

Supporting Information

for

Synthesis of diverse indole libraries on polystyrene resin – Scope and limitations of an organometallic reaction on solid supports

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Experimental details

(3-Nitrophenyl)carboxymethyl-polystyrene (1{a}): According to GP 1 3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.807 mmol/g (93% conversion). Anal. calcd for $C_{83}H_{80}NO_4$: C 86.27, H 6.98, N 1.21; found C 85.91, H 7.25, N 1.13. ($C_{81}H_{78}NO_4$); IR (KBr): 3816 (m), 3576 (s), 3441 (s), 3060 (s), 3026 (s), 2913 (vs), 2256 (m), 1944 (m), 1873 (m), 1804 (m), 1736 (s), 1601 (m), 1535 (m), 1452 (m), 1351 (s), 1261 (m), 1132 (m), 1069 (m), 963 (m), 907 (m), 759 (m), 706 (m) cm^{-1} .

(2-Methyl-3-nitrophenyl)carboxymethyl-polystyrene (1{b}): According to GP 1 2-methyl-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.813 mmol/g (95% conversion). Anal. calcd for $C_{84}H_{82}NO_4$: C 86.24, H 7.07, N 1.20; found C 84.15, H 6.74, N 1.14; IR (KBr): 3580 (s), 3434 (m), 3026 (vs), 2927 (vs), 2399 (m), 1945 (m), 1873 (m), 1804 (m), 1726 (s), 1602 (m), 1531 (m), 1452 (m), 1358 (s), 1280 (s), 1120 (m), 1030 (m), 965 (m), 761 (s), 706 (m) cm^{-1} .

(2-Chloro-3-nitrophenyl)carboxymethyl-polystyrene (1{c}): According to GP 1 2-chloro-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.763 mmol/g (90% conversion). Anal. calcd for $C_{84}H_{79}ClNO_4Cl$: C 83.94, H 6.62; N 1.17; found C 83.72, H 6.91, N 1.05; IR (KBr): 3803 (m), 3587 (s), 3450 (s), 3060 (s), 3028 (m), 2907 (vs), 2721 (m), 2398 (m), 2256 (m), 1945 (m), 1872 (m), 1803 (m), 1745 (s), 1600 (m), 1542 (m), 1454 (m), 1362 (m), 1291 (s), 1149 (m), 1102 (m), 1057 (m), 963 (s), 907 (m), 757 (m), 708 (m), 622 (m) cm^{-1} .

(2-Bromo-3-nitrophenyl)carboxymethyl-polystyrene (1{d}): According to GP 1 2-bromo-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.745 mmol/g (91% conversion). Anal. calcd for $C_{81}H_{77}BrNO_4$: C 80.94, H 6.39; N 1.12; found C 81.23, H 6.66, N 1.02; IR (KBr): 3587 (m), 3462 (s), 3336 (m), 3082 (m), 3027 (m), 2936 (s), 2849 (m), 2728 (m), 2398 (m), 2257 (m), 1944 (m), 1872 (m), 1803 (s), 1742 (s), 1601 (m), 1541 (m), 1455 (m), 1364 (m), 1289 (s), 1141 (m), 1029 (m), 963 (s), 770 (m), 708 (m) cm^{-1} .

(4-Methyl-3-nitrophenyl)carboxymethyl-polystyrene (1{e}): According to GP 1 4-methyl-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g)

and washed following the general washing procedure to give the product resin with a loading of 0.721 mmol/g (83% conversion). Anal. calcd for $C_{84}H_{82}NO_4$: C 86.24, H 7.07, N 1.20; found C 84.80, H 7.11, N 1.00; IR (KBr): 3817 (m), 3568 (m), 3443 (vs), 3027 (m), 2925 (s), 2849 (m), 1944 (m), 1870 (m), 1803 (m), 1733 (m), 1601 (m), 1539 (m), 1453 (m), 1353 (m), 1256 (s), 1119 (m), 963 (m), 760 (m), 700 (m), 621 (m) cm^{-1} .

(4-Hydroxy-3-nitrophenyl)carboxymethyl-polystyrene (1{f}): According to GP 1 4-hydroxy-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.168 mmol/g (16% conversion). Anal. calcd for $C_{83}H_{80}NO_5$: C 85.09, H 6.88, N 1.20; found C 87.67, H 7.63, N 0.19; IR (KBr): 3817 (m), 3588 (s), 3441 (m), 3027 (vs), 2848 (vs), 2337 (m), 1944 (m), 1873 (m), 1804 (m), 1725 (s), 1603 (m), 1540 (m), 1454 (m), 1375 (m), 1269 (s), 1182 (m), 1112 (m), 1029 (m), 965 (m), 907 (m), 841 (m), 765 (m), 707 (s), 622 (m) cm^{-1} .

(4-Methoxy-3-nitrophenyl)carboxymethyl-polystyrene (1{g}): According to GP 1 4-methoxy-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.795 mmol/g (94% conversion). Anal. calcd for $C_{84}H_{82}NO_5$: C 85.10, H 6.97, N 1.18; found C 84.67, H 7.54, N 1.11; IR (KBr): 3821 (m), 3587 (s), 3435 (m), 3059 (s), 3029 (m), 2914 (s), 2852 (m), 2631 (vs), 2071 (m), 2027 (m), 1945 (m), 1875 (m), 1805 (m), 1730 (s), 1619 (m), 1540 (m), 1454 (m), 1355 (m), 1285 (vs), 1123 (m), 1082 (m), 1019 (m), 963 (m), 908 (m), 830 (m), 763 (m), 704 (m) cm^{-1} .

(4-Chloro-3-nitrophenyl)carboxymethyl-polystyrene (1{h}) [1]: According to GP 1 4-chloro-3-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.836 mmol/g (quantitative conversion). Anal. calcd for $C_{83}H_{79}ClNO_4Cl$: C 83.77, H 6.69; N 1.18; found C 81.79, H 6.74, N 1.90; IR (KBr): 3936 (m), 3815 (s), 3439 (vs), 3060 (s), 3025 (m), 2912 (s), 2850 (m), 2727 (m), 1944 (m), 1873 (m), 1729 (s), 1608 (m), 1545 (m), 1452 (m), 1355 (m), 1240 (s), 1110 (m), 964 (m), 908 (m), 842 (m), 758 (m), 706 (m) cm^{-1} .

(3-Methyl-4-nitrophenyl)carboxymethyl-polystyrene (1{i}) [1]: According to GP 1 3-methyl-4-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a

loading of 0.295 mmol/g (35% conversion). Anal. calcd for $C_{84}H_{82}NO_4$: C 86.24, H 7.07, N 1.20; found C 85.95, H 7.50, N 0.42; IR (KBr): 3583 (s), 3436 (m), 3060 (m), 3026 (m), 2952 (s), 2847 (m), 2337 (m), 2310 (m), 1943 (m), 1871 (m), 1803 (m), 1733 (m), 1601 (m), 1529 (m), 1453 (m), 1348 (m), 1256 (s), 1191 (m), 1113 (m), 1069 (m), 1029 (m), 959 (m), 906 (m), 834 (m), 762 (s), 704 (m) cm^{-1} .

(3-Hydroxy-4-nitrophenyl)carboxymethyl-polystyrene (1{j}): According to GP 1 3-hydroxy-4-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.096 mmol/g (10% conversion). Anal. calcd for $C_{83}H_{80}NO_5$: C 85.09, H 6.88, N 1.20; found C 87.87, H 7.58, N 0.18; IR (KBr): 3823 (m), 3587 (s), 3061 (s), 3027 (m), 2915 (s), 2853 (m), 1944 (m), 1873 (m), 1804 (m), 1730 (m), 1682 (m), 1602 (m), 1540 (m), 1453 (m), 1320 (s), 1269 (m), 1106 (m), 965 (m), 908 (m), 757 (s), 704 (m) cm^{-1} .

(3-Methoxy-4-nitrophenyl)carboxymethyl-polystyrene (1{k}): According to GP 1 3-methoxy-4-nitrobenzoic acid was attached to 5.00 g of Merrifield-resin (0.97 mmol/g) and washed following the general washing procedure to give the product resin with a loading of 0.78 mmol/g (92% conversion). Anal. calcd for $C_{84}H_{82}NO_5$: C 85.10, H 6.97, N 1.18; found C 84.90, H 7.26, N 1.09; IR (KBr): 3581 (s), 3432 (m), 3061 (m), 3024 (m), 2952 (vs), 2727 (m), 2399 (m), 2336 (m), 2070 (m), 1943 (m), 1871 (m), 1803 (m), 1733 (s), 1617 (m), 1534 (m), 1495 (m), 1448 (m), 1350 (m), 1242 (s), 1112 (m), 1069 (m), 1016 (m), 962 (m), 907 (m), 829 (m), 761 (s), 707 (m) cm^{-1} .

1H-Indole-6-carboxymethyl-polystyrene and 1H-indole-4-carboxymethyl-polystyrene (3{a,a}): According to GP 2 1.00 g of (3-nitrophenyl)carboxymethyl-polystyrene (**1{a}**) 0.807 mmol/g was reacted with vinylmagnesium bromide (**2{a}**) to give the product resin with a loading of 0.802 mmol/g. Anal. calcd for $C_{85}H_{82}NO_2$: C 88.81, H 7.19; N 1.22; found C 78.92, H 7.22, N 1.01; IR (KBr): 3650 (vs), 3025 (vs), 2912 (vs), 1944 (m), 1873 (m), 1804 (m), 1724 (s), 1601 (m), 1494 (m), 1452 (m), 1372 (vs), 1072 (s), 1029 (s), 907 (m), 766 (s) cm^{-1} .

7-Methyl-1H-indole-6-carboxymethyl-polystyrene (3{b,a}): According to GP 2 1.00 g of (2-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{b}**) 0.813 mmol/g was reacted with vinylmagnesium bromide (**2{a}**) to give the product resin with a loading of 0.808 mmol/g. Anal. calcd for $C_{86}H_{84}NO_2$: C 88.77, H 7.28; N 1.20; found C 82.14, H 7.15, N 1.22; IR (KBr): 3858 (m), 3369 (vs), 3026 (m), 2923 (s), 2849 (m),

1944 (m), 1873 (m), 1804 (m), 1724 (s), 1602 (m), 1453 (m), 1371 (m), 1254 (s), 1188 (m), 1029 (s), 765 (m) cm^{-1} .

3,7-Dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (3{b,b}): According to GP 2 1.00 g of (2-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{b}**) 0.813 mmol/g) was reacted with 1-propenylmagnesium bromide (**2{b}**) to give the product resin with a loading of 0.798 mmol/g. Anal. calcd for $\text{C}_{87}\text{H}_{87}\text{NO}_2$: C 88.66, H 7.44; N 1.19; found C 80.69, H 7.27, N 1.50; IR (KBr): 3366 (vs), 3060 (s), 3027 (m), 2927 (vs), 2399 (m), 1944 (m), 1873 (m), 1804 (m), 1726 (s), 1602 (m), 1532 (m), 1453 (m), 1371 (m), 1260 (s), 1031 (m), 766 (m) cm^{-1} .

2,7-Dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (3{b,c}): According to GP 2 1.00 g of (2-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{b}**) 8.13 mmol/g) was reacted with isopropenylmagnesium bromide (**2{c}**) to give the product resin with a loading of 0.798 mmol/g. Anal. calcd for $\text{C}_{87}\text{H}_{87}\text{NO}_2$: C 88.66, H 7.44; N 1.19; found C 81.01, H 7.28, N 1.35; IR (KBr): 3434 (vs), 3060 (m), 2924 (s), 2337 (m), 2311 (m), 1944 (m), 1874 (m), 1804 (m), 1711 (s), 1452 (m), 1374 (m), 1256 (m), 1191 (m), 1153 (m), 1031 (s), 964 (m), 906 (m), 823 (m), 759 (m) cm^{-1} .

2,3,7-Trimethyl-1*H*-indole-6-carboxymethyl-polystyrene (3{b,d}): According to GP 2 1.00 g of (2-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{b}**) 0.813 mmol/g) was reacted with 1-methyl-1-propenylmagnesium bromide (**2{d}**) to give the product resin with a loading of 0.790 mmol/g. Anal. calcd for $\text{C}_{88}\text{H}_{88}\text{NO}_2$: C 88.70, H 7.44; N 1.18; found C 79.81, H 7.49, N 1.40; IR (KBr): 3348 (vs), 3061 (m), 2911 (vs), 1944 (m), 1873 (m), 1804 (m), 1725 (s), 1602 (m), 1453 (m), 1371 (m), 1260 (m), 1147 (m), 1048 (s), 766 (s), 629 (m) cm^{-1} .

7-Chloro-1*H*-indole-6-carboxymethyl-polystyrene (3{c,a}): According to GP 2 1.00 g of (2-chloro-3-nitrophenyl)carboxymethyl-polystyrene (**1{c}**) 0.763 mmol/g) was reacted with vinylmagnesium bromide (**2{a}**) to give the product resin with a loading of 0.758 mmol/g. Anal. calcd for $\text{C}_{85}\text{H}_{81}\text{ClNO}_2$: C 86.22, H 6.90; N 1.18; found C 78.64, H 7.05, N 0.67; IR (KBr): 3408 (vs), 3025 (vs), 2912 (vs), 2337 (m), 1944 (m), 1873 (m), 1804 (m), 1726 (s), 1601 (m), 1494 (m), 1452 (m), 1260 (vs), 1188 (m), 1153 (m), 1068 (m), 1029 (m), 907 (m), 758 (s) cm^{-1} .

7-Chloro-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (3{c,b}): According to GP 2 1.00 g of (2-chloro-3-nitrophenyl)carboxymethyl-polystyrene (**1{c}**) 0.763 mmol/g) was reacted with 1-propenylmagnesium bromide (**2{b}**) to give the product resin with a loading of 0.750 mmol/g. Anal. calcd for $\text{C}_{86}\text{H}_{83}\text{ClNO}_2$: C 86.22,

H 6.98; N 1.17; found C 79.03, H 7.28, N 1.22; IR (KBr): 3567 (vs), 3060 (s), 3025 (m), 2912 (vs), 1944 (m), 1872 (m), 1803 (m), 1739 (s), 1602 (m), 1454 (m), 1374 (vs), 1184 (m), 1149 (m), 1030 (s), 907 (m), 761 (s), 707 (m) cm^{-1} .

7-Chloro-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (3{c,c}): According to GP 2 1.00 g of (2-chloro-3-nitrophenyl)carboxymethyl-polystyrene (1{c}) 0.763 mmol/g) was reacted with isopropenylmagnesium bromide (2{c}) to give the product resin with a loading of 0.750 mmol/g. Anal. calcd for $\text{C}_{86}\text{H}_{83}\text{ClNO}_2$: C 86.22, H 6.98; N 1.17; found C 79.00, H 6.91, N 1.50; IR (KBr): 3416 (vs), 3024 (vs), 2910 (vs), 1945 (m), 1873 (m), 1804 (m), 1743 (s), 1601 (m), 1537 (m), 1452 (m), 1371 (vs), 1193 (m), 1156 (m), 1054 (m), 1029 (m), 908 (m), 761 (m), 663 (m) cm^{-1} .

7-Chloro-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (3{c,d}): According to GP 2 1.00 g of (2-chloro-3-nitrophenyl)carboxymethyl-polystyrene (1{c}) 0.763 mmol/g) was reacted with 1-methyl-1-propenylmagnesium bromide (2{d}) to give the product resin with a loading of 0.743 mmol/g. Anal. calcd for $\text{C}_{87}\text{H}_{85}\text{ClNO}_2$: C 86.21, H 7.07; N 1.16; found C 78.94, H 7.31, N 0.85; IR (KBr): 3701 (m), 3060 (s), 3025 (m), 2923 (s), 2848 (m), 1944 (m), 1873 (m), 1803 (m), 1726 (s), 1601 (m), 1452 (m), 1373 (vs), 1147 (s), 1029 (m), 908 (m), 761 (m), 704 (m), 663 (m) cm^{-1} .

7-Bromo-1*H*-indole-6-carboxymethyl-polystyrene (3{d,a}): According to GP 2 1.00 g of (2-bromo-3-nitrophenyl)carboxymethyl-polystyrene (1{d}) 0.745 mmol/g) was reacted with vinylmagnesium bromide (2{a}) to give the product resin with a loading of 0.741 mmol/g. Anal. calcd for $\text{C}_{85}\text{H}_{81}\text{BrNO}_2$: C 83.10, H 6.65; N 1.14; found C 79.74, H 6.97, N 1.38; IR (KBr): 3421 (vs), 3060 (m), 3026 (m), 2926 (s), 2850 (m), 1944 (m), 1872 (m), 1803 (m), 1739 (m), 1667 (m), 1601 (m), 1540 (m), 1453 (m), 1372 (m), 1286 (s), 1182 (m), 1144 (m), 1029 (m), 762 (m), 704 (m) cm^{-1} .

7-Bromo-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (3{d,b}): According to GP 2 1.00 g of (2-bromo-3-nitrophenyl)carboxymethyl-polystyrene (1{d}) 0.745 mmol/g) was reacted with 1-propenylmagnesium bromide (2{b}) to give the product resin with a loading of 0.733 mmol/g. Anal. calcd for $\text{C}_{86}\text{H}_{83}\text{BrNO}_2$: C 83.13, H 6.73; N 1.13; found C 77.22, H 6.93, N 0.92; IR (KBr): 3349 (vs), 3059 (s), 3026 (m), 2911 (s), 2851 (m), 1944 (m), 1874 (m), 1804 (m), 1742 (s), 1666 (m), 1602 (m), 1545 (m), 1453 (m), 1370 (m), 1291 (s), 1143 (m), 1030 (m), 770 (m) cm^{-1} .

7-Bromo-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (3{d,c}): According to GP 2 1.00 g of (2-bromo-3-nitrophenyl)carboxymethyl-polystyrene (1{d}) 0.745 mmol/g) was reacted with isopropenylmagnesium bromide (2{c}) to give the

product resin with a loading of 0.733 mmol/g. Anal. calcd for $C_{86}H_{83}BrNO_2$: C 83.13, H 6.73; N 1.13; found C 77.11, H 7.06, N 0.55; IR (KBr): 3366 (vs), 2927 (s), 1944 (m), 1873 (m), 1804 (m), 1726 (s), 1602 (m), 1452 (m), 1314 (s), 1194 (m), 1154 (m), 1029 (m), 907 (m), 823 (m), 758 (m), 663 (m) cm^{-1} .

7-Bromo-2,3-dimethyl-1H-indole-6-carboxymethyl-polystyrene (3{d,d}):

According to GP 2 1.00 g of (2-bromo-3-nitrophenyl)carboxymethyl-polystyrene (**1{d}**) 0.745 mmol/g) was reacted with 1-methyl-1-propenylmagnesium bromide (**2{d}**) to give the product resin with a loading of 0.725 mmol/g. Anal. calcd for $C_{87}H_{85}BrNO_2$: C 83.16, H 6.82; N 1.11; found C 76.89, H 7.16; N 0.84; IR: 3060 (s), 3027 (m), 2916 (vs), 1944 (m), 1873 (m), 1804 (m), 1727 (s), 1602 (m), 1453 (m), 1289 (s), 1144 (s), 1029 (m), 907 (m), 769 (m), 625 (m) cm^{-1} .

7-Methyl-1H-indole-4-carboxymethyl-polystyrene (3{e,a}): According to GP 2 1.00 g of (4-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{e}**) 0.721 mmol/g) was reacted with vinylmagnesium bromide (**2{a}**) to give the product resin with a loading of 0.716 mmol/g. Anal. calcd for $C_{86}H_{84}NO_2$: C 88.77, H 7.28; N 1.20; found C 82.14, H 7.15, N 1.22; IR (KBr): 3858 (m), 3304 (s), 3026 (m), 2924 (s), 2849 (m), 1944 (s), 1873 (s), 1804 (m), 1721 (vs), 1603 (m), 1494 (m), 1452 (m), 1375 (vs), 1254 (s), 1100 (m), 1029 (s), 907 (m), 765 (m), 702 (m), 548 (s) cm^{-1} .

3,7-Dimethyl-1H-indole-4-carboxymethyl-polystyrene (3{e,b}): According to GP 2 1.00 g of (4-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{e}**) 0.721 mmol/g) was reacted with 1-propenylmagnesium bromide (**2{b}**) to give the product resin with a loading of 0.709 mmol/g. Anal. calcd for $C_{87}H_{87}NO_2$: C 88.66, H 7.44; N 1.19; found C 80.69, H 7.27, N 1.50; IR (KBr): 3306 (vs), 3027 (vs), 2929 (vs), 2399 (m), 1944 (s), 1873 (s), 1803 (s), 1715 (s), 1601 (m), 1493 (m), 1452 (m), 1375 (m), 1100 (s), 1029 (vs), 907 (m), 843 (m), 765 (m), 702 (m), 548 (m) cm^{-1} .

2,7-Dimethyl-1H-indole-4-carboxymethyl-polystyrene (3{e,d}): According to GP 2 1.00 g of (4-methyl-3-nitrophenyl)carboxymethyl-polystyrene (**1{e}**) 0.721 mmol/g) was reacted with 1-methyl-1-propenylmagnesium bromide (**2{d}**) to give the product resin with a loading of 0.702 mmol/g. Anal. calcd for $C_{88}H_{88}NO_2$: C 88.70, H 7.44; N 1.18; found C 81.01, H 7.28, N 1.35; IR (KBr): 3304 (vs), 3060 (m), 2922 (s), 2337 (m), 1943 (s), 1871 (s), 1804 (m), 1716 (s), 1602 (m), 1452 (m), 1374 (s), 1289 (s), 1258 (m), 11821 (m), 1104 (s), 1028 (m), 963 (s), 907 (m), 842 (m), 759 (s), 702 (m), 538 (m) cm^{-1} .

7-Chloro-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (3{h,d}) [1]:

According to GP 2 1.00 g of (4-chloro-3-nitrophenyl)carboxymethyl-polystyrene (**1{h}**) (0.836 mmol/g) was reacted with 1-methyl-1-propenylmagnesium bromide (**2{d}**) to give the product resin with a loading of 0.812 mmol/g. Anal. calcd for C₈₇H₈₅ClNO₂: C 86.21, H 7.07; N 1.16; found C 79.02, H 7.19, N 1.64; IR (KBr): 3701 (m), 3649 (s), 3324 (vs), 3061 (s), 3028 (m), 2911 (vs), 1944 (m), 1873 (m), 1804 (m), 1727 (s), 1602 (m), 1453 (m), 1375 (vs), 1105 (m), 1029 (m), 908 (m), 842 (m), 768 (m), 706 (m) cm⁻¹.

7-Methyl-1*H*-indole-5-carboxymethyl-polystyrene (3{i,a}) [1]: According to GP 2 1.00 g of (3-methyl-4-nitrophenyl)carboxymethyl-polystyrene (**1{i}**), 0.295 mmol/g) was reacted with vinylmagnesium bromide (**2{a}**) to give the product resin with a loading of 0.294 mmol/g. Anal. calcd for C₈₆H₈₄NO₂: C 88.77, H 7.28; N 1.20; found C 79.77, H 7.23, N 1.04; IR (KBr): 3641 (vs), 3319 (vs), 3027 (vs), 2951 (m), 2845 (s), 1943 (m), 1871 (m), 1802 (m), 1723 (s), 1603 (m), 1528 (m), 1448 (s), 1348 (s), 1186 (s), 1106 (m), 908 (m), 844 (m), 776 (m) cm⁻¹.

7-(4-*tert*-Butylphenyl)-1*H*-indole-6-carboxymethyl-polystyrene 3{l,a}: According to GP 3 1.00 g of 7-bromo-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,a}**, 0.741 mmol/g) was reacted with 4-*tert*-butylphenylboronic acid to give the product resin with a loading of 0.713 mmol/g. Anal. calcd for C₉₅H₉₄NO₂: C 89.02, H 7.39, N 1.09; found C 79.12, H 7.14, N 1.47; IR (KBr): 3425 (vs), 3059 (m), 2918 (vs), 1944 (m), 1872 (m), 1803 (m), 1716 (s), 1601 (m), 1453 (m), 1374 (m), 1262 (m), 1192 (m), 1071 (s), 1029 (m), 907 (m), 760 (s), 703 (m) cm⁻¹.

7-(4-*tert*-Butylphenyl)-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene 3{l,b}: According to GP 3 1.00 g of 7-bromo-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,b}**, 0.733 mmol/g) was reacted with 4-*tert*-butylphenylboronic acid to give the product resin with a loading of 0.705 mmol/g. Anal. calcd for C₉₆H₉₆NO₂: C 88.98, H 7.47, N 1.08; found C 79.44, H 7.13, N 0.96; IR (KBr): 3822 (m), 3427 (vs), 3060 (m), 3026 (m), 2924 (vs), 1944 (m), 1872 (m), 1803 (m), 1721 (s), 1601 (m), 1453 (m), 1373 (m), 1269 (s), 1152 (vs), 1029 (s), 843 (m), 762 (m), 703 (m) cm⁻¹.

7-(4-*tert*-Butylphenyl)-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene 3{l,c}: According to GP 3 1.00 g of 7-bromo-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,c}**, 0.733 mmol/g) was reacted with 4-*tert*-butylphenylboronic acid to give the product resin with a loading of 0.705 mmol/g. Anal. calcd for C₉₆H₉₆NO₂: C 88.98, H 7.47, N 1.08; found C 78.40, H 6.99, N 1.44; IR (KBr): 3420 (vs), 3031

(vs), 2895 (vs), 1944 (m), 1873 (m), 1804 (m), 1723 (s), 1601 (vs), 1372 (s), 1193 (m), 1154 (vs), 1029 (s), 908 (m), 824 (m), 769 (s) cm^{-1} .

7-(4-*tert*-Butylphenyl)-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene

3{l,d}: According to GP 3 1.00 g of 7-bromo-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,d}**, 0.725 mmol/g) were reacted with 4-*tert*-butylphenylboronic acid to give the product resin with a loading of 0.698 mmol/g. Anal. calcd for $\text{C}_{97}\text{H}_{98}\text{NO}_2$: C 88.95, H 7.54, N 1.07; found C 79.10, H 7.17, N 1.31; IR (KBr): 3425 (vs), 3059 (m), 2923 (vs), 1944 (m), 1871 (m), 1803 (m), 1719 (s), 1602 (m), 1452 (m), 1375 (m), 1305 (s), 1210 (m), 1155 (m), 1120 (m), 1028 (m), 906 (m), 844 (m), 758 (m), 702 (m) cm^{-1} .

7-[(4-Methoxyphenyl)ethynyl]-1*H*-indole-6-carboxymethyl-polystyrene 3{n,a}:

According to GP 4 1.00 g of 7-bromo-1*H*-indole-6-carboxymethyl-polystyrene **3{d,a}**, 0.741 mmol/g) was reacted with 4-ethynylanisole to give the product resin with a loading of 0.714 mmol/g. Anal. calcd for $\text{C}_{94}\text{H}_{88}\text{NO}_3$: C 88.22, H 6.93; N 1.10; found C 83.84, H 6.96, N 0.96; IR (KBr): 3432 (vs), 3024 (vs), 2949 (m), 2843 (s), 2544 (s), 2202 (m), 2048 (m), 1943 (m), 1874 (m), 1804 (m), 1690 (s), 1600 (s), 1511 (m), 1450 (m), 1335 (s), 1246 (m), 1181 (m), 1028 (m), 966 (m), 907 (m), 832 (m), 750 (m), 701 (m) cm^{-1} .

7-[(4-Methoxyphenyl)ethynyl]-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene

3{n,b}: According to GP 4 1.00 g of 7-bromo-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,b}**, 0.733 mmol/g) was reacted with 4-ethynylanisole to give the product resin with a loading of 0.706 mmol/g. Anal. calcd for $\text{C}_{95}\text{H}_{90}\text{NO}_3$: C 88.20, H 7.01, N 1.08; found C 84.90, H 7.07, N 0.89; IR (KBr): 3809 (m), 3643 (m), 3433 (vs), 3024 (vs), 2842 (vs), 2539 (m), 2337 (m), 2310 (m), 2203 (m), 2054 (m), 1943 (m), 1873 (m), 1803 (m), 1723 (s), 1603 (s), 1511 (m), 1451 (m), 1327 (vs), 1180 (m), 1030 (s), 831 (m), 750 (m), 701 (m) cm^{-1} .

7-[(4-Methoxyphenyl)ethynyl]-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene

3{n,c}: According to GP 4 1.00 g of 7-bromo-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,c}**, 0.733 mmol/g) was reacted with 4-ethynylanisole to give the product resin with a loading of 0.706 mmol/g. Anal. calcd for $\text{C}_{95}\text{H}_{90}\text{NO}_3$: C 88.20, H 7.01, N 1.08; found C 83.89, H 6.86, N 0.98; IR (KBr): 3460 (vs), 3059 (s), 3024 (m), 2841 (s), 2538 (m), 2204 (m), 2054 (m), 1943 (m), 1872 (m), 1803 (m), 1697 (s), 1604 (m), 1511 (m), 1450 (m), 1346 (s), 1246 (m), 1181 (m), 1029 (m), 976 (m), 832 (m), 762 (m), 700 (m) cm^{-1} .

7-[(4-Methoxyphenyl)ethynyl]-2,3-dimethyl-1*H*-indole-6-carboxymethyl-

polystyrene 3{n,d}: According to GP 4 1.00 g of 7-bromo-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,d}**, 0.725 mmol/g) was reacted with 4-ethynylanisole to give the product resin with a loading of 0.699 mmol/g. Anal. calcd for C₉₄H₉₀NO₃: C 88.09, H 7.08, N 1.09; found C 84.64, H 7.05, N 0.90; IR (KBr): 3448 (vs), 3024 (s), 2845 (s), 2539 (m), 2310 (m), 2206 (m), 2050 (m), 1943 (m), 1874 (m), 1804 (m), 1691 (s), 1666 (m), 1603 (s), 1511 (m), 1451 (m), 1322 (s), 1246 (m), 1181 (m), 1028 (s), 831 (m), 747 (m), 699 (m) cm⁻¹.

7-Vinyl-1*H*-indole-6-carboxymethyl-polystyrene 3{m,a}: According to GP 5 1.00 g of 7-bromo-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,a}**, 0.741 mmol/g) was reacted with tributyl(vinyl)tin to give the product resin with a loading of 0.771 mmol/g. Anal. calcd for C₈₇H₈₄NO₂: C 88.88, H 7.20; N 1.19; found C 81.59, H 6.90, N 0.98; IR (KBr): 3433 (vs), 3058 (s), 3025 (m), 2913 (vs), 1943 (m), 1872 (m), 1803 (m), 1708 (s), 1601 (m), 1451 (m), 1344 (vs), 1182 (m), 1137 (s), 1028 (s), 907 (m), 823 (m), 763 (m), 701 (m) cm⁻¹.

7-Vinyl-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene 3{m,b}: According to GP 5 1.00 g of 7-bromo-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,b}**, 0.733 mmol/g) was reacted with tributyl(vinyl)tin to give the product resin with a loading of 0.763 mmol/g. Anal. calcd for C₈₈H₈₆NO₂: C 88.85, H 7.29; N 1.18; found C 81.92, H 7.14, N 0.90; IR (KBr): 3435 (vs), 3059 (s), 3025 (m), 2908 (s), 1943 (m), 1872 (m), 1803 (m), 1704 (s), 1601 (m), 1451 (m), 1316 (s), 1256 (m), 1152 (m), 1056 (m), 1029 (s), 908 (m), 759 (m), 700 (m) cm⁻¹.

7-Vinyl-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene 3{m,c}: According to GP 5 1.00 g of 7-bromo-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,c}**, 0.733 mmol/g) was reacted with tributyl(vinyl)tin to give the product resin with a loading of 0.763 mmol/g. Anal. calcd for C₈₈H₈₆NO₂: C 88.85, H 7.29; N 1.18; found C 81.52, H 7.13, N 0.98; IR (KBr): 3639 (m), 3470 (vs), 3059 (s), 3024 (m), 2906 (s), 2337 (m), 2039 (m), 1943 (m), 1871 (m), 1802 (m), 1697 (s), 1601 (m), 1451 (m), 1346 (s), 1245 (m), 1183 (m), 1134 (m), 1028 (m), 908 (m), 822 (m), 762 (m), 700 (m) cm⁻¹.

7-Vinyl-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene 3{m,d}: According to GP 5 1.00 g of 7-bromo-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{d,d}**, 0.725 mmol/g) was reacted with tributyl(vinyl)tin to give the product resin with a loading of 0.754 mmol/g. Anal. calcd for C₈₉H₈₈NO₂: C 88.81, H 7.37; N 1.16; found

C 83.38, H 7.27, N 0.88; IR (KBr): 3580 (s), 3470 (vs), 3024 (vs), 2950 (m), 2843 (m), 1942 (m), 1870 (m), 1802 (m), 1698 (s), 1601 (s), 1450 (m), 1344 (s), 1244 (m), 1182 (m), 1028 (s), 908 (m), 820 (m), 748 (m), 700 (m) cm^{-1} .

Methyl 1*H*-indole-4-carboxylate (4{a,a}): According to GP 6 cleavage of 500 mg (401 μmol) of 1*H*-indole-6-carboxymethyl-polystyrene (0.802 mmol/g) (**3{a,a}**) gave 15.0 mg (85.6 μmol , 21%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1). R_f : 0.36 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 3.94 (s, 3 H, OCH_3), 6.60–6.62 (m, 1 H, 3-H), 7.35–7.38 (m, 1 H, 2-H), 7.71 (dd, $^3J = 7.99$ Hz, $^4J = 0.52$ Hz, 1 H, 4-H), 7.87 (dd, $^3J = 7.99$ Hz, $^4J = 0.88$ Hz, 1 H, 5-H), 8.16 (m, 1 H, 7-H), 8.29 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 51.9 (+, OCH_3), 103.3 (+, C-3), 113.6 (+, C-7), 120.5 (+, C-4), 121.1 (+, C-5), 127.6 (C_q , C-6), 131.9 (C_q , C-3a), 134.8 (C_q , C-7a), 166.9 (C_q , COOCH_3); EI (m/z): 175 (100) $[\text{M}]^+$, 144 (100), 116 (40), 97 (10), 89 (20), 63 (10).

Methyl 1*H*-indole-6-carboxylate (4{a,a'}): According to GP 6 cleavage of 500 mg (401 μmol) of 1*H*-indole-6-carboxymethyl-polystyrene (0.802 mmol/g) (**3{a,a}**) gave 15.0 mg (85.6 μmol , 21%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.36 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 3.99 (s, 3 H, OCH_3), 6.60–6.62 (m, 1 H, 3-H), 7.35–7.38 (m, 1 H, 2-H), 7.37 (ddd, $^3J = 7.99$ Hz, 1 H, 6-H), 7.82 (dd, $^3J = 7.99$ Hz, $^4J = 0.88$ Hz, 1 H, 7-H), 8.16 (dd, $^3J = 7.99$ Hz, $^4J = 0.88$ Hz, 1 H, 5-H), 8.29 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 52.1 (+, OCH_3), 104.2 (+, C-3), 116.0 (C_q , C-4), 120.5 (+, C-6), 121.4 (+, C-2), 123.6 (C_q , C-7a), 126.3 (+, C-5), 135.3 (C_q , C-3a), 166.9 (C_q , COOCH_3); EI (m/z): 175 (100) $[\text{M}]^+$, 144 (100), 116 (40), 97 (10), 89 (20), 63 (10).

Methyl 7-methyl-1*H*-indole-6-carboxylate (4{b,a}): According to GP 6 cleavage of 500 mg (404 μmol) of 7-methyl-1*H*-indole-6-carboxymethyl-polystyrene (**3{b,a}**) (0.808 mmol/g) gave 10.5 mg (55.5 μmol , 14%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.50 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.79 (s, 3 H, CH_3), 3.91 (s, 3 H, OCH_3), 6.58 (d, $^3J = 5.81$ Hz, 1 H, 3-H), 7.35 (d, $^3J = 5.81$ Hz, 1 H, 2-H), 7.50 (d, $^3J = 8.41$ Hz, 1 H, 4-H), 7.74 (d, 1 H, 5-H), 8.38 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 14.9 (+, CH_3), 51.8 (+, OCH_3), 103.5 (+, C-3), 111.5 (C_q , C-7), 117.9 (+, C-4), 122.4 (+, C-5), 124.2 (C_q , C-6), 127.0 (+, C-2), 130.3 (C_q , C-3a), 136.1 (C_q , C-7a), 169.1 (C_q , COOCH_3); EI (m/z): 189 (100) $[\text{M}]^+$, 158 (100), 130 (40), 105 (15), 91 (15), 77 (10); HRMS ($\text{C}_{11}\text{H}_{11}\text{NO}_2$): 189.0790; found 189.0791).

Methyl 3,7-dimethyl-1*H*-indole-6-carboxylate 4{b,b}: According to GP 6 cleavage of 500 mg (399 μ mol) of 3,7-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (0.798 mmol/g) (**3{b,b}**) gave 12.8 mg (63.0 μ mol, 16%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.53 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.33 (d, $^4J = 1.05$ Hz, 3-CH₃), 2.76 (s, 3 H, 7-CH₃), 3.91 (s, 3 H, OCH₃), 7.12 (d, $^4J = 1.05$ Hz, 1 H, 2-H), 7.43 (d, $^3J = 8.47$ Hz, 1 H, 5-H), 7.74 (d, $^3J = 8.47$ Hz, 1 H, 4-H), 8.09 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 9.7 (+, 3-CH₃), 14.7 (+, 7-CH₃), 51.7 (+, OCH₃), 111.5 (C_q, C-7), 112.8 (C_q, C-39), 116.0 (+, C-4), 121.8 (+, C-5), 124.1 (C_q, C-6), 124.6 (+, C-2), 130.5 (C_q, C-7a), 136.4 (C_q, C-3a), 169.2 (C_q, COOCH_3); EI (m/z): 203 (100) $[\text{M}]^+$, 172 (75), 144 (35), 105 (75), 91 (60), 57 (40); HRMS ($\text{C}_{12}\text{H}_{13}\text{NO}_2$:203.0946; found 203.0946).

Methyl 2,7-dimethyl-1*H*-indole-6-carboxylate 4{b,c}: According to GP 6 cleavage of 500 mg (399 μ mol) of 2,7-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (0.798 mmol/g) (**3{b,c}**) gave 14.7 mg (72.3 μ mol, 18%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.52 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.49 (d, $^4J = 0.76$ Hz, 3 H, 2-CH₃), 2.76 (s, 3 H, 7-CH₃), 3.90 (s, 3 H, OCH₃), 6.25 (d, $^4J = 0.76$ Hz, 1 H, 3-H), 7.35 (d, $^3J = 8.34$ Hz, 1 H, 5-H), 7.71 (d, $^3J = 8.34$ Hz, 1 H, 4-H), 8.09 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0 (+, 2-CH₃), 14.8 (+, 7-CH₃), 51.7 (+, OCH₃), 101.6 (+, C-3), 116.7 (+, C-4), 121.2 (C_q, C-7), 122.5 (+, C-5), 123.3 (C_q, C-6), 131.7 (C_q, C-3a), 136.2 (C_q, C-7a), 138.3 (C_q, C-2), 169.2 (C_q, COOCH_3); EI (m/z): 203 (100) $[\text{M}]^+$, 172 (75), 144 (35), 105 (75), 91 (60), 57 (40); HRMS ($\text{C}_{12}\text{H}_{13}\text{NO}_2$:203.0946; found 203.0952).

Methyl 2,3,7-trimethyl-1*H*-indole-6-carboxylate 4{b,d}: According to GP 6 cleavage of 500 mg (395 μ mol) of 2,3,7-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (0.790 mmol/g) (**3{b,d}**) gave 17.3 mg (79.6 μ mol, 20%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.56 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.22 (s, 3 H, 3-CH₃), 2.41 (s, 3 H, 2-CH₃), 2.74 (s, 3 H, 7-CH₃), 3.90 (s, 3 H, OCH₃), 7.31 (d, $^3J = 8.47$ Hz, 1 H, 5-H), 7.72 (d, $^3J = 8.47$ Hz, 1 H, 4-H), 7.92 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 8.5 (+, 3-CH₃), 11.9 (+, 2-CH₃), 14.8 (+, 7-CH₃), 51.6 (+, OCH₃), 108.4 (C_q, C-3), 115.0 (+, C-4), 121.2 (C_q, C-7), 122.0 (+, C-5), 123.1 (C_q, C-6), 131.8 (C_q, C-2), 134.2 (C_q, C-3a), 135.2 (C_q, C-7a), 169.3 (C_q, COOCH_3); EI (m/z): 217 (100) $[\text{M}]^+$,

186 (85), 158 (40), 105 (75), 91 (80), 71 (70), 57 (95); HRMS ($C_{13}H_{15}NO_2$:217.1103; found 217.1095).

Methyl 7-chloro-1*H*-indole-6-carboxylate (4{c,a}): According to GP 6 cleavage of 500 mg (379 μ mol) of 7-chloro-1*H*-indole-6-carboxymethyl-polystyrene (0.758 mmol/g) (**3{c,a}**) gave 4.80 mg (22.9 μ mol, 6%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.50 (cyclohexane/ethyl acetate, 3:1); 1H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3 H, OCH_3), 6.62 (dd, $^3J = 5.44$ Hz, $^4J = 0.76$ Hz, 1 H, 3-H), 7.40 (d, $^3J = 5.44$ Hz, 1 H, 2-H), 7.55 (t, $^3J = 8.33$ Hz, 1 H, 4-H), 7.72 (d, $^3J = 8.33$ Hz, 1 H, 5-H) 8.65 (bs, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.1 (+, OCH_3), 103.0 (+, C-3), 117.1 (C_q , C-6), 117.7 (+, C-4), 121.5 (C_q , C-7), 120.5 (+, C-5), 126.6 (+, C-2), 130.5 (C_q , C-3a), 133.0 (C_q , C-7a), 165.6 (C_q , $\underline{COOCH_3}$); EI (m/z): 210/208 ($[M]^+$, 20/60), 177 (100), 149 (25), 88 (10), 57 (5); HRMS ($C_{10}H_8ClNO_2$:209.0244; found 209.0248).

Methyl 7-chloro-3-methyl-1*H*-indole-6-carboxylate 4{c,b}: According to GP 6 cleavage of 500 mg (375 μ mol) of 7-chloro-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.750 mmol/g) (**3{c,b}**) gave 12.1 mg (56.6 μ mol, 15%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.53 (cyclohexane/ethyl acetate, 3:1); 1H NMR (400 MHz, $CDCl_3$) δ 2.33 (d, $^4J = 1.14$ Hz, 3 H, CH_3), 3.95 (s, 3 H, OCH_3), 7.16 (dd, $^4J = 1.14$ Hz, $^4J = 1.14$ Hz, 1 H, 2-H), 7.48 (d, $^3J = 8.34$ Hz, 1 H, 5-H), 7.71 (d, $^3J = 8.34$ Hz, 1 H, 4-H), 8.39 (bs, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9 (+, CH_3) 51.1 (+, OCH_3), 112.2 (C_q , C-3), 115.9 (+, C-4), 120.3 (C_q , C-7), 121.2 (+, C-5), 124.3 (+, C-2), 127.8 (C_q , C-6), 130.8 (C_q , C-3a), 133.3 (C_q , C-7a), 165.7 (C_q , $\underline{COOCH_3}$); EI (m/z): 225/223 $[M]^+$, 30/100), 191 (100), 177 (20), 127 (15), 57 (5); HRMS ($C_{11}H_{10}ClNO_2$: 223.0400; found 223.0404).

Methyl 7-chloro-2-methyl-1*H*-indole-6-carboxylate 4{c,c}: According to GP 6 cleavage of 500 mg (375 μ mol) of 7-chloro-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.750 mmol/g) (**3{c,c}**) gave 5.00 mg (22.4 μ mol, 6%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.47 (cyclohexane/ethyl acetate, 3:1); 1H NMR (400 MHz, $CDCl_3$) δ 2.51 (d, $^4J = 0.95$ Hz, 3 H, CH_3), 3.94 (s, 3 H, OCH_3), 6.29 (dd, $^4J = 1.14$ Hz, $^4J = 0.95$ Hz 1 H, 3-H), 7.40 (d, $^3J = 8.34$ Hz, 1 H, 4-H), 7.68 (d, $^3J = 8.34$ Hz, 1 H, 5-H), 8.35 (bs, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (+, CH_3) 52.1 (+, OCH_3), 102.1 (+, C-3), 117.3 (C_q , C-7), 117.6 (+, C-5), 120.4 (C_q , C-6), 123.2 (+, C-4), 133.0 (C_q , C-3a), 134.2 (C_q ,

C-2), 139.4 (C_q, C-7a), 166.9 (C_q, COOCH₃); EI (*m/z*): 225/223 ([M]⁺, 25/80), 191 (100), 163 (20), 127 (10), 71 (15); HRMS (C₁₁H₁₀ClNO₂: 223.0400; found 223.0403).

Methyl 7-chloro-2,3-dimethyl-1*H*-indole-6-carboxylate 4{c,d}: According to GP 6 cleavage of 500 mg (372 μmol) of 7-chloro-2,3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.743 mmol/g) (**4{c,d}**) gave 8.60 mg (36.2 μmol, 10%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.56 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 2.22 (s, 3 H, 3-CH₃), 2.42 (s, 3 H, 2-CH₃), 3.94 (s, 3 H, OCH₃), 7.36 (d, ³*J* = 8.33 Hz, 1 H, 5-H), 7.69 (d, ³*J* = 8.34 Hz, 1 H, 4-H), 8.19 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 8.6 (+, 3-CH₃), 12.0 (+, 2-CH₃), 52.1 (+, OCH₃), 109.1 (C_q, C-3), 116.0 (+, C-4), 117.2 (C_q, C-7), 120.2 (C_q, C-6), 122.6 (+, C-5), 128.5 (C_q, C-3a), 133.2 (C_q, C-2), 135.4 (C_q, C-7a), 167.0 (C_q, COOCH₃); EI (*m/z*): 239/237 ([M]⁺, 30/100), 206 (90), 177 (20), 71 (15), 57 (15); HRMS (C₁₂H₁₃ClNO₂: 237.0557; found 237.0560).

Methyl 7-bromo-1*H*-indole-6-carboxylate 4{d,a}: According to GP 6 cleavage of 500 mg (371 μmol) of 7-bromo-1*H*-indole-6-carboxymethyl-polystyrene (0.741 mmol/g) (**3{d,a}**) gave 11.7 mg (47.7 μmol, 13%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f 0.50 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 3.96 (s, 3 H, OCH₃), 6.67 (dd, ³*J* = 5.68 Hz, ⁴*J* = 1.01 Hz, 1 H, 3-H), 7.41 (dd, ³*J* = 5.68 Hz, ⁴*J* = 0.63 Hz, 1 H, 2-H), 7.59 (dd, ³*J* = 8.33 Hz, ⁴*J* = 0.63 Hz, 1 H, 4-H), 7.71 (d, ³*J* = 8.33 Hz, 1 H, 5-H) 8.71 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 52.3 (+, OCH₃), 104.2 (+, C-3), 106.4 (C_q, C-7), 115.4 (+, C-4), 119.5 (+, C-5), 123.1 (+, C-2), 130.9 (C_q, C-6), 131.2 (C_q, C-7a), 135.7 (C_q, C-3a), 167.1 (C_q, COOCH₃); EI (*m/z*): 255/253 ([M]⁺, 80/85), 222 (100), 196 (20), 140 (35), 115 (40); HRMS (C₁₀H₈BrNO₂: 252.9738; found 252.9737).

Methyl 7-bromo-3-methyl-1*H*-indole-6-carboxylate 4{d,b}: According to GP 6 cleavage of 500 mg (367 μmol) of 7-bromo-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.733 mmol/g) (**3{d,b}**) gave 12.1 mg (45.1 μmol, 12%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f 0.53 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 2.33 (d, ⁴*J* = 1.01 Hz, 3 H, CH₃), 3.95 (s, 3 H, OCH₃), 7.17 (dd, ³*J* = 3.28 Hz, ⁴*J* = 1.01 Hz, 1 H, 2-H), 7.52 (d, ³*J* = 8.21 Hz, 1 H, 5-H), 7.70 (d, ³*J* = 8.21 Hz, 1 H, 4-H), 8.39 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 9.8 (+, CH₃), 52.2 (+, OCH₃), 106.4 (C_q, C-7), 113.4 (C_q, C-3), 117.6 (+, C-4), 122.5 (+, C-5), 125.4 (+, C-2), 128.2 (C_q, C-6), 131.5 (C_q,

C-7a), 136.0 (C_q, C-3a), 167.2 (C_q, COOCH₃); EI (*m/z*): 269/267 (100/95) [M]⁺, 236 (90), 208 (15), 105 (35), 91 (30); HRMS (C₁₁H₁₀BrNO₂: 266.9895; found 266.9900).

Methyl 7-bromo-2-methyl-1*H*-indole-6-carboxylate (4{d,c}): According to GP 6 cleavage of 500 mg (367 μmol) of 7-bromo-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.733 mmol/g) (**3{d,c}**) gave 6.50 mg (24.2 μmol, 7%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.47 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 2.50 (d, ⁴*J* = 0.63 Hz, 3 H, CH₃), 3.94 (s, 3 H, OCH₃), 6.33 (dd, ⁴*J* = 1.01 Hz, ⁴*J* = 0.63 Hz, 1 H, 3-H), 7.44 (d, ³*J* = 8.21 Hz, 1 H, 4-H), 7.68 (d, ³*J* = 8.21 Hz, 1 H, 5-H), 8.37 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 14.0 (+, CH₃), 52.2 (+, OCH₃), 102.2 (+, C-3), 105.5 (C_q, C-7), 118.2 (+, C-4), 123.2 (+, C-5), 128.4 (C_q, C-6), 132.5 (C_q, C-3a), 135.8 (C_q, C-2), 139.5 (C_q, C-7a), 167.1 (C_q, COOCH₃); EI (*m/z*): 269/267 ([M]⁺, 95/90), 236 (100), 208 (15), 105 (35), 91 (30); HRMS (C₁₁H₁₀BrNO₂: 266.9895; found 266.9900).

Methyl 7-methyl-1*H*-indole-4-carboxylate (4{e,a}): According to GP 6 cleavage of 500 mg (358 μmol) of 7-methyl-1*H*-indole-4-carboxymethyl-polystyrene (0.716 mmol/g) (**3{e,a}**) gave 9.40 mg (49.7 μmol, 14%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.50 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 2.56 (s, 3 H, CH₃), 3.98 (s, 3 H, OCH₃), 7.05 (d, ³*J* = 7.05 Hz, 1 H, 3-H), 7.21 (d, ³*J* = 7.05 Hz, 1 H, 2-H), 7.36 (d, ³*J* = 7.55 Hz, 1 H, 5-H), 7.85 (d, ³*J* = 7.55 Hz, 1 H, 6-H), 8.27 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 17.1 (+, CH₃), 51.8 (+, OCH₃), 104.7 (+, C-3), 119.7 (C_q, C-3a), 122.2 (+, C-5), 124.0 (+, C-6), 125.9 (+, C-2), 126.0 (C_q, C-7), 127.1 (C_q, C-4), 136.1 (C_q, C-7a), 169.1 (C_q, COOCH₃); EI (*m/z*): 189 ([M]⁺, 35), 158 (35), 127 (10), 111 (10), 97 (15), 57 (15).

Methyl 7-bromo-2,3-dimethyl-1*H*-indole-6-carboxylate (4{d,d}): According to GP 6 cleavage of 500 mg (363 μmol) of 7-bromo-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (0.725 mmol/g) (**3{d,d}**) gave 13.6 mg (48.2 μmol, 13%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.56 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 2.21 (s, 3 H, 3-CH₃), 2.42 (s, 3 H, 2-CH₃), 3.94 (s, 3 H, OCH₃), 7.39 (d, ³*J* = 8.28 Hz, 1 H, 5-H), 7.68 (d, ³*J* = 8.28 Hz, 1 H, 4-H), 8.19 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 8.7 (+, 3-CH₃), 11.9 (+, 2-CH₃), 52.1 (+, OCH₃), 105.4 (C_q, C-3), 109.1 (C_q, C-7), 116.6 (+, C-4), 122.6 (+, C-5), 128.2 (C_q, C-6), 132.7 (C_q, C-2), 134.8 (C_q, C-3a), 135.4 (C_q, C-7a),

167.3 (C_q , $COOCH_3$); EI (m/z): 283/281 ($[M]^+$, 95/100), 252 (80), 143 (25), 105 (45), 91 (45); HRMS ($C_{12}H_{12}BrNO_2$: 281.0051; found 281.0032).

Methyl 3,7-dimethyl-1*H*-indole-4-carboxylate (4{e,b}): According to GP 6 cleavage of 500 mg (355 μ mol) of 3,7-dimethyl-1*H*-indole-4-carboxymethyl-polystyrene (0.709 mmol/g) (**3{e,b}**) gave 10.0 mg (49.2 μ mol 14%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f 0.53 (cyclohexane/ethyl acetate, 3:1); 1H NMR (400 MHz, $CDCl_3$) δ 2.43 (d, 4J = 1.32 Hz, 3 H, 2- CH_3), 2.51 (s, 3 H, 7- CH_3), 3.94 (s, 3 H, OCH_3), 7.00 (d, 3J = 7.55 Hz, 1 H, 5-H), 7.10 (d, 4J = 1.32 Hz, 1 H, 2-H), 7.59 (d, 3J = 7.55 Hz, 1 H, 6-H), 8.00 (bs, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (+, 2- CH_3), 22.8 (+, 7- CH_3), 51.8 (+, OCH_3), 113.4 (C_q , C-3), 121.8 (+, C-5), 122.1 (C_q , C-7), 123.2 (+, C-6), 124.8 (+, C-2), 125.0 (C_q , C-3a), 137.3 (C_q , C-7a), 162.1 (C_q , $\underline{COOCH_3}$); EI (m/z): 203 ($[M]^+$, 95), 179 (60), 172 (55), 148 (100), 135 (20).

Methyl 2,3,7-trimethyl-1*H*-indole-4-carboxylate (4{e,d}): According to GP 6 cleavage of 500 mg (351 μ mol) of 2,3,7-trimethyl-1*H*-indole-4-carboxymethyl-polystyrene (0.702 mmol/g) (**3{e,d}**) gave 11.6 mg (53.4 μ mol, 15%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.52 (cyclohexane/ethyl acetate, 3:1); 1H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3 H, 7- CH_3), 2.52 (d, 6 H, 2- CH_3 , 3- CH_3), 3.96 (s, 3 H, OCH_3), 6.95 (d, 3J = 7.55 Hz, 1 H, 5-H), 7.79 (d, 3J = 7.55 Hz, 1 H, 6-H), 7.97 (bs, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (+, 3- CH_3), 14.3 (+, 7- CH_3), 17.1 (+, 2- CH_3), 51.7 (+, OCH_3), 102.7 (+, C-3), 118.5 (C_q , C-7), 121.3 (+, C-5), 123.7 (+, C-6), 125.0 (C_q , C-4), 128.5 (C_q , C-3a), 136.3 (C_q , C-2), 137.3 (C_q , C-7a), 168.4 (C_q , $\underline{COOCH_3}$); EI (m/z): 217 ($[M]^+$, 10), 166 (45), 135 (100), 107 (15), 77 (20).

Methyl 7-chloro-2,3-dimethyl-1*H*-indole-4-carboxylate (4{h,d}) [1]: According to GP 6 cleavage of 500 mg (406 μ mol) of 7-chloro-2,3-dimethyl-1*H*-indole-4-carboxymethyl-polystyrene (0.812 mmol/g) (**3{h,d}**) gave 23.8 mg (100 μ mol, 25%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.60 (cyclohexane/ethyl acetate, 3:1); 1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3 H, 3- CH_3), 2.43 (s, 3 H, 2- CH_3), 3.94 (s, 3 H, OCH_3), 7.09 (d, 3J = 8.09 Hz, 1 H, 6-H), 7.51 (d, 3J = 8.09 Hz, 1 H, 5-H), 8.16 (bs, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7 (+, 3- CH_3), 12.2 (+, 2- CH_3), 52.0 (+, OCH_3), 109.4 (C_q , C-3), 119.4 (+, C-5), 119.8 (C_q , C-4), 122.1 (C_q , C-7), 123.2 (+, C-6), 128.2 (C_q , C-3a), 133.4 (C_q , C-2),

134.8 (C_q, C-7a), 168.6 (C_q, C=OCH₃); EI (*m/z*): 237 (100) [M]⁺, 222 (35), 177 (85), 105 (15), 71 (10), 57 (10); HRMS (C₁₂H₁₃ClNO₂: 237.0557; found 237.0557).

Methyl 7-methyl-1*H*-indole-5-carboxylate 4{i,a} [1]: According to GP 6 cleavage of 500 mg (147 μmol) of 7-methyl-1*H*-indole-5-carboxymethyl-polystyrene (0.294 mmol/g) (**3{i,a}**) gave 15.0 mg (79.3 μmol, 54%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.37 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (300 MHz, CDCl₃) δ 2.53 (s, 3 H, CH₃), 3.93 (s, 3 H, OCH₃), 6.65 (d, ³*J* = 3.02 Hz, 1 H, 3-H), 7.28 (d, ³*J* = 3.02 Hz, 1 H, 2-H), 7.72 (s, 1 H, 6-H) 8.28 (s, 1 H, 4-H), 8.35 (bs, 1 H, NH); ¹³C NMR (75 MHz, CDCl₃) δ 16.7 (+,CH₃), 52.0 (+,OCH₃), 104.7 (+, C-3), 120.1 (C_q, C-5), 121.8 (+, C-4), 122.2 (C_q, C-7), 123.7 (+, C-2), 125.3 (+, C-6), 127.1 (C_q, C-3a), 138.3 (C_q, C-7a), 168.5 (C_q, COOCH₃); EI (*m/z*): 189 ([M]⁺, 90), 158 (100), 130 (40), 103 (30), 77 (15).

Methyl 7-[4-(*tert*-butyl)phenyl]-1*H*-indole-6-carboxylate 4{l,a}: According to GP 6 cleavage of 500 mg (357 μmol) of 7-(4-*tert*-butylphenyl)-1*H*-indole-6-carboxymethyl-polystyrene (0.713 mmol/g) (**3{l,a}**) gave 11.6 mg (37.7 μmol, 11%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.61 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 1.40 (s, 9 H, C(CH₃)₃), 3.65 (s, 3 H, OCH₃), 6.61 (dd, ³*J* = 5.18 Hz, ⁴*J* = 2.02 Hz, 1 H, 3-H), 7.27 (d, ³*J* = 5.21 Hz, 1 H, 2-H), 7.30 (dt, ³*J* = 8.46 Hz, ⁴*J* = 2.15 Hz, 2 H, 2'/2''-H), 7.50 (dt, ³*J* = 8.46 Hz, ⁴*J* = 2.02 Hz, 2 H, 3'/3''-H), 7.64 (dd, ³*J* = 8.47 Hz, ⁴*J* = 0.63 Hz, 1 H, 4-H), 7.77 (d, ³*J* = 8.47 Hz, 1 H, 5-H), 8.15 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 31.6 (+, C(CH₃)₃), 34.8 (C_q, C(CH₃)₃), 51.7 (+, OCH), 103.2 (+, C-3), 122.1 (+, C-4), 122.7 (C_q, C-2), 125.6 (+, C-2'/2''), 127.3 (+, C-5), 128.0 (C_q, C-6), 128.6 (+, C-3'/3''), 130.5 (C_q, C-1'), 134.7 (C_q, C-7a), 135.4 (C_q, C-3a), 150.5 (C_q, C-4'), 169.0 (C_q, C=OCH₃); EI (*m/z*): 307 (100) [M]⁺, 292 (75), 220 (20), 148 (20), 97 (10), 57 (15); HRMS (C₂₀H₂₁NO₂: 307.1572; found 307.1579).

Methyl 7-[4-(*tert*-butyl)phenyl]-3-methyl-1*H*-indole-6-carboxylate 4{l,b}: According to GP 6 cleavage of 500 mg (353 μmol) of 7-(4-*tert*-butylphenyl)-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.705 mmol/g) (**4{l,b}**) gave 18.3 mg (56.9 μmol, 16%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.65 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 1.40 (s, 9 H, C(CH₃)₃), 2.63 (d, ⁴*J* = 1.08 Hz, 3 H, CH₃), 3.65 (s, 3 H, OCH₃), 7.04 (dd, ³*J* = 3.10 Hz, ⁴*J* = 1.08 Hz, 1 H, 2-H), 7.31 (dt, ³*J* = 8.34 Hz, ⁴*J* = 2.21 Hz, 2 H, 2'/2''-H), 7.49 (dt, ³*J* = 8.34 Hz, ⁴*J* = 2.21 Hz, 2 H, 3'/3''-H), 7.58

(d, $^3J = 8.40$ Hz, 1 H, 5-H), 7.77 (d, $^3J = 8.40$ Hz, 1 H, 4-H), 7.88 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 9.8 (+, CH_3), 31.6 (+, $\text{C}(\underline{\text{CH}}_3)_3$), 34.8 (C_q , $\underline{\text{C}}(\text{CH}_3)_3$), 51.7 (+, OCH_3), 112.3 (C_q , C-7), 117.6 (+, C-4), 121.5 (+, C-5), 122.6 (C_q , C-3), 124.9 (+, C-2), 125.5 (+, C-2'/2''), 127.9 (C_q , C-6), 128.6 (+, C-3'/3''), 130.7 (C_q , C-1'), 134.8 (C_q , C-4'), 135.7 (C_q , C-7a), 150.4 (C_q , C-3a), 169.1 (C_q , COOCH_3); EI (m/z): 321 (100) $[\text{M}]^+$, 306 (40), 234 (10), 138 (5), 71 (5), 57 (5); HRMS ($\text{C}_{21}\text{H}_{23}\text{NO}_2$: 321.1729; found 321.1732).

Methyl 7-[4-(*tert*-butyl)phenyl]-2-methyl-1*H*-indole-6-carboxylate (4{l,c}):

According to GP 6 cleavage of 500 mg (353 μmol) of 7-(4-*tert*-butylphenyl)-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.705 mmol/g) (**3{l,c}**) gave 7.30 mg (22.7 μmol , 6%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.68 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 1.41 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.40 (d, $^4J = 0.82$ Hz, 3 H, CH_3), 3.63 (s, 3 H, 9-H), 6.29 (dd, $^4J = 0.82$ Hz, $^4J = 0.89$ Hz, 1 H, 3-H), 7.31 (dt, $^3J = 8.40$ Hz, $^4J = 2.24$ Hz, 2 H, 2'/2''-H), 7.50 (dt, $^3J = 8.40$ Hz, $^4J = 2.24$ Hz, 2 H, 3'/3''-H), 7.50 (d, $^3J = 8.34$ Hz, 1 H, 5-H), 7.73 (d, $^3J = 8.34$ Hz, 1 H, 4-H), 7.81 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0 (+, CH_3), 31.6 (+, $\text{C}(\underline{\text{CH}}_3)_3$), 34.8 (C_q , $\underline{\text{C}}(\text{CH}_3)_3$), 51.6 (+, OCH_3), 101.3 (+, C-3), 118.2 (+, C-4), 121.6 (C_q , C-7), 122.2 (C_q , C-5), 125.5 (+, C-2'/2''), 127.2 (C_q , C-6), 128.6 (+, C-3'/3''), 131.8 (C_q , C-1'), 135.0 (C_q , C-2), 135.5 (C_q , C-7a), 138.8 (C_q , C-3a), 150.3 (C_q , C-4'), 169.0 (C_q , $\underline{\text{COOCH}}_3$); EI (m/z): 321 (100) $[\text{M}]^+$, 306 (40), 237 (85), 206 (70), 191 (70), 148 (25), 57 (15); HRMS ($\text{C}_{21}\text{H}_{23}\text{NO}_2$: 321.1729; found 321.1732).

Methyl 7-[4-(*tert*-butyl)phenyl]-2,3-dimethyl-1*H*-indole-6-carboxylate (4{l,d}):

According to GP 6 cleavage of 500 mg (349 μmol) of 7-(4-*tert*-butylphenyl)-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (0.698 mmol/g) (**3{l,d}**) gave 12.4 mg (37.0 μmol , 11%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.66 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 1.29 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.22 (s, 3 H, 3- CH_3), 2.42 (s, 3 H, 2- CH_3), 3.94 (s, 3 H, OCH_3), 6.77 (dt, $^3J = 8.71$ Hz, $^4J = 2.15$ Hz, 2 H, 2'/2''-H), 7.24 (dt, $^3J = 8.71$ Hz, $^4J = 2.15$ Hz, 2 H, 3'/3''-H), 7.39 (d, $^3J = 8.28$ Hz, 1 H, 5-H), 7.69 (d, $^3J = 8.28$ Hz, 1 H, 4-H), 8.20 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 8.7 (+, 3- CH_3), 12.0 (+, 2- CH_3), 31.7 (+, $\text{C}(\underline{\text{CH}}_3)_3$), 34.2 (C_q , $\underline{\text{C}}(\text{CH}_3)_3$), 52.2 (+, OCH_3), 105.4 (C_q , C-7), 109.2 (C_q , C-3), 114.9 (+, C-4), 116.6 (+, C-2'/2''), 121.9 (C_q , C-6), 122.7 (+, C-3'/3''), 126.5 (+, C-5), 132.8 (C_q , C-2), 134.8 (C_q , C-1'), 135.4 (C_q , C-7a), 143.6 (C_q ,

C-4'), 153.4 (C_q, C-3a), 169.0 (C_q, COOCH₃); EI (*m/z*): 335 ([M]⁺, 5), 281 (100), 250 (80), 222 (20), 143 (50), 135 (30); HRMS (C₂₂H₂₅NO₂: 335.1885; found 335.1889).

Methyl 7-[(4-methoxyphenyl)ethynyl]-1*H*-indole-6-carboxylate (4{n,a}):

According to GP 6 cleavage of 500 mg (357 μmol) of 7-[(4-methoxyphenyl)ethynyl]-1*H*-indole-6-carboxymethyl-polystyrene (0.714 mmol/g) (**3{n,a}**) gave 16.0 mg (52.4 μmol, 15%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.35 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 3.85 (s, 3 H, PhOCH₃), 3.98 (s, 3 H, COOCH₃), 6.62 (d, ³*J* = 3.15 Hz, 1 H, 3-H), 6.91 (dt, ³*J* = 8.94 Hz, ⁴*J* = 2.14 Hz, 2 H, 3'/3''-H), 7.41 (d, ³*J* = 3.15 Hz, 1 H, 2-H), 7.58 (dt, ³*J* = 8.94 Hz, ⁴*J* = 2.14 Hz, 2 H, 2'/2''-H), 7.63 (d, ³*J* = 8.43 Hz, 1 H, 4-H), 7.82 (d, ³*J* = 8.43 Hz, 1 H, 5-H), 8.79 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 52.1 (+, COOCH₃), 55.5 (+, PhOCH₃), 83.4 (C_q, C≡CPhOCH₃), 98.9 (C_q, C≡CPhOCH₃), 103.8 (+, C-3), 108.5 (C_q, C-7), 114.3 (+, C-3'/3''), 115.5 (C_q, C-1'), 120.2 (+, C-4), 122.3 (+, C-3), 124.6 (C_q, C-6), 127.3 (+, C-5), 130.1 (C_q, C-3a), 133.4 (+, C-2'/2''), 137.3 (C_q, C-7a), 160.1 (C_q, C-4'), 167.5 (C_q, COOCH₃); EI (*m/z*): 303 (100) [M]⁺, 247 (60), 175 (45), 144 (45), 97 (25), 71 (20), 57 (40).

Methyl 7-[(4-methoxyphenyl)ethynyl]-3-methyl-1*H*-indole-6-carboxylate 4{n,b}:

According to GP 6 cleavage of 500 mg (353 μmol) of 7-[(4-methoxyphenyl)ethynyl]-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.706 mmol/g) (**4{n,b}**) gave 19.0 mg (59.5 μmol, 17%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); *R*_f: 0.35 (cyclohexane/ethyl acetate, 3:1); ¹H NMR (400 MHz, CDCl₃) δ 2.35 (s, 3 H, CH₃), 3.85 (s, 3 H, PhOCH₃), 3.98 (s, 3 H, COOCH₃), 6.91 (dt, ³*J* = 9.45 Hz, ⁴*J* = 2.64 Hz, 2 H, 3'/3''-H), 7.17 (d, ⁴*J* = 0.88 Hz, 1 H, 2-H), 7.55 (d, ³*J* = 8.43 Hz, 1 H, 5-H), 7.58 (dt, ³*J* = 9.45 Hz, ⁴*J* = 2.64 Hz, 2 H, 2'/2''-H), 7.81 (d, ³*J* = 8.43 Hz, 1 H, 4-H), 8.52 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 9.8 (+, CH₃), 52.1 (+, COOCH₃), 55.5 (+, PhOCH₃), 83.5 (C_q, C≡CPhOCH₃), 98.7 (C_q, C≡CPhOCH₃), 113.0 (C_q, C-7), 114.2 (+, C-3), 115.6 (C_q, C-1'), 118.4 (+, C-3'/3''), 121.6 (+, C-4), 124.4 (+, C-2), 124.9 (+, C-5), 130.4 (C_q, C-6), 133.4 (+, C-2'/2''), 137.7 (C_q, C-7a), 138.4 (C_q, C-3a), 160.1 (C_q, C-4'), 167.7 (C_q, COOCH₃); EI (*m/z*): 318 ([M - H]⁺, 5), 303 (100), 247 (50), 189 (20), 97 (15), 71 (10), 57 (20); HRMS (C₂₀H₁₇NO₃: 319.1208; found 319.1213).

Methyl 7-[(4-methoxyphenyl)ethynyl]-2-methyl-1*H*-indole-6-carboxylate (4{n,c}):

According to GP 6 cleavage of 500 mg (353 μmol) of 7-[(4-methoxyphenyl)ethynyl]-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.706 mmol/g) (**3{n,c}**) gave 23.0 mg

(72.0 μmol , 20%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.33 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.52 (s, 3 H, CH_3), 3.84 (s, 3 H, PhOCH_3), 3.96 (s, 3 H, COOCH_3), 6.28 (d, $^4J = 1.01$ Hz, 1 H, 3-H), 6.91 (dt, $^3J = 8.81$ Hz, $^4J = 2.65$ Hz, 2 H, 3'/3''-H), 7.47 (d, $^3J = 8.31$ Hz, 1 H, 5-H), 7.50 (dt, $^3J = 8.81$ Hz, $^4J = 2.65$ Hz, 2 H, 2'/2''-H), 7.78 (d, $^3J = 8.31$ Hz, 1 H, 4-H), 8.48 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1 (+, CH_3), 52.0 (+, COOCH_3), 55.5 (+, PhOCH_3), 83.5 (C_q , $\text{C}\equiv\text{CPhOCH}_3$), 98.9 (C_q , $\text{C}\equiv\text{CPhOCH}_3$), 101.7 (+, C-3), 107.4 (C_q , C-7), 114.2 (+, C-3'/3''), 115.6 (C_q , C-1'), 119.0 (+, C-4), 122.3 (+, C-5), 123.1 (C_q , C-6), 131.4 (C_q , C-3a), 133.4 (+, C-2'/2''), 137.6 (C_q , C-2), 138.9 (C_q , C-7a), 160.0 (C_q , C-4'), 167.6 (C_q , COOCH_3); EI (m/z): 319 ($[\text{M}]^+$, 15), 303 (20), 247 (20), 189 (100), 97 (25), 57 (20); HRMS ($\text{C}_{20}\text{H}_{17}\text{NO}_3$: 319.1208; found 319.1213).

Methyl 7-[(4-methoxyphenyl)ethynyl]-2,3-dimethyl-1H-indole-6-carboxylate (4{n,d}): According to GP 6 cleavage of 500 mg (350 μmol) of 7-[(4-methoxyphenyl)ethynyl]-2,3-dimethyl-1H-indole-6-carboxymethyl-polystyrene (0.699 mmol/g) (**3{n,d}**) gave 15.8 mg (47.4 μmol , 14%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.35 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.24 (s, 3 H, 3- CH_3), 2.44 (s, 3 H, 2- CH_3), 3.85 (s, 3 H, PhOCH_3), 3.96 (s, 3 H, COOCH_3), 6.92 (dt, $^3J = 8.81$ Hz, $^4J = 2.01$ Hz, 2 H, 3'/3''-H), 7.43 (d, $^3J = 8.43$ Hz, 1 H, 5-H), 7.59 (dt, $^3J = 8.81$ Hz, $^4J = 2.01$ Hz, 2 H, 2'/2''-H), 7.78 (d, $^3J = 8.43$ Hz, 1 H, 4-H), 8.28 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 8.6 (+, 3- CH_3), 12.0 (+, 2- CH_3), 52.0 (+, COOCH_3), 55.5 (+, PhOCH_3), 83.7 (C_q , $\text{C}\equiv\text{CPhOCH}_3$), 98.2 (C_q , $\text{C}\equiv\text{CPhOCH}_3$), 107.1 (C_q , C-7), 108.7 (C_q , C-3), 114.2 (+, C-3'/3''), 115.7 (C_q , C-1'), 117.4 (+, C-4), 121.7 (+, C-5), 123.3 (C_q , C-6), 131.6 (C_q , C-2), 133.4 (+, C-2'/2''), 134.7 (C_q , C-7a), 136.7 (C_q , C-3a), 147.0 (C_q , C-4'), 160.0 (C_q , COOCH_3); EI (m/z): 333 ($[\text{M}]^+$, 5), 303 (100), 247 (20), 191 (5), 111 (5), 97 (5), 57 (5).

Methyl 7-vinyl-1H-indole-6-carboxylate (4{m,a}): According to GP 6 cleavage of 500 mg (386 μmol) of 7-vinyl-1H-indole-6-carboxymethyl-polystyrene (0.771 mmol/g) (**3{m,a}**) gave 14.6 mg (72.6 μmol , 19%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.38 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 3.91 (s, 3 H, OCH_3), 5.66 (dd, $^3J = 11.45$ Hz, 2 H, CH_2), 6.60 (d, $^3J = 5.29$ Hz, $^4J = 2.14$ Hz, 1 H, 3-H), 7.36 (d, $^3J = 5.22$ Hz, 1 H, 2-H), 7.50 (d, $^3J = 11.45$ Hz, 1 H, $\text{CH}_{\text{aliph.}}$), 7.56 (d, $^3J = 8.44$ Hz, 1 H,

5-H), 7.78 (d, $^3J = 8.44$ Hz, 1 H, 4-H), 8.73 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 51.9 (+, OCH_3), 103.4 (+, C-3), 117.4 (–, CH_2), 119.4 (+, C-5), 121.2 (C_q , C-7), 122.1 (+, C-4), 125.7 (C_q , C-6), 127.4 (+, C-2), 131.2 (C_q , C-7a), 134.0 (+, C-3a), 135.3 (+, $\text{CH}_{\text{aliph.}}$), 168.4 (C_q , COOCH_3); EI (m/z): 201 (100) $[\text{M}]^+$, 170 (60), 141 (20), 115 (15), 89 (5), 57 (5); HRMS ($\text{C}_{12}\text{H}_{11}\text{NO}_2$: 201.0790; found 201.0788).

Methyl 7-vinyl-3-methyl-1*H*-indole-6-carboxylate (4{m,b}): According to GP 6 cleavage of 500 mg (382 μmol) of 7-vinyl-3-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.763 mmol/g) (**4{m,b}**) gave 13.1 mg (60.9 μmol , 16%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.42 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.35 (s, 3 H, CH_3), 3.91 (s, 3 H, OCH_3), 5.63 (dd, $^3J = 11.45$ Hz, 2 H, CH_2), 7.13 (dd, $^3J = 3.40$ Hz, $^4J = 1.13$ Hz, 1 H, 2-H), 7.48 (dt, $^3J = 11.45$ Hz, 1 H, $\text{CH}_{\text{aliph.}}$), 7.49 (d, $^3J = 8.44$ Hz, 1 H, 5-H), 7.77 (d, $^3J = 8.44$ Hz, 1 H, 4-H), 8.45 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 9.7 (+, CH_3), 51.9 (+, OCH_3), 112.5 (C_q , C-3), 117.3 (–, CH_2), 117.5 (+, C-4), 121.0 (C_q , C-7), 121.5 (+, C-5), 125.1 (+, C-2), 125.5 (C_q , C-6), 131.4 (C_q , C-7a), 134.4 (C_q , C-3a), 135.2 (+, $\text{CH}_{\text{aliph.}}$), 168.5 (C_q , COOCH_3); EI (m/z): 215 (100) $[\text{M}]^+$, 184 (50), 154 (15), 97 (5), 77 (5), 57 (5); HRMS ($\text{C}_{13}\text{H}_{13}\text{NO}_2$: 215.0946; found 215.0950).

Methyl 7-vinyl-2-methyl-1*H*-indole-6-carboxylate (4{m,c}): According to GP 6 cleavage of 500 mg (382 μmol) of 7-vinyl-2-methyl-1*H*-indole-6-carboxymethyl-polystyrene (0.763 mmol/g) (**3{m,c}**) gave 13.2 mg (61.3 μmol , 16%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.44 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.48 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 5.64 (dd, $^3J = 11.46$ Hz, 2 H, CH_2), 6.27 (d, $^4J = 1.26$ Hz, 1 H, 3-H), 7.41 (t, $^3J = 8.43$ Hz, 1 H, 5-H), 7.47 (dd, $^3J = 11.46$ Hz, 1 H, $\text{CH}_{\text{aliph.}}$), 7.74 (d, $^3J = 8.43$ Hz, 1 H, 4-H), 8.40 (bs, 1 H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1 (+, CH_3), 51.8 (+, OCH_3), 101.5 (+, C-3), 117.1 (–, CH_2), 118.2 (+, C-4), 120.0 (C_q , C-7), 122.2 (+, C-5), 124.9 (C_q , C-6), 132.6 (C_q , C-2), 134.1 (C_q , C-7a), 135.5 (+, $\text{CH}_{\text{aliph.}}$), 138.8 (C_q , C-3a), 168.5 (C_q , COOCH_3); EI (m/z): 215 (100) $[\text{M}]^+$, 184 (50), 154 (15), 97 (5), 77 (5), 57 (5).

Methyl 7-vinyl-2,3-dimethyl-1*H*-indole-6-carboxylate (4{m,d}): According to GP 6 cleavage of 500 mg (377 μmol) of 7-vinyl-2,3-dimethyl-1*H*-indole-6-carboxymethyl-polystyrene (0.754 mmol/g) (**3{m,d}**) gave 15.0 mg (65.4 μmol , 17%) of the product as a pale yellow solid after preparative TLC (cyclohexane/ethyl acetate, 3:1); R_f : 0.44 (cyclohexane/ethyl acetate, 3:1); ^1H NMR (400 MHz, CDCl_3) δ 2.23 (s, 3 H, 3- CH_3),

2.40 (s, 3 H, 2-CH₃), 3.89 (s, 3 H, OCH₃), 5.64 (dd, ³J = 11.46 Hz, 2 H, CH₂), 7.37 (d, ³J = 8.44 Hz, 1 H, 4-H), 7.46 (dd, ³J = 11.46 Hz, 1 H, CH_{aliph.}), 7.74 (d, ³J = 8.44 Hz, 1 H, 5-H), 8.24 (bs, 1 H, NH); ¹³C NMR (100 MHz, CDCl₃) δ 7.4 (+, 3-CH₃), 10.8 (+, 2-CH₃), 50.6 (+, OCH₃), 107.2 (C_q, C-3), 115.4 (–, CH₂), 115.9 (+, C-4), 118.8 (C_q, C-6), 120.4 (+, C-5), 123.5 (C_q, C-7), 127.8 (C_q, C-2), 131.5 (C_q, C-7a), 133.7 (C_q, C-3a), 134.4 (+, CH_{aliph.}), 167.5 (C_q, COOCH₃); EI (*m/z*): 229 ([M]⁺, 95), 198 (45), 149 (30), 127 (25), 97 (5), 57 (5).

References

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