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Selective Functionalization of the 1*H*-Imidazo[1,2-*b*]pyrazole Scaffold. A new Potential Bioisostere of Indole and a Precursor of Push-Pull Dyes

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Supporting Information

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General information

All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H-NMR (25 °C) and capillary GC. All reagents were obtained from commercial sources and used without further purification unless otherwise stated. Reaction mixtures were cooled using an acetone / dry ice bath. The suspension formed during the work-up of reactions containing CuCN·2LiCl was dissolved by adding appropriate amounts of concentrated aqueous ammonia solution.

Solvents

CH_2Cl_2 was predried over $CaCl_2$ and distilled from CaH_2 under nitrogen atmosphere.

THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen and stored over molecular sieves.

All other solvents were purchased from chemical suppliers (*Merck*, *Acros Organics*) and used without further purification.

Solvents for reaction workups and column chromatography were distilled prior to use.

Reagents

***n*BuLi** solutions in hexane were purchased from Albemarle or Sigma Aldrich and the concentration was determined by titration against *N*-benzylbenzamide in THF at –40 °C.[1]

TMPH was purchased from Albemarle (Frankfurt, Germany), freshly distilled over CaH_2 and stored under argon.

CuCN·2LiCl solution (1.00 M in THF) was prepared by drying CuCN (8.96 g, 100 mmol, 1.00 equiv) and LiCl (8.48 g, 200 mmol, 2.00 equiv) in a *Schlenk*-flask under vacuum for 5 h at 150 °C. After cooling to 25 °C, dry THF (100 mL) was added and the resulting mixture was stirred until the salts were dissolved.

[1] A. F. Burchat, J. M. Chong and N. Nielsen, *J. Organomet. Chem.*, 1997, **542**, 281.

$ZnCl_2$ solution (1.00 M in THF) was prepared by drying $ZnCl_2$ (27.3 g, 200 mmol) in a *Schlenk*-flask under vacuum for 5 h at 150 °C. After cooling to 25 °C, dry THF (200 mL) was added and the resulting mixture was stirred until the salts were dissolved.

***i*PrMgCl·LiCl** in THF was prepared by flame drying magnesium turnings (24 g, 1.0 mol, 2.0 equiv) and anhydrous LiCl (25 g, 0.60 mol, 1.2 equiv) in a *Schlenk*-flask under vacuum at 450 °C. After the addition of anhydrous THF (500 mL), *i*PrCl (39 g, 0.50 mol, 1.0 equiv) was added dropwise at 25 °C using a dropping funnel until the reaction started. Then the reaction mixture was cooled to 0 °C and the addition was continued overnight while allowing the flask to warm up to 25 °C. The remaining solids were filtered off and the *i*PrMgCl·LiCl solution was titrated against iodine.

Chromatography

Flash column chromatographical purifications were performed using SiO_2 60 (0.040–0.063 mm, 230–400 mesh ASTM) or Florisil® PR grade (149-250 µm, 60-100 mesh) from Merck. Thin layer chromatography (TLC) was performed using aluminium plates covered with SiO_2 (Merck 60, F–254). Spots were visualized by UV light irradiation and/or by staining of the TLC plate with one of the reagents below, followed by heating with a heat gun if necessary.

- $KMnO_4$ (0.3 g), K_2CO_3 (20 g) and KOH (0.3 g) in water (300 mL).
- Neat iodine absorbed on silica gel (no heating required).

Preparative HPLC

For purification, an *Agilent Technologies* 1260 Infinity HPLC-System was used, consisting of two prep-pumps (acetonitrile/water, no additives), a MWD-detector (210 nm wavelength, 40 nm bandwidth, ref-wavelength 400 nm, ref-bandwidth 100 nm) and a fraction collector. Three different columns were used: 1) *Kinetix* EVO C18 5 µm column (length: 150 mm, diameter: 10 mm), 2) *Kinetix* EVO C18 5 µm column (length: 150 mm, diameter: 21.2 mm) and 3) *Waters* XBridge Prep C8 5 µm column (length: 150 mm, diameter: 30 mm).

Analytical data

NMR spectra were recorded on *Bruker* ARX 200, AC 300, WH 400 or AMX 600 instruments. Chemical shifts are reported as δ-values in ppm relative to the deuterated solvent peak:

$CDCl_3$ (δ_H: 7.26; δ_C: 77.16). For the observation of the observed signal multiplicities, the following abbreviations and combinations thereof were used: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet) and br (broad). If not otherwise noted, the coupling constants given are either H-H or H-F coupling constants for proton signals and C-F coupling constants for carbon signals.

Melting points are uncorrected. and were measured on a *Büchi* B.540 apparatus.

Infrared spectra were recorded from 4000-400 cm^{-1} on a *Perkin Elmer* Spectrum BX-59343 instrument. For detection a Smiths Detection DuraSampl IR II Diamond ATR sensor was used. The main absorption peaks are reported in cm^{-1}.

Gas chromatographical analysis (GC) was performed with instruments of the type Hewlett-Packard 6890 or 5890 Series II, using a column of the type HP 5 (Hewlett-Packard, 5% phenylmethylpolysiloxane; length: 10 m, diameter: 0.25 mm, film thickness 0.25 µm). The detection was accomplished using a flame ionization detector. Mass spectra (MS) and high resolution mass spectra (HRMS) were recorded on a *Finnigan* MAT 95Q or *Finnigan* MAT 90 instrument for electron impact ionization (EI). For the combination of gas chromatography with mass spectroscopic detection, a GC–MS of the type *Hewlett-Packard* 6890/MSD 5793 networking was used (column: HP 5–MS, Hewlett–Packard; 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm, film thickness: 0.25 µm).

Single crystals of compounds suitable for **X-ray diffraction** were obtained by slow evaporation of either EtOAc or $CDCl_3$ solutions. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K_α radiation (λ = 0.71071 Å).

Data collection was performed with the CrysAlis CCD software;[2] CrysAlis RED software[3] was used for data reduction. Absorption correction using the SCALE3 ABSPACK multiscan method[4] was applied. The structures were solved with SHELXS-97,[5] refined with SHELXL-97[6] and finally checked using PLATON.[7] Details for data collection and structure refinement are summarized in the tables at the end of this document.

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[2] CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).
[3] CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01-04-2005 CrysAlis171.NET) (compiled Apr 1 2005, 17:53:34).
[4] SCALE3 ABSPACK – An Oxford Diffraction Program (1.0.4, gui:1.0.3) (C), Oxford Diffraction, Ltd., 2005.
[5] G. M. Sheldrick (1997) SHELXS-97: *Program for Crystal Structure Solution*, University of Göttingen, Germany.

UV/vis spectra were recorded on a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm InGaAs integrating sphere. Absorbance spectra of **14** were measured with 50 µM solutions. Compounds **14a-d** were dissolved in anhydrous chloroform, compound **14e** was dissolved using anhydrous acetonitrile.

Photoluminescence (PL) spectra were performed using a PicoQuant FluoTime 300 spectrometer equipped with a 375 nm picosecond diode laser for illumination of the samples.

The **1-octanol/water partitioning coefficient (logP)** was determined using a miniaturized Shake-Flask equilibrium method. Prior to start the experiment the two phases were pre-saturated, so ’water-saturated 1-octanol‘ and ’1-octanol-saturated water‘ were used. The samples were initially dissolved in DMSO as a 10 mM stock concentration. The samples and an internal standard were dispensed in a 1 ml deep-well plate and the DMSO was evaporated prior to dissolution in 1-octanol at a target concentration of 150 µM by shaking at 1000 rpm during 8 hours. The pH 7.4 buffer was added with a phase ratio K of 1 (where K = $V_{water}/V_{octanol}$) and then the samples were shaken 4 hours on a shaker at 1000 rpm. The deep-well plate was centrifuged at 3000 rpm prior to phase separation. A x10 dilution for the aqueous phase and a x1000 dilution for the octanol phase were prepared and quantified by LC-HRMS (Exactive-Plus) against an internal standard (Dexamethasone) with a known logD=1.9 with the following equation:

$$logD = log\left(\frac{Analyte\ peak\ area\ in\ octanol * 1000 \Big/ IS\ peak\ area\ in\ octanol \Big/ 0.794}{Analyte\ peak\ area\ in\ aqueous * 10 \Big/ IS\ peak\ area\ in\ aqueous}\right)$$

Column used: Zorbax_SB_AQ 50 x 2.1 mm 1.8 µm – Column oven temperature = 50 °C

The method utilized small amounts of 10 mM DMSO compound stock and subsequently removed the DMSO to generate solid-like material for logP or logD measurement. Sample preparation and phase separation was automated using liquid handling workstations with 8 or 96 tip pipettors. Both 1-octanol and buffer phases were quantified in triplicate and logP or logD was derived from the ratio of peak area responses in the MS corrected for volume and using an internal standard. The assay has been validated using literature compounds and

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[6] G. M. Sheldrick (1997) SHELXS-97: *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.
[7] A. L. Spek (1999) PLATON: *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, the Netherlands.

Novartis compounds with diverse ionization and lipophilicity values ranging from -2 to +5.5. The standard logD pH is 7.4 but the assay can be modified to measure logD at any pH. Further, the pH where a compound is unionized can be chosen to measure logP. This is a direct method of lipophilicity and can be compared with values obtained from traditional methods such as shake-flask/HPLC or dual-phase potentiometric titration.

Mobile phase: A= 100% water UHPLC grade + 0.08% Formic acid. B= 100% ACN + 0.08% Formic acid. Flow rate = 0.5 ml/min. Gradient mode: starting at 95% A up to 95% B in 0.5 min and kept constant during 1min before to restore initial conditions within 0.1min. Vinj = 5µl. Full MS acquisition mode – Full scan 130 to 1800 m/z and Resolution = 35'000. [M+H]+ ion chromatogram was extracted for each compounds.

High-throughput Equilibrium Solubility measurement:

Compounds were first solubilized at 10 mM in pure DMSO. 15 µL of each 10 mM DMSO compound solution was dispensed as triplicates for each media in 96-well polypropylene plates. The DMSO was evaporated at 40.0°C under 1 mbar in a Combidancer. 200 µL of media was added (pH 6.8 buffer, chlorine-free phosphate buffer 0.067 M), the plate was sealed and shaken for a minimum 20 hours. The plates were centrifuged for 15 min at 3600 rpm (about 2000 G). The sample solutions were pooled by 3 and then diluted 200 times in Acetonitrile/water + internal standard. A 4-point calibration curve was prepared and analytics were performed on a LC-HRMS (Exactive-Plus) system. The same analytical conditions were used as the logP determination.

UV-metric pK_a determination

UV-metric ionization constants[8] were determined on the commercial Spectral Gradient Analyser (SGA) or T3 instrument (Sirius Analytical, sirius-analytical.com). Test compounds were diluted to 0.04 mM in a co-solvent mixture and titrated three times in 20-40%wt methanol. The titrations were performed at 25°C and 0.15 M ionic strength, from pH 2 to 12 or 12 to 2 (with delta pH of 0.2) depending on the acidic or basic nature of the test compound. A linear buffer was added to allow fast pH stabilization after each titrant addition. Wavelengths from 230-450 nm were typically monitored for UV absorbance change due to the ionization state of the compound. Target Factor Analysis (TFA) was used to calculate apparent pK_a's from the multi-wavelength absorption data at a given % of co-solvent (psKa), followed by Yasuda-Shedlovsky extrapolation to 0% methanol to provide the aqueous pKa.

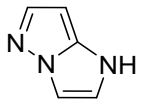
[8] R. I. Allen, K. J. Box, J. E. A. Comer, C. Peake and K. Y. Tam, *J. Pharm. Biomed. Anal.*, 1998, **17**, 699.

Acid/base assignment was performed based on the slope of extrapolation. Experimental variability was determined from 183 duplicate measurements from different days and experimentalists, with a standard deviation of 0.17 (0.35 log units).

Preparation of starting materials

The following reagents were prepared according to literature procedures: *S*-phenyl benzenesulfonothioate,[8] *S*-methyl benzenesulfonothioate,[9] 6-(4-chlorophenyl)-1H-imidazo[1,2-b]-pyrazole[10] and 7-(4-(4-fluorophenethyl)piperazine-1-carbonyl)-1*H*-indole-3-carbonitrile (pruvanserin).[11]

1H-Imidazo[1,2-*b*]pyrazole (1)



1H-Imidazo[1,2-*b*]pyrazole was synthesized using a slightly modified literature procedure:[9] A solution of $N_2H_4 \cdot H_2O$ (77 mL, 500 mmol) in absolute ethanol (250 mL) was heated to reflux before adding bromoacetaldehyde diethyl acetal (121 mL, 2.5 mol) dropwise over 45 min. The resulting solution was refluxed for an additional 3 h and the solvents were removed *in vacuo*. The residue was taken up in aqueous NaOH (35%, 60 mL) and a saturated aqueous solution of NaCl (50 mL) and the mixture was extracted with toluene (2x250 mL).

The resulting solution of (2,2-diethoxyethyl)hydrazine in toluene was treated with ethyl 2-cyano-3-ethoxyacrylate (85 g, 500 mmol) under argon atmosphere and stirred at 25 °C over night. Then the reaction mixture was heated for 3.5 h while distilling of an azeotrope of toluene, ethanol and water at around 73 °C. The remaining toluene was removed *in vacuo* and the residue containing ethyl 5-amino-1-(2,2-diethoxyethyl)-1*H*-pyrazole-4-carboxylate was treated with NaOH (4 M, 1 L) and heated to 110 °C for 2 h. The mixture was cooled down, extracted with DCM (2x200mL) and the organic phase was washed with brine (50 mL). The combined aqueous phases were cooled to 0 °C and treated with HCl (6 M) until pH 4.5. The resulting solid was filtered off, washed with cold water and dried to obtain

[9] K. Fujiki, N. Tanifuji, Y. Sasaki and T. Yokoyama, *Synthesis*, 2002, **3**, 343.
[10] P. Seneci, M. Nicola, M. Inglesi, E. Vanotti and G. Resnati, *Synth. Commun.*, 1999, **29**, 311.
[11] *Ger. Pat.*, DE 101 02 944 A1, 2002.

pure 5-amino-1-(2,2-diethoxyethyl)-1*H*-pyrazole-4-carboxylic acid (97 g, 400 mmol, 80% over 3 steps) as a colorless solid.

The 5-amino-1-(2,2-diethoxyethyl)-1*H*-pyrazole-4-carboxylic acid was dissolved in absolute ethanol (100 mL) and H_2SO_4 (20%, 700 mL) and heated to 75 °C for 75 min. After cooling to 25 °C the mixture was poured on crushed ice (1 L) and slowly treated with solid $NaHCO_3$ until pH 9. The formed solid was filtered off and washed with cold water. The aqueous phase was extracted with EtOAc (3x500 mL), the combined organic phase was dried over $MgSO_4$ and evaporated. The resulting solid was combined with the solid from the filtration and purified via flash column chromatography (silica gel, EtOAc/MeOH = 49:1) to yield *1H*-imidazo[1,2-*b*]pyrazole (**1**, 25 g, 240 mmol, 60%) as a slightly red solid.

^{1}H-NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ = δ 10.96 (brs, 1 H), 7.48 (dd, *J* = 2.1, 0.7 Hz, 1 H), 7.44 (dd, *J* = 2.1, 1.3 Hz, 1 H), 7.13 (dd, *J* = 2.1, 1.3 Hz, 1 H), 5.61 (dd, *J* = 2.2, 0.7 Hz, 1 H).

^{13}C-NMR (DMSO-*d*$_6$, 101 MHz, ppm): δ = 141.9, 141.0, 117.9, 107.3, 78.3.

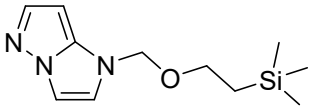
MS (70 eV, EI) *m/z* (%): 107 (100) $[M]^{\cdot+}$, 106 (17), 80 (27), 79 (15), 44 (21).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3157, 3132, 3051, 3005, 2741, 2691, 1594, 1463, 1441, 1393, 1348, 1282, 1171, 1097, 1074, 1045, 957, 914, 867, 831, 789, 763, 697, 677.

HRMS (EI) calculated for $C_5H_5N_3^{\cdot+}$: 107.0478, found 107.0478 $[M]^{\cdot+}$.

mp: 149.5 – 151.2 °C.

1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (15a)



To a solution of *1H*-imidazo[1,2-*b*]pyrazole (**1**, 4.0 g, 38 mmol, 1.3 equiv) in DMF (100 mL) was slowly added sodium hydride (1.3 g, 56 mmol, 1.9 equiv) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h before adding SEMCl (5.0 g, 30 mmol, 1.0 equiv). The reaction was warmed to 25 °C and stirred for 2.5 h before slowly adding a concentrated aqueous solution of NH_4Cl (20 mL). The reaction mixture was extracted with EtOAc (3x30 mL), washed with brine (3 x 30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1) yielded the title compound **15a** (5.8 g, 25 mmol, 82%) as a slightly yellow liquid.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.65 – 7.60 (m, 1 H), 7.33 (d, *J* = 1.9 Hz, 1 H), 6.83 – 6.80 (m, 1 H), 5.75 (d, *J* = 1.8 Hz, 1 H), 5.22 (s, 2 H), 3.52 (t, *J* = 8.2 Hz, 2 H), 0.90 (t, *J* = 8.2 Hz, 2 H), −0.04 (s, 9 H).

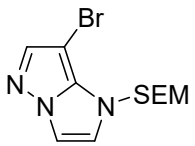
^{13}C-NMR ($CDCl_3$, 101 MHz, ppm): δ = 144.5, 143.7, 120.6, 110.4, 80.6, 78.3, 68.1, 19.1, 0.0.

MS (70 eV, EI) *m/z* (%): 237 (16) $[M]^+$, 179 (70), 151 (10), 121 (33), 120 (56), 103 (11), 93 (16), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3131, 2952, 2892, 1589, 1547, 1463, 1412, 1379, 1315, 1282, 1247, 1229, 1210, 1193, 1178, 1070, 1032, 973, 936, 917, 856, 831, 758, 690.

HRMS (EI) calculated for $C_{11}H_{19}N_3OSi^{\cdot+}$: 237.1292, found 237.1291 $[M]^{\cdot+}$.

7-Bromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (5a)



To a solution of 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (**15a**, 1.3 g, 5.4 mmol, 1.0 equiv) in MeCN (15 mL) was added *N*-bromosuccinimide (0.95 g, 5.4 mmol, 1.0 equiv) and the resulting mixture was stirred at 25 °C for 8 min. The solvent was removed *in vacuo* at 30 °C and the crude product was directly purified via column chromatography (silica gel, *i*Hex/EtOAc = 4:1) to yield the title compound **5a** (1.7 g, 5.3 mmol, 98%) as a colorless liquid. The compound was protected from light during the purification and stored in the dark as a solid at −30 °C to prevent decomposition.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.55 (s, 1 H), 7.34 – 7.31 (m, 1 H), 6.86 (s, 1 H), 5.41 (s, 2 H), 3.60 (t, *J* = 8.2 Hz, 2 H), 0.91 (t, *J* = 8.2 Hz, 2 H), −0.03 (s, 9 H).

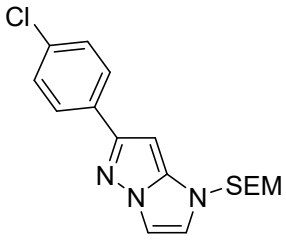
^{13}C-NMR ($CDCl_3$, 101 MHz, ppm): δ = 143.2, 138.3, 120.1, 109.7, 75.5, 66.7, 64.8, 17.9, −1.3.

MS (70 eV, EI) *m/z* (%): 317 (13), 315 (13) $[M]^+$, 259 (53), 257 (53), 200 (31), 198 (33), 178 (25), 151 (13), 119 (33), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3133, 2952, 2895, 1736, 1606, 1551, 1463, 1412, 1378, 1324, 1294, 1276, 1247, 1210, 1194, 1177, 1153, 1081, 1069, 1027, 1003, 972, 916, 857, 833, 758, 689.

HRMS (EI) calculated for $C_{11}H_{18}BrN_3OSi^{\cdot+}$: 315.0397, found 315.0397 $[M]^{\cdot+}$.

6-(4-Chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (15b)



To a solution of 6-(4-chlorophenyl)-1H-imidazo[1,2-b]pyrazole (2.5 g, 12 mmol, 1.0 equiv) in DMF (100 mL) was slowly added sodium hydride (407 mg, 17 mmol, 1.5 equiv) at 0 °C. The resulting mixture was stirred at 0 °C for 30 min before adding SEMCl (3.0 mL, 17 mmol, 1.5 equiv). The reaction was warmed to 25 °C and stirred for 2 h before slowly adding a concentrated aqueous solution of NH_4Cl (20 mL). The reaction mixture was extracted with EtOAc (3x30 mL), washed with brine (3x30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1) yielded the title compound **15b** (1.7 g, 5.0 mmol, 42%) as a yellow solid.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.78 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 7.33 (d, *J* = 2.3 Hz, 1 H), 6.82 (d, *J* = 2.3 Hz, 1 H), 6.07 (s, 1 H), 5.25 (s, 2 H), 3.56 (t, *J* = 8.2 Hz, 2 H), 0.92 (t, *J* = 8.2 Hz, 2 H), –0.02 (s, 9 H).

^{13}C-NMR ($CDCl_3$, 101 MHz, ppm): δ = 154.3, 143.2, 133.4, 133.2, 128.9, 127.0, 119.3, 109.0, 77.4, 77.0, 66.9, 17.8, –1.3.

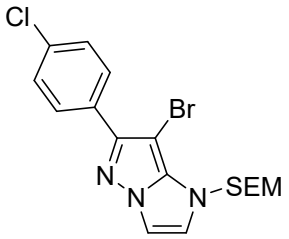
MS (70 eV, EI) *m/z* (%): 349 (12), 347 (33) $[M]^{\cdot+}$, 291 (18), 289 (54), 274 (22), 247 (10), 233 (18), 232 (20), 231 (56), 230 (61), 216 (10), 195 (18), 152 (12), 151 (27), 137 (12), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3157, 3125, 2952, 2895, 2359, 1590, 1568, 1547, 1511, 1456, 1447, 1397, 1378, 1317, 1302, 1289, 1266, 1242, 1227, 1193, 1175, 1096, 1072, 1027, 1013, 982, 955, 914, 832, 786, 748, 729, 718, 709, 699, 687, 667.

HRMS (EI) calculated for $C_{17}H_{22}ClN_3OSi^{\cdot+}$: 347.1215, found 347.1216 $[M]^{\cdot+}$.

mp: 65.9 – 66.9 °C.

7-Bromo-6-(4-chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole (5b)



To a solution of 6-(4-chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole (**15b**, 522 mg, 1.5 mmol, 1.0 equiv) in MeCN (5 mL) was added *N*-bromosuccinimide (267 mg, 1.5 mmol, 1.0 equiv) and the resulting mixture was stirred at 25 °C for 8 min. The solvent was removed *in vacuo* at 30 °C and the crude product was directly purified via column chromatography (silica gel, *i*Hex/EtOAc = 4:1) to yield the title compound **5b** (472 mg, 1.1 mmol, 74%) as a slightly red oil. The compound was protected from light during the purification and stored in the dark as a solid at –30 °C to prevent decomposition.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.08 (d, *J* = 8.6 Hz, 2 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 6.71 (d, *J* = 2.3 Hz, 1 H), 5.93 (d, *J* = 2.3 Hz, 1 H), 4.80 (s, 2 H), 3.40 (t, *J* = 7.8 Hz, 2 H), 0.78 (t, *J* = 7.8 Hz, 2 H), –0.09 (s, 9 H).

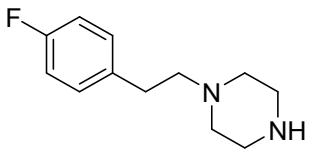
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 151.1, 139.6, 134.2, 132.7, 129.8, 128.9, 119.8, 109.1, 74.8, 66.3, 63.5, 17.8, –1.3.

MS (70 eV, EI) *m/z* (%): 427, 425 (6) $[M]^{\cdot+}$, 369 (13), 366 (10), 309 (9), 307 (7), 103 (10), 101 (6), 74 (7), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3110, 3061, 2952, 2925, 2887, 1682, 1603, 1568, 1551, 1508, 1458, 1444, 1435, 1408, 1397, 1381, 1313, 1291, 1265, 1246, 1234, 1214, 1168, 1149, 1094, 1066, 1026, 1013, 1001, 940, 924, 857, 833, 825, 800, 772, 756, 721, 703, 697, 687, 673.

HRMS (EI) calculated for $C_{17}H_{21}BrClN_3OSi^{\cdot+}$: 425.0320, found 425.0314 $[M]^{\cdot+}$.

1-(4-Fluorophenethyl)piperazine (20)



To a solution of *tert*-butyl piperazine-1-carboxylate (4.47 g, 24.0 mmol, 1.00 equiv) in MeCN (50 mL) was added K_2CO_3 (6.63 g, 48.0 mmol, 2.00 equiv) and 1-(2-bromoethyl)-4-fluoro-benzene (4.87 g, 24.0 mmol, 1.00 equiv). The mixture was then heated to 60 °C and stirred for 19 h. Then water (50 mL) was added, the aqueous phase was extracted with DCM (3 x 50 mL), the combined organic phases dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude *tert*-butyl 4-(4-fluorophenethyl)piperazine-1-carboxylate was dissolved in DCM (100 mL), cooled to 0 °C and treated with trifluoroacetic acid (50 mL). The solution was warmed up to 25 °C and stirred for 1 h. Then the mixture was diluted with EtOAc (100 mL) and treated with concentrated aqueous Na_2CO_3 until the gas evolution stopped. The aqueous phase was extracted with EtOAc (3 x 50 mL), the combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude 1-(4-fluorophenethyl)piperazine (**20**, slightly yellow solid containing traces of EtOAc, ~5.0 g) was used in the amide coupling without further purification.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.71 (brs, 1 H), 7.13 (dd, *J* = 8.5, 5.5 Hz, 2 H), 6.97 (t, *J* = 8.7 Hz, 2 H), 3.19 – 3.07 (m, 4 H), 2.79 – 2.58 (m, 8 H).[12]

TMPMgCl·LiCl (8)

TMPH (14.8 g, 105 mmol, 1.05 equiv) was slowly added to a solution of *i*PrMgCl·LiCl in dry THF (1.05 M, 95 mL, 1.0 equiv). The resulting mixture was stirred under argon at 25 °C for 3 days before titrating the base against benzoic acid using 4-(phenylazo)-diphenylamine as an indicator.

$TMP_2Zn·MgCl_2·2LiCl$ (9)

Magnesium shavings (182 mg, 7.5 mmol) were placed in a *Schlenk*-flask under vacuum and dried with a heat gun at 650 °C for 5 min. After the flask was cooled down it was filled with argon and THF (15 mL). 1,2-Dichloroethane (0.59 mL, 7.5 mmol) was added dropwise over

[12] K. Kumar, D. Michalik, I. G. Castro, A. Tillack, A. Zapf, M. Arlt, T. Heinrich, H. Böttcher and M. Beller, *Chem. Eur. J.*, 2004, **10**, 746.

20 min, leading to gas evolution. The reaction was stirred for at least 1 h, leading to the formation of a 0.50 M solution of $MgCl_2$ in THF. In a second *Schlenk*-flask TMPH (1.9 mL, 11 mmol, 1.0 equiv) was dissolved in THF (11 mL) and cooled to –40 °C. Then freshly titrated BuLi (1.40 M in hexane, 7.86 mL, 11 mmol, 1.0 equiv) was added and the resulting solution was stirred for 30 min. Then the freshly prepared $MgCl_2$ solution (0.50 M in THF, 11 mL, 5.5 mmol, 0.50 equiv) and $ZnCl_2$ solution (1.0 M in THF, 5.5 mL, 5.5 mmol, 0.50 equiv) were added. The resulting mixture was brought to room temperature, protected from light with aluminium foil and stirred for at least 1 h before titration against benzoic acid using 4-(phenylazo)-diphenylamine as an indicator. The base was stored in a closed *Schlenk*-flask covered with aluminium foil at room temperature for up to one week without a significant change in reactivity.

Typical procedures

TP1: Bromine-magnesium exchange of 7-bromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (5a) followed by electrophile trapping

To a solution of 7-bromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (**5a**, 1.0 equiv) in THF (0.5 M) was added *i*PrMgCl·LiCl (**6**, 2.1 equiv) dropwise at 0 °C. The reaction mixture was warmed up to 25 °C and stirred for 1 h before adding the respective electrophile. After stirring for the indicated time a saturated aqueous solution of NH_4Cl was added. The reaction was extracted with EtOAc (3x), washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified via silica gel column chromatography to yield the desired 7-substituted 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole of type **7**.

TP2: Metalation of 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (7b) with TMPMgCl·LiCl (8) followed by electrophile trapping

To a solution of 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (**7b**, 1.0 equiv) in THF (0.5 M) was added a solution of TMPMgCl·LiCl (**8**, typically 0.95-1.05 M in THF, 1.5 equiv) dropwise at –20 °C. The mixture was stirred at –20 °C for 2 h before adding the respective electrophile. After stirring for the indicated time a saturated aqueous solution of NH_4Cl was added. The reaction was extracted with EtOAc (3x), washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified via silica gel column chromatography to yield the desired 3-substituted 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile of type **10**.

TP3: Metalation of ethyl 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate (10c) with $TMP_2Zn{\cdot}MgCl_2{\cdot}2LiCl$ (9) followed by electrophile trapping

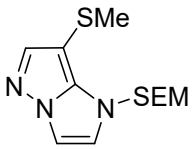
To a solution of 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (**10c**, 1.0 equiv) in THF (0.20 mL) was added a solution of $TMP_2Zn{\cdot}MgCl_2{\cdot}2LiCl$ (**9**, typically 0.14-0.16 M in THF, 0.65 equiv for allylations and acylations, 0.55 equiv for cross-couplings) dropwise at 0 °C. The mixture was stirred at 0 °C for 30 min before adding the respective electrophile. After stirring for the indicated time a saturated aqueous solution of NH_4Cl was added. The reaction was extracted with EtOAc (3x), washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified via silica gel column chromatography to yield the desired 2-substituted ethyl 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate of type **11**.

TP4: Metalation of 2-functionalized ethyl 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylates of type 11 with $TMP_2Zn{\cdot}MgCl_2{\cdot}2LiCl$ (9) leading to push-pull dyes of type 14

To a solution of the respective 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate of type **11** (1.0 equiv) in THF (0.5 M) was added a solution of $TMP_2Zn{\cdot}MgCl_2{\cdot}LiCl$ (**9**, typically 0.14-0.16 M in THF, 0.65 equiv) dropwise at 0 °C. The mixture was stirred at 0 °C for the indicated time before adding a saturated aqueous solution of NH_4Cl. The reaction was extracted with EtOAc (3x), washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified via column chromatography on Florisil® (*i*Hex/EtOAc = 4:1, then *i*Hex/ EtOAc = 1:1, then EtOAc, then EtOAc/MeOH = 10:1) to yield the desired push-pull dye of type **14**.

Products

7-(Methylthio)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (7a)



7-(Methylthio)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole was synthesized according to **TP1** on a 0.88 mmol scale using *S*-methyl benzenesulfonothioate (412 mg, 2.2 mmol, 2.5 equiv) as electrophile (30 min, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1) yielded the title compound **7a** (206 mg, 0.73 mmol, 83%) as a colorless solid.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.60 (d, *J* = 1.1 Hz, 1 H), 7.27 (d, *J* = 2.3 Hz, 1 H), 6.83 (t, *J* = 2.3, 1.1 Hz, 1 H), 5.50 (s, 2 H), 3.57 (t, *J* = 8.1 Hz, 2 H), 2.23 (s, 3 H), 0.89 (t, *J* = 8.3 Hz, 2 H), −0.06 (s, 9 H).

^{13}C-NMR ($CDCl_3$, 101 MHz, ppm): δ = 148.7, 141.3, 119.6, 109.5, 84.9, 75.4, 66.5, 22.7, 17.9, −1.4.

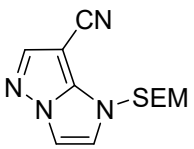
MS (70 eV, EI) *m/z* (%): 283 (27) $[M]^{+\cdot}$, 225 (14), 210 (19), 166 (21), 111 (9), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3156, 3111, 3055, 2951, 2917, 1588, 1539, 1466, 1442, 1416, 1317, 1288, 1273, 1248, 1218, 1172, 1151, 1096, 1069, 1009, 971, 930, 857, 834, 766, 728, 718, 706, 683.

HRMS (EI) calculated for $C_{12}H_{21}N_3OSSi^{+\cdot}$: 283.1169, found 283.1164 $[M]^{+\cdot}$.

mp: 63.6 – 65.0 °C.

1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (7b)



1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP1** on a 5.0 mmol scale using tosyl cyanide (2.2 g, 11 mmol, 2.2 equiv) as electrophile (1 h, 25 °C). The white solid that was formed during the reaction was filtered off

through a pad of Celite before the work-up. Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1 + 5% NEt_3) yielded the title compound **7b** (1.31 g, 4.79 mmol, 96%) as a slightly yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.56 (d, *J* = 1.1 Hz, 1 H), 6.62 (d, *J* = 2.3 Hz, 1 H), 5.86 (dd, *J* = 2.2, 1.2 Hz, 1 H), 4.62 (s, 2 H), 3.42 (t, *J* = 8.1 Hz, 2 H), 0.79 (t, *J* = 8.1 Hz, 2 H), −0.08 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 146.3, 141.7, 120.0, 114.3, 109.9, 76.1, 67.7, 67.3, 17.7, −1.4.

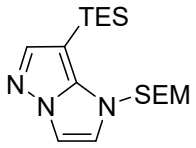
MS (70 eV, EI) *m/z* (%): 262 (24) $[M]^{+\cdot}$, 219 (14), 204 (100), 189 (30), 145 (14), 73 (65).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3150, 3102, 3055, 2953, 2920, 2896, 2869, 2216, 1611, 1543, 1491, 1478, 1454, 1399, 1381, 1335, 1309, 1289, 1260, 1245, 1225, 1196, 1179, 1123, 1085, 1068, 1035, 1018, 972, 916, 875, 843, 832, 779, 742, 721, 709, 690, 663.

HRMS (EI) calculated for $C_{12}H_{18}N_4OSi^{+\cdot}$: 262.1244, found 262.1245 $[M]^{+\cdot}$.

mp: 79.0 – 79.6 °C.

7-(Triethylsilyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (7c)



7-(Triethylsilyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole was synthesized according to **TP1** on a 0.20 mmol scale using TESCl (75 mg, 0.50 mmol, 2.5 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1) yielded the title compound **7c** (53 mg, 0.15 mmol, 76%) as a colorless liquid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.92 (s, 1 H), 6.99 (d, *J* = 2.3 Hz, 1 H), 6.03 – 6.01 (m, 1 H), 4.74 (s, 2 H), 3.23 (t, *J* = 8.0 Hz, 2 H), 1.04 (t, *J* = 7.8 Hz, 9 H), 0.87 (q, *J* = 7.7 Hz, 6 H), 0.79 (t, *J* = 8.1 Hz, 2 H), −0.09 (s, 9 H).

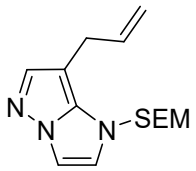
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 150.4, 145.8, 119.6, 108.4, 82.4, 77.0, 65.9, 17.7, 7.9, 5.1, −1.4.

MS (70 eV, EI) *m/z* (%): 351 (16) $[M]^{\cdot+}$, 292 (14), 264 (52), 250 (14), 236 (12), 234 (38), 220 (24), 208 (28), 192 (16), 178 (14), 165 (21), 164 (11), 150 (20), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3132, 2952, 2874, 1565, 1543, 1458, 1413, 1376, 1321, 1248, 1158, 1075, 1041, 1003, 971, 916, 833, 691.

HRMS (EI) calculated for $C_{17}H_{33}N_3OSi_2^{\cdot+}$: 351.2157, found 351.2156 $[M]^{\cdot+}$.

7-Allyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (7d)



7-Allyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole was synthesized according to **TP1** on a 1.69 mmol scale using allyl bromide (0.37 mL, 4.23 mmol, 2.5 equiv) and CuCN·2LiCl (1.0 M in THF, 0.34 mL, 0.34 mmol, 0.20 equiv) as electrophile (30 min, 25 °C.). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 3:7) yielded the title compound **7d** (438 mg, 1.58 mmol, 94%) as a colorless liquid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.67 (s, 1 H), 6.93 (d, *J* = 2.3 Hz, 1 H), 6.03 – 5.93 (m, 2 H), 5.09 – 4.95 (m, 2 H), 4.65 (s, 2 H), 3.37 – 3.31 (m, 2 H), 3.23 (t, *J* = 7.8 Hz, 2 H), 0.74 (t, *J* = 7.8 Hz, 2 H), −0.11 (s, 9 H).

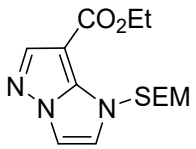
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 143.8, 139.9, 139.4, 119.4, 114.6, 108.5, 92.6, 76.4, 65.8, 28.4, 17.7, −1.4.

MS (70 eV, EI) *m/z* (%): 277 (38) $[M]^{\cdot+}$, 219 (27), 218 (36), 204 (21), 192 (34), 191 (14), 160 (42), 133 (22), 119 (14), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3130, 2952, 2894, 1638, 1609, 1544, 1490, 1413, 1379, 1322, 1247, 1216, 1169, 1074, 994, 914, 832, 758, 688.

HRMS (EI) calculated for $C_{14}H_{23}N_3OSi^{\cdot+}$: 277.1605, found 277.1603 $[M]^{\cdot+}$.

Ethyl 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate (7e)



Ethyl 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate was synthesized according to **TP1** on a 0.20 mmol scale using ethyl cyanoformate (0.05 mL, 0.5 mmol, 2.5 equiv) and CuCN·2LiCl (1.0 M in THF, 0.20 mL, 0.20 mmol, 1.0 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1) yielded the title compound **7e** (31 mg, 0.10 mmol, 50%) as a colorless liquid.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.02 (d, *J* = 1.1 Hz, 1 H), 7.37 (d, *J* = 2.2 Hz, 1 H), 6.95 (t, *J* = 2.2, 1.1 Hz, 1 H), 5.82 (s, 2 H), 4.28 (q, *J* = 7.1 Hz, 2 H), 3.56 (t, *J* = 8.2 Hz, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H), 0.88 (t, *J* = 8.2 Hz, 2 H), −0.07 (s, 9 H).

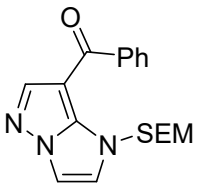
^{13}C-NMR ($CDCl_3$, 101 MHz, ppm): δ = 163.2, 146.2, 140.8, 120.2, 110.1, 91.9, 76.8, 66.4, 59.9, 17.9, 14.7, −1.4.

MS (70 eV, EI) *m/z* (%): 309 (9) $[M]^{\cdot+}$, 279 (10), 251 (37), 250 (42), 238 (11), 236 (34), 223 (13), 208 (49), 206 (14), 192 (25), 182 (13), 164 (35), 148 (29), 134 (18), 133 (100), 73 (49).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3132, 2953, 2898, 1687, 1597, 1548, 1488, 1394, 1375, 1344, 1292, 1269, 1248, 1204, 1194, 1174, 1085, 1056, 971, 916, 856, 833, 768, 731, 691.

HRMS (EI) calculated for $C_{14}H_{23}N_3O_3Si^{\cdot+}$: 309.1503, found 309.1502 $[M]^{\cdot+}$.

Phenyl(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)methanone (7f)



Phenyl(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)methanone was synthesized according to **TP1** on a 0.2 mmol scale using benzoyl chloride (0.035 mL, 0.50 mmol, 2.5 equiv) as electrophile and $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5%) as catalyst

(2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 7:3) yielded the title compound **7f** (41 mg, 0.12 mmol, 60%) as a colorless liquid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.04 – 8.00 (m, 1 H), 7.94 (dd, *J* = 7.9, 1.6 Hz, 2 H), 7.21 – 7.10 (m, 3 H), 6.85 (d, *J* = 2.0 Hz, 1 H), 6.24 (dd, *J* = 2.1, 1.2 Hz, 1 H), 5.83 (s, 2 H), 3.65 (t, *J* = 8.0 Hz, 2 H), 0.89 (t, *J* = 8.0 Hz, 2 H), −0.09 (s, 9 H).

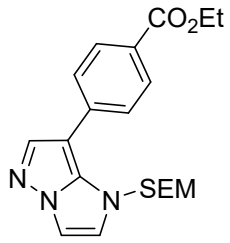
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 186.6, 148.0, 142.0, 140.8, 131.2, 129.1, 128.5, 120.6, 109.8, 102.6, 77.3, 66.2, 17.9, −1.4.

MS (70 eV, EI) *m/z* (%): 341 (12) $[M]^{\cdot+}$, 298 (13), 283 (10), 282 (100), 269 (10), 268 (83), 255 (25), 241 (11), 240 (54), 224 (11), 206 (14), 73 (19).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3128, 3066, 2952, 2892, 1614, 1599, 1568, 1481, 1418, 1365, 1324, 1293, 1269, 1248, 1217, 1195, 1176, 1124, 1068, 1028, 1013, 982, 936, 916, 899, 857, 831, 795, 760, 736, 694, 663.

HRMS (EI) calculated for $C_{18}H_{23}N_3O_2Si^{\cdot+}$: 341.1554, found 341.1549 $[M]^{\cdot+}$.

Ethyl 4-(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)benzoate (7g)



Ethyl 4-(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)benzoate was synthesized according to **TP1** on a 0.2 mmol scale using ethyl 4-iodobenzoate (166 mg, 0.60 mmol, 3.0 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (4 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1) yielded the title compound **7g** (63 mg, 0.16 mmol, 82%) as a slightly yellow oil.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.27 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 1.1 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 6.91 (d, *J* = 2.3 Hz, 1 H), 6.00 (dd, *J* = 2.1, 1.1 Hz, 1 H), 4.65 (s, 2 H), 4.18 (q, *J* = 7.1 Hz, 2 H), 3.14 (t, *J* = 7.9 Hz, 2 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.65 (t, *J* = 7.9 Hz, 2 H), −0.16 (s, 9 H).

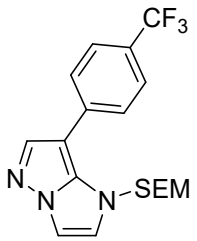
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 166.3, 143.2, 138.7, 138.4, 130.7, 127.7, 127.0, 120.8, 108.7, 99.1, 76.1, 66.2, 60.7, 17.7, 14.4, −1.5.

MS (70 eV, EI) *m/z* (%): 385 (13) $[M]^{+}$, 327 (43), 268 (12), 210 (12), 209 (100), 195 (13), 194 (17), 181 (42), 154 (13), 73 (53).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3134, 2981, 2951, 2915, 1699, 1608, 1563, 1548, 1520, 1474, 1414, 1368, 1347, 1309, 1270, 1249, 1220, 1181, 1149, 1121, 1099, 1066, 1042, 1024, 1013, 993, 983, 935, 834, 772, 743, 715, 695.

HRMS (EI) calculated for $C_{20}H_{28}N_3O_3Si^{+}$: 385.1816, found 385.1815 $[M]^{+}$.

7-(4-(Trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole (7h)



7-(4-(Trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole was synthesized according to **TP1** on a 0.2 mmol scale using 1-iodo-4-(trifluoromethyl)-benzene (163 mg, 0.60 mmol, 3.0 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (2 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 1:1) yielded the title compound **7h** (67 mg, 0.18 mmol, 88%) as a slightly yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.85 (s, 1 H), 7.51 – 7.39 (m, 4 H), 6.89 (d, *J* = 2.3 Hz, 1 H), 5.95 (s, 1 H), 4.58 (s, 2 H), 3.10 (t, *J* = 7.9 Hz, 2 H), 0.64 (t, *J* = 7.9 Hz, 2 H), −0.16 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 143.1, 138.3, 137.8, 127.4, 127.2 (q, *J* = 32.4 Hz), 126.0 (q, *J* = 3.9 Hz), 125.6 (q, *J* = 271.9 Hz) 120.7, 108.7, 98.4, 76.0, 66.2, 17.6, −1.5.

^{19}F-NMR (C_6D_6, 377 MHz, ppm): δ = −61.8 (s).

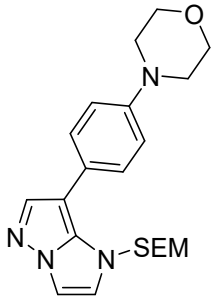
MS (70 eV, EI) *m/z* (%): 381 (20) $[M]^{+}$, 323 (56), 264 (47), 231 (36), 230 (38), 204 (12), 196 (11), 195 (15), 194 (22), 181 (17), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3178, 3114, 3069, 2952, 2892, 1614, 1592, 1553, 1523, 1481, 1464, 1416, 1367, 1325, 1298, 1260, 1249, 1223, 1193, 1174, 1162, 1150, 1105, 1061, 1031, 1012, 982, 937, 897, 859, 850, 831, 760, 745, 736, 671, 694, 686, 671, 666.

HRMS (EI) calculated for $C_{18}H_{22}F_3N_3OSi^{\cdot+}$: 381.1479, found 381.1477 $[M]^{\cdot+}$.

mp: 65.5 – 66.4 °C.

4-(4-(1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)phenyl)-morpholine (7i)



4-(4-(1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)phenyl)morpholino was synthesized according to **TP1** on a 0.2 mmol scale using 4-(4-iodophenyl)morpholine (174 mg, 0.60 mmol, 3.0 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (2 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 1:1) yielded the title compound **7i** (54 mg, 0.14 mmol, 68%) as a slightly yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.02 (d, *J* = 1.0 Hz, 1 H), 7.53 (d, *J* = 8.7 Hz, 2 H), 6.97 (d, *J* = 2.3 Hz, 1 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 6.04 – 5.99 (m, 1 H), 4.78 (s, 2 H), 3.59 (t, *J* = 4.8 Hz, 4 H), 3.19 (t, *J* = 7.9 Hz, 2 H), 2.80 (t, *J* = 4.7 Hz, 4 H), 0.70 (t, *J* = 7.9 Hz, 2 H), −0.14 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 149.9, 142.9, 138.5, 129.0, 125.5, 120.2, 116.5, 108.8, 99.1, 75.8, 67.0, 66.1, 49.7, 17.8, −1.4.

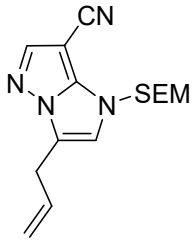
MS (70 eV, EI) *m/z* (%): 398 (17) $[M]^{\cdot+}$, 340 (11), 299 (12), 281 (36), 267 (19), 265 (12), 240 (13), 225 (60), 209 (31), 208 (14), 207 (100), 194 (15), 191 (23), 181 (15), 155 (14), 75 (28), 73 (46), 44 (23).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3105, 2813, 1653, 1591, 1558, 1521, 1506, 1484, 1447, 1376, 1363, 1340, 1312, 1259, 1250, 1242, 1232, 1220, 1183, 1118, 1069, 1048, 991, 927, 853, 844, 828, 763, 739, 722, 702, 655.

HRMS (EI) calculated for $C_{21}H_{30}N_4O_2SI^{\cdot+}$: 398.2133, found 398.2134 $[M]^{\cdot+}$.

mp: 149.7 – 150.9 °C.

3-Allyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10a)



3-Allyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale using allyl bromide (0.04 mL, 0.44 mmol, 2.2 equiv) and CuCN·2LiCl (1.0 M in THF, 0.04 mL, 0.04 mmol, 0.20 equiv) as electrophile (5 min, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) yielded the title compound **10a** (39 mg, 0.13 mmol, 65%) as a colorless liquid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.55 (d, *J* = 1.1 Hz, 1 H), 5.77 (d, *J* = 1.1 Hz, 1 H), 5.71 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1 H), 5.02 – 4.93 (m, 2 H), 4.69 (s, 2 H), 3.50 (t, *J* = 8.0 Hz, 2 H), 3.19 – 3.13 (m, 2 H), 0.83 (t, *J* = 8.1 Hz, 2 H), −0.06 (s, 9 H).

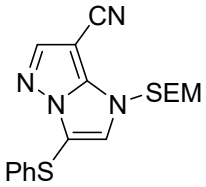
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 146.0, 141.6, 132.2, 122.4, 118.0, 116.4, 114.5, 76.0, 67.9, 67.3, 27.7, 17.8, −1.4.

MS (70 eV, EI) *m/z* (%): 302 (2) $[M]^{\cdot+}$, 259 (13), 245 (11), 244 (100), 243 (95), 229 (11), 217 (12), 185 (25), 73 (66).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3121, 2952, 2894, 2215, 1613, 1600, 1488, 1457, 1419, 1379, 1335, 1302, 1248, 1221, 1183, 1104, 1080, 1031, 992, 970, 916, 856, 833, 748, 693, 667.

HRMS (EI) calculated for $C_{15}H_{22}N_4OSi^{\cdot+}$: 302.1557, found 302.1558 $[M]^{\cdot+}$.

3-(Phenylthio)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10b)



3-(Phenylthio)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale using *S*-methyl benzenesulfonothioate (75 mg, 0.30 mmol, 1.5 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) and HPLC yielded the title compound **10b** (51 mg, 0.14 mmol, 69%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.46 (d, *J* = 1.0 Hz, 1 H), 7.37 – 7.31 (m, 2 H), 6.96 – 6.89 (m, 2 H), 6.88 – 6.82 (m, 1 H), 6.24 (d, *J* = 1.1 Hz, 1 H), 4.59 (s, 2 H), 3.41 (t, *J* = 8.0 Hz, 2 H), 0.79 (t, *J* = 8.1 Hz, 2 H), –0.09 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 146.2, 142.0, 134.3, 129.7, 129.5, 127.8, 127.7, 126.0, 113.8, 76.4, 69.4, 67.5, 17.8, –1.4.

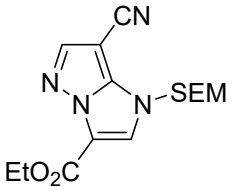
MS (70 eV, EI) *m/z* (%): 370 (8) $[M]^+$, 313 (19), 312 (86), 285 (13), 253 (15), 121 (11), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3128, 3058, 2949, 2893, 2862, 2221, 1603, 1583, 1538, 1474, 1454, 1440, 1398, 1377, 1334, 1296, 1281, 1242, 1196, 1180, 1169, 1136, 1085, 1022, 997, 977, 922, 909, 857, 835, 781, 755, 735, 715, 695, 686, 670.

HRMS (EI) calculated for $C_{18}H_{22}N_4OSSi^{\cdot+}$: 370.1278, found 370 1276 $[M]^{\cdot+}$.

mp: 74.0 – 75.5 °C.

Ethyl 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (10c)



Ethyl 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP2** on a 0.2 mmol scale using ethyl cyanoformate (30 mg, 0.30 mmol, 1.5 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1 + 5% NEt_3) yielded the title compound **10c** (43 mg, 0.13 mmol, 65%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.56 (d, *J* = 1.3 Hz, 1 H), 6.89 (d, *J* = 1.2 Hz, 1 H), 4.60 (s, 2 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 3.39 (t, *J* = 8.0 Hz, 2 H), 1.05 (t, *J* = 7.1 Hz, 3 H), 0.80 (t, *J* = 8.0 Hz, 2 H), −0.07 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 158.0, 146.6, 142.1, 126.9, 116.6, 113.6, 76.7, 69.0, 67.7, 61.3, 17.8, 14.3, −1.4.

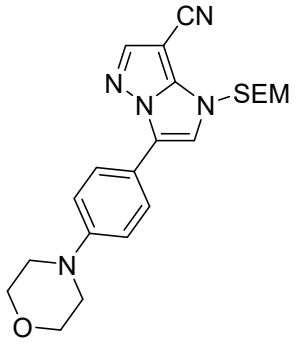
MS (70 eV, EI) *m/z* (%): 334 (4) $[M]^{\cdot+}$, 291 (11), 277 (12), 276 (57), 204 (10), 158 (7), 74 (8), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3158, 3112, 2953, 2895, 2219, 1704, 1603, 1581, 1471, 1451, 1398, 1370, 1249, 1318, 1258, 1249, 1192, 1094, 1036, 948, 933, 918, 856, 833, 768, 749, 710, 684.

HRMS (EI) calculated for $C_{15}H_{22}N_4O_3SSi^{\cdot+}$: 334.1456, found 334.1456 $[M]^{\cdot+}$.

mp: 105.2 – 107.7 °C.

3-(4-Morpholinophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10d)



3-(4-Morpholinophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding 4-(4-iodophenyl)morpholine (46 mg, 0.16 mmol, 0.8 equiv) as electrophile and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5%) in combination with SPhos (8.2 mg, 0.02 mmol, 10%) as catalyst (2 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1 + 5% NEt_3) and HPLC yielded the title compound **10d** (67 mg, 0.14 mmol, 89%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.02 (d, *J* = 8.8 Hz, 2 H), 7.72 – 7.58 (m, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.44 – 6.37 (m, 1 H), 4.82 (s, 2 H), 3.61 – 3.42 (m, 6 H), 2.79 – 2.66 (m, 4 H), 0.87 (t, *J* = 8.0 Hz, 2 H), −0.05 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 151.5, 146.1, 142.1, 126.5, 124.6, 118.5, 115.4, 114.5, 114.3, 76.2, 67.8, 67.4, 66.7, 48.6, 17.8, −1.4.

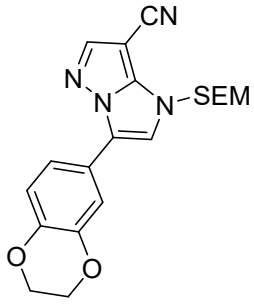
MS (70 eV, EI) *m/z* (%): 423 (19) $[M]^{\cdot+}$, 366 (23), 365 (100), 311 (6), 307 (7), 306 (14), 234 (5), 73 (33).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3118, 2951, 2922, 2895, 2857, 2210, 1606, 1557, 1512, 1485, 1458, 1449, 1428, 1379, 1336, 1316, 1306, 1263, 1248, 1229, 1221, 1192, 1120, 1099, 1072, 1055, 1029, 1003, 975, 933, 921, 902, 858, 826, 815, 770, 753, 743, 712, 682, 665.

HRMS (EI) calculated for $C_{22}H_{29}N_5O_2Si$:423.2091, found 423.2090 [M].

mp: 118.9 – 120.1 °C.

3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-7-carbonitrile (10e)



3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding 6-iodo-2,3-dihydrobenzo[*b*][1,4]dioxine (42 mg, 0.16 mmol, 0.8 equiv) as electrophile and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5%) in combination with SPhos (8.2 mg, 0.02 mmol, 10%) as catalyst (2 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 2:1 + 5% NEt_3) yielded the title compound **10e** (42 mg, 0.11 mmol, 66%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.91 (d, *J* = 2.1 Hz, 1 H), 7.57 (d, *J* = 1.2 Hz, 1 H), 7.53 (dd, *J* = 8.5, 2.2 Hz, 1 H), 6.99 (d, *J* = 8.5 Hz, 1 H), 6.22 (d, *J* = 1.3 Hz, 1 H), 4.73 (s, 2 H), 3.55 – 3.47 (m, 6 H), 0.86 (t, *J* = 8.0 Hz, 2 H), −0.06 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 146.0, 144.4, 142.0, 127.9, 124.0, 121.1, 119.0, 118.1, 115.0, 114.8, 114.4, 76.1, 67.8, 67.3, 64.3, 64.2, 17.8, −1.4.

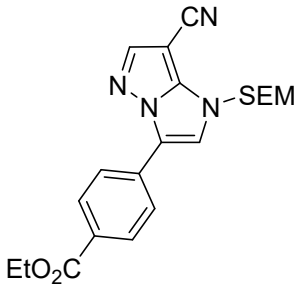
MS (70 eV, EI) *m/z* (%): 396 (10) $[M]^{+}$, 340 (5), 339 (20), 338 (100), 284 (14), 279 (15), 265 (5), 73 (56).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2950, 2358, 2340, 2217, 1613, 1593, 1579, 1558, 1539, 1506, 1490, 1468, 1456, 1436, 1424, 1395, 1381, 1333, 1324, 1287, 1262, 1248, 1241, 1223, 1191, 1179, 1134, 1109, 1081, 1068, 1054, 1044, 1032, 945, 923, 890, 879, 866, 831, 772, 762, 750, 726, 701, 676, 668, 660.

HRMS (EI) calculated for $C_{20}H_{24}N_4O_3Si^{+}$: 396.1612, found 396.1608 $[M]^{+}$.

mp: 147.2 – 148.5 °C.

Ethyl 4-(7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-3-yl)-benzoate (10f)



Ethyl 4-(7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-3-yl)benzoate was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding ethyl 4-iodo benzoate (44 mg, 0.16 mmol, 0.8 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (2 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) yielded the title compound **10f** (55 mg, 0.13 mmol, 84%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.23 (d, *J* = 8.6 Hz, 2 H), 7.97 (d, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 1.1 Hz, 1 H), 6.25 (d, *J* = 1.1 Hz, 1 H), 4.73 (s, 2 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 3.54 (t, *J* = 8.1 Hz, 2 H), 1.04 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 8.1 Hz, 2 H), −0.04 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 165.8, 146.2, 142.2, 131.5, 130.43, 130.39, 124.9, 123.2, 117.3, 114.1, 76.3, 68.2, 67.6, 61.1, 17.9, 14.3, −1.4.

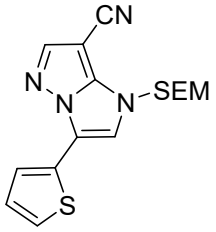
MS (70 eV, EI) *m/z* (%): 367 (8) $[M-C_3H_8]^{\cdot+}$, 353 (20), 352 (100), 298 (13), 293 (12), 281 (11), 234 (20), 225 (14), 207 (29), 75 (11), 73 (63).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3124, 2958, 2219, 1700, 1606, 1590, 1558, 1488, 1456, 1368, 1338, 1326, 1289, 1275, 1248, 1195, 1177, 1109, 1089, 1066, 1049, 1035, 1019, 941, 919, 862, 837, 790, 768, 741, 725, 707, 697, 660.

HRMS (EI) calculated for $C_{18}H_{19}N_4O_3Si^{\cdot+}$: 367.1221, found 367.1221 $[M-C_3H_8]^{\cdot+}$.

mp: 136.0 – 137.6 °C.

3-(Thiophen-2-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10g)



3-(Thiophen-2-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding 2-iodotiophene (34 mg, 0.16 mmol, 0.8 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (2 h, 60 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) yielded the title compound **10g** (41 mg, 0.12 mmol, 74%) as a colorless oil.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.93 (dd, *J* = 3.5, 1.3 Hz, 1 H), 7.56 (d, *J* = 1.3 Hz, 1 H), 6.77 – 6.70 (m, 2 H), 6.21 (d, *J* = 1.2 Hz, 1 H), 4.63 (s, 2 H), 3.47 (t, *J* = 8.0 Hz, 2 H), 0.84 (t, *J* = 8.0 Hz, 2 H), −0.06 (s, 9 H).

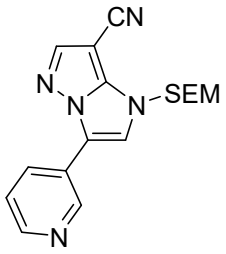
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 146.3, 143.4, 141.5, 127.9, 126.2, 124.8, 119.8, 115.0, 114.1, 76.1, 68.3, 67.4, 17.8, −1.4.

MS (70 eV, EI) *m/z* (%): 344 (1) $[M]^{\cdot+}$, 287 (12), 286 (100), 259 (12), 232 (28), 227 (22), 213 (10), 207 (24), 159 (11), 73 (29).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3107, 2951, 2897, 2215, 1605, 1510, 1484, 1418, 1379, 1335, 1307, 1247, 1220, 1185, 1081, 1046, 1014, 939, 915, 856, 833, 738, 722, 692, 661.

HRMS (EI) calculated for $C_{16}H_{20}N_4OSSi^{\cdot+}$: 344.1122, found 344.1121 $[M]^{\cdot+}$.

3-(Pyridin-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10h)



3-(Pyridin-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding 3-iodopyridine (33 mg, 0.16 mmol, 0.8 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (2 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 1:1 + 5% NEt_3) yielded the title compound **10h** (45 mg, 0.13 mmol, 83%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 9.03 (d, *J* = 1.8 Hz, 1 H), 8.41 (dd, *J* = 4.8, 1.5 Hz, 1 H), 8.35 (dt, *J* = 8.0, 1.9 Hz, 1 H), 7.55 (d, *J* = 1.0 Hz, 1 H), 6.78 (dd, *J* = 7.8, 5.0 Hz, 1 H), 6.27 (d, *J* = 1.0 Hz, 1 H), 4.74 (s, 2 H), 3.53 (t, *J* = 8.1 Hz, 2 H), 0.88 (t, *J* = 8.1 Hz, 2 H), −0.04 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 149.3, 146.5, 146.3, 142.0, 131.9, 123.8, 123.5, 121.1, 116.5, 114.1, 76.3, 68.3, 67.6, 17.9, −1.4.

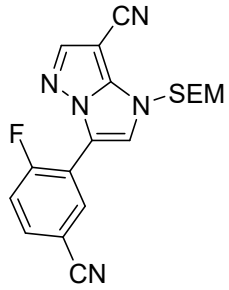
MS (70 eV, EI) *m/z* (%): 339 (0.3) $[M]^{\cdot+}$, 296 (9), 282 (14), 281 (100), 254 (10), 227 (10), 222 (15), 208 (9), 73 (46).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3048, 2951, 2925, 1619, 1568, 1558, 1490, 1456, 1413, 1394, 1380, 1340, 1262, 1249, 1210, 1178, 1130, 1108, 1088, 1072, 1025, 938, 928, 905, 862, 832, 810, 768, 759, 748, 719, 708, 687.

HRMS (EI) calculated for $C_{17}H_{21}N_5OSi^{\cdot+}$: 339.1510, found 339.1511 $[M]^{\cdot+}$.

mp: 92.5 – 93.9 °C.

3-(5-Cyano-2-fluorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10i)



3-(5-Cyano-2-fluorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding 3-bromo-4-fluorobenzonitrile (32 mg, 0.16 mmol, 0.8 equiv) as electrophile and PEPPSI-*i*Pr (2.7 mg, 0.004 mmol, 2%) as catalyst (17 h, 60 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) yielded the title compound **10i** (50 mg, 0.13 mmol, 82%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 9.15 (dd, *J* = 7.1, 2.1 Hz, 1 H), 7.53 (d, *J* = 1.3 Hz, 1 H), 6.89 (dd, *J* = 3.2, 1.3 Hz, 1 H), 6.71 (ddd, *J* = 8.6, 4.8, 2.1 Hz, 1 H), 6.38 (dd, *J* = 11.2, 8.6 Hz, 1 H), 4.72 (s, 2 H), 3.52 (t, *J* = 8.1 Hz, 2 H), 0.88 (t, *J* = 8.1 Hz, 2 H), −0.04 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 160.1 (d, *J* = 258.1 Hz), 146.1, 141.4, 132.7, 131.3, 121.2 (d, *J* = 17.3 Hz), 117.9, 117.6 (d, *J* = 13.2 Hz), 116.5 (d, *J* = 23.3 Hz), 116.0 (d, *J* = 2.9 Hz), 113.7, 109.8 (d, *J* = 3.5 Hz), 76.5, 68.6, 67.7, 17.9, −1.4.

^{19}F-NMR (C_6D_6, 377 MHz, ppm): δ = −104.6 (m).

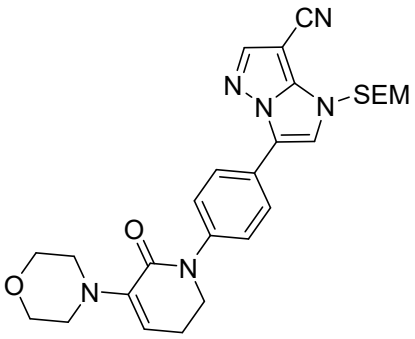
MS (70 eV, EI) *m/z* (%): 381 (3) $[M]^{\cdot+}$, 338 (10), 325 (5), 324 (17), 323 (86), 264 (9), 250 (5), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3132, 3067, 2952, 2228, 2215, 1604, 1576, 1505, 1489, 1456, 1394, 1340, 1323, 1297, 1245, 1229, 1187, 1167, 1124, 1109, 1080, 1052, 1038, 1027, 935, 911, 894, 861, 824, 754, 728, 714, 697, 669.

HRMS (EI) calculated for $C_{19}H_{20}FN_5OSi$: 381.1421, found 381.13422 [M].

mp: 144.0 – 144.0 °C.

3-(4-(5-Morpholino-6-oxo-3,6-dihydropyridin-1(2*H*)-yl)phenyl)-1-((2-(trimethylsilyl)-ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10j)



3-(4-(5-Morpholino-6-oxo-3,6-dihydropyridin-1(2*H*)-yl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP2** on a 0.2 mmol scale. After the metalation a $ZnCl_2$ solution (1.0 M in THF, 0.30 mL, 0.30 mmol, 1.5 equiv) was added before adding 1-(4-iodophenyl)-3-morpholino-5,6-dihydropyridin-2(1*H*)-one (62 mg, 0.16 mmol, 0.8 equiv) as electrophile and PEPPSI-*i*Pent (4.8 mg, 0.006 mmol, 3%) as catalyst (2 h, 60 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:6 + 5% NEt_3) yielded the title compound **10j** (47 mg, 0.09 mmol, 57%) as a colorless solid.

^{1}H-NMR (CD_2Cl_2, 400 MHz, ppm): δ = 8.06 (d, *J* = 8.6 Hz, 2 H), 7.98 (s, 1 H), 7.44 (d, *J* = 8.6 Hz, 2 H), 7.29 (s, 1 H), 5.68 (t, *J* = 4.7 Hz, 1 H), 5.48 (s, 2 H), 3.83 – 3.73 (m, 6 H), 3.68 (t, *J* = 8.3 Hz, 2 H), 2.87 (t, *J* = 4.4 Hz, 4 H), 2.50 (q, *J* = 6.5 Hz, 2 H), 0.98 (t, *J* = 8.3 Hz, 2 H), −0.01 (s, 9 H).

^{13}C-NMR (CD_2Cl_2, 101 MHz, ppm): δ = 161.8, 146.7, 144.2, 143.6, 142.3, 126.0, 125.8, 124.9, 124.2, 116.6, 115.3, 114.6, 77.3, 67.9, 67.2, 51.0, 49.2, 23.9, 18.2, 1.3, −1.3.

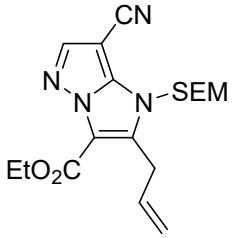
MS (70 eV, EI) *m/z* (%): 518 (15) $[M]^{\cdot+}$, 461 (25), 460 (81), 443 (16), 442 (41), 402 (10), 401 (25), 73 (100), 44 (20).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3117, 2952, 2928, 2846, 2823, 2208, 1652, 1605, 1512, 1486, 1472, 1452, 1418, 1378, 1349, 1338, 1327, 1310, 1261, 1250, 1217, 1208, 1192, 1111, 1048, 1025, 975, 948, 930, 921, 902, 857, 831, 795, 780, 750, 712, 682.

HRMS (EI) calculated for $C_{27}H_{34}N_6O_3Si^{\cdot+}$: 518.2456, found 518.2457 $[M]^{\cdot+}$.

mp: 232.7 – 234.4 °C.

Ethyl 2-allyl-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11a)



Ethyl 2-allyl-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using allyl bromide (0.03 mL, 0.33 mmol, 1.7 equiv) and CuCN·2LiCl (1 M in THF, 0.04 mL, 0.04 mmol, 0.20 equiv) as electrophile (20 min, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 9:1 + 5% NEt_3) yielded the title compound **11a** (54 mg, 0.14 mmol, 72%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.56 (s, 1 H), 5.66 (ddt, *J* = 16.6, 10.3, 6.2 Hz, 1 H)., 4.95 – 4.88 (m, 2 H), 4.84 (s, 2 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 3.63 (d, *J* = 6.2 Hz, 2 H), 3.55 (t, *J* = 8.2 Hz, 2 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.86 (t, *J* = 8.2 Hz, 2 H), −0.05 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 159.1, 145.7, 141.5, 139.7, 132.8, 117.7, 114.0, 113.5, 73.8, 68.5, 67.7, 61.2, 28.3, 17.9, 14.3, −1.4.

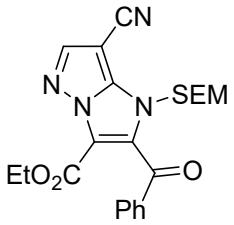
MS (70 eV, EI) *m/z* (%): 374 (1) $[M]^{\cdot+}$, 317 (11), 316 (70), 281 (21), 270 (37), 254 (11), 253 (10), 243 (10), 209 (14), 208 (13), 207 (100), 198 (21), 197 (15), 191 (18), 170 (20), 169 (11), 143 (22), 75 (14), 73 (70), 44 (15).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2924, 2218, 1716, 1642, 1601, 1565, 1479, 1467, 1446, 1407, 1375, 1351, 1317, 1275, 1265, 1248, 1183, 1139, 1108, 1088, 1066, 1046, 1019, 991, 940, 922, 883, 859, 835, 807, 769, 701, 672.

HRMS (EI) calculated for $C_{18}H_{26}N_4O_3Si^{\cdot+}$: 374.1769, found 374.1769 $[M]^{\cdot+}$.

mp: 51.5 – 53.7 °C.

Ethyl 2-benzoyl-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11b)



Ethyl 2-benzoyl-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using benzoyl chloride (42 mg, 0.30 mmol, 1.5 equiv) and CuCN·2LiCl (1 M in THF, 0.10 mL, 0.10 mmol, 0.50 equiv) as electrophile (1 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 9:1 + 5% NEt_3) yielded the title compound **11b** (55 mg, 0.13 mmol, 63%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.64 (d, *J* = 7.2 Hz, 2 H), 7.60 (s, 1 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 6.95 (t, *J* = 7.6 Hz, 2 H), 5.06 (s, 2 H), 3.74 (q, *J* = 7.1 Hz, 2 H), 3.34 (t, *J* = 8.2 Hz, 2 H), 0.59 (dt, *J* = 11.5, 7.7 Hz, 5 H), −0.18 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 185.4, 157.1, 147.6, 142.2, 137.3, 134.3, 133.7, 129.7, 128.9, 115.9, 113.3, 74.8, 69.3, 67.6, 61.5, 17.6, 13.5, −1.5.

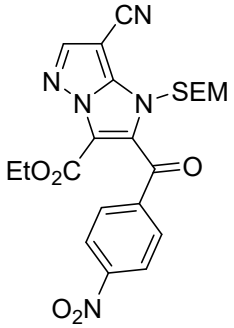
MS (70 eV, EI) *m/z* (%): 438 (2) $[M]^{\cdot+}$, 395 (11), 381 (18), 380 (65), 366 (21), 365 (75), 293 (14), 262 (23), 105 (22), 91 (15), 77 (13), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2945, 2220, 1731, 1666, 1614, 1597, 1562, 1556, 1482, 1461, 1448, 1375, 1349, 1320, 1278, 1242, 1234, 1191, 1174, 1146, 1113, 1094, 1024, 962, 941, 920, 861, 838, 760, 709, 688, 676.

HRMS (EI) calculated for $C_{22}H_{26}N_4O_4Si^{\cdot+}$: 438.1718, found 438.1718 $[M]^{\cdot+}$.

mp: 127.6 – 128.5 °C.

Ethyl 7-cyano-2-(4-nitrobenzoyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate (11c)



Ethyl 7-cyano-2-(4-nitrobenzoyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using 4-nitrobenzoyl chloride (56 mg, 0.30 mmol, 1.5 equiv) and CuCN·2LiCl (1 M in THF, 0.10 mL, 0.10 mmol, 0.50 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) yielded the title compound **11c** (59 mg, 0.12 mmol, 61%) as a yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.71 (d, *J* = 8.8 Hz, 2 H), 7.55 (s, 1 H), 7.39 (d, *J* = 8.8 Hz, 2 H), 5.05 (s, 2 H), 3.77 (q, *J* = 7.1 Hz, 2 H), 3.36 (t, *J* = 8.2 Hz, 2 H), 0.75 – 0.57 (m, 5 H), –0.17 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 184.3, 157.2, 150.9, 147.9, 142.4, 141.0, 132.6, 130.2, 123.9, 116.6, 113.0, 74.6, 69.3, 67.8, 62.0, 17.6, 13.7, –1.6.

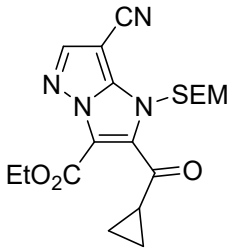
MS (70 eV, EI) *m/z* (%): 483 (0.3) $[M]^{+\cdot}$, 426 (12), 425 (43), 410 (20), 307 (8), 103 (7), 74 (7), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3108, 2951, 2226, 1727, 1690, 1664, 1605, 1562, 1551, 1524, 1475, 1409, 1369, 1344, 1312, 1276, 1245, 1231, 1179, 1137, 1110, 1020, 967, 942, 911, 853, 835, 803, 789, 760, 753, 735, 702, 665.

HRMS (EI) calculated for $C_{22}H_{25}N_5O_6Si^{+\cdot}$: 483.1569, found 483.1561 $[M]^{+\cdot}$.

mp: 164.9 – 166.3 °C.

Ethyl 7-cyano-2-(cyclopropanecarbonyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11d)



Ethyl 7-cyano-2-(cyclopropanecarbonyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using cyclopropanecarbonyl chloride (31 mg, 0.30 mmol, 1.5 equiv) and CuCN·2LiCl (1 M in THF, 0.10 mL, 0.10 mmol, 0.50 equiv) as electrophile (1 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) yielded the title compound **11d** (65 mg, 0.16 mmol, 81%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.55 (s, 1 H), 5.13 (s, 2 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.49 (t, *J* = 8.1 Hz, 2 H), 2.20 (tt, *J* = 7.9, 4.5 Hz, 1 H), 1.33 – 1.26 (m, 2 H), 1.02 (t, *J* = 7.1 Hz, 3 H), 0.83 (t, *J* = 8.1 Hz, 2 H), 0.72 (dd, *J* = 7.6, 3.6 Hz, 2 H), −0.08 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 194.4, 158.0, 147.7, 142.0, 135.4, 116.2, 113.3, 74.8, 69.1, 67.7, 62.0, 24.1, 17.9, 14.4, 14.1, −1.4.

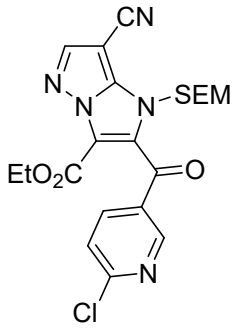
MS (70 eV, EI) *m/z* (%): 402 (1) [M], 345 (10), 344 (35), 330 (11), 329 (45), 283 (18), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2952, 2226, 1724, 1686, 1674, 1612, 1556, 1481, 1441, 1405, 1377, 1359, 1346, 1315, 1305, 1276, 1263, 1247, 1196, 1184, 1166, 1111, 1086, 1057, 1039, 1017, 1002, 945, 921, 897, 860, 834, 792, 772, 759, 723, 697, 682, 666.

HRMS (EI) calculated for $C_{19}H_{26}N_4O_4Si$: 402.1723, found 402.1724 [M].

mp: 85.2 – 86.4 °C.

Ethyl 2-(6-chloronicotinoyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate (11e)



Ethyl 2-(6-chloronicotinoyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using 6-chloronicotinoyl chloride (53 mg, 0.30 mmol, 1.5 equiv) and CuCN·2LiCl (1 M in THF, 0.10 mL, 0.10 mmol, 0.50 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 9:1 + 5% NEt_3) yielded the title compound **11e** (67 mg, 0.14 mmol, 71%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.59 (s, 1 H), 7.55 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.21 (dd, *J* = 5.0, 1.2 Hz, 1 H), 6.83 (dd, *J* = 5.0, 3.0 Hz, 1 H), 4.68 (s, 2 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 3.68 – 3.60 (m, 2 H), 0.98 (t, *J* = 7.1 Hz, 3 H), 0.88 – 0.82 (m, 2 H), −0.03 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 183.5, 157.3, 157.0, 151.5, 147.8, 142.4, 138.5, 132.5, 131.6, 124.7, 116.6, 113.1, 74.7, 69.3, 67.8, 62.1, 17.6, 13.7, −1.6.

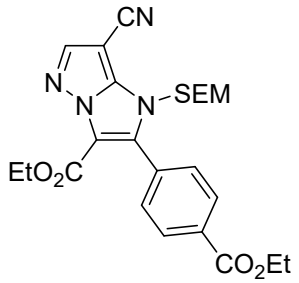
MS (70 eV, EI) *m/z* (%): 473 (2) $[M]^{\cdot+}$, 417 (18), 416 (12), 415 (45), 400 (22), 297 (10), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2952, 2220, 1731, 1676, 1607, 1583, 1563, 1478, 1412, 1363, 1311, 1291, 1275, 1245, 1186, 1134, 1093, 1068, 1021, 980, 963, 935, 923, 860, 836, 820, 783, 765, 741, 707, 692.

HRMS (EI) calculated for $C_{21}H_{24}ClN_5O_4Si^{\cdot+}$: 473.1281, found 473.1281 $[M]^{\cdot+}$.

mp: 137.5 – 139.2 °C.

Ethyl 7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11f)



Ethyl 7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using ethyl 4-iodo benzoate (44 mg, 0.16 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol, 3%) as catalyst (90 min, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 7:1 + 5% NEt_3) yielded the title compound **11f** (51 mg, 0.11 mmol, 66%) as a slightly yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.17 (d, *J* = 8.5 Hz, 2 H), 7.64 (s, 1 H), 7.37 (d, *J* = 8.5 Hz, 2 H), 4.66 (s, 2 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 4.01 (q, *J* = 7.1 Hz, 2 H), 3.63 – 3.49 (m, 2 H), 1.03 (t, *J* = 7.1 Hz, 3 H), 0.91 (t, *J* = 7.1 Hz, 3 H), 0.88 – 0.80 (m, 2 H), –0.05 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 165.5, 158.0, 146.3, 141.9, 139.2, 132.7, 131.7, 130.6, 129.5, 113.9, 113.7, 74.2, 69.0, 68.0, 61.3, 61.2, 18.2, 14.2, 14.1, –1.4.

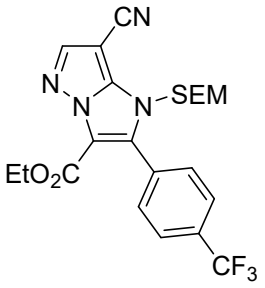
MS (70 eV, EI) *m/z* (%): 424 (3) $[M–C_4H_{10}]^{\cdot+}$, 281 (22), 225 (60), 209 (30), 208 (13), 207 (100), 191 (25), 73 (11).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3097, 2952, 2223, 1709, 1602, 1574, 1503, 1479, 1443, 1392, 1376, 1314, 1274, 1250, 1195, 1171, 1088, 1019, 938, 914, 883, 857, 835, 763, 743, 717, 695, 666.

HRMS (EI) calculated for $C_{24}H_{30}N_4O_5Si^{\cdot+}$: 482.1980, found 482.1975 $[M]^{\cdot+}$.

mp: 110.4 – 111.5 °C.

Ethyl 7-cyano-2-(4-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11g)



Ethyl 7-cyano-2-(4-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using 1-iodo-4-(trifluoromethyl)benzene (44 mg, 0.16 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol, 3%) as catalyst (90 min, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 7:1 + 5% NEt_3) yielded the title compound **11g** (53 mg, 0.11 mmol, 69%) as a slightly yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.61 (s, 1 H), 7.37 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 4.58 (s, 2 H), 4.00 (q, *J* = 7.1 Hz, 2 H), 3.62 – 3.54 (m, 2 H), 0.91 (t, *J* = 7.1 Hz, 3 H), 0.88 – 0.82 (m, 2 H), −0.04 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 158.0, 146.4, 141.9, 138.5, 132.2 (q, *J* = 32.7 Hz), 132.2, 130.0, 125.8 (q, *J* = 272.7 Hz), 125.2 (q, *J* = 3.6 Hz), 113.8, 113.8, 74.2, 69.0, 68.2, 61.3, 18.2, 14.0, −1.5.

^{19}F-NMR (C_6D_6, 377 MHz, ppm): δ = −62.7 (s).

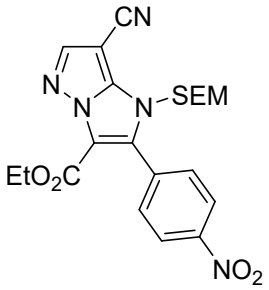
MS (70 eV, EI) *m/z* (%): 478 (0.2) $[M]^{+}$, 435 (21), 421 (22), 420 (96), 349 (12), 348 (72), 328 (18), 320 (12), 315 (14), 302 (26), 287 (12), 275 811), 256 (33), 172 (10), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2954, 2221, 1720, 1606, 1572, 1513, 1478, 1443, 1409, 1378, 1354, 1321, 1274, 1249, 1167, 1127, 1101, 1068, 1018, 942, 915, 834, 765, 722, 692, 671.

HRMS (EI) calculated for $C_{22}H_{25}F_3N_4O_3Si^{+}$: 478.1643, found 478.1643 $[M]^{+}$.

mp: 96.8 – 98.5 °C.

Ethyl 7-cyano-2-(4-nitrophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate (11h)



Ethyl 7-cyano-2-(4-nitrophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.3 mmol scale using 1-iodo-4-nitrobenzene (60 mg, 0.24 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol, 3%) as catalyst (130 min, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) and HPLC yielded the title compound **11h** (63 mg, 0.14 mmol, 58%) as a yellow oil.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.85 (d, *J* = 8.9 Hz, 2 H), 7.63 (s, 1 H), 7.20 (d, *J* = 8.9 Hz, 2 H), 4.60 (s, 2 H), 4.02 (q, *J* = 7.1 Hz, 2 H), 3.72 – 3.58 (m, 2 H), 0.94 (t, *J* = 7.1 Hz, 3 H), 0.91 – 0.84 (m, 2 H), –0.02 (s, 9 H).

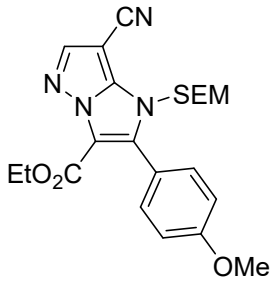
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 157.9, 149.0, 146.5, 142.0, 137.8, 132.5, 132.0, 123.2, 113.9, 113.8, 74.3, 69.0, 68.4, 61.4, 18.3, 14.1, –1.4.

MS (70 eV, EI) *m/z* (%): 455 (0.3) $[M]^{\cdot+}$, 397 (7), 325 (5), 279 (3), 207 (4), 103 (3), 75 (4), 74 (5), 73 (100), 45 (4).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3107, 2952, 2895, 2220, 1716, 1604, 1571, 1522, 1492, 1475, 1443, 1377, 1347, 1312, 1273, 1248, 1172, 1083, 1043, 1015, 975, 943, 915, 880, 855, 834, 767, 710, 700, 694.

HRMS (EI) calculated for $C_{21}H_{25}N_5O_5Si^{\cdot+}$: 455.1619, found 455.1620 $[M]^{\cdot+}$.

Ethyl 7-cyano-2-(4-methoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate (11i)



Ethyl 7-cyano-2-(4-methoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.2 mmol scale using 1-iodo-4-methoxybenzene (37 mg, 0.16 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (6.9 mg, 0.006 mmol, 3%) as catalyst (80 min, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3) and HPLC yielded the title compound **11i** (37 mg, 0.08 mmol, 53%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.65 (s, 1 H), 7.37 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.8 Hz, 2 H), 4.73 (s, 2 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 3.63 (t, *J* = 8.3 Hz, 2 H), 3.25 (s, 3 H), 0.98 (t, *J* = 7.1 Hz, 3 H), 0.87 (t, *J* = 8.3 Hz, 2 H), −0.03 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 161.6, 158.4, 146.0, 141.7, 140.7, 133.2, 118.3, 114.1, 113.9, 113.2, 74.1, 69.0, 67.9, 61.0, 54.9, 18.2, 14.2, −1.4.

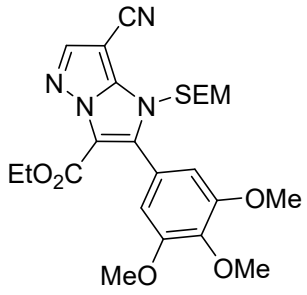
MS (70 eV, EI) *m/z* (%): 440 (2) $[M]^{\cdot+}$, 397 (15), 383 (22), 382 (100), 311 (10), 310 (60), 282 (31), 277 (11), 264 (31), 256 (13), 236 (11), 209 (10), 183 (20), 73 (34).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2980, 2930, 2220, 1720, 1604, 1582, 1568, 1510, 1477, 1462, 1438, 1412, 1376, 1344, 1314, 1296, 1265, 1256, 1248, 1180, 1171, 1119, 1088, 1056, 1036, 1024, 1014, 1008, 944, 933, 916, 874, 858, 838, 790, 768, 758, 728, 701, 686, 676.

HRMS (EI) calculated for $C_{22}H_{28}N_4O_4Si^{\cdot+}$: 440.1874, found 440.1876 $[M]^{\cdot+}$.

mp: 100.7 – 101.8 °C.

Ethyl 7-cyano-2-(3,4,5-trimethoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11j)



Ethyl 7-cyano-2-(3,4,5-trimethoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.3 mmol scale using 5-iodo-1,2,3-trimethoxybenzene (71 mg, 0.24 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol, 5%) as catalyst (4 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 6:1 + 5% NEt_3) yielded the title compound **11j** (60 mg, 0.12 mmol, 50%) as a slightly yellow solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.68 (s, 1 H), 6.74 (s, 2 H), 4.82 (s, 2 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.83 (s, 3 H), 3.65 (t, *J* = 8.4 Hz, 2 H), 3.54 (s, 6 H), 0.98 (t, *J* = 7.1 Hz, 3 H), 0.88 (t, *J* = 8.4 Hz, 2 H), −0.03 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 158.4, 153.7, 146.2, 141.6, 141.1, 140.7, 121.0, 114.1, 113.2, 109.6, 74.4, 69.0, 68.0, 61.0, 60.6, 56.1, 18.4, 14.2, −1.4.

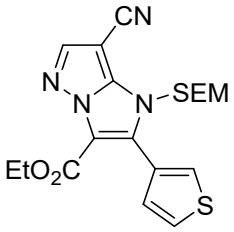
MS (70 eV, EI) *m/z* (%): 500 (5) $[M]^+$, 443 (27), 442 (100), 418 (10), 427 (42), 381 (10), 370 (20), 355 (13), 342 (13), 324 (15), 243 (10), 73 (32).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3094, 2946, 2836, 2214, 1719, 1612, 1591, 1560, 1509, 1493, 1467, 1456, 1421, 1395, 1382, 1366, 1358, 1353, 1317, 1281, 1249, 1228, 1181, 1165, 1128, 1098, 1067, 1033, 990, 945, 931, 859, 834, 791, 772, 758, 748, 724, 711, 691.

HRMS (EI) calculated for $C_{24}H_{32}N_4O_6Si^{\cdot+}$: 500.2086, found 500.2087 $[M]^{\cdot+}$.

mp: 153.8 – 155.3 °C.

Ethyl 7-cyano-2-(thiophen-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate (11k)



Ethyl 7-cyano-2-(thiophen-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** on a 0.30 mmol scale using 3-iodothiophene (34 mg, 0.16 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol, 5%) as catalyst (4 h, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 7:1 + 5% NEt_3) yielded the title compound **11k** (54 mg, 0.13 mmol, 54%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.59 (s, 1 H), 7.55 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.21 (dd, *J* = 5.0, 1.2 Hz, 1 H), 6.83 (dd, *J* = 5.0, 3.0 Hz, 1 H), 4.68 (s, 2 H), 4.07 (q, *J* = 7.1 Hz, 2 H), 3.67 – 3.61 (m, 2 H), 0.98 (t, *J* = 7.1 Hz, 3 H), 0.88 – 0.82 (m, 2 H), −0.03 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 158.3, 146.1, 141.7, 135.5, 130.2, 130.1, 125.9, 125.4, 114.0, 113.4, 74.2, 68.8, 68.1, 61.1, 18.2, 14.2, −1.4.

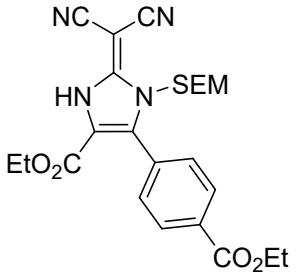
MS (70 eV, EI) *m/z* (%): 416 (1) $[M]^{\cdot+}$, 373 (12), 359 (19), 358 (100), 286 (68), 258 (38), 253 (17), 240 (43), 232 (13), 225 (10), 212 (12), 207 (10), 159 (16), 73 (74).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3097, 2945, 2218, 1713, 1606, 1582, 1519, 1501, 1476, 1443, 1416, 1373, 1337, 1310, 1267, 1243, 1220, 1189, 1166, 1088, 1060, 1018, 942, 912, 837, 810, 764, 721, 711, 689, 660.

HRMS (EI) calculated for $C_{19}H_{24}N_4O_3SSi^{\cdot+}$: 416.1333, found 416.1334 $[M]^{\cdot+}$.

mp: 100.1 – 102.8 °C.

Ethyl 2-(dicyanomethylene)-5-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14a)



Ethyl 2-(dicyanomethylene)-5-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate was synthesized according to **TP4** on a 0.087 mmol scale. The reaction was completed within 40 min and yielded the title compound **14a** (32 mg, 0.066 mmol, 76%) as a slightly yellow solid.

^{1}H-NMR (acetone-d$_6$, 400 MHz, ppm): δ = 8.08 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 5.19 (s, 2 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 3.49 (t, *J* = 8.2 Hz, 2 H), 1.39 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H), 0.85 (t, *J* = 8.2 Hz, 2 H), –0.03 (s, 9 H).

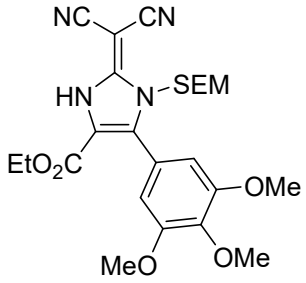
^{13}C-NMR (acetone-d$_6$, 101 MHz, ppm): δ = 166.4, 165.0, 153.1, 136.2, 135.1, 132.1, 131.2, 129.5, 129.4, 128.2, 125.2, 73.0, 65.7, 61.6, 61.0, 24.6, 18.4, 14.6, 14.2, –1.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2953, 2186, 2143, 1714, 1694, 1612, 1575, 1519, 1466, 1403, 1378, 1366, 1270, 1248, 1180, 1101, 1079, 1025, 963, 939, 916, 859, 834, 774, 759, 724, 706, 667.

HRMS (ESI) calculated for $C_{24}H_{29}N_4O_5Si^-$: 481.1913, found 481.19113 $[M-H]^-$.

mp: 84.0 – 93.0 °C.

Ethyl 2-(dicyanomethylene)-5-(3,4,5-trimethoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14b)



Ethyl 2-(dicyanomethylene)-5-(3,4,5-trimethoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate was synthesized according to **TP4** on a 0.148 mmol scale. The reaction was completed within 40 min and yielded the title compound **14b** (71 mg, 0.142 mmol, 96%) as a slightly yellow solid.

^{1}H-NMR (acetone-d$_6$, 400 MHz, ppm): δ = 6.80 (s, 2 H), 5.20 (s, 2 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 3.85 (s, 6 H), 3.78 (s, 3 H), 3.59 – 3.47 (m, 2 H), 1.09 (t, *J* = 7.1 Hz, 3 H), 0.92 – 0.84 (m, 2 H), −0.02 (s, 9 H).

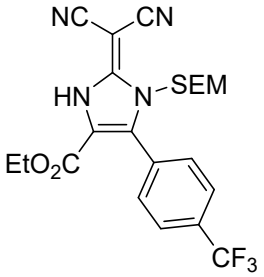
^{13}C-NMR (acetone-d$_6$, 101 MHz, ppm): δ = 165.4, 153.7, 152.2, 139.5, 137.7, 127.3, 125.4, 125.3, 109.5, 72.9, 65.6, 60.8, 60.6, 56.5, 24.4, 18.6, 14.3, −1.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2951, 2184, 2140, 1687, 1605, 1584, 1520, 1500, 1464, 1411, 1379, 1364, 1341, 1319, 1245, 1189, 1124, 1077, 1028, 1003, 938, 834, 788, 769, 726, 693.

HRMS (ESI) calculated for $C_{24}H_{31}N_4O_6Si^-$: 499.2018, found 499.20173 $[M-H]^-$.

mp: 68.5 – 70.0 °C.

Ethyl 2-(dicyanomethylene)-5-(4-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14c)



Ethyl 2-(dicyanomethylene)-5-(4-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate was synthesized according to **TP4** on a 0.096 mmol scale. The reaction was completed within 30 min and yielded the title compound **14c** (30 mg, 0.064 mmol, 67%) as a slightly orange solid.

^{1}H-NMR (acetone-d$_6$, 400 MHz, ppm): δ = 7.89 (q, *J* = 8.4 Hz, 4 H), 5.30 (s, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 3.57 – 3.44 (m, 2 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.93 – 0.80 (m, 2 H), −0.03 (s, 9 H).

^{13}C-NMR (acetone-d$_6$, 101 MHz, ppm): δ = 159.7, 152.0, 136.5, 133.0, 132.0 (q, *J* = 32.4 Hz) 131.71, 131.69, 126.0 (q, *J* = 3.8 Hz), 125.1 (q, *J* = 271.7 Hz), 120.6, 119.7, 73.6, 66.5, 61.9, 28.2, 18.3, 14.1, –1.3.

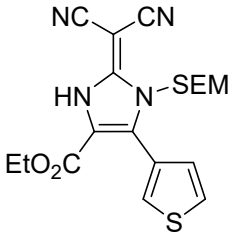
^{19}F-NMR (acetone-d$_6$, 377 MHz, ppm): δ = –63.3 (s).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3050, 2954, 2897, 2746, 2213, 2171, 2149, 1725, 1614, 1599, 1518, 1465, 1431, 1408, 1371, 1323, 1298, 1262, 1250, 1228, 1214, 1203, 1184, 1163, 1126, 1108, 1082, 1067, 1026, 1013, 947, 924, 854, 835, 774, 758, 743, 711, 697, 674.

HRMS (ESI) calculated for $C_{22}H_{24}F_3N_4O_3Si^-$: 477.1575, found 477.15753 $[M–H]^-$.

mp: 134.1 – 135.4 °C.

Ethyl 2-(dicyanomethylene)-5-(thiophen-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14d)



Ethyl 2-(dicyanomethylene)-5-(thiophen-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate was synthesized according to **TP4** on a 0.115 mmol scale. The reaction was completed within 150 min at 25 °C and yielded the title compound **14d** (41 mg, 0.098 mmol, 86%) as a slightly yellow solid.

^{1}H-NMR (acetone-d_6, 400 MHz, ppm): δ = 7.67 (dd, *J* = 3.0, 1.1 Hz, 1 H), 7.54 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.28 (dd, *J* = 5.0, 1.1 Hz, 1 H), 5.21 (s, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 3.54 (t, *J* = 8.1 Hz, 2 H), 1.12 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 8.1 Hz, 2 H), –0.01 (s, 9 H).

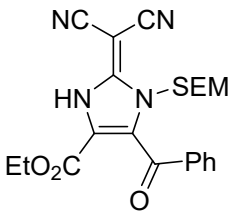
^{13}C-NMR (acetone-d_6, 101 MHz, ppm): δ = 165.3, 152.4, 132.6, 132.6, 131.1, 129.9, 129.4, 127.9, 127.7, 125.4, 72.8, 65.7, 60.9, 24.5, 18.4, 14.2, –1.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2953, 2184, 2142, 1683, 1629, 1521, 1396, 1377, 1341, 1262, 1248, 1189, 1077, 1027, 964, 939, 916, 857, 833, 809, 785, 756, 722, 692, 668.

HRMS (ESI) calculated for $C_{19}H_{23}N_4O_3SSi^-$: 415.1266, found 415.12650 $[M–H]^-$.

mp: 95.5 – 98.2 °C.

Ethyl 5-benzoyl-2-(dicyanomethylene)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14e)



Ethyl 5-benzoyl-2-(dicyanomethylene)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate was synthesized according to **TP4** on a 0.185 mmol scale. The

reaction was completed within 40 min and yielded the title compound **14e** (68 mg, 0.156 mmol, 84%) as a bright yellow solid.

^{1}H-NMR (acetone-d$_6$, 400 MHz, ppm): δ = 7.80 (d, *J* = 7.0 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 5.64 (s, 2 H), 3.75 (q, *J* = 7.1 Hz, 2 H), 3.54 – 3.43 (m, 2 H), 0.77 – 0.67 (m, 5 H), −0.10 (s, 9 H).

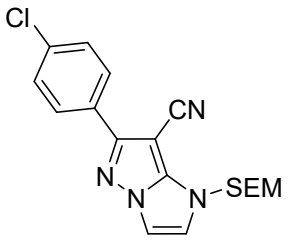
^{13}C-NMR (acetone-d$_6$, 101 MHz, ppm): δ = 186.1, 163.4, 154.7, 139.8, 135.6, 132.6, 129.8, 129.0, 128.3, 127.8, 123.6, 72.5, 65.2, 60.3, 25.0, 17.4, 12.7, −2.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2950, 2359, 2194, 2150, 1703, 1638, 1599, 1581, 1543, 1518, 1494, 1473, 1449, 1423, 1402, 1363, 1354, 1340, 1307, 1277, 1262, 1249, 1218, 1205, 1179, 1143, 1082, 1063, 1033, 998, 956, 936, 919, 861, 848, 835, 812, 790, 761, 733, 724, 695, 683.

HRMS (ESI) calculated for $C_{22}H_{25}N_4O_4Si^-$: 437.1651, found 437.16495 $[M-H]^-$.

mp: 249.8 – 250.9 °C.

6-(4-Chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (7j)



6-(4-Chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile was synthesized according to **TP1** using 7-bromo-6-(4-chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (**5b**, 448 mg, 1.0 mmol, 1.0 equiv) as staring material and tosyl cyanide (472 mg, 2.6 mmol, 2.6 equiv) as electrophile (2 h, 25 °C). The white solid that was formed during the reaction was filtered off through a pad of Celite before the work-up. Purification via column chromatography (silica gel, *i*Hex/EtOAc = 4:1 + 5% NEt_3 then *i*Hex/EtOAc = 4:1 + 5% NEt_3) and HPLC yielded the title compound **7j** (286 mg, 0.77 mmol, 77%) as a slightly blue solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.16 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H), 6.56 (d, *J* = 2.2 Hz, 1 H), 5.80 (d, *J* = 2.2 Hz, 1 H), 4.66 (s, 2 H), 3.48 (t, *J* = 8.0 Hz, 2 H), 0.83 (t, *J* = 8.0 Hz, 2 H), –0.06 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 156.0, 143.0, 135.5, 131.1, 129.4, 128.5, 119.8, 115.3, 109.7, 75.9, 67.3, 65.6, 17.8, –1.4.

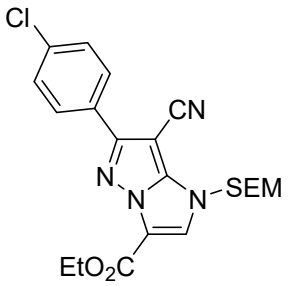
MS (70 eV, EI) *m/z* (%): 372 (7) $[M]^{\cdot+}$, 329 (9), 316 (26), 315 (15), 314 (72), 255 (7), 111 (6), 74 (8), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3114, 3062, 2951, 2918, 2213, 1605, 1572, 1547, 1508, 1475, 1466, 1454, 1434, 1389, 1373, 1311, 1294, 1246, 1219, 1198, 1109, 1093, 1088, 1056, 1022, 1011, 942, 922, 861, 834, 822, 810, 760, 736, 722, 704, 685, 655.

HRMS (EI) calculated for $C_{18}H_{21}ClN_4OSi^{\cdot+}$: 372.1168, found 372.1165 $[M]^{\cdot+}$.

mp: 70.3 – 71.5 °C.

Ethyl 6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (10k)



Ethyl 6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP2** using 6-(4-chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (**7j**, 127 mg, 0.34 mmol, 1.0 equiv) as staring material, ethyl cyanoformate (0.065 mL, 0.68 mmol, 2.0 equiv) as electrophile and $Pd(PPh_3)_4$ (19 mg, 0.017 mmol, 5%) as a catalyst (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 5:1 + 5% NEt_3) yielded the title compound **10k** (66 mg, 0.15 mmol, 44%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.19 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H), 6.80 (s, 1 H), 4.59 (s, 2 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 3.43 (t, *J* = 8.0 Hz, 2 H), 1.06 (t, *J* = 7.1 Hz, 3 H), 0.83 (t, *J* = 8.0 Hz, 2 H), –0.05 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 157.8, 156.3, 143.4, 135.7, 130.8, 129.4, 128.7, 126.4, 116.4, 114.7, 76.5, 67.7, 66.8, 61.3, 17.8, 14.3, –1.4.

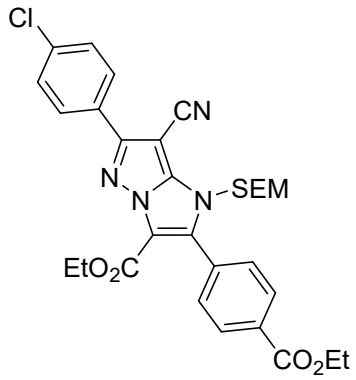
MS (70 eV, EI) *m/z* (%): 444 (5) $[M]^{+}$, 401 (9), 388 (32), 387 (21), 386 (94), 268 (13), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3105, 2950, 2926, 2891, 2219, 1697, 1605, 1578, 1567, 1506, 1469, 1440, 1423, 1397, 1366, 1353, 1313, 1298, 1278, 1251, 1204, 1169, 1137, 1093, 1049, 1013, 963, 929, 856, 835, 799, 768, 754, 727, 696, 674.

HRMS (EI) calculated for $C_{21}H_{25}ClN_4O_3Si^{+}$: 444.1379, found 444.1378 $[M]^{+}$.

mp: 161.9 – 162.3 °C.

Ethyl 6-(4-chlorophenyl)-7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)-ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11l)



Ethyl 6-(4-chlorophenyl)-7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** using ethyl 6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (**10k**, 51 mg, 0.12 mmol, 1.0 equiv) as starting material, ethyl 4-iodo benzoate (25 mg, 0.092 mmol, 0.8 equiv) as electrophile and $Pd(PPh_3)_4$ (4.0 mg, 0.0035 mmol, 3%) as catalyst (100 min, 40 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 9:1 + 5% NEt_3) yielded the title compound **11l** (43 mg, 0.073 mmol, 79%) as a slightly yellow oil.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.25 (d, *J* = 8.6 Hz, 2 H), 8.20 (d, *J* = 8.3 Hz, 2 H), 7.43 (d, *J* = 8.3 Hz, 2 H), 7.15 (d, *J* = 8.6 Hz, 2 H), 4.76 (s, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 4.02 (q, *J* = 7.1 Hz, 2 H), 3.62 (t, *J* = 8.2 Hz, 2 H), 1.04 (t, *J* = 7.1 Hz, 2 H), 0.92 – 0.80 (m, 6 H), –0.04 (s, 9 H).

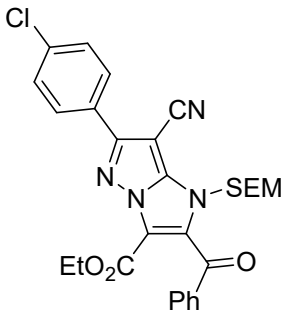
^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 165.5, 157.9, 156.0, 143.3, 138.8, 135.8, 132.8, 131.8, 130.8, 130.7, 129.5, 129.5, 128.8, 115.0, 113.6, 74.0, 68.0, 66.8, 61.4, 61.2, 18.2, 14.2, 14.0, –1.4.

MS (70 eV, EI) *m/z* (%): 592 (4) $[M]^{\cdot+}$, 549 (9), 537 (12), 536 (38), 535 (32), 534 (100), 462 (10), 418 (8), 46 (23), 73 (68).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2980, 2953, 2898, 2214, 1716, 1603, 1579, 1570, 1506, 1465, 1442, 1424, 1404, 1387, 1367, 1270, 1249, 1193, 1093, 1078, 1013, 957, 940, 915, 889, 858, 833, 791, 754, 728, 697, 676.

HRMS (EI) calculated for $C_{30}H_{33}ClN_4O_5Si^{\cdot+}$: 592.1903, found 592.1903 $[M]^{\cdot+}$.

Ethyl 2-benzoyl-6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11m)



Ethyl 2-benzoyl-6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate was synthesized according to **TP3** using ethyl 6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (**10k**, 122 mg, 0.27 mmol, 1.0 equiv) as starting material and benzoyl chloride (50 mg, 0.41 mmol, 1.5 equiv) as well as CuCN·2LiCl (1 M in THF, 0.13 mL, 0.13 mmol, 0.50 equiv) as electrophile (2 h, 25 °C). Purification via column chromatography (silica gel, *i*Hex/EtOAc = 7:1 + 5% NEt_3) yielded the title compound **11m** (98 mg, 0.18 mmol, 66%) as a colorless solid.

^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 8.22 (d, *J* = 8.5 Hz, 2 H), 7.71 (d, *J* = 7.5 Hz, 2 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 7.06 (t, *J* = 7.2 Hz, 1 H), 6.97 (t, *J* = 7.5 Hz, 2 H), 5.21 (s, 2 H), 3.76 (q, *J* = 7.1 Hz, 2 H), 3.40 (t, *J* = 8.1 Hz, 2 H), 0.64 (t, *J* = 8.1 Hz, 2 H), 0.55 (t, *J* = 7.1 Hz, 3 H), –0.17 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 185.4, 157.3, 157.0, 143.6, 137.4, 136.0, 134.3, 133.1, 130.5, 129.7, 129.5, 129.0, 128.8, 127.9, 115.9, 114.4, 74.7, 67.6, 61.6, 17.6, 13.4, –1.5.

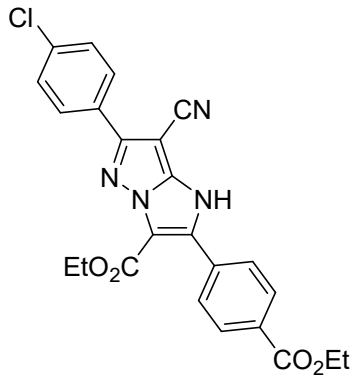
MS (70 eV, EI) *m/z* (%): 548 (3) $[M]^{+}$, 493 (10), 492 (28), 491 (23), 490 (68), 478 (10), 477 (30), 476 (24), 475 (75), 372 (23), 105 (24), 91 (14), 77 (10), 73 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3068, 2952, 2924, 2895, 2876, 2214, 1712, 1661, 1613, 1596, 1566, 1508, 1466, 1450, 1440, 1422, 1397, 1385, 1362, 1339, 1324, 1300, 1288, 1273, 1261, 1250, 1227, 1185, 1161, 1143, 1085, 1053, 1014, 966, 943, 923, 877, 842, 831, 770, 762, 747, 728, 717, 703, 680.

HRMS (EI) calculated for $C_{28}H_{29}ClN_4O_4Si^{+}$: 548.1641, found 548.1673 $[M]^{+}$.

mp: 115.3 – 116.4 °C.

Ethyl 6-(4-chlorophenyl)-7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (12a)



To a solution of ethyl 6-(4-chlorophenyl)-7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (**11l**, 34 mg, 0.059 mmol, 1.0 equiv) in THF (0.12 mL) was added a solution of TBAF (1.0 M in THF, 0.36 mL, 0.36 mmol, 6.0 equiv) at 0 °C. Then the solution was warmed up to 25 °C and stirred for 16 h. The solvent was removed *in vacuo* and the crude residue was purified directly via column chromatography (silica gel, *i*Hex/EtOAc = 7:3 then *i*Hex/EtOAc = 1:1) to yield the title compound **12a** (22 mg, 0.048 mmol, 81%) as a colorless solid.

^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): δ = 8.08 (d, *J* = 8.4 Hz, 2 H), 7.95 (d, *J* = 8.6 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.6 Hz, 2 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

^{13}C-NMR (DMSO-d_6, 101 MHz, ppm): δ = 165.3, 158.1, 154.4, 142.5, 138.5, 134.1, 132.6, 131.0, 130.6, 130.5, 129.2, 128.8, 128.2, 115.1, 110.9, 64.6, 61.2, 60.9, 14.2, 13.9.

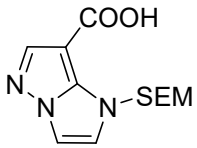
MS (70 eV, EI) *m/z* (%): 464 (33), 463 (29), 462 (100)$[M]^{\cdot+}$, 417 (9), 390 (10), 325 (24), 176 (17), 148 (13).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3153, 2918, 2223, 1732, 1705, 1631, 1581, 1506, 1463, 1445, 1424, 1384, 1273, 1191, 1129, 1144, 1098, 1015, 859, 850, 825, 761, 726, 708, 695, 655.

HRMS (EI) calculated for $C_{24}H_{19}ClN_4O_4^{\cdot+}$: 462.1089, found 462.1083 $[M]^{\cdot+}$.

mp: 262.1 – 263.4 °C.

1-((2-(Trimethylsilyl)ethoxy)methyl)-1H-imidazo[1,2-b]pyrazole-7-carboxylic acid (19)



Ethyl 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate (**7e**, 566 mg, 1.83 mmol, 1.00 equiv) was dissolved in MeOH (18 mL) and treated with aqueous NaOH (32%, 10 mL, 108 mmol, 59 equiv). The mixture was then heated to 50 °C and stirred for 32 h). Then the MeOH was removed *in vacuo*, the residue was diluted with distilled H_2O (10 mL) and extracted with DCM (3 x 10 mL). The aqueous phase was then treated with concentrated aqueous HCl until the pH reached 2. The formed precipitate was filtered off, washed with cold diluted aqueous HCl (pH = 2) and dried under high vacuum to yield the title compound **19** (349 mg, 1.24 mmol, 68%) as a colorless solid.

^{1}H-NMR (DMSO-d_6, 400 MHz, ppm): δ = 11.99 (s, 1 H), 7.90 (s, 1 H), 7.79 (d, *J* = 2.2 Hz, 1 H), 7.46 (s, 1 H), 5.75 (s, 2 H), 3.52 (t, *J* = 8.0 Hz, 2 H), 0.80 (t, *J* = 8.0 Hz, 2 H), –0.10 (s, 9 H).

^{13}C-NMR (DMSO-d_6, 101 MHz, ppm): δ = 163.6, 145.4, 140.1, 122.1, 109.7, 91.5, 75.8, 65.1, 17.2, –1.5.

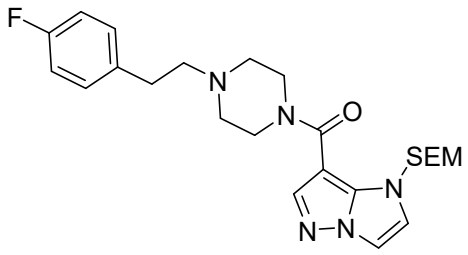
MS (70 eV, EI) *m/z* (%): 281 (11) $[M]^{\cdot+}$, 223 (21), 208 (25), 164 (29), 134 (17), 133 (51), 73 (100).

IR (ATR) $\tilde{\nu}$ **(cm^{-1}):** 3131, 2951, 2918, 2607, 1641, 1591, 1551, 1488, 1452, 1434, 1381, 1345, 1317, 1300, 1267, 1250, 1219, 1209, 1180, 1169, 1106, 1093, 1075, 1046, 1013, 933, 857, 848, 832, 764, 735, 711, 694.

HRMS (EI) calculated for $C_{12}H_{19}N_3O_3Si^{\cdot+}$: 281.1190, found 281.1189 $[M]^{\cdot+}$.

mp: 151.8 – 153.7 °C.

(4-(4-Fluorophenethyl)piperazin-1-yl)(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazol-7-yl)methanone (21)



1-((2-(Trimethylsilyl)ethoxy)methyl)-1H-imidazo[1,2-b]pyrazole-7-carboxylic acid (**19**, 189 mg, 0.67 mmol, 1.0 equiv) was dissolved in a mixture of dry MeCN (6.7 mL) and DMF (2.0 mL), treated with triethylamine (67 mg, 0.67 mmol, 1.0 equiv) and stirred at 25 °C for 5 min. Then bis(pentafluorophenyl) carbonate (288 mg, 0.74 mmol, 1.1 equiv) was added and the mixture was stirred at 25 °C for 1 h. 1-(4-Fluorophenethyl)piperazine (**20**, 697 mg, 3.4 mmol, 5.0 equiv) and more triethylamine (67 mg, 0.67 mmol, 1.0 equiv) and the mixture was stirred at 25 °C over night (21 h) before adding an aqueous solution of NH_4Cl (10 mL). The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic phases were washed with brine (3 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification via column chromatography (silica gel, EtOAc/MeOH = 9:1) yielded the title compound **21** (231 mg, 0.49 mmol, 74%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.69 (d, *J* = 1.1 Hz, 1 H), 7.35 (d, *J* = 2.3 Hz, 1 H), 7.18 – 7.12 (m, 2 H), 6.99 – 6.93 (m, 3 H), 5.70 (s, 2 H), 3.81 (t, *J* = 4.8 Hz, 4 H), 3.55 (t, *J* = 8.1 Hz, 2 H), 2.81 – 2.75 (m, 2 H), 2.63 – 2.53 (m, 6 H), 0.87 (t, *J* = 8.1 Hz, 2 H), –0.06 (s, 9 H).

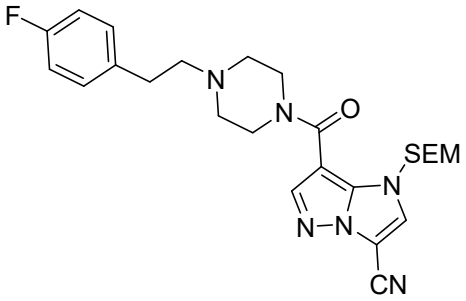
^{13}C-NMR ($CDCl_3$, 101 MHz, ppm): δ = 163.6, 161.5 (d, *J* = 243.9 Hz), 142.8, 141.8, 135.7 (d, *J* =3.2 Hz), 130.1 (d, *J* = 7.8 Hz), 120.5, 115.3 (d, *J* = 21.2 Hz), 109.3, 93.6, 76.9, 66.4, 60.5, 53.5, 45.4, 32.8, 18.0, –1.2.

^{19}F-NMR ($CDCl_3$, 377 MHz, ppm): δ = −117.2 (tt, J = 8.5, 5.3 Hz).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3446, 3123, 2949, 2808, 1597, 1548, 1508, 1486, 1429, 1368, 1332, 1313, 1272, 1247, 1215, 1157, 1126, 1073, 999, 916, 857, 832, 756, 738, 692, 667.

HRMS (ESI) calculated for $C_{24}H_{36}FN_5O_2Si^+$: 472.2539, found 472.25392 $[M+H]^+$.

7-(4-(4-Fluorophenethyl)piperazine-1-carbonyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carbonitrile (22)



To a solution of (4-(4-fluorophenethyl)piperazin-1-yl)(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)methanone (**21**, 184 mg, 0.39 mmol, 1.0 equiv) in THF (1 mL) was added a solution of TMPMgCl·LiCl (**8**, 0.90 M in THF, 0.66 mL, 0.59 mmol, 1.5 equiv) dropwise at −20 °C. The mixture was stirred at −20 °C for 50 min before adding a solution of CuCN·2LiCl in THF (1.0 M, 0.39 mL, 0.39 mmol, 1.0 equiv) and tosyl cyanide (177 mg, 0.98 mmol, 2.5 equiv). After stirring for 2 h at room temperature a saturated aqueous solution of NH_4Cl (1 mL) was added. The reaction was extracted with EtOAc (3 x 2 mL), washed with brine, dried over $MgSO_4$, concentrated *in vacuo* and purified via column chromatography (silica gel, EtOAc + 5% NEt_3) to yield the title compound **22** (163 mg, 0.33 mmol, 85%) as a colorless oil.

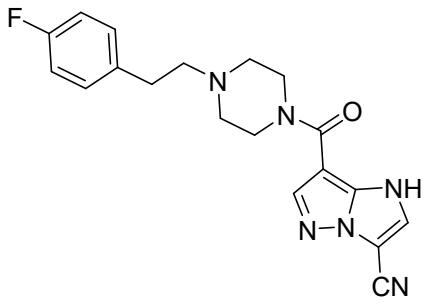
^{1}H-NMR (C_6D_6, 400 MHz, ppm): δ = 7.71 (d, *J* = 1.1 Hz, 1 H), 6.86 – 6.81 (m, 4 H), 6.12 (d, *J* = 1.1 Hz, 1 H), 5.38 (s, 2 H), 3.58 (t, *J* = 4.9 Hz, 4 H), 3.43 (t, *J* = 7.9 Hz, 2 H), 2.52 – 2.42 (m, 2 H), 2.29 – 2.21 (m, 2 H), 2.10 (t, *J* = 4.9 Hz, 4 H), 0.83 (t, *J* = 7.9 Hz, 2 H), –0.08 (s, 9 H).

^{13}C-NMR (C_6D_6, 101 MHz, ppm): δ = 162.3, 162.0 (d, *J* = 243.5 Hz), 143.7, 141.6, 136.3 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 7.7 Hz), 129.3, 115.4 (d, *J* = 21.0 Hz), 109.6, 96.4, 96.4, 77.6, 66.9, 60.2, 53.3, 45.3, 32.9, 18.0, –1.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2949, 2809, 2232, 1597, 1508, 1478, 1429, 1369, 1341, 1315, 1270, 1247, 1217, 1195, 1157, 1119, 1080, 999, 946, 915, 856, 832, 756, 738, 720, 692, 664.

HRMS (ESI) calculated for $C_{25}H_{34}FN_6O_2Si^+$: 497.2491, found 497.24921 $[M+H]^+$.

7-(4-(4-Fluorophenethyl)piperazine-1-carbonyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carbonitrile (4)



7-(4-(4-Fluorophenethyl)piperazine-1-carbonyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carbonitrile (**22**, 50 mg, 0.10 mmol, 1.0 equiv) was dissolved in MeCN (1.0 mL) and treated with 18-crown-6 (30 mg, 0.11 mmol, 1.1 equiv) and CsF (76 mg, 0.50 mmol, 5.0 equiv). The mixture was heated to 85 °C and stirred for 26 h. Then the solvent was removed *in vacuo* and the residue directly purified via column chromatography (silica gel, EtOAc/MeOH = 9:1 + 5% NEt_3 then EtOAc/MeOH = 4:1 + 5% NEt_3 then EtOAc/MeOH = 2:1 + 5% NEt_3) to yield the title compound **4** (21 mg, 0.057 mmol, 57%) as a colorless solid.

^{1}H-NMR (DMSO-*d*$_6$, 400 MHz, ppm): δ = 8.19 (s, 1 H), 7.96 (s, 1 H), 7.32 – 7.23 (m, 2 H), 7.14 – 7.06 (m, 2 H), 3.72 (s, 4 H), 2.80 – 2.73 (m, 2 H), 2.65 – 2.52 (m, 6 H).

^{13}C-NMR (DMSO-*d*$_6$, 101 MHz, ppm): δ = 162.3, 160.7 (d, *J* = 241.2 Hz), 143.7, 143.0, 136.2 (d, *J* = 2.9 Hz), 133.3, 130.4 (d, *J* = 7.9 Hz), 115.0 (d, *J* = 20.9 Hz), 112.0, 94.8, 92.5, 59.2, 52.7, 43.7, 31.4.

^{19}F-NMR (DMSO-*d*$_6$, 377 MHz, ppm): δ = −117.5 (m).

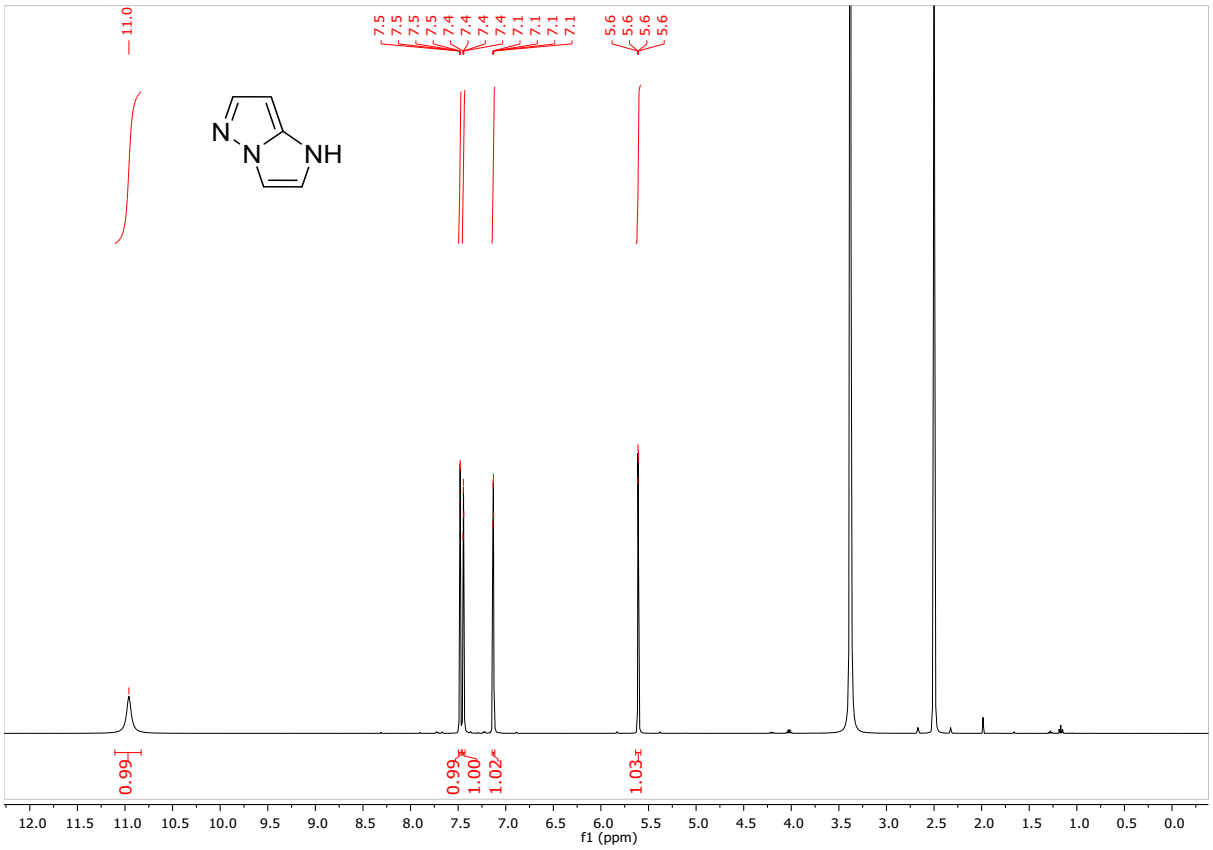
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3371, 3136, 2940, 2864, 2824, 2509, 2296, 2225, 1598, 1507, 1478, 1465, 1441, 1362, 1350, 1319, 1266, 1215, 1199, 1181, 1156, 1126, 1100, 1040, 1001, 948, 885, 859, 833, 817, 804, 759, 690, 672.

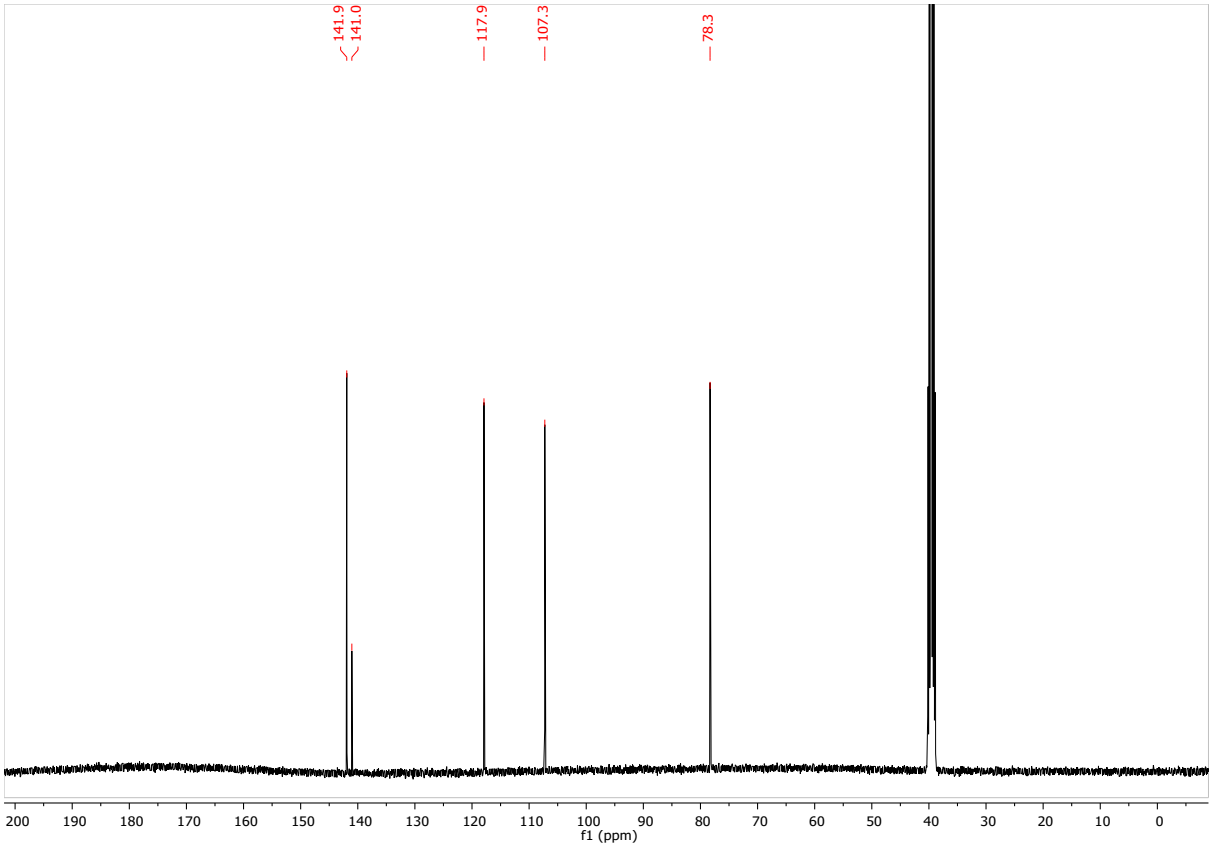
HRMS (ESI) calculated for $C_{18}H_{20}FN_6O^-$: 365.1532, found 365.15332 $[M-H]^-$.

mp: decomposition above 210 °C.

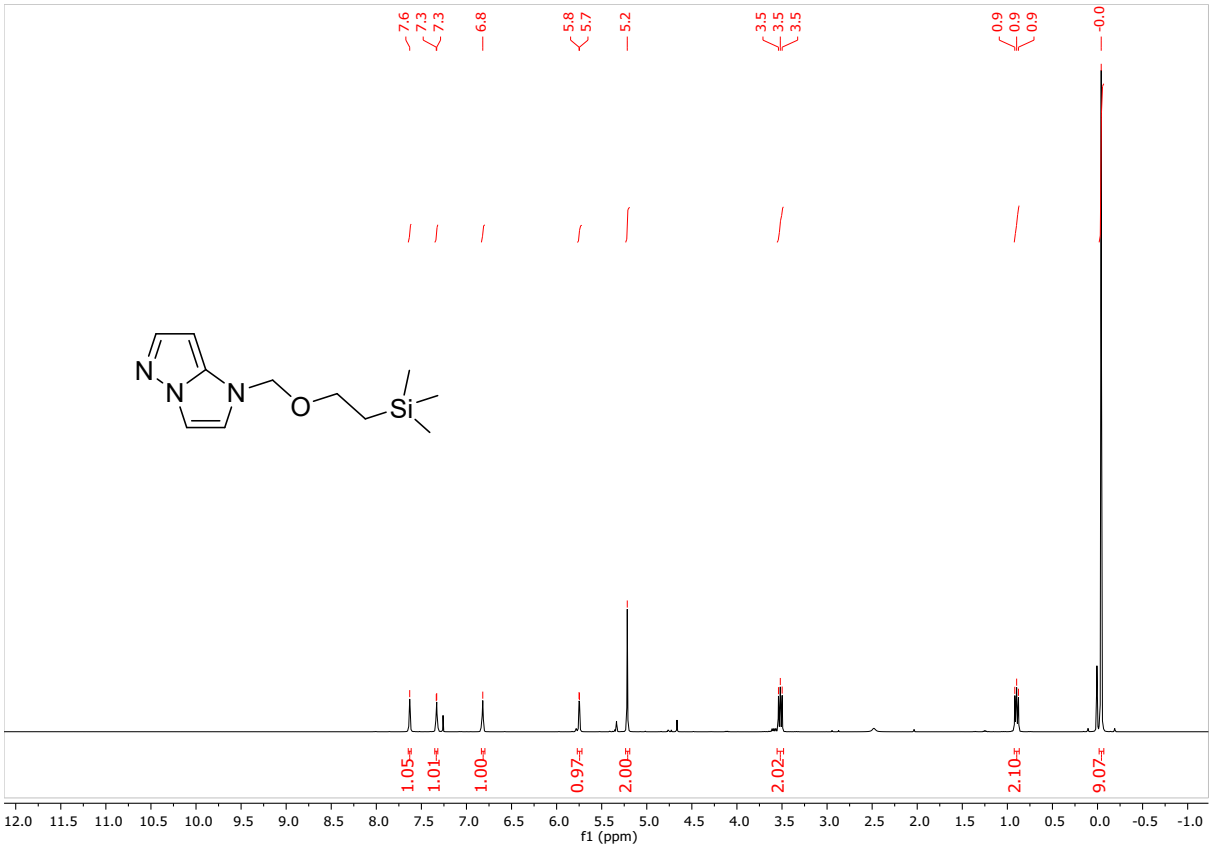
NMR Spectra

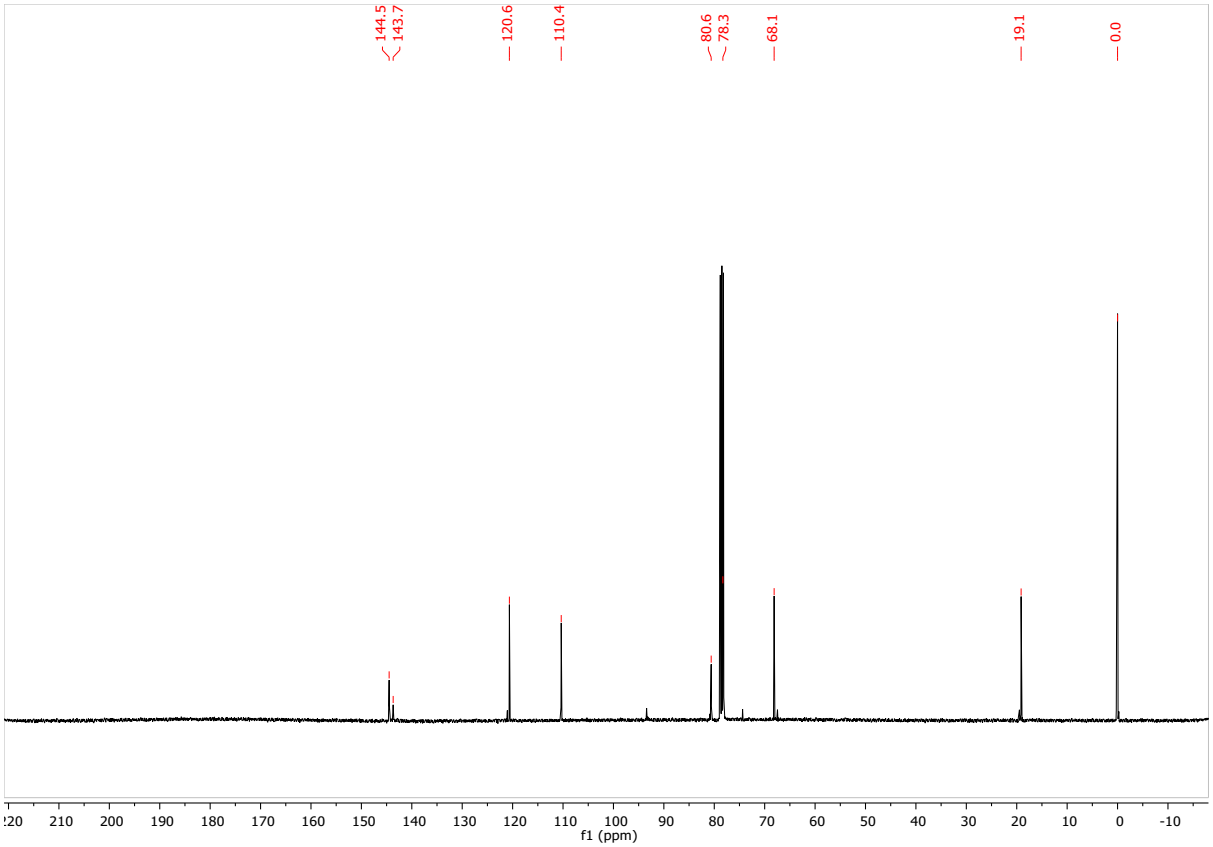
1*H*-Imidazo[1,2-*b*]pyrazole (1)



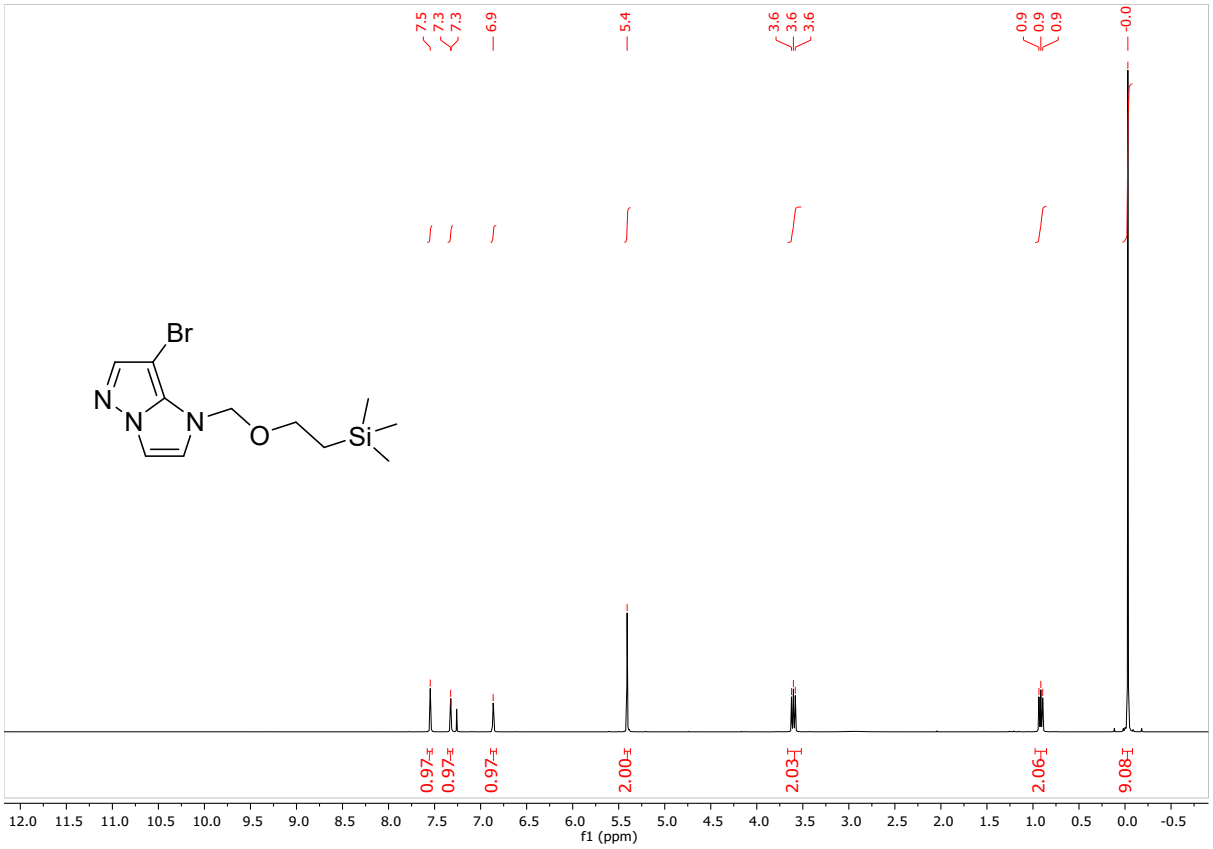


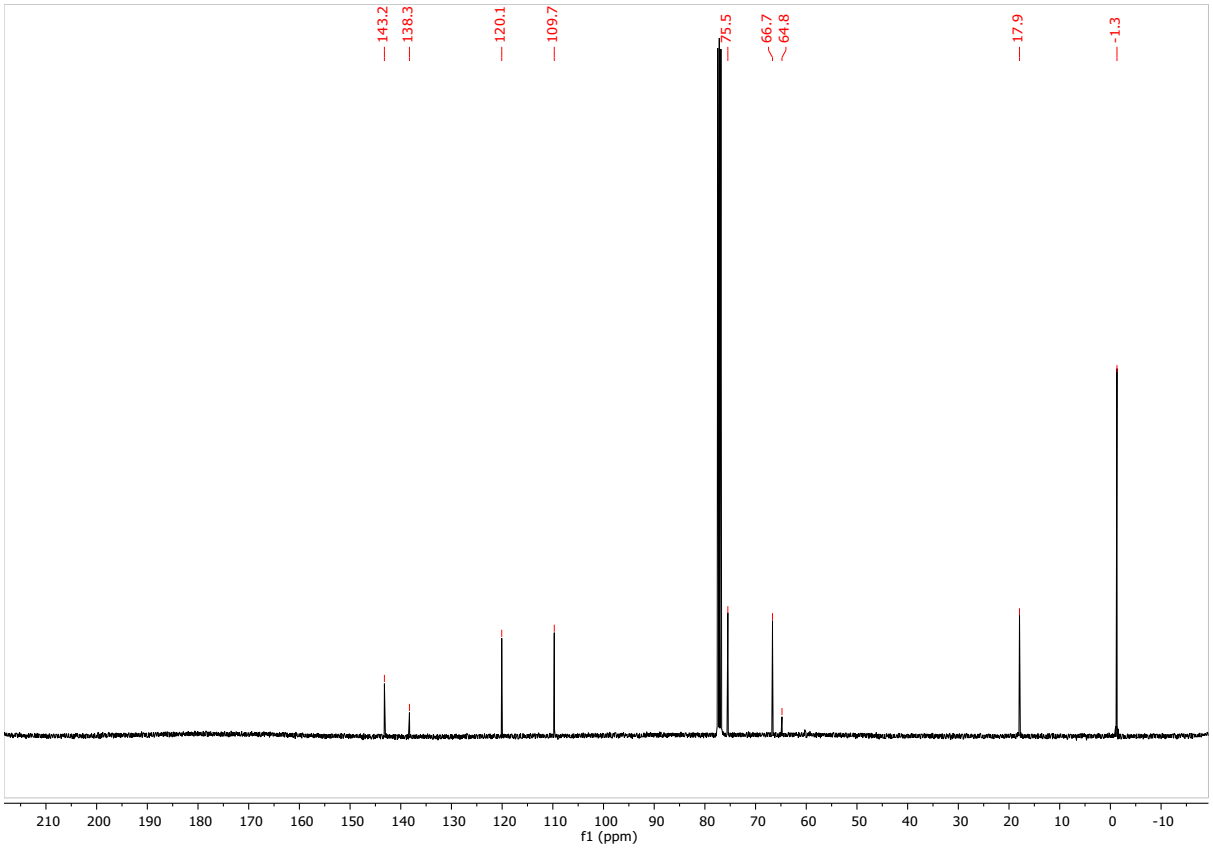
1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (15a)



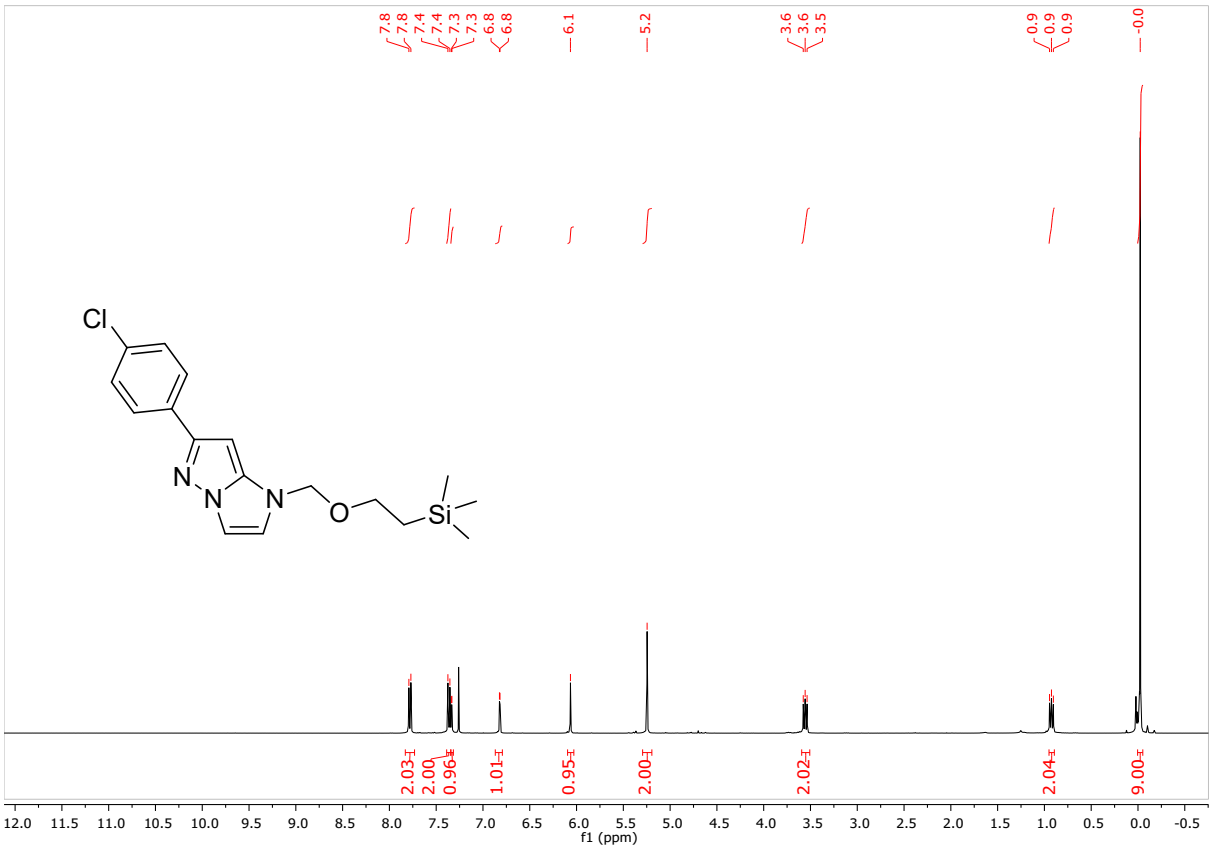

144.5
143.7
120.6
110.4
80.6
78.3
68.1
19.1
0.0
f1 (ppm)

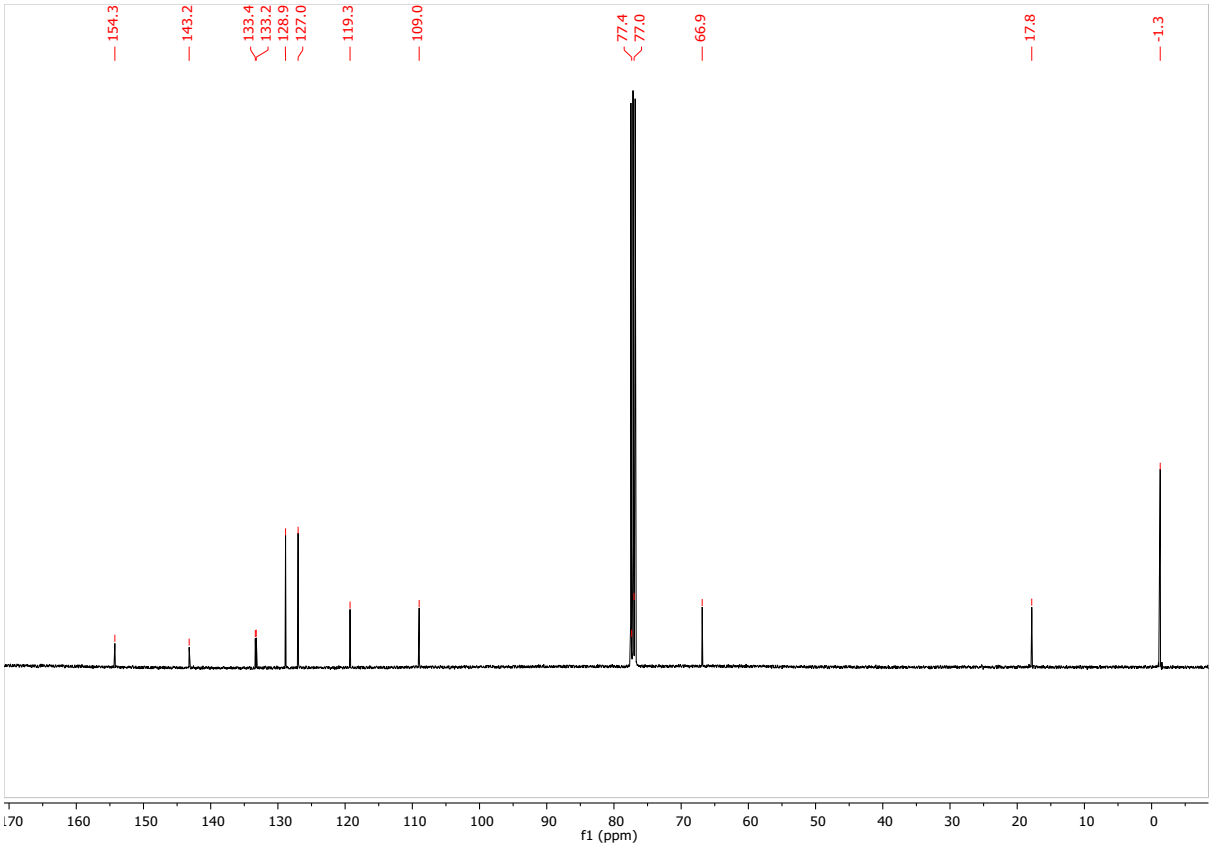
7-Bromo-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (5a)



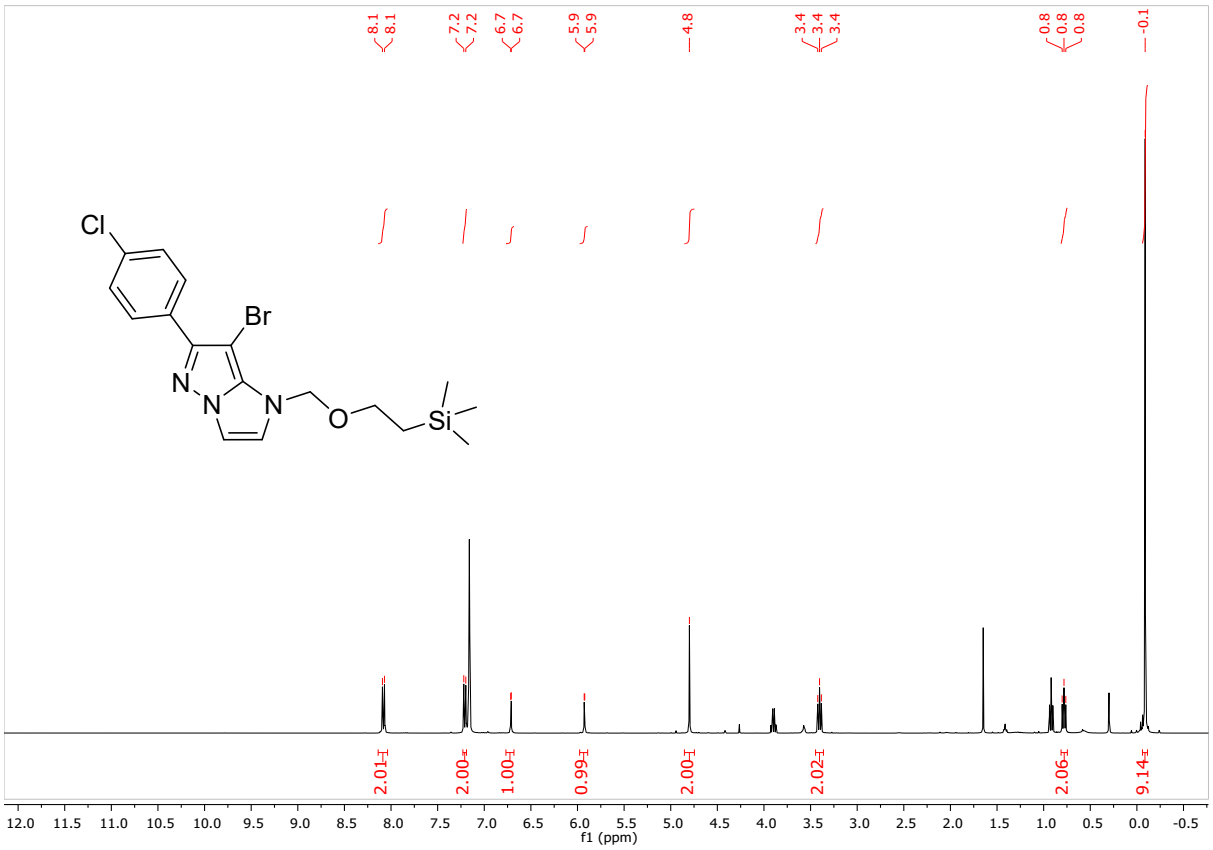


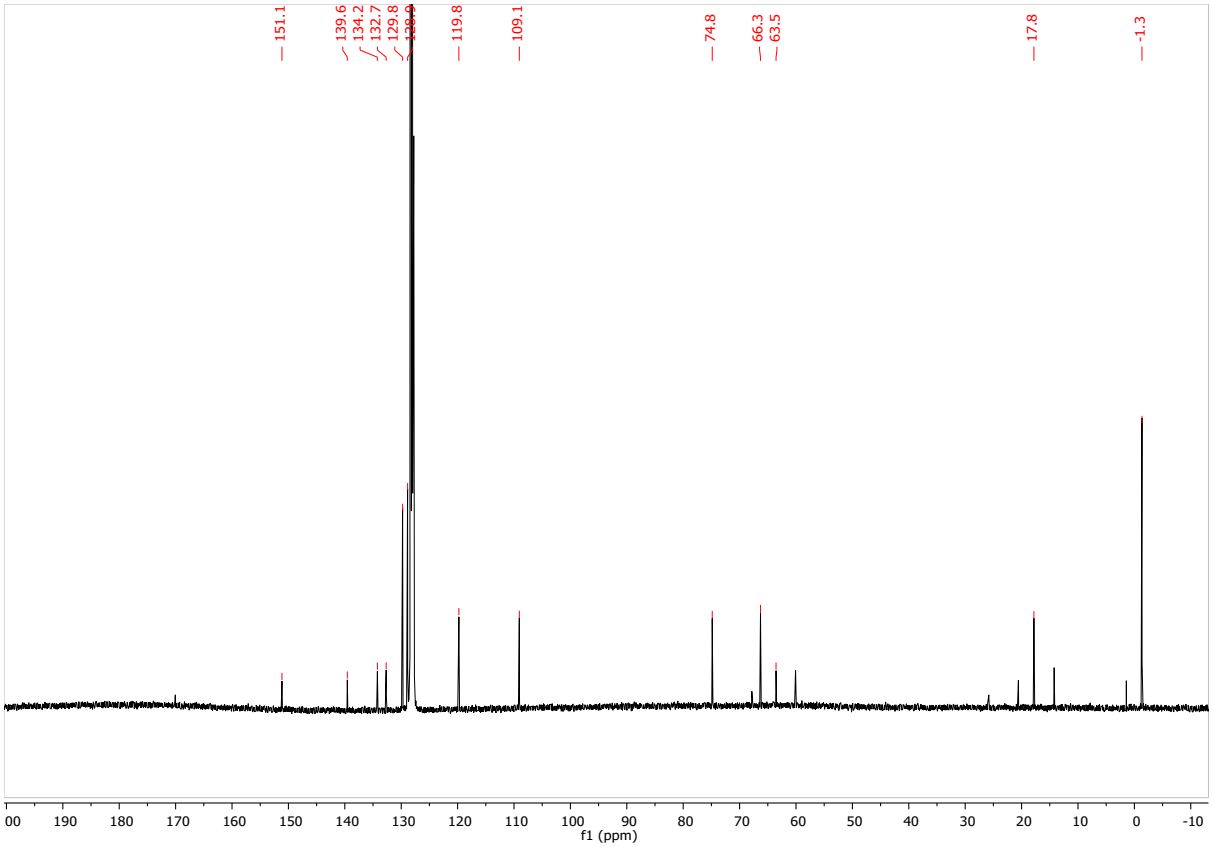
6-(4-Chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (15b)



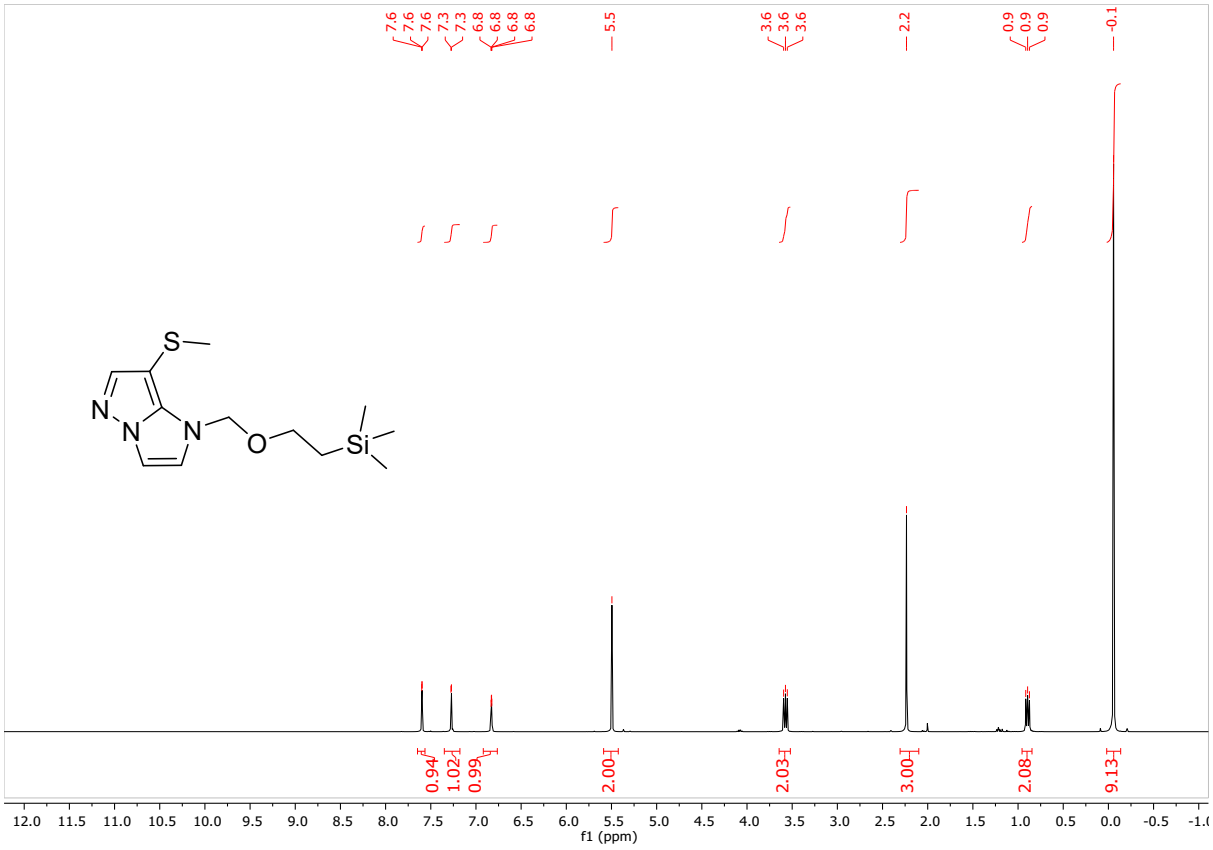

154.3
143.2
133.4
133.2
128.9
127.0
119.3
109.0
77.4
77.0
66.9
17.8
-1.3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

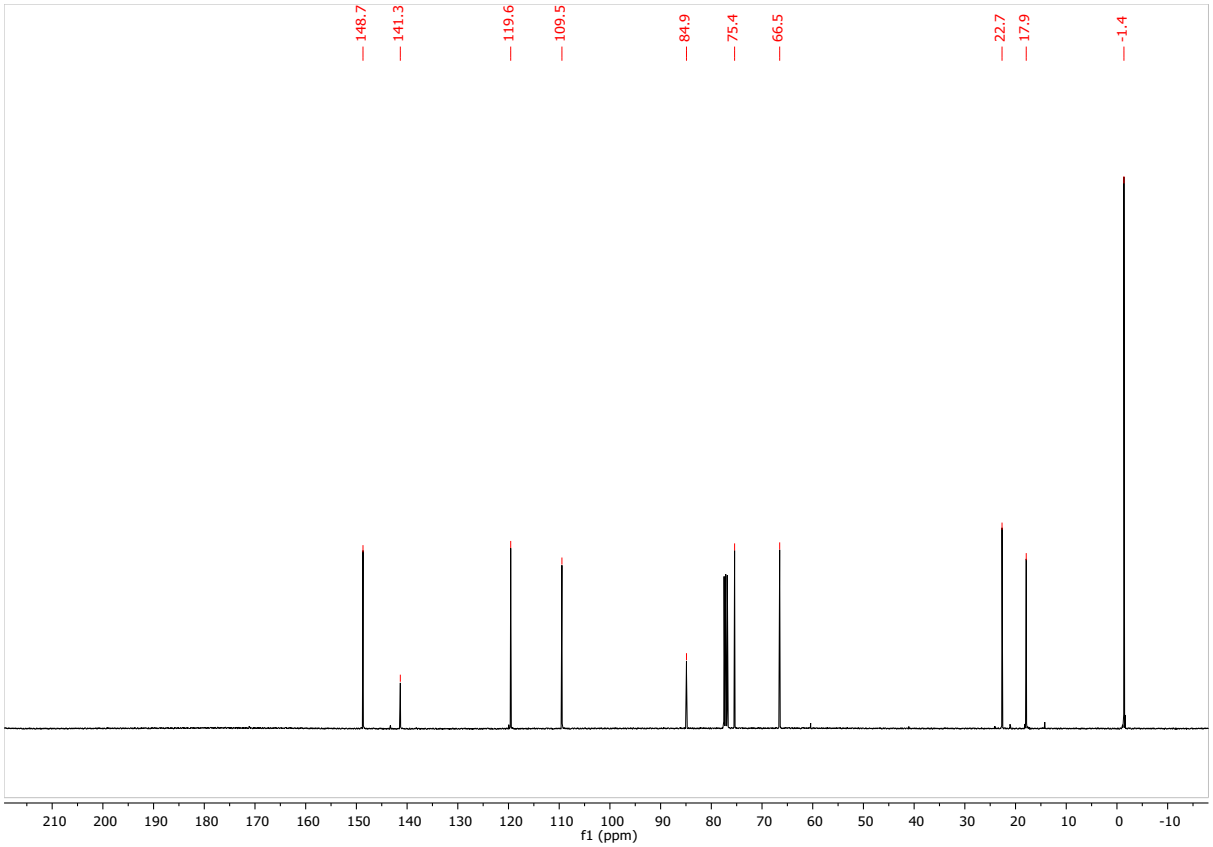
7-Bromo-6-(4-chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole (5b)



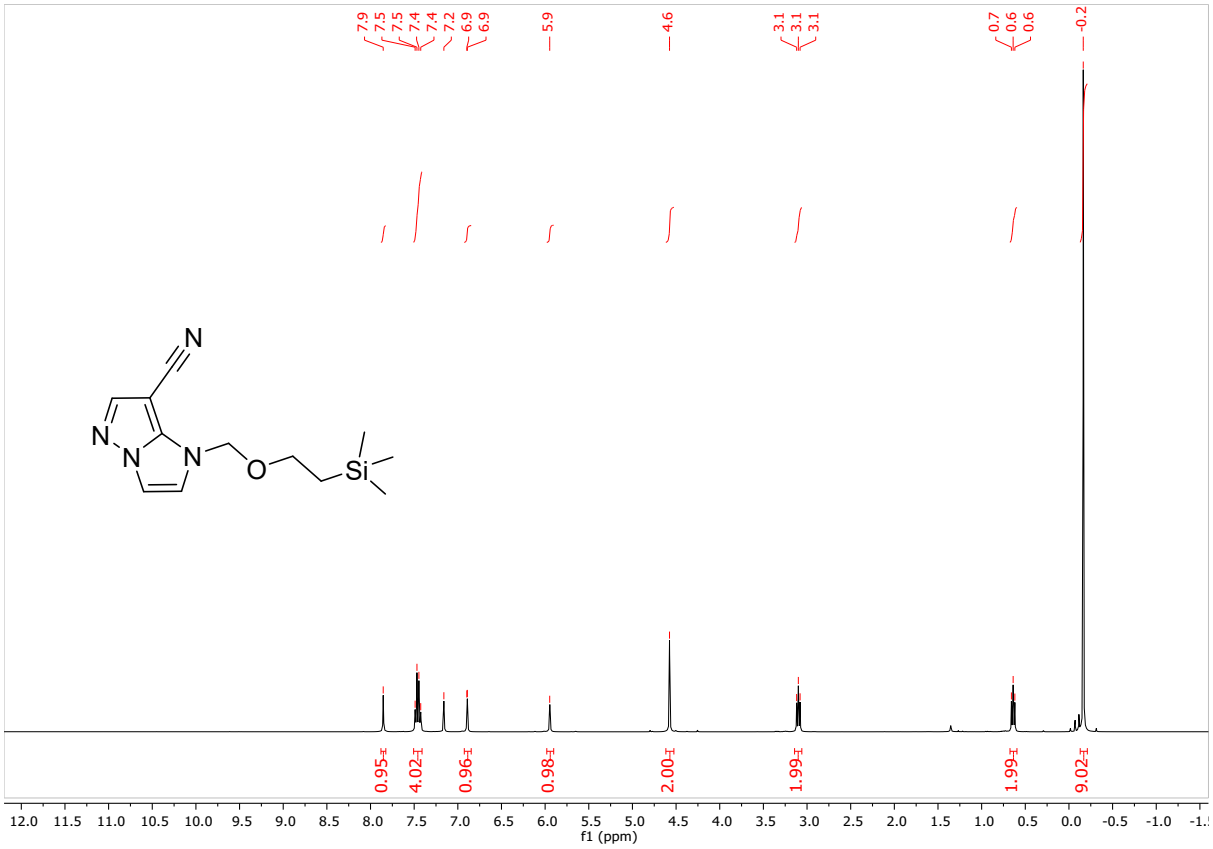


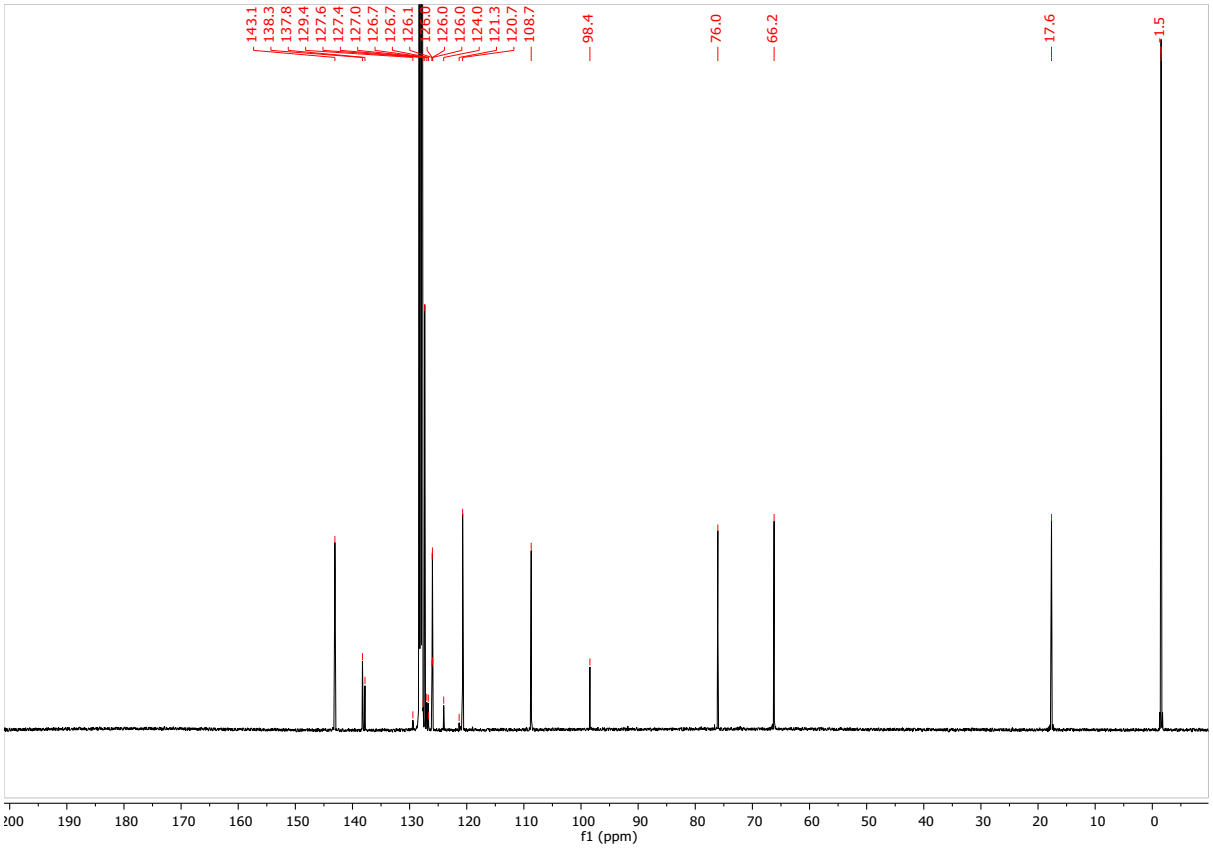
7-(Methylthio)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (7a)



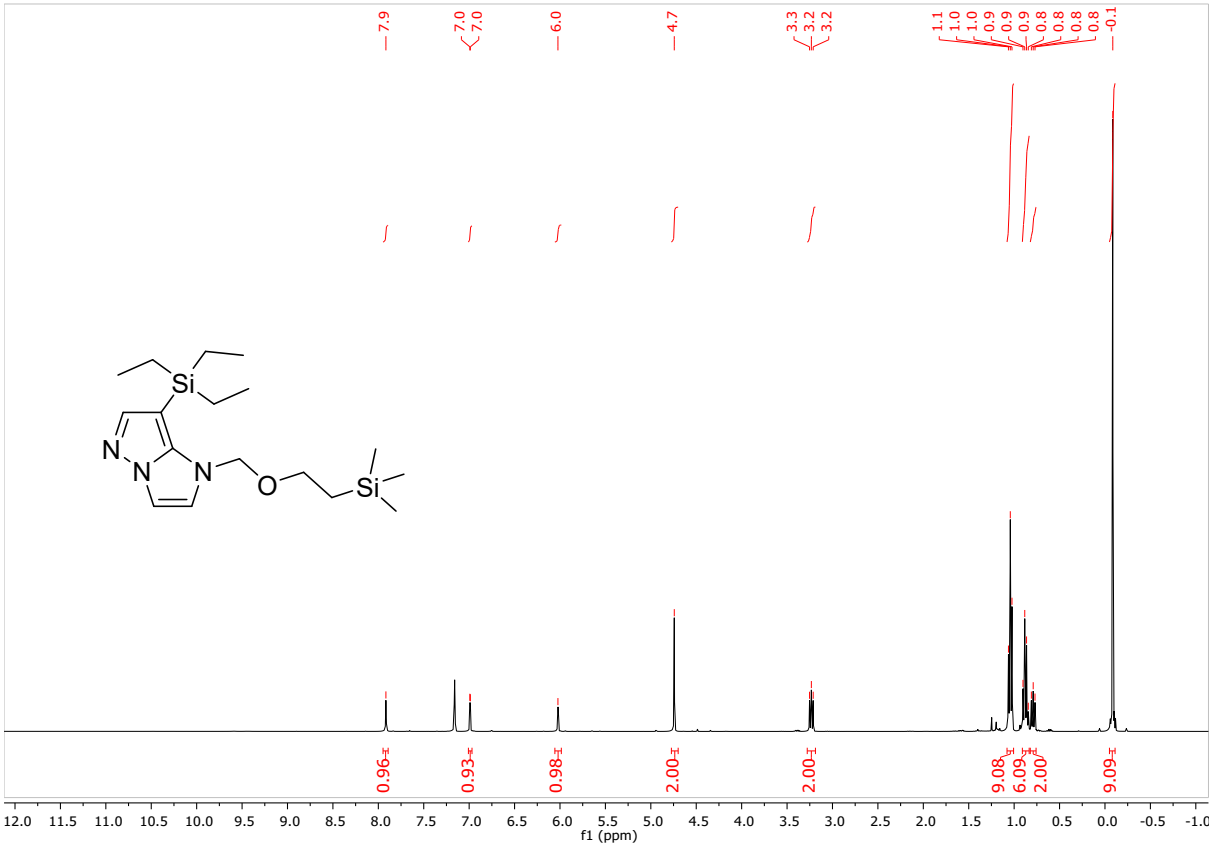

148.7
141.3
119.6
109.5
84.9
75.4
66.5
22.7
17.9
-1.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

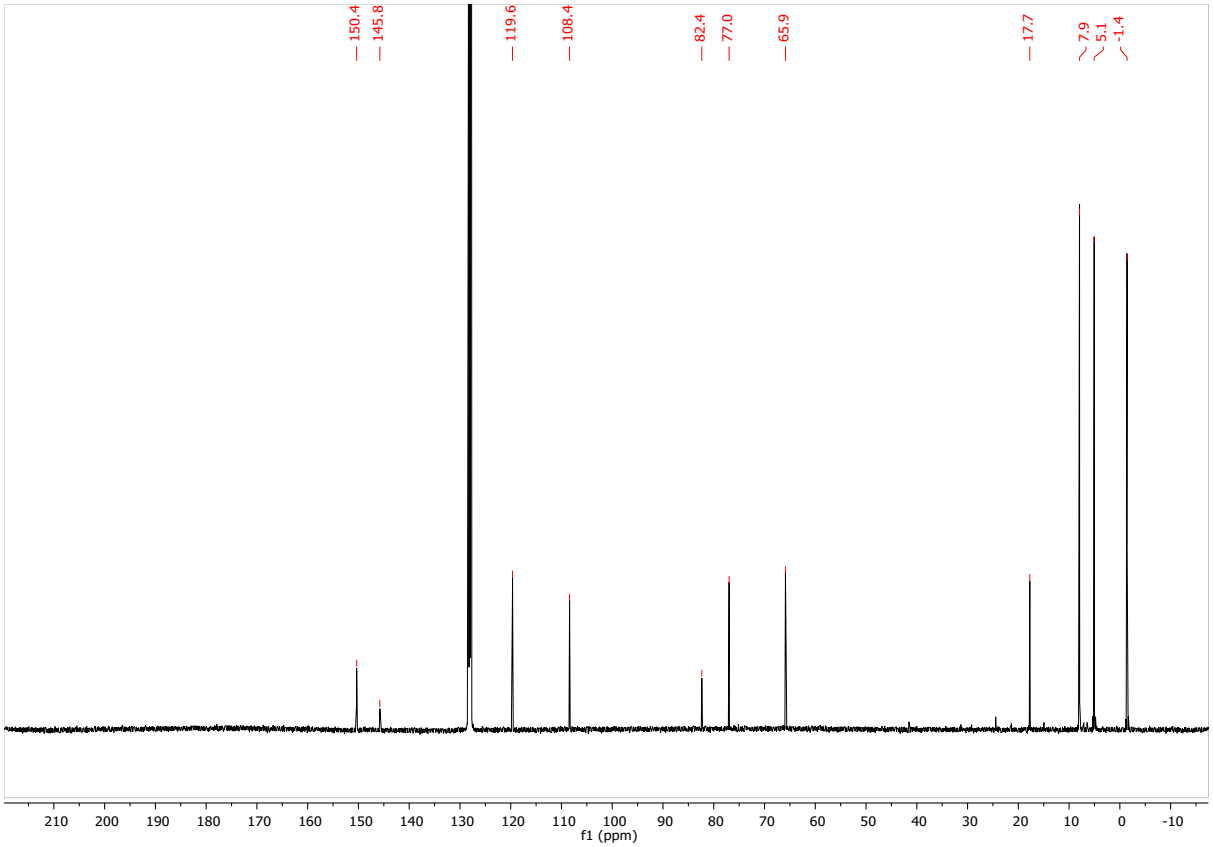
1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (7b)



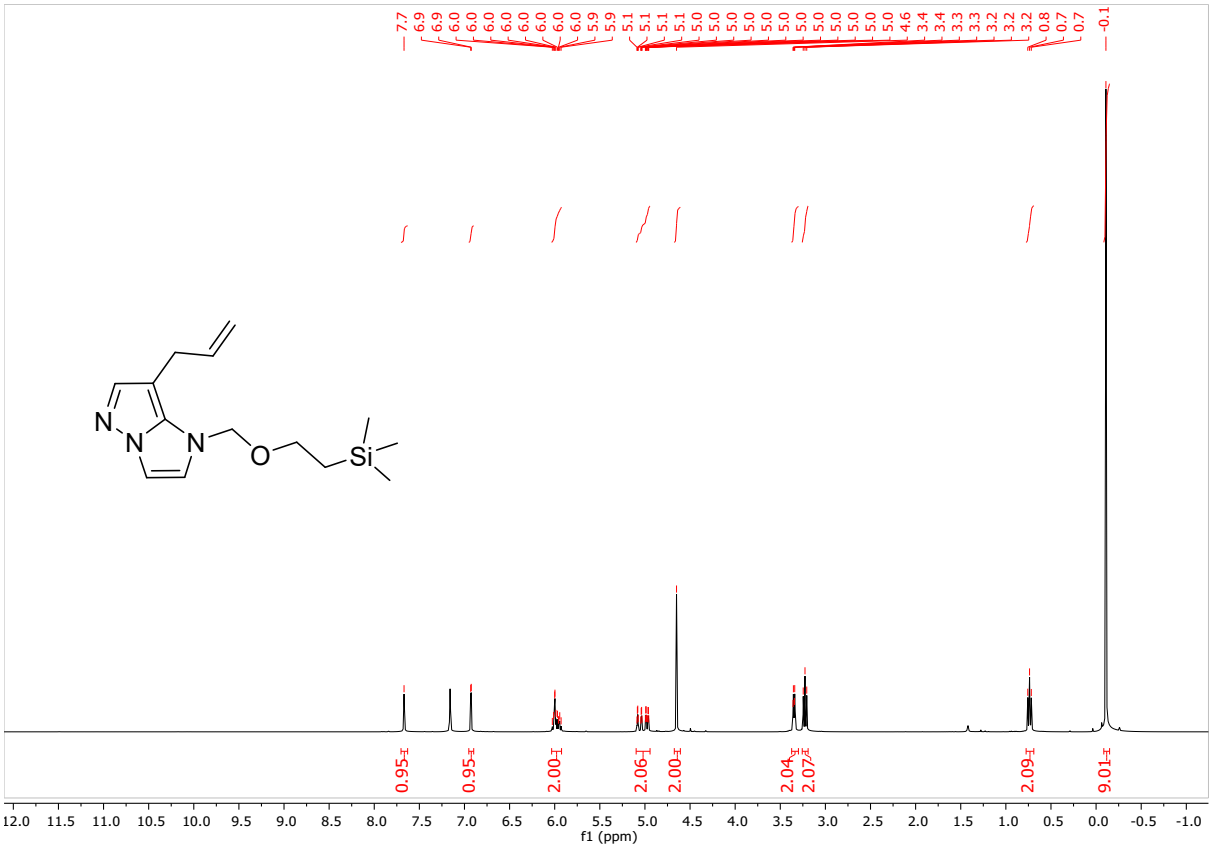


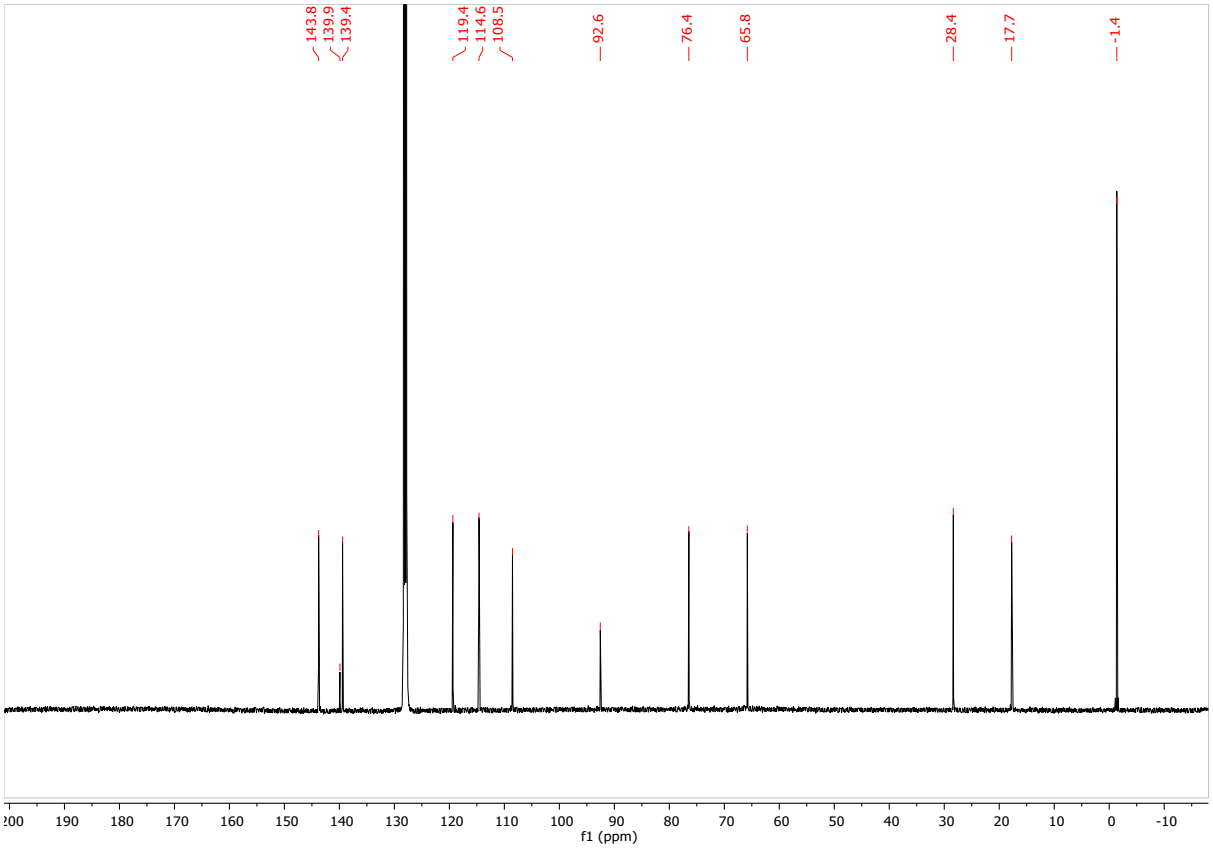
7-(Triethylsilyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (7c)



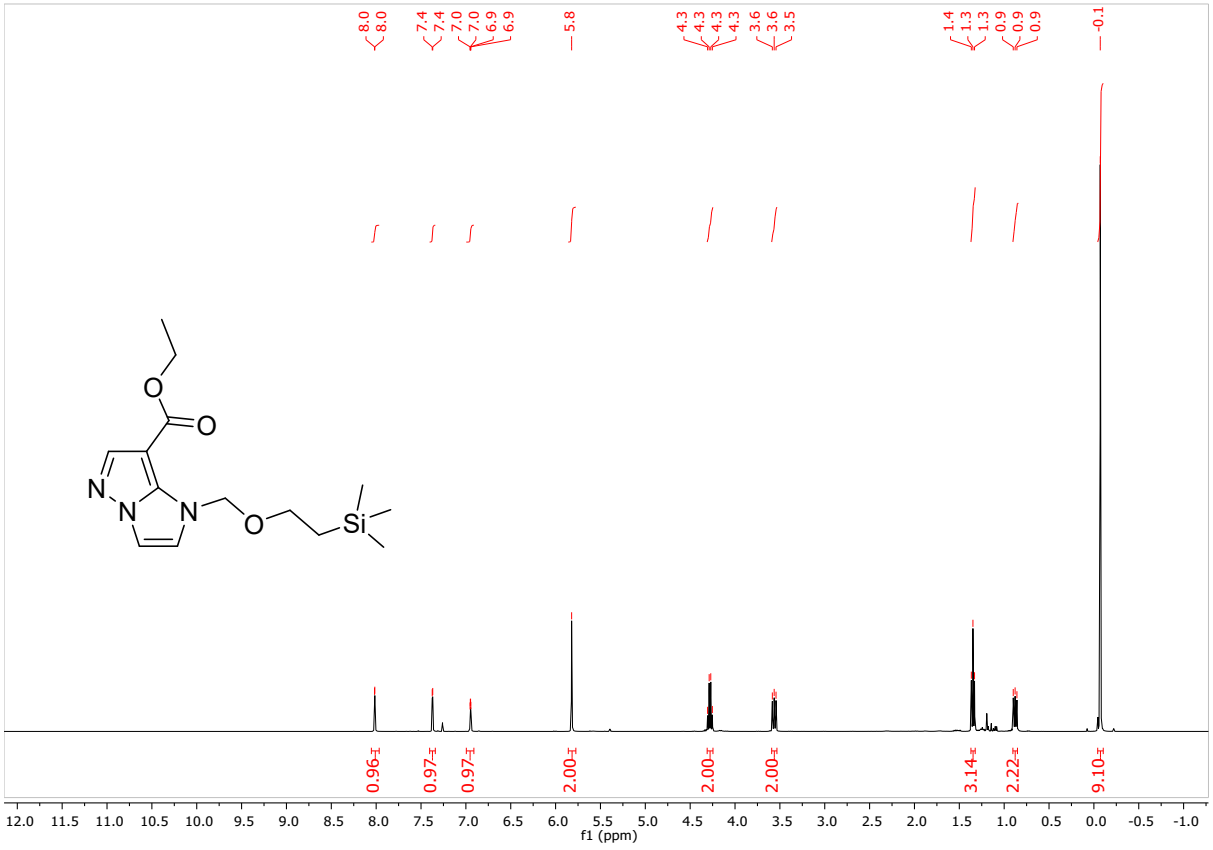

150.4
145.8
119.6
108.4
82.4
77.0
65.9
17.7
7.9
5.1
-1.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

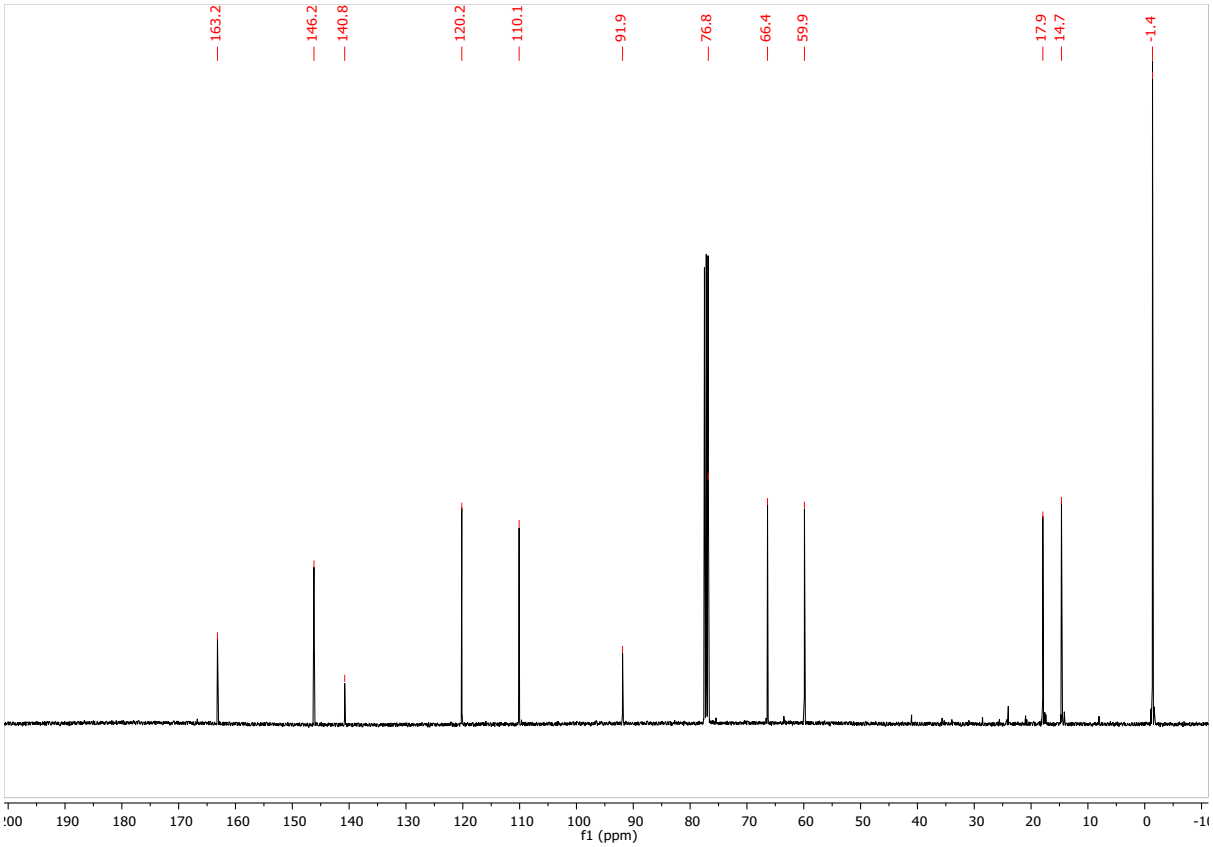
7-Allyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole (7d)



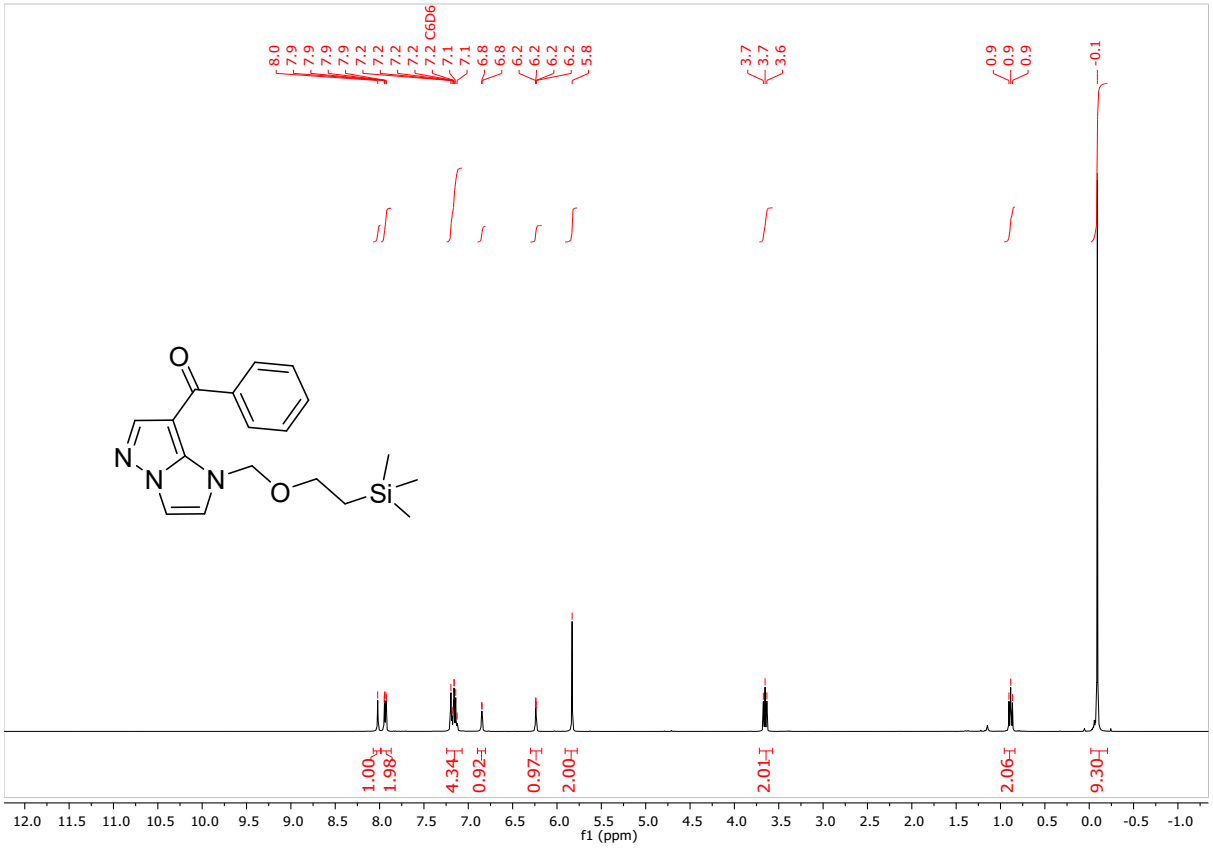


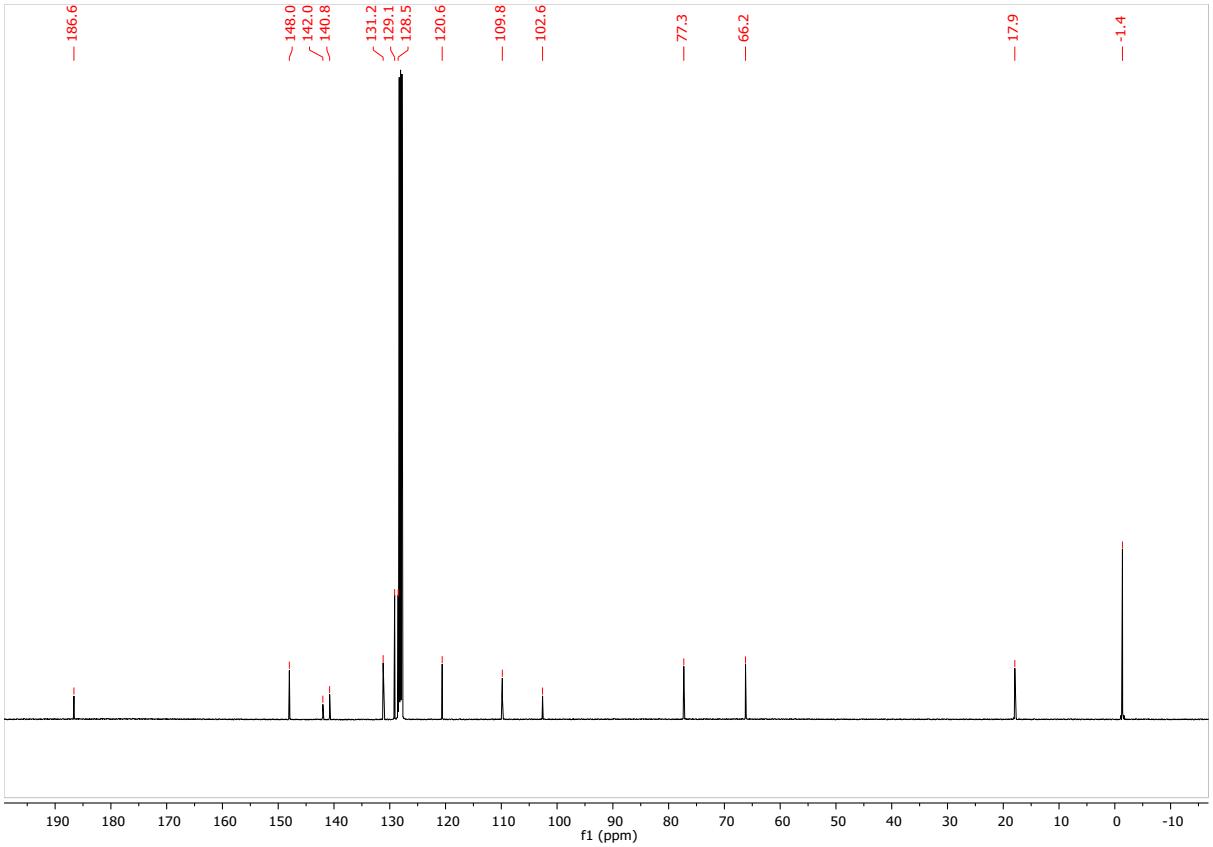
Ethyl 1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carboxylate (7e)



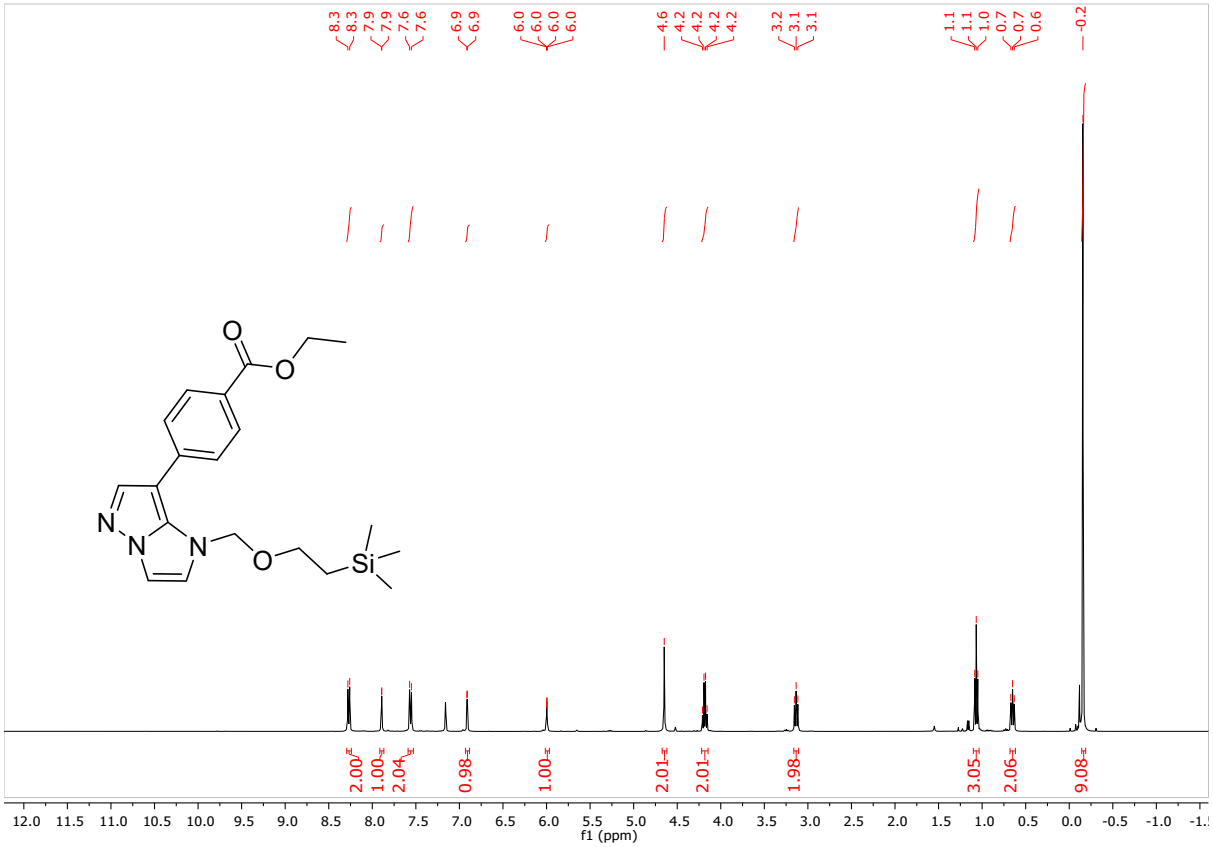

163.2
146.2
140.8
120.2
110.1
91.9
76.8
66.4
59.9
17.9
14.7
-1.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

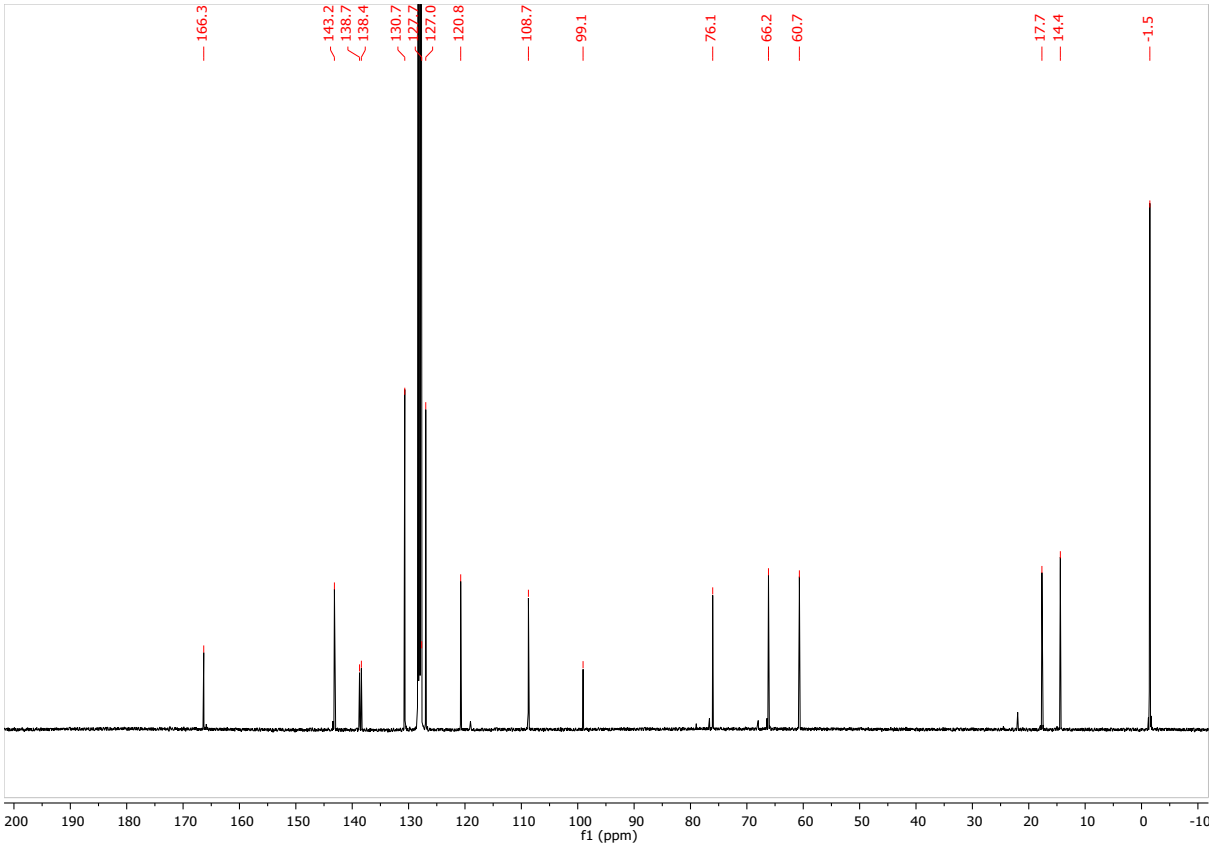
Phenyl(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)methanone (7f)



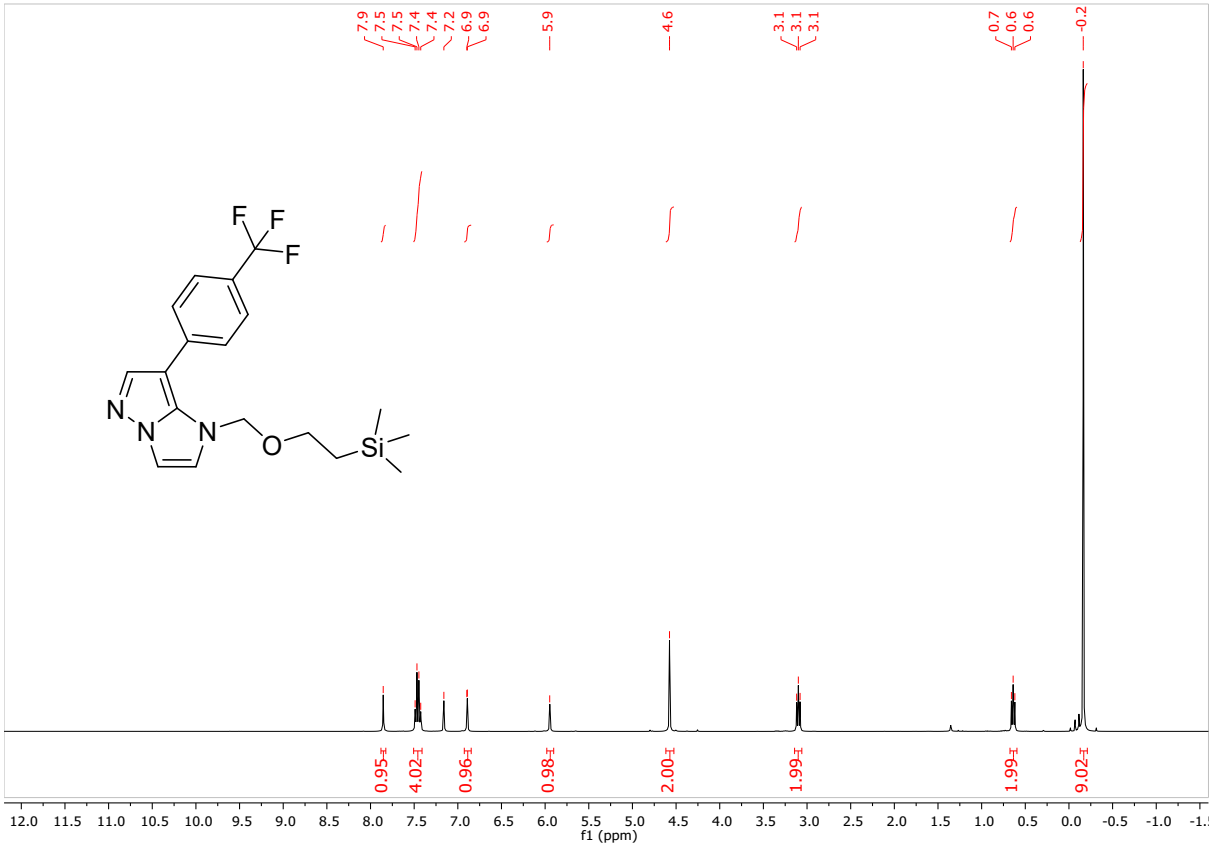

186.6
148.0
142.0
140.8
131.2
129.1
128.5
120.6
109.8
102.6
77.3
66.2
17.9
-1.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

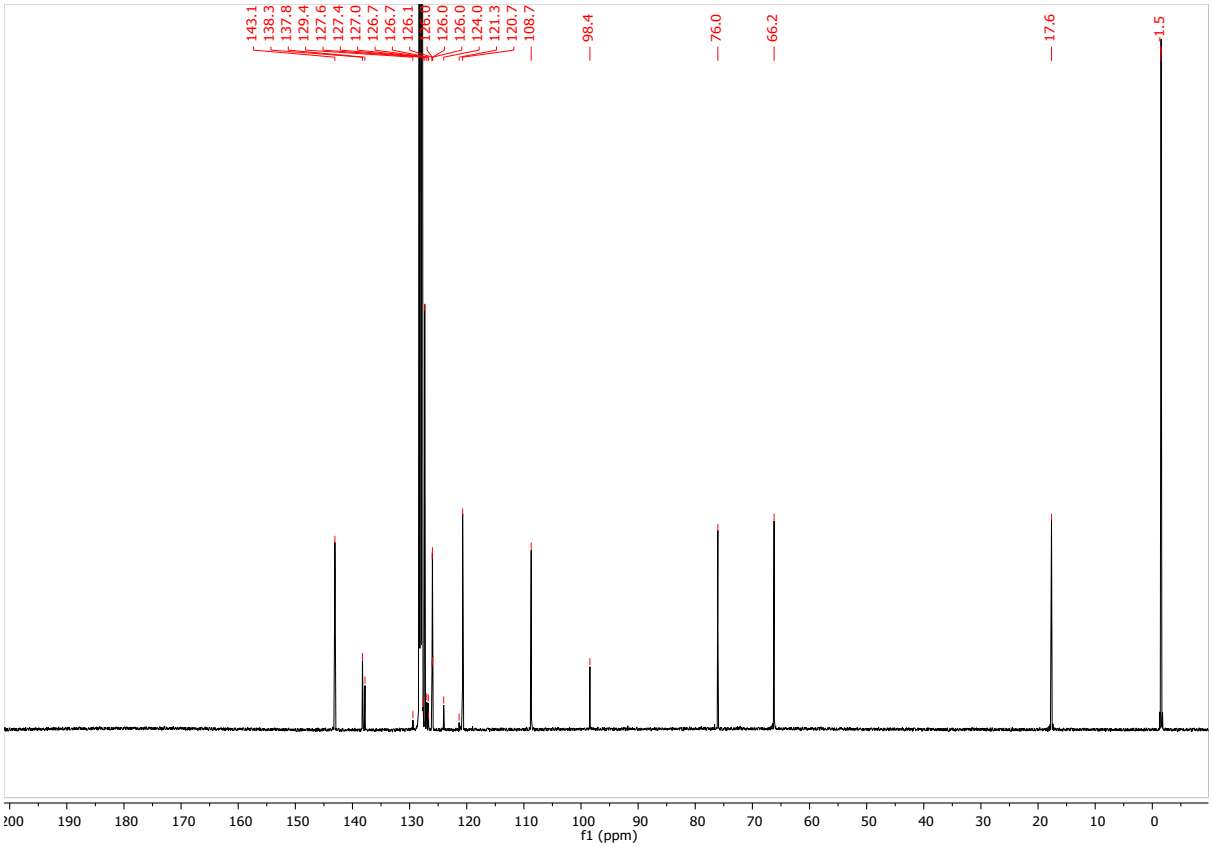
Ethyl 4-(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)benzoate (7g)



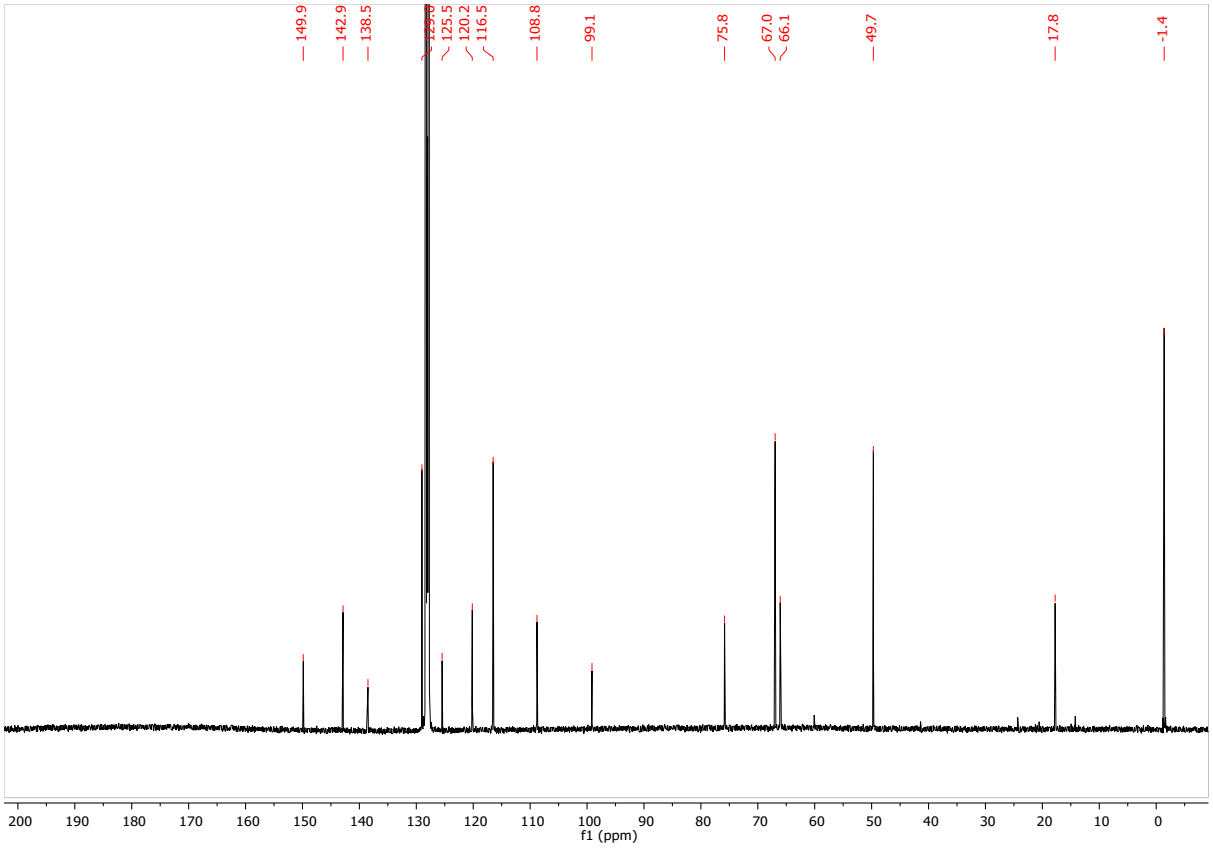

166.3
143.2
138.7
138.4
130.7
127.7
127.0
120.8
108.7
99.1
76.1
66.2
60.7
17.7
14.4
-1.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7-(4-(Trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole (7h)

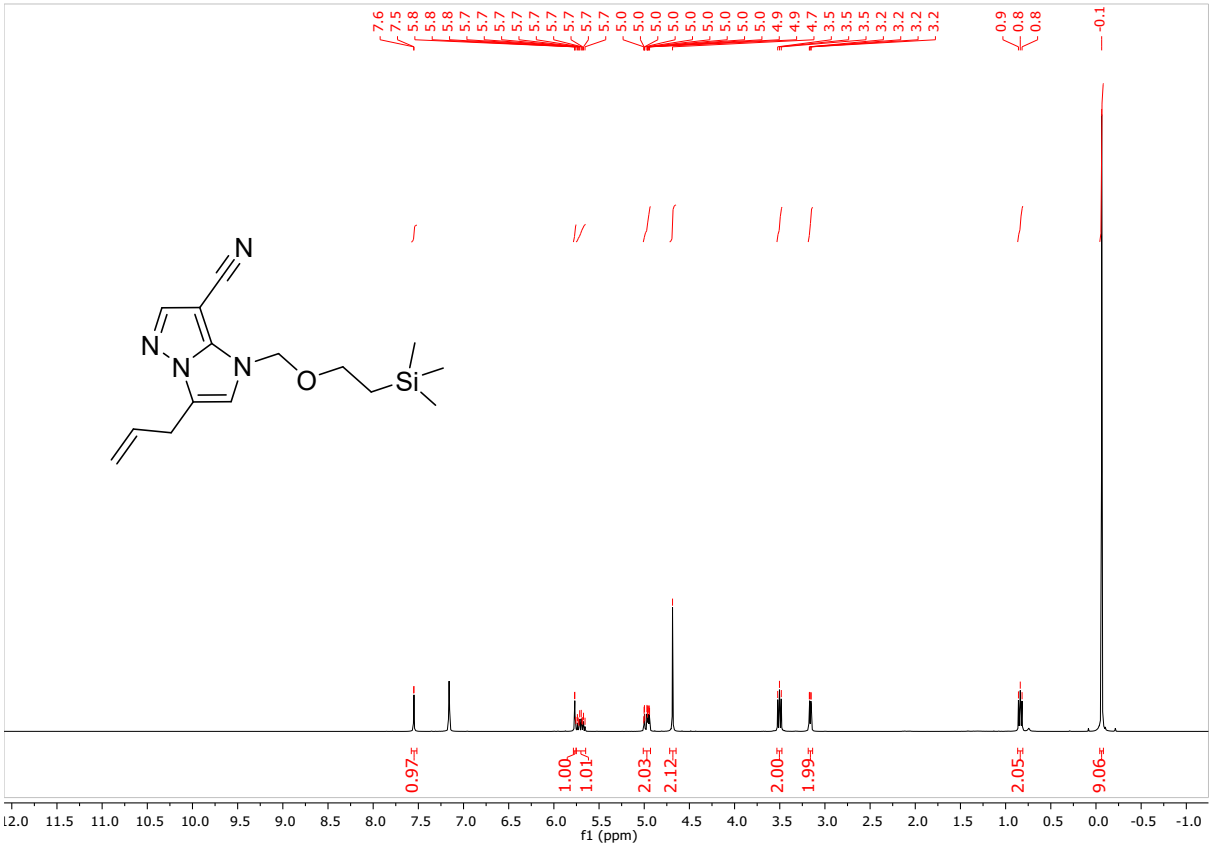


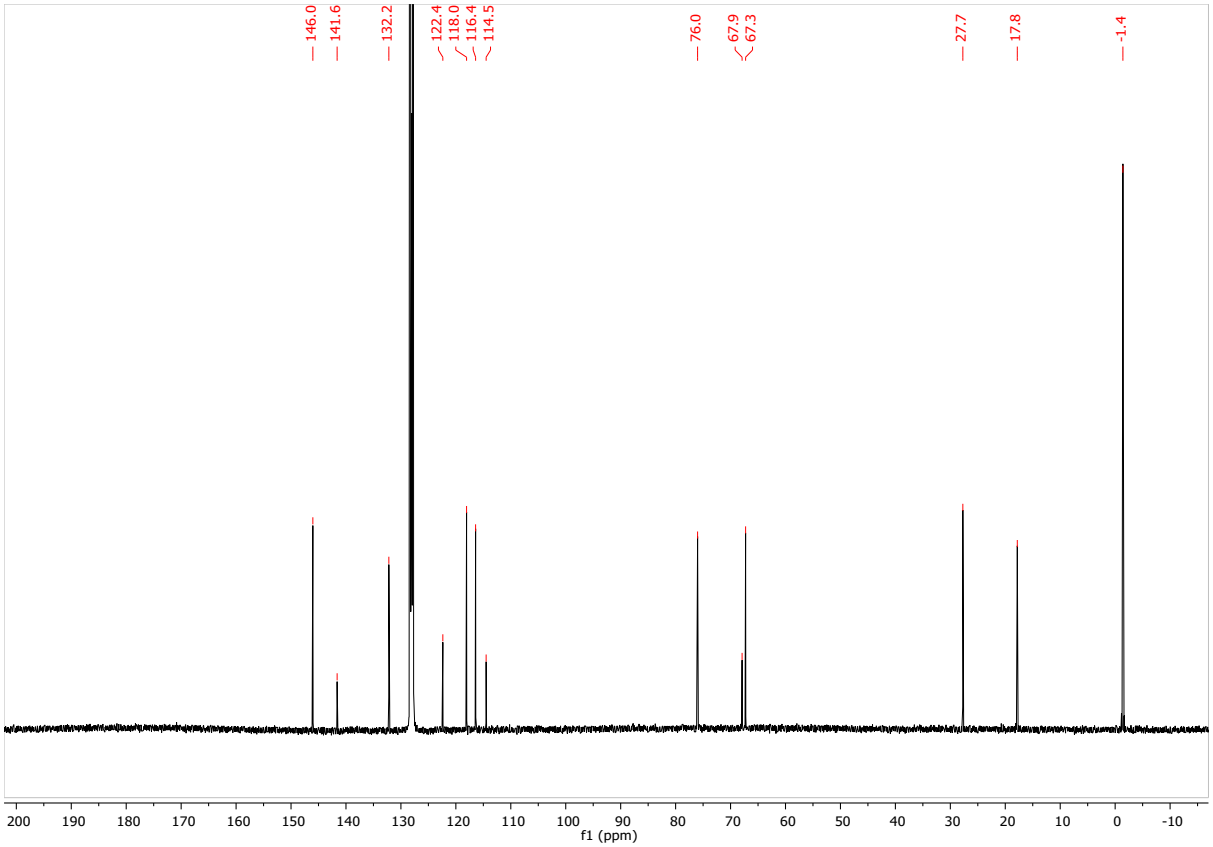

143.1
138.3
137.8
129.4
127.6
127.4
127.0
126.7
126.7
126.1
126.0
126.0
126.0
124.0
121.3
120.7
108.7
98.4
76.0
66.2
17.6
1.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4-(4-(1-((2-(Trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-7-yl)phenyl)-morpholine (7i)

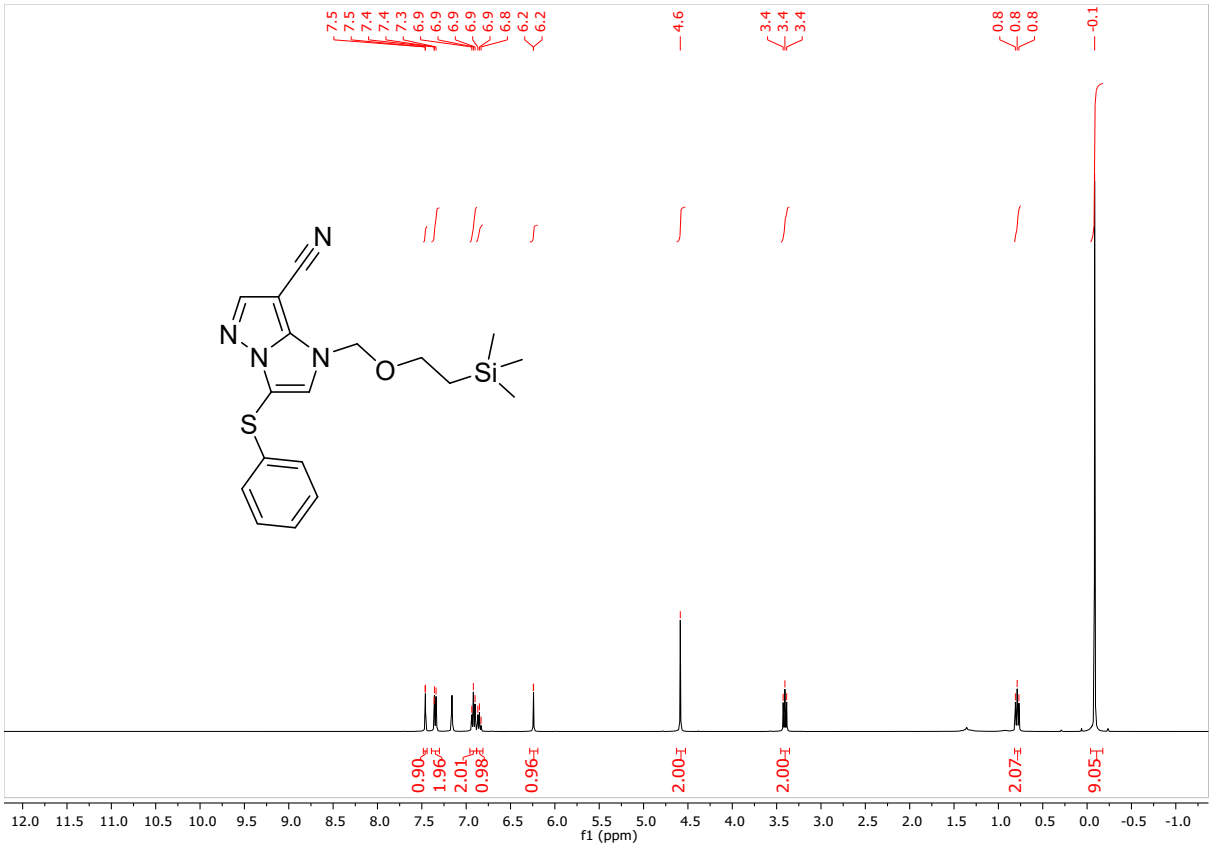

149.9
142.9
138.5
129.6
125.5
120.2
116.5
108.8
99.1
75.8
67.0
66.1
49.7
17.8
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

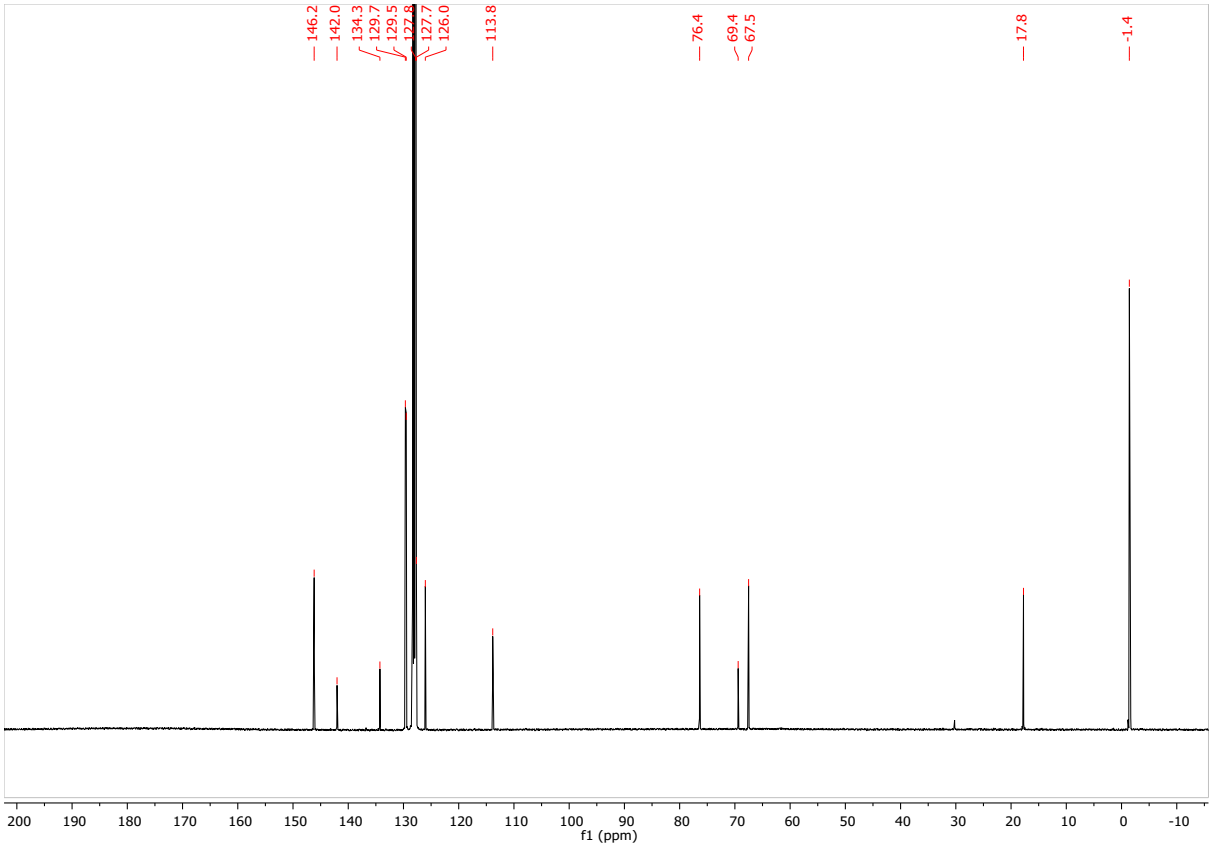
3-Allyl-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10a)



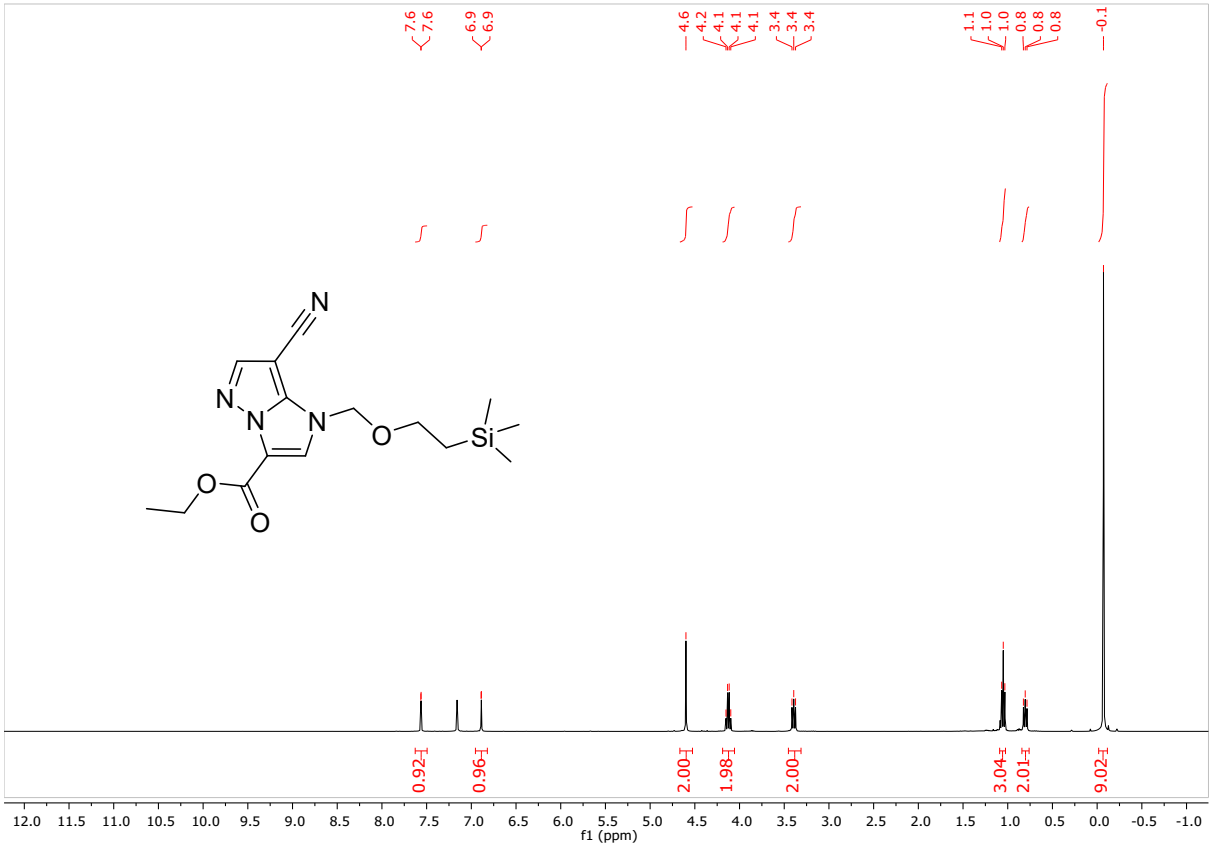


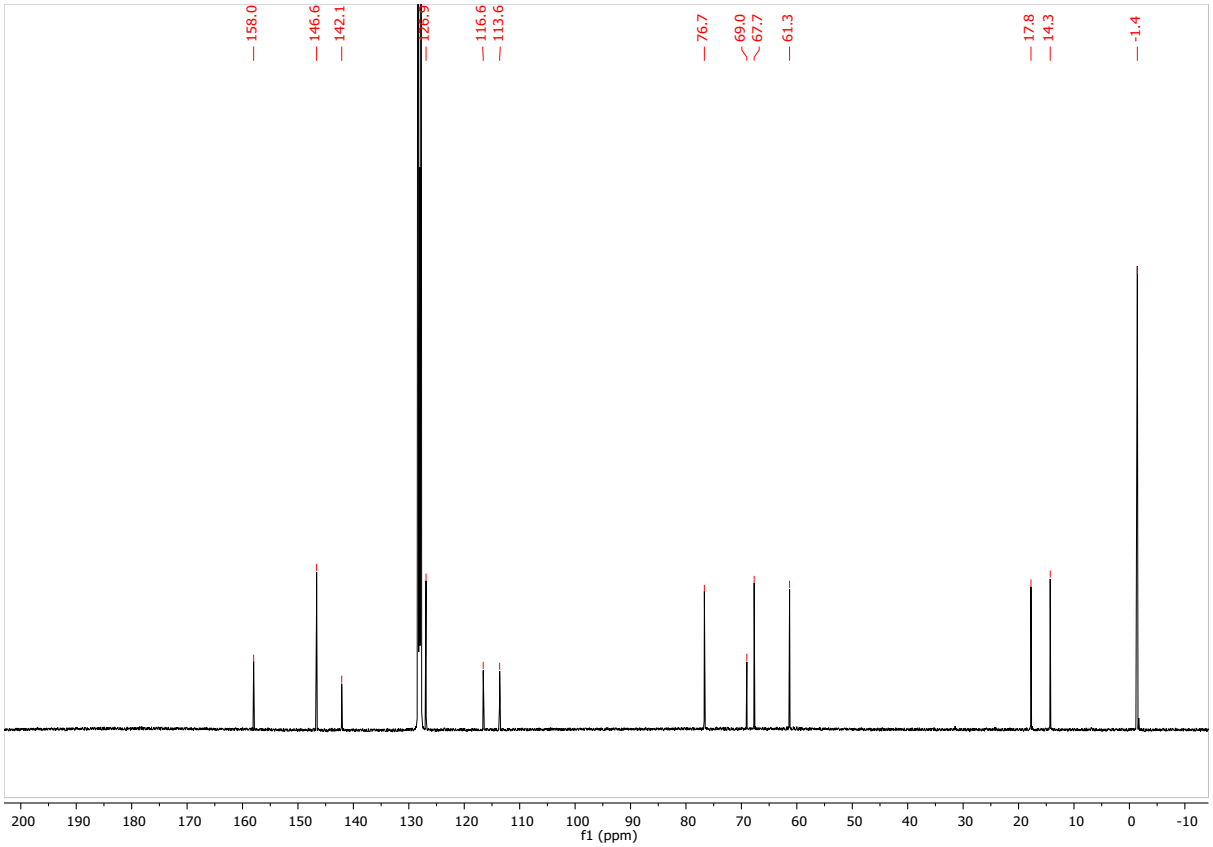
3-(Phenylthio)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10b)


7.5
7.5
7.4
7.4
7.3
6.9
6.9
6.9
6.9
6.8
6.2
6.2
4.6
3.4
3.4
3.4
0.8
0.8
0.8
-0.1
N
N
N
N
O
Si
S
0.90
1.96
2.01
0.98
0.96
2.00
2.00
2.07
9.05
f1 (ppm)

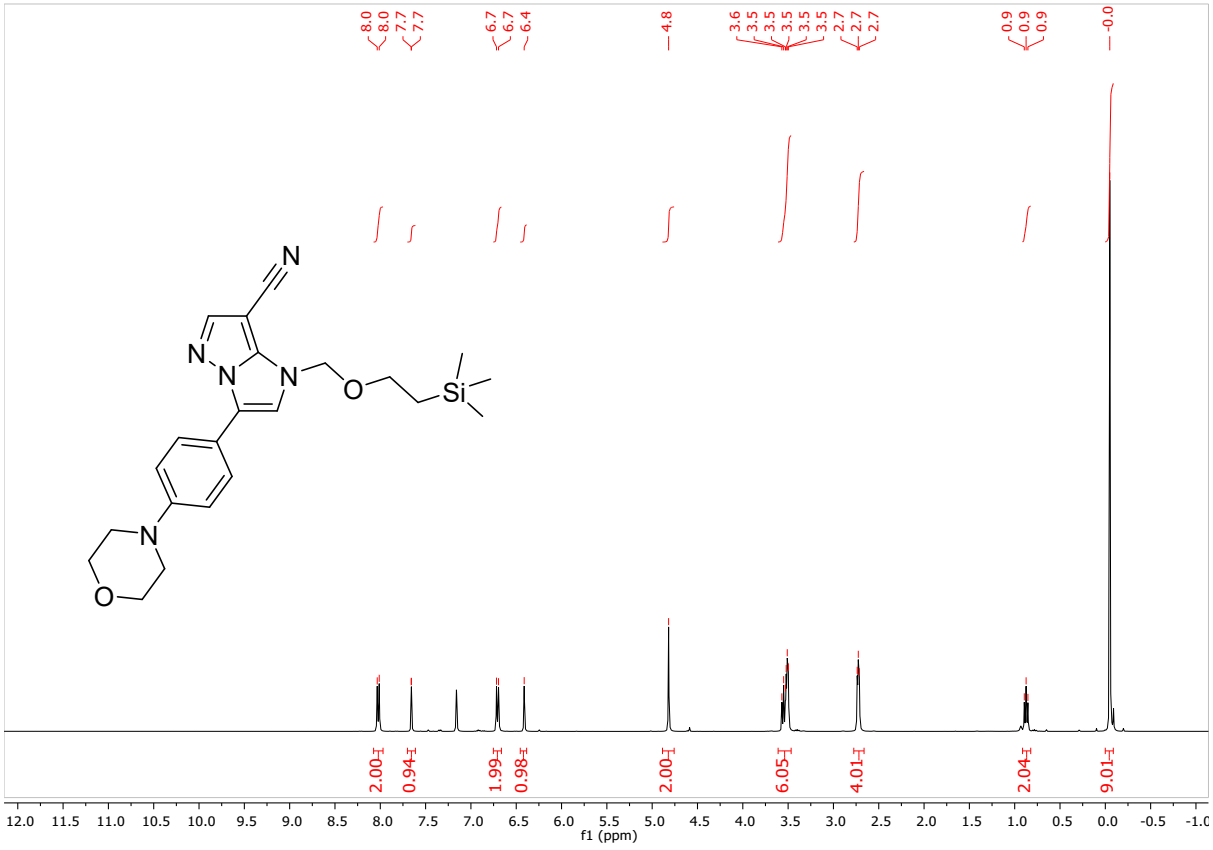

146.2
142.0
134.3
129.7
129.5
127.8
127.7
126.0
113.8
76.4
69.4
67.5
17.8
-1.4
f1 (ppm)

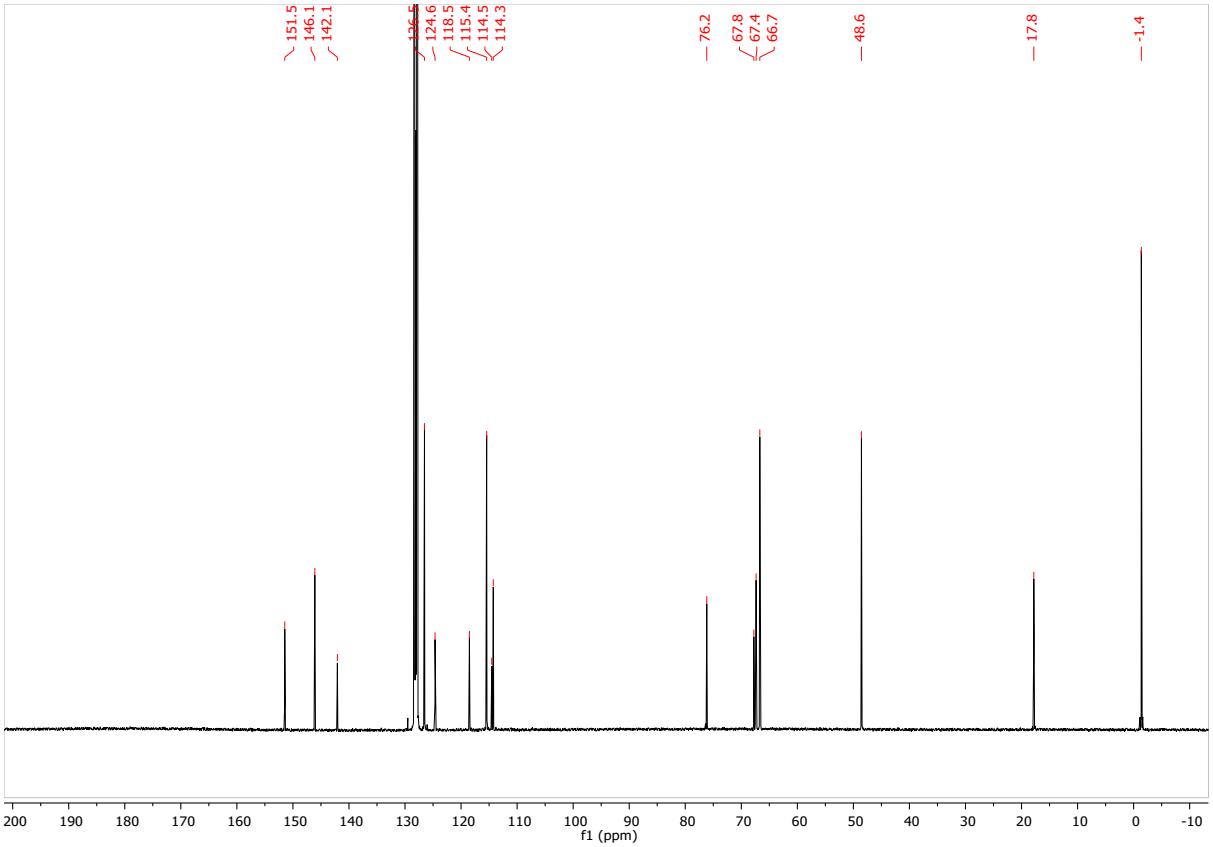
Ethyl 7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (10c)



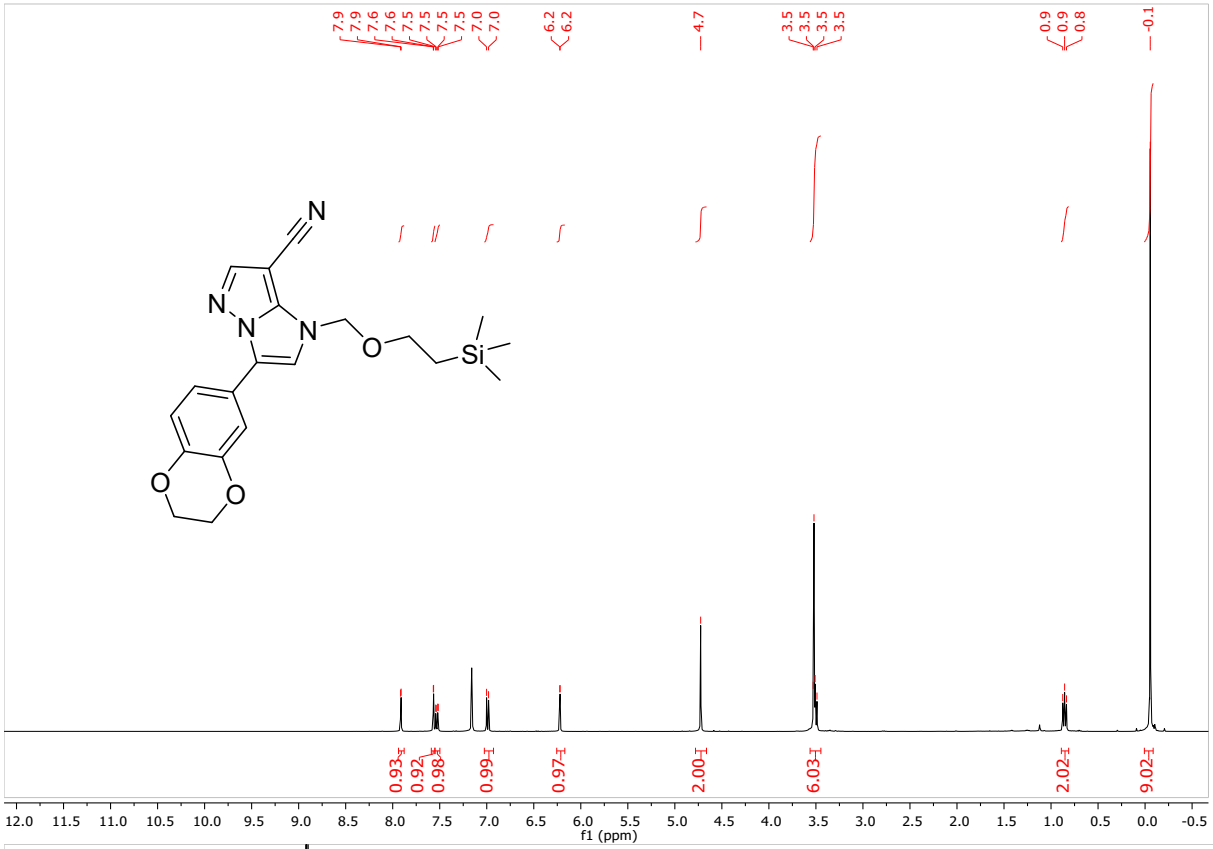

158.0
146.6
142.1
126.9
116.6
113.6
76.7
69.0
67.7
61.3
17.8
14.3
-1.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

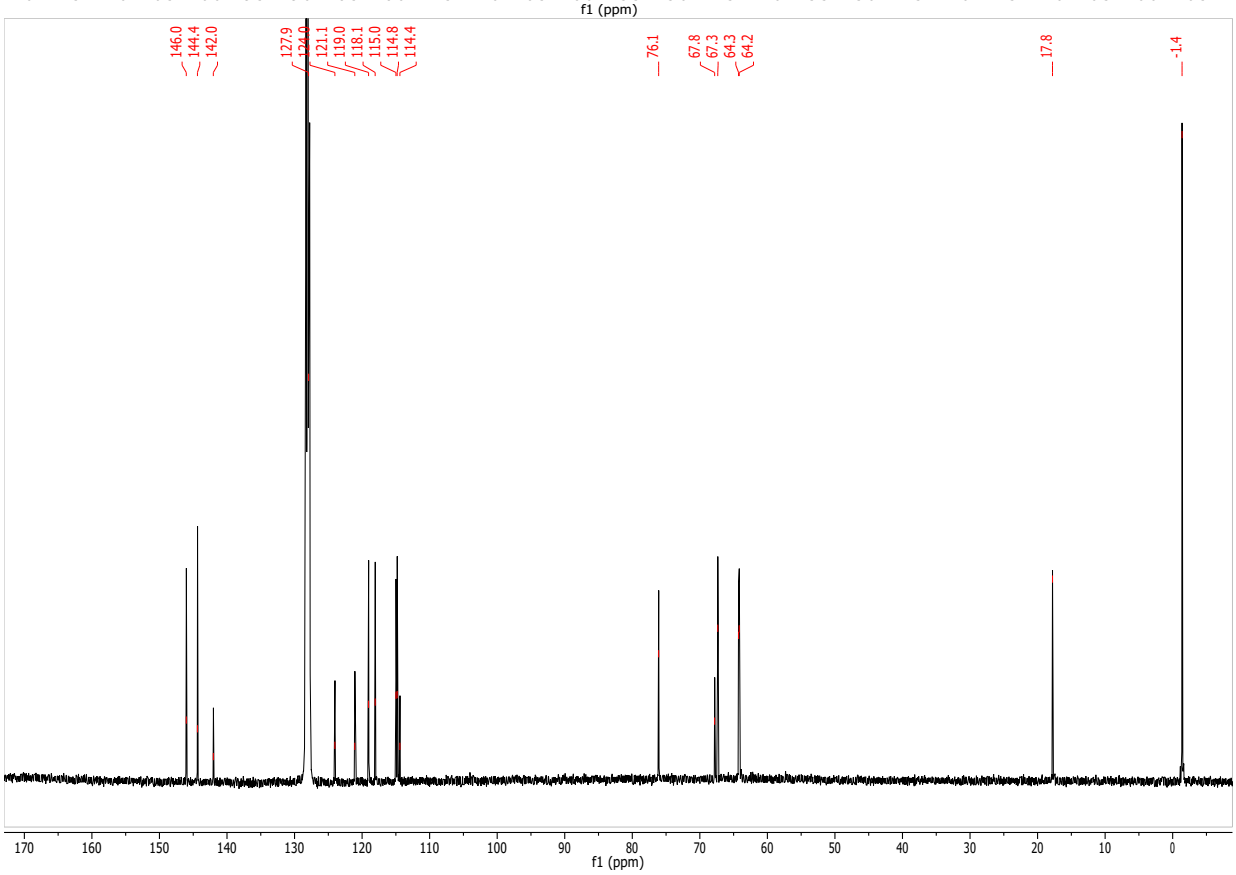
3-(4-Morpholinophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10d)



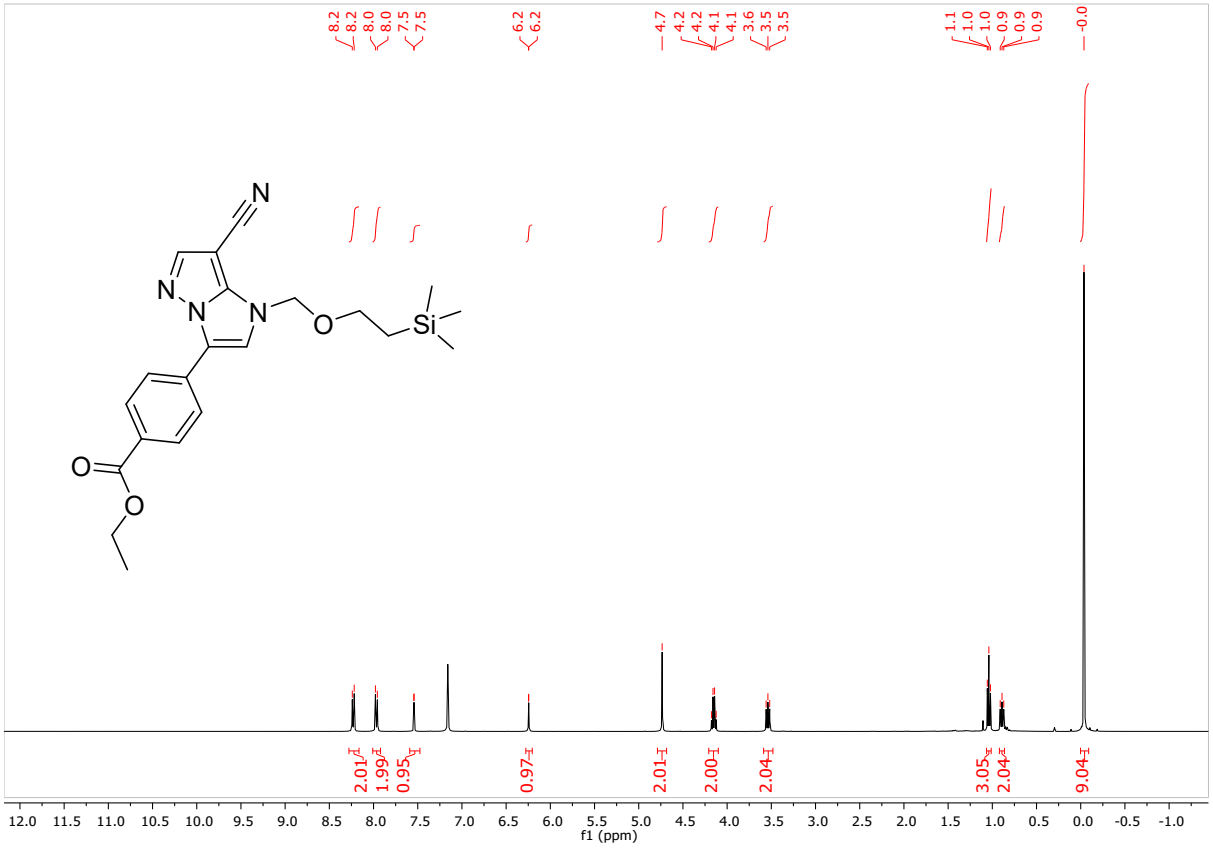

151.5
146.1
142.1
136.5
124.6
118.5
115.4
114.5
114.3
76.2
67.8
67.4
66.7
48.6
17.8
-1.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

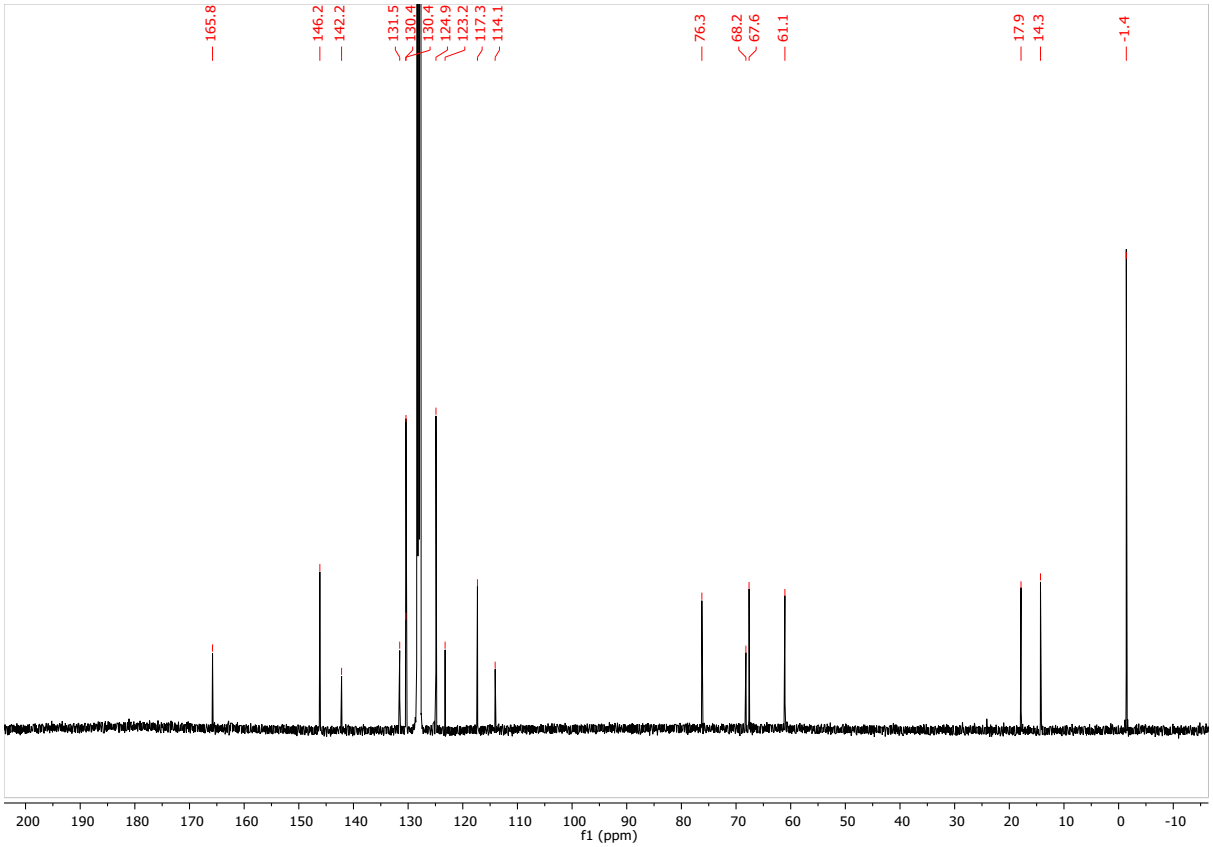
3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-7-carbonitrile (10e)



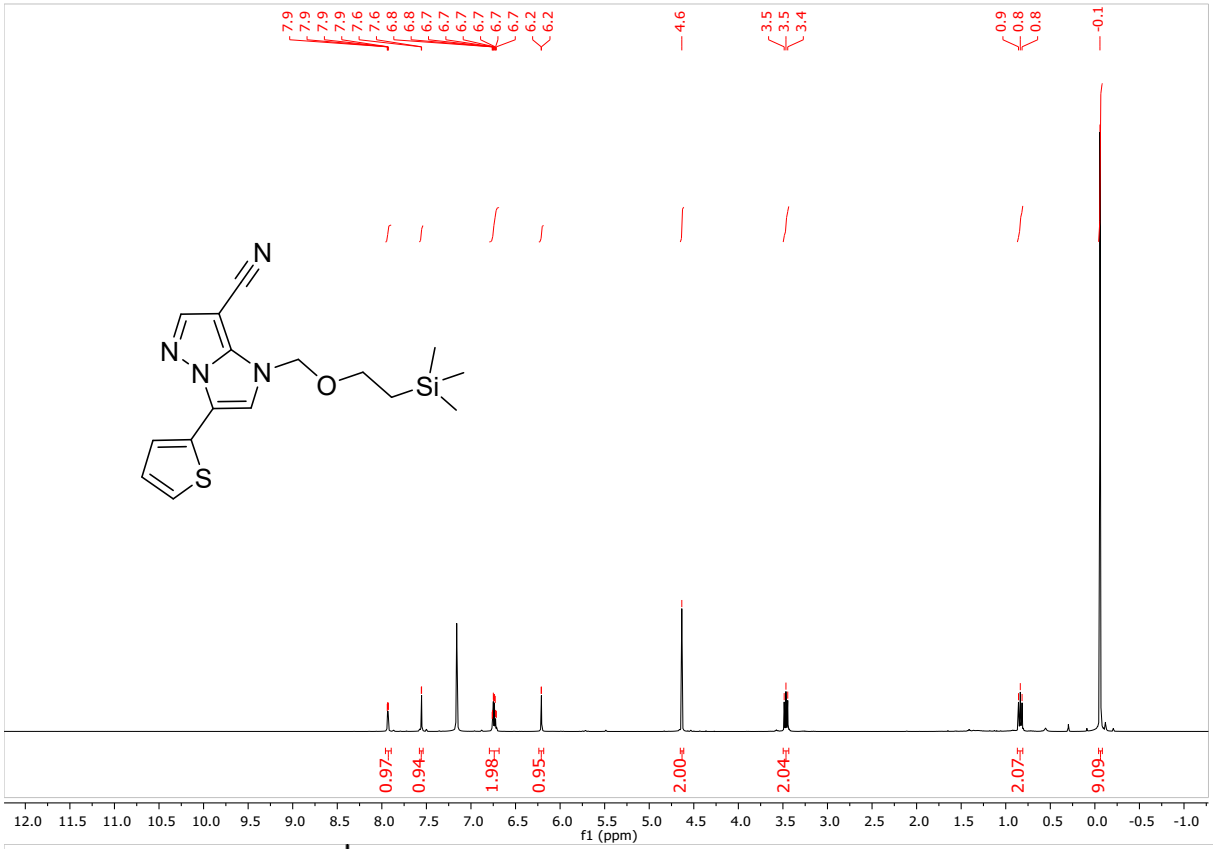


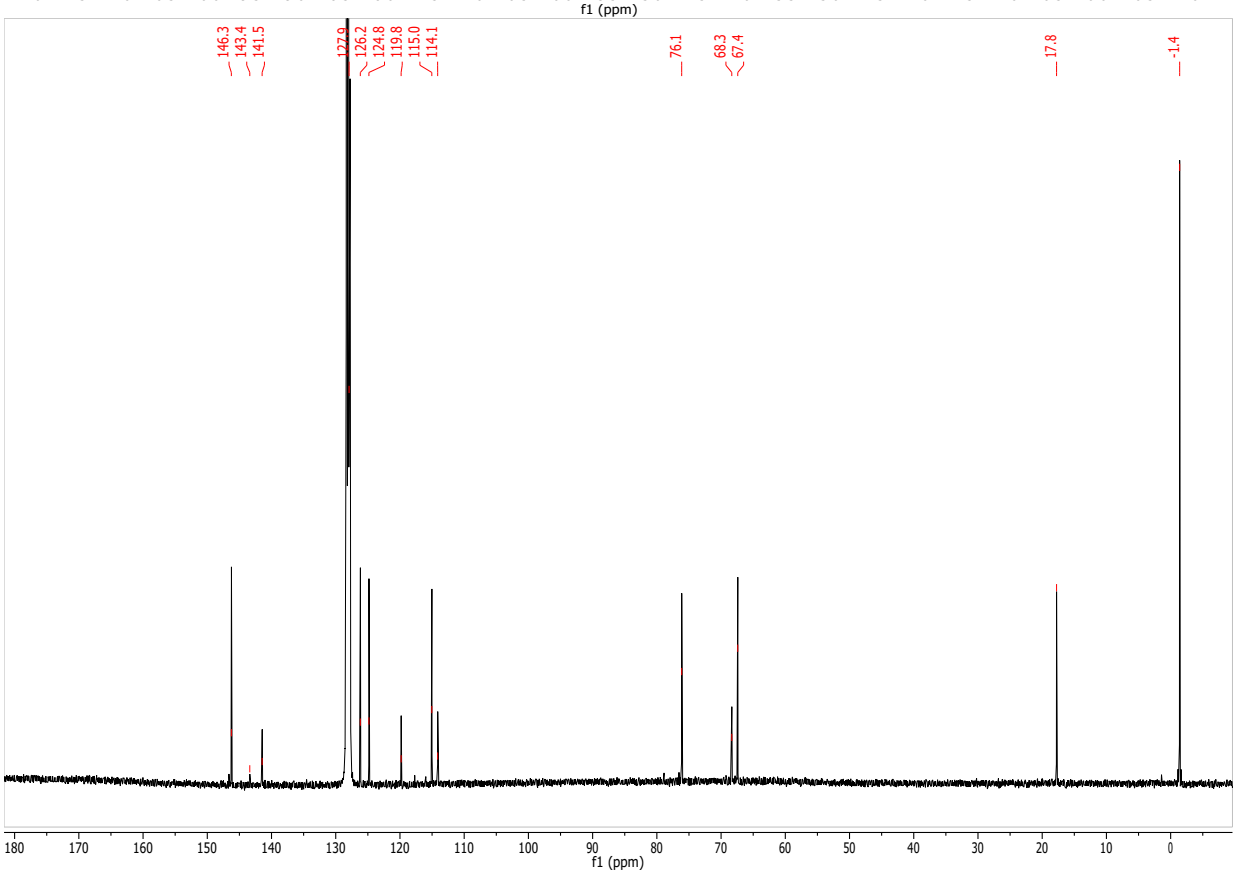
Ethyl 4-(7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazol-3-yl)-benzoate (10f)



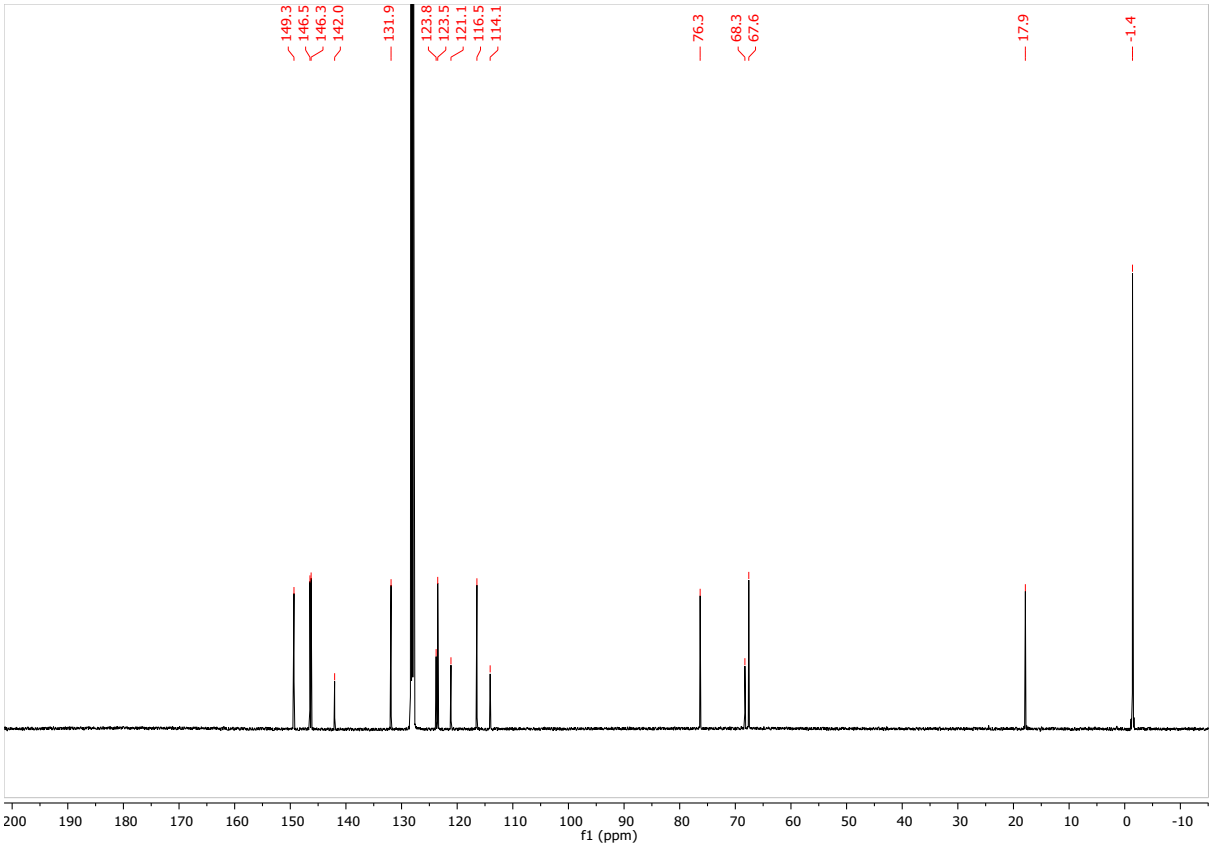

165.8
146.2
142.2
131.5
130.4
130.4
124.9
123.2
117.3
114.1
76.3
68.2
67.6
61.1
17.9
14.3
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3-(Thiophen-2-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10g)

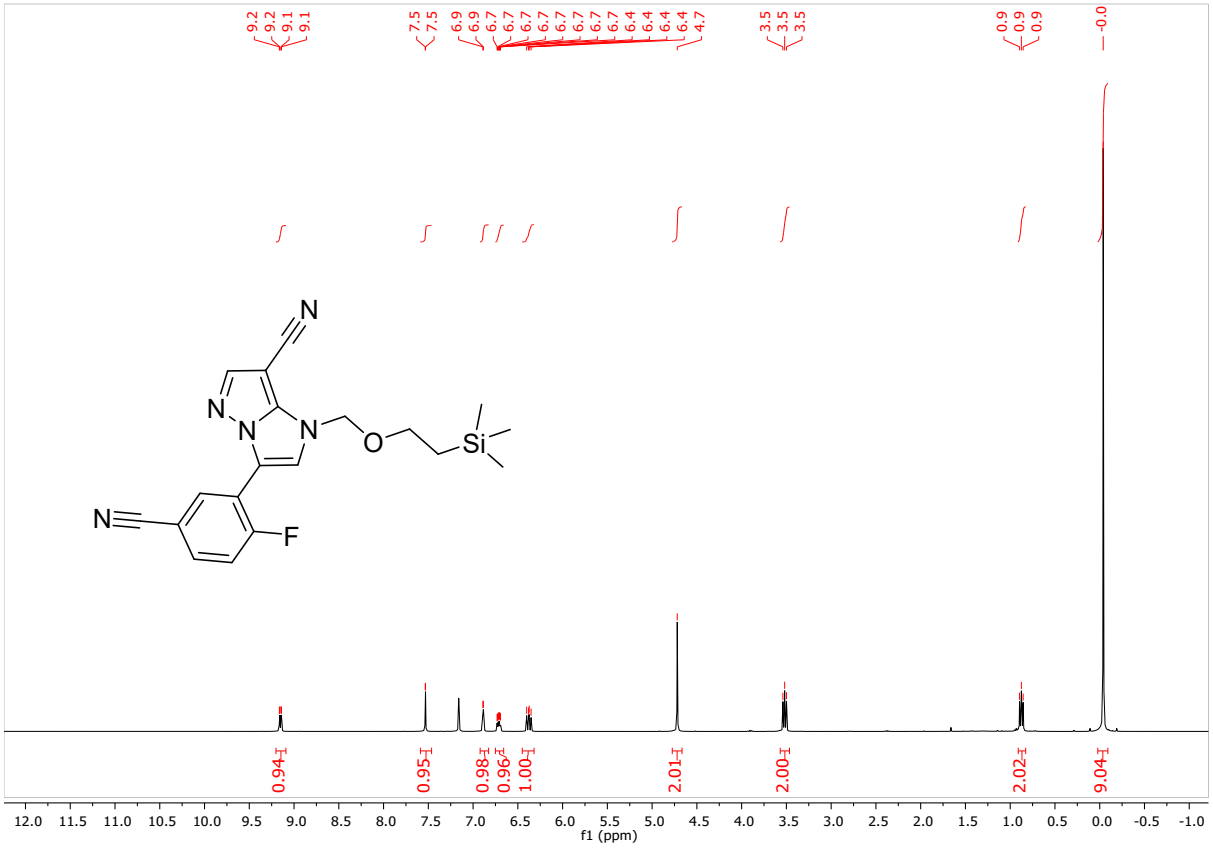


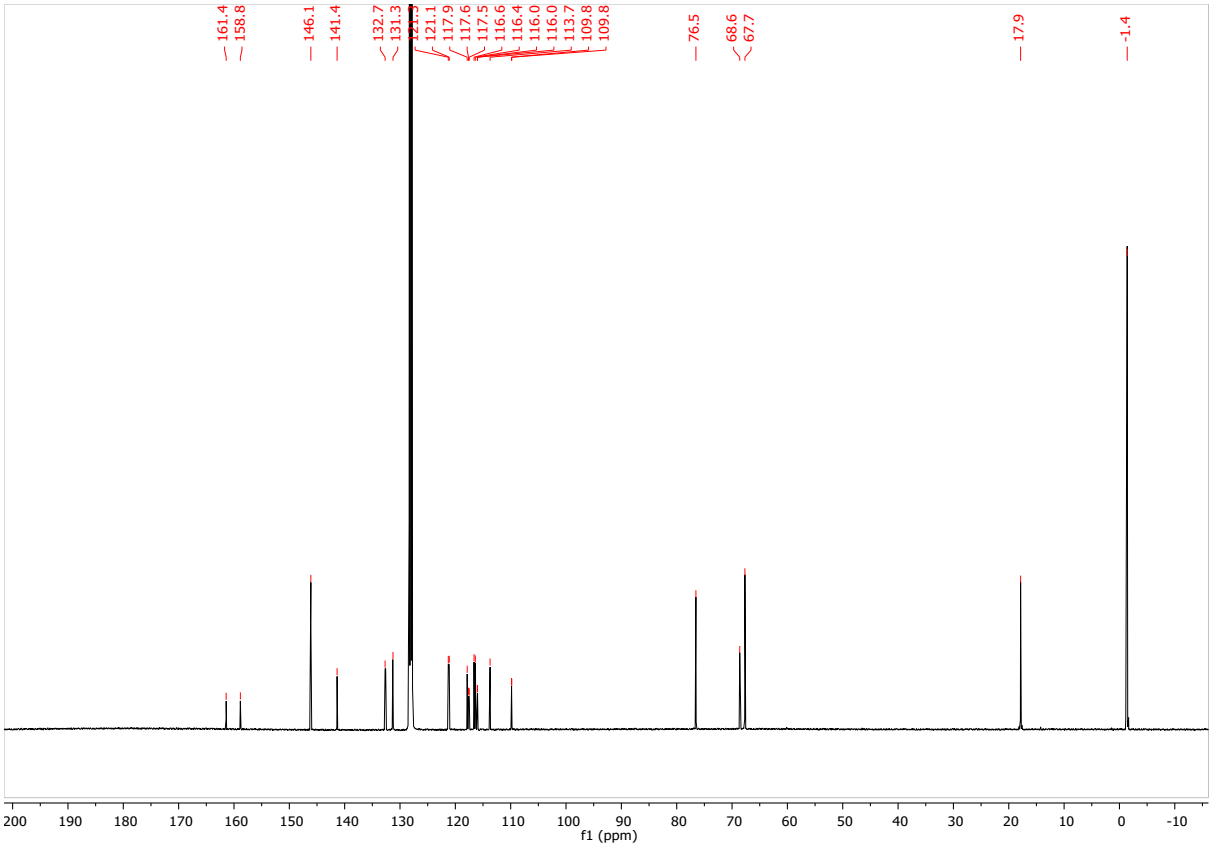


3-(Pyridin-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10h)

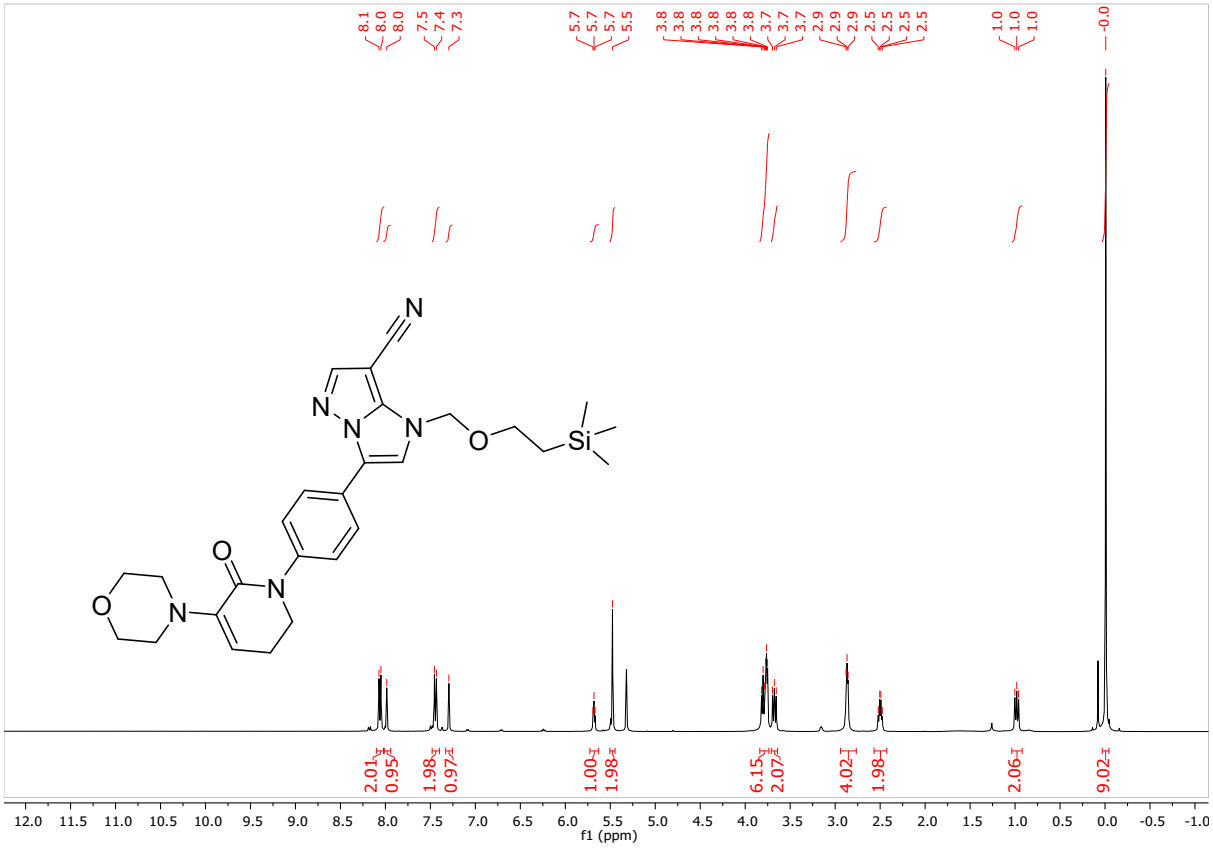

149.3
146.5
146.3
142.0
131.9
123.8
123.5
121.1
116.5
114.1
76.3
68.3
67.6
17.9
-1.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

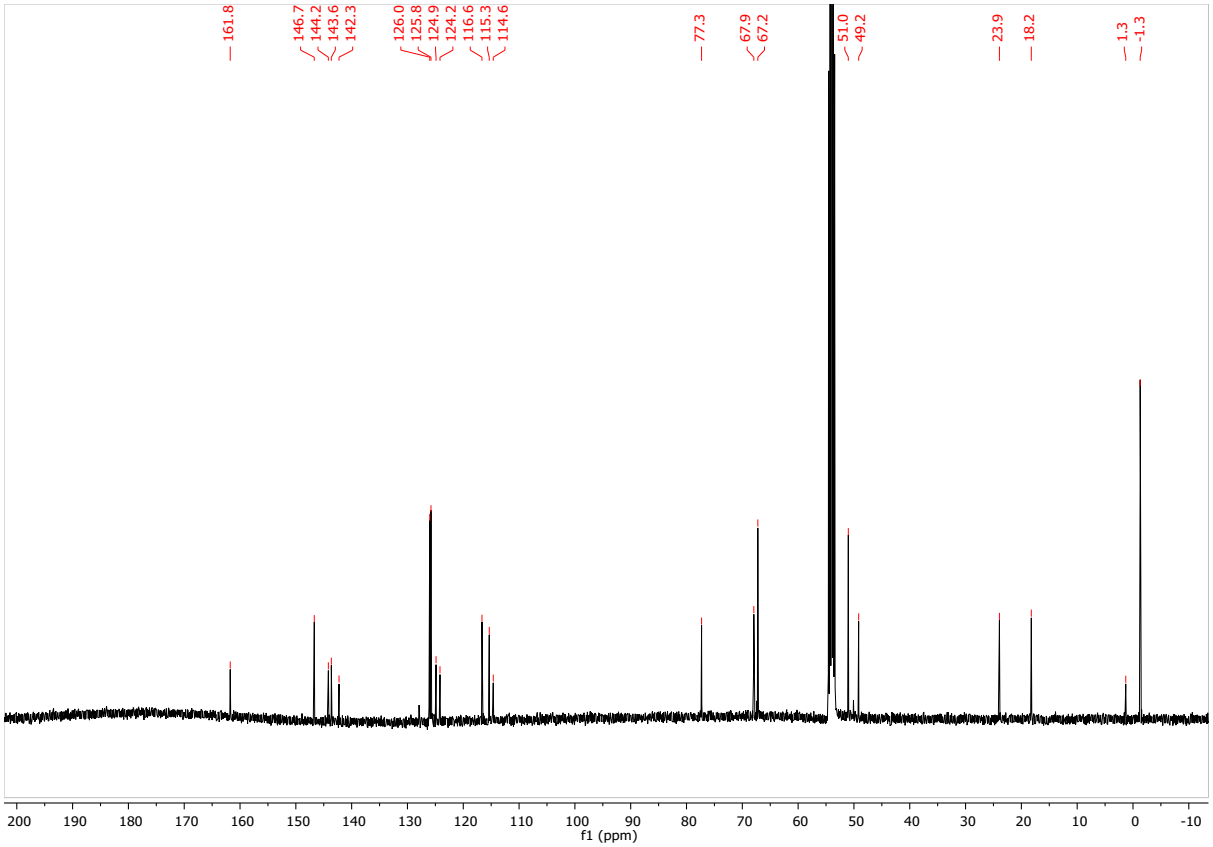
3-(5-Cyano-2-fluorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10i)



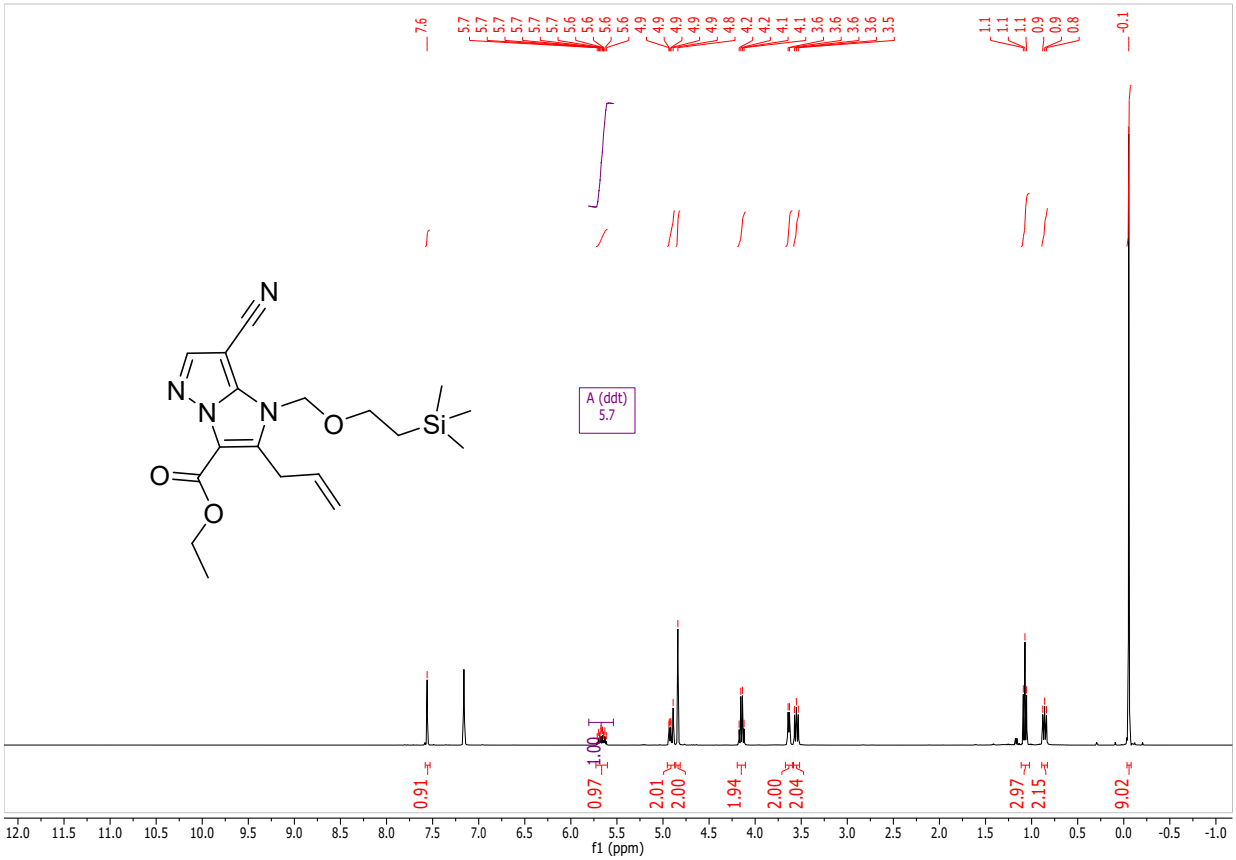

161.4
158.8
146.1
141.4
132.7
131.3
121.5
121.1
117.9
117.6
117.5
116.6
116.4
116.0
116.0
113.7
109.8
109.8
76.5
68.6
67.7
17.9
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

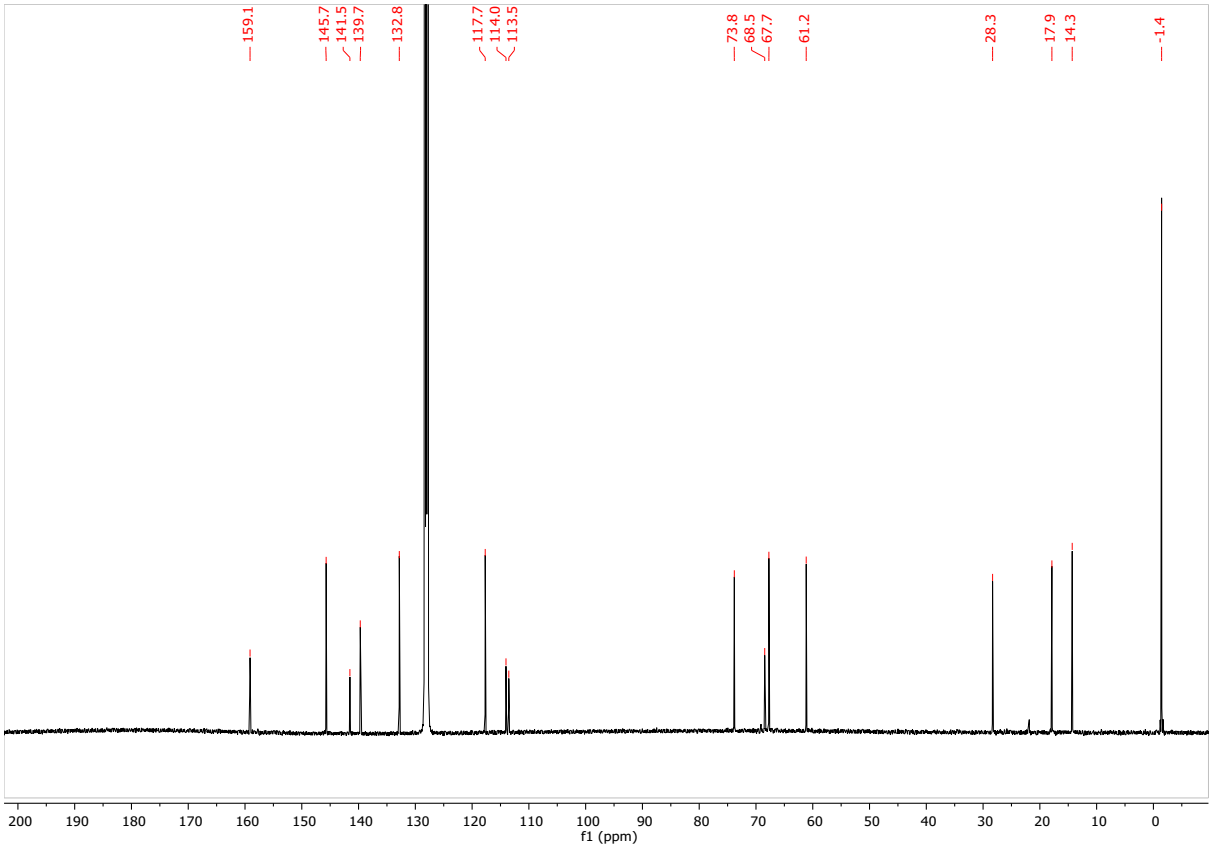
3-(4-(5-Morpholino-6-oxo-3,6-dihydropyridin-1(2*H*)-yl)phenyl)-1-((2-(trimethylsilyl)-ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (10j)



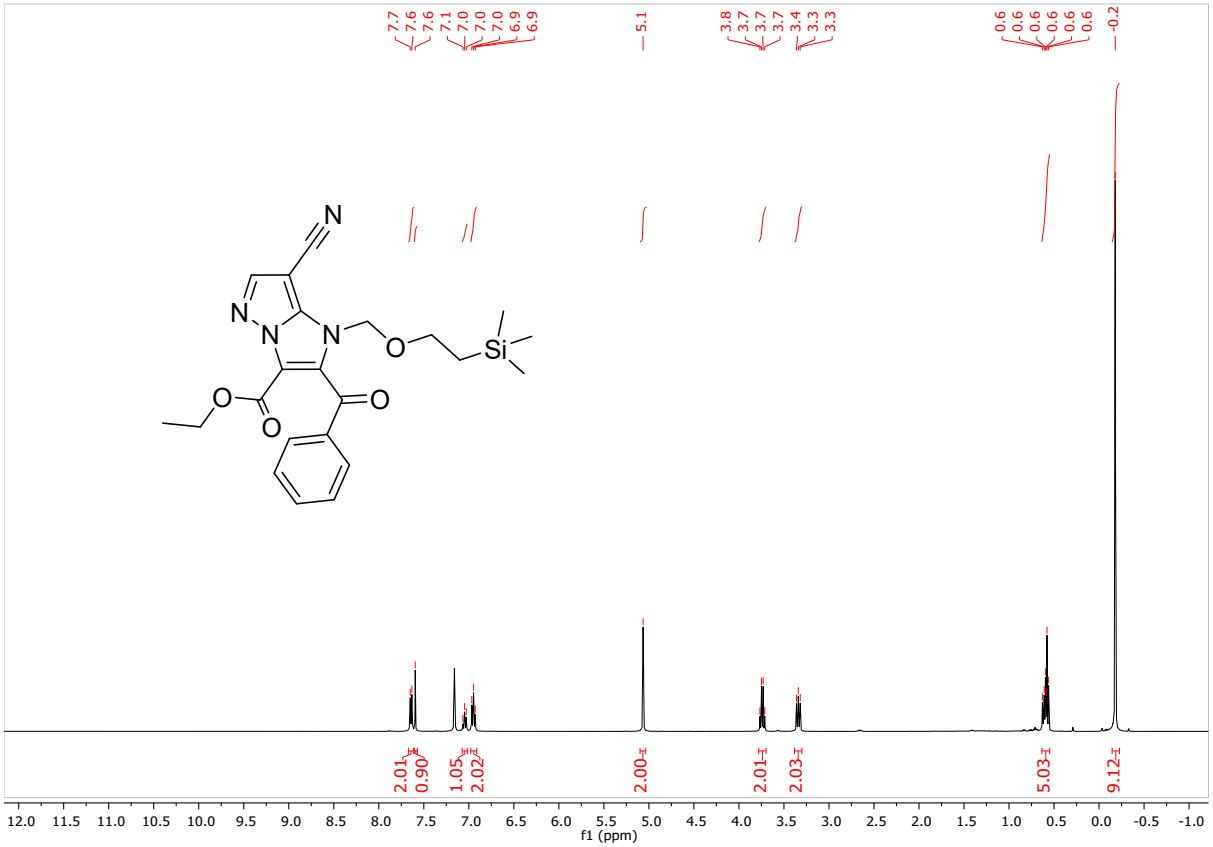

161.8
146.7
144.2
143.6
142.3
126.0
125.8
124.9
124.2
116.6
115.3
114.6
77.3
67.9
67.2
51.0
49.2
23.9
18.2
1.3
-1.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

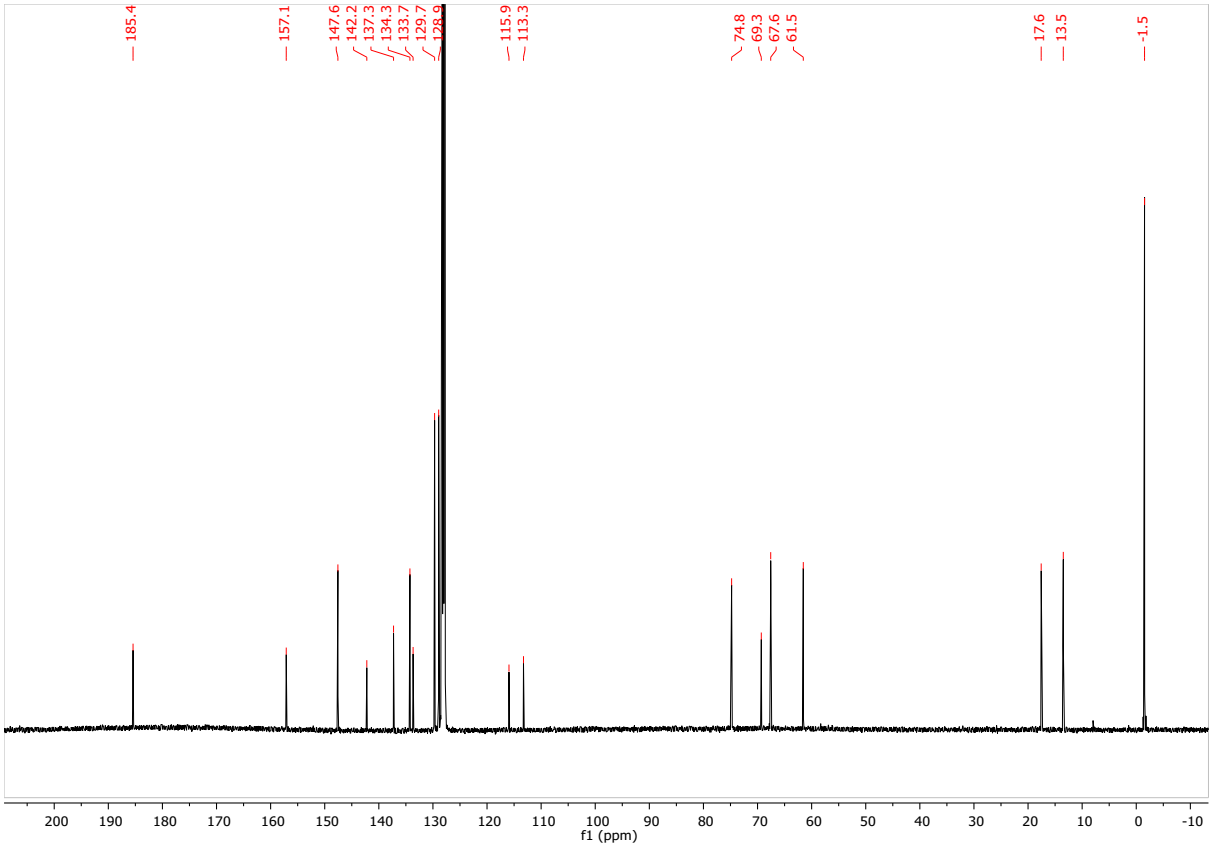
Ethyl 2-allyl-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11a)



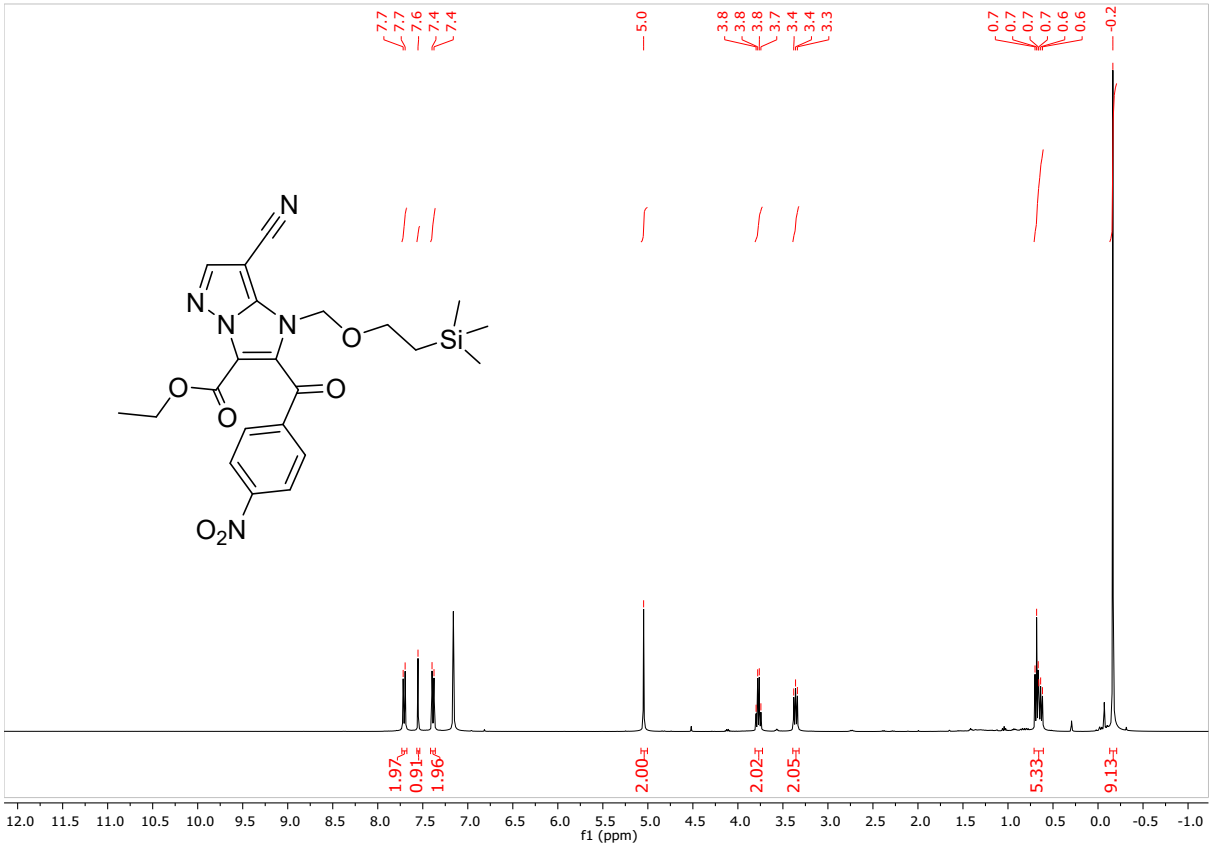


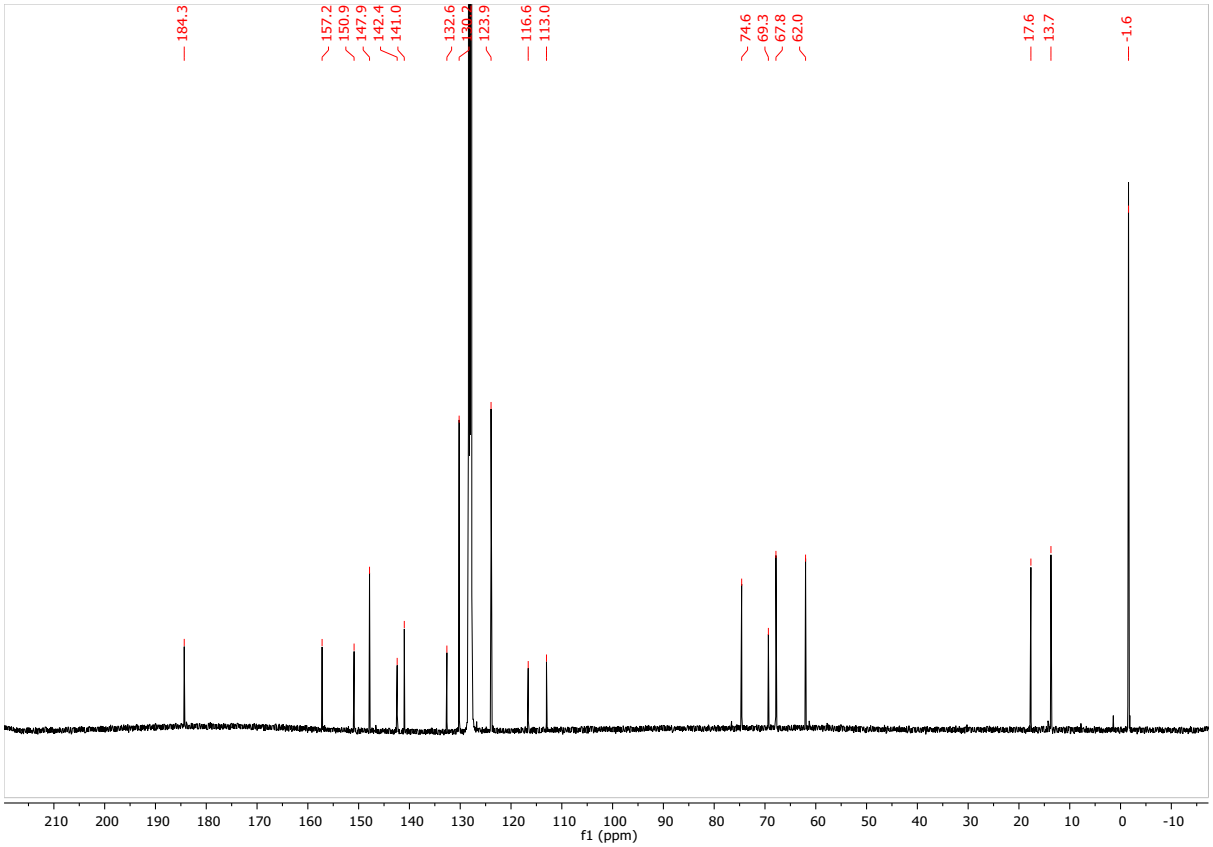
Ethyl 2-benzoyl-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11b)



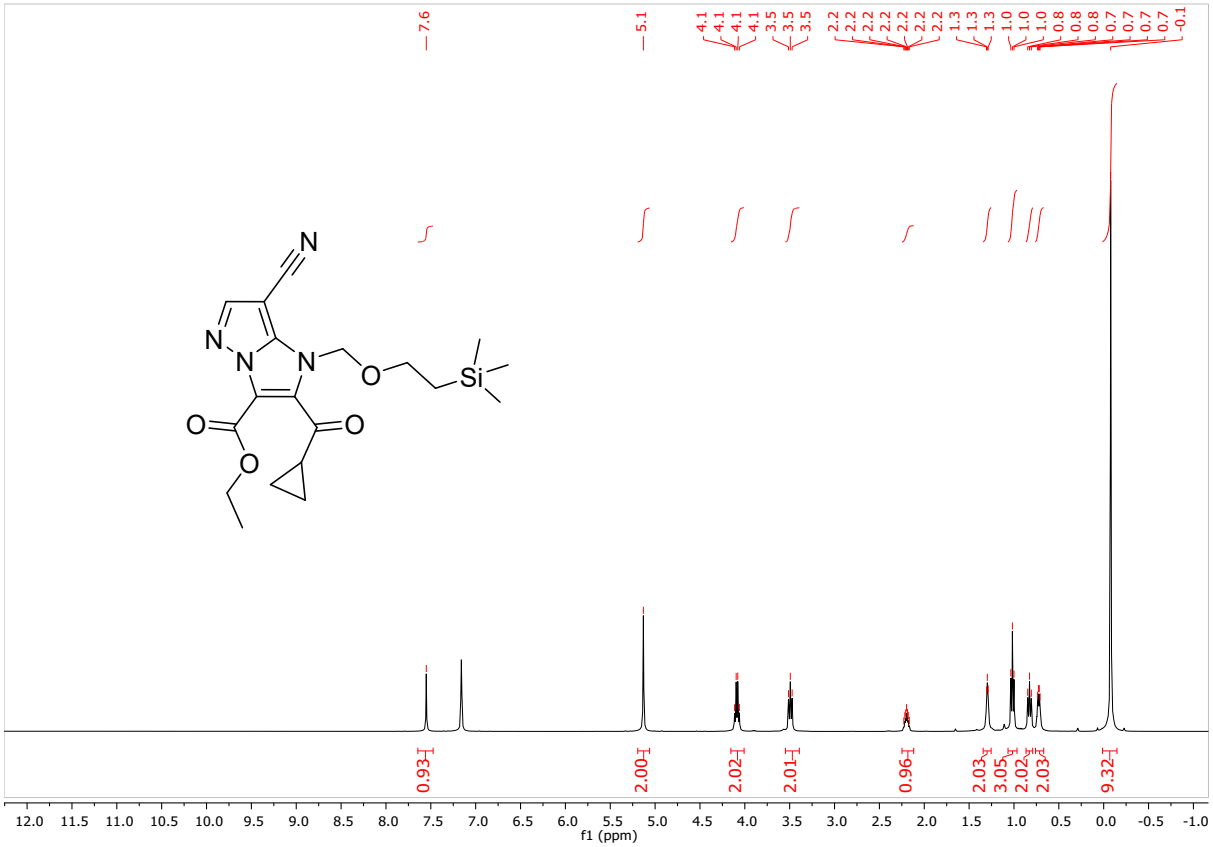

185.4
157.1
147.6
142.2
137.3
134.3
133.7
129.7
128.9
115.9
113.3
74.8
69.3
67.6
61.5
17.6
13.5
-1.5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

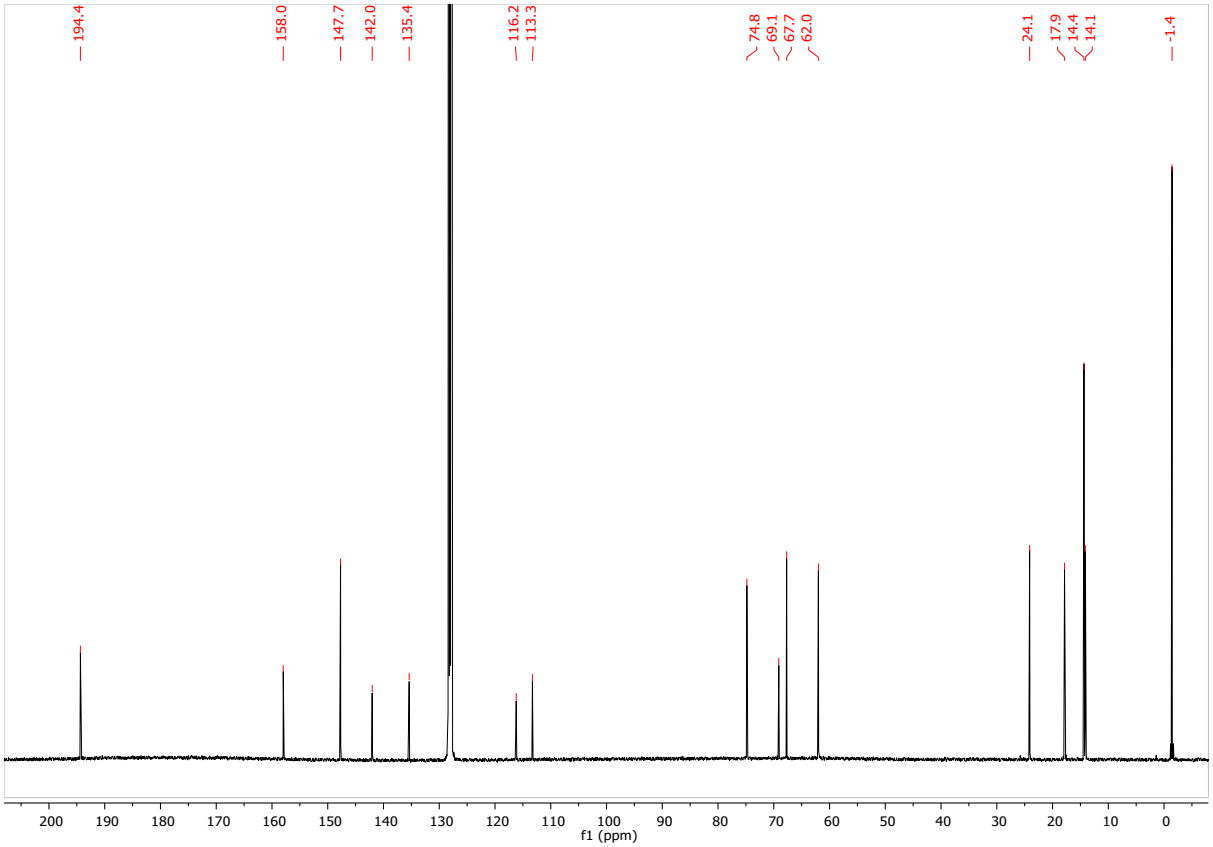
Ethyl 7-cyano-2-(4-nitrobenzoyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate (11c)



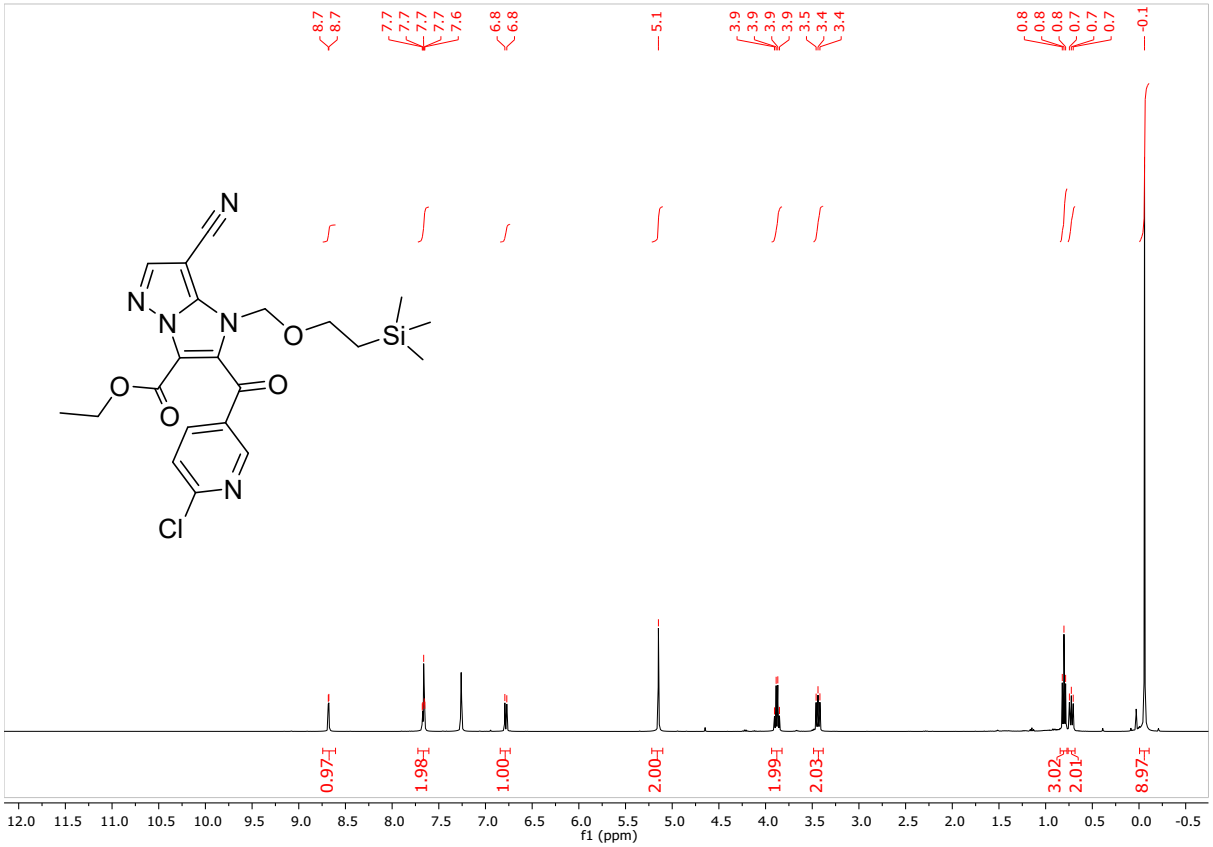

184.3
157.2
150.9
147.9
142.4
141.0
132.6
130.2
123.9
116.6
113.0
74.6
69.3
67.8
62.0
17.6
13.7
-1.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

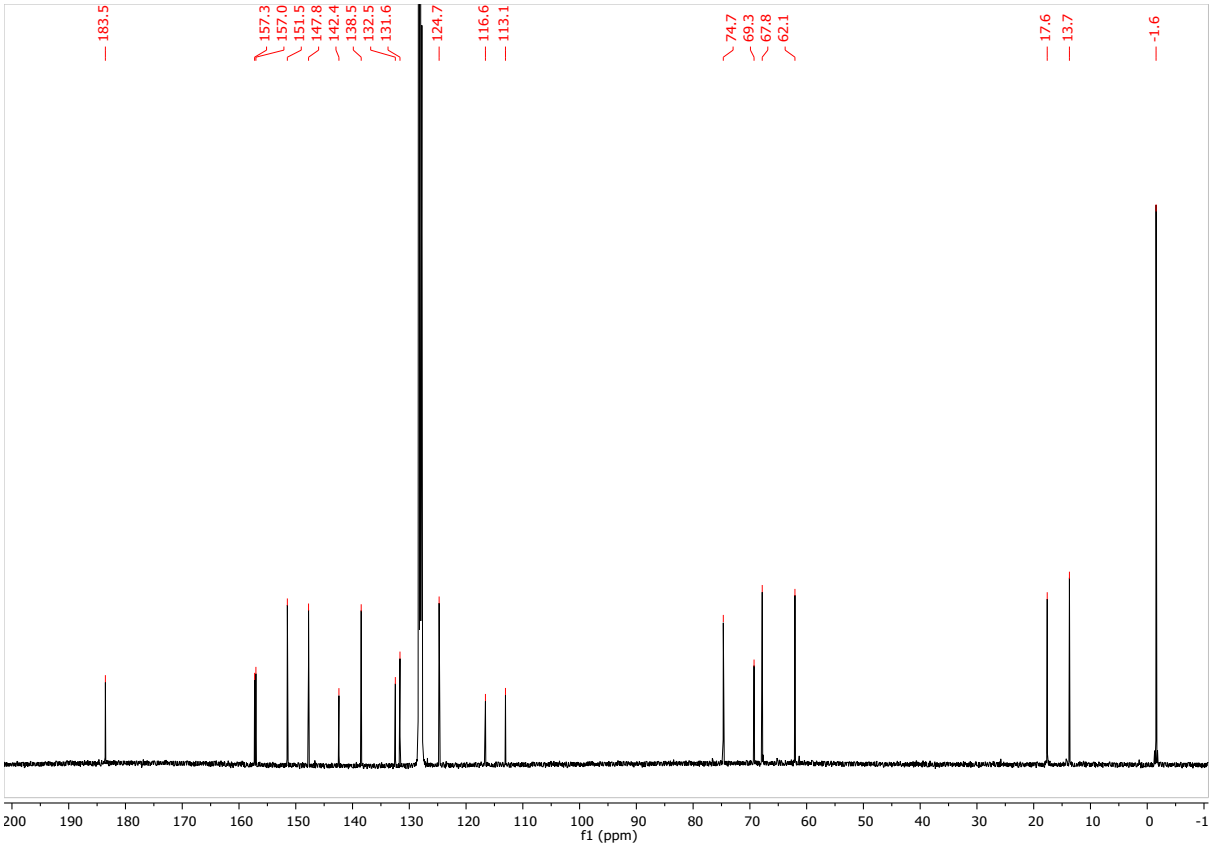
Ethyl 7-cyano-2-(cyclopropanecarbonyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11d)



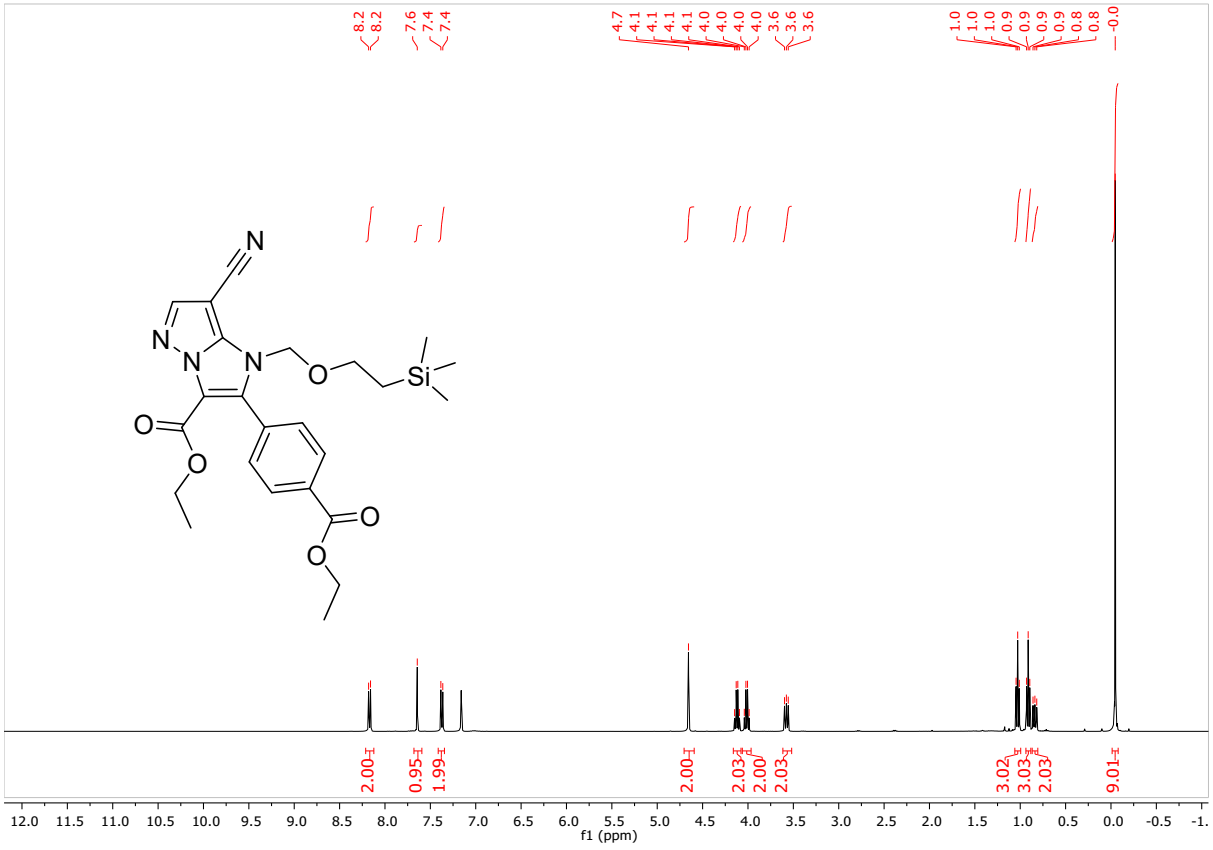

194.4
158.0
147.7
142.0
135.4
116.2
113.3
74.8
69.1
67.7
62.0
24.1
17.9
14.4
14.1
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

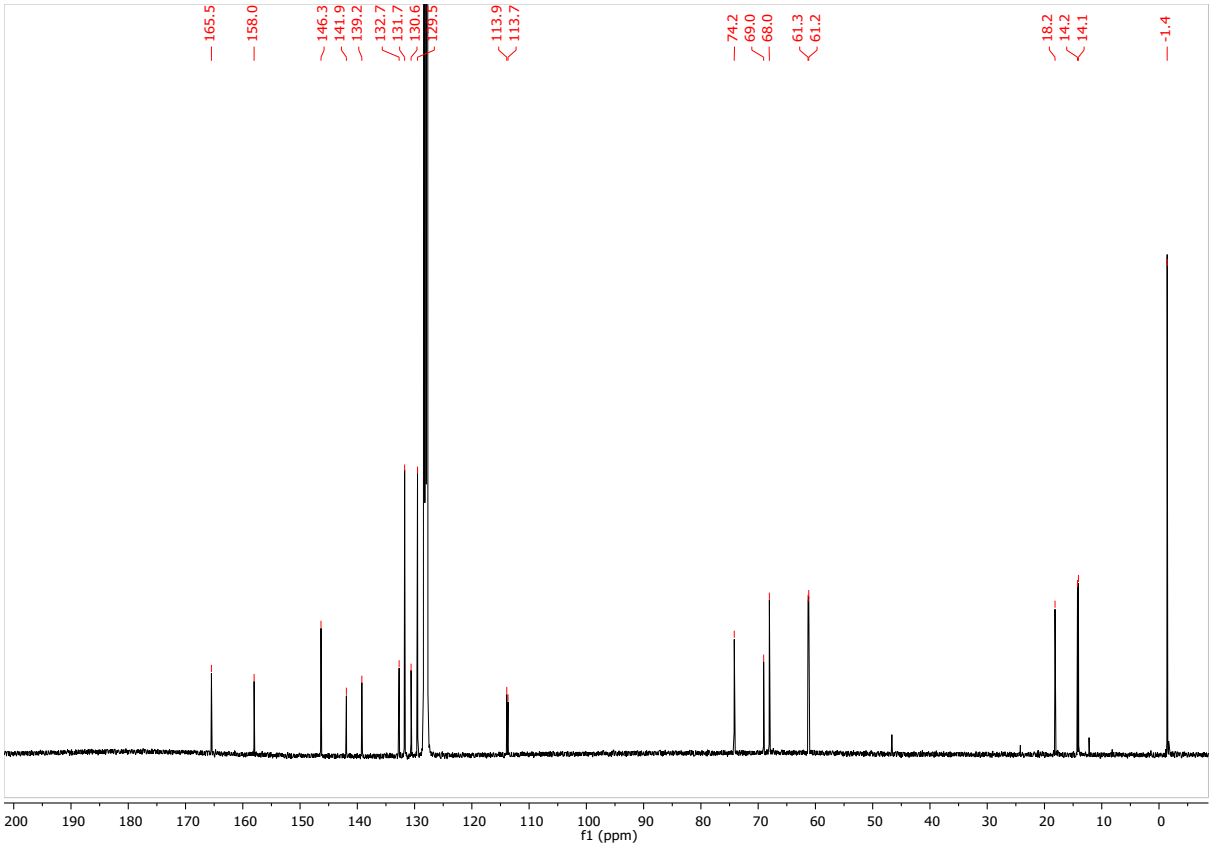
Ethyl 2-(6-chloronicotinoyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate (11e)



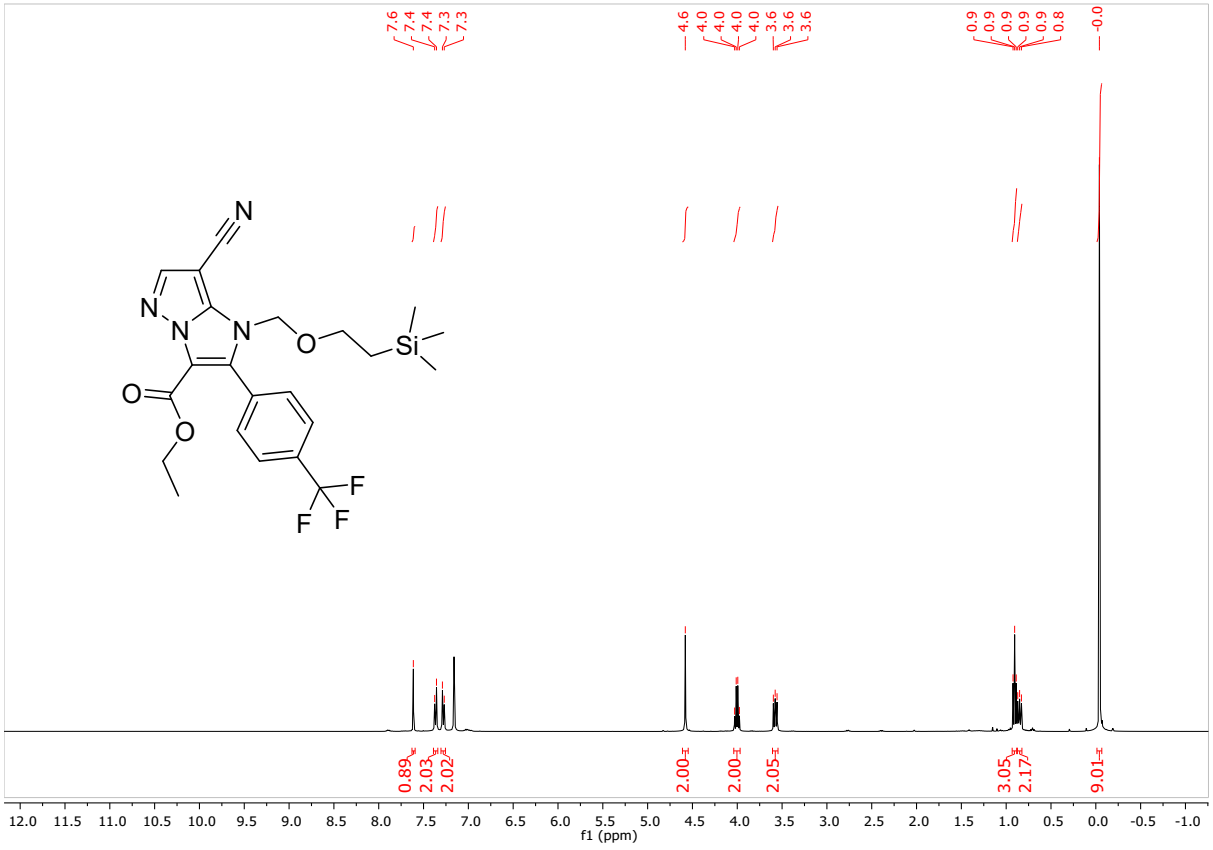

183.5
157.3
157.0
151.5
147.8
142.4
138.5
132.5
131.6
124.7
116.6
113.1
74.7
69.3
67.8
62.1
17.6
13.7
-1.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

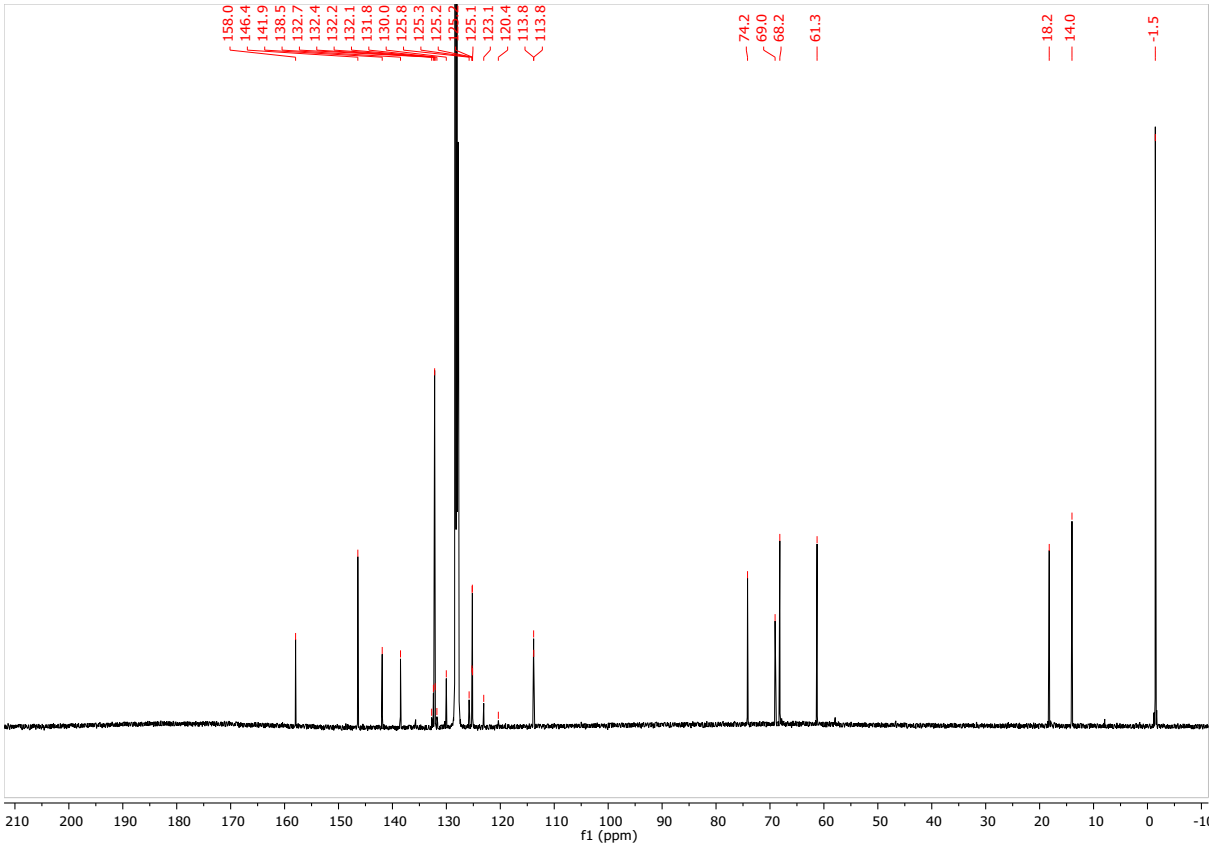
Ethyl 7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11f)



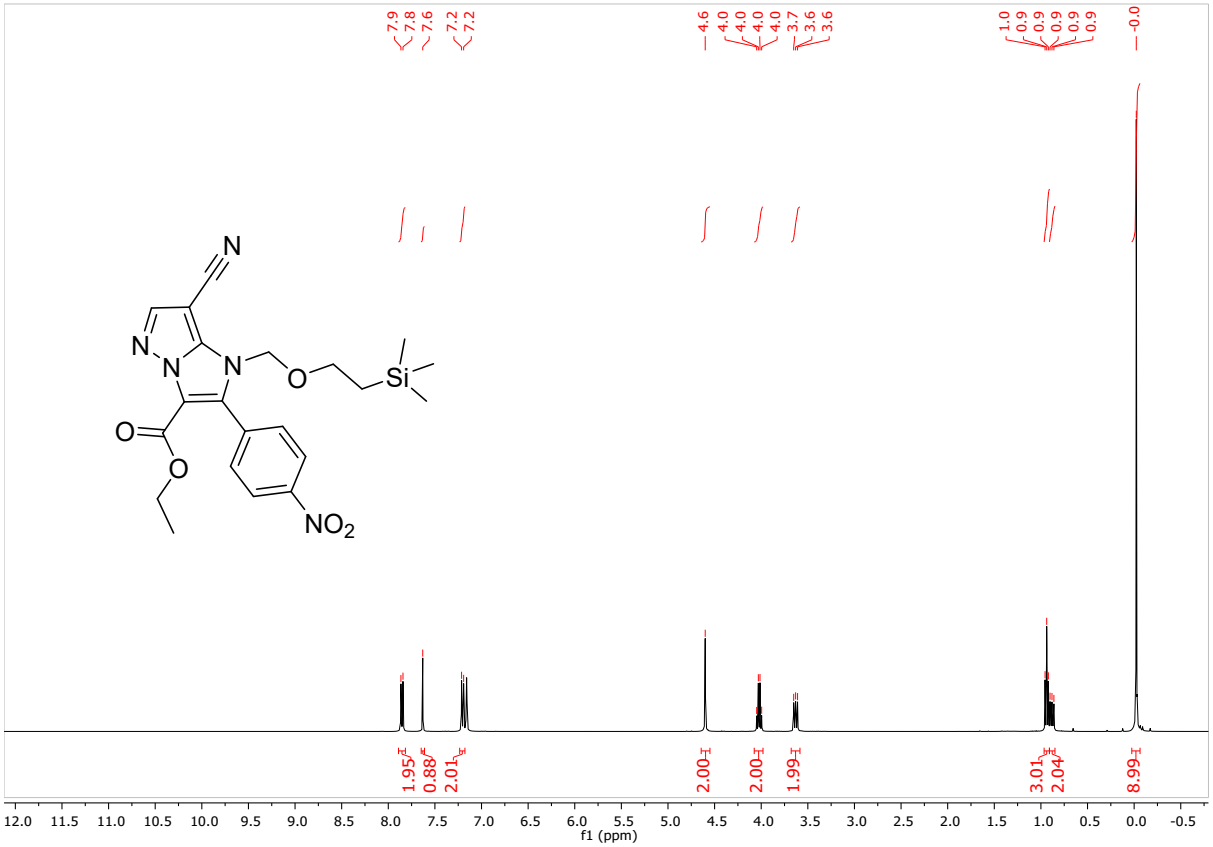

165.5
158.0
146.3
141.9
139.2
132.7
131.7
130.6
129.5
113.9
113.7
74.2
69.0
68.0
61.3
61.2
18.2
14.2
14.1
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

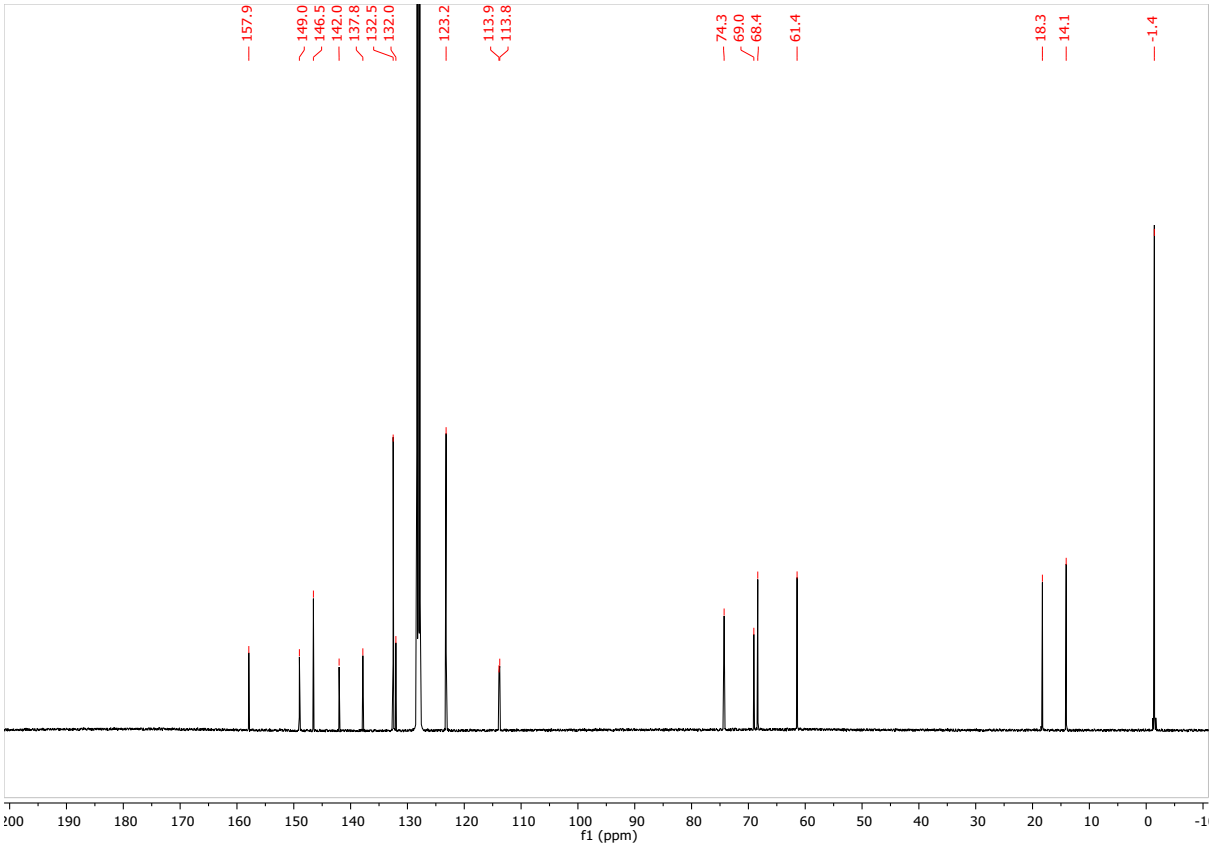
Ethyl 7-cyano-2-(4-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11g)



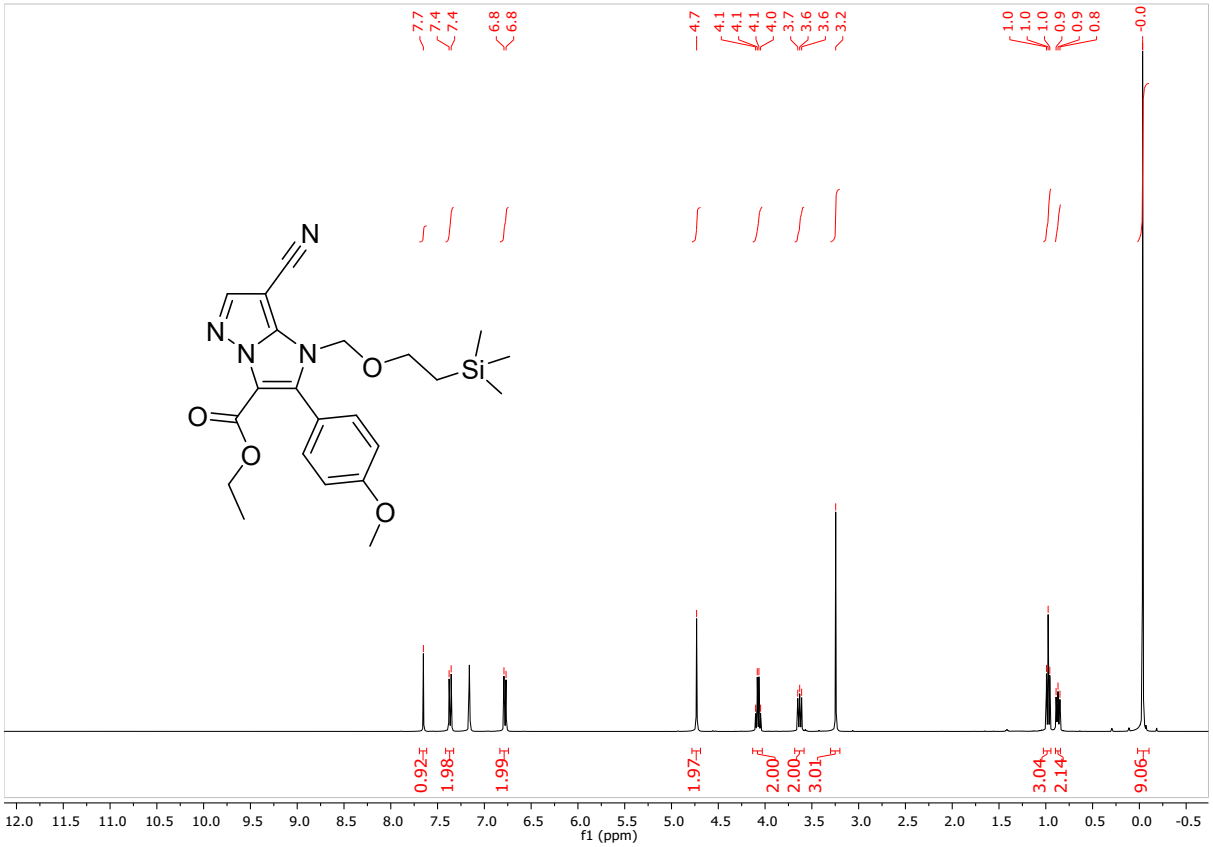

158.0
146.4
141.9
138.5
132.7
132.4
132.2
132.1
131.8
130.0
125.8
125.3
125.2
125.1
123.1
120.4
113.8
113.8
74.2
69.0
68.2
61.3
18.2
14.0
-1.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

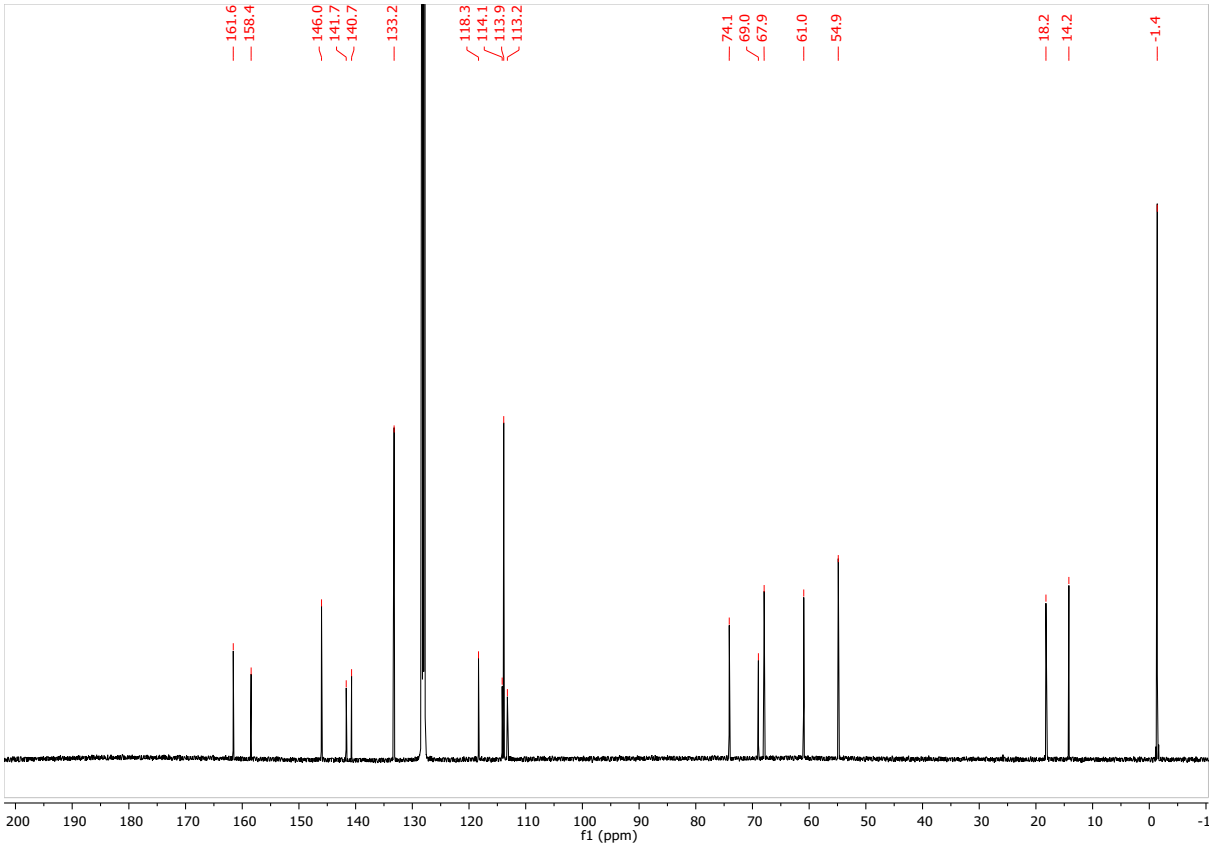
Ethyl 7-cyano-2-(4-nitrophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate (11h)



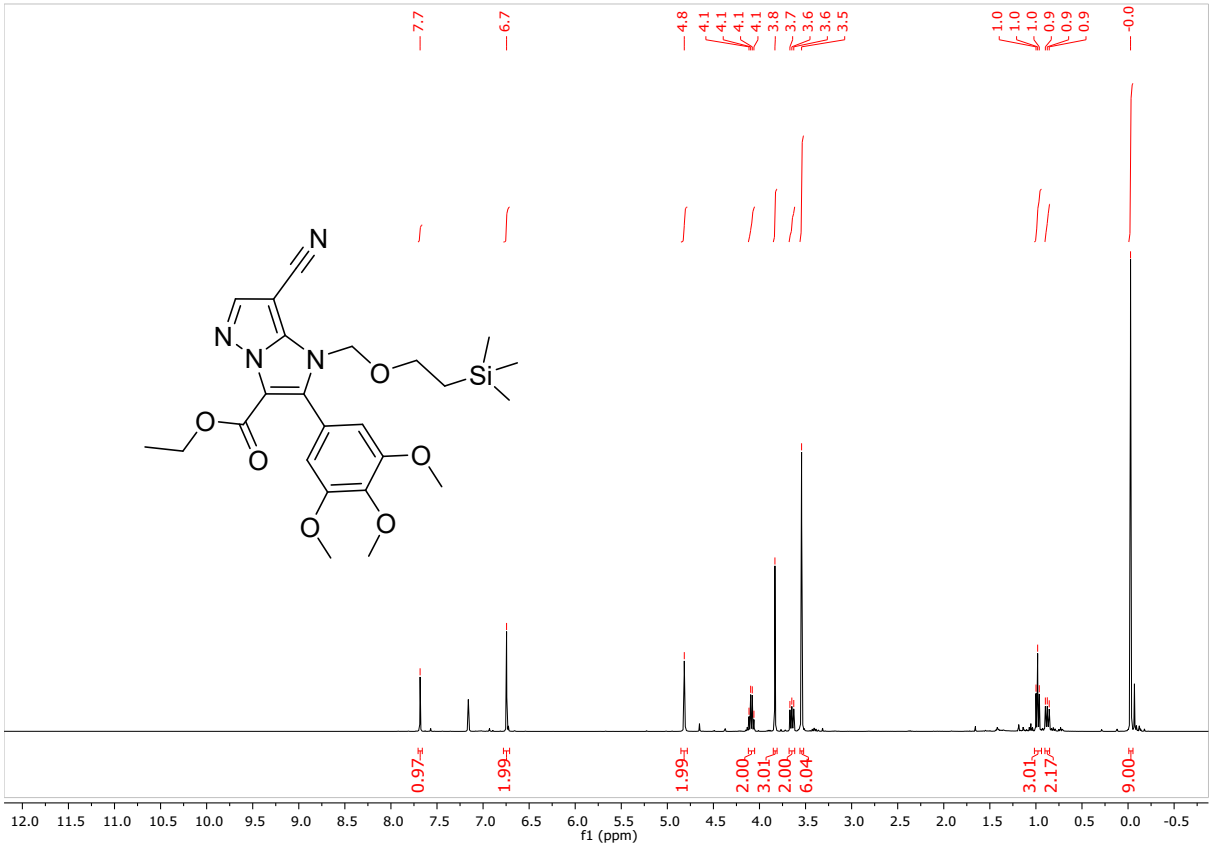

157.9
149.0
146.5
142.0
137.8
132.5
132.0
123.2
113.9
113.8
74.3
69.0
68.4
61.4
18.3
14.1
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

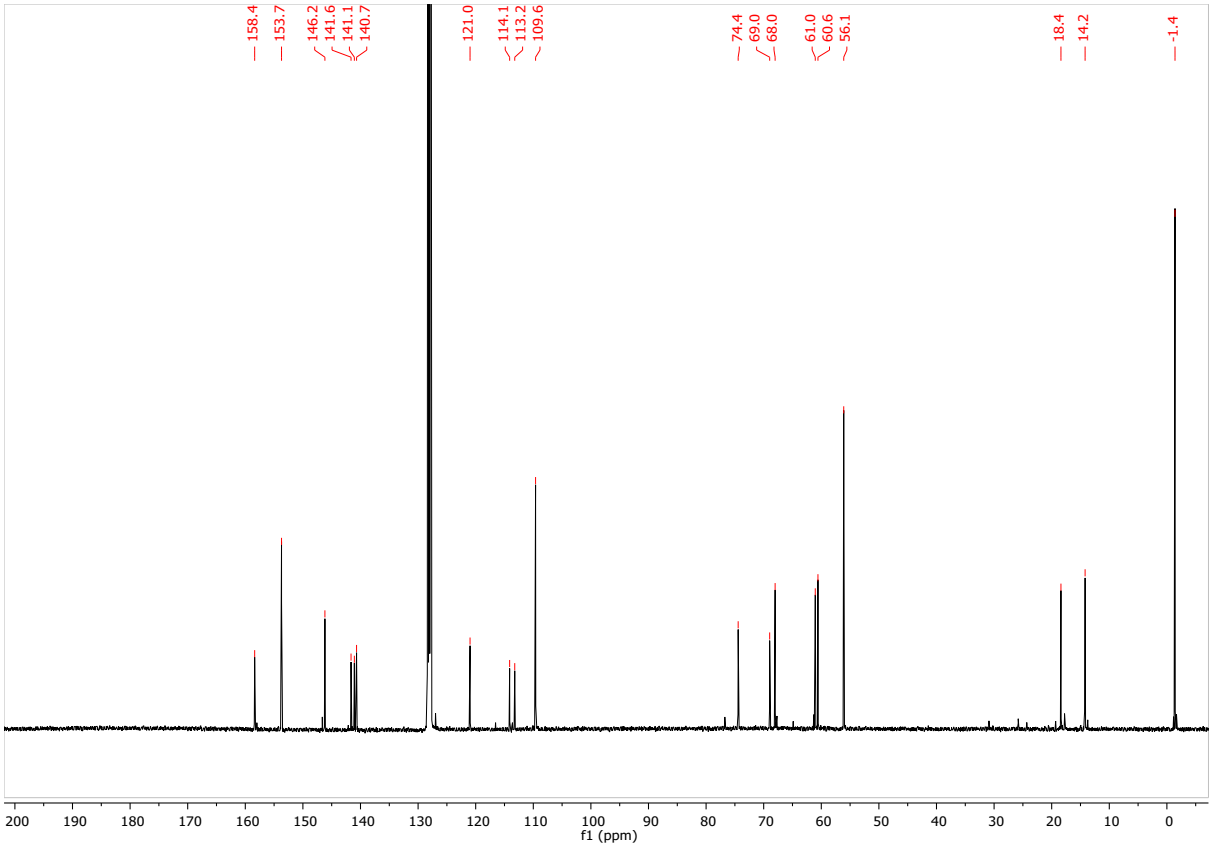
Ethyl 7-cyano-2-(4-methoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazole-3-carboxylate (11i)



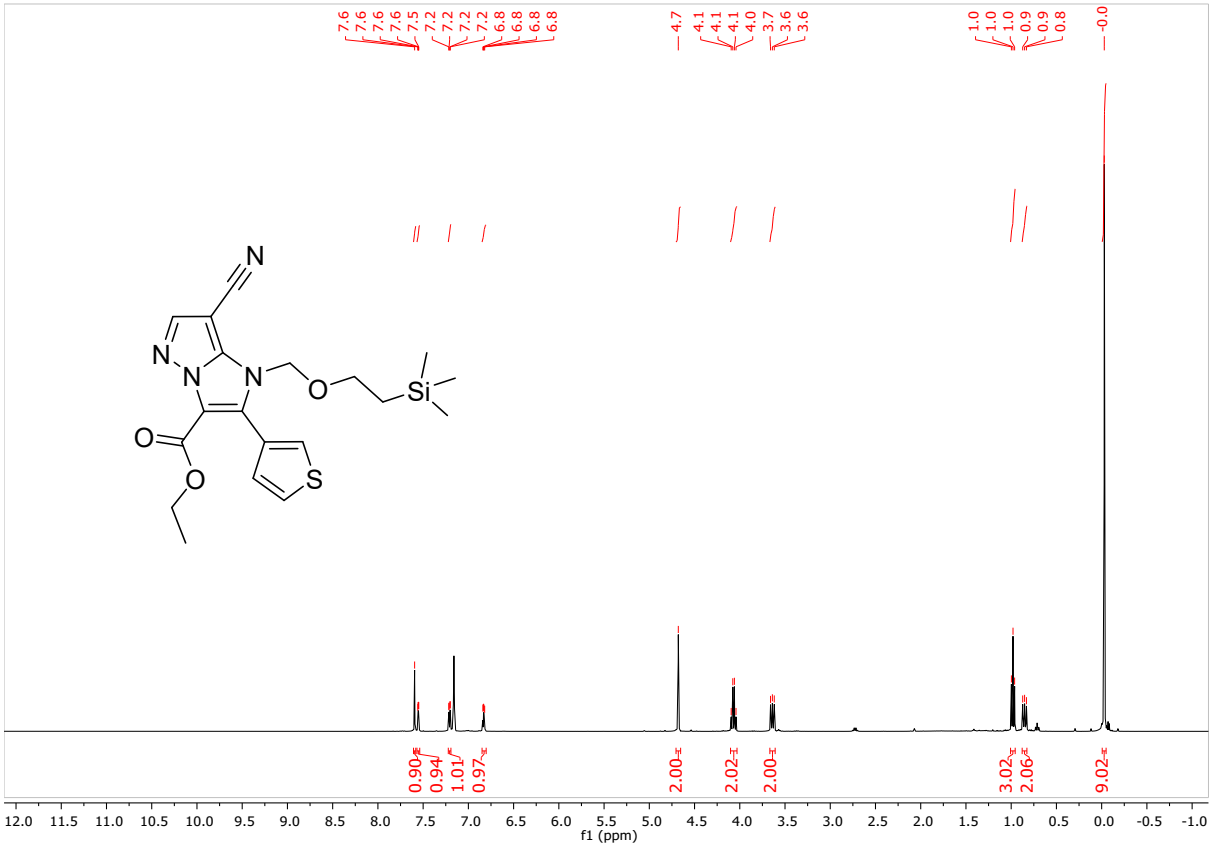

161.6
158.4
146.0
141.7
140.7
133.2
118.3
114.1
113.9
113.2
74.1
69.0
67.9
61.0
54.9
18.2
14.2
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

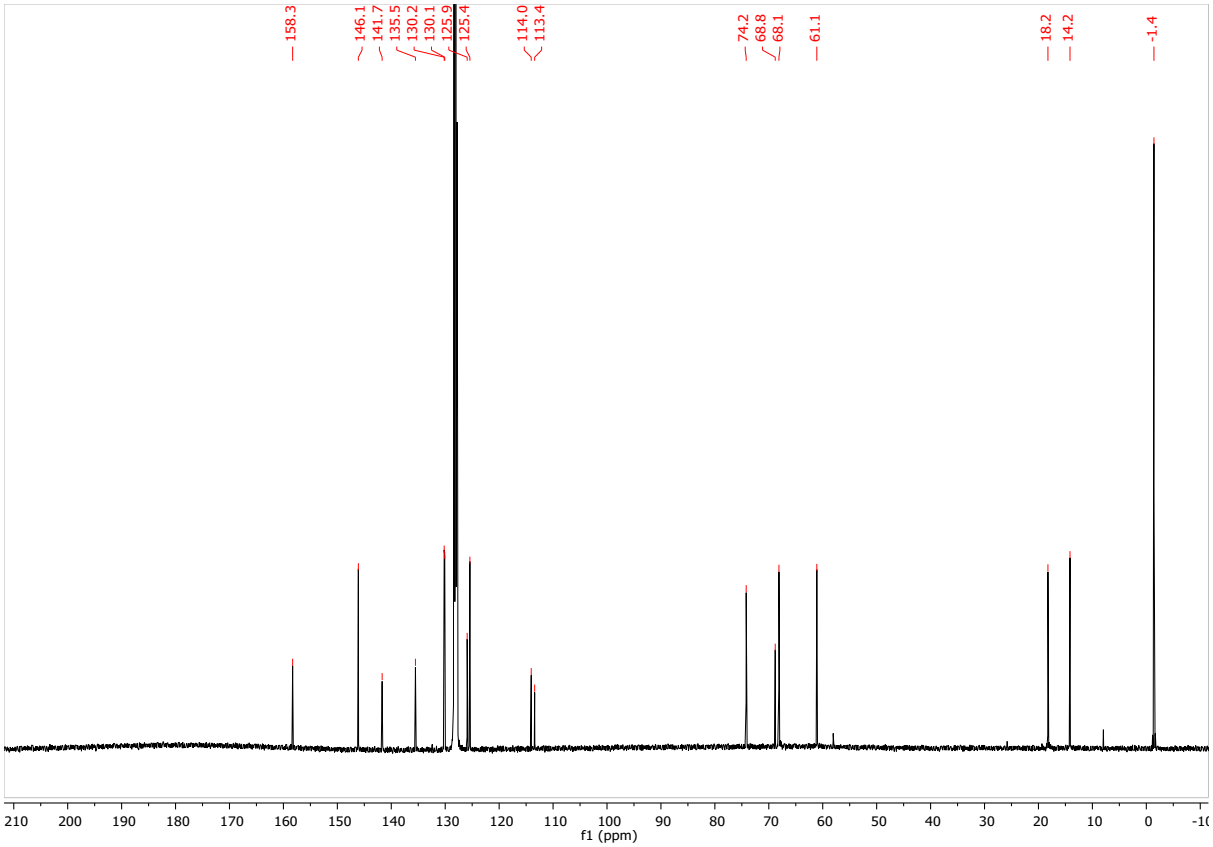
Ethyl 7-cyano-2-(3,4,5-trimethoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11j)



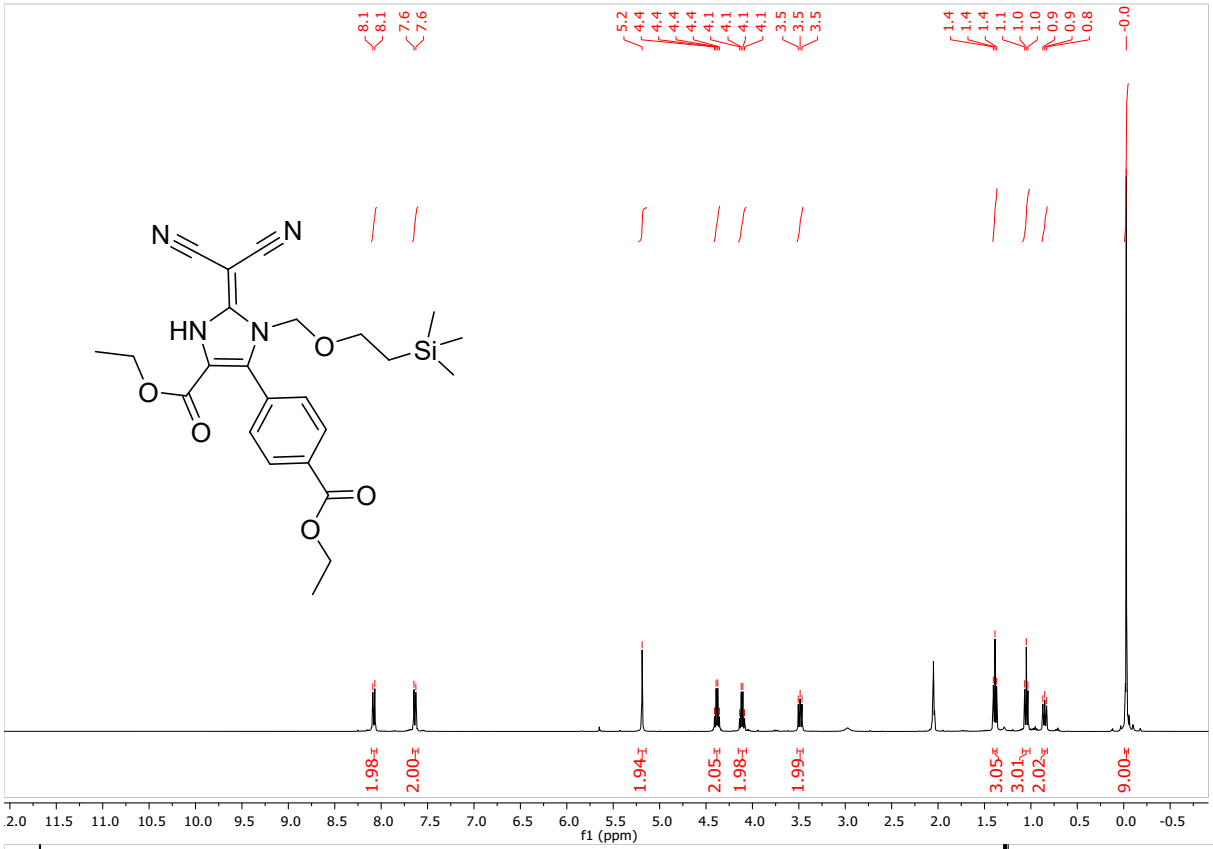

158.4
153.7
146.2
141.6
141.1
140.7
121.0
114.1
113.2
109.6
74.4
69.0
68.0
61.0
60.6
56.1
18.4
14.2
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

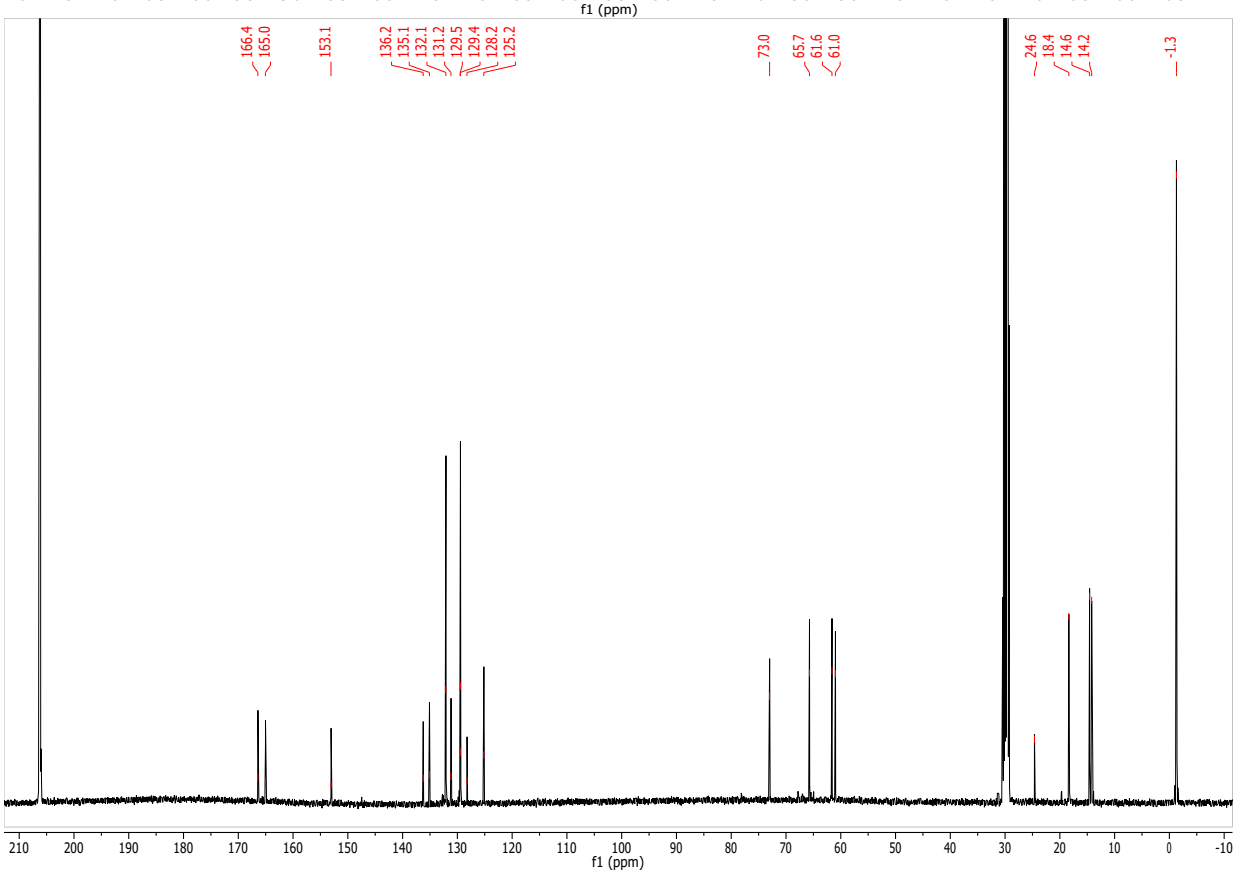
Ethyl 7-cyano-2-(thiophen-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]-pyrazole-3-carboxylate (11k)



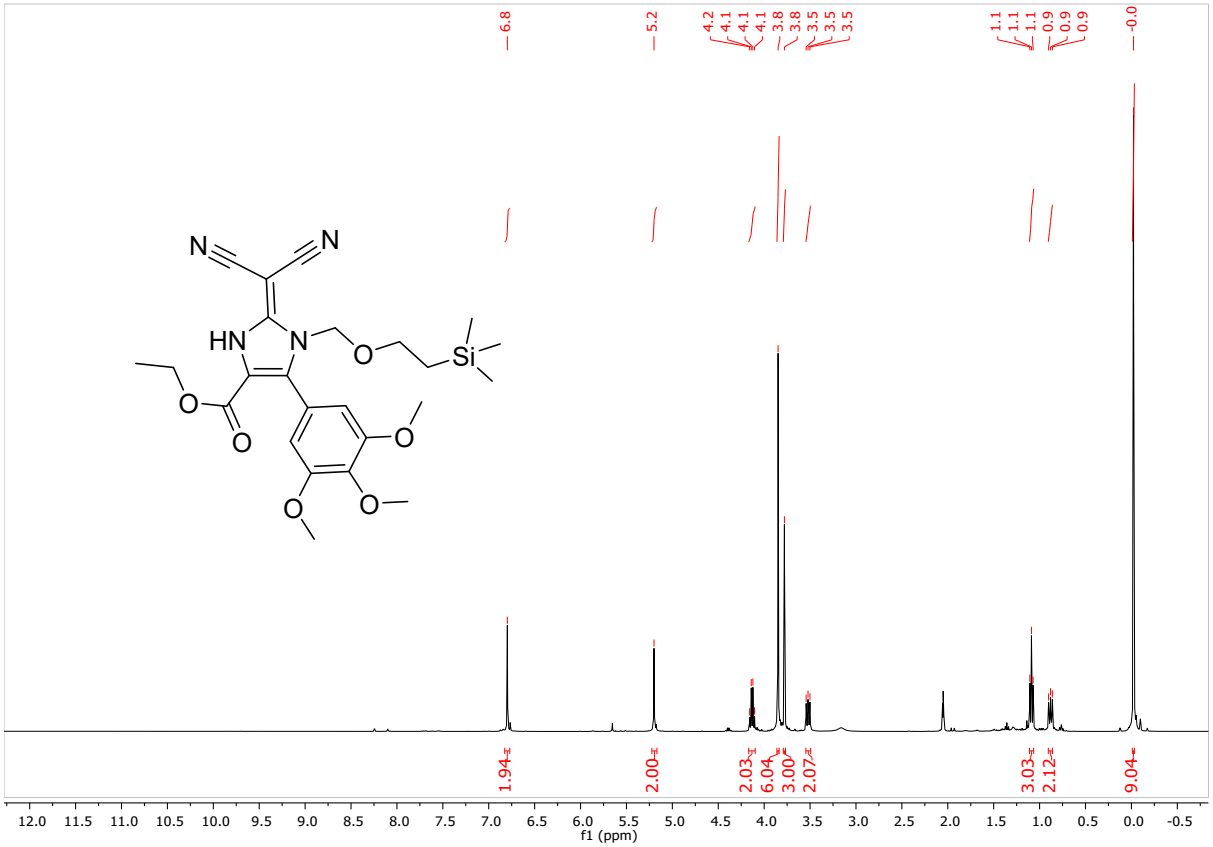

158.3
146.1
141.7
135.5
130.2
130.1
125.9
125.4
114.0
113.4
74.2
68.8
68.1
61.1
18.2
14.2
-1.4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

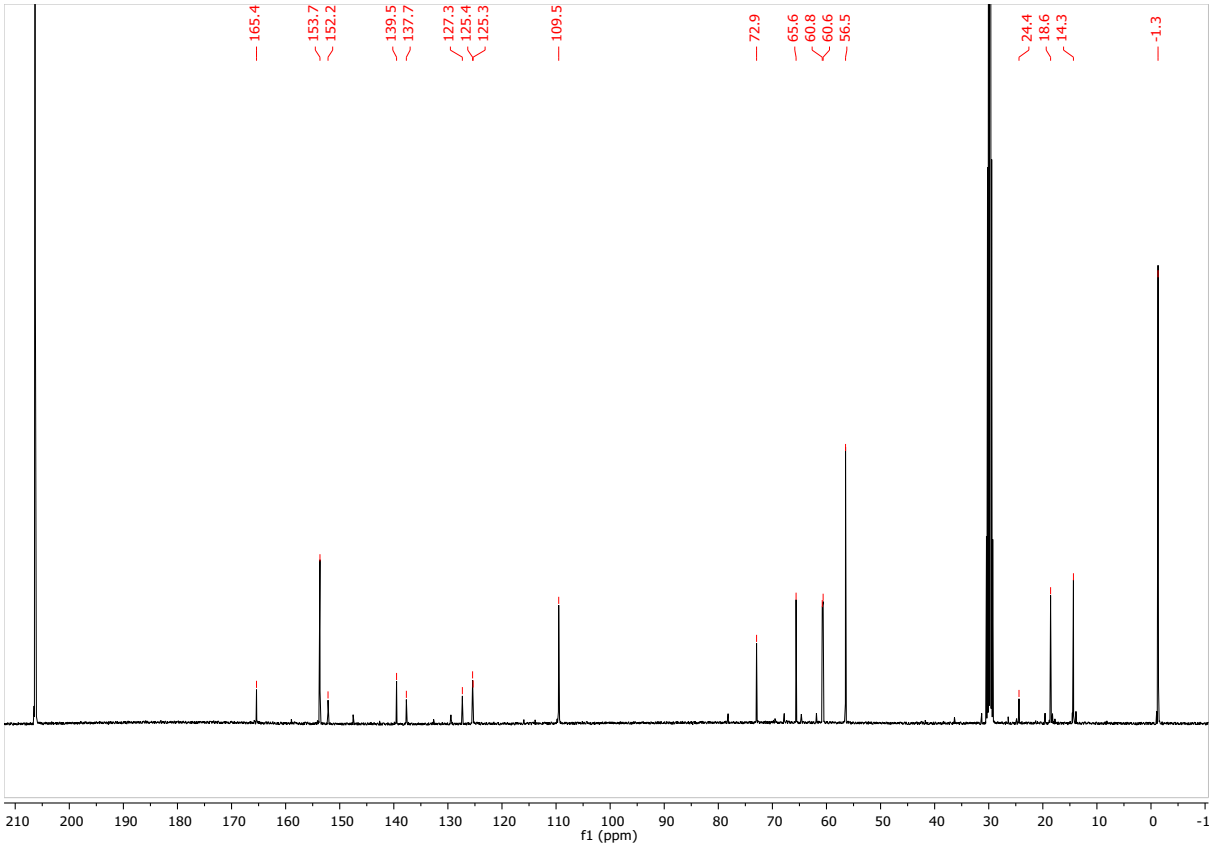
Ethyl 2-(dicyanomethylene)-5-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14a)



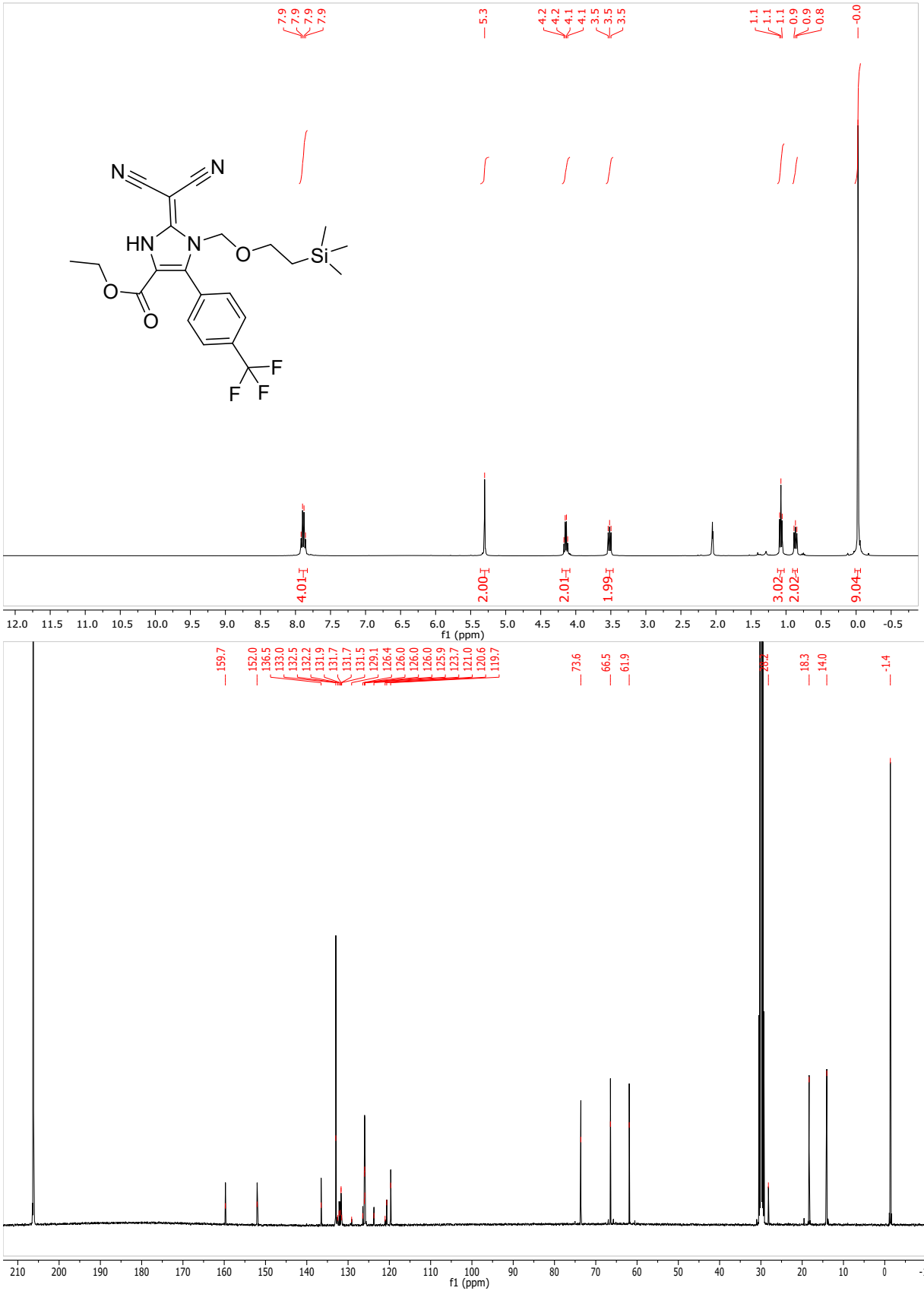


Ethyl 2-(dicyanomethylene)-5-(3,4,5-trimethoxyphenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14b)

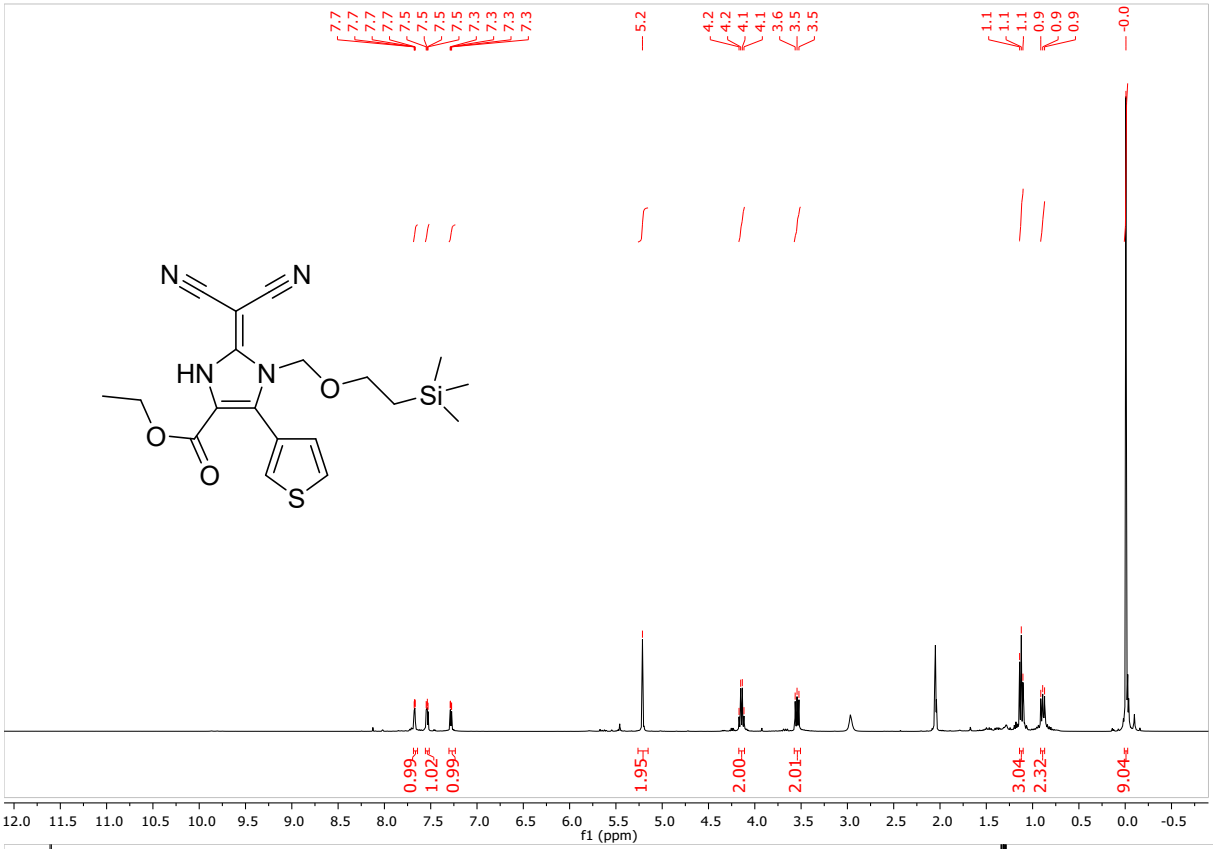


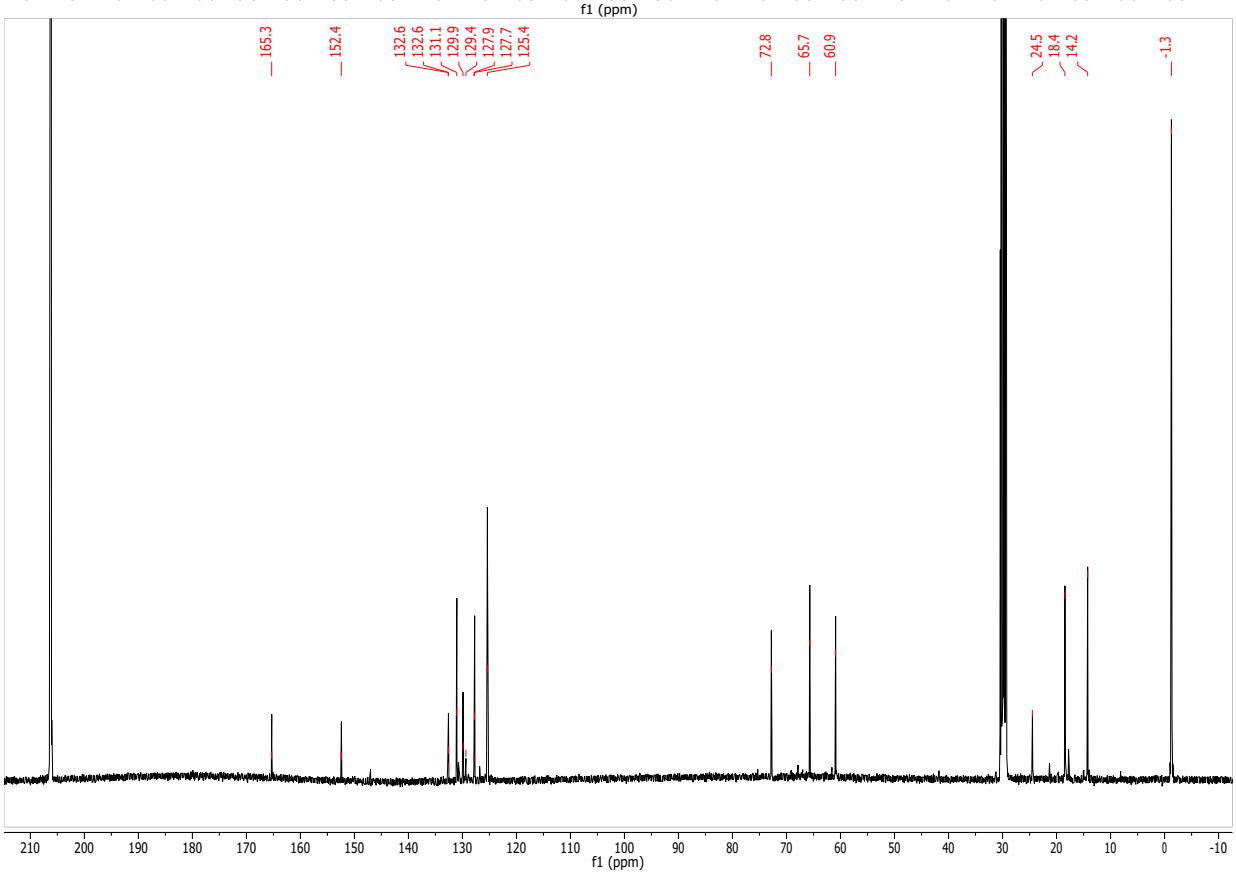

165.4
153.7
152.2
139.5
137.7
127.3
125.4
125.3
109.5
72.9
65.6
60.8
60.6
56.5
24.4
18.6
14.3
-1.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

Ethyl 2-(dicyanomethylene)-5-(4-(trifluoromethyl)phenyl)-1-((2-(trimethylsilyl)ethoxy)-methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14c)

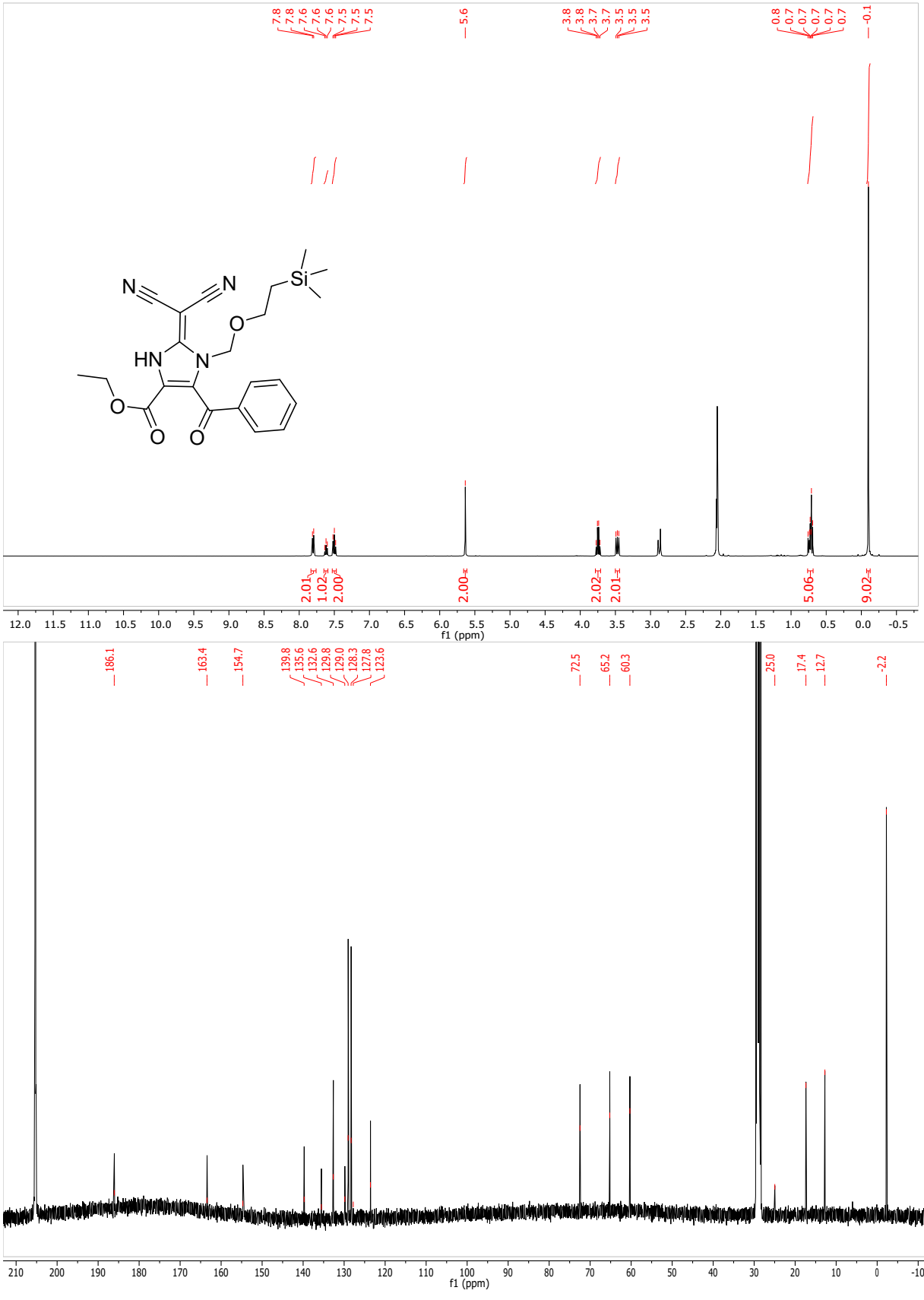


Ethyl 2-(dicyanomethylene)-5-(thiophen-3-yl)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14d)

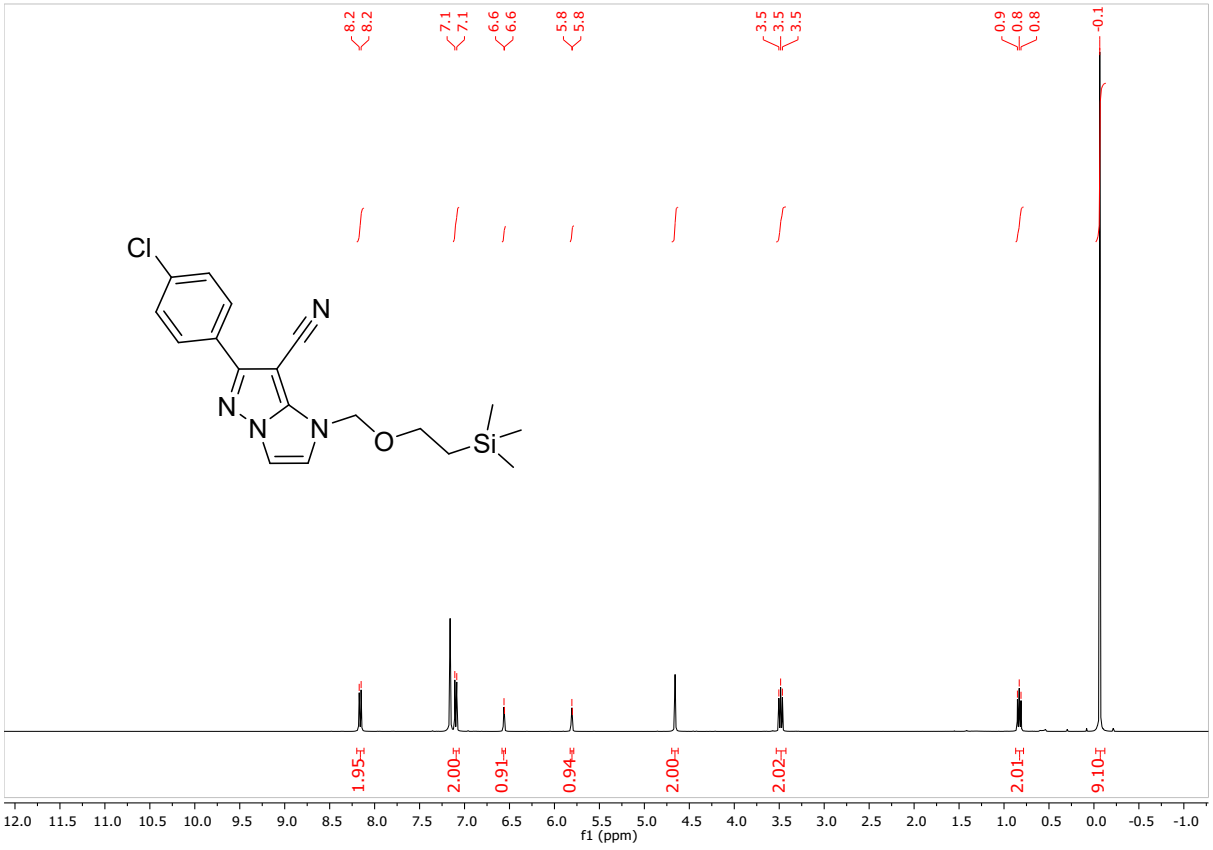


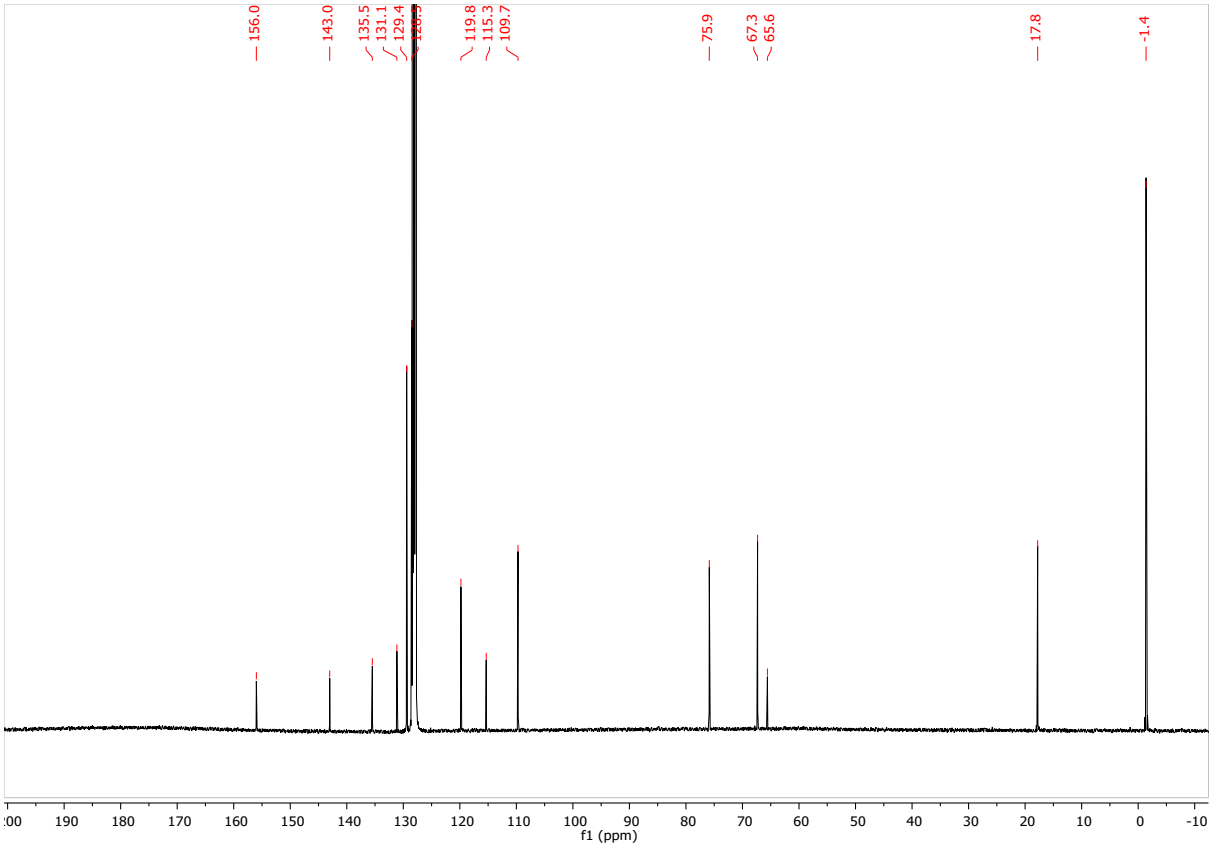


Ethyl 5-benzoyl-2-(dicyanomethylene)-1-((2-(trimethylsilyl)ethoxy)methyl)-2,3-dihydro-1*H*-imidazole-4-carboxylate (14e)

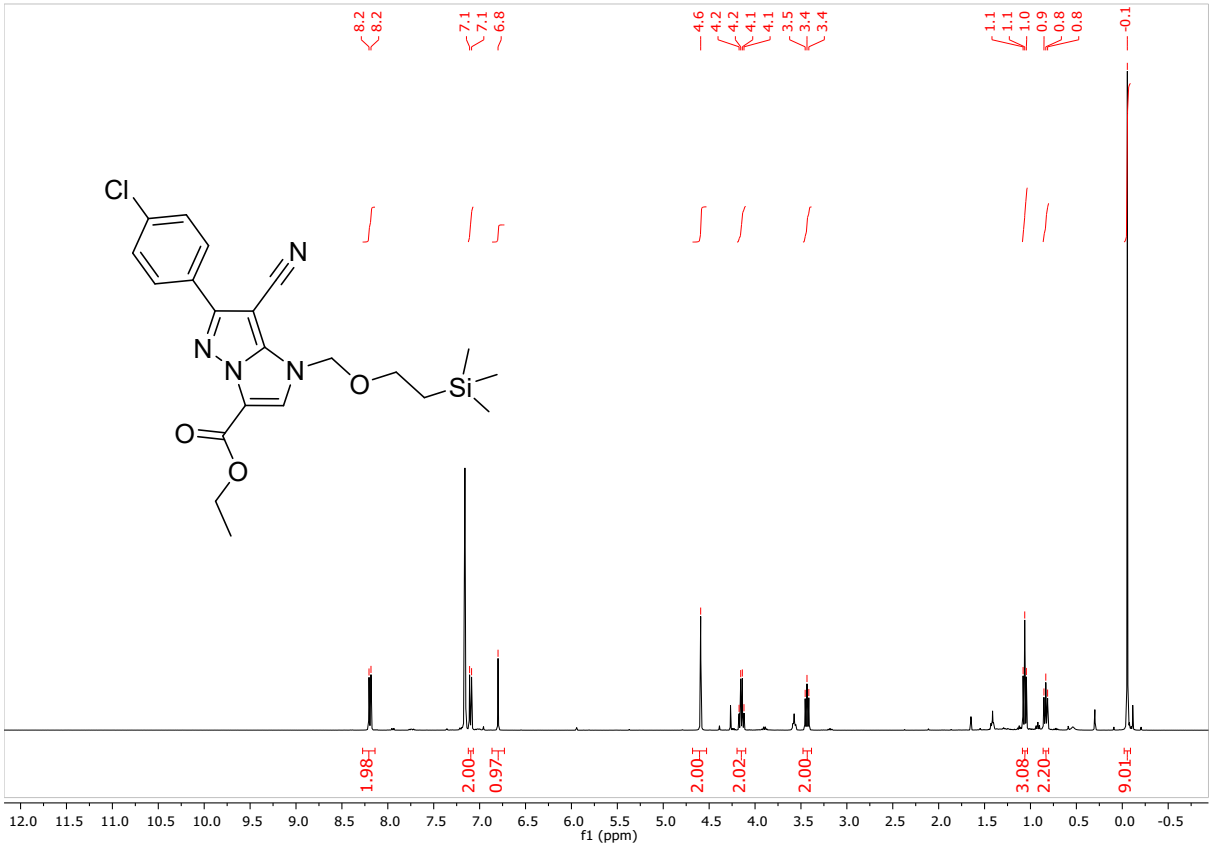


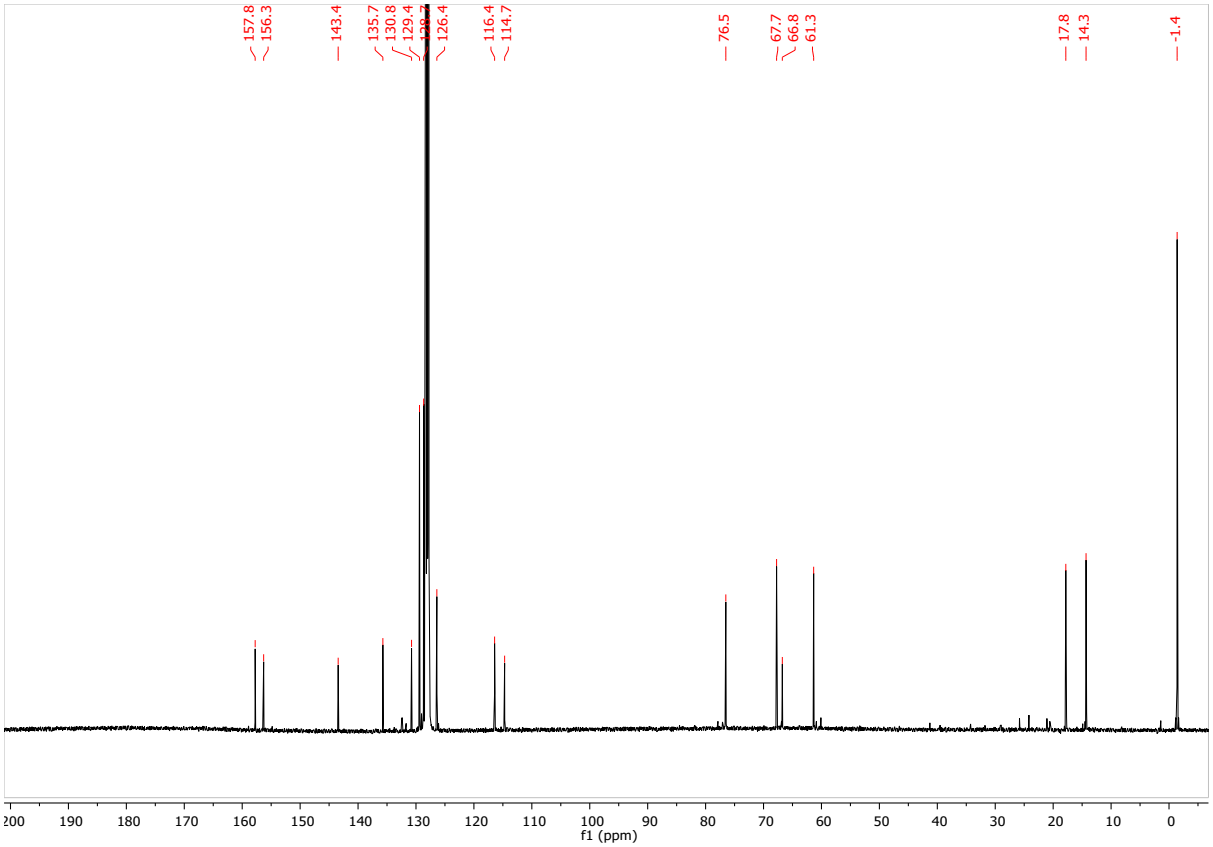
6-(4-Chlorophenyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-7-carbonitrile (7j)



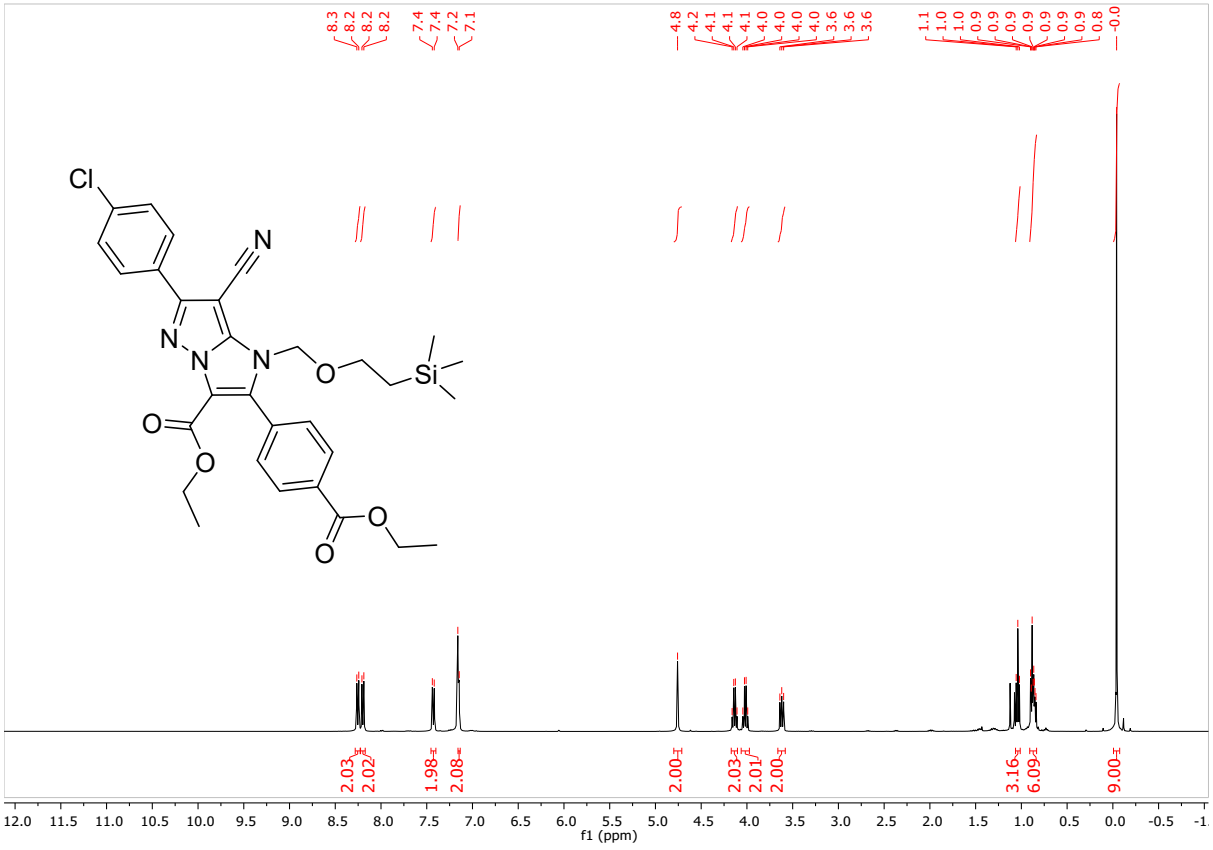

156.0
143.0
135.5
131.1
129.4
119.8
115.3
109.7
75.9
67.3
65.6
17.8
-1.4
f1 (ppm)

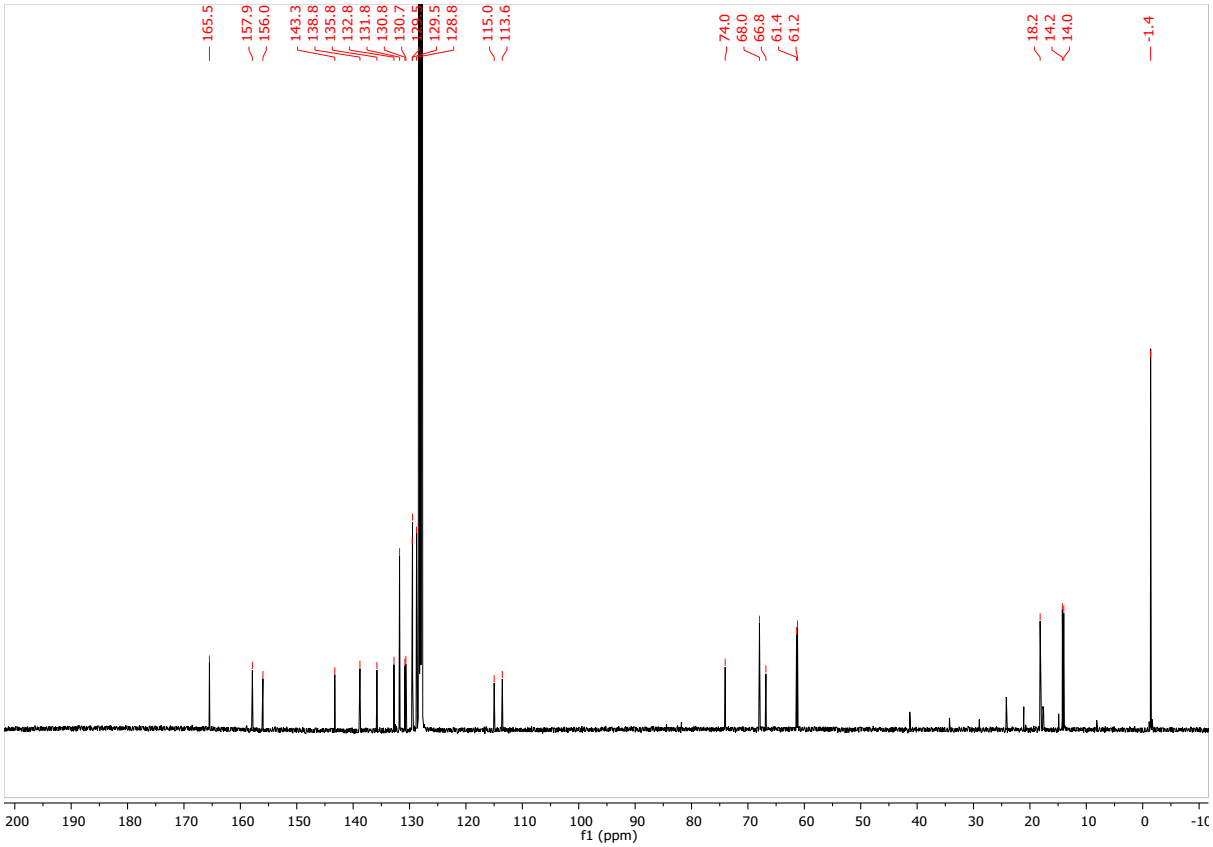
Ethyl 6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (10k)



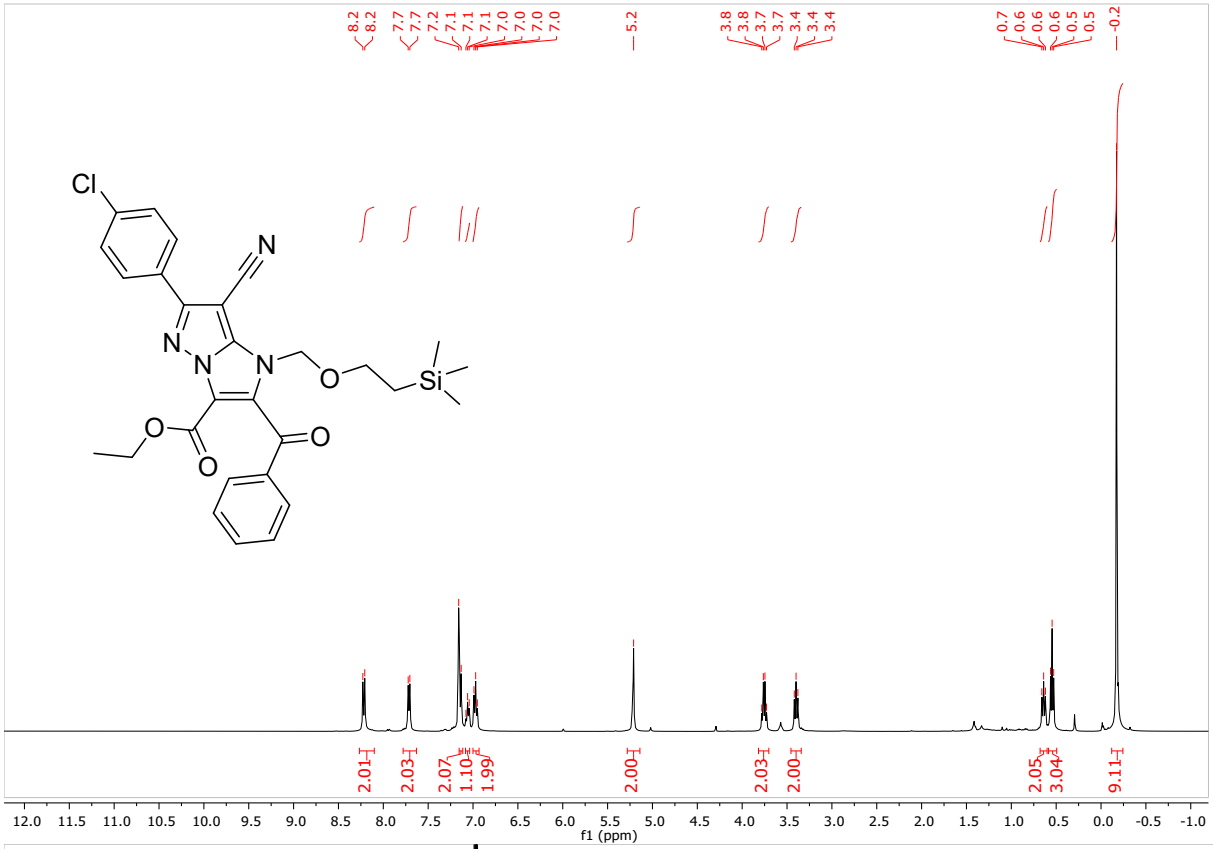

157.8
156.3
143.4
135.7
130.8
129.4
126.4
116.4
114.7
76.5
67.7
66.8
61.3
17.8
14.3
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

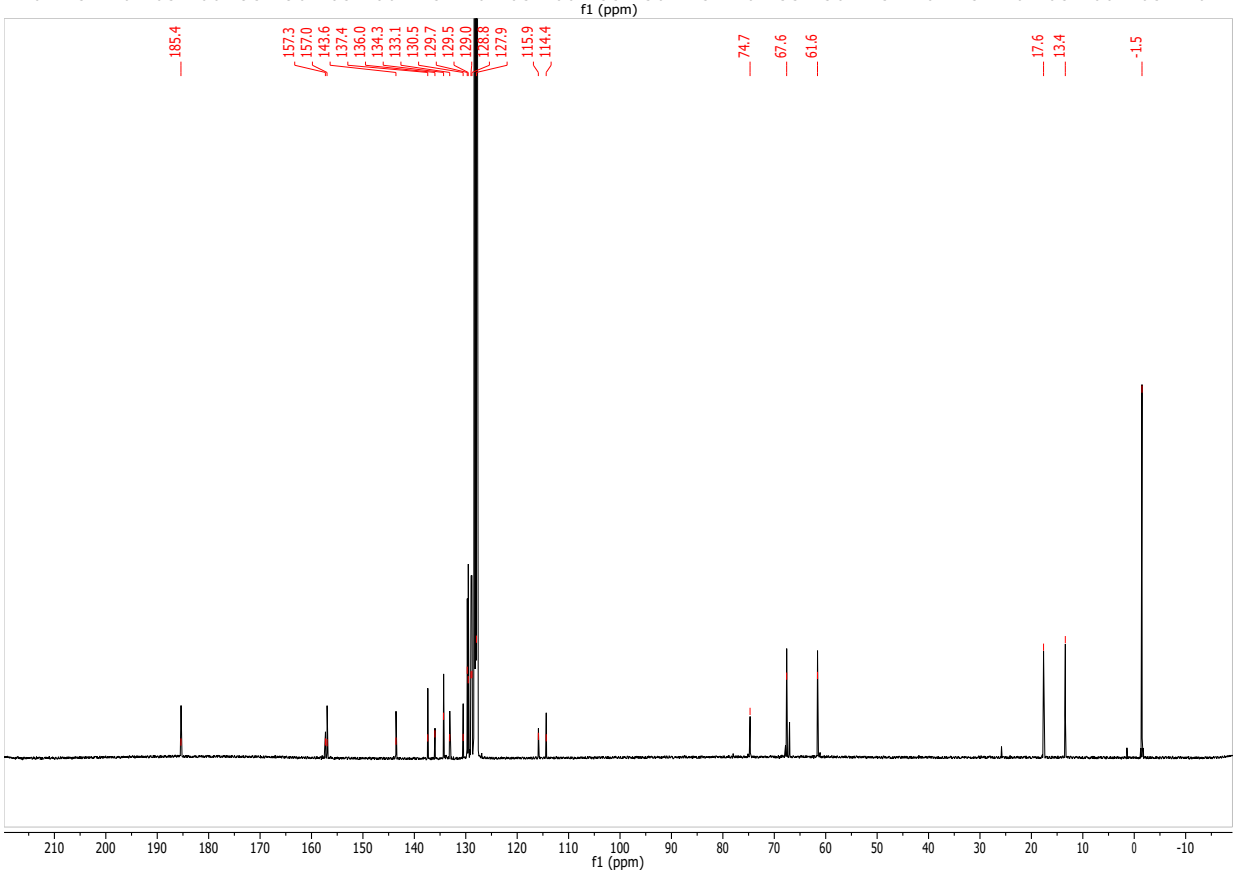
Ethyl 6-(4-chlorophenyl)-7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1-((2-(trimethylsilyl)-ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11l)



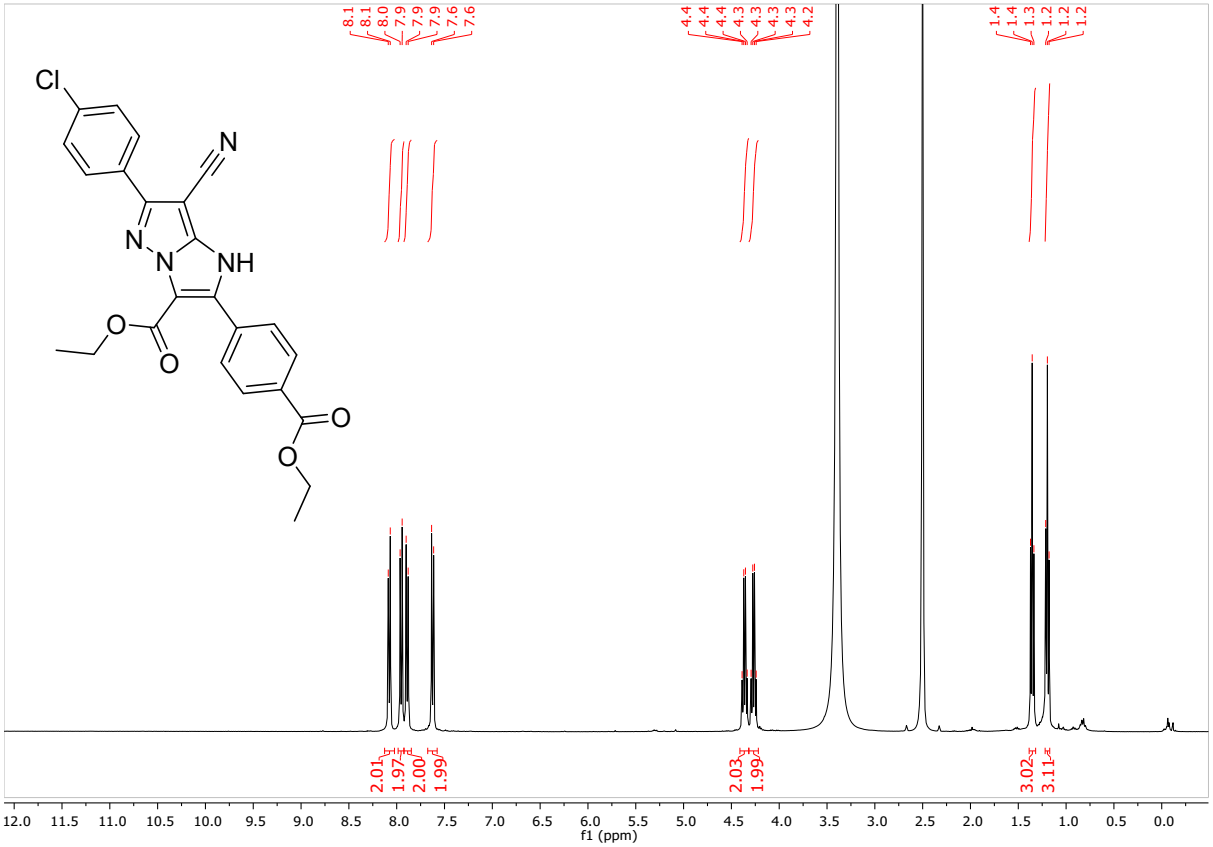

165.5
157.9
156.0
143.3
138.8
135.8
132.8
131.8
130.8
130.7
129.5
128.8
115.0
113.6
74.0
68.0
66.8
61.4
61.2
18.2
14.2
14.0
-1.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

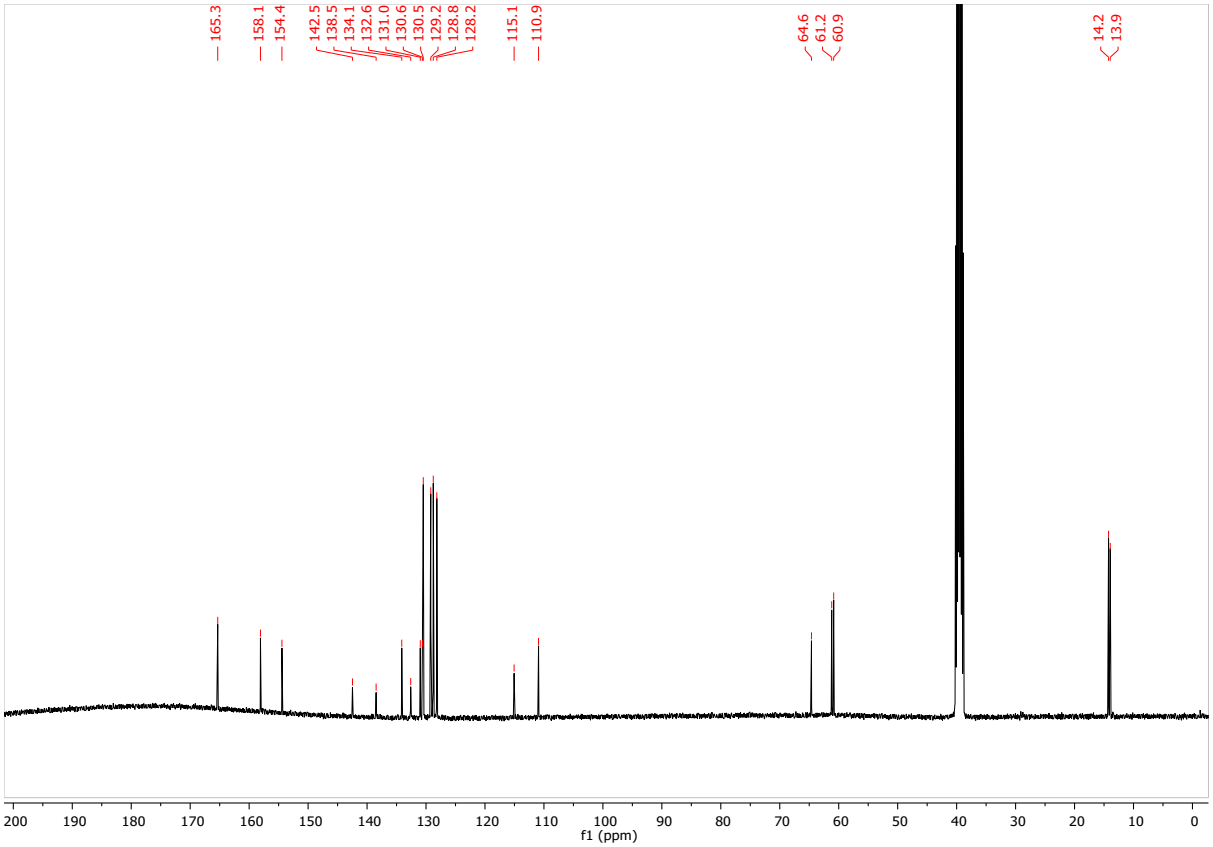
Ethyl 2-benzoyl-6-(4-chlorophenyl)-7-cyano-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (11m)



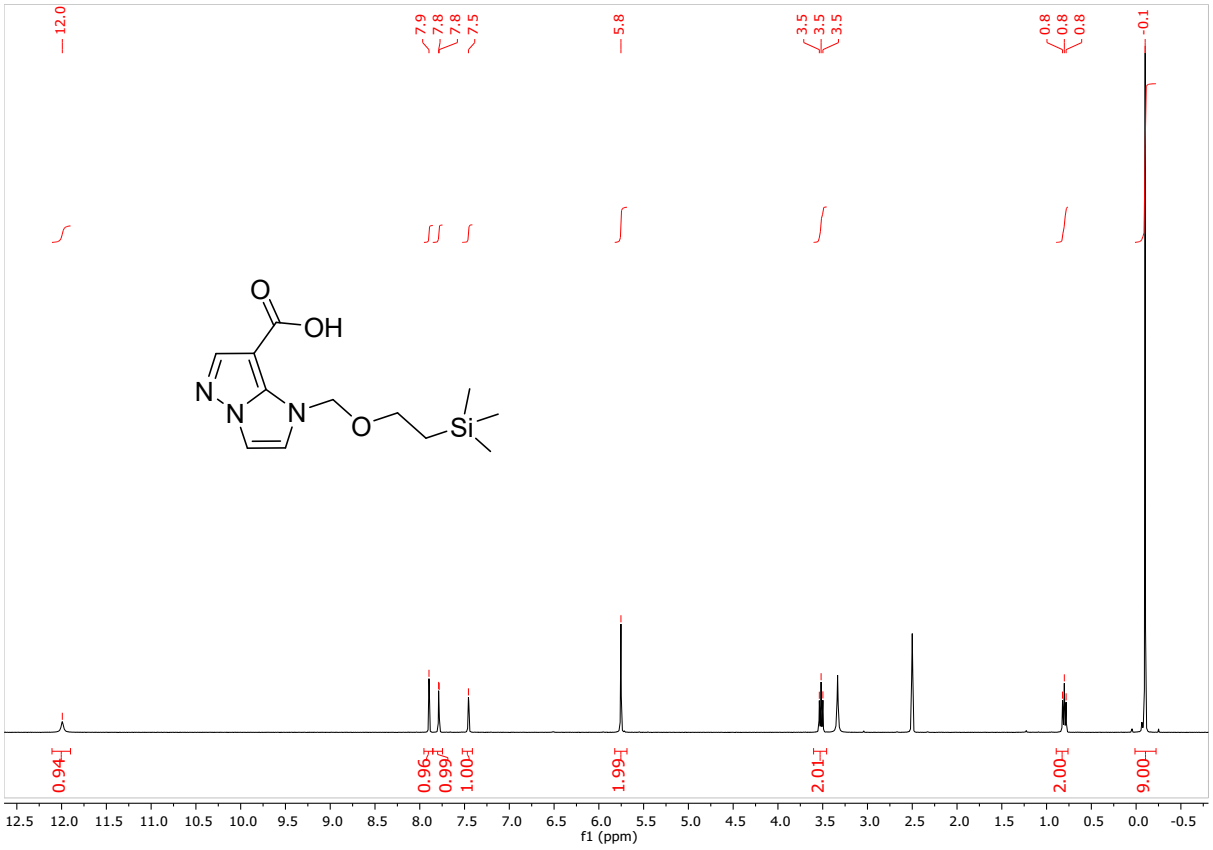


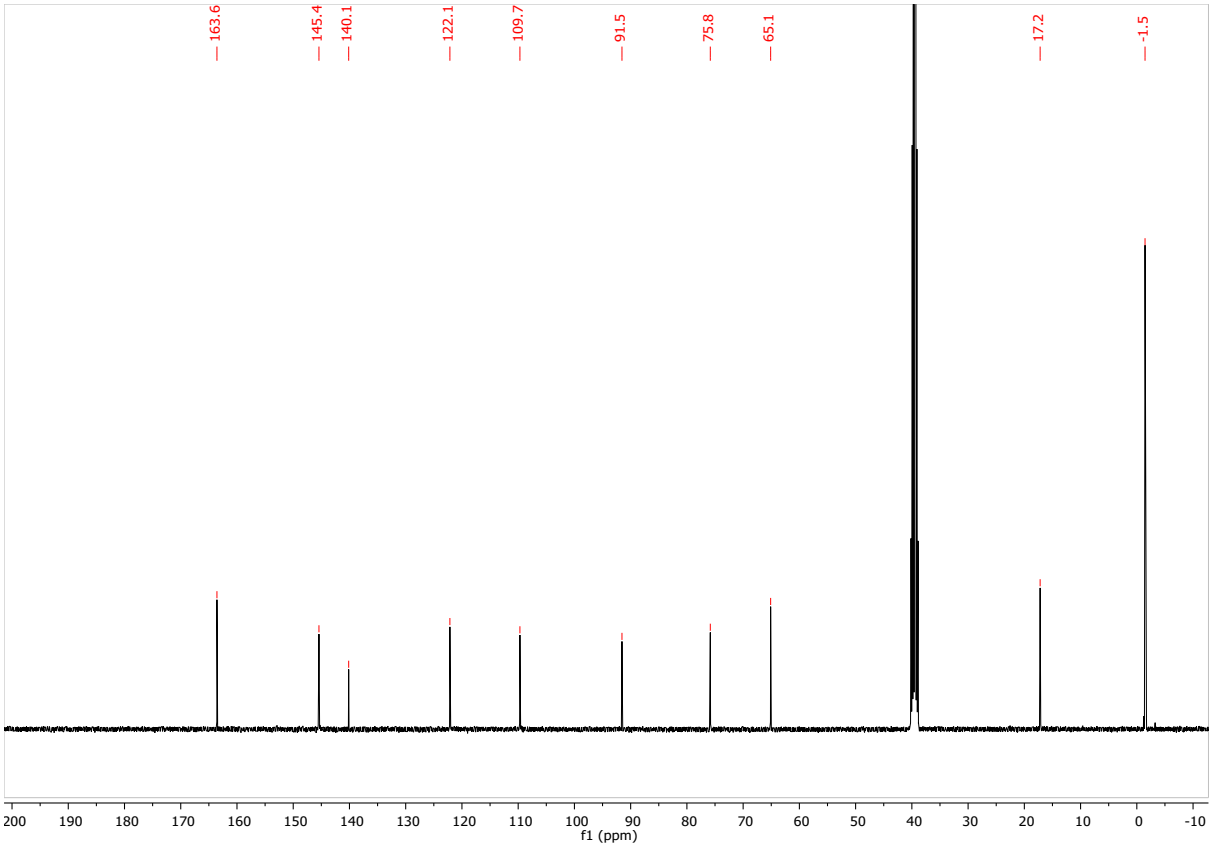
Ethyl 6-(4-chlorophenyl)-7-cyano-2-(4-(ethoxycarbonyl)phenyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carboxylate (12a)



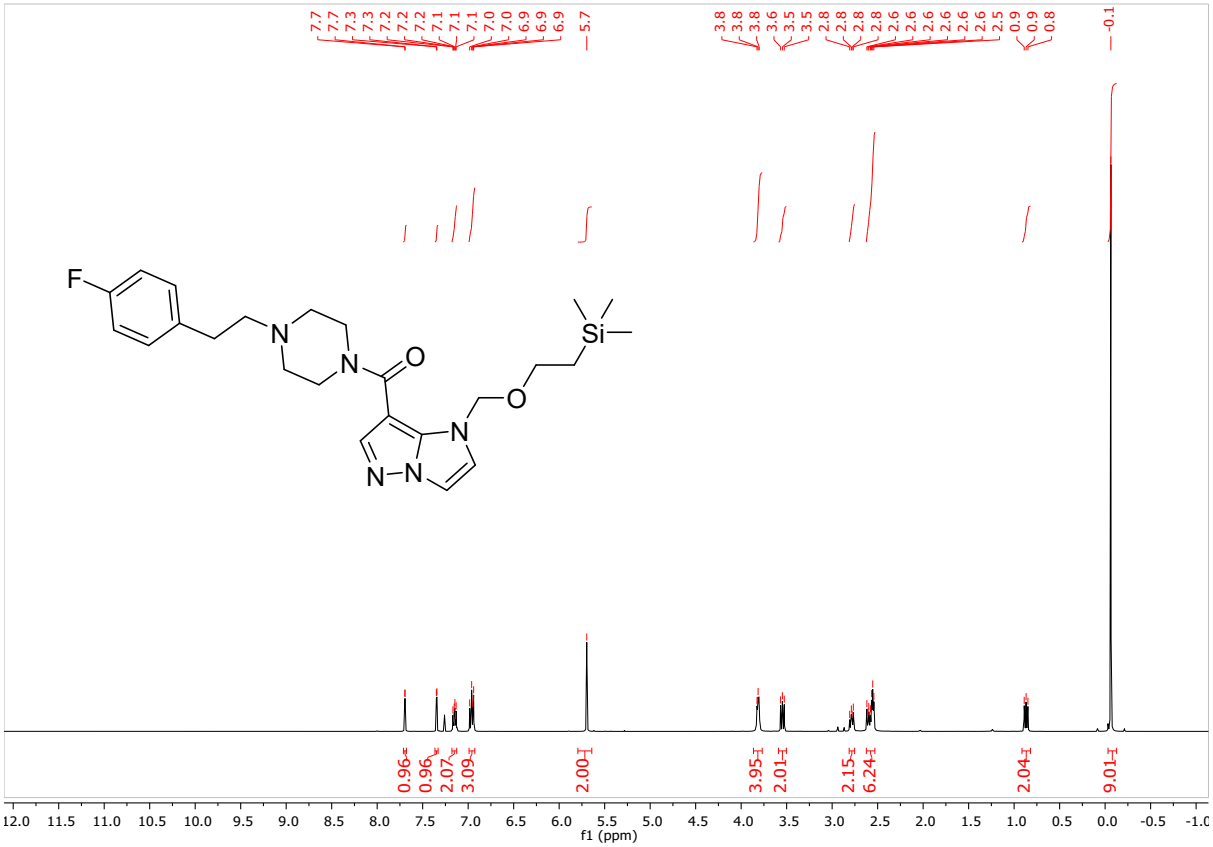


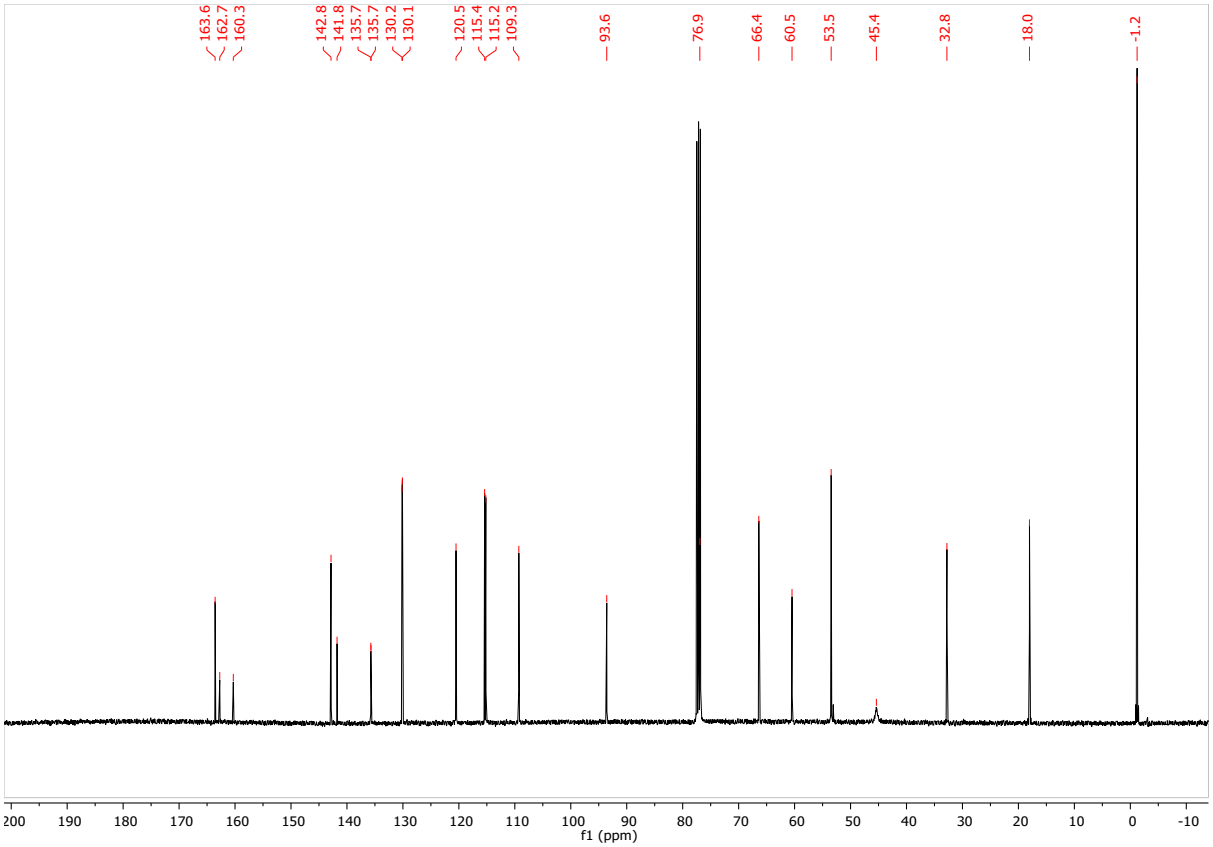
1-((2-(Trimethylsilyl)ethoxy)methyl)-1H-imidazo[1,2-b]pyrazole-7-carboxylic acid (19)



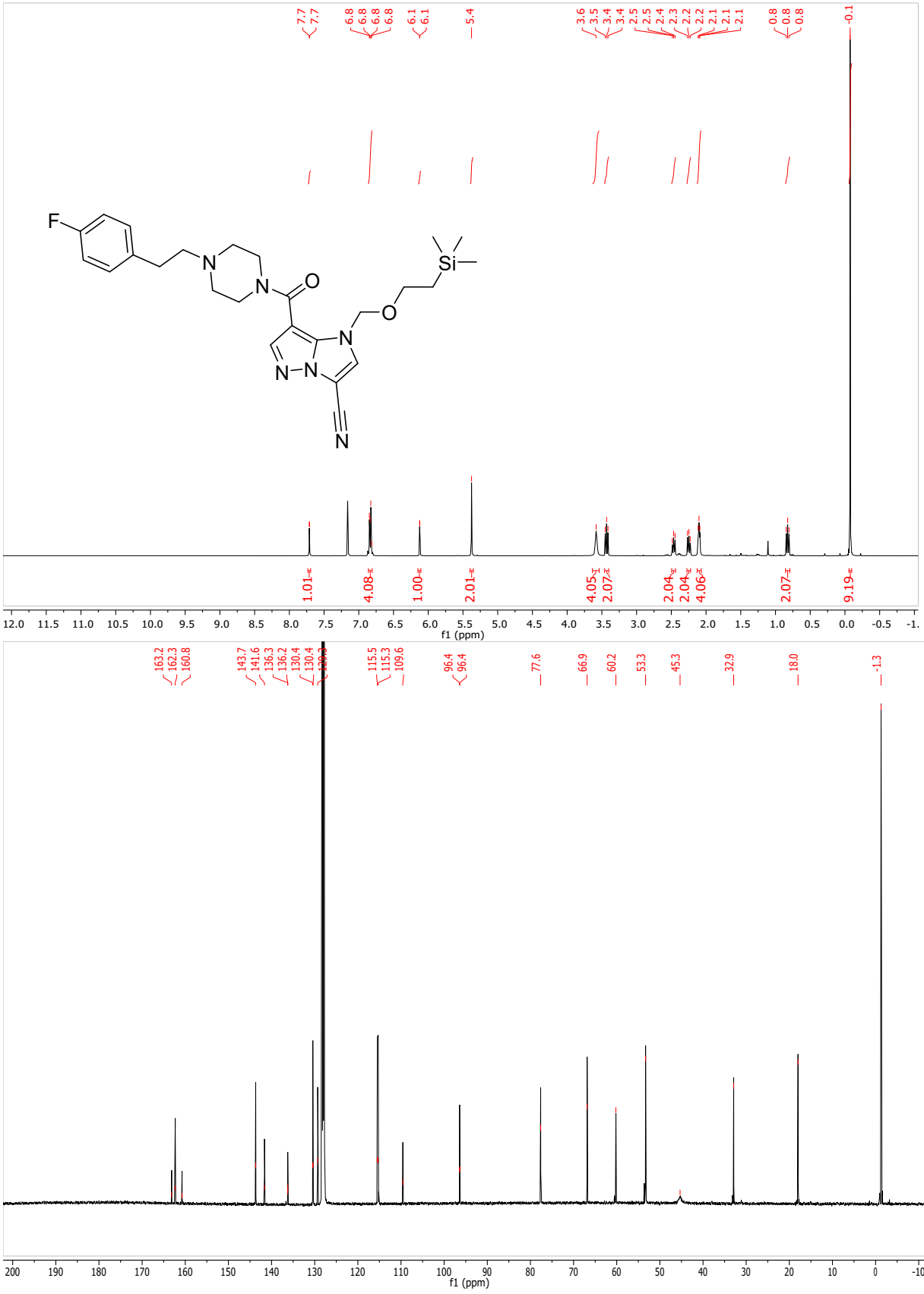

163.6
145.4
140.1
122.1
109.7
91.5
75.8
65.1
17.2
-1.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(4-(4-Fluorophenethyl)piperazin-1-yl)(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo-[1,2-*b*]pyrazol-7-yl)methanone (21)

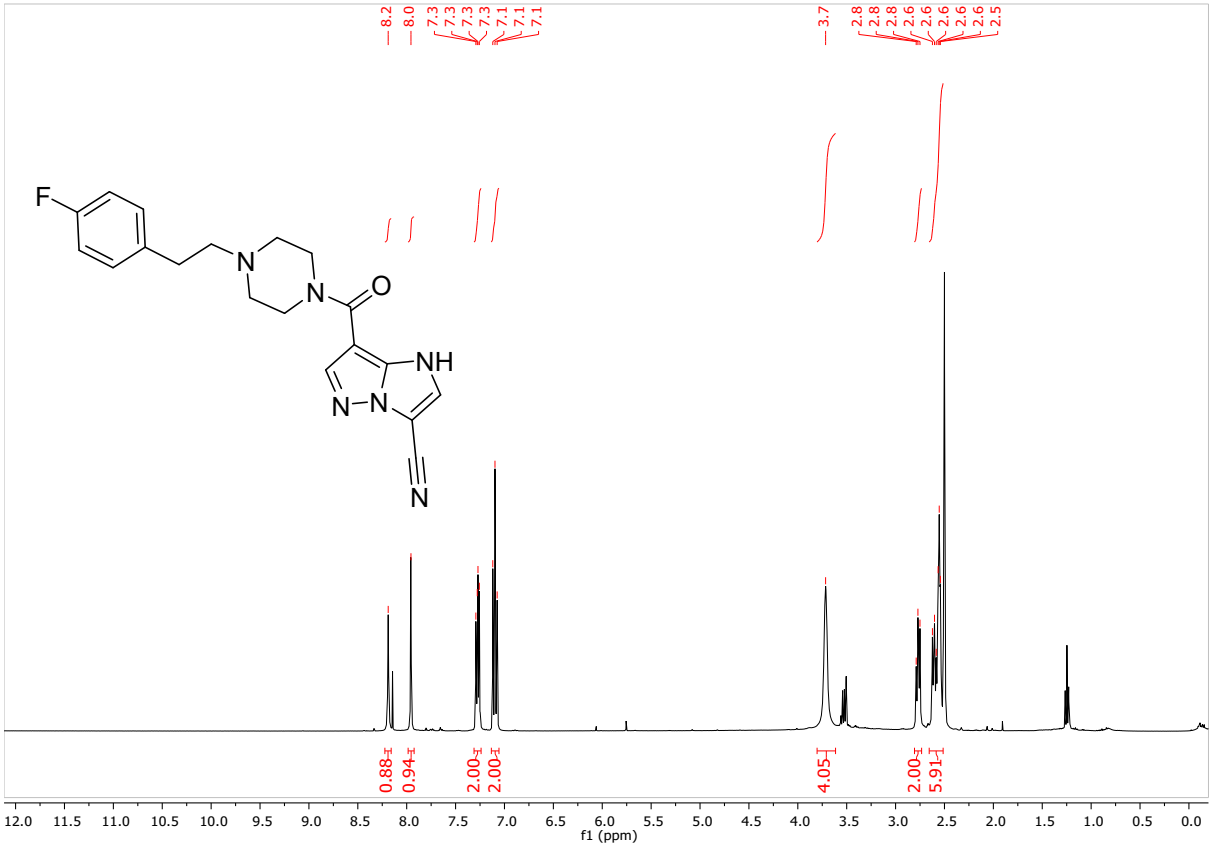


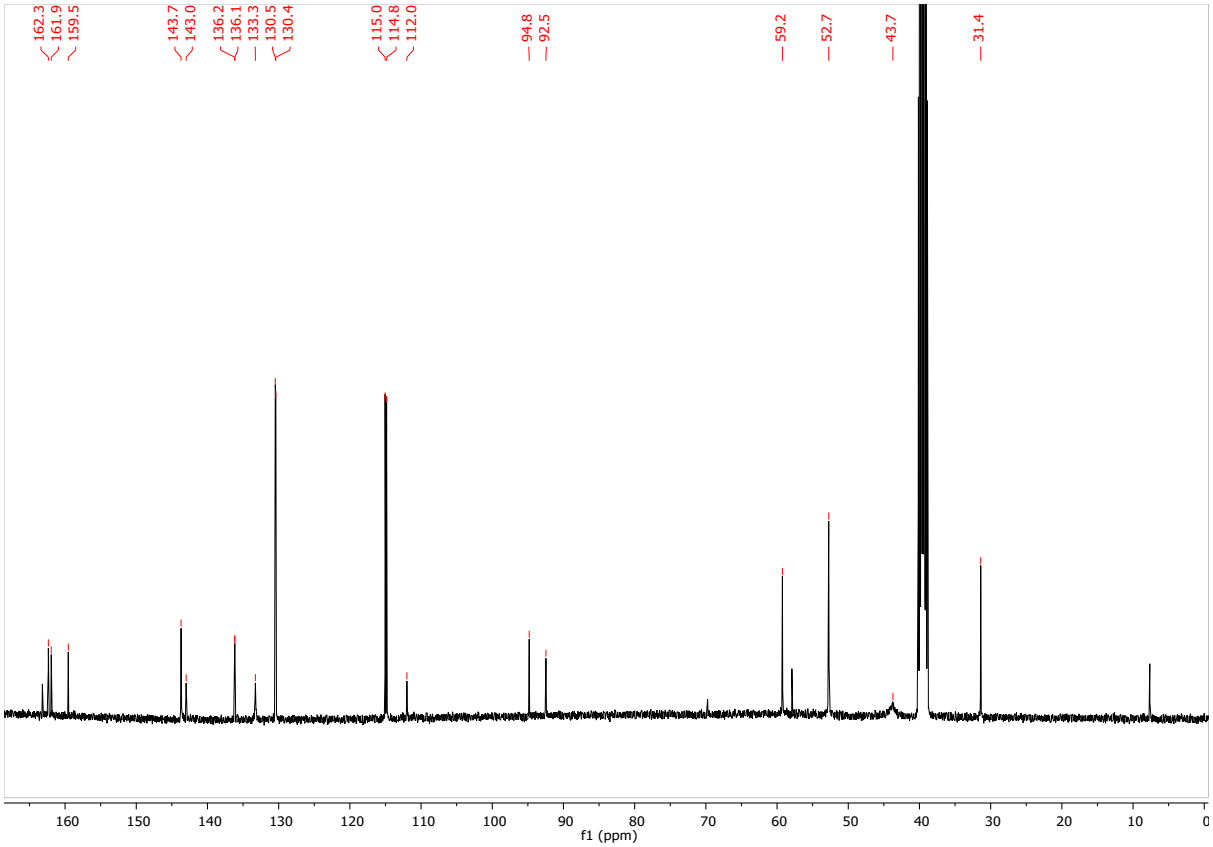

163.6
162.7
160.3
142.8
141.8
135.7
135.7
130.2
130.1
120.5
115.4
115.2
109.3
93.6
76.9
66.4
60.5
53.5
45.4
32.8
18.0
-1.2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

7-(4-(4-Fluorophenethyl)piperazine-1-carbonyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carbonitrile (22)

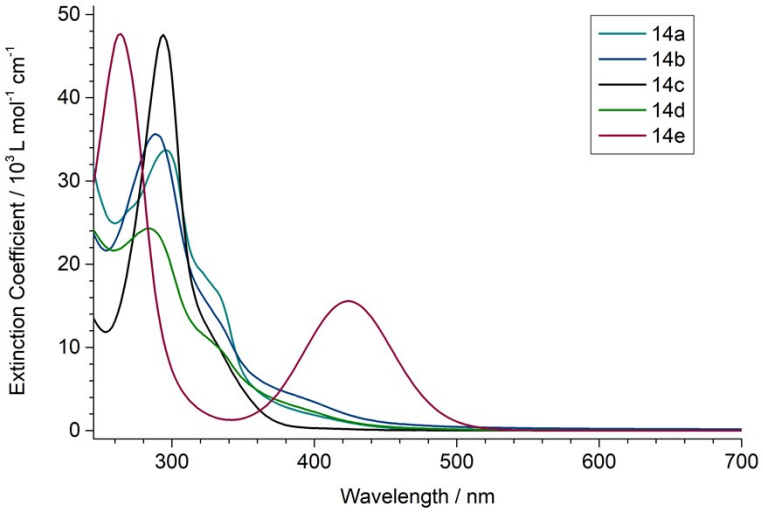


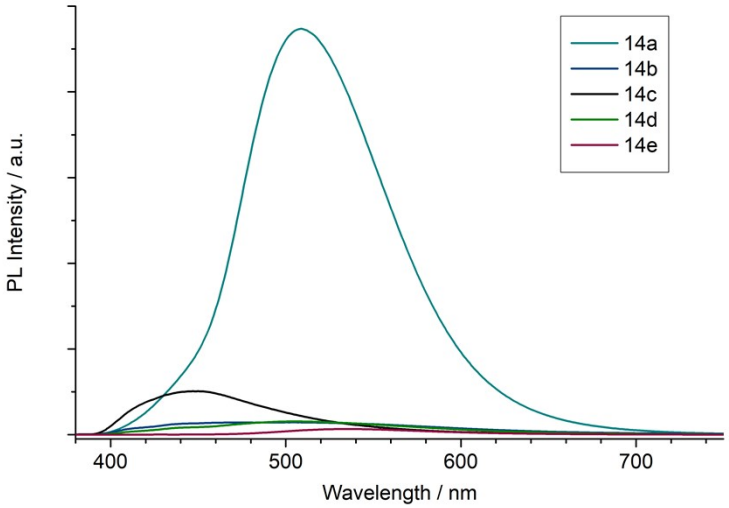
7-(4-(4-Fluorophenethyl)piperazine-1-carbonyl)-1*H*-imidazo[1,2-*b*]pyrazole-3-carbonitrile (4)

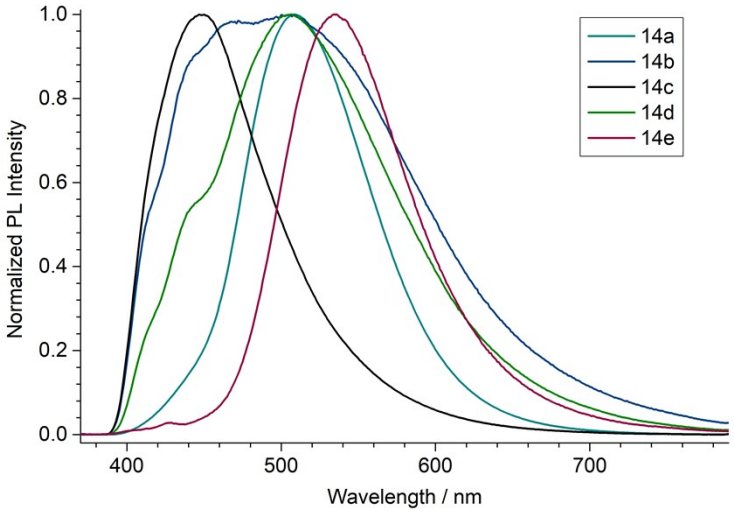



162.3
161.9
159.5
143.7
143.0
136.2
136.1
133.3
130.5
130.4
115.0
114.8
112.0
94.8
92.5
59.2
52.7
43.7
31.4
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

UV/vis and PL spectra







Details for X-ray data collection and structure refinement

Table 1. Details for X-ray data collection and structure refinement for compound **7a**.

	7a
Empirical formula	$C_{12}H_{21}N_3OSSi$
Formula mass	283.47
T[K]	123(2)
Crystal size [mm]	0.25 × 0.05 × 0.02
Crystal description	colorless platelet
Crystal system	monoclinic
Space group	*P*21/*c*
a [Å]	15.4782(12)
b [Å]	8.4222(7)
c [Å]	12.5728(9)
α [°]	90.0
β [°]	102.656(8)
γ [°]	90.0
V [Å^3]	1599.2(2)
Z	4
$\rho_{calcd.}$ [g cm^{-3}]	1.177
μ [mm^{-1}]	0.271
F(000)	608
Θ range [°]	2.76 – 25.24
Index ranges	$-19 \leq h \leq 17$
	$-10 \leq k \leq 9$
	$-15 \leq l \leq 15$
Reflns. collected	10569
Reflns. obsd.	1968
Reflns. unique	3139 (R_{int} = 0.0776)
R_1, wR_2 (2σ data)	0.0568, 0.0844
R_1, wR_2 (all data)	0.1074, 0.0998
GOOF on F^2	0.988
Peak/hole [e Å^{-3}]	0.276 / -0.281

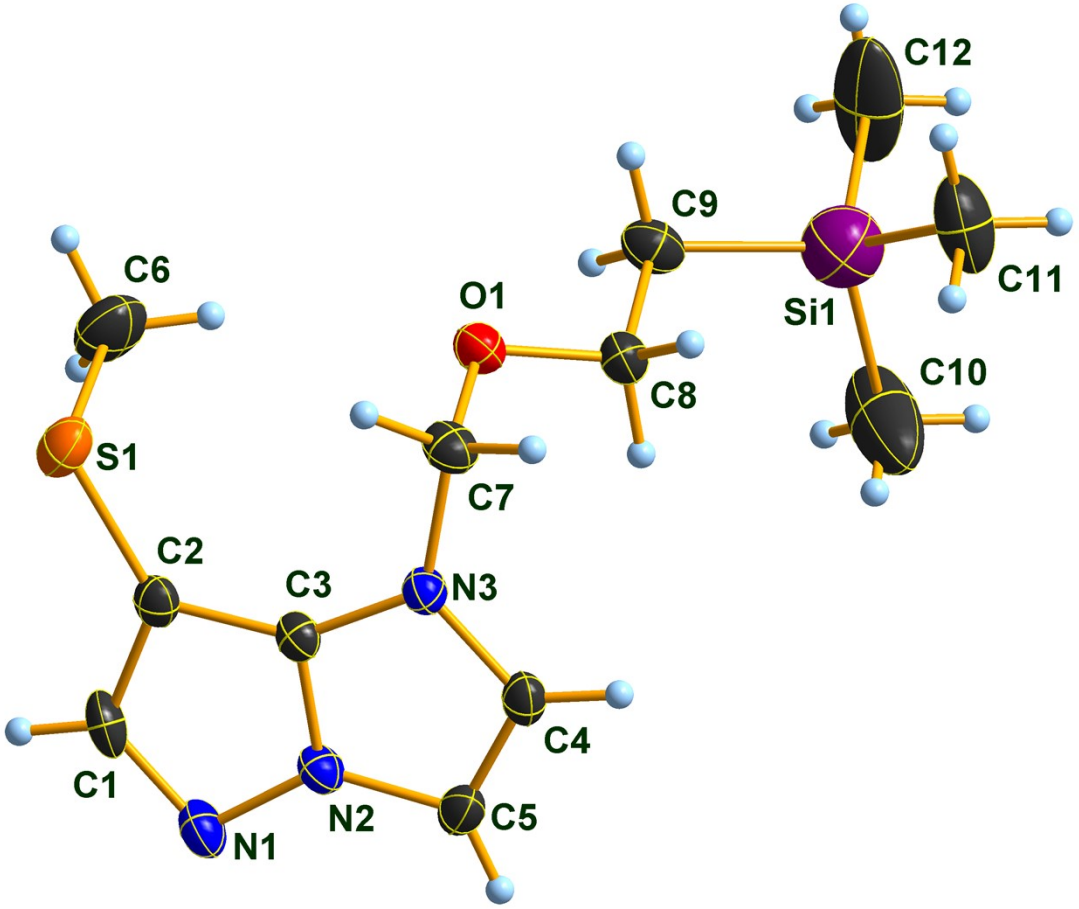


Figure 1. Molecular structure of compound **7a** in the crystal. DIAMOND[e)] representation; thermal ellipsoids are drawn at 50 % probability level.

Table 2. Selected bond lengths (Å) of compound **7a**.

S1 – C2	1.745(3)	C8 – C9	1.506(4)
S1 – C6	1.795(3)	C3 – N2	1.348(3)
C1 – N1	1.341(3)	C3 – C2	1.388(3)
C1 – C2	1.398(4)	N2 – N1	1.368(3)
Si1 – C12	1.843(4)	N2 – C5	1.388(3)
Si1 – C11	1.850(3)	C4 – C5	1.345(3)
Si1 – C10	1.862(4)	N3 – C3	1.372(3)
Si1 – C9	1.876(3)	N3 – C4	1.385(3)
O1 – C7	1.406(3)	N3 – C7	1.455(3)
O1 – C8	1.435(3)		

Table 3. Selected bond angles (°) of compound **7a**.

C2 – S1 – C6	101.3(1)	O1 – C7 – N3	113.0(2)
N1 – C1 – C2	115.6(3)	C8 – C9 – Si1	113.0(2)
C12 – Si1 – C11	109.6(2)	O1 – C8 – C9	110.5(2)
C12 – Si1 – C10	109.8(2)	N3 – C3 – C2	145.1(3)
C11 – Si1 – C10	108.3(2)	C3 – N2 – N1	113.1(2)
C12 – Si1 – C9	109.4(2)	C3 – N2 – C5	110.4(2)
C11 – Si1 – C9	109.7(1)	N1 – N2 – C5	136.4(2)
C10 – Si1 – C9	109.9(2)	C3 – C2 – C1	101.8(2)
C7 – O1 – C8	112.2(2)	C3 – C2 – S1	128.6(2)
C3 – N3 – C4	107.6(2)	C1 – C2 – S1	129.5(2)
C3 – N3 – C7	124.4(2)	C5 – C4 – N3	109.4(2)
C4 – N3 – C7	127.5(2)	C4 – C5 – N2	105.8(2)
N2 – C3 – N3	106.7(2)	C1 – N1 – N2	101.3(2)
N2 – C3 – C2	108.1(2)		

Table 4. Selected torsion angles (°) of compound **7a**.

C4 – N3 – C3 – N2	0.5(3)	C3 – N3 – C4 – C5	-1.0(3)
C7 – N3 – C3 – N2	173.5(2)	C7 – N3 – C4 – C5	-173.8(2)
C4 – N3 – C3 – C2	-179.3(4)	N3 – C4 – C5 – N2	1.0(3)
C7 – N3 – C3 – C2	-6.3(6)	C3 – N2 – C5 – C4	-0.7(3)
N3 – C3 – N2 – N1	-180.0(2)	N1 – N2 – C5 – C4	179.4(3)
C2 – C3 – N2 – N1	-0.1(3)	C2 – C1 – N1 – N2	-0.4(3)
N3 – C3 – N2 – C5	0.1(3)	C3 – N2 – N1 – C1	0.3(3)
C2 – C3 – N2 – C5	-179.9(2)	C5 – N2 – N1 – C1	-179.9(3)
N2 – C3 – C2 – C1	-0.2(3)	C7 – O1 – C8 – C9	-177.9(2)
N3 – C3 – C2 – C1	179.7(4)	C8 – O1 – C7 – N3	-78.8(3)
N2 – C3 – C2 – S1	176.9(2)	C3 – N3 – C7 – O1	-80.4(3)
N3 – C3 – C2 – S1	-3.3(6)	C4 – N3 – C7 – O1	91.3(3)
N1 – C1 – C2 – C3	0.3(3)	O1 – C8 – C9 – Si1	177.1(2)
N1 – C1 – C2 – S1	-176.6(2)	C12 – Si1 – C9 – C8	-176.3(2)
C6 – S1 – C2 – C3	84.8(3)	C11 – Si1 – C9 – C8	-56.0(3)
C6 – S1 – C2 – C1	-99.0(3)	C10 – Si1 – C9 – C8	63.0(3)