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Supporting Information for

An Approach to C-N Activation: Coupling of Arenesulfonyl Hydrazides and Arenesulfonyl Chlorides with *tert*-Amines via a Metal-, Oxidant- and Halogen-free Anodic Oxidation

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I-General Information

¹H and ¹³CNMR spectra were recorded on 400 and 500 MHz NMR instruments. TMS and CDCl₃ used as the internal standards for ¹HNMR and ¹³CNMR, respectively. Graphite anodes and cathodes were 2.0 mm 2B pencil graphite purchased from the supermarket.

II-Experimental Procedures

II-I-Typical procedure for the synthesis of arenesulfonyl hydrazides¹

Into a 25 mL round-bottomed flask, are added 10 mmol of arenesulfonyl chloride and 3.5 mL of tetrahydrofuran. The mixture is cooled to 10 °C and 1.5 mL hydrazine hydrated (85% hydrazine hydrate, 20 mmol) is added. Stirring is continued for further 15 minutes and then the reaction mixture is transferred to a separatory funnel. The organic layer is filtered and washed with 2.5 mL tetrahydrofuran. The colorless filtrates are stirred during the drop-wise addition of 12 mL of distilled water. Arenenesulfonyl hydrazide separates as fluffy crystalline needles. The product is washed several times with distilled water, and air-dried.

II-II-Electrochemical synthesis of sulfonamides from arenesulfonyl chlorides

An undivided cell was equipped with two pencil graphite electrodes (2.0 mm, 2B) and connected with a DC power supply (Figure S1). A mixture of arenesulfonyl chloride (0.5 mmol), *tert*-amine (1 mmol), and Na_2SO_4 (1.25 mmol, 0.5 M) in H₂O (2.5 mL) was added to the cell. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 10 mA (electrode square 1.7 cm²) at room temperature for 3.2 h until the quantity of the electricity 2.4 F/mol was passed. After washing the mixture with 10% brine solution and extraction with ethyl acetate, the organic layer was dried over sodium sulfate and evaporated under reduced pressure. The organic residue was purified by a silica loaded column chromatography with 1:20 ethyl acetate in hexane as eluent.

II-III-Electrochemical synthesis of sulfonamides from arenesulfonyl hydrazides

An undivided cell was equipped with two pencil graphite electrodes (2.0 mm, 2B) and connected with a DC power supply (Figure S1). A mixture of arenesulfonyl hydrazide (0.5 mmol), *tert*-amine (1 mmol), and Na₂SO₄ (1.25 mmol, 0.5 M) in water/acetonitrile (1:1, 2.5 mL) was added to the cell. The electrolyte was allowed to stir and the electrolysis was carried out at a constant current of 10 mA (electrode square 1.7 cm²) at room temperature for 9 h until the quantity of the electricity 6.7 F/mol was passed. After washing the mixture with 10% brine solution and extraction with ethyl acetate, the organic layer was dried over sodium sulfate and evaporated under reduced pressure. The organic residue was purified by a silica loaded column chromatography with 1:20 ethyl acetate in hexane as eluent.

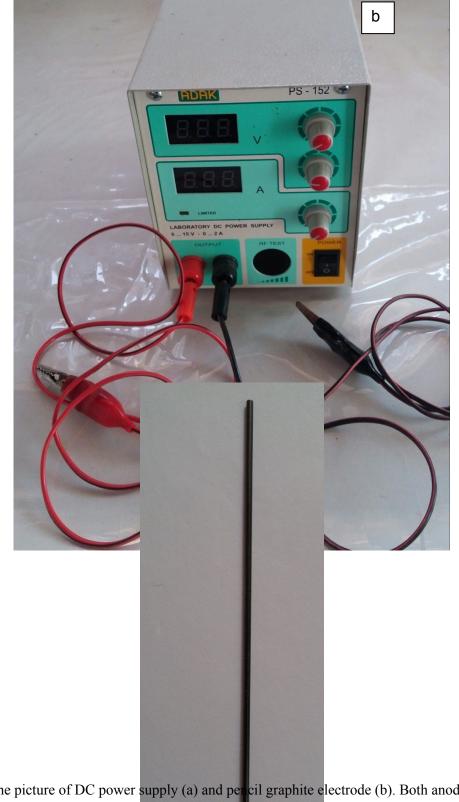
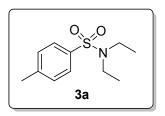


Figure S1. The picture of DC power supply (a) and pencil graphite electrode (b). Both anode and cathode were 2.0 mm 2B pencil leads.

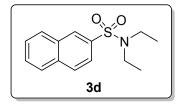


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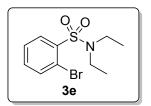
III-Spectral data



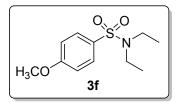
N,*N*-Diethyl-4-methylbenzenesulfonamide (3a): 71% yield. White crystal, mp 60-62 °C; ¹HNMR (500 MHz, CDCl₃) δ 7.68 (d, *J*= 8.0 Hz, 2H), 7.27 (d, *J*= 8.0 Hz, 2H), 3.22 (q, *J*= 7.0, 4H), 2.41 (s, 3H), 1.12 (t, *J*= 7.0 Hz, 6H); ¹³CNMR (125 MHz, CDCl₃) δ 142.8, 137.5, 129.6, 127.1, 42.0, 21.4, 14.1. Known compound.²



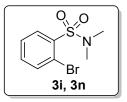
N,*N*-diethylnaphthalene-2-sulfonamide (3d): 72% yield. White crystal, mp 81-83 °C; ¹HNMR (400 MHz, DMSO-d6) δ 8.49 (d, *J* = 1.2 Hz, 1H), 8.20 (d, *J*= 7.6 Hz, 1H), 8.14 (d, *J*= 8.4 Hz, 1H), 8.06 (d, *J*= 8.0 Hz, 1H), 7.82 (dd, *J*=8.4, 1.6 Hz, 1H), 7.66-7.74 (m, 2H), 3.23 (q, *J*= 7.2 Hz, 4H), 1.05 (t, *J*= 7.2 Hz, 6H). Anal. Calcd for C₁₄H₁₇NO₂S: C, 63.85; H, 6.51; N, 5.32; S, 12.18. Found: C, 63.81; H, 6.50; N, 5.33; S, 12.10. Known comound.³



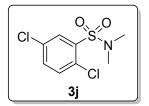
2-Bromo-*N*,*N*-diethylbenzenesulfonamide (3e): 70% yield. White crystal, mp 74-76 °C; ¹HNMR (400 MHz, CDCl₃) δ 7.55-7.69 (m, 3H), 7.40 (d, *J*= 8.4 Hz, 1H), 3.16 (q, *J*= 7.2 Hz, 4H), 1.06 (t, *J*= 7.2 Hz, 6H). Anal. Calcd for C₁₀H₁₄BrNO₂S: C, 41.11; H, 4.83; N, 4.79; 10.97. Found: C, 41.02; H, 4.76; N, 4.86; S, 11.04.



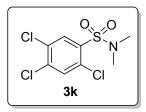
N,*N*-Diethyl-4-methoxybenzenesulfonamide (3f): 77% yield. White crystal, mp 60-62 °C; ¹HNMR (500 MHz, CDCl₃) δ 7.76 (d, *J*= 7.0 Hz, 2H), 6.97 (d, *J*= 7.0 Hz, 2H), 3.88 (s, 3H), 3.23 (q, *J*= 7.1 Hz, 4H), 1.40 (t, *J*= 7.1 Hz, 6H). Known compound.⁴



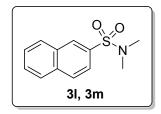
N,N-Dimethyl-2-bromosulfonamide (3i, 3n): 72% yield (74% yield for 3n). Pale crystal, mp 87-89 °C; ¹HNMR (400 MHz, CDCl₃) δ 7.75 (d, *J*= 8.4 Hz, 1H), 7.72 (d, *J*= 8.8 Hz, 1H), 7.67 (d, *J*= 8.8 Hz, 1H), 7.55 (d, *J*= 8.4 Hz, 1H), 2.74 (s, 6H); ¹³CNMR (100 MHz, CDCl₃) δ 134.5, 132.3, 129.4, 129.2, 129.1, 127.8, 37.9. Anal. Calcd for C₈H₁₀BrNO₂S: C, 36.38; H, 3.82; N, 5.30; S, 12.14. Found: C, 36.30; H, 3.73; N, 5.31; S, 12.12.



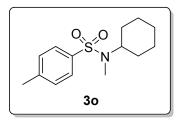
N,*N*-Dimethyl-2,5-dichlorobenzenesulfonamide (3j): 76% yield. White crystal, mp 73-76 °C; ¹HNMR (500 MHz, CDCl₃) δ 8.06 (s, 1H), 7.46-7.48 (m, 2H), 2.94 (s, 6H). Anal. Calcd for C₈H₉Cl₂NO₂S: C, 37.81; H, 3.57; N, 5.51; S 12.62. Found: C, 37.76; H, 3.51; N, 5.48; S, 12.65. Known compound.⁵



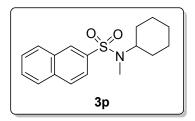
N,*N*-Dimethyl-2,4,5-trichlorobenzenesulfonamide (3k): 72% yield. White crystal, mp 105-106 °C; ¹HNMR (500 MHz, CDCl₃) δ 8.17 (s, 1H), 7.66 (s, 1H), 2.92 (s, 6H). Anal. Calcd for C₈H₈Cl₃NO₂S: C, 33.30; H, 2.79; N, 4.85; S, 11.11. Found: C, 33.21; H, 2.73; N, 4.78; S, 11.00. Known compound.⁶



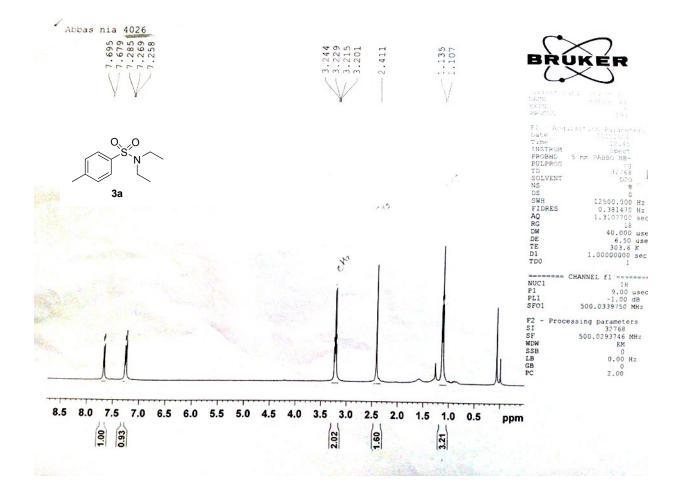
N,*N*-Dimethyl-naphthalene-2-sulfonamide (3l, 3m): 71% yield (78% yield for 3m). White crystal, mp 93-96 °C; ¹HNMR (400 MHz, CDCl₃) δ 8.21 (d, *J*= 1.2 Hz, 1H), 7.90-7.95 (m, 3H), 7.68 (td, *J*= 7.2, 1.2 Hz, 1H), 7.63 (td, *J*= 7.2, 1.2 Hz, 1H), 7.52 (dd, *J*= 8.8, 2.0 Hz, 1H), 7.29-7.35 (m, 3H), 7.13-7.16 (m, 2H). Known compound.⁷

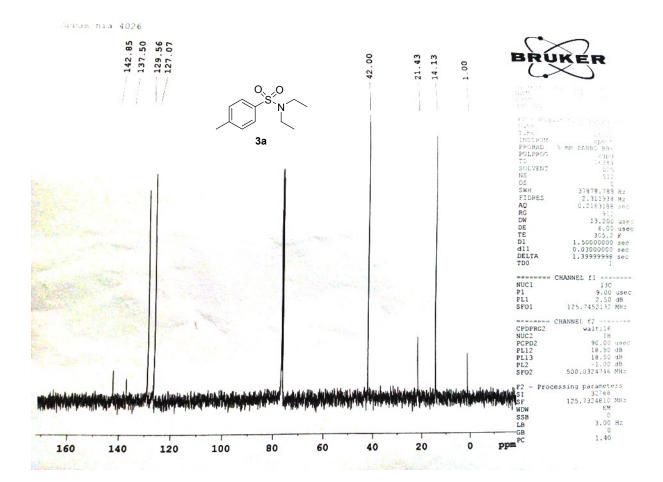


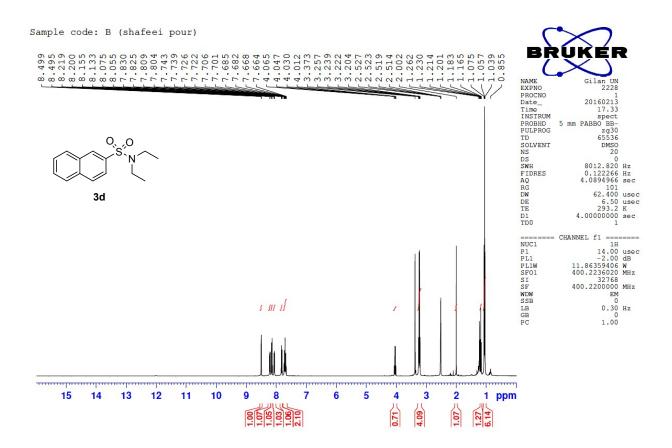
N-Cyclohexyl-*N*-methyl-4-methylbenzenesulfonamide (**30**): 69% yield. White crystal, mp 73-76 °C; ¹HNMR (500 MHz, CDCl₃) δ 7.70 (d, *J*= 8.3 Hz, 2H), 7.29 (d, *J*= 8.3 Hz, 2H), 3.77 (m, 1H), 2.74 (s, 3H), 2.43 (s, 3H), 1.47-1.74 (m, 5H), 1.25-1.34 (m, 4H), 0.89-1.04 (m, 1H). Known compound.⁸

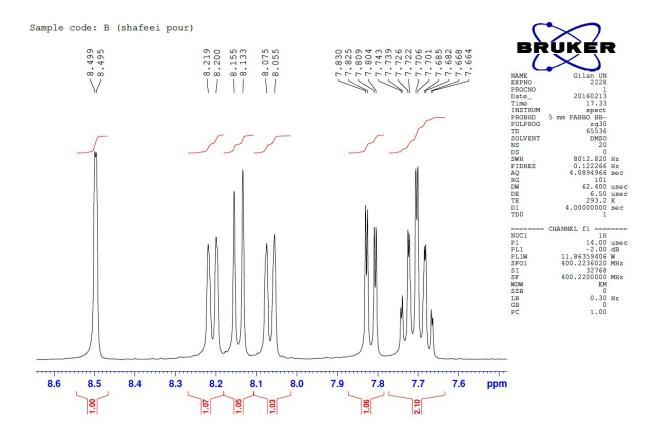


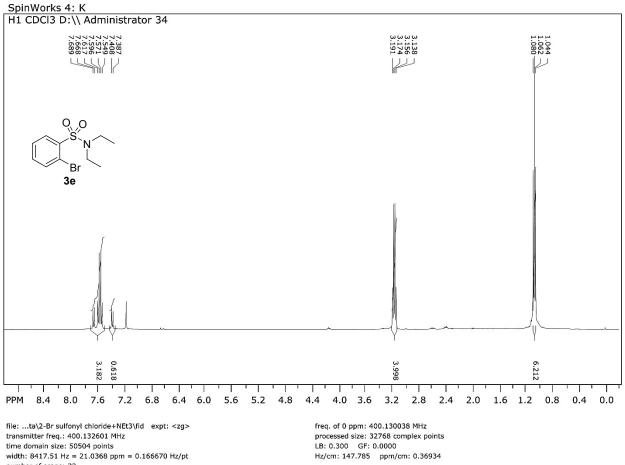
N-Cyclohexyl-*N*-methylnaphthalene-2-sulfonamide (3p): 75% yield. White crystal, mp 76-79 °C; ¹HNMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 7.96-7.99 (m, 2H), 7.92 (d, *J*= 7.6, 1H), 7.81 (dd, *J*= 8.6 Hz, 1.7 Hz, 1H), 7.61-7.65 (m, 2H), 3.86-3.90 (m, 1H), 2.82 (s, 3H), 1.54-1.74 (m, 5H), 1.27-1.37 (m, 4H), 0.92-1.03 (m, 1H). ¹³CNMR (100 MHz, CDCl₃) δ 137.3, 134.6, 132.2, 129.3, 129.2, 128.5, 128.1, 127.9, 127.4, 122.5, 56.9, 30.4, 28.7, 25.8, 25.3. Anal. Calcd for C₁₇H₂₁NO₂S: C, 67.30; H, 6.98; N, 4.62; S, 10.57. Found: C, 67.21; H, 6.91; N, 4.56; S, 10.52. IV-Copies of ¹H- and ¹³CNMR



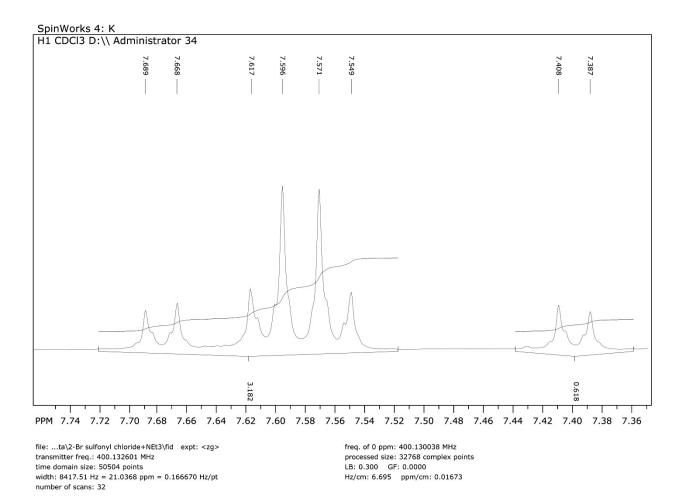




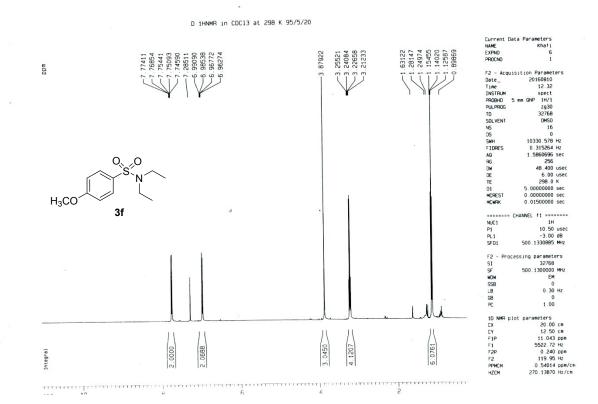


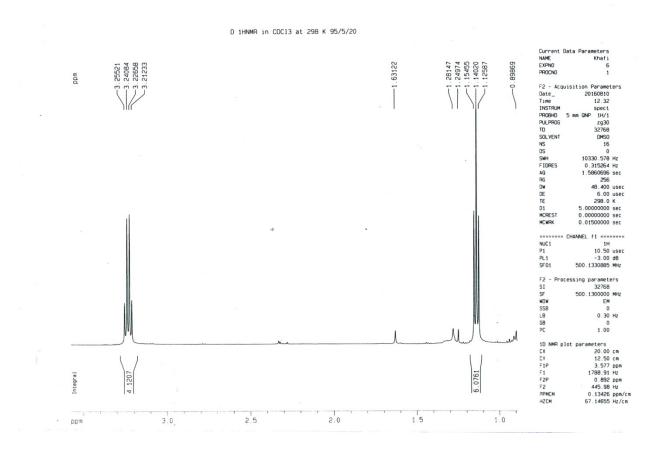


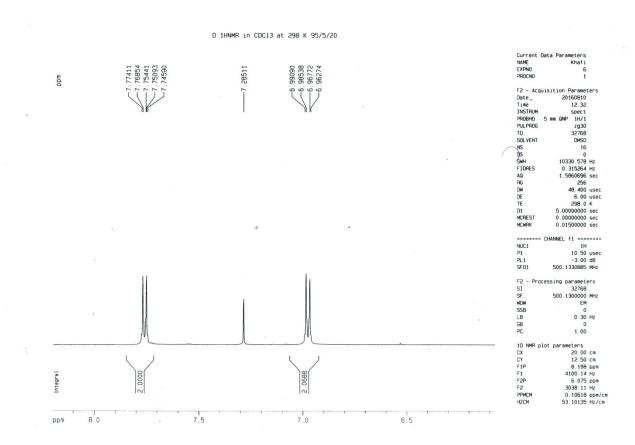
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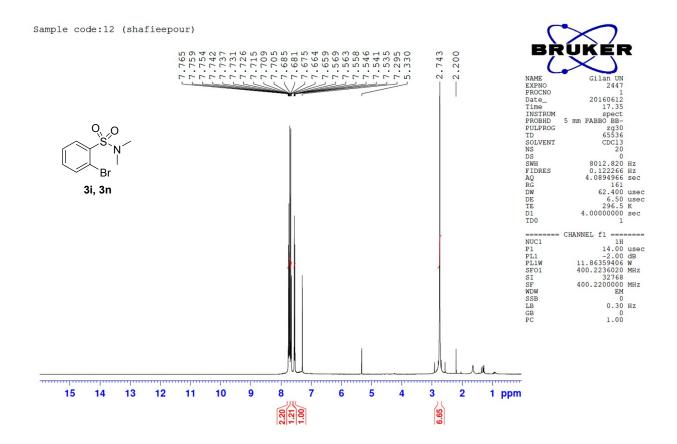


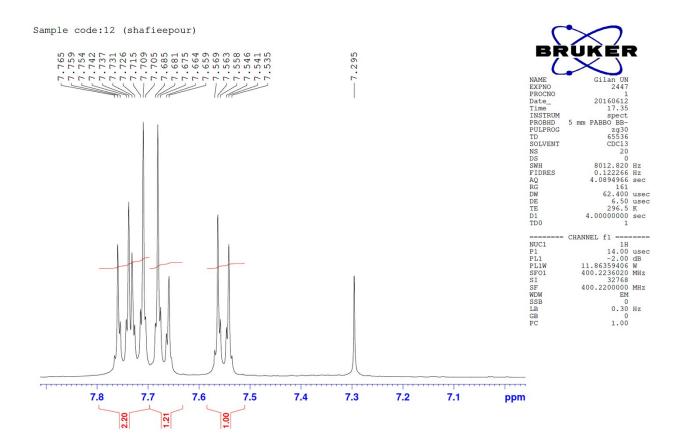
S15

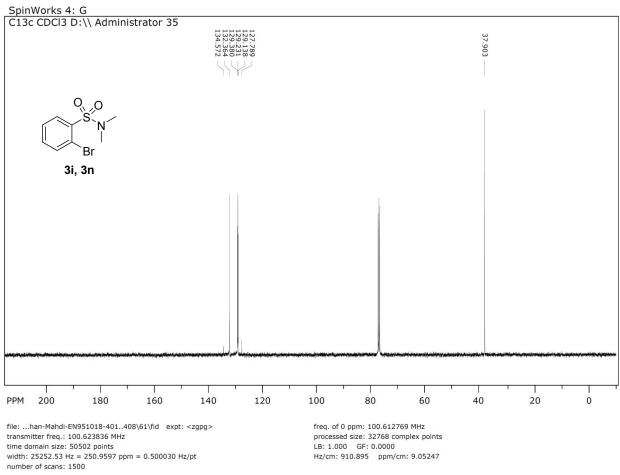




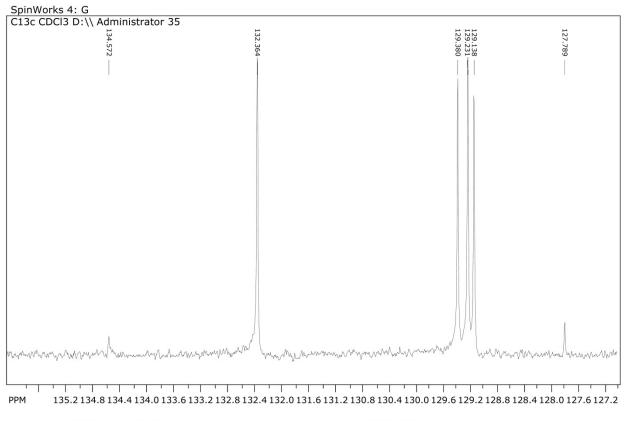




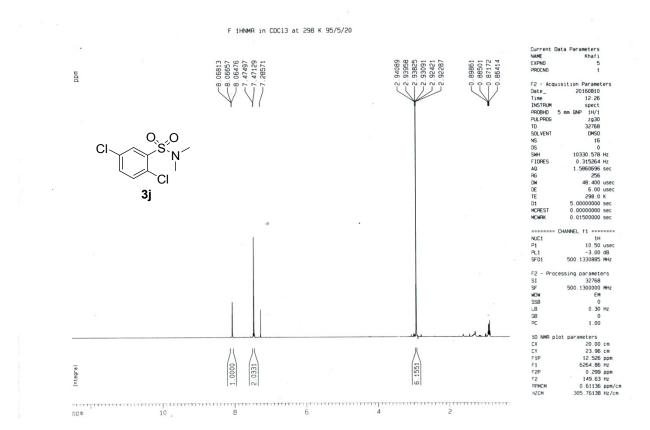


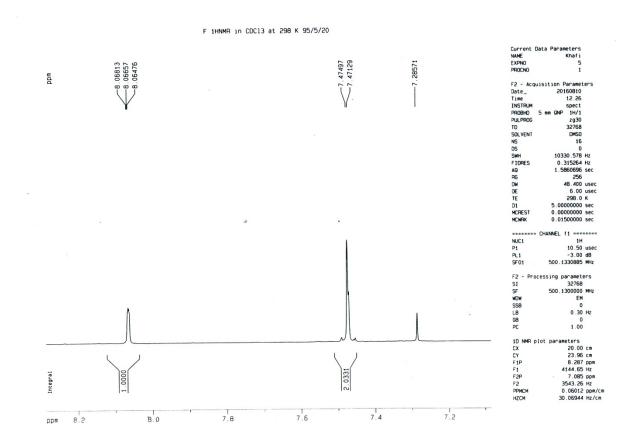


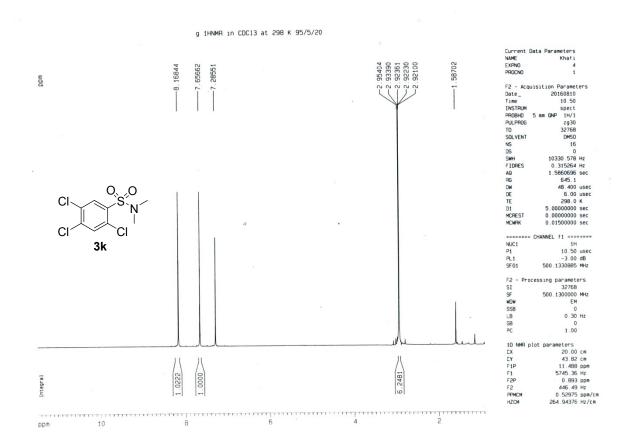
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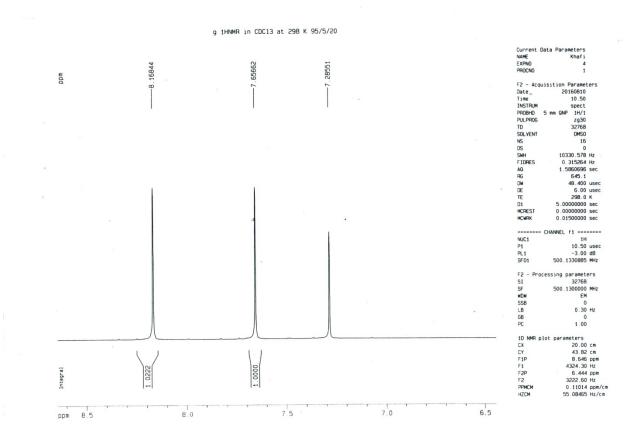


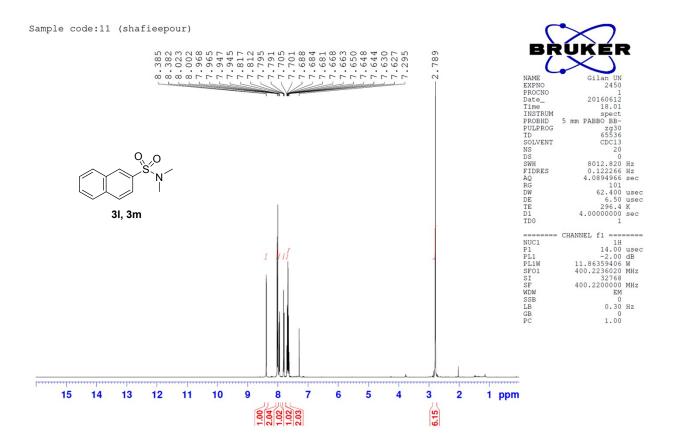
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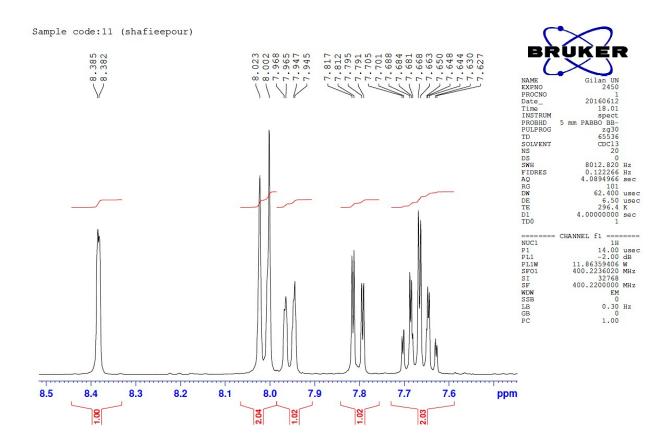


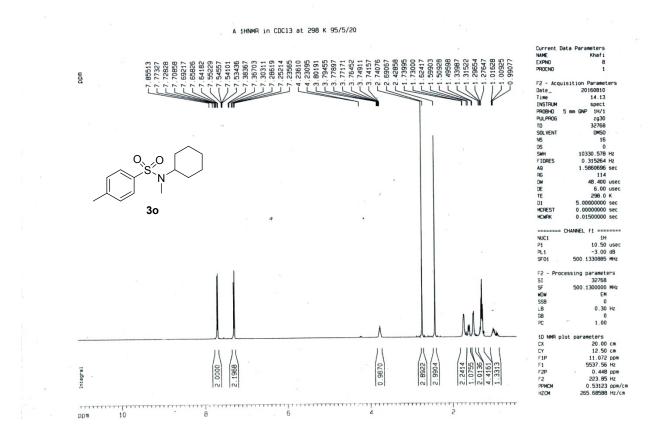


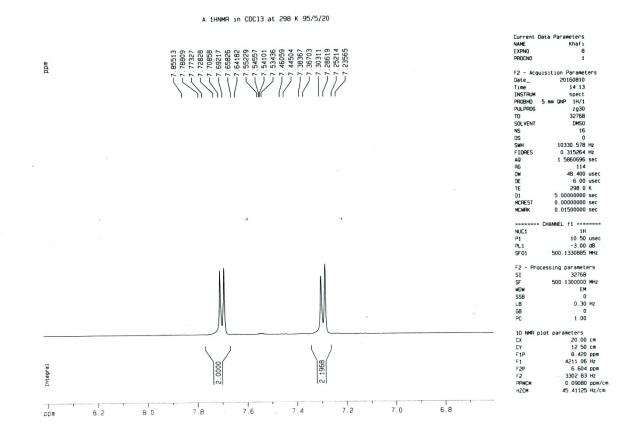


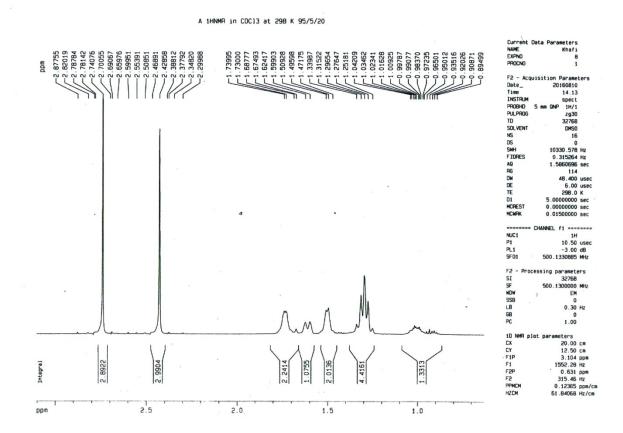


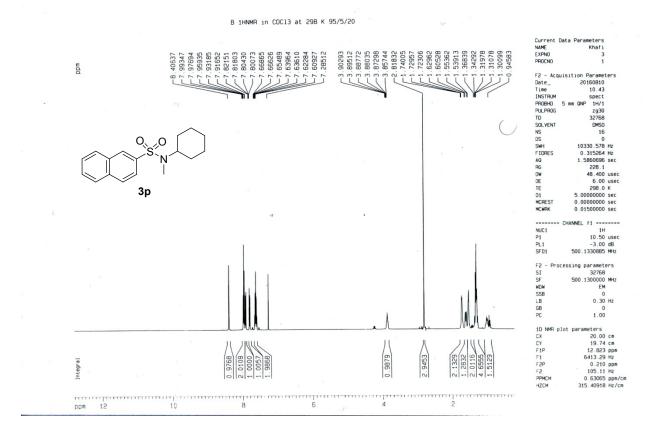


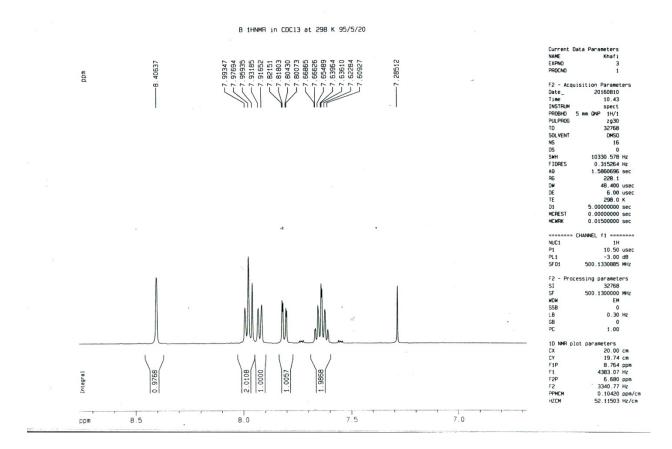


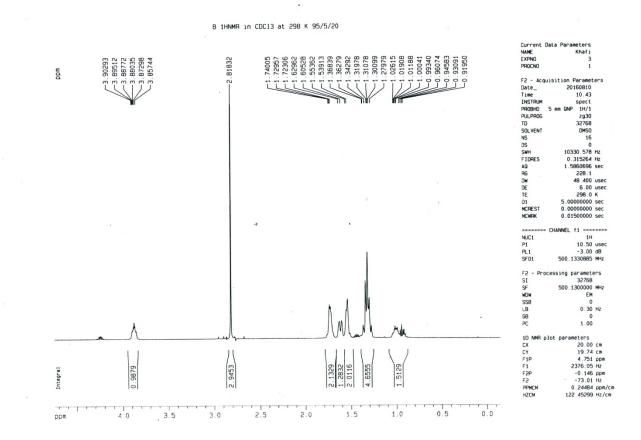


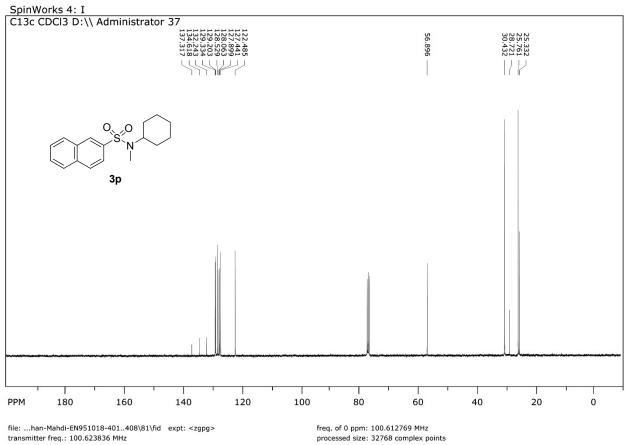






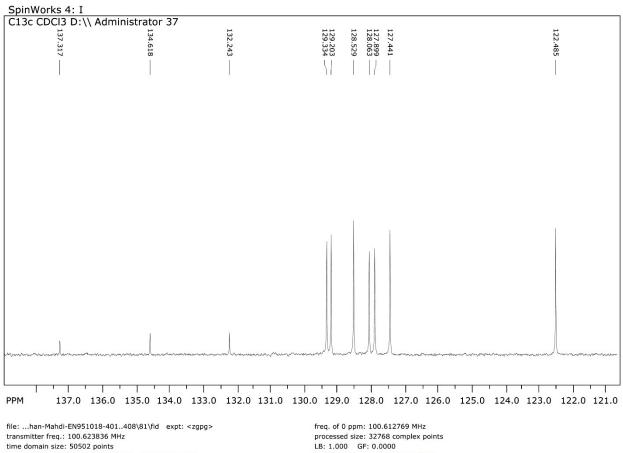






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width: 25252.53 Hz = 250.9597 ppm = 0.500030 Hz/pt number of scans: 1500

freq. of 0 ppm: 100.612769 MHz processed size: 32768 complex points LB: 1.000 GF: 0.0000 Hz/cm: 73.843 ppm/cm: 0.73385

V-References:

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