Supporting Information

Dienylation of *N*-benzoylhydrazones with CF_3-substituted Homoallenylboronates in Water.

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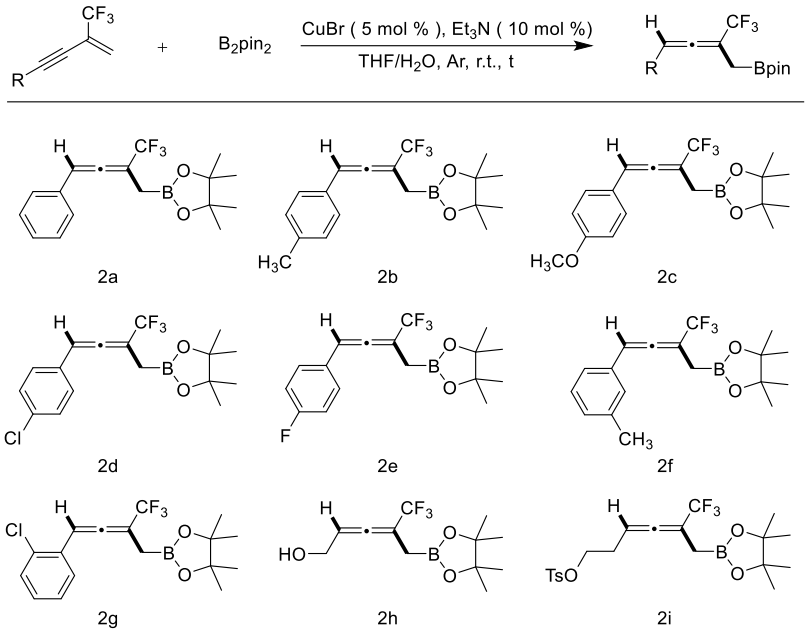
1. General Experimental Information

Unless otherwise noted, reagents were used as supplied commercially without further purification. ^{1}H NMR, ^{11}B NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 25 ºC on a Bruker Advance 400 M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts of ^{1}H, ^{11}B, ^{19}F and ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as a *J* value in Hertz (Hz). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF or Thermo Scientific Q Exactive GC Orbitrap. Enantiomeric excesses of chiral compounds were determined by chiral high-performance liquid chromatography analyses which were performed on an Agilent 1260 Infinity equipped with a Daicel Chiralpak IC, IC-3 or Daicel Chiralcel OJ, OJ-3, OD-H, OD-3 column. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. All hydrazones were prepared according to the literature procedures[1].

2. General Procedures

2.1 Synthesis of Starting Materials.

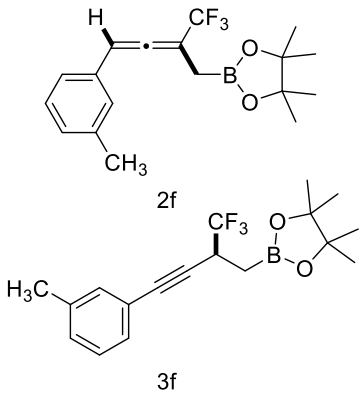
The starting materials **2a**-**2i** were prepared according to the literature procedure[2].



Under argon atmosphere, CuBr (5 mol %) and B_2pin_2 (1.25 equiv) were added into a Schlenk tube. And then, THF/H_2O (2:1), triethylamine (10 mol %), and the corresponding enyne (1.0 equiv) were added sequentially. The mixture was stirred at room temperature, monitored by TLC to the end, diluted and extracted with DCM, washed by H_2O, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by flash column chromatography.

(**2a**-**2g** were synthetized according to the above general procedure; but **2h** and **2i** were synthetized by using 1,4-dioxane/H_2O = 2:1 as solvent.)

4,4,5,5-tetramethyl-2-(4-(m-tolyl)-2-(trifluoromethyl)buta-2,3-dien-1-yl)-1,3,2-dioxaborolane. (**2f**)



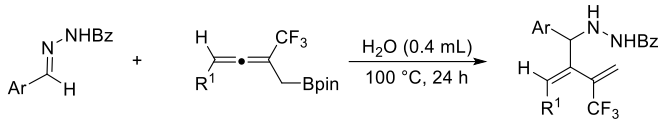
2f

3f

Pale yellow oil, (2f:3f = 97:3), R_f = 0.55 (ethyl acetate/petroleum ether 1:20). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 1H), 7.18 – 7.14 (m, 2H), 7.09 – 7.03 (m, 1H), 6.54 – 6.45 (m, 1H), 2.34 (s, 3H), 1.92 – 1.79 (m, 2H), 1.22 (s, 6H), 1.19 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -65.14, -65.15. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 32.64. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.47 (q, *J* = 4.1 Hz), 138.40, 132.27 (q, *J* = 1.1 Hz), 128.98, 128.65, 128.34, 125.00, 123.77 (q, *J* = 275.2 Hz), 100.66, 98.91 (q, *J* = 35.1 Hz), 84.04, 24.93, 24.78, 21.46. **HRMS (ESI)**: m/z calculated for $C_{18}H_{23}BF_3O_2$ $[M+H]^+$: 339.1743, found: 339.1740.

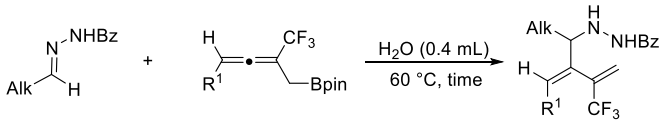
2.2 General Procedure for the Reactions of Hydrazones with Homoallylboronates in Water.

Procedure A:



Under air atmosphere, aromatic hydrazone (0.2 mmol, 1.0 equiv), homoallylboronate (0.24 mmol, 1.2 equiv) and water (0.4 mL) were added into a Schlenk tube. The mixture was stirred at 100 °C for 24 h, diluted and extracted with DCM, washed with saturated brine, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) or preparative thin layer chromatography using ethyl acetate/petroleum ether as eluent.

Procedure B:

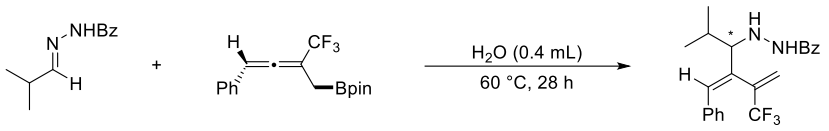


Under air atmosphere, aliphatic hydrazone (0.2 mmol, 1.0 equiv), homoallylboronate (0.22 mmol, 1.1 equiv) and water (0.4 mL) were added into a Schlenk tube. The mixture was stirred at 60 °C, monitored by TLC to the end, diluted and extracted with DCM, washed with saturated brine, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-

300 mesh) or preparative thin layer chromatography using ethyl acetate/petroleum ether as eluent.

2.3 General Procedures for Chirality Transfer and Derivatization Reaction.

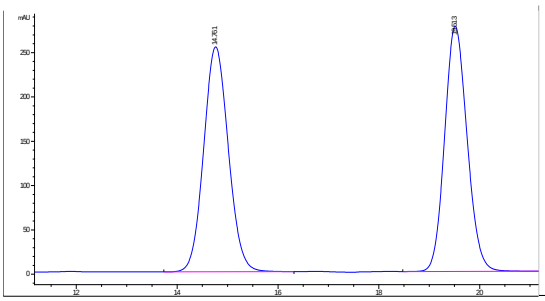
2.3.1 General Procedure for Chirality Transfer



1g (*S*)-**2a**, 90% ee **4**, 97% 64% ee, *E*/*Z* > 99:1

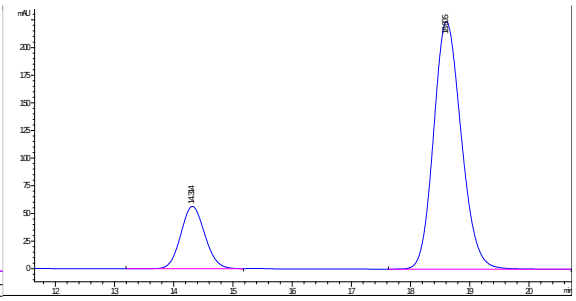
Under air atmosphere, hydrazone **1g** (0.2 mmol, 1.0 equiv), chiral homoallylboronate **(*R*)-2a** (0.24 mmol, 1.1 equiv) and water (0.4 mL) were added into a Schlenk tube. The mixture was stirred at 60 °C for 28 h, diluted and extracted with DCM, washed with saturated brine, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) using ethyl acetate/petroleum ether as eluent to afford the product **4** as white solid (97% yield, 64% ee, *E*/*Z* > 99:1).

The enantiomeric excess of **4** was determined by chiral HPLC analysis on Daicel Chiralcel OD-H column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.6 mL/min, column temperature = 25 ˚C, UV-Vis detection at λ = 254 nm, t_{R1} = 14.314 min (minor), t_{R2} = 18.605 min (major).



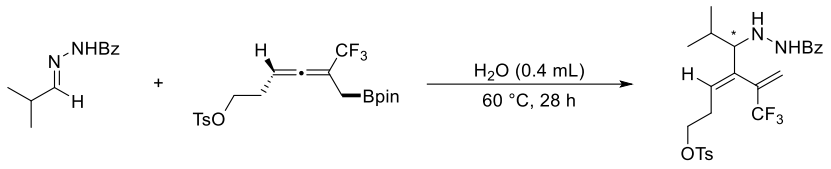
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.761	BB	0.5314	8638.98145	253.64568	50.1760
2	19.513	BB	0.4819	8578.39258	276.54562	49.8240
Totals :				1.72174e4	530.19130	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

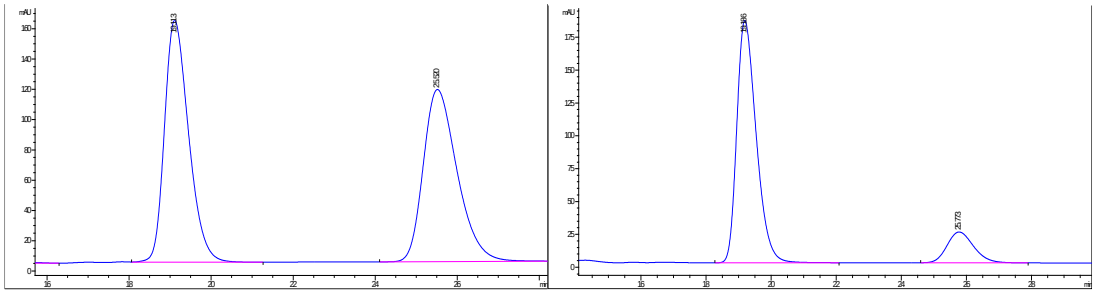
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.314	BB	0.4394	1590.54053	56.32703	17.9676
2	18.605	BB	0.5042	7261.70654	223.99356	82.0324
Totals :				8852.24707	280.32059	



1g **(*S*)-2i**, 95% ee **5,** 92%
70% ee, *E*/*Z* > 99:1

Under air atmosphere, hydrazone **1g** (0.2 mmol, 1.0 equiv), chiral homoallylboronate **(*R*)-2i** (0.24 mmol, 1.1 equiv) and water (0.4 mL) were added into a Schlenk tube. The mixture was stirred at 60 °C for 28 h, diluted and extracted with DCM, washed with saturated brine, dried over anhydrous Na_2SO_4. After concentration under vacuum, the residue was purified by column chromatography over silica gel (200-300 mesh) using ethyl acetate/petroleum ether as eluent to afford the product **5** as pale yellow solid (92% yield, 70% ee, *E*/*Z* > 99:1).

The enantiomeric excess of **5** was determined by chiral HPLC analysis on Daicel Chiralcel OD-H column. Conditions: hexane/isopropanol = 90:10, flow rate = 0.6 mL/min, column temperature = 25 ˚C, UV-Vis detection at λ = 254 nm, t_{R1} = 19.186 min (major), t_{R2} = 25.773 min (minor).



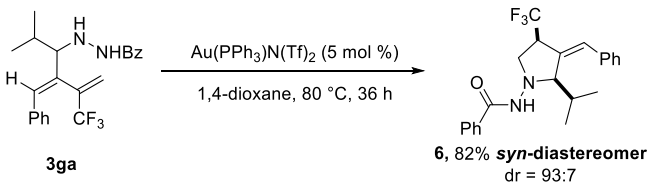
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.113	BB	0.6293	6529.05420	159.57851	50.1083
2	25.520	BBA	0.8775	6500.83838	113.62487	49.8917
Totals :				1.30299e4	273.20338	

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.186	BB	0.6387	7632.02393	184.44621	85.1568
2	25.773	BB	0.8664	1330.29028	23.43032	14.8432
Totals :				8962.31421	207.87654	

2.3.2 General Procedure for Derivatization Reaction of Compound 3ga.



3ga **6,** 82% ***syn*-diastereomer**
dr = 93:7

Under argon atmosphere, the 2-aminomethyl-1,3-diene derivative **3ga** (0.1 mmol, 1.0 equiv) were added into a Schlenk tube. After that, $Au(PPh_3)N(Tf)_2$ (5 mol %) were added in the glove box. Then, 1, 4-dioxane (0.5 mL) was added and the mixture was

stirred at 80 °C for 36 h. When the reaction was finished, solvent was removed under vacuum and the crude residue was purified by preparative thin layer chromatography using isopropyl amine/petroleum ether (1:20) as eluent and the *syn* product **6** could be obtained as pale yellow solid in 82% yield (93:7 dr ratio was determined by ^{1}H NMR analysis of the crude reaction mixture).

2.4 X-Ray Crystallographic Data of 6.

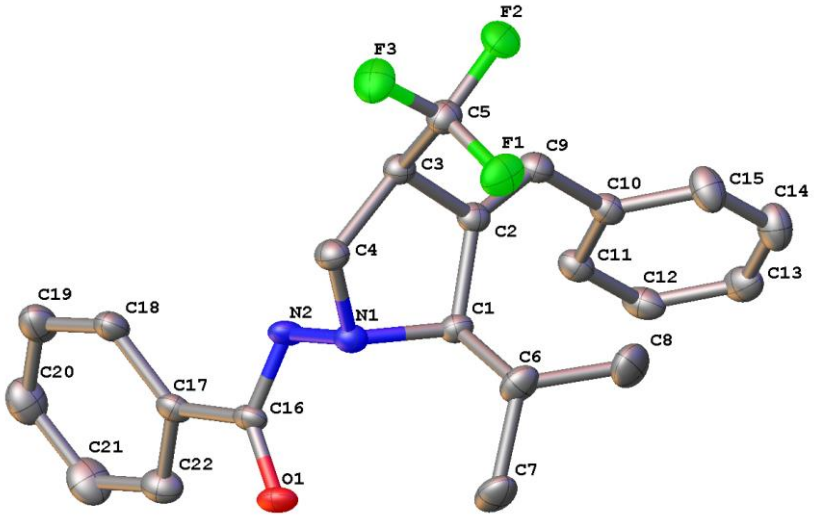


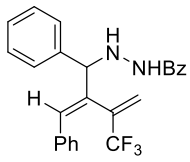
Table S1. Crystal data and structure refinement for **6**

Identification code	**6**
Empirical formula	$C_{22}H_{23}F_3N_2O$
Formula weight	388.42
Temperature/K	170.04
Crystal system	trigonal
Space group	R3c
a/Å	32.7473(4)
b/Å	32.7473(4)
c/Å	9.72720(10)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	9033.8(2)

Z	18
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	0.529
F(000)	3672.0
Crystal size/mm^3	0.12 × 0.08 × 0.06
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	9.398 to 109.85
Index ranges	-39 ≤ h ≤ 39, -39 ≤ k ≤ 39, -8 ≤ l ≤ 11
Reflections collected	32549
Independent reflections	3536 [Rint = 0.0488, Rsigma = 0.0267]
Data/restraints/parameters	3536/1/255
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0729
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0771
Largest diff. peak/hole / e Å^{-3}	0.11/-0.17
Flack parameter	-0.07(7)

3. Characterization Data and Spectrum of Products.

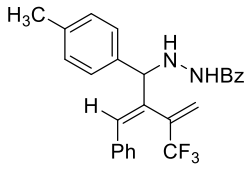
(*E*)-*N'*-(2-benzylidene-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3aa**)



Following the general procedure A, **3aa** was obtained as white solid. Yield = 84%, (*E*/*Z* > 99:1), R_f = 0.39 (ethyl acetate/petroleum ether 1:4), mp 130−131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.63 – 7.57 (d, *J* = 5.8 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.42 – 7.31 (m, 8H), 7.31 – 7.21 (m, 3H), 5.75 (q, *J* =1.5 Hz, 1H), 5.26 (d, *J* = 6.2 Hz, 1H), 4.97 (q, *J* =1.1 Hz, 1H), 4.90 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.90. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.59, 138.26, 136.25 (q, *J* = 31.1 Hz), 135.86, 134.73, 132.96, 131.99, 131.94, 129.16, 128.81, 128.73, 128.66, 128.41, 128.38, 127.84, 127.00, 125.48 (q, *J* = 5.1 Hz), 123.06 (q, *J* = 275.5

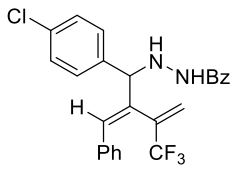
Hz), 69.04. **HRMS (ESI)**: m/z calculated for $C_{25}H_{21}F_3N_2ONa$ $[M+Na]^+$: 445.1504, found: 445.1509.

(*E*)-*N'*-(2-benzylidene-1-(p-tolyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ba**)



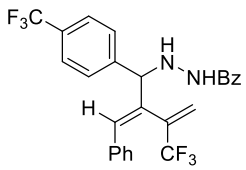
Following the general procedure A, **3ba** was obtained as white solid. Yield = 95%, (*E*/*Z* > 99:1), R_f = 0.41 (ethyl acetate/petroleum ether 1:4), mp 113−114 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.60 (d, *J* = 6.4 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.43 – 7.35 (m, 5H), 7.35 – 7.33 (m, 1H), 7.33 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 5.75 (q, *J* = 1.4 Hz, 1H), 5.23 (d, *J* = 6.7 Hz, 1H), 4.98 (q, *J* = 1.2 Hz, 1H), 4.85 (s, 1H), 2.34 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.92. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.51, 138.14, 136.30 (q, *J* = 31.1 Hz), 135.94, 135.19, 134.88, 133.02, 131.96, 131.69, 129.43, 129.16, 128.81, 128.58, 128.37, 127.79, 126.99, 125.41 (q, *J* = 5.1 Hz), 123.01 (q, *J* =275.7 Hz), 68.79, 21.31. **HRMS (ESI)**: m/z calculated for $C_{26}H_{23}F_3N_2ONa$ $[M+Na]^+$: 459.1660, found: 459.1660.

(*E*)-*N'*-(2-benzylidene-1-(4-chlorophenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ca**)



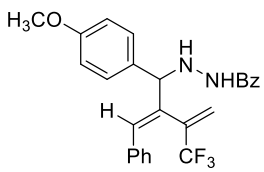
Following the general procedure A, **3ca** was obtained as white solid. Yield = 92%, (*E*/*Z* > 99:1), R_f = 0.39 (ethyl acetate/petroleum ether 1:4), mp 95−96 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.60 (s, 1H), 7.53 – 7.47 (m, 1H), 7.44 – 7.37 (m, 6H), 7.36 – 7.22 (m, 6H), 5.77 (q, *J* = 1.5 Hz, 1H), 5.20 (s, 1H), 5.01 – 4.97 (m, 1H), 4.89 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.86. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.73, 136.91, 136.15 (q, *J* = 31.2 Hz), 135.61, 134.40, 134.24, 132.77, 132.34, 132.14, 129.98, 129.16, 128.96, 128.88, 128.44, 128.01, 126.99, 125.69 (q, *J* = 5.0 Hz), 122.98 (q, *J* = 276.4 Hz), 68.33. **HRMS (ESI)**: m/z calculated for $C_{25}H_{20}ClF_3N_2ONa$ $[M+Na]^+$: 479.1114, found: 479.1104.

(*E*)-*N*′-(2-benzylidene-3-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzohydrazide (**3da**)



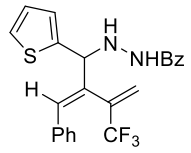
Following the general procedure A, **3da** was obtained as white solid. Yield = 75%, (*E*/*Z* > 99:1), R_f = 0.41 (ethyl acetate/petroleum ether 1:4), mp 41−42 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 3H), 7.62 – 7.57 (m, 4H), 7.53 – 7.48 (m, 1H), 7.43 – 7.36 (m, 4H), 7.33 – 7.28 (m, 3H), 7.28 – 7.23 (m, 1H), 5.79 (q, *J* = 1.3 Hz, 1H), 5.24 (dd, *J* = 6.6, 1.9 Hz, 1H), 5.0 – 4.97 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.53, -63.81. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.86, 142.56, 136.08 (q, *J* = 31.3 Hz), 135.47, 134.10, 132.97, 132.67, 132.21, 130.60 (q, *J* = 32.4 Hz), 129.16, 128.92, 128.90, 128.47, 128.12, 127.00, 125.85 (q, *J* = 5.1 Hz), 125.71 (q, *J* = 3.8 Hz), 124.15 (q, *J* =273.3Hz), 122.96 (q, *J* =276.3 Hz), 68.54. **HRMS (ESI)**: m/z calculated for $C_{26}H_{20}F_6N_2ONa$ $[M+Na]^+$: 513.1378, found: 513.1379.

(*E*)-*N*′-(2-benzylidene-1-(4-methoxyphenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ea**)



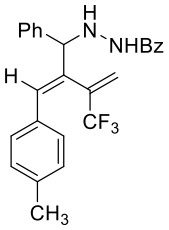
Following the general procedure A, **3ea** was obtained as white solid. Yield = 89%, (*E*/*Z* = 25:75), R_f = 0.27 (ethyl acetate/petroleum ether 1:4), mp 132−133 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 1H), 7.68 – 7.62 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.35 (m, 6H), 7.33 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 6.90 – 6.80 (m, 2H), 5.79 – 5.73 (m, 1H), 5.32 – 5.12 (m, 1H), 4.99 – 4.96 (m, 1H), 4.88 – 4.82 (m, 1H), 3.79 – 3.77 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.95. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.56, 159.61, 138.49, 136.32 (q, *J* = 31.3 Hz), 135.91, 134.90, 132.98, 131.92, 131.38, 130.17, 129.88, 129.12, 128.76, 128.35, 126.98, 125.34 (q, *J* = 5.1 Hz), 123.04 (q, *J* = 275.4 Hz), 114.03, 68.39, 55.33. **HRMS (ESI)**: m/z calculated for $C_{26}H_{23}F_3N_2O_2Na$ $[M+Na]^+$: 475.1609, found: 475.1608.

(*E*)-*N*′-(2-benzylidene-1-(thiophen-2-yl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3fa**)



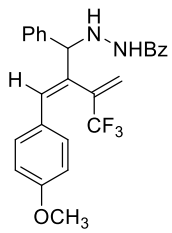
Following the general procedure A, **3fa** was obtained as pale yellow solid. Yield = 78%, (*E*/*Z* = 88:12), R_f = 0.37 (ethyl acetate/petroleum ether 1:4), mp 133−134 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.57 (d, *J* = 6.3 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.43 – 7.39 (m, 2H), 7.37 – 7.28 (m, 3H), 7.24 (dt, *J* = 5.1, 1.0 Hz, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.93 (q, *J* = 1.5 Hz, 1H), 5.24 (d, *J* = 6.6 Hz, 1H), 5.16 (q, *J* = 1.2 Hz, 1H), 4.88 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.02. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.62, 138.79, 138.23, 135.94 (q, *J* = 31.4 Hz), 132.94, 132.01, 131.98, 130.29, 128.83, 128.76, 128.59, 128.45, 127.11 (q, *J* = 4.9 Hz), 127.01, 126.83, 126.75, 125.06, 123.02 (q, *J* = 276.6 Hz), 68.77. **HRMS (ESI)**: m/z calculated for $C_{23}H_{19}F_3N_2OSNa$ $[M+Na]^+$: 451.1068, found: 451.1064.

(*E*)-*N*′-(2-(4-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ab**)



Following the general procedure A, **3ab** was obtained as white solid. Yield = 64%, (*E*/*Z* > 99:1), R_f = 0.41 (ethyl acetate/petroleum ether 1:4), mp 113−114 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 3H), 7.51 – 7.43 (m, 3H), 7.40 – 7.27 (m, 8H), 7.11 (s, 1H), 7.09 (s, 1H), 5.75 (q, *J* = 1.5 Hz, 1H), 5.25 (d, *J* = 6.6 Hz, 1H), 4.97 (q, *J* = 1.1 Hz, 1H), 4.88 (s, 1H), 2.32 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.91. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.55, 138.40, 137.82, 136.45 (q, *J* = 31.0 Hz), 133.64, 132.99, 132.93, 131.96, 131.91, 129.11, 128.80, 128.69, 128.65, 128.35, 127.00, 125.33 (q, *J* = 5.1 Hz), 123.11 (d, *J* = 276.7 Hz), 69.18, 21.32. **HRMS (ESI)**: m/z calculated for $C_{26}H_{23}F_3N_2ONa$ $[M+Na]^+$: 459.1660, found: 459.1662.

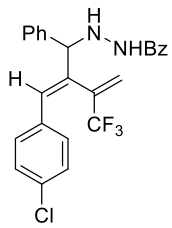
(*E*)-*N*′-(2-(4-methoxybenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ac**)



Following the general procedure A, **3ac** was obtained as white solid. Yield = 52%, (*E*/*Z* = 60:40), R_f = 0.31 (ethyl acetate/petroleum ether 1:4), mp 128−129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 3H), 7.53 – 7.42 (m, 2H), 7.44 – 7.32 (m, 6H), 7.36 – 7.26 (m, 2H),

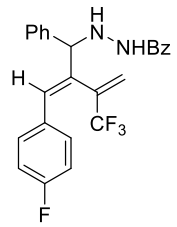
7.28 – 7.19 (m, 1H), 6.86 – 6.80 (m, 2H), 5.78 (q, *J* = 1.5 Hz, 1H), 5.25 (d, *J* = 6.2 Hz, 1H), 5.00 – 4.97 (m, 1H), 4.87 (s, 1H), 3.79 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.01. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.53, 159.32, 138.53, 136.57 (q, *J* = 31.0 Hz), 135.93, 134.97, 133.01, 131.96, 131.52, 130.57, 129.90, 128.81, 128.69, 128.63, 126.99, 125.31 (q, *J* = 5.1 Hz), 123.14 (q, *J* = 276.6 Hz), 113.82, 69.35, 55.36. **HRMS (ESI)**: m/z calculated for $C_{26}H_{23}F_3N_2O_2Na$ $[M+Na]^+$: 475.1609, found: 475.1608.

(*E*)-*N*′-(2-(4-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ad**)



Following the general procedure A, **3ad** was obtained as white solid. Yield = 64%, (*E*/*Z* > 99:1), R_f = 0.36 (ethyl acetate/petroleum ether 1:4), mp 107−108 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.61 (d, *J* = 6.3 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.27 (m, 9H), 7.26 – 7.23 (m, 1H), 5.76 (q, *J* = 1.4 Hz, 1H), 5.23 (d, *J* = 6.0 Hz, 1H), 4.96 (q, *J* = 1.2 Hz, 1H), 4.89 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.98. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.68, 138.06, 136.02 (q, *J* = 31.2 Hz), 135.49, 134.35, 133.60, 132.87, 132.01, 130.67, 130.36, 128.79, 128.76, 128.61, 128.56, 128.48, 126.99, 125.67 (q, *J* = 5.1 Hz), 122.92 (q, *J* = 276.5 Hz), 69.01. **HRMS (ESI)**: m/z calculated for $C_{25}H_{20}ClF_3N_2ONa$ $[M+Na]^+$: 479.1114, found: 479.1113.

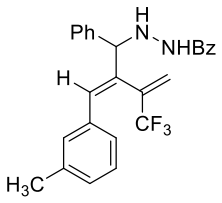
(*E*)-*N*′-(2-(4-fluorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ae**)



Following the general procedure A, **3ae** was obtained as white solid. Yield = 59%, (*E*/*Z* > 99:1), R_f = 0.33 (ethyl acetate/petroleum ether 1:4), mp 128−129 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.59 (d, *J* = 6.6 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.42 – 7.31 (m, 7H), 7.28 (s, 1H), 7.01 – 6.95 (m, 2H), 5.77 (q, *J* = 1.4 Hz, 1H), 5.28 – 5.20 (m, 1H), 4.97 (q, *J* = 1.2 Hz, 1H), 4.89 (s, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.05, -113.64 (tt, *J* = 8.5, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.63, 162.29 (d, *J* = 249.5 Hz), 138.23, 136.15 (q, *J* = 31.2 Hz), 134.60 (d, *J* = 1.0 Hz), 132.94, 132.05, 131.95 (d, *J* = 3.5 Hz),

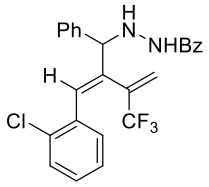
130.87, 130.85, 130.79, 128.81 (d, J = 7.0 Hz), 128.63, 128.47, 126.99, 125.65 (q, J = 5.1 Hz), 123.00 (q, J = 276.4 Hz), 115.38 (d, J = 21.5 Hz), 69.15. **HRMS (ESI)**: m/z calculated for $C_{25}H_{20}F_4N_2ONa$ $[M+Na]^+$: 463.1410, found: 463.1411.

(*E*)-*N*′-(2-(3-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3af**)



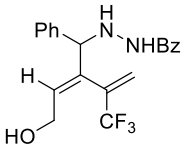
Following the general procedure A, **3af** was obtained as white solid. Yield = 71%, (*E*/*Z* > 99:1), R_f = 0.44 (ethyl acetate/petroleum ether 1:4), mp 109−110 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 5.8 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.50 – 7.44 (m, 3H), 7.41 – 7.28 (m, 6H), 7.23 – 7.14 (m, 3H), 7.08 – 7.02 (m, 1H), 5.74 (q, J = 1.4 Hz, 1H), 5.24 (d, J = 6.1 Hz, 1H), 4.96 (q, J = 1.1 Hz, 1H), 4.89 (s, 1H), 2.31 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.79. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.57, 138.31, 137.93, 136.38 (q, J = 31.1 Hz), 135.76, 134.45, 132.96, 132.05, 131.96, 130.10, 128.78, 128.69, 128.64, 128.58, 128.37, 128.25, 127.00, 126.04, 125.38 (q, J = 5.1 Hz), 123.08 (q, J = 276.4 Hz), 69.07, 21.48. **HRMS (ESI)**: m/z calculated for $C_{26}H_{23}F_3N_2ONa$ $[M+Na]^+$: 459.1660, found: 459.1664.

(*E*)-*N*′-(2-(2-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3ag**)



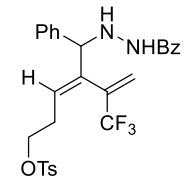
Following the general procedure A, **3ag** was obtained as white solid. Yield = 80%, (*E*/*Z* > 99:1), R_f = 0.49 (ethyl acetate/petroleum ether 1:4), mp 116−118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 6.5 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.57 – 7.46 (m, 4H), 7.44 – 7.29 (m, 6H), 7.27 – 7.23 (m, 1H), 7.23 – 7.13 (m, 2H), 5.63 (q, J = 1.5 Hz, 1H), 5.26 (d, J = 5.8 Hz, 1H), 4.95 – 4.89 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.37. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.53, 137.78, 137.29, 135.41 (q, J = 31.4 Hz), 135.12, 133.93, 132.93, 131.99, 130.38, 129.48, 129.18, 128.91, 128.88, 128.81, 128.78, 128.56, 126.99, 126.62, 125.59 (q, J = 5.2 Hz), 122.76 (q, J = 276.2 Hz), 68.26. **HRMS (ESI)**: m/z calculated for $C_{25}H_{20}ClF_3N_2ONa$ $[M+Na]^+$: 479.1114, found: 479.1109.

(*E*)-*N*′-(4-hydroxy-1-phenyl-2-(3,3,3-trifluoroprop-1-en-2-yl)but-2-en-1-yl)benzohydrazide (**3ah**)



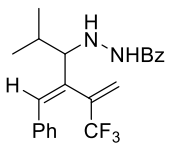
Following the general procedure A, **3ah** was obtained as white solid. Yield = 35%, (*E*/*Z* > 99:1), R_f = 0.35 (ethyl acetate/petroleum ether 1:2), mp 115−117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.70 – 7.58 (m, 2H), 7.53 – 7.44 (m, 1H), 7.43 – 7.36 (m, 4H), 7.36 – 7.28 (m, 3H), 6.54 (t, *J* = 6.6 Hz, 1H), 5.76 (q, *J* = 1.5 Hz, 1H), 4.89 (s, 1H), 4.75 (s, 1H), 4.30 – 4.14 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -65.67. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.76, 138.07, 136.13, 134.95 (q, *J* = 31.3 Hz), 132.93, 131.97, 131.82, 128.75, 128.72, 128.63, 128.44, 127.08, 124.44 (q, *J* = 5.2 Hz), 122.74 (q, *J* = 275.5 Hz), 67.89, 60.11. **HRMS (ESI)**: m/z calculated for $C_{20}H_{19}F_3N_2O_2Na$ $[M+Na]^+$: 399.1296, found: 399.1298.

(*E*)-4-((2-benzoylhydrazinyl)(phenyl)methyl)-5-(trifluoromethyl)hexa-3,5-dien-1-yl 4-methylbenzenesulfonate (**3ai**)



Following the general procedure A, **3ai** was obtained as white solid. Yield = 33%, (*E*/*Z* > 99:1), R_f = 0.43 (ethyl acetate/petroleum ether 1:2), mp 114−116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.79 – 7.70 (m, 4H), 7.51 – 7.45 (m, 1H), 7.44 – 7.29 (m, 10H), 6.51 – 6.44 (m, 1H), 5.74 (q, *J* = 1.5 Hz, 1H), 4.86 (q, *J* = 1.3 Hz, 1H), 4.73 (s, 1H), 4.24 – 4.09 (m, 2H), 2.60 – 2.45 (m, 2H), 2.44 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -65.69. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.61, 145.12, 138.12, 137.33, 135.39 (q, *J* = 31.2 Hz), 133.14, 132.92, 131.88, 130.06, 128.71, 128.70, 128.69, 128.40, 127.94, 127.55, 127.21, 124.45 (q, *J* = 5.4 Hz), 122.82 (q, *J* = 275.6 Hz), 69.57, 68.37, 29.13, 21.78. **HRMS (ESI)**: m/z calculated for $C_{28}H_{27}F_3N_2O_4SNa$ $[M+Na]^+$: 567.1541, found: 567.1535.

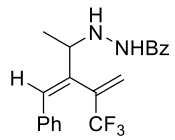
(*E*)-*N*′-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3ga**)



Following the general procedure B, **3ga** was obtained as white solid. Yield = 96%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h),

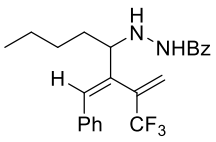
R_f = 0.41 (ethyl acetate/petroleum ether 1:4), mp 105−106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.53 (s, 1H), 7.51 – 7.46 (m, 1H), 7.42 – 7.37 (m ,2H), 7.35 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 6.98 (s, 1H), 5.92 (q, *J* = 1.4 Hz, 1H), 5.47 (q, *J* = 1.2 Hz, 1H), 5.24 (s, 1H), 3.57 (d, *J* = 6.0 Hz,1H), 2.04-1.92 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.96. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.24, 137.37 (q, *J* = 30.9 Hz), 136.11, 134.63, 133.85, 133.04, 131.86, 129.01, 128.80, 128.37, 127.58, 126.88, 125.19 (q, *J* = 5.2 Hz), 123.20 (q, *J* = 276.5 Hz), 70.59, 29.51, 20.36, 17.49. **HRMS (ESI)**: m/z calculated for $C_{22}H_{23}F_3N_2ONa$ $[M+Na]^+$: 411.1660, found: 411.1657.

(*E*)-*N*′-(3-benzylidene-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide (**3ha**)



Following the general procedure B, **3ha** was obtained as white solid. Yield = 99%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.29 (ethyl acetate/petroleum ether 1:4), mp 86−87 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.72 – 7.68 (m, 2H), 7.50 – 7.44 (m, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.31 (m 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 6.95 (s, 1H), 5.93 (q, *J* = 1.5 Hz, 1H), 5.53-5.48 (m, 1H), 4.97 (s, 1H), 3.88 (q, *J* = 6.6 Hz, 1H), 1.30 (d, *J* = 6.6 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.50. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.58, 136.86 (q, *J* = 31.2 Hz), 136.50, 135.92, 132.94, 132.44, 131.92, 129.02, 128.78, 128.30, 127.67, 126.95, 124.92 (q, *J* = 5.1 Hz), 123.07 (q, *J* = 276.3 Hz), 60.90, 18.75. **HRMS (ESI)**: m/z calculated for $C_{20}H_{19}F_3N_2ONa$ $[M+Na]^+$: 383.1347, found: 383.1344.

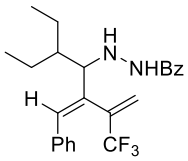
(*E*)-*N*′-(3-benzylidene-2-(trifluoromethyl)oct-1-en-4-yl)benzohydrazide (**3ia**)



Following the general procedure B, **3ia** was obtained as white solid. Yield = 99%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.36 (ethyl acetate/petroleum ether 1:4), mp 52−53 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.7 – 7.64 (m, 3H), 7.51 – 7.45 (m, 1H), 7.42 – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.30 (m, 2H), 7.25 – 7.20 (m 1H), 6.92 (s, 1H), 5.95 – 5.92 (m, 1H), 5.49 (s, 1H), 5.08 (s, 1H), 3.74 (t, *J* = 6.4 Hz, 1H), 1.73 – 1.56 (m, 2H), 1.53 – 1.44 (m, 2H), 1.42 – 1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{19}F**

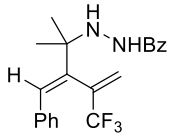
NMR (376 MHz, $CDCl_3$) δ -63.10. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.40, 137.05 (q, *J* = 31.0 Hz), 135.95, 135.50, 133.40, 132.99, 131.91, 129.04, 128.80, 128.33, 127.67, 126.91, 125.00 (q, *J* = 5.1 Hz), 123.16 (q, *J* = 275.5 Hz), 65.99, 32.30, 28.17, 22.82, 14.07. **HRMS (ESI)**: m/z calculated for $C_{23}H_{25}F_3N_2ONa$ $[M+Na]^+$: 425.1817, found: 425.1820.

(*E*)-*N*′-(3-benzylidene-5-ethyl-2-(trifluoromethyl)hept-1-en-4-yl)benzohydrazide (**3ja**)



Following the general procedure B, **3ja** was obtained as white solid. Yield = 96%, (*E*/*Z* > 99:1, and reaction time was extended to 40 h), R_f = 0.54 (ethyl acetate/petroleum ether 1:4), mp 64−66 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.53 (s, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.07 (s, 1H), 5.91 (q, *J* = 1.5 Hz, 1H), 5.40 (q, *J* = 1.2 Hz, 1H), 5.19 (s, 1H), 3.83 (d, *J* = 4.2 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.66 – 1.58 (m, 2H), 1.50 – 1.42 (m, 1H), 1.38 – 1.25 (m, 1H), 1.05 – 0.99 (t, *J* = 7.4 Hz, 3H), 0.98 – 0.92 (m, *J* = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.12. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.20, 137.24 (q, *J* = 30.7 Hz), 136.21, 134.97, 133.12, 132.96, 131.84, 129.02, 128.79, 128.38, 127.51, 126.90, 125.26 (q, *J* = 5.2 Hz), 123.14 (q, *J* = 275.6 Hz), 66.11, 42.22, 23.09, 20.51, 12.09, 12.01. **HRMS (ESI)**: m/z calculated for $C_{24}H_{27}F_3N_2ONa$ $[M+Na]^+$: 439.1973, found: 439.1972.

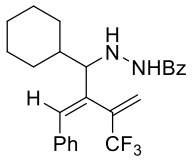
(*E*)-*N*′-(3-benzylidene-2-methyl-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide (**3ka**)



Following the general procedure B, **3ka** was obtained as white solid. Yield = 91%, (*E*/*Z* > 99:1, and reaction time was extended to 40 h), R_f = 0.23 (ethyl acetate/petroleum ether 1:4), mp 99−101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.38 (m, 3H), 7.34 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.04 (s, 1H), 6.03 (q, *J* = 1.4 Hz, 1H), 5.65 (s, 1H), 1.41 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.15. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.16, 138.71, 137.24 (q, *J* = 31.9 Hz), 136.30, 132.95, 132.50, 131.93, 129.11, 128.87, 128.25, 127.66, 126.86, 125.86 (q, *J* = 4.8 Hz), 123.12

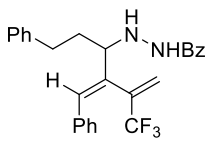
(q, J = 276.4 Hz), 61.44, 26.01. **HRMS (ESI)**: m/z calculated for $C_{21}H_{21}F_3N_2ONa$ $[M+Na]^+$: 397.1504, found: 397.1503.

(*E*)-*N*′-(2-benzylidene-1-cyclohexyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide (**3la**)



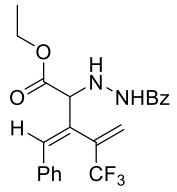
Following the general procedure B, **3la** was obtained as white solid. Yield = 93%, (*E*/*Z* > 99:1, and reaction time was extended to 36 h), R_f = 0.49 (ethyl acetate/petroleum ether 1:4), mp 121−122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.62 – 7.55 (d, J = 6.4 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 6.94 (s, 1H), 5.93 (q, J = 1.5 Hz, 1H), 5.47 (q, J = 1.1 Hz, 1H), 5.26 (d, J = 6.1 Hz, 1H), 3.57 (d, J = 6.1 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.89 – 1.76 (m, 3H), 1.72 – 1.57 (m, 2H), 1.38 – 1.12 (m, 5H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.91. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.11, 137.35 (q, J = 31.0 Hz), 136.08, 134.18, 133.97, 133.02, 131.83, 129.02, 128.77, 128.34, 127.57, 126.87, 125.16 (q, J = 5.1 Hz), 123.21 (q, J = 276.5 Hz), 70.31, 39.31, 30.89, 27.99, 26.55, 26.52, 26.50. **HRMS (ESI)**: m/z calculated for $C_{25}H_{27}F_3N_2ONa$ $[M+Na]^+$: 451.1973, found: 451.1984.

(*E*)-*N*′-(4-benzylidene-1-phenyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3ma**)



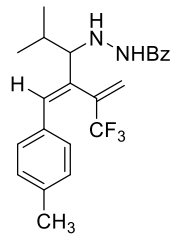
Following the general procedure B, **3ma** was obtained as white solid. Yield = 99%, (*E*/*Z* > 99:1, and reaction time was extended to 32 h), R_f = 0.28 (ethyl acetate/petroleum ether 1:4), mp 69−70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.62 (s, 1H), 7.51 – 7.46 (m, 1H), 7.42 – 7.36 (m, 2H), 7.35 – 7.26 (m, 6H), 7.25 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 6.95 (s, 1H), 5.94 (q, J =1.5 Hz, 1H), 5.52 (s, 1H), 5.12 (s, 1H), 3.83 (t, J = 6.3 Hz, 1H), 2.88 – 2.76 (m, 2H), 2.05 – 1.89 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.03. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.50, 141.62, 136.92 (q, J = 31.2 Hz), 135.81, 134.92, 133.92, 132.90, 131.98, 129.06, 128.83, 128.60, 128.47, 128.38, 127.78, 126.92, 126.15, 125.27 (q, J = 5.1 Hz), 123.14 (q, J = 276.1 Hz), 65.77, 34.20, 32.31. **HRMS (ESI)**: m/z calculated for $C_{27}H_{25}F_3N_2ONa$ $[M+Na]^+$: 473.1817, found: 473.1809.

Ethyl (*E*)-2-(2-benzoylhydrazinyl)-3-benzylidene-4-(trifluoromethyl)pent-4-enoate (**3na)**



Following the general procedure B, **3na** was obtained as white solid. Yield = 96%, (*E*/*Z* > 99:1, and reaction time was extended to 36 h), R_f = 0.13 (ethyl acetate/petroleum ether 1:4), mp 100−101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.7 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.53 – 7.47 (m, 1H), 7.45 – 7.38 (m, 2H), 7.34 – 7.21 (m, 5H), 6.98 (s, 1H), 5.99 (s, 1H), 5.70 (s, 1H), 5.43 (d, *J* = 3.9 Hz, 1H), 4.56 (s, 1H), 4.27 – 4.27 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.83. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.53, 167.36, 137.04, 136.04 (q, *J* = 31.6 Hz), 135.13, 132.55, 132.09, 129.12, 129.00, 128.79, 128.35, 128.29, 127.03, 126.11 (q, *J* = 5.0 Hz), 112.87 (q, *J* = 276.3 Hz), 67.63, 61.69, 14.10. **HRMS (ESI)**: m/z calculated for $C_{22}H_{21}F_3N_2O_3Na$ $[M+Na]^+$: 441.1402, found: 441.1394.

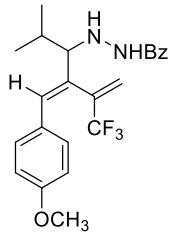
(*E*)-*N*′-(2-methyl-4-(4-methylbenzylidene)-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3gb**)



Following the general procedure B, **3gb** was obtained as white solid. Yield = 91%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.40 (ethyl acetate/petroleum ether 1:4), mp 76−77 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.53 – 7.45 (m, 2H), 7.43 – 7.35 (m, 2H), 7.27 – 7.22 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.92 (s, 1H), 5.92 (q, *J* = 1.4 Hz, 1H), 5.48 (q, *J* = 1.2 Hz, 1H), 5.24 (s, 1H), 3.54 (d, *J* = 6.1 Hz, 1H), 2.32 (s, 3H), 2.03 – 1.90 (m, 1H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.97. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.18, 137.58 (q, *J* = 30.8 Hz), 137.57, 133.85, 133.60, 133.16, 133.10, 131.86, 129.11, 129.00, 128.81, 126.88, 125.05 (q, *J* = 5.1 Hz), 123.27 (q, *J* = 275.5 Hz), 70.89, 29.51, 21.30, 20.41, 17.57. **HRMS (ESI)**: m/z calculated for $C_{23}H_{25}F_3N_2ONa$ $[M+Na]^+$: 425.1817, found: 425.1817.

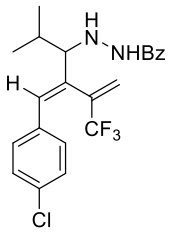
(*E*)-*N*′-(4-(4-methoxybenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-

yl)benzohydrazide (**3gc**)



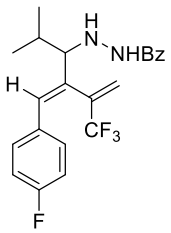
Following the general procedure B, **3gc** was obtained as white solid. Yield = 91%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.30 (ethyl acetate/petroleum ether 1:4), mp 40−42 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.53 (m, 1H), 7.50 – 7.45 (m, 1H), 7.42 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 6.88 (s, 1H), 6.85 – 6.80 (m, 2H), 5.95 (q, *J* = 1.4 Hz, 1H), 5.53-5.48 (m, 1H), 5.23 (d, *J* = 5.3 Hz, 1H), 3.79 (s, 3H), 3.52 (d, *J* = 6.2 Hz, 1H), 1.96 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.03. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.16, 159.13, 137.69 (q, *J* = 30.7 Hz), 133.41, 133.10, 132.30, 131.83, 130.40, 128.79, 128.52, 126.87, 124.97 (q, *J* = 5.1 Hz), 123.29 (q, *J* = 276.6 Hz), 113.80, 71.08, 55.34, 29.52, 20.43, 17.62. **HRMS (ESI)**: m/z calculated for $C_{23}H_{25}F_3N_2O_2Na$ $[M+Na]^+$: 441.1766, found: 441.1766.

(*E*)-*N*′-(4-(4-chlorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3gd**)



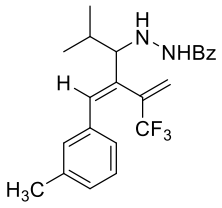
Following the general procedure B, **3gd** was obtained as white solid. Yield = 94%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.35 (ethyl acetate/petroleum ether 1:4), mp 102−104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.57 (d, *J* = 5.0 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.43 – 7.36 (m, 2H), 7.24 (s, 4H), 6.92 (s, 1H), 5.92 (q, *J* = 1.4 Hz, 1H), 5.48 – 5.46 (m, 1H), 5.21 (d, *J* = 5.9 Hz, 1H), 3.56 (d, *J* = 5.9 Hz, 1H). 1.96 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.04. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.32, 137.19 (q, *J* = 30.9 Hz), 135.44, 134.60, 133.35, 132.98, 132.53, 131.92, 130.24, 128.81, 128.57, 126.87, 125.37 (q, *J* = 5.2 Hz), 123.09 (q, *J* = 275.7 Hz), 70.54, 29.49, 20.35, 17.46. **HRMS (ESI)**: m/z calculated for $C_{22}H_{22}ClF_3N_2ONa$ $[M+Na]^+$: 445.1270, found: 445.1261.

(*E*)-*N*′-(4-(4-fluorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3ge**)



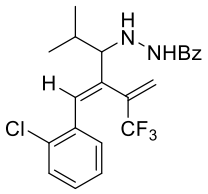
Following the general procedure B, **3ge** was obtained as white solid. Yield = 93%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.35 (ethyl acetate/petroleum ether 1:4), mp 126−127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.37 (m, 2H), 7.32 – 7.26 (m, 2H), 7.01 – 6.94 (m, 2H), 6.92 (s, 1H), 5.94 (q, *J* = 1.4 Hz, 1H), 5.48 (q, *J* = 1.2 Hz, 1H), 5.22 (d, *J* = 6.1 Hz, 1H), 3.55 (d, *J* = 6.1 Hz, 1H), 2.03 – 1.91 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.08, -114.03 (tt, *J* = 8.6, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.29, 162.13 (d, *J* = 247.6 Hz), 137.32 (q, *J* = 30.9 Hz), 134.55 (d, *J* = 1.5 Hz), 133.05, 132.70, 132.18 (d, *J* = 3.5 Hz), 131.93, 130.67 (d, *J* = 8.0 Hz), 128.85, 126.87, 125.31 (q, *J* = 5.2 Hz), 123.16 (q, *J* = 276.4 Hz), 115.36 (d, *J* = 21.4 Hz), 70.77, 29.51, 20.40, 17.55. **HRMS (ESI)**: m/z calculated for $C_{22}H_{22}F_4N_2ONa$ $[M+Na]^+$: 429.1566, found: 429.1563.

(*E*)-*N*′-(2-methyl-4-(3-methylbenzylidene)-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3gf**)



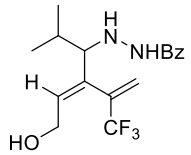
Following the general procedure B, **3gf** was obtained as white solid. Yield = 97%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.38 (ethyl acetate/petroleum ether 1:4), mp 100−101 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.61 (s, 1H), 7.50 – 7.44 (m, 1H), 7.41 – 7.35 (m, 2H), 7.20 – 7.11 (m, 3H), 7.07 – 7.00 (m, 1H), 6.94 (s, 1H), 5.90 (q, *J* = 1.4 Hz, 1H), 5.47 (q, *J* = 1.2 Hz, 1H), 5.24 (s, 1H), 3.55 (d, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 2.04 – 1.90 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.20, 137.91, 137.50 (q, *J* = 30.7 Hz), 136.02, 134.32, 133.96, 133.05, 131.82, 129.93, 128.76, 128.32, 128.23, 126.88, 125.92, 125.09 (q, *J* = 5.2 Hz), 123.23 (q, *J* = 276.5 Hz), 70.65, 29.49, 21.44, 20.34, 17.49. **HRMS (ESI)**: m/z calculated for $C_{23}H_{25}F_3N_2ONa$ $[M+Na]^+$: 425.1817, found: 425.1813.

(*E*)-*N*′-(4-(2-chlorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide (**3gg**)



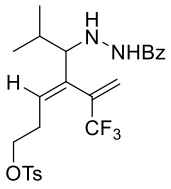
Following the general procedure B, **3gg** was obtained as white solid. Yield = 95%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.43 (ethyl acetate/petroleum ether 1:4), mp 116−118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 3H), 7.52 – 7.45 (m, 1H), 7.44 – 7.32 (m, 3H), 7.24 – 7.13 (m, 4H), 5.80 (q, *J* = 1.4 Hz, 1H), 5.39 (q, *J* = 1.2 Hz, 1H), 5.26 (s, 1H), 3.67 (d, *J* = 5.2 Hz, 1H), 2.11 – 1.95 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.38. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.24, 137.25, 136.67 (q, *J* = 30.9 Hz), 135.54, 133.73, 133.05, 131.85, 131.50, 130.40, 129.18, 128.77, 128.71, 126.89, 126.59, 125.29 (q, *J* = 5.3 Hz), 122.92 (q, *J* = 276.3 Hz), 69.27, 29.68, 20.15, 17.21. **HRMS (ESI)**: m/z calculated for $C_{22}H_{22}ClF_3N_2ONa$ $[M+Na]^+$: 445.1270, found: 445.1269.

(*E*)-*N*′-(6-hydroxy-2-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hex-4-en-3-yl)benzohydrazide (**3gh**)



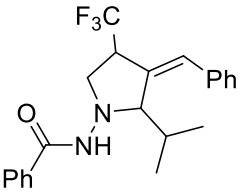
Following the general procedure B, **3gh** was purified by preparative thin layer chromatography using ethyl acetate/petroleum ether =1:2 as eluent and was obtained as white solid. Yield = 70%, (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.28 (ethyl acetate/petroleum ether 1:2), mp 61−62 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.72 – 7.64 (m, 2H), 7.52 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 6.22 (dd, *J* = 7.2, 5.9 Hz, 1H), 5.95 (q, *J* = 1.4 Hz, 1H), 5.40 (q, *J* = 1.3 Hz, 1H), 4.24 – 4.11 (m, 2H), 3.42 (d, *J* = 5.6 Hz, 1H), 1.96 – 1.81 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.61. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.50, 136.44 (q, *J* = 30.8 Hz), 135.72, 133.42, 133.08, 131.84, 128.75, 127.00, 123.97 (q, *J* = 5.4 Hz), 122.84 (q, *J* = 276.0 Hz), 68.86, 59.92, 29.88, 20.13, 17.46. **HRMS (ESI)**: m/z calculated for $C_{17}H_{21}F_3N_2O_2Na$ $[M+Na]^+$: 365.1453, found: 365.1446.

(*E*)-5-(2-benzoylhydrazinyl)-6-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hept-3-en-1-yl 4-methylbenzenesulfonate (**3gi**)



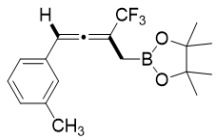
Following the general procedure B, **3gi** was obtained as white solid. Yield = 94% (*E*/*Z* > 99:1, and reaction time was extended to 28 h), R_f = 0.43 (ethyl acetate/petroleum ether 1:2), mp 44−45 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.78 – 7.70 (m, 4H), 7.52 – 7.45 (m, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 2H), 6.10 (dd, *J* = 8.4, 6.1 Hz, 1H), 5.95 (q, *J* = 1.4 Hz, 1H), 5.39 (q, *J* = 1.2 Hz, 1H), 4.19 – 4.03 (m, 2H), 3.46 (d, *J* = 5.1 Hz, 1H), 2.60 – 2.43 (m, 2H), 2.43 (s, 3H), 1.94 – 1.80 (m, 1H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.71. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.28, 145.08, 136.94, 136.64 (q, *J* = 30.9 Hz), 133.04, 132.97, 131.73, 130.00, 129.06, 128.68, 127.87, 127.11, 124.02 (q, *J* = 5.2 Hz), 122.89 (q, *J* = 275.9 Hz), 69.65, 69.14, 29.54, 29.08, 21.73, 20.21, 16.99. **HRMS (ESI)**: m/z calculated for $C_{25}H_{29}F_3N_2O_4SNa$ $[M+Na]^+$: 533.1698, found: 533.1697.

(*Z*)-N-(3-benzylidene-2-isopropyl-4-(trifluoromethyl)pyrrolidin-1-yl)benzamide (**6)**

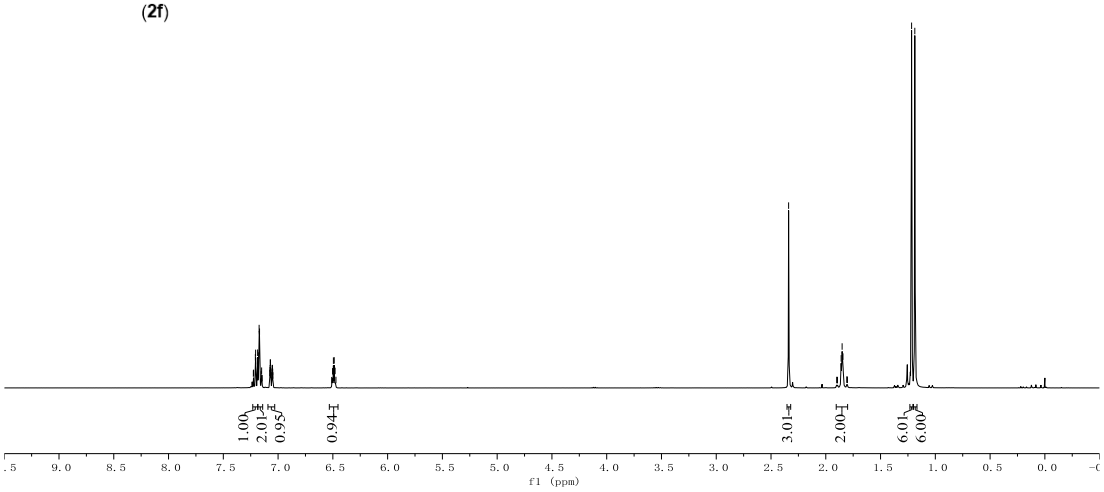


The *syn*-configured product **6** was obtained as pale yellow solid in 82% yield (93:7 dr ratio was determined by ^{1}H NMR analysis of the crude reaction mixture), R_f = 0.35 (isopropylamine/petroleum ether 1:20), mp 116−117 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.61 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.19 (m, 3H), 6.80 (s, 1H), 4.57 (s, 1H), 3.84 – 3.68 (m, 2H), 3.56 – 3.47 (m, 1H), 1.90 – 1.78 (m, 1H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.95 (d, *J* = 8.8 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.42, 136.92, 133.62, 132.00, 129.14, 128.88, 128.48, 128.39, 127.37, 126.97, 126.45 (q, *J* = 279.8 Hz), 71.95, 53.24, δ 48.09 (q, *J* = 28.0 Hz), 30.15, 21.06, 17.68. **HRMS (ESI)**: m/z calculated for $C_{22}H_{23}F_3N_2ONa$ $[M+Na]^+$: 411.1660, found: 411.1659.

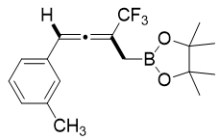
4,4,5,5-tetramethyl-2-(4-(*m*-tolyl)-2-(trifluoromethyl)buta-2,3-dien-1-yl)-1,3,2-dioxaborolane



(**2f**)



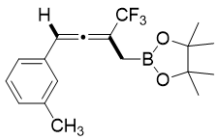
4,4,5,5-tetramethyl-2-(4-(*m*-tolyl)-2-(trifluoromethyl)buta-2,3-dien-1-yl)-1,3,2-dioxaborolane



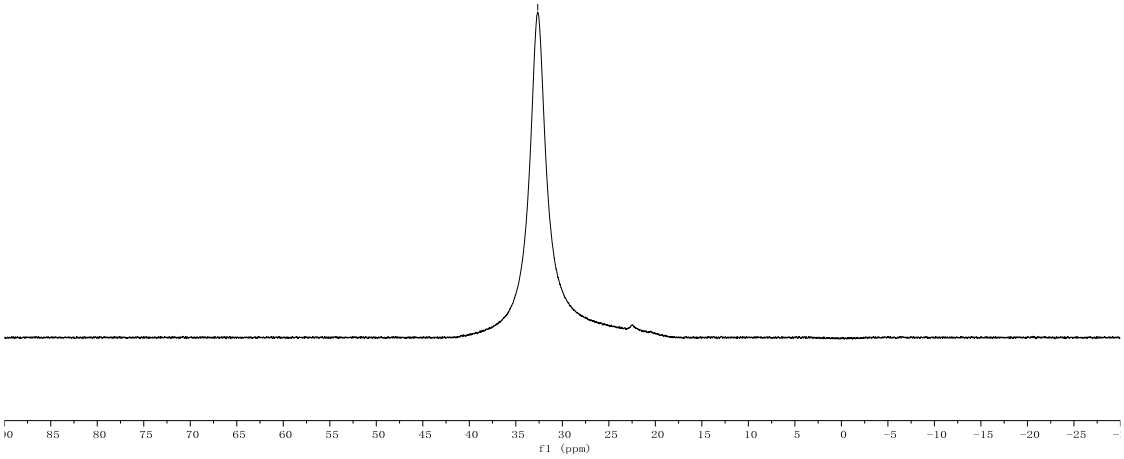
(**2f**)

— 32.64

4,4,5,5-tetramethyl-2-(4-(*m*-tolyl)-2-(trifluoromethyl)buta-2,3-dien-1-yl)-1,3,2-dioxaborolane

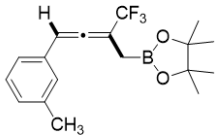


(**2f**)

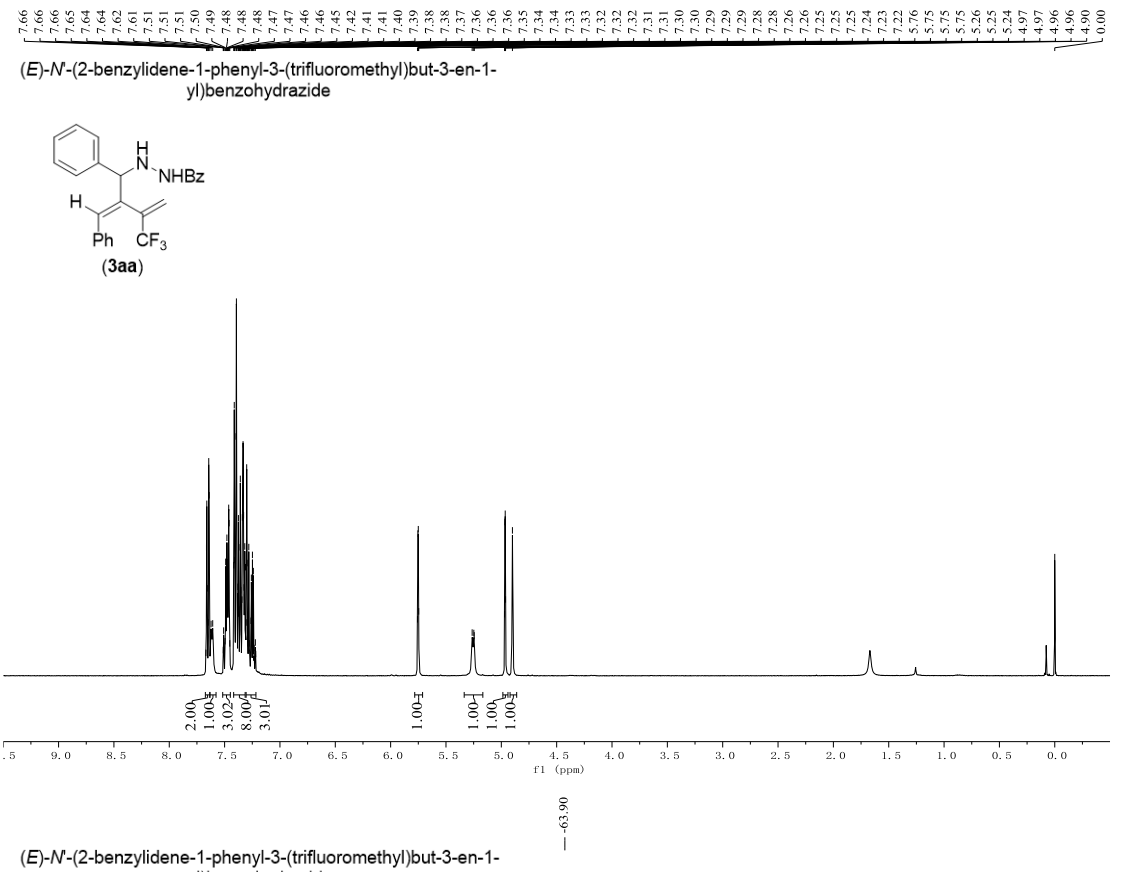


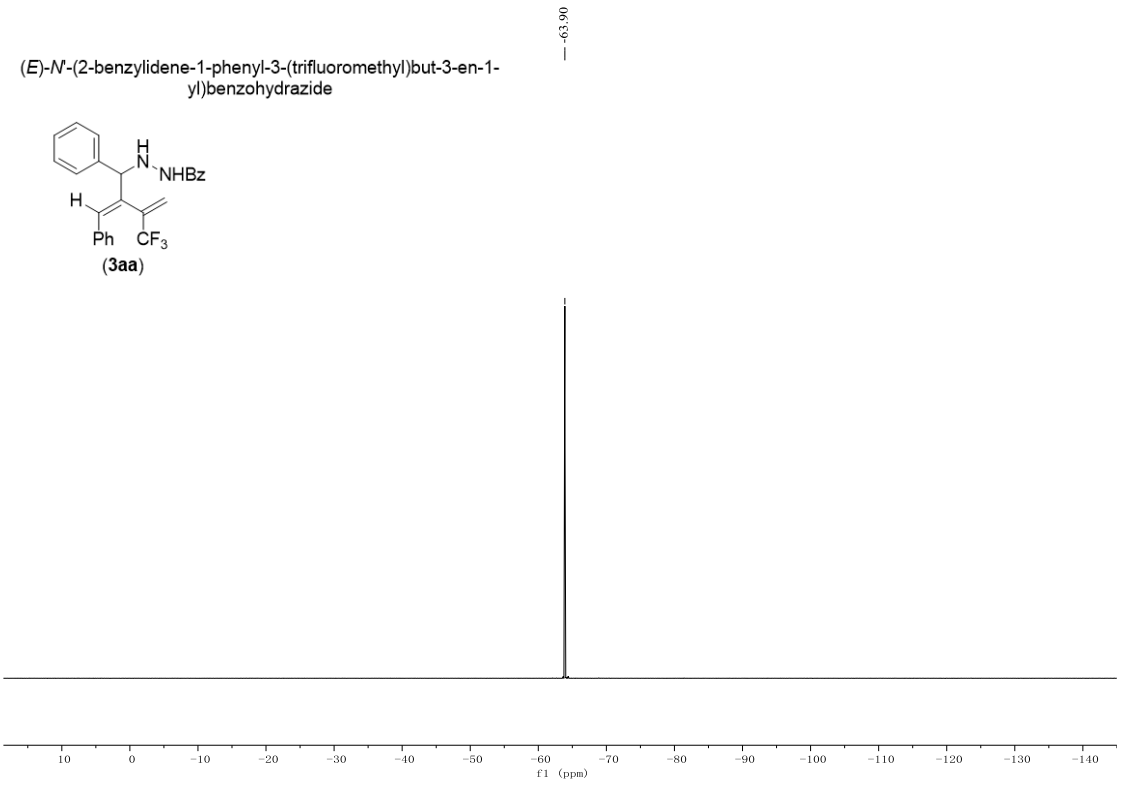
204.53
204.49
204.45
204.41
138.40
132.28
132.26
128.98
128.65
128.34
127.85
125.13
122.41
119.68
100.66
99.43
99.08
98.74
98.39
84.04
77.48
77.16
76.84
24.93
24.78
21.46

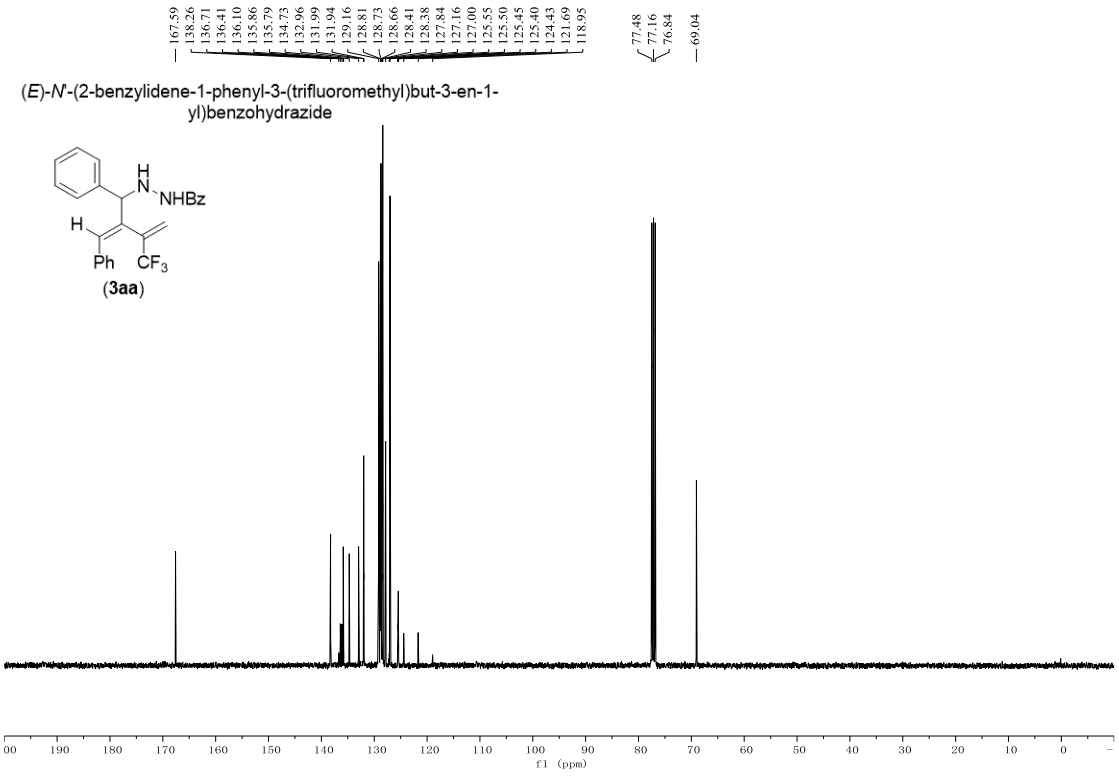
4,4,5,5-tetramethyl-2-(4-(*m*-tolyl)-2-(trifluoromethyl)buta-2,3-dien-1-yl)-1,3,2-dioxaborolane

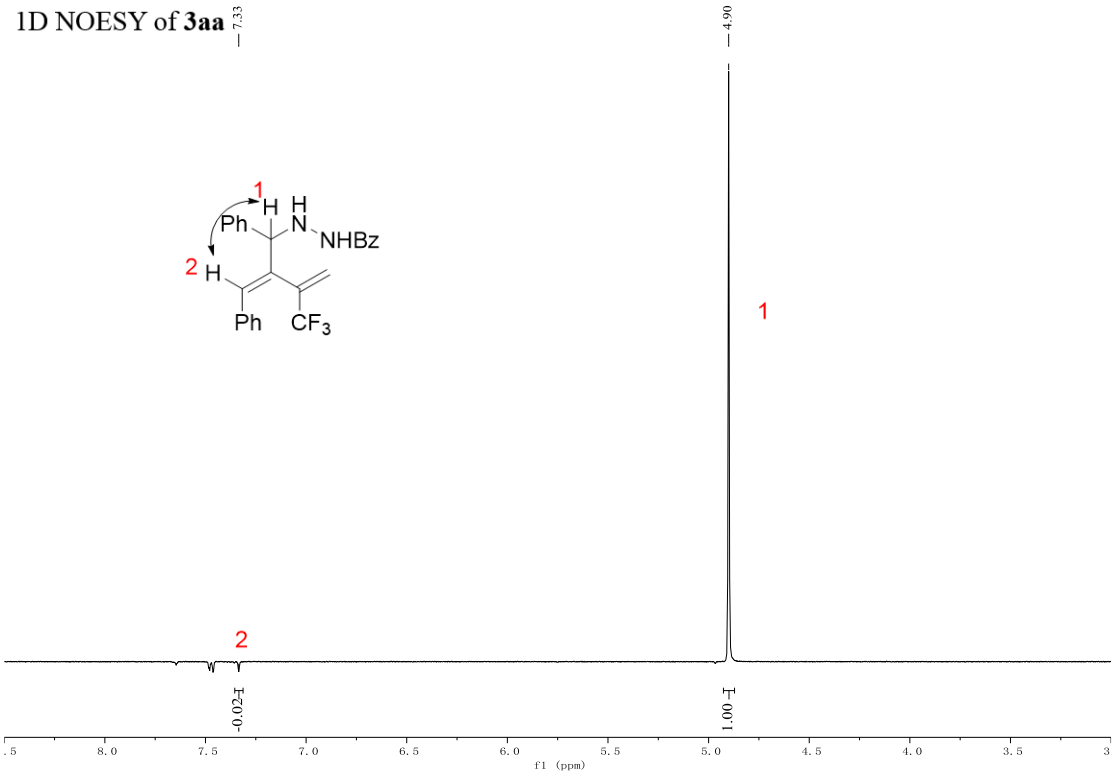


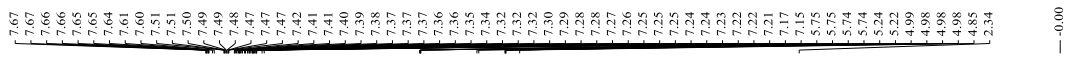
(**2f**)


(E)-N'-(2-benzylidene-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
NHBz
H
Ph
CF3
(3aa)
2.00
1.00
3.02
8.00
3.01
1.00
1.00
1.00
1.00
f1 (ppm)

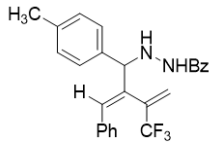

-63.90
(E)-N'-(2-benzylidene-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
NHBz
H
Ph
CF3
(3aa)
f1 (ppm)


167.59
138.26
136.71
136.41
136.10
135.86
135.79
134.73
132.96
131.99
131.94
129.16
128.81
128.73
128.66
128.41
128.38
127.84
127.16
127.00
125.55
125.50
125.45
125.40
124.43
121.69
118.95
77.48
77.16
76.84
69.04
(E)-N'-(2-benzylidene-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
H
N
NHBz
H
Ph
CF3
(3aa)
f1 (ppm)

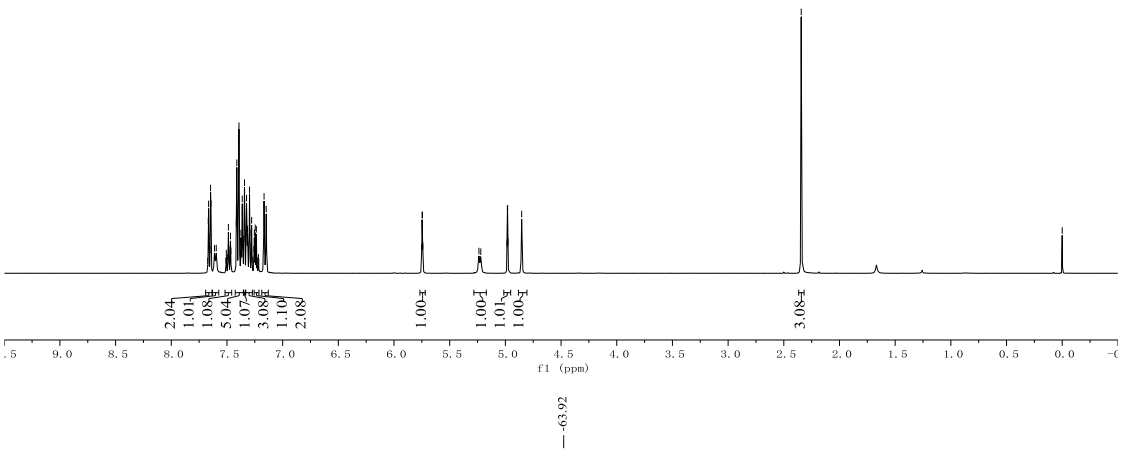

1D NOESY of 3aa
7.33
4.90
1
H
H
N
Ph
NHBz
2
H
Ph
CF3
1
2
-0.02
1.00
f1 (ppm)

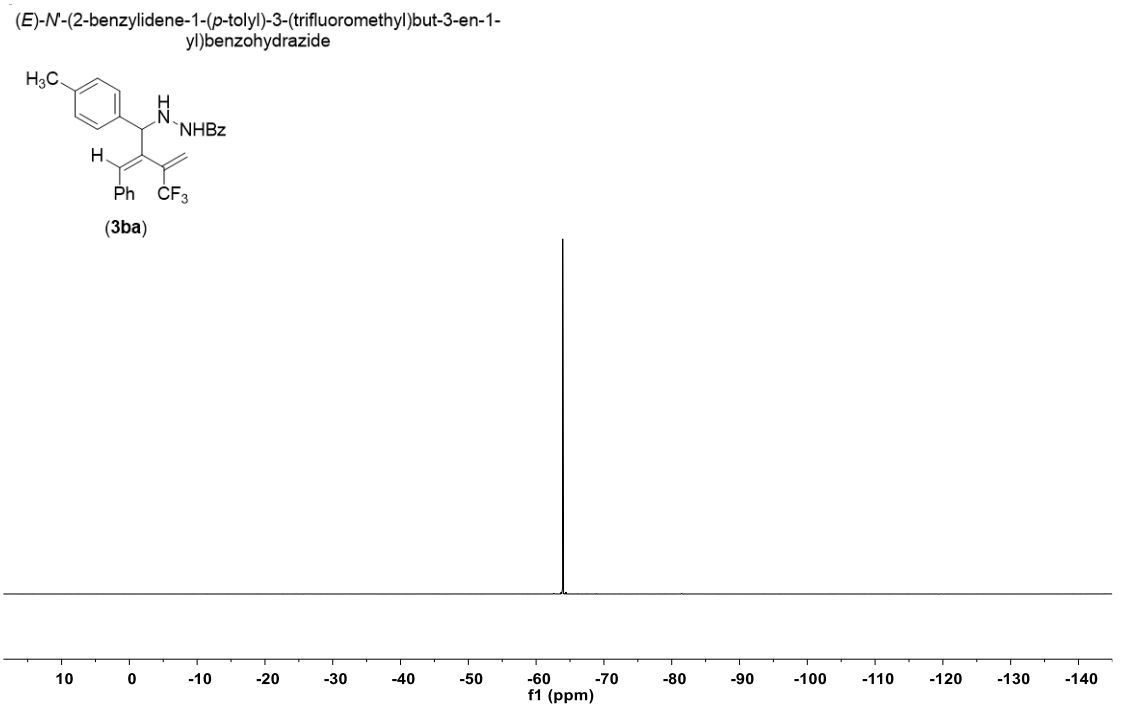


(*E*)-*N*'-(2-benzylidene-1-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



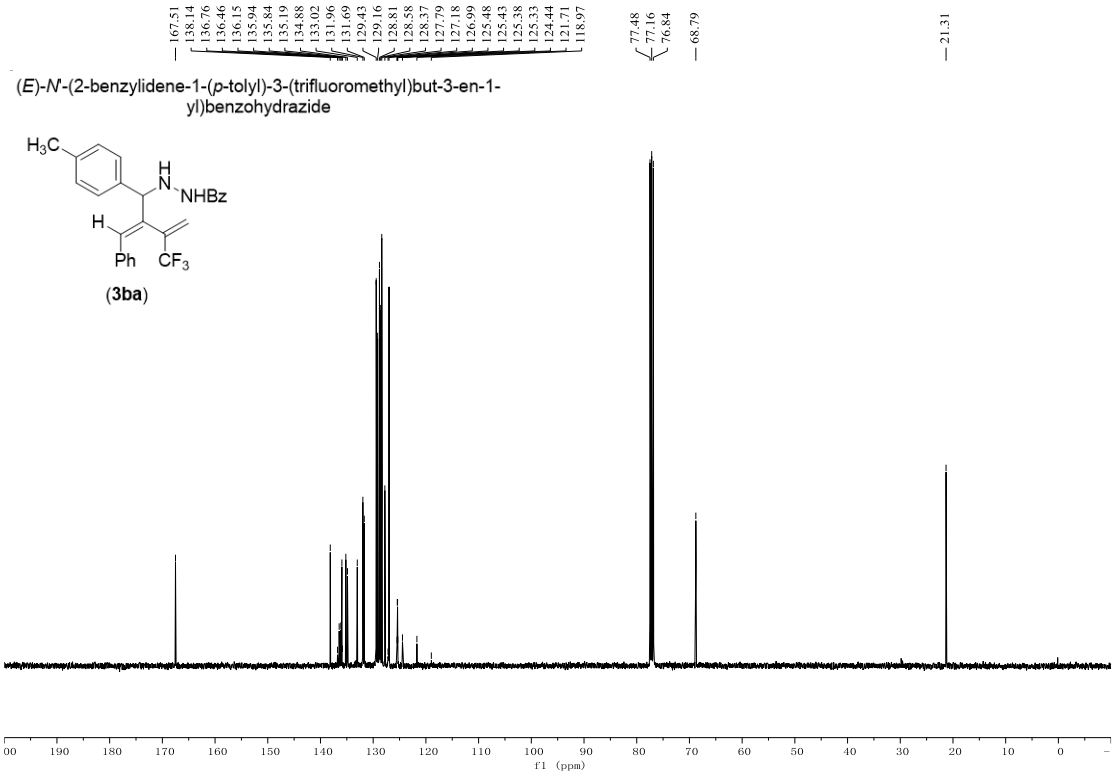
(**3ba**)

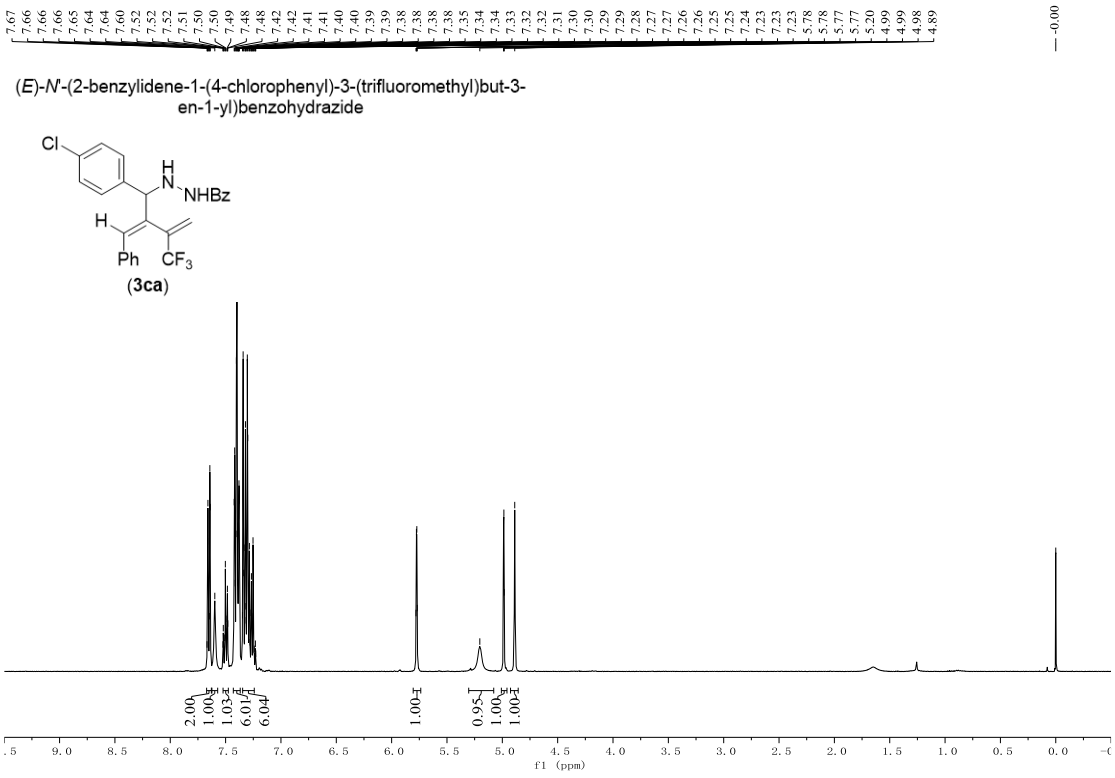


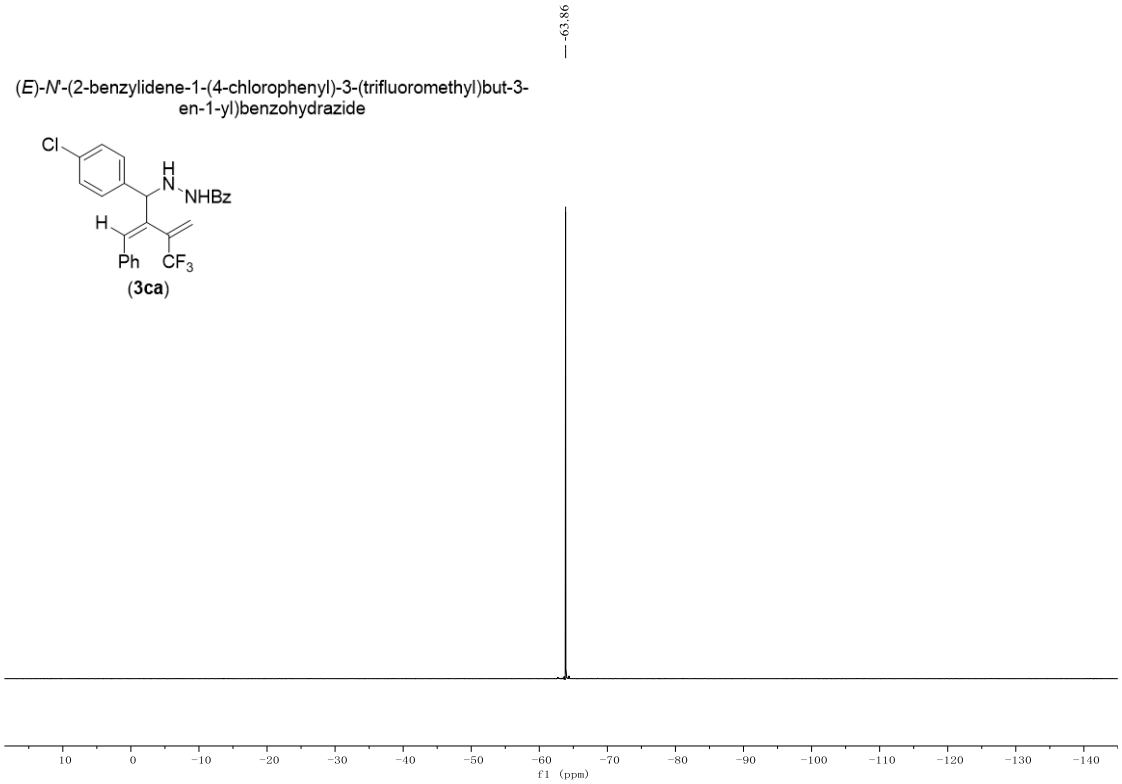


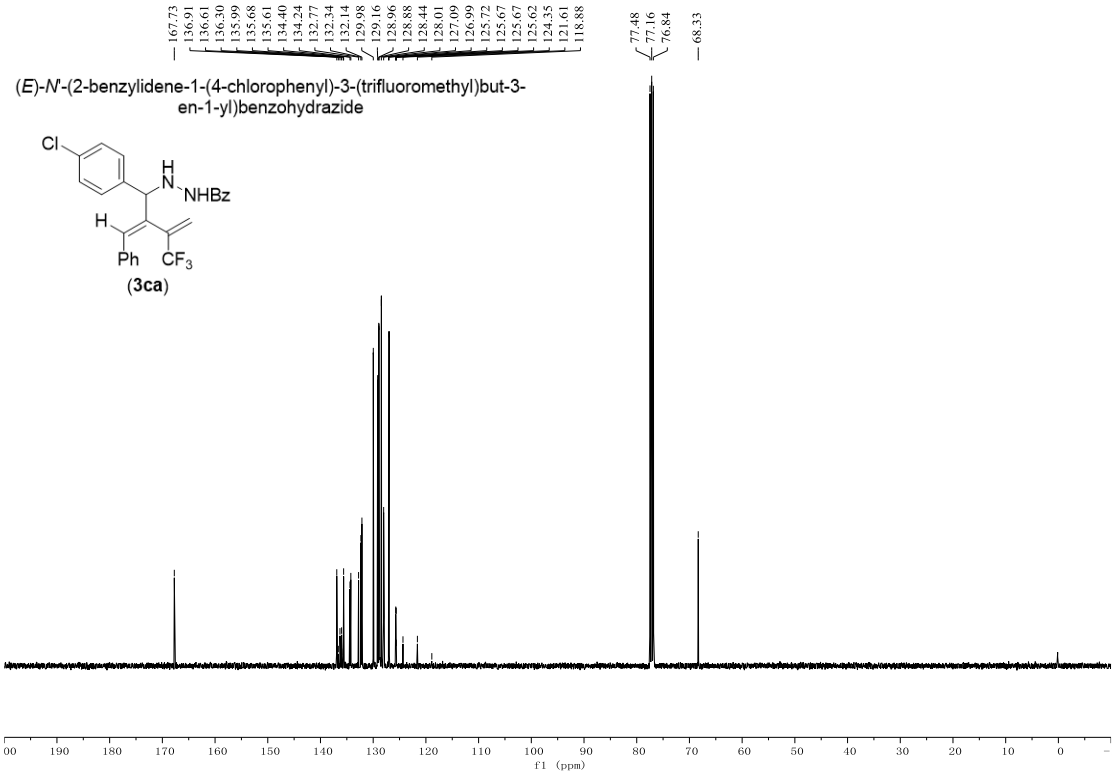
(*E*)-*N*'-(2-benzylidene-1-(*p*-tolyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

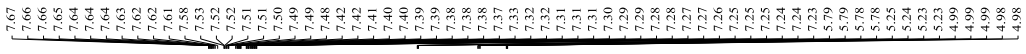
(**3ba**)


(E)-N'-(2-benzylidene-1-(p-tolyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
(3ba)
f1 (ppm)

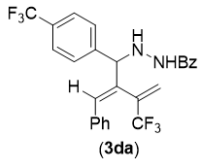

(E)-N'-(2-benzylidene-1-(4-chlorophenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
(3ca)
f1 (ppm)


-63.86
(E)-N'-(2-benzylidene-1-(4-chlorophenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
Cl
H
N
NHBz
H
Ph
CF3
(3ca)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

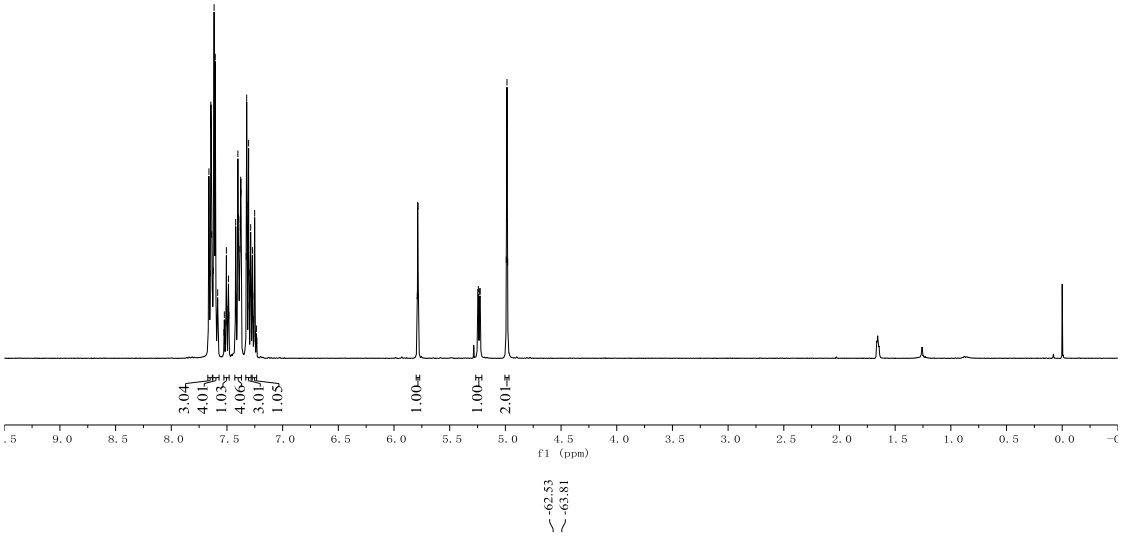

167.73
136.91
136.61
136.30
135.99
135.68
135.61
134.40
134.24
132.77
132.34
132.14
129.98
129.16
128.96
128.88
128.44
128.01
127.09
126.99
125.72
125.67
125.67
125.62
124.35
121.61
118.88
77.48
77.16
76.84
68.33
(E)-N'-(2-benzylidene-1-(4-chlorophenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
Cl
H
N
NHBz
H
Ph
CF3
(3ca)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



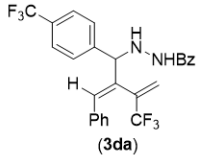
(*E*)-*N*-(2-benzylidene-3-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzohydrazide



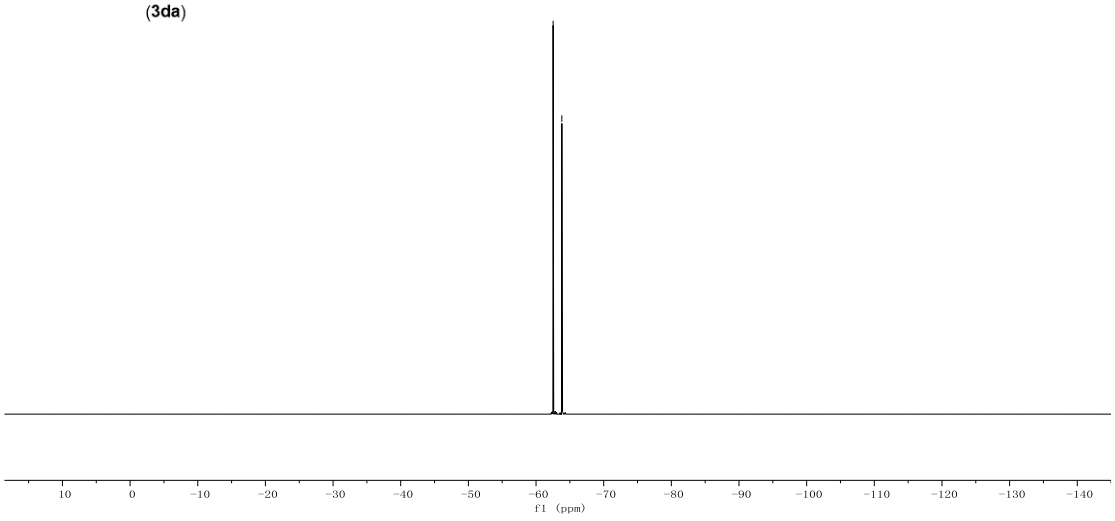
(**3da**)

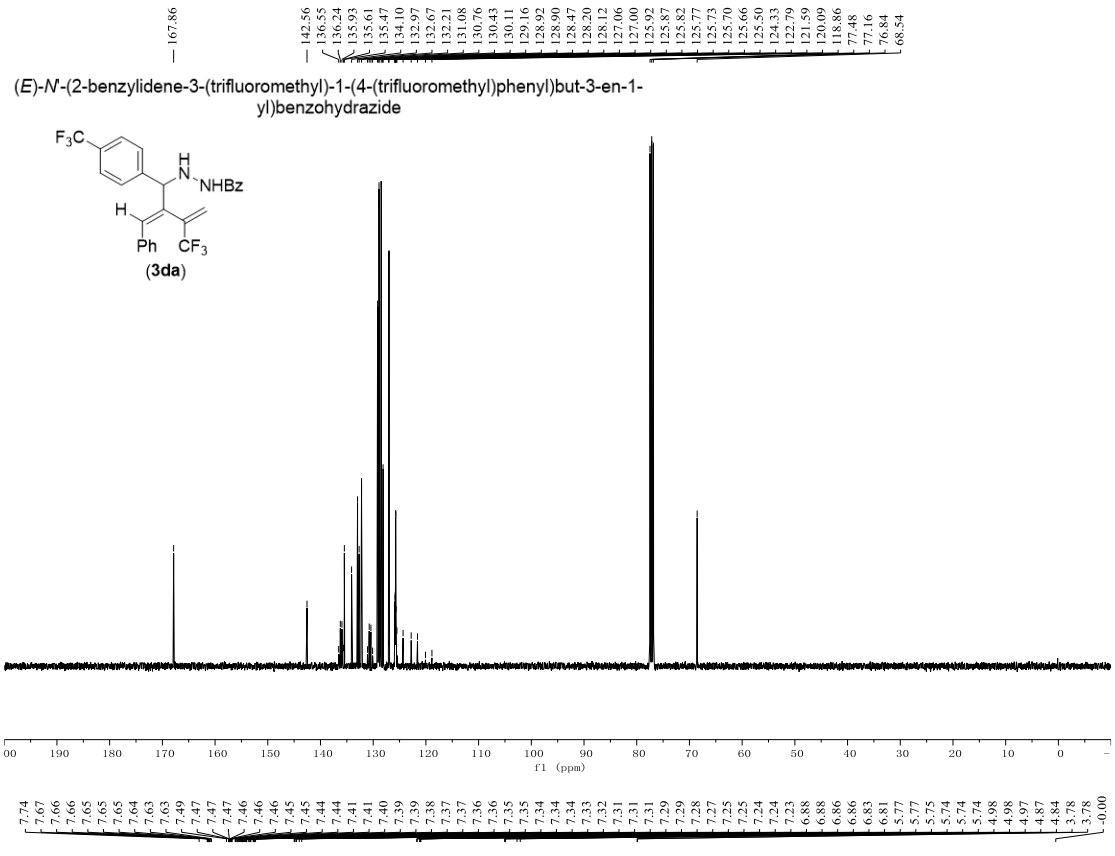


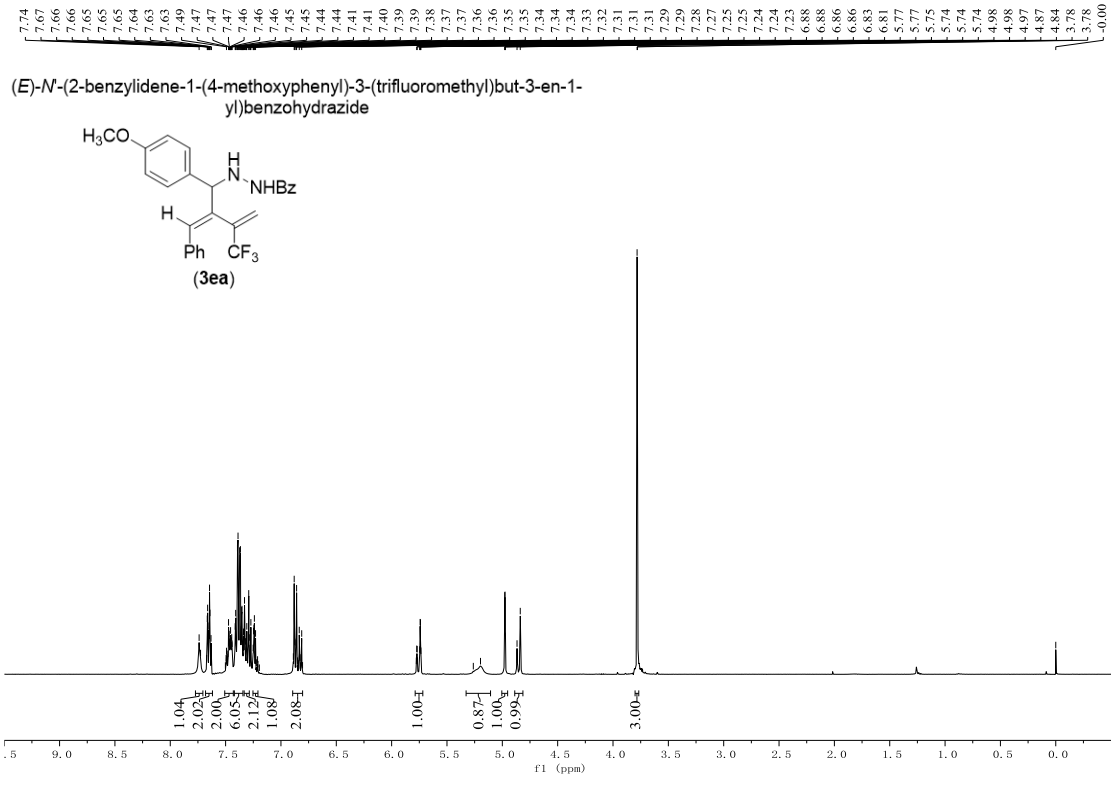
(*E*)-*N*-(2-benzylidene-3-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzohydrazide



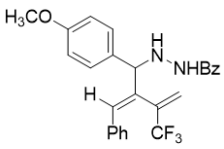
(**3da**)




(E)-N'-(2-benzylidene-3-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzohydrazide
(3da)
f1 (ppm)

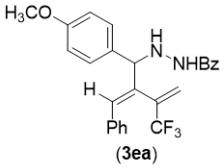

(E)-N'-(2-benzylidene-1-(4-methoxyphenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
(3ea)
f1 (ppm)

(*E*)-*N*'-(2-benzylidene-1-(4-methoxyphenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

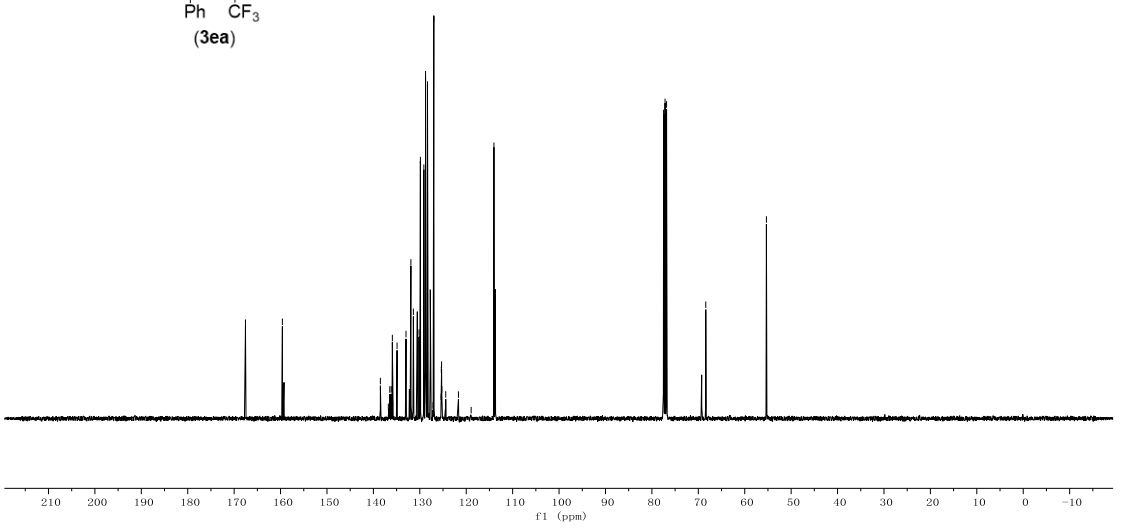


(**3ea**)

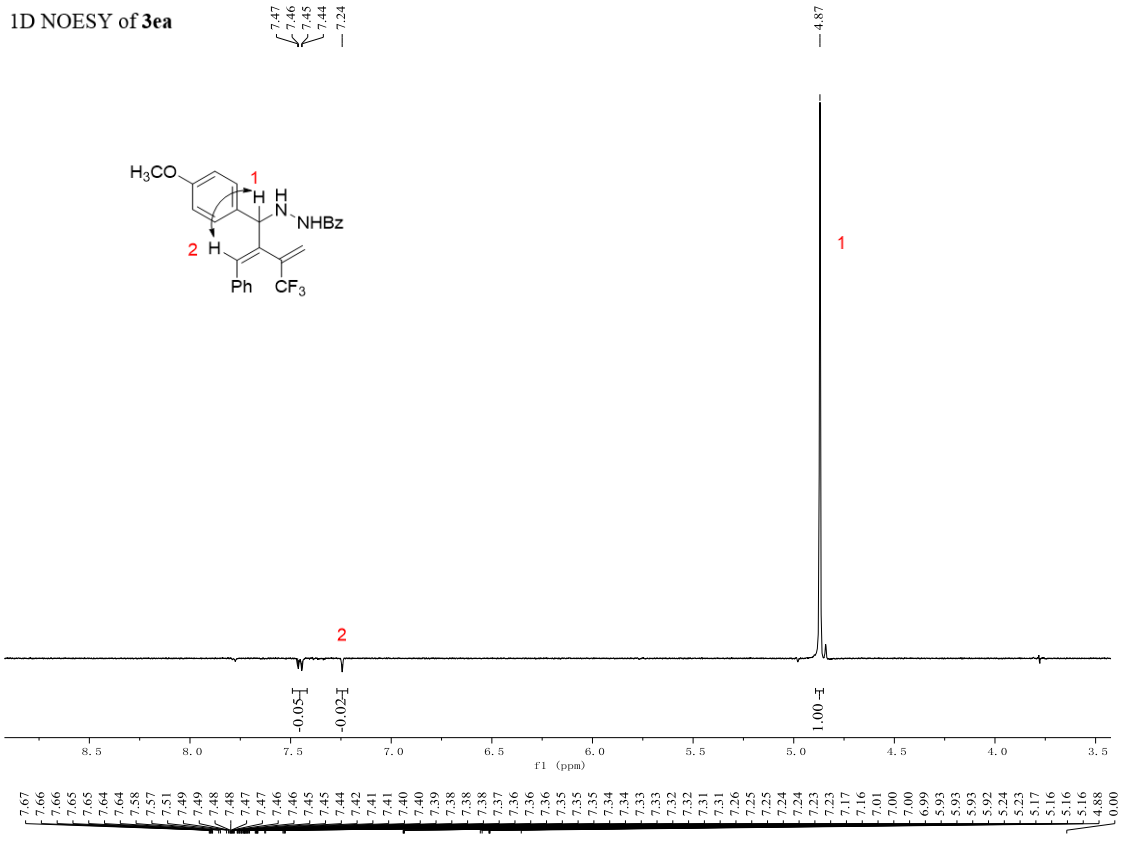
(*E*)-*N*'-(2-benzylidene-1-(4-methoxyphenyl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



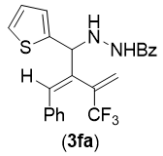
(**3ea**)



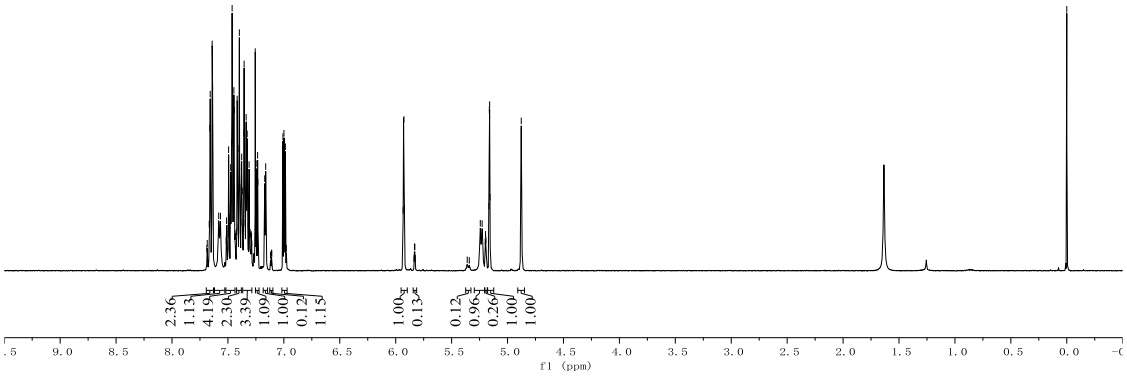
1D NOESY of **3ea**



(*E*)-*N*'-(2-benzylidene-1-(thiophen-2-yl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

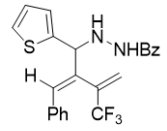


(**3fa**)

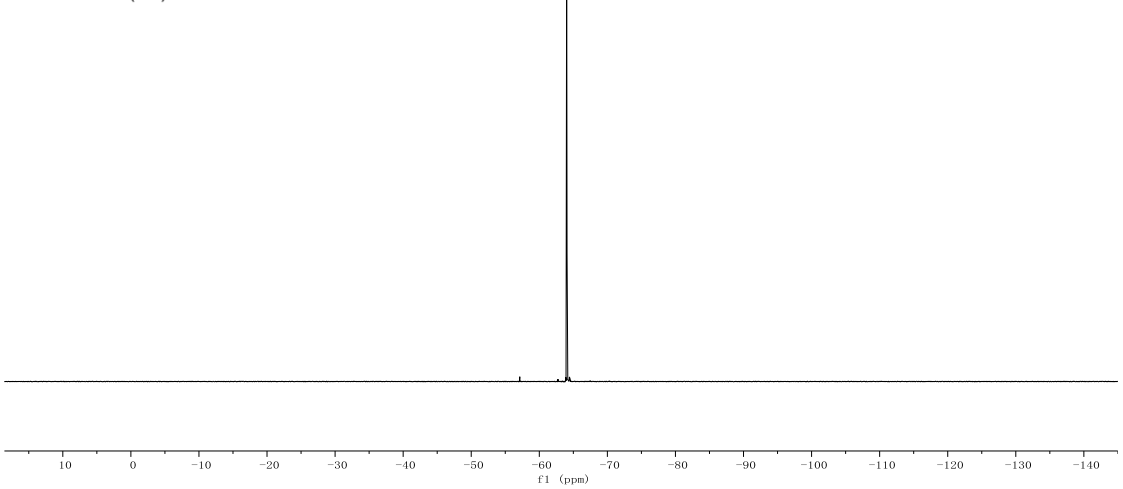


-64.02

(*E*)-*N*'-(2-benzylidene-1-(thiophen-2-yl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

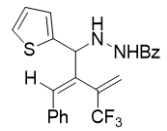


(**3fa**)

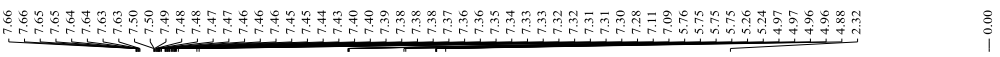


167.62
138.79
138.23
136.41
136.10
135.78
135.47
132.94
132.01
131.98
130.29
128.83
128.76
128.59
128.45
127.19
127.14
127.09
127.01
126.83
126.75
125.06
124.39
121.65
118.91
77.48
77.16
76.84
68.77

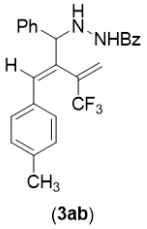
(*E*)-*N*'-(2-benzylidene-1-(thiophen-2-yl)-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



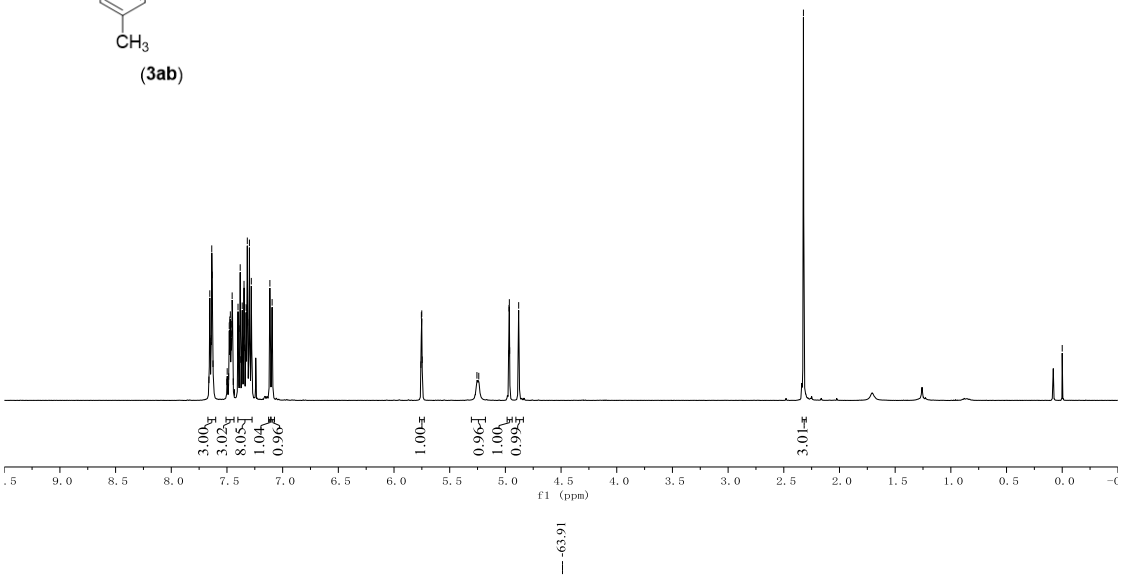
(**3fa**)



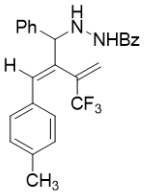
(*E*)-*N*'-(2-(4-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



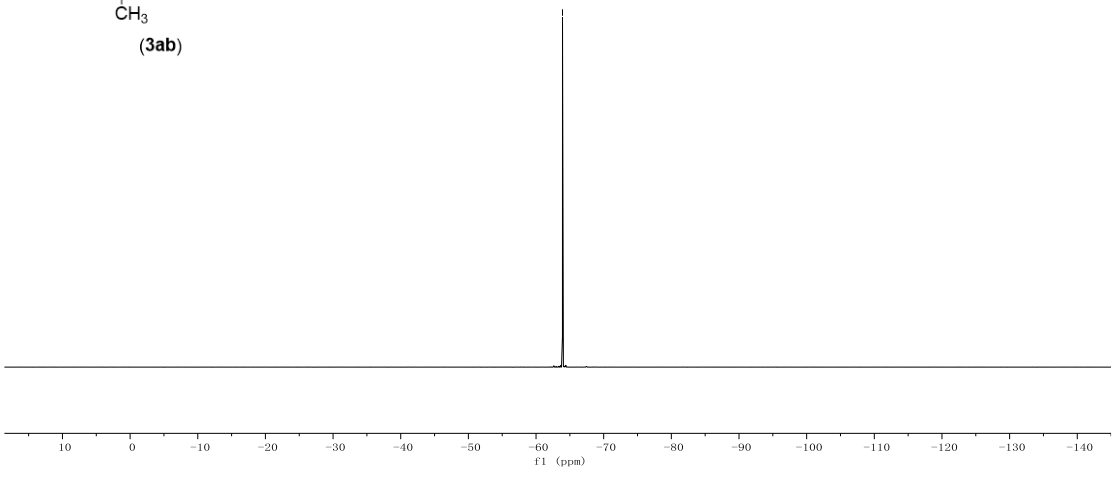
(**3ab**)

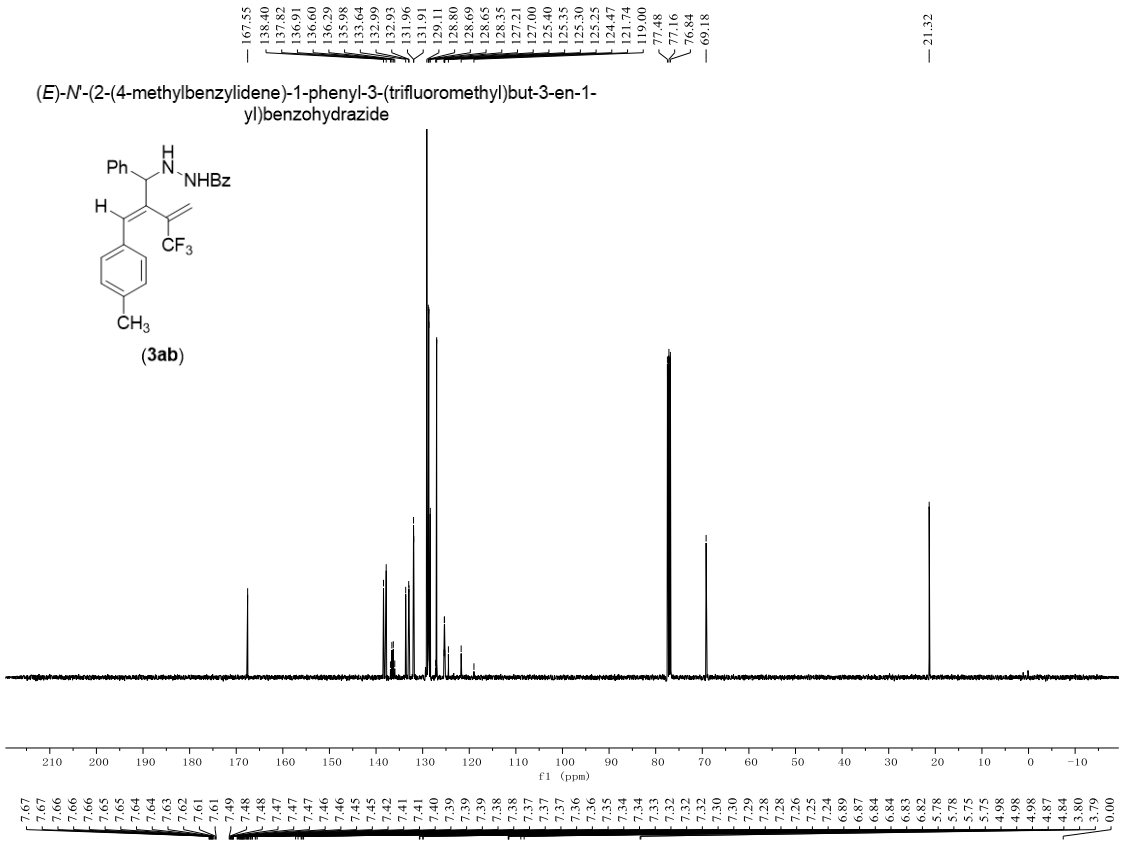


(*E*)-*N*'-(2-(4-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



(**3ab**)

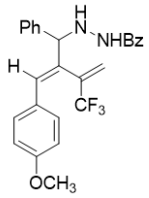




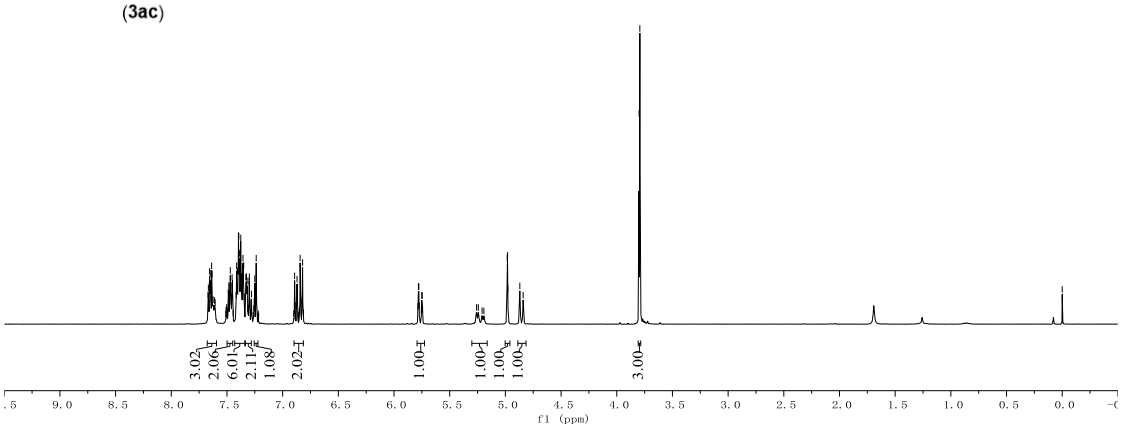
(*E*)-*N*'-(2-(4-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

(**3ab**)

(*E*)-*N*'-(2-(4-methoxybenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



(**3ac**)



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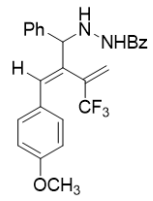
(*E*)-*N*'-(2-(4-methoxybenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



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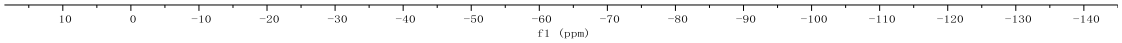
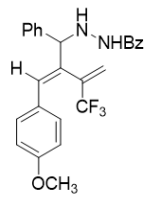


167.53
159.32
138.53
137.03
136.72
136.41
136.10
135.93
134.97
133.01
131.96
131.52
130.57
129.90
128.81
128.69
128.63
127.25
126.99
125.39
125.33
125.28
125.23
124.51
121.77
119.03
113.82
77.48
77.16
76.84
69.35
55.36

(*E*)-*N*'-(2-(4-methoxybenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



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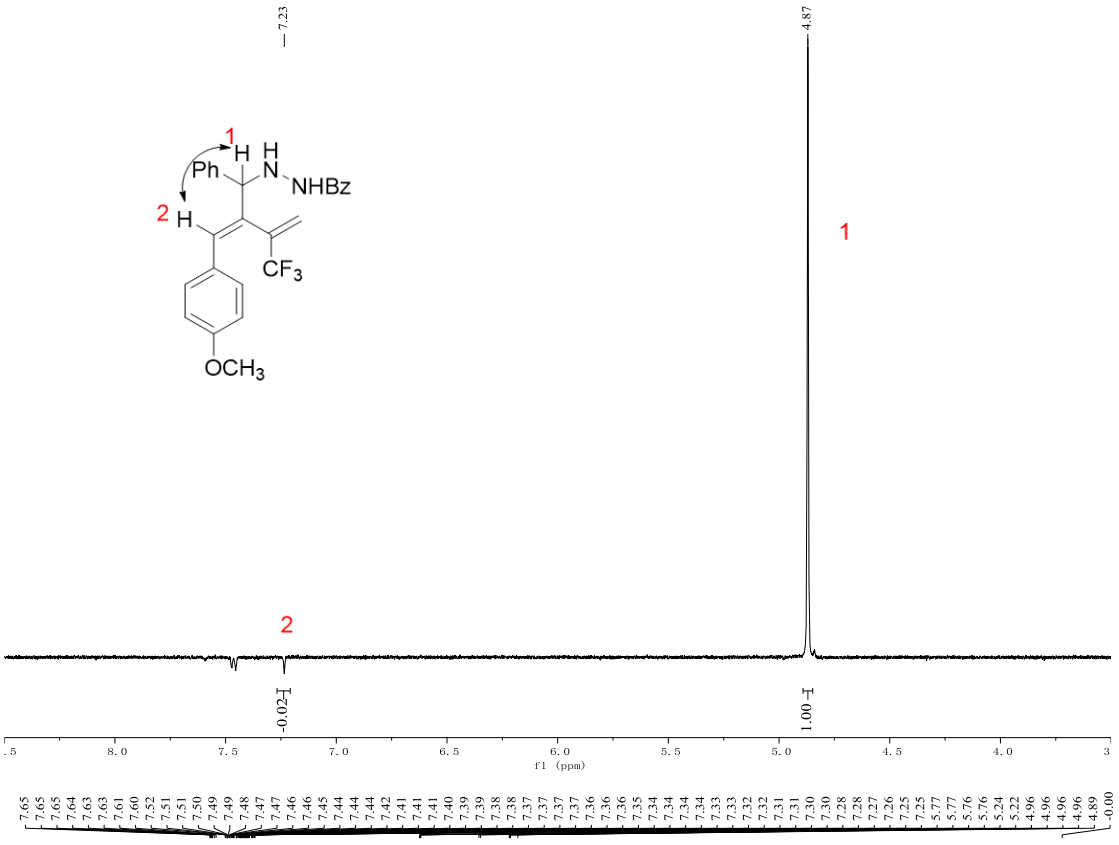
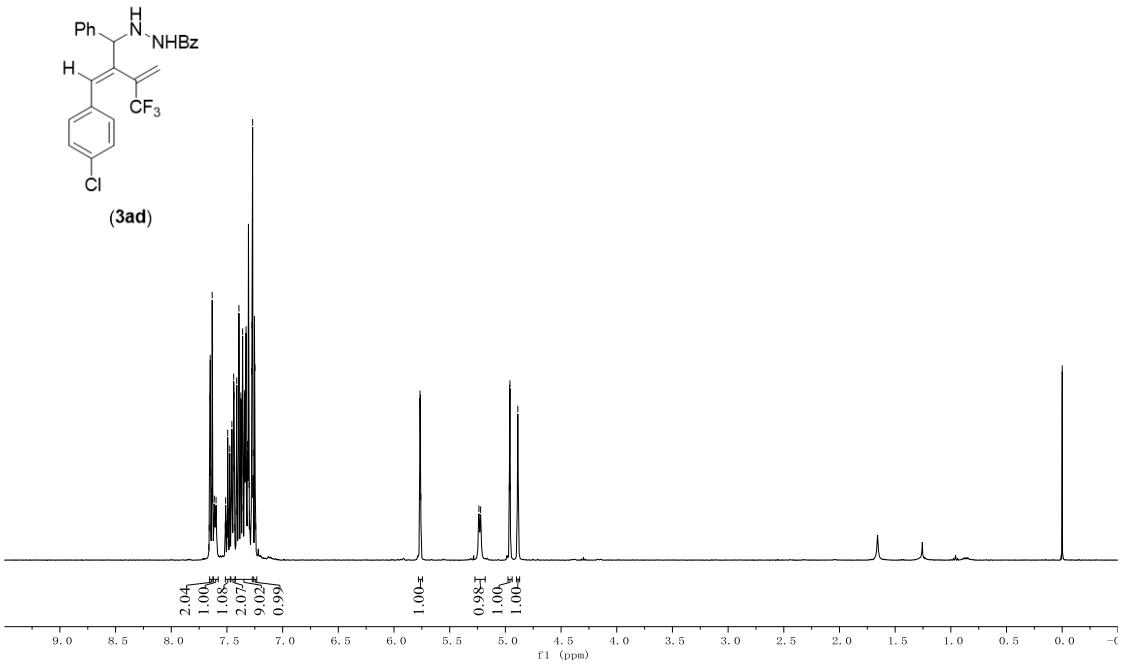
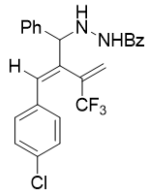


(*E*)-*N*'-(2-(4-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



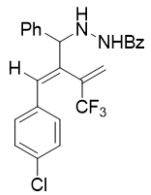
(**3ad**)

(*E*)-*N*'-(2-(4-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

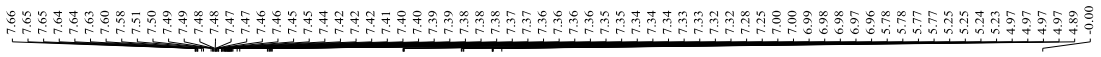


(**3ad**)

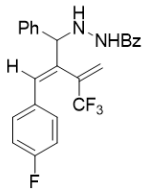
(*E*)-*N*'-(2-(4-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



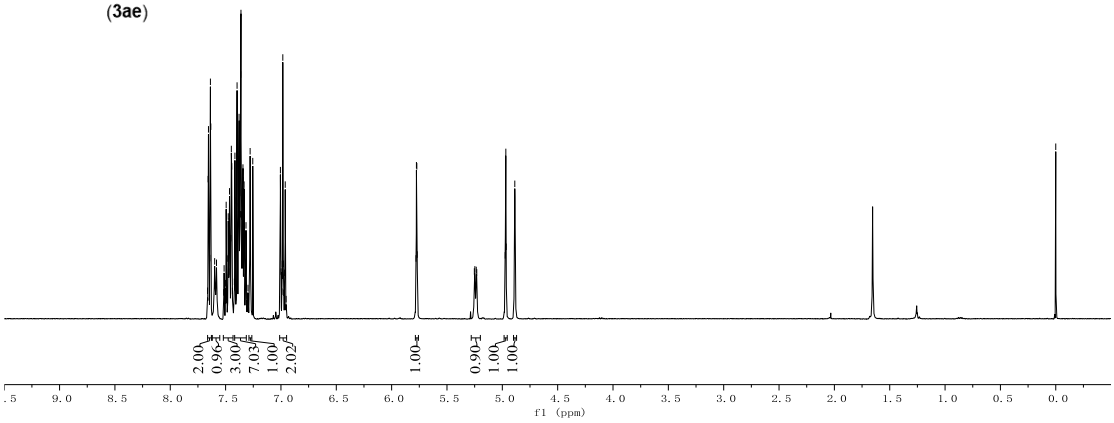
(**3ad**)

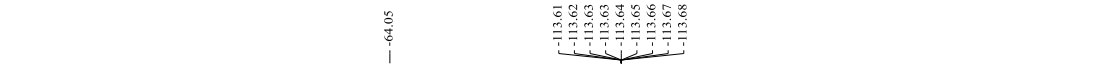


(*E*)-*N*'-(2-(4-fluorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

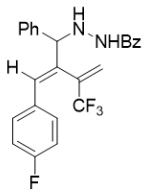


(**3ae**)





(*E*)-*N*'-(2-(4-fluorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



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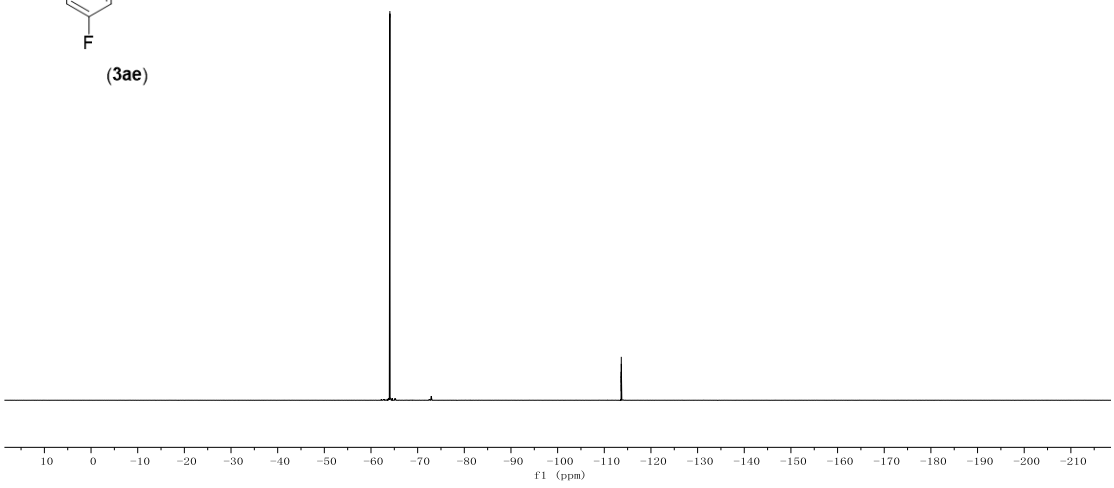
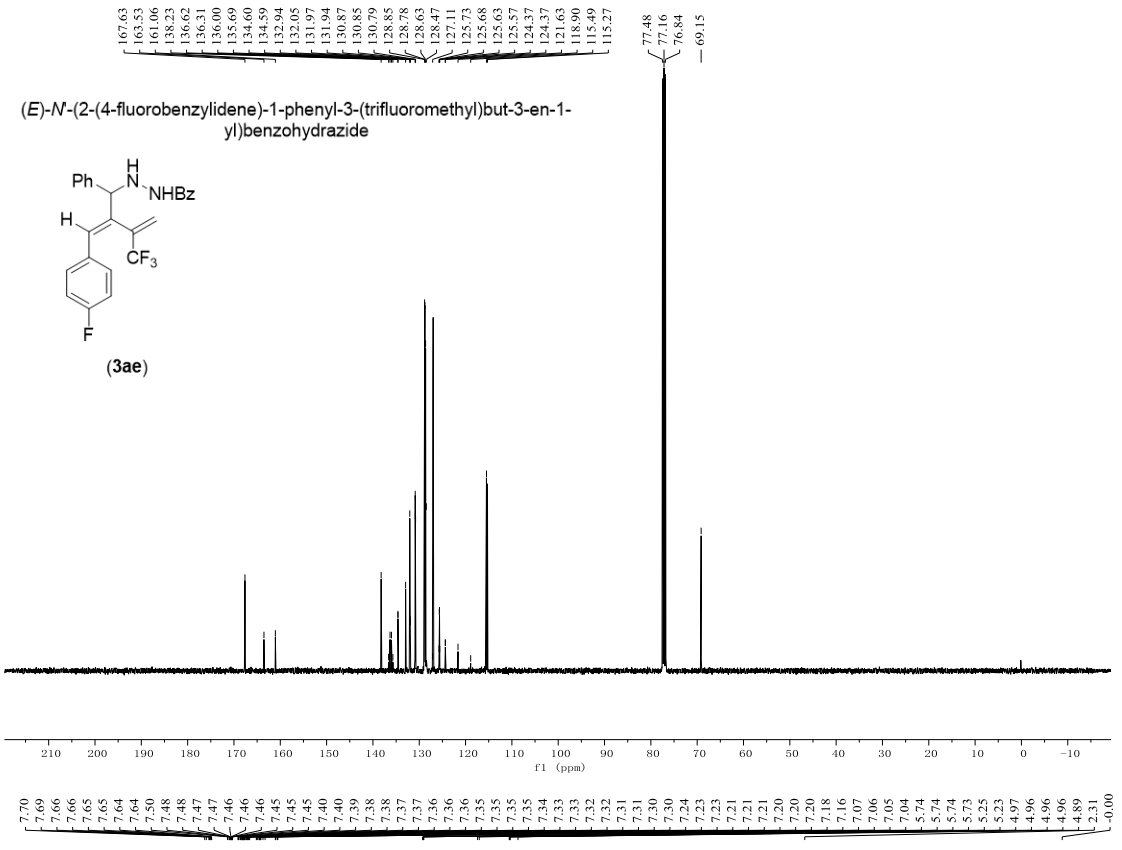
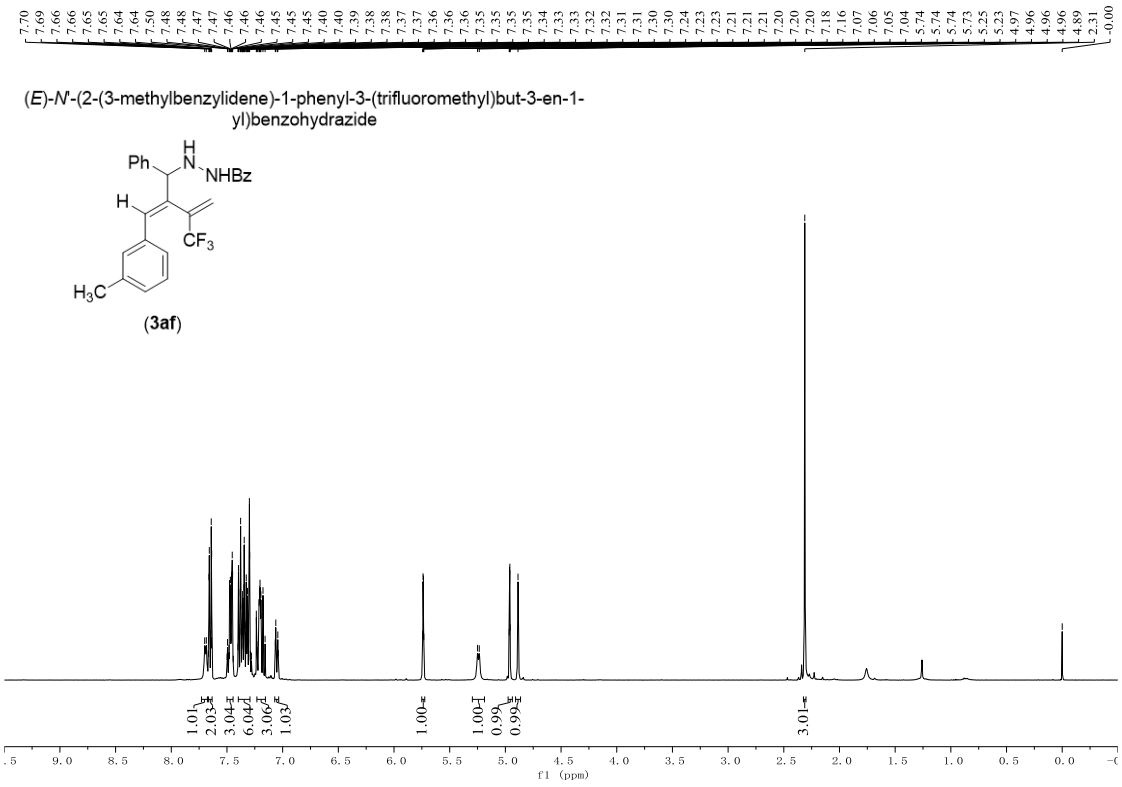




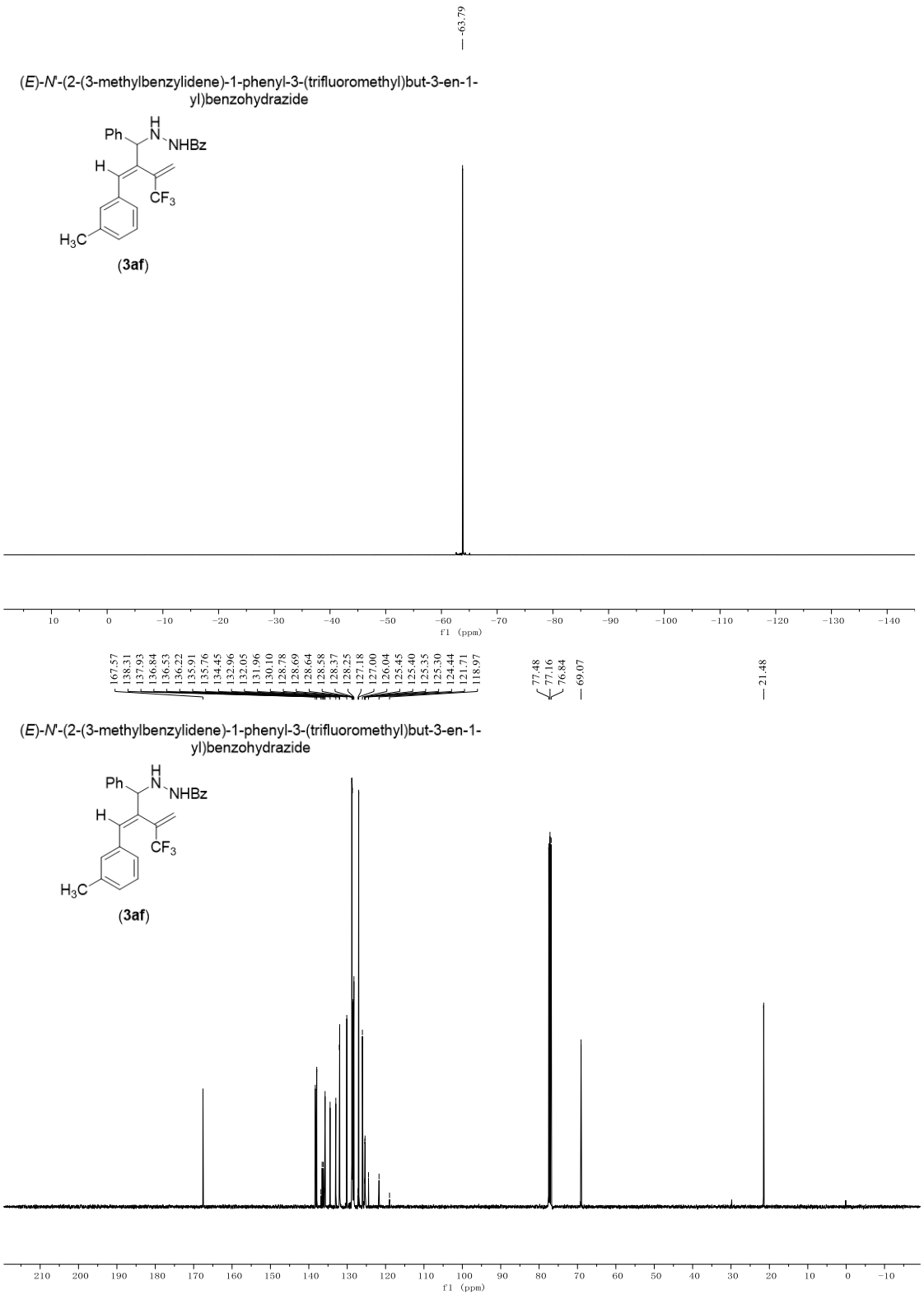
(*E*)-*N*'-(2-(4-fluorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

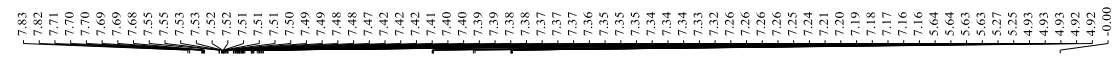
(**3ae**)



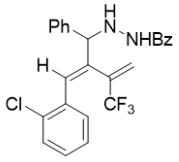
(*E*)-*N*'-(2-(3-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

(**3af**)

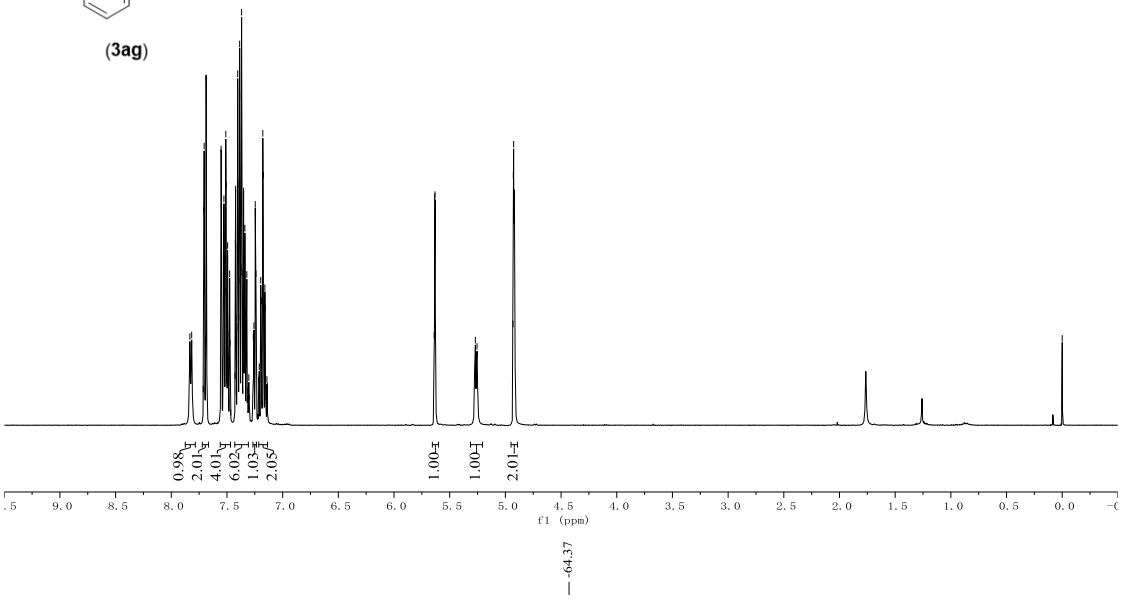

— -63.79
(E)-N'-(2-(3-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
Ph
H
N
NHBz
H
CF3
H3C
(3af)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140
f1 (ppm)
167.57
138.31
137.93
136.84
136.53
136.22
135.91
135.76
134.45
132.96
132.05
131.96
130.10
128.78
128.69
128.64
128.58
128.37
128.25
127.18
127.00
126.04
125.45
125.40
125.35
125.30
124.44
121.71
118.97
77.48
77.16
76.84
— 69.07
— 21.48
(E)-N'-(2-(3-methylbenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide
Ph
H
N
NHBz
H
CF3
H3C
(3af)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



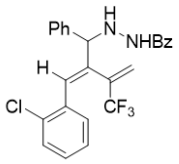
(*E*)-*N*'-(2-(2-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



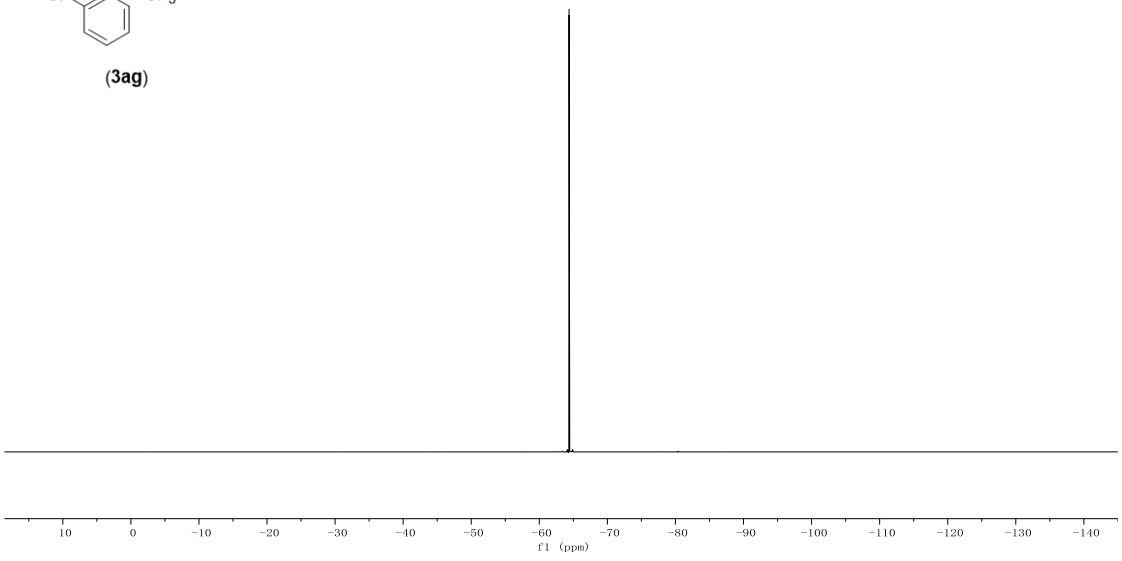
(**3ag**)

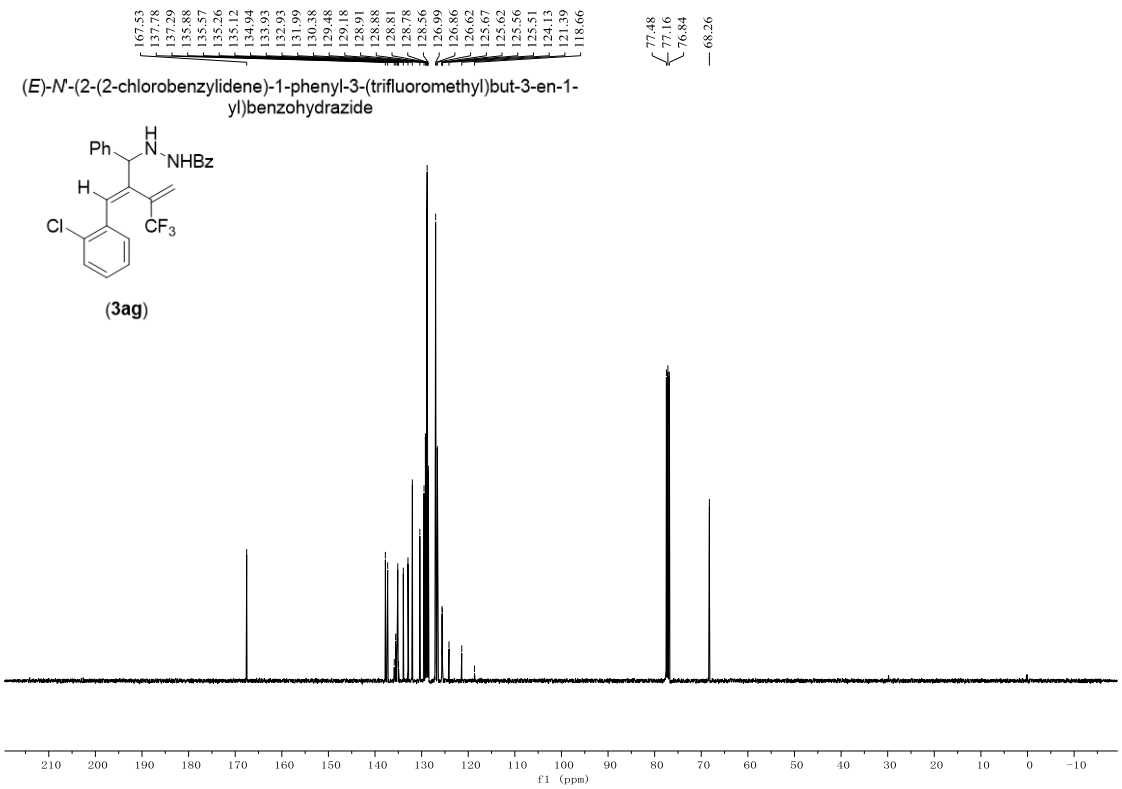


(*E*)-*N*'-(2-(2-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



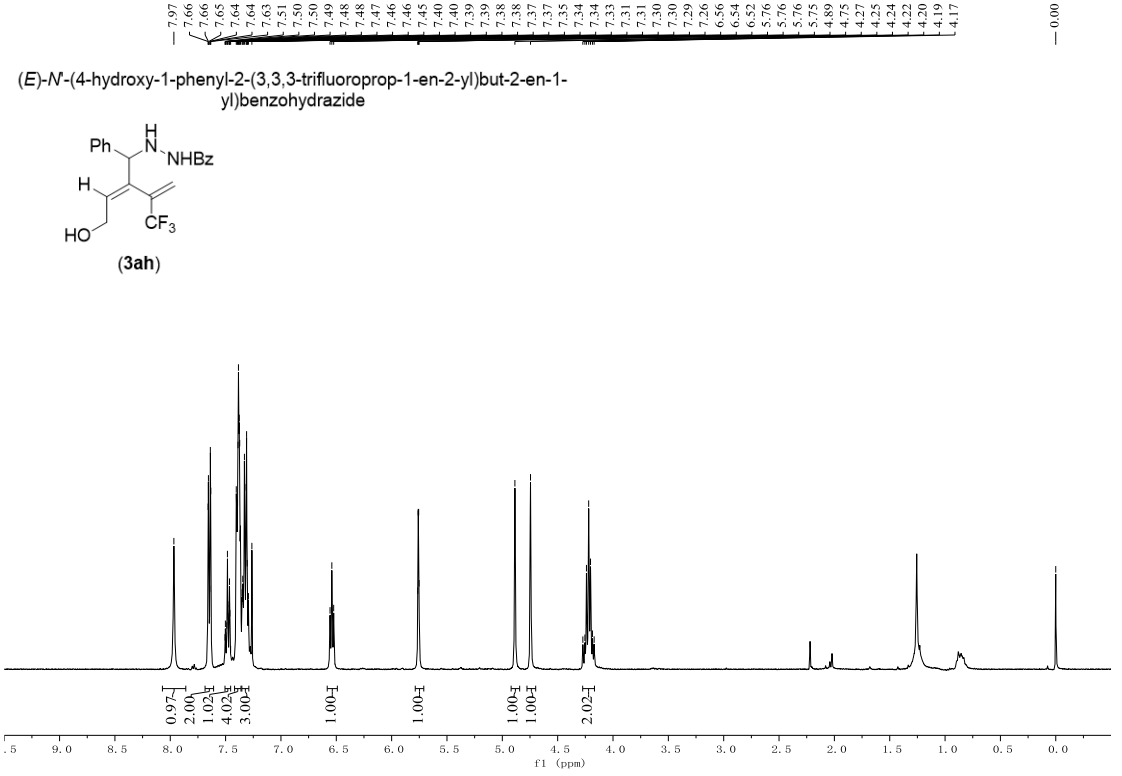
(**3ag**)





(*E*)-*N*'-(2-(2-chlorobenzylidene)-1-phenyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide

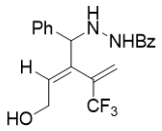
(**3ag**)



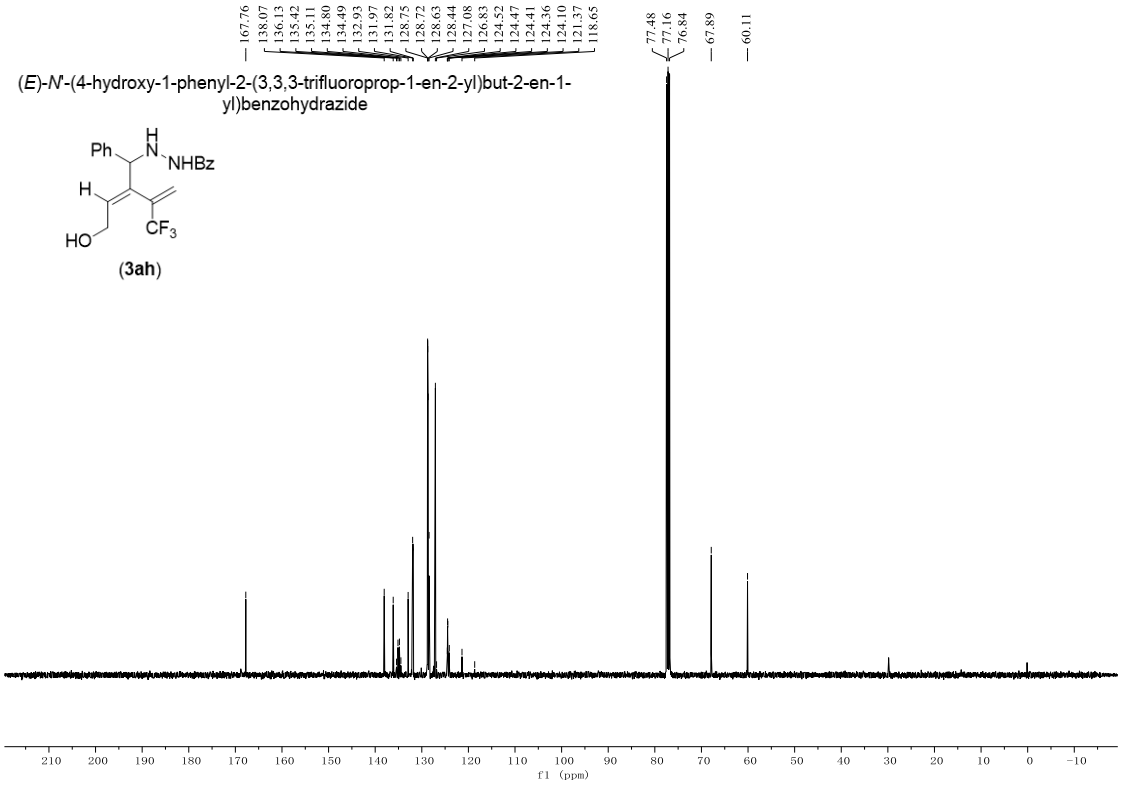
(*E*)-*N*'-(4-hydroxy-1-phenyl-2-(3,3,3-trifluoroprop-1-en-2-yl)but-2-en-1-yl)benzohydrazide

(**3ah**)

(*E*)-*N*'-(4-hydroxy-1-phenyl-2-(3,3,3-trifluoroprop-1-en-2-yl)but-2-en-1-yl)benzohydrazide

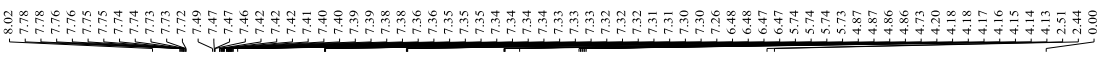


(**3ah**)

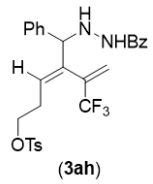


(*E*)-*N*'-(4-hydroxy-1-phenyl-2-(3,3,3-trifluoroprop-1-en-2-yl)but-2-en-1-yl)benzohydrazide

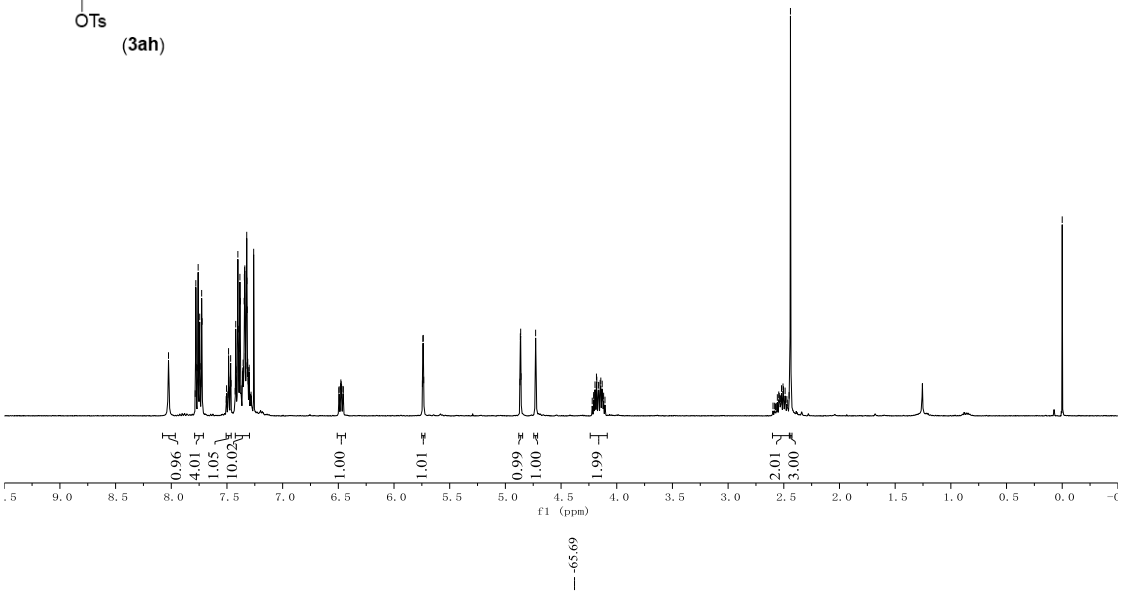
(**3ah**)



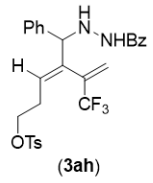
(*E*)-4-((2-benzoylhydrazinyl)(phenyl)methyl)-5-(trifluoromethyl)hexa-3,5-dien-1-yl 4-methylbenzenesulfonate



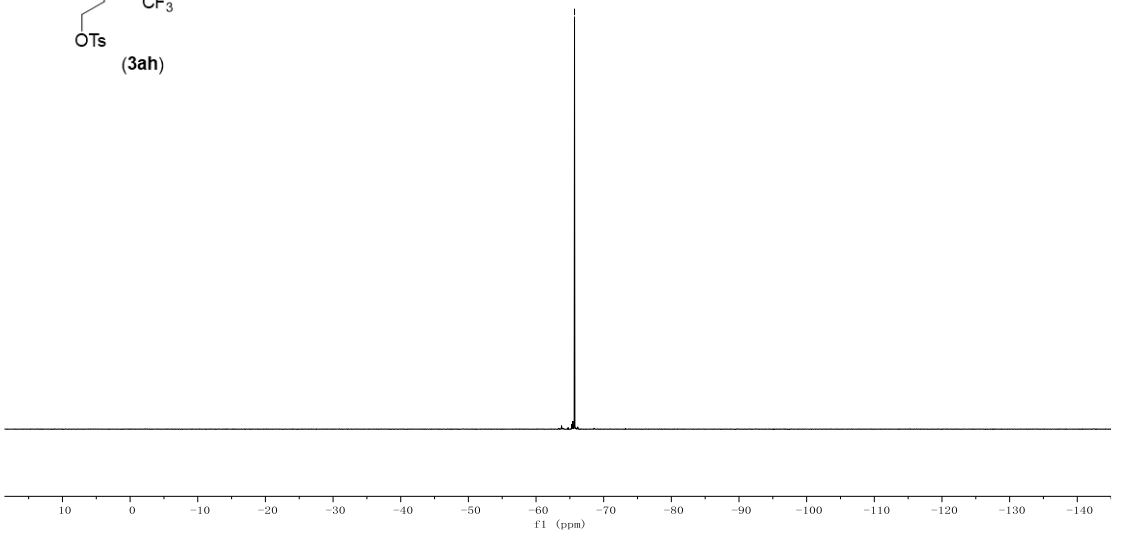
(**3ah**)

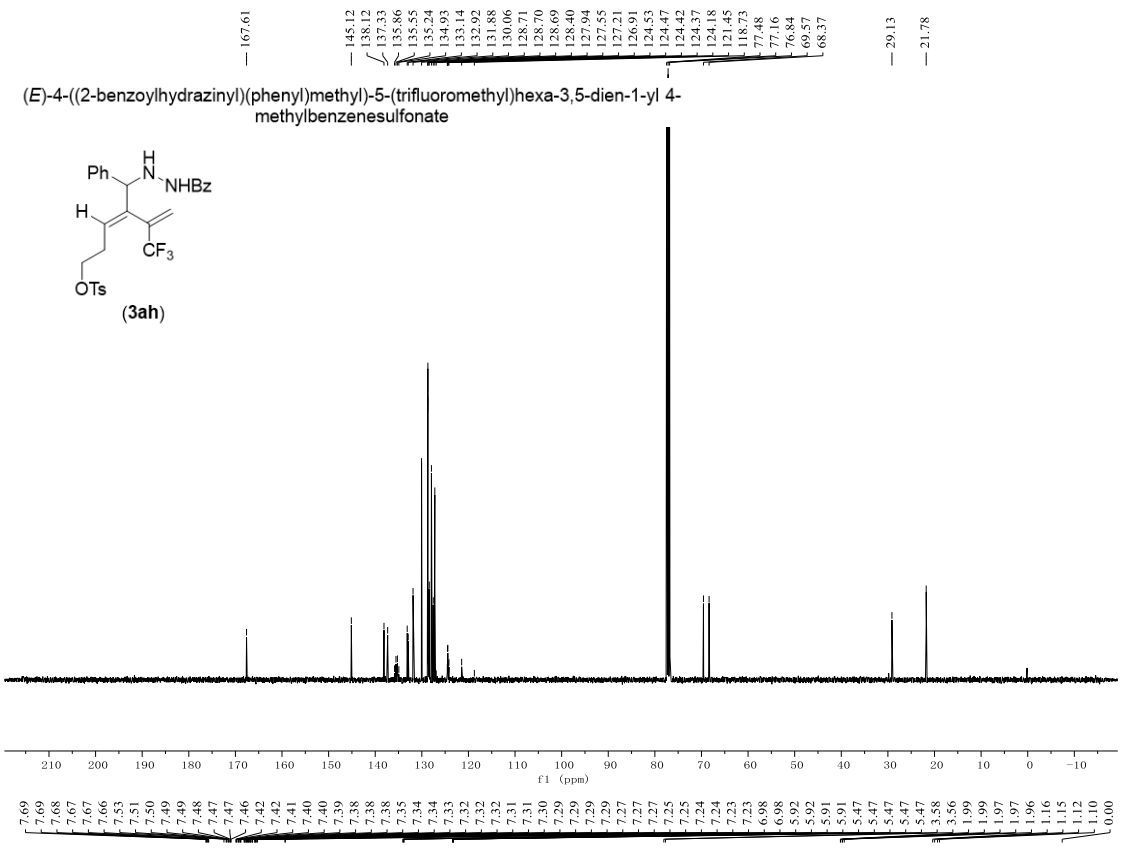


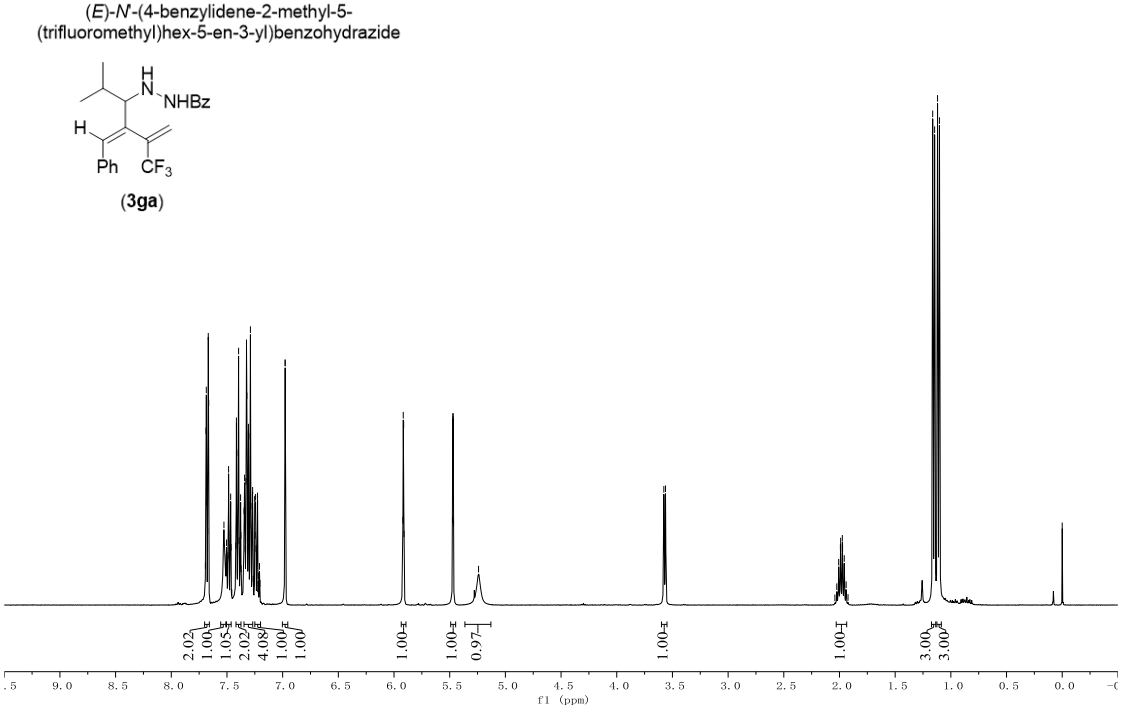
(*E*)-4-((2-benzoylhydrazinyl)(phenyl)methyl)-5-(trifluoromethyl)hexa-3,5-dien-1-yl 4-methylbenzenesulfonate



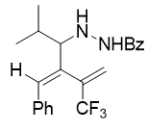
(**3ah**)




(E)-4-((2-benzoylhydrazinyl)(phenyl)methyl)-5-(trifluoromethyl)hexa-3,5-dien-1-yl 4-methylbenzenesulfonate
(3ah)
f1 (ppm)

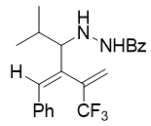

(E)-N'-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide
(3ga)
f1 (ppm)

(*E*)-*N*'-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



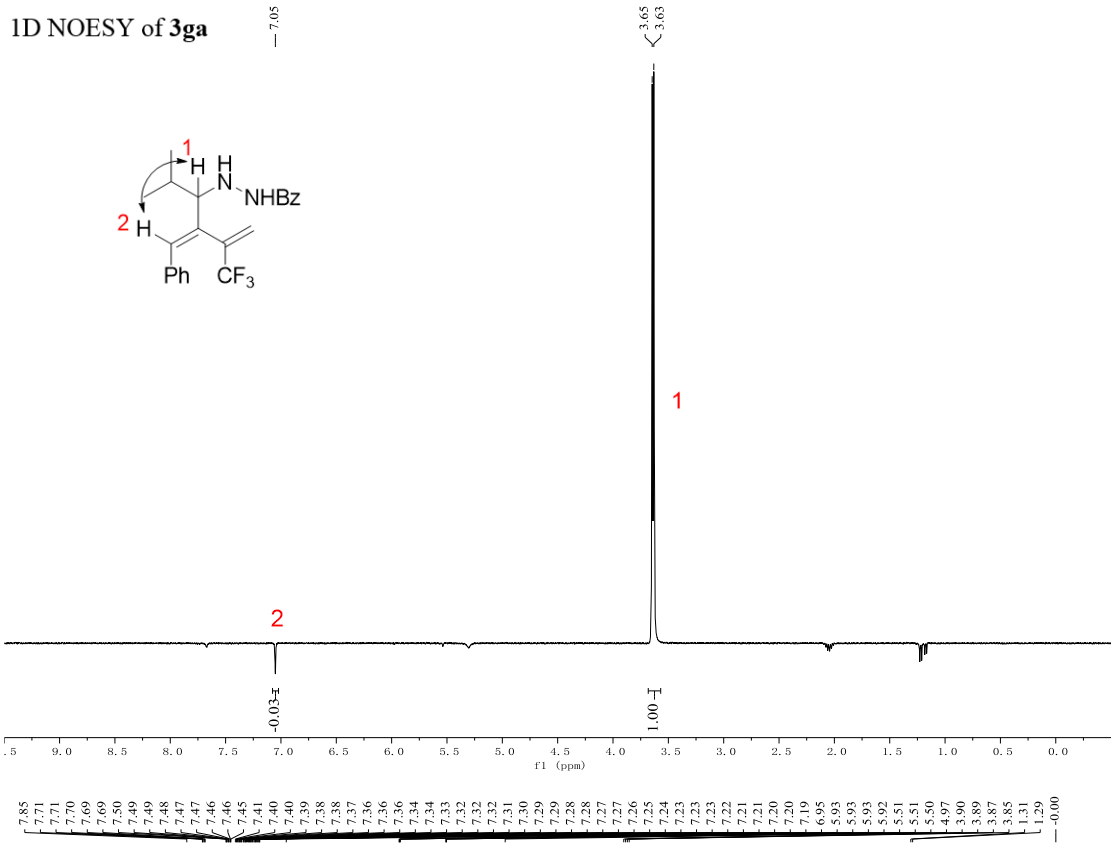
(**3ga**)

(*E*)-*N*'-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



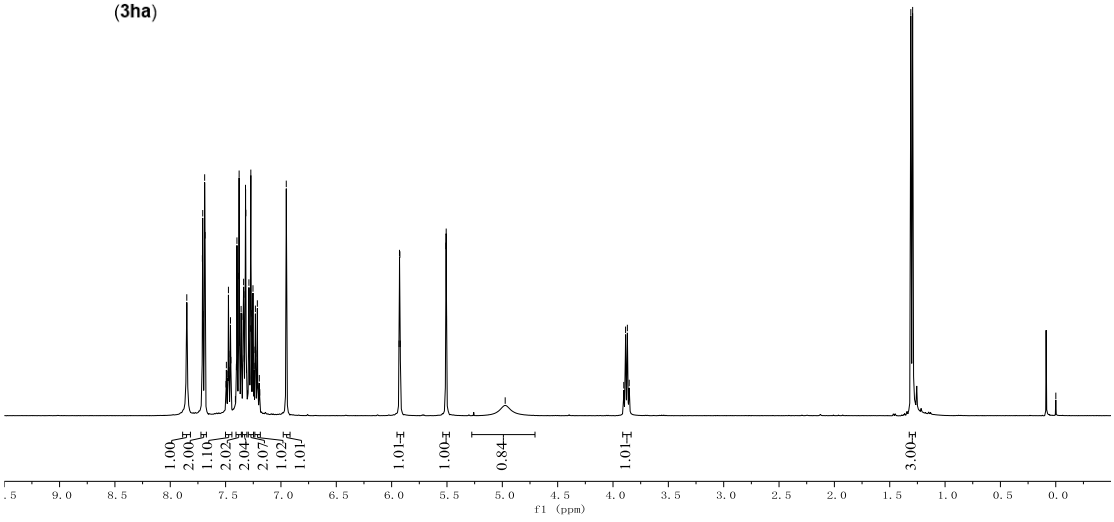
(**3ga**)

1D NOESY of **3ga**

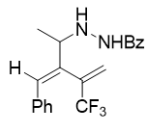


(*E*)-*N*′-(3-benzylidene-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide

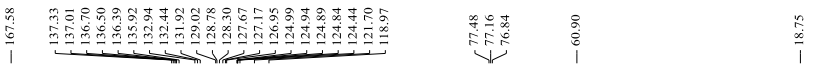
(**3ha**)



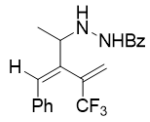
(*E*)-*N*'-(3-benzylidene-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide



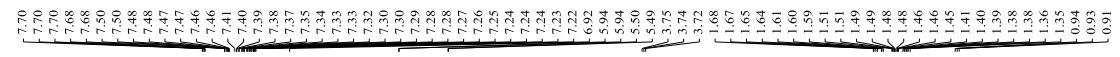
(**3ha**)



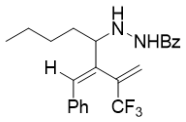
(*E*)-*N*'-(3-benzylidene-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide



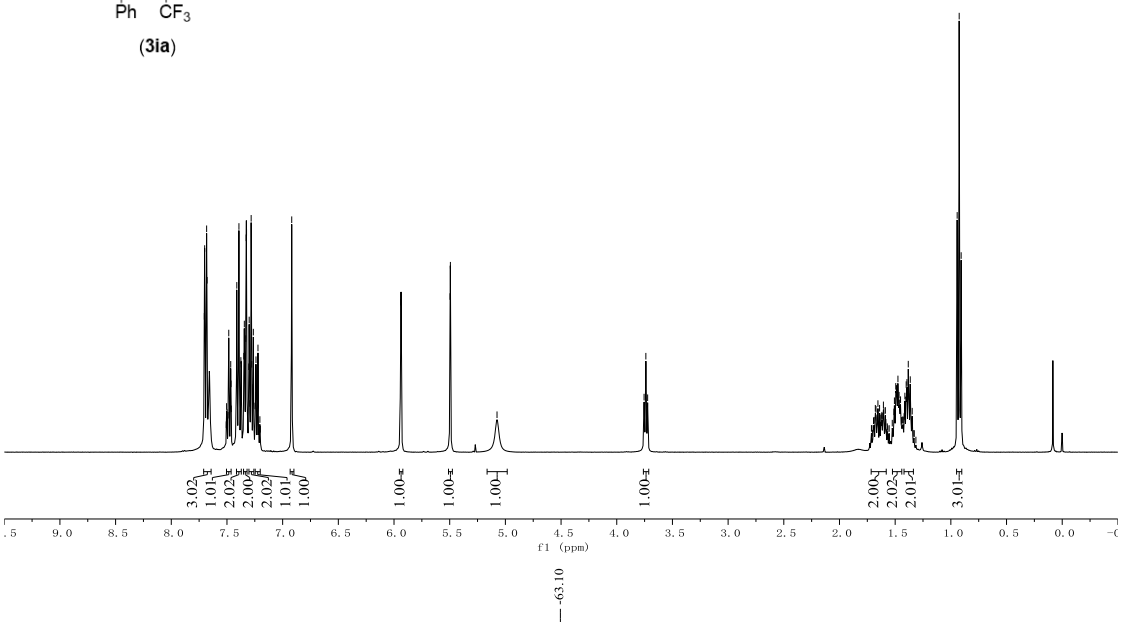
(**3ha**)

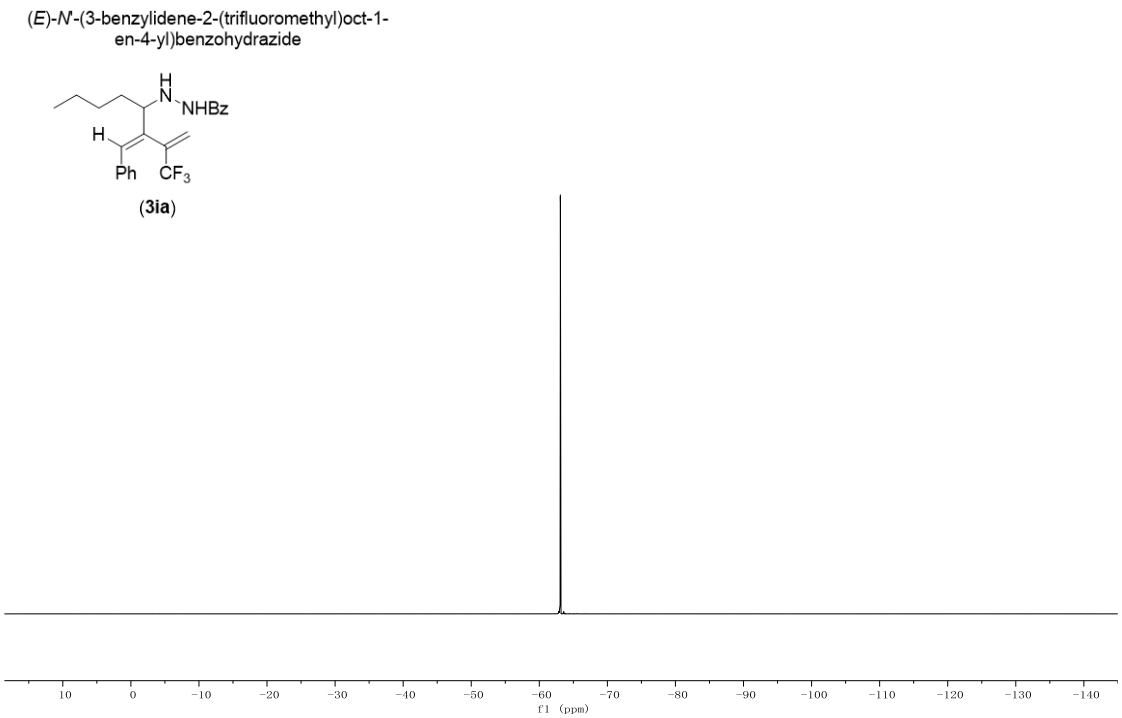


(*E*)-*N*-(3-benzylidene-2-(trifluoromethyl)oct-1-en-4-yl)benzohydrazide



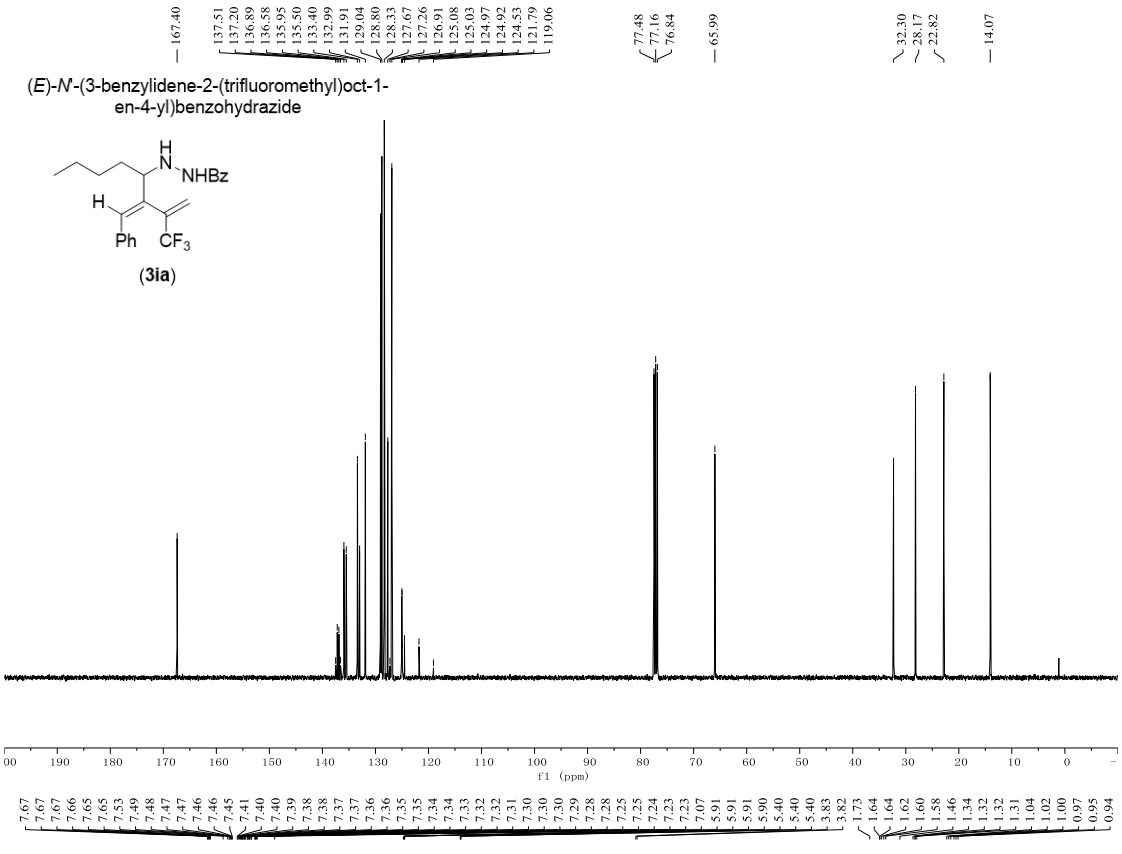
(**3ia**)

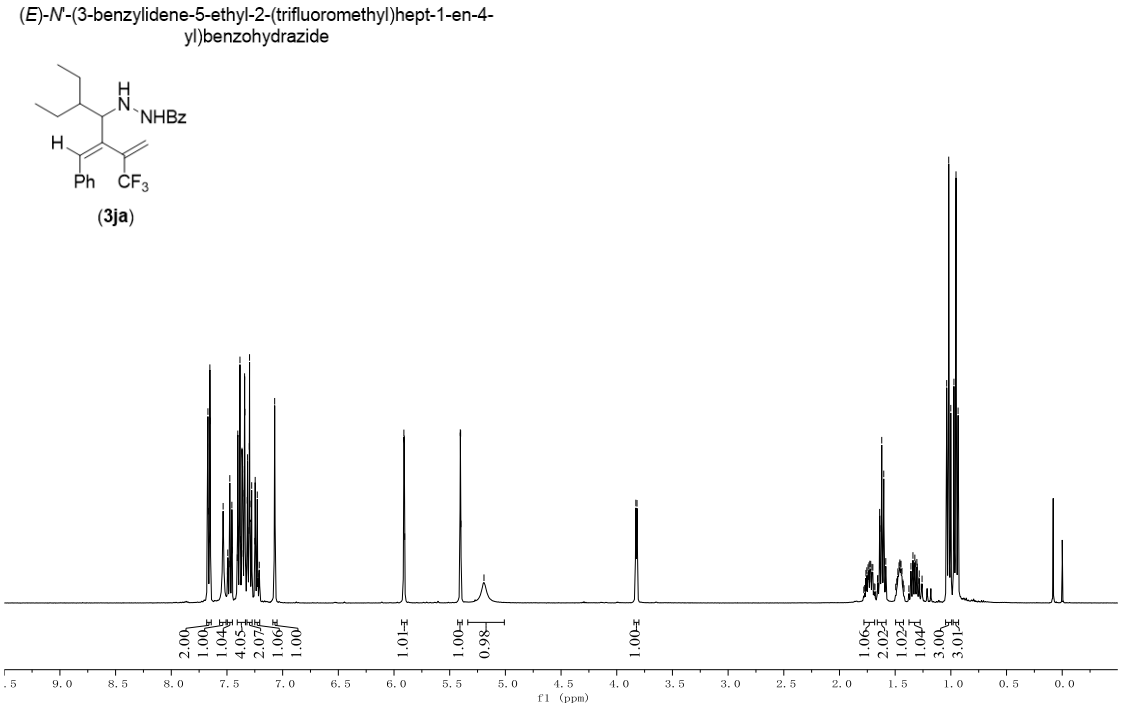




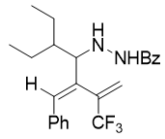
(*E*)-*N*-(3-benzylidene-2-(trifluoromethyl)oct-1-en-4-yl)benzohydrazide

(**3ia**)


(E)-N'-(3-benzylidene-2-(trifluoromethyl)oct-1-en-4-yl)benzohydrazide
NHBz
H
Ph
CF3
(3ia)
f1 (ppm)

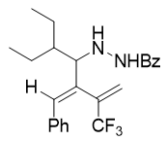

(E)-N'-(3-benzylidene-5-ethyl-2-(trifluoromethyl)hept-1-en-4-yl)benzohydrazide
NHBz
H
Ph
CF3
(3ja)
f1 (ppm)

(*E*)-*N'*-(3-benzylidene-5-ethyl-2-(trifluoromethyl)hept-1-en-4-yl)benzohydrazide

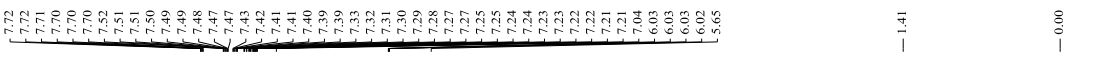


(**3ja**)

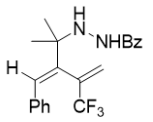
(*E*)-*N'*-(3-benzylidene-5-ethyl-2-(trifluoromethyl)hept-1-en-4-yl)benzohydrazide



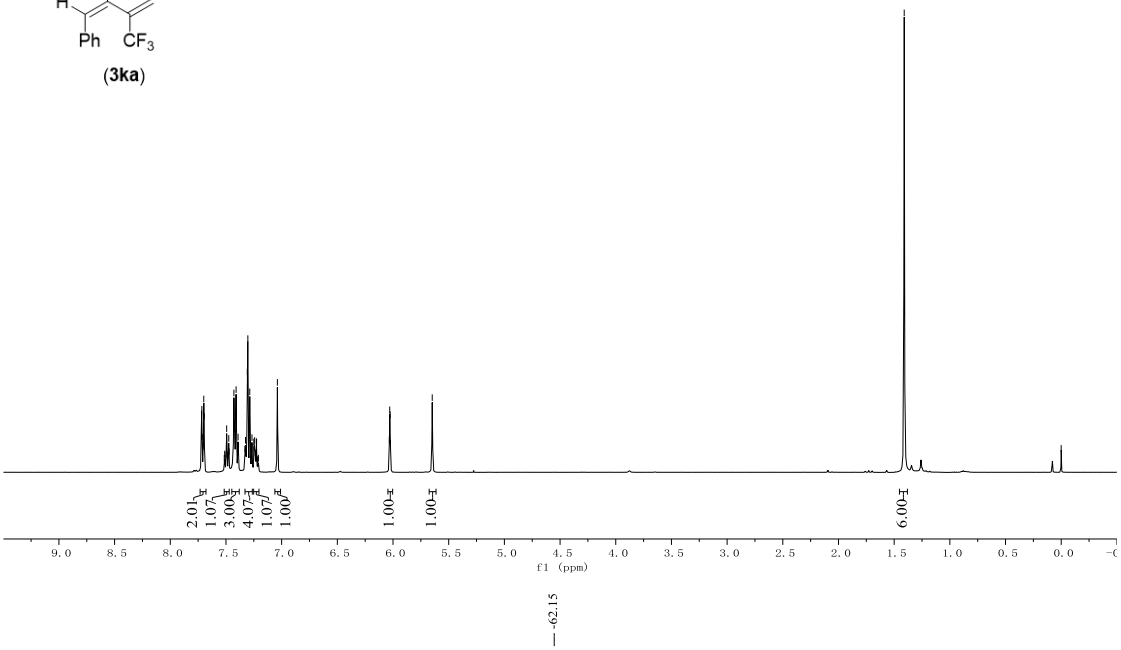
(**3ja**)



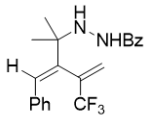
(*E*)-*N*'-(3-benzylidene-2-methyl-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide



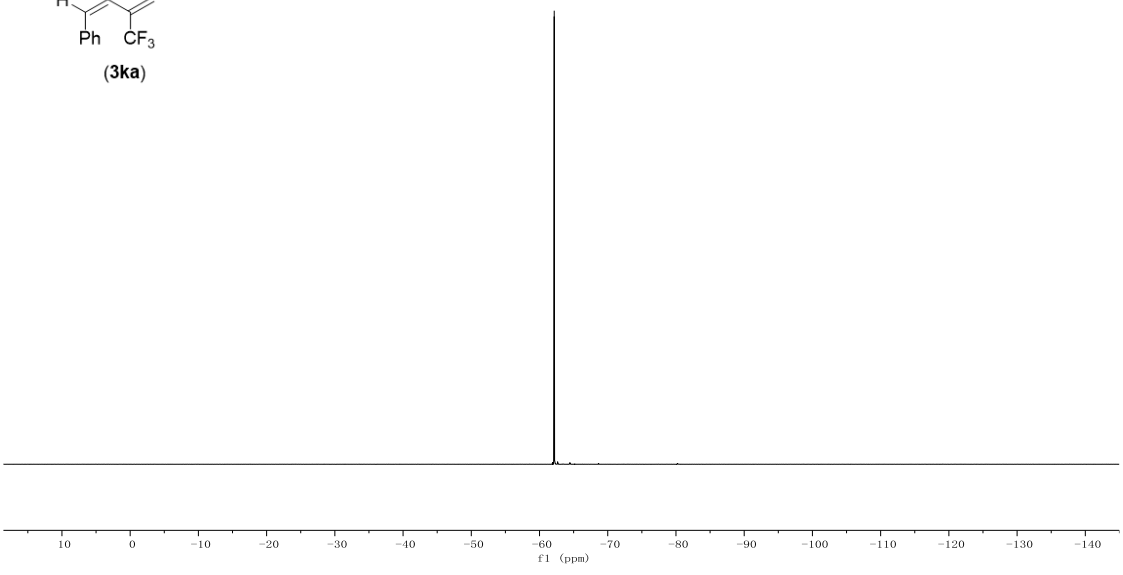
(**3ka**)

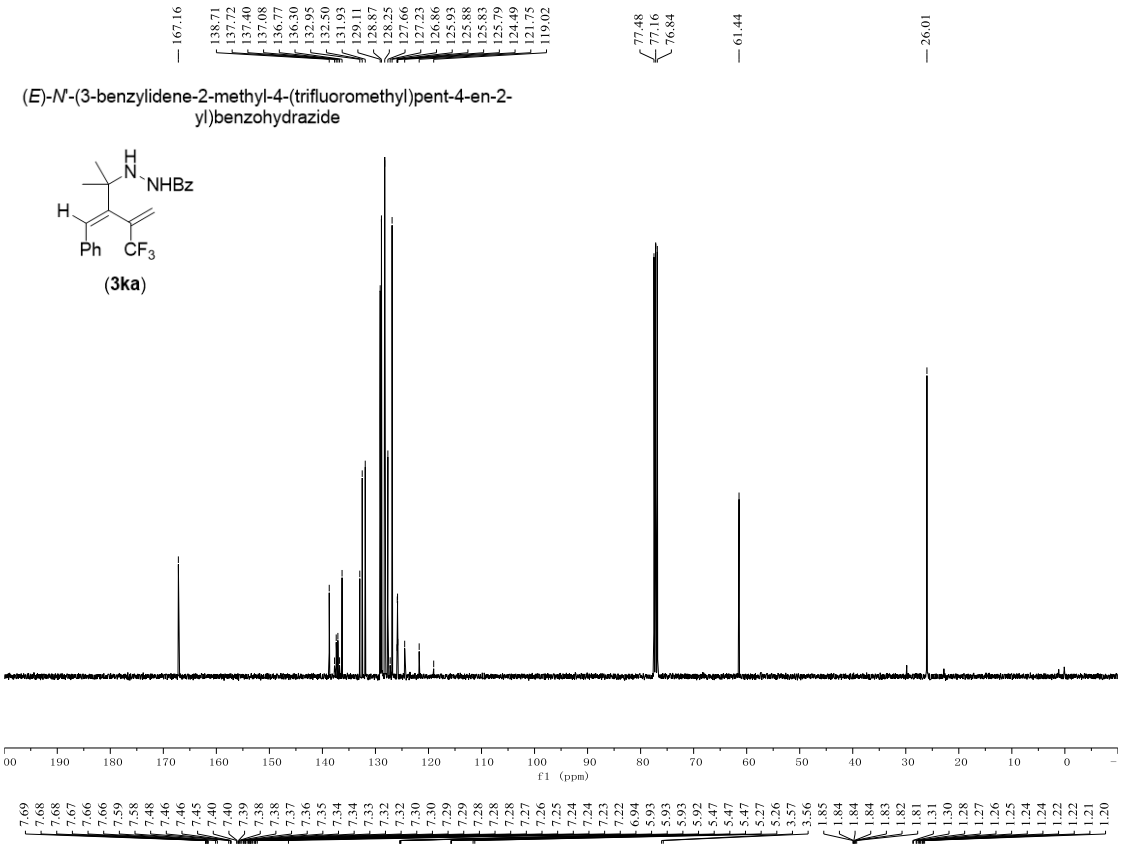


(*E*)-*N*'-(3-benzylidene-2-methyl-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide



(**3ka**)

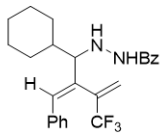




(*E*)-*N*'-(3-benzylidene-2-methyl-4-(trifluoromethyl)pent-4-en-2-yl)benzohydrazide

(**3ka**)

(*E*)-*N*'-(2-benzylidene-1-cyclohexyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



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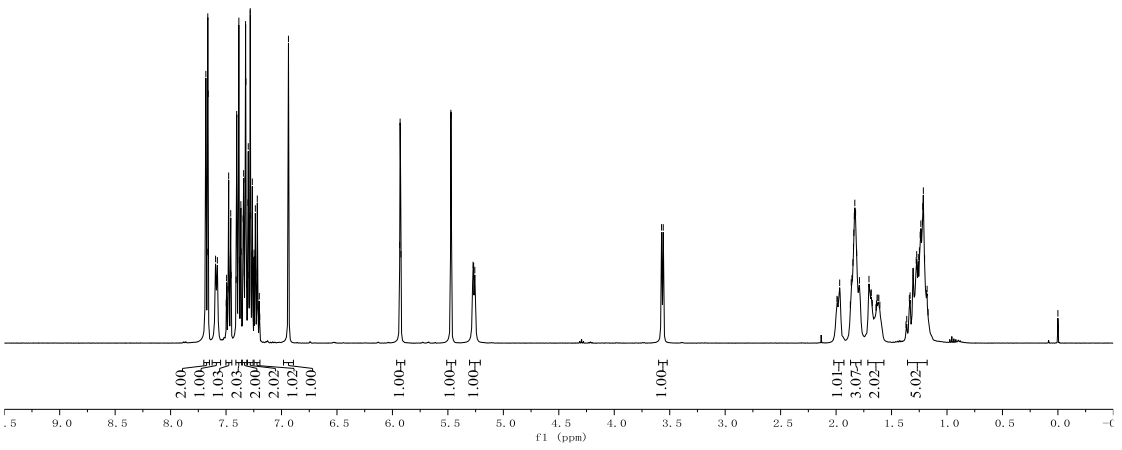
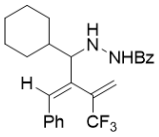
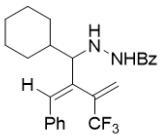


(*E*)-*N*'-(2-benzylidene-1-cyclohexyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



(**3la**)

(*E*)-*N*'-(2-benzylidene-1-cyclohexyl-3-(trifluoromethyl)but-3-en-1-yl)benzohydrazide



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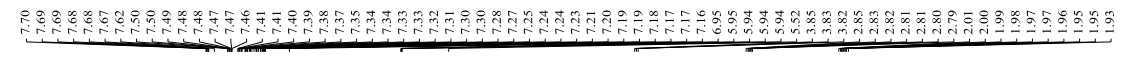
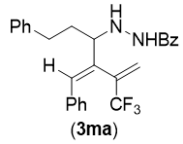
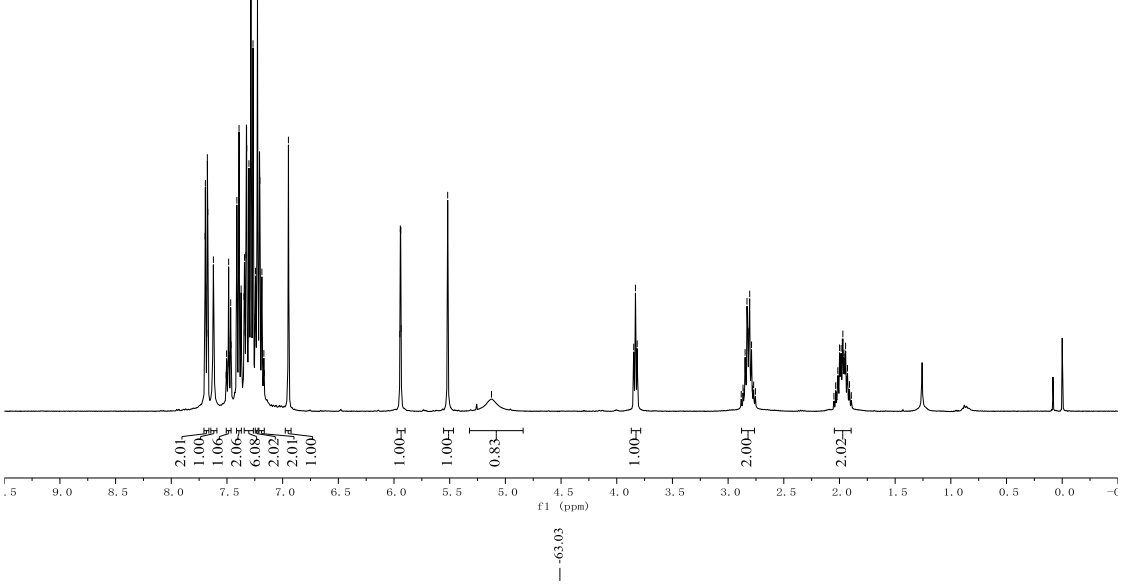


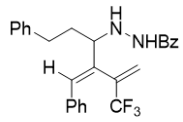
(*E*)-*N*'-(4-benzylidene-1-phenyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3ma**)



(*E*)-*N*'-(4-benzylidene-1-phenyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



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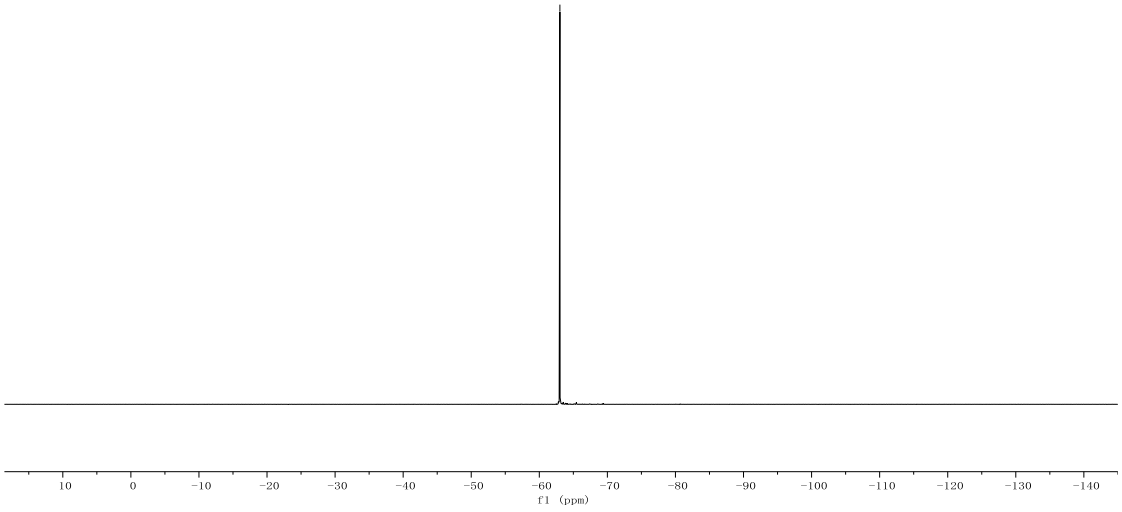
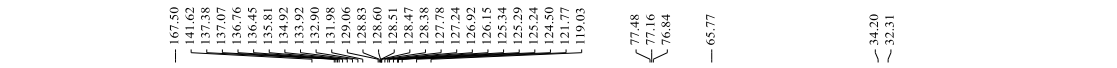
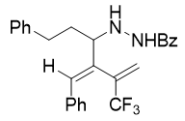
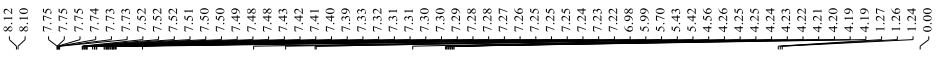




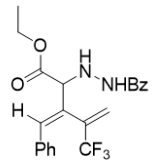
(*E*)-*N*'-(4-benzylidene-1-phenyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3ma**)

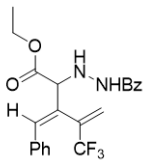


ethyl (*E*)-2-(2-benzoylhydrazinyl)-3-benzylidene-4-(trifluoromethyl)pent-4-enoate



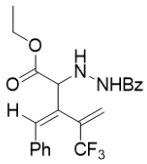
(**3na**)

ethyl (*E*)-2-(2-benzoylhydrazinyl)-3-benzylidene-4-(trifluoromethyl)pent-4-enoate

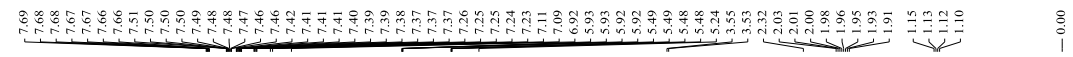


(**3na**)

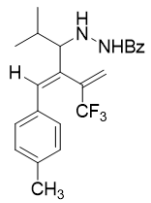
ethyl (*E*)-2-(2-benzoylhydrazinyl)-3-benzylidene-4-(trifluoromethyl)pent-4-enoate



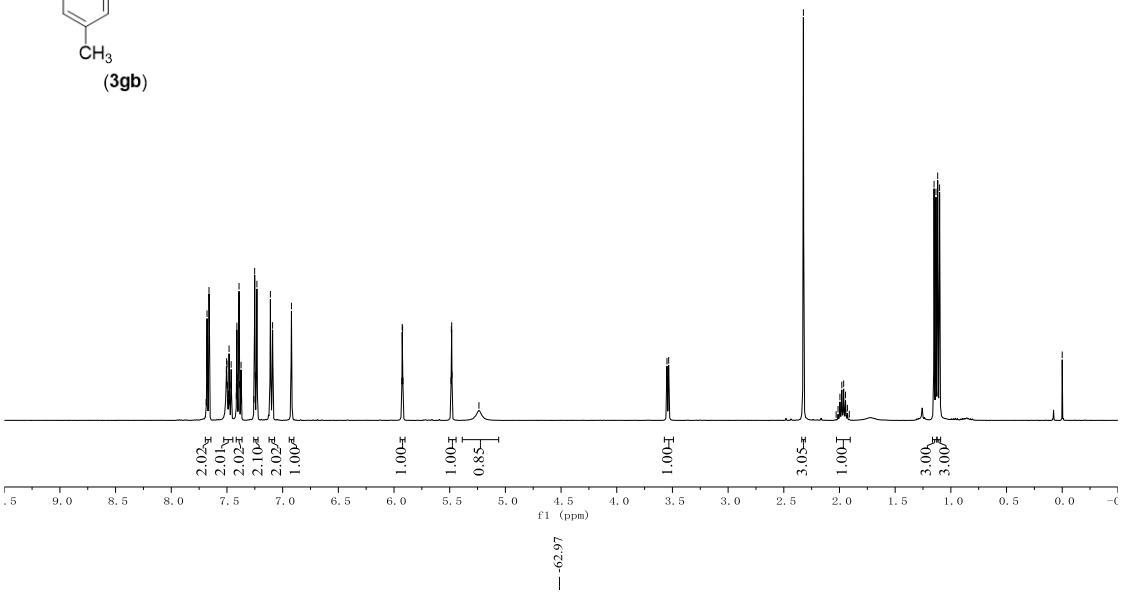
(**3na**)

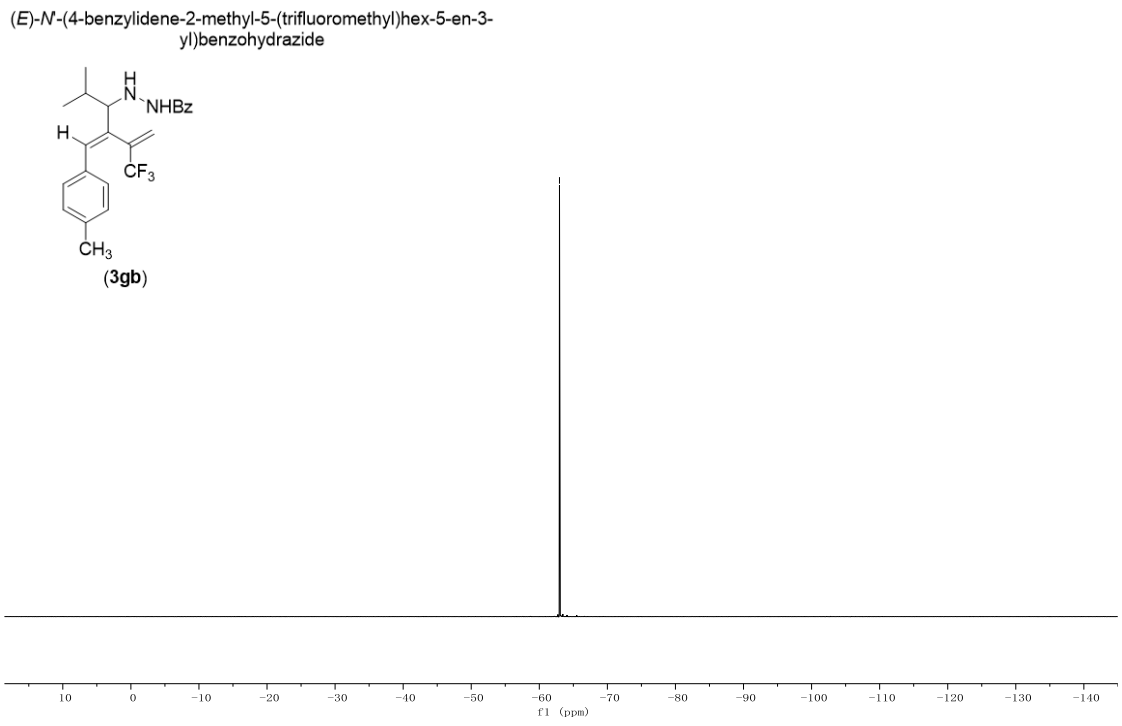


(*E*)-*N*'-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3gb**)

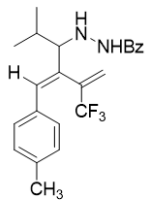




(*E*)-*N*'-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide

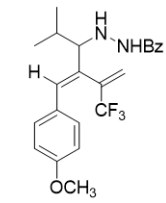
(**3gb**)

(*E*)-*N*'-(4-benzylidene-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



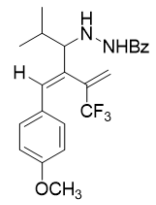
(**3gb**)

(*E*)-*N*'-(4-(4-methoxybenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



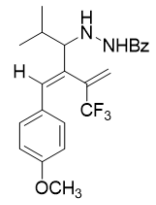
(**3gc**)

(*E*)-*N*'-(4-(4-methoxybenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3gc**)

(*E*)-*N*'-(4-(4-methoxybenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



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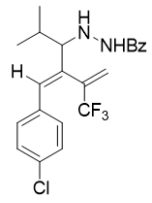
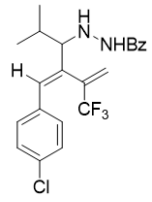
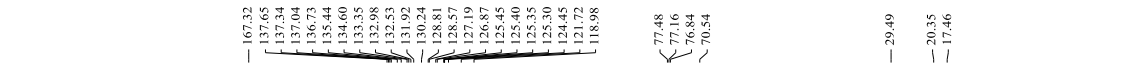


(**3gd**)

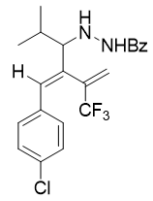
(*E*)-*N'*-(4-(4-chlorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



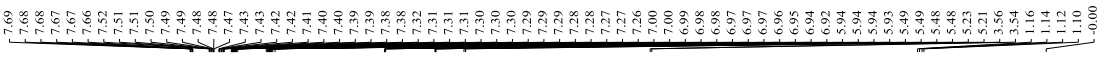
(**3gd**)



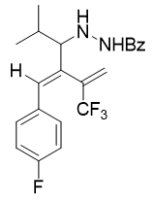
(*E*)-*N*'-(4-(4-chlorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3gd**)



(*E*)-*N*'-(4-(4-fluorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3ge**)

-63.08

-114.00
-114.01
-114.02
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-114.03
-114.04
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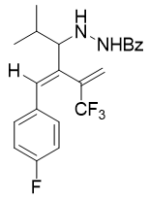
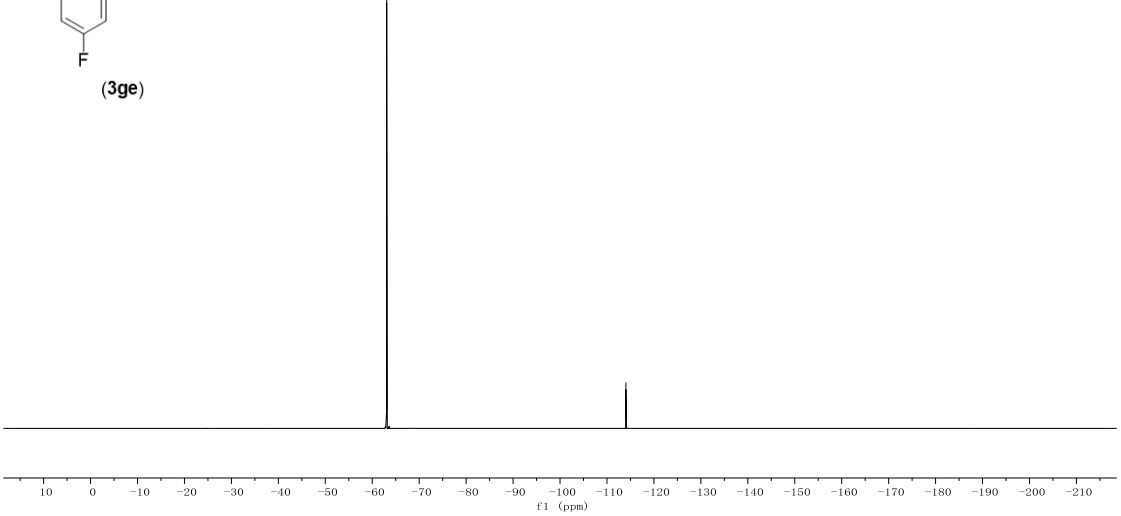
(*E*)-*N*'-(4-(4-fluorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3ge**)



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115.26
77.48
77.16
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20.40
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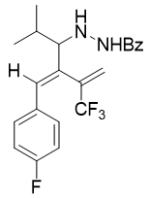
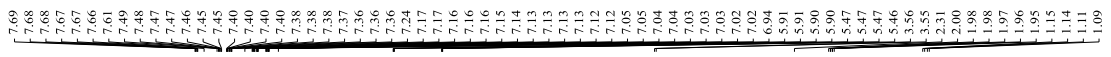
(*E*)-*N*'-(4-(4-fluorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



(**3ge**)



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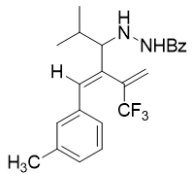
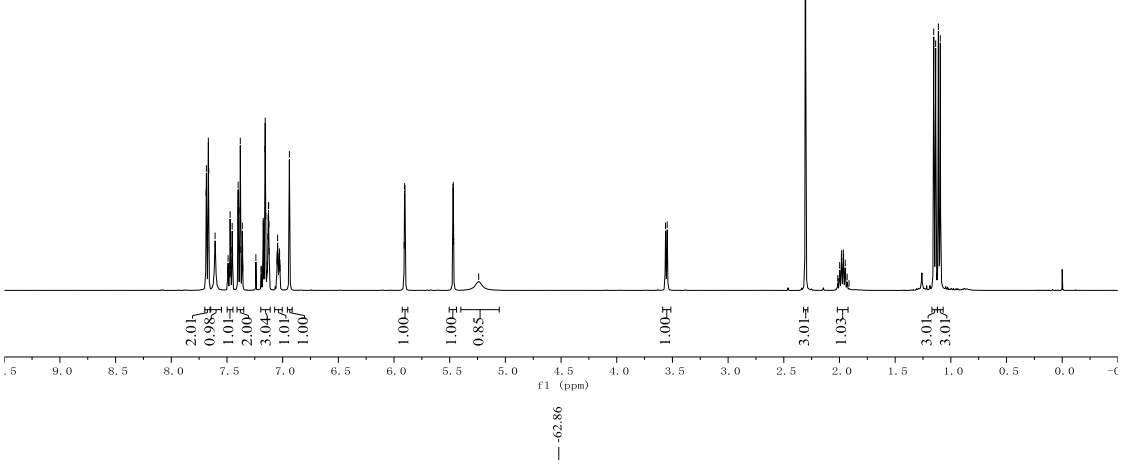
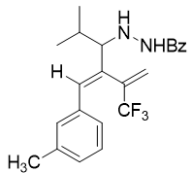


(**3gf**)



(*E*)-*N*'-(2-methyl-4-(3-methylbenzylidene)-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



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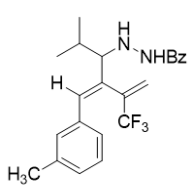
(*E*)-*N*'-(2-methyl-4-(3-methylbenzylidene)-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



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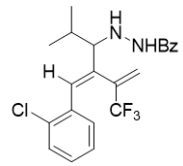

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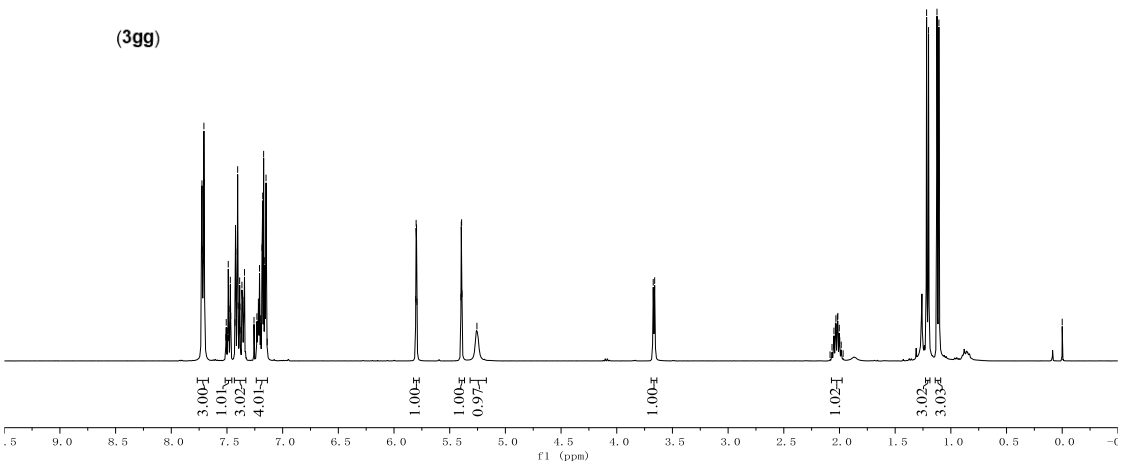
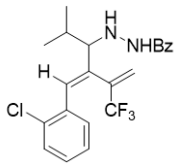


(*E*)-*N*'-(4-(2-chlorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



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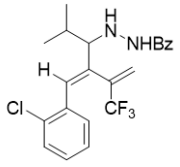
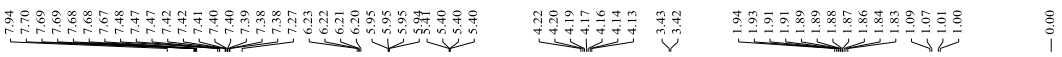
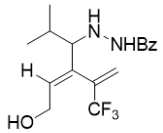
(*E*)-*N*'-(4-(2-chlorobenzylidene)-2-methyl-5-(trifluoromethyl)hex-5-en-3-yl)benzohydrazide



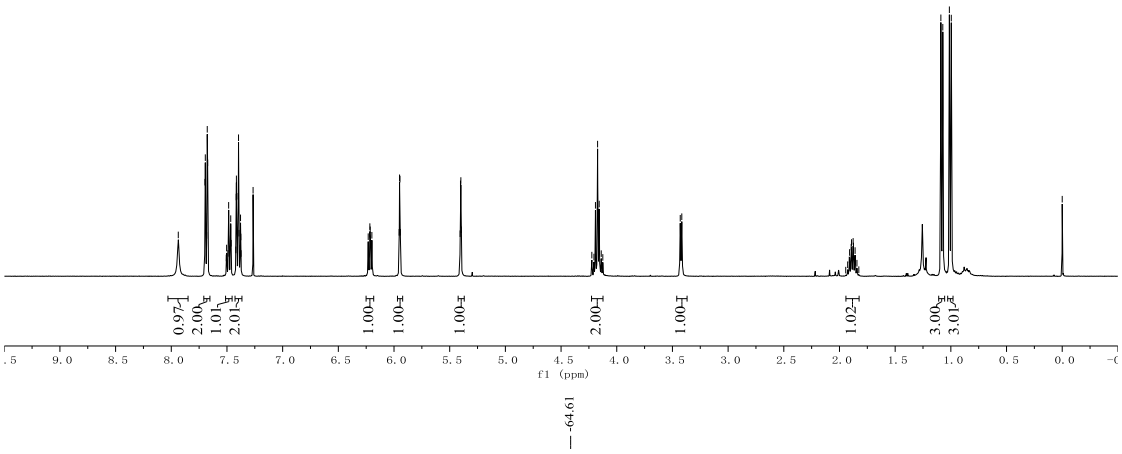
(**3gg**)

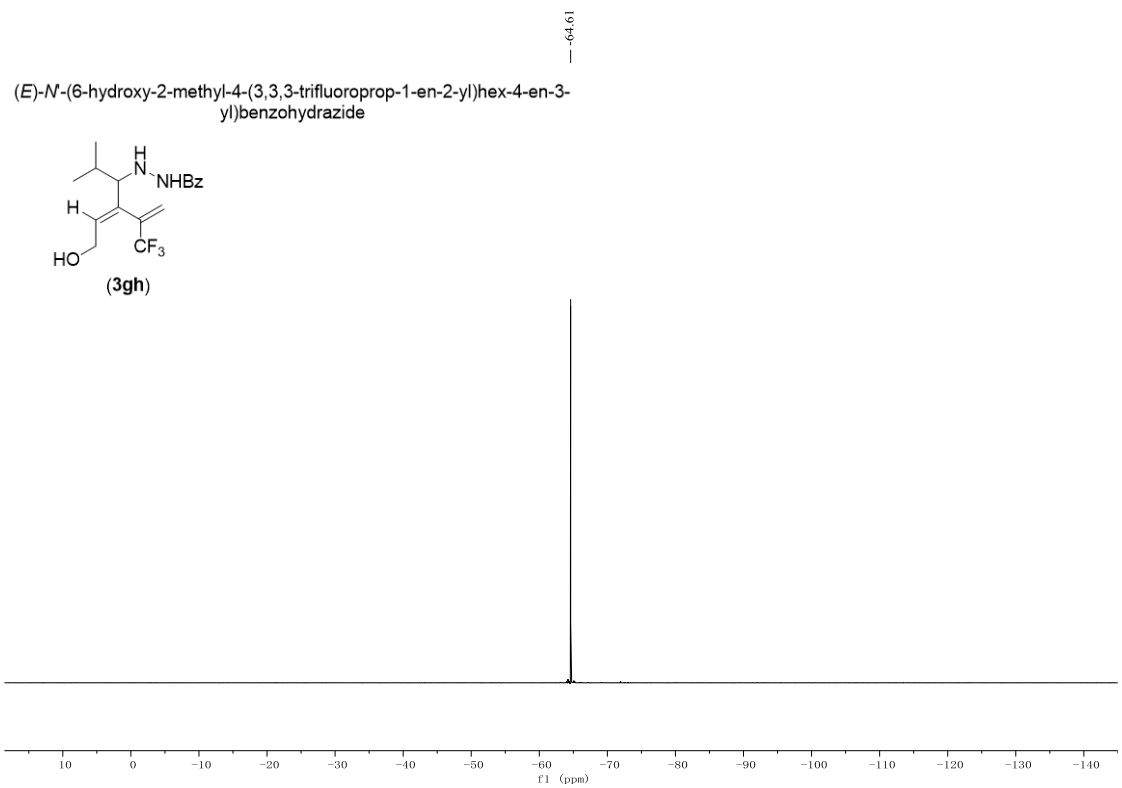


(*E*)-*N*'-(6-hydroxy-2-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hex-4-en-3-yl)benzohydrazide



(**3gh**)

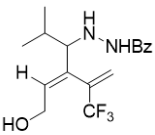




(*E*)-*N*'-(6-hydroxy-2-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hex-4-en-3-yl)benzohydrazide

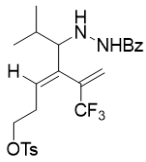
(**3gh**)

(*E*)-*N*'-(6-hydroxy-2-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hex-4-en-3-yl)benzohydrazide



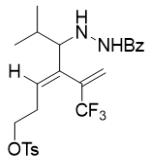
(**3gh**)

(*E*)-5-(2-benzoylhydrazinyl)-6-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hept-3-en-1-yl 4-methylbenzenesulfonate



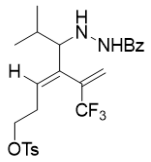
(**3gi**)

(*E*)-5-(2-benzoylhydrazinyl)-6-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hept-3-en-1-yl 4-methylbenzenesulfonate

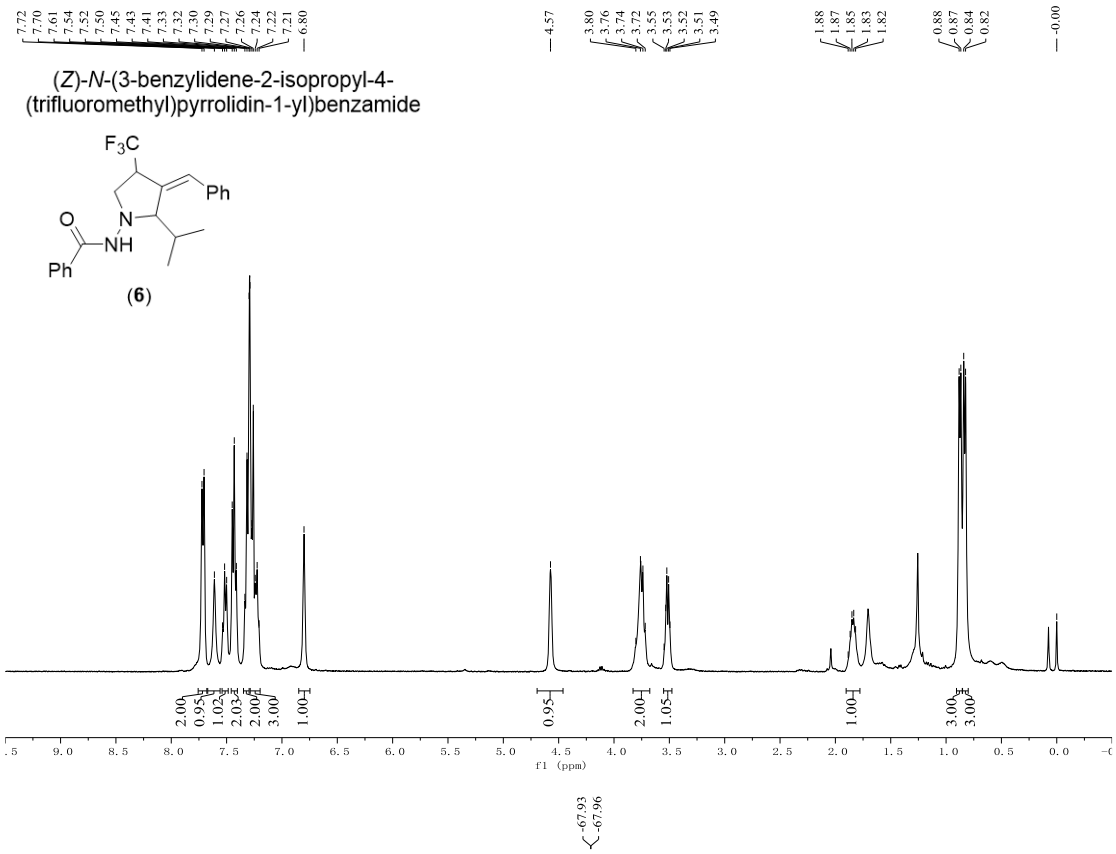


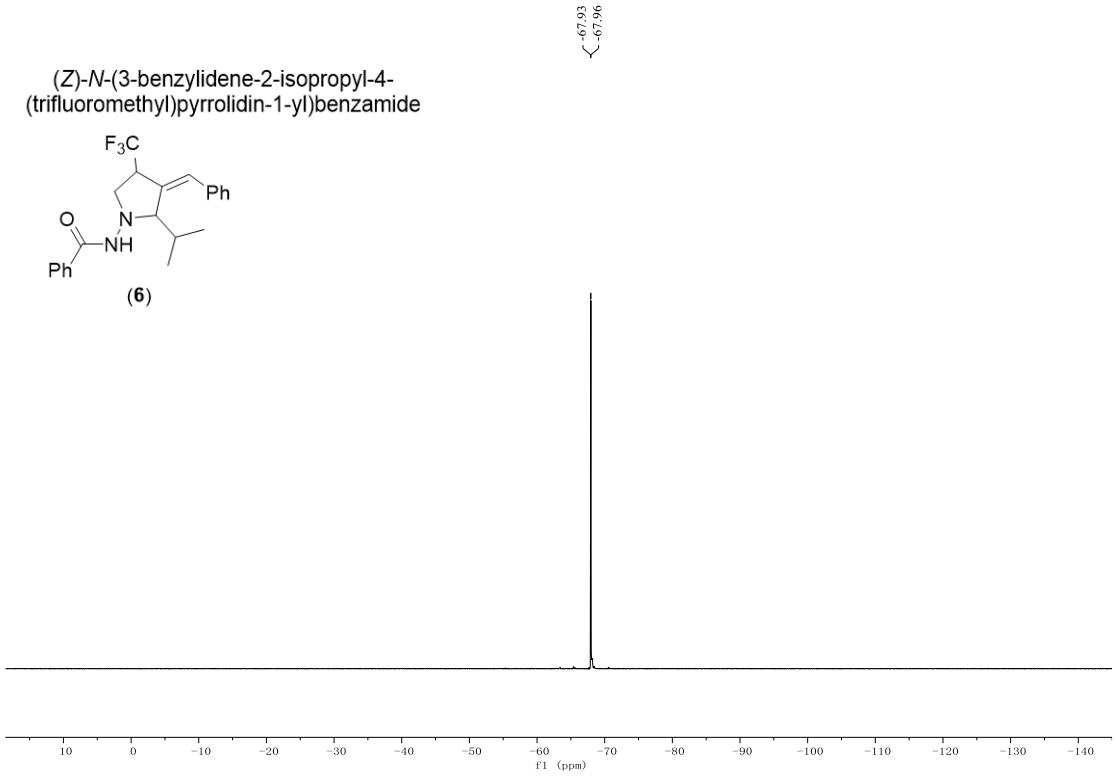
(**3gi**)

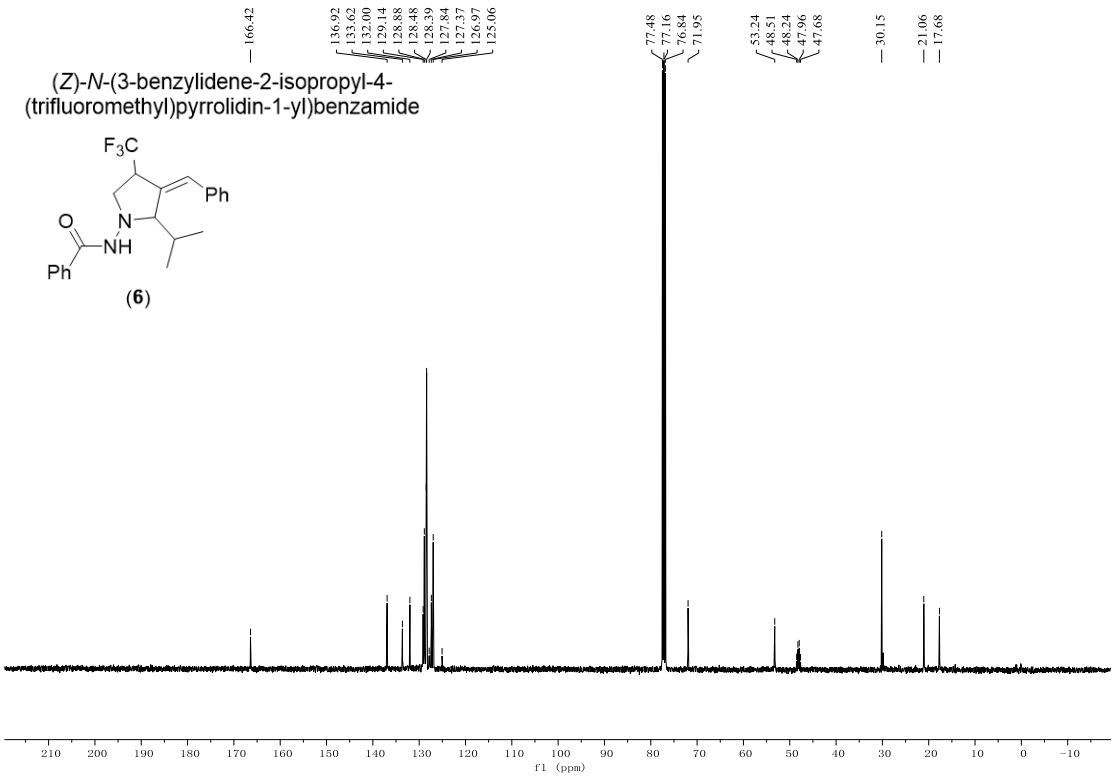
(*E*)-5-(2-benzoylhydrazinyl)-6-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)hept-3-en-1-yl 4-methylbenzenesulfonate



(**3gi**)


7.72
7.70
7.61
7.54
7.52
7.50
7.45
7.43
7.41
7.33
7.32
7.30
7.29
7.27
7.26
7.24
7.22
7.21
6.80
4.57
3.80
3.76
3.74
3.72
3.55
3.53
3.52
3.51
3.49
1.88
1.87
1.85
1.83
1.82
0.88
0.87
0.84
0.82
0.00
(Z)-N-(3-benzylidene-2-isopropyl-4-(trifluoromethyl)pyrrolidin-1-yl)benzamide
F3C
Ph
O
N
NH
Ph
(6)
2.00
0.95
1.02
2.03
2.00
3.00
1.00
0.95
2.00
1.05
1.00
3.00
3.00
f1 (ppm)


-67.93
-67.96
(Z)-N-(3-benzylidene-2-isopropyl-4-(trifluoromethyl)pyrrolidin-1-yl)benzamide
F3C
Ph
O
N
NH
Ph
(6)
f1 (ppm)



4. References.

1. (a) S. Kobayashi, R. Hirabayashi, *J. Am. Chem. Soc*., 1999, **121**, 6942–6943. (b) M. Rueping, M. Sudan Maji, H. Bas, P. Küçük, and I. Atodiresei, *Angew. Chem. Int. Ed*., 2012, **51**, 12864–12868; *Angew. Chem*. 2012, **124**, 13036–13040.
2. C. Yang, Z.-L. Liu, D.-T. Dai, Q. Li, W.-W. Ma, M. Zhao and Y.-H. Xu, *Org. Lett.*, 2020, **22**, 1360−1367.