Unusually Stable, Versatile, and Pure Arenediazonium Tosylates: their Preparation, Structures, and Synthetic Applicability

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Supporting information

Typical procedure for the diazotization: 'Resin-NO_2^-' (4.5 g, containing 15.75 mmol NO_2^-) was added at rt to a solution of monohydrate of *p*-toluenesulfonic acid (2.97 g, 15.75 mmol) in AcOH (8 mL) and stirred for 5 min. The corresponding aniline (5.25 mmol) was added in four times and the mixture was stirred for 5-20 min until TLC indicated the complete consumption of the amine (hexane-ether 1:1). The mixture was filtered from the resin and the filtrate was poured into ether (100-140 mL). The resulting solid was filtered, washed by ether (20-40 ml) and dried under vacuum.
Caution! In our two laboratories there was no case of sudden decomposition during the preparation, purification, and handling of salts **1a-18a**. Nevertheless it must be born in mind that in general diazonium salts in the dry state are potentially explosive. Therefore they must be carefully stored and handled.

Spectral Data and Melting Points (uncorrected and checked by MEL-TEMP) of 1a-18a:
Benzenediazonium 4-methylbenzenesulfonate (1a). mp 224 ^{0}C. IR (KBr): 2295 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.29 (s, 3H), 7.13 (d, *J*=7.5 Hz, 2H), 7.35 (d, *J*=7.5 Hz, 2H), 7.36-7.52 (m, 5H). ^{13}C NMR (75 MHz, DMSO): δ 20.50, 123.15, 123.54, 128.25, 128.38, 129.91, 131.84, 138.41, 144.72.

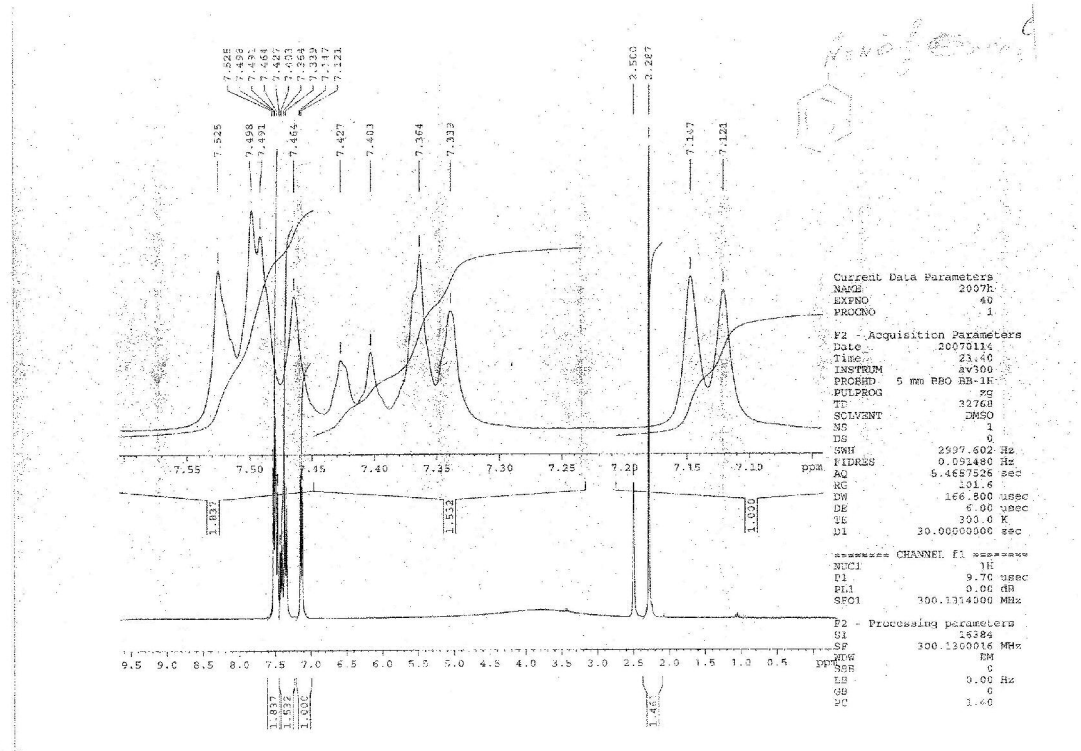

Figure S1. ^{1}H NMR of benzenediazonium tosylate (**1a**) (300 MHz, DMSO-d6)

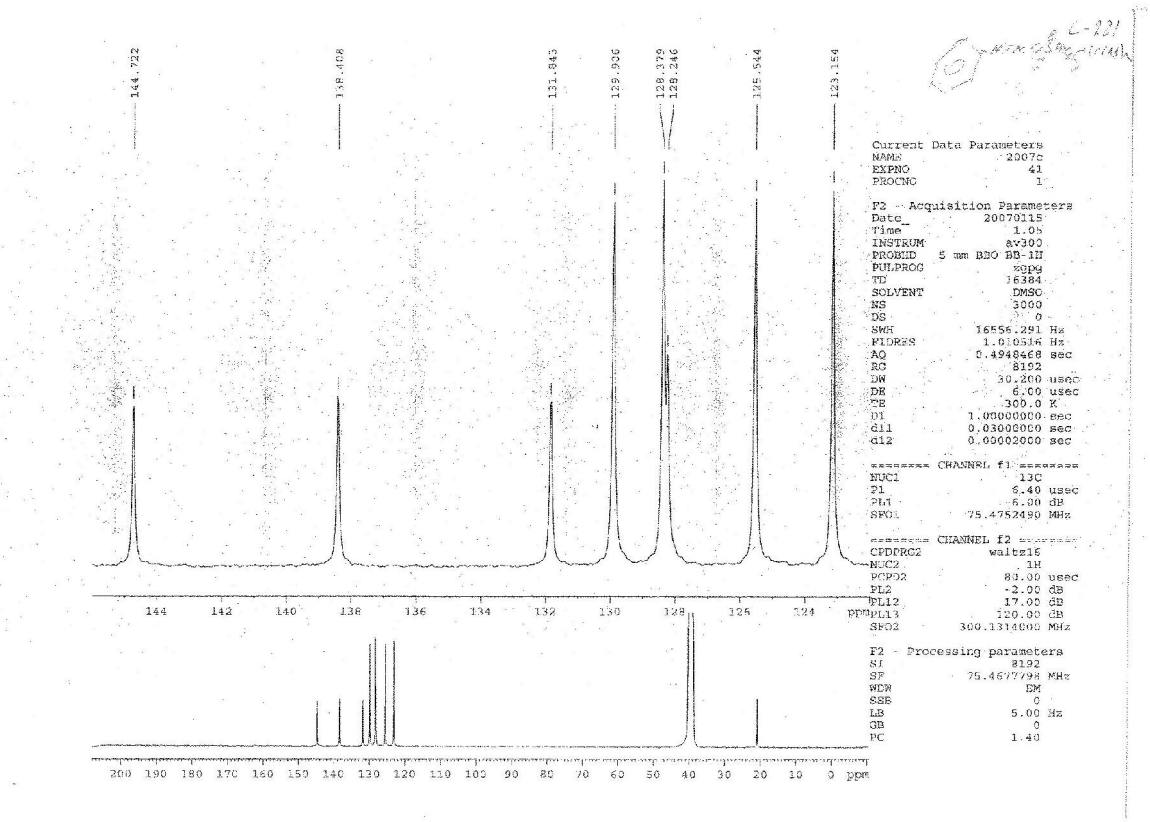

Figure S2. ^{13}C NMR of benzenediazonium tosylate (**1a**) (75 MHz, DMSO-d6)

2-Methylbenzenediazonium 4-methylbenzenesulfonate (2a). mp 182 ^{0}C. IR (KBr): 2064 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.29 (s, 3H), 2.32 (s, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.25-7.40 (m, 4H), 7.51 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 16.78, 20.85, 123.10, 125.44, 127.20, 128.24, 130.60, 131.42, 131.60, 138.13, 144.85.

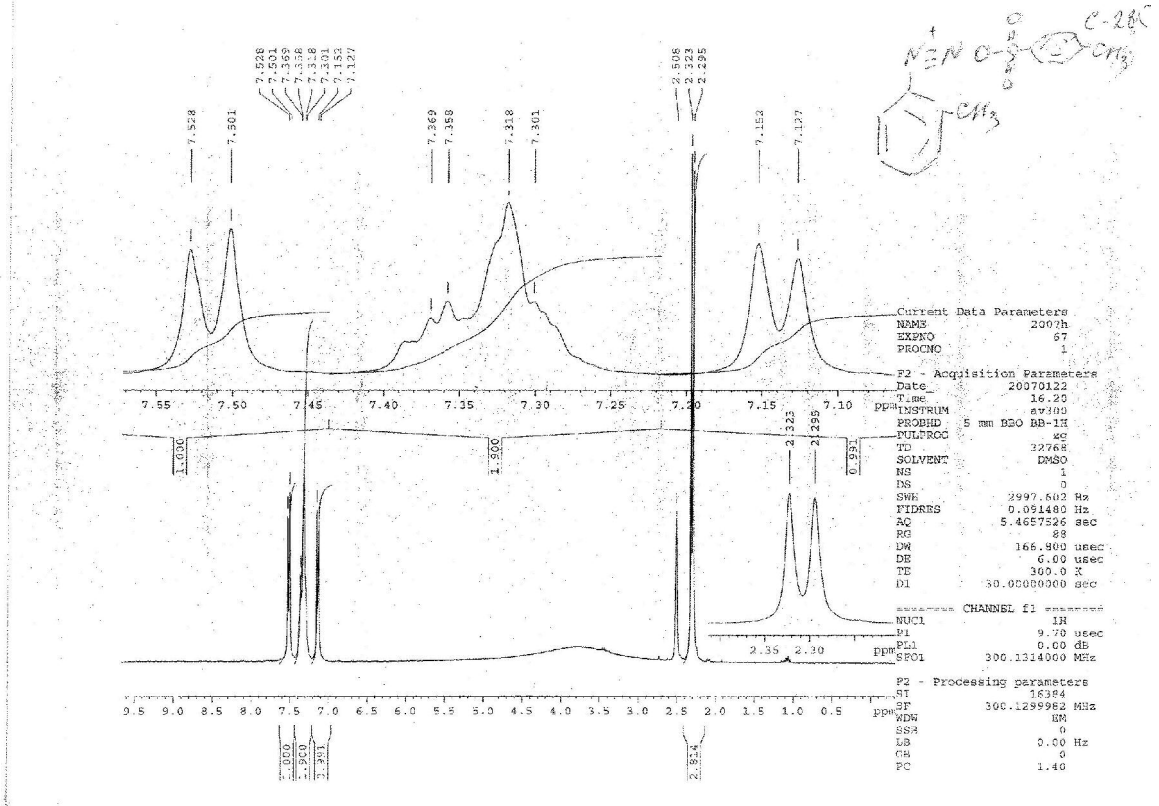

Figure S3. ^{1}H NMR of 2-methylbenzenediazonium tosylate (**2a**) (300 MHz, DMSO-d6)

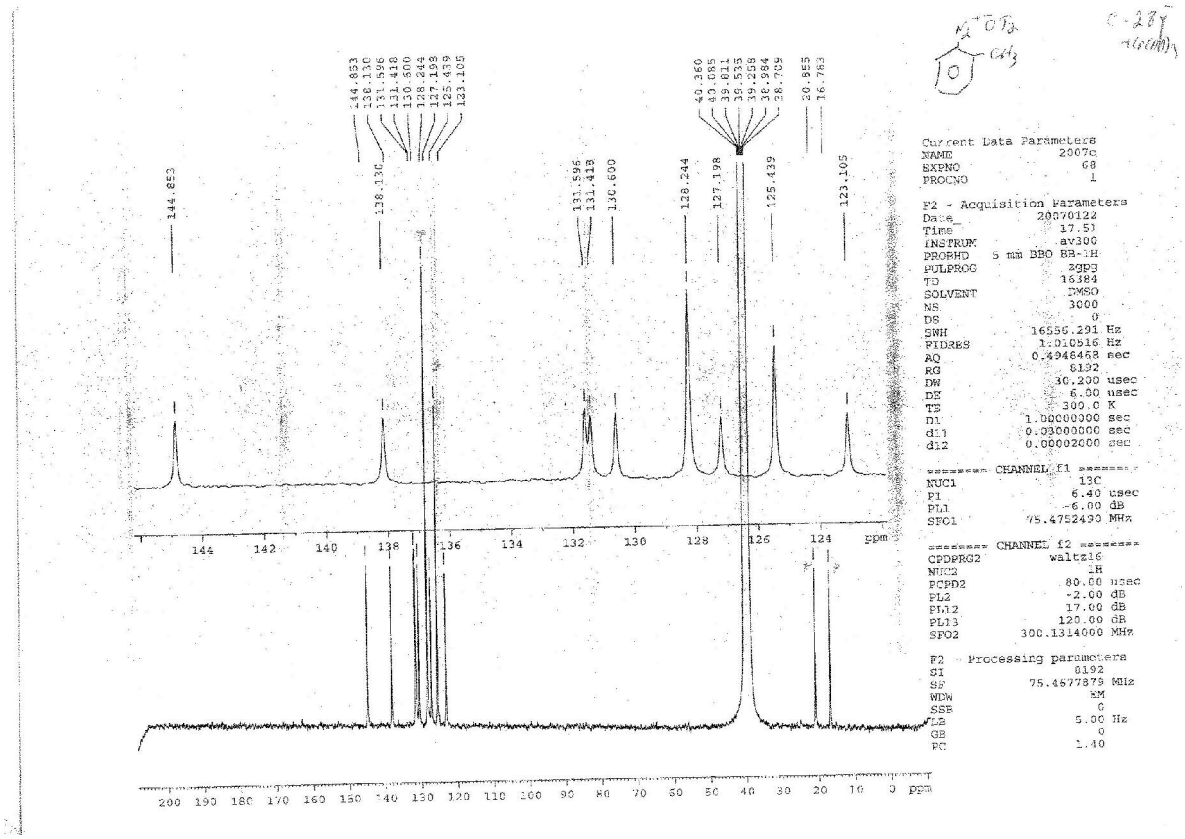

Figure S4. ^{13}C NMR 2-methylbenzenediazonium tosylate (**2a**) (75 MHz, DMSO-d6)

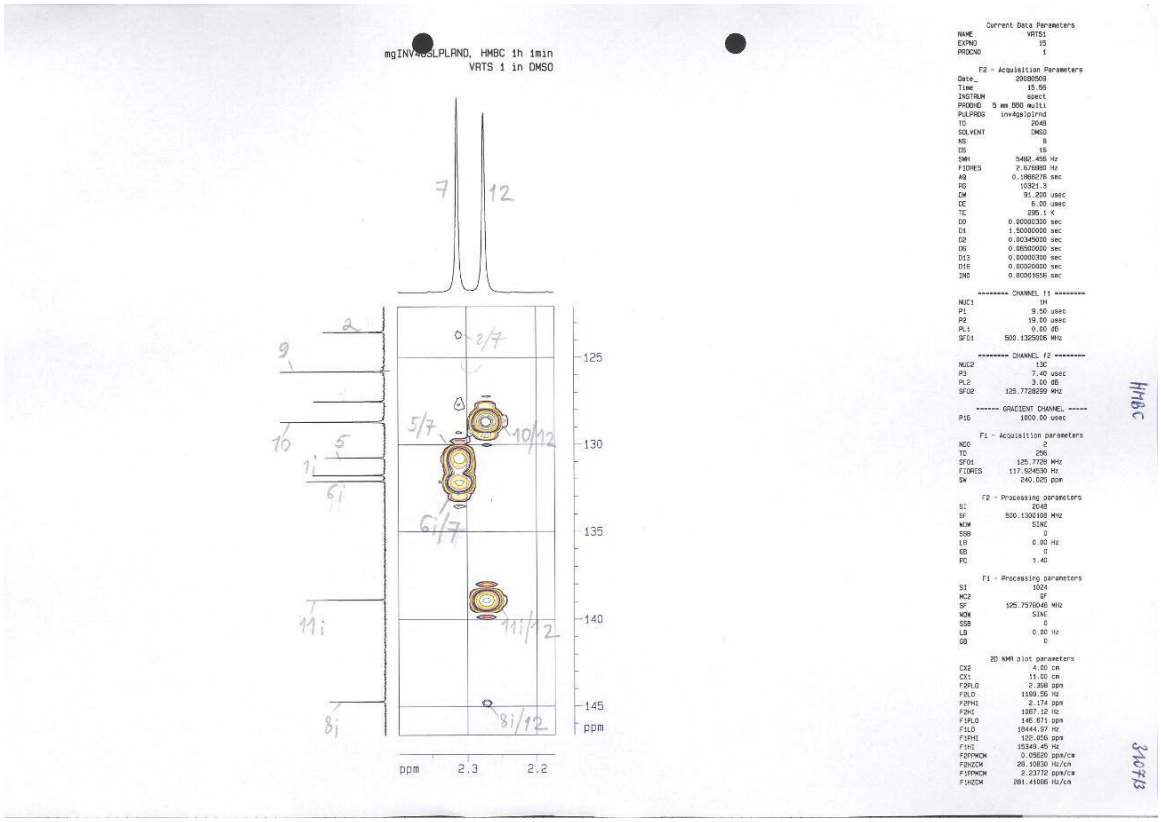

Figure S5. NMR COSYGS of 2-methylbenzenediazonium tosylate (**2a**) (500, 125 MHz)

3-Methylbenzenediazonium 4-methylbenzenesulfonate (3a). mp 158-161 ^{0}C. IR (KBr): 2068 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 2.31 (s, 3H), 7.13-7.24 (m, 5H), 7.34-7.39 (m, 1H), 7.52 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.86, 120.26, 123.54, 125.53, 128.35, 128.98, 129.72, 131.49, 138.36, 139.61, 144.76.

4-Methylbenzenediazonium 4-methylbenzenesulfonate (4a). mp 120 ^{0}C. IR (KBr): 2288 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 2.31 (s, 3H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.24-7.71 (m, 4H), 7.51 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.59, 20.86, 123.12, 125.54, 128.30, 128.76, 130.27, 138.00, 138.22, 144.96.

3,4-Dimethylbenzenediazonium 4-methylbenzenesulfonate (5a). mp 182 ^{0}C. IR (KBr): 2280 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.20 (s, 6H), 2.28 (s, 3H), 7.05-7.16 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 19.16, 19.58, 21.06, 120.48, 123.94, 125.69, 128.55, 129.12, 130.82, 136.64, 138.36, 138.62, 144.77.

2-Methoxybenzenediazonium 4-methylbenzenesulfonate (6a). mp 149-151 ^{0}C. IR (KBr): 2209 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 3.87 (s, 3H), 7.02 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.35-7.41 (m, 2H), 7.50 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.82, 56.10, 112.49, 120.89, 120.91, 123.83, 125.48, 128.18, 129.55, 138.00, 145.00, 152.80.

4-Methoxybenzenediazonium 4-methylbenzenesulfonate (7a). mp 118-120 ^{0}C. IR (KBr): 2243 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 3.76 (s, 3H), 7.03 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.82, 55.54, 114.96, 123.86, 124.40, 125.49, 128.19, 138.02, 145.19, 158.89.

4-Aminobenzenediazonium 4-methylbenzenesulfonate (8a). mp 149-151 ^{0}C. IR (KBr): 2234 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 6.81 (d, *J* = 9.0 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 2H), 8.36 (s, 2H, NH_2). ^{13}C NMR (75 MHz, DMSO): δ 21.01, 89.04, 115.55, 125.67, 128.48, 135.32, 138.45, 145.06, 159.42.

2-Nitrobenzenediazonium 4-methylbenzenesulfonate (9a). mp 155 ^{0}C. IR (KBr): 2303 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 8.37-8.60 (m, 2H), 8.77 (d, *J* = 8.4 Hz, 1H), 9.11 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, DMSO): δ 20.89, 120.30, 123.58, 125.56, 128.40, 129.02, 129.74, 131.51, 138.49, 139.80, 144.87.

3-Nitrobenzenediazonium 4-methylbenzenesulfonate (10a). mp 134 ^{0}C. IR (KBr): 2307 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.29 (s, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 8.20-8.26 (m, 1H), 8.97 (d, *J* = 8.1 Hz, 1H), 9.05 (d, *J* = 8.1 Hz, 1H), 9.61 (s, 1H). ^{13}C NMR (75 MHz, DMSO): δ 20.85, 118.31, 125.54, 128.22, 132.79, 134.99, 138.02, 145.34, 147.60.

4-Nitrobenzenediazonium 4-methylbenzenesulfonate (11a). mp 132 ^{0}C. IR (KBr): 2308 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 7.10 (d, *J*=7.5 Hz, 2H), 7.47 (d, *J*=7.5 Hz, 2H), 8.69 (d, *J*=9.3 Hz, 2H), 8.89 (d, *J*=9.3 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.84, 121.96, 125.57, 126.04, 128.18, 134.60, 137.85, 145.55, 153.22.

4-Cyanobenzenediazonium 4-methylbenzenesulfonate (12a). mp 124 ^{0}C. IR (KBr): 2235 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 7.10 (d, *J*=7.5 Hz, 2H), 7.46 (d, *J*=7.5 Hz, 2H), 8.42 (d, *J*=9.0 Hz, 2H), 8.85 (d, *J*=9.0 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.87, 116.45, 121.11, 121.72, 125.57, 128.25, 133.17, 134.81, 137.97, 145.39.

2-Carboxybenzenediazonium 4-methylbenzenesulfonate (13a). mp 128 ^{0}C. IR (KBr): 2289 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.27 (s, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 8.12-8.17 (m, 1H), 8.27-8.37 (m, 2H), 8.90 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO): δ 21.14, 116.02, 125.75, 128.61, 132.75, 134.91, 135.50, 138.59, 141.12, 144.96, 162.70.

4-Carboxybenzenediazonium 4-methylbenzenesulfonate (14a). mp 114-115 ^{0}C. IR (KBr): 2303 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.27 (s, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 8.36 (d, *J* = 8.7 Hz, 2H), 8.76 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 21.11, 119.78, 125.77, 128.57, 131.55, 133.38, 138.55, 140.98, 145.03, 165.14.
4-Iodobenzenediazonium 4-methylbenzenesulfonate (15a). mp 124-126 ^{0}C. IR (KBr): 2210 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 8.34-8.41 (m, 4H). ^{13}C NMR (75 MHz, DMSO): δ 20.86, 113.60, 115.12, 125.49, 128.17, 132.91, 137.87, 140.20, 145.31.
2,4,6-Tribromobenzenediazonium 4-methylbenzenesulfonate (16a). mp 152 ^{0}C. IR (KBr): 2284 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.28 (s, 3H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 2H), 8.71 (s, 2H). ^{13}C NMR (75 MHz, DMSO): δ 20.93, 92.00, 124.95, 125.54, 126.21, 128.35, 138.34, 144.65.
Naphthalene-1-diazonium 4-methylbenzenesulfonate (17a). mp 134-136 ^{0}C. IR (KBr): 2222 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.27 (s, 3H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.46-7.78 (m, 5H), 7.90-8.07 (m, 4H). ^{13}C NMR (75 MHz, DMSO): δ 20.89, 121.43, 125.57, 127.07, 127.50, 127.82, 127.98, 128.37, 128.83, 129.00, 130.06, 132.00, 132.87, 138.48, 144.86.
4-Benzylbenzenediazonium 4-methylbenzenesulfonate (18a). mp 246 ^{0}C. IR (KBr): 2293 (N≡N). ^{1}H NMR (300 MHz, DMSO): δ 2.27 (s, 3H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 21.10, 123.53, 125.73, 128.57, 129.84, 130.33, 138.60, 141.45, 144.92.

Typical procedures for the subsequent transformations of arenediazonium salts:
4-Iodoaniline. Potassium iodide (0.42 g, 2.5 mmol) was added at rt to a solution of **8a** (0.40 g, 1.0 mmol) in water (6 mL), and the mixture was stirred for 50 min until a negative diazonium test with 2-naphthol. Precipitated pure 4-iodoaniline was filtered and washed with distilled water. Yield 0.20 g (100%), mp 64 ^{0}C.
4-Bromobenzonitrile. Potassium bromide (0.52 g, 2.5 mmol) was added at rt to a solution of **12a** (0.30 g, 1.0 mmol) in water (6 mL), and the mixture was stirred for 100 min until a negative diazonium test with 2-naphthol. Precipitated pure 4-bromobenzonitrile was filtered and washed with distilled water. Yield 0.13 g (74%), mp 113 ^{0}C.
1,4-Dinitrobenzene. Potassium nitrite (0.17 g, 2.5 mmol) was added at rt to a solution of **11a** (0.32 g, 1.0 mmol) in water (6 mL) and the mixture was stirred for 30 min until a negative diazonium test with 2-naphthol. Precipitated pure 1,4-dinitrobenzene was filtered and washed with distilled water. Yield 0.12 g (74%), mp 171-173 ^{0}C.
1-((4-Nitrophenyl)diazenyl)piperidine (19). Piperidine (0.34 g, 4 mmol) was dissolved in methanol (20 mL) and the solution was cooled at 0-5 ^{0}C. The cooled solution of piperidine was added to a solution of **11a** (0.64 g, 2 mmol) in methanol (10 mL), and the mixture was stirred at 0-5 ^{0}C for 20 min until a negative diazonium test with 2-naphthol. The mixture was poured in water (50 mL) and the solid product was filtered, washed with distilled water, and dried. Yield 0.40 g (97%), mp 88-90 ^{0}C (EtOH) (lit. mp. 87-88 ^{0}C [1]). ^{1}H NMR (300 MHz, DMSO): δ 1.69 (m, 3H), 3.85 (m, 2H), 7.48 (d, *J*=8.7 Hz, 2H), 8.18 (d, *J*=8.7 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 23.5, 43.7, 53.2, 120.5, 125.2, 144.0, 156.0; MS m/z 234 (M^+).
(*E*)-4-Nitrostilbene (20). A mixture of 4-nitrobenzenediazonium tosylate (**11a**) (0.55 g, 1.5 mmol), styrene (0.19 g, 1.8 mmol) and $Pd(OAc)_2$ (0.004 g, 0.015 mmol) in 95% aqueous EtOH (15 ml) was stirred at 70 ^{0}C for 20 min until a negative diazonium test with 2-naphthol. The reaction mixture was filtered through silica gel and cooled. (*E*)-4-Nitrostilbene was isolated by filtration. Yield 0.25 g (75%); mp 154–157 ^{0}C (EtOH) (lit.mp 155-156 ^{0}C [2]). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (d, *J* = 16.5 Hz, 1H), 7.24 (d, *J* = 16.5 Hz, 1H), 7.38 (m, 1H), 7.54 (d, *J* = 6.3 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.0, 126.2, 126.8, 126.9, 128.8, 133.3, 136.0, 143.7, 146.6.

(*E*)-2-Styrylbenzoic acid (21) and (*E*)-4-styrylbenzoic acid (22) were prepared by the same method with styrene and diazonium salts **13a** or **14a** respectively. **21**: Yield 0.21 g (65%), mp 153-155 ^{0}C (EtOH) (lit mp 159-160 ^{0}C [3]). ^{1}H NMR and ^{13}C NMR identical to the reported data [3]. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.14 (d, *J* = 16.2 Hz, 1H), 7.26-7.42 (m, 4H), 7.56-7.61 (m, 3H), 7.85-7.87 (m, 1H), 7.99-8.02 (m, 1H), 8.12 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) 127.5, 128.1, 128.2, 128.6, 129.5, 129.8, 131.7, 131.9, 133.1, 138.5, 139.8, 160.9; **22**: yield 0.22 g, (67%), mp 250-253 ^{0}C (EtOH) (lit. mp. 257-258 ^{0}C [4]) ^{1}H NMR and ^{13}C NMR identical to the reported data [5]. ^{1}H NMR (300 MHz, DMSO): δ 7.27 (d, *J* = 16.5 Hz, H), 7.29-7.41 (m, 4H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): δ 126.7, 127.0, 127.5, 128.4, 128.9, 129.6, 129.9, 131.2, 136.7, 141.5, 167.2.

X-ray Crystallography of Arenediazonium Tosylates 9a, 12a and 15a:

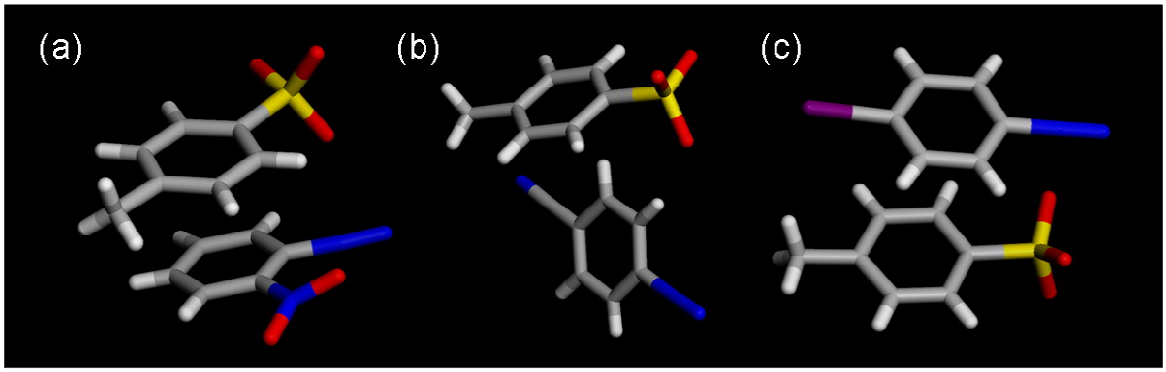

Figure S6. X-ray crystal structures of arenediazonium tosylates (a) **9a**, (b) **12a** and (c) **15a**

The diffraction data were collected with synchrotron radiation (λ = 0.80000 Å) at the Wiggler Beamline 4A, Pohang Accelerator Laboratory (PAL). Data reduction and adsorption correction were performed with HKL2000 package. The structures were solved by direct methods and refined by full-matrix least squares method with SHELXTL package. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were found in the difference electron density map with reasonable bond distances except **15a**.

X-ray data of **9a**: $C_{13}H_{11}N_3O_5S$ *M* = 321.31, Triclinic, *P*-1 (No. 2), *a* = 7.509(2) Å, *b* = 7.546(2) Å, *c* = 13.672(3) Å, α = 78.64(3)°, β = 75.67(3)°, γ = 75.60(3)°, *V* = 719.4(2) Å^3, *Z* = 2, *T* = 90 K, $\mu(\lambda = 0.80000$ Å) = 0.343 mm^{-1}, d_{calc} = 1.483 g/cm^3, 2571 reflections measured, 2571 unique, R_1 = 0.0392, wR_2 =0.1220 ($I > 2\sigma(I)$), R_1 = 0.0398, wR_2 =0.1231 (all data), GOF = 1.055.

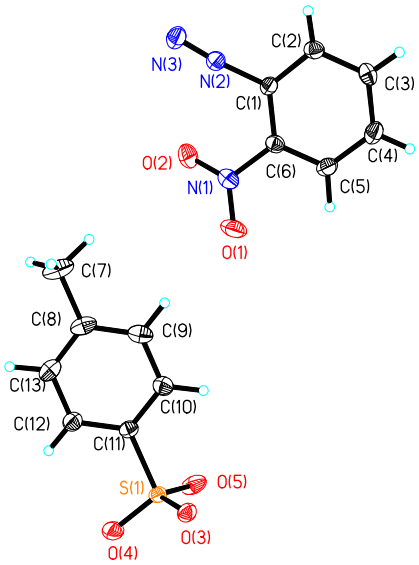

Figure S7. X-ray crystal structure of *o*-nitrobenzenediazonium tosylate (**9a**) with 50 % ellipsoid.

X-ray data of **12a**: $C_{14}H_{11}N_3O_3S$ M = 301.32, monoclinic, $P2_1/c$ (No. 14), a = 5.845(1) Å, b = 8.847(2) Å, c = 26.65(1) Å, β = 94.29(3)°, V = 1374.2(5) Å^3, Z = 4, T = 90 K, $\mu(\lambda = 0.80000$ Å) = 0.338 mm^{-1}, d_{calc} = 1.456 g·cm^{-3}, 4808 reflections measured, 2681 unique (R_{int} = 0.0476), R_1 = 0.0429, wR_2 =0.1242 ($I > 2\sigma(I)$), R_1 = 0.0438, wR_2 = 0.1256 (all data), GOF = 1.036.

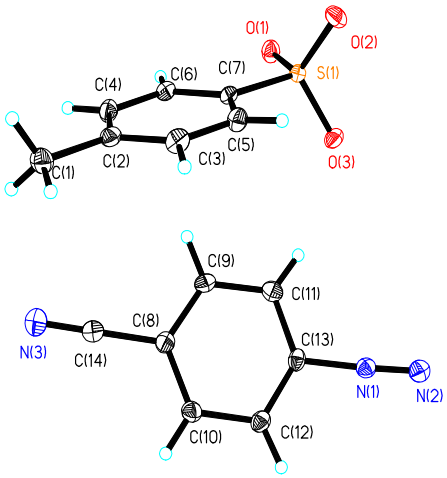

Figure S8. X-ray crystal structure of *p*-cyanobenzenediazonium tosylate (**12a**) with 50% thermal ellipsoid. Distance of triple bond is 1.094 (2) Å.

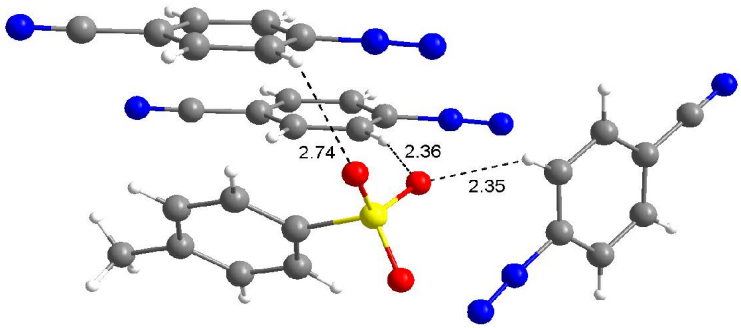

Figure S9. There are three *p*-cyanobenzenediazonium cations connected through hydrogen bonds with a *p*-toluenesulfonate.

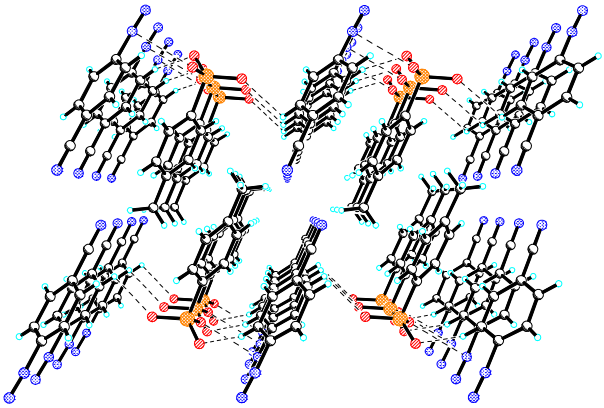

Figure S10. Packing of diazonium salt with ball and stick model. Phenyl groups of *p*-cyanobenzenediazonium ions have hydrogen bonds with a tosylate.

X-ray data of **15a**: $C_{13}H_{11}N_2O_3SI$ M = 402.20, Triclinic, P-1 (No. 2), a = 7.678(2) Å, b = 10.149(2) Å, c = 18.657(4) Å, α = 77.15(3)°, β = 88.73(3)°, γ = 77.04(3)°, V = 1380.7(5) Å^3, Z = 4, T = 90 K, $\mu(\lambda$ = 0.80000 Å) = 3.367 mm^{-1}, d_{calc} = 1.935 g/cm^3, 4411 reflections measured, 4411 unique, R_1 = 0.0793, wR_2 =0.2202 ($I > 2\sigma(I)$), R_1 = 0.0814, wR_2 = 0.2253 (all data), GOF = 1.041.

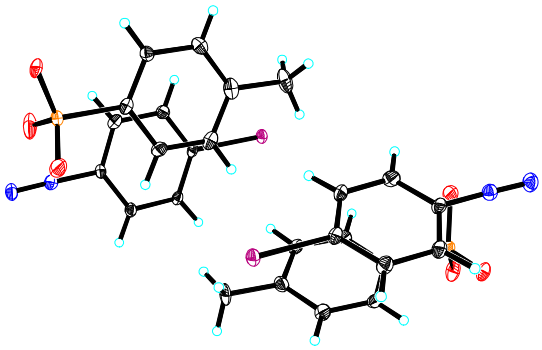

Figure S11. X-ray crystal structure of *p*-iodobenzenediazonium tosylate (**15a**) with 50% thermal ellipsoid.

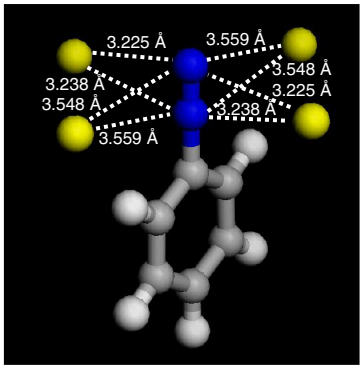

Figure S12. Reported X-ray crystal structure of benzenediazonium chloride from Cambridge Structure Data (CSD)

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