

Catalytic Preparation of 1-Aryl Substituted 1,2,4-Triazolium Salts

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3. NMR Spectra of Isolated Triazolium Salts

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Figure S073: ^{13}C NMR spectrum of 4-cyclohexyl-1-mesityl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[4b]OTf**) (100 MHz, DMSO-*d*₆, 298 K).

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Figure S075: ^{13}C NMR spectrum of 4-((3*s*,5*s*,7*s*)-adamantan-1-yl)-1-mesityl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[4c]OTf**) (100 MHz, DMSO-*d*₆, 298 K).

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Figure S079: ^{13}C NMR spectrum of 1-mesityl-4-phenyl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[4d]OTf**) (100 MHz, DMSO-*d*₆, 298 K).

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Figure S083: ^{13}C NMR spectrum of 4-(4-fluorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[4i]OTf**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S084: ^{19}F NMR spectrum of 4-(4-fluorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[4i]OTf**) (376 MHz, DMSO-*d*₆, 298 K).

Figure S085: ^1H NMR spectrum of 4-(4-chlorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[4k]OTf**) (400 MHz, DMSO-*d*₆, 298 K).

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Figure S092: ^{13}C NMR spectrum of 1-(naphthalen-1-yl)-4-phenyl-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[5d]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

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Figure S094: ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-4-phenyl-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[6d]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S095: ^1H NMR spectrum of 1-(4-methoxyphenyl)-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[6m]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

Figure S096: ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[6m]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S097: ^1H NMR spectrum of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[7d]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

Figure S098: ^{13}C NMR spectrum of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[7d]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S099: ^{19}F NMR spectrum of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[7d]BF₄**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

Figure S100: ^1H NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[7e]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

Figure S101: ^{13}C NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[7e]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S102: ^{19}F NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i^{um} tetrafluoroborate (**[7e]BF₄**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

Figure S103: ^1H NMR spectrum of 1-(4-fluorophenyl)-4-phenyl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[8d]OTf**) (400 MHz, DMSO-*d*₆, 298 K).

Figure S104: ^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-phenyl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[8d]OTf**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S105: ^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-phenyl-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[8d]OTf**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

Figure S106: ^1H NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[8e]OTf**) (400 MHz, DMSO-*d*₆, 298 K).

Figure S107: ^{13}C NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[8e]OTf**) (100 MHz, DMSO-*d*₆, 298 K).

Figure S108: ^{19}F NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4*H*-1,2,4-triazol-1-i^{um} trifluoromethanesulfonate (**[8e]OTf**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

1. Reaction Setup



Figure S001: Left: Microwave tube used for 0.5 mmol scale reactions. Right: Schlenk flask with PTFE screw cap used for 1 mmol scale reactions.

2. NMR Spectra for Conversion and Yields

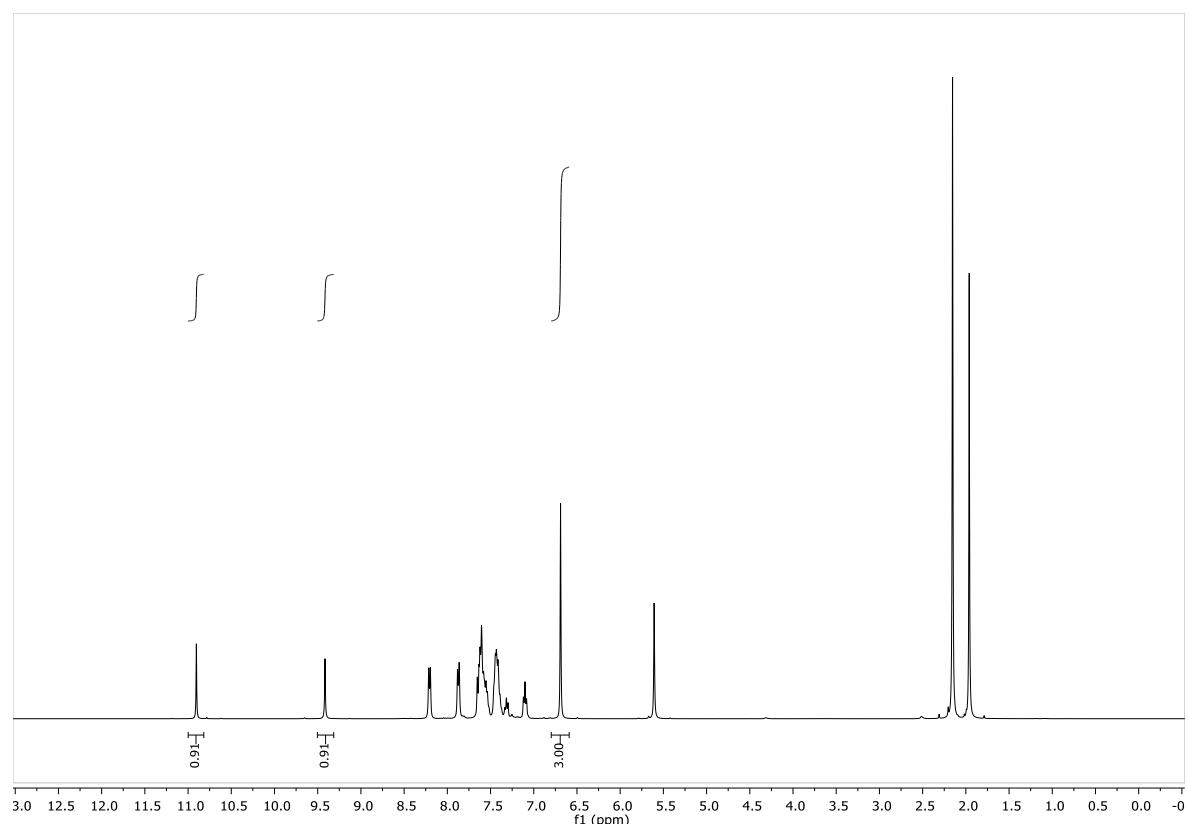


Figure S002: NMR yield of 4-benzyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[2a]BF_4$)

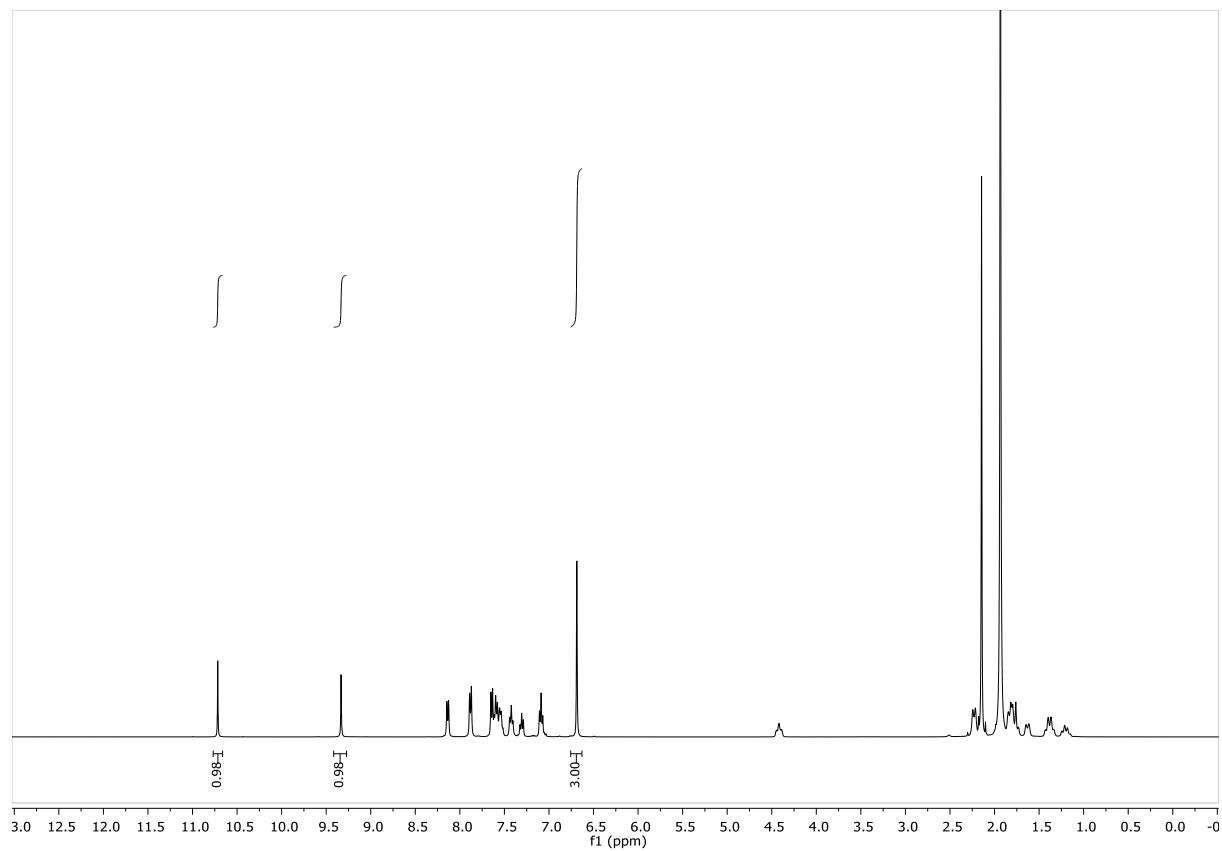


Figure S003: NMR yield of 4-cyclohexyl-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2b]BF₄)

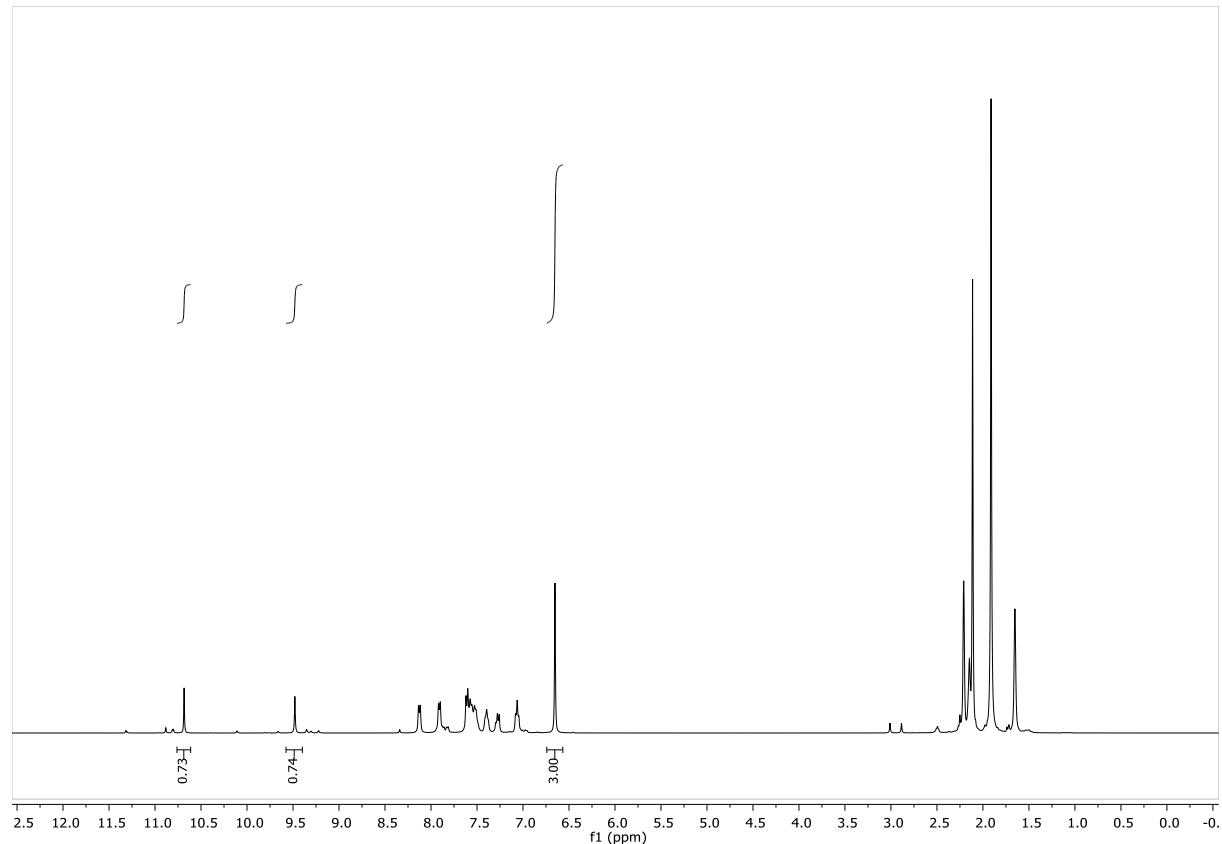


Figure S004: NMR yield of 4-((3s,5s,7s)-adamantan-1-yl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2c]BF₄)

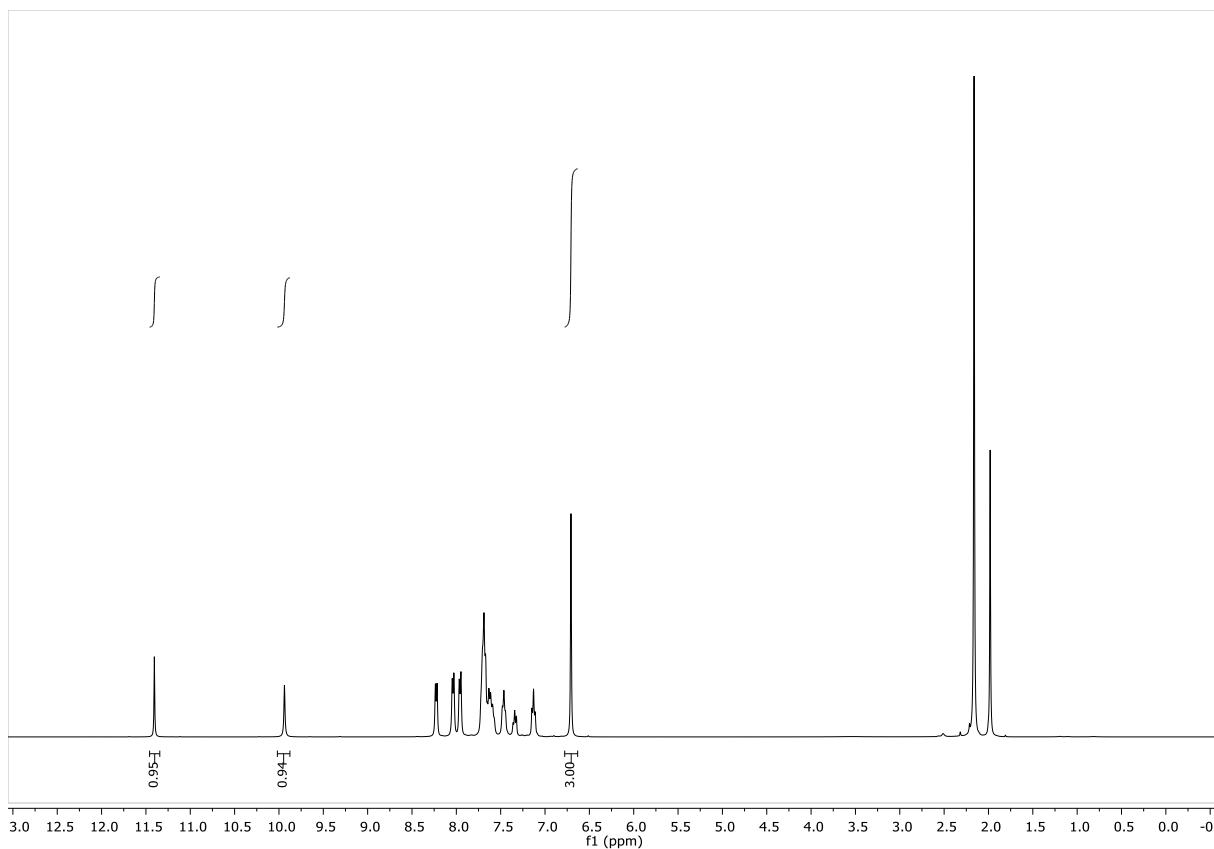


Figure S005: NMR yield of 1,4-diphenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ([2d]BF₄)

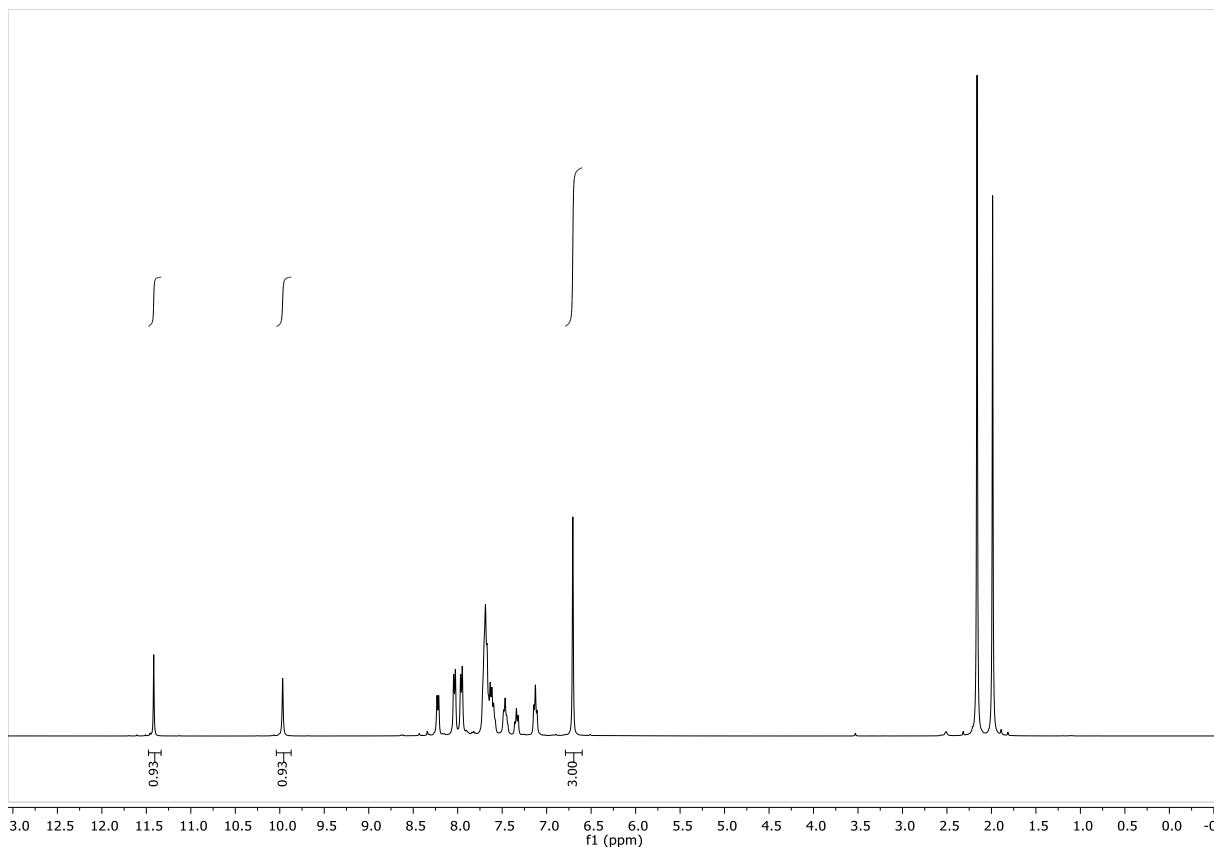


Figure S006: NMR yield of 1,4-diphenyl-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate ([2d]OTf)

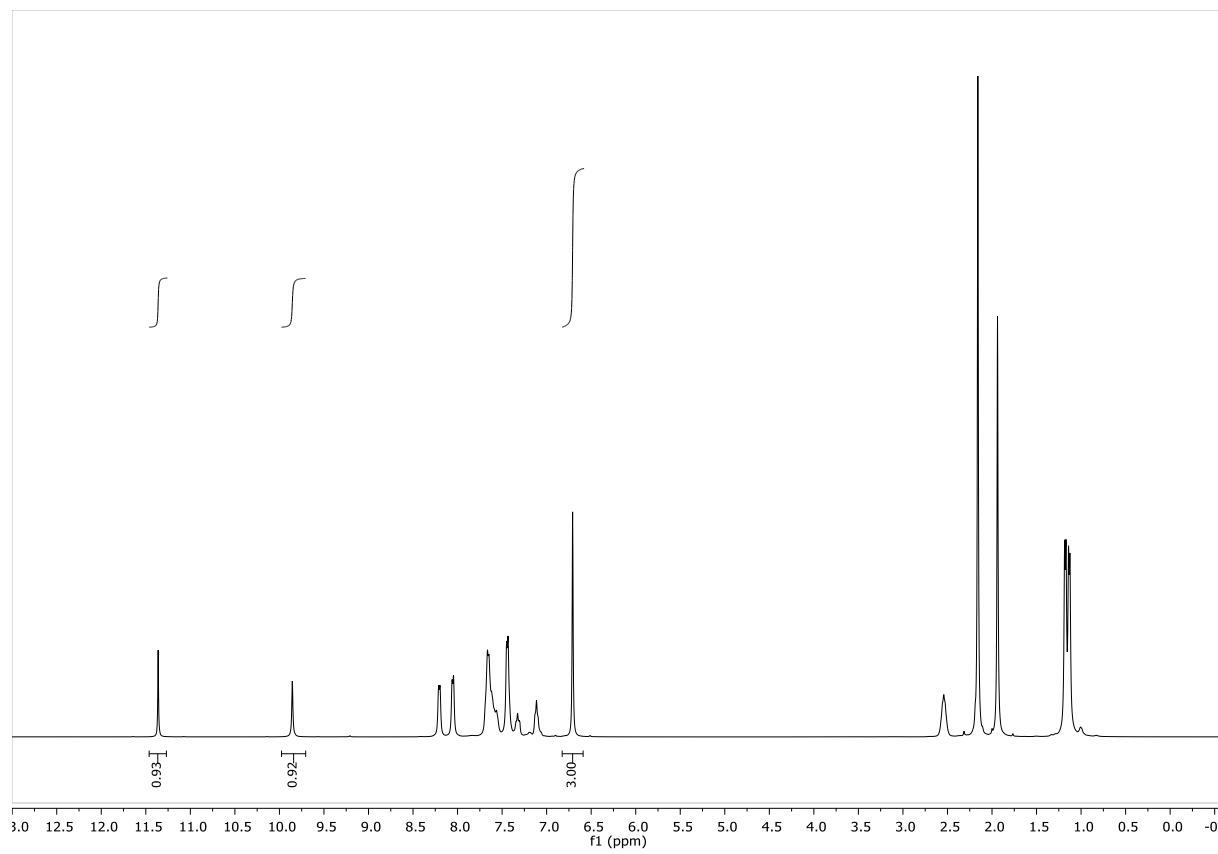


Figure S007: NMR yield of 4-(2,6-diisopropylphenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2e]\text{BF}_4$)

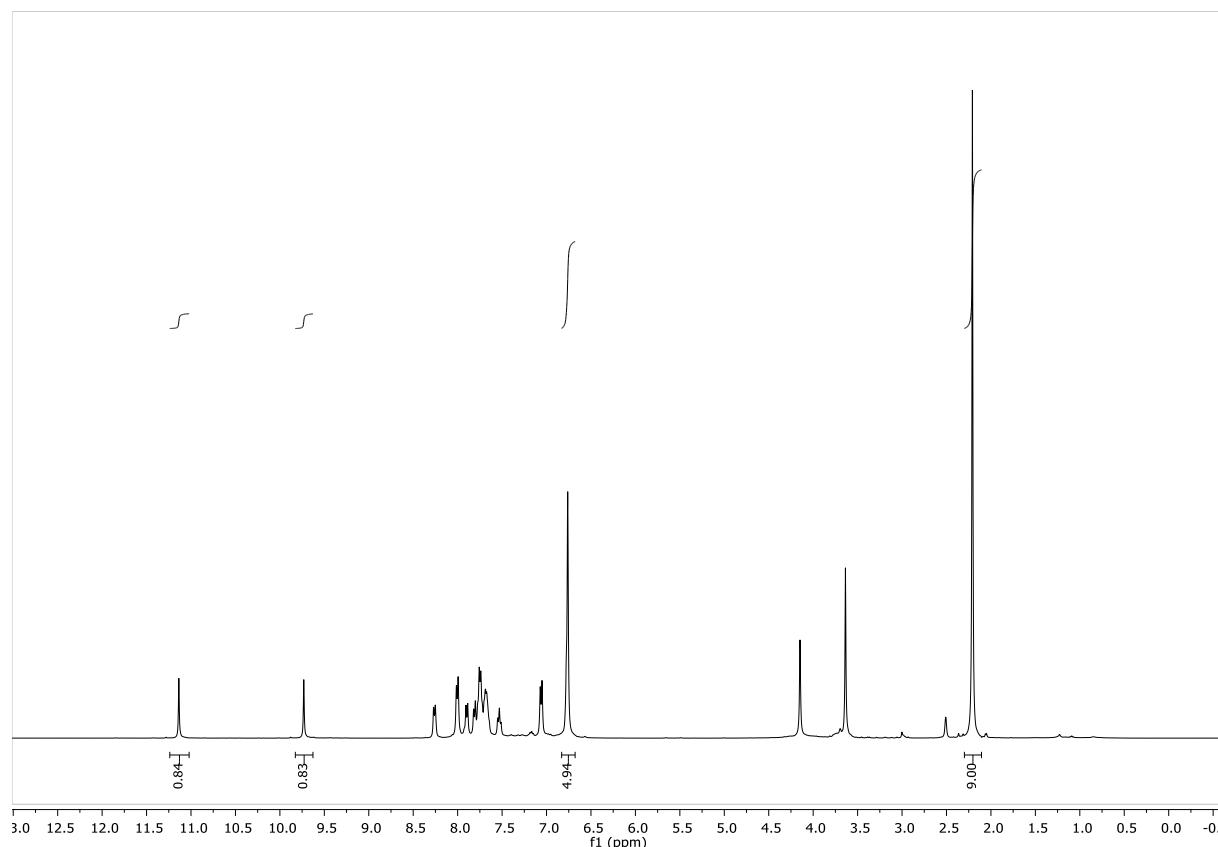


Figure S008: NMR yield of 1-phenyl-4-(2-((4-methoxybenzyl)thio)phenyl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2f]BF₄)

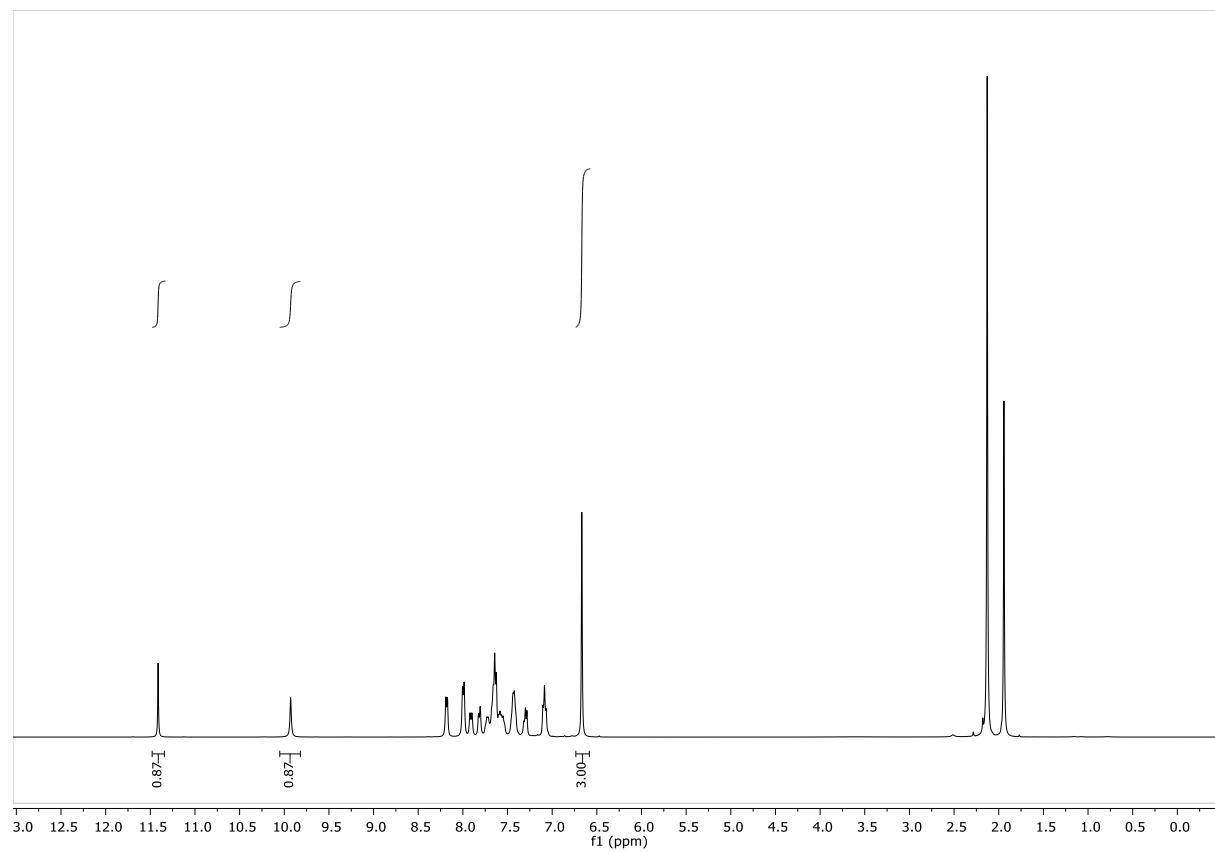


Figure S009: NMR yield of 4-(2-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2g]BF₄)

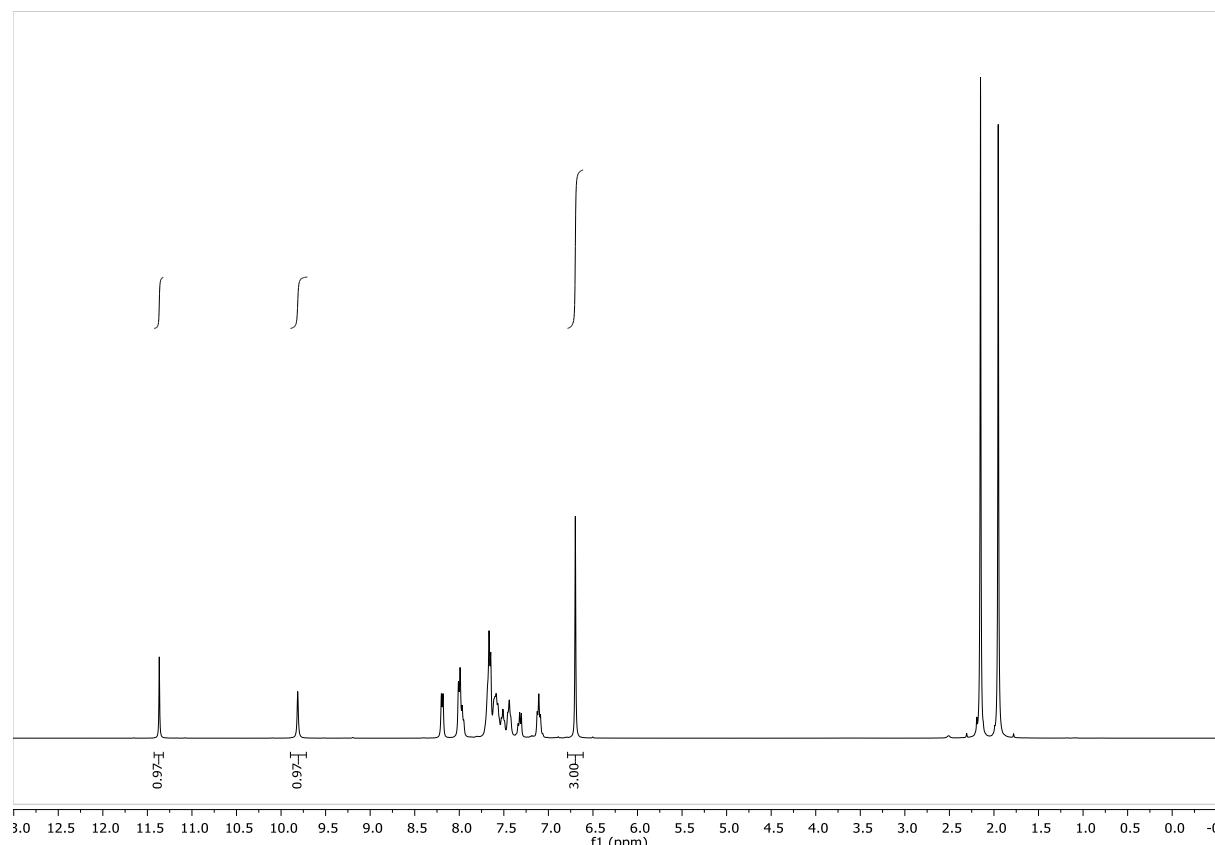


Figure S010: NMR yield of 4-(3-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2h]BF₄)

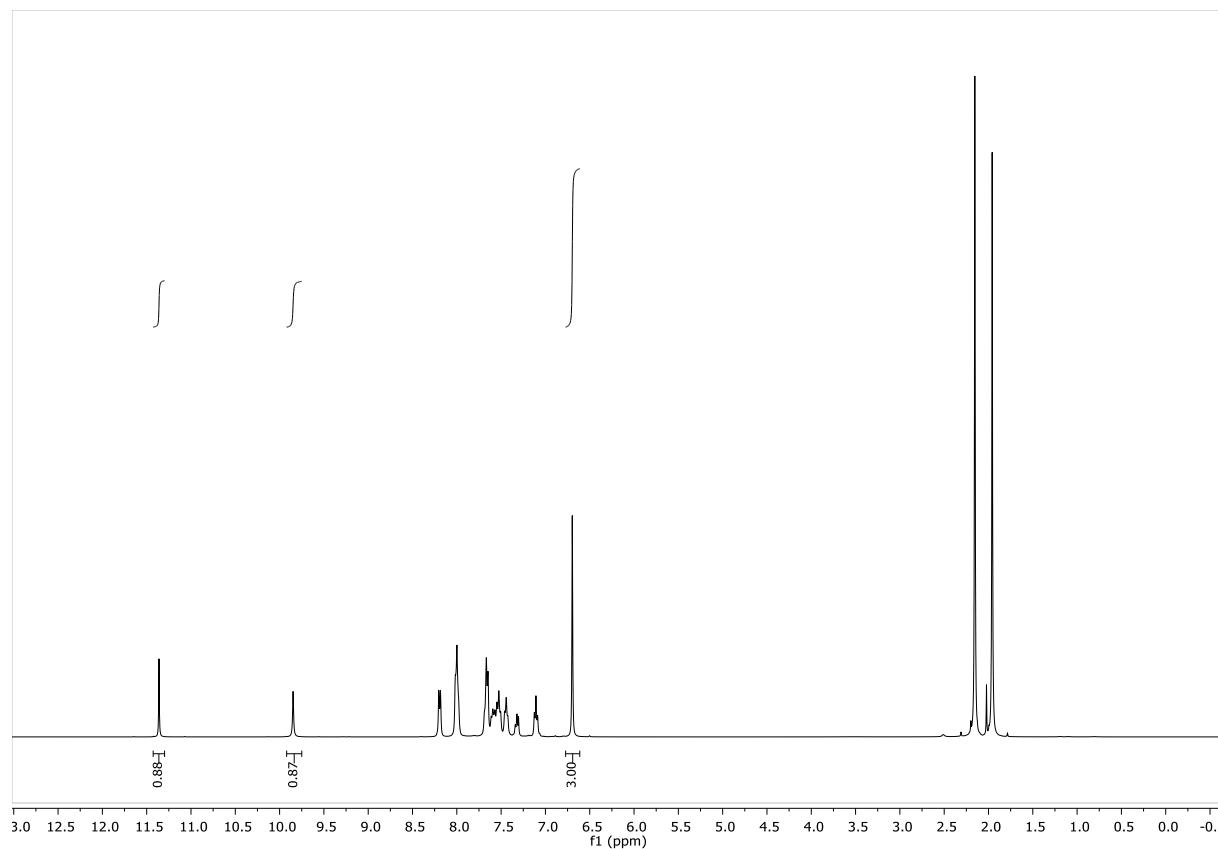


Figure S011: NMR yield of 4-(4-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2*i*]BF₄)

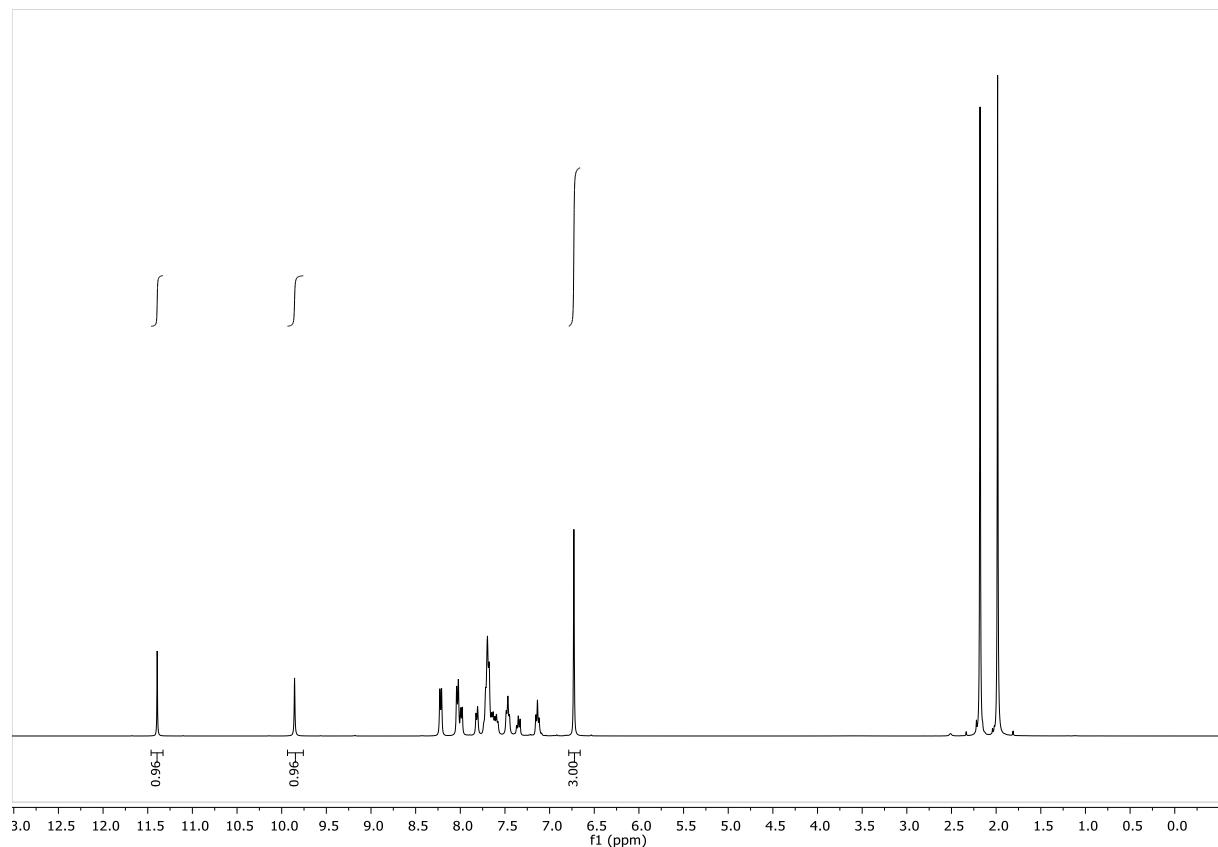


Figure S012: NMR yield of 4-(2-chlorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2*j*]BF₄)

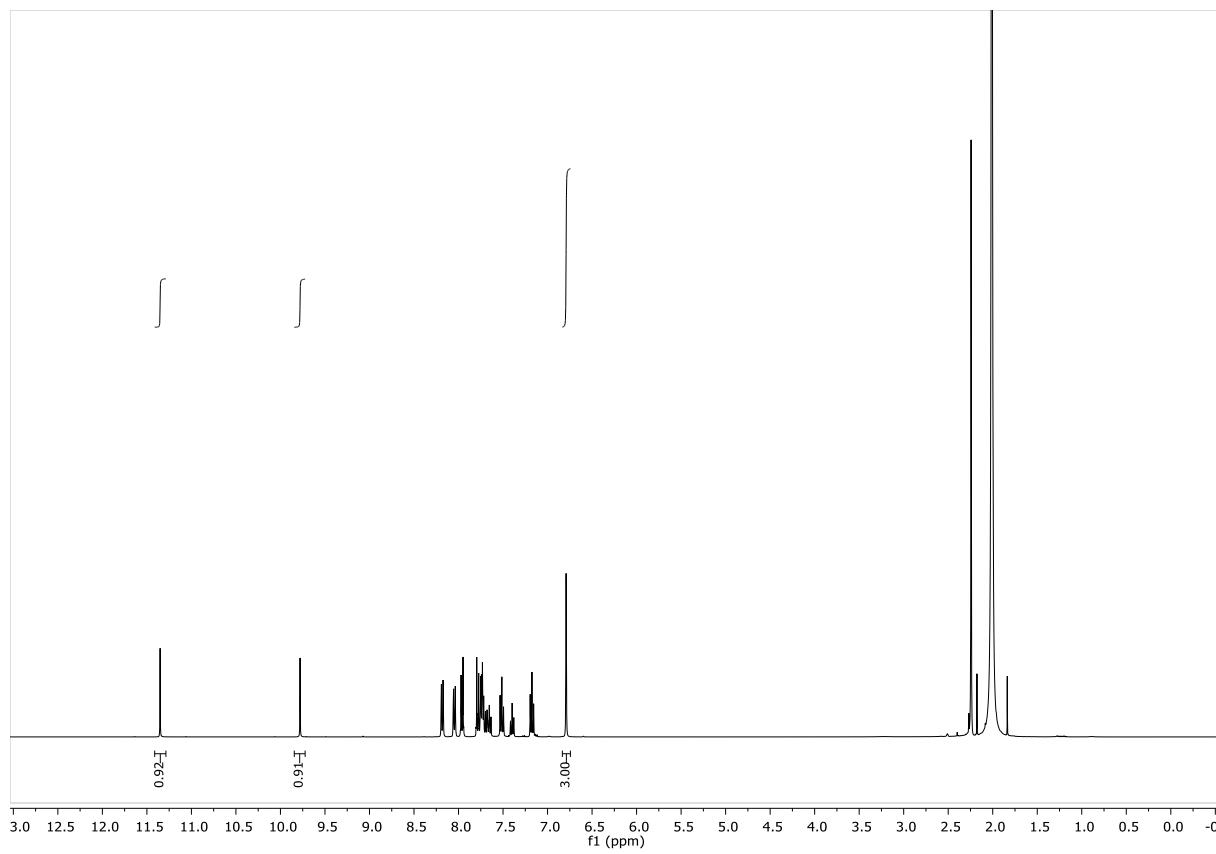


Figure S013: NMR yield of 4-(4-chlorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2k]BF_4$)

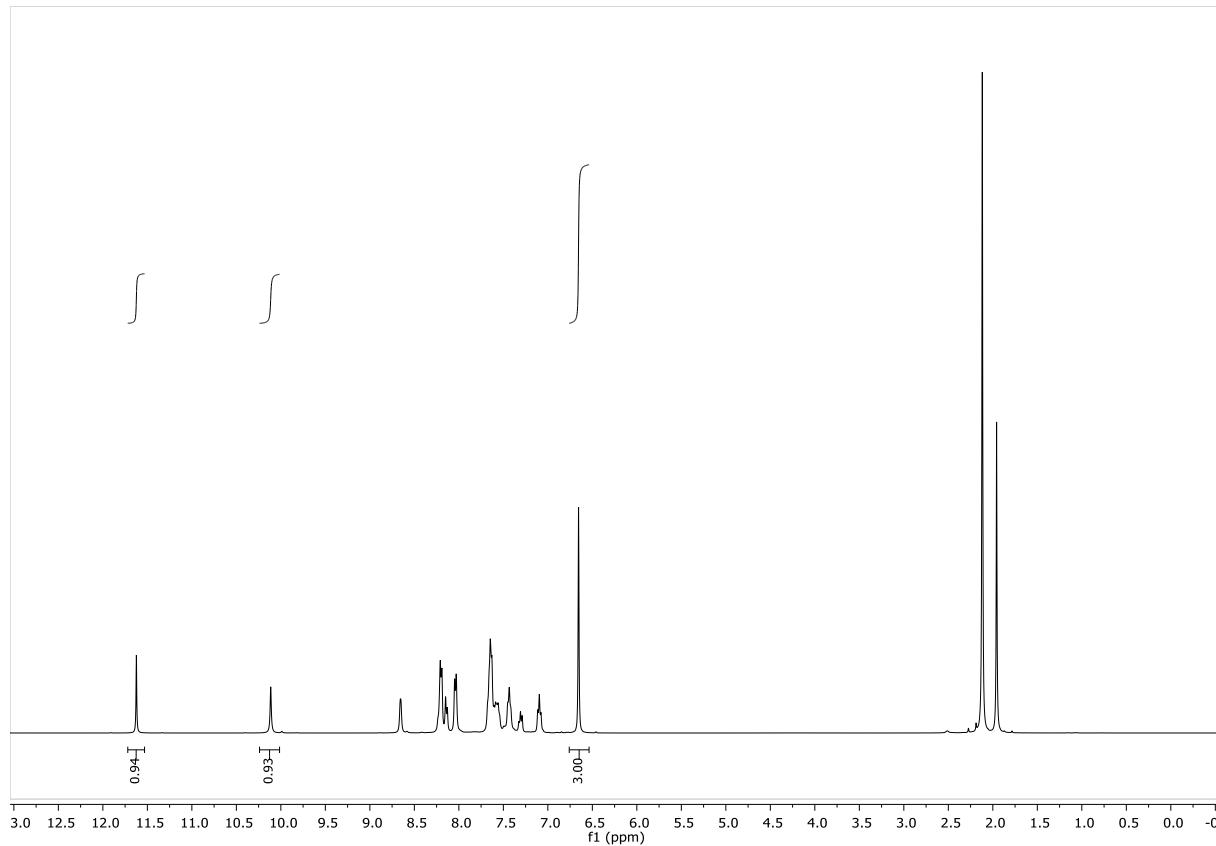


Figure S014: NMR yield of 1-phenyl-4-(pyridin-2-yl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2l]BF_4$)

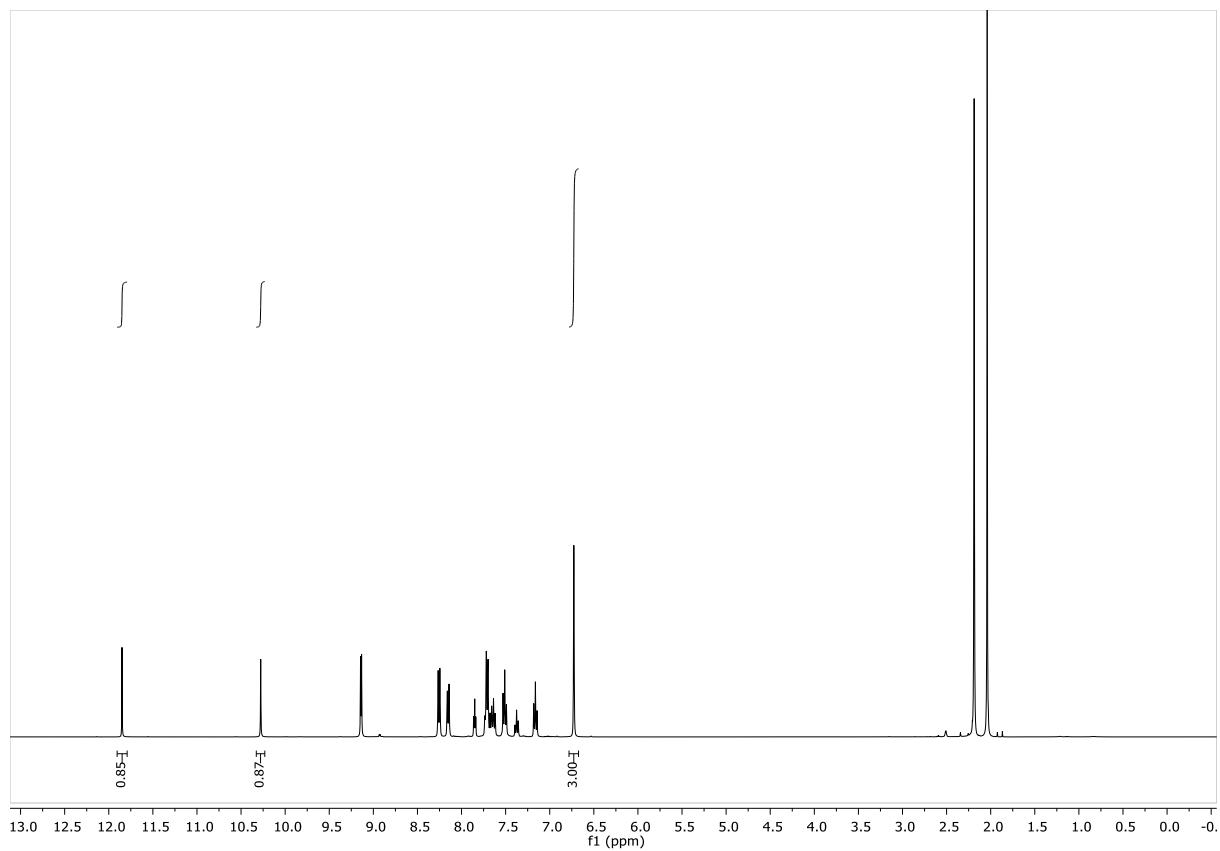


Figure S015: NMR yield of 1-phenyl-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2m]BF₄)

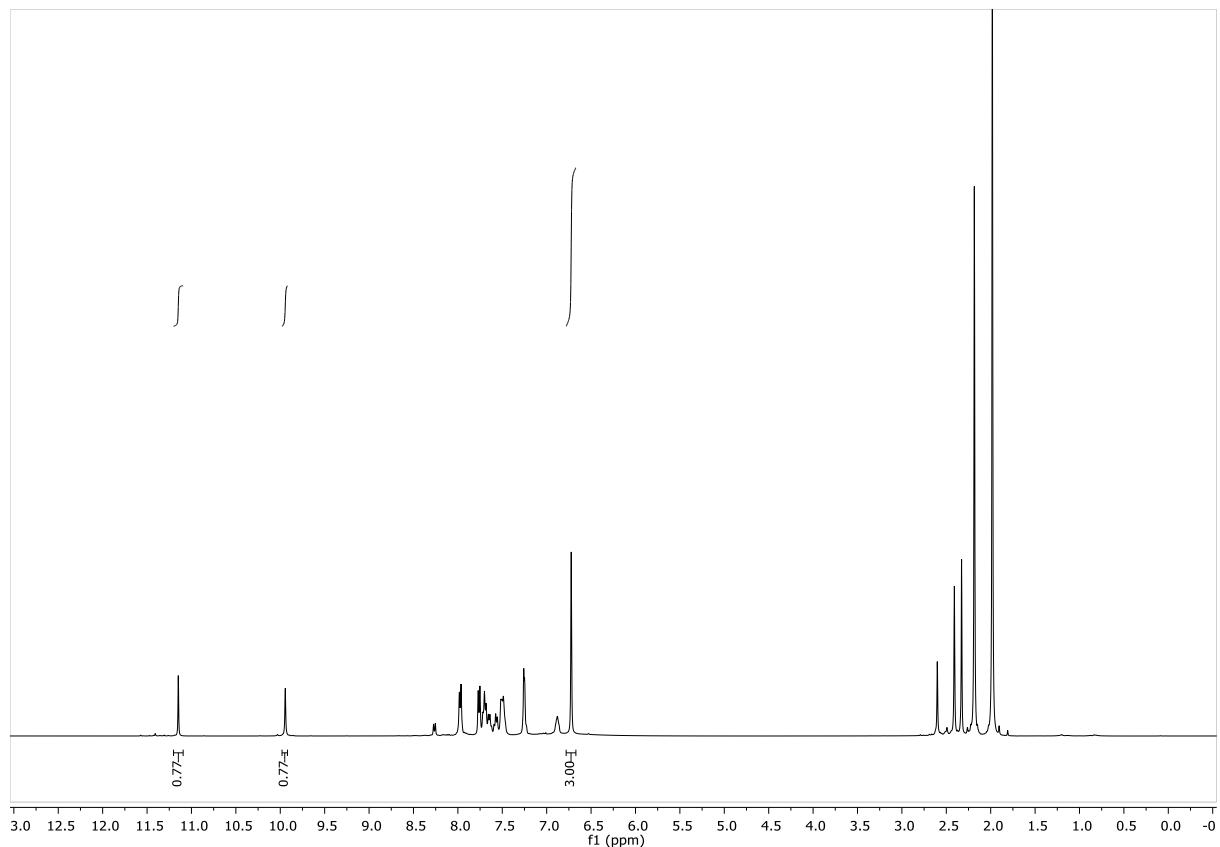


Figure S016: NMR yield of 4-phenyl-1-(o-tolyl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([3d]OTf)

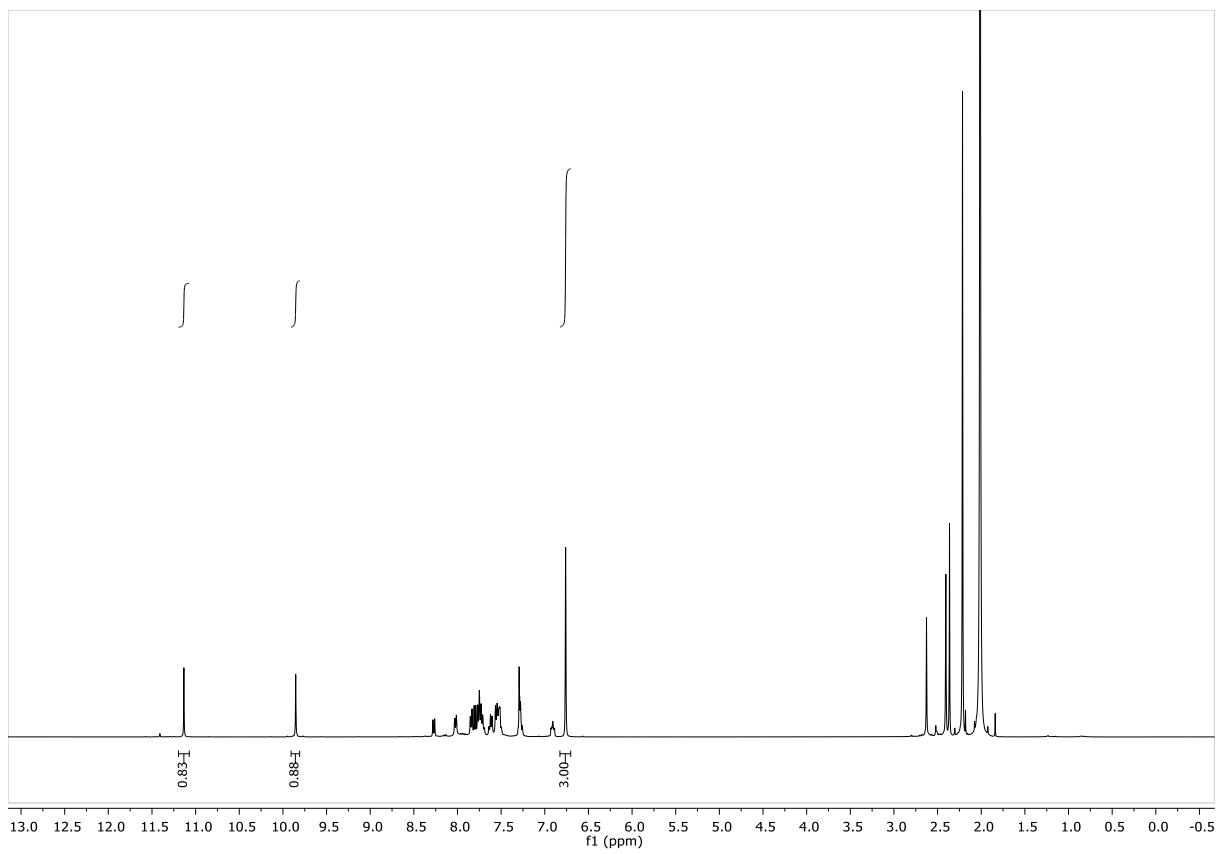


Figure S017: NMR yield of 4-(2-chlorophenyl)-1-(o-tolyl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([3j]OTf)

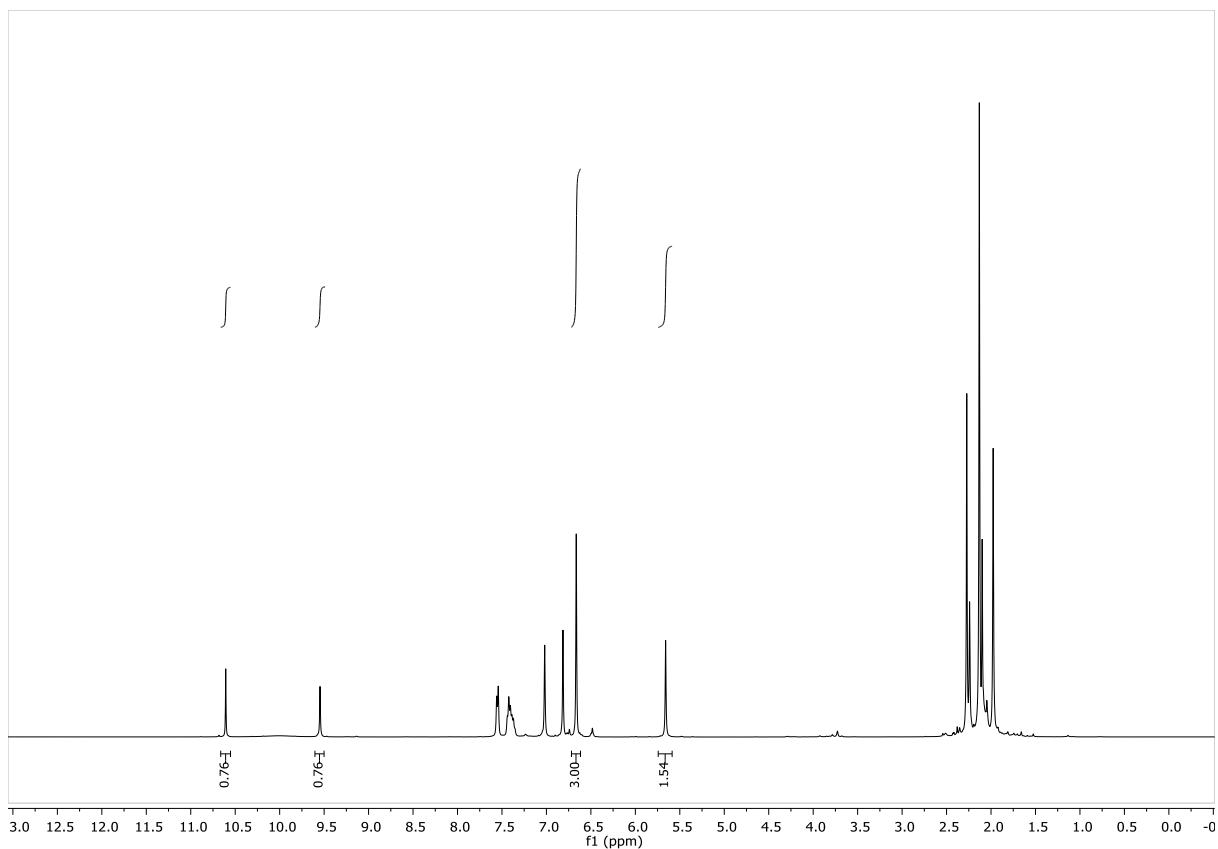


Figure S018: NMR yield of 4-benzyl-1-mesityl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4a]OTf)

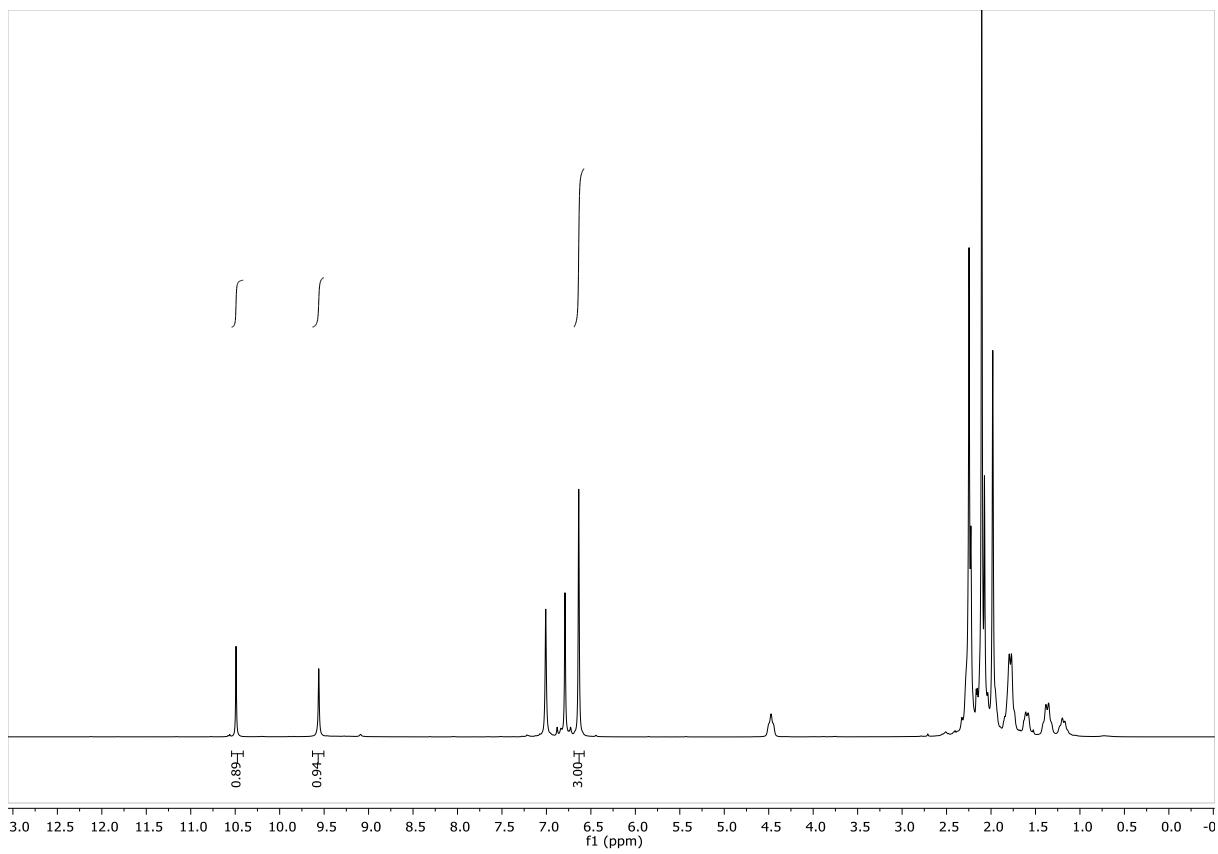


Figure S019: NMR yield of 4-cyclohexyl-1-mesityl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4b]OTf)

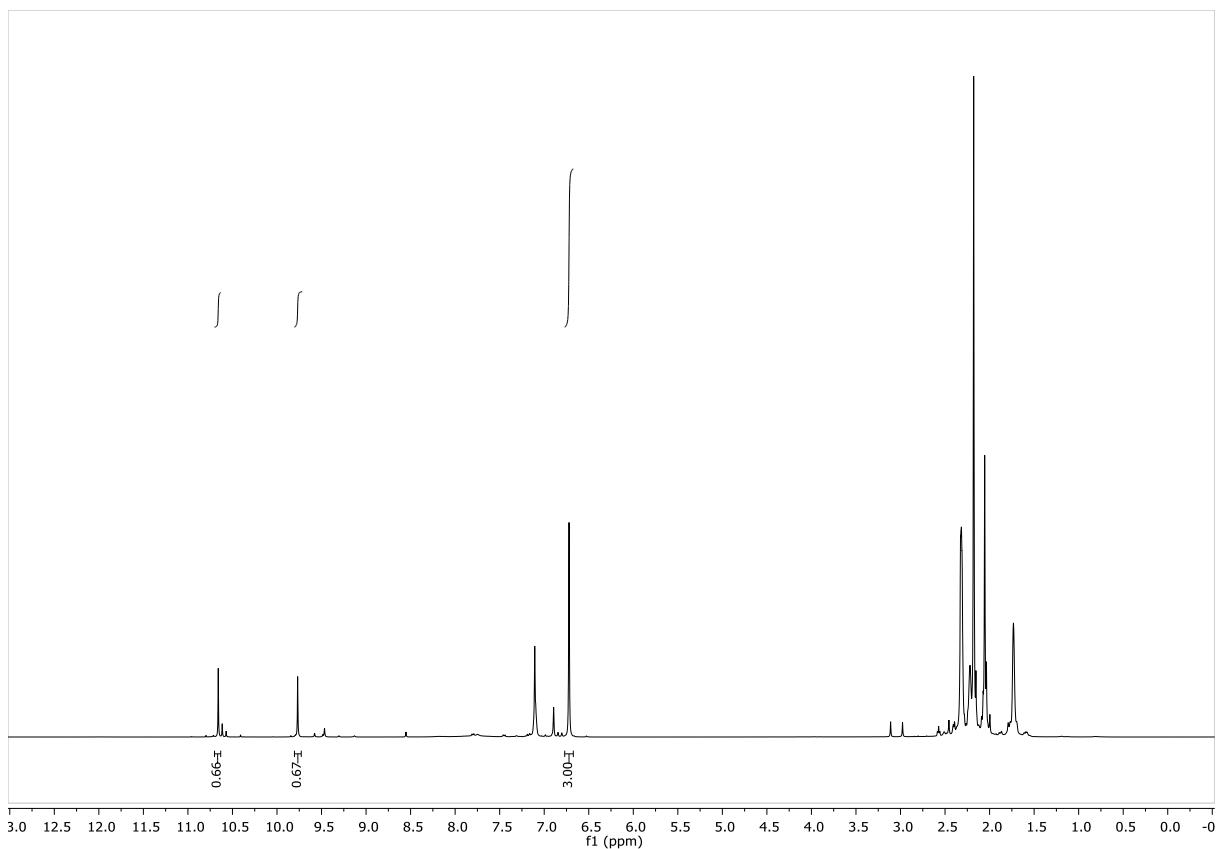


Figure S020: NMR yield of 4-((3*s*,5*s*,7*s*)-adamantan-1-yl)-1-mesityl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4c]OTf)

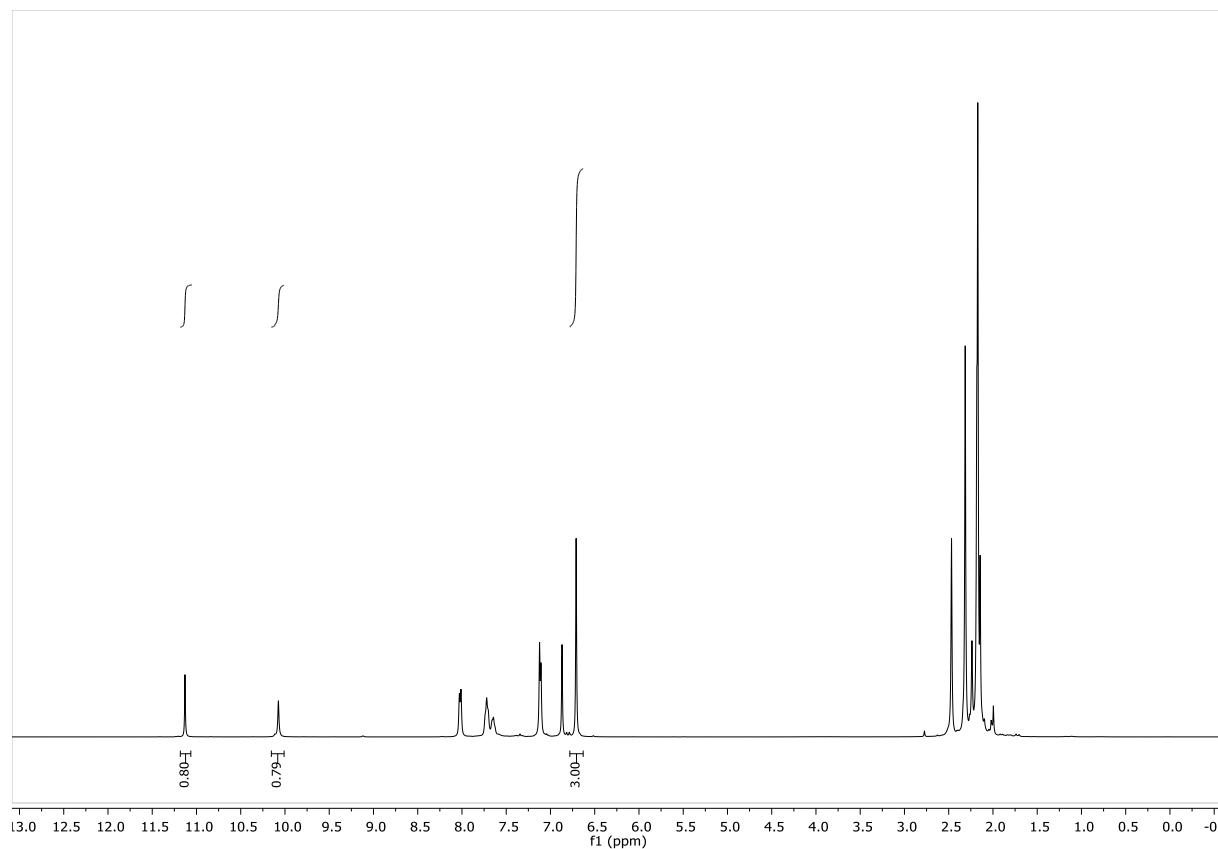


Figure S021: NMR yield of 1-mesityl-4-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[4d]BF_4$)

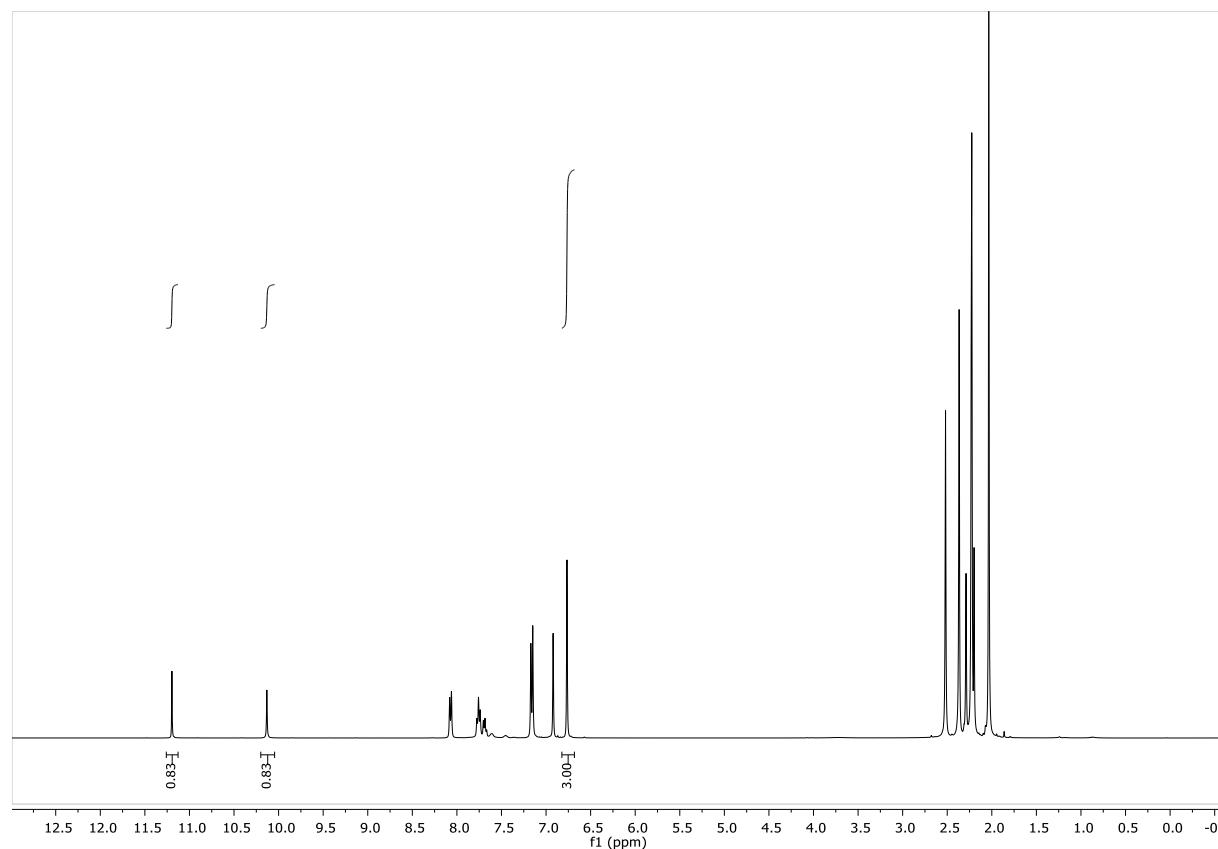


Figure S022: NMR yield of 1-mesityl-4-phenyl-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate ($[4d]OTf$)

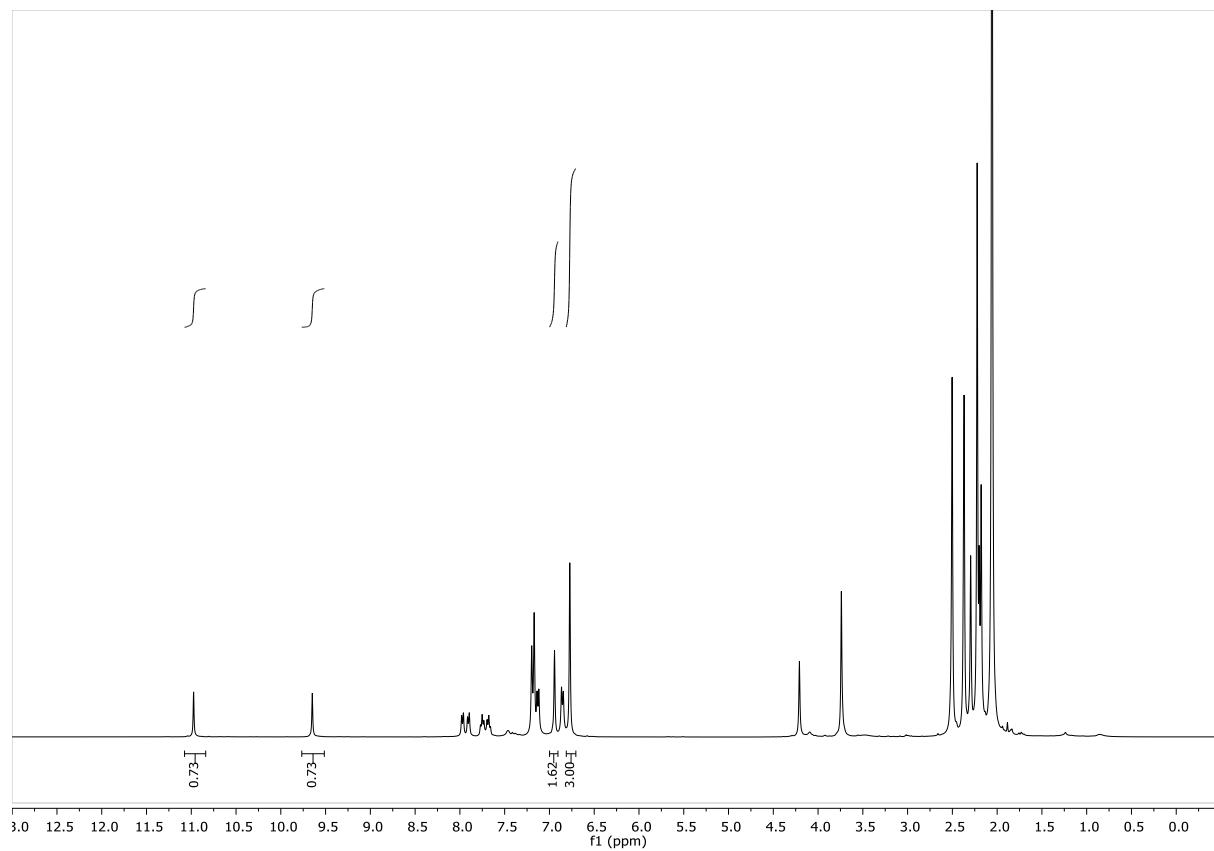


Figure S023: NMR yield of 1-mesityl-4-(2-((4-methoxybenzyl)thio)phenyl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4f]OTf)

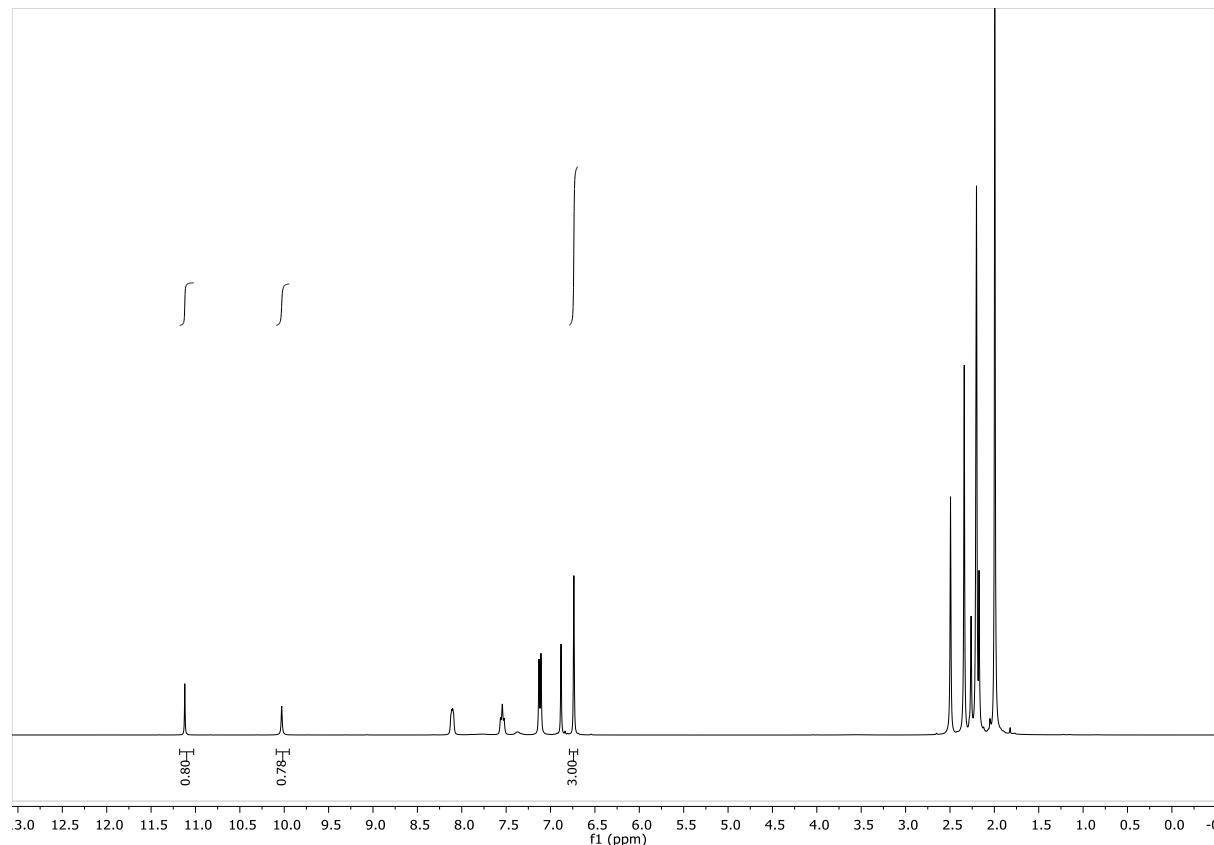


Figure S024: NMR yield of 4-(4-fluorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4i]OTf)

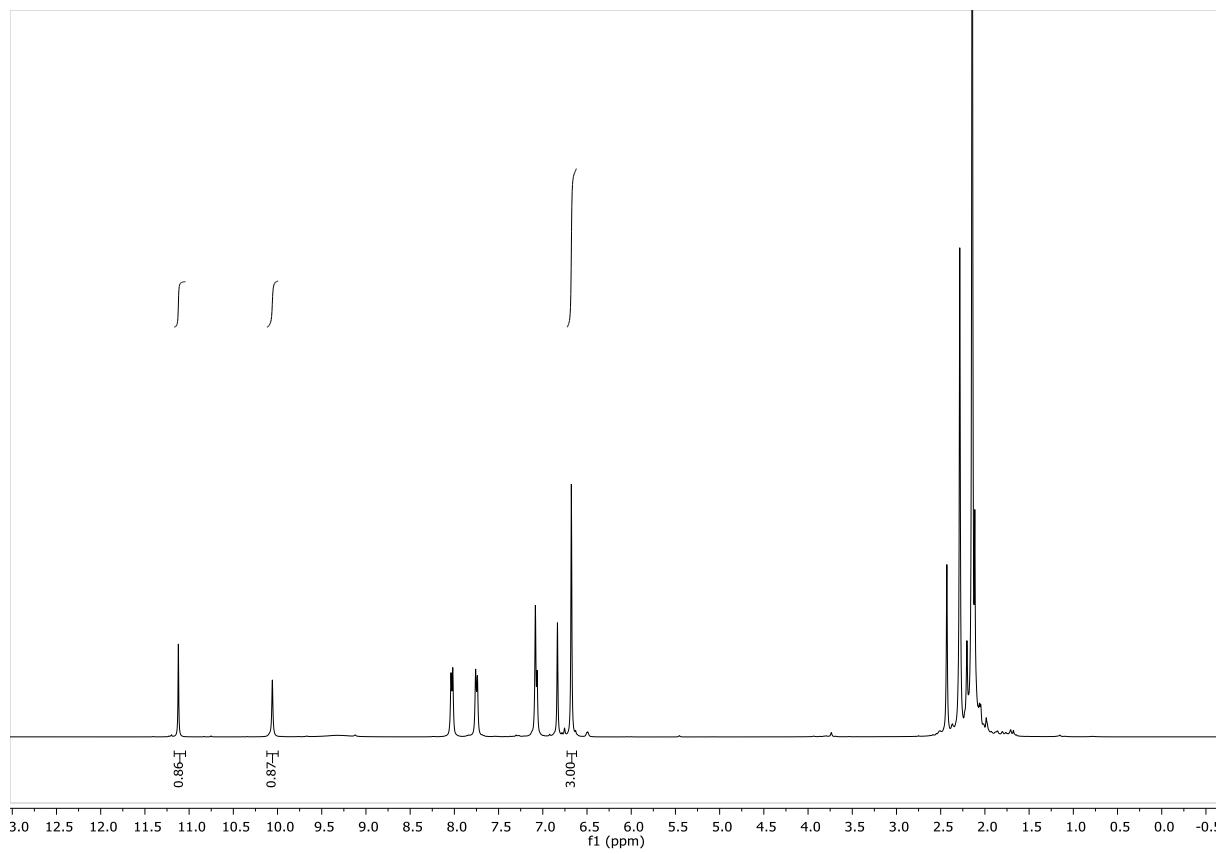


Figure S025: NMR yield of 4-(4-chlorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate ([4k]OTf)

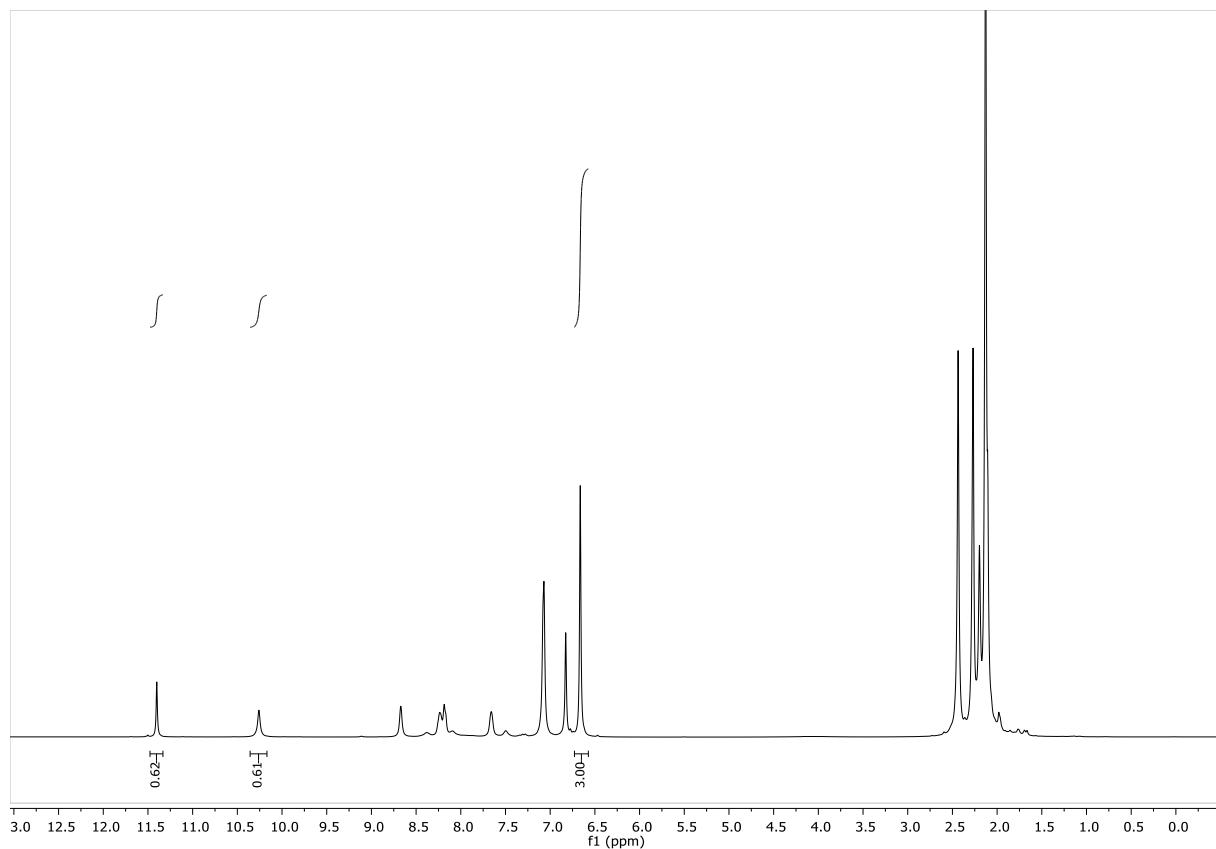


Figure S026: NMR yield of 1-mesityl-4-(pyridin-2-yl)-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate ([4l]OTf)

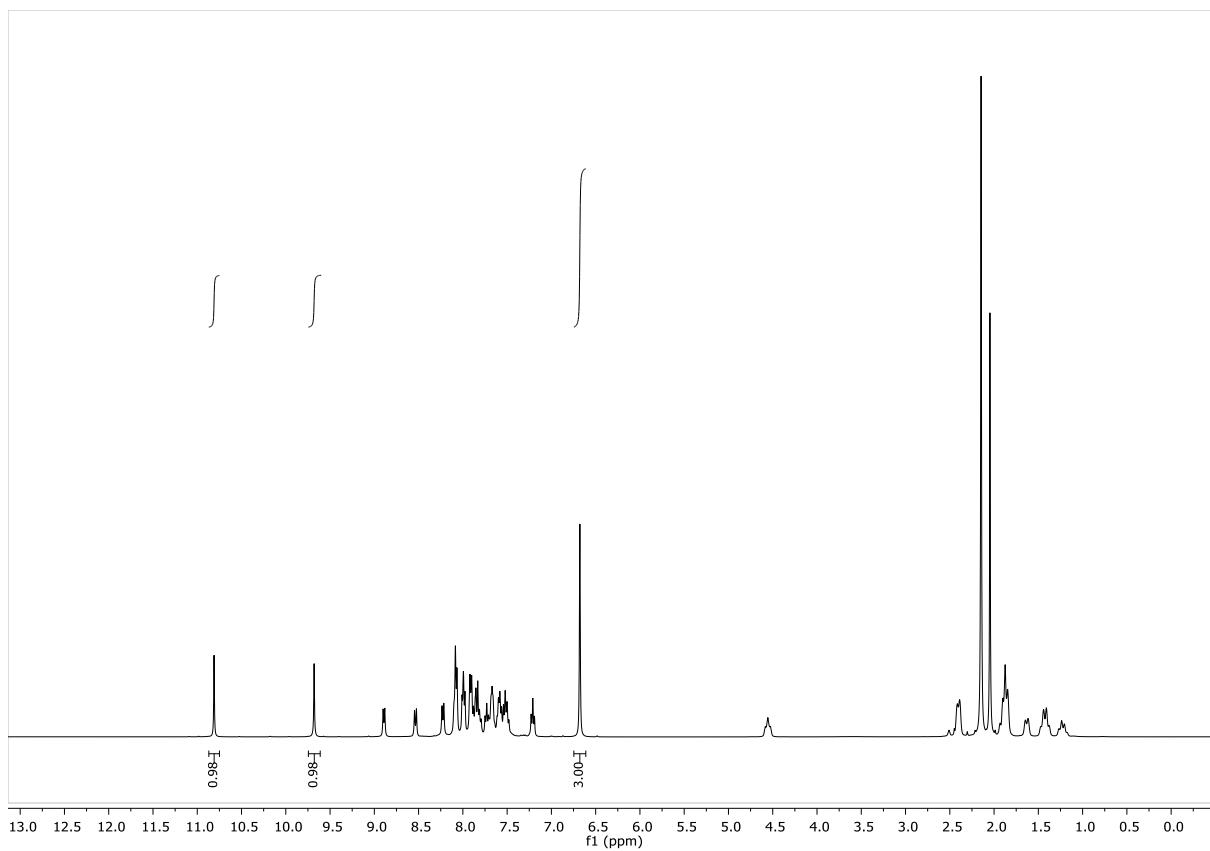


Figure S027: NMR yield of 4-cyclohexyl-1-(naphthalen-1-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[5b]BF_4$)

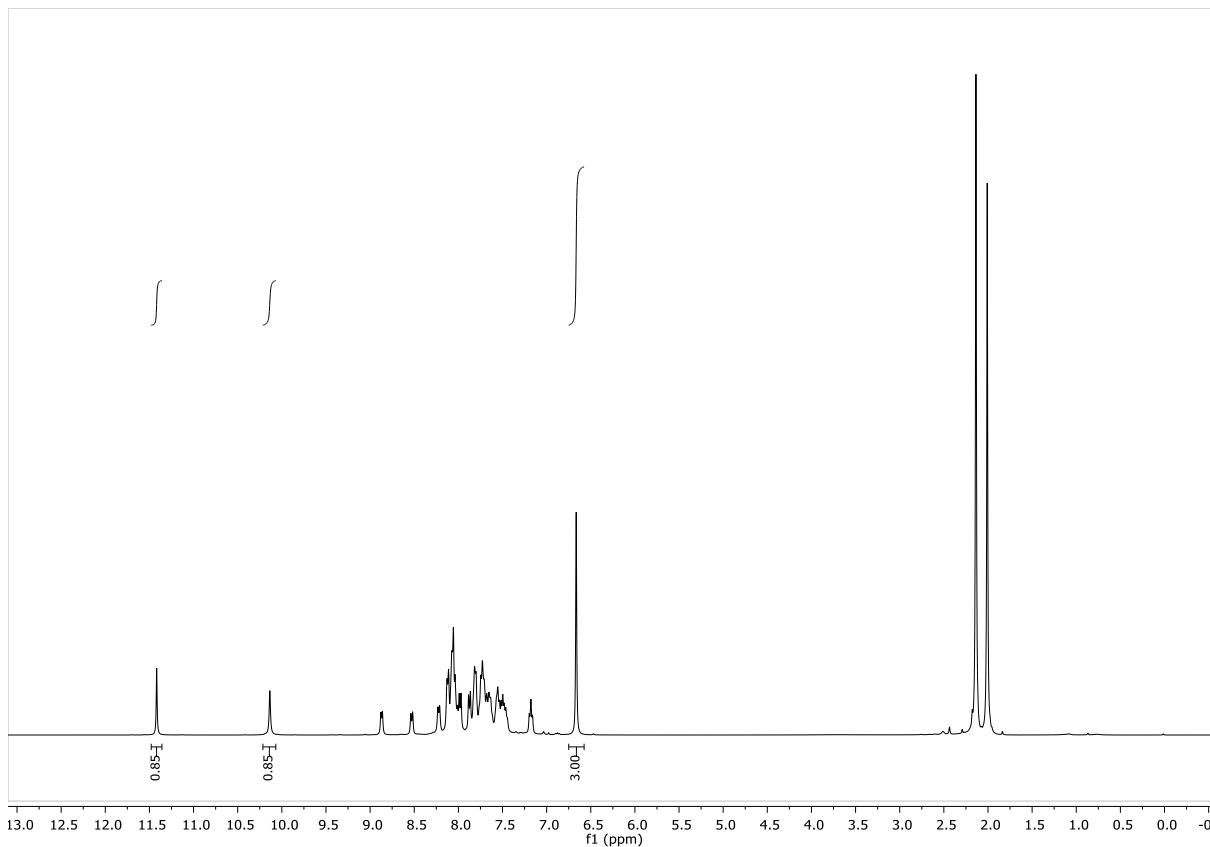


Figure S028: NMR yield of 1-(naphthalen-1-yl)-4-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[5d]BF_4$)

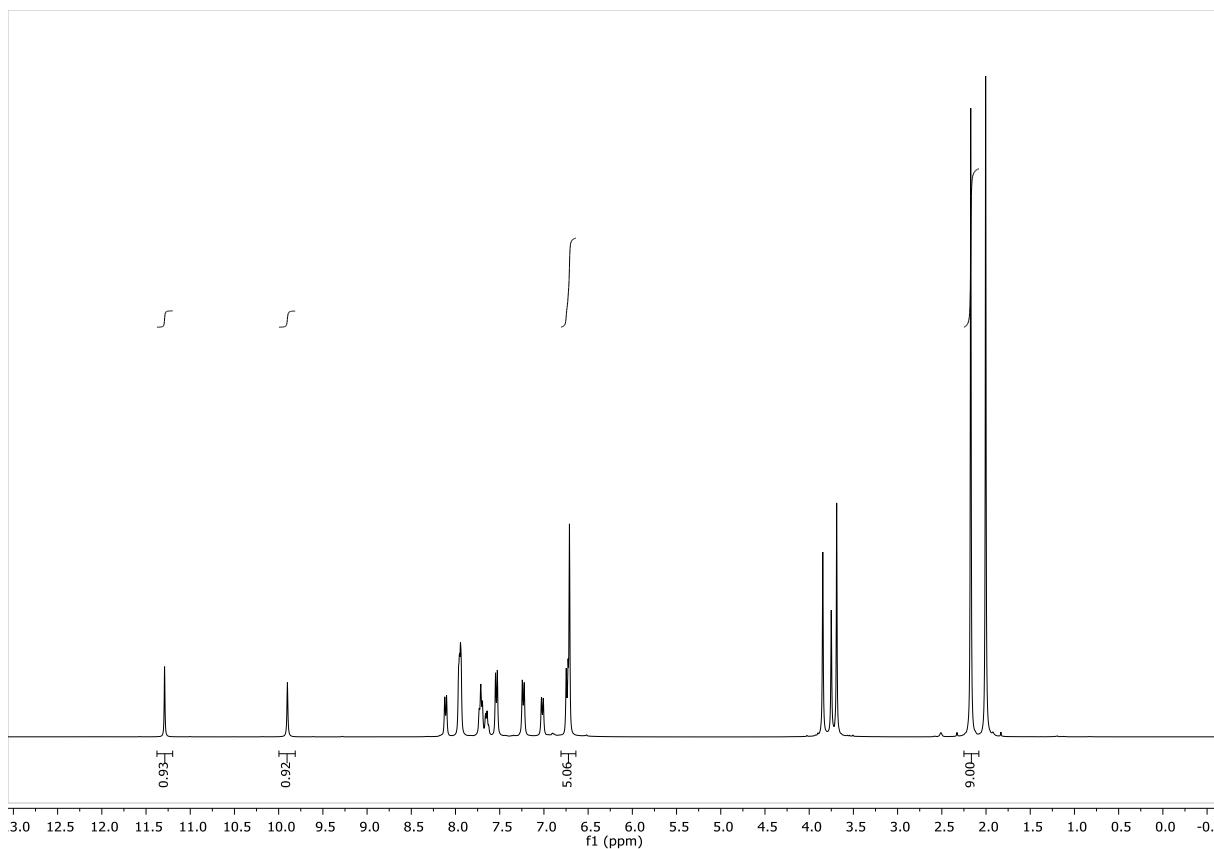


Figure S029: NMR yield of 1-(4-methoxyphenyl)-4-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([6d]BF₄)

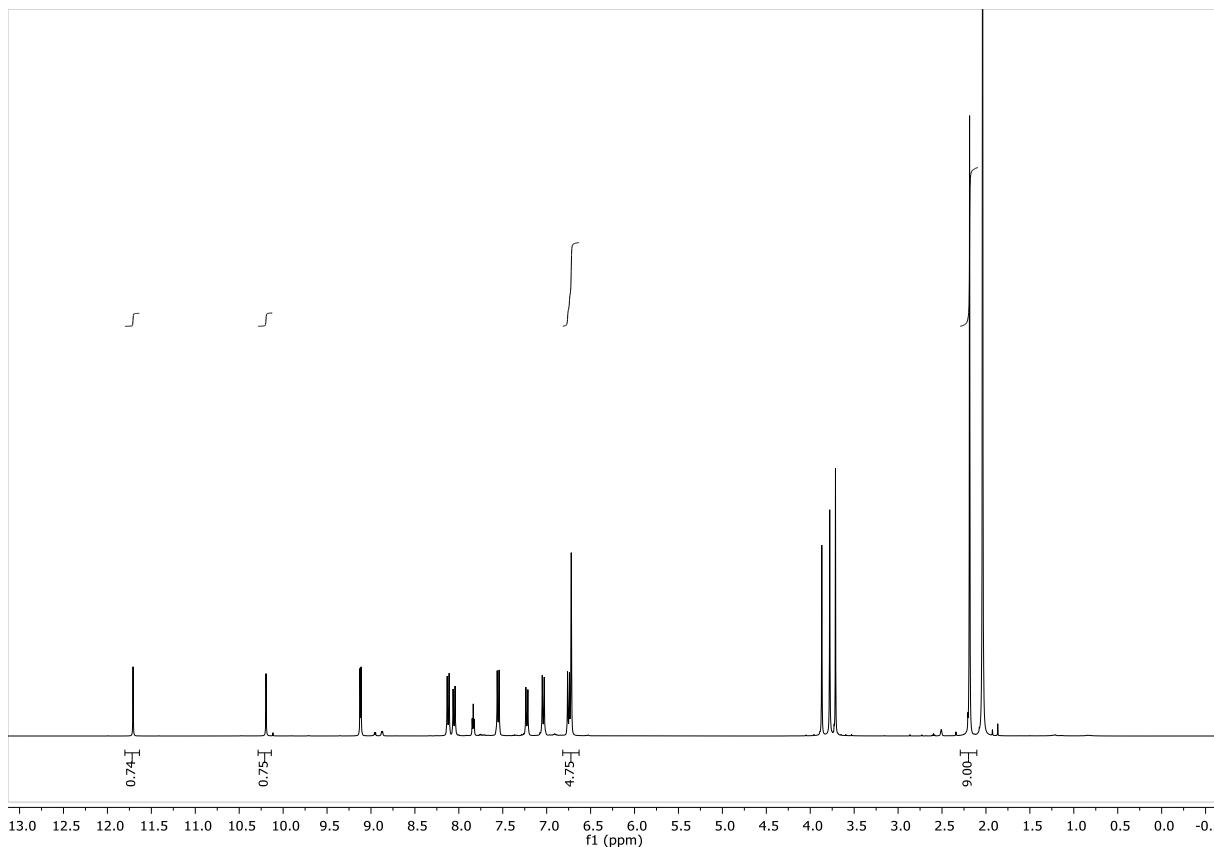


Figure S030: NMR yield of 1-(4-methoxyphenyl)-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([6m]BF₄)

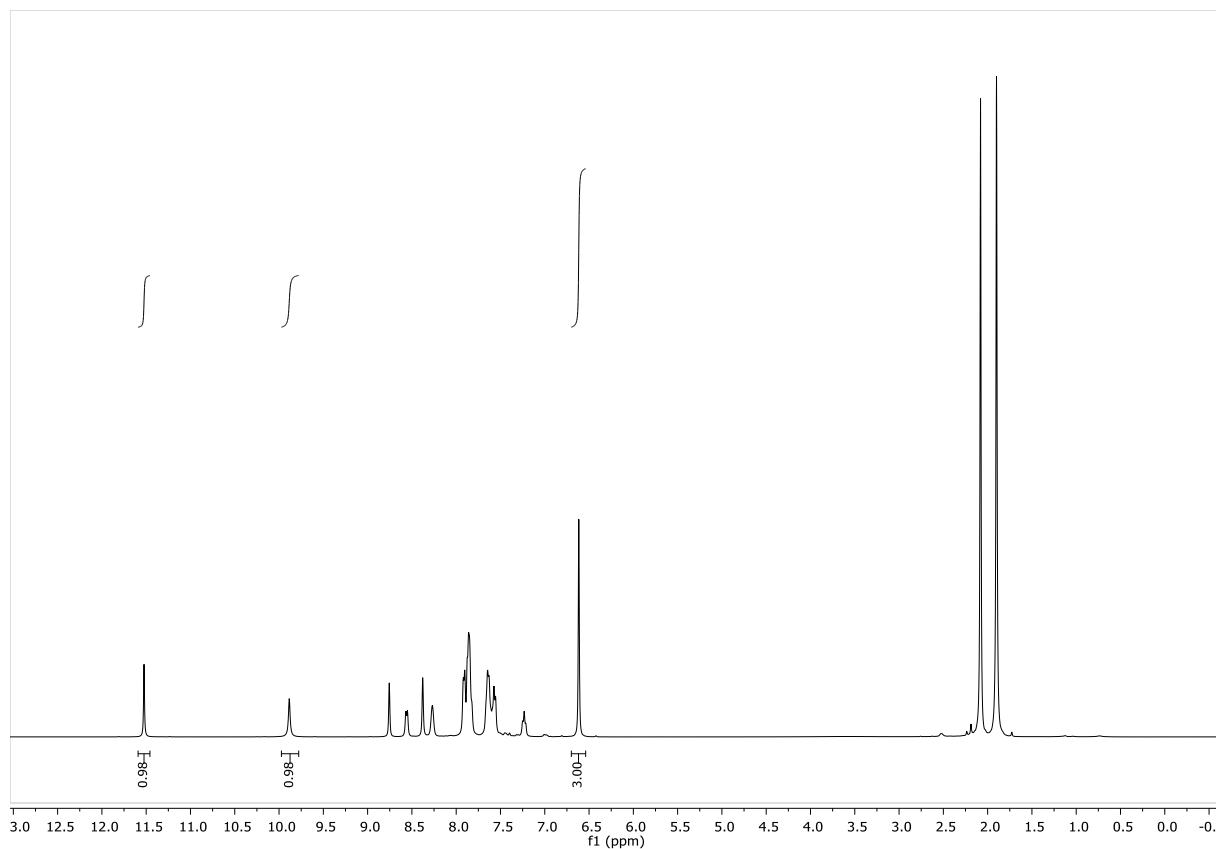


Figure S031: NMR yield of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[7d]BF_4$)

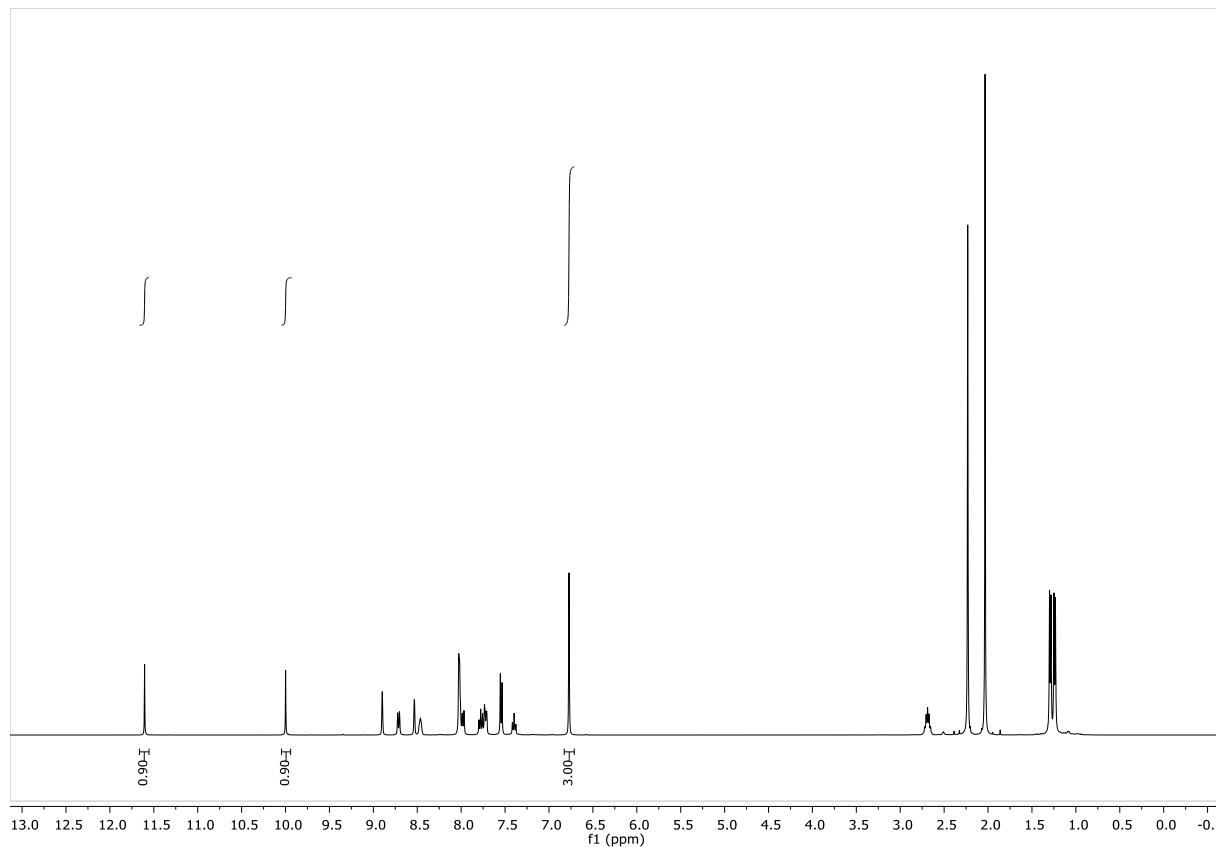


Figure S032: NMR yield of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[7e]BF_4$)

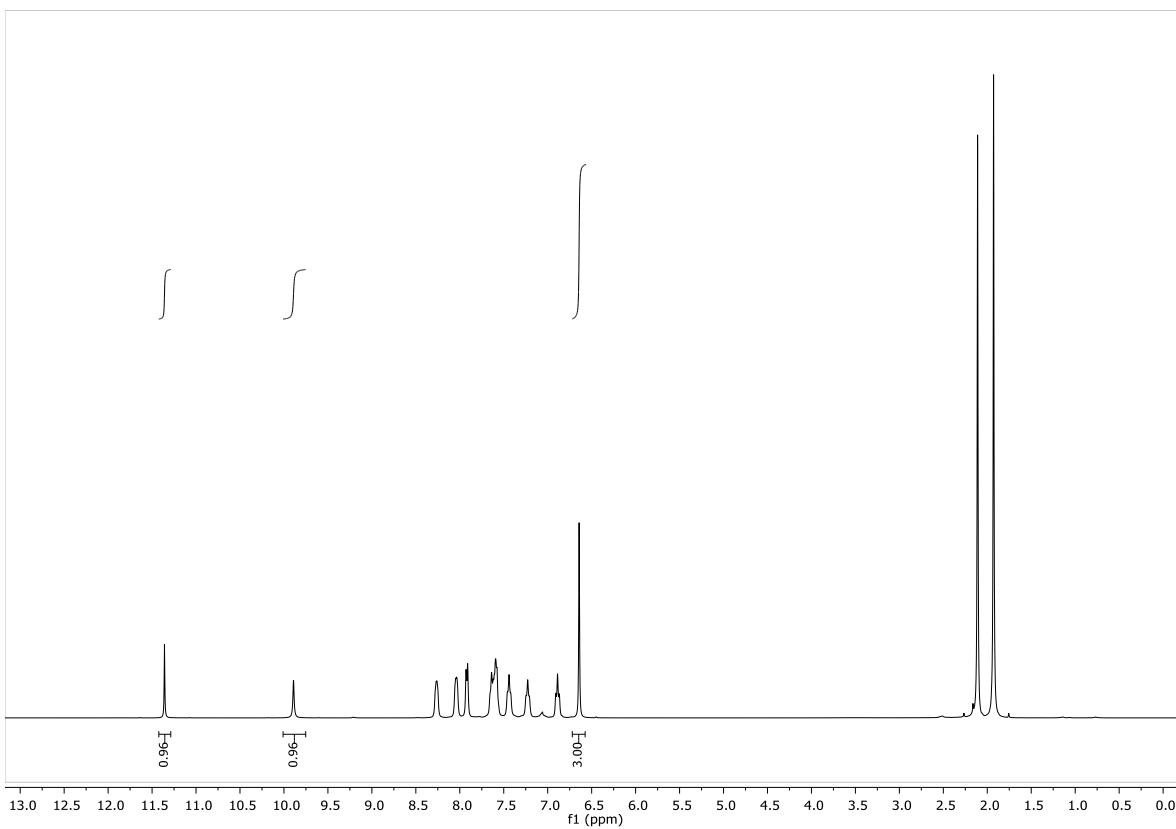


Figure S033: NMR yield of 1-(4-fluorophenyl)-4-phenyl-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate ([8d]OTf)

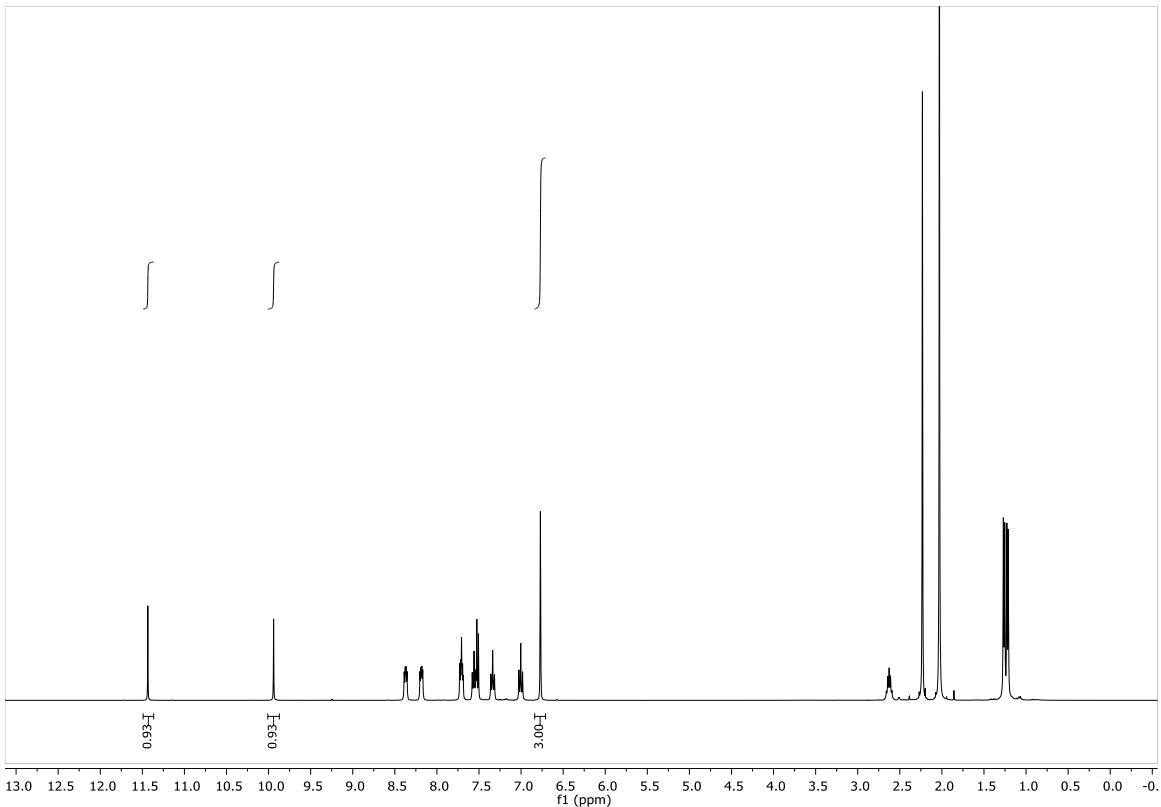


Figure S034: NMR yield of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate ([8e]OTf)

3. NMR Spectra of Isolated Triazolium Salts

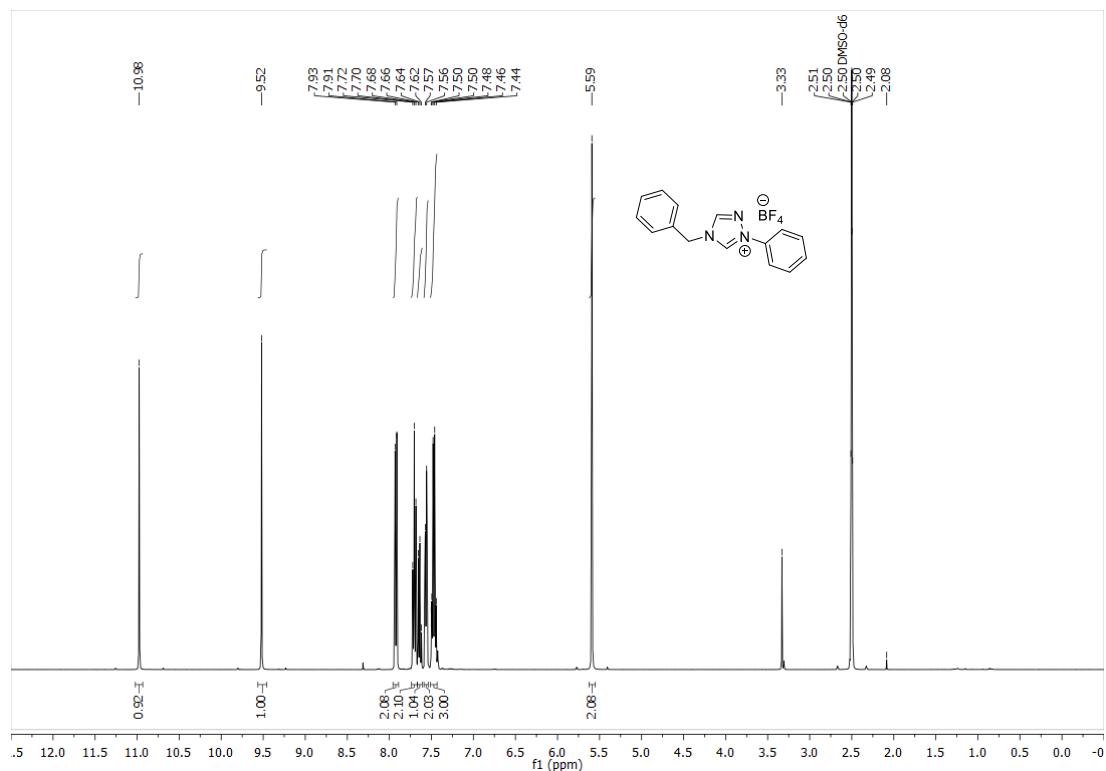


Figure S035: ¹H NMR spectrum of 4-benzyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ([2a]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

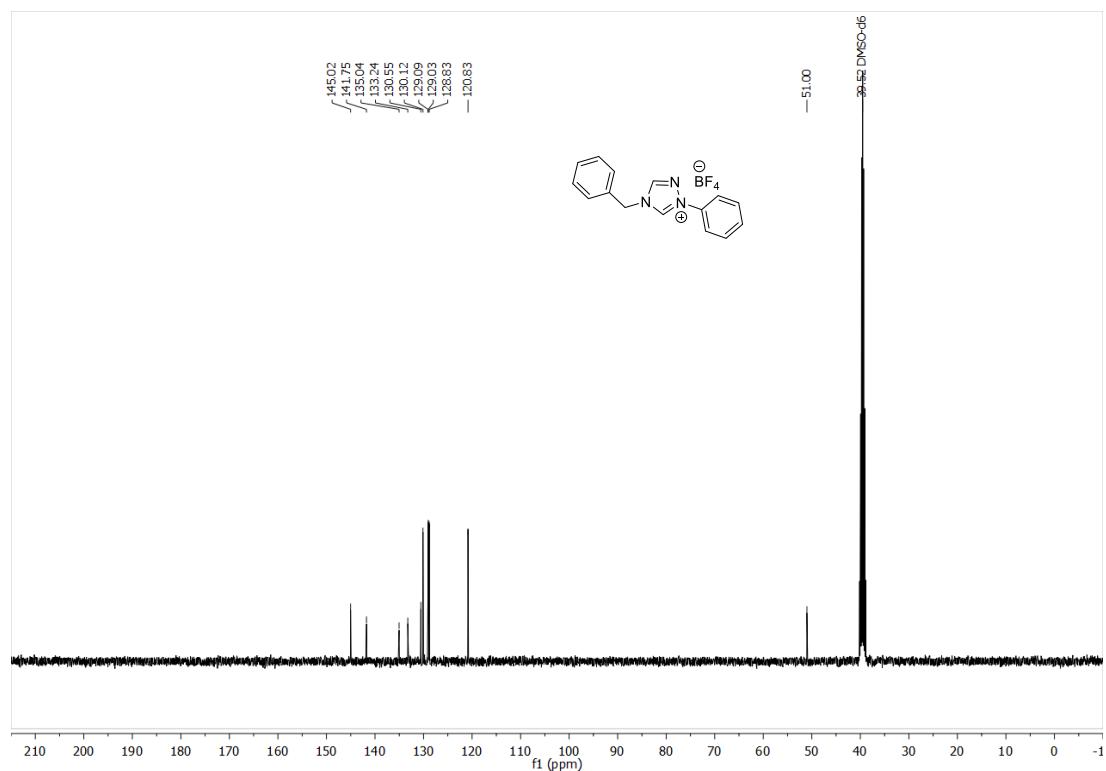


Figure S036: ¹³C NMR spectrum of 4-benzyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ([2a]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

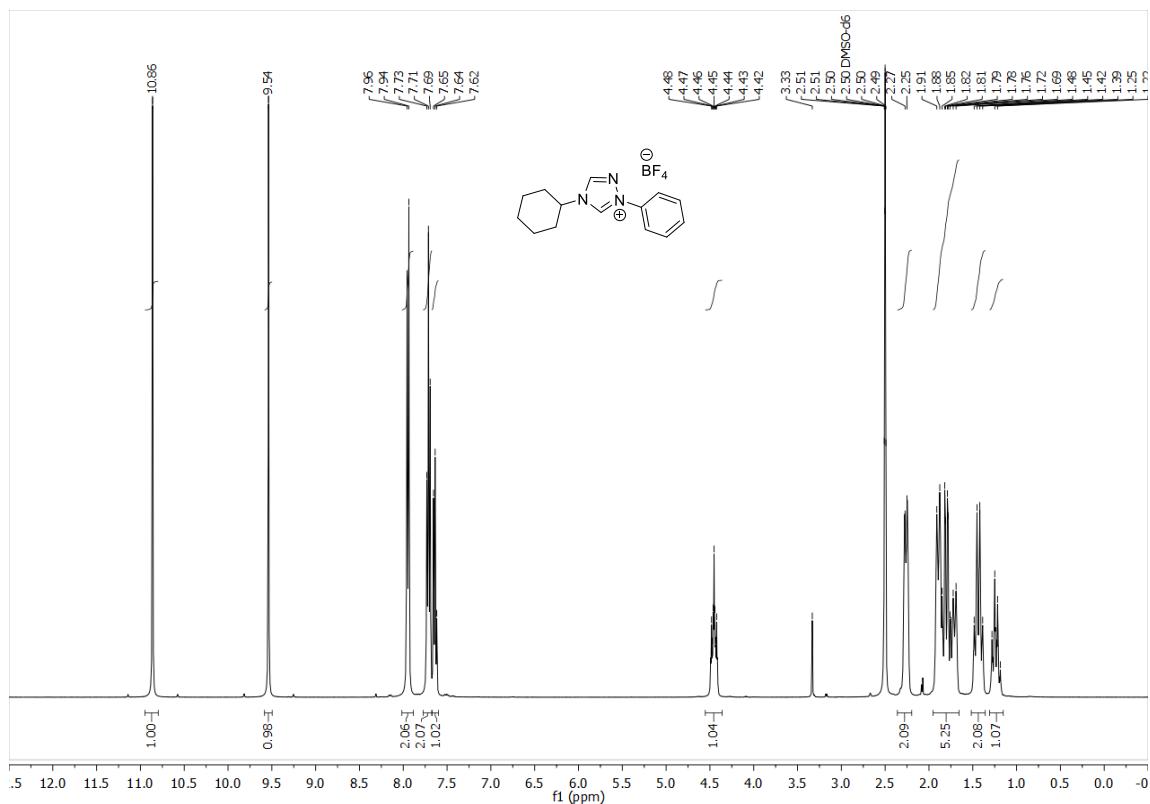


Figure S037: ¹H NMR spectrum of 4-cyclohexyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[2b]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

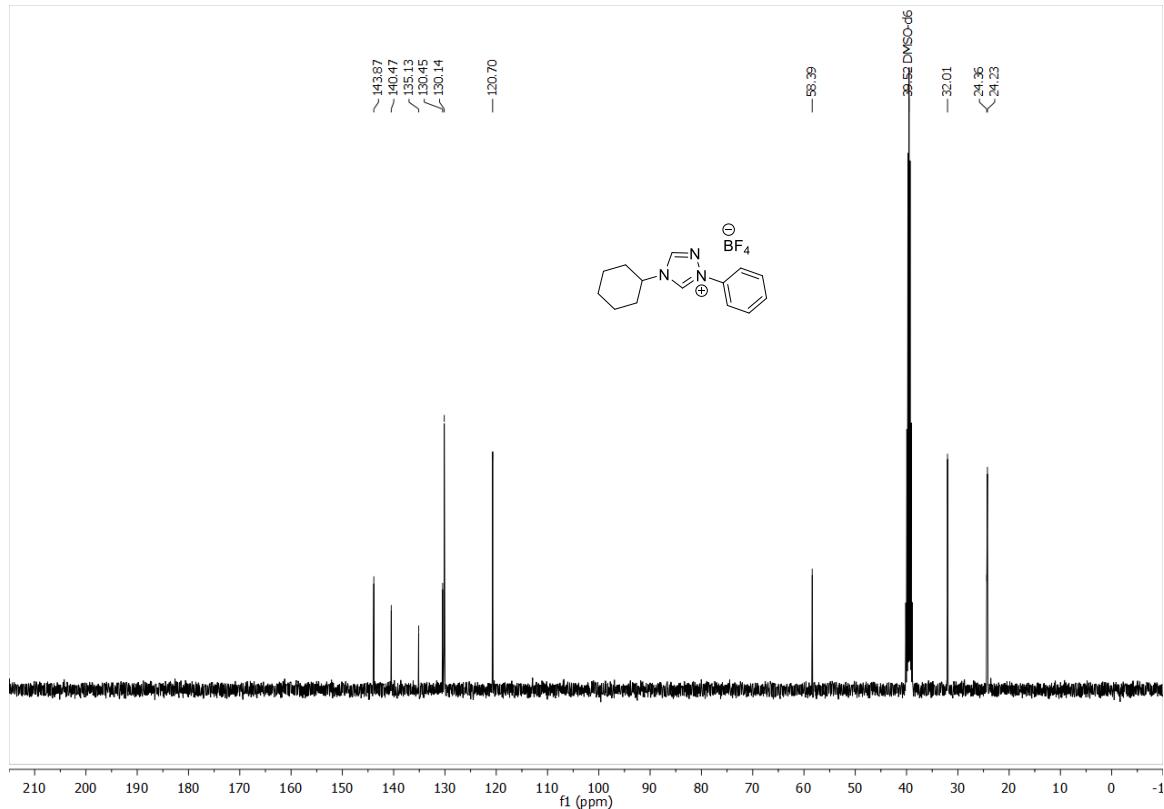


Figure S038: ¹³C NMR spectrum of 4-cyclohexyl-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[2b]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

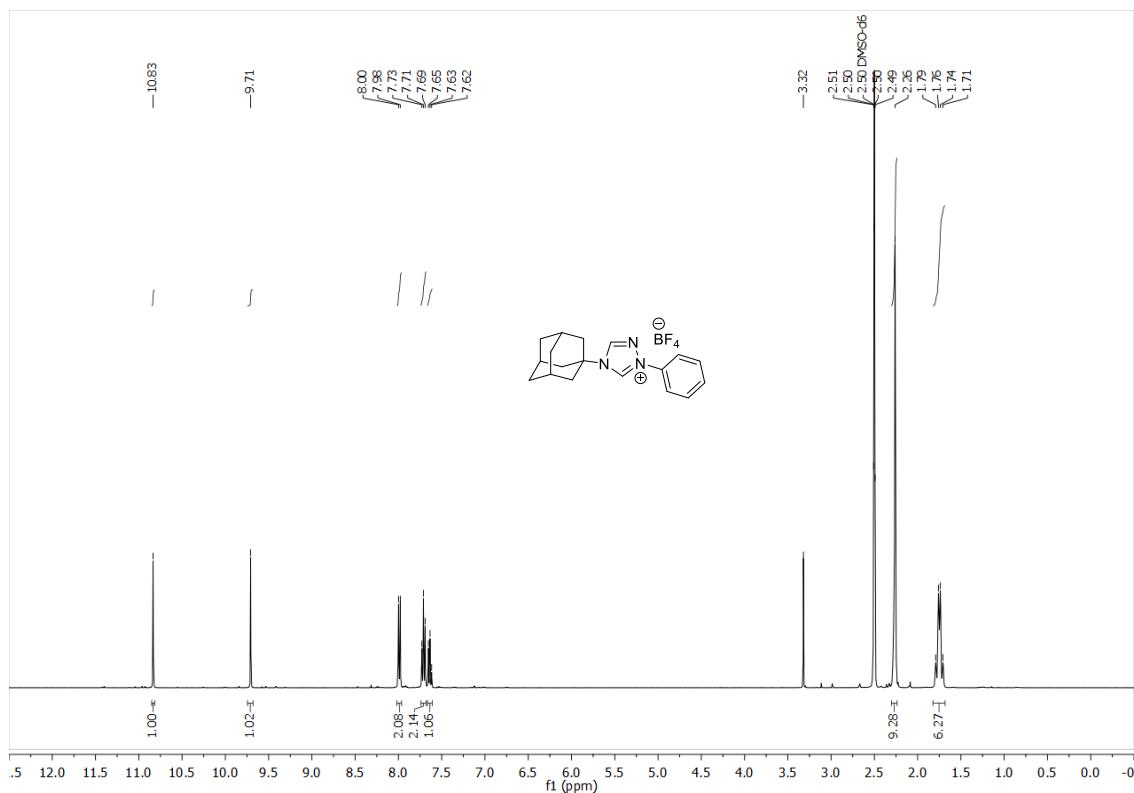


Figure S039: ^1H NMR spectrum of 4-((3s,5s,7s)-adamantan-1-yl)-1-phenyl-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ([2c]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

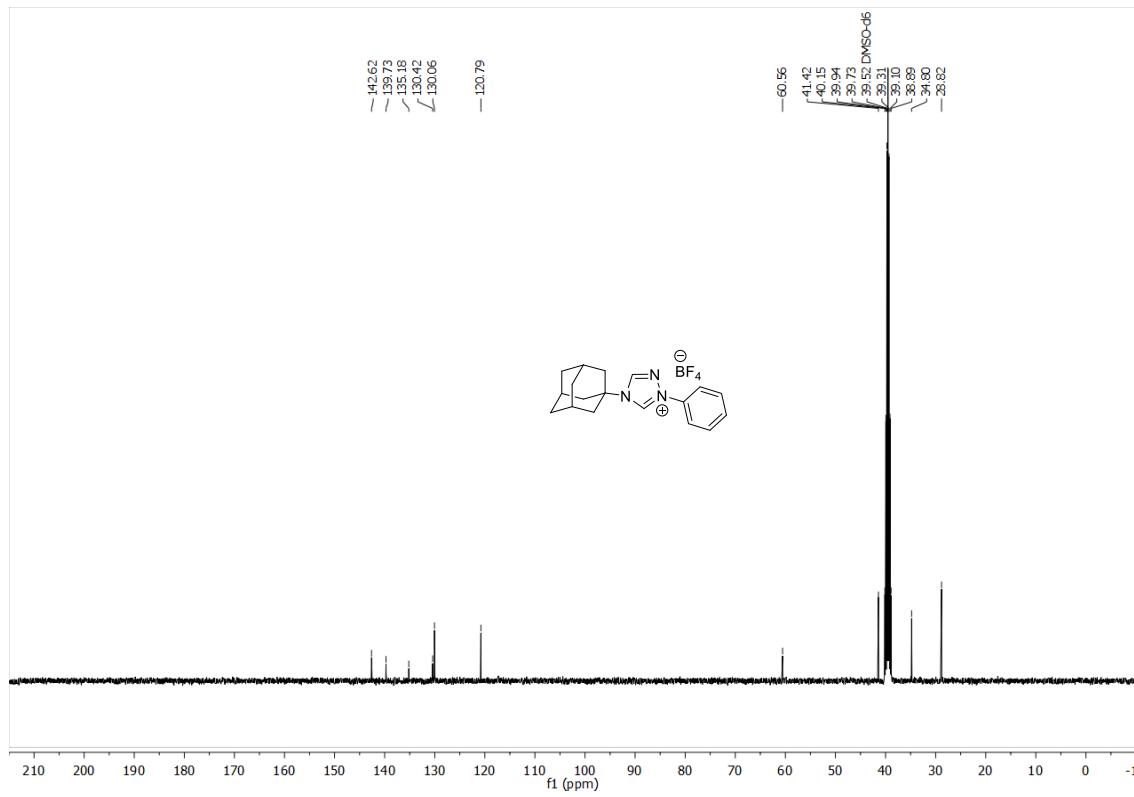


Figure S040: ^{13}C NMR spectrum of 4-((3s,5s,7s)-adamantan-1-yl)-1-phenyl-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ([2c]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

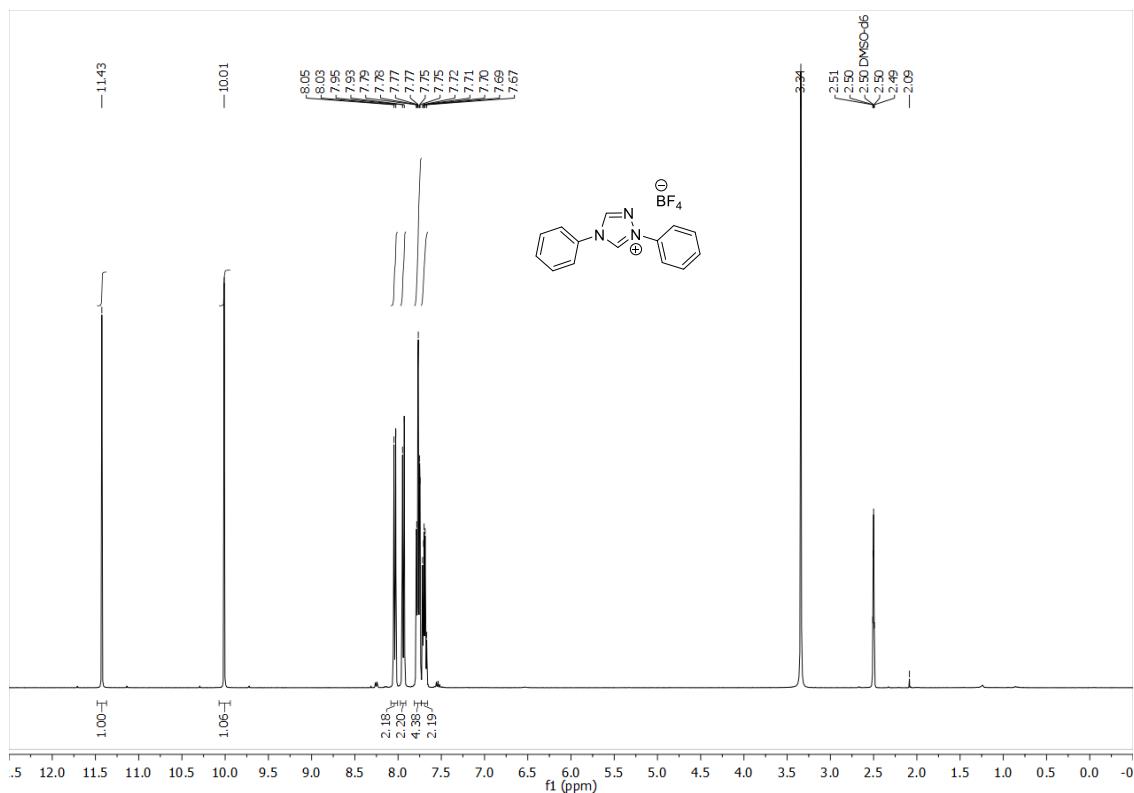


Figure S041: ¹H NMR spectrum of 1,4-diphenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[2d]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

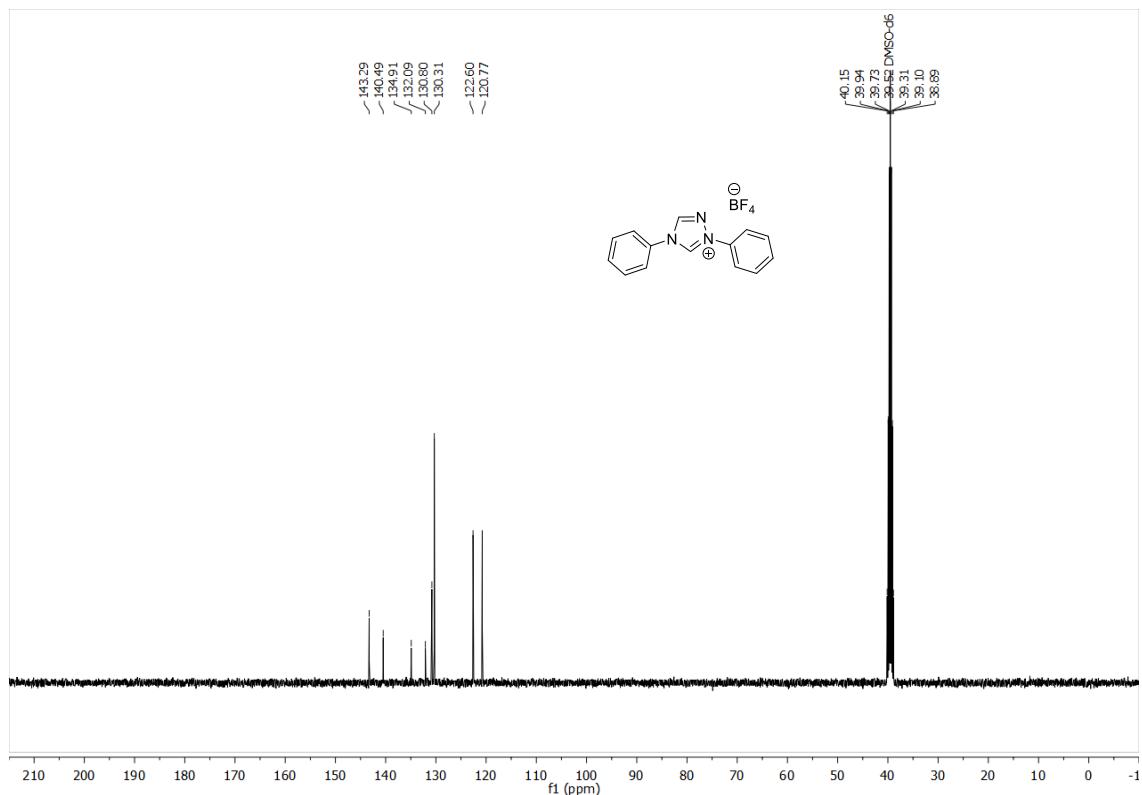


Figure S042: ¹³C NMR spectrum of 1,4-diphenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[2d]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

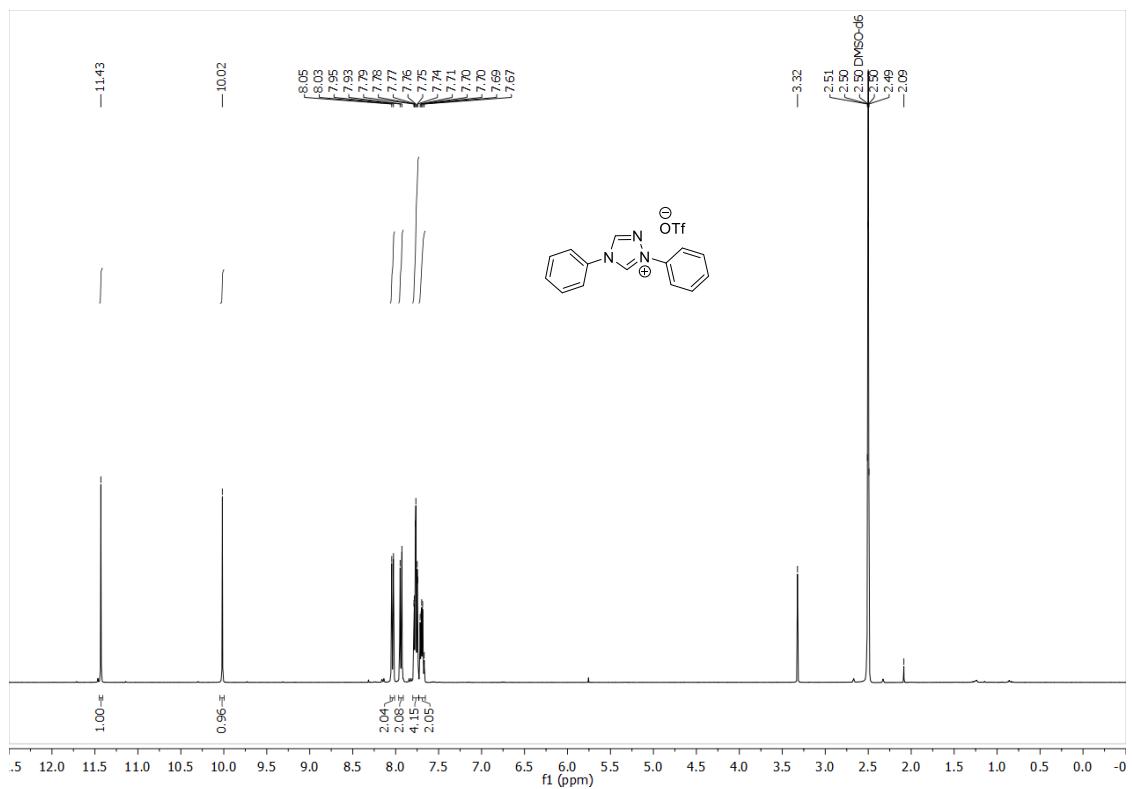


Figure S043: ¹H NMR spectrum of 1,4-diphenyl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([2d]OTf) (400 MHz, DMSO-*d*₆, 298 K).

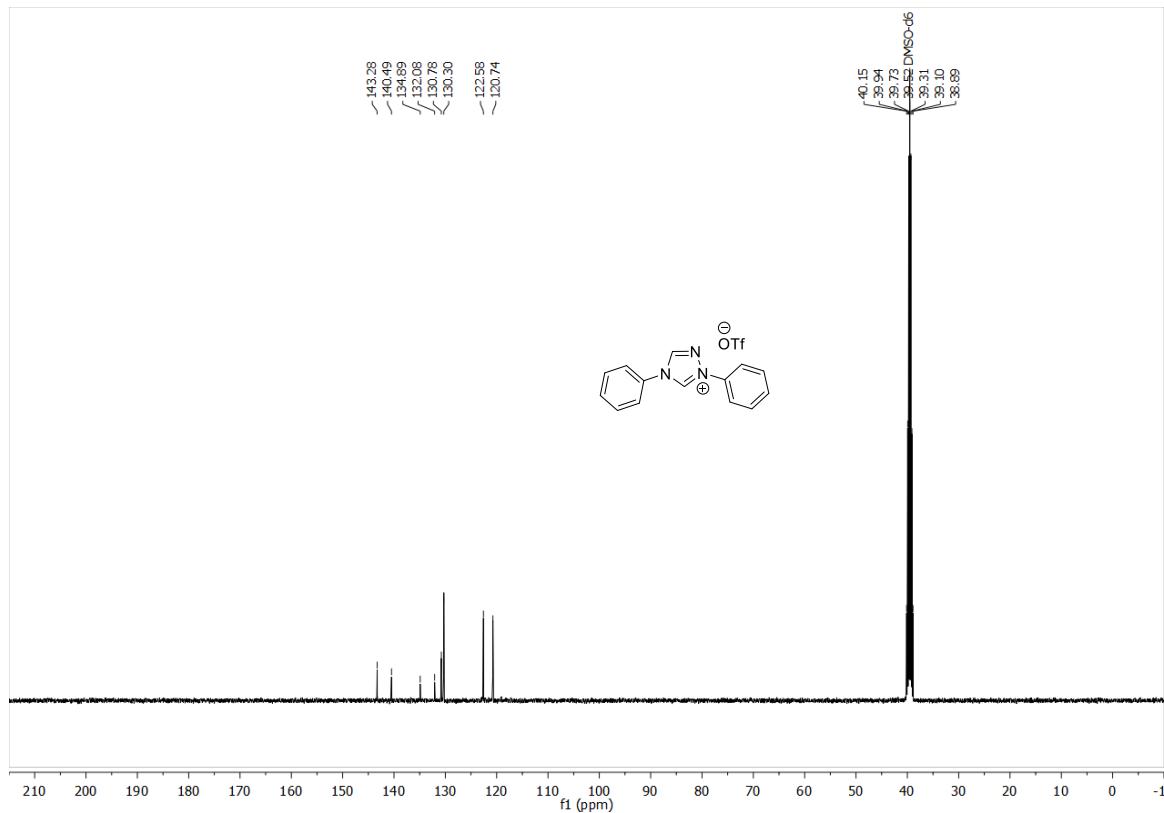


Figure S044: ¹³C NMR spectrum of 1,4-diphenyl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([2d]OTf) (100 MHz, DMSO-*d*₆, 298 K).

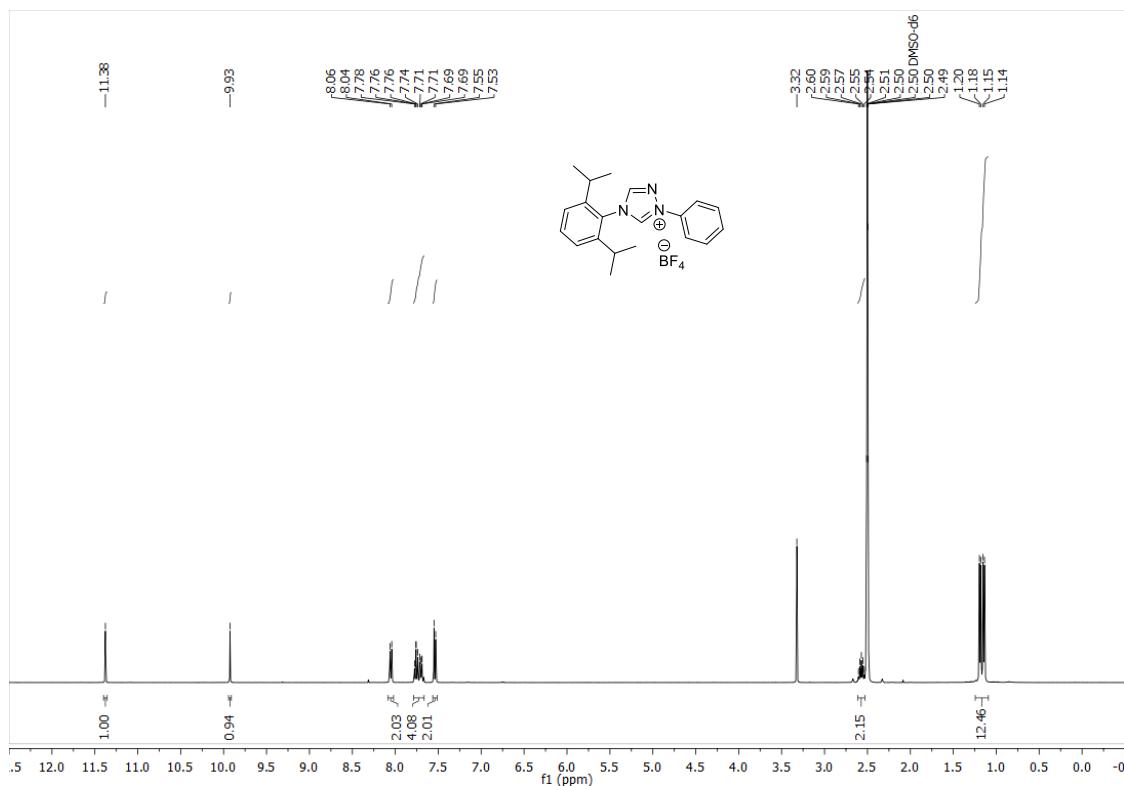


Figure S045: ^1H NMR spectrum of 4-(2,6-diisopropylphenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2\mathbf{e}]\text{BF}_4$) (400 MHz, $\text{DMSO}-d_6$, 298 K).

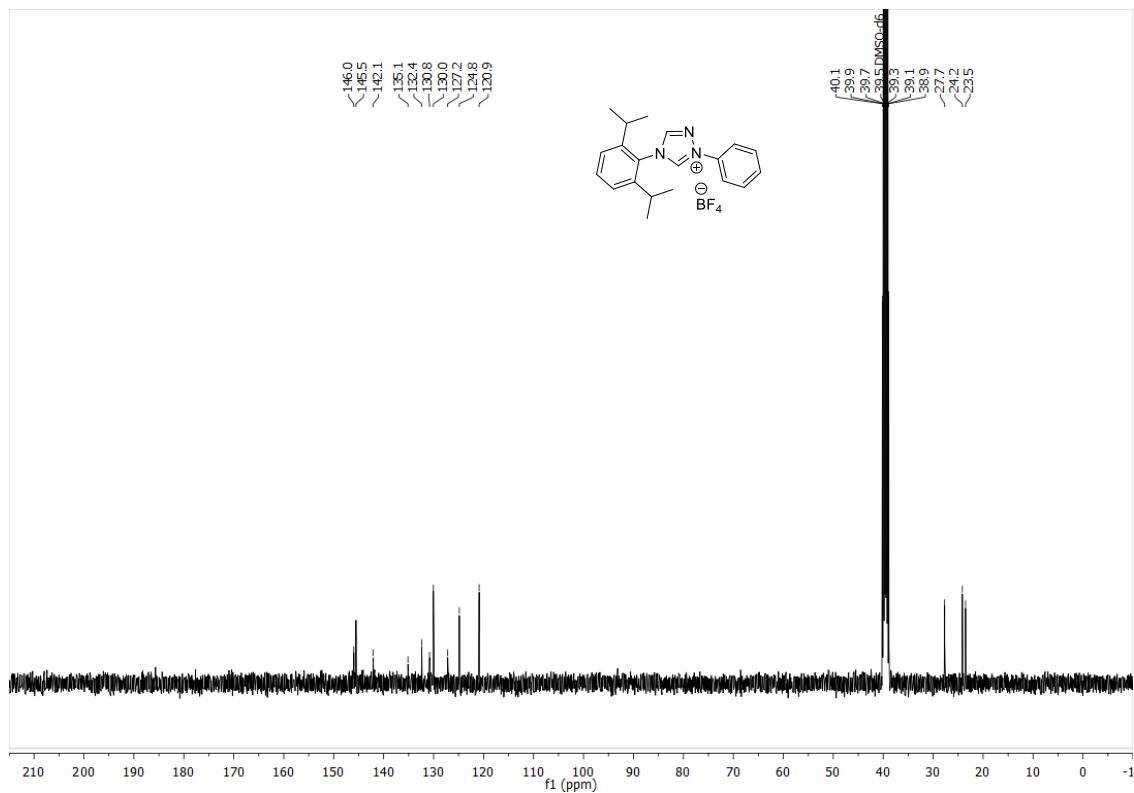


Figure S046: ^{13}C NMR spectrum of 4-(2,6-diisopropylphenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2\mathbf{e}]\text{BF}_4$) (100 MHz, $\text{DMSO}-d_6$, 298 K).

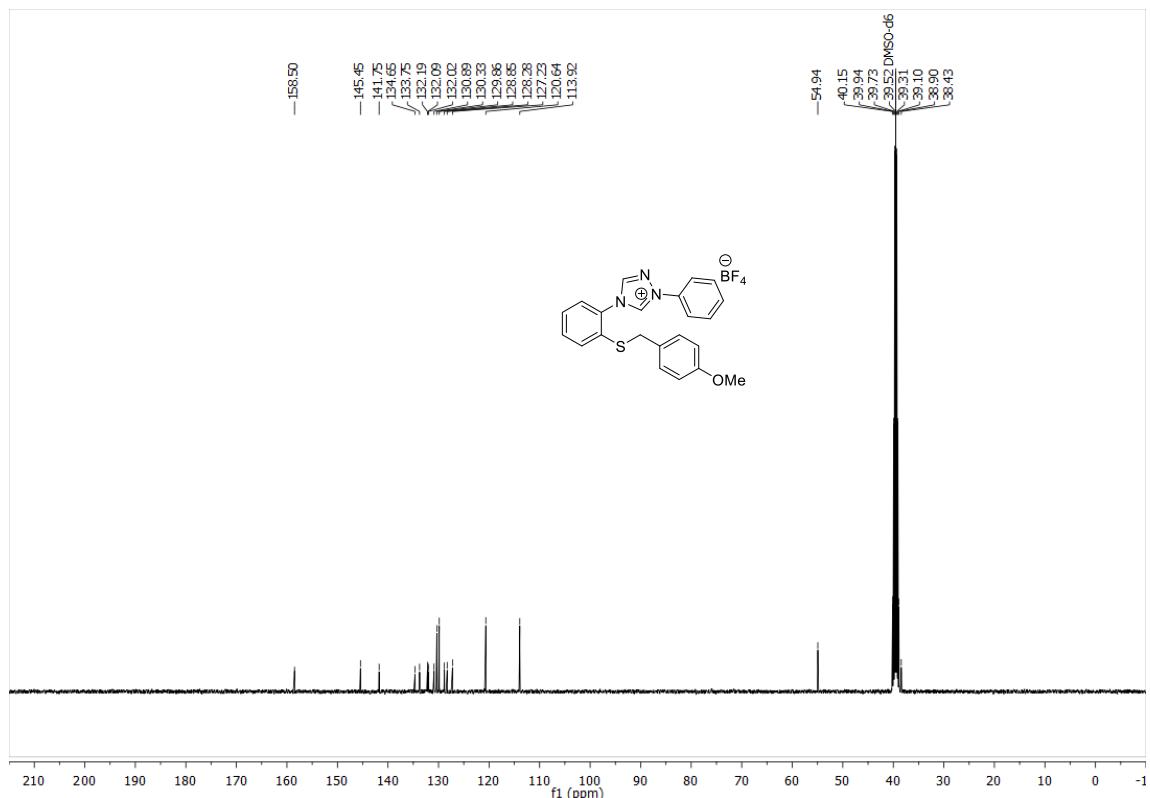
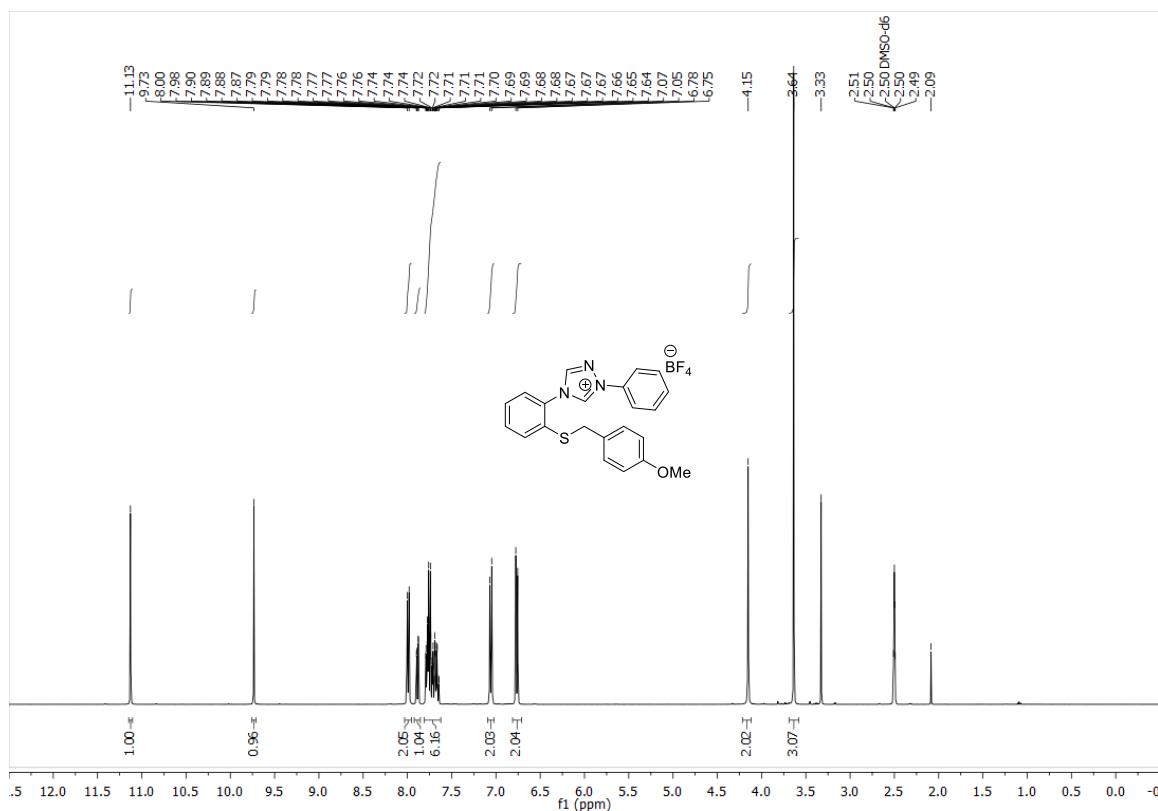


Figure S048: ^{13}C NMR spectrum of 1-phenyl-4-(2-((4-methoxybenzyl)thio)phenyl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2f]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

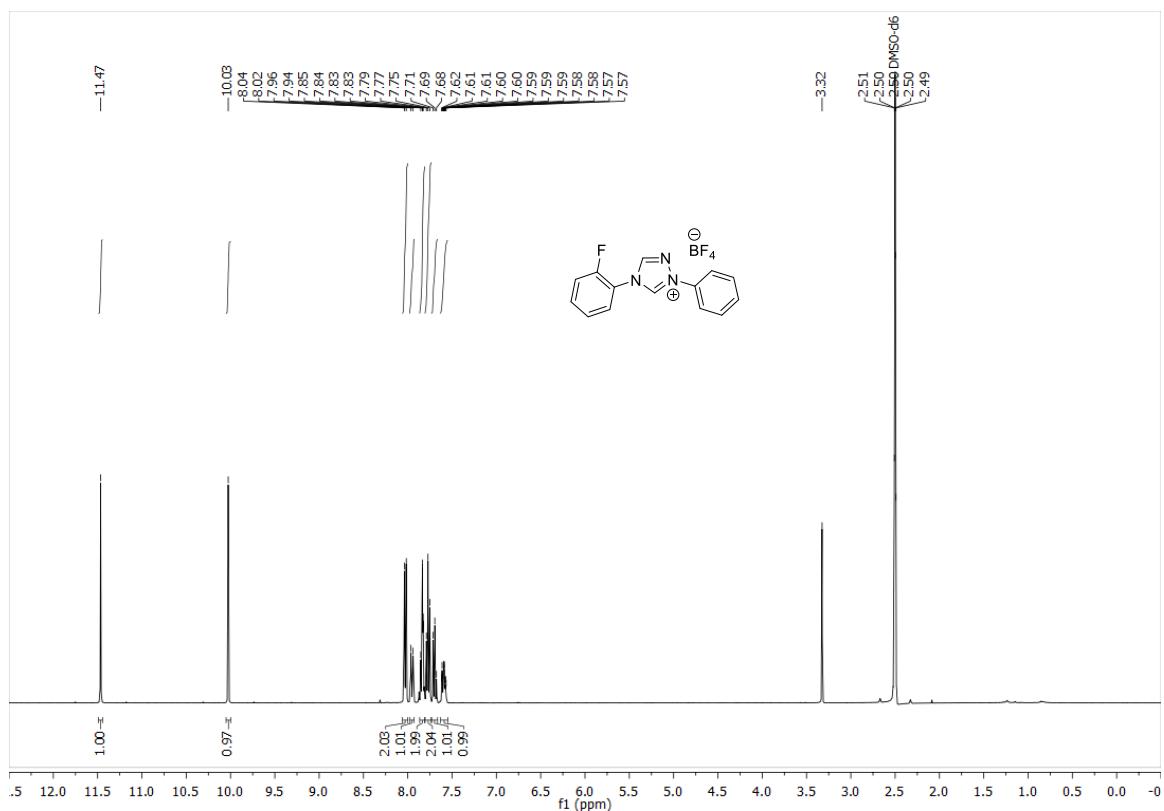


Figure S049: ¹H NMR spectrum of 4-(2-fluorophenyl)-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ([2g]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

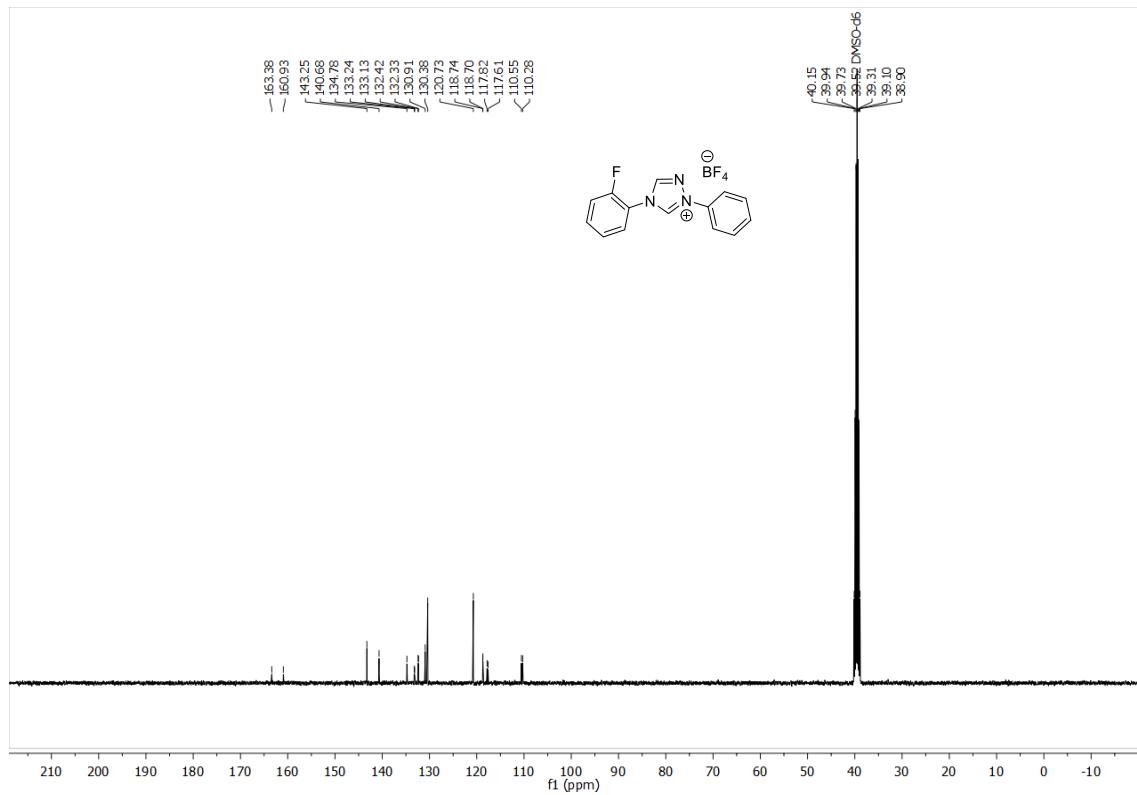


Figure S050: ¹³C NMR spectrum of 4-(2-fluorophenyl)-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ([2g]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

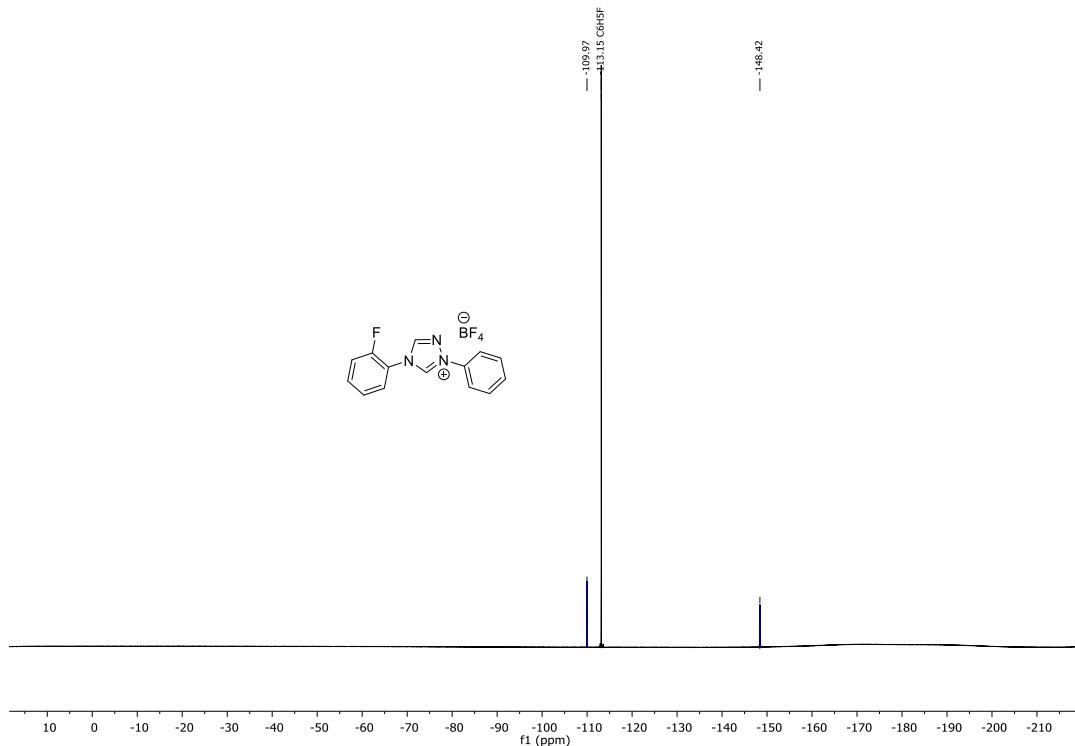


Figure S051: ^{19}F NMR spectrum of 4-(2-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2g]BF₄) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

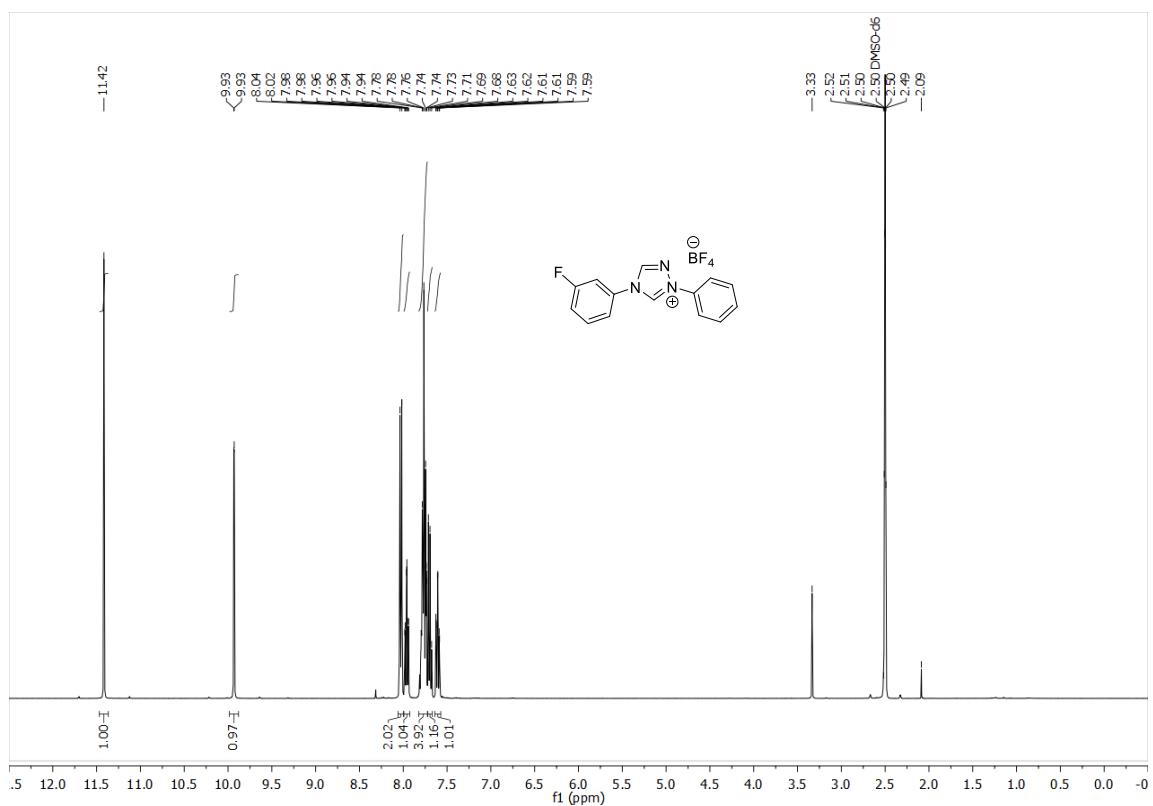


Figure S052: ^1H NMR spectrum of 4-(3-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ($[2\text{h}]\text{BF}_4^-$) (400 MHz, $\text{DMSO}-d_6$, 298 K).

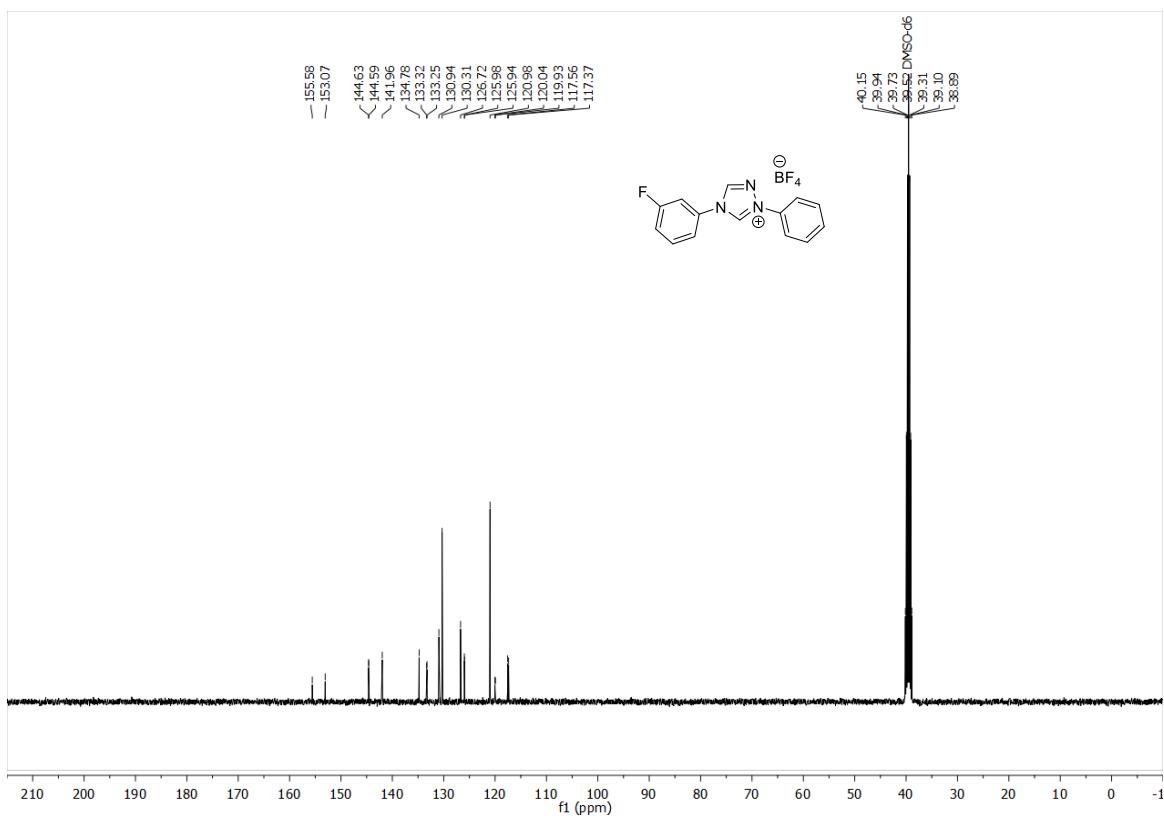


Figure S053: ^{13}C NMR spectrum of 4-(3-fluorophenyl)-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[2\text{h}]\text{BF}_4$) (100 MHz, $\text{DMSO}-d_6$, 298 K).

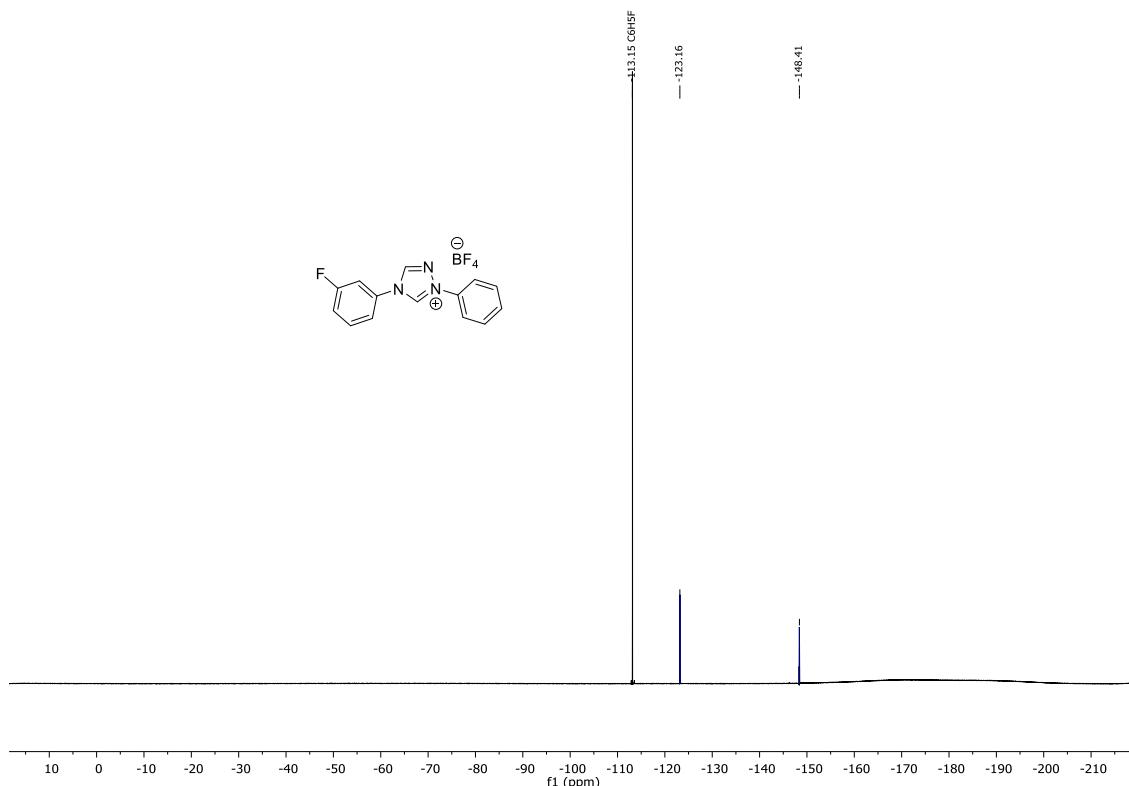


Figure S054: ^{19}F NMR spectrum of 4-(3-fluorophenyl)-1-phenyl-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[2\text{h}]\text{BF}_4$) (376 MHz, $\text{DMSO}-d_6$, 298 K, referenced to fluorobenzene).

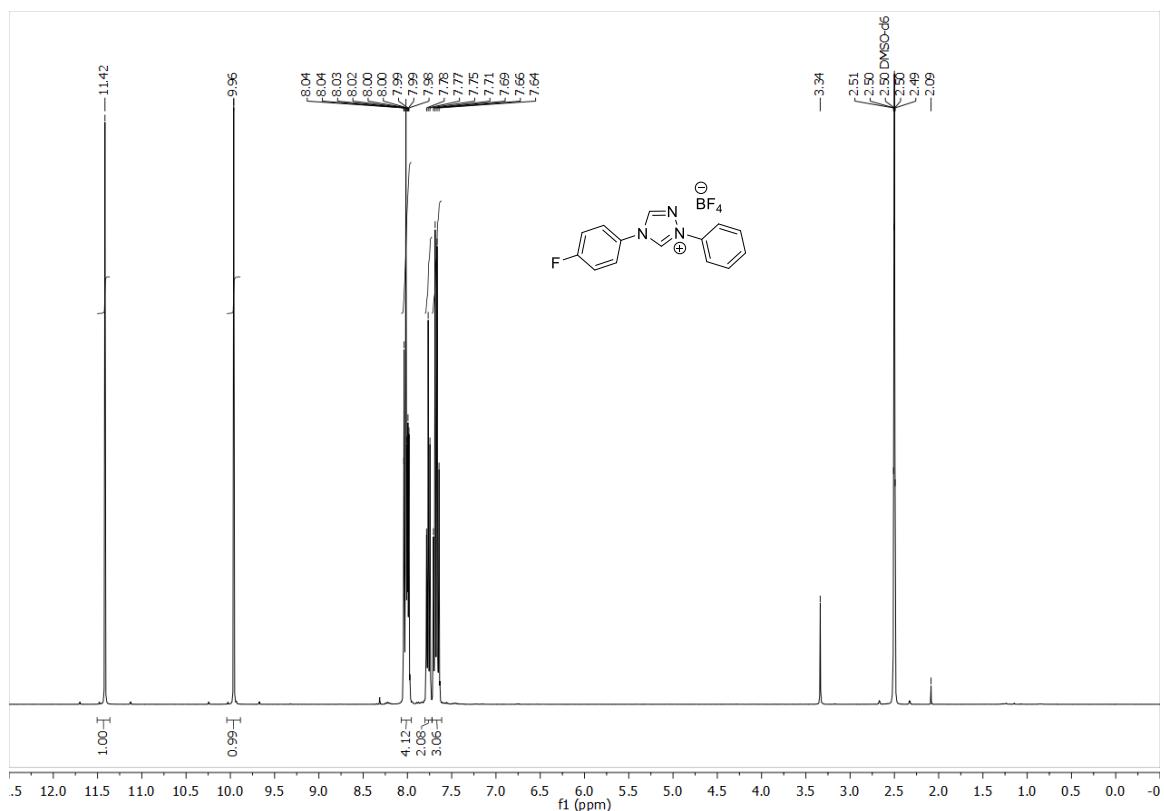


Figure S055: ¹H NMR spectrum of 4-(4-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2i]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

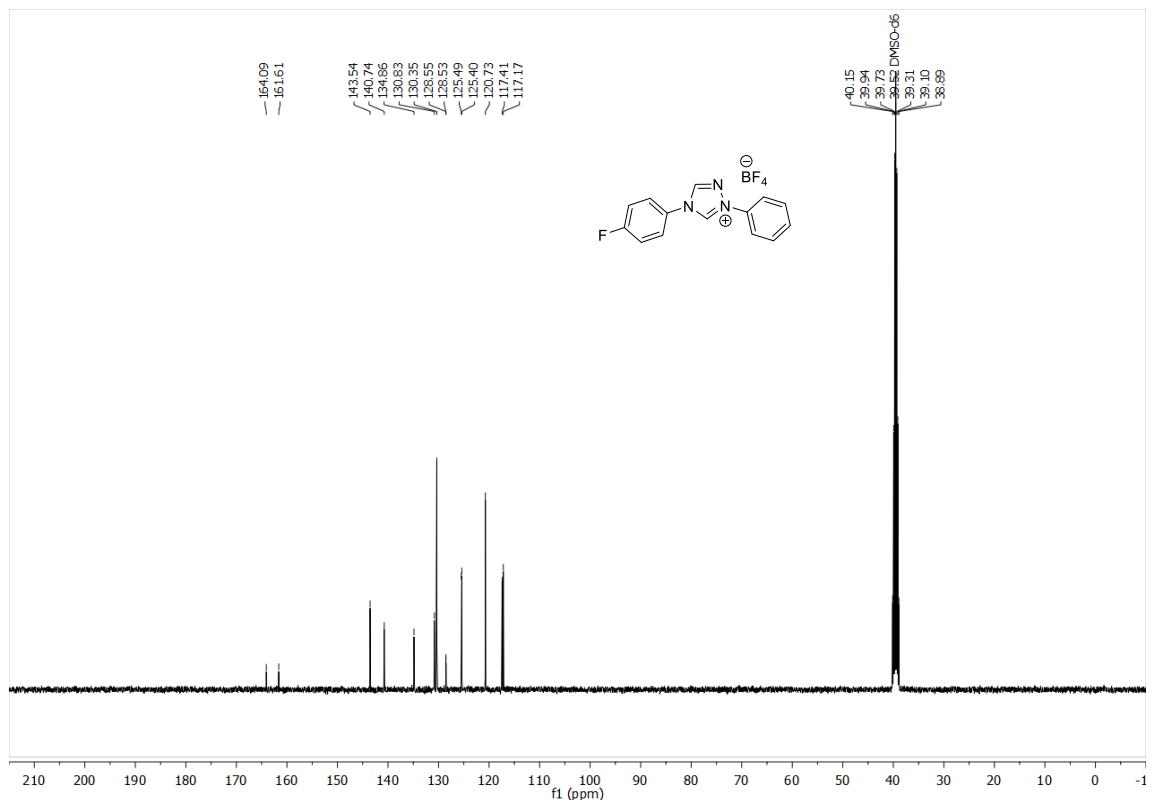


Figure S056: ¹³C NMR spectrum of 4-(4-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([2i]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

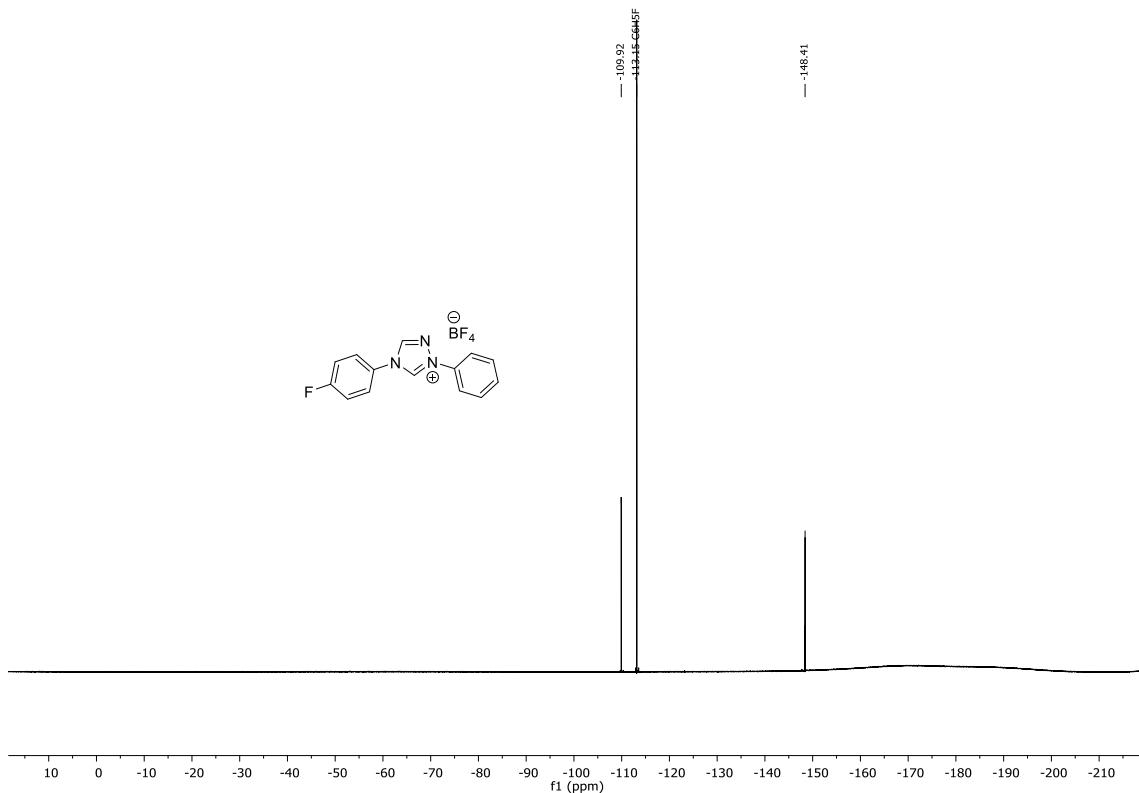


Figure S057: ¹⁹F NMR spectrum of 4-(4-fluorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[2i]BF₄**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

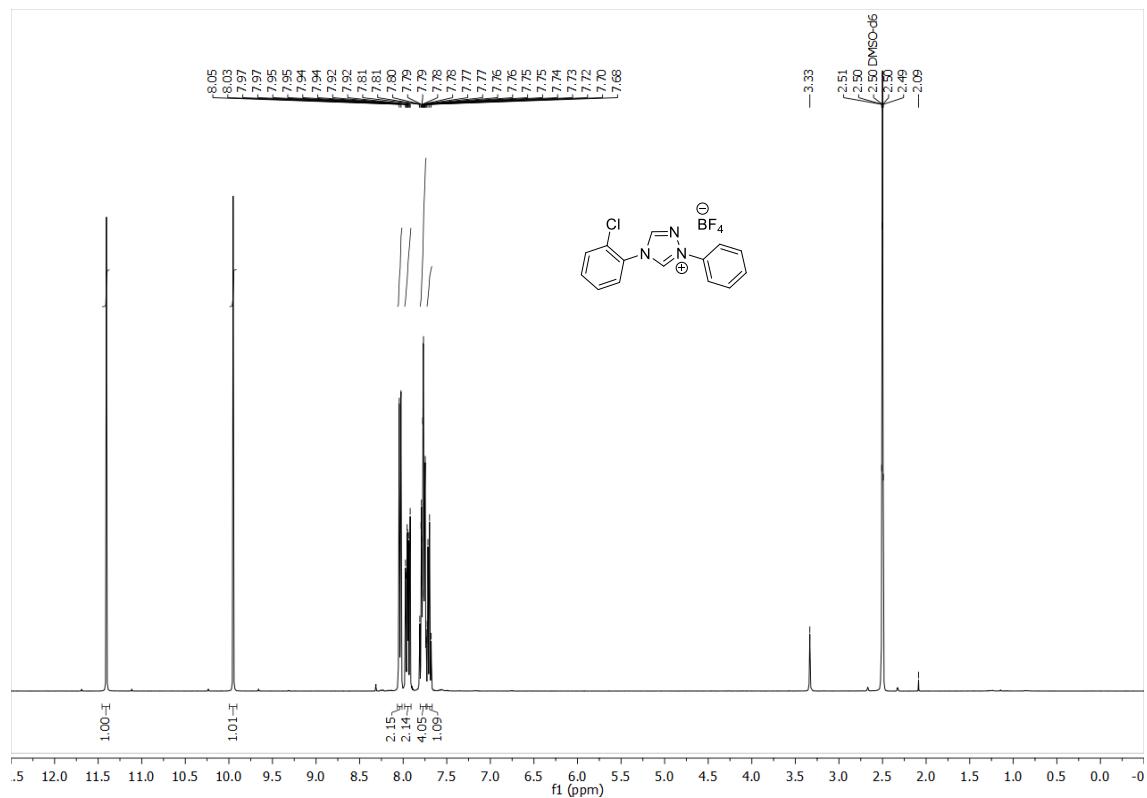


Figure S058: ¹H NMR spectrum of 4-(2-chlorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[2j]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

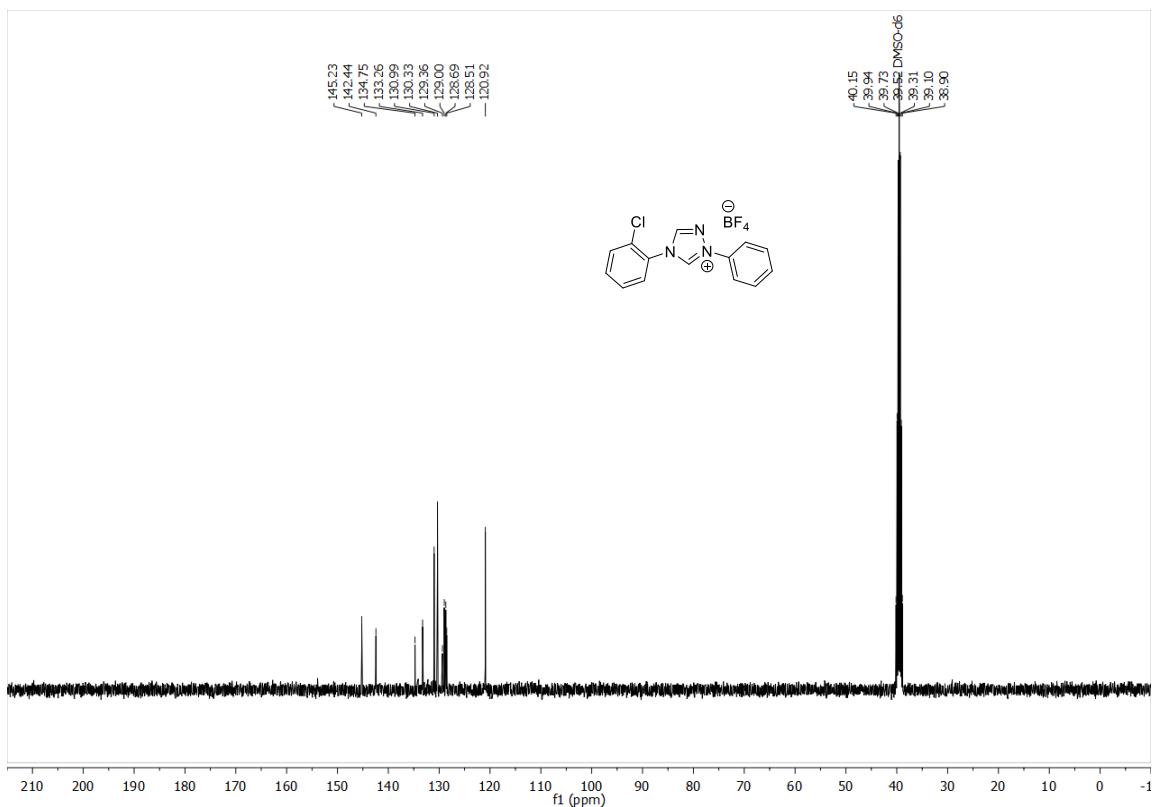


Figure S059: ^{13}C NMR spectrum of 4-(2-chlorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[2j]BF₄**) (100 MHz, DMSO- d_6 , 298 K).

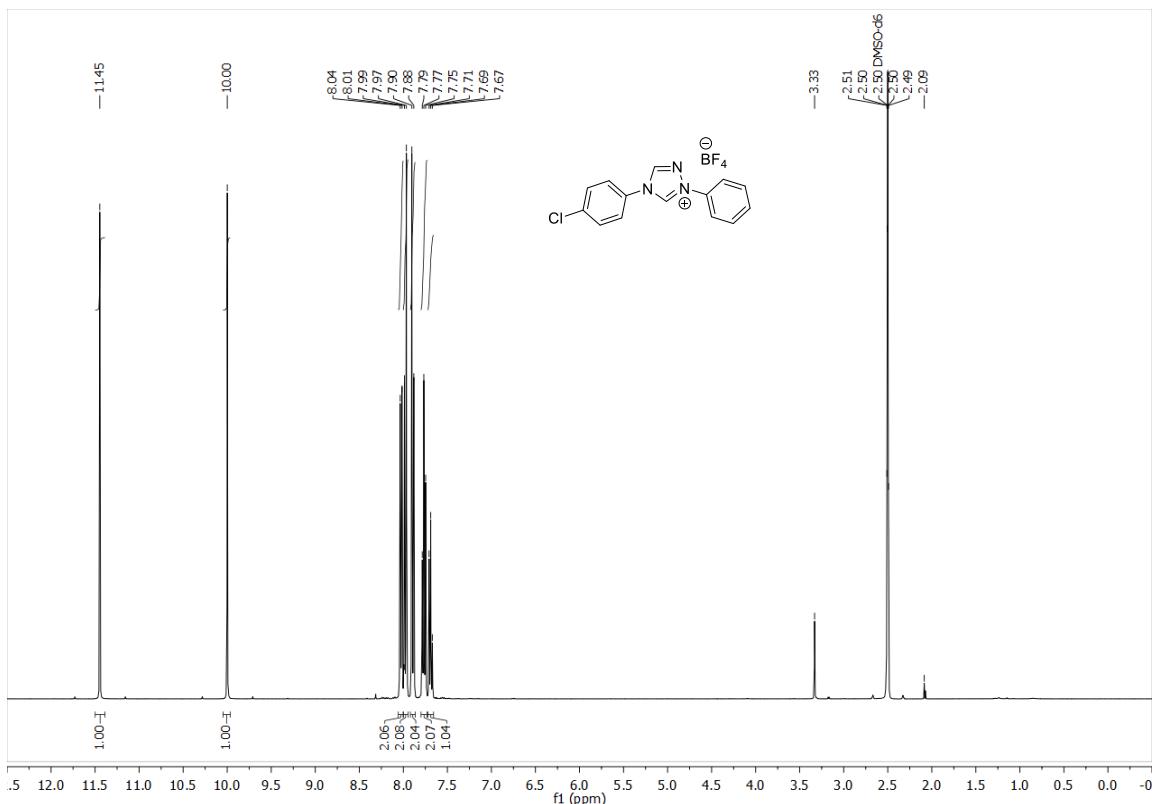


Figure S060: ^1H NMR spectrum of 4-(4-chlorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[2k]BF₄**) (400 MHz, DMSO- d_6 , 298 K).

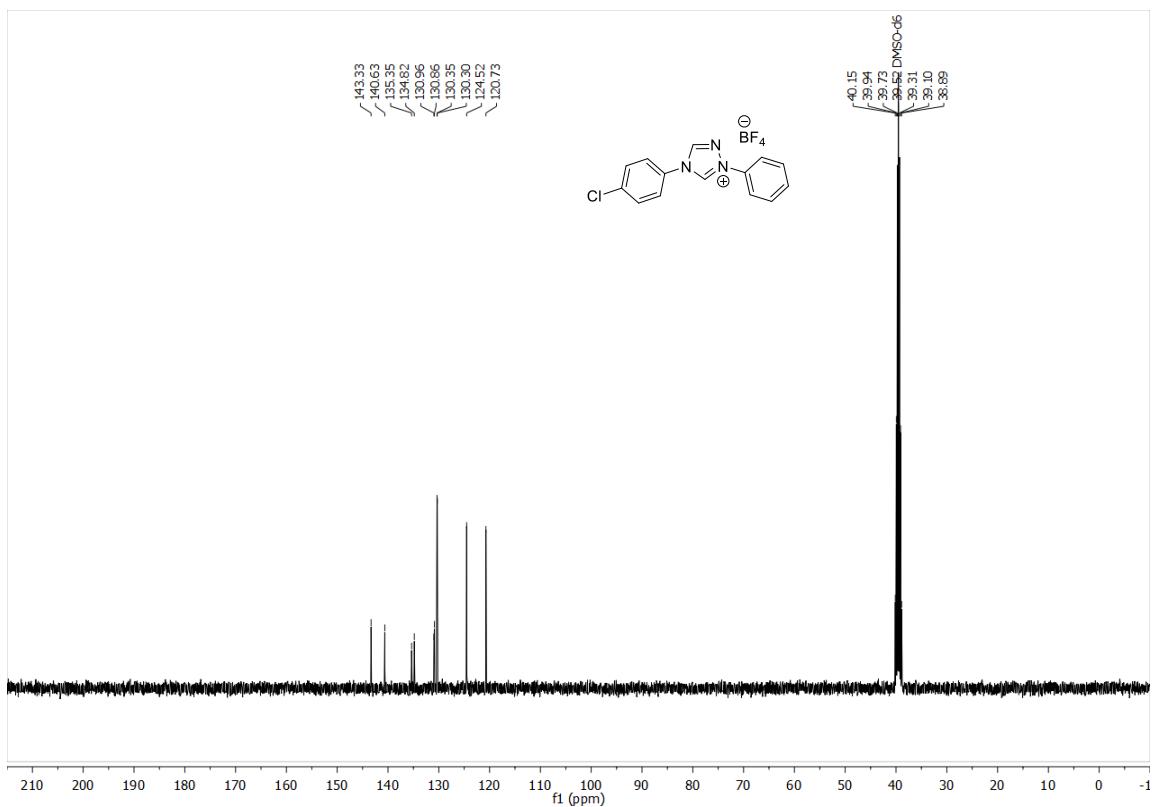


Figure S061: ^{13}C NMR spectrum of 4-(4-chlorophenyl)-1-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[2k]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

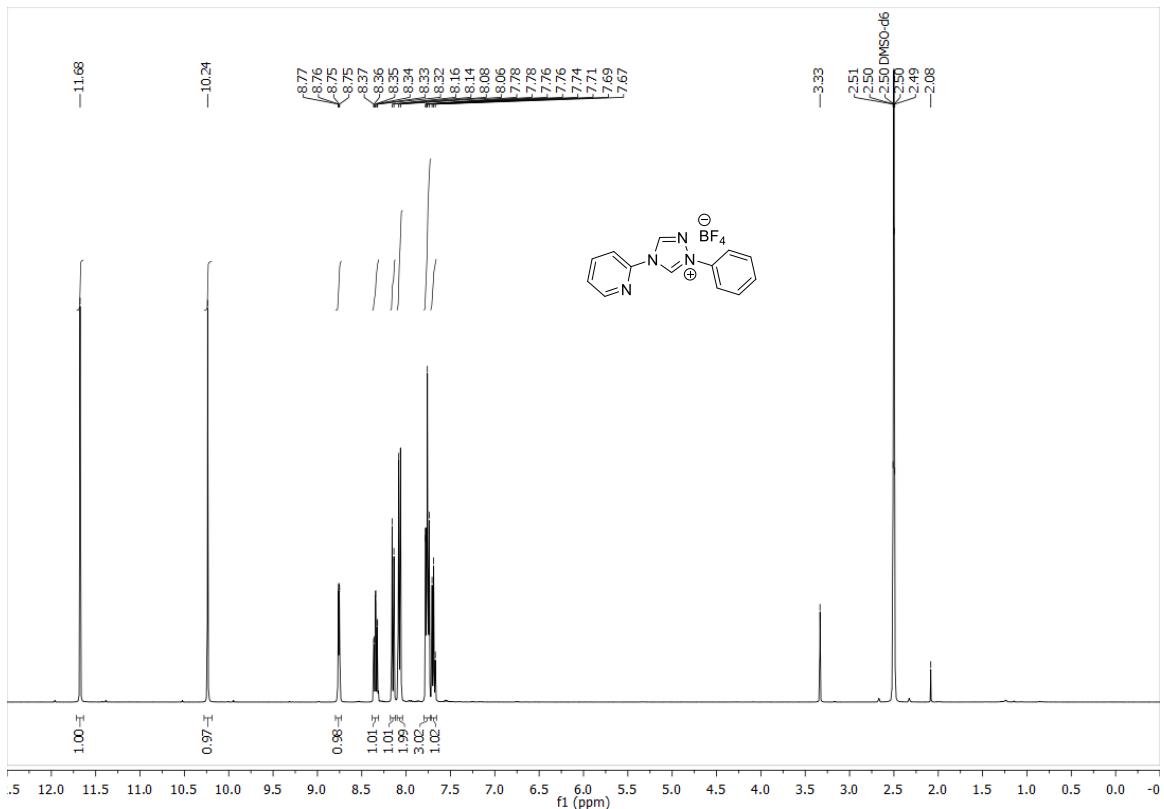


Figure S062: ^1H NMR spectrum of 1-phenyl-4-(pyridin-2-yl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[2l]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

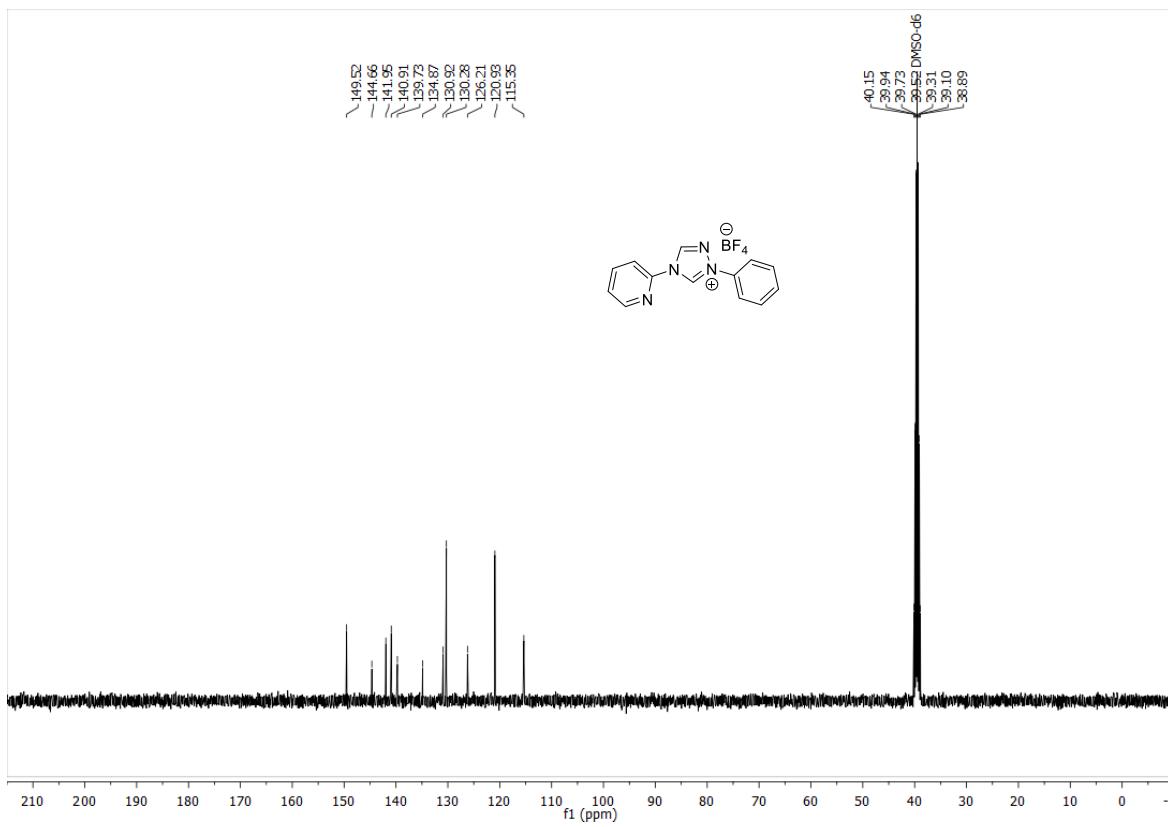


Figure S063: ^{13}C NMR spectrum of 1-phenyl-4-(pyridin-2-yl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2\text{l}]\text{BF}_4^-$) (100 MHz, $\text{DMSO}-d_6$, 298 K).

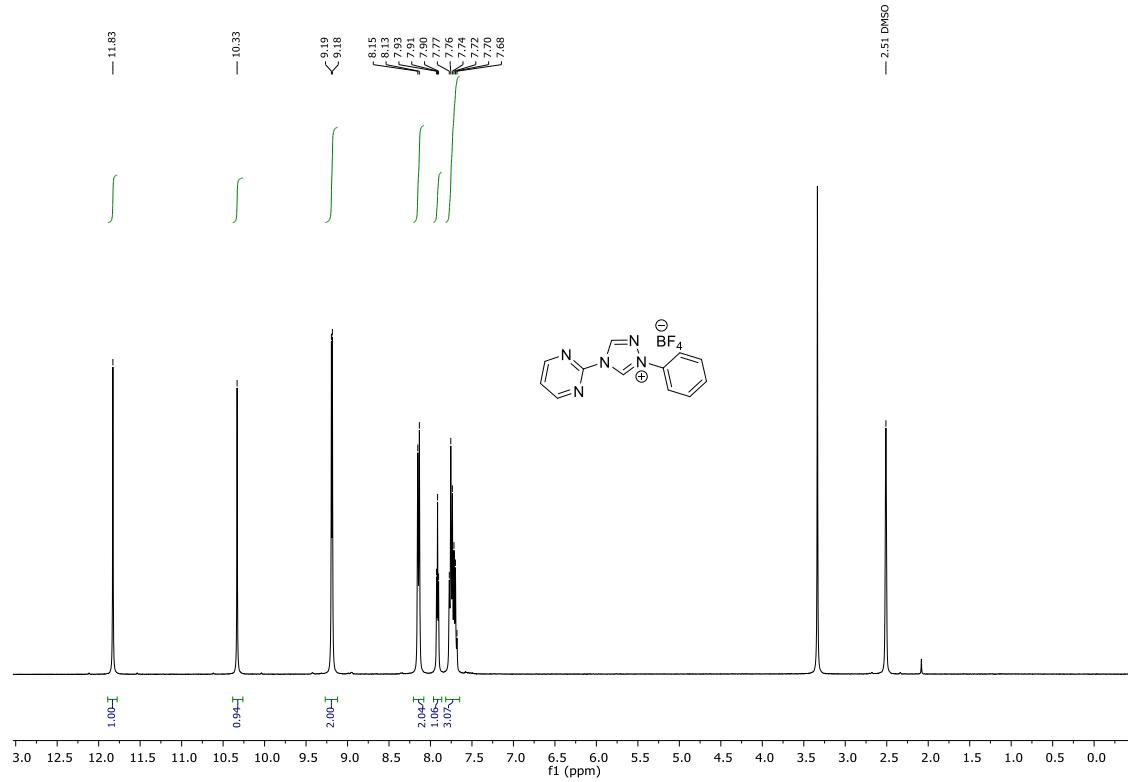


Figure S064: ^1H NMR spectrum of 1-phenyl-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ($[2\text{m}]\text{BF}_4^-$) (400 MHz, $\text{DMSO}-d_6$, 298 K).

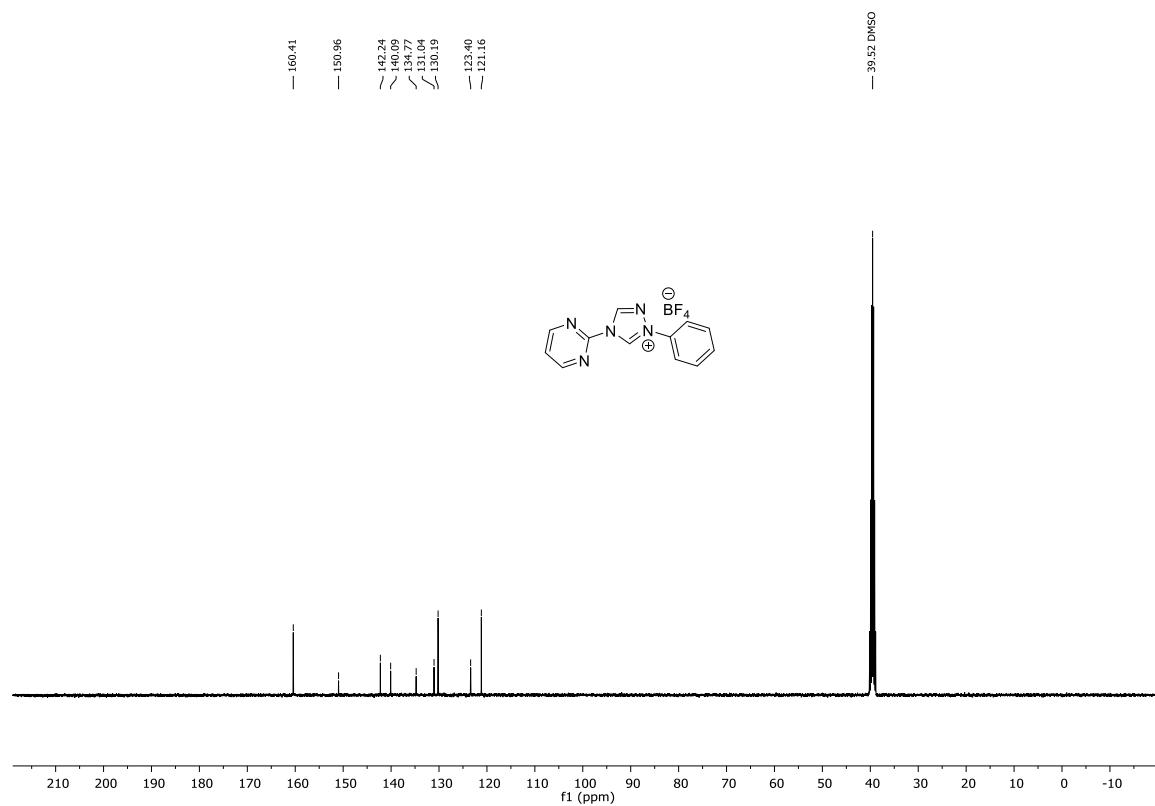


Figure S065: ^{13}C NMR spectrum of 1-phenyl-4-(pyrimidin-2-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[2\mathbf{m}]\text{BF}_4$) (100 MHz, $\text{DMSO}-d_6$, 298 K).

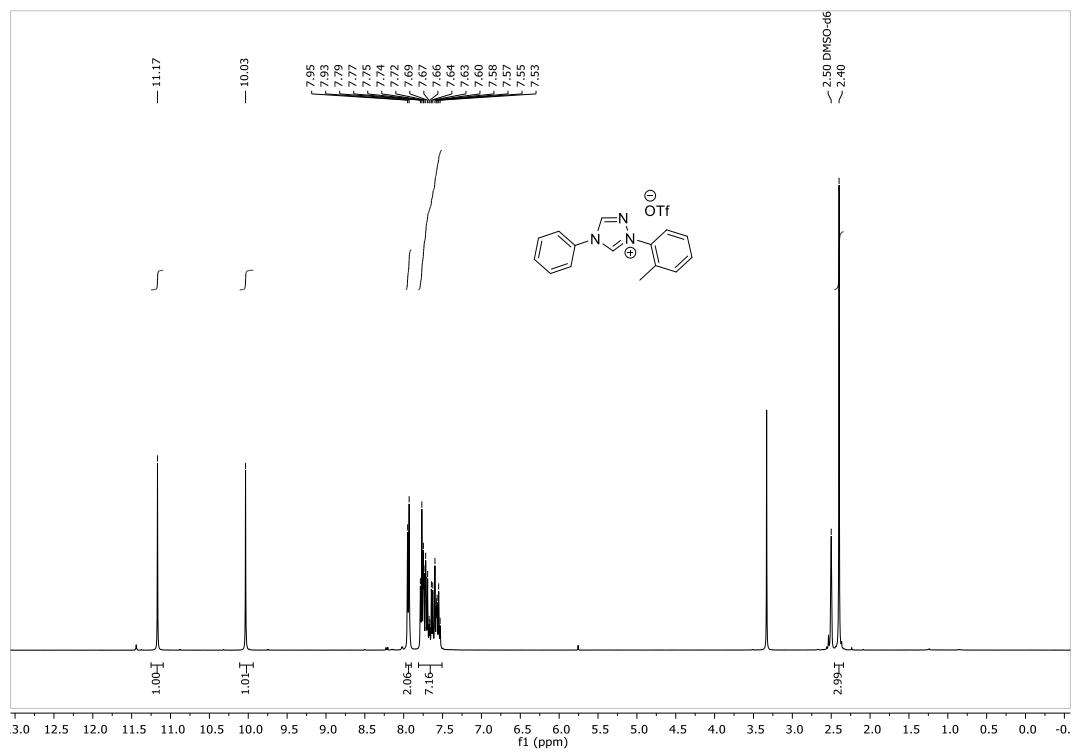


Figure S066: ^1H NMR spectrum of 4-phenyl-1-(o-tolyl)-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate ($[3\mathbf{d}]\text{OTf}$) (400 MHz, $\text{DMSO}-d_6$, 298 K).

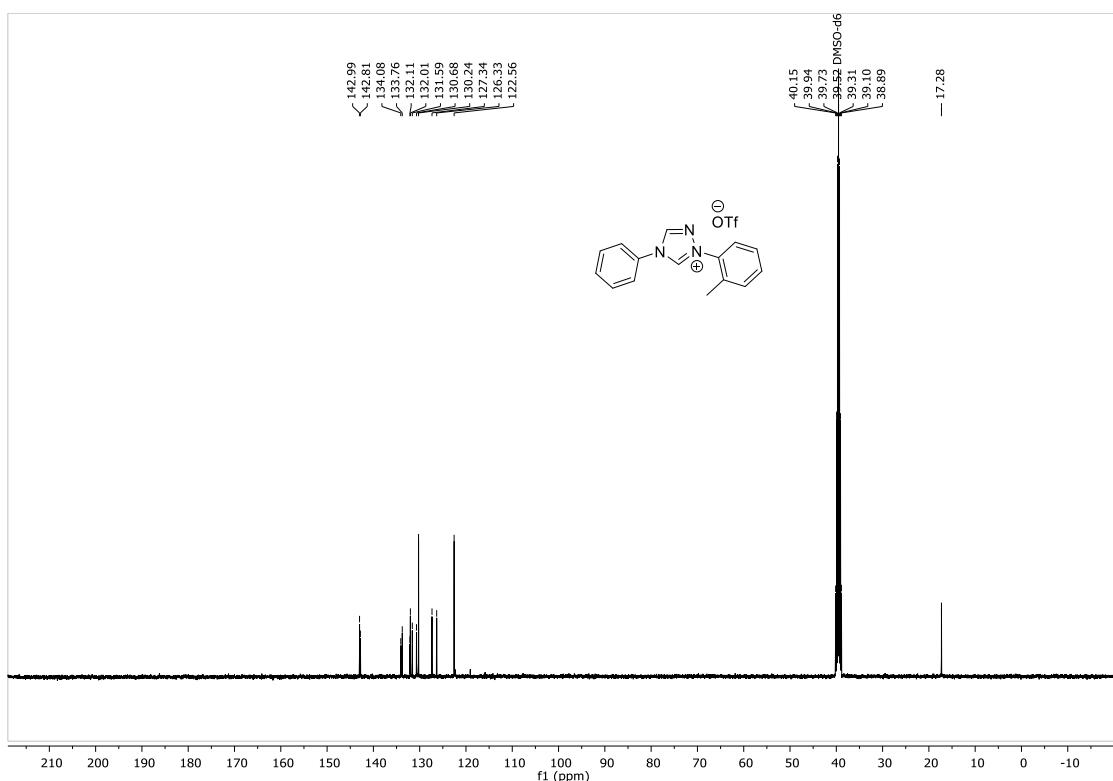


Figure S067: ¹³C NMR spectrum of 4-phenyl-1-(o-tolyl)-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[3d]OTf**) (100 MHz, DMSO-d₆, 298 K).

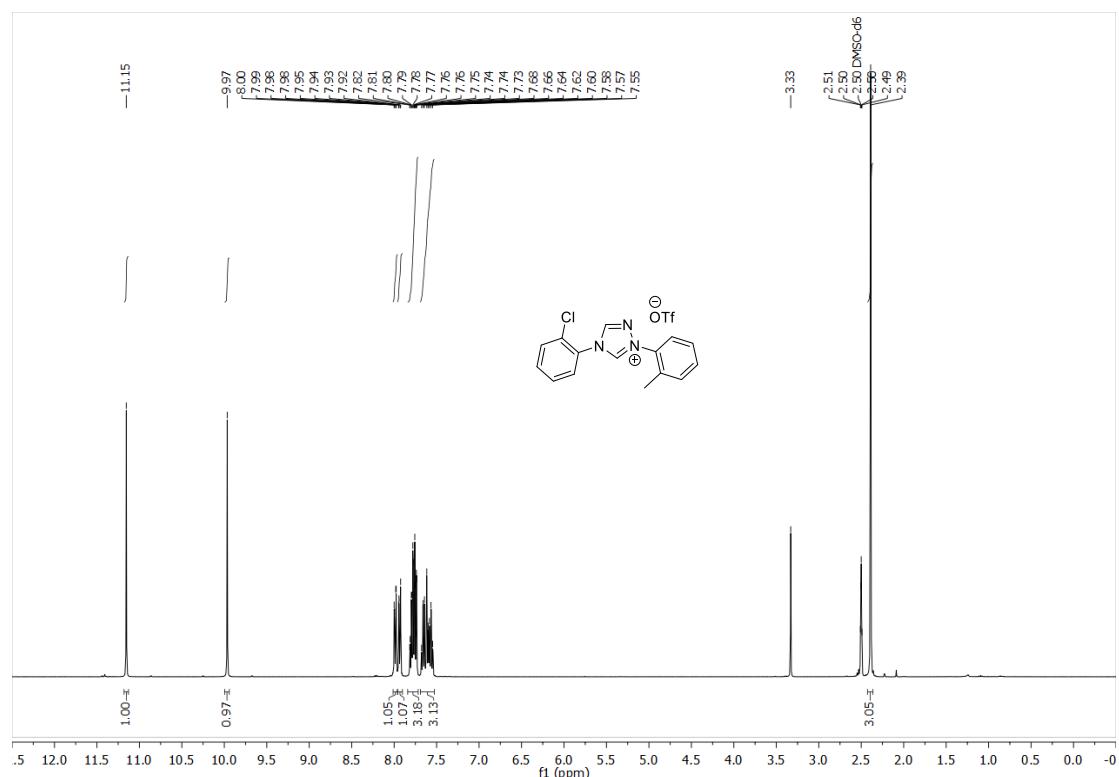


Figure S068: ¹H NMR spectrum of 4-(2-chlorophenyl)-1-(o-tolyl)-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[3j]OTf**) (400 MHz, DMSO-d₆, 298 K).

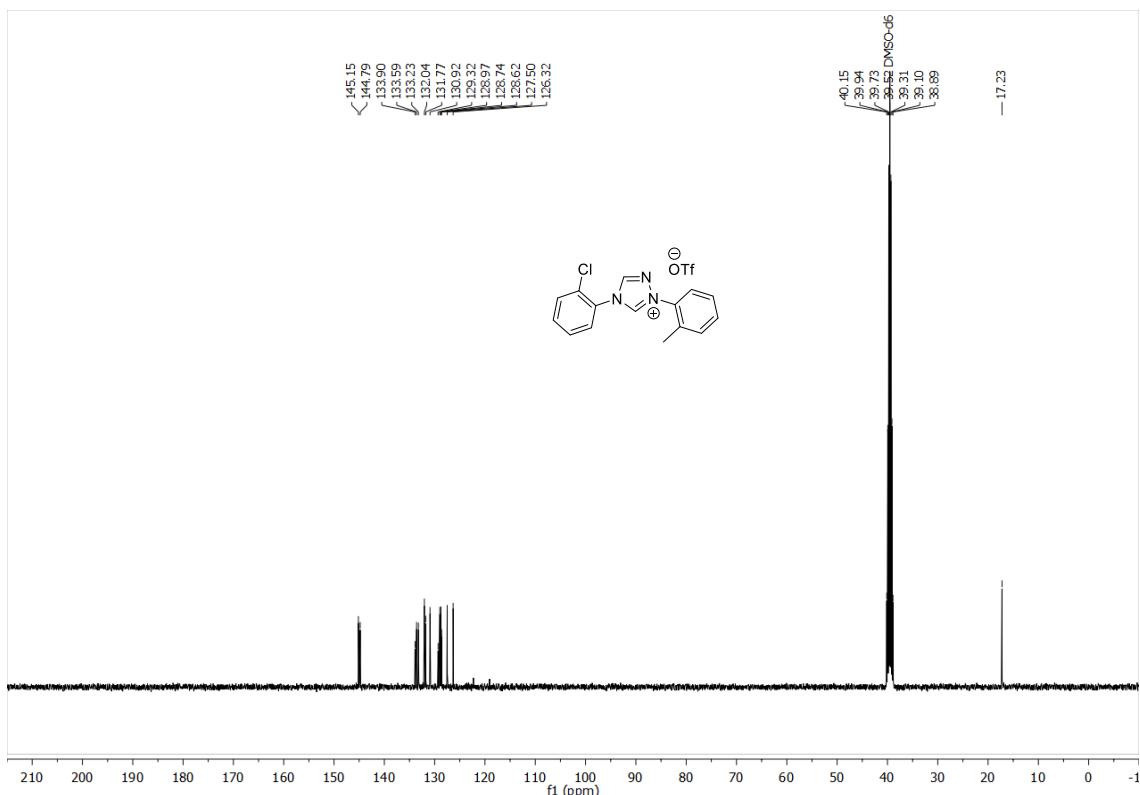


Figure S069: ^{13}C NMR spectrum of 4-(2-chlorophenyl)-1-(o-tolyl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate (**[3j]OTf**) (100 MHz, $\text{DMSO}-d_6$, 298 K).

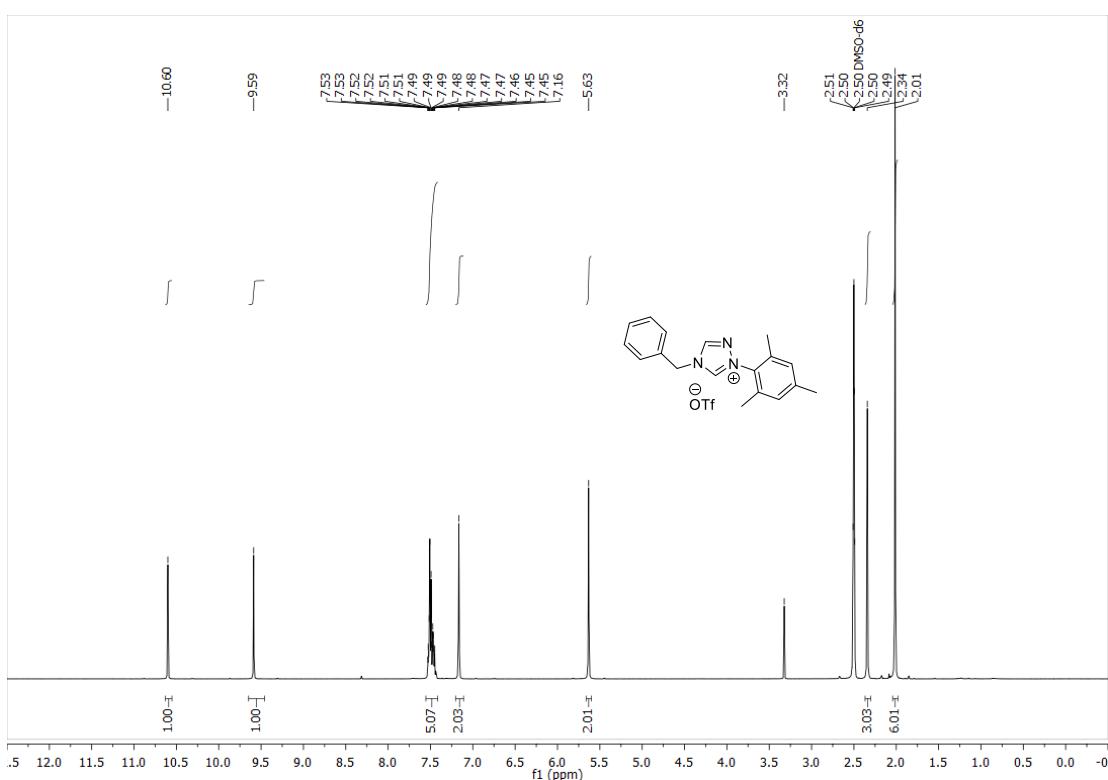


Figure S070: ^1H NMR spectrum of 4-benzyl-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate ([4a]OTf) (400 MHz, $\text{DMSO}-d_6$, 298 K).

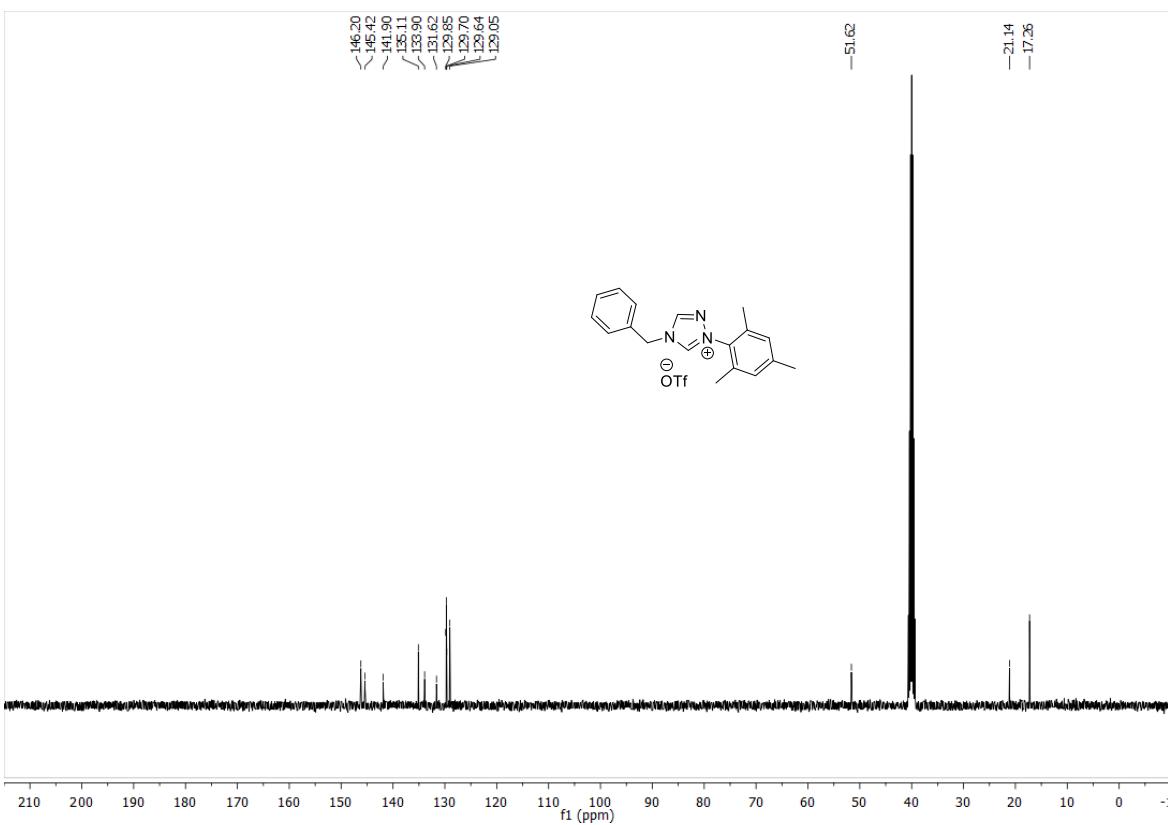


Figure S071: ^{13}C NMR spectrum of 4-benzyl-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4a]OTf**) (100 MHz, $\text{DMSO}-d_6$, 298 K).

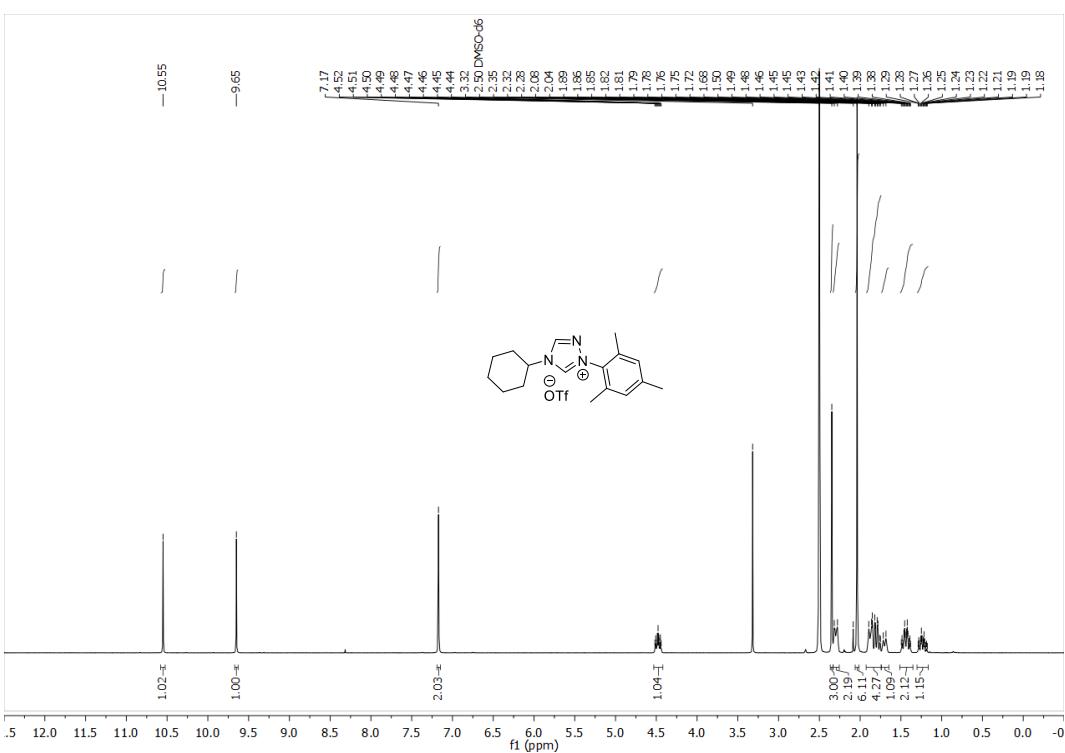


Figure S072: ^1H NMR spectrum of 4-cyclohexyl-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4b]OTf**) (400 MHz, $\text{DMSO}-d_6$, 298 K).

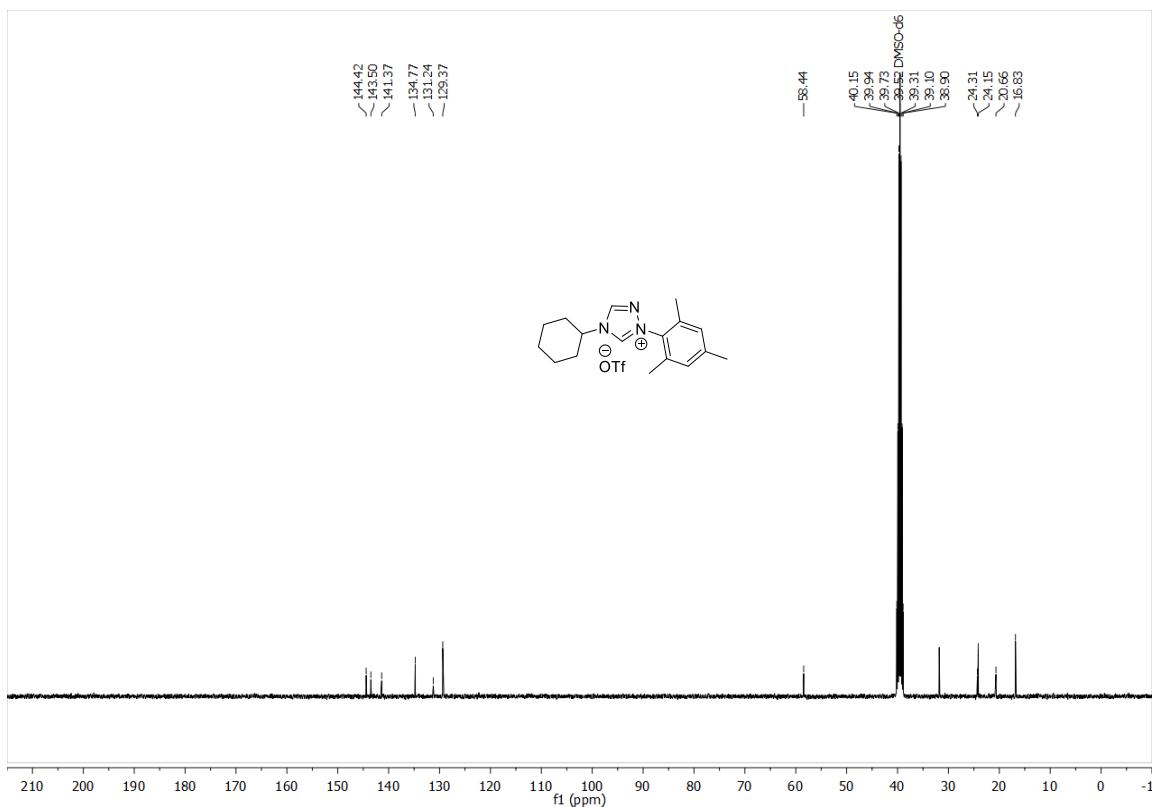


Figure S073: ^{13}C NMR spectrum of 4-cyclohexyl-1-mesityl-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate (**[4b]OTf**) (100 MHz, DMSO-d_6 , 298 K).

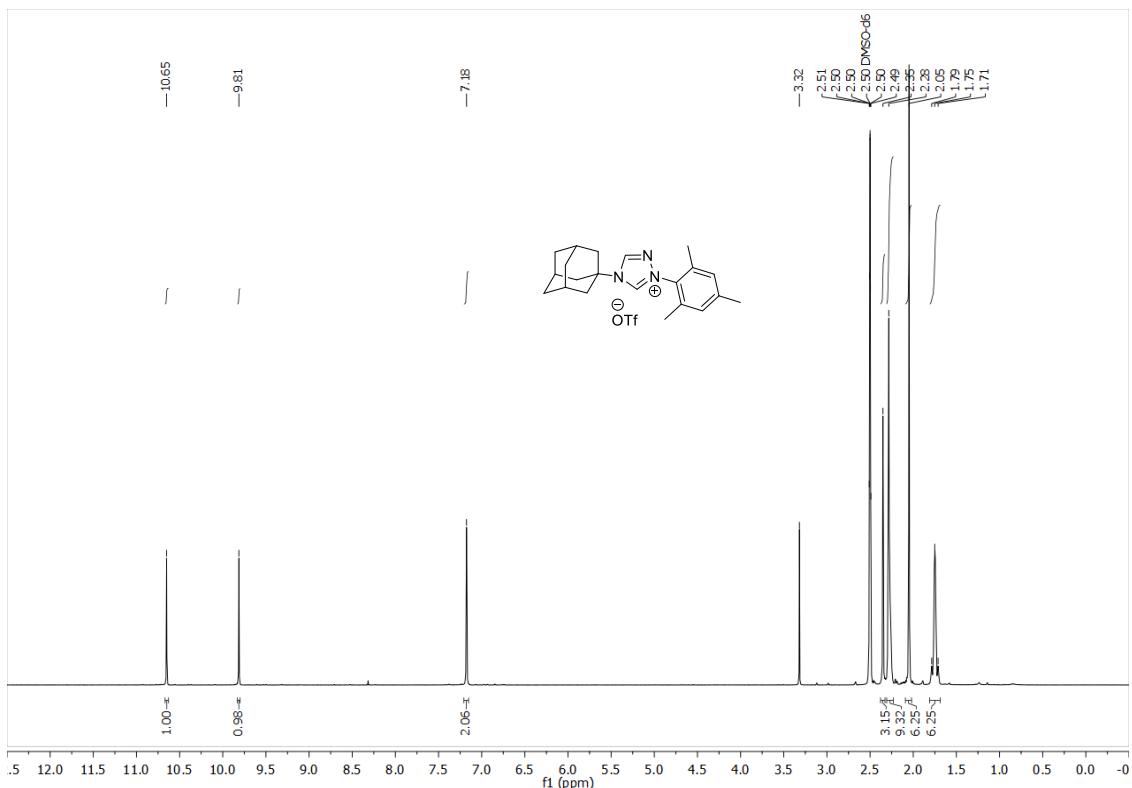


Figure S074: ^1H NMR spectrum of 4-((3s,5s,7s)-adamantan-1-yl)-1-mesityl-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate (**[4c]OTf**) (400 MHz, DMSO-d_6 , 298 K).

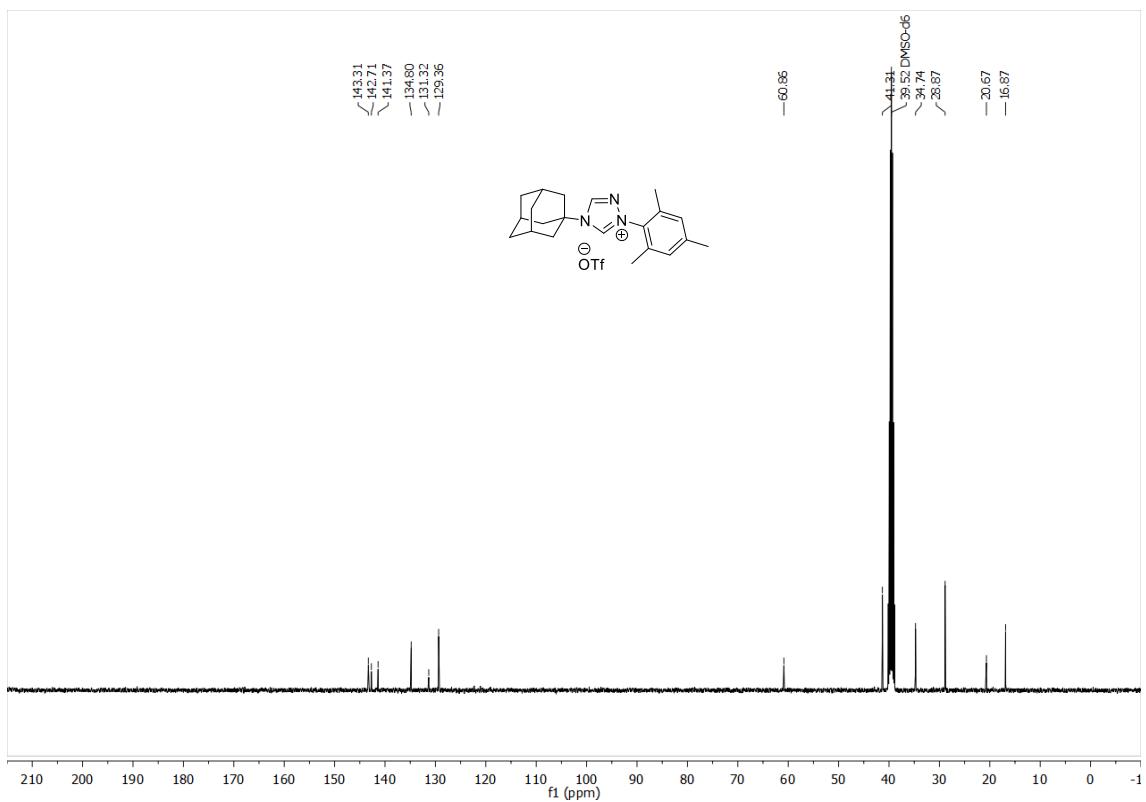


Figure S075: ^{13}C NMR spectrum of 4-((3s,5s,7s)-adamantan-1-yl)-1-mesityl-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate ([4c]OTf) (100 MHz, DMSO-*d*₆, 298 K).

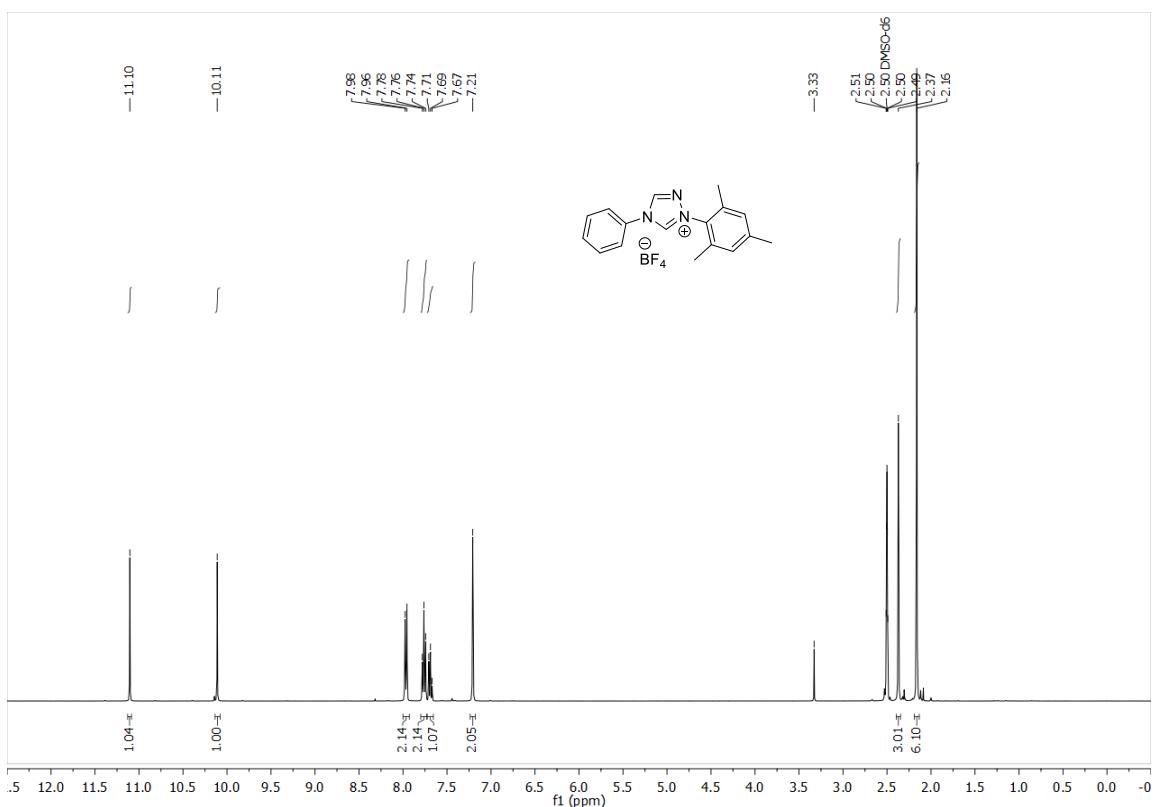


Figure S076: ^1H NMR spectrum of 1-mesityl-4-phenyl-4H-1,2,4-triazol-1-i um tetrafluoroborate ([4d]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

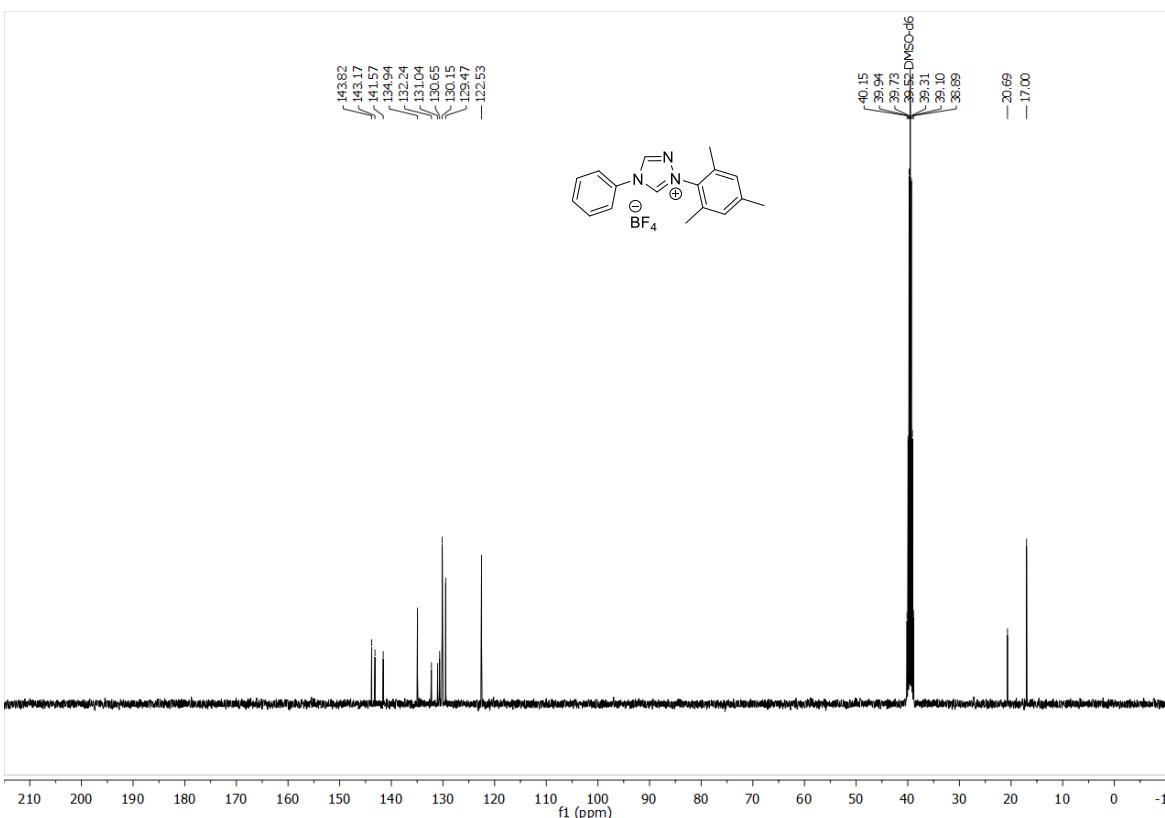


Figure S077: ^{13}C NMR spectrum of 1-mesityl-4-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[4d]BF₄**) (100 MHz, DMSO-*d*₆, 298 K).

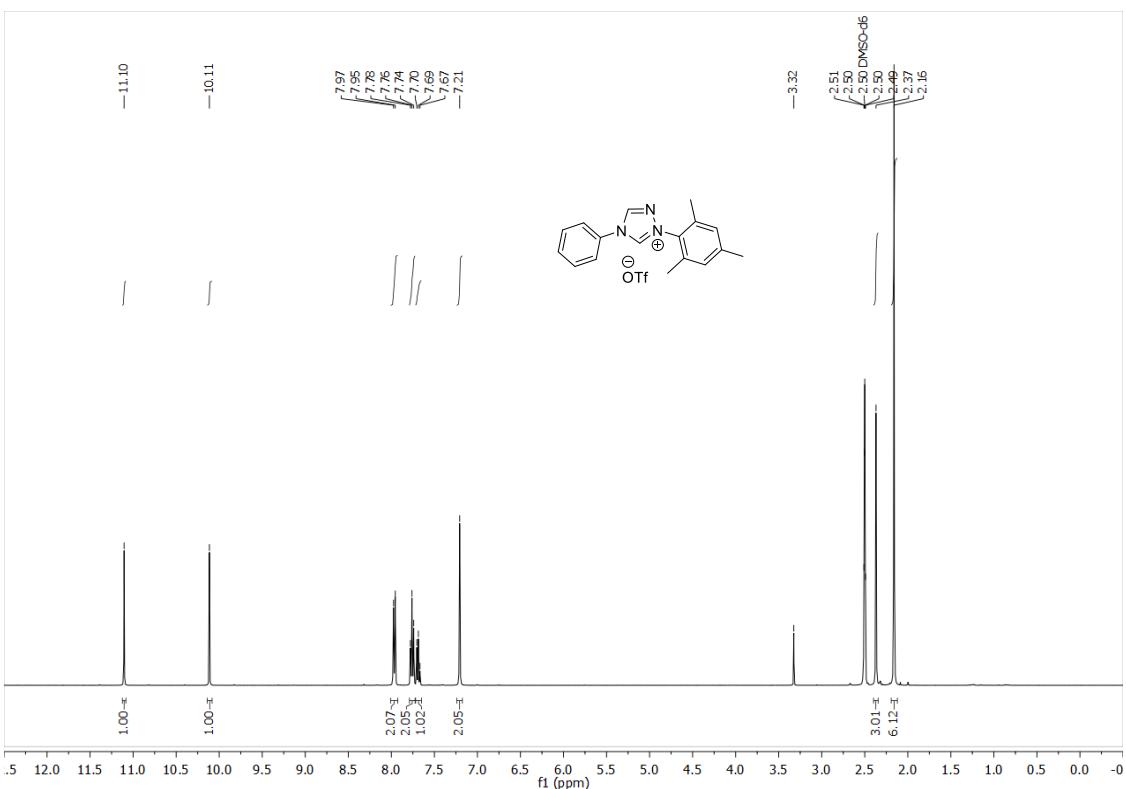


Figure S078: ^1H NMR spectrum of 1-mesityl-4-phenyl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate (**[4d]OTf**) (400 MHz, DMSO-*d*₆, 298 K).

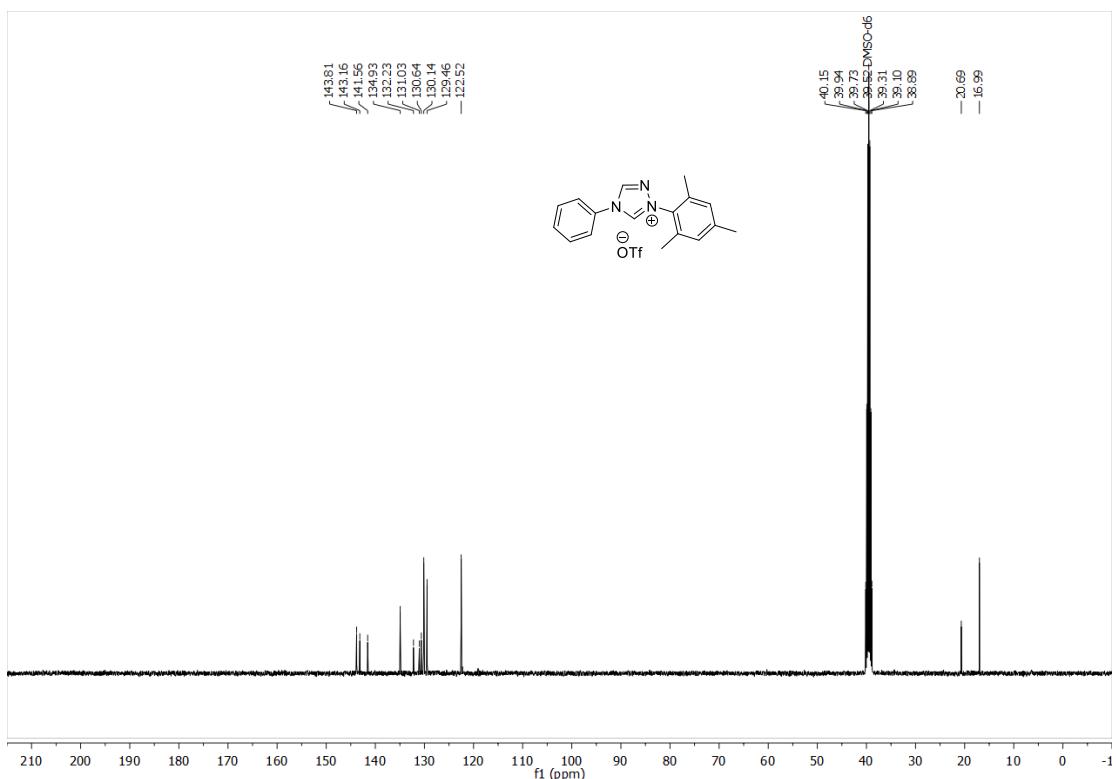


Figure S079: ^{13}C NMR spectrum of 1-mesyl-4-phenyl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4d]OTf**) (100 MHz, $\text{DMSO}-d_6$, 298 K).

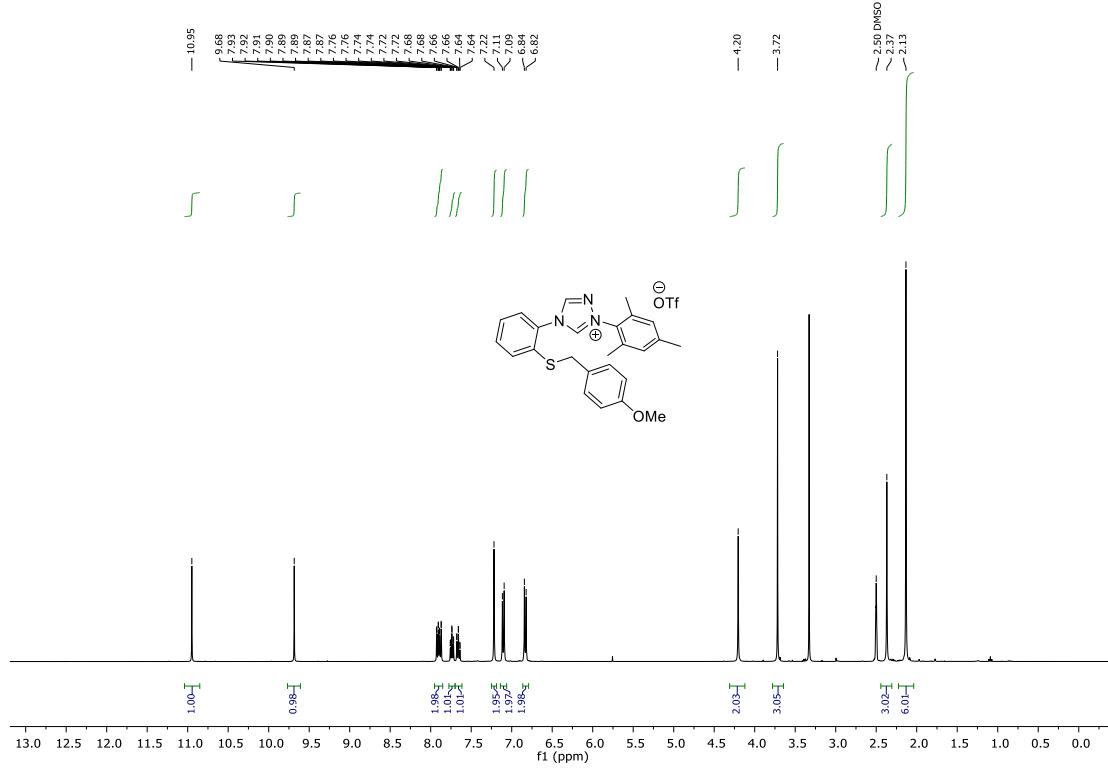


Figure S080: ^1H NMR spectrum of 1-mesityl-4-(2-((4-methoxybenzyl)thio)phenyl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([**4f**]OTf) (400 MHz, DMSO-*d*₆, 298 K).

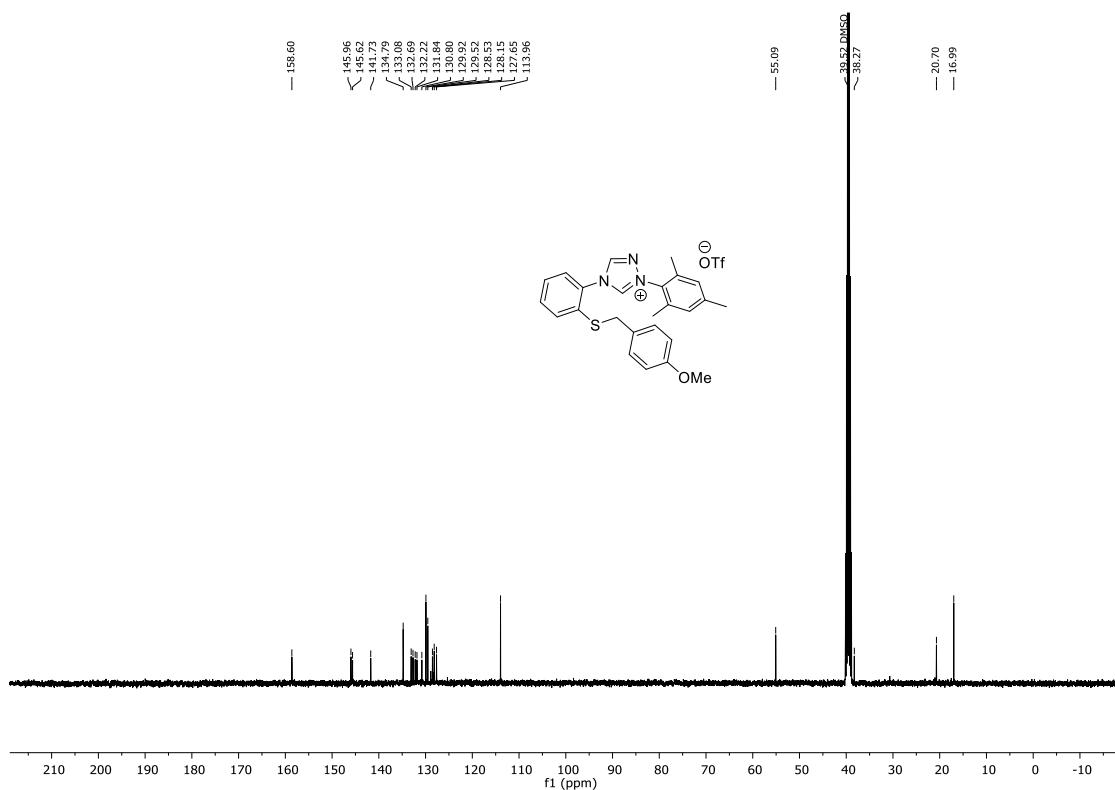


Figure S081: ^{13}C NMR spectrum of 1-mesityl-4-(2-((4-methoxybenzyl)thio)phenyl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ($[4\mathbf{f}]\text{OTf}$) (100 MHz, $\text{DMSO}-d_6$, 298 K).

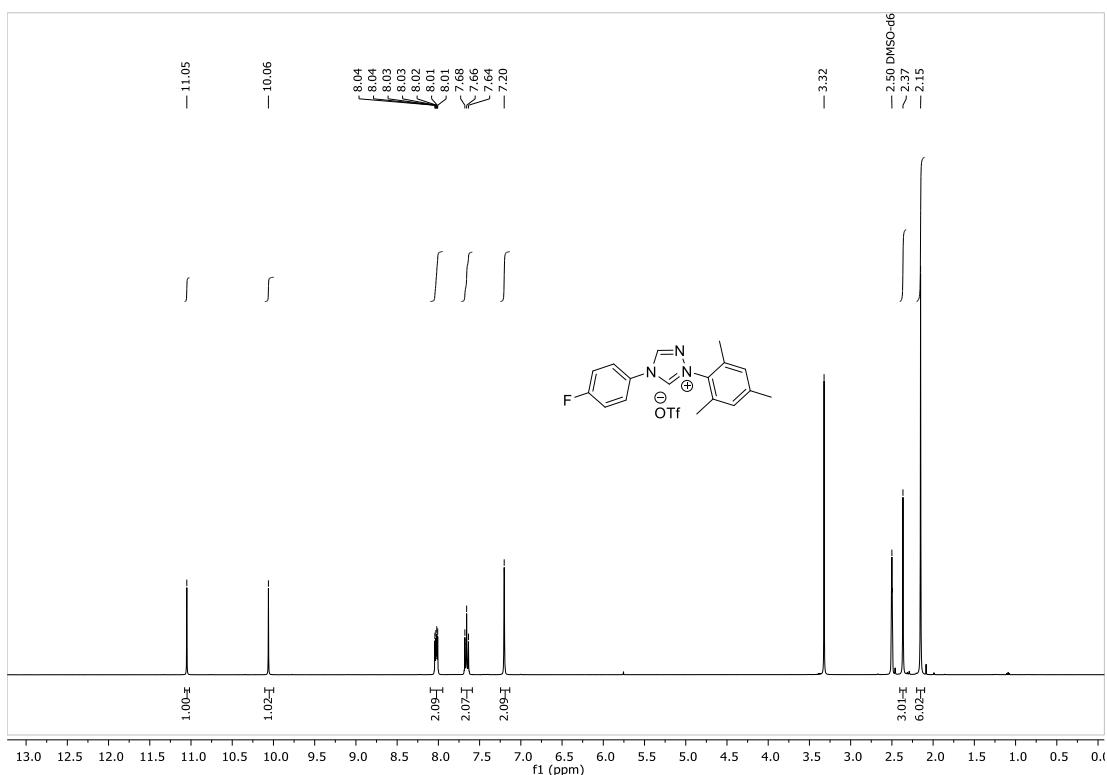


Figure S082: ^1H NMR spectrum of 4-(4-fluorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ($[4\mathbf{i}]\text{OTf}$) (400 MHz, $\text{DMSO}-d_6$, 298 K).

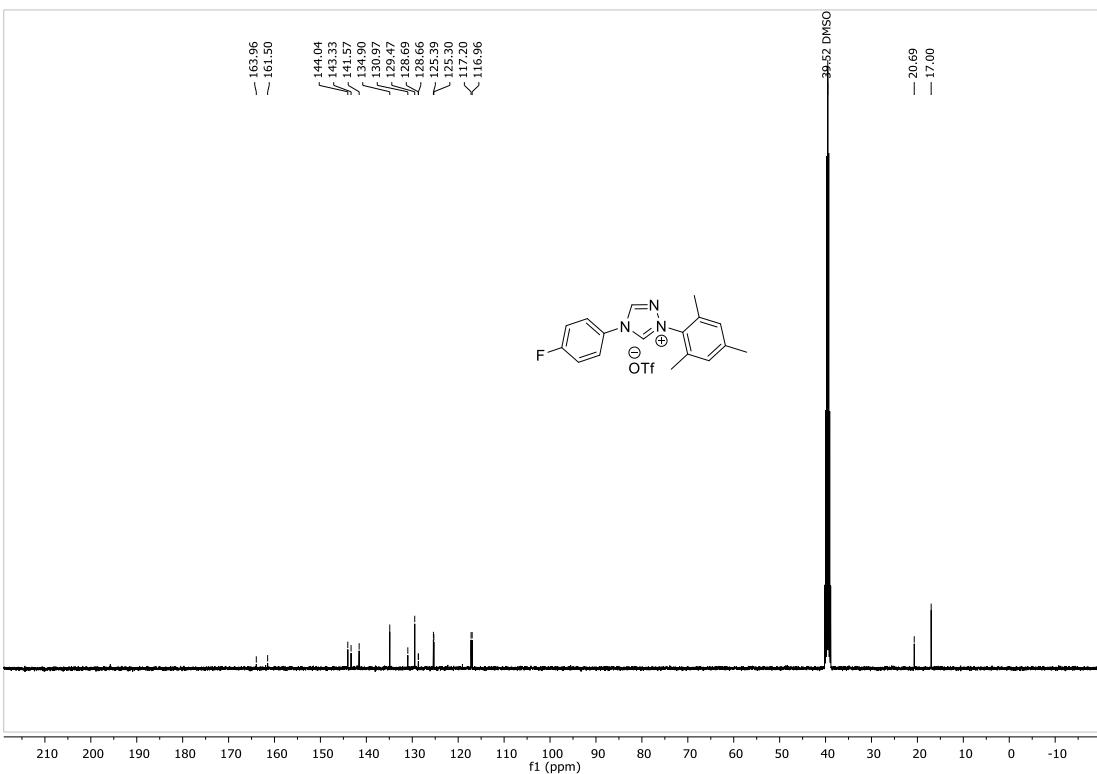


Figure S083: ^{13}C NMR spectrum of 4-(4-fluorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4i]OTf**) (100 MHz, $\text{DMSO}-d_6$, 298 K).



Figure S084: ^{19}F NMR spectrum of 4-(4-fluorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4i]OTf**) (376 MHz, $\text{DMSO}-d_6$, 298 K).

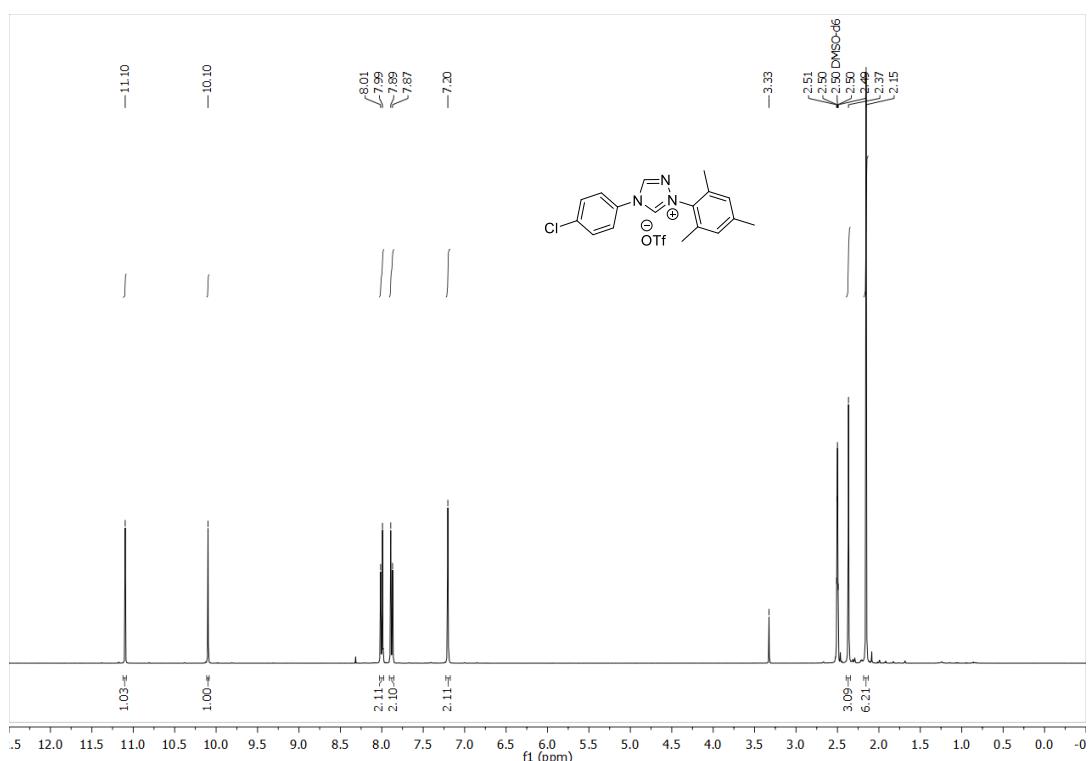


Figure S085: ^1H NMR spectrum of 4-(4-chlorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4k]OTf**) (400 MHz, $\text{DMSO}-d_6$, 298 K).

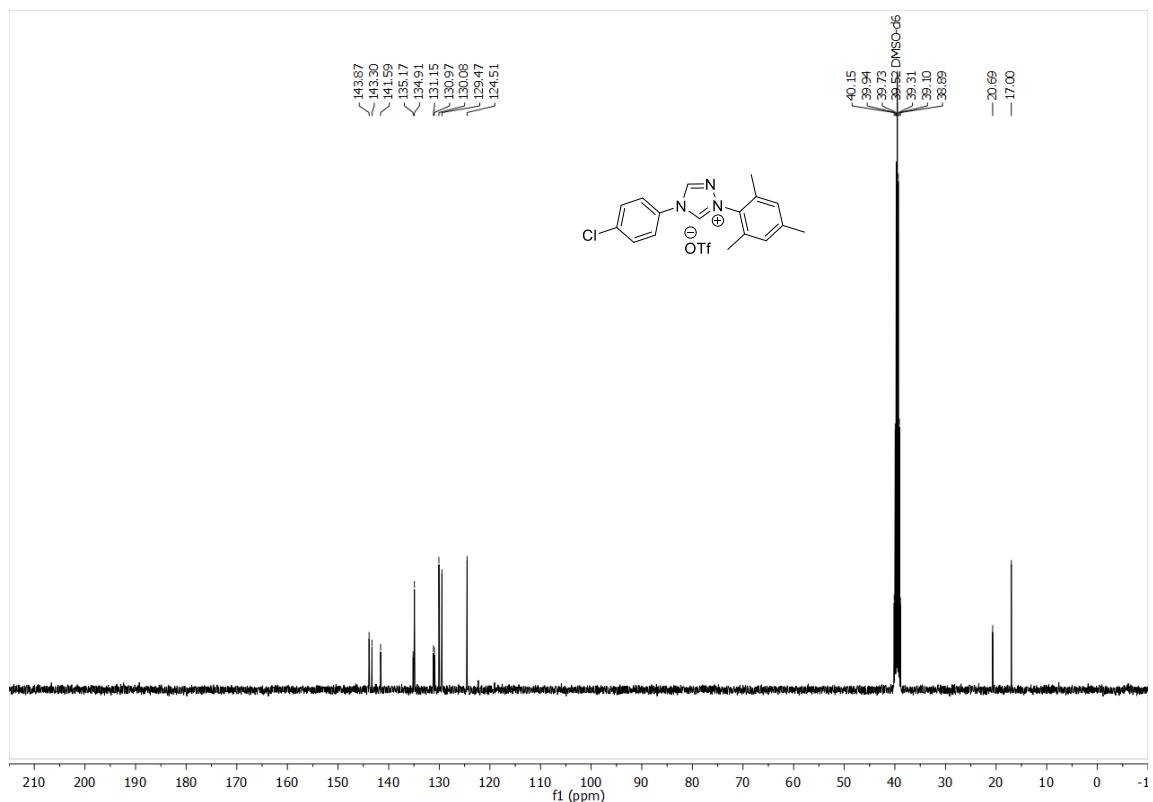


Figure S086: ^{13}C NMR spectrum of 4-(4-chlorophenyl)-1-mesityl-4*H*-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[4k]OTf**) (100 MHz, $\text{DMSO}-d_6$, 298 K).

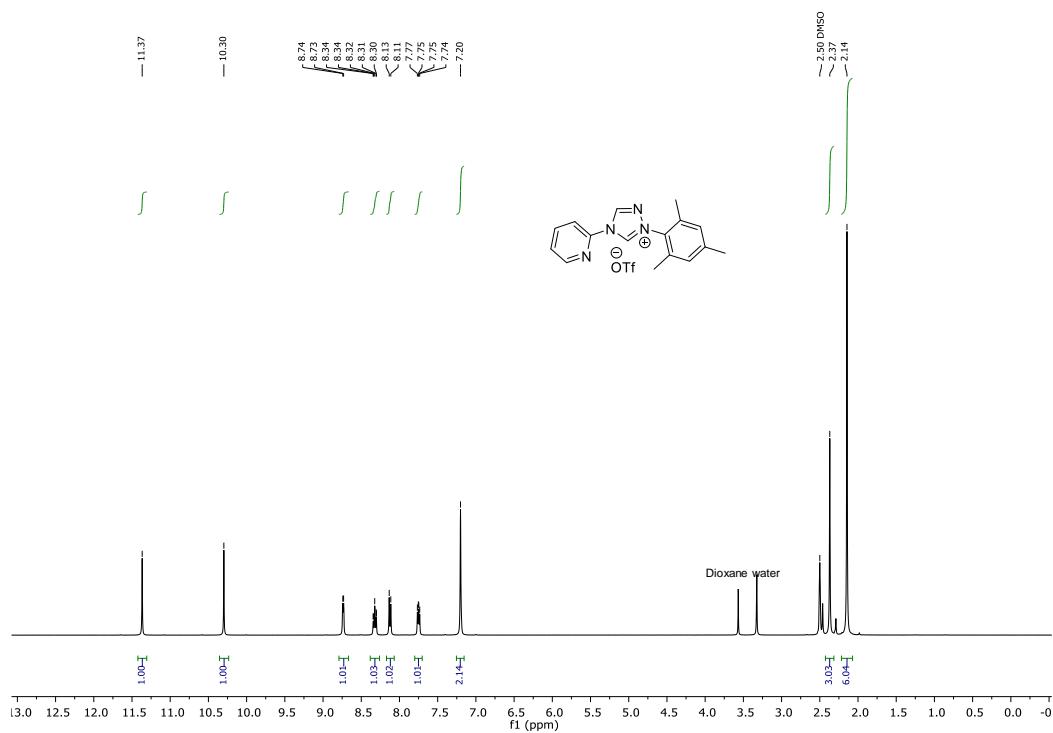


Figure S087: ¹H NMR spectrum of 1-mesityl-4-(pyridin-2-yl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4l]OTf) (400 MHz, DMSO-*d*₆, 298 K).

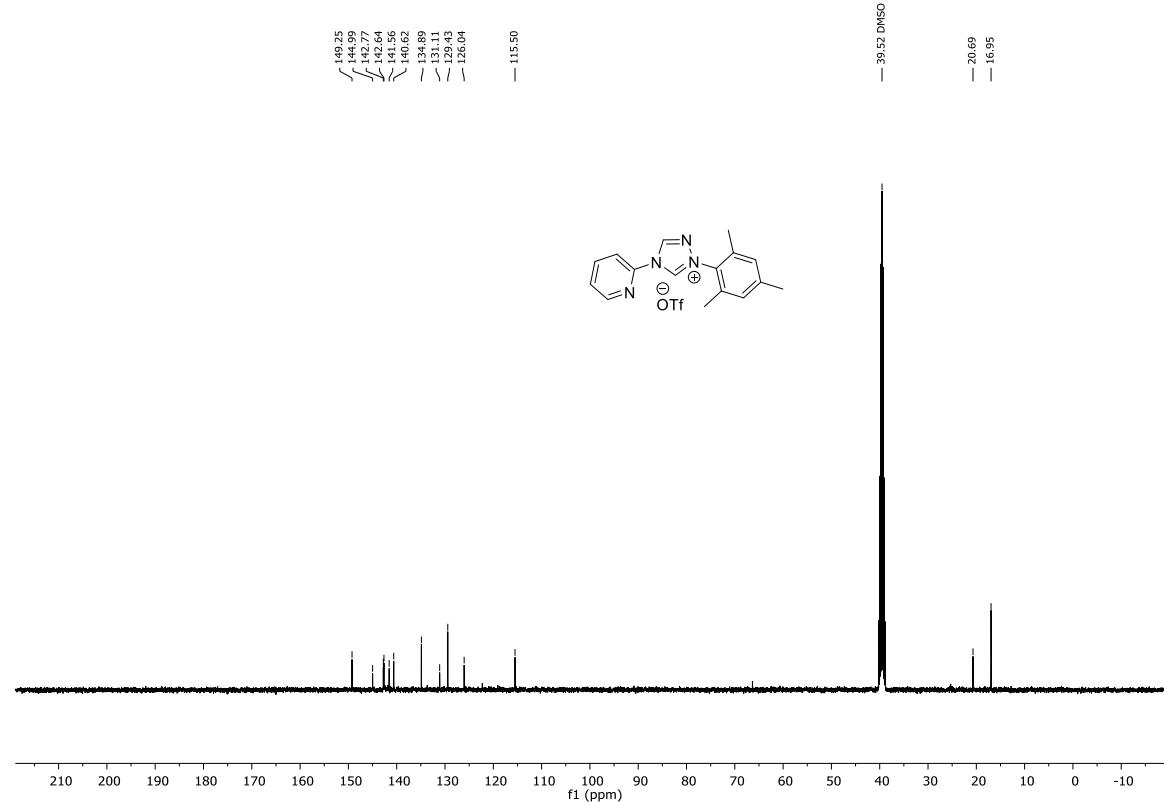


Figure S088: ¹³C NMR spectrum of 1-mesityl-4-(pyridin-2-yl)-4*H*-1,2,4-triazol-1-ium trifluoromethanesulfonate ([4l]OTf) (100 MHz, DMSO-*d*₆, 298 K).

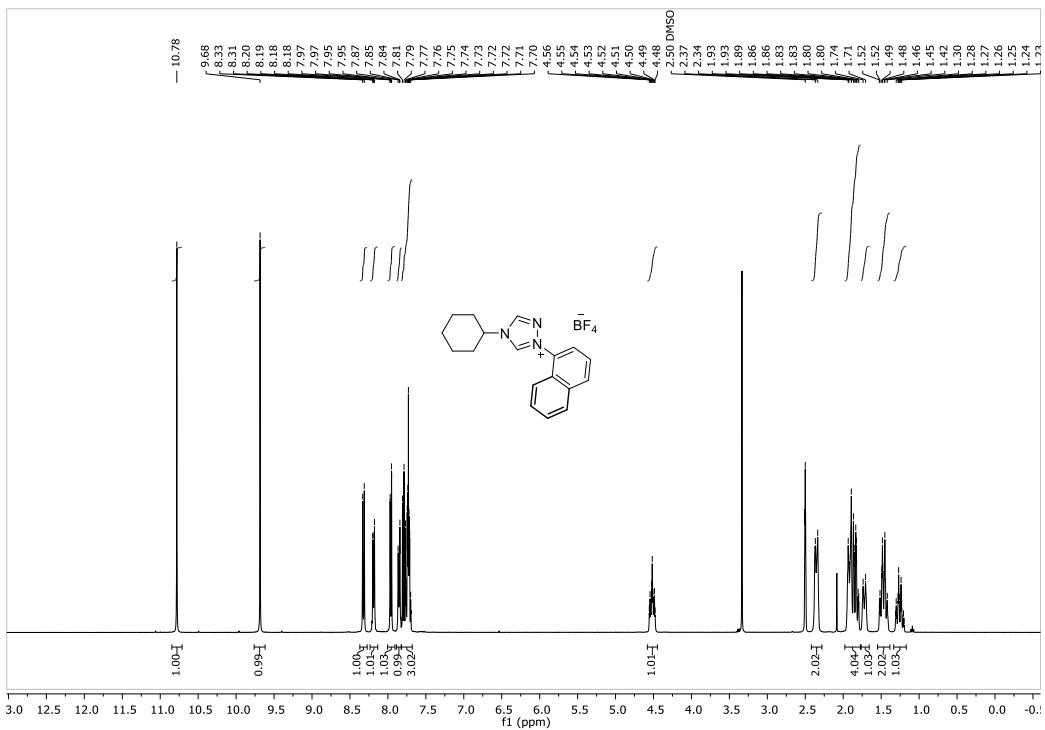


Figure S089: ^1H NMR spectrum of 4-cyclohexyl-1-(naphthalen-1-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[5b]BF₄**) (400 MHz, DMSO- d_6 , 298 K).

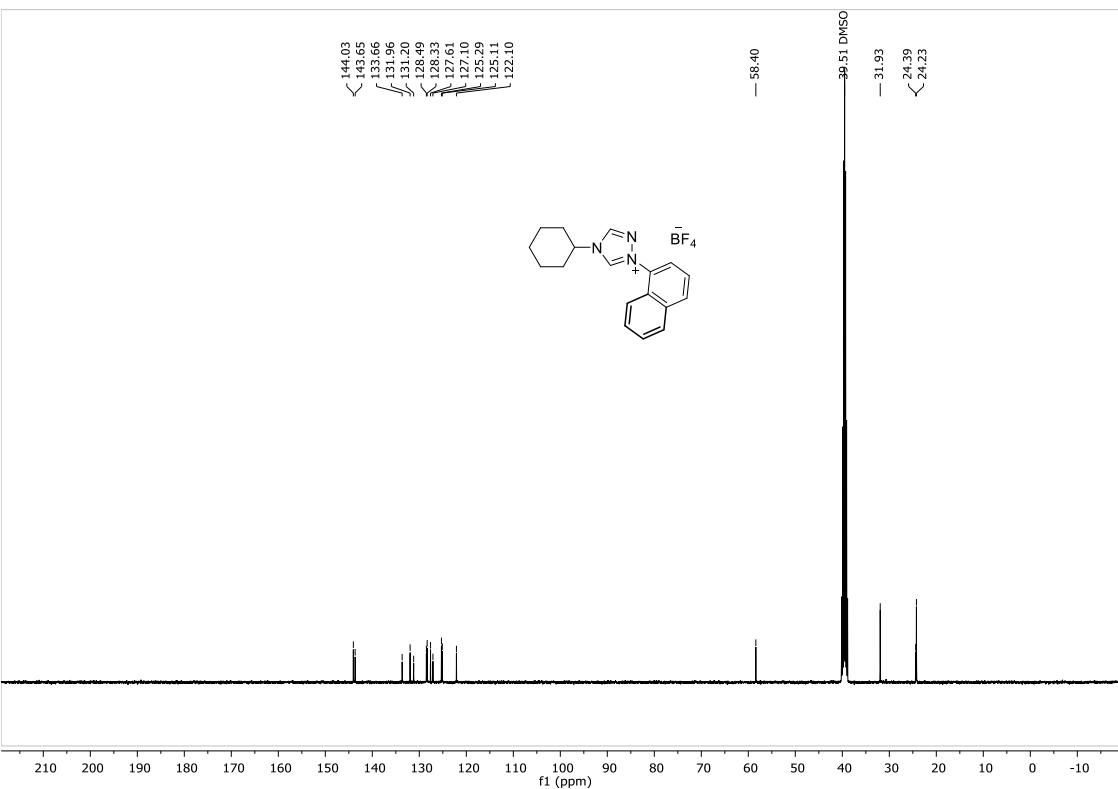


Figure S090: ^{13}C NMR spectrum of 4-cyclohexyl-1-(naphthalen-1-yl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[5b]BF₄**) (100 MHz, DMSO- d_6 , 298 K).

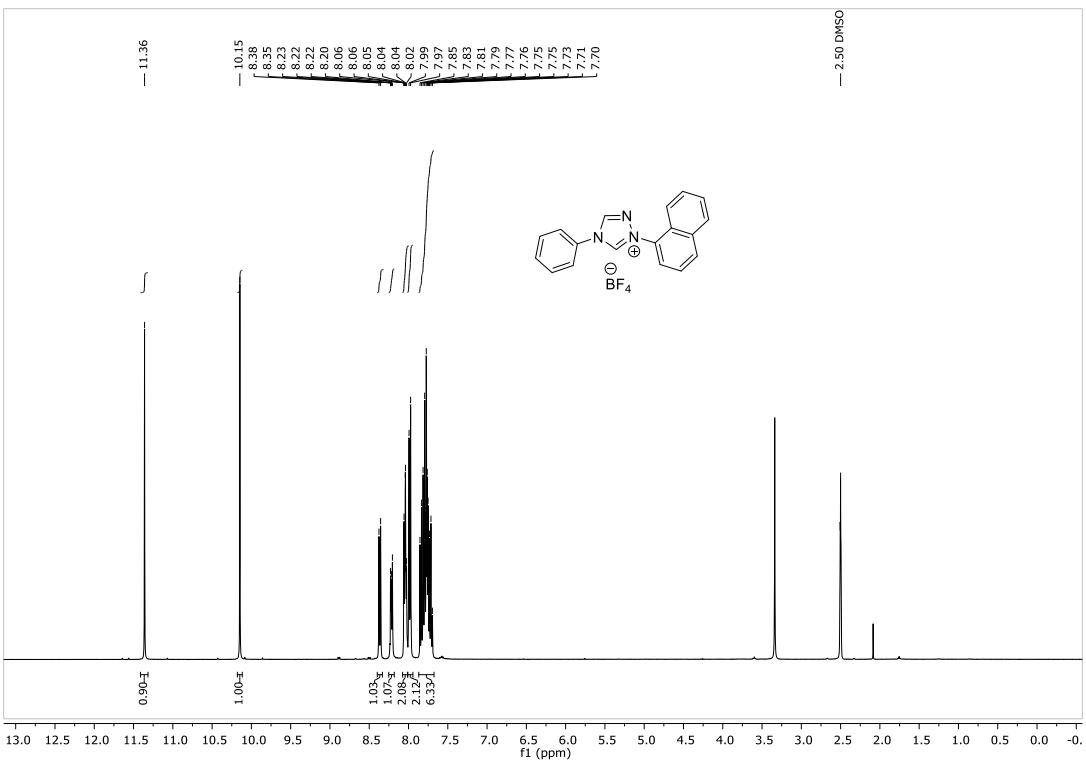


Figure S091: ¹H NMR spectrum of 1-(naphthalen-1-yl)-4-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([5d]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

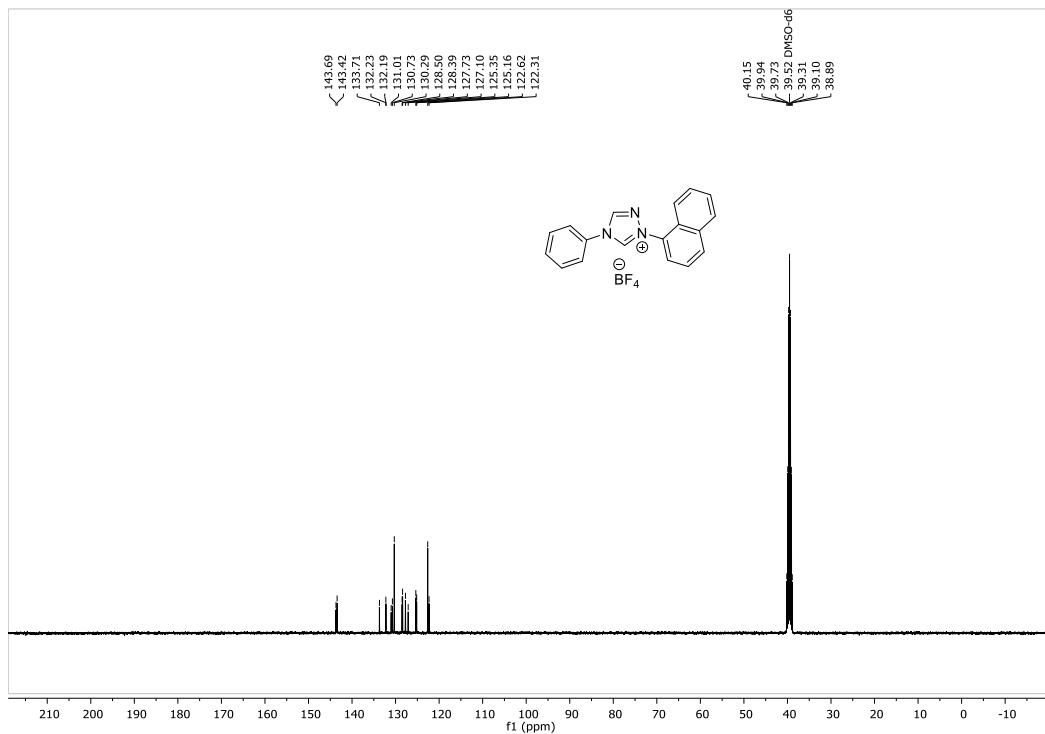


Figure S092: ¹³C NMR spectrum of 1-(naphthalen-1-yl)-4-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([5d]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

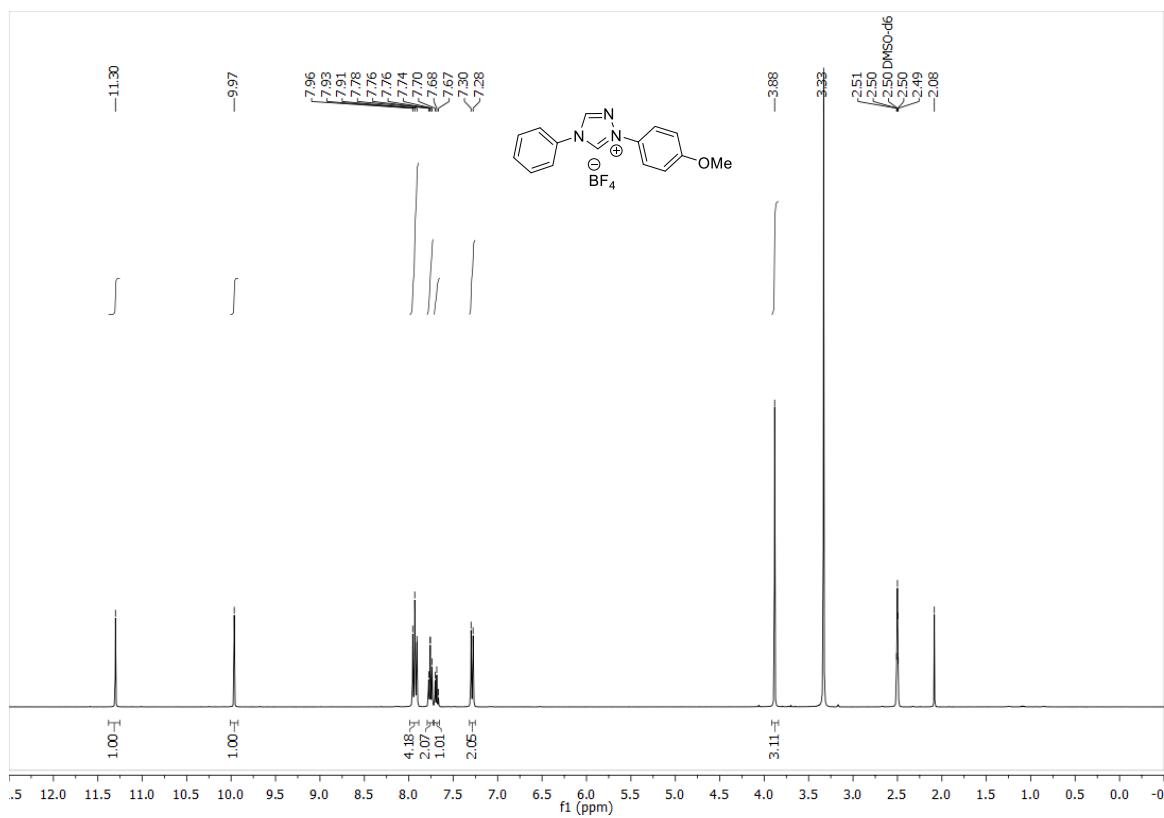


Figure S093: ¹H NMR spectrum of 1-(4-methoxyphenyl)-4-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([6d]BF₄) (400 MHz, DMSO-*d*₆, 298 K).

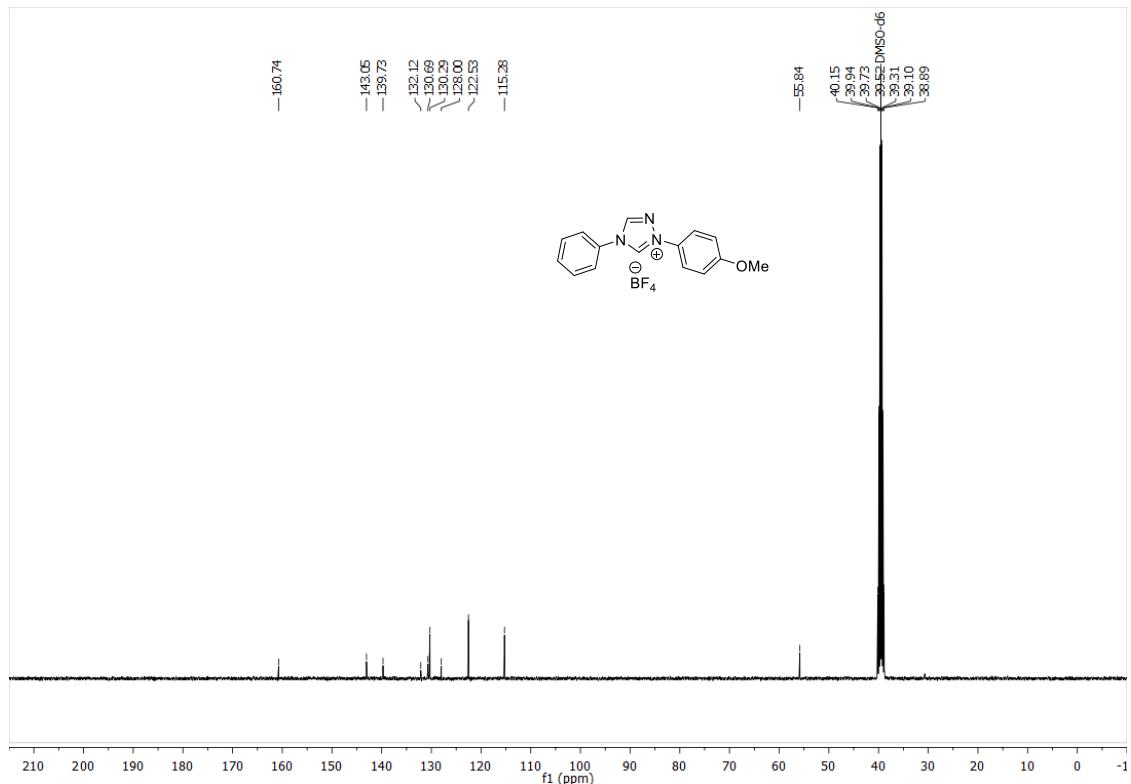


Figure S094: ¹³C NMR spectrum of 1-(4-methoxyphenyl)-4-phenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate ([6d]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

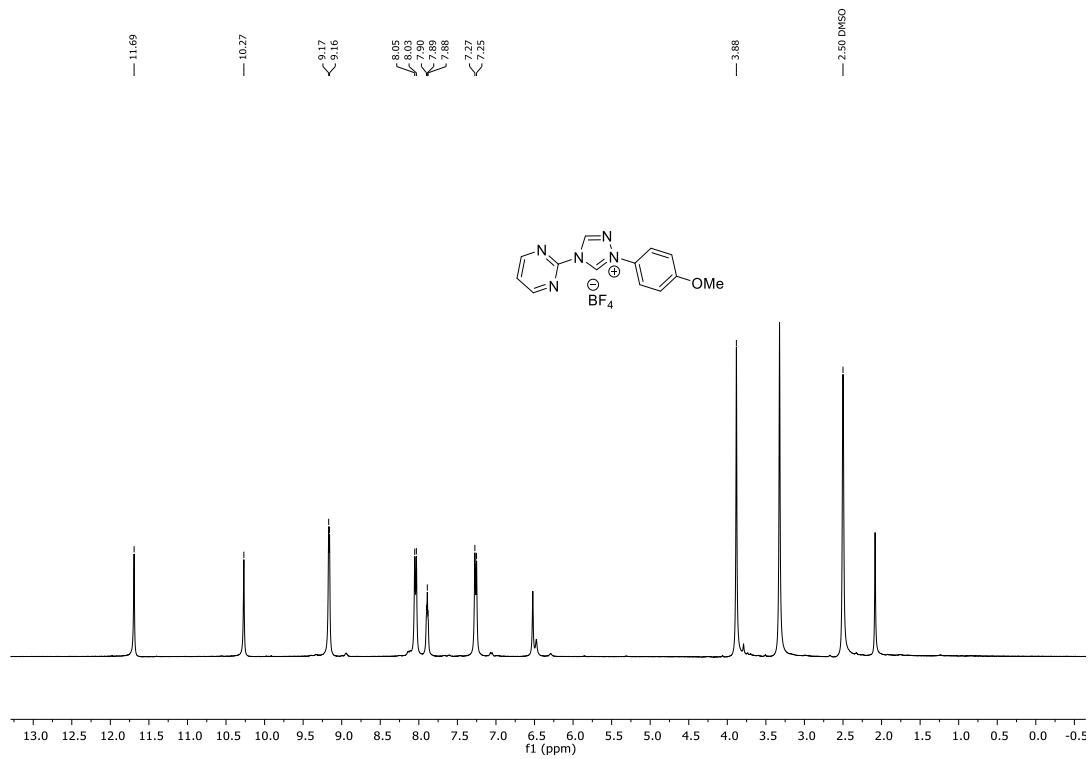


Figure S095: ^1H NMR spectrum of 1-(4-methoxyphenyl)-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ([6m]BF₄) (400 MHz, DMSO-*d*₆, 298 K). The impurities around 6.6 ppm were introduced during the extraction with (impure) acetone and could not be removed by recrystallization.

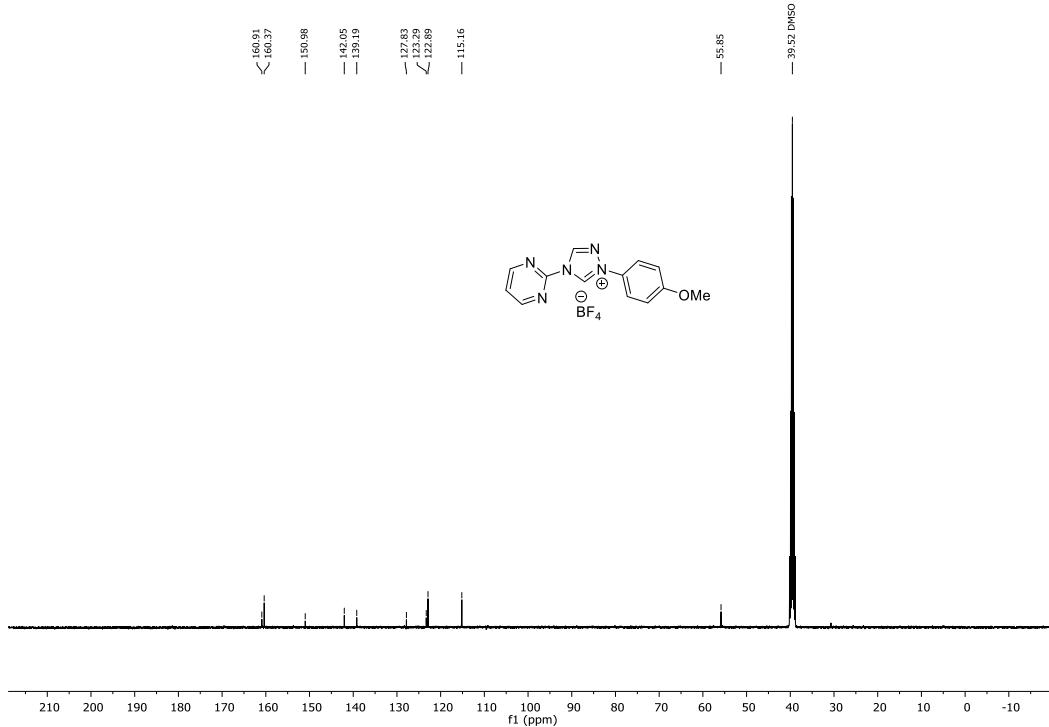


Figure S096: ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-4-(pyrimidin-2-yl)-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ([6m]BF₄) (100 MHz, DMSO-*d*₆, 298 K).

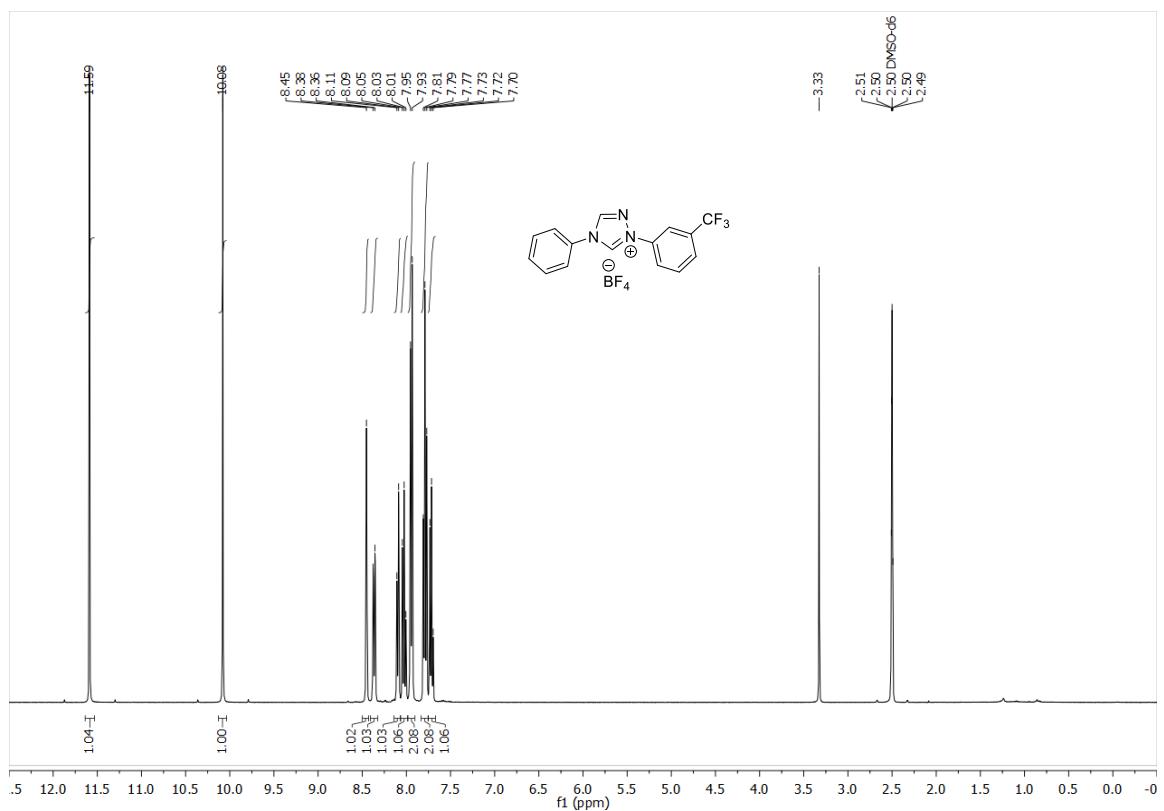


Figure S097: ^1H NMR spectrum of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ([7d] BF_4^-) (400 MHz, $\text{DMSO}-d_6$, 298 K).

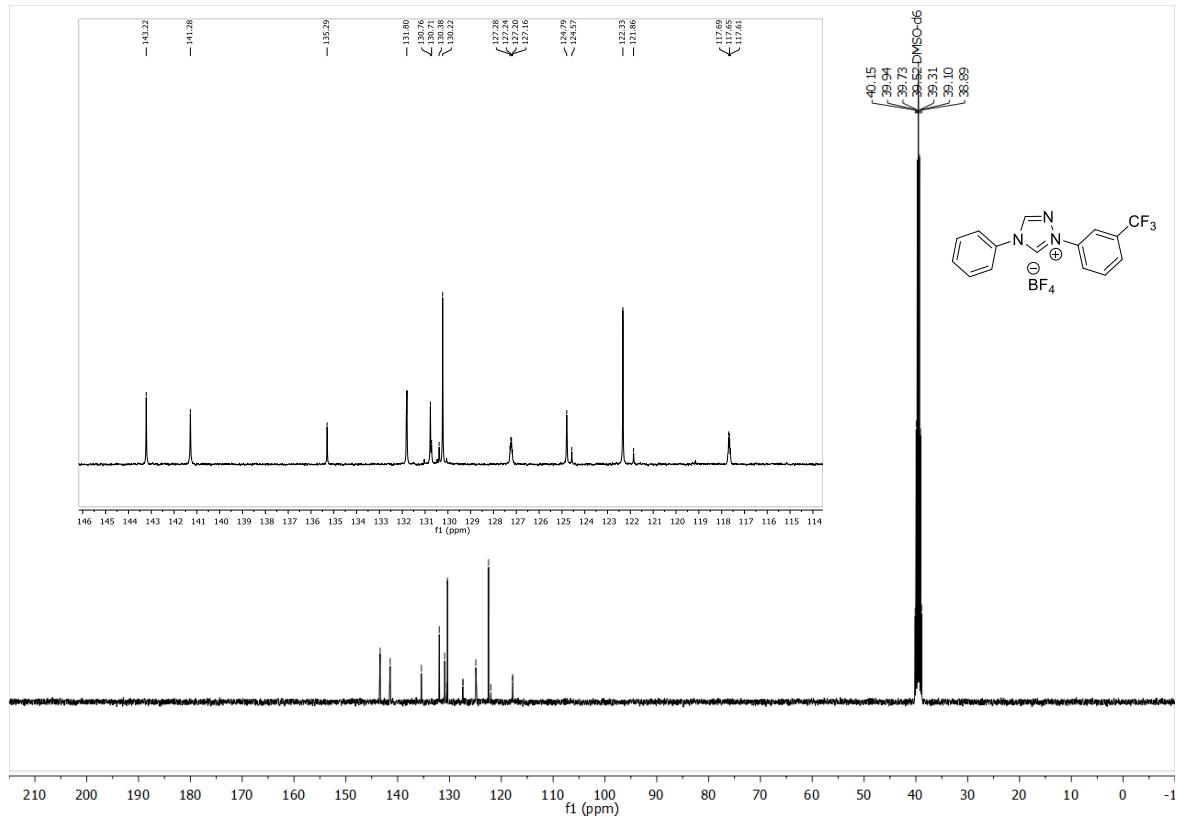


Figure S098: ^{13}C NMR spectrum of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-i um tetrafluoroborate ([7d] BF_4^-) (100 MHz, $\text{DMSO}-d_6$, 298 K).

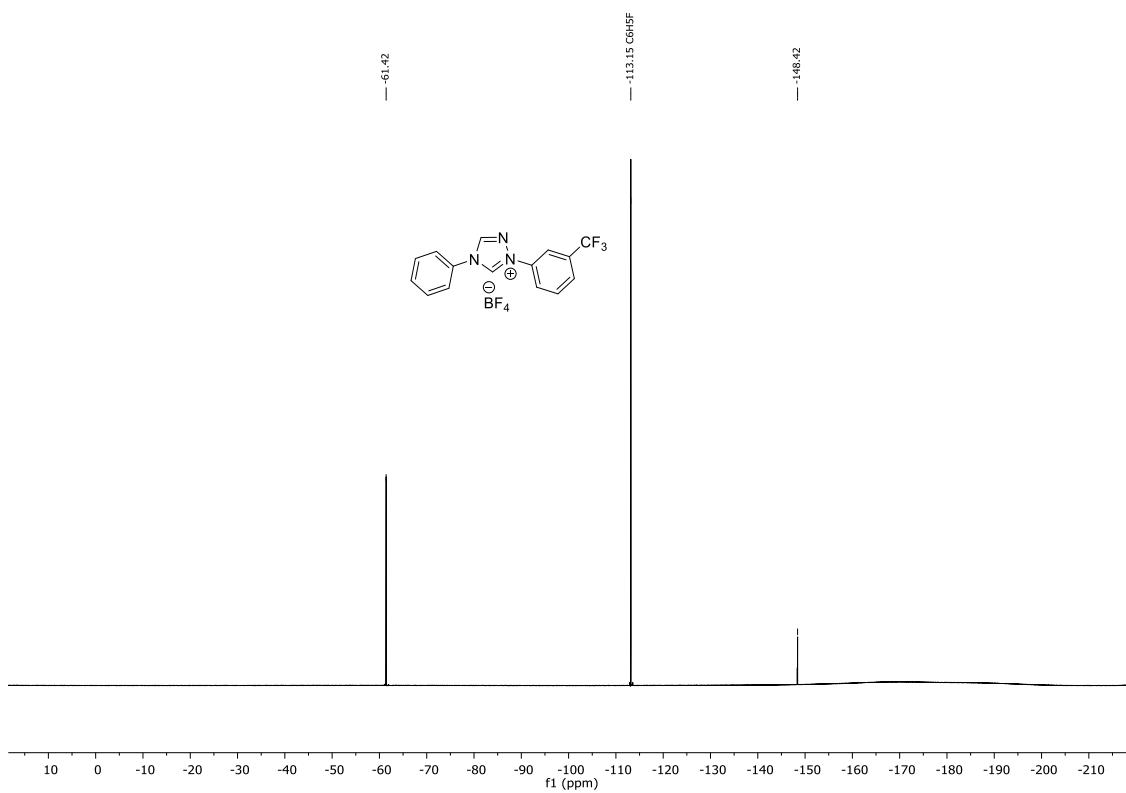


Figure S099: ^{19}F NMR spectrum of 4-phenyl-1-(3-(trifluoromethyl)phenyl)-4*H*-1,2,4-triazol-1-ium tetrafluoroborate (**[7d]BF₄**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

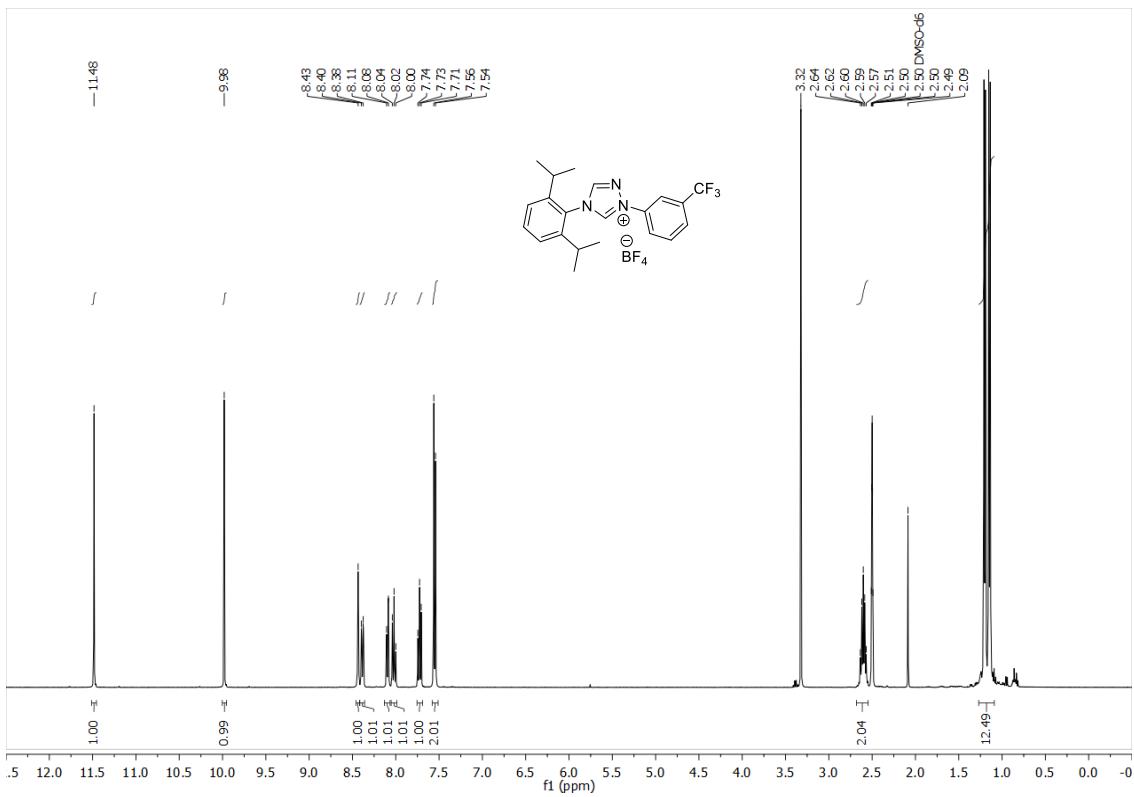


Figure S100: ^1H NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(trifluoromethyl)phenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate (**[7e]BF₄**) (400 MHz, DMSO-*d*₆, 298 K).

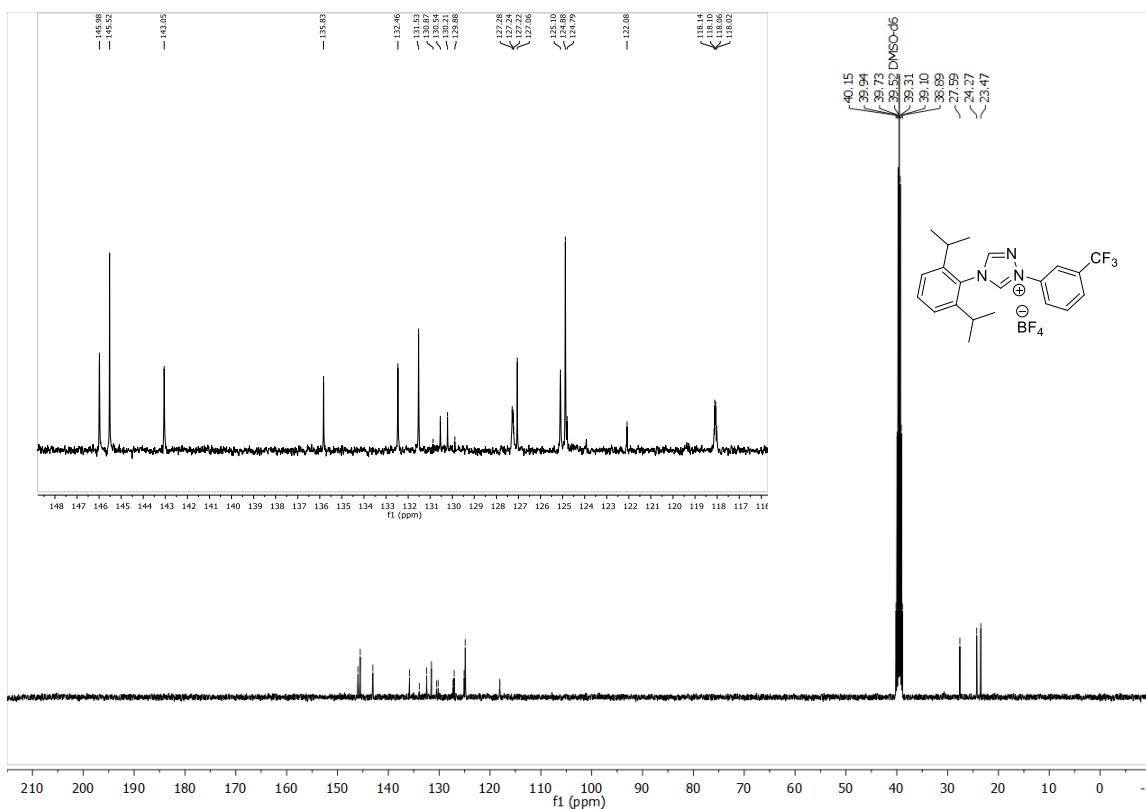


Figure S101: ^{13}C NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)phenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[7\text{e}]\text{BF}_4$) (100 MHz, $\text{DMSO}-d_6$, 298 K).

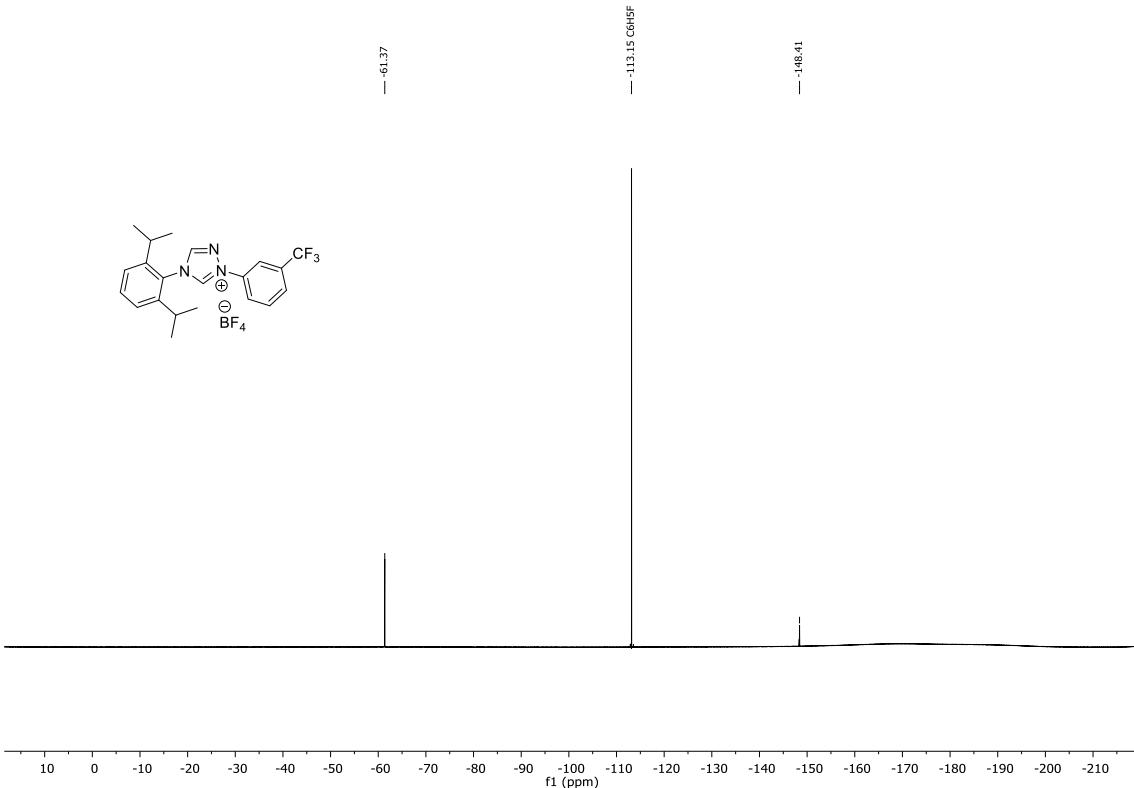


Figure S102: ^{19}F NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)phenyl)-4H-1,2,4-triazol-1-ium tetrafluoroborate ($[7\text{e}]\text{BF}_4$) (376 MHz, $\text{DMSO}-d_6$, 298 K, referenced to fluorobenzene).

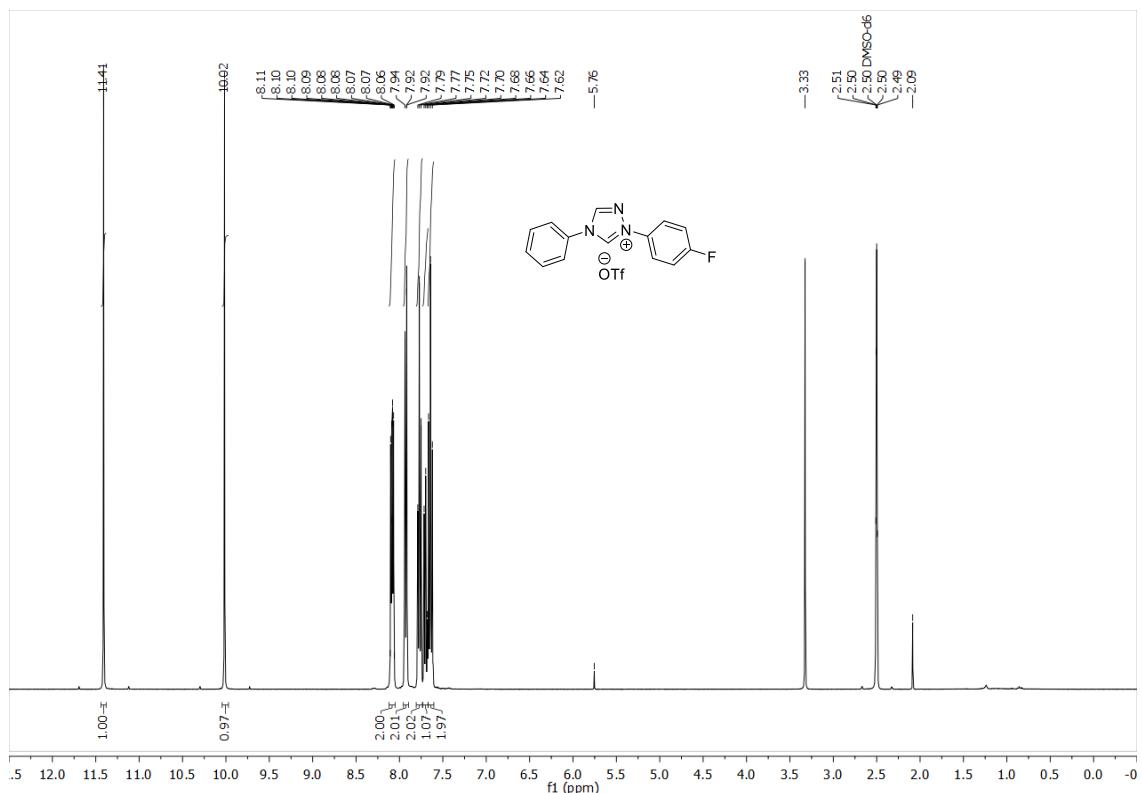


Figure S103: ¹H NMR spectrum of 1-(4-fluorophenyl)-4-phenyl-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate ([8d]OTf) (400 MHz, DMSO-*d*₆, 298 K).

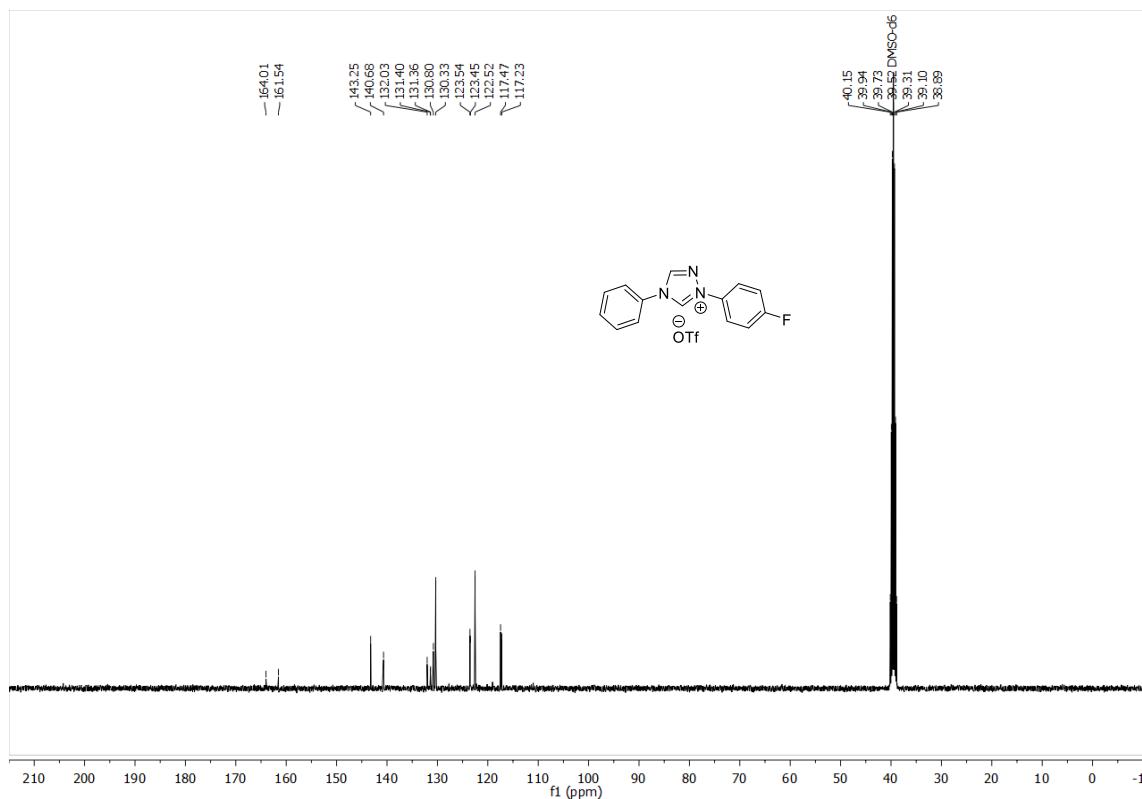


Figure S104: ¹³C NMR spectrum of 1-(4-fluorophenyl)-4-phenyl-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate ([8d]OTf) (100 MHz, DMSO-*d*₆, 298 K).

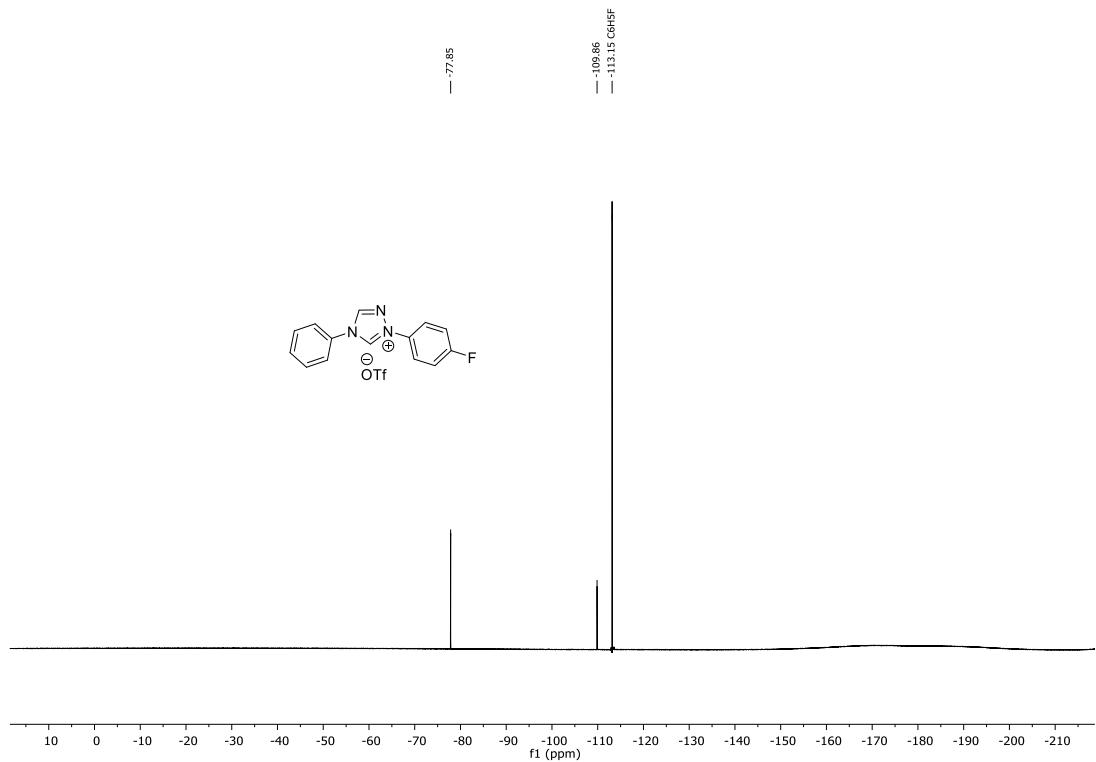


Figure S105: ¹⁹F NMR spectrum of 1-(4-fluorophenyl)-4-phenyl-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate (**[8d]OTf**) (376 MHz, DMSO-*d*₆, 298 K, referenced to fluorobenzene).

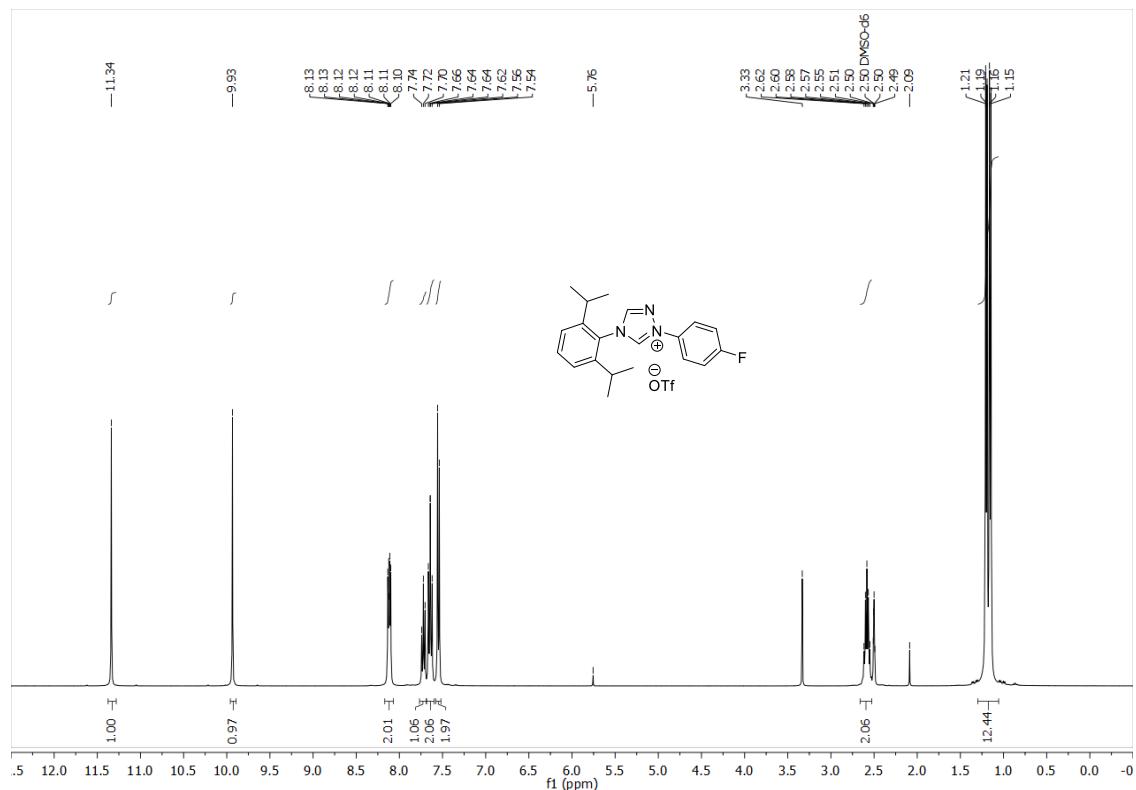


Figure S106: ¹H NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4H-1,2,4-triazol-1-ium trifluoromethanesulfonate (**[8e]OTf**) (400 MHz, DMSO-*d*₆, 298 K).

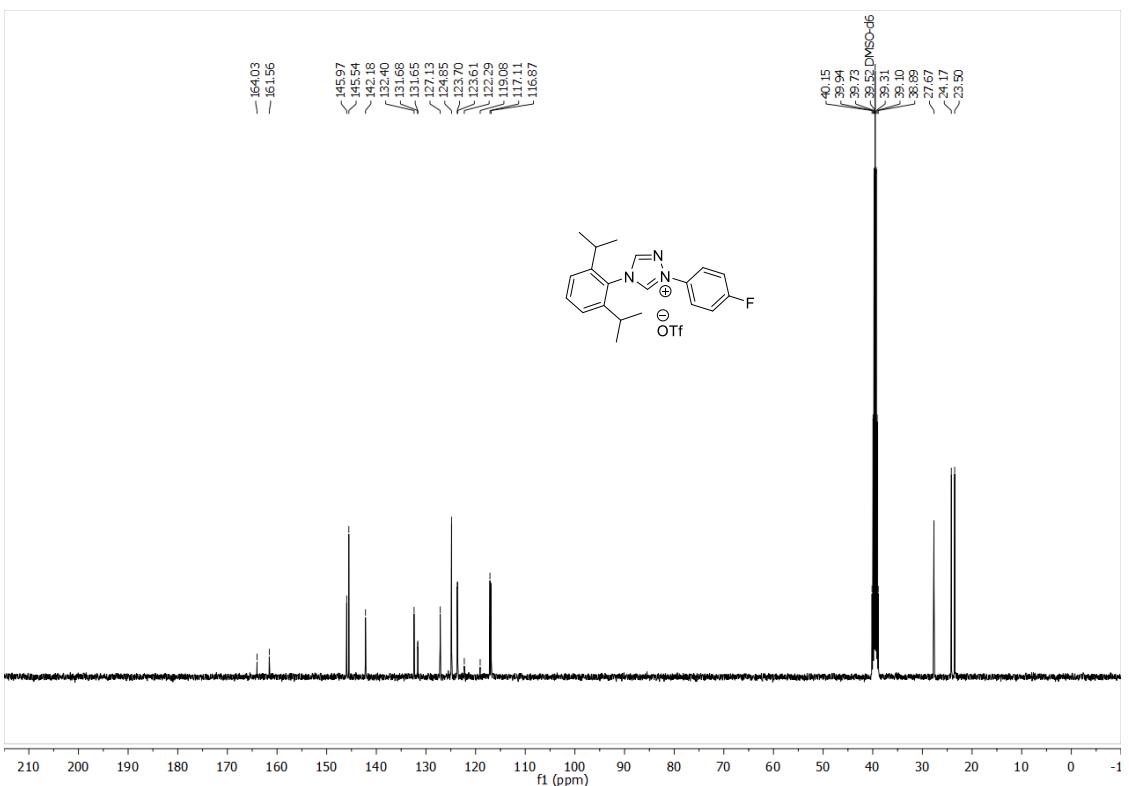


Figure S107: ^{13}C NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[8e]OTf**) (100 MHz, $\text{DMSO}-d_6$, 298 K).



Figure S108: ^{19}F NMR spectrum of 4-(2,6-diisopropylphenyl)-1-(4-fluorophenyl)-4H-1,2,4-triazol-1-i um trifluoromethanesulfonate (**[8e]OTf**) (376 MHz, $\text{DMSO}-d_6$, 298 K, referenced to fluorobenzene).