Progress Toward the Synthesis of Diazonamide A. Preparation of a 3-(Oxazol-5-yl)-4-trifluormethanesulfonyloxyindole and Its Use in Biaryl Coupling Reactions

Edwin Vedejs* and David A. Barda

*Department of Chemistry, University of Wisconsin-Madison, 1101
University Avenue, Madison, Wisconsin 53706.*

J. Org. Lett. **2000**, *2*, 0000

Supporting Information

4-Benzyloxy-1-(triisopropylsilyl)indole. To a 0 °C solution of 4-benzyloxyindole (21.7g, 97.2 mmol) in THF (250 mL) was added a 1.6 M solution of *n*-BuLi in hexanes (60.7 mL, 97.2 mmol) dropwise. After 5 min, the reaction mixture was cooled to -78 °C and chlorotriisopropylsilane (21.8 mL, 102.1 mmol) was added slowly. After 2 h at -78 °C, the reaction was warmed to 0 °C and poured into a saturated solution of $NaHCO_3$ (250 mL). The aqueous layer was extracted with ether (3 x 100 mL) and the combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude residue was purified by column chromatography with silica gel (20:1 hexanes/CH_2Cl_2) to afford 36.8 g (100% yield); analytical tlc on silica gel 60 F254, 10:1 hexane/CH_2Cl_2, Rf= 0.16. Pure material was obtained by crystallization from hexane/CH_2Cl_2, mp 67-68 °C. Molecular ion calcd for $C_{24}H_{33}NOSi$: 379.23320; found m/e= 379.2327; base peak= 288 amu; IR (KBr, cm^{-1}) 1608, C=N; 1570, C=C; 300 MHz NMR ($CDCl_3$, ppm) δ 7.52 (2H, br d, J= 7.5 Hz) 7.42-7.30 (3H, m) 7.16 (1H, s) 7.16 (1H, d, J= 7.5 Hz) 7.05 (1H, d, J= 7.8 Hz) 6.80 (1H, dd, J= 3.0, 0.6 Hz) 6.60 (1H, d, J= 7.2 Hz) 5.21 (2H, s) 1.70 (3H, sept, J= 7.4 Hz) 1.14 (18H, d, J= 7.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 152.4, 142.3, 137.8, 129.6, 128.4

4-Benzyloxy-3-bromo-1-(triisopropylsilyl)indole (9). To a -78 °C solution of 4-benzyloxy-1-(triisopropylsilyl)indole (36.8 g, 97.2 mmol) in THF (300 mL) was added *N*-bromosuccinimide (17.3 g, 97.2 mmol) in five equal portions. The reaction mixture was stirred for 2 h and allowed to warm to room temperature. To the mixture was added pyridine (1 mL) and hexanes (100 mL) and the mixture was concentrated to dryness. The precipitate was washed thoroughly with hexanes and the combined filtrates were concentrated. The residue was purified by column chromatography with silica gel (10:1 hexanes/CH_2Cl_2) to afford 40.1 g (90% yield); analytical tlc on silica gel 60 F254, 10:1 hexane/CH_2Cl_2, Rf= 0.20. Pure material was obtained by crystallization from hexane, mp 80.5-82.0 °C. Molecular ion calcd for $C_{24}H_{32}BrNOSi$: 459.14180; found m/e= 457.1433; base peak= 368 amu; IR (KBr, cm^{-1}) 1607, C=N; 1570, C=C; 300 MHz NMR ($CDCl_3$, ppm) δ 7.61 (2H, d, J= 7.5 Hz) 7.41-7.36 (2H, m) 7.32-7.27 (1H, m) 7.13 (1H, s) 7.12-7.02 (2H, m) 6.61 (1H, d, J= 7.2 Hz) 6.60 (2H, s) 1.65 (3H, sept, J= 7.8 Hz) 1.12 (18H, d, J= 7.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 152.6, 142.1, 137.4, 129.5, 128.3, 127.5, 127.1, 123.0, 119.2, 107.8, 102.2, 90.5, 70.1, 18.0, 12.8.

4-Benzyloxy-3-methoxycarbonyl-1-(triisopropylsilyl)indole (10). To a -78 °C solution of **9** (31.5 g, 68.7 mmol) in THF (325 mL) was added a 1.7 M solution of *t*-BuLi (80.6 mL, 137 mmol) slowly. After 15 min at -78 °C, methyl chloroformate (6.37 mL, 82.4 mmol) was added dropwise. After 30 min at -78 °C, the reaction was warmed to 0 °C for 30 min, then poured over 500 mL of a saturated solution of $NaHCO_3$. The mixture was extracted with ether (3 x 200 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (10:1 to 4:1 hexanes/ether) to afford 24.7 g (82% yield); analytical tlc on silica gel 60 F254, 5:1 hexane/ether, Rf= 0.23. Pure material was obtained by crystallization from hexane, mp 94-95 °C. Molecular ion calcd for $C_{26}H_{35}NO_3Si$: 437.23860; found m/e= 437.2383, error= 1 ppm; base peak= 346 amu; IR (KBr, cm^{-1}) 1726, C=O; 1694, C=C; 300 MHz NMR ($CDCl_3$, ppm) δ 7.87 (1H, s) 7.58 (2H, br d, J= 6.6 Hz) 7.41-7.35 (2H, m) 7.32-7.27 (1H, m) 7.16-7.08 (2H, m) 6.73 (1H, dd, J= 6.6, 1.8 Hz) 5.21 (2H, s) 3.67 (3H, s) 1.70 (3H, sept, J= 7.6 Hz) 1.14 (18H, d, J= 7.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 165.6, 153.0, 143.3, 137.8, 137.5, 128.2, 127.5, 127.5, 123.3, 118.2, 111.2, 107.6, 104.1, 70.4, 51.0, 17.9, 12.6.

4-Benzyloxy-3-(5-oxazolyl)indole (12). To a -78 °C solution of methyl isocyanide (0.827 mL, 15.1 mmol) in THF (20 mL) was added a 1.5 M solution of *n*-BuLi in hexanes (5.0 mL, 7.55 mmol). The mixture was stirred for 10 min and warmed to -45 °C. To the reaction mixture was added **10** (0.661 g, 1.51 mmol) as a solution in THF (5 mL) dropwise. The mixture was stirred at -45 °C for 30 min and warmed to 0 °C for an additional 30 min. The mixture was poured into a saturated solution of $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3 x 30 mL). The combined extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (2:1 to 3:1 ether/hexane) to afford a 4:1 mixture of oxazole to keto isocyanide products. The mixture of products was dissolved in CH_2Cl_2 (15 mL) and treated with pyridinium *p*-toluenesulfonate (PPTS) (0.076 g, 0.302 mmol) for 2 h. The mixture was concentrated and filtered through a plug of silica gel with ether as eluent to afford 0.310 g (71% yield) of **12** as a white solid; analytical tlc on silica gel 60 F254, 3:1 ether/hexane, Rf= 0.29. Pure material was obtained by crystallization from CH_2Cl_2, mp 167-168 °C. Molecular ion calcd for $C_{18}H_{14}N_2O_2$: 290.10560; found m/e= 290.1055, error= 0 ppm; IR

(KBr, cm^{-1}) 1588, C=N; 1523, C=C; 300 MHz NMR (CD_2Cl_2, ppm) δ 8.85 (1H, br s) 7.75 (1H, s) 7.50-7.46 (3H, m) 7.42-7.34 (3H, m) 7.27 (1H, s) 7.15 (1H, t, J= 8.0 Hz) 7.05 (1H, dd, J= 8.4, 0.9 Hz) 6.67 (1H, d, J= 7.5 Hz) 5.23 (2H, s). ^{13}C NMR (75.4 MHz, CD_2Cl_2, ppm) δ 153.3, 149.2, 148.4, 138.7, 137.2, 128.9, 128.5, 124.2, 123.0, 122.7, 114.9, 105.5, 105.4, 102.4, 70.7.

4-Benzyloxy-1-(*t*butyloxycarbonyl)-3-(5-oxazolyl)indole. To a 0 °C solution of **12** (1.06 g, 3.66 mmol) in THF (20 mL) was added NaH as a 60% dispersion in mineral oil (0.161 g, 4.03 mmol). The reaction was stirred for 30 min at which time the bubbling had stopped. To the reaction mixture was added di-*t*-butyl dicarbonate (0.926 mL, 4.03 mmol) via syringe. The reaction was warmed to r.t. and stirred 2 h. The mixture was diluted with ether (50 mL) and poured into a saturated solution of $NaHCO_3$ (50 mL). The aqueous layer was extracted with ether (30 mL). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (1:1 hexane/ether) to afford 1.30 g (91% yield) of the title compound as a white solid; analytical tlc on silica gel 60 F254, 1:1 hexane/ether, Rf= 0.30. Pure material was obtained by crystallization from hexane, mp 130-131 °C. Molecular ion calcd for $C_{23}H_{22}N_2O_4$: 390.1580; found m/e= 390.1584, error= 1 ppm; base peak= 334 amu; IR (KBr, cm^{-1}) 1734, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 7.86 (1H, d, J= 8.4 Hz) 7.82 (1H, s) 7.75 (1H, s) 7.41-7.30 (5H, m) 7.34 (1H, s) 7.25 (1H, t, J= 8.4 Hz) 6.76 (1H, d, J= 8.1 Hz) 5.17 (2H, s) 1.67 (9H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 152.4, 149.5, 149.1, 146.3, 137.3, 136.0, 128.6, 128.2, 127.9, 125.9, 124.9, 122.9, 116.6, 108.9, 108.5, 105.2, 84.3, 70.4, 28.0.

1-(*t*-Butyloxycarbonyl)-4-hydroxy-3-(5-oxazolyl)indole (13). To a suspension of 4-benzyloxy-

1-(*t*butyloxycarbonyl)-3-(5-oxazolyl)indole (1.30 g, 3.33 mmol) in ethanol (30 mL; purged with nitrogen) was added 10% Pd/C hydrogenation catalyst (130 mg). The suspension was stirred vigorously under an atmosphere of hydrogen gas for 20 h. The mixture was filtered through a plug of silica gel and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by column chromatography with silica gel (2:1 ether/hexane) toe afford 1.00 g (100% yield) of **13** as a white solid; analytical tlc on silica gel 60 F254, 2:1 ether/hexane, Rf= 0.20. Pure material was obtained by crystallization from chloroform, mp 148-149 ºC. Molecular ion calcd for $C_{16}H_{16}N_2O_4$: 300.1110; found m/e= 300.1123, error= 4 ppm; base peak= 200 amu; IR (KBr, cm^{-1}) 3501, O-H; 1730, C=O; 300 MHz NMR (acetone-d_6, ppm) δ 9.31 (1H, br s) 8.15 (1H, s) 7.86 (1H, s) 7.82 (1H, s) 7.78 (1H, d, J= 8.1 Hz) 7.22 (1H, t, J= 8.1 Hz) 6.81 (1H, d, J= 8.1 Hz) 1.71 (9H, s). ^{13}C NMR (75.4 MHz, acetone-d_6, ppm) δ 151.8, 151.0, 149.9, 147.3, 138.8, 127.1, 125.8, 122.8, 116.1, 109.9, 109.5, 107.9, 85.0, 28.1.

1-(*t*-Butyloxycarbonyl)-3-(5-oxazolyl)-4-(trifluoromethylsulfonyloxy)indole (3). To a 0 ºC solution of **13** (1.00 g, 3.33 mmol) in THF (25 mL) was added NaH as a 60% dispersion in mineral oil (0.147 g, 3.66 mmol). The reaction was stirred for 15 min at which time the bubbling had stopped. To the reaction mixture was added *N*-phenyltrifluorosulfonimide (1.31 g, 3.66 mmol) as a solution in THF (5 mL) dropwise via cannula. The reaction was stirred for 2 h at room temperature and then poured in a saturated solution of $NaHCO_3$ (50 mL) and ether (50 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (2:1 hexane/ether) to afford 1.31 g (91% yield) of **3** as a white solid; analytical tlc on silica gel 60 F254, 2:1 hexane/ether, Rf= 0.18. Pure material was obtained by crystallization from hexane, mp 108-109 °C. Molecular ion calcd for $C_{17}H_{15}F_3N_2O_6S$: 432.06030; found m/e= 432.0605, error= 0 ppm; base peak= 172 amu; IR (KBr, cm^{-1}) 1744, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 8.32 (1H, d, J= 8.4 Hz) 7.99 (1H, s) 7.90 (1H, s) 7.42 (1H, t, J= 8.4 Hz) 7.34 (1H, s) 7.29 (1H, d, J= 8.4 Hz) 1.70 (9H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 151.0, 148.5, 144.0, 142.1, 137.7, 127.0, 125.6, 125.0, 120.0, 118.6 (q, J= 321 Hz) 115.7, 115.6, 106.6, 85.6, 28.0.

1-(*t*-Butyloxycarbonyl)-4-(2-methoxyphenyl)-3-(5-oxazolyl)indole (15). To a degassed suspension of triflate **3** (0.100 g, 0.231 mmol), boronic acid **14** (0.44 g, 0.289 mmol), and tripotassium phosphate (0.74 g, 0.347 mmol) in THF (1.5 mL) was added [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II), complex with dichloromethane (1:1) (0.0047 g, 0.00576 mmol). The mixture was heated at 65 ºC for 4.5 h and poured into a mixture of ether (30 mL) and a saturated solution of $NaHCO_3$ (30 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (2:1 to 1:1 hexane/ether) to afford 0.83 g of **15** as an oil; analytical tlc on silica gel 60 F254, 5:3 hexane/ether, Rf= 0.13. Molecular ion calcd for $C_{23}H_{22}N_2O_4$: 390.1580; found m/e= 390.1582, error= 1 ppm; IR (neat, cm^{-1}) 1739, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 8.28 (1H, d, J= 8.1 Hz) 7.82 (1H, s) 7.45 (1H, t, J= 7.8 Hz) 7.44 (1H, s) 7.31 (1H, dt, J= 1.8, 8.4 Hz) 7.25-7.20 (2H, m) 6.97 (1H, dt, J= 0.9, 7.2 Hz) 6.71 (1H, d, J= 7.5 Hz) 6.11 (1H, s) 3.45 (3H, s) 1.69 (9H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 156.8, 149.8, 149.2, 145.7, 135.6, 132.1, 130.9, 129.1, 129.1, 126.0, 126.0, 125.4, 124.9, 123.1, 120.2, 114.5, 110.1, 109.7, 84.3, 54.9, 28.1.

1-(3-Bromo-2-methoxy-phenyl)-2-phenoxyethanone (18). To a solution of ketone **17** (3.43g, 13.0 mmol) and potassium carbonate (5.40 g, 39.1 mmol) in dichloroethane (20 mL) was added phenol (3.68 g, 39.1 mmol). The mixture was heated to reflux for 5 h and then cooled to room temperature and combined with ether (150 mL), hexanes (50 mL), and water (75 mL). The organic layer was washed with 1 N NaOH (100 mL), water (100 mL), and brine (50 mL) and then dried over anhydrous $MgSO_4$, filtered, and concentrated. The essentially pure product (4.23 g, 100%) was used in the next step without further purification. An analytical sample was obtained by column chromatography with silica gel (10:1 hexane/ether); analytical tlc on silica gel 60 F254, 10:1 hexane/ether, Rf= 0.19. Molecular ion calcd for $C_{15}H_{13}BrO_3$: 322.00280; found m/e= 322.0036, error= 2 ppm; base peak= 213 amu; IR (neat, cm^{-1}) 1698, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 7.75 (1H, dd, J= 8.1, 1.5 Hz) 7.66 (1H, dd, J= 8.0, 1.7 Hz) 7.31-7.26 (2H, m) 7.11 (1H, t, J= 8.1 Hz) 6.98 (1H, t, J= 7.5 Hz) 6.93-6.90 (2H, m) 5.22 (2H, s) 3.96 (3H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 196.2, 157.9, 156.3, 138.0, 132.2, 129.5, 129.4, 125.8, 121.6, 117.8, 114.7, 73.0, 62.5.

3-(3-Bromo-2-methoxy-phenyl)-benzofuran (19). To phosporous pentoxide (8g) was added methanesulfonic acid (80g) in one portion. The mixture was stirred for 4 h with occasional heating to dissolve all of the solid. The resulting thick liquid was filtered through a plug of glass wool into a flask containing **18** (4.24 g, 13.0 mmol). The mixture slowly became dark green and was stirred for 24 h. The reaction was poured onto cold water (300 mL) stirred for 15 min, and extracted with CH_2Cl_2 (3 x 200 mL). The combined extracts were washed with a saturated solution of $NaHCO_3$ (100 mL) and water (100 mL), and then dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (1:0 to 50:1 hexane/ether) to afford 2.44 g (62% yield) of **19** as a clear oil; analytical tlc on silica gel 60 F254, 10:1 hexane/ether, Rf= 0.63. Molecular ion calcd for $C_{15}H_{11}BrO_2$: 303.99230; found m/e= 303.9894, error= 9 ppm; base peak= 194 amu; IR (neat, cm^{-1}) 1415, C≡C; 300 MHz NMR ($CDCl_3$, ppm) δ 8.00 (1H, s) 7.77 (1H, br d, J= 7.5 Hz) 7.56 (3H, d, J= 7.8 Hz) 7.36 (1H, dt, J= 1.5, 7.6 Hz) 7.30 (1H, dt, J= 1.5, 7.5 Hz) 7.09 (1H, t, J= 8.1 Hz) 3.58 (3H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 155.3, 154.7, 143.8, 132.5, 129.4, 127.4, 126.4, 125.5, 124.6, 123.0, 121.0, 118.4, 117.2, 111.6, 60.2.

3-(3-Bromo-2-methoxy-phenyl)-3*H*-benzofuran-2-one (20). To a solution of benzofuran **19** (1.31 g, 4.32 mmol) in CH_2Cl_2 (260 mL) was added 32% peracetic acid (26 mL). The reaction was stirred vigorously for 20 h and poured into cold water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic extracts were washed with water (100 mL), 10% $NaHSO_3$ (100 mL), and a saturated solution of $NaHCO_3$ (100 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (10:1 hexanes/ether) to afford 1.10 g (80% yield) of **20**; analytical tlc on silica gel 60 F254, 10:1 hexane/ether, Rf= 0.18. Pure material was obtained by crystallization from hexanes, mp 77-79 °C. Molecular ion calcd for $C_{15}H_{11}BrO_3$: 319.98720; found m/e= 317.9889; base peak= 137 amu; IR (neat, cm^{-1}) 1806, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 7.53 (1H, dd, J= 8.1, 1.5 Hz) 7.33 (1H, br t, J= 7.5 Hz) 7.18 (1H, br d, J= 7.8 Hz) 7.11 (2H, dt, J= 0.9, 7.5 Hz) 7.05 (1H, br d, J= 7.2 Hz) 6.98 (1H, t, J= 7.2 Hz) 5.02 (1H, s) 3.64 (3H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm) δ 175.0, 155.5, 153.9, 134.2, 131.8, 129.6, 129.2, 127.9, 125.5, 124.5, 124.4, 117.1, 110.7, 61.2, 46.5.

2-Methoxy-3-(2-oxo-2,3-dihydrobenzofuran-3-yl)-phenylboronic Acid (22). To a 0 °C solution of lactone **21** (0.136 g, 0.426 mmol) in THF (5.0 mL) was added NaH as a 60% dispersion in mineral oil (0.034 g, 0.852 mmol) at once. The mixture was stirred for 30 min until the bubbling stopped. The reaction was cooled to -78 °C and *n*-butyllithium was added as a 1.6 M solution in hexanes (0.533 mL, 0.852 mmol). The reaction was stirred for 30 min and then trimethylborate (0.143 mL, 1.28 mmol) was added via syringe. The reaction was allowed to warm to room temperature over 30 min and then treated with 1 N HCl (15 mL) and stirred overnight. The mixture was extracted with ether (3 x 20 mL). The combined extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel (1:1 to 2:1 ether/hexane) to afford 0.080 g (66% yield) of **22** as a white solid; analytical tlc on silica gel 60 F254, 1:1 hexane/ether, Rf= 0.19. Pure material was obtained by crystallization from ether/hexane, mp 133-134 °C. Molecular ion calcd for $C_{15}H_{13}BO_5$: 284.08550; found m/e= 284.0870, error= 5 ppm; base peak= 181 amu; 300 MHz NMR (acetone-d_6, ppm) δ 7.64 (1H, dd, J= 7.5, 1.8 Hz) 7.42 (1H, dd, J= 7.5, 1.8 Hz) 7.39-7.33 (2H, m) 7.20 (1H, d, J= 8.1 Hz) 7.15-7.07 (1H, m) 7.13 (1H, t, J= 7.5 Hz) 5.15 (1H, s) 3.44 (3H, s) 2.98 (2H, s).

***tert*-Butyl 4-[2-Methoxy-3-(2-oxo-2,3-dihydro-benzofuran-3-yl)-phenyl]-3-oxazol-5-yl-indole-1-carboxylate (23).** To a degassed suspension of triflate **3** (0.017 g, 0.0393 mmol), boronic acid **22** (0.014 g, 0.0419 mmol), and tripotassium phosphate (0.013 g, 0.0589 mmol) in THF (1.0 mL) was added [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II), complex with dichloromethane (1:1) (0.0008 g, 0.000983 mmol). The mixture was heated at 65 °C for 5 h and poured into a mixture of ether (30 mL) and a saturated solution of $NaHCO_3$ (30 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with silica gel (1:1 hexane/ether) to afford 0.013 g (63% yield) of **23** as a white solid; analytical tlc on silica gel 60 F254, 1:1 hexane/ether, Rf= 0.17. Pure material was obtained by crystallization from ether/hexane, mp 85-100 °C. Molecular ion calcd for $C_{31}H_{26}N_2O_6$: 522.17910; found m/e= 522.1773, error= 3 ppm; base peak= 422 amu; IR (neat, cm^{-1}) 1812, C=O; 1741, C=O; 300 MHz NMR ($CDCl_3$, 23 °C, ppm) δ 8.30 (0.5H, d, J= 7.0 Hz) 8.28 (0.5H, d, J= 7.0 Hz) 7.83 (0.5H, s) 7.80 (0.5H, s) 7.57 (0.5H, s) 7.42 (0.5H, s) 7.43 (0.5H, t, J= 8.4 Hz) 7.41 (0.5H, t, J= 8.4 Hz) 7.33 (0.5H, dd, J= 7.7, 1.1 Hz) 7.22 (0.5 H, dd, J= 7.5, 0.9 Hz) 7.31-7.28 (1H, m) 7.18-7.10 (4H, m) 7.02-6.88 (2H, m) 6.27 (1H, s) 5.00 (0.5H, s) 4.94 (0.5H, s) 3.05 (1.5H, s) 2.93 (1.5H, s) 1.70 (4.5H, s) 1.69 (4.5H, s).