Supporting Information

Radical Selenylative Cyclization of Trifluoromethyl Propargyl Imines for the Synthesis of Trifluoromethyl-

and Seleno-Azaspiro[4,5]-tetraenones and Quinolines

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Contents

1. General Information	S1
1.1. Preparation of Fluorinated Imidoyl Chlorides	S1
1.2. Preparation of Trifluoromethyl Propargyl Imines	S2
1.3. Preparation of Diselenides	S2
2. Experimental Procedures	S3
2.1. General Procedure for the Synthesis of Products 3	S3
2.2. General Procedure for the Synthesis of Products 4	S3
2.3. Control Experiments	S4
2.4. Scale-up Reaction and Synthetic Transformation	S6
3. The Crystal Structure of Product 4g	S7
4. Characterization Data of the Corresponding Products	S8
5. References	S28
6. Copy of ¹ H, ¹³ C and ¹⁹ F NMR Spectra of Products.	S29

1. General Information

Unless otherwise noted, all reactions were carried out under N₂ atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ¹NMR spectra were recorded on a Bruker Avance operating at for ¹H NMR at 400 MHz, ¹³C NMR at 100 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl₃ (¹H NMR δ 7.26, ¹³C NMR δ 77.16) or DMSO-D₆ (¹H NMR δ 2.50, ¹³C NMR δ 39.52) as solvent. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected.

1.1 Preparation of Fluorinated Imidoyl Chlorides¹

$$R-NH_2 + CF_3COOH \xrightarrow{PPh_3, Et_3N} CF_3 \xrightarrow{CI} CF_3 \xrightarrow{R} R$$

A 100 mL two-necked flask equipped with a septum cap, a condenser, and a Teflon-coated magnetic stir bar was charged with PPh₃ (9.84 g, 37.5 mmol), Et₃N (2.1 mL, 15 mmol), CCl₄ (20.0 mL), and TFA (1.2 mL, 15 mmol). After the solution was stirred for about 10 min (ice bath), amine (15 mmol) dissolved in CCl₄ (20.0 mL) was added. The mixture was then refluxed under stirring (3 h). After the reaction was completed, residual solid Ph₃PO, PPh₃ and Et₃N-HCl were washed with petroleum ether several times. Then the petroleum ether was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel or neutral alumina to afford the corresponding product.

1.2 Preparation of Trifluoromethyl Propargyl Imines²



Under Nitrogen atmosphere, DABCO (9.0 mmol, 3.0 equiv), Pd(PPh₃)₄ (2.0 mol %), trifluoroacetimide chloride (3.0 mmol, 1.0 equiv), alkyne (3.6 mmol, 1.2 equiv) in toluene (8 mL) were added to an oven-dried 50 mL small flask. Then the mixture was stirred at 110 °C (oil bath) for 16 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×20 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the trifluoromethyl propargyl imine products.

1.3 Preparation of Diselenides³

Aryl or alkyl iodide (5.0 mmol, 1.0 equiv), Se (552.7 mg, 7.0 mmol, 1.4 equiv), and CuO (10 mol %), KOH (448.0 mg, 8.0 mmol, 1.6 equiv) in DMSO (3 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the mixture was stirred at 90 °C (oil bath) for 1 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give diselenide products.

2.Experimental Procedures

2.1 General Procedure for the Synthesis of Products 3



Oxone (0.25 mmol, 1.25 equiv), trifluoromethyl propargyl imine **1** (0.2 mmol, 1.0 equiv) and diselenide **2** (0.2 mmol, 1.0 equiv) in acetonitrile (2.0 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the mixture was stirred under air at 80 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give azaspiro[4,5]-tetraenone products **3**.

2.2 General Procedure for the Synthesis of Products 4



Oxone (0.25mmol, 1.25 equiv), trifluoromethyl propargyl imine **1** (0.2 mmol, 1.0 equiv) and diphenyl diselenide **2a** (0.2 mmol, 1.0 equiv) in acetonitrile (2 mL) were added to an oven-dried 15 mL *In-Ex* tube. Then the mixture was stirred under air at 80 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give quinoline products **4**.

2.3 Control Experiments



Oxone (153.6 mg, 0.25 mmol, 1.25 equiv), trifluoromethyl propargyl imine **1a** (60.6 mg, 0.2 mmol, 1.0 equiv), diphenyl diselenide **2a** (62.4 mg, 0.2 mmol, 1.0 equiv), TEMPO or BHT or 1,1-DPE (0.4 mmol, 2.0 equiv), in CH₃CN (2.0 mL) was added to an oven-dried 15 mL *In-Ex* tube, respectively. The mixture was stirred at 80 $^{\circ}$ C (oil bath) for 12 hours. After completion of the reaction, the mixture was slowly cooled to room temperature, the reaction mixture was concentrated under vacuum. The desired product **3a** was not detected at all from the above three reactions and the radical coupling product **5a** for 1,1-DPE was isolated in 68% yield.





Oxone (153.6 mg, 0.25 mmol, 1.25 equiv), trifluoromethyl propargyl imine **1y** (54.6 mg, 0.2 mmol, 1.0 equiv), diphenyl diselenide **2a** (62.4 mg, 0.2 mmol, 1.0 equiv), TEMPO or BHT (0.4 mmol, 2.0 equiv), in CH₃CN (2.0 mL) was added to an oven-dried 15 mL *In-Ex* tube, respectively. The mixture was stirred at 80 °C (oil bath) for 12 hours. After completion of the reaction, the mixture was slowly cooled to room temperature, the reaction mixture was concentrated under vacuum. The desired product **4a** was not detected at all from the above two reactions and the radical coupling product **5b** for TEMPO was isolated in 36% yield.





Oxone (153.6 mg, 0.25 mmol, 1.25 equiv), trifluoromethyl propargyl imine **1a** (60.6 mg, 0.2 mmol, 1.0 equiv) in CH₃CN (2.0 mL) was added to an oven-dried 15 mL *In-Ex* tube. The mixture was stirred at 80 °C (oil bath) for 12 hours. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The desired product **3a**' was not detected in the reaction.

2.4 Scale-up Reaction and Synthetic Transformation



Scale-up Reaction:

Oxone (1.10 g, 1.8 mmol, 0.6 equiv), trifluoromethyl propargyl imine **1a** (909.2 mg, 3 mmol, 1.0 equiv), diphenyl diselenide **2a** (941.7 mg, 3.0 mmol, 1.0 equiv) in CH₃CN (30.0 mL) (extra dry) was added to a dry 50 mL *In-Ex* tube. Then, the mixture was stirred at 80 °C (oil bath) for 12 hours. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×50 mL). The extract was combined and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the product **3a** as a yellow liquid (0.78 g, 60 %).

Synthetic Transformation:

(a) Compound **3a** (89.0 mg, 0.2 mmol, 1.0 equiv), *m*-CPBA (37.9 mg, 0.22 mmol, 1.1 equiv) in DCM (2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 0 °C (ice bath) for 0.5 h. After completion of the reaction, the reaction mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to give product **5** as a yellow liquid (67.3 mg, 73 %).

(b) Under nitrogen atmosphere, compound **3a** (89.0 mg, 0.2 mmol, 1.0 equiv), ethylmagnesium bromide (79.9 mg, 0.6 moml, 3.0 equiv) in THF (2 mL) (extra dry) was added to an over-dried 15 mL *In-Ex* tube. The tube was sealed and the mixture was stirred at 0 °C for 0.5 hours and allowed to react for overnight at room temperature. After the reaction was completed, the mixture was quenched by water, extracted with ethyl acetate, and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the product **6** as a colorless liquid (44.6 mg, 47%).

3. The Crystal Structure of Product 4g



4. Characterization Data of the Corresponding Products



4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8one (**3a**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10: 1, Rf = 0.4) to give the titled product **3a** as a yellow liquid (80.1 mg, 90%).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.28 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.10 (m, 7H), 6.49 (d, *J* = 9.9 Hz, 2H), 6.23 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 173.1, 169.6 (q, J = 35.3 Hz), 140.5, 132.7, 132.6, 131.3, 130.0, 129.4, 128.7, 128.5, 128.0, 127.8, 125.2, 119.0 (q, J = 276.0 Hz), 83.2.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.1.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₂H₁₅F₃NOSe⁺ 447.0344, found 447.0342.



3-(phenylselanyl)-4-(*o*-tolyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-one (**3b**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10: 1, Rf = 0.4) to give the titled product **3b** as a yellow liquid (69.0 mg, 76%).

¹**H** NMR (400 MHz, CDCl₃) δ 7.18 – 7.02 (m, 7H), 6.87 (t, J = 7.4 Hz, 1H), 6.48 – 6.42 (m, 2H), 6.32 – 6.30 (m, 1H), 6.26 – 6.18 (m, 2H), 2.11 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 184.5, 173.1, 169.0 (q, J = 35.6 Hz), 140.0, 139.8, 135.3, 134.4, 132.7, 132.1, 130.5, 130.2, 129.3, 129.2, 128.5, 128.4, 125.4, 119.1 (q, J = 275.9 Hz), 84.9, 20.4.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.5.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₃H₁₇F₃NOSe⁺ 460.0422, found 460.0426.



4-(phenylselanyl)-4-(*m*-tolyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-one (**3c**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3c** as a yellow liquid (59.9 mg, 65%).

¹**H NMR (400 MHz, CDCl₃)** δ 7.18 (t, *J* = 7.3 Hz, 3H), 7.13 – 7.08 (m, 4H), 6.94 (d, *J* = 7.0 Hz, 1H), 6.89 (s, 1H), 6.48 (d, *J* = 10.0 Hz, 2H), 6.22 (d, *J* = 10.0 Hz, 2H), 2.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 173.2, 169.6 (q, J = 35.2 Hz), 140.6, 138.1, 132.7, 132.6, 131.2, 130.7, 129.3, 128.7, 128.5, 128.4, 128.0, 125.5, 124.8, 119.0 (q, J = 276.0 Hz), 83.2, 21.4.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₃H₁₇F₃NOSe⁺ 460.0422, found 460.0423.



3-(phenylselanyl)-4-(*p*-tolyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-one (**3d**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3d** as a yellow liquid (74.7 mg, 82%).

¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.17 (m, 3H), 7.16 – 7.13 (m, 4H), 7.06 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 10.0 Hz, 2H), 6.23 (d, J = 10.0 Hz, 2H), 2.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 184.7, 173.7, 169.7 (q, J = 35.2 Hz), 140.8, 140.5, 132.6, 132.1, 129.4, 129.2, 129.1, 128.4, 127.9, 127.8, 124.2, 119.0 (q, J = 276.1 Hz), 83.0, 21.5.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{17}F_3NOSe^+$ 460.0422, found 460.0418.



4-(4-methoxyphenyl)-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6 ,9-tetraen-8-one (**3e**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.3) to give the titled product **3e** as a yellow liquid (74.8 mg, 79%).

¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 8.8 Hz, 2H), 7.21 – 7.13 (m, 5H), 6.77 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 10.0 Hz, 2H), 6.24 (d, J = 10.0 Hz, 2H), 3.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 184.7, 172.8, 169.9 (q, J = 35.0 Hz), 161.2, 141.3, 132.5, 131.7, 129.6, 129.5, 129.3, 127.8, 123.2, 122.7, 119.0 (q, J = 276.1 Hz). 114.0, 82.7, 55.4.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{17}F_3NO_2Se^+$ 476.0371, found 476.0376.



4-(4-fluorophenyl)-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9tetraen-8-one (**3f**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3f** as a yellow liquid (84.2 mg, 91%).

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.10 (m, 7H), 6.91 (t, J = 8.6 Hz, 2H), 6.49 (d, J = 10.0 Hz, 2H), 6.20 (d, J = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.4, 171.2, 169.5 (q, J = 35.5 Hz) 164.7, 162.2, 140.4, 132.7, 132.7, 130.0, 129.9, 129.5, 128.2, 119.0 (q, J = 276.0 Hz), 115.9, 115.7, 83.2.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4, -109.6.

HRMS (ESI): [M+H]⁺ calcd. for C₂₂H₁₄F₄NOSe⁺ 464.0171, found 464.0177.



4-(4-bromophenyl)-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9 -tetraen-8-one (**3g**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3g** as a yellow liquid (92.4 mg, 88%).

¹**H NMR (400 MHz, CDCl₃)** *δ* 7.33 (d, *J* = 8.5 Hz, 2H), 7.21 – 7.16 (m, 3H), 7.14 – 7.10 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 10.0 Hz, 2H), 6.19 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.3, 170.8, 169.4 (q, J = 35.5 Hz), 140.2, 132.9, 132.7, 131.7, 130.1, 129.5, 129.3, 128.3, 128.2, 126.1, 124.4, 118.9 (q, J = 276.1 Hz), 83.2.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₂H₁₄BrF₃NOSe⁺ 523.9371, found 523.9372.



4-(2-chlorophenyl)-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9tetraen-8-one (**3h**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3h** as a yellow liquid (39.6 mg, 42%).

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.24 (m, 3H), 7.18 (m, 7.20 – 7.16, 2H), 7.07 (t, J = 7.5 Hz, 2H), 7.02 – 6.98(m, 1H), 6.61 (dd, J = 7.7, 1.4 Hz, 1H), 6.47 (dd, J = 10.0,

0.9 Hz, 1H), 6.41 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.33 (dd, *J* = 10.0, 0.9 Hz, 1H), 6.18 (dd, *J* = 9.9, 2.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 168.5 (q, J = 33.5 Hz), 140.4, 139.3, 134.5, 132.9, 132.6, 131.9, 130.6, 130.0, 129.9, 129.3, 129.2, 128.7, 126.7, 126.4, 120.4 (q, J = 276.0 Hz), 84.8.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.5.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₂H₁₄ClF₃NOSe⁺ 479.9876, found 479.9876.



4-(naphthalen-1-yl)-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9 -tetraen-8-one (**3i**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3i** as a yellow liquid (58.2 mg, 58%).

¹**H NMR (400 MHz, CDCl₃)** δ 7.80 – 7.77 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.13 – 7.10 (m, 1H), 7.02 – 6.98 (m, 1H), 6.83 – 6.82 (m, 4H), 6.76 – 6.74 (m, 1H), 6.53 (dd, J = 9.7, 1.2 Hz, 1H), 6.34 – 6.28 (m, 2H), 6.11 (dd, J = 9.7, 1.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 184.5, 169.0 (q, J = 32.6 Hz), 140.4, 139.6, 134.5, 133.4, 132.9, 132.1, 129.7, 129.6, 128.9, 128.7, 128.5, 128.2, 126.9, 126.6, 126.3, 124.8, 124.6, 119.2 (q, J = 275.9 Hz), 85.1.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₆H₁₇F₃NOSe⁺ 496.0422, found 496.0426.



4-cyclopropyl-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetra en-8-one (**3**k)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3k** as a yellow liquid (53.9 mg, 66%).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.26 (m, 5H), 6.56 (d, *J* = 9.9 Hz, 2H), 6.16 (d, *J* = 10.0 Hz, 2H), 1.92 – 1.85 (m, 1H), 1.20 – 1.16 (m, 2H), 0.95 – 0.90 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 184.8, 179.9, 170.0 (q, *J* = 34.7 Hz), 141.3, 132.4, 130.6, 130.4, 129.7, 127.6, 120.9, 119.0 (q, *J* = 276.0 Hz), 81.9, 13.7, 9.9. ¹⁹F NMR (377 MHz, CDCl₃) δ -67.6.

HRMS (ESI): $[M+H]^+$ calcd. for C₁₉H₁₅F₃NOSe⁺ 410.0265, found 410.0271.

4-ethyl-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-o ne (**3**l)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3l** as a yellow liquid (24.6 mg, 31%).

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.34 (m, 2H), 7.28 – 7.26 (m, 3H), 6.58 (d, J = 9.9 Hz, 2H), 6.08 (d, J = 9.9 Hz, 2H), 2.32 – 2.28 (m, 2H), 1.30 – 1.25 (m, 8H), 0.84 (t, J = 6.9 Hz, 3H).

13C NMR (101 MHz, DMSO) *δ* 183.8, 172, 168.5 (q, *J* = 34.5 Hz), 140.7, 131.6, 1303, 129.1, 127.0, 118.5 (q, *J* = 275.8 Hz), 84, 78.3, 78.0, 77.7, 30.4, 28.7, 27.9, 21.6, 13.4.

¹⁹F NMR (**377** MHz, CDCl₃) δ -67.7.

HRMS (ESI): [M+H]⁺ calcd. for C₂₂H₂₃F₃NOSe⁺ 454.0891, found 454.0896.



3,4-bis(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-one (**3m'**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.3) to give the titled product **3m** as a yellow liquid (74.7 mg, 72%).

¹**H NMR (400 MHz, CDCl₃)** δ 7.48 – 7.31 (m, 8H), 7.21 (t, J = 6.6 Hz, 2H), 6.31 (d, J = 9.2 Hz, 2H), 6.04 (d, J = 9.3 Hz, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 183.8, 173.4, 166.7 (q, J = 34.4 Hz), 140.52, 137.2, 130.5, 130.1, 130.0, 129.8, 129.0, 128.9, 127.3, 123.1, 122.6, 118.8 (q, J = 276.1 Hz), 83.6.

¹⁹F NMR (377 MHz, CDCl₃) δ -66.7.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{15}F_3NOSe_2^+$ 525.9431, found 525.9434.



2-(chlorodifluoromethyl)-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-1,3,6,9-tetr aen-8-one (**3n**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3n** as a yellow liquid (37.5 mg, 41%).

¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.24 (m, 1H), 7.21 – 7.05 (m, 9H), 6.47 (d, J = 10.0 Hz, 2H), 6.23 (d, J = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.7, 172.8, 172.3 (t, J = 28.6 Hz), 140.7, 132.8, 132.6, 131.5, 129.8, 129.3, 129.0, 128.5, 128.0, 127.8, 125.6, 121.4 (t, J = 292.3 Hz), 82.8.

¹⁹F NMR (377 MHz, CDCl₃) δ -56.8.

HRMS (ESI): [M+H]⁺ calcd. for C₂₂H₁₅ClF₂NOSe⁺ 461.9970, found 461.9968.



2-(perfluoroethyl)-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-o ne (**30**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **30** as a yellow liquid (87.5 mg, 89%).

¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.24 (m, 1H), 7.21 – 7.14 (m, 5H), 7.09 – 7.06 (m, 4H), 6.47 (d, J = 10.0 Hz, 2H), 6.19 (d, J = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 172.3, 169.4 (t, J = 27.4 Hz), 140.3, 132.9, 132.7, 131.4, 129.7, 129.3, 128.8, 128.4, 128.0, 127.8, 126.7, 118.4 (qt, J = 286.5, 34.6 Hz), 110.1 (tq, J=257.6, J = 38.7 Hz), 84.1.

¹⁹F NMR (377 MHz, CDCl₃) δ -81.3, -114.1.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₃H₁₅F₅NOSe⁺ 496.0234, found 496.0231.



2-(3,3,3,3,3,3,3,3-heptafluoro-318-prop-1-yn-1-yl)-4-phenyl-3-(phenylselanyl)-1-azaspir o[4.5]deca-1,3,6,9-tetraen-8-one (**3p**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3p** as a yellow liquid (101.2 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.22 (m, 1H), 7.18 – 7.10 (m, 5H), 7.07 – 7.03 (m, 4H), 6.46 (d, J = 10.0 Hz, 2H), 6.17 (d, J = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 172.3, 169.8 (t, J = 25.7 Hz), 140.3, 133.0, 132.7, 131.5, 129.7, 129.3, 128.8, 128.5, 128.0, 127.7, 127.3, 117.8 (qt, J = 287.9, 33.8 Hz), 113.2 (tt, J = 260.2, 31.6 Hz), 84.1.

¹⁹F NMR (377 MHz, CDCl₃) δ -79.8 (t, J = 9.3 Hz), -111.8 (q, J = 9.3 Hz), -124.7 (s).

HRMS (ESI): $[M+H]^+$ calcd. for C₂₄H₁₅F₇NOSe⁺ 546.0202, found 546.0207.



3-((4-fluorophenyl)selanyl)-4-phenyl-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9tetraen-8-one (**3q**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3q** as a yellow liquid (72.1 mg, 78%).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 5H), 7.21 (dd, J = 7.7, 1.7 Hz, 2H), 7.05 (t, J = 8.9 Hz, 2H), 6.75 – 6.65 (m, 2H), 6.48 (d, J = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 174.3, 168.5 (q, J = 35.7 Hz), 161.8 (d, J = 244.5 Hz), 141.8, 133.3 (d, J = 8.0 Hz), 132.0, 131.5, 129.9, 128.4, 127.9, 124.3, 123.8, 119.7 (q, J = 274.7 Hz), 116.7 (d, J = 21.9 Hz), 83.3.

¹⁹F NMR (377 MHz, DMSO) δ -66.5, -114.7.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₂H₁₄F₄NOSe⁺ 464.0171, found 464.0176.



3-((4-chlorophenyl)selanyl)-4-phenyl-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9tetraen-8-one (**3r**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.3) to give the titled product **3r** as a yellow liquid (32.4 mg, 34%).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 1H), 7.26 – 7.23 (m, 2H), 7.14 – 7.05 (m, 6H), 6.48 (d, J = 10.0 Hz, 2H), 6.20 (d, J = 10.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.4, 173.1, 169.2 (q, J = 35.4 Hz), 140.2, 134.6, 134.3, 132.7, 131.2, 130.1, 129.5, 128.6, 127.8, 126.5, 125.1, 119.0 (q, J = 276.0 Hz), 83.3.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.1.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₂H₁₄ClF₃NOSe⁺ 479.9876, found 479.9875.



4-phenyl-3-((4-(trifluoromethoxy)phenyl)selanyl)-2-(trifluoromethyl)-1-azaspiro[4.5] deca-1,3,6,9-tetraen-8-one (**3s**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **4s** as a reddish-brown liquid (53.6 mg, 51%).

¹**H NMR (400 MHz, DMSO)** δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.22 – 7.18 (m, 4H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.50 (d, *J* = 10.0 Hz, 2H).

¹³C NMR (101 MHz, DMOS) δ 183.6, 175.8, 170.4 (q, J = 34.5 Hz), 141.5, 133.9, 132.3, 132.3, 131.8, 131.2, 129.7, 128.2, 127.6, 127.1, 126.5, 122.0, 119.9 (q, J = 274.0 Hz), 83.2.

¹⁹F NMR (377 MHz, DMSO) δ - 56.9, -66.6.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{14}F_6NO_2Se^+$ 530.0088, found 530.0099.



3-((2,4-dimethylphenyl)selanyl)-4-phenyl-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3 ,6,9-tetraen-8-one (**3t**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.3) to give the titled product **4t** as a yellow liquid (38.6 mg, 41%).

¹**H NMR (400 MHz, CDCl₃)** δ 7.23 (d, J = 7.5 Hz, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 7.4 Hz, 2H), 6.96 (d, J = 7.9 Hz, 1H), 6.85 (s, 1H), 6.69 (d, J = 7.8 Hz, 1H), 6.47 (d, J = 10.0 Hz, 2H), 6.22 (d, J = 10.0 Hz, 2H), 2.21 (s, 3H), 2.19 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 184.7, 171.6, 169.5 (q, J = 35.8 Hz), 140.7, 139.5, 138.5, 133.5, 132.6, 131.3, 131.1, 129.7, 129.0, 128.3, 127.63, 127.6, 125.7, 119.1 (q, J = 275.1 Hz), 65.7, 22.3, 21.0.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.6.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{19}F_3NOSe^+$ 474.0578, found 474.0590.



3-(naphthalen-1-ylselanyl)-4-phenyl-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-t etraen-8-one (**3u**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3u** as a yellow liquid (25.6 mg, 26%).

¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.91 (m, 1H), 7.75 – 7.73 (m, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.42 (d, J = 7.1 Hz, 1H), 7.08 (t, J = 7.8 Hz, 2H),

6.97 (t, *J* = 7.2 Hz, 2H), 6.76 – 6.74 (m, 2H), 6.38 (d, *J* = 10.1 Hz, 2H), 6.10 (d, *J* = 10.1 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.6, 170.8, 169.6 (q, J = 34.7 Hz), 140.5, 134.2, 134.0, 133.2, 132.5, 131.0, 129.8, 129.4, 128.9, 128.1, 127.3, 127.1, 127.0, 126.5, 126.4, 125.6, 125.4, 119.2 (q, J = 275.7 Hz), 83.6.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.5.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{17}F_3NOSe^+$ 496.0422, found 496.0427.



7-methyl-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9tetraen-8-one (**3w**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.4) to give the titled product **3w** as a yellow liquid (67.1 mg, 73%).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.15 (m, 10H), 6.52 – 6.49 (m, 1H), 6.22 (d, J = 9.8 Hz, 1H), 6.03 (s, 1H), 1.95 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 185.3, 173.6, 169.1 (q, J = 35.2 Hz), 140.1, 139.9, 134.9, 132.4, 131.5, 129.9, 129.4, 128.9, 128.4, 127.9, 127.8, 124.3, 119.1 (q, J = 275.9 Hz), 83.7, 16.1.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.4.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₃H₁₇F₃NOSe⁺ 460.0422, found 460.0430.



7-methoxy-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,
9-tetraen-8-one (3x)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3x** as a yellow liquid (44.4 mg, 47%).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.10 (m, 10H), 6.52 (d, J = 9.8 Hz, 1H), 6.17 (dd, J = 9.8, 2.5 Hz, 1H), 5.13 (d, J = 2.5 Hz, 1H), 3.65 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.0, 173.8, 168.7 (q, J = 35.5 Hz), 153.9, 140.8, 132.7, 132.5, 131.5, 130.0, 129.4, 128.8, 128.6, 128.1, 127.8, 124.0, 120.5 (q, J = 275.8 Hz, 106.8, 84.3, 55.5.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.5.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₃H₁₇F₃NO₂Se⁺ 476.0371, found 476.0374.



5,6-dimethoxy-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (3x')

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 10:1, Rf = 0.4) to give the titled product **3x'** as a yellow liquid (37.1 mg, 38%).

¹**H NMR (400 MHz, CDCl₃)** *δ* 7.55 (s, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.1 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 7.3 Hz, 2H), 6.59 (s, 1H), 4.06 (s, 3H), 3.68 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.8, 153.9, 151.6, 147.8 (q, J = 31.3 Hz), 143.8, 137.8, 133.2, 131.3, 129.2, 128.8, 128.1, 128.0, 126.6, 125.5, 122.26 (q, J = 276.1 Hz), 118.4, 108.5, 104.2, 56.6, 56.0.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.0.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{19}F_3NO_2Se^+$ 490.0528, found 490.0527.

4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4a)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 3:1, Rf = 0.4) to give the titled product **4a** as a yellow liquid (41.5 mg, 49%).

¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 8.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.54 – 7.50 (m, 1H), 7.44 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 7.12 – 7.08 (m, 1H), 7.03 – 6.99 (m, 2H), 6.96 – 6.94 (m, 2H), 6.90 – 6.88 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 158.1, 149.5 (q, J = 31.7 Hz), 146.2, 137.3, 132.8, 131.7, 131.2, 130.4, 129.4, 129.1, 128.9, 128.1, 128.0, 127.0, 126.8, 121.5, 121.4 (q, J = 270.9 Hz), 120.7.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.5.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{15}F_3NSe^+$ 430.0316, found 430.0325.



4-(4-methoxyphenyl)-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4b)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4b** as a yellow liquid (90.8 mg, 99%).

¹**H NMR (400 MHz, CDCl₃)** δ 8.24 (d, J = 8.3 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.71 – 7.67 (m, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.11 – 7.02 (m, 5H), 6.92 – 6.88 (m, 4H), 3.39 (s, 3H).

13C NMR (101 MHz, DMSO) *δ* 159.1, 158.4, 148.2 (q, *J* = 31.2 Hz), 145.4, 132.6, 131.8, 130.4, 129.8, 129.6, 129.1, 128.9, 126.9, 126.3, 120.3 (q, *J* = 276.6 Hz), 119.1, 113.3, 55.1.

19F NMR (377 MHz, DMSO) *δ* -61.7.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₃H₁₇F₃NOSe⁺ 460.0422, found 460.0422.



4-(4-ethylphenyl)-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4c)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4c** as a white solid (81.9 mg, 90%).

¹**H NMR (400 MHz, CDCl₃)** δ 8.26 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.53 – 7.47 (m, 2H), 7.14 – 7.08 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.88 (t, *J* = 8.0 Hz, 4H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.2, 149.3 (q, J = 31.5 Hz), 146.2, 144.3, 134.6, 132.8, 131.8, 131.1, 130.3, 129.4, 129.0, 128.9, 127.5, 127.1, 126.8, 122.0 (q, J = 276.5 Hz), 28.9, 15.7.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.2.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₄H₁₉F₃NSe⁺ 458.0629, found 458.0635.



4-(naphthalen-2-yl)-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4d)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4d** as a yellow liquid (59.0 mg, 62%).

¹**H NMR (400 MHz, CDCl₃)** δ 8.30 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.60 – 7.54 (m, 2H), 7.51 – 7.44 (m, 3H), 7.27 – 7.26 (m, 1H), 7.16 – 7.14 (m, 1H), 7.03 (t, J = 7.3 Hz, 1H), 6.86 (t, J = 7.7 Hz, 2H), 6.79 – 6.77 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.9, 149.5 (q, J = 31.5 Hz), 146.2, 134.6, 132.8, 132.8, 132.7, 131.9, 131.2, 130.4, 129.5, 129.2, 129.0, 128.8, 128.4, 127.8, 127.7, 127.1, 127.0, 126.8, 126.4, 122.0 (q, J = 276.7 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ -62.5.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₆H₁₇F₃NSe⁺ 480.0473, found 480.0482.



4-(4-methoxyphenyl)-3-(thiophen-3-yl)-5-(trifluoromethyl)-4H-1,2,4-triazole (4e)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4e** as a yellow liquid (45.0 mg, 52%).

¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.20 – 7.13 (m, 5H), 5.08 (s, 1H), 2.44 (d, J = 17.1 Hz, 1H), 2.11 – 2.07 (m, 2H), 1.92 – 1.72 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 161.6, 149.8 (q, J = 31.4 Hz), 146.4, 135.0, 134.6, 131.2, 130.5, 129.7, 129.0, 129.0, 128.6, 126.6, 126.5, 121.9 (q, J = 276.6 Hz), 118.3, 29.8, 25.3, 22.9, 21.9.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.2.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{19}F_3NSe^+$ 434.0629, found 434.0635.



4-cyclopropyl-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4f)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4f** as a yellow liquid (51.2 mg, 65%).

¹**H** NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.68 – 7.64 (m, 1H), 7.27 – 7.25 (m, 2H), 7.18 – 7.16 (m, 3H), 1.54 – 1.47 (m, 1H), 1.33 – 1.28 (m, 2H), 0.93 – 0.89 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 155.3, 149.3 (q, J = 31.4 Hz), 146.0, 132.9, 131.3, 130.8, 130.6, 129.4, 128.6, 127.0, 125.5, 125.0, 122.0 (q, J = 276.6 Hz), 116.4, 15.0, 11.5.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.6.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{15}F_3NSe^+$ 394.0316, found 394.0324.



6-methyl-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4g)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4g** as a yellow solid (60.2 mg, 68%).

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.6 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.42 – 7.38 (m, 1H), 7.32 (t, J = 7.4 Hz, 3H), 7.18 (s, 1H), 7.12 – 7.08 (m, 1H), 7.03 – 7.00 (m, 2H), 6.96 – 6.94 (m, 2H), 6.90 – 6.88 (m, 2H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.3, 148.6 (q, J = 31.5 Hz), 144.8, 139.6, 137.5, 133.5, 133.0, 131.5, 130.0, 129.4, 128.9, 128.0, 128.0, 126.7, 125.7,122.1 (q, J = 276.5 Hz), 120.6, 22.1.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.4.

М.р. 120.8-123.3 °С

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{17}F_3NSe^+$ 444.0473, found 444.0477.



8-methyl-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4h)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4h** as a yellow liquid (54.0 mg, 61%).

¹**H NMR (400 MHz, CDCl₃)** δ 7.68 (d, J = 6.9 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.35 – 7.28 (m, 3H), 7.15 – 7.11 (m, 1H), 7.04 (t, J = 7.6 Hz, 2H), 6.98 – 6.93 (m, 4H), 2.94 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.0, 148.1 (q, J = 31.7 Hz), 145.3, 138.8, 137.8, 133.0, 131.6, 131.2, 129.4, 128.9, 128.8, 128.0, 127.9, 126.7, 124.9, 122.1 (q, J = 276.5 Hz), 120.1, 17.9.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.8.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{17}F_3NSe^+$ 444.0473, found 444.0478.



3-6-(tert-butyl)-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)quinoline (4i)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.3) to give the titled product **4i** as a white solid (41.8 mg, 43%).

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.9 Hz, 1H), 7.92 – 7.89 (m, 1H), 7.38 – 7.26 (m, 4H), 7.09 (t, J = 7.3 Hz, 1H), 7.02 – 6.95 (m, 4H), 6.88 (d, J = 7.5 Hz, 2H), 1.23 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 158.0, 148.1 (q, J = 31.7 Hz), 145.3, 138.8, 137.8, 133.0, 131.6, 131.2, 129.4, 128.9, 128.8, 128.0, 127.9, 126.7, 124.9, 122.1 (q, J = 276.5 Hz), 120.8, 17.9.

¹⁹F NMR (377 MHz, CDCl₃) δ -62.4.

M.p. 106.3-108.5 °C

HRMS (ESI): $[M+H]^+$ calcd. for C₂₆H₂₃F₃NSe⁺ 486.0942, found 486.0948.



4-2-(3,3,3,3,3,3,3,3,-heptafluoro-318-prop-1-yn-1-yl)-4-phenyl-3-(phenylselanyl)quinoli ne (4j)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 50:1, Rf = 0.4) to give the titled product **4j** as a reddish-brown liquid (79.4 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 8.4 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.53 – 7.49 (m, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.26 (m, 2H), 7.12 – 7.08 (m, 1H), 7.00 (t, J = 7.6 Hz, 2H), 6.94 – 6.92 (m, 2H), 6.88 – 6.89 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 149.3 (t, J = 24.1 Hz), 146.0, 137.4, 133.2, 131.7, 131.1, 130.4, 129.5, 129.3, 129.0, 128.9, 128.0, 128.0, 126.9, 126.7, 122.0, 118.5 (qt, *J* = 288.2, 34.6 Hz), 113.6 (tt, *J* = 258.4, 29.5 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ -78.7 (t, J = 9.6 Hz), -102.2 (q, J = 19.3 Hz), -122.0 (s).

HRMS (ESI): $[M+H]^+$ calcd. for C₂₄H₁₅F₇NSe⁺ 530.0252, found 530.0260.



5-phenyl-3-(phenylseleninyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-tetraen-8-one (5)

¹**H NMR (400 MHz, CDCl₃)** δ 7.45 – 7.37 (m, 6H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.14 (m, 2H), 6.52 – 6.46 (m, 3H), 6.18 – 6.13 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 184.0, 178.7, 166.0 (q, J = 38.6 Hz) 138.8, 138.2, 133.6, 133.4, 131.7, 131.1, 129.7, 129.2, 128.8, 128.3, 126.1, 118.6 (q, J = 275.7 Hz), 83.9.

¹⁹F NMR (377 MHz, CDCl₃) δ -66.3.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₂H₁₅F₃NO₂Se⁺ 462.0215, found 462.0218.



8-ethyl-4-phenyl-3-(phenylselanyl)-2-(trifluoromethyl)-1-azaspiro[4.5]deca-1,3,6,9-te traen-8-ol (6)

¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.08 (m, 10H), 6.12 (d, J = 9.9 Hz, 2H), 5.23 (d, J = 9.9 Hz, 2H), 1.31 (q, J = 7.6 Hz, 2H), 0.48 (t, J = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 179.0, 166.6 (q, J = 35.0 Hz), 137.2, 132.6, 132.1, 129.7, 129.3, 129.2, 128.3, 128.0, 127.6, 121.9, 121.7, 119.3 (q, J = 275.8 Hz), 82.8, 67.8, 33.3, 7.7.

¹⁹F NMR (377 MHz, CDCl₃) δ -67.1.

HRMS (ESI): $[M+H]^+$ calcd. for C₂₄H₂₁F₃NOSe⁺ 476.0735, found 476.0733.

5 References

(1) K. Tamura, H. Mizukami, K. Maeda, H. Watanabe, K. Uneyama, J. Org. Chem. **1993**, 58, 32-35.

(2) M. Chen, Q. Zhang, X. Zhang, P. Zhong, M. Hu. J. Chem. Res. 2008, 11, 637-639.

(3) D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues, A.
L. Braga, *Org. Lett.* 2010, *12*, 3288-3291.

6 Copy of ¹H, ¹³C and ¹⁹F NMR Spectra of Products.





¹H NMR (400 MHz, CDCl₃)

7.00 . 20 7.15 f1 (ppm) 7.05 7.10





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 fl (ppm)



¹³C NMR (101 MHz, CDCl₃)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 fl (ppm)


















77.72 77.72 77.73 77.74 77.74 6.49 6.49 6.49 6.47 6.41 6.41











----67.46





¹⁹F NMR (377 MHz, CDCl₃)



----67.35





< •= SePh `N≓∕ 3k `CF₃ ¹⁹F NMR (377 MHz, CDCl₃)

----67.63







¹H NMR (400 MHz, CDCl₃)





SePh 0= `N≦ ℃F₃ 31 ¹⁹F NMR (377 MHz, CDCl₃)

---67.72







----66.66







---------56.81





S56



S57















CI 3r

¹⁹F NMR (377 MHz, DMSO)

----67.12



OCF3 0 3s

¹⁹F NMR (377 MHz, DMSO)







0= 3t ¹⁹F NMR (377 MHz, CDCl₃)

---67.62

0= 3u

¹H NMR (400 MHz, CDCl₃)





0= CF₃ 3u

¹⁹F NMR (377 MHz, CDCl₃)

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

----67.53





SePh 0= N≊ CF₃ 3w ¹⁹F NMR (377 MHz, CDCl₃)

---67,39


¹H NMR (400 MHz, CDCl₃)





6. 2

6.0

7.0 6.8 6.6 6.4 f1 (ppm)

¹³C NMR (101 MHz, CDCl₃)



MeQ SePh /N= 3x 0= `CF₃

¹⁹F NMR (377 MHz, CDCl₃)

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

---67.45



---4.06 ---3.68





----62.01

A 528 A 528



S76















8.24 8.22 8.22 8.22 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.84 7.7.19 7.7.119 7.7.119 7.7.119 ~2.42 2.42 2.42 2.42 2.03 7.2.09 1.1.92 1.1.74 1.1.74 1.1.75 1.1.73





----62.21







------62.56















-----62.78





-1.23



-----62.41

2.8 4.8 28 2.9 2.9 29 2.1 2.1 20 2.1 2.1 20 2.1 2.1 20 2.1 2.2 20 2.1 2.







 $O = \underbrace{\bigvee_{N=1}^{Ph} \bigcup_{CF_3}^{O} O_{L}}_{Se-Ph}$

¹H NMR (400 MHz, CDCl₃)







¹³C NMR (101 MHz, CDCl₃)





----66.31





----67.06