An efficient catalyst for Pd-catalyzed carbonylation of aryl arenesulfonates

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Part A: Typical Experimental Procedures

General

All chemicals except aryl p-fluorobenzenesulfonates were obtained from commercial sources and used without further purification. The ferrocenyl phosphine ligands were purchased from Solvias AG. Aryl p-fluorobenzenesulfonates were prepared from the corresponding phenols and p-fluorobenzenesulfonyl chloride according to the procedure in reference 4. Anhydrous solvents were used as were purchased without further distillation throughout the entire experiment. Reactions were analyzed by reversed phase HPLC, conducted on an Agilent 1100 Series instrument with DAD using a 96-well plate auto sampler. NMR experiments were conducted on a Bruker NMR (400 or 500 MHz) instrument.

Milligram-scale screening procedure

Symyx Technology's software and hardware were used to conduct the entire milligram-scale screening experiments from library design, liquid and solid dispense, reaction heating and agitation, to HPLC analysis (<http://www.symyx.com>). The 96-well reactor block has the capacity to run 96 milligram-scale reactions in parallel. For all milligram-scale reactions, most pipetting jobs were conducted by the Cavo robot. An organic substance was usually charged as a stock solution, and an inorganic base was dispensed as slurry, usually in dichloroethane suspension. Solid dispense by PowderNium robot was used in some cases. In a typical screening procedure, under a N₂ atmosphere, a reactor block containing 96 disposable glass reaction vials (40 mm height × 8 mm diameter) was dispensed with ligands (0.44 or 0.80 μmol) and Pd(OAc)₂ (0.4 μmol, 4 mol% Pd loading relative to p-tolyl p-fluorobenzenesulfonate), and aged at room temperature for ~1 h. A ligand-to-palladium ratio of 1.1 was employed for a bidentate ligand, and 2.0 for a monodentate ligand. Ligands and Pd(OAc)₂ were dissolved in a 1:1 toluene/dichloroethane mixture. p-Tolyl p-fluorobenzenesulfonate (2.66 mg, 10 μmol) and base (2.0 equivs) were then dispensed. The reaction mixture was concentrated down in vacuum to remove all unwanted solvents from stock solutions (or slurries) prior to the addition of solvents (200 μL) to be screened. The reactor block was then sealed, leak tested, and purged first by 3 times of 40 psi N₂, followed by 3 times 40 psi CO before it was pressurized to 90 psi CO. The reactor block was agitated and heated at desired temperature for certain hours. An internal standard (4,4-dimethylbiphenyl) was added to the reaction mixture for the calculations of HPLC assay yields.

Gram-scale autoclave procedure

To a 50 mL autoclave were charged with an aryl arenesulfonate (~1.0 g, 4 mmol), NaOAc (0.7 g, 8 mmol), and 20 mL EtOH (~100 ppm water content). The reaction mixture was then mechanically stirred at 200 rpm and degassed with 40 psi N₂ three times. Under a N₂ atmosphere, Pd(OAc)₂ (36 mg, 0.16 mmol), Josiphos Et₂P-Fc-PtBu₂ (90 mg, 0.17 mmol) and 2 mL DCE were added to an 8 mL vial, and aged at room temperature for more than 1 hour. The catalyst solution was added to the autoclave, and

the vessel was purged with 40 psi CO three times, and then pressurized with 90 psi CO. The reaction mixture was stirred at 1000 rpm while heating to 130 °C over 30 minutes. The reaction was aged at 130 °C overnight. After completion, the reaction mixture was first filtered to remove inorganic solid, then concentrated to remove solvents. The residue was subjected to flash chromatography on silica gel to purify the product.

Part B: Reaction Kinetic Profile

The reaction progress can be monitored by in situ IR. A Mettler Toledo MultiMax ReactIR instrument was used for this task. An example of reaction kinetic profile is plotted in Figure 1. The initial temperature profile was indicated in the plot. The reaction did not proceed at an appreciable rate at temperatures below 120 °C.

Figure 1. Carbonyl absorbance of 1-heptyl 4-methylbenzoate vs. reaction time at 1722 cm^{-1} . Reaction temperature was ramped from r.t. to 100 °C in 15 min, held for 20 min; then to 110 °C in 5 min, held for 1 h; then to 120 °C in 5 min, held for 10 min; then to 125 °C in 5 min. Other conditions same as Table 1. The data was recorded by subtracting baseline absorbance at 1706 cm^{-1} .

Part C: Analytical Data

1-heptyl 4-methylbenzoate (1): ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, 2H, $J = 8.4$), 7.24 (d, 2H, $J = 8.1$), 4.31 (t, 2H, $J = 6.7$), 2.42 (s, 3H), 1.77 (p, 2H, $J = 7.0$), 1.27-1.48 (m, 8H), 0.90 (t, 3H, $J = 6.7$); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 143.6, 129.8, 129.2, 128.0, 65.2, 32.0, 29.2, 29.0, 26.2, 22.8, 21.8, 14.3; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd 235.16926, found 235.17031.

ethyl 4-methylbenzoate (2): ^1H NMR (400 MHz, CDCl_3): δ 7.94 (dt, 2H, $J = 8.4$, 2.0), 7.23 (d, 2H, $J = 8.8$), 4.36 (q, 2H, $J = 7.1$), 2.40 (s, 3H), 1.39 (t, 3H, $J = 7.2$); ^{13}C NMR (100 MHz, CDCl_3): δ 166.8, 143.5, 129.7, 129.1, 128.0, 60.8, 21.7, 14.5.

ethyl 4-acetobenzoate (3): ^1H NMR (400 MHz, CDCl_3): δ 8.13 (d, 2H, $J = 8.4$), 8.00 (d, 2H, $J = 8.4$), 4.41 (q, 2H, $J = 7.1$), 2.65 (s, 3H), 1.42 (t, 3H, $J = 7.2$); ^{13}C NMR (100 MHz, CDCl_3): δ 197.7, 165.9, 140.4, 134.5, 130.0, 128.4, 61.7, 27.1, 14.5.

ethyl benzoate (4): ^1H NMR (400 MHz, CDCl_3): δ 8.06 (dd, 2H, $J = 8.8$, 1.6), 7.56 (tt, 1H, $J = 7.4$, 1.2), 7.44 (t, 2H, $J = 7.6$), 4.39 (q, 2H, $J = 7.1$), 1.41 (t, 3H, $J = 7.1$); ^{13}C NMR (100 MHz, CDCl_3): δ 166.9, 133.0, 130.7, 129.7, 128.5, 61.1, 14.5.

ethyl 2-methylbenzoate (5): ^1H NMR (400 MHz, CDCl_3): δ 7.92 (dd, 1H, $J = 8.4$, 2.0), 7.40 (dt, 1H, $J = 7.4$, 1.6), 7.25 (m, 2H), 4.37 (q, 2H, $J = 7.1$), 2.61 (s, 3H), 1.41 (t, 3H, $J = 7.0$); ^{13}C NMR (100 MHz, CDCl_3): δ 167.9, 140.2, 132.0, 131.8, 130.7, 130.2, 125.9, 60.9, 21.9, 14.5.

ethyl 4-methoxybenzoate (6): ^1H NMR (400 MHz, CDCl_3): δ 8.00 (dt, 2H, $J = 8.8, 2.0$), 6.92 (dt, 2H, $J = 8.4, 2.0$), 4.35 (q, 2H, $J = 7.1$), 3.86 (s, 3H), 1.38 (t, 3H, 7.2); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 163.5, 131.7, 123.2, 113.7, 60.8, 55.6, 14.6.

ethyl 2-methoxybenzoate (7): ^1H NMR (400 MHz, CDCl_3): δ 7.78 (dd, 1H, $J = 8.0, 1.8$), 7.45 (ddd, 1H, $J = 7.8, 7.2, 2.0$), 6.97 (m, 2H), 4.36 (q, 2H, $J = 7.2$), 3.90 (s, 3H), 1.38 (t, 3H, $J = 7.0$); ^{13}C NMR (100 MHz, CDCl_3): δ 166.4, 159.3, 133.5, 131.6, 120.7, 120.3, 112.2, 60.9, 56.1, 14.5.

ethyl 2-cyanobenzoate (8): ^1H NMR (400 MHz, CDCl_3): δ 8.11 (dd, 1H, $J = 6.8, 2.0$), 7.77 (dd, 1H, $J = 7.2, 2.0$), 7.65 (m, 2H), 4.44 (q, 2H, $J = 7.2$), 1.42 (t, 3H, $J = 7.0$); ^{13}C NMR (100 MHz, CDCl_3): δ 164.1, 134.8, 132.8, 132.7, 132.6, 131.2, 117.6, 113.0, 62.3, 14.2.

ethyl 4-chlorobenzoate (9): ^1H NMR (400 MHz, CDCl_3): δ 7.96 (dt, 2H, $J = 8.8, 2.0$), 7.39 (dt, 2H, $J = 8.8, 2.0$), 4.36 (q, 2H, $J = 7.2$), 1.38 (t, 3H, $J = 7.0$); ^{13}C NMR (100 MHz, CDCl_3): δ 165.9, 139.4, 131.1, 129.1, 128.8, 61.3, 14.4.

diethyl terephthalate (10): ^1H NMR (400 MHz, CDCl_3): δ 8.10 (s, 4H), 4.41 (q, 4H, $J = 7.3$), 1.41 (t, 6H, $J = 7.0$); ^{13}C NMR (100 MHz, CDCl_3): δ 166.0, 134.4, 129.7, 61.6, 14.5.

ethyl 4-fluorobenzoate (11): ^1H NMR (400 MHz, CDCl_3): δ 8.05 (dd, 2H, $J = 8.8, 5.4$), 7.10 (tt, 2H, $J = 8.6, 1.8$), 4.37 (q, 2H, $J = 7.1$), 1.39 (t, 3H, $J = 7.0$); ^{13}C NMR (100 MHz, CDCl_3): δ 165.9 (d, $J_{\text{C-F}} = 253.4$), 165.8, 132.2 (d, $J_{\text{C-F}} = 9.4$), 126.9 (d, $J_{\text{C-F}} = 2.9$), 115.6 (d, $J_{\text{C-F}} = 22.1$), 61.2, 14.5.

ethyl nicotinate (12): ^1H NMR (400 MHz, CDCl_3): δ 9.17 (d, 1H, $J = 1.6$), 8.71 (dd, 1H, $J = 4.8, 1.6$), 8.24 (dt, 1H, $J = 8.4, 2.4$), 7.33 (ddd, 1H, $J = 8.0, 4.8, 0.8$), 4.36 (q, 2H, $J = 7.1$), 1.35 (t, 3H, $J = 7.2$); ^{13}C NMR (100 MHz, CDCl_3): δ 165.3, 153.4, 150.9, 137.1, 126.4, 123.3, 61.5, 14.3.

ethyl 4-cyanomethylbenzoate (13): ^1H NMR (400 MHz, CDCl_3): δ 8.06 (dt, 2H, $J = 8.4, 2.0$), 7.42 (dd, 2H, $J = 8.0, 0.8$), 4.39 (q, 2H, $J = 7.2$), 3.82 (s, 2H), 1.41 (t, 3H, $J = 7.1$); ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 134.9, 130.7, 130.6, 128.1, 117.3, 61.4, 23.9, 14.5.

4-acetylphenyl 4-fluorobenzenesulfonate (14): ^1H NMR (400 MHz, CDCl_3): δ 7.93 (m, 4H), 7.23 (m, 2H), 7.11 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 196.7, 166.4 (d, $J_{\text{C-F}} = 258.2$), 152.9, 136.1, 131.6 (d, $J_{\text{C-F}} = 9.7$), 131.3 (d, $J_{\text{C-F}} = 3.3$), 130.3, 122.6, 117.0 (d, $J_{\text{C-F}} = 22.7$), 26.8.

phenyl 4-fluorobenzenesulfonate (15): ^1H NMR (400 MHz, CDCl_3): δ 7.85 (m, 2H), 7.30 (m, 3H), 7.20 (m, 2H), 6.99 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.2 (d, $J_{\text{C-F}} = 257.1$), 149.7, 131.6 (d, $J_{\text{C-F}} = 3.5$), 131.6 (d, $J_{\text{C-F}} = 9.6$), 129.9, 127.5, 122.5, 116.7 (d, $J_{\text{C-F}} = 22.6$).

4-methylphenyl 4-fluorobenzenesulfonate (16): ^1H NMR (400 MHz, CDCl_3): δ 7.84 (m, 2H), 7.21 (m, 2H), 7.13 (m, 2H), 6.86 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.2 (d, $J_{\text{C-F}} = 257.0$), 147.5, 137.4, 131.6 (d, $J_{\text{C-F}} = 4.0$), 131.5 (d, $J_{\text{C-F}} = 9.6$), 130.4, 122.2, 116.7 (d, $J_{\text{C-F}} = 22.9$), 21.1.

2-methylphenyl 4-fluorobenzenesulfonate (17): ^1H NMR (500 MHz, CDCl_3): δ 7.91 (m, 2H), 7.19 (m, 5H), 7.01 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.2 (d, $J_{\text{C-F}} = 257.3$), 148.4, 132.4 (d, $J_{\text{C-F}} = 3.3$), 131.9, 131.7, 131.5 (d, $J_{\text{C-F}} = 9.6$), 127.4, 127.2, 122.4, 116.8 (d, $J_{\text{C-F}} = 23.6$), 16.5.

4-methoxyphenyl 4-fluorobenzenesulfonate (18): ^1H NMR (400 MHz, CDCl_3): δ 7.83 (m, 2H), 7.21 (m, 2H), 6.89 (m, 2H), 6.79 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.2 (d, $J_{\text{C-F}} = 257.2$), 158.6, 143.1, 131.6 (d, $J_{\text{C-F}} = 9.7$), 131.5 (d, $J_{\text{C-F}} = 3.4$), 123.5, 116.7 (d, $J_{\text{C-F}} = 22.8$), 114.8, 55.8.

2-methoxyphenyl 4-fluorobenzenesulfonate (19): ^1H NMR (500 MHz, CDCl_3): δ 7.91 (m, 2H), 7.22 (m, 4H), 6.93 (m, 1H), 6.86 (d, 1H, $J = 8.1$), 3.56 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.1 (d, $J_{\text{C-F}} = 256.7$), 151.8, 138.4, 132.5 (d, $J_{\text{C-F}} = 3.2$), 131.7 (d, $J_{\text{C-F}} = 9.5$), 128.5, 124.4, 121.0, 116.2 (d, $J_{\text{C-F}} = 22.7$), 112.9, 55.7; HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd 283.04348, found 235.04386.

2-cyanophenyl 4-fluorobenzenesulfonate (20): ^1H NMR (500 MHz, CDCl_3): δ 8.00 (m, 2H), 7.68 (m, 1H), 7.62 (m, 1H), 7.55 (m, 1H), 7.43 (m, 1H), 7.28 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.8 (d, $J_{\text{C-F}} = 258.7$), 150.2, 134.6, 134.0, 132.0 (d, $J_{\text{C-F}} = 9.9$), 130.7 (d, $J_{\text{C-F}} = 3.2$), 127.8, 124.1, 117.1 (d, $J_{\text{C-F}} = 22.9$), 114.5, 107.9.

4-chlorophenyl 4-fluorobenzenesulfonate (21): ^1H NMR (400 MHz, CDCl_3): δ 7.86 (m, 2H), 7.25 (m, 4H), 6.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.4 (d, $J_{\text{C-F}} = 258.0$), 148.1, 133.3, 131.7 (d, $J_{\text{C-F}} = 9.8$), 131.6 (d, $J_{\text{C-F}} = 4.0$), 130.1, 123.9, 116.9 (d, $J_{\text{C-F}} = 22.7$).

4-fluorophenyl 4-fluorobenzenesulfonate (22): ^1H NMR (500 MHz, CDCl_3): δ 7.86 (m, 2H), 7.24 (m, 2H), 6.99 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.3 (d, $J_{\text{C-F}} = 257.8$), 161.4 (d, $J_{\text{C-F}} = 247.1$), 145.4 (d, $J_{\text{C-F}} = 2.9$), 131.7 (d, $J_{\text{C-F}} = 9.7$), 131.3 (d, $J_{\text{C-F}} = 3.2$), 124.2 (d, $J_{\text{C-F}} = 8.7$), 116.9 (d, $J_{\text{C-F}} = 22.8$), 116.7 (d, $J_{\text{C-F}} = 23.7$).

pyridin-3-yl 4-fluorobenzenesulfonate (23): ^1H NMR (400 MHz, CDCl_3): δ 8.52 (m, 1H), 8.19 (d, $J = 2.5$ Hz, 1H), 7.87 (m, 2H), 7.48 (m, 1H), 7.32 (m, 1H), 7.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.5 (d, $J_{\text{C-F}} = 258.7$), 148.7, 146.5, 144.1, 131.6 (d, $J_{\text{C-F}} = 9.7$), 130.9 (d, $J_{\text{C-F}} = 3.3$), 130.3, 124.5, 117.1 (d, $J_{\text{C-F}} = 22.8$).

4-methylphenyl 4-methylbenzenesulfonate (24): ^1H NMR (400 MHz, CDCl_3): δ 7.71 (m, 2H), 7.31 (m, 2H), 7.07 (m, 2H), 6.86 (m, 2H), 2.46 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 147.7, 145.4, 137.1, 132.8, 130.3, 129.9, 128.8, 122.3, 21.9, 21.1.

Part D: Spectroscopic Data

1-heptyl 4-methylbenzoate (1)

1-heptyl 4-methylbenzoate (1)

ethyl 4-methylbenzoate (2)

ethyl 4-methylbenzoate (2)

ethyl 4-acetobenzoate (3)

ethyl 4-acetobenzoate (3)

ethyl benzoate (4)

ethyl benzoate (4)

ethyl 2-methylbenzoate (5)

ethyl 2-methylbenzoate (5)

ethyl 4-methoxybenzoate (6)

ethyl 4-methoxybenzoate (6)

ethyl 2-methoxybenzoate (7)

ethyl 2-methoxybenzoate (7)

ethyl 2-cyanobenzoate (8)

ethyl 2-cyanobenzoate (8)

ethyl 4-chlorobenzoate (9)

ethyl 4-chlorobenzoate (9)

diethyl terephthalate (10)

diethyl terephthalate (10)

ethyl 4-fluorobenzoate (11)

ethyl 4-fluorobenzoate (11)

ethyl nicotinate (12)

ethyl nicotinate (12)

ethyl 4-cyanomethylbenzoate (13)

ethyl 4-cyanomethylbenzoate (13)

4-acetylphenyl 4-fluorobenzenesulfonate (14)

4-acetylphenyl 4-fluorobenzenesulfonate (14)

phenyl 4-fluorobenzenesulfonate (15)

Current Data Parameters
NAME 89451-177
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6561.680 Hz
FIDRES 0.200247 Hz
AQ 2.4969716 sec
RG 256
DW 76.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -5.00 dB
SFO1 400.1322007 MHz

F2 - Processing parameters
SI 16384
SF 400.1300056 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

nmr400c h1
89451-177
phenyl
E-benzene sulfonate

Chemical structure: O=S(=O)(Oc1ccccc1)c2ccc(F)cc2

Spectrum plot showing intensity versus frequency (ppm). The x-axis ranges from 13 ppm to -1 ppm. A large peak is visible at approximately 7.8 ppm.

4-methylphenyl 4-fluorobenzenesulfonate (16)

4-methylphenyl 4-fluorobenzenesulfonate (16)

2-methylphenyl 4-fluorobenzenesulfonate (17)

2-methylphenyl 4-fluorobenzenesulfonate (17)

4-methoxyphenyl 4-fluorobenzenesulfonate (18)

4-methoxyphenyl 4-fluorobenzenesulfonate (18)

2-methoxyphenyl 4-fluorobenzenesulfonate (19)

2-methoxyphenyl 4-fluorobenzenesulfonate (19)

2-cyanophenyl 4-fluorobenzenesulfonate (20)

2-cyanophenyl 4-fluorobenzenesulfonate (20)

4-chlorophenyl 4-fluorobenzenesulfonate (21)

Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6561.680 Hz
FIDRES 0.200247 Hz
AQ 2.4969716 sec
RG 406.4
DW 76.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -5.00 dB
SFO1 400.1322007 MHz

F2 - Processing parameters
SI 16384
SF 400.1300056 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

nmr400c h1
89451-187
Cl-phenyl
F benzene sulfonate

Clc1ccc(cc1)OS(=O)(=O)c2ccc(F)cc2

1 2 3 4 5 6 7 8 9 10 11 12 13

4-fluorophenyl 4-fluorobenzenesulfonate (22)

4-fluorophenyl 4-fluorobenzenesulfonate (22)

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Current Data Parameters
NAME      89594-187
EXPNO     1
PROCNO    1

nmr500c h-1
89594-187

p-F-Benzzenesulfonate
```

pyridin-3-yl 4-fluorobenzenesulfonate (23)

nmr400c h1
89451-176
pyridyl (3)
F benzene sulfonate

F2 - Acquisition Parameters
Date_ 20051019
Time_ 15.54
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6561.680 Hz
FIDRES 0.200247 Hz
AQ 2.4969716 sec
RG 256
DW 76.200 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -5.00 dB
SFO1 400.1322007 MHz

F2 - Processing parameters
SI 16384
SF 400.1300056 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

Chemical structure: O=S(=O)(Oc1cccnc1)c2ccc(F)cc2

The NMR spectrum displays several sharp peaks in the aromatic region between 7.22 and 7.34 ppm. The x-axis is labeled 'ppm' and ranges from 13 to -1. The peaks are clustered around 7.3 ppm, with some smaller peaks visible at lower chemical shifts.

4-methylphenyl 4-methylbenzenesulfonate (24)

4-methylphenyl 4-methylbenzenesulfonate (24)