Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Tunable chiral triazole-based halogen bond donors: assessment of donor strength in solution with nitrogen-containing acceptors

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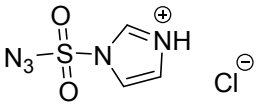
I) Synthetic procedures

General Information

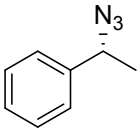
NMR spectra were measured on a Bruker Avance III 400 MHz instrument. The spectra are reported in parts per million (δ) referenced to the residual solvent signal [$CDCl_3$ δ = 7.26 ppm, CD_3OD δ = 3.31 ppm, [D_6]DMSO δ = 2.50 ppm, [D_6]Acetone δ = 2.05 ppm (for ^{1}H NMR), $CDCl_3$ δ = 77.16 ppm, CD_3OD δ = 49.00 ppm, [D_6]DMSO δ = 39.52 ppm, [D_6]Acetone δ = 29.84 ppm (for ^{13}C NMR)]). High resolution mass spectra were recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS spectrometer with AJ-ESI ionization. Optical rotations were obtained using an Anton Paar GWB Polarimeter MCP 500. Infrared absorption frequencies in wavenumbers are listed, with the relative strength in parentheses (w = weak, m = medium, s = strong, br = broad). Precoated silica gel 60 F_{254} plates from Merck were used for TLC, whereas for column chromatography silica gel Kieselgel 40-63 µm was used. The measured melting points are uncorrected. Purchased chemicals and solvents were used as received. DCM was distilled over phosphorous pentoxide and MeOH was dried by distillation over sodium metal. Petroleum ether (PE) had a boiling point of 40-60°C. The reactions were performed without additional moisture elimination unless stated otherwise.

Imidazole-1-sulfonyl azide hydrochloride (Cas No. 952234-36-5)



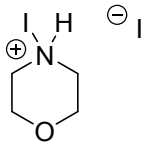
The azidating agent was prepared starting from imidazole, following the literature procedures,[1] and obtained as colourless crystals (9.85 g, 75% yield). ^{1}H NMR (400 MHz, D_2O) δ 9.14, 7.95, 7.53. ^{13}C NMR (101 MHz, D_2O) δ 137.7, 125.1, 119.7.

(*R*)-(1-azidoethyl)benzene (Cas No. 129575-56-0)



The azide was prepared starting from (*R*)-(+)-α-methylbenzylamine, following the literature procedure,[2] and obtained as a colourless liquid (0.72 g, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 4.62 (q, *J* = 6.8 Hz, 1H), 1.54 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 128.9, 128.3, 126.5, 61.2, 21.7.

4-iodomorpholine hydroiodide (Cas No. 120972-13-6)

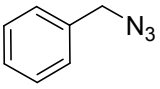


The iodination agent was prepared starting from morpholine, following the literature procedure, [3] and obtained as orange crystals (6.48 g, 84% yield). ^{1}H NMR (400 MHz, [D_6]DMSO) δ 4.06 – 3.79 (broad s, 1H), 3.77 – 3.71 (m, 4H), 3.06 – 2.99 (m, 4H).

***tert*-Butyl azide (Cas No. 13686-33-4)**

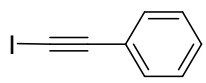
The azide was prepared starting from *tert*-butanol, following the literature procedure,[4] and obtained as a colourless liquid (3.77 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H).

Benzyl azide (Cas No. 622-79-7)



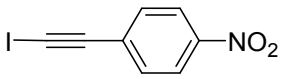
The azide was prepared starting from benzyl bromide, following the literature procedure,[5] and obtained as a colourless liquid (0.62 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 2H), 7.38 – 7.27 (m, 3H), 4.32 (s, 2H).

(Iodoethynyl)benzene (Cas No. 932-88-7)



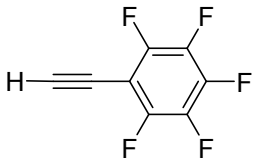
The alkyne was prepared starting from ethynylbenzene, following the literature procedure,[3] and obtained as an orange oil (0.634 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.36 – 7.27 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 128.9, 128.4, 123.5, 94.3, 6.3.

1-(iodoethynyl)-4-nitrobenzene (Cas No. 66535-27-1)



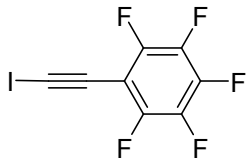
Iodoform (4.10 g, 10.42 mmol), triphenylphosphine (2.87 g, 10.94 mmol) and *t*BuOK (1.11 g, 9.93 mmol) were added to THF (20 mL) under argon atmosphere. The suspension was stirred at r.t. for 5 minutes and turned brown. 4-nitrobenzaldehyde (0.75 g, 4.96 mmol) was added. After 30 minutes, the brown suspension was cooled to -78 °C and *t*BuOK (2.80 g, 24.95 mmol) was added. After an additional 30 minutes the reaction was quenched with brine (90 mL) at -78 °C. After warming to r.t. the two layers were separated and the aqueous phase was extracted with ether (3 x 90 mL). The combined organic phase was passed through a phase separator, concentrated and purified by column chromatography on silica gel (starting from 0% of EtOAc in petroleum ether) to provide 1-(iodoethynyl)-4-nitrobenzene as a yellow solid (1.17 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.15 (m, 2H), 7.62 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 133.3, 130.1, 123.7, 92.5, 14.3.

1-ethynyl-2,3,4,5,6-pentafluorobenzene (Cas No. 5122-07-6)



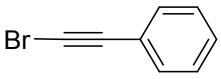
Bromopentafluorobenzene (3.0 mL, 24.1 mmol), $PdCl_2(PPh_3)_2$ (0.342 g, 0.49 mmol), and CuI (0.187 g, 0.46 mmol) were dissolved in THF (60 mL). Hünig's base (16.0 mL, 89.9 mmol) was added, followed by ethynyltrimethylsilane (6.8 mL, 49.1 mmol), and the mixture was stirred for 24 h at 72 °C. The suspension was poured onto a pad of Celite®, washed with THF and the filtrate was concentrated under reduced pressure. Purification by flash column chromatography on silica gel (100% petroleum ether) and concentration under reduced pressure afforded the silylated coupling product and the Glaser coupling product as a mixture. The mixture was dissolved in MeOH (100 mL) and KOH (50%, 0.078 mL) was added. The reaction was stirred for 1 h, then quenched with H_2O (30 mL) and acidified with HCl (7 mL, 1M). The combined organic phase was dried over anhydrous $MgSO_4$, then filtered. Purification by distillation (130 °C, 1 atm) gave 1-ethynyl-2,3,4,5,6-pentafluorobenzene as an orange oil (0.74 g, 16% yield, solvent impurities were not completely removed). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 – 3.61 (m, 1H).

1,2,3,4,5-pentafluoro-6-(iodoethynyl)benzene (Cas No. 66535-27-1)



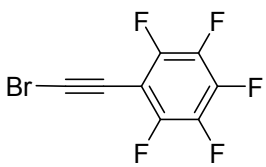
1-ethynyl-2,3,4,5,6-pentafluorobenzene (0.30 g, 1.56 mmol), dissolved in THF (4 mL), was treated with CuI (0.029 g, 0.15 mmol) and 4-iodomorpholine hydroiodide (0.59 g, 2.0 mmol) and the reaction mixture was stirred at r.t. for 3.5 h. The suspension was poured onto a pad of neutral alumina, the solid phase was washed with THF and CH_2Cl_2, and the filtrate was concentrated under reduced pressure. The combined organic fractions were pooled and washed with a solution of $Na_2S_2O_3$ (100 mL, 5% w/w) and a solution of saturated NaCl (50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography on silica gel (petroleum ether) to provide 1,2,3,4,5-pentafluoro-6-(iodoethynyl)benzene as an orange oil (0.35 g, 70% yield). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1 – 147.0 (m), 139.2 – 136.1 (m), 143.5 – 140.4 (m), 100.5 – 99.9 (m), 77.7 (q, J = 3.6 Hz), 21.7 (q, J = 3.9 Hz).

(bromoethynyl)benzene (Cas No. 932-87-6)



To ethynylbenzene (0.75 mL, 6.85 mmol), dissolved in acetone (70 mL), were added NBS (1.35 g, 7.59 mmol) and $AgNO_3$ (0.119 g, 0.70 mmol). The resulting mixture was stirred at r.t. for 3.5 h. The suspension was filtered and the filtrate was concentrated under reduced pressure. Then, the resulting crude mixture was added to water (50 mL) and extracted with Et_2O (3 × 50 mL). The combined organic phase was dried over anhydrous K_2CO_3, filtered, concentrated and purified by column chromatography on silica gel (petroleum ether) to provide (bromoethynyl)benzene as a yellow oil (1.13 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 2H), 7.42 – 7.28 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1, 128.8, 128.5, 122.8, 80.2, 49.9.

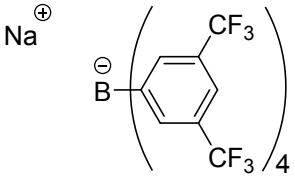
1-(bromoethynyl)-2,3,4,5,6-pentafluorobenzene (Cas No. 66535-26-0)



To bromoform (2.37 g, 7.15 mmol) and 2,3,4,5,6-pentafluorobenzaldehyde (0.70 g, 3.57 mmol) in CH_2Cl_2 (20 mL) under argon atmosphere at 0 °C was added triphenylphosphine (3.74 g, 14.3 mmol). The suspension was stirred at r.t. for 1 h during which it changed colour from yellow to orange. The suspension was then cooled

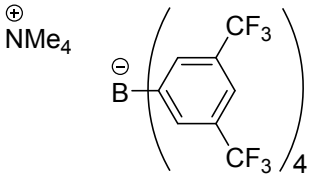
to -78 °C and *t*BuOK (1.60 g, 14.3 mmol) was added. After stirring for 35 min. the reaction was quenched with brine (9 mL) at -78 °C. Then the reaction mixture was warmed to r.t. and an additional amount of brine (30 mL) was added, the two layers were separated and the aqueous phase was extracted with ether (3 x 25 mL). The combined organic phase was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration, the crude product was purified by column chromatography on silica gel (petroleum ether). Removal of solvent under reduced pressure provided 1-(bromoethynyl)-2,3,4,5,6-pentafluorobenzene as a yellow oil (0.39 g, 40% yield). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7 – 146.8 (m), 143.6 – 140.4 (m), 139.3 – 136.1 (m), 100.3 – 99.4 (m), 64.6 (q, J = 3.8 Hz), 63.6 (q, J = 3.8 Hz).

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Cas No. 79060-88-1)



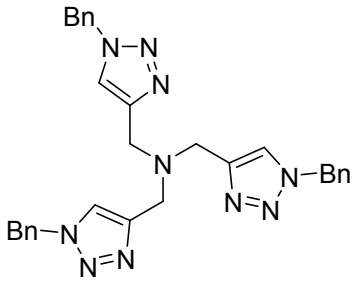
A three-neck round bottom flask fitted with a reflux condenser was evacuated, flame dried and filled with argon prior to use. Magnesium (1.11 g, 45.7 mmol), $NaBF_4$ (0.71 g, 6.4 mmol) and Et_2O (150 mL) were added to the flask. To start the reaction dibromoethane (0.49 mL, 5.7 mmol) was added and the flask was heated for 5 minutes followed by dropwise addition of 3,5-bis(trifluoromethyl)bromobenzene (5.0 mL, 35.9 mmol) dissolved in Et_2O (40 mL) over 70 min. The solution was then stirred at r. t. over night. As all of the magnesium had not reacted the reaction was refluxed for an additional 24 h. Then the reaction mixture was quenched by the addition of Na_2CO_3 (16.2 g, 153 mmol) dissolved in H_2O (200 mL) and stirred for 1 h and filtered. The aqueous phase was extracted three times with Et_2O (50 mL), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed and the remaining crude product was dissolved in toluene (50 mL) and concentrated to remove remaining traces of water, this was repeated three more times. The product was dried under reduced pressure with heating (100 °C) for 10 h to yield a brown solid. This solid was washed with CH_2Cl_2 and toluene, dried under reduced pressure with heating (100 °C) in the presence of P_2O_5 for 2 days to yield the NaBARF as a pale grey solid (2.70 g, 47% yield). ^1H NMR (400 MHz, [D_6]DMSO) δ 7.64 (s, 4H), 7.61 (s, 8H). ^{13}C NMR (101 MHz, [D_6]DMSO) δ 161.0 (q, J = 49.9 Hz), 134.9, 129.1 – 127.9 (m), 124.0 (q, J = 272.2 Hz), 118.0 – 117.1 (m).

Tetramethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Cas No. 144699-38-7)



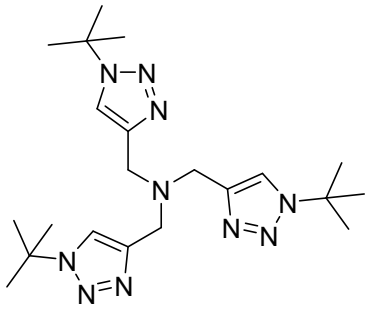
To NaBARF (1.76 g, 1.99 mmol) suspended in CH_2Cl_2 (100 mL) was added tetramethylammonium iodide (0.60 g, 2.98 mmol). The reaction mixture was stirred at r.t. for 3 days open to air (moisture helps to increase the solubility of NaBARF). Then the mixture was filtered and concentrated under reduced pressure. The precipitate was suspended in Et_2O and filtered (to remove excess Me_4NI). The Et_2O was evaporated and the resulting solid was recrystallized from CH_2Cl_2 at 0 °C for three times to yield the tetramethylammonium BARF salt as a colourless powder (in total: 1.49 g, 80% yield). ^1H NMR (400 MHz, [D_6]DMSO) δ 7.66 (s, 4H), 7.64 – 7.57 (m, 8H), 3.10 (s, 12H). ^{13}C NMR (101 MHz, [D_6]DMSO) δ 161.0 (q, J = 49.9 Hz), 134.0 (s), 129.1 – 127.9 (m), 124.0 (q, J = 272.4 Hz). 117.9 – 117.27 (m), 54.7 – 54.0 (m).

tris((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)amine (Cas No. 510758-28-8)



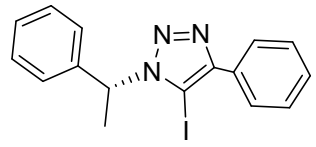
CuI (0.037 g, 0.193 mmol) and Et_3N (0.57 mL, 5.63 mmol) were dissolved in freshly distilled THF (10 mL) under argon atmosphere and stirred at r.t for 30 min. Then benzyl azide (0.74 mL, 5.9 mmol) and tripropargylamine (0.27 mL, 1.9 mmol) were added and the reaction mixture was stirred at r.t. for 21 h. Then Et_2O (10 mL) and NH_4OH (4 mL, 8% w/w) were added and the precipitate was filtered. The solid was dissolved in CH_2Cl_2 (10 mL), and NH_4OH (18 mL, 8% w/w) and trilon B (0.074 g, 0.19 mmol) were added. The mixture was stirred at r.t. for 2 h and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated to provide TBTA as a colourless solid (0.80 g, 79% yield). M.p.: 146 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 3H), 7.39 – 7.21 (m, 15H), 5.49 (s, 6H), 3.69 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 134.9, 129.2, 128.8, 128.1, 123.8, 54.2, 47.2.

tris((1-(tert-butyl)-1H-1,2,3-triazol-4-yl)methyl)amine (Cas No. 862678-56-6)



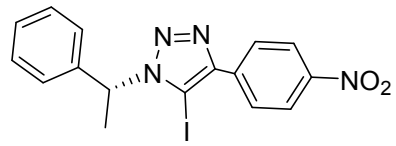
Tripropargylamine (0.66 g, 5.0 mmol) was dissolved in MeCN (7 mL) and H_2O (2 mL). Then *tert*-Butyl azide (2.23 mL, 22.5 mmol), sodium ascorbate (0.15 g, 0.75 mmol) and $CuSO_4$ x $5H_2O$ (0.125 mg, 0.50 mmol) were added and the reaction mixture was stirred at r.t. for 7 days. The reaction mixture was concentrated and NH_4OH (20 mL, 10% w/w) was added and the aqueous layer was extracted with CH_2Cl_2 (5 x 20 mL). The combined organic phase was washed with an aqueous solution of saturated NaCl. The combined organic phase was dried over anhydrous K_2CO_3, filtered and concentrated. The triazole was crystallized from CH_2Cl_2 (4 mL) and Et_2O (20 mL) and then recrystallized from CH_2Cl_2 (4 mL) and Et_2O (20 mL) to provide the product as a colourless solid (1.24 g, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 3H), 3.78 (s, 6H), 1.69 (s, 27H).

(*R*)-5-iodo-4-phenyl-1-(1-phenylethyl)-1*H*-1,2,3-triazole (Cas No. 2109806-82-6)



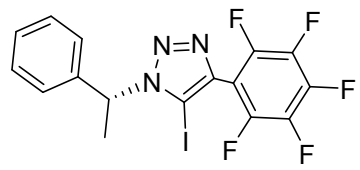
The triazole was prepared starting from 1-iodo-phenylacetylene and (*R*)-(1-azidoethyl)benzene,[6] following the literature procedure, as colourless crystals (0.240 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.28 (m, 6H), 5.80 (q, J = 7.1 Hz, 1H), 2.12 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 140.3, 130.5, 129.0, 128.7, 128.6, 128.4, 127.8, 126.7, 77.0, 61.6, 22.5.

(*R*)-5-iodo-4-(4-nitrophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole



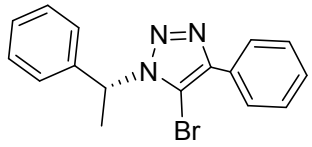
CuI (0.006 g, 0.032 mmol) and TTTA (0.015 mg, 0.035 mmol) were dissolved in freshly distilled THF (3.5 mL) under argon atmosphere and stirred at r.t. for 30 min. Then 1-(iodoethynyl)-4-nitrobenzene (0.186 g, 0.681 mmol) and (*R*)-(1-azidoethyl)benzene (0.097 mL, 0.680 mmol) were added and the reaction mixture was stirred at r.t. for 5 h. The reaction mixture was concentrated, NH_4OH (20 mL, 10 % w/w) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated and purified by column chromatography on silica gel (from 10% of EtOAc in petroleum ether) to provide the triazole as yellow crystals (0.253 g, 88% yield). M.p.: decomposes above 153 °C in the presence of visible light; $[\alpha]_D^{20}$ = 25.9 (c = 0.16 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.28 (m, 2H), 8.23 – 8.14 (m, 2H), 7.41 – 7.29 (m, 5H), 5.82 (q, J = 7.1 Hz, 1H), 2.14 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 147.6, 139.8, 136.8, 129.1, 128.6, 128.1, 126.7, 124.0, 78.3, 62.0, 22.5. IR (KBr) ν=: 2992 (w), 2937 (w), 1602 (s), 1521 (s), 1458 (m), 1382 (m), 1346 (s), 1288 (m), 1245 (w), 1110 (m), 989 (m), 977 (m), 855 (s), 712 (s), 604 (w), 540 (w) cm^{-1}. HRMS (ESI): m/z calc. $C_{16}H_{13}IN_4O_2$ $[M + H]^+$: 421.0156**;** found: 421.0151.

(*R*)-5-iodo-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole



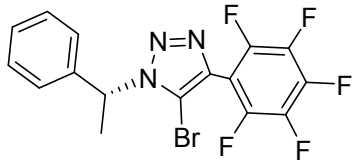
CuI (0.006 g, 0.032 mmol) and TTTA (0.015 mg, 0.035 mmol) were dissolved in freshly distilled THF (3.5 mL) under argon atmosphere and stirred at r.t. for 30 min. Then (*R*)-(1-azidoethyl)benzene (0.097 µL, 0.680 mmol) and 1,2,3,4,5-pentafluoro-6-(iodoethynyl)benzene (0.215 g, 0.676 mmol) were added and the reaction mixture was stirred at r.t. for 23 h. The reaction mixture was concentrated, NH_4OH (20 mL, 10 % w/w) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic phase was passed through a phase separator, concentrated and purified by column chromatography on silica gel (from 10% of EtOAc in petroleum ether) to provide the triazole as colourless crystals (0.271 g, 86% yield). M.p.: 157 – 160 °C; $[\alpha]_D^{20}$ = 32.0 (c = 0.21 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 5.79 (q, J = 7.1 Hz, 1H), 2.14 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 129.2, 128.6, 126.7, 82.7, 62.3, 22.4 (The Ar^F C-atoms and the C-atom of C4 in the triazole could not be detected because of low intensity of the signals). IR (KBr) ν=: 1659 (w), 1554 (m), 1495 (s), 1413 (w), 1393 (w), 1238 (m), 1165 (m), 1126 (m), 1046 (m), 987 (s), 917 (w), 841 (s), 765 (m), 698 (s) cm^{-1}. HRMS (ESI): m/z calc. $C_{16}H_9F_5IN_3$ $[M + H]^+$: 465.9834**;** found: 465.9831**.**

(*R*)-5-bromo-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole



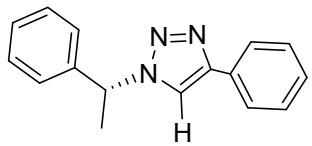
$Cu(OAc)_2$ (0.024 g, 0.132 mmol) CuBr (0.019 g, 0.132 mmol) and TTTA (0.058 mg, 0.135 mmol) were dissolved in freshly distilled THF (6.0 mL) under argon atmosphere and stirred at r.t. for 30 min. (bromoethynyl)benzene (0.239 g, 1.32 mmol) and (*R*)-(1-azidoethyl)benzene (0.194 g, 1.32 mmol) were added and the reaction mixture was stirred at 60 °C for two weeks. The reaction mixture was concentrated, NH_4OH (28 mL, 18 % w/w) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (from 10% of EtOAc in petroleum ether) to provide the triazole as colourless crystals (0.176 g, 41% yield). $[\alpha]_D^{20}$ = 27.0 (*c* = 0.18 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.48 – 7.41 (m, 2H), 7.41 – 7.28 (m, 6H), 5.78 (q, *J* = 7.1 Hz, 1H), 2.11 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 140.0, 129.8, 129.0, 128.7, 128.6, 128.4, 127.0, 126.6, 108.1, 60.0, 22.0. IR (KBr) ν=: 3031 (w), 2988 (m), 2943 (w), 1607 (w), 1494 (m), 1477 (m), 1447 (m), 1374 (m), 1306 (w), 1280 (m), 1232 (s), 1049 (m), 989 (m), 975 (m), 771 (s), 733 (s), 698 (s), 536 (m) cm^{-1}. HRMS (ESI): m/z calc. $C_{16}H_{14}BrN_3$ $[M + H]^+$: 328.0444**;** found: 328.0439 (^{79}Br).

(*R*)-5-bromo-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole



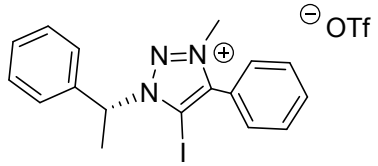
$Cu(OAc)_2$ (0.010 g, 0.054 mmol) and CuBr (0.008 g, 0.054 mmol) were suspended in freshly distilled THF (0.5 mL) under argon atmosphere and stirred at r.t. for 30 min. 1-(bromoethynyl)-2,3,4,5,6-pentafluorobenzene (0.070 g, 0.258 mmol) and (*R*)-(1-azidoethyl)benzene (0.040 g, 0.272 mmol) were added and the reaction mixture was stirred at 50 °C for 1 day. As no reaction had occurred TTTA (0.025 g, 0.058 mmol) was added and the reaction mixture was stirred at 50 °C for 8 days. The reaction mixture was concentrated, NH_4OH (20 mL, 10 % w/w) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phase was dried over anhydrous K_2CO_3, filtered, then concentrated and purified by column chromatography on silica gel (starting from 10% of EtOAc in petroleum ether) to provide the triazole as a colourless oil (0.051 g, 47% yield). $[\alpha]_D^{20}$ = 14.4 (*c* = 0.08, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.79 (q, *J* = 7.1 Hz, 1H), 2.13 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 129.2, 128.7, 126.6, 113.0, 60.8, 21.9 (The Ar^F C-atoms and the C-atom of C4 in the triazole could not be detected because of low intensity of the signals). HRMS (ESI): m/z calc. $C_{16}H_9BrF_5N_3$ $[M + H]^+$: 417.9973**;** found: 417.9989 (^{79}Br).

(*R*)-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole (Cas No. 1657030-97-1)



CuI (0.010 g, 0.053 mmol) and TTTA (0.021 mg, 0.049 mmol) were dissolved in freshly distilled THF (3.5 mL) under argon atmosphere and stirred at r.t. for 30 min. Phenylacetylene (0.231 g, 1.013 mmol) and (*R*)-(1-azidoethyl)benzene (0.150 g, 1.019 mmol) dissolved in THF (2.0 mL) were added and the reaction mixture was stirred at r.t. for 21 h. The reaction mixture was concentrated, NH_4OH (20 mL, 10 % w/w) was added and the aqueous phase was extracted with CH_2Cl_2 (4 x 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (from 0% of EtOAc in petroleum ether) to provide the triazole as colourless crystals (0.320 g, 84% yield). M.p.: 115 – 116 °C; $[\alpha]_D^{20}$ = -48.9 (*c* = 0.20 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 2H), 7.64 (s, 1H), 7.47 – 7.28 (m, 8H), 5.87 (q, *J* = 7.1 Hz, 1H), 2.03 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 140.0, 130.8, 129.2, 128.9, 128.7, 128.2, 126.7, 125.8, 118.5, 60.4, 21.5. IR (KBr) ν=: 3121 (m), 3091 (w), 2985 (m), 1606 (w), 1496 (m), 1481 (m), 1463 (m), 1449 (m), 1356 (m), 1232 (m), 1219 (m), 1153 (m), 1075 (s),1026 (m), 992 (m), 916 (w), 818 (m), 764 (s), 714 (s), 692 (s), 521 (m) cm^{-1}. HRMS (ESI): m/z calc. $C_{16}H_{15}N_3$ $[M + H]^+$: 250.1339**;** found: 250.1336.

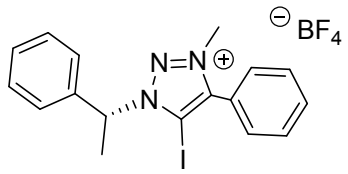
(*R*)-5-iodo-3-methyl-4-phenyl-1-(1-phenylethyl)-1*H*-1,2,3-triazol-3-ium trifluoromethanesulfonate (Cas No. 2109807-19-2): 1-OTf



The triazolium salt was prepared starting from the corresponding triazole, following the literature procedure[6] and obtained as colourless crystals (0.065 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.53 (m, 5H), 7.47 – 7.33 (m, 5H), 5.96 (q, *J* = 6.9 Hz, 1H), 4.27 (s, 3H), 2.14 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 136.8, 132.2, 130.4, 129.8, 129.7, 129.6, 127.2, 122.4,

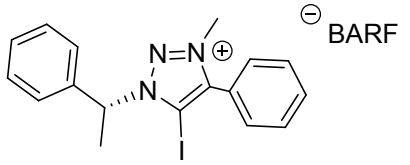
88.1, 66.7, 39.7, 21.7 (The C-atom of the triflate could not be detected because of low intensity of the signal).

(*R*)-5-iodo-3-methyl-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium tetrafluoroborate: 1-BF$_4$



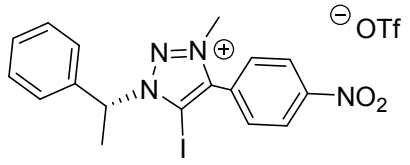
The corresponding triazole (0.124 g, 0.330 mmol) was dissolved in CH_2Cl_2 (6.5 mL) under argon atmosphere. Trimethyloxonium tetrafluoroborate (0.061 mg, 0.412 mmol) was added and the reaction mixture was stirred at r.t. for 24 h. The reaction was quenched by adding MeOH (10.0 mL) and stirred for 1 h. After removal of the solvents under reduced pressure the crude produce was dissolved in MeOH (10.0 mL), then Et_2O (5.0 mL) was added to the solution and a fine precipitate formed which was filtered. The crystallization was repeated a second time using MeOH (5.0 mL) and Et_2O (25.0 mL) to provide **1-BF$_4$** as colourless crystals (in total: 0.140 g, 89% yield). M.p.: 193 – 195 °C; $[\alpha]_D^{20}$ = 36.0 (*c* = 0.16 in MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.77 – 7.57 (m, 5H), 7.55 – 7.37 (m, 5H), 6.23 (q, *J* = 6.9 Hz, 1H), 4.27 (s, 3H), 2.12 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 148.6, 138.8, 133.1, 131.4, 130.7, 130.4, 130.3, 128.2, 124.3, 91.3, 67.4, 39.8, 22.0. HRMS (ESI): m/z calcd for $C_{17}H_{17}IN_3$ $[M - BF_4]^+$: 390.0462; found: 390.0455; m/z calcd for BF_4 $[BF_4]^-$: 86.0071; found: 87.0037 (^{11}B).

(*R*)-5-iodo-3-methyl-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate: 1-BARF



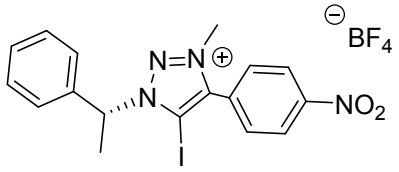
Triazolium **1-OTf** (0.153 g, 0.284 mmol) was dissolved in a mixture of CH_2Cl_2 (17.4 mL) and MeOH (5.8 mL), tetramethylammonium BARF (0.293 g, 0.313 mmol) was added and the reaction mixture was stirred at r.t. for 22 h. After removal of the solvents under reduced pressure the precipitate was suspended in Et_2O (11.5 mL) and stirred for 45 minutes at 0 °C. The precipitate was removed by filtration and discarded. The filtrate was concentrated under reduced pressure and the obtained solid was suspended in $CHCl_3$ (11.5 mL), then stirred for 30 minutes at 0 °C. The precipitate was removed by filtration and the mother liquid was concentrated under reduced pressure to provide **1-BARF** as colourless crystals (0.342 g, 96% yield). M.p.: 173 – 174 °C; $[\alpha]_D^{20}$ = 12.5 (*c* = 0.37 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 9H), 7.53 – 7.47 (m, 2H), 7.43 (s, 4H), 7.39 – 7.30 (m, 3H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 5.87 (q, *J* = 7.0 Hz, 1H), 4.04 (s, 3H), 1.99 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (q, *J* = 49.9 Hz), 147.9, 135.1 – 134.8 (m), 135.0, 133.5, 130.7, 130.5, 130.0, 129.7 – 128.5 (m), 129.3, 127.0, 124.63 (q, $J = 272.6$ Hz), 120.6, 117.8 – 117.5 (m), 86.4, 67.7, 39.5, 21.3. IR (KBr) ν=: 1610 (m), 1355 (s), 1277 (s), 1131 (s), 888 (m), 839 (m), 763 (w), 745 (m), 715 (m), 697 (m), 683 (m), 670 (m) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{17}IN_3$ $[M - C_{32}H_{12}BF_{24}]^+$: 390.0462; found: 390.0460; m/z calcd for $C_{32}H_{12}BF_{24}$ $[BARF]^-$: 862.0691; found: 862.0696 (^{10}B).

(*R*)-5-iodo-3-methyl-4-(4-nitrophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium trifluoromethanesulfonate: 2-OTf



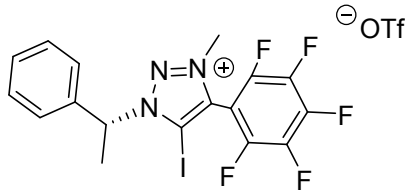
The corresponding triazole (0.102 g, 0.243 mmol) was dissolved in CH_2Cl_2 (5.0 mL) under argon atmosphere. Methyl triflate (0.041 mL, 0.363 mmol) was added dropwise and the reaction mixture was stirred at r.t. for 23 h. The reaction mixture was concentrated and dissolved in CH_2Cl_2 (1.5 mL). Et_2O (10.0 mL) was added to the reaction mixture and a precipitate formed after 20 minutes which, was filtered to provide **2-OTf** as colourless crystals (0.123 g, 87% yield). M.p.: 84 – 87 °C; $[\alpha]_D^{20}$ = 34.8 (*c* = 0.25 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.36 (m, 2H), 8.01 – 7.89 (m, 2H), 7.51 – 7.37 (m, 5H), 6.02 (q, *J* = 6.9 Hz, 1H), 4.32 (s, 3H), 2.19 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 145.4, 136.4, 132.1, 129.7, 129.6, 128.4, 127.1, 124.6, 120.5 (q, *J* = 320.0 Hz), 88.7, 67.0, 39.9, 21.6. IR (KBr) ν=: 3107 (w), 1605 (m), 1527 (s), 1488 (w), 1454 (w), 1349 (s), 1277 (s), 1158 (s), 1030 (s), 856 (m), 757 (w), 704 (m), 638 (s), 600 (w), 574 (w) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{16}IN_4O_2$ $[M - CF_3O_3S]^+$: 435.0312; found: 435.0327; m/z calcd for CF_3O_3S $[OTf]^-$: 148.9526; found: 148.9549.

(*R*)-5-iodo-3-methyl-4-(4-nitrophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium tetrafluoroborate: 2-BF_4



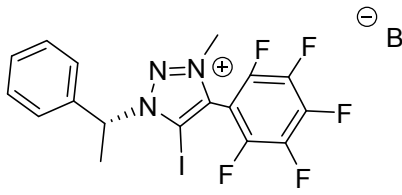
The corresponding triazole (0.112 g, 0.267 mmol) was dissolved in CH_2Cl_2 (5.5 mL) under argon atmosphere. Trimethyloxonium tetrafluoroborate (0.055 mg, 0.372 mmol) was added and the reaction mixture was stirred at r.t. for 3 days. The reaction was quenched by adding MeOH (5.5 mL) and stirred for 40 min. After removal of the solvents under reduced pressure the precipitate was dissolved in CH_2Cl_2 (2.0 mL) and Et_2O (5.0 mL) was added. After 20 minutes a precipitate formed, which was then filtered to provide **2-BF_4** as pale yellow crystals (0.132 g, 95% yield). M.p.: 98 – 101 °C; $[\alpha]_D^{20}$ = 39.4 (*c* = 0.19 in MeOH); ^{1}H NMR (400 MHz, CD_3OD) 8.56 – 8.45 (m, 2H), 8.01 – 7.88 (m, 2H), 7.56 – 7.36 (m, 5H), 6.25 (q, *J* = 6.9 Hz, 1H), 4.32 (s, 3H), 2.13 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) *δ* 151.3, 146.9, 138.7, 133.2, 130.38, 130.37, 130.3, 128.2, 125.5, 92.1, 67.6, 40.0, 22.0. IR (KBr) ν=: 1605 (w), 1526 (s), 1487 (w), 1453 (w), 1348 (s), 1287 (w), 1061 (s), 855 (m), 763 (w), 704 (m), 600 (w) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{16}IN_4O_2$ $[M - BF_4]^+$: 435.0312; found: 435.0315; m/z calcd for BF_4 $[BF_4]^-$: 86.0071; found: 87.0054 (^{11}B).

(*R*)-5-iodo-3-methyl-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium trifluoromethanesulfonate: 3-OTf



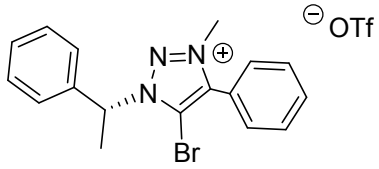
The corresponding triazole (0.200 g, 0.230 mmol) was dissolved in CH_2Cl_2 (9.0 mL) under argon atmosphere. Methyl triflate (0.073 mL, 0.645 mmol) was added dropwise and the reaction mixture was stirred at r.t. for 21 h. After removal of the solvents under reduced pressure the precipitate was dissolved in CH_2Cl_2 (6.0 mL). Et_2O (10.0 mL) was added to the solution and after 10 minutes a fine precipitate formed which was filtered to provide **3-OTf** as colourless crystals (0.231 g, 85% yield). M.p.: 134 – 137 °C; $[\alpha]_D^{20}$ = 12.6 (*c* = 0.21 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.49 – 7.37 (m, 5H), 6.10 (q, *J* = 6.9 Hz, 1H), 4.39 (s, 3H), 2.18 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 136.2, 130.0, 129.8, 127.2, 120.6 (q, *J* = 320.4 Hz), 77.5, 67.5, 40.6, 21.7 (The Ar^F C-atoms and the C4 C-atom of the triazole could not be detected because of low intensity of the signals). IR (KBr) ν=: 3034 (w), 1661 (m), 1505 (s), 1450 (m), 1246 (s), 1161 (s), 1078 (m), 1030 (s),994 (s), 867 (m), 754 (m), 699 (m), 638 (s), 574 (w), 518 (m) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{12}F_5IN_3$ $[M - CF_3O_3S]^+$: 479.9991; found: 479.9998; m/z calcd for CF_3O_3S $[OTf]^-$: 148.9526; found: 148.9550.

(*R*)-5-iodo-3-methyl-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate: 3-BARF



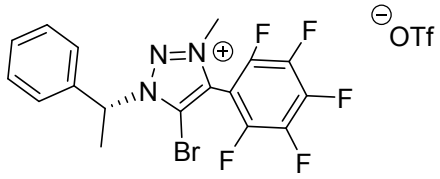
Triazolium **3-OTf** (0.096 g, 0.152 mmol) was dissolved in a mixture of CH_2Cl_2 (9.5 mL) and MeOH (3.2 mL), tetramethylammonium BARF (0.156 g, 0.166 mmol) was added and the reaction mixture was stirred at r.t. for 24 h. After removal of the solvents under reduced pressure the precipitate was suspended in Et_2O (6.5 mL), stirred at r.t. for 10 minutes and 45 minutes at -20 °C. The precipitate was removed by filtration and discarded. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (starting from 5% of MeOH in CH_2Cl_2/petroleum ether 1:1) to provide **3-BARF** as an off white solid (0.184 g, 90% yield). Mp 156–158 °C; $[\alpha]_D^{20}$ = 10.5 (*c* = 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.68 (bs, *J* = 2.1 Hz, 8H), 7.50 (s, 4H), 7.45 – 7.38 (m, 3H), 7.33 – 7.26 (m, 2H), 5.95 (q, *J* = 7.0 Hz, 1H), 4.12 (s, 3H), 2.07 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 161.8 (q, *J* = 49.8 Hz), 134.9, 134.4, 131.0, 130.2, 129.3 – 128.7 (m), 126.8, 124.6 (q, *J* = 272.5 Hz), 117.81 – 117.40 (m), 90.3, 68.8, 40.0, 21.3 (The Ar^F C-atoms and the C4 C-atom of the triazole could not be detected because of low intensity of the signals). IR (KBr) ν=: 2924 (w), 1611 (w), 1518 (s), 1355 (s), 1278 (s), 1134 (s), 1287 (w), 1061 (s), 1000 (w), 889 (w), 716, (w), 683 (w), 670 (w) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{12}F_5IN_3$ $[M - C_{32}H_{12}BF_{24}]^+$: 479.9991; found: 480.008; m/z calcd for $C_{32}H_{12}BF_{24}$ $[BARF]^-$: 862.0691; found: 862.0710 (^{10}B), 863.0682 (^{11}B).

(*R*)-5-bromo-3-methyl-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium trifluoromethanesulfonate: 4-OTf



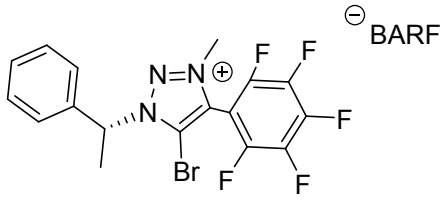
The corresponding triazole (0.096 g, 0.29 mmol) was dissolved in CH_2Cl_2 (6.0 mL) under argon atmosphere. Methyl triflate (0.050 mL, 0.439 mmol) was added dropwise and the reaction mixture was stirred at r.t. for 22 h. After removal of the solvent under reduced pressure the product was purified by column chromatography on silica gel (from 5% of MeOH in CH_2Cl_2) to provide **4-OTf** as an off white oil (0.049 g, 34% yield). $[\alpha]_D^{20}$ = -1.6 (*c* = 0.18 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.55 (m, 5H), 7.49 – 7.37 (m, 5H), 6.06 (q, *J* = 7.0 Hz, 1H), 4.31 (s, 3H), 2.19 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 136.6, 132.4, 130.2, 129.8, 129.8, 129.7, 127.1, 122.4, 120.8 (q, *J* = 320.4 Hz), 116.5, 65.4, 39.9, 21.3. IR (film) ν=: 3063 (w), 1566 (w), 1493 (m), 1455 (m), 1266 (s), 1225 (m), 1154 (s), 1031 (s), 795 (w), 760 (m), 702 (s), 638 (s), 573 (w) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{17}BrN_3$ [M - CF_3O_3S]$^+$: 342.0600; found: 342.0601 (^{79}Br); m/z calcd for CF_3O_3S [OTf]$^-$: 148.9526; found: 148.9525.

(*R*)-5-bromo-3-methyl-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium trifluoromethanesulfonate: 5-OTf



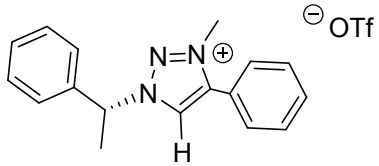
The corresponding triazole (0.050 g, 0.120 mmol) was dissolved in CH_2Cl_2 (2.4 mL) under argon atmosphere. Methyl triflate (0.021 mL, 0.185 mmol) was added dropwise and the reaction mixture was stirred at r.t. for 20 h. After removal of the solvents under reduced pressure, the product was crystallized from hot petroleum ether by cooling to r.t., providing **5-OTf** as a beige solid (0.029 g, 41% yield). Mp 75–78 °C; $[\alpha]_D^{20}$ = 10.3 (*c* = 0.14, MeOH) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.32 (m, 5H), 6.12 (q, *J* = 6.9 Hz, 1H), 4.44 (s, 3H), 2.22 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 130.0, 129.8, 127.0, 119.8, 100.1, 66.4, 41.1, 21.3 (The Ar^F C-atoms and C-atom of the triflate could not be detected because of low intensity of the signals). IR ($CHCl_3$) ν=: 1506 (m), 1450 (m), 1259 (s), 1161 (m), 1077 (w), 1032 (m), 994 (w), 867 (w), 639 (m), 518 (w) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrF_5N_3$ [M - CF_3O_3S]$^+$: 432.0129; found: 432.0135 (^{79}Br); m/z calcd for CF_3O_3S [OTf]$^-$: 148.9526; found: 148.9539.

(*R*)-5-bromo-3-methyl-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate: 5-BARF



Triazolium **5-OTf** (0.029 g, 0.050 mmol) was dissolved in a mixture of CH_2Cl_2 (3 mL) and MeOH (1 mL), tetramethylammonium BARF (0.052 g, 0.055 mmol) was added and the reaction mixture was stirred at r.t. for 20 h. After removal of the solvents under reduced pressure the precipitate was suspended in Et_2O (2.5 mL) and stirred for 45 minutes at 0 °C. The precipitate was removed by filtration and discarded. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (starting from 5% of MeOH in CH_2Cl_2/petroleum ether 1:1) to provide **5-BARF** as an off white solid (0.049 g, 75% yield). Mp 145–147 °C; $[\alpha]_D^{20}$ = 4.1 (*c* = 0.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 8H), 7.50 (bs, 4H), 7.45 – 7.37 (m, 3H), 7.33 – 7.27 (m, 2H), 6.00 (q, *J* = 7.0 Hz, 1H), 4.10 (s, 3H), 2.07 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (q, *J* = 49.8 Hz), 134.9 (broad s), 133.9, 131.1, 130.2, 129.6 – 128.4 (m), 126.8, 124.6 (q, *J* = 272.6 Hz), 120.1, 117.9 – 117.5 (m), 103.1, 67.4, 40.3, 20.7 (The Ar^F C-atoms could not be detected because of low intensity of the signals). IR (KBr) ν=: 2925 (w), 1611 (w), 1521 (m), 1355 (s), 1278 (s), 1133 (s), 1287 (w), 1061 (s), 1000 (w), 889 (w), 716, (w), 683 (w), 670 (w) cm^{-1}. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrF_5N_3$ [M – $C_{32}H_{12}BF_{24}$]$^+$: 432.0142; found: 432.0129 (^{79}Br); m/z calcd for $C_{32}H_{12}BF_{24}$ [BARF]$^-$: 862.0691; found: 862.0691 (^{10}B).

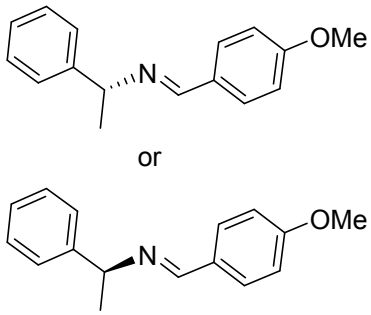
(*R*)- 3-methyl-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazol-3-ium trifluoromethanesulfonate: 6-OTf



The corresponding triazole (0.050 g, 0.201 mmol) was dissolved in CH_2Cl_2 (4.0 mL) under argon atmosphere. Methyl triflate (0.045 mL, 0.401 mmol) was added dropwise and the reaction mixture was stirred at r.t. for 21 h. After removal of the solvent under reduced pressure the product was purified by column chromatography on silica gel (from 3% of MeOH in CH_2Cl_2) to provide

6-OTf as an off white oil (0.074 g, 89% yield). $[\alpha]_D^{20}$ = -27.6 (*c* = 0.09 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.63 – 7.50 (m, 7H), 7.48 – 7.38 (m, 3H), 6.17 (q, *J* = 7.1 Hz, 1H), 4.26 (s, 3H), 2.11 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.7, 132.1, 130.0, 129.8, 129.7, 129.6, 128.0, 127.7, 122.0, 120.9 (q, *J* = 320.3 Hz), 65.4, 38.8, 20.3. HRMS (ESI): m/z calcd for $C_{17}H_{18}N_3$ [M - CF_3O_3S]$^+$: 264.1495; found: 264.1502; m/z calcd for CF_3O_3S [OTf]$^-$: 148.9526; found: 148.9551.

(*R*,*E*)-1-(4-methoxyphenyl)-N-(1-phenylethyl)methanimine (***R*-8**, **Cas. No. 321917-76-4**) and **(*S*,*E*)-1-(4-methoxyphenyl)-N-(1-phenylethyl)methanimine** (***S*-8**, **Cas No. 74879-40-6**)



Anhydrous $MgSO_4$ (3.03 g, 25.2 mmol) was suspended in CH_2Cl_2 (6 mL), then *p*-anisaldehyde (0.79 mL, 6.06 mmol) and α-methylbenzylamine (0.75 mL, 5.82 mmol; in the case of the *R* enantiomer: purity $[\alpha]^{23}$ = +38 (neat) and ; in the case of the *S* enantiomer: purity $[\alpha]_D^{20}$= -37 to -40 (neat)) were added. The reaction mixture was stirred at r.t. for 1 day and filtered. After removal of the solvent under reduced pressure, the crude product was purified by distillation under reduced pressure to yield the imine **8** as a colourless liquid (0.62 g, 45% yield). Bp 190-194 °C (2.3 mbar). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.90 – 7.66 (m, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.33 (m, 2H), 7.29 – 7.22 (m, 1H), 7.09 – 6.79 (m, 2H), 4.53 (q, *J* = 6.6 Hz, 1H), 3.85 (s, 3H), 1.61 (d, *J* = 6.7 Hz, 3H).). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 158.9, 145.6, 129.9, 129.5, 128.5, 126.9, 126.8, 114.0, 69.7, 55.5, 25.0.

II) ^{1}H NMR titration experiments

General information

^{1}H NMR titration experiments were performed on a Bruker AVANCE III 800 MHz spectrometer. The 1 mM (**1-OTf**, **1-BARF**, **2-BF4**, **3-OTf**, **3-BARF**, **5-BARF**, **6-OTf** and **7**) or 1.5 mM (**2-OTf**, **4-OTf**) stock solutions of XB donors were prepared in $CDCl_3$. The XB donor stock solution was added to a vial containing previously weighed sample of the XB acceptor to keep the concentration of XB donor fixed throughout the titration experiment. All the solutions were prepared using Hamilton® Gastight syringes and samples were weighed on a microbalance with an accuracy of 6 µg. $CDCl_3$ was dried over 3Å molecular sieves to keep the water content to a minimum. Small aliquots from the XB acceptor stock solution were added increasingly (from 0 to 150-300 µl) to the NMR tube containing 600 µl of the XB donor stock solution. The concentration of each XB acceptor stock solution was based on the predicted XB binding strength. After every addition the sample was thoroughly shaken using vortex and measured after leaving the sample to thermally equilibrate in the NMR spectrometer for 5 min. For the quantitative measurement, depending on the concentration of the XB donor, 4 or 8 scans were collected with 15 or 20 s relaxation delay and acquisition time set to 2.4 s. The spectra were obtained with power level PLW1= 12.2 W with pulse width set to 3 µs (30° pulse) and at 298 K. All the NMR experiments showed upfield ^{1}H shifts upon addition of quinuclidine and **8** and **9**. The chemical shifts were referenced based on $CHCl_3$ residual peak at 7.26 ppm. K_a values were determined using nonlinear regression analysis. For the fitting of the binding data 1:1 binding isotherm of BindFit was used (freely available at http://supramolecular.org). Herein, the given standard error after each trial depicts error coming from curve fit calculations, whereas the standard errors given in the article Table 1 are the calculated mean values of the two parallel experiments.

1. ^{1}H NMR titration data of [1-OTf-quinuclidine] complex

Trial 1

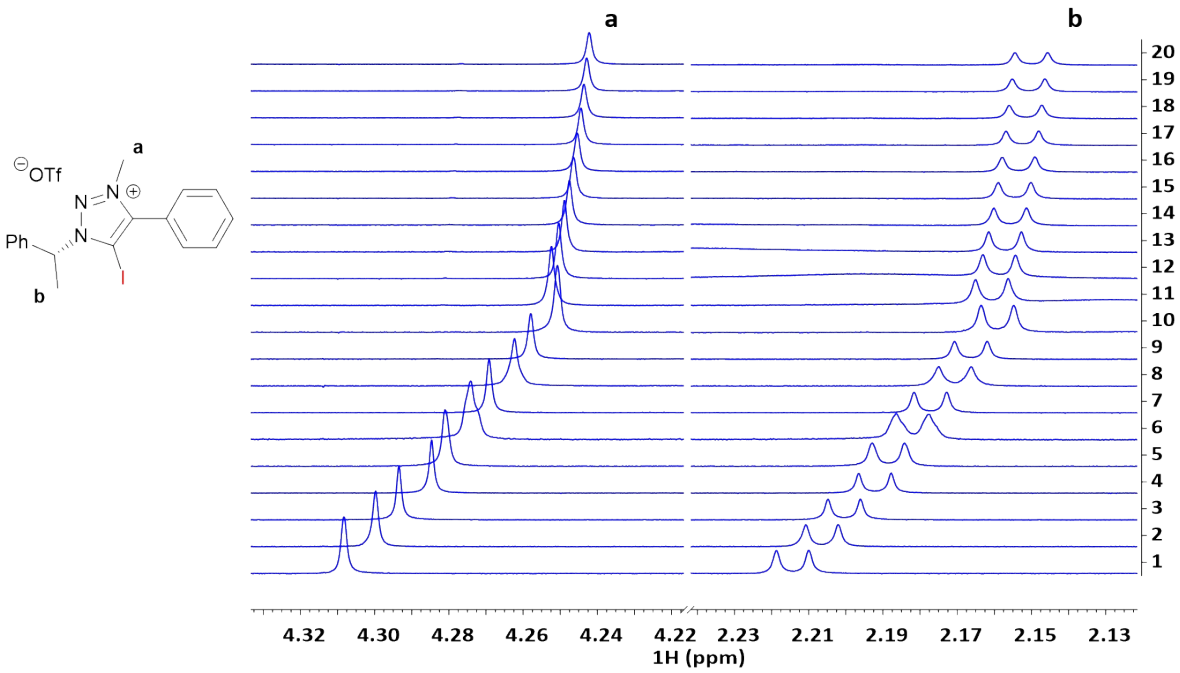


Figure S1. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **1-OTf** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 20 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 2.0, 3.9, 7.7, 9.6, 14.1, 18.6, 27.0, 34.9, 42.4, 49.5, 56.2, 62.5, 68.5, 74.2, 79.7, 84.8, 89.8, 94.5 and 99.0 eq of quinuclidine.

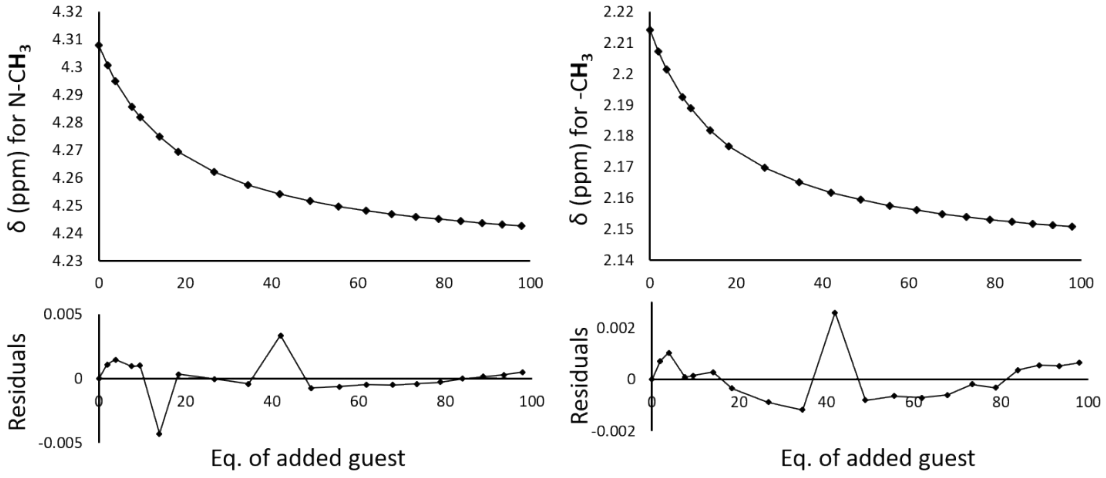


Figure S2. Bindfit output of the binding isotherms for the [**1-OTf**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 55 ± 2 M^{-1}.

Trial 2

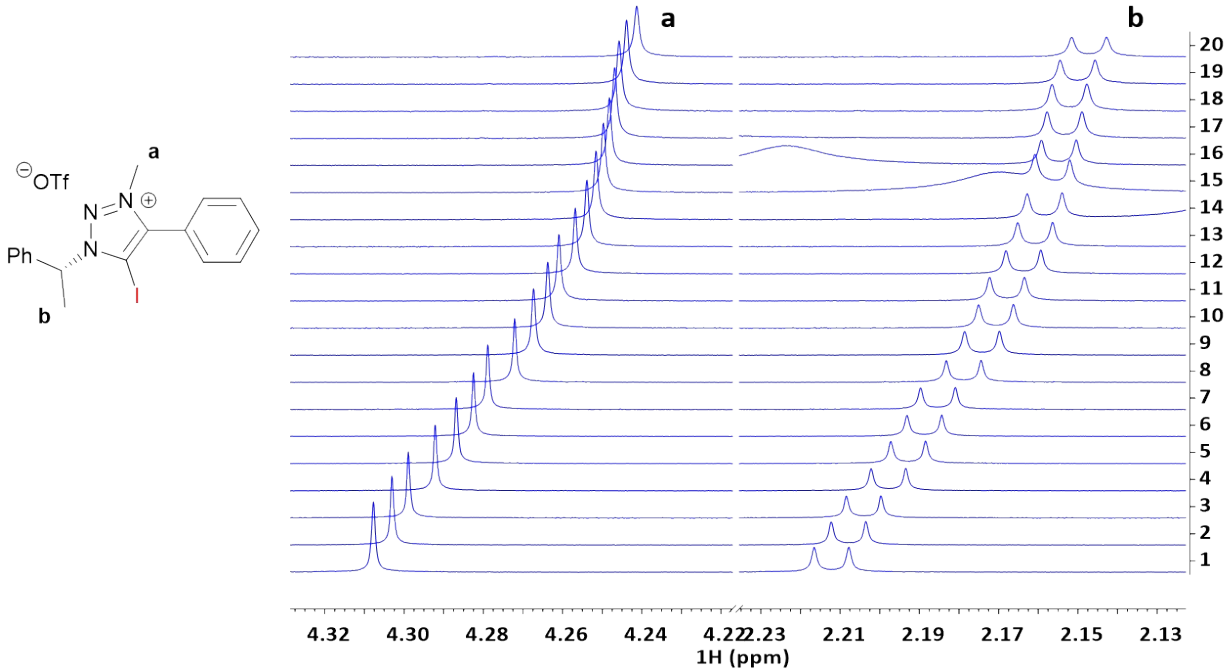


Figure S3. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **1-OTf** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 20 data points of methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 1.1, 2.1, 4.2, 6.2, 8.2, 10.2, 15.1, 19.8, 24.4, 28.8, 37.3, 45.3, 52.8, 60.0, 66.7, 73.1, 79.2, 90.6 and 105.7 eq of quinuclidine.

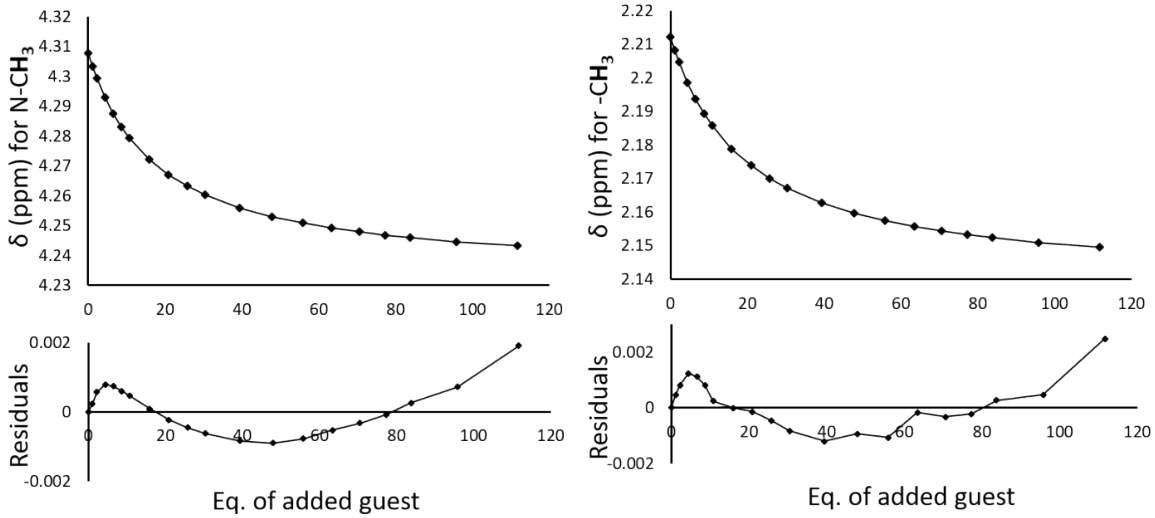


Figure S4. Bindfit output of the binding isotherms for the [**1-OTf**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 60 ± 1 M^{-1}.

2. ^{1}H NMR titration data of [1-BARF-quinuclidine] complex

Trial 1

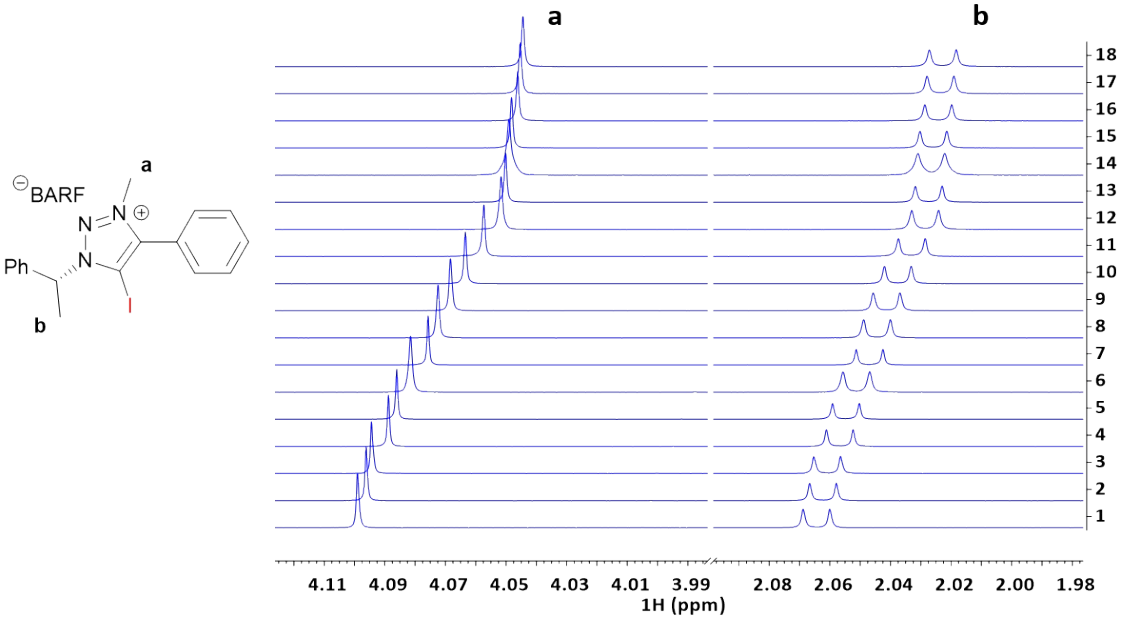


Figure S5. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **1-BARF** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.1, 0.2, 0.4, 0.5, 0.7, 1.0, 1.2, 1.5, 1.9, 2.9, 4.8, 5.6, 6.4, 7.3, 10.5, 12.6 and 15.6 eq of quinuclidine.

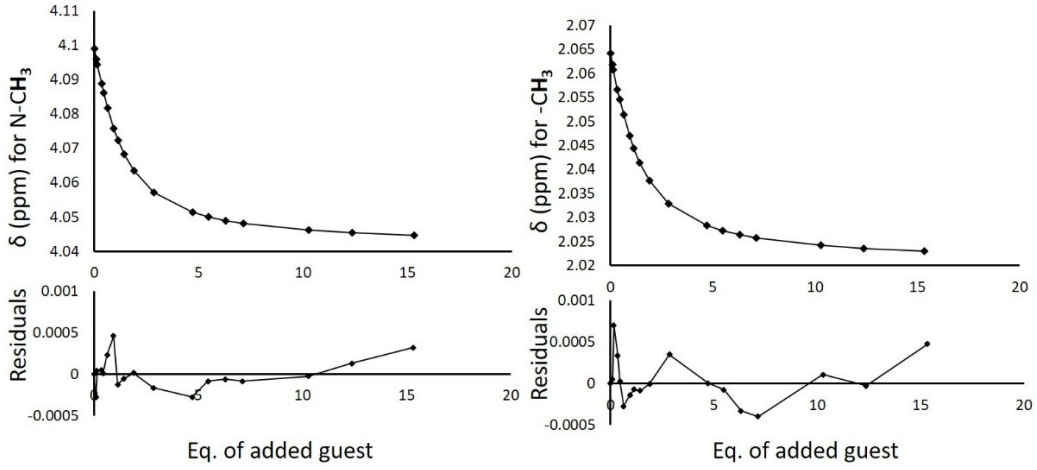


Figure S6. Bindfit output of the binding isotherms for the [**1-BARF**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = (1.23± 0.02) × 10^3 M^{-1}.

Trial 2

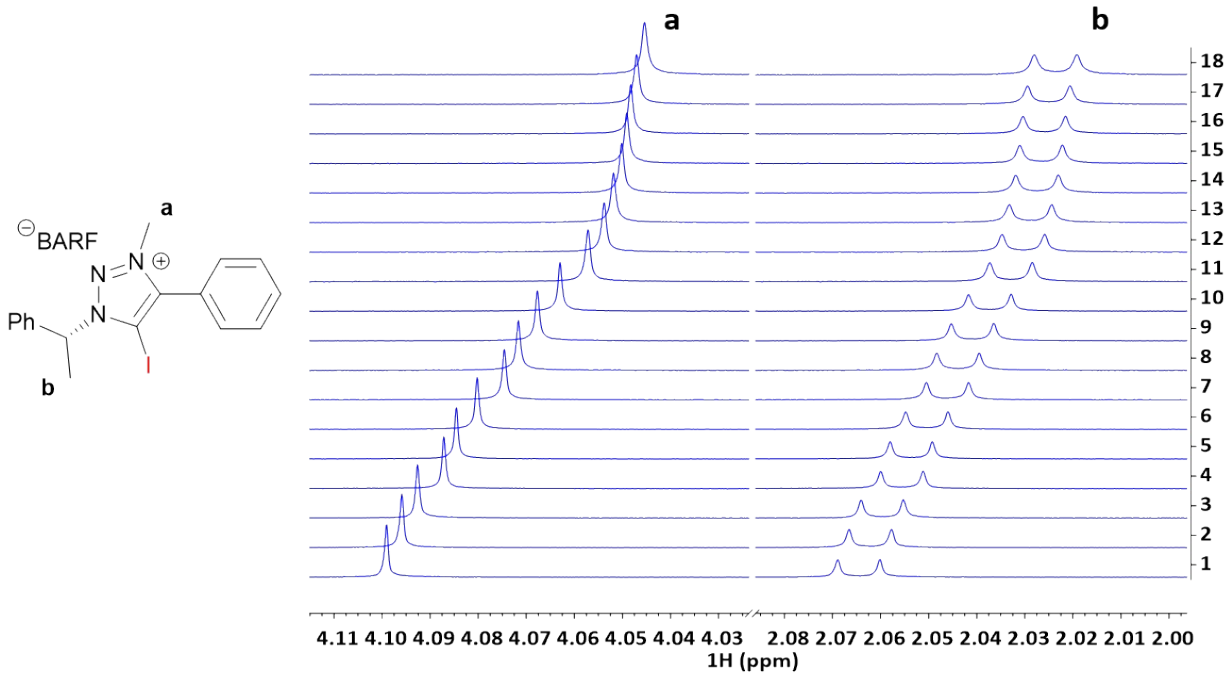


Figure S7. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **1-BARF** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.1, 0.2, 0.4, 0.5, 0.7, 1.0, 1.2, 1.5, 2.0, 3.1, 4.0, 5.0, 5.6, 6.6, 7.4, 8.9 and 12.5 eq of quinuclidine.

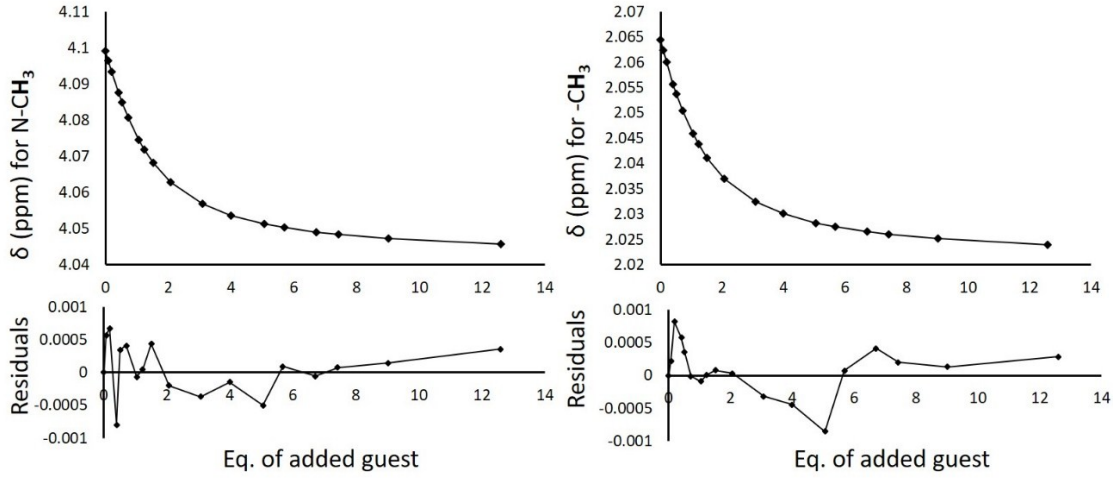


Figure S8. Bindfit output of the binding isotherms for the [**1-BARF**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = (1.22 ± 0.03) × 10^3 M^{-1}.

3. ^{1}H NMR titration data of [2-OTf-quinuclidine] complex

Trial 1

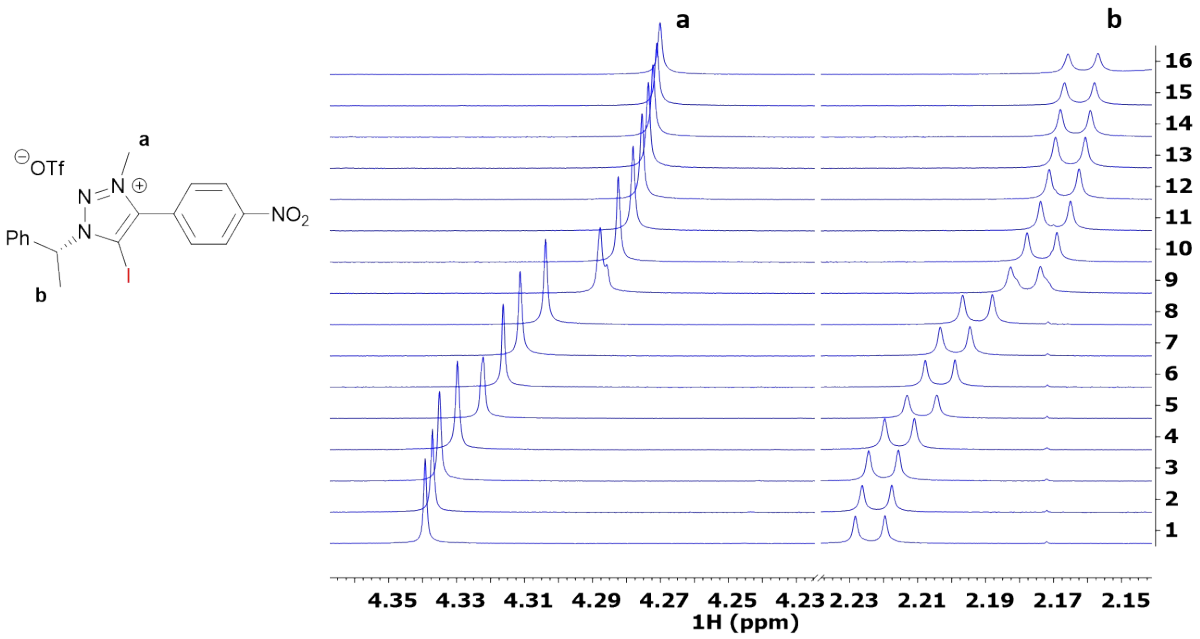


Figure S9. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **2-OTf** (1.5 mM) titration with quinuclidine at 298 K. Showing the collected 16 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.9, 7.6, 10.8, 15.2, 20.2, 24.8, 30.2, 38.3 and 47.3 eq of quinuclidine.

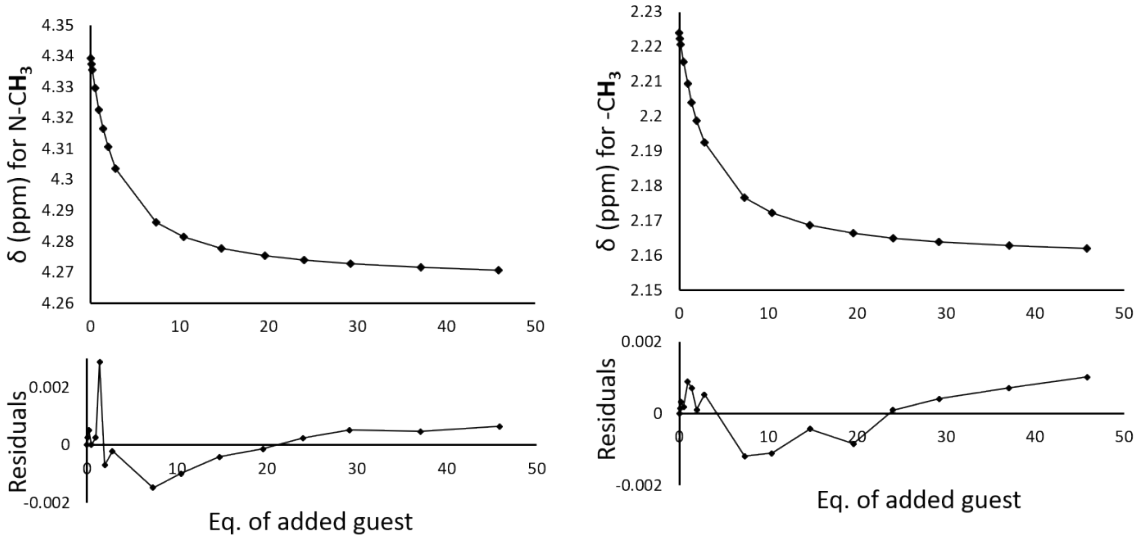


Figure S10. Bindfit output of the binding isotherms for the [**2-OTf**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 263 ± 9 M^{-1}.

Trial 2

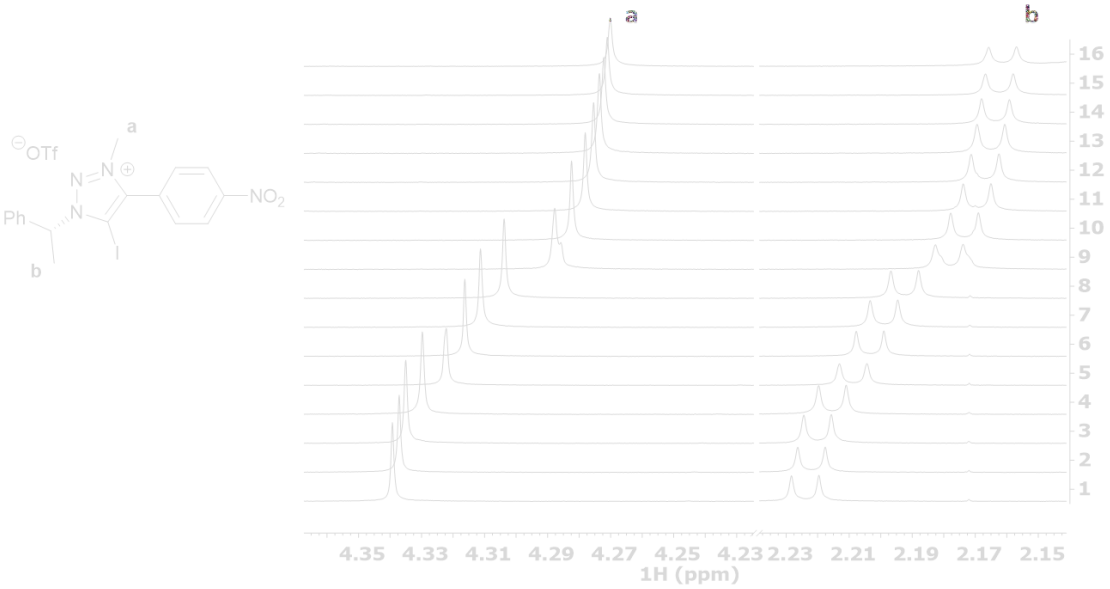


Figure S11. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **2-OTf** (1.5 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.1, 0.2, 0.5, 1.0, 1.4, 2.0, 2.9, 4.7, 6.8, 8.7, 13.5, 17.7, 21.4, 25.7, 29.1, 34.6 and 38.3 eq of quinuclidine.

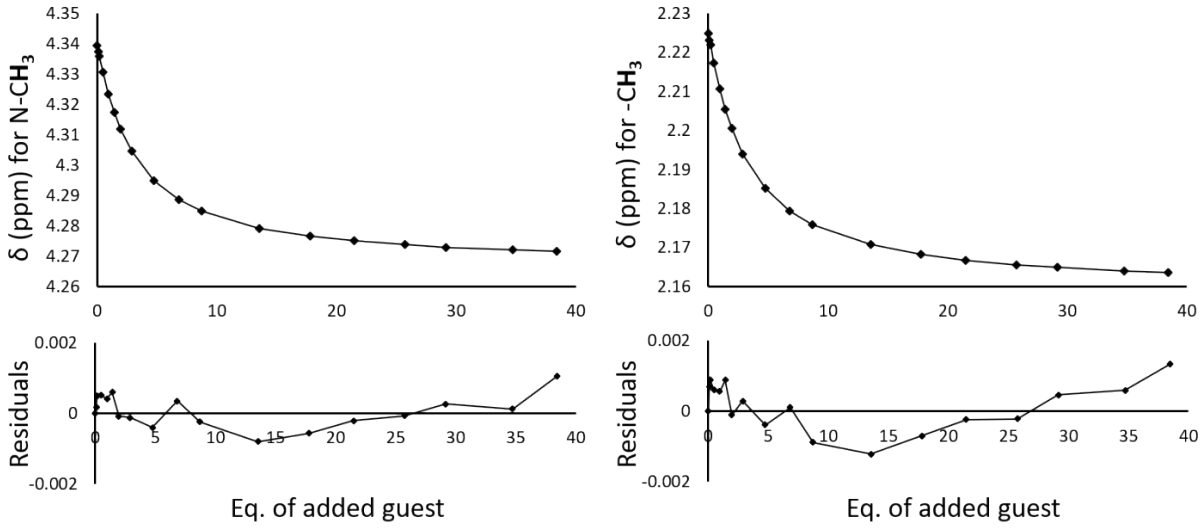


Figure S12. Bindfit output of the binding isotherms for the [**2-OTf**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 250 ± 6 M^{-1}.

4. ^{1}H NMR titration data of [2-BF_4-quinuclidine] complex

Trial 1

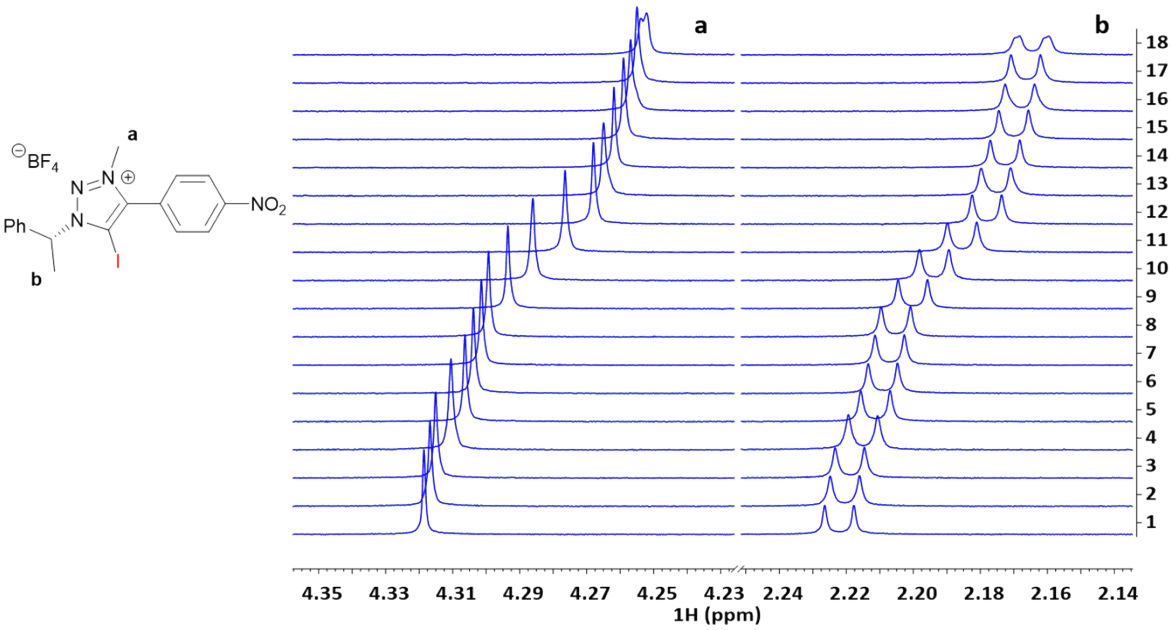


Figure S13. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **2-BF_4** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.1, 0.2, 0.6, 0.9, 1.1, 1.3, 1.5, 2.1, 3.1, 5.1, 8.0, 9.4, 11.4, 14.3, 16.7, 19.6 and 22.4 eq of quinuclidine.

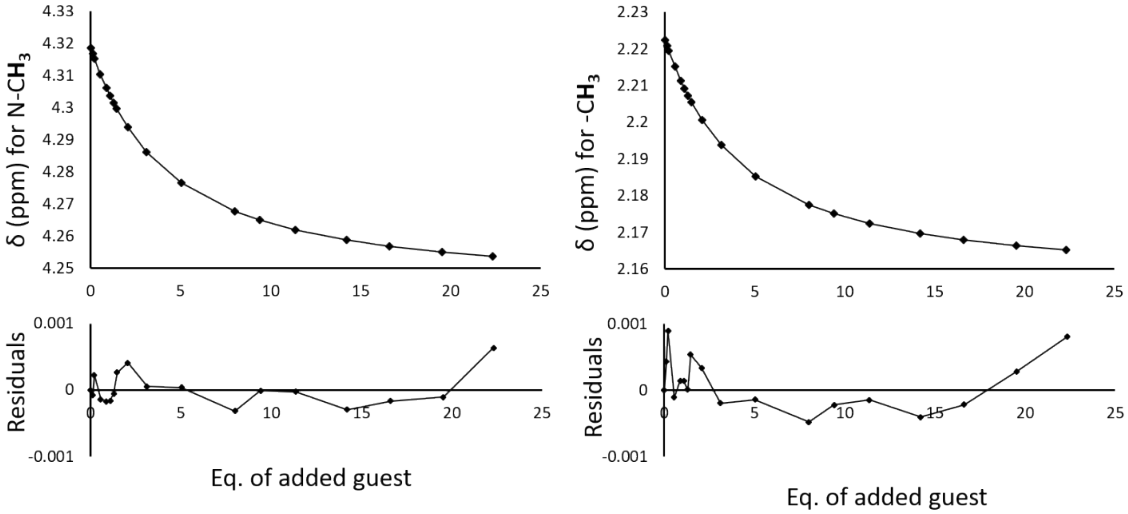


Figure S14. Bindfit output of the binding isotherms for the [**2-BF_4**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 277 ± 3 M^{-1}.

Trial 2

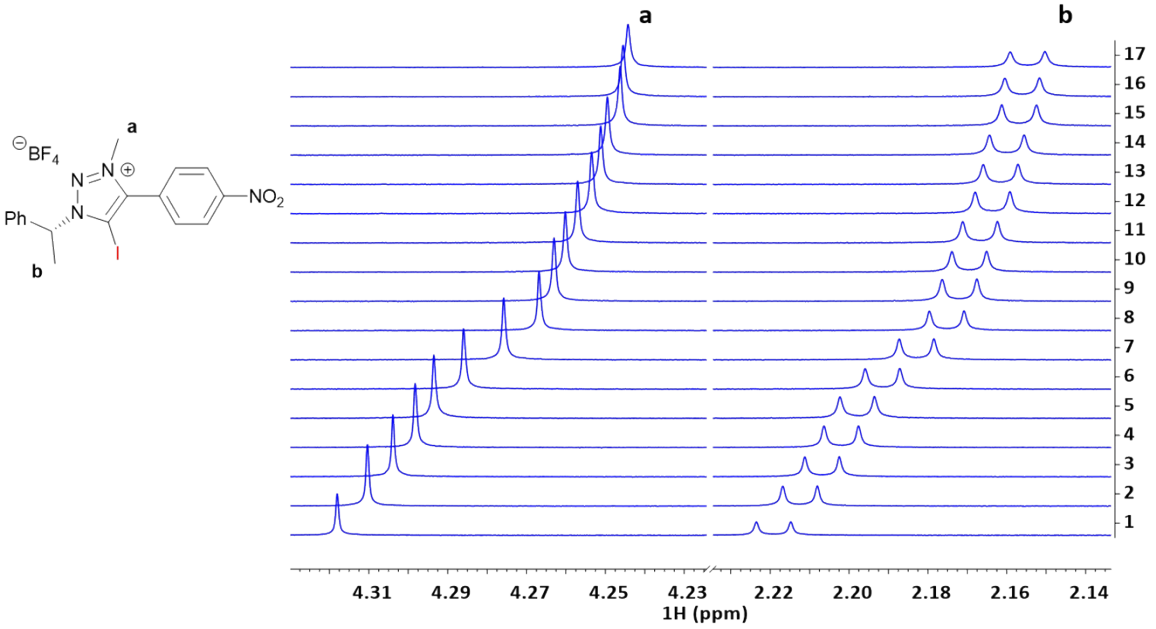


Figure S15. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **2-BF$_4$** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 17 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.5, 0.9, 1.4, 1.9, 2.9, 4.7, 7.8, 9.3, 11.6, 14.0, 20.2, 26.9, 29.1, 43.9, 47.3 and 54.3 eq of quinuclidine.

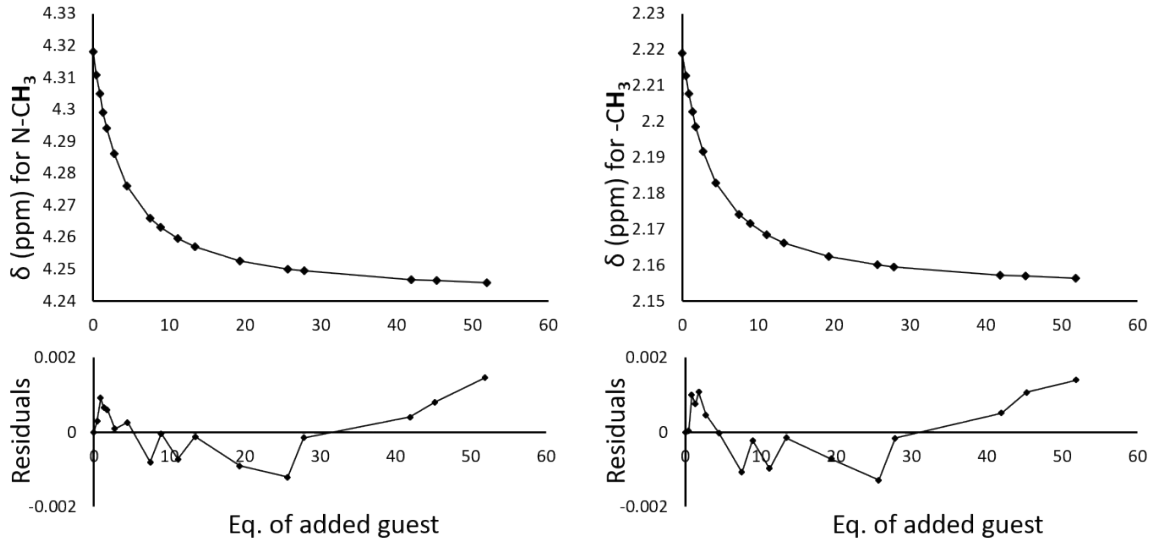


Figure S16. Bindfit output of the binding isotherms for the [**2-BF$_4$**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 290 ± 8 M^{-1}.

5. ^{1}H NMR titration data of [3-OTF-quinuclidine] complex

Trial 1

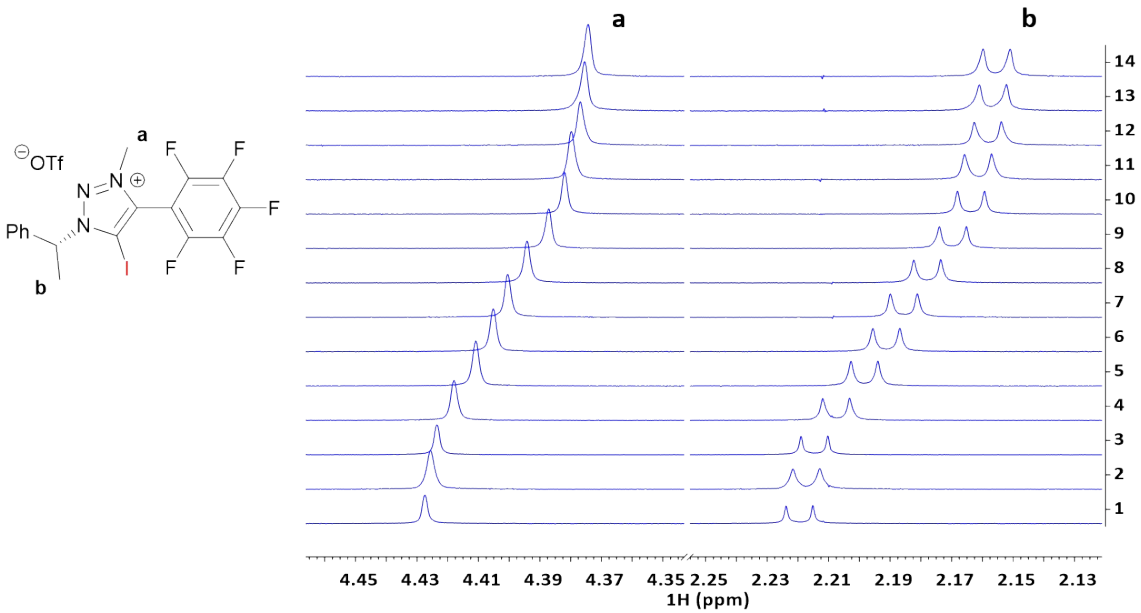


Figure S17. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-OTf** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 14 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.1, 0.2, 0.4, 0.9, 1.3, 1.8, 2.8, 4.4, 6.9, 8.0, 11.4, 14.6 and 17.0 eq of quinuclidine.

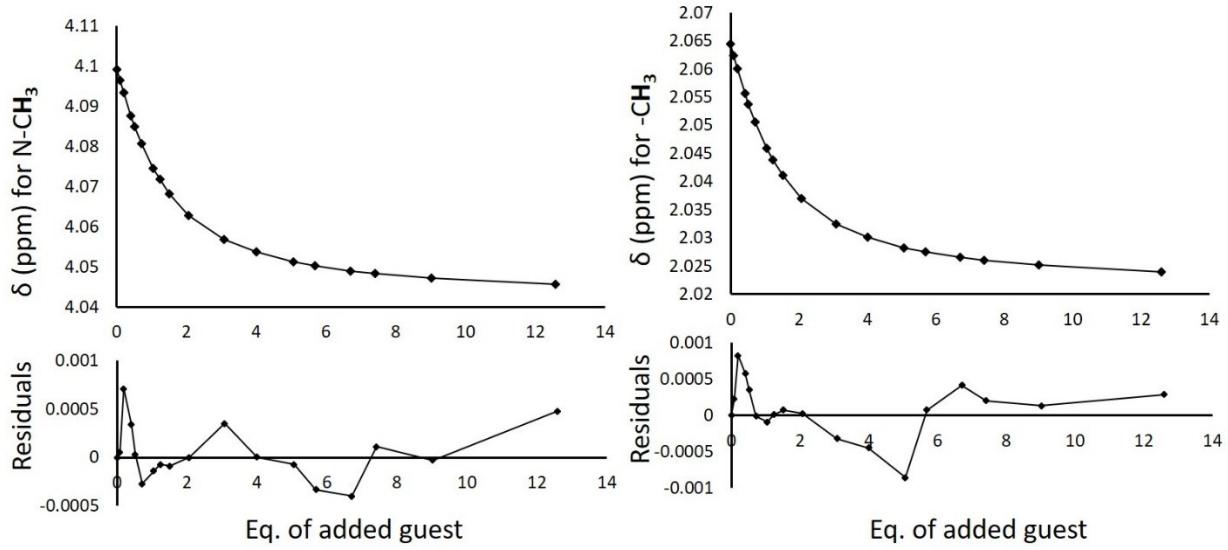


Figure S18. Bindfit output of the binding isotherms for the [**3-OTf**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 700 ± 18 M^{-1}.

Trial 2

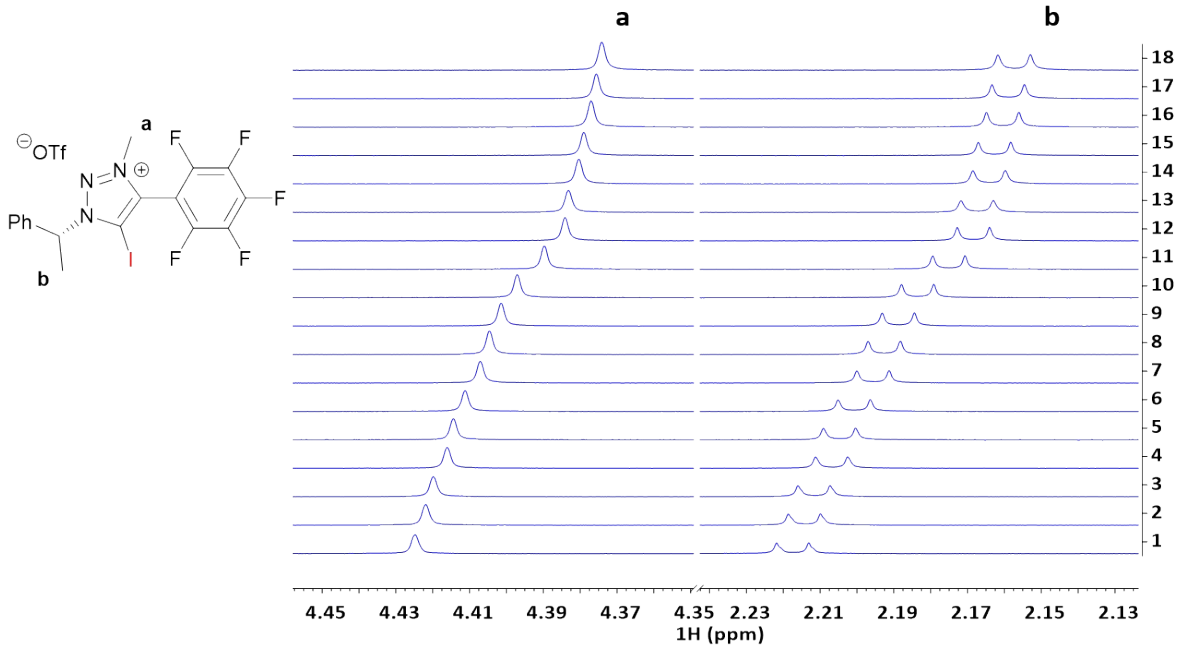


Figure S19. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-OTf** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.1, 0.2, 0.4, 0.5, 0.7, 1.0, 1.2, 1.5, 2.0, 3.0, 4.9, 5.3, 6.2, 7.3, 8.7, 10.5 and 12.9 eq of quinuclidine.

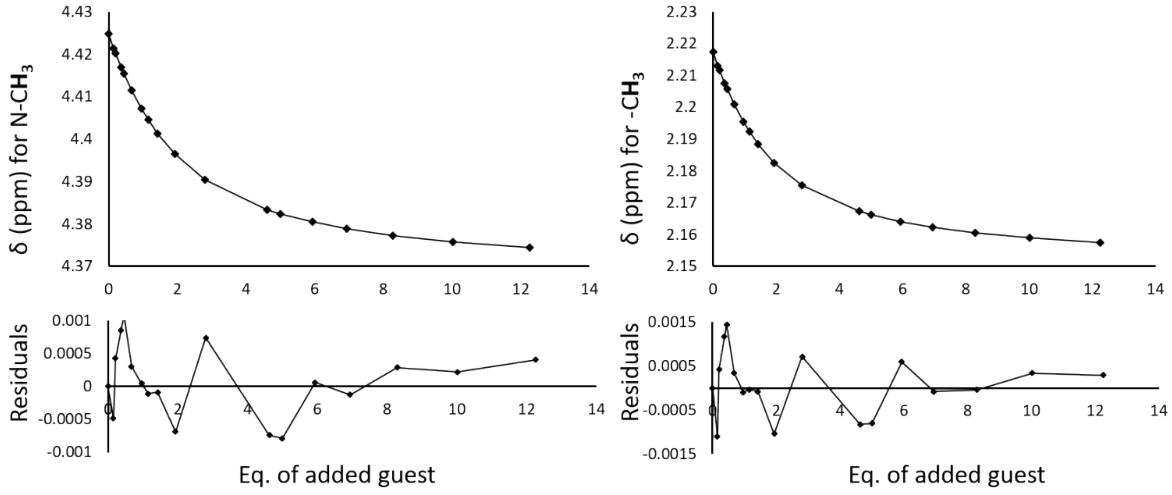


Figure S20. Bindfit output of the binding isotherms for the [**3-OTf**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 706 ± 18 M^{-1}.

6. ^{1}H NMR titration data of [3-BARF-quinuclidine] complex

Trial 1

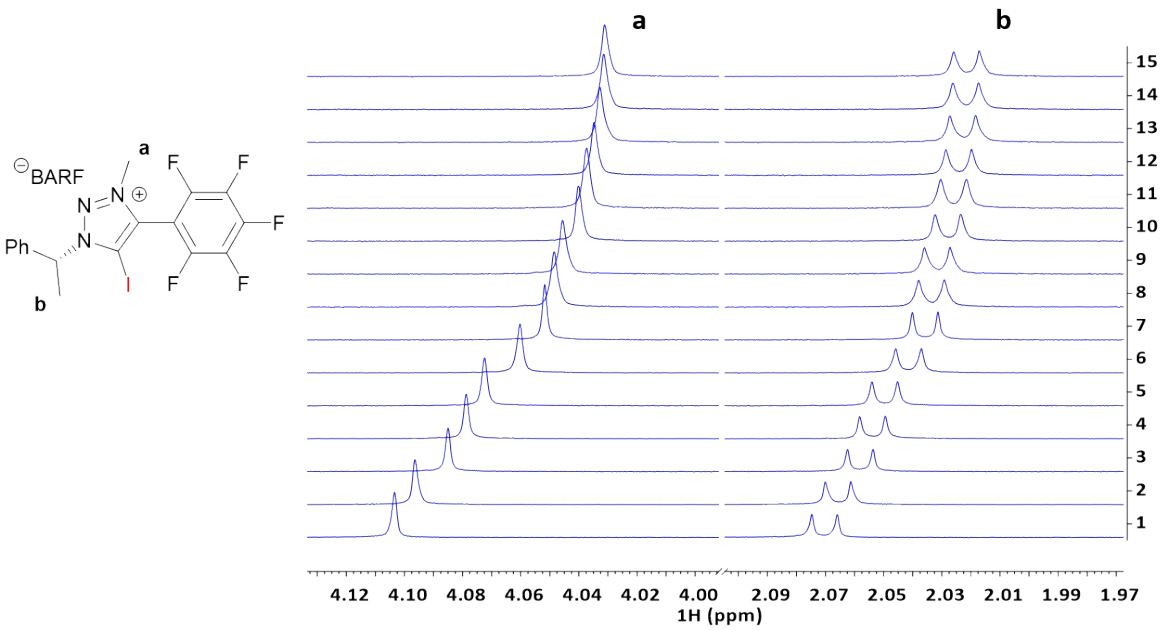


Figure S21. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 15 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.1, 0.3, 0.4, 0.5, 0.7, 0.9, 1.0, 1.1, 1.4, 1.8, 2.2, 3.3, 5.3, 6.1 eq of quinuclidine.

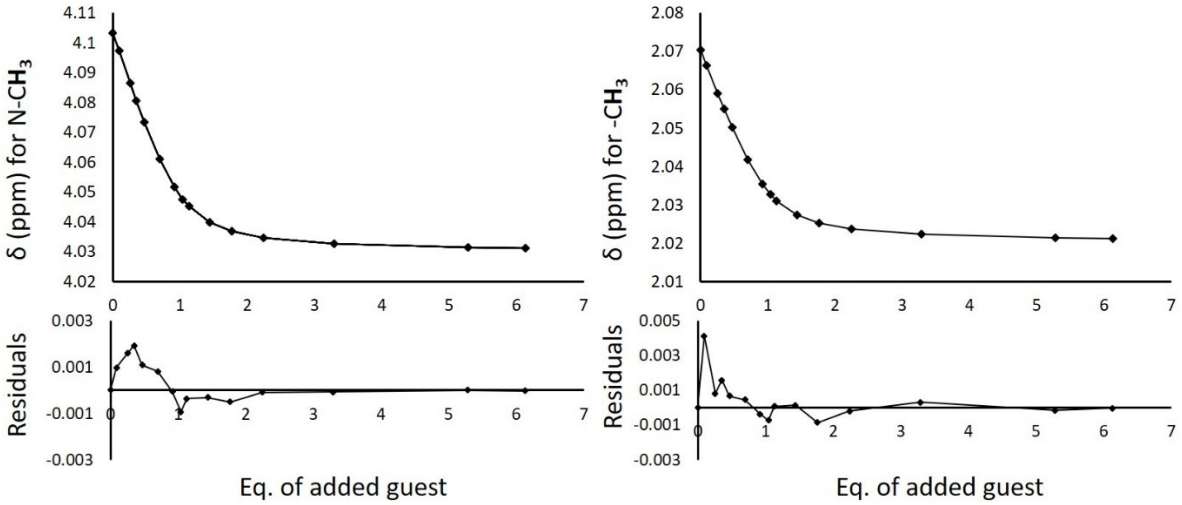


Figure S22. Bindfit output of the binding isotherms for the [**3-BARF**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = (1.1 ± 0.2) × 10^4 M^{-1}.

Trial 2

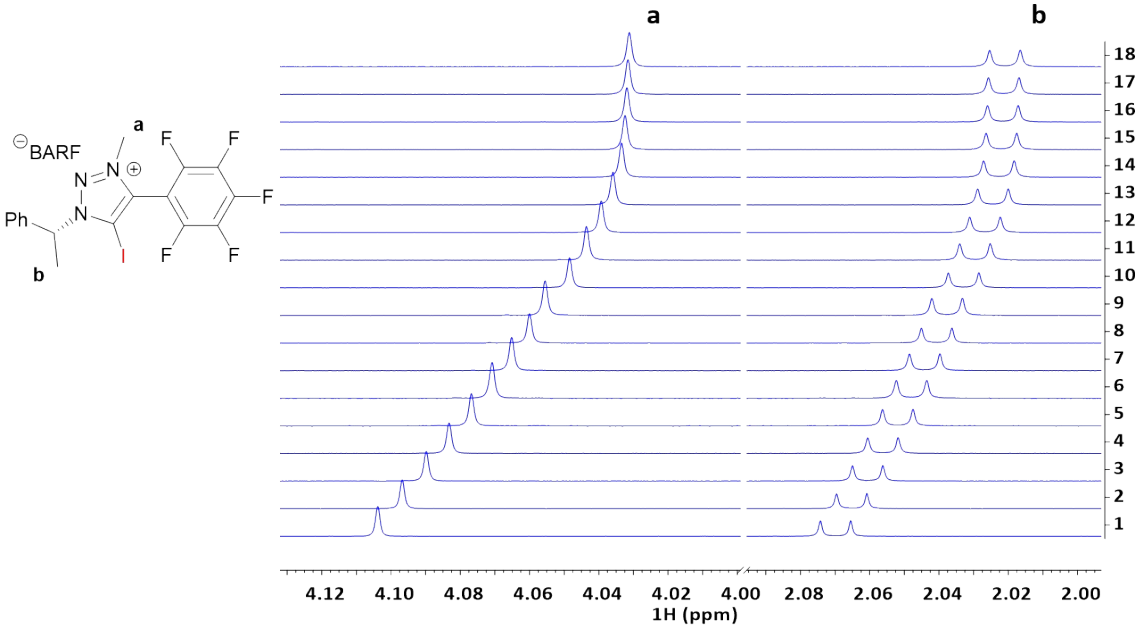


Figure S23. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0, 1.2, 1.5, 2.0, 2.9, 3.8, 4.8, 5.3, 7.1 eq of quinuclidine.

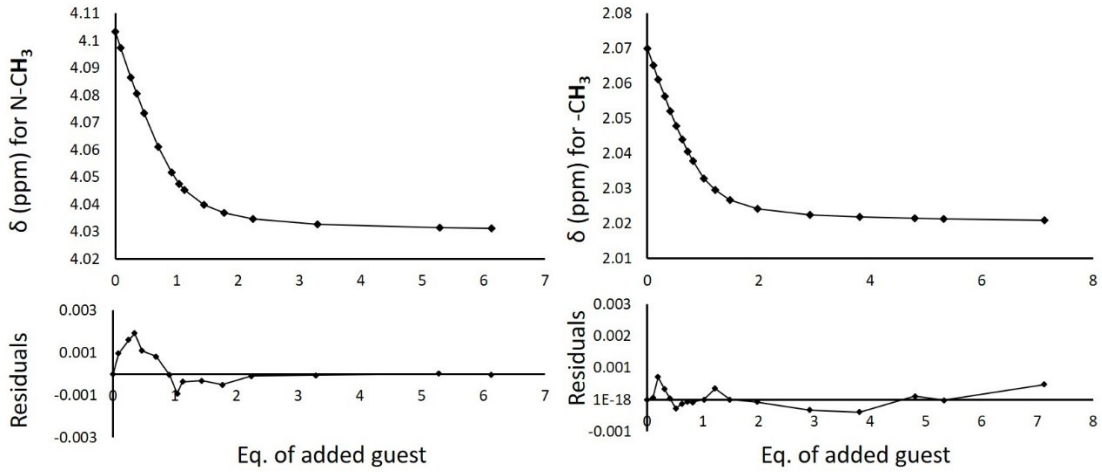


Figure S24. Bindfit output of the binding isotherms for the [**3-BARF**-quinuclidine] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = (1.1 ± 0.03) × 10^4 M^{-1}.

7. ^{1}H NMR titration data of [4-OTf-quinuclidine] complex

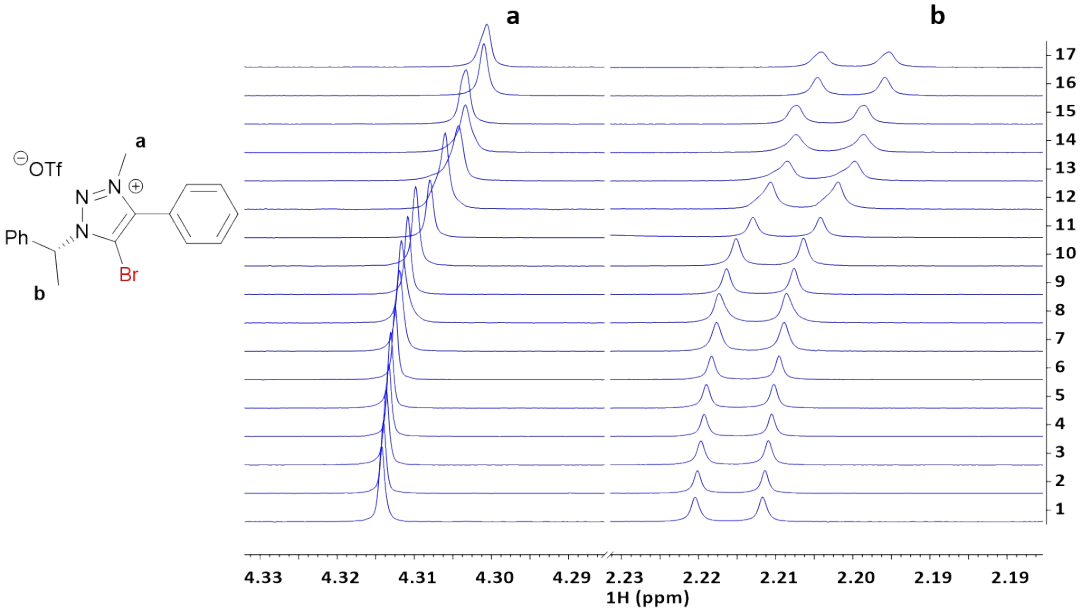


Figure S25. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **4-OTf** (1.5 mM) titration with quinuclidine at 298 K. Showing the collected 17 data points of methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition 0.0, 2.0, 4.9, 7.8, 9.7, 14.3, 18.7, 23.1, 27.2, 35.3, 42.8, 49.9, 63.1, 74.9, 85.6, 95.4, 104.2 and 112.4 eq of quinuclidine. There are no remarkable chemical shifts to be seen when adding up to 112.4 eq of XB acceptor to the **4-OTf** sample. The low value of the calculated association constant *Ka* = (2.98 ± 0.02) × 10^{-3} M^{-1}, evidences low probability of complex formation.

8. ^{1}H NMR titration data of [5-BARF-quinuclidine] complex

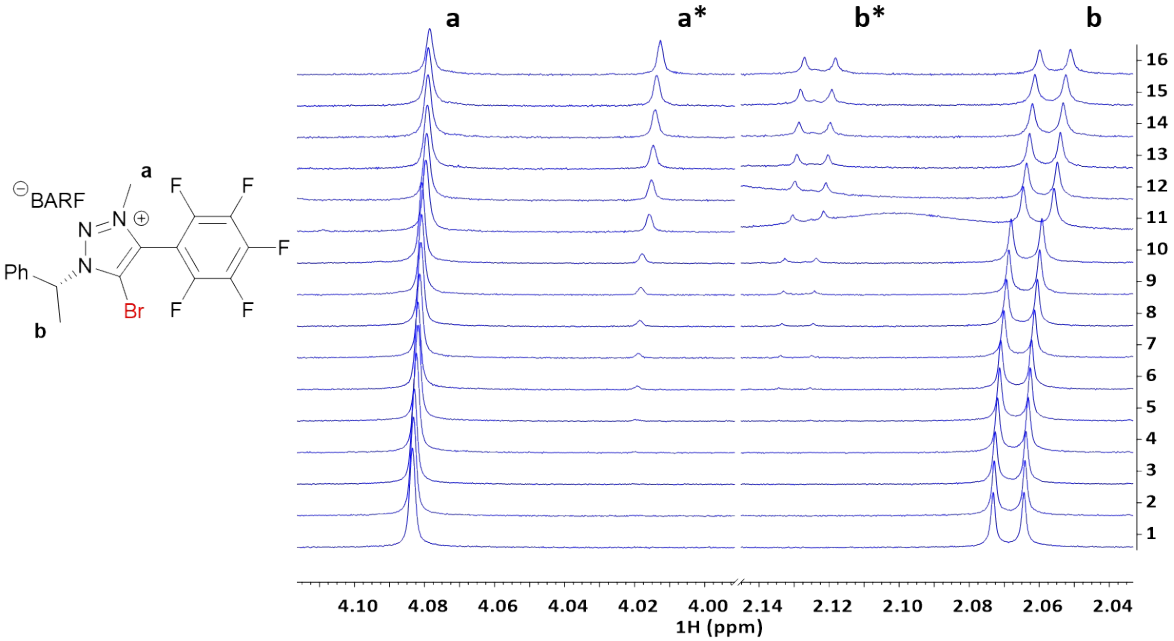


Figure S26. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **5-BARF** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 16 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 1.0, 2.0, 5.0, 7.9, 9.8, 14.4, 18.9, 23.3, 27.5, 35.6, 57.2, 63.6, 69.8, 75.6 and 86.4 eq of quinuclidine. When adding more than 9.8 eq of quinuclidine to **5-BARF**, the XB donor went through noticeable changes in its structure that were evidenced by the duplication of all the **5-BARF** proton signals (only protons **a*** and **b*** shown for clarity). This suggests two species of the triazolium salt being present in the solution due to -Br exchange with -H atom (based on previous similar observations with other triazolium salts, but not during the other titrations described in this study). Therefore, the association constant for [**5-BARF**-quinuclidine] complex could not be determined.

9. ^{1}H NMR titration data of [6-OTf-quinuclidine] complex

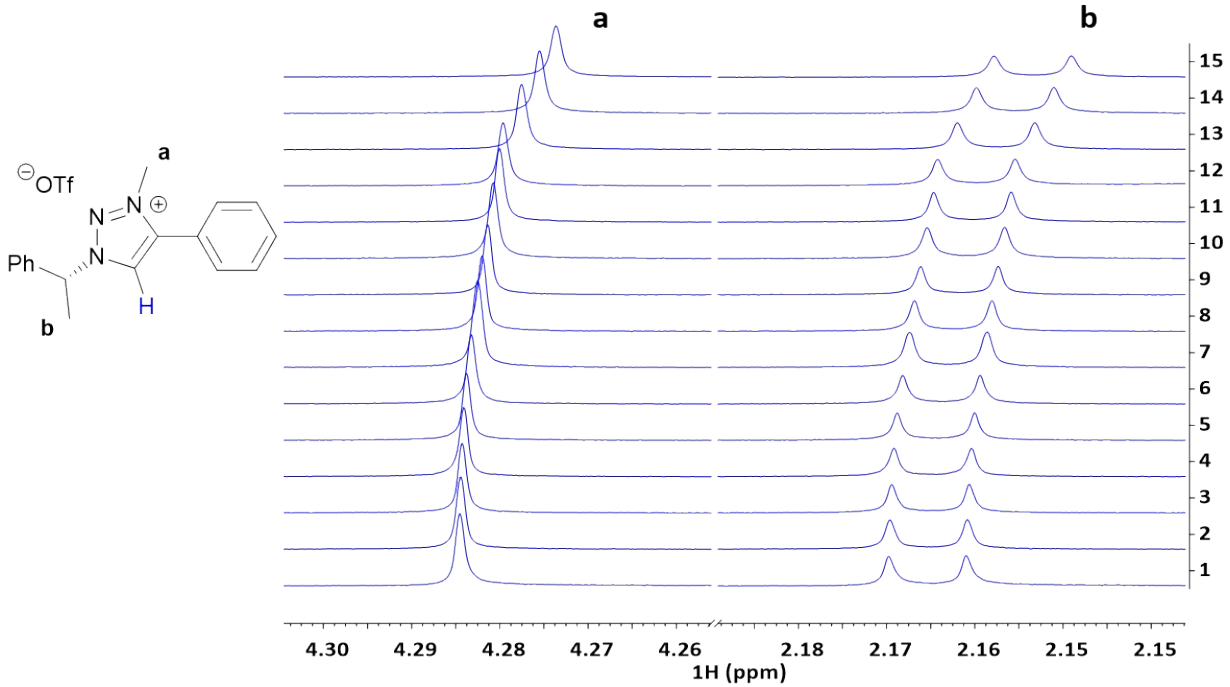


Figure S27. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **6-OTf** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 15 data points of methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition eq of quinuclidine. There are no remarkable chemical shifts to be seen when adding up to 0.0, 1.0, 2.0, 3.9, 5.8, 7.7, 14.2, 18.6, 22.9, 27.0, 31.1, 35.0, 49.6, 62.6 and 74.4 eq of quinuclidine to the **6-OTf** sample. The low value of the calculated association constant *Ka* = (3.17 ± 0.01) × 10^{-5} M^{-1}, evidences low probability of complex formation.

10. ^{1}H NMR titration data of [7-quinuclidine] complex

Trial 1

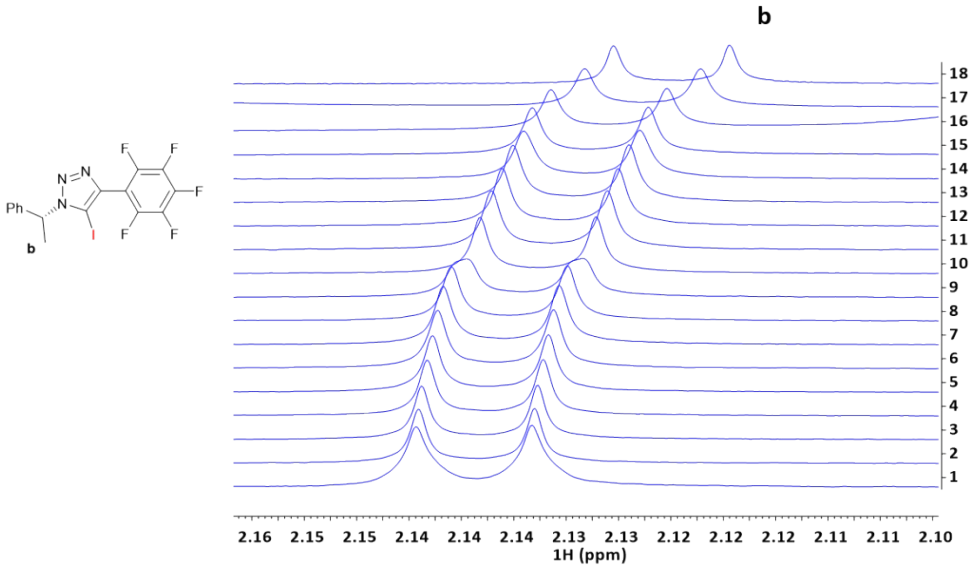


Figure S28. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **7** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **b** (-C**H$_3$**) after the addition of 0.0, 1.0, 3.1, 5.2, 10.2, 15.1, 19.9, 24.6, 29.2, 33.7, 38.0, 46.5, 54.6, 62.3, 69.7, 76.8, 83.6 and 96.5 eq of quinuclidine.

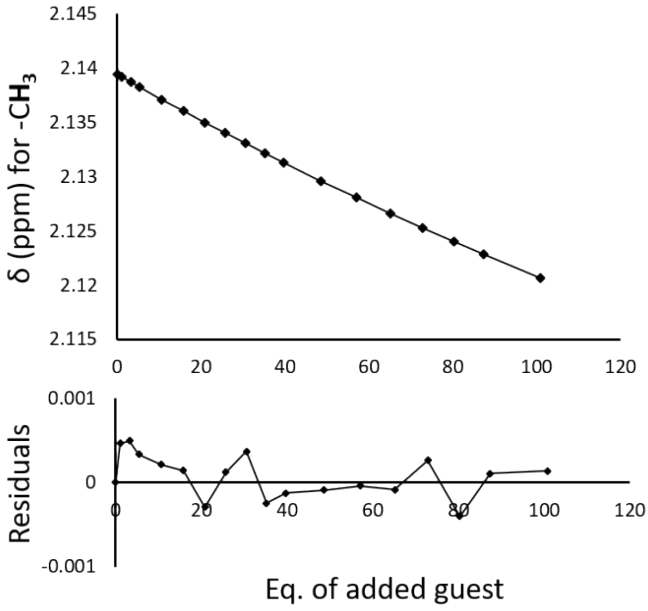


Figure S29. Bindfit output of the binding isotherms for the [**7**-quinuclidine] complex. The global fitting of the methyl protons **b** (-C**H$_3$**) gave average value of K_a = 1.82 ± 0.03 M^{-1}.

Trial 2

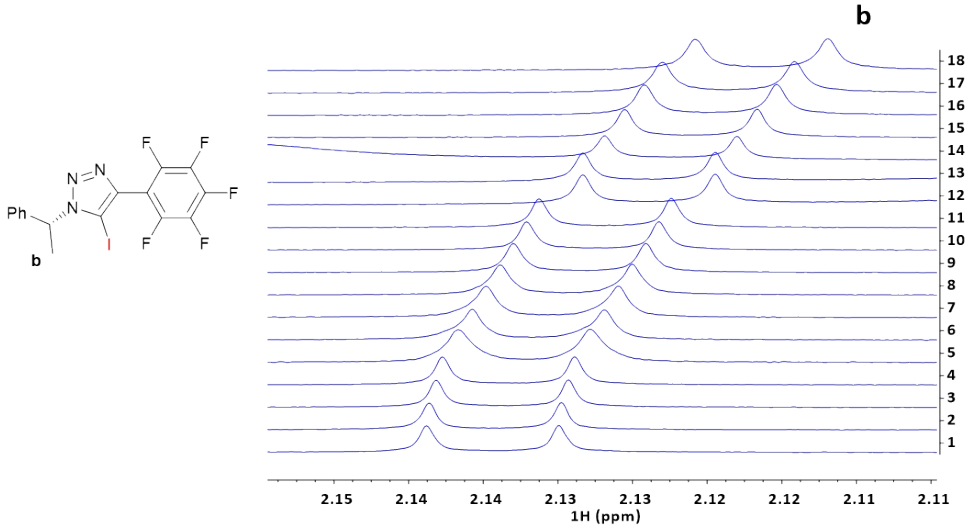


Figure S30. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **7** (1.0 mM) titration with quinuclidine at 298 K. Showing the collected 18 data points of methyl protons **b** (-C**H**$_3$) after the addition of 0.0, 1.0, 3.0, 5.0, 10.0, 14.8, 19.5, 24.0, 28.5, 32.9, 37.2, 41.3, 53.3, 60.9, 68.1, 75.1, 81.8 and 94.3 eq of quinuclidine.

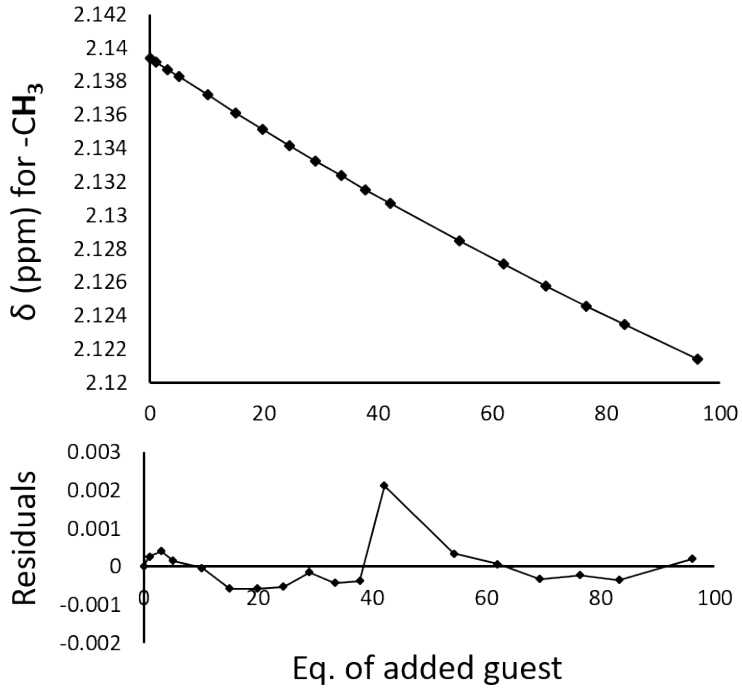


Figure S31. Bindfit output of the binding isotherms for the [**7**-quinuclidine] complex. The global fitting of the methyl protons **b** (-C**H**$_3$) gave average value of K_a = 2.09 ± 0.08 M^{-1}.

11. ^{1}H NMR titration data of [3-BARF-*R*-8] complex

Trial 1

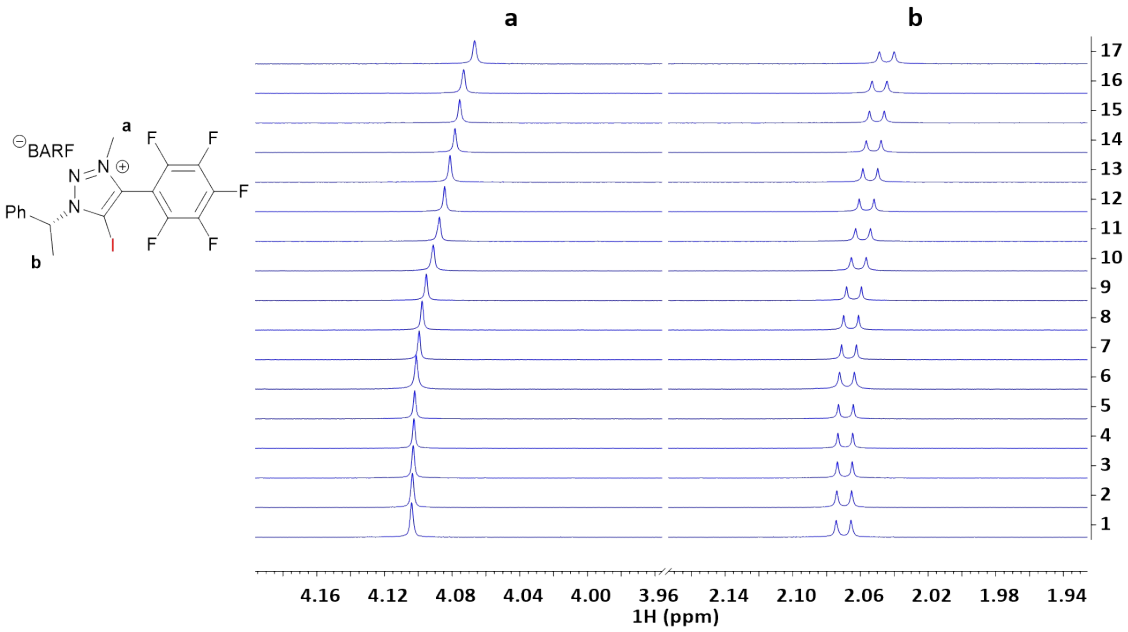


Figure S32. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *R*-imine at 298 K. Showing the collected 17 data points of protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) after the addition of 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.9, 6.8, 9.6, 14.2, 18.7, 23.0, 27.2, 31.2, 35.2, 39.0 and 49.8 eq of ***R*-8**.

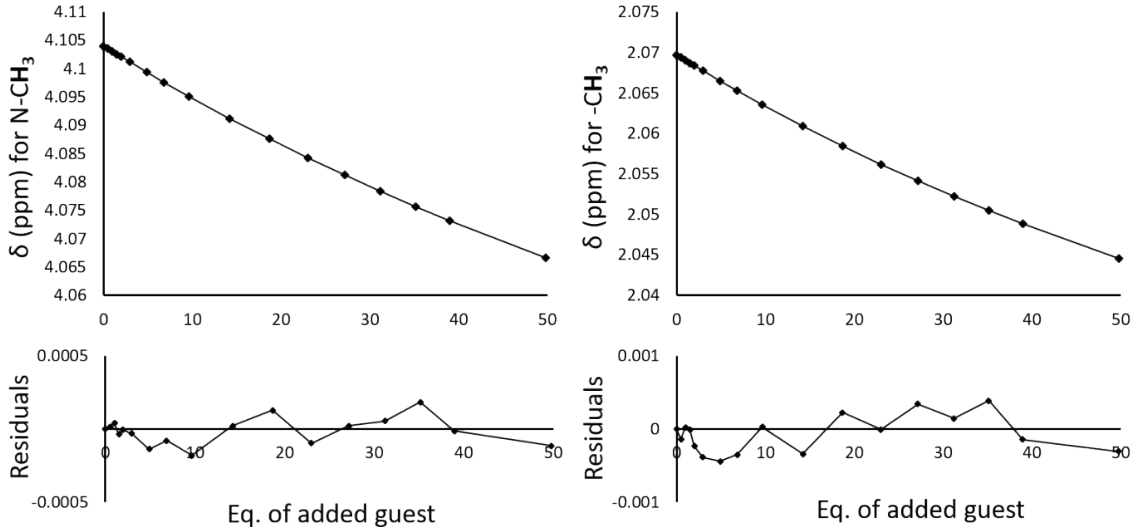


Figure S33. Bindfit output of the binding isotherms for the [**3-BARF-*R*-8**] complex. The global fitting of the methyl protons **a** (N-C**H$_3$**) and **b** (-C**H$_3$**) gave average value of K_a = 6.41 ± 0.04 M^{-1}.

Trial 2

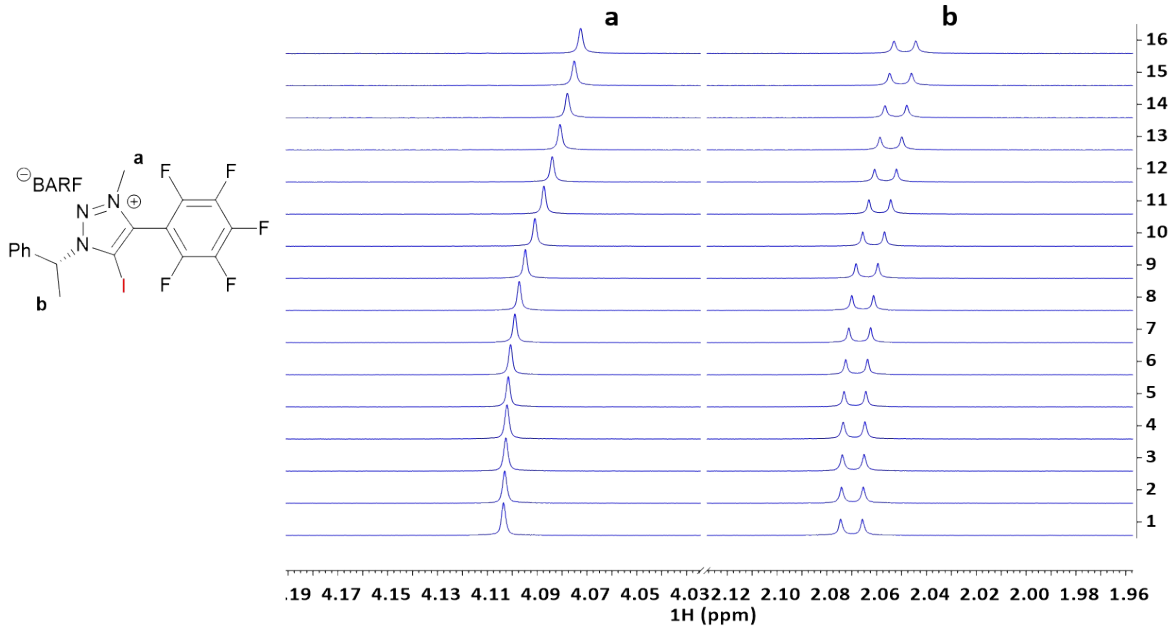


Figure S34. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *R*-imine at 298 K. Showing the collected 16 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.9, 6.8, 9.7, 14.3, 18.8, 23.1, 27.3, 31.4, 35.3 and 39.2 eq of ***R*-8**.

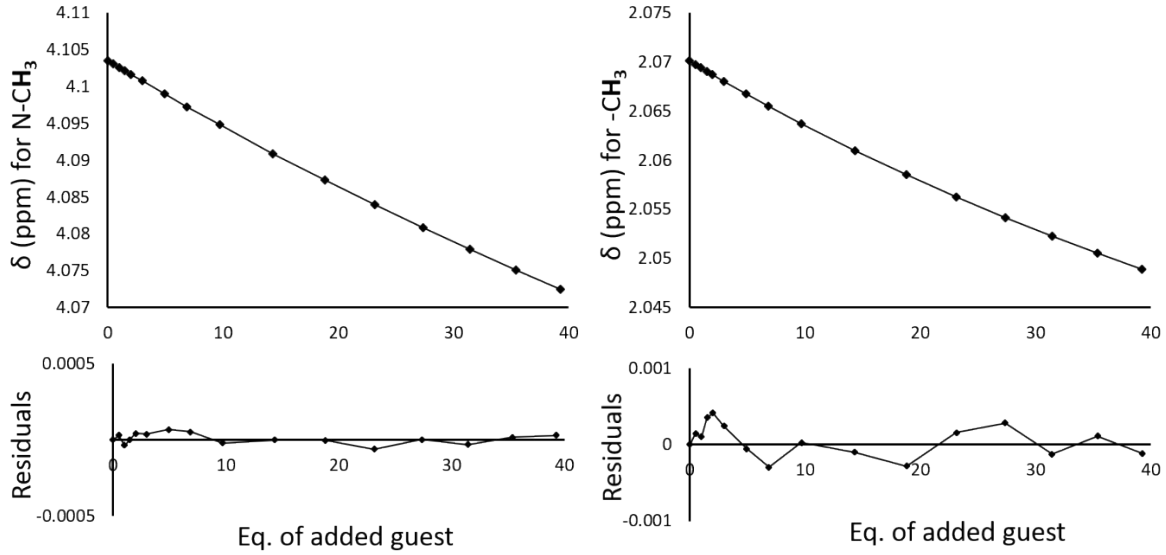


Figure S35. Bindfit output of the binding isotherms for the [**3-BARF**-***R*-8**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 5.90 ± 0.04 M^{-1}.

12. ^{1}H NMR titration data of [3-BARF-*S*-8] complex

Trial 1

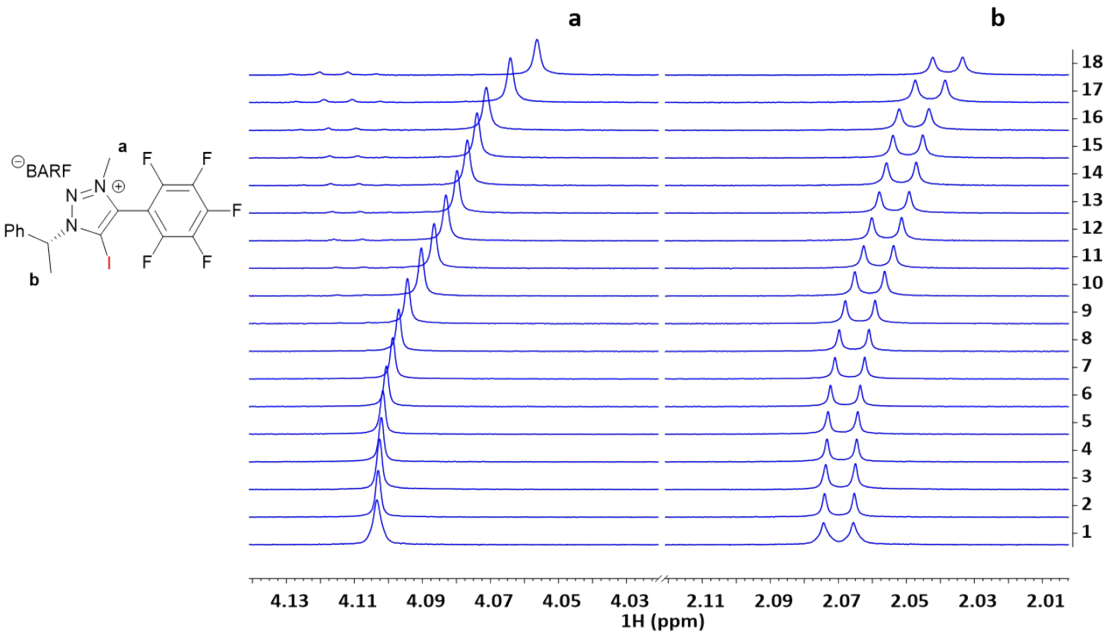


Figure S36. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *S*-imine at 298 K. Showing the collected 18 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.5, 0.9, 1.4, 1.9, 2.8, 4.7, 6.5, 9.2, 13.6, 17.8, 21.9, 25.9, 29.8, 33.6, 37.2, 47.5 and 60.0 eq of ***S*-8**.

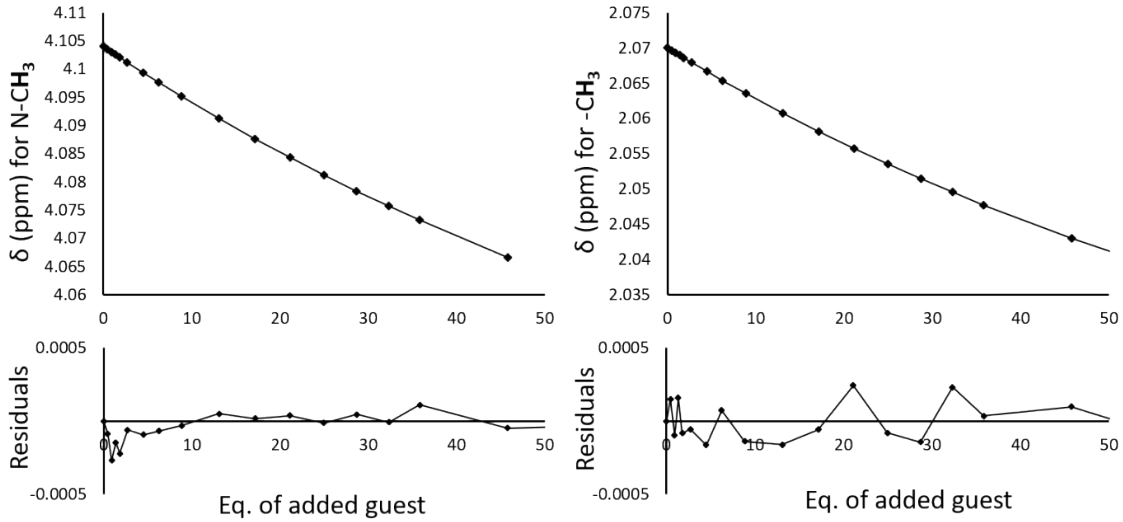


Figure S37. Bindfit output of the binding isotherms for the [**3-BARF-*S*-8**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 5.62 ± 0.02 M^{-1}.

Trial 2

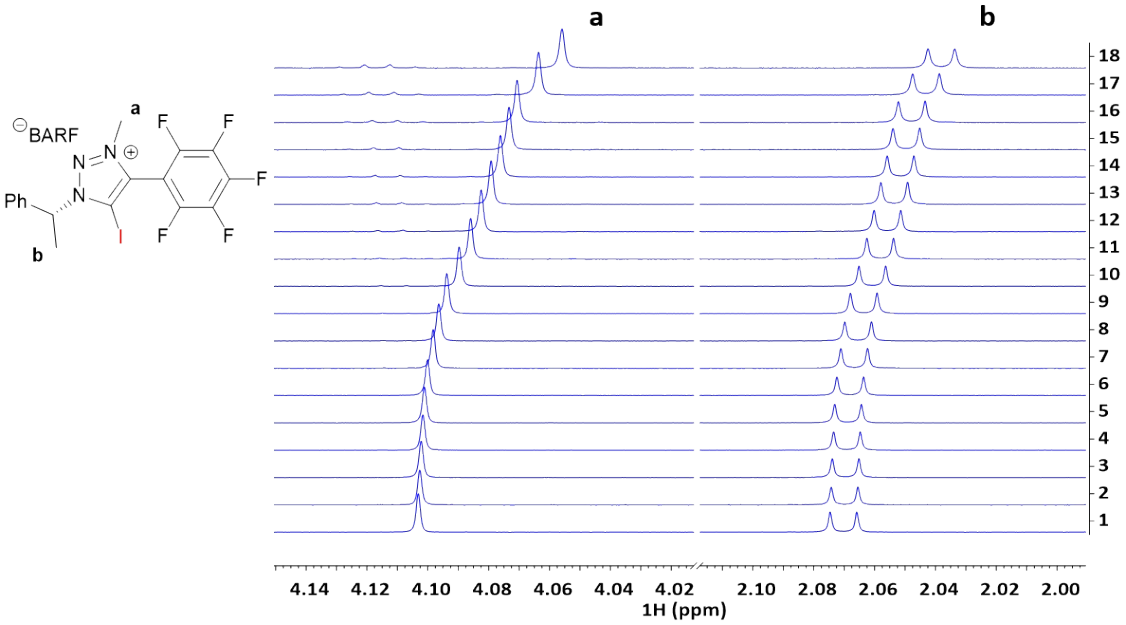


Figure S38. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *S*-imine at 298 K. Showing the collected 18 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.9, 6.8, 9.6, 14.2, 18.6, 22.9, 27.1, 31.1, 35.1, 38.9, 49.7 and 62.7 eq of ***S*-8**.

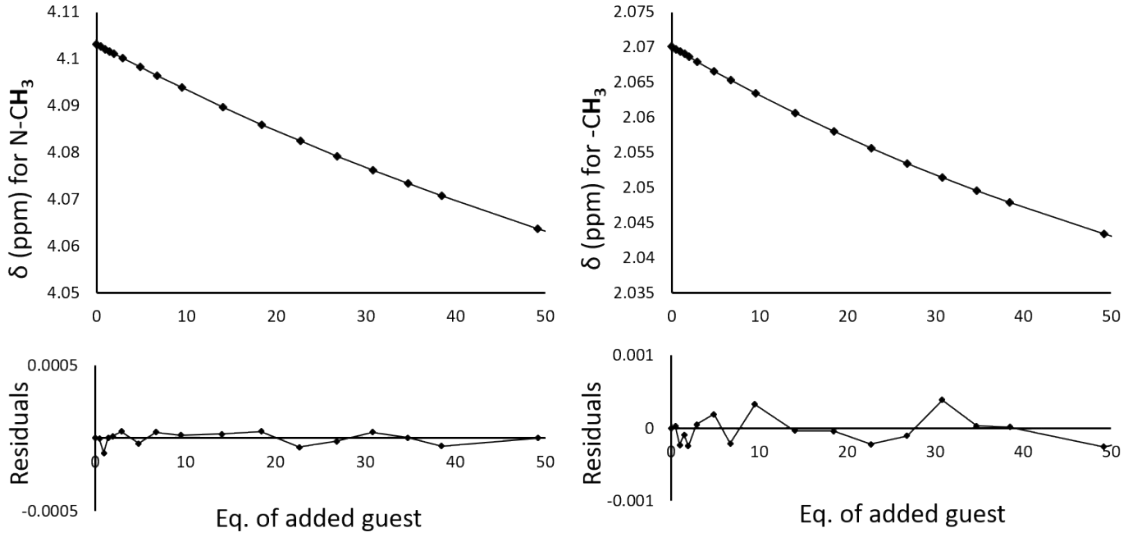


Figure S39. Bindfit output of the binding isotherms for the [**3-BARF**-***S*-8**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 6.34 ± 0.04 M^{-1}.

13. ^{1}H NMR titration data of [3-BARF-*R*-9] complex

Trial 1

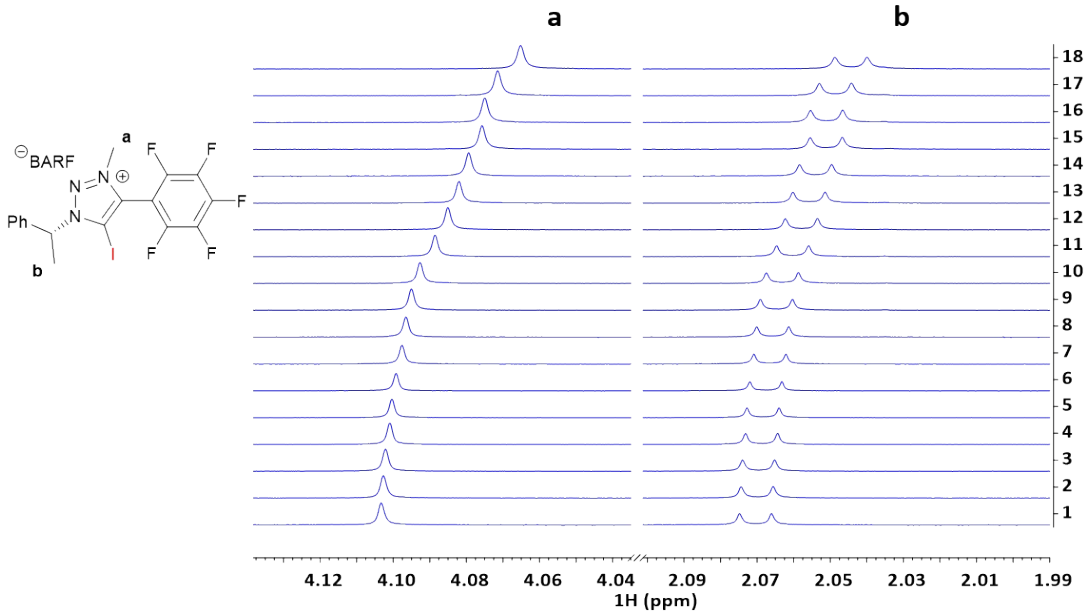


Figure S40. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with R-amine at 298 K. Showing the collected 18 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.1, 0.2, 0.4, 0.5, 0.7, 1.0, 1.2, 1.5, 1.9, 2.8, 3.7, 4.6, 5.4, 6.2, 7.0, 8.5 and 11.9 eq of ***R*-9**.

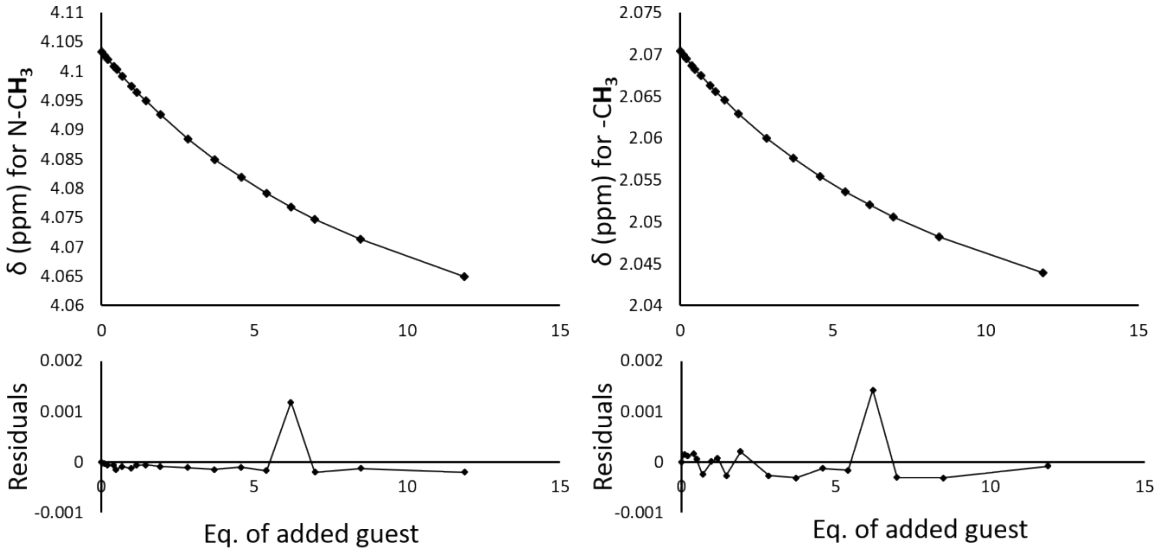


Figure S41. Bindfit output of the binding isotherms for the [**3-BARF-*R*-9**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 97 ± 1 M^{-1}.

Trial 2

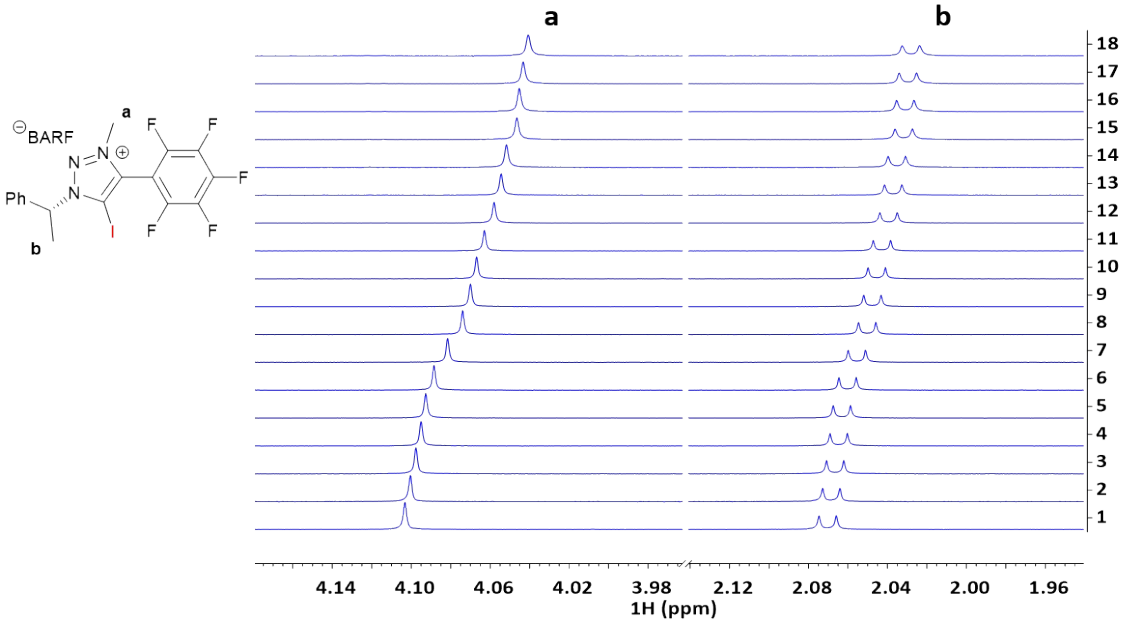


Figure S42. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *R*-amine at 298 K. Showing the collected 18 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.9, 7.8, 9.7, 11.5, 14.3, 18.7, 23.0, 27.2, 39.1, 42.8, 49.9 and 63.0 eq of ***R*-9**.

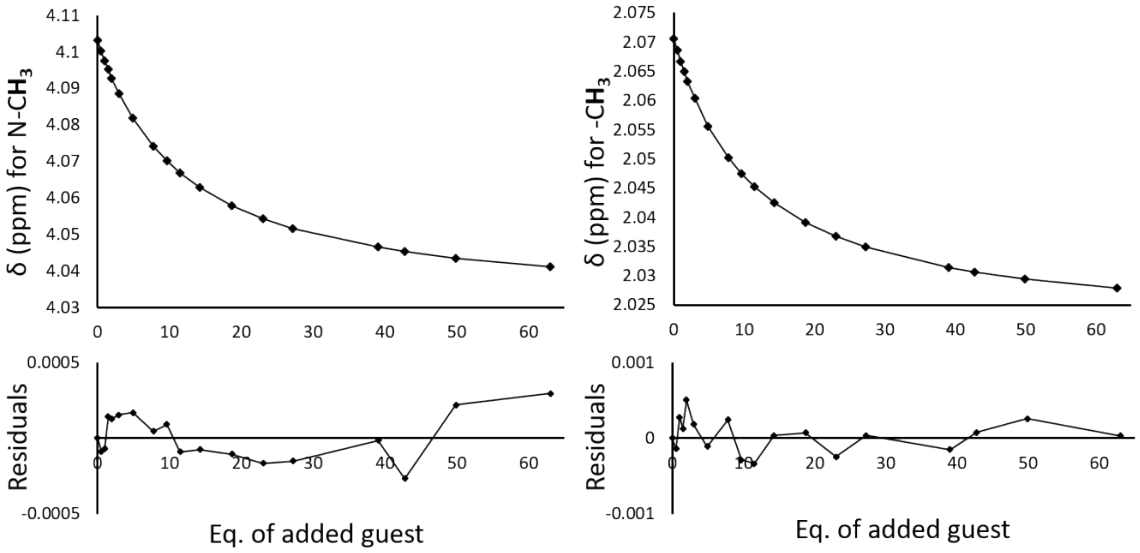


Figure S43. Bindfit output of the binding isotherms for the [**3-BARF**-***R*-9**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 91 ± 1 M^{-1}.

14. ^{1}H NMR titration data of [3-BARF-*S*-9] complex

Trial 1

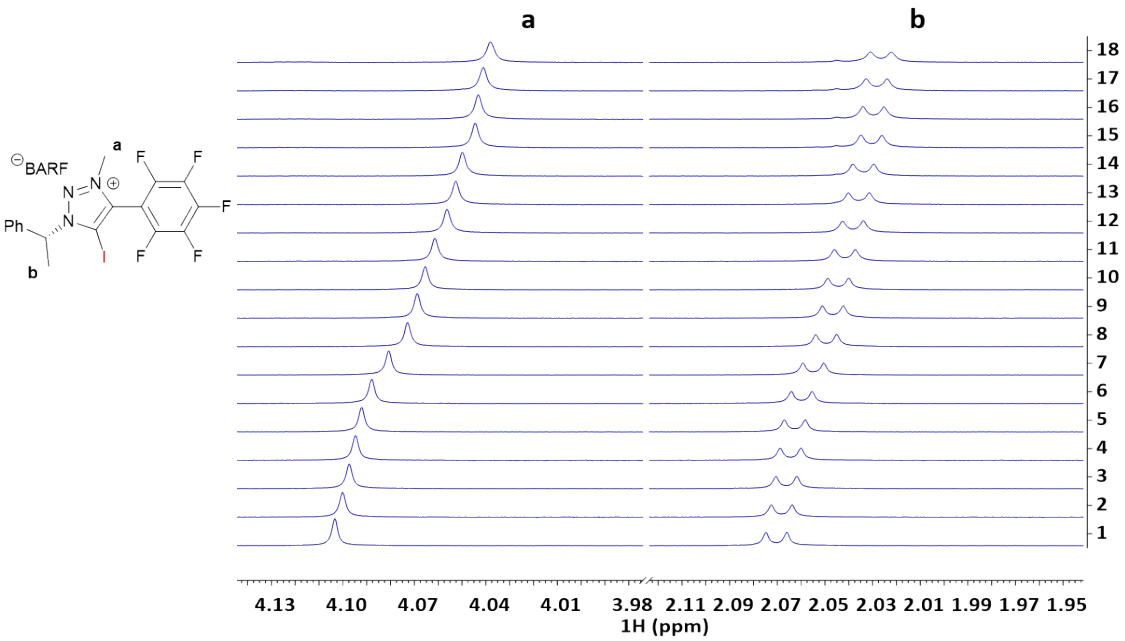


Figure S44. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *S*-amine at 298 K. Showing the collected 18 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.9, 7.7, 9.6, 11.5, 14.2, 18.6, 22.9, 27.1, 38.9, 42.6, 49.7 and 62.8 eq of ***S*-9**.

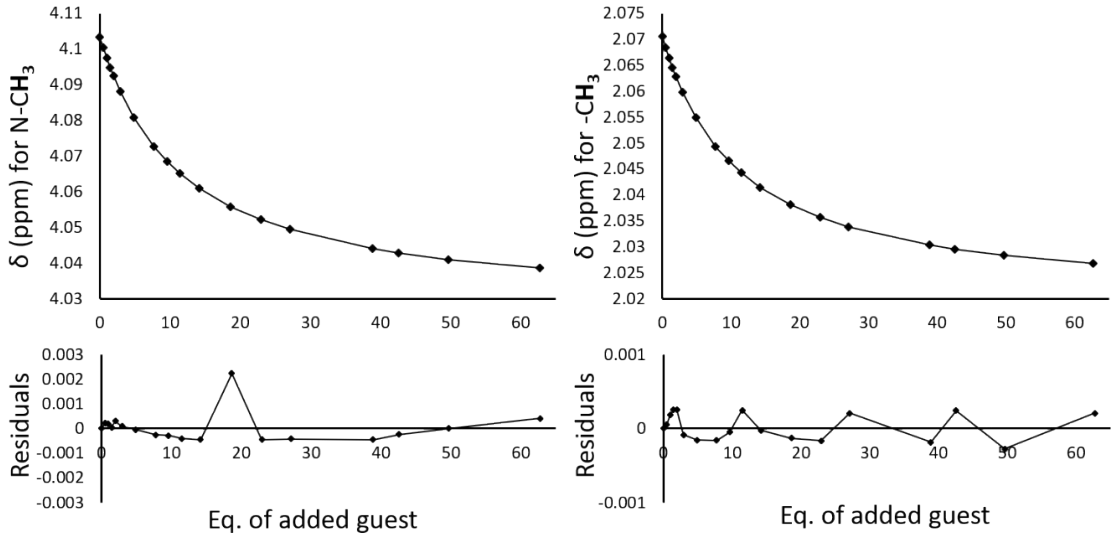


Figure S45. Bindfit output of the binding isotherms for the [**3-BARF-*S*-9**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 93 ± 1 M^{-1}.

Trial 2

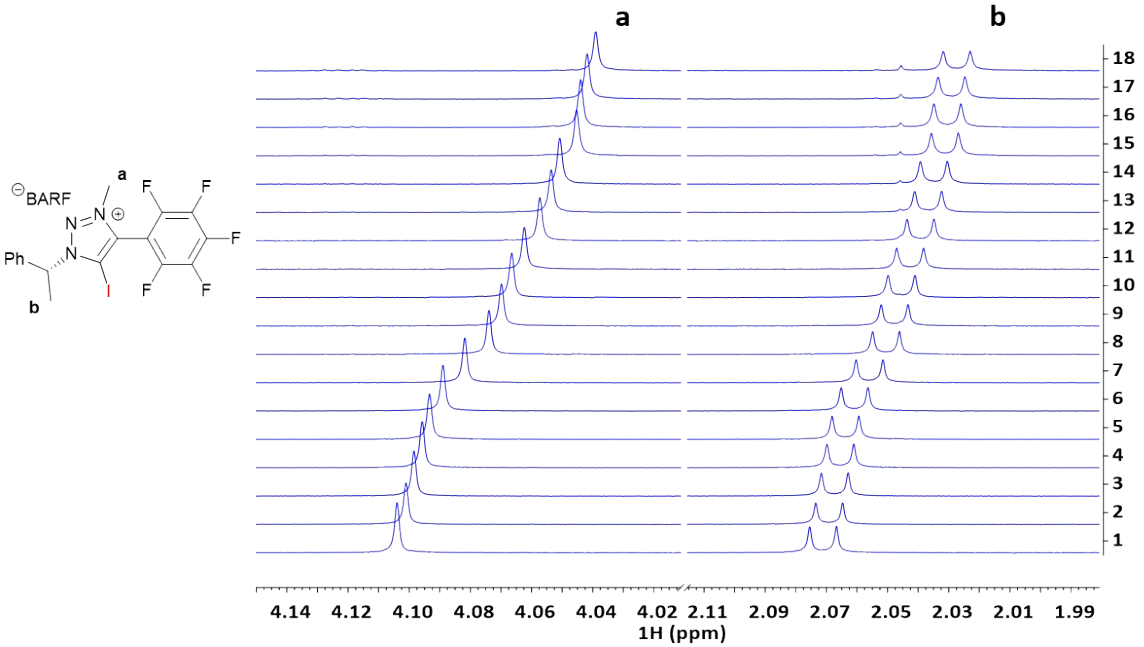


Figure S46. ^{1}H NMR spectra ($CDCl_3$, 800 MHz) of **3-BARF** (1.0 mM) titration with *S*-amine at 298 K. Showing the collected 18 data points of protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) after the addition of 0.0, 0.5, 1.0, 1.5, 2.0, 2.9, 4.9, 7.7, 9.6, 11.4, 14.2, 18.6, 22.9, 27.0, 38.8, 42.5, 49.5 and 62.6 eq of ***S*-9**.

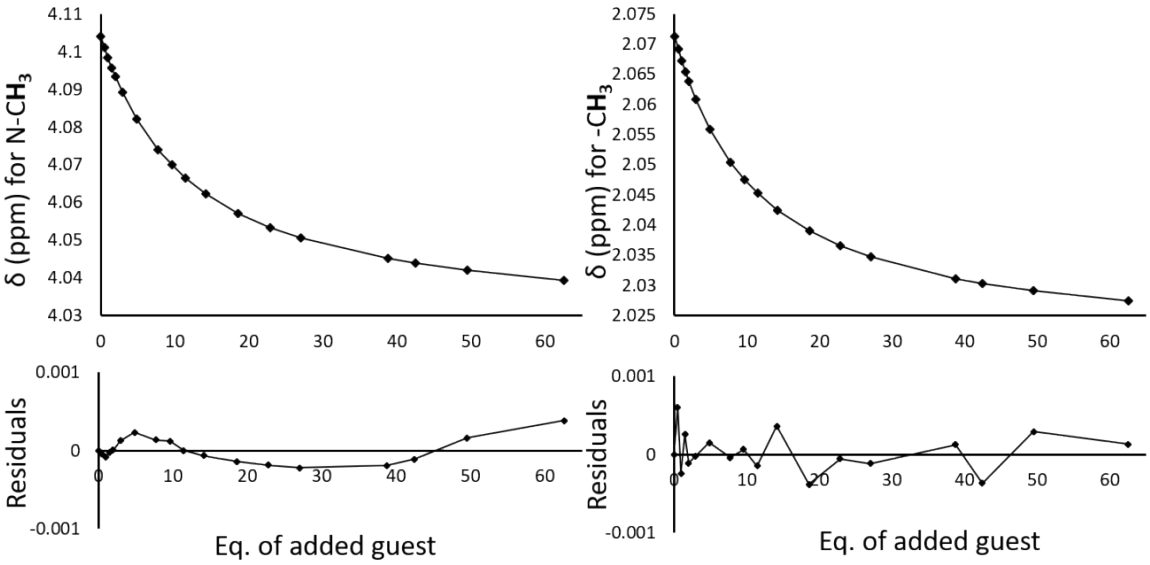


Figure S47. Bindfit output of the binding isotherms for the [**3-BARF**-***S*-9**] complex. The global fitting of the methyl protons **a** (N-C**H**$_3$) and **b** (-C**H**$_3$) gave average value of K_a = 89 ± 1 M^{-1}.

III) Computational Information

All the calculated structures were initially treated with extensive conformational analysis. The conformational scan of the amine **9** and **3-OTF** adduct was performed with the help of VEGA program[7,8] and force field SP4 implemented therein. The details about the conformational search procedure are similar to that described in ref.[9] About 50 generated lowest energy conformers were used as input for quantum mechanical calculations. DFT calculations were carried out with the Gaussian09 program[10] using the CAM-B3LYP functional[11] with the DEF2TZVP[12] basis set. All the generated structures were verified with frequency calculations in order to be sure that imaginary frequencies are not present. The latter step also gives us Gibbs free energy values; this is helpful in order to obtain a minimum energy structure (most stable structure). The energy values for adducts of **3-OTf** with the *R* and *S* enantiomer of **9** are pretty close (Table S1).

In order to evaluate the influence of the solvent (chloroform) effect the polarizable continuum model (PCM) [13] was used in the same Gaussian06 program. The geometries of the adducts (enantiomers of amine **9** with **3-OTF)** in the solvent remained pretty close to those in vacuum. Inclusion of the solvent results in lowering of the Gibbs free energy differences between the diastereomeric adducts (from 0.431 to -0.237 kcal/mol).

Table S1. Relative electronic energies (E) and Gibbs free energies (G) (kcal/mol) of the adducts (enantiomers of amine **9** with **3-OTF**) in vacuum and chloroform.

solvent	adduct of **3-OTf** with enantiomer of **9**	E	G
vacuum	*S*	0.016	0.431
vacuum	*R*	0.000	0.000
chloroform	*S*	0.129	0.000
chloroform	*R*	0.000	0.237

Cartesian coordinates of the minimum energy structures:

S-9 complex with **3-OTf** vacuum:

69
mikk231-clust3-1_cam_tzvp_2.out

O	4.13142	-5.15094	3.20620
S	5.22879	-4.69335	2.37853
O	4.93673	-3.49720	1.61488
O	5.90360	-5.73512	1.63744
C	6.48867	-4.12813	3.59759
F	6.86452	-5.12905	4.39498
F	7.57521	-3.66273	2.97909
F	6.00234	-3.15069	4.36614
N	2.31241	-4.49692	0.12802
C	3.13235	-5.51227	-0.24198
C	4.09966	-4.91069	-1.01216
N	3.76593	-3.59614	-1.03509
N	2.69270	-3.35020	-0.35122
C	5.25832	-5.50009	-1.68721
C	6.56489	-5.09350	-1.43811
C	7.64228	-5.72285	-2.03195
C	7.43017	-6.77975	-2.89545
C	6.14196	-7.19506	-3.17533
C	5.07876	-6.55255	-2.57781
I	3.00506	-7.48667	0.42333
C	1.08980	-4.58498	0.97685
C	0.83670	-3.27793	1.69440
C	-0.05633	-5.10419	0.12490
C	-0.16128	-2.40042	1.29640

***R*-9** complex with **3-OTf** vacuum:

69
mikk232-clust3-1_cam_tzvp_9.out

O	1.84354	1.52570	0.77620
S	1.77394	0.25762	1.47368
O	2.50798	-0.81392	0.83280
O	0.45359	-0.10385	1.93922
C	2.72074	0.56123	3.02422
F	2.15702	1.53205	3.74463
F	2.76725	-0.53787	3.77860
F	3.97600	0.92668	2.75197
N	1.48262	-0.38852	-2.14972
C	0.26937	-0.47623	-1.54985
C	0.22405	-1.75756	-1.05172
N	1.40918	-2.31613	-1.40472
N	2.16230	-1.49290	-2.06425
C	-0.83654	-2.42997	-0.29760
C	-2.12685	-2.48213	-0.81337
C	-3.17664	-3.02658	-0.10515
C	-2.94730	-3.54973	1.15344
C	-1.67286	-3.53424	1.68551
C	-0.63304	-2.98075	0.96336
I	-1.08077	1.09804	-1.29361
C	2.05714	0.79013	-2.85808
C	3.56763	0.77740	-2.78898
C	1.45885	0.85670	-4.25334
C	4.35263	0.40563	-3.87066

C	-0.37351	-1.22029	1.98960
C	0.41375	-0.90806	3.08376
C	1.41223	-1.78083	3.48382
C	1.62281	-2.96214	2.79640
C	4.51002	-2.47369	-1.57998
F	6.81063	-4.07289	-0.63961
F	8.87673	-5.31549	-1.78000
F	8.45702	-7.38405	-3.46786
F	5.93522	-8.19625	-4.02156
F	3.85080	-6.95750	-2.88975
H	1.35638	-5.33230	1.72299
H	0.18679	-6.08032	-0.29098
H	-0.94733	-5.20809	0.74134
H	-0.28067	-4.42603	-0.69727
H	-0.78668	-2.62695	0.44429
H	-1.15716	-0.54502	1.67226
H	0.24832	0.01399	3.62556
H	2.03457	-1.54379	4.33620
H	2.41319	-3.63576	3.10612
H	3.80312	-1.67567	-1.78117
H	5.24213	-2.15979	-0.84021
H	5.00191	-2.78463	-2.49704
C	5.28968	-10.29502	2.09753
C	3.84109	-10.51842	2.50344
C	3.47364	-9.81340	3.79241
N	2.95719	-10.11863	1.38851
C	1.56336	-10.50187	1.57713
C	2.86360	-10.52533	4.81728
C	2.51826	-9.90670	6.00800
C	2.77874	-8.55917	6.18669
C	3.39002	-7.83854	5.17322
C	3.73898	-8.46264	3.98852
H	5.49737	-9.24151	1.91560
H	5.95735	-10.63918	2.88585
H	5.52634	-10.85347	1.18884
H	3.69990	-11.59362	2.68302
H	3.30906	-10.56640	0.54952
H	1.00087	-10.28357	0.67023
H	1.44615	-11.56655	1.81354
H	1.13192	-9.92625	2.39408
H	2.65824	-11.58109	4.68374
H	2.04673	-10.48001	6.79573
H	2.51086	-8.07205	7.11528
H	3.60565	-6.78479	5.28692
H	4.22407	-7.87084	3.22556
C	5.73392	0.42170	-3.77124
C	6.33936	0.80627	-2.58784
C	5.55933	1.17750	-1.50506
C	4.17997	1.16692	-1.60364
C	1.96115	-3.60643	-1.02925
F	-2.37448	-2.01378	-2.03324
F	-4.39561	-3.06189	-0.62771
F	-3.94485	-4.08030	1.83917
F	-1.45270	-4.05308	2.88400
F	0.57304	-3.00995	1.49710
H	1.70099	1.63321	-2.26803
H	0.37441	0.93745	-4.20148
H	1.84289	1.73398	-4.77075
H	1.71024	-0.02741	-4.83758
H	3.89770	0.10184	-4.80310
H	6.33665	0.13286	-4.62220
H	7.41865	0.81830	-2.50986
H	6.02369	1.47652	-0.57500
H	3.57145	1.44711	-0.75203
H	2.68669	-3.88757	-1.78534
H	2.43954	-3.50361	-0.05860
H	1.15854	-4.33674	-0.98408
C	-1.05474	4.52787	0.46617
C	-2.48771	4.01740	0.46980
C	-2.83445	3.18792	1.68707
N	-2.78617	3.23587	-0.75305
C	-2.90950	4.04671	-1.95801
C	-1.96318	2.23879	2.20825
C	-2.33142	1.46839	3.29806
C	-3.57322	1.63967	3.88733
C	-4.44808	2.58560	3.38013
C	-4.07791	3.35148	2.28723
H	-0.86850	5.17127	-0.39371
H	-0.87497	5.11792	1.36409
H	-0.33018	3.71534	0.44780
H	-3.15271	4.89267	0.48004
H	-3.65788	2.74419	-0.59479
H	-3.28843	3.43047	-2.77222
H	-3.58399	4.90136	-1.82340
H	-1.93495	4.42882	-2.25778
H	-0.98602	2.07639	1.77654
H	-1.63209	0.73419	3.67504
H	-3.85689	1.04124	4.74339
H	-5.41753	2.73285	3.83834
H	-4.76263	4.09769	1.89988

***S*-9** complex with **3-OTf** chloroform:

69

mikk231-clust3-1_cam_tzvp_stcm_2.out

O	4.49851	-5.03112	3.61265
S	5.40625	-4.56534	2.58704
O	4.85898	-3.55178	1.71071
O	6.16935	-5.59818	1.92489
C	6.68154	-3.64096	3.54515
F	7.30428	-4.43949	4.41626

***R*-9** complex with **3-OTf** chloroform:

69

mikk232-clust3-1_cam_tzvp_stcm_9.out

O	2.02058	1.57117	1.14845
S	1.92833	0.24722	1.72650
O	2.47917	-0.80833	0.90380
O	0.66673	-0.05891	2.35839
C	3.10341	0.32533	3.14493
F	2.74023	1.26629	4.02113

F	7.60900	-3.11805	2.73713
F	6.13172	-2.63663	4.23510
N	2.30986	-4.51684	0.07847
C	3.16833	-5.51617	-0.23879
C	4.11404	-4.91796	-1.03715
N	3.73224	-3.61962	-1.12731
N	2.64916	-3.38122	-0.45718
C	5.29484	-5.48657	-1.69040
C	6.57866	-5.01242	-1.45062
C	7.68593	-5.59073	-2.03805
C	7.52599	-6.66856	-2.88618
C	6.26095	-7.15577	-3.15239
C	5.16677	-6.56199	-2.56077
I	3.06074	-7.47756	0.47616
C	1.05555	-4.61373	0.87621
C	0.82707	-3.34939	1.67418
C	-0.07377	-5.03193	-0.04975
C	-0.13422	-2.41596	1.31535
C	-0.32919	-1.27945	2.08406
C	0.43752	-1.06689	3.21645
C	1.39994	-1.99604	3.57889
C	1.59267	-3.13237	2.81426
C	4.39717	-2.51812	-1.80745
F	6.76805	-3.97413	-0.65316
F	8.89941	-5.11726	-1.79220
F	8.58159	-7.22743	-3.45323
F	6.10484	-8.18089	-3.98098
F	3.96089	-7.03755	-2.85760
H	1.25862	-5.42093	1.57709
H	0.15359	-5.98882	-0.51680
H	-0.99173	-5.14245	0.52415
H	-0.23902	-4.29648	-0.83545
H	-0.74383	-2.56507	0.43546
H	-1.08388	-0.56006	1.79493
H	0.28494	-0.17987	3.81712
H	2.00501	-1.83773	4.46150
H	2.35660	-3.84545	3.09985
H	3.65162	-1.75621	-2.00555
H	5.17979	-2.12582	-1.16458
H	4.81863	-2.88296	-2.73935
C	5.15663	-10.55449	2.13757
C	3.68687	-10.63083	2.52140
C	3.38622	-9.92669	3.82848
N	2.86624	-10.10433	1.41387
C	1.43986	-10.37102	1.56875
C	2.74262	-10.61057	4.85159
C	2.46686	-9.99163	6.06138
C	2.83206	-8.67148	6.26218
C	3.47680	-7.97791	5.24920
C	3.75324	-8.60284	4.04565
H	5.47530	-9.52438	1.98298
H	5.77425	-10.98647	2.92362
H	5.34228	-11.11221	1.21761
H	3.42981	-11.68855	2.66781
H	3.18793	-10.55288	0.56294
H	0.91436	-10.07101	0.66357
H	1.23022	-11.42975	1.75976
F	3.15171	-0.84056	3.79618
F	4.34235	0.61141	2.73174
N	1.48853	-0.39203	-2.10431
C	0.27433	-0.49745	-1.51113
C	0.20445	-1.80694	-1.10036
N	1.38012	-2.36362	-1.48462
N	2.14875	-1.51254	-2.08759
C	-0.87292	-2.52342	-0.41345
C	-2.14161	-2.58743	-0.97638
C	-3.19188	-3.21148	-0.33817
C	-2.98519	-3.80078	0.89420
C	-1.73271	-3.76643	1.47452
C	-0.69409	-3.13237	0.82239
I	-1.08297	1.06582	-1.20221
C	2.06429	0.80329	-2.78337
C	3.57359	0.80177	-2.68833
C	1.48878	0.88702	-4.18729
C	4.37963	0.43406	-3.75603
C	5.75957	0.46310	-3.63450
C	6.34405	0.85861	-2.44364
C	5.54322	1.22669	-1.37426
C	4.16528	1.20072	-1.49546
C	1.86974	-3.71335	-1.24793
F	-2.36615	-2.05142	-2.17226
F	-4.39168	-3.25780	-0.90342
F	-3.98489	-4.40583	1.51265
F	-1.53427	-4.33949	2.65328
F	0.49444	-3.12279	1.40404
H	1.69138	1.63731	-2.19182
H	0.40338	0.96230	-4.15063
H	1.87569	1.77476	-4.68382
H	1.75194	0.01279	-4.78042
H	3.94214	0.12379	-4.69438
H	6.37775	0.17608	-4.47485
H	7.42178	0.88202	-2.34931
H	5.99168	1.53639	-0.43974
H	3.54332	1.47775	-0.65288
H	2.64895	-3.91217	-1.97518
H	2.26866	-3.77193	-0.23931
H	1.05000	-4.41423	-1.37437
C	-1.28185	4.71453	0.23914
C	-2.65612	4.07320	0.35926
C	-2.88211	3.38097	1.68596
N	-2.89966	3.11832	-0.74420
C	-3.13239	3.76092	-2.03454
C	-1.93672	2.52744	2.24431
C	-2.18653	1.88311	3.44413
C	-3.38494	2.08765	4.10993
C	-4.33260	2.93886	3.56686
C	-4.08015	3.57731	2.36284
H	-1.18395	5.26115	-0.69814
H	-1.13271	5.42282	1.05324
H	-0.48657	3.97209	0.28439
H	-3.40397	4.87415	0.28662
H	-3.71908	2.57305	-0.50242
H	-3.47320	3.01589	-2.75149
H	-3.88352	4.55688	-1.97466

H	1.04425	-9.79106	2.40096
H	2.45365	-11.64395	4.70090
H	1.96591	-10.54345	6.84629
H	2.61861	-8.18473	7.20493
H	3.77240	-6.94582	5.38386
H	4.26264	-8.04002	3.27654
H	-2.20832	4.19212	-2.41589
H	-0.99134	2.35138	1.75086
H	-1.43528	1.21901	3.85028
H	-3.57762	1.58742	5.05007
H	-5.26956	3.10981	4.08098
H	-4.82408	4.24531	1.94472

IV) ^{1}H NMR and ^{13}C NMR spectra of triazoles, triazolium salts and imines

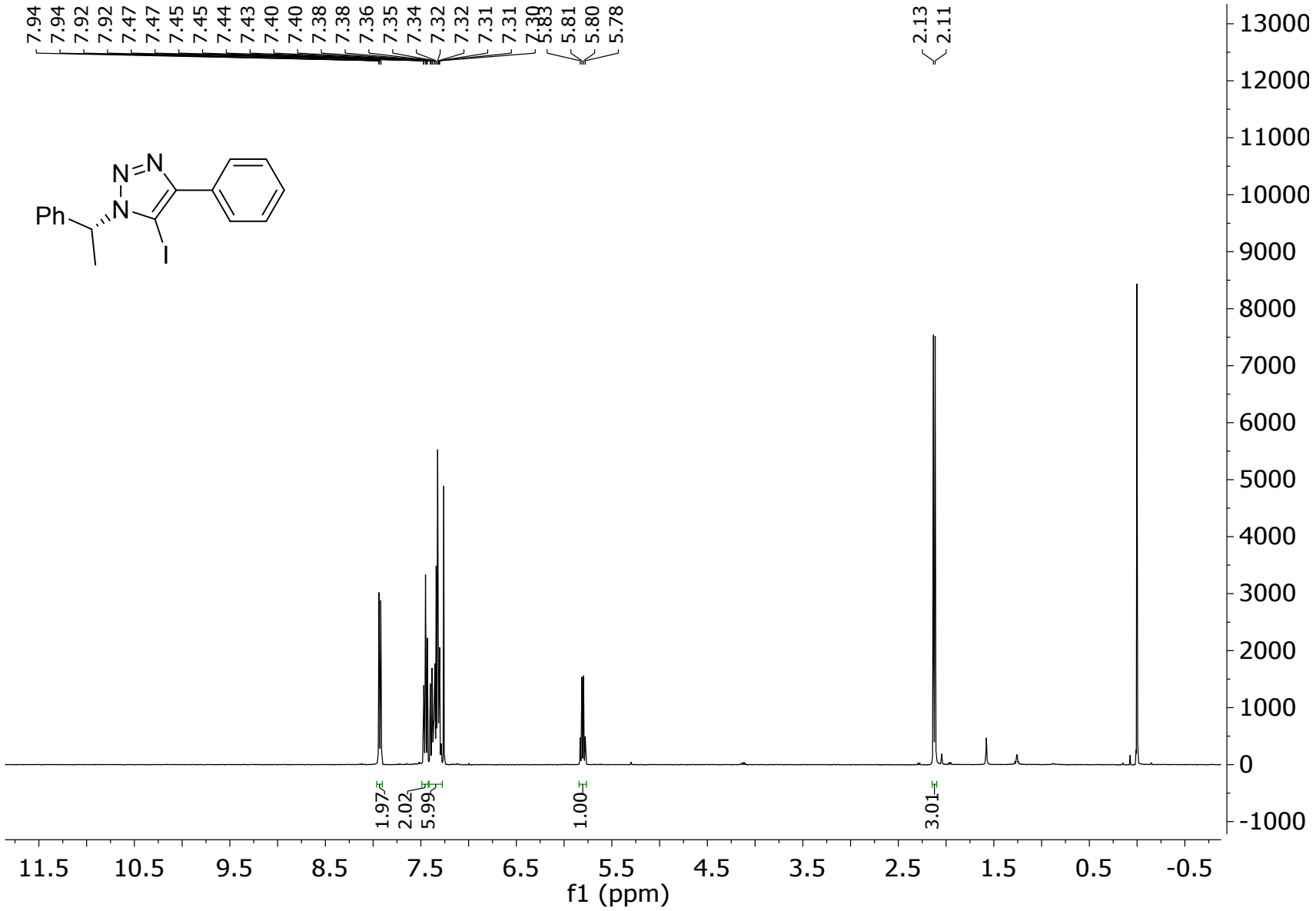


Figure S48. ^{1}H NMR spectrum of **(*R*)-5-iodo-4-phenyl-1-(1-phenylethyl)-1*H*-1,2,3-triazole** ($CDCl_3$, 400 MHz).

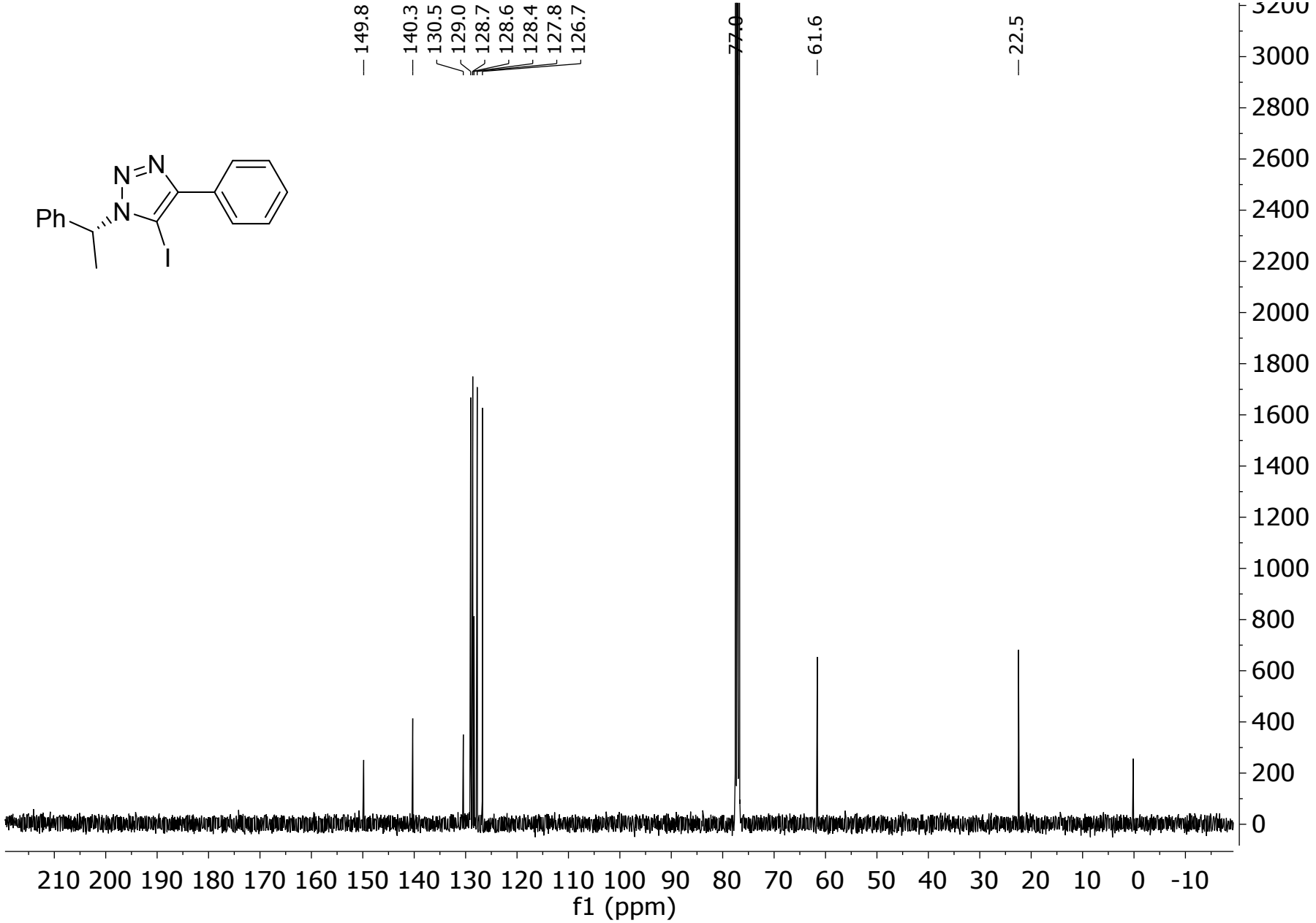


Figure S49. ^{13}C NMR spectrum of **(*R*)-5-iodo-4-phenyl-1-(1-phenylethyl)-1*H*-1,2,3-triazole** ($CDCl_3$, 101 MHz).

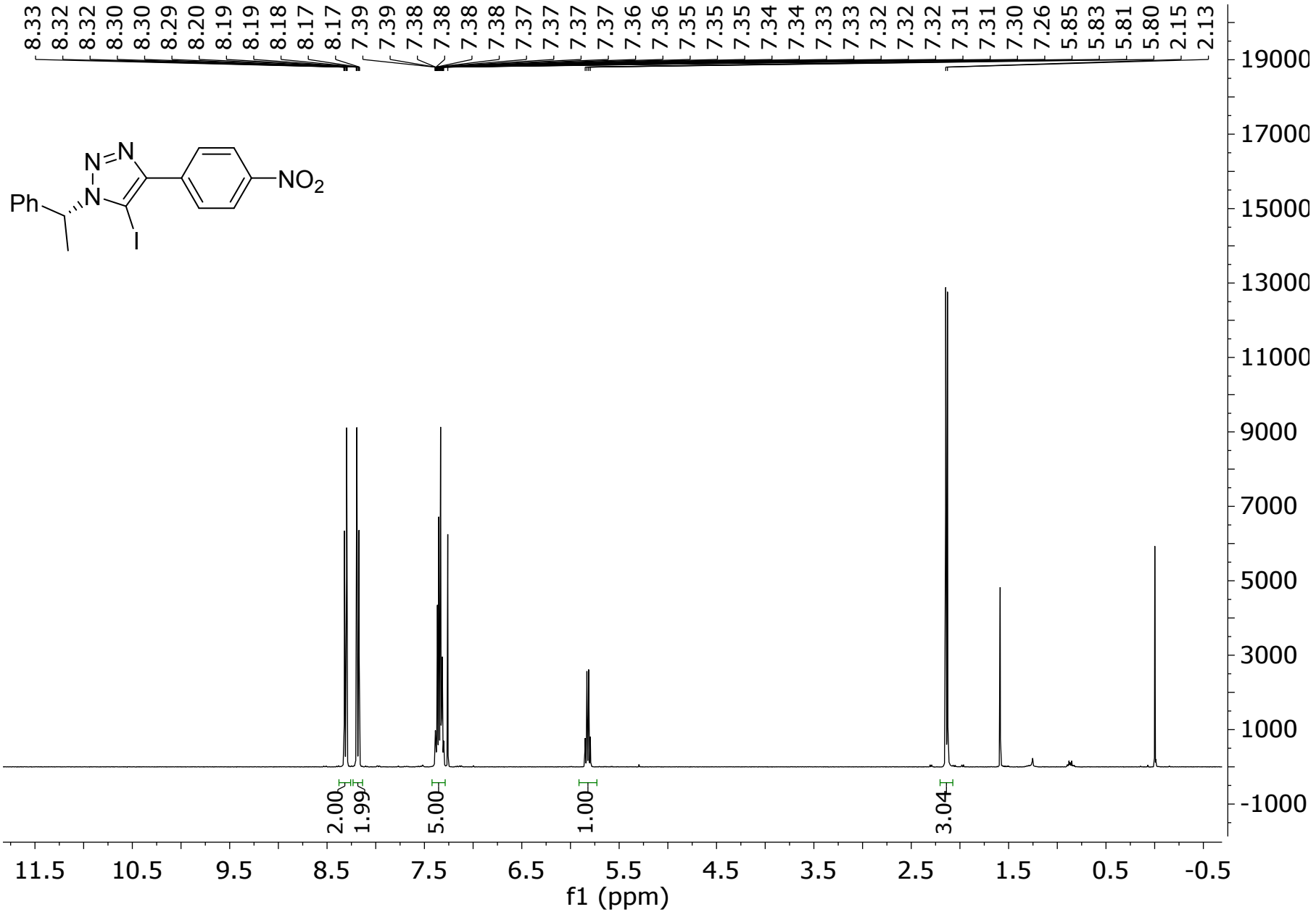


Figure S50. ^{1}H NMR spectrum of **(*R*)-5-iodo-4-(4-nitrophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 400 MHz).

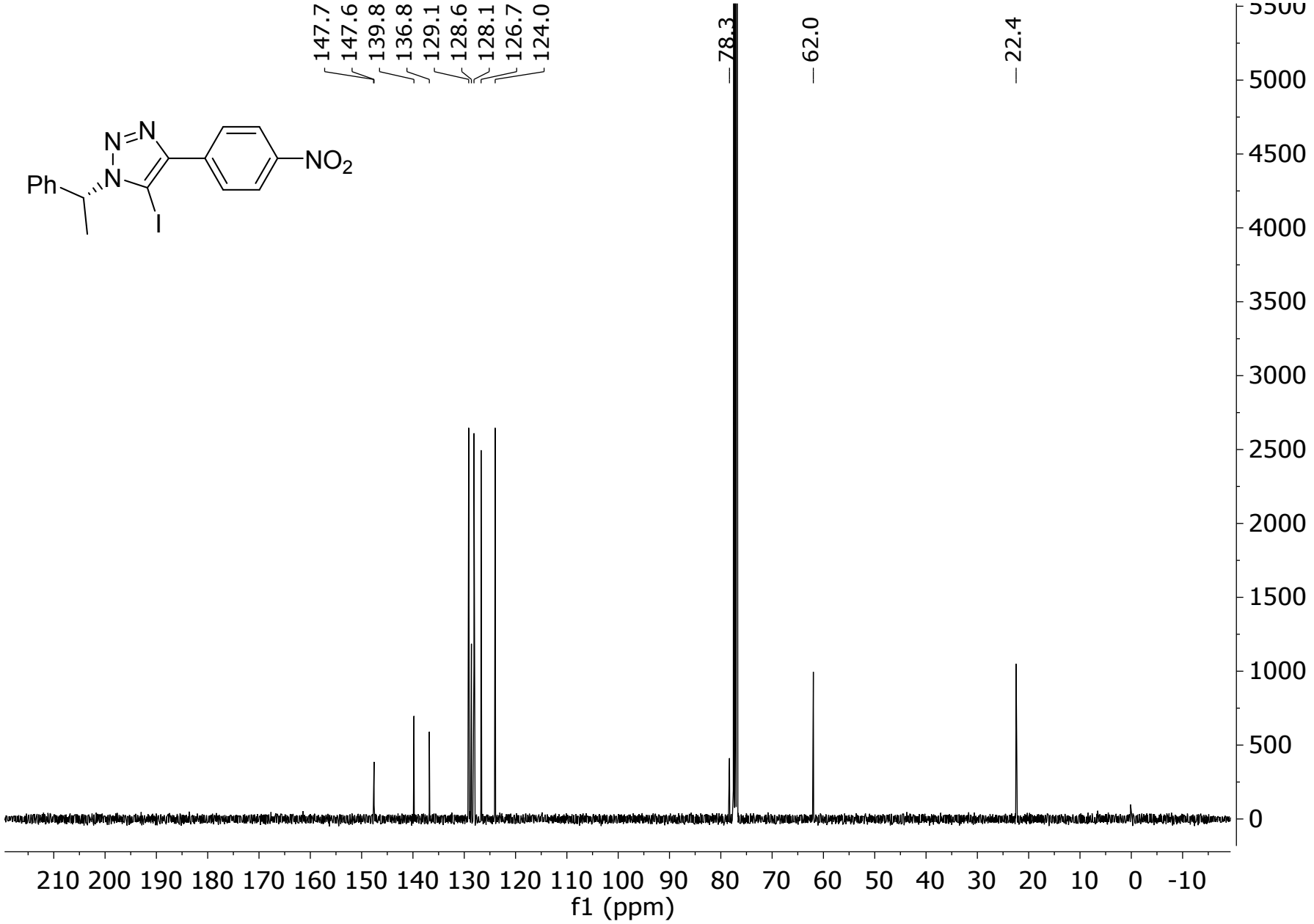


Figure S51. ^{13}C NMR spectrum of **(*R*)-5-iodo-4-(4-nitrophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 101 MHz).

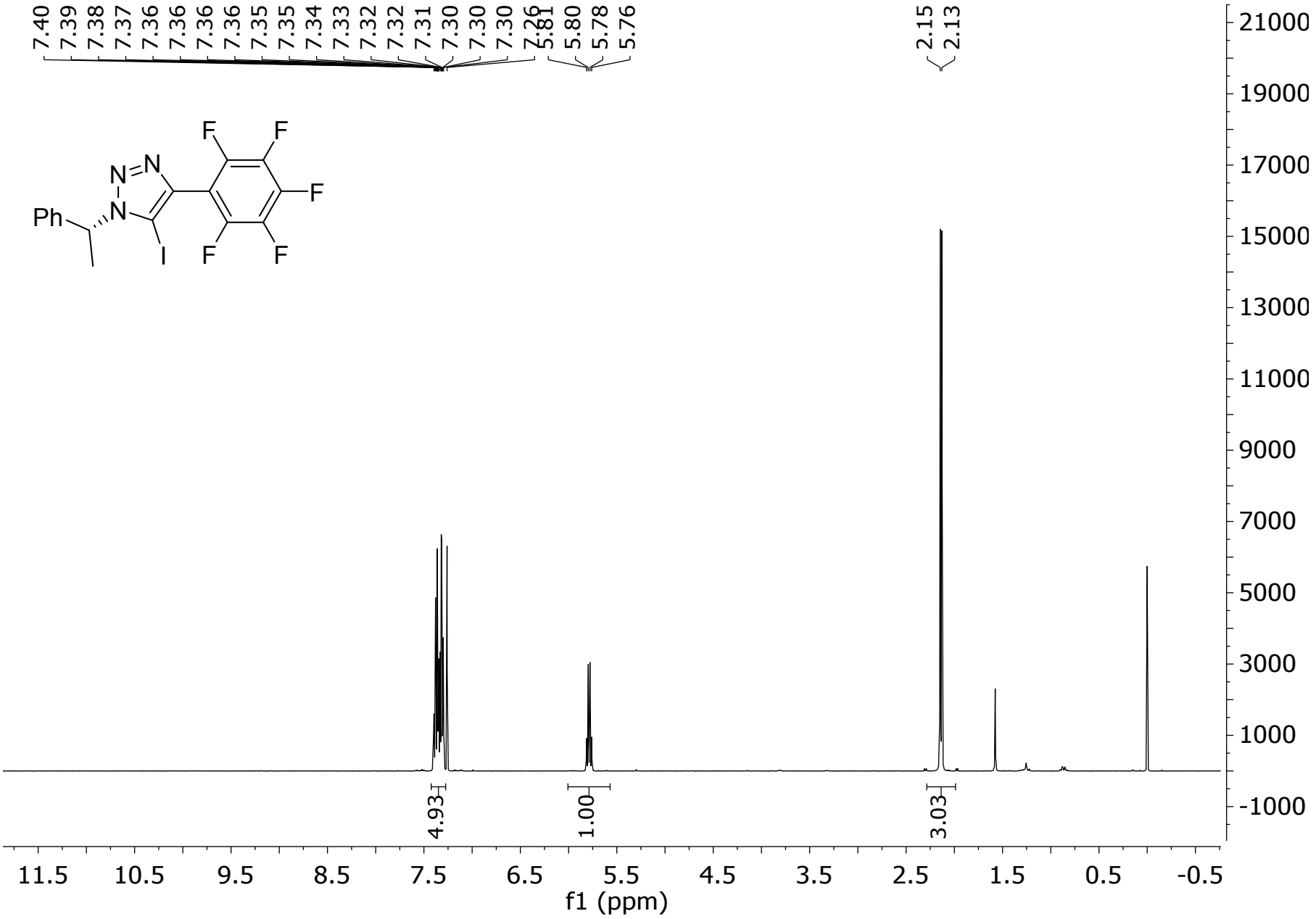


Figure S52. ^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz).

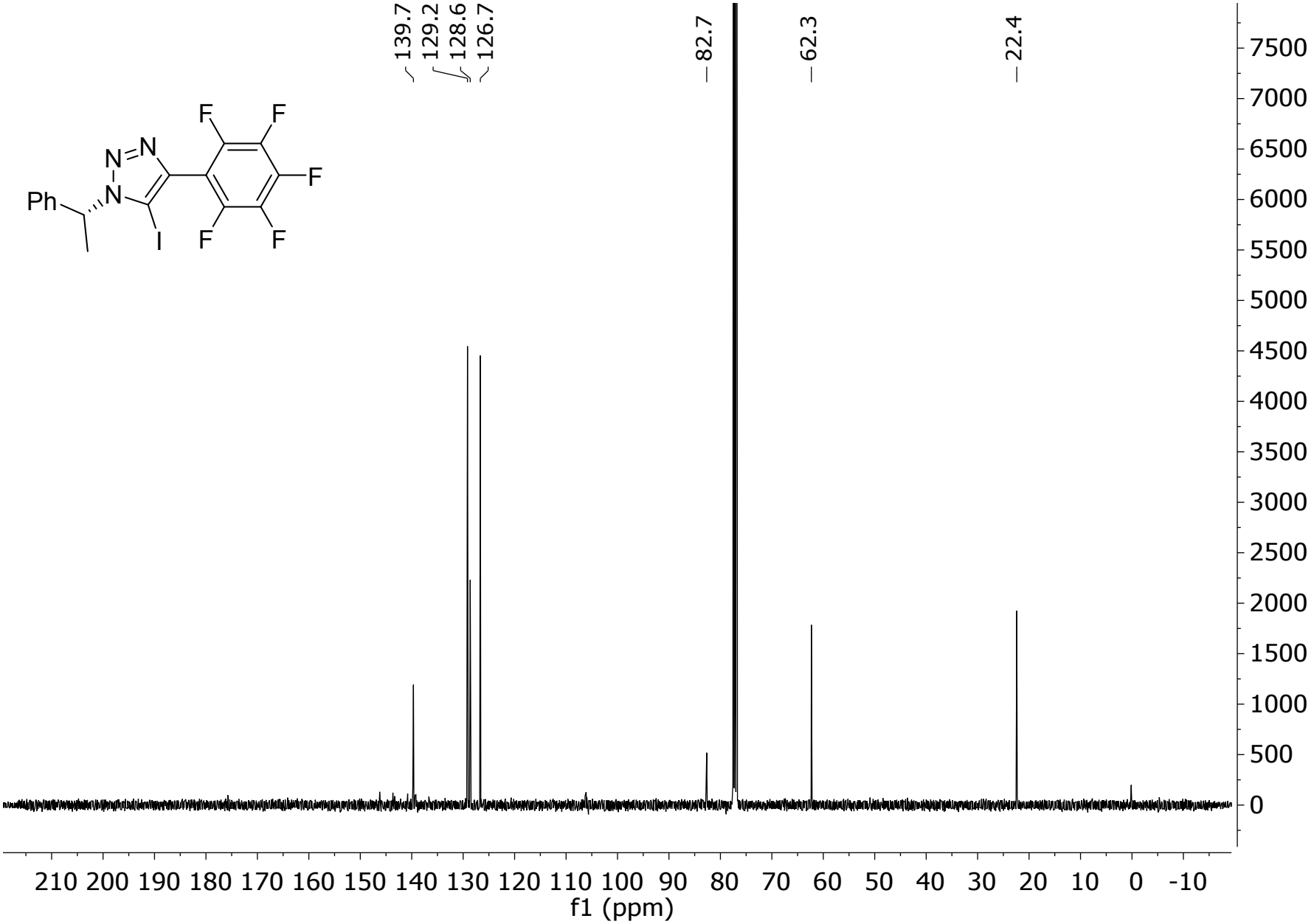


Figure S53. ^{13}C NMR spectrum of **7** ($CDCl_3$, 101 MHz).

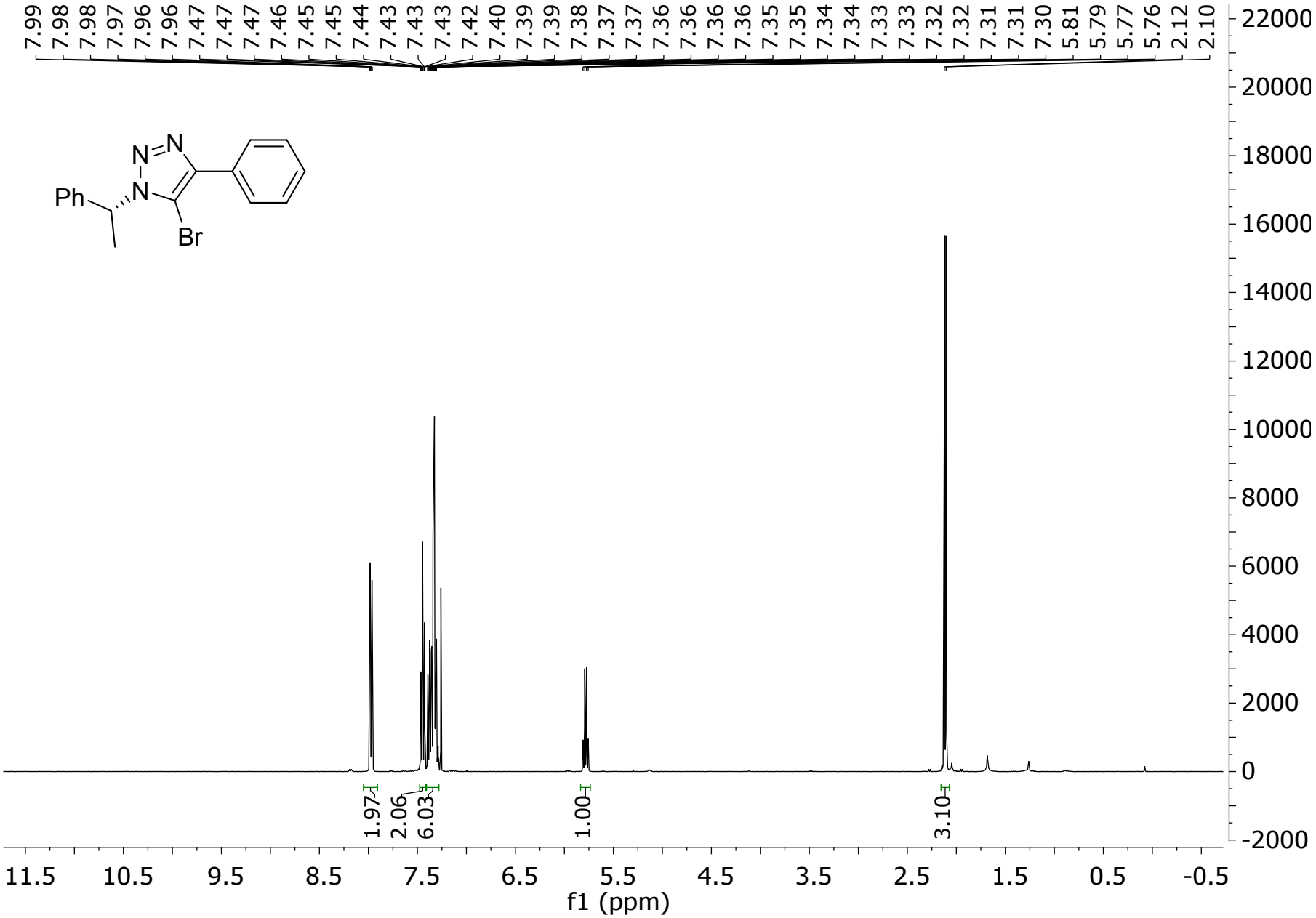


Figure S54. ^{1}H NMR spectrum of **(*R*)-5-bromo-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 400 MHz).

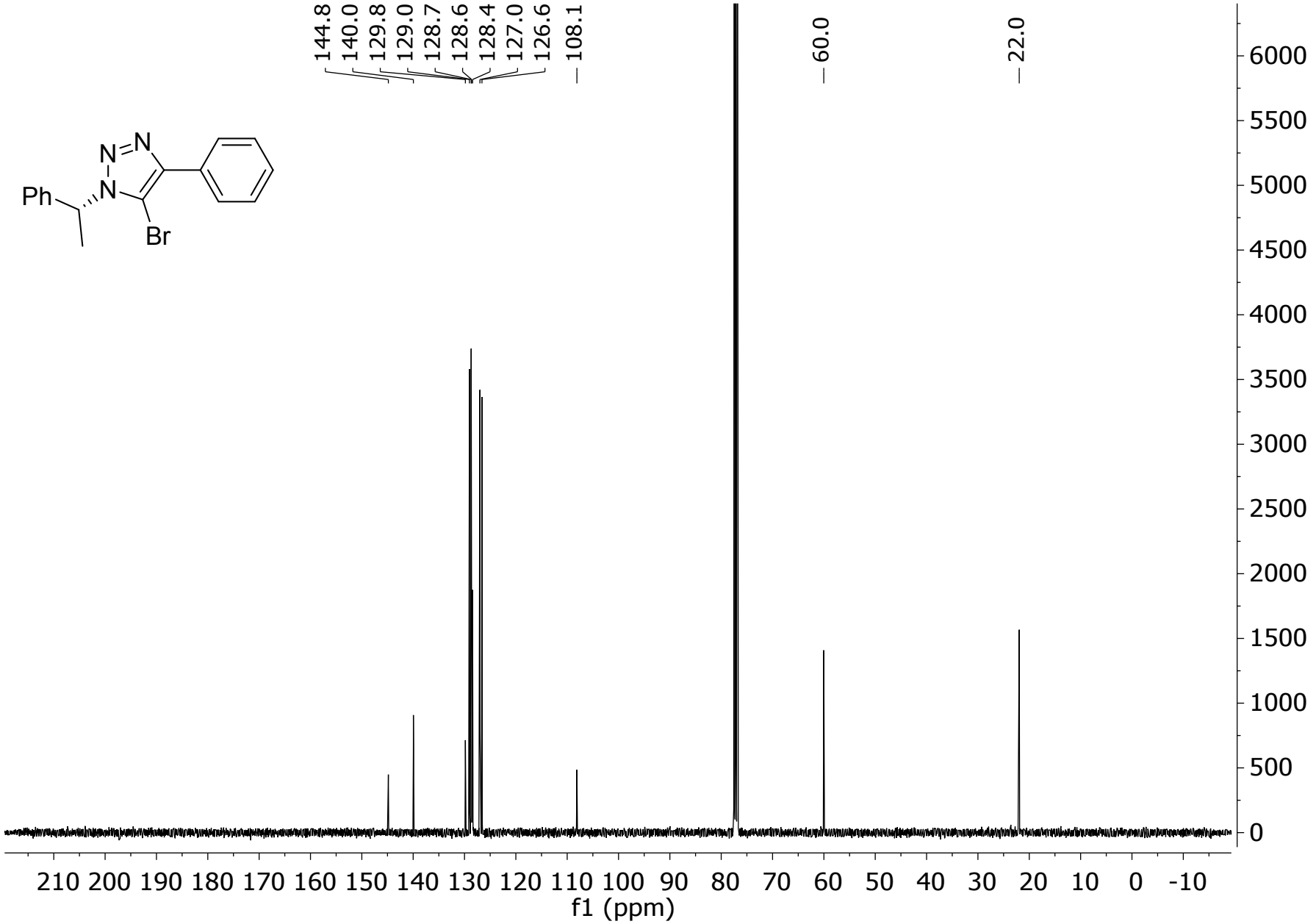


Figure S55. ^{13}C NMR spectrum of **(*R*)-5-bromo-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 101 MHz).

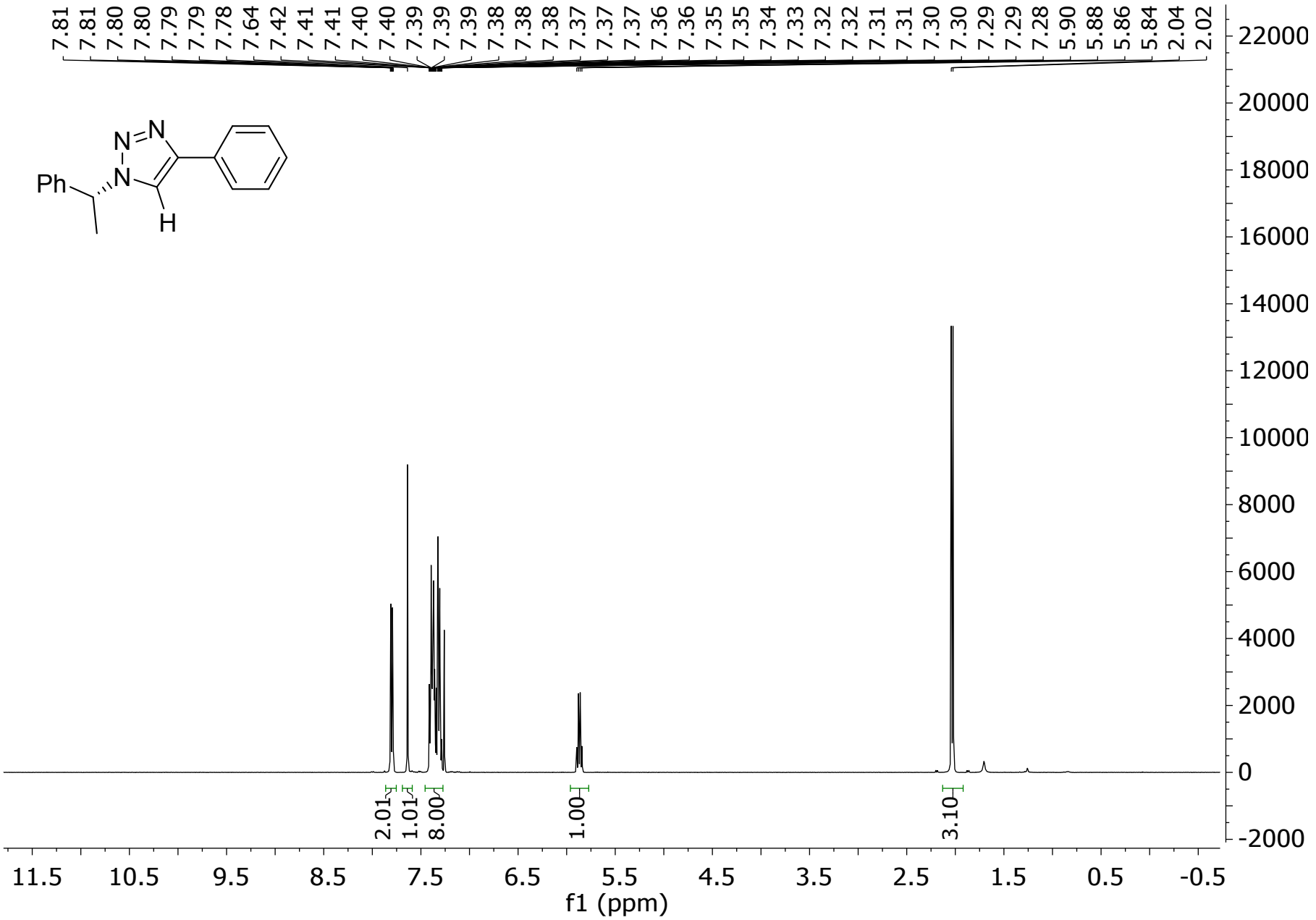


Figure S56. ^{1}H NMR spectrum of **(*R*)-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 400 MHz).

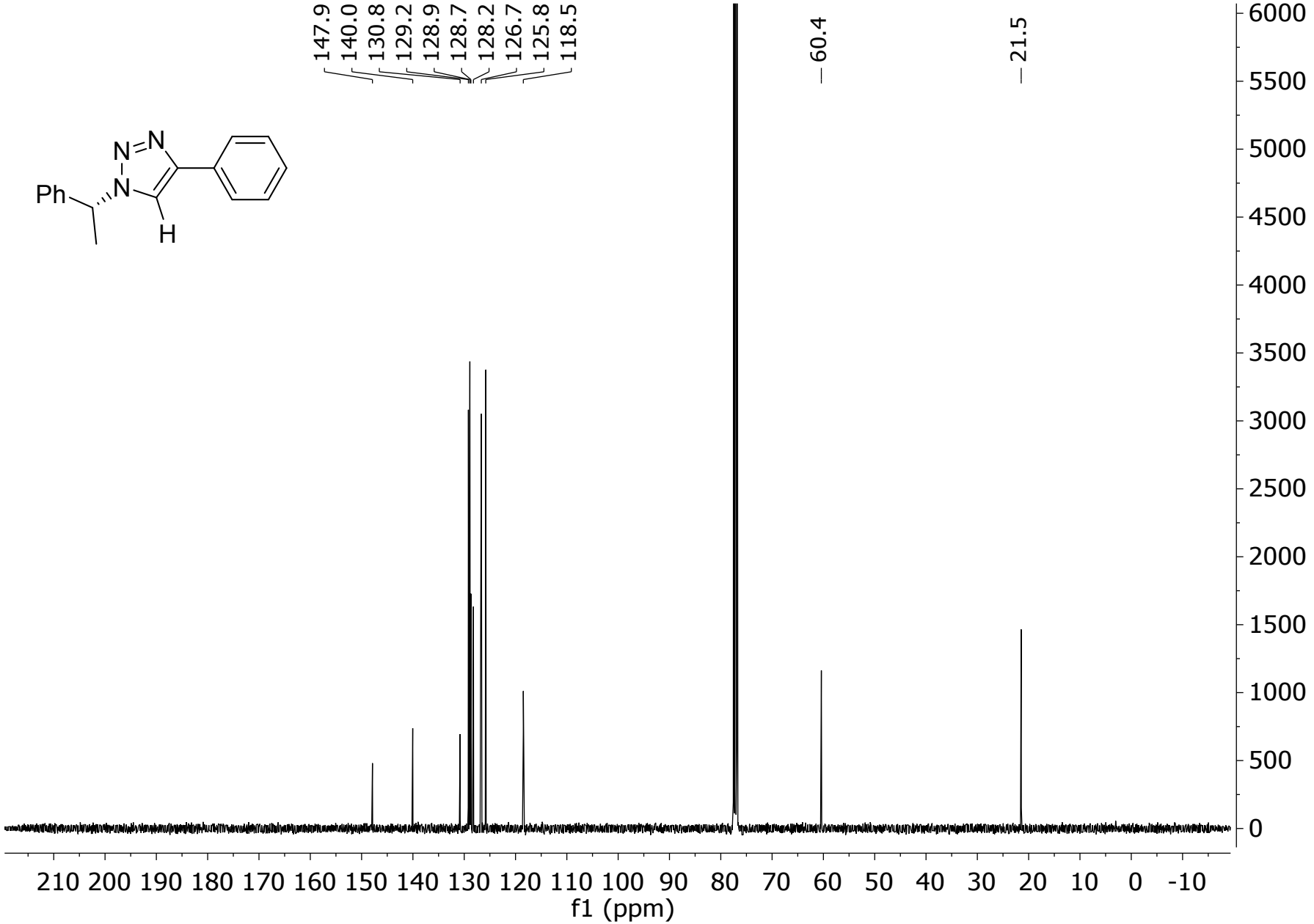


Figure S57. ^{13}C NMR spectrum of **(*R*)-4-phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 101 MHz).

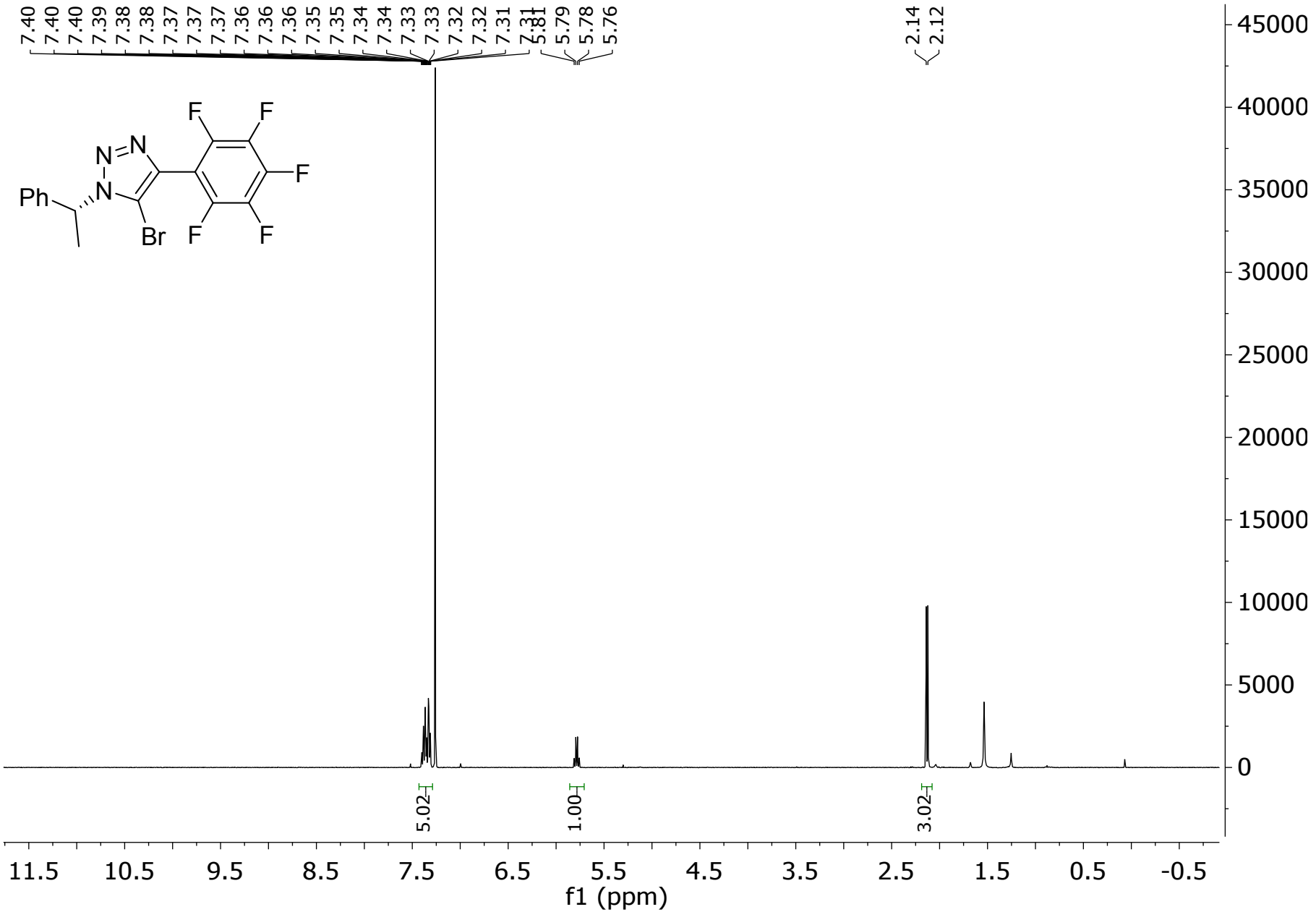


Figure S58. ^{1}H NMR spectrum of ***(R)*-5-bromo-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 400 MHz).

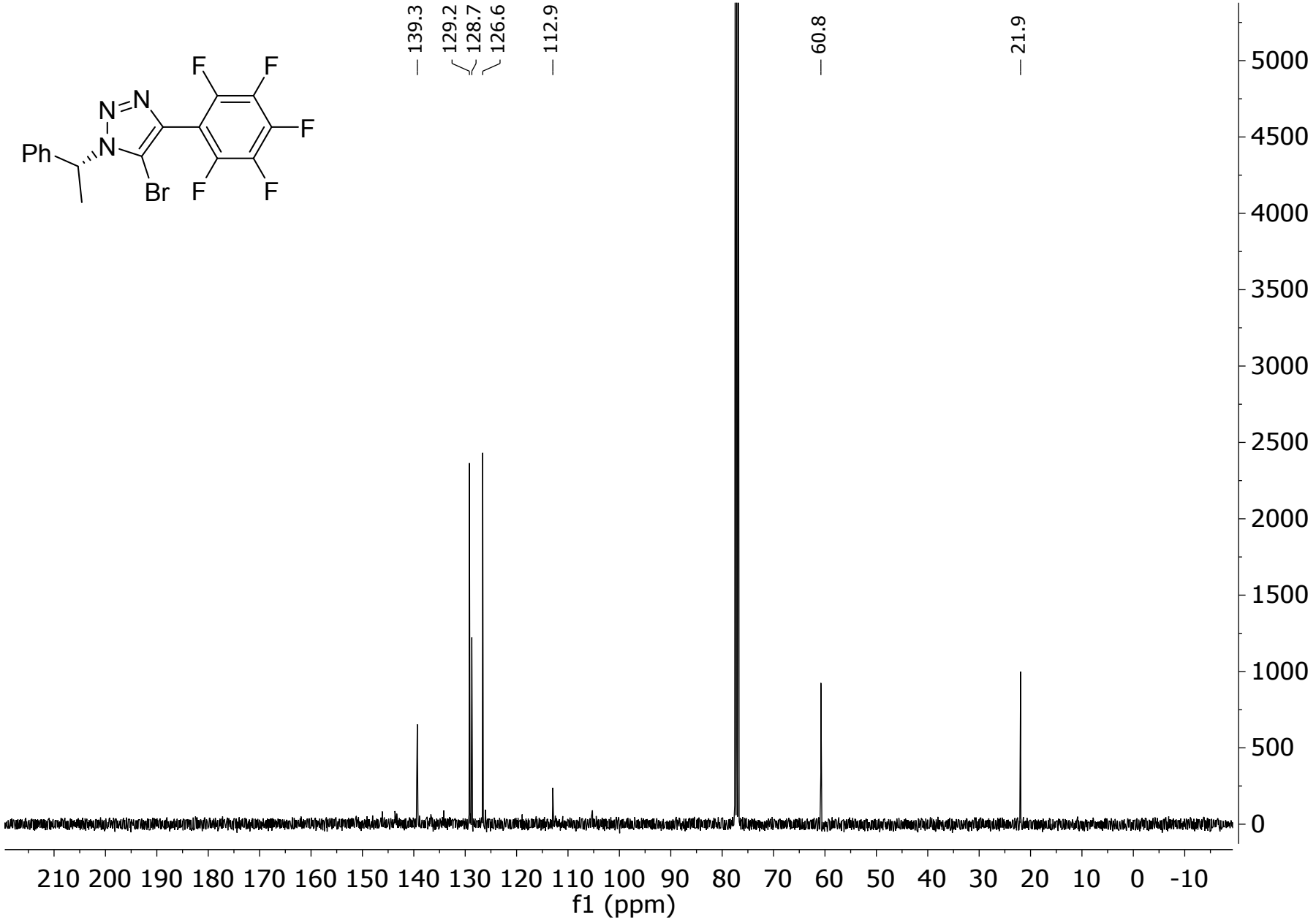


Figure S59. ^{13}C NMR spectrum of ***(R)*-5-bromo-4-(perfluorophenyl)-1-(1-phenylethyl)-1H-1,2,3-triazole** ($CDCl_3$, 101 MHz)

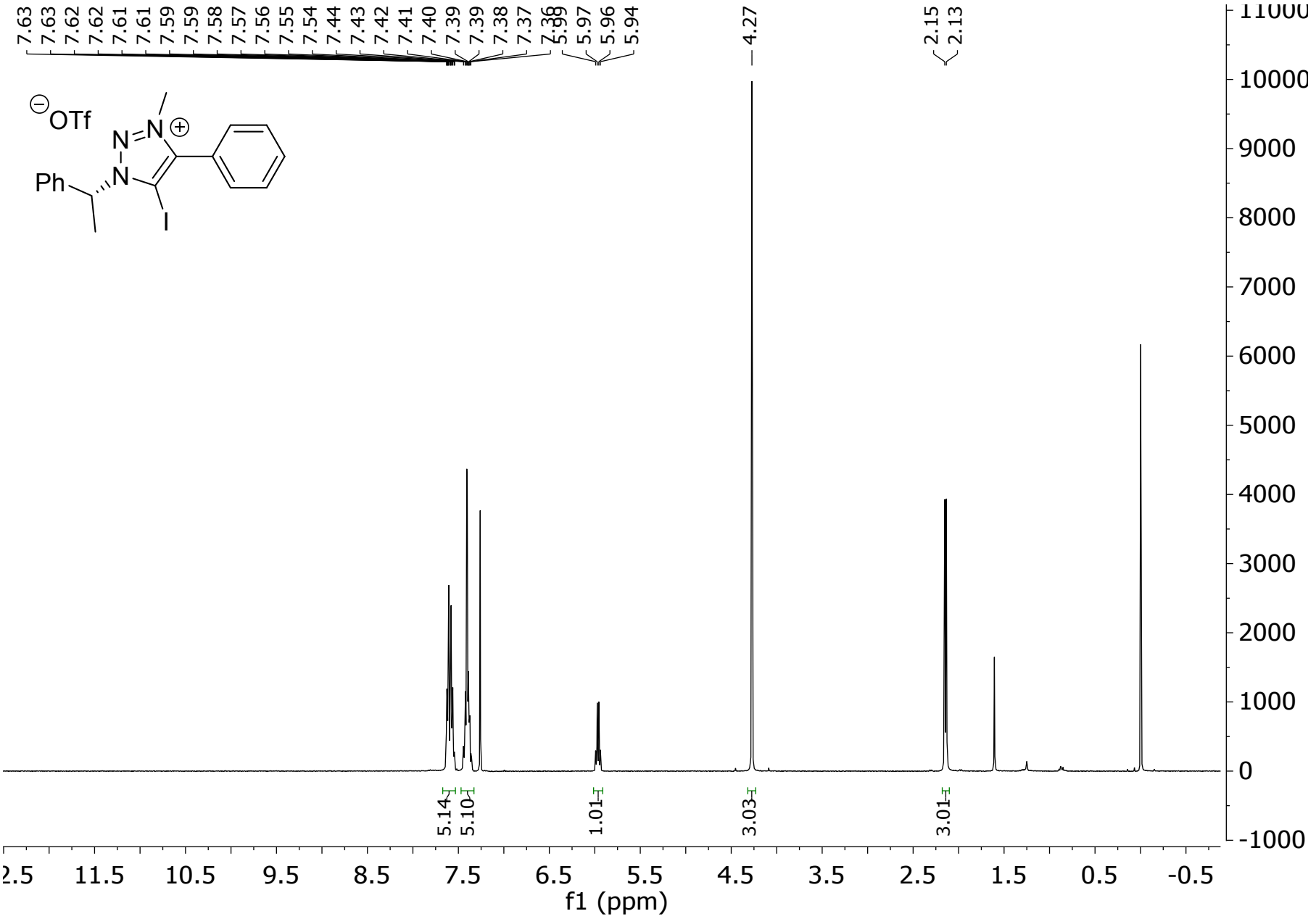


Figure S60. ^{1}H NMR spectrum of **1-OTf** ($CDCl_3$, 400 MHz).

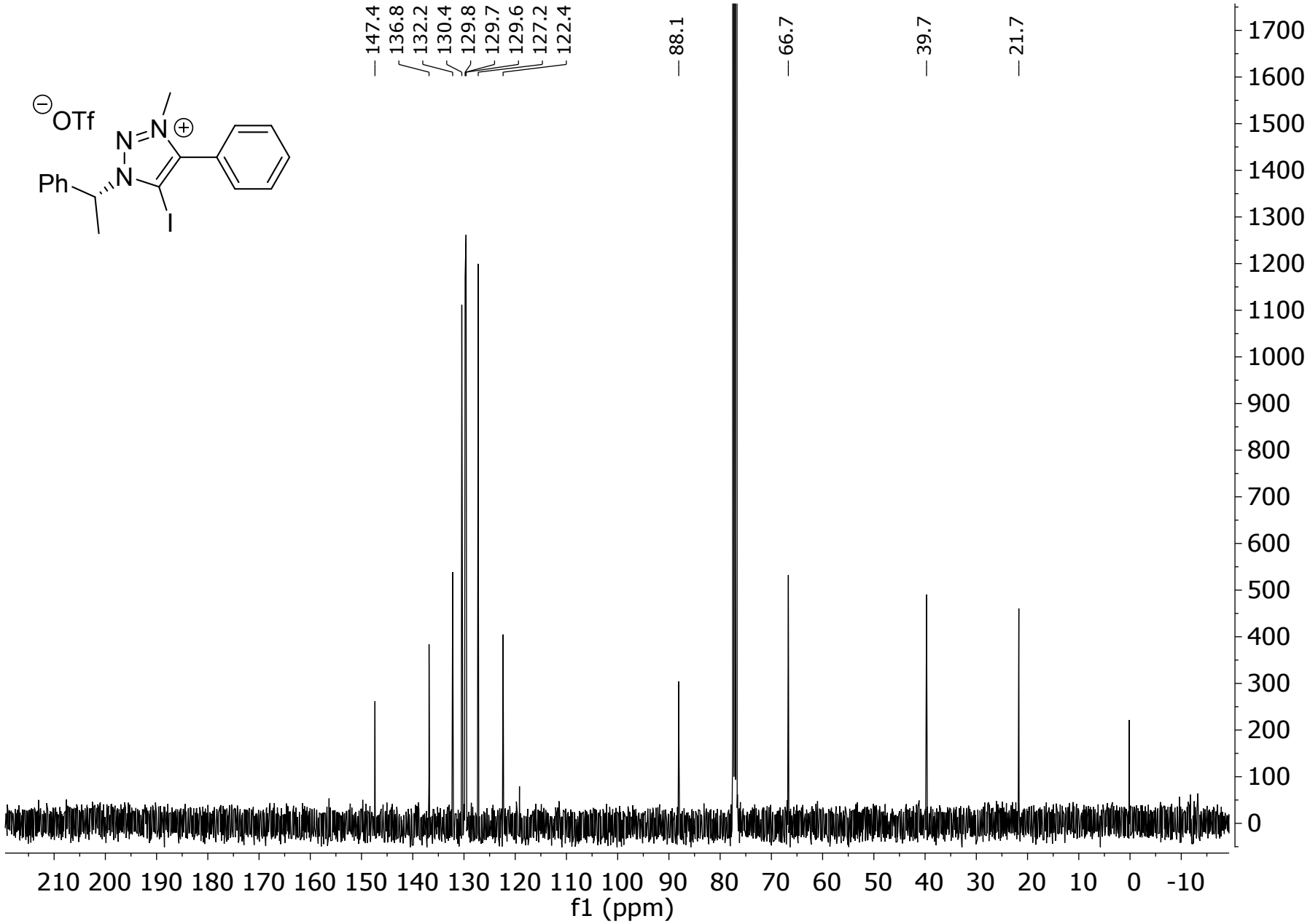


Figure S61. ^{13}C NMR spectrum of **1-OTf** ($CDCl_3$, 101 MHz).

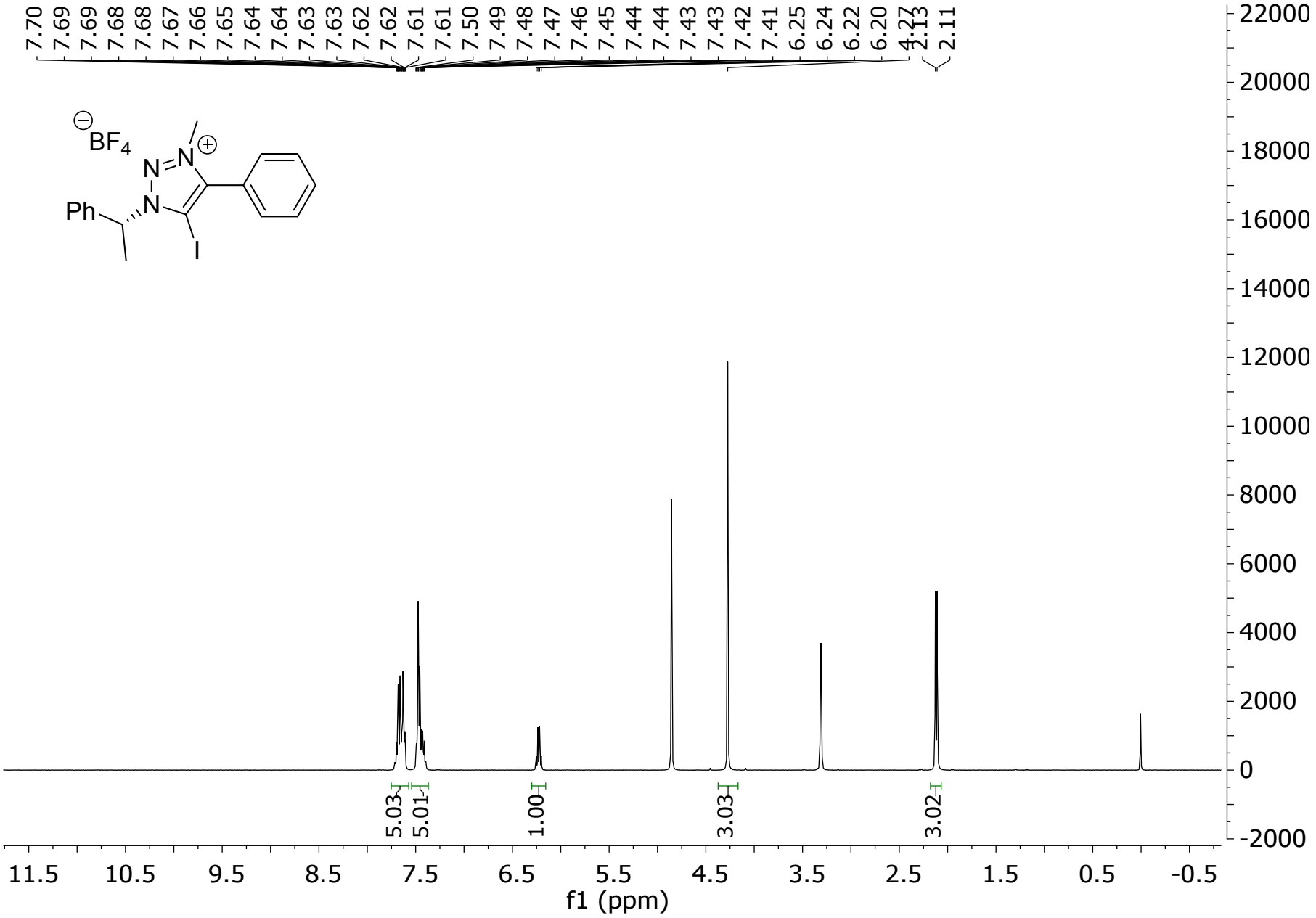


Figure 62. ^{1}H NMR spectrum of **1-BF_4** (CD_3OD, 400 MHz).

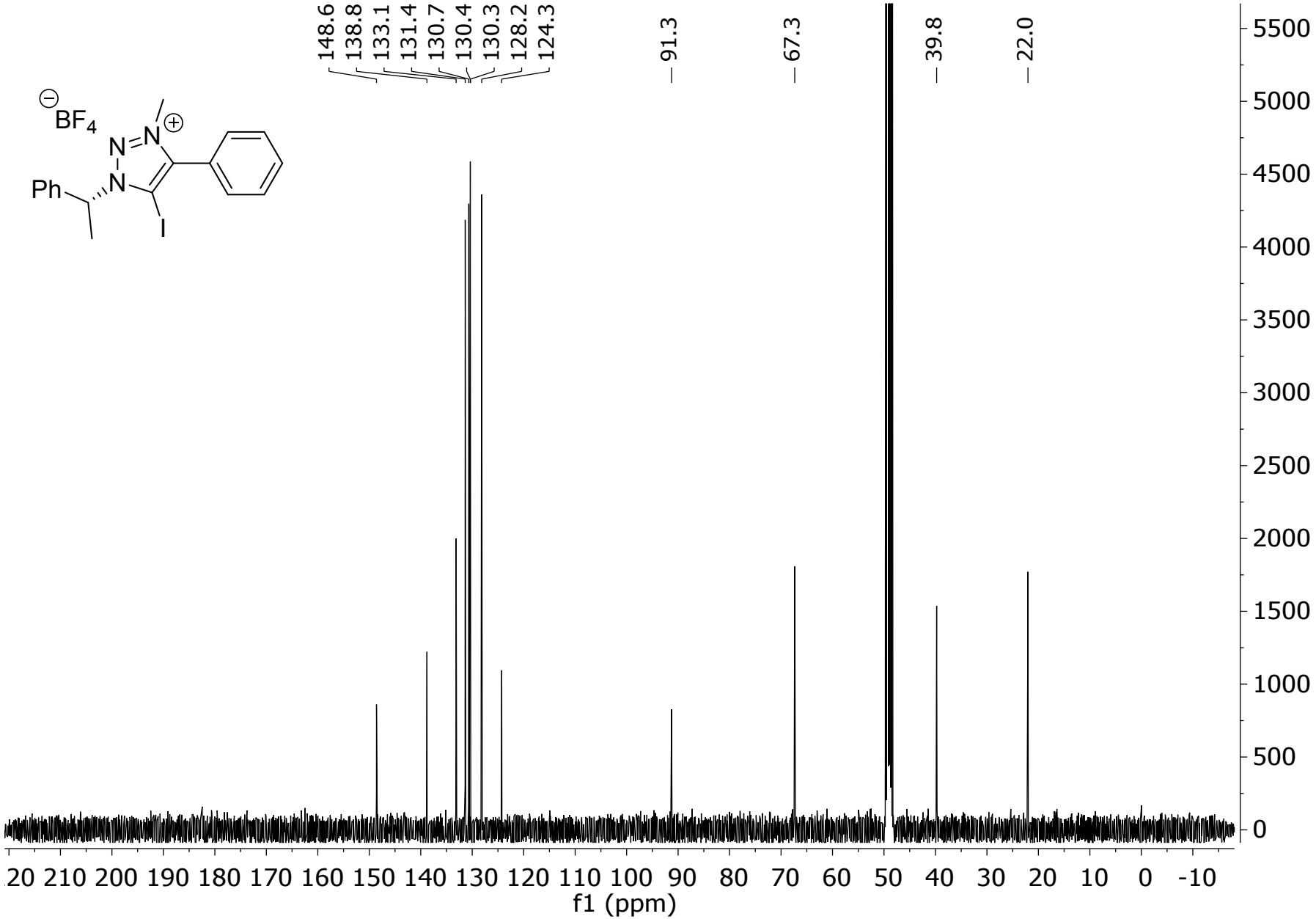


Figure S63. ^{13}C NMR spectrum of **1-BF_4** (CD_3OD, 101 MHz).

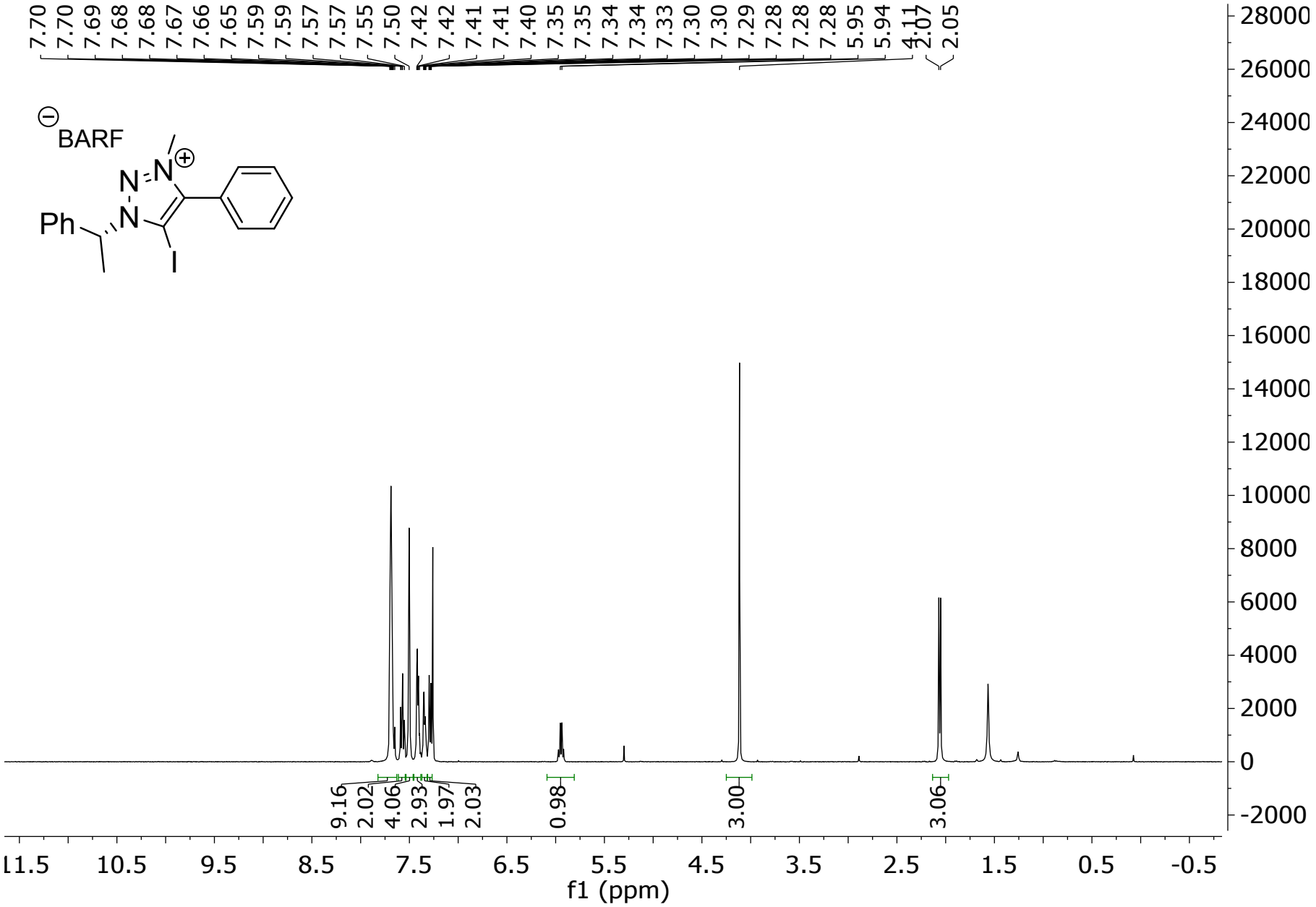


Figure S64. ^{1}H NMR spectrum of **1-BARF** ($CDCl_3$, 400 MHz).

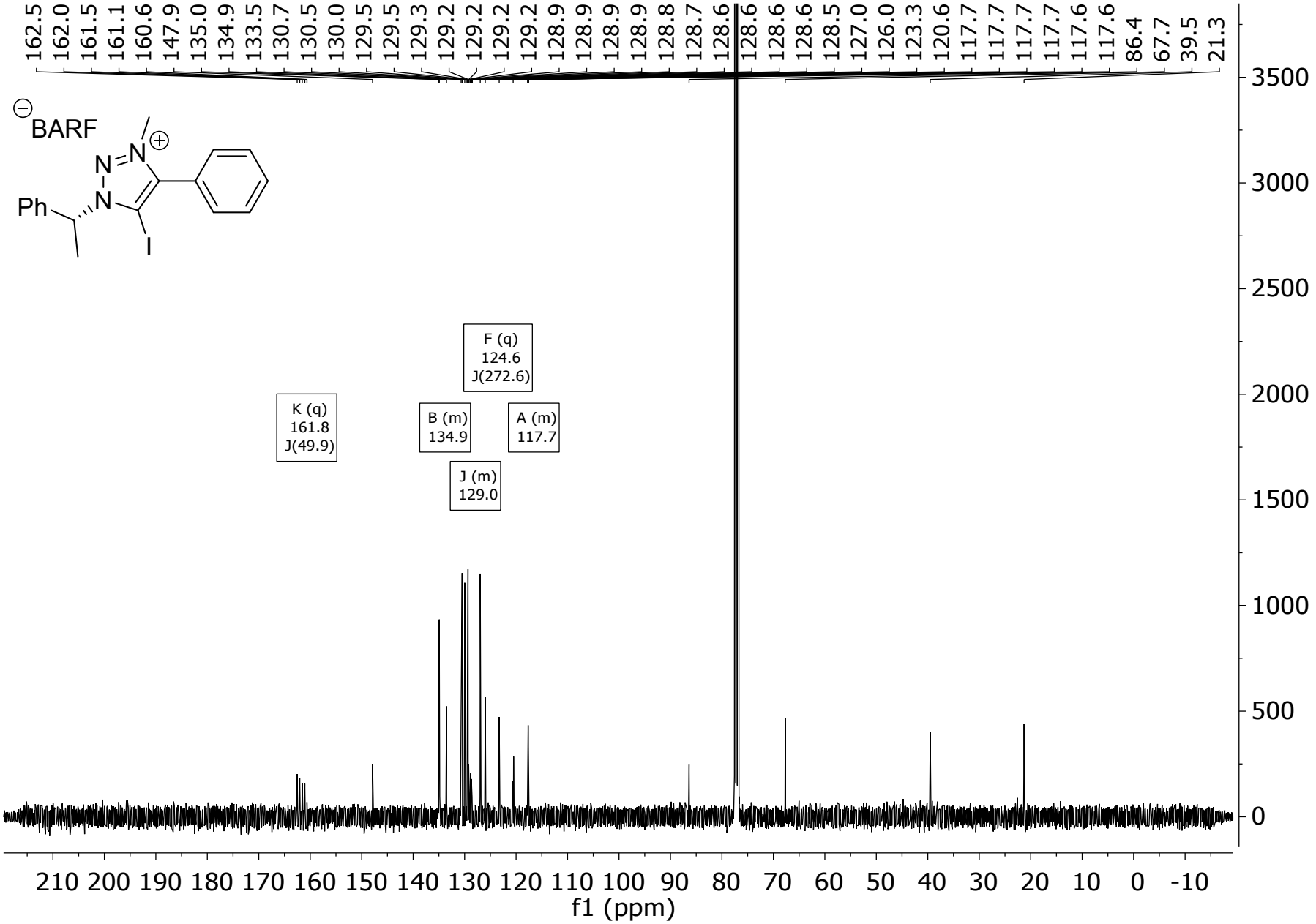


Figure S65. ^{13}C NMR spectrum of **1-BARF** ($CDCl_3$, 101 MHz).

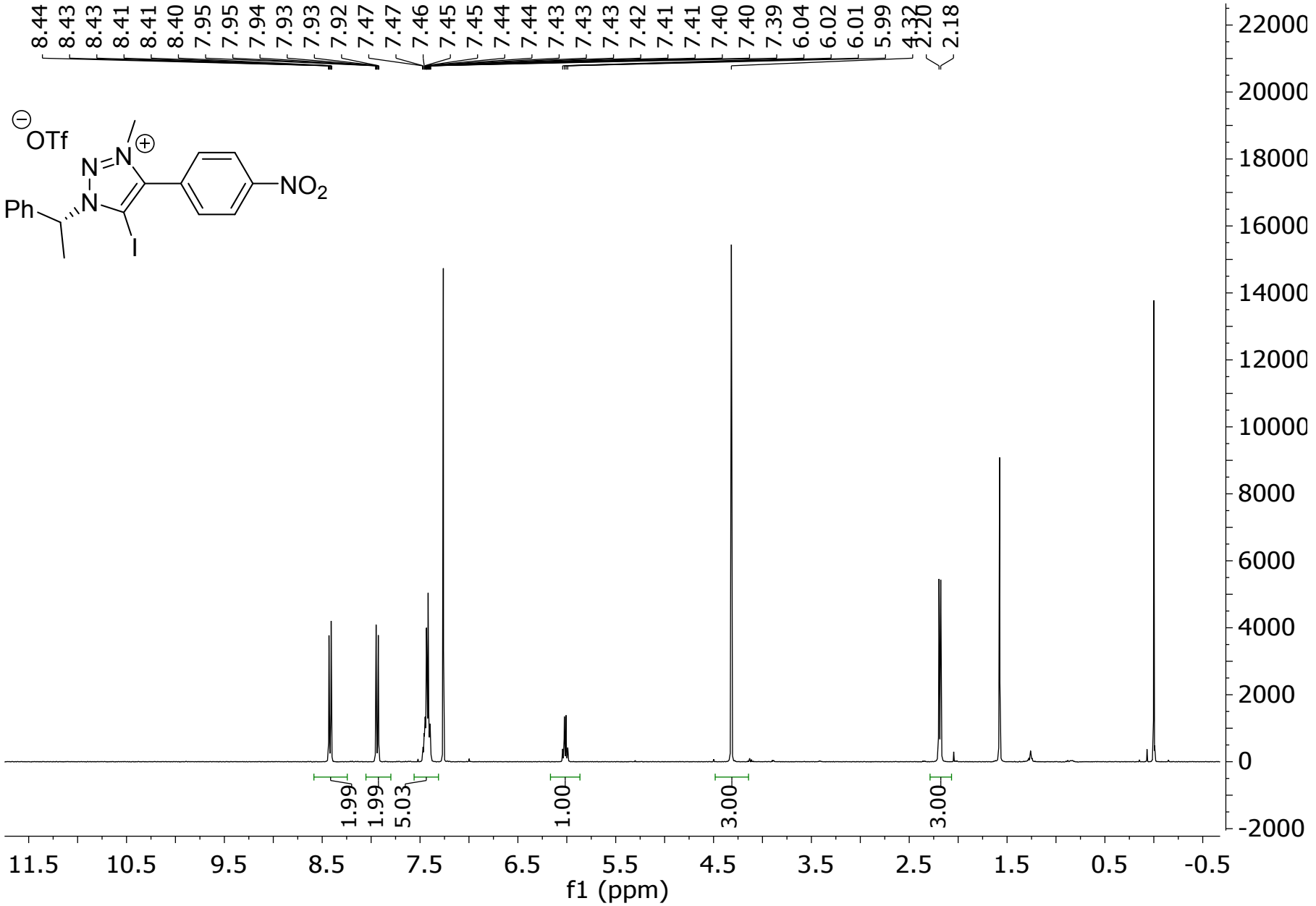


Figure S66. ^{1}H NMR spectrum of **2-OTf** ($CDCl_3$, 400 MHz).

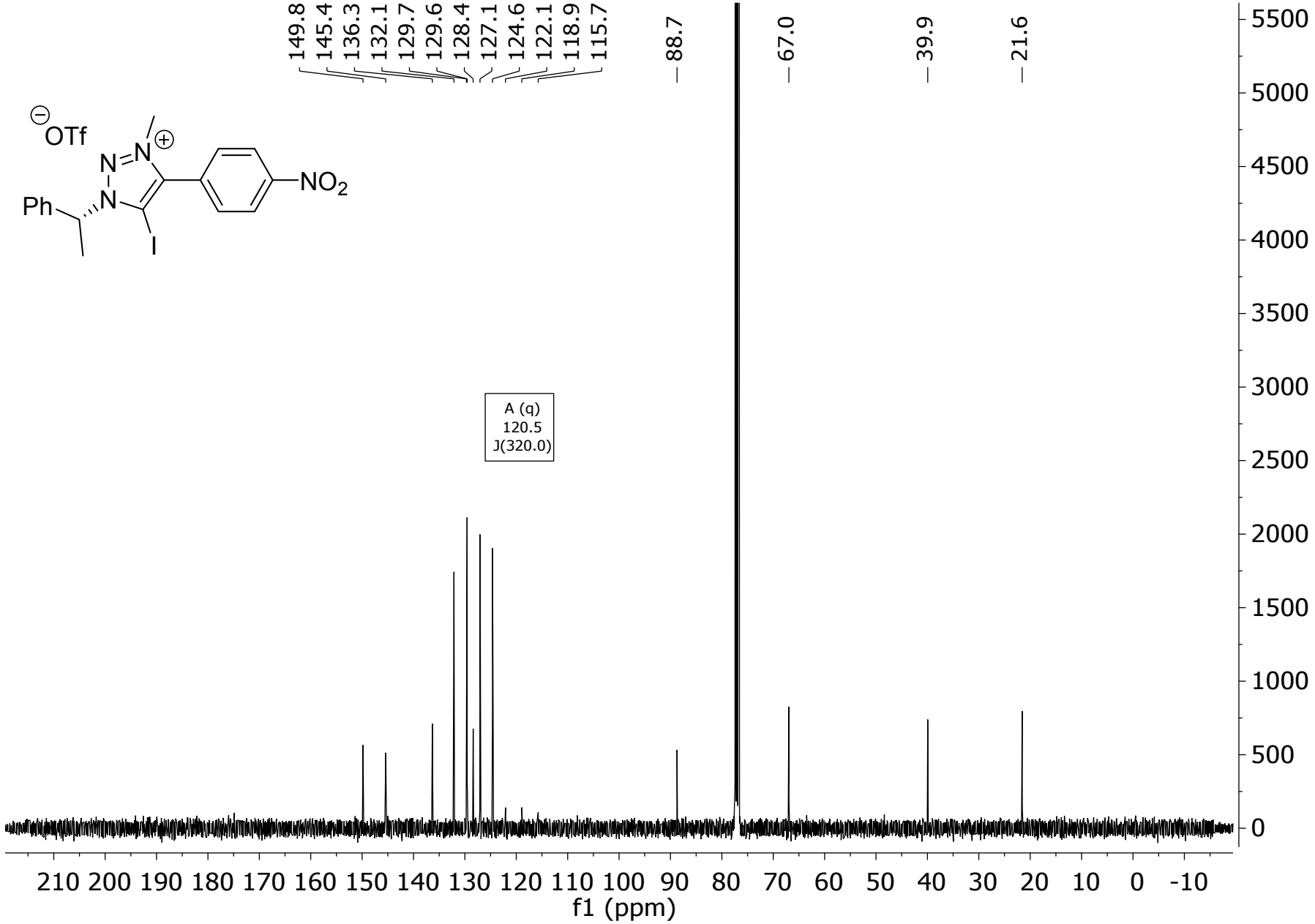


Figure S67. ^{13}C NMR spectrum of **2-OTf** ($CDCl_3$, 101 MHz).

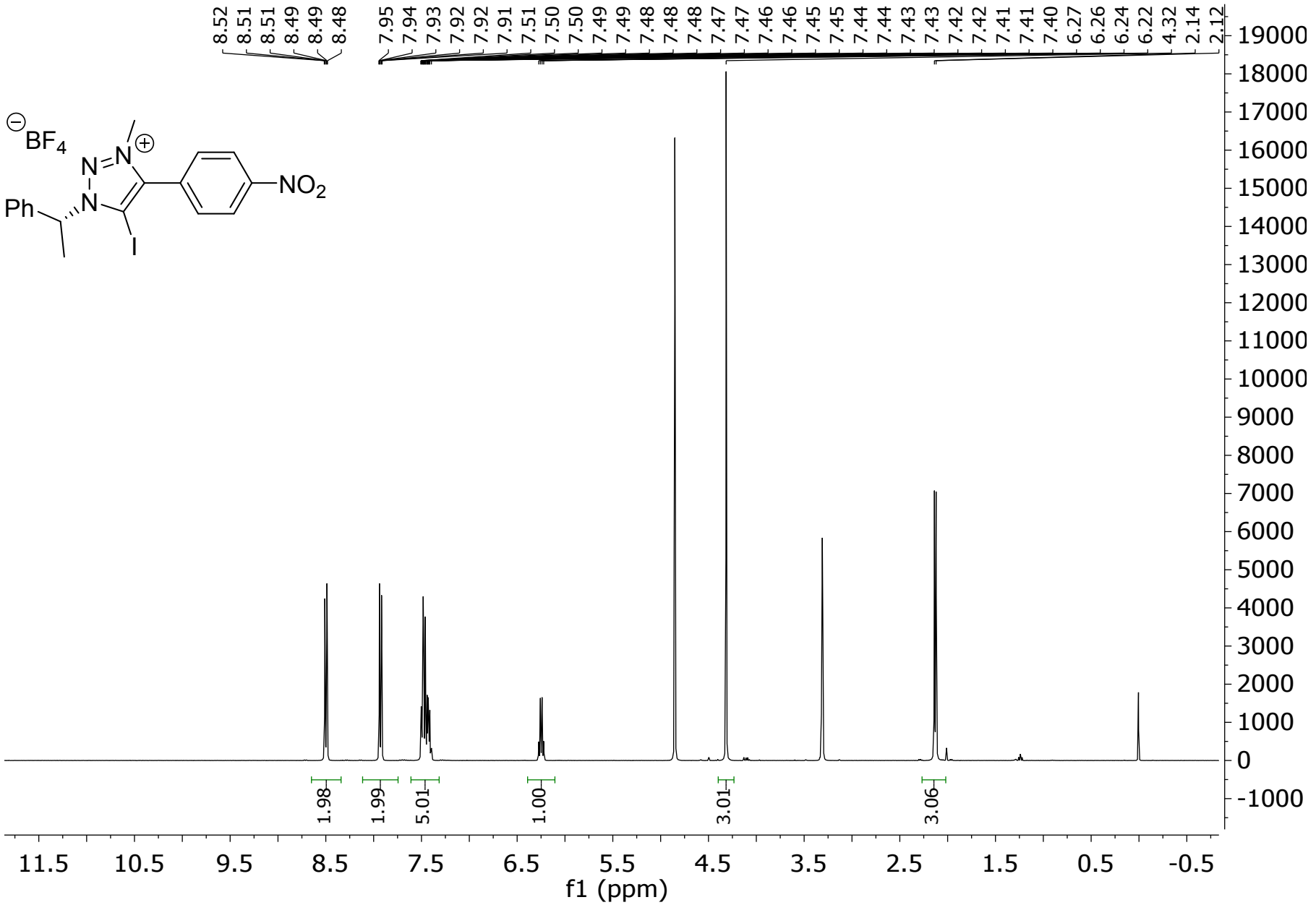


Figure S68. ^{1}H NMR spectrum of **2-BF$_4$** (CD_3OD, 400 MHz).

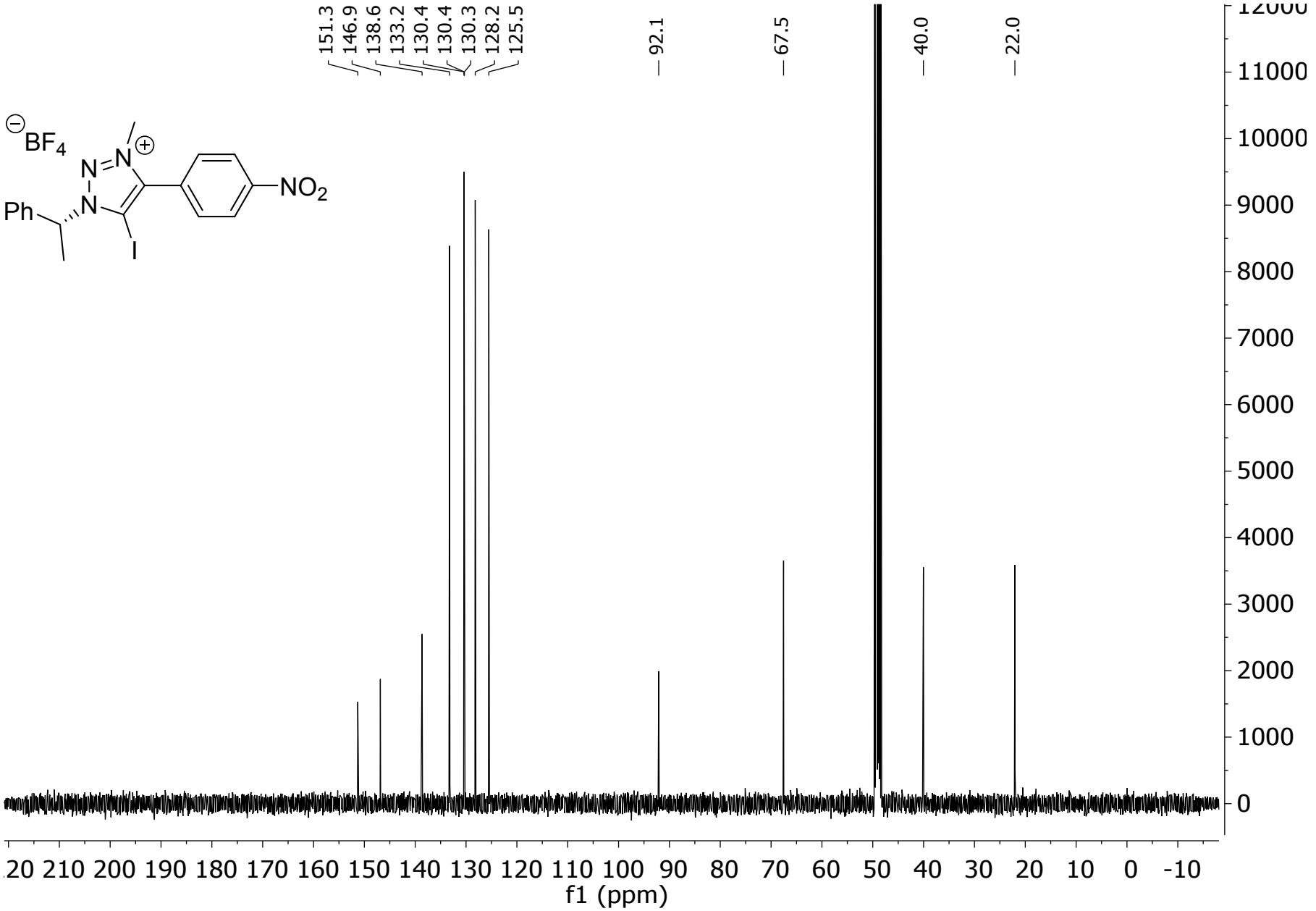


Figure S69. ^{13}C NMR spectrum of **2-BF_4** (CD_3OD, 101 MHz).

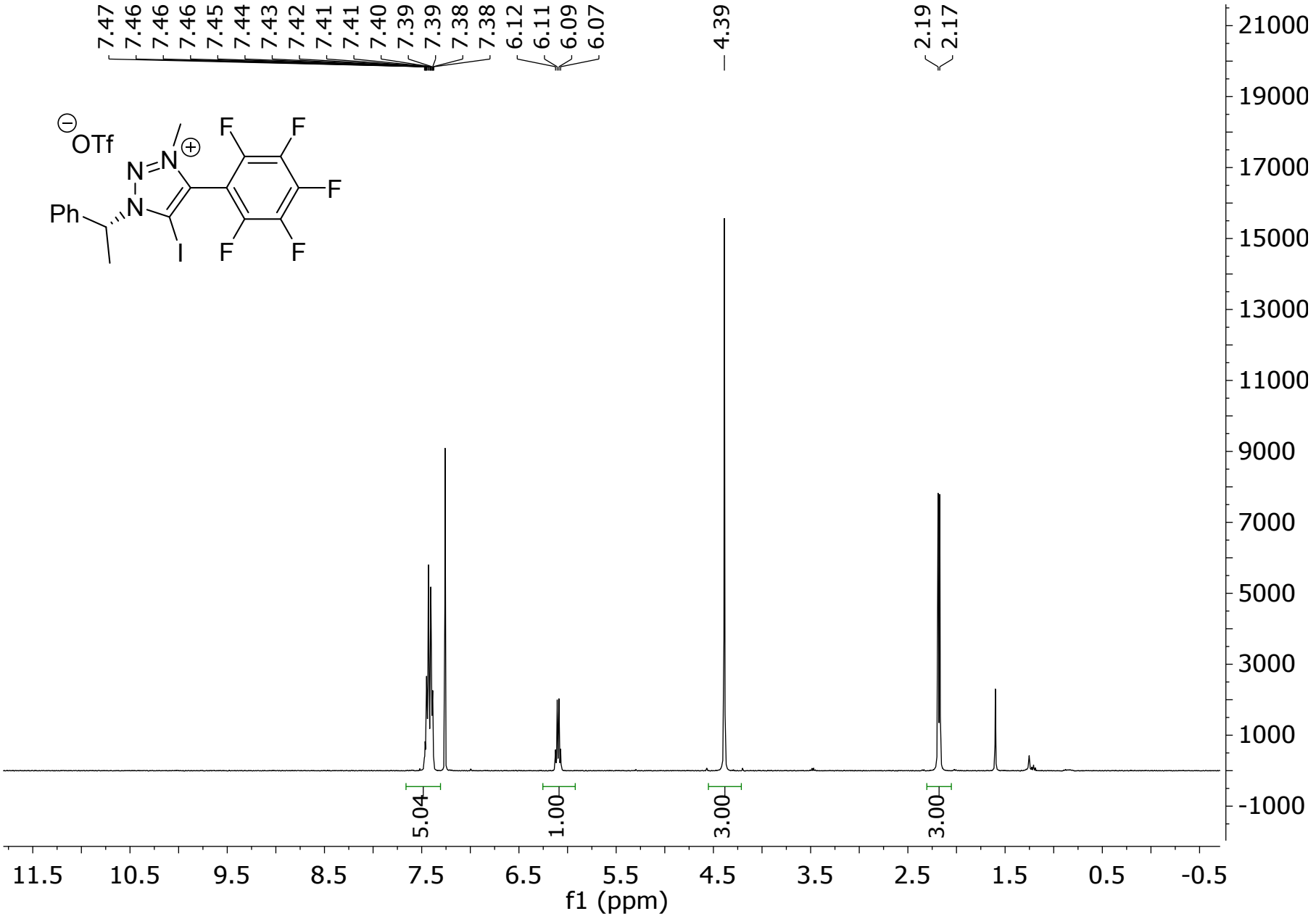


Figure S70. ^{1}H NMR spectrum of **3-OTf** ($CDCl_3$, 400 MHz).

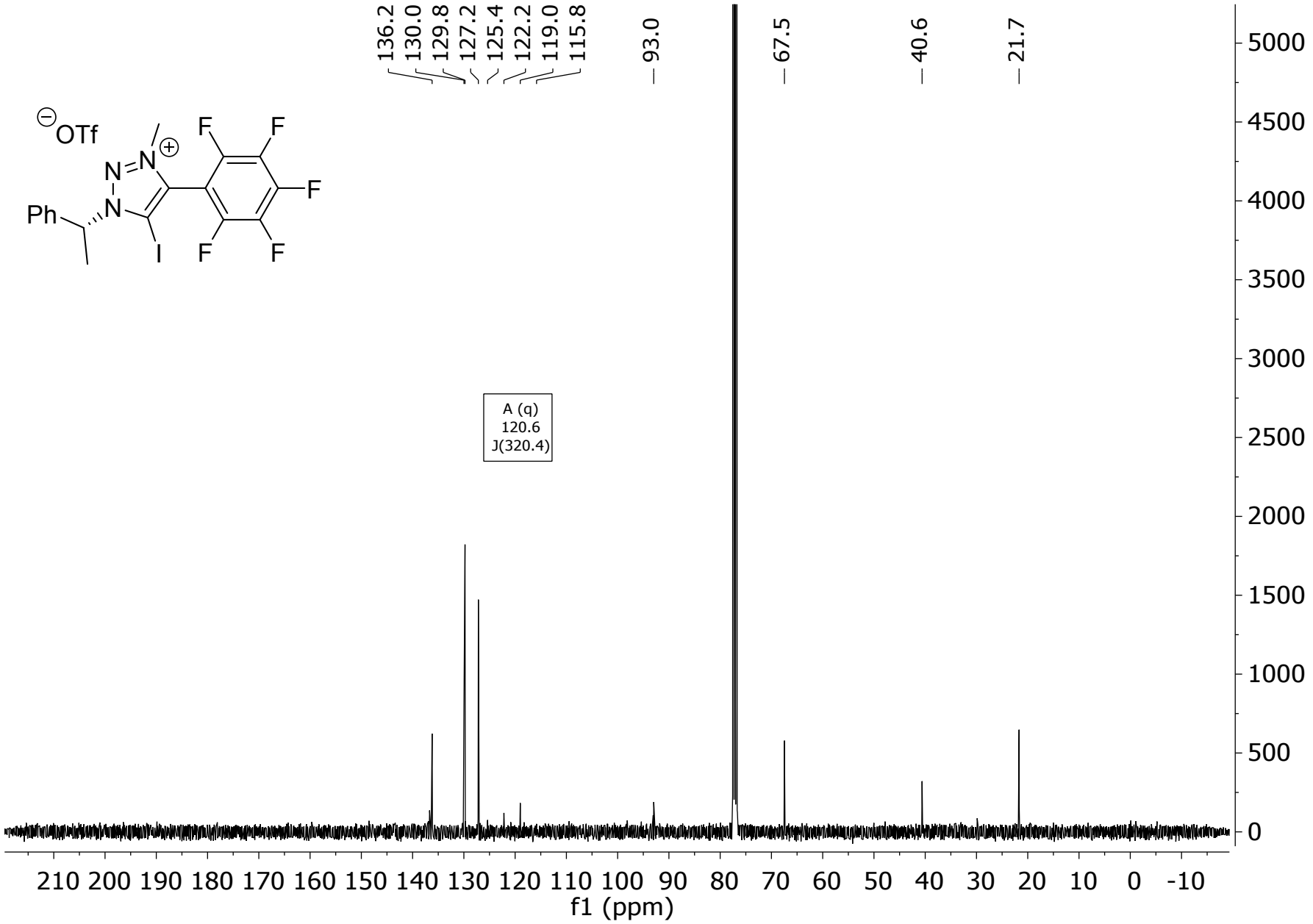


Figure S71. ^{13}C NMR spectrum of **3-OTf** ($CDCl_3$, 101 MHz).

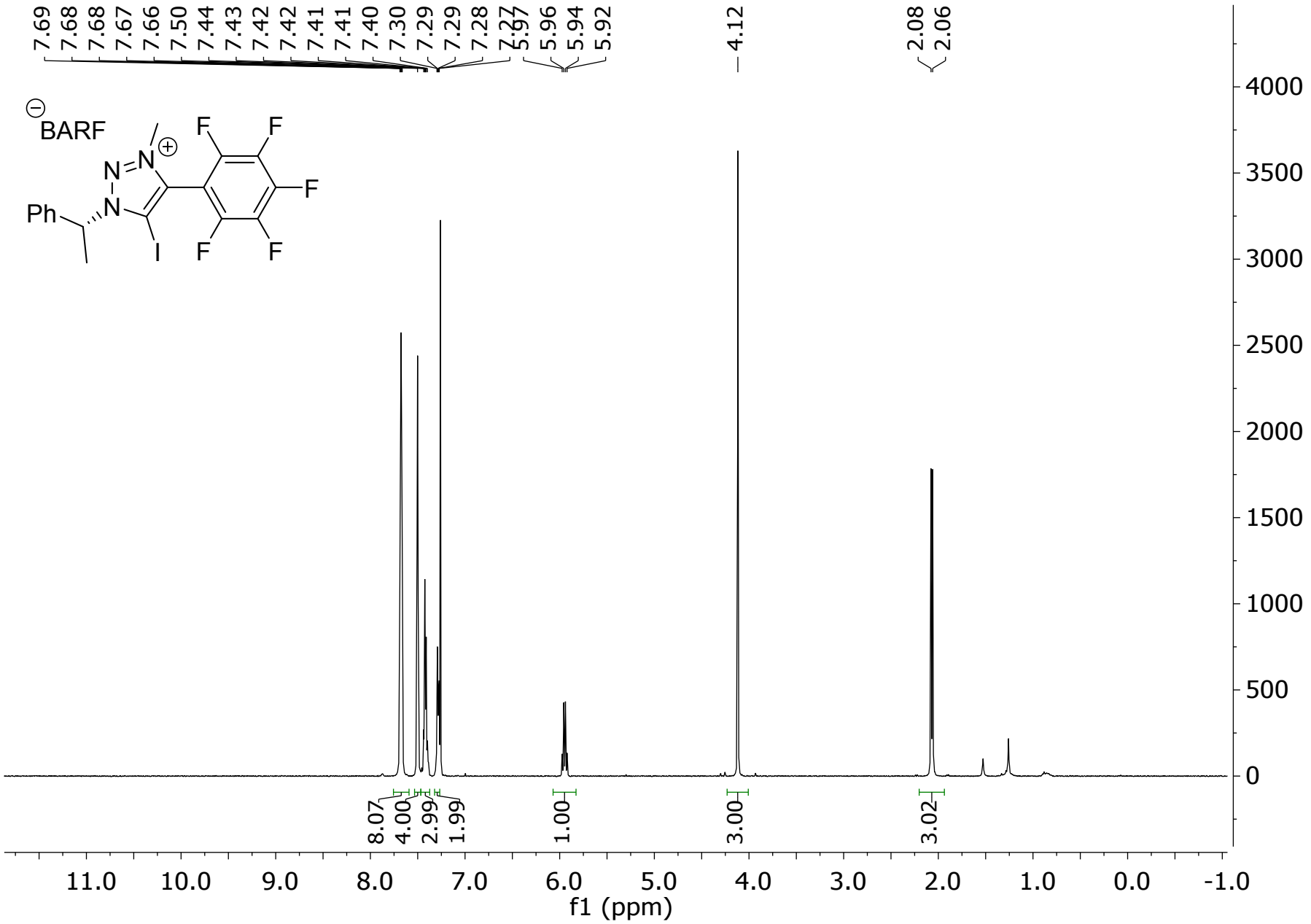


Figure S72. ^{1}H NMR spectrum of **3-BARF** ($CDCl_3$, 400 MHz).

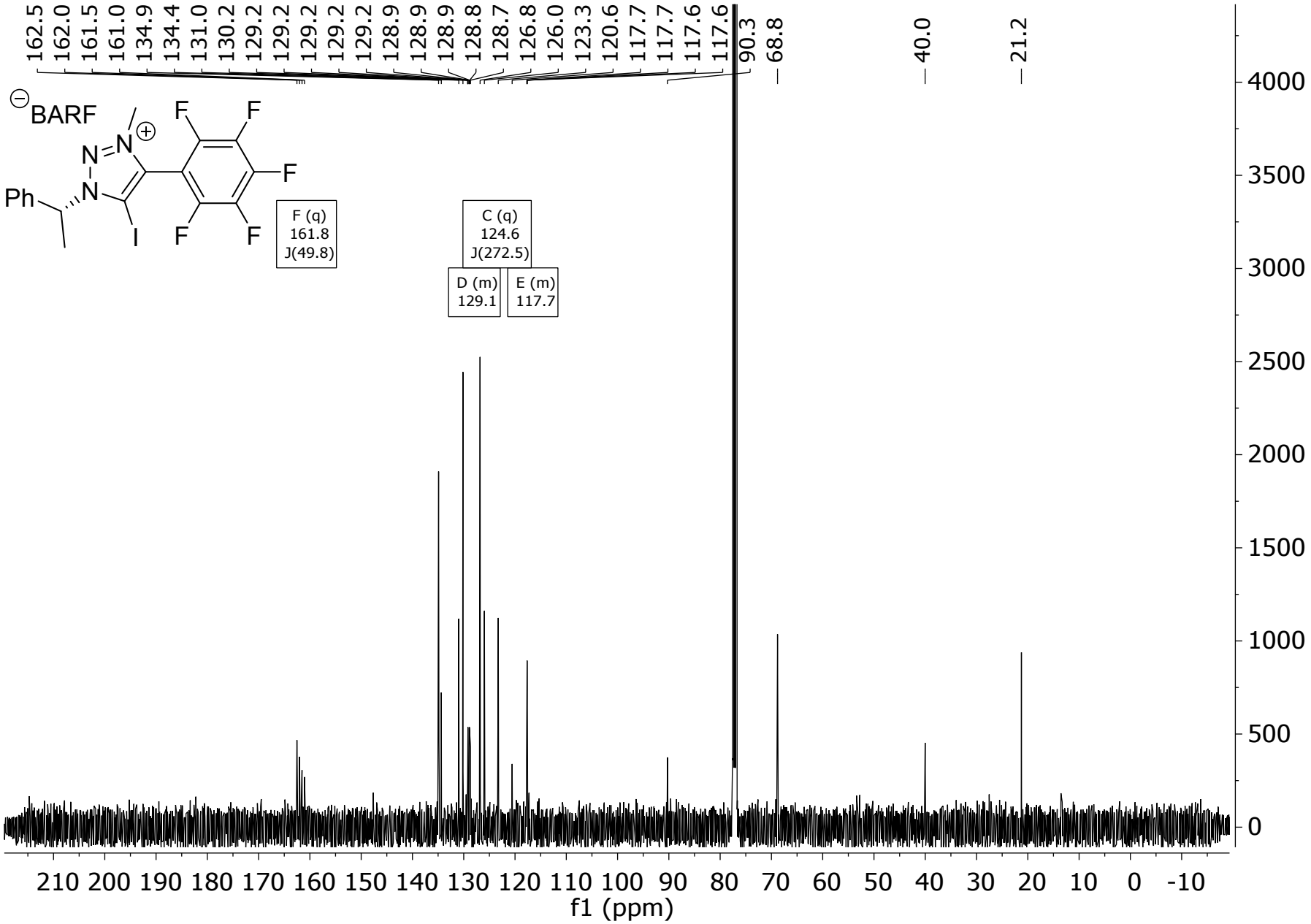


Figure S73. ^{13}C NMR spectrum of **3-BARF** ($CDCl_3$, 101 MHz).

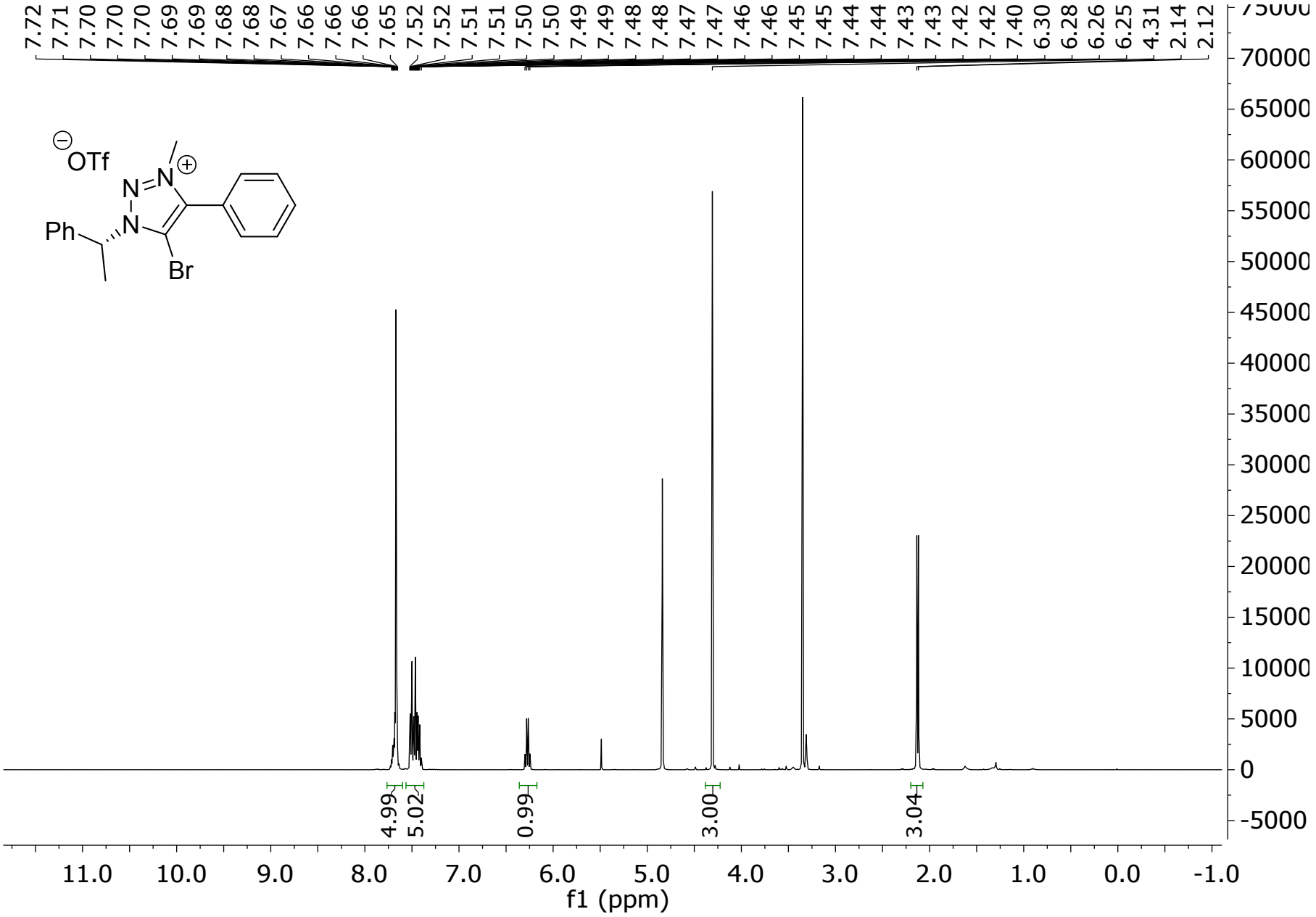


Figure S74. ^{1}H NMR spectrum of **4-OTf** (CD_3OD, 400 MHz).

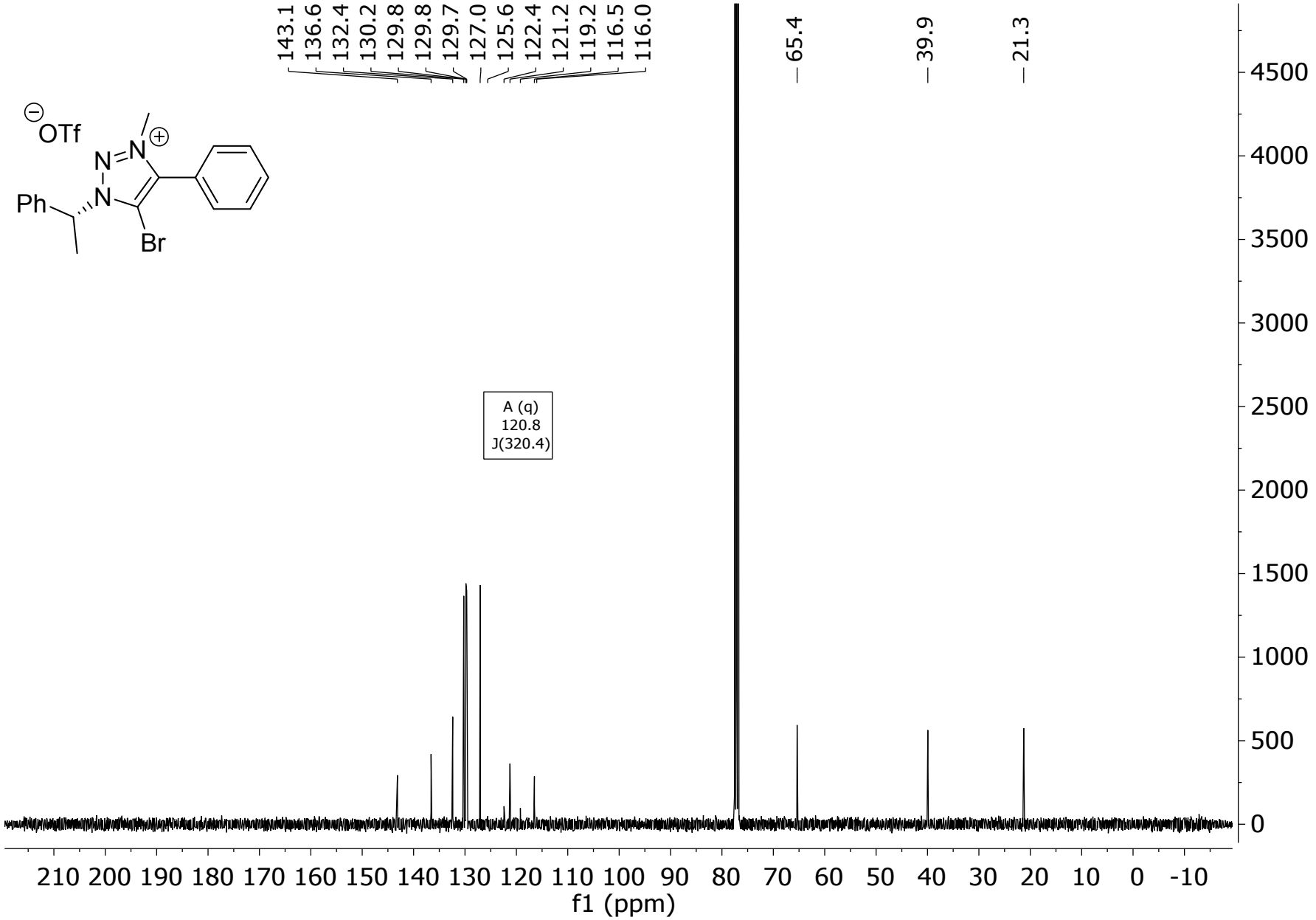


Figure S75. ^{13}C NMR spectrum of **4-OTf** (CD_3OD, 101 MHz).

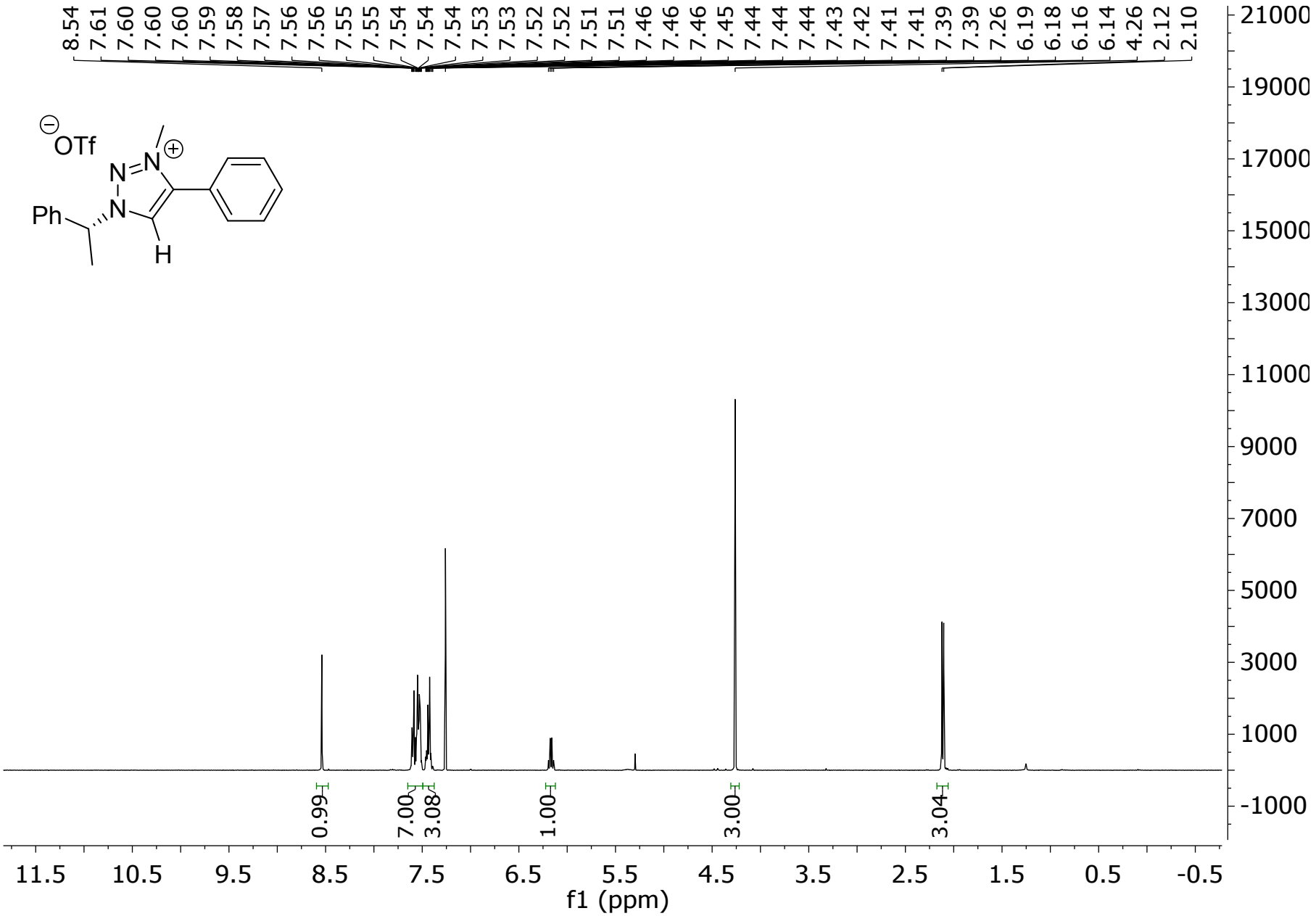


Figure S76. ^{1}H NMR spectrum of **6-OTf** ($CDCl_3$, 400 MHz).

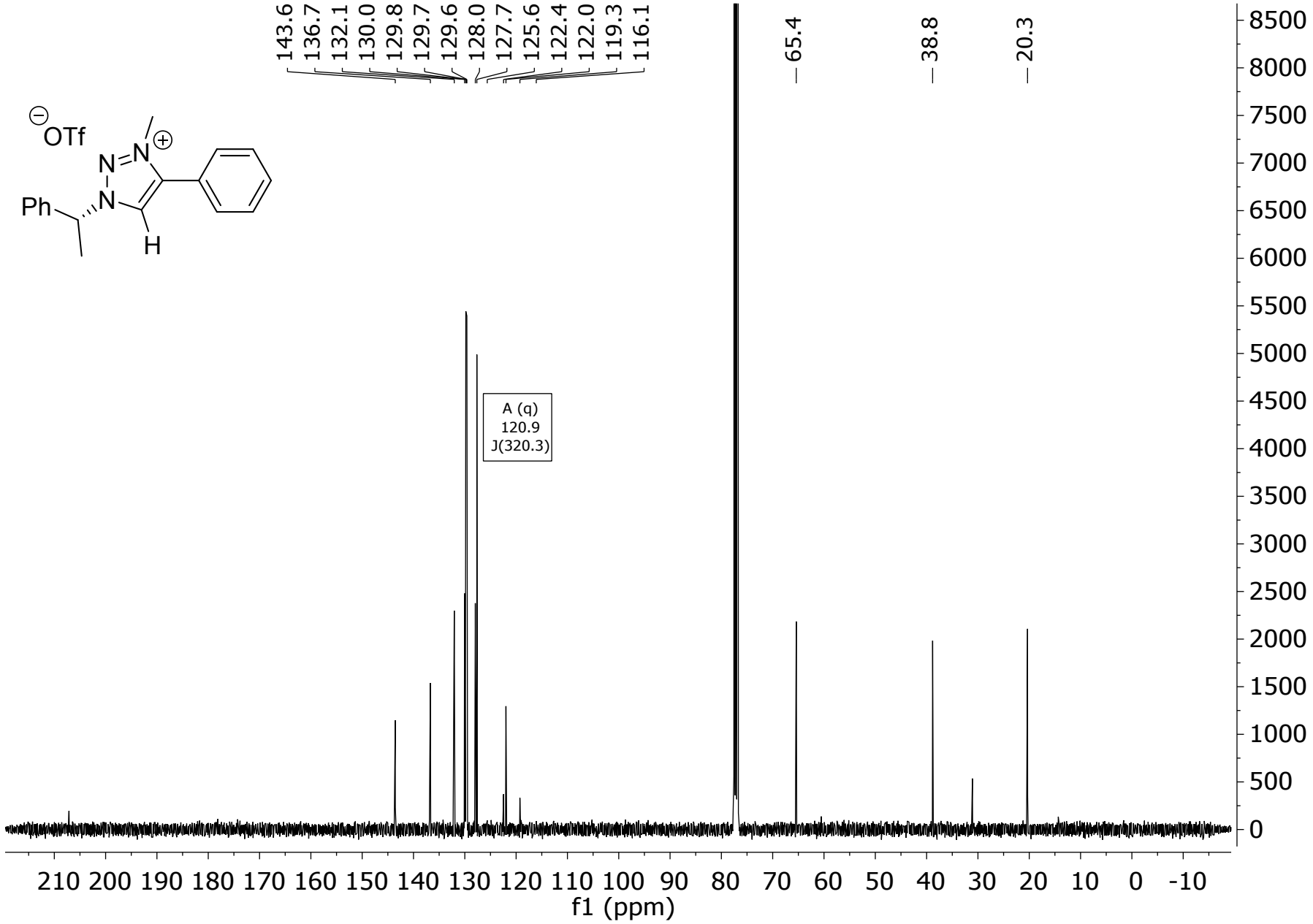


Figure S77. ^{13}C NMR spectrum of **6-OTf** ($CDCl_3$, 101 MHz)

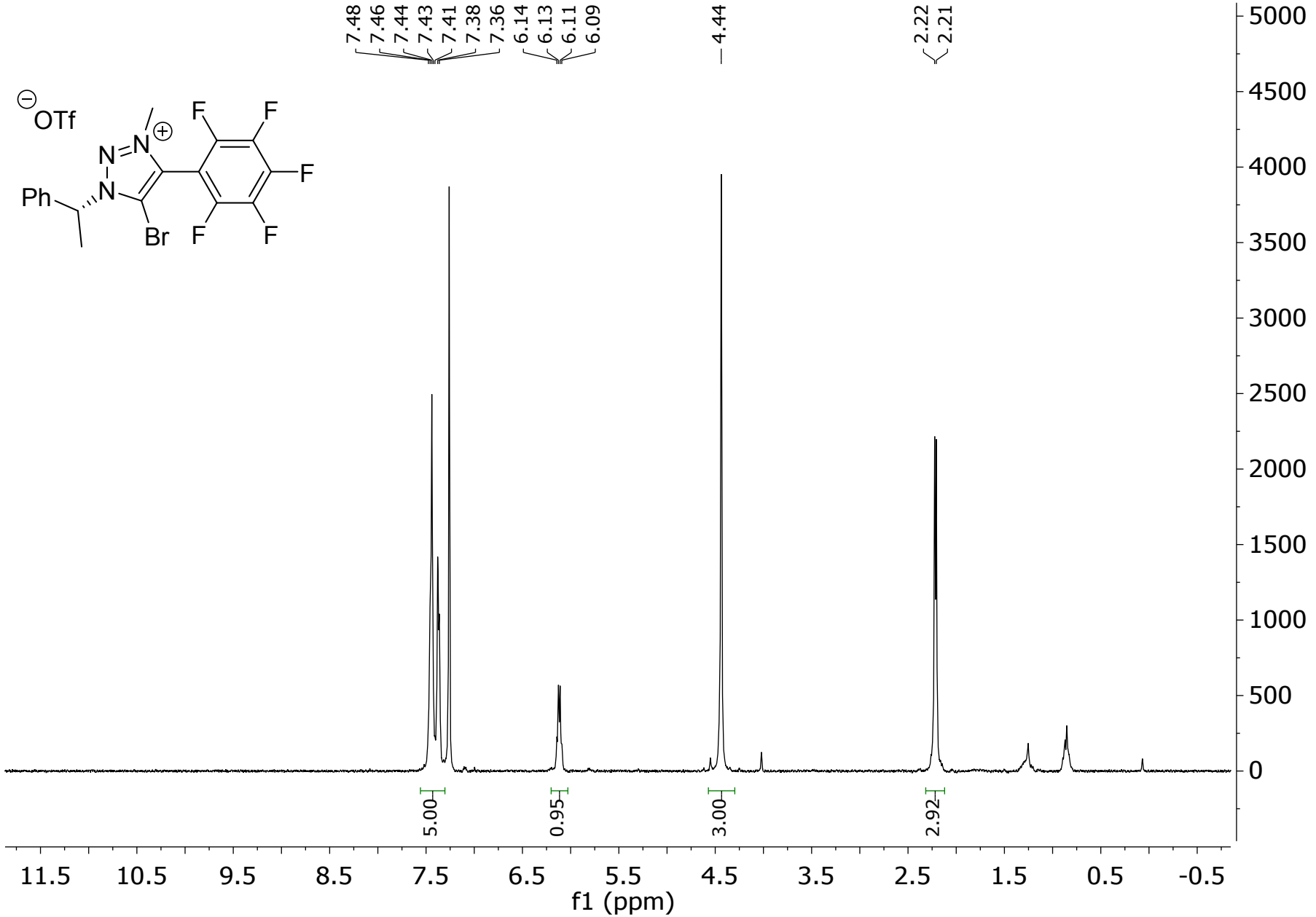


Figure S78. ^{1}H NMR spectrum of **5-OTf** ($CDCl_3$, 400 MHz).

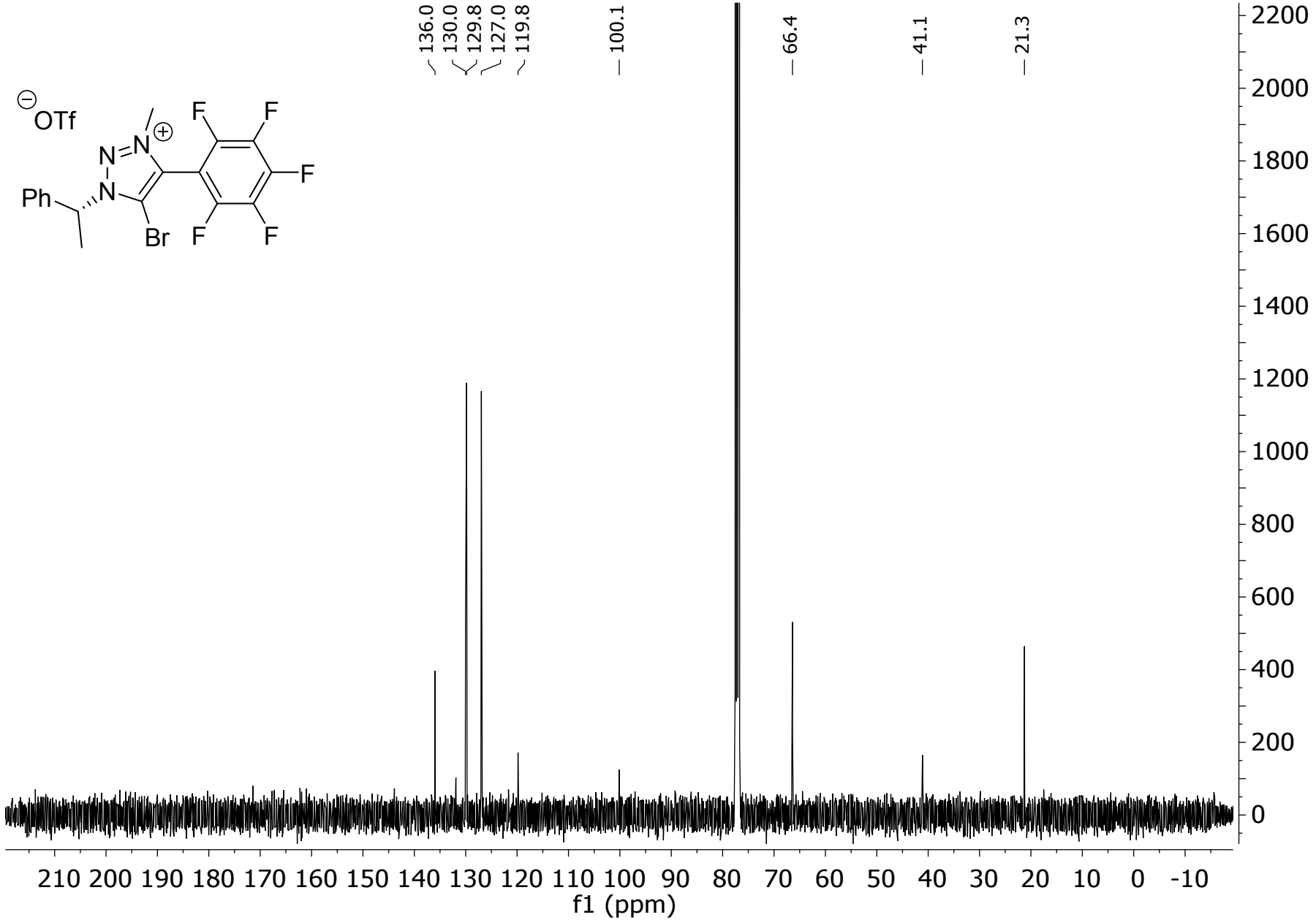


Figure S79. ^{13}C NMR spectrum of **5-OTf** ($CDCl_3$, 101 MHz)

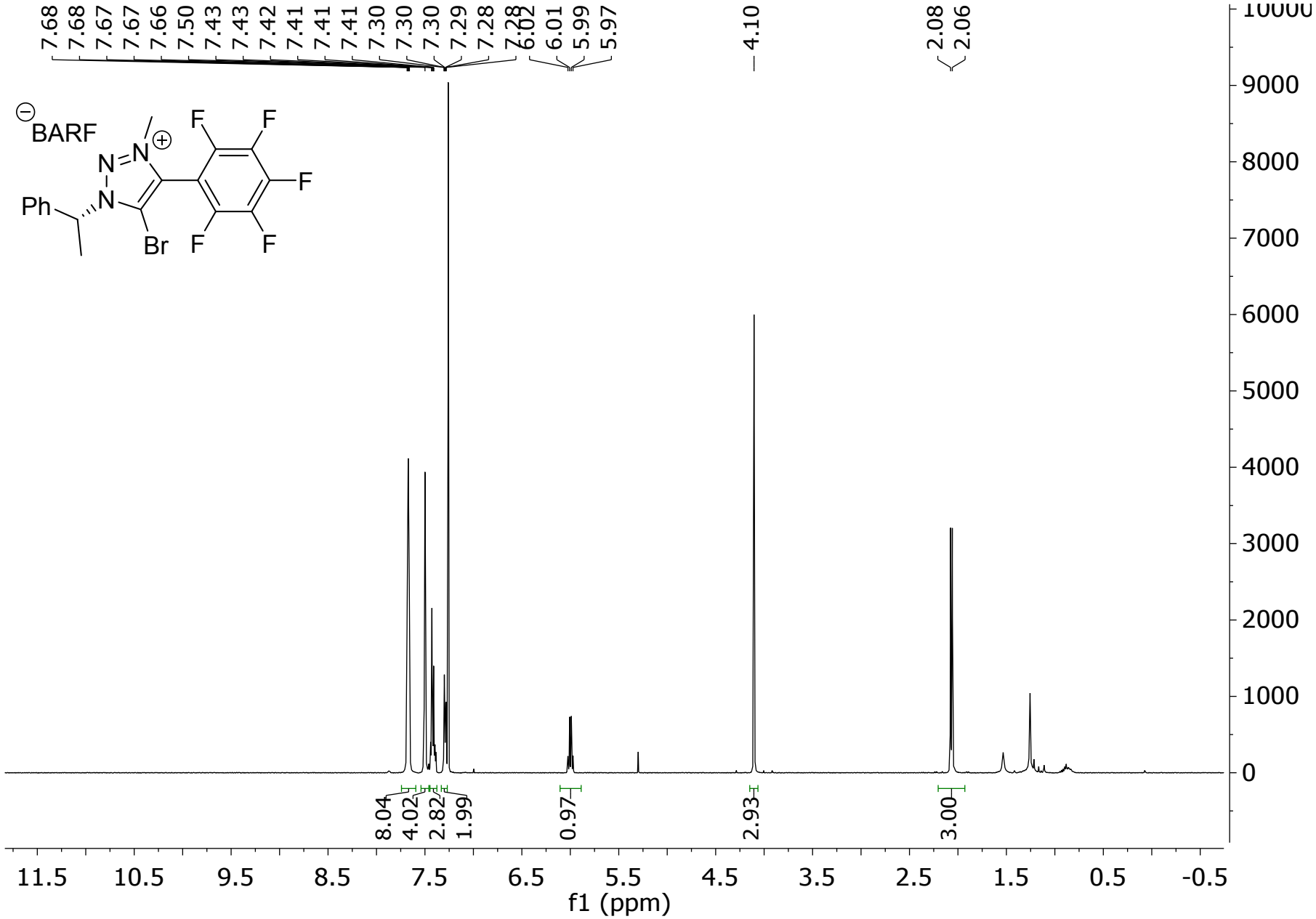


Figure S80. ^{1}H NMR spectrum of **5-BARF** ($CDCl_3$, 400 MHz).

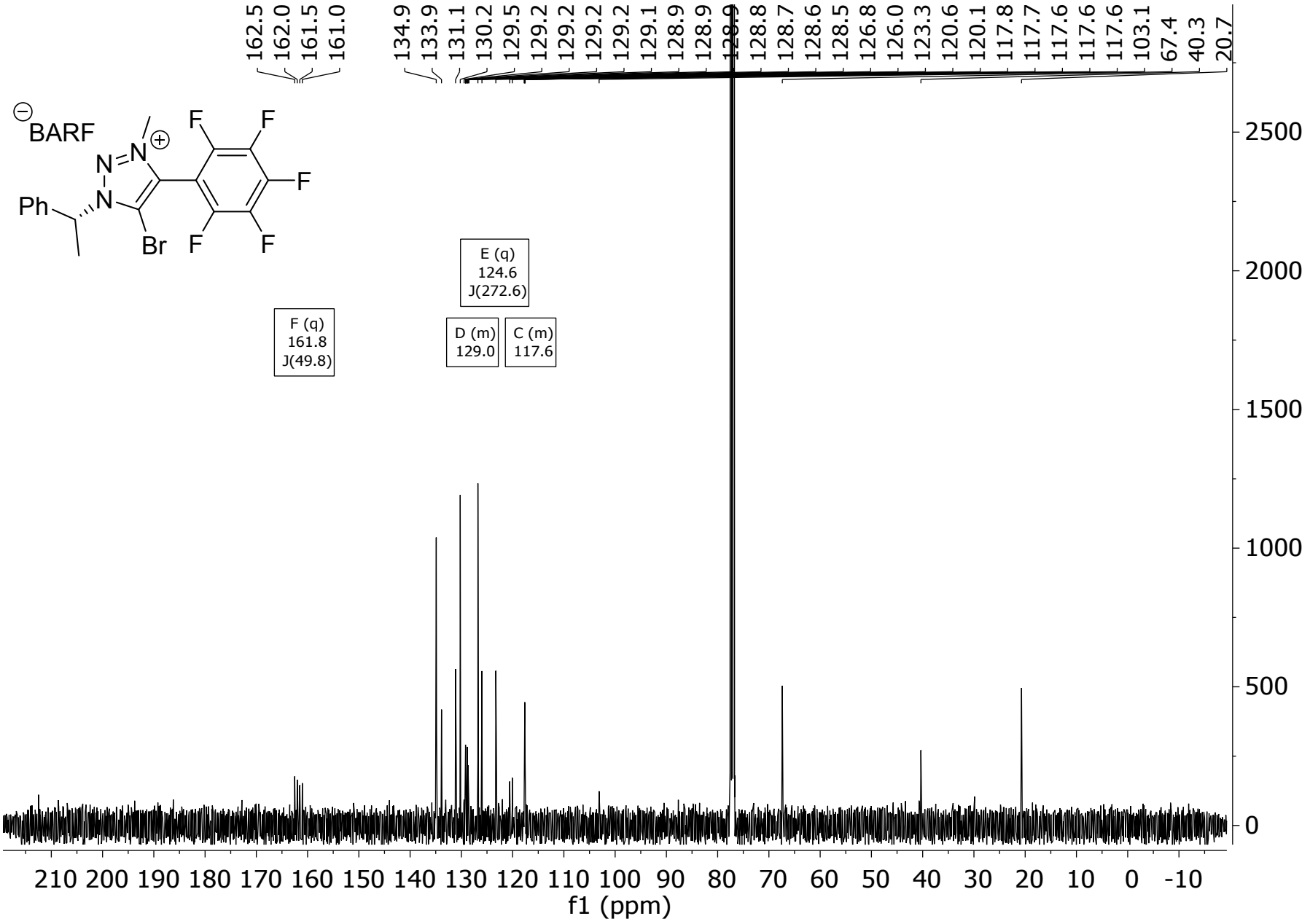


Figure S81. ^{13}C NMR spectrum of **5-BARF** ($CDCl_3$, 101 MHz)

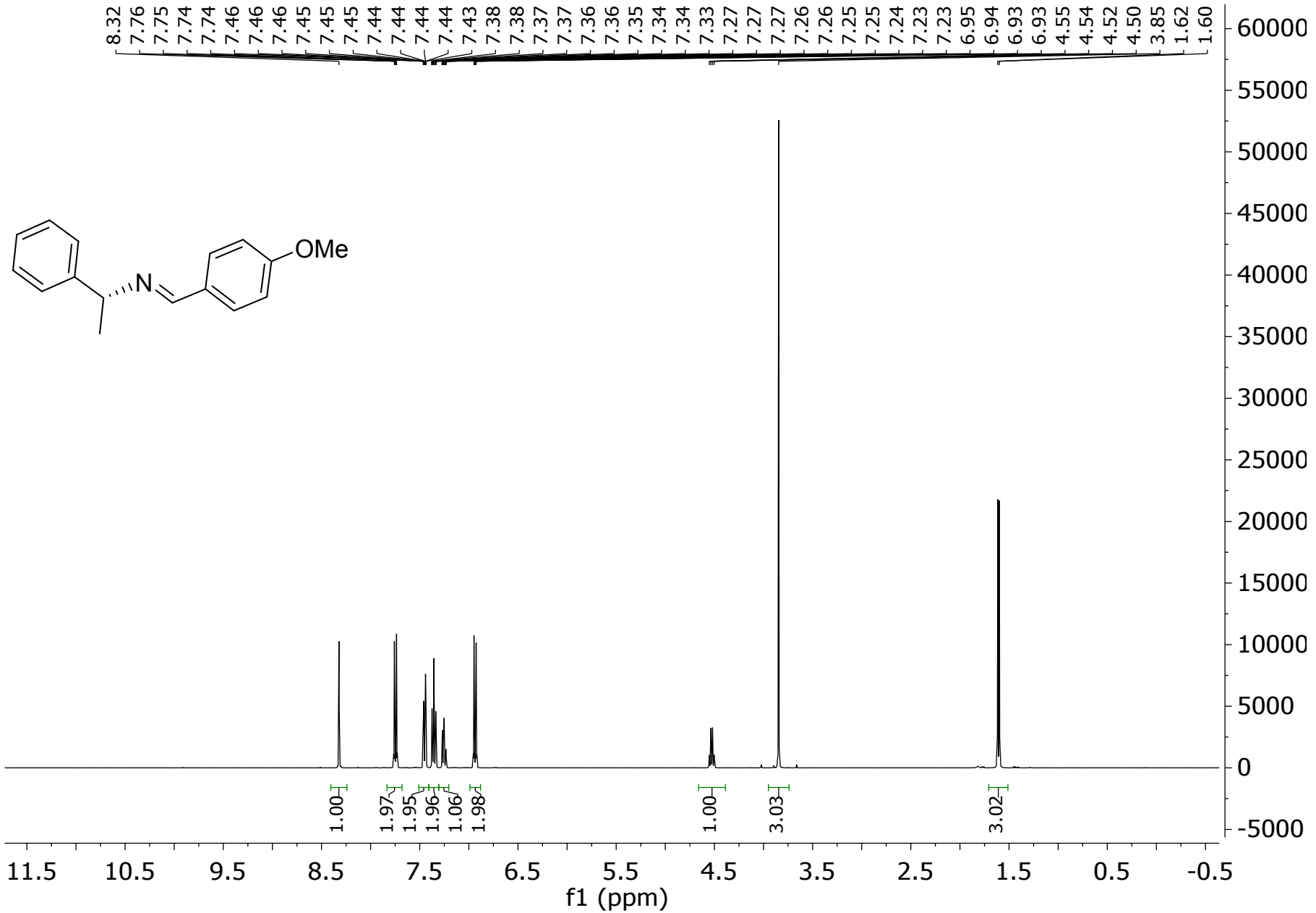


Figure S82. ^{1}H NMR spectrum of ***R*-8** ($CDCl_3$, 400 MHz).

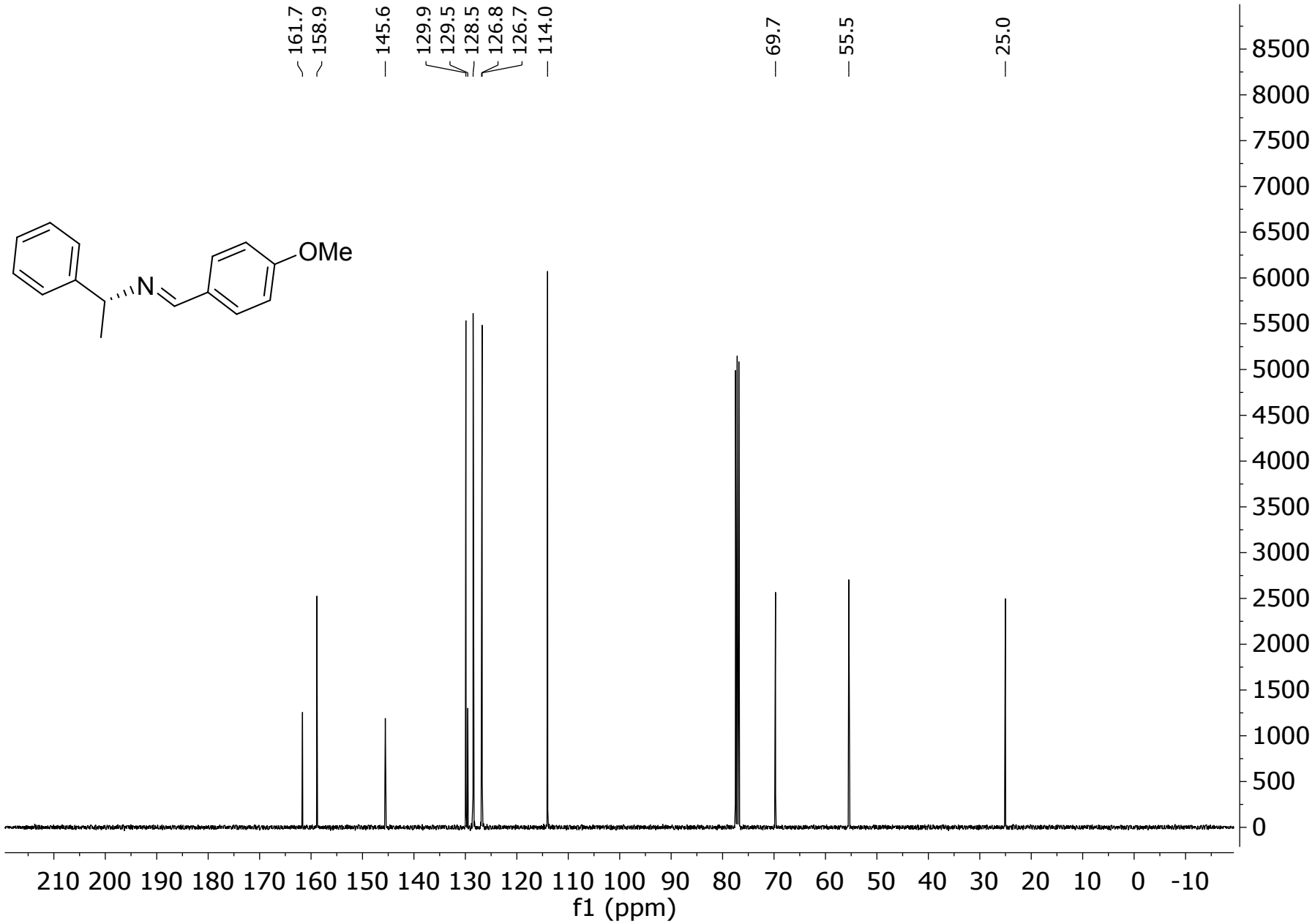


Figure S83. ^{13}C NMR spectrum of ***R*-8** ($CDCl_3$, 101 MHz)

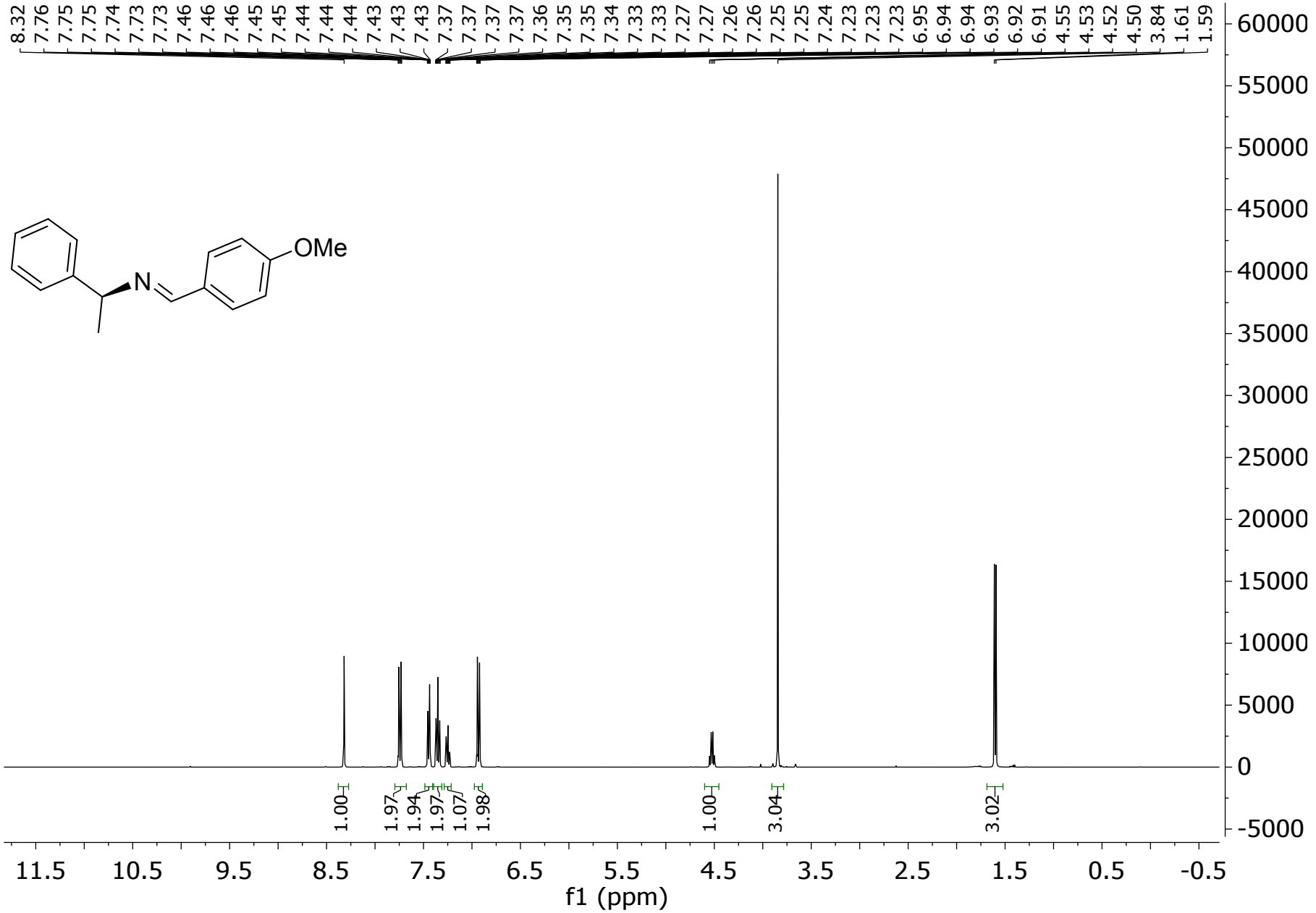


Figure S84. ^{1}H NMR spectrum of ***S*-8** ($CDCl_3$, 400 MHz).

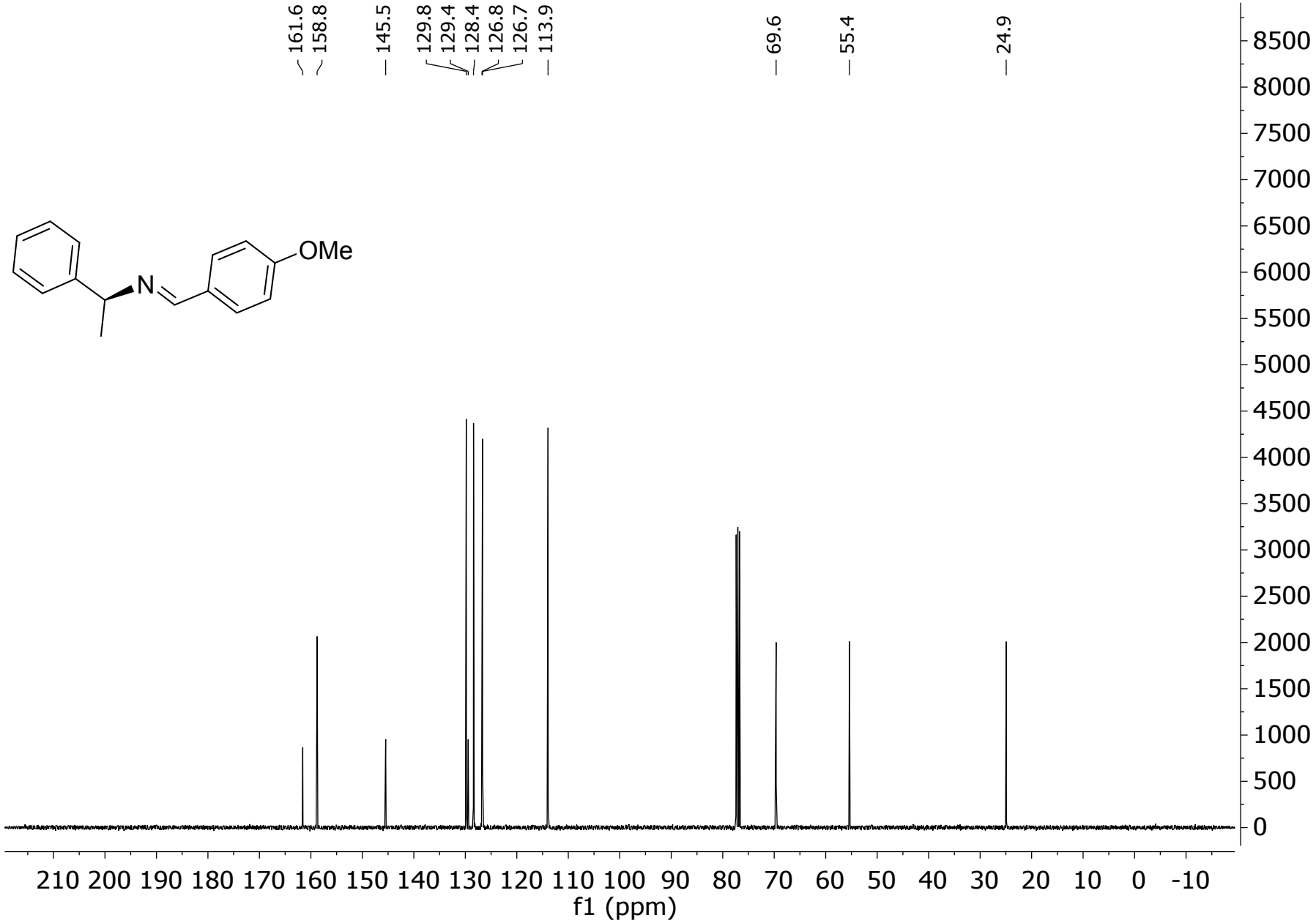


Figure S85. ^{13}C NMR spectrum of ***S*-8** ($CDCl_3$, 101 MHz)

V) References

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