

Supporting Information

Halo- and Azido-dediazoni- ation of Arenediazonium Tetrafluoroborates with Trimethylsilyl halides (TMSX) and Trimethylsilyl azide (TMSN₃) and Sandmeyer Type Bromodediazoni- ation with Cu(I)Br in [BMIM][PF₆] Ionic Liquid.

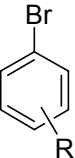
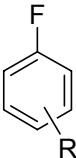
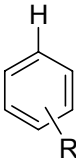
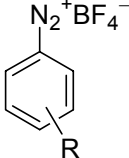
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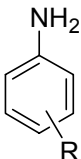
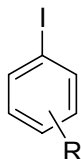
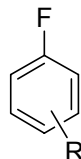
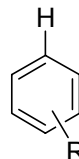
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Table S1. Product Distribution in Dediazonation Reactions in the Presence of TMSBr

Substrate	Temp	Product Distribution % ^{a,b,c}		
				
 1 (R = <i>p</i> - <i>t</i> -Bu)	55 °C	34	55	3
	RT	31	42	9
2 (R = <i>p</i> -Cl)	55 °C	65		35
	RT	70		30
3 (R = <i>p</i> -Me)	55 °C	88	6	6
	RT	91	5	3
4 (R = H)	55 °C	2	96	
	RT	7	88	
5 (R = <i>p</i> -Br)	55 °C	49		34
	RT	67		23
6 (R = <i>p</i> -CH ₃ O)	55 °C	80	5	
	RT	77	6	
7 (R = <i>m</i> -NO ₂)	55 °C	78		13
	RT	67		17
8 (R = 2,4,6-Me ₃)	55 °C	52	48	
	RT	87	13	

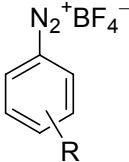
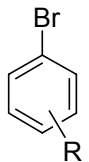
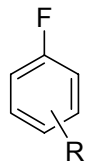
^{a)} Products confirmed by GC coinjection with authentic samples or by GC-MS; ^{b)} Yields determined by GC (traces of unidentified materials were detectable by GC in some cases); ^{c)} No literature data are available under classical/conventional conditions (without IL) for comparison.

Table S2. Product Distribution for *in situ* Diazotization and Iododediazotiation

Substrate	Product Distribution % ^{a,b,c}		
			
R = <i>p-t</i> -Bu	71	9	2
R = <i>p</i> -Me	62	9	9
R = <i>p</i> -Br	74	<1	7
R = <i>p</i> -CH ₃ O	86		

^{a)} Products confirmed by GC coinjection with authentic samples, GC-MS, or by ¹H NMR; ^{b)} Yields determined by GC (traces of unknown compounds with high GC retention times were detectable in some cases, presumably due to minor formation of biaryls); ^{c)} Reactions of TMSX (X = Cl, Br, I) with aniline and substituted anilines with NaNO₂ (or *t*BuONO₂) and C₆H₅CH₂N⁺Et₃ Cl⁻ in CCl₄ at 0 °C have been reported^{S1} (instead of TMSI an equimolar mixture of hexamethyldisilane and I₂ was used). The reported GC yields of ArX were in 70-100% range.^{S1}

Table S3. Product Distribution in Dediazonation Reactions in the presence of TMSBr and Cu(I)Br Immobilized in the IL.

Substrate	Product Distribution % ^{a,b,c}		
			
1 (R = <i>p</i> - <i>t</i> -Bu)	<2	96	<2
2 (R = <i>p</i> -Cl)	4	61	35
3 (R = <i>p</i> -Me)	<2	84	14
5 (R = <i>p</i> -Br)	23		63
6 (R = <i>p</i> -CH ₃ O)	22	59	19
7 (R = <i>m</i> -NO ₂)	75		25
8 (R = 2,4,6-Me ₃)	4	96	

^{a)} Products confirmed by GC coinjection with authentic samples or by GC-MS; ^{b)} Yields determined by GC; ^{c)} No literature data for these reactions are available under classical/conventional conditions (without IL) for comparison.

Experimental

General. All reagents employed in this study were high purity commercial samples, which were used without further purification.

Reactions were carried out in small Schlenk tubes under nitrogen or argon atmosphere.

Diethyl ether used for extraction was distilled over magnesium sulfate or from benzophenone/sodium prior to use.

GC analyses employed a capillary OV101 column. GC-MS analyses were performed on an ion-trap instrument. NMR spectra were recorded on a 400MHz instrument (for product confirmation) and at 500 MHz (for multinuclear studies). IR spectra were obtained on an FT-IR instrument.

Yield Determination by GC. The reaction mixtures in ether were directly analyzed by GC. In each case the GC conversions were determined by taking an average of 3 injections. The use of internal standard for reporting GC conversions became unnecessary since in several control experiments the response factors determined for 1:1 equimolar mixtures of authentic samples of products formed in various reactions were found to be good within 1%.

Preparation of Arenediazonium Salts.⁴ The aniline substrate (4.85 mmol) was dissolved in a minimal amount of water and 48% tetrafluoroboric acid (21.8 mmol, 2.68

mL) was added. In a separate flask, sodium nitrite (0.670 g) was dissolved in a minimal amount of water. The sodium nitrite solution was dropwise added into the aniline/acid solution cooled in an ice/salt bath. The resulting precipitate was washed with cold water (2×5 mL) and purified by re-precipitation from acetonitrile/ether. The pure salt was dried under vacuum and analyzed by IR as a KBr pellet.

p-*tert*-Butylbenzenediazonium tetrafluoroborate (**1**): IR 2286 cm^{-1} (N_2^+)

p-Chlorobenzenediazonium tetrafluoroborate (**2**): IR 2279 cm^{-1} (N_2^+)

p-Toluenediazonium tetrafluoroborate (**3**): IR 2297 cm^{-1} (N_2^+)

Benzenediazonium tetrafluoroborate (**4**): IR 2297.1 cm^{-1} (N_2^+)

p-Bromobenzenediazonium tetrafluoroborate (**5**): IR 2290 cm^{-1} (N_2^+)

p-Methoxybenzenediazonium tetrafluoroborate (**6**): IR 2255 cm^{-1} (N_2^+)

m-Nitrobenzenediazonium tetrafluoroborate (**7**): IR 2307 cm^{-1} (N_2^+)

2,4,6-Trimethylbenzenediazonium tetrafluoroborate (**8**): IR 2257 cm^{-1} (N_2^+)

Procedure for in Situ Diazotization followed by Iododediazotization: Under nitrogen atmosphere, a Schlenk tube equipped with a magnetic stirring bar was charged with [BMIM][PF₆] (3.52 mmol, 0.66 mL) and nitrosonium tetrafluoroborate (32.9 mg, 0.28 mmol). The tube was purged with nitrogen and cooled to 0 °C in an ice/salt bath.

The aniline (0.141 mmol) was added and the resulting mixture was stirred at 0 °C for 30 minutes. Iodotrimethylsilane (0.282 mmol, 38.5 μ L) was then added and the mixture was stirred at room temperature overnight. The mixture was extracted with diethyl ether (0.5 mL \times 3). The ether extract was neutralized directly with sodium bicarbonate and filtered quickly prior to analysis by GC, GC-MS, IR, or NMR.

Sandmeyer type Halodediazotiation in Ionic liquid: Under nitrogen atmosphere, a Schlenk tube equipped with a magnetic stirring bar was charged with [BMIM][PF₆] (3.52 mmol, 0.66 mL) and copper (I) bromide (0.176 mmol, 25.2 mg). The mixture was heated to 65-75 °C until copper (I) bromide was immobilized under argon atmosphere. The arenediazonium salt (0.141 mmol) was added and the resulting mixture was stirred overnight with heating (70 °C). The reaction mixture was extracted with diethyl ether (0.5 mL \times 3). The ether extract was neutralized directly with sodium bicarbonate and filtered quickly prior to analysis by GC, GC-MS, IR, or NMR.

Product Characterizations:

m-Bromonitrobenzene: GC-MS *m/z* (EI) 200.9/202.9 (M^+)

p-Bromo-*tert*-butylbenzene: GC-MS *m/z* (EI) 212.0/214.0 (M^+)

p-*tert*-Butyliodobenzene: ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 1.31 (s, 9H)

p-Bromoiodobenzene: GC-MS *m/z* (EI) 282.0/283.9 (M⁺); ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H)

m-Iodonitrobenzene: ¹H NMR (400 MHz, CDCl₃) δ 8.58 (dd, *J* = 1.8, 1.8 Hz, 1H), 8.21 (m, 1H), 8.03 (m, 1H), 7.29 (dd, *J* = 8.0, 8.0 Hz, 1H)

p-*tert*-Butylphenyl azide:^{S2} GC-MS *m/z* (EI) 175.1 (M⁺); IR (NaCl) 2129, 2094 cm⁻¹ (N₃)

p-Chlorophenyl azide: ^{S3} IR (NaCl) 2133, 2096 cm⁻¹ (N₃)

p-Tolyl azide: ^{S3, S4} GC-MS *m/z* (EI) 133.1 (M⁺); IR (NaCl) 2130, 2106 cm⁻¹ (N₃)

Phenyl azide:^{S3, S4} GC-MS *m/z* (EI) 119.0 (M⁺); IR (NaCl) 2244, 2298 cm⁻¹ (N₃)

p-Bromophenyl azide:^{S3} IR (NaCl) 2249, 2291 cm⁻¹ (N₃)

p-Anisyl azide: ^{S4} GC-MS *m/z* (EI) 149.0 (M⁺); IR (NaCl) 2131, 2016 cm⁻¹ (N₃)

m-Nitrophenyl azide:^{S5} GC-MS *m/z* (EI) 164.1 (M⁺); IR (NaCl) 2191, 2151 cm⁻¹ (N₃)

Mesityl azide:^{S6} GC-MS *m/z* (EI) 161.1 (M⁺); ¹H NMR (400 MHz, CDCl₃) δ 6.83 (s, 2H), 2.32 (s, 6H), 2.24 (s, 3H)

All other products were confirmed by GC coinjection with authentic samples.

References

- S1) Lee, J. G.; Cha, H. T. *Tetrahedron. Lett.* **1992**, 33, 3167-3168
- S2) Barr, L.; Lincoln, S. F.; Easton, C. J. *Supramolecular Chem.* **2005**, 17, 547-555.
- S3) Zhu, W.; Ma, D. *Chem. Commun.* **2004**, 888-889.
- S4) Huber, M. L.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 721-722.
- S5) Liang, T. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, 109, 7803-7810.
- S6) Smith, P. A. S.; Rowe, C. D.; Bruner, L. B. *J. Org. Chem.* **1969**, 34, 3430-3433.

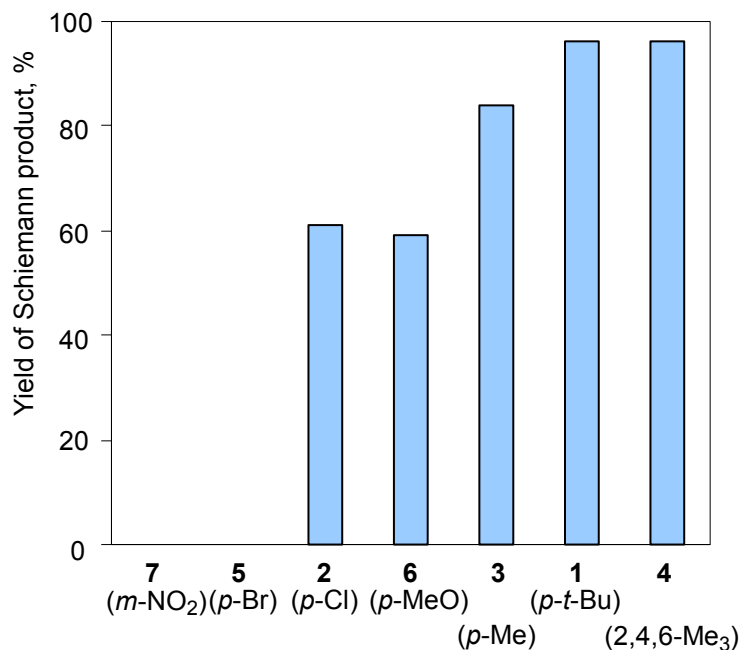


Chart S1. Substituent effect on fluorodediazoniaion product distribution in the presence of Cu(I)Br immobilized in the IL.

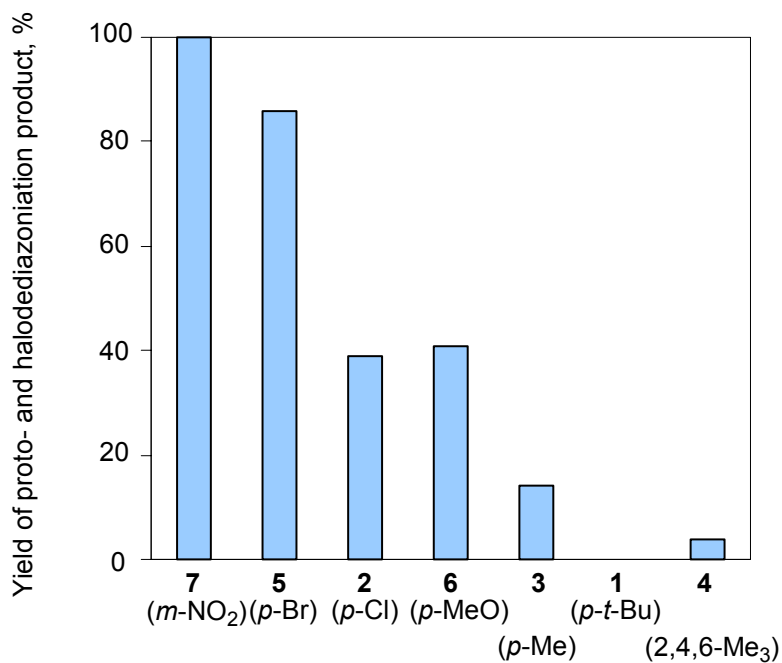


Chart S2. Substituent effect on proto- and halodediazoniaion product distribution in the presence of Cu(I)Br immobilized in the IL.

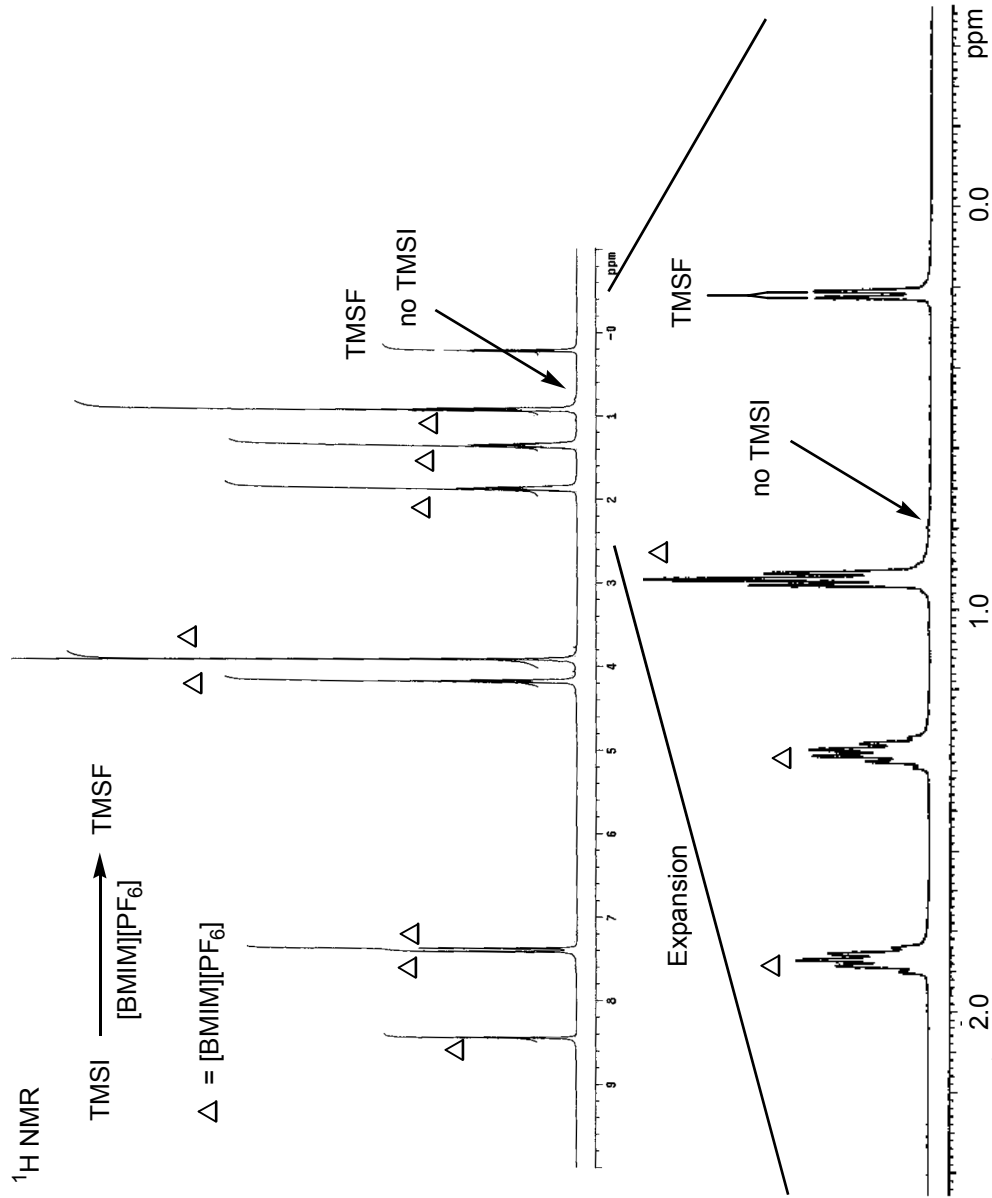


Figure S1. $^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum, showing the formation of fluorotrimethylsilane in the reaction of iodotrimethylsilane in $[\text{BMIM}][\text{PF}_6]$.

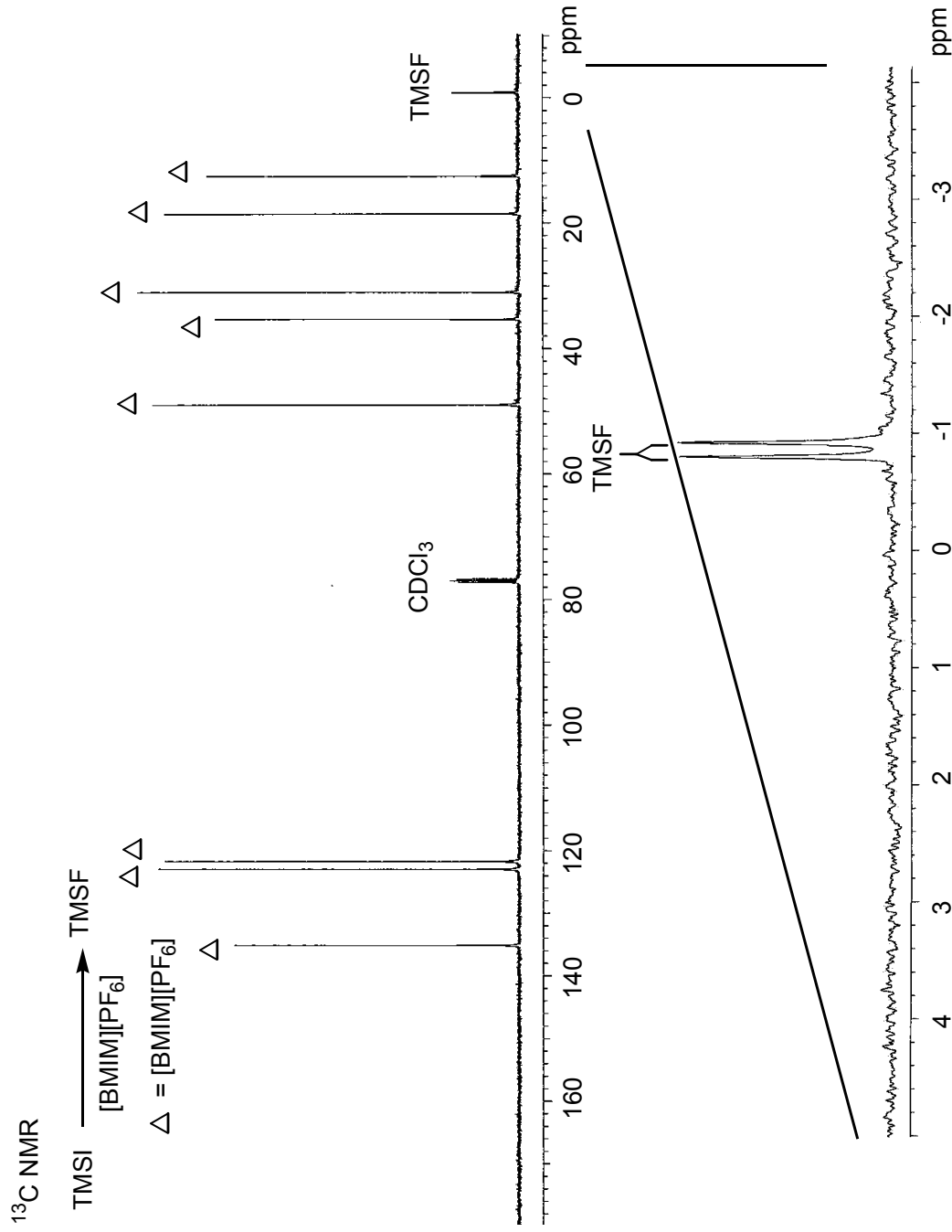


Figure S2. ^{13}C NMR (125 MHz, CDCl_3) spectrum, showing the formation of fluorotrimethylsilane in the reaction of iodotrimethylsilane in $[\text{BMIM}][\text{PF}_6]$.

^{19}F NMR

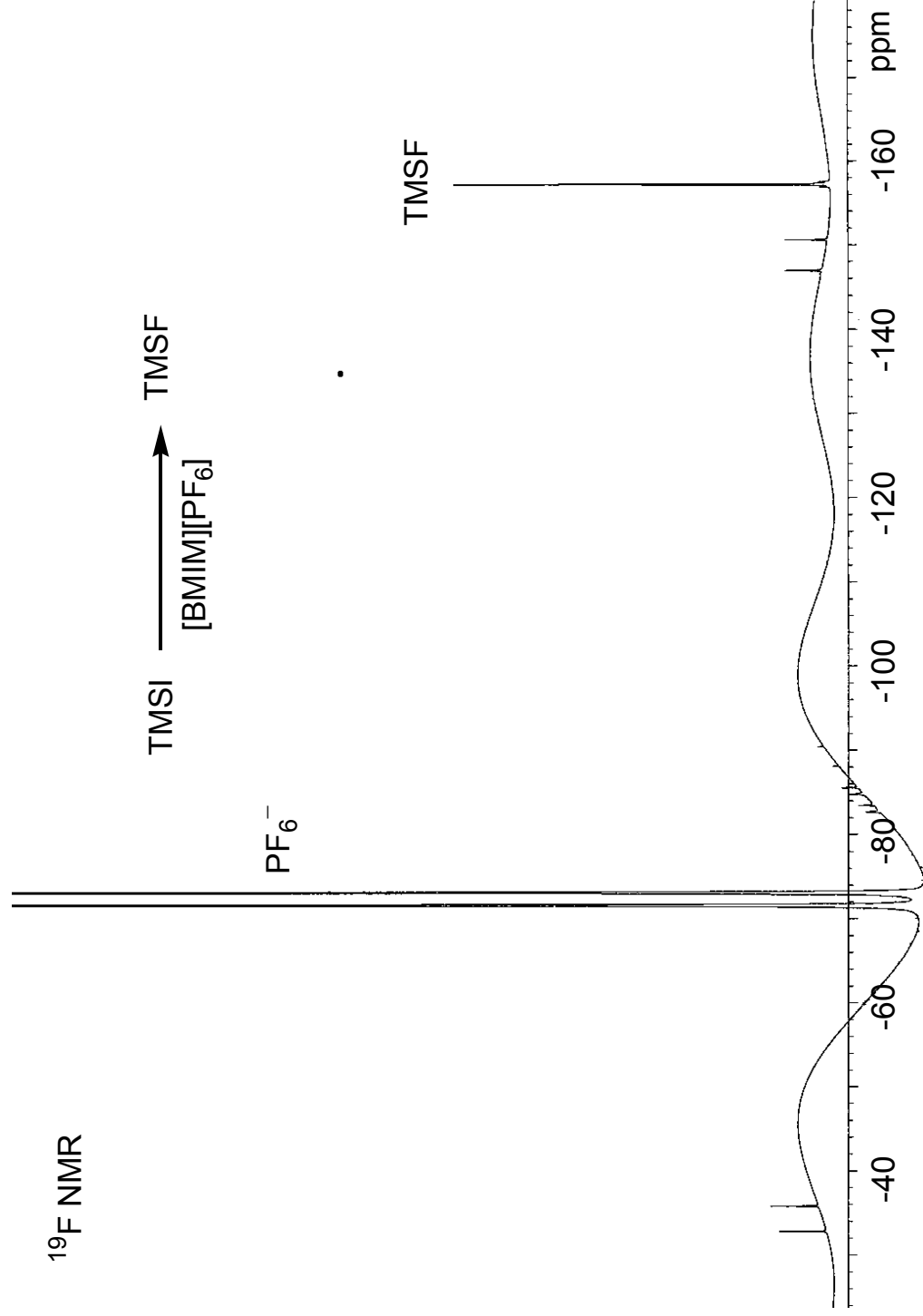
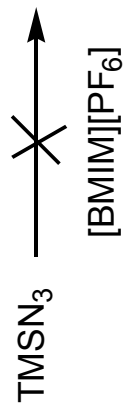


Figure S3. ^{19}F NMR (470 MHz, CDCl_3) spectrum, showing the formation of fluorotrimethylsilane in the reaction of iodotrimethylsilane in $[\text{BMIM}][\text{PF}_6]$.



^{29}Si NMR

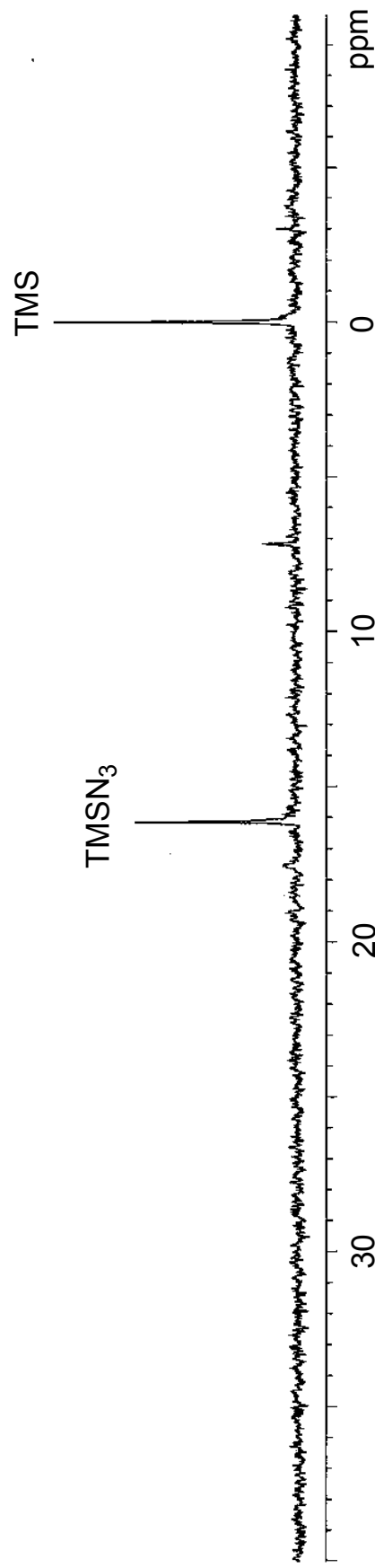


Figure S5. ^{29}Si NMR (99 MHz, CDCl_3) spectrum of azidotrimethylsilane in [BMIM][PF₆].

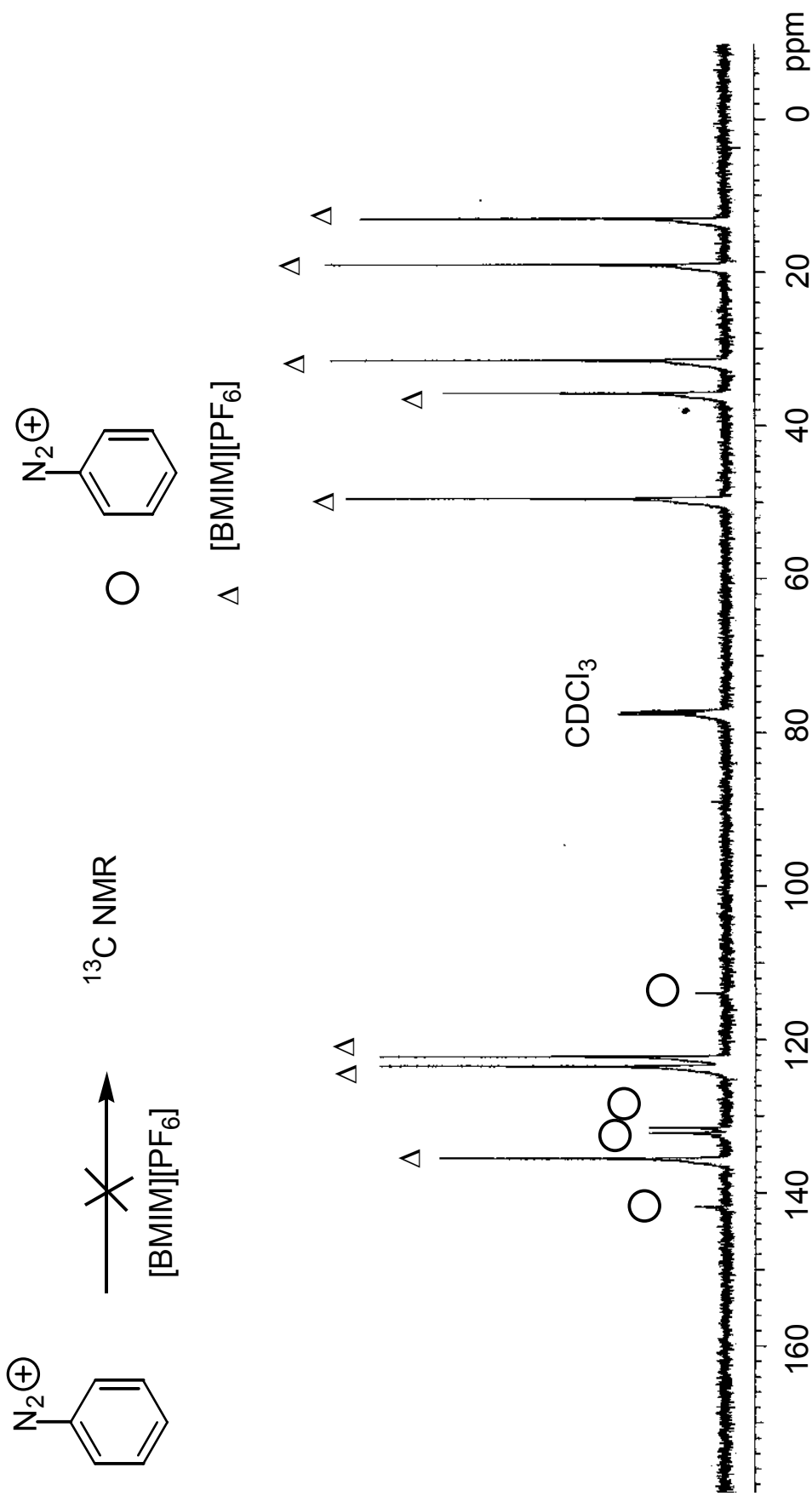


Figure S6. $^{13}\text{C NMR}$ (125 MHz, CDCl₃) spectrum of benzenediazonium tetrafluoroborate immobilized in [BMIM][PF₆].

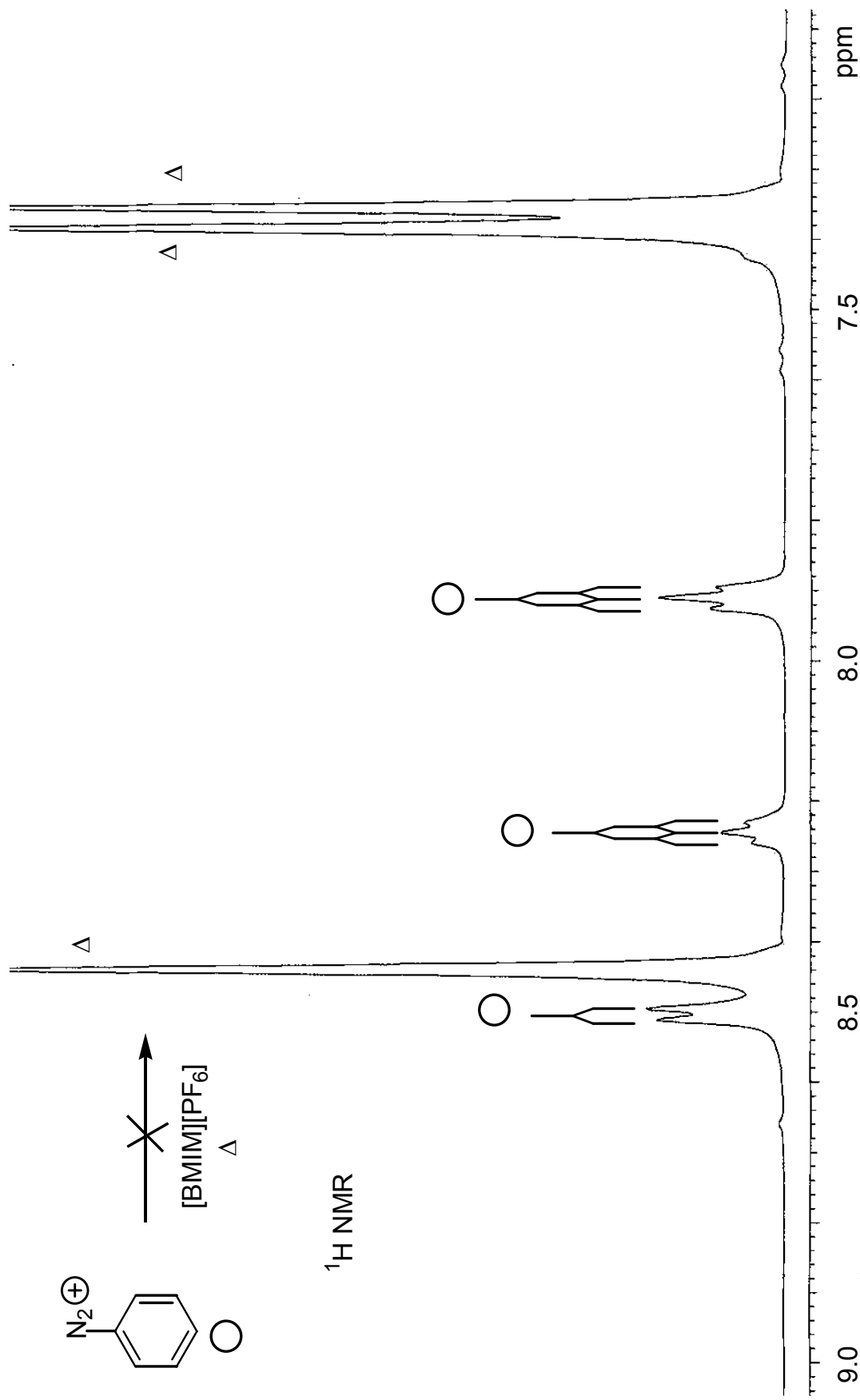


Figure S7. $^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of benzenediazonium tetrafluoroborate immobilized in [BMIM][PF₆].

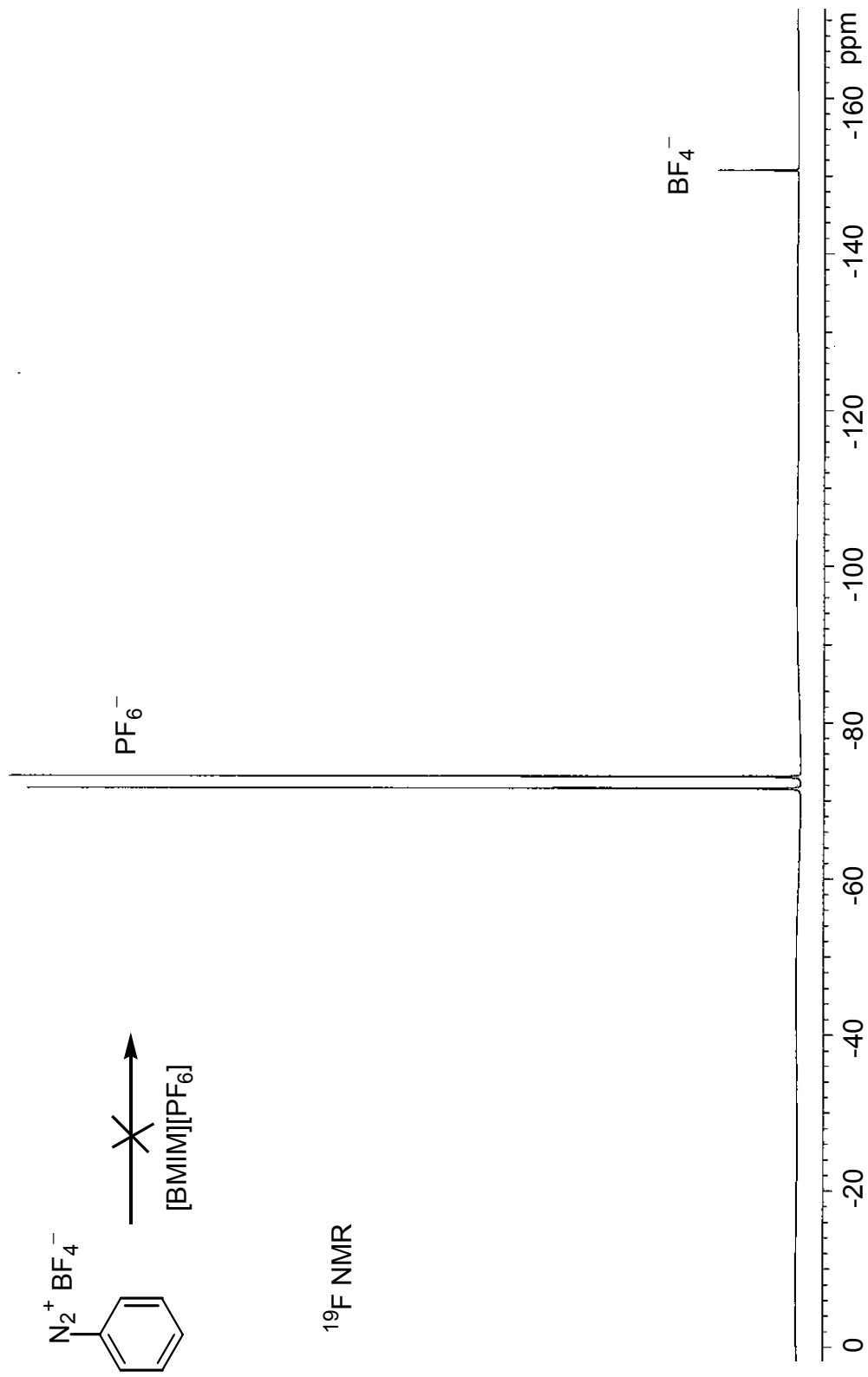


Figure S8. ^{19}F NMR (470 MHz, CDCl_3) spectrum of benzenediazonium tetrafluoroborate immobilized in $[\text{BMIM}][\text{PF}_6]$.

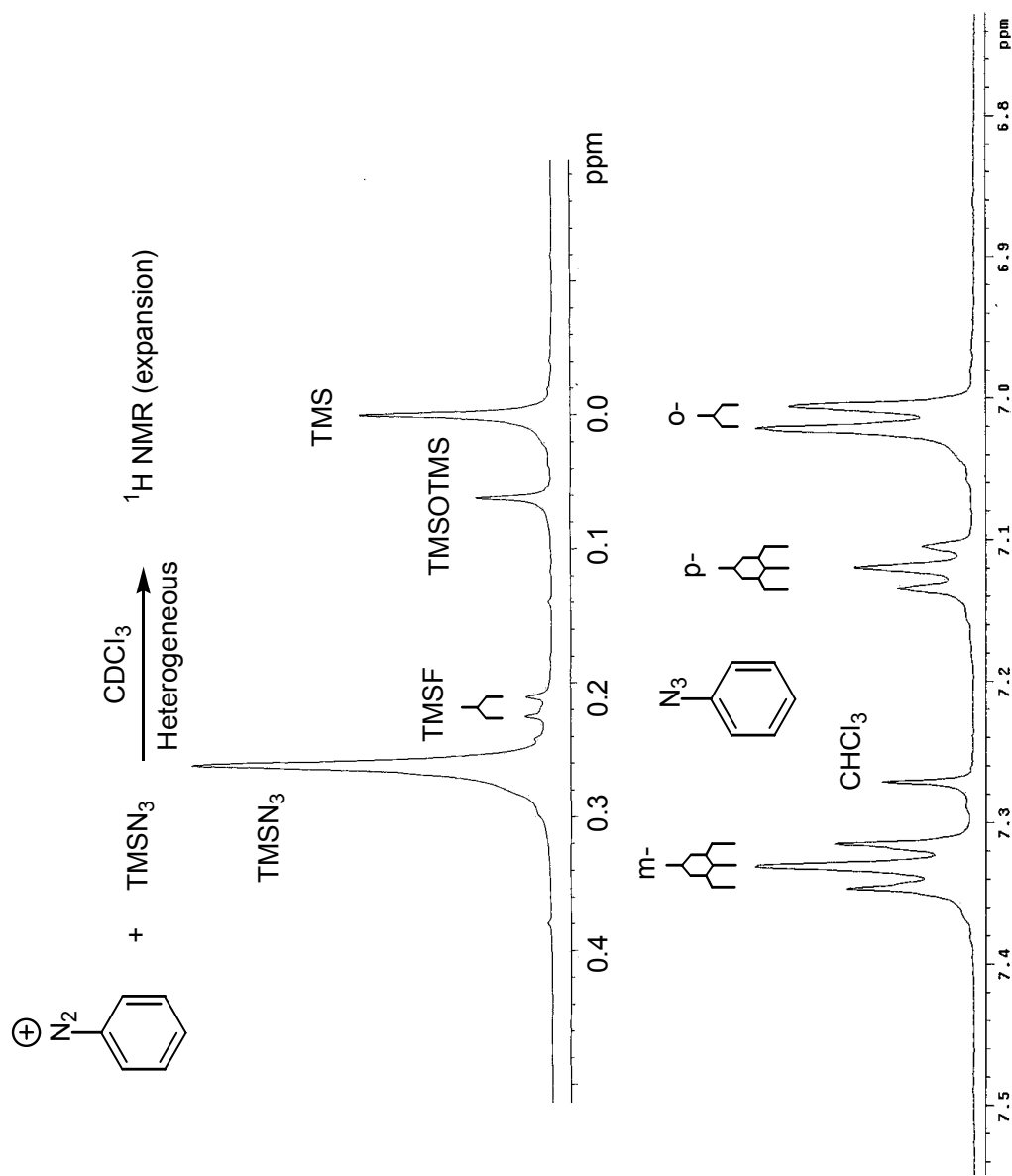


Figure S9. $^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum, showing the formation of phenyl azide and TMSF in the reaction of TMSN_3 with benzenediazonium tetrafluoroborate in CDCl_3 .

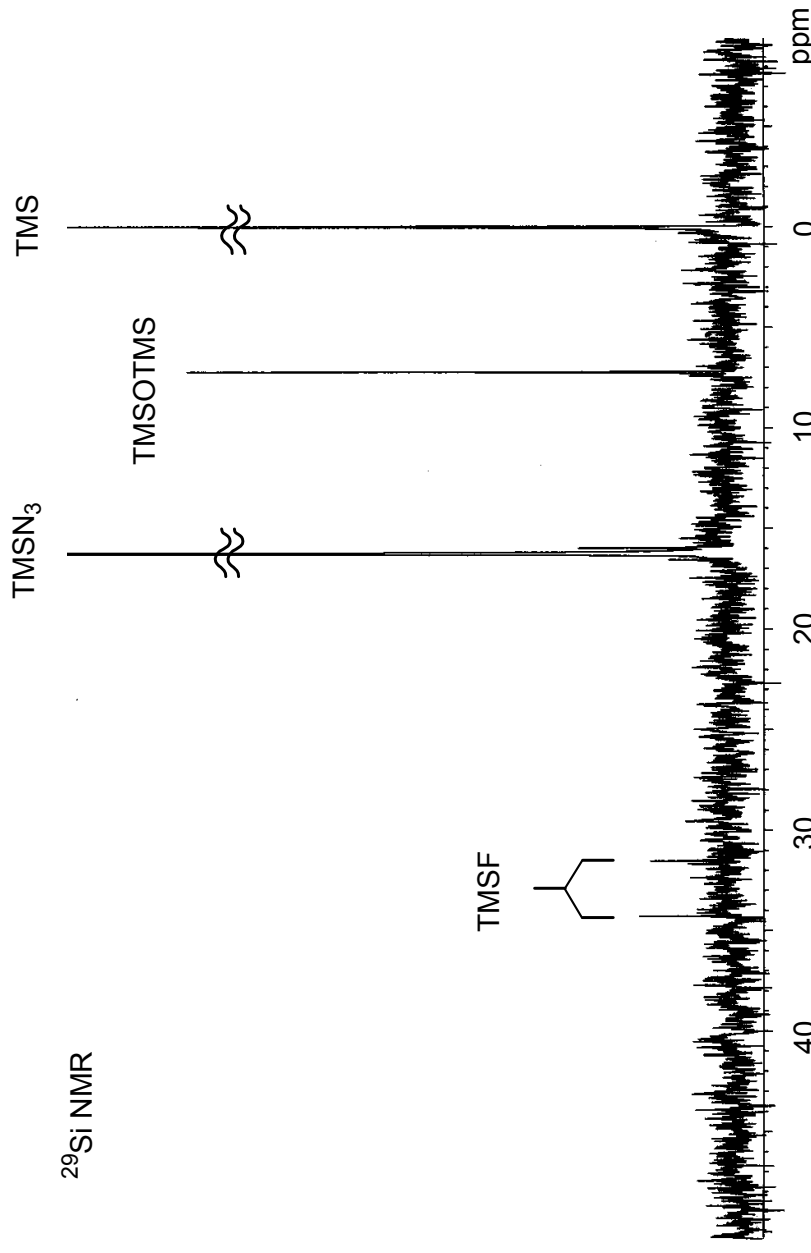
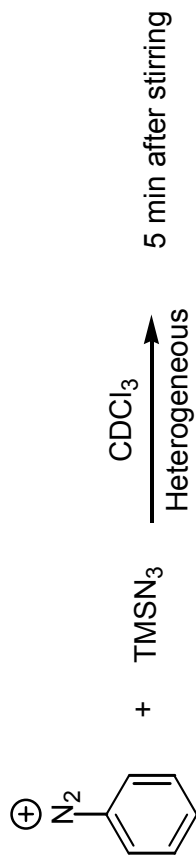


Figure S10. ²⁹Si NMR (99 MHz, CDCl₃) spectrum, showing the formation of TMSF in the reaction of TMSN₃ with benzenediazonium tetrafluoroborate in CDCl₃.

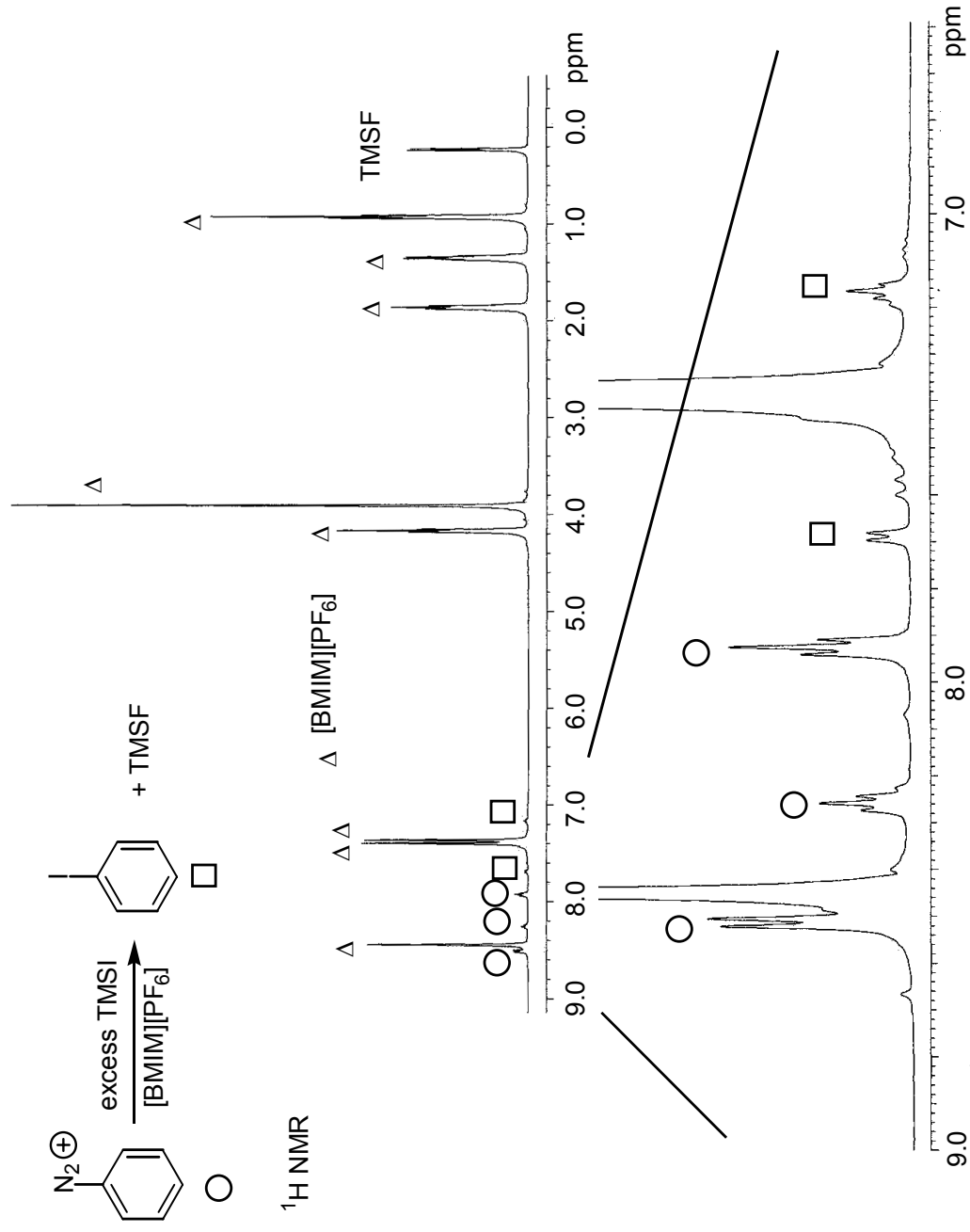


Figure S11. ¹H NMR (500 MHz, CDCl₃) spectrum, showing the formation of iodobenzene and fluorotrimethylsilane in the reaction of benzenediazonium tetrafluoroborate with iodotrimethylsilane in [BMIM][PF₆].

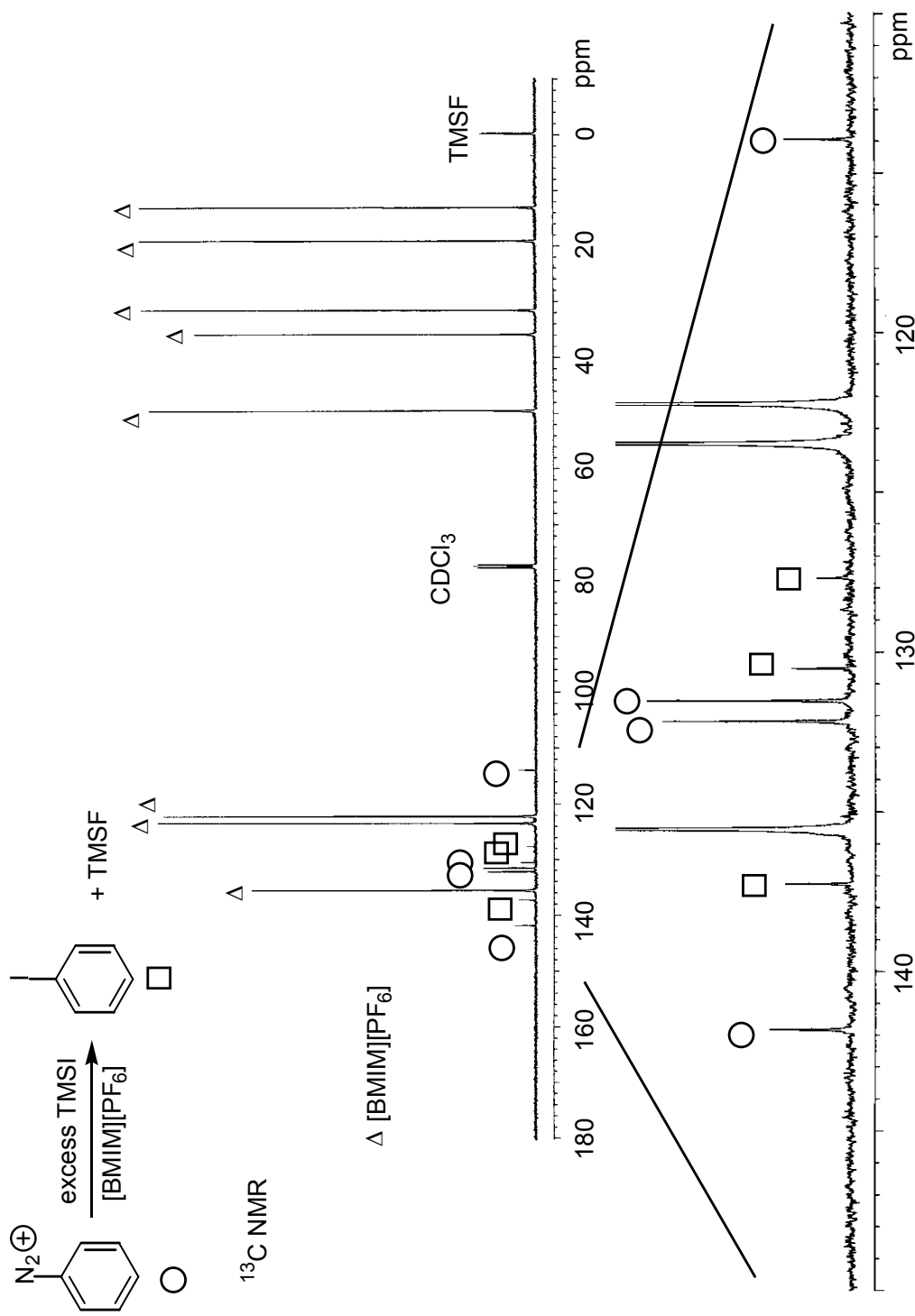


Figure S12. ^{13}C NMR (125 MHz, CDCl_3) spectrum, showing the formation of iodobenzene and fluorotrimethylsilane in the reaction of benzenediazonium tetrafluoroborate with iodotrimethylsilane in [BMIM][PF₆].

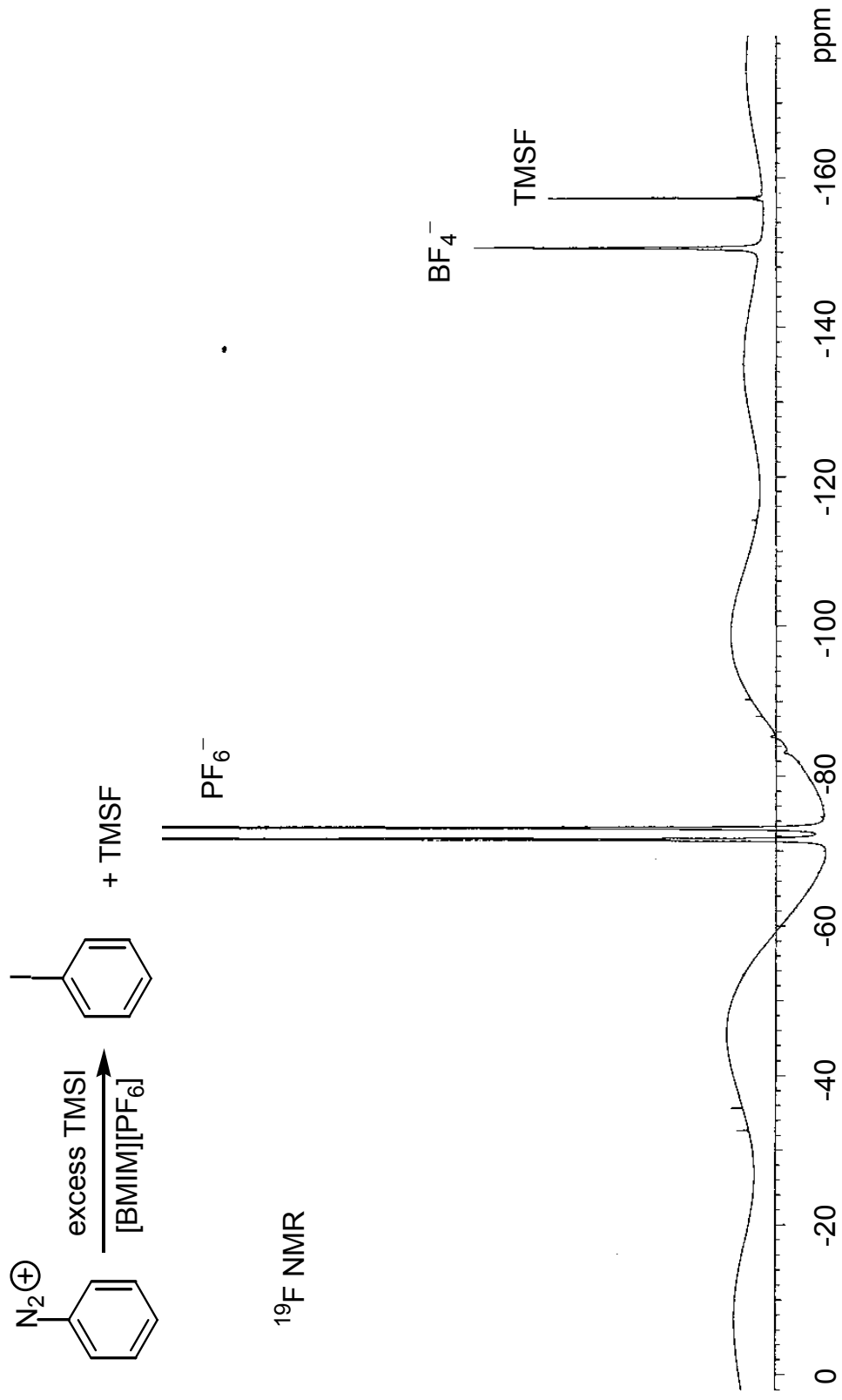


Figure S13. ^{19}F NMR (470 MHz, CDCl_3) spectrum, showing the formation of fluorotrimethylsilane in the reaction of benzenediazonium tetrafluoroborate with iodotrimethylsilane in $[\text{BMIM}][\text{PF}_6]$.

