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Supporting Information

Catalytic Asymmetric Intermolecular Radical Aminotrifluoromethylation of Alkenes with Hydrazines by Cu(I)/CPA Cooperative Catalysis

Zhe Wang⁺, Jiang-Tao Cheng⁺, Zhichao Shi, Na Wang, Feng Zhan, Sheng-Peng Jiang, Jin-Shun Lin,^{*} Yuyang Jiang,^{*} and Xin-Yuan Liu^{*}

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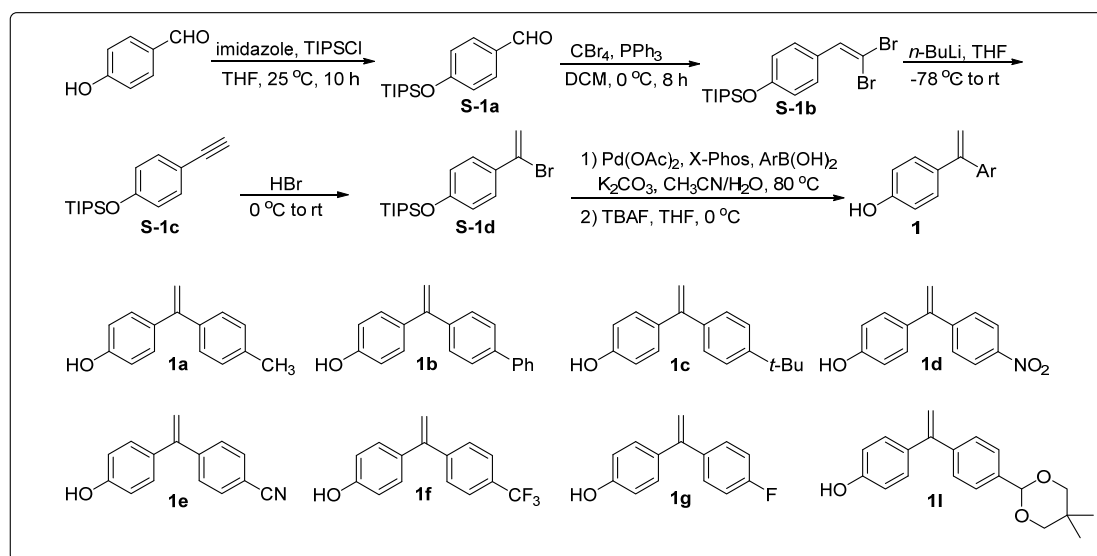
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General information

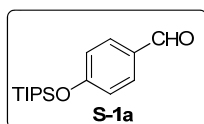
Most of reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuI was purchased from Sigma-Aldrich. Chiral phosphoric acid (CPA) was purchased from Daicel Chiral Technologies (China). Commercial solvents were used without further purification with the following exceptions: CH₂Cl₂ was freshly distilled from CaH₂. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on Bruker 400 MHz spectrometer at 400 MHz for ¹H NMR, 101 MHz for ¹³C NMR and 376 MHz for ¹⁹F NMR in CDCl₃, or CD₃OD with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectral analysis (HRMS) data were obtained using AB SCIEX QSTAR Elite. Enantiomeric excess (ee) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (λ = 254 or 214 nm). Column conditions are reported in the experimental section below. Circular dichroism (CD) spectra were recorded on an Applied PhotoPhysics Chirascan CD spectropolarimeter, using a 10 mm quartz cuvette.

General procedures for the synthesis of substrates:

General synthesis of substrates 1a-1g, 1l



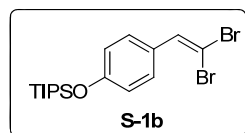
1a-1g, 1l were synthesized according to the procedures previously reported.^[1]



4-((triisopropylsilyloxy)benzaldehyde (S-1a)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.87 (s, 1H), 7.78 (d, $J = 8.6$ Hz, 2H), 6.97 (d, $J = 8.6$ Hz, 2H), 1.33-1.24 (m, 3H), 1.10 (d, $J = 7.4$ Hz, 18H).

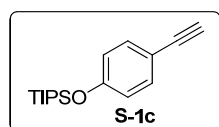
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 190.9, 161.9, 132.0, 130.2, 120.3, 17.9, 12.7.



(4-(2,2-dibromovinyl)phenoxy)triisopropylsilane (S-1b)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.0$ Hz, 2H), 7.39 (s, 1H), 6.86 (d, $J = 7.9$ Hz, 2H), 1.35-1.20 (m, 3H), 1.10 (t, $J = 6.0$ Hz, 18H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.5, 136.4, 129.9, 128.1, 119.8, 87.0, 17.9, 12.7.

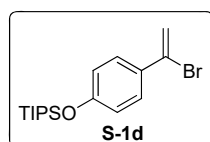


(4-ethynylphenoxy)triisopropylsilane (S-1c)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 2.97 (s, 1H), 1.24 (m, 3H), 1.09 (d, $J = 7.4$ Hz, 18H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.8, 133.6, 120.0, 114.6, 83.8,

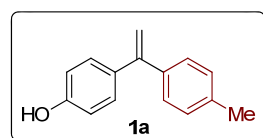
75.8, 17.9, 12.7.



(4-(1-bromovinyl)phenoxy)triisopropylsilane (S-1d)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (d, $J = 8.7$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.01 (d, $J = 2.0$ Hz, 1H), 5.66 (d, $J = 2.0$ Hz, 1H), 1.34-1.17 (m, 3H), 1.10 (d, $J = 7.3$ Hz, 18H).

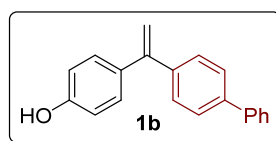
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.1, 131.3, 130.9, 128.6, 119.5, 115.8, 17.9, 12.7.



4-(1-(*p*-tolyl)vinyl)phenol (1a)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36-7.25 (m, 4H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.91-6.83 (m, 2H), 5.39 (dd, $J = 5.3, 1.3$ Hz, 2H), 2.43 (s, 3H).

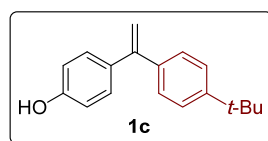
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.6, 149.4, 139.0, 137.5, 134.2, 129.7, 128.9, 128.3, 115.1, 112.3, 21.2.



4-(1-([1,1'-biphenyl]-4-yl)vinyl)phenol (1b)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.47-7.32 (m, 4H), 7.23 (t, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 7.7$ Hz, 2H), 6.82 (dd, $J = 11.4, 2.1$ Hz, 2H), 5.49 (d, $J = 13.4$ Hz, 2H), 4.89 (s, 1H).

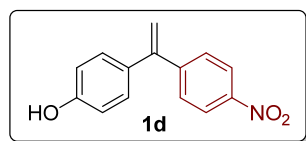
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.4, 149.2, 143.2, 140.7, 140.6, 140.2, 129.5, 128.8, 127.4, 127.0, 121.0, 115.3, 114.7, 114.5.



4-(1-(4-*tert*-butylphenyl)vinyl)phenol (1c)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.1$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 5.99 (s, 1H), 5.44 (d, $J = 5.7$ Hz, 2H), 1.43 (s, 9H).

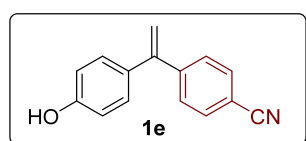
^{13}C NMR (101 MHz, CDCl_3) δ 155.2, 150.8, 149.3, 138.8, 134.5, 129.8, 128.0, 125.2, 115.1, 112.6, 34.7, 31.5.



4-(1-(4-nitrophenyl)vinyl)phenol (1d)

^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.8$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 5.55 (s, 1H), 5.47 (s, 1H).

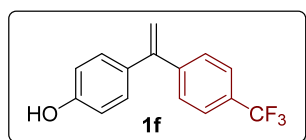
^{13}C NMR (101 MHz, CDCl_3) δ 155.9, 148.5, 147.8, 147.3, 132.8, 129.6, 129.1, 123.6, 115.9, 115.4.



4-(1-(4-cyanobenzene)vinyl)phenol (1e)

^1H NMR (400 MHz, CDCl_3) δ 7.66-7.59 (m, 2H), 7.47-7.40 (m, 2H), 7.20-7.12 (m, 2H), 6.86-6.78 (m, 2H), 5.51 (d, $J = 0.9$ Hz, 1H), 5.42 (d, $J = 0.9$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.0, 148.2, 146.6, 132.7, 132.1, 129.6, 129.0, 119.0, 115.4, 115.4, 111.1.

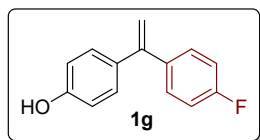


4-(1-(4-(trifluoromethyl)phenyl)vinyl)phenol (1f)

^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 6.91 (d, $J = 8.2$ Hz, 2H), 5.54 (s, 1H), 5.46 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.6, 148.4, 145.4, 133.4, 129.7, 128.7, 125.2 (q, $J = 3.7$ Hz), 124.3 (q, $J = 270.0$ Hz), 115.4, 114.6.

^{19}F NMR (376 MHz, CDCl_3) δ -62.3 (s, 3F).

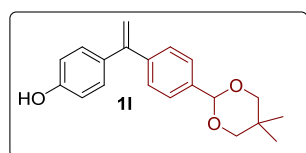


4-(1-(4-fluorophenyl)vinyl)phenol (1g)

^1H NMR (400 MHz, CDCl_3) δ 7.34-7.27 (m, 2H), 7.22-7.16 (m, 2H), 7.05-6.97 (m, 2H), 6.81-6.76 (m, 2H), 5.36 (d, $J = 1.2$ Hz, 1H), 5.30 (d, $J = 1.2$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.5 (d, $J = 246.4$ Hz), 155.6, 148.6, 137.9, 133.9, 130.0 (d, $J = 8.0$ Hz), 129.6, 115.2, 115.0 (d, $J = 21.4$ Hz), 112.9.

^{19}F NMR (376 MHz, CDCl_3) δ -114.8 (s, 1F).

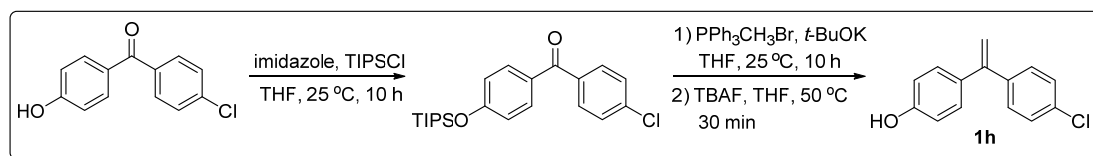


4-(1-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)vinyl)phenol (1i)

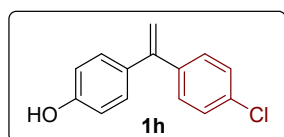
^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.6 (s, 1H), 7.4 (d, $J = 7.9$ Hz, 2H), 7.3 (d, $J = 8.0$ Hz, 2H), 7.1 – 7.0 (m, 2H), 6.8 – 6.7 (m, 2H), 5.4 (s, 1H), 5.4 (s, 1H), 5.3 (s, 1H), 3.6 (q, $J = 10.9$ Hz, 4H), 1.2 (s, 3H), 0.7 (s, 3H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 157.9, 149.2, 142.2, 138.6, 131.8, 129.5, 128.1, 126.6, 115.6, 113.0, 101.0, 77.0, 23.2, 21.9.

General synthesis of substrate 1h



1h was synthesized according to the procedures previously reported.^[2]

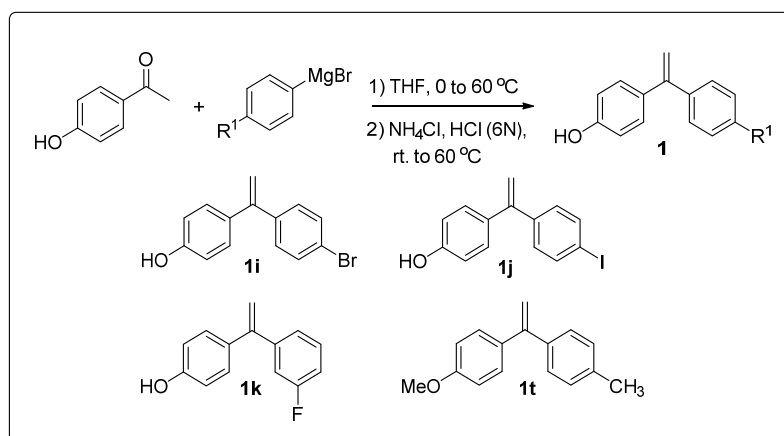


4-(1-(4-chlorophenyl)vinyl)phenol (**1h**)

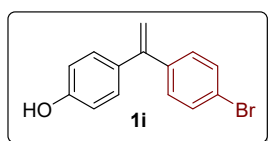
¹H NMR (400 MHz, CDCl₃) δ 7.32-7.26 (m, 4H), 7.23-7.17 (m, 2H), 6.83-6.76 (m, 2H), 5.39 (d, *J* = 1.1 Hz, 1H), 5.33 (d, *J* = 1.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 155.6, 148.5, 140.3, 133.7, 133.6, 129.7, 129.7, 128.4, 115.3, 113.5.

General synthesis of substrates 1i-1k, 1t



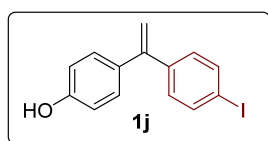
1i-1k, 1t were synthesized according to the procedures previously reported.^[3]



4-(1-(4-bromophenyl)vinyl)phenol (**1i**)

¹H NMR (400 MHz, CDCl₃) δ 7.48-7.42 (m, 2H), 7.20 (m, 4H), 6.82-6.77 (m, 2H), 5.39 (d, *J* = 1.1 Hz, 1H), 5.34 (d, *J* = 1.1 Hz, 1H).

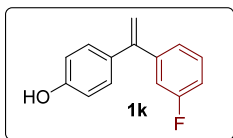
¹³C NMR (101 MHz, CDCl₃) δ 155.5, 148.5, 140.8, 133.7, 131.3, 130.0, 129.6, 121.8, 115.2, 113.5.



4-(1-(4-iodophenyl)vinyl)phenol (**1j**)

¹H NMR (400 MHz, CDCl₃) δ 7.47-7.42 (m, 2H), 7.23-7.17 (m, 4H), 6.82-6.77 (m, 2H), 5.39 (d, *J* = 1.1 Hz, 1H), 5.33 (d, *J* = 1.1 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 163.95, 161.52, 155.68, 148.50, 133.47, 129.64, 129.57, 124.05, 115.17, 113.84

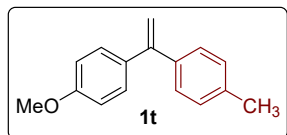


4-(1-(3-fluorophenyl)vinyl)phenol (1k)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32-7.27 (m, 1H), 7.24-7.18 (m, 2H), 7.12 (m, 1H), 7.07-6.97 (m, 2H), 6.83-6.78 (m, 2H), 5.41 (d, $J = 1.2$ Hz, 1H), 5.37 (d, $J = 1.1$ Hz, 1H), 4.85 (s, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.7 (d, $J = 245.4$ Hz), 155.5, 148.5 (d, $J = 2.2$ Hz), 144.1 (d, $J = 7.4$ Hz), 133.6, 129.7, 129.6, 124.0 (d, $J = 2.9$ Hz), 115.2 (d, $J = 21.8$ Hz), 115.1, 114.5 (d, $J = 21.2$ Hz), 113.9.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -113.7.

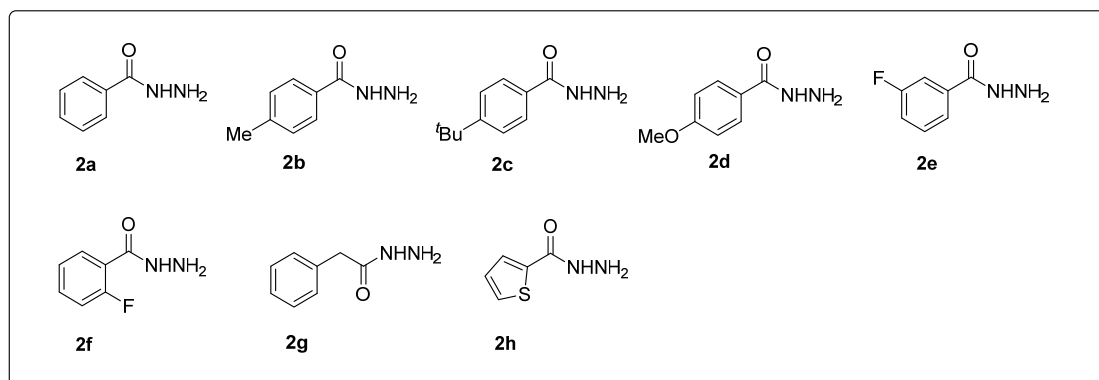


1-methoxy-4-(1-(p-tolyl)vinyl)benzene (1t)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.32-7.22 (m, 4H), 7.15 (d, $J = 8.2$ Hz, 2H), 6.90-6.84 (m, 2H), 5.34 (dd, $J = 6.0, 1.4$ Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).

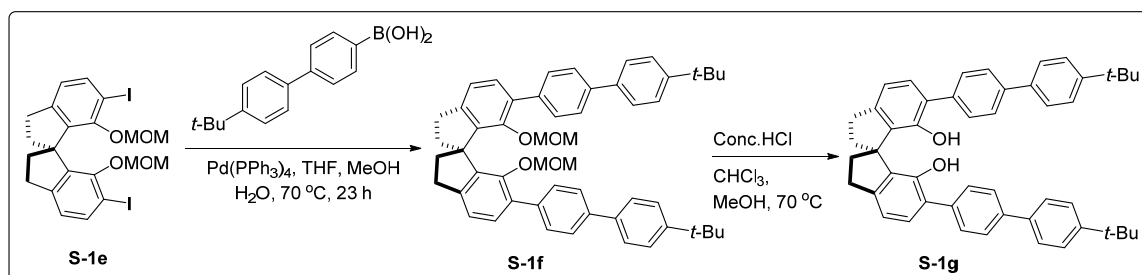
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.3, 149.4, 139.0, 137.5, 134.2, 129.5, 128.9, 128.3, 113.5, 112.4, 55.4, 21.2.

Substituted hydrazines were purchased at the highest commercial quality.



Synthesis of the catalyst (S)-A4

(S)-6,6'-bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diol (S-1f)



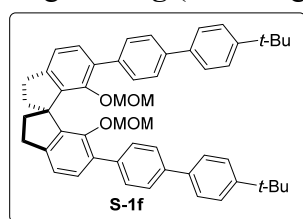
S-1e was synthesized according to the procedures previously reported.^[4]

(S)-6,6'-bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-7,7'-bis(methoxymethoxy)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (S-1f)

S-1e (296 mg, 0.5 mmol), 4'-(*tert*-butyl)-[1,1'-biphenyl]-4-ylboronic acid (381.2 mg, 1.5 mmol, 3 equiv.), K₂CO₃ (414 mg, 3 mmol, 6 equiv.), THF (10 mL), MeOH (0.4 mL) and H₂O (1 mL) were added into an oven-dried resealable Schlenk tube (100 ml) under argon atmosphere. The resulting solution was degassed for 10 minutes, and Pd(PPh₃)₄ (86.67 mg, 0.075 mmol) was added under argon atmosphere. Then the resulting mixture was degassed for 10 minutes and the reaction mixture was heated at 70 °C for 23 h. Upon cooling to room temperature, the resulting mixture was extracted with CH₂Cl₂ (3 times). The combined organic layers were brined, dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (silica gel, eluent: *n*-hexane/ethyl acetate = 100/0-20/1) to give **S-1f** (290.0 mg, 0.38 mmol, 77% yield) as a white solid.

(S)-6,6'-bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diol (S-1g)

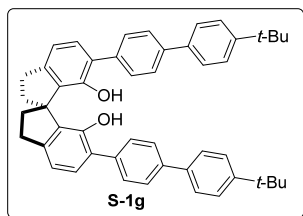
A solution of **S-1f** (290 mg, 0.38 mmol) in a mixture of CHCl₃ (2 mL) and MeOH (3 mL) was treated with conc. HCl (2 mL) and heated to 70 °C for 3 h. After cooling to room temperature, saturated NaHCO₃ solution was added, the layers were separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄ and evaporated to dryness. The resulting residue was purified by flash column chromatography (silica gel, eluent: *n*-hexane/ethyl acetate = 100/0-20/1) to give **S-1g** (210.8 mg, 0.32 mmol, 83% yield) as a white solid.



(S)-6,6'-bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-7,7'-bis(methoxymethoxy)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (S-1f)

¹H NMR (400 MHz, CDCl₃) δ 7.64-7.55 (m, 12H), 7.50-7.45 (m, 4H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H),

4.43 (d, $J = 5.3$ Hz, 2H), 4.29 (d, $J = 5.4$ Hz, 2H), 3.10 (dd, $J = 9.5, 5.2$ Hz, 4H), 2.74 (s, 6H), 2.64-2.52 (m, 2H), 2.39-2.26 (m, 2H), 1.36 (s, 18H)
 ^{13}C NMR (101 MHz, CDCl_3) δ 151.9, 150.3, 145.4, 142.6, 139.4, 138.7, 137.9, 132.7, 130.4, 129.5, 126.9, 126.7, 125.8, 120.3, 98.6, 60.1, 56.4, 39.4, 34.6, 31.4, 31.3.
 HRMS (ESI) m/z calcd. for $\text{C}_{53}\text{H}_{56}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 779.4077, found 779.4074.



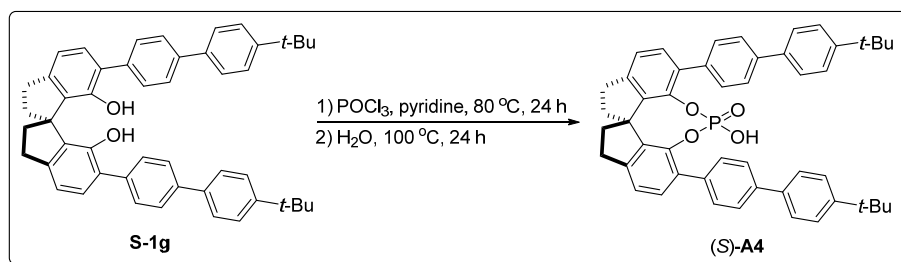
(S)-6,6'-bis(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-7,7'-bis(methoxymethoxy)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (S-1g)

^1H NMR (400 MHz, CDCl_3) δ 7.65-7.59 (m, 4H), 7.58-7.52 (m, 8H), 7.49-7.42 (m, 4H), 7.27-7.22 (m, 2H), 6.96 (d, $J = 7.7$ Hz, 2H), 5.13 (s, 2H), 3.19-3.01 (m, 4H), 2.49-2.34 (m,

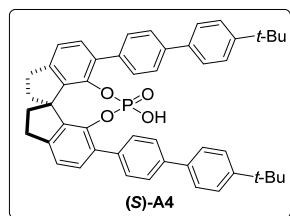
4H), 1.36 (s, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.4, 149.7, 145.4, 140.0, 138.0, 136.3, 132.1, 130.7, 129.7, 127.3, 126.8, 126.7, 125.9, 117.7, 58.5, 37.9, 34.7, 31.5, 31.3.

HRMS (ESI) m/z calcd. for $\text{C}_{49}\text{H}_{48}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 691.3552, found 691.3544.



Chiral Phosphoric Acid (S)-A4. **S-1g** (210.8 mg, 0.32 mmol) was suspended in 3.2 mL of pyridine and treated with 0.32 mL of freshly distilled POCl_3 . The resulting solution was stirred at 80 °C for 24 h. After cooling to room temperature, H_2O (0.3 mL) was added carefully and the resulting mixture was heated to 100 °C for 24 h. The reaction mixture was acidified with HCl (2 N) and extracted with DCM for three times. The combined organic layers were washed with 2 N HCl for two times, dried over anhydrous Na_2SO_4 , filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (silica gel, eluted with $\text{CH}_2\text{Cl}_2/\text{MeOH} = 100/1-20/1$) to give the product as a white solid in 75% yield (197.2 mg, 0.24 mmol).



1,10-bis(4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)-12-hydroxy-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7']fg[1,3,2]dioxaphosphocine 12-oxide

^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.92$ Hz, 4H), 7.29 (d, $J = 7.65$ Hz, 2H), 7.23 (d, $J = 8.11$ Hz, 4H), 7.18 (dd, $J = 9.72, 7.84$ Hz, 6H), 7.11 (d, $J = 8.08$ Hz, 4H), 3.21-3.06 (m,

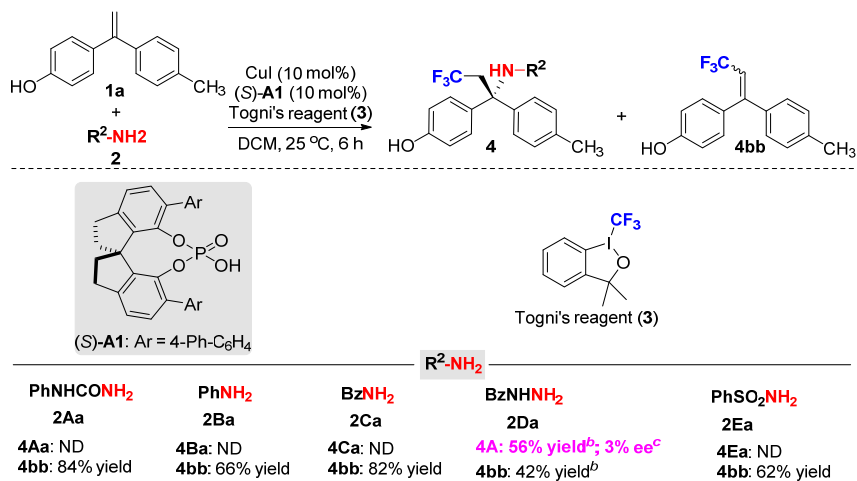
2H), 2.93 (dd, $J = 16.10, 7.70$ Hz, 2H), 2.33 (dd, $J = 12.13, 6.22$ Hz, 2H), 2.24-2.11 (m, 2H), 1.30 (s, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.7, 145.2, 140.7, 139.6, 138.0, 136.6, 134.1, 130.3, 129.7, 127.0, 126.9, 125.3, 122.6, 60.1, 38.6, 34.4, 31.4, 30.4.

^{31}P NMR (162 MHz, CDCl_3) δ -7.5(s, 1P).

HRMS (ESI) m/z calcd. for $\text{C}_{49}\text{H}_{47}\text{O}_4\text{NaP}$ $[\text{M}+\text{Na}]^+$ 753.3110, found 753.3104.

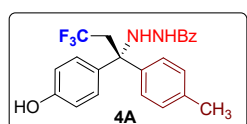
Evaluation of different nitrogen-based nucleophiles with alkenes in the presence of a dual CuI and chiral phosphoric acid catalytic system



^aReaction conditions: **1a** (0.05 mmol), **2** (0.05 mmol), Togni's reagent (0.05 mmol), CuI (10 mol%), CPA (10 mol%), DCM (1.0 mL) under argon. ^b Isolated yield. ^cEe value on HPLC.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 1,1-diaryllalkene substrate **1a** (0.05 mmol, 1.0 equiv.), nucleophiles **2** (0.05 mmol, 1.0 equiv.), Togni's reagent (16.5 mg, 0.05 mmol, 1.0 equiv.), CuI (1 mg, 0.005 mmol, 10 mol%), chiral phosphoric acid ((S)-A1 (3.7 mg, 0.005 mmol, 10 mol%), anhydrous DCM (1.0 mL) at 25 °C, then the sealed tube was stirred at 25 °C for 6 h. Upon completion (monitored by TLC), CH_2Br_2 (internal standard, 0.05 mmol, 1.0 equiv.) was added to the reaction mixture (Yield based on ^1H NMR of the crude product). The reaction mixture was directly purified by a silica gel chromatography (eluent: petroleum ether/ethyl acetate = 10/1-2/1, using petroleum ether (100%) to remove the solvent (CH_2Cl_2) at first) to afford the desired product **4Da**.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use.



(R)-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(p-tolyl)propyl)benzohydrazide (**4A**)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 2/1) to afford desired product **4A** (11.5 mg, 56 %) as a yellow solid.

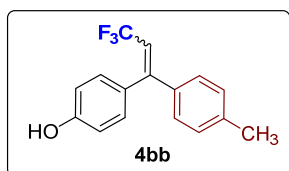
HPLC analysis: Chiralcel IA3(hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 230 nm), t_R (minor) = 16.75 min, t_R (major) = 20.95 min.

^1H NMR (400 MHz, MeOD) δ 7.49-7.42 (m, 3H), 7.33 (dd, J = 25.2, 7.7 Hz, 4H), 7.21 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 6.71 (d, J = 8.2 Hz, 2H), 3.42-3.22 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, MeOD) δ 167.9, 156.4, 139.9, 136.8, 133.5, 133.0, 131.3, 129.0, 128.1, 128.0, 127.7, 127.0, 126.7 (q, $J = 278.7$ Hz), 114.2, 65.6, 41.0 (q, $J = 26.0$ Hz), 19.7.

^{19}F NMR (376 MHz, MeOD) δ -59.3.

HRMS (ESI) m/z calcd. for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_2\text{F}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 437.1453, found 437.1445.



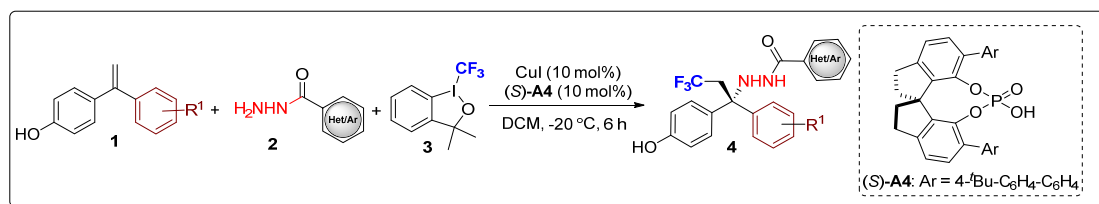
4-(3,3,3-trifluoro-1-(*p*-tolyl)prop-1-en-1-yl)phenol (4bb)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 2/1) to afford desired product **4bb** (6.1 mg, 44 %) as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 7.9$ Hz, 2H), 7.17-7.09 (m, 4H), 6.80-6.73 (m, 2H), 6.01 (q, $J = 8.4$ Hz, 1H), 5.03 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.7, 138.3, 134.6, 133.1, 129.7, 129.1 (q, $J = 2.0$ Hz), 128.7, 122.0 (q, $J = 271.5$ Hz), 115.3, 113.4 (q, $J = 33.6$ Hz), 21.3.

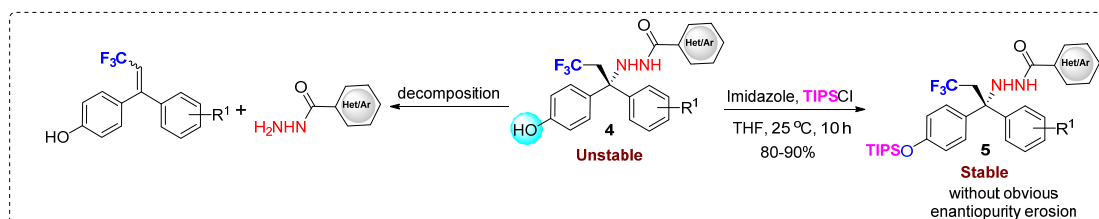
^{19}F NMR (376 MHz, CDCl_3) δ -55.1.



General procedure for direct asymmetric intermolecular three-component radical-initiated aminotrifluoromethylation of alkenes

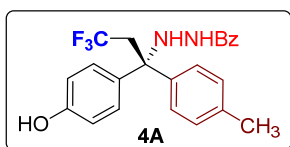
Under argon, an oven-dried Schlenk tube (25mL) equipped with a magnetic stir bar was charged with 1,1-diaryllalkene substrate **1** (0.1 mmol, 1.0 equiv.), substituted hydrazines (0.1 mmol, 1.0 equiv.), CuI (1.9 mg, 0.01 mmol, 10 mol%), chiral phosphoric acid ((*S*)-**A4** (7.4 mg, 0.01 mmol, 10 mol%), Togni's reagent **3** (33.0 mg, 0.1 mmol, 1.0 equiv.) and anhydrous DCM (4.0 mL) at 0 °C, then the sealed tube was stirred at -20 °C for 6 h. Upon completion (monitored by TLC), the reaction mixture was directly purified by a silica gel chromatography [eluent: *n*-hexane/ethyl acetate = 10/1-2/1, using *n*-hexane (100 %) to remove the solvent (DCM) at first] to afford the desired product **4**.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use. The ee value of the products were greatly affected by the size of Schlenk tube largely due to their poor solubility in DCM.



The products **4** bearing a hydroxy group tend to decompose *via* a β -hydride elimination process after they were isolated. Considering the inherent instability of the products **4**, they should be converted to **5** ASAP without the erosion of enantioselectivity after the yield and ee value of **4** were determined.

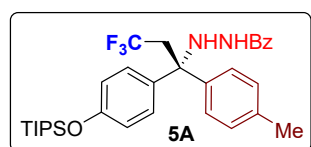
Under argon, an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **4** (0.06 mmol, 1.0 equiv.), imidazole (0.15 mmol, 2.5 equiv.), TIPSCl (0.075 mmol, 1.25 equiv.) and anhydrous THF (1.0 mL), then the sealed tube was stirred at 25 °C for 10 h. Upon completion (monitored by TLC), the reaction mixture was directly purified by a silica gel chromatography [eluent: *n*-hexane/ethyl acetate = 20/0-5/1, using *n*-hexane (100 %) to remove the solvent (THF) at first] to afford the desired product **5**.



(R)-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(p-tolyl)propyl)benzohydrazide (4A)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4A** (38.5 mg, 93 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 17.82 min, t_R (minor) = 22.10 min.



(R)-N'-(3,3,3-trifluoro-1-(p-tolyl)-1-(4-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5A)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5A** as sticky colorless oil.

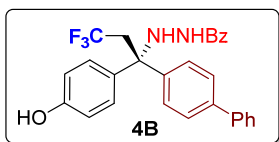
HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 90/10, flow rate 0.4 mL/min, λ = 260 nm), t_R (minor) = 22.08 min, t_R (major) = 26.42 min.

¹H NMR (400 MHz, CDCl₃) δ 7.51-7.42 (m, 3H), 7.39-7.32 (m, 2H), 7.29-7.19 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 6.86-6.80 (m, 2H), 5.97 (s, 1H), 3.20 (q, J = 10.4 Hz, 2H), 2.34 (s, 3H), 1.26-1.18 (m, 3H), 1.07 (d, J = 7.3 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 165.4, 154.4, 138.4, 136.2, 133.8, 131.5, 130.8, 127.8, 127.6, 126.4, 125.7, 124.9 (q, J = 276.8 Hz), 118.6, 64.5, 40.3 (q, J = 25.9 Hz), 20.0, 16.8, 11.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.1.

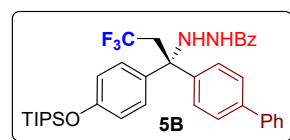
HRMS (ESI) m/z calcd. for C₃₂H₄₁N₂O₂F₃NaSi [M+Na]⁺ 593.2787, found 593.2781.



(R)-N'-(1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoro-1-(4-hydroxyphenyl)propyl)benzohydrazide (4B)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4B** (45.2 mg, 95 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 13.06 min, t_R (minor) = 21.02 min.



(R)-N'-(1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoro-1-(4-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5B)

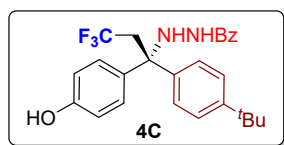
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5B** as sticky colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.64-7.56 (m, 4H), 7.53-7.42 (m, 7H), 7.35 (t, J = 7.5 Hz, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 7.2 Hz, 1H), 6.91-6.85 (m, 2H), 6.07 (d, J = 7.5 Hz, 1H), 3.28 (q, J = 10.4 Hz, 2H), 1.31-1.20 (m, 3H), 1.09 (d, J = 7.4 Hz, 18H)

¹³C NMR (101 MHz, CDCl₃) δ 166.6, 155.6, 141.6, 140.4, 140.3, 134.7, 132.6, 131.9, 129.0, 128.8, 128.7, 128.1, 127.5, 127.1, 126.8, 126.7, 125.9 (q, J = 278.5 Hz), 119.7, 65.8, 41.5 (q, J = 26.0 Hz), 17.9, 12.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -57.9.

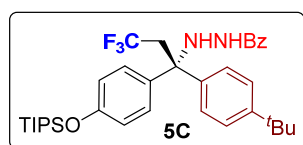
HRMS (ESI) m/z calcd. for $C_{37}H_{43}F_3N_2O_2NaSi$ $[M+Na]^+$ 655.2944, found 655.2926.



(R)-N'-(1-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoro-1-(4-hydroxyphenyl)propyl)benzohydrazide (4C)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4C** (43.3 mg, 95 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 230 nm), t_R (major) = 9.10 min, t_R (minor) = 10.63 min.



(R)-N'-(1-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoro-1-((triisopropylsilyloxy)phenyl)propyl)-benzohydrazide (5C)

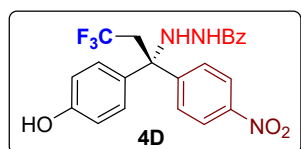
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5C** as sticky colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.42 (m, 3H), 7.37-7.31 (m, 4H), 7.29 (d, J = 8.6 Hz, 2H), 7.26-7.23 (m, 2H), 6.90 (d, J = 7.5 Hz, 1H), 6.87-6.80 (m, 2H), 5.97 (d, J = 7.6 Hz, 1H), 3.21 (q, J = 10.4 Hz, 2H), 1.31 (s, 9H), 1.26-1.19 (m, 3H), 1.07 (d, J = 7.3 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 155.5, 150.5, 139.2, 134.7, 132.8, 131.7, 129.0, 128.6, 127.3, 126.8, 125.9 (q, J = 279.4 Hz), 125.1, 119.6, 65.8, 41.7 (q, J = 26.2 Hz), 34.5, 31.3, 17.9, 12.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.0.

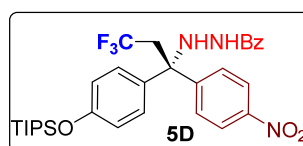
HRMS (ESI) m/z calcd. for $C_{35}H_{47}F_3N_2O_2NaSi$ $[M+Na]^+$ 635.3257, found 635.3253.



(R)-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)benzohydrazide (4D)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4D** (41.8 mg, 94 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 11.15 min, t_R (minor) = 25.79 min.



(R)-N'-(3,3,3-trifluoro-1-(4-nitrophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)-benzohydrazide (5D)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5D** as a colorless solid.

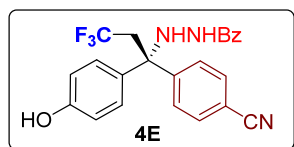
1H NMR (400 MHz, $CDCl_3$) δ 8.21-8.14 (m, 2H), 7.63-7.55 (m, 2H), 7.49 (dd, J = 8.0, 5.9 Hz, 3H), 7.37 (t, J = 7.6 Hz, 2H), 7.21-7.12 (m, 2H), 6.97 (d, J = 7.2 Hz, 1H), 6.91-6.84 (m, 2H), 6.04 (d, J = 7.4 Hz, 1H), 3.27 (q, J = 10.1 Hz, 2H), 1.28-1.15 (m, 3H), 1.06 (d, J = 7.3 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 156.0, 150.0, 147.1, 133.7, 132.2, 131.9, 128.7, 128.7, 128.6, 126.8, 125.6 (q, J = 276.8 Hz), 123.2, 120.0, 65.8, 41.2 (q, J = 27.9 Hz),

17.8, 12.6.

^{19}F NMR (376 MHz, CDCl_3) δ -58.1.

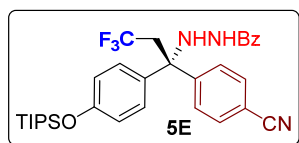
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{38}\text{F}_3\text{N}_4\text{O}_3\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 624.2482, found 624.2472.



(R)-N'-(1-(4-cyanophenyl)-3,3,3-trifluoro-1-(4-hydroxyphenyl)propyl)benzohydrazide (4E)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4E** (38.3 mg, 90 %) as a yellow solid.

HPLC analysis: Chiralcel IA3(hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 260 nm), t_R (major) = 13.98 min, t_R (minor) = 31.85 min.



(R)-N'-(1-(4-cyanophenyl)-3,3,3-trifluoro-1-((triisopropylsilyloxy)phenyl)propyl)-benzohydrazide (5E)

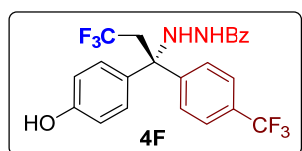
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5E** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.65-7.58 (m, 2H), 7.56-7.43 (m, 5H), 7.37 (dd, J = 8.4, 7.0 Hz, 2H), 7.21-7.11 (m, 2H), 6.95 (s, 1H), 6.90-6.76 (m, 2H), 6.01 (s, 1H), 3.23 (q, J = 10.2 Hz, 2H), 1.28-1.17 (m, 3H), 1.06 (d, J = 7.3 Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 156.0, 148.1, 133.8, 132.2, 132.1, 131.8, 128.8, 128.8, 128.5, 126.8, 125.6 (q, J = 276.7 Hz), 120.0, 118.6, 111.6, 65.9, 41.3 (q, J = 26.2 Hz), 17.9, 12.6.

^{19}F NMR (376 MHz, CDCl_3) δ -58.1.

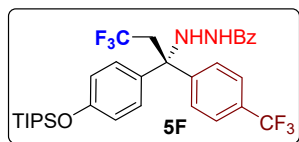
HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{38}\text{F}_3\text{N}_3\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 604.2583, found 604.2578.



(R)-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-(trifluoromethyl)phenyl)propyl)benzohydrazide (4F)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10:1 to 2:1) to afford desired product **4F** (44.5 mg, 95 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 9.96 min, t_R (minor) = 17.56 min.



(R)-N'-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)-1-(4-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5F)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5F** as colorless oil.

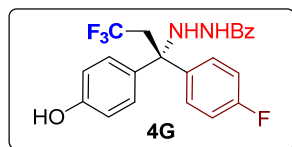
^1H NMR (400 MHz, CDCl_3) δ 7.56 (q, J = 8.5 Hz, 4H), 7.50-7.42 (m, 3H), 7.33 (t, J = 7.6 Hz, 2H), 7.20 (dd, J = 10.2, 7.0 Hz, 3H), 6.91-6.84 (m, 2H), 6.04 (d, J = 7.1 Hz, 1H), 3.39-3.12 (m, 2H), 1.30-1.19 (m, 3H), 1.09 (d, J = 7.5 Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 155.9, 146.7, 134.2, 132.3, 132.0, 129.7 (q, J =

32.5 Hz), 128.9, 128.7, 128.2, 126.8, 125.8 (q, $J = 279.6$ Hz), 126.8, 125.0 (q, $J = 3.8$ Hz), 124.0 (q, $J = 273.1$ Hz), 119.9, 65.8, 41.4 (q, $J = 26.4$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.0, -62.5.

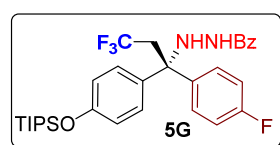
HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{38}\text{F}_6\text{N}_2\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 647.2505, found 604.2501.



(R)-N'-(3,3,3-trifluoro-1-(4-fluorophenyl)-1-(4-hydroxyphenyl)propyl)benzohydrazide (4G)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4G** (33.0 mg, 79 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 11.59 min, t_R (minor) = 21.55 min.



(R)-N'-(3,3,3-trifluoro-1-(4-(triisopropylsilyloxy)phenyl)-1-(4-(trifluoromethyl)phenyl)propyl)benzohydrazide (5G)

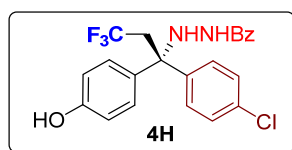
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5G** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.52-7.44 (m, 3H), 7.40-7.31 (m, 4H), 7.23-7.17 (m, 2H), 7.01 (t, $J = 8.7$ Hz, 2H), 6.96 (s, 1H), 6.88-6.81 (m, 2H), 5.95 (br s, 1H), 3.28-3.09 (m, 2H), 1.27-1.19 (m, 3H), 1.07 (d, $J = 7.4$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 162.0 (d, $J = 247.2$ Hz), 155.7, 138.3, 134.6, 132.4, 131.9, 129.5 (d, $J = 8.0$ Hz), 128.9, 128.7, 126.8, 125.8 (q, $J = 278.4$ Hz), 119.8, 115.0 (d, $J = 21.3$ Hz), 65.5, 41.6 (q, $J = 26.0$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.2, -114.7.

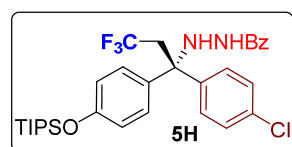
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{38}\text{F}_4\text{N}_2\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 597.2537, found 597.2531.



(R)-N'-(1-(4-chlorophenyl)-3,3,3-trifluoro-1-(4-hydroxyphenyl)propyl)benzohydrazide (4H)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4H** (41.2 mg, 95 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 230$ nm), t_R (major) = 11.64 min, t_R (minor) = 21.46 min.



(R)-N'-(1-(4-chlorophenyl)-3,3,3-trifluoro-1-(4-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5H)

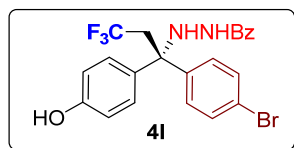
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5H** as colorless solid.

^1H NMR (400 MHz, CDCl_3) δ 7.51-7.43 (m, 3H), 7.40-7.26 (m, 6H), 7.23-7.14 (m, 2H), 6.97 (s, 1H), 6.89-6.81 (m, 2H), 5.96 (d, $J = 5.7$ Hz, 1H), 3.30-3.07 (m, 2H), 1.30-1.17 (m, 3H), 1.07 (d, $J = 7.3$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 155.8, 141.2, 134.4, 133.5, 132.4, 132.0, 129.1, 128.8, 128.7, 128.3, 126.8, 125.8 (q, $J = 278.4$ Hz), 119.8, 65.6, 41.4 (q, $J = 26.3$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.1.

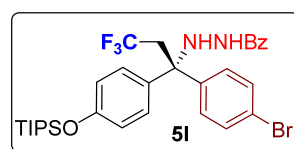
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{38}\text{F}_3\text{ClN}_2\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 613.2241, found 613.2234.



(R)-N'-(1-(4-bromophenyl)-3,3,3-trifluoro-1-(4-hydroxyphenyl)propyl)benzohydrazide (4I)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4I** (37.8 mg, 79 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 11.73 min, t_R (minor) = 21.98 min.



(R)-N'-(1-(4-bromophenyl)-3,3,3-trifluoro-1-(4-((triisopropylsilyl)oxy)phenyl)propyl)-benzohydrazide (5I)

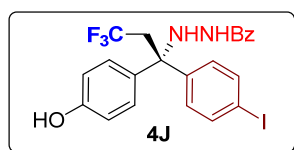
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5I** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.51-7.42 (m, 5H), 7.39-7.33 (m, 2H), 7.27 (dd, $J = 7.5$, 1.5 Hz, 2H), 7.24-7.15 (m, 2H), 6.92 (d, $J = 5.1$ Hz, 1H), 6.87-6.81 (m, 2H), 5.97 (d, $J = 7.5$ Hz, 1H), 3.31-3.05 (m, 2H), 1.27-1.19 (m, 3H), 1.07 (d, $J = 7.3$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 155.7, 141.7, 134.3, 132.3, 132.0, 131.2, 129.4, 128.8, 128.7, 126.8, 125.8 (q, $J = 279.4$ Hz), 121.7, 119.8, 65.5, 41.2 (q, $J = 26.3$ Hz), 17.9, 12.6.

^{19}F NMR (376 MHz, CDCl_3) δ -58.1.

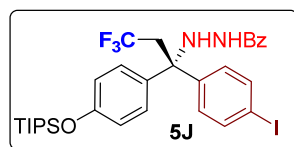
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{38}\text{F}_3\text{BrN}_2\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 657.1736, found 657.1722.



(R)-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-iodophenyl)propyl)benzohydrazide (4J)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4J** (50.0 mg, 95 %) as a yellow solid.

HPLC analysis: Chiralcel IE3 (hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, $\lambda = 260$ nm), t_R (major) = 24.79 min, t_R (minor) = 30.00 min.



(R)-N'-(3,3,3-trifluoro-1-(4-iodophenyl)-1-(4-((triisopropylsilyl)oxy)phenyl)propyl)benzohydrazide (5J)

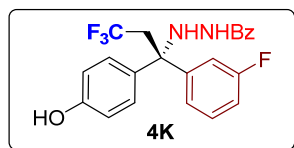
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5J** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.51-7.41 (m, 5H), 7.36 (dd, $J = 8.7$, 6.8 Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.20-7.15 (m, 2H), 6.92 (s, 1H), 6.87-6.79 (m, 2H), 5.98 (s, 1H), 3.28-3.07 (m, 2H), 1.28-1.18 (m, 3H), 1.07 (d, $J = 7.3$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 155.8, 141.7, 134.4, 132.4, 132.0, 131.2, 129.5, 128.8, 128.7, 126.8, 125.8 (q, $J = 279.4$ Hz), 121.7, 119.8, 65.6, 41.4 (q, $J = 26.5$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.1.

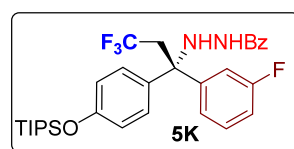
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{38}\text{F}_3\text{N}_2\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 705.1597, found 705.1588.



(R)-N'-(3,3,3-trifluoro-1-(3-fluorophenyl)-1-(4-hydroxyphenyl)propyl)benzohydrazide (4K)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10:1/to 2/1) to afford desired product **4K** (28.8 mg, 69 %) as a solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 11.34min, t_R (minor) = 14.48min.



(R)-N'-(3,3,3-trifluoro-1-(3-fluorophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5K)

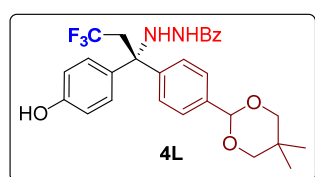
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5K** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.51-7.44 (m, 3H), 7.39-7.33 (m, 2H), 7.33-7.27 (m, 1H), 7.23-7.10 (m, 4H), 7.02-6.95 (m, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 6.88-6.82 (m, 2H), 5.98 (d, $J = 7.5$ Hz, 1H), 3.28-3.11 (m, 2H), 1.27-1.18 (m, 3H), 1.07 (d, $J = 7.4$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 162.6 (d, $J = 245.8$ Hz), 155.8, 145.4 (d, $J = 6.6$ Hz), 134.3, 132.4, 132.0, 129.6 (d, $J = 8.2$ Hz), 128.8, 128.7, 126.8, 125.8 (d, $J = 276.4$ Hz), 123.3 (d, $J = 2.8$ Hz), 119.8, 115.0 (d, $J = 23.2$ Hz), 114.6 (d, $J = 21.1$ Hz), 65.7, 41.4 (q, $J = 26.1$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.2, -112.5.

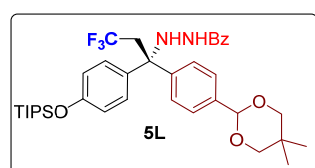
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{38}\text{F}_4\text{N}_2\text{O}_2\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 597.2591, found 597.2531.



(R)-N'-(1-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-3,3,3-trifluoro-1-(4-hydroxyphenyl)propyl)benzohydrazide (4L)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4L** (48.8 mg, 95 %) as a yellow solid.

HPLC analysis: Chiralcel IA3 (hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 12.46 min, t_R (minor) = 14.14 min.



(R)-N'-(1-(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-3,3,3-trifluoro-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5L)

The product was purified by silica gel flash column

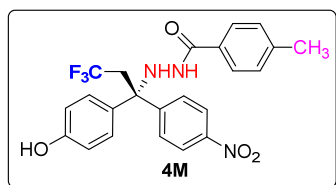
chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5L** as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.54-7.39 (m, 7H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.20-7.14 (m, 2H), 6.87 (s, 1H), 6.83-6.77 (m, 2H), 6.02 (br s, 1H), 5.40 (s, 1H), 3.78 (d, *J* = 11.2 Hz, 2H), 3.66 (d, *J* = 10.9 Hz, 2H), 3.31-3.10 (m, 2H), 1.30 (s, 3H), 1.27-1.18 (m, 3H), 1.06 (d, *J* = 7.3 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 166.5, 155.6, 143.2, 137.8, 134.7, 132.5, 131.8, 128.9, 128.6, 127.7, 126.8, 126.1, 125.8 (q, *J* = 278.5 Hz), 119.6, 101.5, 65.7, 41.4 (q, *J* = 26.5 Hz), 30.3, 23.1, 21.9, 17.9, 12.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.0.

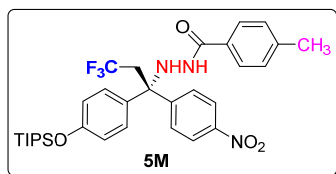
HRMS (ESI) *m/z* calcd. for C₃₇H₄₉F₃N₂O₄NaSi [M+Na]⁺ 693.3312, found 693.3307.



(R)-4-methyl-*N'*-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)benzohydrazide (4M)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4M** (43.6mg, 95%) as a yellow solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 260 nm), *t_R* (major) = 13.57 min, *t_R* (minor) = 23.86 min.



(R)-4-methyl-*N'*-(3,3,3-trifluoro-1-(4-nitrophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5M)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5M** as colorless oil.

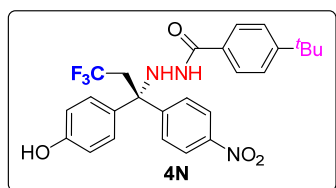
HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 260 nm), *t_R* (major) = 12.08 min, *t_R* (minor) = 15.98 min.

¹H NMR (400 MHz, CDCl₃) δ 8.19-8.10 (m, 2H), 7.62-7.54 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 4H), 7.00 (d, *J* = 5.7 Hz, 1H), 6.89-6.83 (m, 2H), 6.02 (d, *J* = 7.1 Hz, 1H), 3.35-3.13 (m, 2H), 2.36 (s, 3H), 1.27-1.19 (m, 3H), 1.07 (d, *J* = 7.3 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 167.2, 156.0, 150.2, 147.1, 142.8, 133.8, 129.4, 129.2, 128.8, 128.7, 126.8, 125.6 (q, *J* = 279.6 Hz), 123.1, 120.0, 65.8, 41.3 (q, *J* = 26.5 Hz), 21.5, 17.9, 12.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.1.

HRMS (ESI) *m/z* calcd. for C₃₂H₄₀F₃N₃O₄NaSi [M+Na]⁺ 638.2638, found 638.2628.

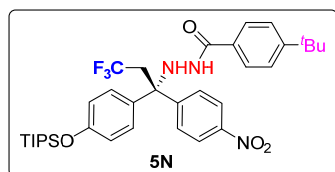


(R)-4-(*tert*-butyl)-*N'*-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)benzohydrazide (4N)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4N** (45.1 mg, 90%) as a yellow

solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 260 nm), t_R (major) = 12.88 min, t_R (minor) = 24.19 min.



(R)-4-(tert-butyl)-N'-(3,3,3-trifluoro-1-(4-nitrophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5N)

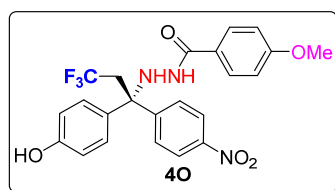
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5N** as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.19-8.14 (m, 2H), 7.62-7.56 (m, 2H), 7.46-7.40 (m, 2H), 7.40-7.34 (m, 2H), 7.19-7.12 (m, 2H), 6.94 (s, 1H), 6.89-6.83 (m, 2H), 6.03 (s, 1H), 3.37-3.13 (m, 2H), 1.30 (s, 9H), 1.27-1.17 (m, 3H), 1.07 (d, J = 7.3 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 167.1, 156.0, 155.9, 150.2, 147.2, 133.8, 129.2, 128.8, 128.7, 126.7, 125.7, 125.6 (q, J = 278.5 Hz), 123.2, 120.0, 65.9, 41.3 (q, J = 26.5 Hz), 35.0, 31.1, 17.9, 12.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.10.

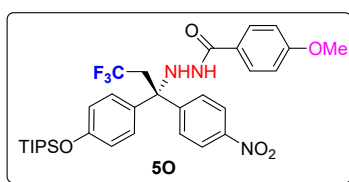
HRMS (ESI) m/z calcd. for C₃₅H₄₆F₃N₃O₄NaSi [M+Na]⁺ 680.3108, found 680.3103.



(R)-4-methoxy-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)benzohydrazide (4O)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4O** (26.6 mg, 56%) as a yellow solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 12.54 min, t_R (minor) = 20.34 min.



(R)-4-methoxy-N'-(3,3,3-trifluoro-1-(4-nitrophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5O)

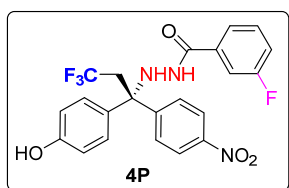
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5O** as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.19-8.11 (m, 2H), 7.62-7.51 (m, 2H), 7.50-7.39 (m, 2H), 7.18-7.09 (m, 2H), 6.95 (s, 1H), 6.89-6.80 (m, 4H), 6.03 (s, 1H), 3.81 (s, 3H), 3.36-3.14 (m, 2H), 1.28-1.17 (m, 3H), 1.07 (d, J = 7.4 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 166.9, 162.7, 156.0, 150.2, 147.1, 133.9, 128.8, 128.77, 128.69, 125.7 (q, J = 278.4 Hz), 124.2, 123.1, 120.0, 114.0, 65.8, 55.5, 41.3 (q, J = 26.4 Hz), 17.9, 12.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.1.

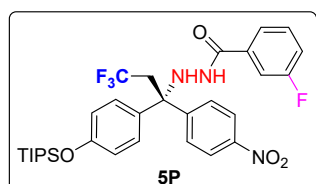
HRMS (ESI) m/z calcd. for C₃₂H₄₀F₃N₃O₅NaSi [M+Na]⁺ 654.2587, found 654.2572.



(R)-3-fluoro-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)benzohydrazide (4P)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4P** (32.0 mg, 69%) as a yellow solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 12.32 min, t_R (minor) = 28.39 min.



(R)-3-fluoro-N'-(3,3,3-trifluoro-1-(4-nitrophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5P)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5P** as colorless solid.

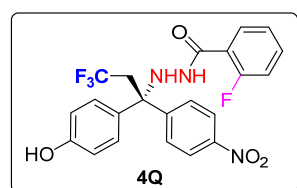
HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 273 nm), t_R (major) = 11.01 min, t_R (minor) = 14.87 min.

¹H NMR (400 MHz, CDCl₃) δ 8.19-8.13 (m, 2H), 7.62-7.56 (m, 2H), 7.37-7.28 (m, 1H), 7.25-7.19 (m, 2H), 7.19-7.12 (m, 3H), 7.09 (d, J = 5.5 Hz, 1H), 6.89-6.83 (m, 2H), 6.01 (d, J = 6.6 Hz, 1H), 3.41-3.09 (m, 2H), 1.25-1.18 (m, 3H), 1.06 (d, J = 7.3 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 165.9, 162.7 (d, J = 248.7 Hz), 156.2, 149.9, 147.2, 134.2 (d, J = 6.9 Hz), 133.6, 130.5 (d, J = 7.9 Hz), 128.8, 128.7, 125.6 (q, J = 278.6 Hz), 123.2, 122.3 (d, J = 2.8 Hz), 120.1, 119.2 (d, J = 21.3 Hz), 114.3 (d, J = 23.0 Hz), 65.9, 41.3 (q, J = 26.5 Hz), 17.8, 12.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.1, -111.0.

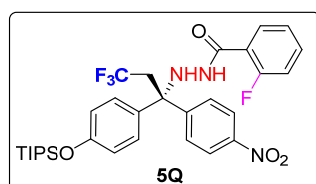
HRMS (ESI) m/z calcd. for C₃₁H₃₇F₄N₃O₄NaSi [M+Na]⁺ 642.2387, found 642.2371.



(R)-2-fluoro-N'-(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)benzohydrazide (4Q)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4Q** (44.0 mg, 95%) as a yellow solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 12.5 min, t_R (minor) = 27.3 min.



(R)-2-fluoro-N'-(3,3,3-trifluoro-1-(4-nitrophenyl)-1-((triisopropylsilyloxy)phenyl)propyl)benzohydrazide (5Q)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5Q** as colorless oil.

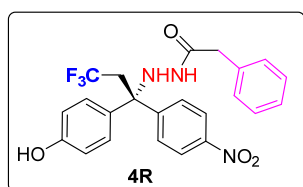
¹H NMR (400 MHz, CDCl₃) δ 8.20-8.14 (m, 2H), 7.92-7.85 (m, 1H), 7.65 (dd, J = 12.49, 7.87 Hz, 1H), 7.62-7.56 (m, 2H), 7.50-7.40 (m, 1H), 7.25-7.19 (m, 1H), 7.18-7.12 (m, 2H), 7.08-6.99 (m, 1H), 6.89-6.83 (m, 2H), 6.17 (dd, J = 8.05, 2.54 Hz, 1H),

3.38-3.12 (m, 2H), 1.26-1.19 (m, 3H), 1.07 (d, $J = 7.33$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.3 (d, $J = 3.5$ Hz), 160.3 (d, $J = 248.0$ Hz), 156.1, 150.0, 147.2, 133.8 (d, $J = 9.3$ Hz), 133.6, 131.8 (d, $J = 2.1$ Hz), 128.7, 128.6, 125.6 (q, $J = 278.4$ Hz), 125.0 (d, $J = 3.1$ Hz), 123.2, 120.1, 118.8 (d, $J = 12.1$ Hz), 116.0 (d, $J = 24.5$ Hz), 65.7, 41.1 (q, $J = 26.7$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.3, -112.4.

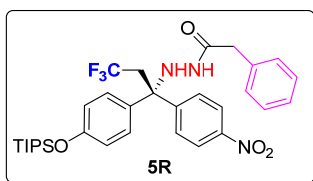
HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{37}\text{F}_4\text{N}_3\text{O}_4\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 642.2387, found 642.2370.



(R)-2-phenyl- N' -(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)acetohydrazide (4R)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4R** (34.0 mg, 74%) as a yellow solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 8.84 min, t_R (minor) = 10.25 min.



(R)-2-phenyl- N' -(3,3,3-trifluoro-1-(4-nitrophenyl)-1-(4-((triisopropylsilyloxy)phenyl)propyl)acetohydrazide (5R)

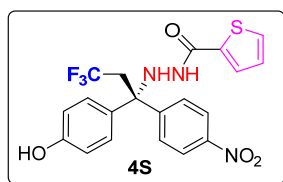
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5R** as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.6$ Hz, 2H), 7.44-7.38 (m, 2H), 7.30-7.24 (m, 3H), 7.02 (dd, $J = 6.6, 3.0$ Hz, 2H), 7.00-6.95 (m, 2H), 6.80-6.75 (m, 2H), 6.40 (d, $J = 7.2$ Hz, 1H), 5.64 (d, $J = 7.3$ Hz, 1H), 3.37 (s, 3H), 3.12-2.97 (m, 2H), 1.27-1.21 (m, 3H), 1.09 (d, $J = 7.3$ Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 156.0, 149.8, 147.1, 133.7, 133.3, 129.0, 128.63, 128.56, 127.6, 125.4 (q, $J = 279.6$ Hz), 123.1, 119.9, 65.6, 41.9, 41.1 (q, $J = 26.7$ Hz), 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -58.3.

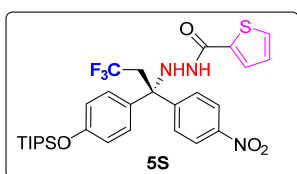
HRMS (ESI) m/z calcd. for $\text{C}_{32}\text{H}_{40}\text{F}_3\text{N}_3\text{O}_4\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 638.2638, found 638.2630.



(R)- N' -(3,3,3-trifluoro-1-(4-hydroxyphenyl)-1-(4-nitrophenyl)propyl)thiophene-2-carbohydrazide (4S)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 10/1 to 2/1) to afford desired product **4S** (32.0 mg, 71%) as a yellow solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 14.90 min, t_R (minor) = 38.28 min.



(R)- N' -(3,3,3-trifluoro-1-(4-nitrophenyl)-1-(4-((triisopropylsilyloxy)phenyl)propyl)thiophene-2-carbohydrazide (5S)

The product was purified by silica gel flash column

chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5S** as colorless oil.

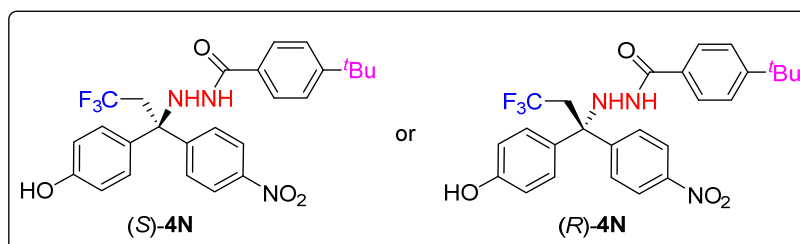
¹H NMR (400 MHz, CDCl₃) δ 8.22-8.10 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 4.8 Hz, 1H), 7.30 (s, 1H), 7.17-7.10 (m, 2H), 7.02 (t, *J* = 4.3 Hz, 1H), 6.96 (s, 1H), 6.90-6.82 (m, 2H), 5.86 (s, 1H), 3.36-3.14 (m, 2H), 1.27-1.19 (m, 3H), 1.07 (d, *J* = 7.3 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 161.8, 156.1, 150.0, 147.2, 135.4, 133.5, 130.6, 128.8, 127.7, 125.6 (q, *J* = 278.9 Hz), 123.2, 120.1, 65.9, 41.2 (q, *J* = 26.7 Hz), 17.9, 12.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.1.

HRMS (ESI) *m/z* calcd. for C₂₉H₃₆SF₃N₃O₄NaSi [M+Na]⁺ 630.2046, found 630.2026.

The absolute configuration of 4N was determined by ECD



Conformations of (*R*)-4N was searched using Conflex 7 (Rev. D). Initial low-energy conformers with larger than 1% distribution in Gibb's free energy were chosen for geometry optimization and frequency calculation at the B3LYP/6-311++G(d,p) level in acetonitrile solvent by a self-consistent reaction field (SCRF) using the SMD implicit solvent model with Gaussian 16. Then, conformers with distinct conformations were further subjected to TD-DFT calculation at the same level as aforementioned for dipole and rotational strengths of the first 40 excited states in the UV range. Next, ECD spectra of (*R*)-4N (Supplementary Figure 1) were calculated from excitation energies and rotational strengths as averages weighed on Boltzmann conformer relative populations as a sum of Gaussian functions centered at the wavelength of each transition with appropriate widths of the band at half-height using SpecDis (version 1.71), respectively. Samples of compounds 4N for ECD were dissolved in CH₃OH, and spectra were acquired in a 10.0-mm pathlength cuvette, respectively. The UV and ECD spectra were recorded using a Chirascan® Spectrophotometer with the following instrumental parameters: 200–400 nm with a 1 nm step and a 1 nm bandwidth with data averaging over 1.0 sec per point. Three spectral acquisitions were taken for each sample and were averaged and smoothed thereafter.

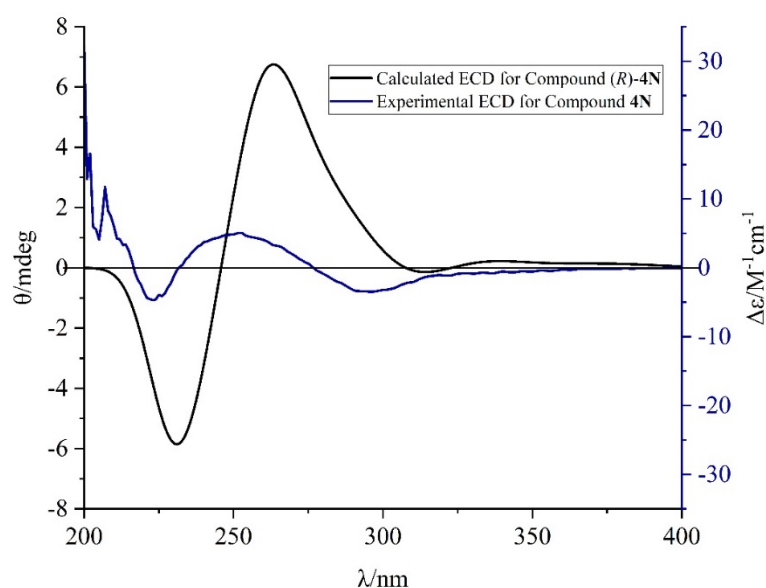
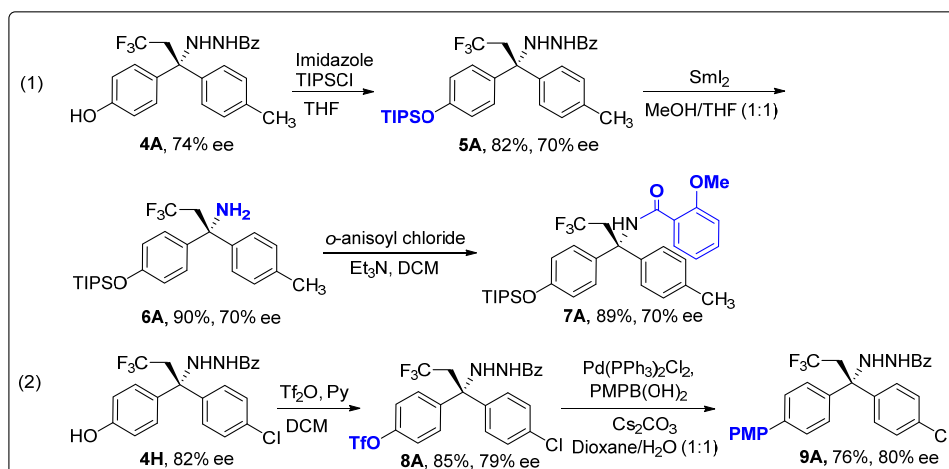


Figure 1. Comparison of the calculated ECD of compound (*R*)-**4N** with the experimental one of compound **4N**.

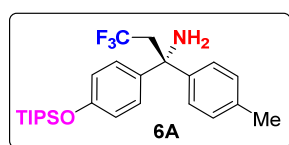
The calculated spectrum for (*R*)-**4N** was basically in accordance with the experimental one, and thus, the absolute configuration of **4N** has been assigned to be *R*.

Representative product transformations



Procedure for synthetic application

Synthesis of **6a**, **7a**: **6a**, **7a** were synthesized according to the procedures previously reported.^[5]



(*R*)-3,3,3-trifluoro-1-(*p*-tolyl)-1-(4-((triisopropylsilyl)oxy)phenyl)propan-1-amine (**6A**)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 10/1) to afford desired product **6A** as colorless oil.

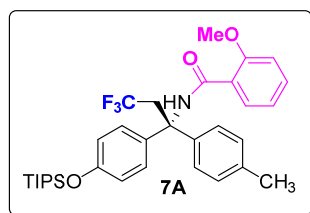
HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 95/05, flow rate 0.4 mL/min, λ = 230 nm), t_R (minor) = 12.54 min, t_R (major) = 17.68 min.

¹H NMR (400 MHz, CDCl₃) δ 7.3-7.1 (m, 6H), 6.8 (d, J = 8.2 Hz, 2H), 3.1 (q, J = 10.7 Hz, 2H), 2.3 (s, 3H), 1.3-1.2 (m, 3H), 1.1 (d, J = 7.4 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 154.9, 144.1, 139.3, 136.6, 128.9, 127.3, 126.3 (q, J = 279.1 Hz), 126.1, 119.6, 58.5, 46.0 (q, J = 24.6 Hz), 20.9, 17.9, 12.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -58.1.

HRMS (ESI) m/z calcd. for C₂₅H₃₆ONF₃S [M+Na]⁺ 474.2416, found 474.2401



(*R*)-2-methoxy-*N*-(3,3,3-trifluoro-1-(*p*-tolyl)-1-(4-((triisopropylsilyl)oxy)phenyl)propyl)benzamide (**7A**)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **7A** as colorless oil.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 14.12 min, t_R (major) = 20.63 min.

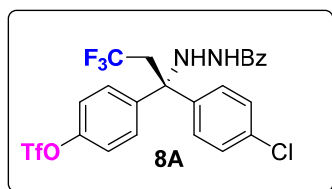
¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 1H), 8.11 (dd, J = 7.78, 1.88 Hz, 1H), 7.50-7.42 (m, 1H), 7.24 (d, J = 8.35 Hz, 2H), 7.20-7.17 (m, 2H), 7.12 (d, J = 8.15 Hz, 2H), 7.09-7.01 (m, 2H), 6.85-6.79 (m, 2H), 4.08 (s, 3H), 3.95-3.78 (m, 1H), 3.76-3.62 (m, 1H), 2.30 (s, 3H), 1.27-1.18 (m, 3H), 1.07 (d, J = 7.30 Hz, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.2, 157.6, 155.0, 142.3, 137.1, 136.6, 132.9, 132.4, 129.1, 127.0, 126.2 (q, $J = 279.8$ Hz), 125.8, 122.1, 121.6, 119.8, 111.5, 60.8, 56.3, 40.1 (q, $J = 25.7$ Hz), 21.0, 17.9, 12.7.

^{19}F NMR (376 MHz, CDCl_3) δ -59.1.

HRMS (ESI) m/z calcd. for $\text{C}_{33}\text{H}_{43}\text{O}_3\text{NF}_3\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 608.2784, found 608.2762.

Synthesis of **9A**: **9A** was synthesized according to the procedures previously reported.^[6]



(R)-4-(1-(2-benzoylhydrazinyl)-1-(4-chlorophenyl)-3,3,3-trifluoropropyl)phenyl trifluoromethanesulfonate (8A)

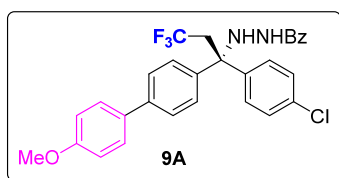
The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 10/1) to afford desired product **8A** as colorless oil.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 20.47 min, t_R (major) = 26.52 min.

^1H NMR (400 MHz, CDCl_3) δ 7.53-7.43 (m, 5H), 7.39 (dd, $J = 8.4, 6.9$ Hz, 2H), 7.31 (q, $J = 8.9$ Hz, 4H), 7.26-7.21 (m, 2H), 7.01 (d, $J = 7.0$ Hz, 1H), 5.97 (d, $J = 7.3$ Hz, 1H), 3.24 (q, $J = 10.1$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.5, 148.9, 142.7, 140.3, 134.2, 132.3, 131.9, 129.7, 129.0, 128.8, 128.6, 126.8, 125.5 (q, $J = 279.4$ Hz), 121.1, 118.7 (q, $J = 322.0$ Hz), 65.6, 41.3 (q, $J = 26.7$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -58.2, -72.8.



(R)-N'-(1-(4-chlorophenyl)-3,3,3-trifluoro-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)propyl)benzohydrazide (9A)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **9A** as a white solid.

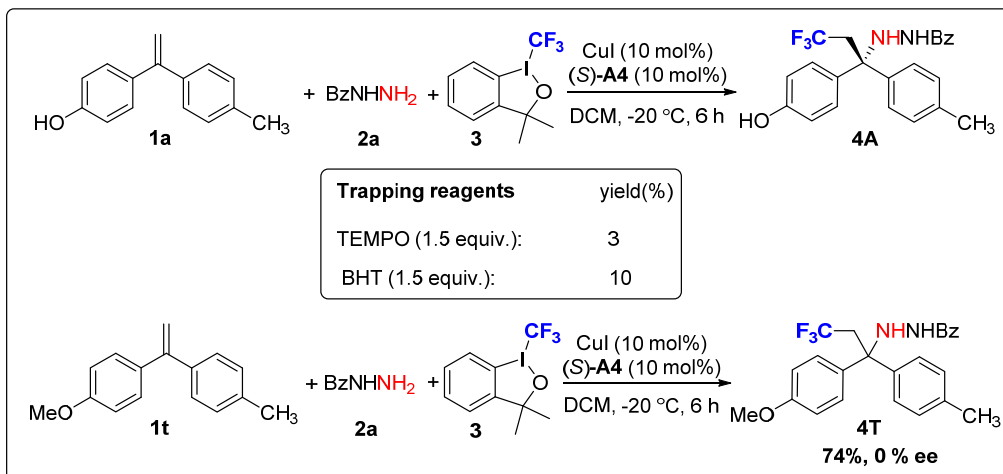
HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 18.83 min, t_R (major) = 24.26 min.

^1H NMR (400 MHz, CDCl_3) δ 7.6-7.4 (m, 7H), 7.41-7.35 (m, 6H), 7.3-7.3 (m, 2H), 7.0 (s, 1H), 7.0-7.0 (m, 2H), 6.1 (s, 1H), 3.8 (s, 3H), 3.35-3.18 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 159.5, 141.0, 140.4, 140.2, 133.7, 132.6, 132.4, 132.1, 129.2, 128.8, 128.4, 128.1, 128.0, 126.8, 126.5, 125.8 (q, $J = 278.5$ Hz), 114.3, 65.7, 55.4, 41.2 (q, $J = 26.3$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -58.0.

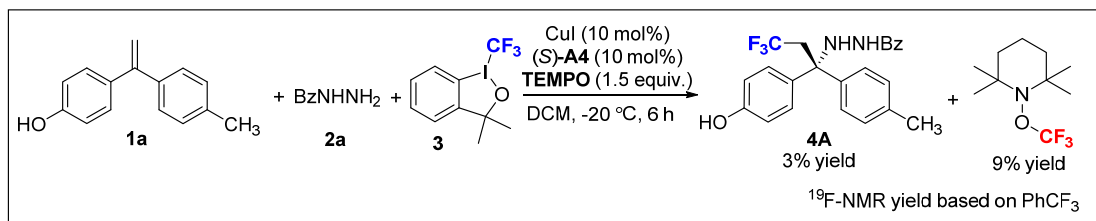
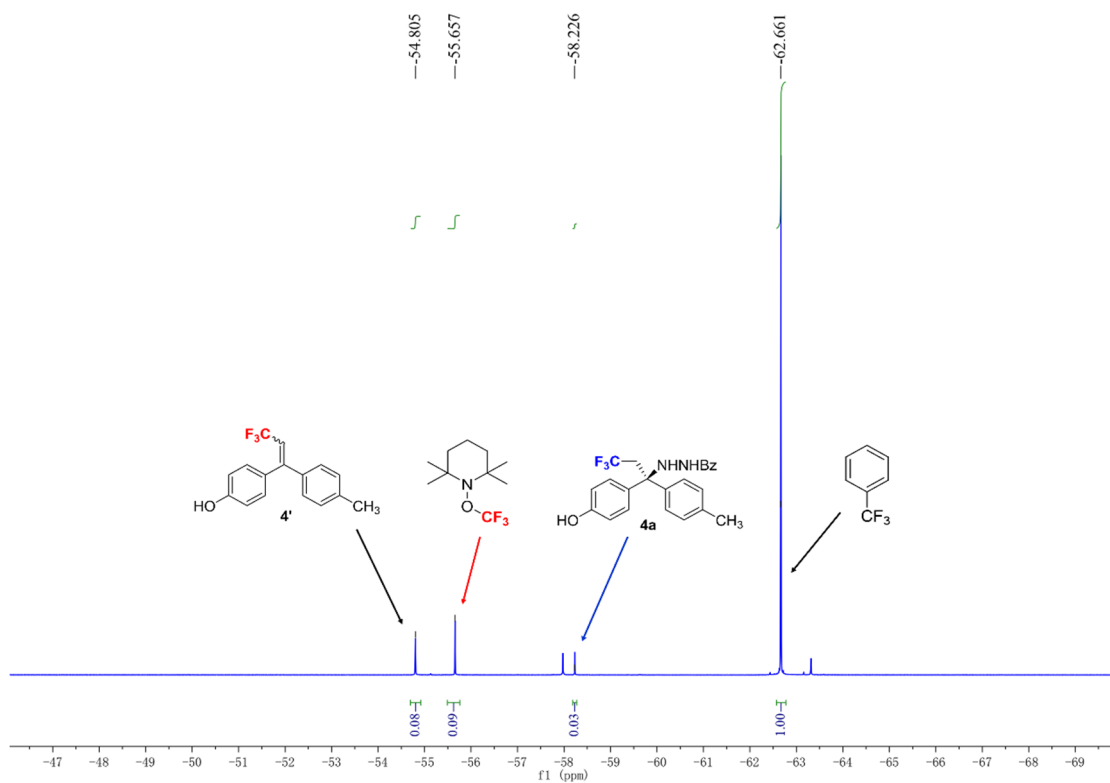
HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{24}\text{O}_2\text{N}_2\text{F}_3\text{ClNa}$ $[\text{M}+\text{Na}]^+$ 547.1365, found 547.1376.

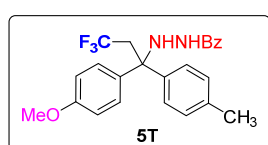
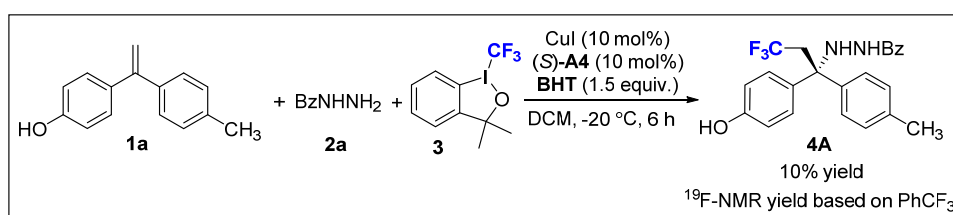
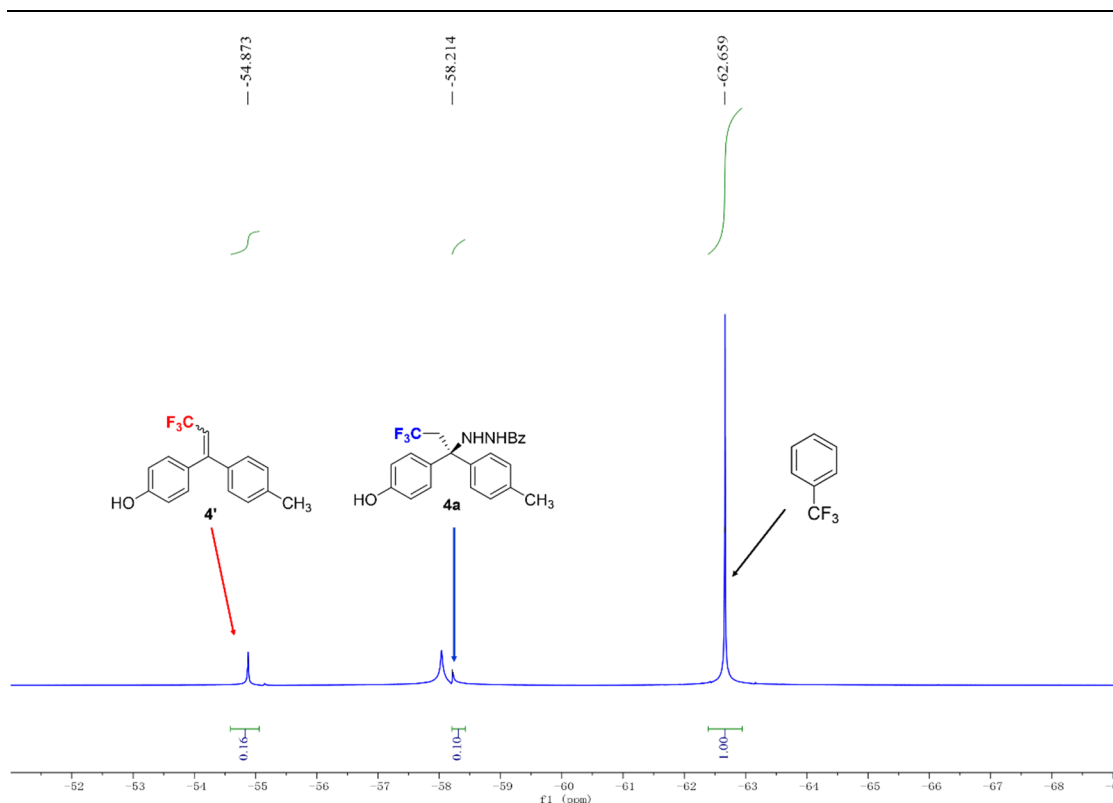


Mechanistic study

Under argon atmosphere, an oven-dried resealable Schlenk tube (**25 mL**) equipped with a magnetic stir bar was charged with 1,1-diaryllkene **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.), CuI (1.0 mg, 0.005 mmol, 10 mol%), chiral phosphoric acid ((*S*)-**A4** (3.7 mg, 0.005 mmol, 10 mol%), Togni's reagent (**3**, 16.5 mg, 0.05 mmol, 1.0 equiv.), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 11.7 mg, 0.075 mmol, 1.5 equiv.) or 2,6-di-*tert*-butyl-4-methylphenol (16.5 mg, 0.075 mmol, 1.5 equiv.), and anhydrous DCM (2 mL) at 0 °C, then the sealed tube was stirred at -20 °C for 6 h. PhCF₃ (internal standard, 0.05 mmol, 1.0 equiv.) was added to the reaction mixture. Yield was based on ¹⁹F NMR analysis of the crude product.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use.





N'-(3,3,3-trifluoro-1-(4-methoxyphenyl)-1-(*p*-tolyl)propyl)-benzohydrazide (**5T**)

The product was purified by silica gel flash column chromatography (*n*-hexane/ethyl acetate = 100/0 to 5/1) to afford desired product **5T** as colorless solid.

HPLC analysis: Chiralcel IA3 (*n*-hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 23.34 min, t_R (major) = 24.35 min.

^1H NMR (400 MHz, CDCl_3) δ 7.54-7.43 (m, 3H), 7.36 (t, J = 7.6 Hz, 2H), 7.33-7.23 (m, 4H), 7.14 (d, J = 7.8 Hz, 2H), 6.96 (s, 1H), 6.89-6.80 (m, 2H), 5.98 (d, J = 7.6 Hz, 1H), 3.80 (s, 3H), 3.22 (q, J = 10.4 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 158.8, 139.5, 137.3, 134.5, 132.6, 131.9, 128.9, 128.9, 128.7, 127.5, 126.8, 125.9 (q, J = 278.4 Hz), 113.4, 65.5, 55.2, 41.3 (q, J = 26.1 Hz), 21.1.

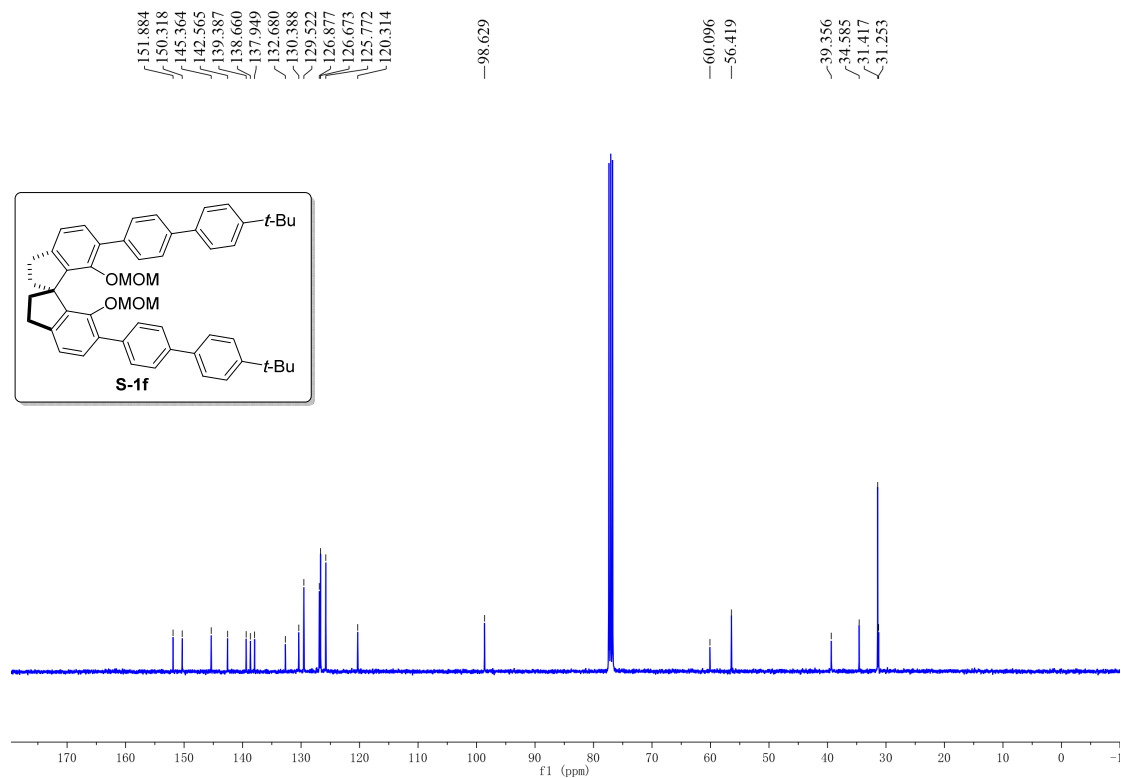
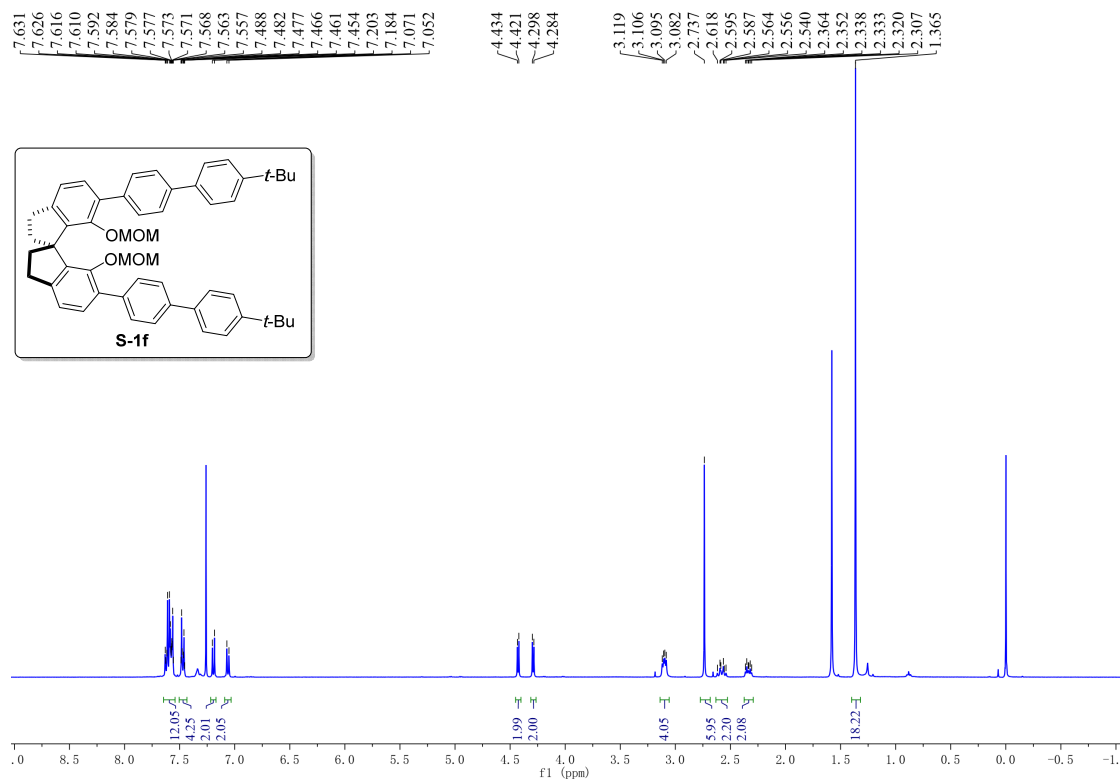
^{19}F NMR (376 MHz, CDCl_3) δ -58.0.

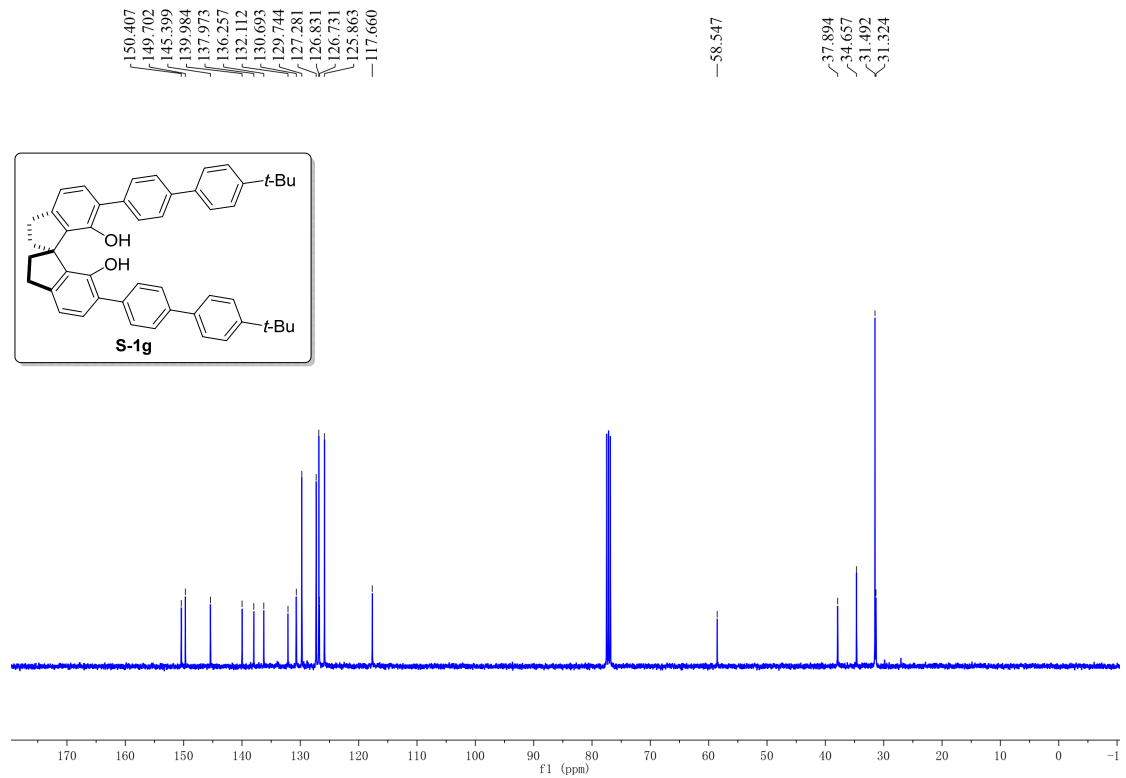
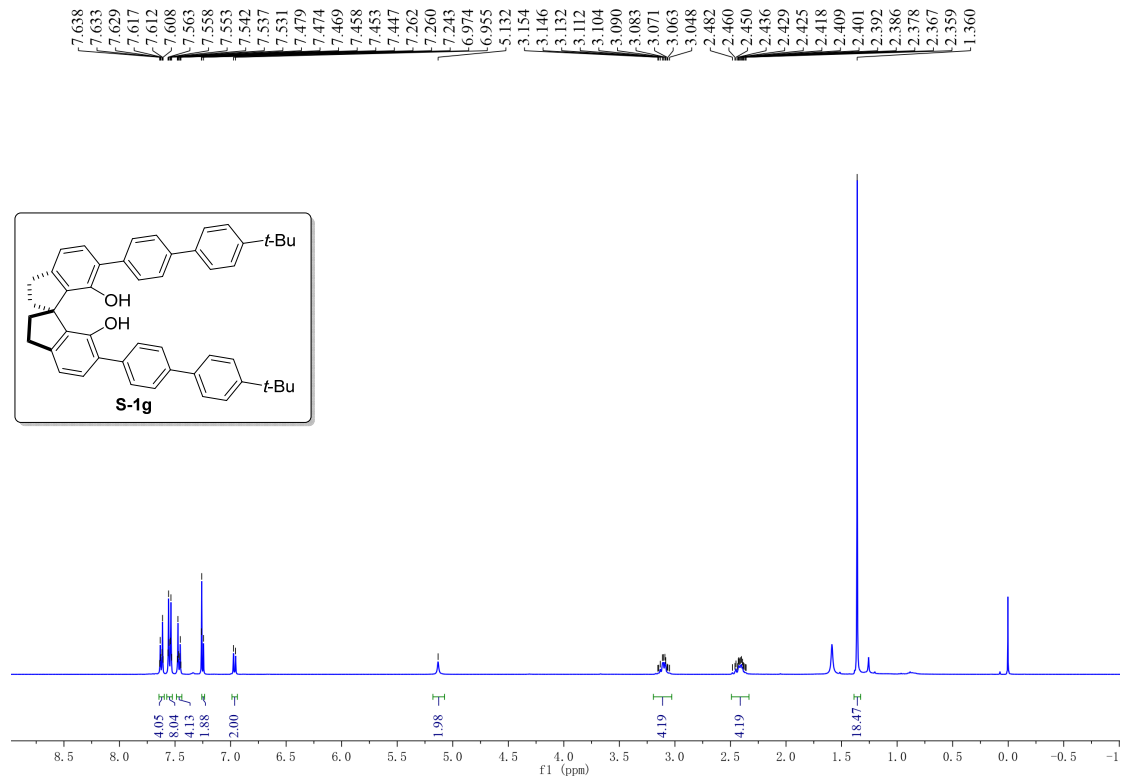
HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 451.1610, found 451.1605.

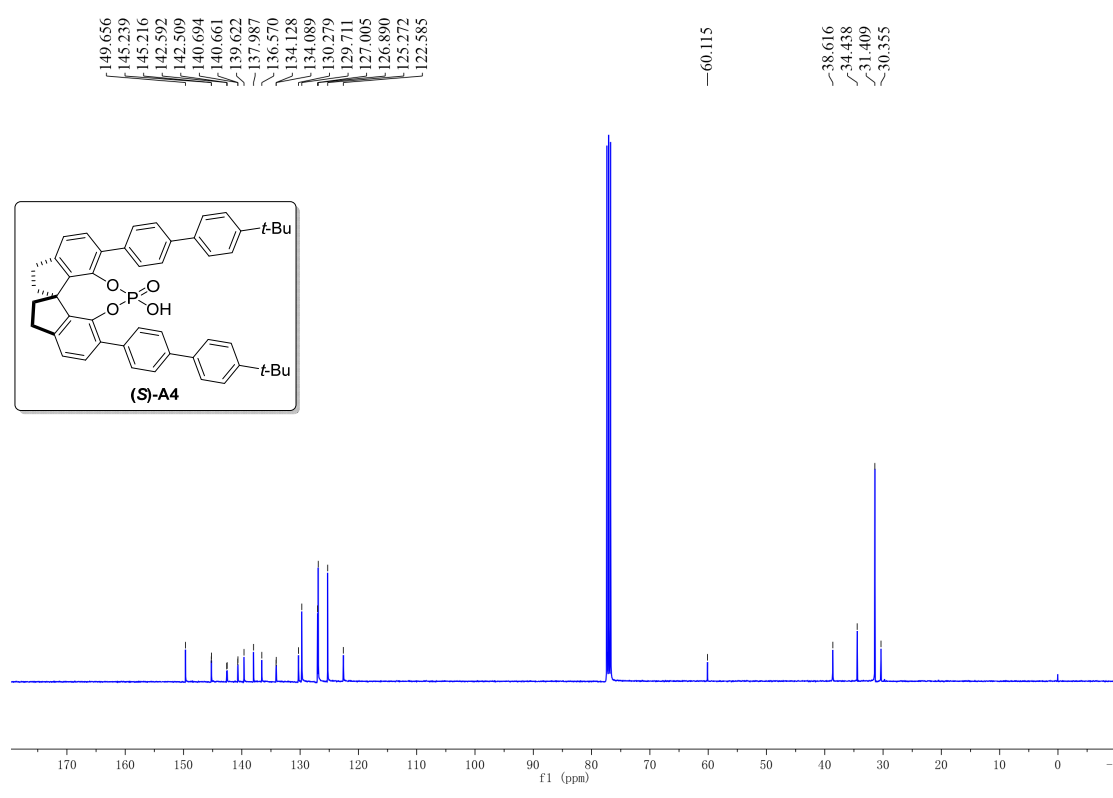
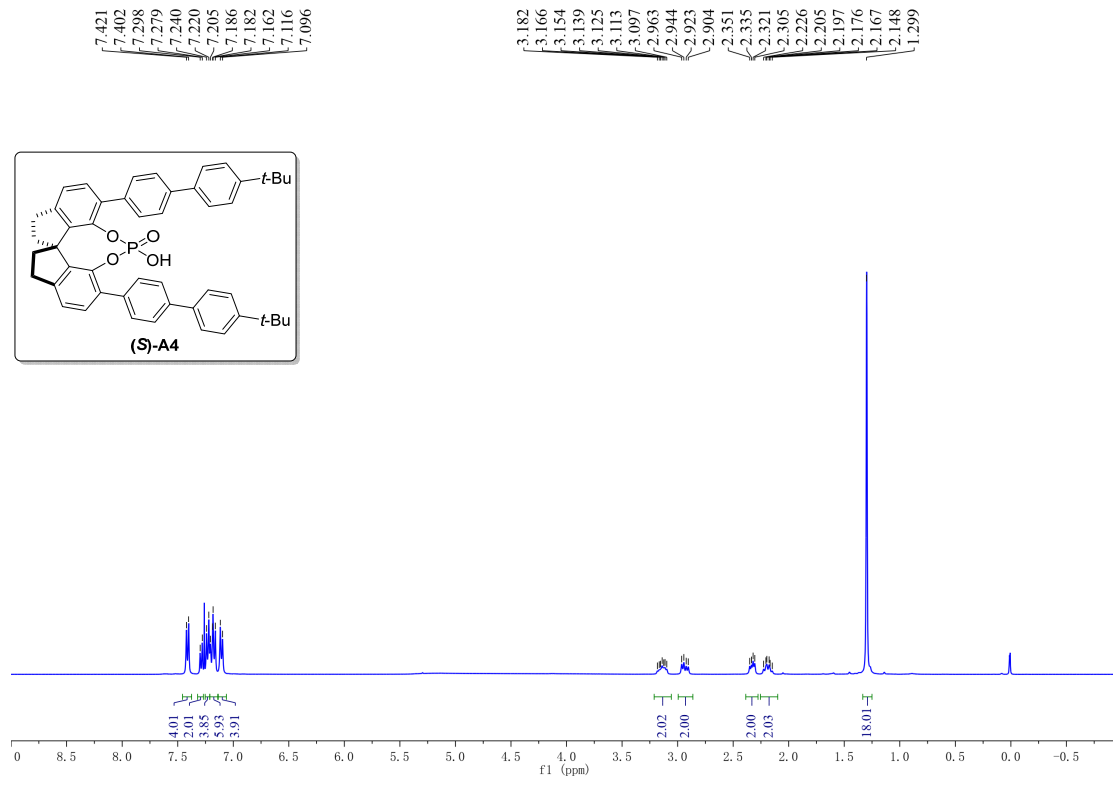
Supplementary References

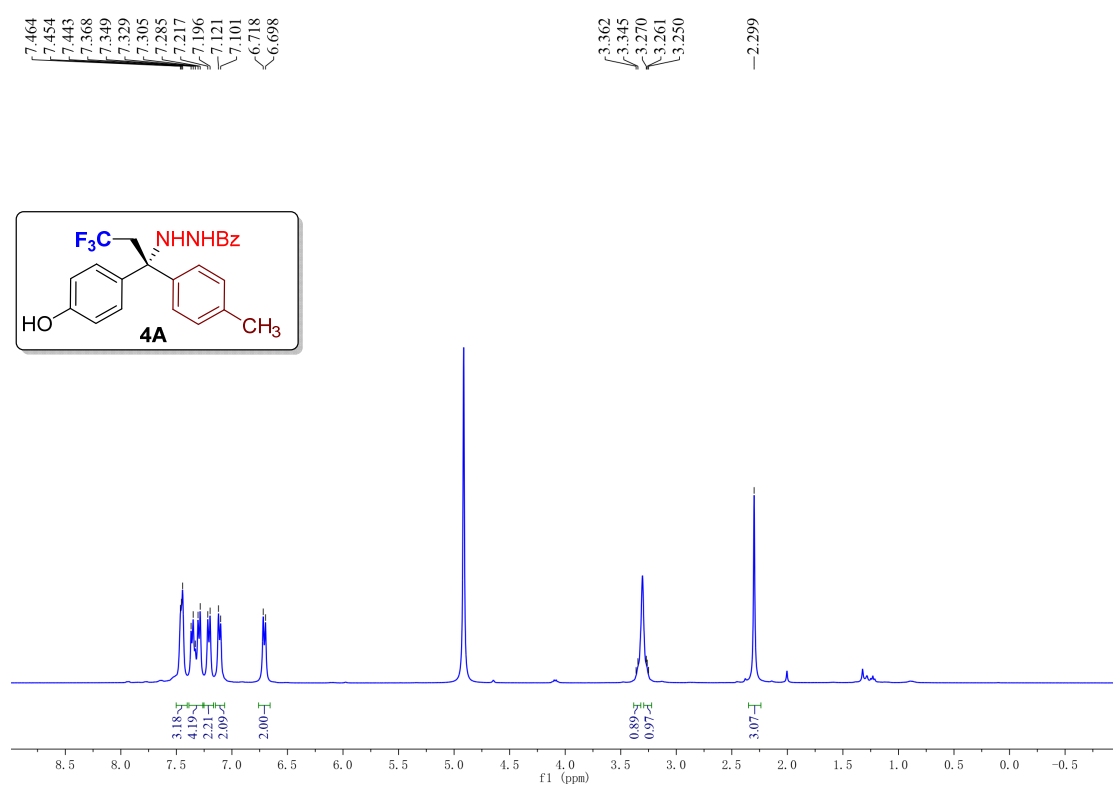
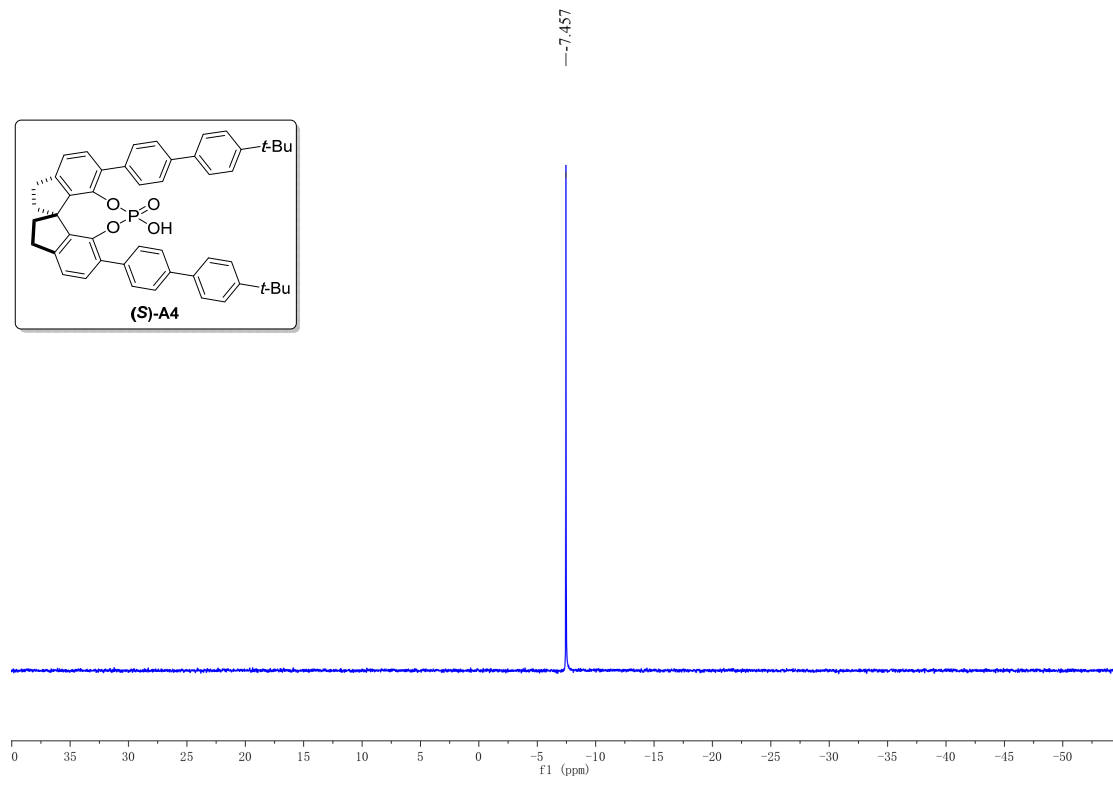
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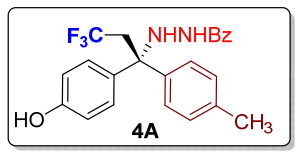
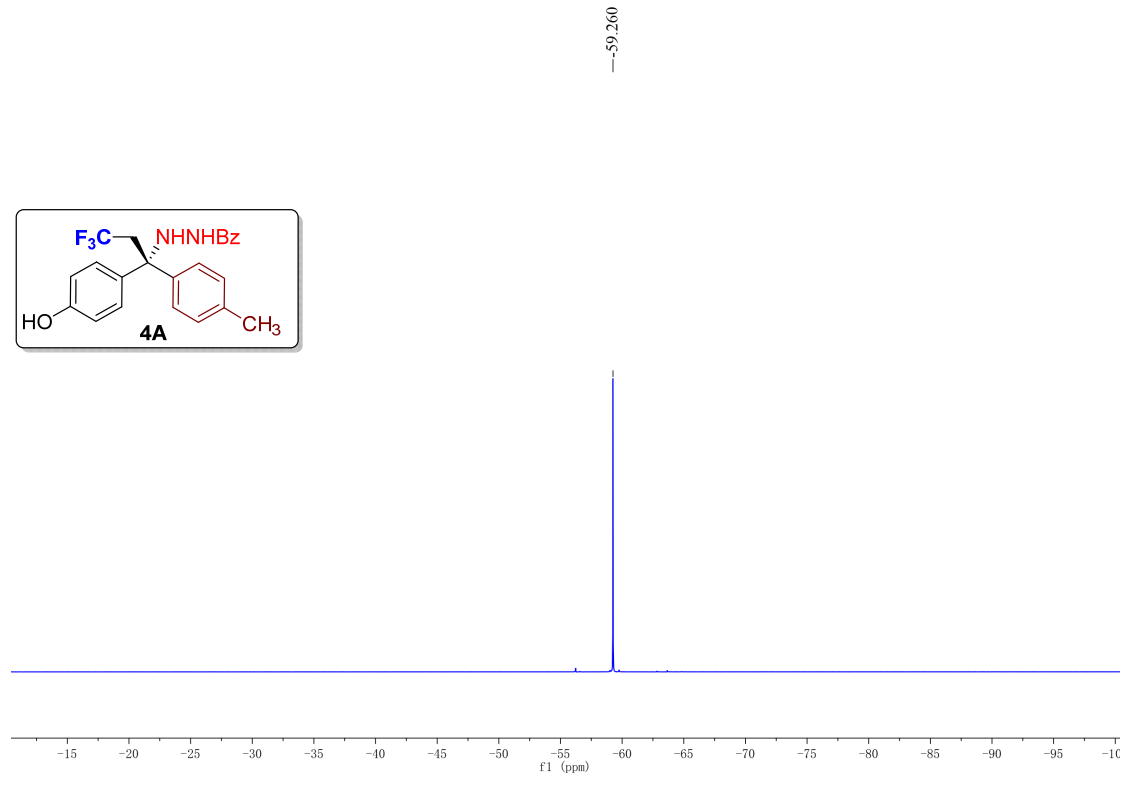
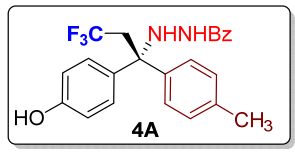
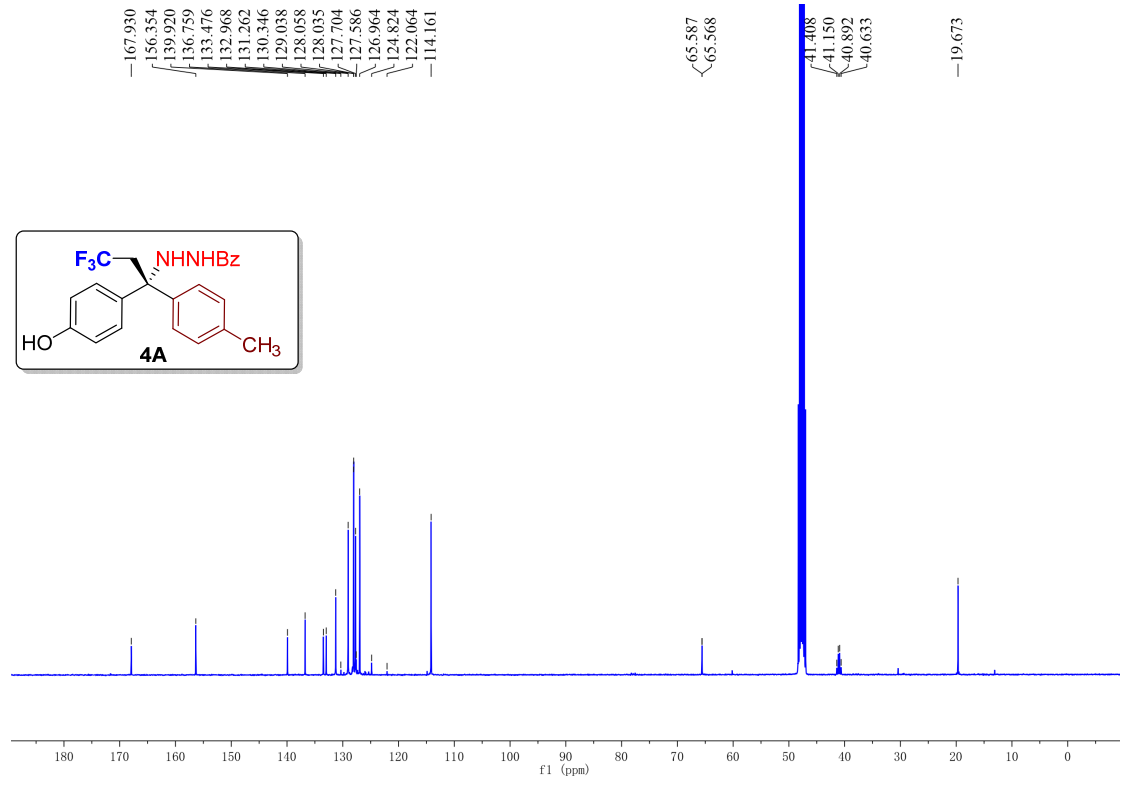
NMR Spectra

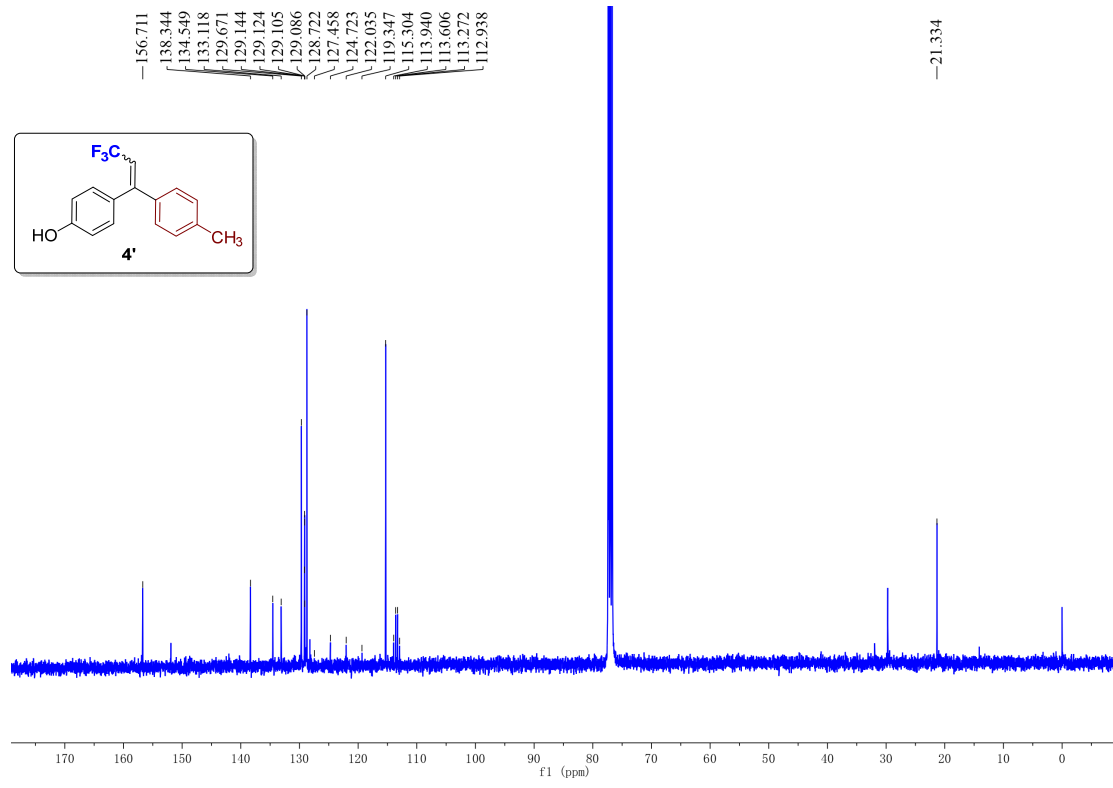
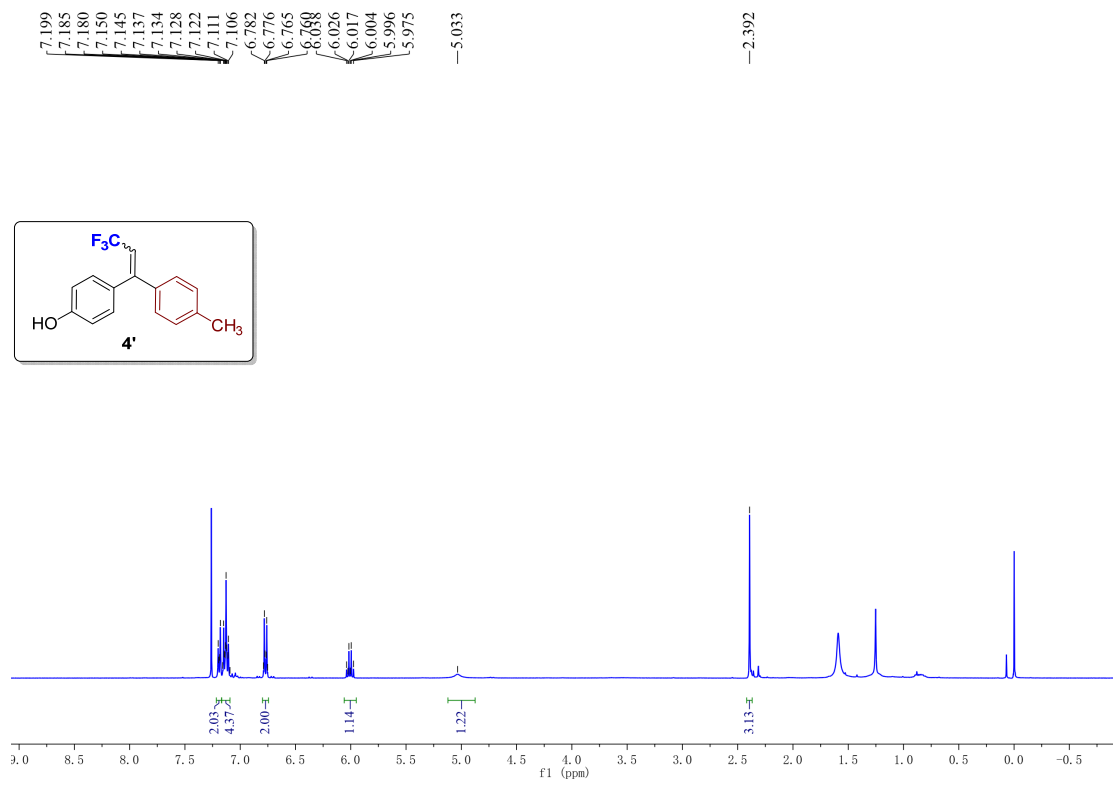




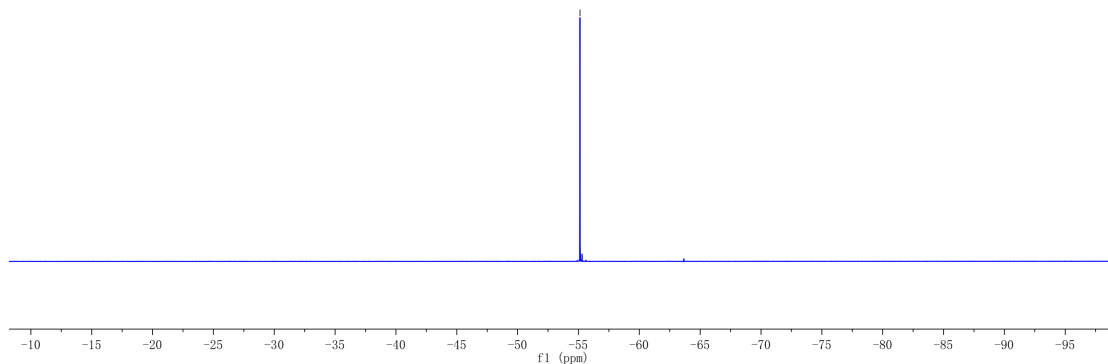
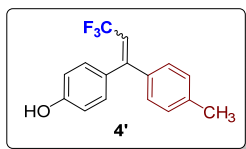




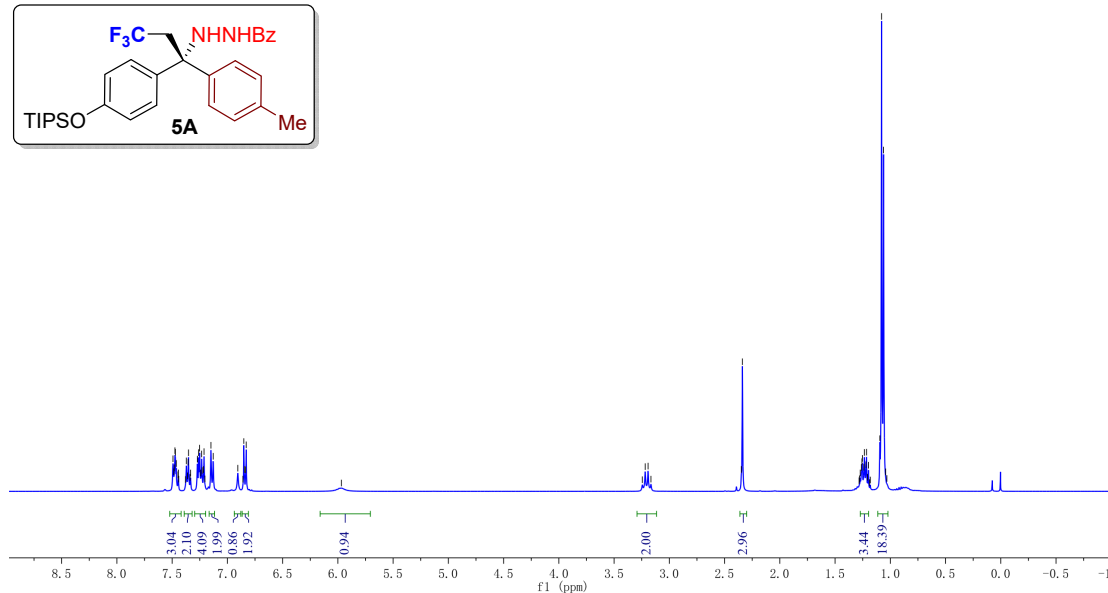
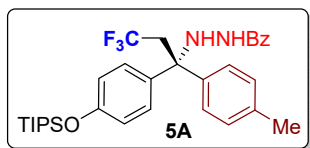


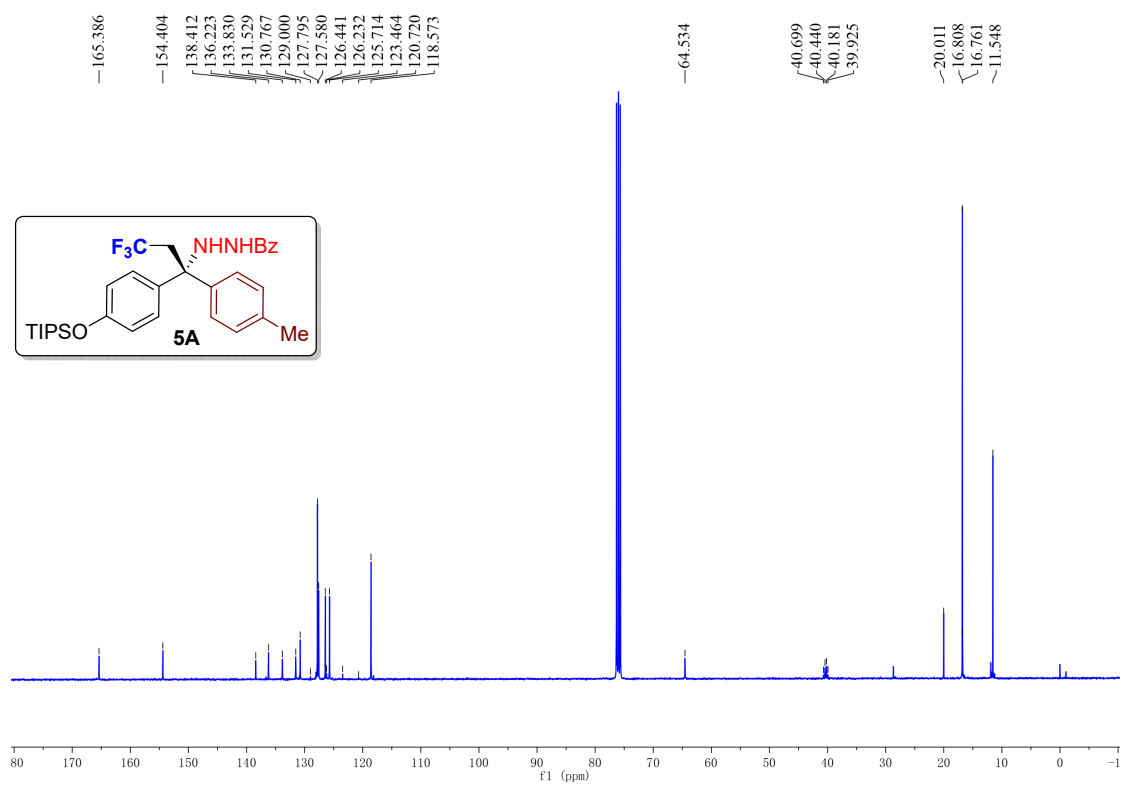


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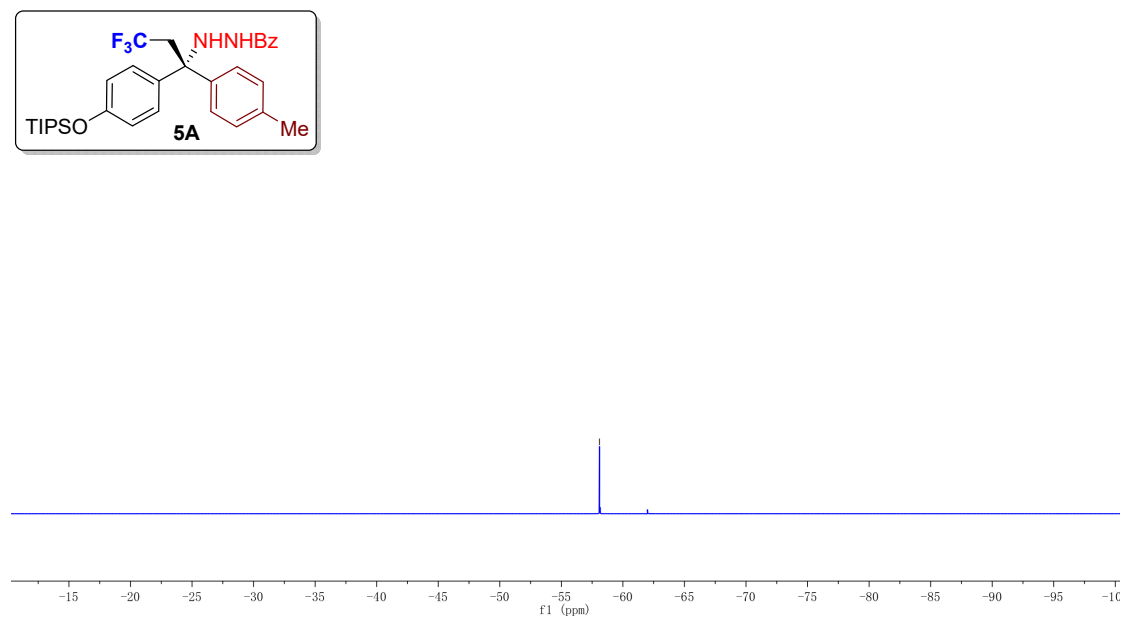


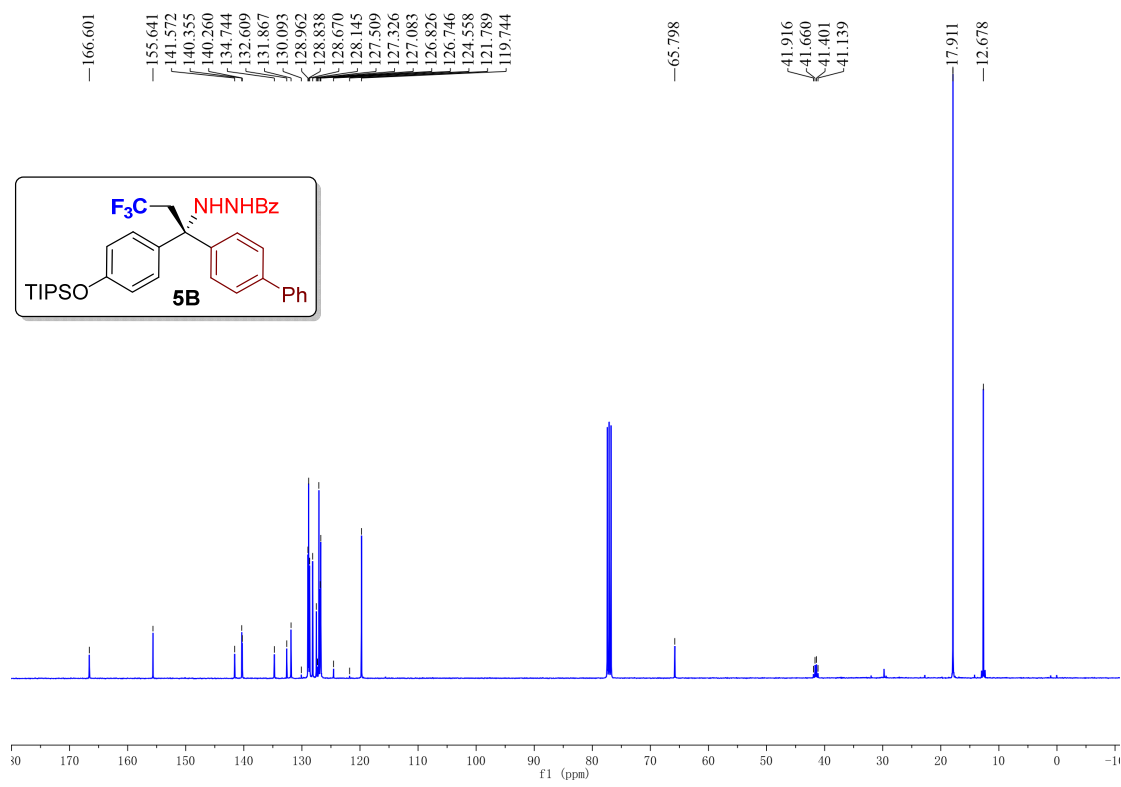
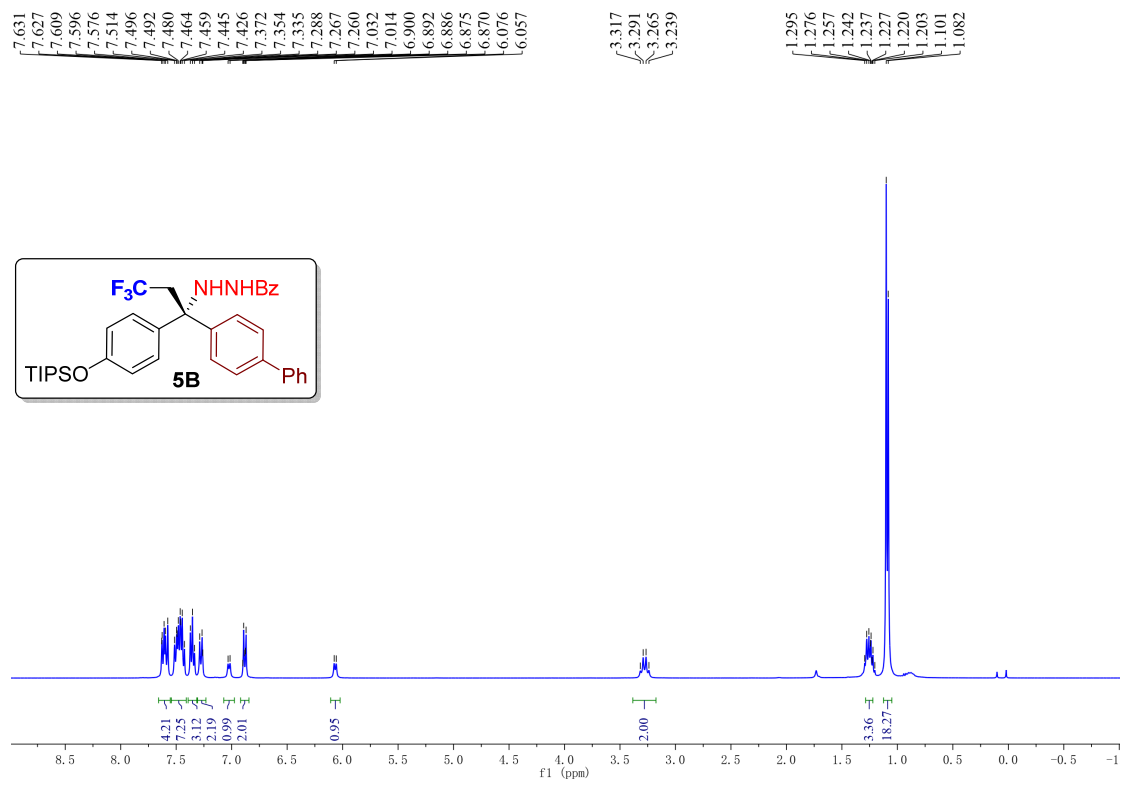
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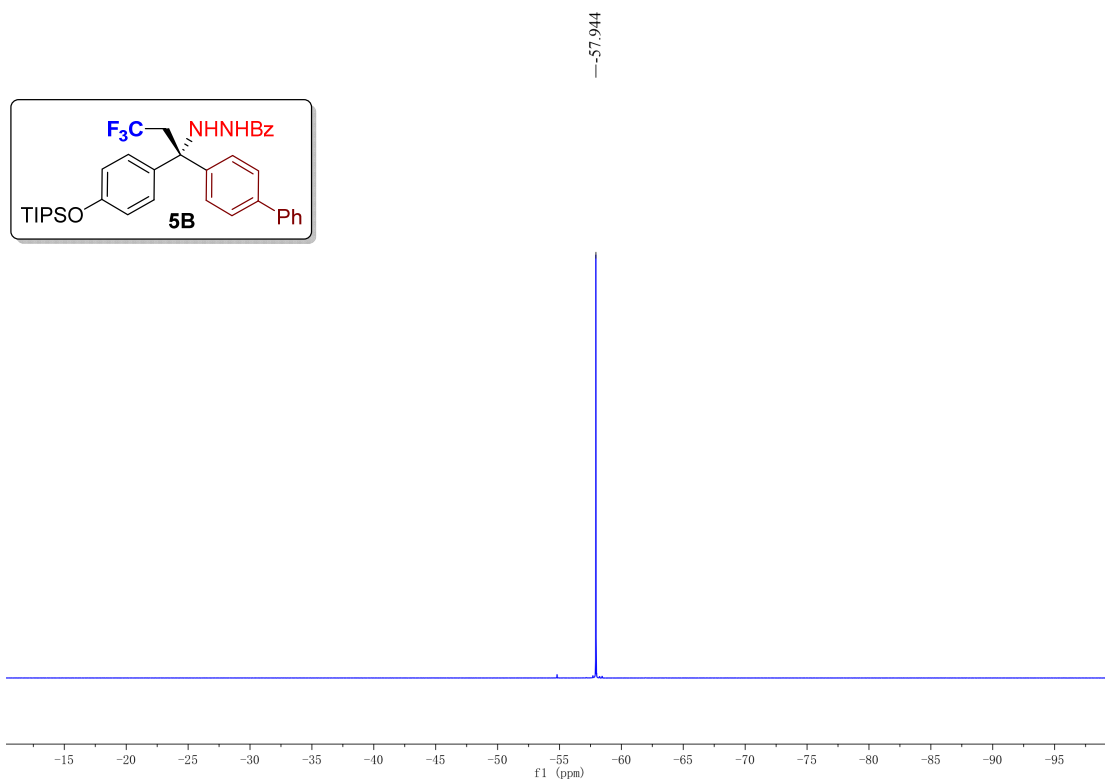




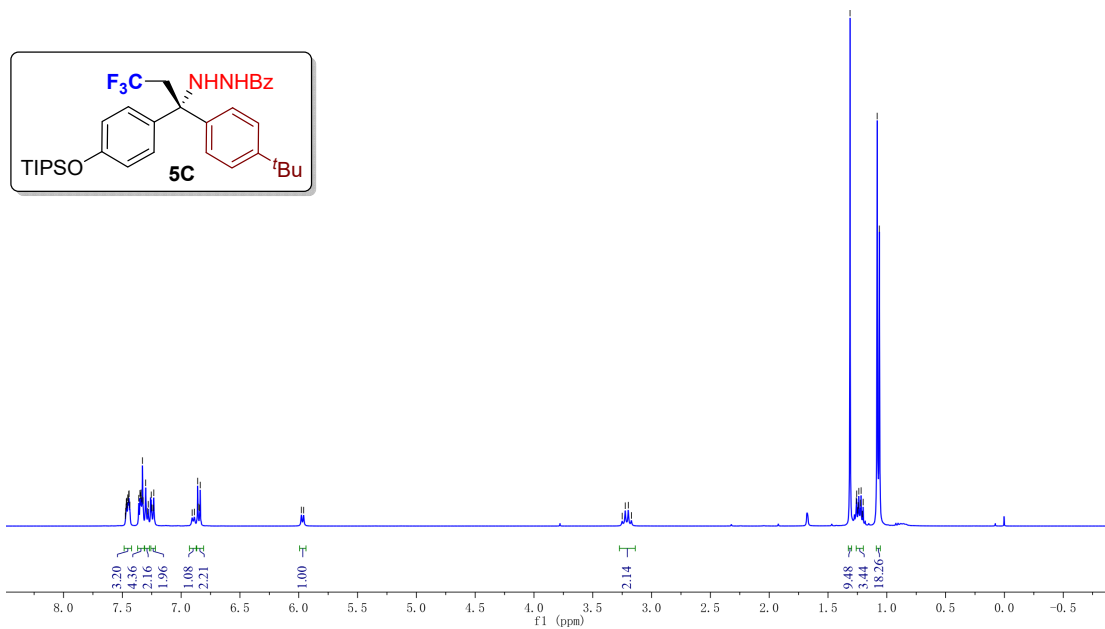
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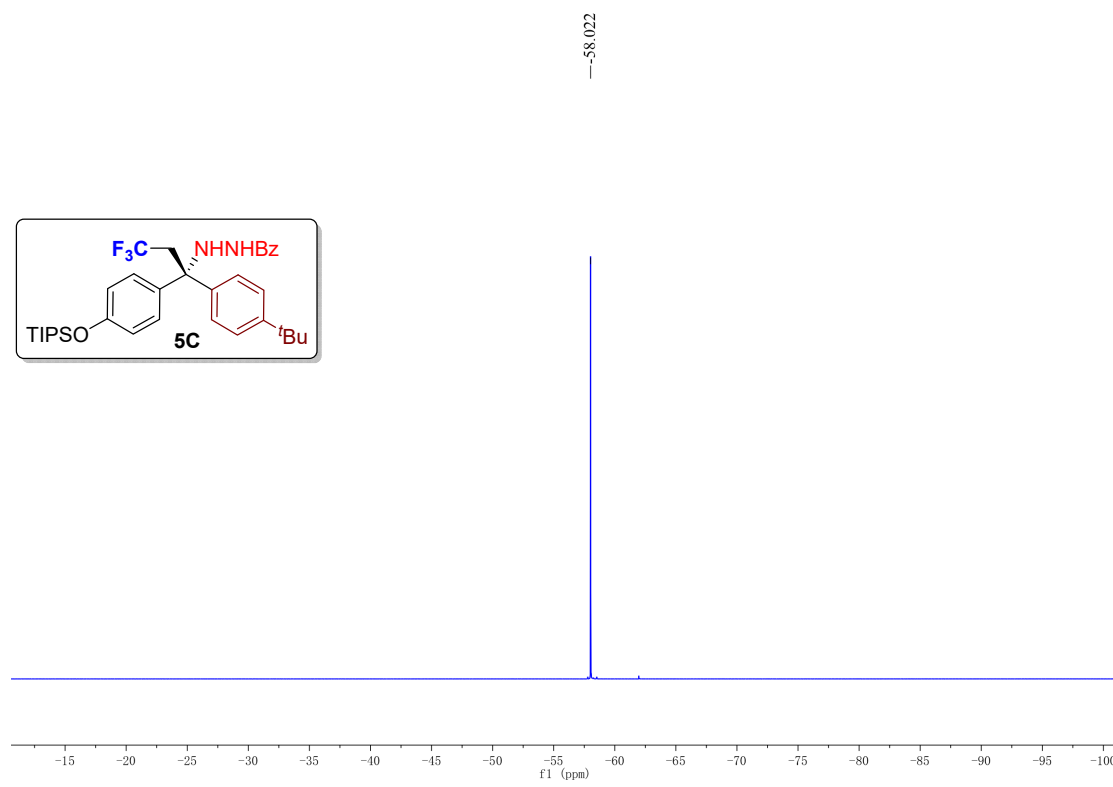
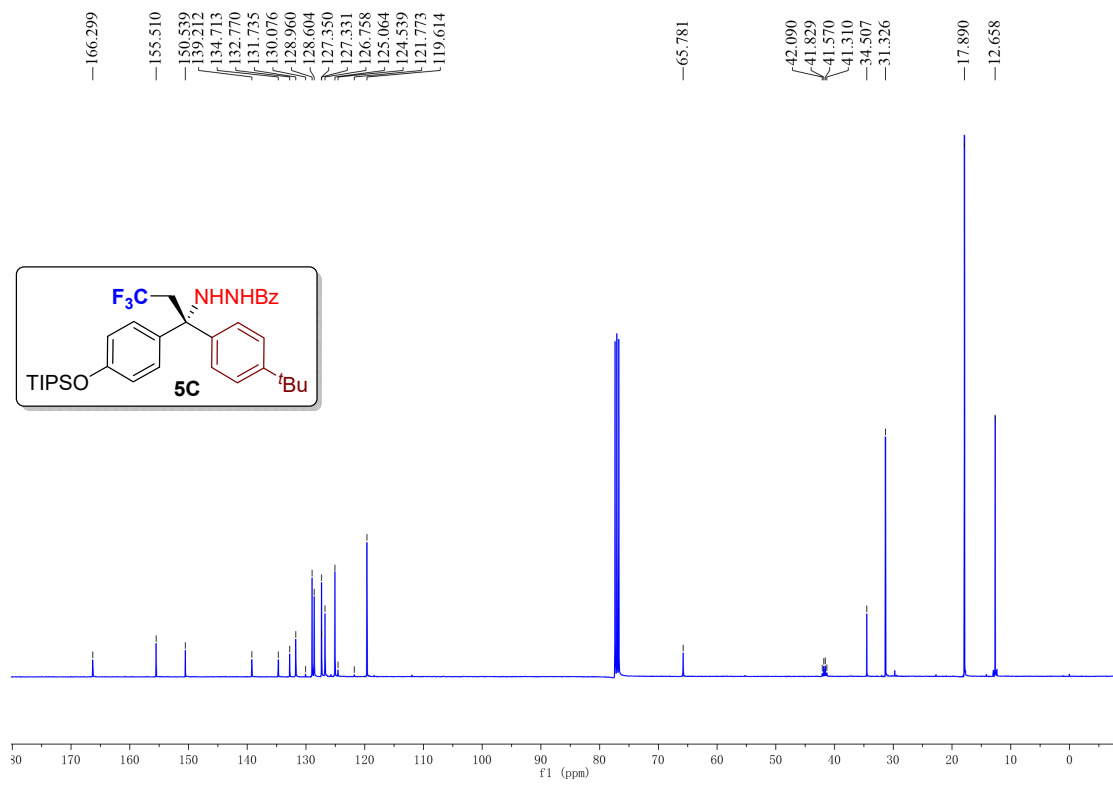


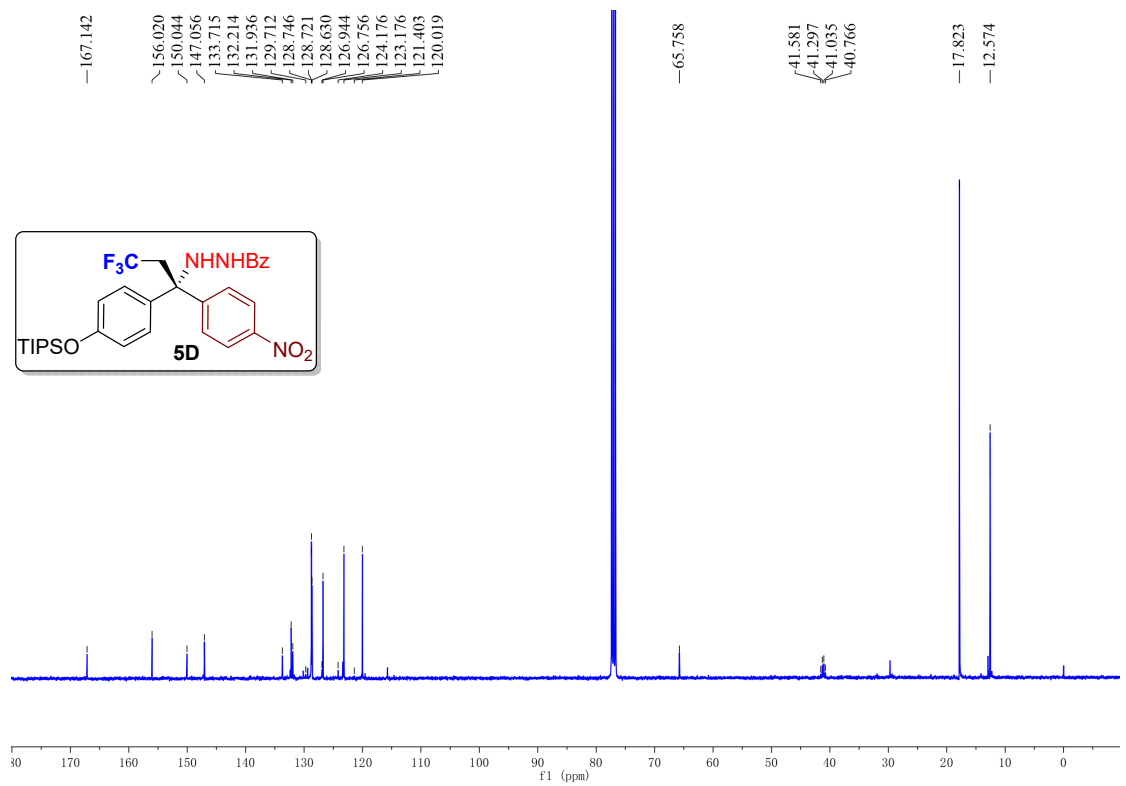
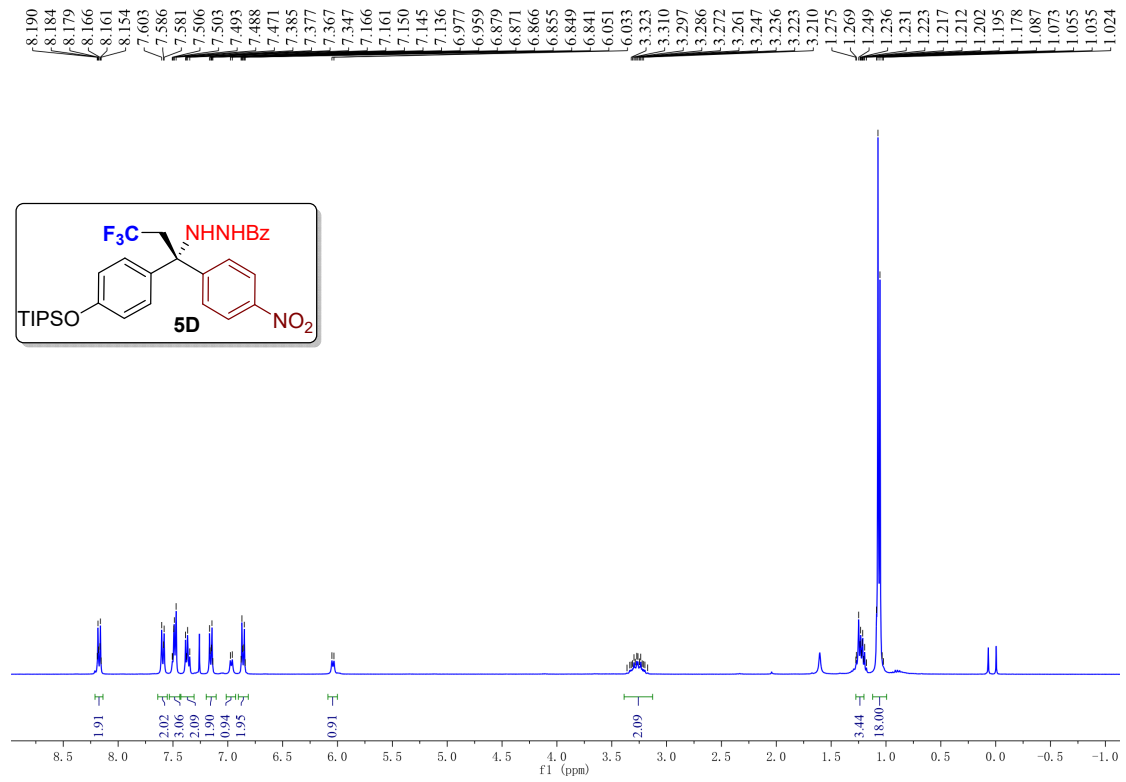


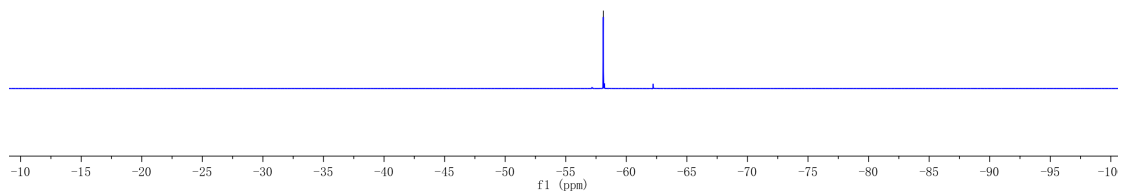
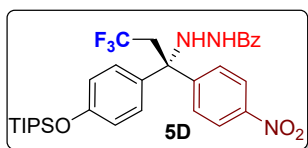
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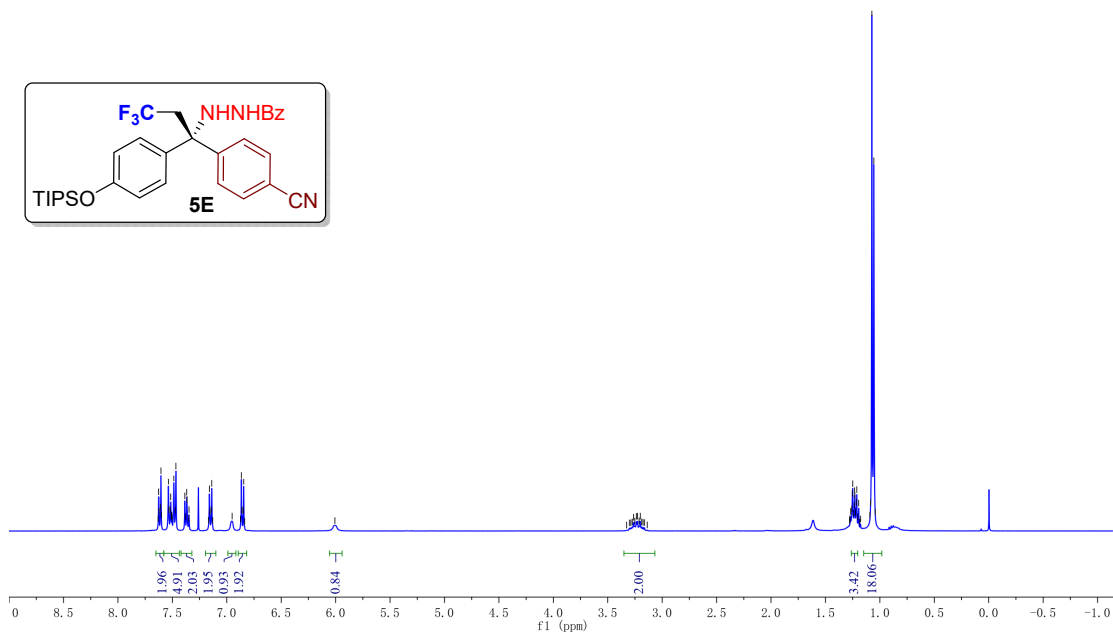
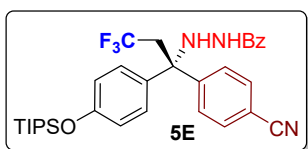
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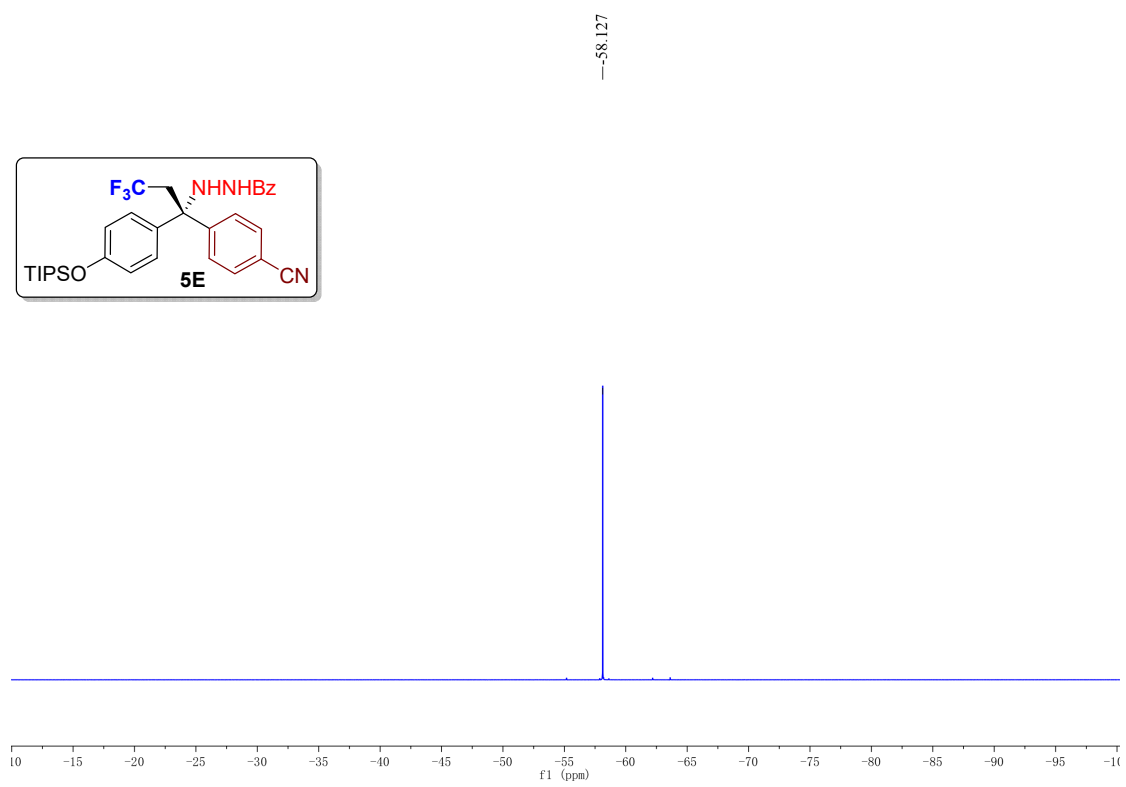
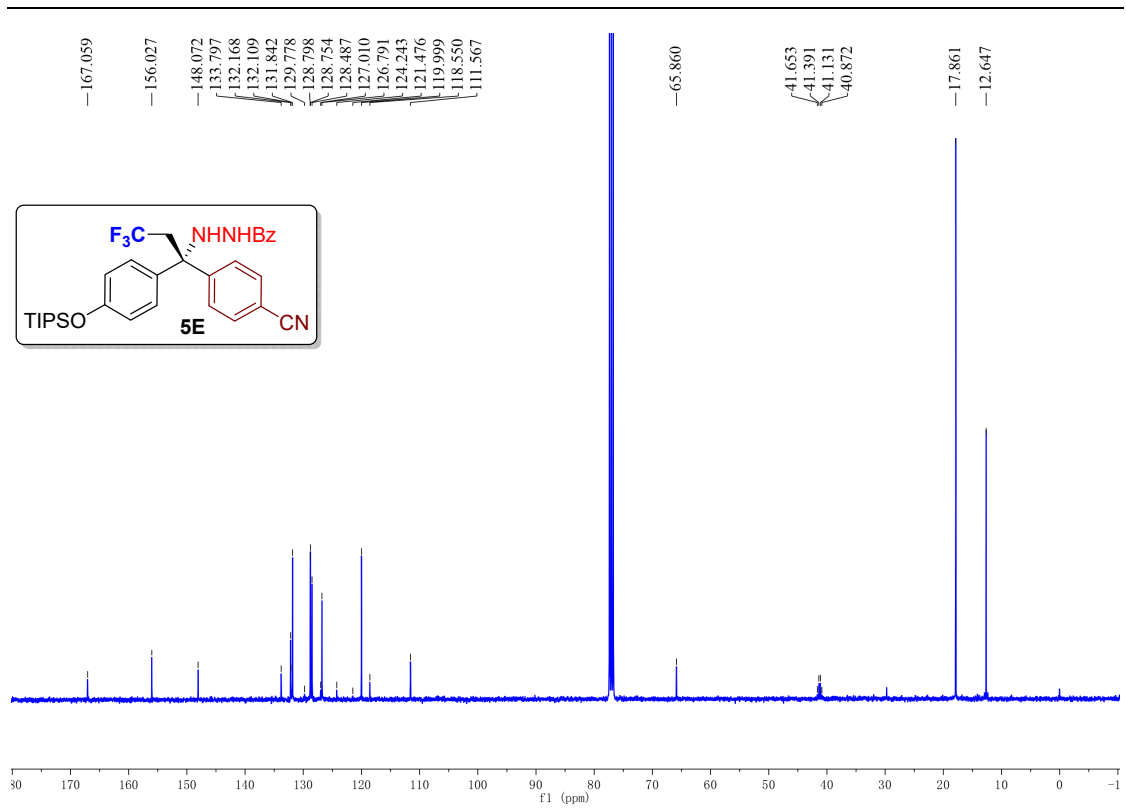


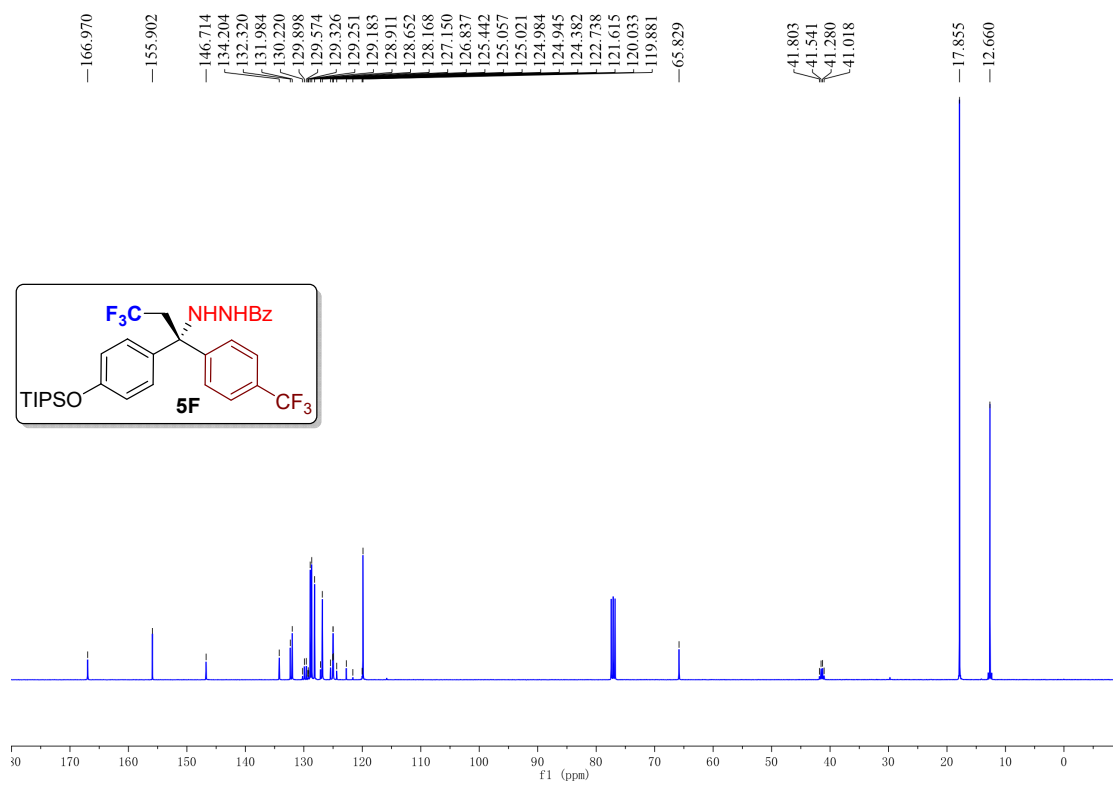
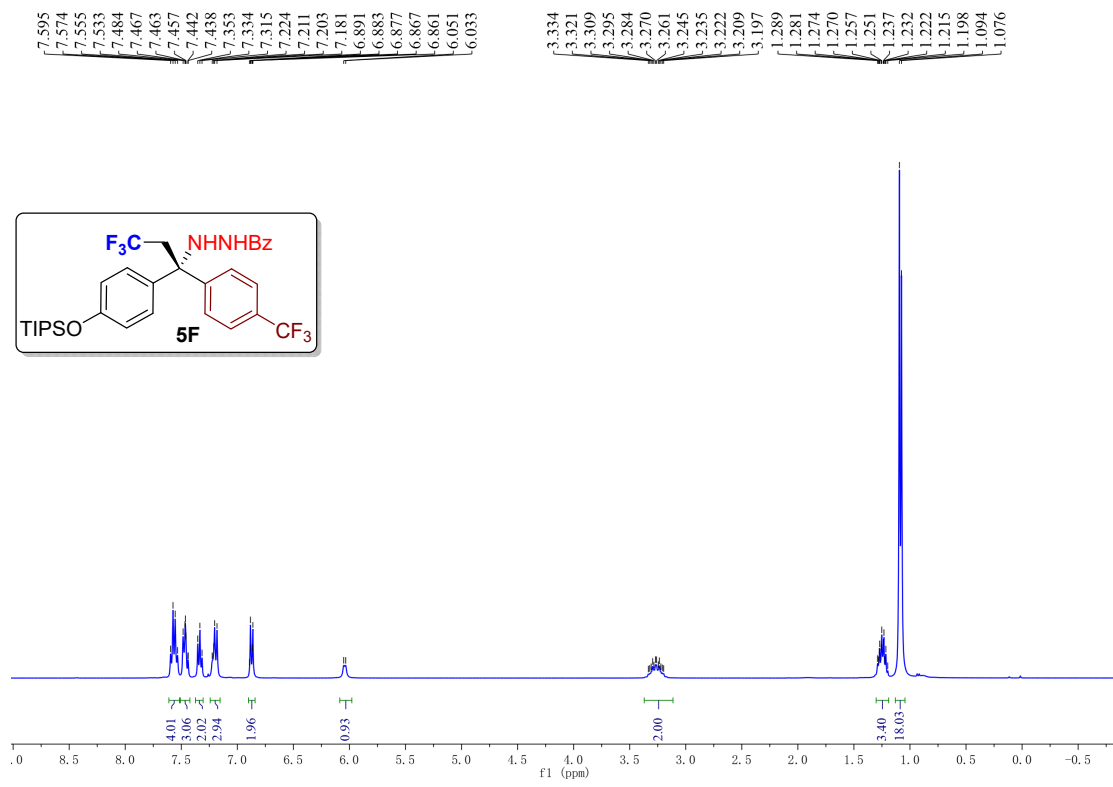


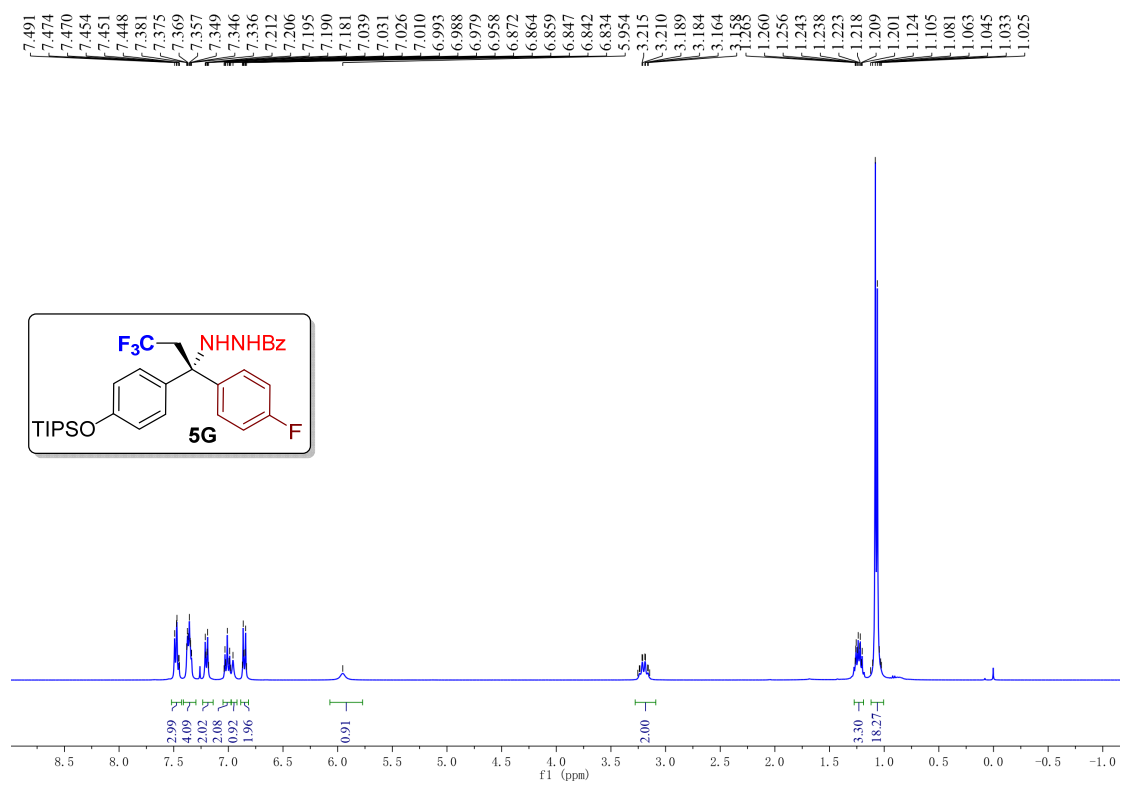
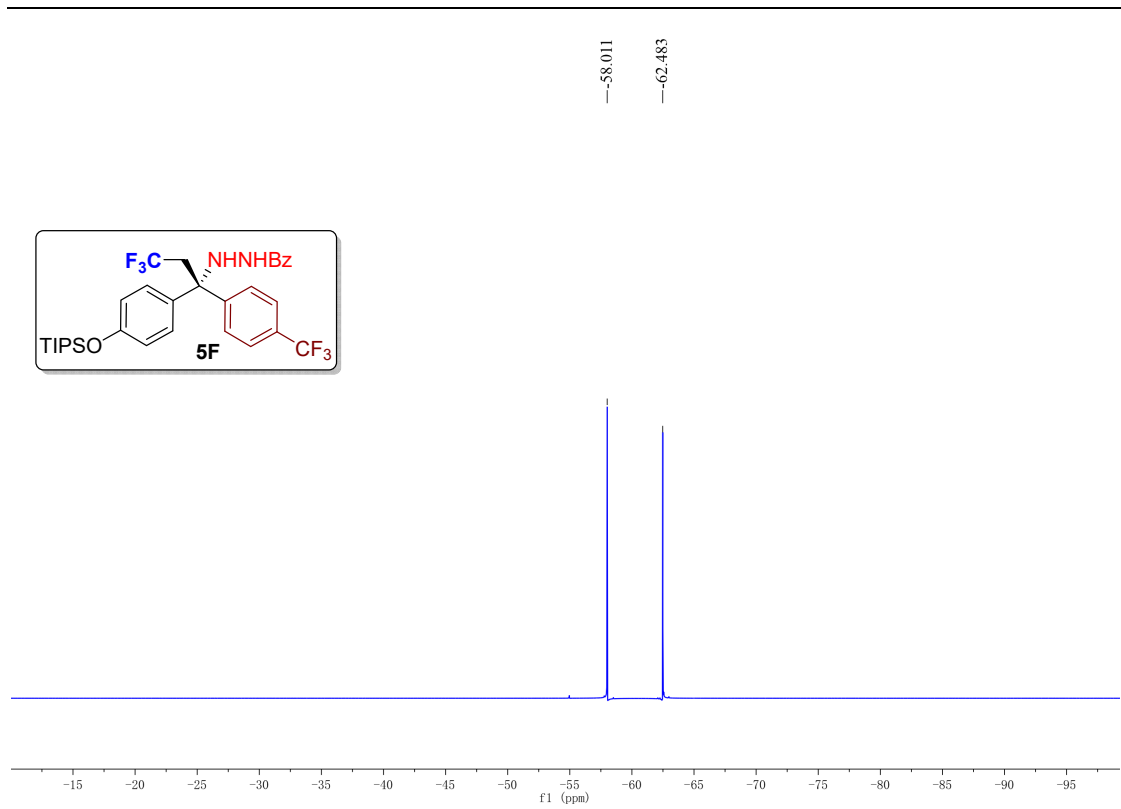


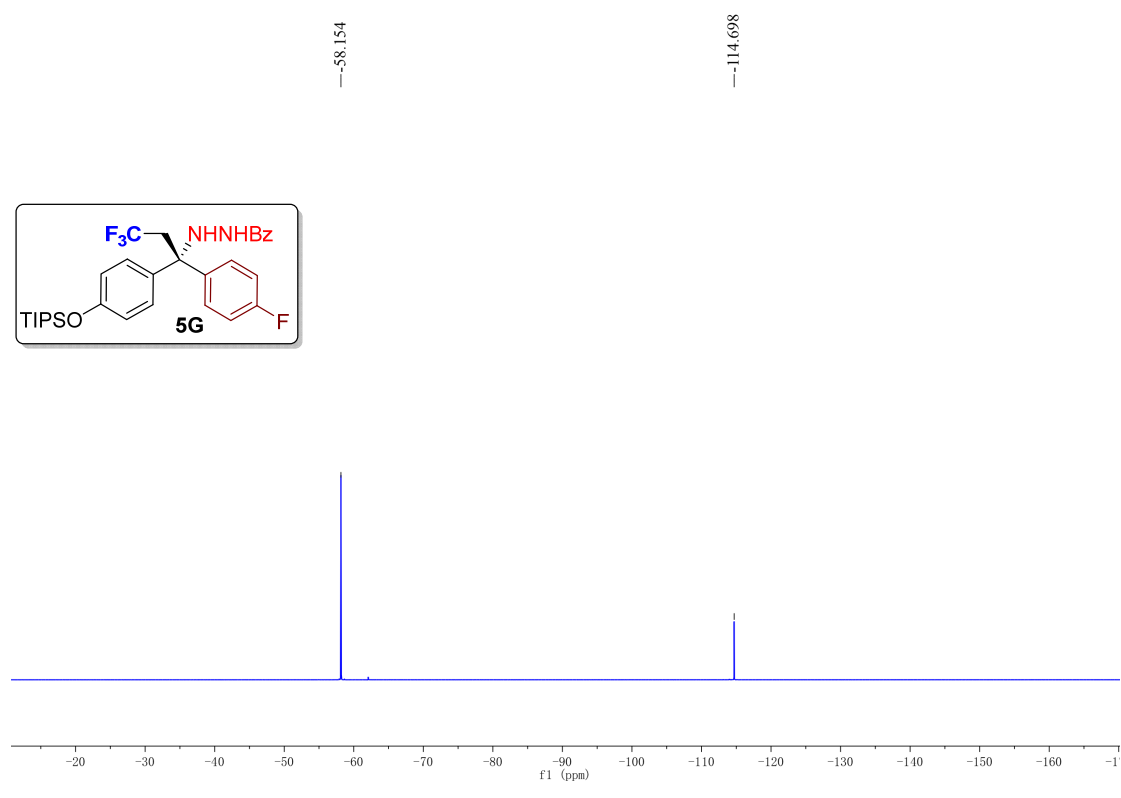
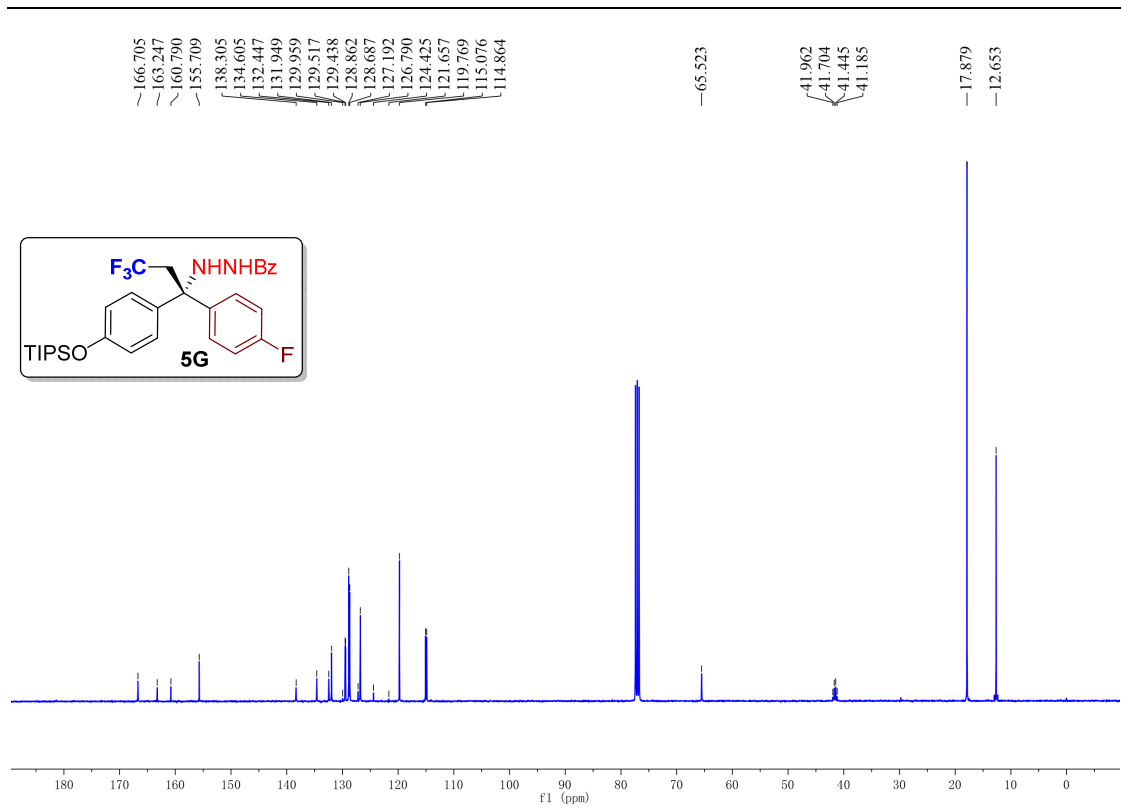
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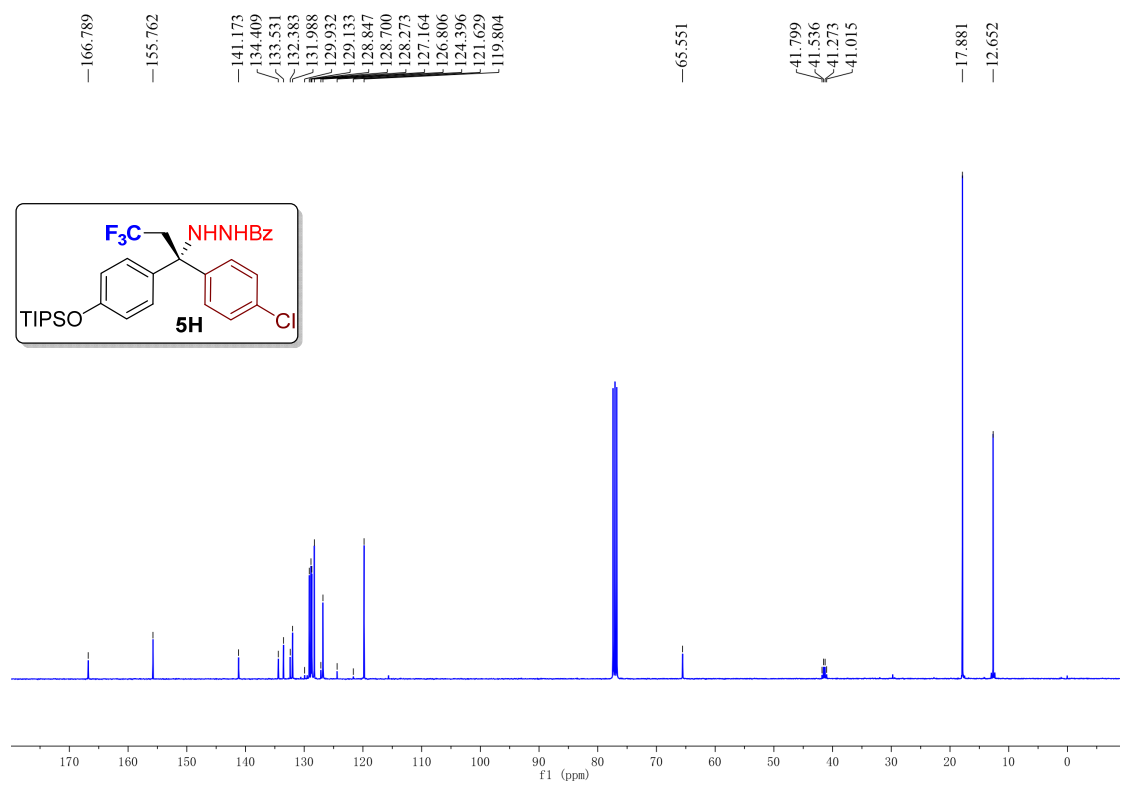
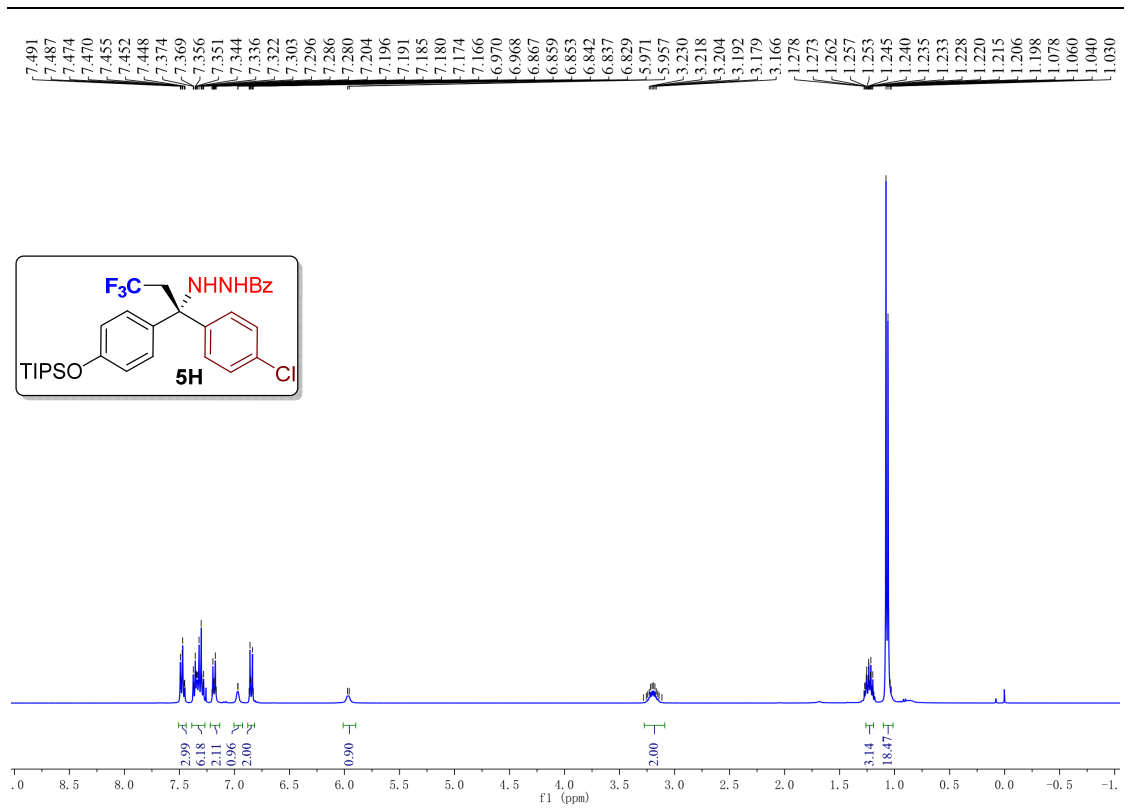




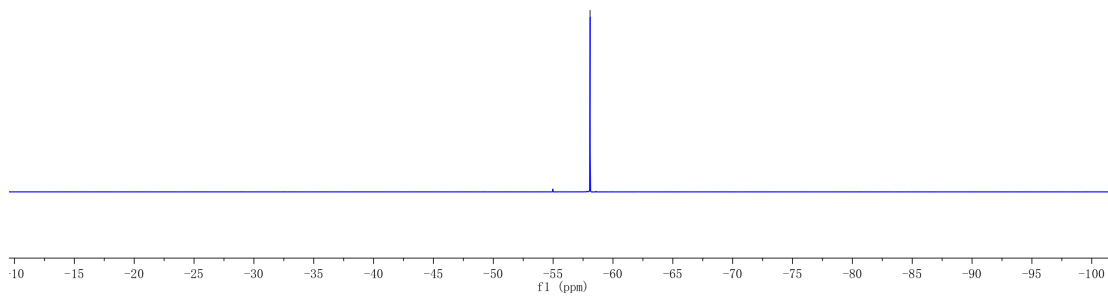
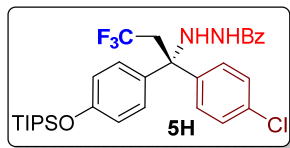




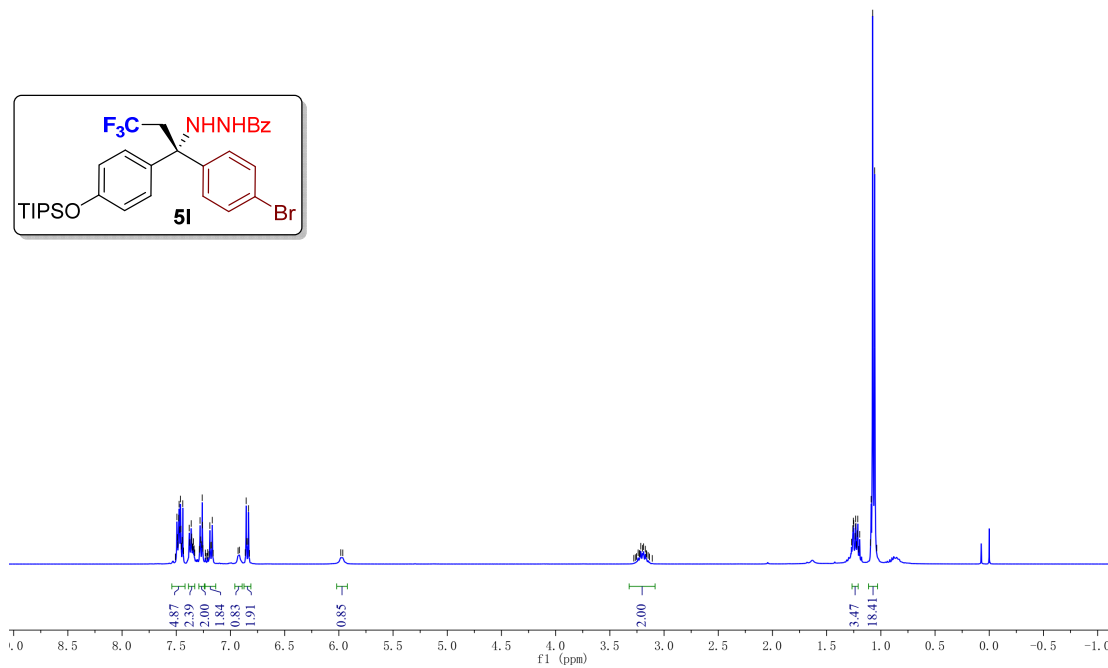
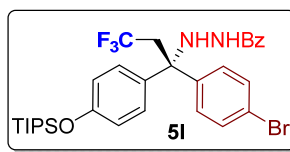


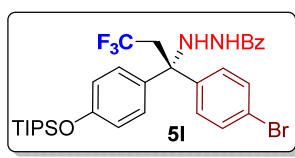
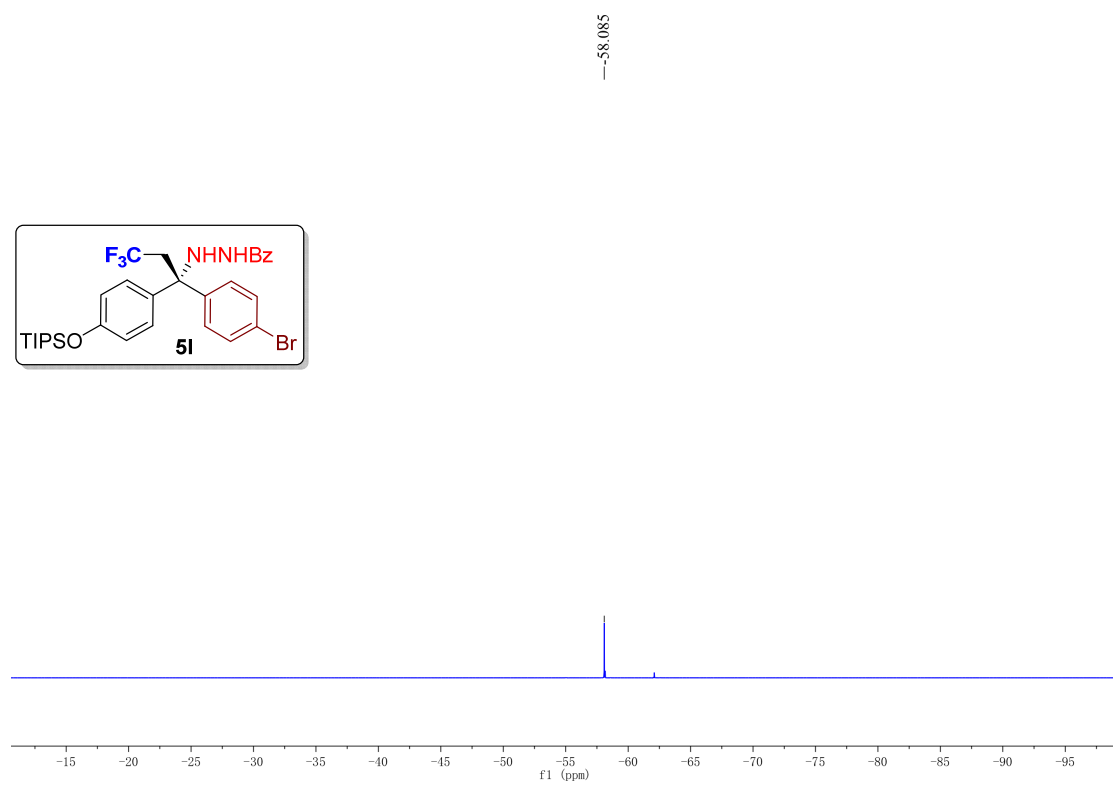
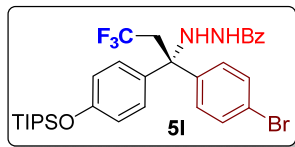
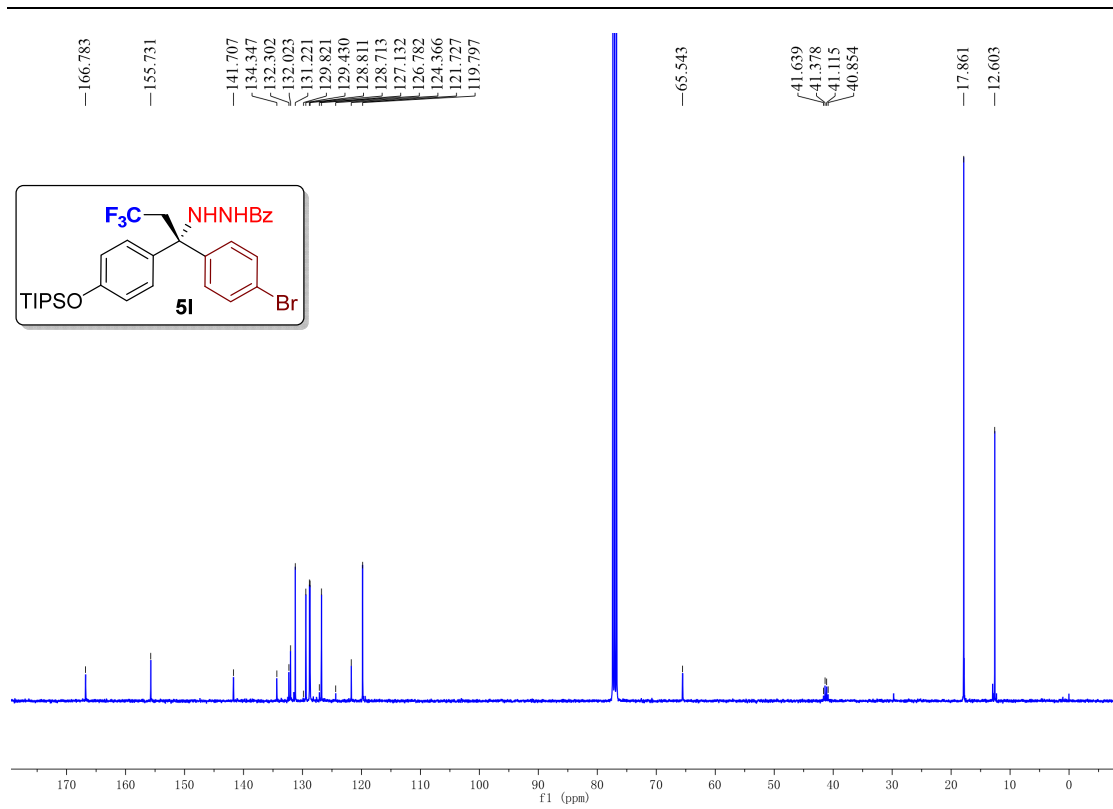


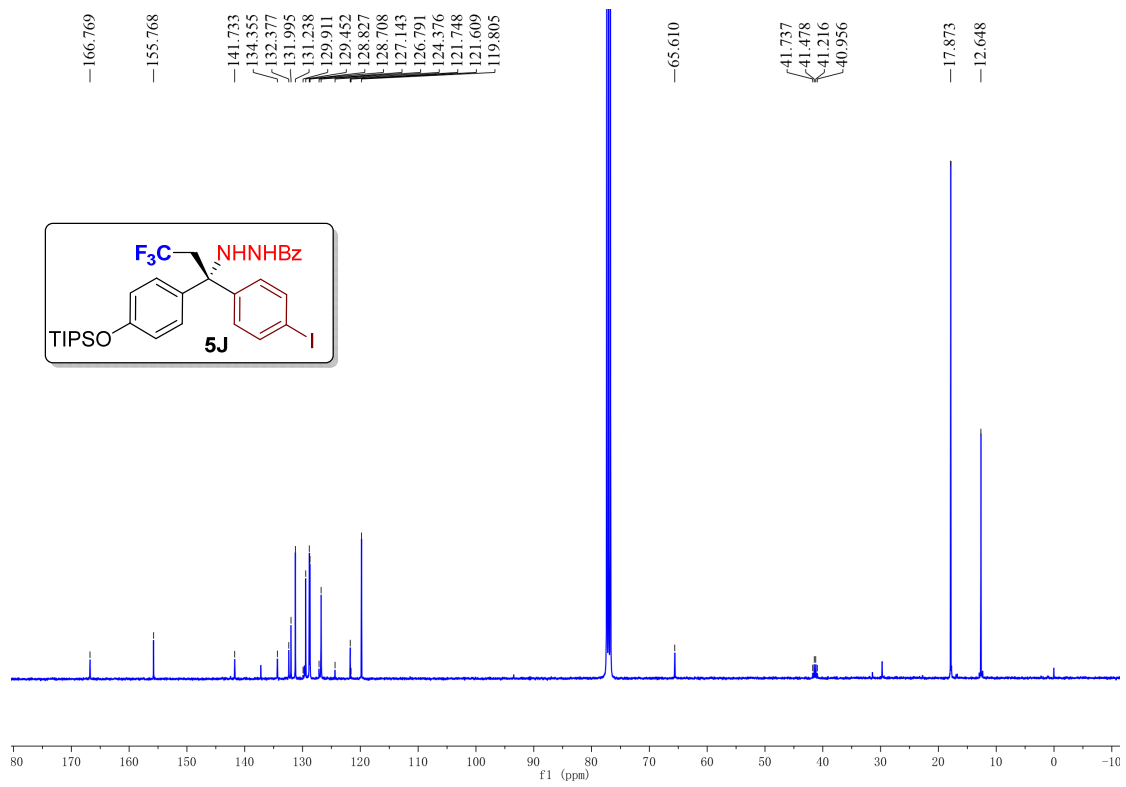
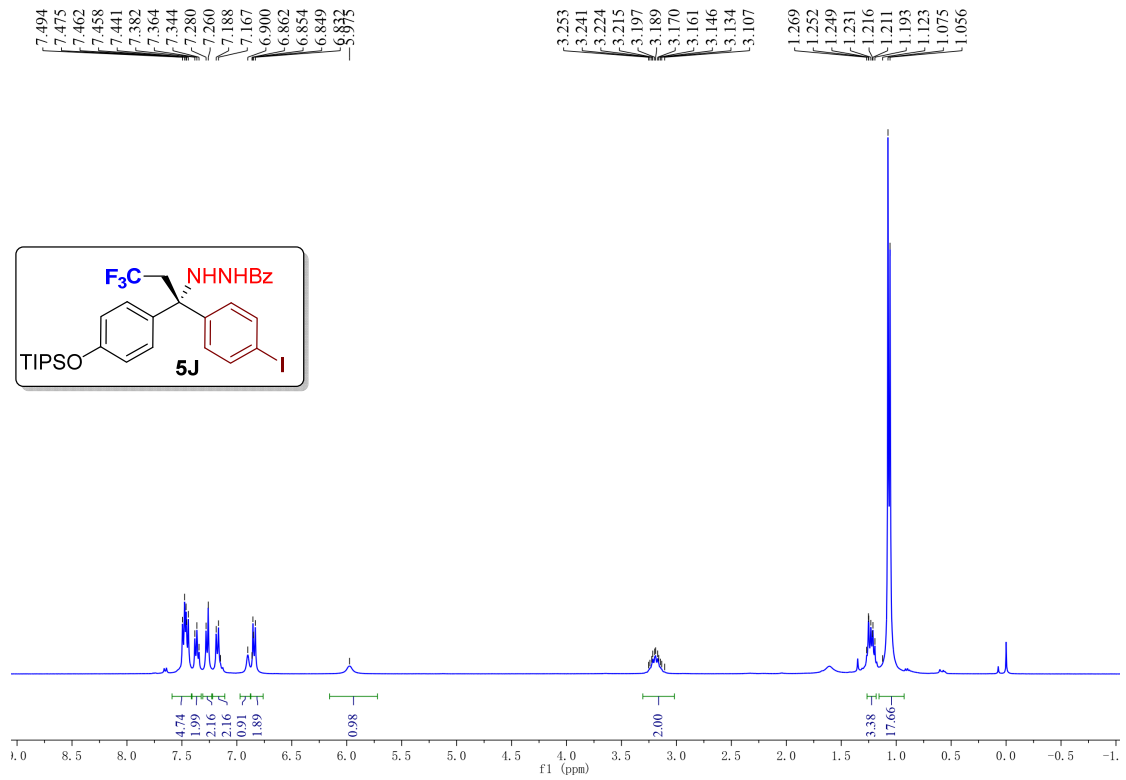
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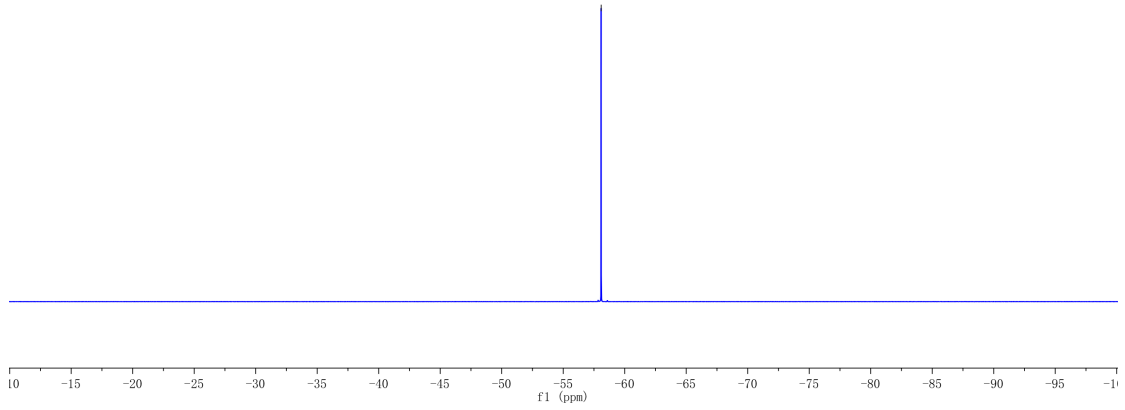
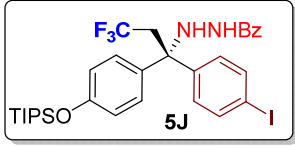
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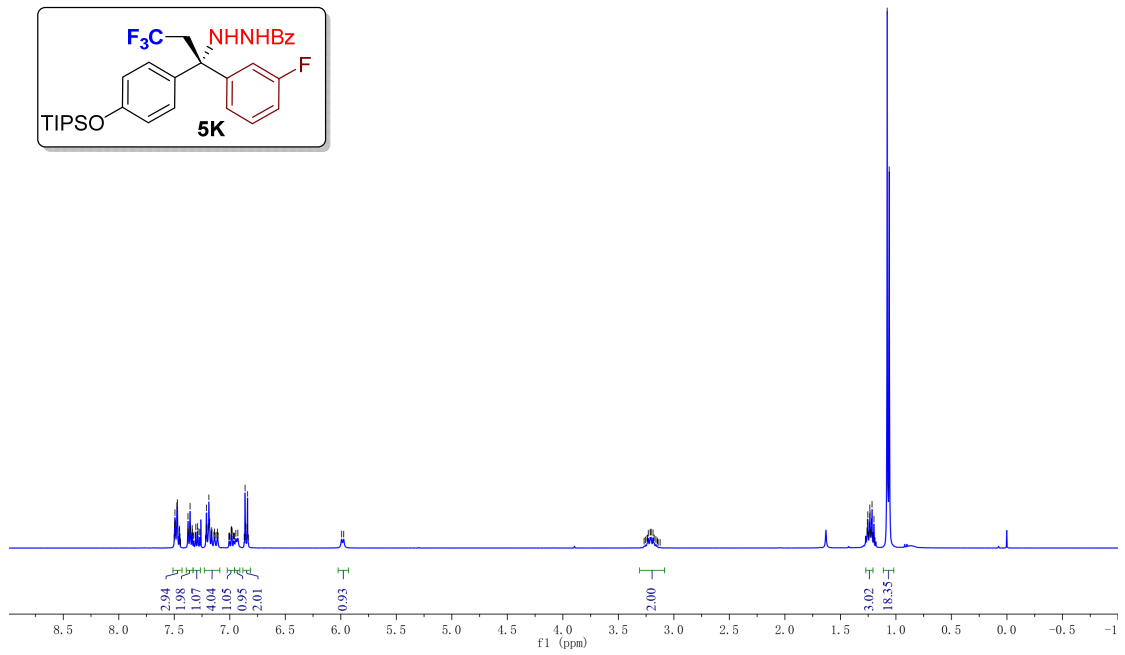
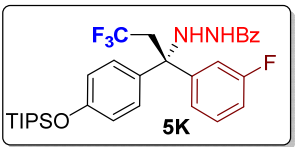


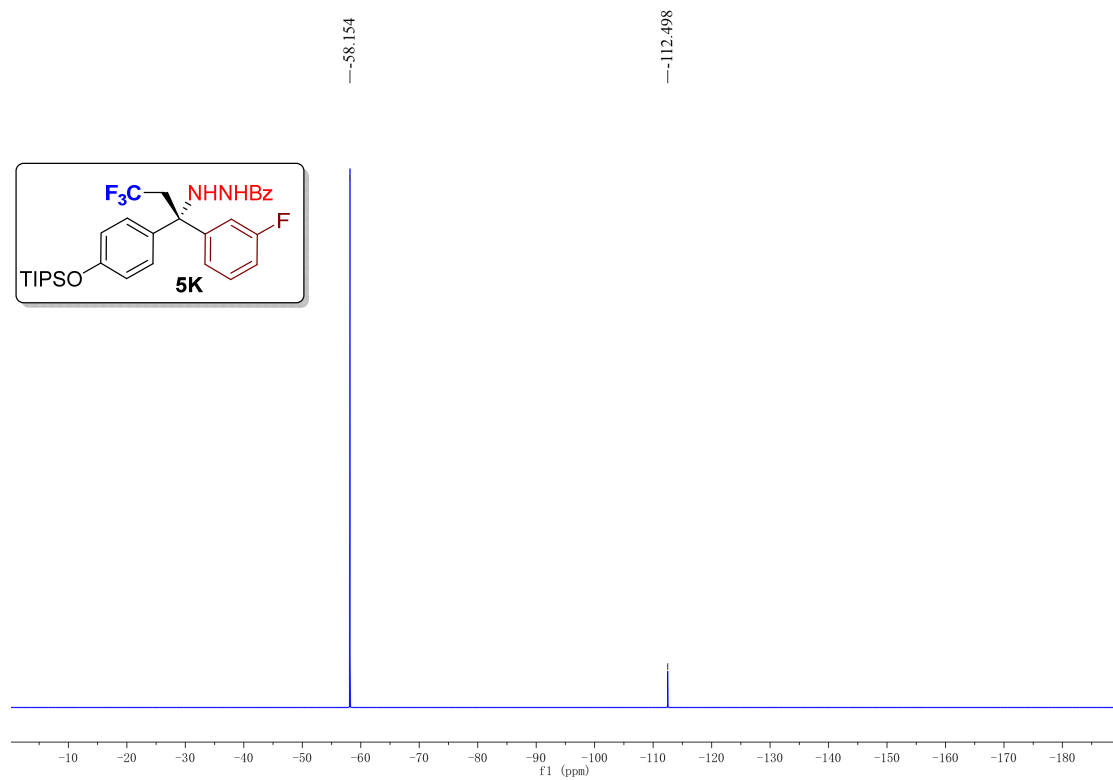
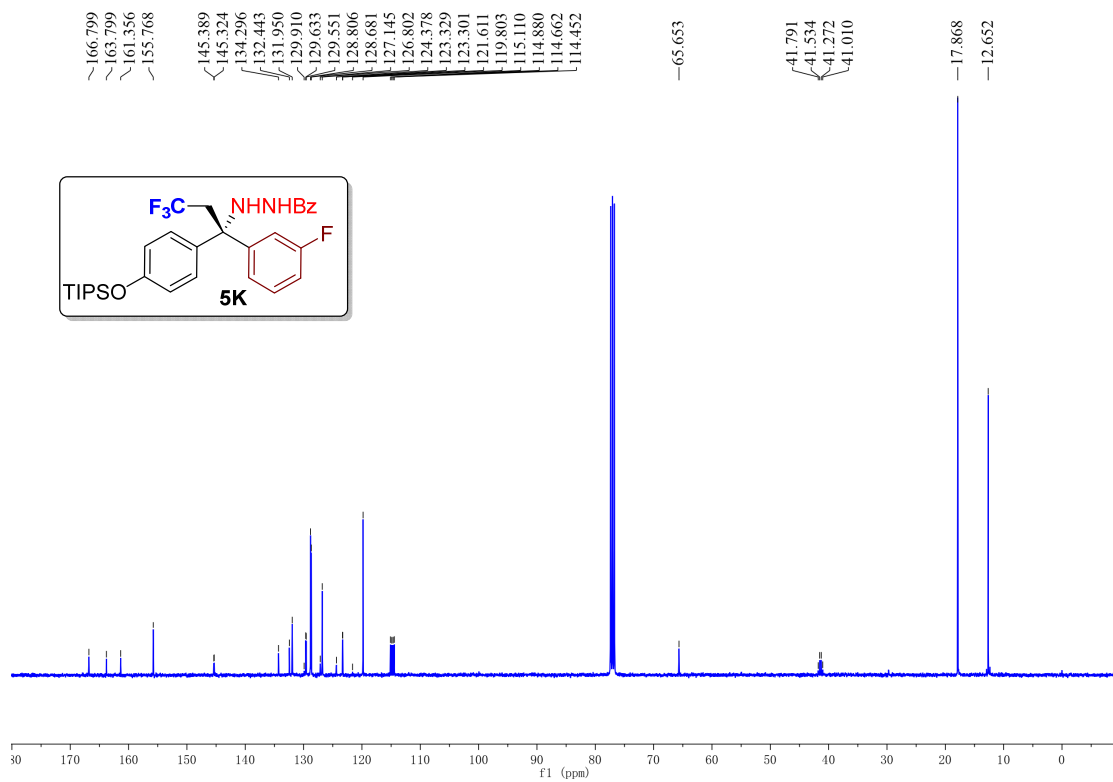


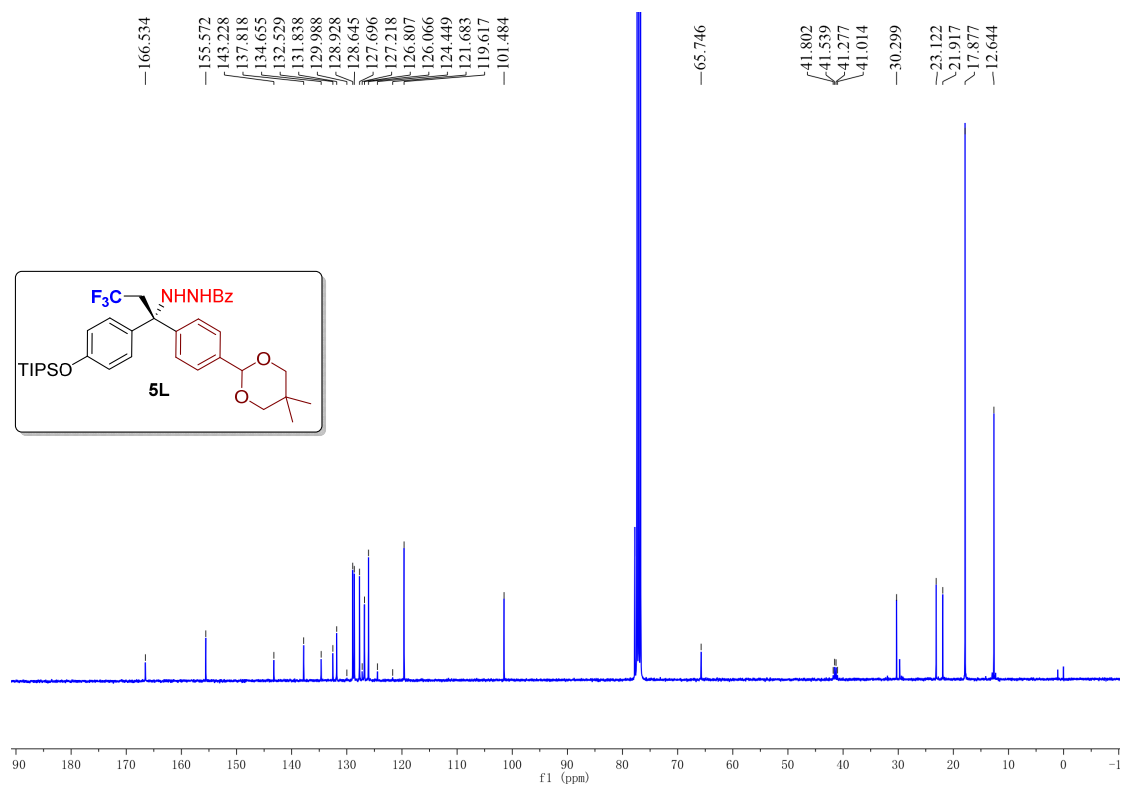
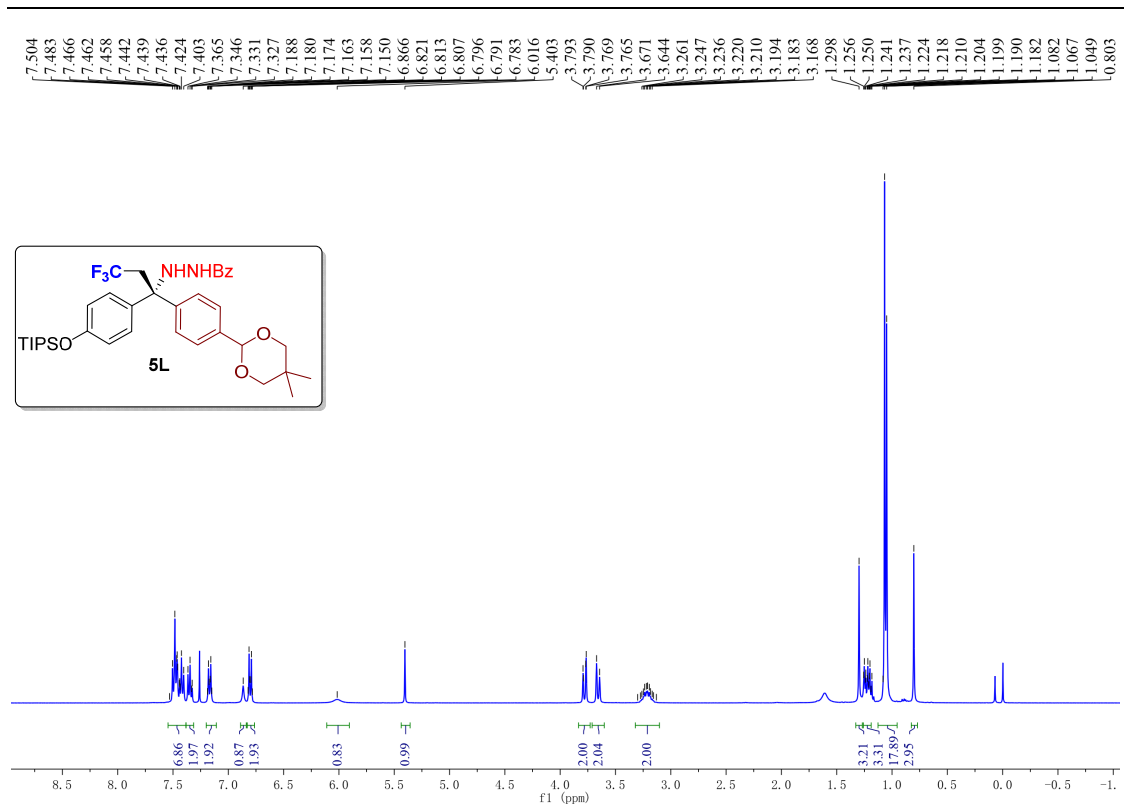
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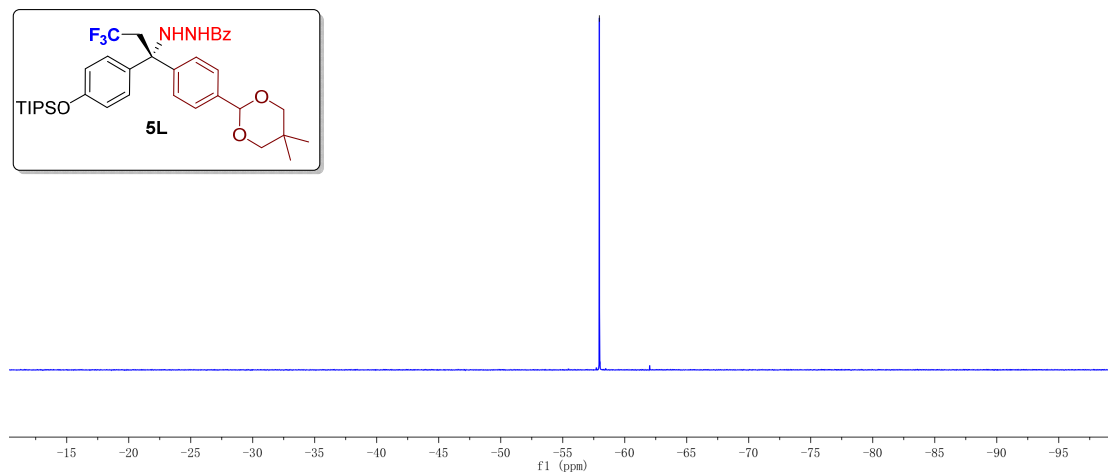
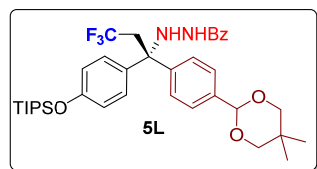


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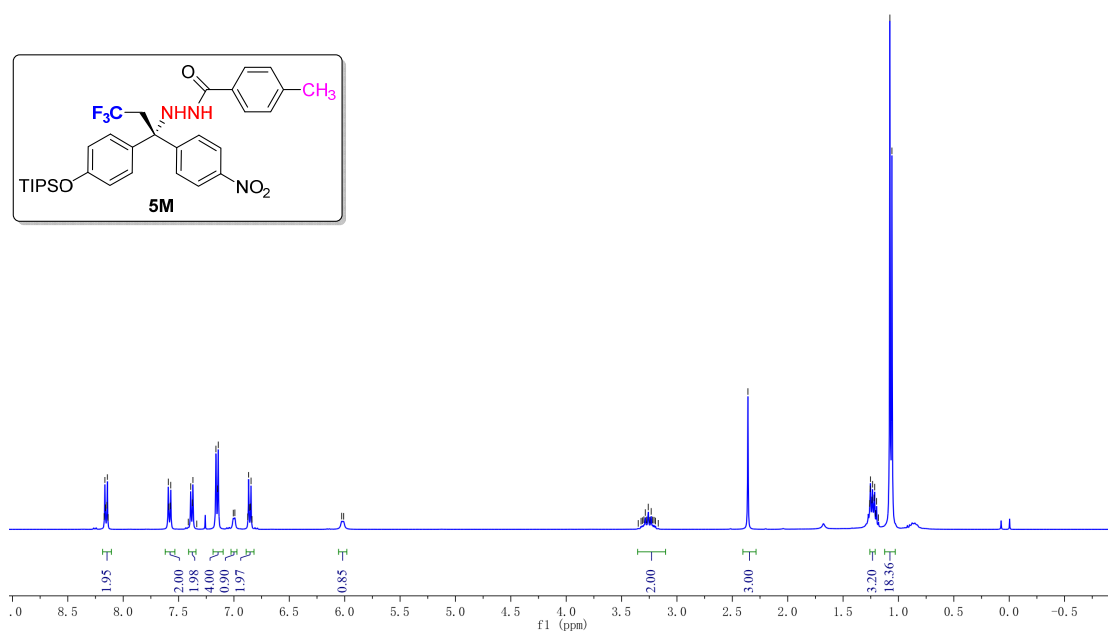
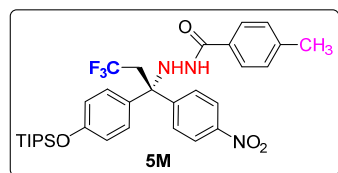


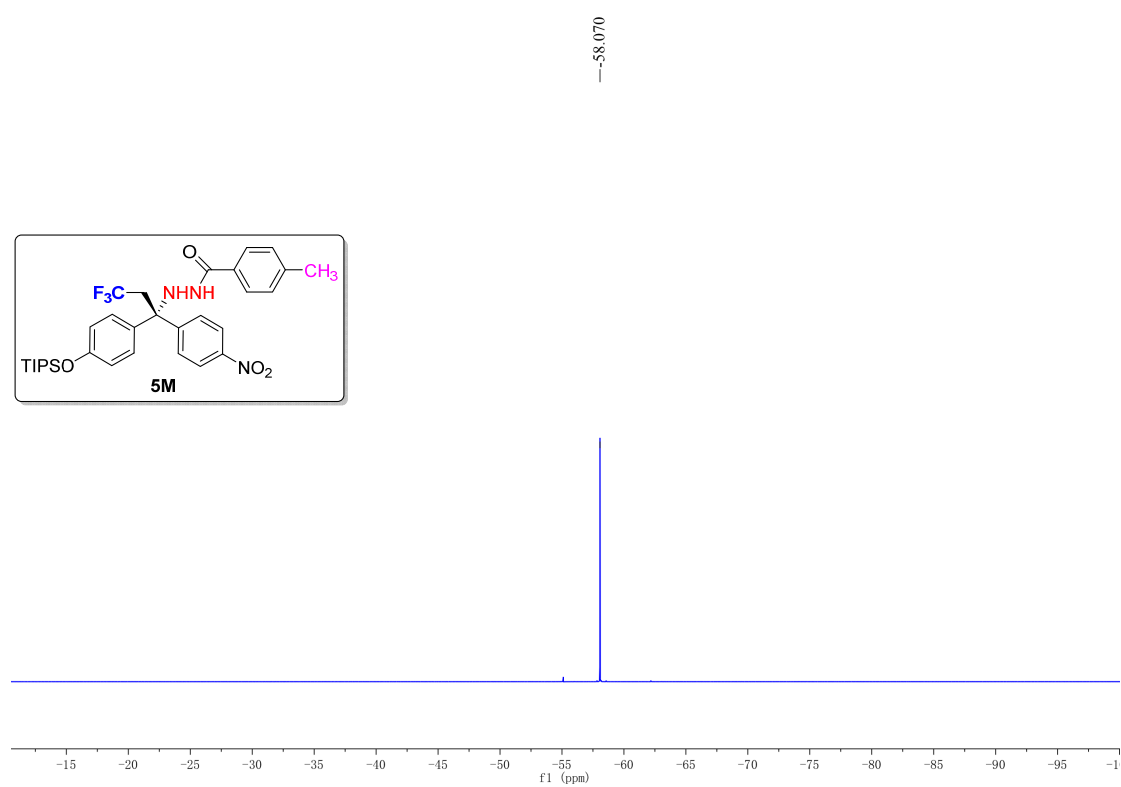
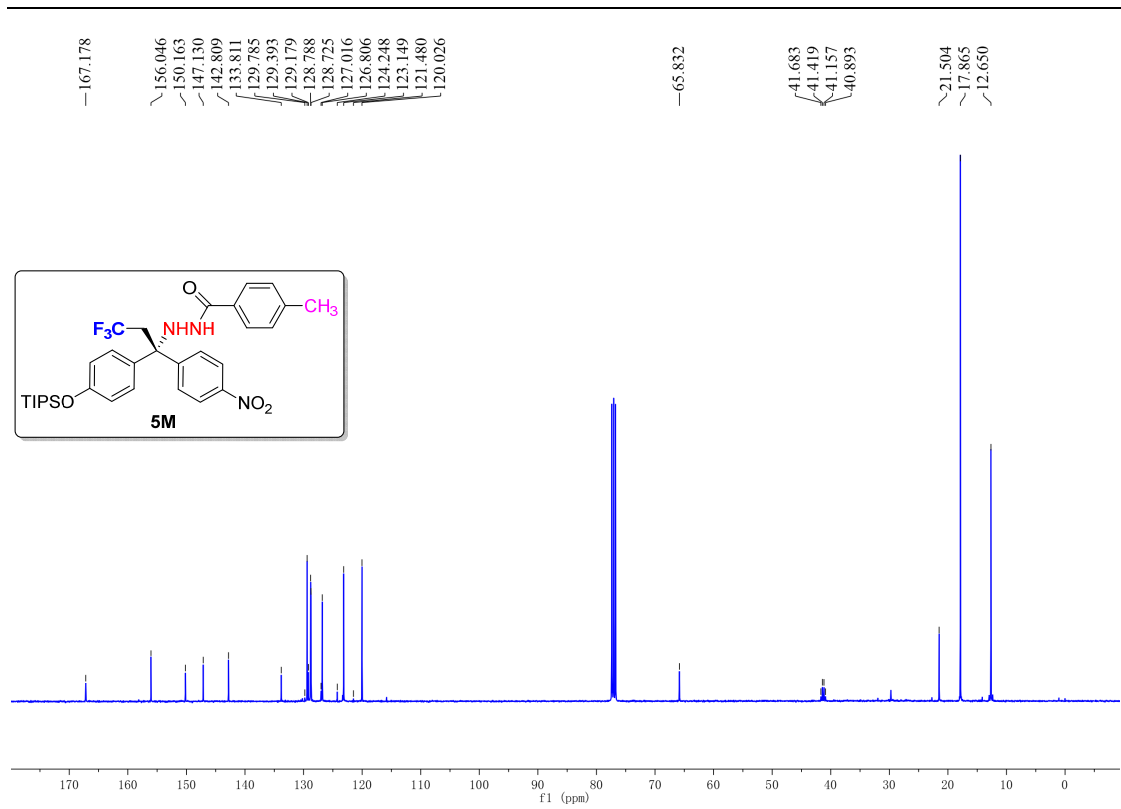


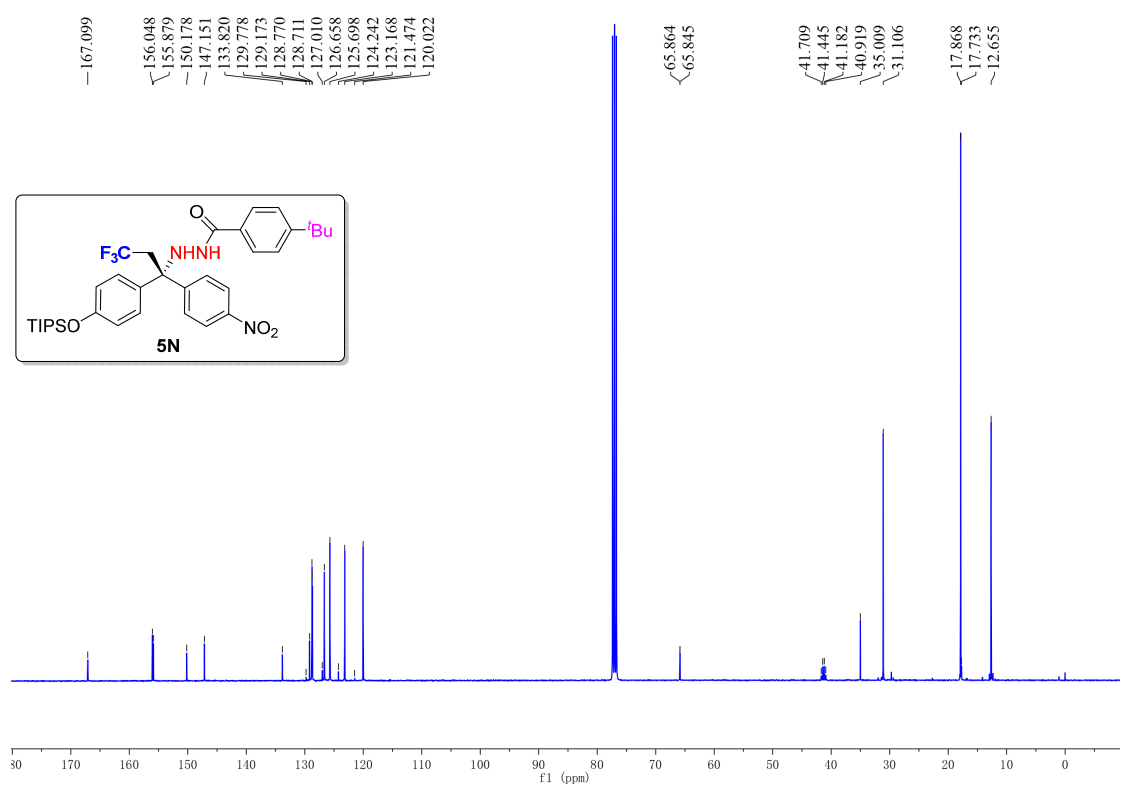
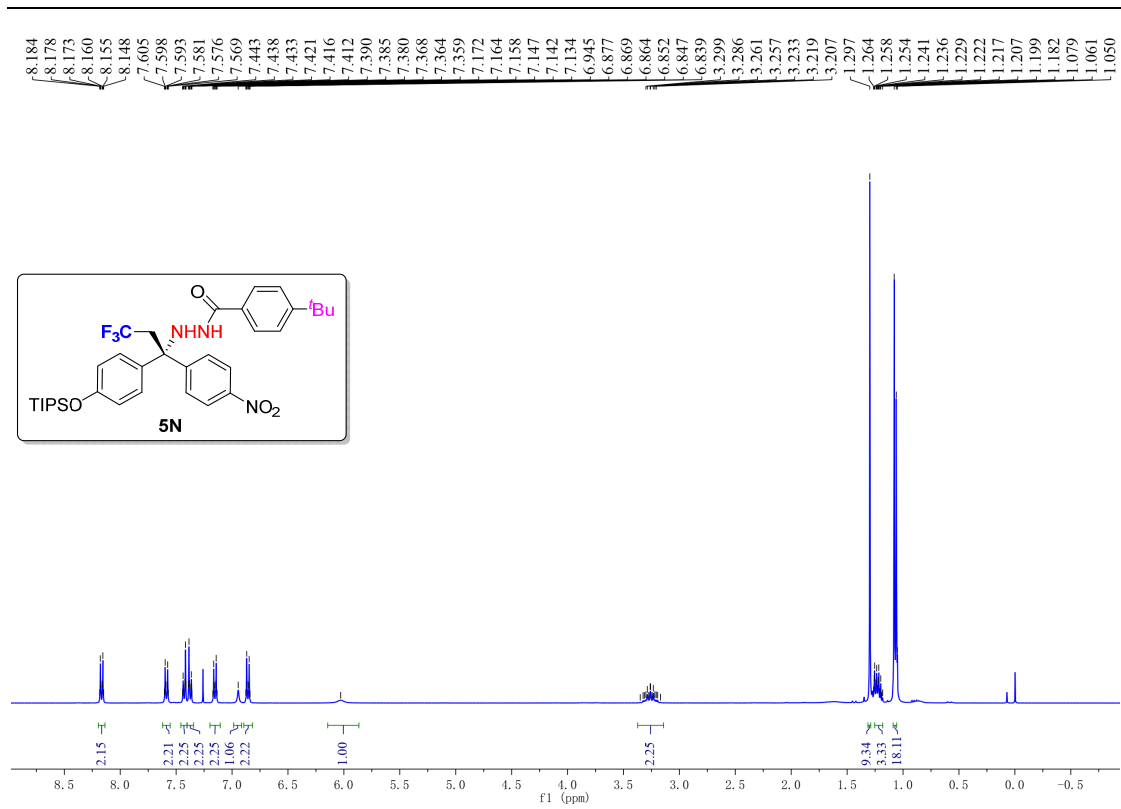


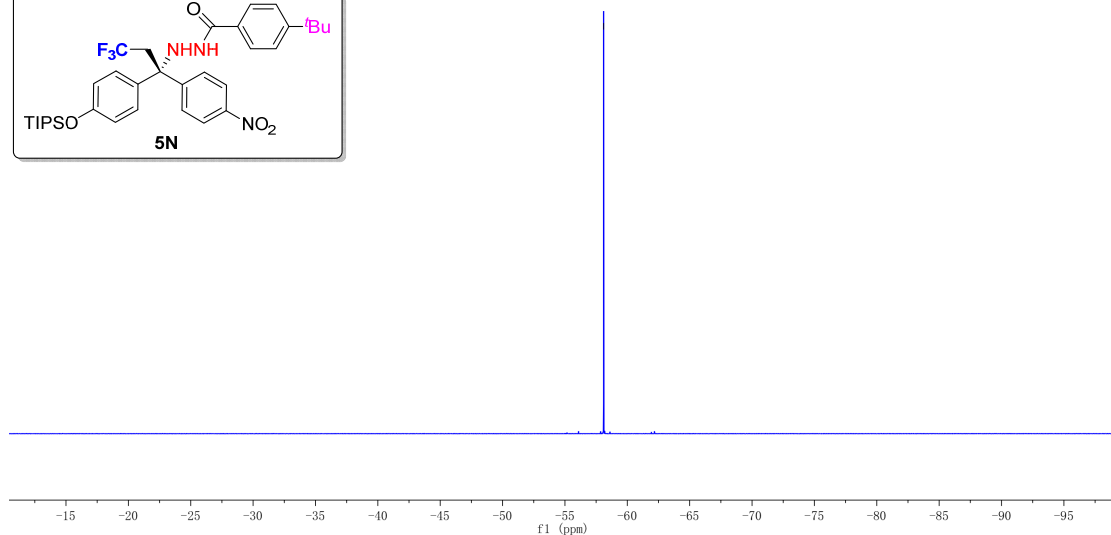
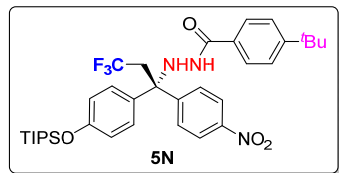


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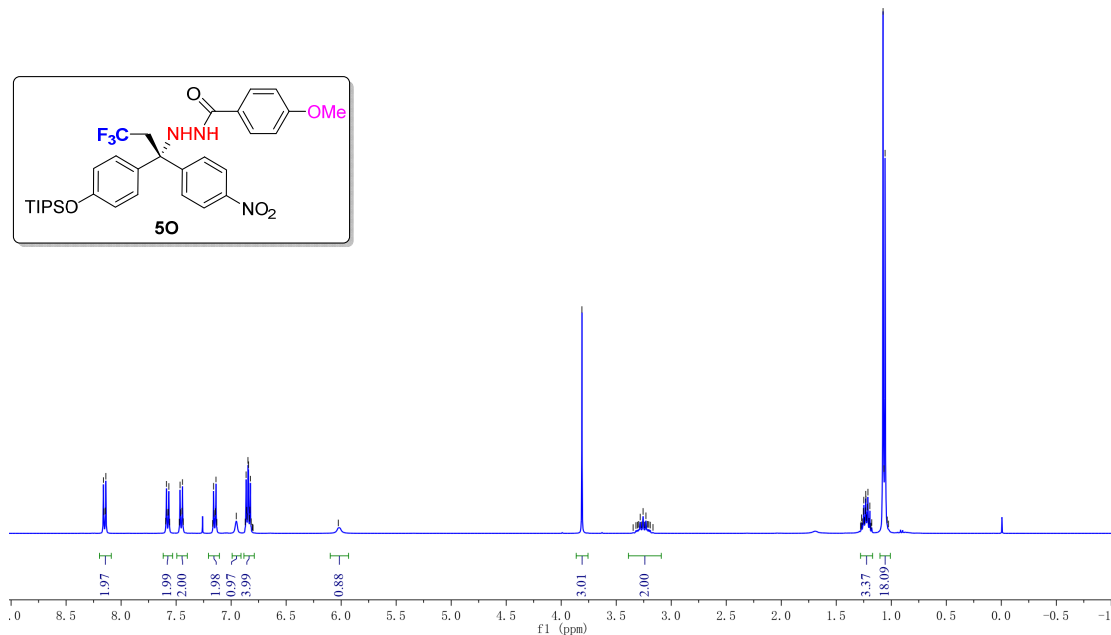
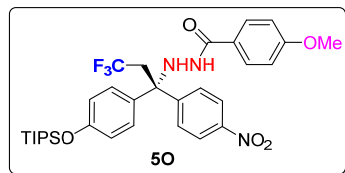


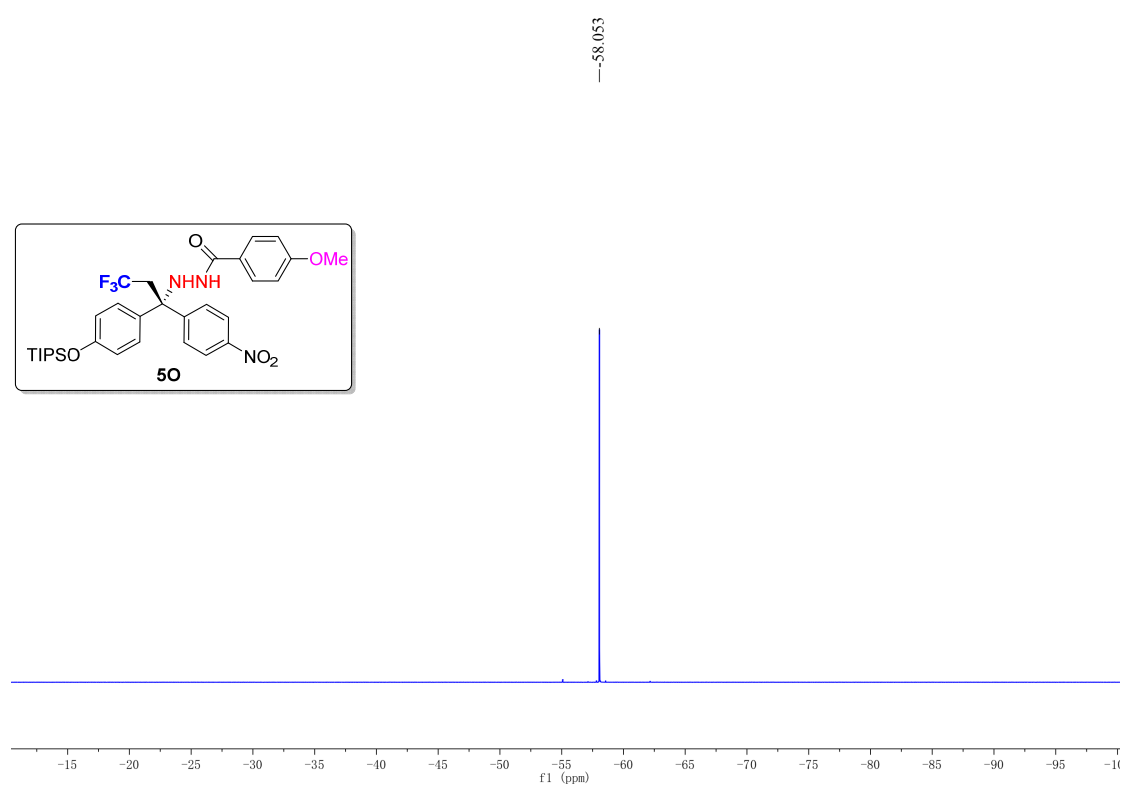
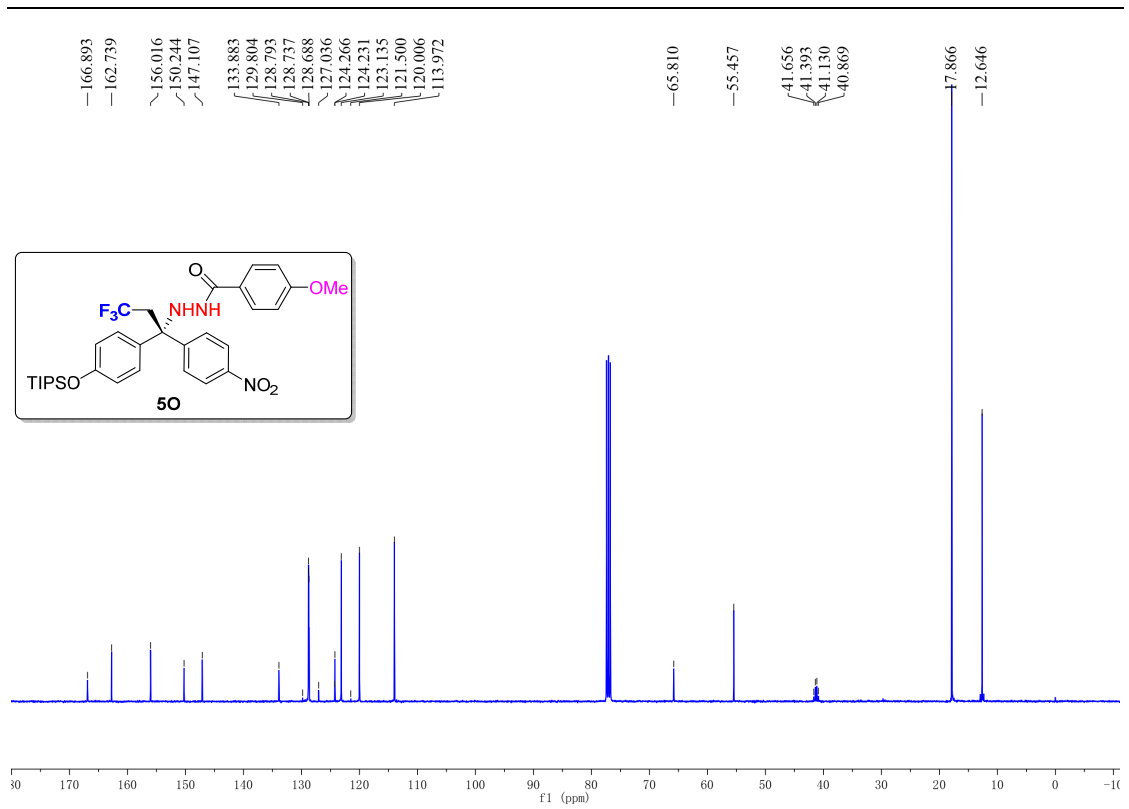


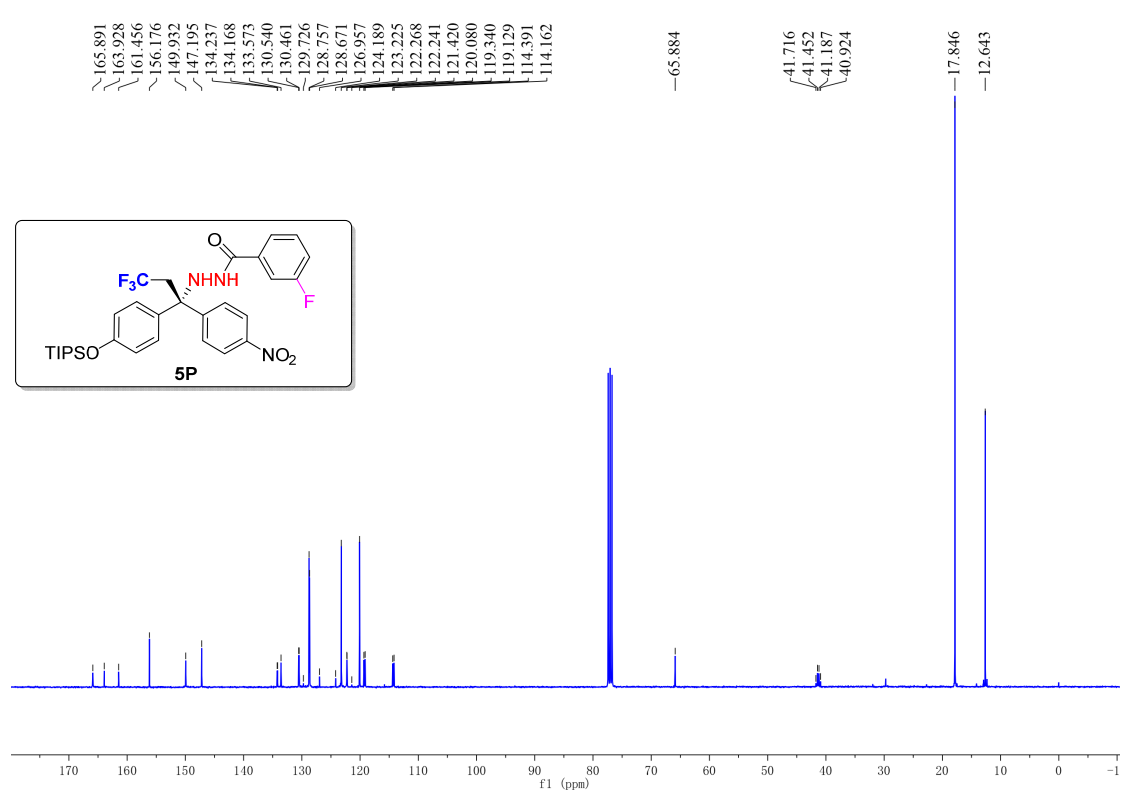
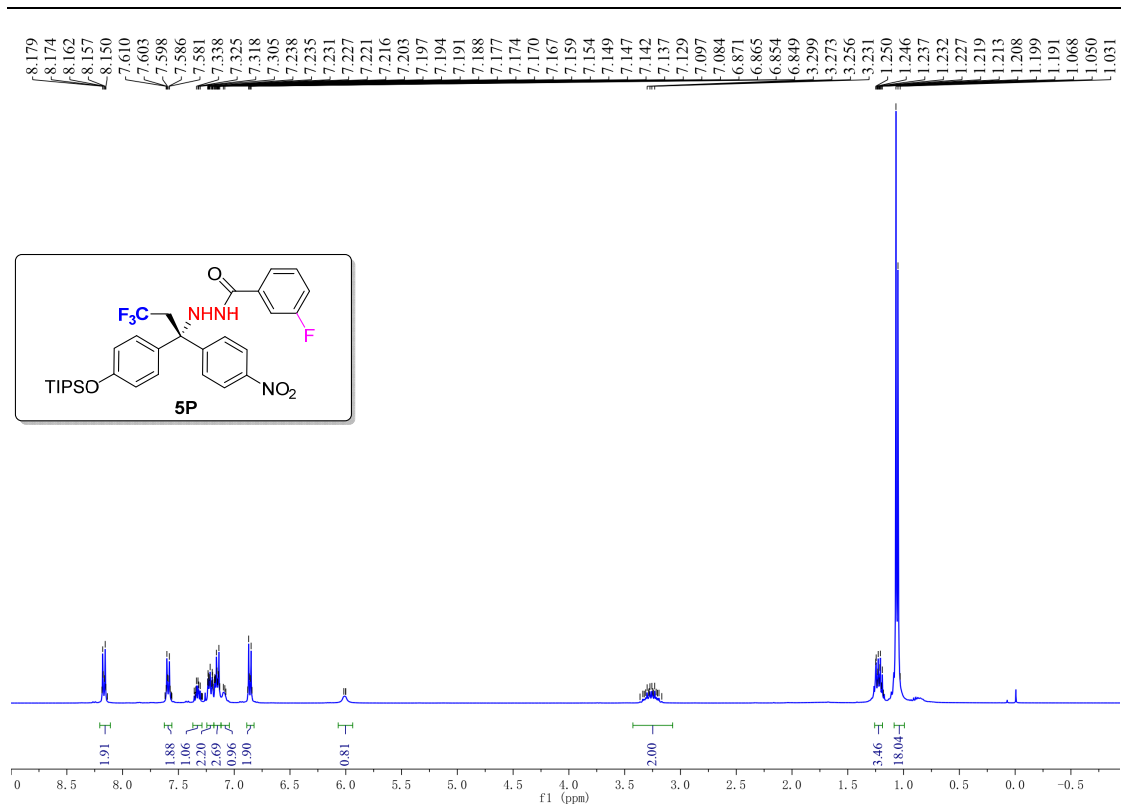


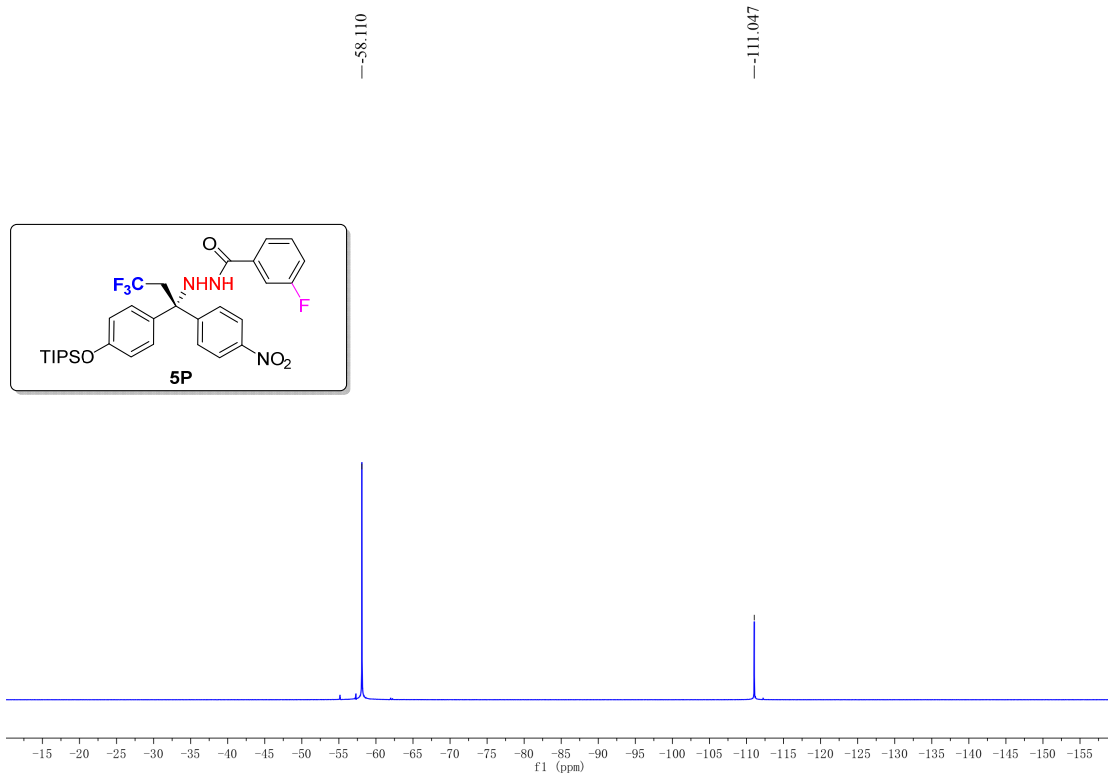


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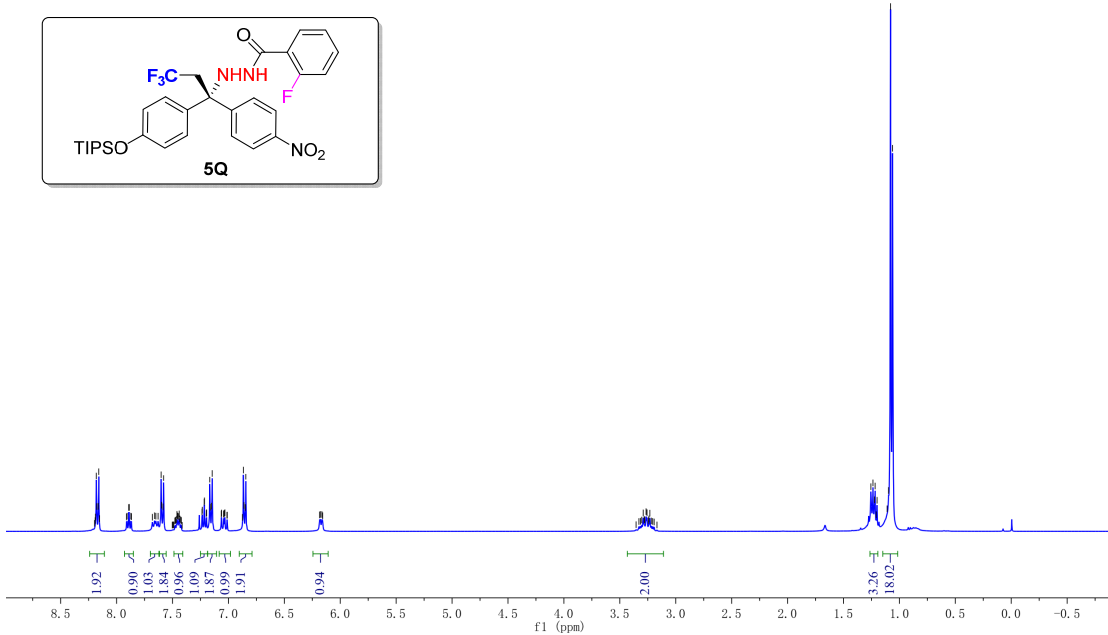


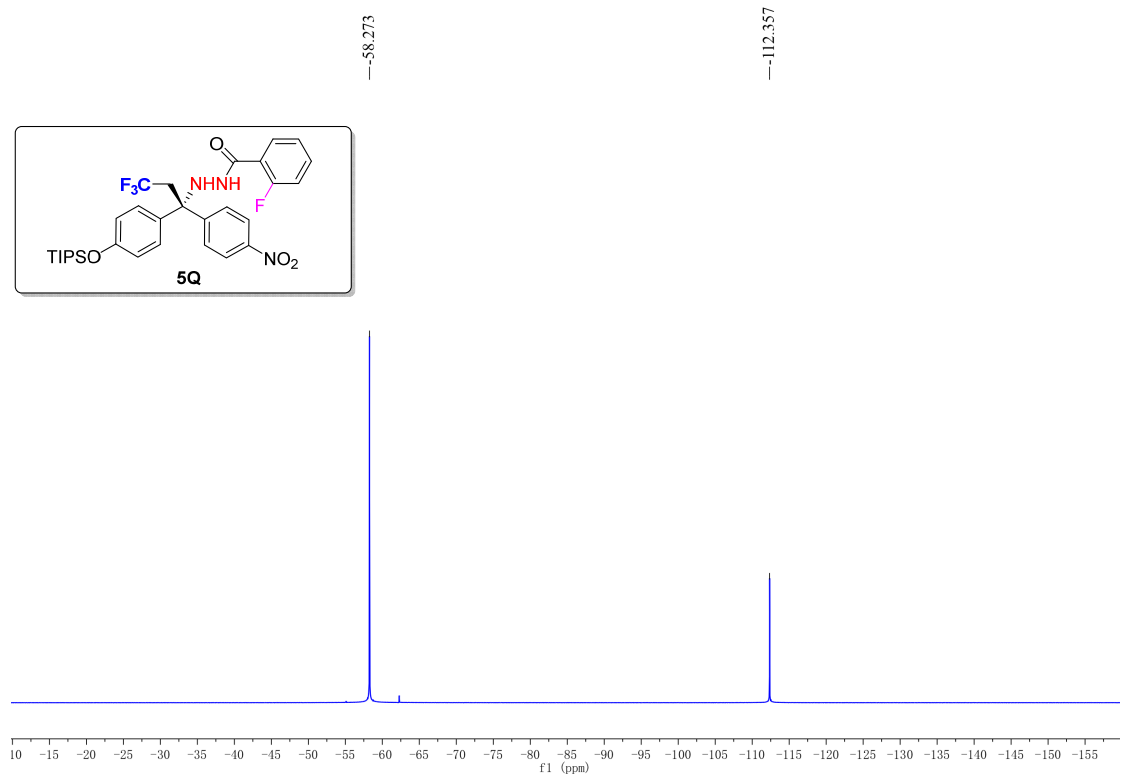
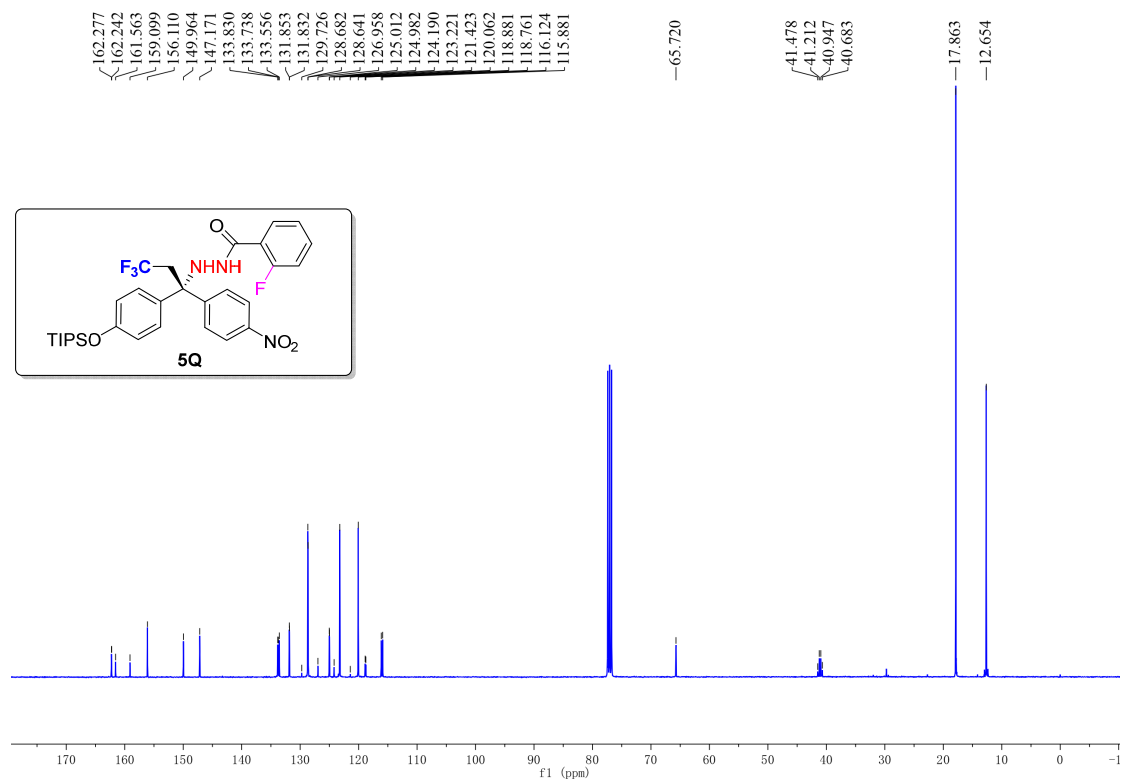


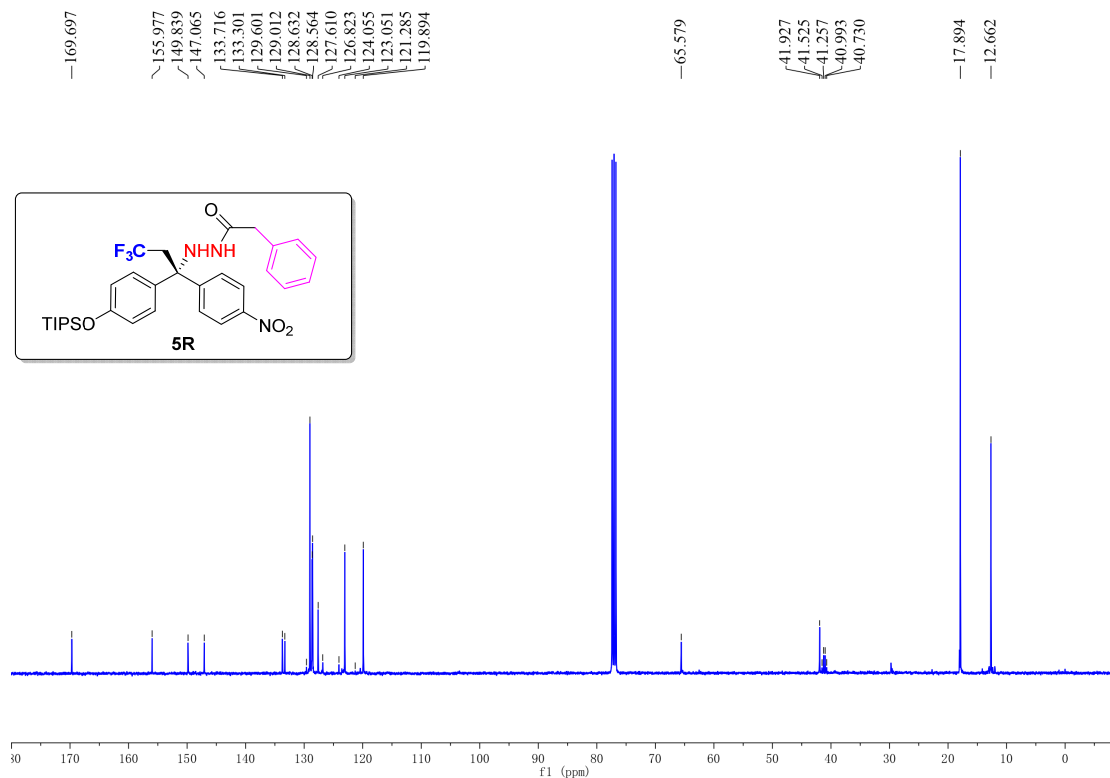
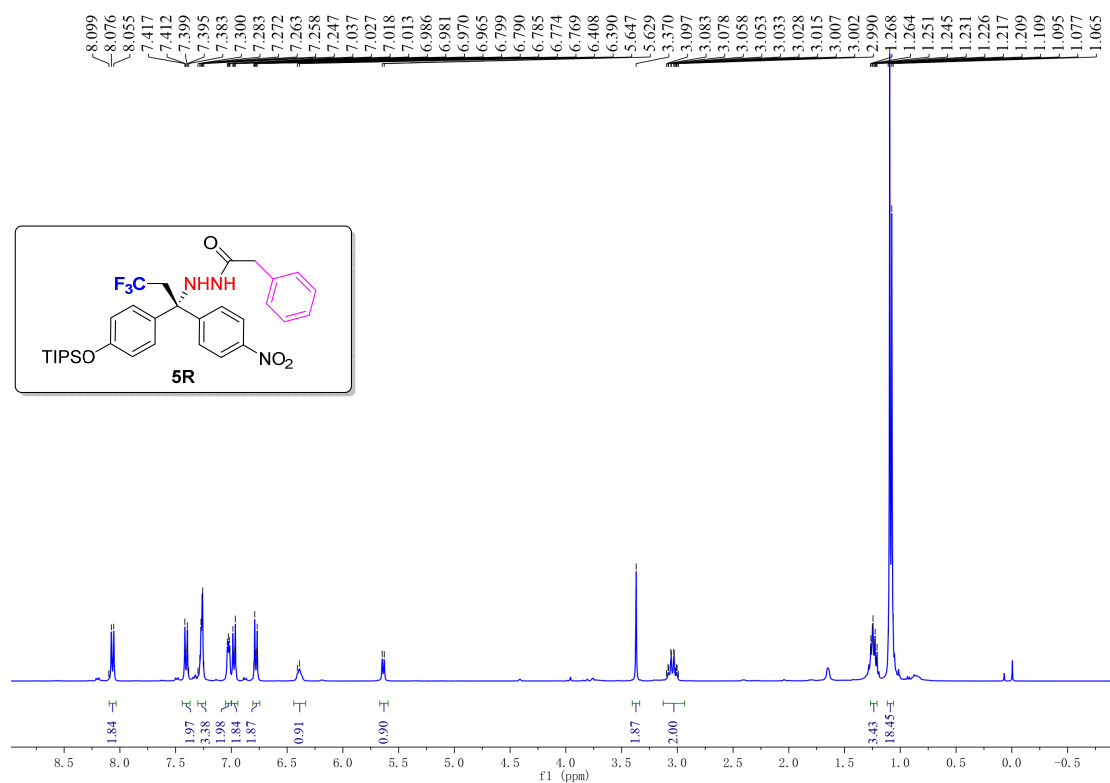




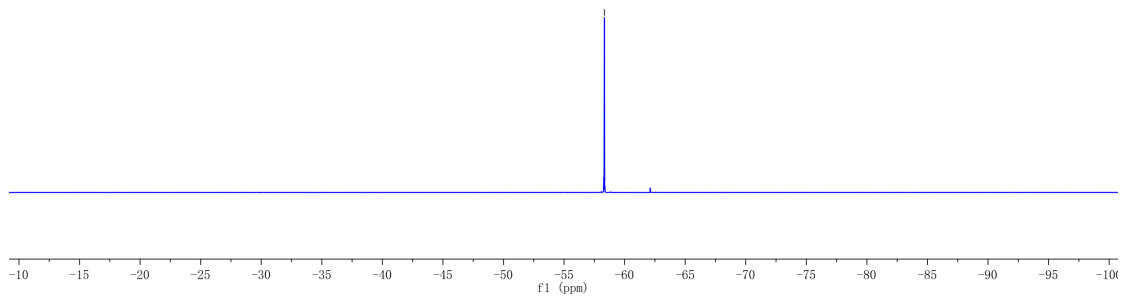
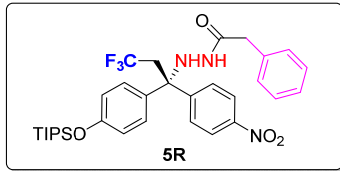
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7.217
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7.040
7.034
7.031
7.013
7.010
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6.861
6.849
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6.178
6.164
6.158
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1.222
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1.061



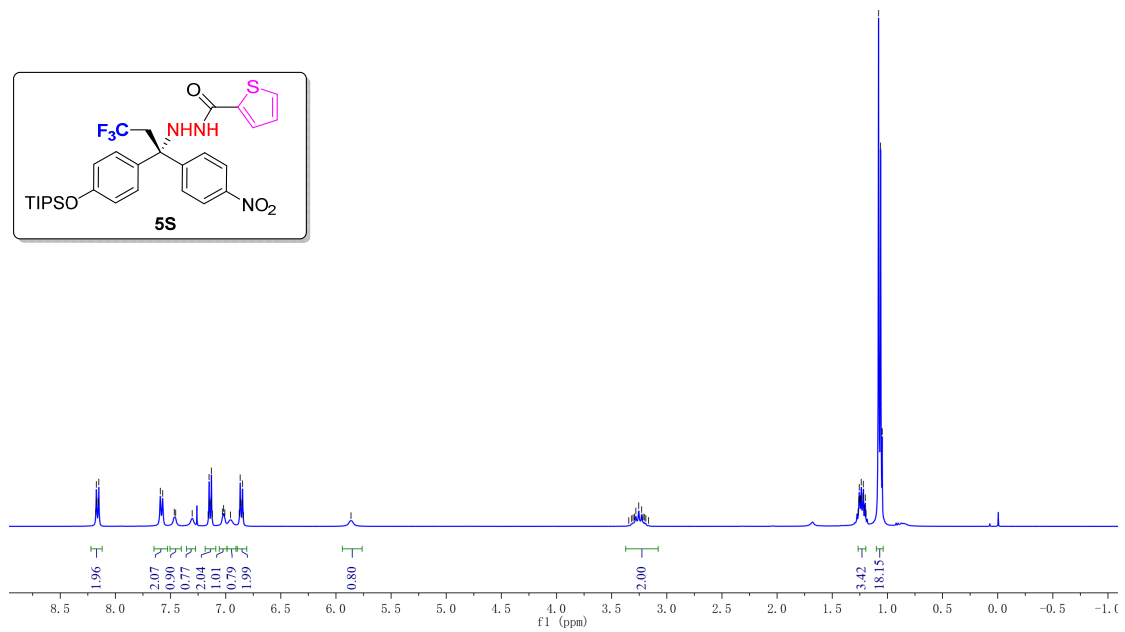
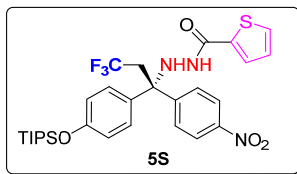


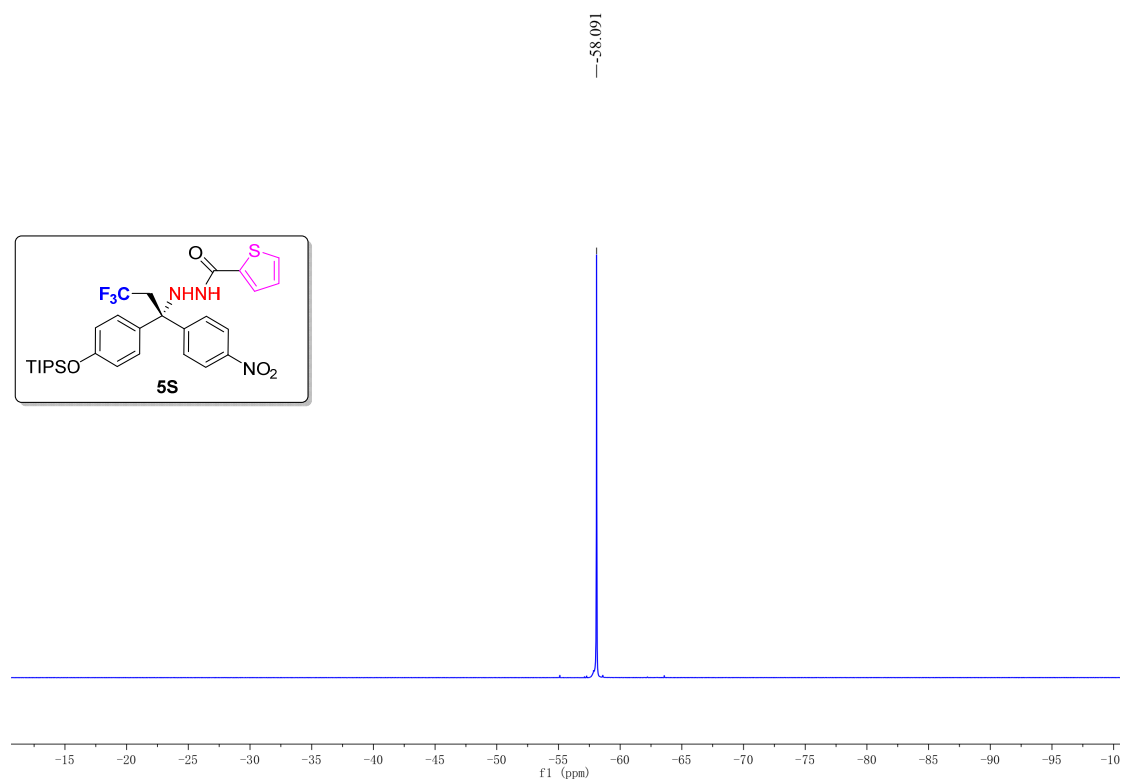
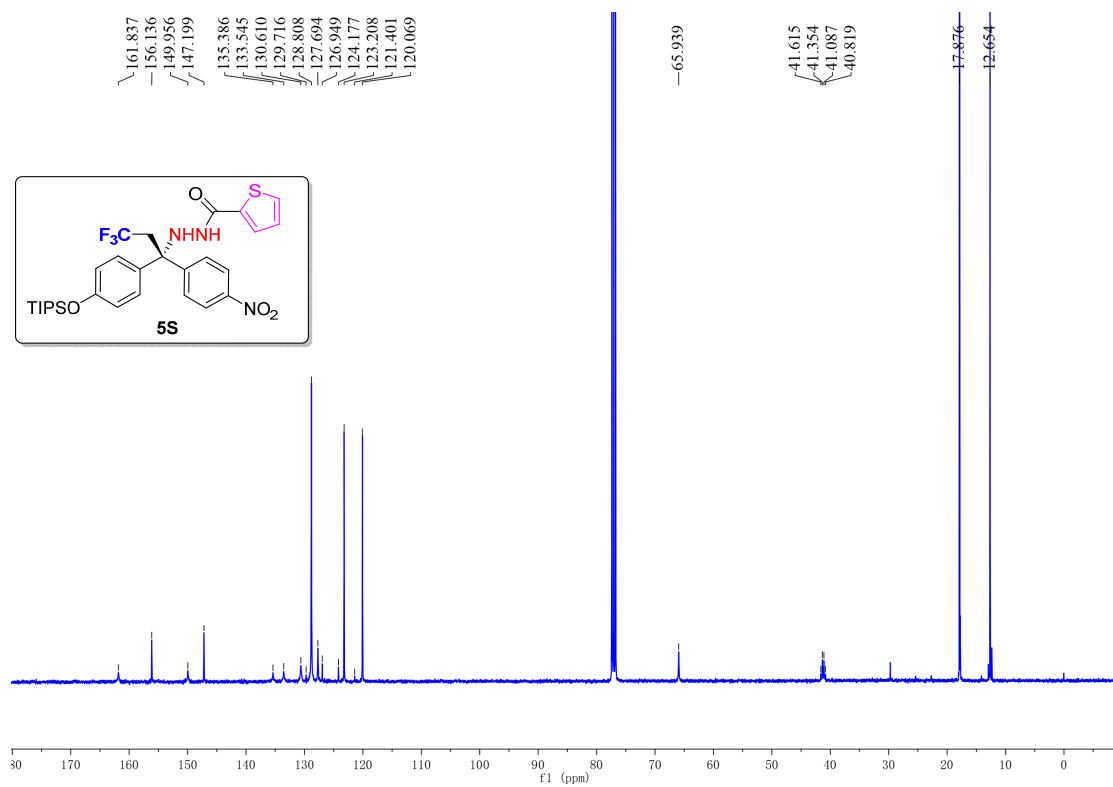


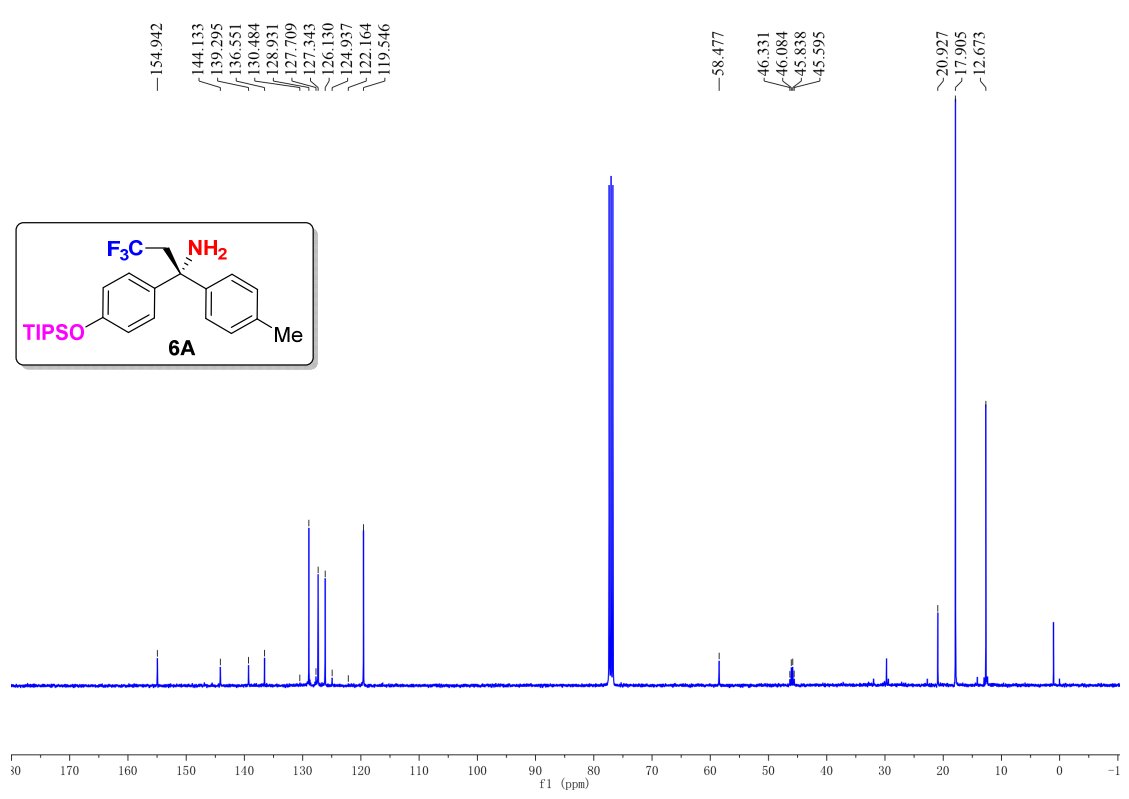
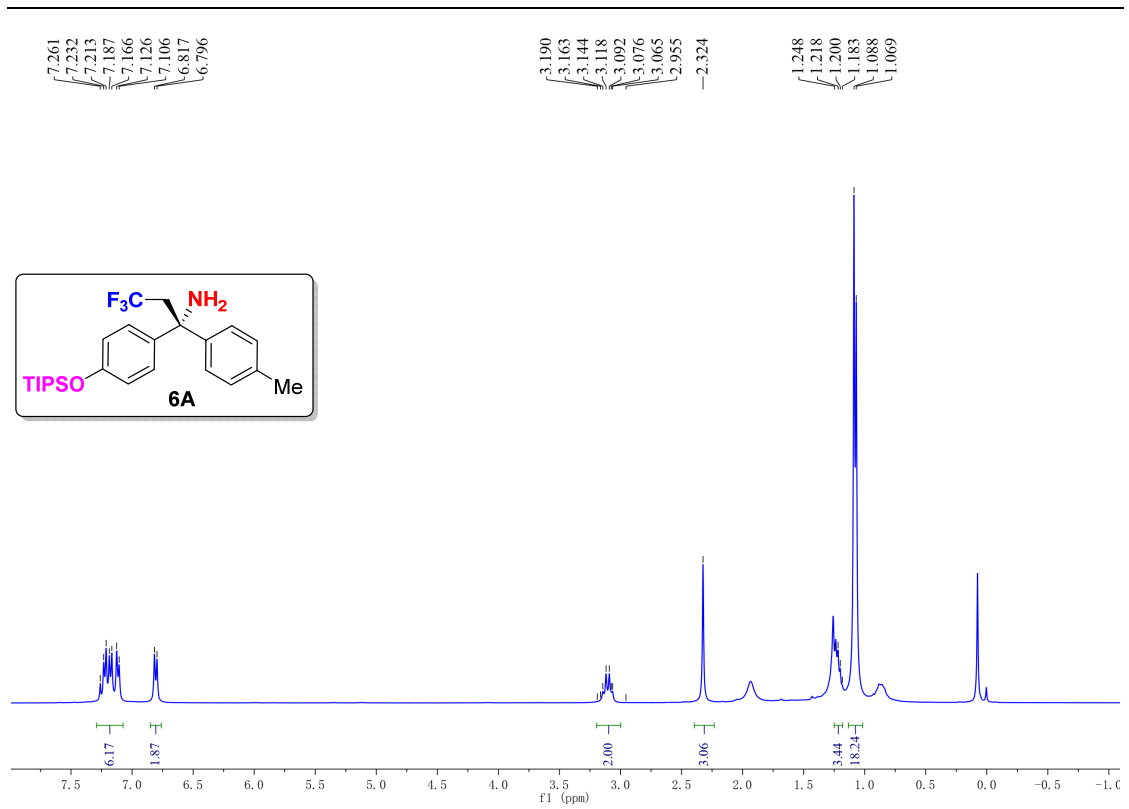
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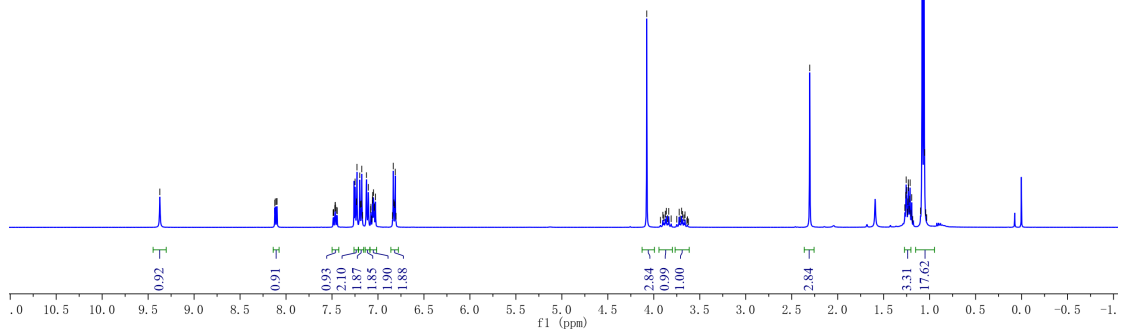
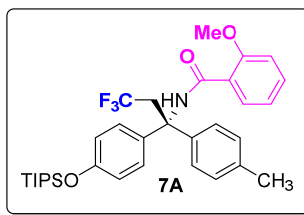
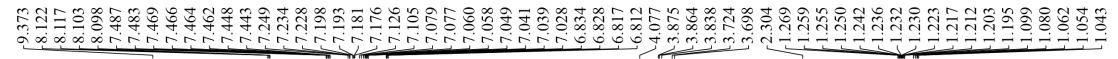
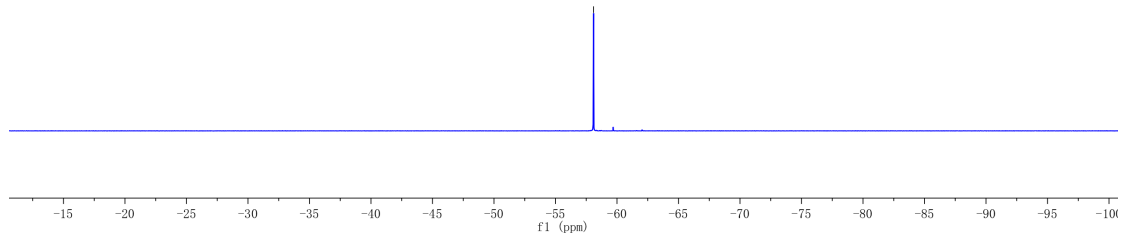
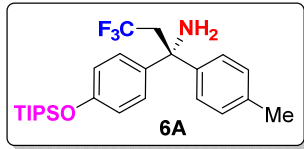


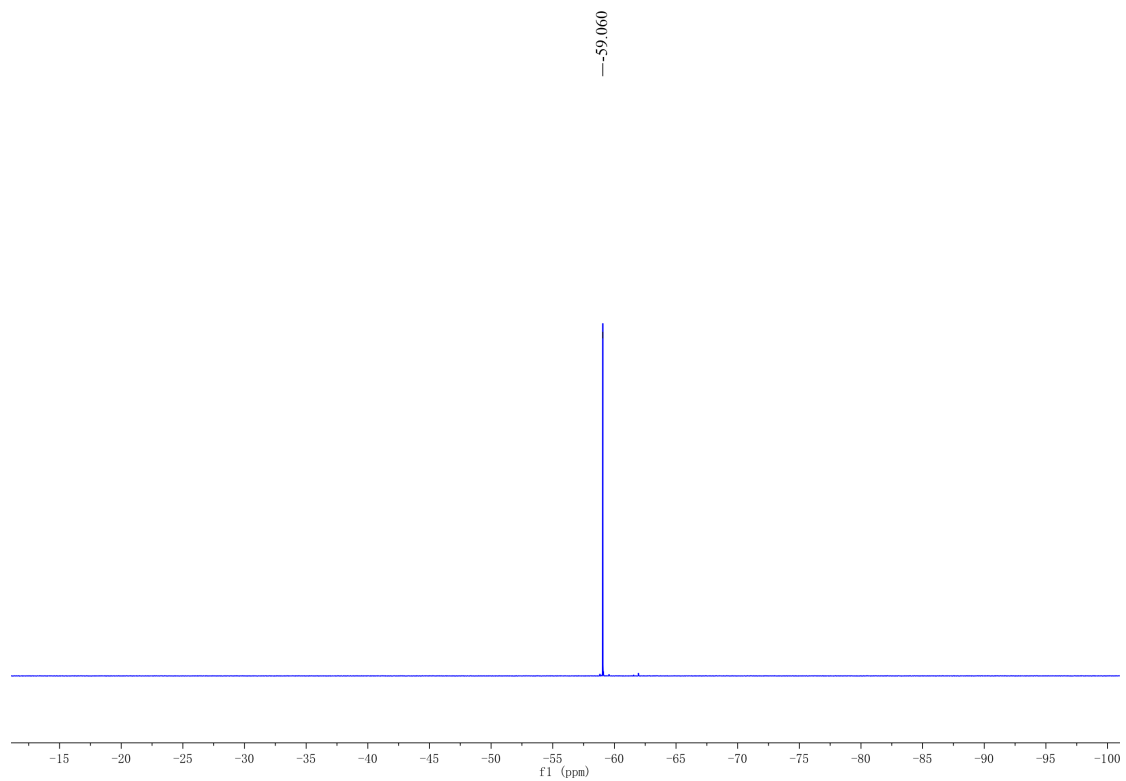
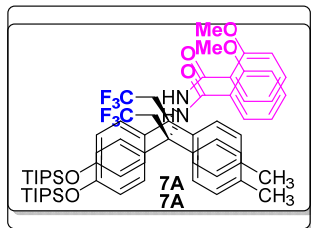
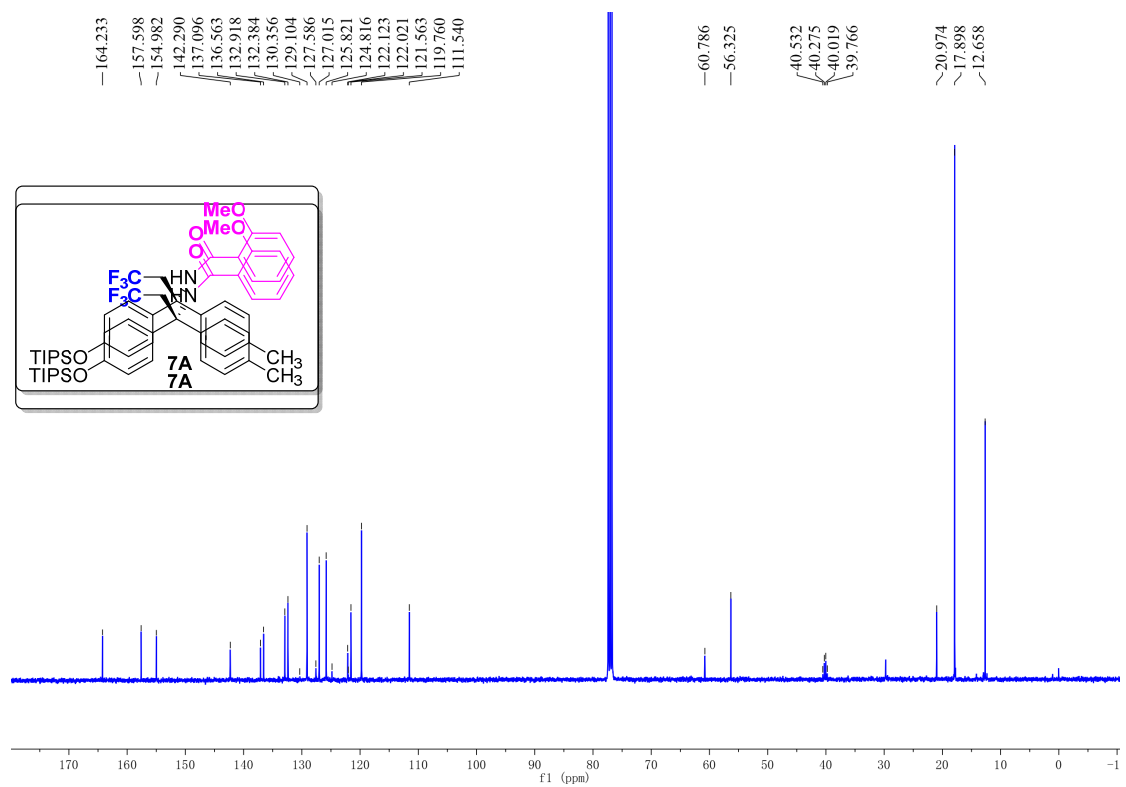
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3.294
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3.215
3.203
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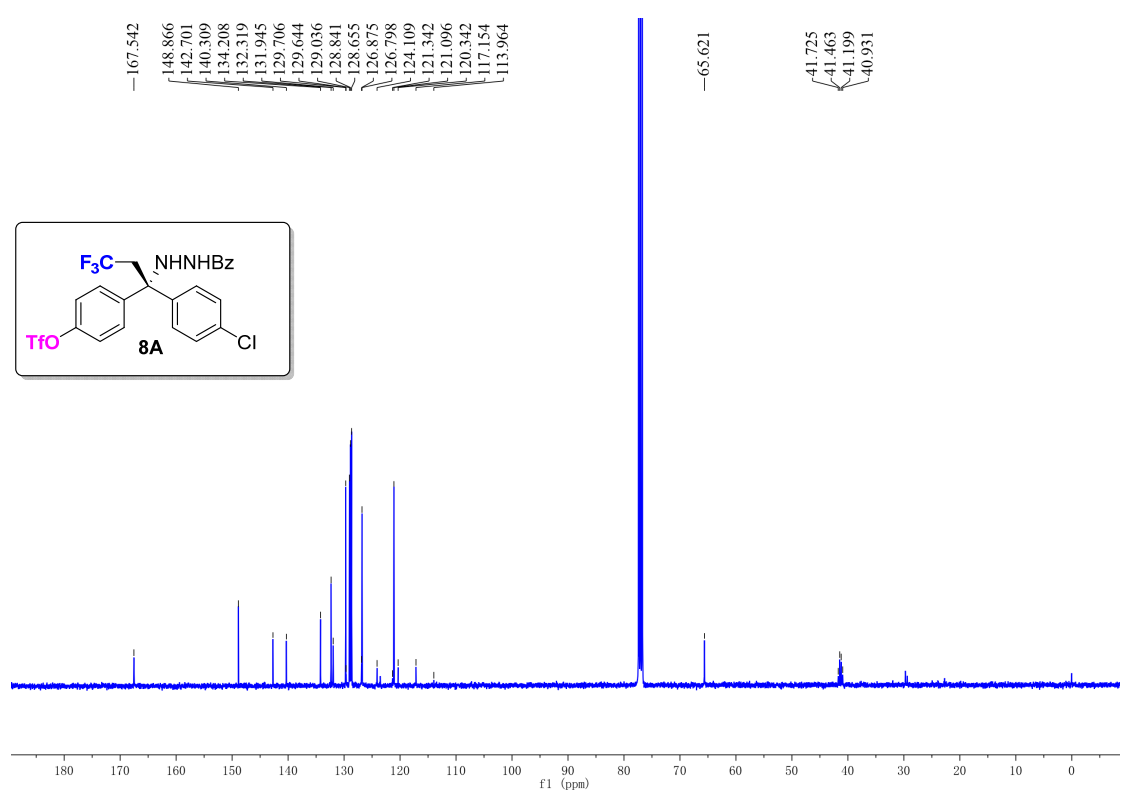
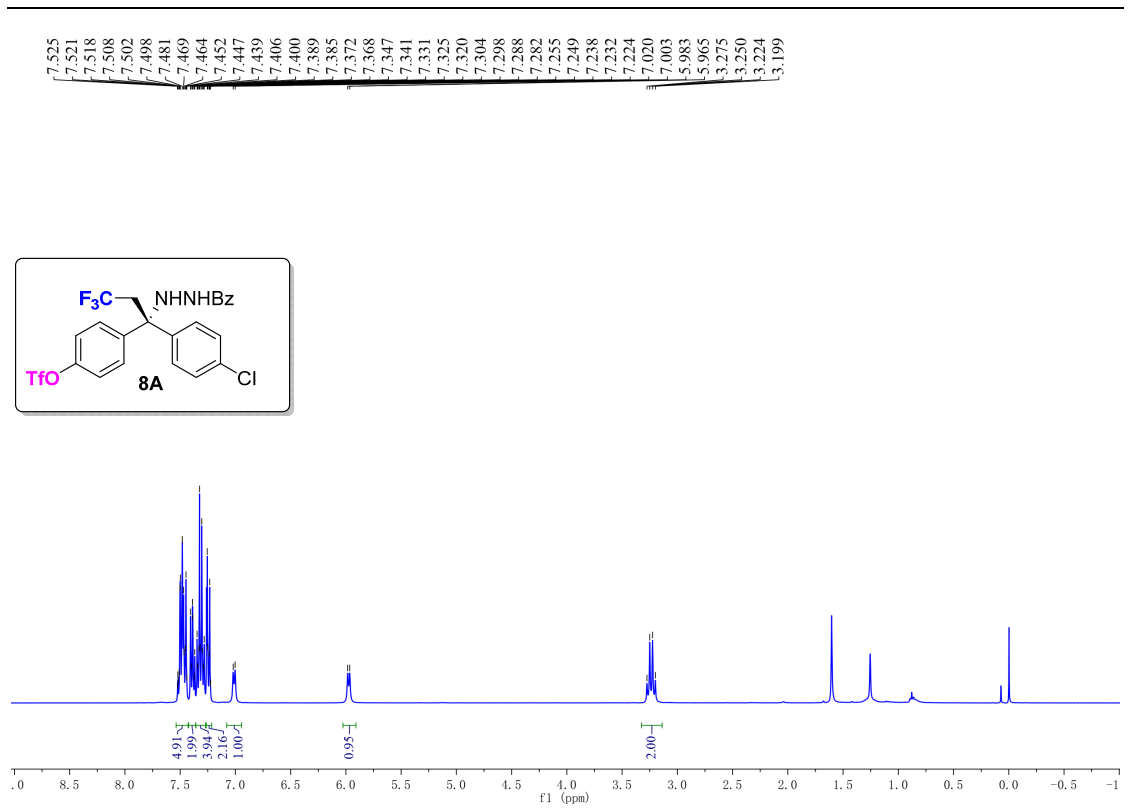


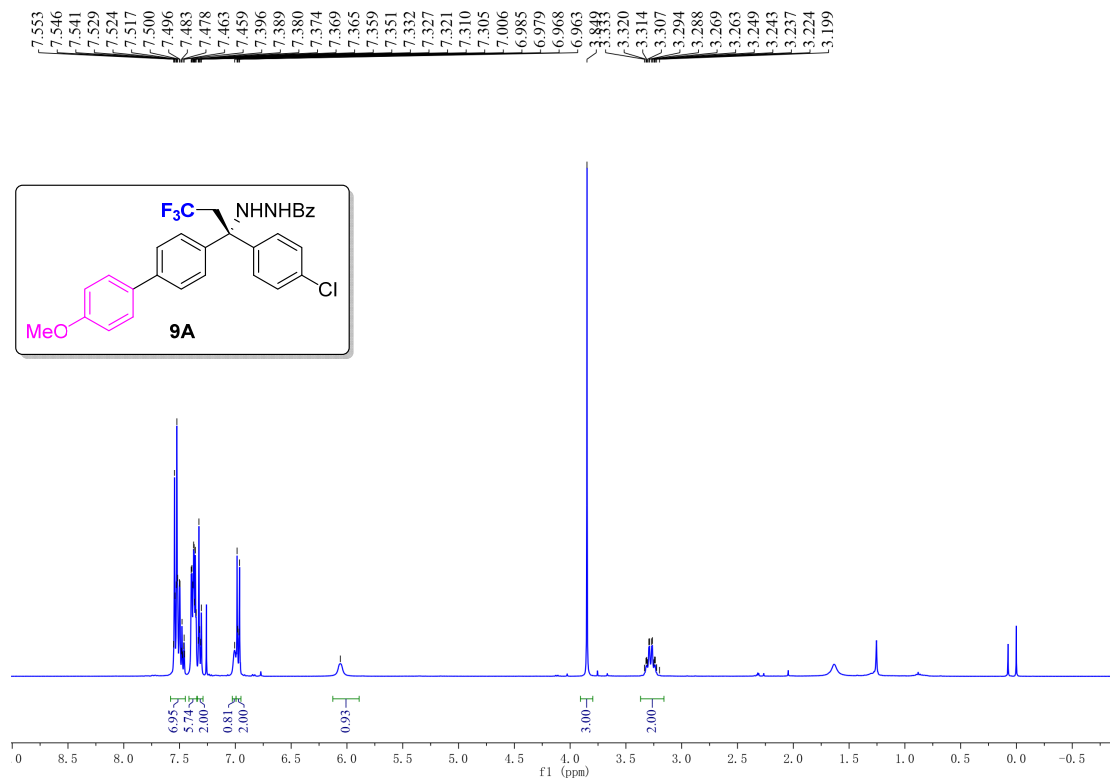
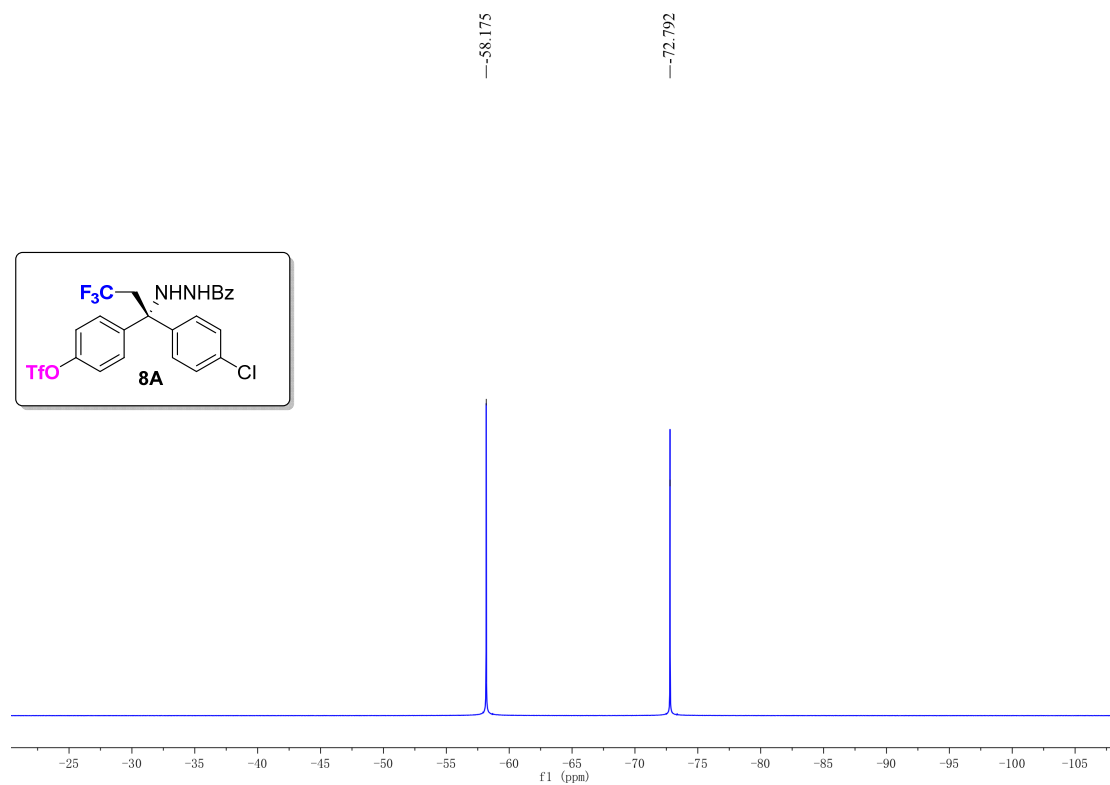


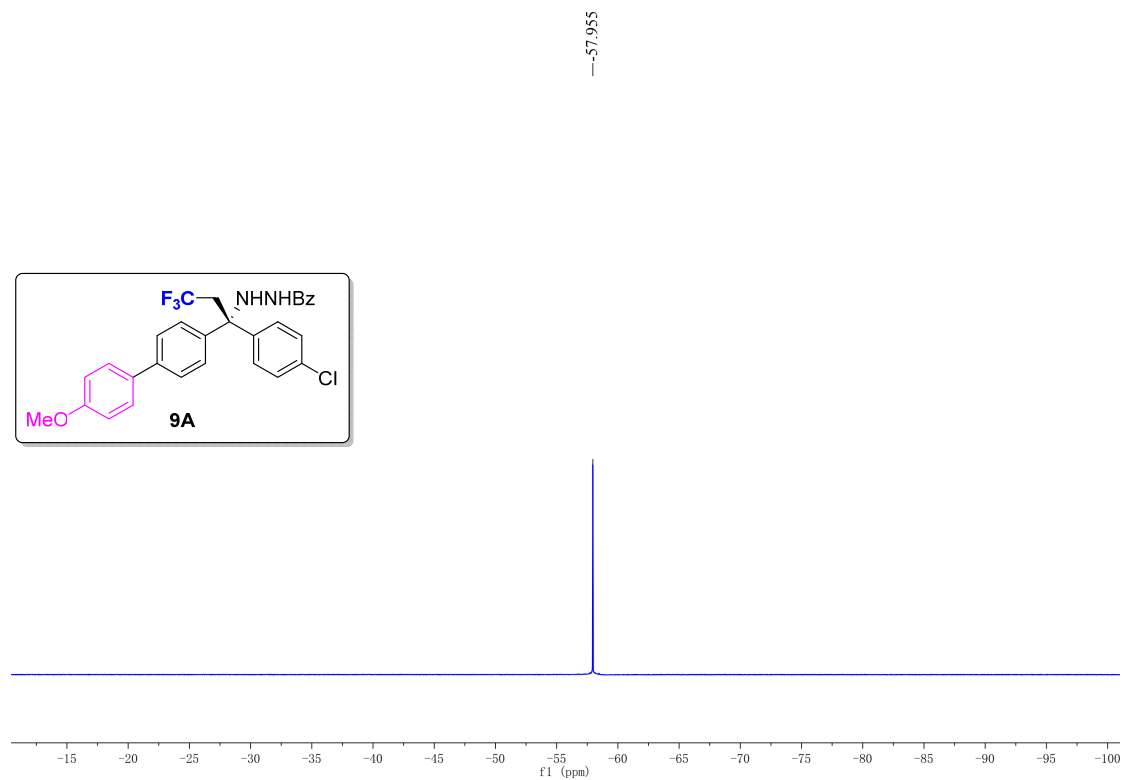
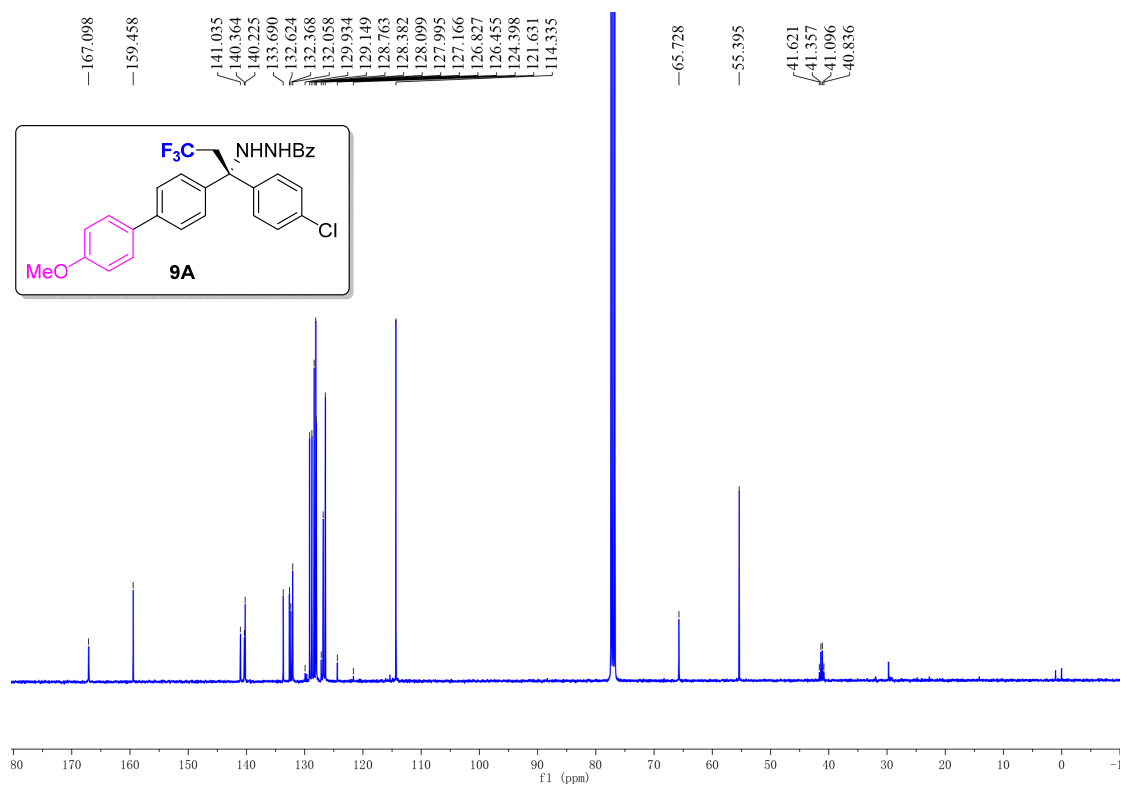


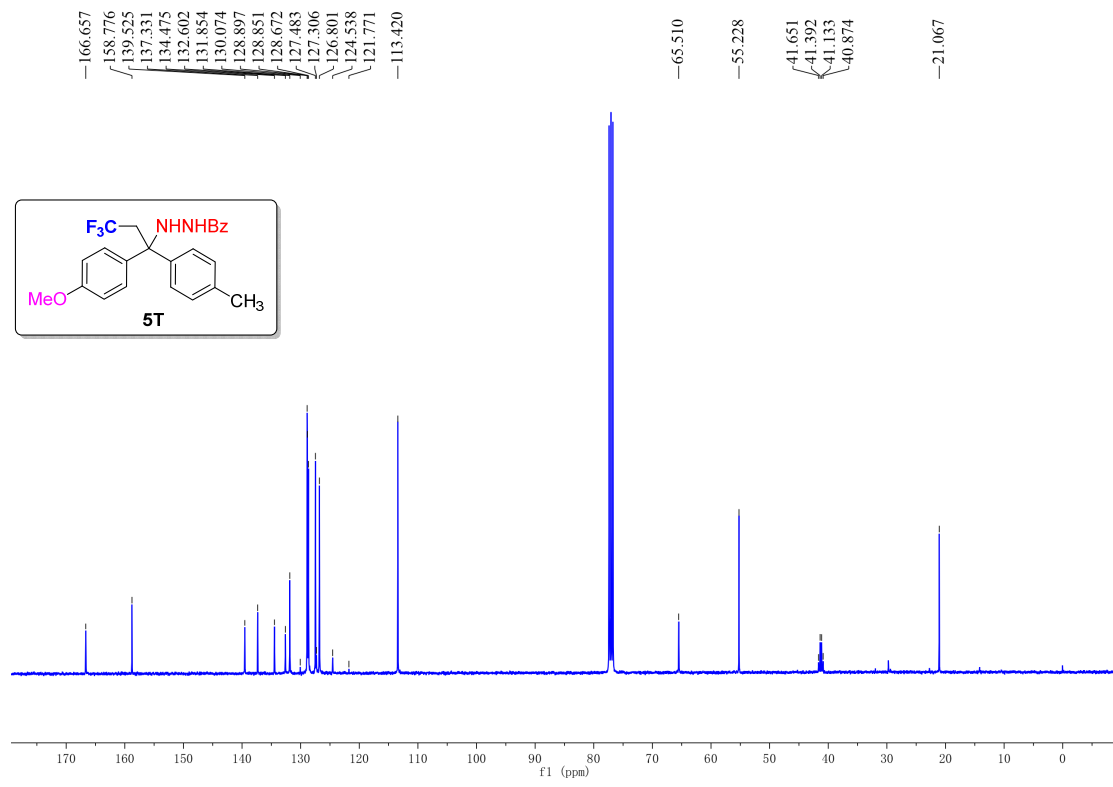
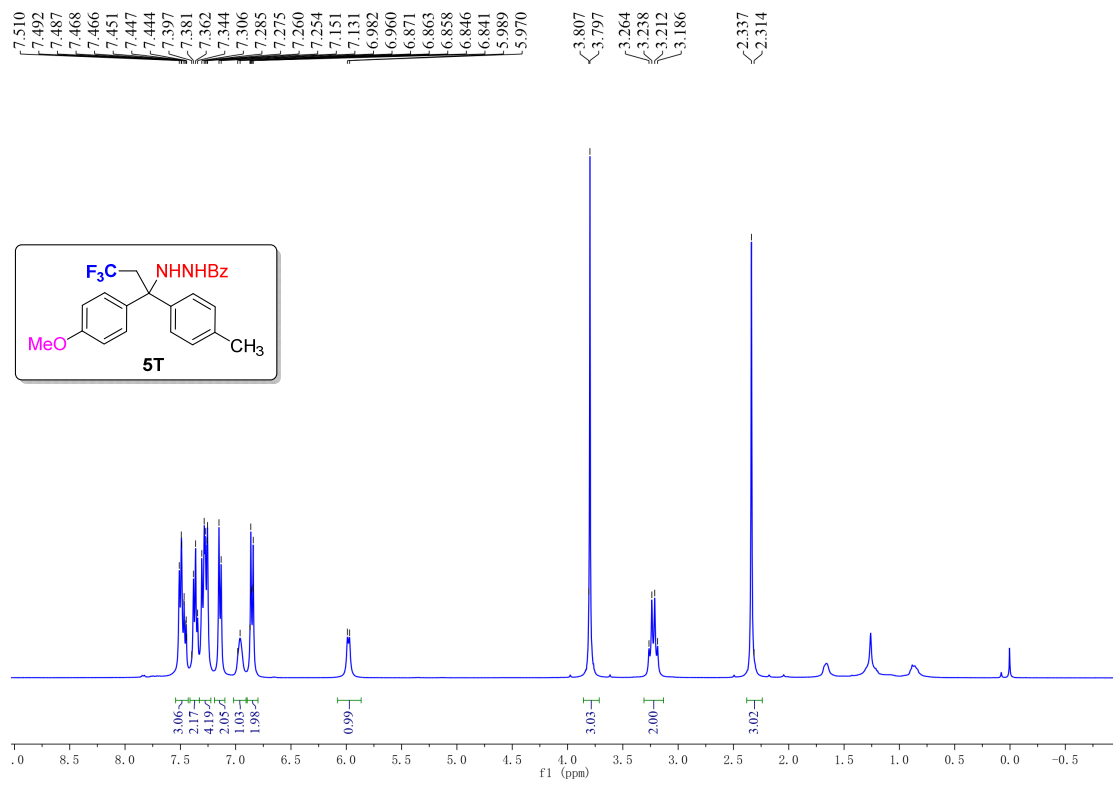




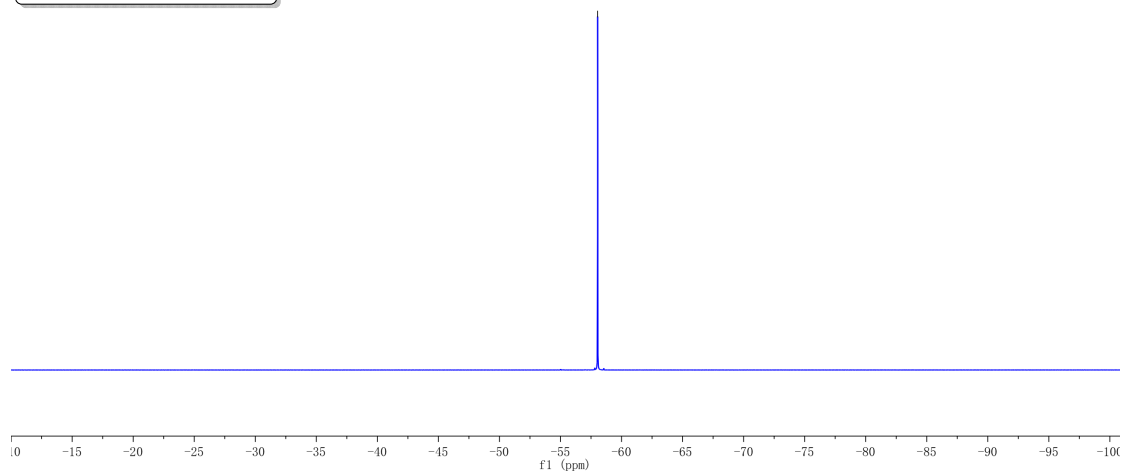
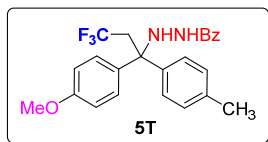




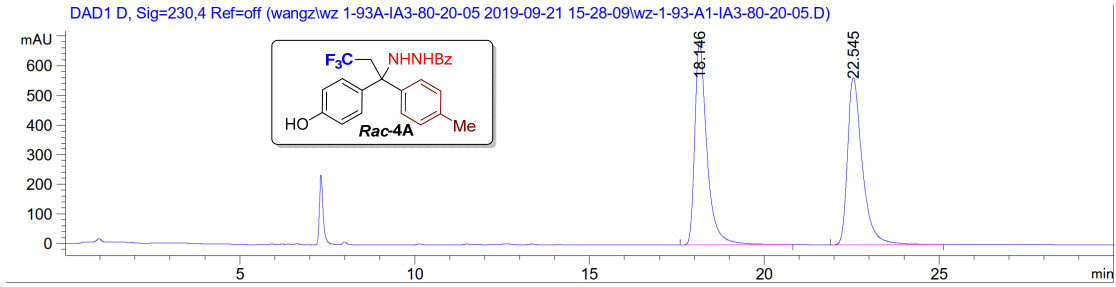




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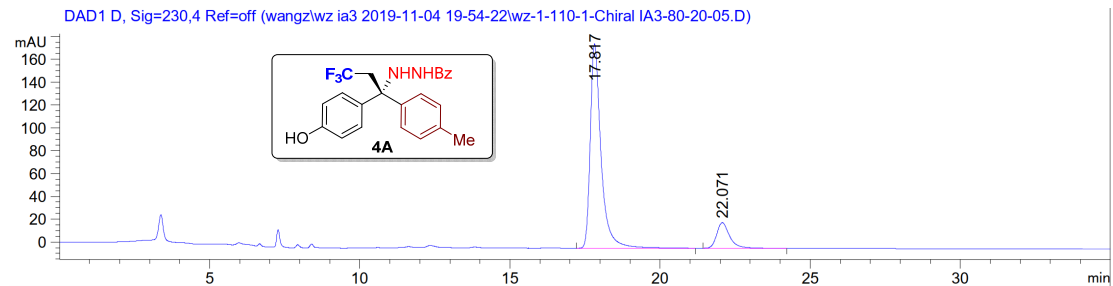
HPLC Spectra



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.146	BB	0.3593	1.65687e4	687.27185	50.0953
2	22.545	BB	0.4415	1.65057e4	563.91663	49.9047

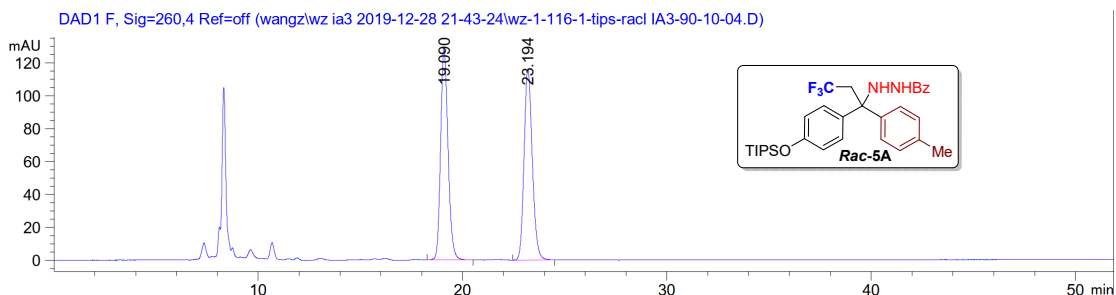
Totals : 3.30744e4 1251.18848



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.817	BB	0.3713	4471.64990	179.07292	86.9269
2	22.071	BB	0.4482	672.49744	22.40514	13.0731

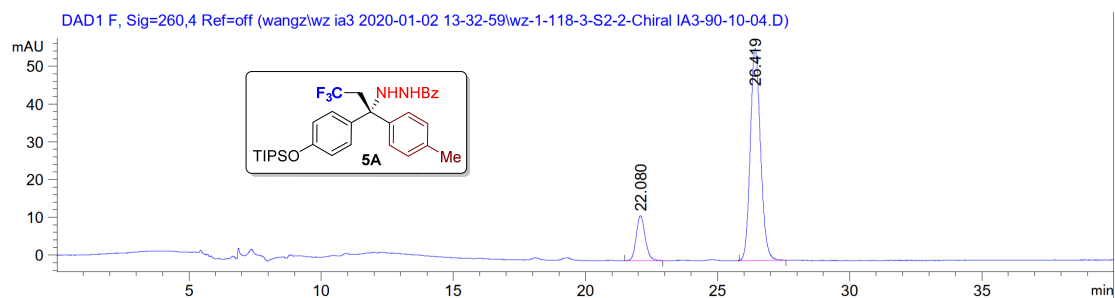
Totals : 5144.14734 201.47806



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.090	BB	0.3864	3259.53906	129.16458	50.0615
2	23.194	BB	0.4327	3251.53198	116.12693	49.9385

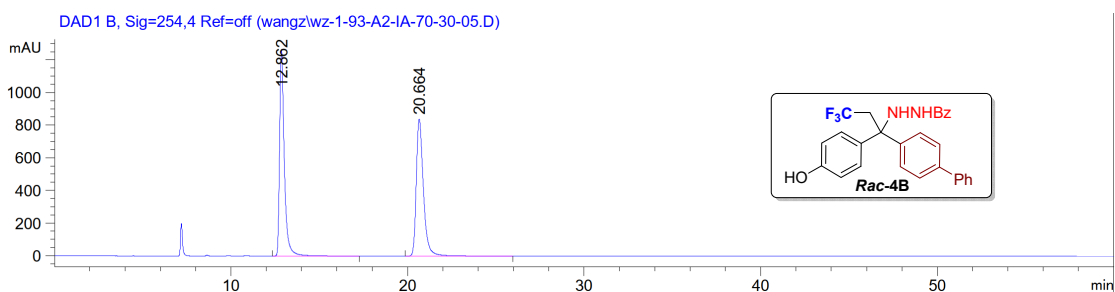
Totals : 6511.07104 245.29151



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.080	BB	0.3558	279.40277	11.90333	15.6186
2	26.419	BB	0.4157	1509.50293	56.13169	84.3814

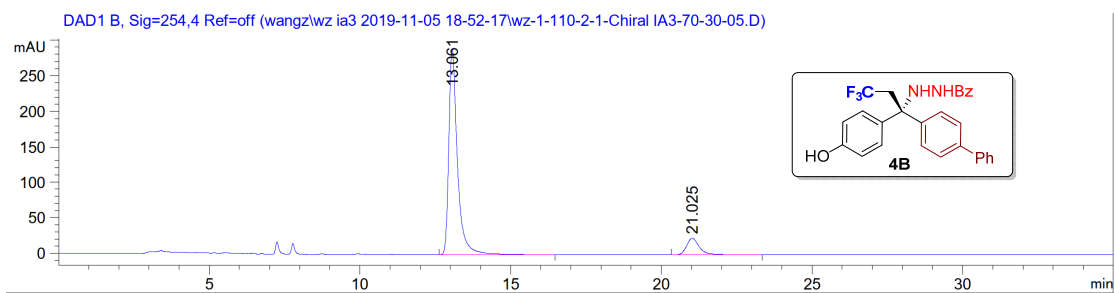
Totals : 1788.90570 68.03502



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.862	BB	0.2771	2.35805e4	1266.96582	50.0008
2	20.664	BB	0.4256	2.35798e4	839.69714	49.9992

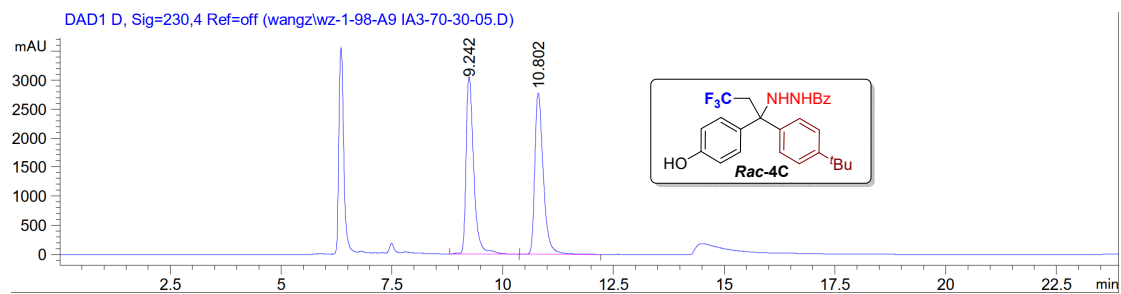
Totals : 4.71603e4 2106.66296



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.061	BB	0.2937	5750.91309	289.52655	89.4448
2	21.025	BB	0.4408	678.65222	23.09534	10.5552

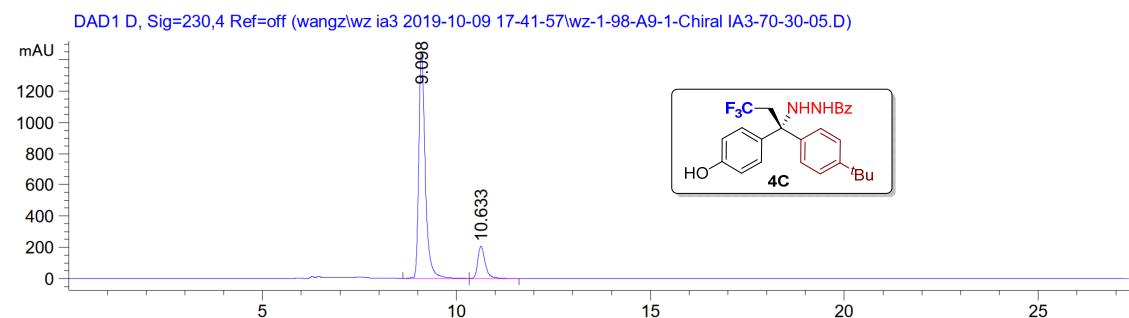
Totals : 6429.56531 312.62189



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.242	VB R	0.1811	3.64815e4	3048.27563	49.8282
2	10.802	BB	0.2029	3.67330e4	2766.81860	50.1718

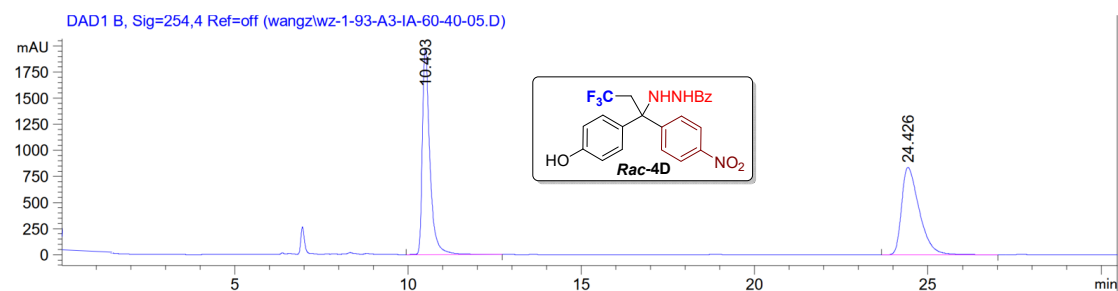
Totals : 7.32145e4 5815.09424



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.098	BV	0.1749	1.67443e4	1448.08093	85.9665
2	10.633	VB	0.2014	2733.39819	205.22334	14.0335

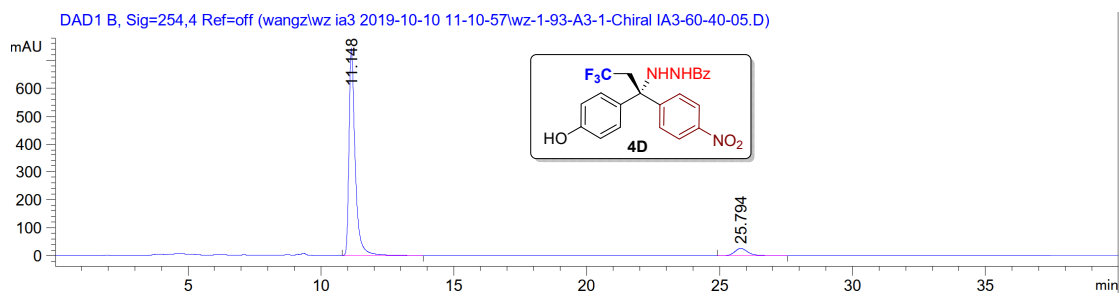
Totals : 1.94777e4 1653.30428



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.493	BB	0.2263	2.98231e4	1973.36804	50.0948
2	24.426	BB	0.5349	2.97102e4	839.45703	49.9052

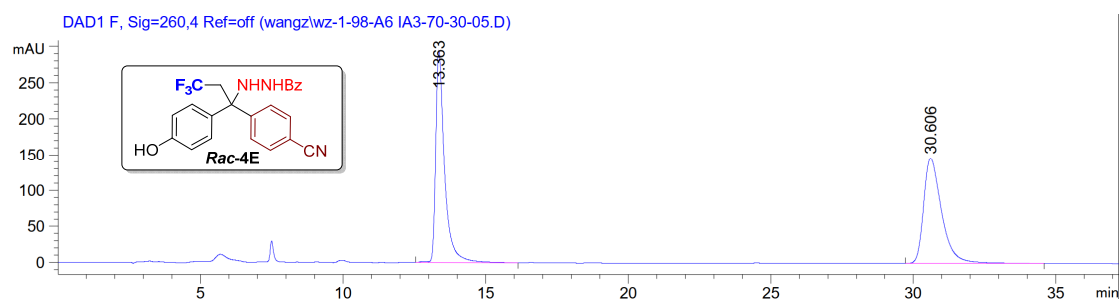
Totals : 5.95333e4 2812.82507



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.148	BB	0.2396	1.19372e4	742.51331	93.1817
2	25.794	BB	0.5186	873.46924	25.69594	6.8183

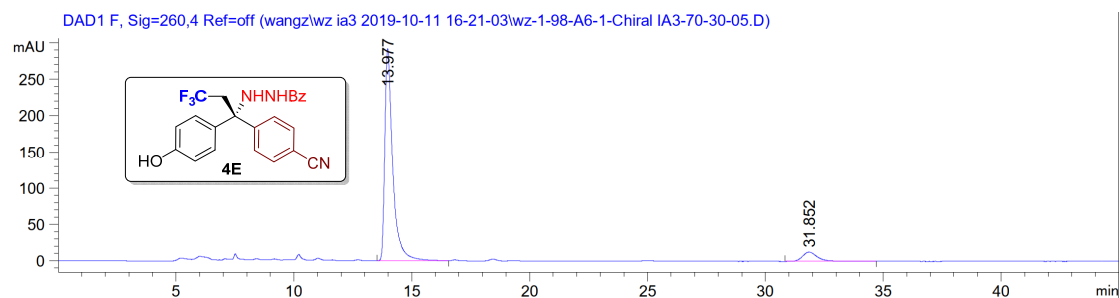
Totals : 1.28107e4 768.20925



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.363	VB R	0.3182	6388.44385	294.13556	49.9366
2	30.606	BB	0.6585	6404.65820	146.36276	50.0634

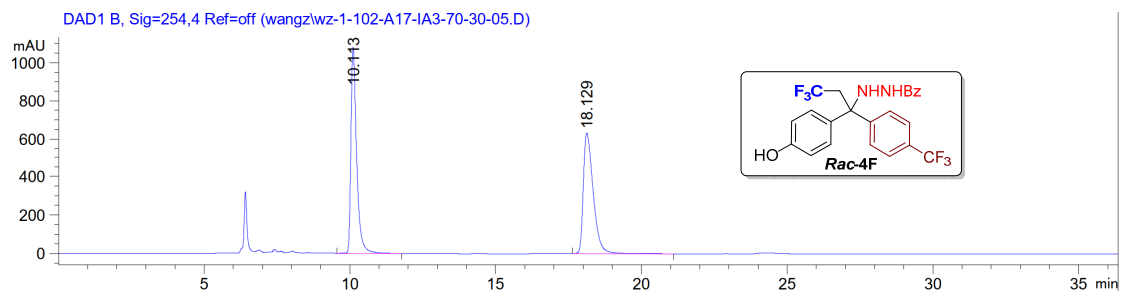
Totals : 1.27931e4 440.49832



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.977	BB	0.3449	6824.37012	291.75912	92.3712
2	31.852	BB	0.6598	563.61072	12.74738	7.6288

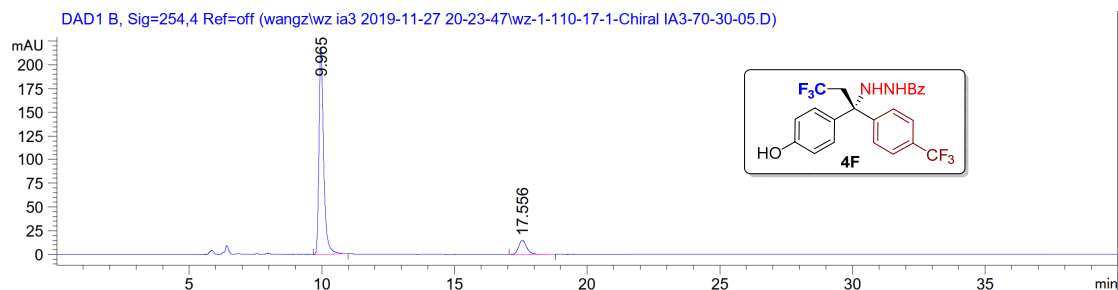
Totals : 7387.98083 304.50651



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.113	BB	0.2018	1.46084e4	1080.25610	49.9604
2	18.129	BB	0.3528	1.46316e4	630.31537	50.0396

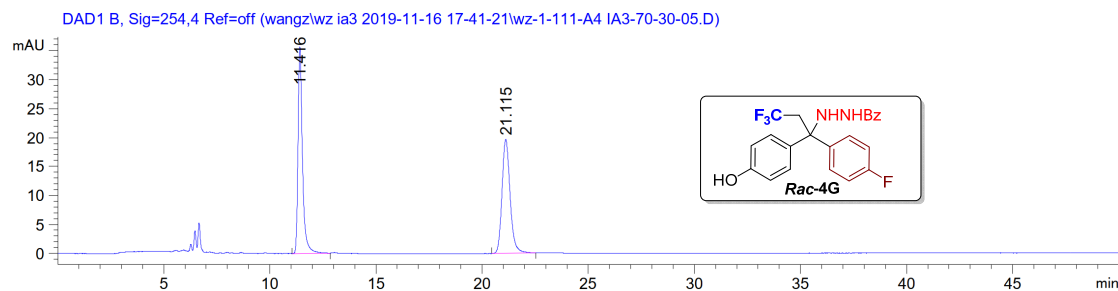
Totals : 2.92400e4 1710.57147



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.965	BB	0.1822	2656.22363	217.98204	89.3130
2	17.556	BB	0.3271	317.83777	14.88322	10.6870

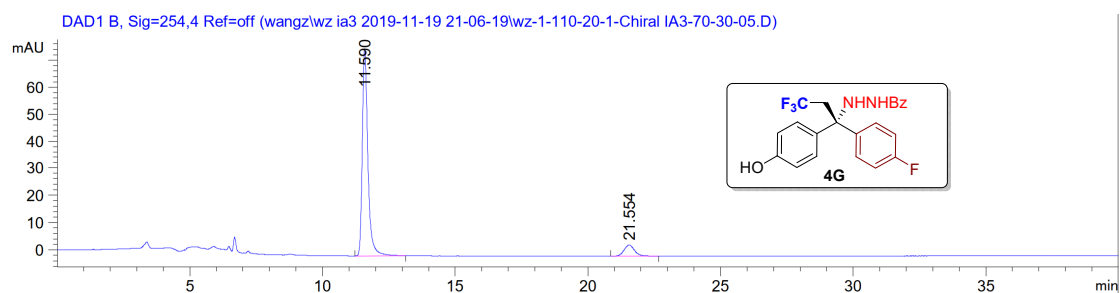
Totals : 2974.06140 232.86526



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.416	BB	0.2182	519.78375	35.63284	50.1132
2	21.115	BB	0.4025	517.43451	19.69266	49.8868

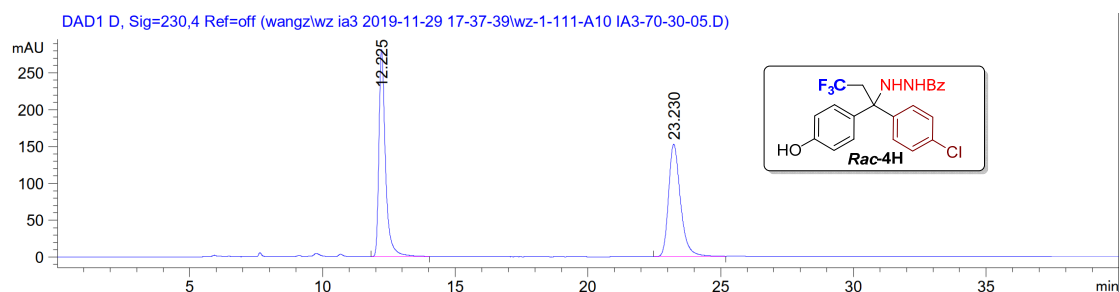
Totals : 1037.21826 55.32550



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.590	BB	0.2204	1112.61011	76.19142	90.7659
2	21.554	BB	0.4160	113.19113	4.07579	9.2341

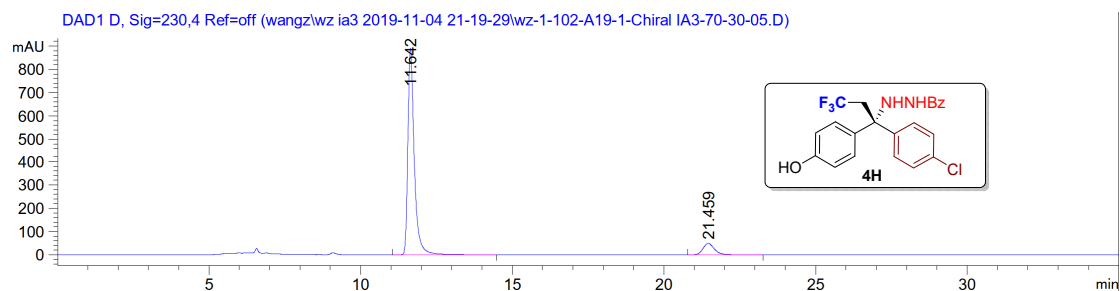
Totals : 1225.80124 80.26721



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.225	BB	0.2548	4792.67236	281.28769	50.0615
2	23.230	BB	0.4776	4780.89893	152.55357	49.9385

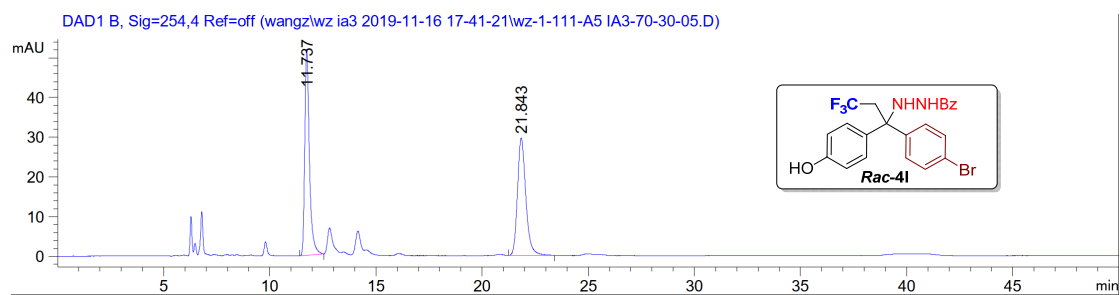
Totals : 9573.57129 433.84126



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.642	BB	0.2191	1.30605e4	890.34204	90.8867
2	21.459	BB	0.4067	1309.59412	48.85733	9.1133

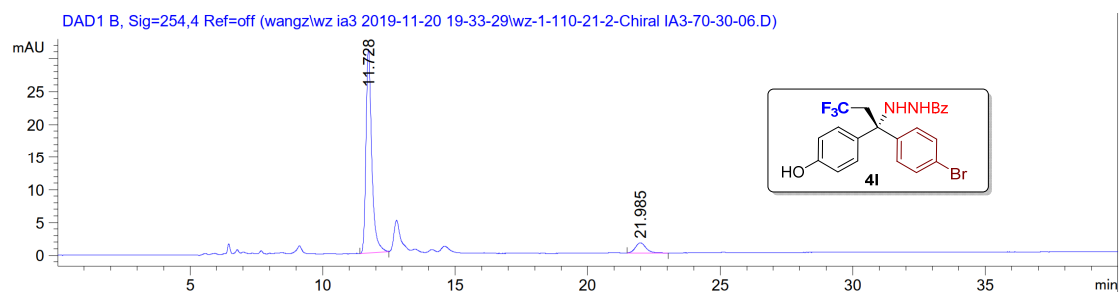
Totals : 1.43701e4 939.19937



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.737	BB	0.2274	789.42633	51.90494	49.5048
2	21.843	BB	0.4143	805.21985	29.51823	50.4952

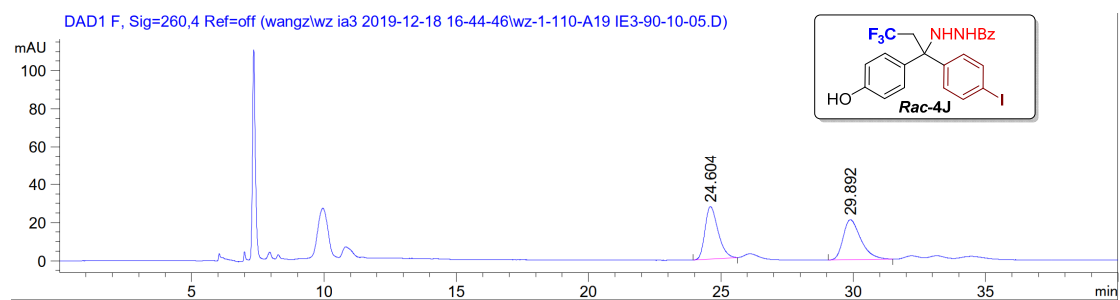
Totals : 1594.64618 81.42317



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.728	BB	0.2271	471.40576	31.05218	91.7577
2	21.985	BB	0.4026	42.34486	1.55049	8.2423

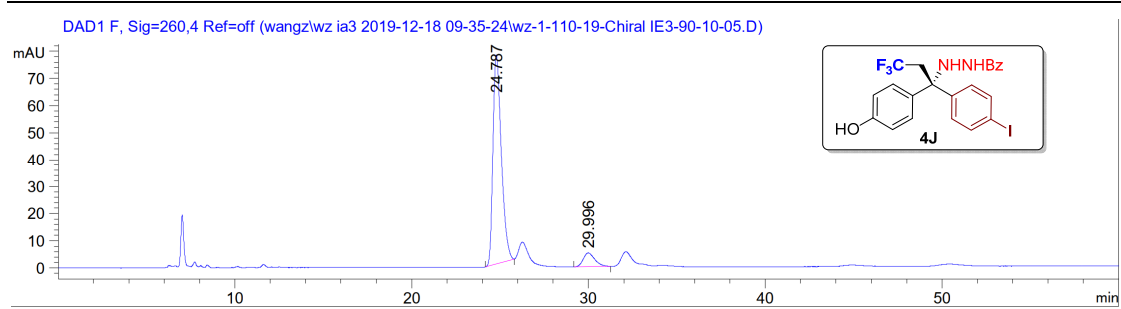
Totals : 513.75062 32.60266



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.604	BB	0.5135	939.83740	27.44592	49.1425
2	29.892	BB	0.6953	972.63824	20.88616	50.8575

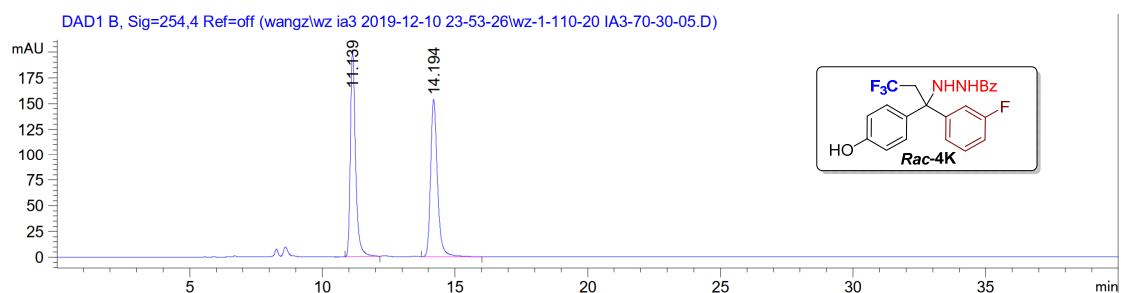
Totals : 1912.47565 48.33207



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.787	BB	0.5050	2535.15552	77.22713	91.6923
2	29.996	BB	0.5718	229.69525	5.05828	8.3077

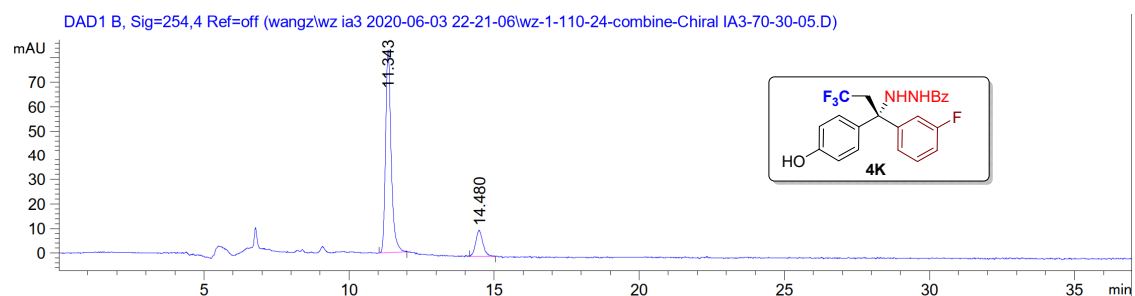
Totals : 2764.85077 82.28541



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.139	BB	0.2012	2712.91333	201.35522	49.7826
2	14.194	BB	0.2698	2736.60376	153.67931	50.2174

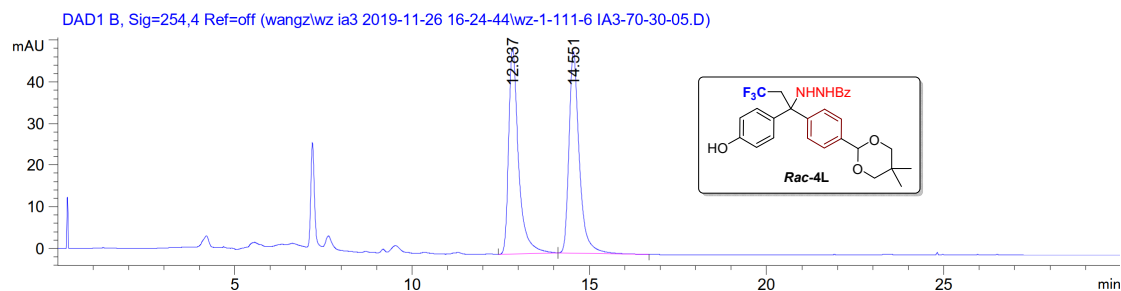
Totals : 5449.51709 355.03453



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.343	BV R	0.2071	1118.11108	83.04435	85.8545
2	14.480	BV R	0.2549	184.22145	10.59282	14.1455

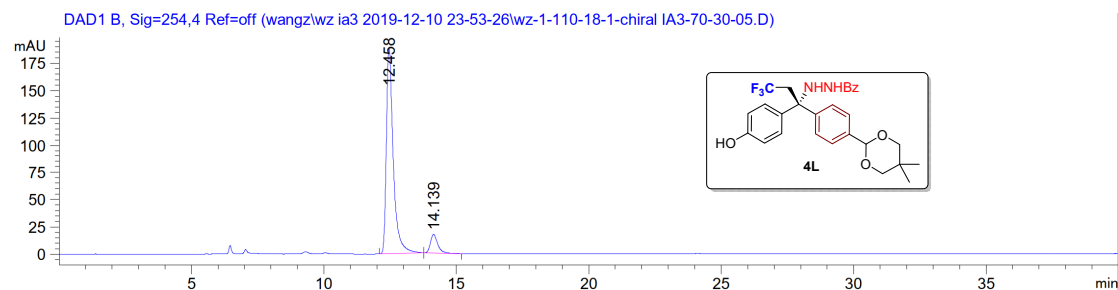
Totals : 1302.33253 93.63717



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.837	BB	0.2871	955.52850	49.53055	49.4739
2	14.551	BB	0.3032	975.85126	48.40446	50.5261

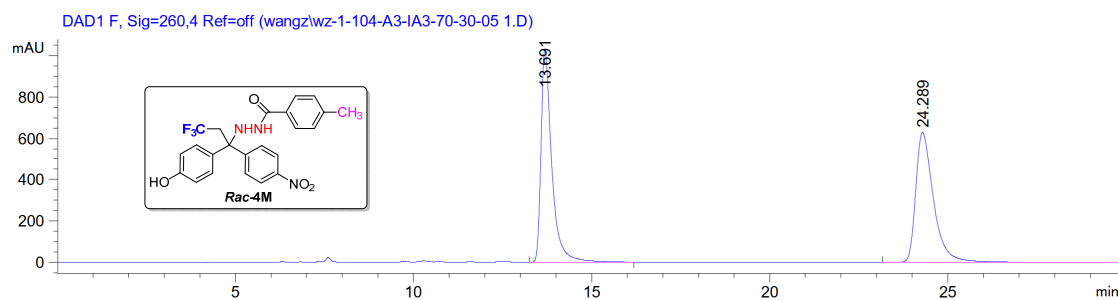
Totals : 1931.37976 97.93501



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.458	BB	0.2685	3406.10962	188.78632	91.3780
2	14.139	BB	0.2884	321.38577	16.85809	8.6220

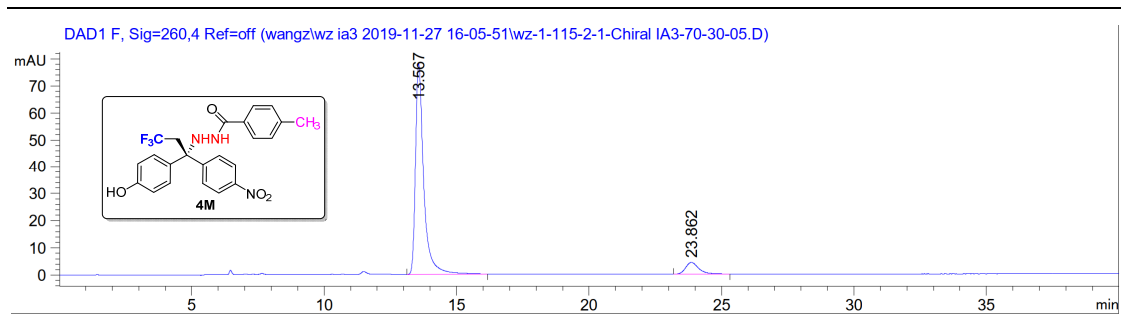
Totals : 3727.49539 205.64440



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.691	BB	0.3144	2.17141e4	1028.22021	49.7315
2	24.289	BBA	0.5209	2.19485e4	632.44281	50.2685

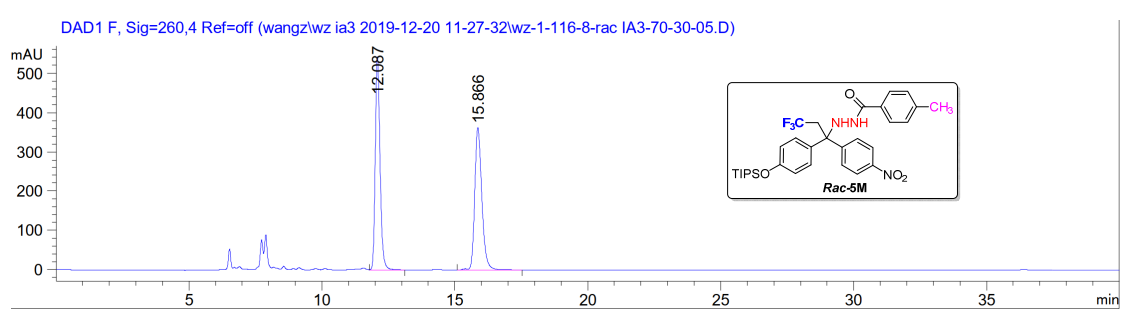
Totals : 4.36626e4 1660.66302



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.567	BB	0.3169	1685.65894	78.38357	91.8888
2	23.862	BB	0.4924	148.79700	4.29224	8.1112

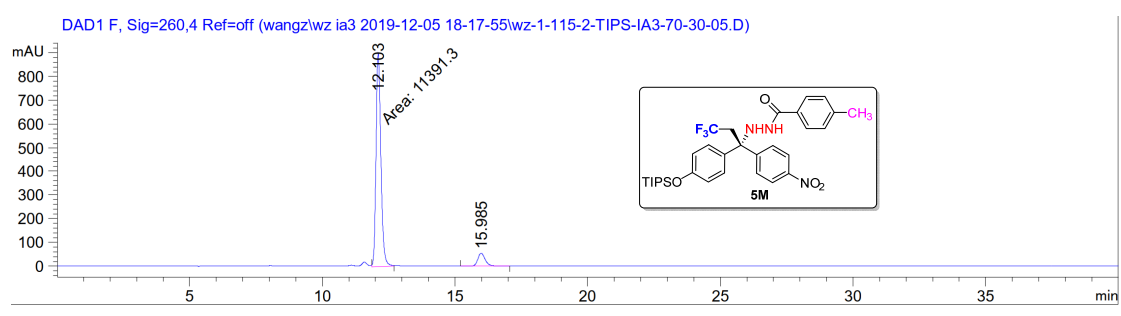
Totals : 1834.45593 82.67581



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.087	VB	0.1916	6772.52930	542.52673	49.9407
2	15.866	VB R	0.2824	6788.61816	363.62561	50.0593

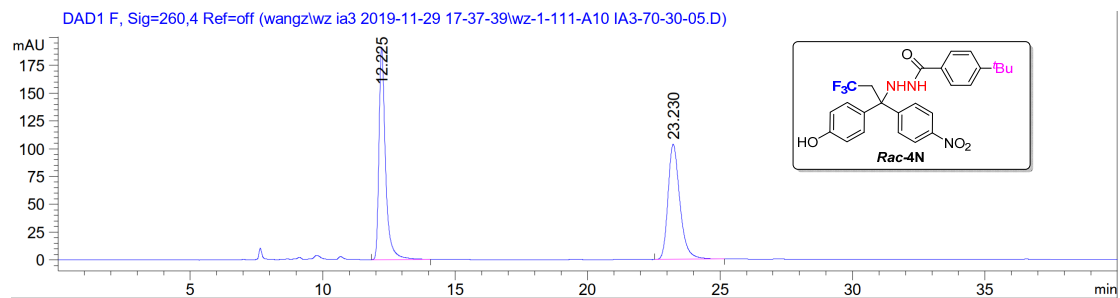
Totals : 1.35611e4 906.15234



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.103	MM	0.2109	1.13913e4	900.19263	91.4364
2	15.985	BB	0.2965	1066.86987	54.47313	8.5636

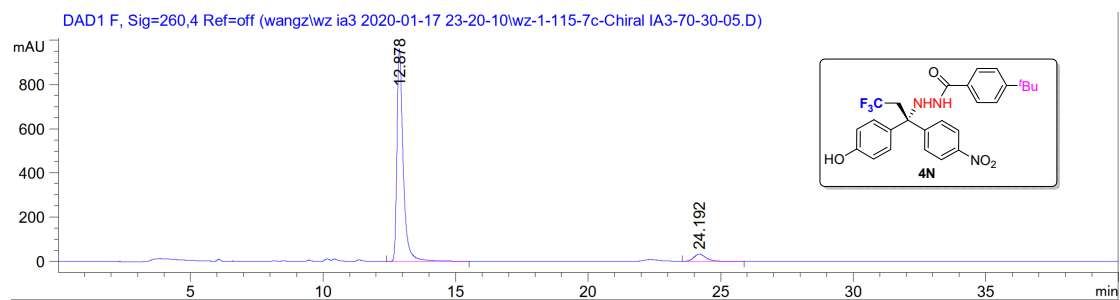
Totals : 1.24581e4 954.66575



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.225	BB	0.2552	3264.77686	191.24953	50.1430
2	23.230	BB	0.4795	3246.15796	103.61681	49.8570

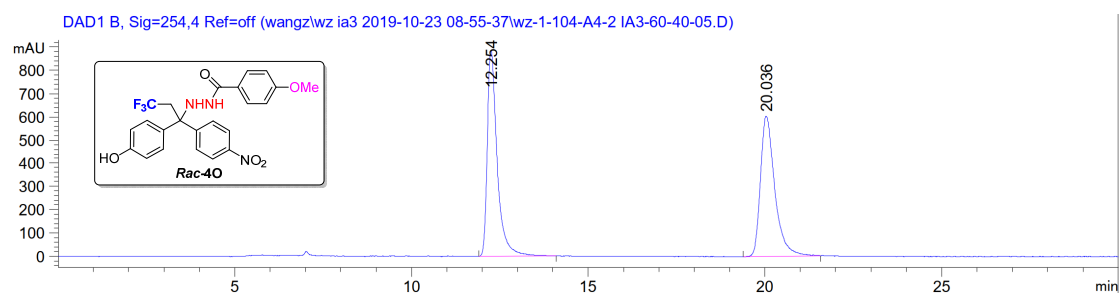
Totals : 6510.93481 294.86634



Signal 6: DAD1 F, Sig=260,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.878	BB	0.2448	1.57251e4	961.27435	93.7955
2	24.192	BB	0.4904	1040.20898	32.41763	6.2045

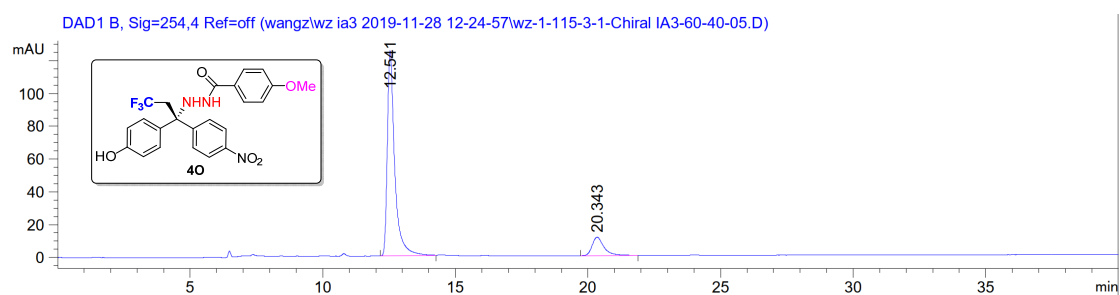
Totals : 1.67653e4 993.69198



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.254	BV R	0.2773	1.73082e4	887.30377	50.4429
2	20.036	BV R	0.3862	1.70042e4	604.43463	49.5571

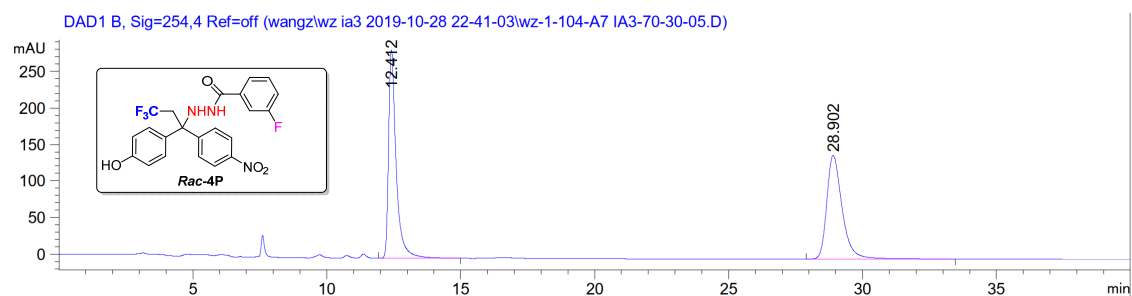
Totals : 3.43124e4 1491.73840



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.541	BB	0.2833	2413.95898	124.97690	87.4197
2	20.343	BB	0.4591	347.38412	11.22356	12.5803

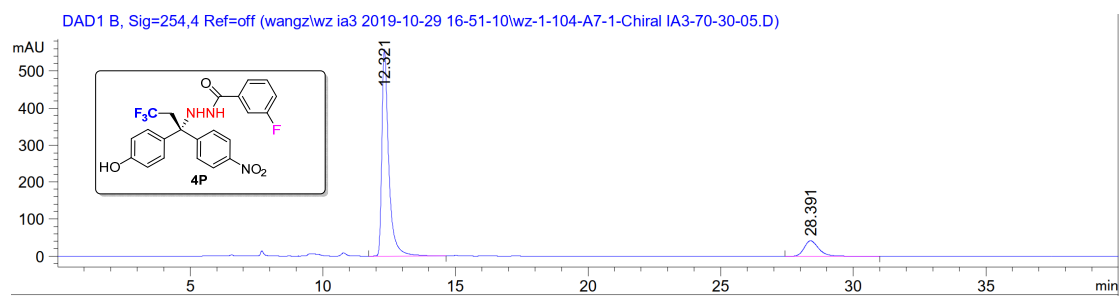
Totals : 2761.34311 136.20045



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.412	BB	0.2924	5613.73926	284.26025	49.9569
2	28.902	BB	0.6050	5623.41602	141.08601	50.0431

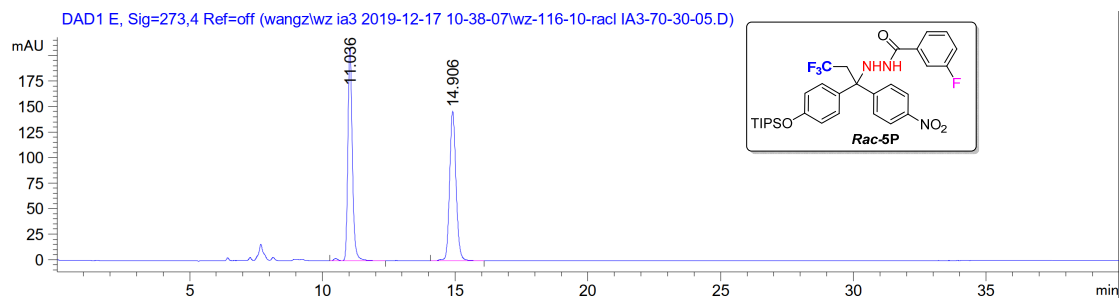
Totals : 1.12372e4 425.34627



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.321	BB	0.2681	1.00506e4	558.22528	86.1408
2	28.391	BB	0.5908	1617.03821	41.66123	13.8592

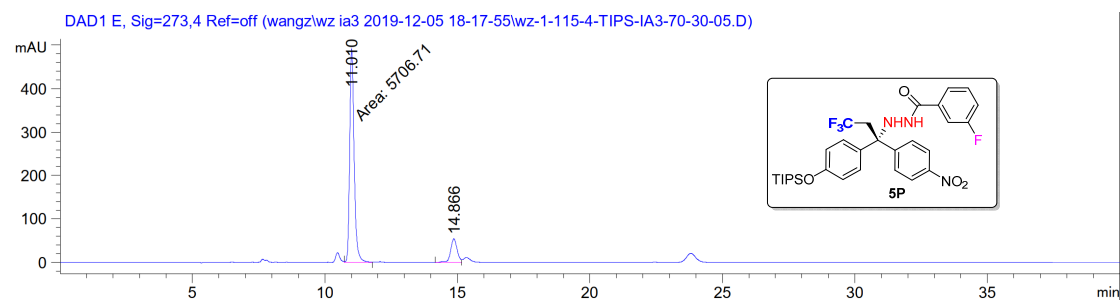
Totals : 1.16676e4 599.88651



Signal 5: DAD1 E, Sig=273,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.036	VB R	0.1783	2467.25146	208.98149	49.9749
2	14.906	BB	0.2586	2469.72974	146.52710	50.0251

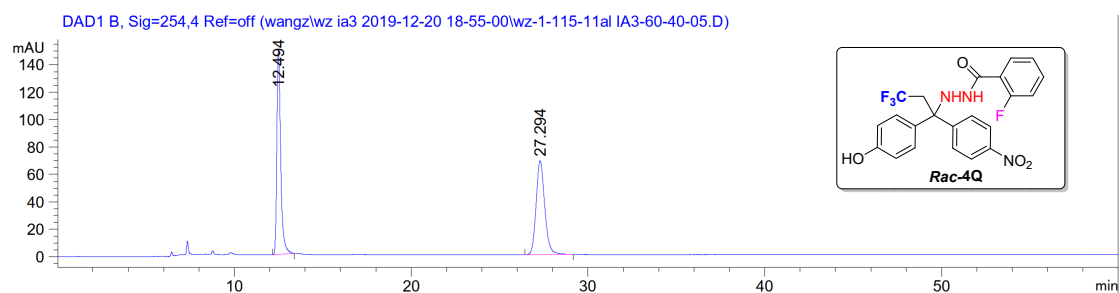
Totals : 4936.98120 355.50859



Signal 5: DAD1 E, Sig=273,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.010	MM	0.1947	5706.70557	488.59232	85.7496
2	14.866	BV	0.2661	948.37268	54.20891	14.2504

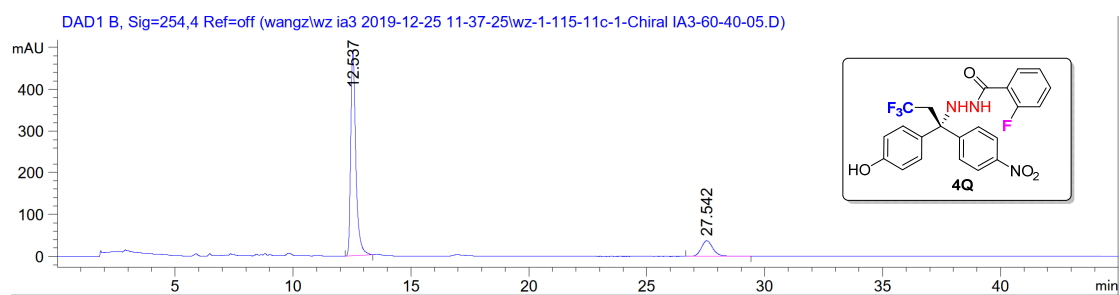
Totals : 6655.07825 542.80123



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.494	BB	0.2257	2251.16577	149.50638	49.2368
2	27.294	BB	0.5219	2320.95581	68.38902	50.7632

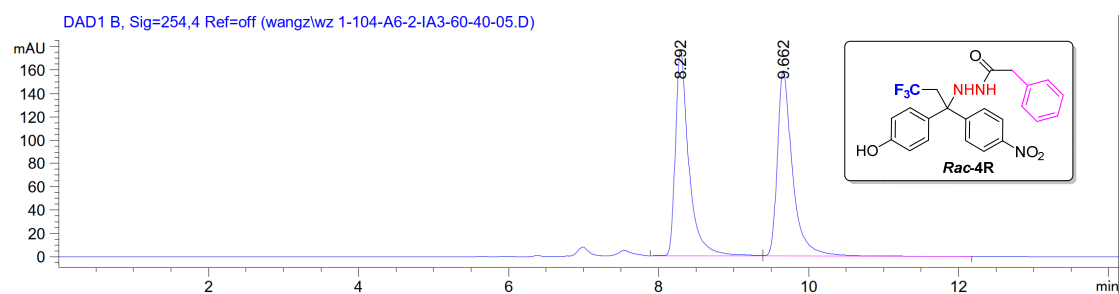
Totals : 4572.12158 217.89539



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.537	BB	0.2235	7317.15381	492.04251	85.1235
2	27.542	BB	0.5277	1278.77100	37.14261	14.8765

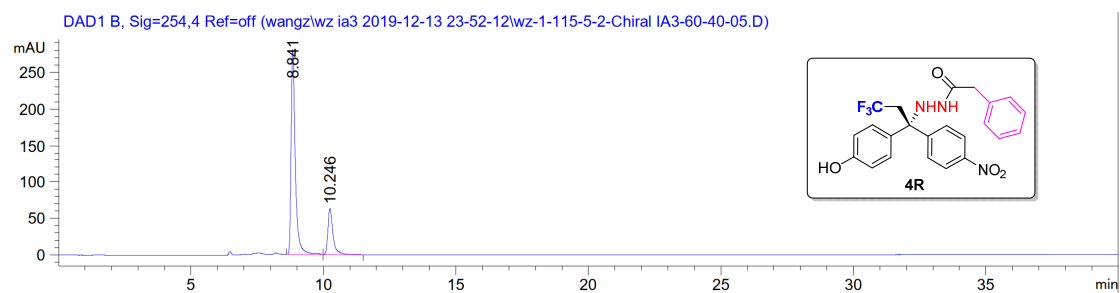
Totals : 8595.92480 529.18512



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.292	VV R	0.1840	2204.10425	176.09476	49.5704
2	9.662	VB	0.2109	2242.30518	158.68575	50.4296

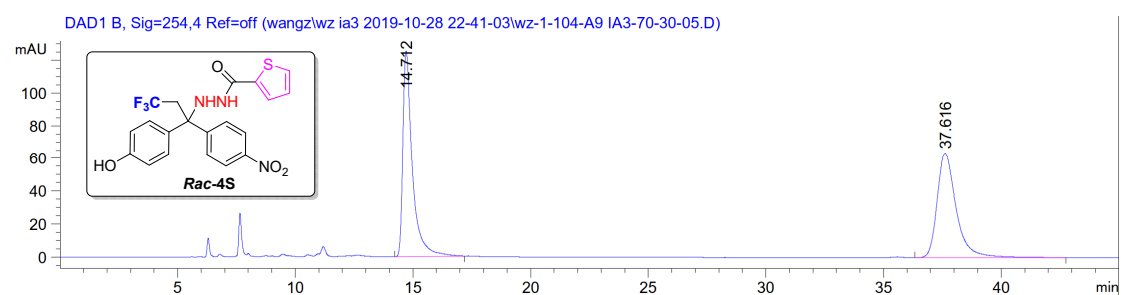
Totals : 4446.40942 334.78050



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.841	BV R	0.1636	3121.02075	280.85043	78.6333
2	10.246	VB	0.1985	848.06427	63.20127	21.3667

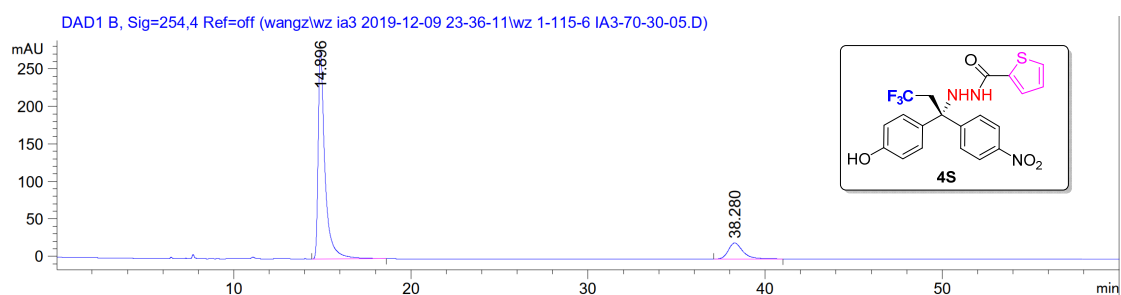
Totals : 3969.08502 344.05170



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.712	BB	0.4076	3503.27563	125.51518	49.6141
2	37.616	BB	0.8397	3557.76587	63.49479	50.3859

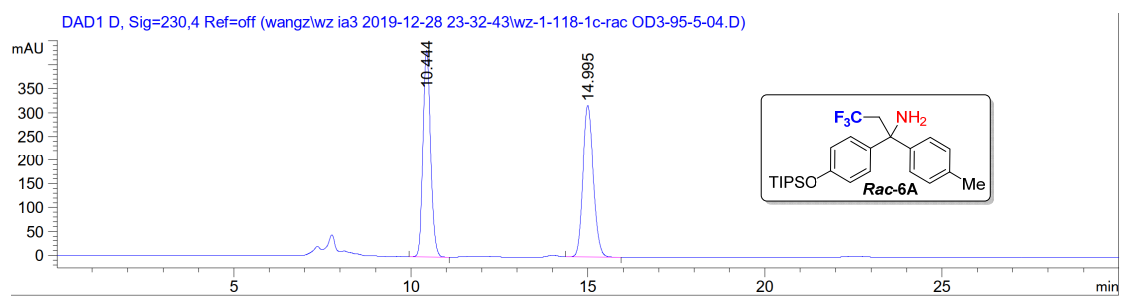
Totals : 7061.04150 189.00997



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.896	BB	0.3922	7491.17627	278.13660	85.9898
2	38.280	BB	0.8335	1220.52832	21.39827	14.0102

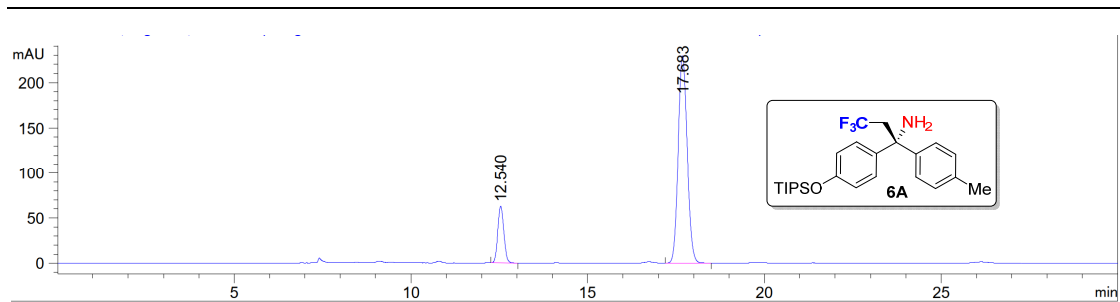
Totals : 8711.70459 299.53487



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.444	BB	0.2305	6481.04541	433.35587	49.9188
2	14.995	BB	0.3160	6502.13818	318.67941	50.0812

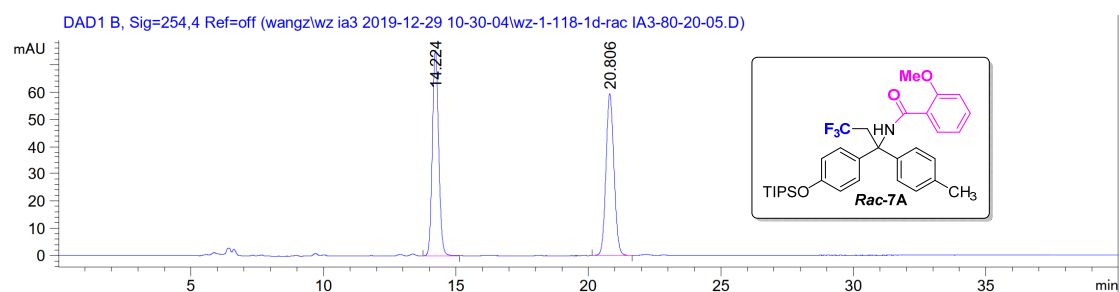
Totals : 1.29832e4 752.03528



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.540	BB	0.1847	742.17566	62.41515	15.4298
2	17.683	BB	0.2771	4067.83521	229.16956	84.5702

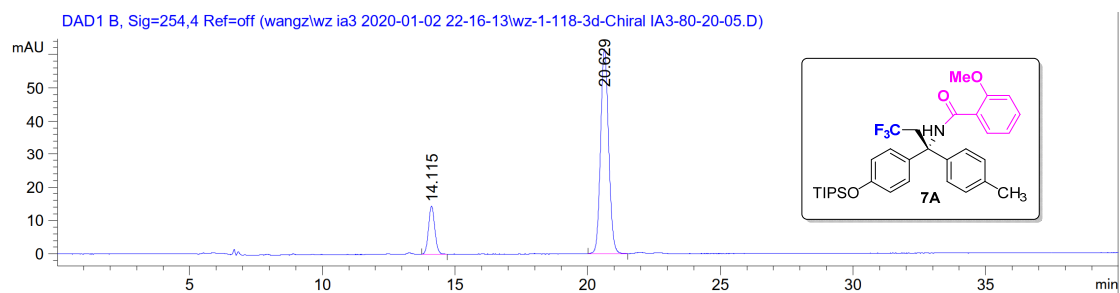
Totals : 4810.01086 291.58471



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.224	BB	0.2545	1241.09839	75.21783	49.9338
2	20.806	BB	0.3248	1244.38745	59.30152	50.0662

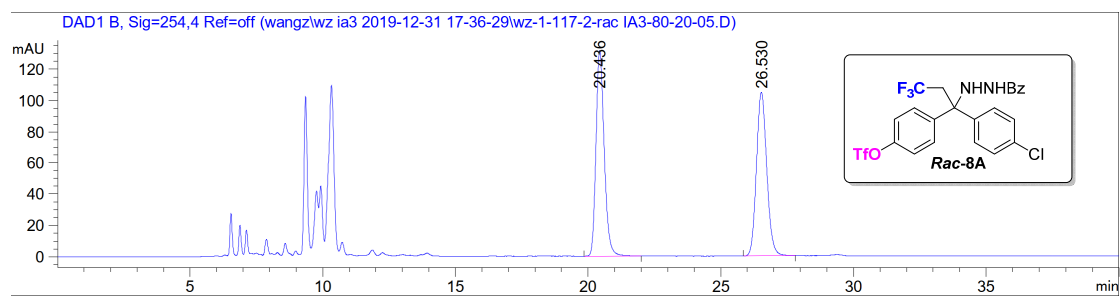
Totals : 2485.48584 134.51934



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.115	BB	0.2554	236.70651	14.42498	15.4731
2	20.629	BB	0.3250	1293.08850	61.58277	84.5269

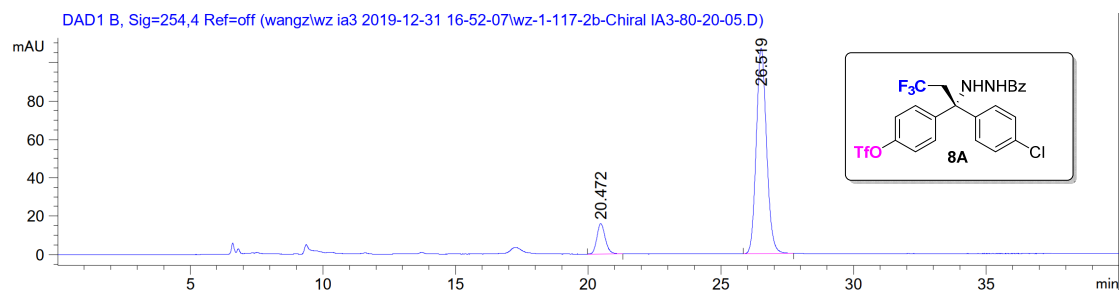
Totals : 1529.79501 76.00775



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.436	BB	0.3295	2833.13477	131.43967	50.0535
2	26.530	BB	0.4168	2827.08081	104.78460	49.9465

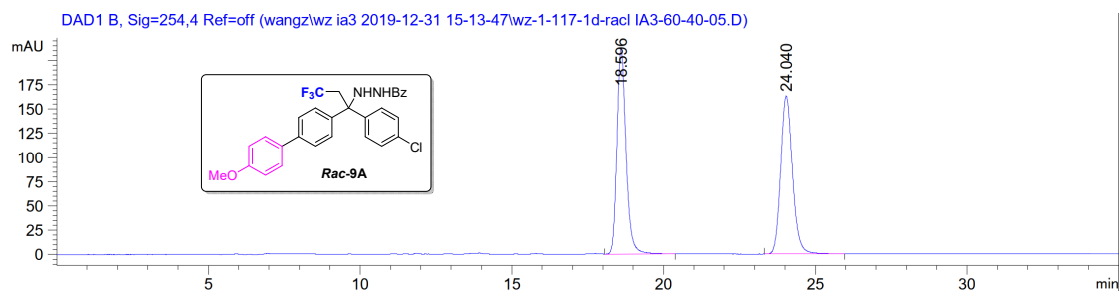
Totals : 5660.21558 236.22427



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.472	BB	0.3351	344.71521	15.76600	10.6981
2	26.519	BB	0.4165	2877.49756	106.75556	89.3019

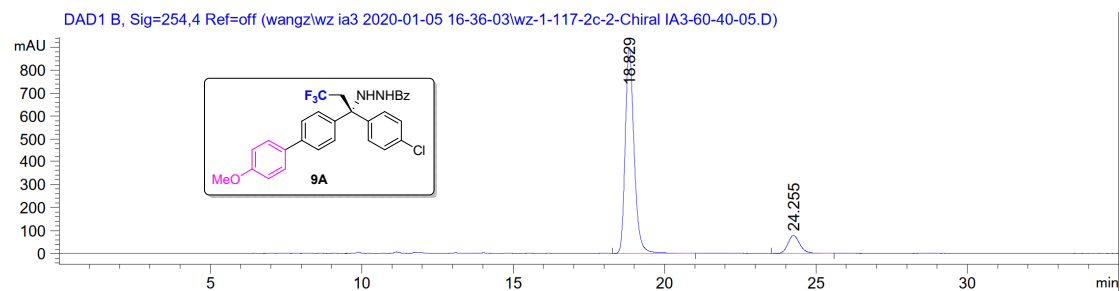
Totals : 3222.21277 122.52156



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.596	BB	0.3166	4406.24365	211.92793	49.9793
2	24.040	BB	0.4162	4409.89941	162.73108	50.0207

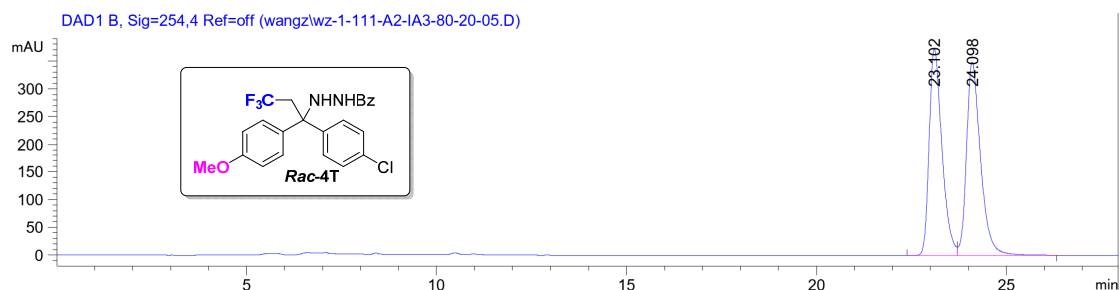
Totals : 8816.14307 374.65901



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.829	BB	0.3079	1.81806e4	899.18823	89.5881
2	24.255	BB	0.4169	2112.93823	77.79408	10.4119

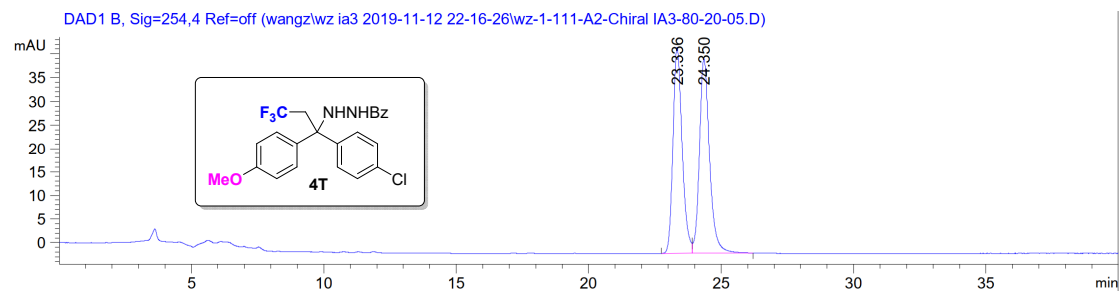
Totals : 2.02935e4 976.98231



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.102	BV	0.3564	8692.26367	372.24265	49.2334
2	24.098	VB	0.3904	8962.94922	348.10040	50.7666

Totals : 1.76552e4 720.34305



Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.336	BV	0.3697	1053.92578	43.64122	49.0319
2	24.350	VB	0.4001	1095.54468	41.21569	50.9681

Totals : 2149.47046 84.85691