Supplementary Information

Access to Amidines via C(sp^2)-*N* Coupling of Trifluoroborate-Iminiums with *N*-Fluorobenzenesulfonimide

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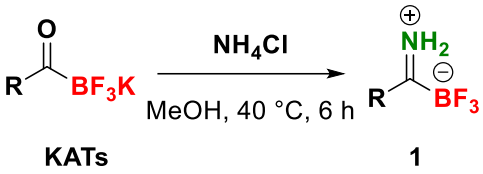
1. General Chemistry Information

The reagents and solvents were used as received from commercial suppliers (Merck-Sigma Aldrich, TCI, Acros Organics, Abcr, Janssen, Fluka, Fluorochem, Alfa Aesar, BLDPharm, Carlo Erba) and were used as supplied unless noted otherwise. After extraction, organic phases were dried over anhydrous sodium sulfate. Reactions were monitored using analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} Al plates (Merck). Developed plates were inspected under UV light and, if necessary, visualized with ninhydrin or phosphomolybdate stains. Column chromatography was performed on silica gel (SiO_2; Silica gel 60, particle size: 0.035–0.070 mm, Merck). Nuclear magnetic resonance spectra were recorded on a Bruker Avance III 400 MHz spectrometer at 400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F nucleus, 128 MHz for ^{11}B nucleus, and 41 MHz for ^{15}N nuclei, using acetone-d_6, MeCN-d_3, $MeOD_4$, DMSO-d_6, $CDCl_3$ and D_2O as solvents. Unless otherwise indicated, the spectra were recorded at 295 K. Chemical shifts are reported in *parts per million* (ppm), with ^{1}H and ^{13}C resonances referenced to the residual non-deuterated solvent signal. ^{11}B, ^{19}F and ^{15}N spectra are not calibrated. Coupling constants *J* are reported in Hz. Continuous wave (cw) X-band electron paramagnetic resonance (EPR) measurements were performed using a Bruker E500 EPR spectrometer, operating at 9.4 GHz, and equipped with a 4122SHQE cylindrical Bruker resonator. Mass spectra were recorded on Thermo Scientific Q Exactive Plus LC-MS/MS (high resolution mass spectrometry, HRMS), and IR spectra on Thermo Nicolet FT-IR. Melting points were determined on a Reichelt hot-stage apparatus and are uncorrected. HPLC analyses were performed on Thermo Scientific Dionex UltiMate 3000 modular system (Thermo Fisher Scientific Inc.). The general method used a Waters Acquity UPLC® HSS C18 SB column (2.1 × 50 mm, 1.8 µm) thermostated at 40 °C, with: injection volume, 5 µL; sample, 0.2 mg/mL in MeOH; flow rate, 0.4 mL/min; detector λ, 220 or 254 nm; mobile phase A: 0.1% TFA (v/v) in MilliQ water; mobile phase B: MeCN. Gradient: 0–2 min, 10% B; 2–5 min, 10%–90% B; 5–8 min, 90% B. LC-MS analyses were performed on Agilent 1260 Infinity modular system coupled with Advion Expression CMS mass spectrometer. The general method used a Waters XBridge® C18 SB column (4.6 × 150 mm, 3.5 µm) thermostated at 40 °C, with: injection volume, 20 µL; sample, 0.1–0.5 mg/mL in MeOH; flow rate, 1.5 mL/min; detector λ, 220 and 254 nm; mobile phase A: 0.1% HCOOH (v/v) in MilliQ water + 1% MeCN (v/v); mobile phase B: MeCN. Gradient: 0–1 min, 25% B; 1–6 min, 25%–98% B; 6–6.5 min, 98% B; 6.5–7 min, 98%–25% B; 7–10 min, 25% B.

General Procedure 1 (GP1) – reversed-phase column chromatography: Certain intermediates and products were purified by reversed-phase column chromatography (RP-CC) (Isolera Biotage One Flash Chromatography system, Biotage® Sfär C18 Duo 100 Å 30 µm column, 30 g, column volume = 45 mL) using a gradient of 0.1% TFA in deionized water and MeCN as eluent (gradient 0–100% MeCN in 6 column volumes (270 mL); 100% MeCN for 2 column volumes (90 mL)). After the RP-CC, fractions

containing the product were combined and organic volatiles were evaporated *in vacuo*. If specified, the remaining aqueous solution was made alkaline (pH 12–14) with 1 M NaOH (aq) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was dried over anhydrous sodium sulfate, filtered, and volatile components evaporated *in vacuo* to afford pure product.

2. Synthesis of Starting Compounds – pTIMs



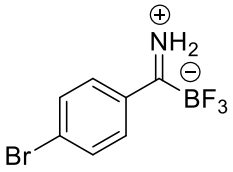
KATs 1

Potassium acyltrifluoroborates (KATs) were purchased from Sigma Aldrich. pTIMs **1** were synthesized following the literature procedure.[S1] Spectral data for **1a–j, 1l–o** and **1r** are reported in our previous publication.[S1]

General Procedure for the Synthesis of pTIMs (1)

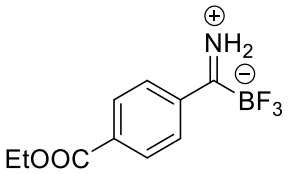
In an oven-dried flask under argon atmosphere, KAT (1 equiv.) and NH_4Cl (5 equiv.) were dissolved in dry MeOH (0.08 M) and stirred at 40 °C for 6 h. The solvent was evaporated under reduced pressure and dry residue was suspended in boiling EtOAc (75–80 °C). The suspension was filtered, washed with EtOAc, and the filtrate was evaporated under reduced pressure to afford pTIM **1**, which were further purified by a filtration over a short path of SiO_2 (gradient, 1) CH_2Cl_2/MeOH = 30/1, 2) CH_2Cl_2/MeOH = 15/1).

((4-Bromophenyl)(iminio)methyl)trifluoroborate (1k)



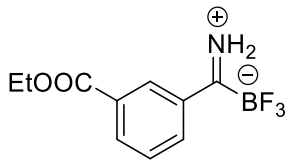
Synthesized from potassium (4-bromobenzoyl)trifluoroborate (568 mg, 1.95 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (385 mg, 79% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.79 – 7.87 (m, 2H, Ar-H), 8.09 – 8.18 (m, 2H, Ar-H), 10.59 – 11.01 (m, 1H, NH_2^+), 11.01 – 11.40 (m, 1H, NH_2^+). **^{11}B NMR** (128 MHz, Acetone-d_6) δ –0.02 (q, J = 38.6 Hz). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 130.53, 132.61, 132.78, 133.25, 206 (br m, extracted from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-d_6) δ –146.03 (dd, J = 77.4, 38.4 Hz). **HRMS** (ESI^-): calc. for $C_7H_5NBBrF_3$ $[M–H]^-$: 249.9656, found: 249.9658.

((4-(Ethoxycarbonyl)phenyl)(iminio)methyl)trifluoroborate (1p)



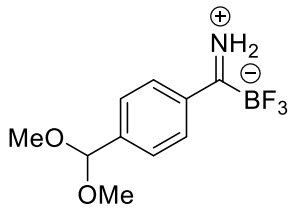
Synthesized from potassium (4-(ethoxycarbonyl)benzoyl)trifluoroborate (500 mg, 1.76 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (212 mg, 62% yield). **^{1}H NMR** (400 MHz, Acetone-*d*$_6$) δ 1.37 (t, *J* = 7.1 Hz, 3H, C$\underline{H}_3$), 4.39 (q, *J* = 7.1 Hz, 2H, C$\underline{H}_2$), 8.16 – 8.21 (m, 2H, Ar-$\underline{H}$), 8.25 – 8.31 (m, 2H, Ar-$\underline{H}$), 10.76 – 11.53 (m, 2H, N$\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-*d*$_6$) δ 0.03 (q, *J* = 38.8 Hz). **^{13}C NMR** (101 MHz, Acetone-*d*$_6$) δ 14.41, 62.15, 130.45, 130.80, 136.23, 137.31, 165.72, 206 (br m, extracted from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-*d*$_6$) δ –146.04 (dd, *J* = 76.5, 37.2 Hz). **HRMS** (ESI$^-$): calc. for $C_{10}H_{10}O_2NBF_3$ [M–H]$^-$: 244.0762, found: 244.0764.

((3-(Ethoxycarbonyl)phenyl)(iminio)methyl)trifluoroborate (1q)



Synthesized from potassium (3-(ethoxycarbonyl)benzoyl)trifluoroborate (1850 mg, 6.51 mmol) according to the General Procedure to afford the title compound as a white solid (1200 mg, 75% yield). **^{1}H NMR** (400 MHz, Acetone-*d*$_6$) δ 1.38 (t, *J* = 7.1 Hz, 3H, C$\underline{H}_3$), 4.40 (q, *J* = 7.1 Hz, 2H, C$\underline{H}_2$), 7.78 (t, *J* = 7.8 Hz, 1H, Ar-$\underline{H}$), 8.34 (dt, *J* = 7.8, 1.5 Hz, 1H, Ar-$\underline{H}$), 8.44 (dt, *J* = 7.9, 1.5 Hz, 1H, Ar-$\underline{H}$), 8.83 (t, *J* = 1.8 Hz, 1H, Ar-$\underline{H}$), 10.62 – 11.67 (m, 2H, N$\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-*d*$_6$) δ 0.05 (q, *J* = 38.8 Hz). **^{13}C NMR** (101 MHz, Acetone-*d*$_6$) δ 14.51, 62.06, 130.37, 131.48, 132.37, 134.03, 135.27, 135.86, 165.71, 206 (br m, extracted from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-*d*$_6$) δ –146.05 (dd, *J* = 76.9, 37.8 Hz). **HRMS** (ESI$^-$): calc. for $C_{10}H_{10}O_2NBF_3$ [M–H]$^-$: 244.0762, found: 244.0764.

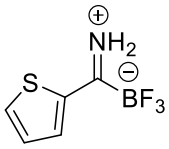
((4-(Dimethoxymethyl)phenyl)(iminio)methyl)trifluoroborate (1s)



Synthesized from potassium (4-formylbenzoyl)trifluoroborate (300 mg, 1.25 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (148 mg, 48% yield). **^{1}H NMR** (400 MHz, Acetone-*d*$_6$) δ 3.32 (s, 6H, OC$\underline{H}_3$), 5.50 (s, 1H, C$\underline{H}$), 7.59 – 7.78 (m, 2H, Ar-$\underline{H}$), 8.16 – 8.31 (m, 2H, Ar-$\underline{H}$), 10.41 – 11.42 (m, 2H, N$\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-*d*$_6$) δ 0.06 (q, *J* = 39.0 Hz). **^{13}C NMR** (101 MHz, Acetone-*d*$_6$) δ 53.05, 102.93, 128.25, 131.01, 133.45, 146.50, 206 (br m, extracted

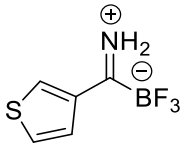
from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-d_6) δ –145.88 (dd, *J* = 77.9, 38.4 Hz). **HRMS** (ESI$^-$): calc. for $C_{10}H_{12}O_2NBF_3$ [M–H]$^-$: 246.0919, found: 246.0920.

(Iminio(thiophen-2-yl)methyl)trifluoroborate (1t)



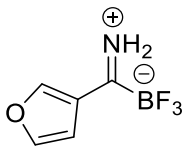
Synthesized from potassium 2-thiophenyltrifluoroborate (500 mg, 2.29 mmol) according to the General Procedure to afford the title compound as a white solid (315 mg, 76% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.41 (dd, *J* = 5.0, 3.9 Hz, 1H, Ar-H), 8.28 (dd, *J* = 4.9, 1.2 Hz, 1H, Ar-H), 8.38 (dd, *J* = 4.0, 1.1 Hz, 1H, Ar-H), 9.85 – 10.87 (m, 2H, NH$_2^+$). **^{11}B NMR** (128 MHz, Acetone-d_6) δ -0.01 (q, *J* = 38.7 Hz). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 130.30, 136.97, 140.21, 141.08, 196 (br m, extracted from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-d_6) δ –146.05 (dd, *J* = 77.4, 38.5 Hz). **HRMS** (ESI$^-$): calc. for $C_5H_4NBF_3S$ [M–H]$^-$: 178.0115, found: 178.0110.

(Iminio(thiophen-3-yl)methyl)trifluoroborate (1u)



Synthesized from potassium 3-thiophenyltrifluoroborate (500 mg, 2.29 mmol) according to the General Procedure to afford the title compound as a white solid (245 mg, 60% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.69 (dd, *J* = 5.2, 2.9 Hz, 1H, Ar-H), 7.88 (dd, *J* = 5.2, 1.3 Hz, 1H, Ar-H), 8.88 (dd, *J* = 3.0, 1.3 Hz, 1H, Ar-H), 10.01 – 10.88 (m, 2H, NH$_2^+$). **^{11}B NMR** (128 MHz, Acetone-d_6) δ 0.11 (q, *J* = 39.7 Hz). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 125.84, 128.95, 136.23, 143.06, 198 (br m). **^{19}F NMR** (376 MHz, Acetone-d_6) δ –145.74 (dd, *J* = 78.7, 38.6 Hz). **HRMS** (ESI$^-$): calc. for $C_5H_4NBF_3S$ [M–H]$^-$: 178.0115, found: 178.0110.

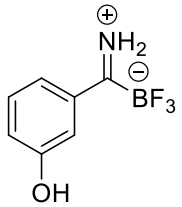
(Furan-3-yl(iminio)methyl)trifluoroborate (1v)



Synthesized from potassium 3-furoyltrifluoroborate (500 mg, 2.48 mmol) according to the General Procedure to afford the title compound as a white solid (218 mg, 60% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.18 (dd, *J* = 2.1, 0.9 Hz, 1H, Ar-H), 7.82 (dd, *J* = 2.1, 1.4 Hz, 1H, Ar-H), 8.63 (s, 1H, Ar-H),

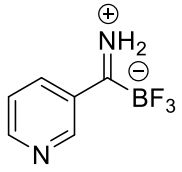
9.96 – 10.82 (m, 2H, N$\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-d_6) δ –0.05 (q, J = 39.2 Hz). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 106.84, 122.59, 143.55, 146.70, 157.02 (q, J = 3.1 Hz), 198 (br m). **^{19}F NMR** (376 MHz, Acetone-d_6) δ –146.73 (dd, J = 78.1, 38.5 Hz). **HRMS** (ESI$^-$): calc. for $C_5H_4ONBF_3$ [M–H]$^-$: 162.0344, found: 162.0336.

((3-Hydroxyphenyl)(iminio)methyl)trifluoroborate (1w)



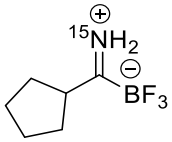
Synthesized from potassium 3-(hydroxy)benzoyltrifluoroborate (500 mg, 2.19 mmol) according to the General Procedure to afford the title compound as a white solid (242 mg, 83% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.18 – 7.26 (m, 1H, Ar-$\underline{H}$), 7.40 – 7.48 (m, 1H, Ar-$\underline{H}$), 7.62 – 7.71 (m, 2H, Ar-$\underline{H}$), 8.98 (br s, 1H, O$\underline{H}$), 10.18 – 11.35 (m, 2H, N$\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-d_6) δ 0.01 (q, J = 39.1 Hz). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 117.80, 121.47, 122.86, 131.05, 134.55, 158.35, 207 (br m, extracted from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-d_6) δ –145.90 (dd, J = 78.0, 38.6 Hz). **HRMS** (ESI$^-$): calc. for $C_7H_6ONBF_3$ [M–H]$^-$: 188.0500, found: 188.0495.

(Iminio(pyridin-3-yl)methyl)trifluoroborate (1x)



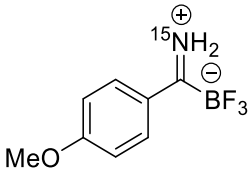
Synthesized from potassium nicotinoyltrifluoroborate (530 mg, 2.49 mmol) according to the General Procedure to afford the title compound as an off-white solid (296 mg, 68% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.66 (ddd, J = 8.1, 4.8, 0.8 Hz, 1H, Ar-$\underline{H}$), 8.54 (dt, J = 8.1, 2.0 Hz, 1H, Ar-$\underline{H}$), 8.89 (dd, J = 4.9, 1.7 Hz, 1H, Ar-$\underline{H}$), 9.33 (d, J = 2.3 Hz, 1H, Ar-$\underline{H}$), 11.17 (br s, 2H, N$\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-d_6) δ 0.05 (q, J = 38.5 Hz). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 124.81, 129.58, 137.86, 151.71, 155.80. Quaternary BF_3-bound carbon suppressed and could not be detected by ^{1}H-^{13}C *gs*-HMBC experiment. **^{19}F NMR** (376 MHz, Acetone-d_6) δ –146.50 (dd, J = 76.9, 38.2 Hz). **HRMS** (ESI$^-$): calc. for $C_6H_5ON_2BF_3$ [M–H]$^-$: 173.0503, found: 173.0499.

(Cyclopentyl(iminio-^{15}N)methyl)trifluoroborate (^{15}N-1f)



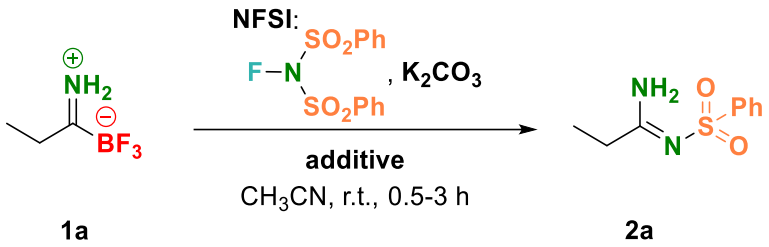
Synthesized from potassium cyclopentanecarbonyltrifluoroborate (61 mg, 0.30 mmol) and $^{15}NH_4Cl$ according to the General Procedure to afford the title compound as a white solid (26 mg, 53% yield). **^{1}H NMR** (400 MHz, Acetone-*d*$_6$) δ 1.58 – 1.71 (m, 2H, C$\underline{H}_2$), 1.71 – 1.85 (m, 2H, C$\underline{H}_2$), 1.85 – 1.99 (m, 4H, C$\underline{H}_2$), 3.03 – 3.17 (m, 1H, C$\underline{H}$), 10.36 – 10.76 (m, 2H, $^{15}N\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-*d*$_6$) δ –0.48 (q, *J* = 40.2 Hz). **^{13}C NMR** (101 MHz, Acetone-*d*$_6$) δ 26.47, 30.35, 48.79. Quaternary BF_3-bound carbon suppressed and could not be obtained even by ^{1}H-^{13}C *gs*-HMBC experiment. **^{19}F NMR** (376 MHz, Acetone-*d*$_6$) δ –148.02 (dd, *J* = 80.4, 40.0 Hz). **^{15}N NMR** (41 MHz, Acetone-*d*$_6$) δ 182.84. **HRMS** (ESI$^+$): calc. for $C_6H_{11}{}^{15}NBF_3Na$ [M+Na]$^+$: 189.07992, found: 189.07995.

((Iminio-^{15}N)(4-methoxyphenyl)methyl)trifluoroborate (^{15}N-1m)



Synthesized from potassium (4-anisoyl)trifluoroborate (175 mg, 0.72 mmol) and $^{15}NH_4Cl$ according to the General Procedure to afford the title compound as a white solid (127 mg, 86% yield). **^{1}H NMR** (400 MHz, Acetone-*d*$_6$) δ 3.94 (s, 3H, C$\underline{H}_3$), 7.10 – 7.20 (m, 2H, Ar-$\underline{H}$), 8.21 – 8.32 (m, 2H, Ar-$\underline{H}$), 10.19 (d, *J* = 94.1 Hz, 1H, $^{15}N\underline{H}_2^+$), 10.59 (d, *J* = 65.7 Hz, 1H, $^{15}N\underline{H}_2^+$). **^{11}B NMR** (128 MHz, Acetone-*d*$_6$) δ 0.15 (q, *J* = 40.0 Hz). **^{13}C NMR** (101 MHz, Acetone-*d*$_6$) δ 56.24, 115.37, 125.45, 134.22, 166.43, 203 (br m, extracted from ^{1}H-^{13}C *gs*-HMBC spectrum). **^{19}F NMR** (376 MHz, Acetone-*d*$_6$) δ –145.28 (dd, *J* = 79.7, 39.4 Hz). **^{15}N NMR** (41 MHz, Acetone-*d*$_6$) δ 166.13. **HRMS** (ESI$^–$): calc. for $C_8H_8O{}^{15}NBF_3$ [M–H]$^–$: 203.06269, found: 203.06209.

3. Reaction Optimization for the Synthesis of Unsubstituted *N*-Sulfonyl Amidines



1a **2a**

General Procedure for the Reaction Optimization

To a stirred suspension of NFSI and K_2CO_3 in dry MeCN (0.1 M), pTIM **1a** (0.2 mmol) was added, followed by the addition of deionized water (equivalents defined in Table 1). If molecular sieves were used, they were added to an oven-dried flask under argon prior to the addition of reactants. The reaction mixture was stirred at room temperature for 3 h and samples of reaction mixture (50 µL) were collected at 0.5 h, 1 h and 3 h using a needle equipped with syringe, diluted with acetone-d_6 (600 µL), and ^{1}H NMR spectra were recorded (Figures S1–S8). The amount of **2a** formed was determined by ^{1}H-NMR and was calculated as $I_{2a}/(I_{1a}+I_{2a})\times100\%$, where I_{1a} and I_{2a} are integrals for CH_3 of **1a** and **2a,** respectively.

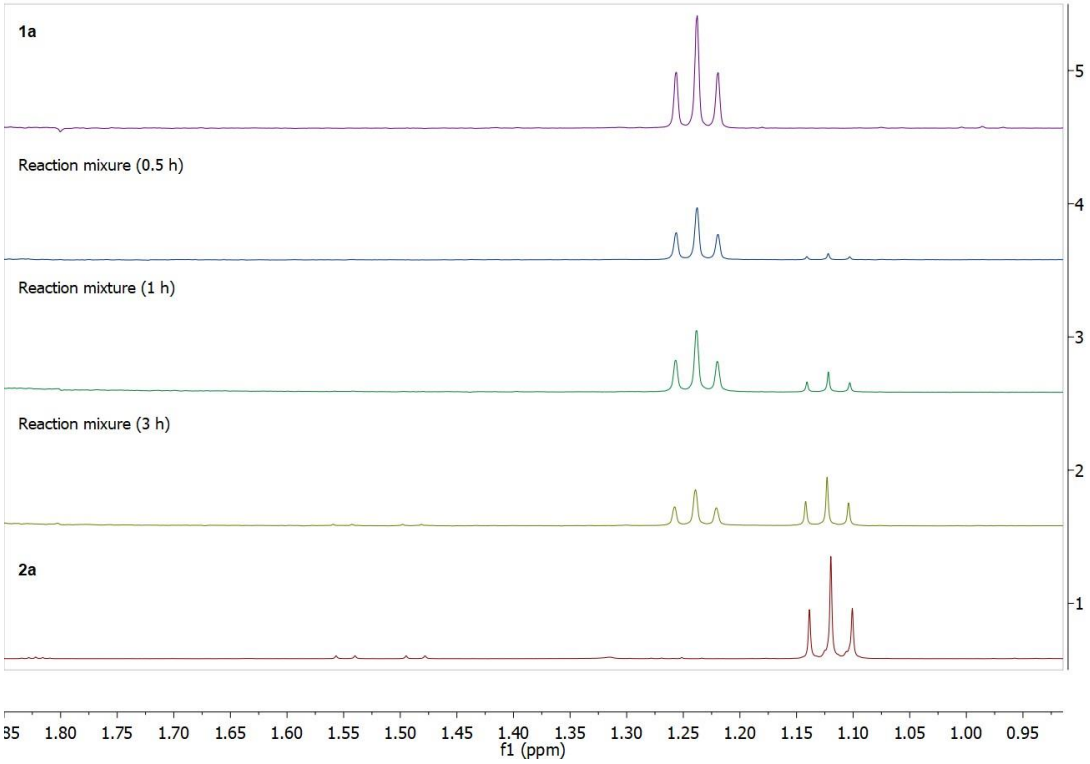


Figure S1. ^{1}H NMR of reaction conditions optimization (Table 1, entry 1).

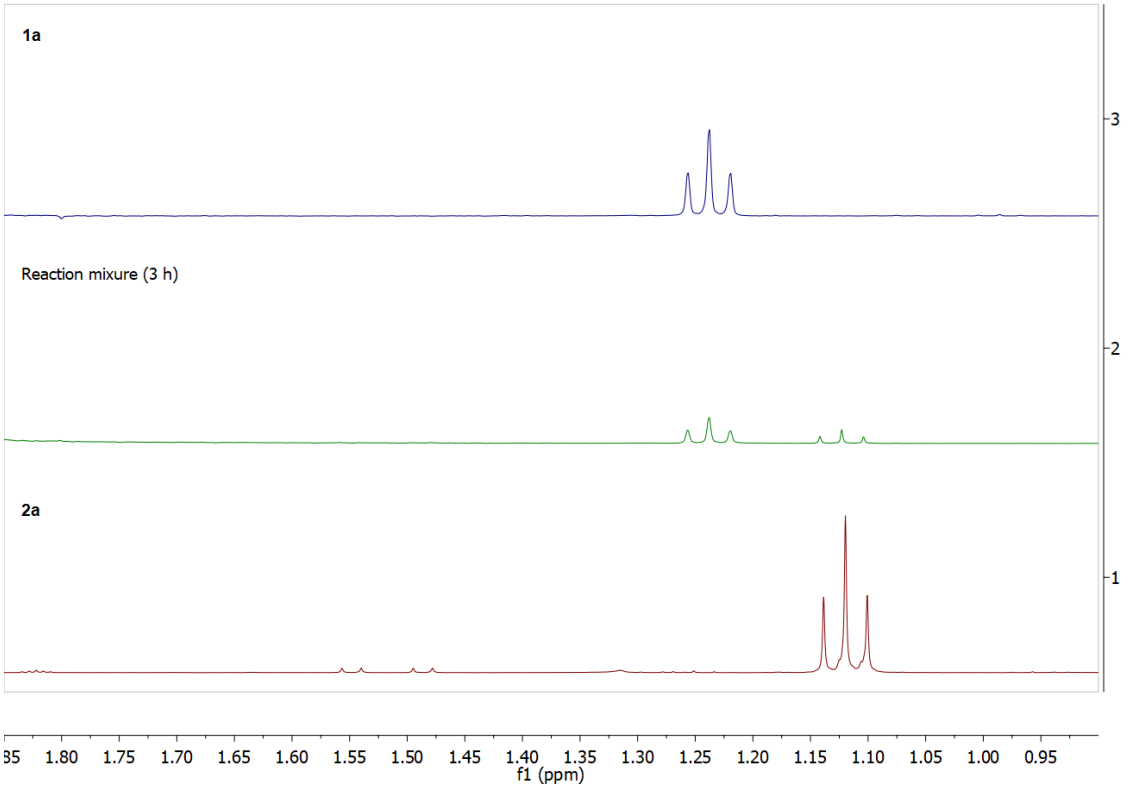


Figure S2. ^{1}H NMR of reaction conditions optimization (Table 1, entry 2).

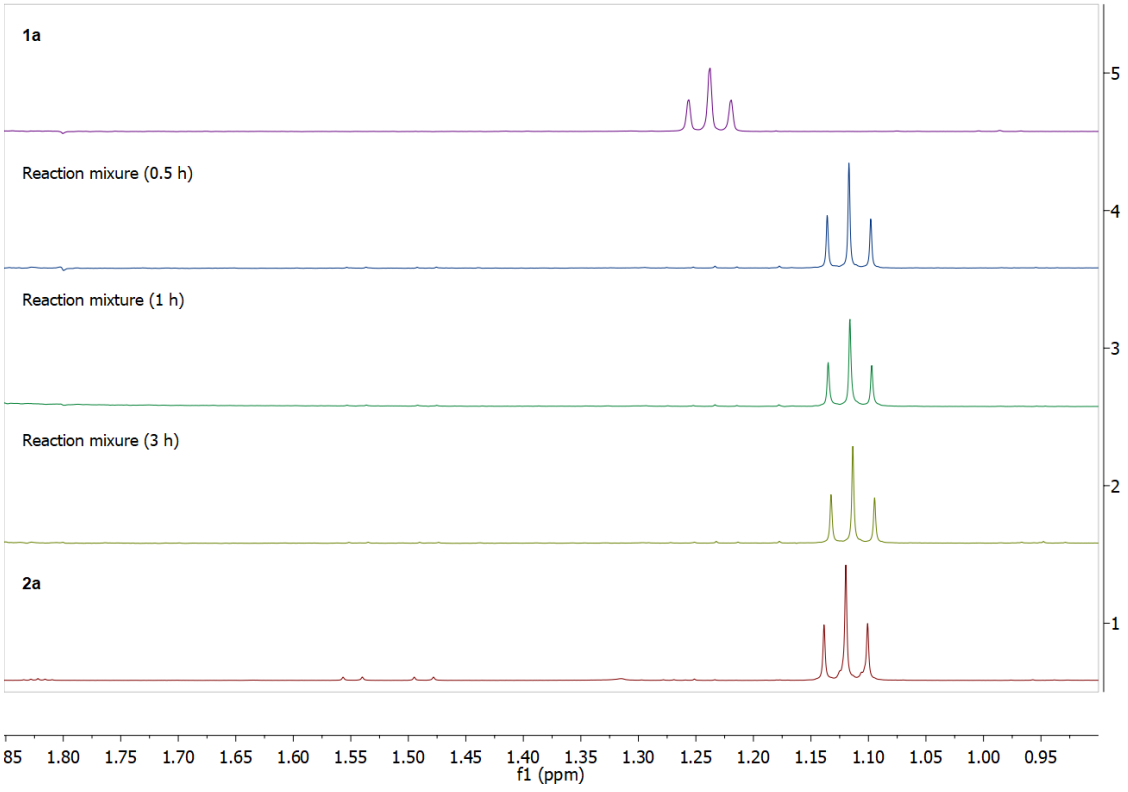


Figure S3. ^{1}H NMR of reaction conditions optimization (Table 1, entry 3).

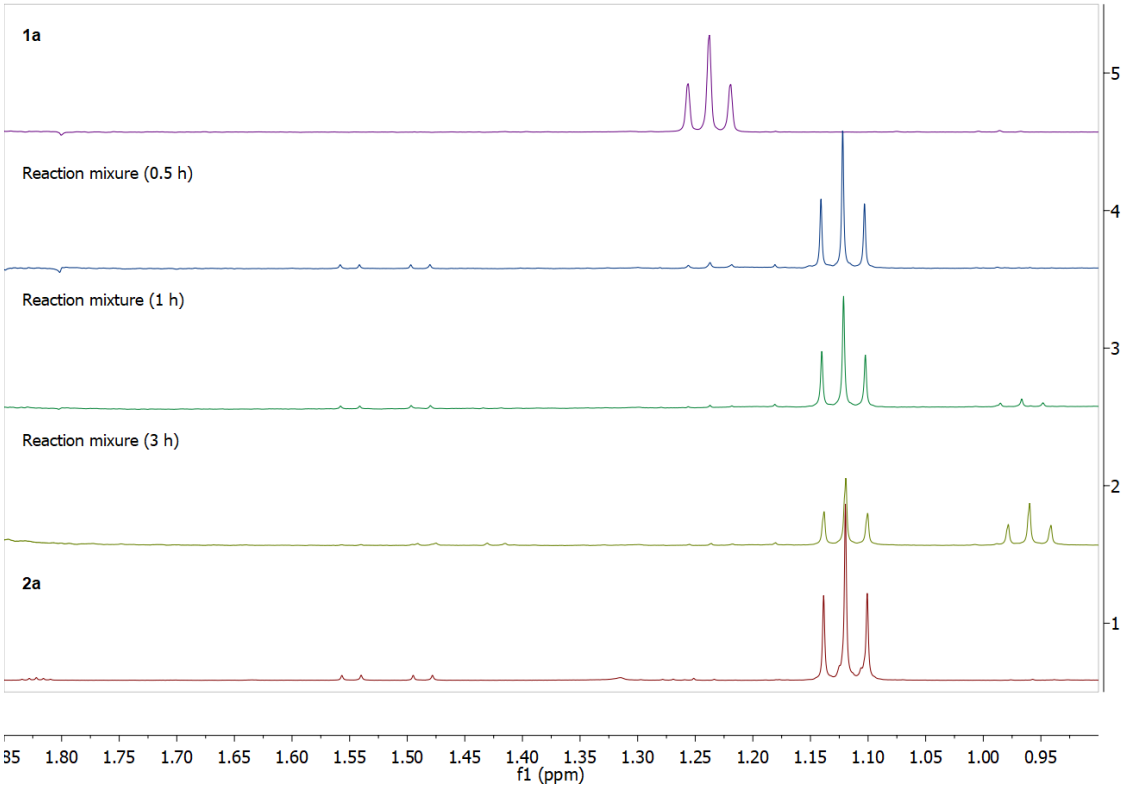


Figure S4. ^{1}H NMR of reaction conditions optimization (Table 1, entry 4).

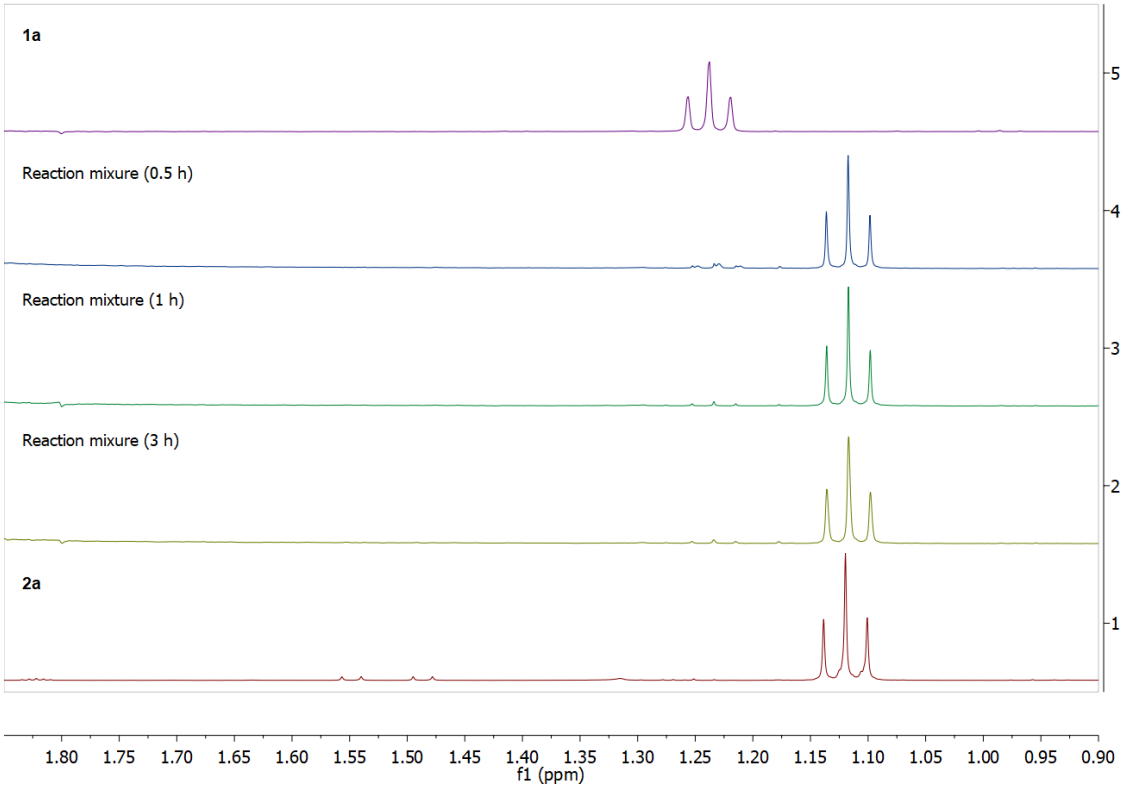


Figure S5. ^{1}H NMR of reaction conditions optimization (Table 1, entry 5).

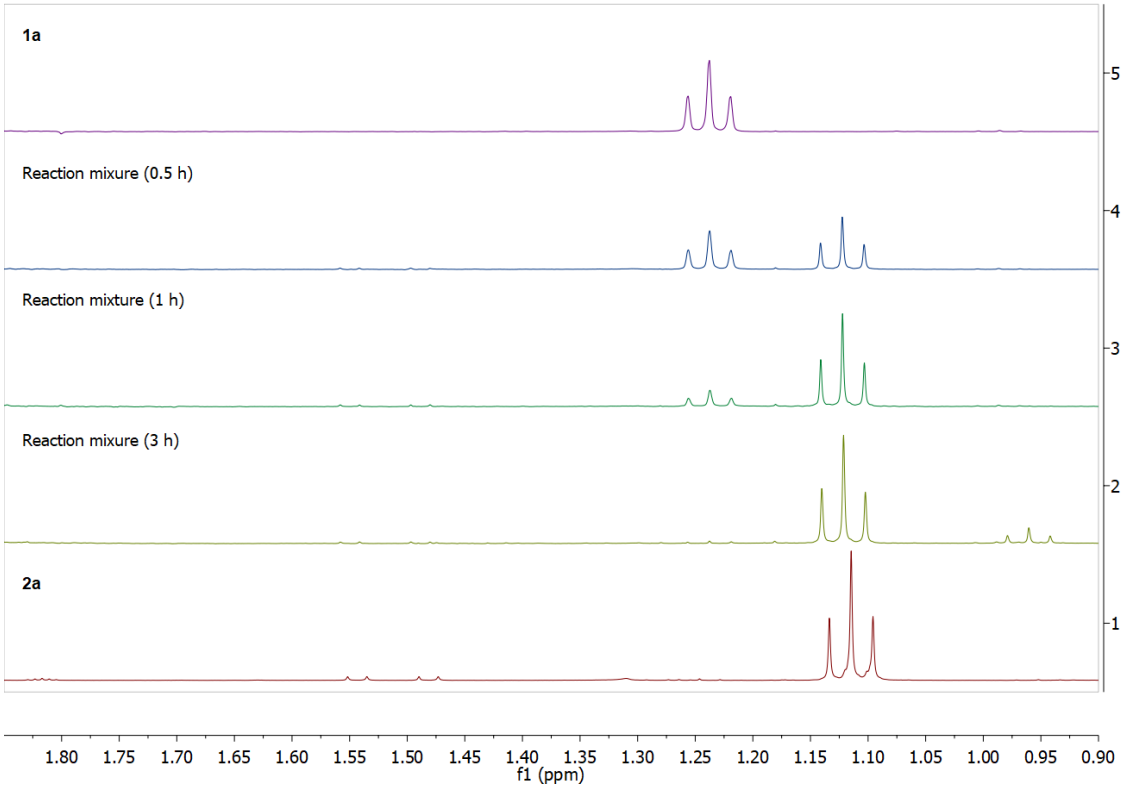


Figure S6. ^{1}H NMR of reaction conditions optimization (Table 1, entry 6).

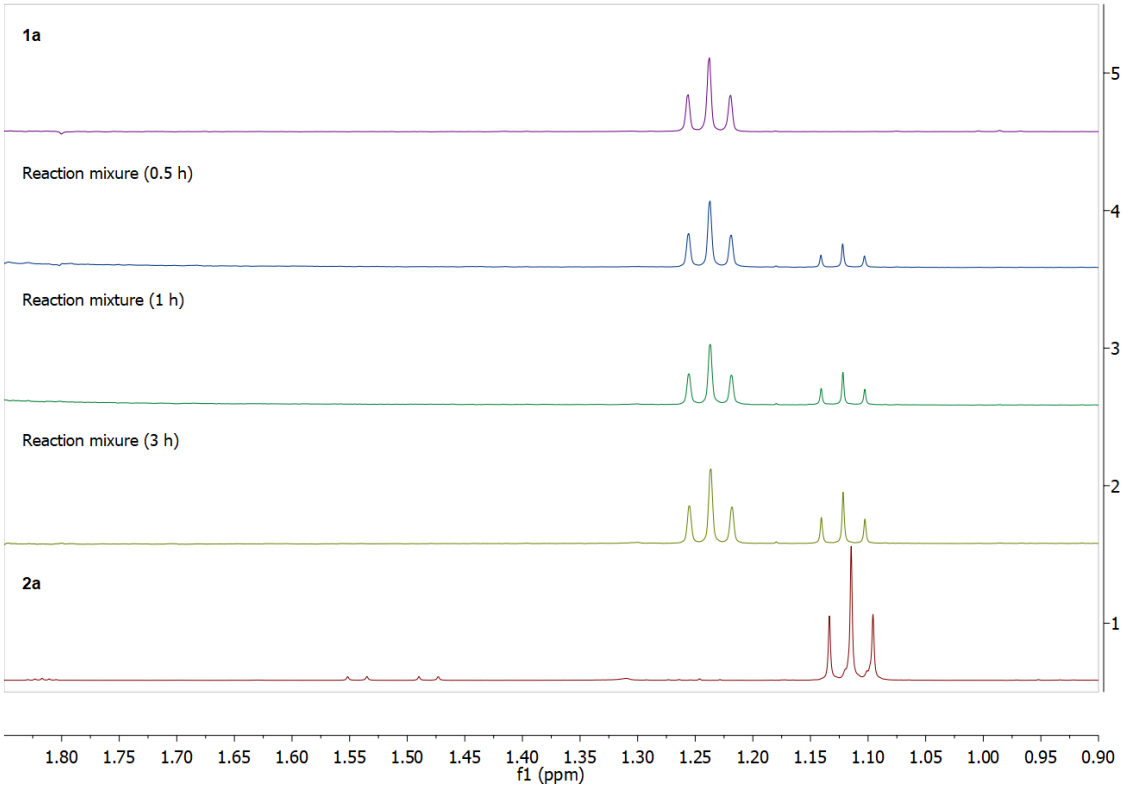


Figure S7. ^{1}H NMR of reaction conditions optimization (Table 1, entry 7).

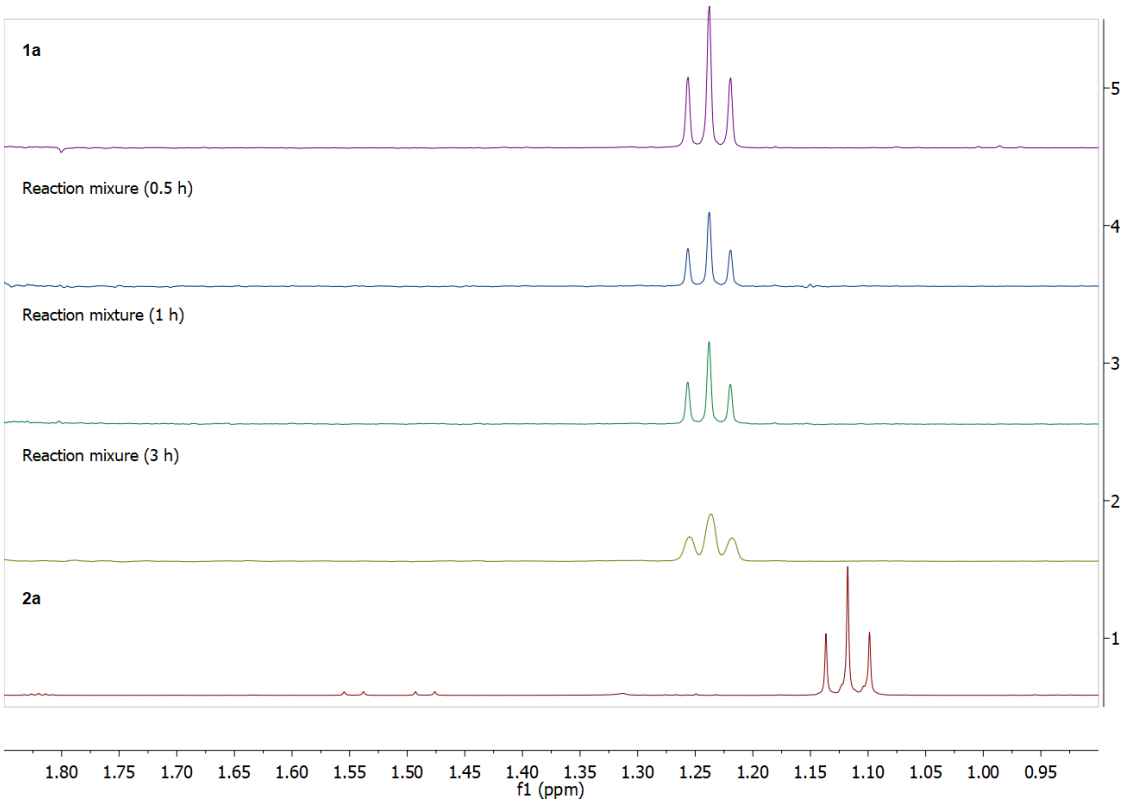
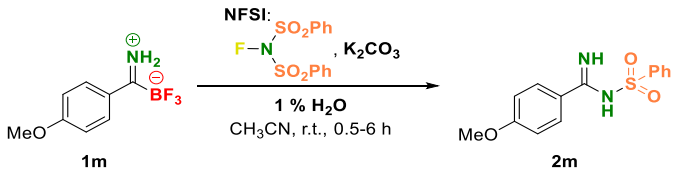


Figure S8. ^{1}H NMR of reaction conditions optimization (Table 1, entry 8).

Table S1. Reaction of pTIM **1m** with NFSI.



entry[a]	*NFSI (equiv.)*	*K_2CO_3 (equiv.)*	*additive*	*time*	*Conv. [%]*[b]
1	***1***	***1***	***1% H_2O***	***0.5 h***	***21***
2	***1***	***1***	***1% H_2O***	***1 h***	***80***
3	***1***	***1***	***1% H_2O***	***3 h***	***100***
4	***1***	***1***	***1% H_2O***	***6 h***	***100***

To a stirred suspension of NFSI (63 mg, 0.2 mmol) and K_2CO_3 (28 mg, 0.2 mmol) in MeCN (2 mL), pTIM **1m** (41 mg, 0.2 mmol) was added, followed by the addition of deionized water (20 µL). The reaction mixture was stirred at room temperature for 6 h and samples of reaction mixture (50 µL) were collected at 0.5 h, 1 h, 3 h and 6 h, diluted with acetone-d_6 (600 µL), and ^{1}H NMR spectra were recorded (Figure S9). The amount of **2m** formed was determined by ^{1}H-NMR and was calculated as $I_{2m}/(I_{1m}+I_{2m})\times100\%$, where I_{1m} and I_{2m} are integrals for 2×Ar-H on 4-methoxy moiety of **1m** and **2m**, respectively.

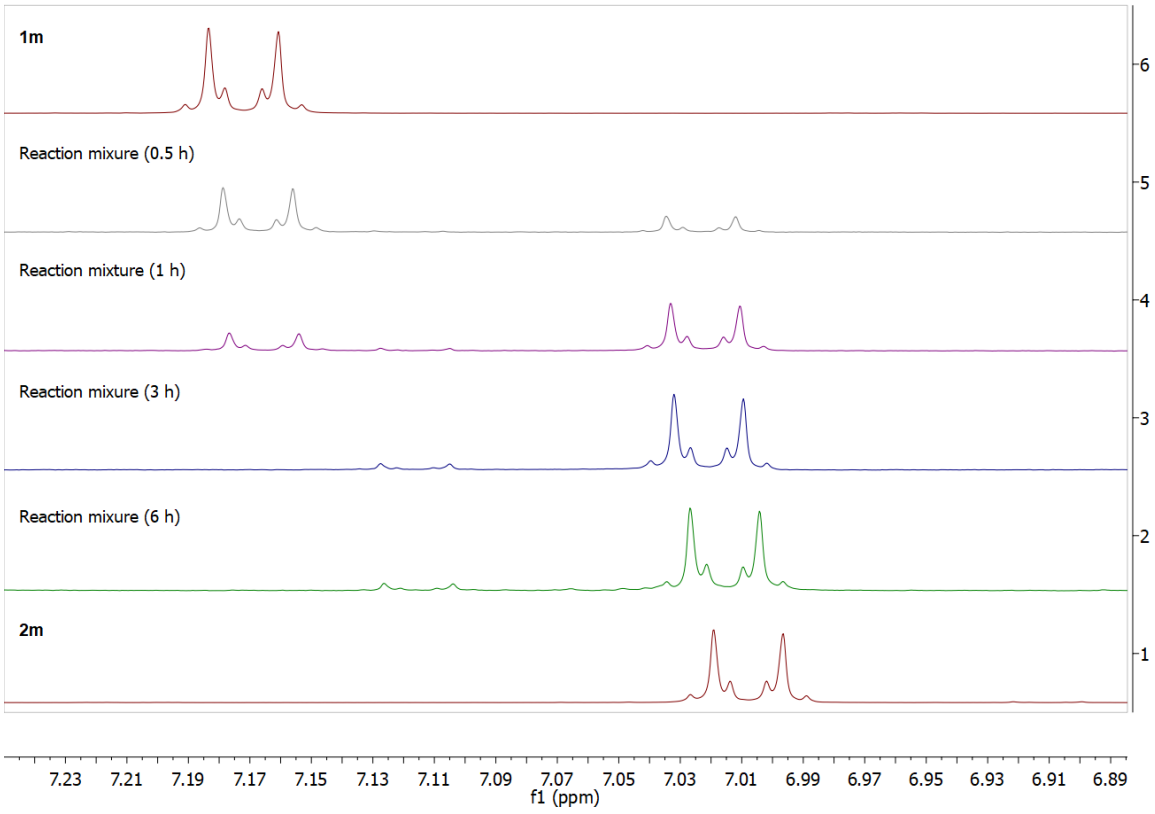


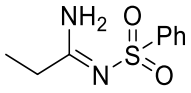
Figure S9. ^{1}H NMR of reaction conditions optimization – transformation of **1m** into **2m** (Table S1).

4. Synthesis of Unsubstituted *N*-Sulfonyl Amidines

General Procedure for the Synthesis of Unsubstituted *N*-Sulfonyl Amidines

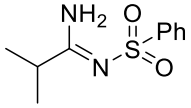
To a stirred suspension of NFSI (1 equiv.) and K_2CO_3 (1 equiv.) in MeCN (0.1 M), pTIM **1** (1 equiv., 0.20–0.50 mmol) was added, followed by the addition of deionized water (1% v/v with regard to MeCN). The reaction mixture was stirred at room temperature for 3 h for aliphatic substrates and 6 h for aromatic substrates, followed by the addition of deionized water (20% v/v with regard to MeCN), and stirring for an additional hour. The solvent was removed under reduced pressure and the dry residue was re-suspended in MeCN (0.05 M), which was again removed under reduced pressure. This procedure was repeated thrice, and the residue was dried at 0.05 mbar, 60 °C for 1 h to remove volatile benzenesulfonyl fluoride and nitrile side products. The residue was suspended in EtOAc (50 mL) and washed with 1 M NaOH (aq) (2 × 50 mL) and saturated brine (2 × 10 mL), the organic dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford product **2**.

(*Z*)-*N*'-(Phenylsulfonyl)propionimidamide (2a)



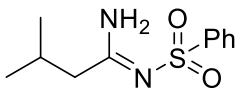
Synthesized from **1a** (31 mg, 0.25 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (45 mg, 85% yield). **m.p.** = 99–100 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.6 Hz, 3H, C<u>H</u>$_3$), 2.32 (q, *J* = 7.6 Hz, 2H, C<u>H</u>$_2$), 6.03 (br s, 1H, N<u>H</u>), 7.45 – 7.50 (m, 2H, Ar-<u>H</u>), 7.52 – 7.57 (m, 1H, Ar-<u>H</u>), 7.90 – 7.95 (m, 2H, Ar-<u>H</u>), 8.02 (br s, 1H, N<u>H</u>). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 10.71, 31.22, 126.45, 128.87, 132.40, 142.21, 170.28. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 784, 887, 1085, 1131, 1260, 1417, 1447, 1545, 1641, 3240, 3317, 3401. **HRMS** (ESI$^+$): calc. for $C_9H_{13}O_2N_2S$ $[M+H]^+$: 213.0692, found: 213.0688.

(*Z*)-*N*'-(Phenylsulfonyl)isobutyrimidamide (2b)



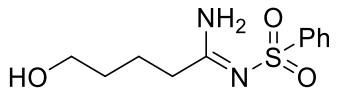
Synthesized from **1b** (97 mg, 0.7 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (116 mg, 73% yield). **m.p.** = 68–69 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.12 (d, *J* = 6.9 Hz, 6H, (C<u>H</u>$_3$)$_2$), 2.44 (hept, *J* = 6.8 Hz, 1H, C<u>H</u>), 6.37 (br s, 1H, N<u>H</u>), 7.42 – 7.48 (m, 2H. Ar-<u>H</u>), 7.49 – 7.55 (m, 1H, Ar-<u>H</u>), 7.86 – 7.91 (m, 2H, Ar-<u>H</u>), 7.97 (br s, 1H, N<u>H</u>). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 20.02, 36.86, 126.22, 128.80, 132.27, 142.27, 174.14. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 718, 755, 790, 853, 1084, 1132, 1260, 1450, 1474, 1538, 1631, 2975, 3227, 3307, 3421. **HRMS** (ESI$^+$): calc. for $C_{10}H_{15}O_2N_2S$ $[M+H]^+$: 227.0849, found: 227.0847.

(*Z*)-3-Methyl-*N*'-(phenylsulfonyl)butanimidamide (2c)



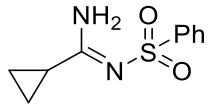
Synthesized from **1c** (122 mg, 0.8 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (119 mg, 62% yield). **m.p.** = 77–78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.87 (d, *J* = 6.4 Hz, 6H, (C<u>H</u>$_3$)$_2$), 1.99 – 2.09 (m, 1H, C<u>H</u>), 2.11 (d, *J* = 7.0 Hz, 2H, C<u>H</u>$_2$), 5.91 (br s, 1H, NH), 7.45 – 7.51 (m, 2H, Ar-<u>H</u>), 7.51 – 7.57 (m, 1H, Ar-<u>H</u>), 7.90 – 7.96 (m, 2H, Ar-<u>H</u>), 8.09 (br s, 1H, N<u>H</u>). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 21.89, 27.16, 46.46, 126.18, 128.79, 132.35, 142.03, 169.72. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 763, 1085, 1129, 1144, 1276, 1416, 1446, 1534, 1649, 2960, 3392. **HRMS** (ESI$^+$): calc. for $C_{11}H_{17}O_2N_2S$ $[M+H]^+$: 241.1005, found: 241.1000.

(*Z*)-5-Hydroxy-*N*'-(phenylsulfonyl)pentanimidamide (2d)



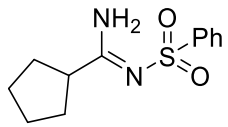
Synthesized from **1d** (85 mg, 0.5 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (100 mg, 78% yield). **m.p.** = 103–104 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.25 – 1.37 (m, 2H, C$\underline{H}_2$), 1.46 – 1.54 (m, 2H, C$\underline{H}_2$), 2.22 (t, *J* = 7.6 Hz, 2H, C$\underline{H}_2$), 3.31 (m, partially hidden under H_2O signal, 2H, C$\underline{H}_2$), 4.38 (br s, 1H, O$\underline{H}$), 7.51 – 7.63 (m, 3H, Ar-$\underline{H}$), 7.79 – 7.85 (m, 2H, Ar-$\underline{H}$), 7.94 (br s, 1H, N$\underline{H}$), 8.59 (br s, 1H, N$\underline{H}$). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 23.29, 31.64, 35.65, 60.22, 125.92, 128.82, 131.92, 142.87, 170.07. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 721, 754, 930, 997, 1025, 1057, 1085, 1141, 1331, 1447, 3248, 3343. **HRMS** (ESI$^+$): calc. for $C_{11}H_{17}O_3N_2S$ [M+H]$^+$: 257.0954, found: 257.0951.

(*Z*)-*N*'-(Phenylsulfonyl)cyclopropanecarboximidamide (2e)



Synthesized from **1e** (68 mg, 0.5 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (75 mg, 67% yield). **m.p.** = 183–184 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 0.77 – 0.86 (m, 4H, 2×C$\underline{H}_2$), 1.64 (tt, *J* = 7.5, 4.9 Hz, 1H, C$\underline{H}$), 7.50 – 7.55 (m, 2H, Ar-$\underline{H}$), 7.55 – 7.61 (m, 1H, Ar-$\underline{H}$), 7.78 (dd, *J* = 7.1, 1.9 Hz, 2H, Ar-$\underline{H}$), 7.90 (br s, 1H, N$\underline{H}$), 8.88 (br s, 1H, N$\underline{H}$). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 8.61, 15.11, 125.77, 128.79, 131.82, 142.79, 170.93. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 780, 799, 817, 851, 867, 947, 1031, 1059, 1078, 1130, 1258, 1417, 1462, 1526, 1617, 2916, 3336, 3437. **HRMS** (ESI$^+$): calc. for $C_{10}H_{13}O_2N_2S$ [M+H]$^+$: 225.0703, found: 225.0693.

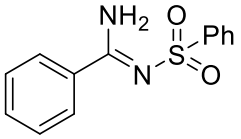
(*Z*)-*N*'-(Phenylsulfonyl)cyclopentanecarboximidamide (2f)



Synthesized from **1f** (82 mg, 0.5 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (99 mg, 79% yield). **m.p.** = 98–99 °C. **^{1}H NMR** (400 MHz, MeCN-d_3) δ 1.50 – 1.72 (m, 6H, C$\underline{H}_2$), 1.78 – 1.90 (m, 2H, C$\underline{H}_2$), 2.56– 2.70 (m, 1H, C$\underline{H}$), 6.90 (br s, 1H, N$\underline{H}$), 7.52 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.55 – 7.63 (m, 1H, Ar-$\underline{H}$), 7,75 (br s, 1H, N$\underline{H}$), 7.85 (dd, *J* = 7.1, 1.8 Hz, 2H). **^{13}C NMR** (101 MHz, MeCN-d_3) δ 26.48, 31.89, 47.35, 126.88, 129.81, 133.08, 143.78, 174.59. **IR**

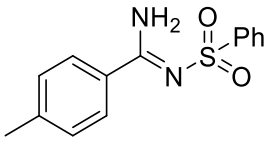
(ν/cm^{-1}, ATR) $\nu_{max.}$ = 719, 761, 1136, 1258, 1449, 1540, 1634, 2967, 3306, 3408. **HRMS** (ESI$^+$): calc. for $C_{12}H_{17}O_2N_2S$ $[M+H]^+$: 253.1005, found: 253.1003.

(*Z*)-*N*'-(Phenylsulfonyl)benzimidamide (2g)



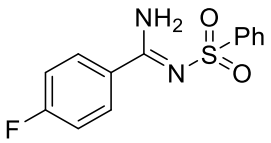
Synthesized from **1g** (35 mg, 0.2 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (38 mg, 72% yield). **m.p.** = 112–114 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.44 – 7.50 (m, 2H, Ar-H), 7.54 – 7.64 (m, 4H, Ar-H), 7.92 – 7.96 (m, 2H, Ar-H), 7.99 – 8.02 (m, 2H, Ar-H), 8.32 (br s, 1H, NH), 8.39 (br s, 1H, NH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 127.07, 128.53, 129.41, 129.62, 132.89, 133.34, 134.50, 144.09, 163.91. **HRMS** (ESI$^+$): calc. for $C_{13}H_{13}O_2N_2S$ $[M+H]^+$: 261.0692, found: 261.0691.

(*Z*)-4-Methyl-*N*'-(phenylsulfonyl)benzimidamide (2h)



Synthesized from **1h** (42 mg, 0.23 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (55 mg, 87% yield). **m.p.** = 116–117 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 2.38 (s, 3H, CH$_3$), 7.29 (d, J = 8.1 Hz, 2H, Ar-H), 7.52 – 7.64 (m, 3H, Ar-H), 7.82 – 7.91 (m, 2H, Ar-H), 7.95 – 8.05 (m, 2H, Ar-H), 8.32 (br s, 2H, 2×NH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 21.37, 127.03, 128.55, 129.59, 130.00, 131.56, 132.81, 144.07, 144.20, 163.79. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 754, 798, 843, 1079, 1136, 1155, 1268, 1402, 1447, 1509, 1613, 1629, 3247, 3314, 3402. **HRMS** (ESI$^+$): calc. for $C_{14}H_{15}O_2N_2S$ $[M+H]^+$: 275.0849, found: 275.0842.

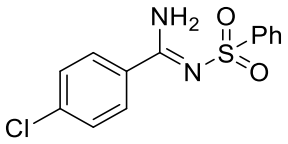
(*Z*)-4-Fluoro-*N*'-(phenylsulfonyl)benzimidamide (2i)



Synthesized from **1i** (95 mg, 0.5 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (115 mg, 83% yield). **m.p.** = 115–116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.60 (br s, 1H, NH), 7.03 – 7.11 (m, 2H, Ar-H), 7.46 – 7.59 (m, 3H, Ar-H), 7.77 – 7.86 (m, 2H, Ar-H), 7.96 – 8.00 (m, 2H, Ar-H), 8.34 (br s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 116.10 (d, $^2J_{CF}$ = 22.1

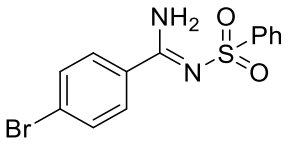
Hz), 126.51, 128.99jj, 129.36 (d, $^4J_{CF}$ = 3.0 Hz), 130.08 (d, $^3J_{CF}$ = 9.1 Hz), 132.58, 142.07, 162.00, 165.67 (d, $^1J_{CF}$ = 254.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ –105.55. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 755, 810, 1082, 1112, 1133, 1155, 1227, 1284, 1433, 1511, 1600, 1645, 3088, 3386. **HRMS** (ESI$^+$): calc. for $C_{13}H_{12}O_2N_2FS$ $[M+H]^+$: 279.0598, found: 279.0593.

(*Z*)-4-Chloro-*N*'-(phenylsulfonyl)benzimidamide (2j)



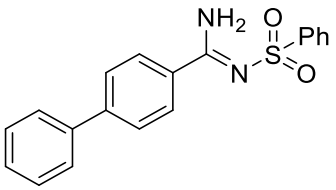
Synthesized from **1j** (104 mg, 0.5 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (106 mg, 72% yield). **m.p.** = 136–138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.28 (br s, 1H, NH), 7.38 – 7.43 (m, 2H, Ar-H), 7.48 – 7.59 (m, 3H, Ar-H), 7.70 – 7.76 (m, 2H, Ar-H), 7.98 – 8.02 (m, 2H, Ar-H), 8.37 (br s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 126.62, 128.90, 129.00, 129.30, 131.80, 132.65, 139.47, 142.03, 161.83. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 836, 1079, 1136, 1153, 1270, 1404, 1519, 1595, 1630, 3243, 3309, 3390, 3407. **HRMS** (ESI$^+$): calc. for $C_{13}H_{12}O_2N_2ClS$ $[M+H]^+$: 295.0303, found: 295.0299.

(*Z*)-4-Bromo-*N*'-(phenylsulfonyl)benzimidamide (2k)



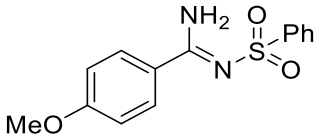
Synthesized from **1k** (63 mg, 0.25 mmol) according to the General Procedure to afford the title compound as an off-white crystalline solid (71 mg, 84% yield). **m.p.** = 124–125 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.53 – 7.63 (m, 3H, Ar-H), 7.63 – 7.69 (m, 2H, Ar-H), 7.84 – 7.90 (m, 2H, Ar-H), 7.97 – 8.02 (m, 2H, Ar-H), 8.40 (br s, 2H, NH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 127.08, 127.50, 129.64, 130.47, 132.55, 132.99, 133.64, 143.83, 162.92. **HRMS** (ESI$^+$): calc. for $C_{13}H_{12}O_2N_2BrS$ $[M+H]^+$: 338.9797, found: 338.9799.

(*Z*)-*N*'-(Phenylsulfonyl)-[1,1'-biphenyl]-4-carboximidamide (2l)



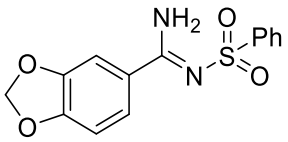
Synthesized from **1l** (100 mg, 0.4 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (119 mg, 88% yield). Due to poor solubility of **2l** in $CDCl_3$, ^{13}C NMR spectrum was recorded in a 2:1 mixture of $CDCl_3$ and MeOD. **m.p.** = 164–165 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.29 (br s, 1H, NH), 7.36 – 7.61 (m, 8H, Ar-H), 7.62 – 7.69 (m, 2H, Ar-H), 7.82 – 7.93 (m, 2H, Ar-H), 8.00 – 8.07 (m, 2H, Ar-H), 8.40 (br s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$:MeOD = 2:1) δ 126.15, 127.06 (2C), 128.14, 128.20, 128.74, 128.85, 131.69, 132.28, 139.53, 142.04, 145.46, 163.40. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 796, 1087, 1149, 1285, 1306, 1415, 1446, 1519, 1571, 1587, 1608, 3310, 3447. **HRMS** (ESI$^+$): calc. for $C_{19}H_{17}O_2N_2S$ $[M+H]^+$: 337.1005, found: 337.0999.

(*Z*)-4-Methoxy-*N*'-(phenylsulfonyl)benzimidamide (2m)



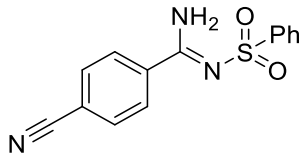
Synthesized from **1m** (51 mg, 0.25 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (60 mg, 83% yield). **m.p.** = 125–127 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 3.86 (s, 3H, CH_3), 6.97 – 7.04 (m, 2H, Ar-H), 7.51 – 7.63 (m, 3H, Ar-H), 7.92 – 8.01 (m, 4H, Ar-H), 8.18 (br s, 1H, NH), 8.30 (br s, 1H, NH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 55.94, 114.68, 126.26, 127.04, 129.59, 130.56, 132.74, 144.45, 163.33, 164.27. **HRMS** (ESI$^+$): calc. for $C_{14}H_{15}O_3N_2S$ $[M+H]^+$: 291.0798, found: 291.0798.

(*Z*)-*N*'-(Phenylsulfonyl)benzo[*d*][1,3]dioxole-5-carboximidamide (2n)



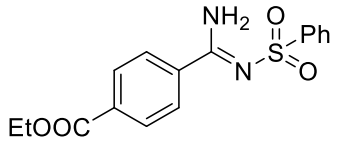
Synthesized from **1n** (109 mg, 0.5 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (119 mg, 78% yield). **m.p.** = 139–141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.04 (s, 2H, CH_2), 6.12 (br s, 1H, NH), 6.83 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.29 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.33 (dd, *J* = 8.2, 1.9 Hz, 1H, Ar-H), 7.47 – 7.58 (m, 3H, Ar-H), 7.98 – 8.02 (m, 2H, Ar-H), 8.30 (s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 102.24, 108.05, 108.41, 122.48, 126.58, 127.31, 128.93, 132.45, 142.35, 148.44, 151.86, 162.22. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 804, 822, 878, 918, 1034, 1079, 1100, 1143, 1178, 1256, 1352, 1393, 1446, 1503, 1611, 1628, 3313, 3441. **HRMS** (ESI$^+$): calc. for $C_{14}H_{13}O_4N_2S$ $[M+H]^+$: 305.0590, found: 305.0584.

(*Z*)-4-Cyano-*N*'-(phenylsulfonyl)benzimidamide (2o)



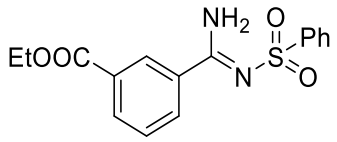
Synthesized from **1o** (50 mg, 0.25 mmol) according to the General Procedure to afford the title compound as white crystalline solid (52 mg, 73% yield). **m.p.** = 89–90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.71 (br s, 1H, NH), 7.48 – 7.54 (m, 2H, Ar-H), 7.56 – 7.61 (m, 1H, Ar-H), 7.67 – 7.72 (m, 2H, Ar-H), 7.88 – 7.93 (m, 2H, Ar-H), 7.95 – 8.00 (m, 2H, Ar-H), 8.40 (br s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 116.31, 117.78, 126.61, 128.31, 129.10, 132.66, 132.94, 137.47, 141.58, 161.13. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 837, 1081, 1135, 1155, 1283, 1445, 1520, 1578, 1634, 2242, 2928, 3192, 3320, 3400. **HRMS** (ESI^+): calc. for $C_{14}H_{12}O_2N_3S$ $[M+H]^+$: 286.0645, found: 286.0640.

Ethyl (*Z*)-4-(*N*'-(phenylsulfonyl)carbamimidoyl)benzoate (2p)



Synthesized from **1p** (124 mg, 0.5 mmol) according to the General Procedure and purified by column chromatography (SiO_2; CH_2Cl_2/MeOH = 20/1) to afford the title compound as a white amorphous solid (108 mg, 65% yield). **m.p.** = 108–110 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.32 (t, J = 7.1 Hz, 3H, CH_3), 4.33 (q, J = 7.1 Hz, 2H, CH_2), 7.55 – 7.61 (m, 2H, Ar-H), 7.61 – 7.65 (m, 1H, Ar-H), 7.93 – 7.98 (m, 4H, Ar-H), 8.00 – 8.04 (m, 2H, Ar-H), 8.40 (br s, 1H, NH), 9.26 (br s, 1H, NH). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 14.11, 61.19, 126.13, 128.32, 129.00, 129.11, 132.35, 132.97, 137.47, 142.20, 161.81, 165.00. **HRMS** (ESI^+): calc. for $C_{16}H_{17}O_4N_2S$ $[M+H]^+$: 333.0904, found: 333.0903.

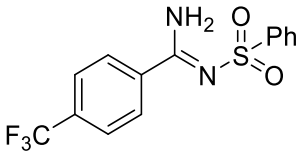
Ethyl (*Z*)-3-(*N*'-(phenylsulfonyl)carbamimidoyl)benzoate (2q)



Synthesized from **1q** (61 mg, 0.25 mmol) according to the General Procedure and purified by column chromatography (SiO_2; CH_2Cl_2/MeOH = 50/1) to afford the title compound as a white amorphous solid (60 mg, 72% yield). **m.p.** = 101–103 °C. **^{1}H NMR** ^{1}H NMR (400 MHz, Acetone-d_6) δ 1.34 (t, J = 7.1 Hz, 3H, CH_3), 4.35 (q, J = 7.1 Hz, 2H, CH_2), 7.51 – 7.65 (m, 4H, Ar-H), 8.02 – 8.08 (m, 2H, Ar-H), 8.12 – 8.19 (m, 2H, Ar-H), 8.46 – 8.59 (m, 3H, 2 × NH + Ar-H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 14.51, 61.89,

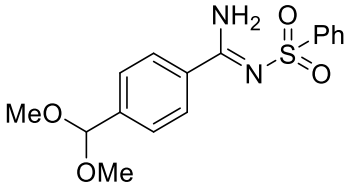
127.11, 129.33, 129.67, 129.84, 131.86, 132.87, 133.02, 133.77, 135.05, 143.86, 163.11, 165.86. **HRMS** (ESI^+): calc. for $C_{16}H_{17}O_4N_2S$ $[M+H]^+$: 333.0904, found: 333.0901.

(*Z*)-*N*'-(Phenylsulfonyl)-4-(trifluoromethyl)benzimidamide (2r)



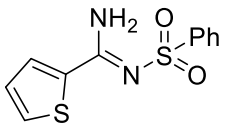
Synthesized from **1r** (94 mg, 0.4 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (98 mg, 75% yield). **m.p.** = 126–127 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.54 – 7.67 (m, 3H, Ar-H), 7.84 (d, *J* = 8.3 Hz, 2H, Ar-H), 8.01 (dd, *J* = 6.9, 1.7 Hz, 2H, Ar-H), 8.15 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.48 (br s, 1H, NH), 8.53s (br s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 123.52 (q, *J* = 273.0 Hz), 125.83 (q, *J* = 3.6 Hz), 126.51, 128.17, 129.04, 132.78, 134.34 (q, *J* = 32.7 Hz), 136.63, 141.72, 161.87. **^{19}F NMR** (376 MHz, Acetone-d_6) δ –63.52. **IR** (ν/cm^{-1}, ATR) $\nu_{max.}$ = 822, 850, 1017, 1066, 1091, 1115, 1157, 1272, 1314, 1328, 1422, 1522, 1619, 3316, 3439. **HRMS** (ESI^+): calc. for $C_{14}H_{12}O_2N_2F_3S$ $[M+H]^+$: 329.0566, found: 329.0560.

(*Z*)-4-(Dimethoxymethyl)-*N*'-(phenylsulfonyl)benzimidamide (2s)



Synthesized from **1s** (62 mg, 0.25 mmol) according to the General Procedure to afford the title compound as a white amorphous solid (63 mg, 75% yield). **m.p.** = 119–121 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 3.27 (s, 6H, CH_3), 5.44 (s, 1H, CH), 7.51 – 7.64 (m, 5H, Ar-H), 7.94 – 7.99 (m, 2H, Ar-H), 7.99 – 8.02 (m, 2H, Ar-H), 8.33 (br s, 1H, NH), 8.40 (br s, 1H, NH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 52.87, 102.98, 127.07, 127.76, 128.41, 129.62, 132.90, 134.37, 143.98, 144.03, 163.57. **HRMS** (ESI^+): calc. for $C_{16}H_{19}O_4N_2S$ $[M+H]^+$: 335.1060, found: 335.1058.

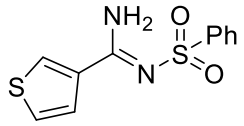
(*Z*)-*N*'-(Phenylsulfonyl)thiophene-2-carboximidamide (2t)



Synthesized from **1t** (90 mg, 0.5 mmol) according to the General Procedure to afford the title compound as an off-white solid (95 mg, 71% yield). **m.p.** = 98–100 °C. **^{1}H NMR** (400 MHz, Acetone-d_6)

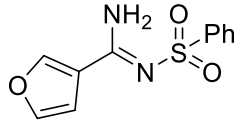
δ 7.16 (dd, *J* = 5.0, 3.9 Hz, 1H, Ar-H), 7.53 – 7.62 (m, 3H, Ar-H), 7.78 (dd, *J* = 5.0, 1.1 Hz, 1H, Ar-H), 7.96 – 8.00 (m, 3H, Ar-H), 8.31 (br s, 1H, NH), 8.33 (br s, 1H, NH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 126.99, 129.06, 129.61, 130.92, 132.92, 133.95, 138.76, 143.96, 158.48. **HRMS** (ESI$^-$): calc. for $C_{11}H_9O_2N_2S_2$ $[M+H]^+$: 265.0111, found: 265.0115.

(*Z*)-*N*'-(Phenylsulfonyl)thiophene-3-carboximidamide (2u)



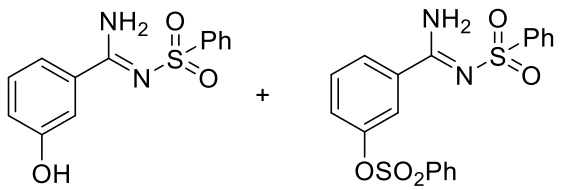
Synthesized from **1u** (45 mg, 0.25 mmol) according to the General Procedure to afford the title compound as an off-white solid (50 mg, 75% yield). **m.p.** = 106–108 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.52 – 7.64 (m, 5H, Ar-H), 7.96 – 8.02 (m, 2H, Ar-H), 8.21 (br s, 1H, NH), 8.30 (br s, 1H, NH), 8.32 (dd, *J* = 3.0, 1.4 Hz, 1H, Ar-H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 127.03, 127.48, 127.84, 129.58, 131.33, 132.81, 137.20, 144.22, 159.11. **HRMS** (ESI$^+$): calc. for $C_{11}H_{11}O_2N_2S_2$ $[M+H]^+$: 267.0257, found: 267.0256.

(*Z*)-*N*'-(Phenylsulfonyl)furan-3-carboximidamide (2v)



Synthesized from **1v** (41 mg, 0.25 mmol) according to the General Procedure to afford the title compound as an off-white solid (50 mg, 80% yield). **m.p.** = 105–107 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 6.93 (dd, *J* = 2.0, 0.8 Hz, 1H, Ar-H), 7.52 – 7.63 (m, 3H, Ar-H), 7.65 – 7.67 (m, 1H, Ar-H), 7.94 – 7.99 (m, 2H, Ar-H), 8.10 (br s, 1H, NH), 8.28 (br s, 1H, NH), 8.29 (dd, *J* = 1.6, 0.9 Hz, 1H, Ar-H). **^{13}C NMR** (101 MHz, Acetone) δ 109.48, 123.40, 127.02, 129.57, 132.81, 144.21, 145.45, 147.42, 158.90. **HRMS** (ESI$^+$): calc. for $C_{11}H_{11}O_3N_2S$ $[M+H]^+$: 251.0485, found: 251.0485.

(*Z*)-3-Hydroxy-*N*'-(phenylsulfonyl)benzimidamide (2w) and (*Z*)-3-(*N*'-(phenylsulfonyl)carbamimidoyl)phenyl benzenesulfonate (2w')



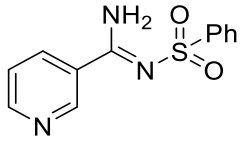
Synthesized from **1w** (47 mg, 0.25 mmol) according to the General Procedure, omitting the extraction with 1 M NaOH (aq) (2 × 50 mL), and purified by column chromatography (SiO_2; gradient, 1)

CH_2Cl_2/MeOH = 50/1, 2) CH_2Cl_2/MeOH = 20/1) to afford the title compound as white solid (19 mg, 28% yield). Column chromatography also yielded compound **2w'** as white solid (43 mg, 41% yield). Overall yield of C-N coupling was thus 69 %.

For **2w**: **m.p.** = 128–130 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 6.98 – 7.10 (m, 1H, Ar-H), 7.30 (t, *J* = 8.1 Hz, 1H, Ar-H), 7.37 – 7.44 (m, 2H, Ar-H), 7.54 – 7.66 (m, 3H, Ar-H), 7.95 – 8.04 (m, 2H, Ar-H), 8.22 (br s, 1H, NH), 8.34 (br s, 1H, NH), 8.70 (br s, 1H, OH). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 115.49, 119.41, 120.35, 127.05, 129.62, 130.55, 132.87, 135.94, 144.14, 158.37, 163.89. **HRMS** (ESI$^+$): calc. for $C_{13}H_{13}O_3N_2S$ $[M+H]^+$: 277.0641, found: 277.0642.

For **2w'**: **m.p.** = 132–134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.68 (br s, 1H, NH), 7.13 (ddd, *J* = 8.2, 2.4, 0.9 Hz, 1H, Ar-H), 7.33 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.41 (t, *J* = 2.0 Hz, 1H, Ar-H), 7.45 – 7.53 (m, 4H, Ar-H), 7.53 – 7.61 (m, 1H, Ar-H), 7.61 – 7.67 (m, 1H, Ar-H), 7.70 (ddd, *J* = 7.9, 1.7, 1.0 Hz, 1H, Ar-H), 7.77 – 7.82 (m, 2H, Ar-H), 7.93 (d, *J* = 1.5 Hz, 2H, Ar-H), 8.27 (br s, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 121.69, 126.40, 126.52, 126.63, 128.55, 128.97, 129.45, 130.29, 132.66, 134.75, 134.88, 135.19, 141.82, 149.62, 161.36. **HRMS** (ESI$^+$): calc. for $C_{19}H_{17}O_5N_2S_2$ $[M+H]^+$: 417.0573, found: 417.0572.

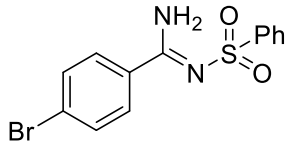
(*Z*)-*N*'-(Phenylsulfonyl)nicotinimidamide (2x)



Synthesized from **1x** (43 mg, 0.25 mmol) according to the General Procedure and purified by column chromatography (SiO_2; 100 % EtOAc) to afford the title compound as brownish solid (27 mg, 41% yield). **m.p.** = 97–100 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.49 (ddd, *J* = 8.1, 4.8, 0.8 Hz, 1H, Ar-H), 7.55 – 7.67 (m, 3H, Ar-H), 8.00 – 8.04 (m, 2H, Ar-H), 8.26 (ddd, *J* = 8.1, 2.4, 1.7 Hz, 1H, Ar-H), 8.46 (br s, 1H, NH), 8.52 (br s, 1H, NH), 8.75 (dd, *J* = 4.8, 1.6 Hz, 1H, Ar-H), 9.09 (dd, *J* = 2.3, 0.7 Hz, 1H, Ar-H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 124.21, 127.16, 129.70, 130.49, 133.07, 136.17, 143.83, 149.63, 153.90, 162.31. **HRMS** (ESI$^+$): calc. for $C_{12}H_{12}O_2N_3S$ $[M+H]^+$: 262.0645, found: 262.0644.

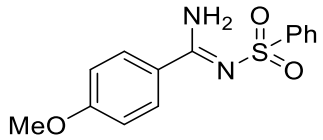
4.1. Gram Scale Synthesis of Unprotected *N*-Sulfonyl Amidines

(*Z*)-4-Bromo-*N'*-(phenylsulfonyl)benzimidamide (2k)



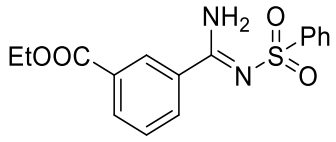
Synthesized from **1k** (1.0 g, 3.97 mmol) according to the General Procedure to afford the title compound as white crystalline solid (1.22 g, 91% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.54 – 7.64 (m, 3H, Ar-H), 7.64 – 7.70 (m, 2H, Ar-H), 7.86 – 7.91 (m, 2H, Ar-H), 7.98 – 8.02 (m, 2H, Ar-H), 8.40 (br s, 2H, NH_2).

(*Z*)-4-Methoxy-*N'*-(phenylsulfonyl)benzimidamide (2m)



Synthesized from **1m** (1.0 g, 4.93 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (1.02 g, 71% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 3.86 (s, 3H, CH_3), 6.98 – 7.04 (m, 2H, Ar-H), 7.52 – 7.63 (m, 3H, Ar-H), 7.92 – 8.01 (m, 4H, Ar-H), 8.17 (br s, 1H, NH), 8.30 (br s, 1H, NH).

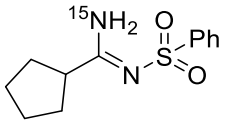
Ethyl (*Z*)-3-(*N*'-(phenylsulfonyl)carbamimidoyl)benzoate (2q)



Synthesized from **1q** (0.80 g, 3.26 mmol) according to the General Procedure and purified by column chromatography (SiO_2; CH_2Cl_2/MeOH = 50/1) to afford the title compound as a white amorphous solid (0.81 g, 74% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 1.36 (t, *J* = 7.1 Hz, 3H, CH_3), 4.37 (q, *J* = 7.1 Hz, 2H, CH_2), 7.54 – 7.68 (m, 4H, Ar-H), 7.99 – 8.04 (m, 2H, Ar-H), 8.15 – 8.22 (m, 2H, Ar-H), 8.47 (br s, 1H, NH), 8.54 (br s, 1H, NH), 8.54 (t, *J* = 1.8 Hz, 1H, Ar-H).

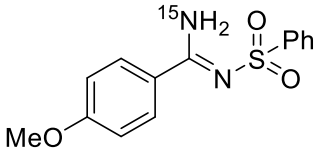
4.2. Synthesis of ^{15}N-Labeled Unprotected *N*-Sulfonyl Amidines

^{15}N-(*Z*)-*N*'-(Phenylsulfonyl)cyclopentanecarboximidamide (^{15}N-2f)



Synthesized from **^{15}N-1f** (25 mg, 0.15 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (27 mg, 70% yield). **m.p.** = 95–97 °C. **^{1}H NMR** (400 MHz, MeCN-d_3) δ 1.47 – 1.72 (m, 6H, C$\underline{H}_2$), 1.74 – 1.89 (m, 2H, C$\underline{H}_2$), 2.53 – 2.70 (m, 1H, C$\underline{H}$), 6.92 (dd, *J* = 93.2, 2.5 Hz, 1H, ^{15}N$\underline{H}$), 7.47 – 7.57 (m, 2H, Ar-$\underline{H}$), 7.54 – 7.64 (m, 1H, Ar-$\underline{H}$), 7.76 (dd, *J* = 91.1, 2.7 Hz, 1H, ^{15}N$\underline{H}$), 7.83 – 7.87 (m, 3H, Ar-$\underline{H}$). **^{13}C NMR** (101 MHz, MeCN-d_3) δ 26.47, 31.88, 47.32 (d, *J* = 3.4 Hz), 126.86, 129.80, 133.07, 143.74, 174.58 (d, *J* = 14.2 Hz). **^{15}N NMR** (41 MHz, Acetone-d_6) δ 106.98. **HRMS** (ESI$^-$): calc. for $C_{12}H_{15}O_2N^{15}NS$ [M–H]$^-$: 252.08301, found: 252.08303.

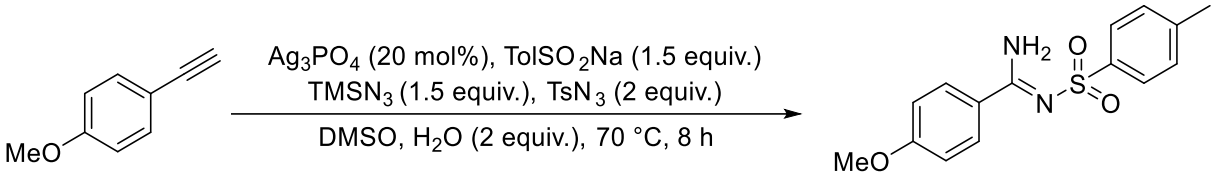
^{15}N-(*Z*)-4-Methoxy-*N*'-(phenylsulfonyl)benzimidamide (^{15}N-2m)



Synthesized from **^{15}N-1m** (41 mg, 0.20 mmol) according to the General Procedure to afford the title compound as a white crystalline solid (42 mg, 72% yield). **m.p.** = 121–122 °C. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 3.85 (s, 3H, OC$\underline{H}_3$), 6.96 – 7.03 (m, 2H, Ar-$\underline{H}$), 7.52 – 7.61 (m, 3H, Ar-$\underline{H}$), 7.93 – 7.97 (m, 2H, Ar-$\underline{H}$), 7.97 – 8.02 (m, 2H, Ar-$\underline{H}$), 8.19 (dd, *J* = 92.9, 1.5 Hz, 1H, ^{15}N$\underline{H}$), 8.32 (dd, *J* = 91.2, 1.3 Hz, 1H, ^{15}N$\underline{H}$). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 55.92, 114.65, 126.17 (d, *J* = 3.5 Hz), 127.00, 129.57, 130.54, 132.74, 144.35, 163.32 (d, *J* = 15.1 Hz), 164.22. **^{15}N NMR** (41 MHz, Acetone-d_6) δ 98.29. **HRMS** (ESI$^+$): calc. for $C_{14}H_{15}O_3N^{15}NS$ [M+H]$^+$: 292.07682, found: 292.07669.

4.3. Synthesis of Unprotected *N*-Sulfonyl Amidine According to the Bi's Procedure[S2] for the Comparative Structure Determination

(*Z*)-4-Methoxy-*N'*-tosylbenzimidamide (2y)



4-ethynylanisole **2y**, 33%

Synthesized following the procedure reported by Bi et al.[S2] To a 25 mL sealed tube 4-ethynylanisole (130 µL, 1 mmol), dry DMSO (4 mL), $TMSN_3$ (260 µL, 2 mmol), H_2O (36 µL, 2 mmol), $TolSO_2Na$ (270 mg, 1.5 mmol), TsN_3 (300 mg, 1.5 mmol, dissolved in 1 mL of toluene), and Ag_3PO_4 (84 mg, 0.2 mmol) were added, then the mixture was stirred at 70 °C for 8 h. The crude reaction was quenched with H_2O (30 mL), extracted with CH_2Cl_2 (3 × 25 mL), combined organic layers washed with saturated brine (30 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The product by purified by flash column chromatography (SiO_2; 1) petroleum ether/EtOAc = 5/1, 2) petroleum ether/EtOAc = 1/1) to afford the title compound as white solid (99 mg, 33% yield). **m.p.** = 129–131 °C. **^{1}H NMR** (400 MHz, MeCN-d_3) δ 2.39 (s, 3H, C<u>H</u>$_3$), 3.83 (s, 3H, OC<u>H</u>$_3$), 6.94 – 7.00 (m, 2H, Ar-<u>H</u>), 7.23 (br s, 1H, N<u>H</u>), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-<u>H</u>), 7.74 – 7.85 (m, 4H, Ar-<u>H</u>), 8.03 (br s, 1H, N<u>H</u>). **^{13}C NMR** (101 MHz, MeCN-d_3) δ 21.47, 56.31, 114.87, 126.06, 127.09, 130.39, 130.60, 140.95, 144.11, 163.63, 164.36. **HRMS** (ESI$^+$): calc. for $C_{15}H_{17}O_3N_2S$ $[M+H]^+$: 305.09544, found: 305.09544.

5. Structure Determination of Unsubstituted *N*-Sulfonyl Amidines by NMR and X-ray Single Crystal Analysis

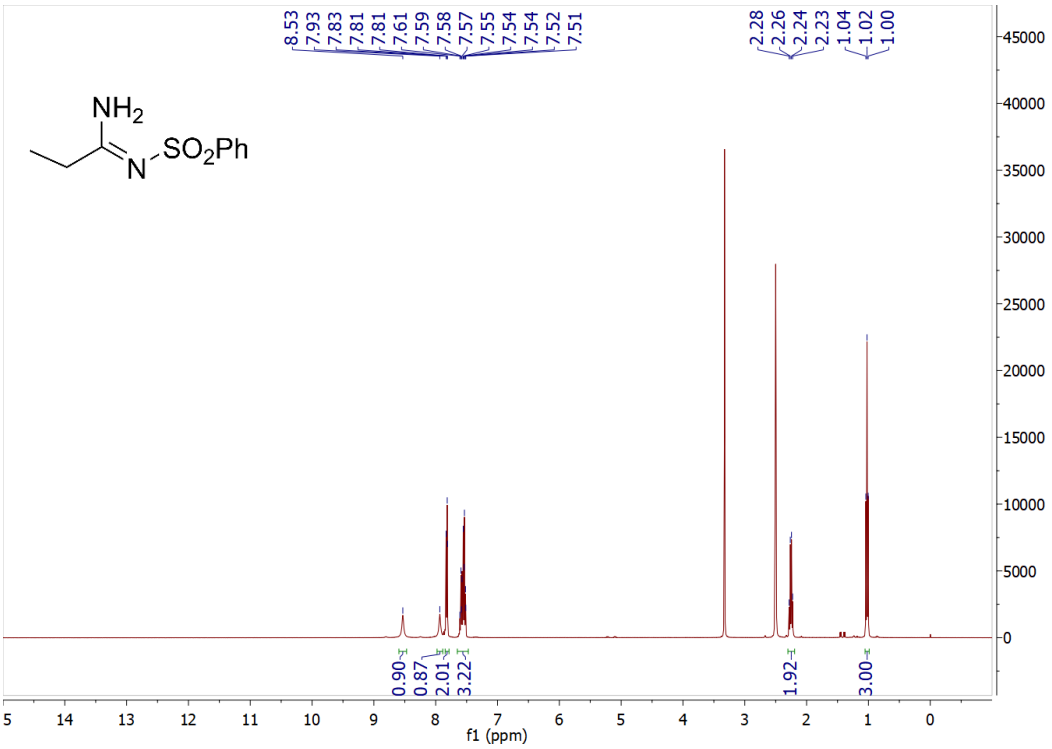


Figure S10. ^{1}H NMR of **2a** in DMSO-d_6 at 295 K.

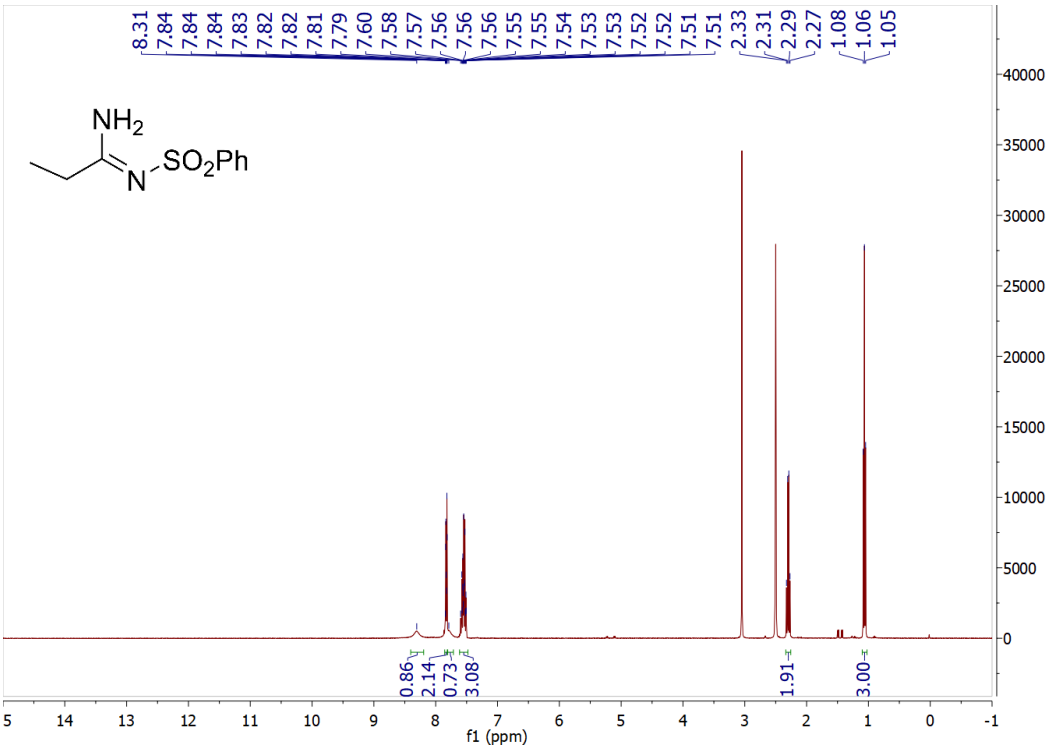


Figure S11. ^{1}H NMR of **2a** in DMSO-d_6 at 353 K.

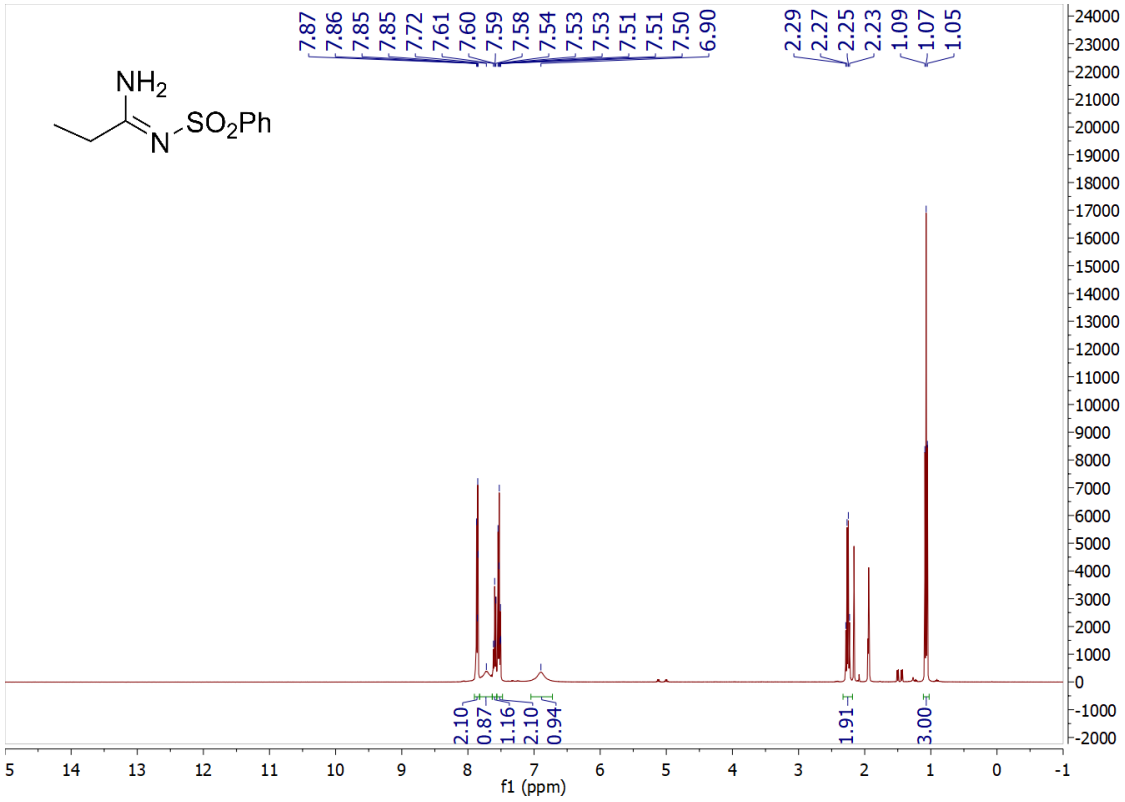


Figure S12. ^{1}H NMR of **2a** in MeCN-d_3 at 295 K.

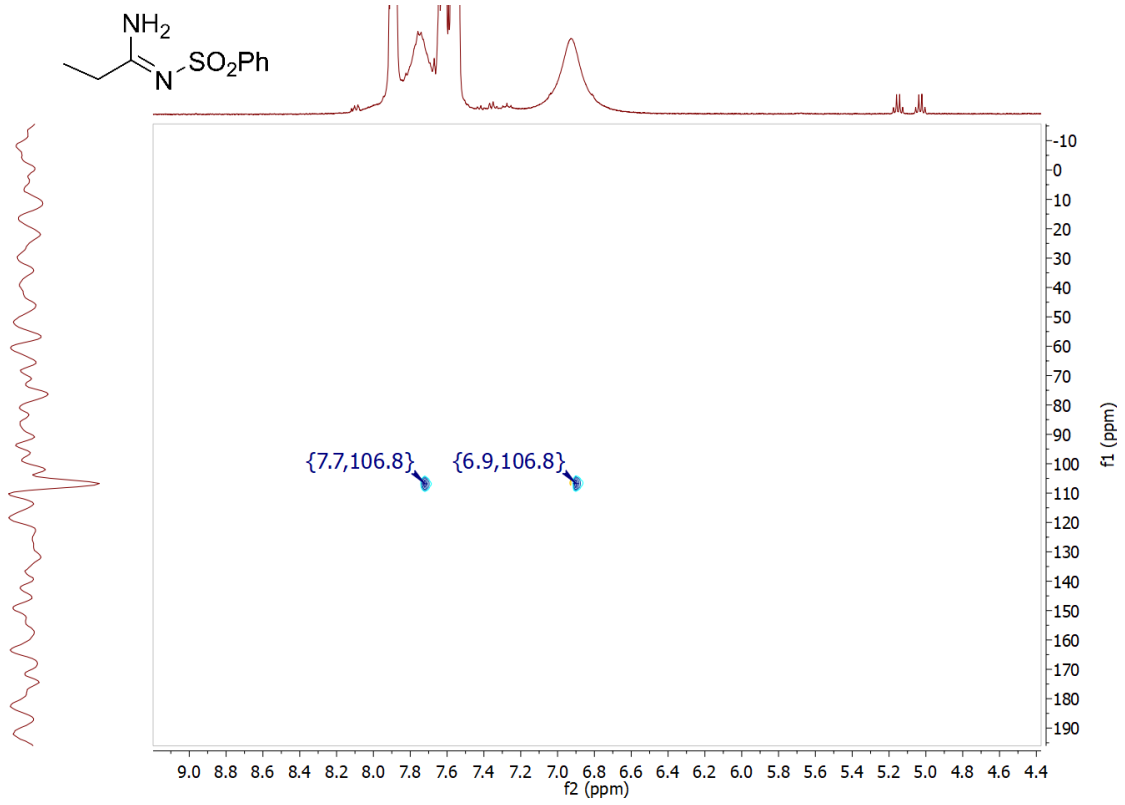


Figure S13. ^{1}H-^{15}N HSQC of **2a** in MeCN-d_3 at 295 K.

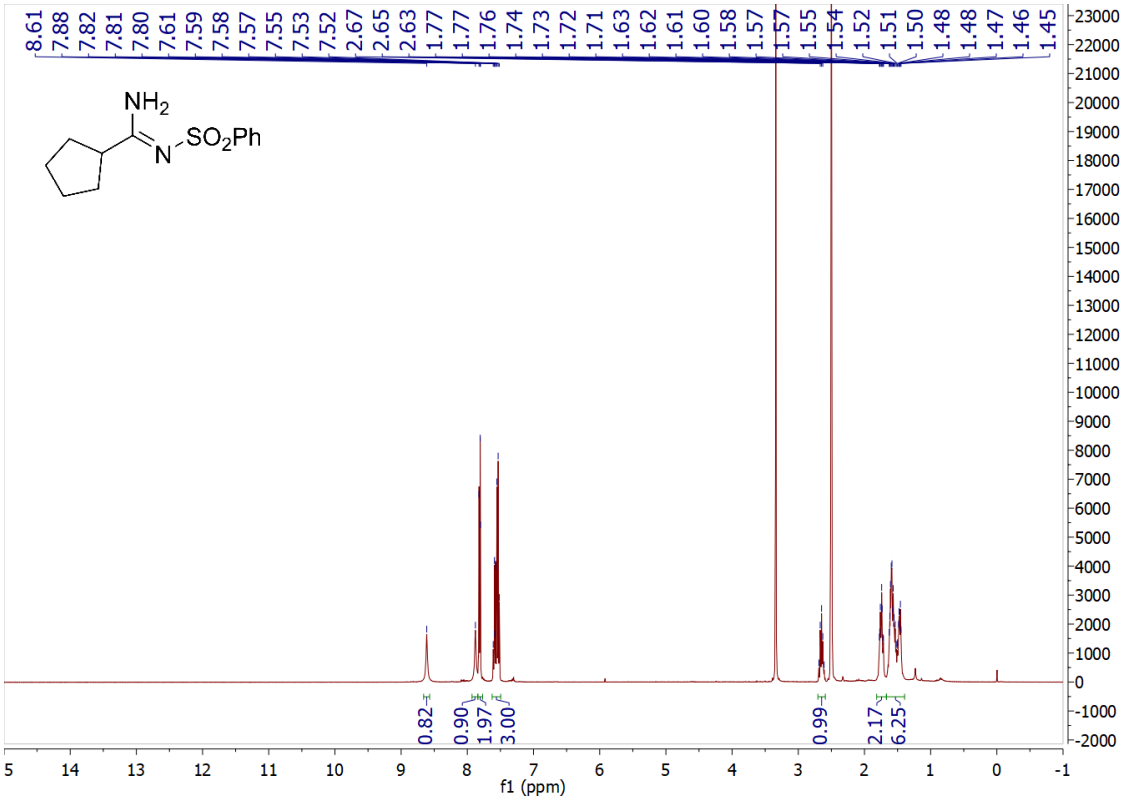


Figure S14. ^{1}H NMR of **2f** in DMSO-d_6 at 295 K.

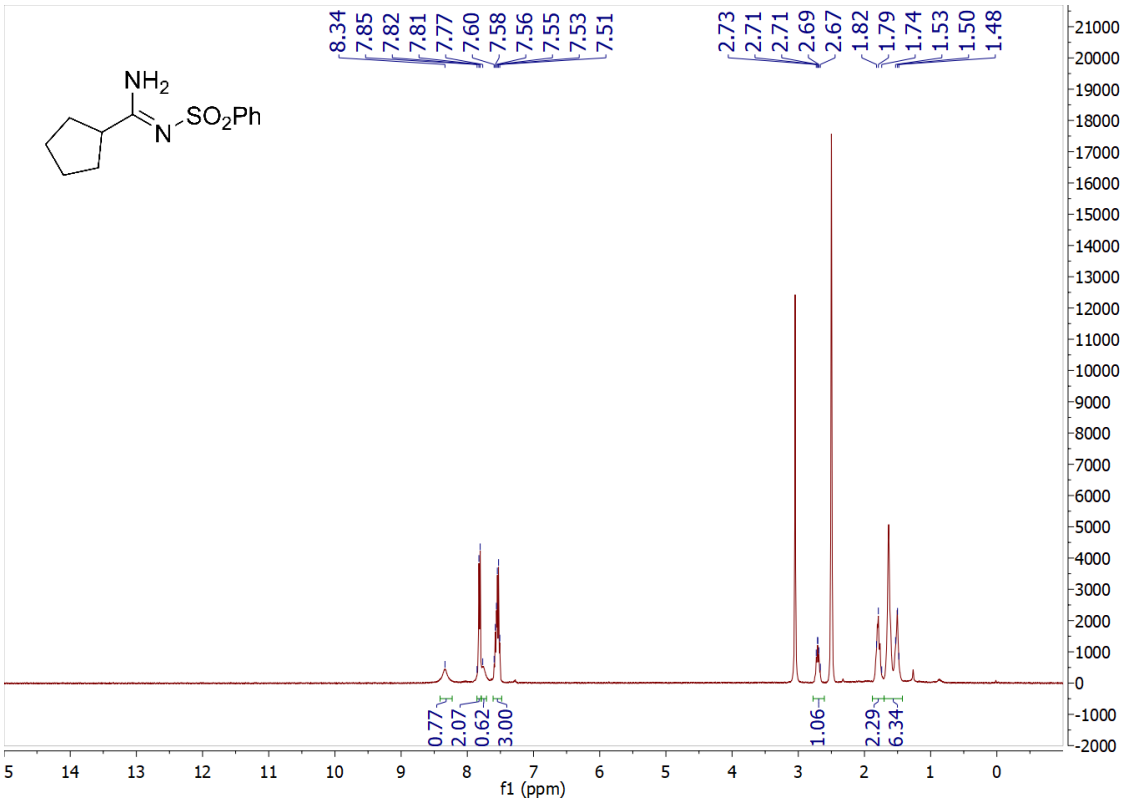


Figure S15. ^{1}H NMR of **2f** in DMSO-d_6 at 353 K.

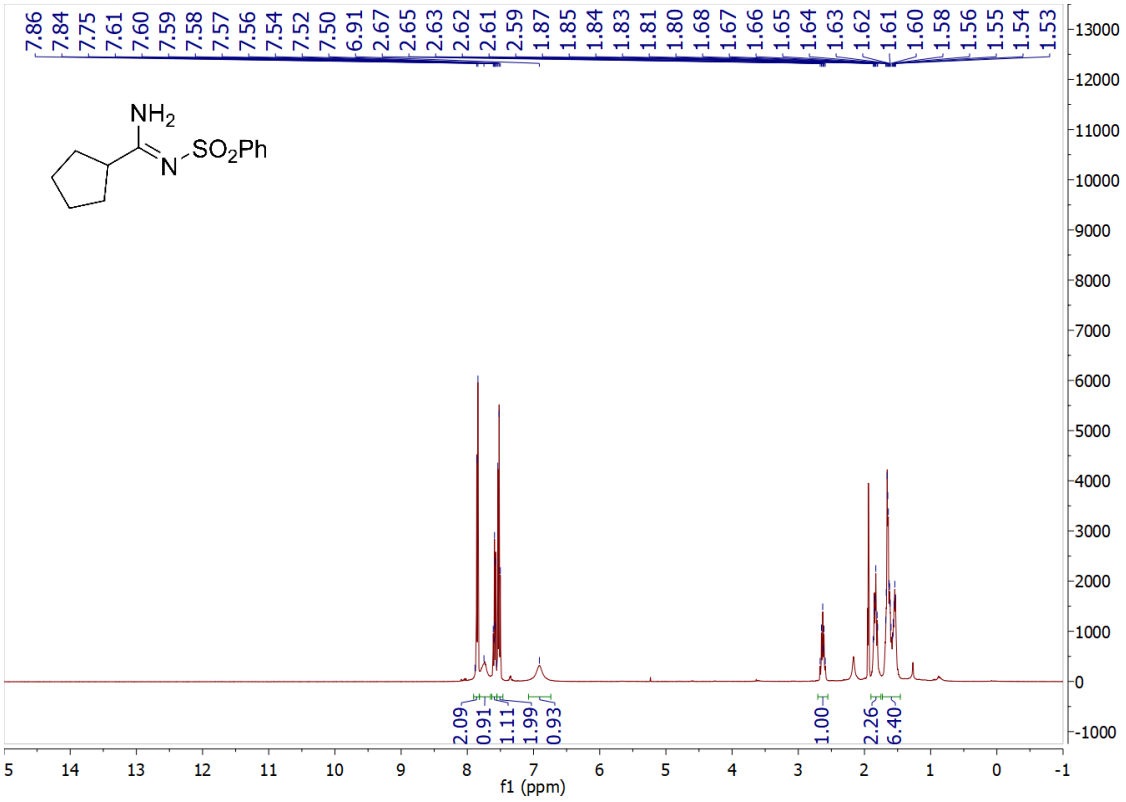


Figure S16. ^{1}H NMR of **2f** in MeCN-d_3 at 295 K.

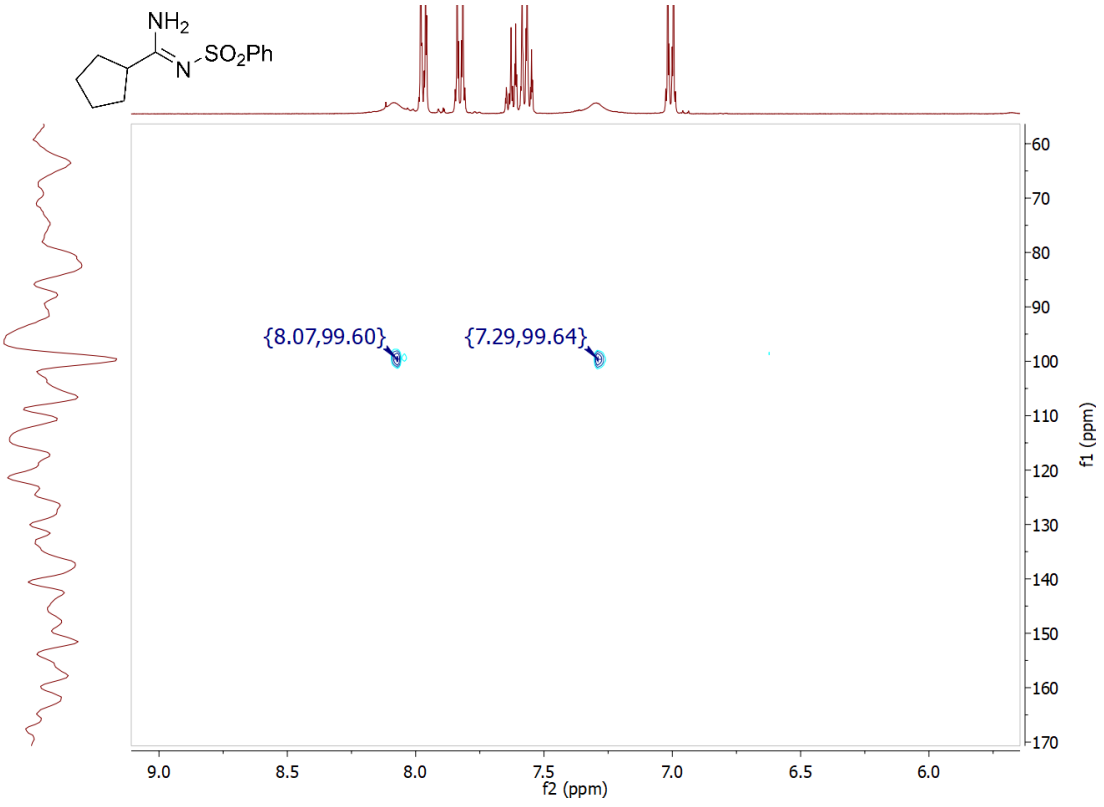


Figure S17. ^{1}H-^{15}N HSQC of **2f** in MeCN-d_3 at 295 K.

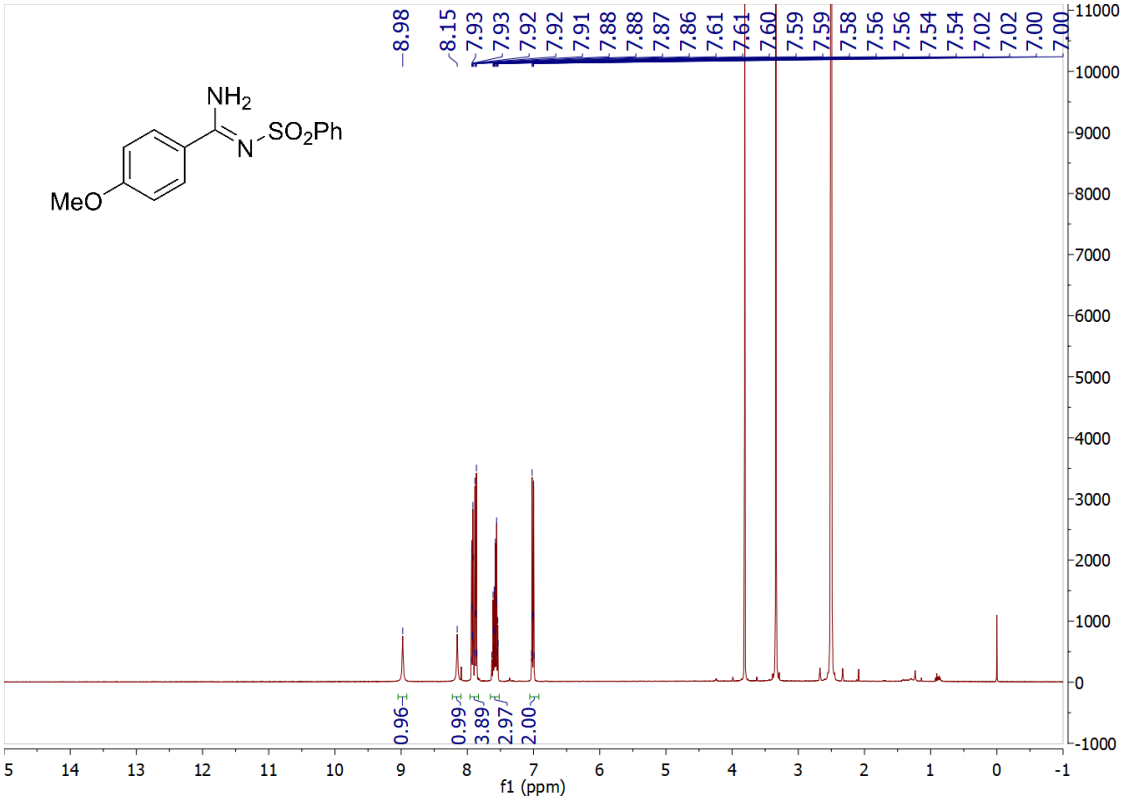


Figure S18. ^{1}H NMR of **2m** in DMSO-d_6 at 295 K.

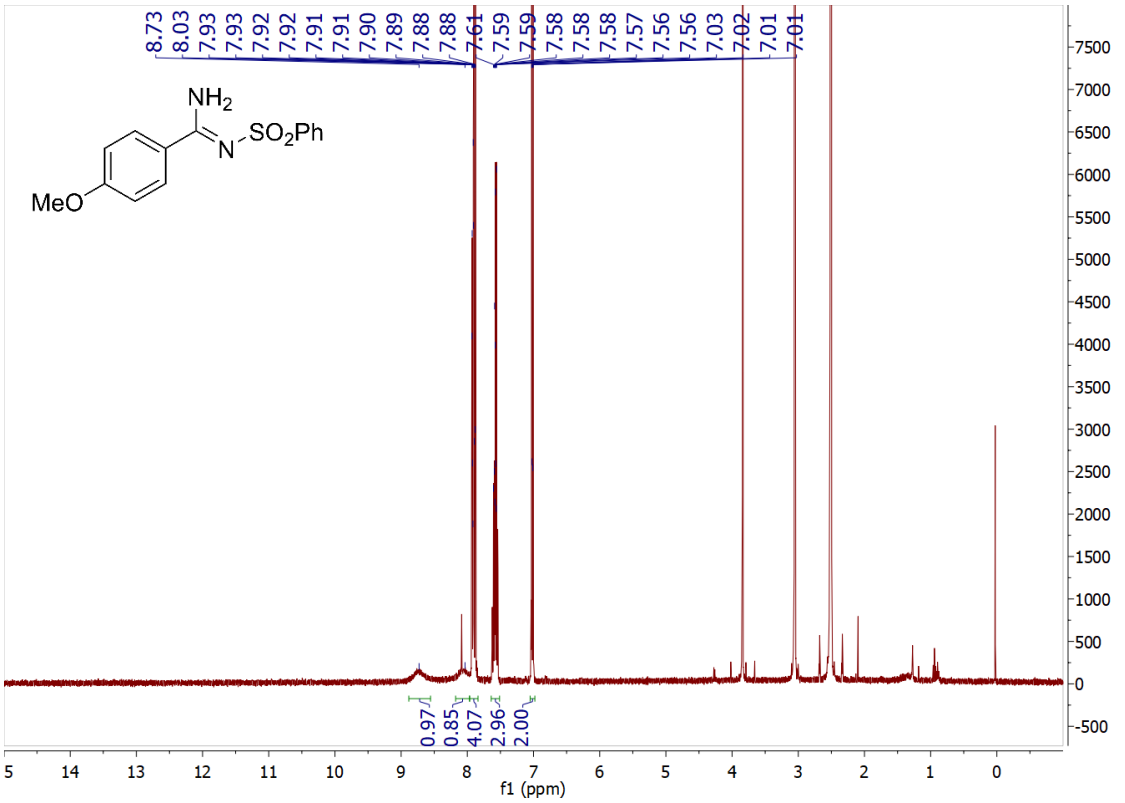


Figure S19. ^{1}H NMR of **2m** in DMSO-d_6 at 353 K.

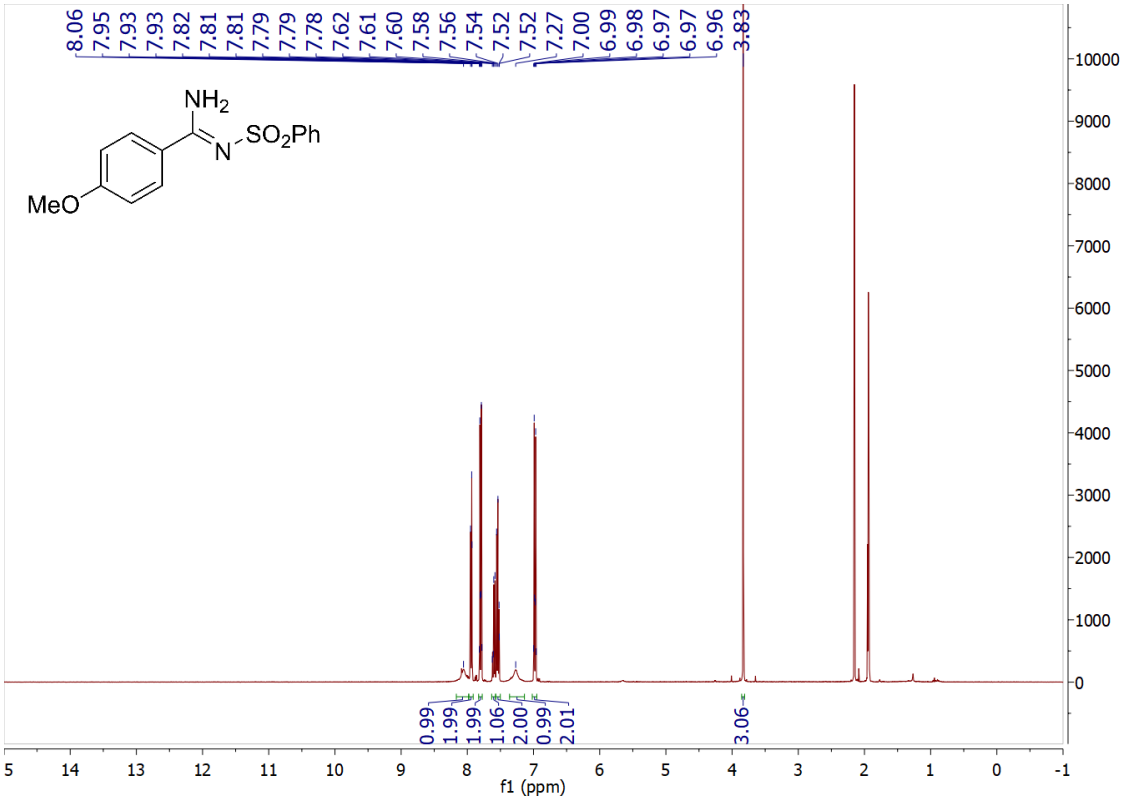


Figure S20. ^{1}H NMR of **2m** in MeCN-d_3 at 295 K.

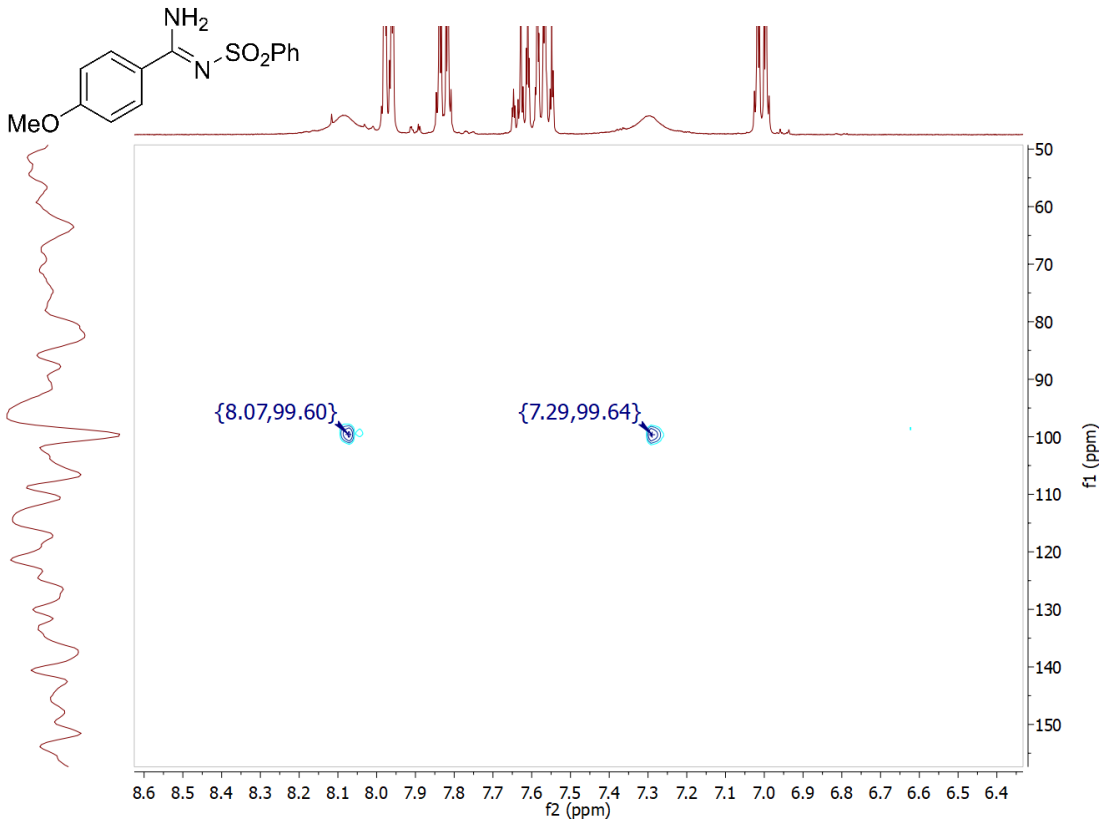


Figure S21. ^{1}H-^{15}N HSQC of **2m** in MeCN-d_3 at 295 K.

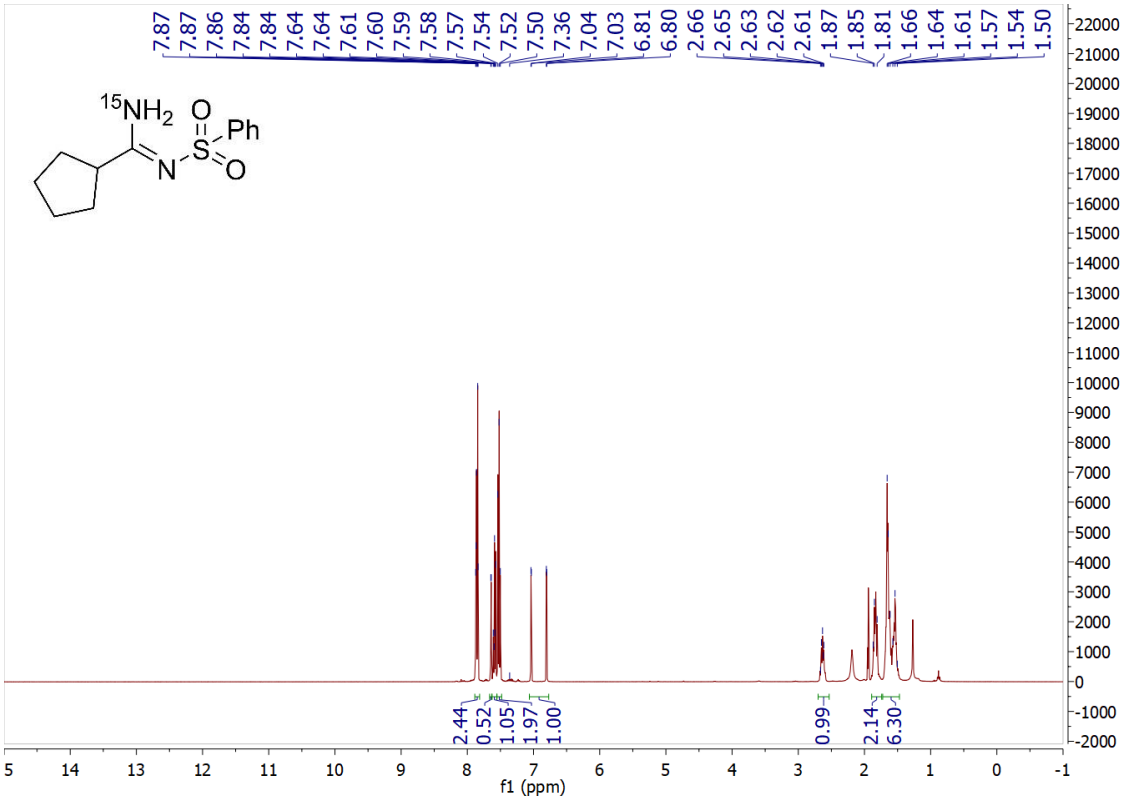


Figure S22. ^{1}H NMR of ^{15}N-**2f** in MeCN-d_3 at 295 K.

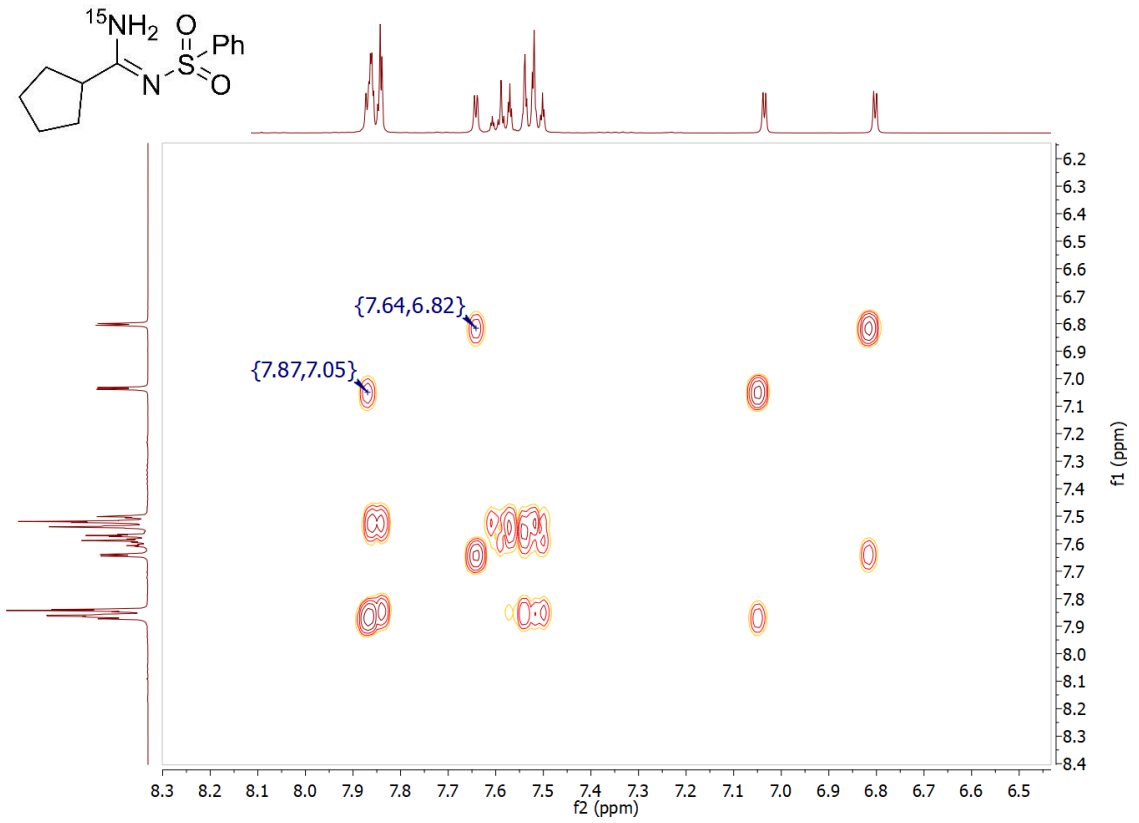


Figure S23. ^{1}H-^{1}H COSY NMR of ^{15}N-**2f** in MeCN-d_3 at 295 K.

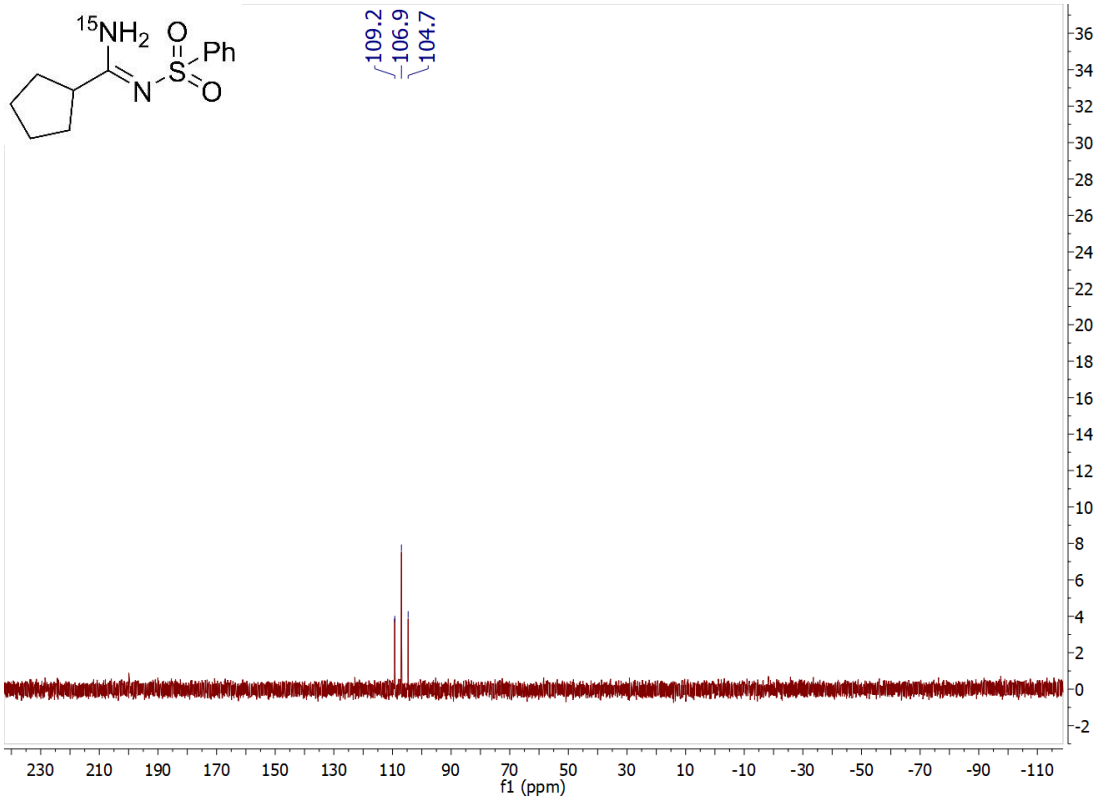


Figure S24. ^{1}H-^{15}N coupled ^{15}N NMR of ^{15}N-**2f** in MeCN-d_3 at 295 K.

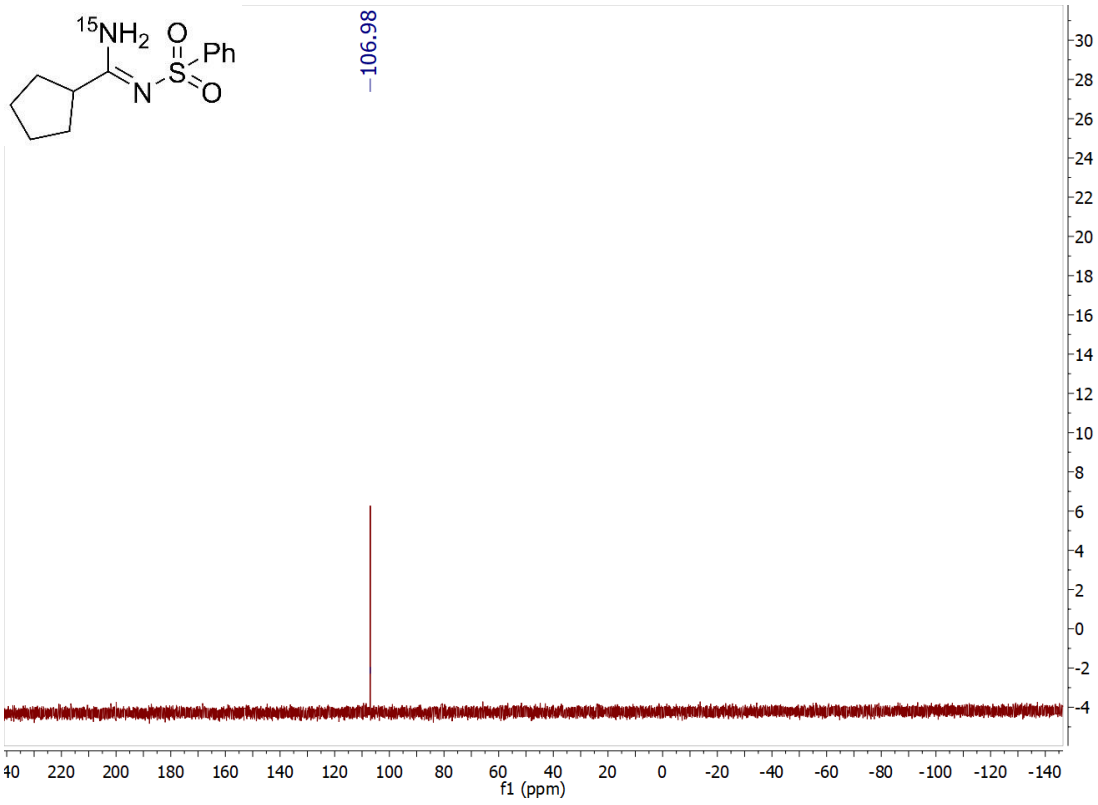


Figure S25. ^{1}H-decoupled ^{15}N NMR of ^{15}N-**2f** in MeCN-d_3 at 295 K.

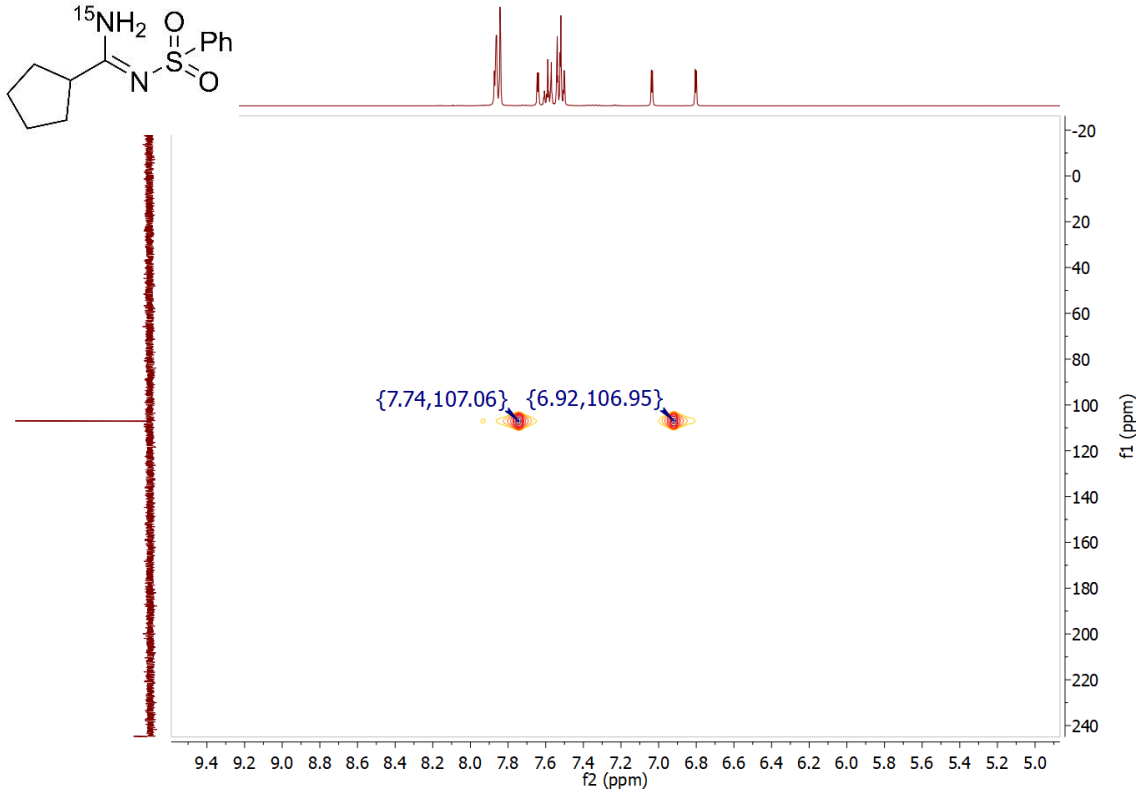


Figure S26. ^{1}H-^{15}N HSQC NMR of ^{15}N-**2f** in MeCN-d_3 at 295 K.

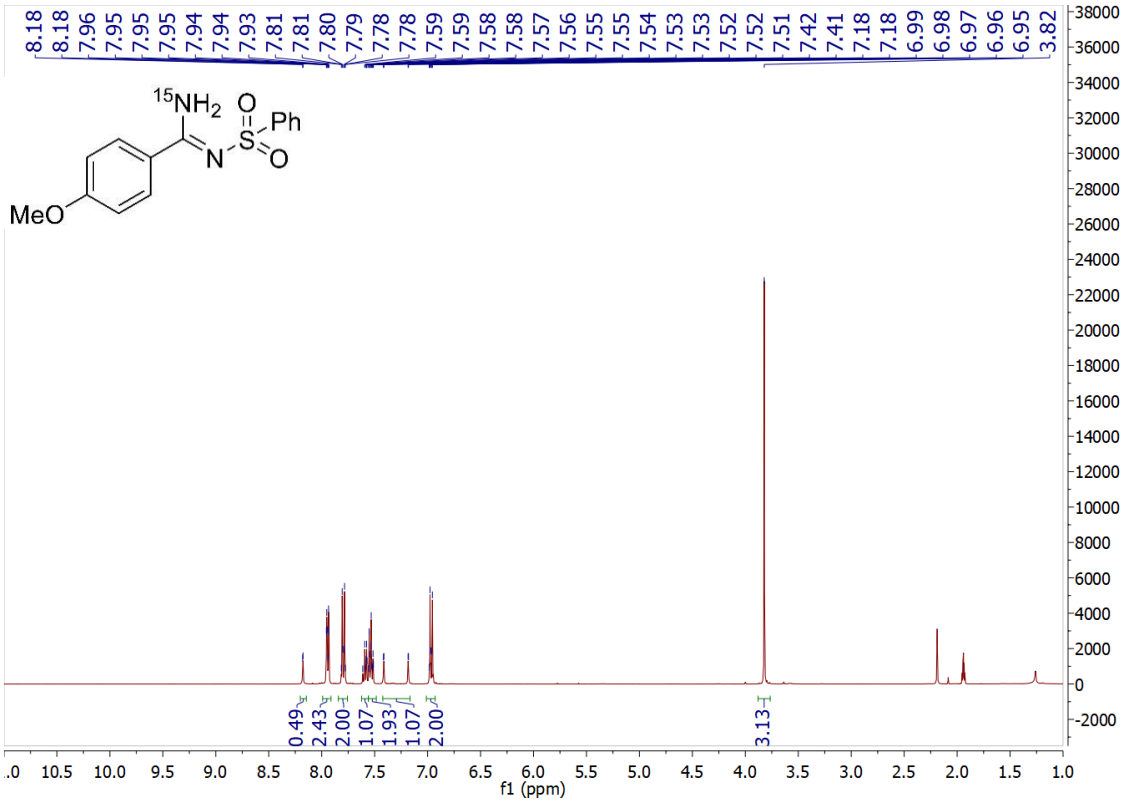


Figure S27. ^{1}H NMR of ^{15}N-**2m** in MeCN-d_3 at 295 K.

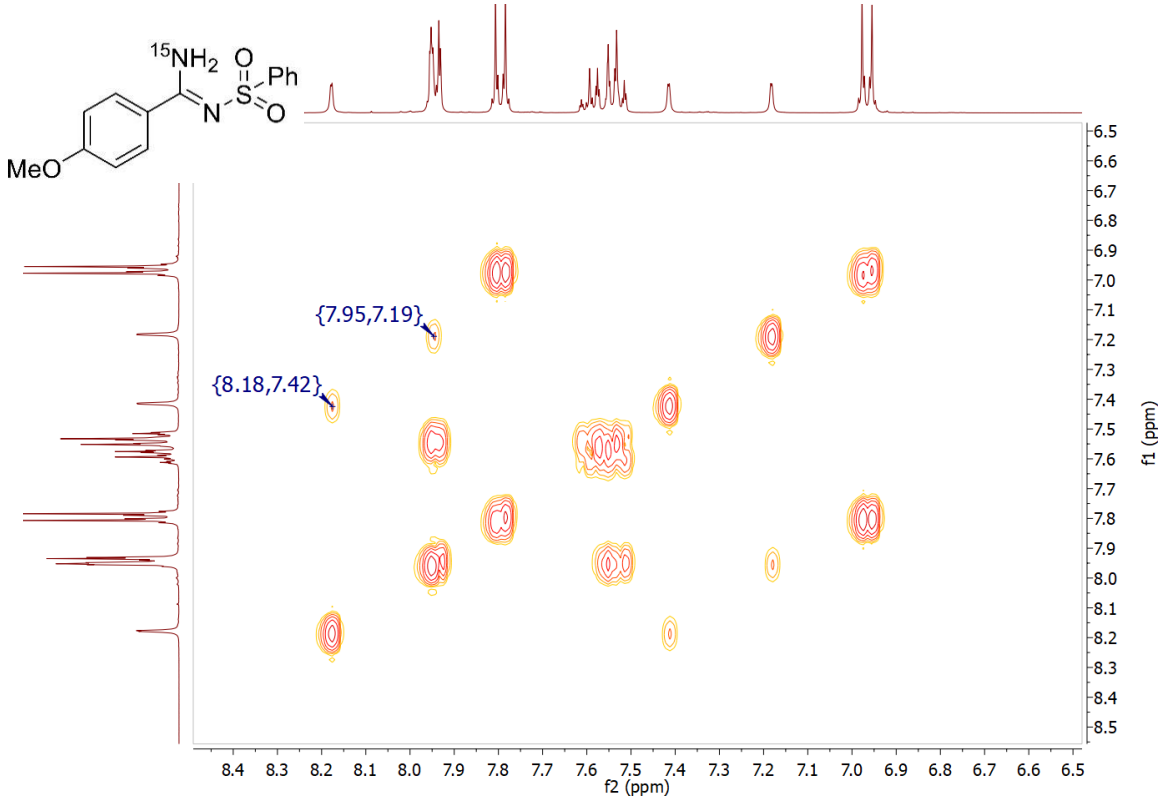


Figure S28. ^{1}H-^{1}H COSY NMR of ^{15}N-**2m** in MeCN-d_3 at 295 K.

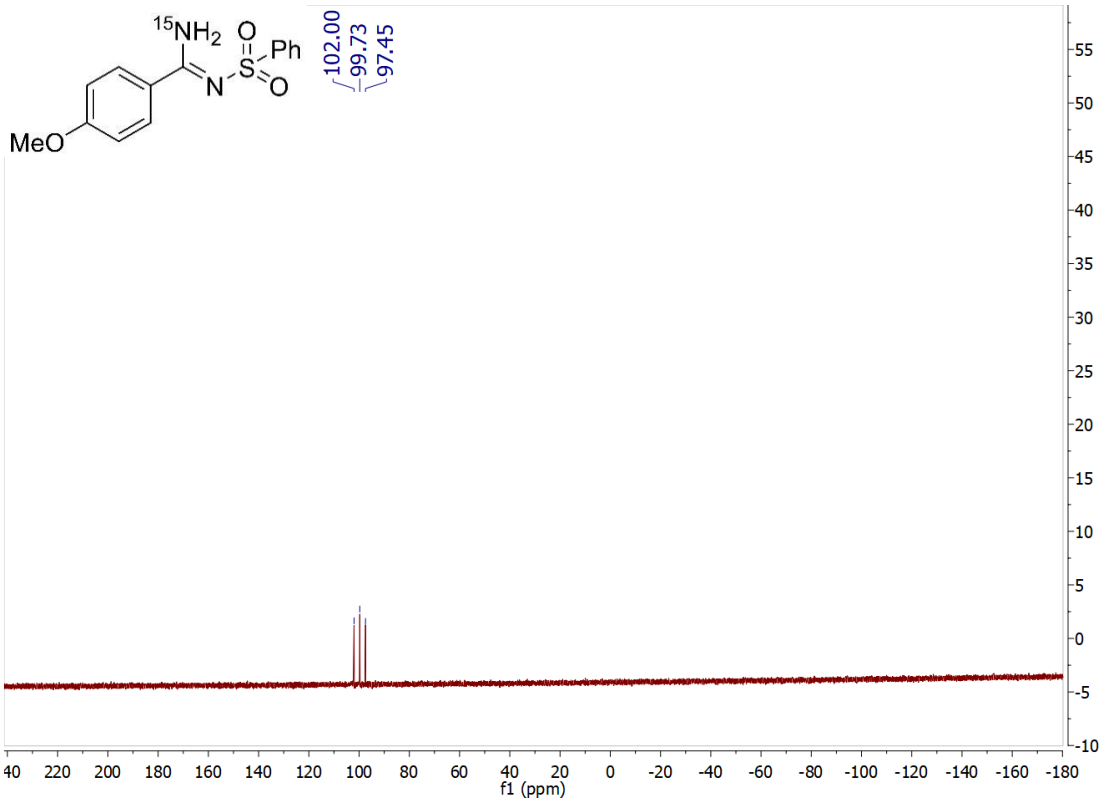


Figure S29. ^{1}H-^{15}N coupled ^{15}N NMR of ^{15}N-**2m** in MeCN-d_3 at 295 K.

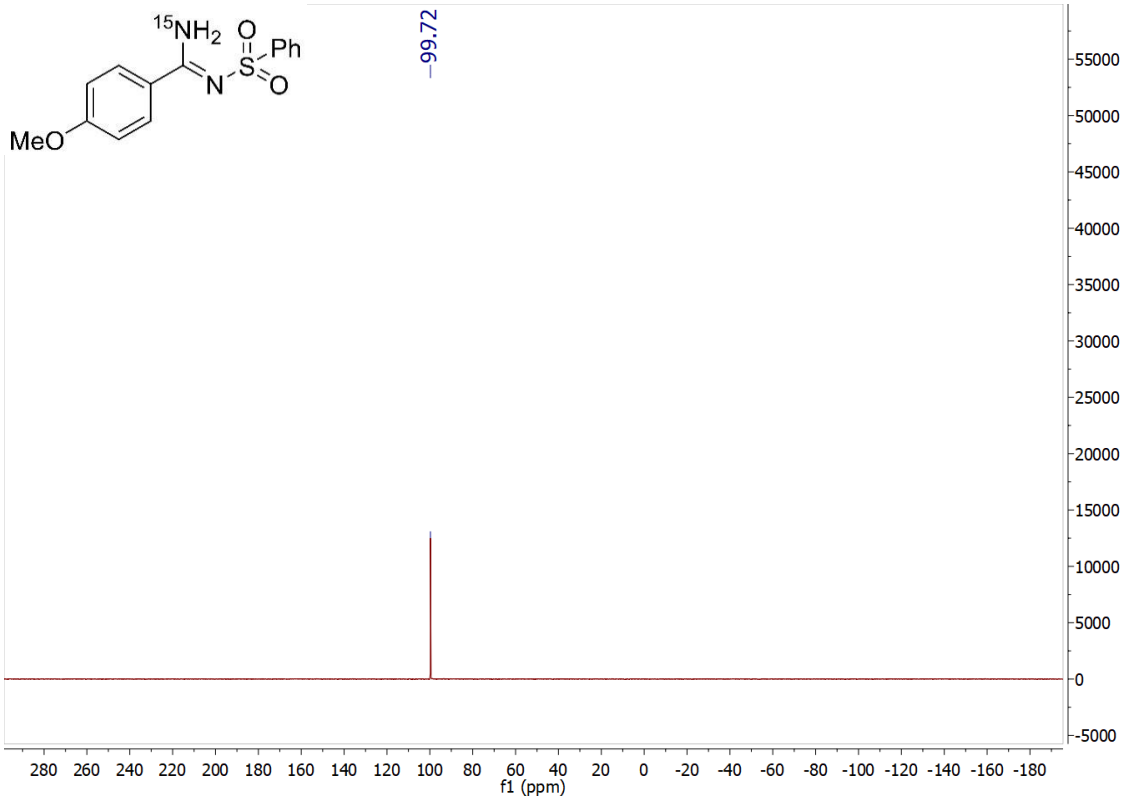


Figure S30. ^{1}H-decoupled ^{15}N NMR of ^{15}N-**2m** in MeCN-d_3 at 295 K.

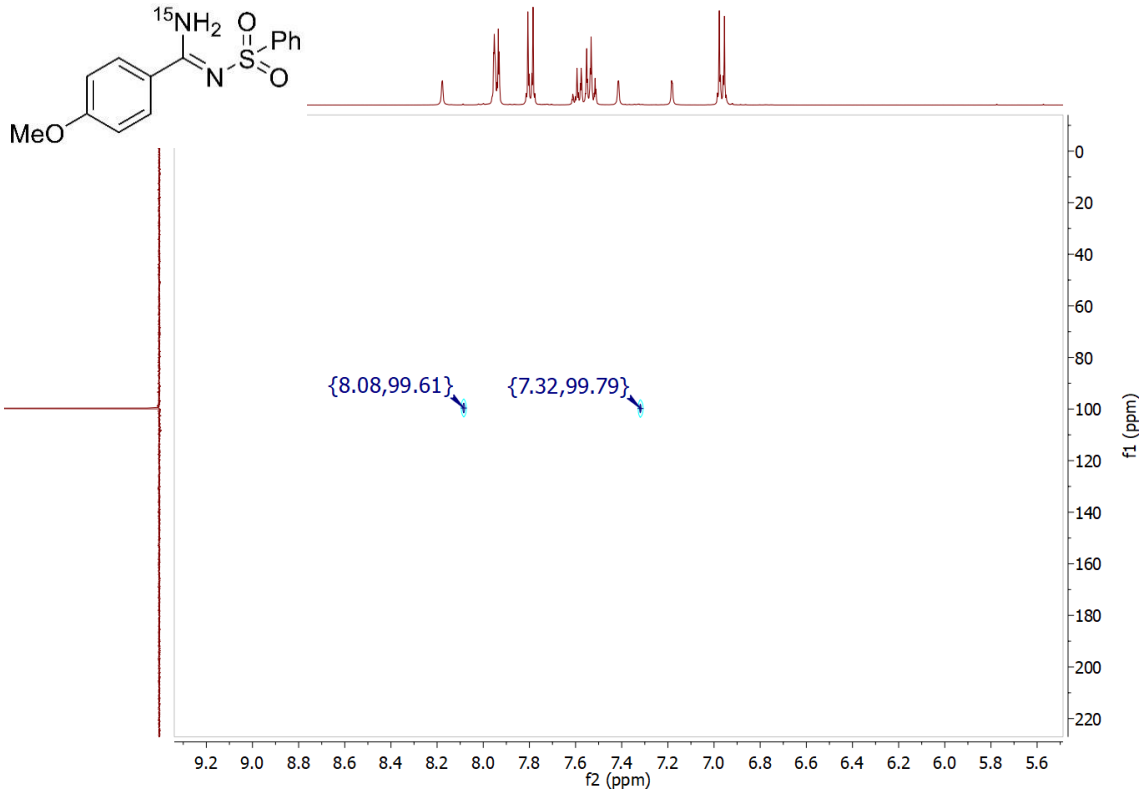


Figure S31. ^{1}H-^{15}N HSQC NMR of ^{15}N-**2m** in MeCN-d_3 at 295 K.

Single-crystal X-ray diffraction data were collected at 150 K on an Agilent Technologies SuperNova Dual diffractometer with an Atlas detector using monochromated Mo-*K*α radiation (*λ* = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å). The data were processed using CrysAlis Pro.[S4] Structures were solved by SHELXT program[S5] and refined by a full-matrix least-squares procedure based on F^2 with SHELXL[S6] using the Olex2 program suite.[S7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were readily located in difference Fourier maps. Hydrogen atoms bonded to carbon atoms were subsequently treated as riding atoms in geometrically idealized positions with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms. Hydrogen atoms bonded to nitrogen atoms were refined fixing isotropic temperature factors as U_{iso}(H) = 1.2U_{eq}(N) and N–H bond length were refined restraining bonding distances. The crystallographic data are listed in Tables S2 and S3. The observed C–N_{amide} and C–N_{imine} bond lengths are very similar in the studied systems and are comparable with the observed ones in sulfonyl amides with tautomer A found in the CCDC (Table S4).

Table S2. Crystallographic Data for Reported Structures.

	2a	**2e**	**2h**	**2j**
CCDC number	2400597	2400598	2400599	2400600
Formula	$C_9H_{12}N_2O_2S$	$C_{10}H_{12}N_2O_2S$	$C_{14}H_{14}N_2O_2S$	$C_{13}H_{11}ClN_2O_2S$
M_r	212.27	224.28	274.33	294.75
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*–1	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	7.2268(4)	8.4203(6)	8.5461(2)	8.5033(3)
b (Å)	7.9865(6)	17.4676(10)	23.1470(7)	23.1754(7)
c (Å)	9.2053(8)	7.2129(5)	20.3641(6)	20.2967(6)
α (°)	103.537(7)	90	90	90
β (°)	92.512(6)	110.069(8)	92.362(3)	92.005(3)
γ (°)	108.209(6)	90	90	90
Volume (Å^3)	486.72(7)	996.47(12)	4024.93(19)	3997.4(2)
Z	2	4	12	12
D_c (g/cm^3)	1.448	1.495	1.358	1.469
μ (mm^{-1})	0.307	0.305	0.240	0.441
F(000)	224.0	472.0	1728.0	1824.0
Reflections collected	4769	7114	37373	35775
Independent reflections (R_{int})	2232 (0.0319)	2291 (0.0335)	9219 (0.0310)	9145 (0.0341)
Data/restraints/parameters	2232/2/134	2291/2/142	9219/6/535	9145/6/532
R, wR_2 [$I > 2\sigma(I)$] [a]	1.072	1.025	1.037	1.035
R, wR_2 (all data) [a]	0.0409, 0.0872	0.0367, 0.0877	0.0375, 0.0908	0.0357, 0.0841
GOF, S [b]	0.0552, 0.0979	0.0492, 0.0948	0.0483, 0.0972	0.0469, 0.0899
Largest diff. peak/hole (e Å^{-3})	0.36/–0.44	0.45/–0.45	0.39/–0.41	0.54/–0.45

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$, where n is the number of reflections and p is the total number of refined parameters.

Table S2. *Continuation.*

	2m	**2p**	**2u**	**2y**
CCDC number	2400601	2400602	2400603	2400604
Formula	$C_{14}H_{14}N_2O_3S$	$C_{16}H_{16}N_2O_4S$	$C_{11}H_{10}N_2O_2S_2$	$C_{15}H_{16}N_2O_3S$
M_r	290.33	332.37	266.33	304.36
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/c$	$P2_1$
a (Å)	14.3193(2)	7.62600(10)	11.5242(2)	7.8160(2)
b (Å)	7.07640(10)	10.8033(2)	9.8469(2)	5.54900(10)
c (Å)	27.0199(3)	36.3680(7)	10.7702(2)	16.7197(4)
α (°)	90	90	90	90
β (°)	90	90	98.211(2)	97.198(2)
γ (°)	90	90	90	90
Volume (Å^3)	2737.90(6)	2996.21(9)	1209.65(4)	719.43(3)
Z	8	8	4	2
D_c (g/cm^3)	1.409	1.474	1.462	1.405
μ (mm^{-1})	2.190	2.131	3.932	2.109
F(000)	1216.0	1392.0	552.0	320.0
Reflections collected	13827	11983	8114	7568
Independent reflections (R_{int})	2602 (0.0555)	2844 (0.0560)	2295 (0.0319)	2399 (0.0575)
Data/restraints/parameters	2602/2/189	2844/2/216	2295/2/160	2399/3/198
R, wR_2 [$I > 2\sigma(I)$] [a]	1.069	1.066	1.045	1.069
R, wR_2 (all data) [a]	0.0388, 0.1026	0.0476, 0.1204	0.0359, 0.0982	0.0390, 0.1033
GOF, S [b]	0.0452, 0.1106	0.0552, 0.1290	0.0398, 0.1020	0.0408, 0.1053
Largest diff. peak/hole (e Å^{-3})	0.26/–0.42	0.39/–0.56	0.33/–0.43	0.32/–0.56
Flack parameter	/	/	/	0.059(17)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$, where n is the number of reflections and p is the total number of refined parameters.

Table S3. Hydrogen Bonds for Reported Structures [Å and °].

D–H···A	*d*(D–H)	d(H···A)	d(D···A)	<(DHA)
2a				
N1–H1a···O1	0.854(16)	2.26(2)	2.869(2)	128.0(18)
N1–H1a···O1^{i}	0.854(16)	2.261(18)	3.017(2)	147.6(19)
N1–H1b···O2^{ii}	0.879(15)	2.119(17)	2.978(2)	165(2)
2e				
N1–H1a···O1	0.859(15)	2.215(19)	2.850(2)	130.6(18)
N1–H1b···O2^{i}	0.867(15)	2.172(16)	3.005(2)	161.1(19)
2h				
N1–H1a···O1	0.894(15)	2.117(17)	2.7943(18)	131.9(16)
N1–H1b···O6^{i}	0.872(14)	2.060(15)	2.9188(17)	168.1(18)
N5–H5a···O1	0.867(15)	2.275(18)	2.9011(18)	129.2(17)
N5–H5a···O5	0.867(15)	2.103(18)	2.7649(18)	132.7(17)
N5–H5b···O4	0.867(15)	2.068(16)	2.8966(19)	159.7(18)
N3–H3a···O5^{i}	0.867(15)	2.245(17)	2.9076(17)	133.1(16)
N3–H3a···O3	0.867(15)	2.052(18)	2.7102(18)	132.1(17)
2j				
N1–H1a···O1	0.879(15)	2.130(18)	2.7939(19)	131.8(17)
N1–H1b···O6	0.866(15)	2.034(15)	2.8764(18)	163.8(19)
N5–H5a···O5	0.864(15)	2.092(18)	2.7521(18)	132.7(17)
N5–H5b···O4^{i}	0.868(15)	2.075(16)	2.8953(19)	157.4(19)
N3–H3a···O5	0.872(15)	2.241(18)	2.8941(18)	131.5(16)
N3–H3a···O3	0.872(15)	2.030(18)	2.7015(19)	133.0(17)
2m				
N1–H1a···O1	0.879(10)	2.073(17)	2.7681(19)	135(2)
N1–H1b···O2^{i}	0.875(10)	1.990(12)	2.8404(19)	163(2)
2p				
N1–H1a···O1	0.872(10)	2.35(2)	2.886(2)	120(2)
N1–H1a···O2^{i}	0.872(10)	2.180(15)	2.976(2)	152(2)
N1–H1b···O3^{ii}	0.877(10)	2.426(15)	3.228(2)	152(2)
2u				
N1–H1a···O1	0.870(10)	2.115(19)	2.777(2)	132(2)
N1–H1b···O2^{i}	0.882(10)	2.039(12)	2.887(2)	161(2)
2y				
N1–H1a···O1	0.873(13)	2.21(4)	2.783(4)	123(4)
N1–H1a···O2^{i}	0.873(13)	2.15(3)	2.857(4)	138(4)
N1–H1b···N2^{i}	0.877(13)	2.54(3)	3.215(4)	134(3)

Symmetry codes for **2a**: (i) 1 – *x*, 2 – *y*, 2 – *z*; (ii) 1 + *x*, *y*, *z*; for **2e**: (i) *x*, *y*, –1 + *z*; for **2h**: (i) *x*, ½ – *y*, –½ + *z*; for **2j**: (i) *x*, 1½ – *y*, ½ + *z*; for **2m**: *x*, 1 + *y*, *z*; for **2p**: (i) 1½ – *x*, –½ + *y*, *z*; (ii) 1 – *x*, –½ + *y*, ½ – *z*; for **2u**: *x*, ½ – *y*, –½ + *z*; for **2y**: *x*, –1 + *y*, *z*.

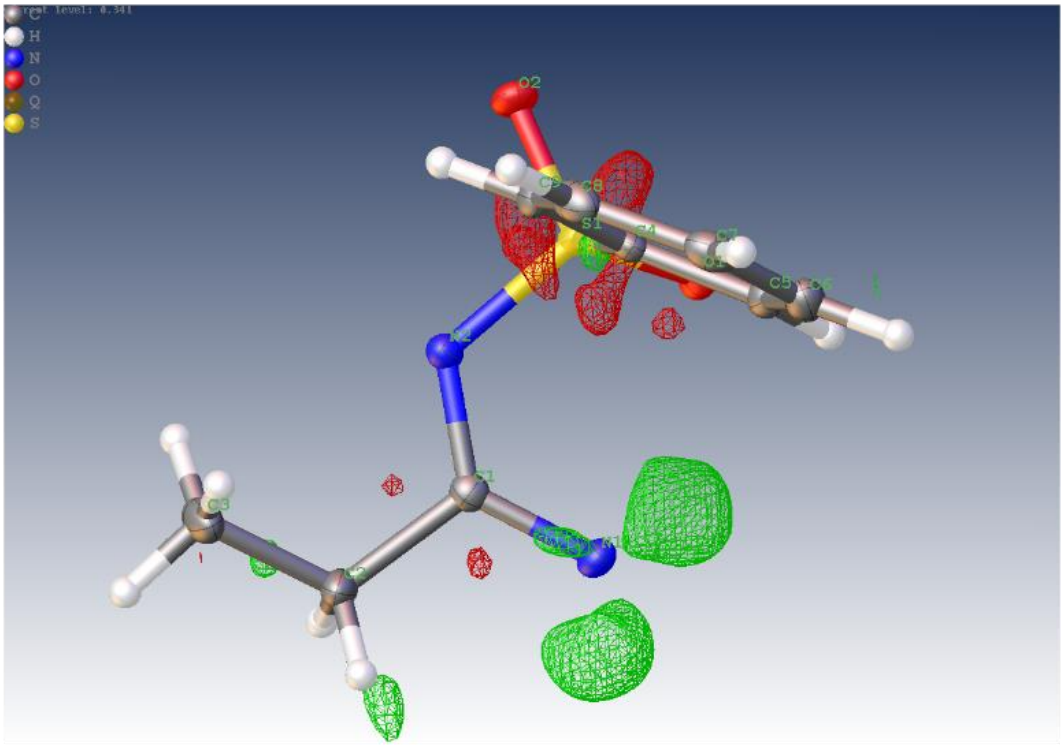


Figure S32. Fourier difference electron density maps showing the electron density associated with two H-atoms in **2a**.

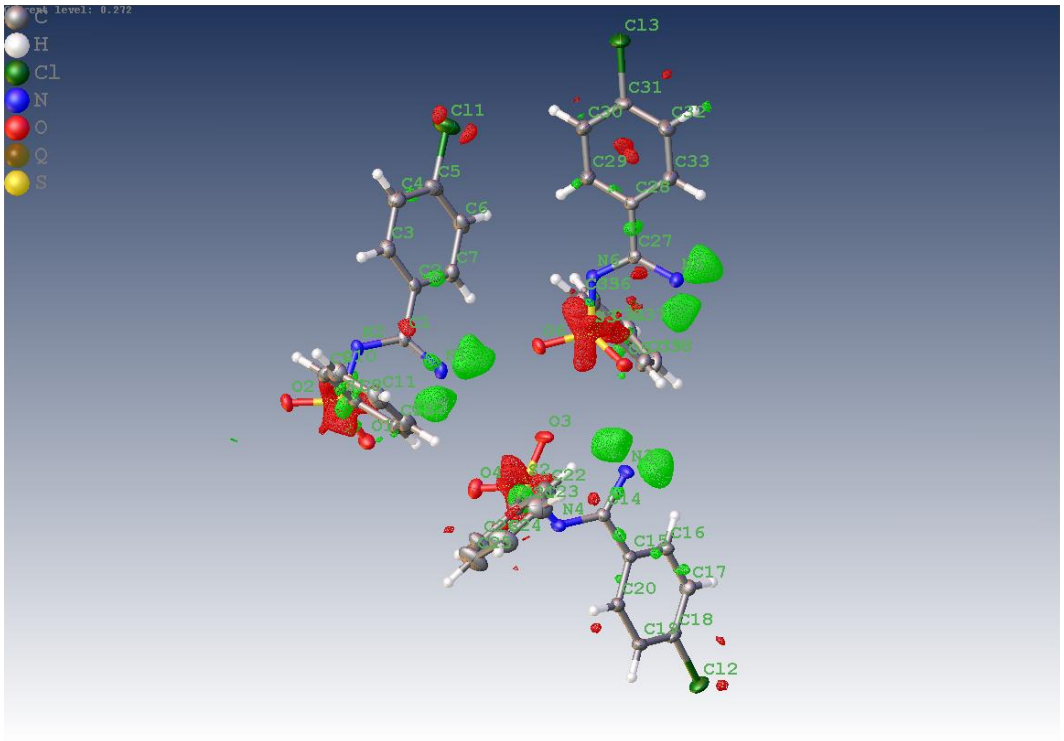


Figure S33. Fourier difference electron density maps showing the electron density associated with two H-atoms in **2j**.

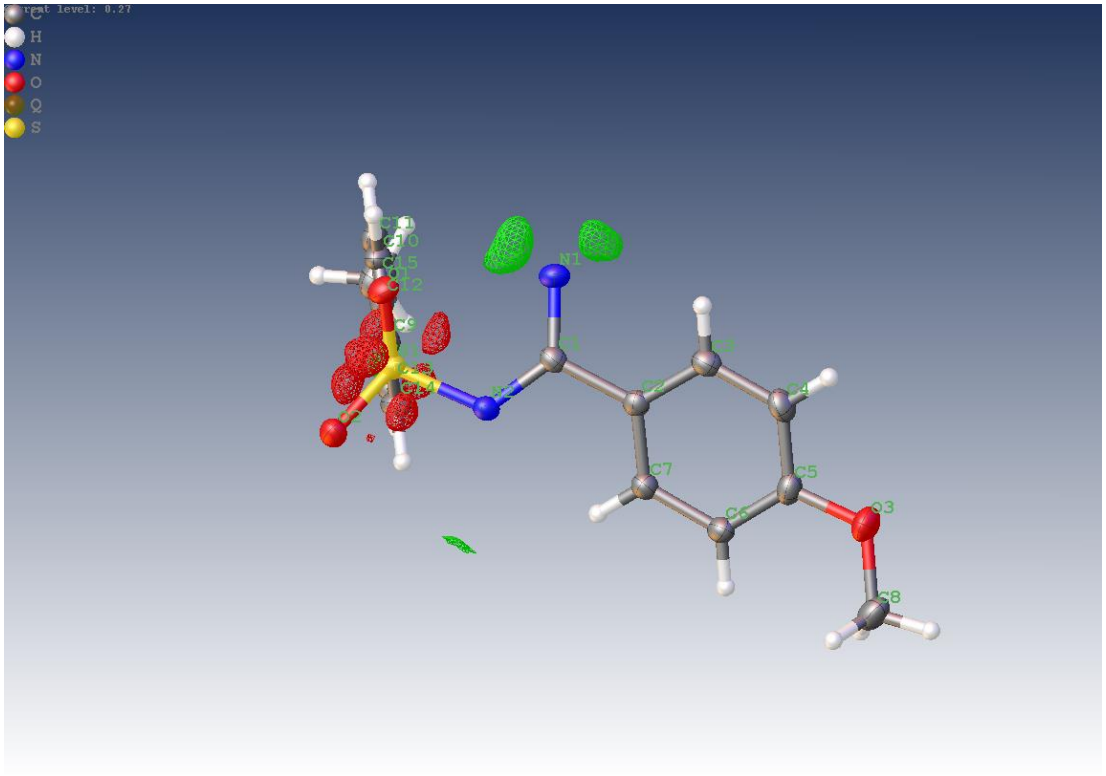


Figure S34. Fourier difference electron density maps showing the electron density associated with two H-atoms in **2y**.

Table S4. Selected C–N bond distances [Å].

	C1–N1	C1–N2	C–N3	C–N4	C–N5	C–N6
2a	1.322(2)	1.324(2)				
2e	1.320(2)	1.328(2)				
2h	1.323(2)	1.3278(19)	1.3233(19)	1.3254(19)	1.320(2)	1.322(2)
2j	1.319(2)	1.331(2)	1.324(2)	1.320(2)	1.317(2)	1.324(2)
2m	1.322(2)	1.326(2)				
2p	1.325(3)	1.317(3)				
2u	1.327(2)	1.332(2)				
2y	1.316(4)	1.325(4)				

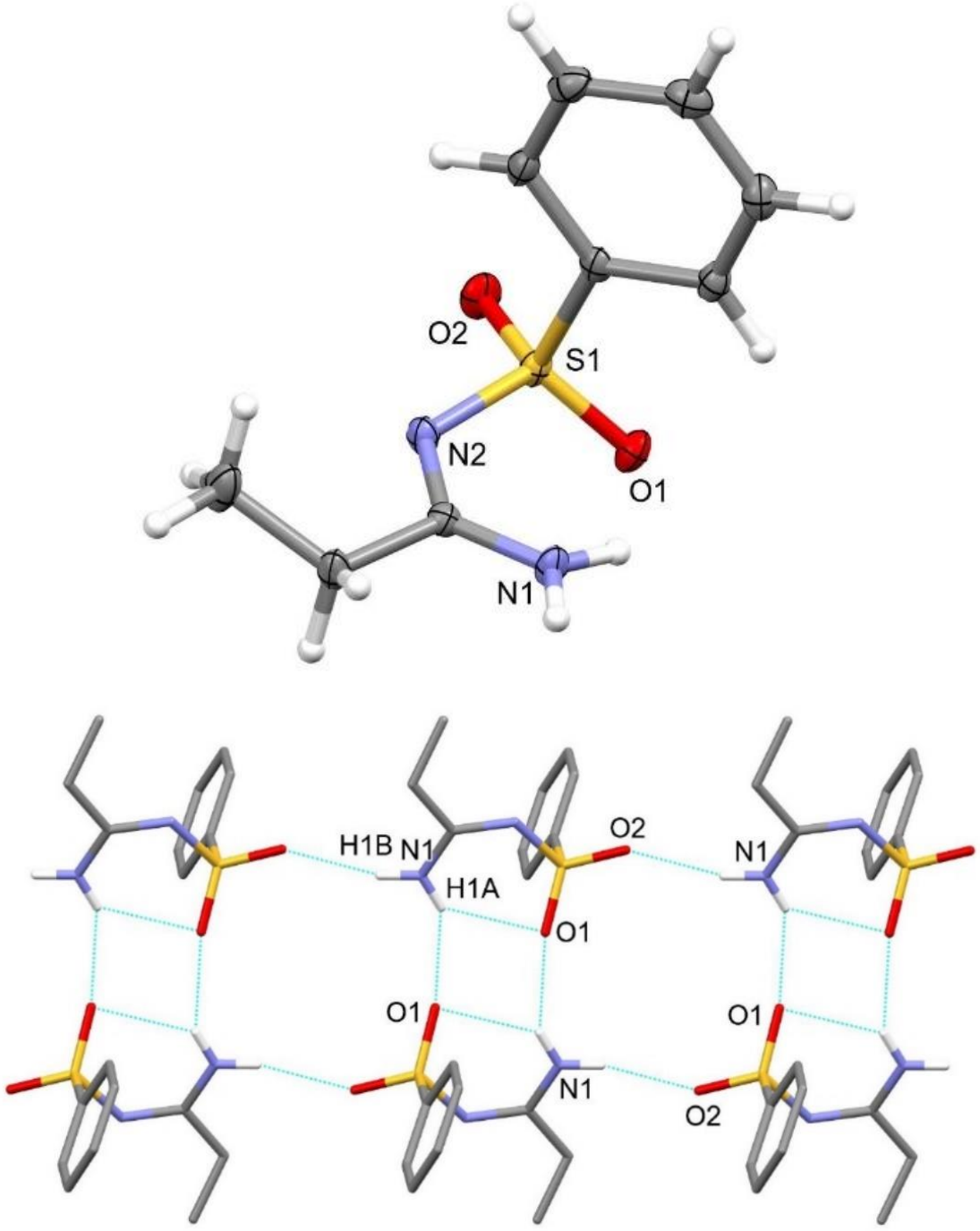


Figure S35. Top: X-Ray crystal structure of **2a**. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded belt formation in **2a**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

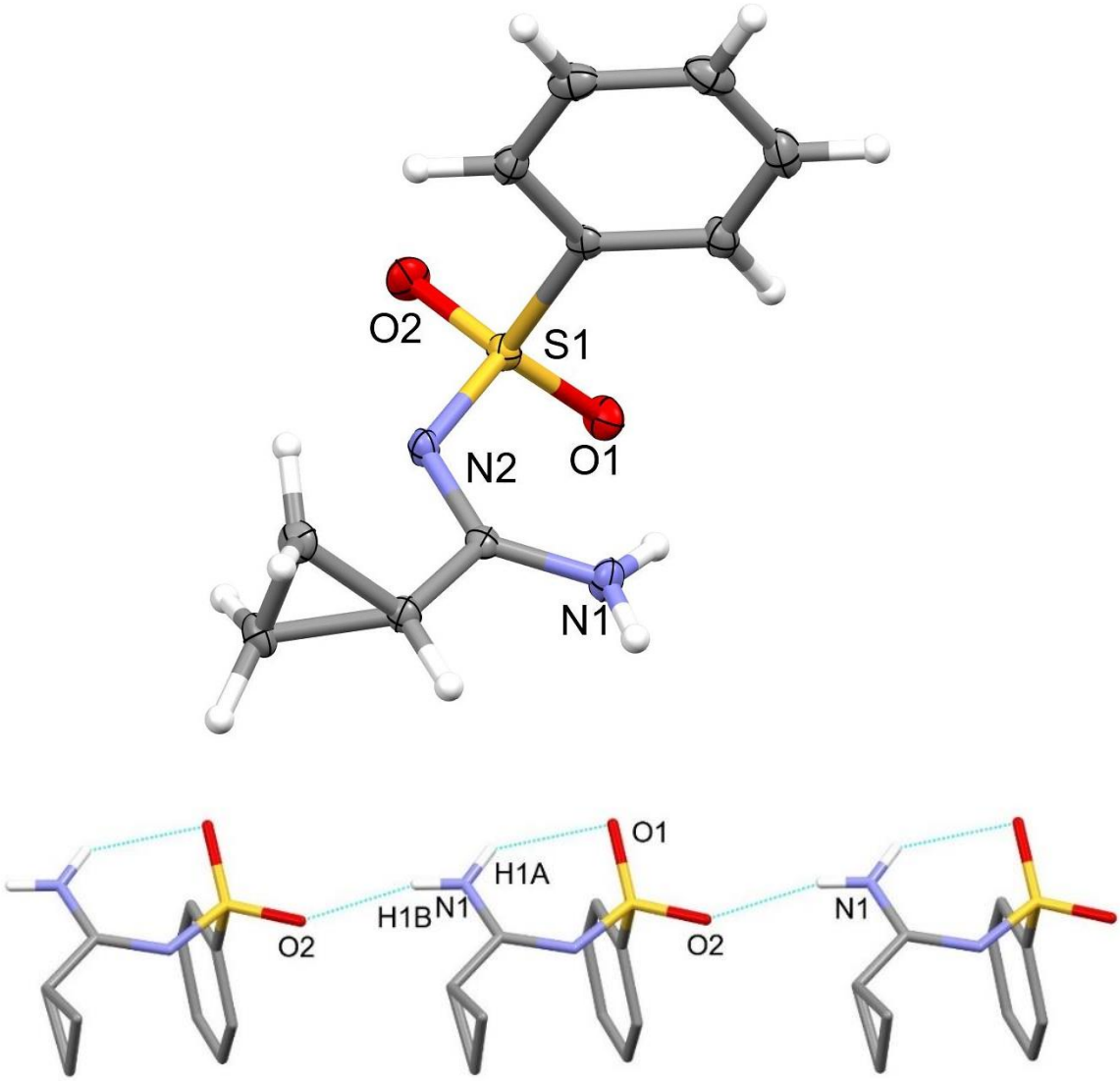


Figure S36. Top: X-Ray crystal structure of **2e**. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded belt formation in **2e**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

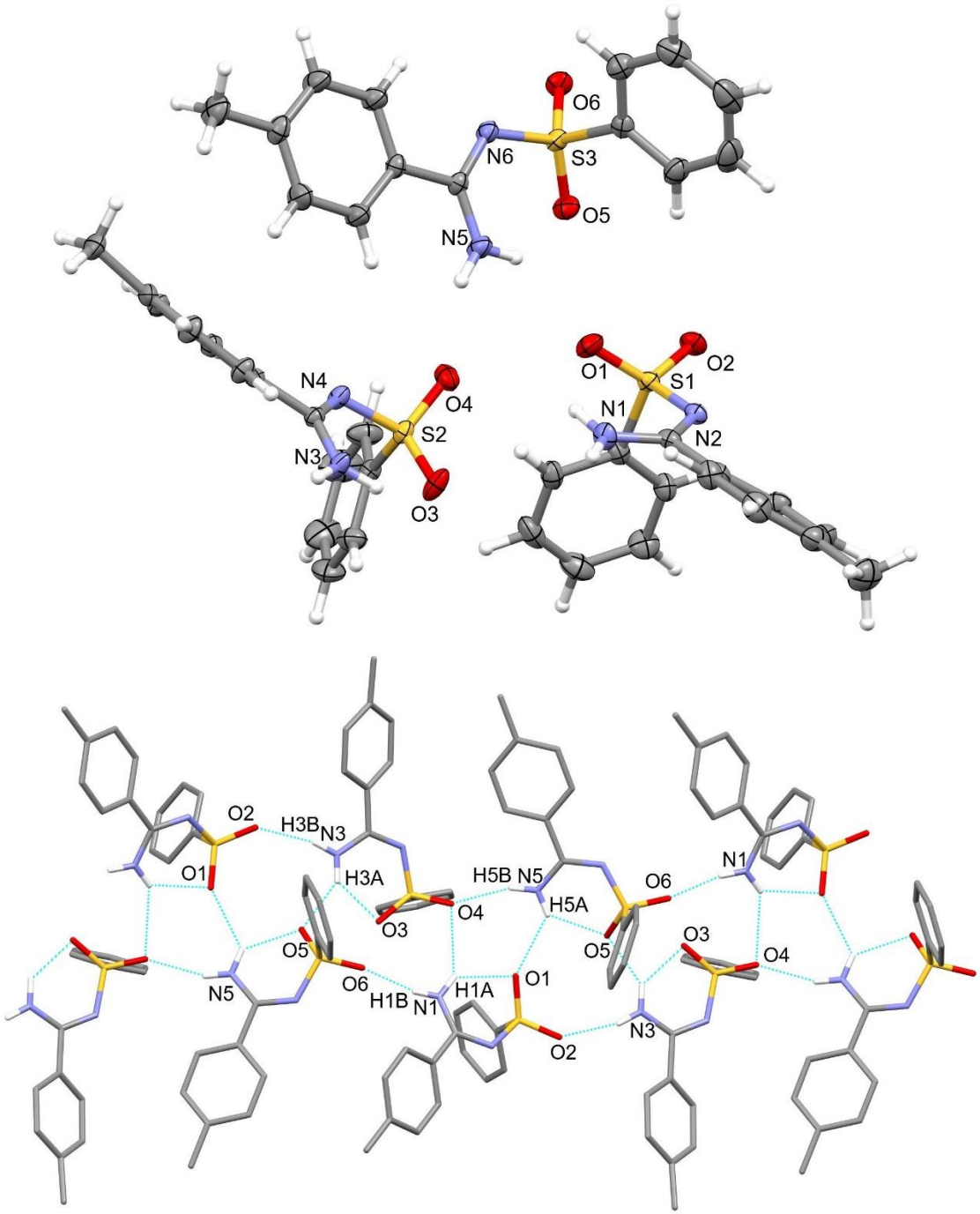


Figure S37. Top: Asymmetric unit of **2h** with three crystallographically independent molecules. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Bottom: Hydrogen-bonded belt formation in **2h**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

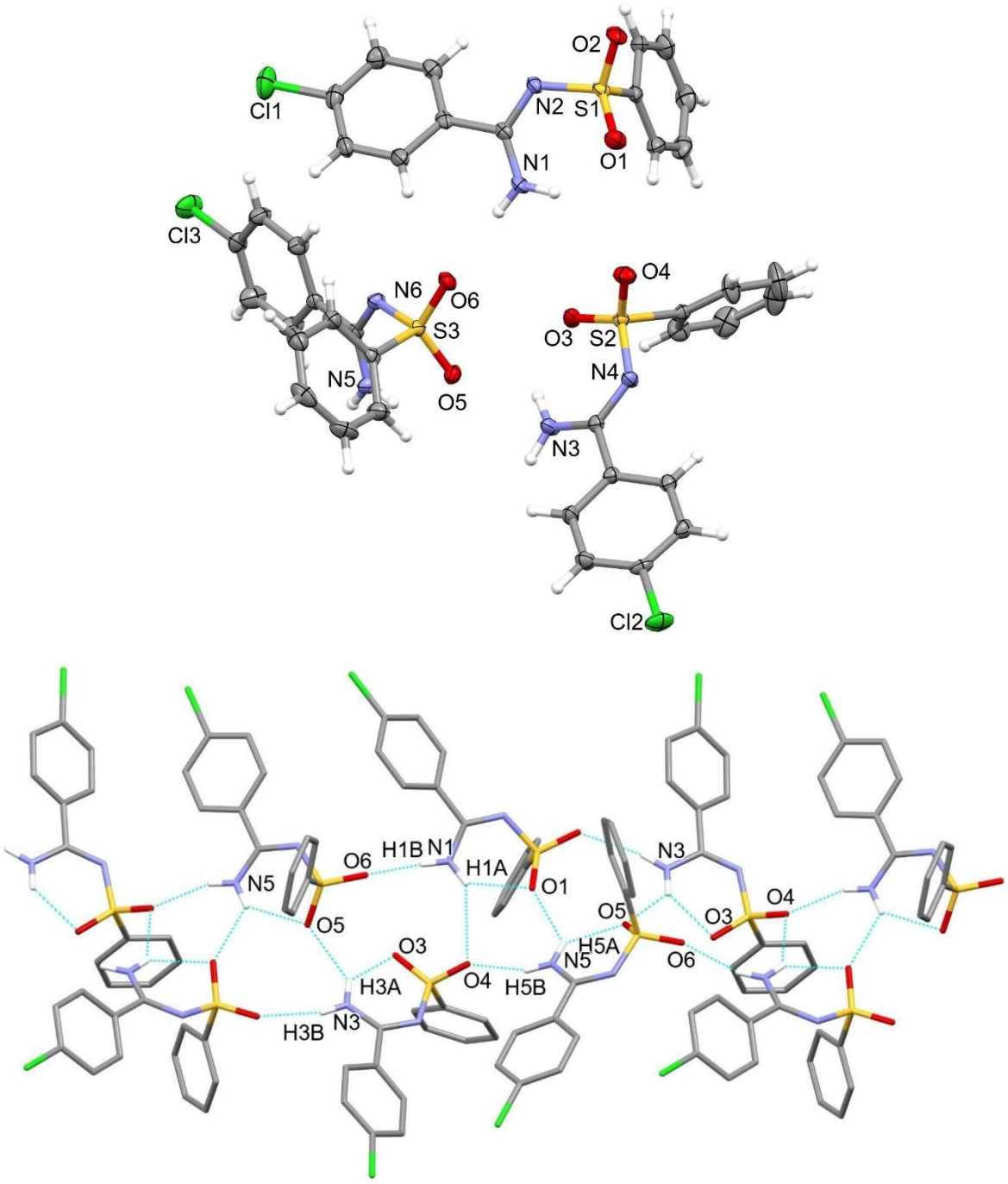


Figure S38. Top: Asymmetric unit of **2j** with three crystallographically independent molecules. Displacement. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded belt formation in **2j**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

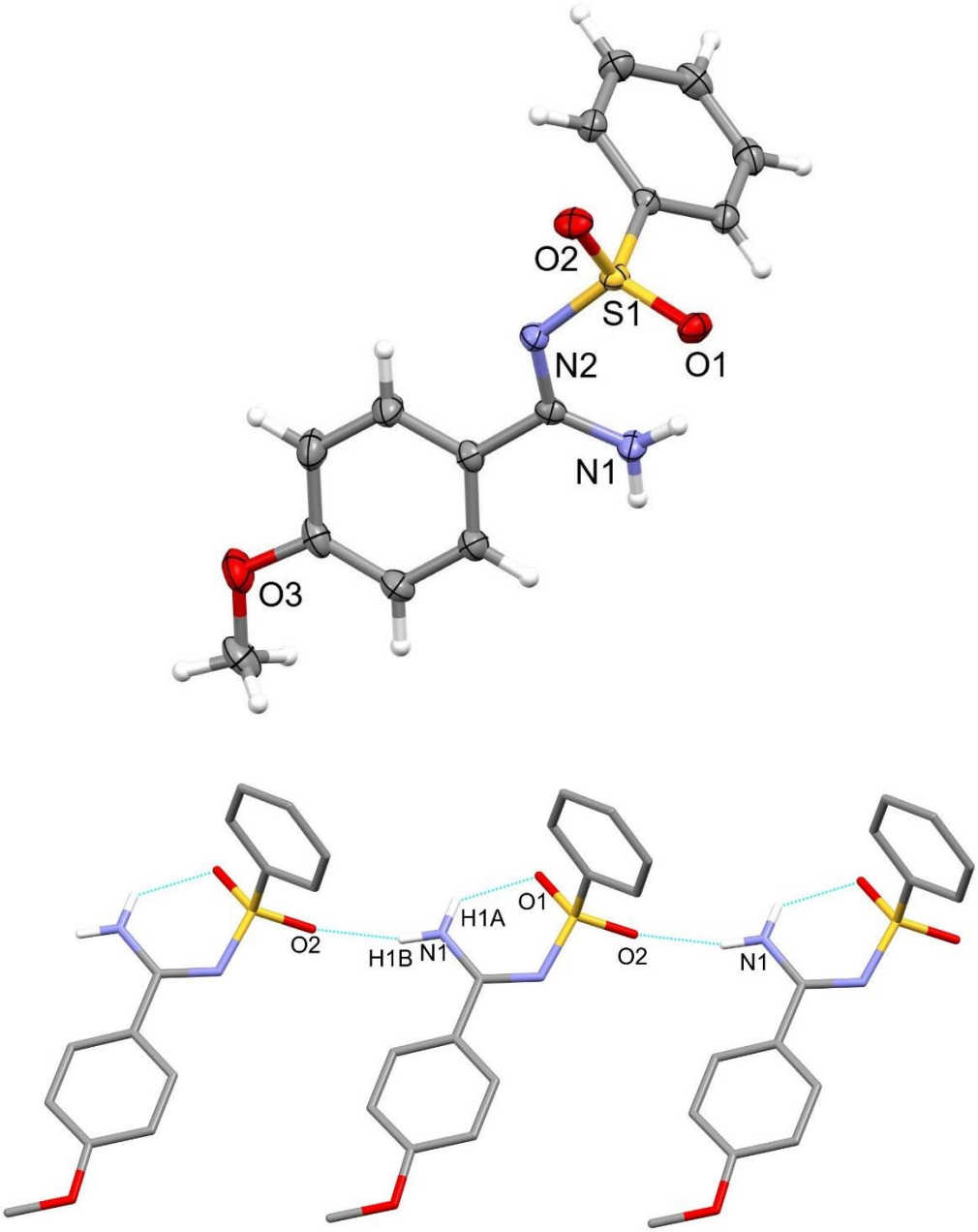


Figure S39. Top: X-Ray crystal structure of **2m**. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded chain formation in **2m**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

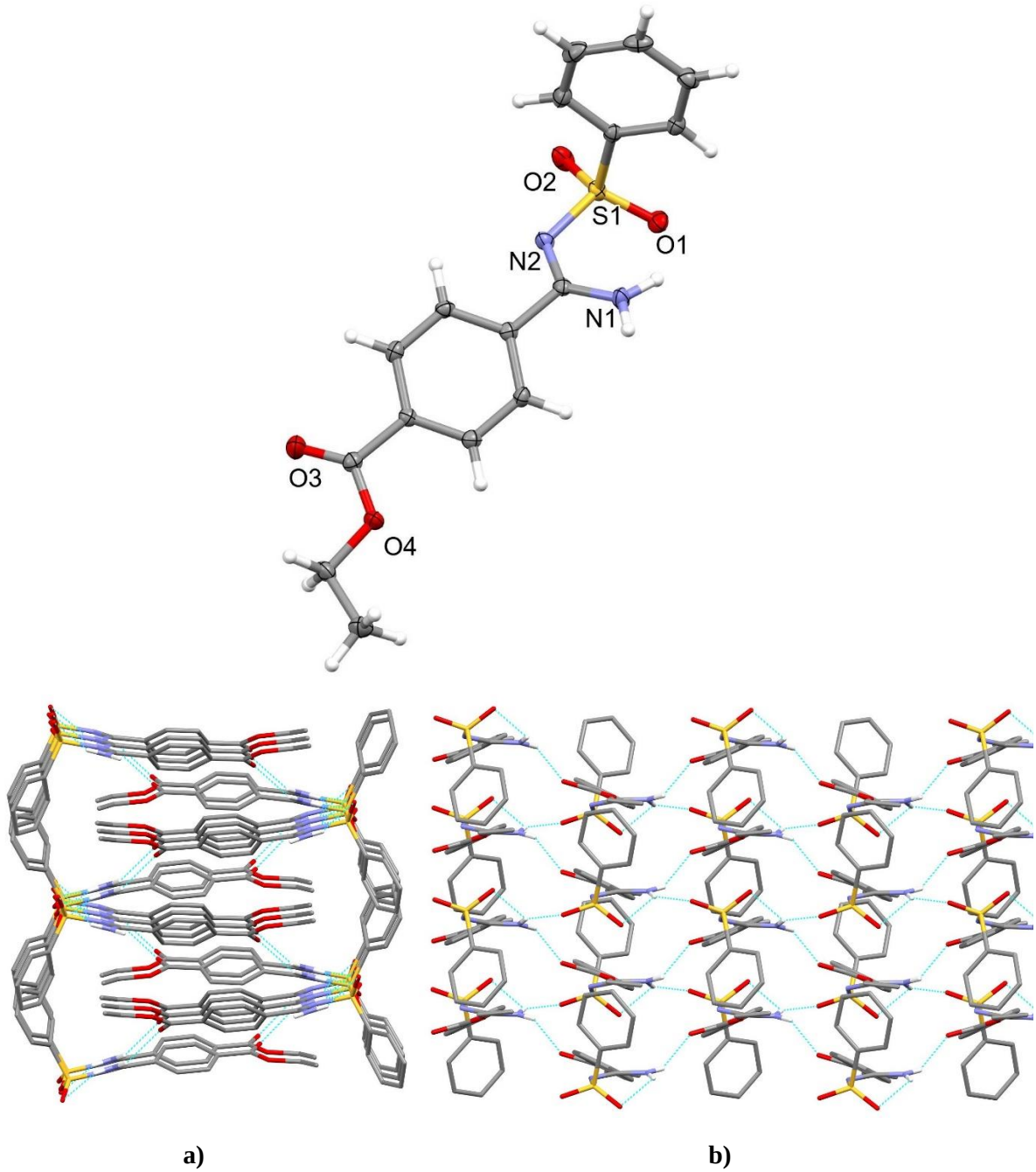


Figure S40. Top: X-Ray crystal structure of **2p**. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded layer formation in **2p**: **a)** view along a-axis, **b)** view along c-axis. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

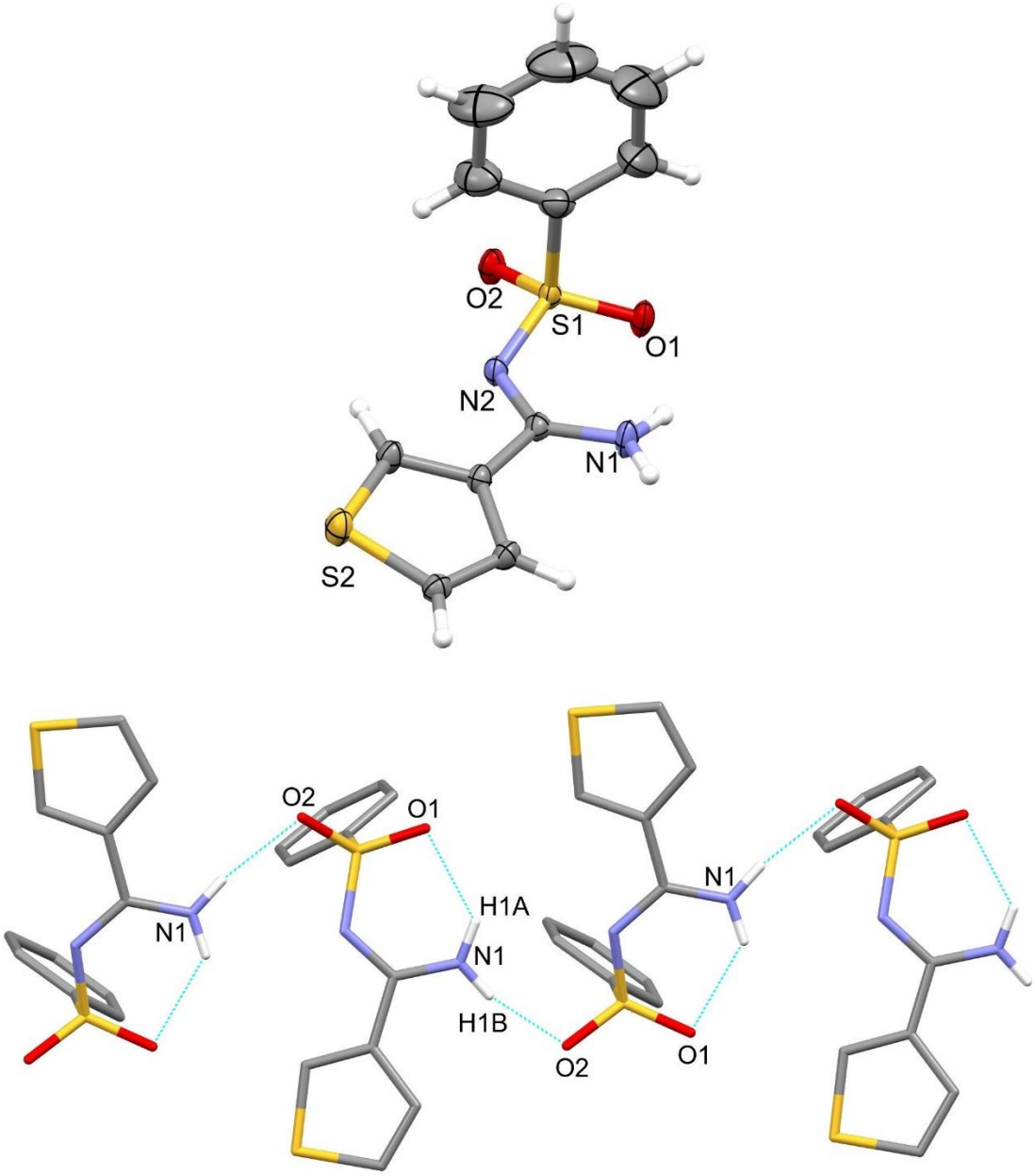


Figure S41. Top: X-Ray crystal structure of **2u**. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded chain formation in **2u**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

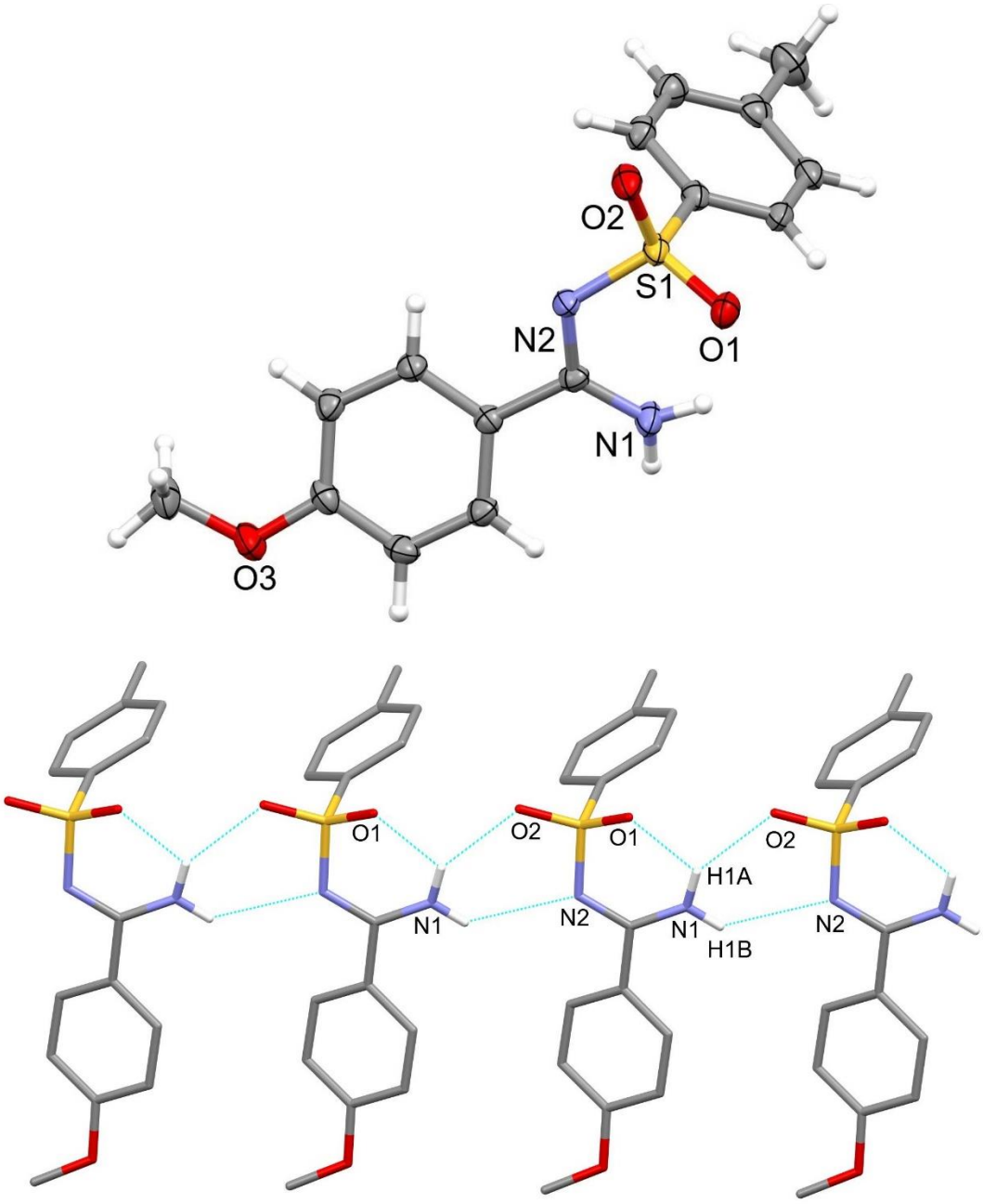


Figure S42. Top: X-Ray crystal structure of **2y**. Displacement ellipsoids are drawn at the 50% probability level. Bottom: Hydrogen-bonded chain formation in **2y**. Hydrogen bonds are represented by dashed blue lines. Hydrogen atoms not involved in the motif shown have been omitted for clarity.

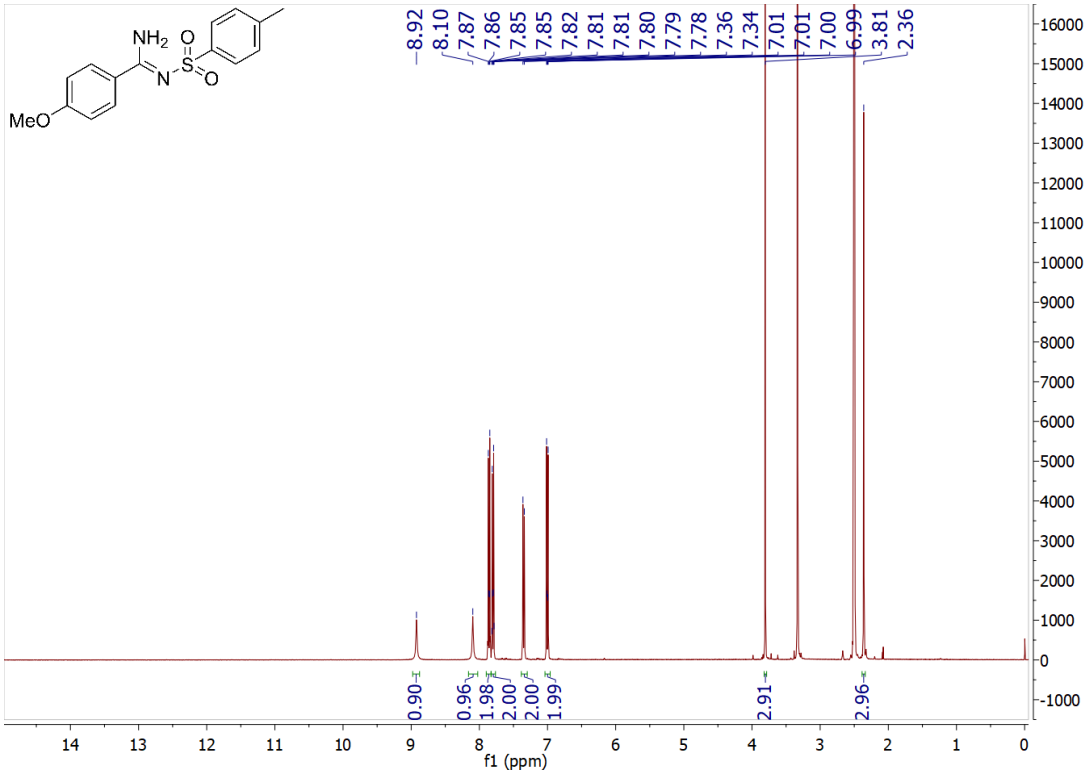


Figure S43. ^{1}H NMR of **2y** in DMSO-d_6 at 295 K.

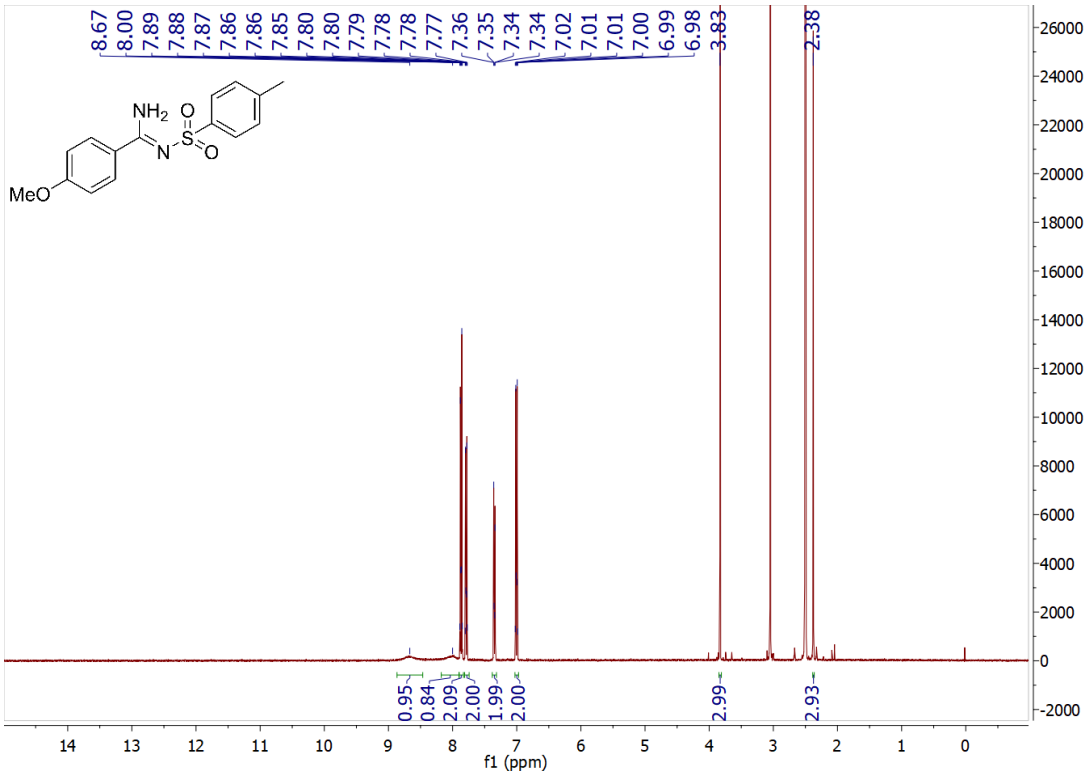


Figure S44. ^{1}H NMR of **2y** in DMSO-d_6 at 353 K.

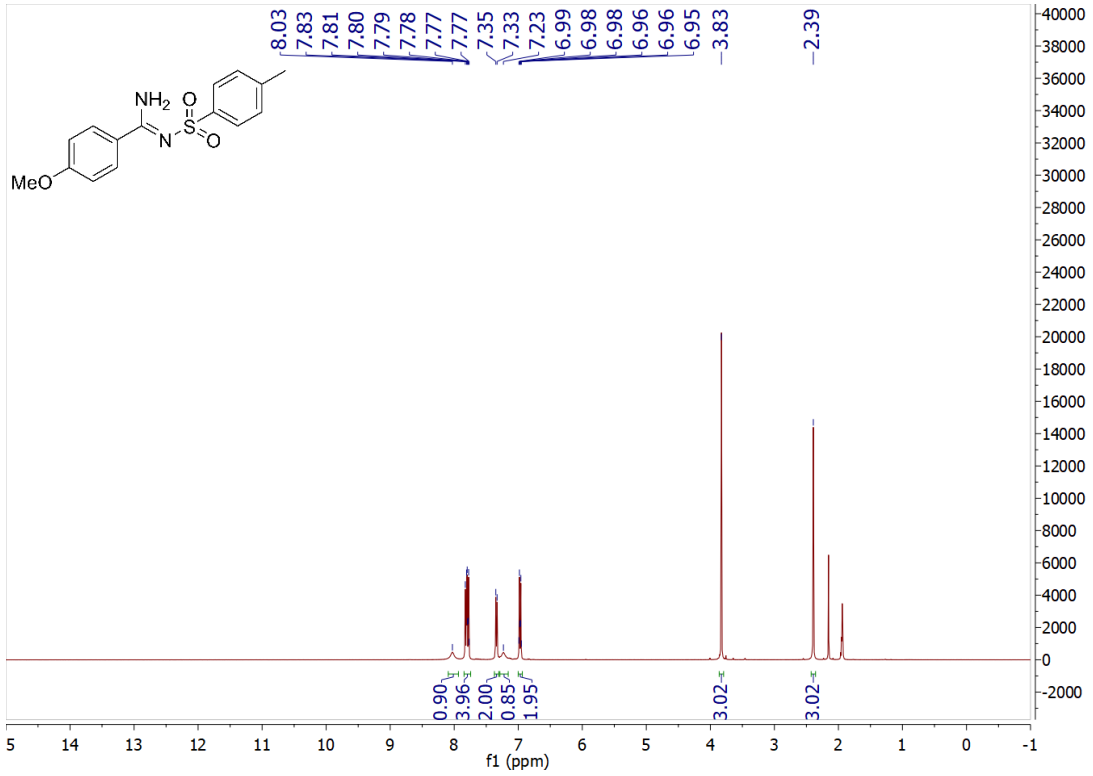


Figure S45. ^{1}H NMR of **2y** in MeCN-d_3 at 295 K.

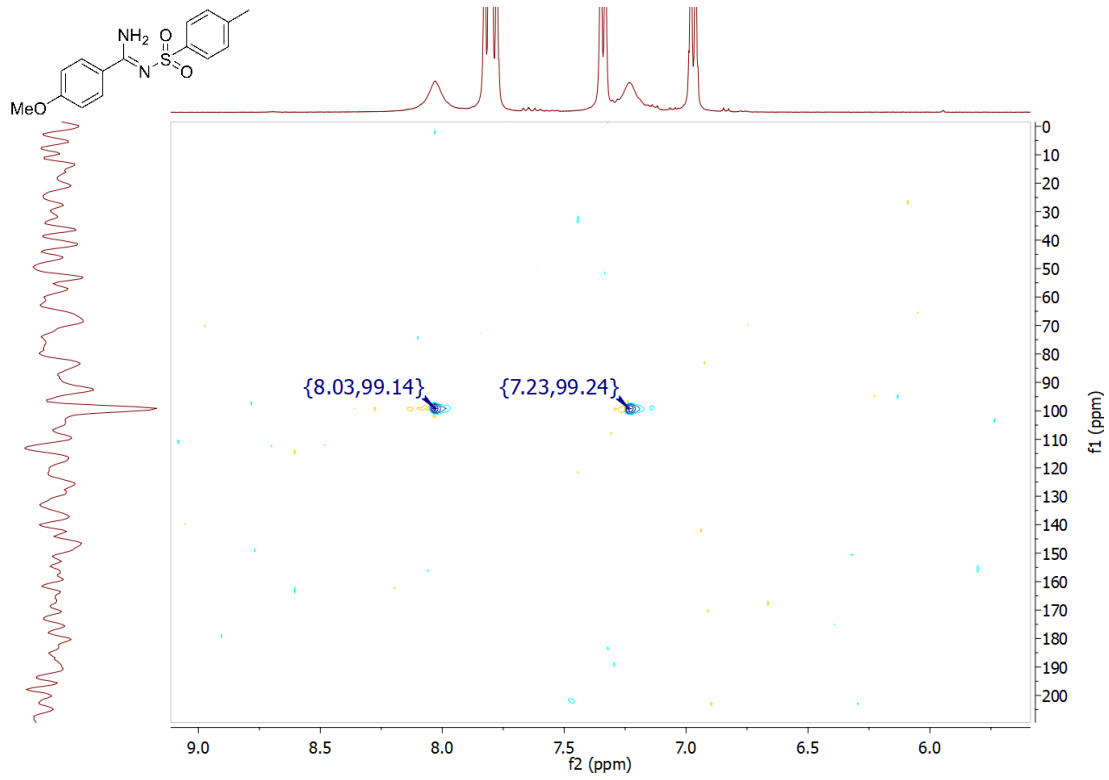


Figure S46. ^{1}H-^{15}N HSQC of **2y** in MeCN-d_3 at 295 K.

6. Removal of Benzenesulfonyl Group and Synthesis of Amidine Bearing Compounds

6.1. Removal of Benzenesulfonyl Group

Treatment of **2h** with NaOH in MeOH at reflux as reported by Bi and co-workers[S2] did not provide the corresponding amidine **3h** (Figure S47). Different methodologies previously reported in the literature for deprotection of sulfonamides were thus further explored using **2m** as the exemplary unprotected *N*-sulfonyl amidine, and the reaction progress was monitored by TLC and/or LC-MS (Figure S47, Table S5). This investigation demonstrated that only modified TfOH/phenol couple[S8] or $HClO_4$ in AcOH[S19] enabled the sulfonyl group deprotection of unprotected *N*-sulfonyl amidines **2** to amidines **3**, while other methods failed (Table S5) either due to a notable degradation of the starting material, a high extent of side reactions, or no conversion. Thus, **2k** and **2m** were treated with 5 equiv. of TfOH/2 equiv. phenol mixture in 1,2-dichloroethane at 85 °C for 24 h to provide the corresponding amidines **3k** and **3m** in 79% and 61% yield, respectively (Figure S47). The carboxylic acid derivative **4**, prepared from the ester derivative **2q** via alkaline hydrolysis (*vide infra*), was deprotected with 70% $HClO_4$ (aq) in glacial AcOH at 105 °C for 15 h to provide the corresponding amidine **5** in 51% yield.

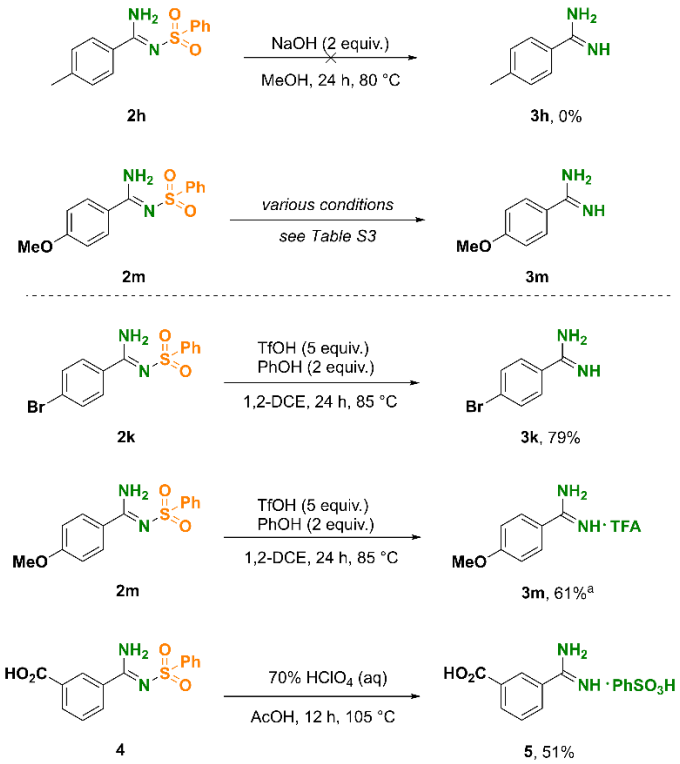
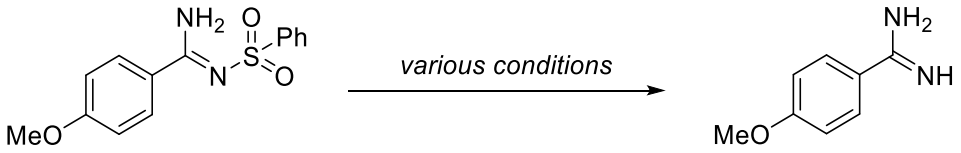


Figure S47. Desulfonation of Unprotected *N*-Sulfonyl Amidines. [a] Compound **3m** was obtained as TFA salts, due to the use of TFA in RP-CC purification (following *GP1*).

Table S5. Screening of Desulfonation Conditions.[a]



2m **3m**

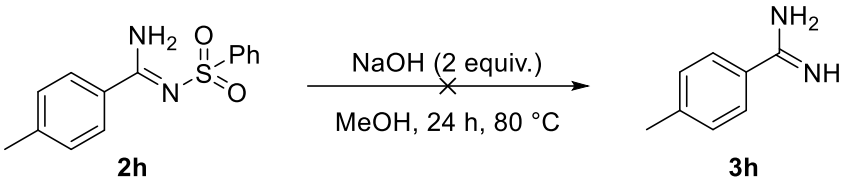
Entry	Reagents, conditions, literature reference	Reaction comment
1	**2m** (29 mg, 0.1 mmol), TFA (250 µL), CH_2Cl_2 (3 mL), 24 h, rt.	Starting **2m**
2	**2m** (29 mg, 0.1 mmol), 4 M HCl in 1,4-dioxane (250 µL), 1,4-dioxane (3 mL), 24 h, rt.	Starting **2m**
3	**2m** (29 mg, 0.1 mmol), NaOH (40 mg, 1 mmol), MeOH (3 mL), 24 h, 60 °C, under argon atmosphere.	Starting **2m**, minor side products
4	**2m** (29 mg, 0.1 mmol), NaOH (40 mg, 1 mmol), MeOH (3 mL), H_2O (2 mL), 24 h, 60 °C.	Starting **2m**, minor side products
5	**2m** (29 mg, 0.1 mmol), 6 M HCl (2 mL), 1,4-dioxane (3 mL), 24 h, 60 °C.	Starting **2m**, minor side products
6	**2m** (29 mg, 0.1 mmol), NaOH (60 mg, 1.5 mmol), MeOH (3 mL), 24 h, 80 °C, under argon atmosphere.	Starting **2m**, minor side products
7	**2m** (29 mg, 0.1 mmol), 4 M HCl in 1,4-dioxane (5 mL), 1,4-dioxane (5 mL), 24 h, 100 °C.	Decomposition of **2m**
8	**2m** (29 mg, 0.1 mmol), 13.2 M HBr (aq) (1 mL), AcOH (3 mL), 24 h, 100 °C.	Starting **2m**, minor *O*-desmethylated **2m**
9	**2m** (29 mg, 0.1 mmol), TfOH (27 µL, 0.3 mmol), 1,2-dichloroethane (2.5 mL), 24 h, 80 °C (sealed tube). Ref[S8]	Starting **2m,** benzamidine **3m**
10	**2m** (29 mg, 0.1 mmol), TfOH (54 µL, 0.6 mmol), 1,2-dichloroethane (2.5 mL), 24 h, 80 °C (sealed tube). Ref[S8]	Benzamidine **3m**, side products
11	**2m** (29 mg, 0.1 mmol), Mg (24 mg, 1.0 mmol), dry MeOH (2 mL), 20 min, rt, ultrasound, under argon atmosphere. Ref[S9]	Complete degradation of starting **2m**, traces of benzamidine **3m**
12	**2m** (29 mg, 0.1 mmol), TMSiI (43 µL, 0.3 mmol), dry MeCN (2 mL), 6 h, 80 °C, under argon atmosphere. Ref[S10]	Starting **2m**
13	**2m** (29 mg, 0.1 mmol), SmI_2 (0.1 M in THF; 10 mL, 1.0 mmol), dry THF (5 mL), H_2O (5 µL, 0.3 mmol), pyrrolidine (16 µL, 0.2 mmol), 1 h, rt, under argon atmosphere. Ref[S11]	Starting **2m**
14	**2m** (58 mg, 0.2 mmol), SmI_2 (0.1 M in THF; 6 mL, 0.3 mmol), dry THF (5 mL), 1 h, 0 °C, then 1 h, rt, under argon atmosphere. Ref[S12]	Starting **2m**
15	**2m** (29 mg, 0.1 mmol), SmI_2 (0.1 M in THF; 6 mL, 0.6 mmol), dry DMA (0.5 mL), 1 h, 0 °C, then 1 h, rt, under argon atmosphere. Ref[S11]	Starting **2m**
16	**2m** (58 mg, 0.2 mmol), Ti(O-*i*-Pr)$_4$ (59 µL, 0.2 mmol), TMSCl (38 µL, 0.3 mmol), Mg (24 mg, 1.0 mmol), dry THF (2 mL), 24 h, 50 °C, under argon atmosphere. Ref[S13]	Starting **2m**

17	**2m** (58 mg, 0.2 mmol), pyridine-70% HF (2.5 mL), anisole (43 µL, 0.4 mmol), 72 h, rt, under argon atmosphere. Ref[S14]	Starting **2m**
18	**2m** (58 mg, 0.2 mmol), TBAF (1 M in THF; 400 µL, 0.4 mmol), dry THF (2 mL), 24 h, 65 °C, under argon atmosphere. Ref[S15]	Starting **2m**
19	**2m** (58 mg, 0.2 mmol), Hantzsch ester (51 mg, 0.2 mmol), KO*t*Bu (49 mg, 0.44 mmol), dry DMSO (2 mL), 24 h, rt, irradiation under Hg lamp, under argon atmosphere. Ref[S16]	Starting **2m**
20	**2m** (58 mg, 0.2 mmol), Vitride-Red-Al (>60% in toluene; 260 µL, 0.8 mmol), dry toluene (2 mL), 24 h, 110 °C, under argon atmosphere. Ref[S17]	Complete degradation of starting **2m**, traces of benzamidine **3m**
21	**2m** (58 mg, 0.2 mmol), Bu_3SnH (121 µL, 0.45 mmol), AIBN (33 mg, 0.2 mmol), dry toluene (5 mL), 24 h, 110 °C, under argon atmosphere. Ref[S12]	Starting **2m**
22	$TiCl_4$ (66 µL, 0.6 mmol), Zn (262 mg, 4.0 mmol), dry THF (5 mL), 2 h, 65 °C, then **2m** (58 mg, 0.2 mmol), 24 h, 65 °C, under argon atmosphere. Ref[S12]	Starting **2m**
23	Na (23 mg, 1.0 mmol), naphthalene (66 µL, 0.6 mmol), dry DME (5 mL), 1 h, rt, then **2m** (58 mg, 0.2 mmol), 1 h, rt, under argon atmosphere, quench with 1 M HCl (aq).	Starting **2m**, traces of benzamidine **3m**
24	Na (23 mg, 1.0 mmol), naphthalene (66 µL, 0.6 mmol), dry THF (5 mL), 1 h, rt, then **2m** (58 mg, 0.2 mmol), 12 h, rt, under argon atmosphere, quench with 1 M HCl (aq).	Complete degradation of starting **2m**
25	**2m** (58 mg, 0.2 mmol), $LiAlH_4$ (2.4 M in THF; 167 µL, 0.4 mmol), dry THF (3 mL), 24 h, 60 °C, under argon atmosphere. Ref[S17]	Full consumption of starting **2m**, traces of benzamidine **3m**
26	**2m** (58 mg, 0.2 mmol), $Bu_4N{\times}HSO_4$ (170 mg), MeCN (5 mL), 1 h, rt, $2e^-$ (graphite/Ni electrode), Ep,e = 2.5 V, n = 5 F/mol. Ref[S18]	Starting **2m**
27	**2m** (58 mg, 0.2 mmol), $Bu_4N{\times}HSO_4$ (170 mg), MeCN (5 mL), H_2O (250 µL) 1 h, rt, $2e^-$ (graphite/Ni electrode), Ep,e = 2.5 V, n = 5 F/mol. Ref[S18]	Starting **2m**
28	**2m** (58 mg, 0.2 mmol), 70% $HClO_4$ (aq) (3.5 mL), AcOH (1.5 mL), 12 h, rt. Ref[S19]	Starting **2m**, traces of benzamidine **3m**
29	**2m** (58 mg, 0.2 mmol), 70% $HClO_4$ (aq) (3.5 mL), AcOH (1.5 mL), 4 h, 105 °C. Ref[S19]	Full consumption of starting **2m**, benzamidine **3m**, side products
30	**2m** (58 mg, 0.2 mmol), 70% $HClO_4$ (aq) (3.5 mL), 4 h, 80 °C.	Full consumption of starting **2m**, benzamidine **3m**, side products
31	**2m** (58 mg, 0.2 mmol), TfOH (88 µL, 1.0 mmol), 1,2-metcaptoethanol (87 µL, 1.0 mmol), 1,2-dichloroethane (5 mL), 24 h, 85 °C (sealed tube).	Starting **2m**, traces of benzamidine **3m**
32	**2m** (58 mg, 0.2 mmol), TfOH (176 µL, 2.0 mmol), 1,2-metcaptoethanol (87 µL, 1.0 mmol), 1,2-dichloroethane (5 mL), 24 h, 85 °C (sealed tube).	Starting **2m**, traces of benzamidine **3m**
33	**2m** (58 mg, 0.2 mmol), TfOH (88 µL, 1.0 mmol), phenol (38 mg, 0.4 mmol), 1,2-dichloroethane (10 mL), 24 h, 85 °C (sealed tube).	Full consumption of starting **2m**, benzamidine **3m**

[a] Reactions were performed using **2m** (29 mg, 0.1 mmol or 58 mg, 0.2 mmol) under the conditions reported in Table S5. The reaction progress was monitored by TLC and/or LC-MS.

Deprotection Experiments

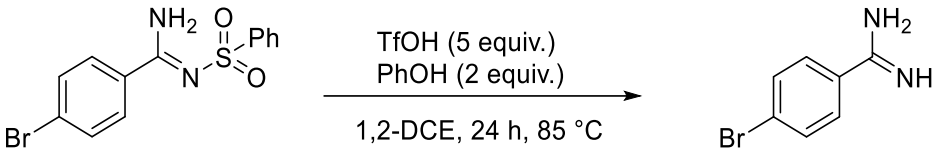
4-Methylbenzimidamide (3h)



2h **3h**

Synthesized following the procedure reported by Bi et al.[S2] To a 25 mL sealed tube **2h** (55 mg, 0.2 mmol), MeOH (2 mL), and NaOH (16 mg, 0.4 mmol) were added, and the mixture was stirred at 80 °C for 24 h. The LC-MS and TLC analyses showed the presence of the starting material and smaller quantity of side products.

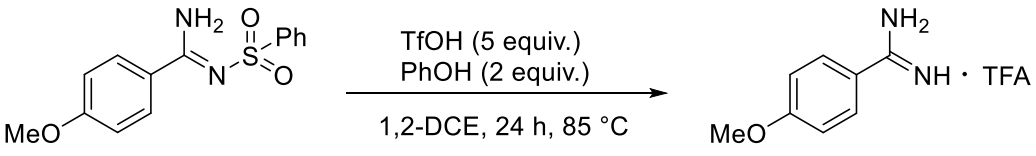
4-Bromobenzimidamide (3k)



2k **3k**, 79%

To a 25 mL sealed tube, **2k** (136 mg, 0.4 mmol), 1,2-dichloroethane (10 mL), TfOH (177 µL, 2.0 mmol) and phenol (75 mg, 0.8 mmol) were added, and the mixture was stirred at 85 °C for 24 h. The solvent was evaporated under reduced pressure, and oily residue was taken up in EtOAc (50 mL), washed with 1 M NaOH (aq) (2 × 25 mL), and saturated brine (2 × 10 mL), the organic dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford crude **3k**, which was purified by RP-CC (*GP1*) to afford the title compound as white solid (63 mg, 79% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.54 (br s, 2H, N$\underline{H_2}$), 7.55 – 7.64 (m, 2H, Ar-$\underline{H}$), 7.69 – 7.75 (m, 2H, Ar-$\underline{H}$). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 123.32, 128.77, 130.95, 135.32, 161.47. **HRMS** (ESI$^+$): calc. for $C_7H_8N_2Br$ $[M+H]^+$: 198.98654, found: 198.98632.

4-Methoxybenzimidamidinium trifluoroacetate (3m)



2m **3m**, 61%

To a 25 mL sealed tube, **2m** (200 mg, 0.69 mmol), 1,2-dichloroethane (10 mL), TfOH (310 µL, 3.5 mmol) and phenol (130 mg, 1.38 mmol) were added, and the mixture was stirred at 85 °C for 24 h. The solvent

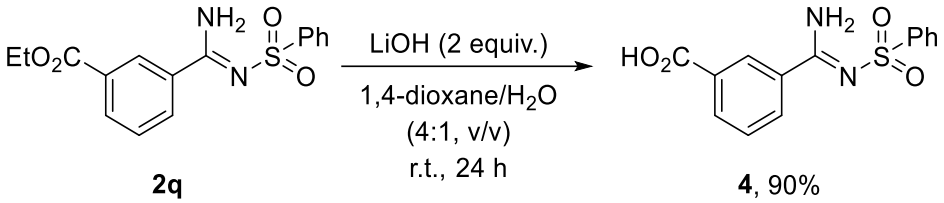
was evaporated under reduced pressure, and oily residue was taken up in EtOAc (50 mL), washed with 1 M NaOH (aq) (2 × 25 mL), and saturated brine (2 × 10 mL), the organic dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford crude **3m**, which was purified by RP-CC (*GP1*, without final neutralization and extraction) to afford the title compound as off-white semi-solid (111 mg, 61% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 3.86 (s, 3H, OC$\underline{H}_3$), 7.13 – 7.19 (m, 2H, Ar-$\underline{H}$), 7.80 – 7.86 (m, 2H, Ar-$\underline{H}$), 9.10 (br s, 4H, N$\underline{H}_3$ + N$\underline{H}$). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 55.78, 114.38, 117.20 (q, J = 286.0 Hz), 119.65, 130.16, 158.45 (q, J = 32.3 Hz), 163.60, 164.74. **^{19}F NMR** (376 MHz, DMSO-d_6) δ –73.65. **HRMS** (ESI$^+$): calc. for $C_8H_{11}ON_2$ $[M+H]^+$: 151.08659, found: 151.08647.

6.2. Synthesis of Bioactive, Amidine Group Containing Compounds

Furthermore, to demonstrate the utility of our methodology, we conducted the synthesis of factor Xa inhibitor derivative **7** and furamidine **10**,[S20] a trypanocide agent[S21] (Scheme 3). We started the synthesis of factor Xa inhibitor derivative **7** (Scheme 3B) with the hydrolysis of the ester **2q**. Ester moiety in **2q** was hydrolyzed using 2 equiv. of LiOH in 1,4-dioxane/H_2O mixture (v/v, 4/1) at room temperature for 24 h, which provided carboxylic acid derivative **4** in 90% yield. Subsequently, the sulfonyl protecting group was removed with 70% $HClO_4$ (aq) in AcOH at 105 °C in 12 h, to furnish the amidine derivative **5** in 47% yield. In the last step, the acid **5** was coupled with (*R*)-2-amino-1-(4-benzylpiperidin-1-yl)-2-phenylethan-1-one (**6**) in the presence of 1-hydroxybenzotriazole (HOBt) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) in DMF at room temperature to afford the factor Xa inhibitor derivative **7** in 48% yield and 95% purity (Scheme 3B). The synthesis of furamidine **10** began with the Suzuki-Miyaura coupling of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)furan (**8**) with sulfonyl amidine **2p** in the presence of $Pd(PPh_3)_4$ catalyst (5 mol%) in DMF at 100 °C for 24 h (Scheme 3C). The desired *N*-sulfonyl protected furamidine **9** was obtained in 48% yield. Subsequent deprotection of sulfonyl protecting groups in **9** with 10 equiv. of TfOH/10 equiv. phenol mixture in 1,2-dichloroethane at 85 °C for 24 h afforded the desired furamidine **10** in 52% yield (Scheme 3C). Therefore, C(sp^2)-N bond-forming reaction using pTIMs and NFSI allowed us to obtain both factor Xa inhibitor derivative **7** and furamidine **10** in only four and three steps, respectively, from readily accessible pTIMs as starting materials, demonstrating the convenience and simplicity of this methodology.

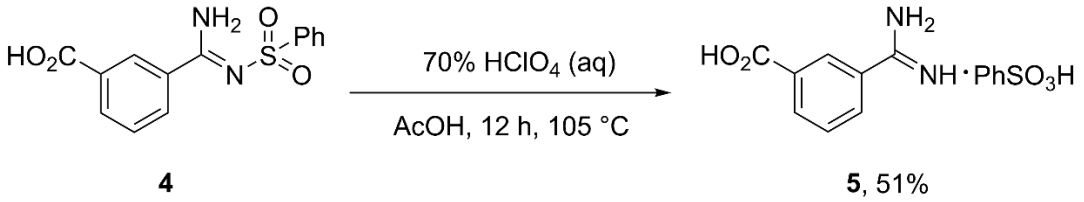
Synthesis of Factor Xa Inhibitor

(*Z*)-3-(*N*'-(Phenylsulfonyl)carbamimidoyl)benzoic acid (4)



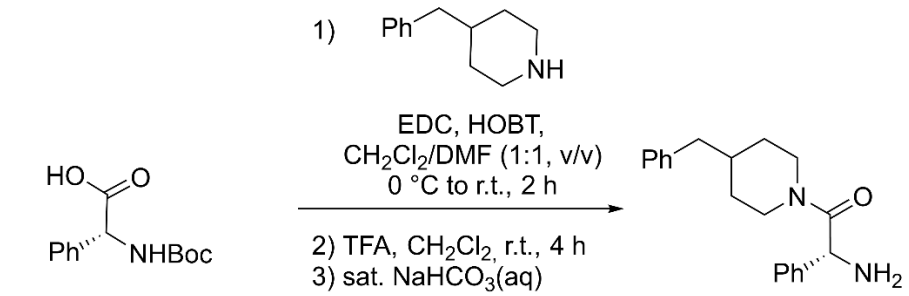
To a solution of **2q** (810 mg, 2.44 mmol) in 1,4-dioxane/H_2O (20 mL + 5 mL), LiOH (117 mg, 4.88 mmol) was added, and the mixture was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure and the resultant slurry was dissolved in H_2O (30 mL), acidified with 6 M HCl (aq) to pH = 1, extracted with EtOAc (3 × 40 mL). The combined organic phases were washed with saturated brine (50 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford the title compound as white solid (670 mg, 90% yield). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.55 – 7.67 (m, 4H, Ar-H), 8.01 (d, *J* = 1.6 Hz, 1H, Ar-H), 8.03 (q, *J* = 2.1, 1.7 Hz, 1H, Ar-H), 8.19 (ddd, *J* = 7.9, 1.9, 1.2 Hz, 1H, Ar-H), 8.22 (dt, *J* = 7.7, 1.4 Hz, 1H, Ar-H), 8.48 (br s, 1H, NH_2), 8.48 (br s, 1H, NH_2), 8.56 (t, *J* = 1.8 Hz, 1H, Ar-H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 127.16, 129.65, 129.70, 129.88, 131.94, 132.94, 133.03, 134.14, 135.09, 143.98, 163.12, 166.72. **HRMS** (ESI^-): calc. for $C_8H_9O_2N_2$ $[M–H]^-$: 303.04450, found: 303.04465.

3-Carbamimidoylbenzoic acid, benzesulfonate salt (5)



To a solution of **4** (350 mg, 1.15 mmol) in AcOH (5 mL), 70% $HClO_4$ (aq) (10 mL) was added, and the mixture was stirred at 105 °C for 12 h. The solvent was evaporated under reduced pressure and the residue purified by RP-CC (*GP1*, without final neutralization and extraction) to afford the title compound as pink solid (189 mg, 51% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.28 – 7.38 (m, 3H, Ar-H), 7.60 (dd, *J* = 7.4, 2.3 Hz, 2H, Ar-H), 7.76 (t, *J* = 7.8 Hz, 1H, Ar-H), 8.03 (ddd, *J* = 7.8, 1.9, 1.2 Hz, 1H, Ar-H), 8.26 (dt, *J* = 7.8, 1.3 Hz, 1H, Ar-H), 8.34 (t, *J* = 1.6 Hz, 1H, Ar-H), 9.03 (br s, 2H, NH_2), 9.45 (br s, 2H, NH_2), 13.50 (s, 1H, COOH). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 125.46, 127.69, 128.51, 128.78, 128.97, 129.53, 131.50, 132.40, 134.09, 148.11, 165.08, 166.22. **HRMS** (ESI^+): calc. for $C_8H_9O_2N_2$ $[M+H]^+$: 165.06585, found: 165.06585.

(*R*)-2-Amino-1-(4-benzylpiperidin-1-yl)-2-phenylethan-1-one (6)[S20]

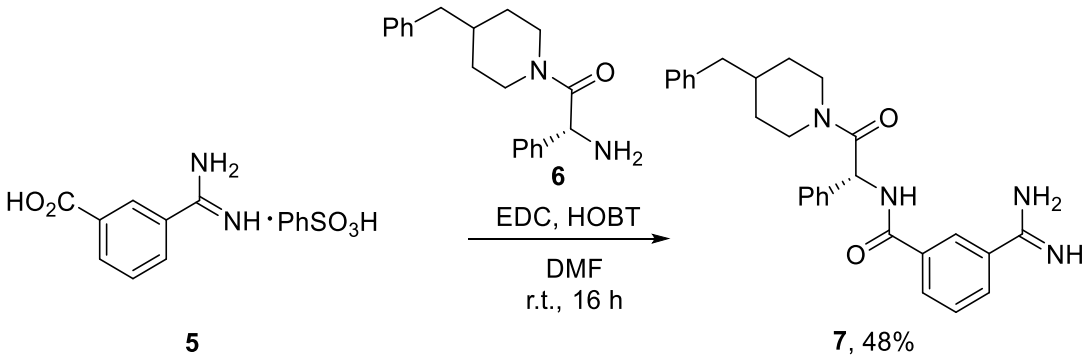


Boc-D-phenylglycine **6**, 90%

To a cooled solution (0 °C) of Boc-D-phenylglycine (754 mg, 3.0 mmol) in CH_2Cl_2/DMF (10 mL + 10 mL), EDC×HCl (631 mg, 3.3 mmol), HOBT (496 mg, 3.3 mmol) and 4-benzylpiperidine (585 µL, 3.3 mmol) were added consecutively and the mixture was stirred at room temperature for 2 h. Volatiles were then removed under reduced pressure and the resulting oil extracted with Et_2O (3 × 20 mL). Combined ethereal phases were washed with 1 M NaOH (aq) (2 × 20 mL), 1 M HCl (aq) (2 × 20 mL) and saturated brine (40 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford crude intermediate **6a** – *tert*-butyl (*R*)-(2-(4-benzylpiperidin-1-yl)-2-oxo-1-phenylethyl)carbamate (1.161 g, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.08 – 0.22 (m, 0.5H), 0.86 – 1.01 (m, 0.5H), 1.11 – 1.30 (m, 1H), 1.39 and 1.41 (2 × s, 9H), 1.50 – 1.74 (m, 2H), 2.24 – 2.39 (m, 1H), 2.46 – 2.61 (m, 2.5H), 2.84 – 2.93 (m, 0.5H), 3.69 – 3.83 (m, 1H), 4.60 (t, *J* = 15.1 Hz, 1H), 5.56 (dd, *J* = 12.5, 7.7 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.0 Hz, 1H), 7.05 – 7.41 (m, 9H), set of two conformers. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 28.38, 31.08, 31.41, 31.58, 32.15, 37.89, 38.02, 42.63, 42.71, 45.51, 45.69, 54.98, 55.19, 79.52, 126.00, 126.06, 127.55, 127.71, 127.98, 128.08, 128.23, 128.29, 128.91, 128.95, 128.99, 129.02, 129.07, 138.42, 138.58, 139.67, 139.75, 155.03, 167.89, 168.13, set of two conformers. **HRMS** (ESI^+): calc. for $C_{25}H_{33}O_3N_2$ $[M+H]^+$: 409.24857, found: 409.24807. Removal of the Boc protecting group was carried out using TFA (5 mL) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 4 h, then the volatiles were evaporated under reduced pressure. The resultant oil was dissolved in EtOAc (50 mL), washed with saturated $NaHCO_3$ (aq) (2 × 50 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford the title compound as orange semi-solid (786 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.15 (qd, *J* = 12.5, 4.2 Hz, 0.5H), 0.93 (qd, *J* = 12.9, 4.5 Hz, 0.5H), 1.11 – 1.34 (m, 1H), 1.44 – 1.74 (m, 2.5H), 2.32 (d, *J* = 6.4 Hz, 1H), 2.39 – 2.55 (m, 2H), 2.85 (t, *J* = 13.0 Hz, 0.5H), 3.52 – 3.82 (m, 4H), 4.55 (d, *J* = 13.3 Hz, 1H), 4.96 (s, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.12 – 7.39 (m, 8H). set of two conformers. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 31.22, 31.51, 31.67, 32.16, 37.96, 38.14, 42.78, 42.83, 42.91, 42.99, 45.46, 45.57, 56.38, 126.09, 126.14, 127.51, 127.71, 128.33, 128.37, 128.52, 129.06, 129.13,

129.27, 129.35, 138.93, 139.13, 139.82, 139.96, 169.36, 169.77, set of two conformers. **HRMS** (ESI$^+$): calc. for $C_{20}H_{25}ON_2$ $[M+H]^+$: 309.19614, found: 309.19556.

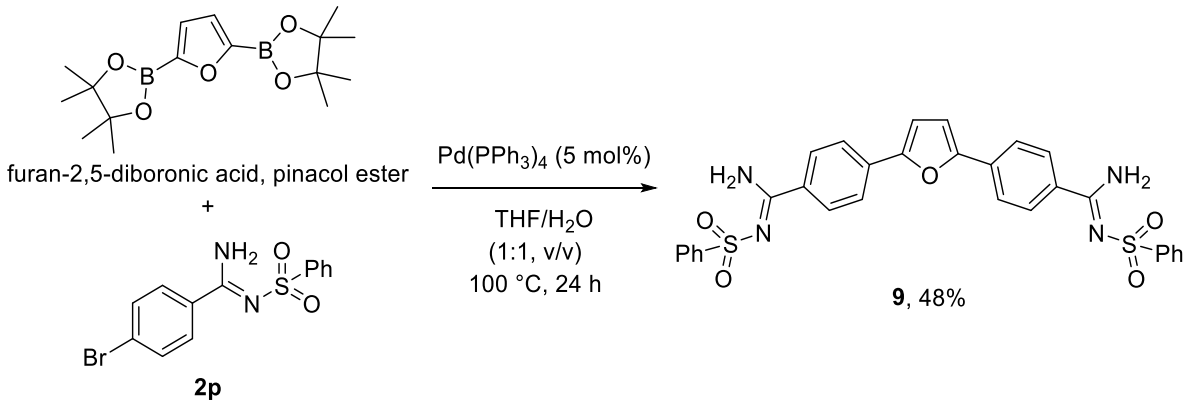
(*R*)-*N*-(2-(4-Benzylpiperidin-1-yl)-2-oxo-1-phenylethyl)-3-carbamimidoylbenzamide (7)[S20]



To a solution of **5** (150 mg, 0.47 mmol) in DMF (5 mL), EDC×HCl (90 mg, 0.47 mmol), HOBT (71 mg, 1.1 mmol) and **6**[S20] (145 mg, 0.47 mmol) were added consecutively, and the mixture was stirred at room temperature for 16 h, then H_2O (50 mL) was added and the product extracted with EtOAc (3 × 40 mL). Combined organic phases were washed with 1 M NaOH (aq) (40 mL) and saturated brine (40 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford crude **7**, which was purified by RP-CC (*GP1*) to afford the title compound as white solid (102 mg, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.18 (qd, *J* = 12.6, 4.1 Hz, 0.5H), 0.97 (qd, *J* = 12.8, 4.3 Hz, 0.5H), 1.12 – 1.37 (m, 1.5H), 1.55 – 1.80 (m, 2.5H), 2.34 (dd, *J* = 7.0, 2.7 Hz, 1H), 2.47 – 2.70 (m, 2.5H), 2.93 (td, *J* = 13.0, 2.7 Hz, 0.5H), 3.75 – 3.92 (m, 1H), 4.49 – 4.68 (m, 1H), 5.74 (br s, 2H), 5.99 and 6.06 (2 × s, 1H), 6.98 – 7.05 (m, 1H), 7.06 – 7.13 (m, 1H), 7.14 – 7.21 (m, 1H), 7.21 – 7.27 (m, 2H), 7.27 – 7.49 (m, 6H), 7.67 (t, *J* = 6.8 Hz, 1H), 7.77 – 7.89 (m, 1H), 8.03 (d, *J* = 10.2 Hz, 1H), set of two conformers. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 31.13, 31.45, 31.67, 32.23, 37.89, 38.09, 42.72, 42.77, 42.91, 42.95, 45.70, 45.87, 54.46, 54.67, 125.19, 126.12, 126.17, 127.99, 128.02, 128.16, 128.19, 128.34, 128.40, 128.44, 128.94, 129.04, 129.07, 129.12, 129.32, 129.35, 134.47, 134.50, 136.15, 136.22, 137.46, 137.65, 139.70, 139.80, 165.01, 165.47, 165.52, 167.77, 167.98, set of two conformers. **HRMS** (ESI$^+$): calc. for $C_{28}H_{31}O_2N_4$ $[M+H]^+$: 455.24415, found: 455.24373. **HPLC purity**: 95.9% (t_R= 4.693 min, 220 nm).

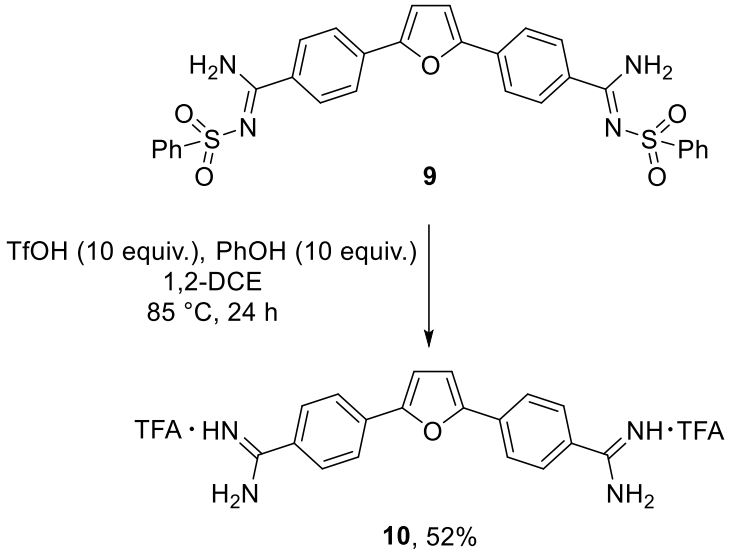
Synthesis of Furamidine

(1*Z*,1'*Z*)-1,1'-(Furan-2,5-diylbis(4,1-phenylene))bis(*N*'-(phenylsulfonyl)formimidamide) (9)



To a degassed solution of furan-2,5-diboronic acid, pinacol ester (72 mg, 0.23 mmol), **2p** (190 mg, 0.58 mmol) and K_2CO_3 (95 mg, 0.69 mmol) in THF/H_2O (5 mL + 5 mL) in sealed tube, $Pd(PPh_3)_4$ (13 mg, 5 mol%) was added and the mixture was stirred at 100 °C for 24 h. The volatiles were then evaporated under the reduced pressure and the residue extraced with EtOAc (2 × 20 mL) and H_2O (30 mL). Combined organic phases were washed with saturated brine (40 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford crude **7**, which was purified by flash column chromatography (SiO_2; 1) EtOAc/*n*-hex = 1/1, 2) EtOAc/*n*-hex = 4/1) to afford the title compound as yellow solid (79 mg, 48% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.33 (s, 2H), 7.56 – 7.65 (m, 6H), 7.91 – 7.99 (m, 12H), 8.30 (br s, 2H), 9.15 (br s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 110.97, 123.44, 126.08, 128.72, 128.98, 131.84, 132.23, 133.20, 142.48, 152.54, 161.87. **HRMS** (ESI^+): calc. for $C_{30}H_{25}O_5N_4S_2$ $[M+H]^+$: 585.12609, found: 585.12561.

4,4'-(Furan-2,5-diyl)dibenzimidamide, bistrifluoroacetate salt (10)



To a 25 mL sealed tube, **9** (103 mg, 0.18 mmol), 1,2-dichloroethane (5 mL), TfOH (156 µL, 1.76 mmol) and phenol (166 mg, 1.76 mmol) were added, and the mixture was stirred at 85 °C for 24 h. The solvent was evaporated under reduced pressure, and oily residue was taken up in EtOAc (50 mL), washed with 1 M NaOH (aq) (2 × 25 mL), and saturated brine (2 × 10 mL), the organic dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford crude **3m**, which was purified by RP-CC (*GP1*, without final neutralization and extraction) to afford the title compound as off-white semi-solid (49 mg, 52% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.47 (s, 2H), 7.93 (d, *J* = 8.5 Hz, 4H), 8.12 (d, *J* = 8.5 Hz, 4H), 9.18 (s, 4H), 9.36 (s, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) 111.76, 123.86, 126.72, 128.96, 134.25, 152.44, 164.82. **^{19}F NMR** (376 MHz, DMSO-d_6) δ –73.62. **HRMS** (ESI$^+$): calc. for $C_{18}H_{17}ON_4$ $[M+H]^+$: 305.13969, found: 305.13915.

7. NMR, EPR and LC-HRMS Study of the Reaction Mechanism

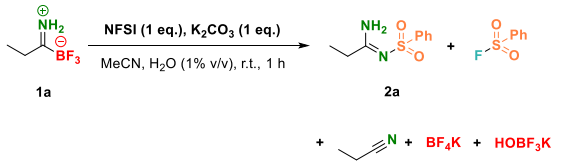
To better understand the reaction, we monitored the conversion of **1a** to **2a** and **1m** to **2m** (Figure S48A and S48B) by ^{1}H-, ^{11}B- and ^{19}F-NMR in order to identify key species formed in the reaction mixture (Figures S49–S76). Enclosed are the spectra of pure starting materials recorded in MeCN-d_3 (Figures S49–S56). Spectra for compounds considered as possible reaction side products were also recorded in MeCN-d_3 or in MeCN-d_3/D_2O mixture to ensure sufficient solubility of inorganic salts (Figures S57–S69). KBF_3OH was synthesized according to a literature procedure.[S22]

When monitoring the conversion of **1a** to **2a**, ^{1}H NMR spectrum in the spectral window of 0.7 to 3.3 ppm (Figure S71) at the end of reaction (60 min) in MeCN-d_3 showed the formation of two products: desired **2a** (t, δ_H 1.05 ppm, J = 7.7 Hz and q, δ_H 2.25 ppm, J = 7.5 Hz) as a predominant product, and propionitrile (t, δ_H 1.19 ppm, J = 7.5 Hz and q, δ_H 1.36 ppm, J = 7.6 Hz) as a minor side product, which was identified by comparison with an authentic reference compound (Figure S68). Interestingly, during our work, we have observed that the extent of side reaction leading to nitrile side products is higher when crude pTIMs[S1] were used compared to the pTIMs that were additionally purified via filtration over silica gel, where the presence of nitrile side product was marginal. In addition, monitoring of the reaction progress with ^{19}F NMR (Figures S73–S75) revealed that benzenesulfonyl fluoride ($PhSO_2F$; s, δ_F –64.5 ppm), potassium tetrafluoroborate (KBF_4; s, δ_F –151.9 ppm) and potassium hydroxytrifluoroborate (KBF_3OH; dd, δ_F, –144.0 ppm, J = 83.0, 41.3 Hz) were formed during the reaction (identified by comparison with authentic reference compounds for $PhSO_2F$ (Figure S60) and KBF_4 (Figure S64) and an authentic sample of KBF_3OH (Figure S67) synthesized according to the literature procedure.[S22] Moreover, the formation of KBF_4 and KBF_3OH species was also confirmed in ^{11}B NMR by using the above-mentioned reference compounds (Figures S63 and S66). Indeed, ^{11}B NMR spectrum at the end of reaction (60 min) in MeCN-d_3 showed beside major KBF_3OH (q, δ_B 0.32 ppm, J = 14.7 Hz) two minor boron containing species: KBF_4 (s, δ_B –1.30 ppm) and unidentified boron-containing species (q, δ_B –3.72 ppm, J = 26.5 Hz) (Figure S72). We have also monitored the reaction progress with ^{1}H NMR using substrate **1m** (Figure S48B, Figure S76). Similarly, formation of benzenesulfonyl fluoride and 4-methoxybenzonitrile in this reaction was easily confirmed by comparison with authentic reference compounds (Figures S59 and S69).

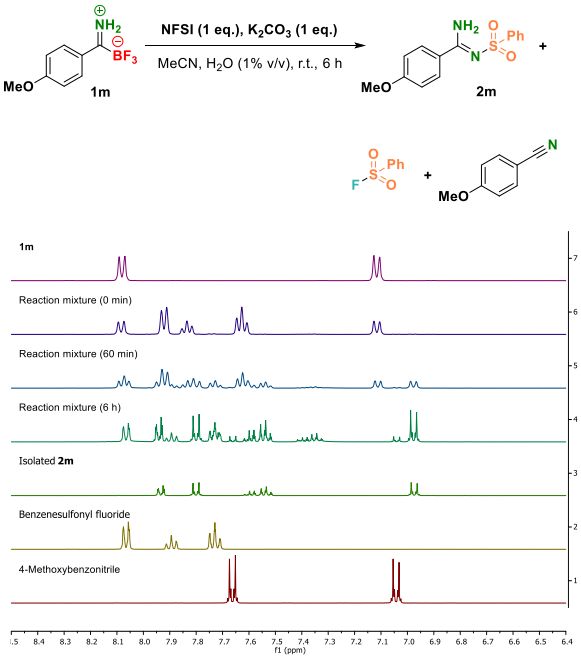
When **1m** was subjected to standard reaction conditions described in Figure S48C and protected from direct sun light using deuterated solvents to facilitate the reaction progress monitoring by ^{1}H NMR, the reaction proceeded normally and afforded full conversion in 6 h (Figure S48C(i), Figure S77). The addition of radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT) in stoichiometric amount under standard reaction conditions had no effect on the reaction progress, which was completed as expected

in 6 h (Figure S48C(ii), Figure S78). Interestingly, when radical scavengers galvinoxyl free radical and 2,2,6,6-tetramethylpiperidinyloxyl free radical (TEMPO) were added to the reaction mixture in stoichiometric amounts, the reaction appeared less clean and was slowed down giving a full conversion in 48 h (Figure S48C(iii)–(iv), Figures S79–S80). It is known that NFSI interacts with TEMPO,[S23] which could be the reason for the observed reaction slowdown. To verify this, the reaction mixture containing added TEMPO free radical was monitored by EPR spectroscopy over 7 hours, which revealed that the concentration of TEMPO was decreasing over time, while no other radical species were observed in the EPR spectra (Figure S81). When mixture of TEMPO and NFSI was reacted in MeCN similar observation was made (Figure S82). To fully exclude the presence of radical species in the reaction we have also monitored the reaction progress over 5 hours directly by EPR spectroscopy. These measurements demonstrated that the reaction mixture is EPR silent (Figure S48D, Figure S83), which indicates that a mechanism that involves free radical species is not likely. The presence of the product at the end of the EPR experiment was also confirmed by LC-MS analysis (Figure S84). Next, the reaction of potassium acyltrifluoroborate **1m**' under standard reaction procedure afforded no reaction (Figure S48E, Figure S85), which confirmed the importance of imine/iminium structure of substrate. Since a minor amount of nitrile products was observed in all reactions, we wanted to verify if nitrile is an intermediate or a side product of the reaction. Thus, we designed a set of experiments involving 4-methoxybenzonitrile **1m''** (Figure S48F). First, the reaction of **1m''** with dibenzenesulfonimide (1 equiv.) under standard reaction condition (1 equiv. K_2CO_3 in MeCN in the presence of 1 vol% of water for 6 h) afforded no product **2m** (Figure S48F(i), Figure S86). The same observation was made when benzenesulfonamide (1 equiv.) was used as a nitrogen nucleophile (Figure S48F(ii), Figure S87). Moreover, a reaction of **1m''** with NFSI under standard reaction conditions provided no reaction (Figure S48F(iii), Figure S88). These experiments affirmed that nitriles represent a side product of the reaction, and precluded their role as possible intermediates in the reaction sequence. Next, the reaction of **1m** with dibenzenesulfonimide in the presence of Selectfluor under standard reaction conditions did not afford **2m** (Figure S48G, Figure S89), which eliminated possible involvement of electrophilic fluorine species in the reaction mechanism. Moreover, when KF was used instead of K_2CO_3 as a base in the reaction between **1m** and NFSI, **2m** was again detected as a main product by LC-MS and ^{1}H NMR analysis (Figure S48H, Figures S90–S91). Independent reaction between **1m** and KF revealed that the latter can deprotonate **1m** (checked by ^{1}H NMR) and promote the reaction to product **2m** formation (Figure S92).

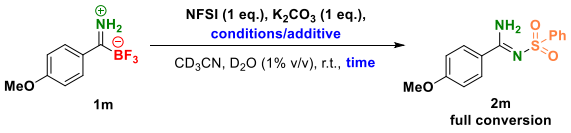
A) Determination of by-products and side products:



B) Reaction progress monitoring by ^{1}H NMR:

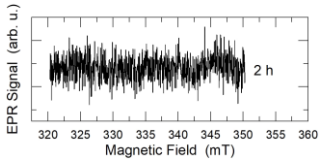


C) Radical reaction control experiments:

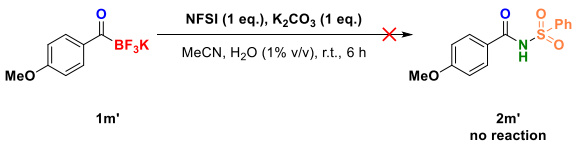


	conditions/additive	time [h]
(i)	absence of sun light	6
(ii)	TEMPO (1 eq.)	6
(iii)	galvinoxyl free radical (1 eq.)	48
(iv)	BHT (1 eq.)	48

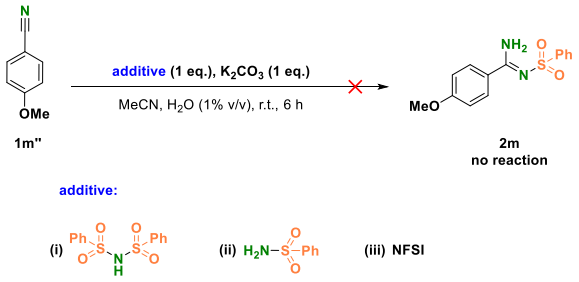
D) Reaction monitoring with EPR after 2 h reaction time:



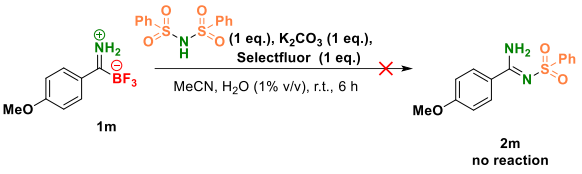
E) Reaction of KAT with NFSI:



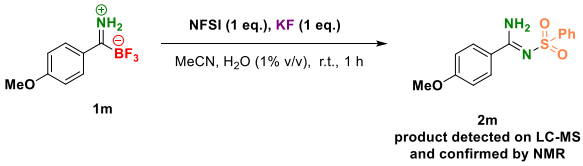
F) Reactions of 4-methoxybenzonitrile:



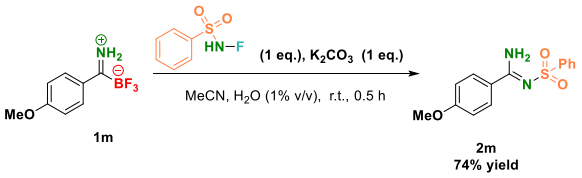
G) Reaction of TIM with dibenzenesulfonimide in the presence of Selectfluor:



H) Reaction of TIM with NFSI with KF as a base:



I) Reaction of TIM with *N*-fluorobenzenesulfonamide in the presence of base:



J) Reaction of TIM with *N*-fluorobenzenesulfonamide without the presence of base:

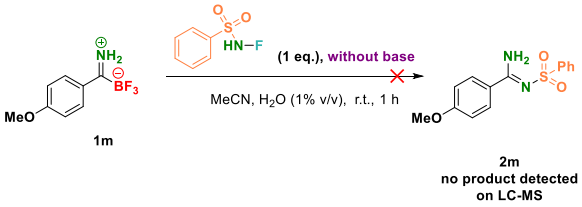


Figure S48. Reaction by-products, side products, reaction progress monitoring and control experiments.

General Procedure for Mechanism Investigation by NMR

To a stirred suspension of NFSI (63 mg, 0.2 mmol) and K_2CO_3 (28 mg, 0.2 mmol) in dry MeCN-d_3 (0.1 M, 2 mL) under argon atmosphere, **1a** (25 mg, 0.2 mmol) [or **1m** (41 mg, 0.2 mmol)] was added. For reaction of **1a**, after 20 min, the first sample was taken for NMR (designated as "Reaction mixture – no water (20 min)", Figures S71–S75), and at that time D_2O (20 µL) was added to the reaction mixture. The reaction mixture was stirred and samples were taken from the mixture at the reported time-points for NMR measurements in MeCN-d_3 (designated as "Reaction mixture - water added (20 min and 60 min)", Figures S71–S75). Deionized water (20% v/v with regard to MeCN) was added thereafter and the reaction mixture stirred for an additional hour. Then, the solvent was removed under reduced pressure and the dry residue was re-suspended in MeCN (0.05 M), which was again removed under reduced pressure. This procedure was repeated thrice, and the residue was dried at 0.05 mbar, 60 °C for 1 h (designated as "Reaction mixture - evaporated", Figures S71–S75). For reaction of **1m**, additives (if present) and D_2O (20 µL) were added immediately and samples were taken from the reaction mixture at the reported time-points for NMR measurements in MeCN-d_3.

Control Reactions

Reaction of KAT with NFSI: Synthesis according to the "*General Procedure for the Synthesis of Unsubstituted N-Sulfonyl Amidines*" using potassium trifluoro(4-methoxybenzoyl)borate **1m'** (61 mg, 0.25 mmol) instead of pTIM **1m**. Only starting **1m'** was isolated.

Reaction of 4-methoxybenzonitrile with dibenzenesulfonimide/benzensulfonamide/NFSI: Synthesis according to the "*General Procedure for the Synthesis of Unsubstituted N-Sulfonyl Amidines*" using 4-methoxybenzonitrile **1m''** (67 mg, 0.5 mmol) instead of pTIM **1m**, the corresponding additive (either dibenzenesulfonimide, benzensulfonamide or NFSI; 0.5 mmol, 1 equiv.) and K_2CO_3 (69 mg, 0.5 mmol) in MeCN (0.1 M) and H_2O (50 µL).

*Reaction of pTIM **1m** with dibenzenesulfonimide in the presence of Selectfluor:* Synthesis according to the "*General Procedure for the Synthesis of Unsubstituted N-Sulfonyl Amidines*" using **1m** (51 mg, 0.25 mmol), dibenzenesulfonimide (74 mg, 0.25 mmol), Selectfluor (89 mg, 0.25 mmol) and K_2CO_3 (35 mg, 0.25 mmol) in MeCN (0.1 M) and H_2O (25 µL).

*Reaction of pTIM **1m** with NFSI with KF as a base:* Synthesis according to the "*General Procedure for the Synthesis of Unsubstituted N-Sulfonyl Amidines*" using **1m** (41 mg, 0.2 mmol), NFSI (63 mg, 0.2 mmol) and KF (12 mg, 0.25 mmol) in MeCN (0.1 M) and H_2O (20 µL).

For the deprotonation of **1a** with K_2CO_3, **1a** (20 mg, 0.1 mmol) was dissolved in MeCN-d_3 (1 mL), and K_2CO_3 (14 mg, 0.1 mmol) was added, mixed thoroughly and ^1H NMR spectra recorded. For the

deprotonation of **1m** with KF, **1m** (20 mg, 0.1 mmol) was dissolved in MeCN-d_3 (1 mL), and KF (6 mg, 0.1 mmol) was added, mixed thoroughly and ^{1}H NMR spectra recorded.

Preparation of N-fluorobenzenesulfonamide ($PhSO_2NHF$): $PhSO_2NHF$ was prepared according to the procedure described by Qing and co-workers.[S24] To a solution of NFSI (3.153 g, 10 mmol) in MeOH (10 mL), pyridine (0.97 mL, 12 mmol) was added and the reaction was stirred at room temperature for 16 h. The solution was diluted with EtOAc (50 mL), washed with 2 M HCl (aq) (2 × 30 mL), water (30 mL), saturated brine (30 mL), dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to obtain crude product, which was purified by flash column chromatography (SiO_2; petroleum ether/EtOAc = 5/1) to afford *N*-fluorobenzenesulfonamide as colorless viscous oil (1250 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.63 (m, 2H, Ar-H), 7.73 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.92 – 8.03 (m, 2H, Ar-H), 9.02 (d, *J* = 52.1 Hz, 1H, NH). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.12, 129.66, 134.23, 135.32. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –91.37, –91.23. **HRMS** (ESI^-): calc. for $C_6H_5O_2NFS$ $[M–H]^-$: 174.0031, found: 174.0024.

*Reaction of pTIM **1m** with N-fluorobenzenesulfonamide in the presence of* K_2CO_3: To a stirred solution of $PhSO_2NHF$ (35 mg, 0.2 mmol) and K_2CO_3 (28 mg, 0.2 mmol) in MeCN (0.1 M, 2 mL), pTIM **1m** (41 mg, 0.2 mmol) was added, followed by the addition H_2O (20 µL). The reaction mixture was stirred at room temperature for 1 h and the reaction samples were taken at 15 min, 30 min and 60 min (for ^{1}H NMR analysis), followed by the addition of deionized water (20% v/v with regard to MeCN), and stirring for an additional hour. The solvent was removed under reduced pressure and the dry residue was re-suspended in MeCN (0.05 M), which was again removed under reduced pressure. This procedure was repeated thrice, and the residue was dried at 0.05 mbar and 60 °C for 1 h. The residue was suspended in EtOAc (50 mL) and washed with 1 M NaOH (aq) (2 × 50 mL) and saturated brine (2 × 10 mL), the organic dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure to afford (*Z*)-4-methoxy-*N*'-(phenylsulfonyl)benzimidamide (**2m**) as an off-white solid (43 mg, 74% yield).

Reaction of pTIM with N-fluorobenzenesulfonamide in the absence of K_2CO_3: To a stirred solution of $PhSO_2NHF$ (35 mg, 0.2 mmol) in MeCN (0.1 M, 2 mL), pTIM **1m** (41 mg, 0.2 mmol) was added, followed by the addition H_2O (20 µL). The reaction mixture was stirred at room temperature for 1 h. The reaction mixture did not contain the (*Z*)-4-methoxy-*N*'-(phenylsulfonyl)benzimidamide (**2m**) as determined by LC-MS (Figure S96).

General Procedure for Mechanism Investigation by EPR

To a suspension of NFSI (32 mg, 0.1 mmol) and K_2CO_3 (14 mg, 0.1 mmol) in MeCN (0.1 M), pTIM **1m** (21 mg, 0.1 mmol), H_2O (10 µL) [and if indicated, TEMPO (16 mg, 0.1 mmol)] were added, shaken well, and MeCN solutions injected into 1 mm thin-wall capillaries, which were then inserted into standard 4 mm quartz EPR tubes for EPR measurements. For comparison, solutions of TEMPO at 0.1 M and 0.01 M concentrations in MeCN and toluene were also prepared and measured by the EPR. Continuous wave (cw) X-band EPR measurements were performed using a Bruker E500 EPR spectrometer, operating at 9.4 GHz, and equipped with a 4122SHQE cylindrical Bruker resonator. The EPR spectra were measured at 1 mW microwave power, while the modulation field was set to 0.01 mT amplitude and 100 kHz modulation frequency. When measuring the reaction mixture alone (i.e. without TEMPO), larger 0.1 mT modulation amplitude was used.

The reaction mixture alone has no detectable EPR signal close to g = 2 field range at all times of measurement during the reaction process (Figure S83). Initially, the EPR spectrum of the reaction mixture with added TEMPO radical consists of a strong signal with nearly Lorentzian lineshape (Figure S81(a)). With the reaction time, the fine structure of the measured EPR signal starts to emerge, clearly revealing the splitting into three equidistant lines. This is a hallmark of hyperfine interaction of the unpaired electron with the nitrogen (^{14}N) nuclear spin of the TEMPO radical (Figure S82(c)). Notably, the measured EPR signal intensity monotonically decreases with time and the effective ^{14}N hyperfine splitting of the EPR lines gradually increases, reaching a final value of a_N = 1.3 mT (Figure S82(b)). The absence of pronounced ^{14}N hyperfine splitting in the initial EPR spectra is due to the interaction between highly concentrated TEMPO radical molecules (Figure S82(c)).

The decrease of the EPR signal intensity of TEMPO in the reaction mixture is due to TEMPO interacting with the NFSI reactant, where TEMPO is converted to the EPR-silent form of $TEMPO^+$. This is confirmed with the control EPR measurements of the TEMPO signal in MeCN with added NFSI only (Figure S82(a)). In these measurements we observe a similar EPR spectra time evolution and a concomitant decrease of TEMPO EPR signal intensity and an increase of effective ^{14}N hyperfine splitting (Figure S82(b)).

The initial TEMPO signal, consisting of a single Lorentzian line rather than a characteristic triplet of lines, is due to a relatively high spin concentration. In this limit, TEMPO molecules get close enough for the electron spins to interact either via dipolar or exchange interactions, where the ^{14}N hyperfine interaction is effectively averaged-out. As a result, the measured spectrum consists only of a single Lorentzian line. When TEMPO reacts with NFSI and forming EPR silent $TEMPO^+$, the EPR-active TEMPO concentration drops and the average distance between the radical molecules increases. The

interaction between TEMPO molecules is now significantly weaker and consequently the ^{14}N hyperfine split triplet of lines becomes clearly visible in the measured EPR spectra. This concentration-driven effect is confirmed with separate EPR measurements of TEMPO in MeCN and in toluene with two radically different concentrations where the same transition between the single Lorentzian and ^{14}N hyperfine split lines are observed (Figure S82(c) and (d), respectively).

Starting Materials

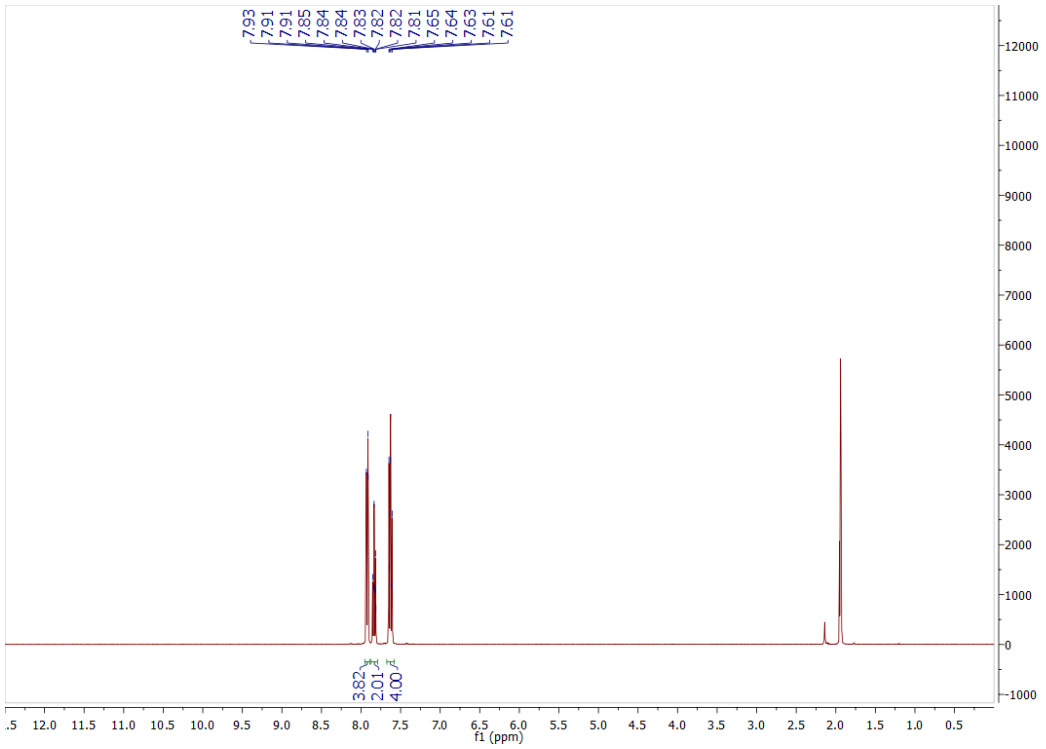


Figure S49. ^{1}H NMR (400 MHz, MeCN-d_3) for **NFSI**.

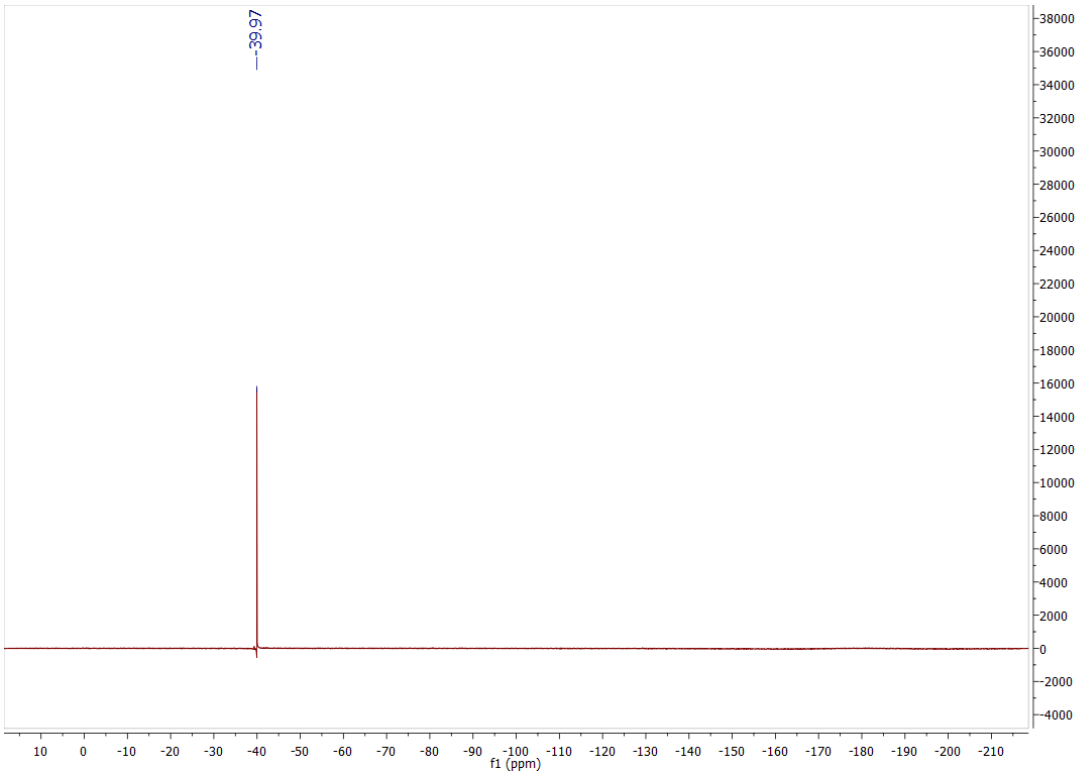


Figure S50. ^{19}F NMR (376 MHz, MeCN-d_3) for **NFSI**.

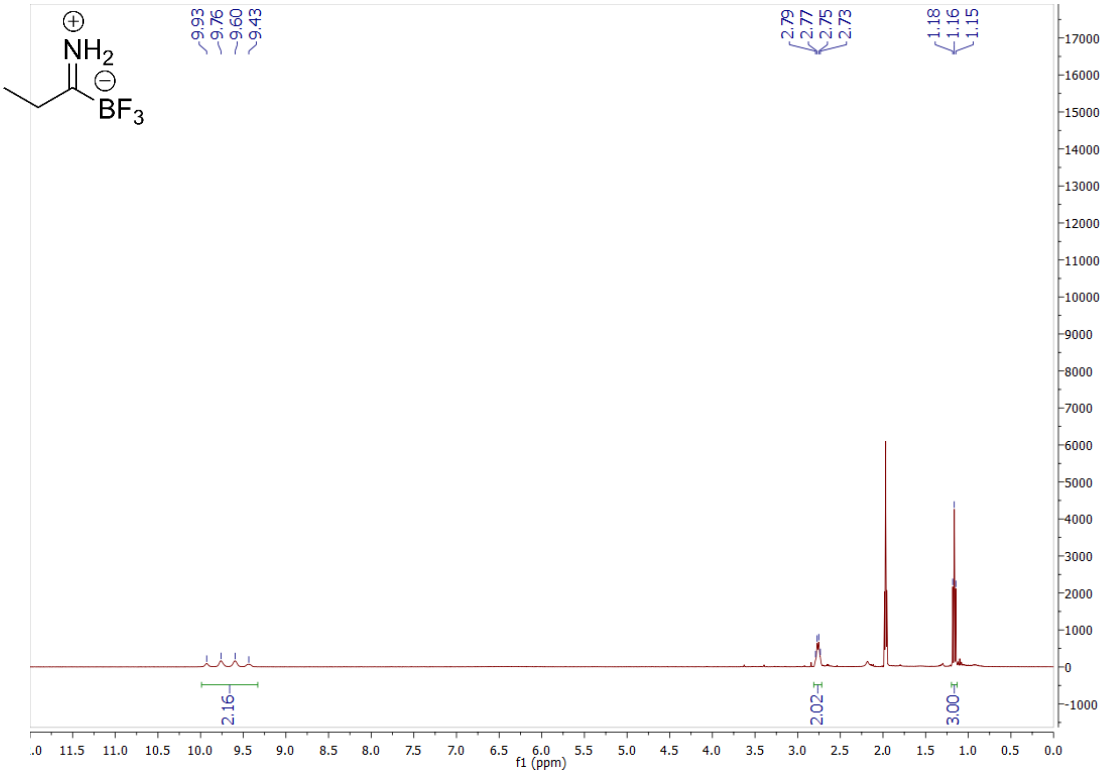


Figure S51. ^{1}H NMR (400 MHz, MeCN-d_3) for **1a**.

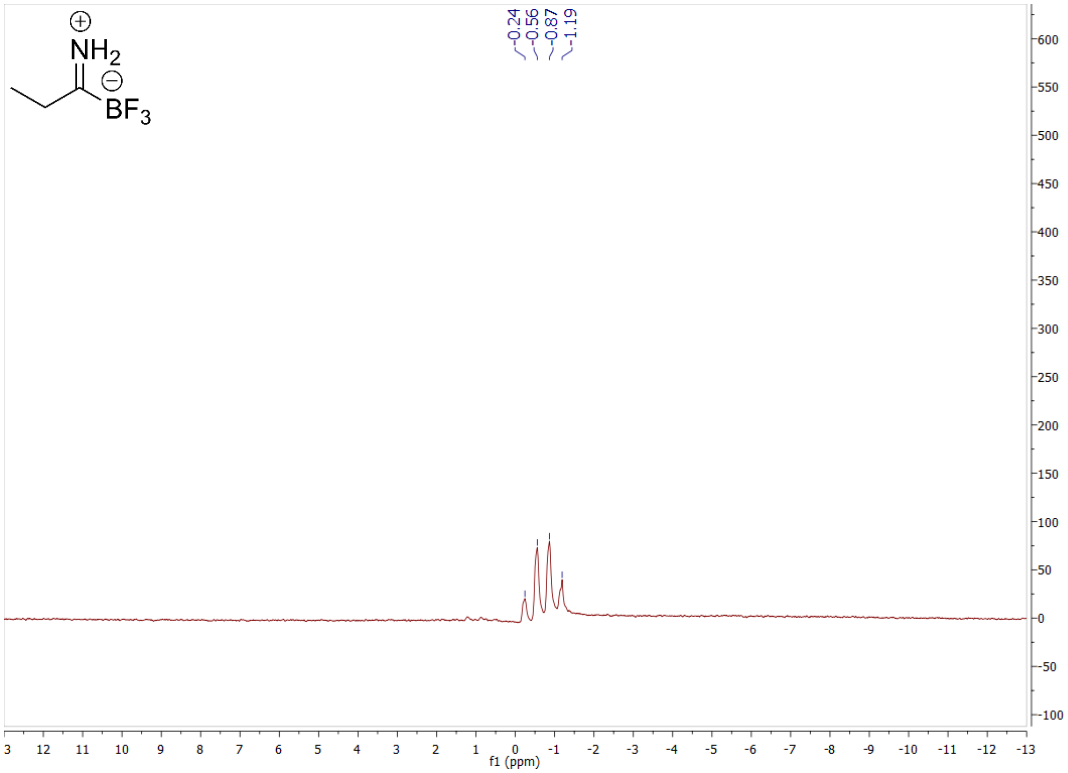


Figure S52. ^{11}B NMR (128 MHz, MeCN-d_3) for **1a**.

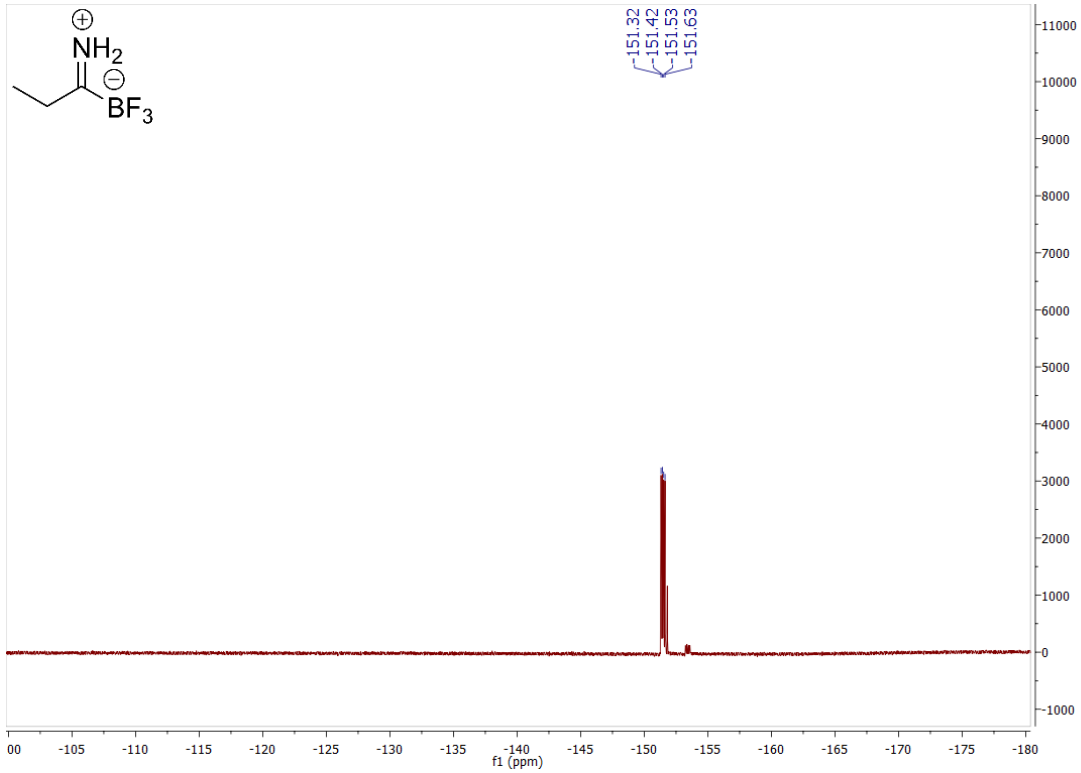


Figure S53. ^{19}F NMR (376 MHz, MeCN-d_3) for **1a**.

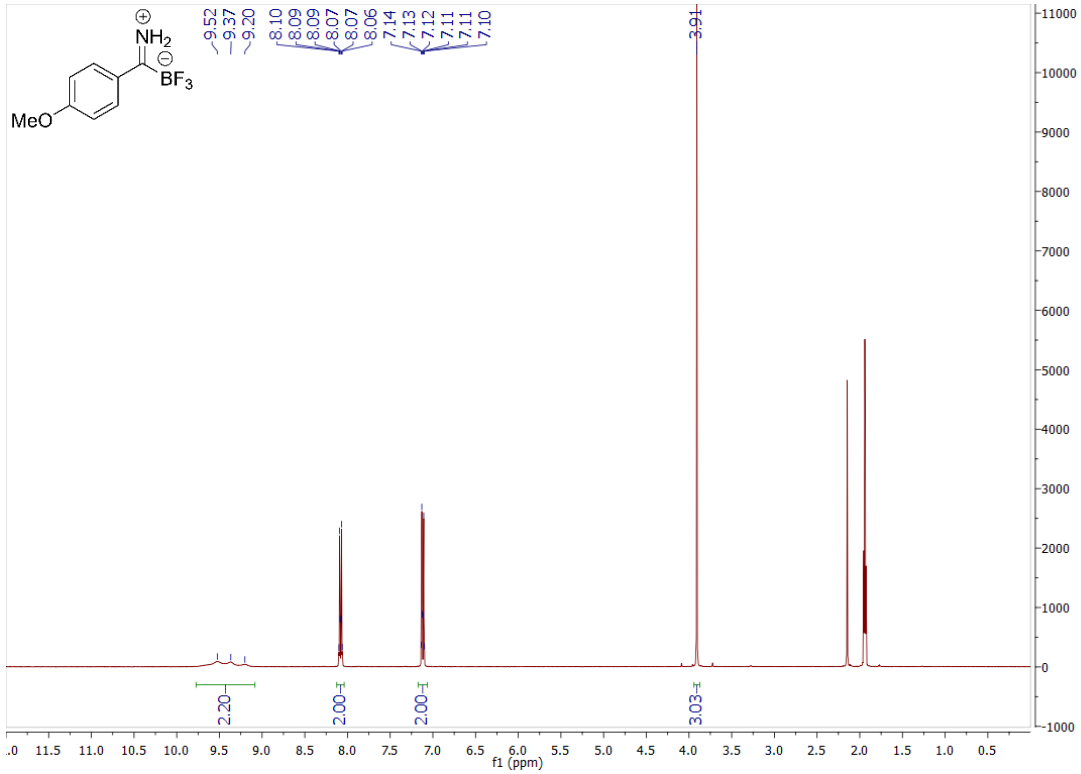


Figure S54. ^{1}H NMR (400 MHz, MeCN-d_3) for **1m**.

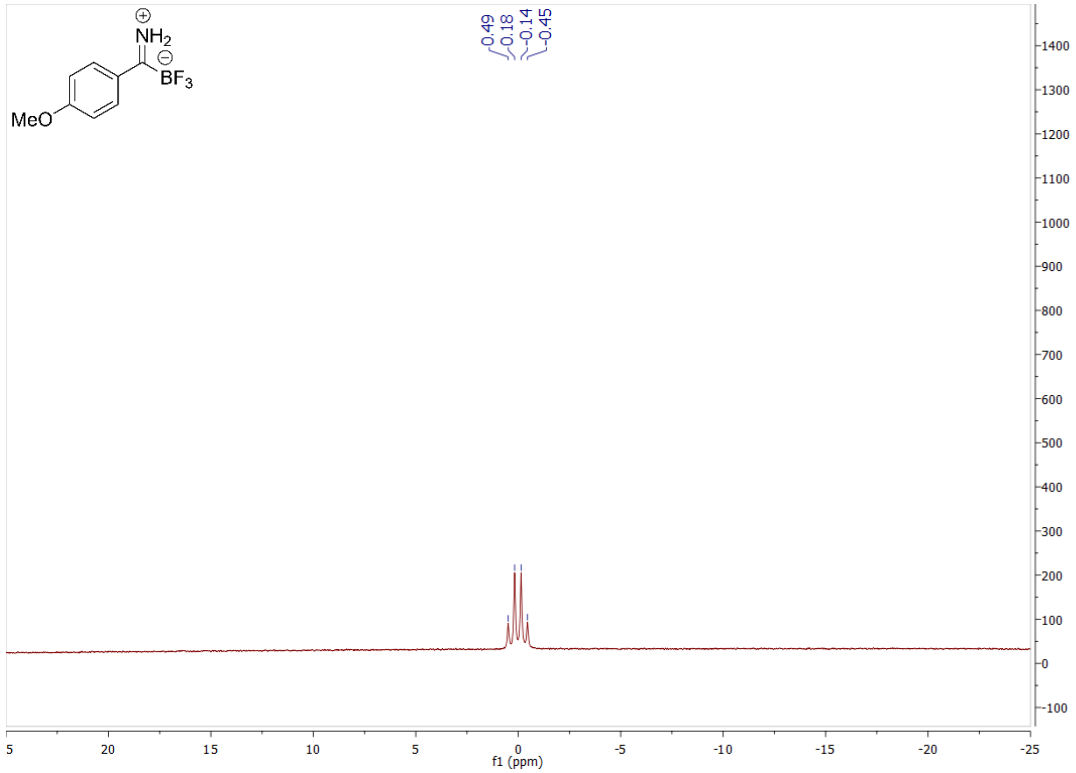


Figure S55. ^{11}B NMR (128 MHz, MeCN-d_3) for **1m**.

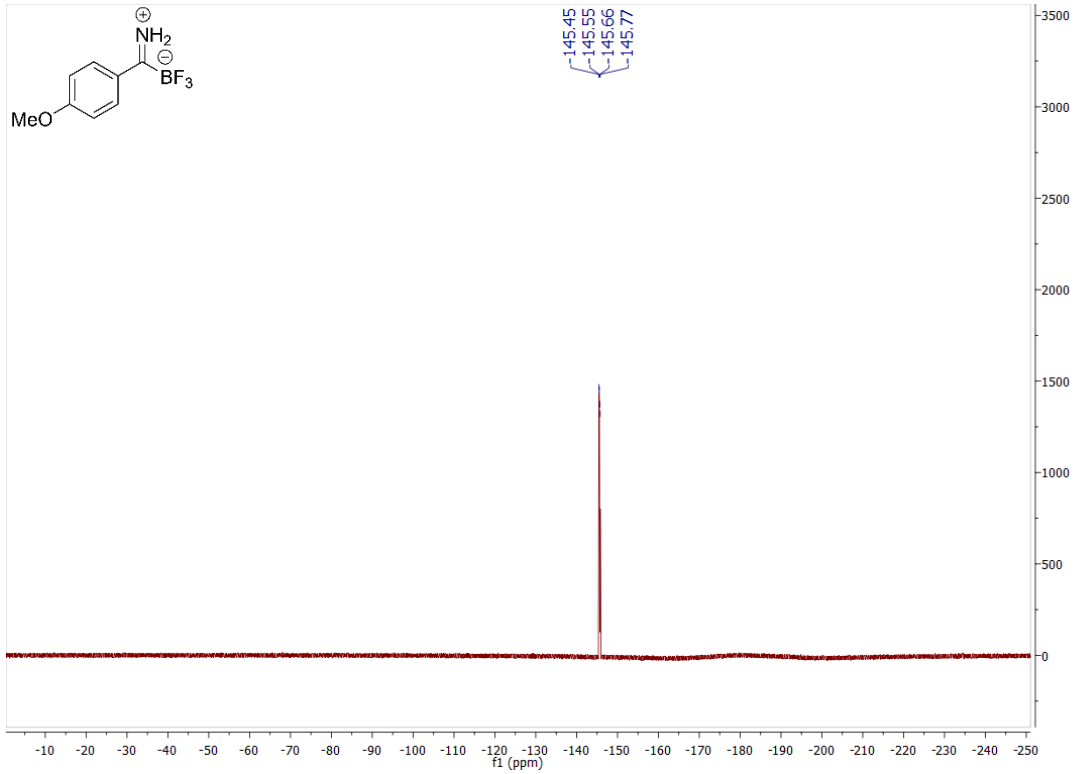


Figure S56. ^{19}F NMR (376 MHz, MeCN-d_3) for **1m**.

Products and Possible Side Products

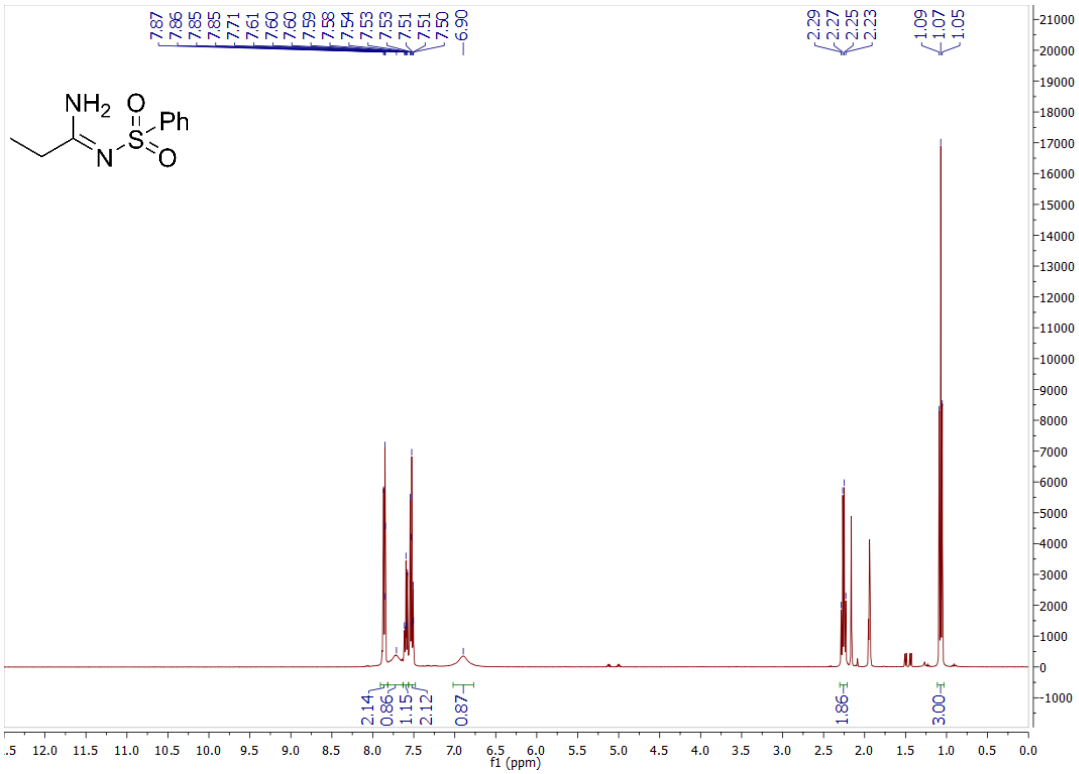


Figure S57. ^{1}H NMR (400 MHz, MeCN-d_3) for **2a**.

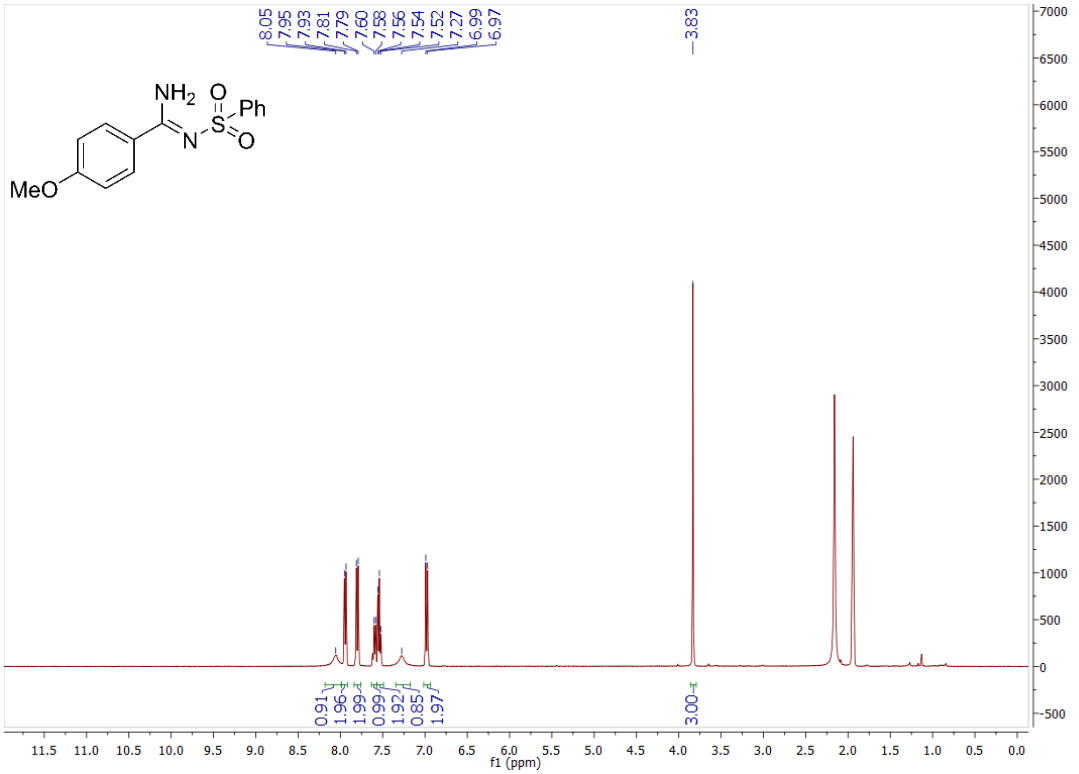


Figure S58. ^{1}H NMR (400 MHz, MeCN-d_3) for **2m**.

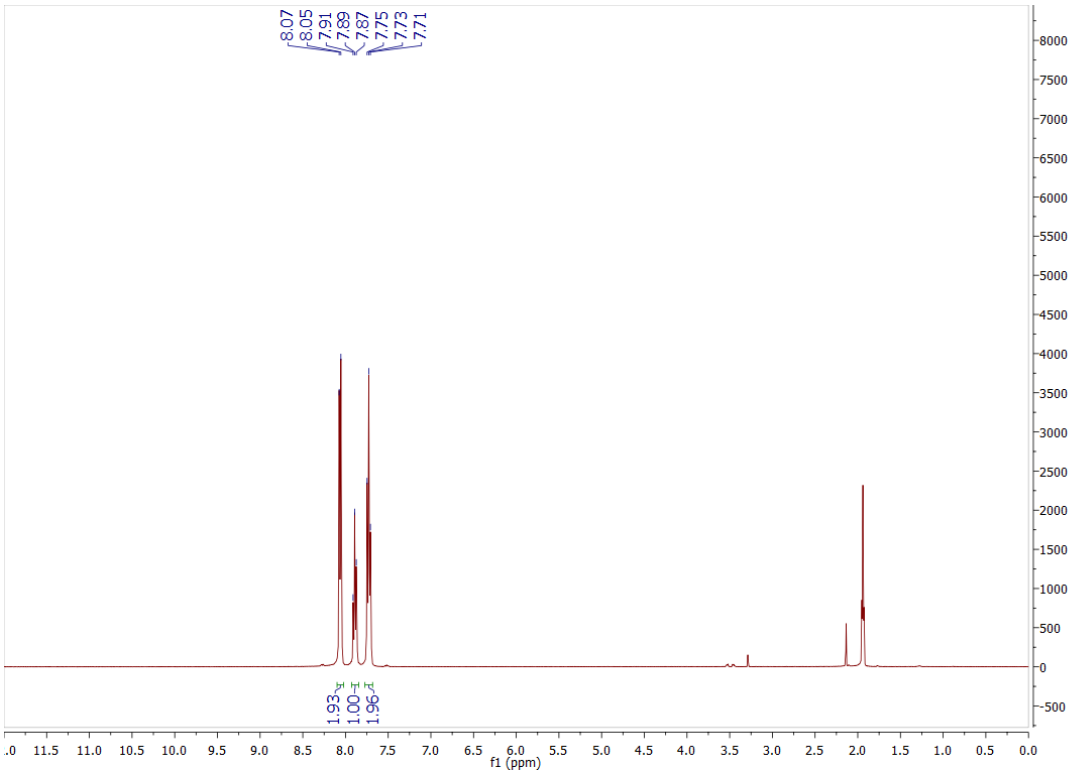


Figure S59. ^{1}H NMR (400 MHz, MeCN-d_3) for **benzenesulfonyl fluoride**.

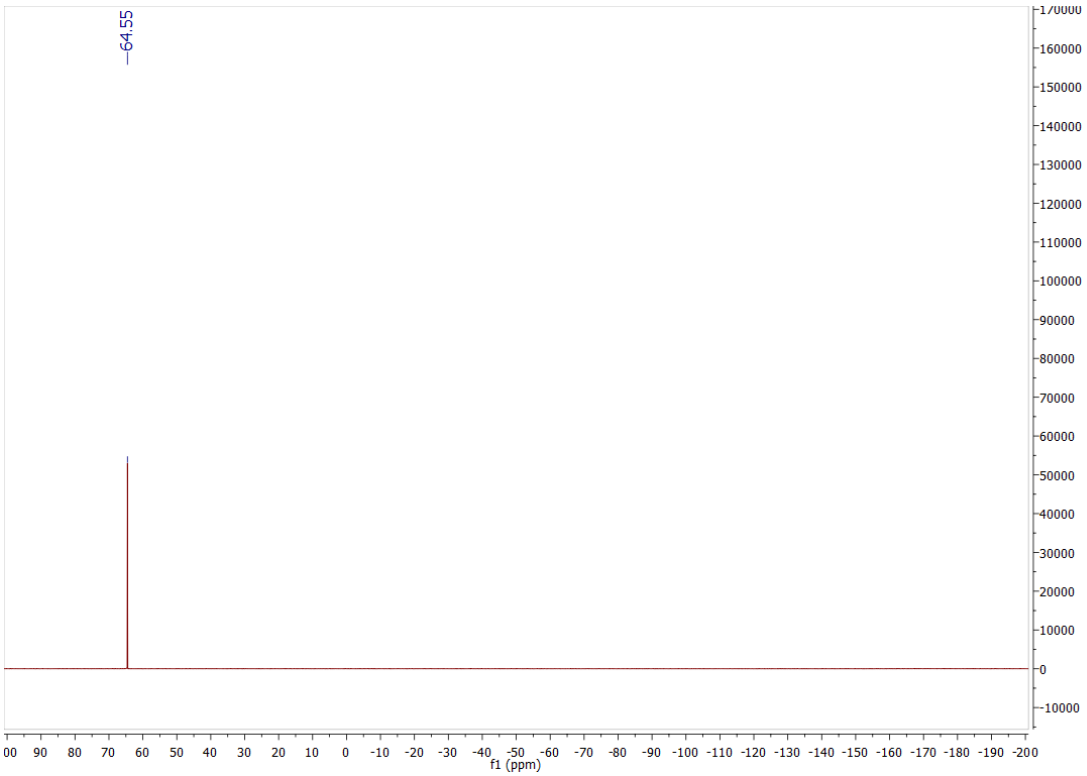


Figure S60. ^{19}F NMR (376 MHz, MeCN-d_3) for **benzenesulfonyl fluoride**.

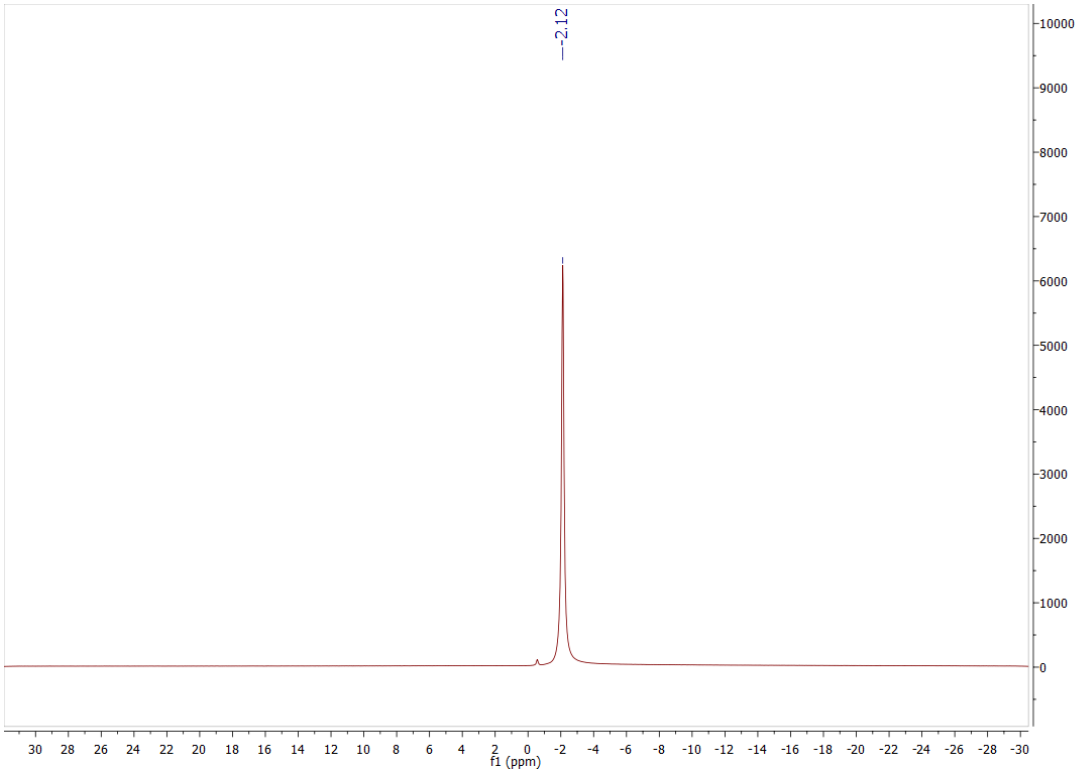


Figure S61. ^{11}B NMR (128 MHz, MeCN-d_3) for **BF_3×MeCN**.

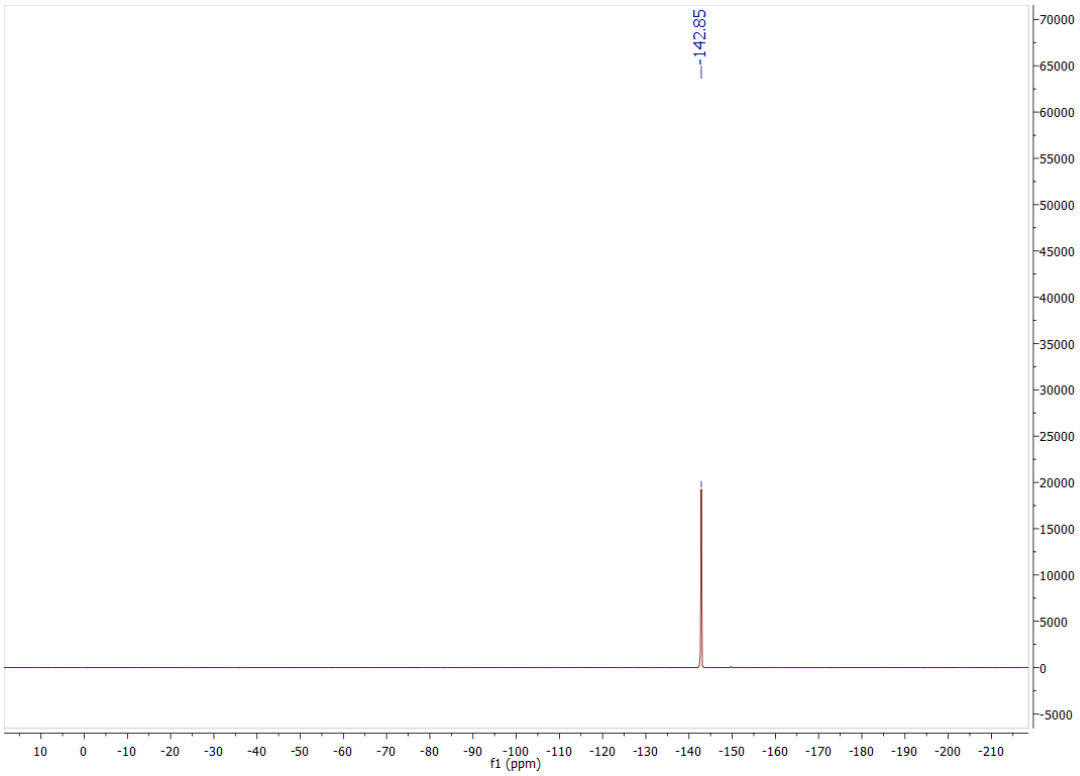


Figure S62. ^{19}F NMR (376 MHz, MeCN-d_3) for **BF_3×MeCN**.

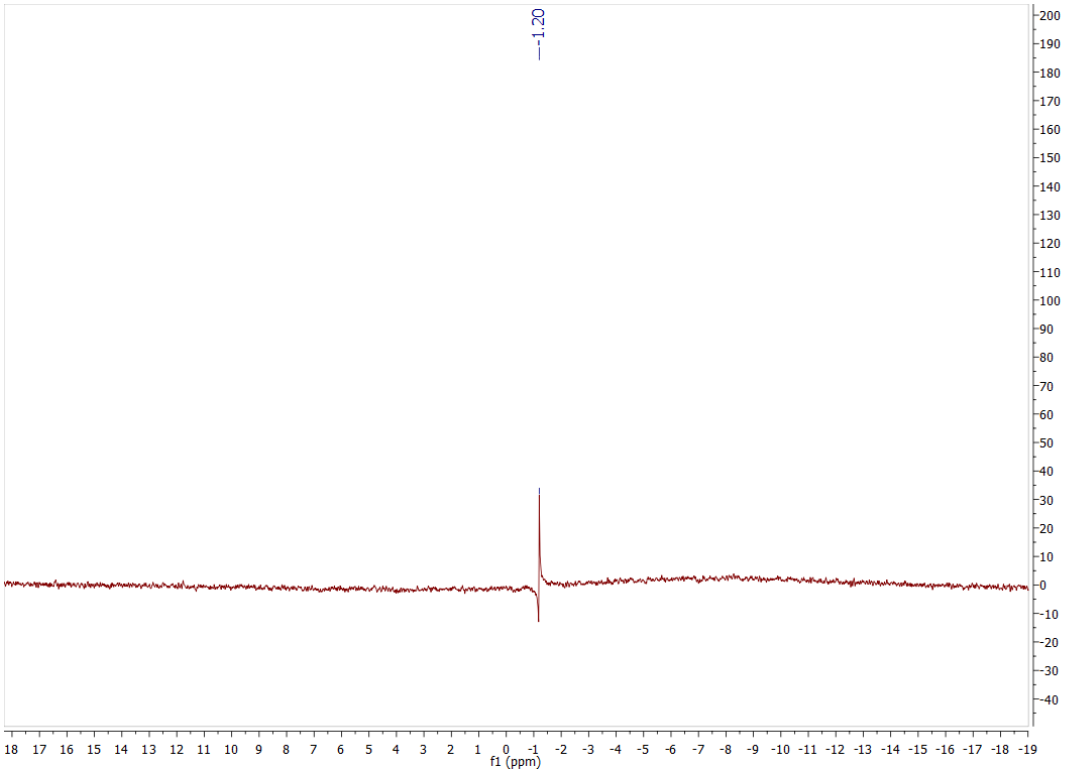


Figure S63. ^{11}B NMR (128 MHz, MeCN-d_3:D_2O = 2:1) for **KBF_4**.

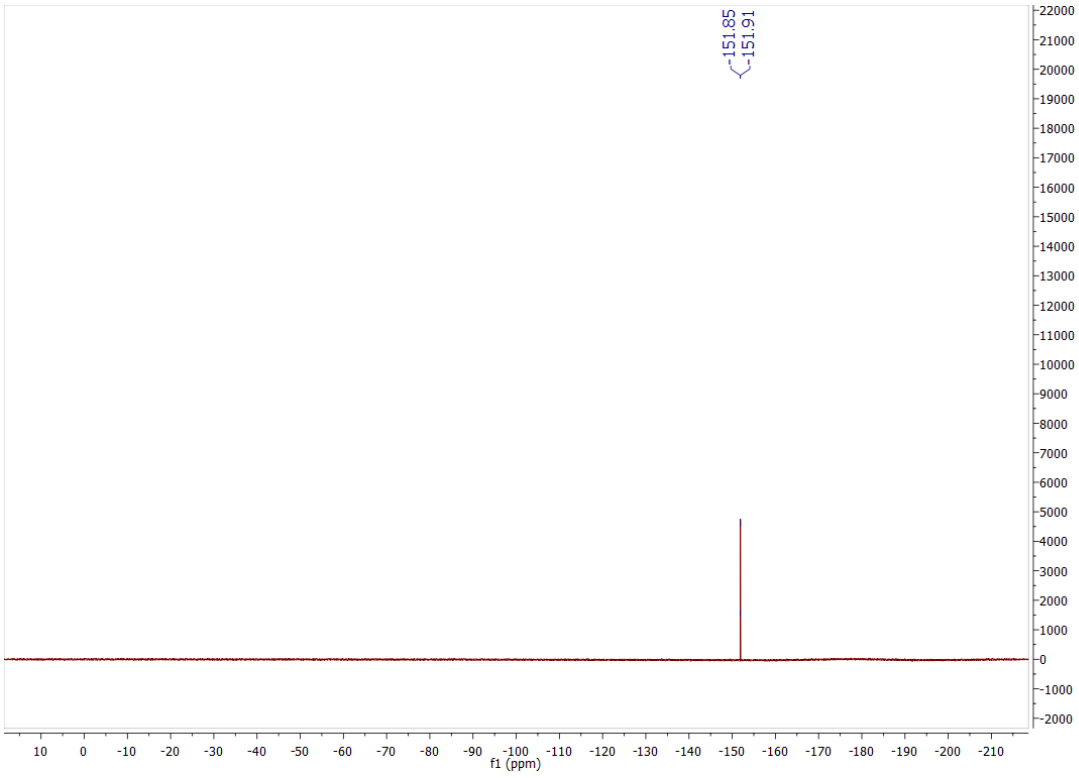


Figure S64. ^{19}F NMR (376 MHz, MeCN-d_3:D_2O = 2:1) for **KBF_4**.

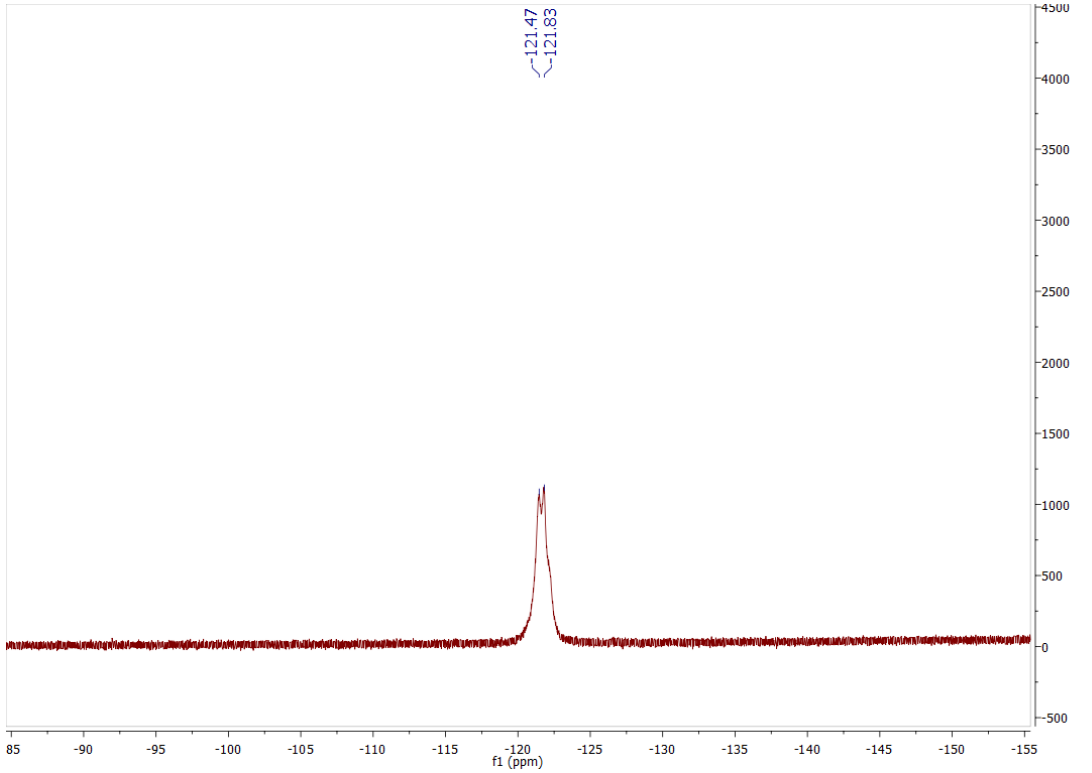


Figure S65. ^{19}F NMR (376 MHz, MeCN-d_3:D_2O = 2:1) for **KF**.

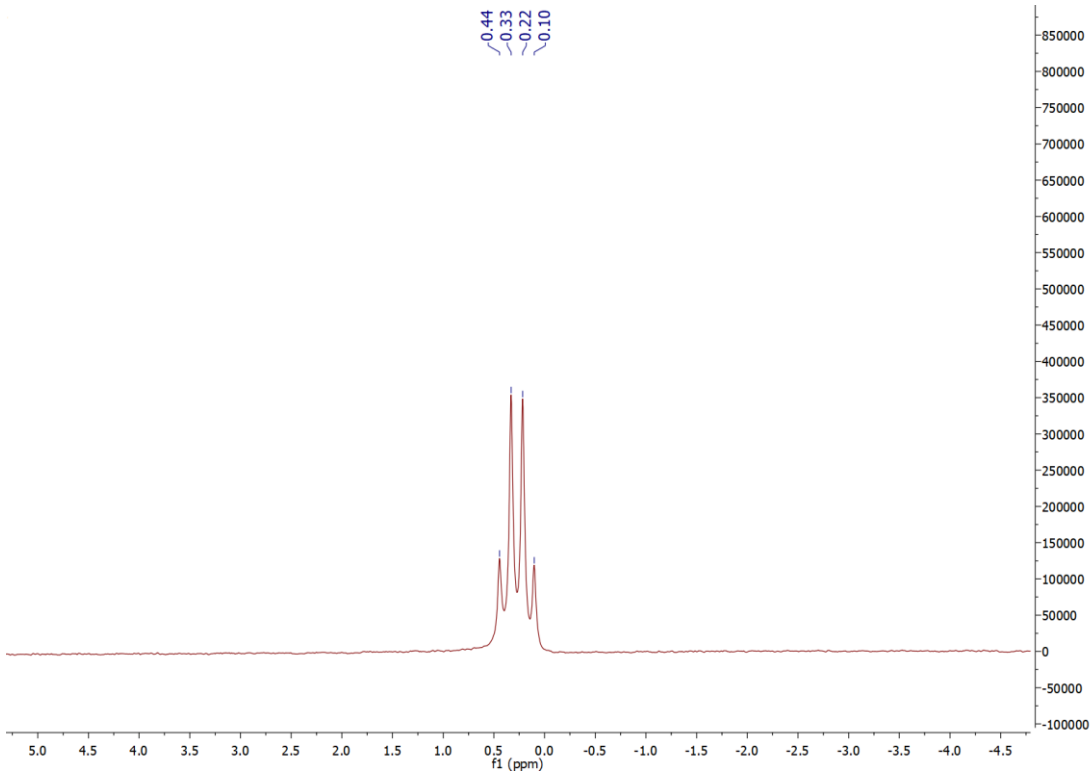


Figure S66. ^{11}B NMR (128 MHz, MeCN-d_3:D_2O = 2:1) for **KBF_3OH**.

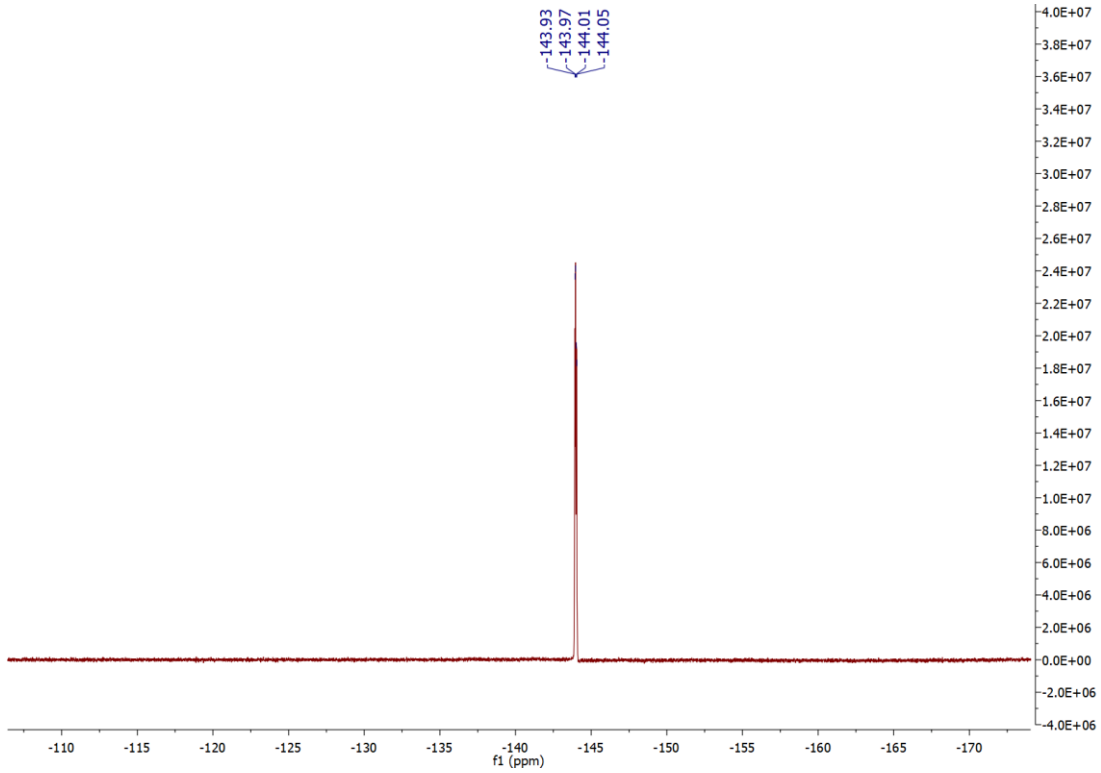


Figure S67. ^{19}F NMR (376 MHz, MeCN-d_3:D_2O = 2:1) for **KBF_3OH**.

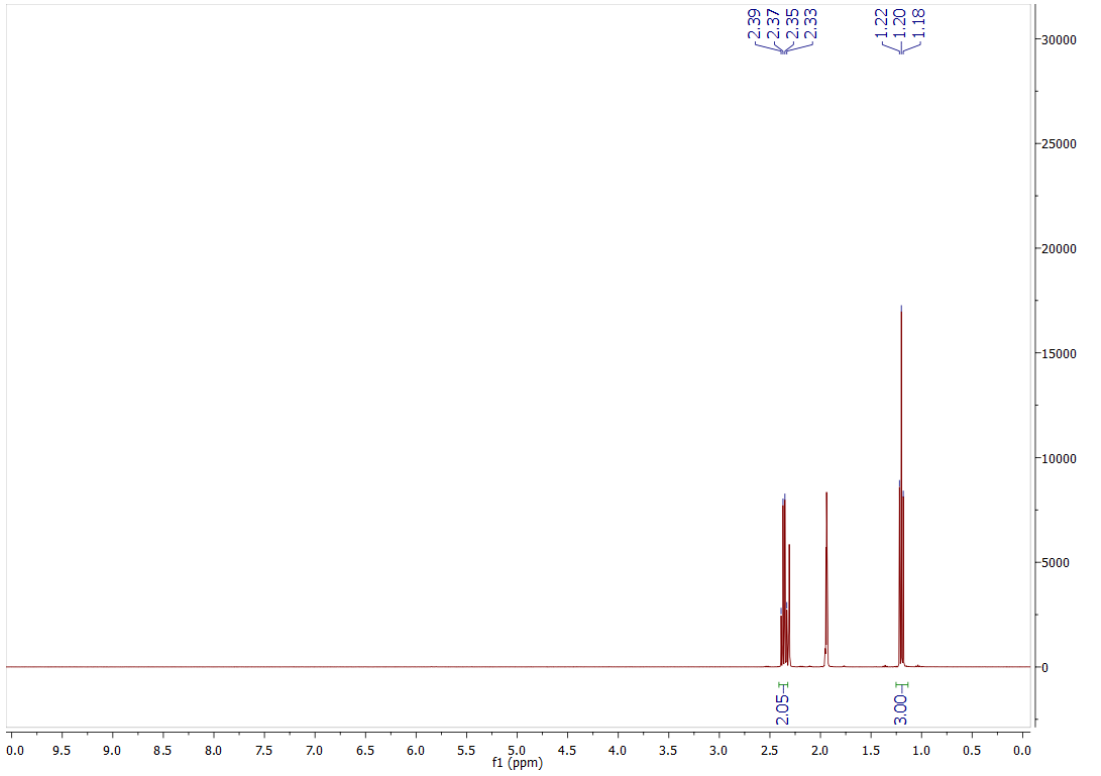


Figure S68. ^{1}H NMR (400 MHz, MeCN-d_3) for **propionitrile**.

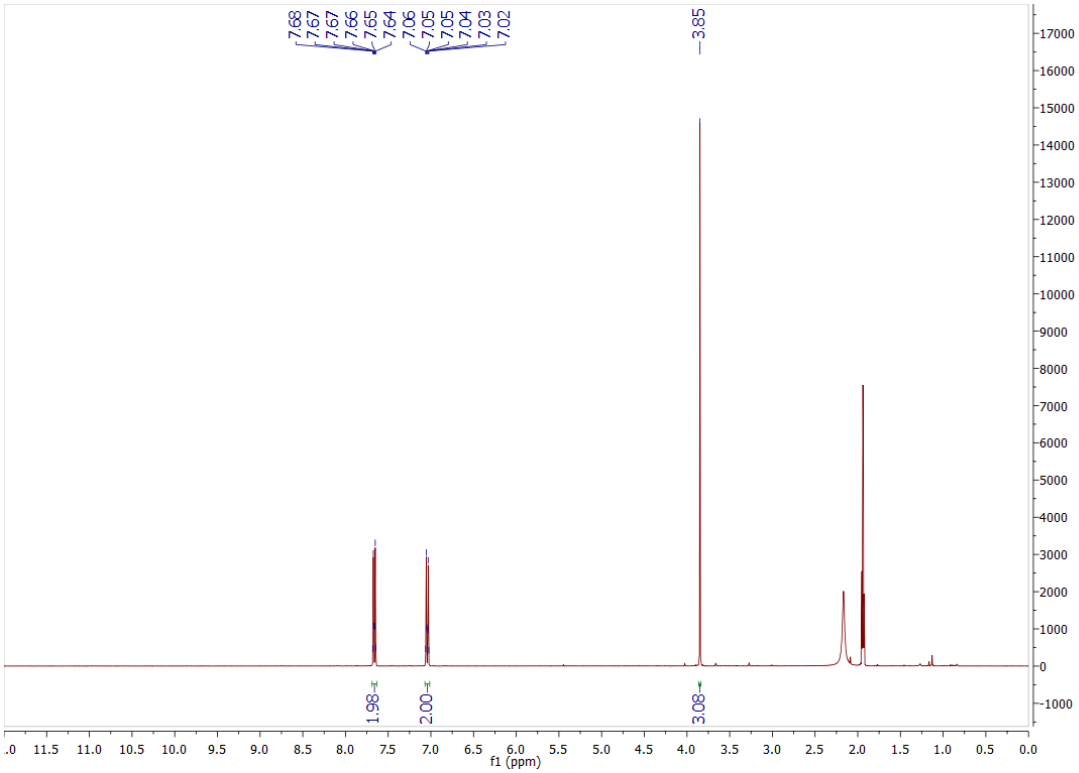


Figure S69. ^{1}H NMR (400 MHz, MeCN-d_3) for **4-methoxybenzonitrile**.

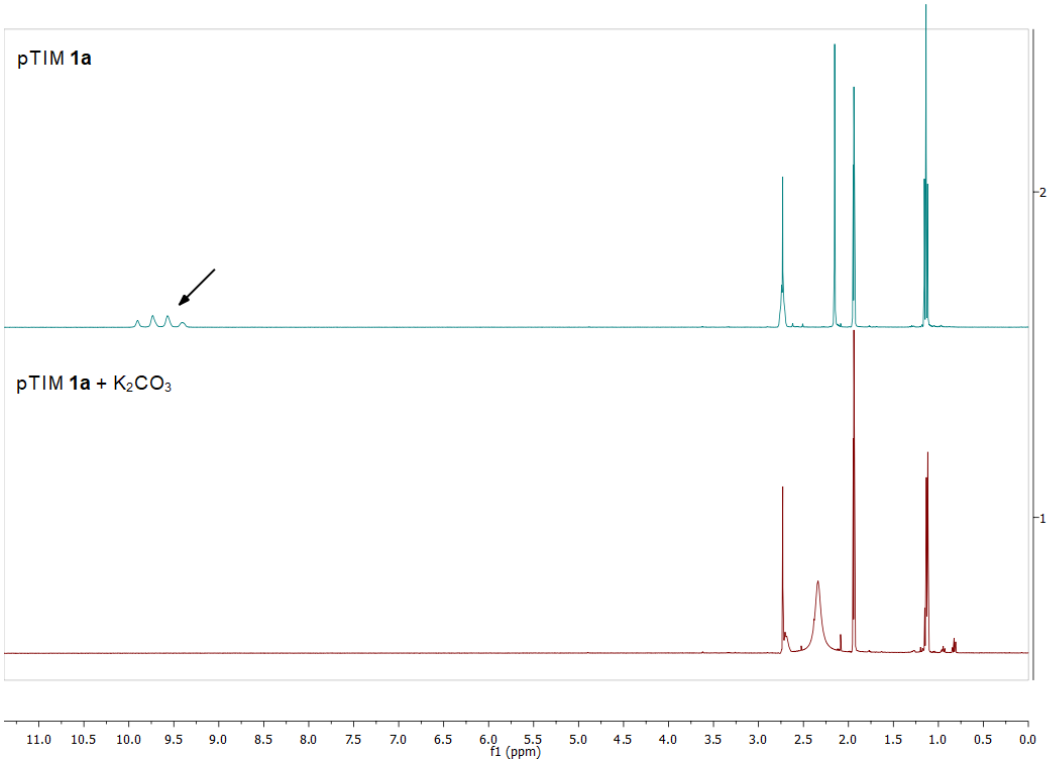


Figure S70. ^{1}H NMR (400 MHz, MeCN-d_3) of control experiment – deprotonation of pTIM **1a** with K_2CO_3 as base.

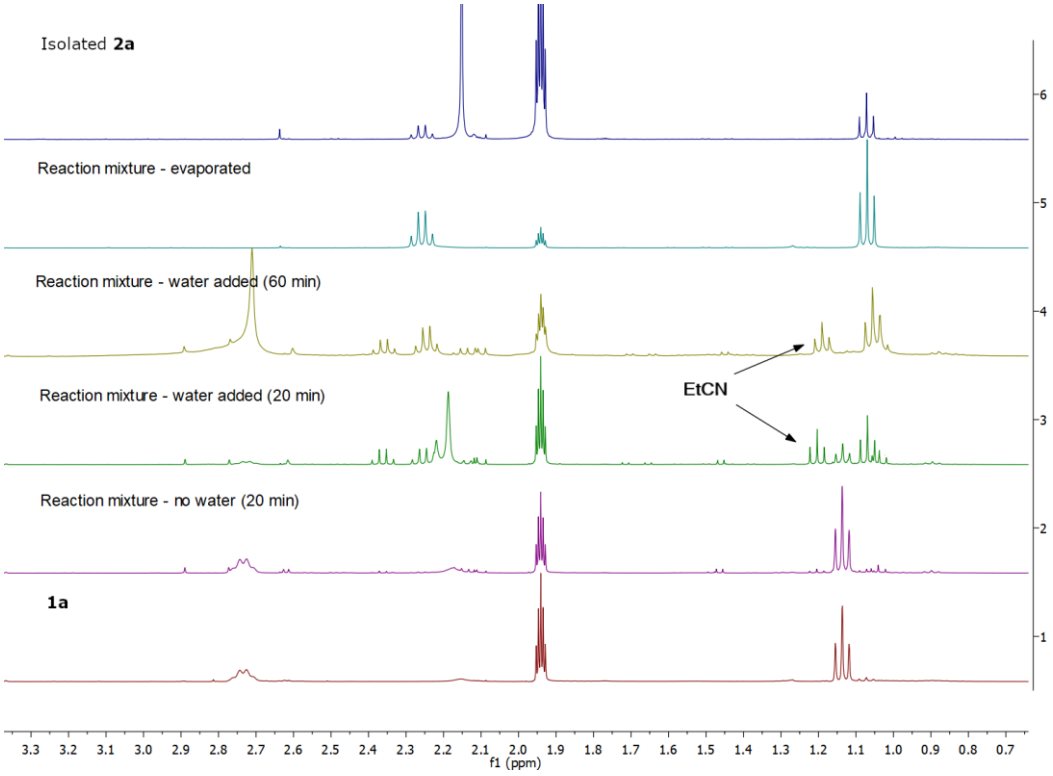


Figure S71. Tracking the conversion of **1a** to **2a**: ^{1}H NMR (400 MHz) of the reaction mixture. Crude **1a** (without filtration over SiO_2) was used to generate more nitrile side product.

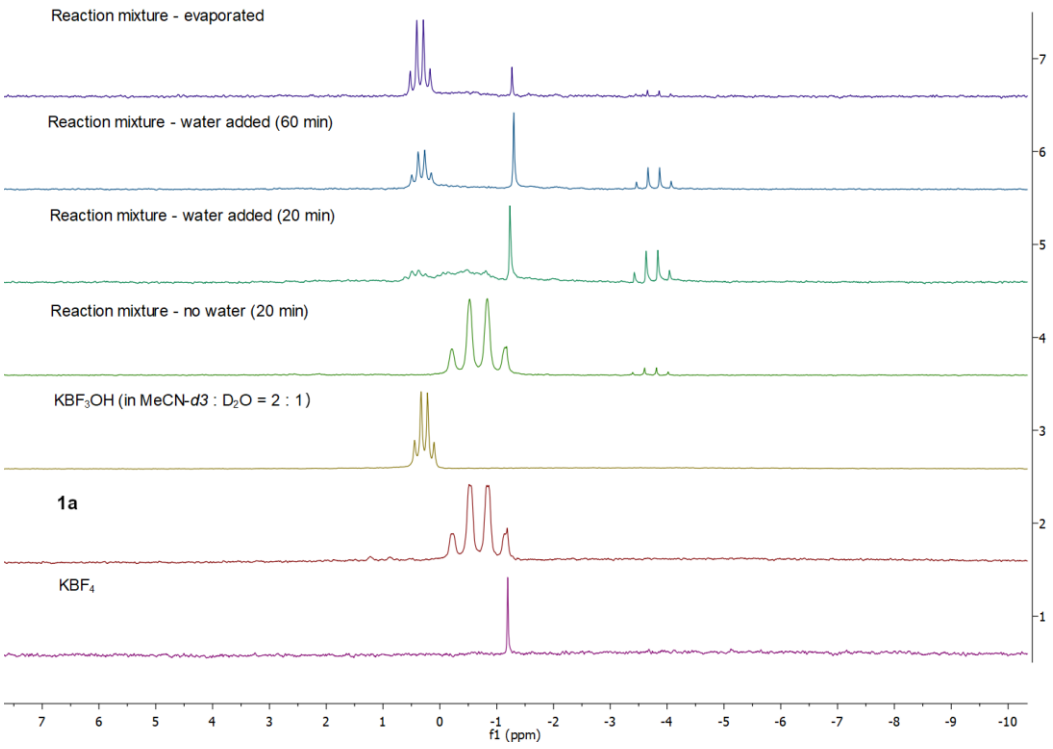


Figure S72. Tracking the conversion of **1a** to **2a**: ^{11}B NMR (128 MHz) of the reaction mixture. Crude **1a** was used.

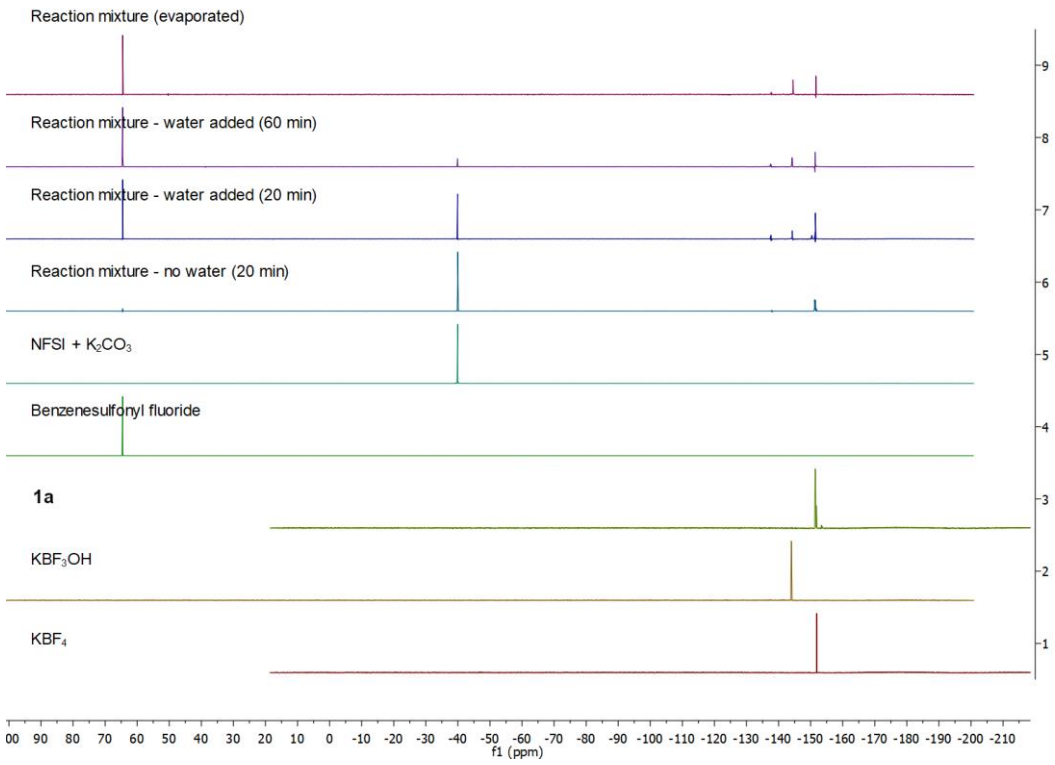


Figure S73. Tracking the conversion of **1a** to **2a**: ^{19}F NMR (376 MHz) of the reaction mixture (whole spectral window). Crude **1a** was used.

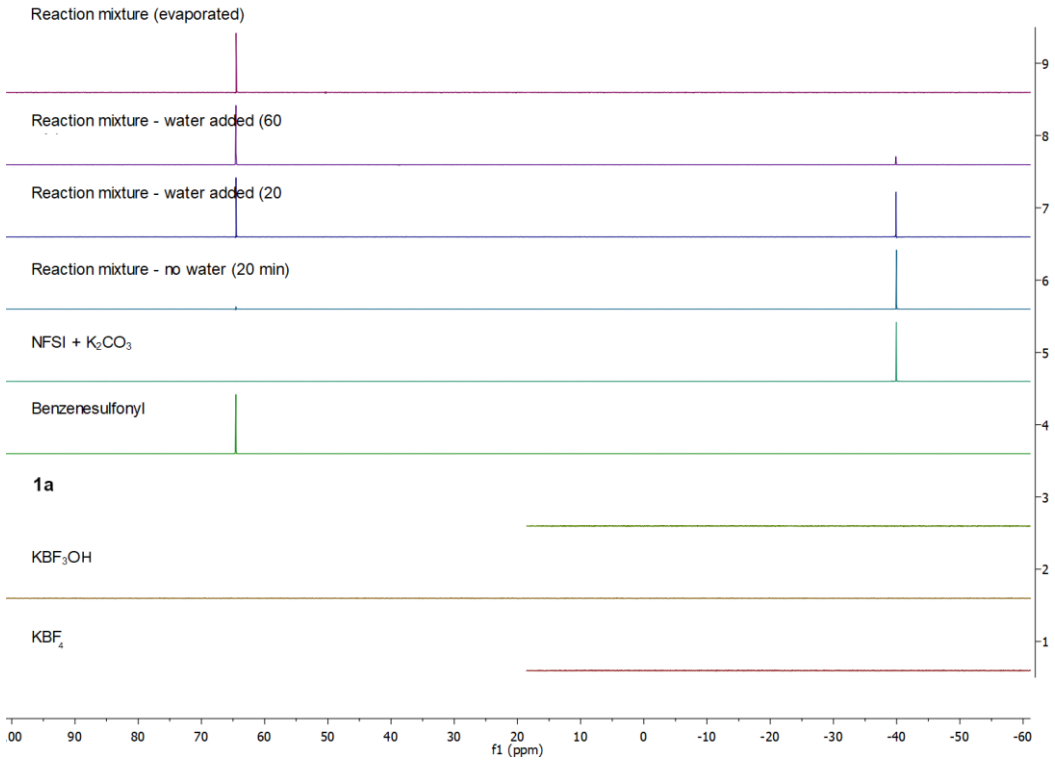


Figure S74. Tracking the conversion of **1a** to **2a**: ^{19}F NMR (376 MHz) of the reaction mixture (spectral window 100 to –60 ppm). Crude **1a** was used.

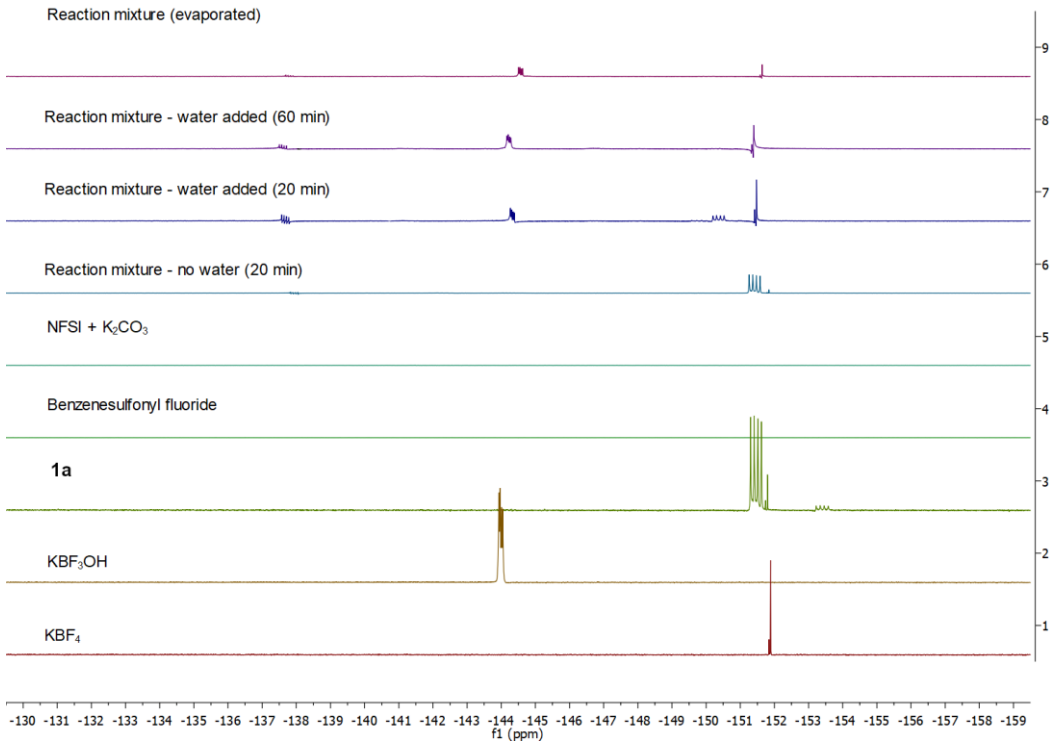


Figure S75. Tracking the conversion of **1a** to **2a**: ^{19}F NMR (376 MHz) of the reaction mixture (spectral window –130 to –160 ppm). Crude **1a** was used.

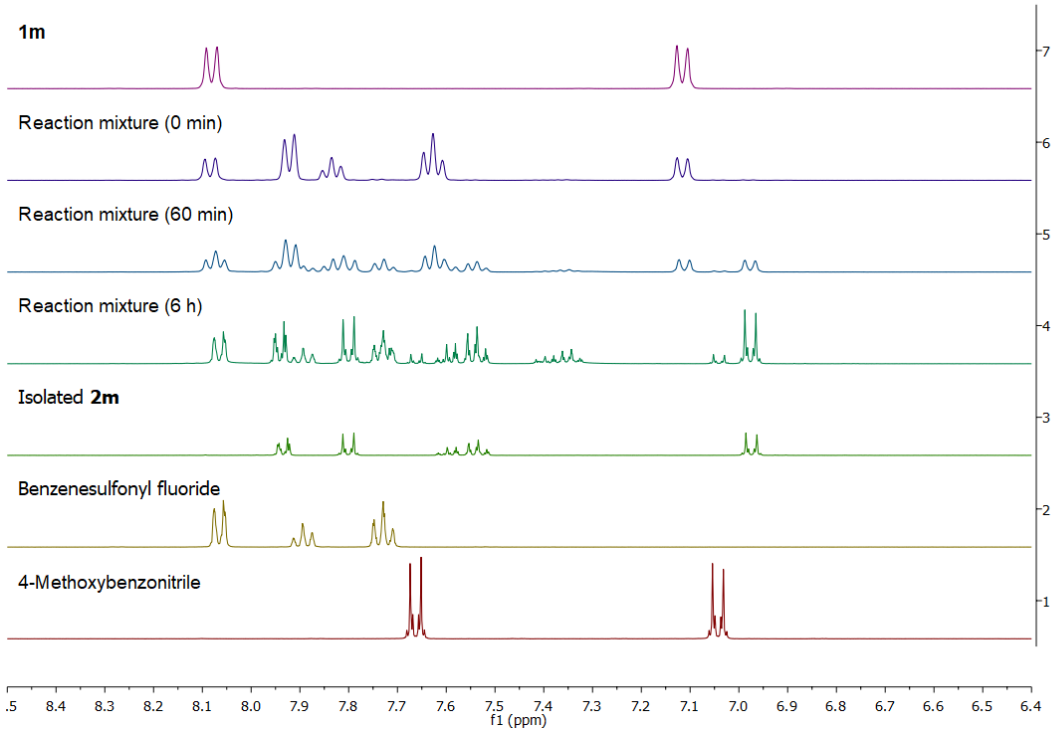


Figure S76. Tracking the conversion of pTIM **1m** to **2m**: ^{1}H NMR (400 MHz) of the reaction mixture.

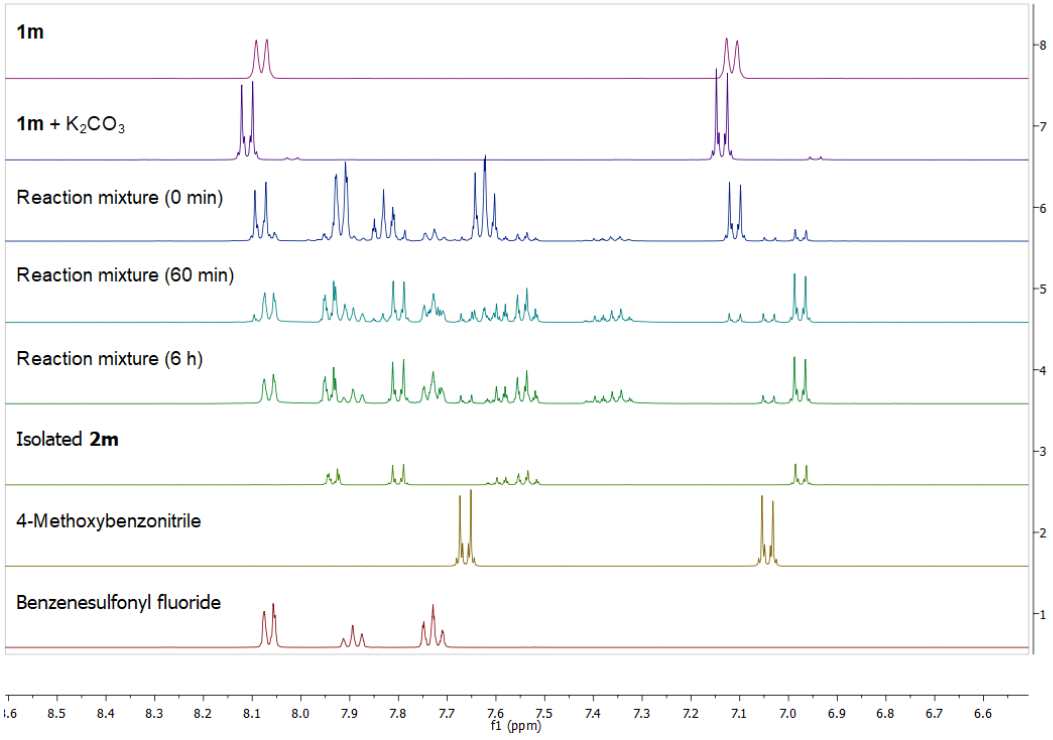


Figure S77. Tracking the conversion of **1m** to **2m**: ^{1}H NMR (400 MHz) of the reaction mixture protected from direct sun light.

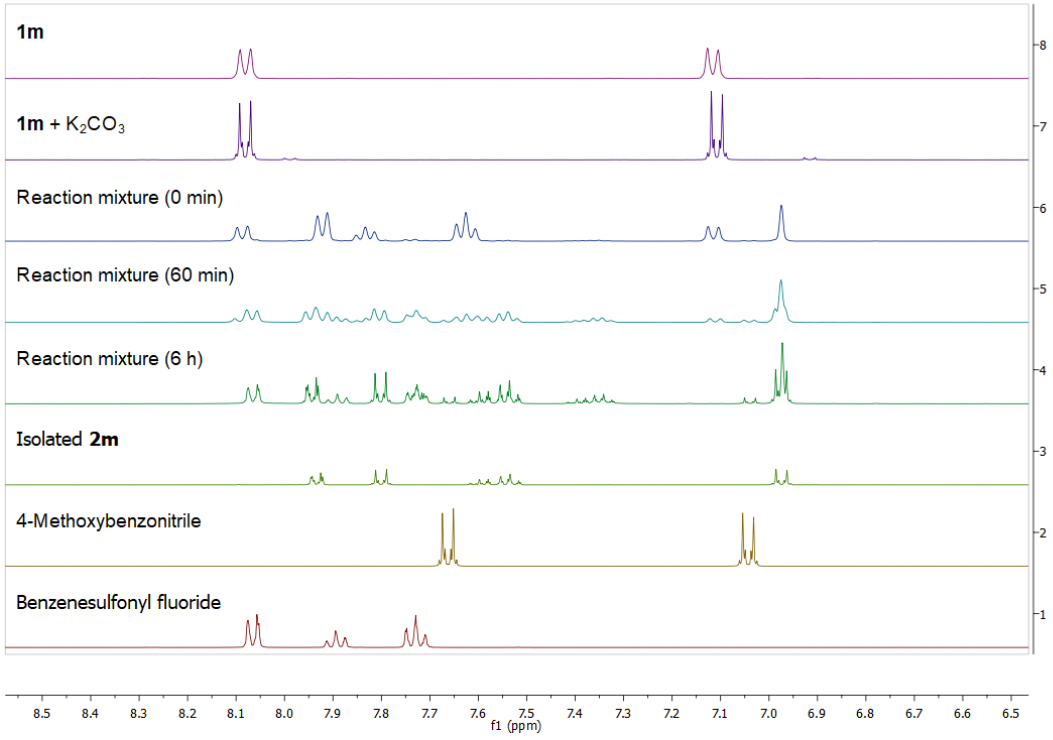


Figure S78. Tracking the conversion of **1m** to **2m**: ^{1}H NMR (400 MHz) of the reaction mixture in the presence of BHT.

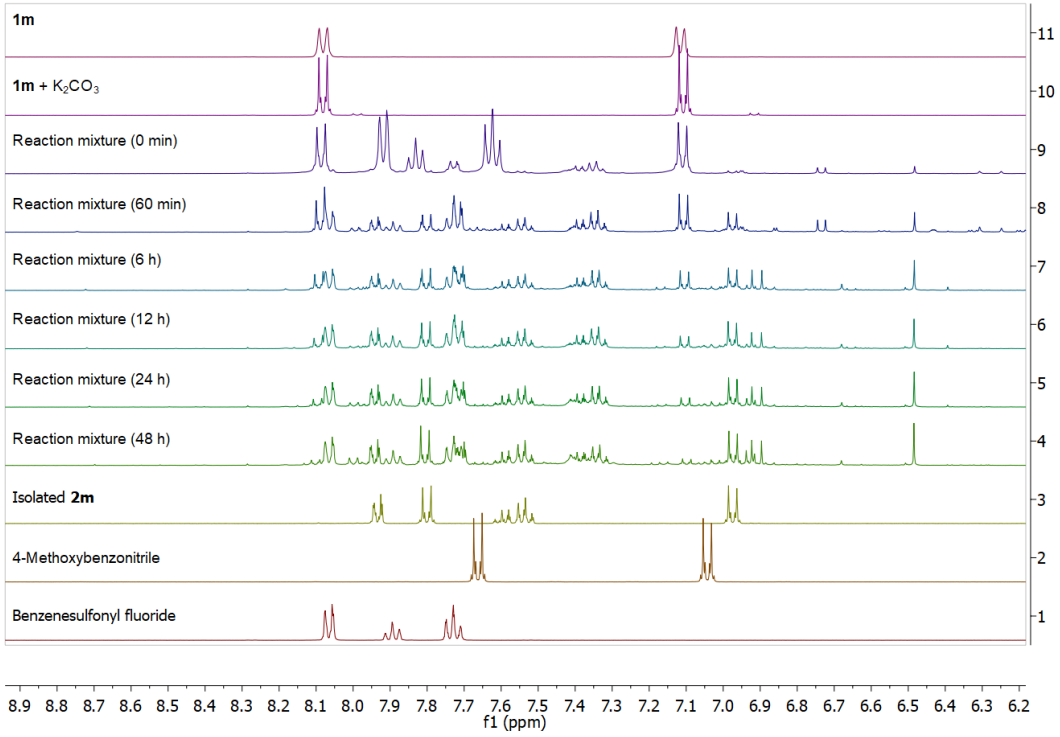


Figure S79. Tracking the conversion of **1m** to **2m**: ^{1}H NMR (400 MHz) of the reaction mixture in the presence of galvinoxyl free radical.

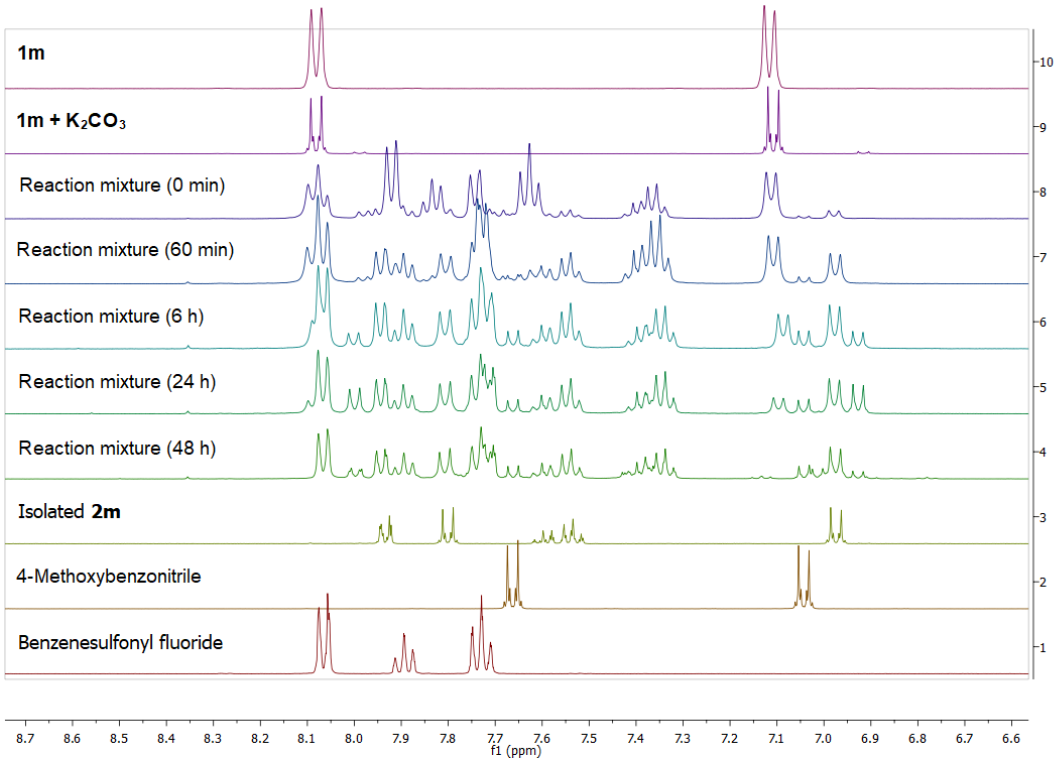


Figure S80. Tracking the conversion of **1m** to **2m**: ^{1}H NMR (400 MHz) of the reaction mixture in the presence of TEMPO.

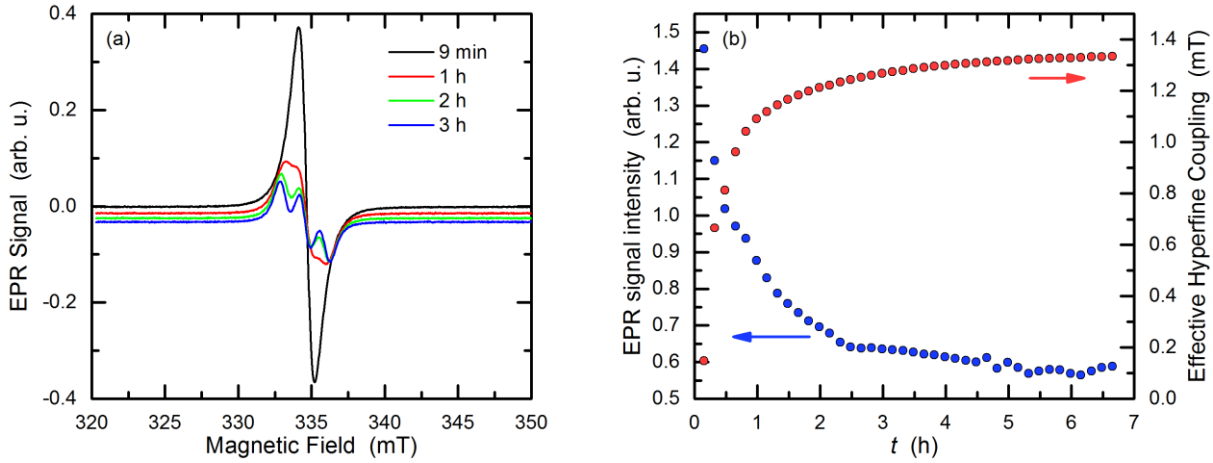


Figure S81. Tracking the conversion of **1m** to **2m** in the presence of TEMPO: Time dependence of the EPR signal of TEMPO in the reaction mixture. (a) Selected EPR spectra of TEMPO in the reaction mixture collected at 9 min, 1 h, 2 h and 3 h after the start of the reaction. (b) Time dependence of the EPR signal intensity (blue circles), and the effective hyperfine coupling – ^{14}N hyperfine splitting of the EPR spectra (red circles).

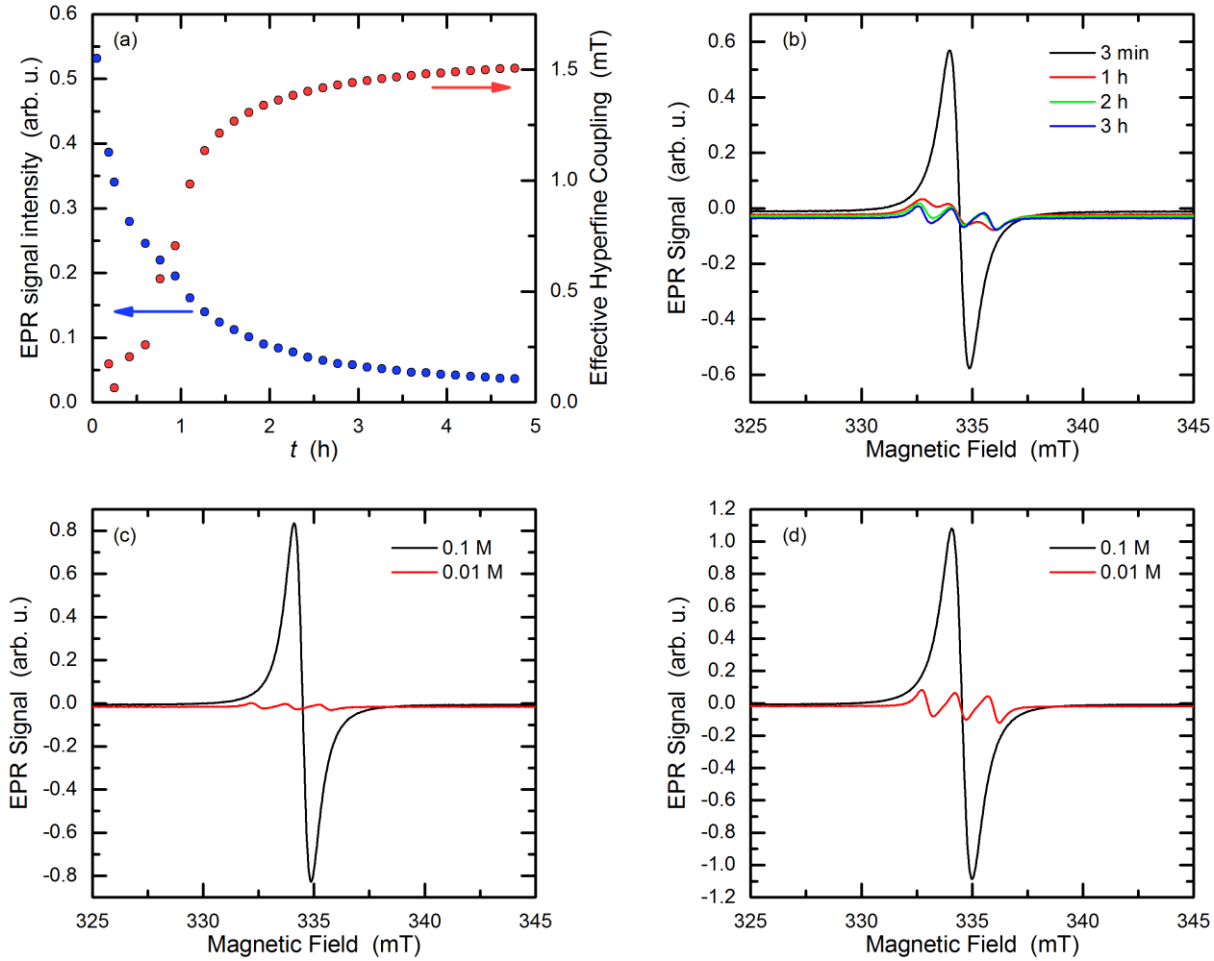


Figure S82. X-band EPR measurements of TEMPO and NFSI in MeCN. (a) Reaction time dependence of TEMPO EPR signal intensity (blue circles) and the effective ^{14}N hyperfine coupling constant determined from the splitting of the EPR spectra (red circles). (b) Selected TEMPO EPR spectra at different reaction times – 3 min, 1 h, 2 h and 3 h. (c) EPR spectra of TEMPO in MeCN at 0.1 M and 0.01 M concentrations. (d) EPR spectra of TEMPO in toluene at 0.1 M and 0.01 M concentrations.

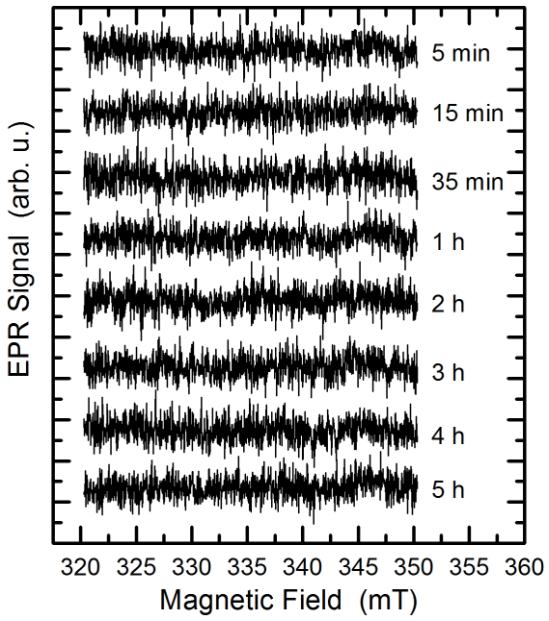


Figure S83. Tracking the conversion of **1m** to **2m**: The EPR measurements of the reaction mixture without TEMPO at selected times. No EPR signal is observed.

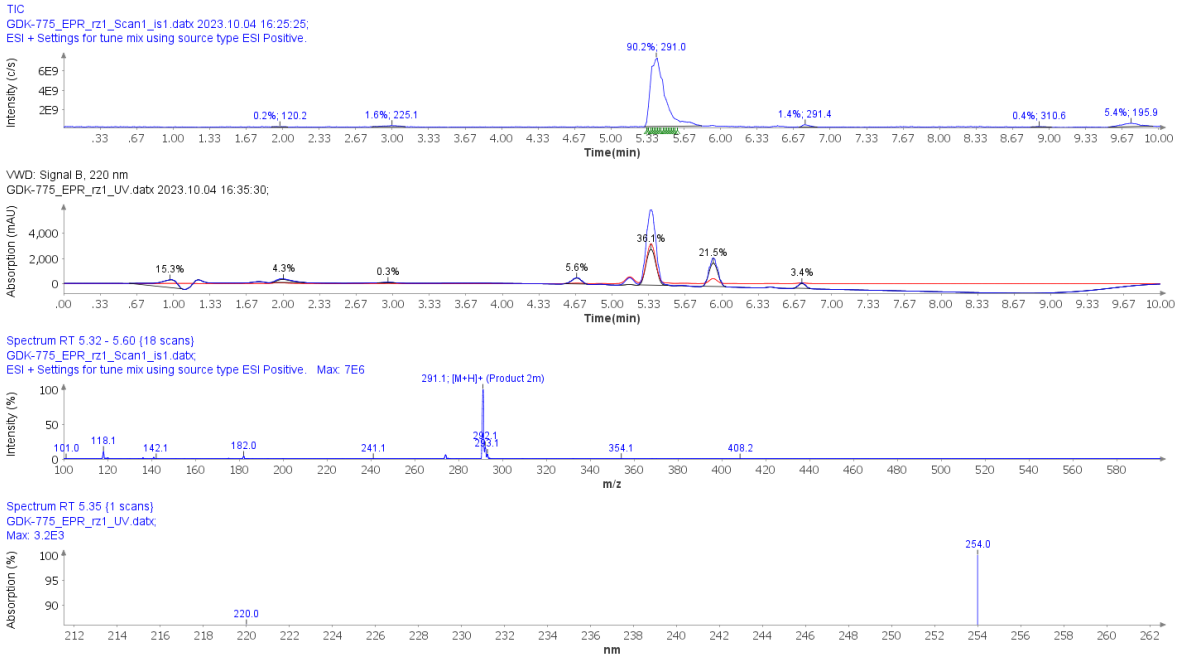


Figure S84. Tracking the conversion of **1m** to **2m** in the presence of TEMPO**:** LC-MS of the reaction mixture from EPR control experiment after 6 h. **2m** was detected ($[M+H]^+$ = 291.1).

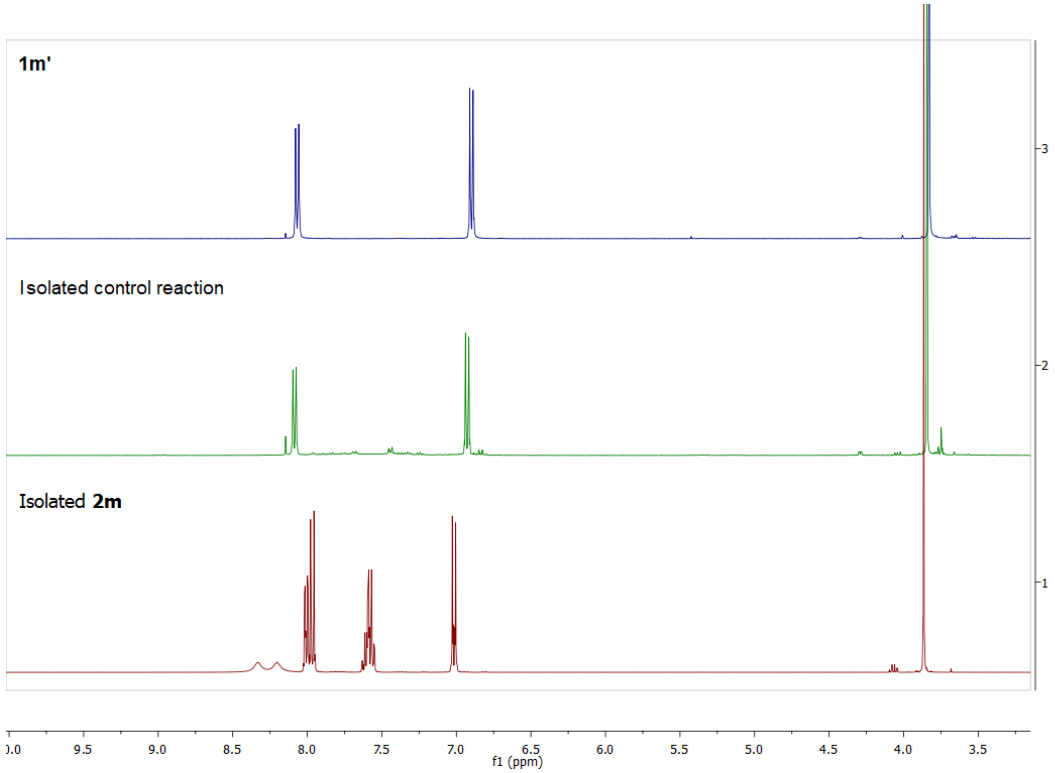


Figure S85. ^{1}H NMR (400 MHz, acetone-d_6) of control experiment – reaction of KAT **1m'** with NFSI. No **2m** was detected.

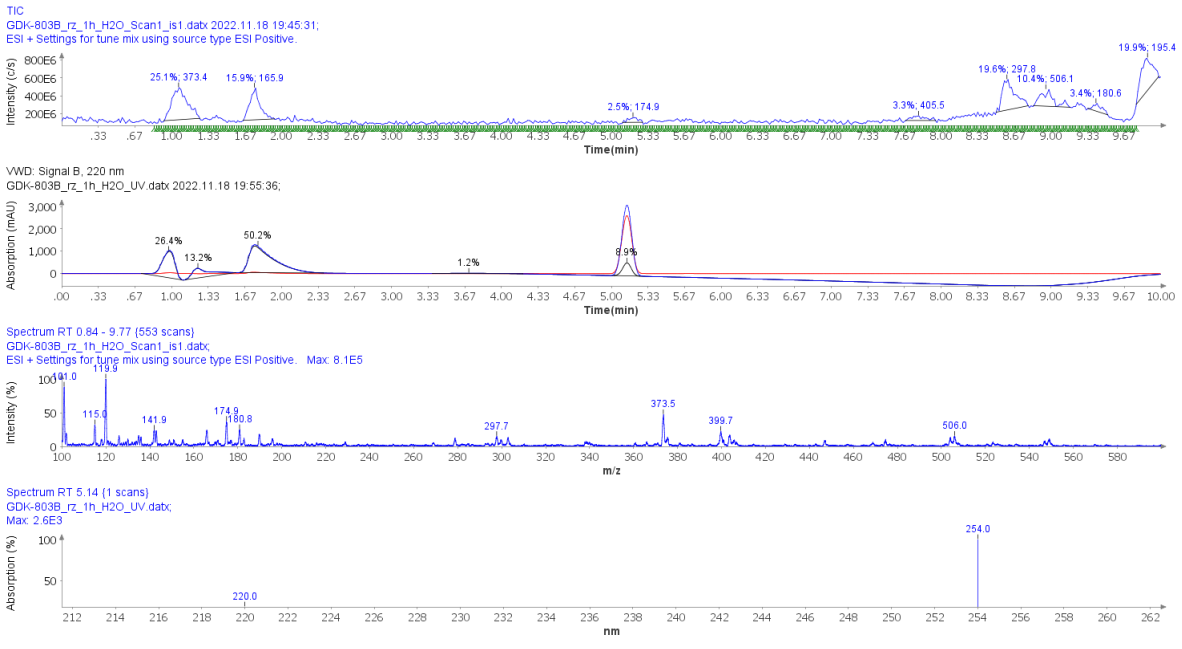


Figure S86. LC-MS of control experiment – reaction of 4-methoxybenzonitrile **1m''** with dibenzenesulfonimide. No **2m** was detected ([M+H]$^{+}$ = 291.1).

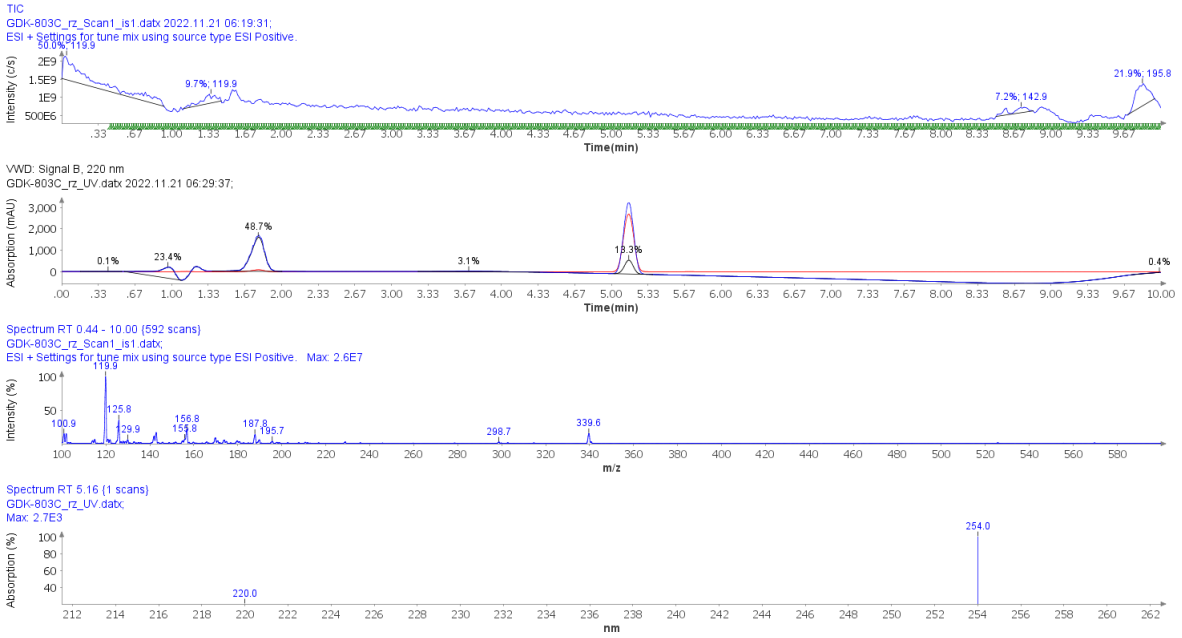


Figure S87. LC-MS of control experiment – reaction of 4-methoxybenzonitrile **1m''** with benzenesulfonamide. No **2m** was detected ($[M+H]^+$ = 291.1).

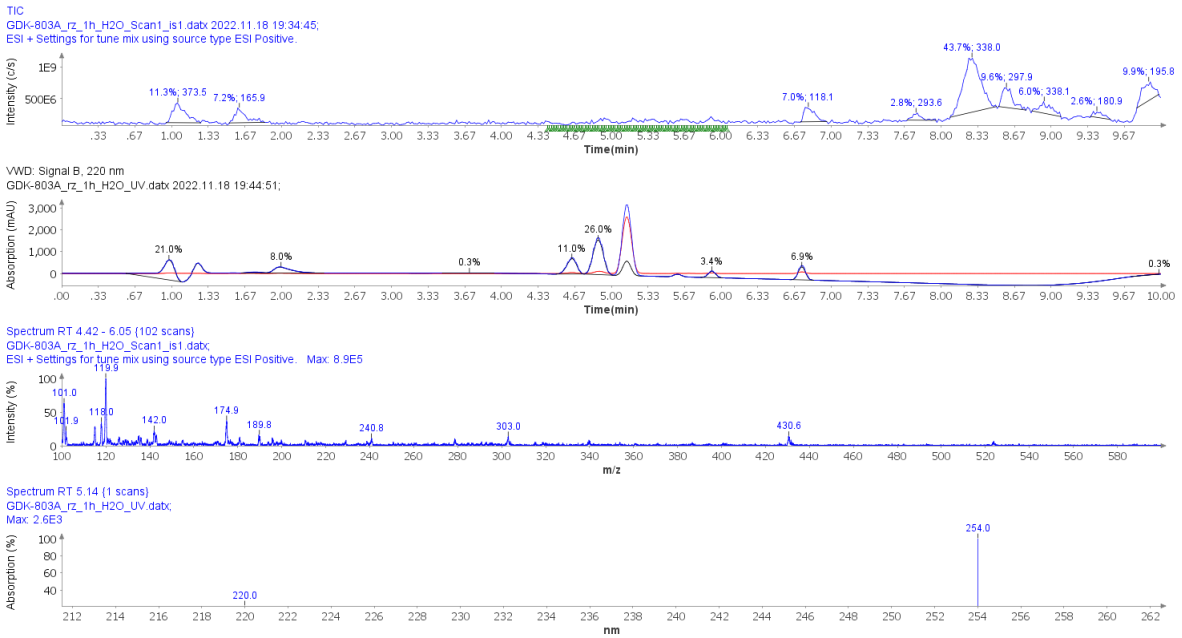


Figure S88. LC-MS of control experiment – reaction of 4-methoxybenzonitrile **1m''** with NFSI. No **2m** was detected ($[M+H]^+$ = 291.1).

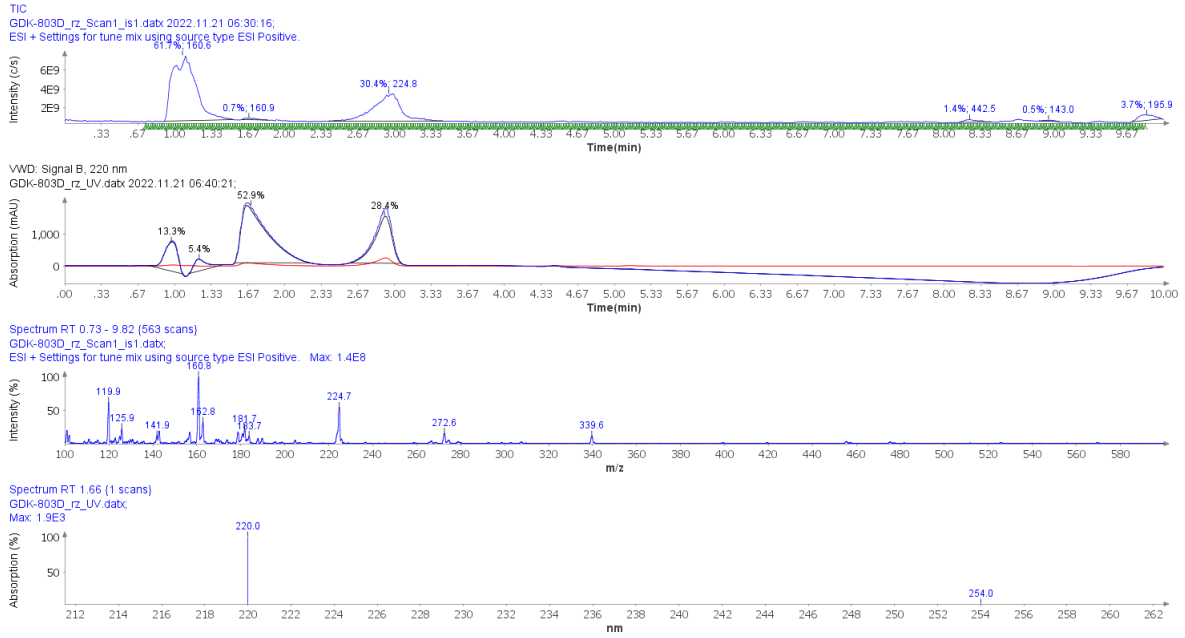


Figure S89. LC-MS of control experiment – reaction of pTIM **1m** with dibenzenesulfonimide in the presence of Selectfluor. No **2m** was detected ($[M+H]^+$ = 291.1).

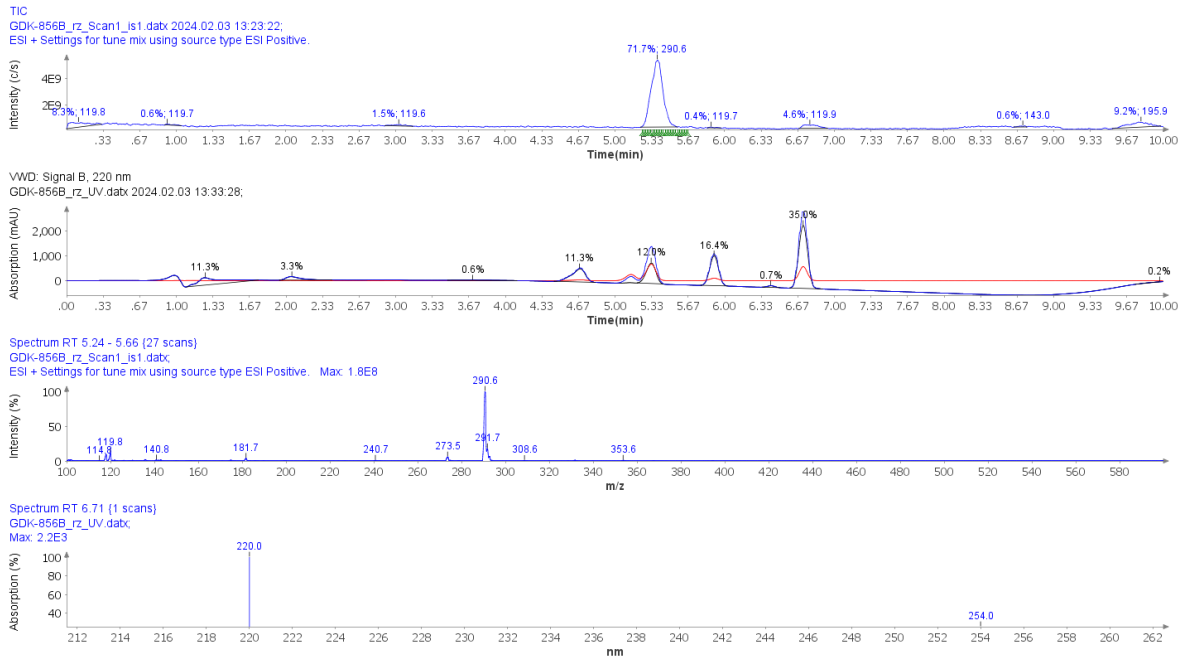


Figure S90. LC-MS of control experiment – reaction of pTIM **1m** with NFSI in the presence of KF as base. **2m** was detected ($[M+H]^+$ = 291.1).

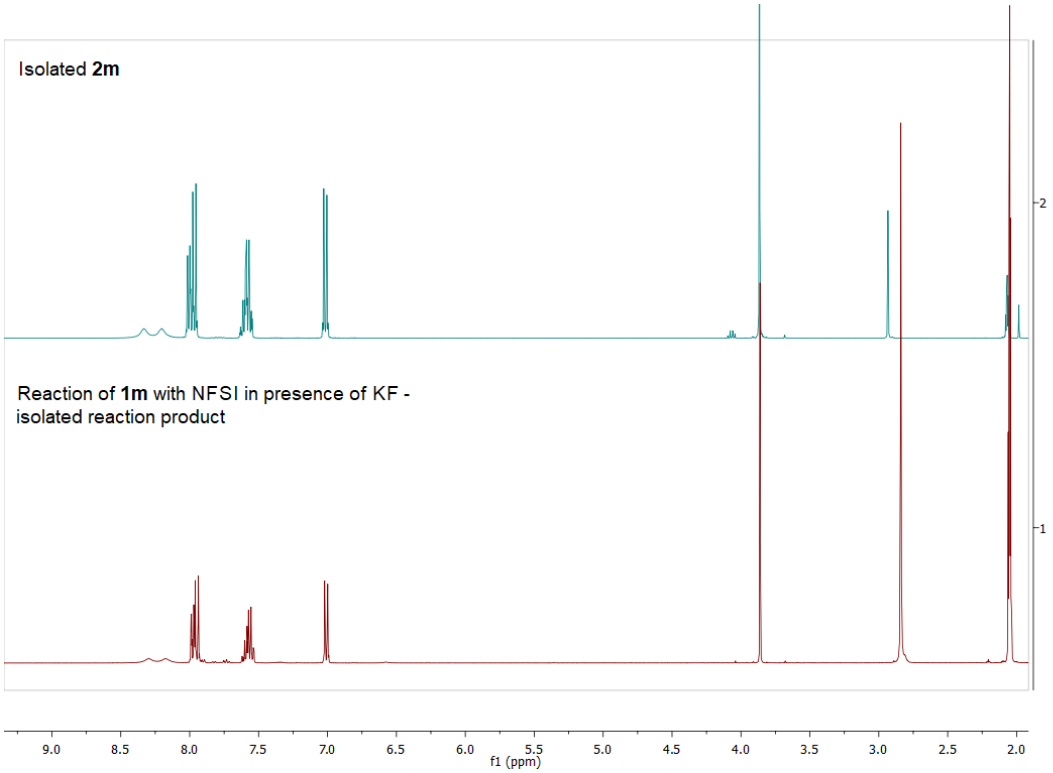


Figure S91. ^{1}H NMR (400 MHz, Acetone-d_6) of control experiment – reaction of pTIM **1m** with NFSI in the presence of KF as base.

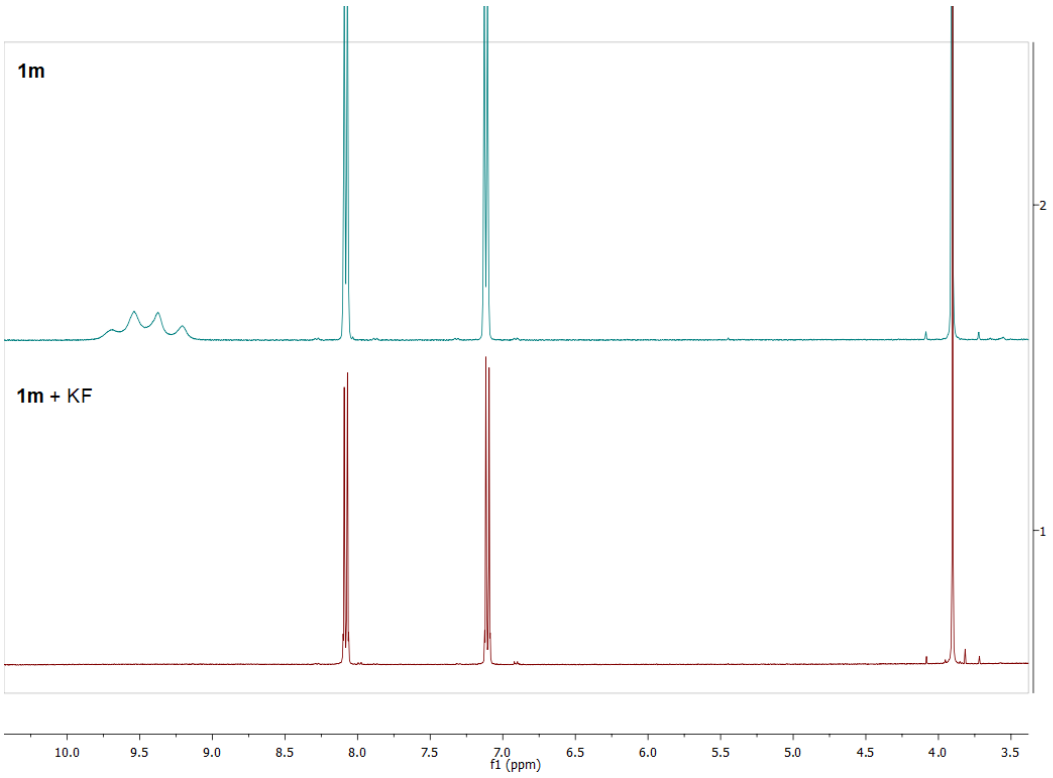


Figure S92. ^{1}H NMR (400 MHz, MeCN-d_3) of control experiment – deprotonation of pTIM **1m** with KF as base.

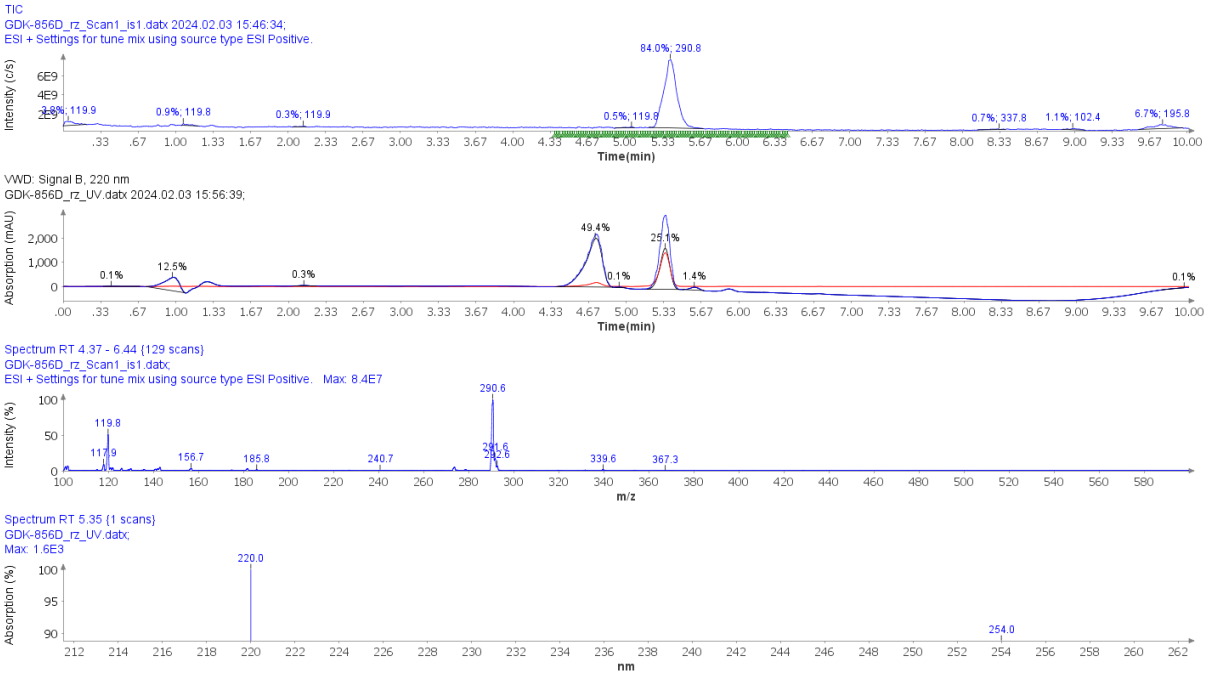


Figure S93. LC-MS of control experiment – reaction of pTIM **1m** with $PhSO_2NHF$ in the presence of K_2CO_3 as base. **2m** was detected ($[M+H]^+$ = 291.1).

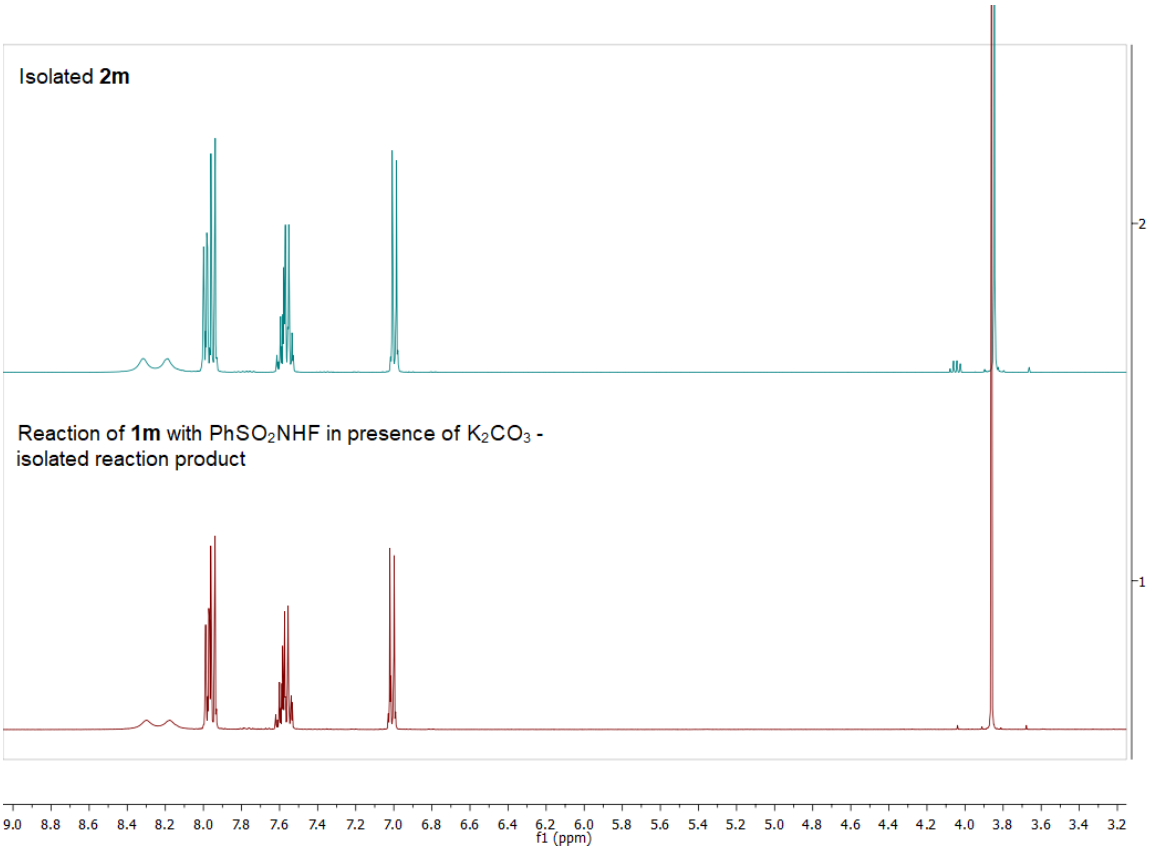


Figure S94. ^1H NMR (400 MHz, Acetone-d_6) of control experiment – reaction of pTIM **1m** with $PhSO_2NHF$ in the presence of K_2CO_3 as base.

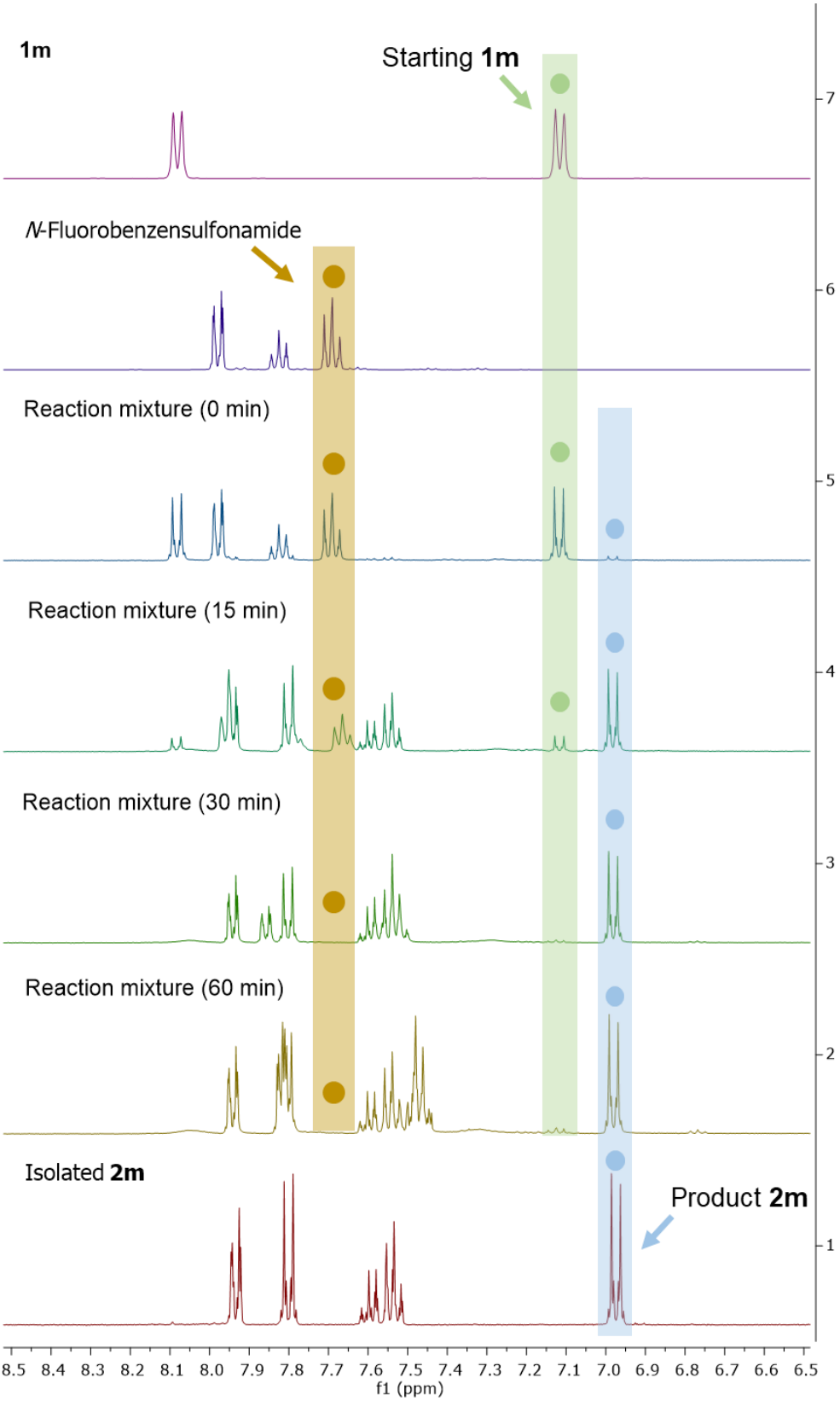


Figure S95. ^{1}H NMR (400 MHz, Acetone-d_6) of control experiment – reaction of pTIM **1m** with $PhSO_2NHF$ in the presence of K_2CO_3 as base (reaction progress monitoring).

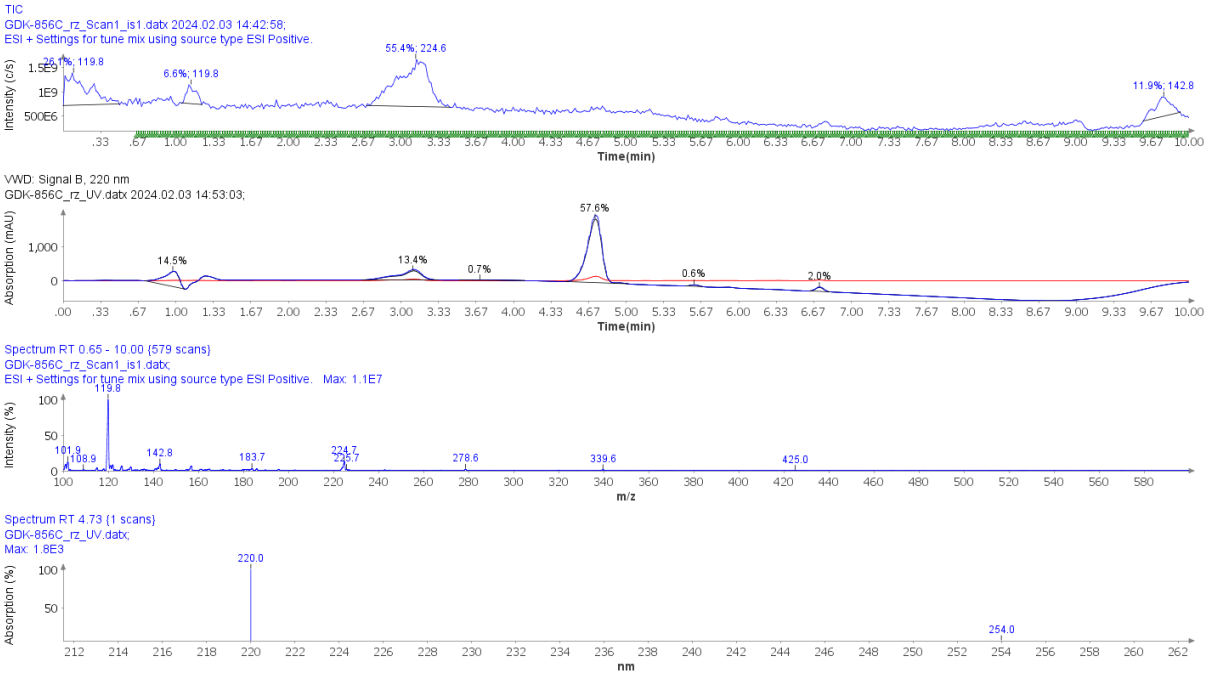


Figure S96. LC-MS of control experiment – reaction of pTIM **1m** with $PhSO_2NHF$ in the absence of K_2CO_3. **2m** was not detected ($[M+H]^+$ = 291.1).

General Procedure for Mechanism Investigation by LC-HRMS

To a solution of NFSI (3.2 mg, 0.01 mmol) and K_2CO_3 (1.4 mg, 0.01 mmol) in MeCN (20 mL), **1m** (2.0 mg, 0.01 mmol; 0.1 mg/mL = 0.0005 M), H_2O (200 µL) were added, and sonicated on ultrasonic bath for 5 min to ensure complete dissolution of all reagents. Sample was analyzed after 1.5 h either by direct injection HRMS or by LC-HRMS (Figure S97, Tables S6 and S7).

For the (LC-)HRMS analysis HPLC Thermo Scientific UltiMate™ 3000 modular system coupled to Thermo Scientific Q Exactive Plus LC-MS/MS mass spectrometer was used. The general LC method used a Waters Acquity UPLC® BEH C18 column (2.1 × 50 mm, 1.7 µm) and Waters Vanguard UPLC® BEH C18 precolumn (2.1 × 5 mm, 1.7 µm) thermostated at 40 °C, with: injection volume, 1 µL; flow rate, 0.4 mL/min; detector λ, 220 and 254 nm; mobile phase A: 0.1% HCOOH (v/v) in MilliQ water; mobile phase B: 0.1% HCOOH (v/v) in MeCN. Gradient: 0–2 min, 5% B; 2–7 min, 5%–95% B; 7–9 min, 95% B; 9–9.5 min, 5% B; 9.5–12 min, 5% B. Data was analyzed using Freestyle v1.6 software (Thermo Scientific).

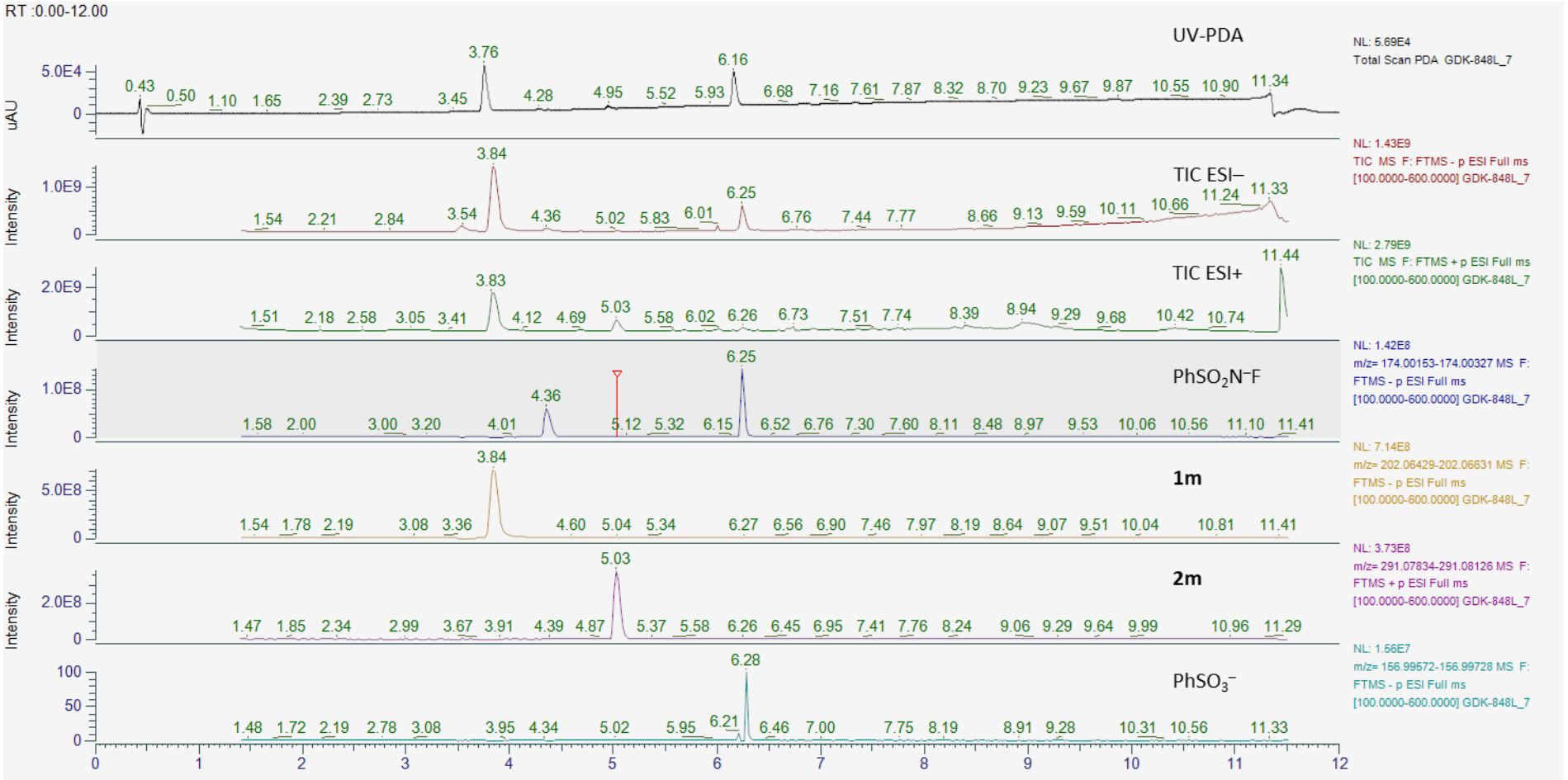


Figure S97. LC-HRMS analysis – reaction of pTIM **1m** with NFSI/K_2CO_3 in MeCN + H_2O (1% v/v). For starting materials, intermediates and side products identified see Table S6.

Table S6. LC-HRMS analysis – reaction of pTIM **1m** with NFSI/K_2CO_3 in MeCN + H_2O (1% v/v). Detected starting materials, intermediates and products.

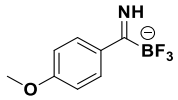
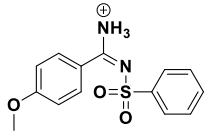
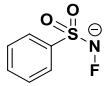
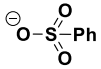
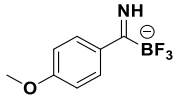
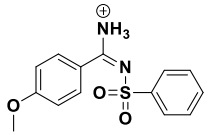
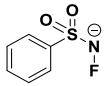
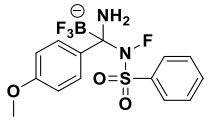
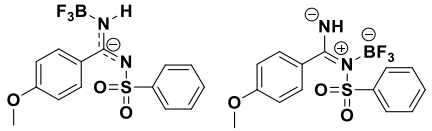
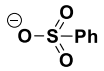
Detected ion	Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank
	202.0653	$C_8H_8ON^{11}BF_3$	26.5023440720565	4.50	-1.86	202.06565	1
	291.0793	$C_{14}H_{15}O_3N_2{}^{32}S$	40.9212479869484	8.50	-1.84	291.07979	1
	174.0024	$C_6H_5O_2NF^{32}S$	29.9232928561241	4.50	-3.76	174.00305	1
	156.9958	$C_6H_5O_3{}^{32}S$	26.1192882693514	4.50	-4.55	156.99649	1

Table S7. HRMS analysis, direct injection – reaction of pTIM **1m** with NFSI/K_2CO_3 in MeCN + H_2O (1% v/v). Detected starting materials, intermediates (Figures S98–S100) and products.

Detected ion	Peak Mass	Display Formula	Combined Fit	RDB	Delta [ppm]	Theo. mass	Rank
	202.0650	$C_8H_8ON^{11}BF_3$	43.2758516321631	4.50	-3.22	202.06565	1
	291.0797	$C_{14}H_{15}O_3N_2{}^{32}S$	29.2107684135348	8.50	-0.27	291.07979	1
	174.0022	$C_6H_5O_2NF^{32}S$	25.7371029082838	4.50	-5.17	174.00305	1
	377.0755	$C_{14}H_{14}O_3N_2{}^{11}BF_4{}^{32}S$	29.0113516951809	7.50	-1.19	377.07598	1
	357.0696	$C_{14}H_{13}O_3N_2{}^{11}BF_3{}^{32}S$	29.0662861995331	8.50	-0.39	357.06975	1
	156.9955	$C_6H_5O_3{}^{32}S$	21.7165987727861	4.50	-6.59	156.99649	1

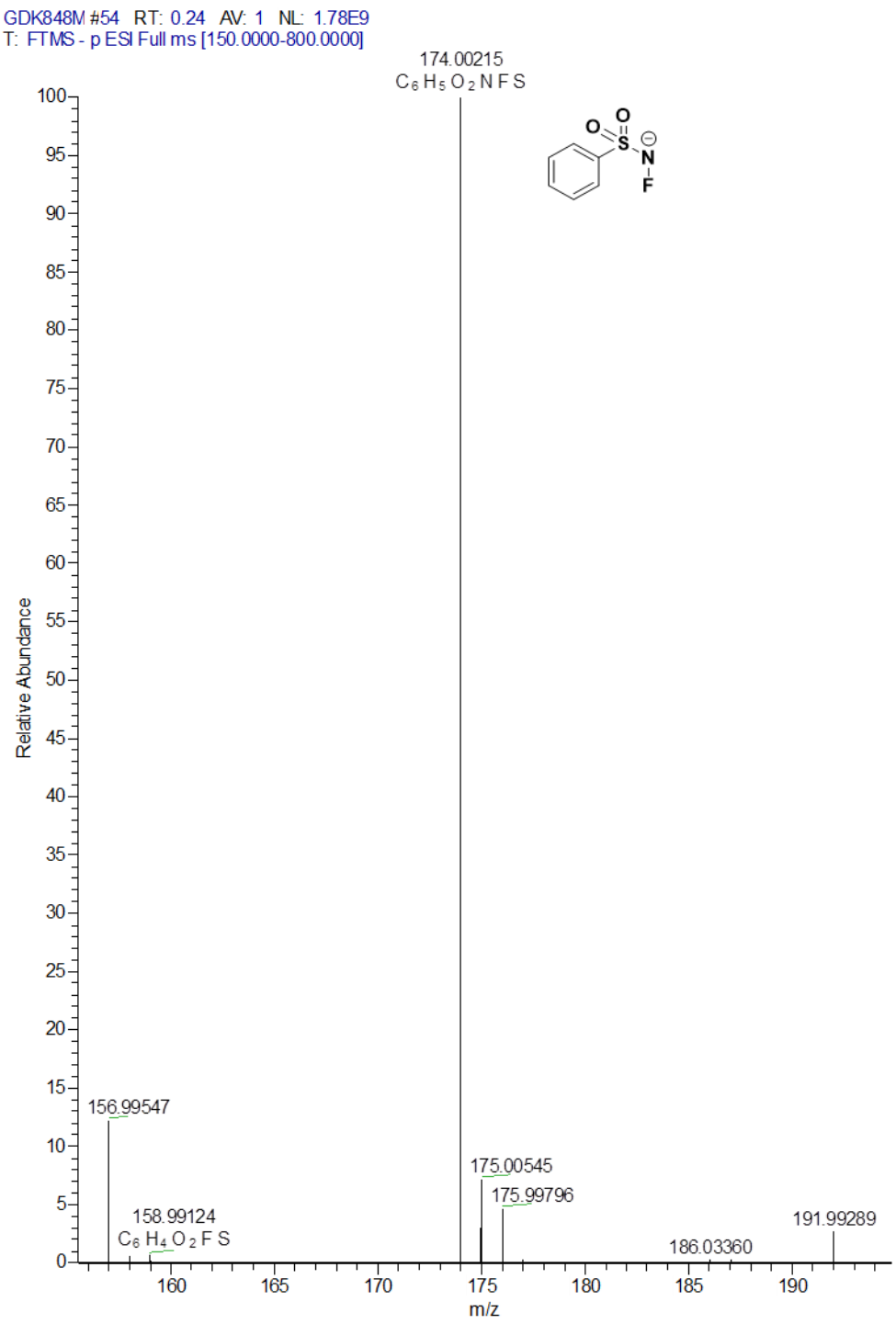


Figure S98. HRMS spectra of *N*-fluorobenzensulfonamide – intermediate **I** (Mechanism **B**, Figure 3) from direct injection: reaction of pTIM **1m** with NFSI/K_2CO_3 in MeCN + H_2O (1% v/v).

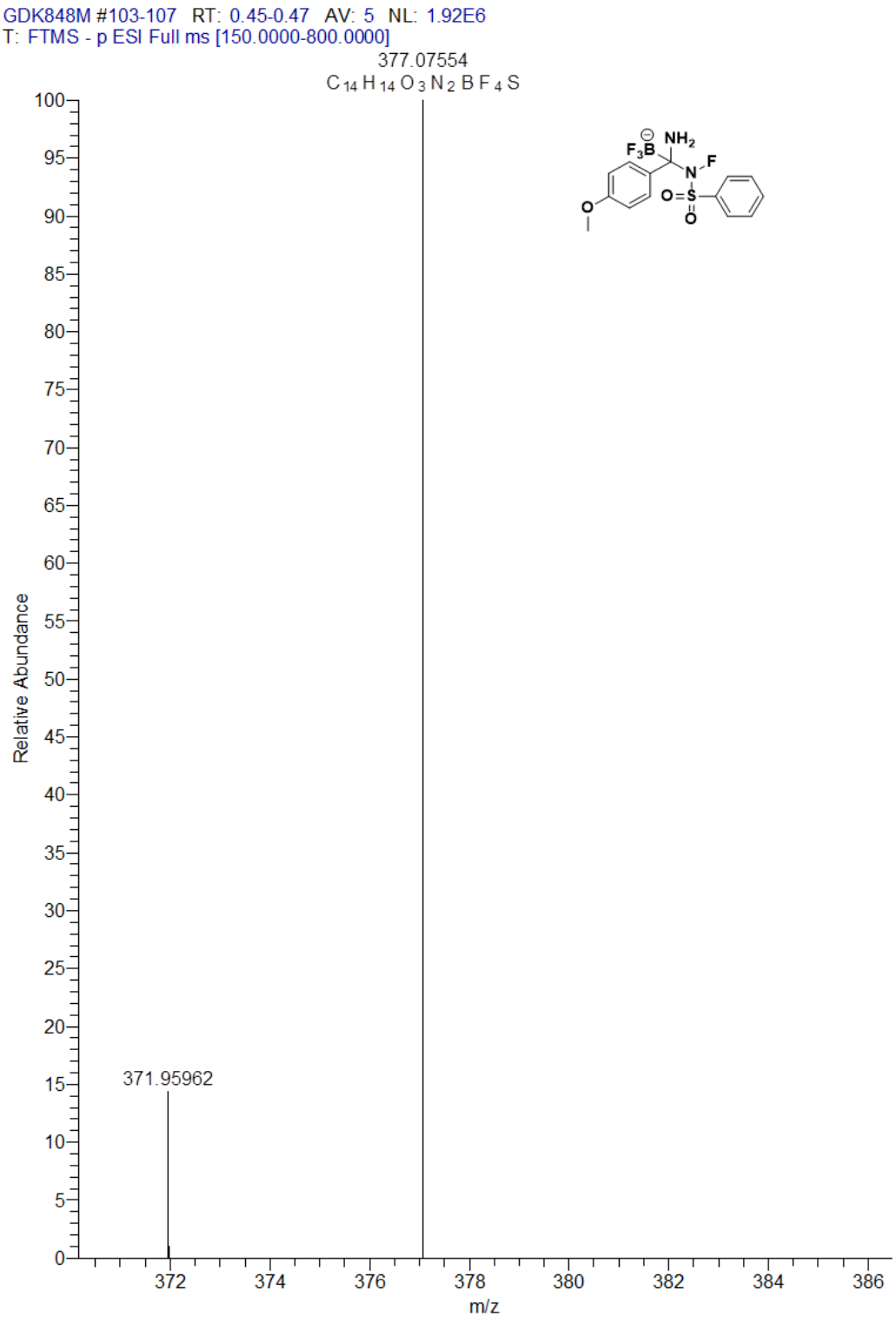


Figure S99. HRMS spectra of intermediate **III** (Mechanism **B**, Figure 3) from direct injection: reaction of pTIM **1m** with NFSI/K_2CO_3 in MeCN + H_2O (1% v/v).

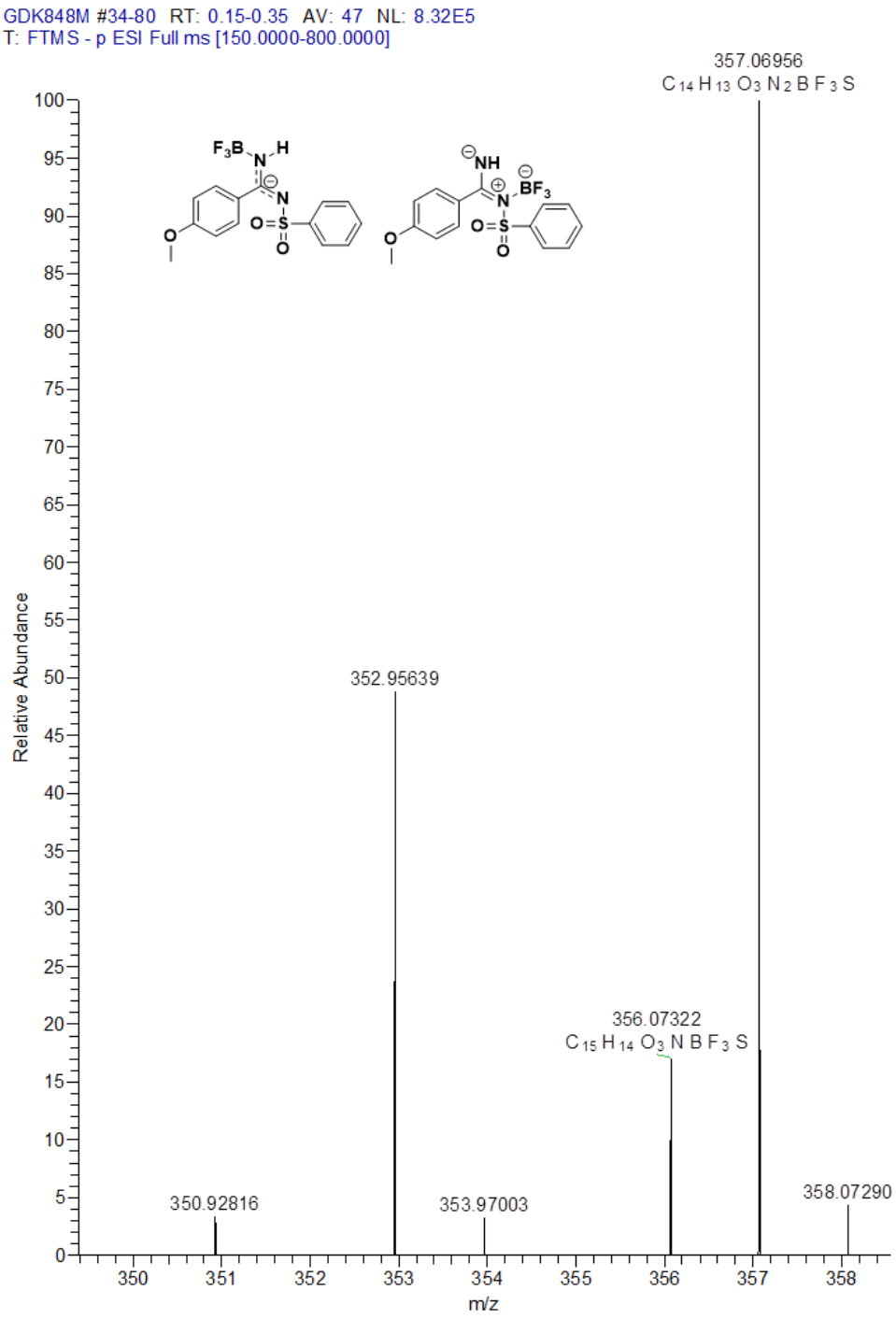


Figure S100. HRMS spectra of intermediates **VII** (Mechanism **A**, Figure 3) and **VIII** (Mechanism **B**, Figure 3) from direct injection: reaction of pTIM **1m** with NFSI/K_2CO_3 in MeCN + H_2O (1% v/v).

8. DFT study

8.1. Computational Details

Density Functional Theory (DFT) calculations were performed with the Gaussian 16 package.[S25] The quantum mechanics calculations were performed within the framework of Density Functional Theory (DFT) by using the ωB97X-D functional.[S26] For all atoms the 6-311+G++(d,p) basis set was used.[S27] Solvent effects of MeCN were included using the implicit solvation model SMD with default parameters.[S28] Free energies were computed at a concentration of 1 M and a temperature of 298.15 K. The structures of the reported mechanisms are also available in the ioChem-BD repository,[S29] and can be accessed via the following link: https://iochem-bd.urv.es/browse/handle/100/2172.

8.2. Analysis of pTIM Deprotonation: Scan of Potential Energy Surface

As discussed in the main text, the deprotonation of pTIM by KOH base to yield compound **II** (Figure 3A) proceeds downhill in energy without barrier in the corresponding potential free-energy surface. Figure S101 shows the detailed, relaxed energy scan of the proton transfer from pTIM reactant to the hydroxide of the base that uses the distance between the proton and the oxygen of the hydroxide as a reaction coordinate. In those cases, we can assume a low Gibbs free-energy barrier of ~3.5 kcal·mol^{-1} associated with the diffusion process of reactants. This was also experimentally observed by ^{1}H NMR (Figure S102).

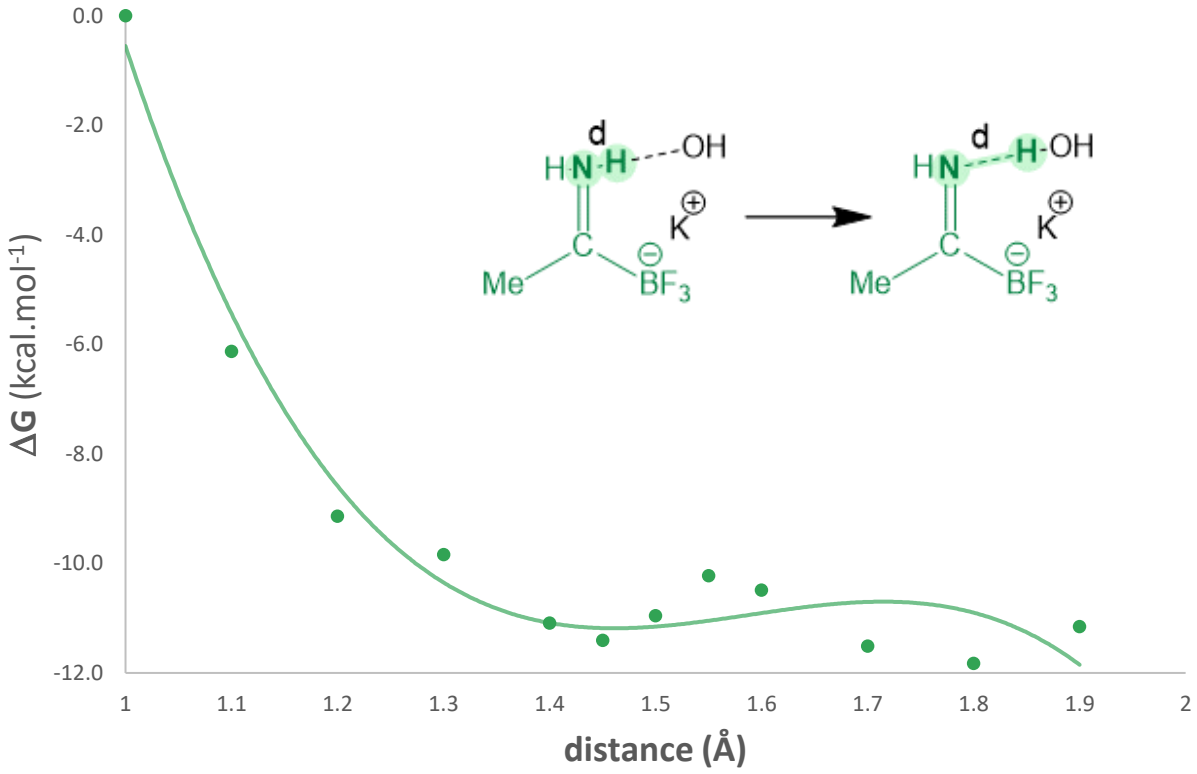


Figure S101. Free-energy scan of the proton transfer from the pTIM to the hydroxide base (Figure S102), using the distance (Å) between a N-bond hydrogen of pTIM and the oxygen of the hydroxide as reaction coordinate. Relative energies in kcal·mol^{-1}.

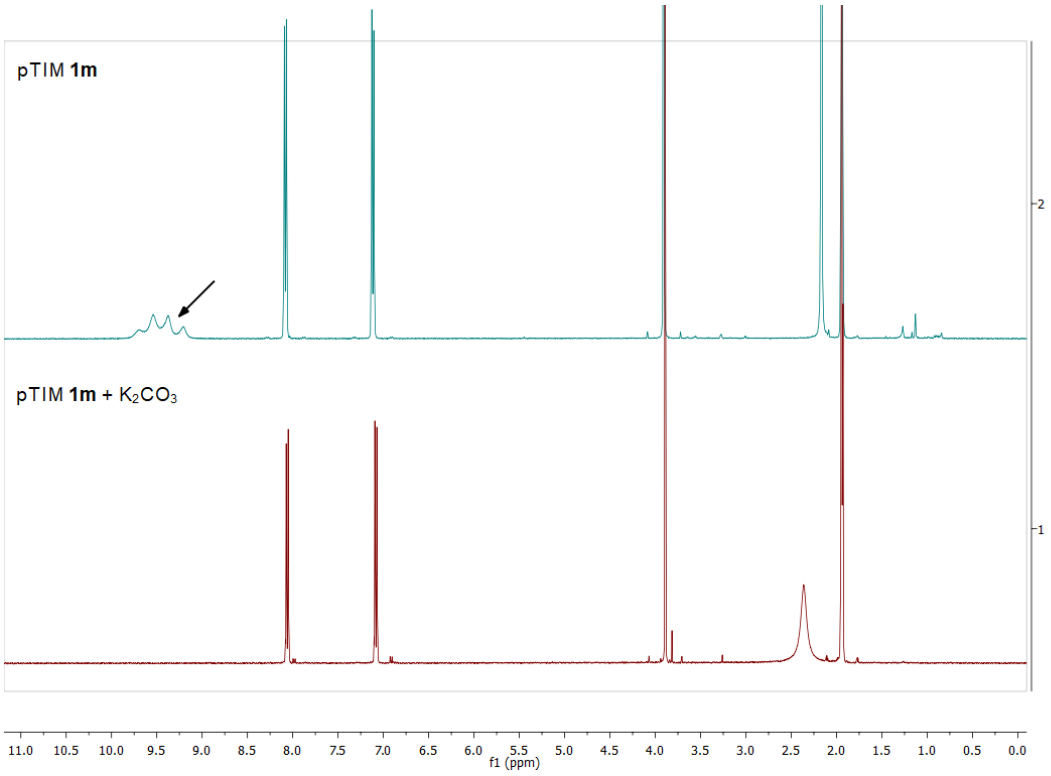


Figure S102. ^{1}H NMR (400 MHz, MeCN-d_3) of control experiment – deprotonation of pTIM **1m** with K_2CO_3 as base.

8.3. Analysis of NFSI Desulfonylation by the Base: Scan of Potential Energy Surface

As discussed in the main text, the activation of NFSI as nucleophile can proceed via desufonylation by KOH base, leading to the formation of the species **I**, which initiates the mechanism **B**. Figure S103 shows a detailed relaxed free-energy scan of this process, using the distance between the sulfur atom and the oxygen of the potassium hydroxide as the reaction coordinate. The energy scan reveals a smooth, downhill energy profile, indicating that the activation occurs without a significant energy barrier. This suggests that the rate of desulfonylation step is likely governed by the diffusion or association of reactants rather than the chemical step itself. In this case, we can also assume a low Gibbs free-energy barrier of ~3.5 kcal·mol^{-1} [1] associated with the diffusion process of reactants.

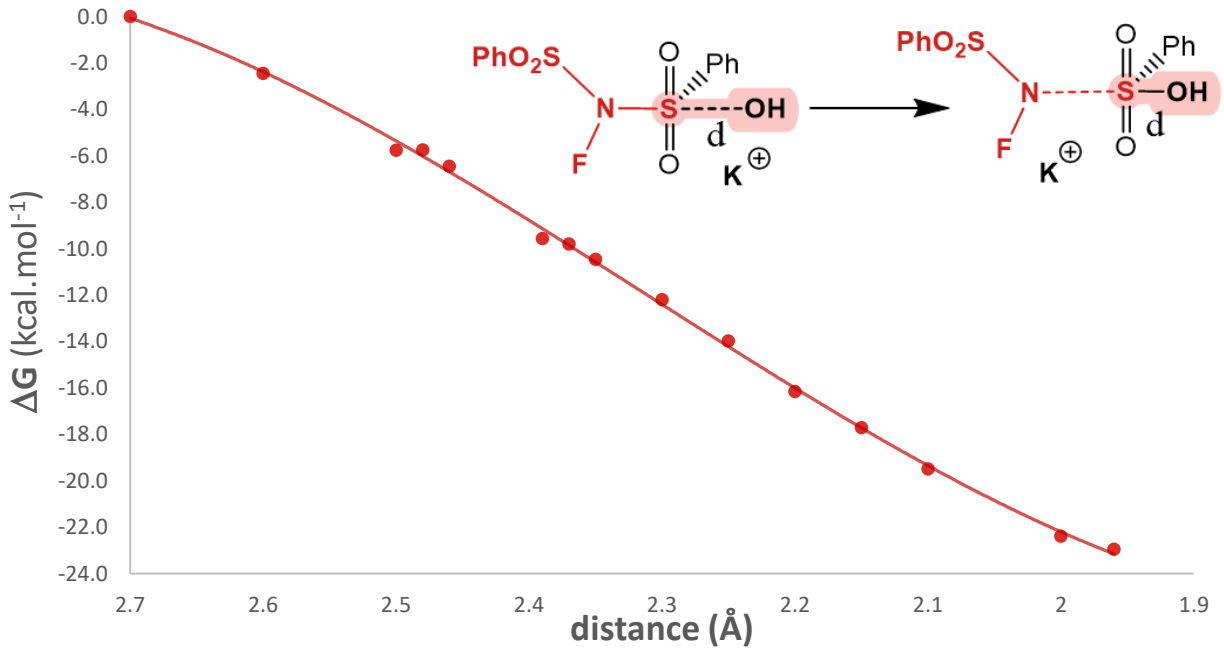


Figure S103. Free-energy scan of desulfonylation of NFSI by hydroxide base, using the distance (Å) between the sulfur atom and the oxygen of the hydroxide as reaction coordinate. Relative energies in kcal·mol^{-1}.

8.4. 3D Structures of the Key Transition States and Intermediates in Mechanisms A and B

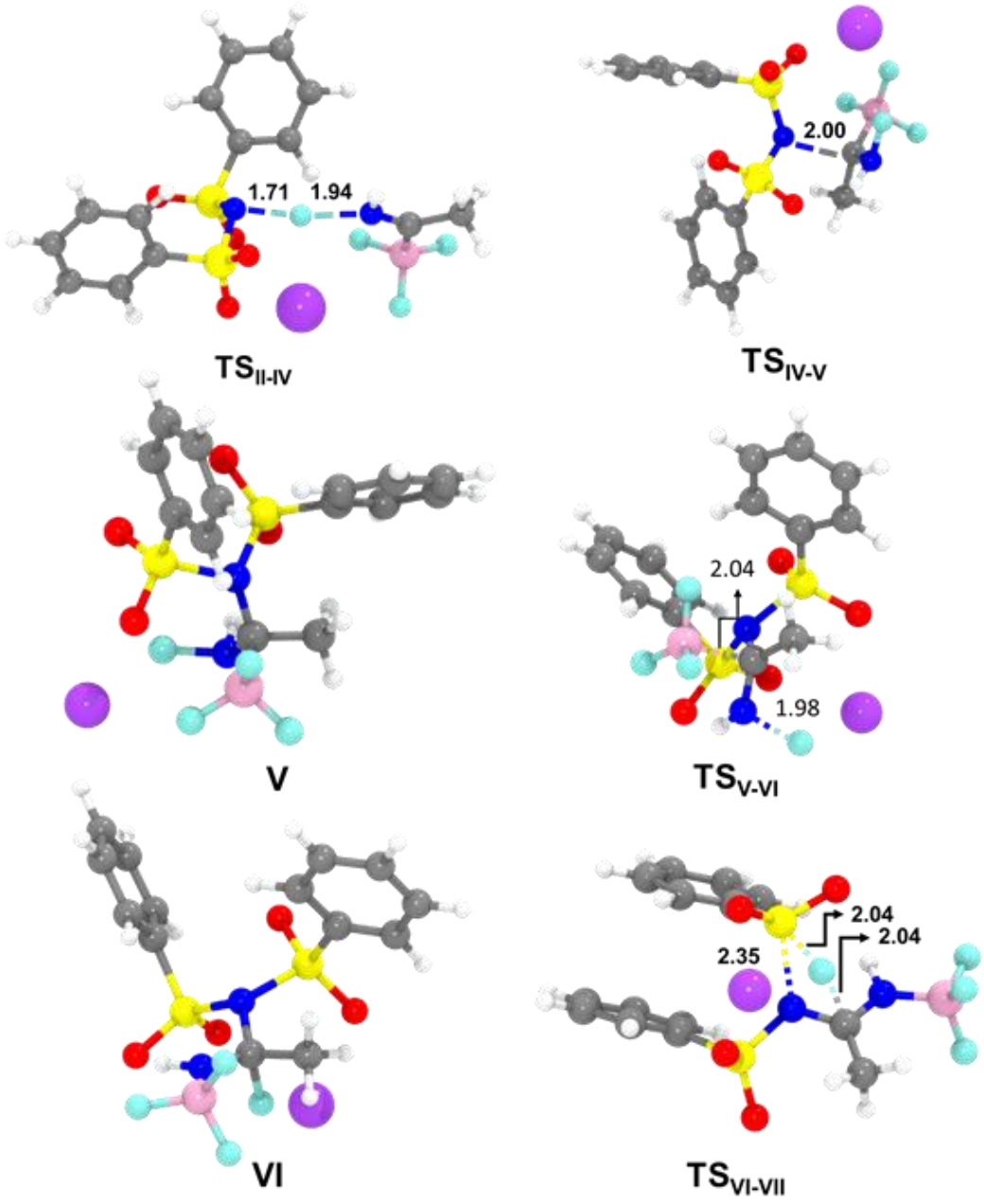


Figure S104. 3D representation of the optimized geometries for key intermediates (**V** and **VI**) and transition states (**TS$_{II-IV}$**, **TS$_{IV-V}$**, **TS$_{V-VI}$** and **TS$_{VI-VII}$**) in mechanism A. The breaking and forming bonds of transition states are represented with dotted squared lines. Selected distances are given in Å. Color code: nitrogen (blue), hydrogen (white), carbon (grey), sulphur (yellow), potassium (purple), fluorine (light blue), oxygen (red), and boron (pink).

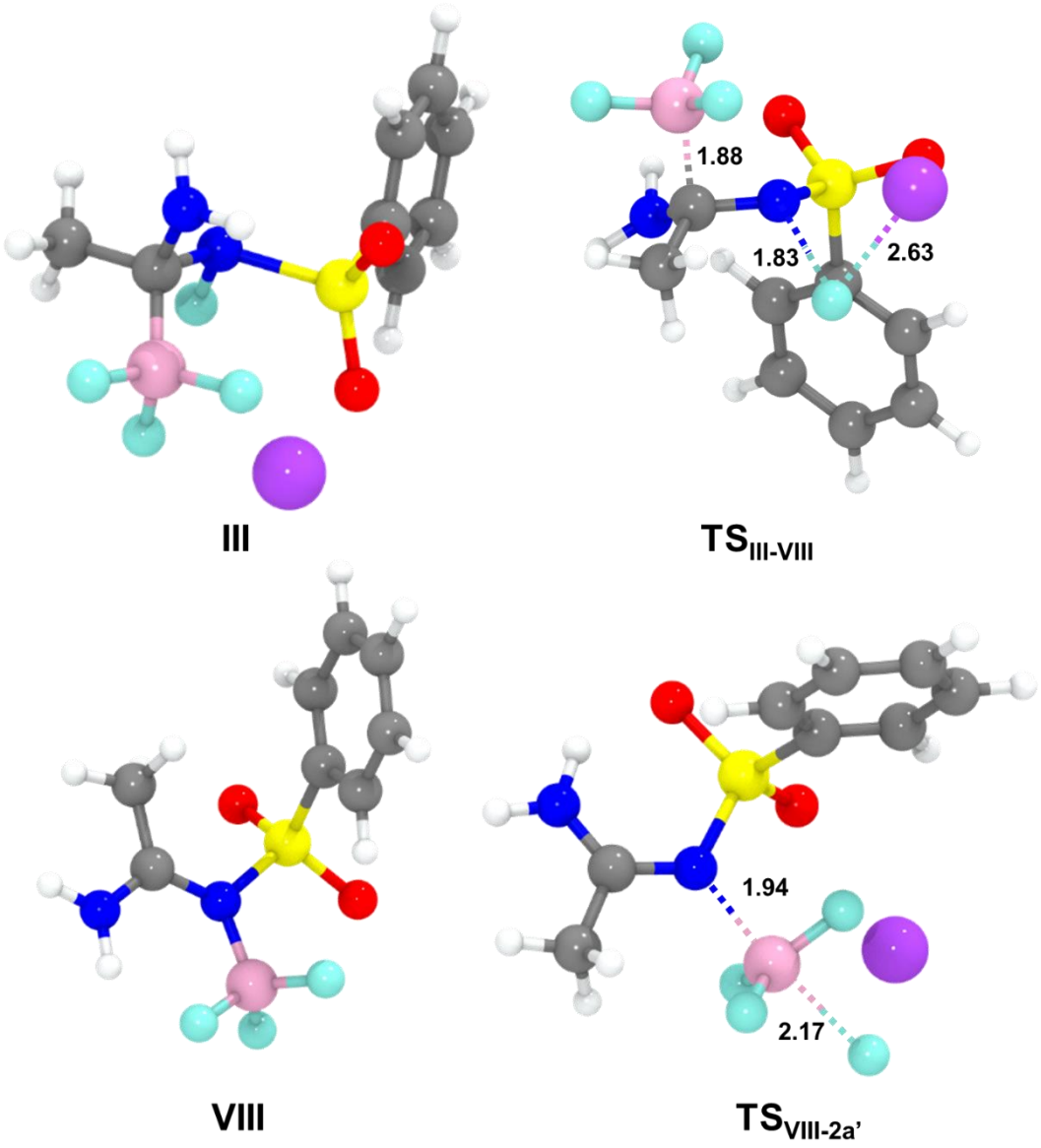


Figure S105. 3D representation of the optimized geometries for key intermediates (**III** and **VIII**) and transition states (**TS**$_{\text{III-VIII}}$ and **TS**$_{\text{VIII-2a'}}$) in mechanism **B**. Selected distances are given in Å. Color code: nitrogen (blue), hydrogen (white), carbon (grey), sulfur (yellow), potassium (purple), fluorine (light blue), oxygen (red), and boron (pink).

8.5. Computational Evaluation of the Thermodynamics of Possible Reactions Between Side Products

BF_3 + KOH ⟶ $HOBF_3K$ ΔG = -79.0

PhO_2OH + KF ⟶ PhO_2OK + HF ΔG = -19.8

BF_3 + KF ⟶ KBF_4 ΔG = -54.7

KBF_4 + KOH ⟶ $HOBF_3K$ + KF ΔG = -24.7

Figure S106. Computed Gibbs free-energies (ΔG) in kcal·mol^{-1} for possible exergonic reactions between side products.

8.6. Computational Analysis of the Stereoselectivity for Mechanisms A and B

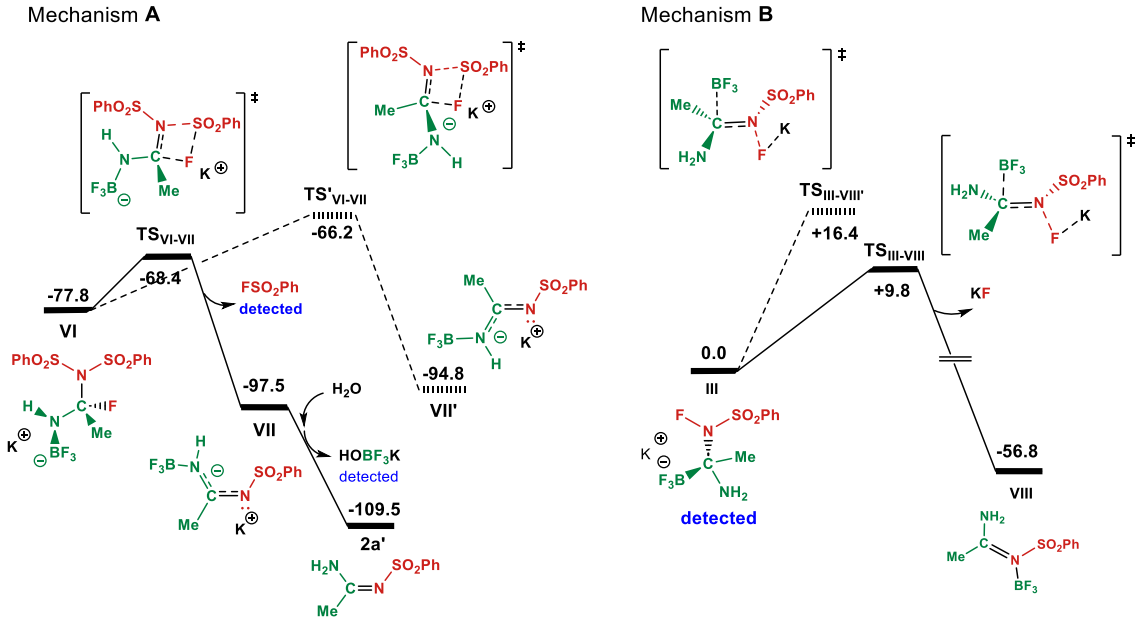


Figure S107. DFT-derived, free-energy profile (kcal·mol^{-1}) of the proposed stereoselectivity-determining steps in mechanisms **A** and **B**, yielding the selective formation of *N*-sulfonyl amidines with the sulfonyl and amino groups in *cis*. The zero of energies is set at species **II** for mechanism **A** and at species **I** for mechanism **B**.

8.7. Cartesian Coordinates and Potential Electronic Energies of the Optimized Structures.

Cartesian coordinates are reported in Å and absolute electronic energies (Eopt) in Hartrees.

BF_3
Eopt -324.494547288
B -0.000241 0.000702 -0.000190
F 1.029845 0.854255 0.000035
F -1.255225 0.463969 0.000035
F 0.225513 -1.318613 0.000035

BF_4K
Eopt -1024.43132168
B 1.059130 -0.000154 0.000143
F 0.180251 -0.018230 1.149973
F 1.827366 1.185421 -0.000494
F 1.881736 -1.147652 0.000606
K -2.206500 -0.000053 0.000021
F 0.180408 -0.019340 -1.150208

$HOBF_3K$
Eopt -1000.39294098
B 1.016857 0.024369 0.000206
F 1.851051 -0.037726 1.172497
F 1.879302 0.007909 -1.152729
K -2.186868 -0.013738 0.000054
F 0.186035 -1.177734 -0.031955
O 0.096083 1.123641 0.010591
H 0.450053 2.018000 0.022908

KF
Eopt -699.831711598
F 0.000000 0.000000 -1.583801
K 0.000000 0.000000 0.750222

KOH
Eopt -675.750873140
O -0.000000 -0.000000 1.513074
H -0.000000 -0.000000 2.480056
K 0.000000 0.000000 -0.767613

PhO_2SF
Eopt -879.757912644
S -1.458728 0.000008 0.167996
C 0.374445 0.000005 0.090947
O -2.056264 -1.379830 0.680059
O -2.056350 1.379944 0.679724
C 1.010821 1.230076 0.057640
C 1.010816 -1.230062 0.057599
C 2.401555 1.214419 -0.004621
H 0.459816 2.158474 0.083544
C 2.401554 -1.214402 -0.004662
H 0.459822 -2.158466 0.083485
C 3.089260 0.000007 -0.035829
H 2.940348 2.149616 -0.027831
H 2.940340 -2.149601 -0.027909
H 4.168526 0.000006 -0.084830
F -1.828777 -0.000148 -1.617678

PhO_2SOH
Eopt -855.728945260
S -1.468321 -0.000008 -0.137583
C 0.372593 -0.000004 -0.081097
O -2.037333 1.382020 -0.735931
O -2.037323 -1.382071 -0.735861
C 1.013094 -1.226562 -0.051539
C 1.013085 1.226558 -0.051555
C 2.405241 -1.213566 0.006114
H 0.458836 -2.153073 -0.080393
C 2.405233 1.213574 0.006098
H 0.458822 2.153066 -0.080423
C 3.094007 0.000006 0.035515
H 2.944514 -2.149015 0.026882
H 2.944499 2.149027 0.026853
H 4.173724 0.000010 0.080857
O -1.749212 0.000042 1.626871
H -2.715820 0.000149 1.805720

PhO_2SOK
Eopt -1455.15988057
S 0.598851 0.840609 0.101622
C -1.107107 0.122869 0.058057
O 0.437228 2.453092 0.280525
O 1.403074 0.085341 1.333159
C -1.243232 -1.246617 0.223868
C -2.172869 0.970887 -0.188699
C -2.524504 -1.789460 0.148550
H -0.385676 -1.872112 0.427229

C -3.449301 0.412528 -0.262569
H -2.011731 2.032811 -0.304677
C -3.622140 -0.961722 -0.096606
H -2.662330 -2.853013 0.281361
H -4.301011 1.050874 -0.449022
H -4.613413 -1.388938 -0.155059
O 1.360246 0.395365 -1.299505
K 3.342268 -0.996878 -0.170254

pTIM
Eopt -458.469433356
C -0.913517 0.107035 -0.000012
N -1.437351 1.288385 -0.000042
H -0.851860 2.113665 0.000103
H -2.438515 1.440561 0.000011
B 0.700839 -0.037914 -0.000062
F 1.306982 1.268281 0.001415
F 1.120638 -0.755727 -1.171434
F 1.120119 -0.758144 1.170170
C -1.779778 -1.092040 -0.000059
H -2.843116 -0.857377 0.000142
H -1.539738 -1.702587 -0.873376
H -1.539382 -1.703044 0.872798

II
Eopt -1057.86156028
C -0.777578 0.935041 -0.000033
N 0.372204 1.528189 0.000106
B -0.858485 -0.669138 -0.000007
F 0.464257 -1.294407 0.001278
F -1.557690 -1.159730 -1.170630
F -1.559866 -1.159339 1.169494
C -2.083912 1.682075 -0.000152
H -1.938432 2.764348 -0.000955
H -2.675230 1.403728 -0.876022
H -2.674482 1.404991 0.876649
H 0.303201 2.551704 0.000068
K 2.616873 0.070641 -0.000032

IV
Eopt -557.598497741
C 0.511225 0.283613 0.000046
N 1.319231 -0.702895 0.000056
H 1.112041 -1.697346 0.000091
F 2.719945 -0.513030 -0.000018
B -1.081159 -0.119210 0.000017
F -1.211929 -1.547923 0.001186
F -1.684541 0.428323 -1.170807
F -1.685217 0.430346 1.169512
C 0.948803 1.691266 0.000019
H 2.025577 1.819574 -0.000831
H 0.513804 2.182906 -0.872594
H 0.515254 2.182457 0.873605

V
Eopt -2772.23921296
N -0.155366 -0.387195 -0.250195
S 1.223206 -0.643133 -1.481341
S -1.034928 1.229394 -0.640429
C 2.677797 -1.086197 -0.416658
O 1.526496 0.806028 -2.132561
O 0.835956 -1.870721 -2.475321
C 0.184247 2.450320 0.034531
O -2.340007 1.288682 0.308547
O -1.344822 1.448330 -2.210128
C 3.315244 -2.289588 -0.653483
C 3.081805 -0.147288 0.515686
C 0.423729 2.395601 1.396884
C 0.741487 3.369080 -0.832991
C 4.436325 -2.576141 0.124074
H 2.955343 -2.980582 -1.401682
C 4.200660 -0.458579 1.284762
H 2.551786 0.783842 0.653249
C 1.310787 3.335146 1.919175
H -0.040604 1.644296 2.019536
C 1.619835 4.302714 -0.285129
H 0.520506 3.345649 -1.888810
C 4.871328 -1.667294 1.089169
H 4.962561 -3.506949 -0.027789
H 4.543029 0.243776 2.030247
C 1.902956 4.282025 1.081321
H 1.534100 3.322952 2.975863
H 2.081346 5.037723 -0.928079
H 5.738179 -1.900606 1.690678
H 2.589557 5.006692 1.495469
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C 0.144853 -2.702701 0.542532
H -0.370993 -3.546287 0.986904
H 0.660943 -3.061246 -0.344983
H 0.863524 -2.321185 1.263538
N -1.736670 -2.233024 -0.807107
B -1.732489 -1.341943 1.639219
F -1.730444 -2.552072 2.433968
F -3.137140 -1.045378 1.454186
F -1.104251 -0.318504 2.426086
K -4.627605 0.165263 -0.146263

H -1.206306 -2.404587 -1.668537
F -2.700354 -1.207700 -1.310829

VI
Eopt -2772.34730593
N -0.037542 0.210158 -0.031394
S 0.204351 -1.198738 -1.247887
S 1.418965 1.415967 -0.208396
C -0.693377 -2.571626 -0.394974
O 1.798596 -1.447603 -1.211001
O -0.460061 -0.871338 -2.690525
C 2.769330 0.544015 0.709985
O 1.010339 2.745396 0.620906
O 1.764373 1.617361 -1.777575
C -1.655336 -3.257359 -1.113860
C -0.307383 -2.861663 0.902479
C 2.515126 0.233866 2.034143
C 3.955818 0.303518 0.045387
C -2.291690 -4.312221 -0.462712
H -1.909745 -2.981556 -2.126484
C -0.963764 -3.917000 1.530897
H 0.451089 -2.288039 1.414824
C 3.545467 -0.382343 2.741723
H 1.562775 0.442937 2.500322
C 4.972260 -0.304902 0.779458
H 4.083145 0.560889 -0.994916
C -1.949044 -4.635138 0.850816
H -3.052410 -4.873924 -0.983958
H -0.703219 -4.172079 2.547209
C 4.765060 -0.647081 2.116472
H 3.390137 -0.650507 3.776153
H 5.918019 -0.513052 0.301461
H -2.452943 -5.451098 1.348379
H 5.557834 -1.124517 2.674207
C -1.369636 0.860576 0.043895
C -2.538850 -0.022617 -0.310048
H -3.432580 0.594620 -0.285160
H -2.450537 -0.426502 -1.312529
H -2.647361 -0.824945 0.414872
N -1.505504 1.612551 1.164727
B -2.780575 1.928307 1.898413
F -3.793690 2.537563 1.059049
F -2.441715 2.856892 2.946221
F -3.386977 0.760362 2.498805
K -0.220126 1.646717 -3.602944
H -0.702208 2.165733 1.432157
F -1.280766 1.828244 -1.254284

VII
Eopt -1892.59297813
N -0.133791 -1.314276 -0.265374
S -1.063428 -0.437293 1.022231
C -1.582989 1.161544 0.242714
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O -2.366094 -1.414619 1.169424
C -2.632936 1.127966 -0.660608
C -0.870182 2.303804 0.566437
C -2.990249 2.326935 -1.273821
H -3.165352 0.212198 -0.873464
C -1.243601 3.492079 -0.060585
H -0.063479 2.279136 1.284277
C -2.296177 3.501059 -0.975843
H -3.808234 2.339701 -1.979325
H -0.710998 4.403245 0.169353
H -2.578612 4.426265 -1.457703
C 1.140254 -0.954204 -0.458460
C 1.783150 -1.634237 -1.628599
H 2.602768 -2.264062 -1.285214
H 1.060332 -2.241155 -2.165056
H 2.192293 -0.887983 -2.308459
N 1.849792 -0.089323 0.265896
H 1.440321 0.246855 1.132241
K -1.901141 -3.431662 -0.509913
B 3.260756 0.402402 -0.004148
F 4.228690 -0.663918 0.018191
F 3.576478 1.341513 1.035403
F 3.368350 1.061516 -1.280681

TS_{VI-VII}
Eopt -2772.33348604
N -0.588287 -0.039749 -0.659203
S 0.382866 1.299188 -1.418082
S -0.278311 -0.135750 1.671827
C 2.096494 0.618012 -1.342371
O 0.358188 2.674048 -0.540683
O -0.055233 1.445439 -2.981074
C 1.176137 -1.292080 1.287011
O -1.418526 -1.125918 2.204281
O 0.432776 1.009983 2.561718
C 3.080234 1.428745 -0.804895
C 2.330901 -0.612150 -1.935116
C 0.891492 -2.537178 0.759540
C 2.440416 -0.852266 1.629824
C 4.393054 0.962010 -0.859081
H 2.836055 2.382509 -0.361108

C 3.648505 -1.059861 -1.972418
H 1.526531 -1.208455 -2.340337
C 1.961319 -3.413535 0.587364
H -0.108282 -2.843661 0.496908
C 3.494027 -1.748994 1.449200
H 2.604198 0.135991 2.027492
C 4.672921 -0.272689 -1.442412
H 5.188530 1.565515 -0.447259
H 3.870248 -2.020023 -2.414429
C 3.254953 -3.020730 0.932780
H 1.775727 -4.398528 0.184983
H 4.496037 -1.440897 1.708961
H 5.692957 -0.627451 -1.480822
H 4.078583 -3.705882 0.791888
C -1.944960 -0.003597 -0.900987
C -2.682596 1.142740 -1.506861
H -3.693592 1.177664 -1.112909
H -2.200965 2.089486 -1.285954
H -2.733514 1.017962 -2.587771
N -2.593349 -1.089137 -0.549850
B -4.107557 -1.355059 -0.597127
F -4.817333 -0.465138 0.272782
F -4.291637 -2.703633 -0.163445
F -4.614116 -1.200222 -1.927283
K -0.463037 3.452530 1.786191
H -2.043302 -1.860685 -0.195686
F -1.695822 1.273648 1.287291

$TS_{V\text{-}VI}$
Eopt -2772.22307838
N -0.019201 -0.364906 0.290950
S 0.731755 -0.144217 -1.428332
S -1.882193 -0.568692 0.061079
C 2.228601 0.895640 -1.128728
O -0.368770 0.739568 -2.214612
O 1.139609 -1.577394 -2.067935
C -2.458702 1.175031 -0.171583
O -2.483174 -1.110084 1.469277
O -2.187636 -1.480069 -1.241909
C 3.450168 0.406123 -1.555149
C 2.021557 2.139634 -0.559270
C -2.201730 2.057627 0.862067
C -3.154415 1.478633 -1.325634
C 4.555522 1.235139 -1.376564
H 3.542198 -0.575685 -1.995430
C 3.144486 2.944934 -0.385885
H 1.041883 2.466255 -0.243792
C -2.677083 3.358794 0.709150
H -1.652610 1.760256 1.743355
C -3.626385 2.783975 -1.449325
H -3.308096 0.742676 -2.099579
C 4.401229 2.493363 -0.792447
H 5.530058 0.893848 -1.692544
H 3.032301 3.919403 0.065508
C -3.385611 3.716357 -0.438997
H -2.493408 4.083920 1.487991
H -4.175071 3.066816 -2.335509
H 5.265857 3.126217 -0.652957
H -3.750895 4.727565 -0.547399
C 0.680903 -1.209445 1.294396
C 2.152980 -1.429833 1.034118
H 2.544381 -2.009502 1.865736
H 2.295010 -2.014107 0.124395
H 2.715146 -0.504342 0.967769
N 0.049521 -2.134910 1.985104
B 0.746321 0.009765 2.929181
F 1.512815 -0.642370 3.877236
F -0.569976 0.259440 3.288027
F 1.381235 1.096654 2.343637
K -0.636298 -3.598612 -1.819693
H -0.971490 -2.069103 2.025167
F -0.396494 -3.517740 0.635963

$TS_{II\text{-}IV}$
Eopt -2772.18536802
N -0.822259 0.453458 0.956602
S -0.751626 1.221285 -0.777308
S -1.784539 -1.177419 1.047078
C 0.583465 2.466621 -0.482414
O -2.177939 1.949485 -1.017243
O -0.265535 0.142525 -1.887771
C -3.488287 -0.705178 0.501012
O -1.735562 -1.490907 2.631111
O -1.192391 -2.291170 0.031289
C 1.889806 2.081567 -0.728657
C 0.198264 3.710591 -0.012724
C -4.243540 0.066370 1.368165
C -3.901893 -1.123328 -0.751350
C 2.882535 3.028566 -0.486105
H 2.133634 1.089647 -1.080544
C 1.210199 4.640130 0.219409
H -0.840077 3.952855 0.159546
C -5.513094 0.442518 0.936963
H -3.870223 0.365308 2.336699
C -5.177196 -0.735884 -1.158001

H -3.266453 -1.726003 -1.383200
C 2.542985 4.297988 -0.015086
H 3.915753 2.768307 -0.663627
H 0.953352 5.624452 0.582028
C -5.973703 0.044324 -0.319383
H -6.135583 1.044351 1.582326
H -5.540778 -1.043621 -2.127204
H 3.321099 5.024584 0.170392
H -6.959600 0.343249 -0.645464
F 0.798784 -0.032711 1.202897
N 2.652681 -0.251915 1.711564
C 3.672590 -0.785623 1.157299
H 2.740917 0.340324 2.535417
C 5.052991 -0.575739 1.715348
H 5.500429 -1.539402 1.965197
H 5.686524 -0.116952 0.952975
H 5.044487 0.057861 2.602553
B 3.494750 -1.699641 -0.158281
F 2.535481 -2.773735 0.059757
F 4.733321 -2.285393 -0.575749
F 2.964640 -0.928948 -1.282985
K 0.677848 -2.274175 -1.765811

TS_{IV-V}
Eopt -2772.22260283
N -0.114886 -0.298081 0.008493
S 1.111955 -0.642950 -1.336183
S -0.721998 1.420349 -0.161996
C 2.500709 -1.445287 -0.408845
O 1.632650 0.753711 -1.990663
O 0.501562 -1.738373 -2.395058
C 0.686969 2.568869 0.203282
O -1.796268 1.573347 1.057384
O -1.421826 1.739199 -1.607549
C 2.949139 -2.676480 -0.851314
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C 1.204850 2.523923 1.486470
C 1.103462 3.438979 -0.785172
C 4.021515 -3.248427 -0.167888
H 2.479249 -3.174776 -1.686329
C 4.122211 -1.334394 1.318550
H 2.666023 0.217119 0.954127
C 2.233556 3.415399 1.787411
H 0.835045 1.825351 2.222945
C 2.126586 4.327239 -0.458560
H 0.664390 3.413479 -1.770473
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H 4.397736 -4.211132 -0.481326
H 4.574322 -0.820484 2.153981
C 2.689093 4.311088 0.818941
H 2.669551 3.407871 2.775558
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H 5.429995 -3.032958 1.437215
H 3.486011 4.999817 1.060807
C -1.395165 -1.837361 0.159599
C -0.357705 -2.888898 0.503412
H -0.888055 -3.734474 0.940446
H 0.189881 -3.252146 -0.361972
H 0.326747 -2.496730 1.249646
N -1.907661 -2.031151 -1.063530
B -2.390920 -1.510953 1.430859
F -2.977376 -2.797320 1.750822
F -3.490070 -0.631796 1.141236
F -1.653151 -1.055933 2.556886
K -4.052440 1.276006 -0.454347
H -1.312470 -2.154908 -1.887559
F -2.957433 -1.119135 -1.457235

TS_{VIII}
Eopt -1293.16756871
N 1.216728 0.352977 -0.017863
S -0.071837 -0.149059 1.228375
C -1.631589 -0.223922 0.225095
O -0.183505 0.995927 2.365186
O 0.330717 -1.622247 1.734801
C -1.638683 -1.061348 -0.877328
C -2.716857 0.509876 0.669263
C -2.826659 -1.143646 -1.600191
H -0.758518 -1.613110 -1.175293
C -3.895388 0.405856 -0.068545
H -2.649887 1.144097 1.540881
C -3.946545 -0.414153 -1.196090
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C 1.179707 1.617762 -0.500314
C 0.045335 2.553141 -0.227686
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H -0.143423 2.659815 0.837000
N 2.140505 2.061137 -1.280943
H 2.091264 2.997527 -1.647833
H 2.923077 1.482586 -1.549071
B 2.249867 -0.781641 -0.346178
F 1.551680 -1.920494 -0.841259
F 3.140044 -0.324842 -1.381852

F 3.024053 -1.103420 0.796541

I

Eopt -1534.42831691
N -1.459712 -0.477092 1.069729
S -0.477989 -0.749736 -0.427678
C 1.213200 -0.027918 -0.201166
O -1.342330 0.245873 -1.427717
O -0.274815 -2.292616 -0.921604
C 2.309181 -0.868938 -0.279978
C 1.302190 1.330649 0.059725
C 3.572905 -0.308889 -0.090336
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C 2.571692 1.873557 0.245170
H 0.419040 1.951395 0.112037
C 3.701143 1.055167 0.171185
H 4.448914 -0.938810 -0.146785
H 2.675852 2.929936 0.446924
H 4.682901 1.483106 0.317658
F -0.725939 -1.245550 2.132955
K -3.425870 1.110137 -0.037694

III

Eopt -1992.92151860
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S 0.657141 -0.283008 0.718530
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O 0.129487 -1.758963 0.294508
O 0.496916 0.181390 2.265646
C 2.919832 -1.093217 -0.688645
C 3.185001 0.855793 0.770466
C 4.258857 -0.980774 -1.061006
H 2.286835 -1.873785 -1.083195
C 4.520119 0.949964 0.383814
H 2.756334 1.551500 1.476983
C 5.051650 0.035899 -0.527820
H 4.675240 -1.686327 -1.764998
H 5.138252 1.734605 0.794840
H 6.088266 0.116363 -0.822657
C -1.458317 1.629353 -0.197084
C -1.693285 2.581541 -1.372876
H -2.635094 3.100193 -1.199789
H -0.891945 3.320630 -1.434445
H -1.757397 2.044200 -2.316347
N -1.342581 2.345794 1.028677
B -2.609660 0.501291 -0.097361
F -3.909960 1.100349 -0.018538
F -2.431924 -0.336524 1.091785
F -2.615942 -0.428191 -1.219123
K -2.204950 -2.755740 -0.012458
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F 0.064293 0.395504 -1.743142

$TS_{I\text{-}III}$

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C -2.545578 0.058331 0.223775
O -0.313460 1.697567 0.513579
O -0.570009 -0.531321 2.173829
C -3.072916 1.075531 -0.552090
C -3.265993 -1.048477 0.642796
C -4.414973 0.977891 -0.919664
H -2.465353 1.917878 -0.847238
C -4.605330 -1.128240 0.266623
H -2.807356 -1.816826 1.248406
C -5.174758 -0.119166 -0.512530
H -4.860049 1.756910 -1.521618
H -5.197684 -1.975210 0.581299
H -6.213867 -0.188335 -0.801981
C 1.955796 -1.670585 -0.162470
C 2.010967 -2.476110 -1.427310
H 3.009702 -2.913529 -1.507155
H 1.278419 -3.283558 -1.422705
H 1.851109 -1.845981 -2.297675
N 1.773529 -2.345012 0.972302
B 2.837115 -0.330034 -0.085251
F 4.231171 -0.689706 -0.065103
F 2.555017 0.442232 1.116704
F 2.626722 0.568562 -1.201704
K 1.900608 2.810277 0.026166
H 1.385324 -3.275015 0.970625
H 1.827379 -1.878197 1.862555
F -0.194261 -0.321903 -1.798361

$TS_{III\text{-}VIII}$

Eopt -1992.90326262
N -0.837212 0.258747 0.260414
S 0.543482 0.188573 -1.091170
C 2.197305 -0.155654 -0.318769
O 0.477896 1.750964 -1.546099
O 0.259915 -0.935818 -2.224261
C 2.949966 0.929147 0.096096
C 2.617466 -1.472725 -0.253280
C 4.215984 0.666027 0.615172

H 2.572549 1.936096 0.013787
C 3.885233 -1.711997 0.274400
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C 4.677640 -0.647924 0.706823
H 4.834092 1.487331 0.947152
H 4.247801 -2.727203 0.341944
H 5.659443 -0.842994 1.114391
C -1.289330 -0.959059 0.747984
C -1.691444 -0.856463 2.218550
H -2.308891 -1.711548 2.482846
H -0.779505 -0.862720 2.814519
H -2.237585 0.059154 2.425120
N -0.591029 -2.135118 0.423916
B -2.875239 -0.837320 -0.139747
F -3.604510 -1.955337 0.328589
F -2.671315 -0.922878 -1.532872
F -3.514975 0.375877 0.224618
K -1.213832 2.934386 0.269396
H -0.602861 -2.874745 1.105925
H -0.593314 -2.440037 -0.537602
F 0.310764 1.117873 1.399008

$TS_{VIII\text{-}2a'}$
Eopt -1993.00086922
N 0.483843 1.285430 -0.091479
S -0.580762 0.475905 1.163014
C -1.963626 -0.267783 0.178202
O -1.236966 1.587315 2.176117
O 0.256954 -0.695730 1.917116
C -2.162578 -1.632805 0.257547
C -2.757643 0.600460 -0.550590
C -3.235921 -2.163930 -0.456386
H -1.508441 -2.260628 0.843497
C -3.821308 0.047620 -1.261223
H -2.565203 1.663563 -0.578962
C -4.057554 -1.327236 -1.212219
H -3.422777 -3.227218 -0.421471
H -4.459819 0.691994 -1.847439
H -4.884955 -1.747622 -1.765855
C 0.616838 2.619858 -0.099977
C 1.556663 3.184924 -1.123636
H 1.580875 4.269745 -1.049827
H 2.560609 2.796676 -0.963789
H 1.241922 2.901463 -2.124271
N -0.009782 3.476312 0.691167
H 0.152584 4.462794 0.580051
H -0.629604 3.162972 1.430296
B 1.653352 -0.054978 -0.871419
F 0.630219 -1.022136 -0.814830
F 1.911087 0.529291 -2.099841
F 2.596057 0.087202 0.161709
F 2.862264 -1.785574 -1.354203
K 2.128212 -2.482311 0.909323

H_2O
Eopt -76.4011520359
O -0.000000 -0.000000 0.112316
H -0.000000 -0.786545 -0.449264
H 0.000000 0.786545 -0.449264

NFSI
Eopt -1714.32969791
N -0.097987 -0.761296 -0.730229
S -1.173366 -0.684971 0.928213
S 1.757291 -1.410560 -0.348429
C -2.570198 0.321795 0.266072
O -0.216674 0.188396 1.887866
O -1.666260 -2.161749 1.327778
C 2.551974 0.244340 -0.155582
O 2.150331 -2.106674 -1.745448
O 1.822081 -2.269542 1.012947
C -3.708419 -0.349064 -0.147813
C -2.388944 1.693536 0.201164
C 2.835119 0.951313 -1.312741
C 2.819647 0.683435 1.129298
C -4.748617 0.427425 -0.654138
H -3.791415 -1.423273 -0.075084
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H -1.475205 2.161412 0.536753
C 3.437719 2.197375 -1.158715
H 2.606207 0.556949 -2.291802
C 3.424910 1.931938 1.254536
H 2.563872 0.089547 1.993164
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C 3.729294 2.681978 0.117583
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H 3.654423 2.312435 2.238691
H -5.427097 2.406940 -1.128462
H 4.196802 3.650027 0.226609
F -0.701828 -1.845670 -1.458340

$(PhSO_2)_2NK$
Eopt -2214.62630867
N -0.059896 0.343046 0.347333

S -1.498460 -0.741185 0.486721
S 1.461351 -0.445004 0.927760
C -2.762522 0.518474 -0.001898
O -1.817995 -1.279576 1.997057
O -1.503626 -1.916660 -0.661031
C 2.644112 0.729773 0.122042
O 1.682325 -1.934990 0.268744
O 1.703327 -0.385011 2.539565
C -3.002326 0.714770 -1.351222
C -3.394893 1.221056 1.009339
C 2.788731 0.663710 -1.254360
C 3.325974 1.620945 0.930783
C -3.944481 1.680066 -1.703712
H -2.485828 0.132622 -2.100098
C -4.334585 2.181050 0.636763
H -3.172521 1.022931 2.047762
C 3.678461 1.553472 -1.852125
H 2.233671 -0.051207 -1.844346
C 4.212456 2.504074 0.313982
H 3.174668 1.622835 2.000370
C -4.605081 2.408731 -0.713369
H -4.159012 1.858191 -2.747460
H -4.850244 2.745392 1.400102
C 4.385253 2.469271 -1.069648
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H -5.334294 3.155187 -0.994759
H 5.073137 3.156847 -1.541136
K 0.394495 -3.540558 -1.201563

2a'

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S -0.464421 0.950559 0.082144
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O -0.902747 1.152653 1.659922
O -0.469197 2.288947 -0.848470
C 2.020566 0.431979 -1.057489
C 1.600140 -0.593842 1.122246
C 3.279781 -0.166506 -1.084507
H 1.680852 1.063761 -1.865276
C 2.862921 -1.182585 1.077242
H 0.942010 -0.737740 1.966812
C 3.696104 -0.970008 -0.022263
H 3.928820 -0.002621 -1.932428
H 3.190533 -1.802805 1.898926
H 4.673692 -1.430166 -0.049925
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C -3.296619 -1.761125 -1.066876
H -3.465218 -2.656939 -0.468466
H -4.266043 -1.364519 -1.371800
N -3.131292 -0.333553 0.886272
H -4.012703 -0.727155 1.167717
H -2.659450 0.309260 1.510552
H -2.725639 -2.022853 -1.952290

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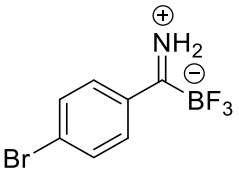
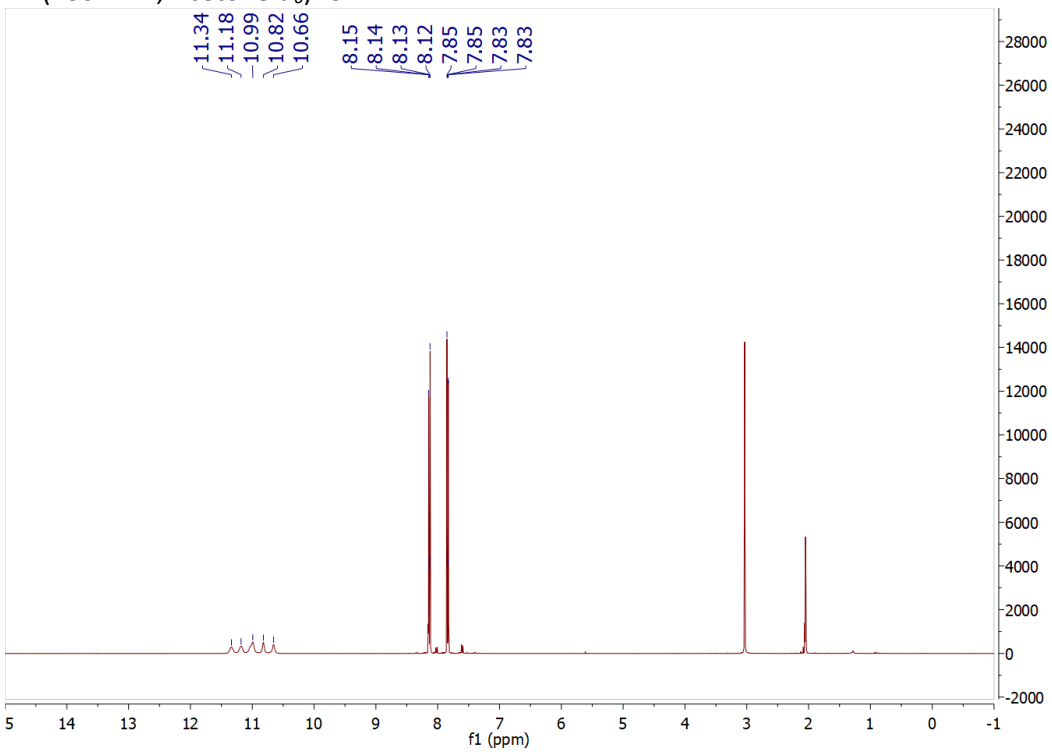
10. NMR Spectra

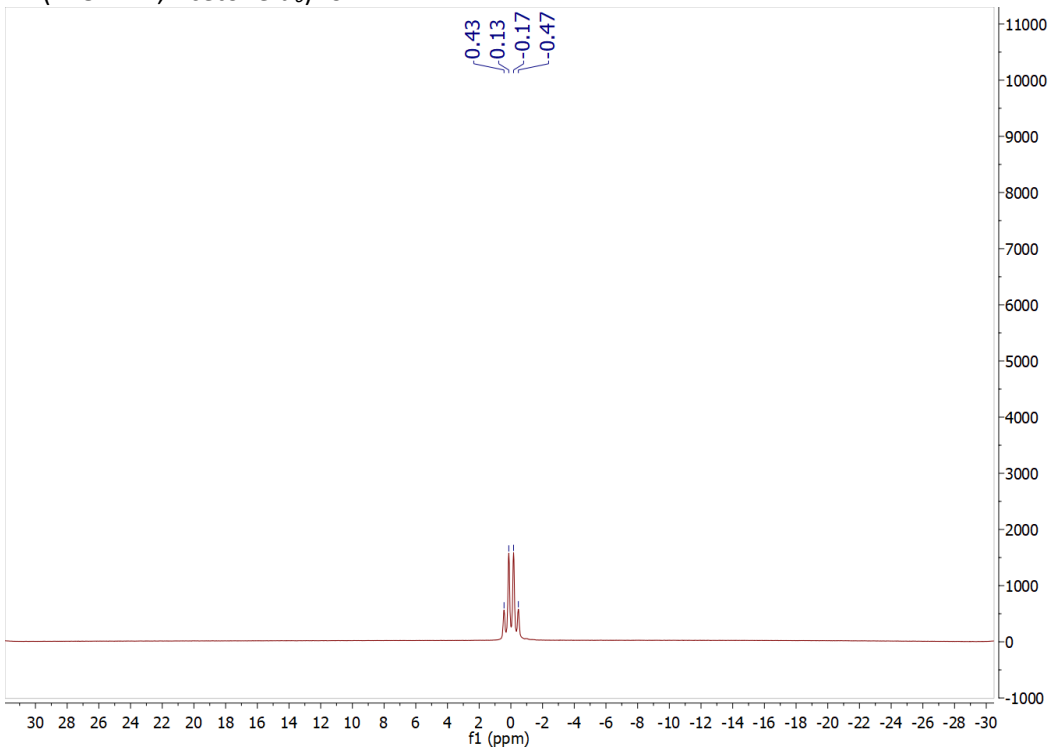
((4-Bromophenyl)(iminio)methyl)trifluoroborate (1k)



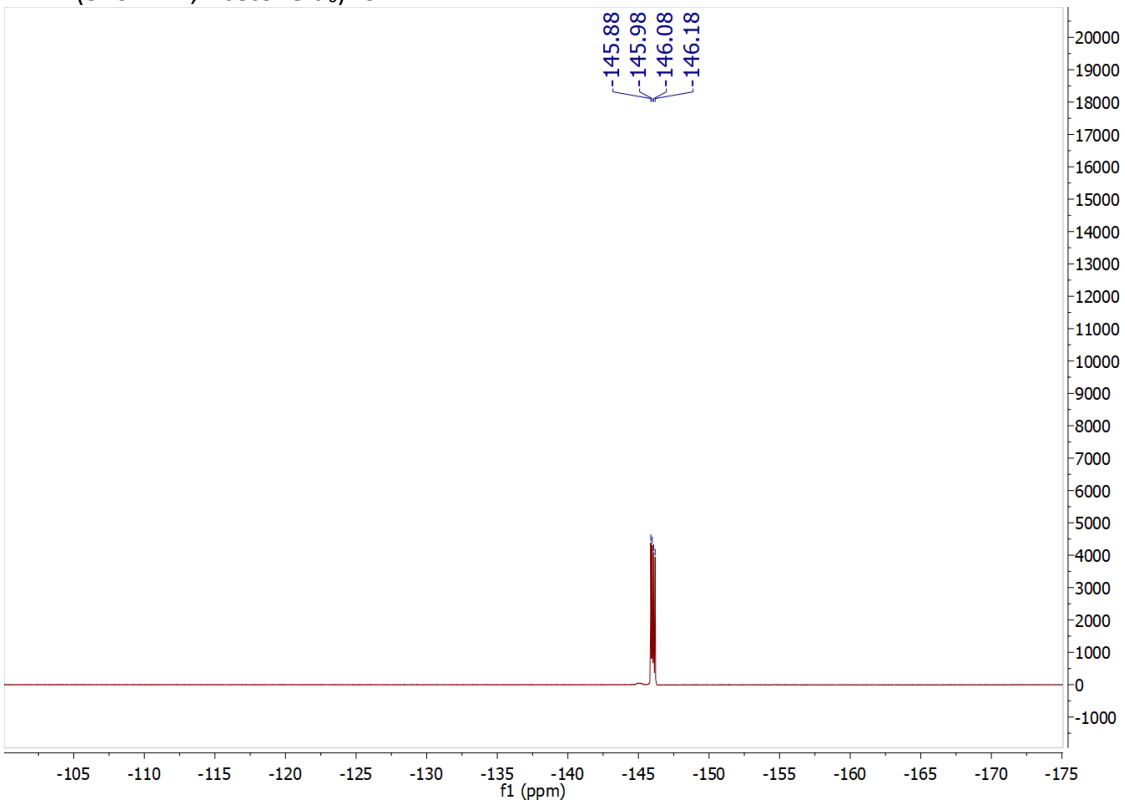
^{1}H NMR (400 MHz, Acetone-d_6) for **1k**:



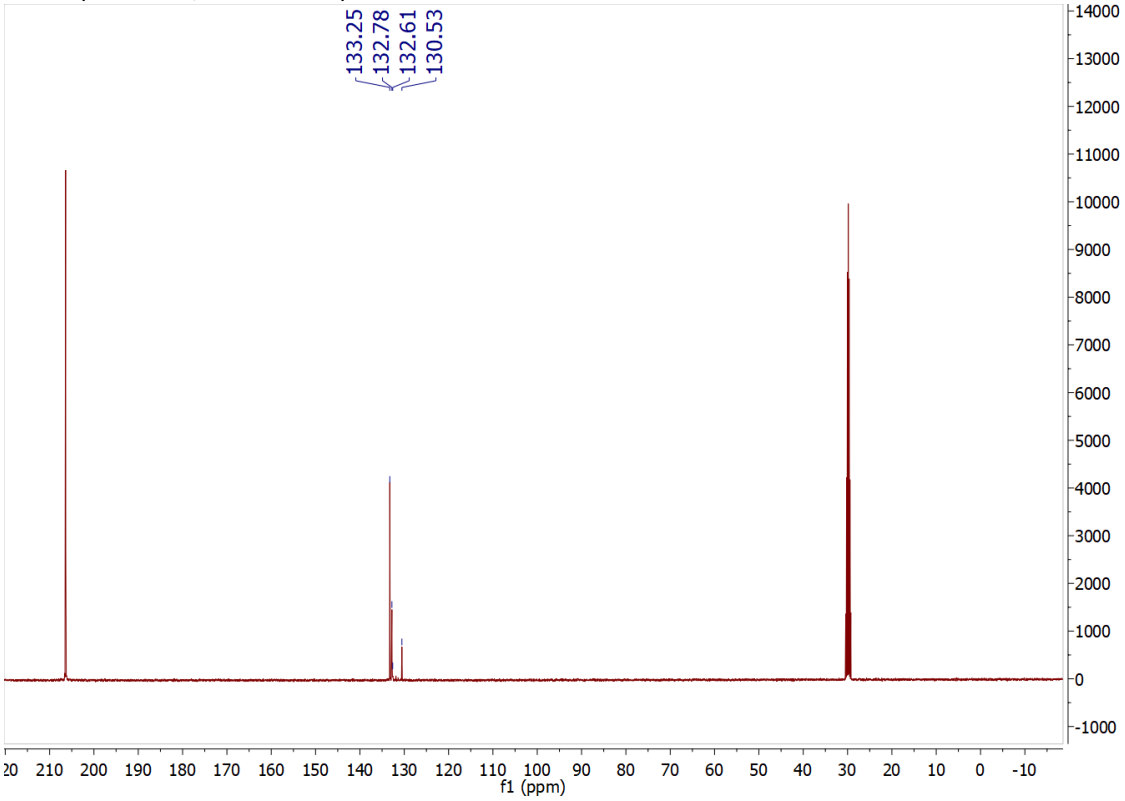
^{11}B NMR (128 MHz, Acetone-d_6) for **1k**:



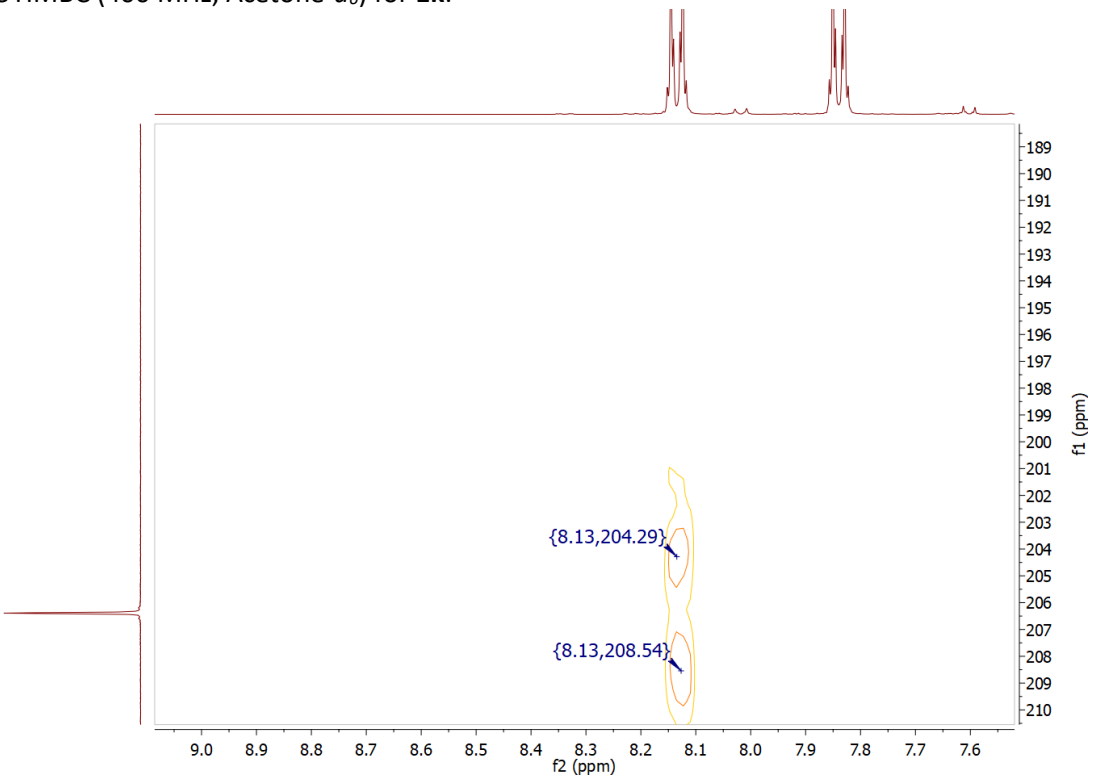
^{19}F NMR (376 MHz, Acetone-d_6) for **1k**:



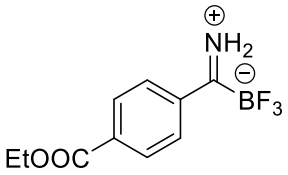
^{13}C NMR (101 MHz, Acetone-d_6) for **1k**:



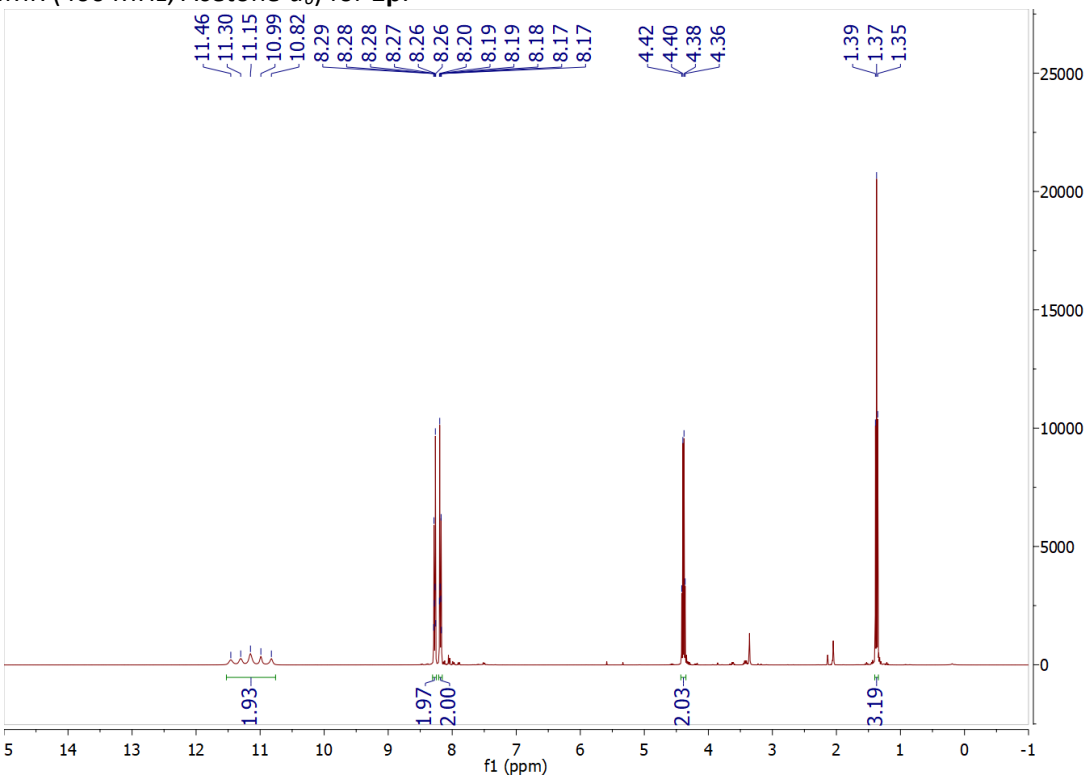
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1k**:



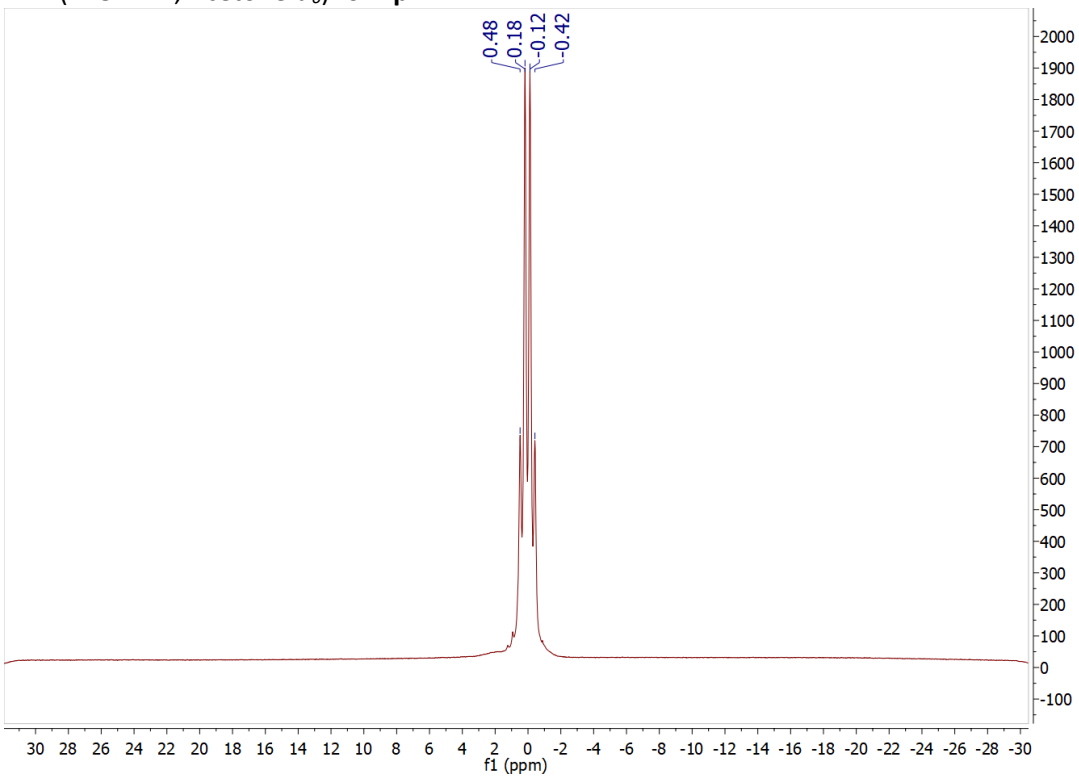
((4-(Ethoxycarbonyl)phenyl)(iminio)methyl)trifluoroborate (1p)



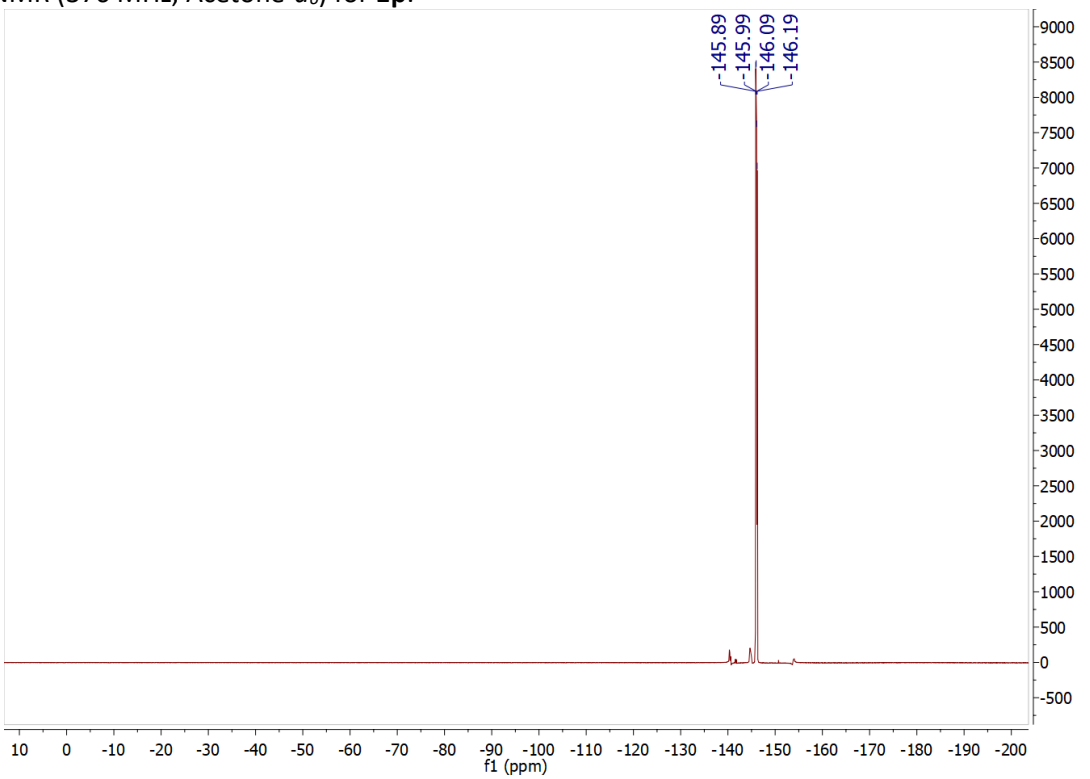
^{1}H NMR (400 MHz, Acetone-d_6) for **1p**:



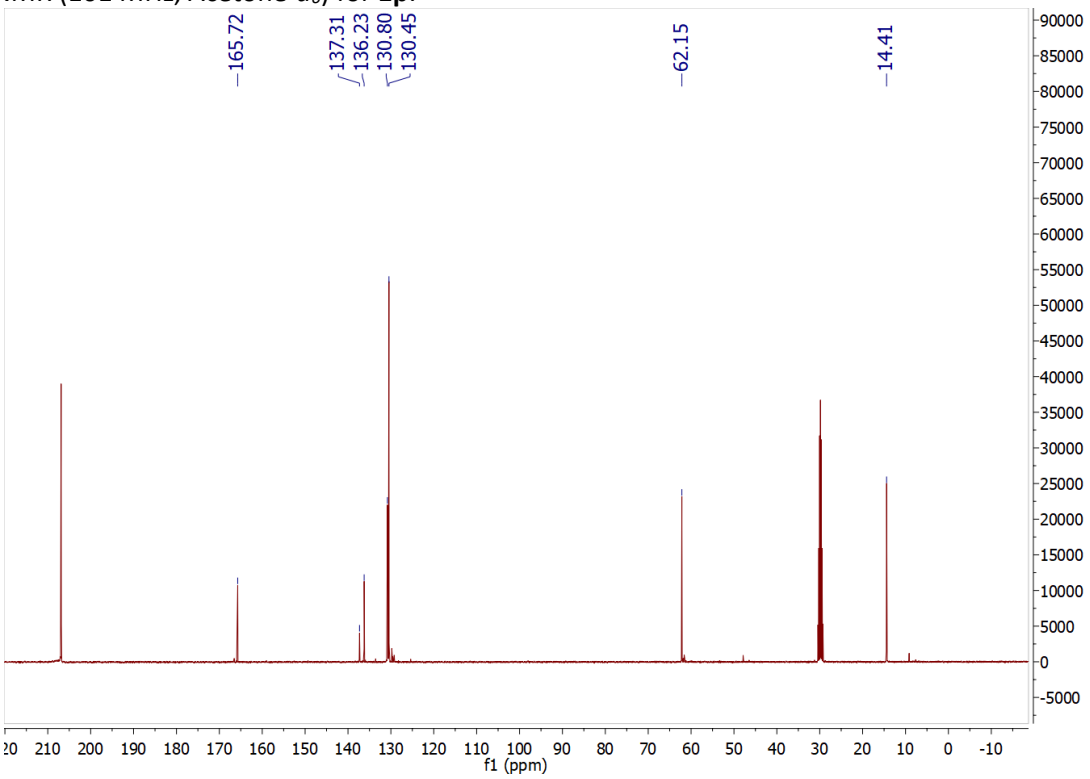
^{11}B NMR (128 MHz, Acetone-d_6) for **1p**:



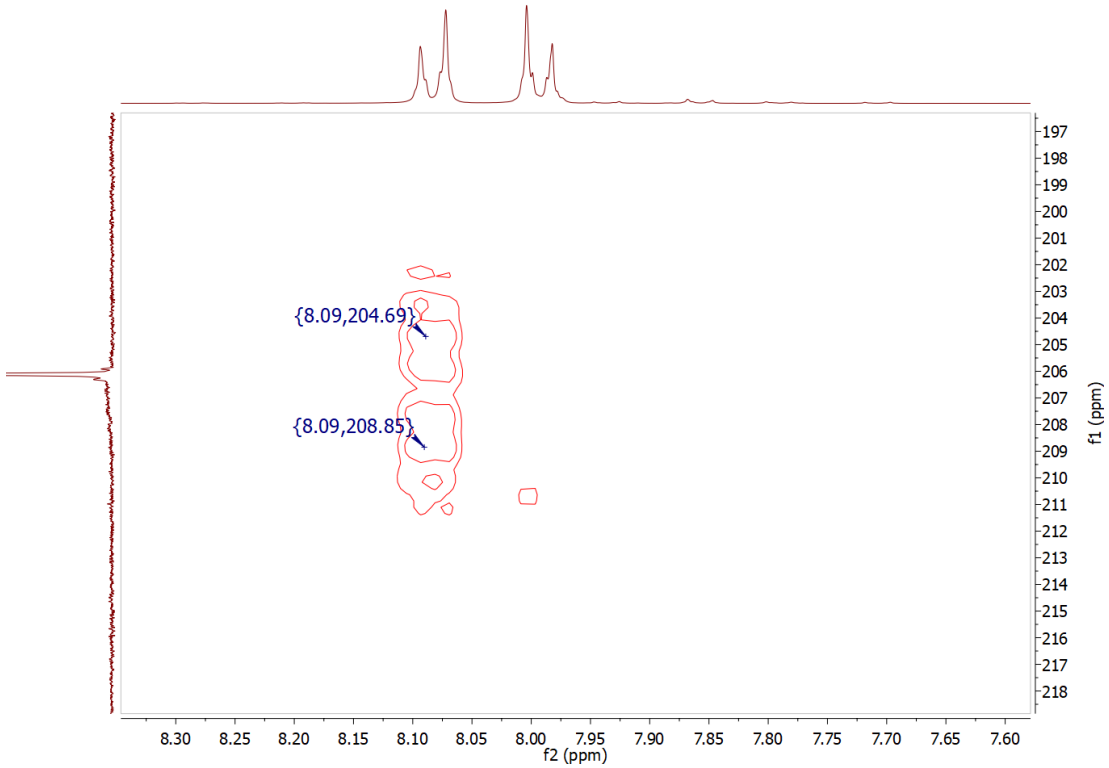
^{19}F NMR (376 MHz, Acetone-d_6) for **1p**:



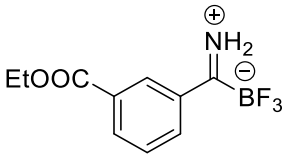
^{13}C NMR (101 MHz, Acetone-d_6) for **1p**:



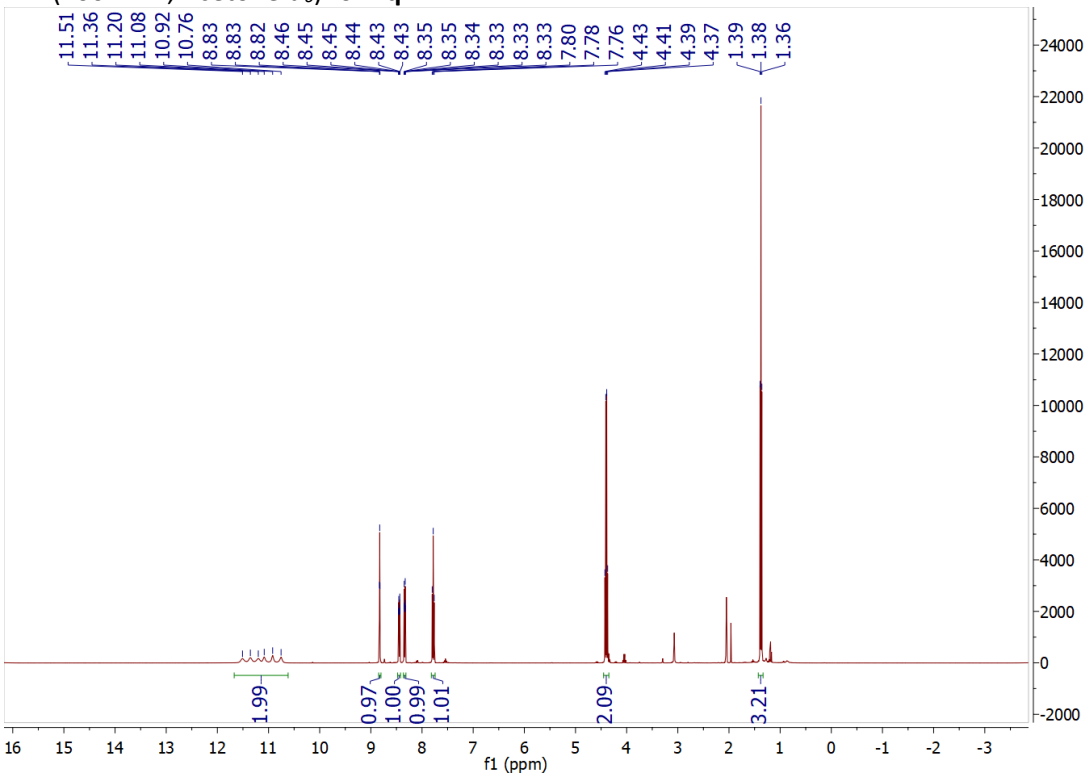
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1p**:



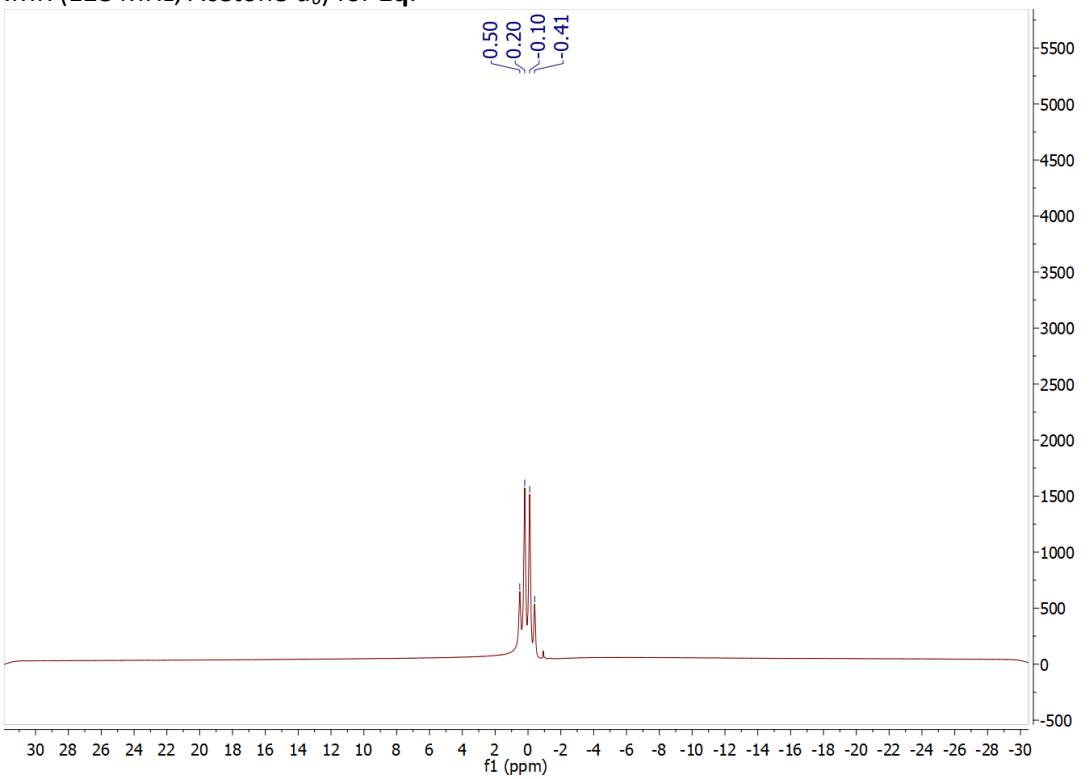
((3-(Ethoxycarbonyl)phenyl)(iminio)methyl)trifluoroborate (1q)



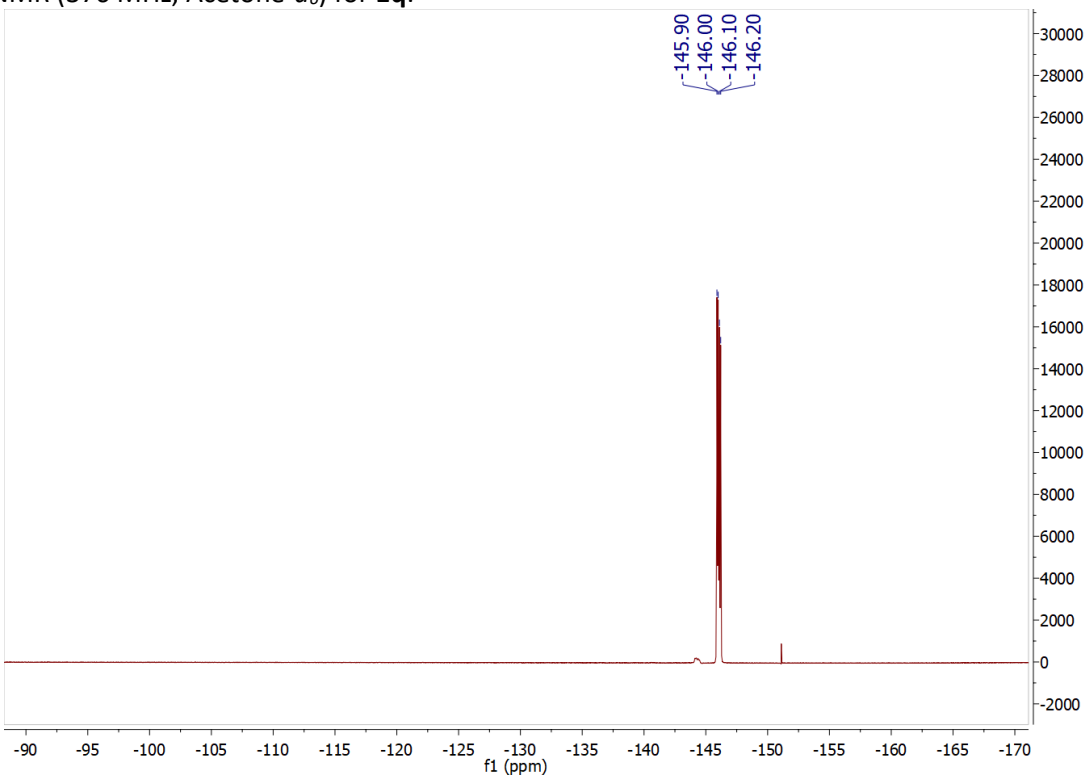
^{1}H NMR (400 MHz, Acetone-d_6) for **1q**:



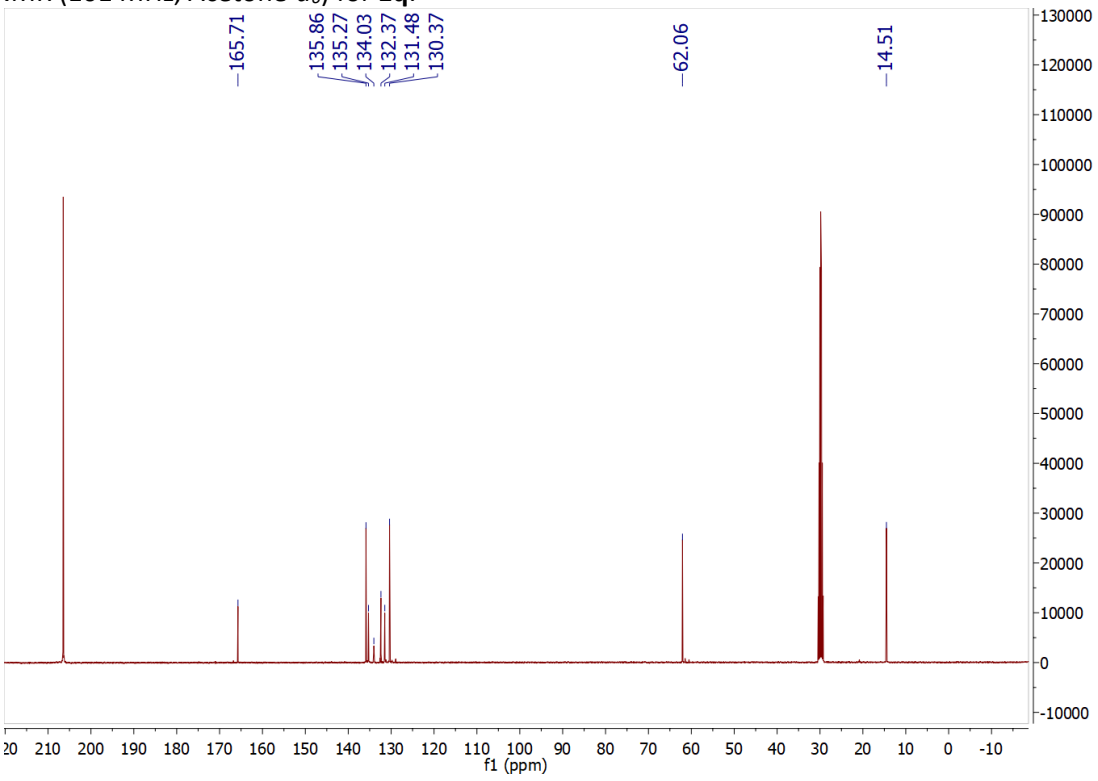
^{11}B NMR (128 MHz, Acetone-d_6) for **1q**:



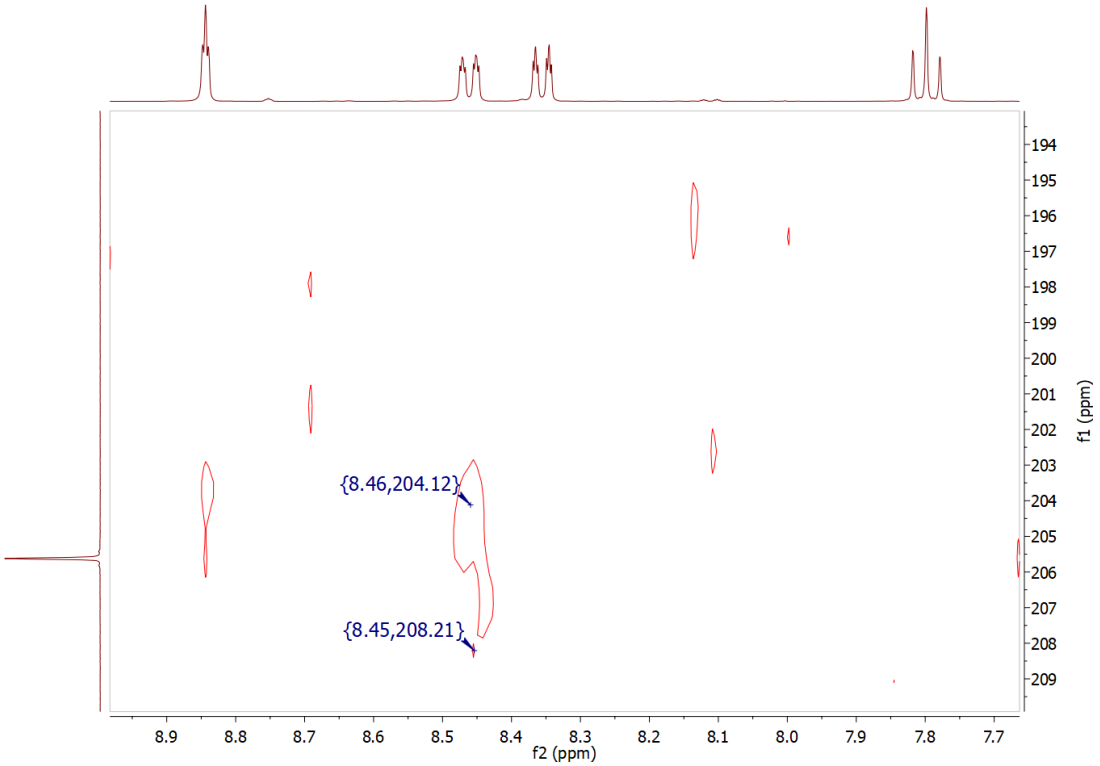
^{19}F NMR (376 MHz, Acetone-d_6) for **1q**:



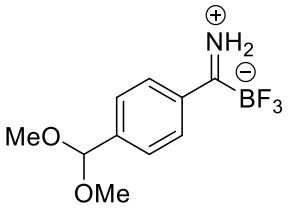
^{13}C NMR (101 MHz, Acetone-d_6) for **1q**:



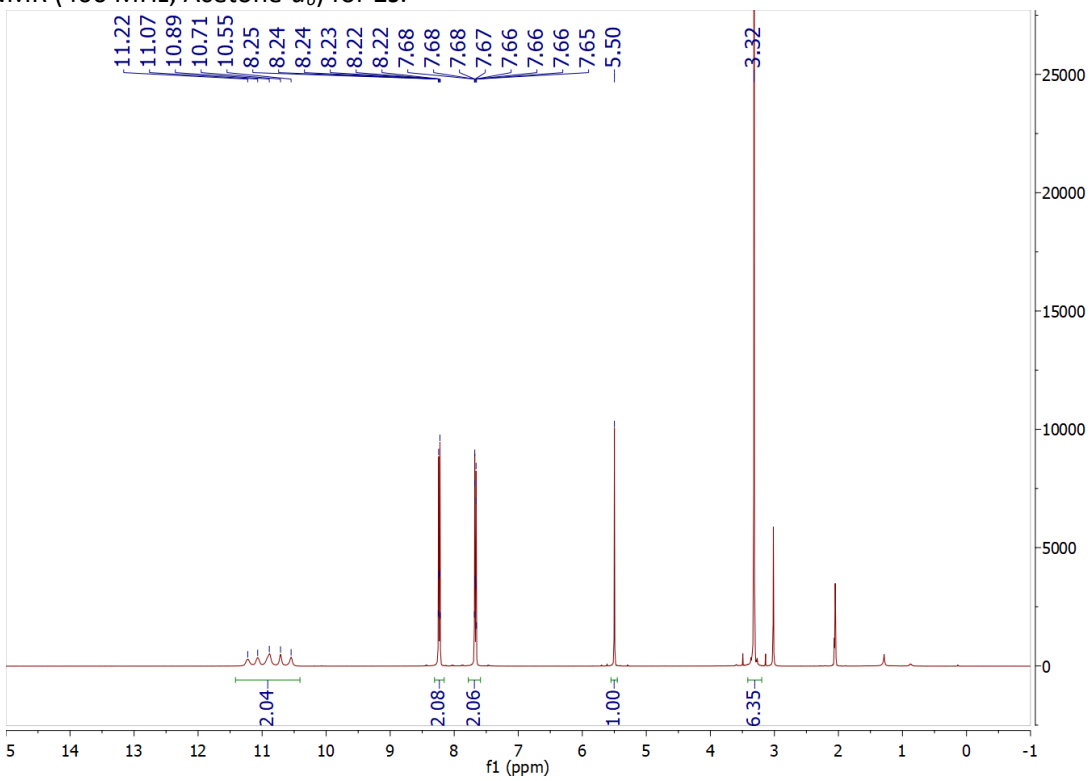
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1q**:



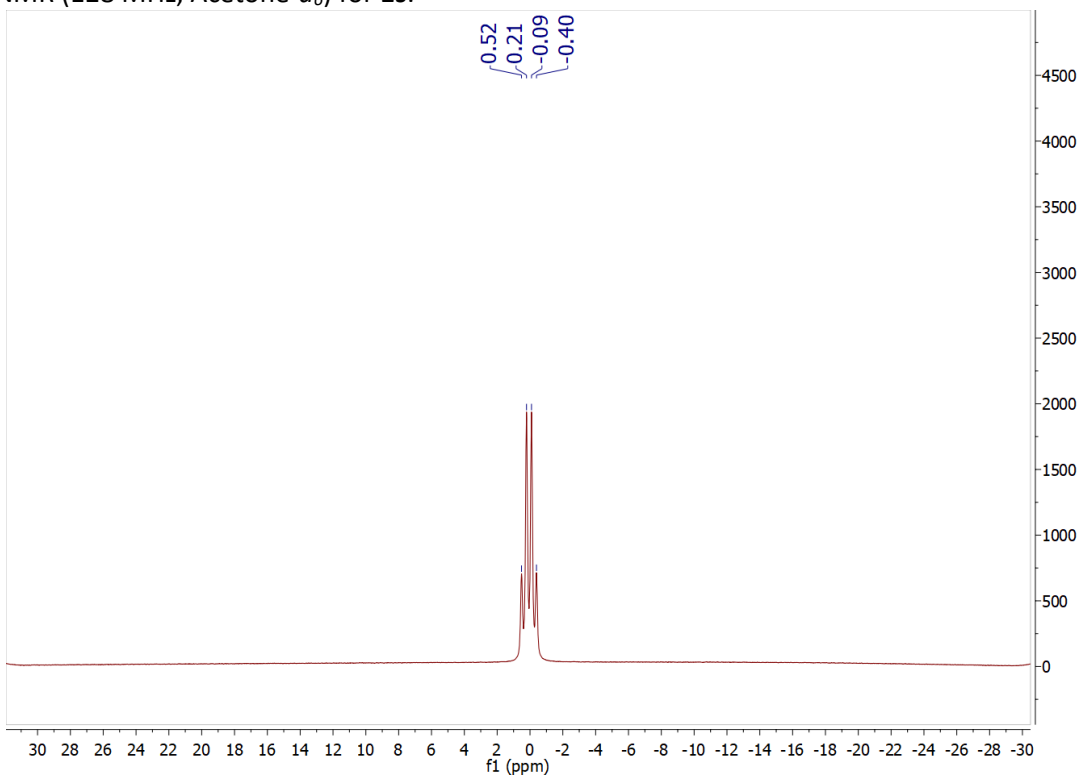
((4-(Dimethoxymethyl)phenyl)(iminio)methyl)trifluoroborate (1s)



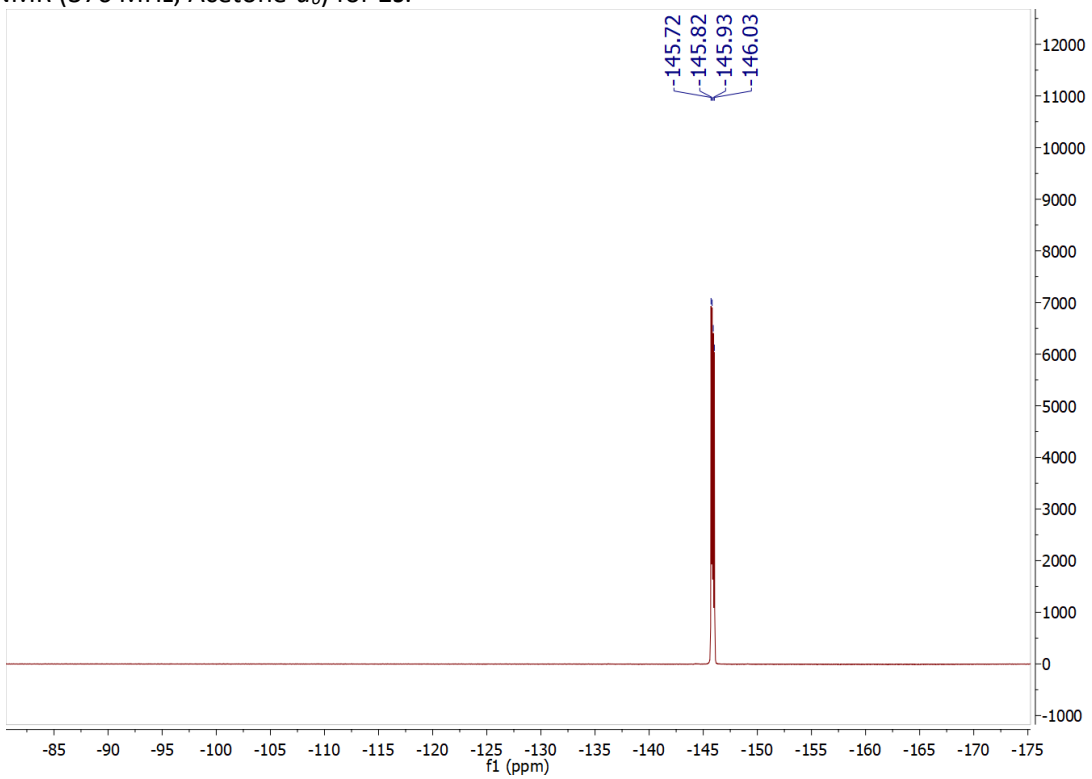
^{1}H NMR (400 MHz, Acetone-d_6) for **1s**:



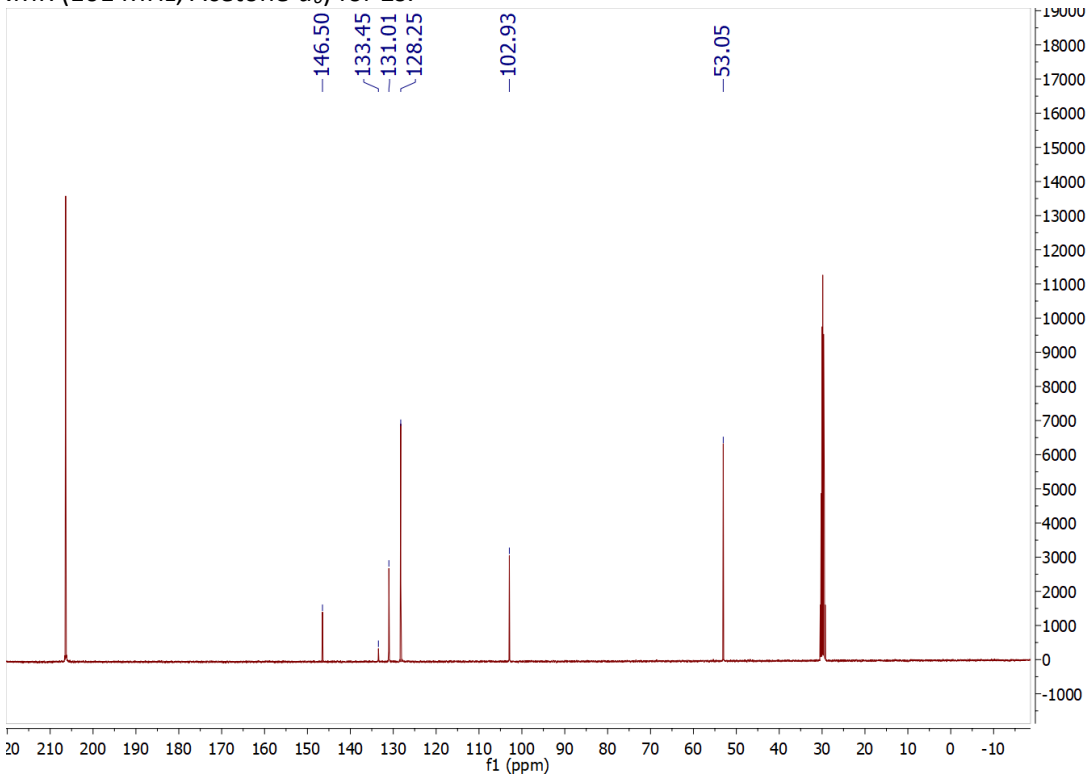
^{11}B NMR (128 MHz, Acetone-d_6) for **1s**:



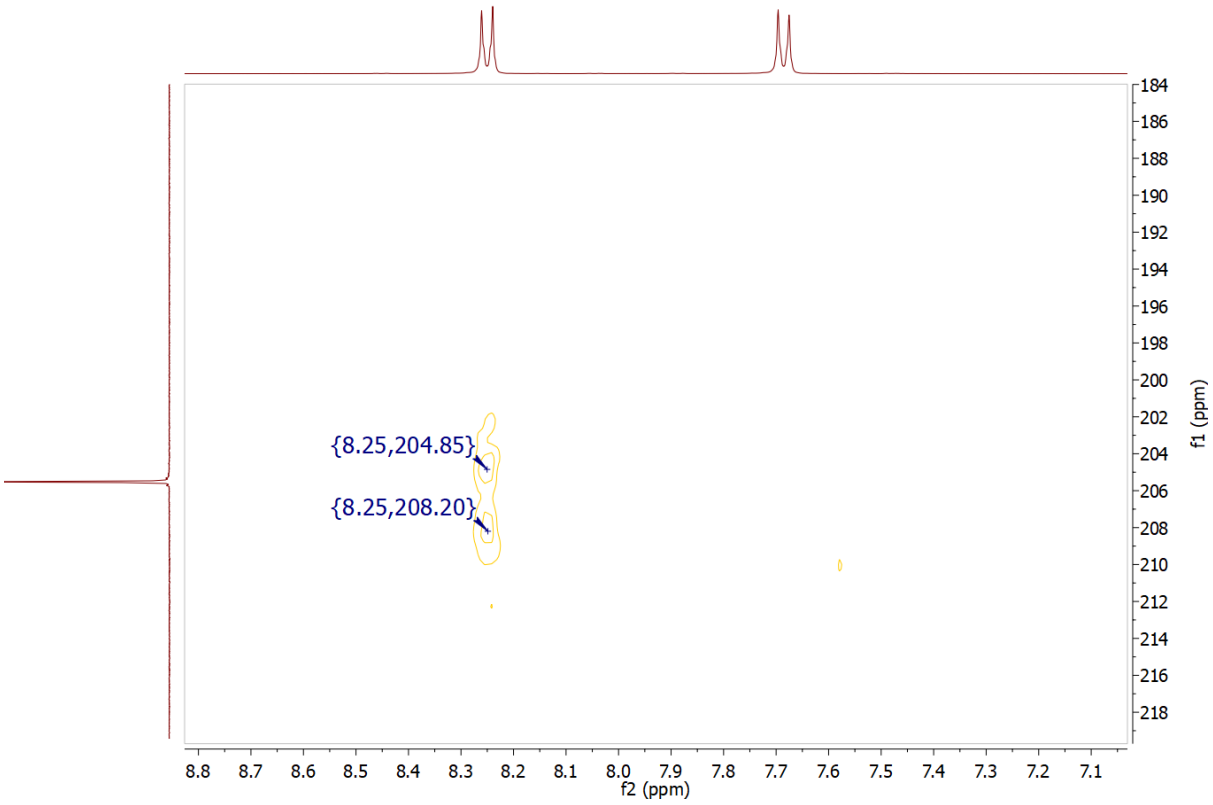
^{19}F NMR (376 MHz, Acetone-d_6) for **1s**:



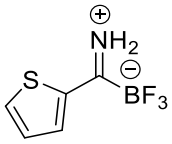
^{13}C NMR (101 MHz, Acetone-d_6) for **1s**:



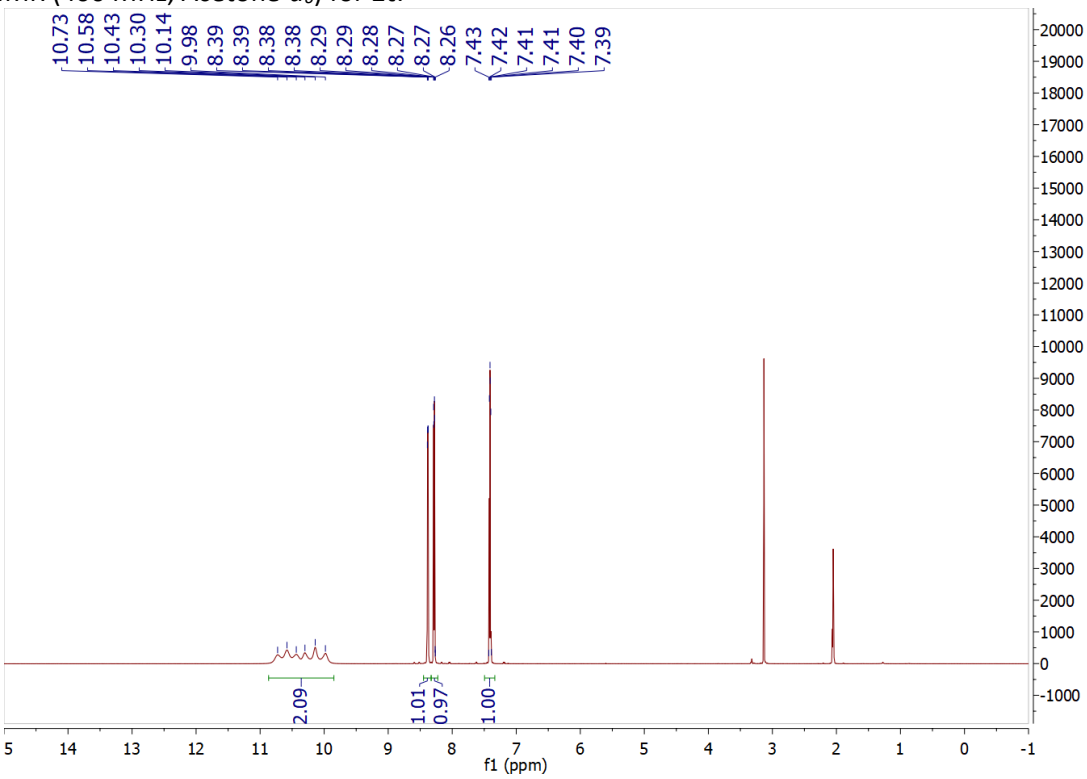
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1s**:



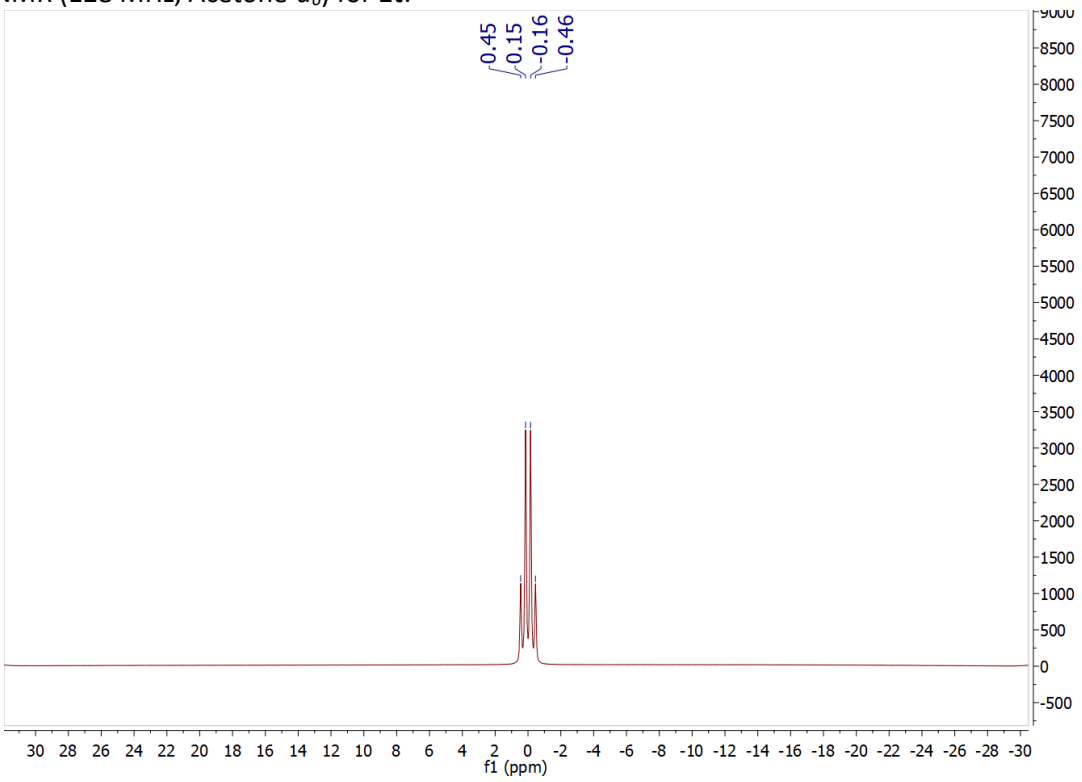
(Iminio(thiophen-2-yl)methyl)trifluoroborate (1t)



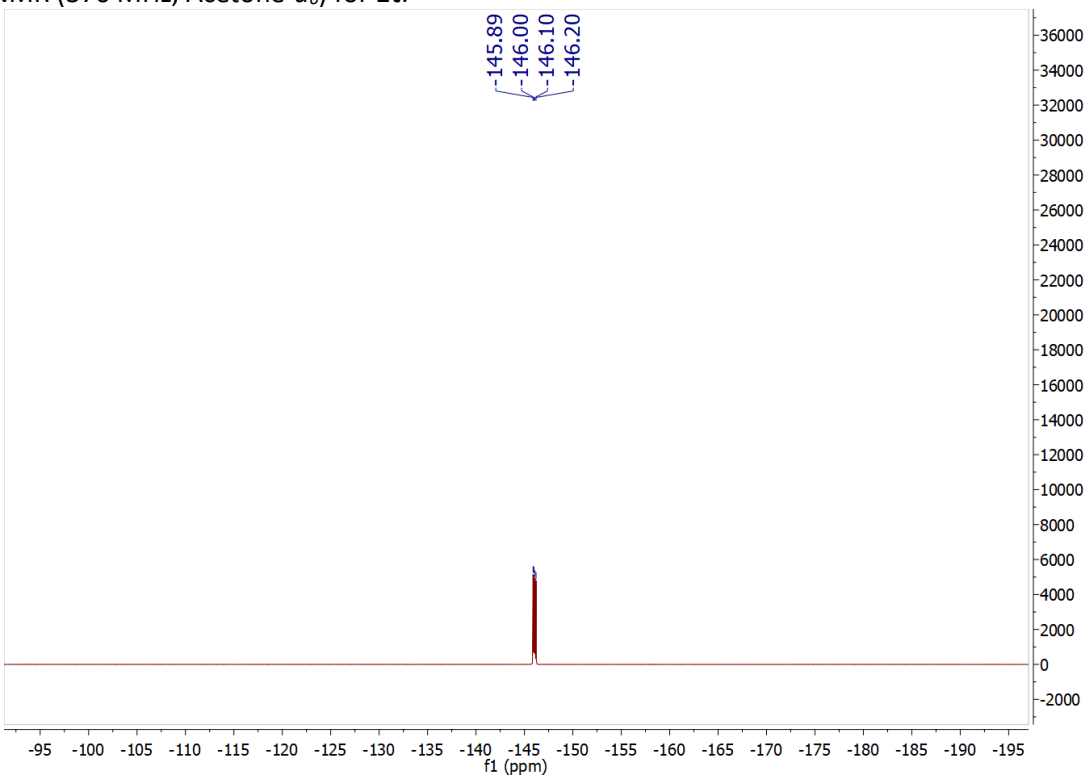
^{1}H NMR (400 MHz, Acetone-d_6) for **1t**:



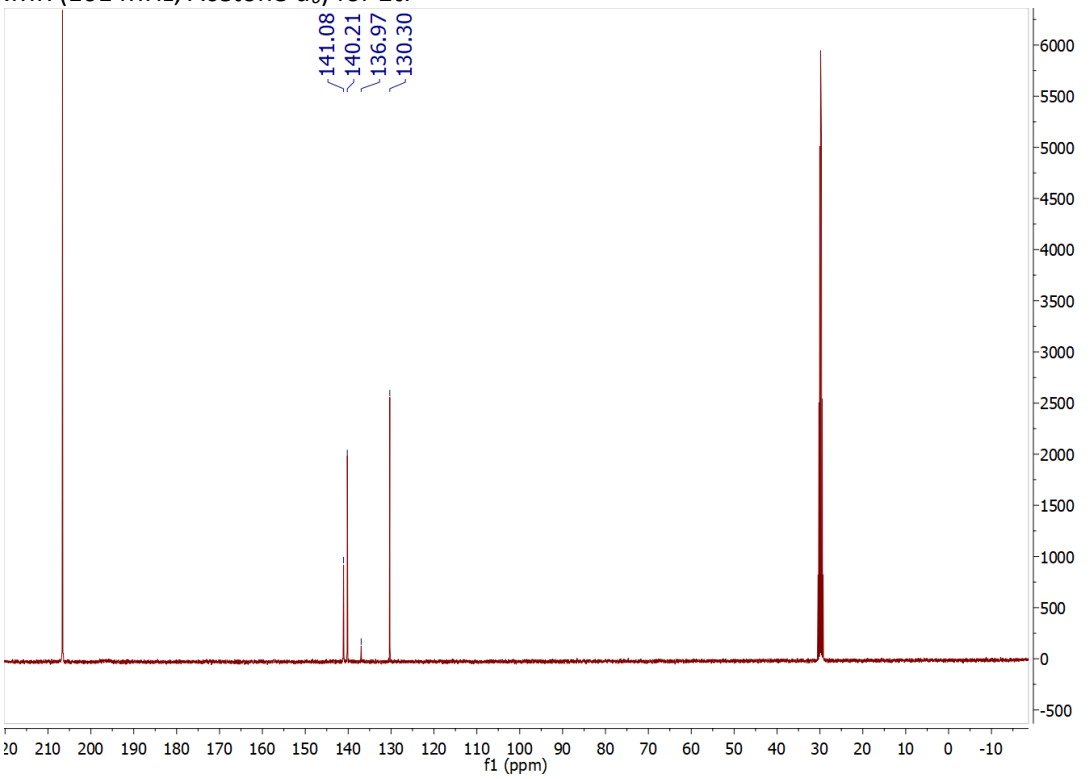
^{11}B NMR (128 MHz, Acetone-d_6) for **1t**:



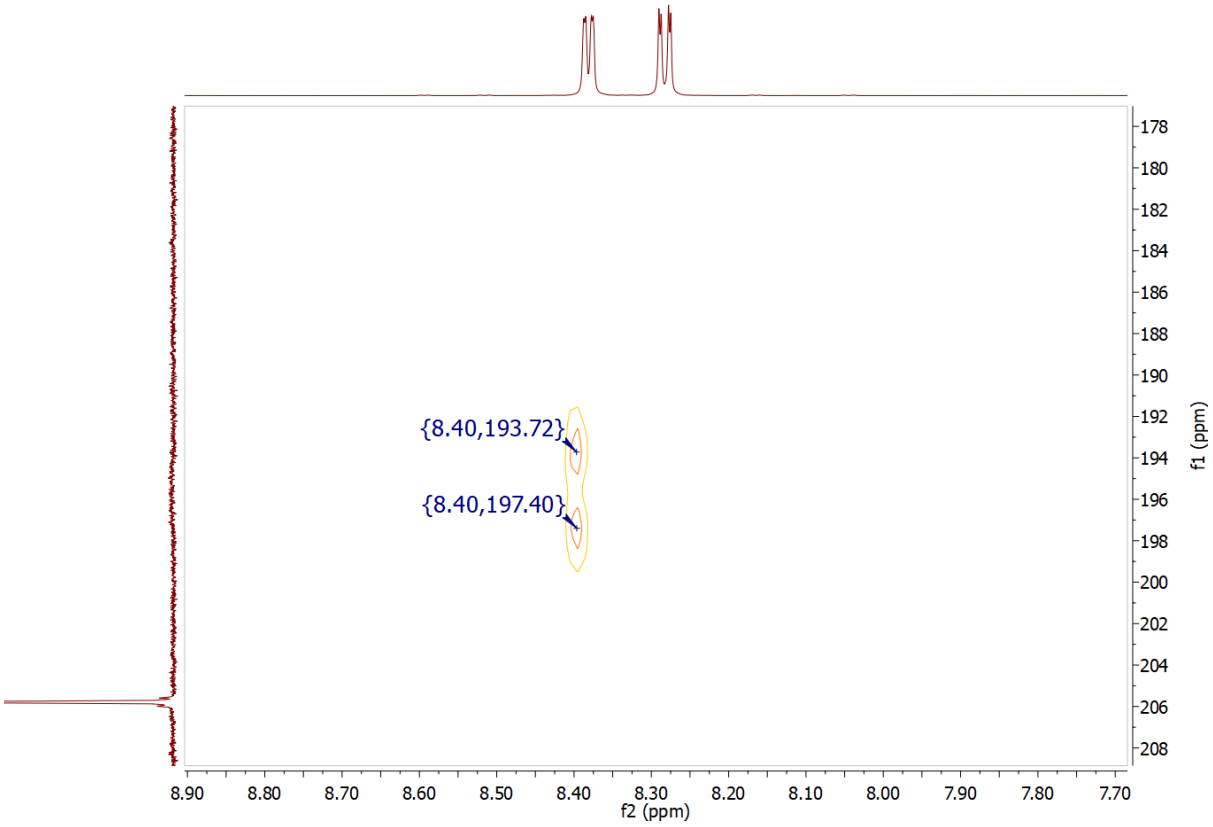
^{19}F NMR (376 MHz, Acetone-d_6) for **1t**:



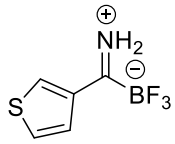
^{13}C NMR (101 MHz, Acetone-d_6) for **1t**:



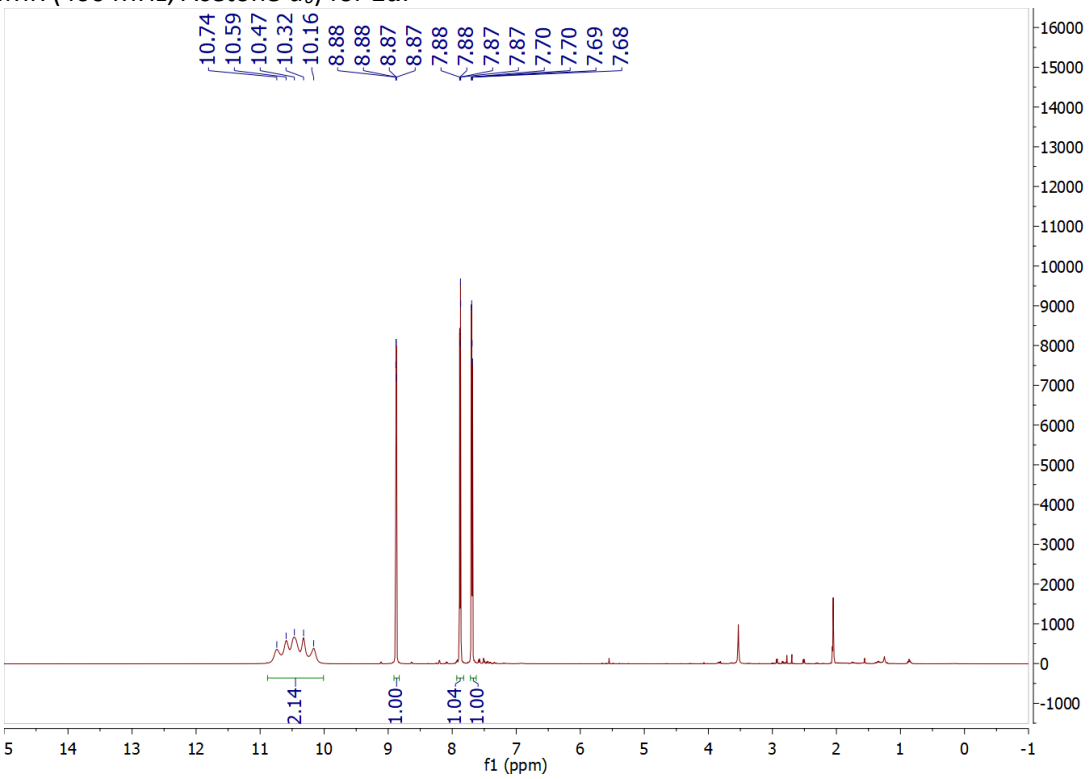
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1t**:



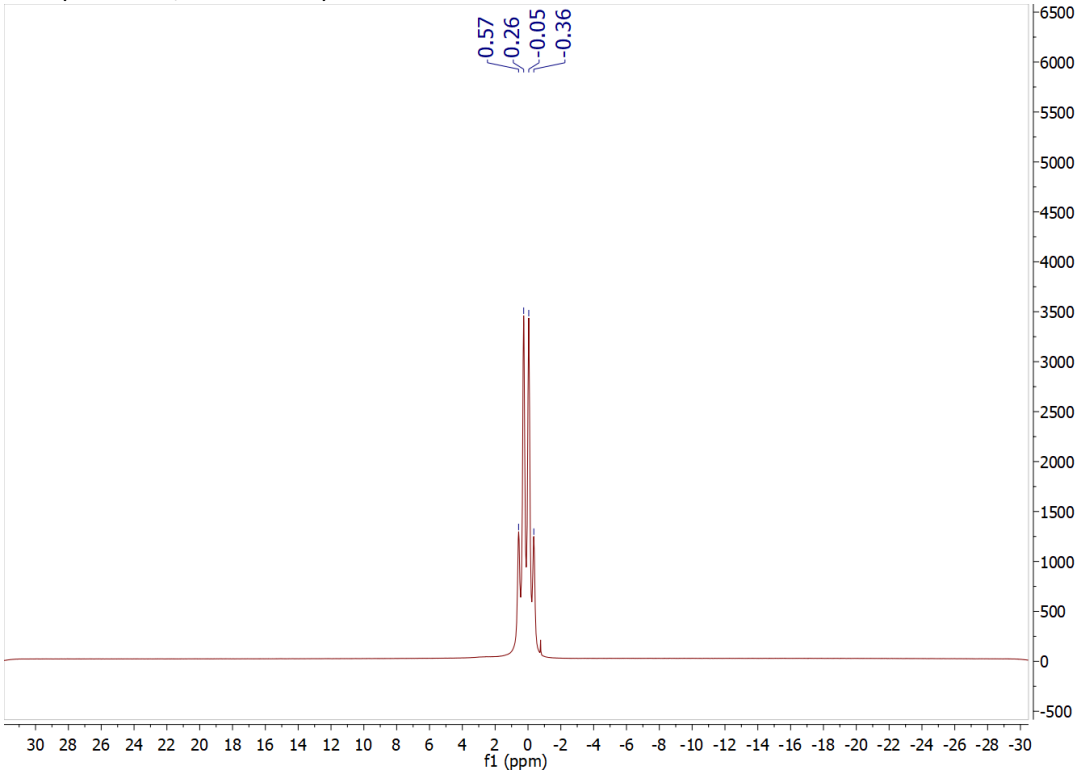
(Iminio(thiophen-3-yl)methyl)trifluoroborate (1u)



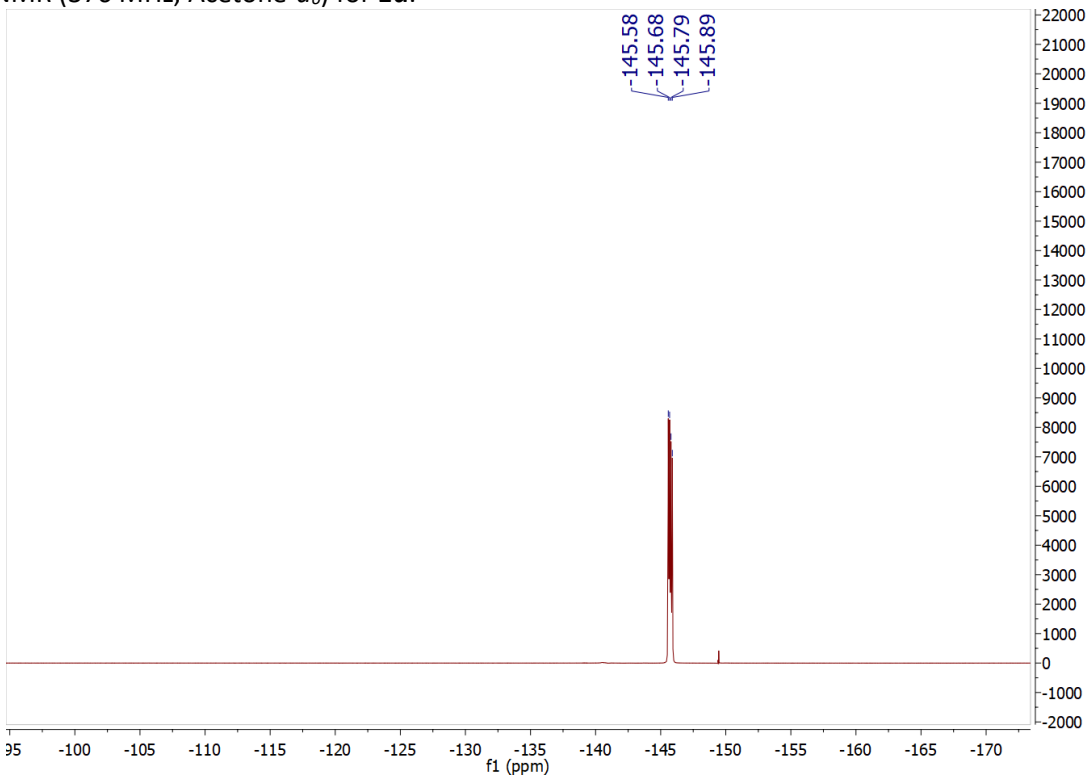
^{1}H NMR (400 MHz, Acetone-d_6) for **1u**:



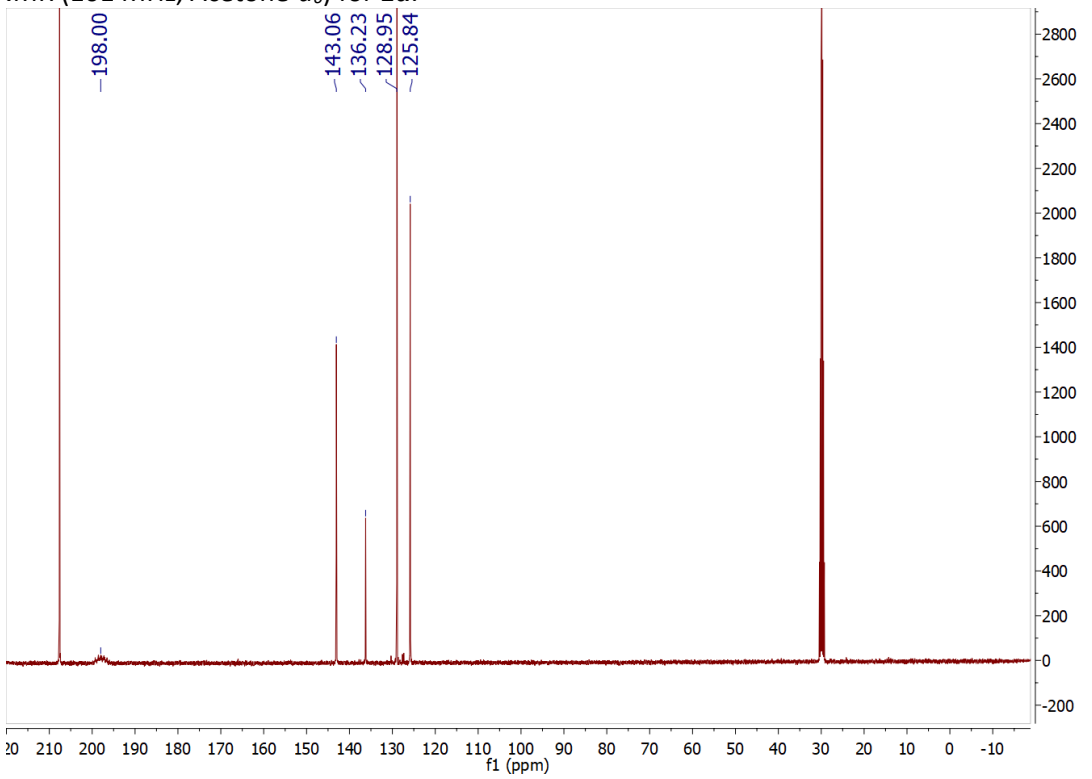
^{11}B NMR (128 MHz, Acetone-d_6) for **1u**:



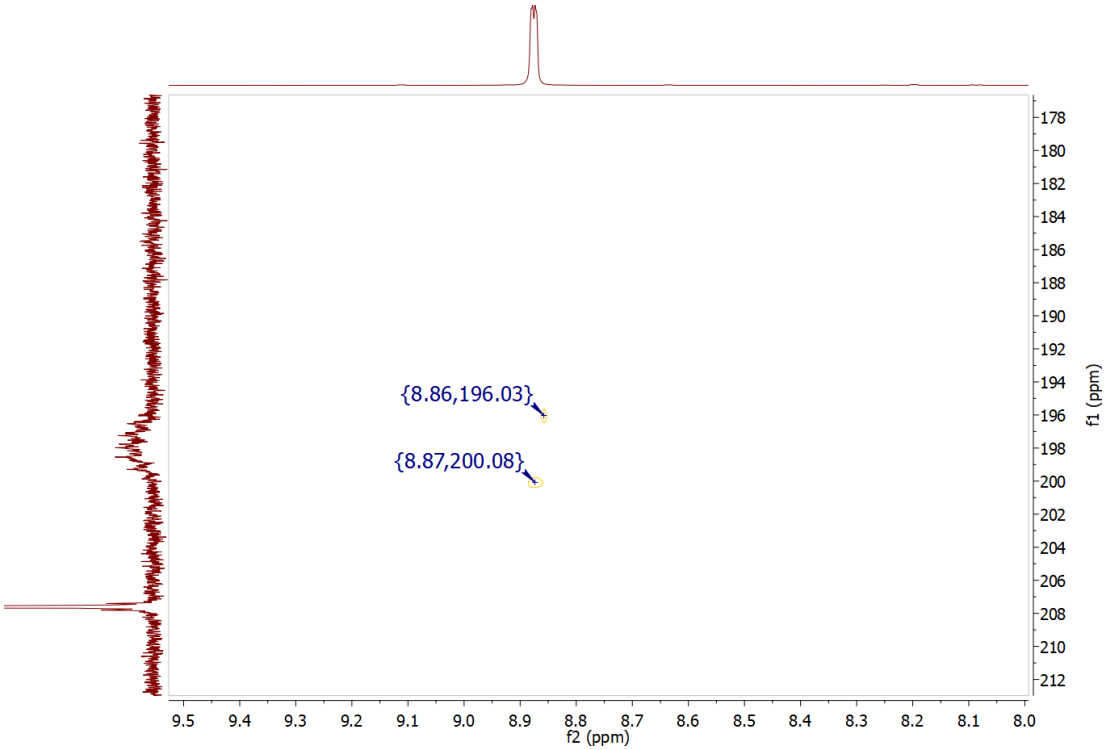
^{19}F NMR (376 MHz, Acetone-d_6) for **1u**:



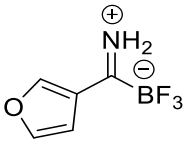
^{13}C NMR (101 MHz, Acetone-d_6) for **1u**:



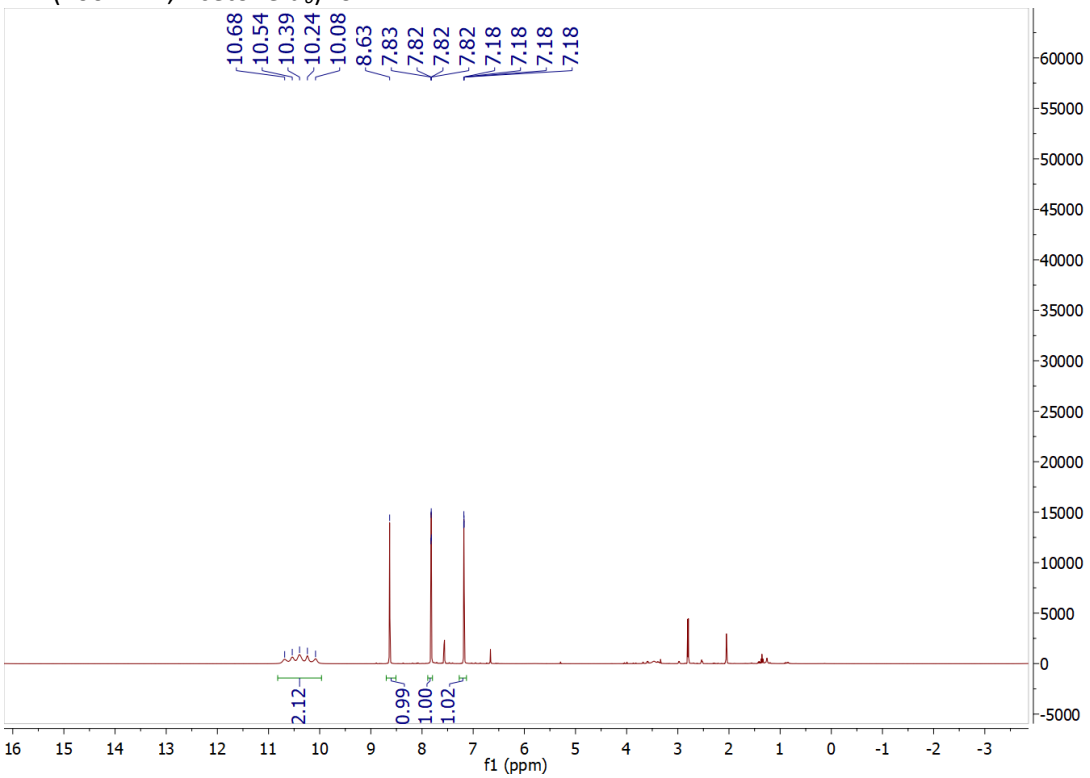
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1u**:



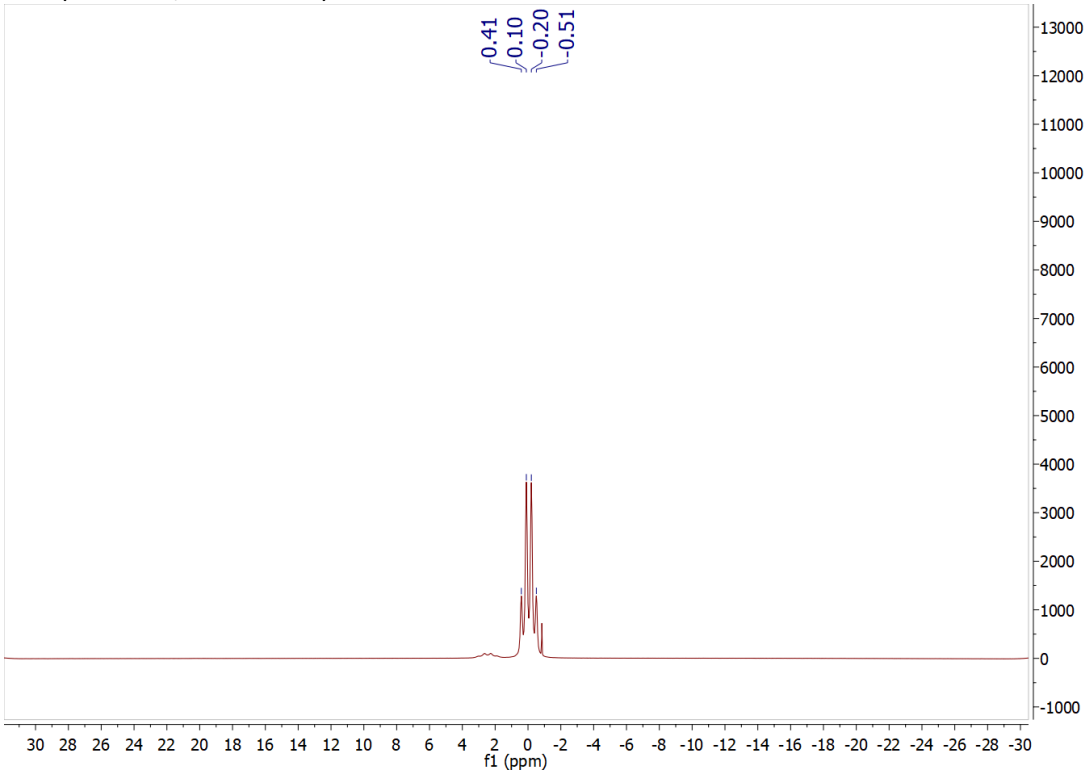
(Furan-3-yl(iminio)methyl)trifluoroborate (1v)



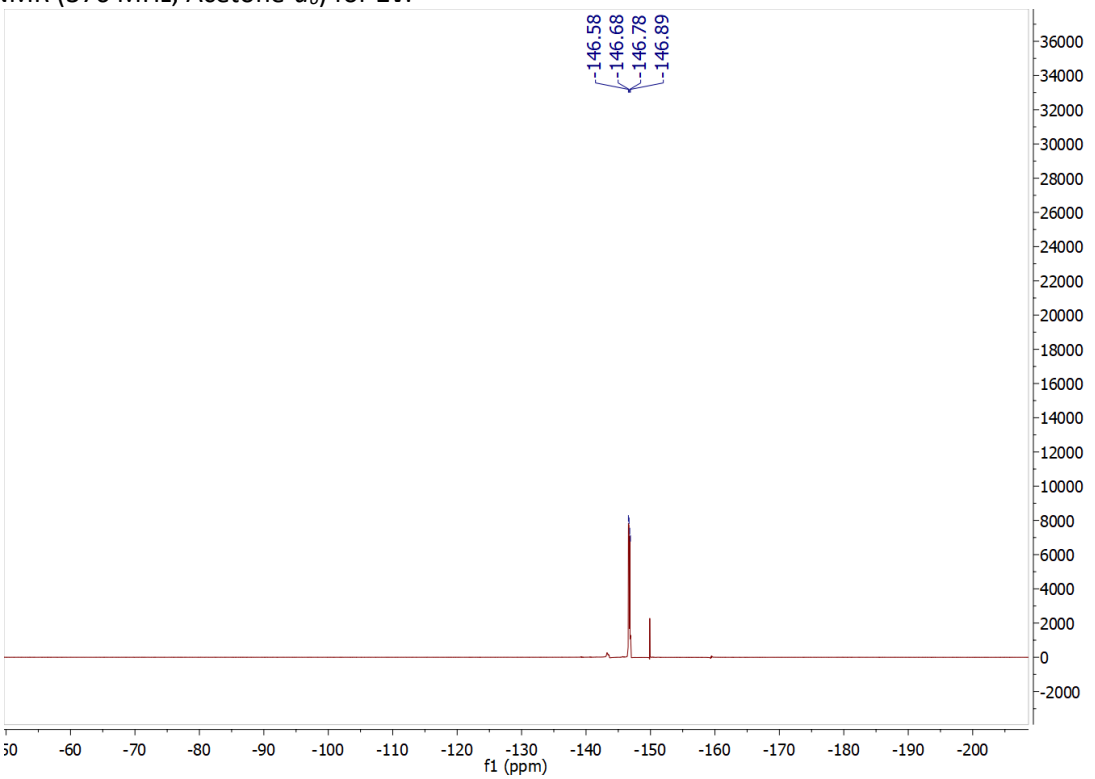
^{1}H NMR (400 MHz, Acetone-d_6) for **1v**:



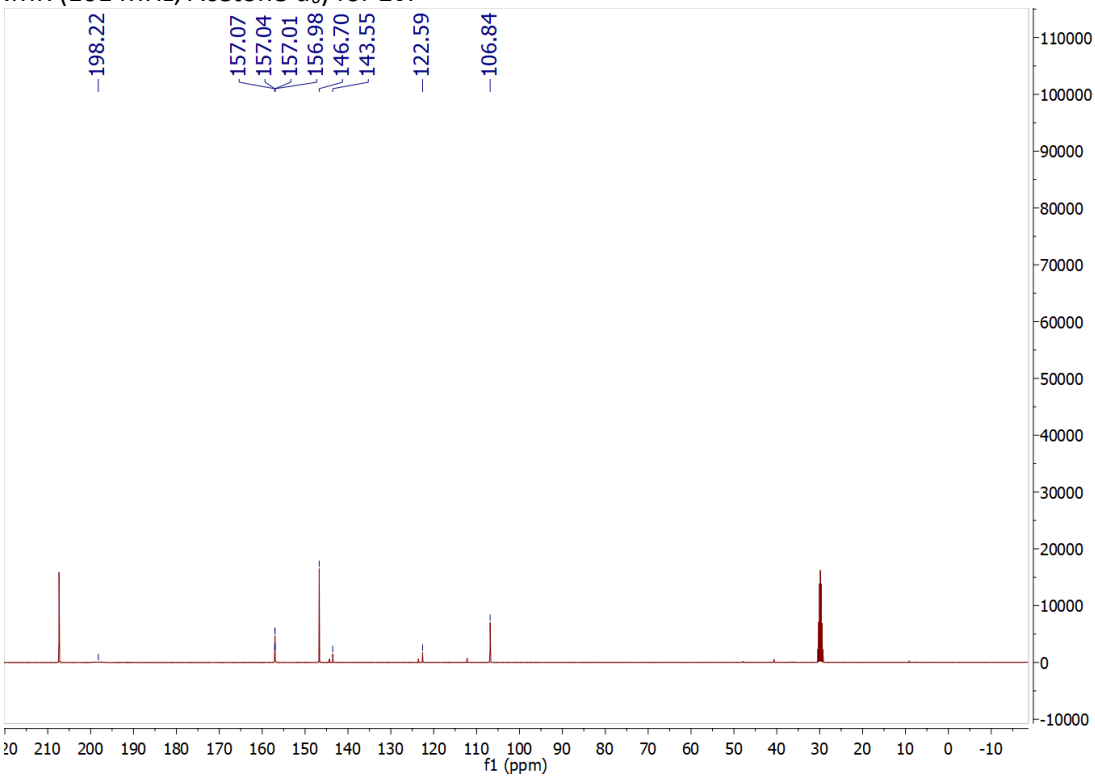
^{11}B NMR (128 MHz, Acetone-d_6) for **1v**:



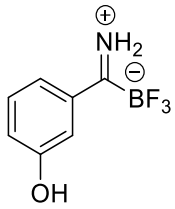
^{19}F NMR (376 MHz, Acetone-d_6) for **1v**:



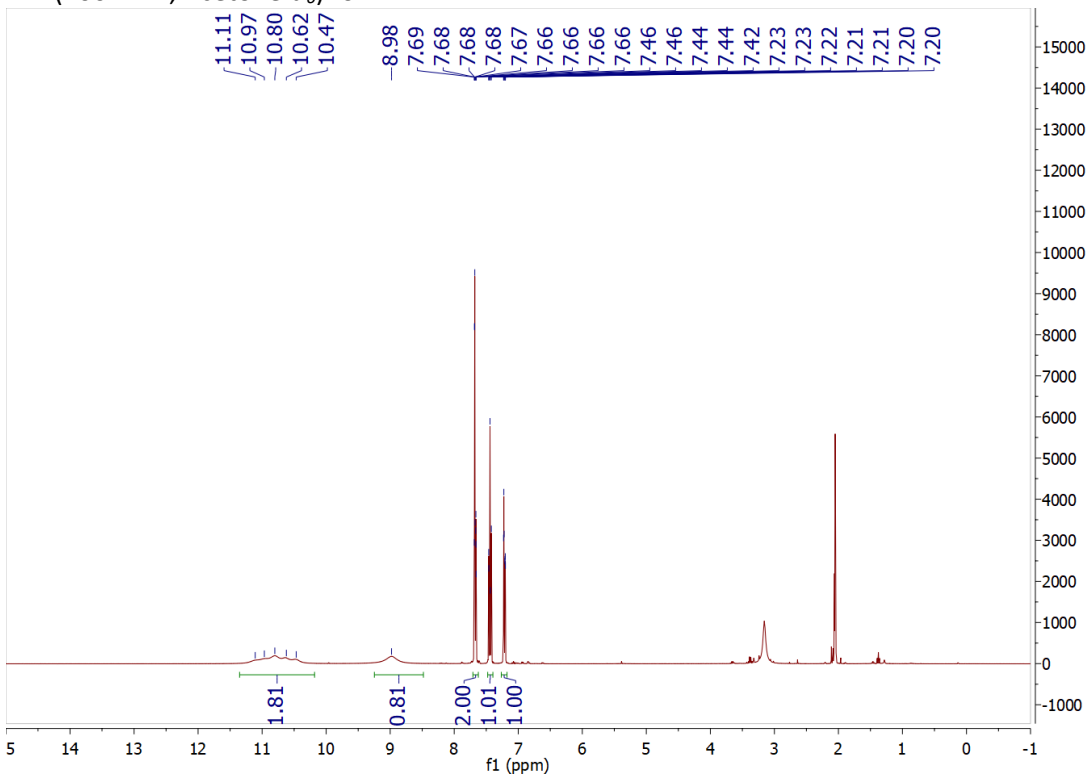
^{13}C NMR (101 MHz, Acetone-d_6) for **1v**:



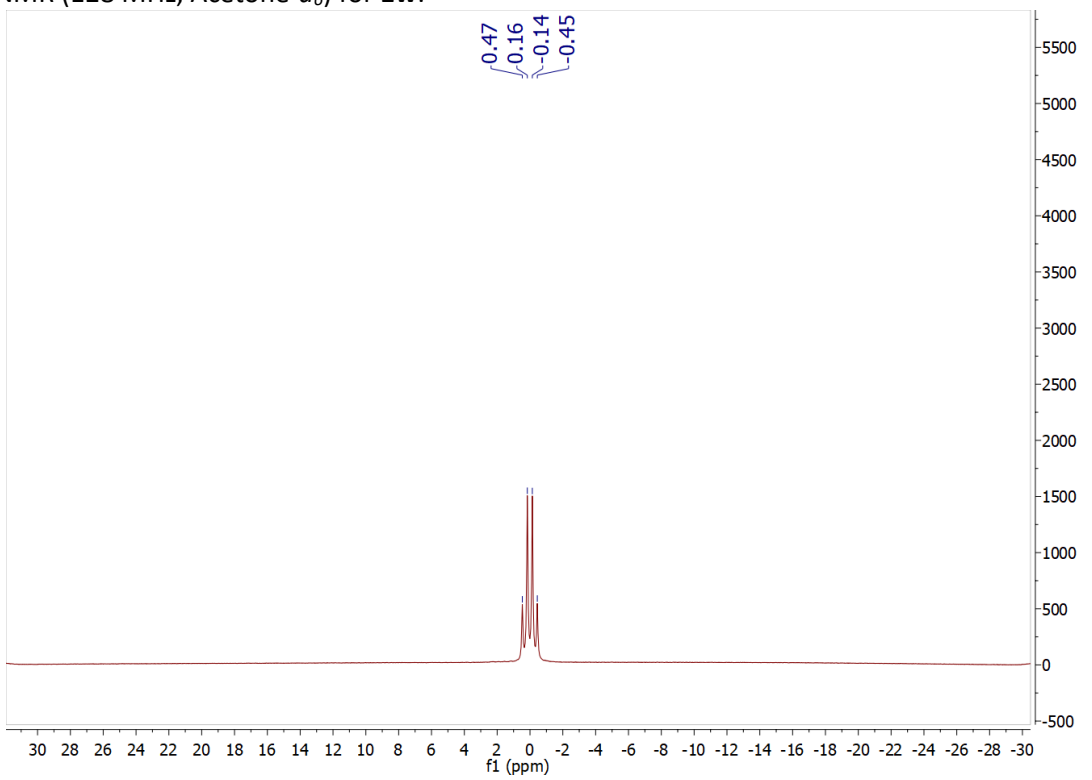
((3-Hydroxyphenyl)(iminio)methyl)trifluoroborate (1w)



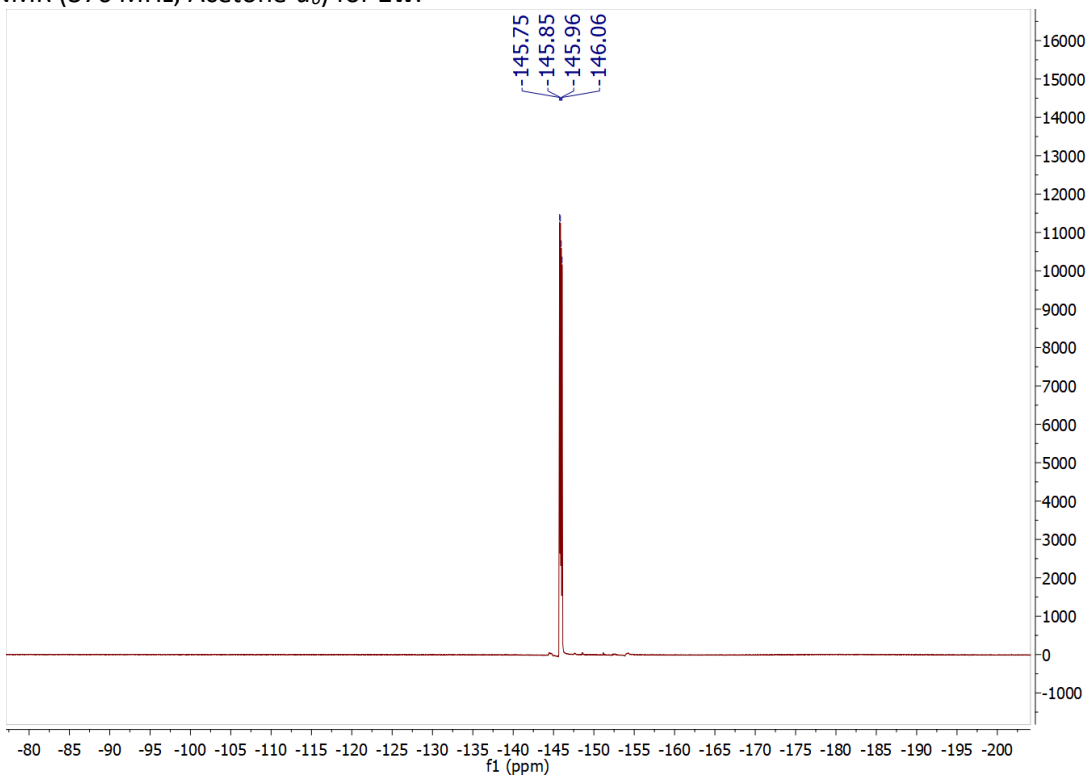
^{1}H NMR (400 MHz, Acetone-d_6) for **1w**:



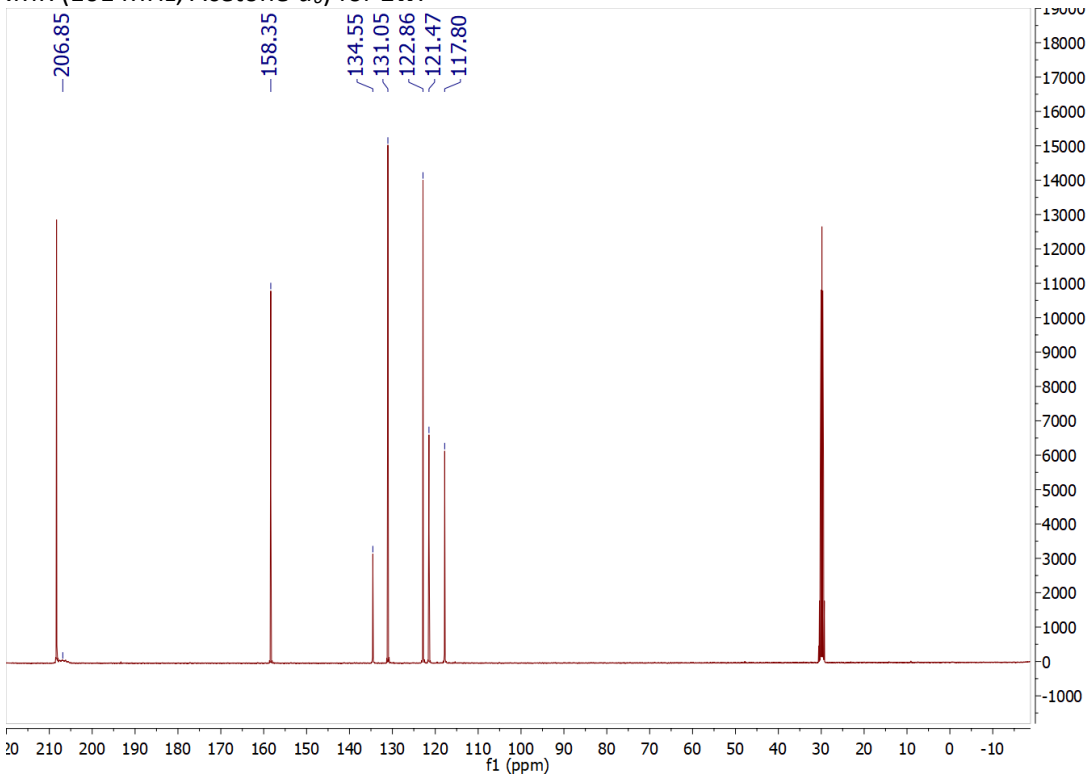
^{11}B NMR (128 MHz, Acetone-d_6) for **1w**:



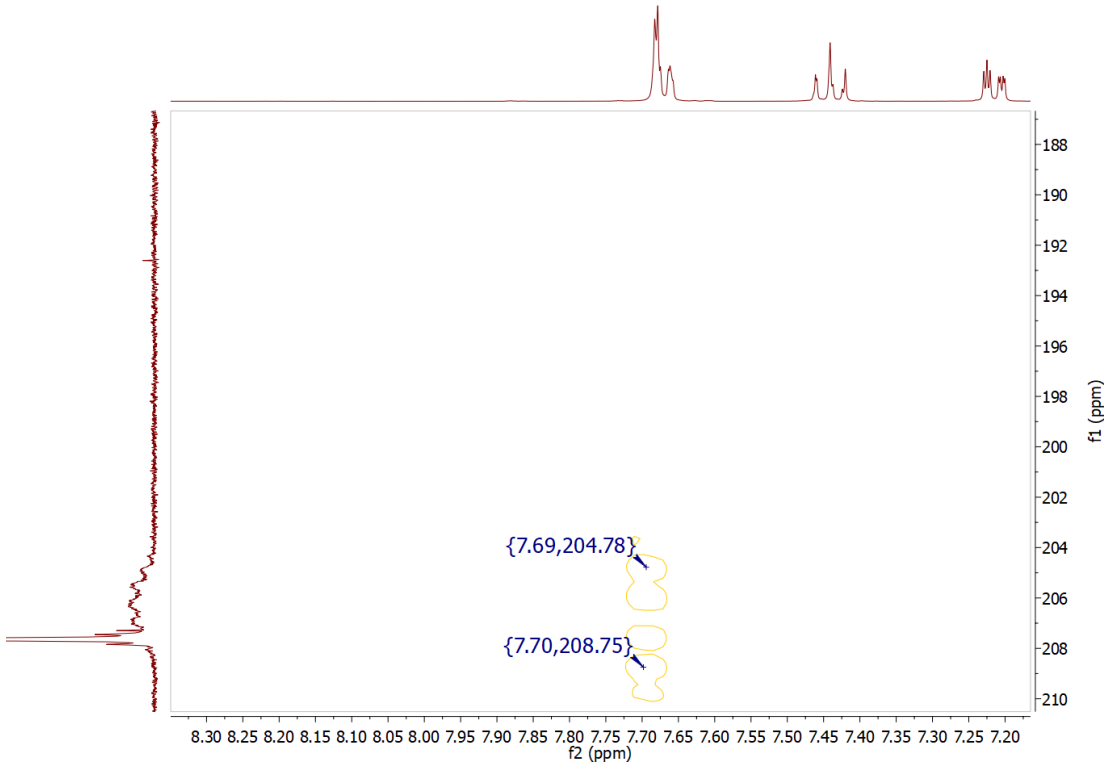
^{19}F NMR (376 MHz, Acetone-d_6) for **1w**:



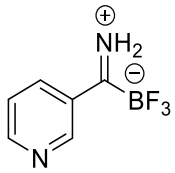
^{13}C NMR (101 MHz, Acetone-d_6) for **1w**:



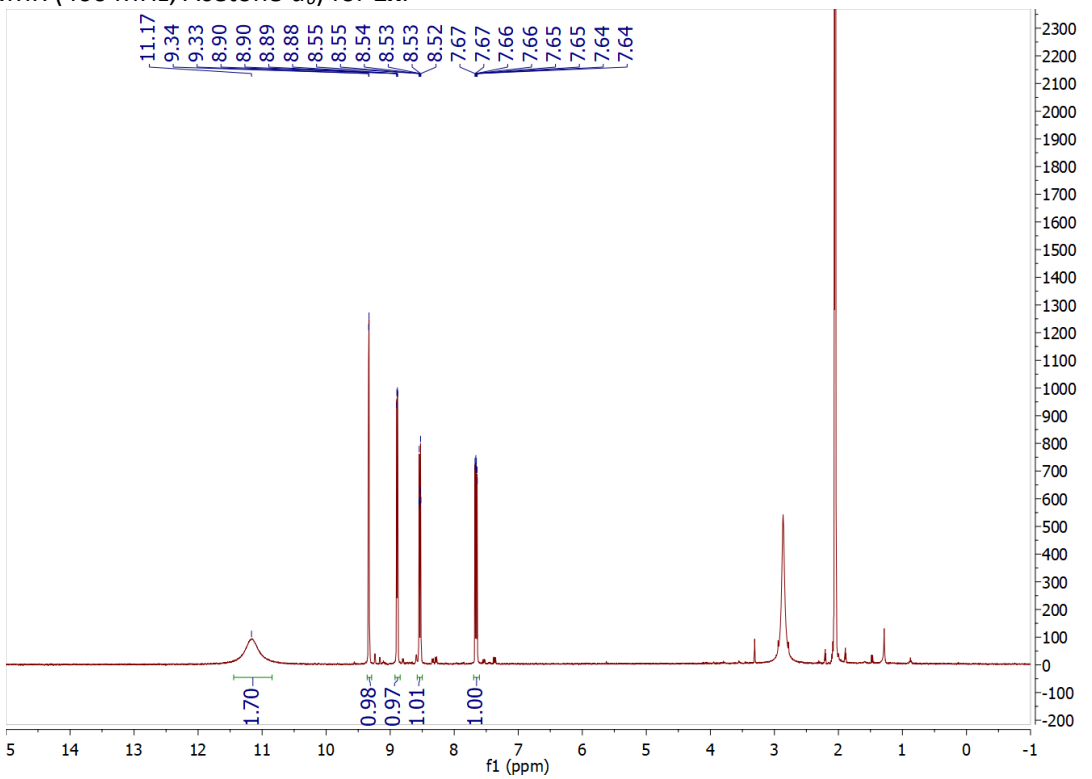
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **1w**:



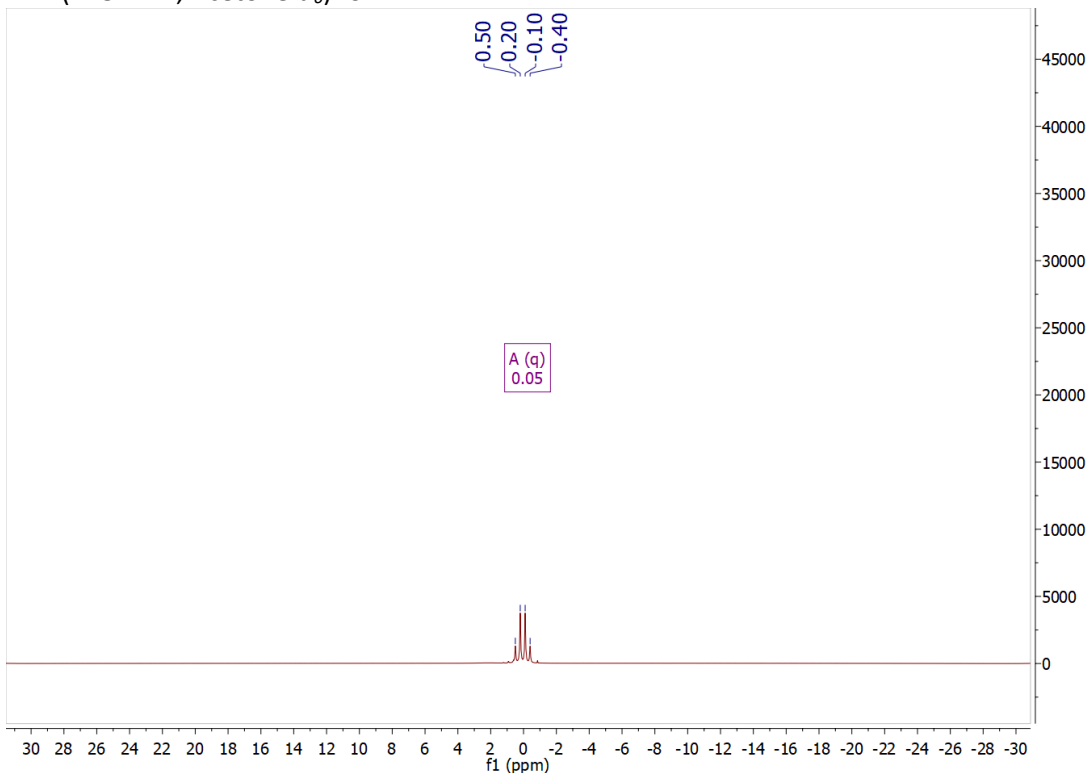
(Iminio(pyridin-3-yl)methyl)trifluoroborate (1x)



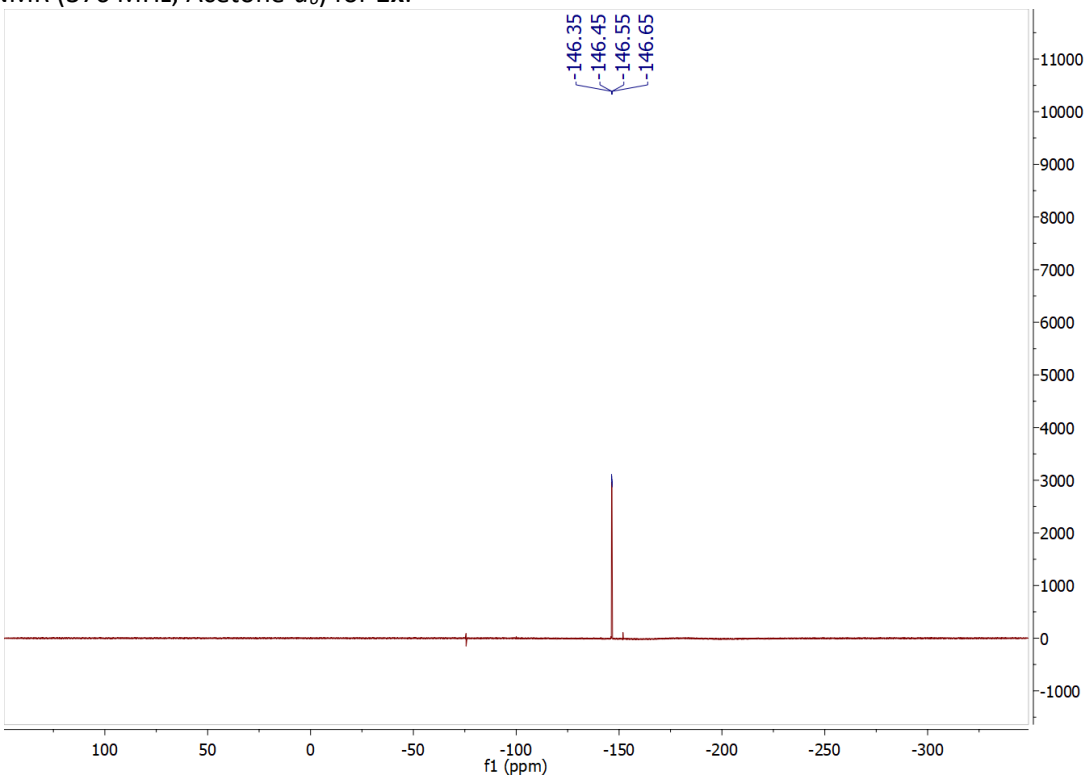
^{1}H NMR (400 MHz, Acetone-d_6) for **1x**:



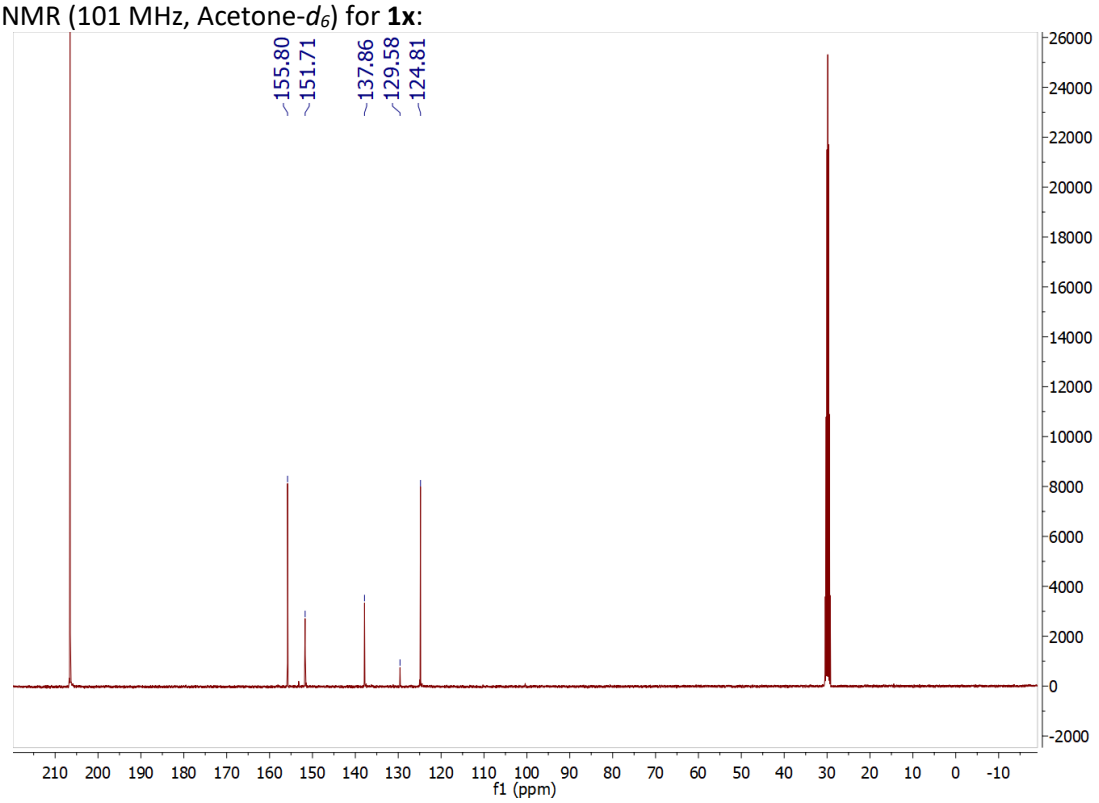
^{11}B NMR (128 MHz, Acetone-d_6) for **1x**:



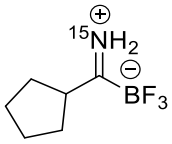
^{19}F NMR (376 MHz, Acetone-d_6) for **1x**:



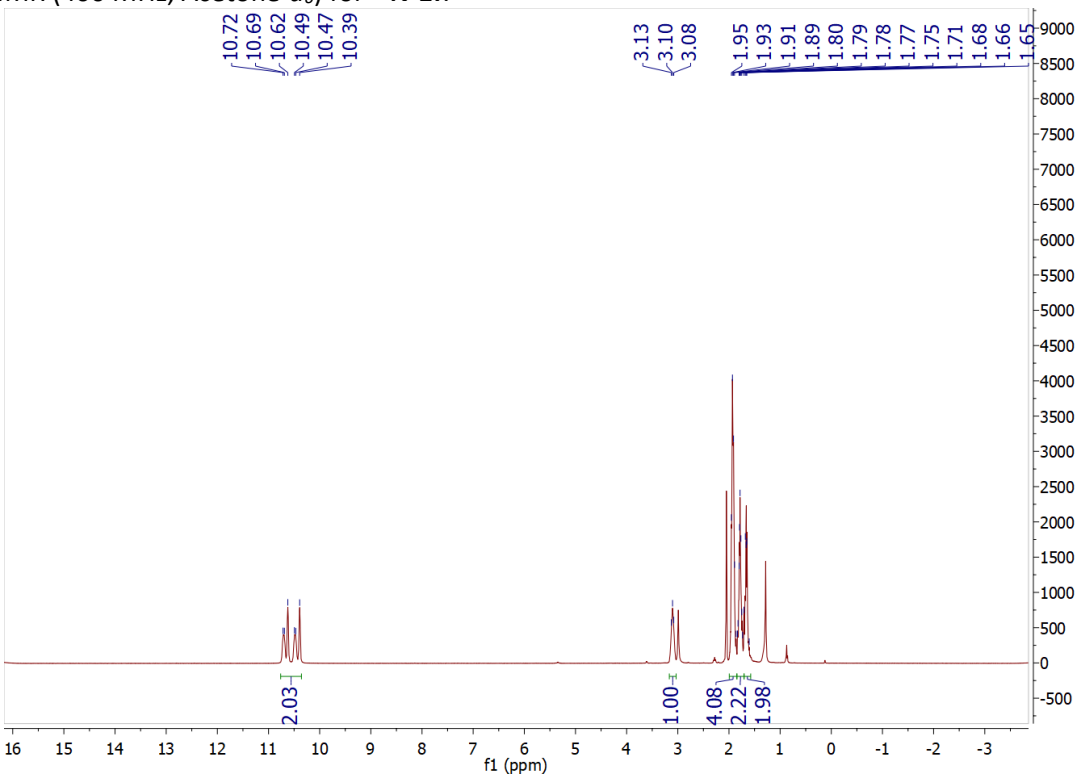
^{13}C NMR (101 MHz, Acetone-d_6) for **1x**:



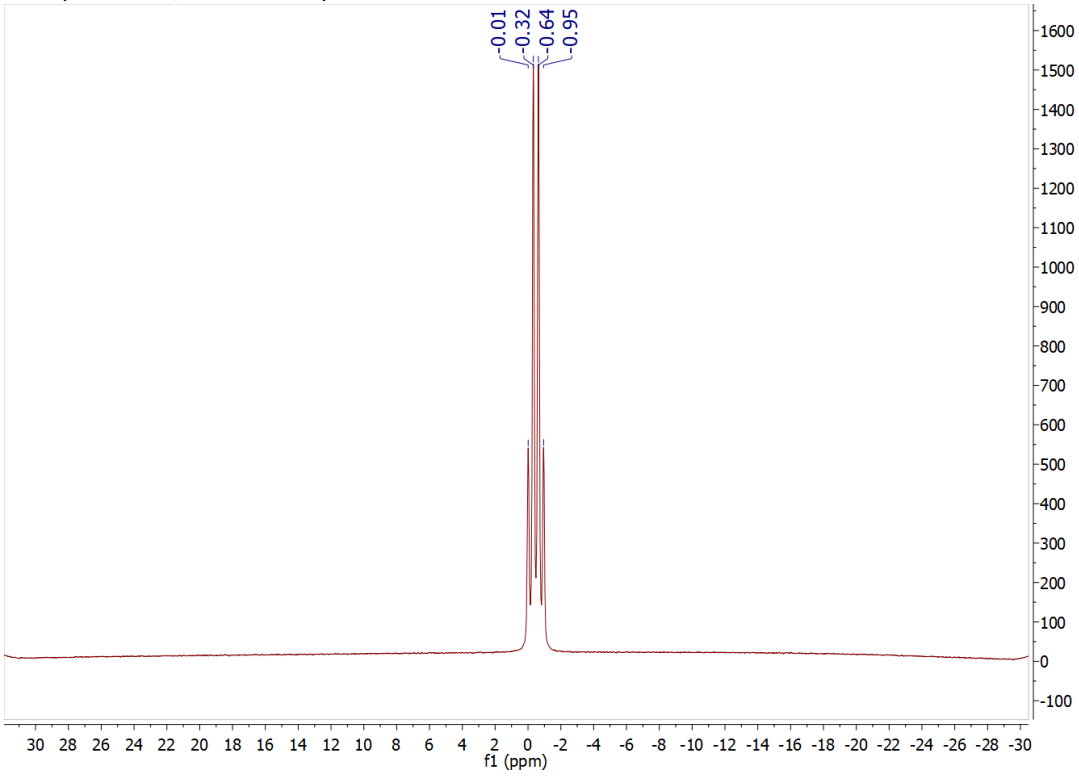
(Cyclopentyl(iminio-^{15}N)methyl)trifluoroborate (^{15}N-1f)



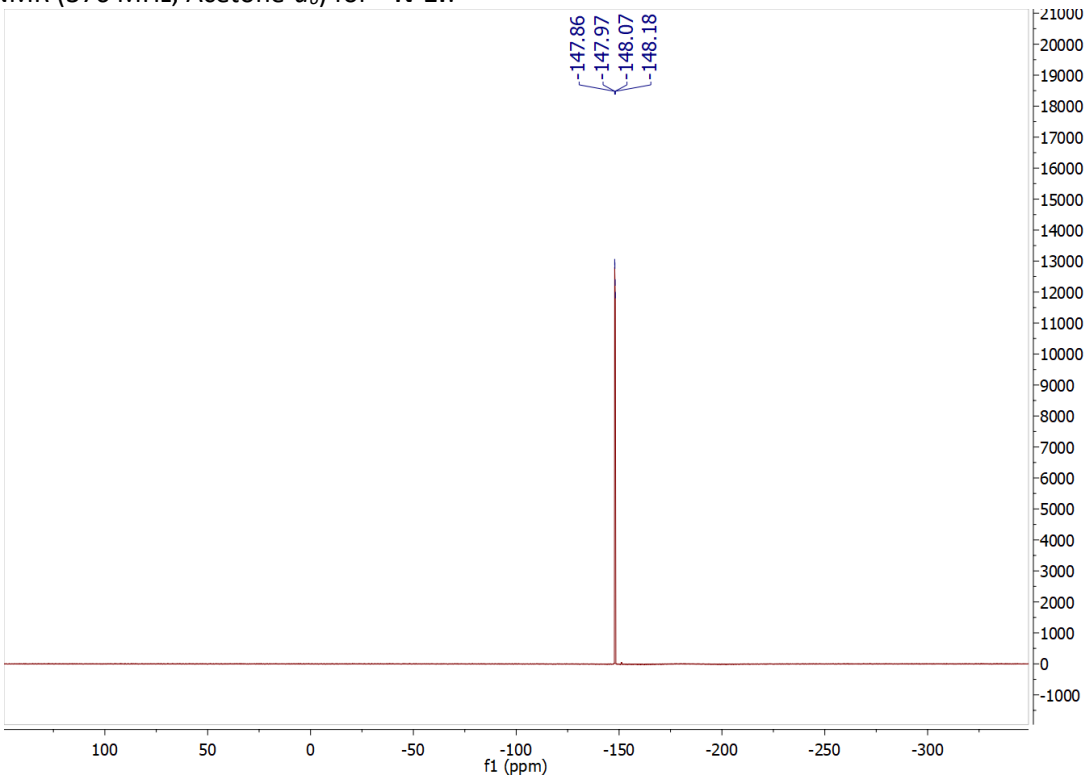
^{1}H NMR (400 MHz, Acetone-d_6) for **^{15}N-1f**:



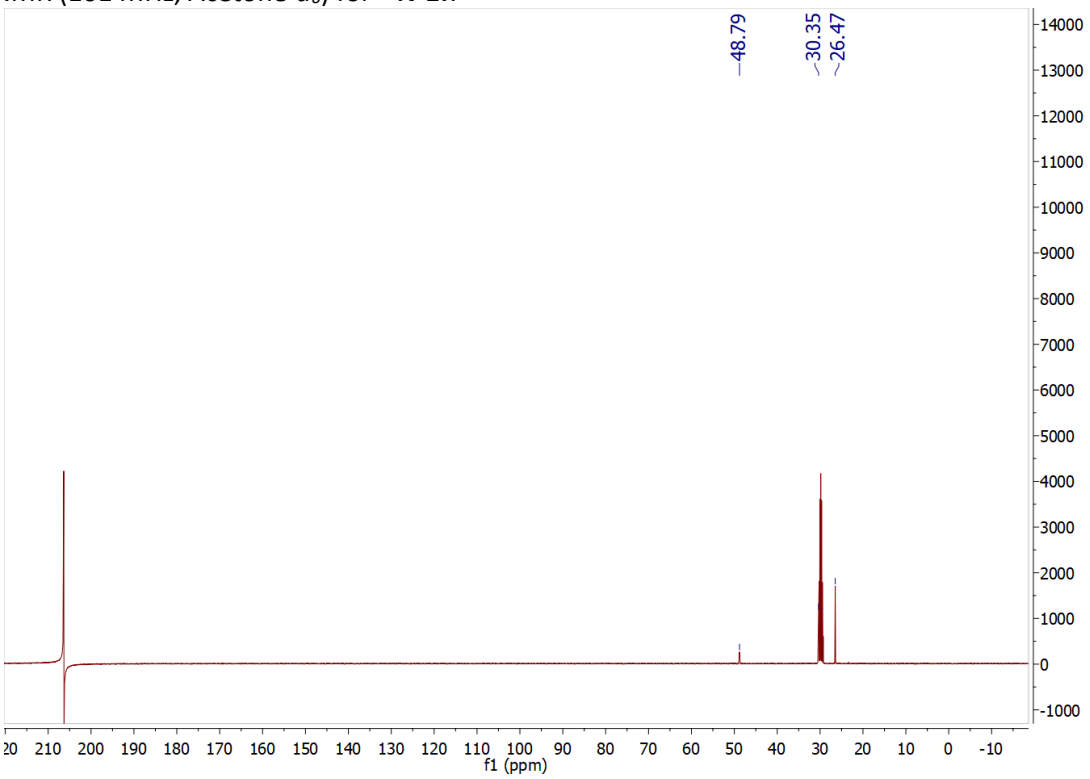
^{11}B NMR (128 MHz, Acetone-d_6) for **^{15}N-1f**:



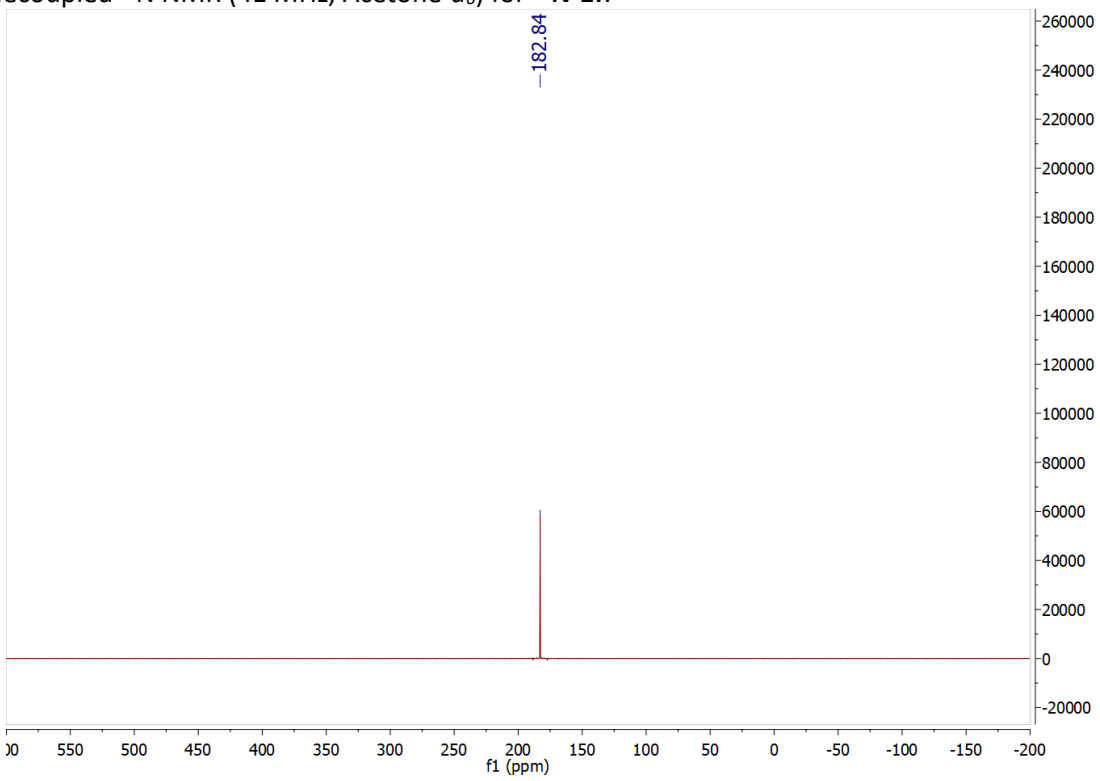
^{19}F NMR (376 MHz, Acetone-d_6) for **^{15}N-1f**:



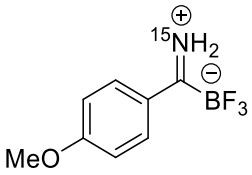
^{13}C NMR (101 MHz, Acetone-d_6) for **^{15}N-1f**:



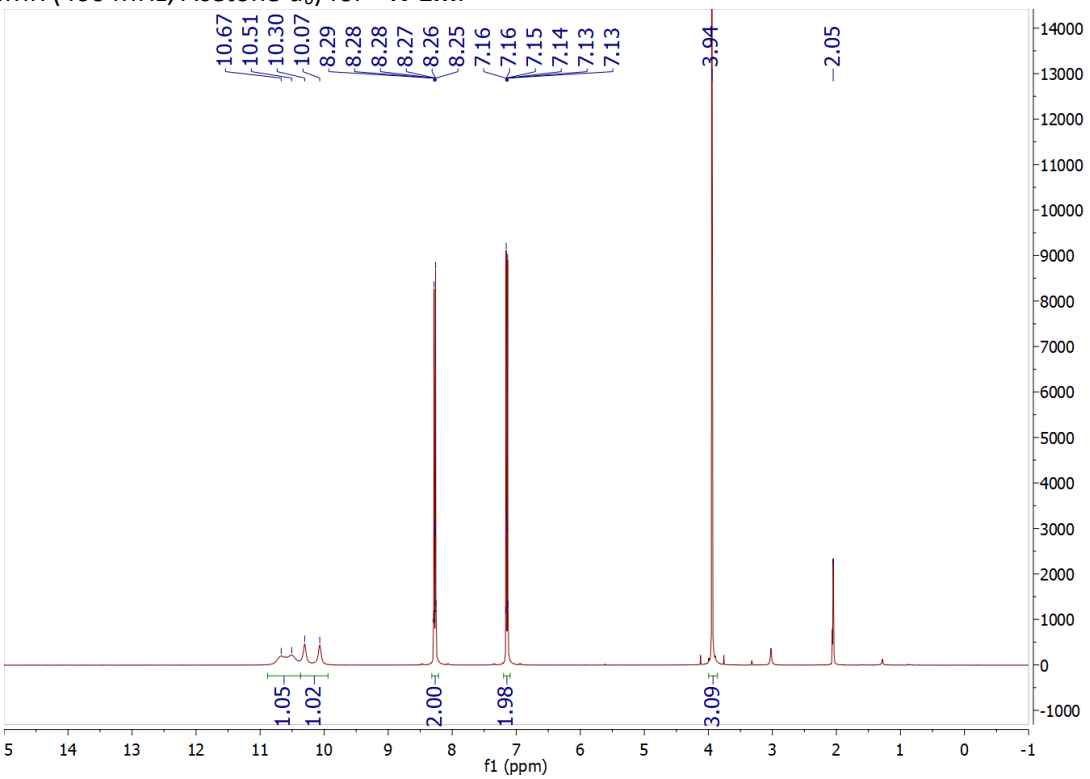
^{1}H decoupled ^{15}N NMR (41 MHz, Acetone-d_6) for **^{15}N-1f**:



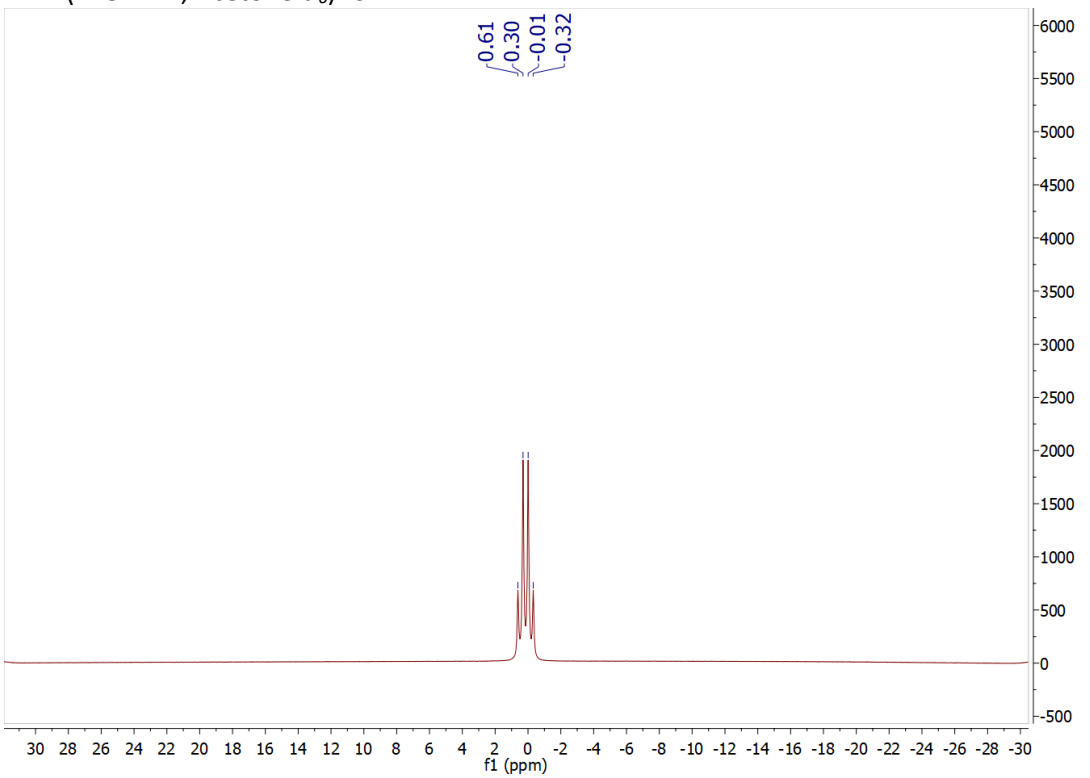
((Iminio-^{15}N)(4-methoxyphenyl)methyl)trifluoroborate (^{15}N-1m)



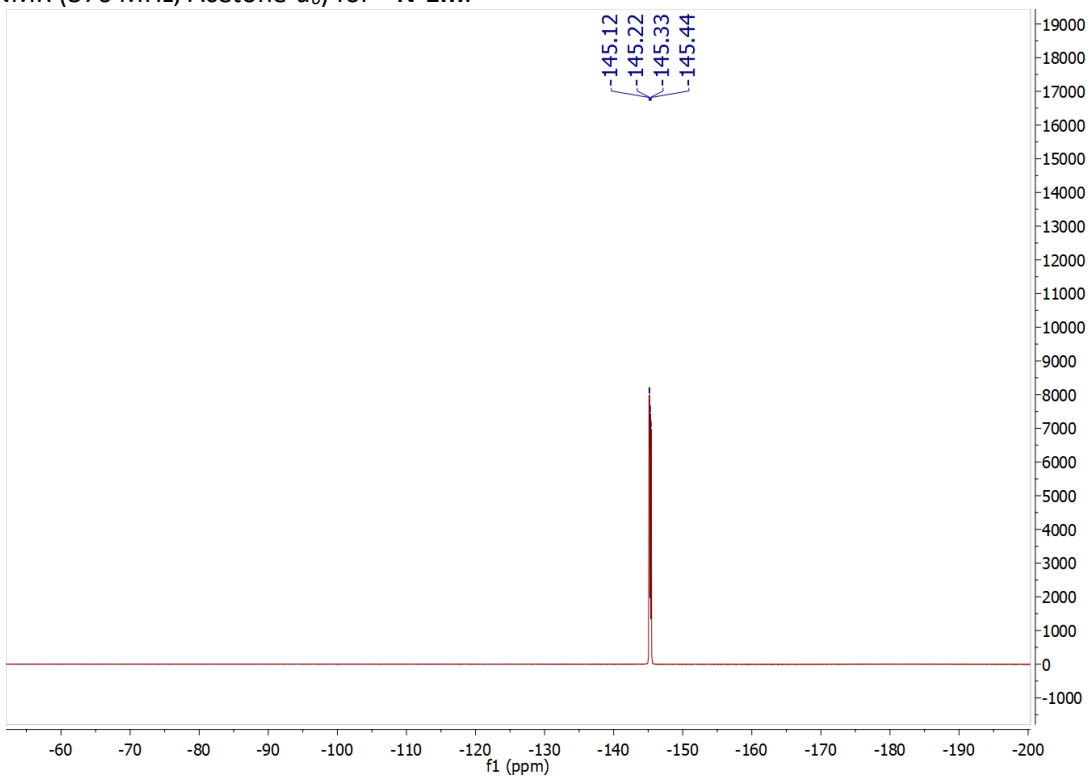
^{1}H NMR (400 MHz, Acetone-d_6) for **^{15}N-1m**:



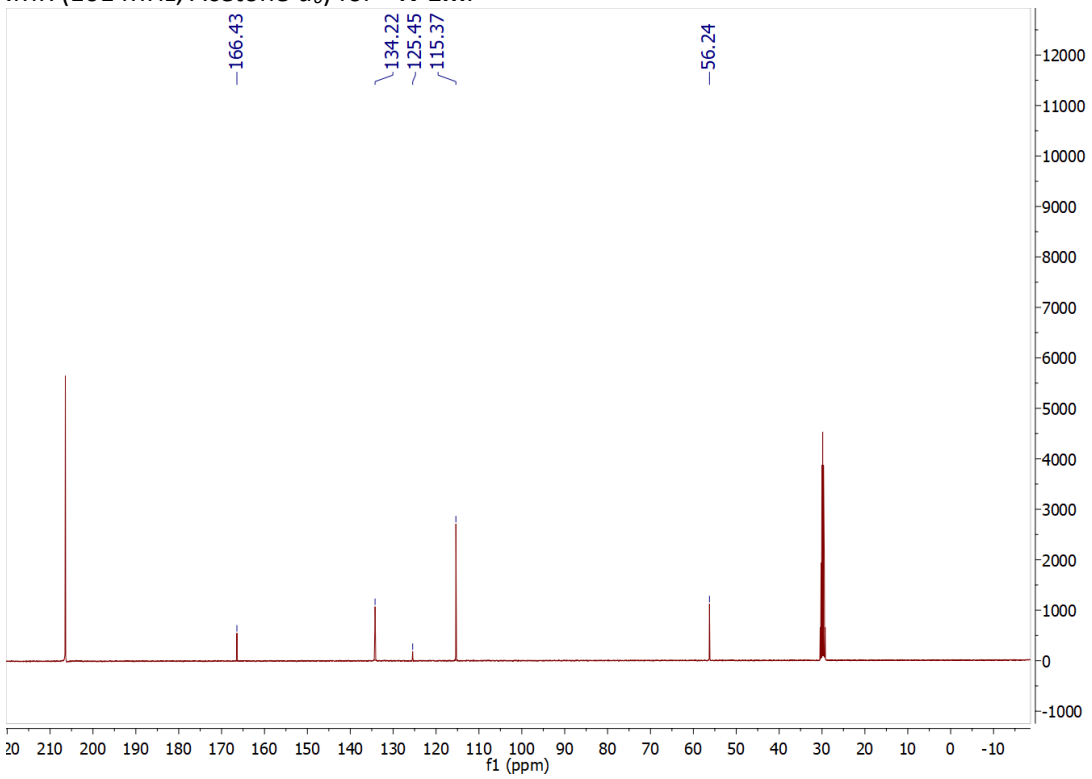
^{11}B NMR (128 MHz, Acetone-d_6) for **^{15}N-1m**:



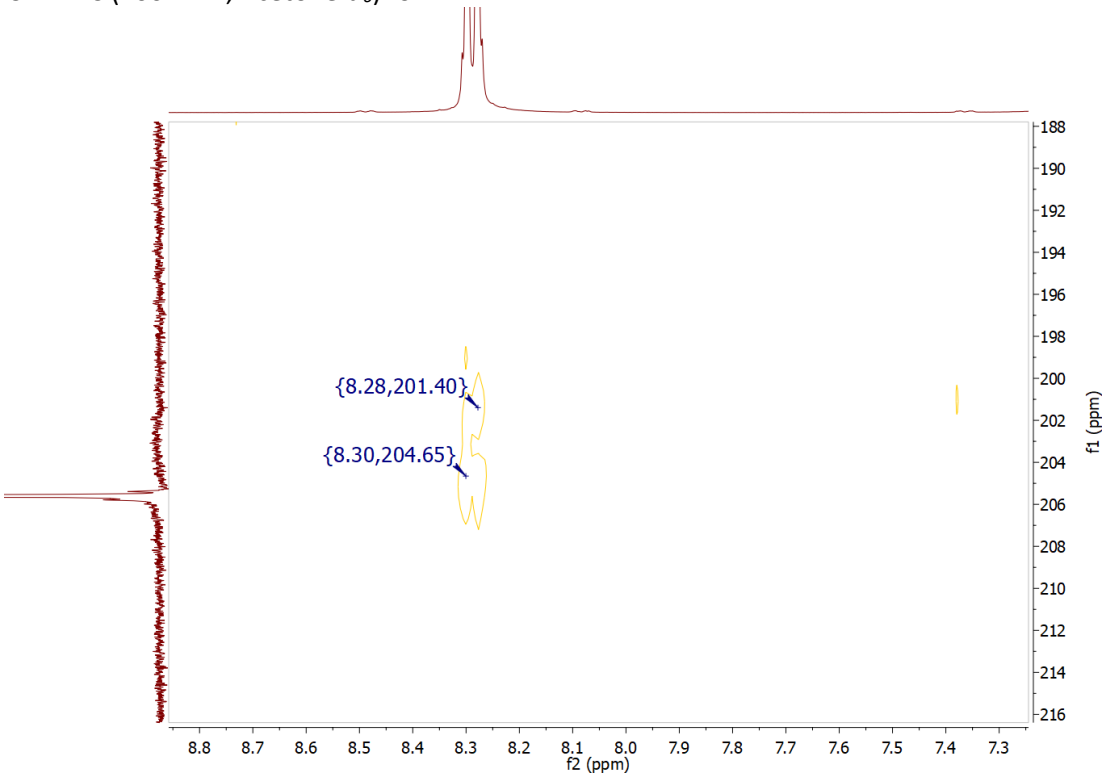
^{19}F NMR (376 MHz, Acetone-d_6) for **^{15}N-1m**:



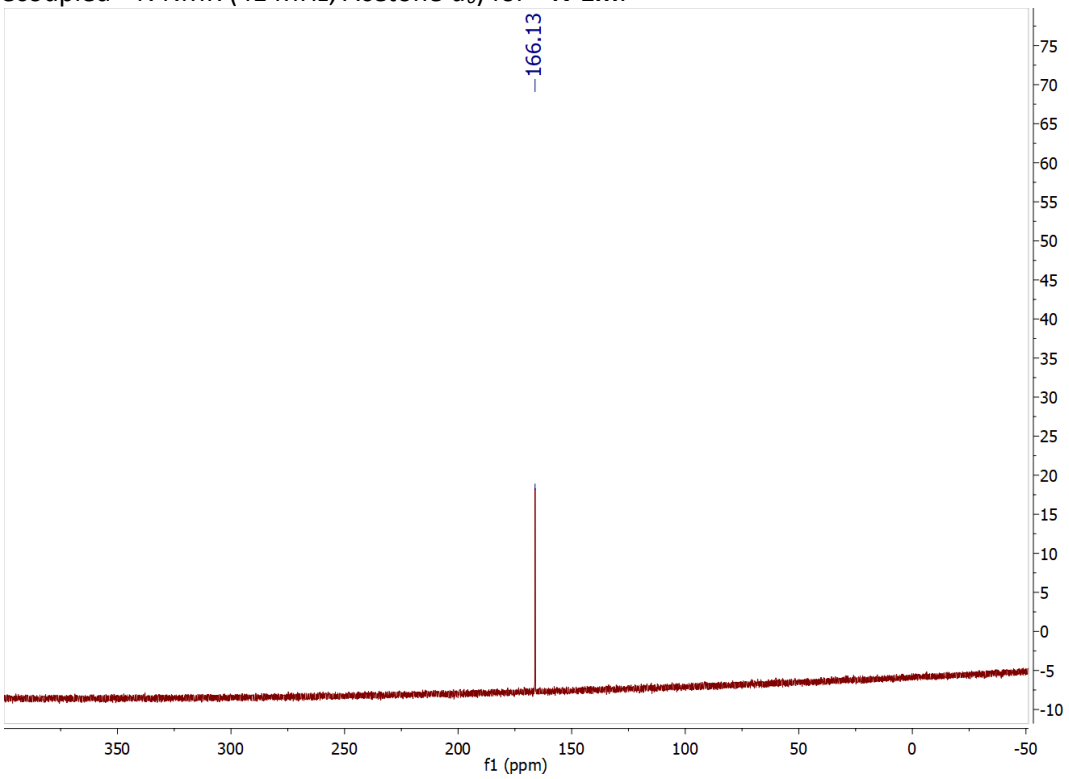
^{13}C NMR (101 MHz, Acetone-d_6) for **^{15}N-1m**:



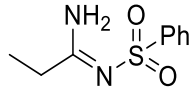
^{1}H-^{13}C HMBC (400 MHz, Acetone-d_6) for **^{15}N-1m**:



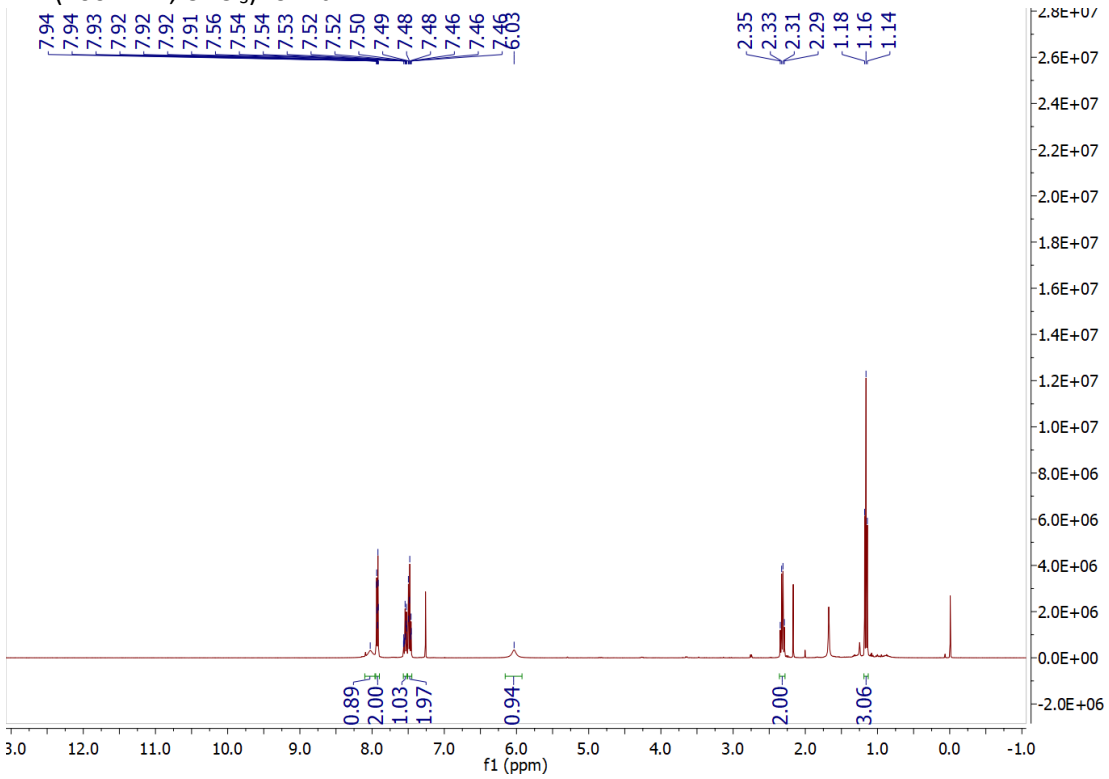
^{1}H decoupled ^{15}N NMR (41 MHz, Acetone-d_6) for **^{15}N-1m**:



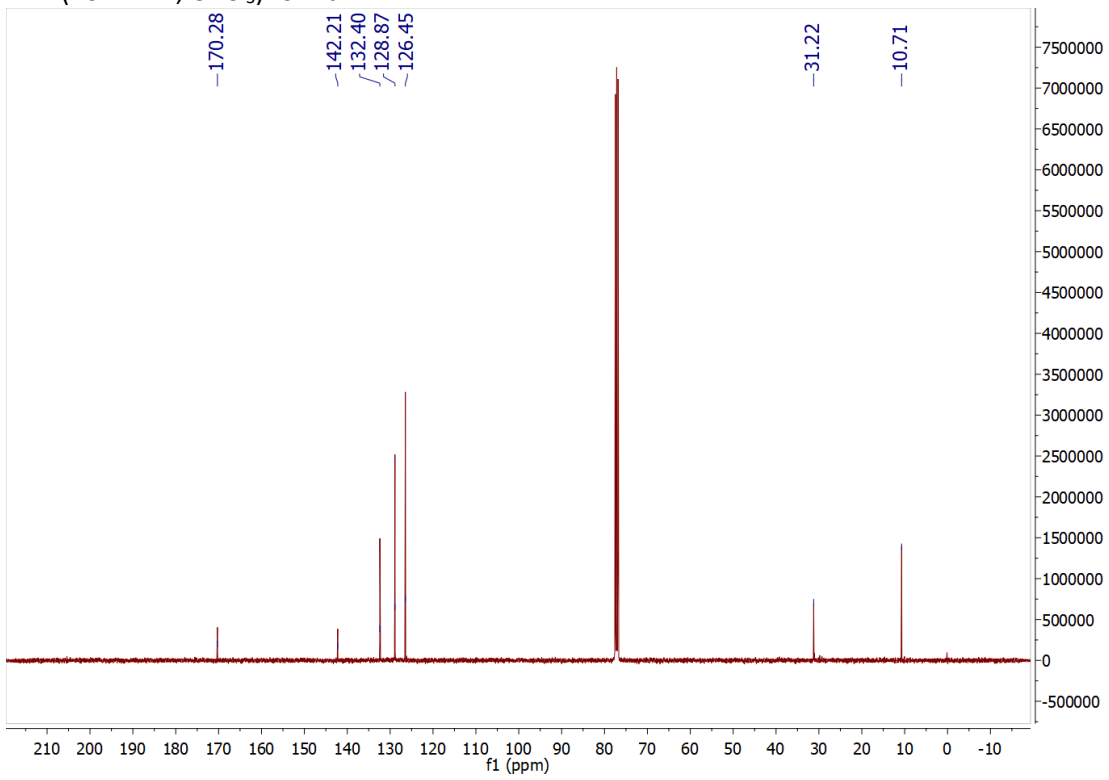
(*Z*)-*N*'-(Phenylsulfonyl)propionimidamide (2a)



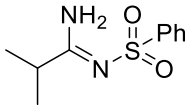
^{1}H NMR (400 MHz, $CDCl_3$) for **2a**:



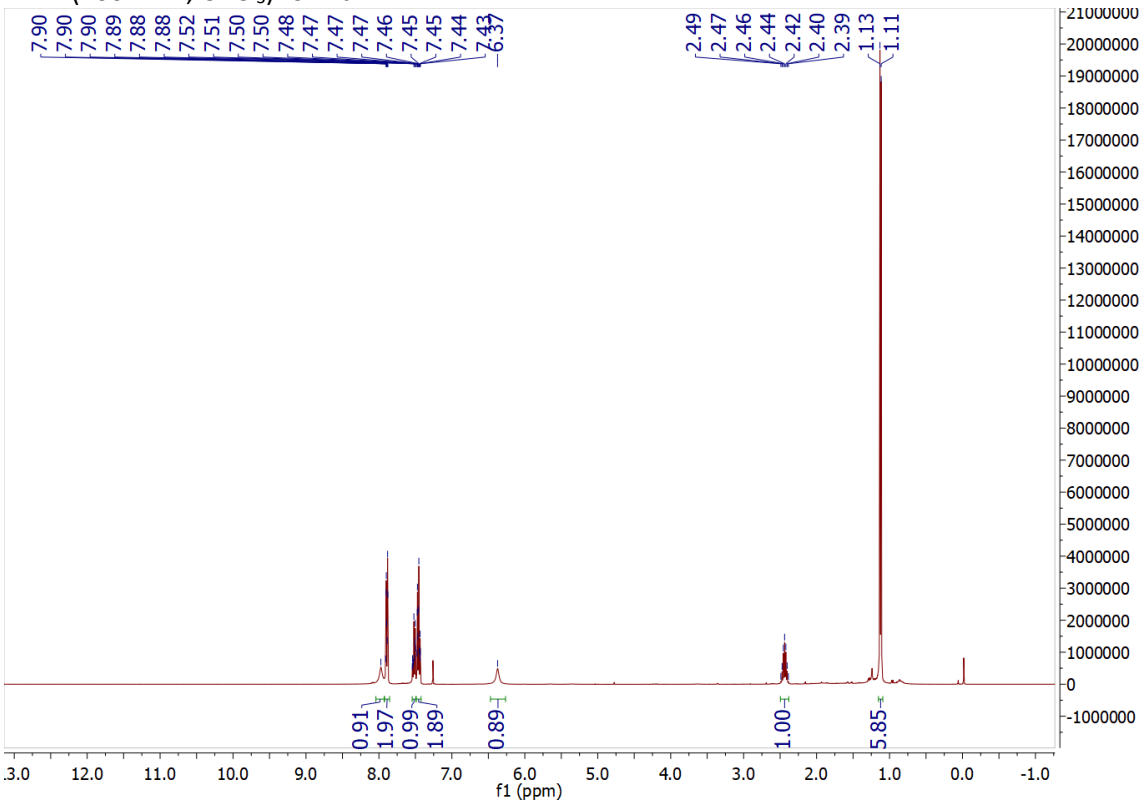
^{13}C NMR (101 MHz, $CDCl_3$) for **2a**:



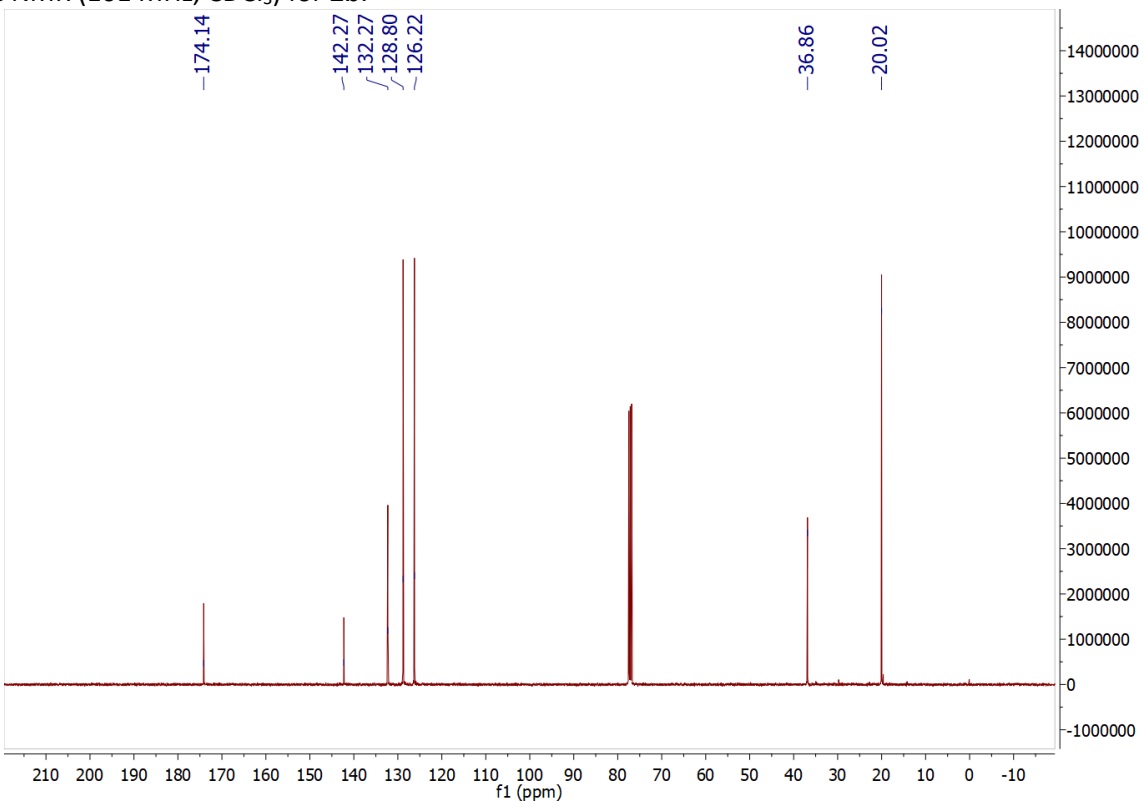
(*Z*)-*N*'-(Phenylsulfonyl)isobutyrimidamide (2b)



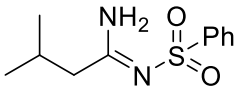
^{1}H NMR (400 MHz, $CDCl_3$) for **2b**:



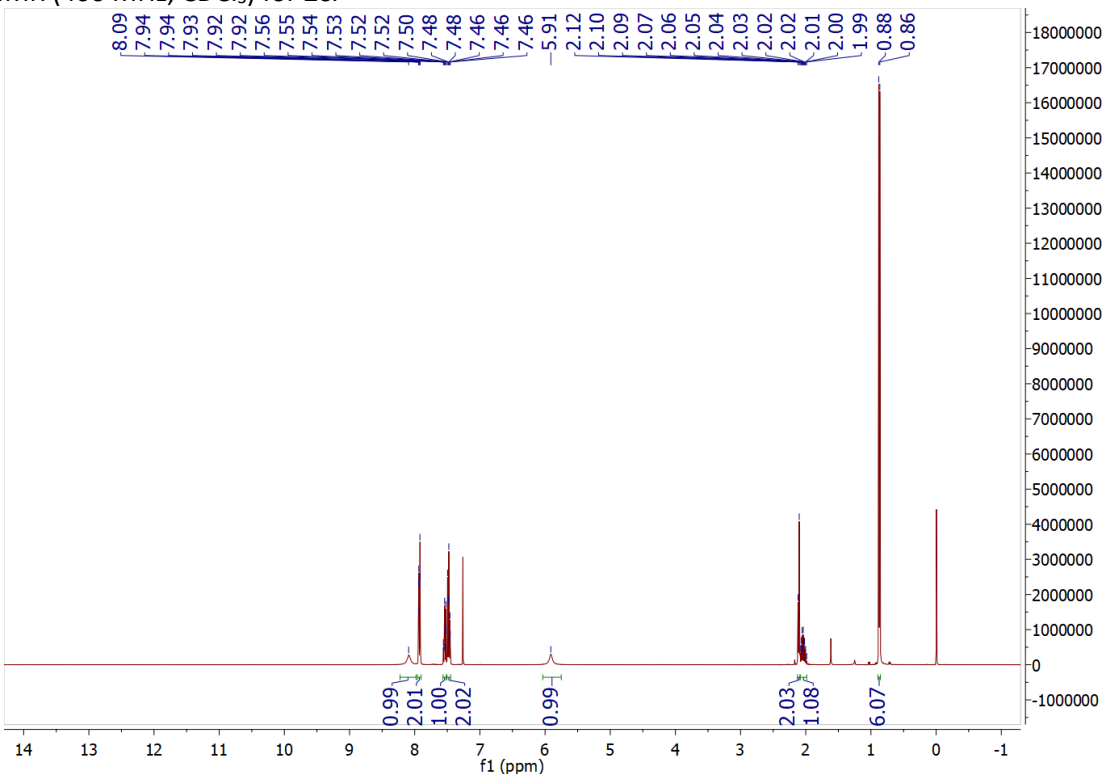
^{13}C NMR (101 MHz, $CDCl_3$) for **2b**:



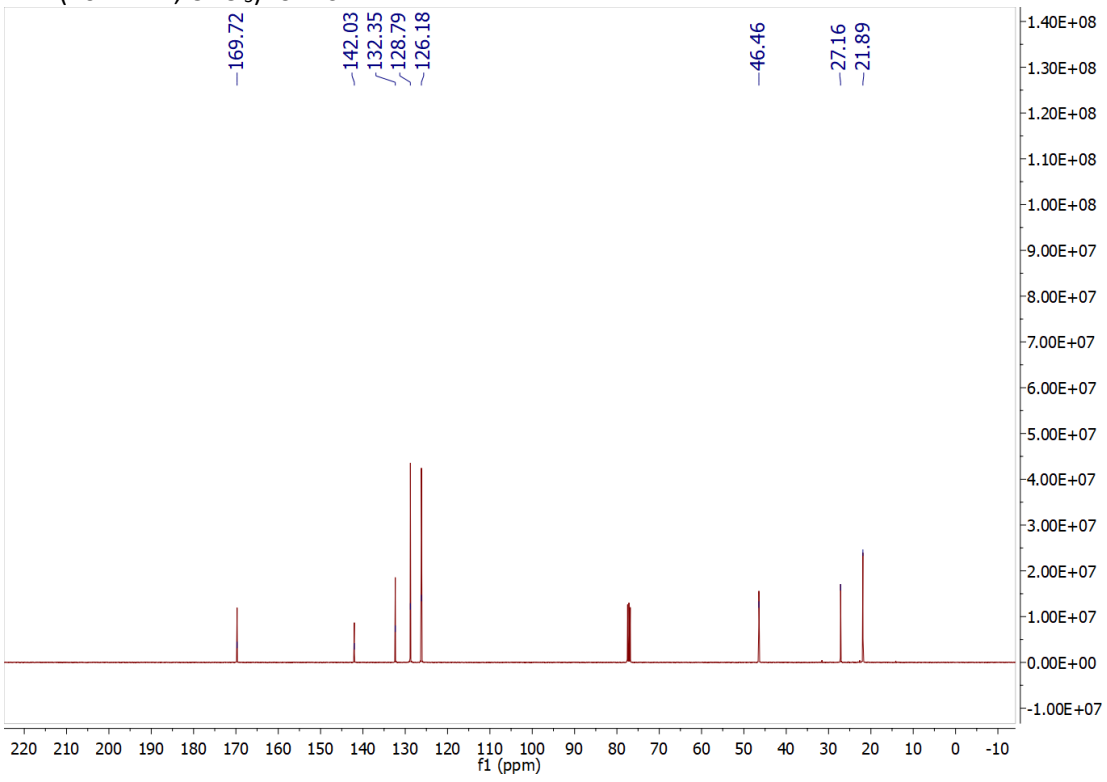
(*Z*)-3-Methyl-*N*'-(phenylsulfonyl)butanimidamide (2c)



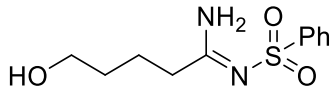
^{1}H NMR (400 MHz, $CDCl_3$) for **2c**:



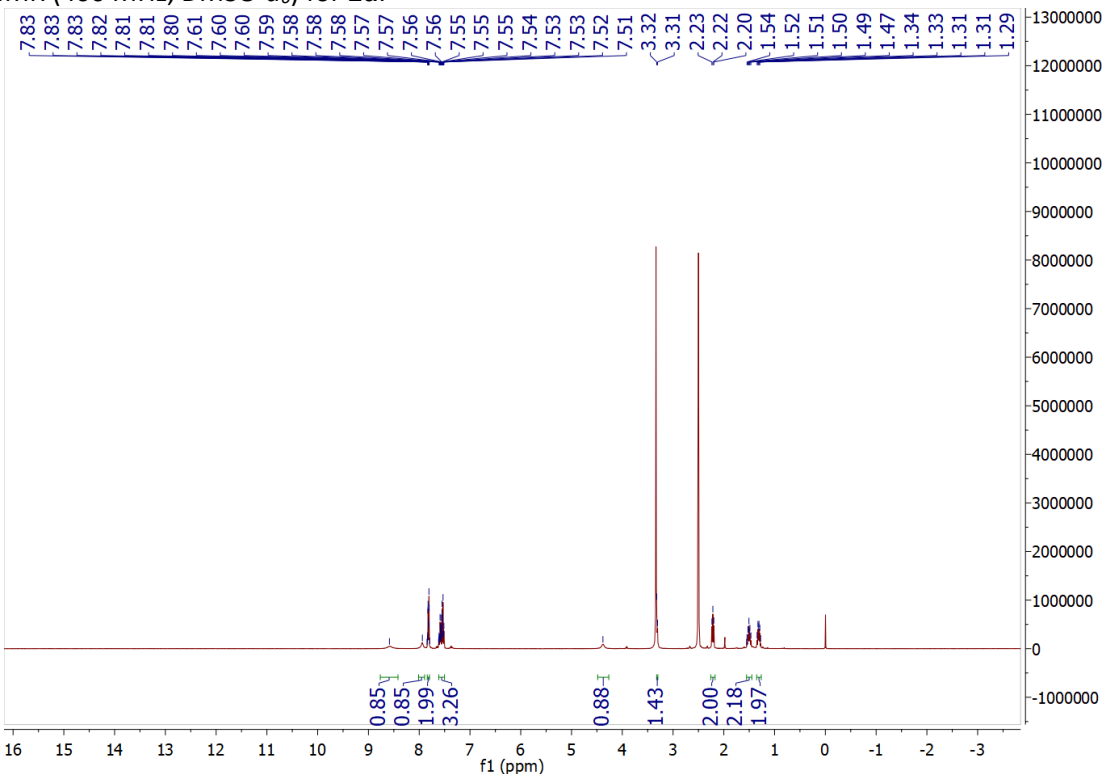
^{13}C NMR (101 MHz, $CDCl_3$) for **2c**:



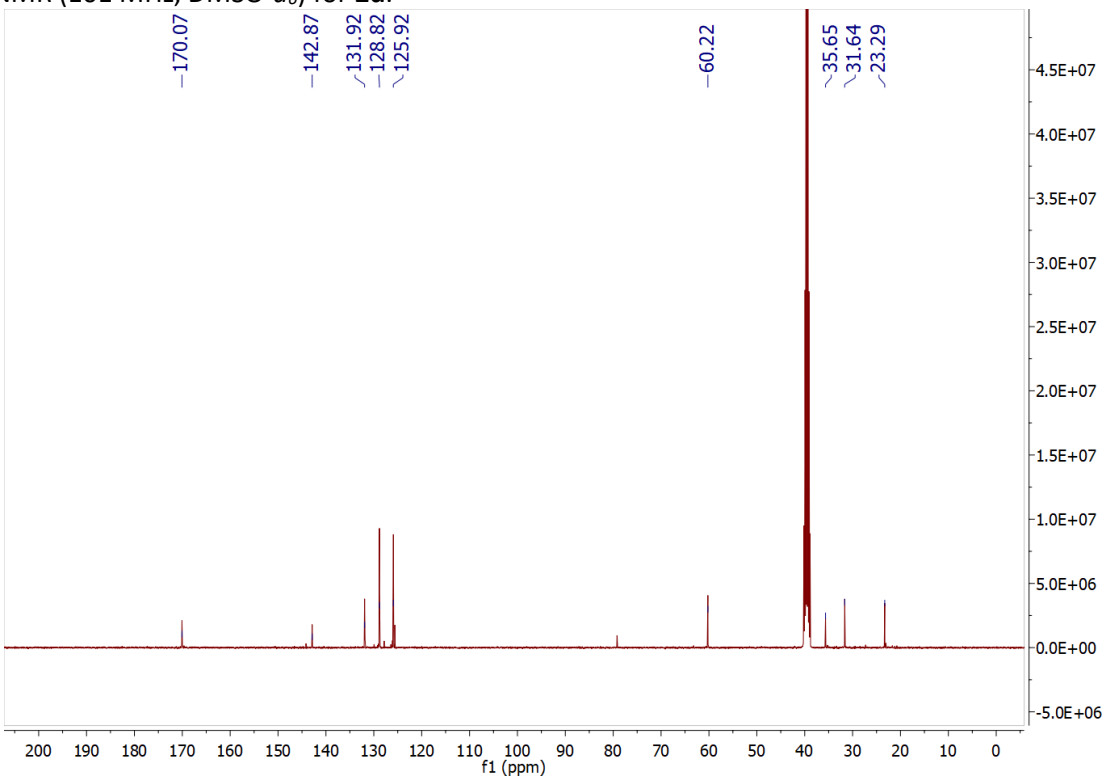
(*Z*)-5-Hydroxy-*N*'-(phenylsulfonyl)pentanimidamide (2d)



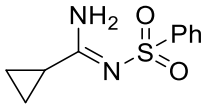
^{1}H NMR (400 MHz, DMSO-d_6) for **2d**:



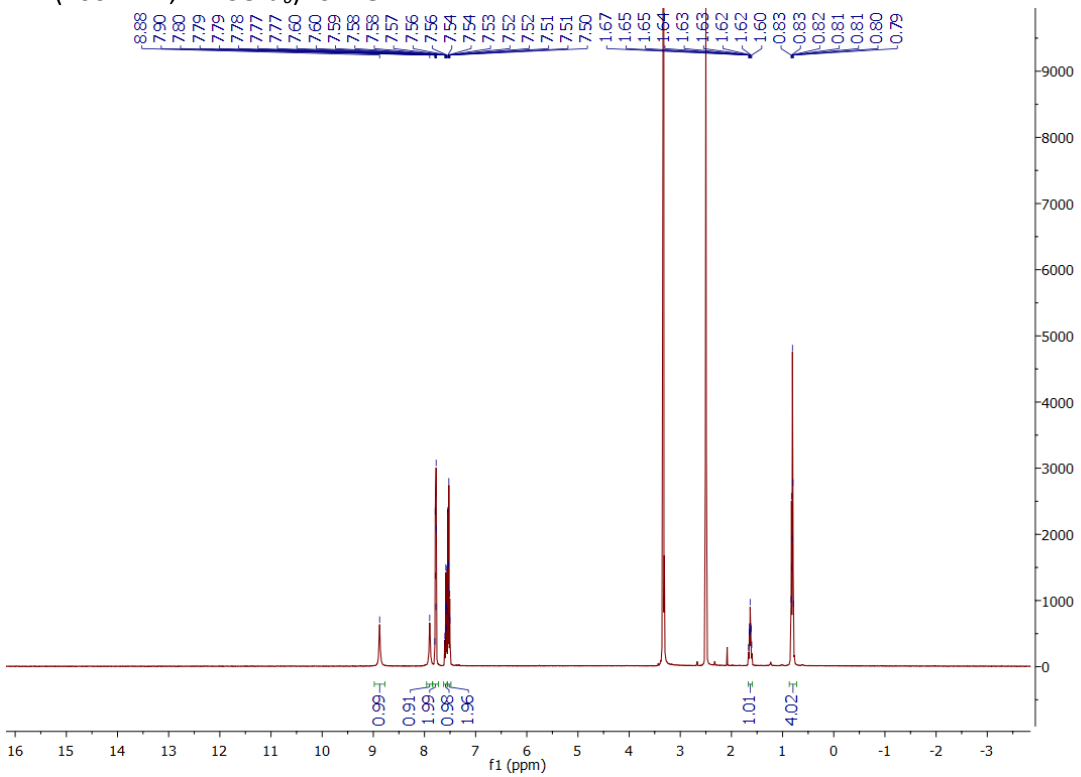
^{13}C NMR (101 MHz, DMSO-d_6) for **2d**:



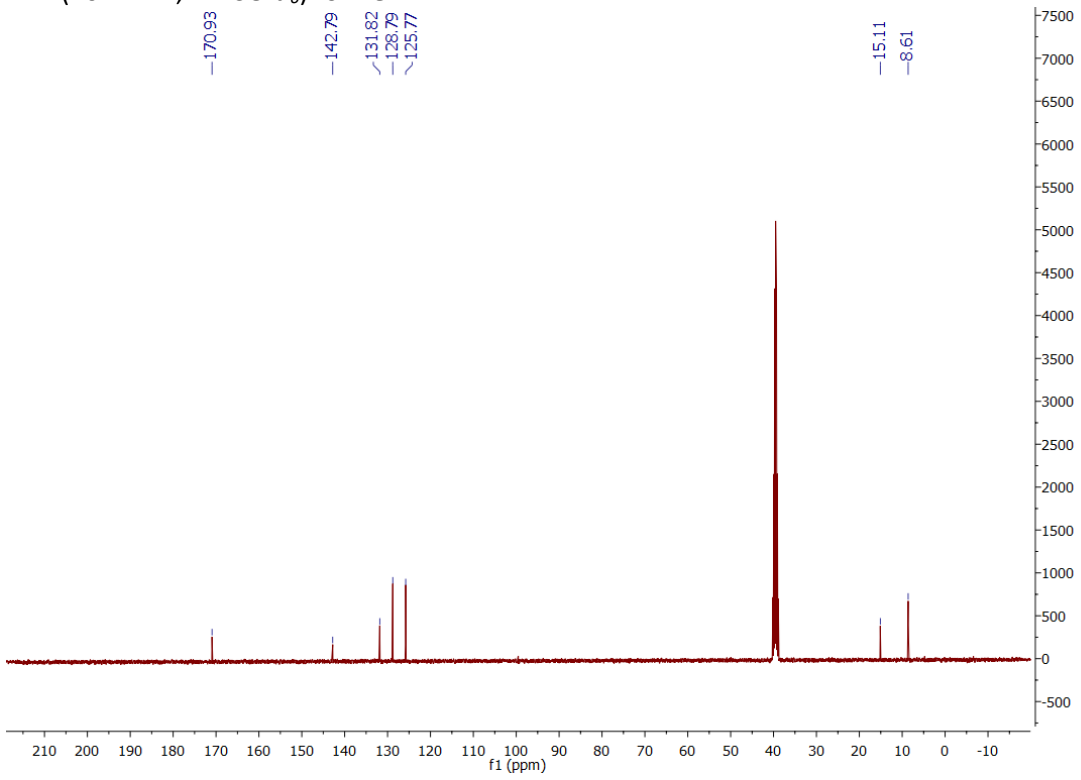
(*Z*)-*N'*-(Phenylsulfonyl)cyclopropanecarboximidamide (2e)



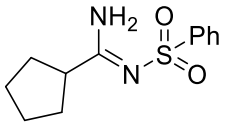
^{1}H NMR (400 MHz, DMSO-d_6) for **2e**:



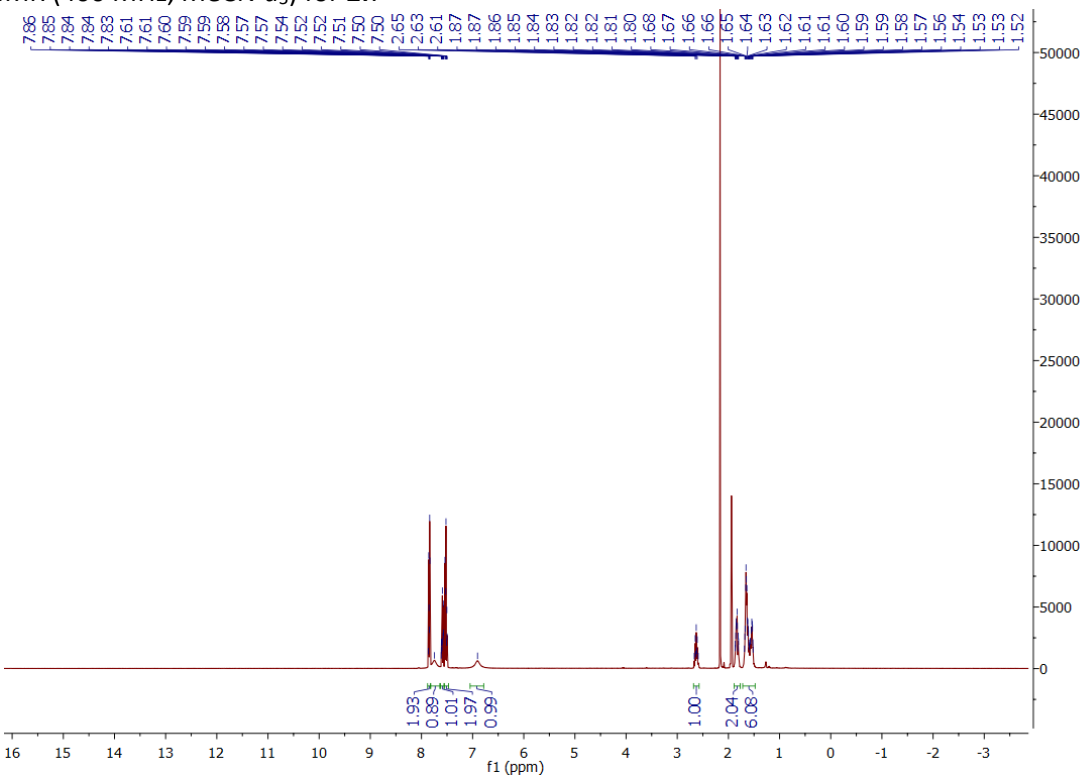
^{13}C NMR (101 MHz, DMSO-d_6) for **2e**:



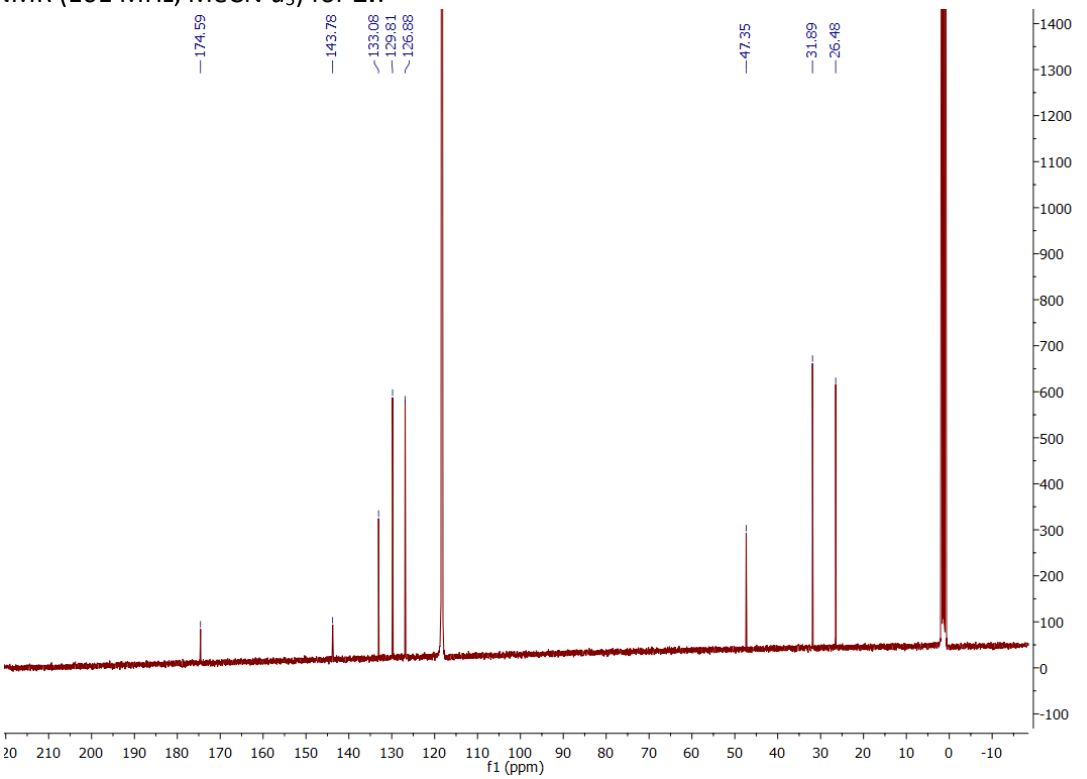
(*Z*)-*N'*-(Phenylsulfonyl)cyclopentanenecarboximidamide (2f)



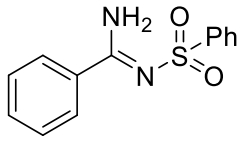
^{1}H NMR (400 MHz, MeCN-d_3) for **2f**:



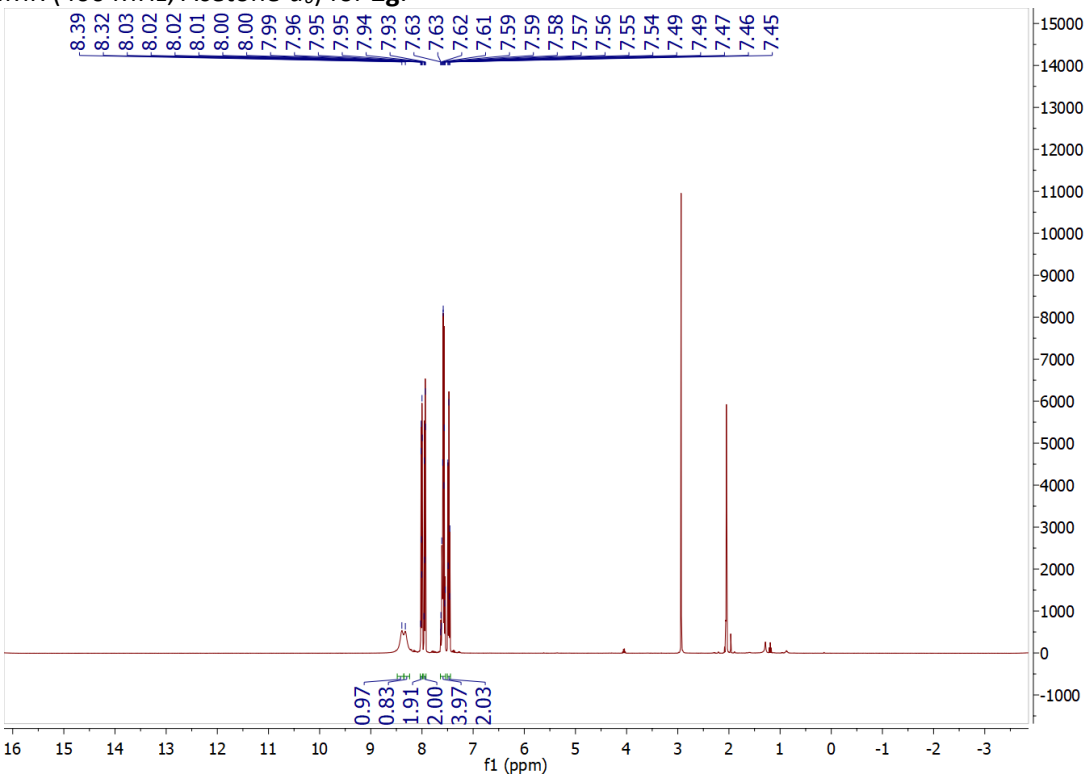
^{13}C NMR (101 MHz, MeCN-d_3) for **2f**:



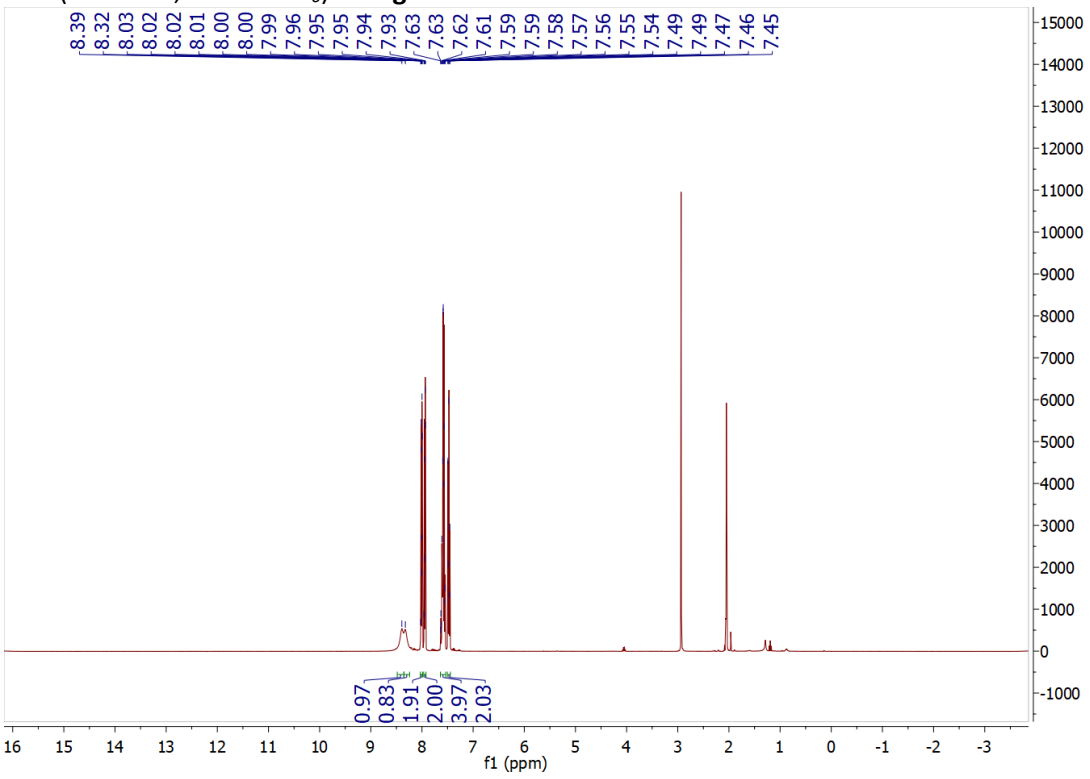
(*Z*)-*N'*-(Phenylsulfonyl)benzimidamide (2g)



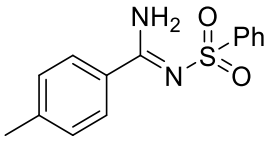
^{1}H NMR (400 MHz, Acetone-d_6) for **2g**:



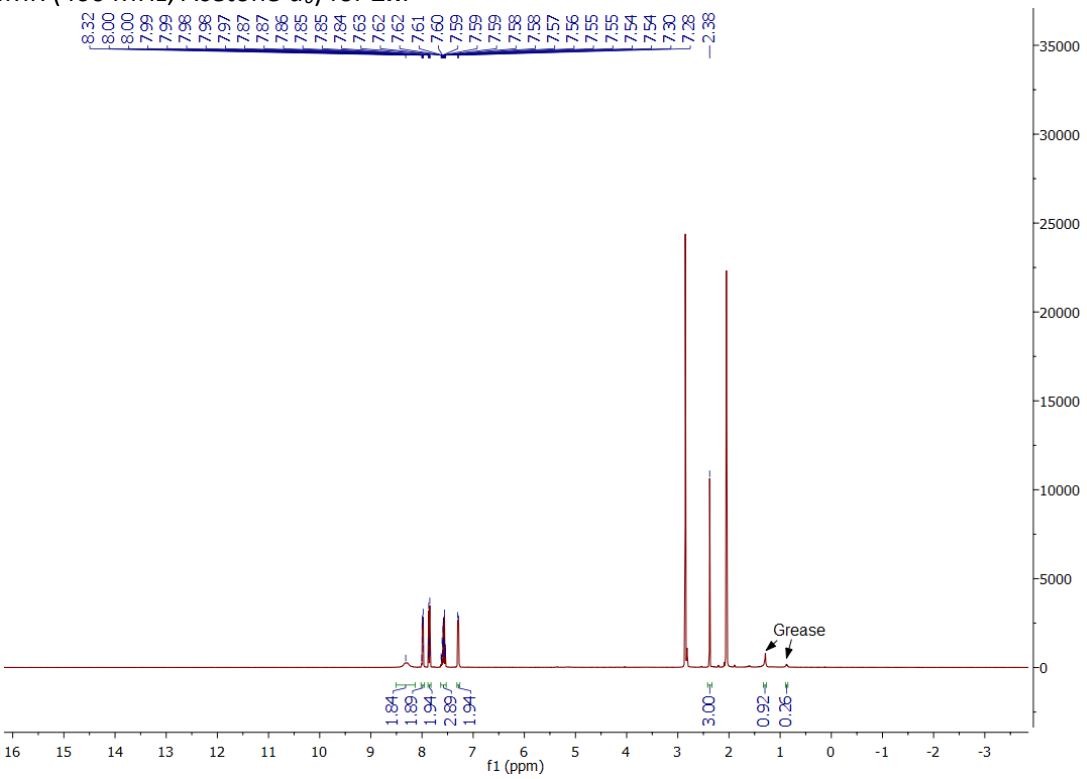
^{13}C NMR (101 MHz, Acetone-d_6) for **2g**:



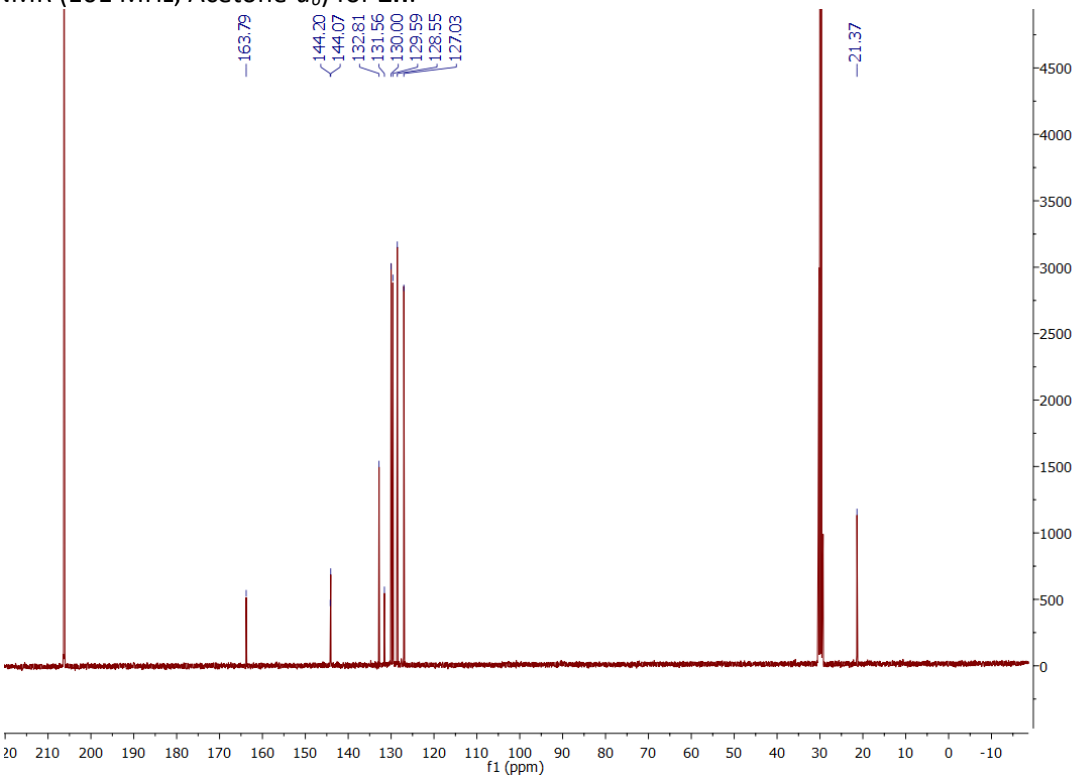
(*Z*)-4-Methyl-*N*'-(phenylsulfonyl)benzimidamide (2h)



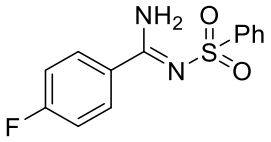
^{1}H NMR (400 MHz, Acetone-d_6) for **2h**:



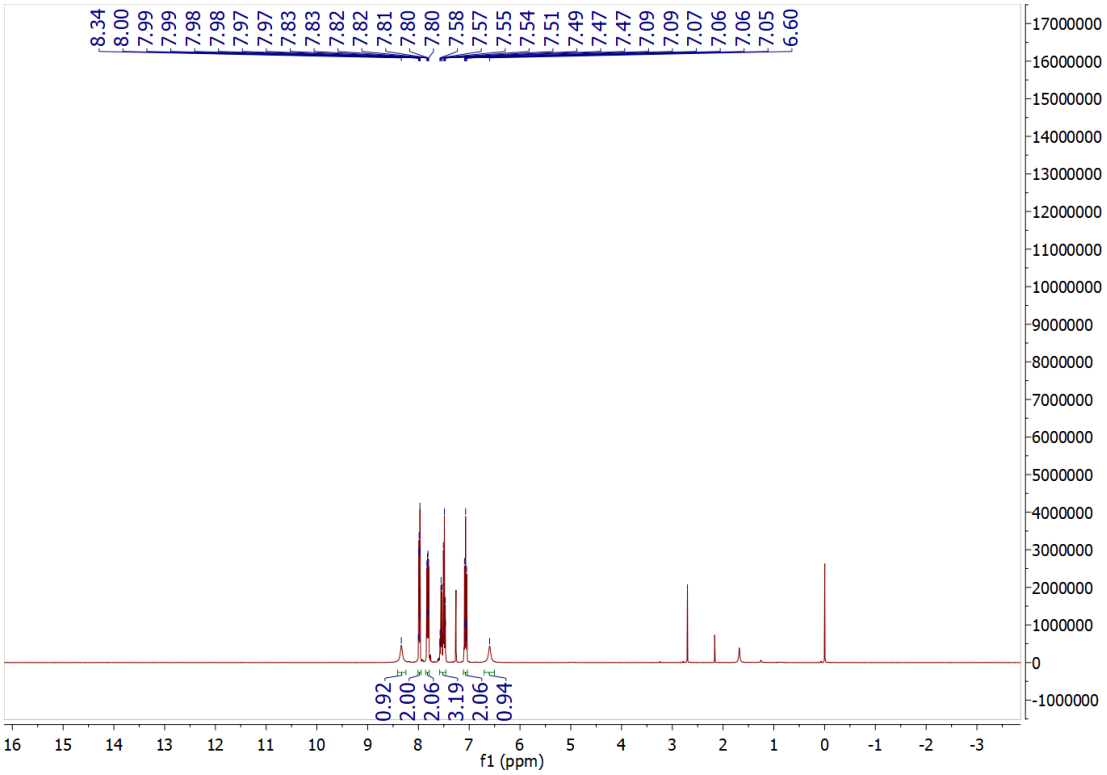
^{13}C NMR (101 MHz, Acetone-d_6) for **2h**:



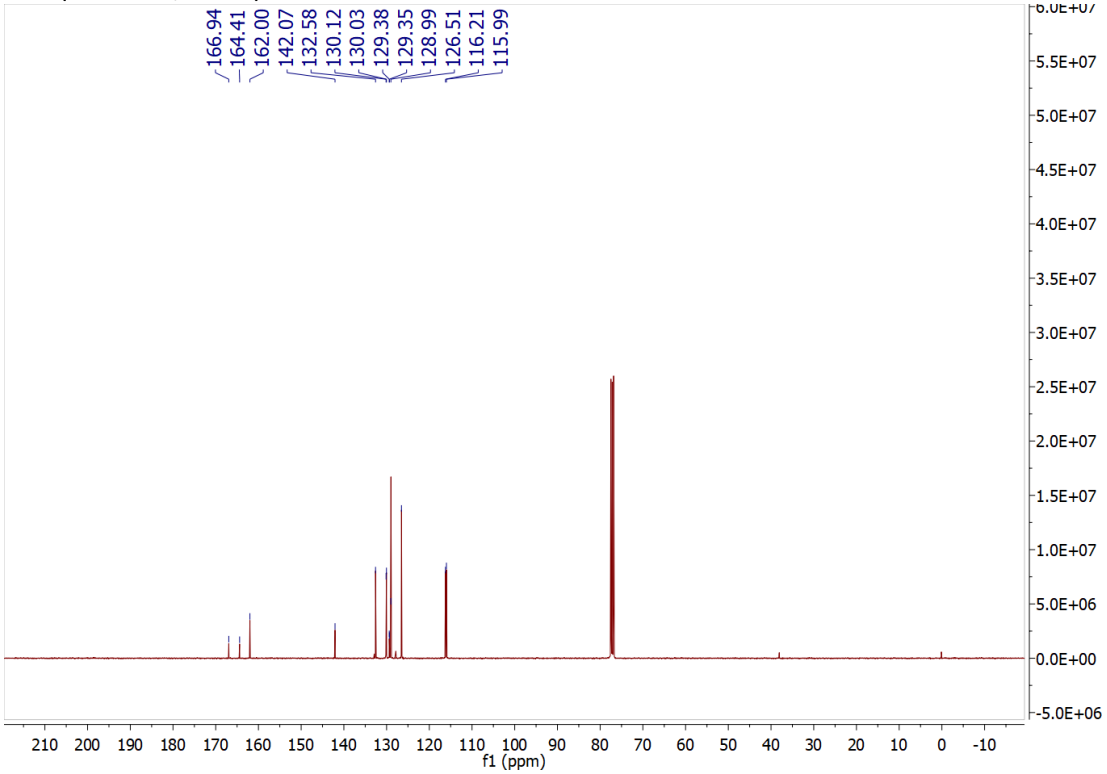
(*Z*)-4-Fluoro-*N'*-(phenylsulfonyl)benzimidamide (2i)



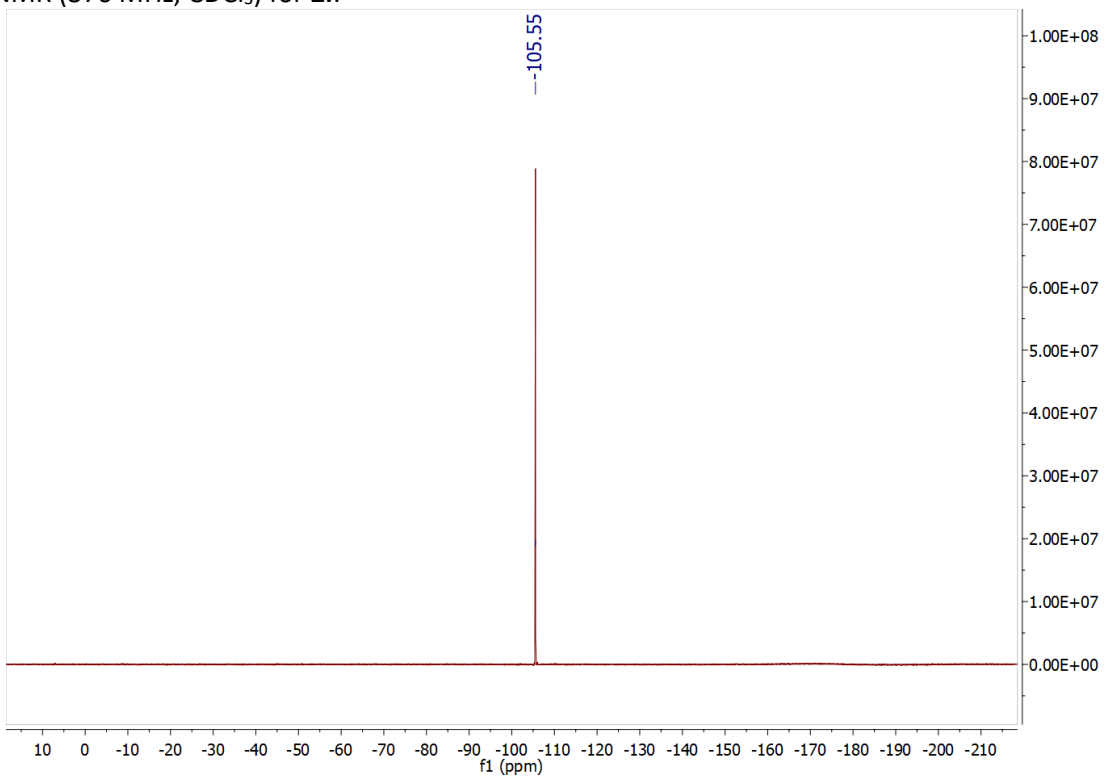
^{1}H NMR (400 MHz, $CDCl_3$) for **2i**:



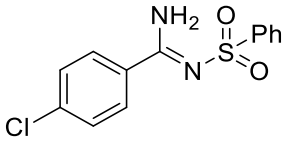
^{13}C NMR (101 MHz, $CDCl_3$) for **2i**:



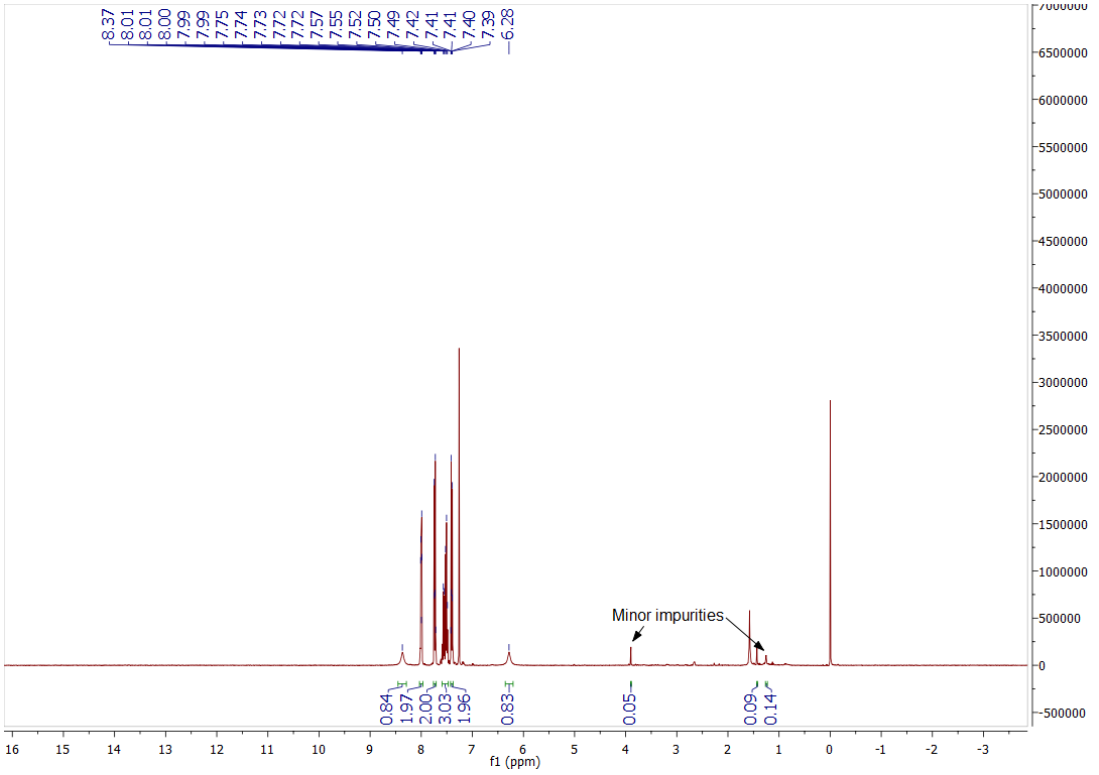
^{19}F NMR (376 MHz, $CDCl_3$) for **2i**:



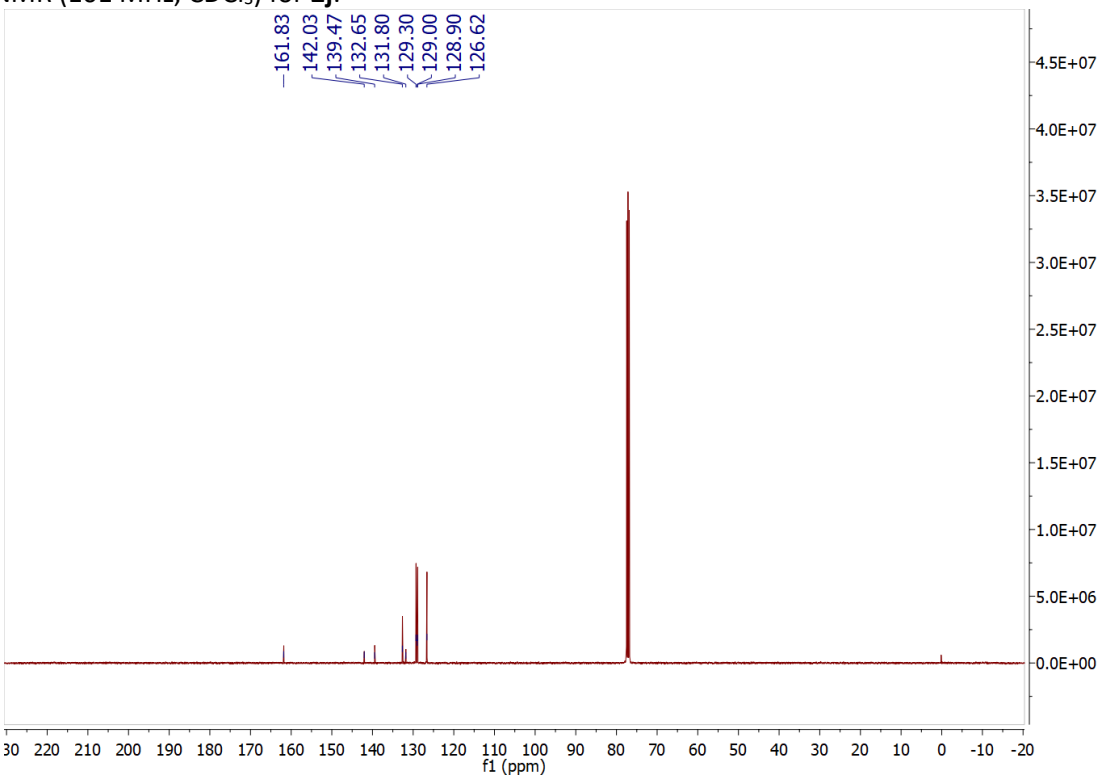
(*Z*)-4-Chloro-*N'*-(phenylsulfonyl)benzimidamide (2j)



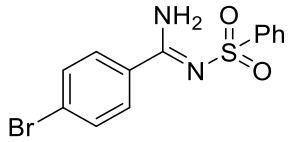
^{1}H NMR (400 MHz, $CDCl_3$) for **2j**:



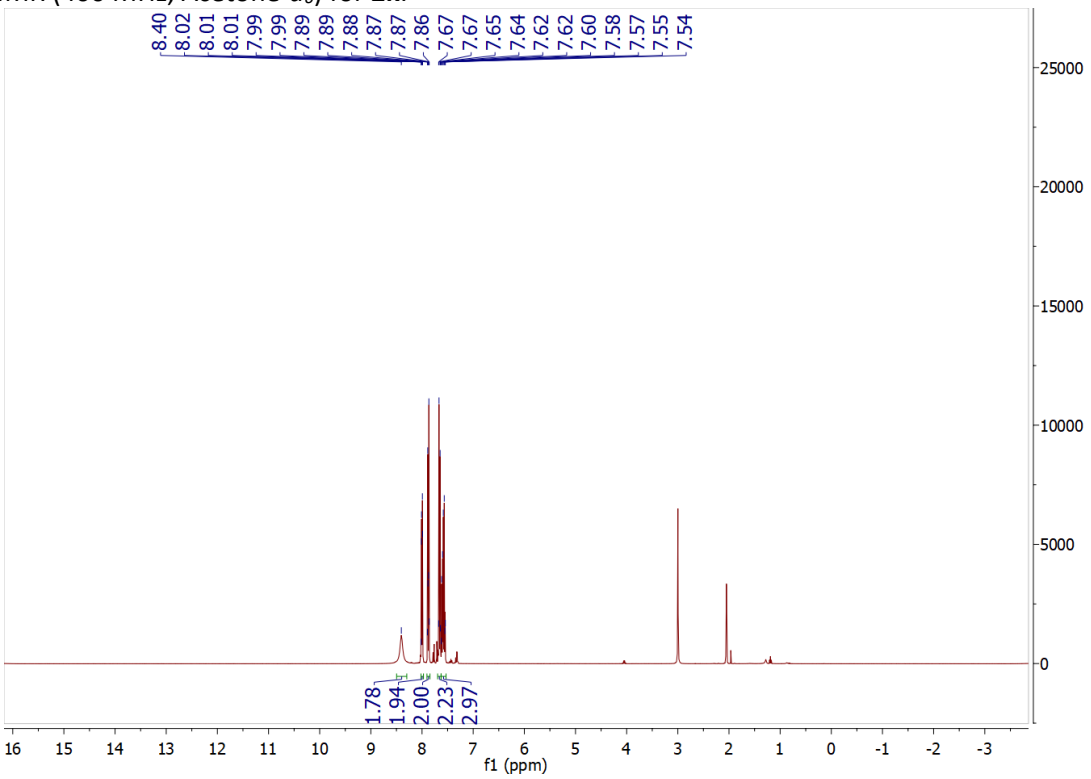
^{13}C NMR (101 MHz, $CDCl_3$) for **2j**:



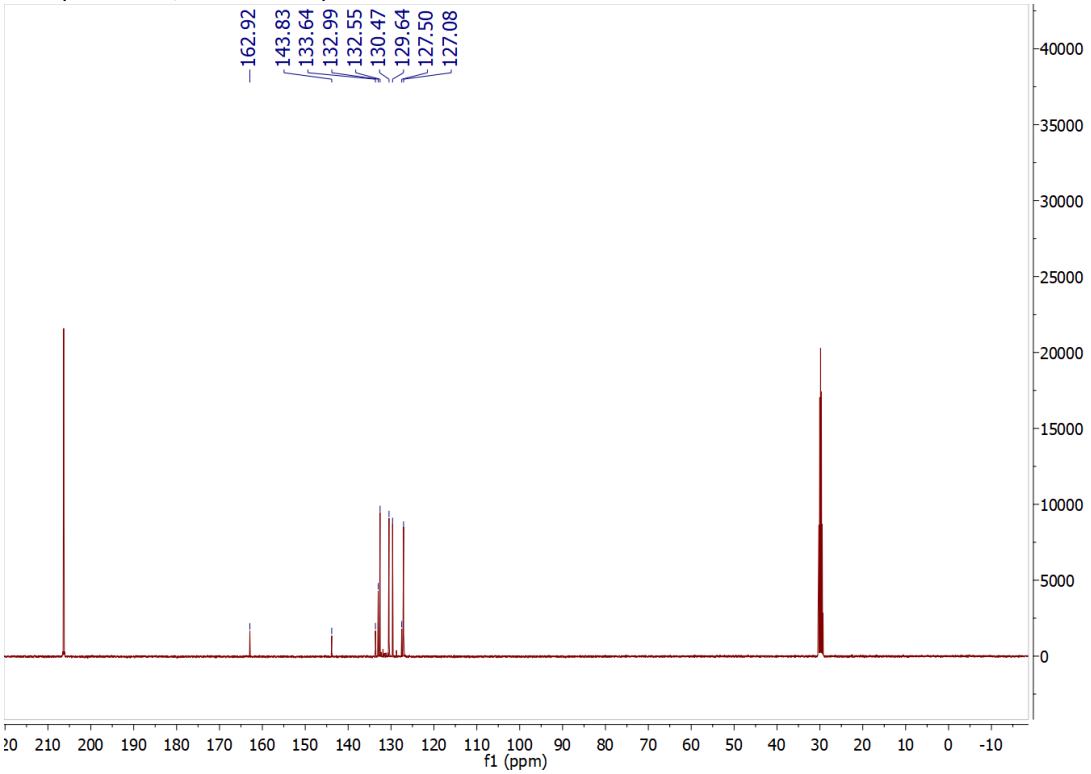
(*Z*)-4-Bromo-*N'*-(phenylsulfonyl)benzimidamide (2k)



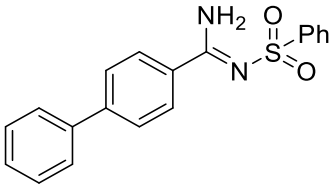
^{1}H NMR (400 MHz, Acetone-d_6) for **2k**:



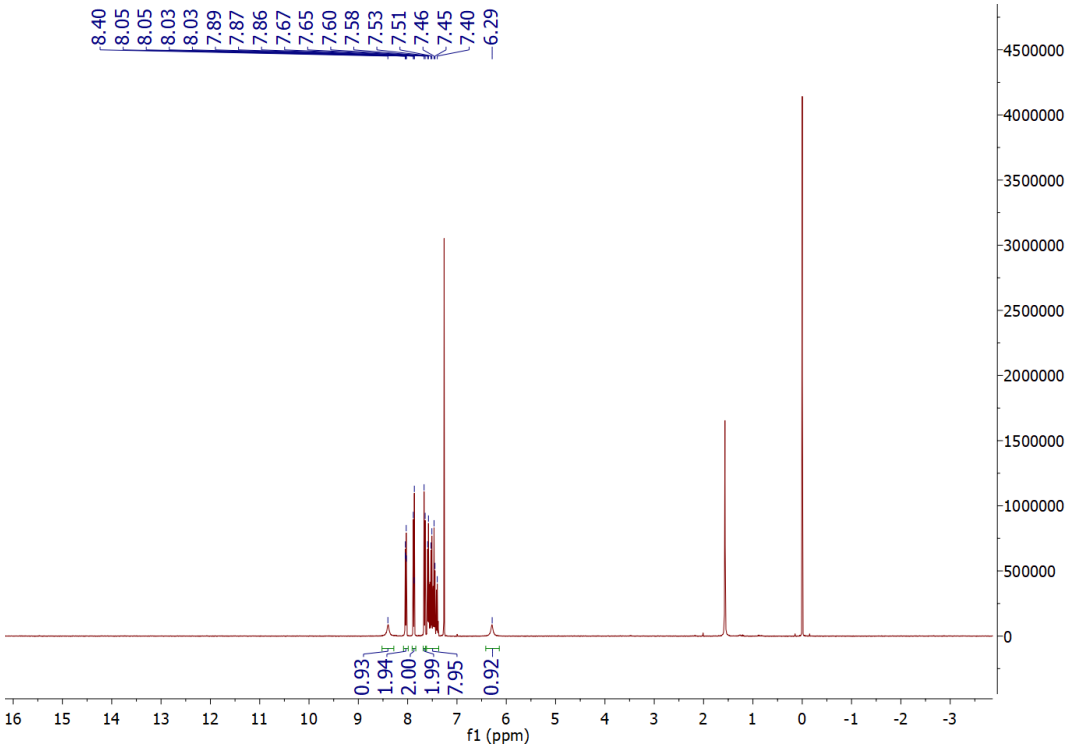
^{13}C NMR (101 MHz, Acetone-d_6) for **2k**:



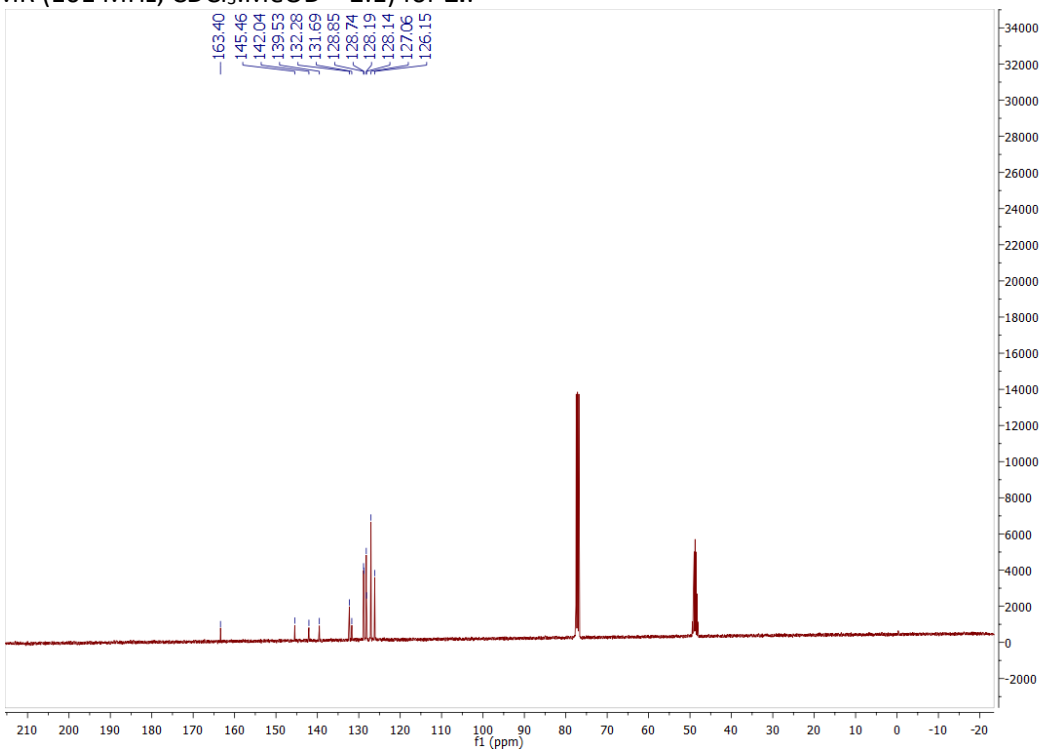
(*Z*)-*N'*-(Phenylsulfonyl)-[1,1'-biphenyl]-4-carboximidamide (2l)



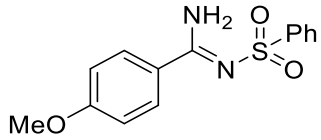
^{1}H NMR (400 MHz, $CDCl_3$) for **2l**:



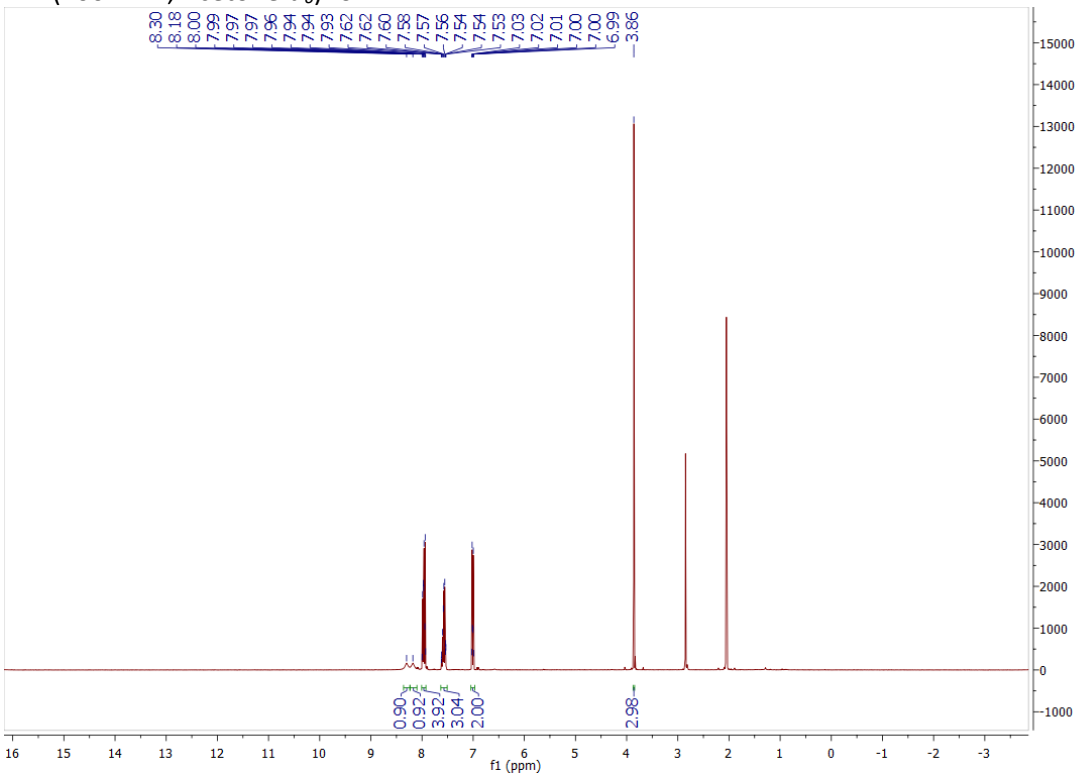
^{13}C NMR (101 MHz, $CDCl_3$:MeOD = 2:1) for **2l**:



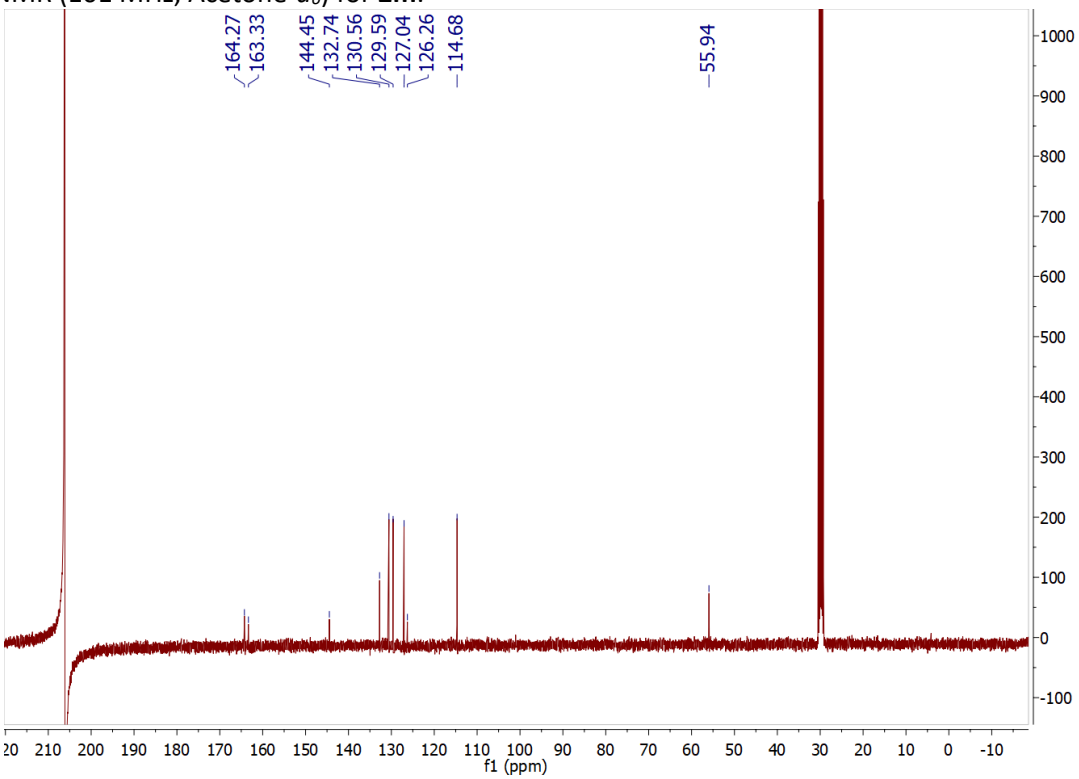
(*Z*)-4-Methoxy-*N'*-(phenylsulfonyl)benzimidamide (2m)



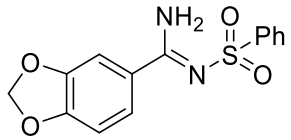
^{1}H NMR (400 MHz, Acetone-d_6) for **2m**:



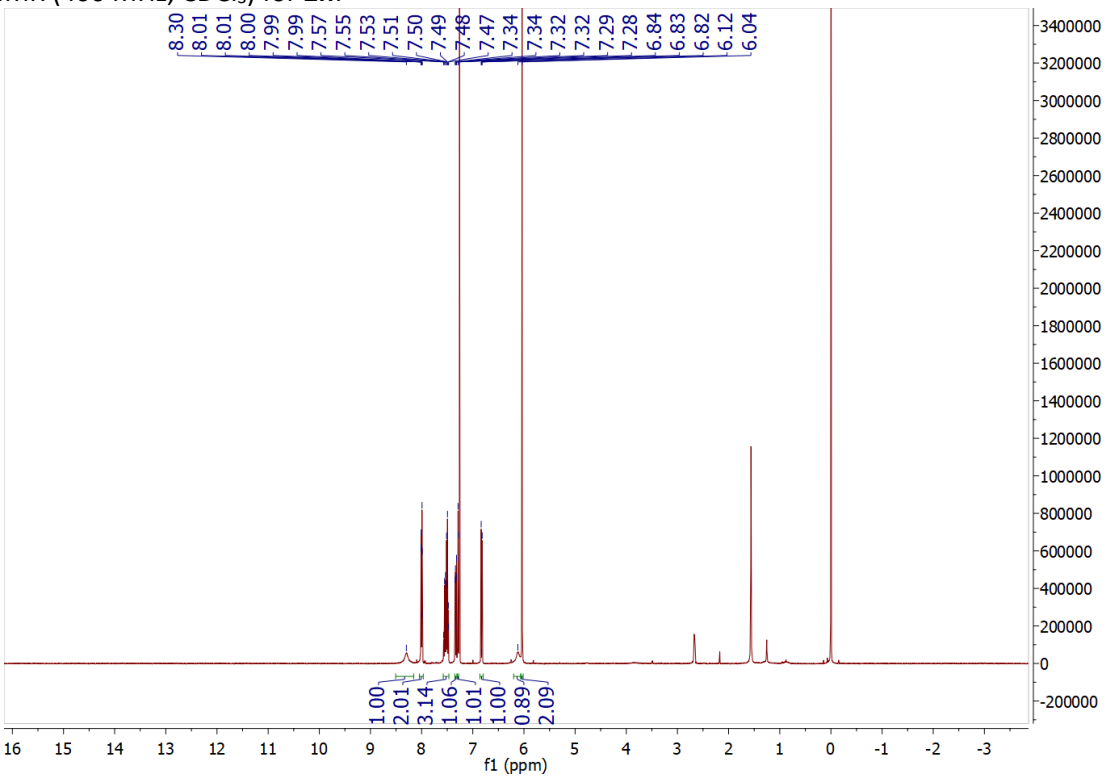
^{13}C NMR (101 MHz, Acetone-d_6) for **2m**:



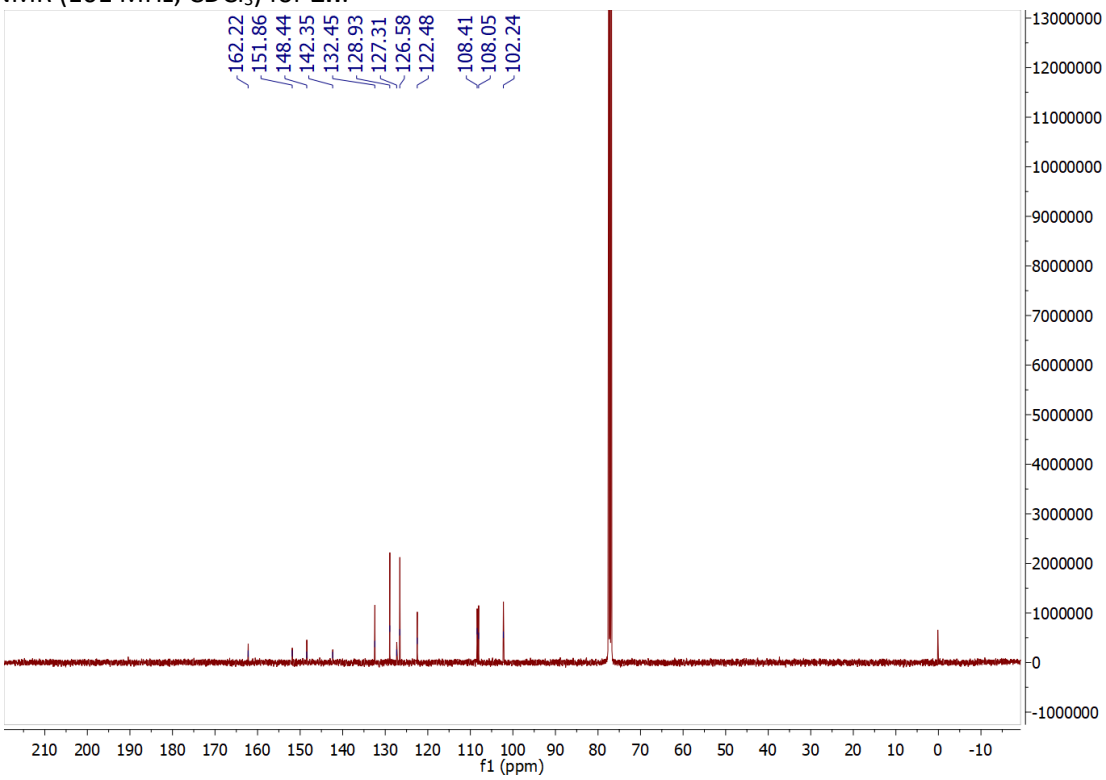
(*Z*)-*N'*-(Phenylsulfonyl)benzo[*d*][1,3]dioxole-5-carboximidamide (2n)



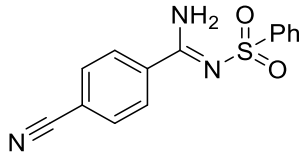
^{1}H NMR (400 MHz, $CDCl_3$) for **2n**:



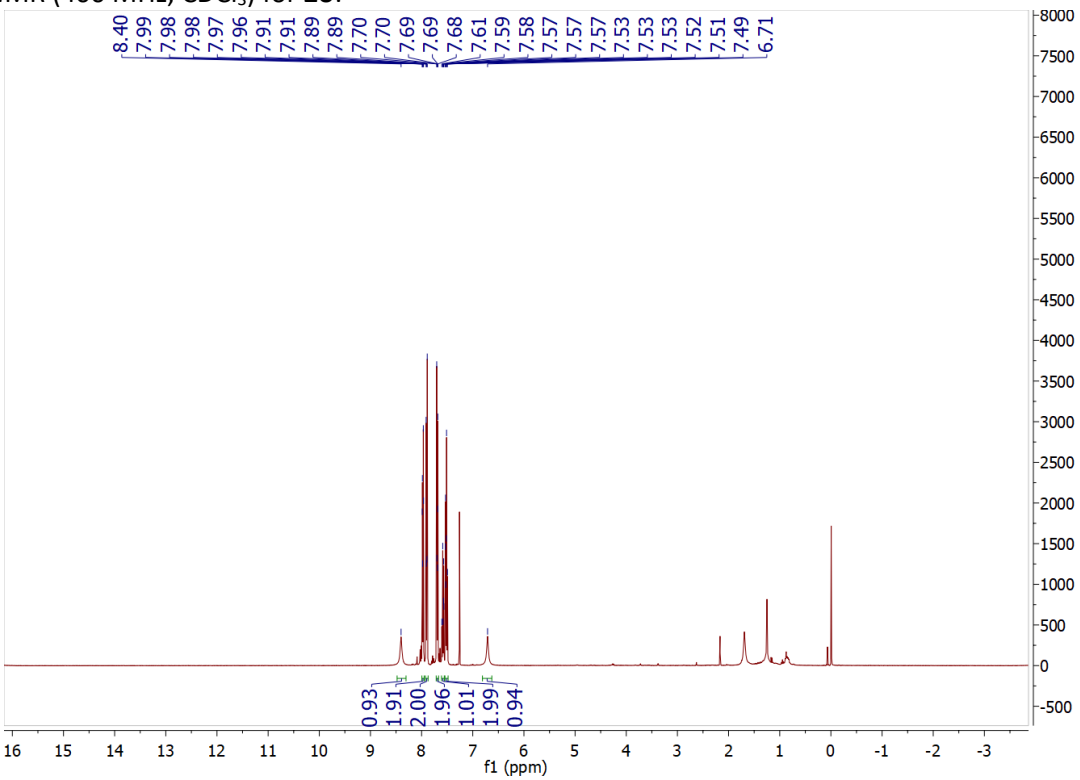
^{13}C NMR (101 MHz, $CDCl_3$) for **2n**:



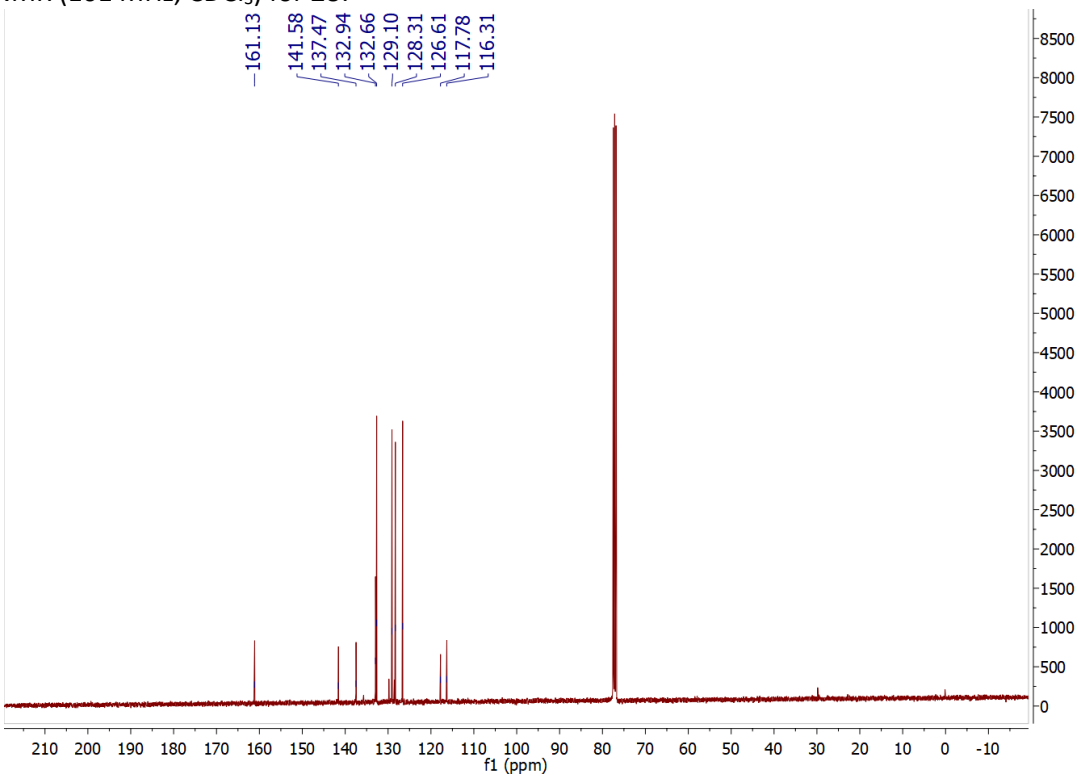
(*Z*)-4-Cyano-*N*'-(phenylsulfonyl)benzimidamide (2o)



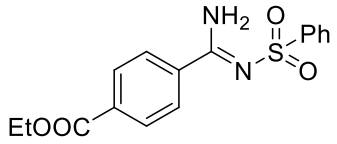
^{1}H NMR (400 MHz, $CDCl_3$) for **2o**:



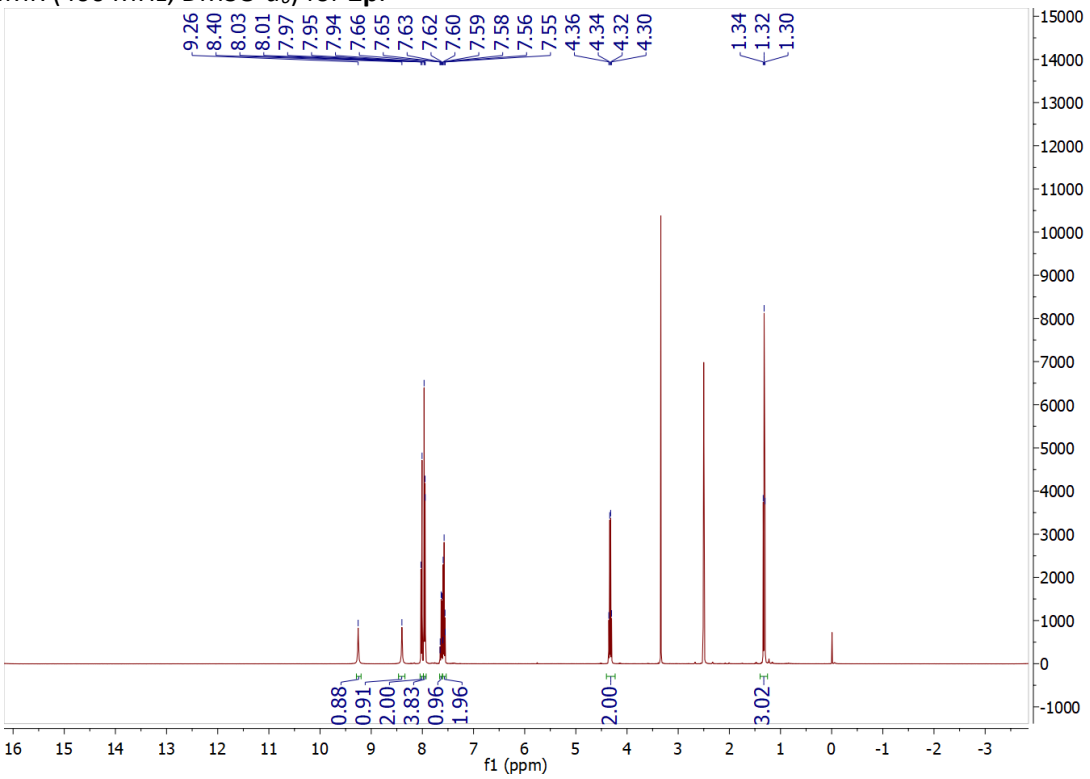
^{13}C NMR (101 MHz, $CDCl_3$) for **2o**:



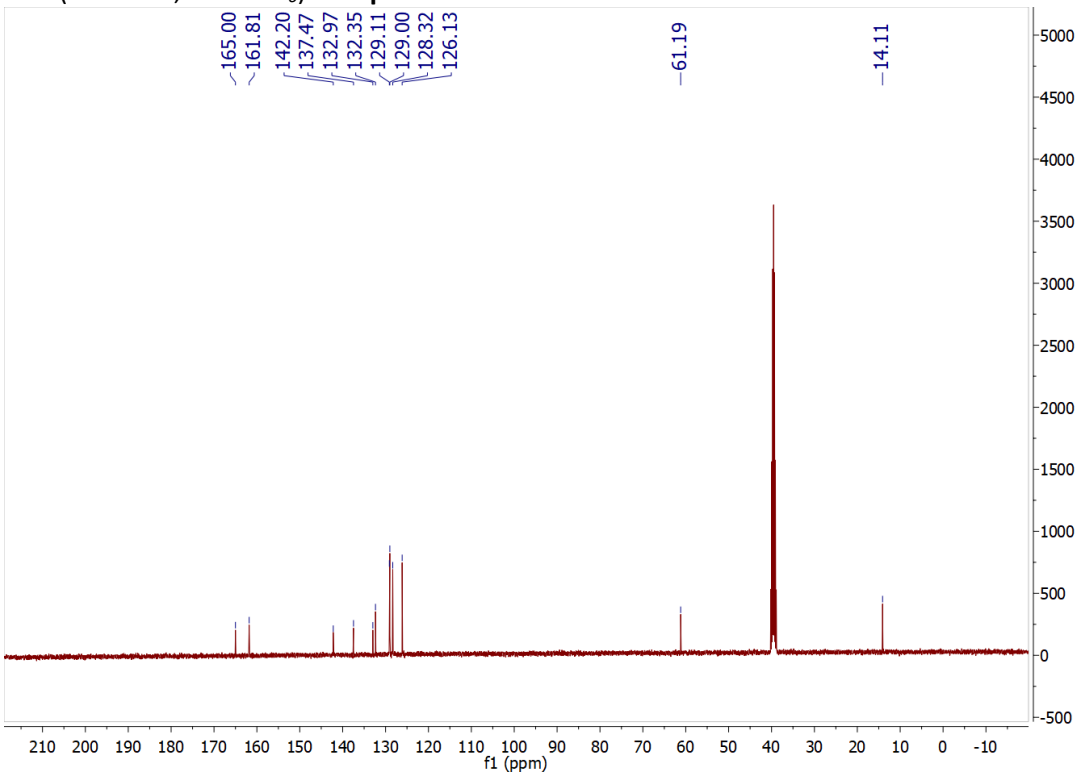
Ethyl (*Z*)-4-(*N*'-(phenylsulfonyl)carbamimidoyl)benzoate (2p)



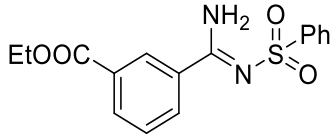
^{1}H NMR (400 MHz, DMSO-d_6) for **2p**:



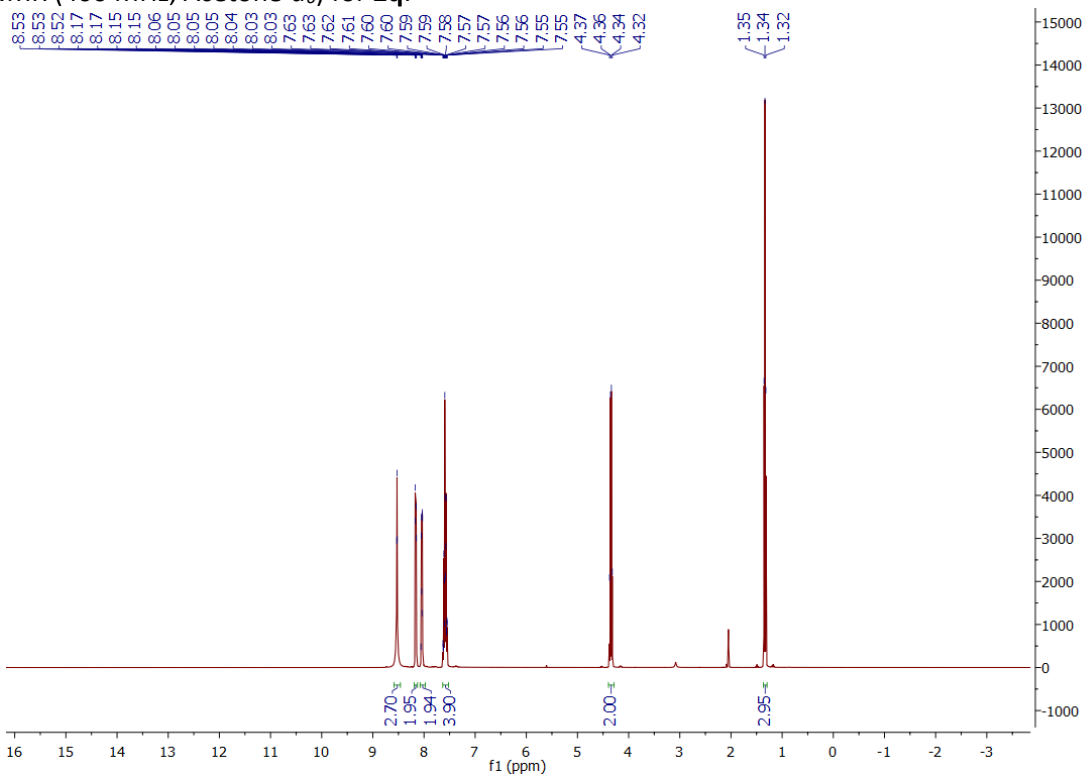
^{13}C NMR (101 MHz, DMSO-d_6) for **2p**:



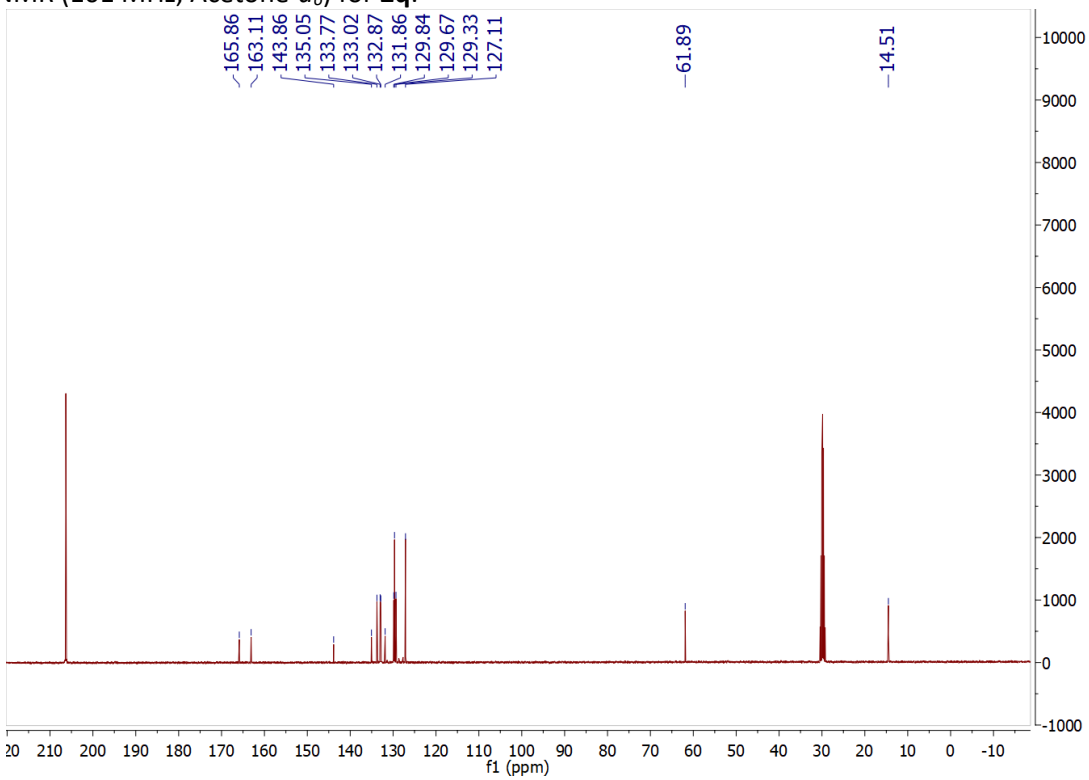
Ethyl (*Z*)-3-(*N*'-(phenylsulfonyl)carbamimidoyl)benzoate (2q)



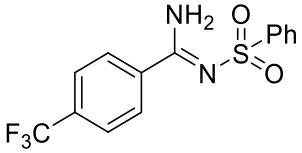
^{1}H NMR (400 MHz, Acetone-d_6) for **2q**:



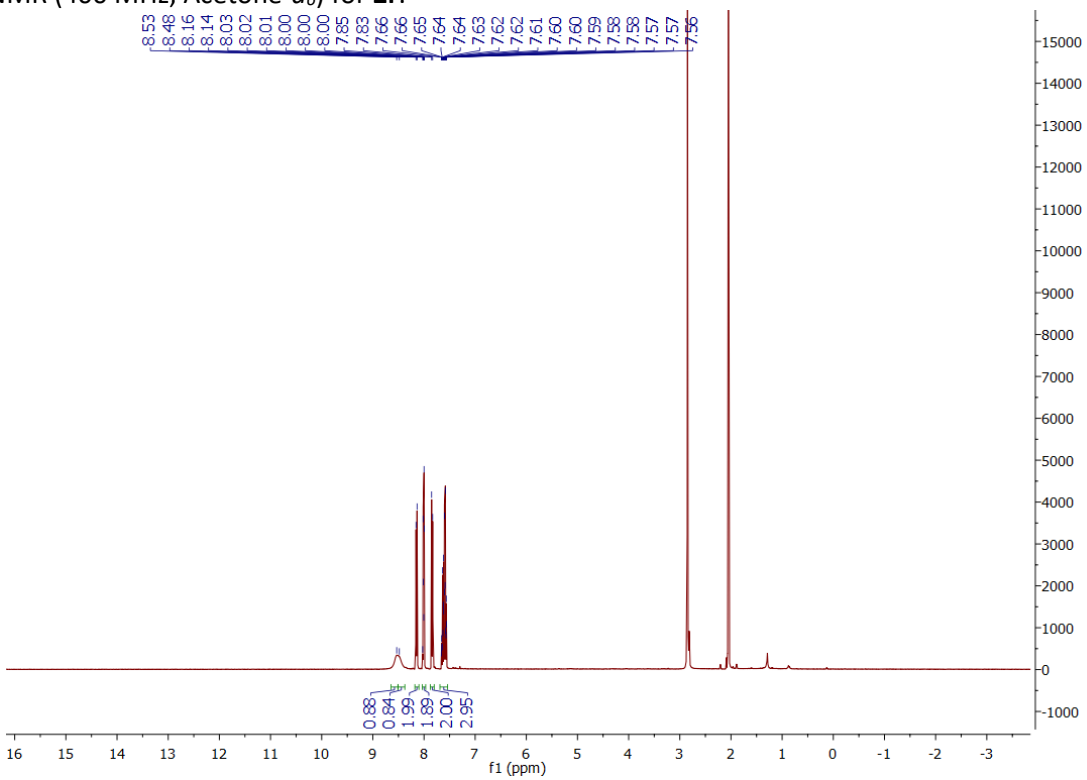
^{13}C NMR (101 MHz, Acetone-d_6) for **2q**:



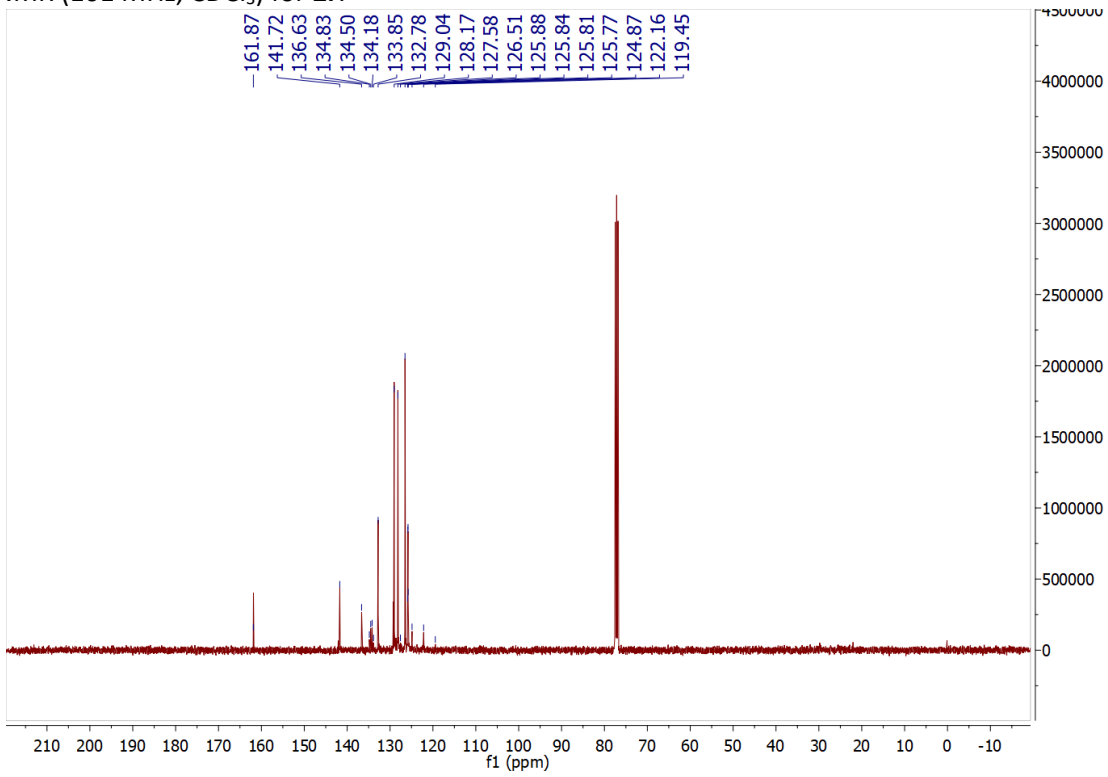
(*Z*)-*N'*-(Phenylsulfonyl)-4-(trifluoromethyl)benzimidamide (2r)



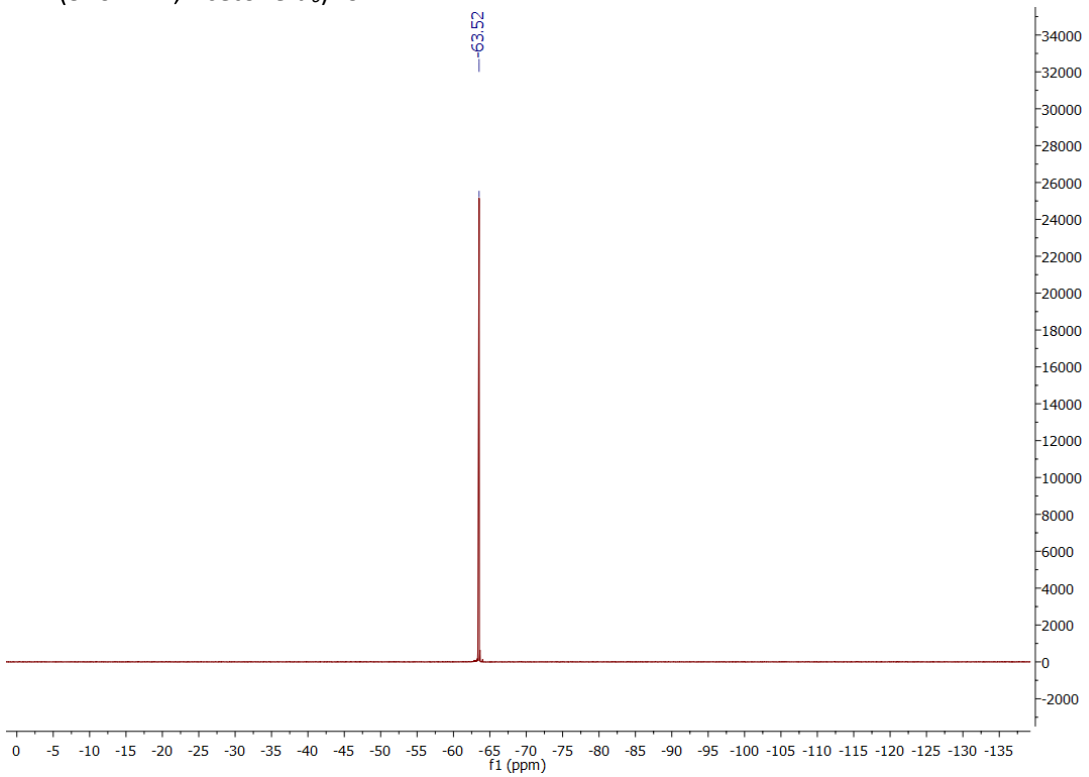
^{1}H NMR (400 MHz, Acetone-d_6) for **2r**:



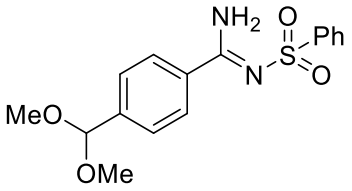
^{13}C NMR (101 MHz, $CDCl_3$) for **2r**:



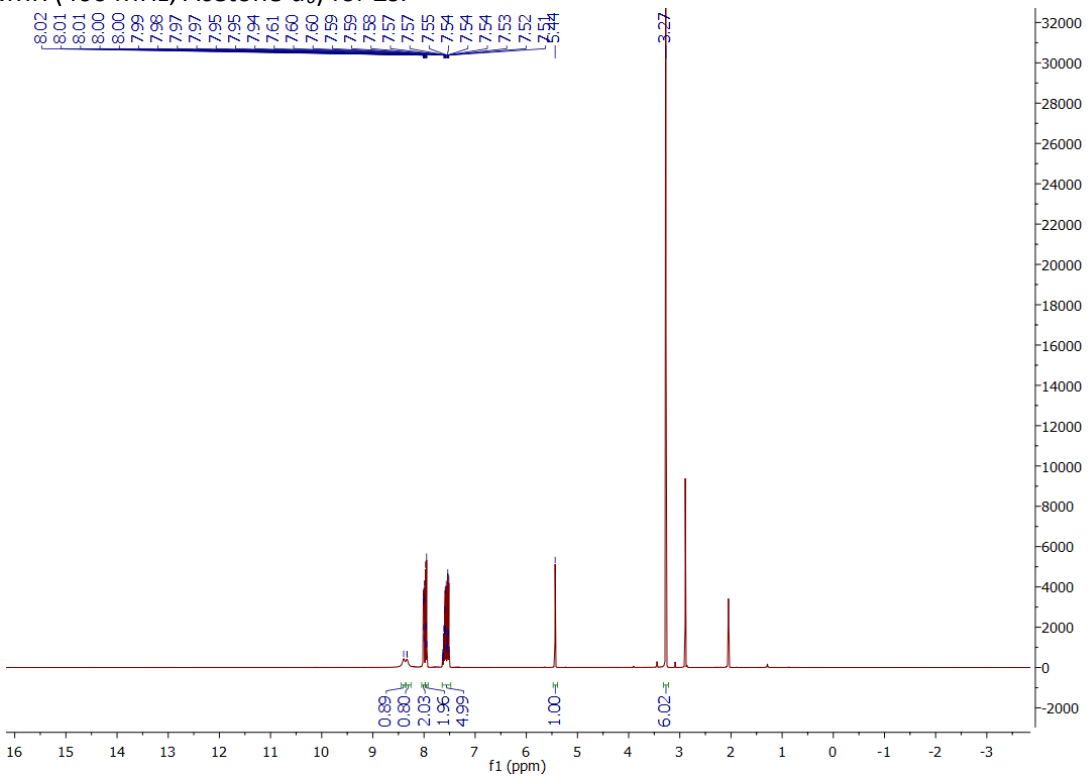
^{19}F NMR (376 MHz, Acetone-d_6) for **2r**:



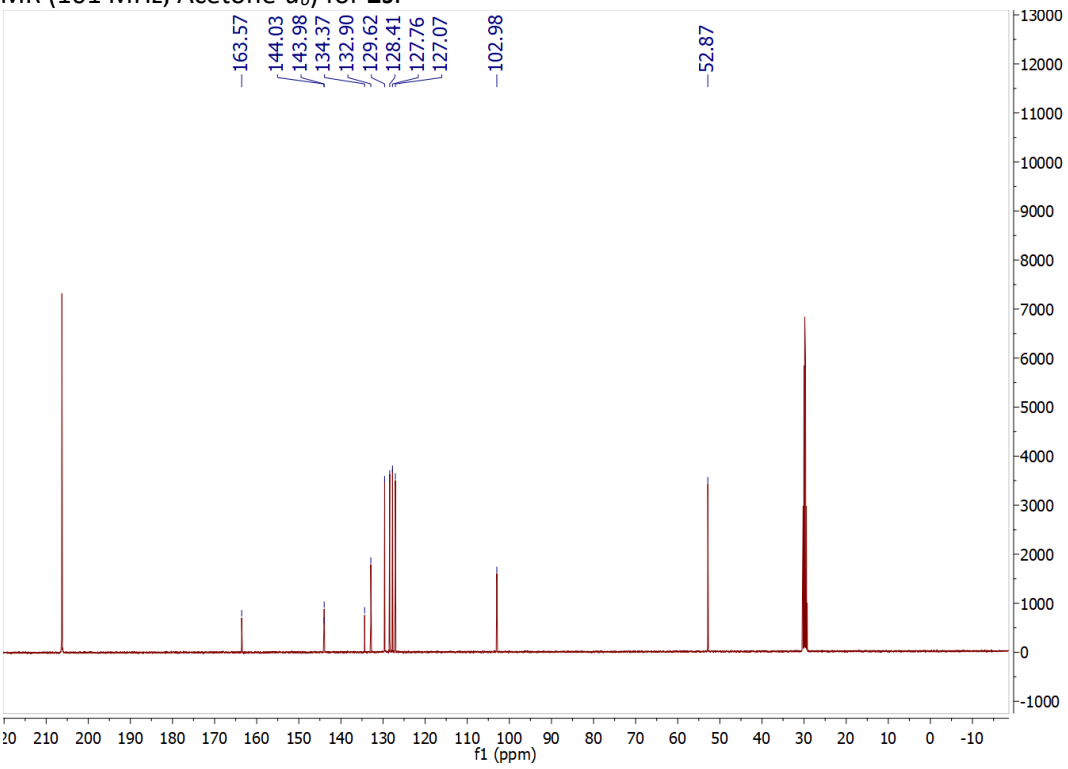
(*Z*)-4-(Dimethoxymethyl)-*N*'-(phenylsulfonyl)benzimidamide (2s)



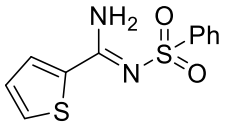
^{1}H NMR (400 MHz, Acetone-d_6) for **2s**:



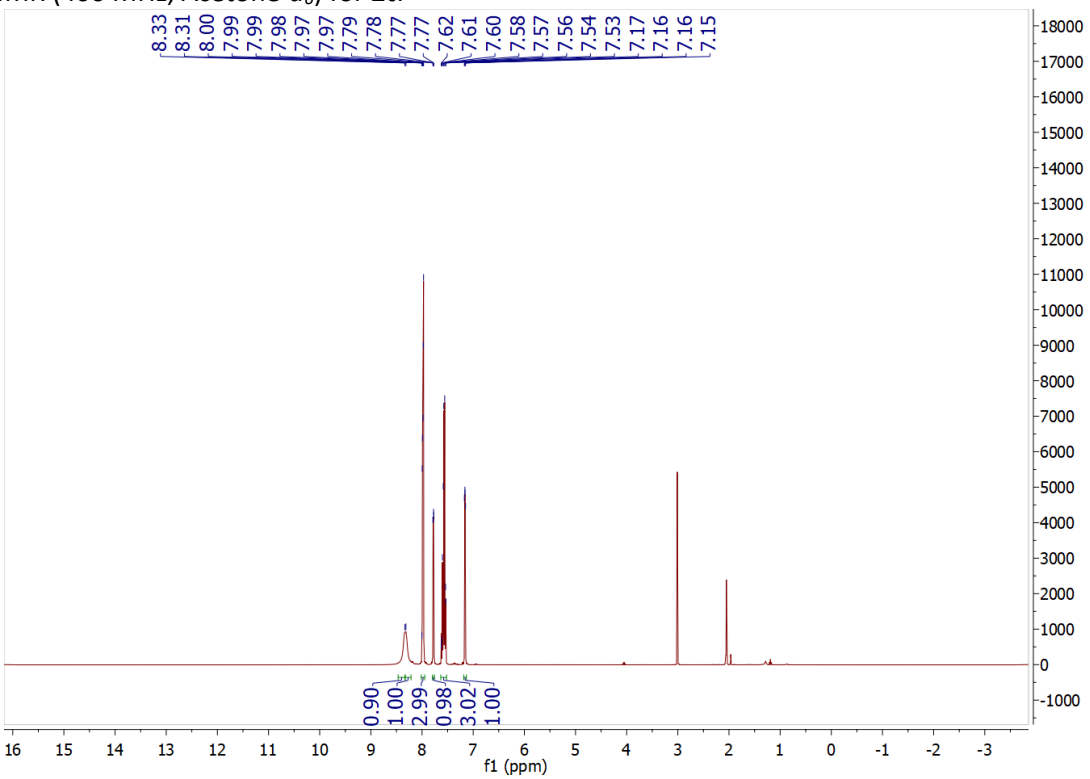
^{13}C NMR (101 MHz, Acetone-d_6) for **2s**:



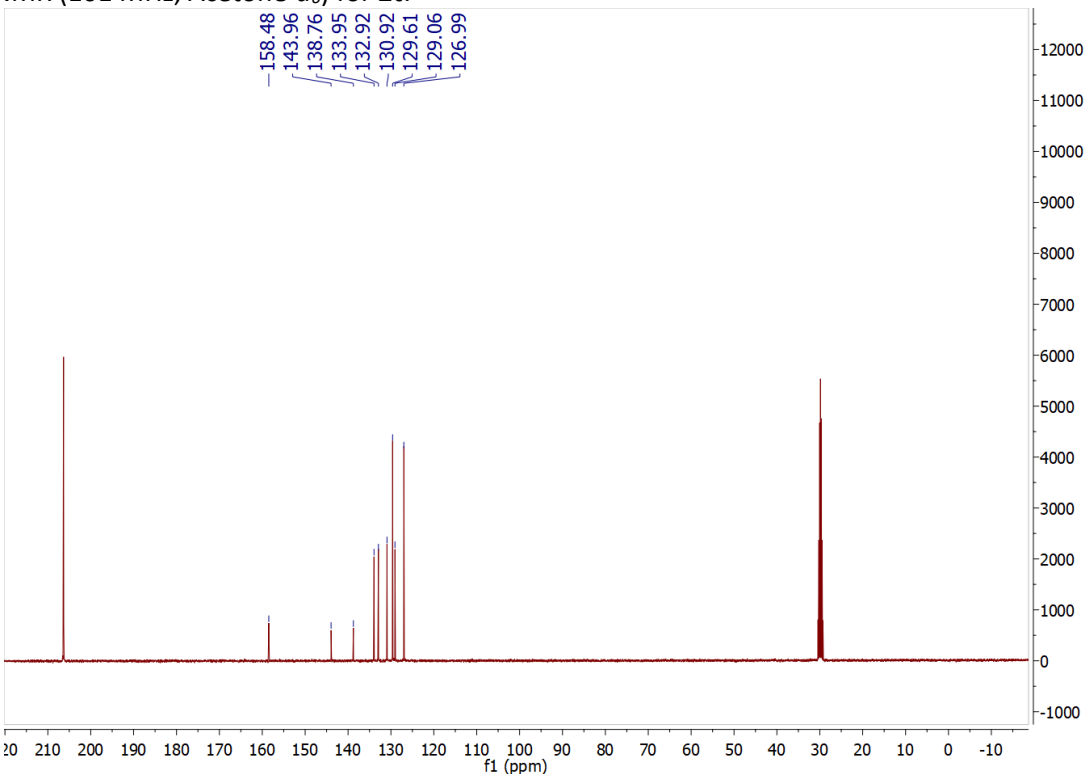
((*Z*)-*N*'-(Phenylsulfonyl)thiophene-2-carboximidamide (2t)



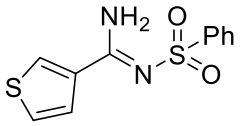
^{1}H NMR (400 MHz, Acetone-d_6) for **2t**:



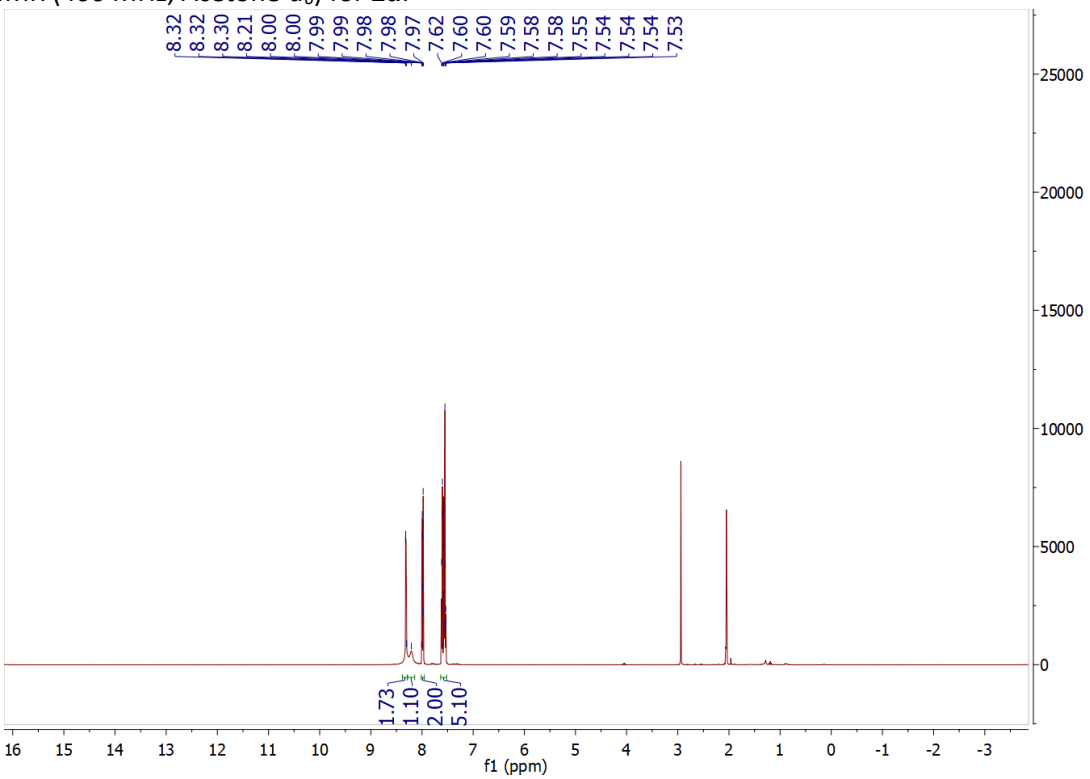
^{13}C NMR (101 MHz, Acetone-d_6) for **2t**:



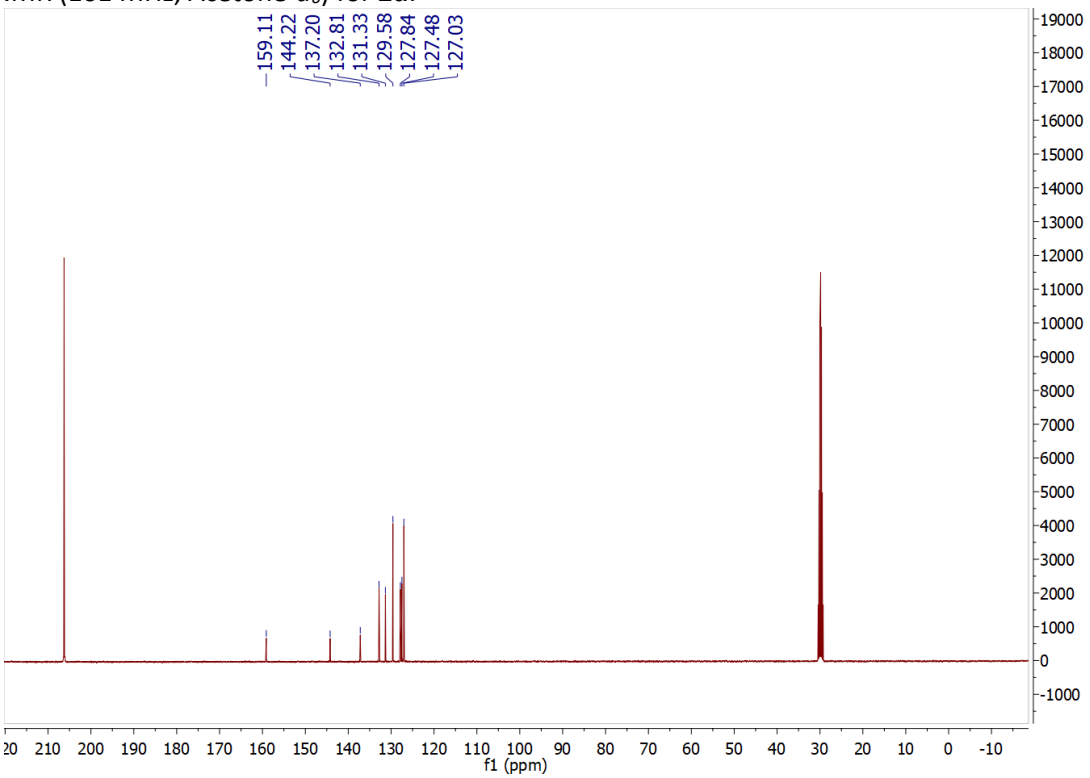
(*Z*)-*N*'-(Phenylsulfonyl)thiophene-3-carboximidamide (2u)



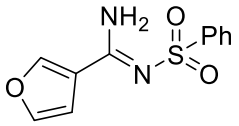
^{1}H NMR (400 MHz, Acetone-d_6) for **2u**:



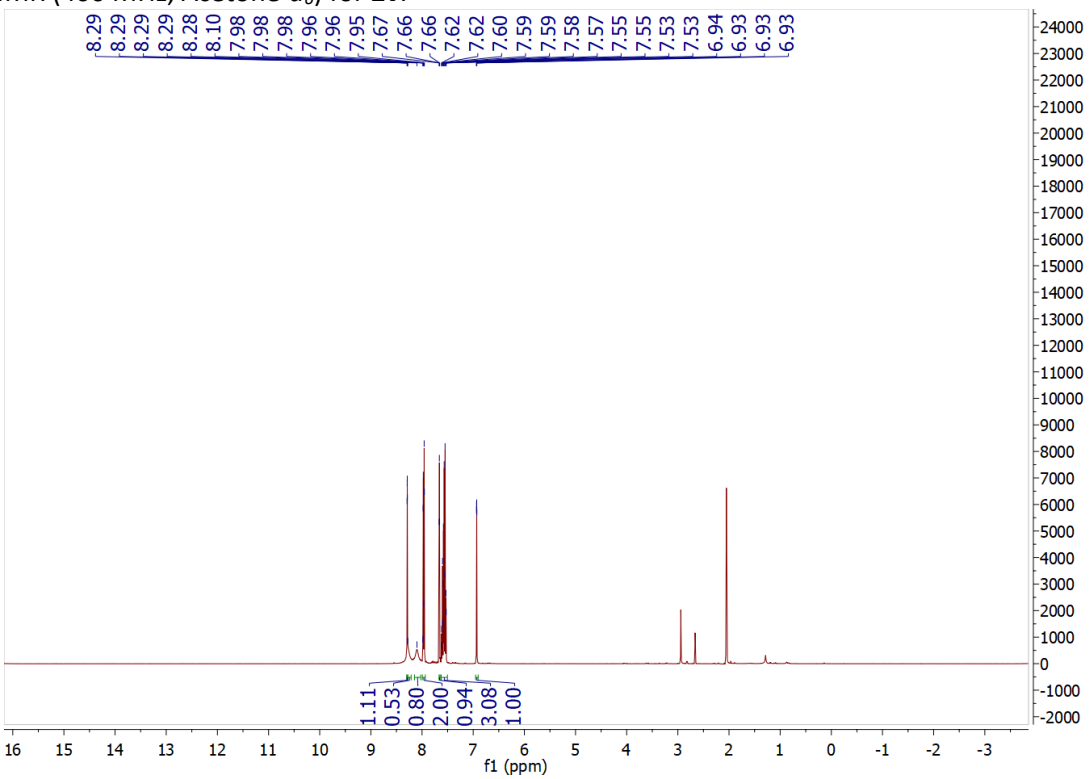
^{13}C NMR (101 MHz, Acetone-d_6) for **2u**:



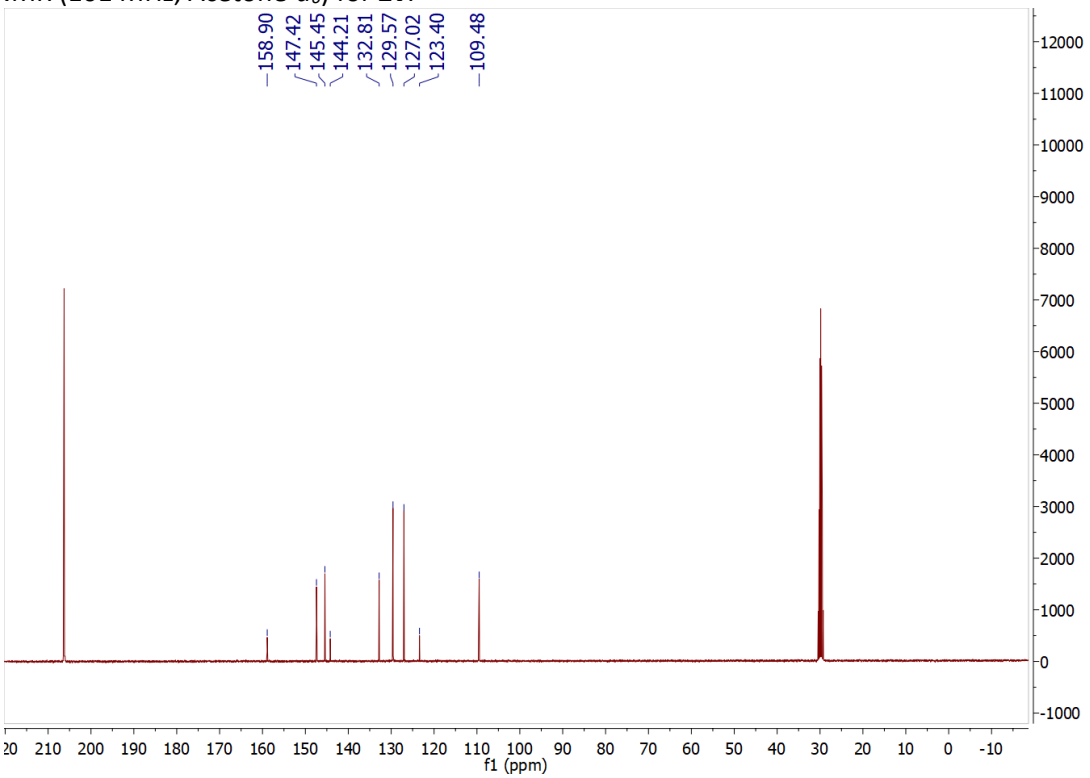
(*Z*)-*N*'-(Phenylsulfonyl)furan-3-carboximidamide (2v)



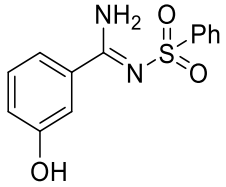
^{1}H NMR (400 MHz, Acetone-d_6) for **2v**:



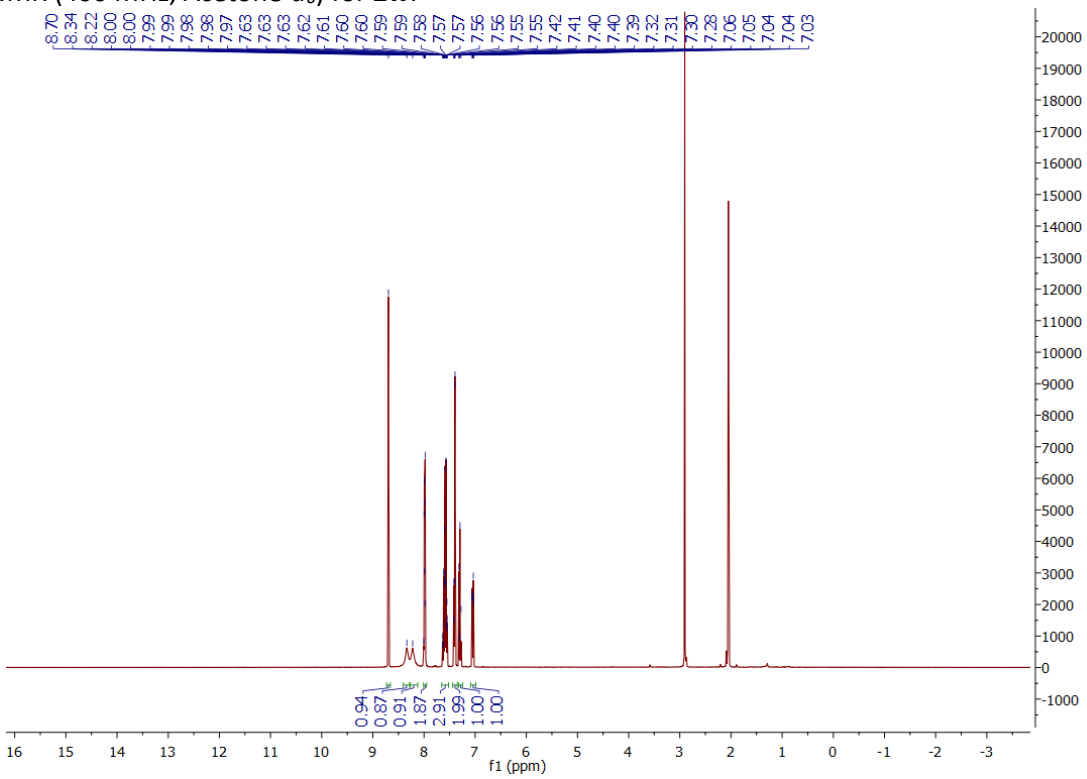
^{13}C NMR (101 MHz, Acetone-d_6) for **2v**:



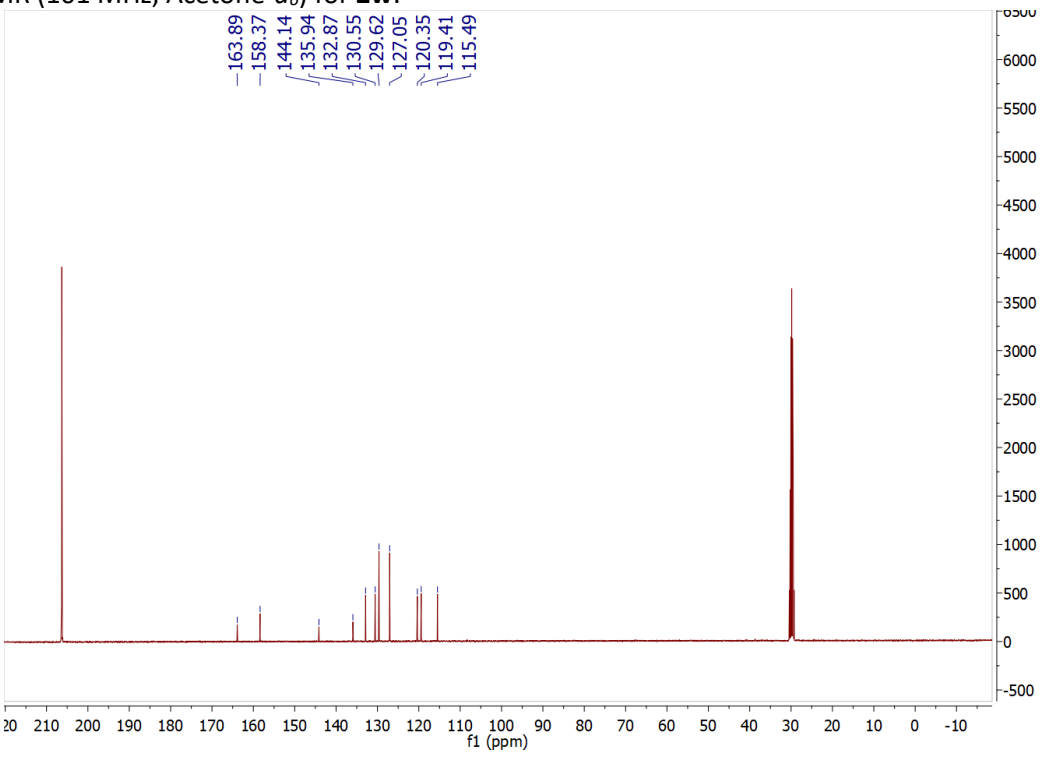
(*Z*)-3-Hydroxy-*N*'-(phenylsulfonyl)benzimidamide (2w)



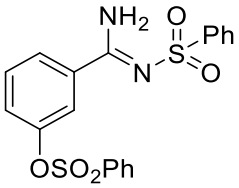
^{1}H NMR (400 MHz, Acetone-d_6) for **2w**:



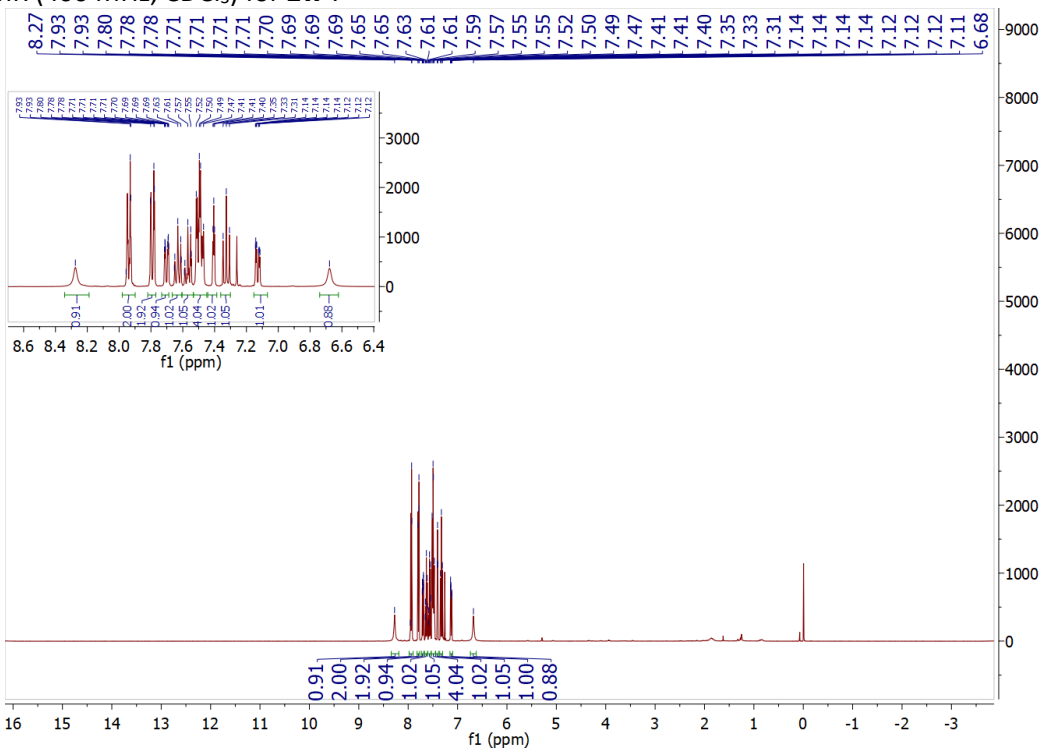
^{13}C NMR (101 MHz, Acetone-d_6) for **2w**:



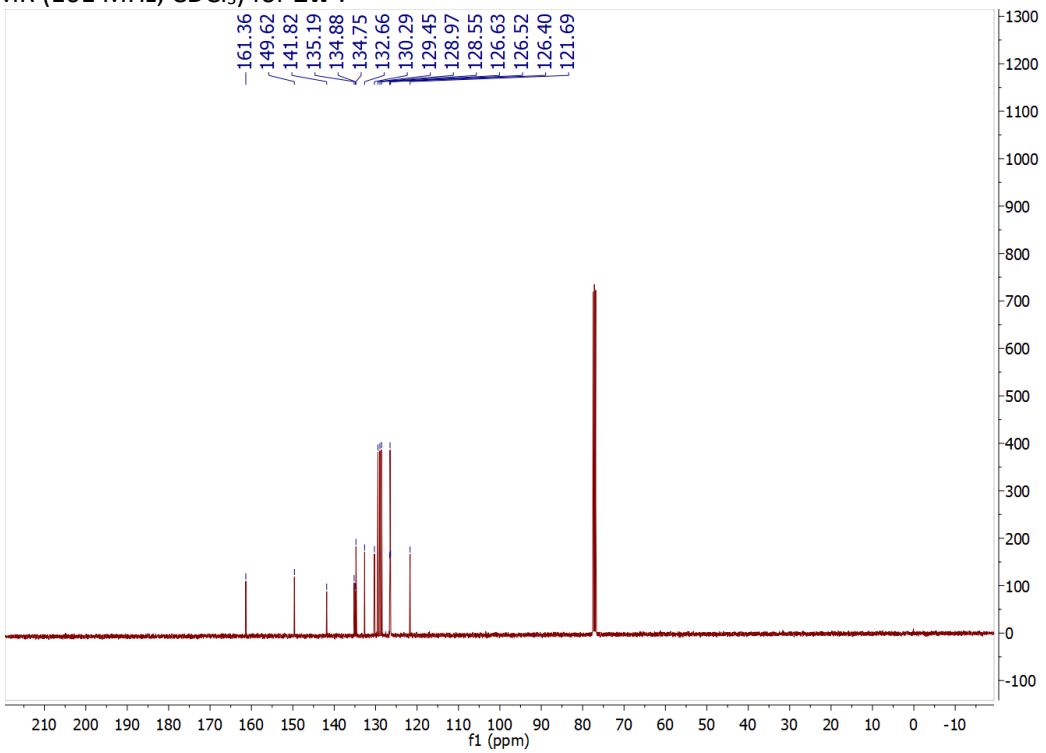
(*Z*)-3-(*N*'-(Phenylsulfonyl)carbamimidoyl)phenyl benzenesulfonate (2w')



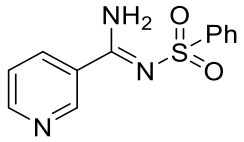
^{1}H NMR (400 MHz, $CDCl_3$) for **2w'**:



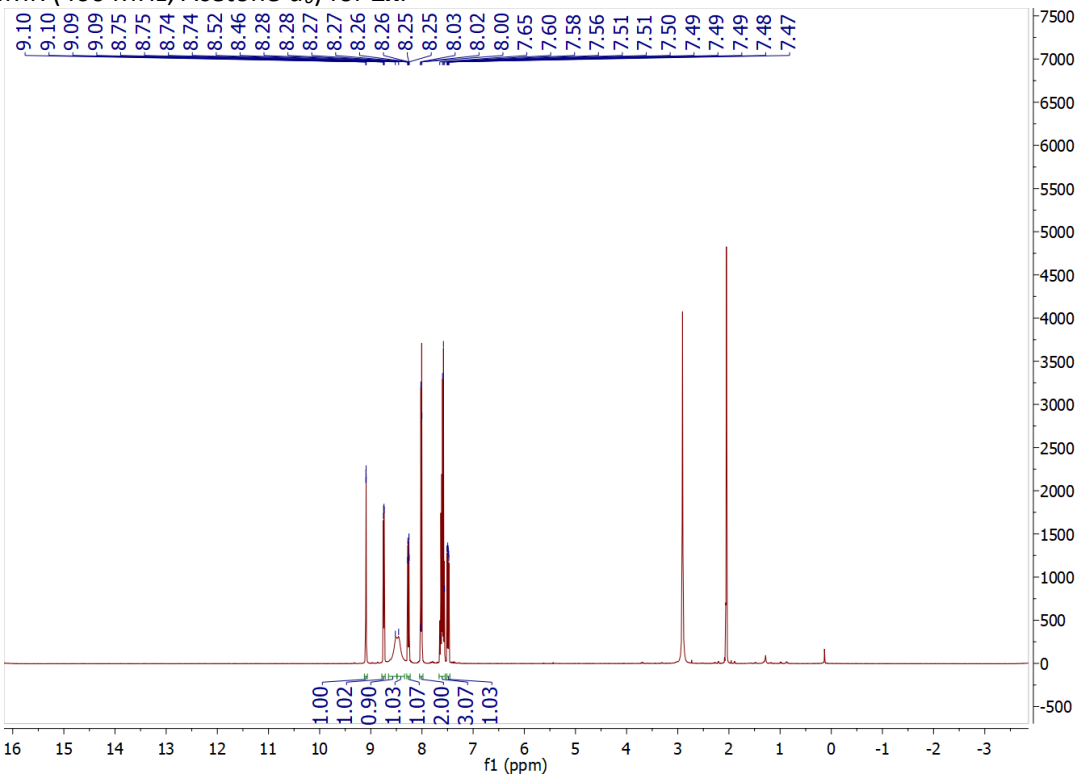
^{13}C NMR (101 MHz, $CDCl_3$) for **2w'**:



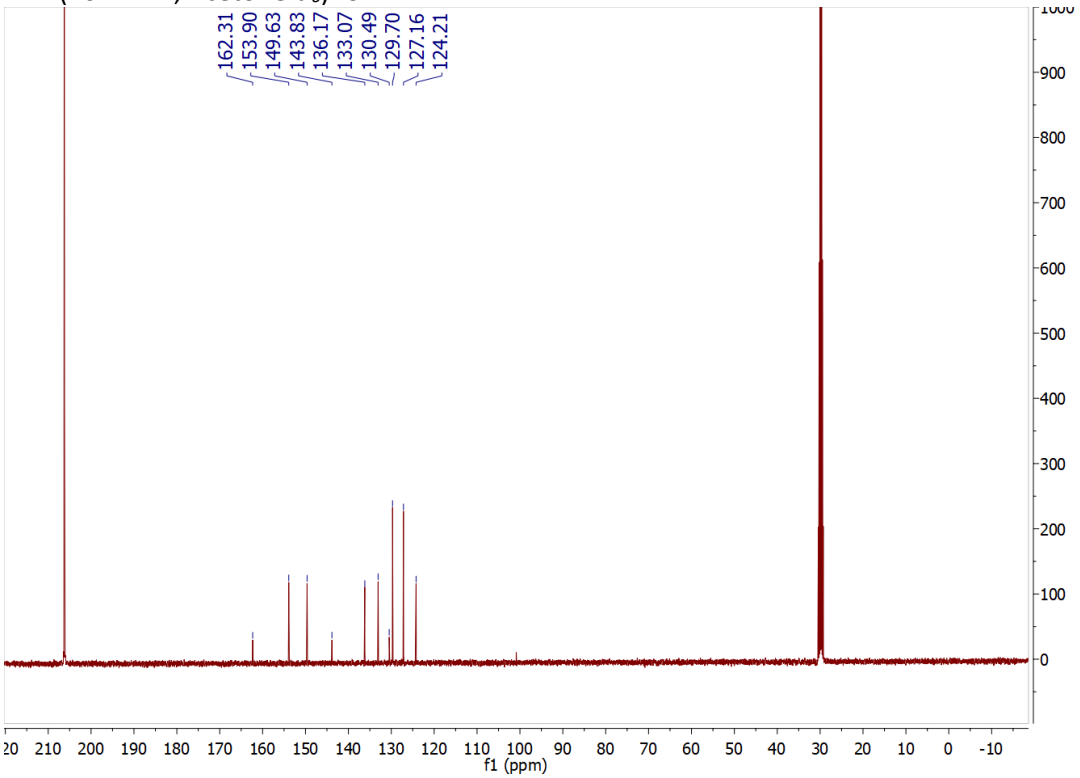
(*Z*)-*N*'-(Phenylsulfonyl)nicotinimidamide (2x)



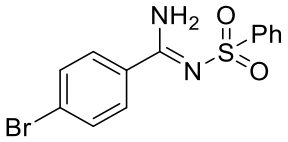
^{1}H NMR (400 MHz, Acetone-d_6) for **2x**:



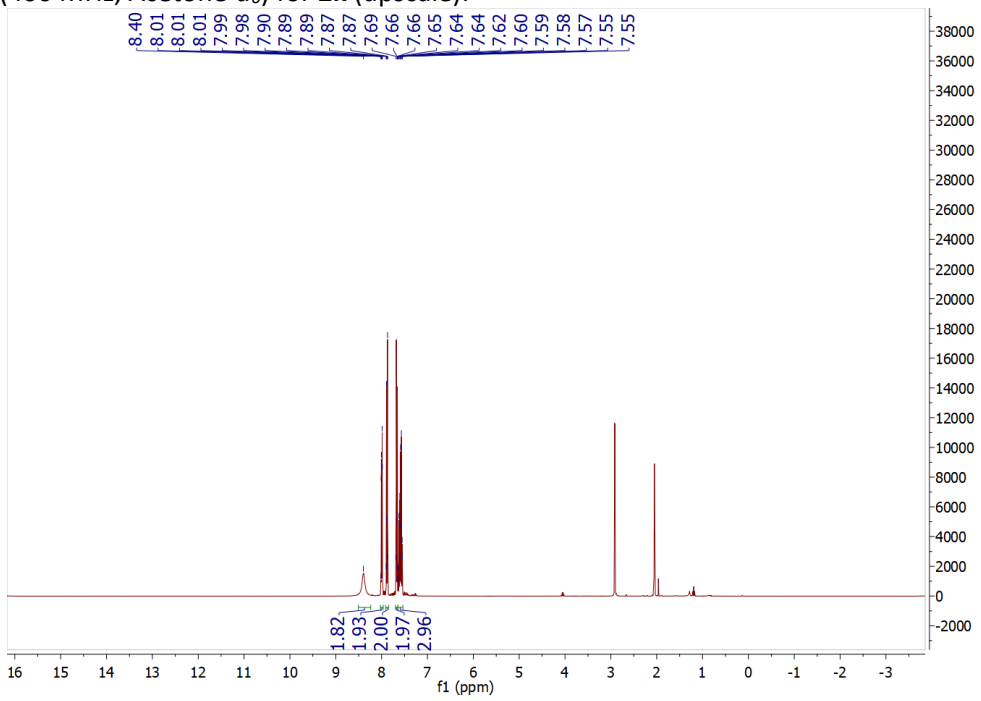
^{13}C NMR (101 MHz, Acetone-d_6) for **2x**:



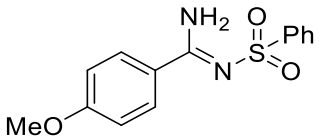
(*Z*)-4-Bromo-*N*'-(phenylsulfonyl)benzimidamide (2k) – upscale



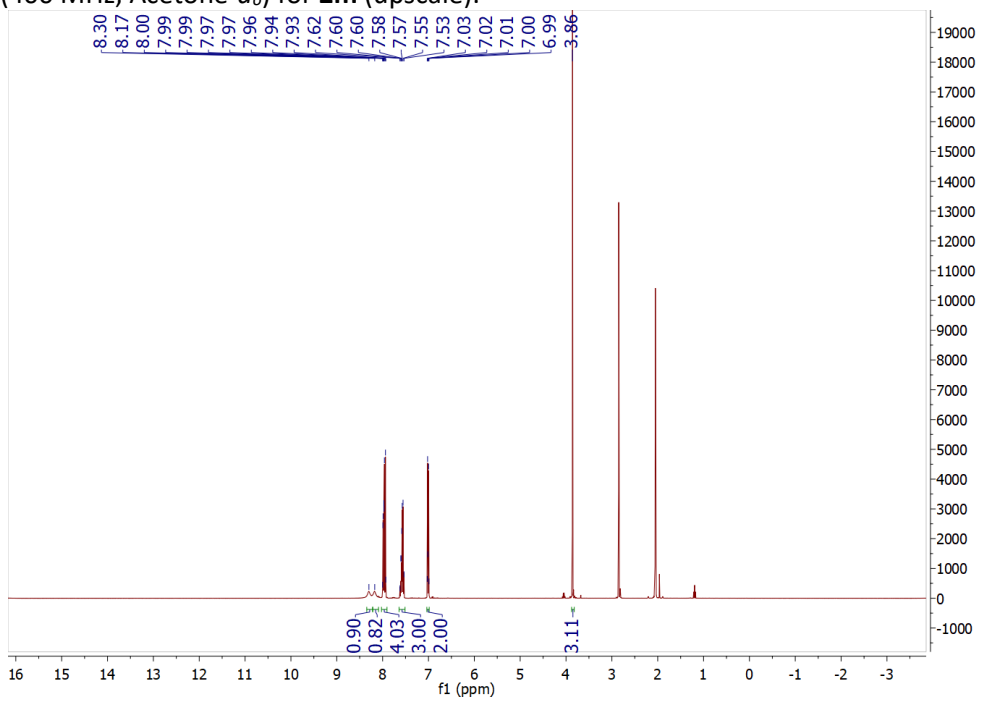
^{1}H NMR (400 MHz, Acetone-d_6) for **2k** (upscale):



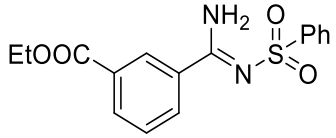
(*Z*)-4-Methoxy-*N*'-(phenylsulfonyl)benzimidamide (2m) – upscale



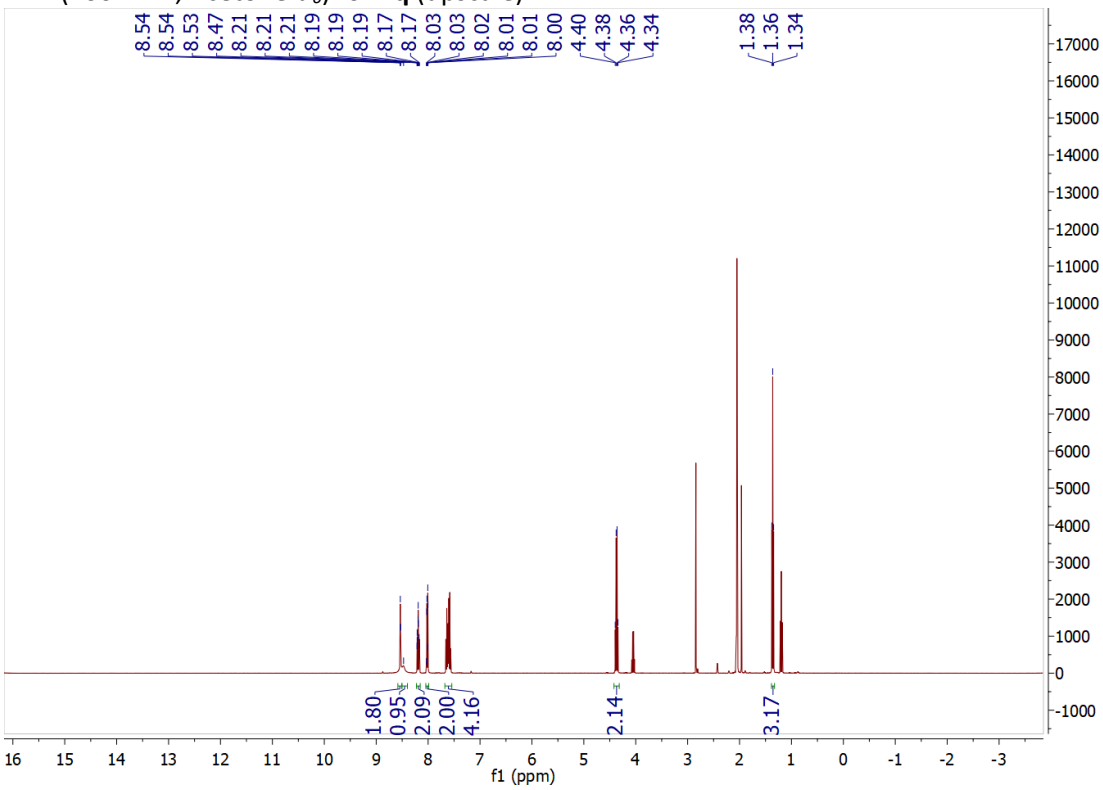
^{1}H NMR (400 MHz, Acetone-d_6) for **2m** (upscale):



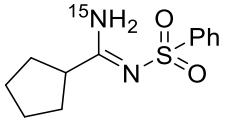
Ethyl (*Z*)-3-(*N*'-(phenylsulfonyl)carbamimidoyl)benzoate (2q) – upscale



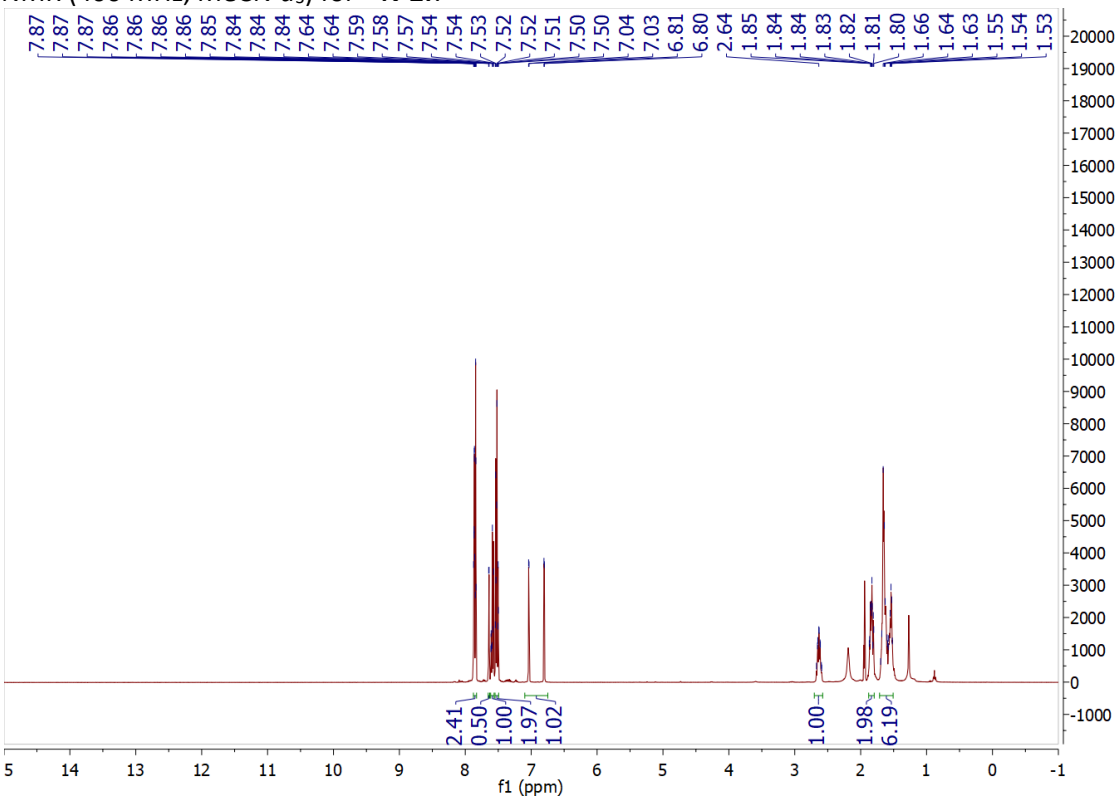
^{1}H NMR (400 MHz, Acetone-d_6) for **2q** (upscale):



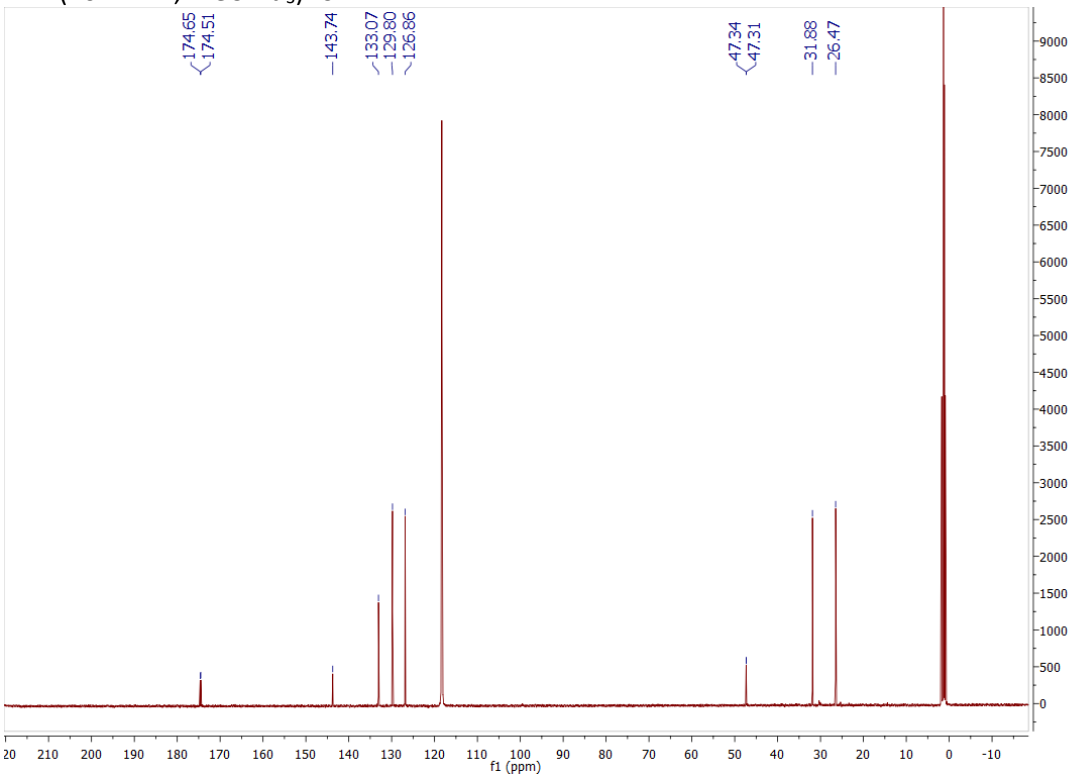
^{15}N-(*Z*)-*N'*-(Phenylsulfonyl)cyclopropanecarboximidamide (^{15}N-2f)



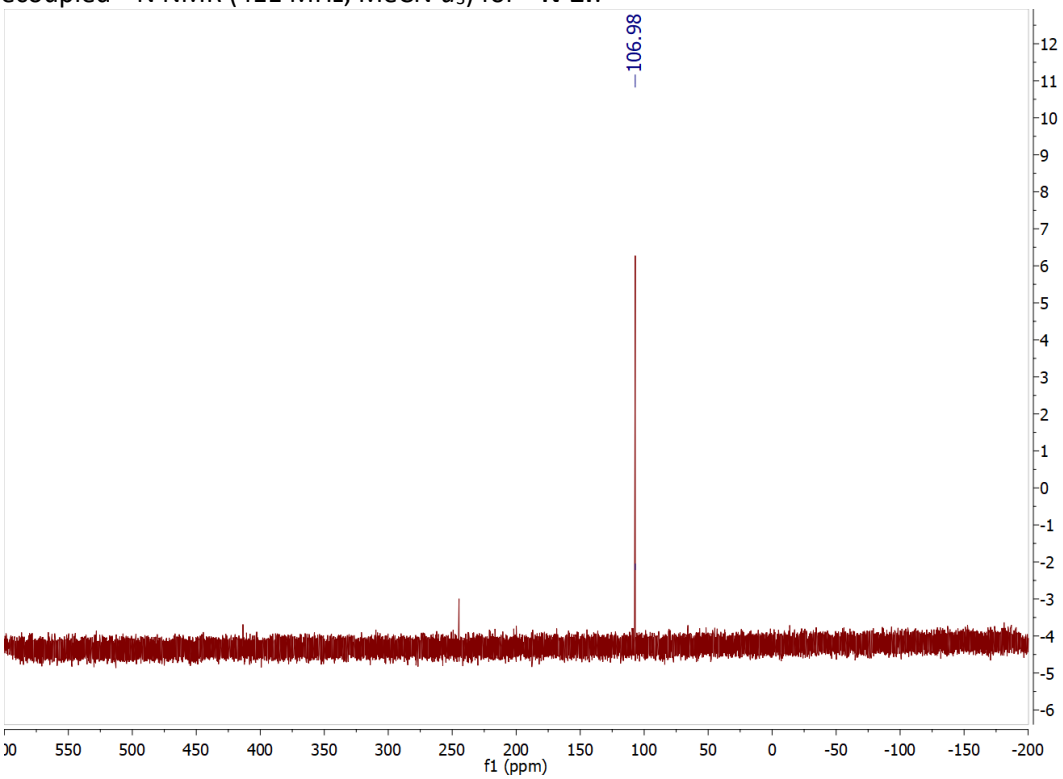
^{1}H NMR (400 MHz, MeCN-d_3) for **^{15}N-2f**:



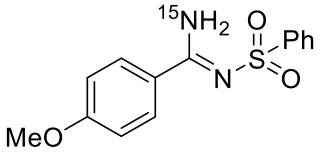
^{13}C NMR (101 MHz, MeCN-d_3) for **^{15}N-2f**:



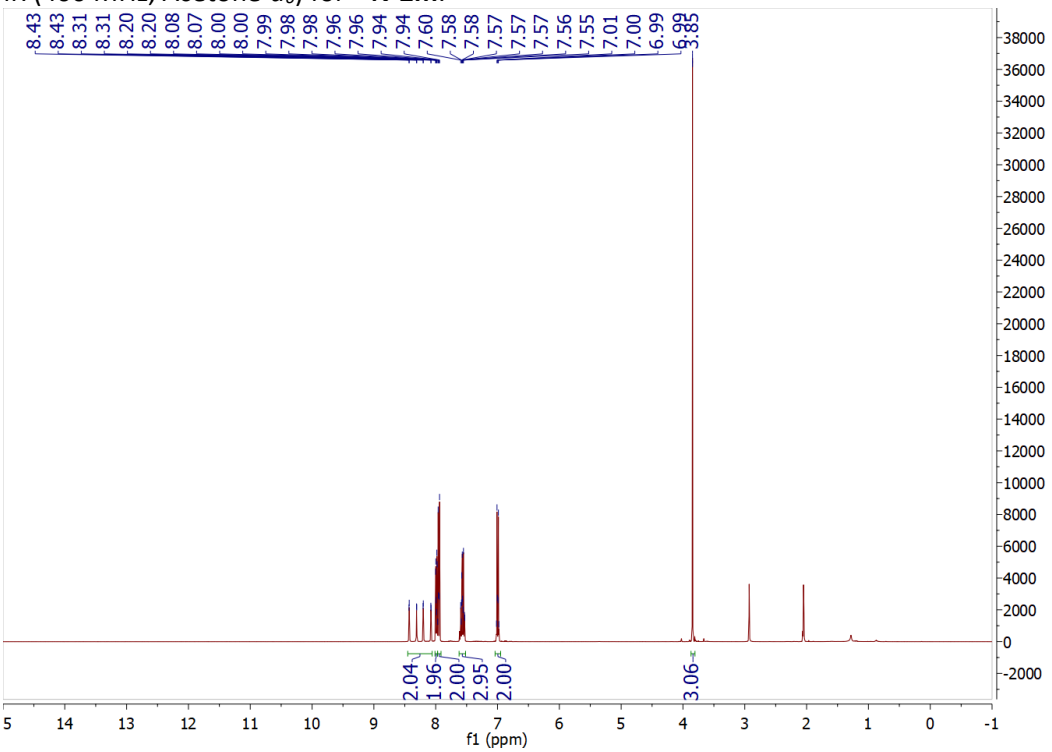
^{1}H decoupled ^{15}N NMR (411 MHz, MeCN-d_3) for **^{15}N-2f**:



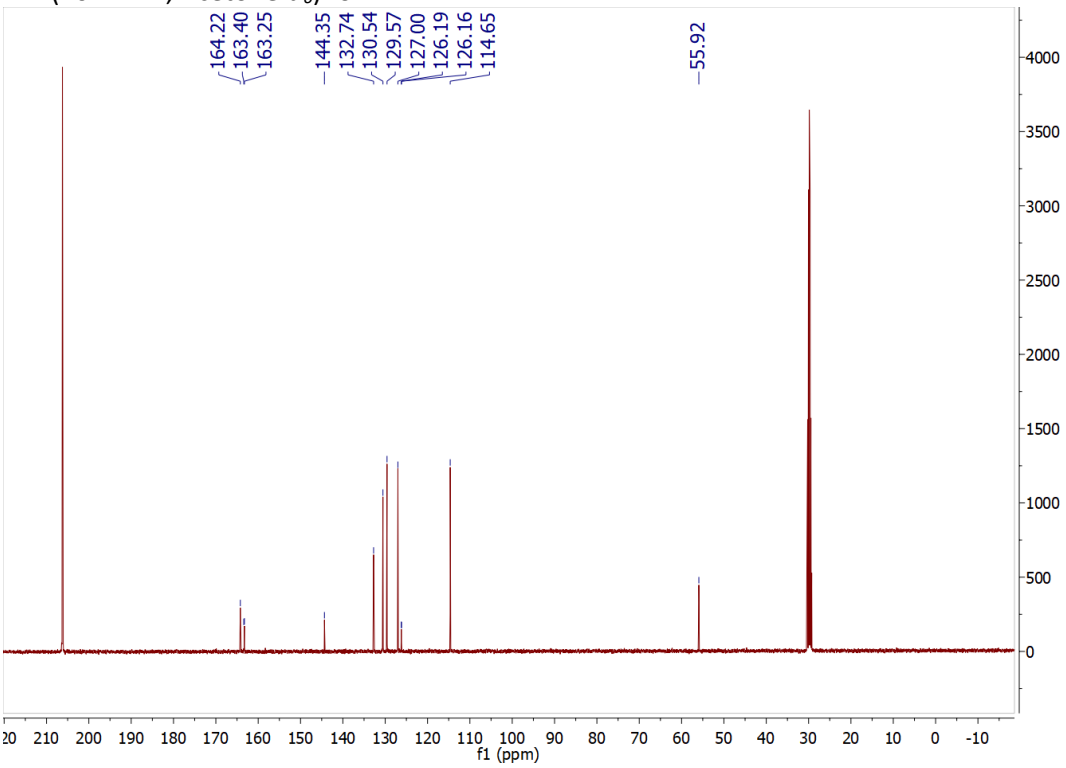
^{15}N-(*Z*)-4-Methoxy-*N*'-(phenylsulfonyl)benzimidamide (^{15}N-2m)



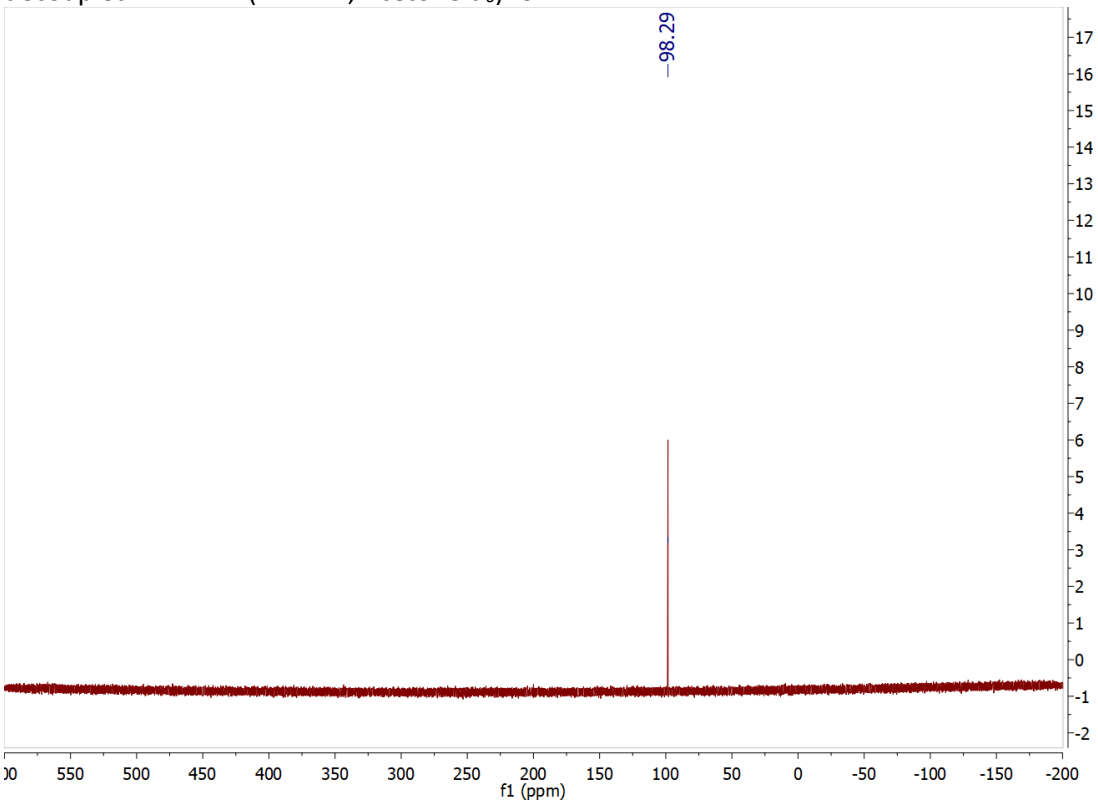
^{1}H NMR (400 MHz, Acetone-d_6) for **^{15}N-2m**:



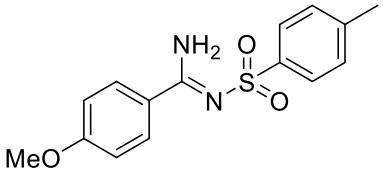
^{13}C NMR (101 MHz, Acetone-d_6) for **^{15}N-2m**:



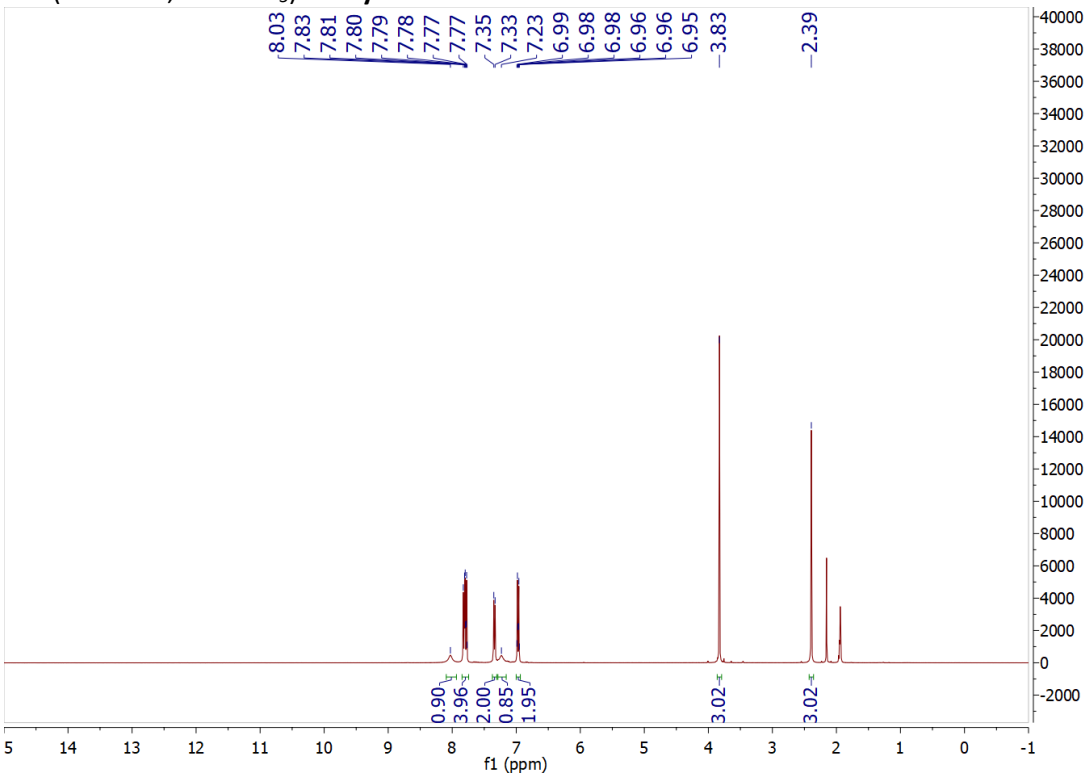
^{1}H decoupled ^{15}N NMR (41 MHz, Acetone-d_6) for **^{15}N-2m**:



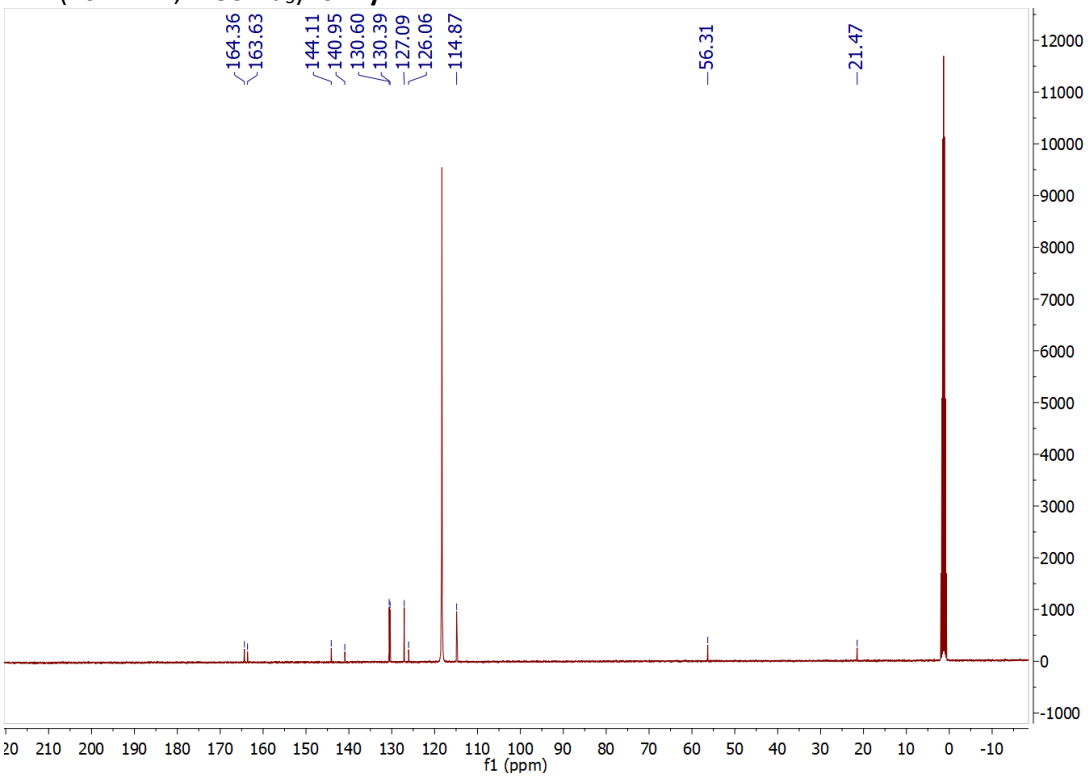
(*Z*)-4-Methoxy-*N'*-tosylbenzimidamide (2y) – obtained by Bi's procedure[S2]



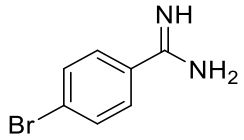
^{1}H NMR (400 MHz, MeCN-d_3) for **2y**:



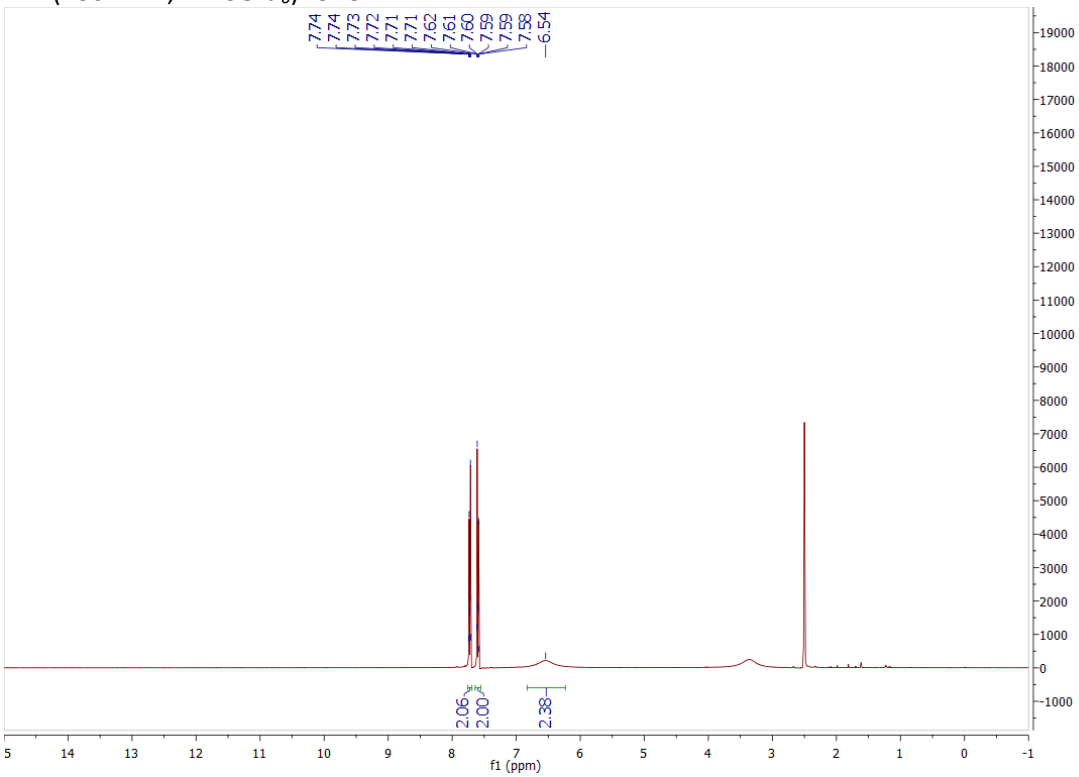
^{13}C NMR (101 MHz, MeCN-d_3) for **2y**:



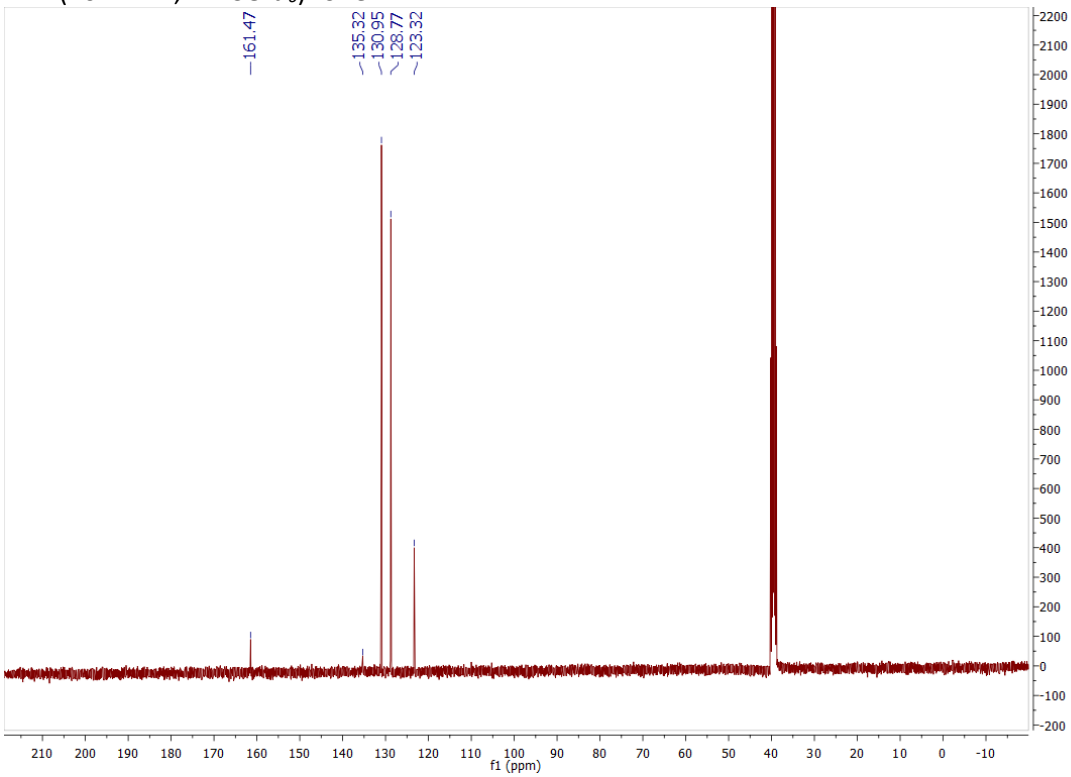
4-Bromobenzimidamide (3k)



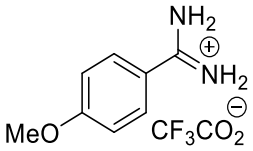
^{1}H NMR (400 MHz, DMSO-d_6) for **3k**:



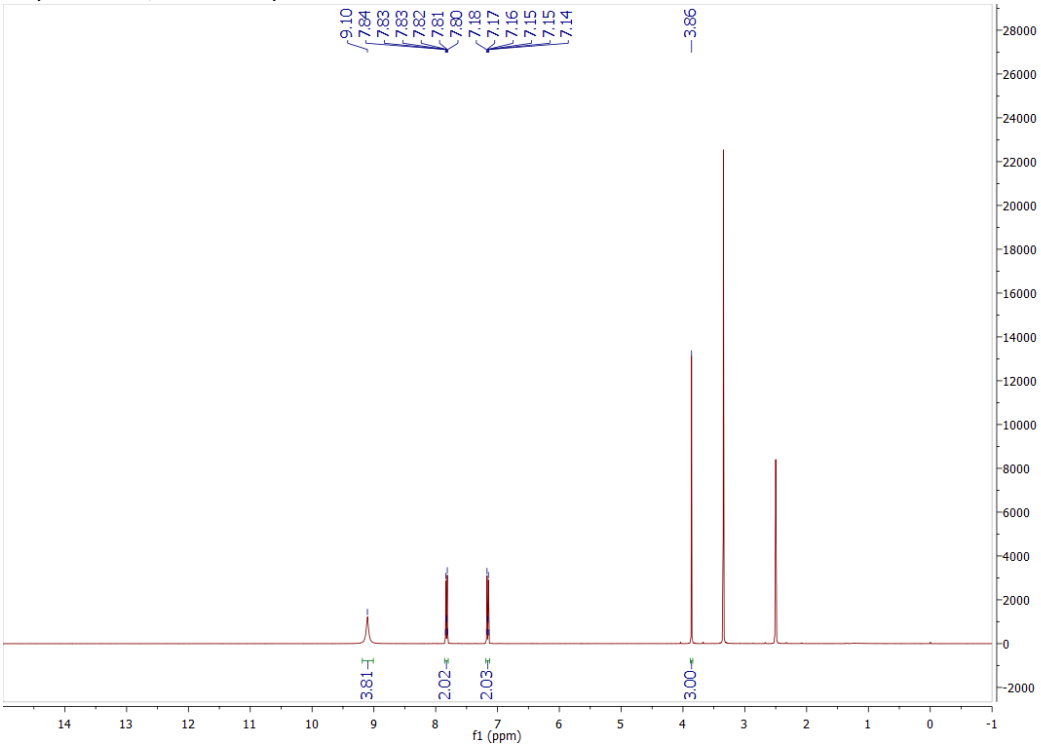
^{13}C NMR (101 MHz, DMSO-d_6) for **3k**:



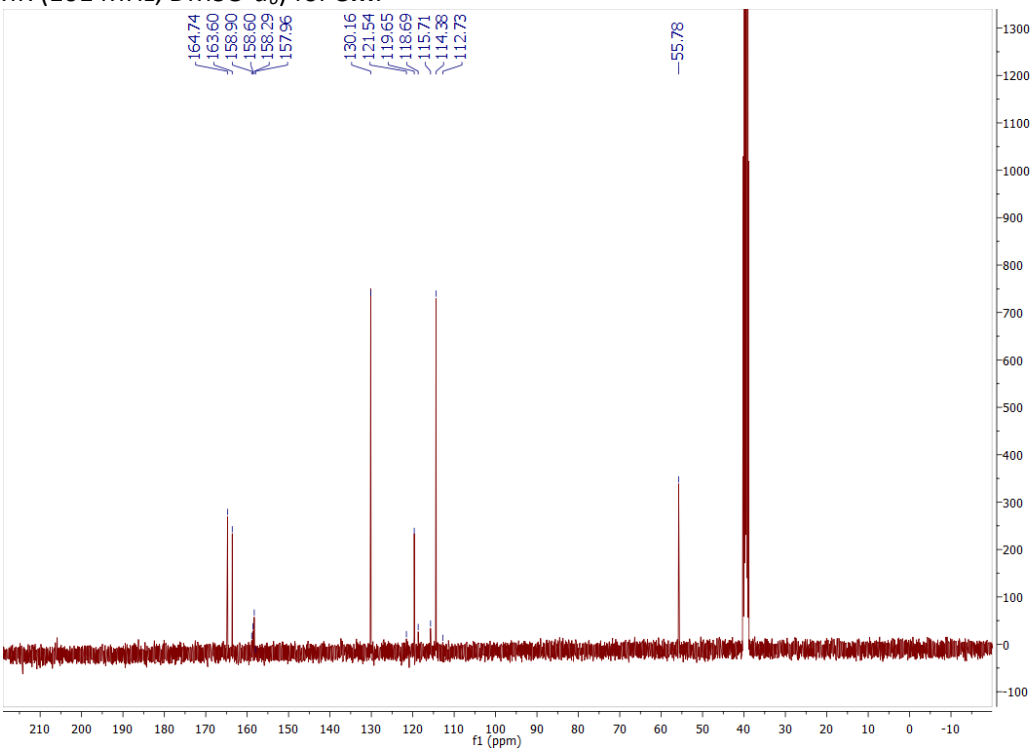
4-Methoxybenzimidamidinium trifluoroacetate (3m)



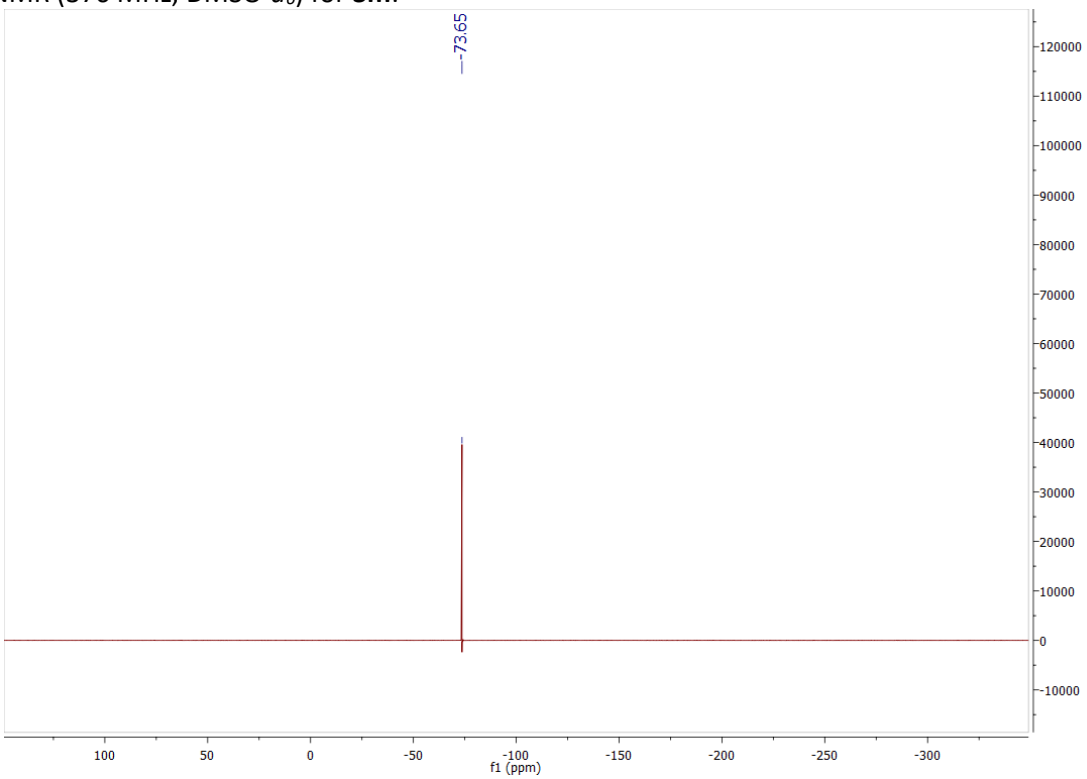
^{1}H NMR (400 MHz, DMSO-d_6) for **3m**:



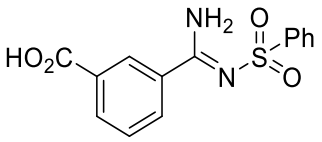
^{13}C NMR (101 MHz, DMSO-d_6) for **3m**:



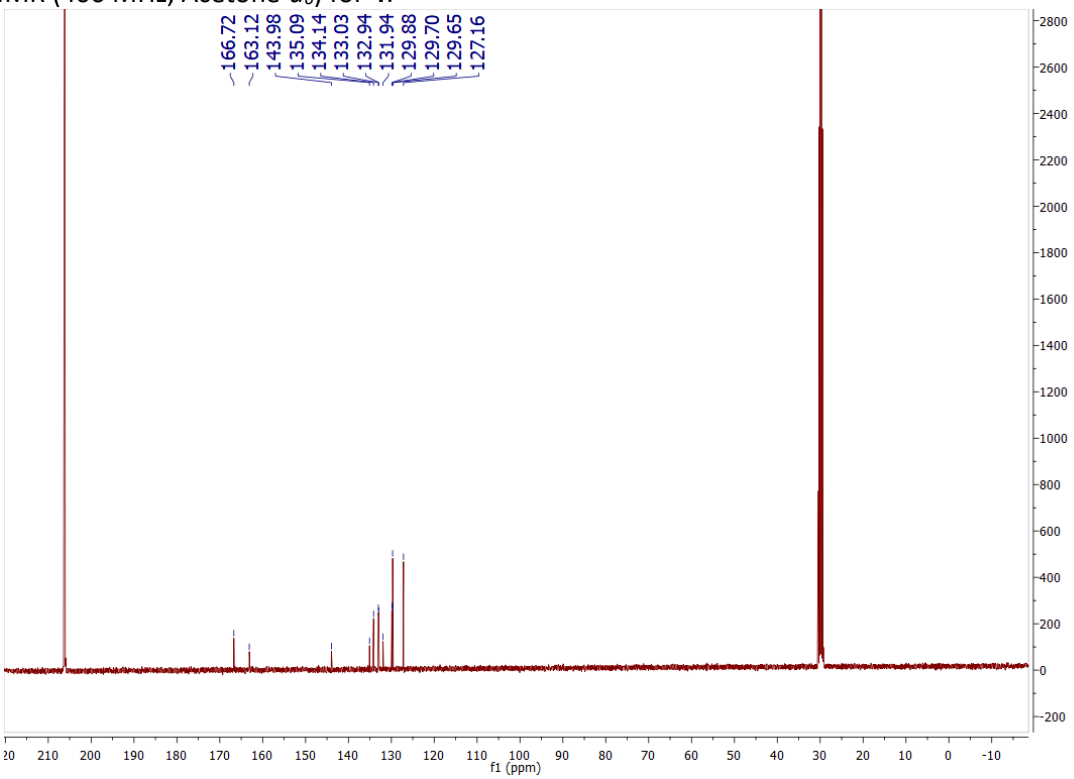
^{19}F NMR (376 MHz, DMSO-d_6) for **3m**:



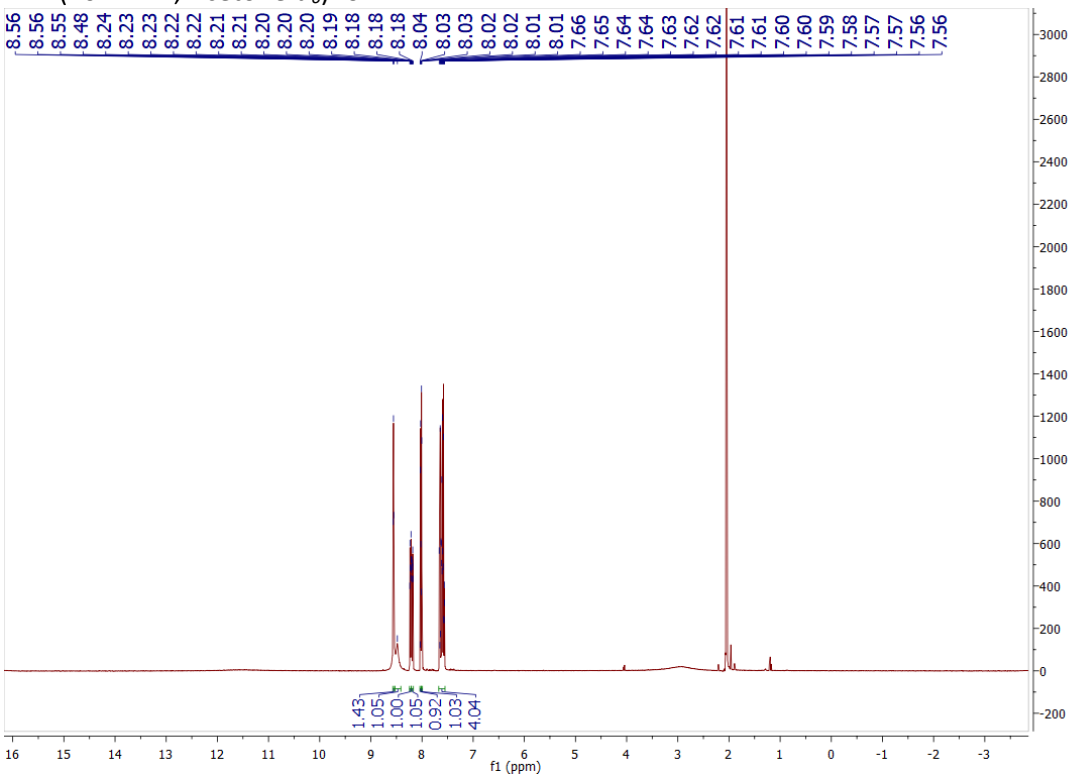
(*Z*)-3-(N'-(Phenylsulfonyl)carbamimidoyl)benzoic acid (4)



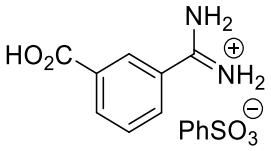
^{1}H NMR (400 MHz, Acetone-d_6) for **4**:



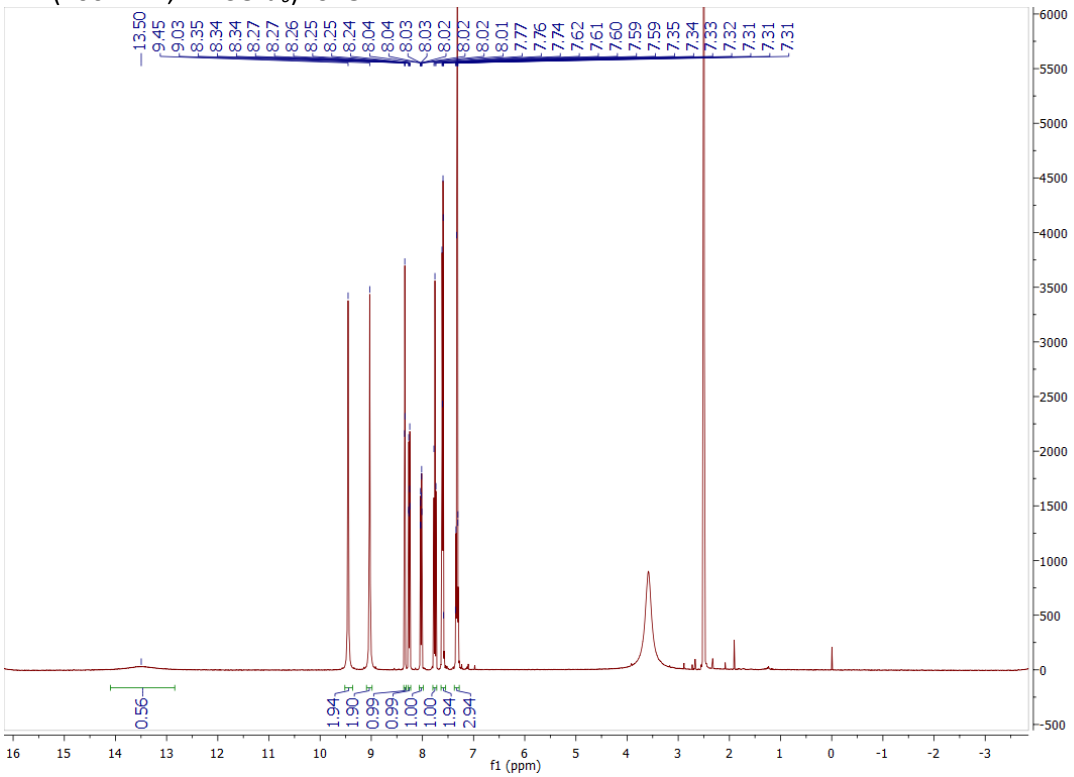
^{13}C NMR (101 MHz, Acetone-d_6) for **4**:



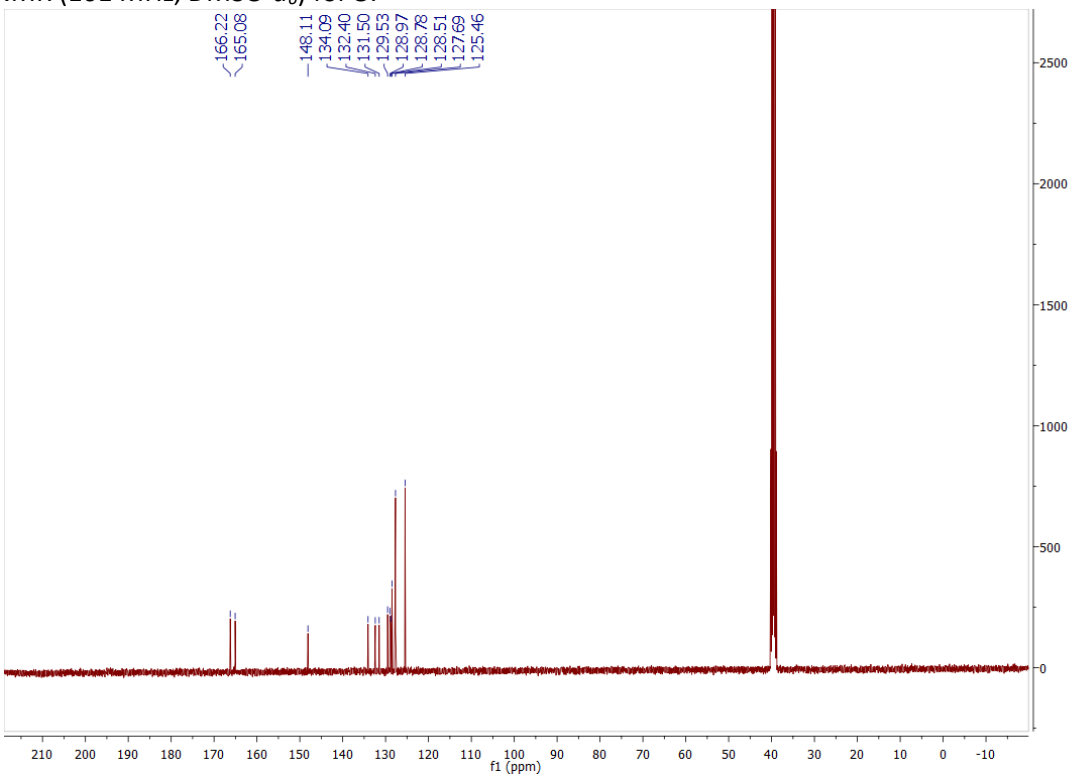
3-Carbamimidoylbenzoic acid, benzesulfonate salt (5)



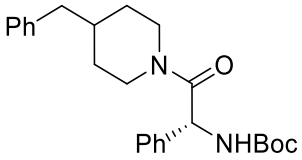
^{1}H NMR (400 MHz, DMSO-d_6) for **5**:



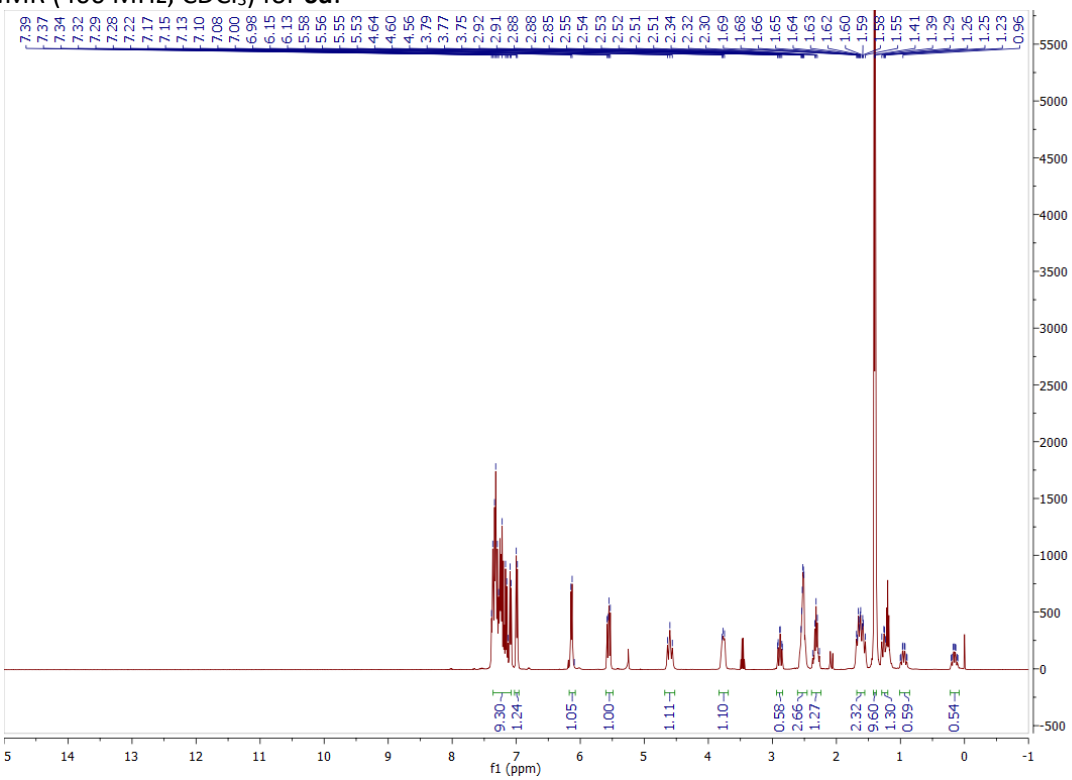
^{13}C NMR (101 MHz, DMSO-d_6) for **5**:



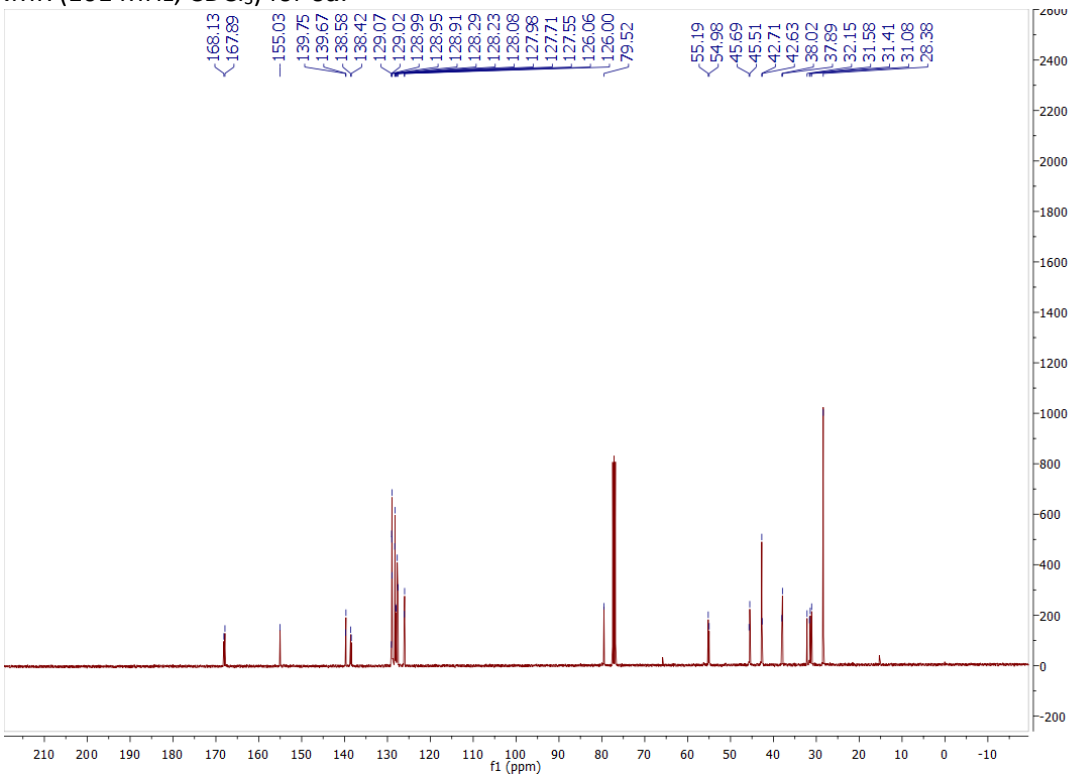
***Tert*-butyl (*R*)-(2-(4-benzylpiperidin-1-yl)-2-oxo-1-phenylethyl)carbamate (6a)**



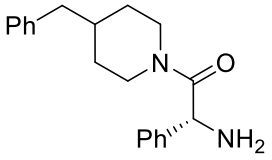
^{1}H NMR (400 MHz, $CDCl_3$) for **6a**:



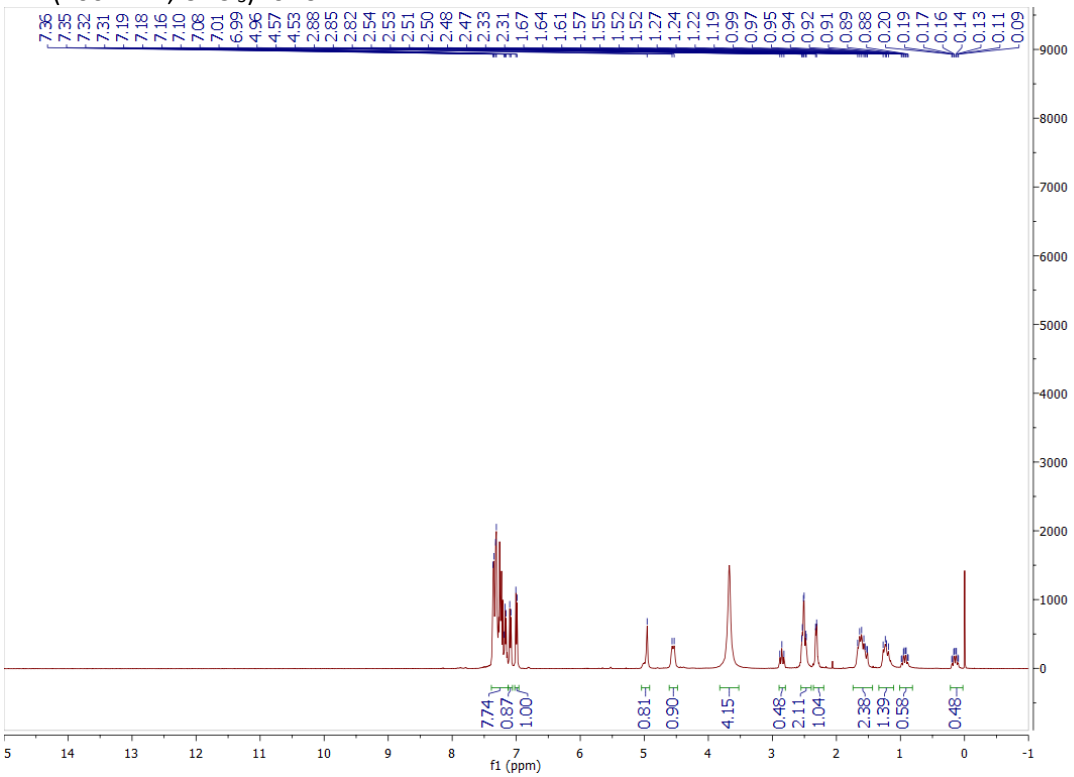
^{13}C NMR (101 MHz, $CDCl_3$) for **6a**:



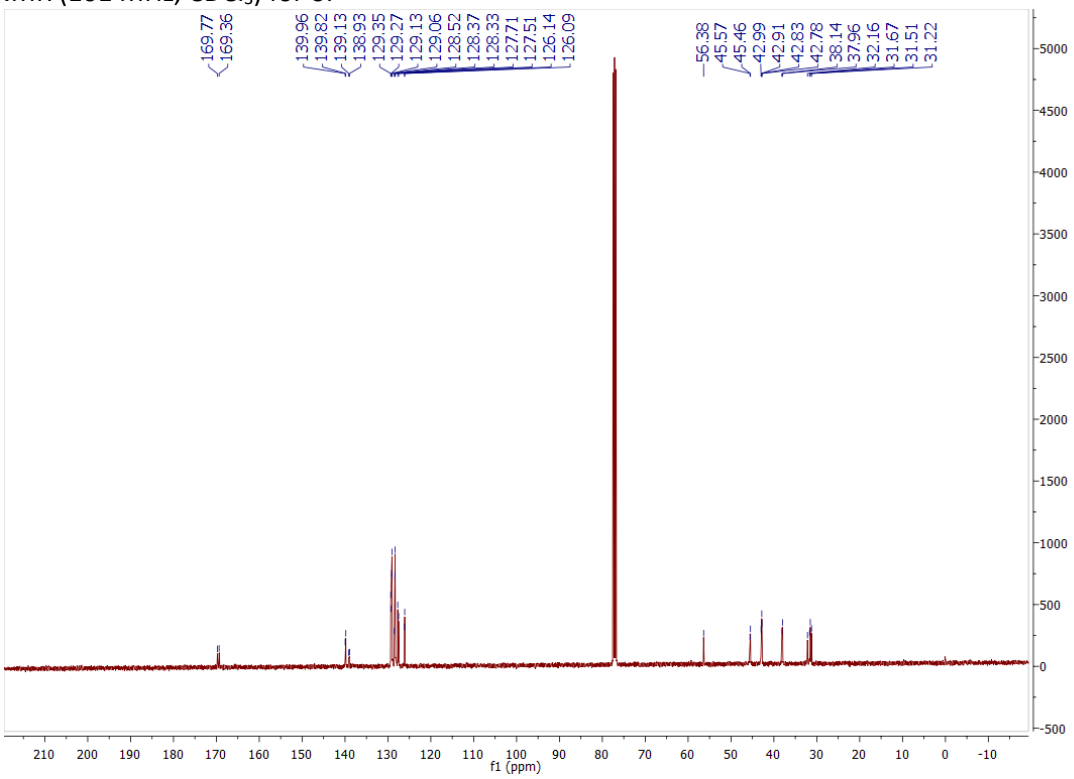
(*R*)-2-Amino-1-(4-benzylpiperidin-1-yl)-2-phenylethan-1-one (6)



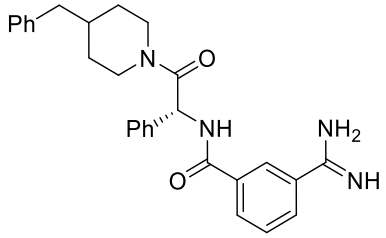
^{1}H NMR (400 MHz, $CDCl_3$) for **6**:



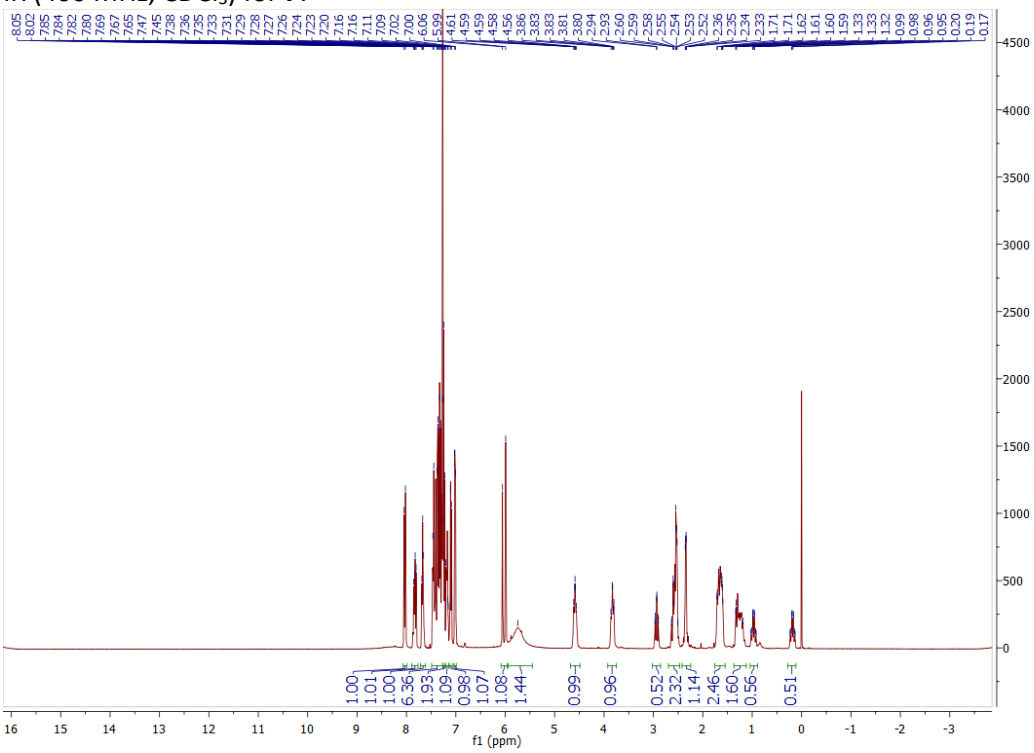
^{13}C NMR (101 MHz, $CDCl_3$) for **6**:



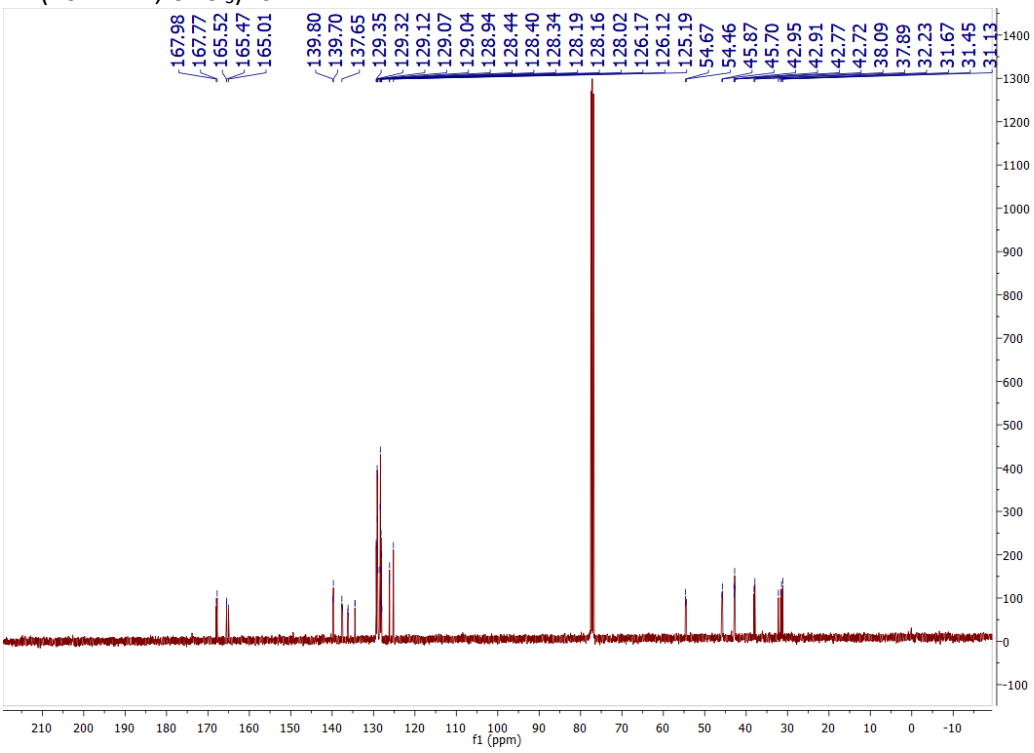
(*R*)-*N*-(2-(4-Benzylpiperidin-1-yl)-2-oxo-1-phenylethyl)-3-carbamimidoylbenzamide (7)



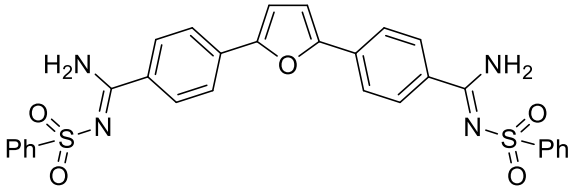
^{1}H NMR (400 MHz, $CDCl_3$) for **7**:



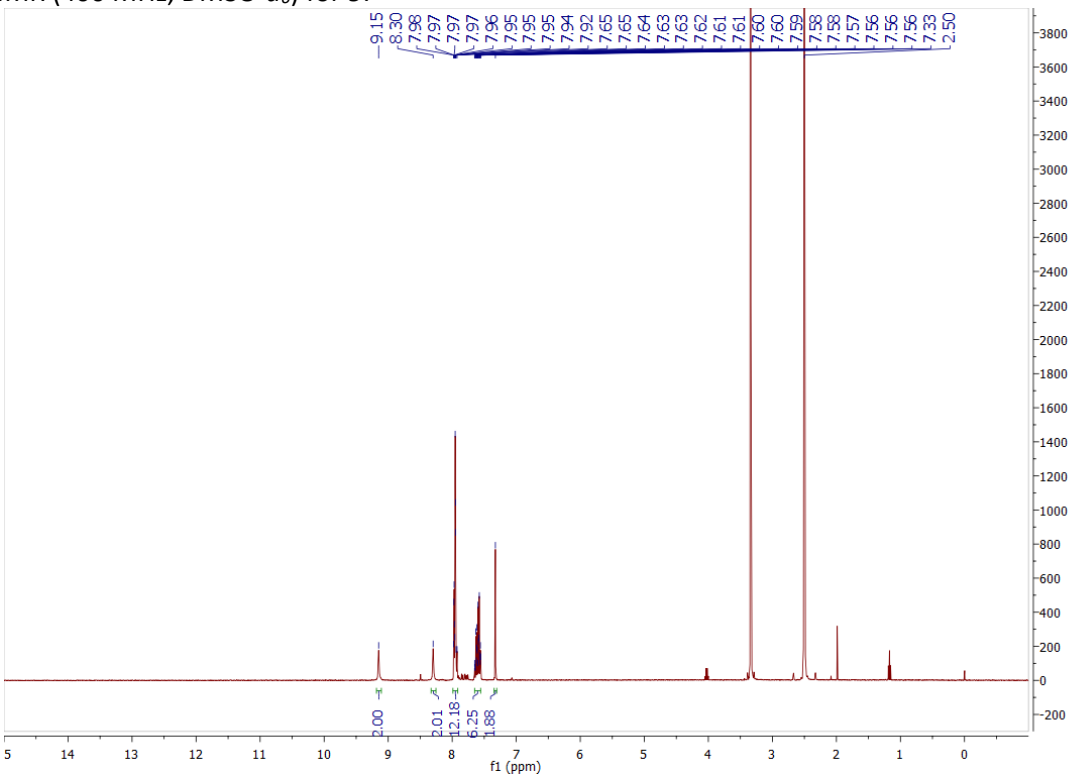
^{13}C NMR (101 MHz, $CDCl_3$) for **7**:



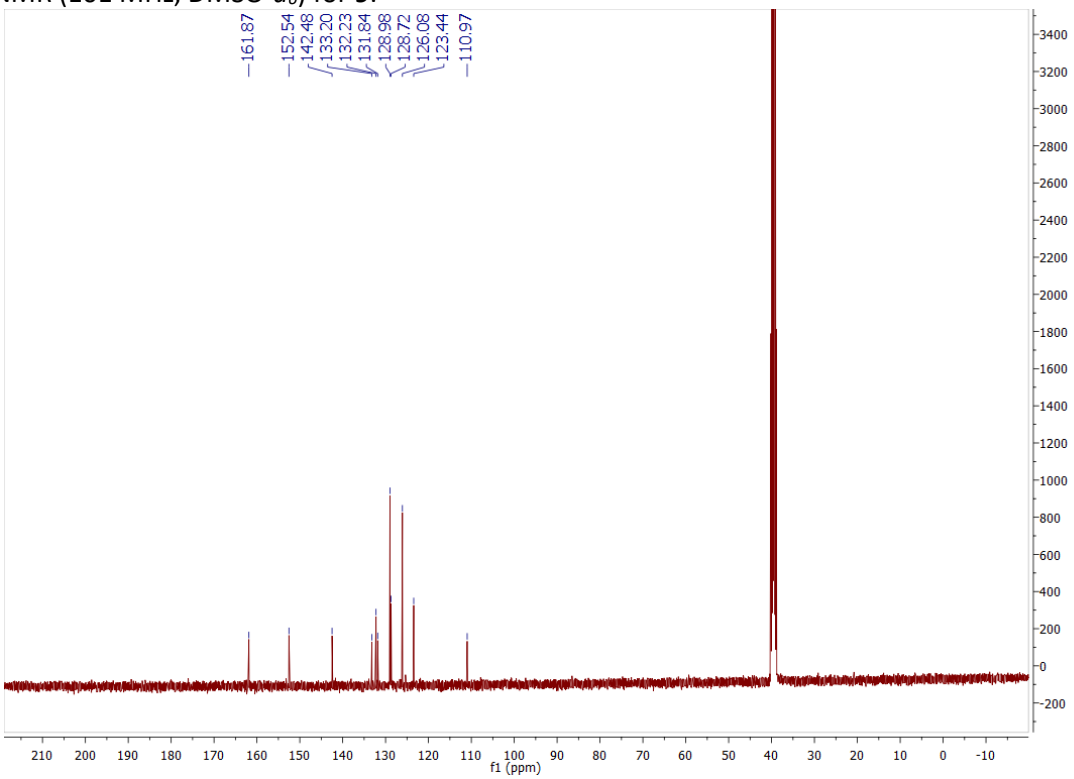
(1*Z*,1'*Z*)-1,1'-(Furan-2,5-diylbis(4,1-phenylene))bis(*N*'-(phenylsulfonyl)formimidamide) (9)



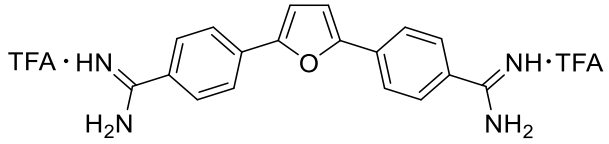
^{1}H NMR (400 MHz, DMSO-d_6) for **9**:



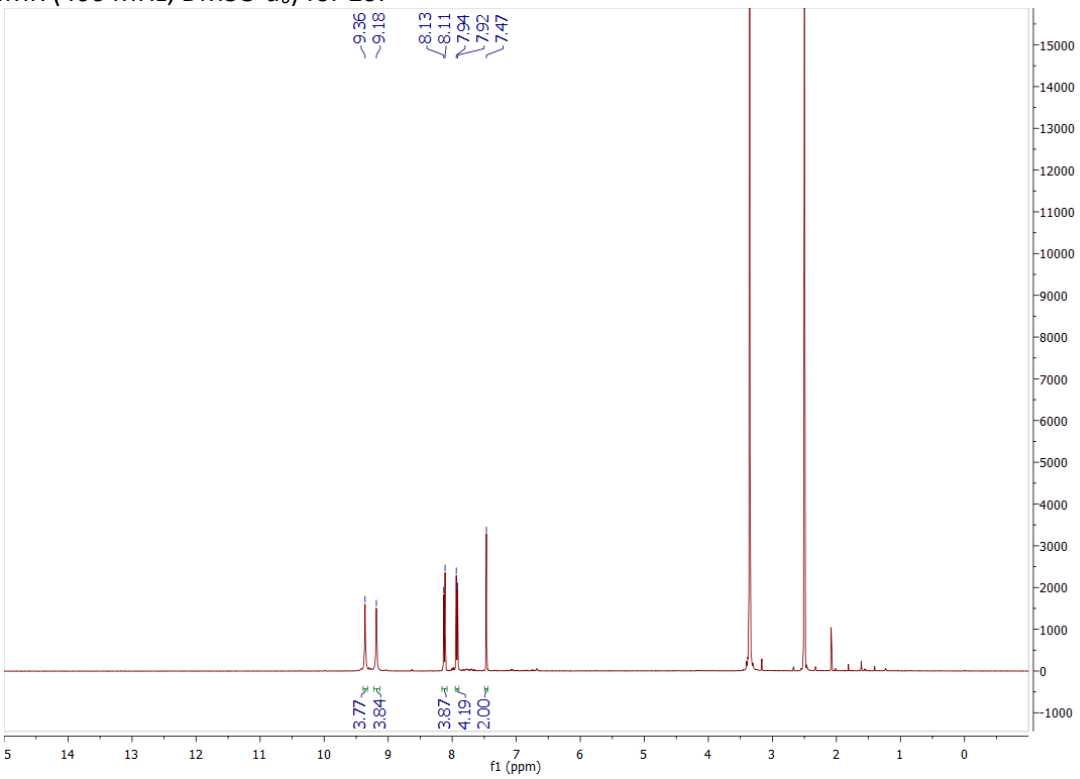
^{13}C NMR (101 MHz, DMSO-d_6) for **9**:



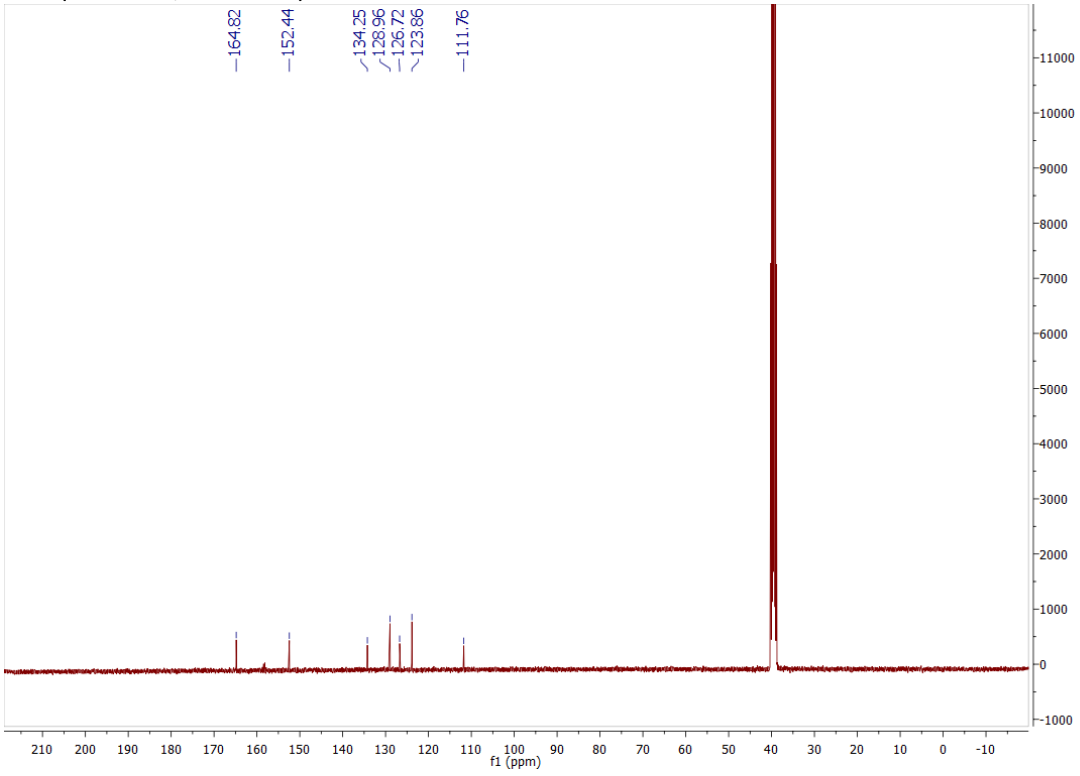
4,4'-(Furan-2,5-diyl)dibenzimidamide, bistrifluoroacetate salt (10)



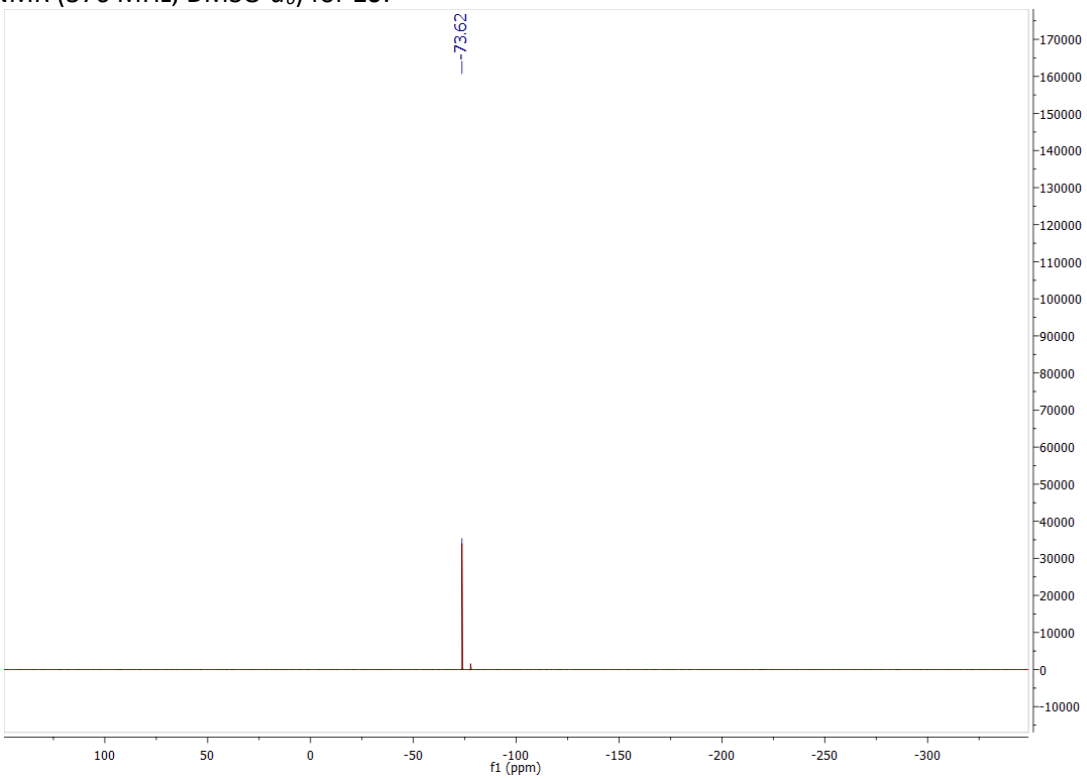
^{1}H NMR (400 MHz, DMSO-d_6) for **10**:



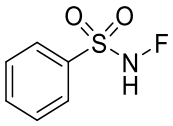
^{13}C NMR (101 MHz, DMSO-d_6) for **10**:



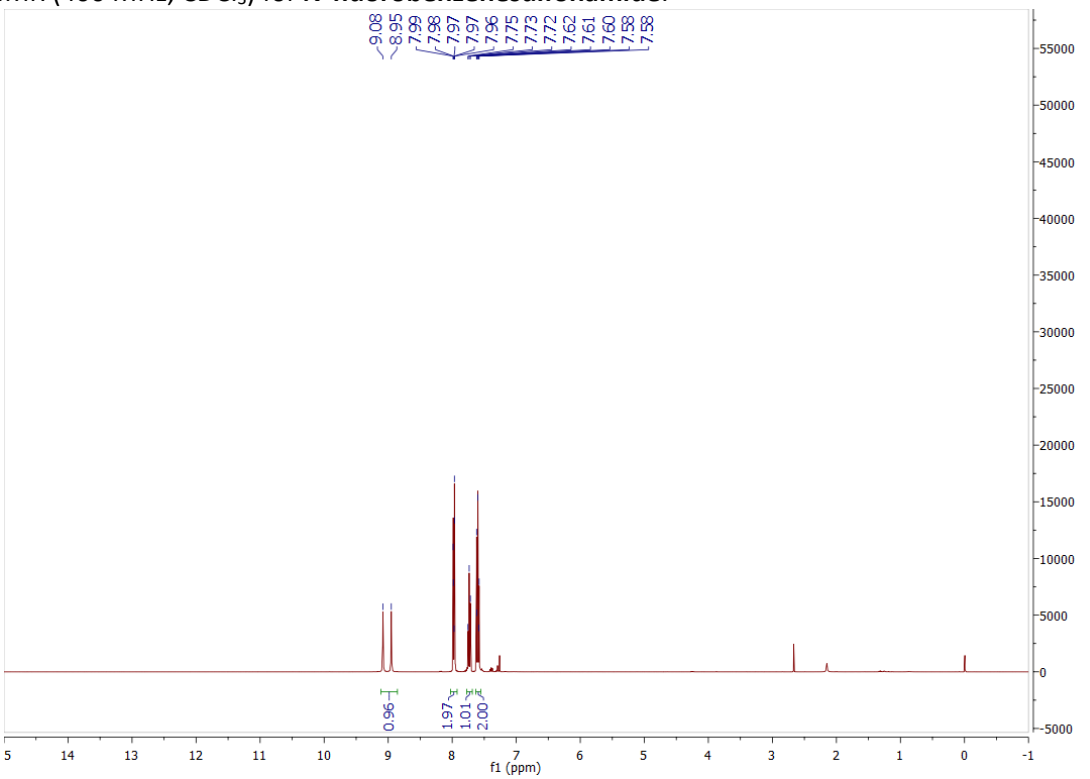
^{19}F NMR (376 MHz, DMSO-d_6) for **10**:



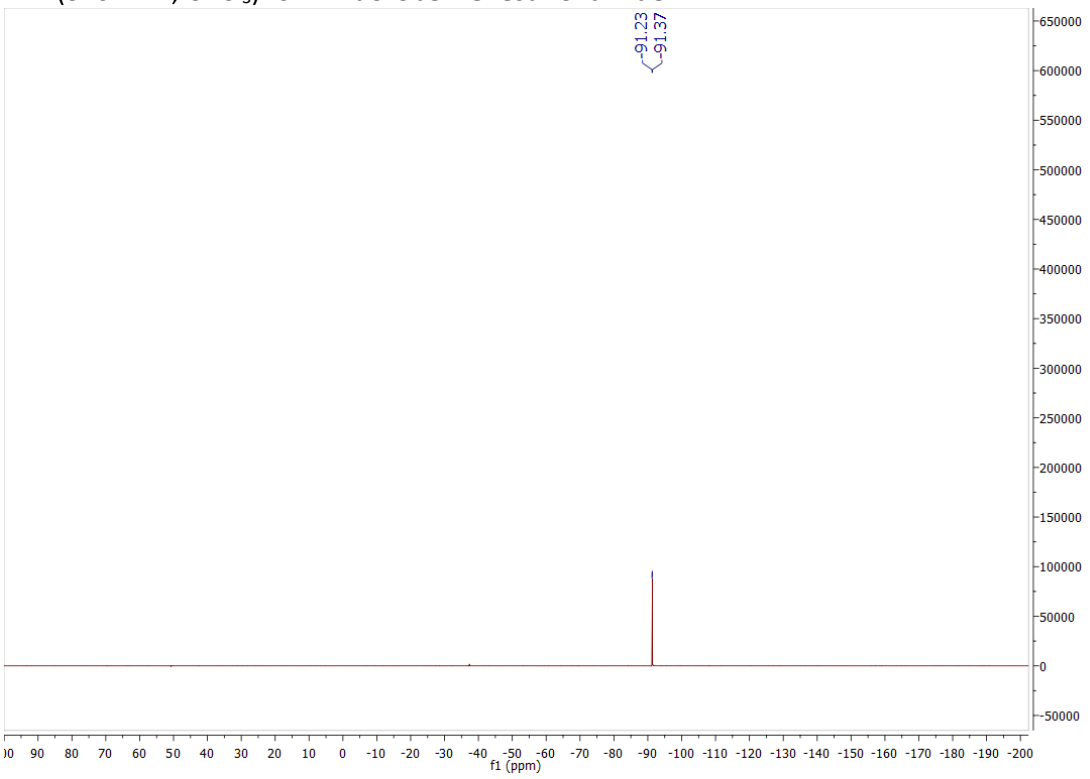
***N*-Fluorobenzenesulfonamide**



^{1}H NMR (400 MHz, $CDCl_3$) for ***N*-fluorobenzenesulfonamide**:



^{19}F NMR (376 MHz, $CDCl_3$) for ***N*-fluorobenzenesulfonamide**:



^{13}C NMR (101 MHz, $CDCl_3$) for ***N*-fluorobenzenesulfonamide**: