

Supporting Information

Tunable Regioselectivity for C–H Alkynylation of Weak Coordinating Amides that Tolerated Strongly Coordinating Heterocycles

Bifu Liu^{a†}, Qiaoya Zhang^{b†}, Jun Zhang^{b†}, Aidong Huang^b, Hulin Zhong^b, Kejun Feng^a,
Yang Gao^b, Yanping Huo^b, Qian Chen^b, Xianwei Li^{*b}

^a *School of Chemistry and Material Engineering, Huizhou University, Huizhou, 516007, China.*

^b *School of Chemical Engineering and Light Industry, Guangdong University of Technology,
Guangzhou, 510006, China.*

[†] *These authors (Bifu Liu, Qiaoya Zhang and Jun Zhang) contributed equally.*

E-mail: xwli@gdut.edu.cn

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A. General Information

^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using CDCl_3 as solvent and TMS as an internal standard. Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); dt (doublets of triplet); dq (doublets of quartet). Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP 5000 spectrometer. HRMS was carried out on a MAT 95XP (Thermo).

B. General procedure

B-1. General reaction procedure for the synthesis of amide:

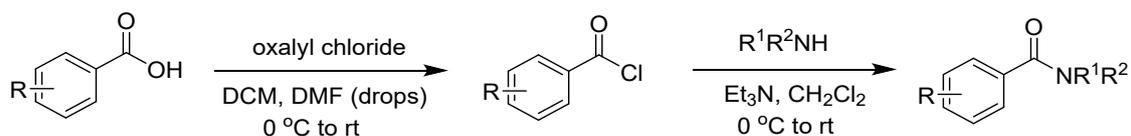


Figure S1. Synthesis of amide substrates.

1) The acid was dissolved in anhydrous CH₂Cl₂ (20 mL) and cooled with ice water. Oxalyl chloride (1.5 eq.) was added dropwise to the solution followed with the addition of catalytic amount of DMF (2 drops). The resulting mixture was allowed to stir at room temperature for additional two hours and the solvent was evaporated to afford crude acid chloride, which was used directly in the next step.

2) To a solution of amine R¹R²NH (1 eq.) in a mixture of Et₃N (1 M), CH₂Cl₂ (1 M), the resulting solution was cooled to 0 °C, followed by dropwise addition of the substituted benzoyl chloride (1.0 eq.). The reaction mixture was warmed to rt and stirred overnight. The organic phase was separated and the aqueous phase was extracted with EtOAc (20 mL×3). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The pure products were obtained by flash column chromatography.

B-2. General procedure for the preparation of haloalkynes bearing propargyl alcohols **2**:

The haloalkynes bearing propargyl alcohols **2** in this work were synthesized using literature procedures from the corresponding ketones or propargyl alcohols:

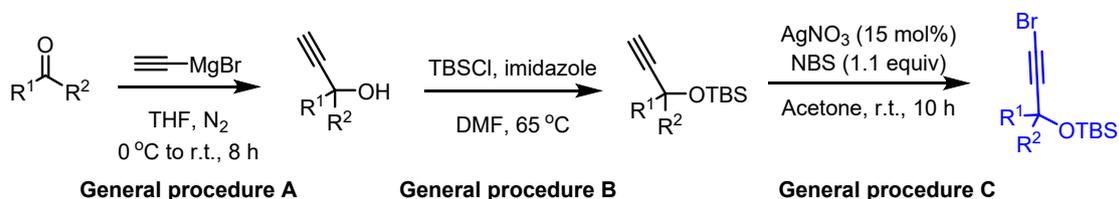


Figure S12. Synthesis of haloalkynes **2**.

General procedure A: Preparation of propargyl alcohols from corresponding ketones.

To a solution of ketone (5 mmol) in THF (5 mL) in ice bath, ethynylmagnesium bromide (0.5 M in THF, 15 mL, 7.5 mmol, 1.5 equiv) was added slowly. Upon completion of addition, ice bath was removed and the mixture was stirred for 4 hours at room temperature. The reaction was quenched with 0.5 N HCl (20 mL). The aqueous layer was extracted with ethyl acetate (40 mL) for three times. Combined organic phases were dried with sodium sulfate and concentrated in vacuo. Desired propargyl alcohol was used directly without further purification.

General procedure B: preparation of OTBS-propargyl alcohols.

To a solution of propargyl alcohol (4 mmol) in DMF (2 mL) was added tert-butyldimethylsilyl chloride (1.2 g, 8 mmol, 2.0 equiv) and imidazole (0.82 g, 12 mmol, 3.0 equiv). The solution was stirred and heated to $55^\circ C$ in oil bath for 24 hours. The reaction was quenched by addition of water (15 mL) and 0.5 N HCl (25 mL). The Aqueous layer was extracted with ethyl acetate (25 mL) for three times. Combined organic phases were dried with sodium sulfate and concentrated. Crude residue was purified by column chromatography (1% ether in hexane) to give desired silyl ether. (T. Liu, J. X. Qiao, M. A. Poss, J.-Q. Yu, Palladium(II)-Catalyzed Site-Selective $C(sp^3)$ -H Alkynylation of Oligopeptides: A Linchpin Approach for Oligopeptide-Drug Conjugation. *Angew. Chem. Int. Ed.* **2017**, *56*, 10924-10927.).

General procedure C: preparation of haloalkynes from terminal alkynes.

To a solution of terminal alkynes (1 mmol) in acetone (5 mL) was added N-bromo succinimide (195 mg, 1.1 mmol, 1.1 equiv) and silver nitrate (8.5 mg, 0.05 mmol, 5 mol%) at room temperature. The solution was stirred for 4 hours at room temperature in darkness. The reaction was quenched with water (5 mL) and extracted with DCM (10 mL) for three times. The combined organic layers were dried with sodium sulfate and concentrated. Crude residue was purified by column chromatography (2% DCM in hexane) to give desired alkynyl bromides.

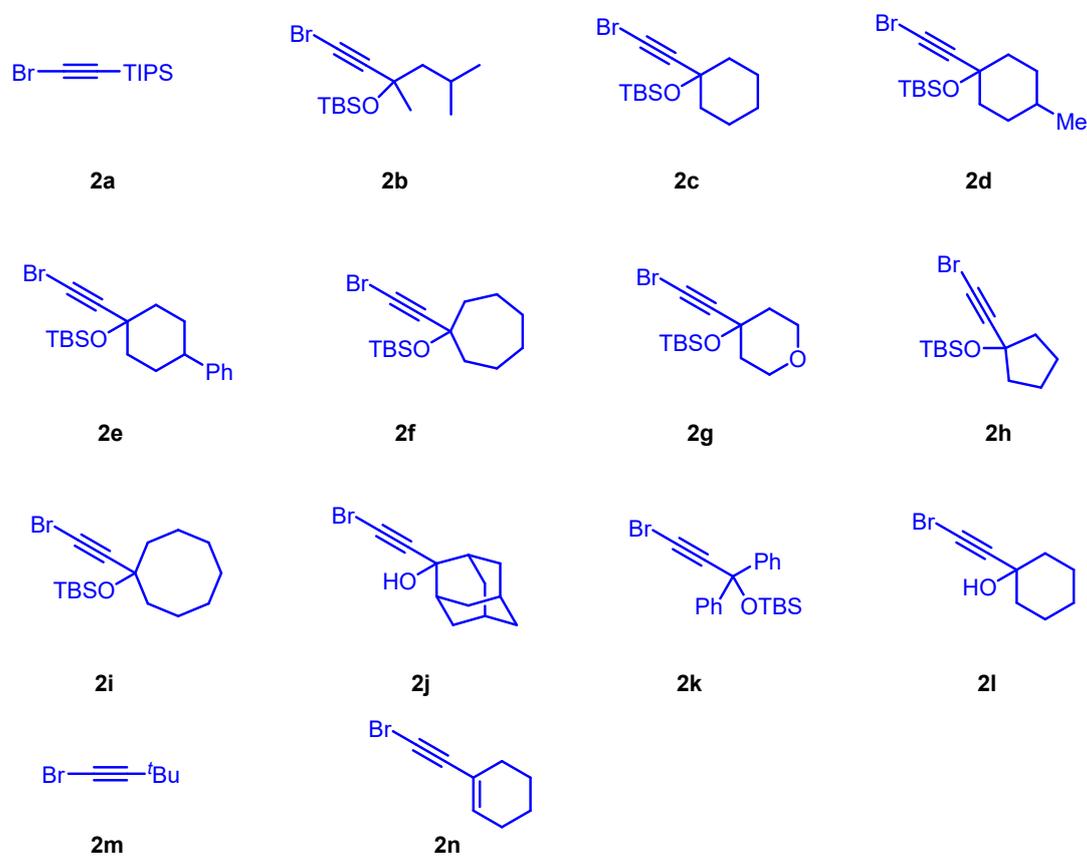


Figure S13. Haloalkynes used in this C–H annulation or alkylation of amides.

To commence this study, we selected benzamide **1a** bearing competing coordinating amine moiety as the model substrate to conduct regioselective C–H alkynylation with haloalkyne **2a** (Table S1). Extensive investigations revealed that optimal result was obtained with [Cp*IrCl₂]₂ (2 mol%), AgNTf₂ (5 mol%), 1-AdCO₂Cs (30 mol%), AgOAc (1.0 equiv) in acetone at 70 °C for 12 hours, furnishing C–H alkynylation product **3a** with and regioselectivity.

Table S1. Optimization of the Reaction Conditions^a.

Entry	Variation of standard condition	Yield ^b (%)
1	None	76
2	Pd(OAc) ₂ (5 mol%), K ₂ S ₂ O ₈ (1.5 equiv)	n. p.
3	NiCl ₂ (5 mol%), Cu(OAc) ₂ (2.0 equiv)	n. p.
4	[RhCp*Cl ₂] ₂ (4 mol%)	72
5	[Ru(<i>p</i> -cymene)Cl ₂] ₂ (4 mol%)	61
6	Without AgNTf ₂	<10
7	AgSbF ₆ instead of AgNTf ₂	46
8	Cu(OAc) ₂ of AgOAc	<10
9	Without 1-AdCO ₂ Cs	23
10	CsOAc instead of 1-AdCO ₂ Cs	48
11	Addition of PivOH (0.5 equiv)	16
12	Toluene or DCE instead of Acetone	n. p. or 71

^a Standard reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), [IrCp*Cl₂]₂ (4 mol%), AgNTf₂ (16 mol%), 1-AdCO₂Cs (30 mol%), AgOAc (1.0 equiv.), acetone (1.0 mL), air, 70 °C, 12 h. ^b Isolated yield.

Ir(III) stood out to be optimal, Rh(III) and Ru(II) complex exhibited moderated efficiency, while Pd(II) or Ni(II) showed no reactivity (entries 1-4). AgNTf₂ was also critical to serve as a halide-scavenger, no or low efficiency were observed in the absence of it, or with AgSbF₆ instead of it. The use of Cu(II) salt to replace AgOAc was deleterious for this regioselective C–H alkynylation (entry 8). Base additive 1-AdCO₂Cs was also indispensable, since the use of CsOAc or PivOH led to significantly low efficiency (entry 9-11). DCE was also an amenable solvent, while the use of toluene totally shut down this reaction (entry 12).

B-3. General procedure for the Ir(III)-Catalyzed C–H alkynylation of amides:

An oven-dried 10 mL Schlenk Tube was charged with **1** (0.1 mmol), [Cp*IrCl₂]₂ (0.004 mmol, 3.2 mg), AgNTf₂ (0.018 mmol, 6.2 mg), 1-AdCO₂Cs (0.03 mmol, 11.5 mg), AgOAc (0.1 mmol, 16.7 mg) in sequence, followed by adding haloalkyne **2** (0.15 mmol) in acetone (1.0 mL) through syringe. The resulting reaction mixture was stirred at 70 °C for 12 h and then diluted with CH₂Cl₂ and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired alkynylation and/or annulation product **3** or **4**.

For the multi-functionalized amides, similar reaction conditions were used for the regioselective C–H alkynylation and/or annulation, notably, for those 1,4-di-alkynylation, 3 equivalents of haloalkynes **2** were added to the standard conditions, furnishing alkyne or heterocycle products **5** or **6**.

C. Mechanistic studies

1) To verify our initial proposal of the mechanism on this Ir(III)-catalyzed C–H bond alkylation of carbonyl compounds, preliminary mechanistic investigations were conducted. We select amide substrate **1g** to perform stoichiometric reaction, based on precedent report by Sukbok Chang. Indeed, cyclometallated intermediate **3g-Int** was obtained in 52%, and the structure was confirmed unambiguously by single crystal diffraction (Figure S7).

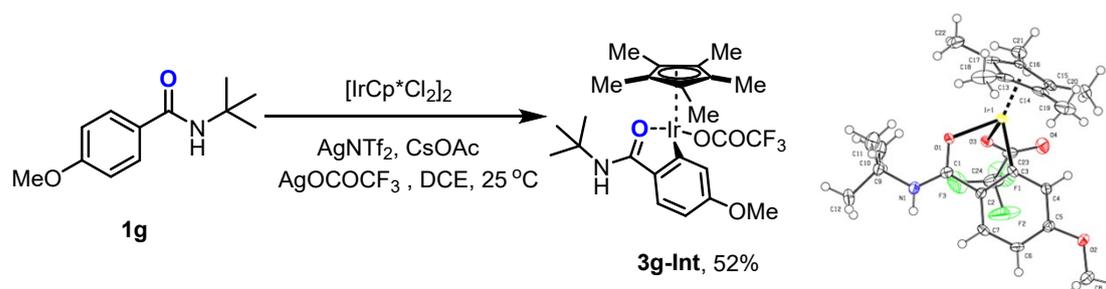


Figure S7. Stoichiometric experiment for the generation of *O*-coordinated iridacycle intermediate.

2) Subsequently, we test the reactivity of **3i-Int** in the catalytic reaction of amide facilitated C–H alkylation, with the assistance of Ag(I), the desired product **3i** was obtained with moderated yield (Kim, H.; Shin, K.; Chang, S. Iridium-Catalyzed C–H Amination with Anilines at Room Temperature: Compatibility of Iridacycles with External Oxidants. *J. Am. Chem. Soc.* **2014**, 136, 5904–5907.). This result supported that **3g-Int** might serve as the key intermediate of this transformation (Figure S8).

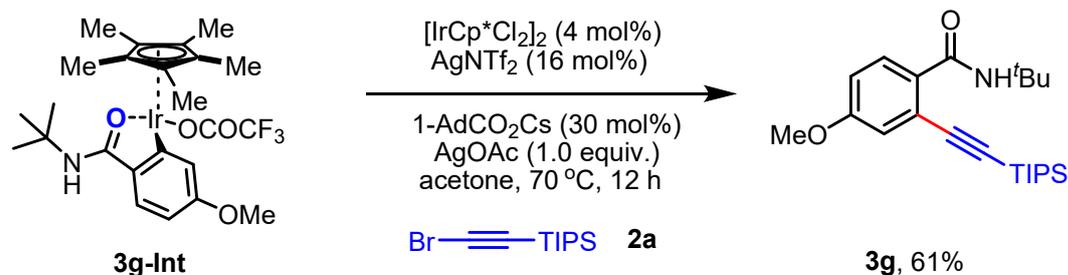


Figure S8. Catalytic reactivity of the generated *O*-coordinated iridacycle for amides enabled C–H alkylation.

3) Compatibility of strongly coordinating heterocycles for this weak coordinating amides enabled C–H alkylation:

To elucidate the mechanistic basis for regiodivergent C–H alkylation of amides bearing strongly coordinating heterocycles, we first examined *N*-pyrazole benzene with distinct haloalkynes (**Figure S9**). And C–H alkylation took place smoothly with TIPS-substituted haloalkyne **2a**, while the use of aliphatic haloalkynes yielded recovery of starting material. These divergent outcomes suggest steric blockade of the iridacycle intermediate by bulky coupling partners and/or coordinative saturation of the Ir-catalyst (**Figure S9**).

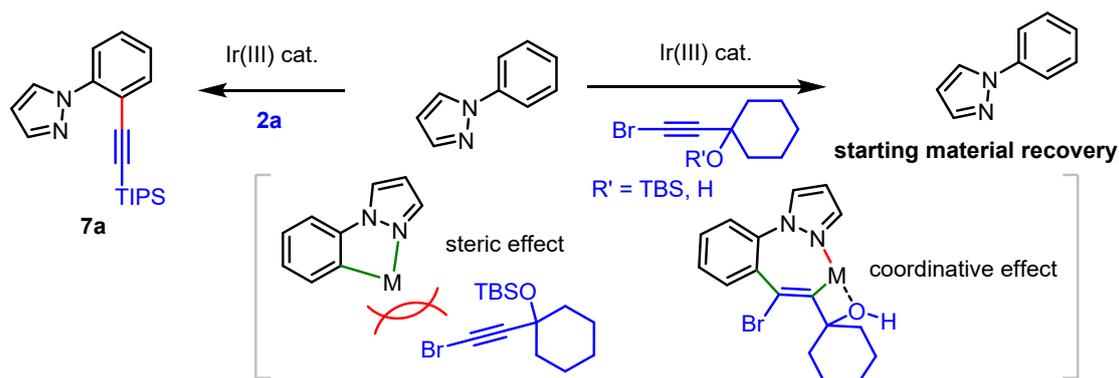


Figure S9. Match and mismatch reactivity of haloalkynes for directed C–H alkylation.

Further studies with conventional *L*-type directing groups (*N*-OMe oxime, *N*-pyrazole benzamides and *N*-(*tert*-butyl)-4-(pyridin-2-yl)benzamide) revealed analogous behavior: alkylation occurred exclusively *ortho* to the DG with **2a**, furnishing alkylation products **6d**, **6e** and **6f**, respectively (Scheme 4B). Strikingly, propargyl alcohol and alkyl-substituted haloalkynes enabled an

unprecedented C–H alkylation/C–O cyclization cascade with complementary regioselectivity, affording annulation products **4v**, **4w** and **4x** (Figure S10).

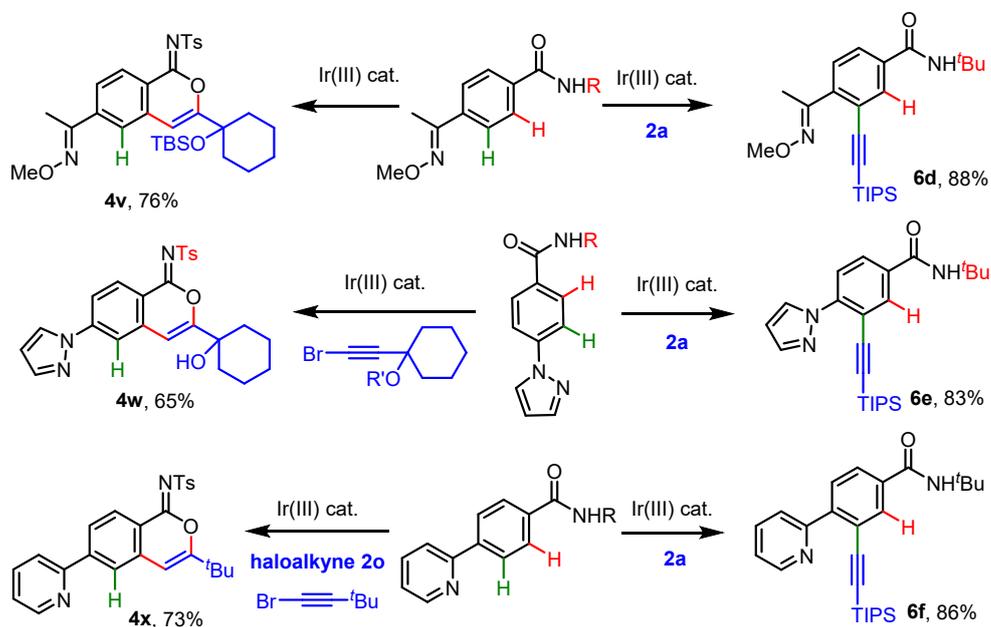


Figure S10. Switchable regioselectivity for C–H alkylation via L-type versus X-type coordination.

Along this line, we further investigated regiodivergent C–H annulation of Celecoxib, by exploiting match/mismatch effect of aliphatic haloalkynes to the benzamides bearing strongly coordinating heterocycles. Delightfully, diverse haloalkynes that are derived from alkyl alkynes and enynes showed complementary regioselectivity for this *N*-sulfonyl amides enabled C–H annulation of Celecoxib derivatives (**4y-4zc**). Notably, C2 and C4-alkynylation/annulation of thiophene substituted Celecoxib analogue was also achieved (**4zd**) (**Figure S11**).

These observations suggest that the sterically demanding aliphatic haloalkynes exhibits mismatched reactivity with pyrazole. Moreover, the alkylation/C–O cyclization cascade to generate heterocyclic products serves as the key thermodynamic driving force, lowering the overall energy barrier and enabling transformations that tolerate strongly coordinating heterocycles. Consequently, the regiodivergent functionalization of Valdecoxib and Celecoxib analogues

arises from complementary reactivity patterns between amide substrates and haloalkynes under Ir(III) catalysis.

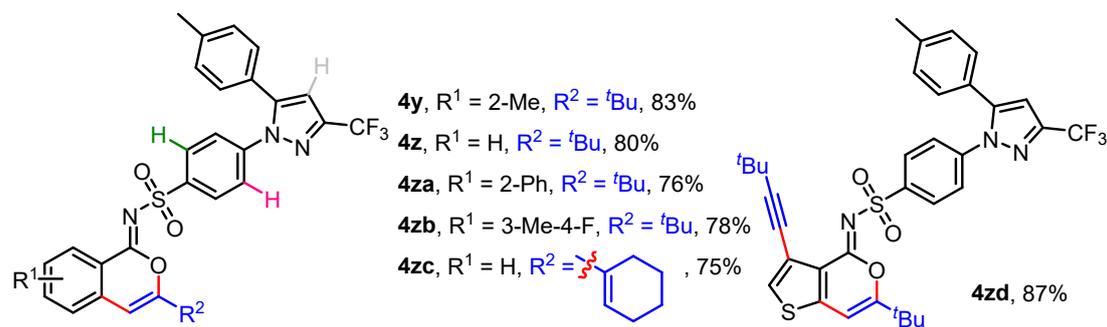


Figure S11. Match/mismatch effect enabled regioselective C–H alkynylation/annulation of benzamides bearing Celecoxib.

Stoichiometric experiment using secondary amide **1g**, and the corresponding 5-membered iridacycle intermediate **3g-Int** was obtained, in which oxygen atom of amide coordinated to the iridium. While the use of *N*-Ts amides led to iridacycle species via *X*-type *O*- or *N*-coordination, which followed by migratory insertion of haloalkynes, and β -Br elimination released alkyne **4w-C**, upon nucleophilic addition, the C–O annulation products were obtained. Thus, *X*-type coordination and nucleophilicity of *N*-Ts facilitated kinetic favored C–H metalation, while the generation of thermodynamically stable annulation products further drove the overall process that tolerated strongly coordinating heterocycles (**Figure S12**).

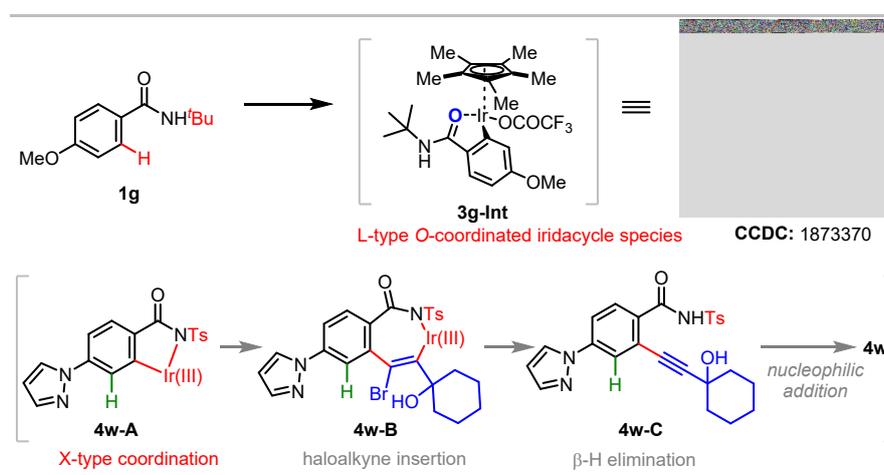
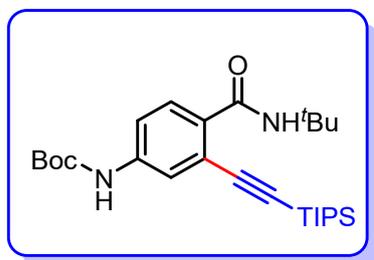


Figure S12. L-Type versus X-type coordination of amides to Ir(III) catalyst enabled regiodivergent C–H alkynylation/annulation that tolerated strongly coordinating heterocycles.

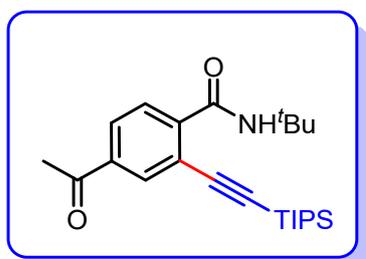
These observations suggest that the sterically demanding cyclohexanol-derived haloalkynes exhibits mismatched reactivity with pyrazole. Moreover, the alkynylation/C–O or C–N cyclization cascade to generate heterocyclic products serves as the key thermodynamic driving force, lowering the overall energy barrier and enabling transformations that tolerate strongly coordinating heterocycles.

Consequently, the regiodivergent functionalization of Valdecoxib and Celecoxib analogues arises from complementary reactivity patterns between amide substrates and haloalkynes under Ir(III) catalysis.

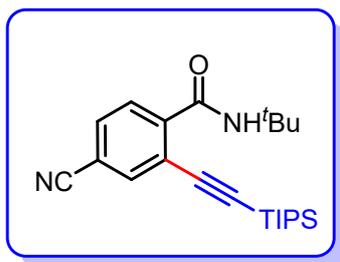
D. Analytical data for the obtained products:



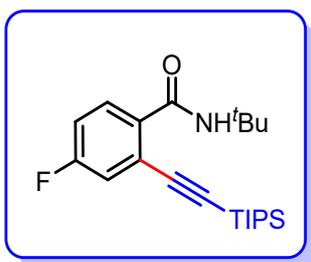
tert-Butyl(4-(tert-butylcarbamoyl)-3-((triisopropylsilyl)ethynyl)phenyl)carbamate (3a), white solid (36 mg, 76% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 117 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.16 (d, $J = 1.6$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.21 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.13 (s, 1H), 5.59 (s, 1H), 1.53 (s, 9H), 1.33 (m, 3H), 1.09 (d, $J = 7.6$ Hz, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.4, 156.7, 152.4, 144.6, 141.3, 126.0, 120.4, 119.1, 109.0, 101.4, 81.8, 28.4, 18.9, 18.5, 11.8. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{45}\text{N}_2\text{O}_3\text{Si}$: 473.3194, found: 473.3194.



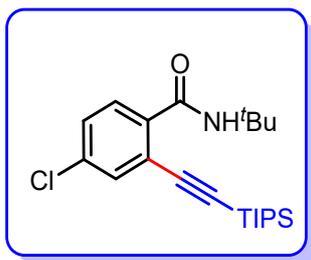
4-Acetyl-N-(tert-butyl)-2-((triisopropylsilyl)ethynyl)benzamide (3b), white solid (28 mg, 71% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 121 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 (d, $J = 2.0$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.91 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.99 (s, 1H), 2.61 (s, 3H), 1.48 (s, 9H), 1.16 (d, $J = 4.0$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.0, 165.0, 140.7, 138.0, 134.7, 130.1, 128.4, 120.4, 104.5, 99.7, 52.4, 28.9, 26.9, 18.9, 11.5. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{38}\text{NO}_2\text{Si}$: 400.2666, found: 400.2672.



***N*-(*tert*-Butyl)-4-cyano-2-((triisopropylsilyl)ethynyl)benzamide (3c)**, white solid (26 mg, 69% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 113 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.94 (s, 1H), 1.47 (s, 9H), 1.15 (d, *J* = 4.0 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 140.7, 138.3, 131.7, 130.5, 121.1, 117.5, 114.2, 103.0, 101.8, 52.6, 28.8, 18.8, 11.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₃H₃₅N₂OSi: 383.2513, found: 383.2519.

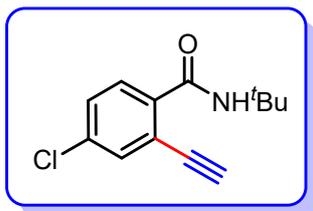


***N*-(*tert*-Butyl)-4-fluoro-2-((triisopropylsilyl)ethynyl)benzamide (3d)**, white solid (28 mg, 76% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 125 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.11-7.06 (m, 2H), 1.47 (s, 9H), 1.14 (d, *J* = 4.0 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 163.1(d, *J* = 250 Hz), 133.1(d, *J* = 3 Hz), 132.3(d, *J* = 9 Hz), 121.7(d, *J* = 10 Hz), 121.2(d, *J* = 23 Hz), 116.5(d, *J* = 21 Hz), 104.4, 100.1, 52.2, 28.9, 18.8, 11.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.69. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₃₅FNOSi: 392.2172, found: 392.2172.

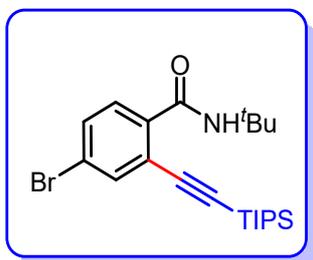


***N*-(*tert*-Butyl)-4-chloro-2-((triisopropylsilyl)ethynyl)benzamide (3e)**, white solid

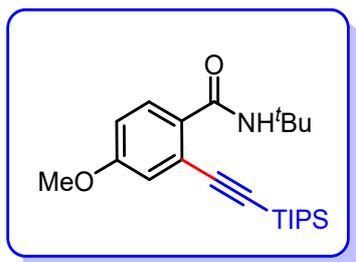
(32 mg, 81% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 129 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.07 (s, 1H), 1.46 (s, 9H), 1.15 (d, *J* = 4.0 Hz, 21H). **¹³C NMR (100 MHz, CDCl₃)** δ 164.7, 136.0, 135.2, 134.2, 131.1, 129.3, 121.2, 104.3, 100.2, 52.2, 28.9, 18.8, 11.4. **HRMS (ESI-TOF) m/z:** [M + H]⁺ Calcd for C₂₂H₃₅ClNOSi: 392.2172, found: 392.2178.



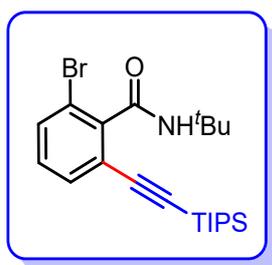
***N*-(*tert*-Butyl)-4-chloro-2-ethynylbenzamide (3e-1)**, white solid (20 mg, 86% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 116 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.99 (s, 1H), 3.51 (s, 1H), 1.46 (s, 9H). **¹³C NMR (100 MHz, CDCl₃)** δ 164.5, 136.4, 136.2, 133.5, 131.2, 129.9, 119.9, 84.7, 81.2, 52.4, 28.8. **HRMS (ESI-TOF) m/z:** [M + H]⁺ Calcd for C₁₃H₁₅ClNO: 236.0837, found: 236.0843.



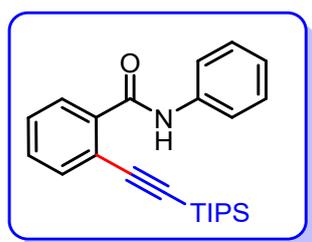
4-Bromo-*N*-(*tert*-butyl)-2-((triisopropylsilyl)ethynyl)benzamide (3f), white solid (32 mg, 74% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 112 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.05 (s, 1H), 1.46 (s, 9H), 1.15 (d, *J* = 3.6 Hz, 21H). **¹³C NMR (100 MHz, CDCl₃)** δ 164.8, 137.1, 135.7, 132.2, 131.4, 124.1, 121.5, 104.1, 100.3, 52.2, 28.9, 18.8, 11.4. **HRMS (ESI-TOF) m/z:** [M + H]⁺ Calcd for C₂₂H₃₅BrNOSi: 436.1666, found: 436.1672.



***N*-(*tert*-Butyl)-4-methoxy-2-((triisopropylsilyl)ethynyl)benzamide (3g)**, white solid (31 mg, 80% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 114 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.8$ Hz, 1H), 7.26 (s, 1H), 7.00 (d, $J = 2.8$ Hz, 1H), 6.92 (dd, $J = 8.8, 2.8$ Hz, 1H), 3.82 (s, 3H), 1.46 (s, 9H), 1.14 (d, $J = 3.6$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.2, 160.6, 131.9, 129.1, 120.9, 119.9, 114.7, 105.8, 98.7, 55.6, 51.9, 28.9, 18.8, 11.4. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{38}\text{NO}_2\text{Si}$: 388.2666, found: 388.2672.

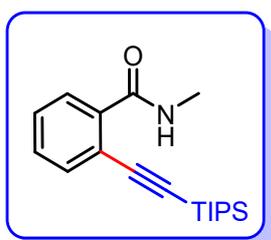


2-Bromo-*N*-(*tert*-butyl)-6-((triisopropylsilyl)ethynyl)benzamide (3h), white solid (32mg, 74% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 129 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.43 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.12 (t, $J = 8.0$ Hz, 1H), 5.48 (s, 1H), 1.47 (s, 9H), 1.11 (d, $J = 1.2$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.8, 141.3, 132.8, 132.6, 129.6, 122.8, 120.0, 103.3, 96.1, 52.4, 28.8, 18.8, 11.4. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{35}\text{BrNOSi}$: 436.1666, found: 436.1672.

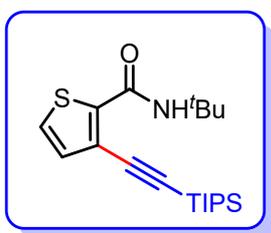


***N*-Phenyl-2-((triisopropylsilyl)ethynyl)benzamide (3i)**, white solid (27 mg, 71% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 123 °C. $^1\text{H NMR}$

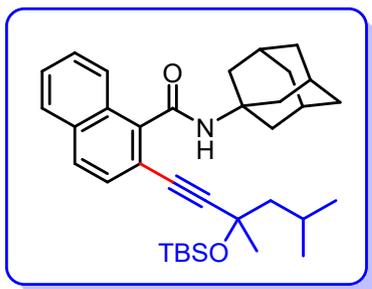
(400 MHz, CDCl₃) δ 9.07 (s, 1H), 8.10-8.04 (m, 1H), 7.62 (td, J = 8.0, 3.2 Hz, 3H), 7.47-7.43 (m, 2H), 7.35 (dd, J = 8.4, 7.2 Hz, 2H), 7.17-7.11 (m, 1H), 1.07 (d, J = 4.0 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 137.8, 136.2, 134.6, 130.8, 130.2, 129.2, 129.0, 124.8, 120.8, 119.9, 105.0, 99.6, 18.7, 11.4. HRMS (ESI-TOF) m/z : [M + H]⁺ Calcd for C₂₄H₃₂NOSi: 378.2448, found: 378.2454.



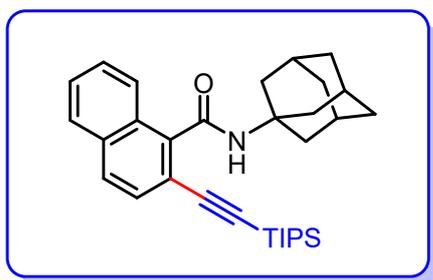
N-Methyl-2-((triisopropylsilyl)ethynyl)benzamide (**3j**), white solid (24 mg, 75% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 120 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, J = 7.6, 2.0 Hz, 1H), 7.78 (s, 1H), 7.53 (dd, J = 6.8, 2.4 Hz, 1H), 7.39 (pd, J = 7.2, 2.0 Hz, 2H), 2.99 (d, J = 4.8 Hz, 3H), 1.14 (d, J = 3.6 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 135.3, 134.4, 130.5, 130.2, 129.1, 119.6, 105.8, 98.5, 26.8, 18.7, 11.3. HRMS (ESI-TOF) m/z : [M + H]⁺ Calcd for C₁₉H₃₀NOSi: 316.2091, found: 316.2098.



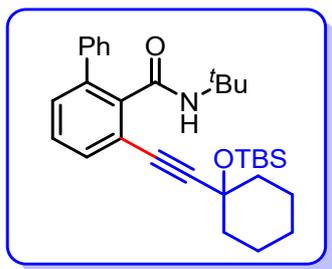
N-(*tert*-Butyl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide (**3k**), white solid (30 mg, 82% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 117°C. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (s, 1H), 7.33 (d, J = 5.2 Hz, 1H), 7.09 (d, J = 5.2 Hz, 1H), 1.46 (s, 9H), 1.14 (d, J = 3.2 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 143.6, 132.8, 128.5, 119.5, 101.2, 99.3, 52.2, 29.0, 18.8, 11.3. HRMS (ESI-TOF) m/z : [M + H]⁺ Calcd for C₂₀H₃₅NOSSi: 364.2125, found: 364.2131.



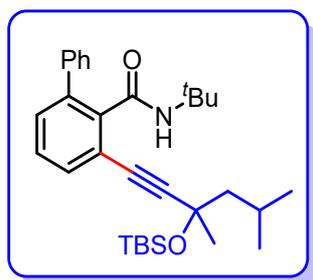
***N*-(Adamantan-1-yl)-2-(3-((*tert*-butyldimethylsilyl)oxy)-3,5-dimethylhex-1-yn-1-yl)-1-naphthamide (3l)**, white solid (37 mg, 68% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 157 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 12.8, 8.0 Hz, 2H), 7.55-7.44 (m, 3H), 5.58 (brs, 1H), 2.24 (d, *J* = 2.4 Hz, 6H), 2.17 (s, 3H), 2.07 (d, *J* = 6.4 Hz, 1H), 1.80-1.73 (m, 6H), 1.70 (dd, *J* = 5.6, 2.0 Hz, 2H), 1.59 (s, 3H), 1.05-1.01 (m, 6H), 0.90 (s, 9H), 0.25 (d, *J* = 4.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 138.4, 132.8, 130.0, 128.8, 128.6, 128.1, 127.5, 126.9, 125.6, 117.3, 98.8, 82.1, 69.9, 53.8, 53.1, 41.9, 36.5, 31.9, 29.7, 25.9, 25.0, 24.6, 24.6, 18.2, -2.4, -2.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₅H₅₀NO₂Si: 544.3605, found: 544.3611.



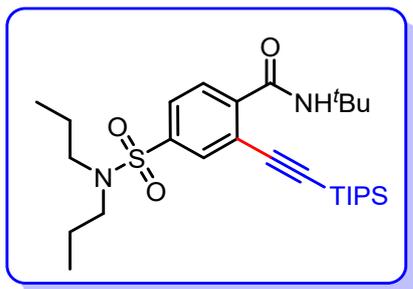
***N*-(Adamantan-1-yl)-2-((triisopropylsilyl)ethynyl)-1-naphthamide (3m)**, white solid (34 mg, 70% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 135 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.78-7.72 (m, 2H), 7.55- 7.46 (m, 3H), 5.65 (brs, 1H), 2.24 (d, *J* = 2.4 Hz, 6H), 2.15 (s, 3H), 1.78-1.71 (m, 6H), 1.18 (s, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 167.2, 138.5, 132.9, 129.9, 129.6, 128.6, 128.0, 127.4, 127.0, 125.7, 117.6, 105.2, 96.0, 53.1, 41.7, 36.5, 29.6, 18.9, 11.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₂H₄₄NOSi: 486.3187, found: 486.3193.



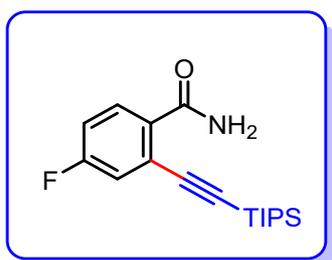
***N*-(*tert*-Butyl)-3-((1-((*tert*-butyldimethylsilyloxy)cyclohexyl)ethynyl)-[1,1'-biphenyl]-2-carboxamide (3n)**, white solid (39 mg, 80% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 116 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.33 (m, 3H), 7.27-7.22 (m, 4H), 7.17 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.94 (brs, 1H), 1.81-1.78 (m, 2H), 1.59-1.49 (m, 7H), 1.35-1.32 (m, 1H), 1.01 (s, 9H), 0.80 (s, 9H), 0.11 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 140.0, 139.9, 139.8, 131.7, 129.6, 128.9, 128.7, 128.4, 127.9, 127.7, 126.2, 121.4, 97.4, 82.5, 69.9, 51.6, 41.2, 28.4, 26.0, 25.5, 22.9, 18.3, -2.6. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₄₄NO₂Si: 490.3136, found: 490.3142.



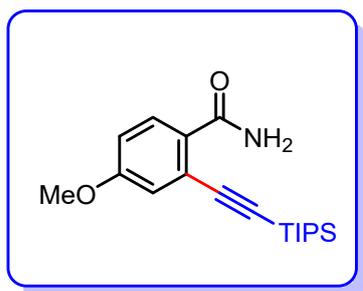
***N*-(*tert*-Butyl)-3-(3-((*tert*-butyldimethylsilyloxy)-3,5-dimethylhex-1-yn-1-yl)-[1,1'-biphenyl]-2-carboxamide (3o)**, white solid (37 mg, 76% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 112 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.43 (m, 3H), 7.40-7.33 (m, 4H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.08 (brs, 1H), 2.02 (d, *J* = 6.4 Hz, 1H), 1.65-1.62 (m, 2H), 1.52 (s, 3H), 1.13 (s, 9H), 1.00 (dd, *J* = 8.8, 6.8 Hz, 6H), 0.89 (s, 9H), 0.24 (d, *J* = 4.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 139.9, 139.8, 139.7, 131.5, 129.6, 128.9, 128.7, 128.4, 127.7, 124.4, 121.4, 100.1, 97.7, 81.6, 69.8, 53.7, 51.6, 32.0, 28.5, 25.9, 25.0, 24.6, 24.5, 18.2, -2.53, -2.77. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₄₆NO₂Si: 492.3292, found: 492.3298.



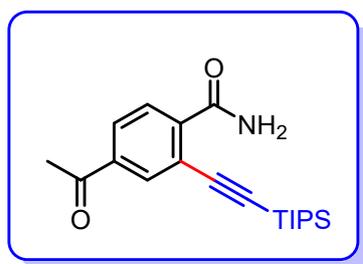
***N*-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2-((triisopropylsilyl)ethynyl)benzamide (3p)**, white solid (39 mg, 75% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 116 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.73 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.90 (s, 1H), 3.12-3.03 (m, 4H), 1.53 (h, *J* = 7.6 Hz, 4H), 1.46 (s, 9H), 1.13 (d, *J* = 4.4 Hz, 21H), 0.86 (t, *J* = 7.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 141.7, 140.3, 133.0, 130.3, 126.8, 120.9, 103.8, 100.8, 52.4, 50.0, 28.8, 22.0, 18.8, 11.4, 11.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₈H₄₉N₂O₃SSi: 521.3228, found: 521.3234.



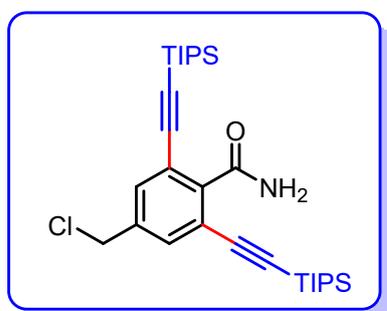
4-Fluoro-2-((triisopropylsilyl)ethynyl)benzamide (3q), white solid (21 mg, 65% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 147 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.19-8.15 (m, 1H), 7.79 (brs, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.39 (brs, 1H), 1.13 (m, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 166.9, 165.0, 162.5, 133.4, 133.3, 130.8, 130.8, 122.6, 122.5, 120.9, 120.7, 116.8, 116.6, 104.5, 104.5, 100.8, 18.7, 11.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -108.80. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₂₇FNOSi: 320.1840, found: 320.1846.



4-Methoxy-2-((triisopropylsilyl)ethynyl)benzamide (3r), white solid (27 mg, 81% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 138 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.8$ Hz, 1H), 7.89 (brs, 1H), 7.02 (d, $J = 2.4$ Hz, 1H), 6.95 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.05 (brs, 1H), 3.85 (s, 3H), 1.12 (d, $J = 4.4$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.5, 161.5, 132.9, 126.8, 121.9, 119.3, 115.0, 105.9, 99.1, 55.6, 18.7, 11.3. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{30}\text{NO}_2\text{Si}$: 332.2040, found: 332.2046.

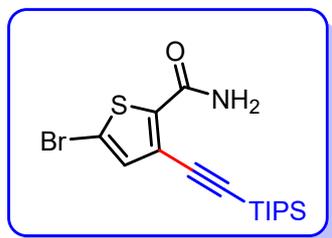


4-Acetyl-2-((triisopropylsilyl)ethynyl)benzamide (3s), white solid (25 mg, 72% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 142 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.24 (d, $J = 8.2$ Hz, 1H), 8.11 (s, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.84 (brs, 1H), 6.20 (brs, 1H), 2.64 (s, 3H), 1.14 (d, $J = 5.2$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.9, 167.1, 138.9, 137.8, 134.2, 131.1, 128.4, 121.0, 104.7, 100.8, 27.0, 18.8, 11.4, 1.2. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{NO}_2\text{Si}$: 344.2040, found: 344.2046.

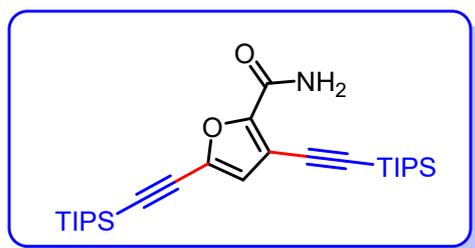


4-(Chloromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (3t), white solid (31 mg, 59% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 141 °C.

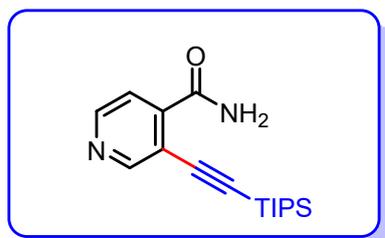
^1H NMR (400 MHz, CDCl_3) δ 7.46 (s, 2H), 5.89 (brs, 1H), 5.79 (brs, 1H), 4.50 (s, 2H), 1.11 (s, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 141.8, 138.5, 132.6, 121.9, 102.7, 96.8, 18.7, 11.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{49}\text{ClNOSi}_2$: 530.3036, found: 530.3042.



5-Bromo-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide (3u), white solid (23 mg, 59% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 129 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (brs, 1H), 7.09 (s, 1H), 6.62 (brs, 1H), 1.10 (d, J = 4.4 Hz, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.2, 142.8, 134.4, 121.9, 118.3, 101.0, 99.5, 18.7, 11.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{25}\text{BrNOSSi}$: 386.0604, found: 386.0610.

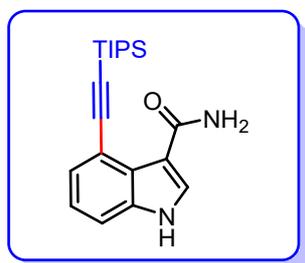


3,5-bis((triisopropylsilyl)ethynyl)furan-2-carboxamide (3v), white solid (33 mg, 71% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 116 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.95 (brs, 1H), 6.70 (s, 1H), 6.13 (brs, 1H), 1.11 (d, J = 4.8 Hz, 42H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 147.4, 138.3, 119.9, 111.8, 101.7, 100.0, 96.7, 94.1, 18.7, 18.4, 11.4, 11.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{46}\text{NO}_2\text{Si}_2$: 472.3062, Found: 472.3068.

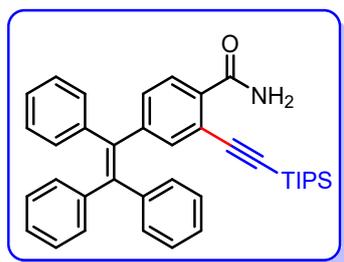


3-((Triisopropylsilyl)ethynyl)isonicotinamide (3w), white solid (10 mg, 31% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 109 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.82 (s, 1H), 8.68 (d, J = 4.8 Hz, 1H), 7.98 (d, J = 5.2 Hz, 1H), 7.82

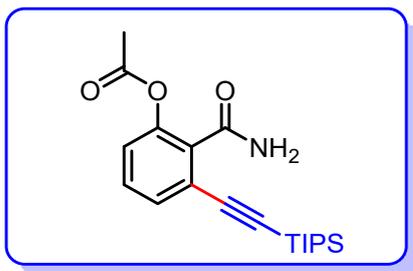
(brs, 1H), 6.20 (brs, 1H), 1.14 (d, $J = 5.2$ Hz, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 154.9, 149.8, 140.7, 123.2, 116.3, 103.3, 102.6, 18.7, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{OSi}$: 303.1887; found: 303.1879.



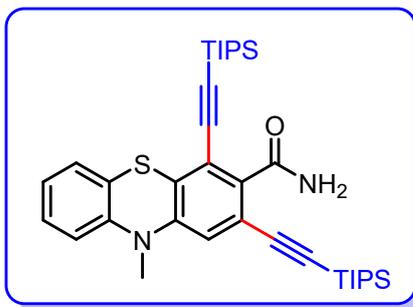
4-((Triisopropylsilyl)ethynyl)-1H-indole-3-carboxamide (3x), white solid (18 mg, 53% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 125 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.85 (s, 1H), 7.57 (s, 1H), 7.55 (s, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.25-7.22 (m, 1H), 6.54 (s, 1H), 6.19 (s, 1H), 1.11 (d, $J = 5.6$ Hz, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.12, 138.7, 132.8, 130.6, 130.3, 129.3, 129.2, 125.3, 123.0, 108.0, 102.5, 18.7, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{29}\text{N}_2\text{OSi}$: 341.2044, found: 341.2050.



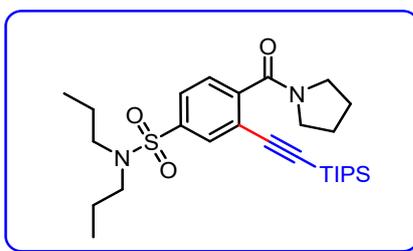
2-((Triisopropylsilyl)ethynyl)-4-(1,2,2-triphenylvinyl)benzamide (3y), white solid (38 mg, 70% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 149 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (s, 1H), 7.14-7.13 (m, 4H), 7.10-7.09 (m, 4H), 7.08 (s, 1H), 7.05 (s, 1H), 7.02-7.00 (m, 7H), 5.77 (brs, 1H), 5.66 (brs, 1H), 1.05 (s, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 144.5, 143.2, 143.2, 142.9, 142.4, 139.4, 138.3, 135.7, 131.6, 131.5, 131.44, 131.41, 131.2, 131.0, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5, 127.2, 127.0, 126.9, 126.63, 126.60, 120.7, 103.3, 95.6, 18.7, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{38}\text{H}_{42}\text{NOSi}$: 556.3030, found: 556.3036.



2-Carbamoyl-3-((triisopropylsilyl)ethynyl)phenyl acetate (3z), white solid (28 mg, 78% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 147 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 1.2$ Hz, 7.6 Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.07 (dd, $J = 0.8$ Hz, 8.0 Hz, 1H), 6.04 (brs, 1H), 5.94 (brs, 1H), 2.30 (s, 3H), 1.12-1.10 (m, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 166.7, 147.8, 131.0, 130.3, 123.5, 122.3, 103.0, 97.3, 20.9, 18.6, 11.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{NO}_3\text{Si}$: 360.1989, found: 360.1993.

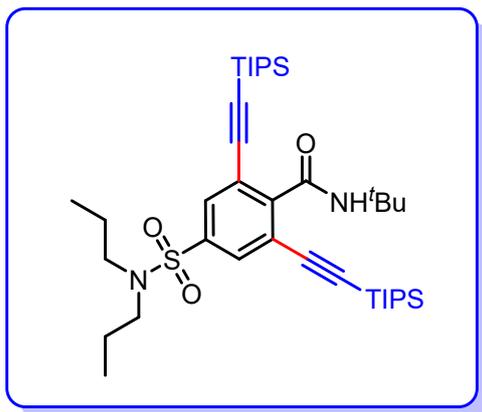


10-Methyl-2, 4-bis((triisopropylsilyl)ethynyl)-10H-phenothiazine-3-carboxamide (3za), white solid (46 mg, 75% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 133 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.16 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 1H), 6.92 (t, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.72 (s, 1H), 5.75 (s, 1H), 5.67 (s, 1H), 3.33 (s, 3H), 1.16 (s, 21H), 1.11 (s, 21H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 145.8, 144.5, 136.2, 129.7, 128.0, 127.5, 123.0, 122.5, 119.7, 118.8, 116.9, 114.4, 103.6, 103.4, 100.2, 95.9, 35.7, 18.8, 18.7, 11.5, 11.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{53}\text{N}_2\text{OS}$: 617.3412, found: 617.3418.

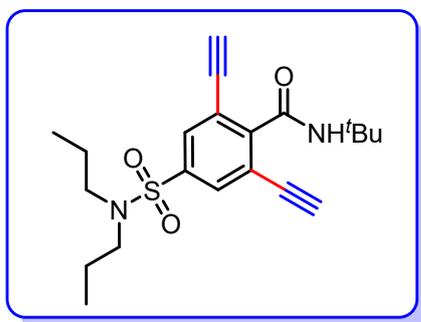


N, N-Dipropyl-4-(pyrrolidine-1-carbonyl)-3-((triisopropylsilyl)ethynyl)benzene sulfonamide (3zb), white solid (32 mg, 62% yield, chromatography on silica gel,

eluent: PE/EA = 10:1), m. p.: 118 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 1.2$ Hz, 1H), 7.72 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 3.60 (t, $J = 6.8$ Hz, 2H), 3.22 (t, $J = 6.0$ Hz, 2H), 3.06 (t, $J = 7.6$ Hz, 4H), 1.95-1.83 (m, 4H), 1.59-1.50 (m, 4H), 1.08 (s, 21H), 0.86 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.0, 144.3, 140.7, 131.5, 127.1, 127.0, 121.3, 102.5, 97.0, 50.1, 47.9, 45.8, 26.0, 24.5, 22.1, 18.7, 11.3, 11.2. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{47}\text{N}_2\text{O}_3\text{SSi}$: 519.3071, Found: 519.3081.

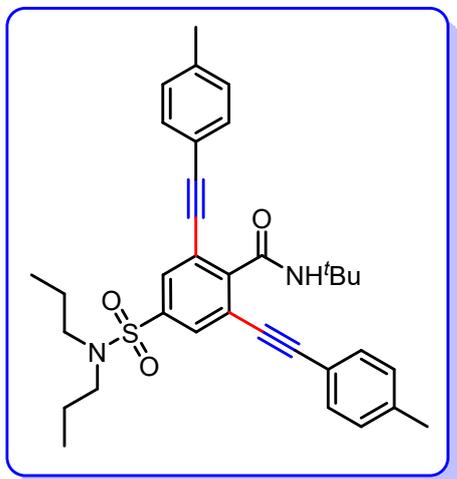


***N*-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (3zc)**, white solid (58 mg, 83% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 126 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (s, 2H), 5.52 (s, 1H), 3.13-3.04 (m, 4H), 1.61-1.51 (m, 4H), 1.47 (s, 9H), 1.11 (d, $J = 2.4$ Hz, 42H), 0.89 (t, $J = 7.6$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.2, 144.7, 140.7, 131.3, 122.7, 102.3, 98.2, 52.4, 50.0, 28.9, 22.1, 18.8, 11.4, 11.3. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{39}\text{H}_{69}\text{N}_2\text{O}_3\text{SSi}_2$: 701.4562, found: 701.4568.

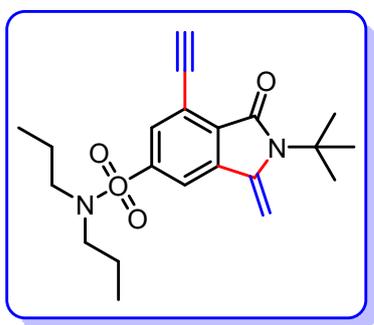


***N*-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2,6-diethynylbenzamide (3zc-1)**, white solid (33 mg, 85% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 119 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (s, 2H), 5.70 (s, 1H), 3.32 (s, 2H), 3.10-

2.98 (m, 4H), 1.56 (h, $J = 7.6$ Hz, 4H), 1.47 (s, 9H), 0.88 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.0, 146.6, 141.0, 131.2, 121.3, 83.3, 79.1, 52.6, 50.4, 28.7, 22.3, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$: 389.1893, found: 389.1899.

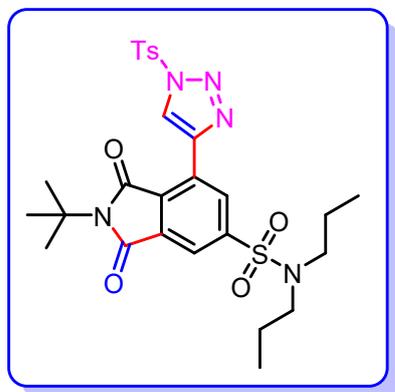


N-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2,6-bis(*p*-tolylethynyl)benzamide (**3zc-2**), white solid (45 mg, 79% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 128 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 2H), 7.42 (d, $J = 8.0$ Hz, 4H), 7.17 (d, $J = 7.6$ Hz, 4H), 5.70 (s, 1H), 3.14-3.06 (m, 4H), 2.37 (s, 6H), 1.66-1.53 (m, 4H), 1.49 (s, 9H), 0.91 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 144.9, 140.7, 139.6, 131.8, 129.7, 129.4, 122.7, 119.2, 95.2, 84.8, 77.5, 50.5, 46.0, 29.0, 22.4, 21.7, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{41}\text{N}_2\text{O}_3\text{S}$: 569.2832, found: 569.2832.

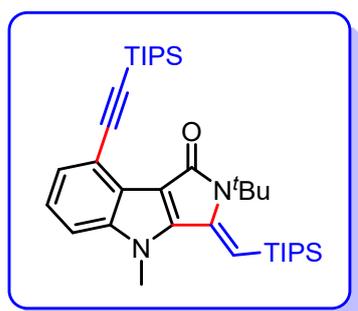


2-(*tert*-Butyl)-7-ethynyl-3-methylene-1-oxo-*N,N*-dipropylisoindoline-5-sulfonamide (**3zc-3**), white solid (32 mg, 82% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 125 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 1.2$ Hz, 1H), 7.92 (d, $J = 1.2$ Hz, 1H), 5.41-5.34 (m, 2H), 3.58 (s, 1H), 3.15-3.05 (m, 4H),

1.75 (s, 9H), 1.55 (h, $J = 7.5$ Hz, 4H), 0.87 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 143.5, 140.1, 138.6, 132.4, 131.7, 119.3, 118.1, 95.4, 85.3, 78.6, 58.7, 50.1, 29.9, 22.1, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$: 389.1893, found: 389.1899.

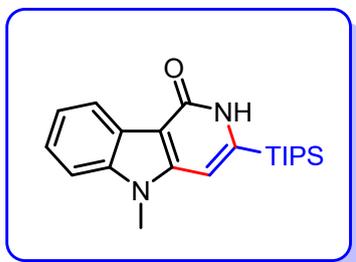


2-(*tert*-Butyl)-1,3-dioxo-*N,N*-dipropyl-7-(1-tosyl-1*H*-1,2,3-triazol-4-yl)isoindoline-5-sulfonamide (3zc-4), white solid (42 mg, 72% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 145 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.54 (s, 1H), 9.08 (d, $J = 1.6$ Hz, 1H), 8.17 (d, $J = 1.6$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 7.6$ Hz, 2H), 3.19-3.10 (m, 4H), 2.46 (s, 3H), 1.73 (s, 9H), 1.57 (q, $J = 7.6$ Hz, 4H), 0.87 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 167.4, 147.8, 146.7, 140.6, 134.4, 133.0, 131.9, 130.7, 129.1, 128.6, 128.1, 126.2, 121.0, 59.1, 50.2, 29.2, 22.2, 22.0, 11.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{34}\text{N}_5\text{O}_6\text{S}_2$: 588.1945, found: 588.1951.

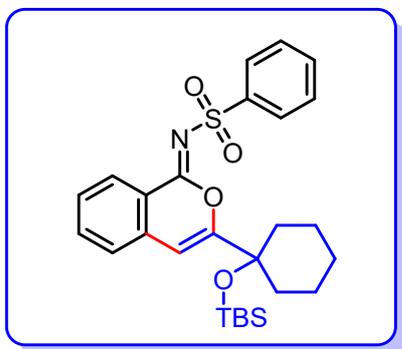


2-(*tert*-Butyl)-4-methyl-8-((triisopropylsilyl)ethynyl)-3-((triisopropylsilyl)methylene)-3,4-dihydropyrrolo[3,4-*b*]indol-1(2*H*)-one (3zd), white solid (37 mg, 63% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 124 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (t, $J = 4.0$ Hz, 1H), 7.18 (d, $J = 4.0$ Hz, 2H), 5.87 (s, 1H), 3.77 (s, 3H), 1.49 (s, 9H), 1.24 – 1.19 (m, 6H), 1.17 (d, $J = 5.4$

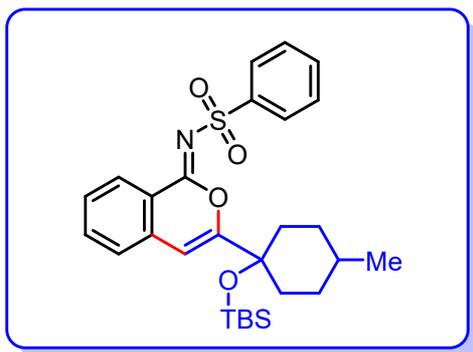
Hz, 36H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.8, 137.1, 129.5, 123.7, 123.5, 122.0, 118.9, 116.5, 109.8, 106.3, 103.3, 96.4, 95.7, 51.6, 30.9, 29.2, 18.9, 18.8, 11.6, 11.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{59}\text{N}_2\text{OSi}_2$: 591.4160, found: 591.4166.



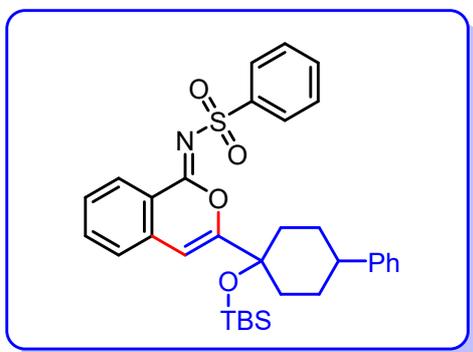
5-Methyl-3-(triisopropylsilyl)-2,5-dihydro-1H-pyrido[4,3-b]indol-1-one (3ze), white solid (19 mg, 55% yield, chromatography on silica gel, eluent: PE/EA = 5:1), m. p.: 115 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 7.6$ Hz, 1H), 7.42-7.40 (m, 2H), 7.38-7.35 (m, 1H), 7.26 (s, 1H), 6.78 (d, $J = 2.0$ Hz, 1H), 3.84 (s, 3H), 1.50-1.42 (m, 3H), 1.18-1.61 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 143.9, 138.5, 124.7, 124.2, 122.6, 121.6, 109.3, 105.1, 101.3, 29.9, 18.5, 10.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{OSi}$: 355.2200, found: 355.2205.



(Z)-N-(3-(1-((tert-Butyldimethylsilyl)oxy)cyclohexyl)-1H-isochromen-1-ylidene)benzenesulfonamide (4a), white solid (42 mg, 85% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 119 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.31 (dd, $J = 1.2$ Hz, 8.4 Hz, 1H), 8.10-8.07 (m, 2H), 7.72 (td, $J = 1.2$ Hz, 7.6 Hz, 1H), 7.55-7.46 (m, 4H), 7.43 (d, $J = 1.2$ Hz, 1H), 6.68 (s, 1H), 2.04-2.00 (m, 2H), 1.86 (td, $J = 3.6$ Hz, 2H), 1.80-1.71 (m, 2H), 1.63-1.51 (m, 4H), 0.92 (s, 9H), -0.05 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 159.4, 135.3, 135.1, 132.1, 129.0, 128.9, 128.6, 126.7, 126.0, 120.8, 104.0, 74.1, 36.1, 25.9, 25.4, 21.9, 18.4, -3.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{36}\text{NO}_4\text{SSi}$: 498.2129, found: 498.2135.

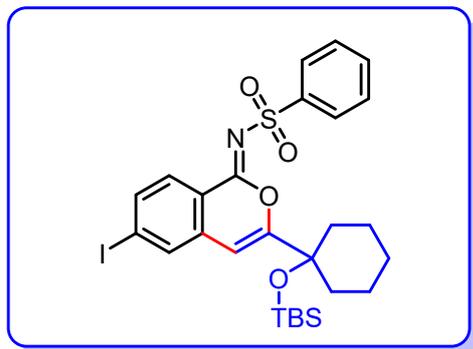


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyl)oxy)-4-methylcyclohexyl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (4b), white solid (37 mg, 73% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 121 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H), 8.10-8.08 (m, 2H), 7.73 (td, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.55-7.47 (m, 4H), 7.45 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 2.53-2.49 (m, 2H), 1.79-1.69 (m, 4H), 1.60-1.53 (m, 1H), 1.08-0.99 (m, 2H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.84 (s, 9H), -0.05 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 158.9, 142.8, 135.3, 135.2, 132.1, 129.0, 128.9, 128.6, 126.7, 126.1, 120.9, 105.2, 75.1, 36.0, 31.5, 31.1, 25.7, 21.0, 18.0, -3.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₈H₃₈NO₄SSi: 512.2285, found: 512.2290.

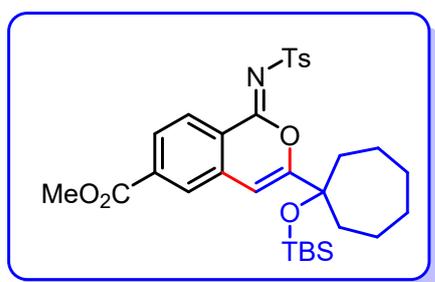


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyl)oxy)-4-phenylcyclohexyl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (4c), white solid (37 mg, 65% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 123 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H), 8.10-8.08 (m, 2H), 7.75 (td, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.54-7.46 (m, 5H), 7.25-7.21 (m, 2H), 7.15-7.12 (m, 3H), 6.75 (s, 1H), 2.74 (d, *J* = 13.6 Hz, 2H), 2.70-2.64 (m, 1H), 2.01-1.95 (m, 2H), 1.88 (td, *J* = 3.6 Hz, 13.6 Hz, 2H), 1.58-1.51 (m, 4H), 0.86 (s, 9H), -0.01 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 158.3, 145.9, 142.7, 135.3, 135.0, 132.1, 128.7, 128.2, 126.8, 126.7, 126.1, 126.0, 121.0,

105.6, 74.9, 43.0, 37.1, 31.2, 25.7, 18.0, -2.9. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{33}H_{40}NO_4SSi$: 574.2442, found: 574.2447.

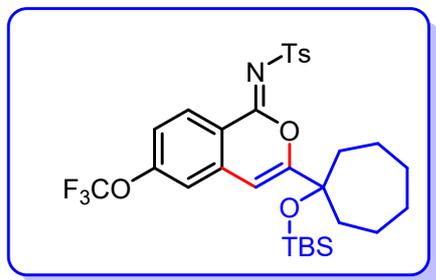


(Z)-N-(3-(1-((tert-Butyldimethylsilyl)oxy)cyclohexyl)-6-iodo-1H-isochromen-1-ylidene)benzenesulfonamide (4d), white solid (38 mg, 62% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 113 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.95 (d, $J = 8.8$ Hz, 1H), 7.82 (d, $J = 1.6$ Hz, 1H), 7.78 (d, $J = 1.6$ Hz, 8.4 Hz, 1H), 7.57-7.49 (m, 3H), 6.57 (s, 1H), 2.02-1.99 (m, 2H), 1.85 (td, $J = 3.6$ Hz, 10.8 Hz, 2H), 1.76-1.68 (m, 2H), 1.60-1.52 (m, 4H), 0.92 (s, 9H), -0.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 158.9, 142.5, 138.0, 136.4, 134.9, 132.2, 129.9, 128.7, 126.7, 120.0, 103.8, 102.5, 74.3, 36.1, 25.9, 25.3, 21.9, 18.4, -2.9. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{27}H_{35}INO_4SSi$: 624.1095, found: 624.1099.

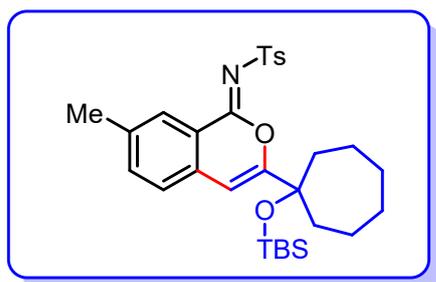


Methyl (Z)-3-(1-((tert-butyl)dimethylsilyloxy)cycloheptyl)-1-(tosylimino)-1H-isochromene-6-carboxylate (4e), white solid (44 mg, 76% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 117 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, $J = 8.4$ Hz, 1H), 8.05 (d, $J = 1.2$ Hz, 1H), 8.00 (dd, $J = 1.6$ Hz, 8.0 Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.79 (s, 1H), 3.97 (s, 3H), 2.44 (s, 3H), 2.33-2.27 (m, 2H), 2.05-1.99 (m, 2H), 1.75-1.71 (m, 4H), 1.68-1.62 (m, 4H), 0.96 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.0, 158.3, 143.0, 139.6, 135.8,

135.3, 129.3, 128.9, 128.6, 127.4, 126.7, 123.6, 102.3, 79.1, 52.7, 40.7, 30.1, 26.0, 22.7, 21.5, 18.4, -2.3. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{31}H_{42}NO_6SSi$: 584.2497, found: 584.2504.

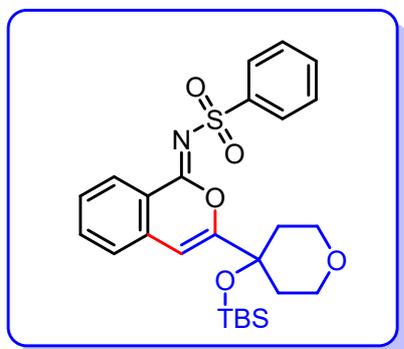


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyl)oxy)cycloheptyl)-6-(trifluoromethoxy)-1H-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4f), white solid (45 mg, 75% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 121 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, $J = 8.8$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.24-7.21 (m, 1H), 7.17 (d, $J = 1.2$ Hz, 1H), 6.72 (s, 1H), 2.44 (s, 3H), 2.31-2.25 (m, 2H), 2.04-1.97 (m, 2H), 1.73-1.64 (m, 8H), 0.95 (m, 9H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 158.0, 154.1, 142.9, 139.7, 137.5, 131.5, 129.3, 126.7, 122.6, 121.5, 120.6, 118.9, 117.7, 116.1, 101.9, 79.2, 40.7, 30.1, 26.0, 22.7, 21.5, 18.4, -2.3. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calcd for $C_{30}H_{39}F_3NO_5SSi$: 610.2265, found: 610.2272.

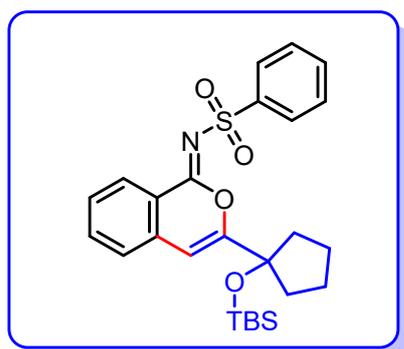


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyl)oxy)cycloheptyl)-6-(trifluoromethoxy)-1H-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4g), white solid (43 mg, 81% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 108 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, $J = 1.2$ Hz, 2.0 Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.51 (dd, $J = 2.0$ Hz, 8.0 Hz, 1H), 7.30 (dd, $J = 4.4$ Hz, 8.0 Hz, 1H), 6.71 (d, $J = 0.8$ Hz, 1H), 2.42 (d, $J = 5.2$ Hz, 6H), 2.27-2.21 (m, 2H), 2.03-1.97 (m, 2H), 1.68-1.62 (m, 8H), 0.93

(s, 9H), 0.02 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.0, 159.6, 142.6, 140.1, 139.1, 136.6, 133.0, 129.2, 128.3, 126.7, 125.9, 120.4, 102.8, 78.9, 40.5, 29.9, 26.0, 22.5, 21.5, 21.4, 18.4, -2.5. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{42}\text{NO}_4\text{SSi}$: 540.2598, found: 540.2604.

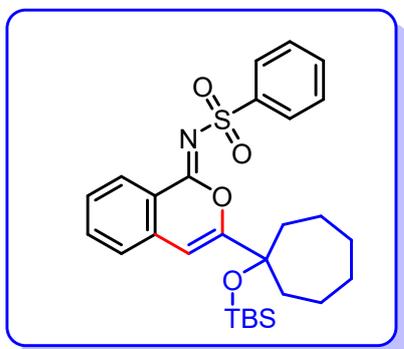


(Z)-N-(3-(4-((tert-Butyldimethylsilyl)oxy)tetrahydro-2H-pyran-4-yl)-1H-isochromen-1-ylidene)benzenesulfonamide (4h), white solid (32 mg, 64% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 113 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 1.6$ Hz, 8.0 Hz, 1H), 8.09-8.06 (m, 2H), 7.74 (td, $J = 1.2$ Hz, 7.6 Hz, 1H), 7.57-7.49 (m, 4H), 7.46 (d, $J = 8.0$ Hz, 1H), 3.94-3.81 (m, 4H), 2.14-2.01 (m, 4H), 0.93 (s, 9H), -0.06 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 158.9, 142.6, 135.4, 134.6, 132.2, 129.3, 128.9, 128.7, 126.7, 126.2, 121.0, 104.1, 71.3, 63.4, 36.0, 25.9, 18.4, -3.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{34}\text{NO}_5\text{SSi}$: 500.1921, found: 500.1927.

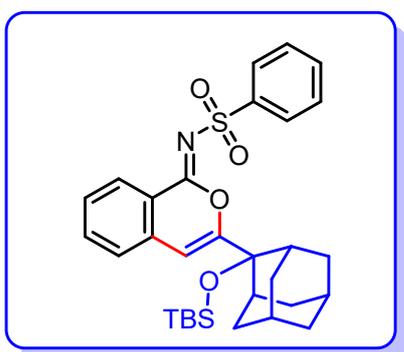


(Z)-N-(3-(1-((tert-Butyldimethylsilyl)oxy)cyclopentyl)-1H-isochromen-1-ylidene)benzenesulfonamide (4i), white solid (33 mg, 69% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 113 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 8.4$ Hz, 1H), 8.07-8.05 (m, 2H), 7.71 (td, $J = 1.2$ Hz, 7.2 Hz, 1H), 7.56-7.49 (m, 3H), 7.47-7.44 (m, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 6.80 (s, 1H), 2.17-2.10 (m, 2H), 1.91-

1.88 (m, 6H), 0.96 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.0, 159.9, 135.5, 135.4, 132.2, 128.9, 128.7, 128.6, 126.6, 125.9, 120.3, 103.2, 84.0, 40.0, 25.9, 24.3, 18.3, -2.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{34}\text{NO}_4\text{SSi}$: 484.1972, found: 484.1977.

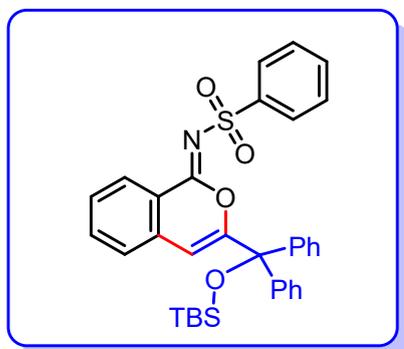


(Z)-N-(3-(1-((tert-Butyldimethylsilyl)oxy)cycloheptyl)-1H-isochromen-1-ylidene)benzenesulfonamide (4j), white solid (30 mg, 60% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 107 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.25 (dd, $J = 1.2$ Hz, 8.0 Hz, 1H), 8.10-8.07 (m, 2H), 7.70 (td, $J = 1.2$ Hz, 7.2 Hz, 1H), 7.57-7.51 (m, 3H), 7.47-7.41 (m, 1H), 7.39 (d, $J = 1.2$ Hz, 1H), 6.76 (d, $J = 0.8$ Hz, 1H), 2.31-2.25 (m, 2H), 2.05-1.98 (m, 2H), 1.73-1.63 (m, 8H), 0.95 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 159.6, 142.8, 135.4, 135.2, 132.1, 128.8, 128.6, 126.6, 126.0, 120.5, 102.8, 79.0, 40.7, 30.0, 26.0, 22.6, 18.4, -2.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{NO}_4\text{SSi}$: 512.2285, found: 512.2290.

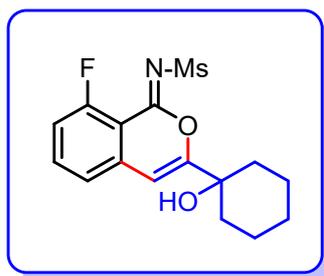


N-((Z)-3-((1R,3S,5r,7r)-2-((tert-Butyldimethylsilyl)oxy)adamantan-2-yl)-1H-isochromen-1-ylidene)benzenesulfonamide (4k), white solid (47 mg, 86% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 113 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.33 (dd, $J = 1.2$ Hz, 8.0 Hz, 1H), 8.10-8.07 (m, 2H), 7.73 (td, $J = 1.2$ Hz, 7.6 Hz, 1H), 7.52-7.44 (m, 5H), 6.70 (s, 1H), 2.37 (d, $J = 12.4$ Hz, 2H), 1.87-1.61

(m, 12H), 0.88 (s, 9H), -0.17 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.5, 158.9, 142.7, 135.3, 135.1, 132.1, 129.1, 128.9, 128.6, 126.6, 126.1, 121.0, 105.6, 78.1, 37.7, 34.9, 32.4, 26.9, 26.0, 18.5, -3.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{40}\text{NO}_4\text{SSi}$: 550.2442, found: 550.2447.

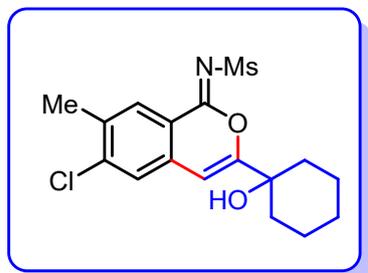


(Z)-N-(3-(((tert-Butyldimethylsilyl)oxy)diphenylmethyl)-1H-isochromen-1-ylidene)benzenesulfonamide (4l), white solid (33 mg, 57% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 113 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.24-8.22 (m, 1H), 7.79 (dd, $J = 1.2$ Hz, 8.4 Hz, 2H), 7.69 (td, $J = 1.6$ Hz, 7.6 Hz, 1H), 7.54-7.51 (m, 4H), 7.48 (d, $J = 7.2$ Hz, 1H), 7.45-7.39 (m, 3H), 7.38-7.34 (m, 7H), 7.25 (s, 1H), 1.08 (s, 9H), -0.39 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 158.9, 141.9, 132.0, 129.2, 128.6, 128.3, 127.9, 126.6, 126.1, 104.7, 82.1, 26.4, 19.1, -3.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{36}\text{NO}_4\text{SSi}$: 582.2129, found: 582.2135.

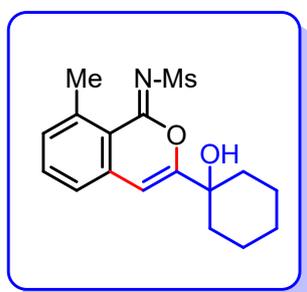


N-(8-Fluoro-3-(1-hydroxycyclohexyl)-1H-isochromen-1-ylidene)methanesulfonamide (4m), white solid (24 mg, 71% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 98 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.65 (td, $J = 8.0, 5.0$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.18 - 7.13 (m, 1H), 6.65 (d, $J = 2.0$ Hz, 1H), 3.19 (s, 3H), 1.98 (td, $J = 13.5, 4.5$ Hz, 2H), 1.84 (d, $J = 13.0$ Hz, 2H), 1.74 - 1.70 (m, 2H), 1.66 - 1.62 (m, 2H), 1.34 (d, $J = 6.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3)

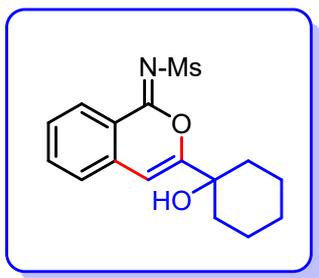
δ 163.29, 162.29, 160.62, 155.91, 155.82, 138.19, 136.46, 136.36, 122.21, 122.16, 116.29, 116.07, 109.64, 109.56, 101.24, 101.21, 72.14, 43.39, 35.00, 25.27, 21.46. ¹⁹F NMR (376 MHz, CDCl₃) δ 101.45. HRMS (ESI-TOF) m/z : [M + H]⁺ Calcd for C₁₆H₁₈FNO₄S: 339.0914, found: 339.0920.



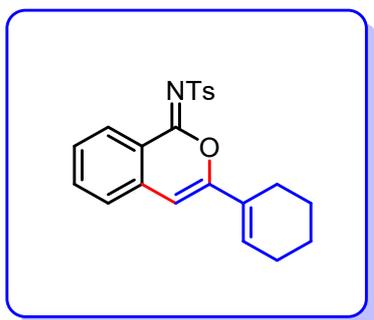
***N*-(6-Chloro-3-(1-hydroxycyclohexyl)-7-methyl-1*H*-isochromen-1-ylidene)methanesulfonamide (4n)**, white solid (19 mg, 53% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 156 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.06 (s, 1H), 7.38 (s, 1H), 6.62 (s, 1H), 3.17 (s, 3H), 2.44 (s, 3H), 1.95 (td, J = 13.0, 4.0 Hz, 2H), 1.82 (d, J = 13.5 Hz, 2H), 1.75 – 1.56 (m, 5H). 1.35 – 1.19 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 162.2, 159.4, 142.8, 137.5, 134.7, 129.9, 126.2, 118.5, 101.0, 72.1, 42.9, 35.0, 25.2, 21.4, 20.3. HRMS (ESI-TOF) m/z : [M + H]⁺ Calcd for C₁₇H₂₀ClNO₄S: 369.0802, found: 369.0808.



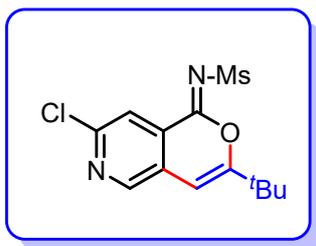
***N*-(3-(1-Hydroxycyclohexyl)-8-methyl-1*H*-isochromen-1-ylidene)methanesulfonamide (4o)**, white solid (26 mg, 78% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 96 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.54 (t, J = 7.2 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 5.86 (s, 1H), 3.21 (s, 3H), 2.62 (s, 3H), 1.93-1.88 (m, 2H), 1.84-1.79 (m, 2H), 1.76-1.69 (m, 2H), 1.50-1.45 (m, 3H), 1.42-1.36 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 162.8, 146.9, 139.2, 138.1, 134.4, 131.9, 124.4, 117.5, 116.8, 71.6, 42.6, 38.2, 25.2, 22.1, 18.4. HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd. for C₁₇H₂₂N₁O₄S⁺: 336.1264, Found: 336.1270.



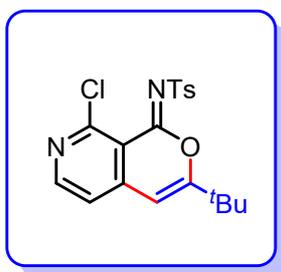
***N*-(3-(1-Hydroxycyclohexyl)-1*H*-isochromen-1-ylidene)methanesulfonamide (4p)**, white solid (20 mg, 62% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 93 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 3.5 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 6.72 (s, 1H), 3.18 (s, 3H), 2.90 (s, 1H), 1.98 (td, *J* = 13.0, 4.0 Hz, 2H), 1.85 (d, *J* = 13.5 Hz, 2H), 1.76 – 1.66 (m, 3H), 1.61 (dd, *J* = 13.0, 4.1 Hz, 1H), 1.40–1.19 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 161.6, 160.1, 135.6, 135.4, 128.8, 128.4, 126.4, 120.2, 102.1, 72.2, 43.0, 35.1, 25.3, 21.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₂₀NO₄S: 321.1035, found: 321.1041.



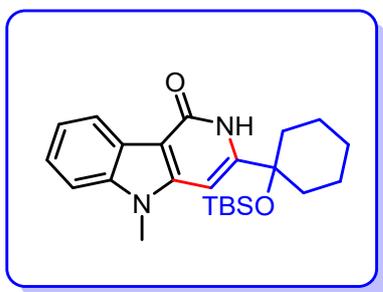
***N*-(3-(Cyclohex-1-en-1-yl)-1*H*-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4q)**, white solid (26 mg, 68% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 158 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.23 (dd, *J* = 8.0, 3.5 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 2H), 7.66-7.62 (m, 1H), 7.41-7.34 (m, 2H), 7.29 (s, 2H), 7.12 – 7.06 (m, 1H), 6.43 (s, 1H), 2.42 (s, 3H), 2.33-2.31 (m, 2H), 2.28-2.25 (m, 2H), 1.78-1.75 (m, 2H), 1.67-1.64 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.4, 154.0, 142.8, 139.6, 136.1, 135.1, 132.1, 129.2, 128.8, 128.1, 127.3, 126.7, 125.9, 120.5, 101.1, 25.9, 23.9, 22.1, 21.7, 21.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd. for C₂₂H₂₂NO₃S⁺: 380.1315, Found: 380.1321.



(Z)-N-(3-(tert-Butyl)-7-chloro-1H-pyrano[4,3-c]pyridin-1-ylidene)methanesulfonamide (4r), white solid (28 mg, 73% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 162 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.61 (d, *J* = 1.0 Hz, 1H), 8.00 (t, *J* = 1.0 Hz, 1H), 6.43 (d, *J* = 0.5 Hz, 1H), 3.20 (s, 3H), 1.36 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 167.15, 156.96, 150.23, 148.67, 128.61, 120.44, 97.21, 43.13, 36.30, 27.82. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₀ClN₂O₃S⁺: 391.0878, Found: 391.0884.

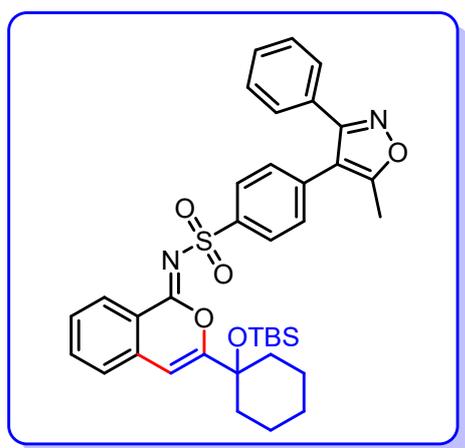


N-(3-(tert-Butyl)-8-chloro-1H-pyrano[3,4-c]pyridin-1-ylidene)-4-methylbenzenesulfonamide (4s), white solid (25 mg, 65% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 165 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.45 (d, *J* = 5.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 5.0 Hz, 1H), 6.33 (s, 1H), 2.43 (s, 3H), 1.41 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 169.9, 155.1, 152.5, 151.6, 146.2, 143.0, 139.5, 129.3, 126.5, 118.6, 114.0, 99.6, 36.2, 27.5, 21.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd. for C₁₉H₂₀ClN₂O₃S⁺: 391.0878, Found: 391.0884.

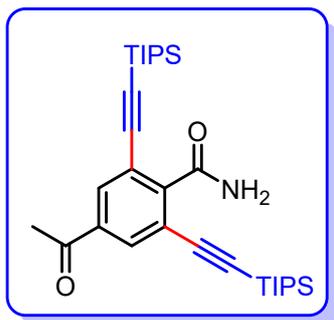


3-(1-((tert-Butyldimethylsilyl)oxy)cyclohexyl)-5-methyl-2,5-dihydro-1H-pyrido[4,3-b]indol-1-one (4t), white solid (29 mg, 72% yield, chromatography on

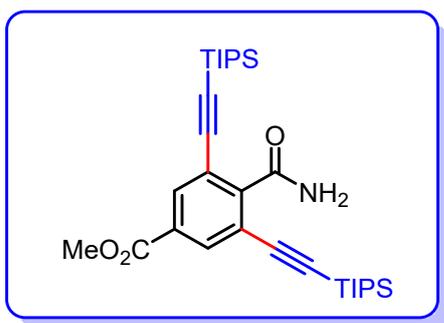
silica gel, eluent: PE/EA = 10:1), m. p.: 128 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.23 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.41 – 7.39 (m, 2H), 7.37 – 7.34 (m, 1H), 6.62 (s, 1H), 3.83 (s, 3H), 2.11 – 2.07 (m, 2H), 1.86 – 1.81 (m, 2H), 1.81 – 1.74 (m, 2H), 1.67 – 1.55 (m, 2H), 1.39 – 1.27 (m, 2H), 0.91 (s, 9H), -0.03 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.5, 159.4, 146.1, 139.1, 124.7, 124.2, 122.7, 121.6, 109.4, 100.0, 91.3, 74.5, 36.6, 30.0, 26.1, 25.7, 22.0, 18.7, -2.8. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{35}\text{N}_2\text{O}_2\text{Si}$: 411.2462, found: 411.2468.



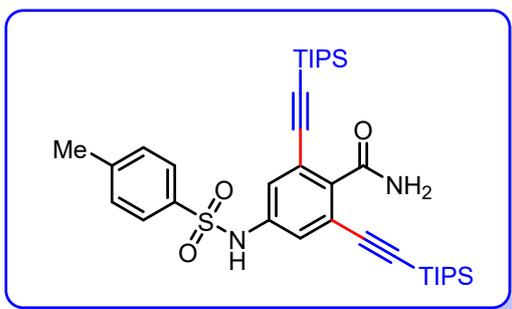
(Z)-N-(3-(1-((*tert*-Butyldimethylsilyl)oxy)cyclohexyl)-1*H*-isochromen-1-ylidene)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide (4u), white solid (44 mg, 68% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 128 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 (dd, $J = 1.2$ Hz, 8.0 Hz, 1H), 8.10-8.08 (m, 2H), 7.72-7.49 (m, 1H), 7.46 (d, $J = 2.0$ Hz, 1H), 7.43-7.37 (m, 3H), 7.35-7.31 (m, 4H), 6.72 (s, 1H), 2.49 (s, 3H), 2.11-2.06 (m, 2H), 1.92-1.86 (m, 2H), 1.80-1.73 (m, 2H), 1.63-1.52 (m, 3H), 1.35-1.25 (m, 1H), 0.92 (s, 9H), -0.04 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.1, 161.0, 160.6, 159.8, 141.9, 135.4, 135.2, 134.5, 129.8, 129.6, 128.6, 128.4, 127.1, 120.6, 114.7, 104.0, 74.0, 36.0, 25.9, 25.4, 18.3, 11.7, -3.0. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{37}\text{H}_{43}\text{N}_2\text{O}_5\text{Si}$: 655.2656, found: 655.2662.



4-Acetyl-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5a), white solid (35 mg, 67% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 114 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (s, 2H), 2.64 (s, 3H), 1.10 (s, 42H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 196.5, 169.4, 141.5, 137.6, 132.2, 122.7, 102.3, 98.0, 26.9, 18.7, 11.3. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{50}\text{NO}_2\text{Si}_2$: 524.3375, Found: 524.3381.

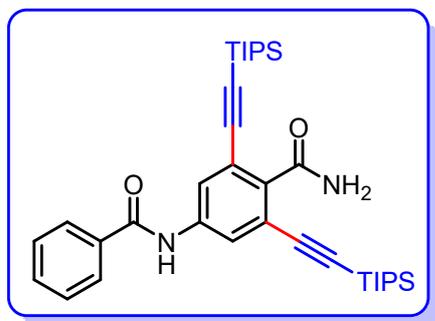


Methyl 4-carbamoyl-3, 5-bis((triisopropylsilyl)ethynyl)benzoate (5b), white solid (38 mg, 71% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 131 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (s, 2H), 5.79 (brs, 2H), 3.94 (s, 3H), 1.12 (s, 21H). $^{13}\text{C NMR}$ (100MHz, CDCl_3) δ 168.2, 165.4, 145.5, 133.5, 131.0, 121.9, 102.3, 97.5, 52.7, 18.7, 11.4. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{50}\text{NO}_3\text{Si}_2$: 540.3324, found: 540.3330.

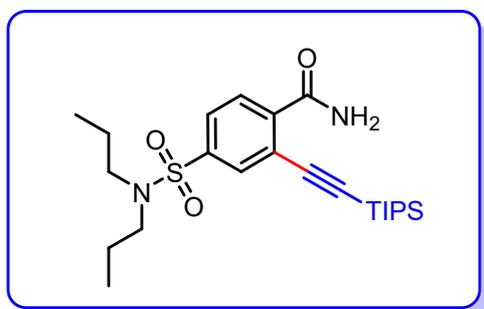


4-((4-Methylphenyl)sulfonamido)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5c), white solid (55 mg, 85% yield, chromatography on silica gel, eluent: PE/EA =

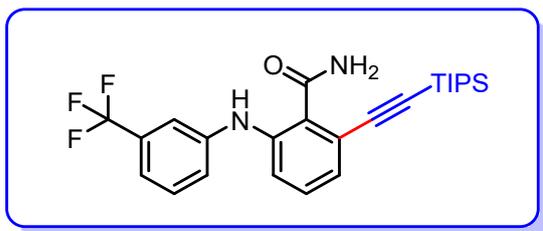
10:1), m. p.: 159 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 2.8$ Hz, 2H), 6.09 (brs, 1H), 5.89 (brs, 1H), 2.51 (s, 3H), 1.19 (s, 42H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.6, 144.7, 138.2, 137.5, 135.8, 130.1, 127.6, 124.1, 122.6, 102.6, 97.2, 21.7, 18.7, 11.4. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{55}\text{N}_2\text{O}_3\text{SSi}_2$: 651.3466, Found: 651.3470.



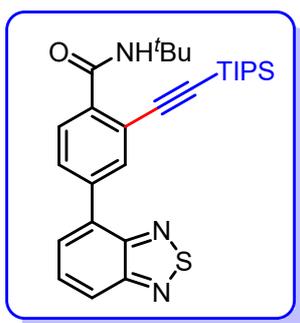
4-Benzamido-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5d), white solid (45 mg, 75% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 159 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (brs, 1H), 7.88 (d, $J = 7.6$ Hz, 2H), 7.77 (s, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 5.83 (s, 1H), 5.73 (s, 1H), 1.11 (s, 42H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.6, 165.8, 138.5, 138.1, 134.3, 132.5, 129.1, 127.2, 124.1, 122.4, 103.0, 96.6, 18.8, 11.4. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{53}\text{N}_2\text{O}_2\text{Si}_2$: 601.3640, found: 601.3646.



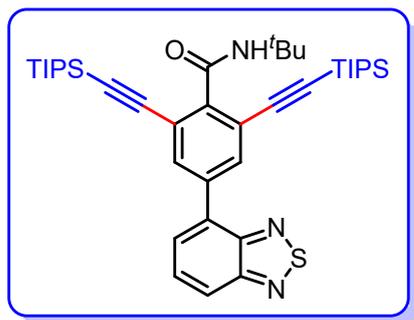
4-(*N,N*-Dipropylsulfamoyl)-2-((triisopropylsilyl)ethynyl)benzamide (5e), white solid (38 mg, 81% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 141 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.4$ Hz, 1H), 7.96 (s, 1H), 7.79 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.70 (brs, 1H), 6.35 (brs, 1H), 3.11 (t, $J = 8.0$ Hz, 4H), 1.60-1.51 (m, 4H), 1.13 (d, $J = 5.2$ Hz, 21H), 0.87 (t, $J = 7.6$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.6, 142.9, 137.7, 132.6, 131.4, 126.8, 121.5, 104.0, 101.9, 50.0, 22.0, 18.7, 11.3, 11.2. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{41}\text{SSi}$: 465.2602; found: 465.2608.



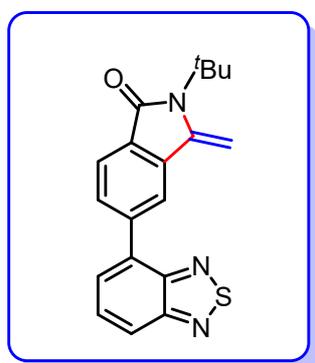
2-((3-(Trifluoromethyl)phenyl)amino)-6-((triisopropylsilyl)ethynyl)benzamide (5f), white solid (28 mg, 61% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 158 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (brs, 1H), 7.54-7.50 (t, J = 8.0 Hz, 2H), 7.40-7.35 (m, 3H), 7.20 (d, J = 8.0 Hz, 1H), 6.13 (brs, 1H), 5.95 (brs, 1H), 1.11 (s, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.1, 154.9, 142.3, 138.9, 138.5, 132.9, 131.1 (q, J = 32 Hz), 130.2, 129.8, 129.5, 123.4, 122.9, 122.6, 103.1, 97.1, 18.7, 11.4. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.57. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{F}_3\text{N}_2\text{OSi}$: 461.2231, found: 461.2236.



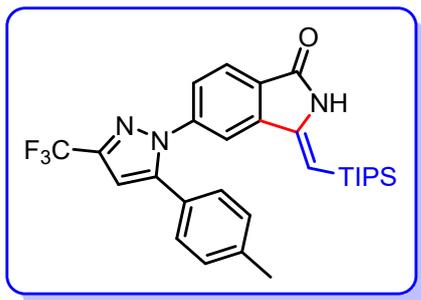
4-(Benzo[c][1,2,5]thiadiazol-4-yl)-N-(tert-butyl)-2-((triisopropylsilyl)ethynyl)benzamide (5g), white solid (42 mg, 85% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 127 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.11 – 8.08 (m, 2H), 8.02 (dd, J = 7.5, 2.0 Hz, 1H), 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.19 (s, 1H), 1.50 (s, 9H), 1.21 – 1.16 (m, 3H), 1.15 (d, J = 5 Hz, 18H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 165.4, 155.6, 153.3, 139.0, 136.4, 135.6, 132.7, 130.0, 129.7, 129.6, 128.1, 121.5, 120.0, 105.6, 98.8, 52.1, 28.9, 18.8, 11.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{N}_3\text{OSSi}$: 492.2499, found: 492.2505.



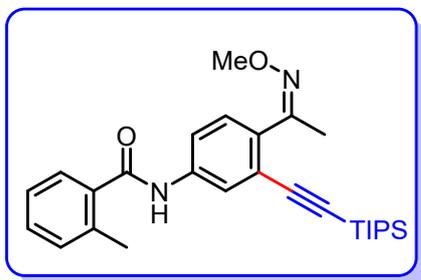
4-(Benzo[c][1,2,5]thiadiazol-4-yl)-N-(tert-butyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5h), white solid (60 mg, 89% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 137 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.92 (s, 2H), 7.72 – 7.63 (m, 2H), 5.63 (s, 1H), 1.49 (s, 9H), 1.12 (s, 42H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.1, 155.5, 153.3, 141.7, 137.8, 134.2, 132.5, 129.6, 128.2, 121.8, 121.5, 103.8, 95.7, 52.1, 29.0, 18.8, 11.4. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{39}\text{H}_{58}\text{N}_3\text{OSSi}_2$: 672.3834, found: 672.3840.



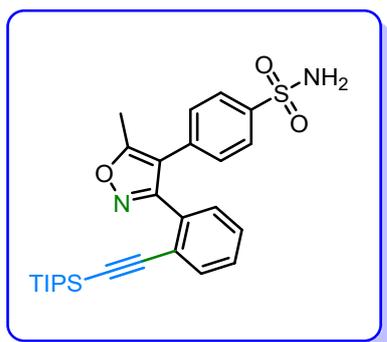
5-(Benzo[c][1,2,5]thiadiazol-4-yl)-2-(tert-butyl)-3-methyleneisoindolin-1-one (5g-1), white solid (30 mg, 90% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 137 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.19 (d, $J = 1.6$ Hz, 1H), 8.05 (dd, $J = 2.0$ Hz, 8.4 Hz, 1H), 7.94 (dd, $J = 1.2$ Hz, 8.0 Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.76–7.69 (m, 2H), 5.39 (d, $J = 2.4$ Hz, 1H), 5.29 (d, $J = 2.4$ Hz, 1H), 1.79 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 168.4, 155.7, 153.5, 142.1, 141.0, 137.7, 134.0, 130.3, 129.7, 129.5, 128.4, 123.0, 121.5, 120.2, 93.6, 58.1, 30.1. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{OS}$: 336.1165, found: 336.1168.



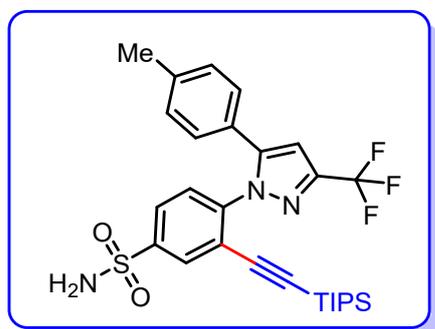
5-(5-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)-3-((triisopropylsilyl)methylene)isoindolin-1-one (5i), white solid (43 mg, 81% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 129 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.77 (s, 1H), 5.59 (s, 1H), 2.37 (s, 3H), 1.39 – 1.32 (m, 3H), 1.11 (d, *J* = 7.5 Hz, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 166.4, 155.6, 145.5, 144.4, 144.3, 140.5, 140.1, 129.8, 128.9, 126.9, 125.8, 125.7, 123.9, 121.1, 117.3, 106.6, 103.3, 21.4, 18.8, 11.7. ¹⁹F NMR (471 MHz, CDCl₃) δ 62.30. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₉H₃₅F₃N₃OSi: 526.2496, found: 526.2502.



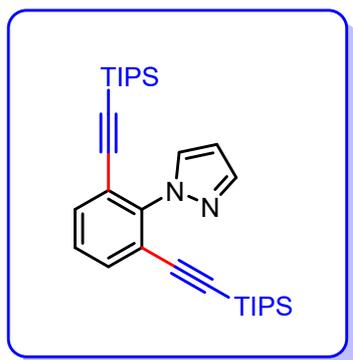
***N*-(4-(1-(Methoxyimino)ethyl)-3-((triisopropylsilyl)ethynyl)phenyl)-2-methylbenzamide (6a)**, white solid (38 mg, 83% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 127 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.64 (s, 1H), 7.62 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37-7.31 (m, 2H), 7.26-7.21 (m, 2H), 3.96 (s, 3H), 2.47 (s, 3H), 2.28 (s, 3H), 1.11 (d, *J* = 2.4 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 156.6, 138.2, 136.7, 131.4, 130.6, 129.3, 126.7, 126.0, 124.4, 122.9, 119.9, 104.8, 96.3, 61.9, 19.9, 18.7, 16.4, 11.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₈H₃₉N₂O₂Si: 463.2775, found: 463.2781.



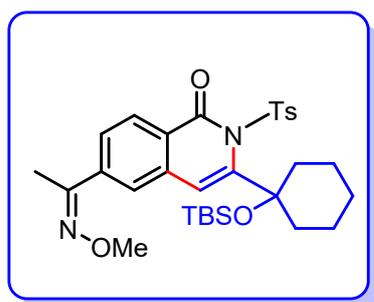
4-(5-Methyl-3-(2-((triisopropylsilyl)ethynyl)phenyl)isoxazol-4-yl)benzenesulfonamide (6b), slightly yellow solid (39 mg, 80% yield, chromatography on silica gel, $R_f = 0.30$, eluent: petroleum ether/ethyl acetate = 2/1, V/V), m.p.: 180 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.4$ Hz, 2H), 7.52 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.27 (d, $J = 2.0$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 2H), 5.21 (s, 2H), 2.52 (s, 3H), 0.98 – 0.94 (m, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 161.2, 140.5, 134.7, 133.1, 131.5, 129.7, 129.3, 129.1, 128.3, 126.5, 124.0, 115.7, 104.2, 95.6, 18.4, 11.9, 11.0. HRMS (ESI-TOF) m/z calcd. for $\text{C}_{27}\text{H}_{35}\text{N}_2\text{O}_3\text{SSi}^+$ $[\text{M}+\text{H}]^+$ 495.2132, found: 495.2137.



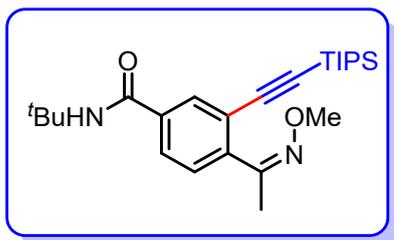
4-(5-(*p*-Tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)-3-((triisopropylsilyl)ethynyl)benzenesulfonamide (6c), white solid (36 mg, 65% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 158 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.8$ Hz, 1H), 7.71 (s, 1H), 7.28 (d, $J = 1.6$ Hz, 1H), 7.26 (s, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.74 (s, 1H), 5.29 (s, 1H), 2.38 (s, 3H), 1.13 (d, $J = 5.2$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.5, 144.41(q, $J = 25.0$ Hz), 142.6, 142.1, 140.1, 130.8, 129.9, 128.9, 128.2, 125.7, 124.6, 121.9, 121.1(q, $J = 178.0$ Hz), 106.7, 103.7, 102.1, 21.5, 18.7, 11.4. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.47. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{28}\text{H}_{35}\text{F}_3\text{N}_3\text{O}_2\text{SSi}$: 562.2166, found: 562.2162.



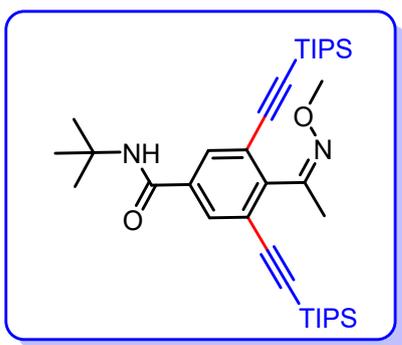
1-(2,6-Bis((triisopropylsilyl)ethynyl)phenyl)-1H-pyrazole (7a), white solid (40 mg, 81% yield, chromatography on silica gel, eluent: PE/EA = 20:1), m. p.: 113 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.62 (m, 2H), 7.53 (s, 1H), 7.51 (s, 1H), 7.31-7.28 (m, 1H), 6.34-6.33 (m, 1H), 0.99 (s, 42H). ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 140.2, 133.2, 131.1, 128.3, 123.0, 105.9, 101.6, 96.6, 18.6, 11.2. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₄₉N₂Si₂: 505.3429, found: 505.3434.



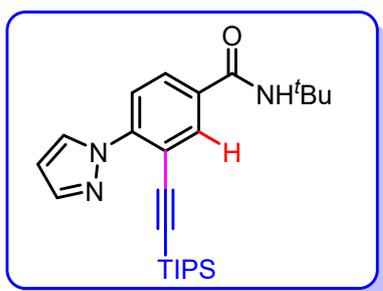
3-(1-((tert-Butyl)dimethylsilyloxy)cyclohexyl)-6-(1-(methoxyimino)ethyl)-2-tosylisoquinolin-1(2H)-one (4v), white solid (44 mg, 76% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 130 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.77 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 4.05 (s, 3H), 2.42 (s, 3H), 2.26 (s, 3H), 2.06 – 2.00 (m, 2H), 1.88 – 1.81 (m, 2H), 1.79 – 1.71 (m, 2H), 1.65 – 1.57 (m, 2H), 1.57 – 1.50 (m, 2H), 0.91 (s, 9H), -0.07 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 161.0, 159.0, 153.1, 143.2, 142.9, 140.0, 135.4, 129.4, 129.2, 126.9, 126.6, 123.3, 121.0, 104.2, 74.2, 62.6, 36.2, 26.1, 25.6, 22.1, 21.7, 18.5, 12.5, -2.9. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₄₃N₂O₅SSi: 583.2656, found: 583.2662.



***N*-(*tert*-Butyl)-4-(1-(methoxyimino)ethyl)-3-((triisopropylsilyl)ethynyl)benzamide (6d)**, white solid (44 mg, 88% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 111 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.12 (s, 1H), 4.01 (s, 3H), 2.20 (s, 3H), 1.47 (s, 9H), 1.15 (d, *J* = 3.6 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 153.1, 138.3, 136.9, 132.3, 129.9, 126.4, 119.8, 105.5, 98.7, 62.3, 52.1, 28.9, 18.8, 12.5, 11.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₄₁N₂O₂Si: 429.2932, found: 429.2938.

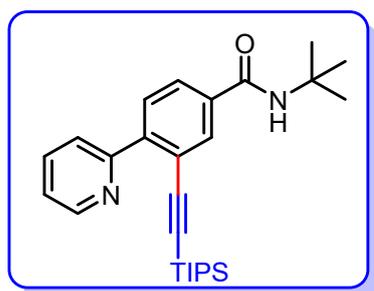


***N*-(*tert*-Butyl)-4-(1-(methoxyimino)ethyl)-3,5-bis((triisopropylsilyl)ethynyl)benzamide (6d-1)**, white solid (53 mg, 88% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 138 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (s, 2H), 5.88 (s, 1H), 3.90 (s, 3H), 2.15 (s, 3H), 1.47 (s, 9H), 1.10 (s, 42H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 154.5, 145.5, 135.9, 130.5, 123.7, 103.3, 96.3, 61.7, 52.2, 28.9, 18.7, 15.9, 11.3. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₆H₆₁N₂O₂Si₂: 609.4266, found: 609.4272.

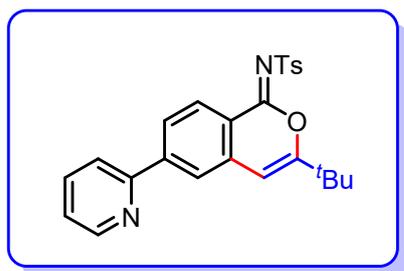


***N*-(*tert*-Butyl)-4-(1*H*-pyrazol-1-yl)-3-((triisopropylsilyl)ethynyl)benzamide (6e)**,

white solid (35 mg, 83% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 127 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.51 (d, $J = 2.4$ Hz, 1H), 7.99 (d, $J = 2.0$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 1.6$ Hz, 1H), 7.69 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.42-6.40 (m, 1H), 6.00 (s, 1H), 1.47 (s, 9H), 1.08 (d, $J = 4.0$ Hz, 21H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.3, 142.9, 141.4, 134.0, 133.8, 133.8, 130.8, 127.4, 124.1, 119.0, 115.8, 106.9, 102.9, 98.5, 52.1, 28.9, 18.7, 11.4. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{38}\text{N}_3\text{OSi}$: 424.2779, found: 424.2785.

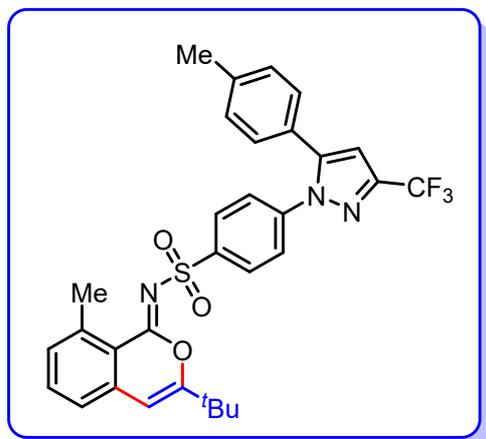


***N*-(*tert*-Butyl)-4-(pyridin-2-yl)-3-((triisopropylsilyl)ethynyl)benzamide (6f)**, white solid (37 mg, 86% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 142 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.66 (d, $J = 4.8$ Hz, 1H), 8.01-7.94 (m, 2H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.70-7.62 (m, 2H), 7.24-7.21 (m, 1H), 6.09 (s, 1H), 1.44 (s, 3H), 1.00 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.8, 156.6, 149.6, 144.5, 135.8, 135.5, 132.7, 129.8, 126.5, 124.8, 122.6, 121.9, 105.3, 95.8, 51.9, 28.9, 18.6, 11.3. **HRMS (ESI-TOF) m/z:** $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{39}\text{N}_2\text{OSi}$: 435.2826, found: 435.2832.

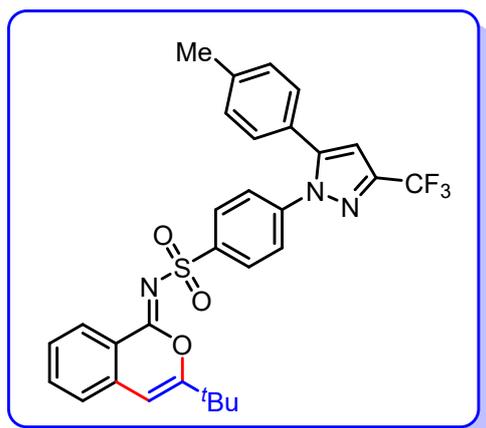


***N*-(3-(*tert*-Butyl)-6-(pyridin-2-yl)-1*H*-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4x)**, white solid (31 mg, 73% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 156 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.73 (dt, $J = 4.8, 1.6$ Hz, 1H), 8.35 (d, $J = 8.4$ Hz, 1H), 8.05 (d, $J = 1.6$ Hz, 1H), 8.02 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 2H), 7.81 (dd, $J = 3.6, 1.2$ Hz, 2H), 7.33-7.29 (m, 3H), 6.51 (s, 1H), 2.42 (s, 3H), 1.34 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.1, 156.0, 155.1, 150.0, 145.5, 142.8, 139.8, 137.1, 136.2, 129.3, 129.1, 126.7, 126.6,

123.8, 123.5, 121.2, 120.3, 101.6, 35.8, 27.8, 21.5. **HRMS (ESI-TOF) m/z :** $[M+H]^+$
Calcd. for $C_{25}H_{25}N_2O_3S^+$: 433.1580, Found: 433.1586.

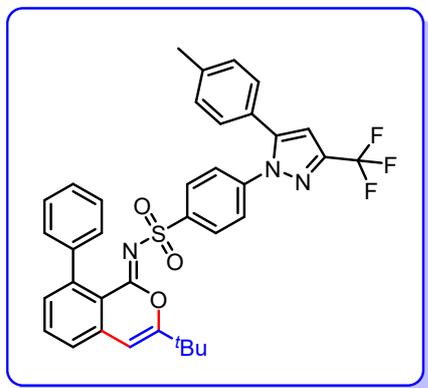


***N*-(3-(*tert*-Butyl)-8-methyl-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4y)**, white solid (48 mg, 83% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 145 °C. **1H NMR (500 MHz, $CDCl_3$) δ** 8.06 (d, J = 9.0 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.26-7.21 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 6.39 (s, 1H), 2.61 (s, 3H), 2.37 (s, 3H), 1.39 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 164.0, 160.4, 145.2, 143.8(q, J = 39.1 Hz), 142.8, 142.4, 141.8, 139.6, 137.8, 134.4, 131.8, 129.6, 128.7, 127.4, 125.7, 125.2, 124.2, 121.1(q, J = 269.6 Hz), 118.5, 106.0, 102.1, 35.5, 27.8, 24.8, 21.2. **^{19}F NMR (471 MHz, $CDCl_3$) δ** -62.21. **HRMS (ESI-TOF) m/z :** $[M+H]^+$ Calcd. for $C_{31}H_{29}F_3N_3O_3S^+$: 580.1876, Found: 580.1882.

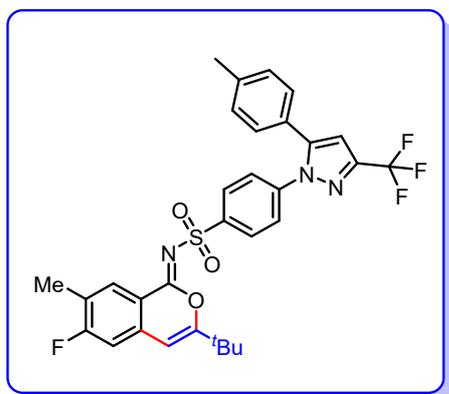


***N*-(3-(*tert*-Butyl)-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4z)**, white solid (45 mg, 80% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 143 °C. **1H NMR (500 MHz, $CDCl_3$) δ** 8.24 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.5 Hz, 2H), 7.74-7.67 (m, 1H), 7.49-7.44 (m, 3H), 7.41 (d, J = 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 8.0

Hz, 2H), 6.73 (s, 1H), 6.46 (s, 1H), 2.37 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.8, 160.7, 145.1, 143.8(q, $J = 39.1$ Hz), 142.2, 142.1, 139.6, 135.9, 135.5, 129.7, 128.7, 128.5, 128.5, 127.7, 125.8, 125.7, 125.1, 121.1(q, $J = 269.6$ Hz), 119.9, 106.1, 101.5, 35.8, 27.8, 21.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{30}\text{H}_{27}\text{F}_3\text{N}_3\text{O}_3\text{S}^+$: 566.1720, Found: 566.1726.

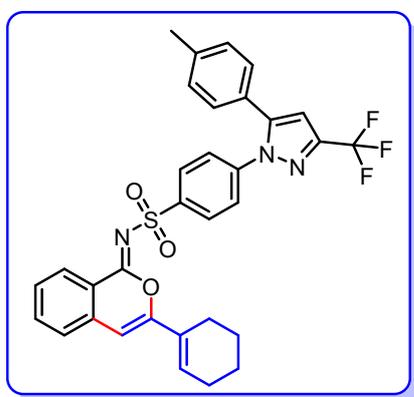


***N*-(3-(*tert*-Butyl)-8-phenyl-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4za)**, white solid (48 mg, 76% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 158 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.65 (t, $J = 7.5$ Hz, 1H), 7.41 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.29 (d, $J = 9.0$ Hz, 2H), 7.25-7.23 (m, 2H), 7.22-7.20 (m, 3H), 7.18 (dd, $J = 8.0, 1.5$ Hz, 2H), 7.14-7.10 (m, 4H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.75 (s, 1H), 6.50 (s, 1H), 2.40 (s, 3H), 1.45 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.6, 159.4, 144.9, 144.8, 143.8(q, $J = 39.1$ Hz), 141.9, 141.8, 141.4, 139.4, 137.6, 133.9, 132.2, 129.6, 128.7, 128.3, 127.6, 127.1, 126.8, 126.0, 125.6, 124.7, 121.1(q, $J = 269.6$ Hz), 16.9, 106.0, 101.7, 35.6, 27.8, 21.2. ^{19}F NMR (471 MHz, CDCl_3) δ -62.12. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{36}\text{H}_{31}\text{F}_3\text{N}_3\text{O}_3\text{S}^+$: 642.2033, Found: 642.2039.

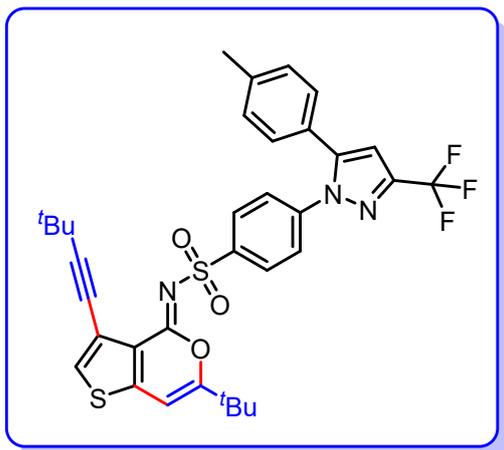


***N*-(3-(*tert*-Butyl)-6-fluoro-7-methyl-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4zb)**, white solid (46 mg,

78% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 151 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, $J = 7.5$ Hz, 1H), 8.06 (d, $J = 9.0$ Hz, 2H), 7.48 (d, $J = 9.0$ Hz, 2H), 7.18 (d, $J = 7.5$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 9.0$ Hz, 1H), 6.74 (s, 1H), 6.38 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.0, 165.3, 165.0, 159.9, 145.1, 143.9 (q, $J = 39.1$ Hz), 142.1 (q, $J = 3.9$ Hz), 139.6, 136.5 (q, $J = 10.9$ Hz), 132.1 (q, $J = 7.6$ Hz), 129.7, 128.7, 127.8, 127.5 (q, $J = 20.2$ Hz), 125.7, 125.2, 121.1 (q, $J = 269.6$ Hz), 116.1, 110.9 (q, $J = 23.9$ Hz), 106.1, 101.0, 35.9, 27.8, 21.3, 14.7, 14.6. ^{19}F NMR (471 MHz, CDCl_3) δ -62.29, -103.82 (t, $J = 9.4$ Hz). HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{31}\text{H}_{28}\text{F}_4\text{N}_3\text{O}_3\text{S}^+$: 598.1782, Found: 598.1788.



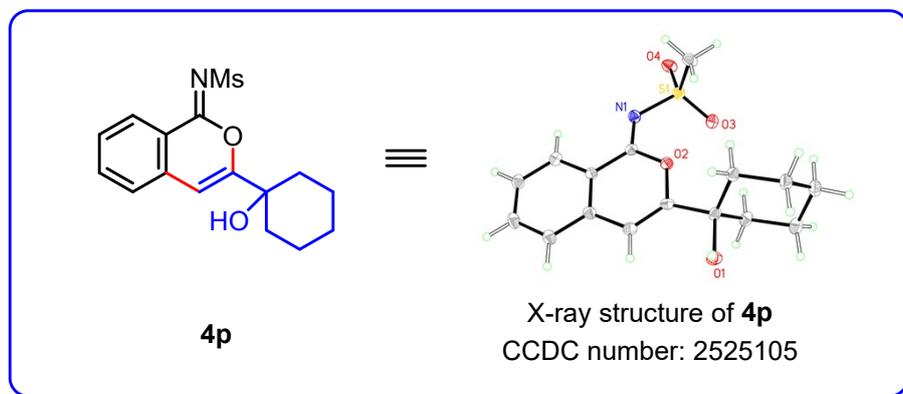
***N*-(3-(Cyclohex-1-en-1-yl)-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4zc)**, white solid (44 mg, 75% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 127 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 8.5$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 2H), 7.70-7.64 (m, 1H), 7.46 (d, $J = 9.0$ Hz, 2H), 7.43-7.38 (m, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.08 (t, $J = 4.0$ Hz, 1H), 6.73 (s, 1H), 6.48 (s, 1H), 2.37 (s, 3H), 2.34-2.23 (m, 4H), 1.80-1.72 (m, 2H), 1.72-1.61 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 160.0, 154.0, 145.1, 143.8 (q, $J = 39.1$ Hz), 142.1, 141.9, 139.6, 136.2, 135.5, 132.2, 129.6, 128.7, 128.6, 128.3, 127.7, 127.3, 126.1, 125.7, 125.1, 121.1 (q, $J = 269.6$ Hz), 120.1, 106.0, 101.4, 25.8, 23.9, 22.0, 21.6, 21.2. ^{19}F NMR (471 MHz, CDCl_3) δ -62.26. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{32}\text{H}_{27}\text{F}_3\text{N}_3\text{O}_3\text{S}^+$: 590.1720, Found: 590.1726.



***N*-(6-(*tert*-Butyl)-3-(3,3-dimethylbut-1-yn-1-yl)-4*H*-thieno[3,2-*c*]pyran-4-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4zd)**, white solid (56 mg, 87% yield, chromatography on silica gel, eluent: PE/EA = 10:1), m. p.: 162 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.32 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 6.64 (s, 1H), 2.37 (s, 3H), 1.36 (s, 9H), 1.09 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 167.3, 156.0, 149.7, 1455.0, 143.7 (q, *J* = 39.1 Hz), 142.5, 142.0, 139.5, 129.6, 128.7, 128.3, 127.8, 125.9, 125.0, 121.6, 121.5, 121.1 (q, *J* = 270.9 Hz), 106.1, 103.3, 98.2, 72.0, 36.2, 30.4, 27.9, 27.9, 21.2. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.26. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd. for C₃₄H₃₃F₃N₃O₃S⁺: 652.1910, Found: 652.1910.

E. X-Ray Crystallographic Analysis for 4p.

The crystal was obtained by slow evaporation of the solution of dichloromethane at room temperature, displacement ellipsoids are drawn at the 50% probability level.



Identification code	cs6_0m
Empirical formula	C ₁₆ H ₁₉ NO ₄ S
Formula weight	321.38
Temperature/K	170
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	6.9274(5)
b/Å	21.8077(16)
c/Å	20.0653(15)
α/°	90
β/°	95.639(4)
γ/°	90
Volume/Å ³	3016.6(4)
Z	8
ρ _{calc} /cm ³	1.415
μ/mm ⁻¹	2.071
F(000)	1360.0
Crystal size/mm ³	0.11 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.002 to 127.728
Index ranges	-7 ≤ h ≤ 8, -25 ≤ k ≤ 25, -23 ≤ l ≤ 22
Reflections collected	21579

Independent reflections	4879 [$R_{\text{int}} = 0.0866$, $R_{\text{sigma}} = 0.0587$]
Data/restraints/parameters	4879/0/401
Goodness-of-fit on F^2	1.089
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0623$, $wR_2 = 0.1534$
Final R indexes [all data]	$R_1 = 0.0804$, $wR_2 = 0.1677$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.44/-0.52

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for cs6_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
S2	6723.8(13)	497.3(4)	7128.3(5)	27.0(2)
S1	3100.7(13)	2904.8(4)	4891.3(5)	27.6(2)
O6	7562(3)	1459.4(11)	6282.7(13)	26.5(6)
O2	2549(4)	3467.9(11)	6136.6(13)	25.8(6)
O1	2478(4)	4817.6(12)	7169.2(13)	29.7(6)
O5	7450(4)	2035.1(12)	4596.1(13)	31.2(6)
O4	3551(4)	2424.3(13)	4434.8(14)	35.7(7)
O8	6470(4)	157.6(12)	7728.9(14)	32.8(6)
O7	5100(4)	489.2(13)	6620.1(15)	35.6(7)
O3	4456(4)	3404.6(13)	4978.3(14)	35.9(7)
N2	7261(4)	1194.1(13)	7370.7(16)	25.5(7)
N1	2820(4)	2553.2(14)	5591.8(16)	27.2(7)
C2	2564(5)	2533.6(17)	6773.8(19)	24.2(8)
C26	7544(5)	2261.7(17)	7100.1(19)	24.7(8)
C27	7453(5)	1619.5(17)	6929.2(19)	24.5(8)
C5	2526(5)	3816.0(17)	6718.5(19)	24.6(8)
C1	2660(5)	2848.4(16)	6142.6(19)	22.9(8)
C18	7607(5)	1575.3(16)	5102.2(19)	24.9(8)
C3	2486(5)	2883.8(17)	7355.5(19)	26.5(8)
C4	2510(5)	3542.1(17)	7306.8(19)	26.8(8)
C15	2555(5)	1893.1(17)	6801(2)	28.4(8)
C6	2532(5)	4490.5(16)	6554.4(19)	24.9(8)
C25	7601(5)	2694.1(17)	6584(2)	25.1(8)
C17	7611(5)	1886.8(16)	5772.6(19)	24.4(8)
C28	7513(5)	2457.8(18)	7763(2)	28.2(8)
C19	9569(5)	1253.2(18)	5046(2)	29.3(8)

C14	2462(5)	1603.4(18)	7406(2)	31.7(9)
C8	824(6)	5331.7(17)	5853(2)	30.6(9)
C31	7586(5)	3321.2(17)	6746(2)	30.1(9)
C7	798(5)	4657.7(17)	6057(2)	27.4(8)
C24	7633(5)	2482.3(17)	5909(2)	26.7(8)
C30	7563(6)	3501.8(18)	7399(2)	32.5(9)
C12	2417(5)	2577.0(18)	7967(2)	31.1(9)
C11	4462(5)	4664.4(17)	6272(2)	30.1(9)
C23	5913(5)	1115.3(17)	4999(2)	29.0(8)
C29	7541(6)	3077.3(18)	7915(2)	32.3(9)
C13	2386(5)	1943.8(19)	7988(2)	34.4(9)
C22	5959(6)	772(2)	4342(2)	37.6(10)
C10	4470(6)	5338.7(18)	6058(2)	35.0(9)
C9	2742(6)	5492.8(18)	5568(2)	34.9(9)
C16	785(6)	3183.5(19)	4604(2)	33.7(9)
C32	8787(6)	191.9(18)	6802(2)	34.2(9)
C20	9577(6)	906(2)	4390(2)	39.2(10)
C21	7901(6)	452(2)	4294(3)	45.7(11)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for cs6_0m.

The Anisotropic displacement factor exponent takes the form: -

$$2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+...].$$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
S2	28.4(5)	23.4(5)	29.4(5)	1.7(4)	3.6(4)	-1.0(3)
S1	30.9(5)	26.2(5)	25.6(5)	0.1(4)	2.8(4)	2.1(3)
O6	32.1(13)	24.7(13)	22.5(15)	0.5(10)	2.6(10)	0.8(10)
O2	33.1(13)	21.4(13)	22.9(14)	-1.5(10)	2.0(10)	0.4(10)
O1	34.0(14)	28.0(14)	26.8(15)	-7.1(11)	1.6(11)	0.3(11)
O5	37.0(14)	33.4(15)	23.6(15)	5.5(11)	4.5(11)	5.2(11)
O4	43.8(15)	37.4(16)	25.9(16)	-6.8(12)	3.8(12)	9.9(12)
O8	38.4(15)	28.1(14)	32.8(16)	7.2(12)	7.8(12)	-1.3(11)
O7	34.6(14)	33.8(16)	36.7(17)	-1.6(12)	-5.6(12)	-7.2(11)
O3	37.8(15)	35.3(16)	34.6(17)	4.6(13)	3.4(12)	-9.3(12)
N2	29.8(15)	21.2(16)	24.8(18)	1.0(13)	-0.2(13)	0.7(12)
N1	30.2(16)	26.1(16)	25.7(19)	0.7(13)	4.6(13)	1.6(12)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for cs6_0m.**The Anisotropic displacement factor exponent takes the form: -**

$$2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+...].$$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	20.5(16)	26.5(19)	25(2)	1.7(15)	0.3(14)	-1.3(13)
C26	19.1(16)	28(2)	26(2)	-0.9(15)	1.2(14)	0.0(14)
C27	20.1(16)	28(2)	25(2)	1.7(16)	1.7(14)	1.5(13)
C5	24.6(17)	27(2)	22(2)	-5.7(15)	0.8(14)	1.0(14)
C1	18.5(16)	22.6(19)	27(2)	-0.2(15)	-0.2(14)	1.2(13)
C18	26.7(18)	21.7(18)	26(2)	-0.2(15)	1.1(15)	3.4(14)
C3	22.0(17)	31(2)	26(2)	2.7(16)	-0.9(14)	1.5(14)
C4	26.0(18)	28(2)	26(2)	-3.0(16)	2.5(15)	1.8(14)
C15	24.2(18)	26(2)	35(2)	0.2(16)	2.9(15)	1.8(14)
C6	28.2(18)	19.9(18)	27(2)	-2.2(15)	5.3(15)	-0.6(14)
C25	19.8(16)	24.9(19)	30(2)	-0.9(16)	1.4(14)	0.4(13)
C17	22.8(16)	24.7(19)	26(2)	6.7(15)	2.8(14)	1.9(14)
C28	25.1(18)	30(2)	30(2)	-1.0(16)	2.9(15)	1.5(15)
C19	27.8(18)	33(2)	26(2)	-4.4(16)	0.2(15)	3.0(15)
C14	29.3(19)	29(2)	37(2)	7.7(17)	1.2(16)	0.4(15)
C8	34(2)	24(2)	34(2)	4.6(16)	1.7(16)	1.1(15)
C31	28.6(19)	23(2)	39(2)	3.6(17)	4.6(16)	1.9(14)
C7	29.4(18)	23.2(19)	29(2)	-0.7(16)	1.1(15)	-0.2(14)
C24	27.7(18)	25(2)	27(2)	1.3(15)	3.0(15)	-0.4(14)
C30	35(2)	25(2)	37(2)	-8.4(17)	2.8(17)	1.2(15)
C12	29.1(19)	34(2)	30(2)	5.7(17)	2.7(16)	2.1(15)
C11	25.9(18)	24(2)	40(2)	-1.9(17)	3.1(16)	1.2(14)
C23	28.8(19)	28(2)	30(2)	-2.4(16)	1.9(15)	-1.4(15)
C29	36(2)	31(2)	30(2)	-6.6(17)	2.7(17)	2.7(16)
C13	32(2)	36(2)	35(2)	14.6(18)	2.2(17)	3.0(16)
C22	38(2)	38(2)	35(3)	-9.8(19)	-1.8(18)	-0.3(17)
C10	31(2)	30(2)	45(3)	3.7(18)	5.6(18)	-2.5(16)
C9	41(2)	26(2)	38(3)	6.9(17)	5.2(18)	-1.0(16)
C16	38(2)	32(2)	30(2)	1.1(17)	-5.7(17)	9.5(17)
C32	39(2)	30(2)	34(2)	4.6(17)	8.0(18)	8.7(16)
C20	37(2)	44(2)	37(3)	-9(2)	3.8(18)	5.8(18)
C21	42(2)	47(3)	47(3)	-20(2)	-1(2)	3.3(19)

Table 4 Bond Lengths for cs6_0m.

Atom	Atom	Length/Å	Atom Atom	Length/Å
S2	O8	1.440(3)	C18 C17	1.507(5)
S2	O7	1.442(3)	C18 C19	1.544(5)
S2	N2	1.627(3)	C18 C23	1.542(5)
S2	C32	1.760(4)	C3 C4	1.439(5)
S1	O4	1.446(3)	C3 C12	1.403(5)
S1	O3	1.438(3)	C15 C14	1.375(6)
S1	N1	1.630(3)	C6 C7	1.528(5)
S1	C16	1.759(4)	C6 C11	1.549(5)
O6	C27	1.353(4)	C25 C31	1.406(5)
O6	C17	1.387(4)	C25 C24	1.433(6)
O2	C5	1.394(4)	C17 C24	1.327(5)
O2	C1	1.353(4)	C28 C29	1.385(6)
O1	C6	1.429(4)	C19 C20	1.519(6)
O5	C18	1.424(4)	C14 C13	1.391(6)
N2	C27	1.299(5)	C8 C7	1.527(5)
N1	C1	1.293(5)	C8 C9	1.538(5)
C2	C1	1.448(5)	C31 C30	1.369(6)
C2	C3	1.400(5)	C30 C29	1.390(6)
C2	C15	1.398(5)	C12 C13	1.382(6)
C26	C27	1.442(5)	C11 C10	1.532(5)
C26	C25	1.404(5)	C23 C22	1.519(6)
C26	C28	1.400(5)	C22 C21	1.527(6)
C5	C4	1.324(5)	C10 C9	1.511(6)
C5	C6	1.507(5)	C20 C21	1.523(6)

Table 5 Bond Angles for cs6_0m.

Atom Atom Atom Angle/°	Atom Atom Atom Angle/°
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Table 5 Bond Angles for cs6_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O8	S2	O7	115.74(17)	C23	C18	C19	111.0(3)
O8	S2	N2	105.87(17)	C2	C3	C4	119.1(3)
O8	S2	C32	106.67(18)	C2	C3	C12	118.5(4)
O7	S2	N2	111.23(16)	C12	C3	C4	122.5(4)
O7	S2	C32	109.8(2)	C5	C4	C3	120.8(4)
N2	S2	C32	107.12(18)	C14	C15	C2	119.6(4)
O4	S1	N1	104.89(16)	O1	C6	C5	107.3(3)
O4	S1	C16	106.81(19)	O1	C6	C7	111.0(3)
O3	S1	O4	116.57(17)	O1	C6	C11	106.9(3)
O3	S1	N1	112.57(17)	C5	C6	C7	110.9(3)
O3	S1	C16	109.97(19)	C5	C6	C11	109.9(3)
N1	S1	C16	105.26(18)	C7	C6	C11	110.7(3)
C27	O6	C17	122.8(3)	C26	C25	C31	118.8(4)
C1	O2	C5	122.8(3)	C26	C25	C24	119.0(3)
C27	N2	S2	119.9(3)	C31	C25	C24	122.2(4)
C1	N1	S1	122.0(3)	O6	C17	C18	111.0(3)
C3	C2	C1	118.6(3)	C24	C17	O6	120.4(3)
C15	C2	C1	120.6(3)	C24	C17	C18	128.6(3)
C15	C2	C3	120.8(4)	C29	C28	C26	120.4(4)
C25	C26	C27	118.7(3)	C20	C19	C18	111.7(3)
C28	C26	C27	121.2(3)	C15	C14	C13	120.4(4)
C28	C26	C25	120.0(3)	C7	C8	C9	110.7(3)
O6	C27	C26	118.3(3)	C30	C31	C25	120.1(4)
N2	C27	O6	119.3(3)	C8	C7	C6	112.1(3)
N2	C27	C26	122.5(3)	C17	C24	C25	120.6(4)
O2	C5	C6	110.4(3)	C31	C30	C29	121.5(4)
C4	C5	O2	120.2(3)	C13	C12	C3	120.3(4)
C4	C5	C6	129.5(3)	C10	C11	C6	111.4(3)
O2	C1	C2	118.3(3)	C22	C23	C18	110.9(3)
N1	C1	O2	119.9(3)	C28	C29	C30	119.2(4)
N1	C1	C2	121.8(3)	C12	C13	C14	120.4(4)
O5	C18	C17	108.2(3)	C23	C22	C21	111.9(4)
O5	C18	C19	105.9(3)	C9	C10	C11	111.8(3)
O5	C18	C23	111.0(3)	C10	C9	C8	111.4(3)
C17	C18	C19	110.3(3)	C19	C20	C21	111.4(4)
C17	C18	C23	110.3(3)	C20	C21	C22	111.2(4)

Table 6 Torsion Angles for cs6_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S2	N2	C27	O6	-12.2(4)	C3	C2	C15	C14	0.3(5)
S2	N2	C27	C26	167.4(3)	C3	C12	C13	C14	1.3(6)
S1	N1	C1	O2	6.0(5)	C4	C5	C6	O1	-1.2(5)
S1	N1	C1	C2	-175.1(3)	C4	C5	C6	C7	-122.6(4)
O6	C17	C24	C25	-0.2(5)	C4	C5	C6	C11	114.7(4)
O2	C5	C4	C3	-1.0(5)	C4	C3	C12	C13	179.6(3)
O2	C5	C6	O1	179.1(3)	C15	C2	C1	O2	176.2(3)
O2	C5	C6	C7	57.7(4)	C15	C2	C1	N1	-2.8(5)
O2	C5	C6	C11	-65.0(4)	C15	C2	C3	C4	179.6(3)
O1	C6	C7	C8	63.9(4)	C15	C2	C3	C12	0.6(5)
O1	C6	C11	C10	-67.4(4)	C15	C14	C13	C12	-0.5(6)
O5	C18	C17	O6	173.9(3)	C6	C5	C4	C3	179.3(3)
O5	C18	C17	C24	-5.3(5)	C6	C11	C10	C9	-54.7(5)
O5	C18	C19	C20	-66.2(4)	C25	C26	C27	O6	4.5(5)
O5	C18	C23	C22	63.2(4)	C25	C26	C27	N2	-175.1(3)
O4	S1	N1	C1	170.4(3)	C25	C26	C28	C29	-0.1(5)
O8	S2	N2	C27	-175.6(3)	C25	C31	C30	C29	-0.4(6)
O7	S2	N2	C27	-49.1(3)	C17	O6	C27	N2	174.6(3)
O3	S1	N1	C1	42.7(3)	C17	O6	C27	C26	-4.9(5)
C2	C3	C4	C5	2.7(5)	C17	C18	C19	C20	177.0(3)
C2	C3	C12	C13	-1.3(5)	C17	C18	C23	C22	-176.8(3)
C2	C15	C14	C13	-0.3(5)	C28	C26	C27	O6	-177.6(3)
C26	C25	C31	C30	1.5(5)	C28	C26	C27	N2	2.9(5)
C26	C25	C24	C17	0.0(5)	C28	C26	C25	C31	-1.3(5)
C26	C28	C29	C30	1.2(6)	C28	C26	C25	C24	179.9(3)
C27	O6	C17	C18	-176.5(3)	C19	C18	C17	O6	-70.7(4)
C27	O6	C17	C24	2.9(5)	C19	C18	C17	C24	110.1(4)
C27	C26	C25	C31	176.7(3)	C19	C18	C23	C22	-54.3(4)
C27	C26	C25	C24	-2.1(5)	C19	C20	C21	C22	55.4(5)
C27	C26	C28	C29	-178.0(3)	C31	C25	C24	C17	-178.8(3)
C5	O2	C1	N1	-174.9(3)	C31	C30	C29	C28	-1.0(6)
C5	O2	C1	C2	6.1(4)	C7	C6	C11	C10	53.6(4)
C5	C6	C7	C8	-176.9(3)	C7	C8	C9	C10	-55.9(5)
C5	C6	C11	C10	176.4(3)	C24	C25	C31	C30	-179.7(3)
C1	O2	C5	C4	-3.6(5)	C12	C3	C4	C5	-178.3(3)
C1	O2	C5	C6	176.1(3)	C11	C6	C7	C8	-54.7(4)
C1	C2	C3	C4	-0.2(5)	C11	C10	C9	C8	55.8(5)
C1	C2	C3	C12	-179.2(3)	C23	C18	C17	O6	52.3(4)
C1	C2	C15	C14	-180.0(3)	C23	C18	C17	C24	-127.0(4)

Table 6 Torsion Angles for cs6_0m.

C18	C17	C24	C25	178.9(3)	C23	C18	C19	C20	54.4(4)
C18	C19	C20	C21	-55.0(5)	C23	C22	C21	C20	-56.1(5)
C18	C23	C22	C21	55.5(5)	C9	C8	C7	C6	55.7(4)
C3	C2	C1	O2	-4.1(5)	C16	S1	N1	C1	-77.1(3)
C3	C2	C1	N1	177.0(3)	C32	S2	N2	C27	70.9(3)

Table 7 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for cs6_0m.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H1	1328.19	4917.8	7216.6	45
H5	6318.22	2177.97	4556.69	47
H4	2515.07	3783.01	7701.41	32
H15	2614.01	1659.37	6404.12	34
H28	7472.01	2164.16	8111.24	34
H19A	10617.72	1563.28	5076.77	35
H19B	9831.92	963.92	5423.87	35
H14	2449.35	1168.16	7425.11	38
H8A	665.31	5593.08	6246.9	37
H8B	-274.35	5414.76	5510.67	37
H31	7592.39	3620.23	6402.11	36
H7A	810.16	4398.02	5653.16	33
H7B	-416.22	4571.03	6262.38	33
H24	7671.78	2770.98	5556	32
H30	7562.88	3927.07	7501.53	39
H12	2391.86	2805.87	8369.33	37
H11A	5555.21	4589.53	6618.64	36
H11B	4648.53	4400.69	5882.16	36
H23A	6002.17	818.63	5374.57	35
H23B	4666.63	1337.59	4998.98	35
H29	7545.37	3210.6	8365.56	39
H13	2312.23	1739.81	8403.45	41
H22A	5718.42	1064.34	3965.48	45
H22B	4907.19	463.07	4301.15	45
H10A	4455.65	5602.72	6459.08	42
H10B	5677.07	5426.08	5849.52	42
H9A	2831.97	5263.01	5146.2	42
H9B	2758.44	5936.15	5462.01	42

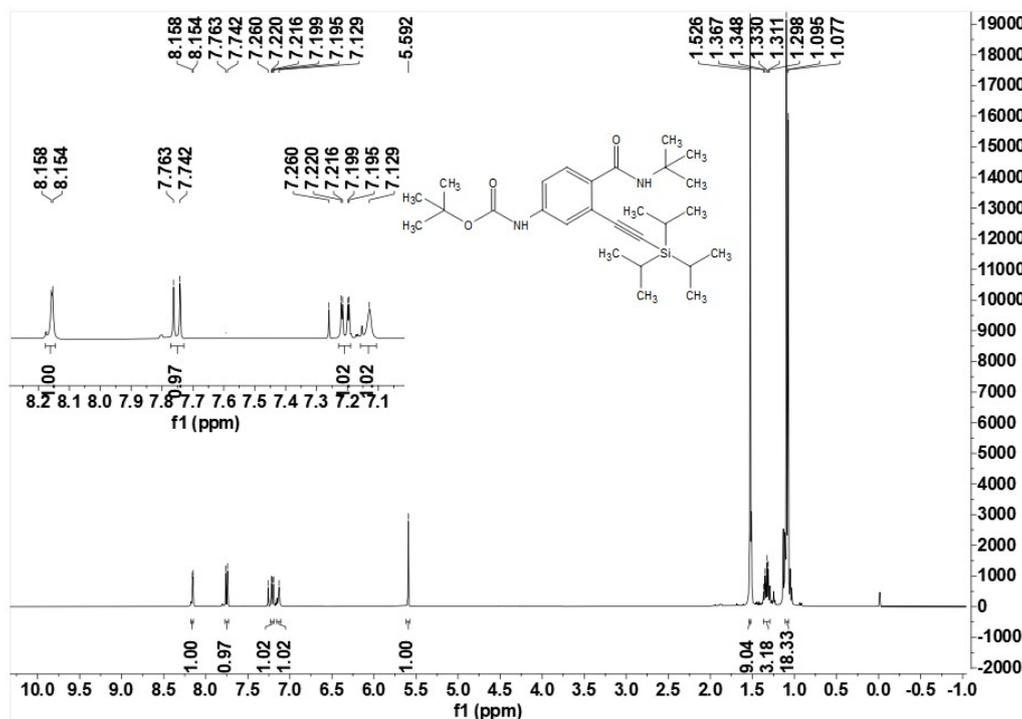
Table 7 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for cs6_0m.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H16A	843.82	3390.8	4172.88	51
H16B	352.72	3474.44	4930.41	51
H16C	-130.81	2840.67	4547.87	51
H32A	9863.56	173.42	7157.23	51
H32B	9149.67	454.18	6438.15	51
H32C	8496.69	-221.88	6630.24	51
H20A	10819.41	681.9	4385.04	47
H20B	9477.73	1200.78	4012.94	47
H21A	8081.67	128.91	4641.35	55
H21B	7897.69	253.15	3850.76	55

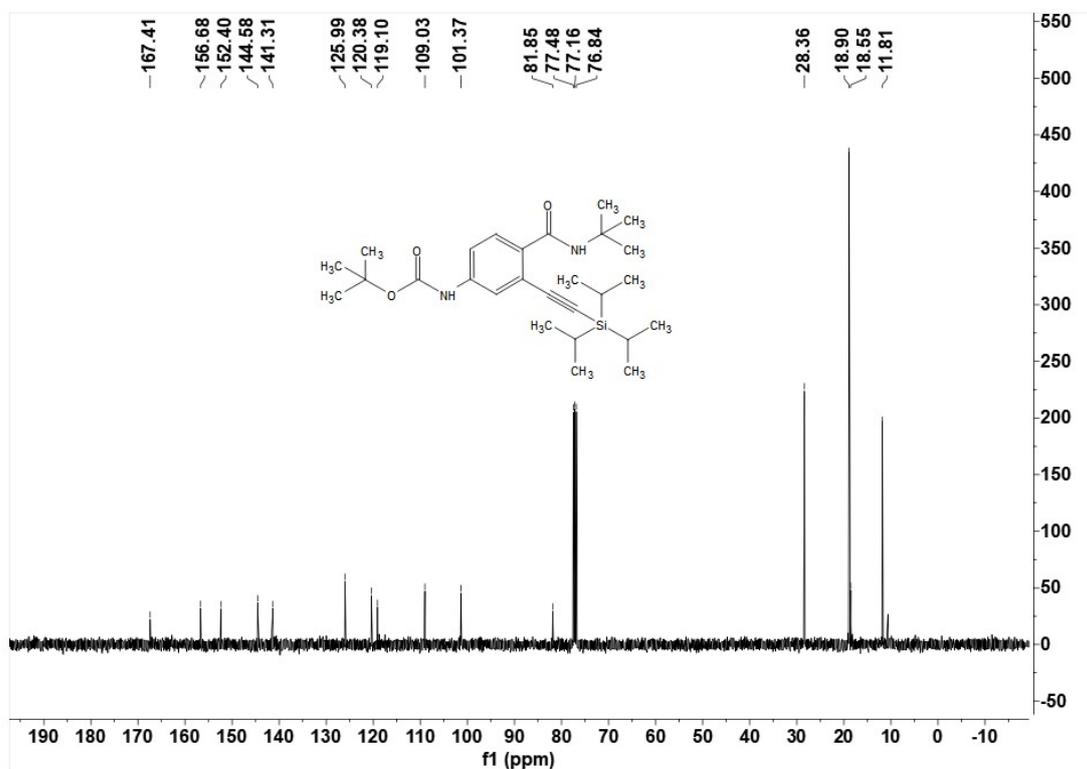
F. NMR spectra

***tert*-Butyl (4-(*tert*-butylcarbamoyl)-3-((triisopropylsilyl)ethynyl)phenyl)carbamate (3a),**

¹H NMR (CDCl₃, 400 MHz)

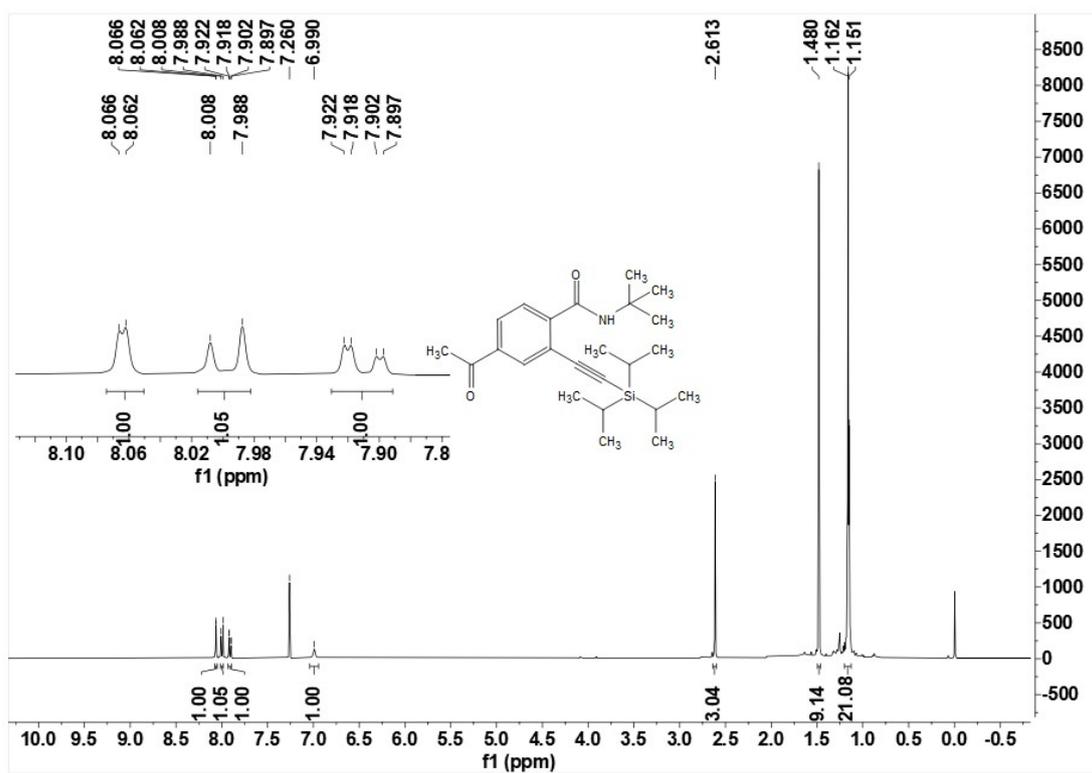


¹³C NMR (100 MHz, CDCl₃)

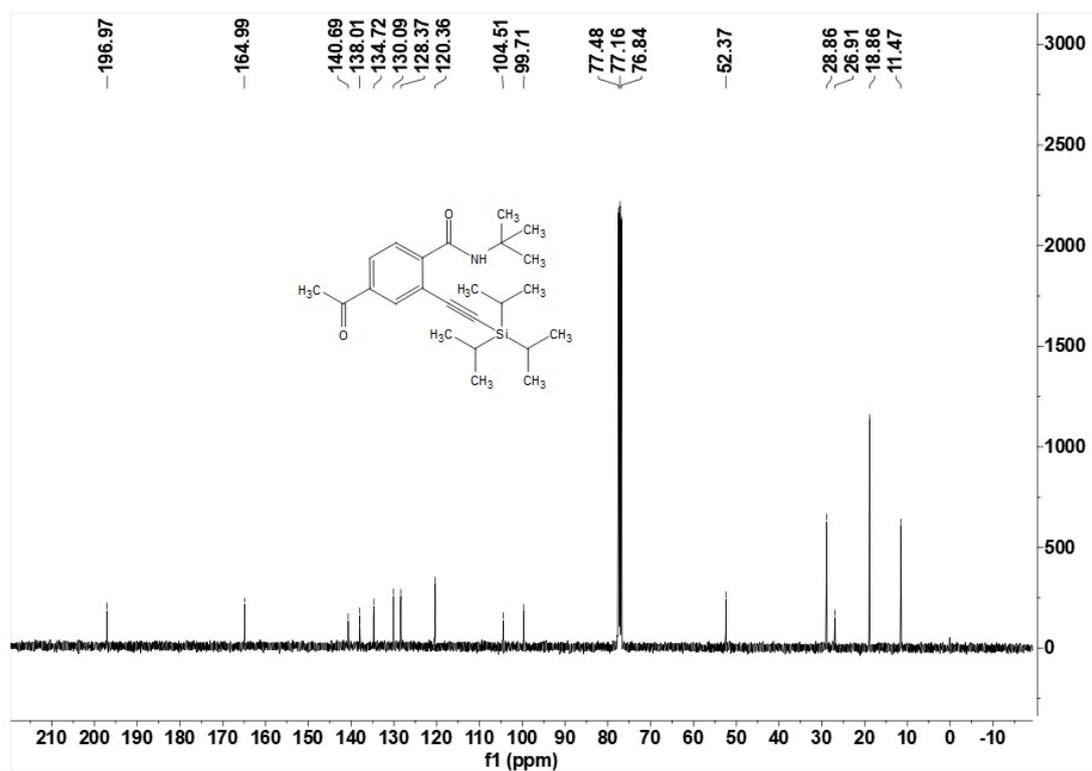


4-Acetyl-*N*-(*tert*-butyl)-2-((triisopropylsilyl)ethynyl)benzamide (3b)

¹H NMR (CDCl₃, 400 MHz)

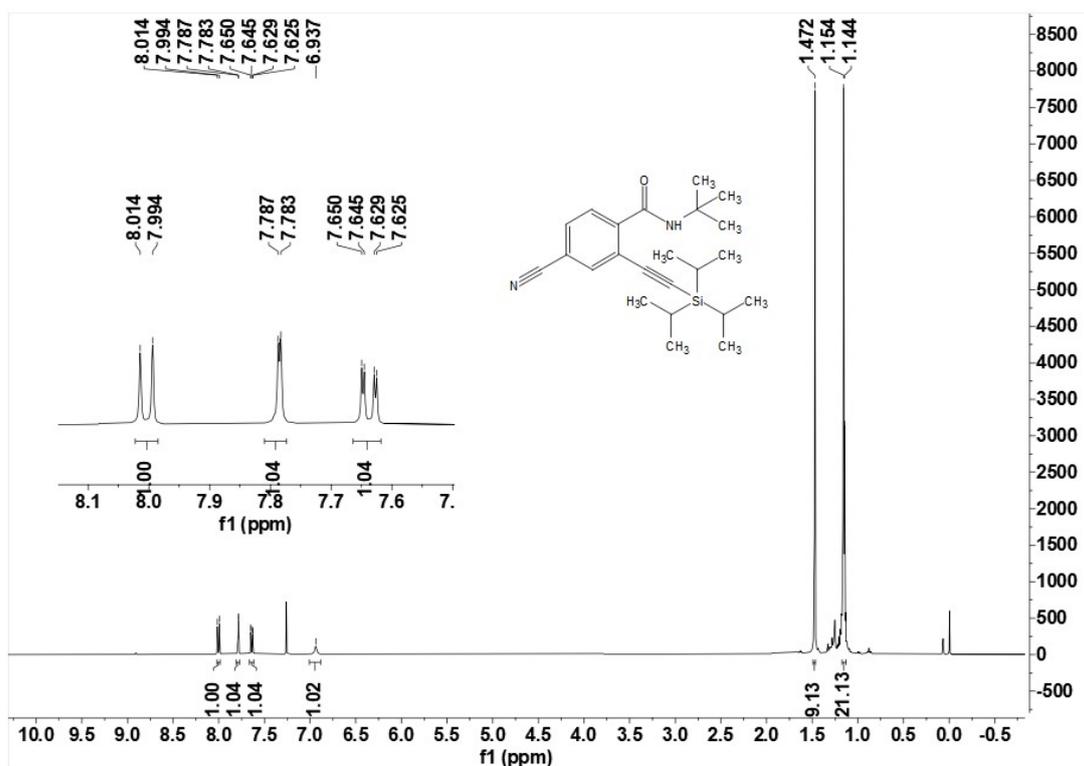


¹³C NMR (100 MHz, CDCl₃)

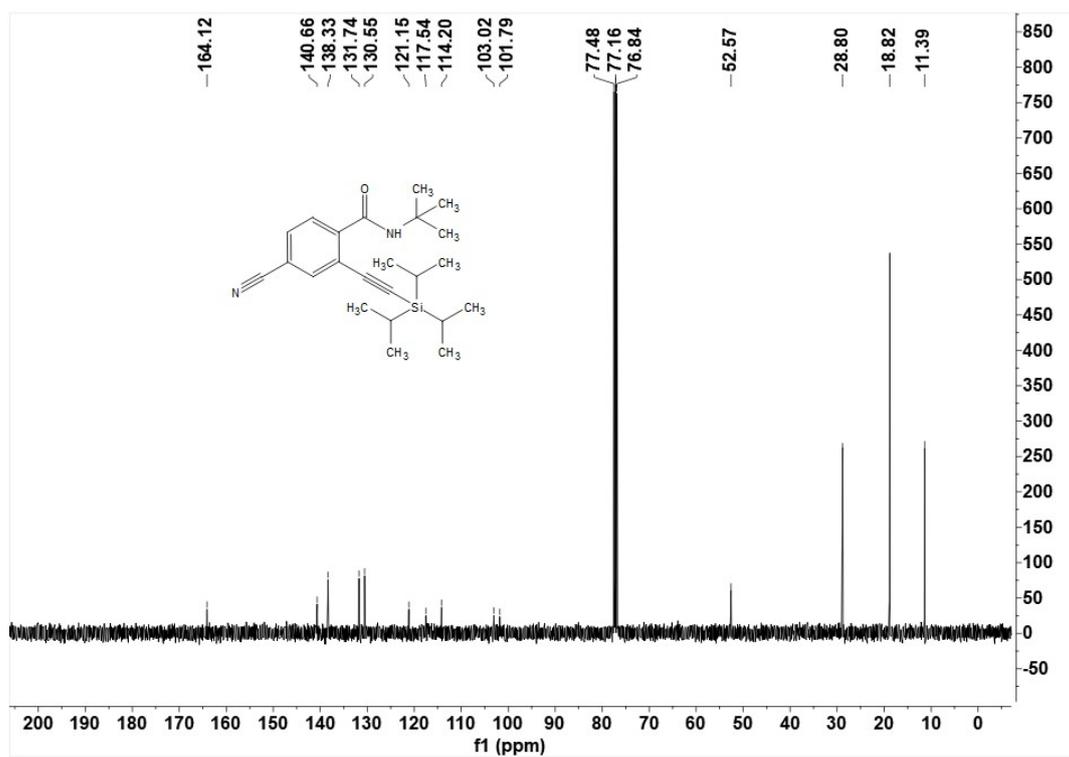


***N*-(*tert*-Butyl)-4-cyano-2-((triisopropylsilyl)ethynyl)benzamide (3c)**

¹H NMR (CDCl₃, 400 MHz)

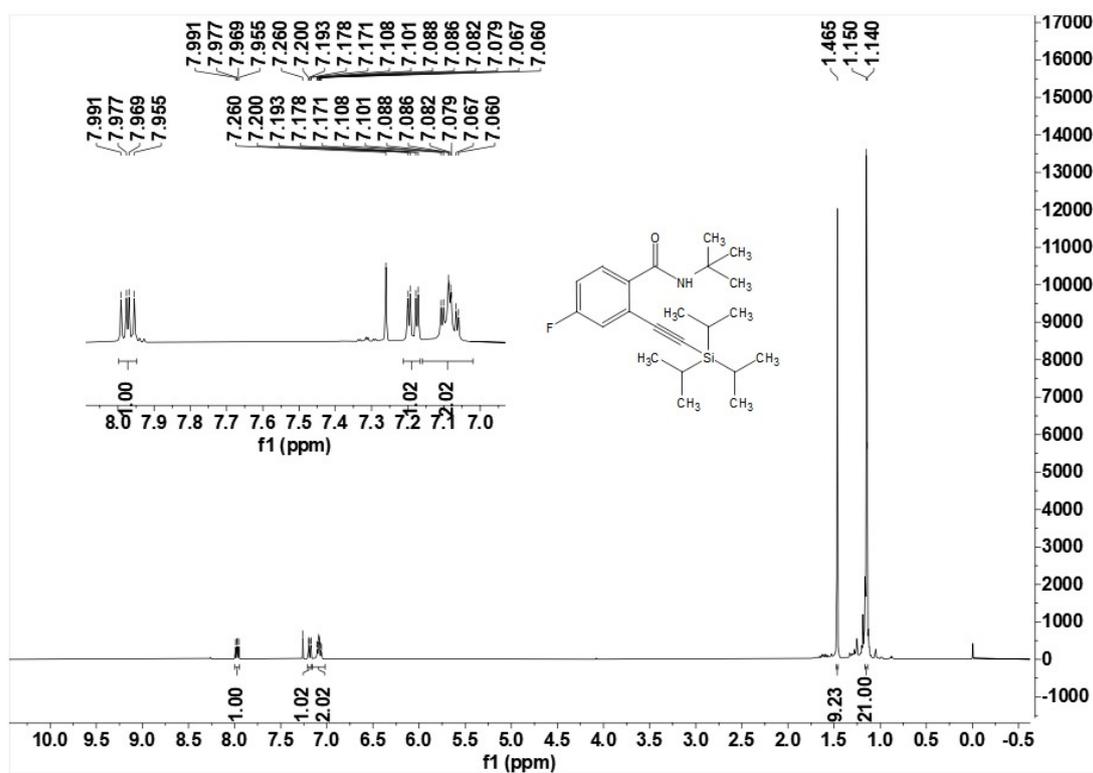


¹³C NMR (100 MHz, CDCl₃)

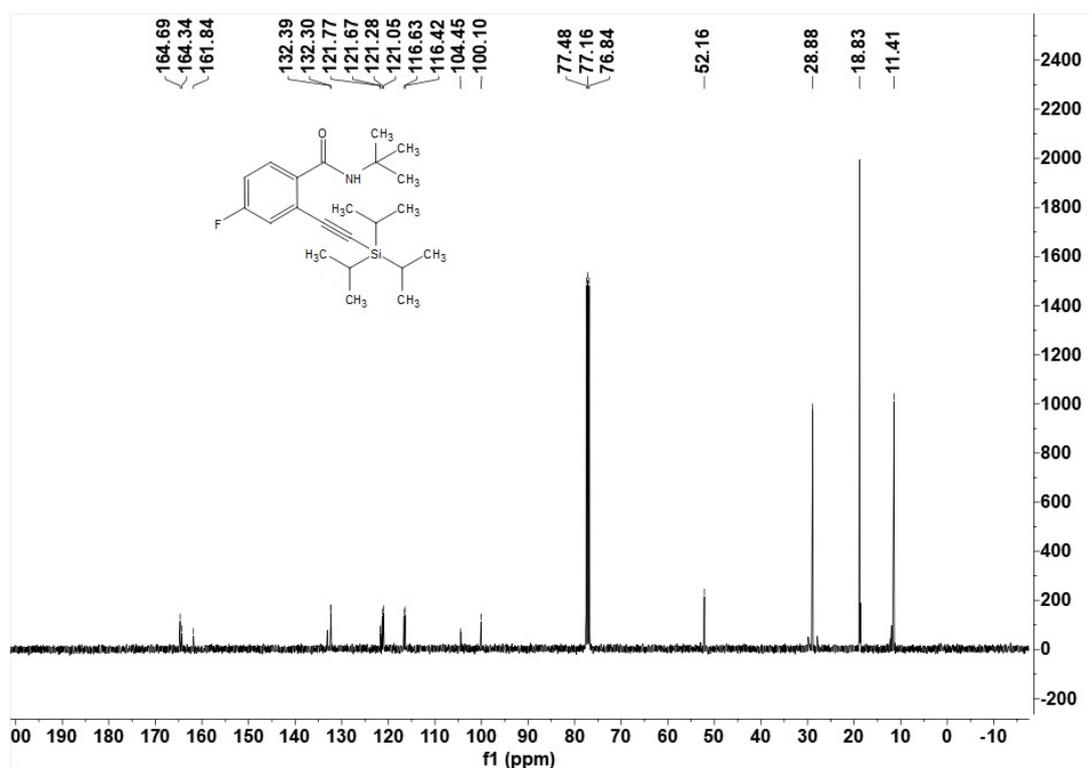


***N*-(*tert*-Butyl)-4-fluoro-2-((triisopropylsilyl)ethynyl)benzamide (3d)**

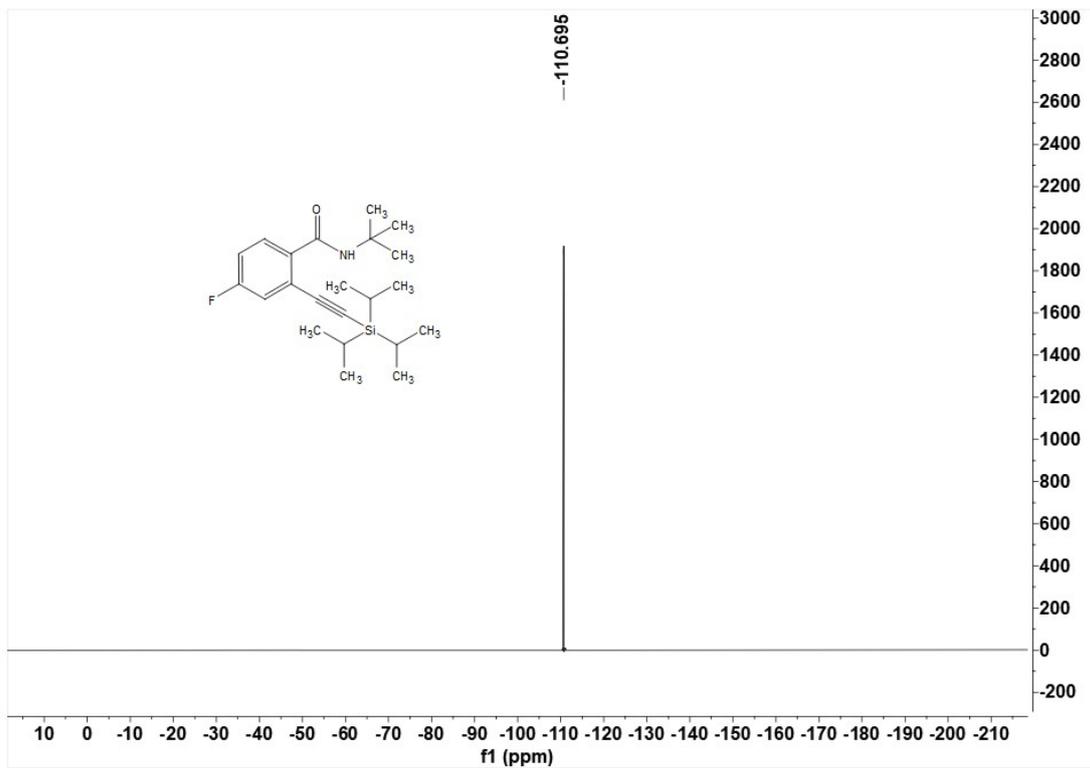
¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (100 MHz, CDCl₃)

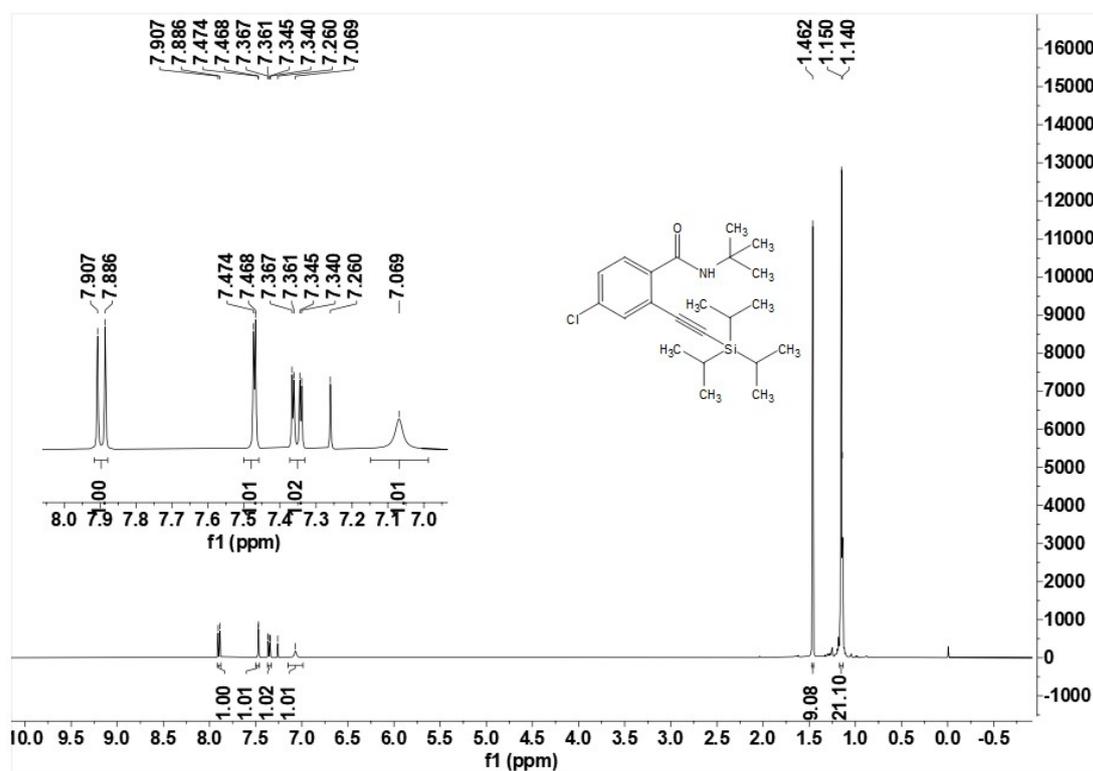


¹⁹F NMR (376 MHz, CDCl₃)

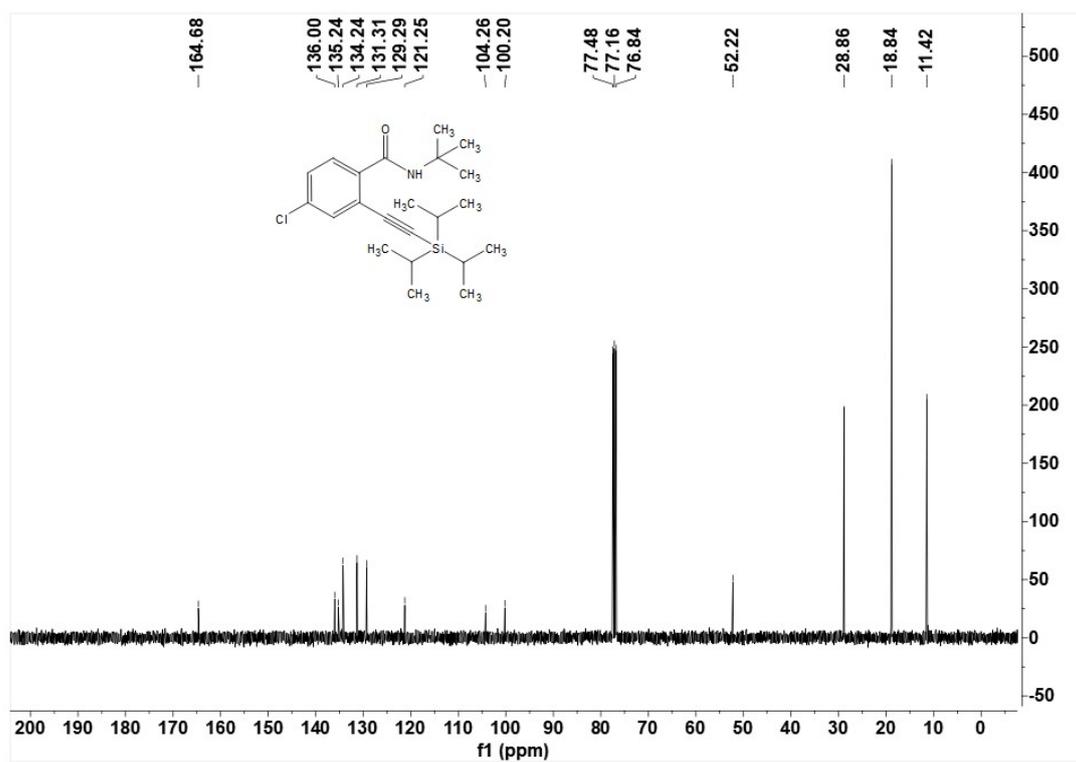


***N*-(*tert*-Butyl)-4-chloro-2-((triisopropylsilyl)ethynyl)benzamide (3e)**

¹H NMR (CDCl₃, 400 MHz)

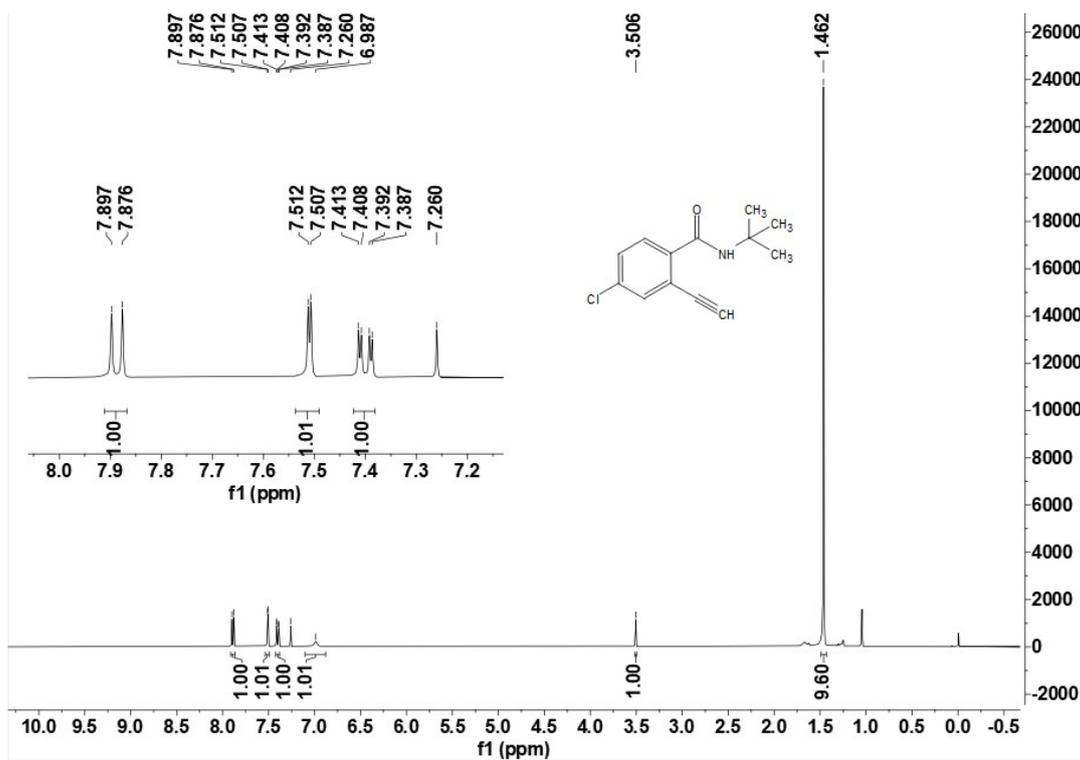


¹³C NMR (100 MHz, CDCl₃)

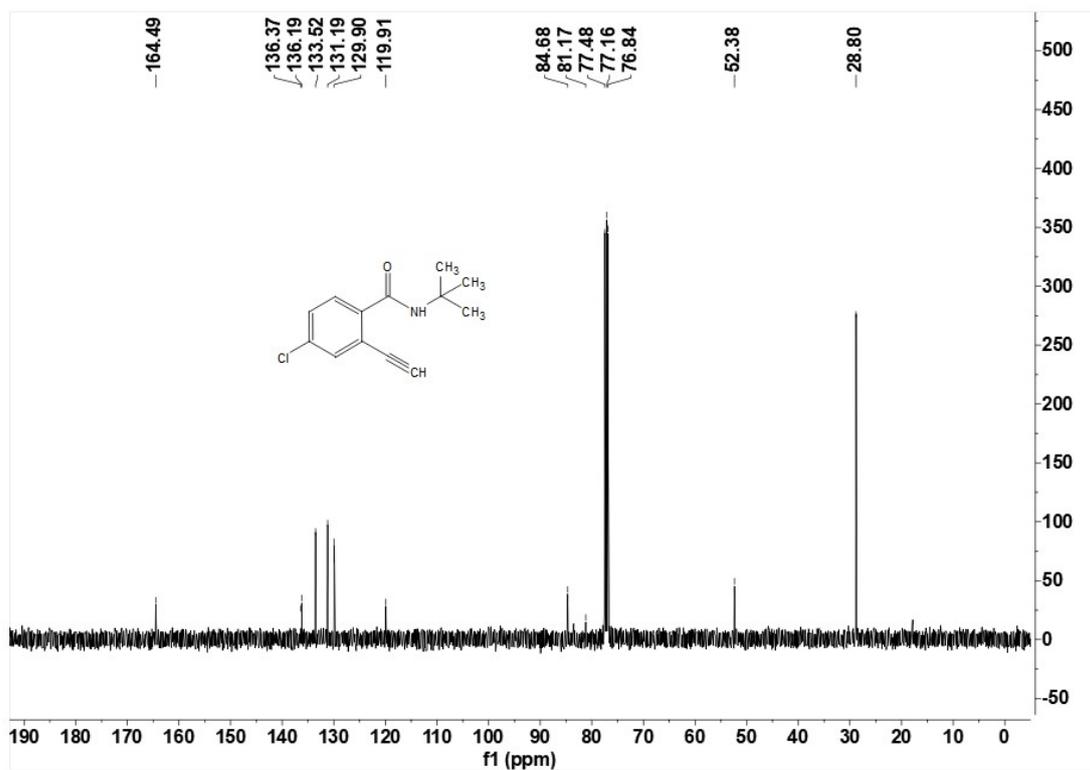


***N*-(*tert*-Butyl)-4-chloro-2-ethynylbenzamide (3e-1)**

^1H NMR (CDCl₃, 400 MHz)

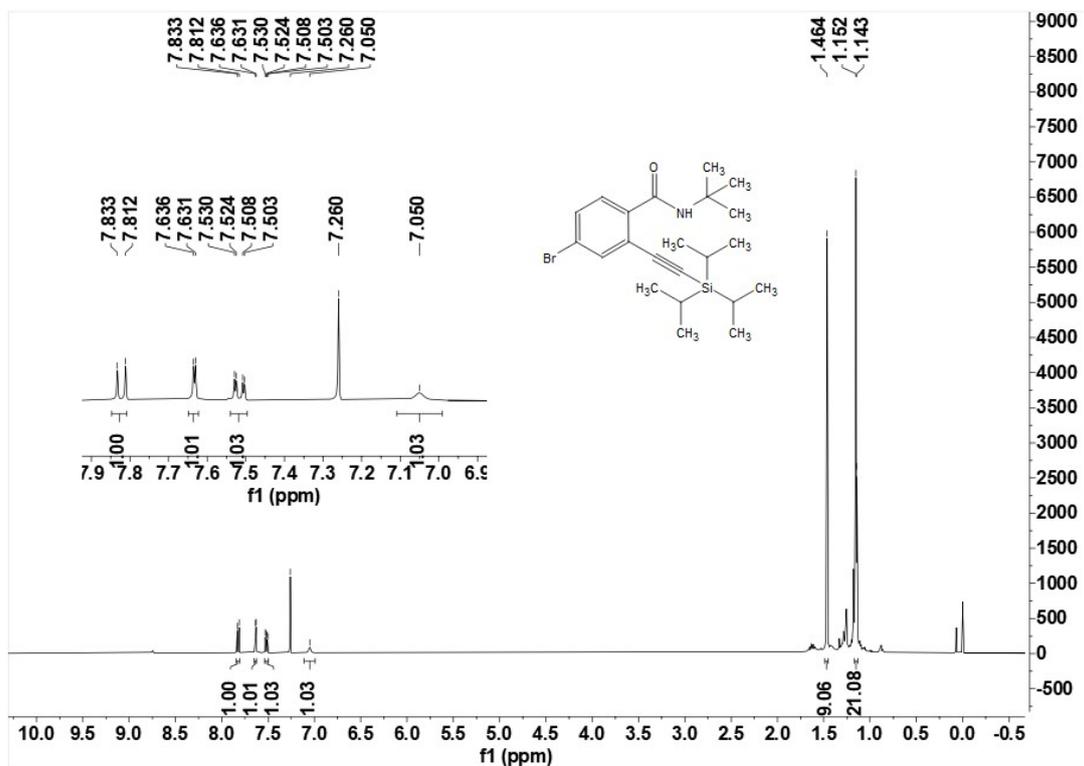


^{13}C NMR (100 MHz, CDCl₃)

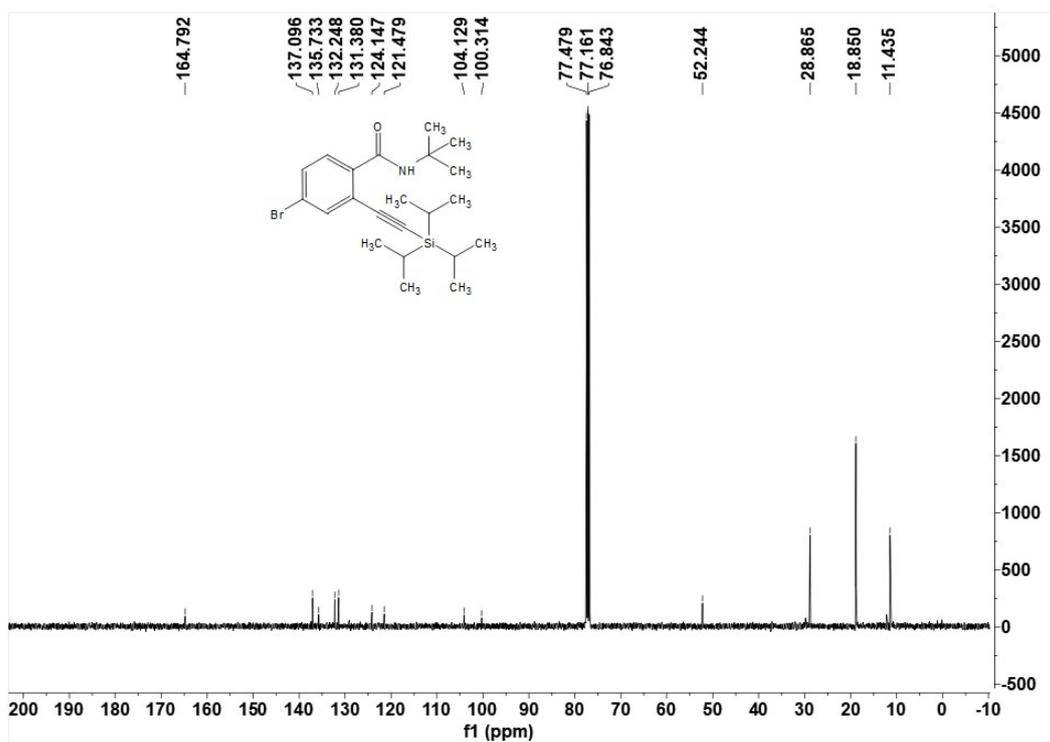


4-Bromo-*N*-(*tert*-butyl)-2-((triisopropylsilyl)ethynyl)benzamide (3f)

^1H NMR (CDCl_3 , 400 MHz)

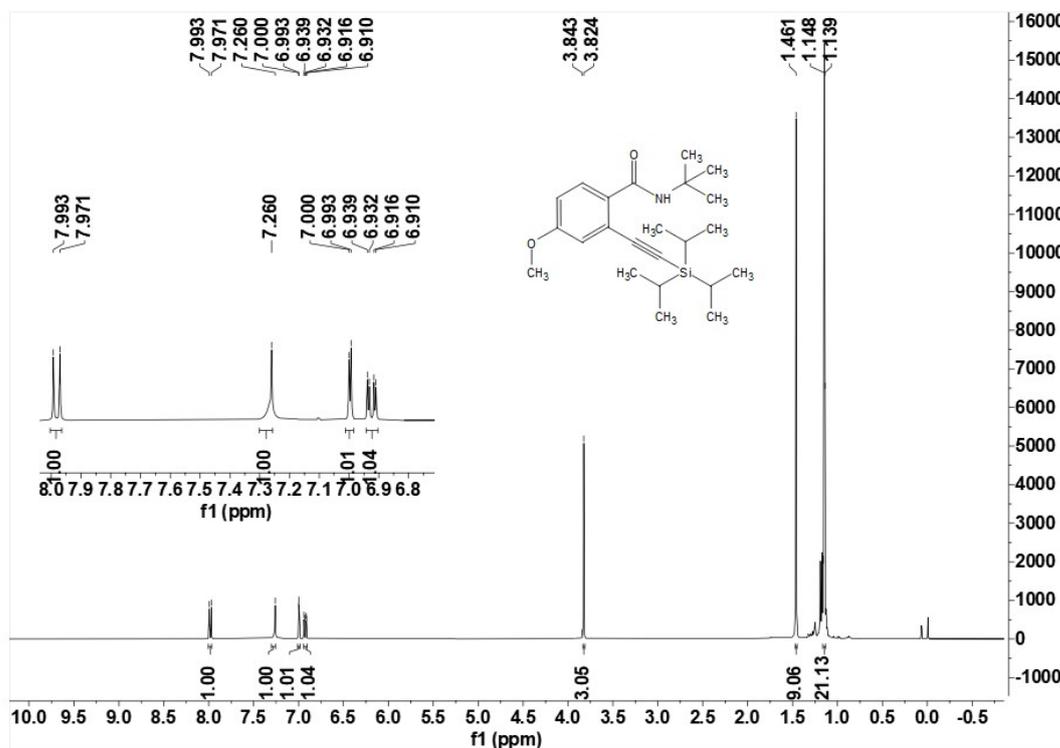


^{13}C NMR (100 MHz, CDCl_3)

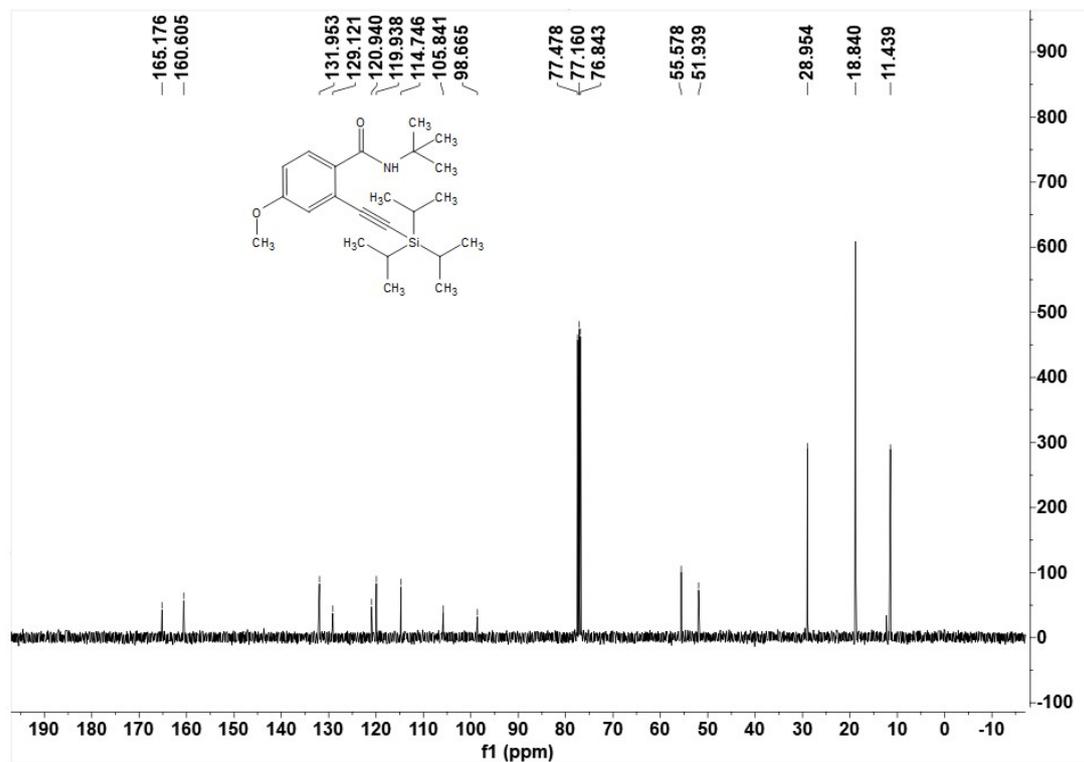


N-(*tert*-Butyl)-4-methoxy-2-((triisopropylsilyl)ethynyl)benzamide (3g)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

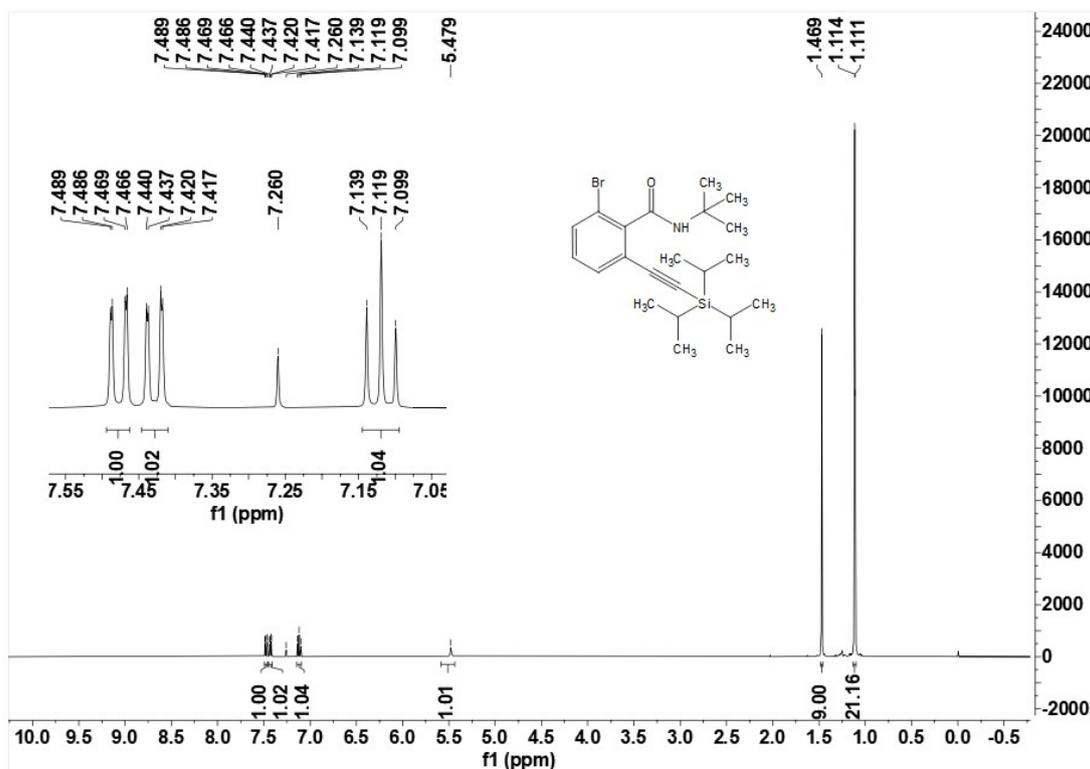


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

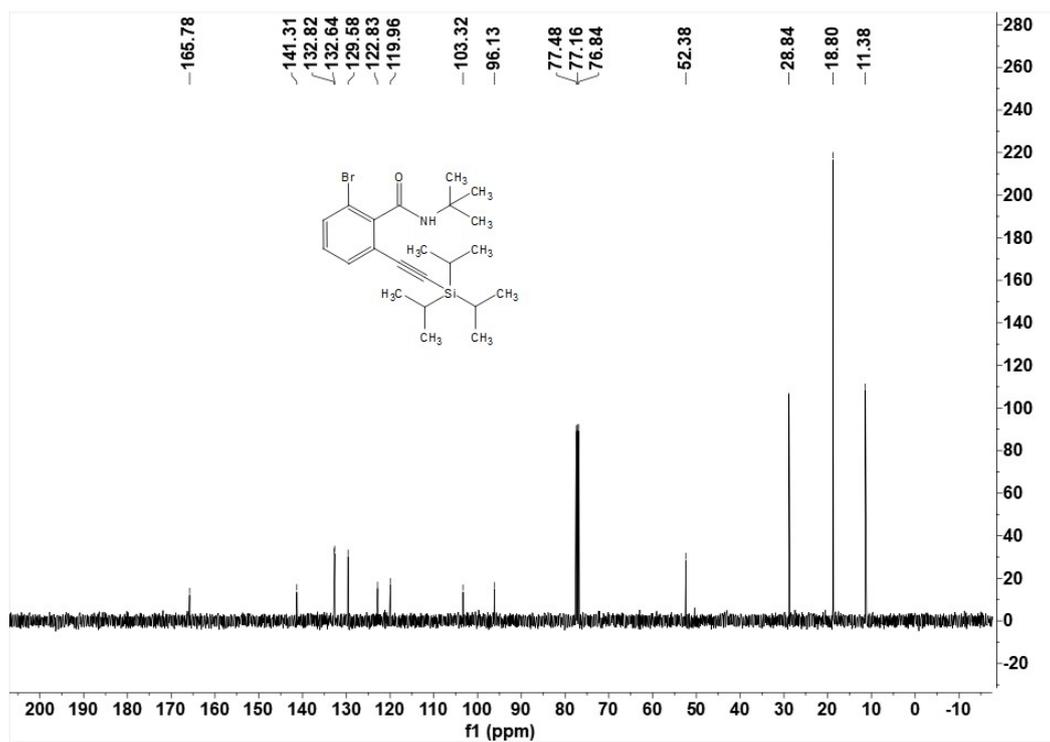


2-Bromo-*N*-(*tert*-butyl)-6-((triisopropylsilyl)ethynyl)benzamide (3h)

^1H NMR (CDCl_3 , 400 MHz)

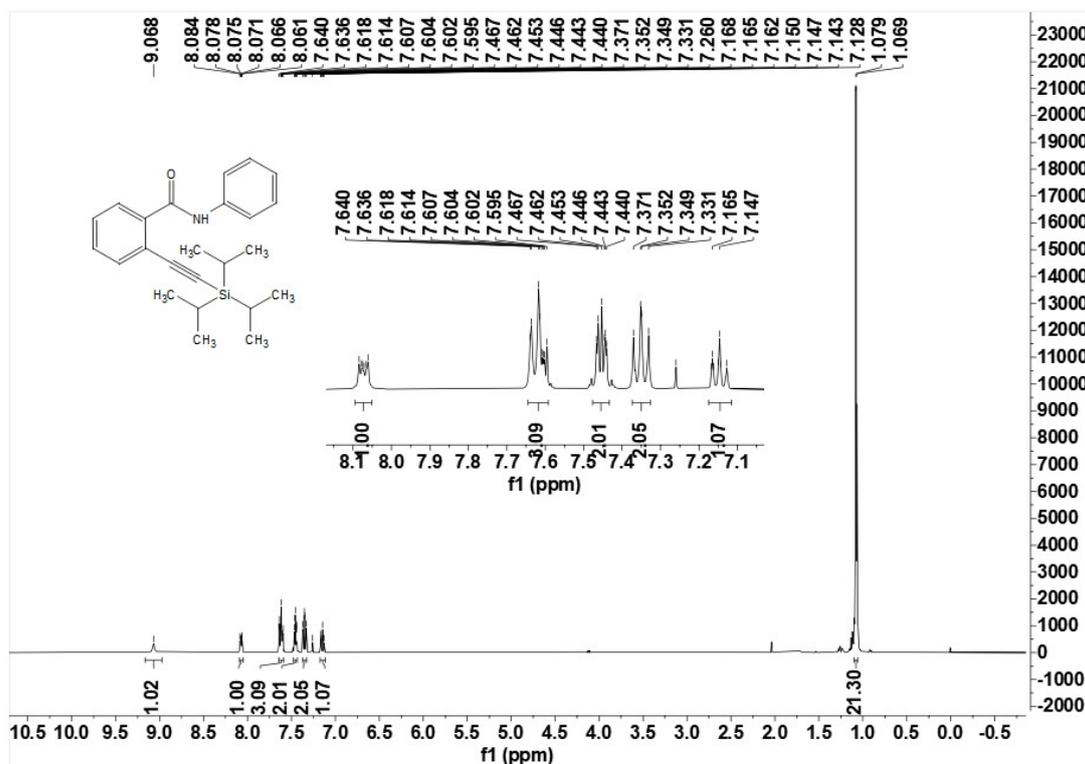


^{13}C NMR (100 MHz, CDCl_3)

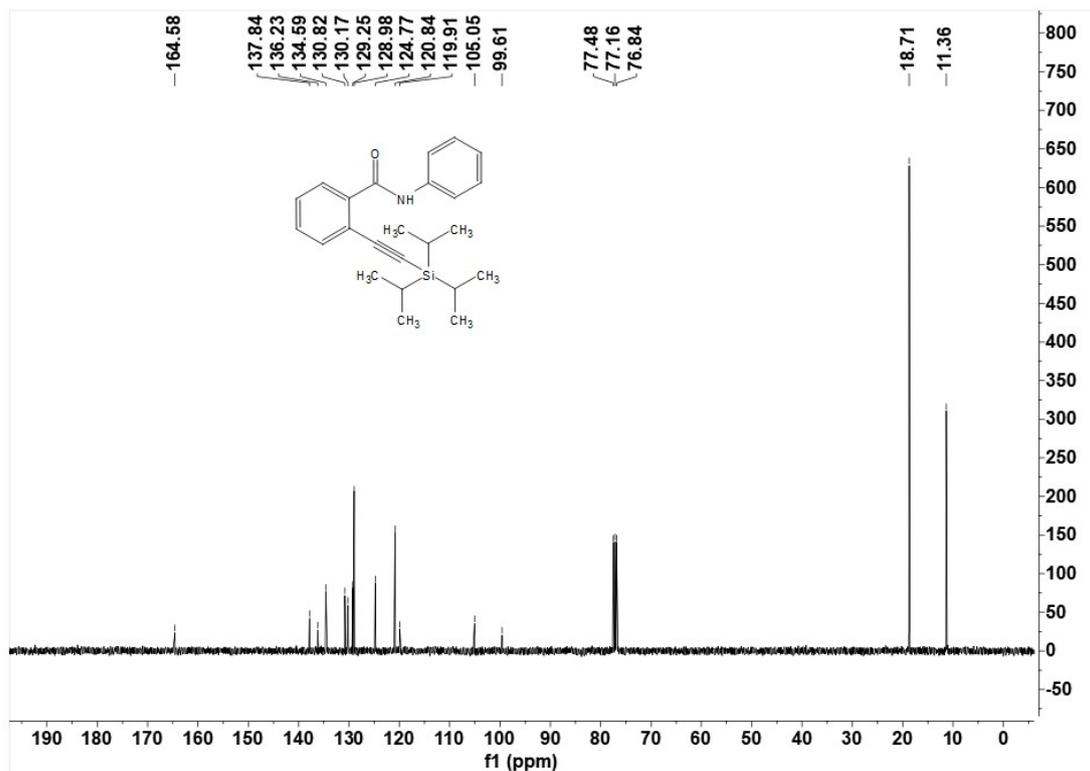


N-Phenyl-2-((triisopropylsilyl)ethynyl)benzamide (3i)

¹H NMR (CDCl₃, 400 MHz)

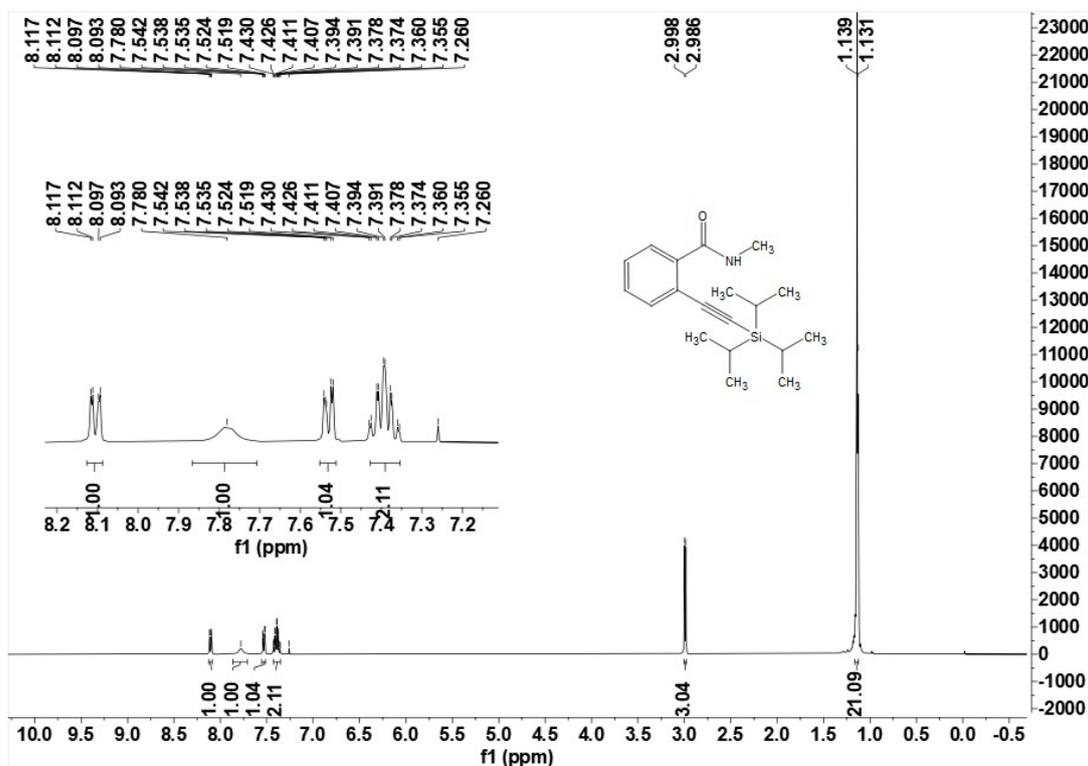


¹³C NMR (100 MHz, CDCl₃)

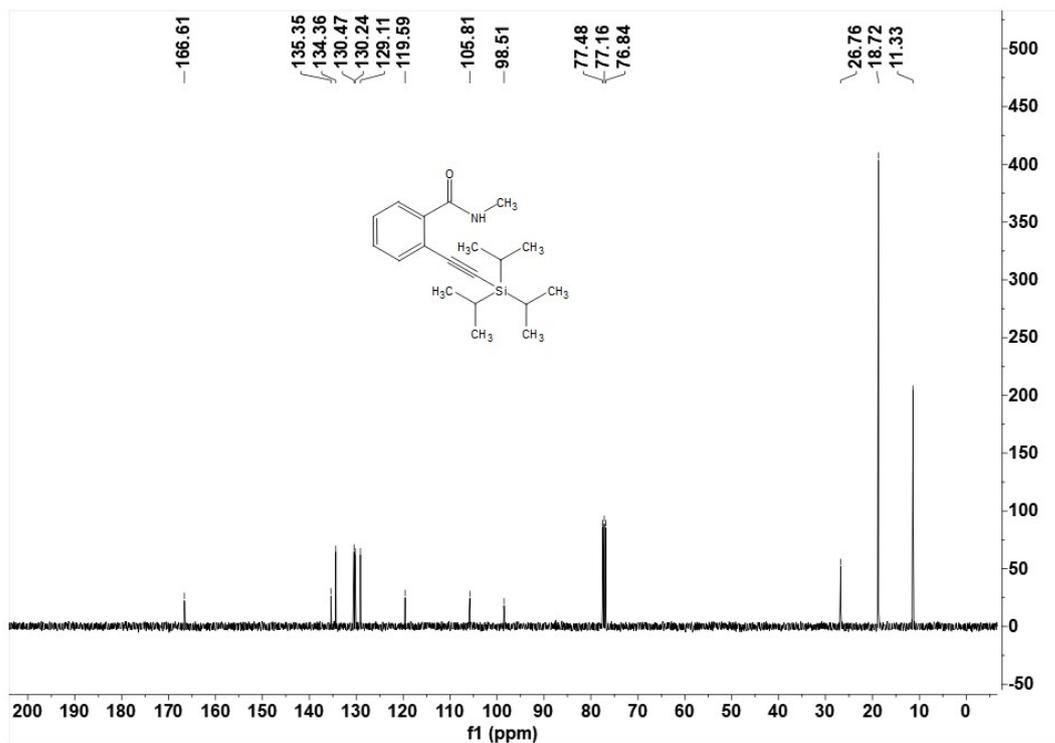


N-Methyl-2-((triisopropylsilyl)ethynyl)benzamide (3j)

¹H NMR (CDCl₃, 400 MHz)

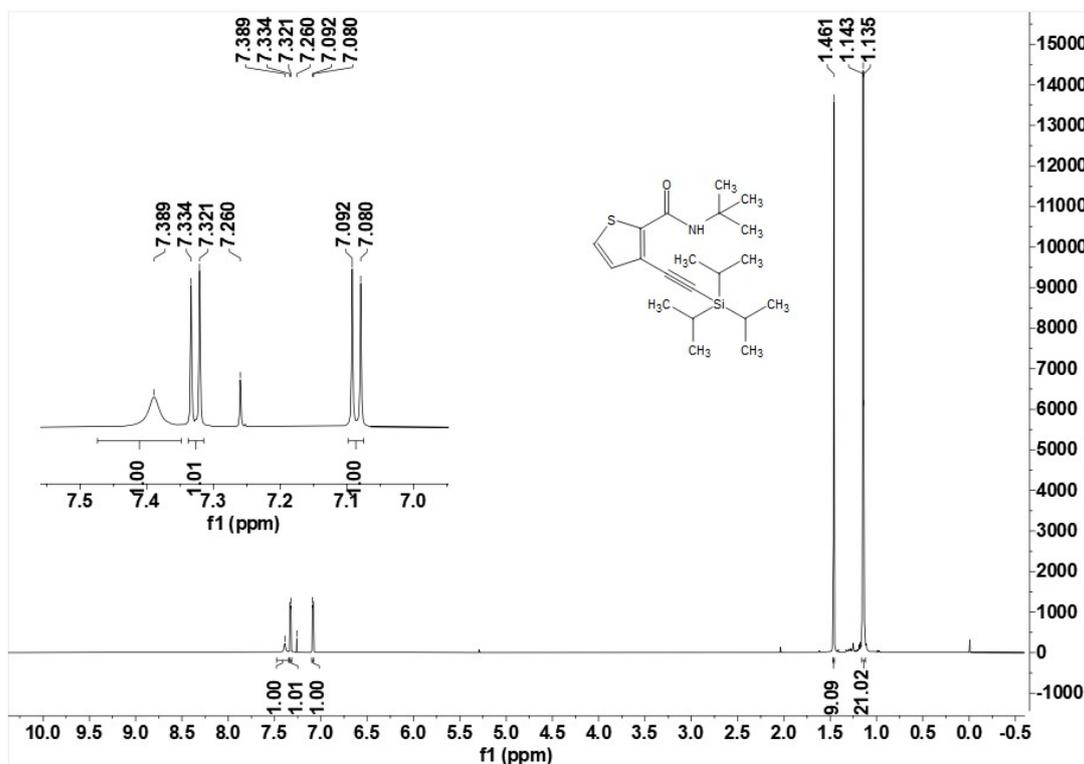


¹³C NMR (100 MHz, CDCl₃)

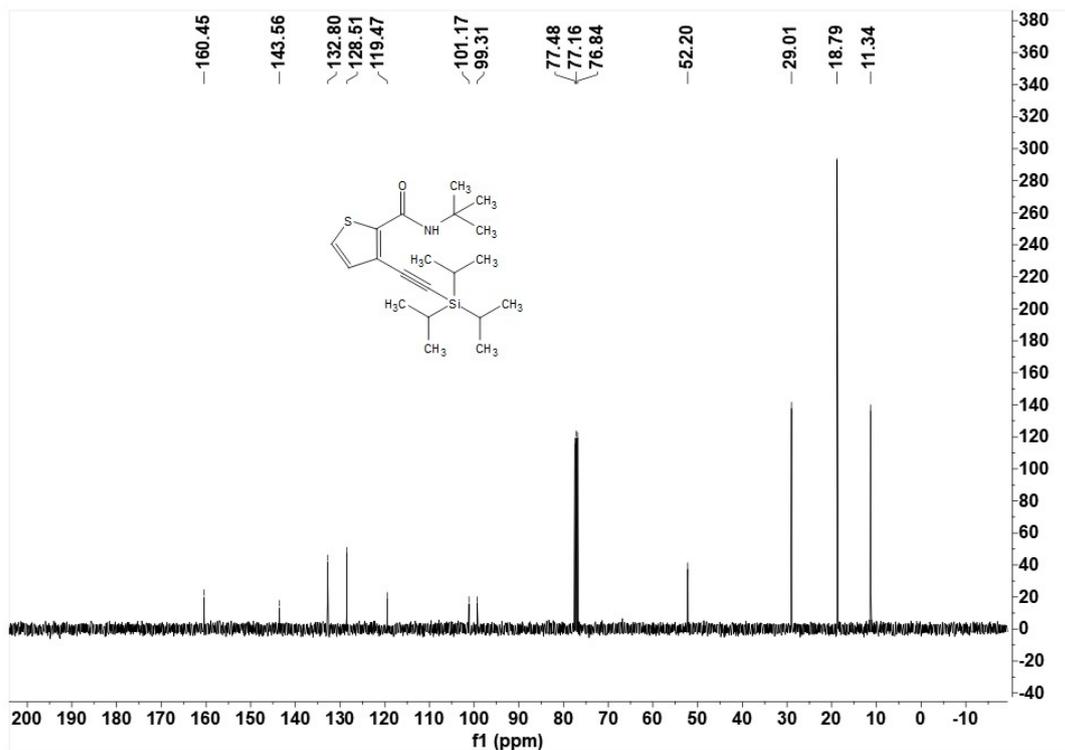


N-(*tert*-Butyl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide (**3k**)

¹H NMR (CDCl₃, 400 MHz)

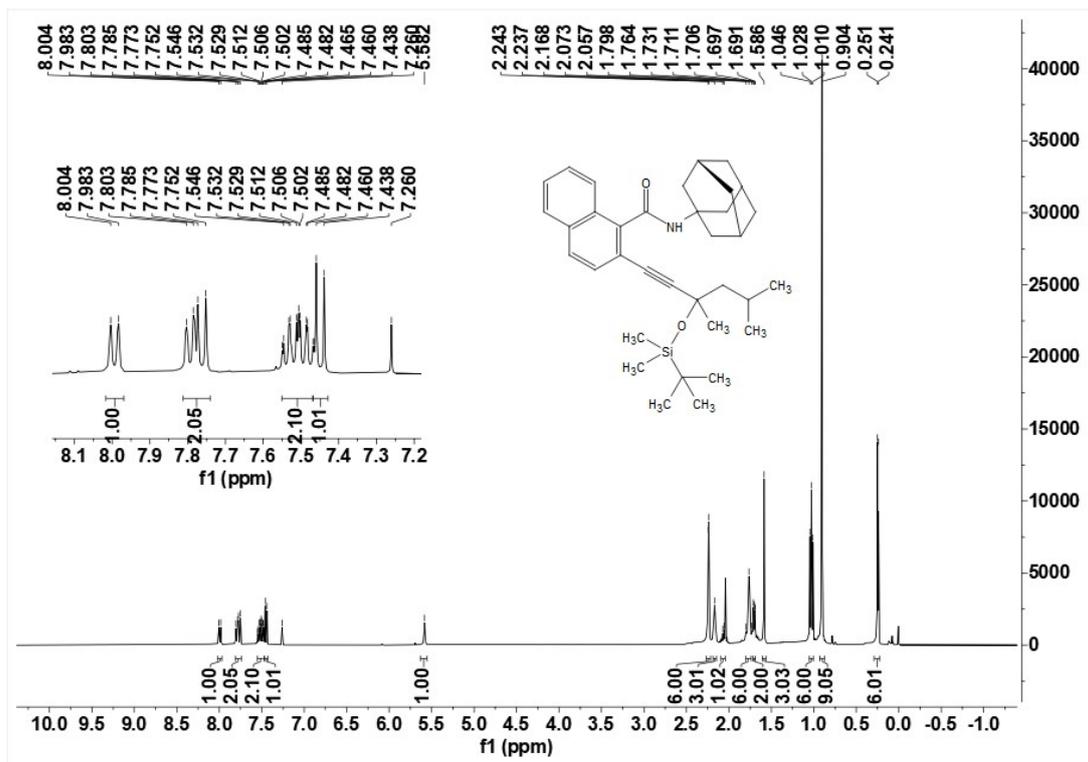


¹³C NMR (100 MHz, CDCl₃)

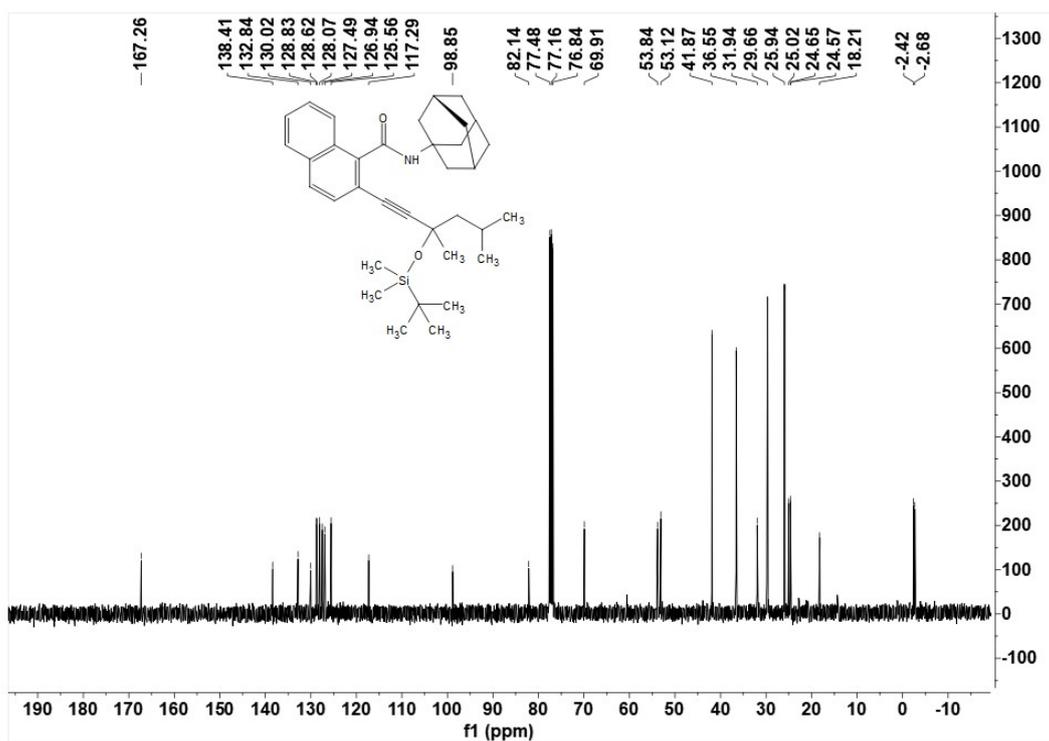


***N*-(Adamantan-1-yl)-2-(3-((*tert*-butyldimethylsilyl)oxy)-3,5-dimethylhex-1-yn-1-yl)-1-naphthamide (3l)**

^1H NMR (CDCl₃, 400 MHz)

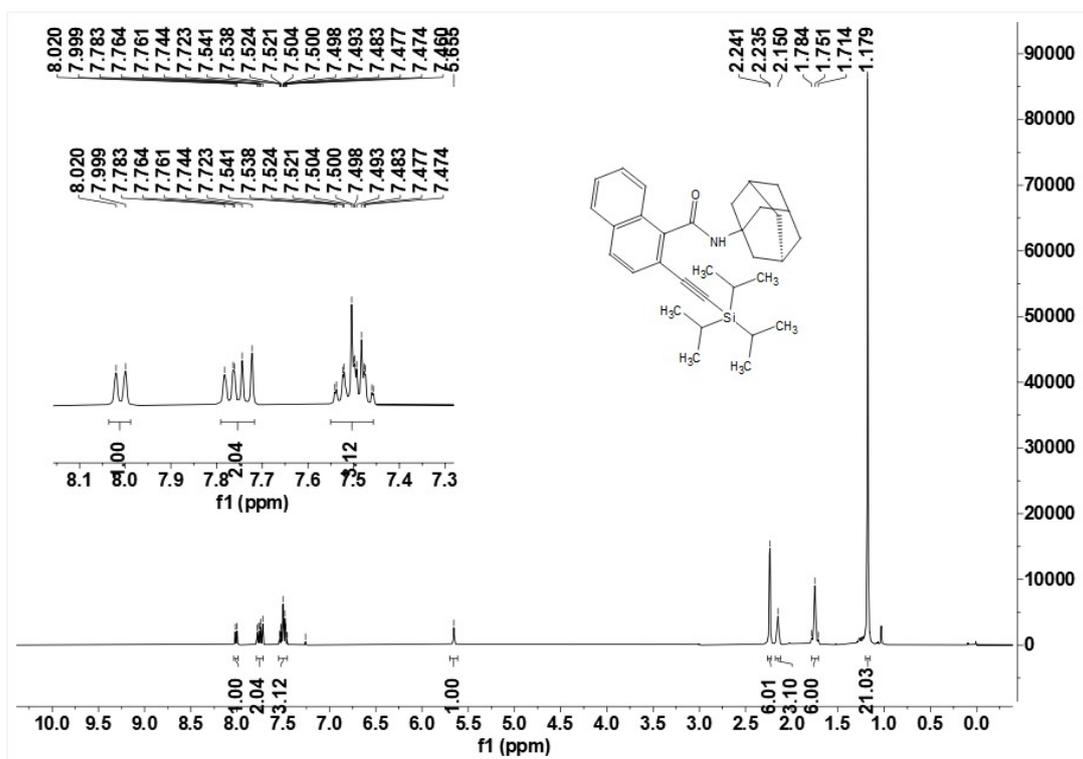


^{13}C NMR (100 MHz, CDCl₃)

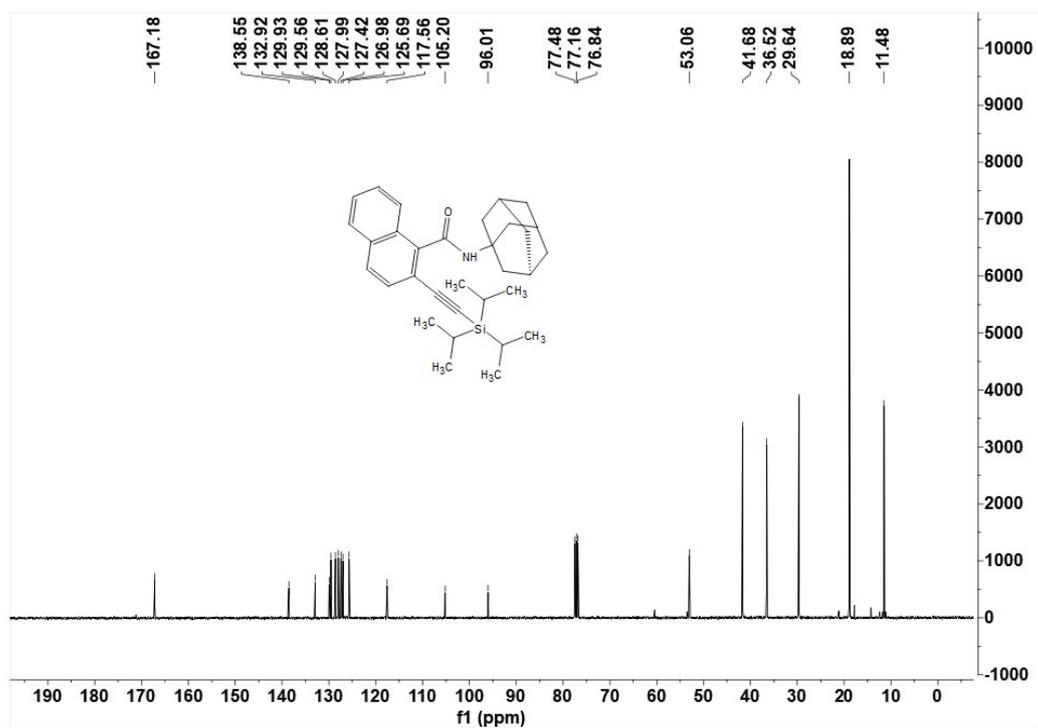


N-(Adamantan-1-yl)-2-((triisopropylsilyl)ethynyl)-1-naphthamide (3m)

¹H NMR (CDCl₃, 400 MHz)

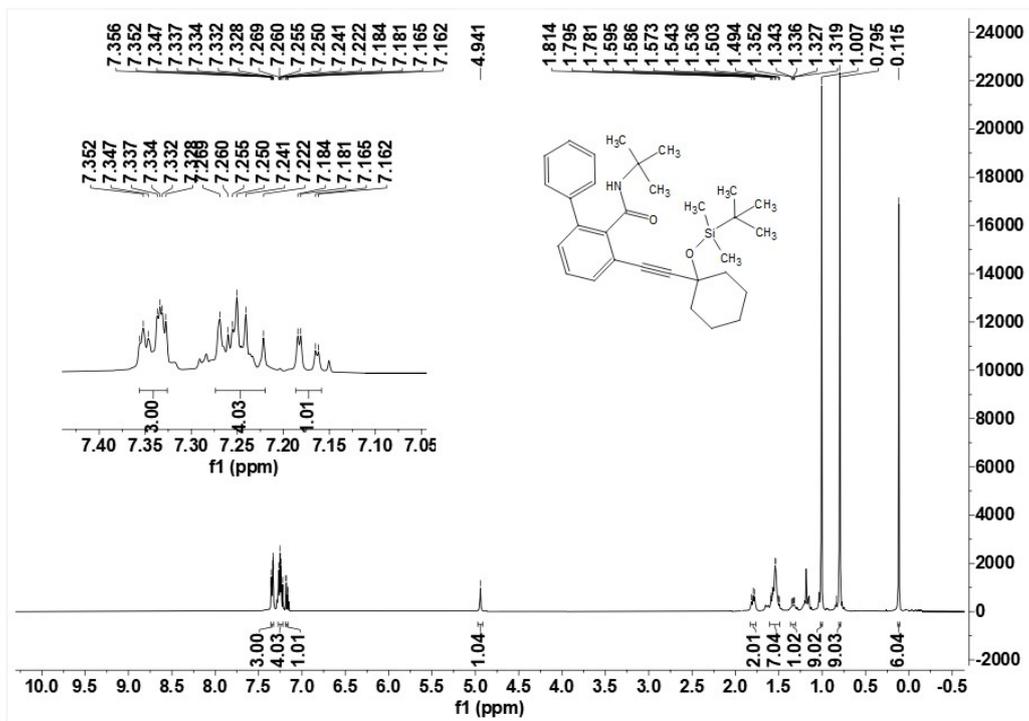


¹³C NMR (100 MHz, CDCl₃)

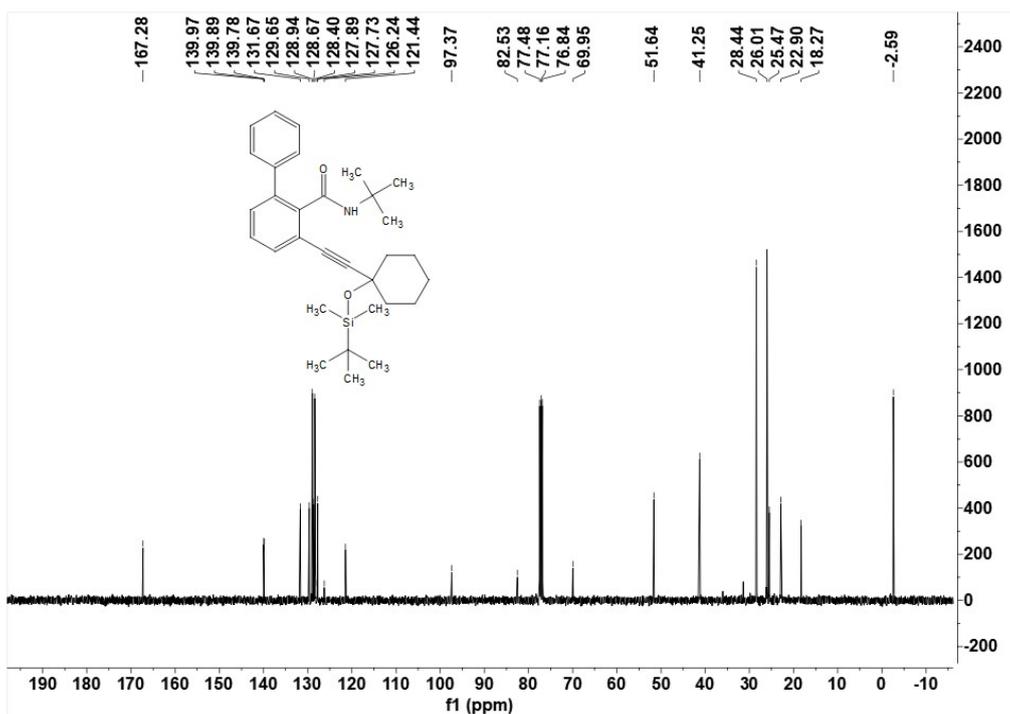


***N*-(*tert*-Butyl)-3-((1-((*tert*-butyldimethylsilyloxy)cyclohexyl)ethynyl)phenyl)-[1,1'-biphenyl]-2-carboxamide (3n)**

¹H NMR (CDCl₃, 400 MHz)

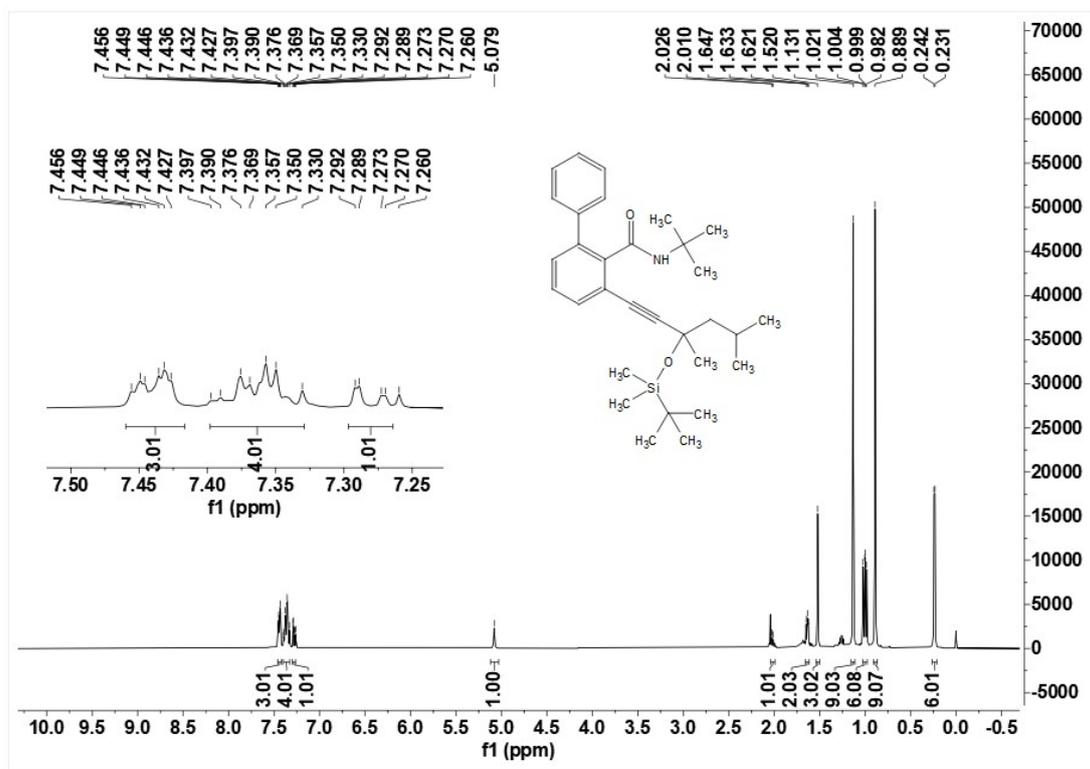


¹³C NMR (100 MHz, CDCl₃)

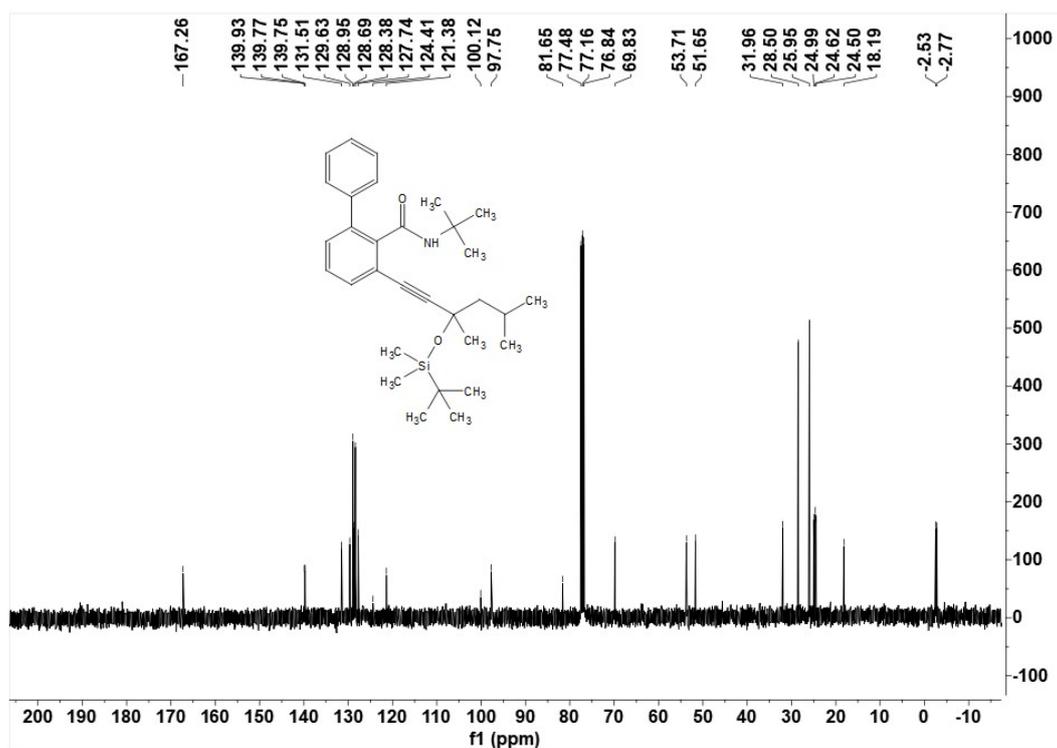


***N*-(*tert*-Butyl)-3-(3-((*tert*-butyldimethylsilyloxy)-3,5-dimethylhex-1-yn-1-yl)-[1,1'-biphenyl]-2-carboxamide (3o)**

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

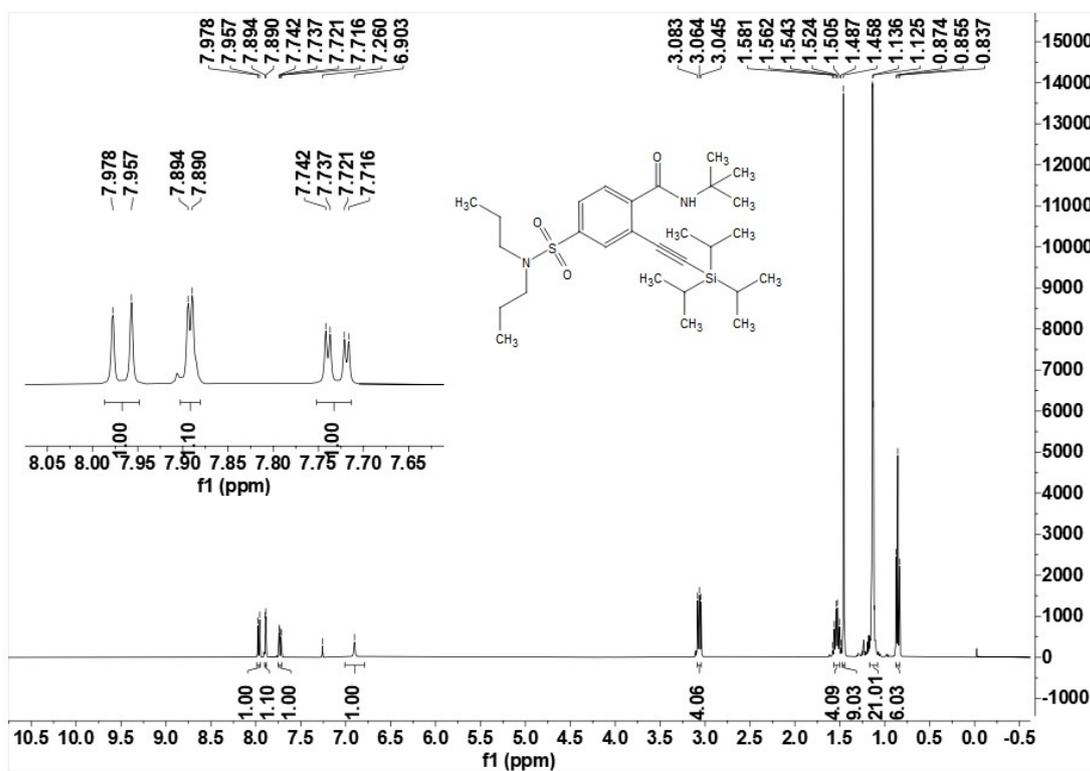


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

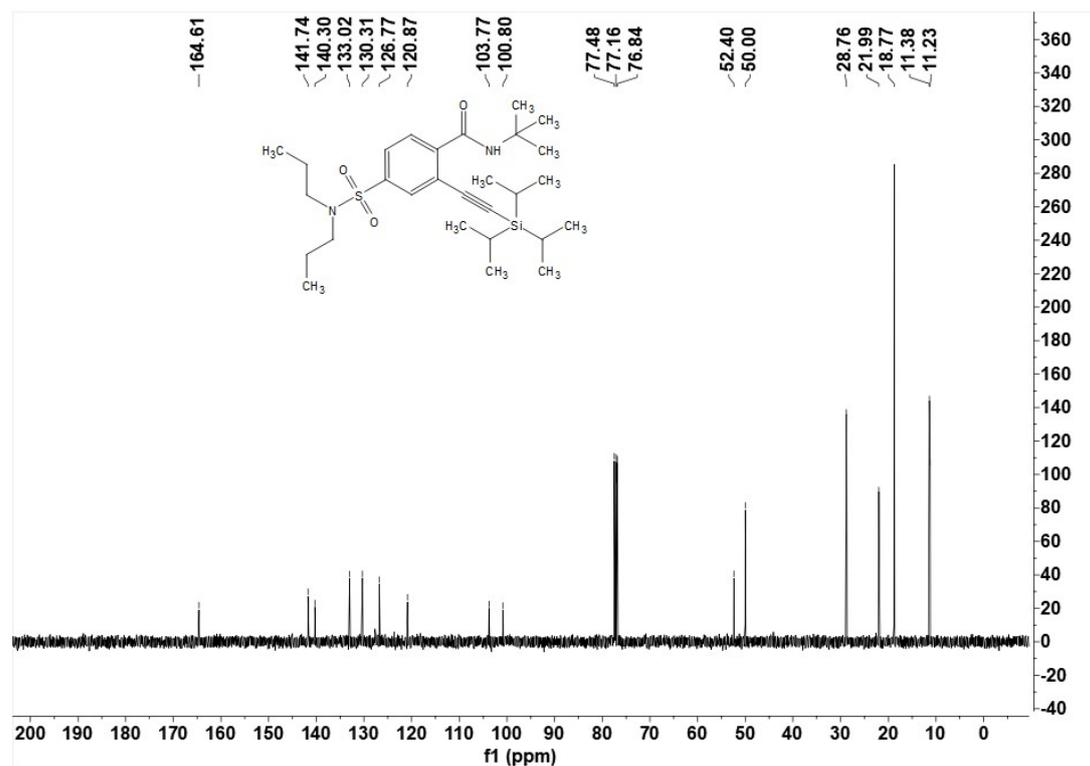


N-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)benzamide (3p)

¹H NMR (CDCl₃, 400 MHz)

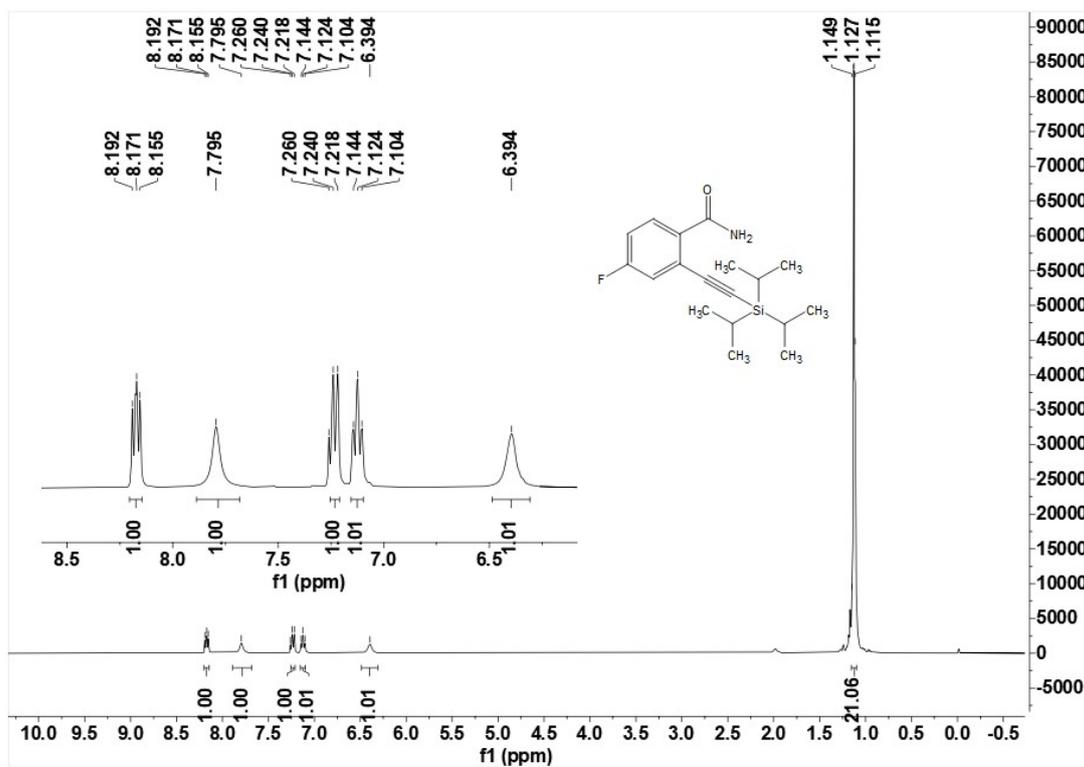


¹³C NMR (100 MHz, CDCl₃)

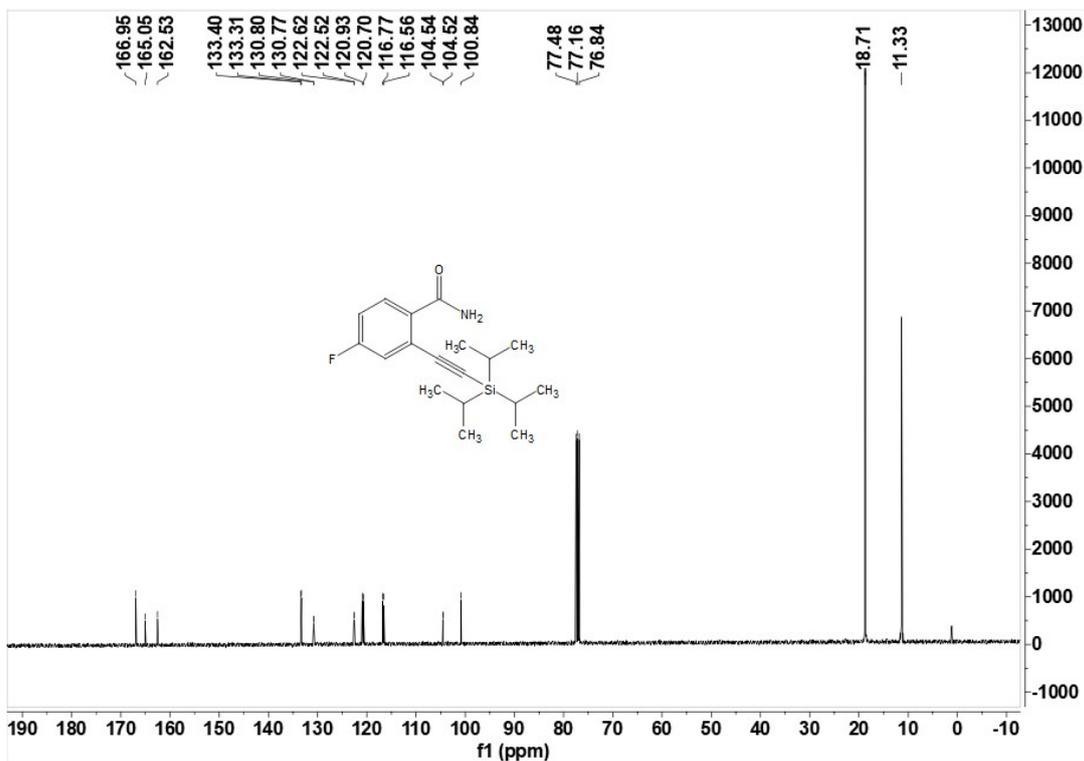


4-Fluoro-2-((triisopropylsilyl)ethynyl)benzamide (3q)

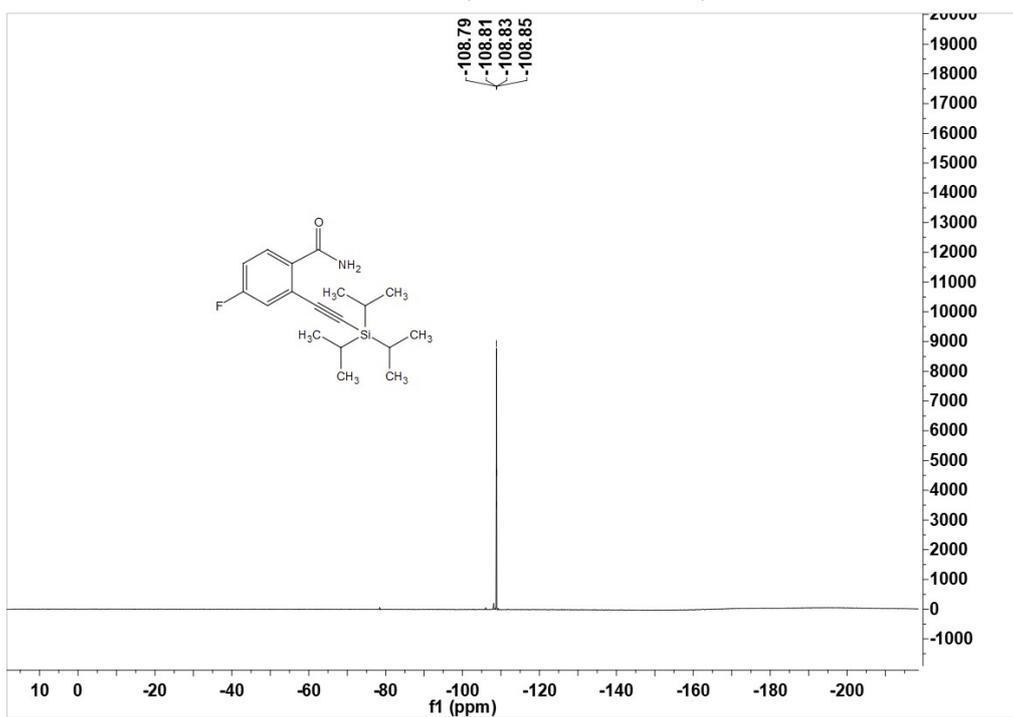
$^1\text{H NMR}$ (CDCl_3 , 400 MHz)



$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

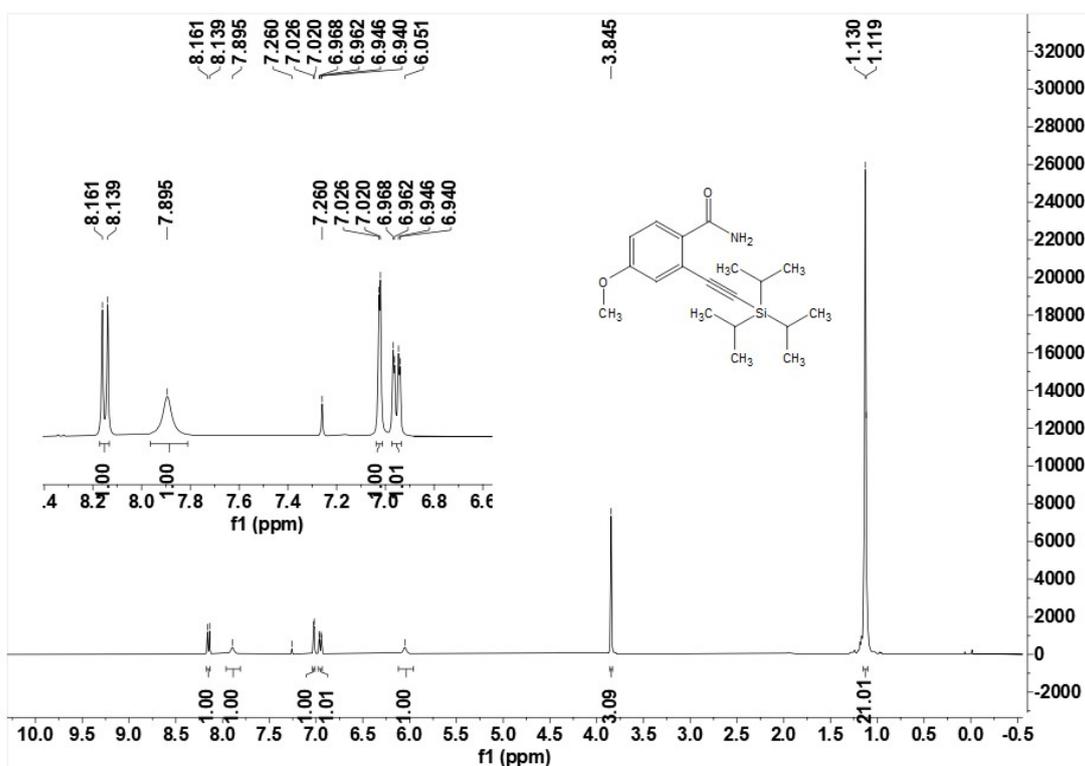


^{19}F NMR (376 MHz, CDCl_3)

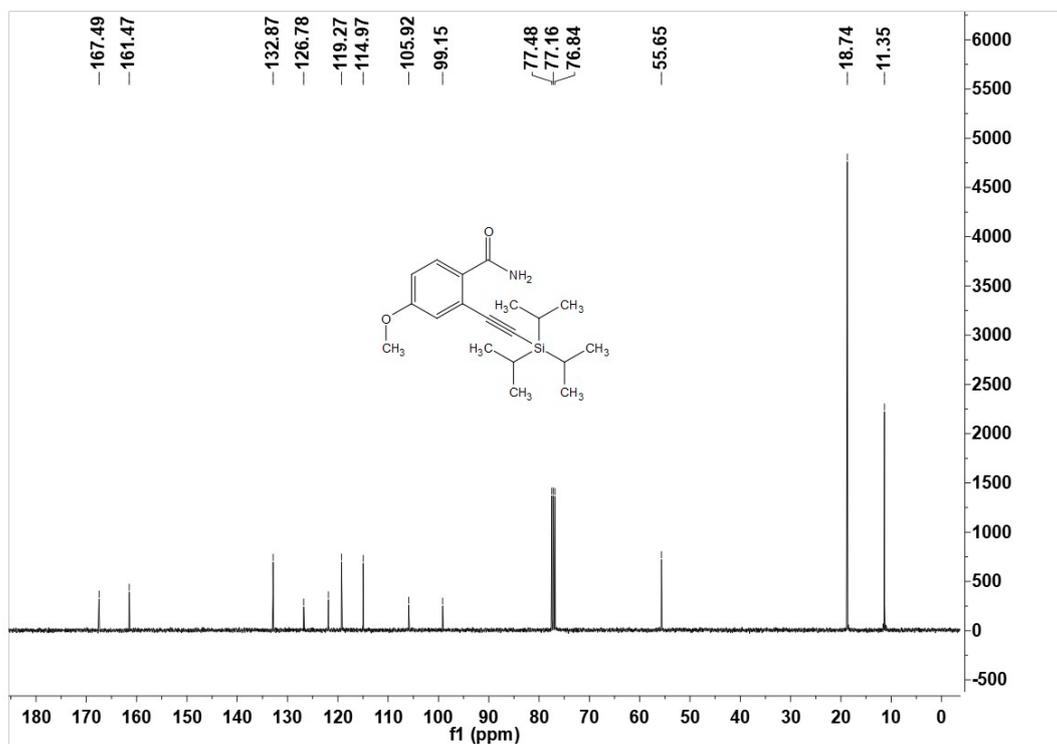


4-Methoxy-2-((triisopropylsilyl)ethynyl)benzamide (3r)

¹H NMR (CDCl₃, 400 MHz)

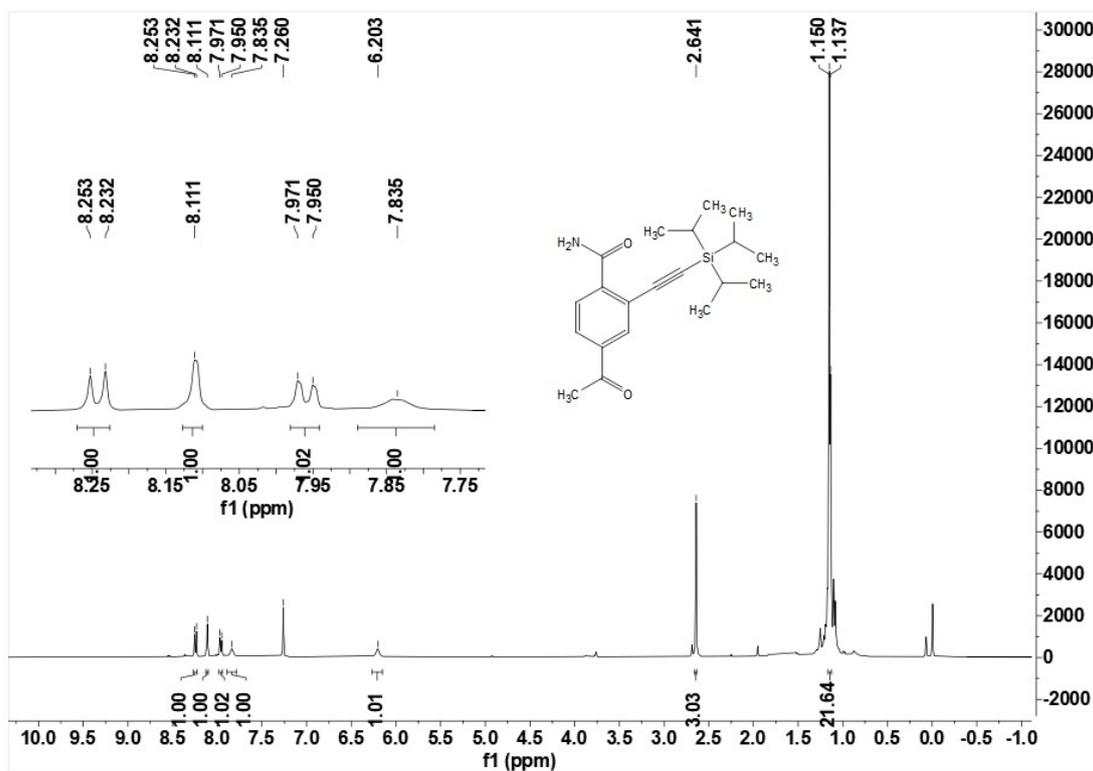


¹³C NMR (100 MHz, CDCl₃)

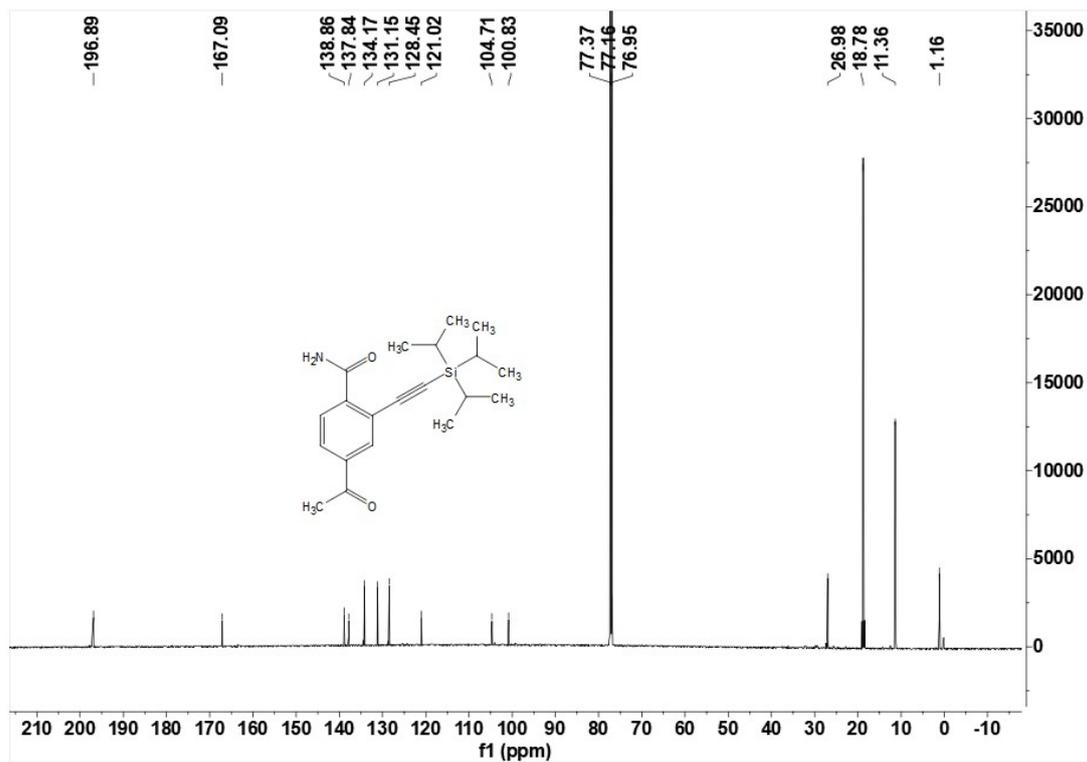


4-Acetyl-2-((triisopropylsilyl)ethynyl)benzamide (3s)

¹H NMR (CDCl₃, 400 MHz)

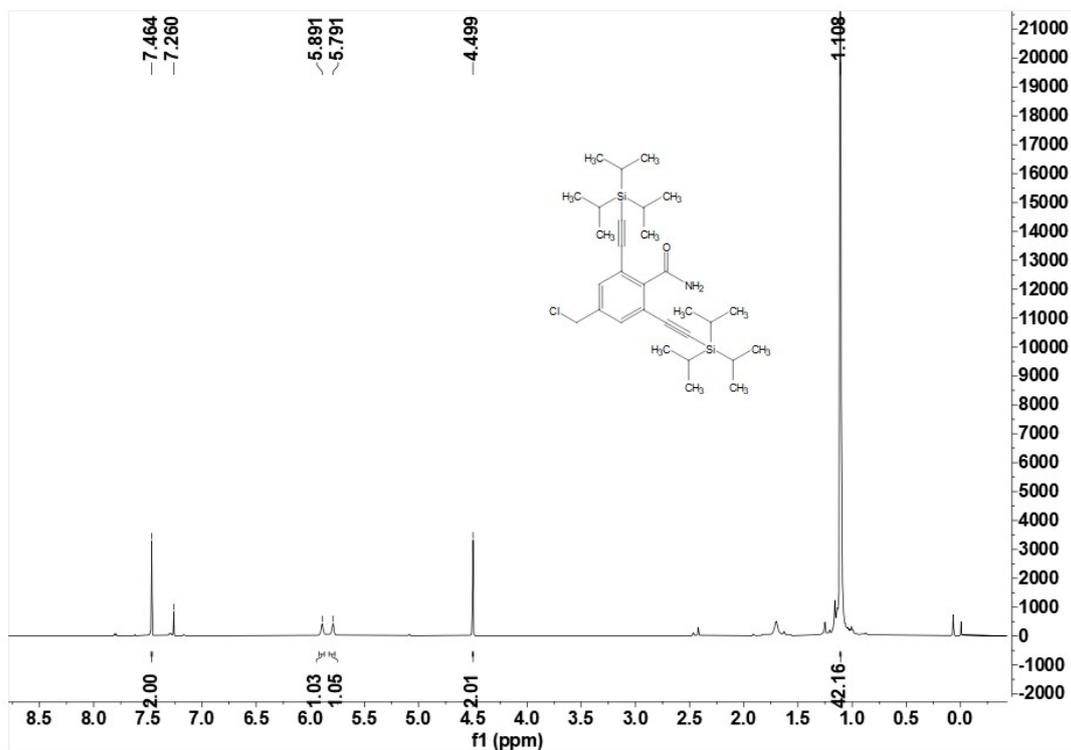


¹³C NMR (100 MHz, CDCl₃)

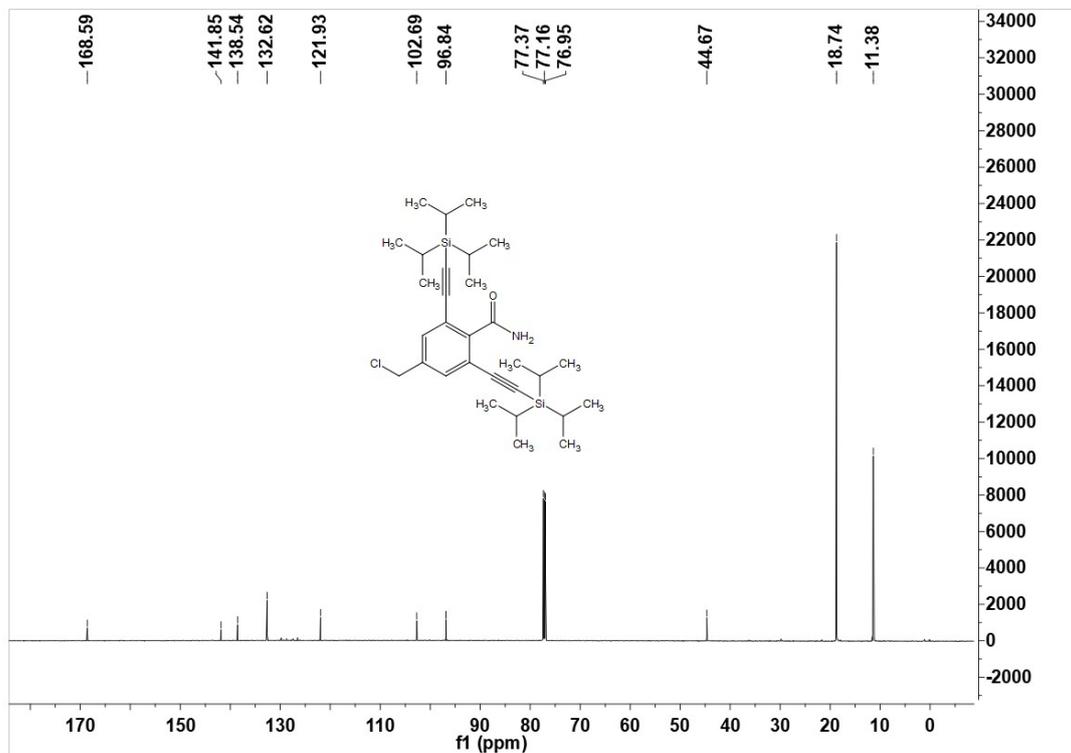


4-(Chloromethyl)-2, 6-bis((triisopropylsilyl)ethynyl)benzamide (3t)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

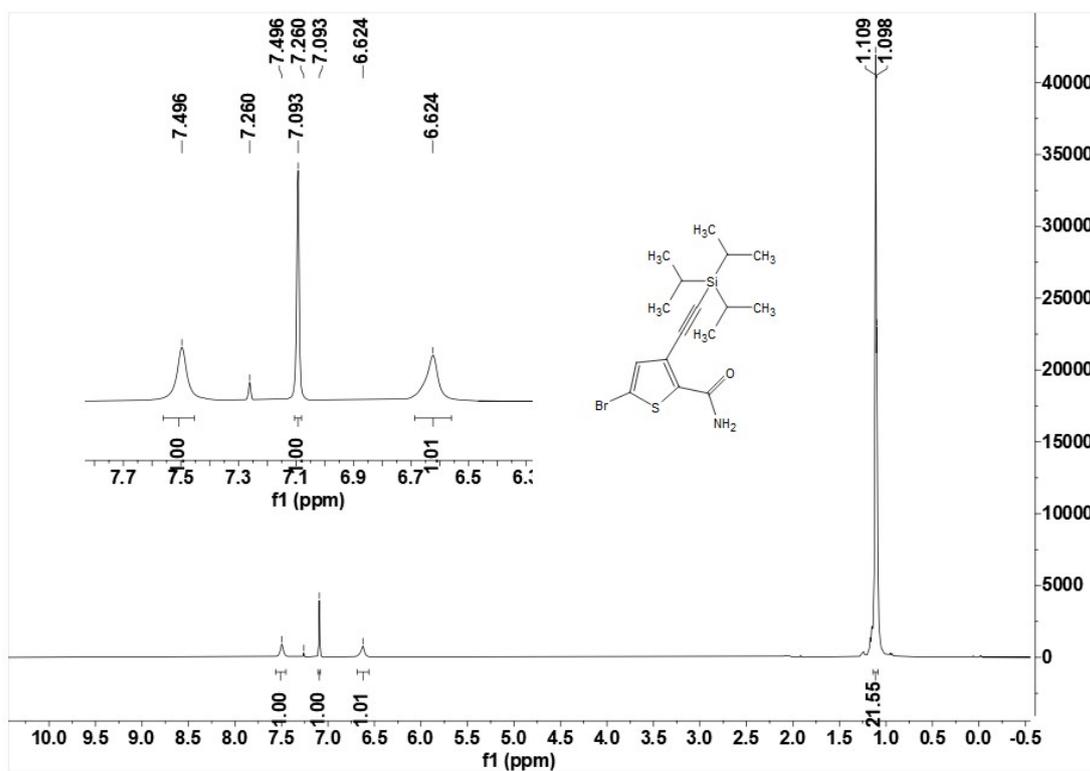


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

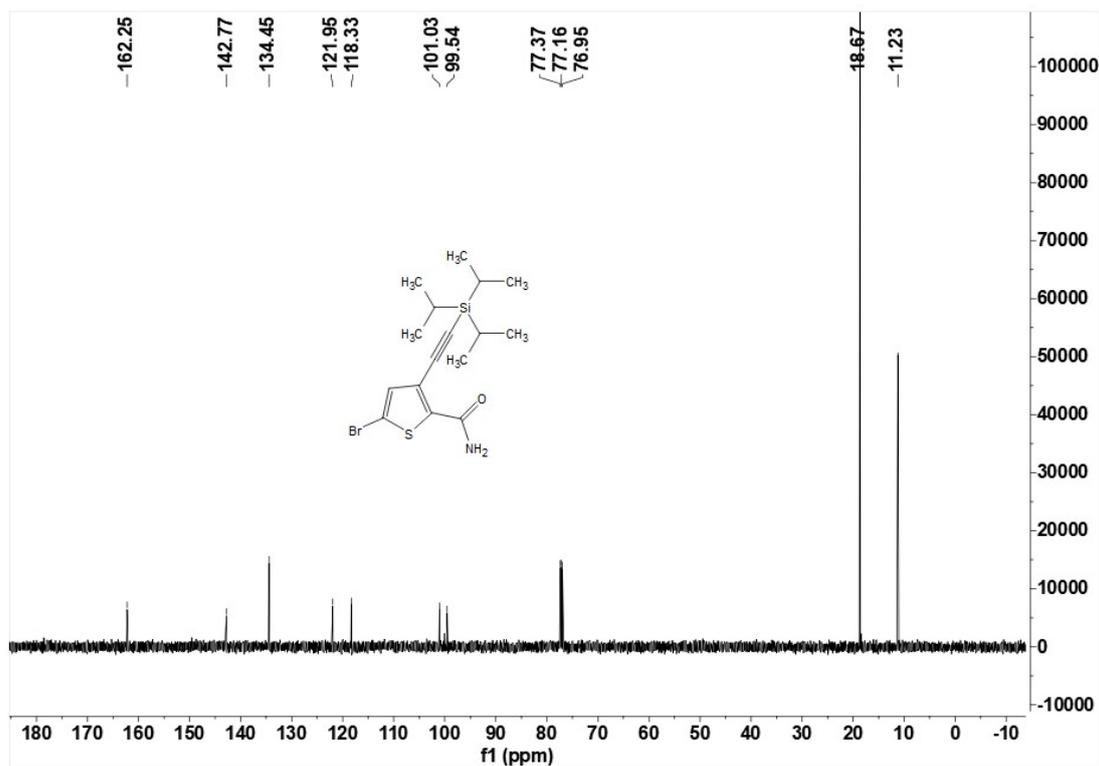


5-Bromo-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide (3u)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

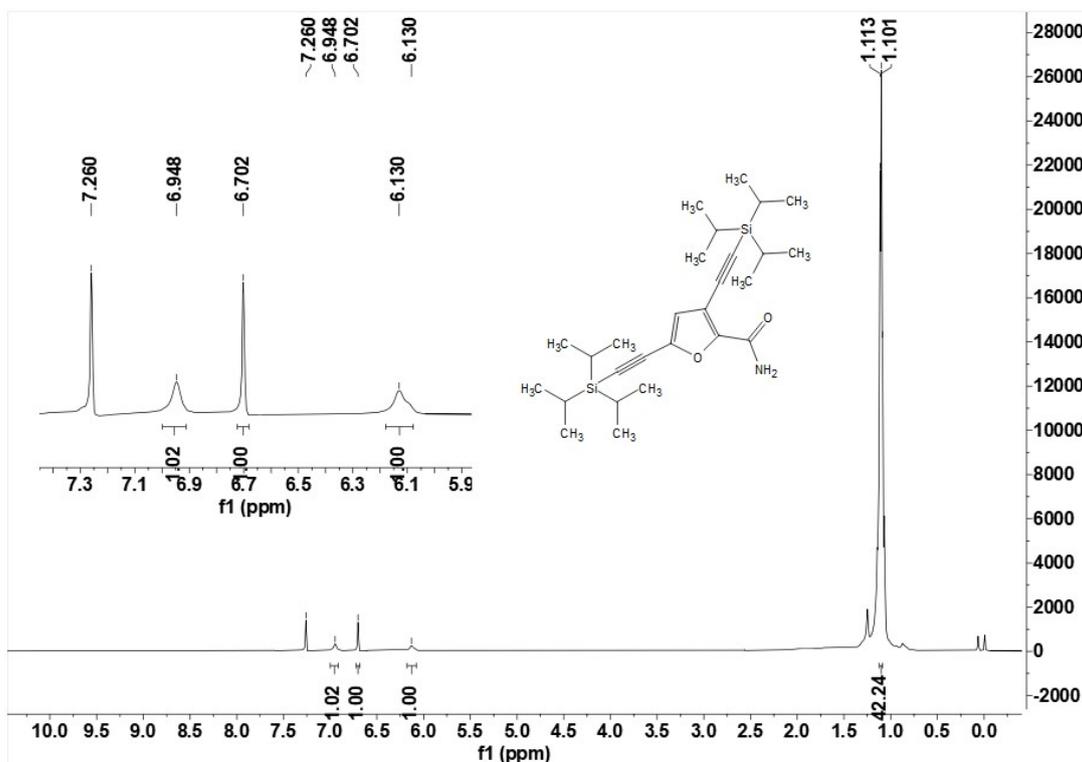


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

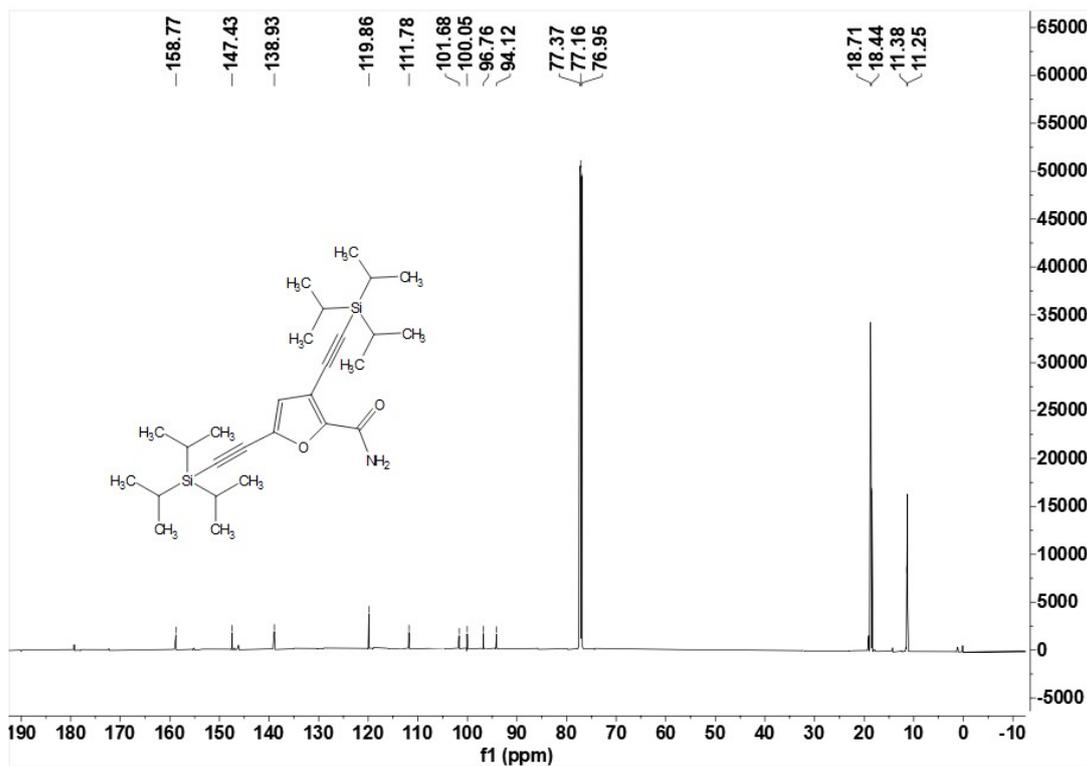


3,5-Bis((triisopropylsilyl)ethynyl)furan-2-carboxamide (3v)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

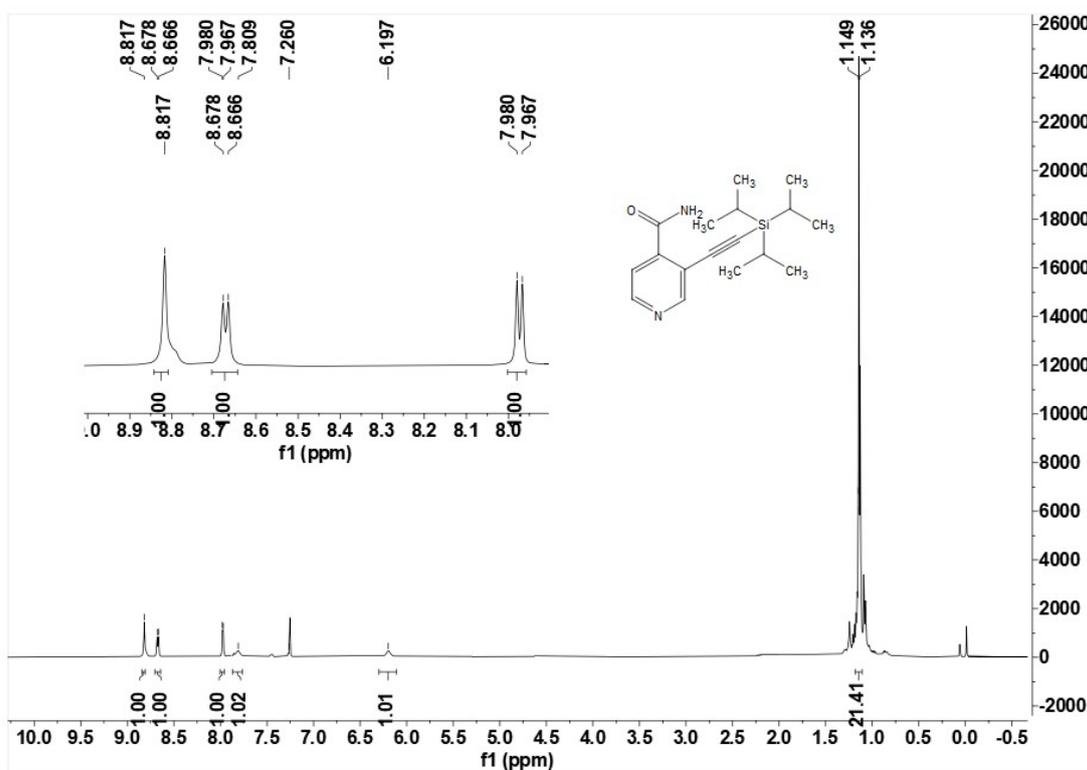


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

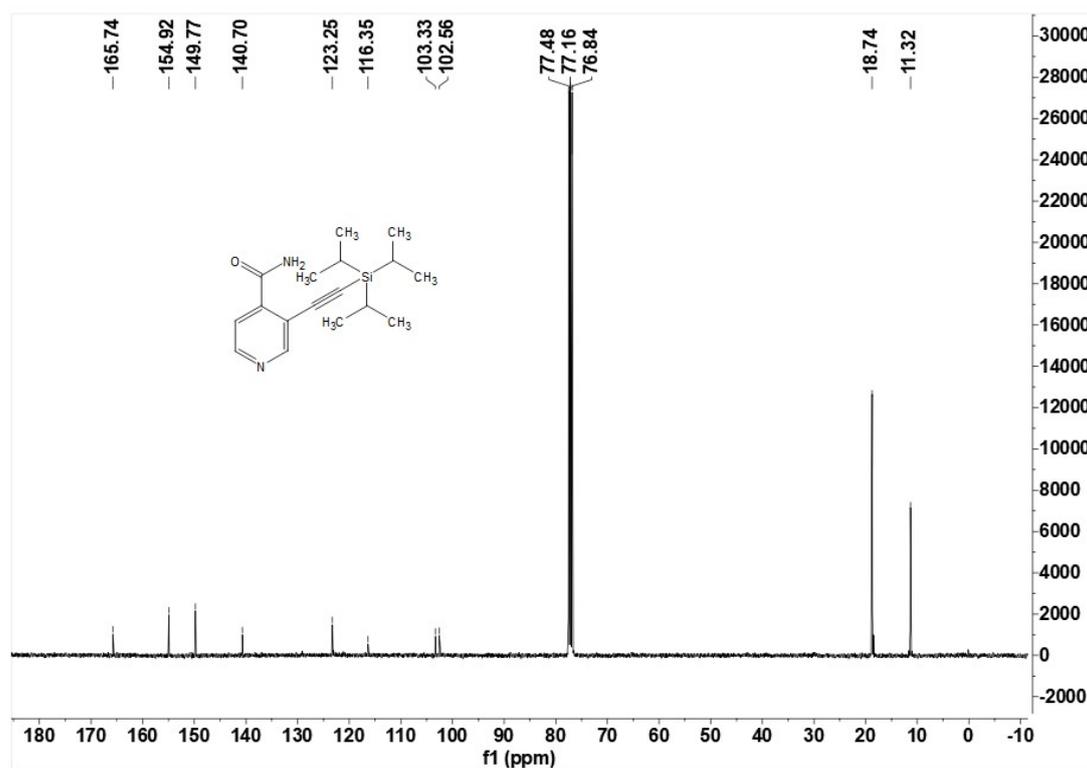


3-((Triisopropylsilyl)ethynyl)isonicotinamide (3w)

¹H NMR (CDCl₃, 400 MHz)

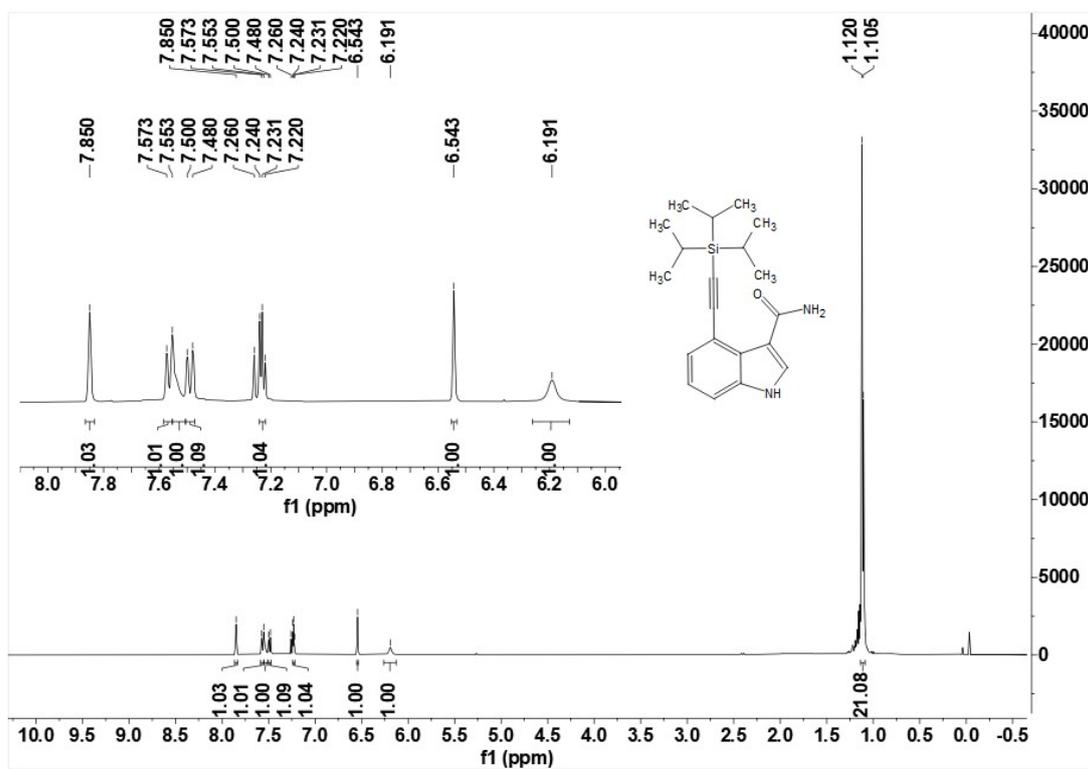


¹³C NMR (100 MHz, CDCl₃)

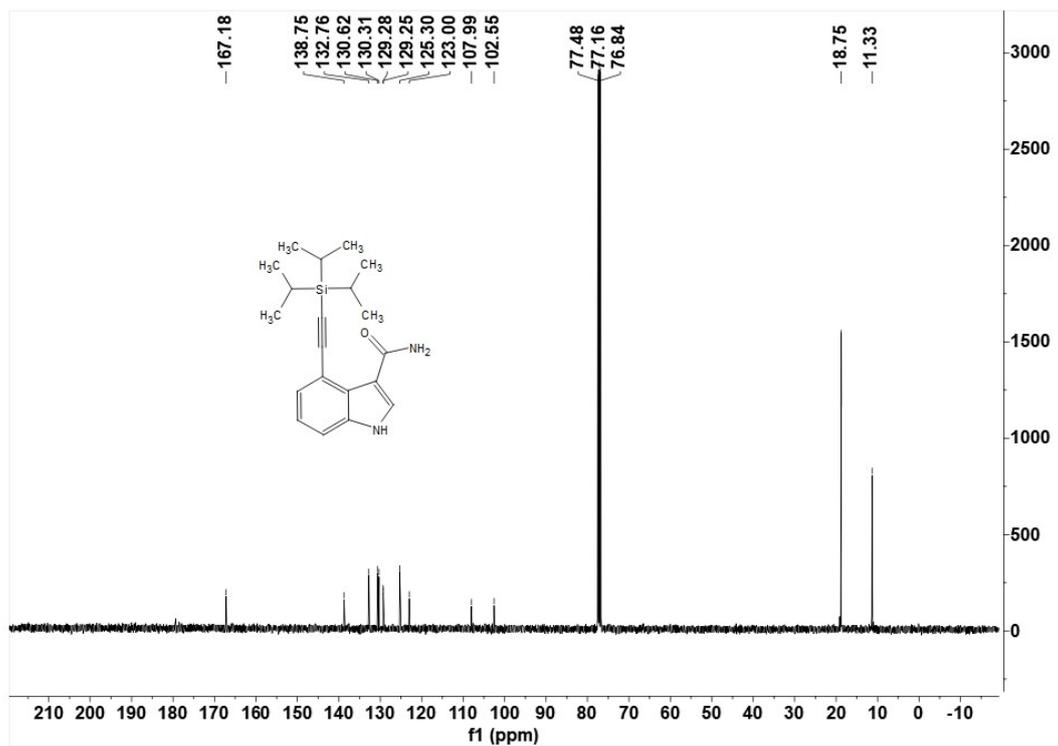


4-((Triisopropylsilyl)ethynyl)-1H-indole-3-carboxamide (3x)

^1H NMR (CDCl_3 , 400 MHz)

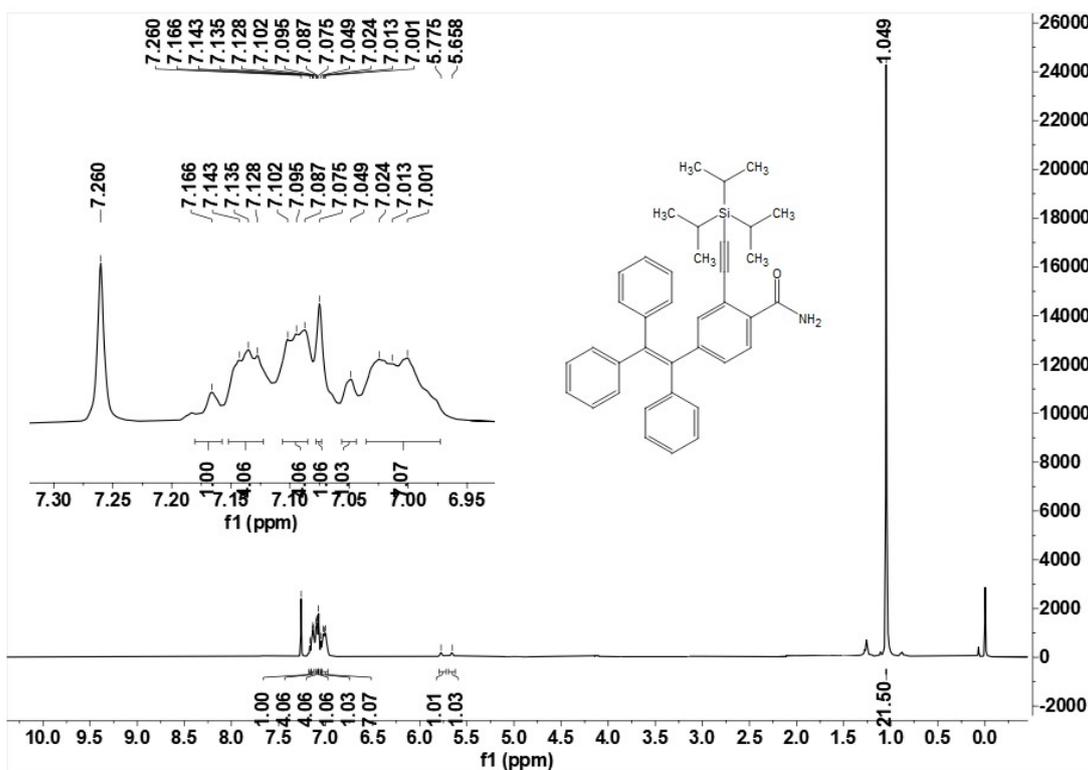


^{13}C NMR (100 MHz, CDCl_3)

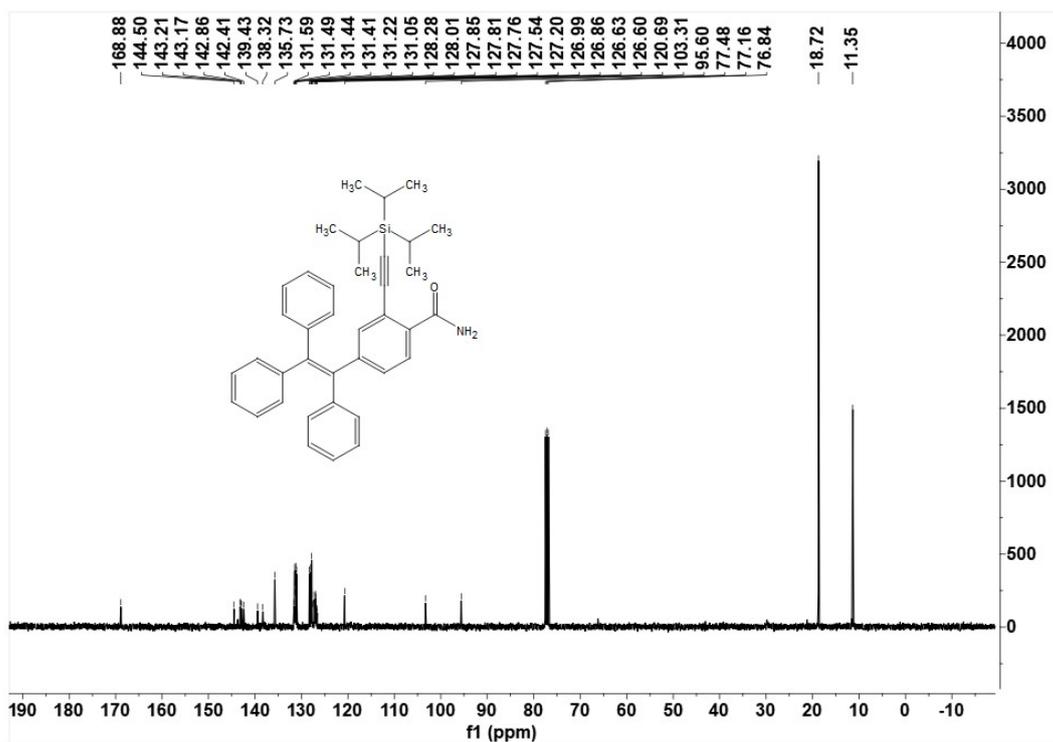


2-((Triisopropylsilyl)ethynyl)-4-(1,2,2-triphenylvinyl)benzamide (3y)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

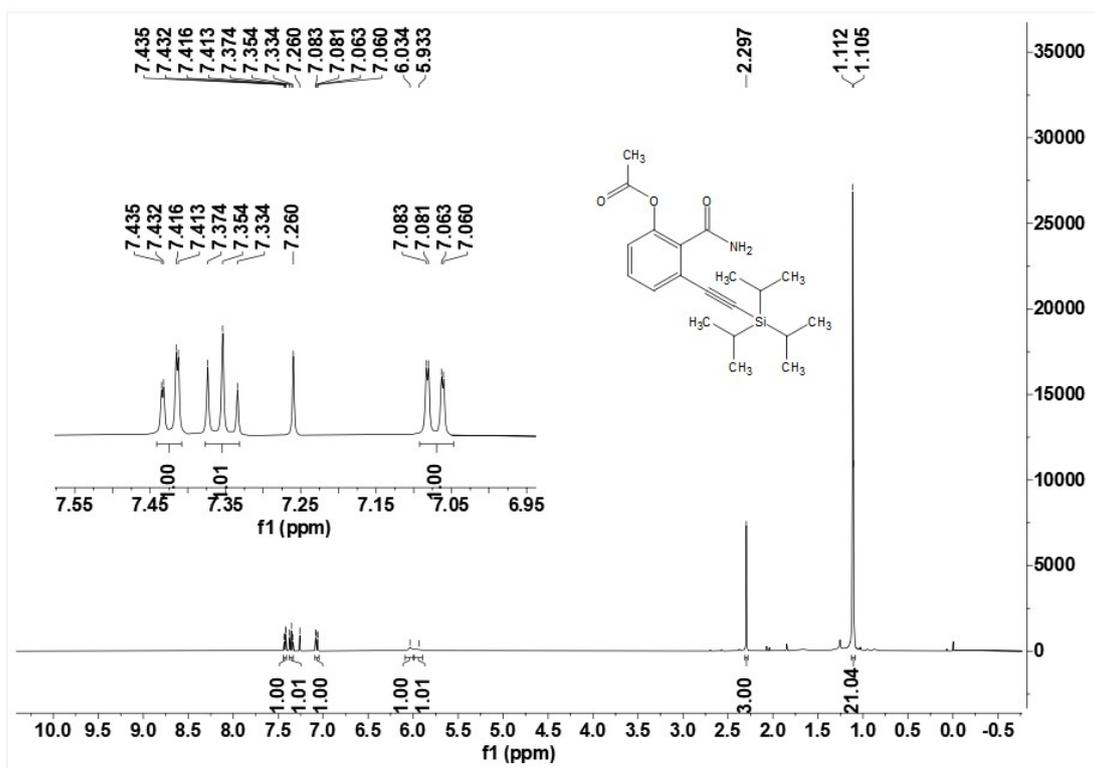


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

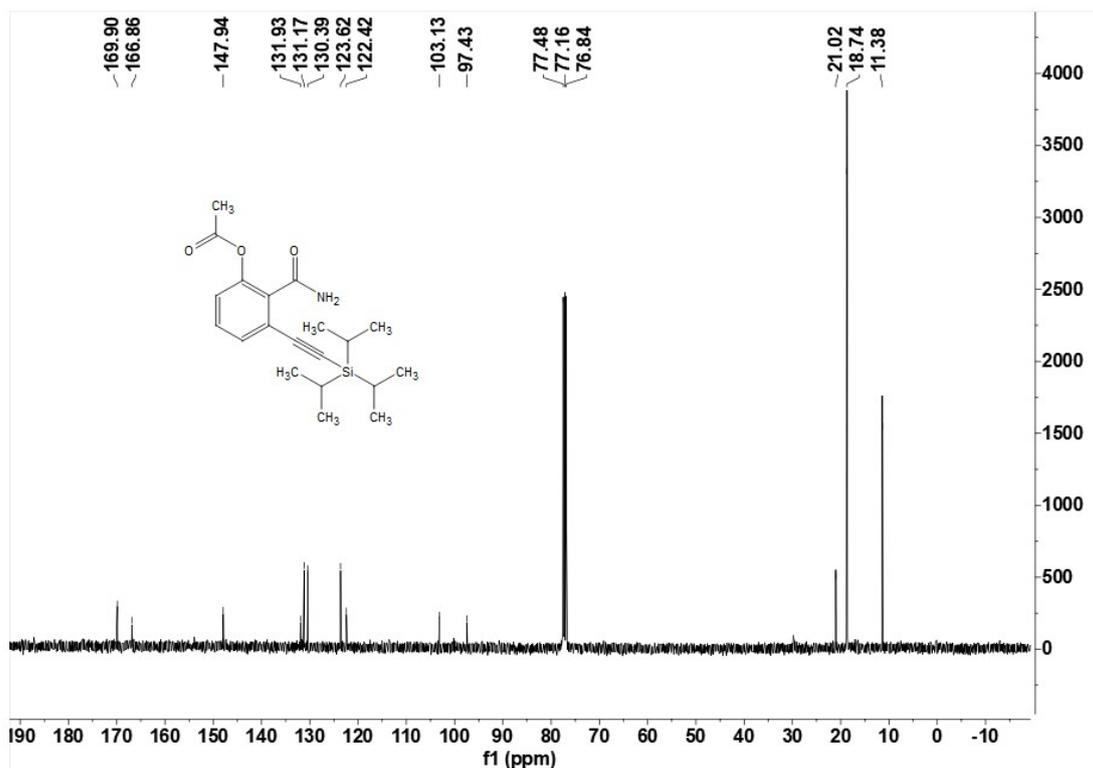


2-Carbamoyl-3-((triisopropylsilyl)ethynyl)phenyl acetate (3z)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

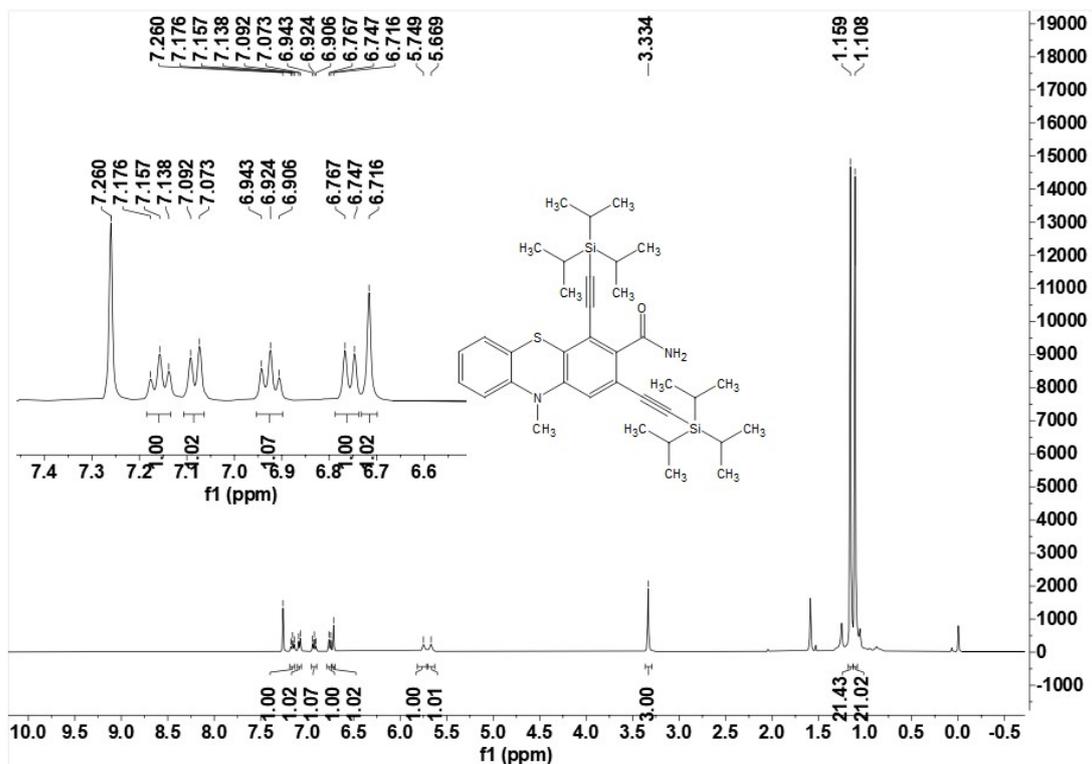


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

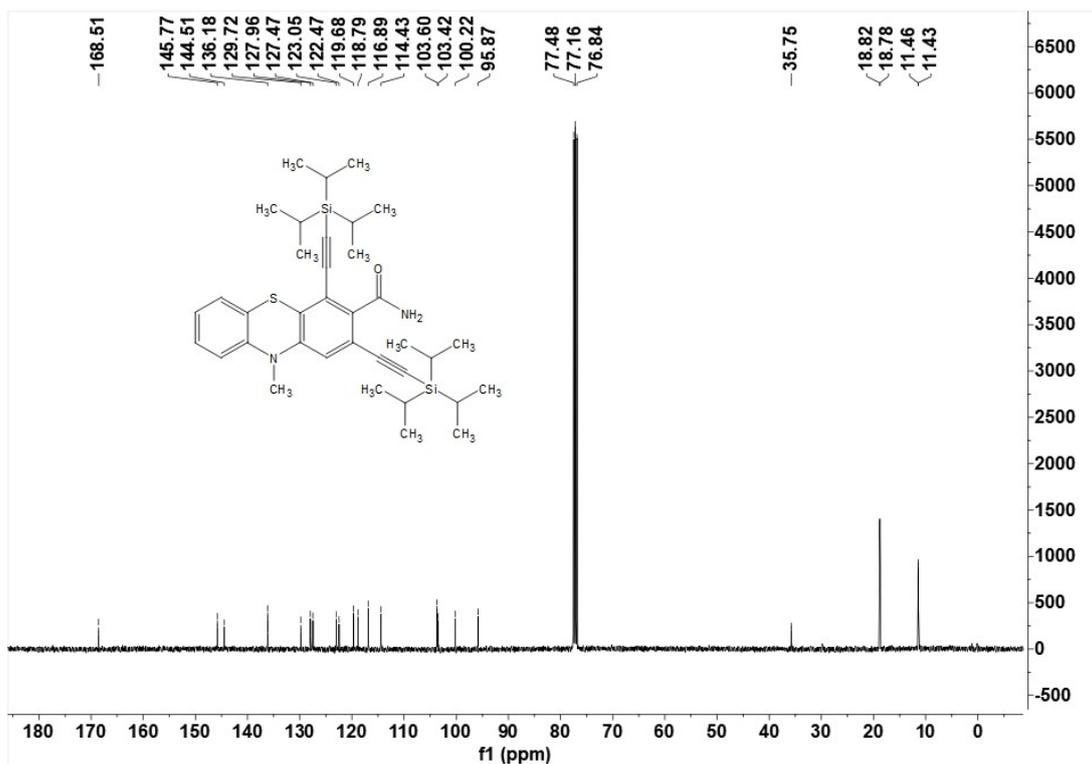


10-Methyl-2,4-bis((triisopropylsilyl)ethynyl)-10H-phenothiazine-3-carboxamide (3za)

^1H NMR (CDCl_3 , 400 MHz)



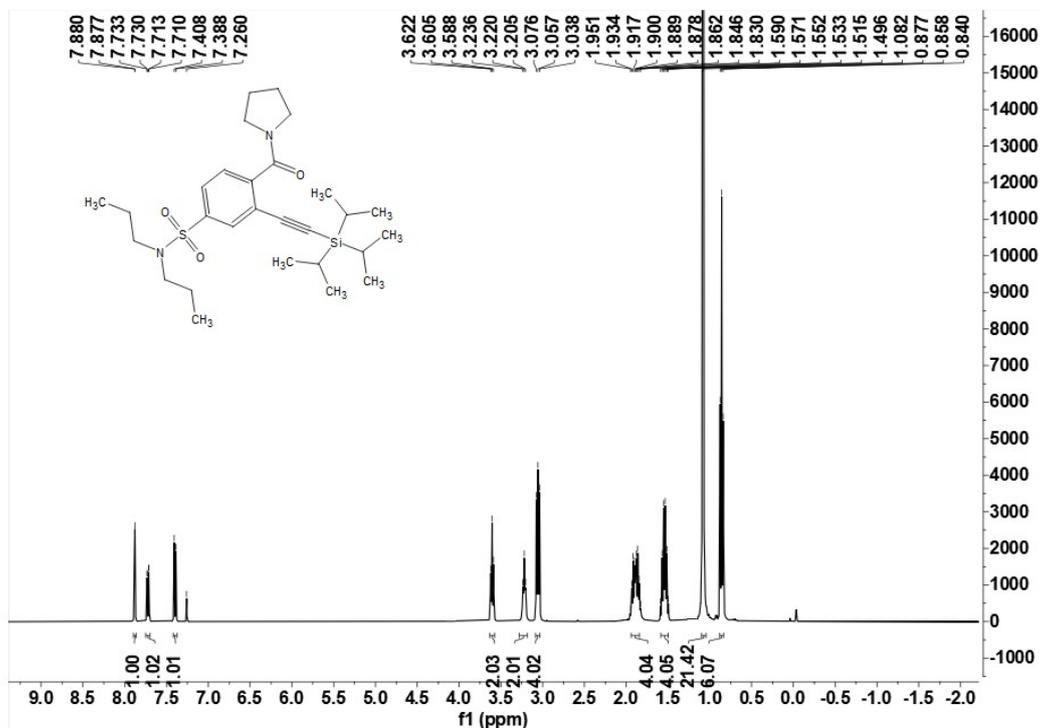
^{13}C NMR (100 MHz, CDCl_3)



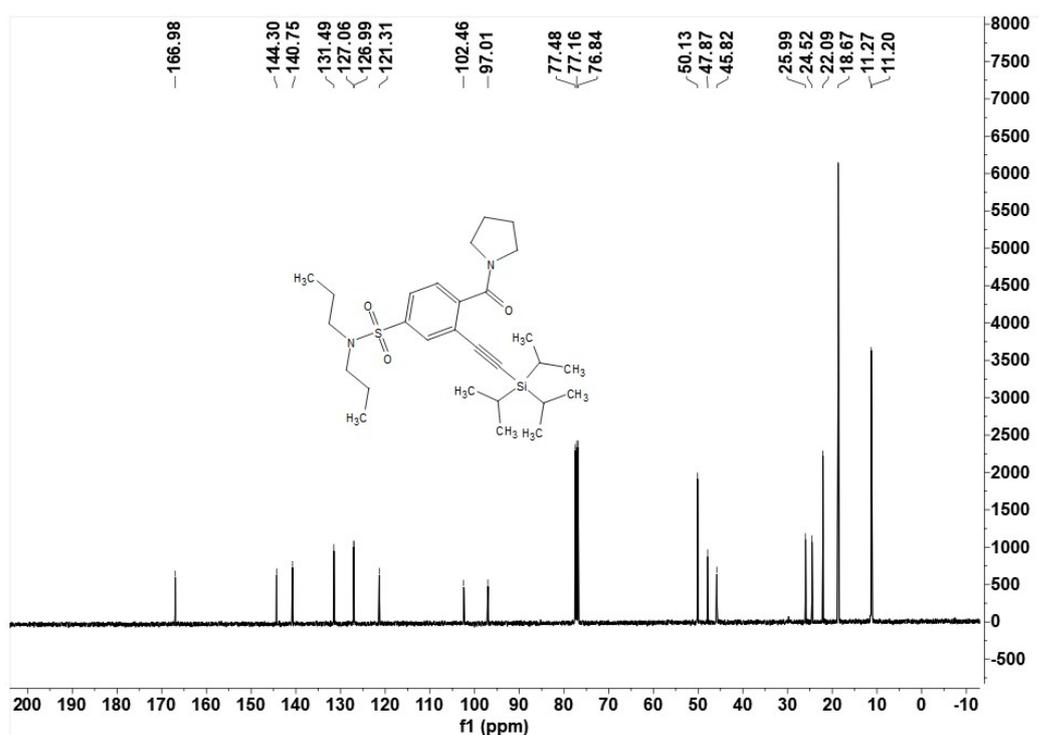
N,N-Dipropyl-4-(pyrrolidine-1-carbonyl)-3-((triisopropylsilyl)ethynyl)benzene

Sulfonamide (3zb)

¹H NMR (CDCl₃, 400 MHz)

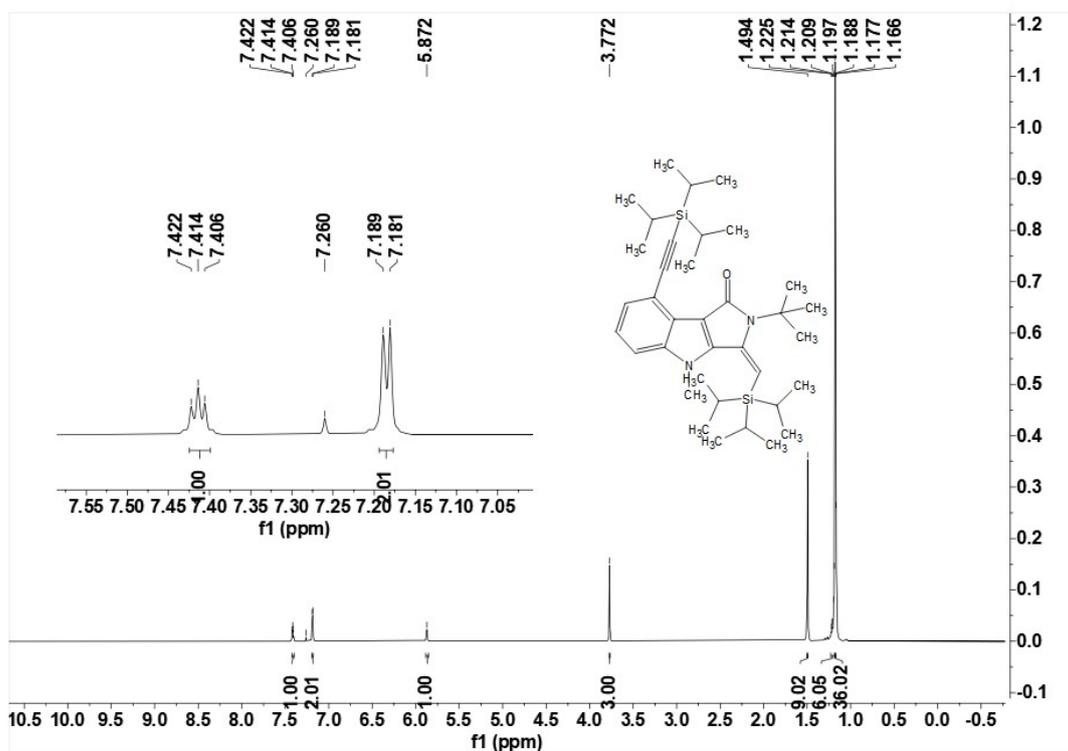


¹³C NMR (100 MHz, CDCl₃)

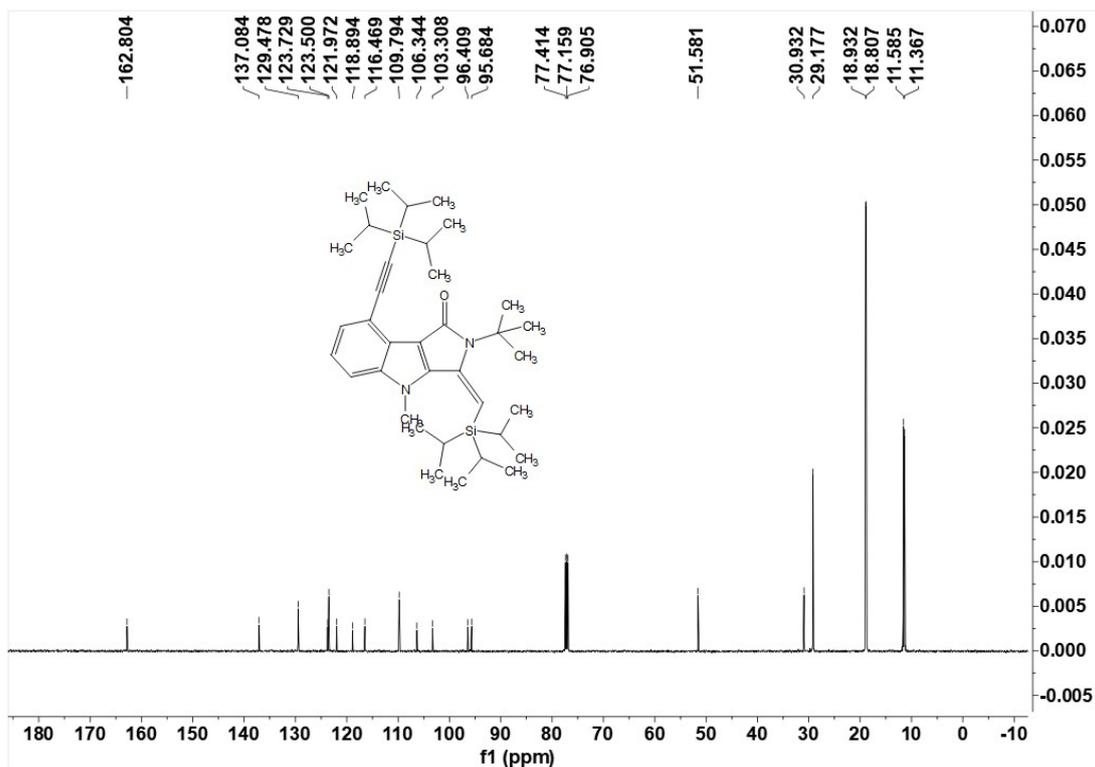


2-(*tert*-Butyl)-4-methyl-8-((triisopropylsilyl)ethynyl)-3-
((triisopropylsilyl)methylene)-3,4-dihydropyrrolo[3,4-*b*]indol-1(2H)-one (3zd)

^1H NMR (CDCl_3 , 500 MHz)

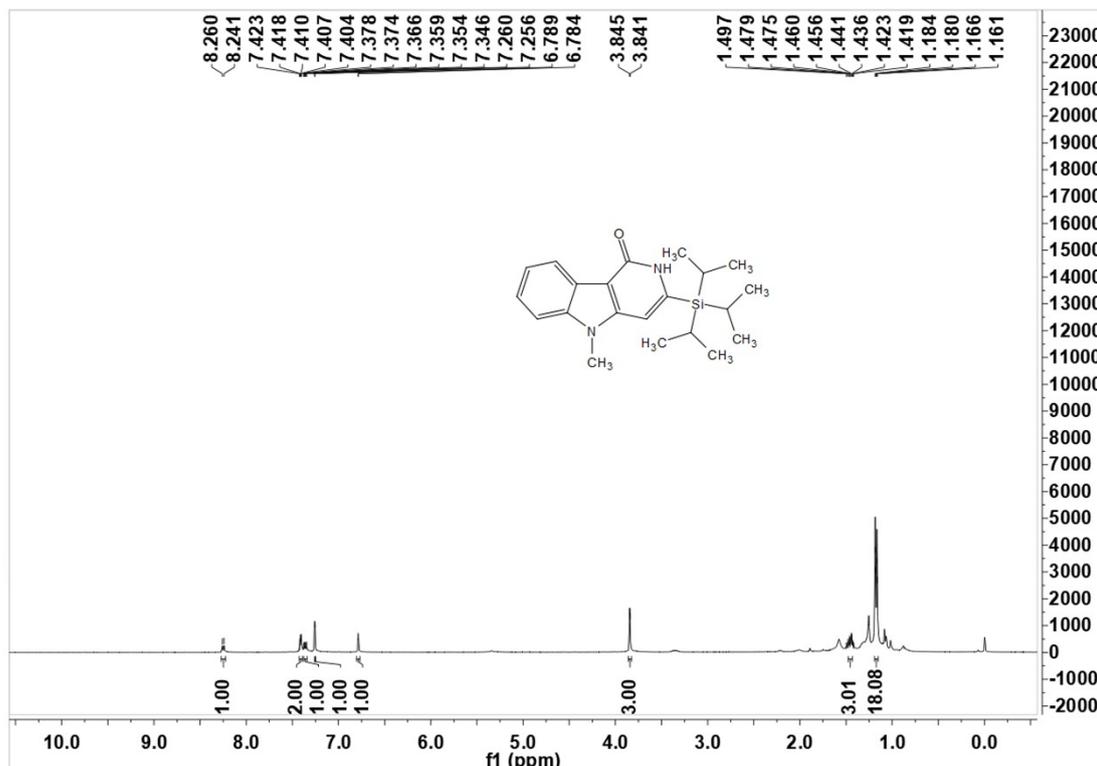


^{13}C NMR (126 MHz, CDCl_3)

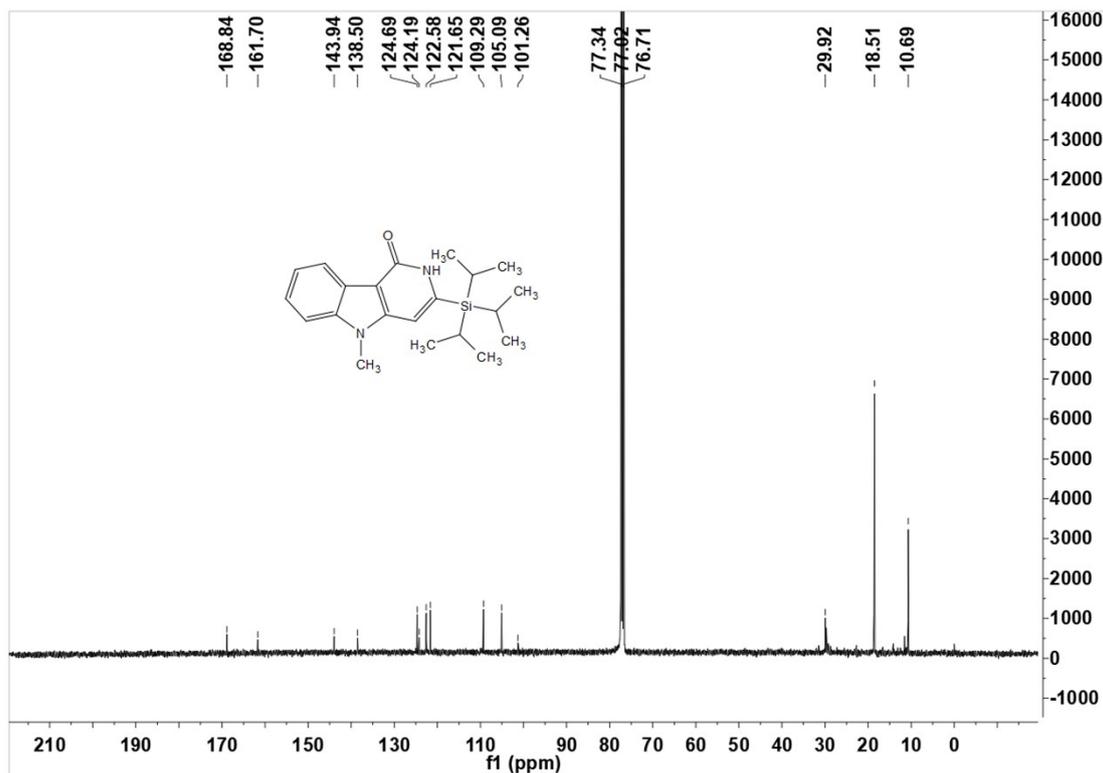


5-Methyl-3-(triisopropylsilyl)-2,5-dihydro-1H-pyrido[4,3-b]indol-1-one (3ze)

¹H NMR (CDCl₃, 400 MHz)

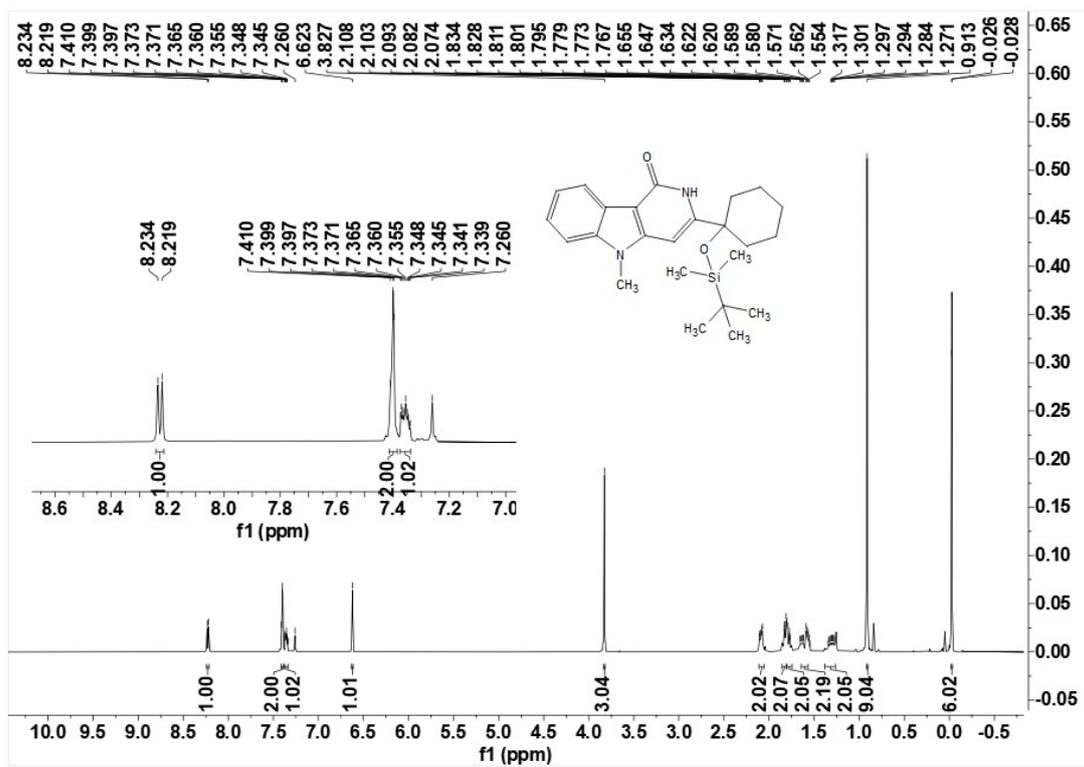


¹³C NMR (100 MHz, CDCl₃)

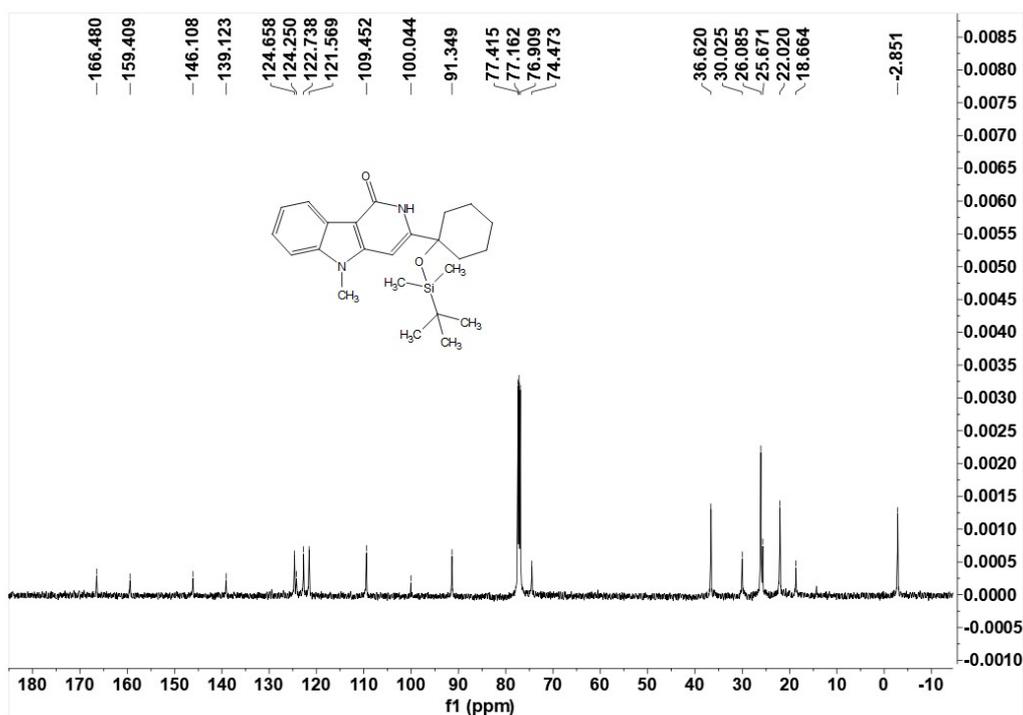


3-(1-((*tert*-Butyldimethylsilyl)oxy)cyclohexyl)-5-methyl-2,5-dihydro-1H-pyrido[4,3-b]indol-1-one (4t)

¹H NMR (500 MHz, CDCl₃)

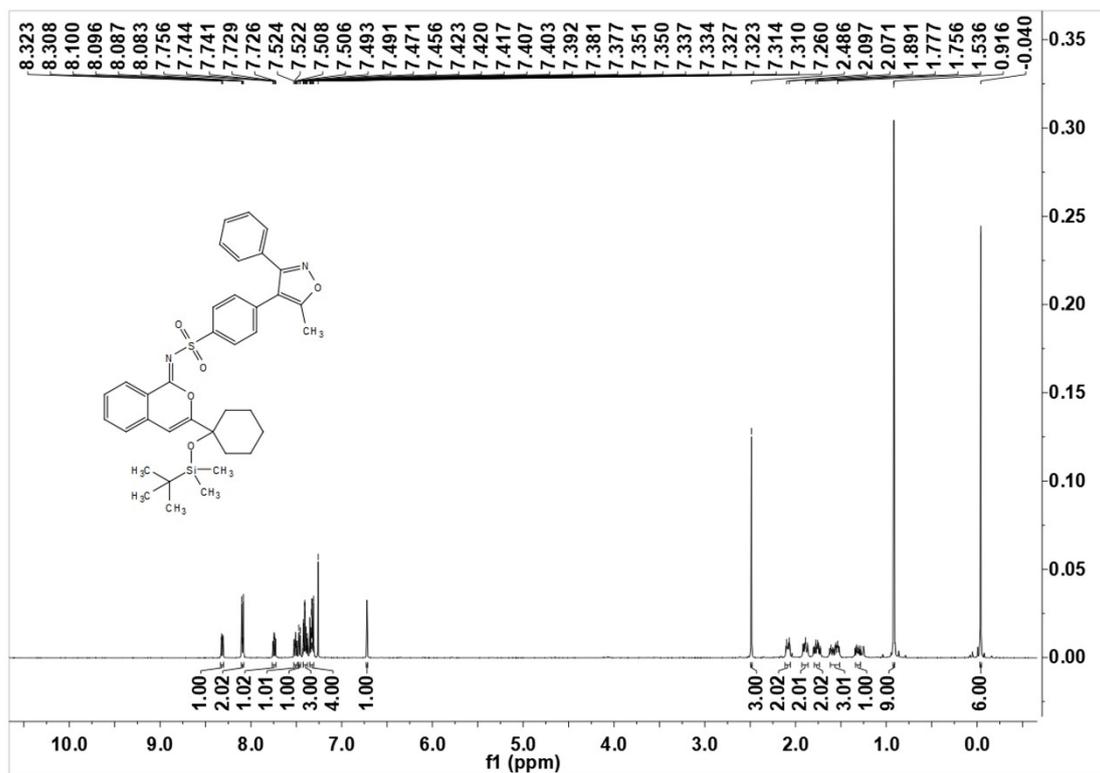


¹³C NMR (126 MHz, CDCl₃)

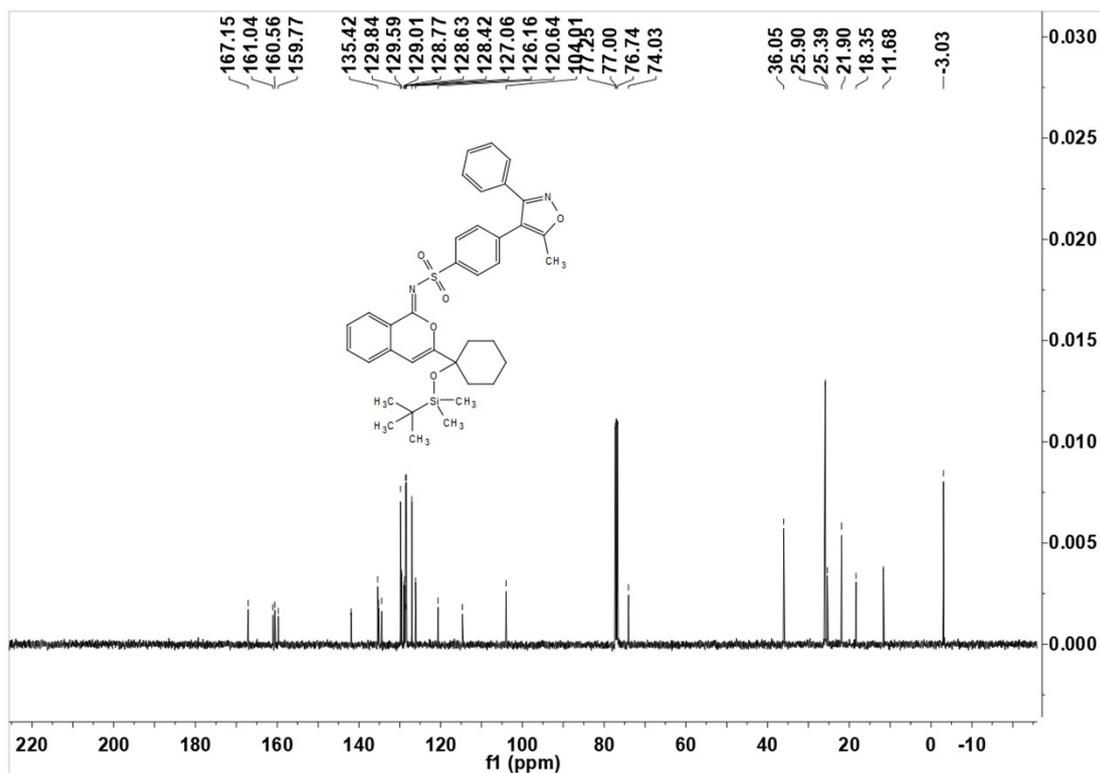


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyloxy)cyclohexyl)-1*H*-isochromen-1-ylidene)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide (4u)

¹H NMR (400 MHz, CDCl₃)

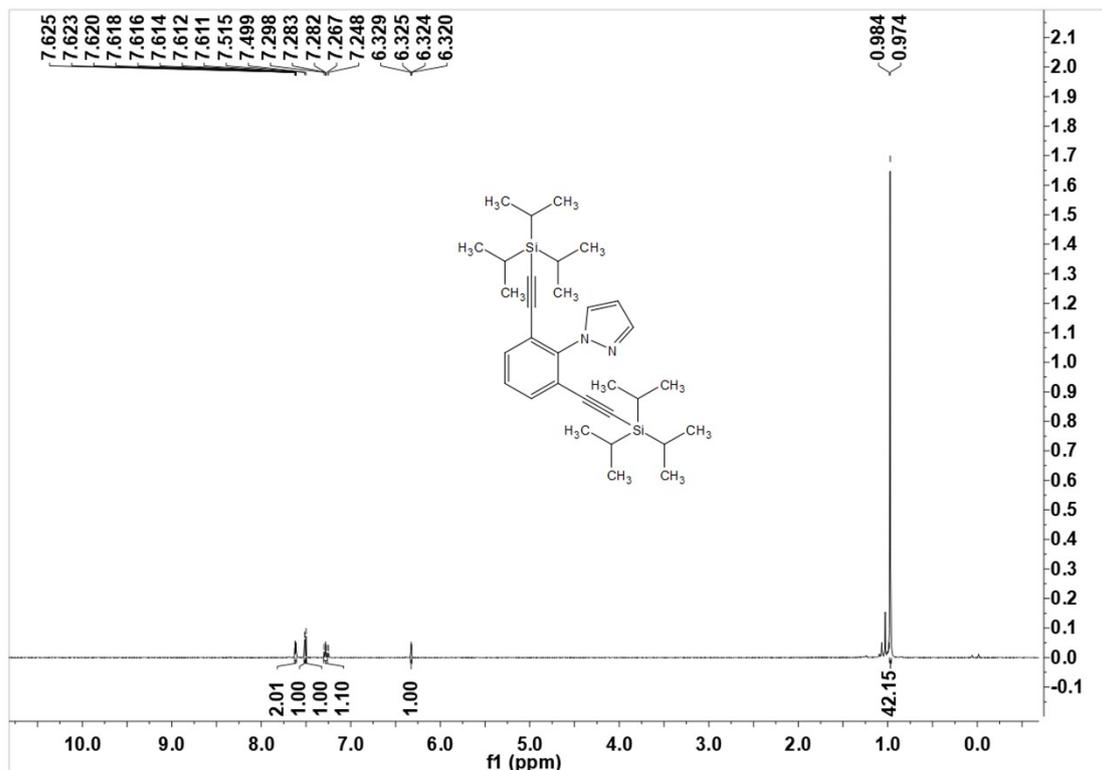


¹³C NMR (100 MHz, CDCl₃)

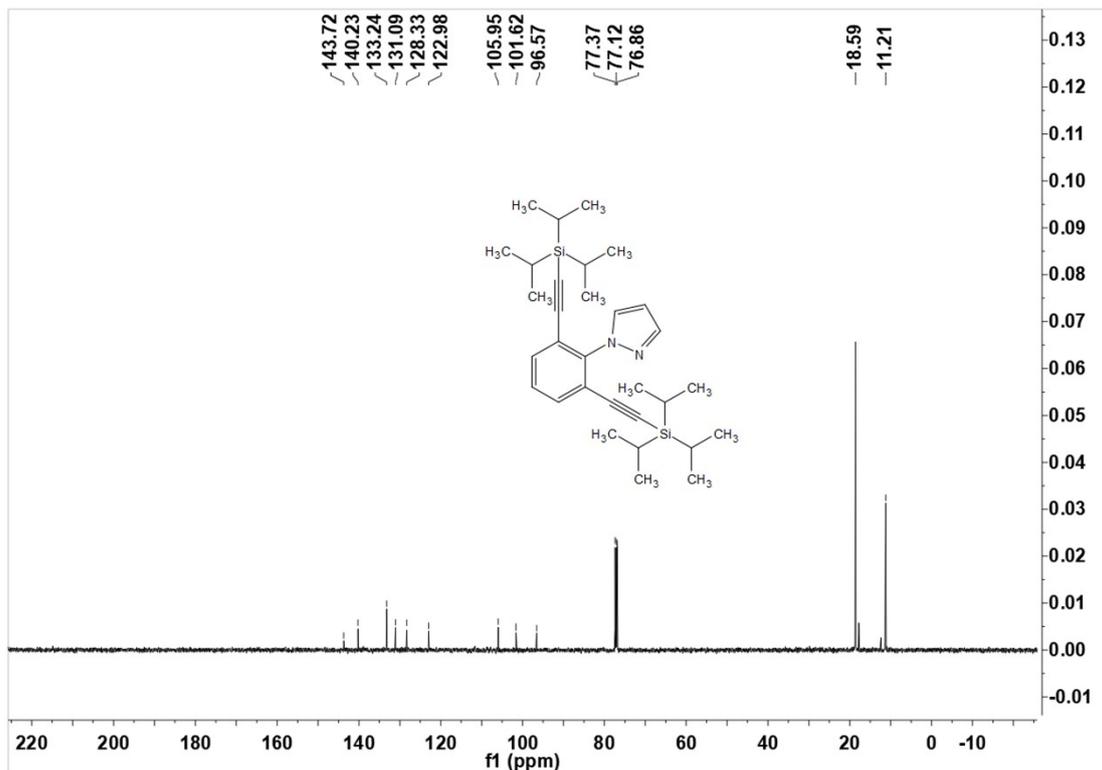


1-(2,6-Bis((triisopropylsilyl)ethynyl)phenyl)-1H-pyrazole (7a)

¹H NMR (400 MHz, CDCl₃)

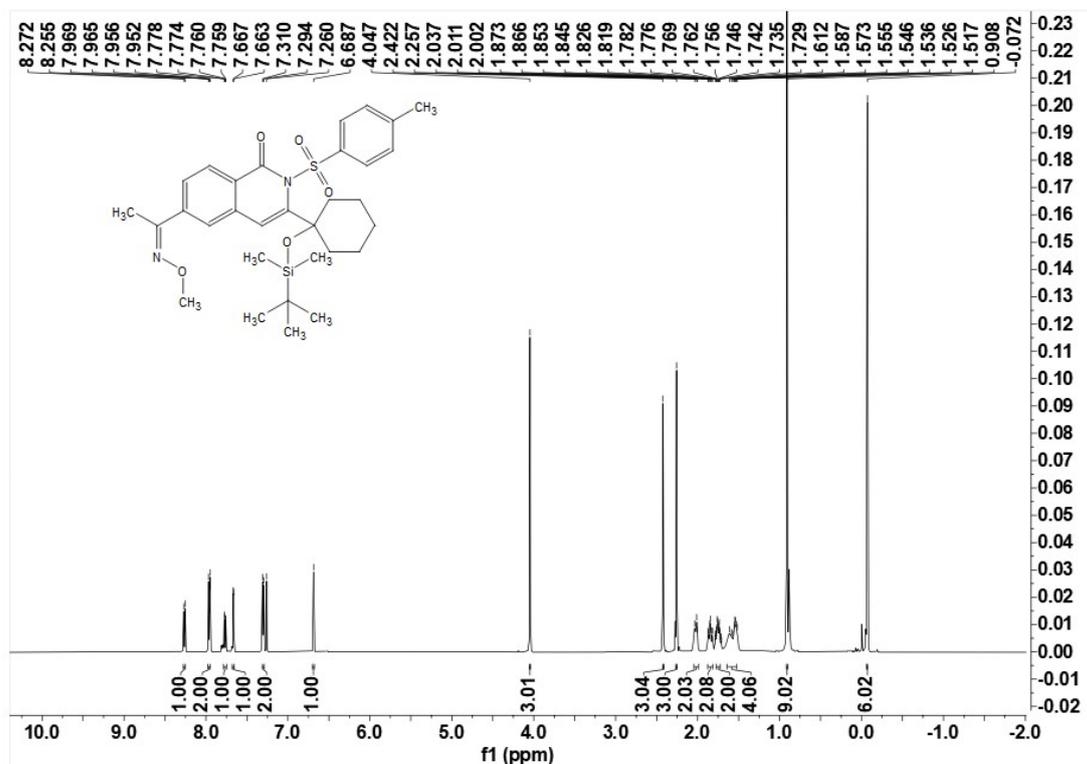


¹³C NMR (100 MHz, CDCl₃)

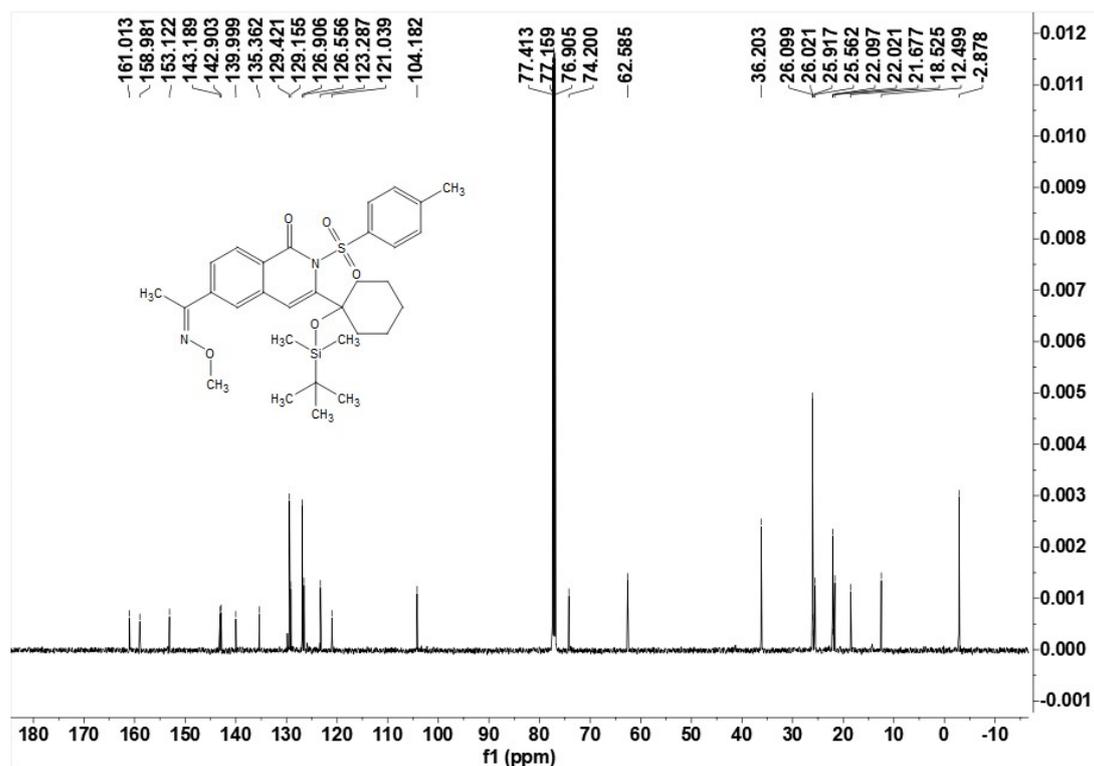


3-(1-((*tert*-Butyldimethylsilyloxy)cyclohexyl)-6-(1-(methoxyimino)ethyl)-2-tosylisoquinolin-1(2*H*)-one (4v)

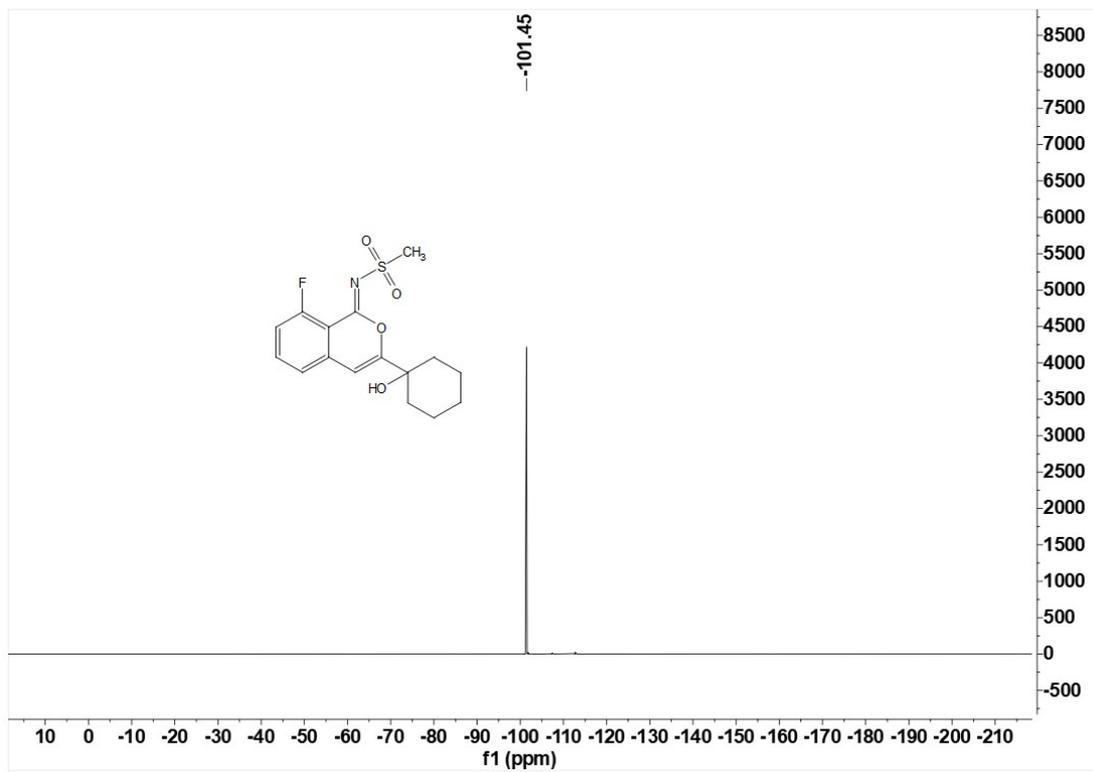
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (100 MHz, CDCl_3)

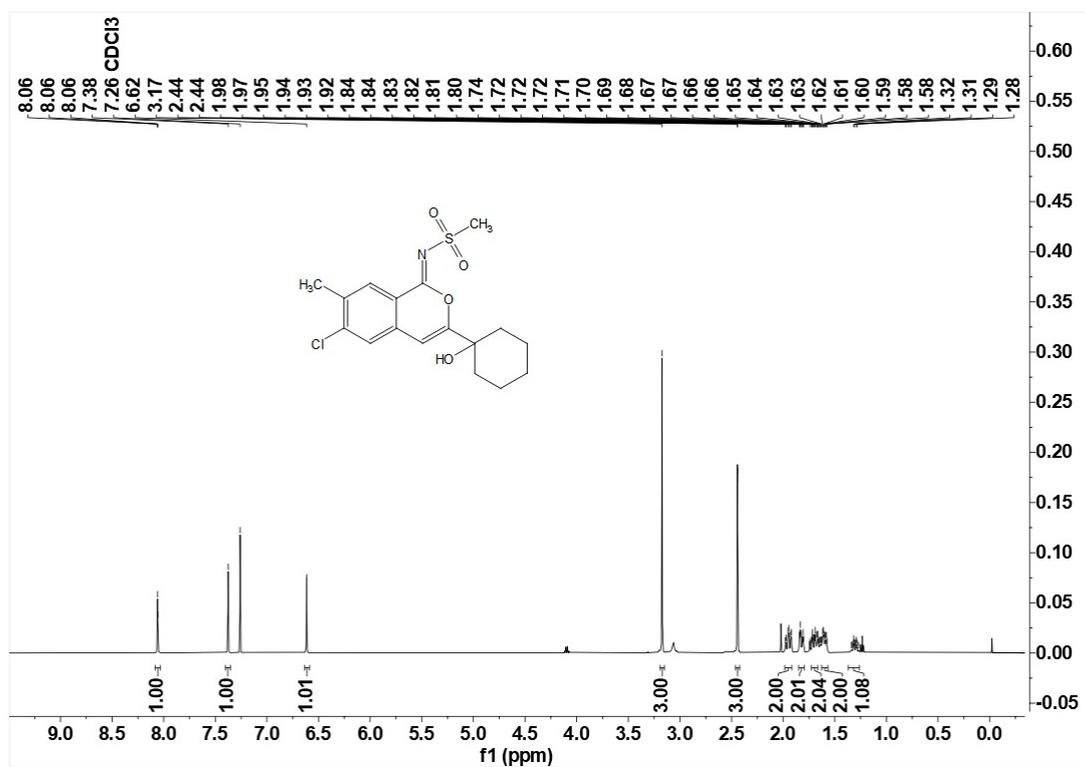


^{19}F NMR (376 MHz, CDCl_3)

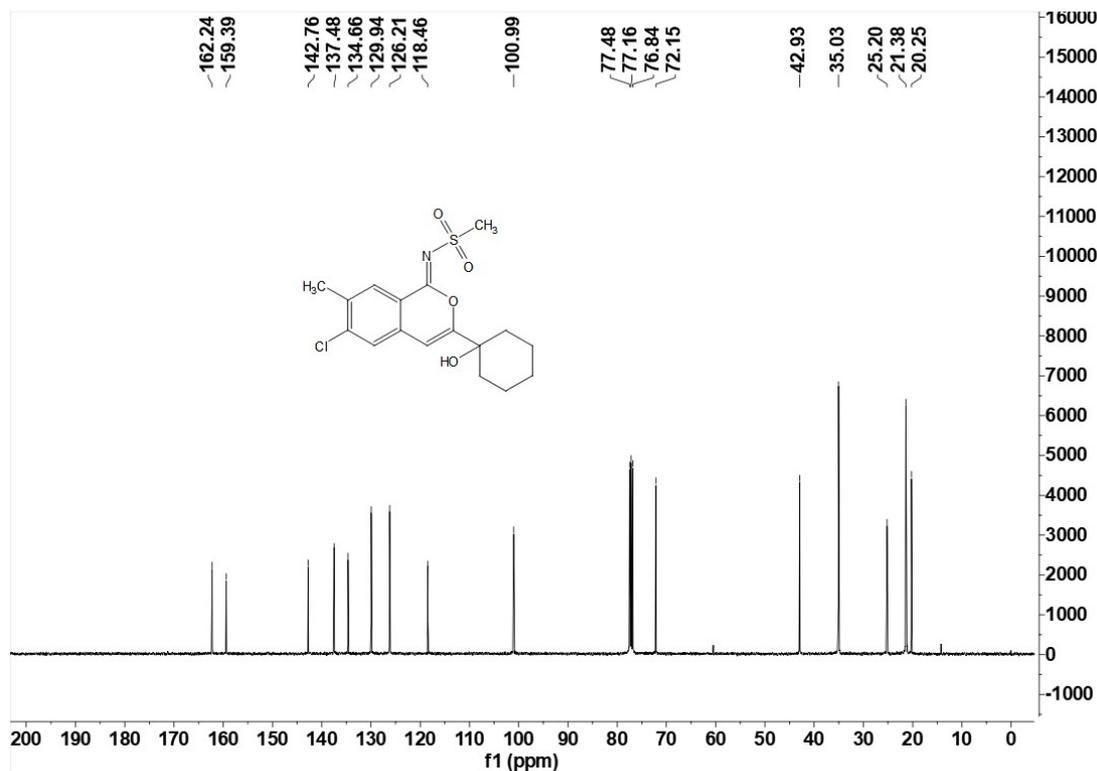


***N*-(6-Chloro-3-(1-hydroxycyclohexyl)-7-methyl-1*H*-isochromen-1-ylidene)methanesulfonamide (4n)**

¹H NMR (500 MHz, CDCl₃)



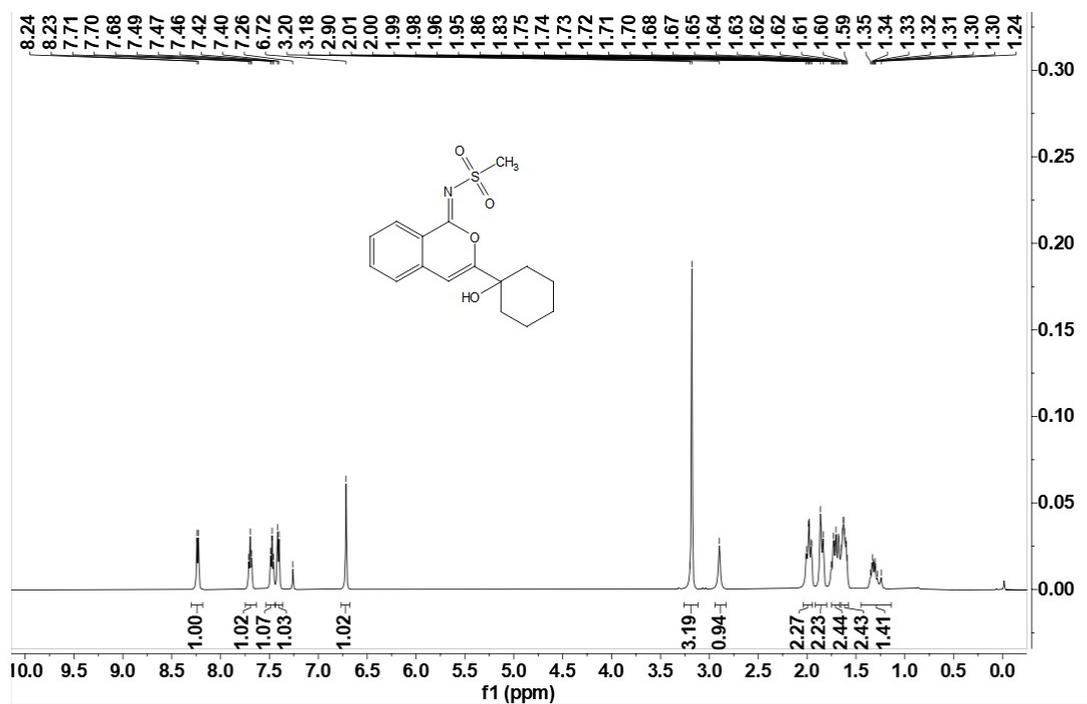
¹³C NMR (125 MHz, CDCl₃)



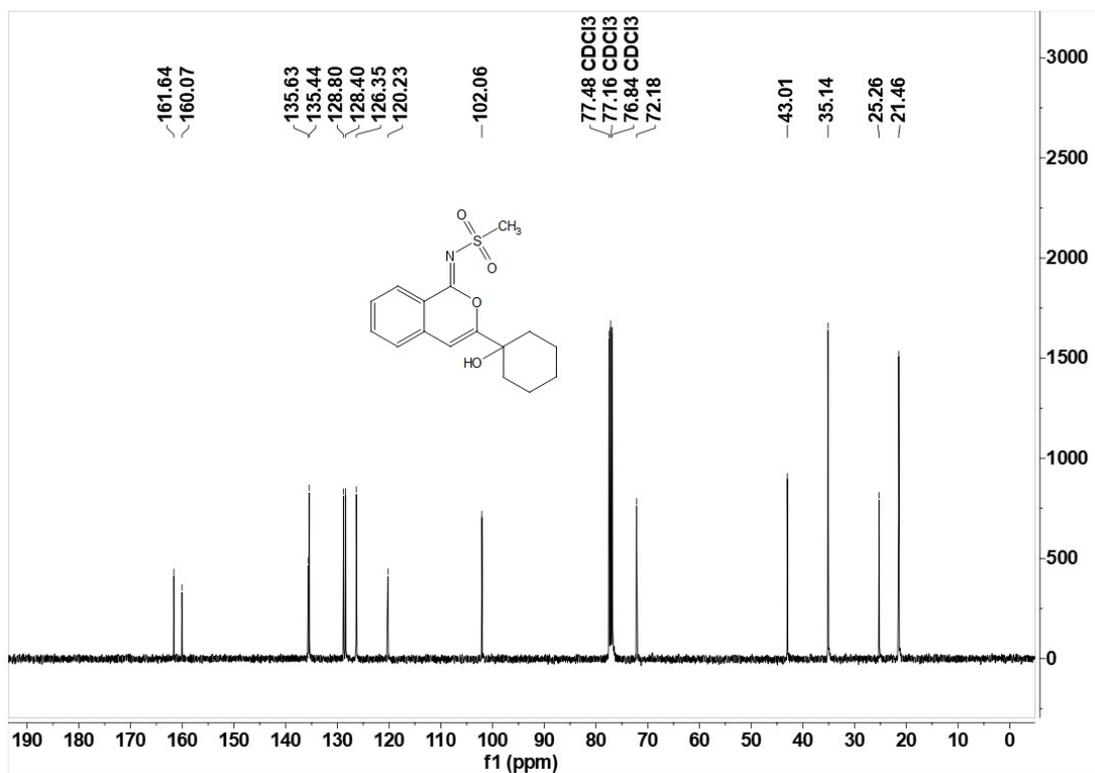
N-(3-(1-hydroxycyclohexyl)-1*H*-isochromen-1-ylidene)methanesulfonamide

(4p)

¹H NMR (CDCl₃, 500 MHz)

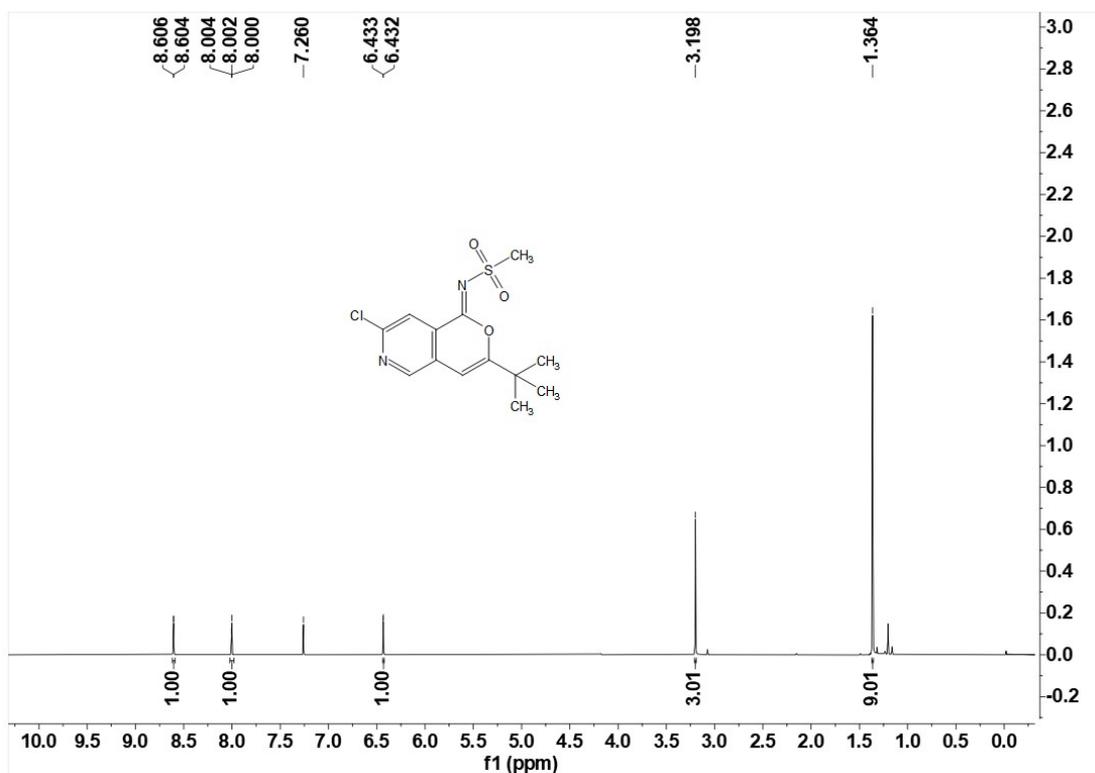


¹³C NMR (125 MHz, CDCl₃)

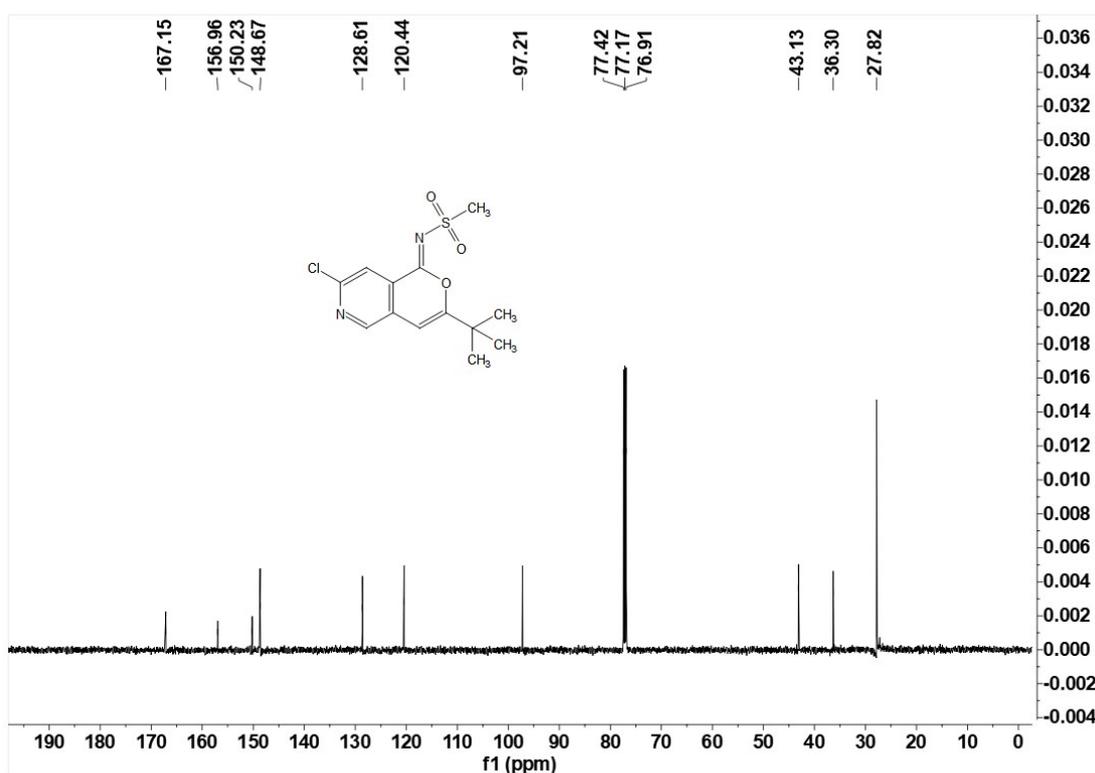


(Z)-N-(3-(*tert*-Butyl)-7-chloro-1*H*-pyrano[4,3-*c*]pyridin-1-ylidene)methanesulfonamide (4r)

¹H NMR (CDCl₃, 500 MHz)

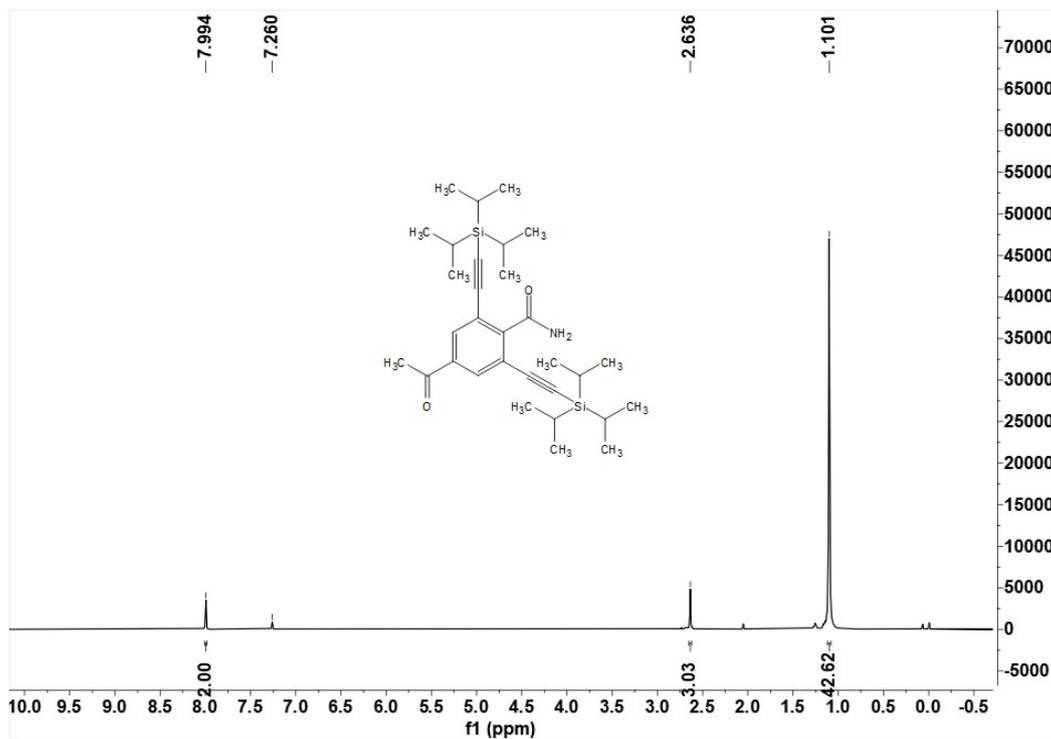


¹³C NMR (125 MHz, CDCl₃)

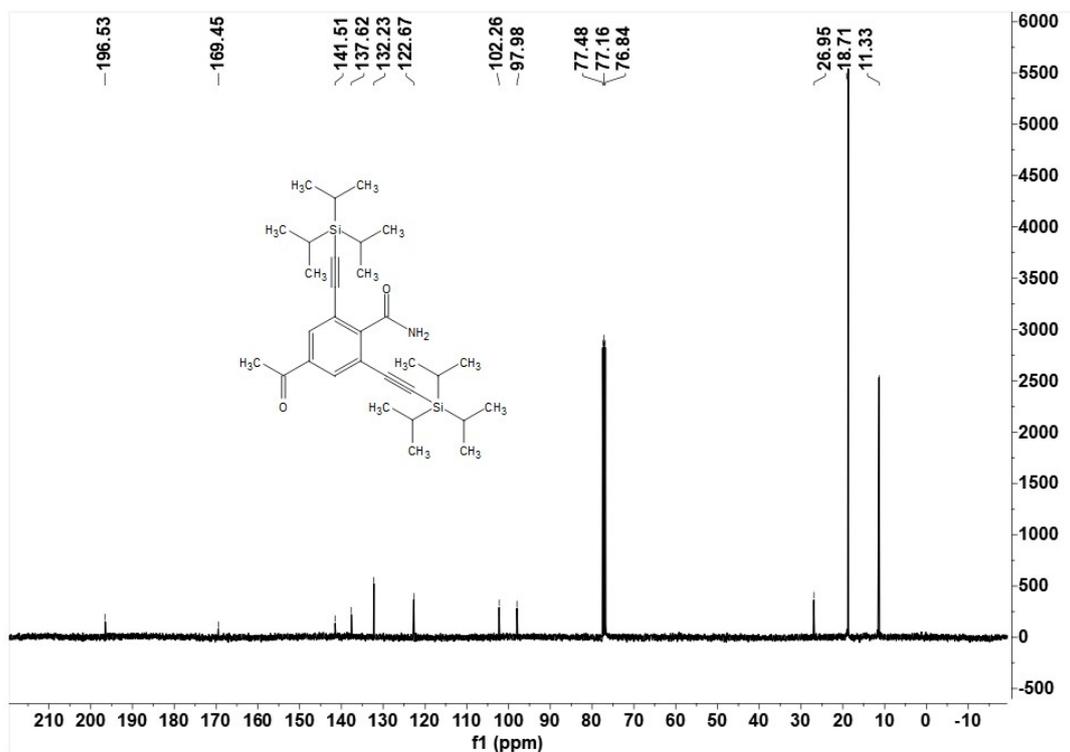


4-Acetyl-2-((triisopropylsilyl)ethynyl)benzamide (5a)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)

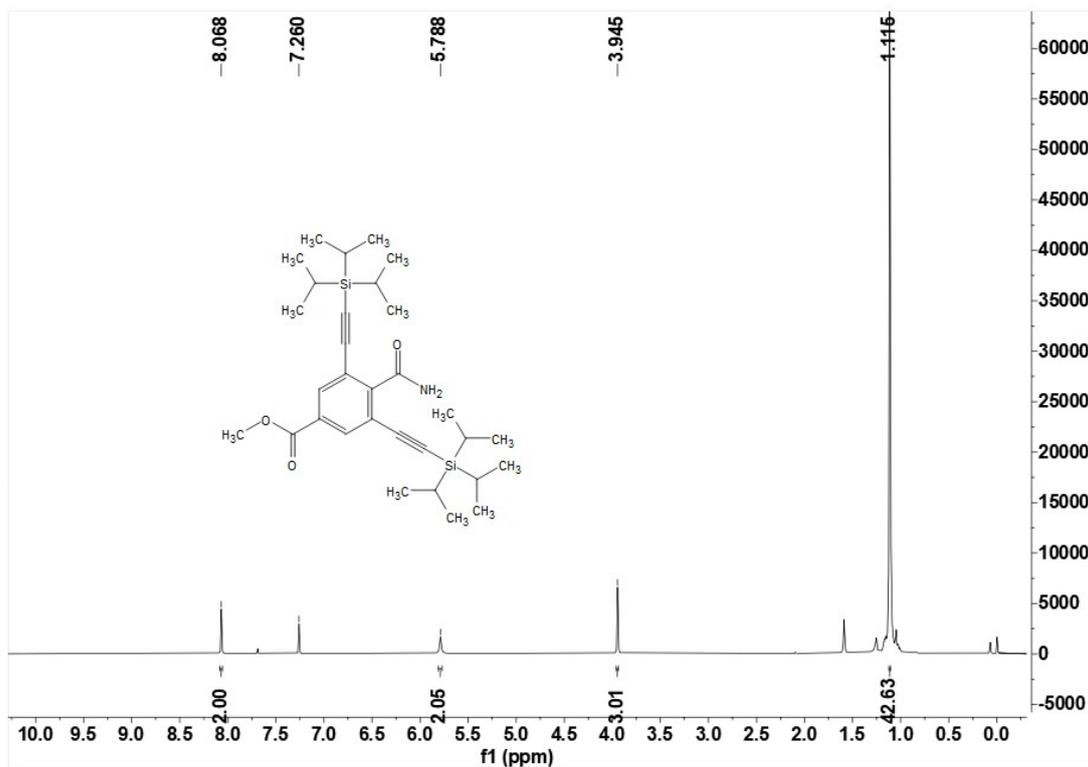


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

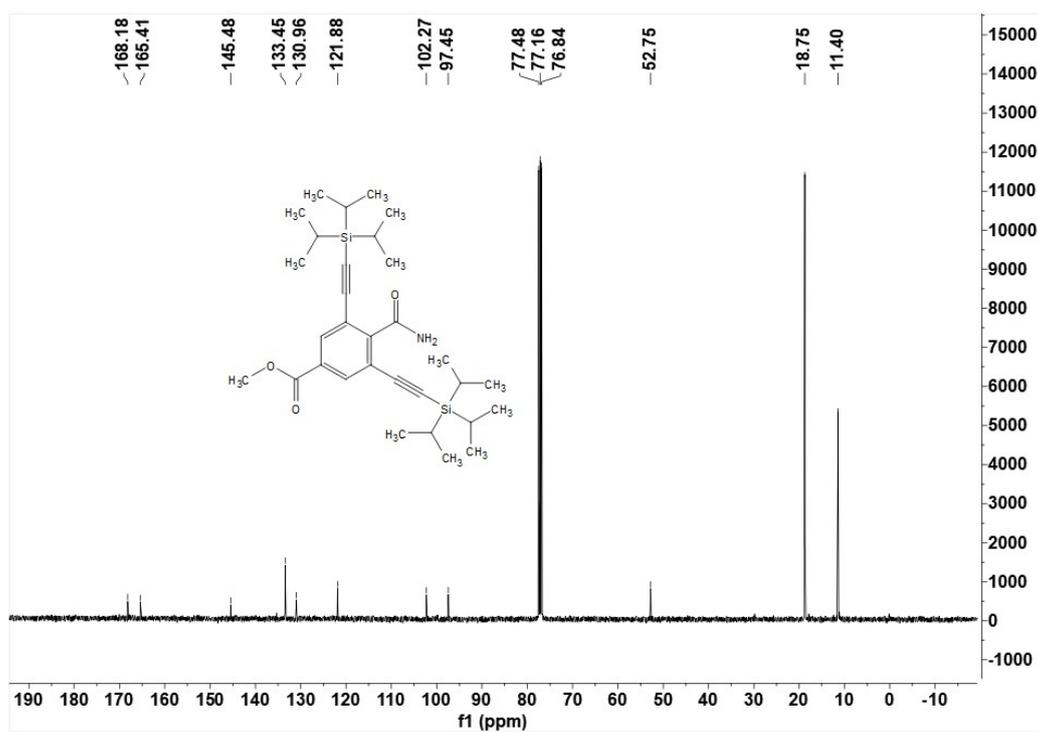


Methyl 4-carbamoyl-3, 5-bis((triisopropylsilyl)ethynyl)benzoate (5b)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz)



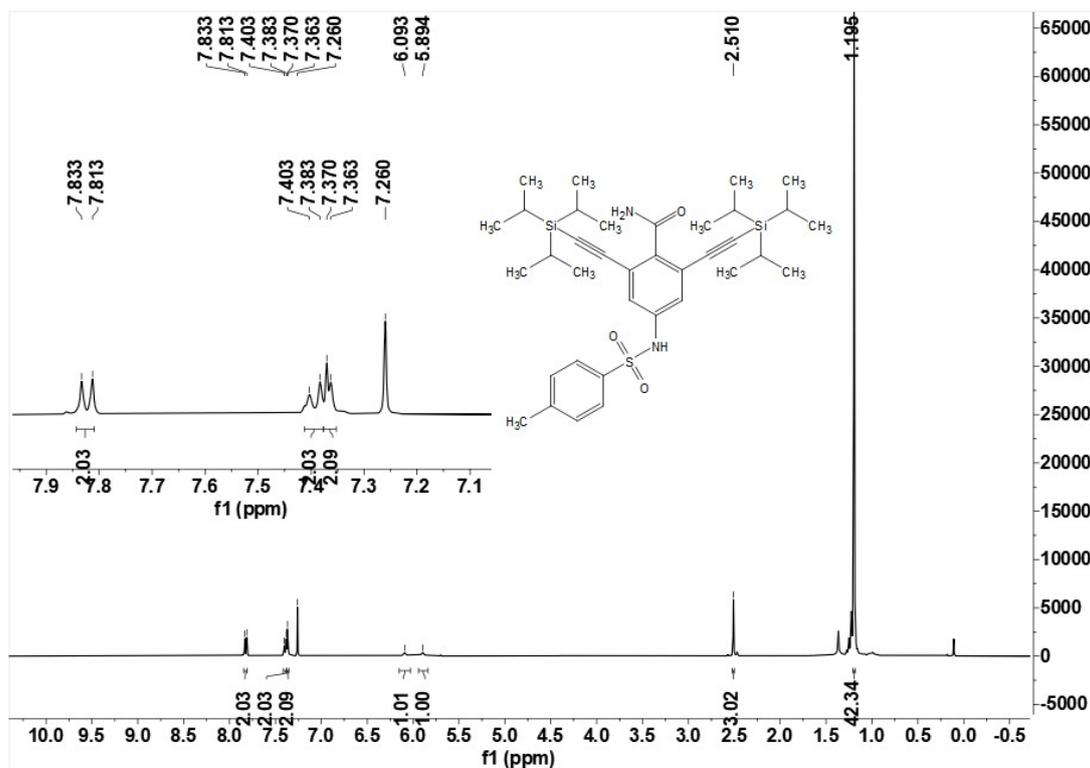
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



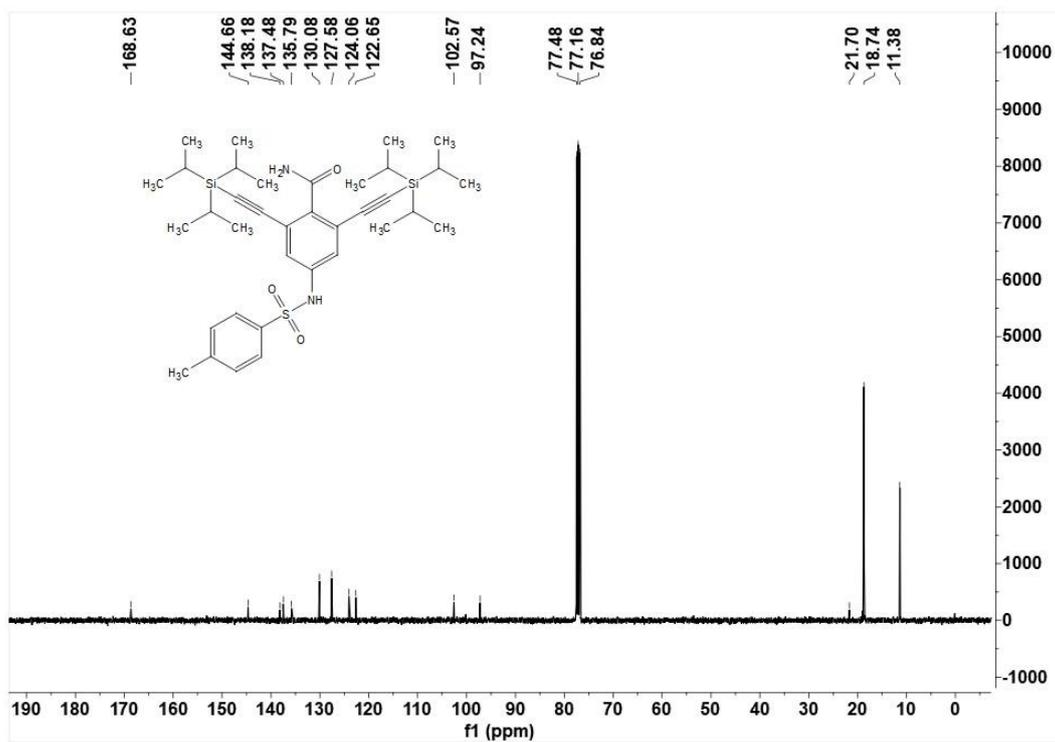
4-((4-Methylphenyl)sulfonamido)-2,6-bis((triisopropylsilyl)ethynyl)benzamide

(5c)

¹H NMR (CDCl₃, 400 MHz)

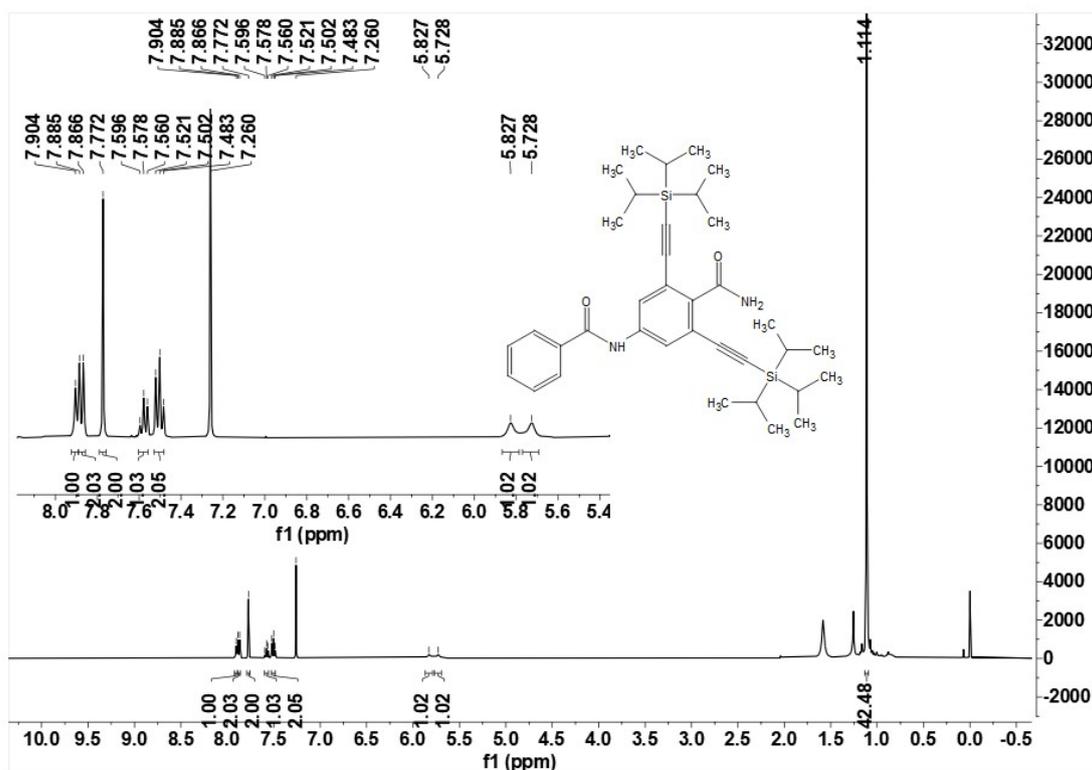


¹³C NMR (100 MHz, CDCl₃)

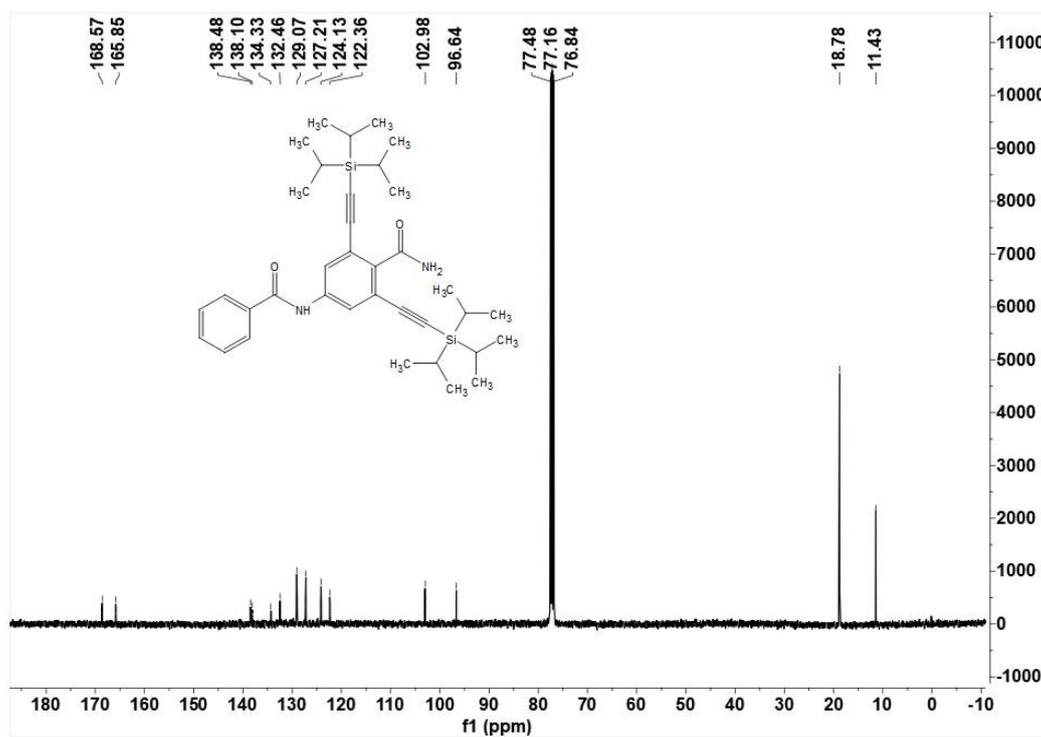


4-Benzamido-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5d)

¹H NMR (CDCl₃, 400 MHz)

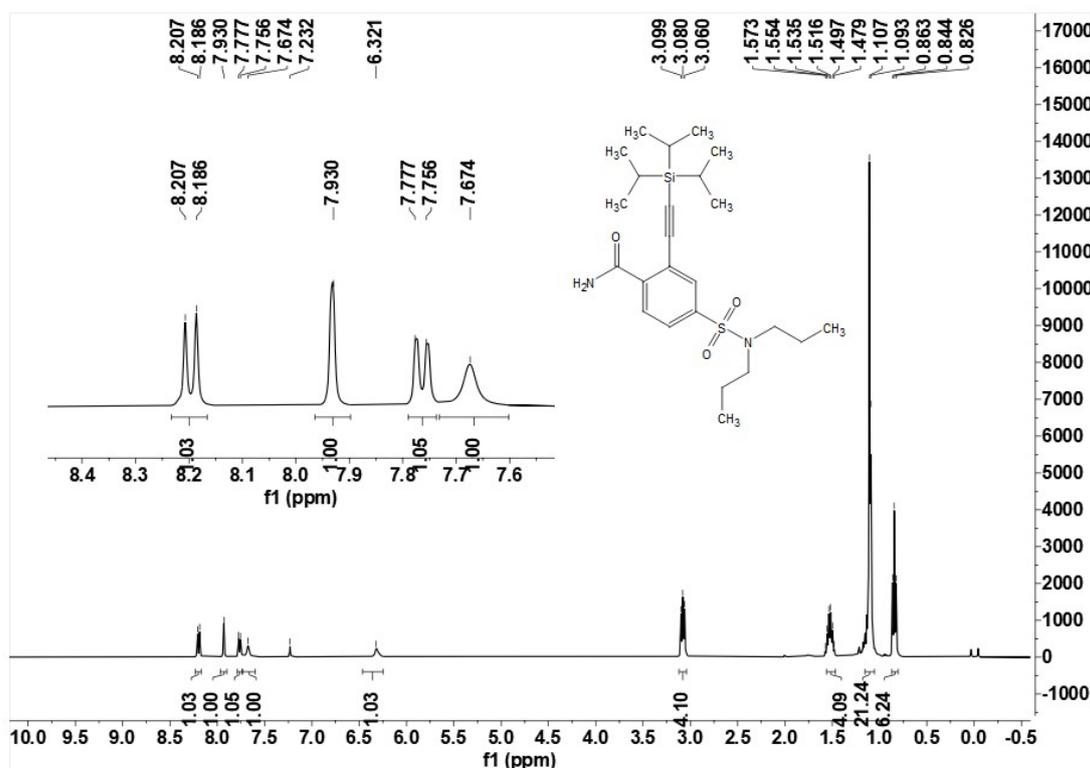


¹³C NMR (100 MHz, CDCl₃)

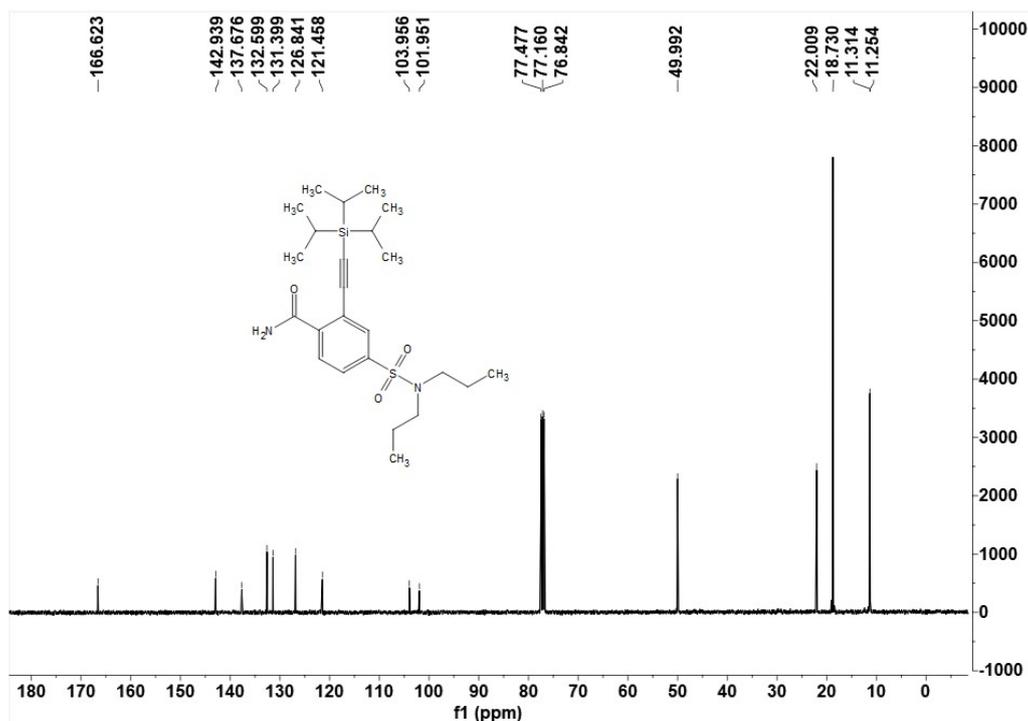


4-(*N,N*-Dipropylsulfamoyl)-2-((triisopropylsilyl)ethynyl)benzamide (5e)

¹H NMR (CDCl₃, 400 MHz)



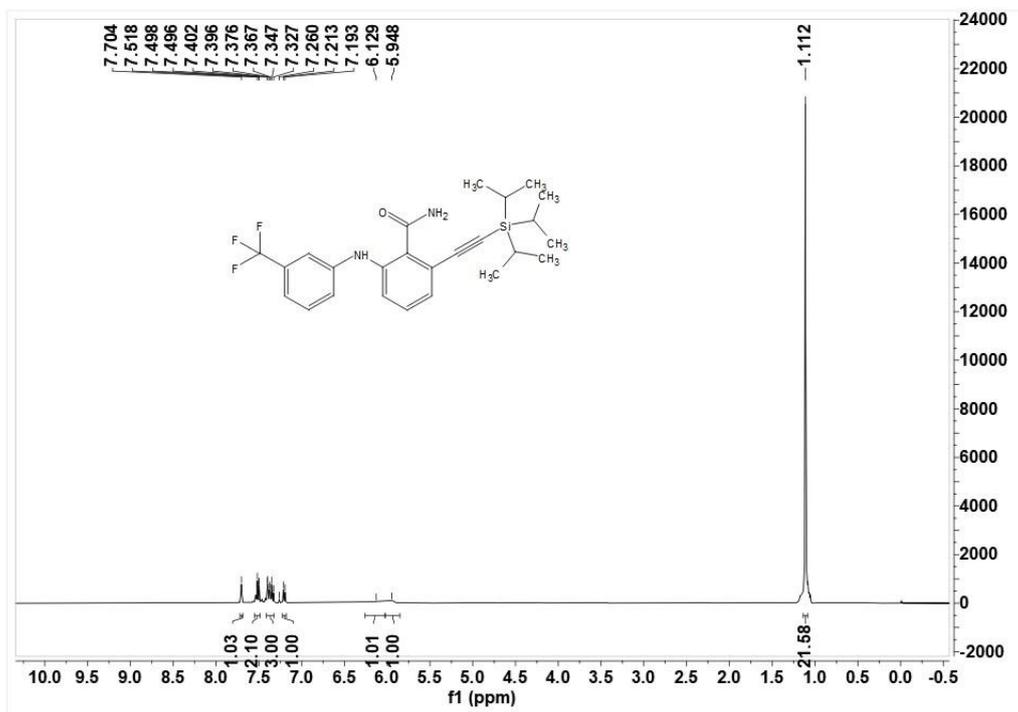
¹³C NMR (100 MHz, CDCl₃)



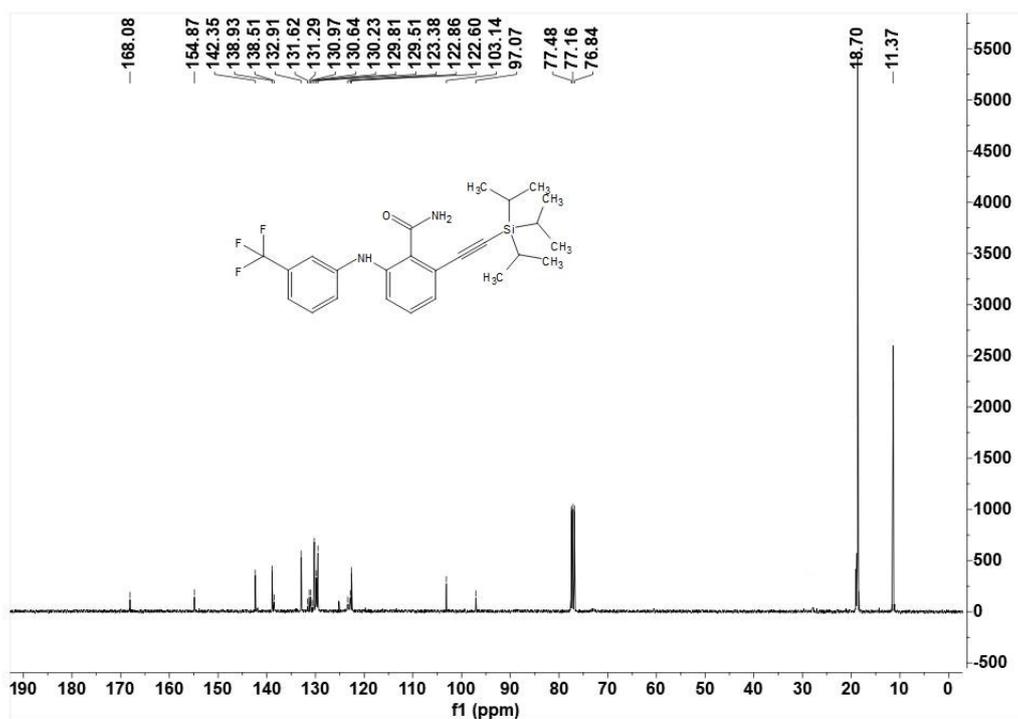
2-((3-(Trifluoromethyl)phenyl)amino)-6-((triisopropylsilyl)ethynyl)benzamide

(5f)

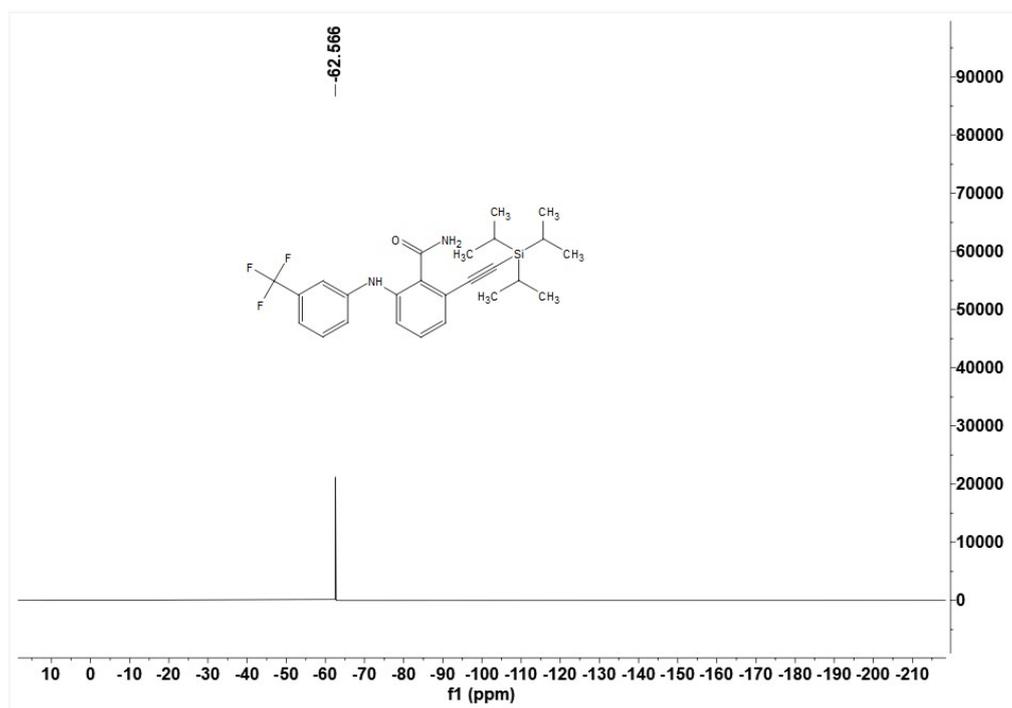
$^1\text{H NMR}$ (CDCl_3 , 400 MHz)



$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

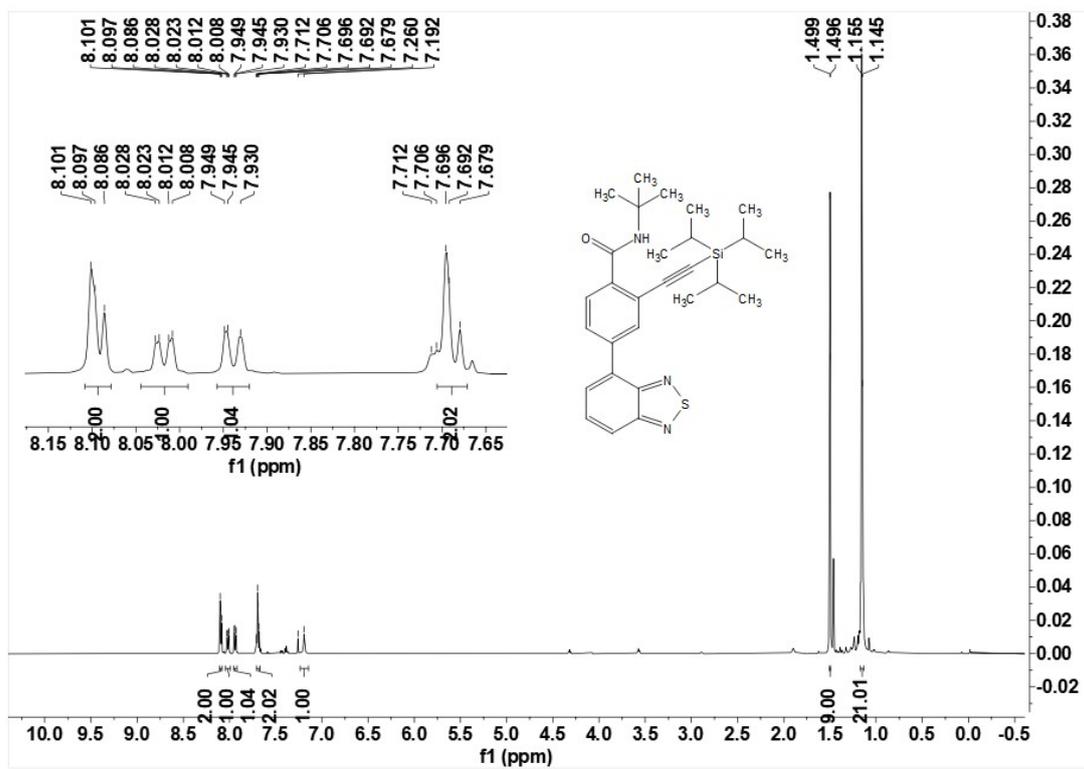


^{19}F NMR (376 MHz, CDCl_3)

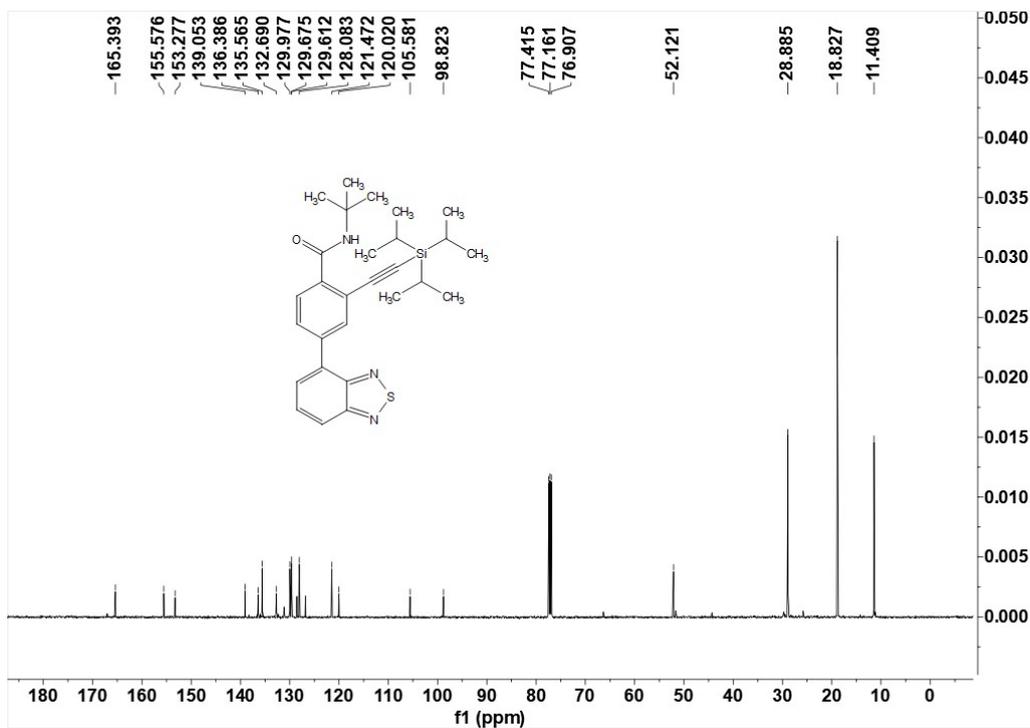


4-(Benzo[c][1,2,5]thiadiazol-4-yl)-*N*-(*tert*-butyl)-2-
 ((triisopropylsilyl)ethynyl)benzamide (5g)

$^1\text{H NMR}$ (CDCl_3 , 500 MHz)



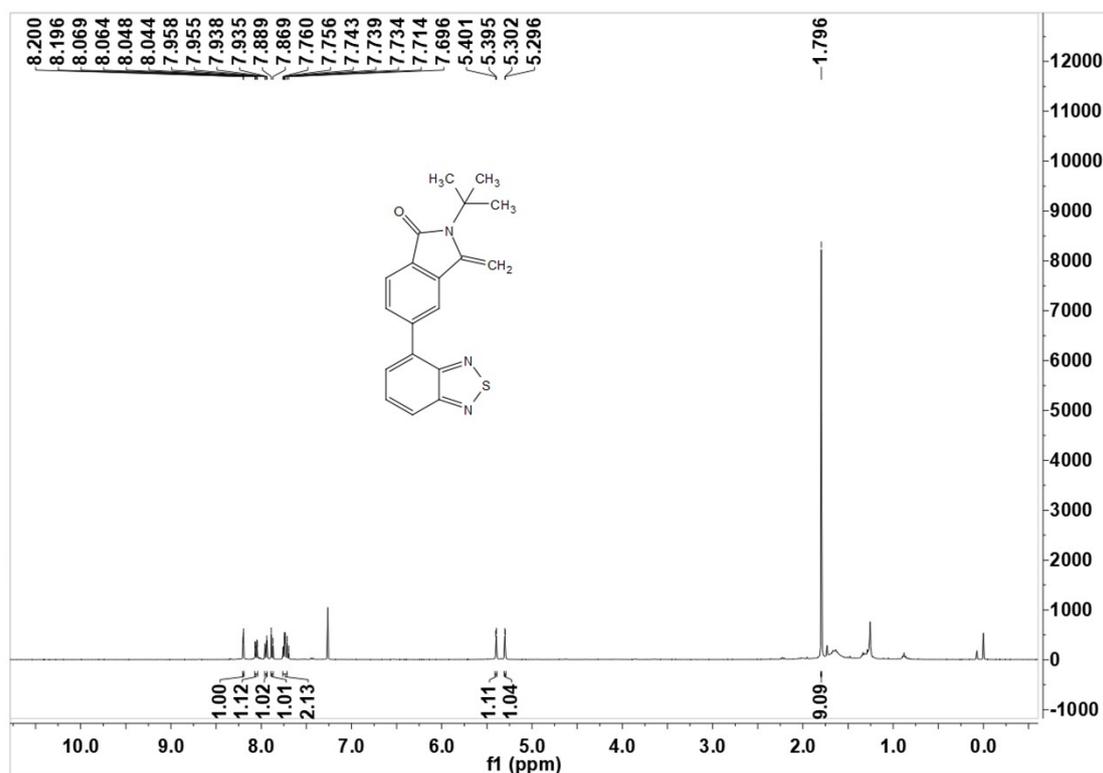
$^{13}\text{C NMR}$ (126 MHz, CDCl_3)



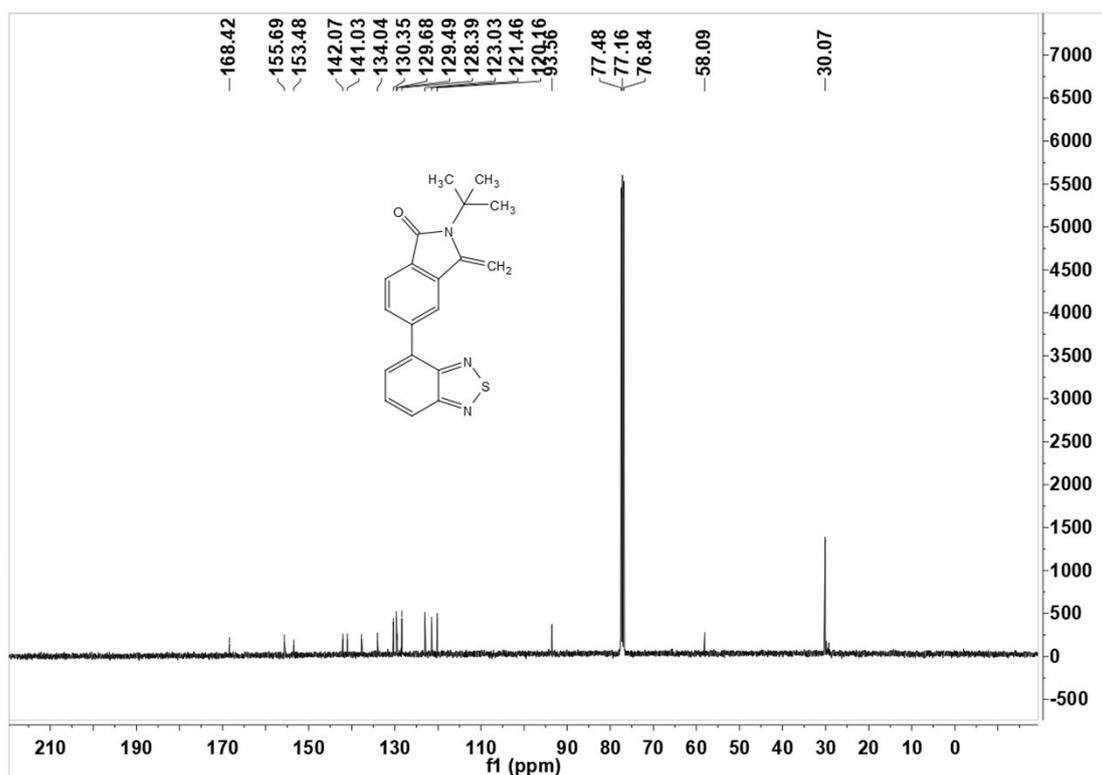
5-(Benzo[c][1,2,5]thiadiazol-4-yl)-2-(*tert*-butyl)-3-methyleneisindolin-1-one

(5g-1)

¹H NMR (CDCl₃, 400 MHz)

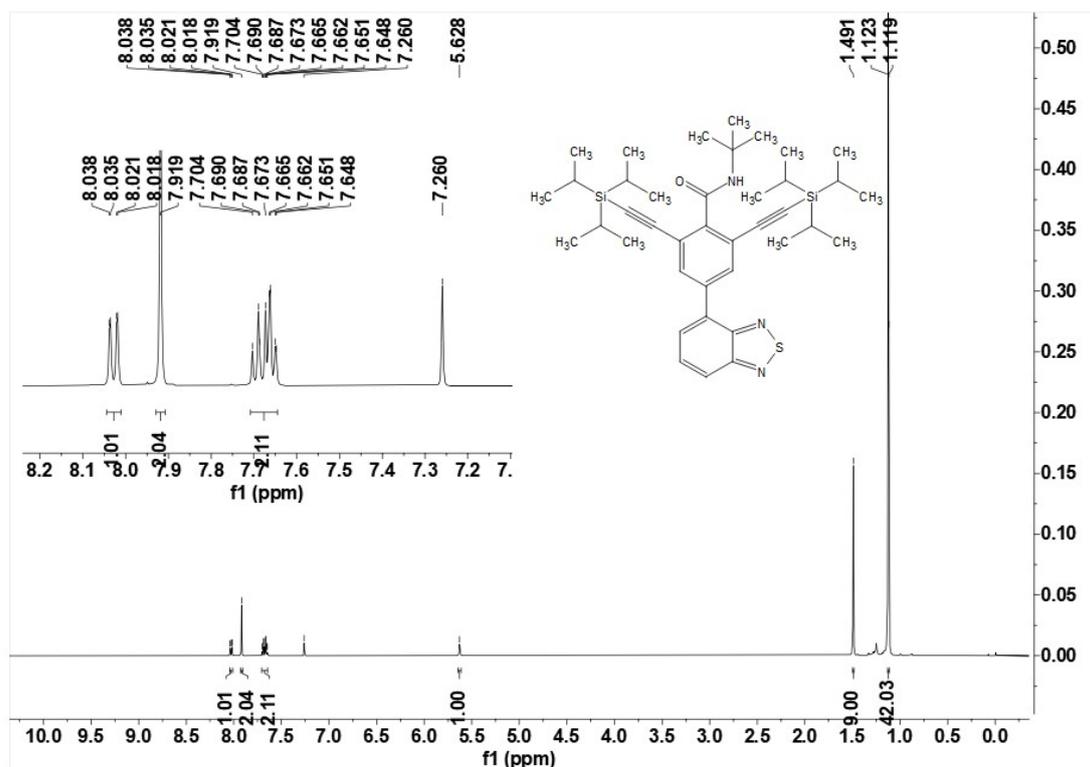


¹³C NMR (100 MHz, CDCl₃)

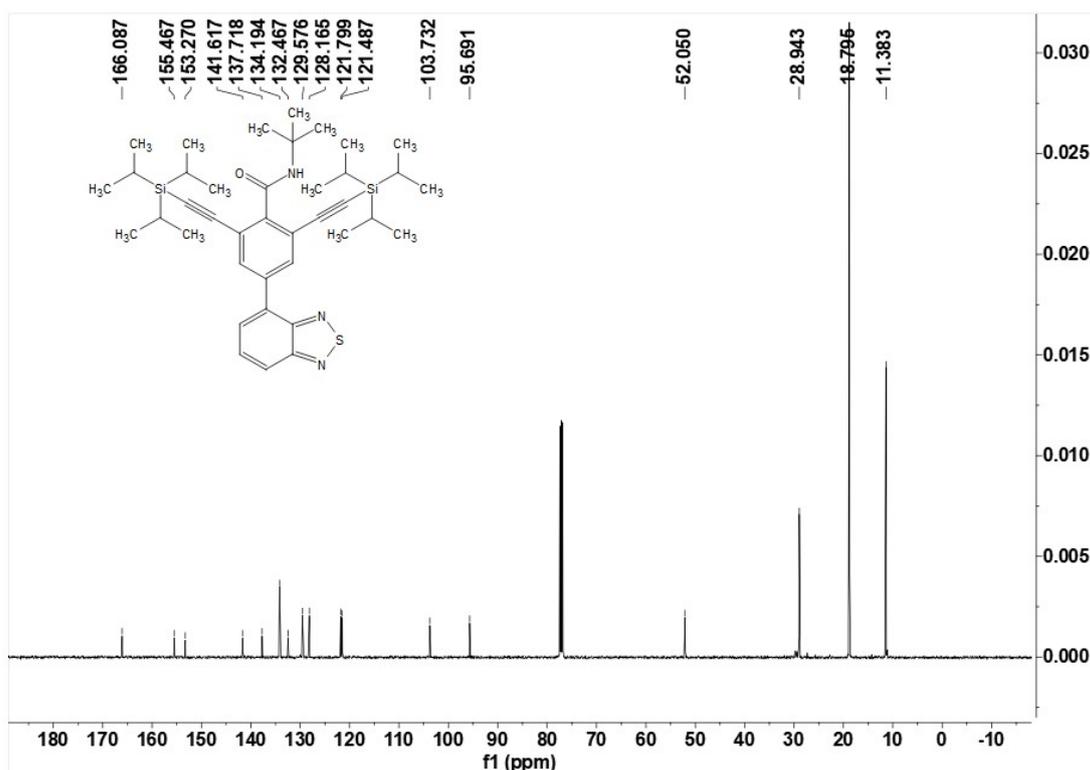


4-(Benzo[c][1,2,5]thiadiazol-4-yl)-*N*-(*tert*-butyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5h)

^1H NMR (CDCl_3 , 500 MHz)

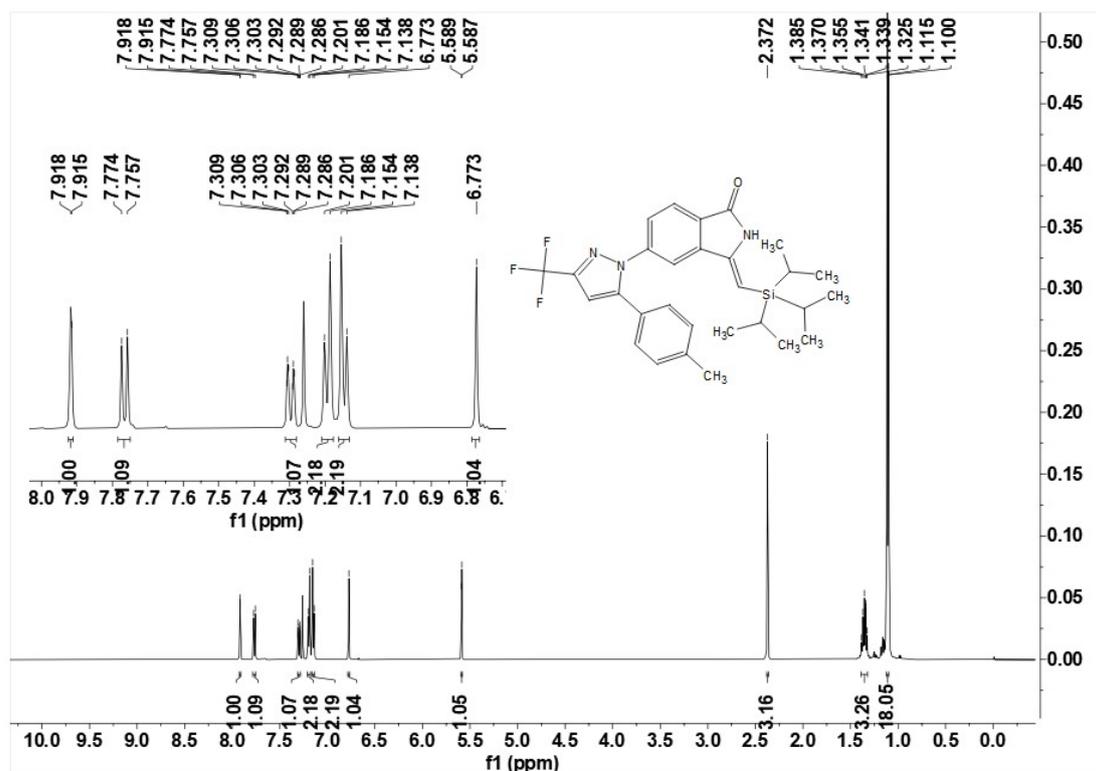


^{13}C NMR (126 MHz, CDCl_3)

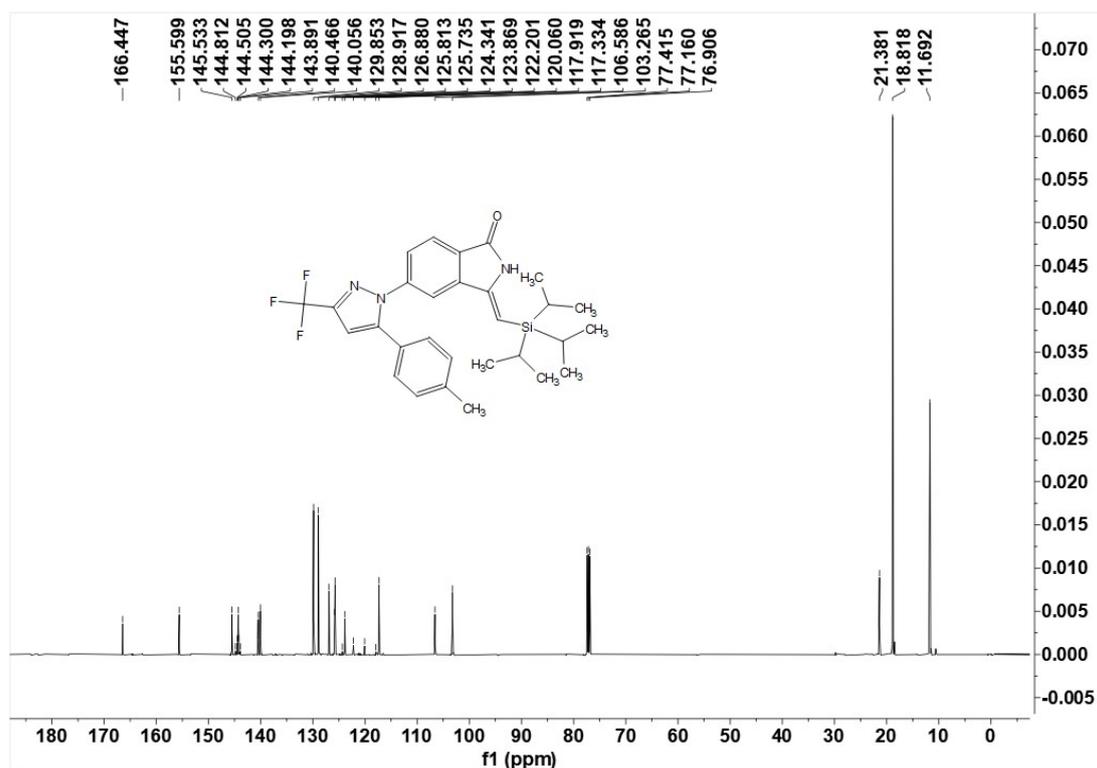


5-(5-(*p*-Tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)-3-
 ((triisopropylsilyl)methylene)isoindolin-1-one (5i)

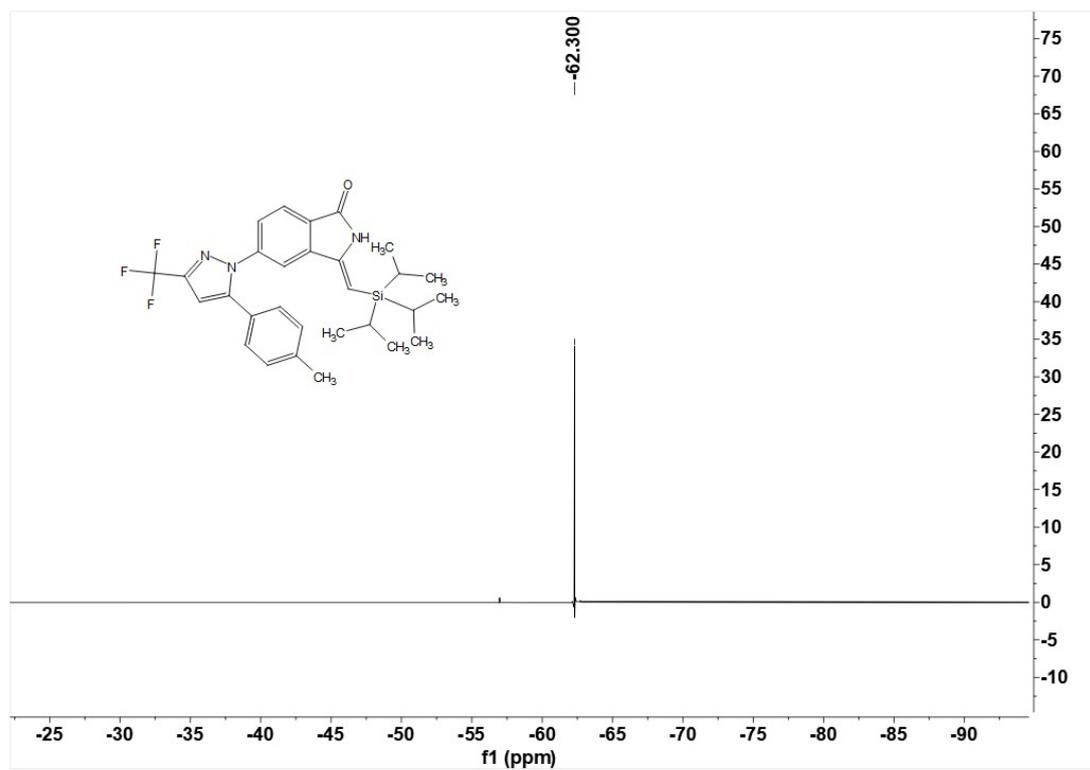
^1H NMR (CDCl_3 , 500 MHz)



^{13}C NMR (126 MHz, CDCl_3)

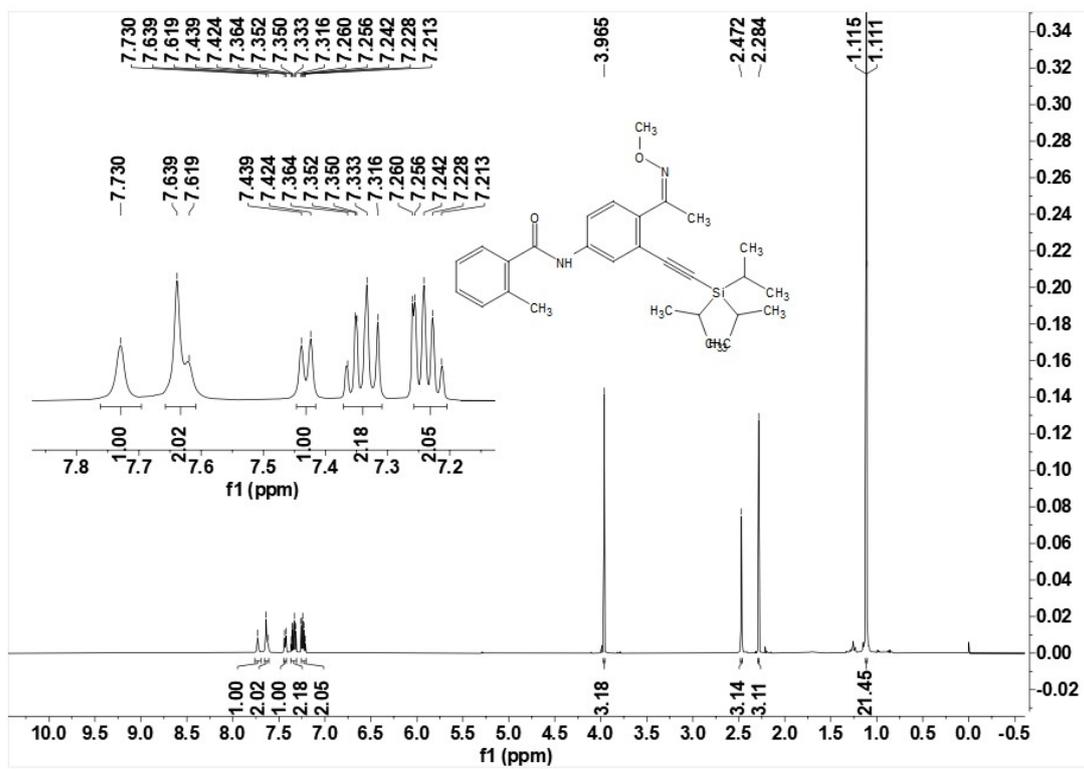


^{19}F NMR (471 MHz, CDCl_3)

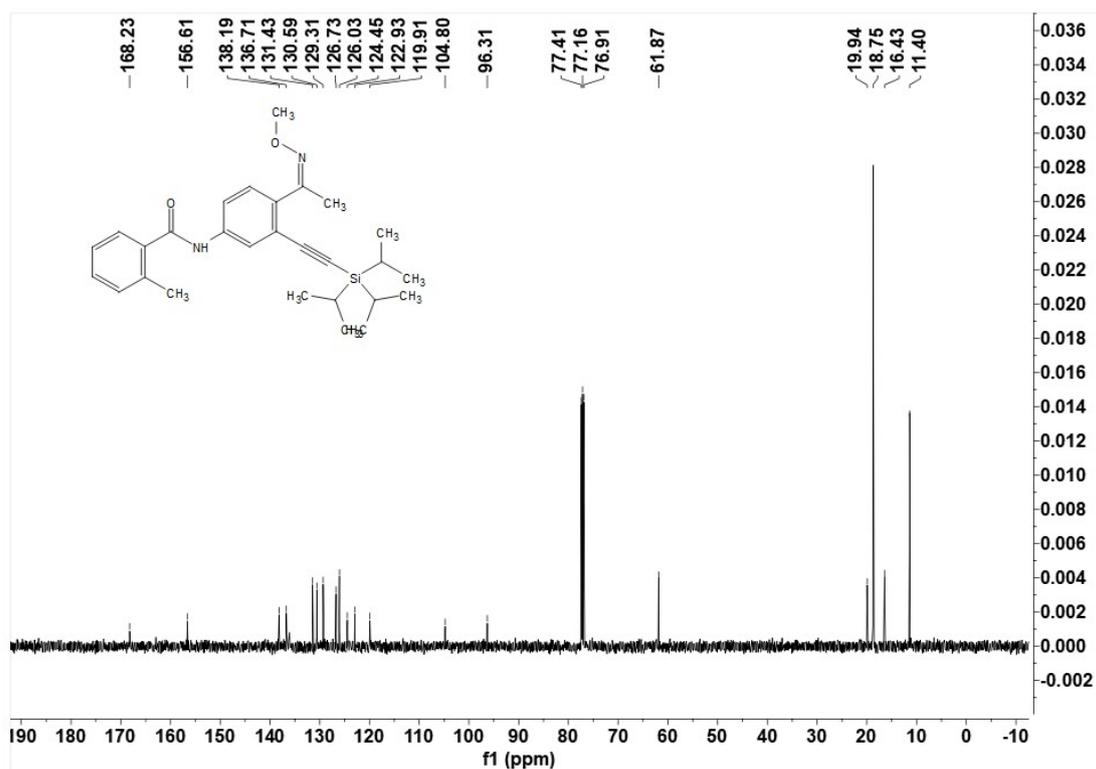


***N*-4-(1-(Methoxyimino)ethyl)-3-((triisopropylsilyl)ethynyl)phenyl)-2-methylbenzamide (6a)**

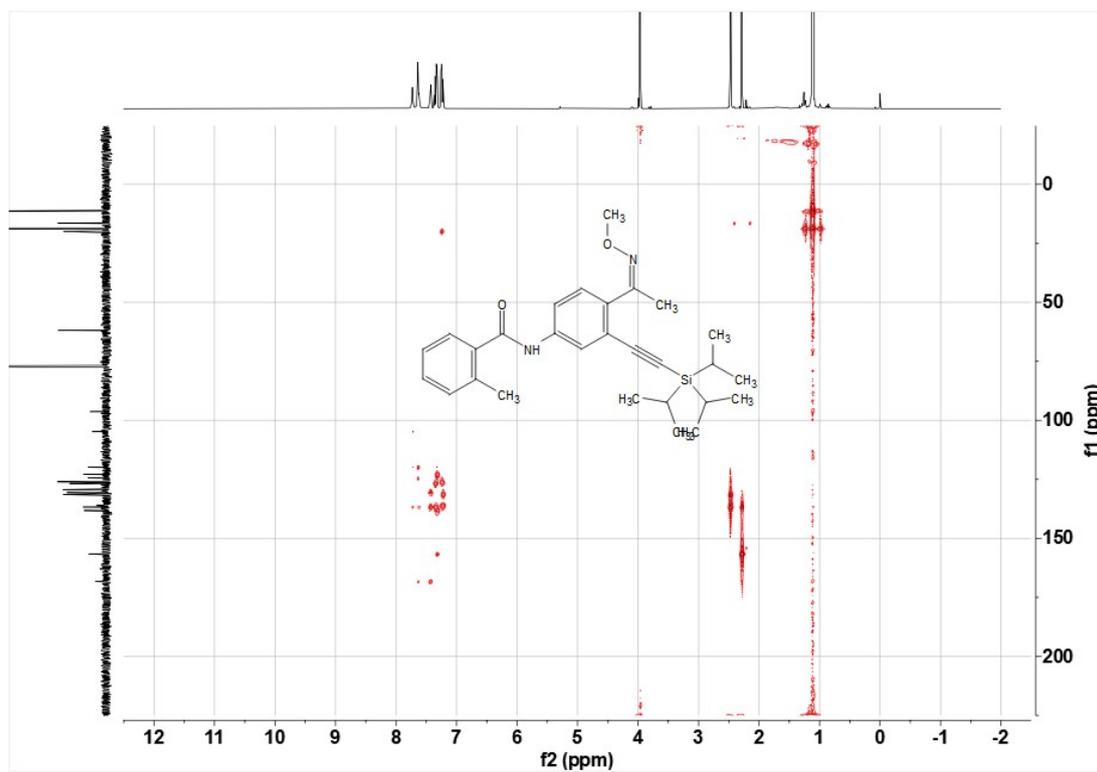
¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (100 MHz, CDCl₃)

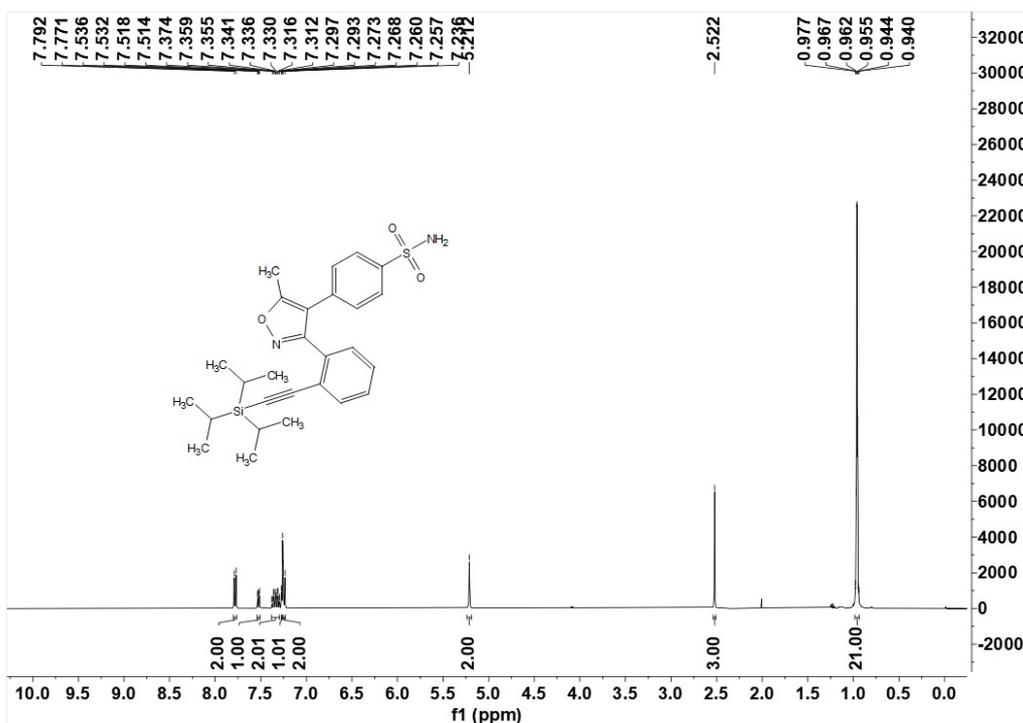


HMBC spectrum of 6a

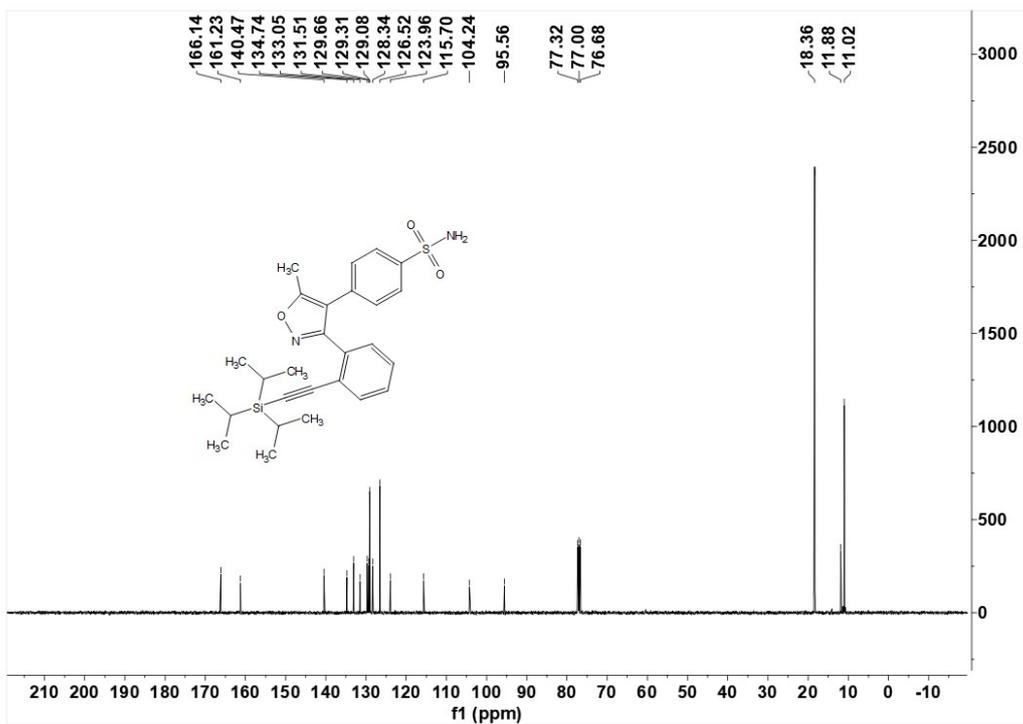


4-(5-Methyl-3-(2-((triisopropylsilyl)ethynyl)phenyl)isoxazol-4-yl)benzenesulfonamide (6b)

¹H NMR (400 MHz, CDCl₃)

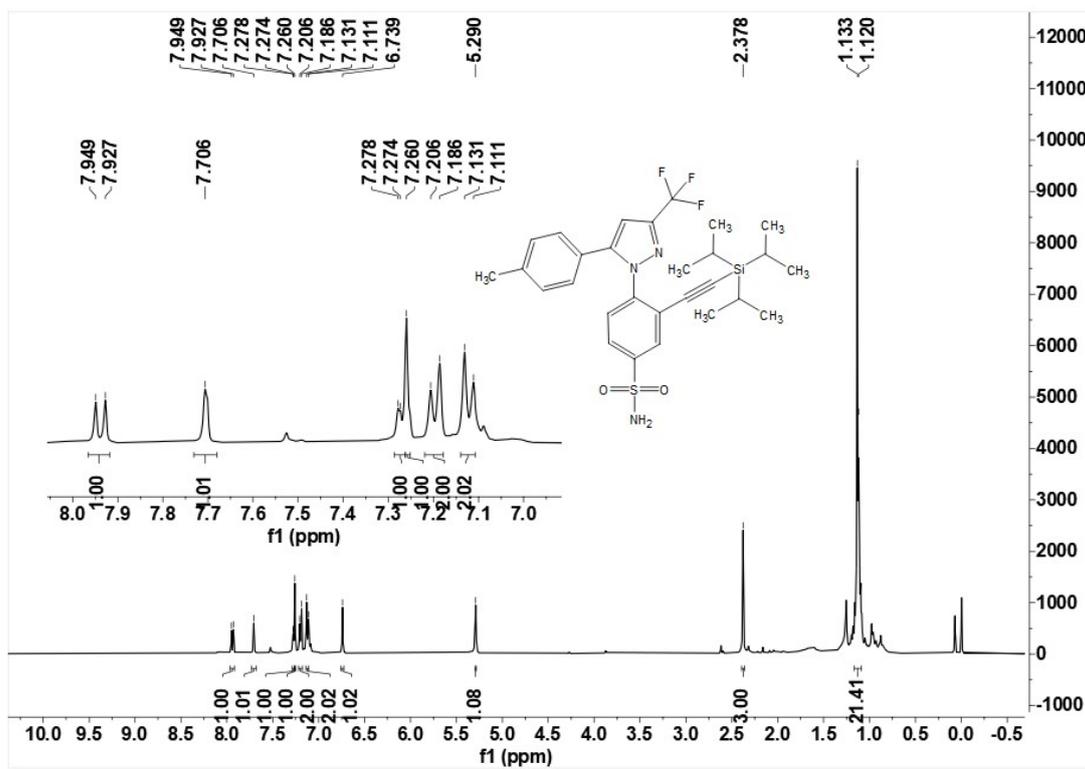


6b, ¹³C NMR (100 MHz, CDCl₃)

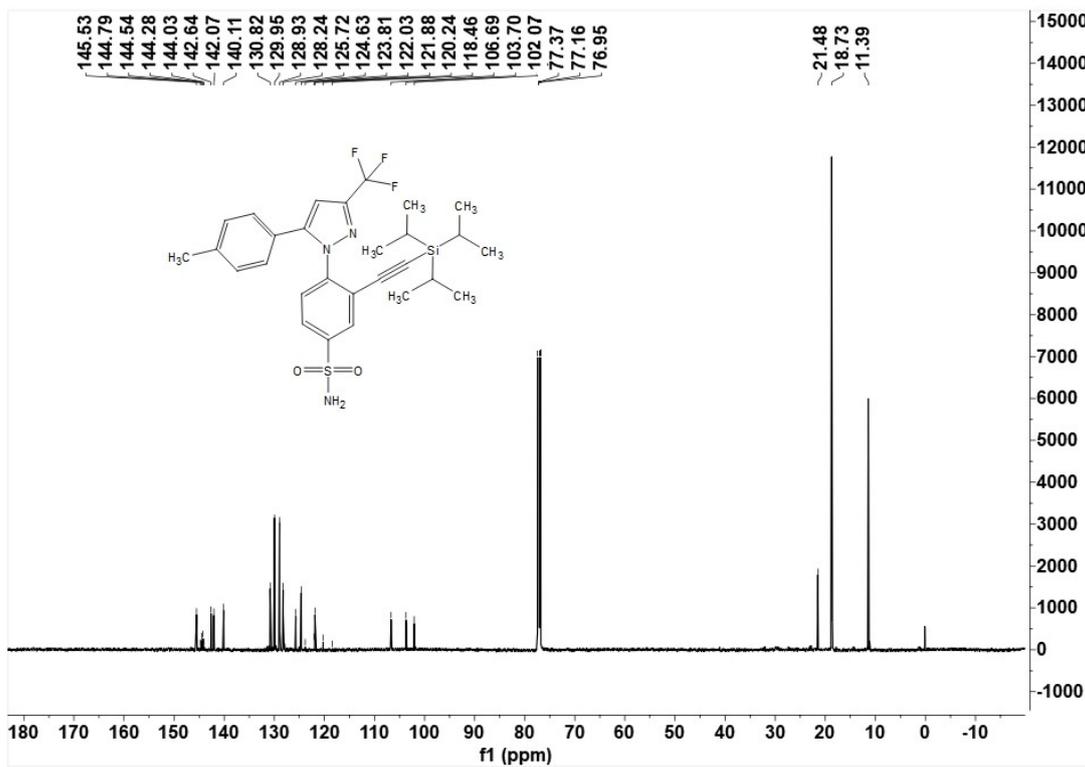


4-(5-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)-3-
((triisopropylsilyl)ethynyl)benzenesulfonamide (6c)

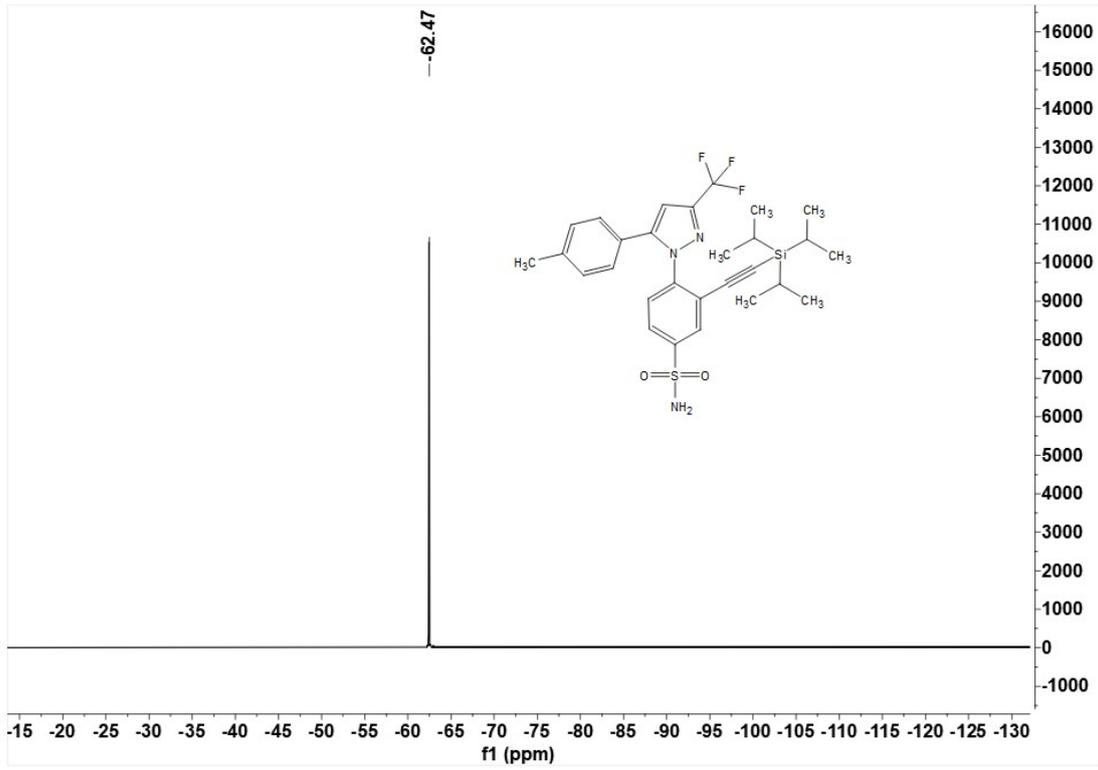
¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (100 MHz, CDCl₃)

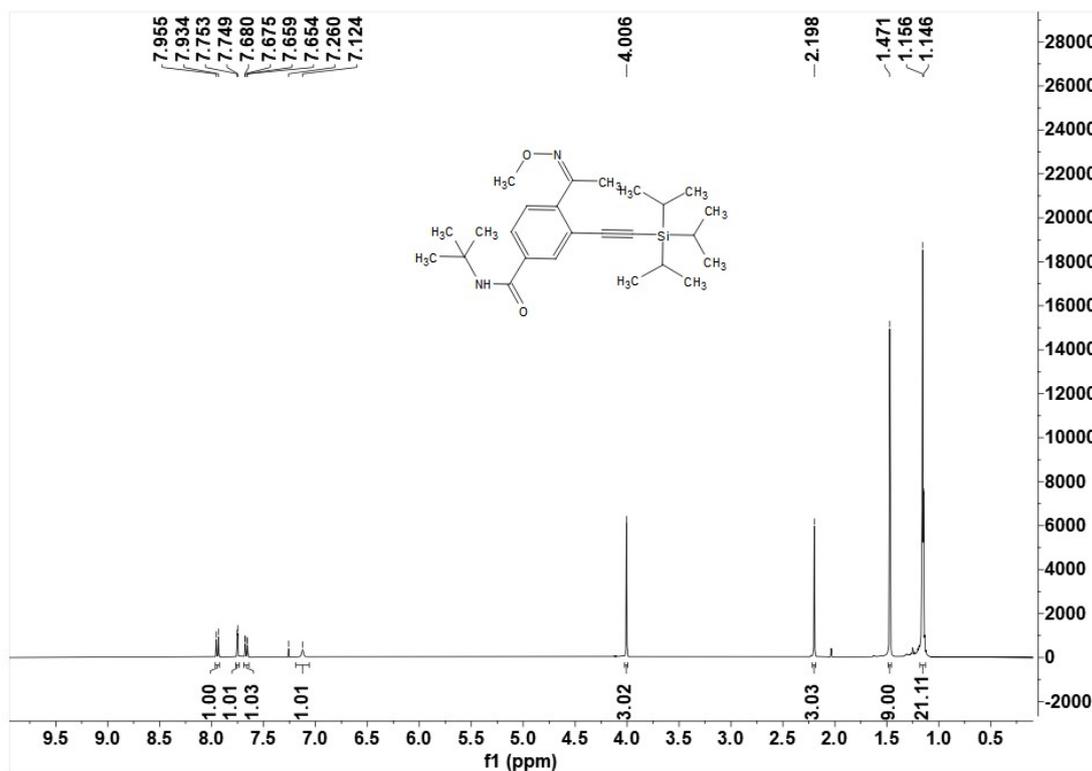


^{19}F NMR (376 MHz, CDCl_3)

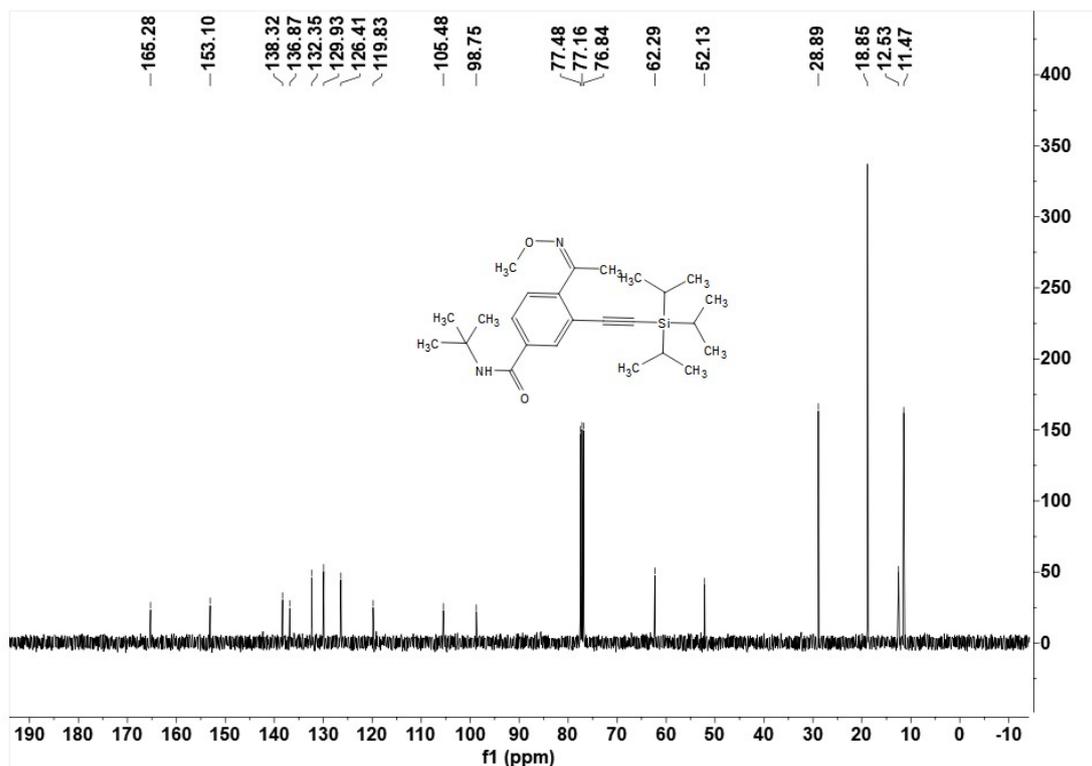


***N*-(*tert*-Butyl)-4-(1-(methoxyimino)ethyl)-3-
((triisopropylsilyl)ethynyl)benzamide (6d)**

¹H NMR (CDCl₃, 400 MHz)

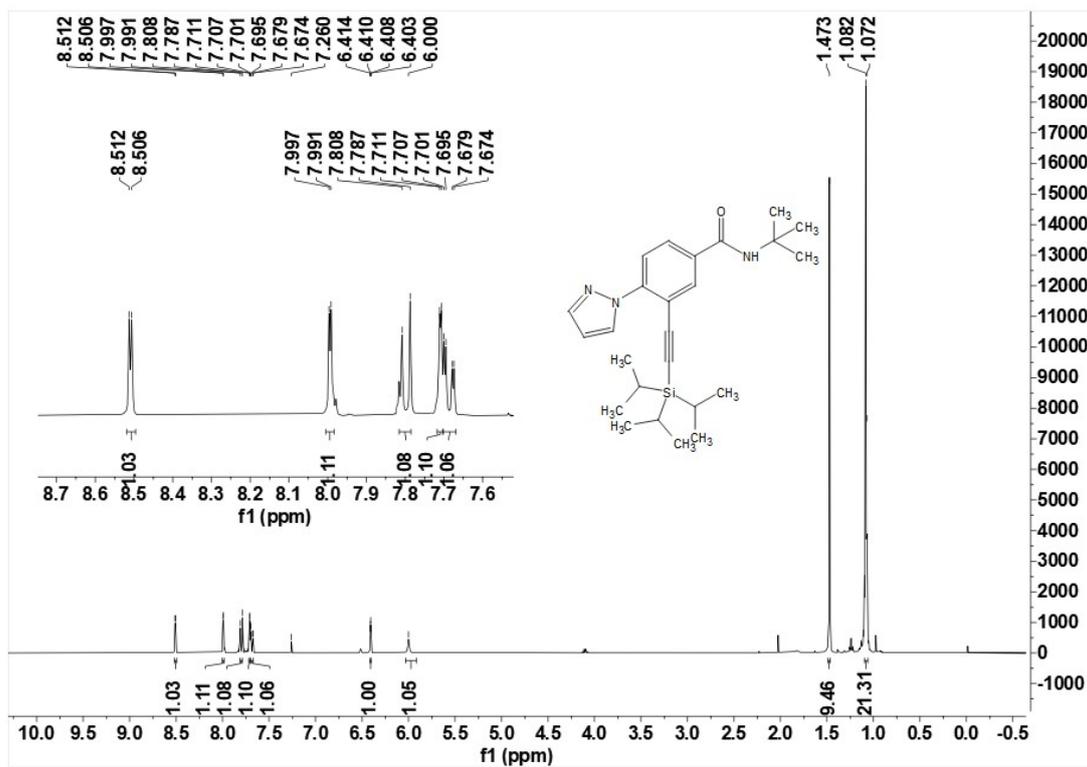


¹³C NMR (100 MHz, CDCl₃)

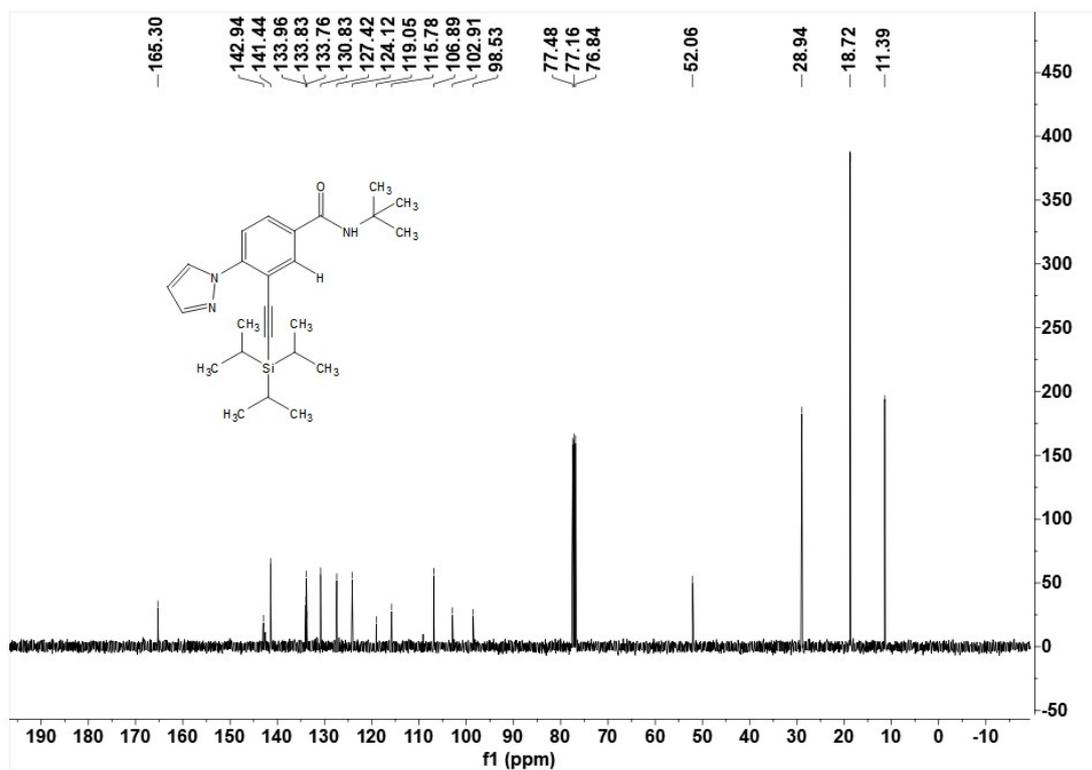


N-(*tert*-Butyl)-4-(1*H*-pyrazol-1-yl)-3-((triisopropylsilyl)ethynyl)benzamide (6e)

¹H NMR (CDCl₃, 400 MHz)

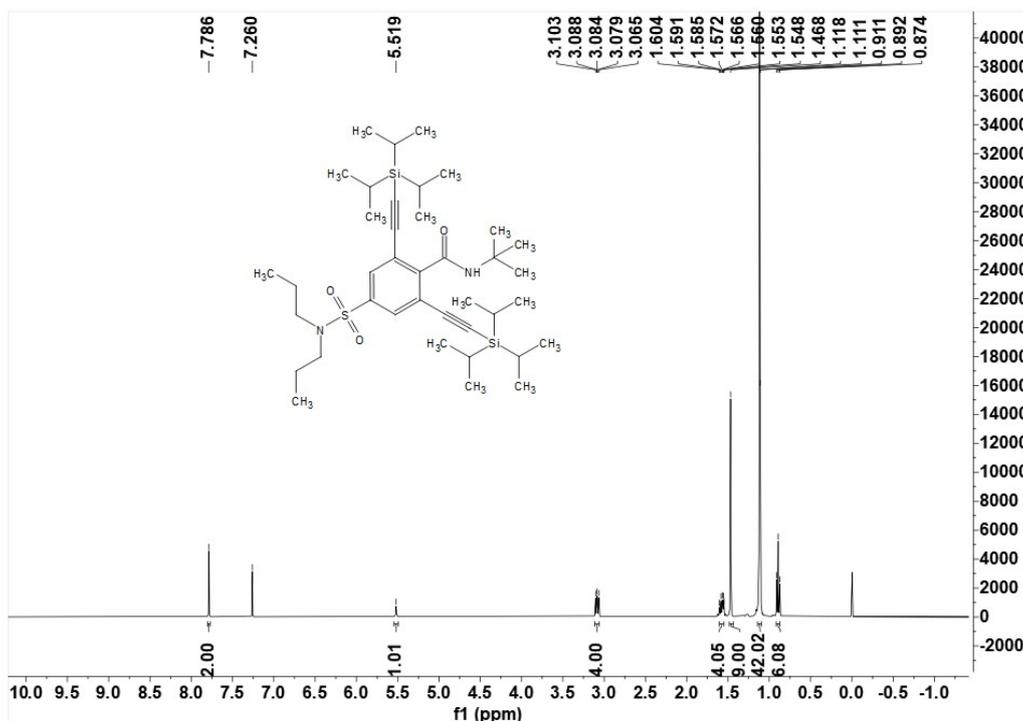


¹³C NMR (100 MHz, CDCl₃)

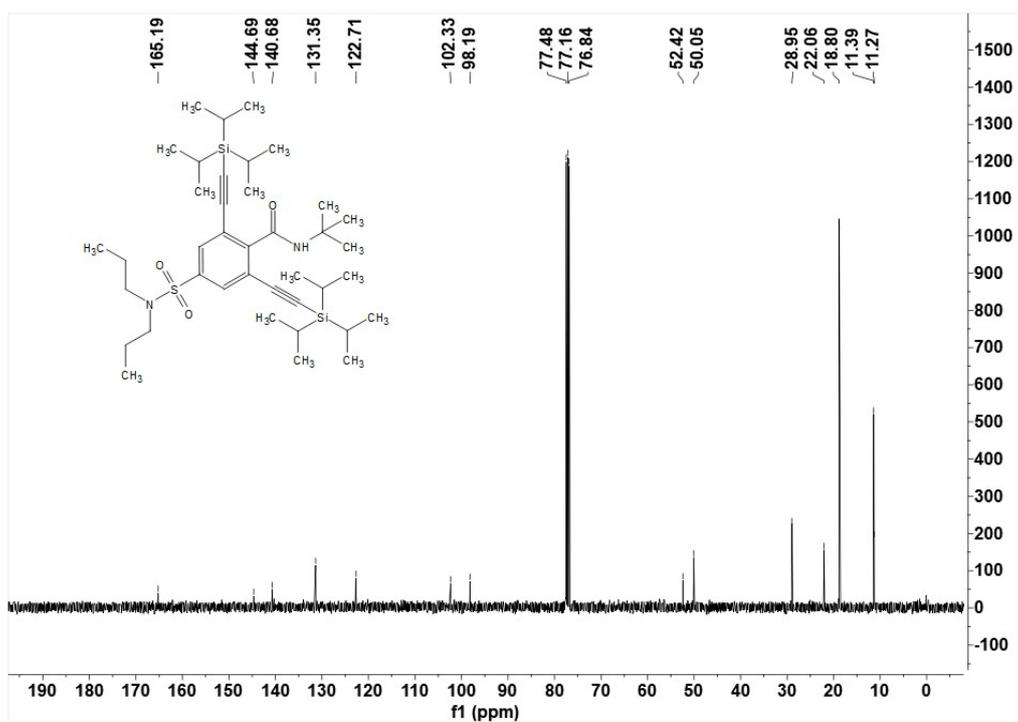


***N*-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2,6-bis((*triisopropylsilyl*)ethynyl)benzamide (3zc)**

^1H NMR (CDCl_3 , 400 MHz)



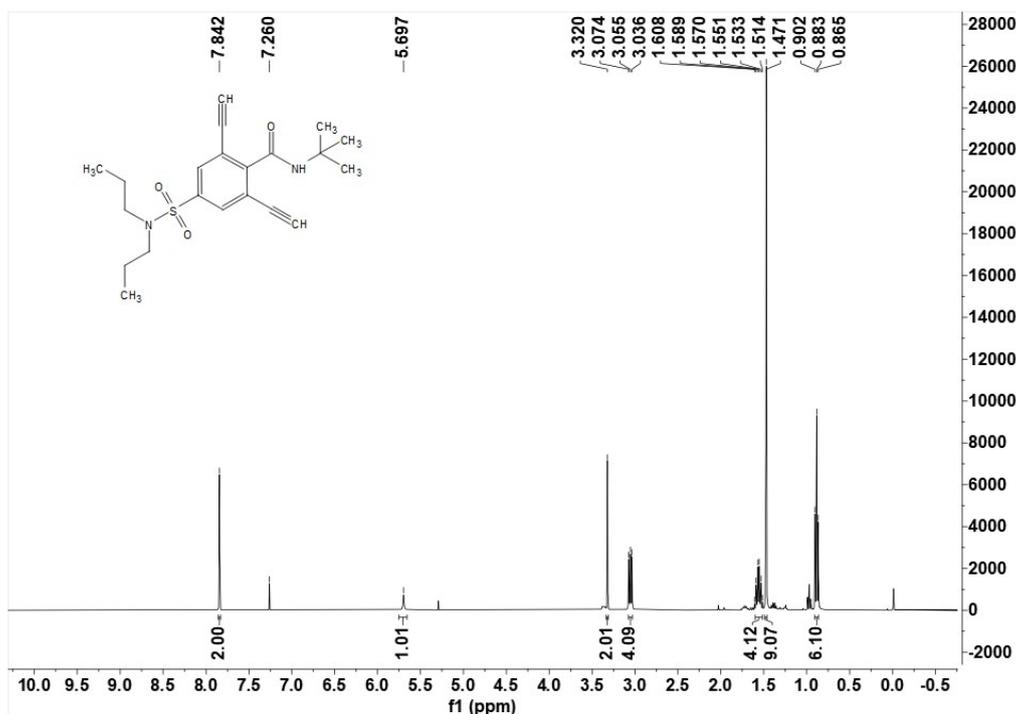
^{13}C NMR (100 MHz, CDCl_3)



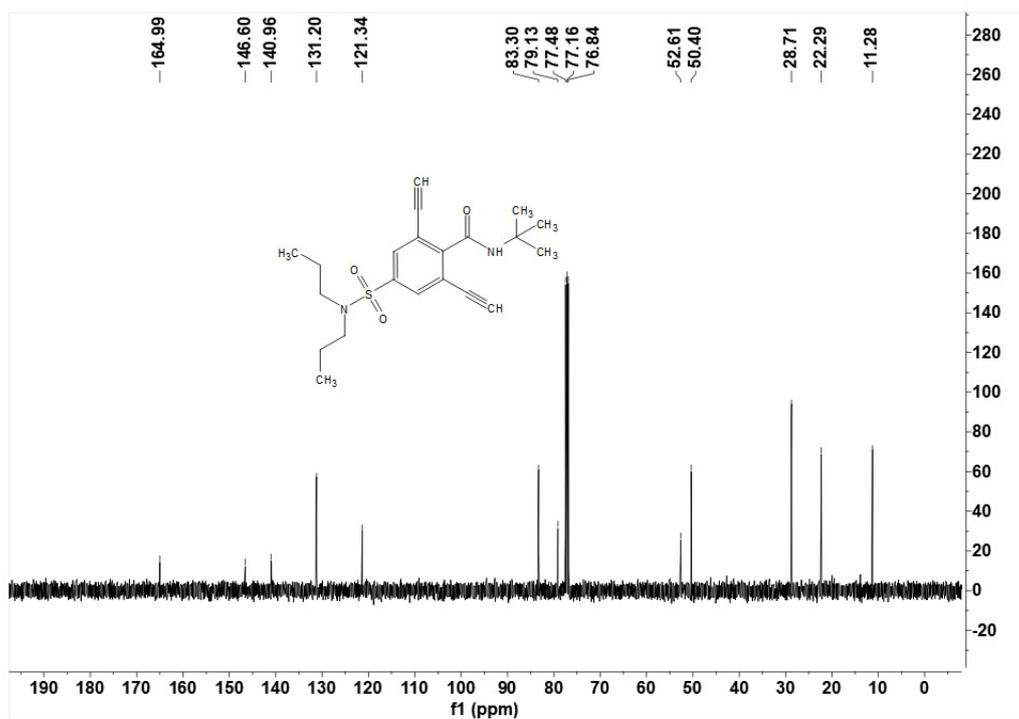
N-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2,6-diethynylbenzamide

(3zc-1)

¹H NMR (CDCl₃, 400 MHz)

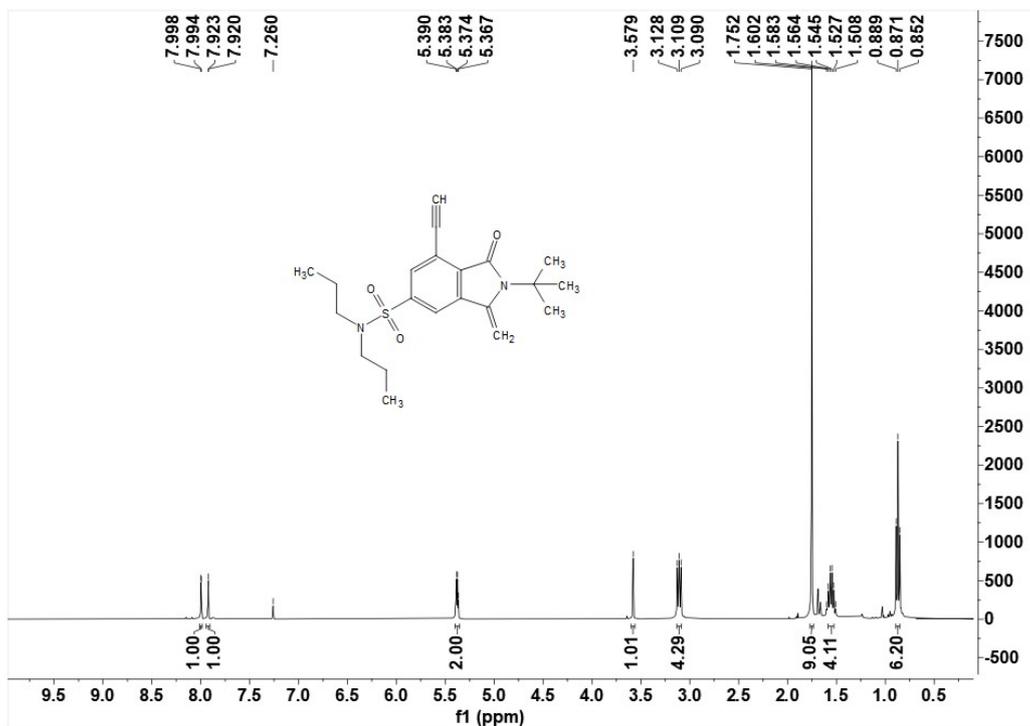


¹³C NMR (100 MHz, CDCl₃)

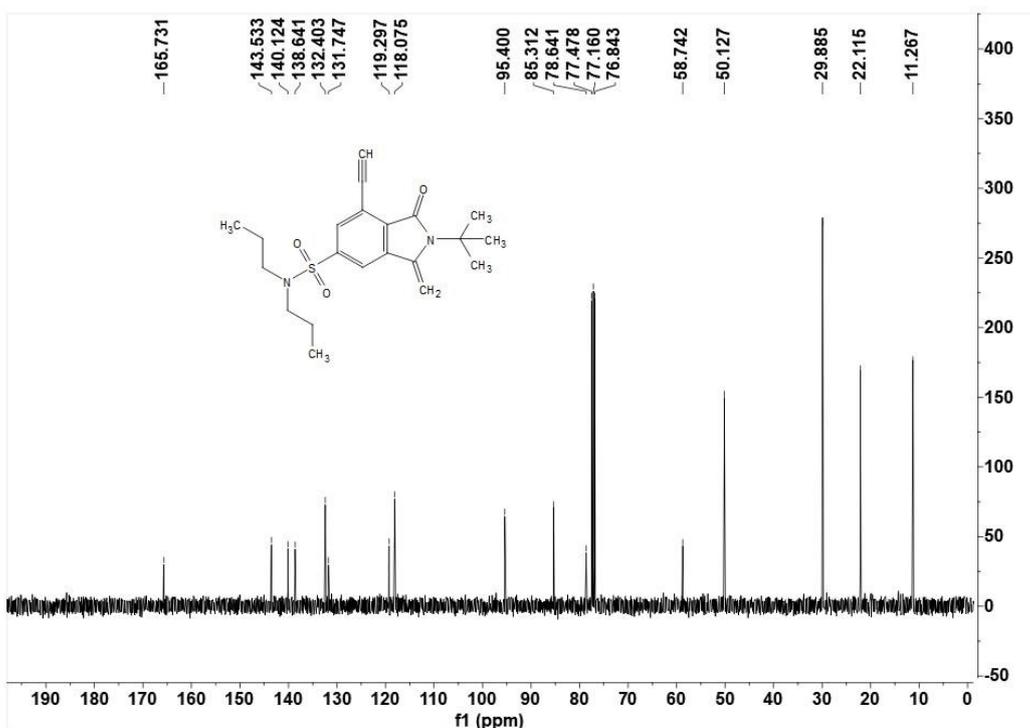


2-(*tert*-Butyl)-7-ethynyl-3-methylene-1-oxo-*N,N*-dipropylisoindoline-5-sulfonamide (3zc-3)

^1H NMR (CDCl_3 , 400 MHz)

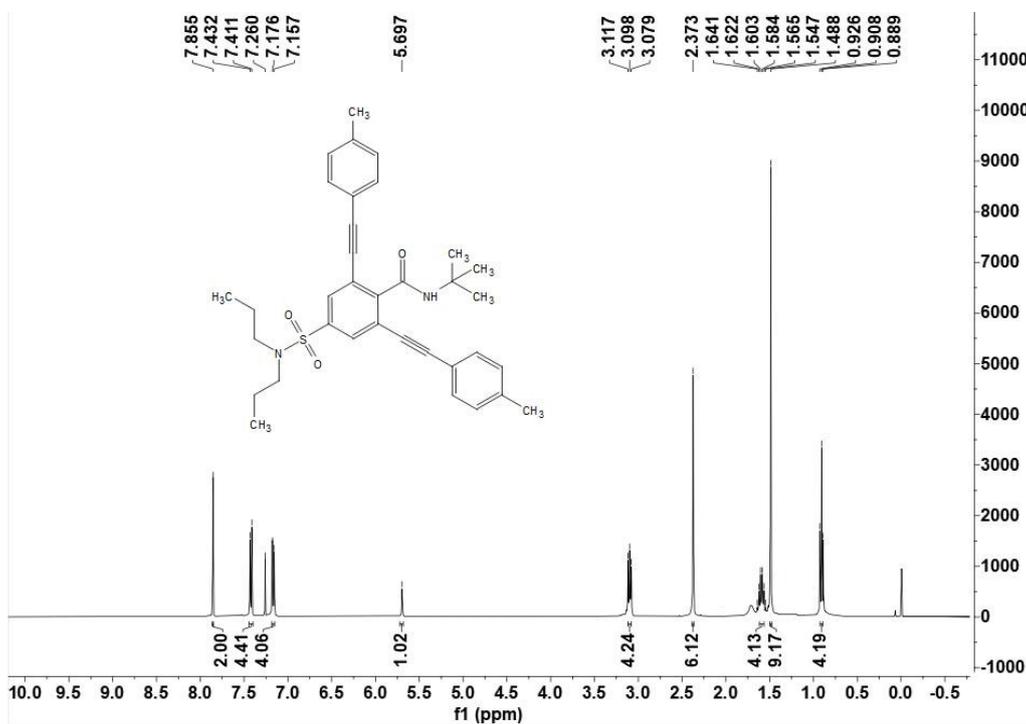


^{13}C NMR (100 MHz, CDCl_3)

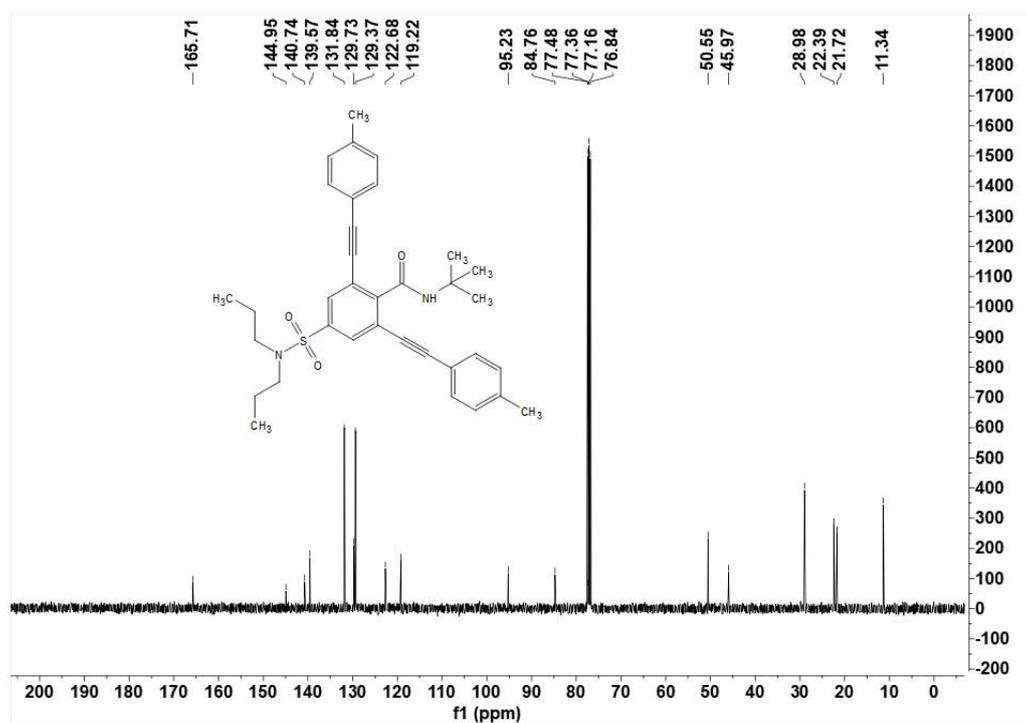


***N*-(*tert*-Butyl)-4-(*N,N*-dipropylsulfamoyl)-2,6-bis(*p*-tolylethynyl)benzamide
(3zc-2)**

¹H NMR (CDCl₃, 400 MHz)

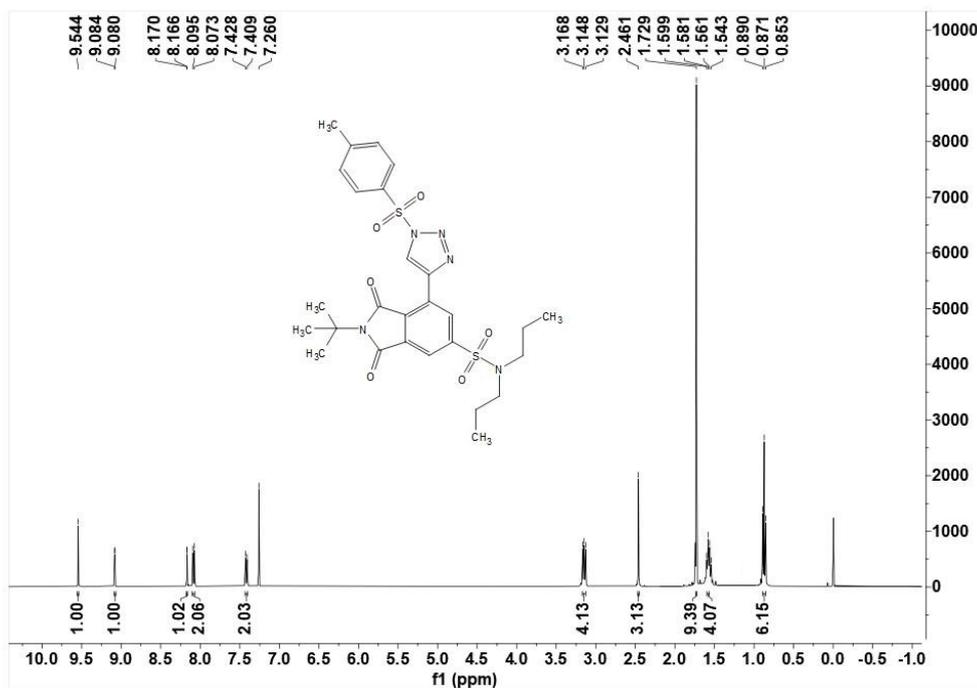


¹³C NMR (100 MHz, CDCl₃)

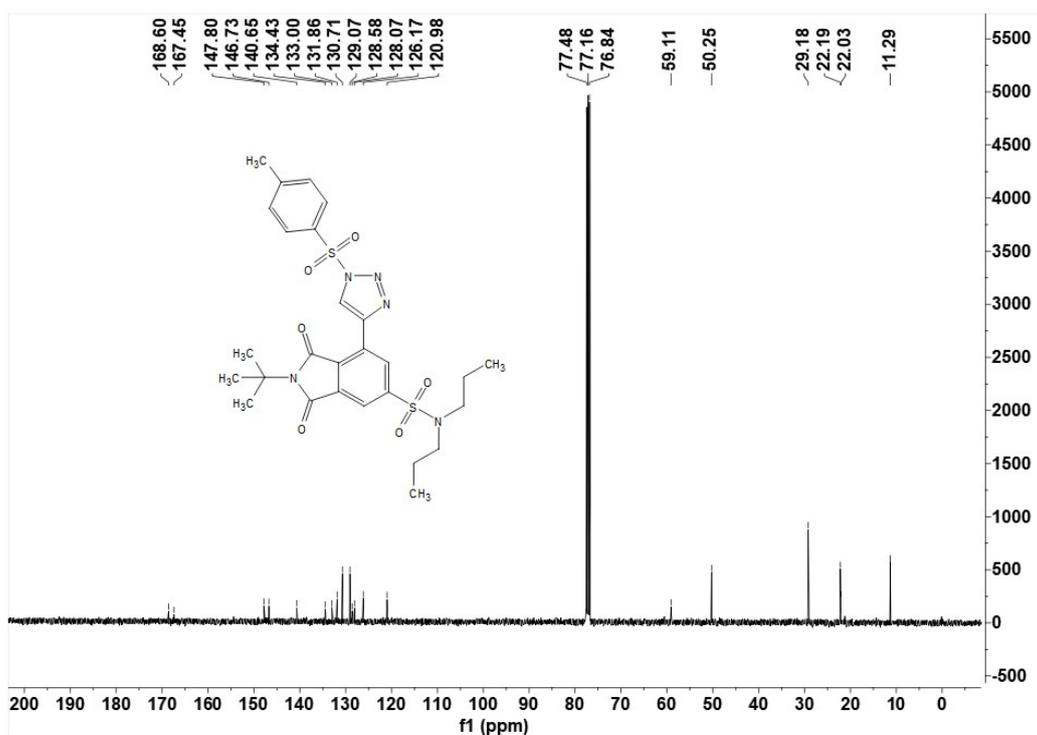


2-(*tert*-Butyl)-1,3-dioxo-*N,N*-dipropyl-7-(1-tosyl-1*H*-1,2,3-triazol-4-yl)isoindoline-5-sulfonamide(3zc-4)

¹H NMR (CDCl₃, 400 MHz)

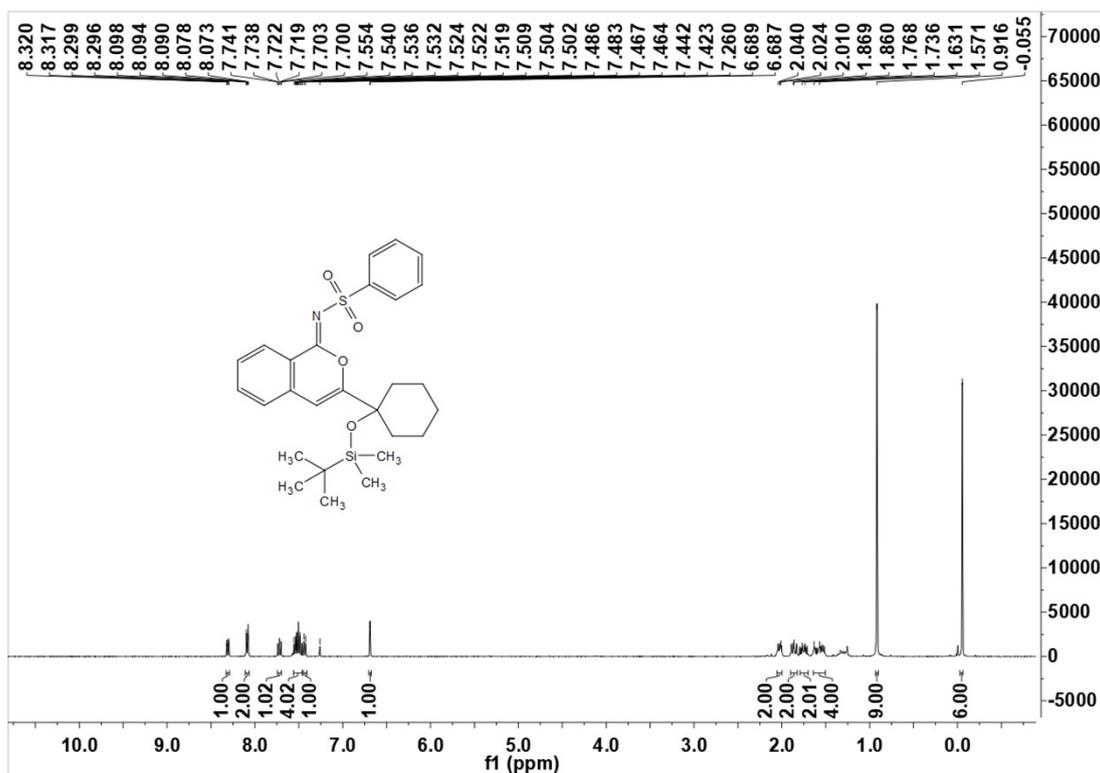


¹³C NMR (100 MHz, CDCl₃)

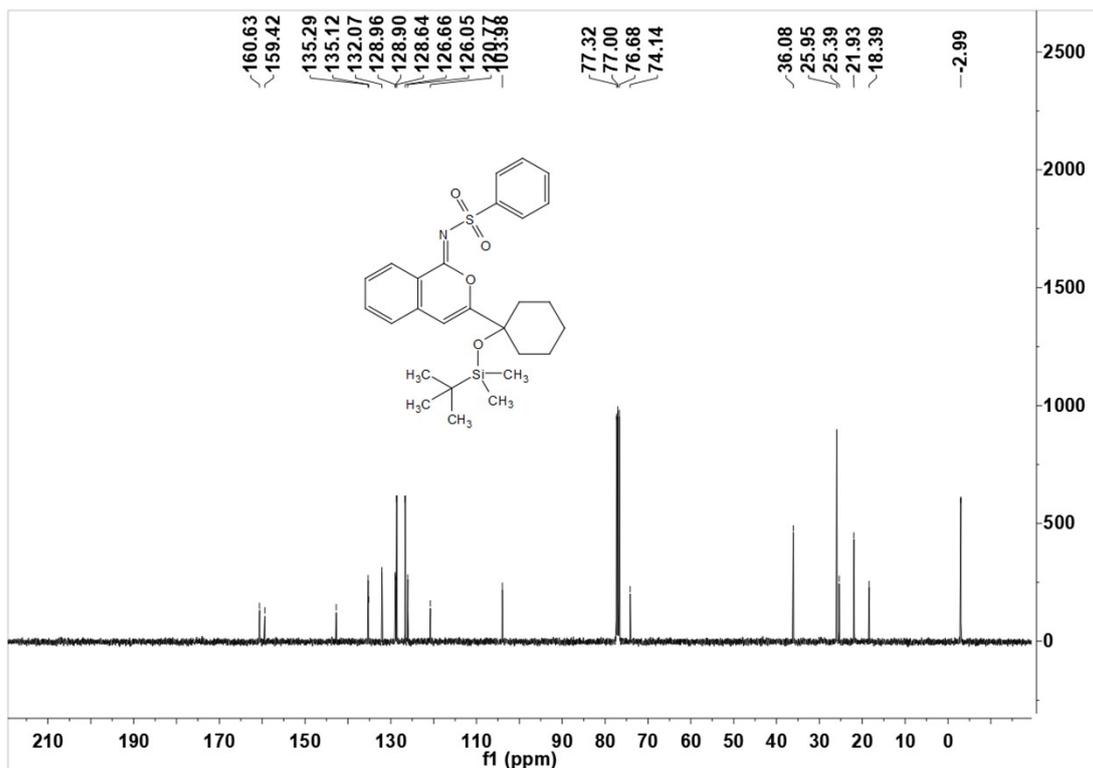


(Z)-N-(3-(1-((*tert*-butyldimethylsilyloxy)cyclohexyl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (4a),

¹H NMR (400 MHz, CDCl₃)

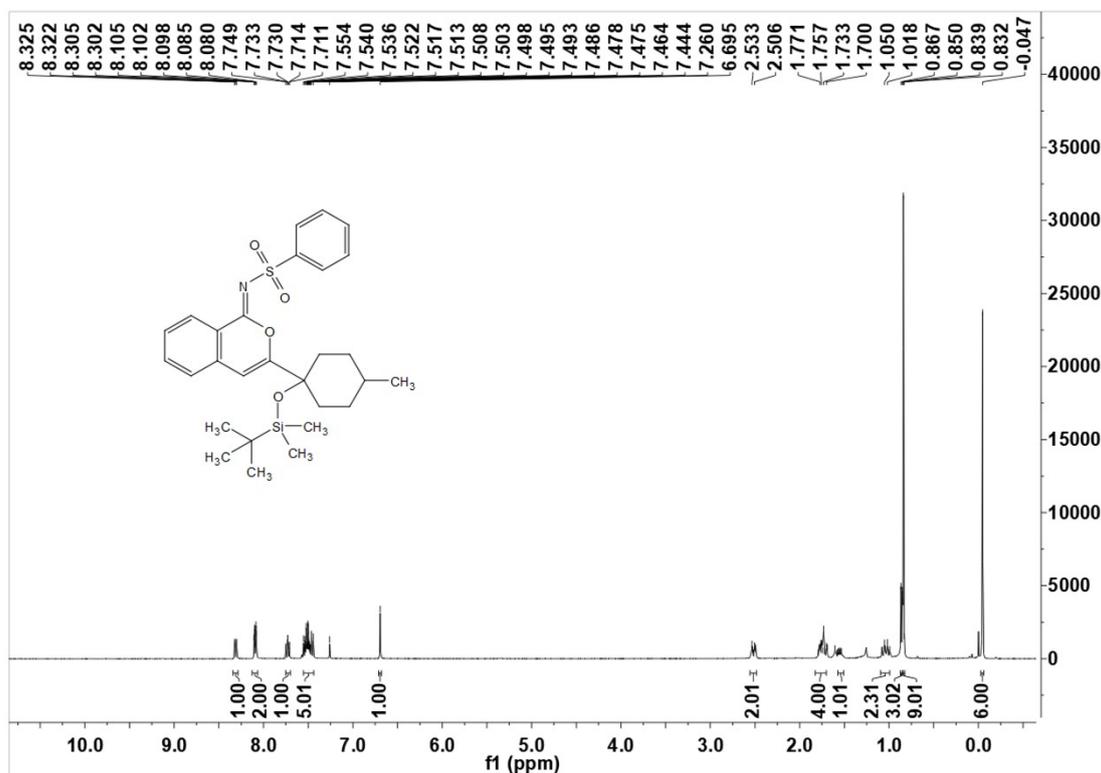


¹³C NMR (100 MHz, CDCl₃)

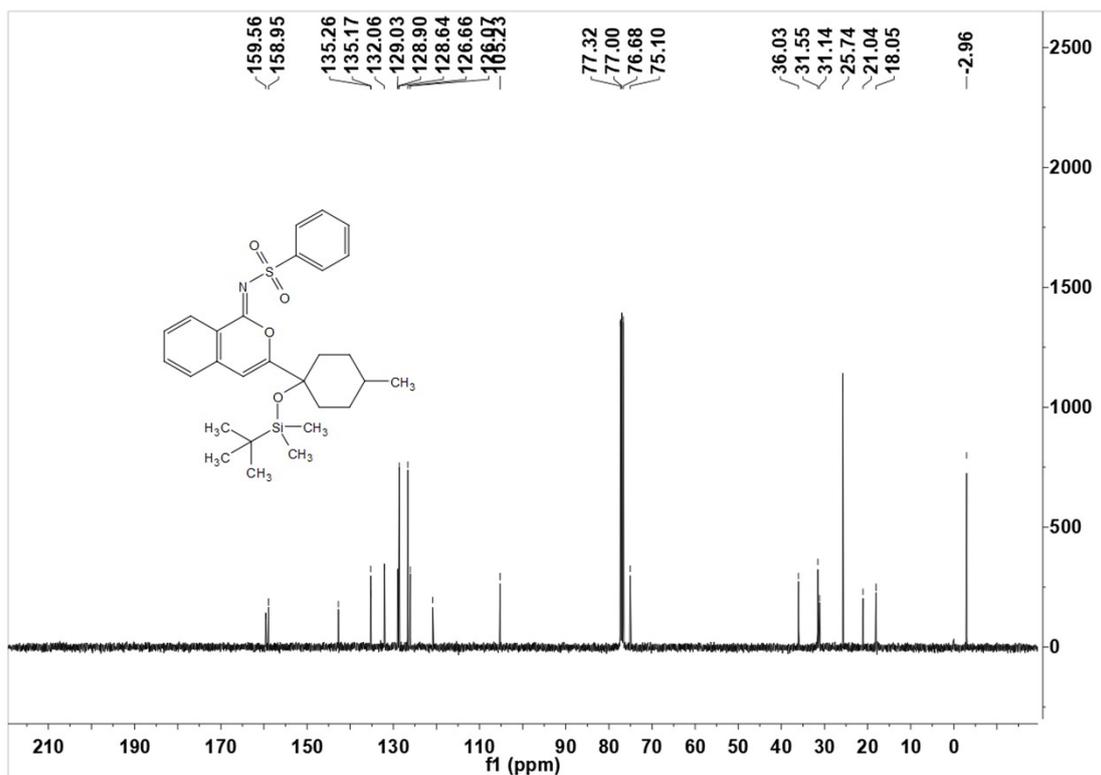


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyloxy)-4-methylcyclohexyl)-1*H*-
isochromen-1-ylidene)benzenesulfonamide (4b)

¹H NMR (400 MHz, CDCl₃)

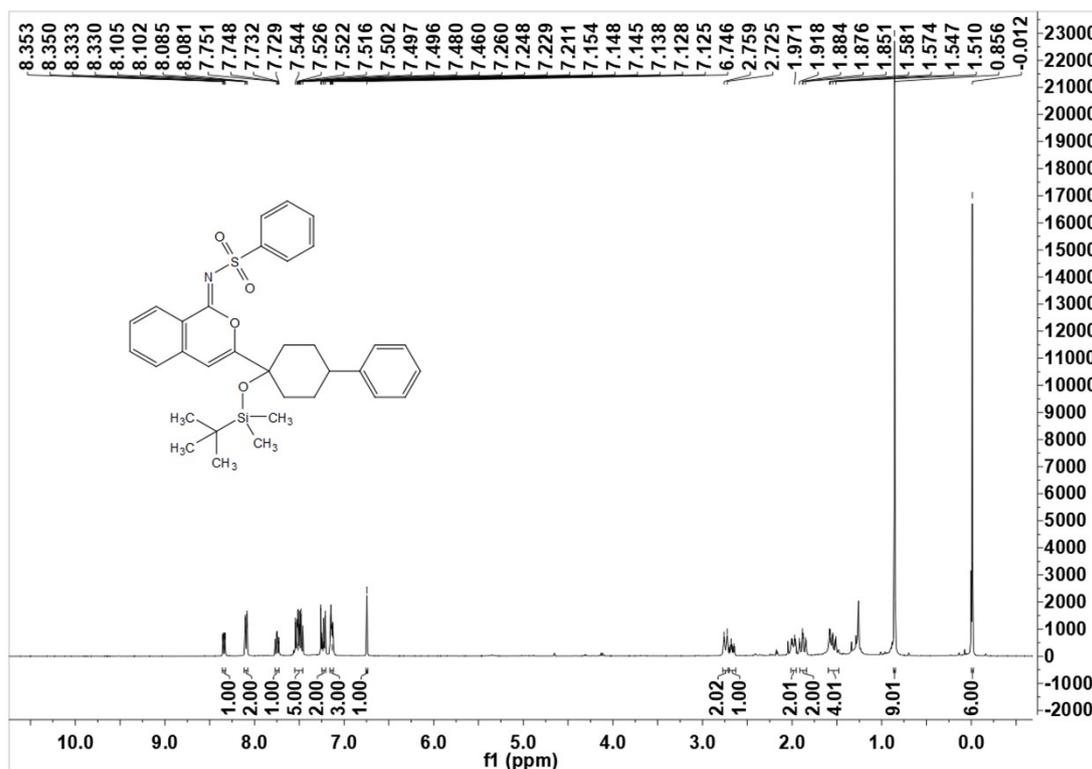


¹³C NMR (100 MHz, CDCl₃)

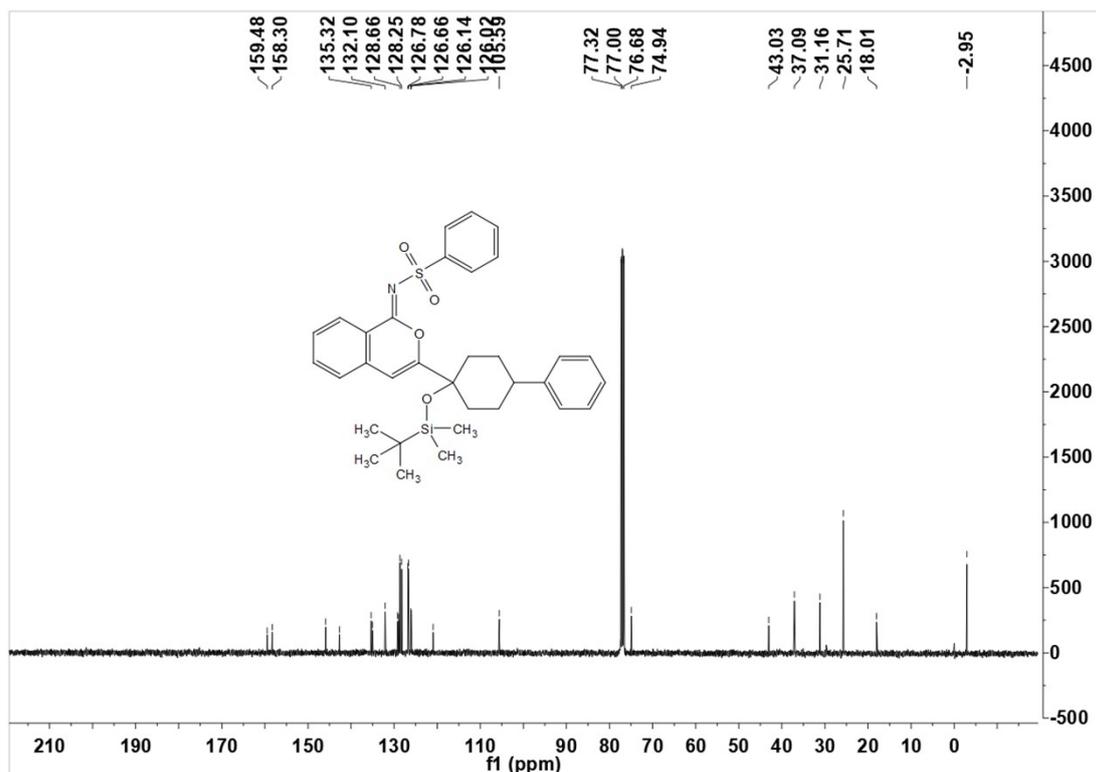


**(Z)-N-(3-(1-((*tert*-Butyldimethylsilyloxy)-4-phenylcyclohexyl)-1*H*-
isochromen-1-ylidene)benzenesulfonamide (4c)**

¹H NMR (400 MHz, CDCl₃)

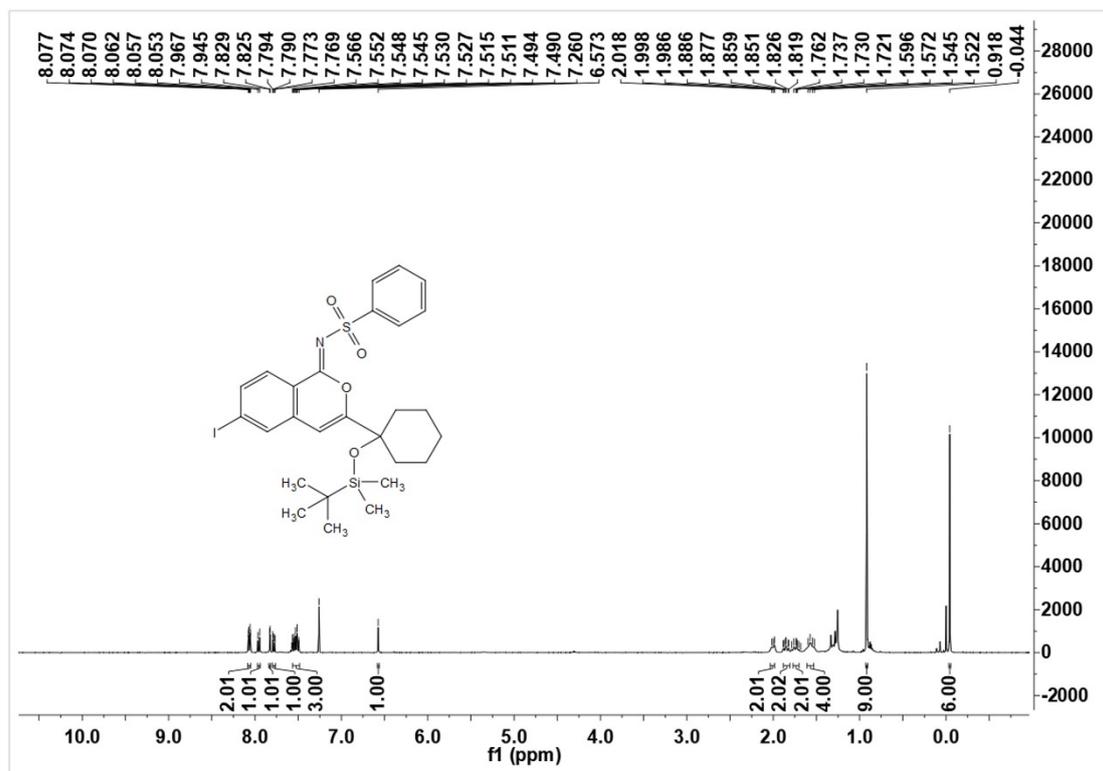


¹³C NMR (100 MHz, CDCl₃)

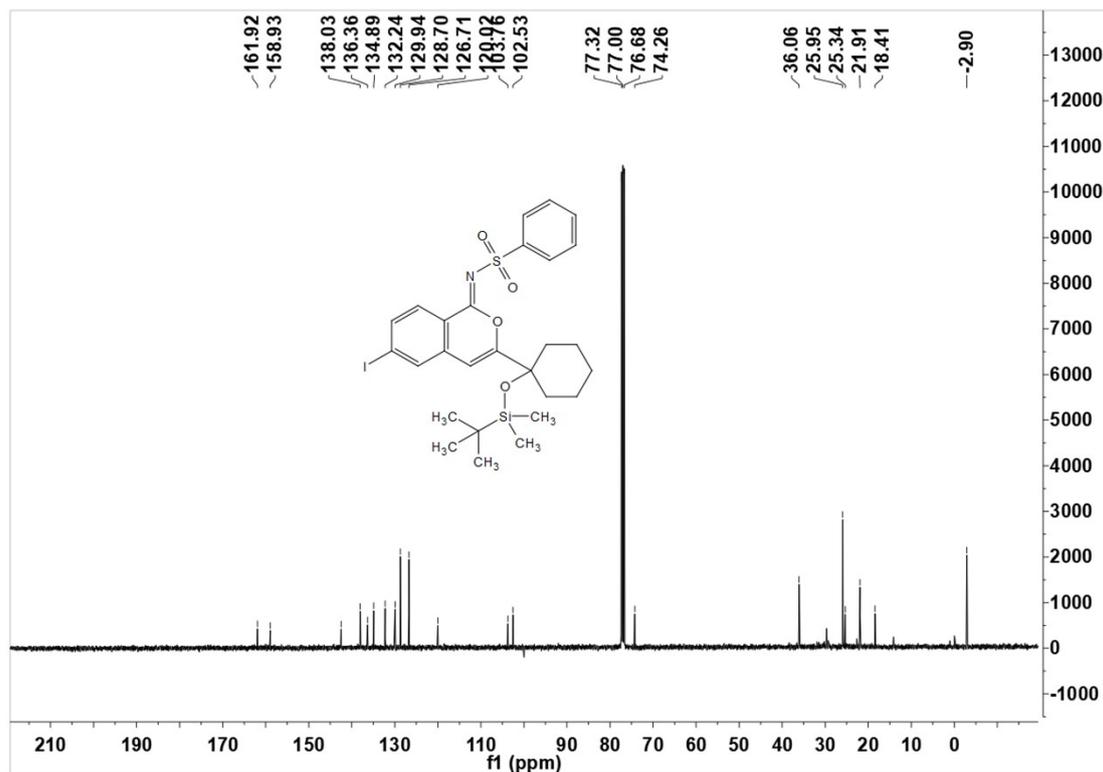


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyloxy)cyclohexyl)-6-iodo-1*H*-isochromen-1-ylidene)benzenesulfonamide (4d)

¹H NMR (400 MHz, CDCl₃)

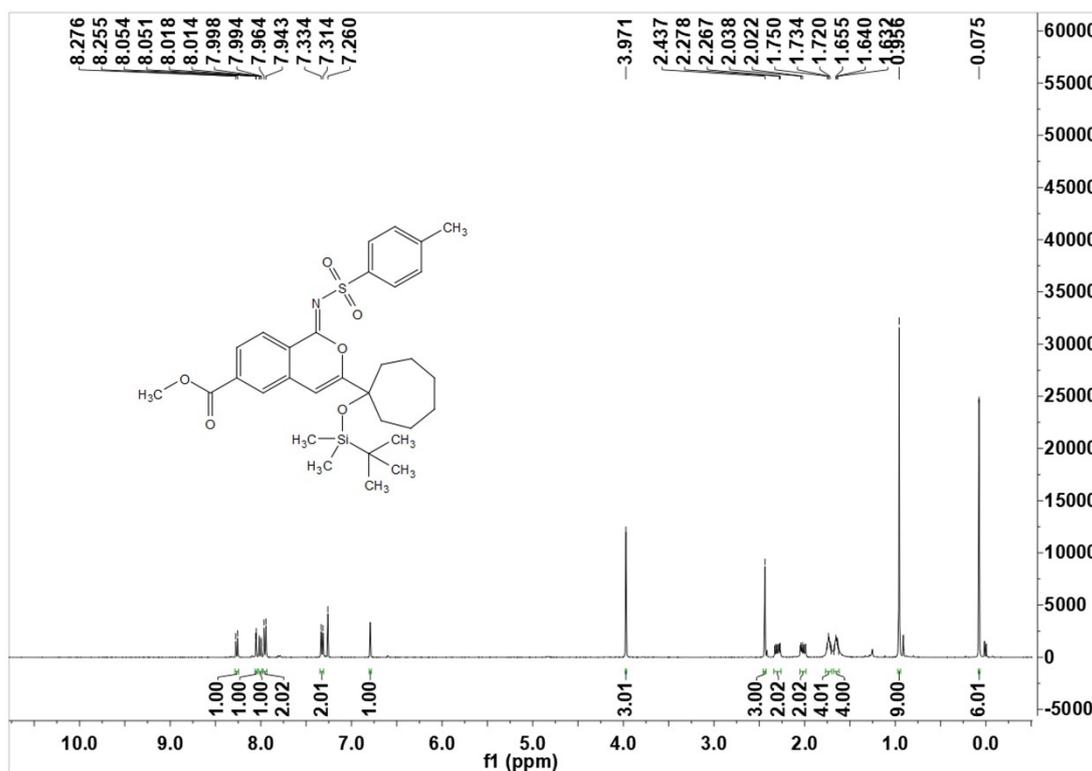


¹³C NMR (100 MHz, CDCl₃)

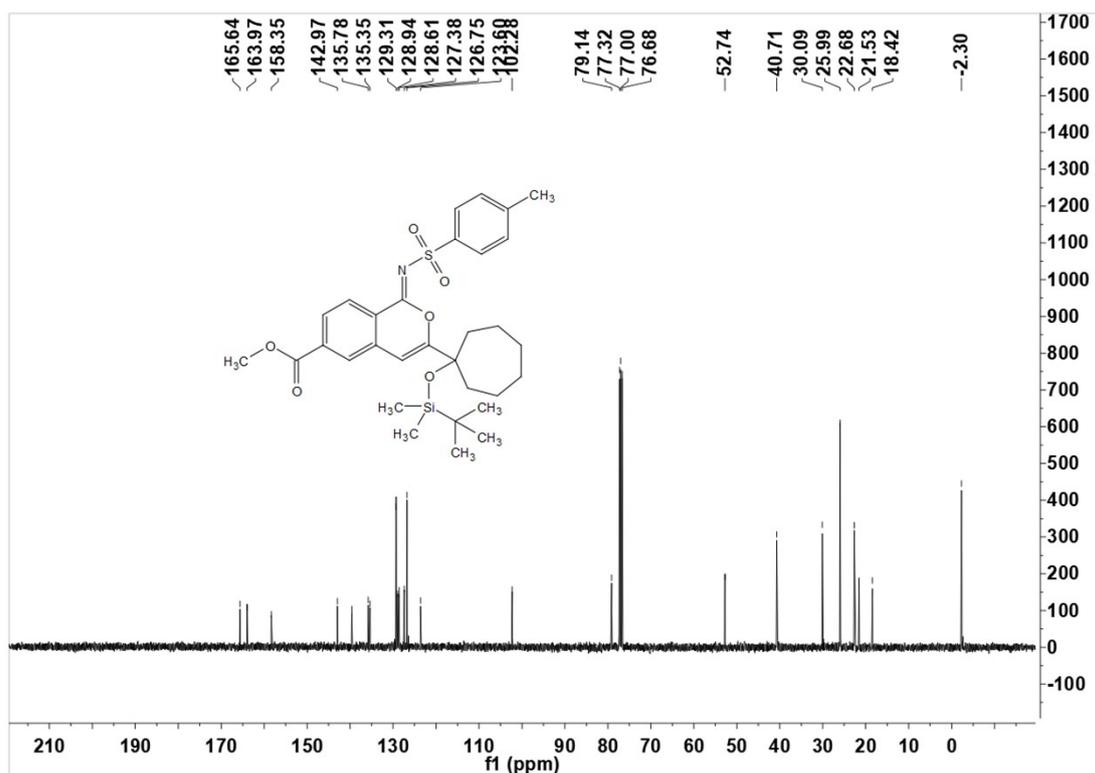


Methyl (Z)-3-(1-((*tert*-butyldimethylsilyloxy)cycloheptyl)-1-(tosylimino)-1H-
isochromene-6-carboxylate (4e)

¹H NMR (400 MHz, CDCl₃)

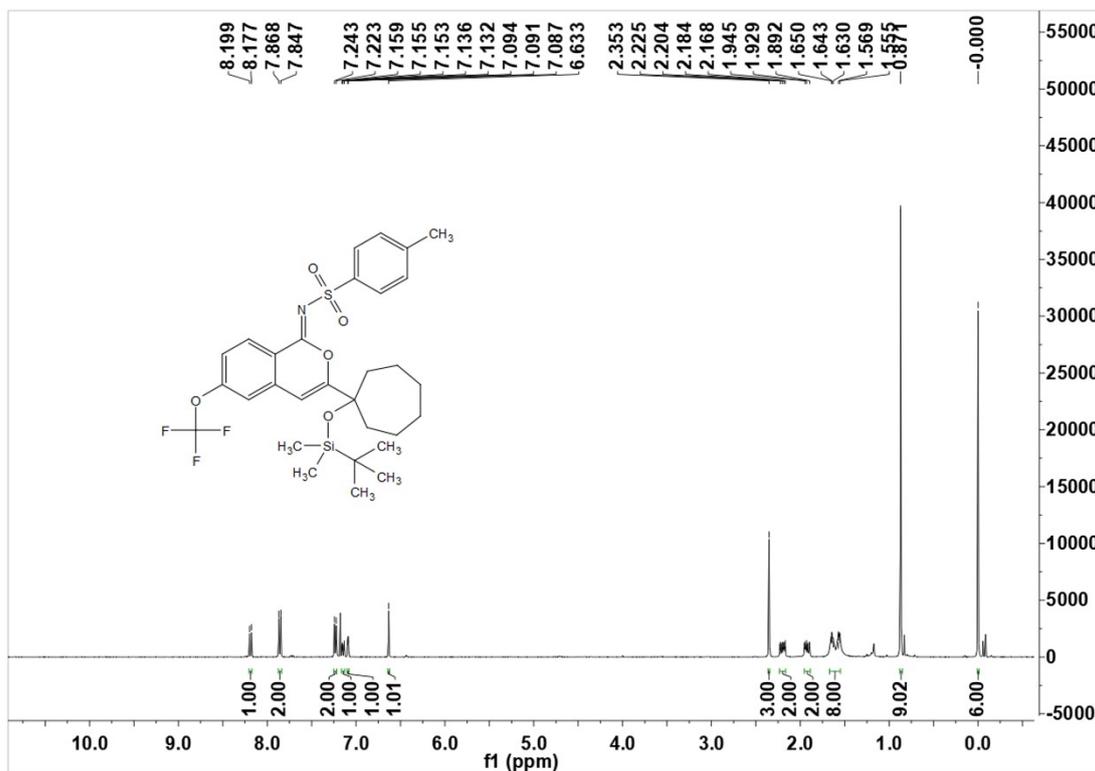


¹³C NMR (100 MHz, CDCl₃)

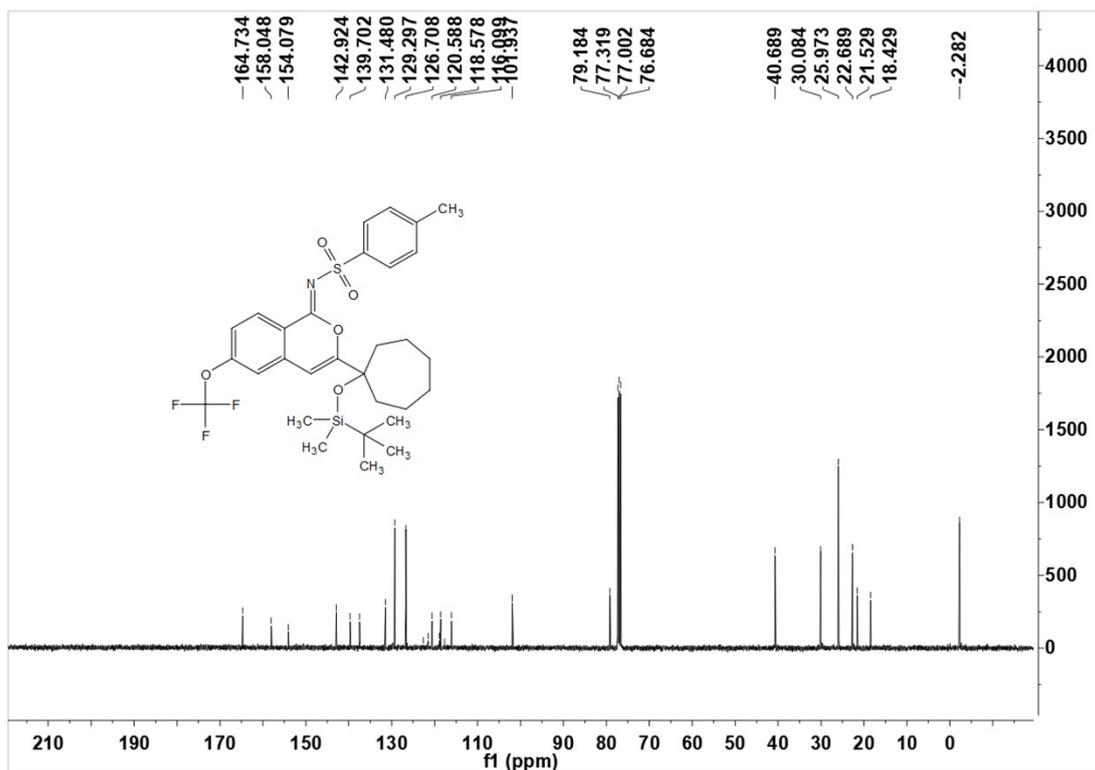


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyloxy)cycloheptyl)-6-(trifluoromethoxy)-1*H*-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4f)

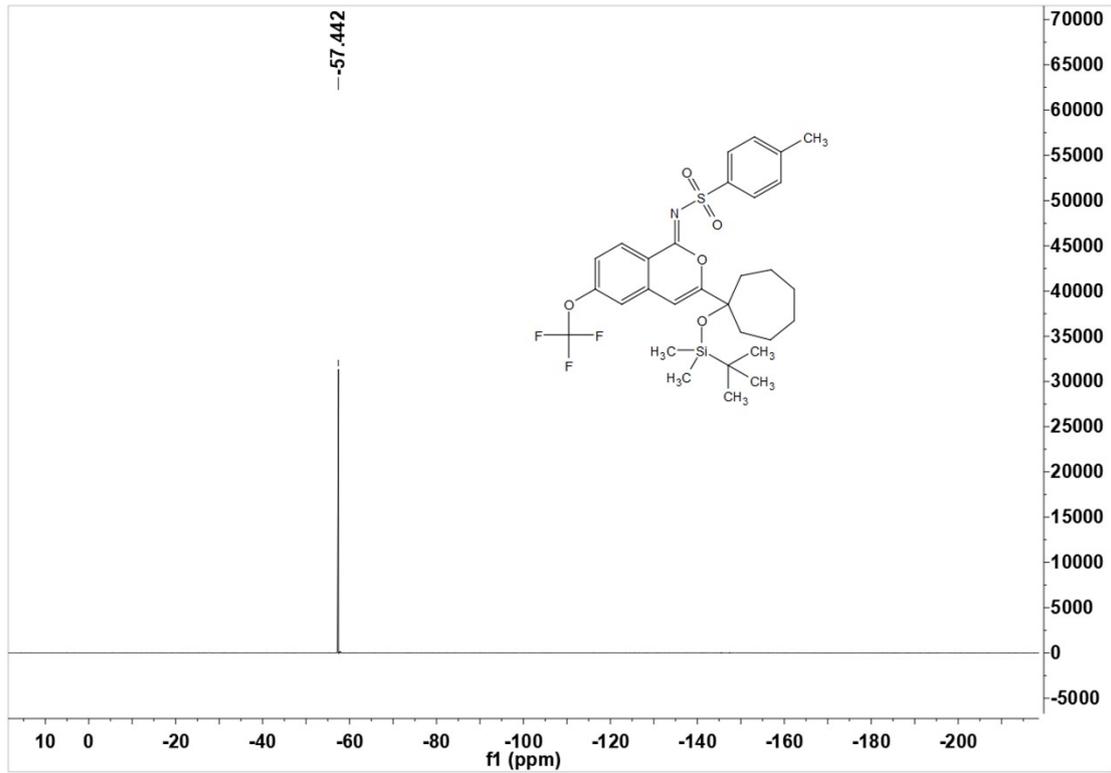
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

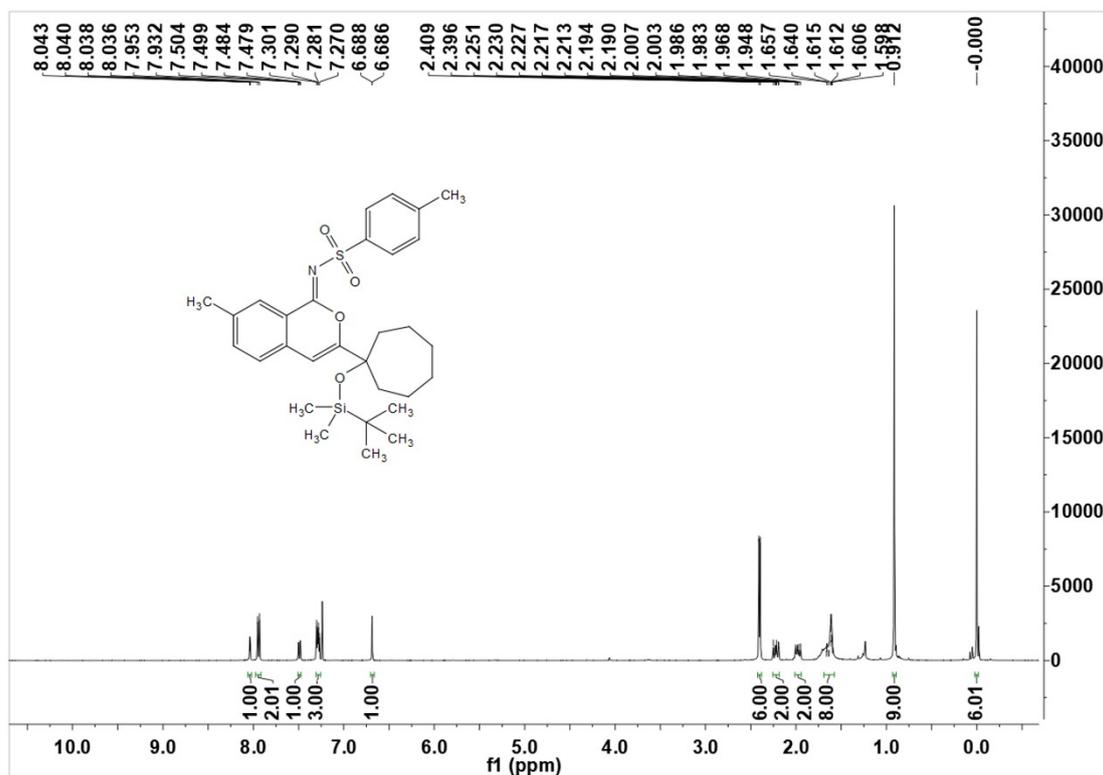


¹⁹F NMR (376 MHz, CDCl₃)

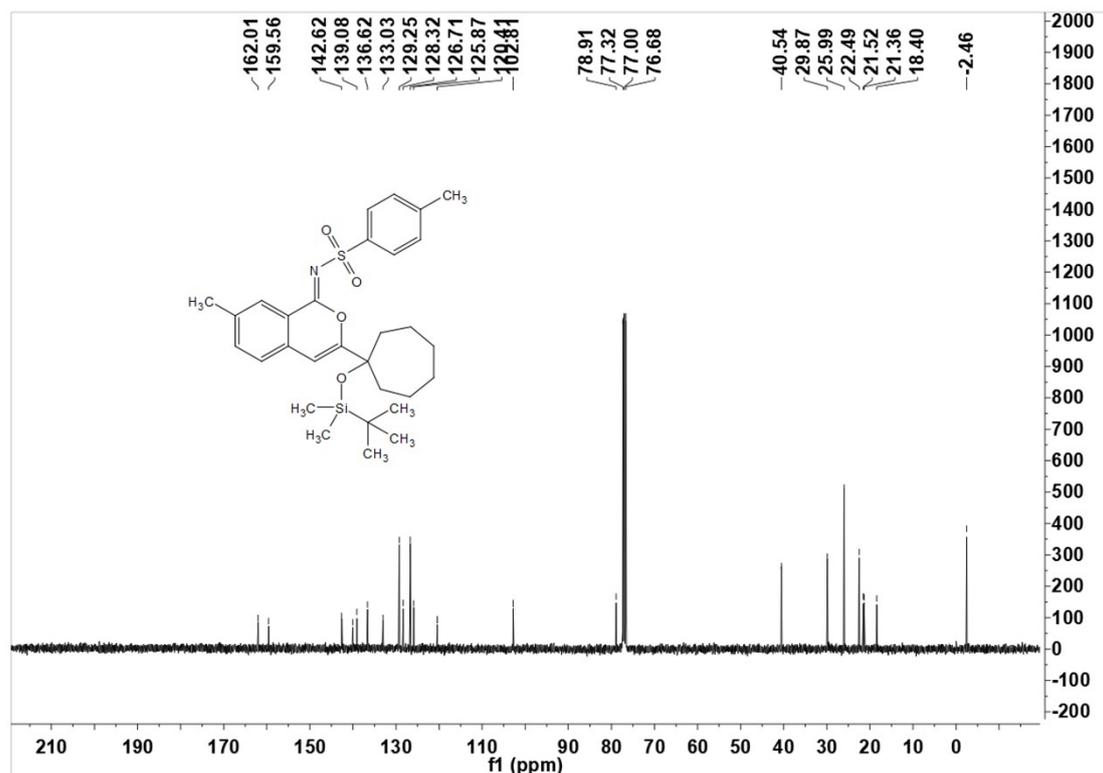


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyl)oxy)cycloheptyl)-6-(trifluoromethoxy)-1*H*-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4g)

¹H NMR (400 MHz, CDCl₃)

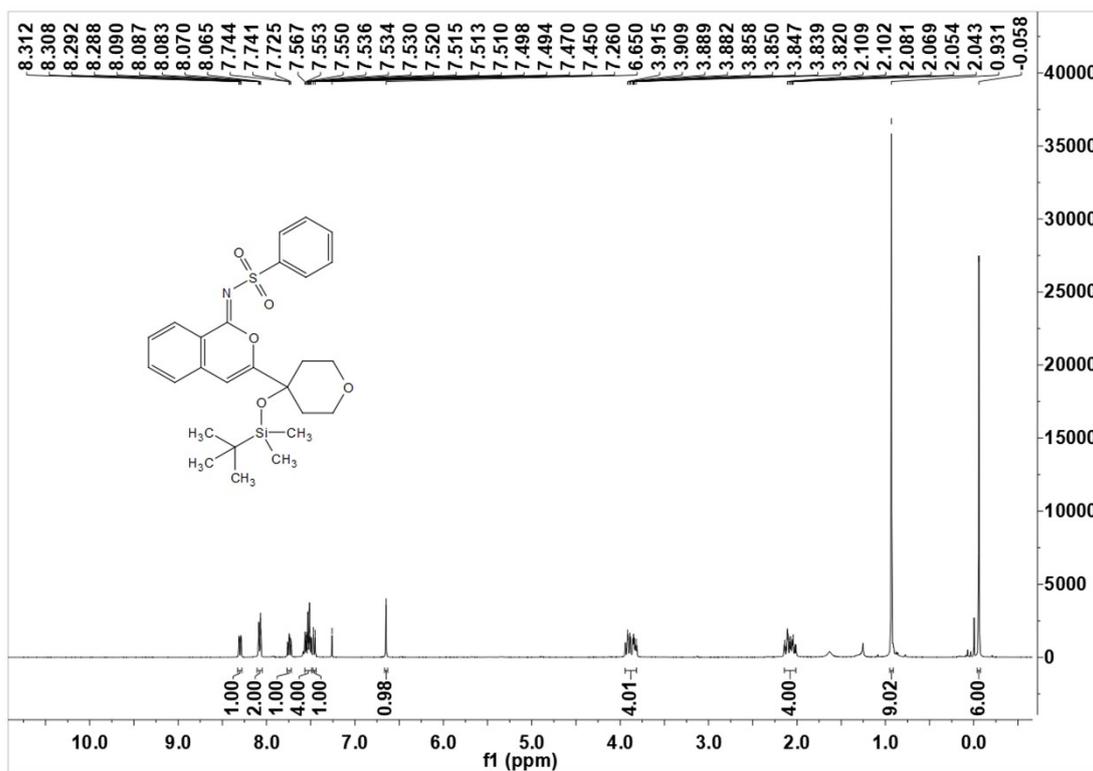


¹³C NMR (100 MHz, CDCl₃)

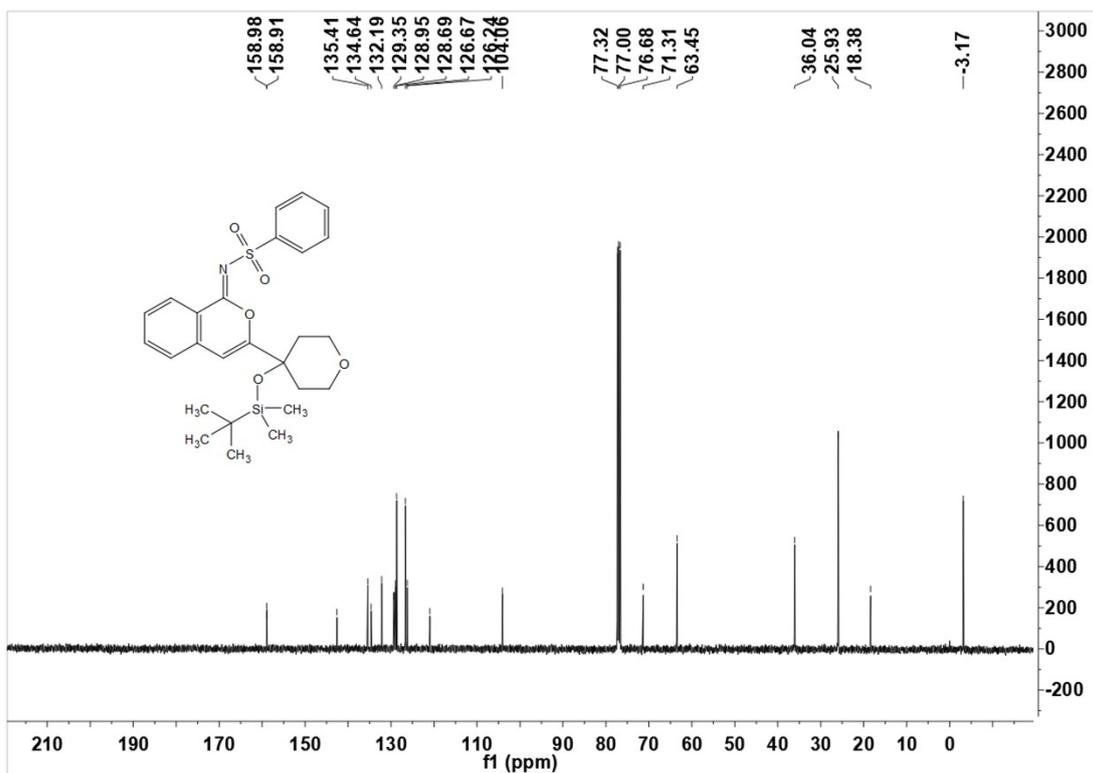


**(Z)-N-(3-(4-((*tert*-butyldimethylsilyl)oxy)tetrahydro-2H-pyran-4-yl)-1H-
isochromen-1-ylidene)benzenesulfonamide (4h)**

¹H NMR (400 MHz, CDCl₃)

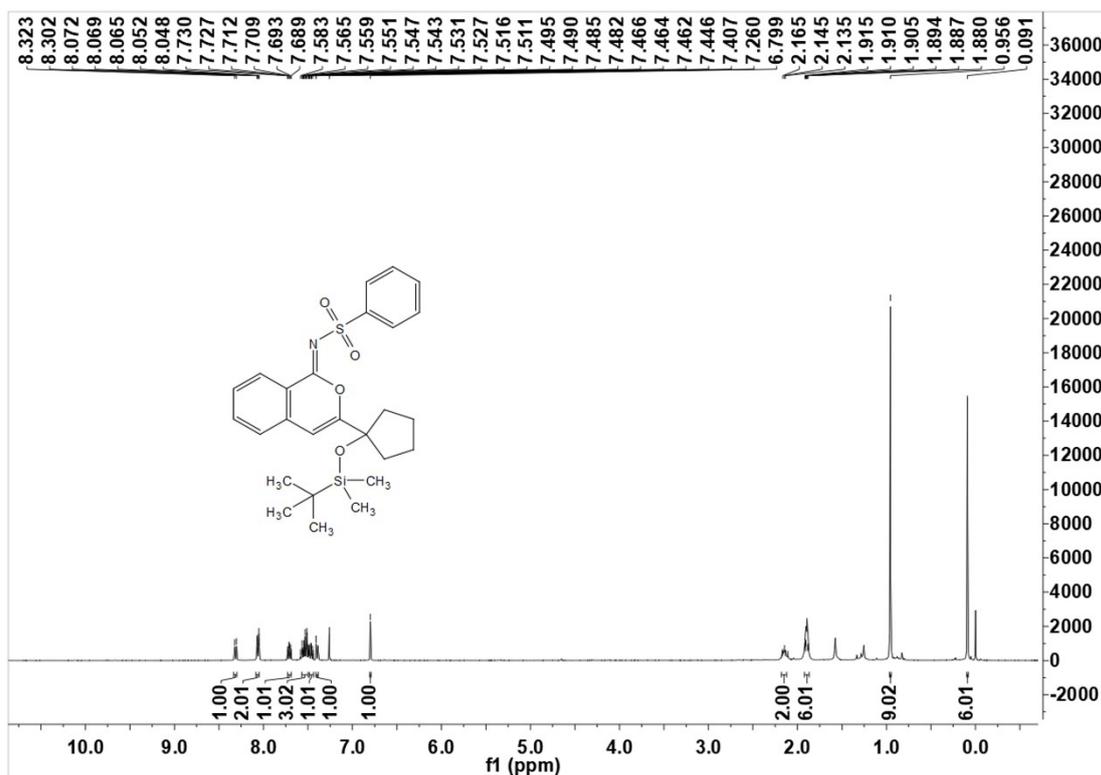


¹³C NMR (100 MHz, CDCl₃)

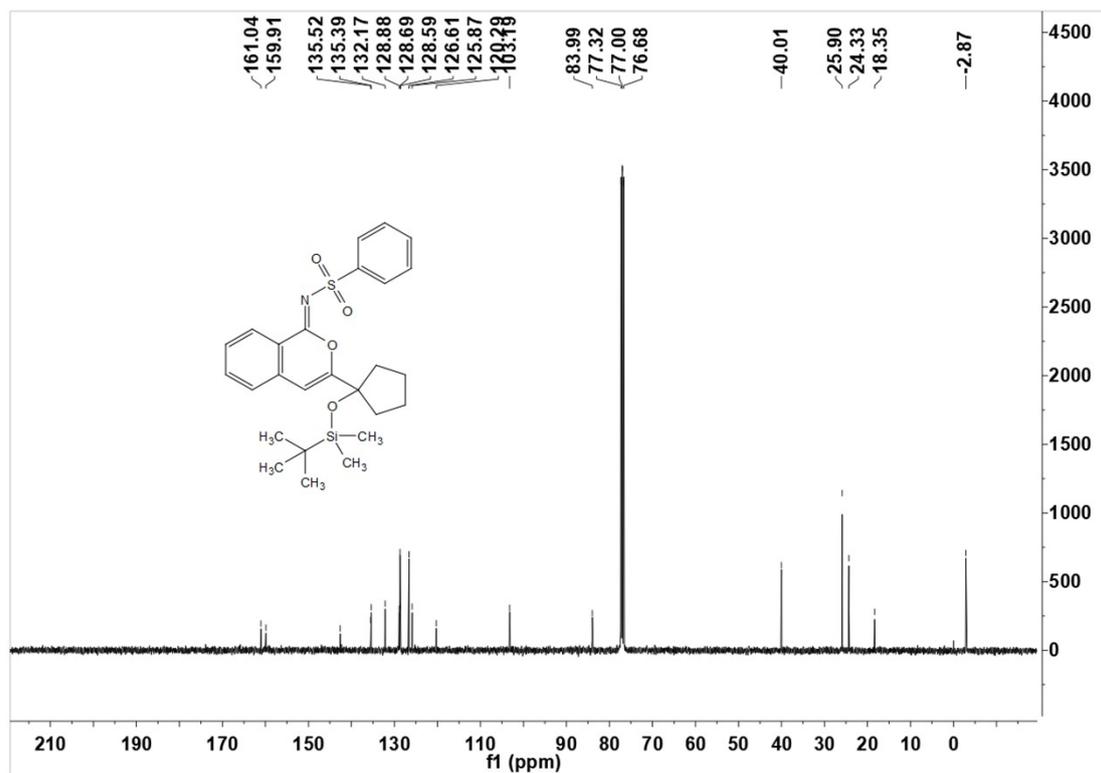


(Z)-N-(3-(1-((*tert*-butyldimethylsilyloxy)cyclopentyl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (4i)

¹H NMR (400 MHz, CDCl₃)

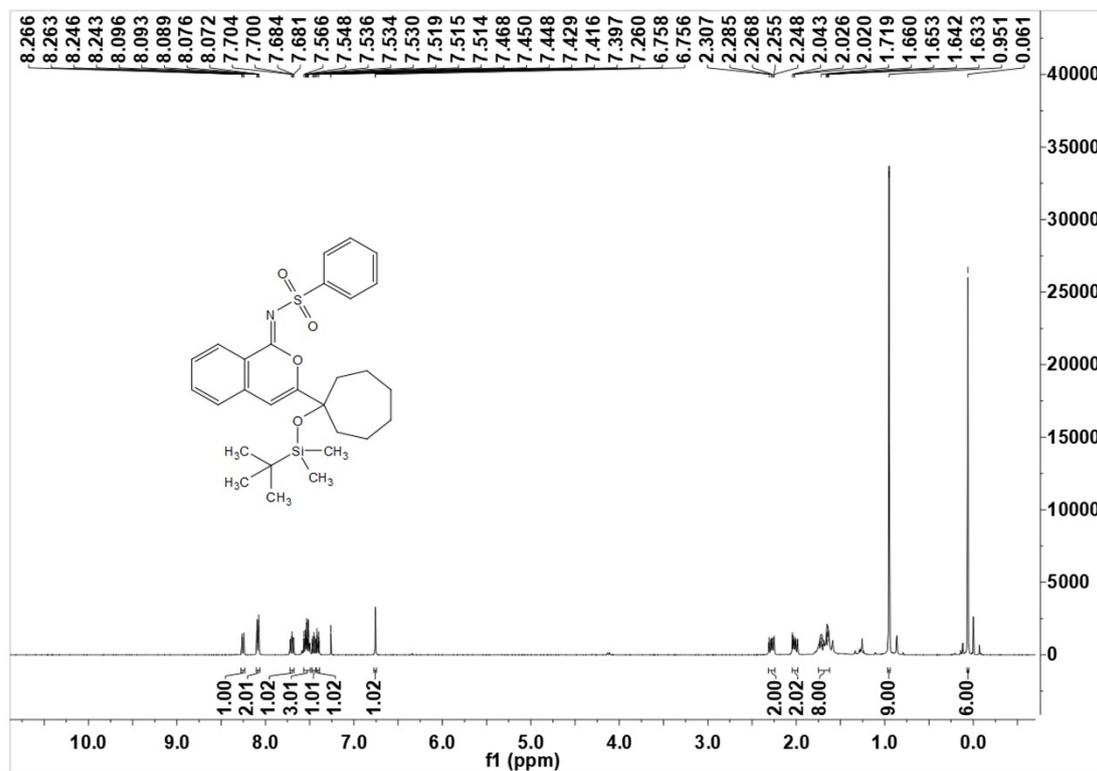


¹³C NMR (100 MHz, CDCl₃)

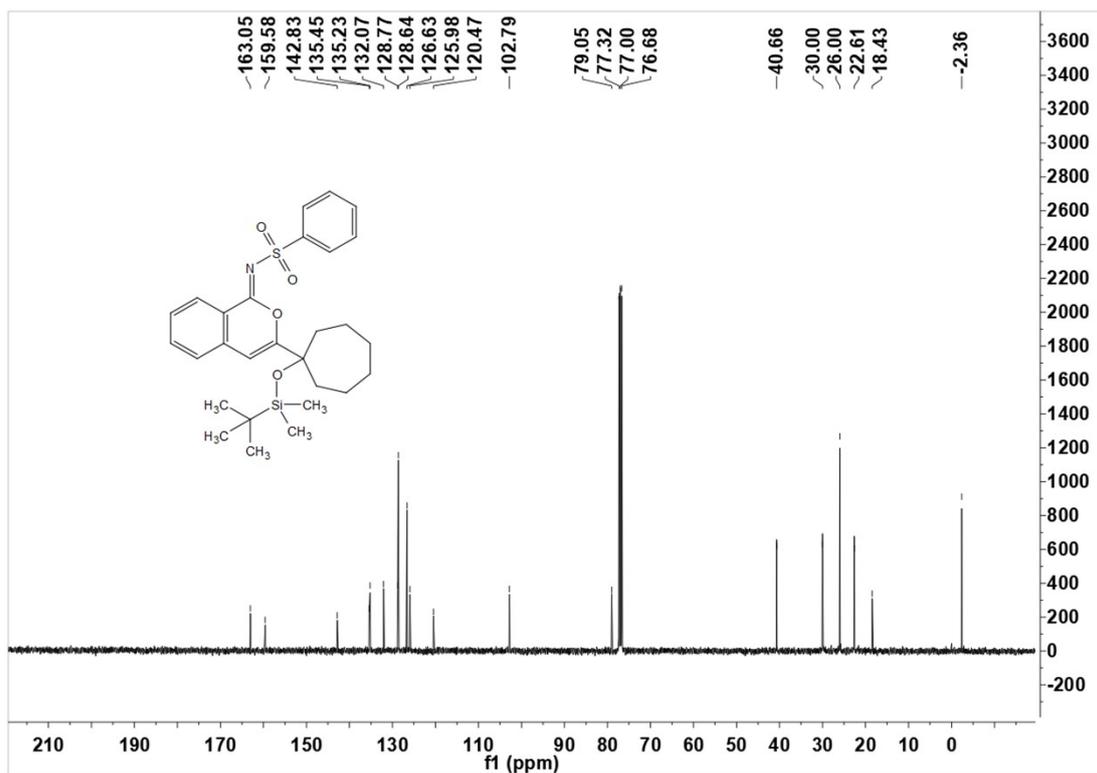


(Z)-N-(3-(1-((*tert*-Butyldimethylsilyloxy)cycloheptyl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (4j)

¹H NMR (400 MHz, CDCl₃)

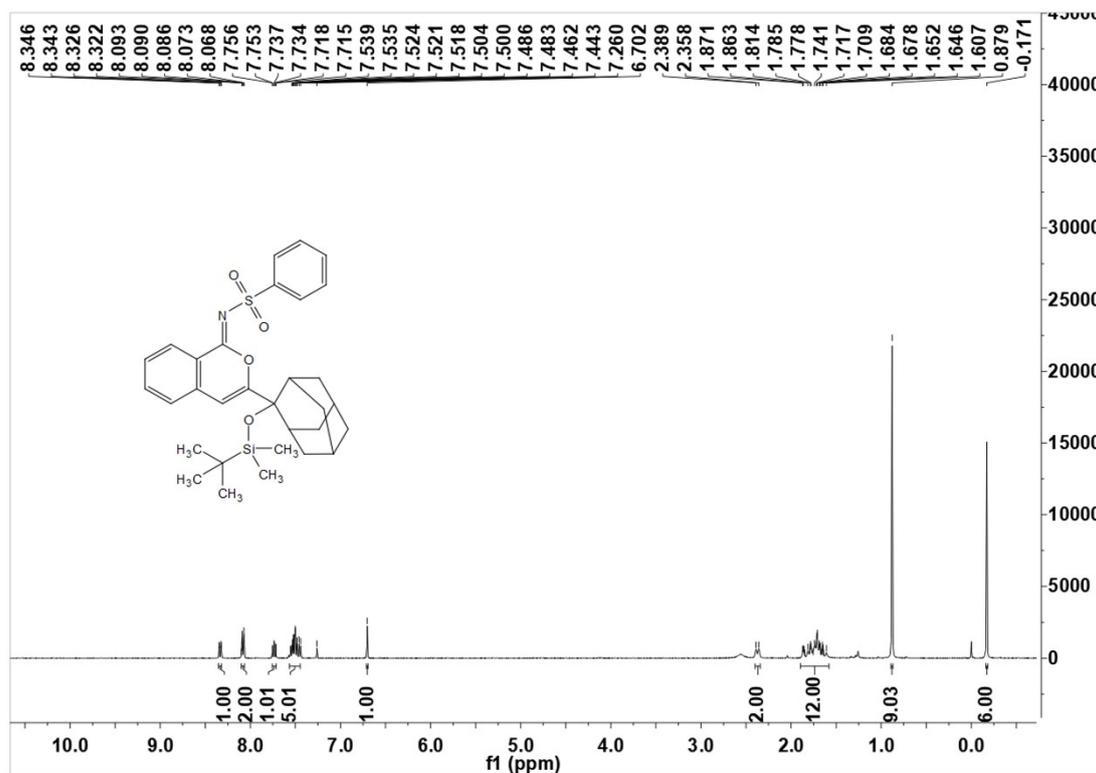


¹³C NMR (100 MHz, CDCl₃)

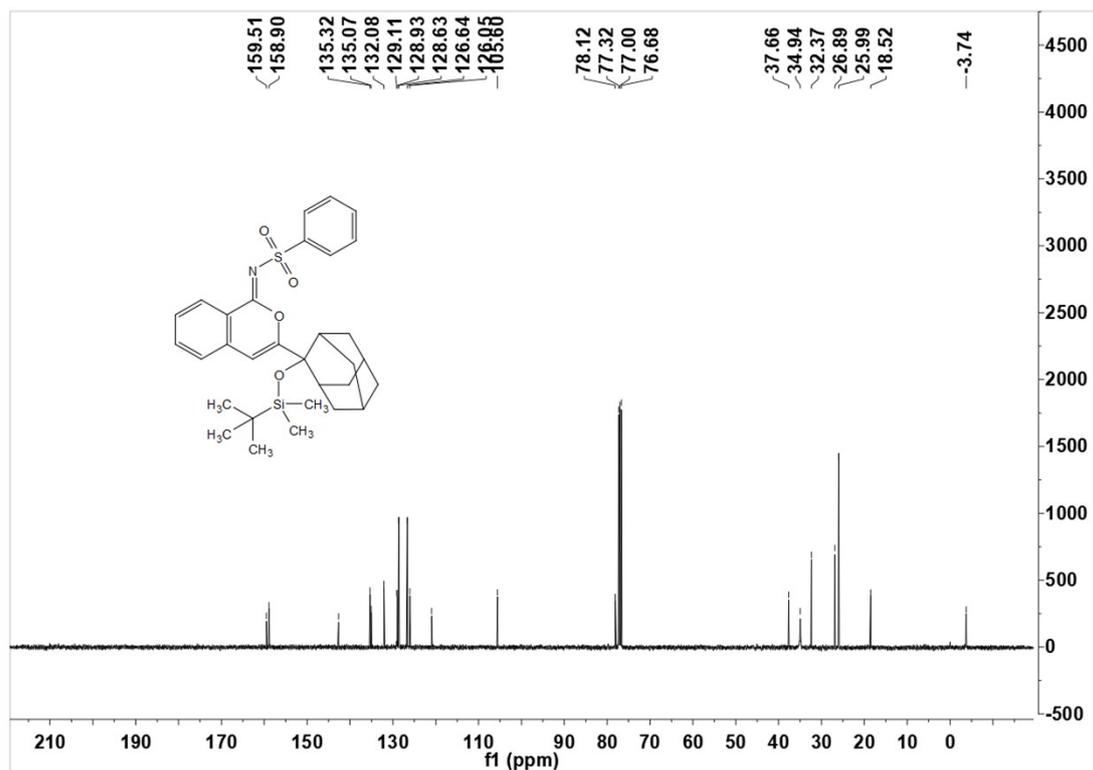


N-((*Z*)-3-((1*R*,3*S*,5*r*,7*r*)-2-((*tert*-butyldimethylsilyl)oxy)adamantan-2-yl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (**4k**)

¹H NMR (400 MHz, CDCl₃)

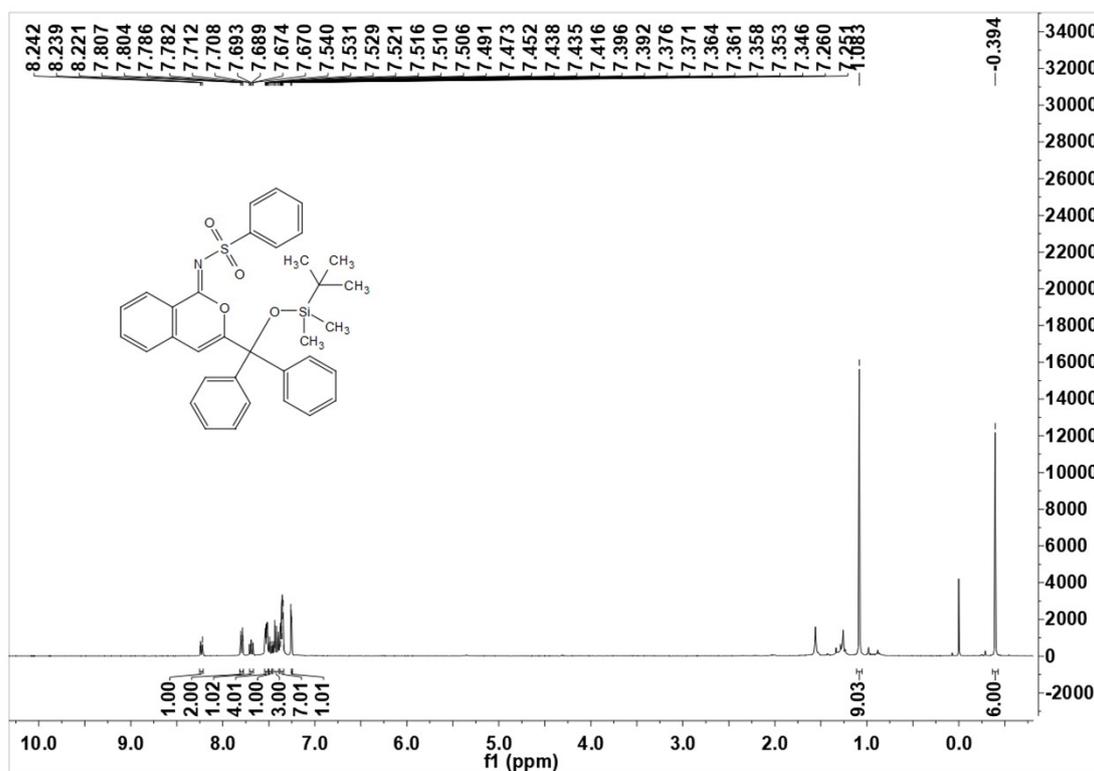


¹³C NMR (100 MHz, CDCl₃)

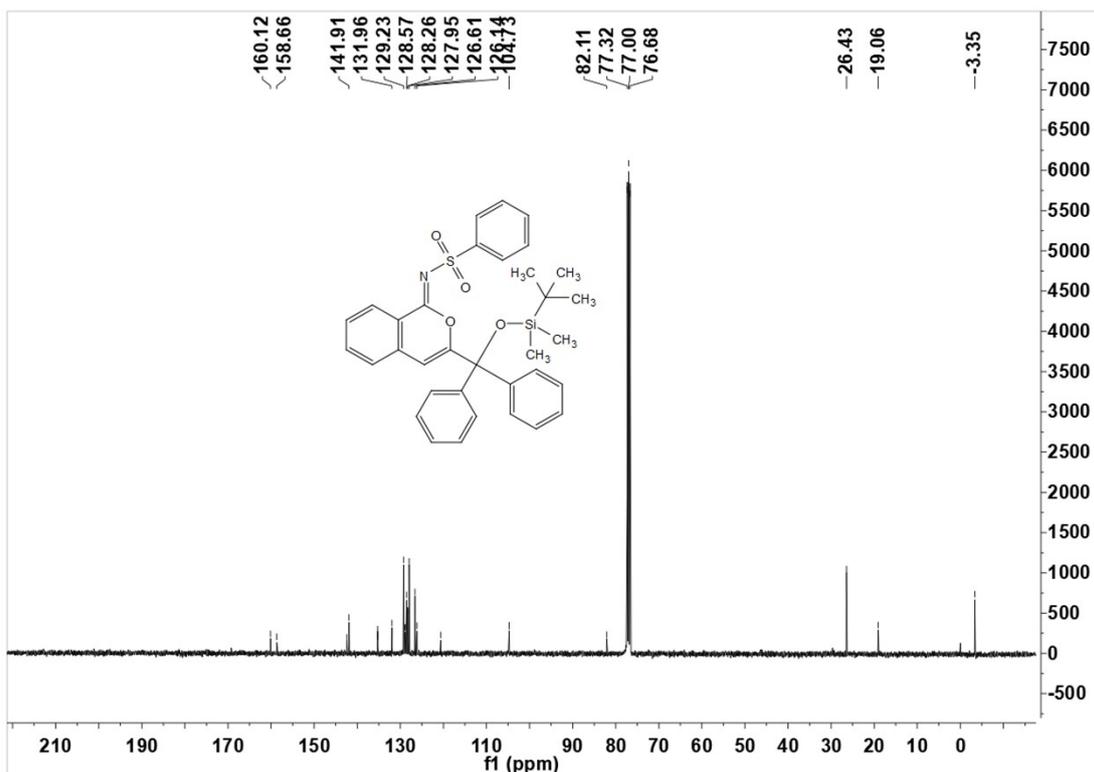


(Z)-N-(3-(((*tert*-butyldimethylsilyloxy)diphenylmethyl)-1*H*-isochromen-1-ylidene)benzenesulfonamide (4l)

¹H NMR (400 MHz, CDCl₃)

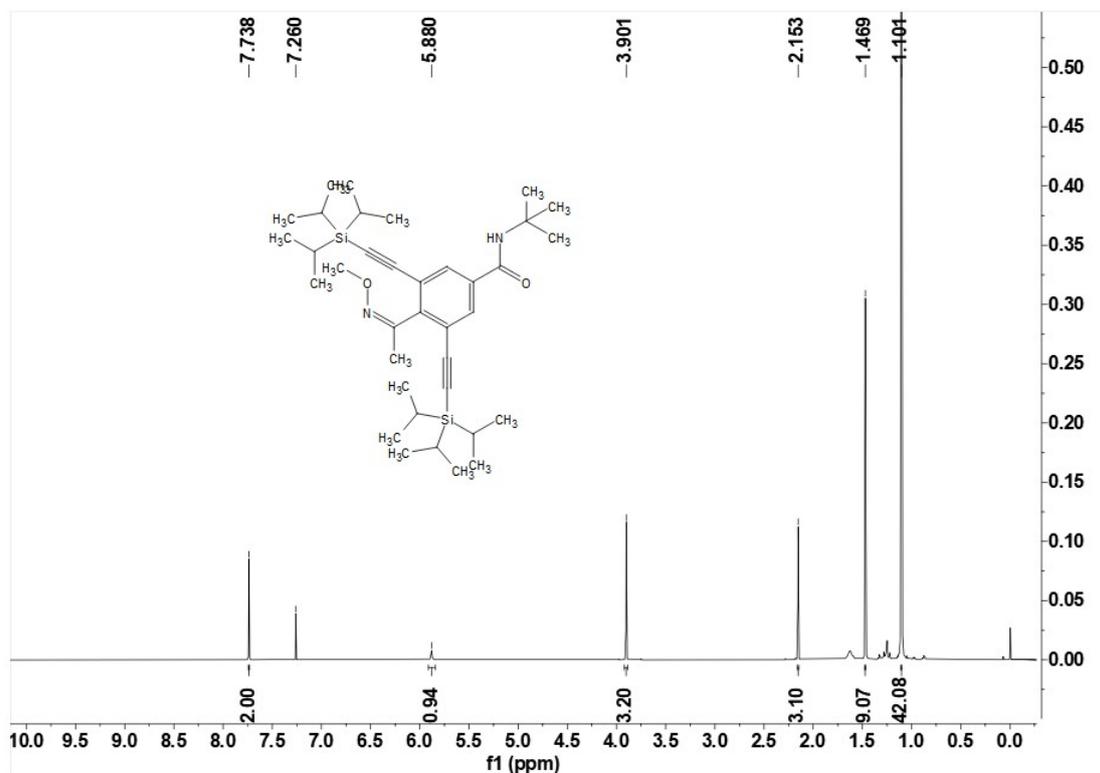


¹³C NMR (100 MHz, CDCl₃)

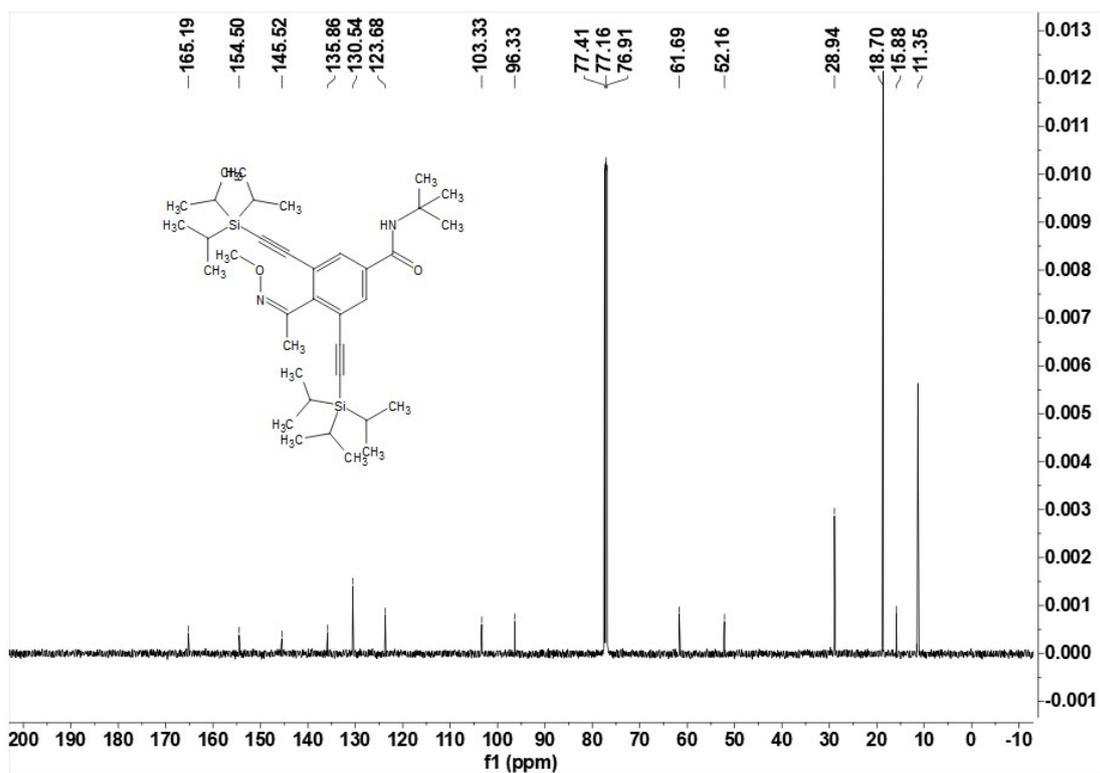


***N*-(*tert*-Butyl)-4-(1-(methoxyimino)ethyl)-3,5-bis((triisopropylsilyl)ethynyl)benzamide (6d-1)**

^1H NMR (CDCl_3 , 400 MHz)

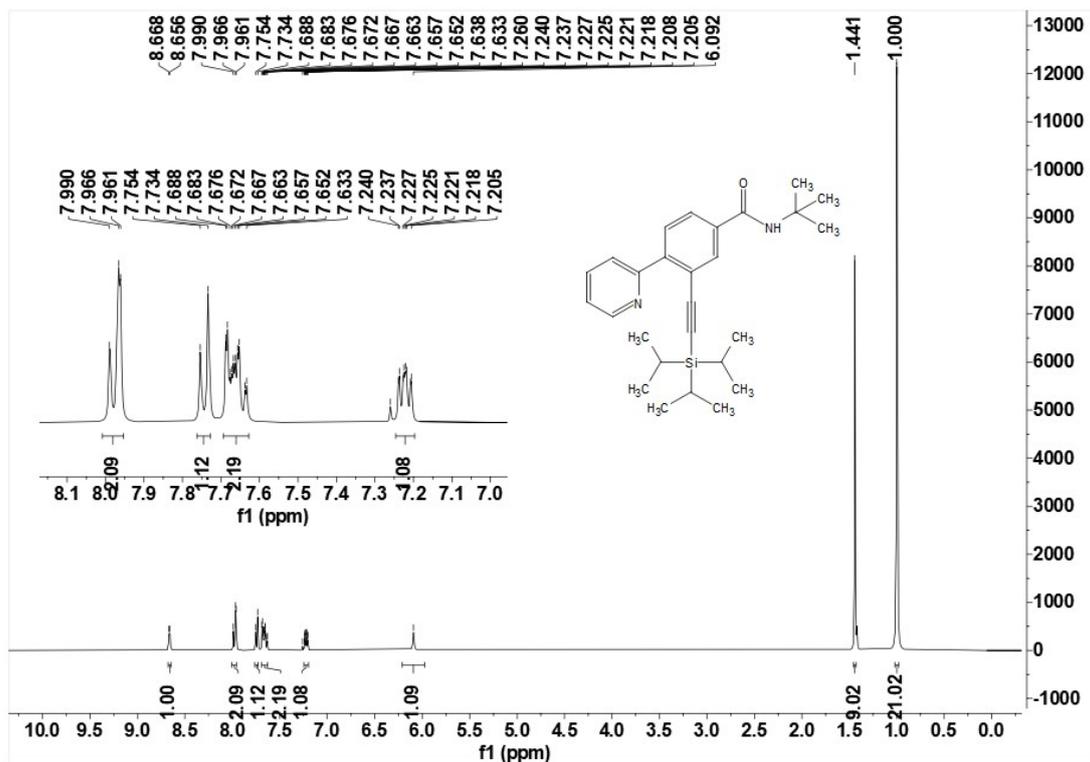


^{13}C NMR (100 MHz, CDCl_3)

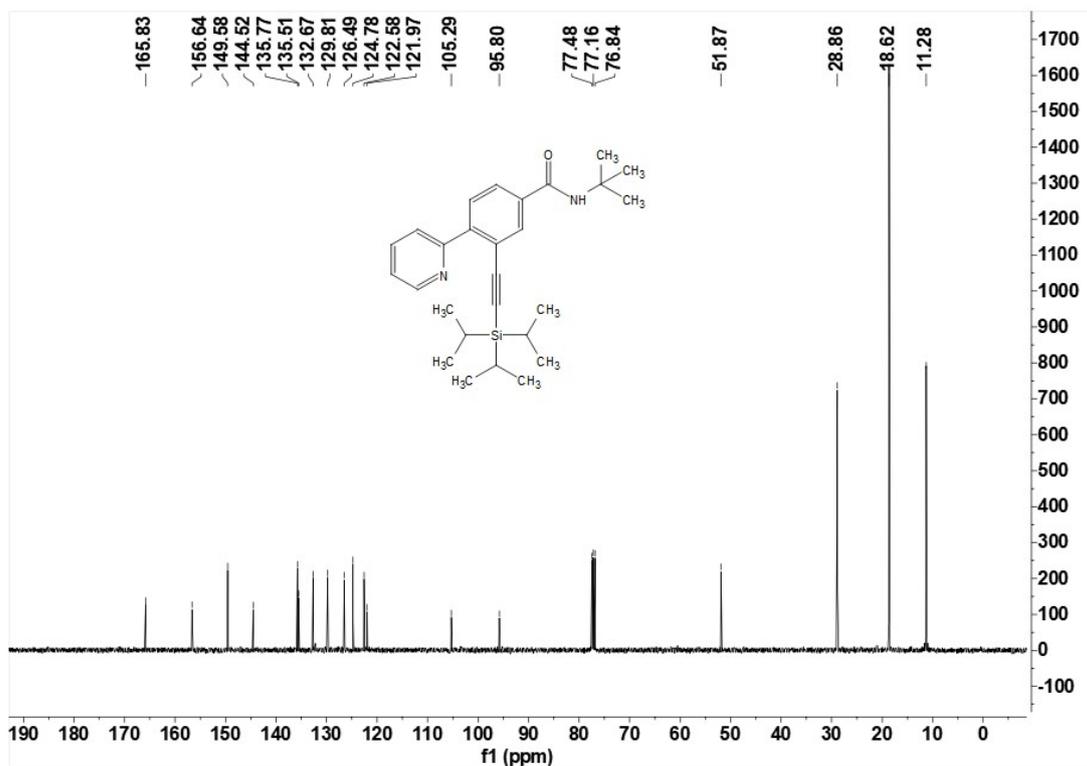


N-(*tert*-Butyl)-4-(pyridin-2-yl)-3-((triisopropylsilyl)ethynyl)benzamide (6f)

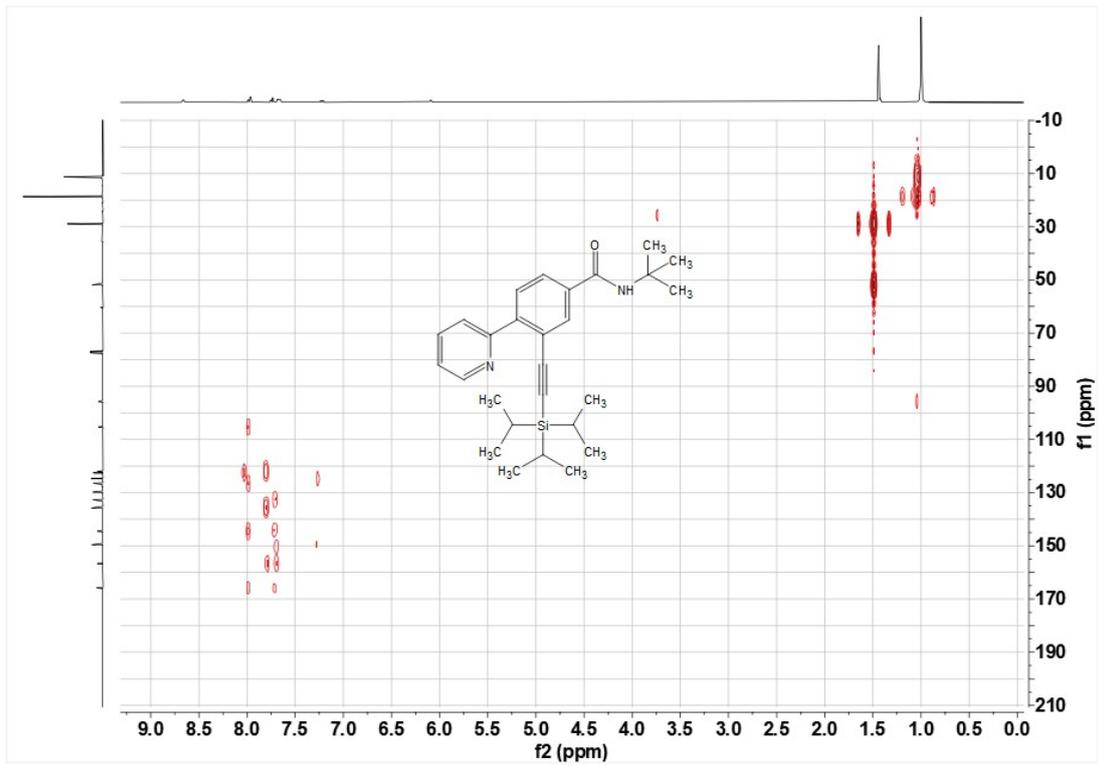
¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (100 MHz, CDCl₃)

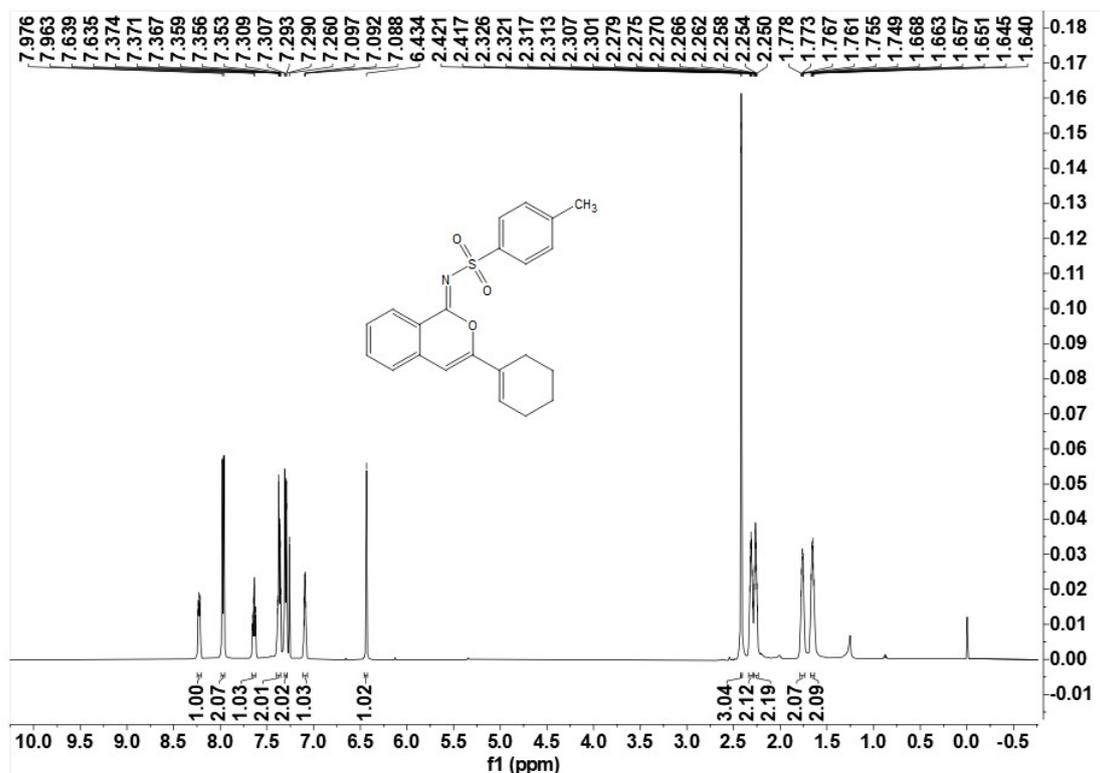


HMBC spectrum of 6f

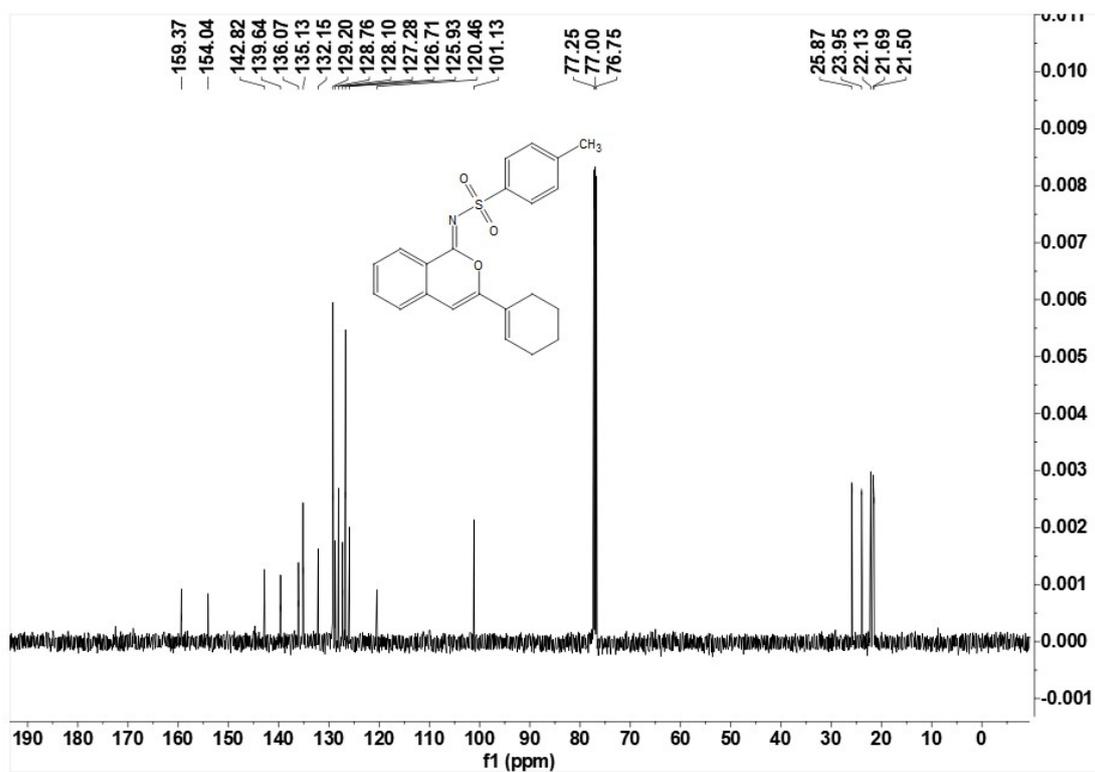


***N*-(3-(Cyclohex-1-en-1-yl)-1*H*-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4q),**

^1H NMR (500 MHz, CDCl_3) δ

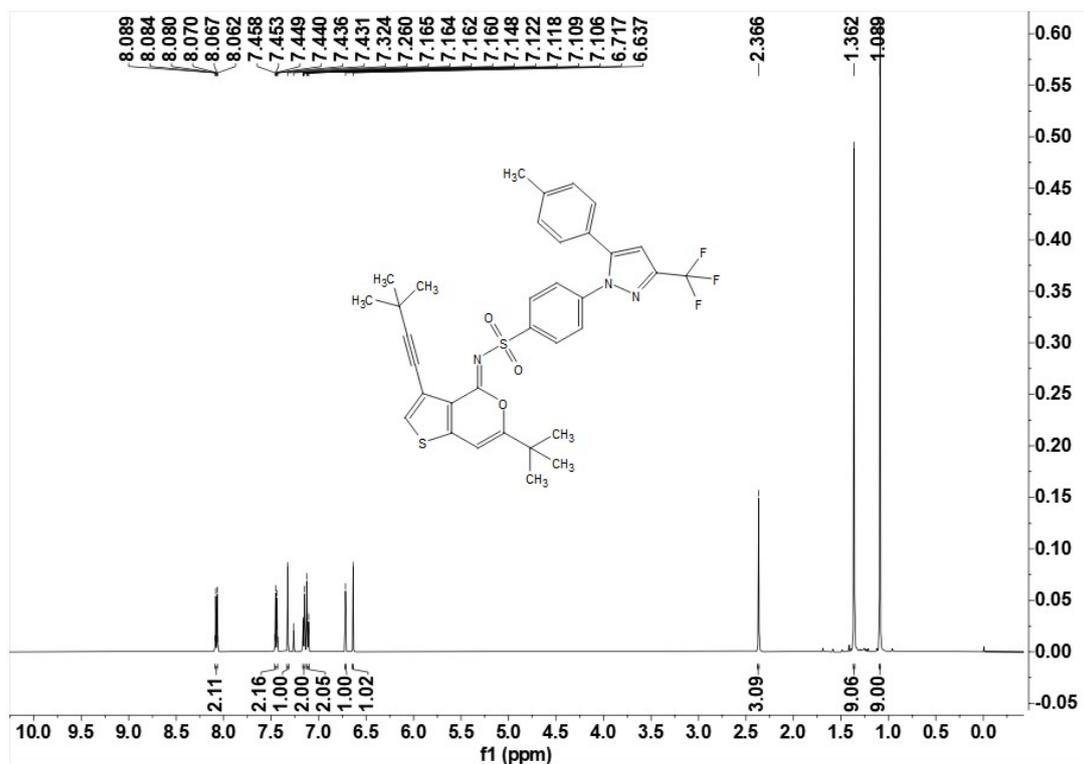


^{13}C NMR (126 MHz, CDCl_3)

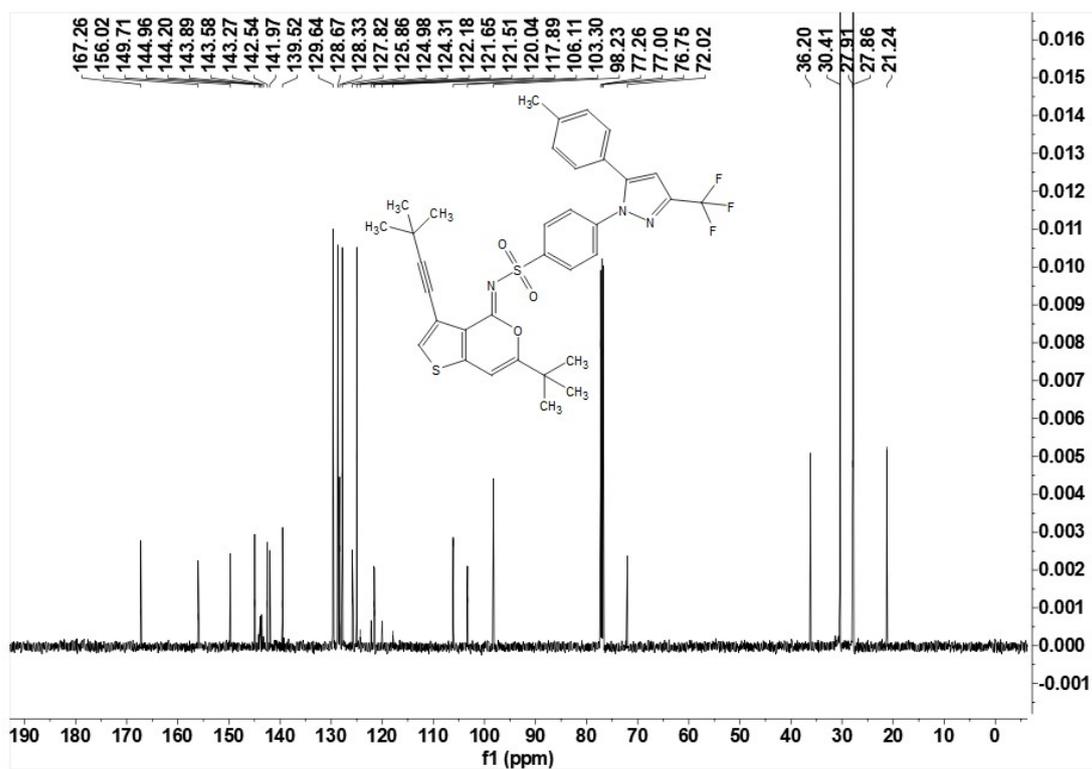


N-(6-(*tert*-Butyl)-3-(3,3-dimethylbut-1-yn-1-yl)-4*H*-thieno[3,2-*c*]pyran-4-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4ze)

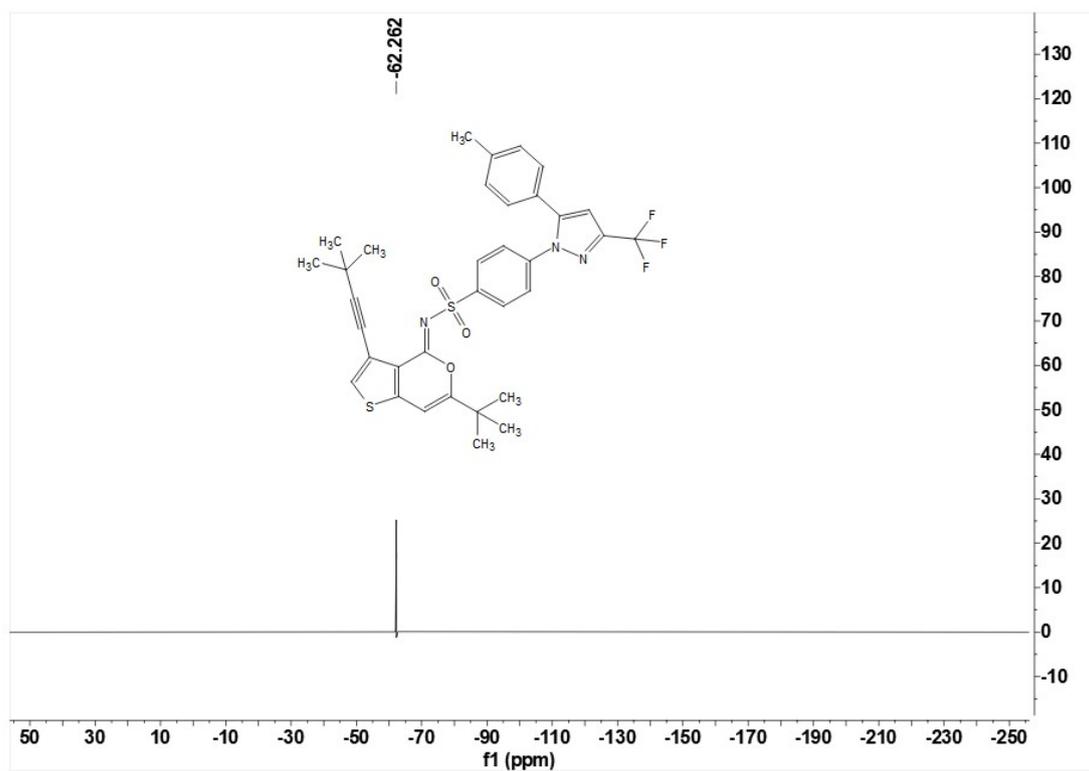
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

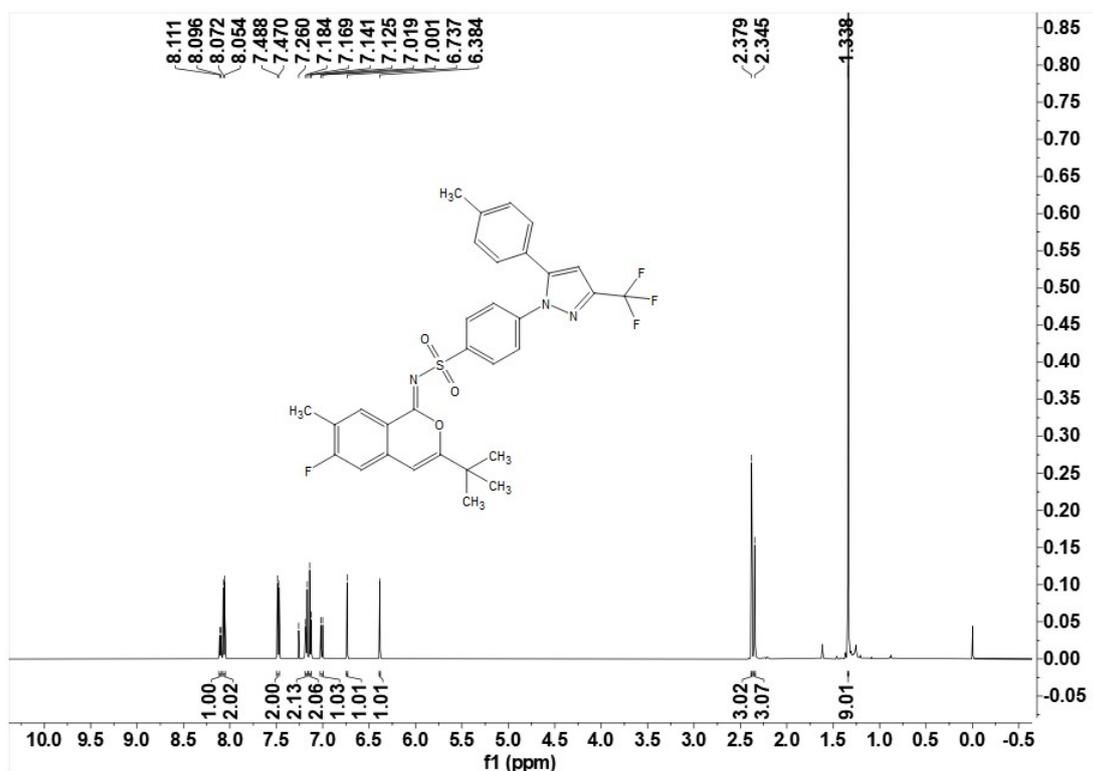


^{19}F NMR (471 MHz, CDCl_3)

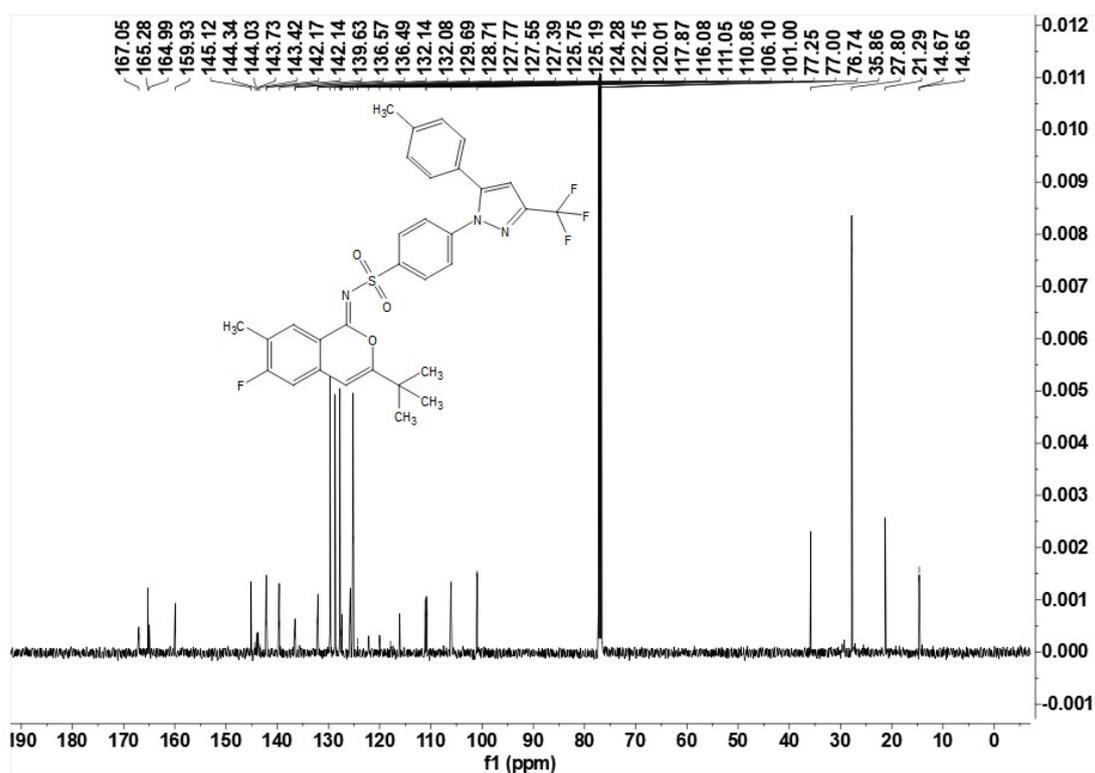


***N*-(3-(*tert*-Butyl)-6-fluoro-7-methyl-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4zc)**

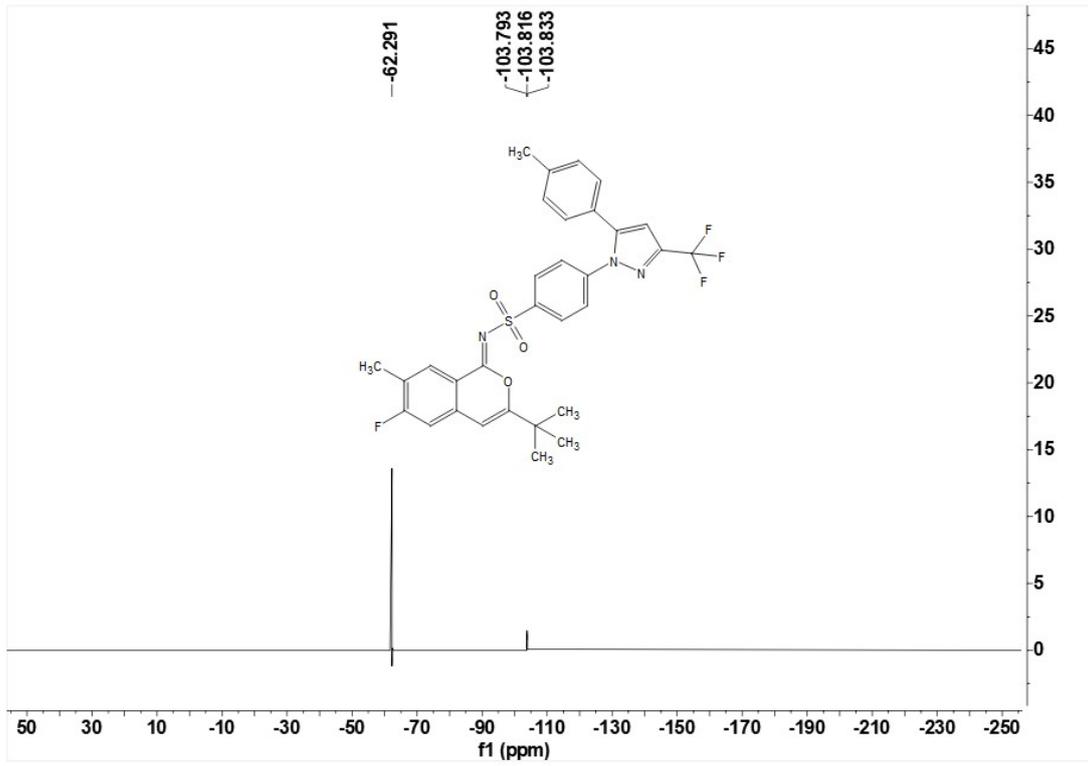
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

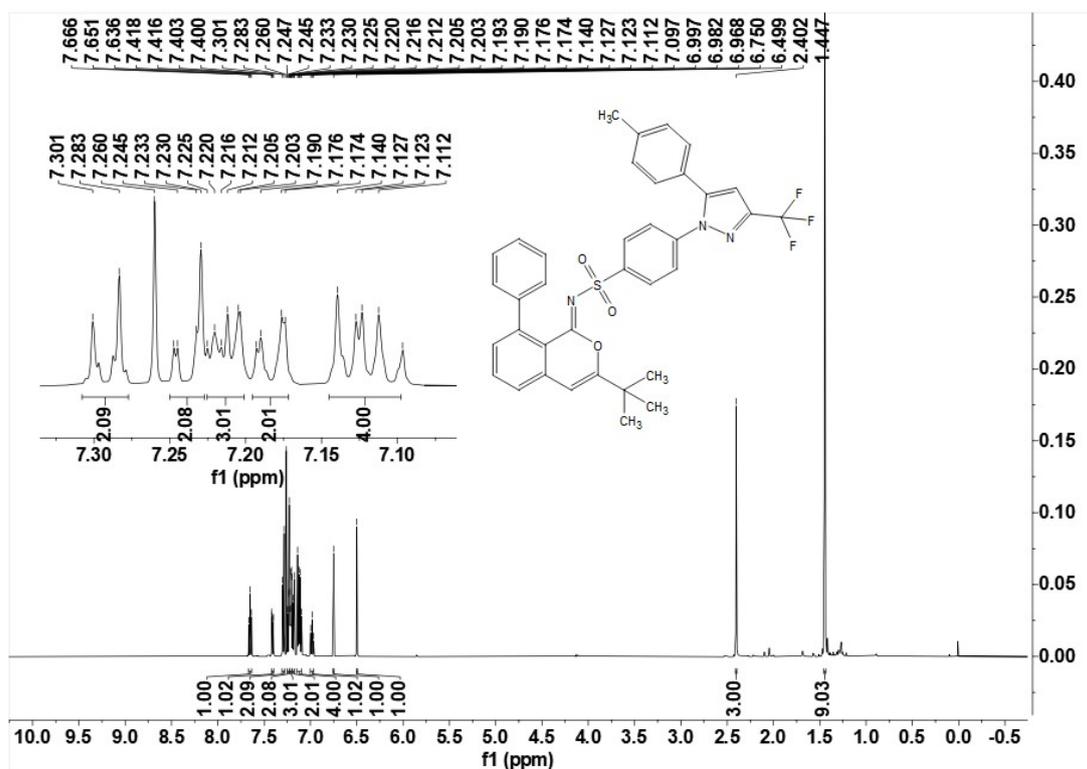


^{19}F NMR (471 MHz, CDCl_3)

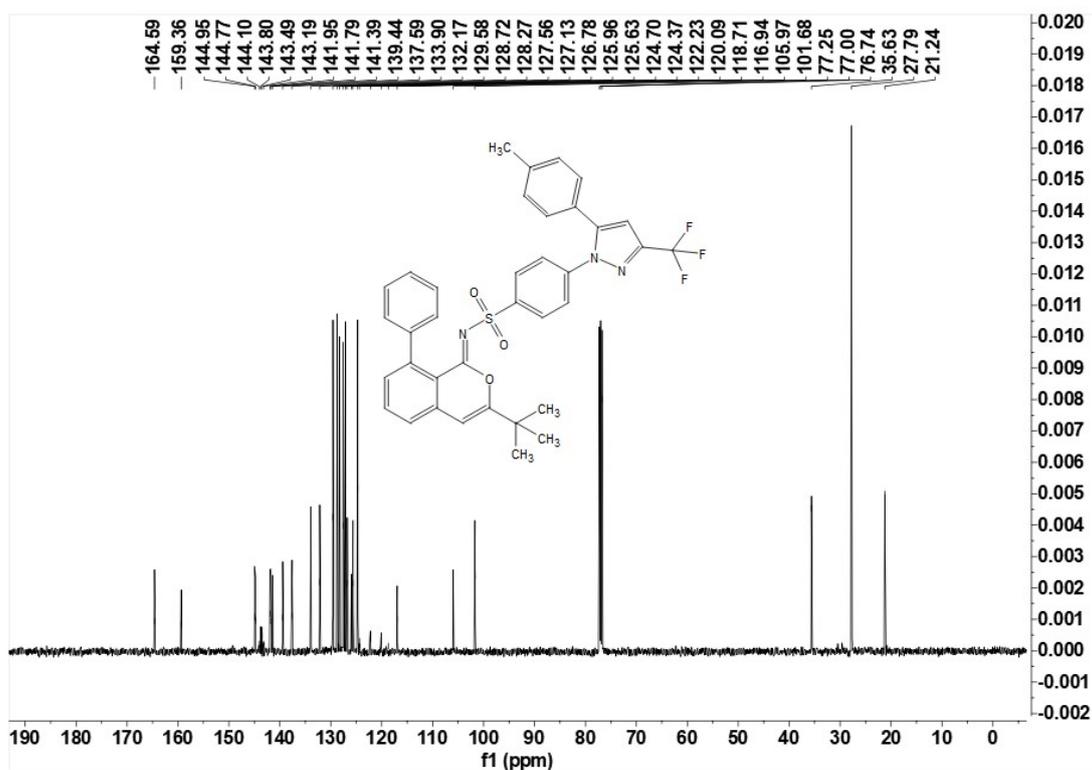


***N*-(3-(*tert*-Butyl)-8-phenyl-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4zb)**

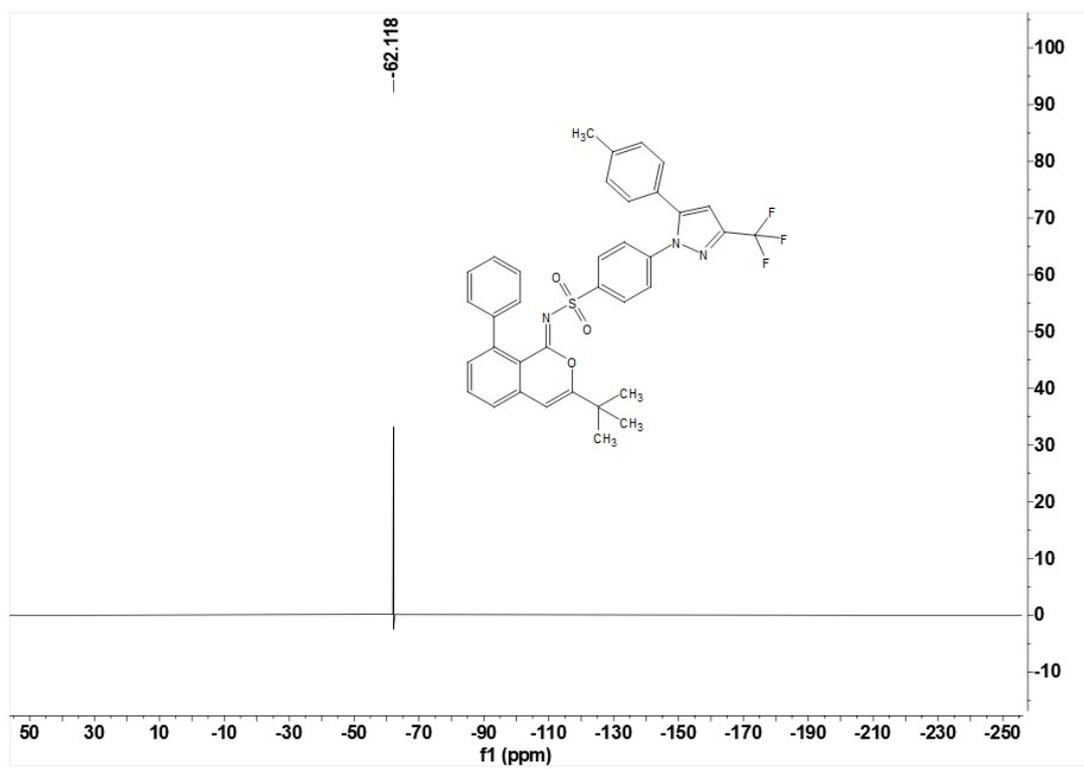
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

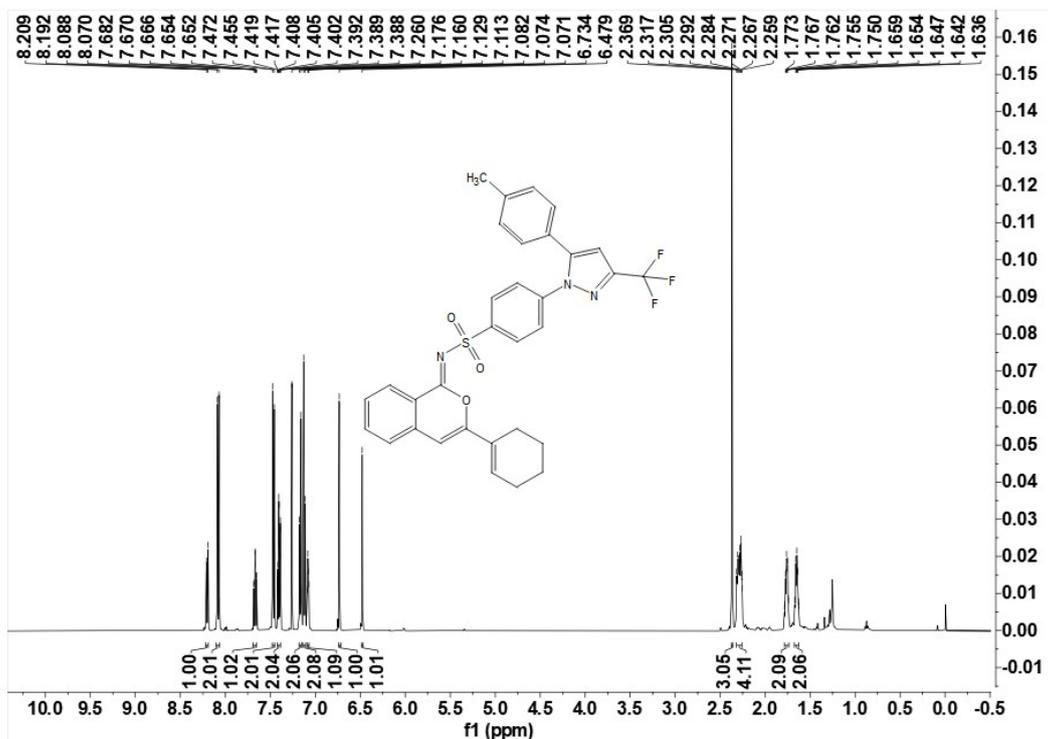


^{19}F NMR (471 MHz, CDCl_3)

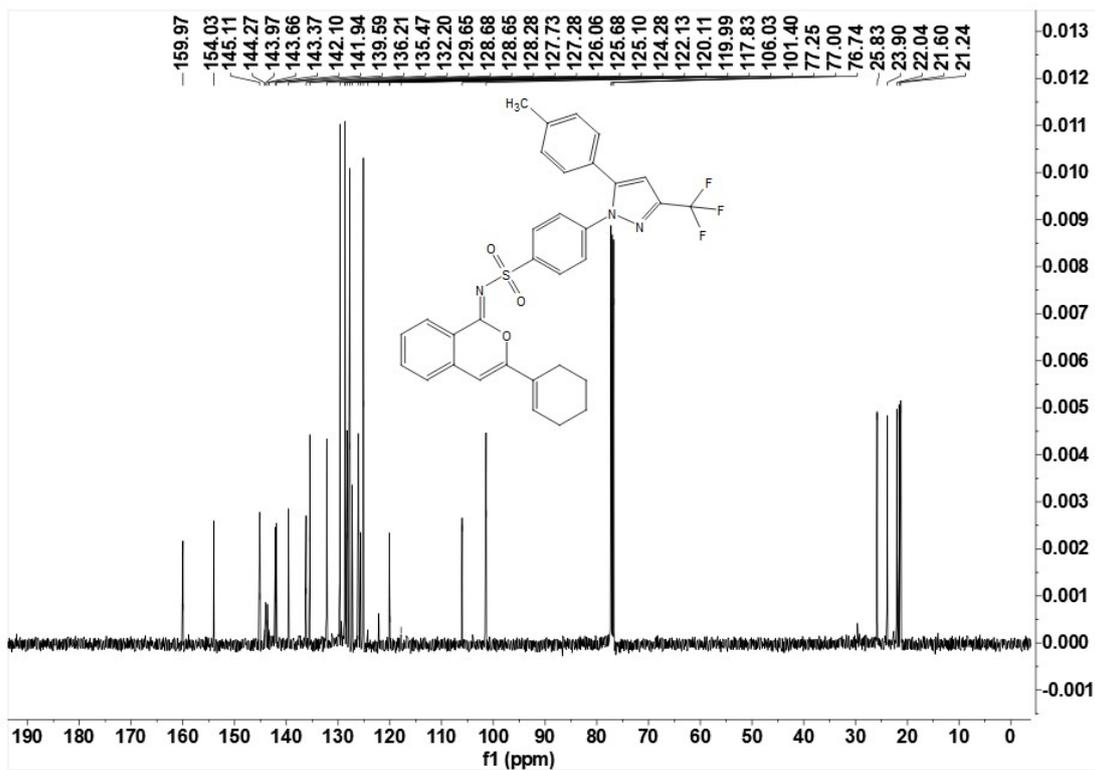


***N*-(3-(Cyclohex-1-en-1-yl)-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4zd)**

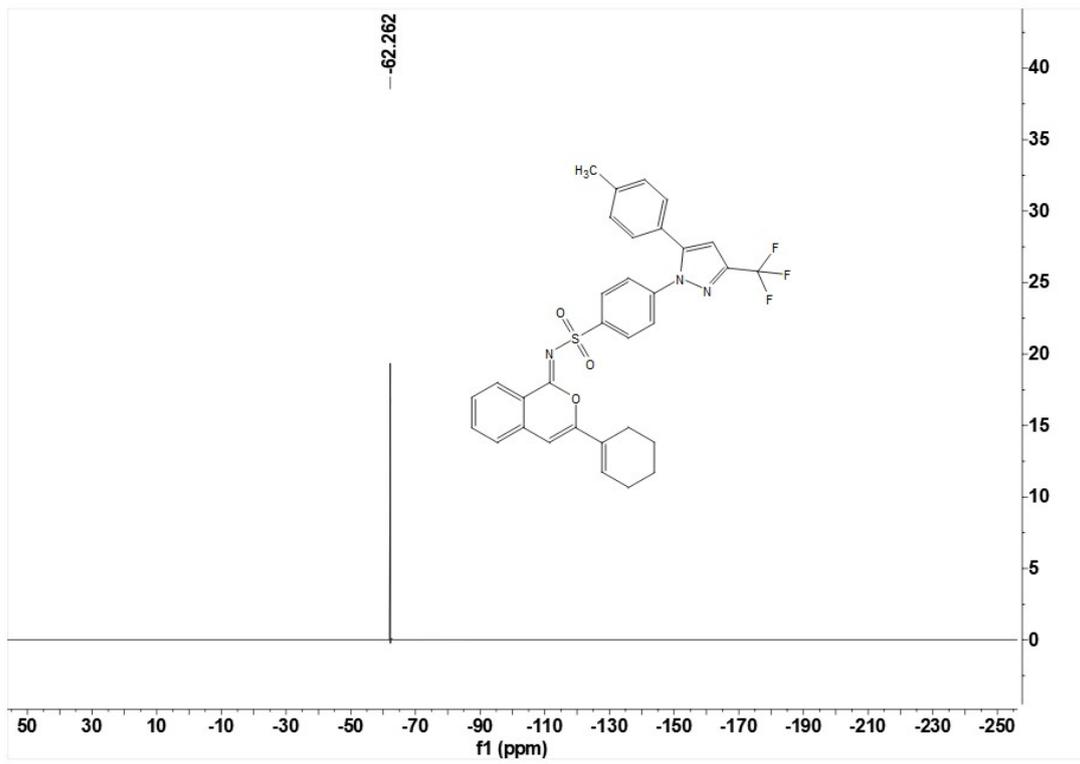
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

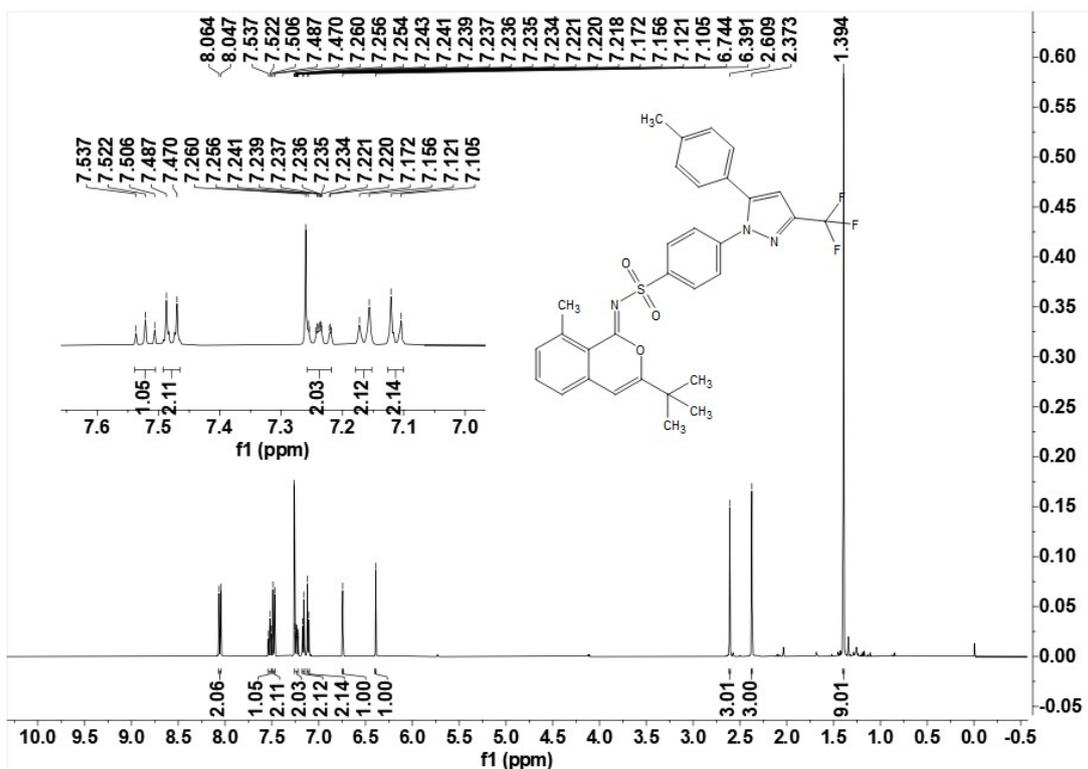


¹⁹F NMR (471 MHz, CDCl₃)

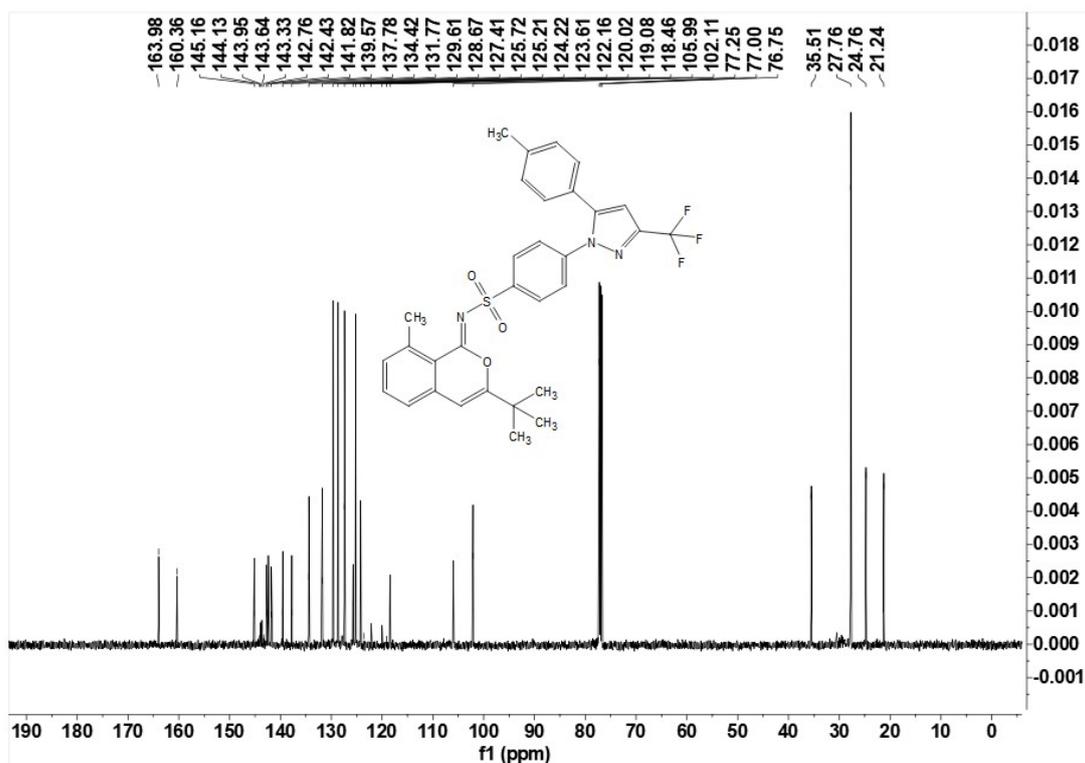


***N*-(3-(*tert*-Butyl)-8-methyl-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4z)**

¹H NMR (500 MHz, CDCl₃)

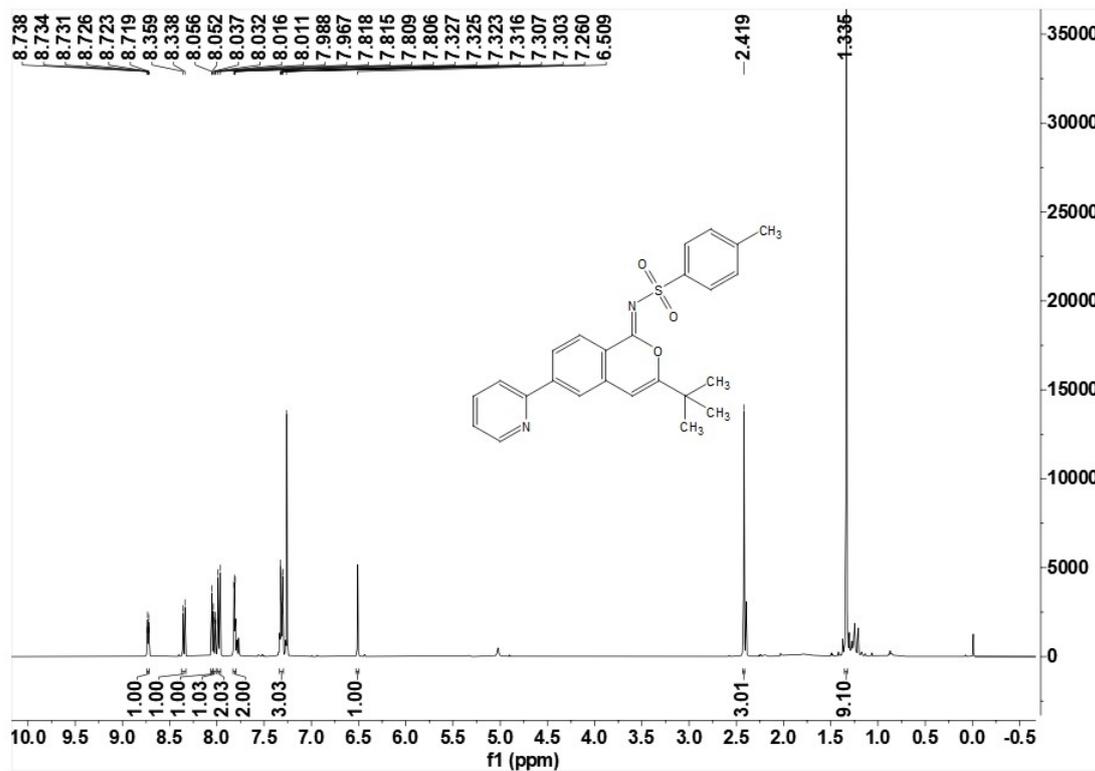


¹³C NMR (126 MHz, CDCl₃)

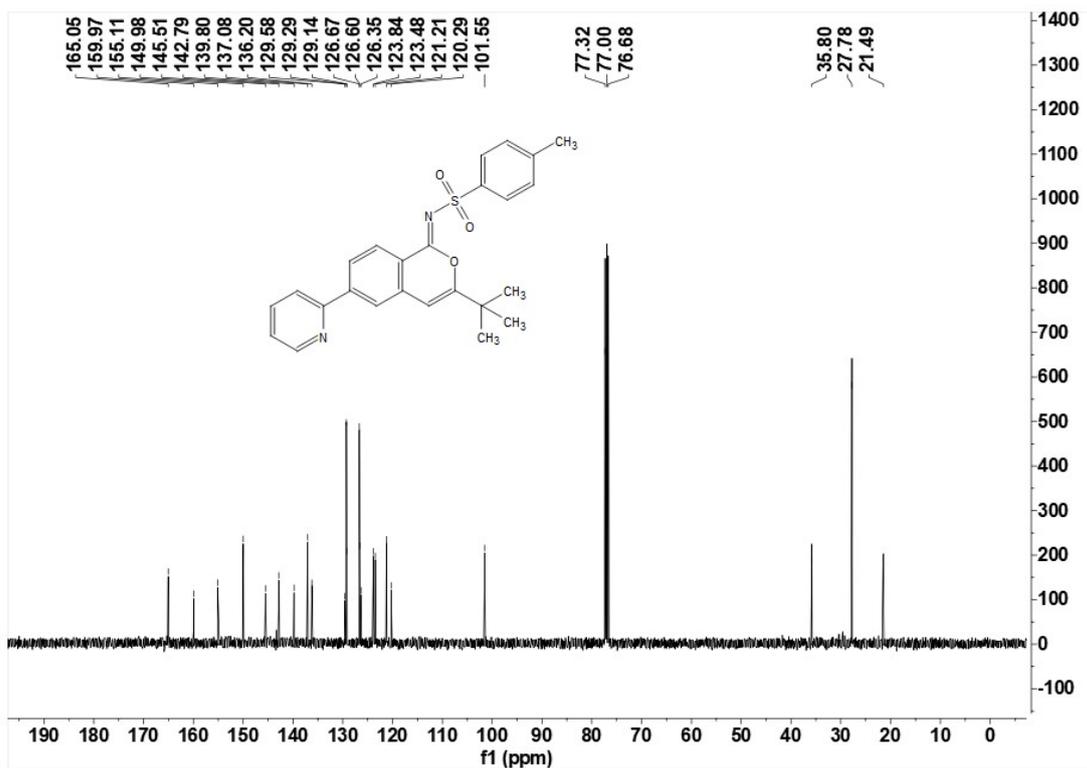


***N*-(3-(*tert*-Butyl)-6-(pyridin-2-yl)-1*H*-isochromen-1-ylidene)-4-methylbenzenesulfonamide (4y)**

¹H NMR (400 MHz, CDCl₃)

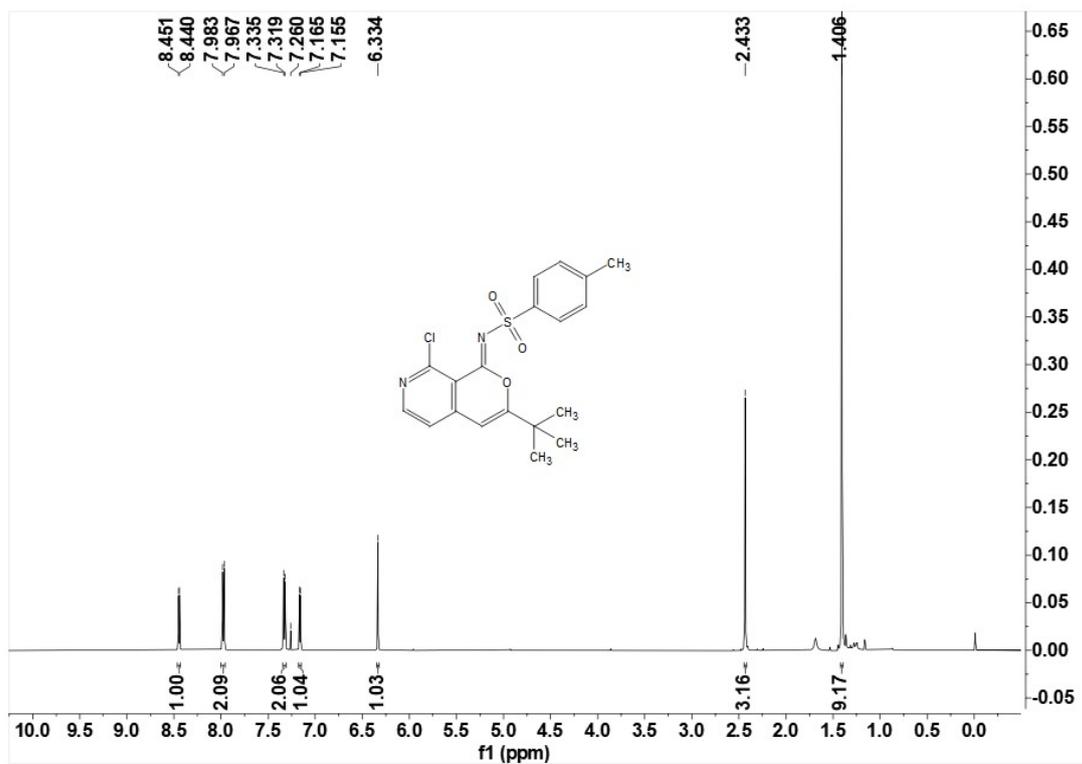


¹³C NMR (100 MHz, CDCl₃)



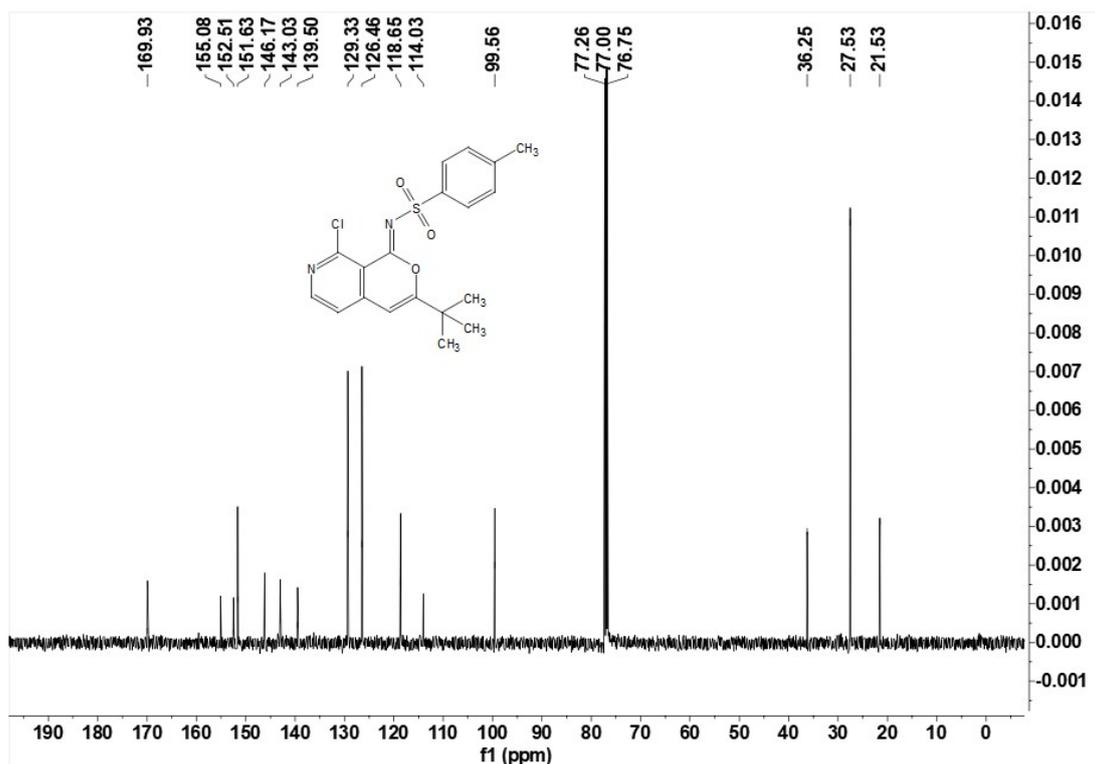
N-(3-(*tert*-Butyl)-8-chloro-1*H*-pyrano[3,4-*c*]pyridin-1-ylidene)-4-methylbenzenesulfonamide (4s)

¹H NMR (500 MHz, CDCl₃)



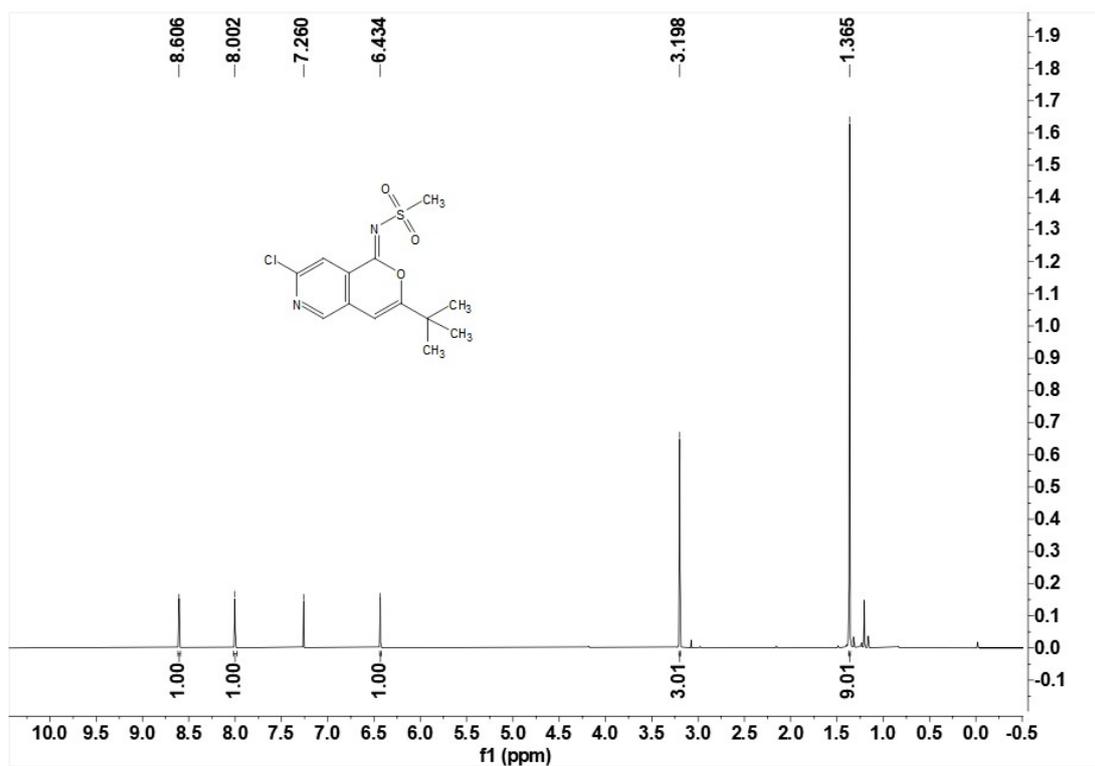
¹³C NMR (126 MHz, CDCl₃)

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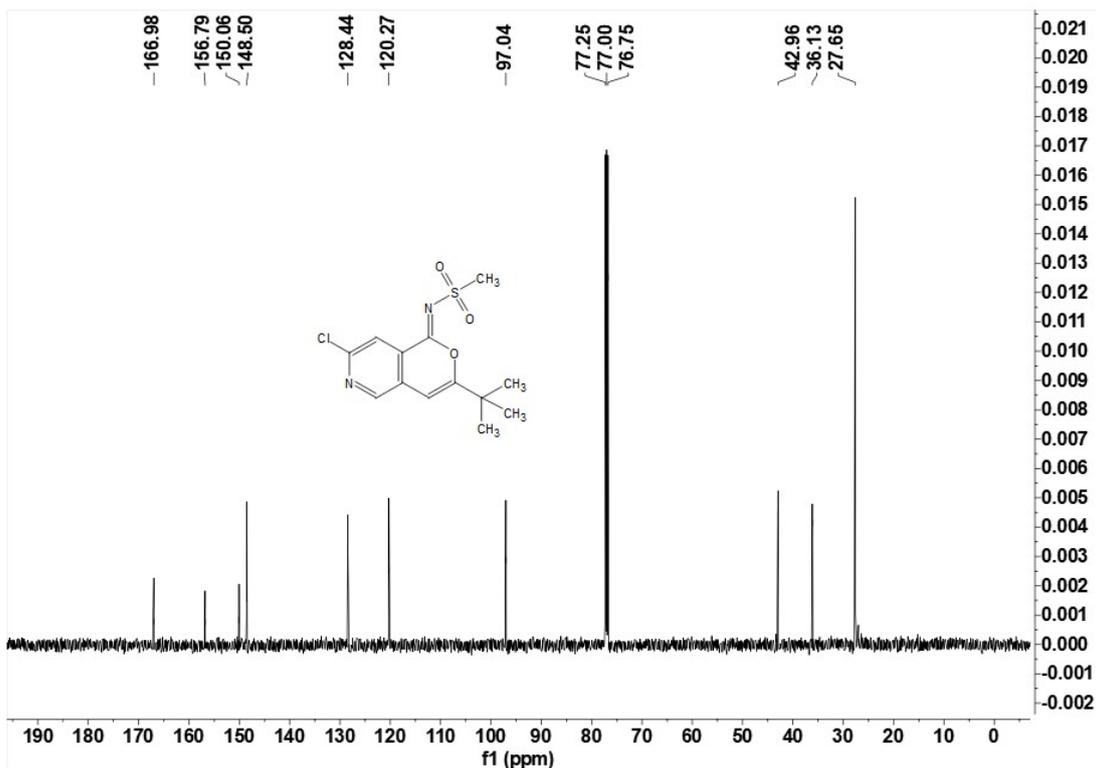


***N*-(3-(*tert*-Butyl)-7-chloro-1*H*-pyrano[4,3-*c*]pyridin-1-ylidene)methanesulfonamide (4s)**

¹H NMR (500 MHz, CDCl₃)

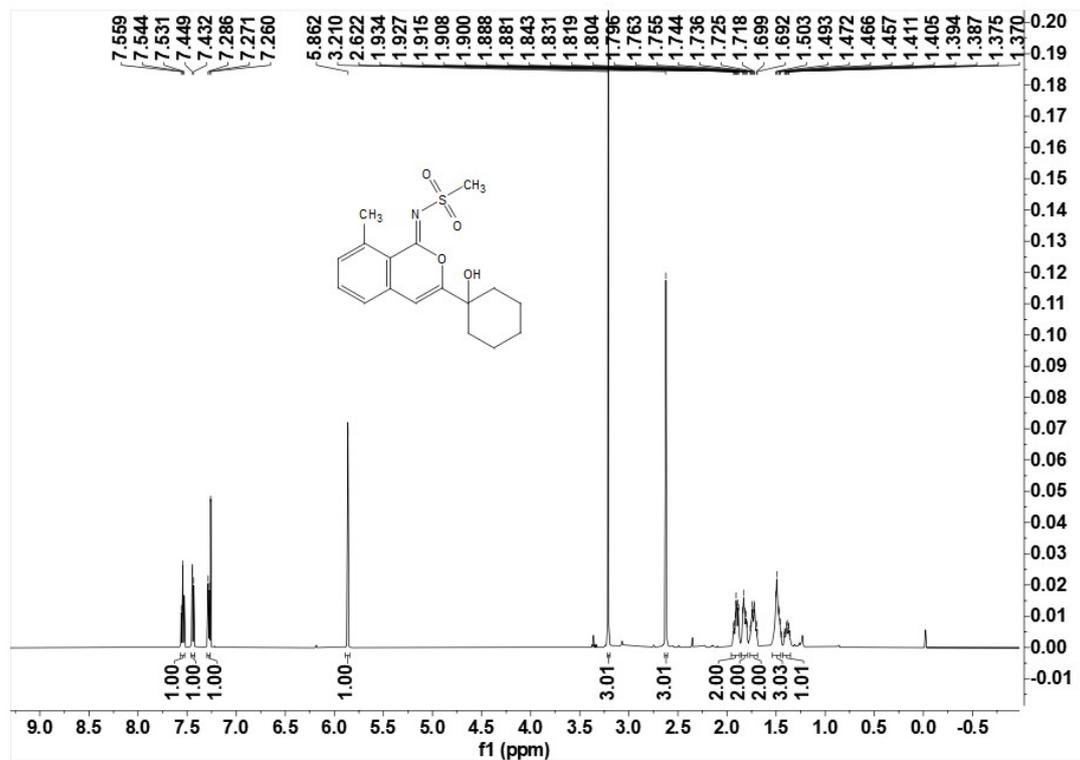


¹³C NMR (126 MHz, CDCl₃)

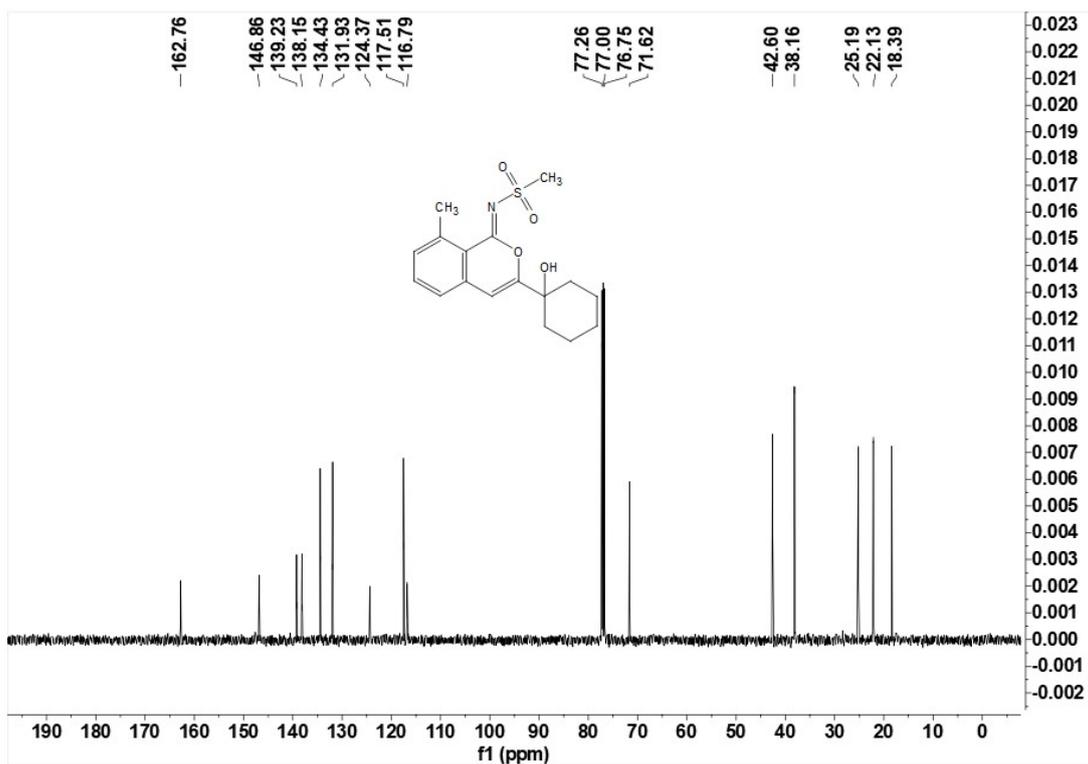


***N*-(3-(1-Hydroxycyclohexyl)-8-methyl-1*H*-isochromen-1-ylidene)methanesulfonamide (4o)**

¹H NMR (500 MHz, CDCl₃)

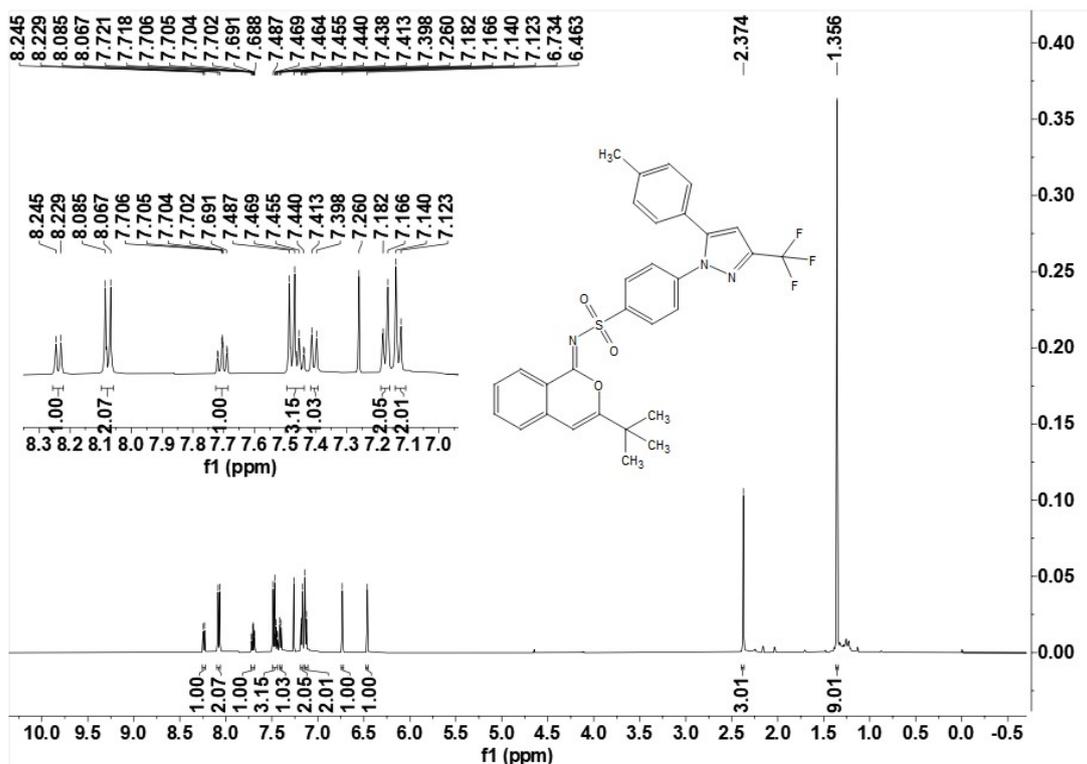


¹³C NMR (126 MHz, CDCl₃)

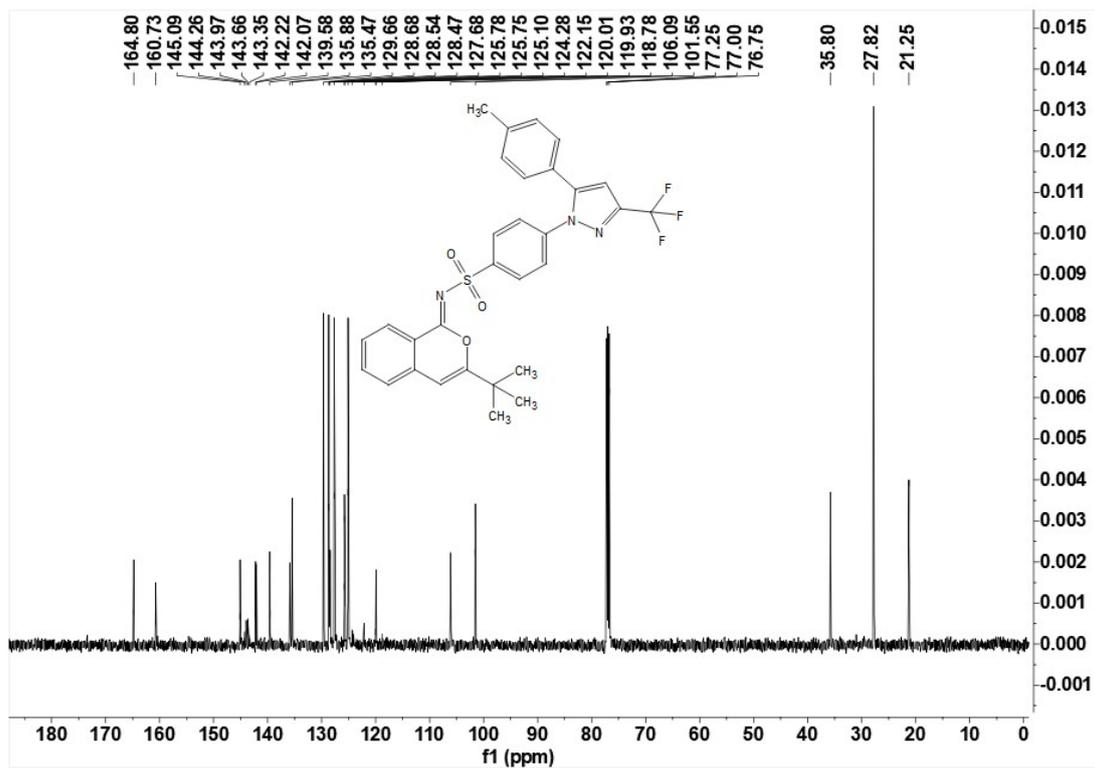


***N*-(3-(*tert*-Butyl)-1*H*-isochromen-1-ylidene)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4z)**

¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)



^{19}F NMR (471 MHz, CDCl_3)

