Supporting information

Highly Enantioselective Organocatalyzed Vinylogous Michael-Type Reaction for the Construction of Trifluoromethylated All-Carbon Quaternary Stereocenters

Qiao Chen, Guoqiang Wang, Xianxing Jiang, Zhaoqing Xu*, Li Lin, and Rui Wang*

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1.0 General Methods

All commercially available reagents were used without further purification unless otherwise stated. All solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel GF254. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian instrument (300 MHz, 75 MHz and 282 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet) and coupling constant in Hertz (Hz). Optical rotations were recorded on a Perkin-Elmer 341 polarimeter. HRMS was measured with an APEX II 47e mass spectrometer. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel OD-H column or Chiracel IC column on Waters with a 2998 UV-detector and the dr (Z:E) was determined by ^{19}F NMR spectroscopic analysis.

Materials:

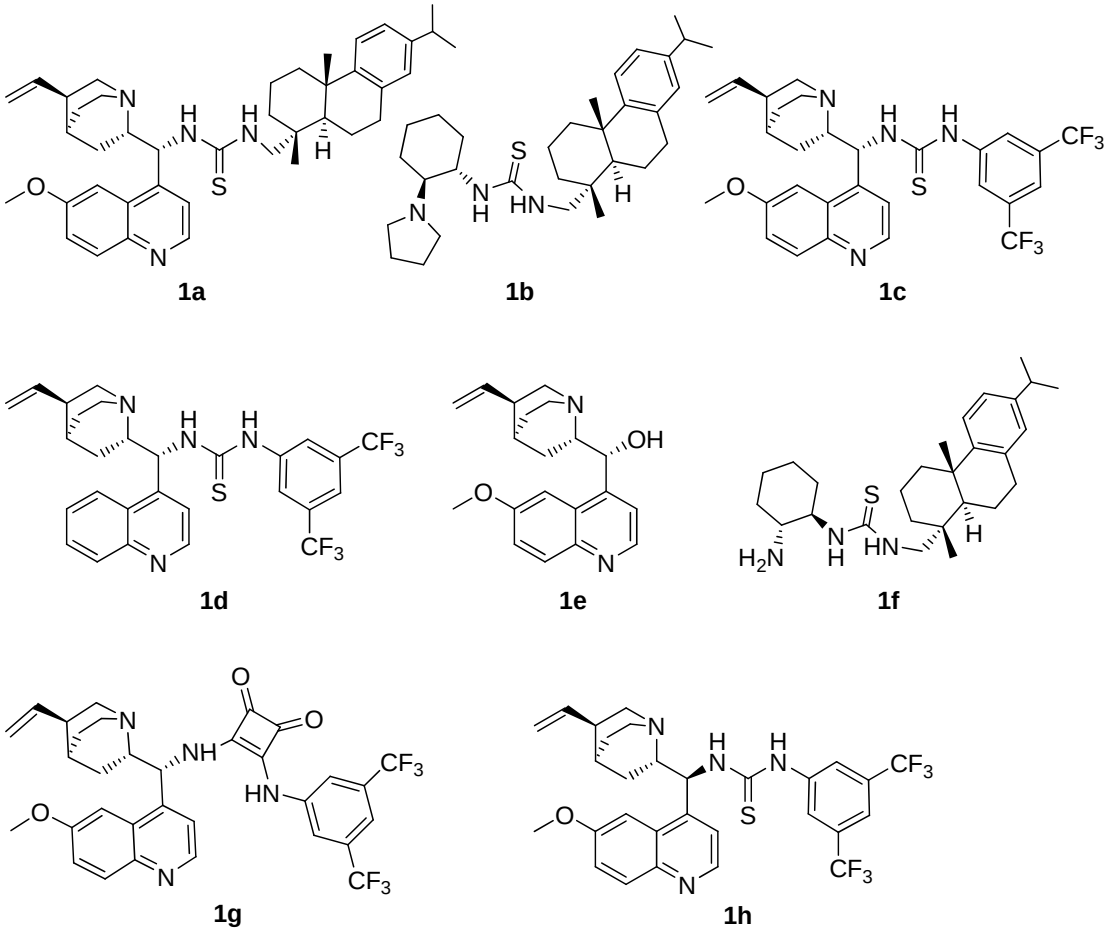
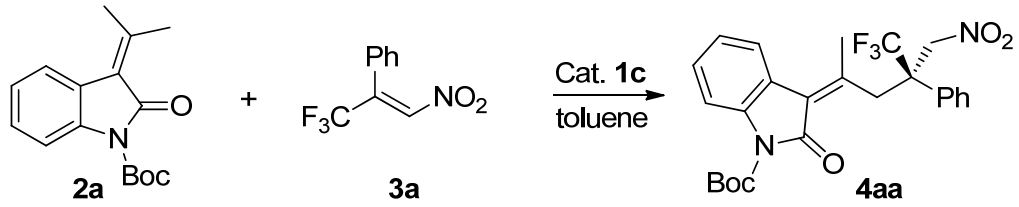


***Figure* S1**: Catalysts for the Asymmetric Vinylogous Michael-Type Reaction.

Catalyst **1e** were commercially available and were used as such without further purification.

Thiourea catalysts **1a**[1], **1b**[1a,2], **1c**[3], **1d**[3b], **1f**[1a,2],**1g**[4], **1h**[3] were prepared according to known procedures, and their spectral and optical data perfectly matched those reported in literature. 3-alkylidene oxindoles **2** were prepared according to literature procedures.[5] Trifluoromethylated nitroalkenes **3** were prepared according to literature procedures.[6]

2.0 General procedure for the asymmetric synthesis of 4:



To a solution of 3-alkylidene oxindole **2a** (0.225 mmol, 1.5 equiv) and catalyst **1c** (0.0225 mmol, 15 mol %) in toluene (0.75 mL) at room temperature, was added trifluoromethylated nitroalkene **3a** (0.15 mmol, 1 equiv). The reaction was kept under vigorous stirring for 36 h at room temperature. The reaction solution was then concentrated in vacuum and the residue was purified by silica gel flash chromatography (petroleum ether/ ethyl acetate 15:1) to yield pure **4aa** as a yellow solid. The enantiomeric ratio was determined by HPLC on a chiral stationary phase, and the dr (Z : E) was determined by ^{19}F NMR spectroscopic analysis. The corresponding opposite enantiomers of the products (*ent*-**4aa**) were obtained using the corresponding opposite enantiomer of the catalyst **1c** (catalyst **1h** in Figure S1) under the same reaction conditions.

2.0 Proposed Model for the Asymmetric Vinylogous Michael-Type Reaction

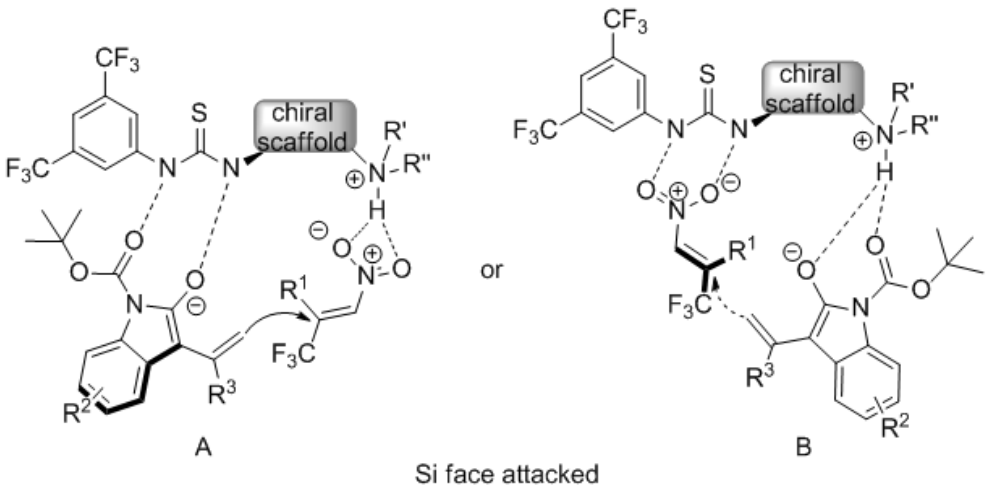
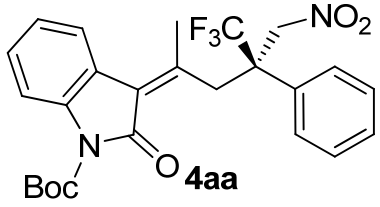


***Figure* S2**: Proposed modes of activation of the substrates.

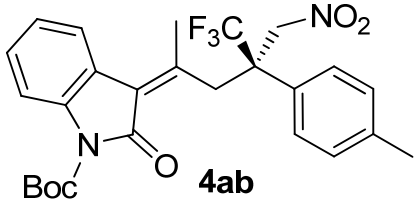
4.0 Characterization Data



(R,Z)-tert-butyl

2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-phenylpentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 92% yield; $[\alpha]_D^{20}$= -150 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 8.9 min, t_{minor} = 10.2 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.31 (m, 4H), 7.18 (td, *J* = 7.7, 1.0 Hz, 1H), 5.50 (dd, *J* = 13.9, 1.1 Hz, 1H), 5.23 (d, *J* = 13.9 Hz, 1H), 3.93 – 3.79 (m, 2H), 2.04 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.10, 151.10, 148.86, 138.31, 134.35, 129.25, 128.81, 128.53, 127.11, 126.86, 124.73, 124.10, 123.06, 114.73, 84.94, 75.72, 55.72, 55.39, 42.01, 28.16, 25.85. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.78 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{25}H_{25}F_3N_2NaO_5$ [M+ Na] $^+$: 513.1608, Found: 513.1609.

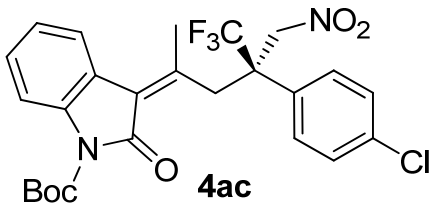


4ab

(R,Z)-tert-butyl

2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-p-tolylpentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 87% yield; $[\alpha]_D^{20}$= -209 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 10.8 min, t_{minor} = 13.5 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 3H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.13 (m, 3H), 5.45 (d, *J* = 13.8 Hz, 1H), 5.22 (d, *J* = 13.8 Hz, 1H), 3.89 (d, *J* = 13.2 Hz, 1H), 3.80 (d, *J* = 13.2 Hz, 1H), 2.37 (s, 3H), 2.04 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.07, 151.40, 148.87, 138.41, 138.28, 131.21, 129.48, 129.18, 126.99, 126.72, 124.71, 124.07, 123.10, 114.70, 84.90, 77.44, 77.02, 76.60, 75.77, 55.45, 55.13, 41.91, 28.15, 25.89, 20.99. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.06 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{26}H_{27}F_3N_2NaO_5$ [M+ Na] $^+$: 527.1764, Found: 527.1767.



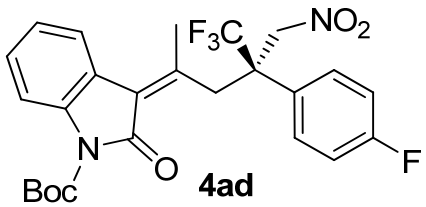
4ac

(R,Z)-tert-butyl

3-(4-(4-chlorophenyl)-5,5,5-trifluoro-4-(nitromethyl)pentan-2-ylidene)-2-oxoindoline-1-carboxyla te

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 91% yield; $[\alpha]_D^{20}$= -99 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 9.9 min, t_{minor} = 12.8 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.50 (d, *J* = 13.8 Hz, 1H), 5.17 (d, *J* = 13.8 Hz, 1H), 3.90 (d, *J* = 13.3 Hz, 1H), 3.72 (d, *J* = 13.3 Hz, 1H), 2.11 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling

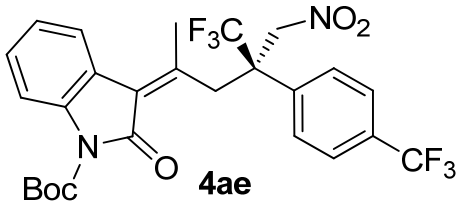
not assigned) δ 166.20, 150.35, 148.77, 138.30, 134.61, 133.04, 129.41, 128.97, 128.65, 127.13, 124.81, 124.22, 122.91, 114.77, 85.07, 77.49, 77.06, 76.64, 75.59, 60.41, 55.50, 55.17, 42.17, 28.14, 26.02. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.85 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}ClF_3N_2NaO_5$ [M+ Na] $^+$: 547.1218, Found: 547.1227.



4ad

(R,Z)-tert-butyl 2-oxo-3-(5,5,5-trifluoro-4-(4-fluorophenyl)-4-(nitromethyl)pentan-2-ylidene)indoline-1-carboxylate

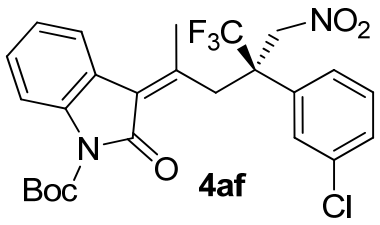
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 84% yield; $[\alpha]_D^{20}$= -247 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 9.5 min, t_{minor} = 12.7 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 8.5, 5.0 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.31 (m, 1H), 7.19 (td, *J* = 7.7, 0.9 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 5.55 – 5.40 (m, 1H), 5.18 (d, *J* = 13.8 Hz, 1H), 3.89 (d, *J* = 13.3 Hz, 1H), 3.76 (d, *J* = 13.3 Hz, 1H), 2.10 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.18, 164.02, 160.71, 150.56, 148.78, 138.30, 130.24, 130.19, 129.38, 129.20, 129.12, 127.07, 124.78, 124.19, 122.94, 115.92, 115.64, 114.77, 85.05, 77.47, 77.04, 76.62, 75.75, 55.40, 55.08, 42.23, 29.70, 28.14, 25.96. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.96 (s, 3F), -113.01(s, 1F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}F_4N_2NaO_5$ [M+ Na] $^+$: 531.1514, Found: 531.1511.



4ae

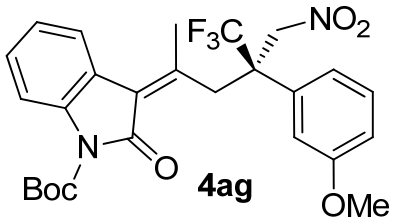
(R,Z)-tert-butyl 2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-(4-(trifluoromethyl)phenyl)pentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 90% yield; $[\alpha]_D^{20}$= -200 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 7.4 min, t_{minor} = 9.5 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 3H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 5.61 (d, *J* = 13.9 Hz, 1H), 5.17 (d, *J* = 13.9 Hz, 1H), 4.03 (d, *J* = 13.3 Hz, 1H), 3.62 (d, *J* = 13.4 Hz, 1H), 2.16 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.25, 149.83, 148.73, 138.79, 138.34, 130.85, 130.42, 129.52, 127.68, 127.36, 125.73, 125.68, 124.85, 124.26, 122.83, 114.81, 85.14, 77.47, 77.05, 76.62, 75.42, 55.84, 55.51, 42.38, 29.70, 28.13, 26.90, 26.03. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.86 (s, 3F), -65.47 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{26}H_{24}F_6N_2NaO_5$ [M+ Na] $^+$: 581.1482, Found: 581.1479.



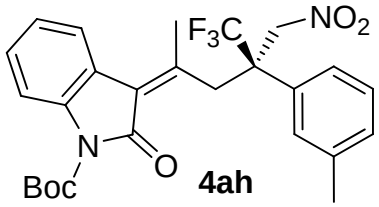
(R,Z)-tert-butyl
3-(4-(3-chlorophenyl)-5,5,5-trifluoro-4-(nitromethyl)pentan-2-ylidene)-2-oxoindoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 88% yield; $[\alpha]_D^{20}$= -168 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 9.8 min, t_{minor} = 12.9 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.64 (s, 1H), 7.60 – 7.55 (m, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.24 – 7.15 (m, 1H), 5.50 (d, *J* = 13.9 Hz, 1H), 5.18 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.3 Hz, 1H), 3.74 (d, *J* = 13.3 Hz, 1H), 2.11 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.13, 150.13, 148.80, 138.34, 136.56, 134.76, 130.03, 129.42, 128.77, 127.46, 127.19, 125.44, 124.81, 124.21, 122.91, 114.78, 85.04, 77.48, 77.06, 76.63, 75.47, 55.62, 55.29, 42.15, 29.70, 28.14, 26.90, 26.00. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.70 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}ClF_3N_2NaO_5$ $[M+Na]^+$: 547.1218, Found: 547.1225.



(R,Z)-tert-butyl
2-oxo-3-(5,5,5-trifluoro-4-(3-methoxyphenyl)-4-(nitromethyl)pentan-2-ylidene)indoline-1-carboxylate

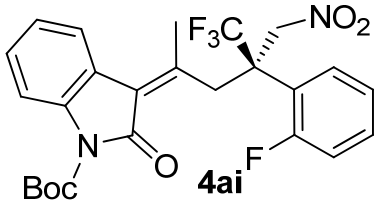
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 82% yield; $[\alpha]_D^{20}$= -259 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 13.3 min, t_{minor} = 16.0 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.24 – 7.13 (m, 3H), 6.91 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.44 (d, *J* = 14.0 Hz, 1H), 5.24 (d, *J* = 14.0 Hz, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 3.82 (s, 3H), 3.77 (d, *J* = 13.2 Hz, 1H), 2.04 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.02, 159.69, 151.06, 148.89, 138.31, 135.81, 129.80, 129.24, 126.83, 124.72, 124.10, 123.06, 119.37, 114.72, 113.85, 113.33, 84.87, 77.48, 77.06, 76.63, 75.74, 55.60, 55.32, 41.85, 29.70, 28.14, 25.76. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.79 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{26}H_{27}F_3N_2NaO_6$ $[M+Na]^+$: 543.1713, Found: 543.1713.



(R,Z)-tert-butyl

2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-m-tolylpentan-2-ylidene)indoline-1-carboxylate

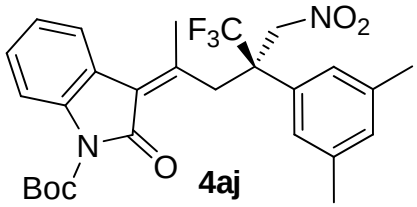
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 90% yield; $[\alpha]_D^{20}$= -146 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 10.0 min, t_{minor} = 13.8 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.42 (s, 2H), 7.33 (dt, *J* = 13.9, 8.1 Hz, 2H), 7.22 – 7.13 (m, 2H), 5.47 (d, *J* = 13.9 Hz, 1H), 5.23 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.2 Hz, 1H), 3.80 (d, *J* = 13.2 Hz, 1H), 2.39 (s, 3H), 2.03 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.06, 151.32, 148.89, 138.43, 138.29, 134.26, 129.28, 129.21, 128.66, 127.68, 126.76, 124.71, 124.10, 123.10, 114.72, 84.90, 77.48, 77.05, 76.63, 75.74, 55.63, 55.31, 41.94, 29.71, 28.15, 25.87, 21.76. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.70 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{26}H_{27}F_3N_2NaO_5$ [M+ Na] $^+$: 527.1764, Found: 527.1762.



(R,Z)-tert-butyl

2-oxo-3-(5,5,5-trifluoro-4-(2-fluorophenyl)-4-(nitromethyl)pentan-2-ylidene)indoline-1-carboxylat e

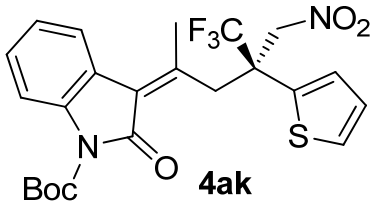
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 83% yield; $[\alpha]_D^{20}$= -113 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 0.6 mL/min, 254 nm; t_{major} = 18.8 min, t_{minor} = 21.5 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.19 – 7.05 (m, 2H), 5.56 (d, *J* = 14.9 Hz, 1H), 5.31 (dd, *J* = 14.9, 1.8 Hz, 1H), 4.20 (d, *J* = 13.2 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 2.03 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 165.78, 163.02, 159.74, 150.43, 148.94, 138.36, 130.87, 130.74, 129.21, 129.13, 126.47, 124.66, 123.97, 123.17, 121.43, 121.30, 117.14, 116.80, 114.64, 84.68, 77.46, 77.04, 76.62, 74.96, 74.85, 54.21, 54.15, 53.83, 38.20, 28.15, 25.33. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.92 (s, 3F), -107.22 (d, *J* = 3.0Hz, 1F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}F_4N_2NaO_5$ [M+ Na] $^+$: 531.1514, Found: 531.1520.



(R,Z)-tert-butyl

3-(4-(3,5-dimethylphenyl)-5,5,5-trifluoro-4-(nitromethyl)pentan-2-ylidene)-2-oxoindoline-1-carboxylate

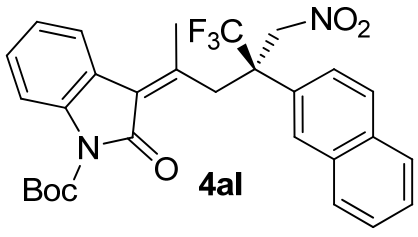
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 92% yield; $[\alpha]_D^{20}$= -179 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 8.2 min, t_{minor} = 10.9 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.29 (m, 1H), 7.23 – 7.13 (m, 3H), 7.00 (s, 1H), 5.44 (d, *J* = 14.8 Hz, 1H), 5.22 (d, *J* = 14.0 Hz, 1H), 3.90 (d, *J* = 13.2 Hz, 1H), 3.78 (d, *J* = 13.1 Hz, 1H), 2.34 (s, 6H), 2.03 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.01, 151.53, 148.92, 138.29, 138.24, 134.18, 130.16, 129.16, 126.67, 124.77, 124.67, 124.07, 123.16, 114.72, 84.86, 77.46, 77.04, 76.61, 75.78, 55.55, 55.22, 41.85, 28.15, 25.90, 21.63. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.63 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{27}H_{29}F_3N_2NaO_5$ [M+ Na] $^+$: 541.1921, Found: 541.1947.



4ak

(R,Z)-tert-butyl 2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-(thiophen-2-yl)pentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 91% yield; $[\alpha]_D^{20}$= -156 (c 1.0, $CHCl_3$), 98% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 13.5 min, t_{minor} = 16.1 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 5.2, 1.0 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 7.17 (td, *J* = 7.7, 0.9 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.8 Hz, 1H), 5.34 (d, *J* = 13.2 Hz, 1H), 5.22 (d, *J* = 13.2 Hz, 1H), 4.27 (d, *J* = 13.0 Hz, 1H), 3.65 (d, *J* = 13.0 Hz, 1H), 2.05 (s, 3H), 1.67 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 165.83, 150.24, 148.86, 138.37, 136.54, 129.30, 127.96, 126.93, 126.81, 126.43, 124.74, 124.08, 123.02, 114.69, 84.86, 77.50, 77.07, 76.65, 53.91, 53.57, 42.20, 28.14, 25.18. ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.22 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{23}H_{23}F_3N_2NaO_5S$ [M+ Na] $^+$: 519.1172, Found: 519.1180.

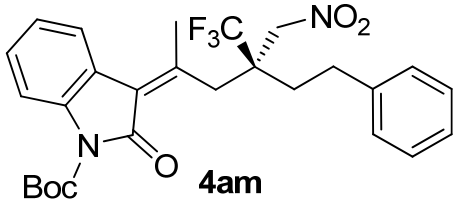


4al

(R,Z)-tert-butyl 2-oxo-3-(5,5,5-trifluoro-4-(naphthalen-2-yl)-4-(nitromethyl)pentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v);

Yellow solid, 82% yield; $[\alpha]_D^{20}$= -302 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 14.7 min, t_{minor} = 16.8 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.88 – 7.76 (m, 4H), 7.59 – 7.50 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.30 (m, 1H), 7.15 (td, *J* = 7.7, 0.8 Hz, 1H), 5.63 (d, *J* = 14.0 Hz, 1H), 5.30 (d, *J* = 13.9 Hz, 1H), 3.99 (d, *J* = 13.2 Hz, 1H), 3.88 (d, *J* = 13.2 Hz, 1H), 2.02 (s, 3H), 1.70 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.18, 151.04, 148.88, 138.30, 132.87, 132.67, 131.67, 129.28, 128.60, 128.57, 127.46, 127.07, 126.91, 126.70, 124.76, 124.43, 124.14, 123.05, 114.74, 84.98, 77.49, 77.07, 76.64, 75.76, 55.97, 55.64, 41.94, 28.17, 26.02. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.55 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{29}H_{27}F_3N_2NaO_5$ [M+ Na] $^+$: 563.1764, Found: 563.1784.

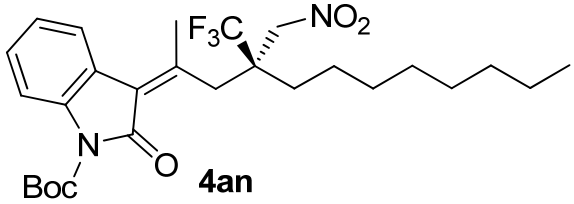


4am

(S,Z)-tert-butyl

3-(4-(nitromethyl)-6-phenyl-4-(trifluoromethyl)hexan-2-ylidene)-2-oxoindoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 93% yield; $[\alpha]_D^{20}$= -57 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 8.5 min, t_{minor} = 13.9 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.26 (m, 5H), 7.26 – 7.18 (m, 2H), 5.21 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.39 (d, *J* = 13.2 Hz, 1H), 3.12 (td, *J* = 12.9, 4.3 Hz, 1H), 2.96 – 2.83 (m, 2H), 2.47 (s, 3H), 2.43 – 2.29 (m, 1H), 2.13 (td, *J* = 13.6, 4.8 Hz, 1H), 1.67 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.08, 151.32, 148.81, 140.65, 138.26, 129.27, 128.66, 128.53, 126.83, 126.37, 124.88, 124.19, 123.06, 114.76, 84.98, 77.47, 77.05, 76.62, 74.92, 50.69, 50.37, 37.71, 34.26, 29.71, 29.54, 28.14, 26.51. ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.76 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{27}H_{29}F_3N_2NaO_5$ [M+ Na] $^+$: 541.1921, Found: 541.1920.



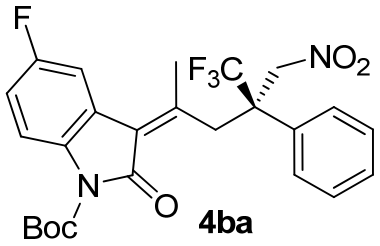
4an

(S,Z)-tert-butyl

3-(4-(nitromethyl)-4-(trifluoromethyl)dodecan-2-ylidene)-2-oxoindoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 60% yield; $[\alpha]_D^{20}$= -47 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 6.3 min, t_{minor} = 13.8 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.22 (td, *J* = 7.7, 1.0 Hz, 1H), 5.08 – 4.97 (m, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 13.2 Hz, 1H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.44 (s, 3H), 2.08 – 1.95 (m, 1H), 1.91 – 1.78 (m, 1H), 1.67 (s, 9H), 1.60 – 1.50 (m, 2H),

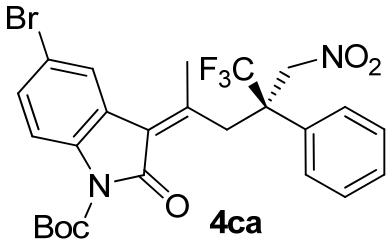
1.35 – 1.26 (m, 10H), 0.93 – 0.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 199.14, 165.97, 151.85, 148.83, 138.21, 129.14, 126.63, 124.82, 124.12, 123.15, 114.71, 84.88, 77.44, 77.02, 76.59, 75.48, 50.64, 50.32, 37.66, 32.03, 31.81, 29.97, 29.29, 29.24, 28.14, 26.43, 26.39, 23.00, 22.65, 14.13. ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.53 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{27}H_{37}F_3N_2NaO_5$ [M+ Na] $^+$: 549.2547, Found: 549.2552.



4ba

(R,Z)-tert-butyl 5-fluoro-2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-phenylpentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 86% yield; $[\alpha]_D^{20}$= -120 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 70/30, 0.4 mL/min, 254 nm; t_{major} = 15.4 min, t_{minor} = 16.4 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.37 (m, 3H), 7.21 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.06 (td, *J* = 8.8, 2.6 Hz, 1H), 5.47 (d, *J* = 13.9 Hz, 1H), 5.23 (d, *J* = 13.9 Hz, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 3.83 (d, *J* = 13.2 Hz, 1H), 2.01 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 165.74, 160.97, 157.76, 153.01, 148.77, 134.35, 134.32, 134.07, 128.86, 128.66, 127.10, 127.08, 126.46, 126.43, 124.23, 124.12, 115.90, 115.79, 115.68, 115.38, 112.21, 111.86, 85.11, 77.45, 77.02, 76.60, 75.69, 55.65, 55.32, 41.63, 29.70, 28.14, 25.65. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.07 (s, 3F), -117.84 (s, 1F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}F_4N_2NaO_5$ [M+ Na] $^+$: 531.1514, Found: 531.1516.

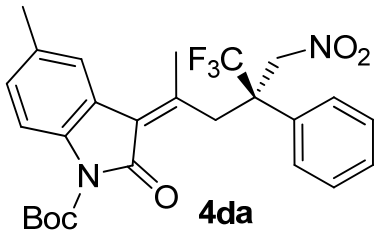


4ca

(R,Z)-tert-butyl 5-bromo-2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-phenylpentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 81% yield; $[\alpha]_D^{20}$= -112 (c 1.0, $CHCl_3$), 98% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 12.2 min, t_{minor} = 13.7 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.51 – 7.37 (m, 4H), 5.44 (d, *J* = 14.1 Hz, 1H), 5.22 (d, *J* = 13.9 Hz, 1H), 3.96 (d, *J* = 13.2 Hz, 1H), 3.81 (d, *J* = 13.2 Hz, 1H), 2.02 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 165.29, 153.30, 148.64, 137.19, 134.01, 131.85, 128.87, 128.68, 127.39, 127.09, 125.90, 124.77, 117.14, 116.24, 85.29, 77.44, 77.02, 76.60, 75.68, 55.93, 55.60, 55.28, 41.57, 28.12, 25.87. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.13 (s,

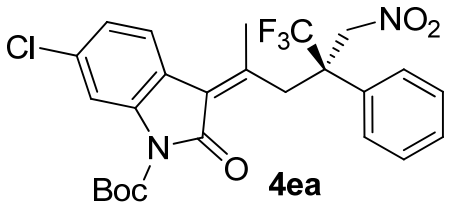
3F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}BrF_3N_2NaO_5$ [M+ Na] $^+$: 591.0713, Found: 591.0716.



4da

(R,Z)-tert-butyl 5-methyl-2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-phenylpentan-2-ylidene)indoline-1-carboxylate

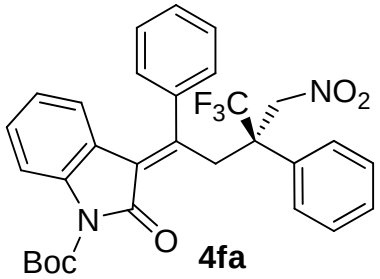
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 81% yield; $[\alpha]_D^{20}$= -181 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 11.9 min, t_{minor} = 15.0 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.36 (m, 3H), 7.30 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 5.49 (d, *J* = 13.9 Hz, 1H), 5.23 (d, *J* = 13.9 Hz, 1H), 3.91 – 3.78 (m, 2H), 2.36 (s, 3H), 2.03 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.33, 150.66, 148.90, 136.07, 134.42, 133.58, 129.76, 128.80, 128.50, 127.12, 127.02, 125.40, 123.09, 114.53, 84.76, 77.47, 77.05, 76.62, 75.71, 55.72, 55.39, 42.11, 28.16, 26.90, 25.95, 21.36. ^{19}F NMR (282 MHz, $CDCl_3$) δ -65.73 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{26}H_{27}F_3N_2NaO_5$ [M+ Na] $^+$: 527.1764, Found: 527.1765.



4ea

(R,Z)-tert-butyl 6-chloro-2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-phenylpentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 87% yield; $[\alpha]_D^{20}$= -181 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 10.7 min, t_{minor} = 12.1 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.37 (m, 4H), 7.15 (dd, *J* = 8.4, 1.9 Hz, 1H), 5.45 (d, *J* = 13.9 Hz, 1H), 5.22 (d, *J* = 13.9 Hz, 1H), 3.91 (d, *J* = 13.3 Hz, 1H), 3.81 (d, *J* = 13.3 Hz, 1H), 2.01 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 165.60, 151.82, 148.58, 139.07, 135.09, 134.11, 128.84, 128.63, 127.11, 126.06, 125.34, 124.11, 121.49, 115.49, 85.45, 77.45, 77.02, 76.60, 75.69, 55.62, 55.30, 54.97, 41.63, 28.11, 25.82. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.05 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{25}H_{24}ClF_3N_2NaO_5$ [M+ Na] $^+$: 547.1218, Found: 547.1218.

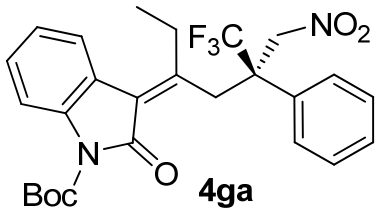


4fa

(R,E)-tert-butyl

2-oxo-3-(4,4,4-trifluoro-3-(nitromethyl)-1,3-diphenylbutylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 91% yield; $[\alpha]_D^{20}$= +122 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{major} = 11.3 min, t_{minor} = 12.4 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.24 (m, 8H), 7.22 – 7.10 (m, 2H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 7.5 Hz, 1H), 5.74 (d, *J* = 7.8 Hz, 1H), 5.12 (d, *J* = 3.6 Hz, 1H), 5.07 (d, *J* = 6.2 Hz, 1H), 4.46 (d, *J* = 15.8 Hz, 1H), 4.34 (d, *J* = 13.3 Hz, 1H), 1.70 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.34, 153.34, 148.98, 138.49, 138.30, 133.07, 129.37, 129.25, 129.04, 128.84, 128.58, 127.74, 127.39, 126.37, 123.52, 123.23, 122.52, 114.30, 84.79, 77.50, 77.07, 76.65, 75.01, 52.73, 52.41, 32.31, 29.71, 28.18. ^{19}F NMR (282 MHz, $CDCl_3$) δ -70.84 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{30}H_{27}F_3N_2NaO_5$ [M+ Na] $^+$: 575.1764, Found: 575.1788.

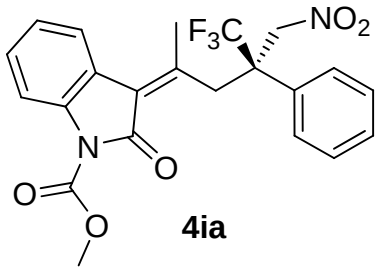


4ga

(R,Z)-tert-butyl

2-oxo-3-(6,6,6-trifluoro-5-(nitromethyl)-5-phenylhexan-3-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 72% yield; $[\alpha]_D^{20}$= -269 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} = 6.9 min, t_{minor} = 8.8 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.29 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.47 (d, *J* = 14.0 Hz, 1H), 5.30 (d, *J* = 14.0 Hz, 1H), 4.06 (d, *J* = 13.1 Hz, 1H), 3.61 (d, *J* = 13.0 Hz, 1H), 2.55 – 2.39 (m, 1H), 2.06 – 1.90 (m, 1H), 1.69 (s, 9H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, C-F coupling not assigned) δ 166.55, 158.35, 148.81, 138.32, 134.00, 129.23, 128.77, 128.53, 127.12, 125.95, 124.30, 124.13, 122.09, 114.72, 84.91, 77.46, 77.04, 76.61, 75.83, 55.71, 55.39, 38.36, 29.54, 28.15, 10.93. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.51 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{26}H_{27}F_3N_2NaO_5$ [M+ Na] $^+$: 527.1764, Found: 527.1789.

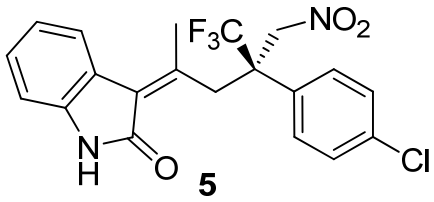


4ia

(R,Z)-methyl

2-oxo-3-(5,5,5-trifluoro-4-(nitromethyl)-4-phenylpentan-2-ylidene)indoline-1-carboxylate

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 81% yield; $[\alpha]_D^{20}$= -175 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel IC column, n-hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} = 17.3 min, t_{minor} = 20.9 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.34 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.44 (d, *J* = 14.1 Hz, 1H), 5.25 (d, *J* = 13.9 Hz, 1H), 4.08 (s, 3H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.80 (d, *J* = 13.3 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.60, 152.02, 151.36, 137.92, 134.10, 129.44, 128.86, 128.64, 127.12, 126.55, 124.67, 124.51, 123.23, 114.96, 77.47, 77.04, 76.62, 75.68, 55.57, 55.25, 54.14, 41.60, 25.83. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.03 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{22}H_{19}F_3N_2NaO_5$ [M+ Na] $^+$: 471.1138, Found: 471.1139.



5

(R,Z)-3-(4-(4-chlorophenyl)-5,5,5-trifluoro-4-(nitromethyl)pentan-2-ylidene)indolin-2-one

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:15 (v/v); Yellow solid, 95% yield; $[\alpha]_D^{20}$= -89 (c 1.0, $CHCl_3$), 99% ee [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} = 8.9 min, t_{minor} = 13.8 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 8.3 Hz, 3H), 7.27 (d, *J* = 9.0 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 5.48 (d, *J* = 14.0 Hz, 1H), 5.26 (d, *J* = 14.0 Hz, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 3.81 (d, *J* = 13.2 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.55, 149.45, 139.79, 134.65, 133.11, 129.40, 128.98, 128.67, 128.50, 125.18, 123.27, 122.44, 109.94, 77.48, 77.06, 76.64, 75.19, 55.06, 54.73, 41.15, 25.22. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.29 (s, 3F). HRMS-ESI (m/z): Calculated for $C_{20}H_{16}ClF_3N_2NaO_3$ [M+ Na] $^+$: 447.0694, Found: 447.0696.

5.0 References

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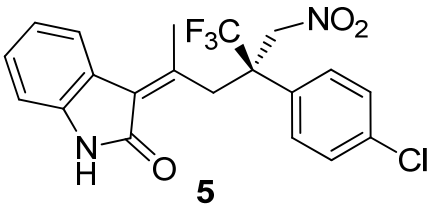
5 a) B. M. Trost, N. Cramer, S. M. Silverman, *J. Am. Chem. Soc.* **2007**, *129*, 12396-12397; b) G. Rassu, V. Zambrano, R. Tanca, A. Sartori, L. Battistini, F. Zanardi, C. Curti, G. Casiraghi, *Eur. J. Org. Chem.* **2012**, 466-470.

6 a) X. Zuo, X. Zhao, B. Liu, S. Yang, L. Fan, *J. Appl. Poly. Sci.* **2009**, *112*, 2781-2791; b) J.-R. Gao, H. Wu, B. Xiang, W.-B. Yu, L. Han, Y.-X. Jia, *J. Am. Chem. Soc.* **2013**, *135*, 2983–2986;

6.0 Absolute Configuration and X-Ray Analysis Data

CCDC 986456 (**5**)



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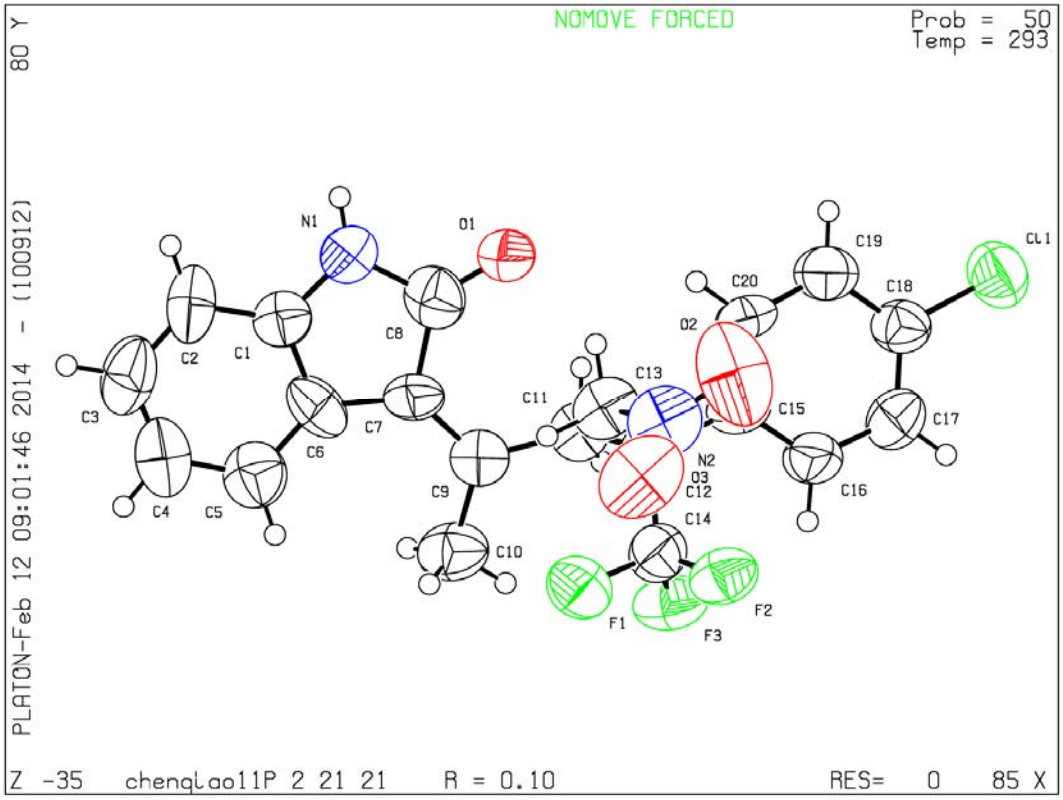
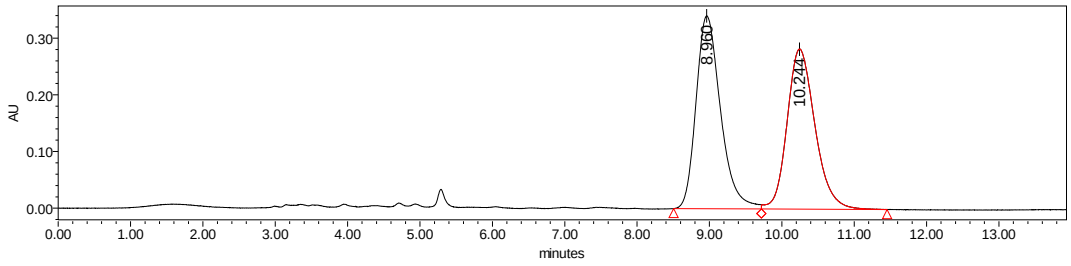


Table 1 Crystal data and structure refinement for **5**

Identification code	chenqiao1126	
Empirical formula	C20 H20 Cl F3 N2 O5	
Formula weight	460.83	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2 21 21	
Unit cell dimensions	a = 7.6488(11) Å	α= 90°.
	b = 16.8386(13) Å	β= 90°.
	c = 17.9210(19) Å	γ = 90°.
Volume	2308.1(5) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	952	
Crystal size	0.420 x 0.320 x 0.280 mm^3	
Theta range for data collection	3.320 to 25.677°.	
Index ranges	-6<=h<=9, -15<=k<=20, -21<=l<=21	
Reflections collected	7371	
Independent reflections	4289 [R(int) = 0.0825]	
Completeness to theta = 25.242°	98.5 %	
Max. and min. transmission	1.000 and 0.440	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4289 / 0 / 264	
Goodness-of-fit on F^2	0.961	
Final R indices [I>2sigma(I)]	R1 = 0.1035, wR2 = 0.2653	
R indices (all data)	R1 = 0.1738, wR2 = 0.3379	
Absolute structure parameter	0.06(13)	
Extinction coefficient	0.032(10)	
Largest diff. peak and hole	0.432 and -0.336 $e.Å^{-3}$	

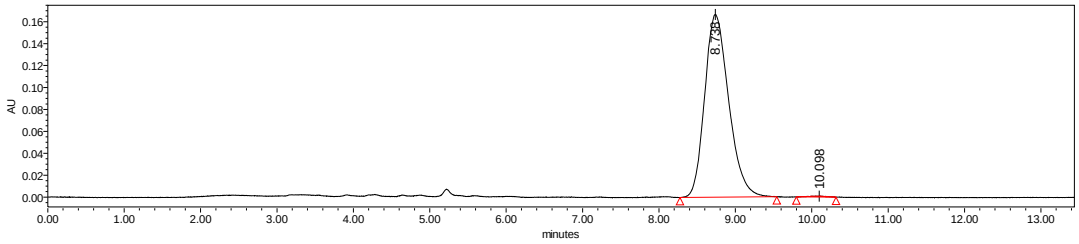
7.0 Copies of HPLC Spectra of Racemic and Chiral Products

4aa + *ent*-**4aa**



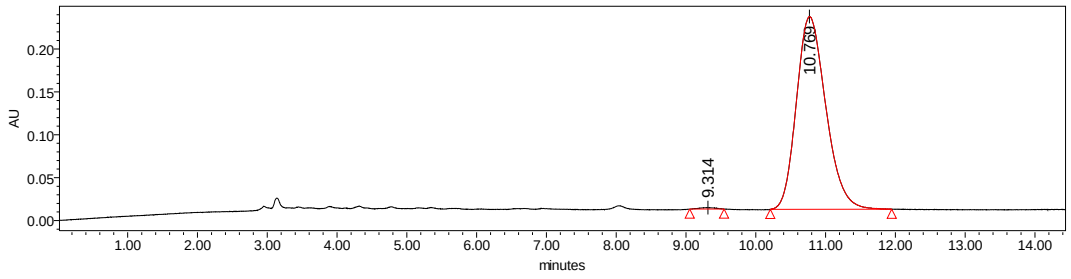
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.960	8002679	51.40	340583	bv
2	10.244	7568020	48.60	282447	vb

4aa



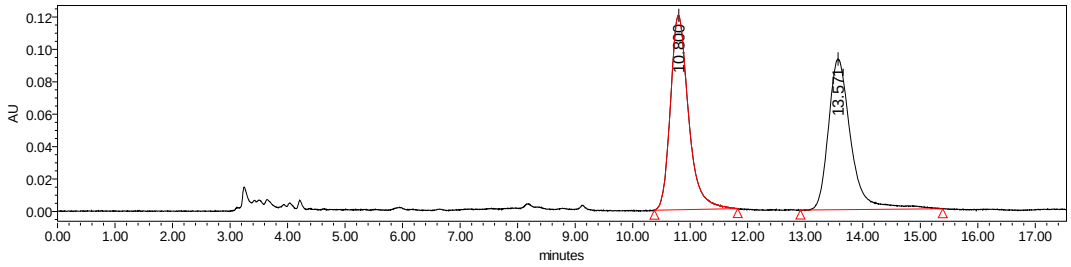
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.738	3639779	99.64	166660	bb
2	10.098	13083	0.36	818	bb

ent-**4aa**



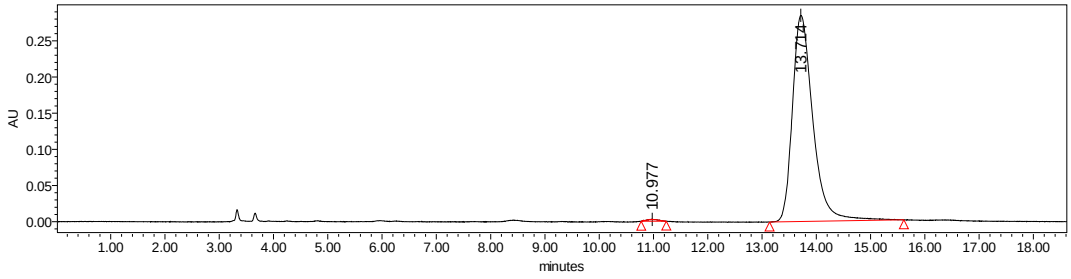
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.314	24711	0.37	1658	bb
2	10.769	6579126	99.63	224910	bb

4ab + *ent*-**4ab**



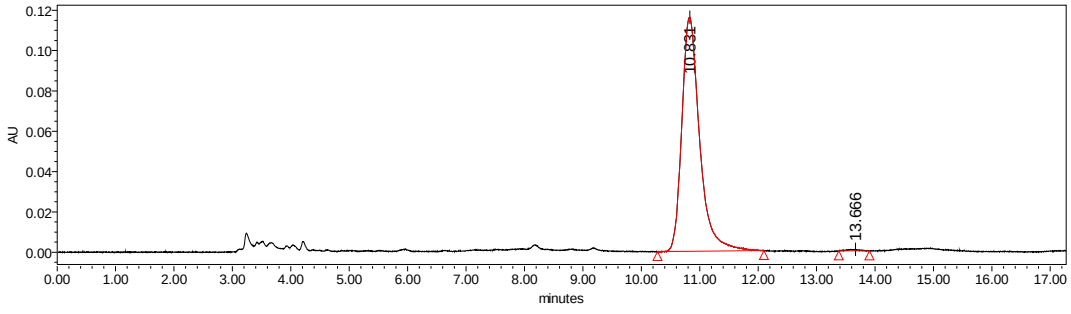
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.800	2616968	50.93	120076	bb
2	13.571	2521601	49.07	93106	bb

4ab



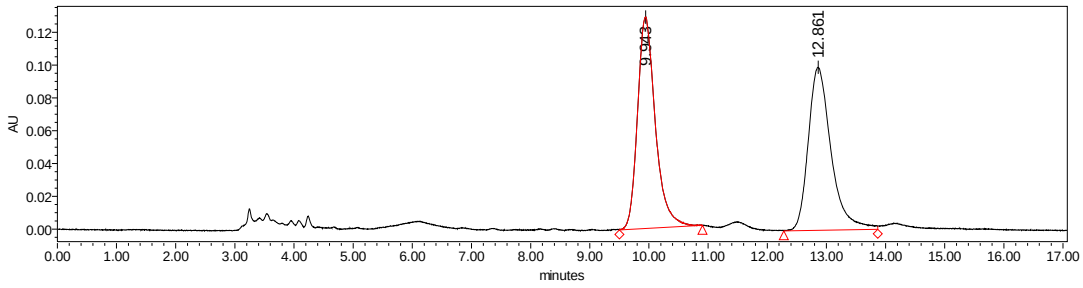
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.977	36866	0.49	2553	bb
2	13.714	7440158	99.51	284993	bb

ent-**4ab**



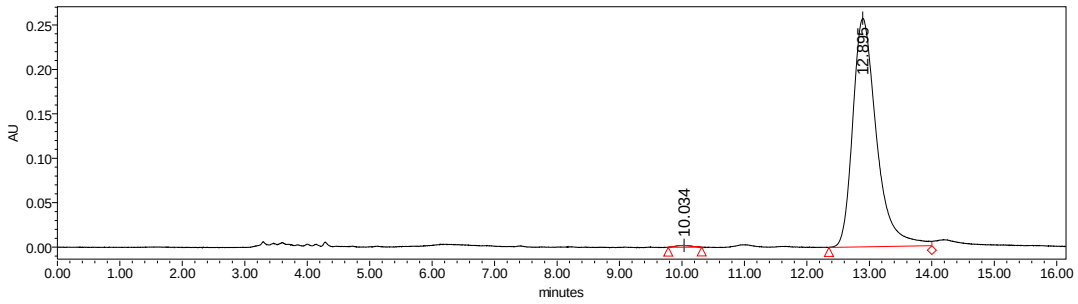
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.831	2443715	99.55	116154	bb
2	13.666	11092	0.45	775	bb

4ac + *ent*-**4ac**



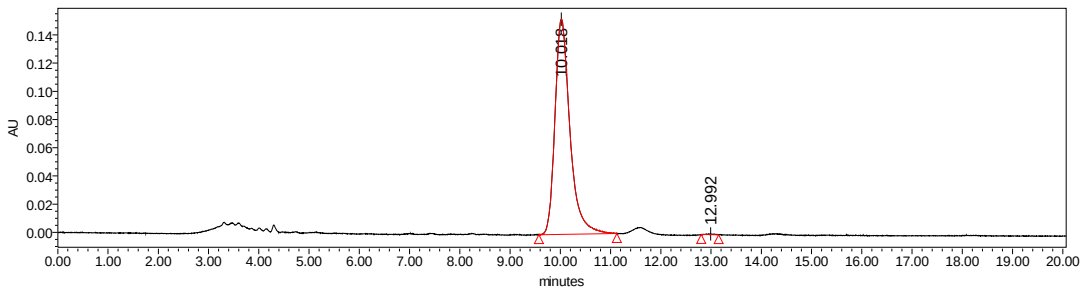
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.943	2690313	50.34	128798	Vb
2	12.861	2653669	49.66	99270	BV

4ac



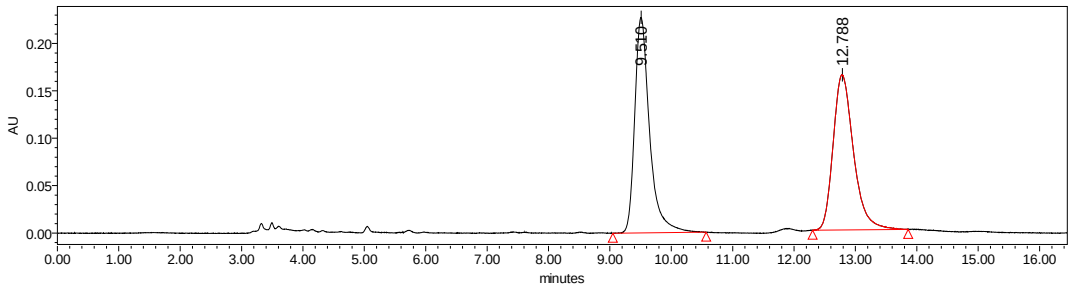
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.034	33827	0.50	2061	bb
2	12.895	6779206	99.50	257308	BV

ent-**4ac**



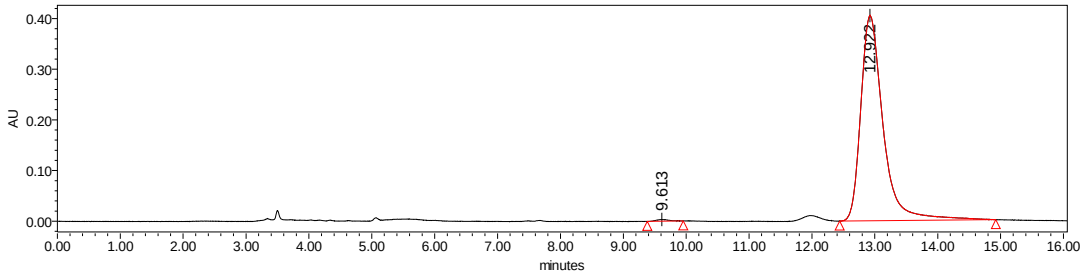
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.018	3153626	99.85	152517	bb
2	12.992	4666	0.15	549	bb

4ad + *ent*-**4ad**



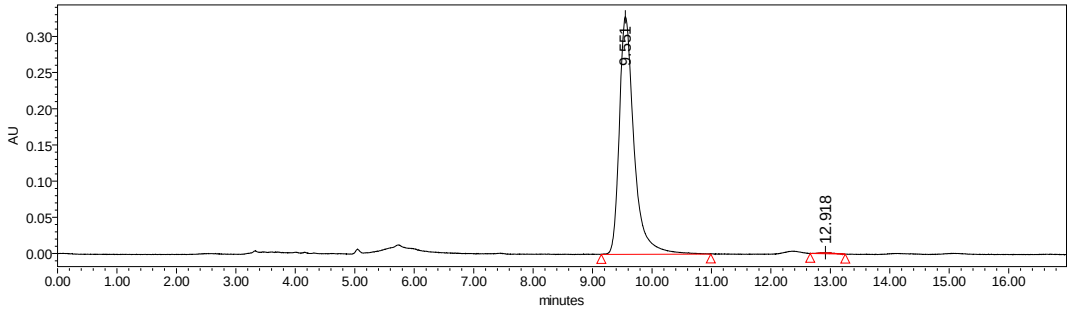
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.510	3821459	50.28	227523	bb
2	12.788	3778595	49.72	163706	bb

4ad



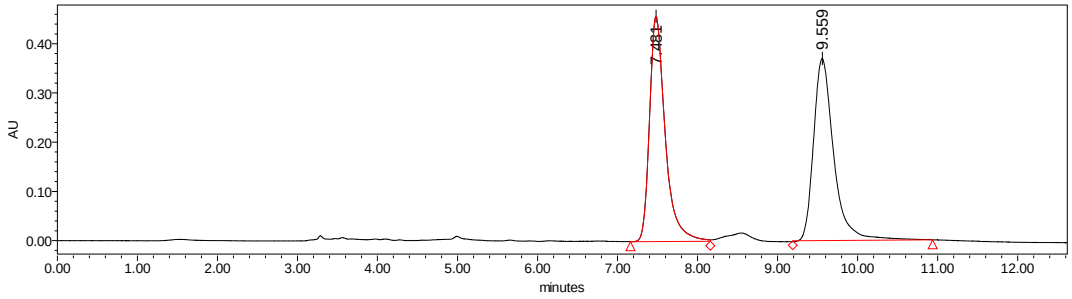
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.613	47293	0.47	3416	bb
2	12.922	9990461	99.53	405040	bb

ent-**4ad**



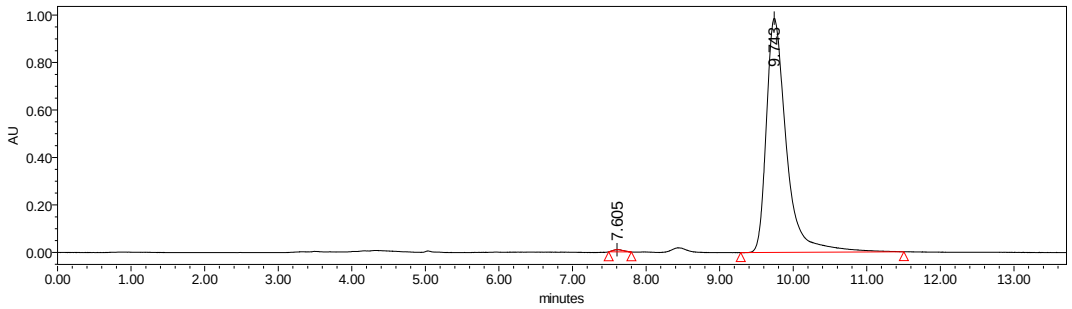
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.551	5643369	99.62	328096	BB
2	12.918	21684	0.38	1392	bb

4ae + *ent*-**4ae**



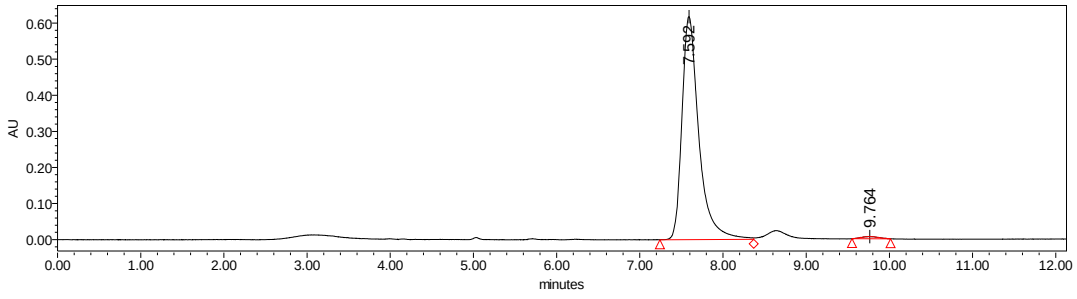
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	7.481	6235344	49.12	457633	BV
2	9.559	6458865	50.88	369995	Vb

4ae



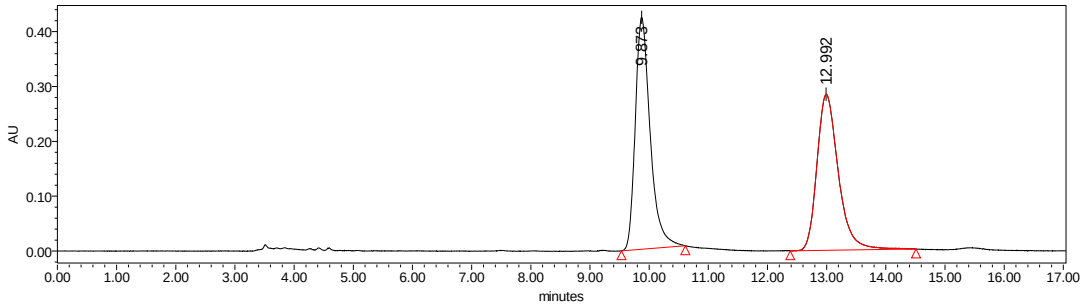
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	7.605	89850	0.48	9338	bb
2	9.743	18673624	99.52	987241	bb

ent-**4ae**



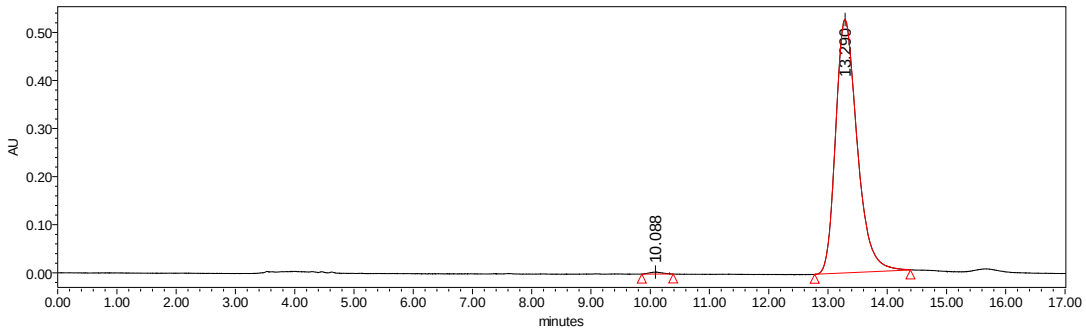
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	7.592	8716214	99.03	617929	BV
2	9.764	85387	0.97	5966	bb

4af + *ent*-**4af**



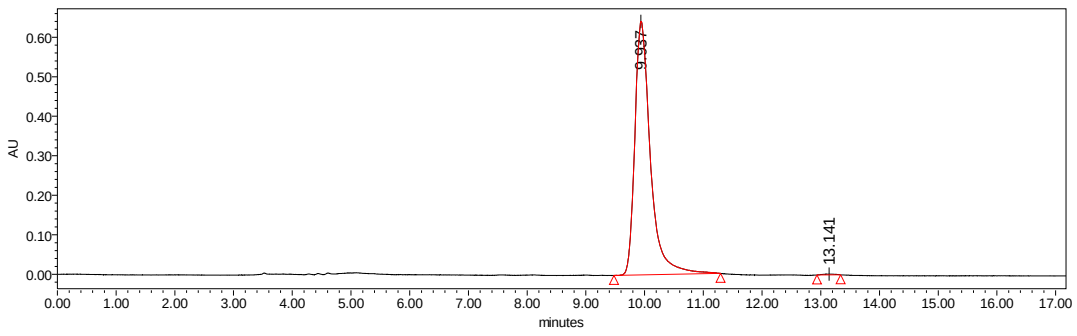
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.873	7406242	50.99	423120	bb
2	12.992	7118106	49.01	284618	bb

4af



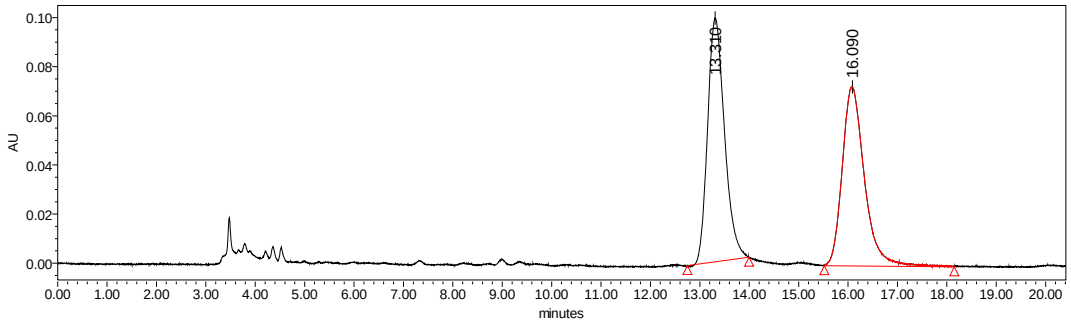
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.088	58604	0.44	3958	bb
2	13.290	13290554	99.56	527225	bb

ent-**4af**



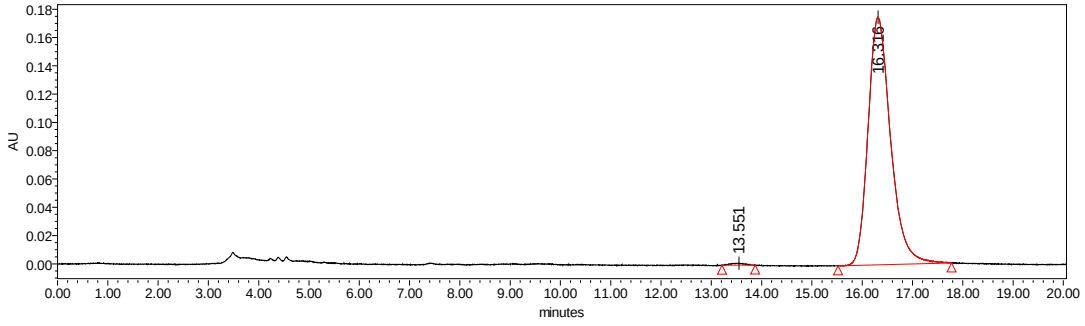
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.937	11841559	99.75	641317	bb
2	13.141	30240	0.25	2142	bb

4ag + *ent*-**4ag**



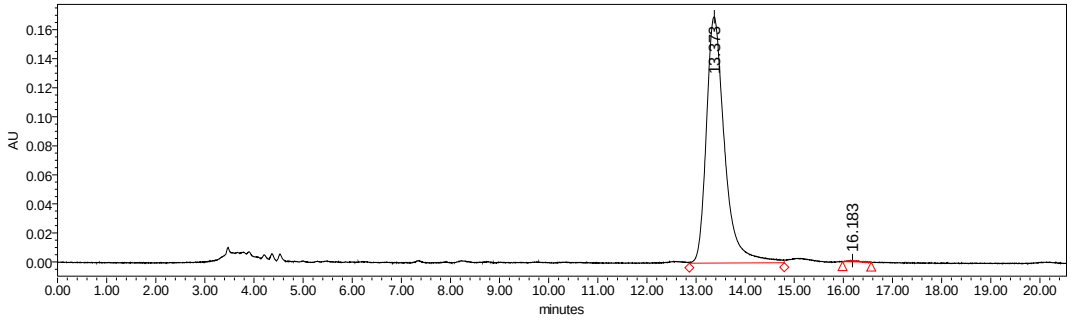
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	13.310	2363194	50.91	99283	bb
2	16.090	2278278	49.09	72900	bb

4ag



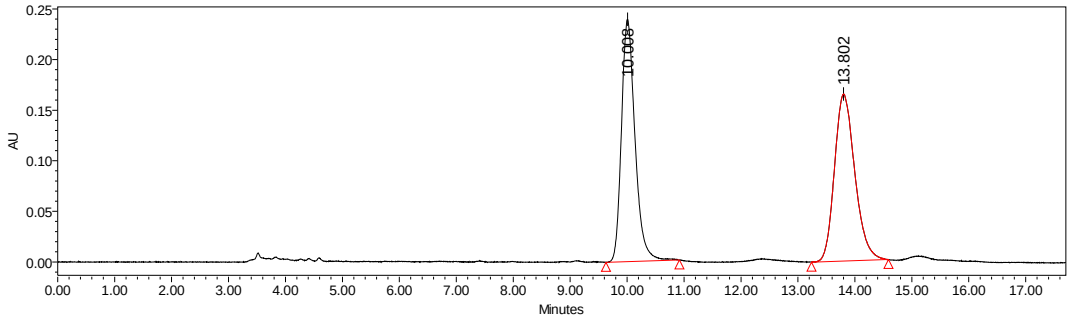
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	13.551	25721	0.47	1365	bb
2	16.316	5449702	99.53	175196	bb

ent-**4ag**



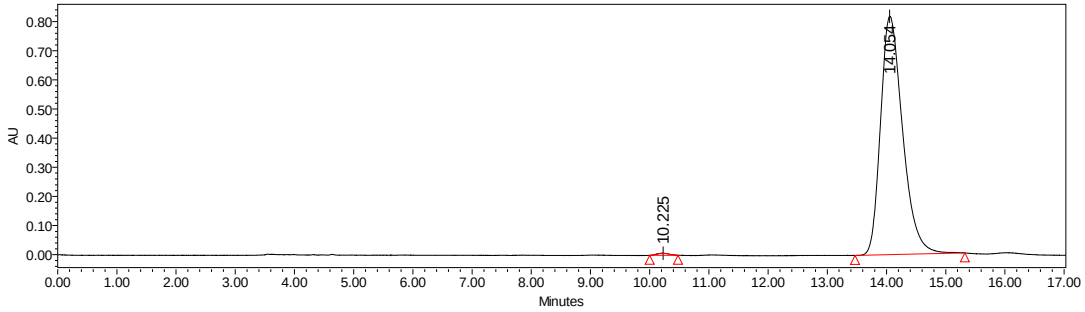
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	13.373	4379980	99.76	169737	VV
2	16.183	10745	0.24	800	bb

4ah + *ent*-**4ah**



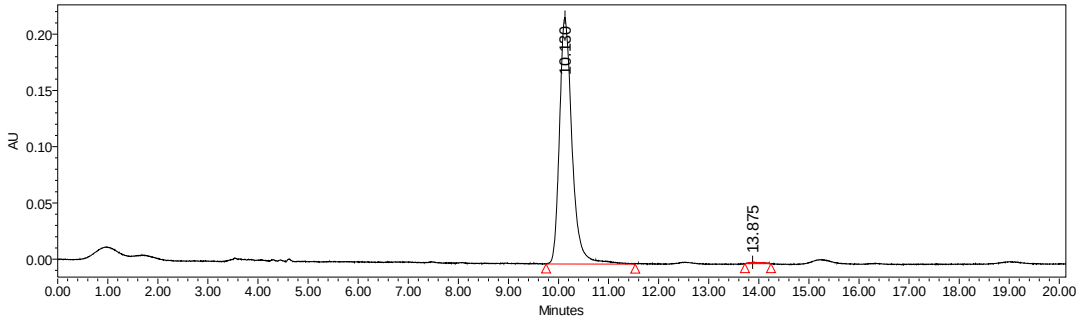
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.008	3968102	49.20	239783	Bb
2	13.802	4097192	50.80	165175	Bb

4ah



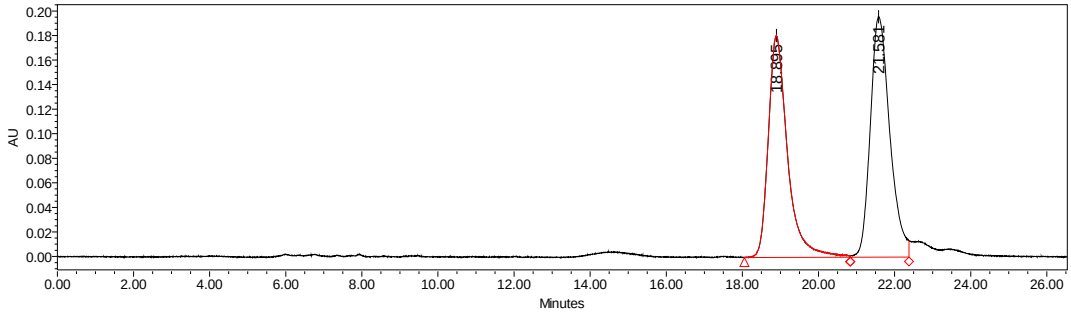
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.225	100233	0.47	7234	bb
2	14.054	21158436	99.53	818111	bb

ent-**4ah**



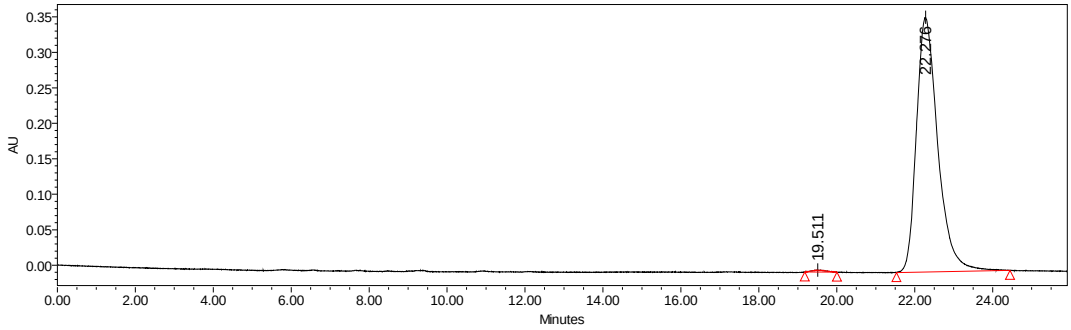
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.130	3825061	99.51	219282	BB
2	13.875	18955	0.49	1174	bb

4ai + *ent*-**4ai**



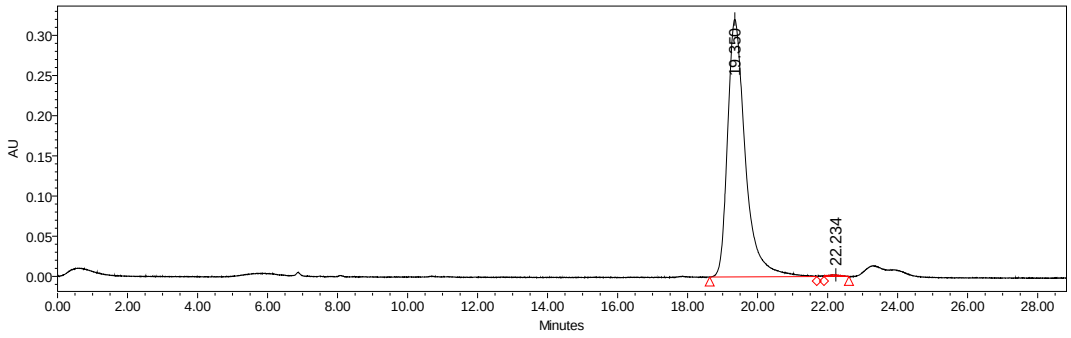
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	18.895	6335740	47.66	180879	BV
2	21.581	6957947	52.34	195843	Vv

4ai



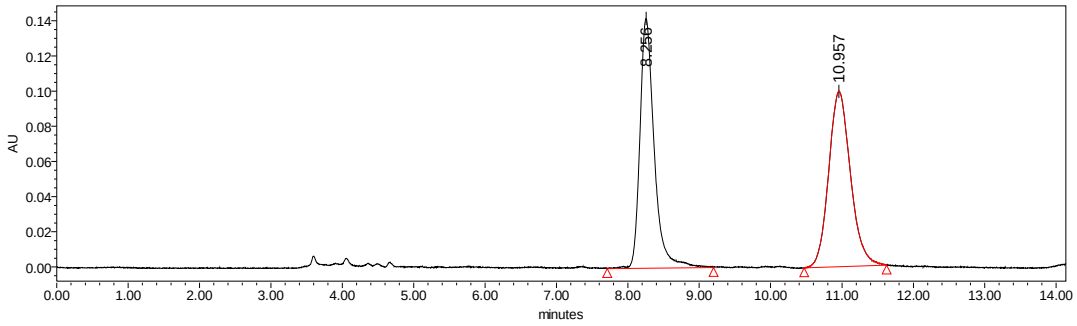
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	19.511	68762	0.50	2858	bb
2	22.276	13638507	99.50	358970	BB

ent-**4ai**



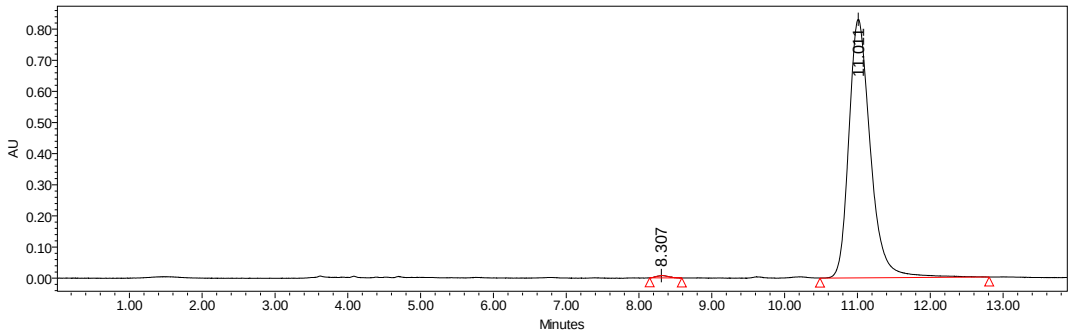
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	19.350	11284098	99.58	321161	BV
2	22.234	48122	0.42	2031	vb

4aj + *ent*-4aj



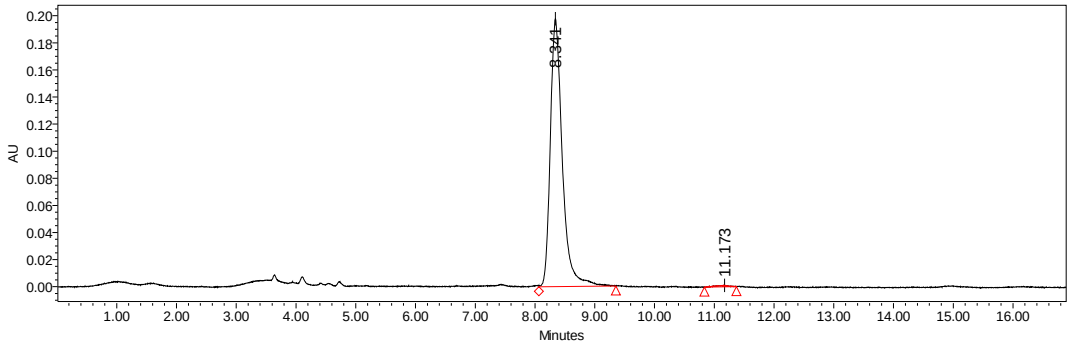
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.256	1977911	48.34	142019	bb
2	10.957	2113665	51.66	99670	bb

4aj



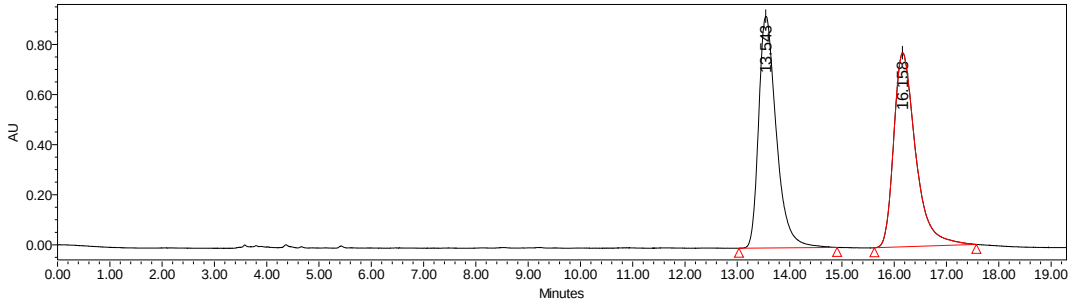
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.307	85304	0.50	7383	bb
2	11.011	17079373	99.50	831424	BB

ent-**4aj**



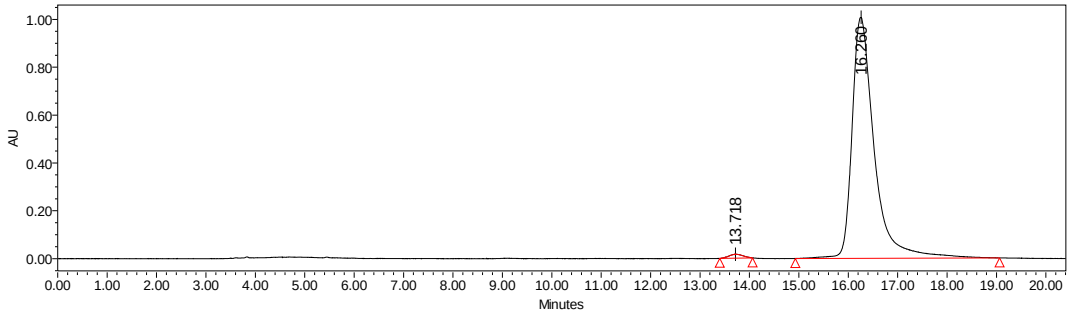
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.341	2758860	99.50	197732	VB
2	11.173	13794	0.50	995	bb

4ak + *ent*-**4ak**



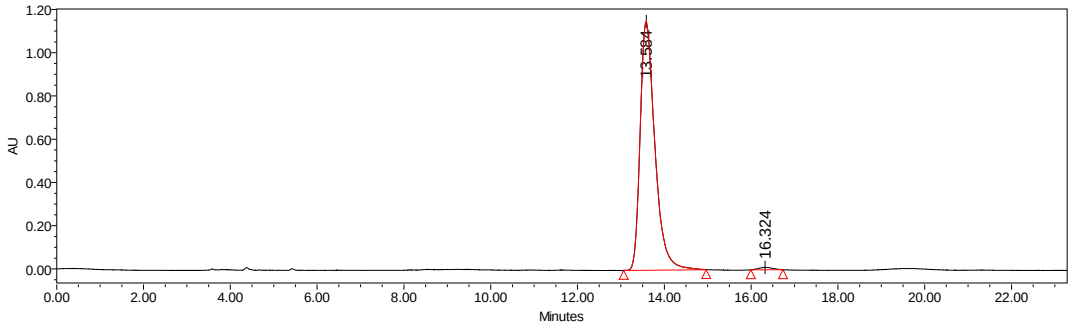
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	13.543	21724603	49.10	926540	Bb
2	16.158	22525448	50.90	775886	bb

4ak



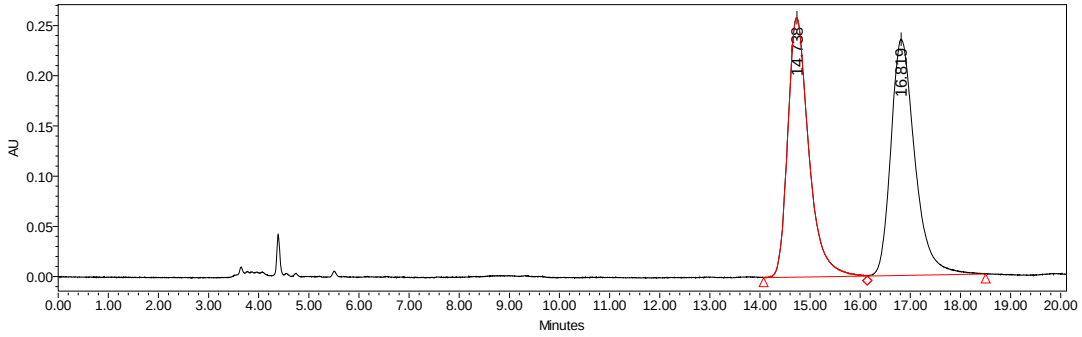
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	13.718	317752	1.00	16212	bb
2	16.260	31401964	99.00	1007877	Bb

ent-**4ak**



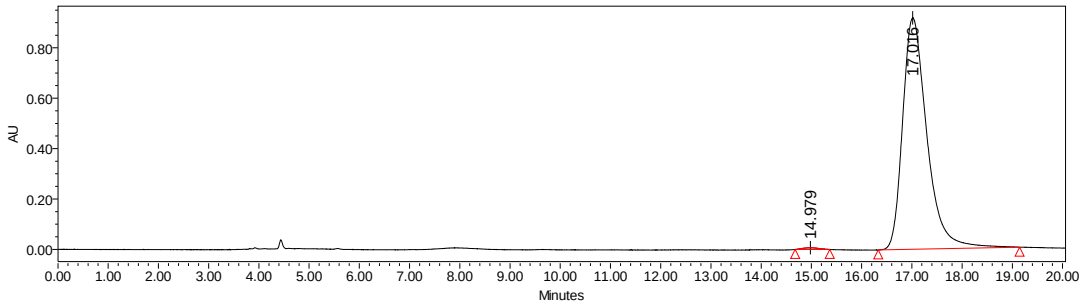
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	13.584	27075667	99.08	1150140	Bb
2	16.324	252777	0.92	11012	bb

4al + *ent*-**4al**



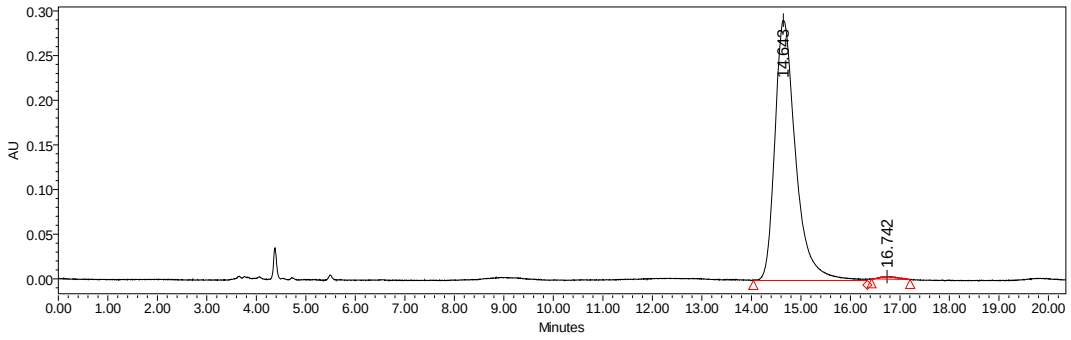
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	14.738	7512457	49.04	258318	BV
2	16.819	7807506	50.96	235159	Vb

4al



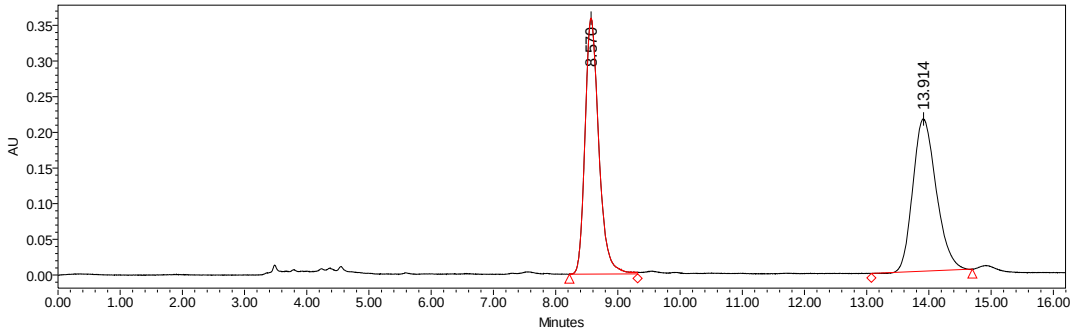
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	14.979	156148	0.50	7230	bb
2	17.016	30790172	99.50	918979	bb

ent-**4al**



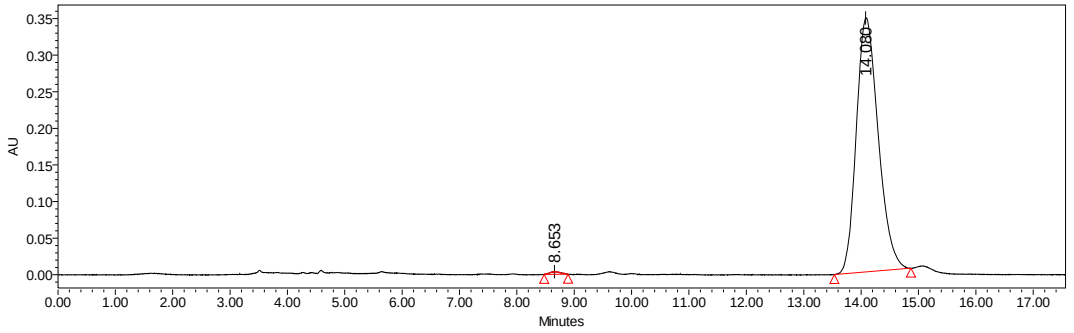
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	14.643	8464691	99.23	291545	BV
2	16.742	65398	0.77	2781	bb

4am + *ent*-4am



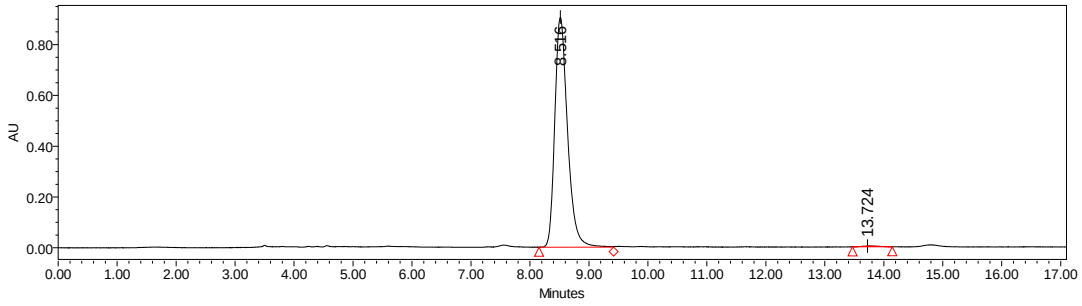
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.570	5522174	49.76	358922	BV
2	13.914	5576555	50.24	213420	Vb

4am



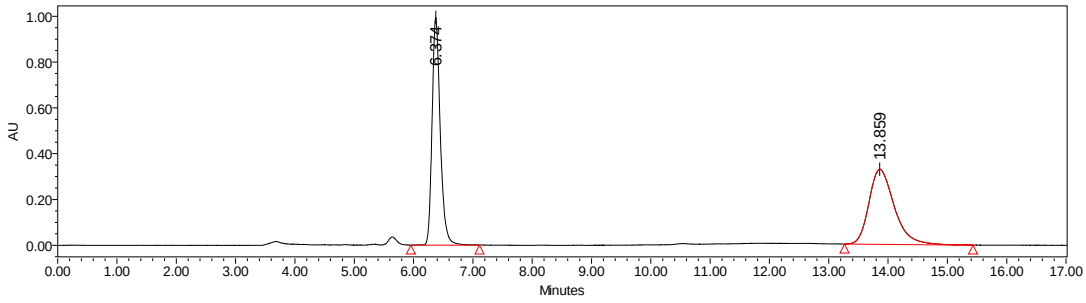
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.653	46165	0.50	3561	bb
2	14.080	9196932	99.50	346910	bb

ent-**4am**



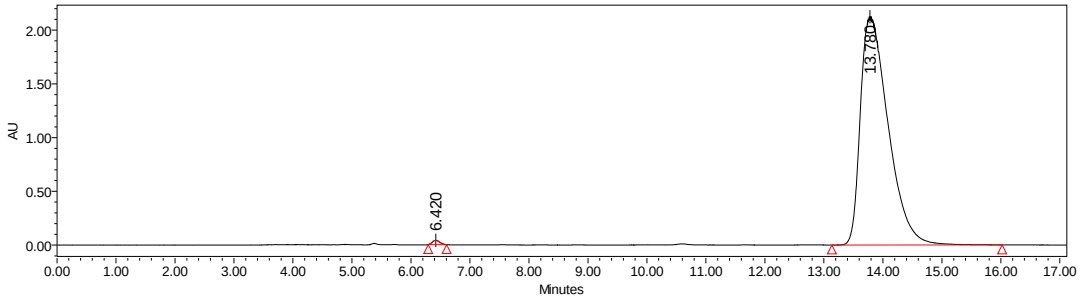
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.516	13586216	99.59	906381	BV
2	13.724	56027	0.41	2774	bb

4an + *ent*-**4an**



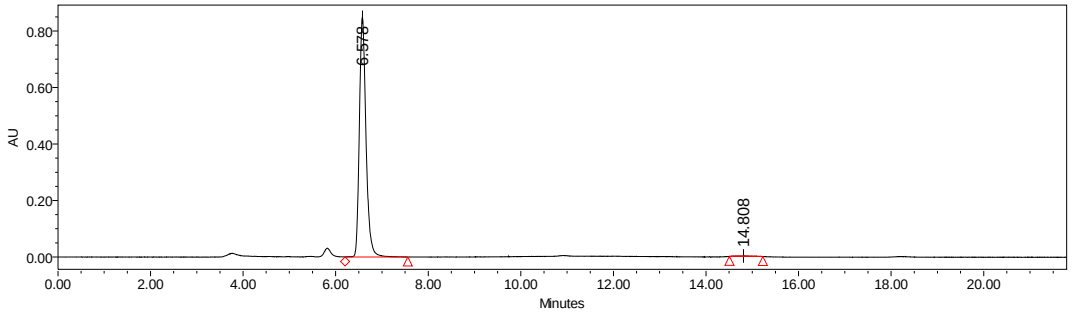
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	6.374	9474418	49.41	994438	BB
2	13.859	9700261	50.59	328099	BB

4an



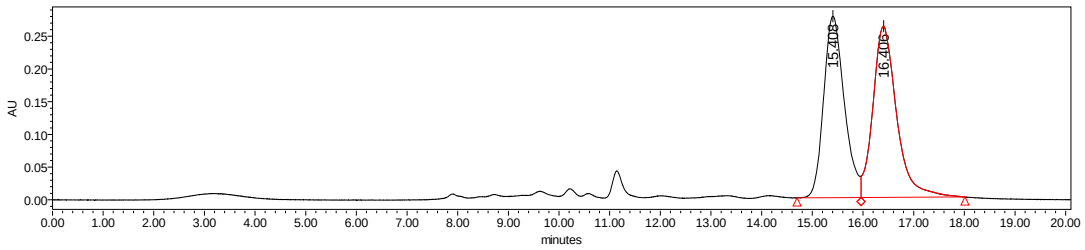
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	6.420	348968	0.50	40316	bb
2	13.780	69426173	99.50	2124022	BB

ent-**4an**



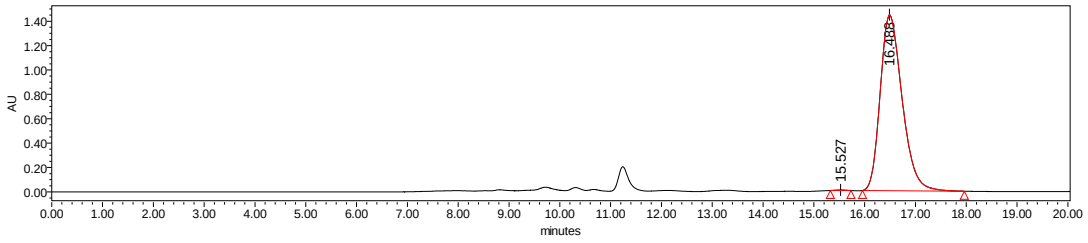
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	6.578	8481901	99.50	849327	VB
2	14.808	42641	0.50	1733	bb

4ba + *ent*-**4ba**



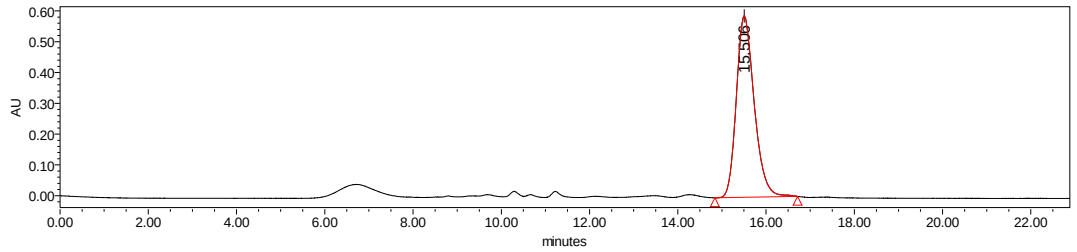
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	15.408	7840575	48.02	277246	bv
2	16.406	8486442	51.98	261472	vb

4ba



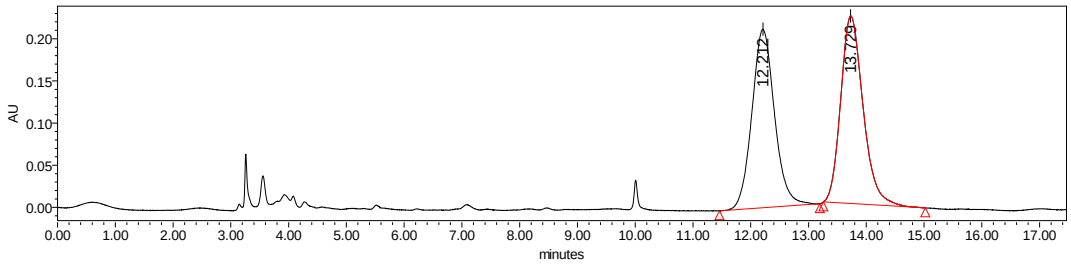
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	15.527	65154	0.15	4499	bb
2	16.488	43087091	99.85	1443633	bb

ent-**4ba**



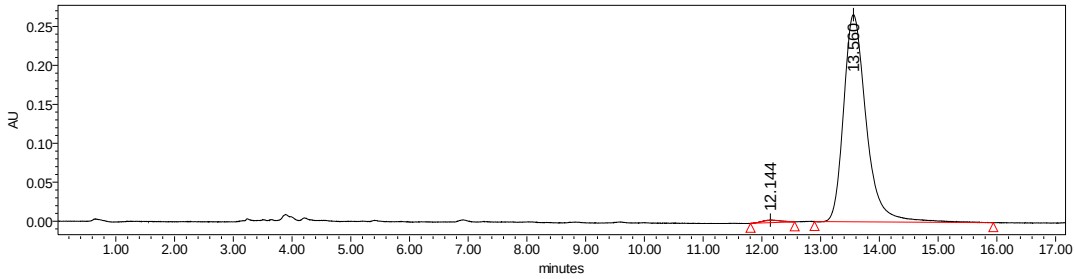
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	15.506	16564923	100.00	588892	bb

4ca + *ent*-**4ca**



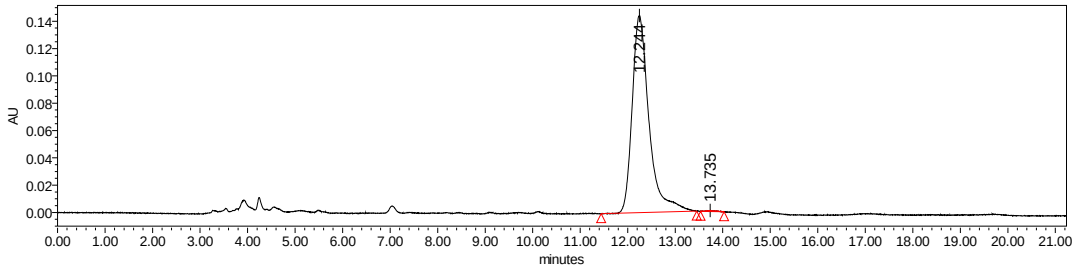
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	12.212	5747553	49.01	211840	Bb
2	13.729	5979836	50.99	222610	bb

4ca



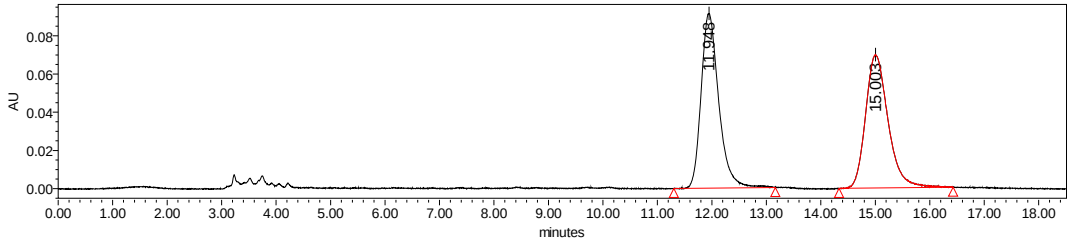
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	12.144	70506	0.98	3340	bb
2	13.560	7090822	99.02	265950	bb

ent-**4ca**



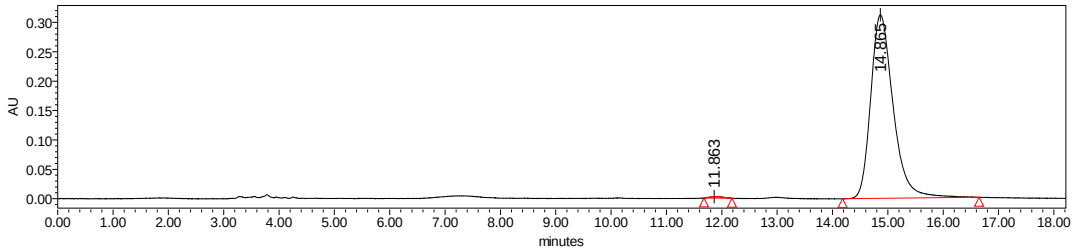
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	12.244	3545262	99.72	144331	bb
2	13.735	9972	0.28	754	bb

4da + *ent*-**4da**



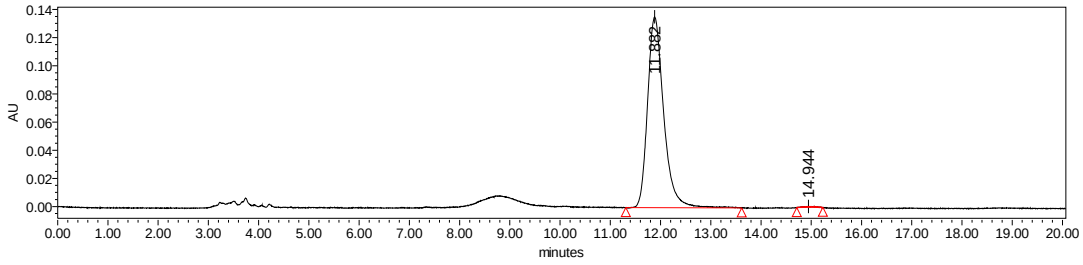
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	11.948	2056541	50.79	91505	bb
2	15.003	1992442	49.21	69794	bb

4da



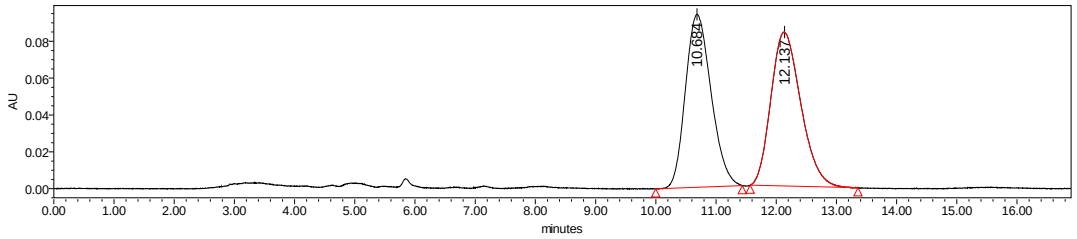
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	11.863	40972	0.46	2560	bb
2	14.865	8786762	99.54	312437	bb

ent-**4da**



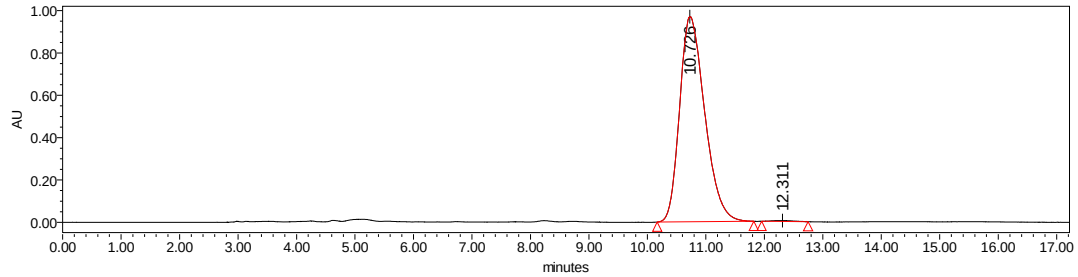
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	11.882	3022490	99.59	135528	bb
2	14.944	12399	0.41	765	bb

4ea + *ent*-4ea



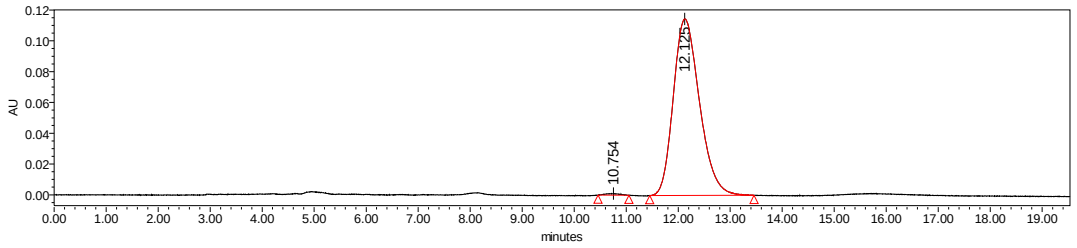
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.684	2777929	49.10	93841	bb
2	12.137	2879665	50.90	83544	bb

4ea



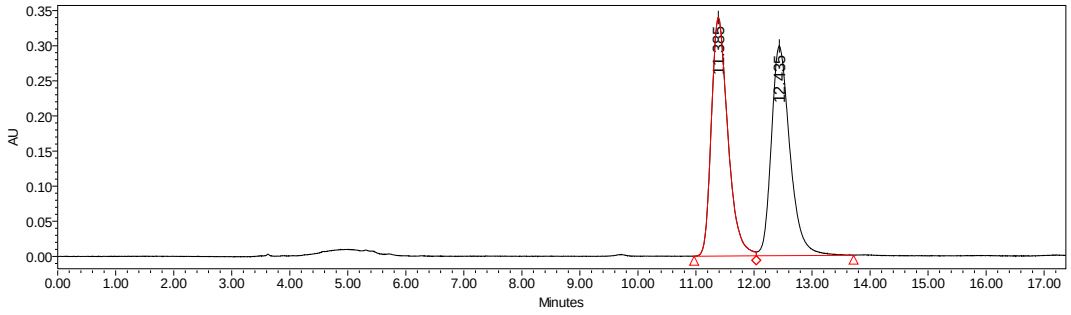
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.726	28916193	99.61	969536	bb
2	12.311	113725	0.39	4421	bb

ent-**4ea**



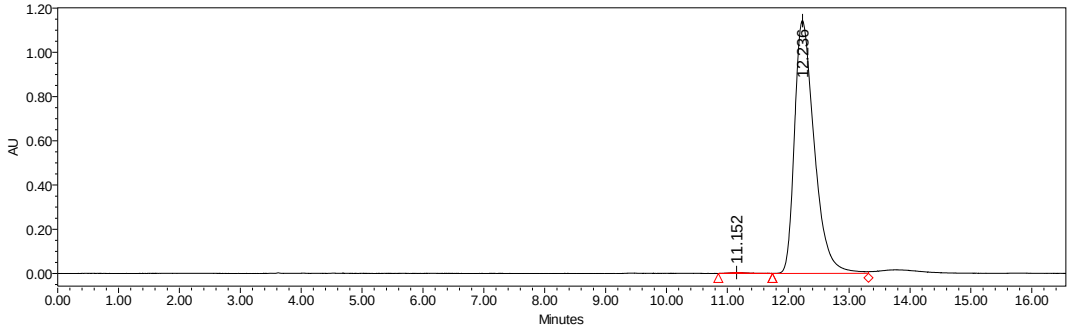
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	10.754	18358	0.46	1021	bb
2	12.125	4003975	99.54	114655	bb

4fa + *ent*-4fa



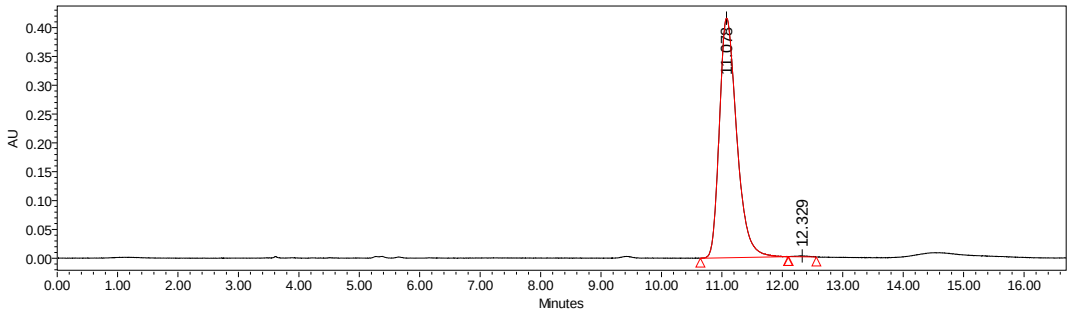
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	11.385	6711423	50.20	339820	BV
2	12.435	6657609	49.80	298553	VB

4fa



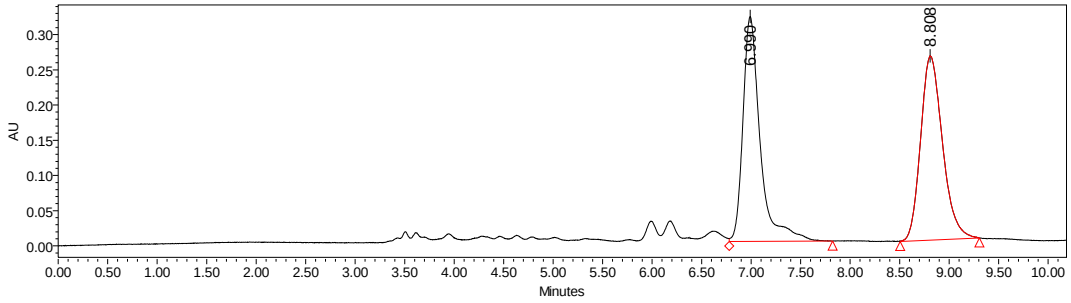
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	11.152	90475	0.35	4515	BB
2	12.236	25753156	99.65	1143645	BV

ent-**4fa**



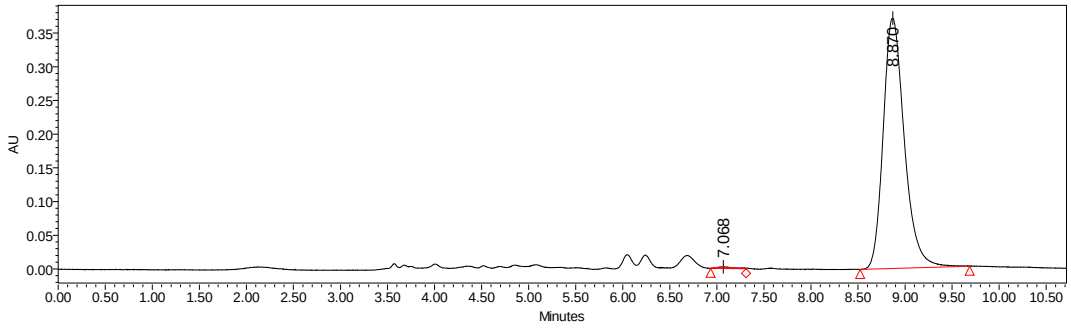
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	11.078	8283267	99.73	415535	Bb
2	12.329	22103	0.27	1482	bb

4ga + *ent*-4ga



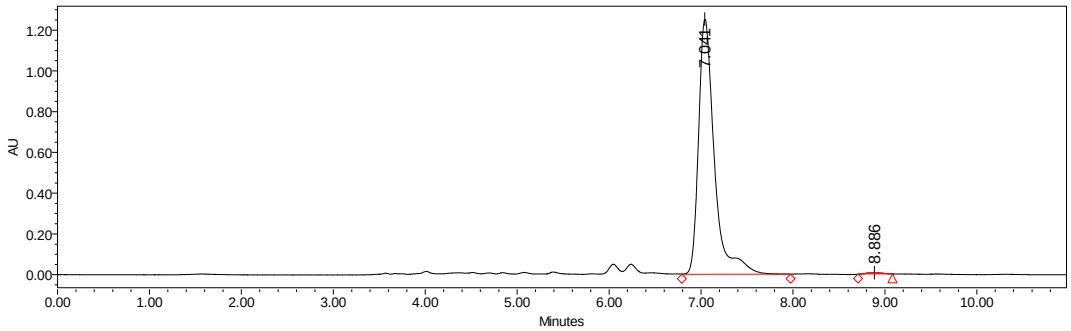
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	6.990	3879315	49.16	319407	VB
2	8.808	4011393	50.84	261688	Bb

4ga



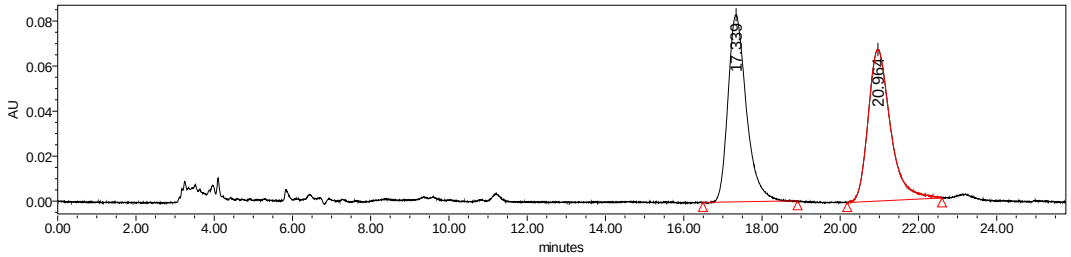
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	7.068	29135	0.50	2512	bV
2	8.870	5794904	99.50	371539	BB

ent-**4ga**



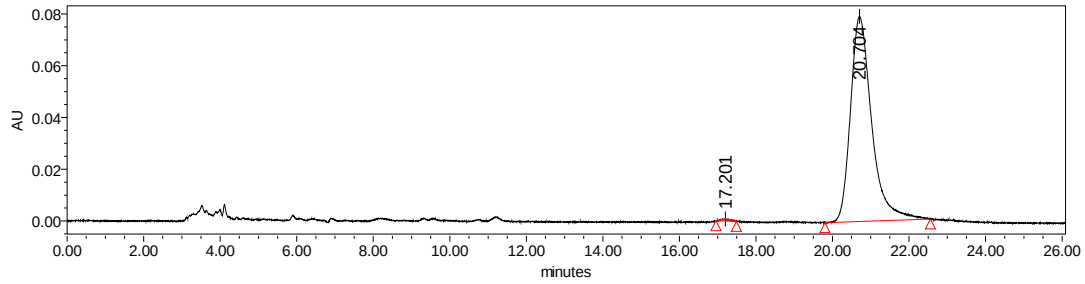
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	7.041	14946051	99.65	1251671	VV
2	8.886	52663	0.35	5083	vb

4ia + *ent*-**4ia**



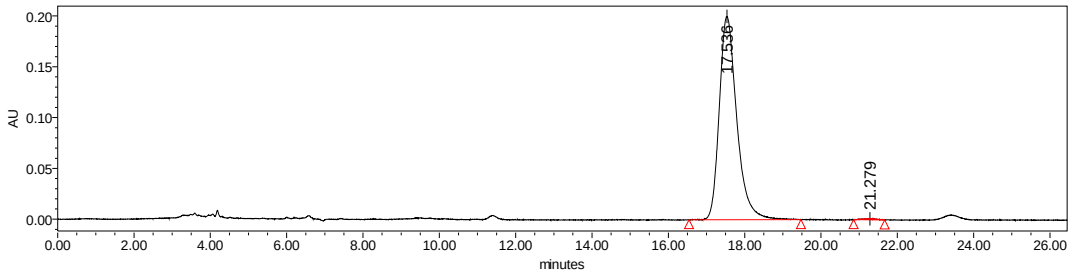
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	17.339	2717959	50.51	83147	bb
2	20.964	2663350	49.49	67305	bb

4ia



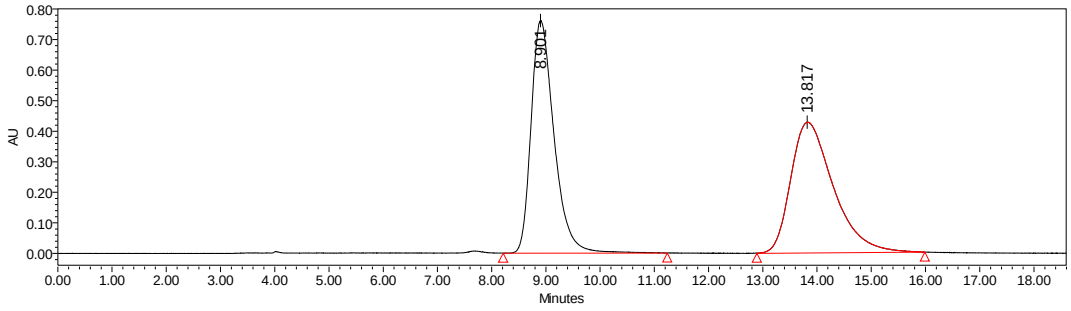
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	17.201	13041	0.43	837	bb
2	20.704	3040303	99.57	79322	bb

ent-**4ia**



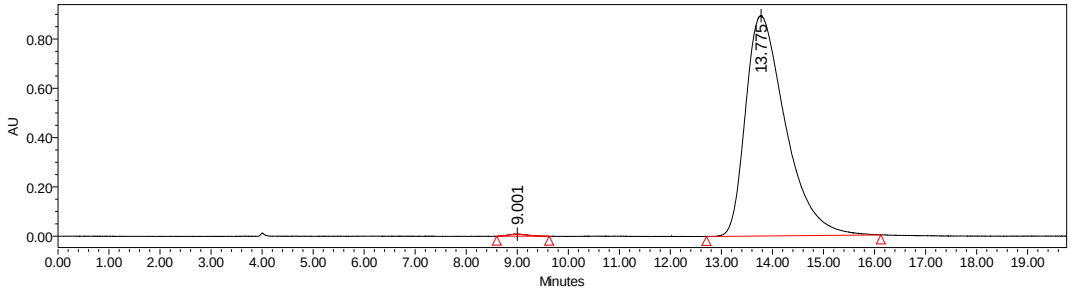
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	17.536	6353843	99.64	200122	bb
2	21.279	23003	0.36	946	bb

5 + *ent*-5



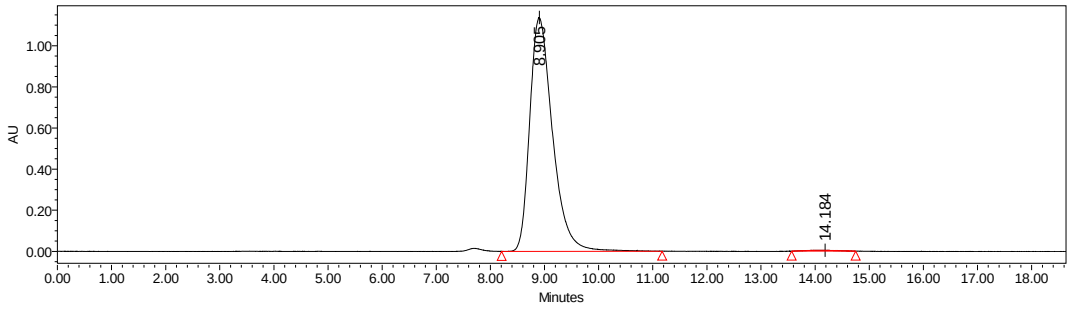
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.901	22476159	49.11	761812	BB
2	13.817	23294896	50.89	428406	Bb

5



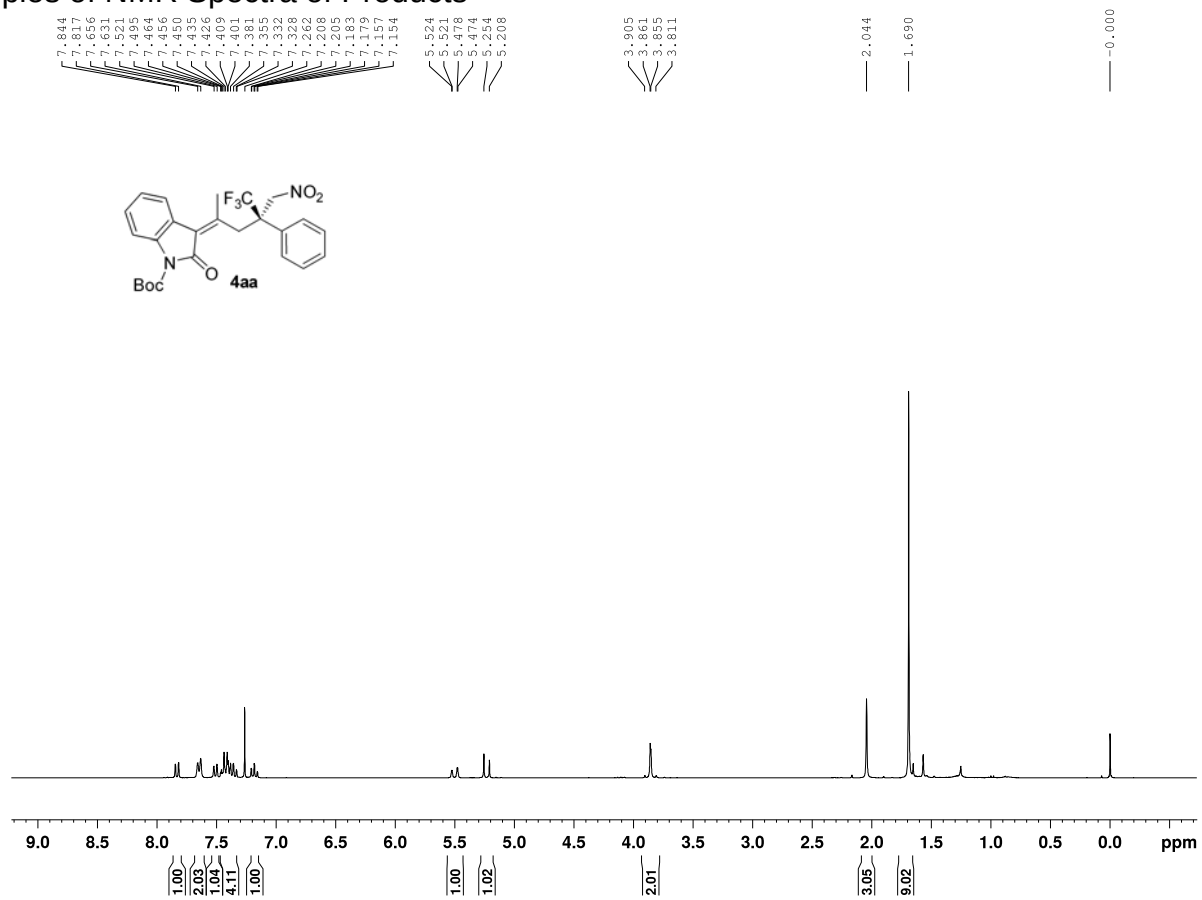
Entry	Retention Time	Area	Area (%)	Height	Int Type
1	9.001	229508	0.47	8731	bb
2	13.775	48493251	99.53	893675	bb

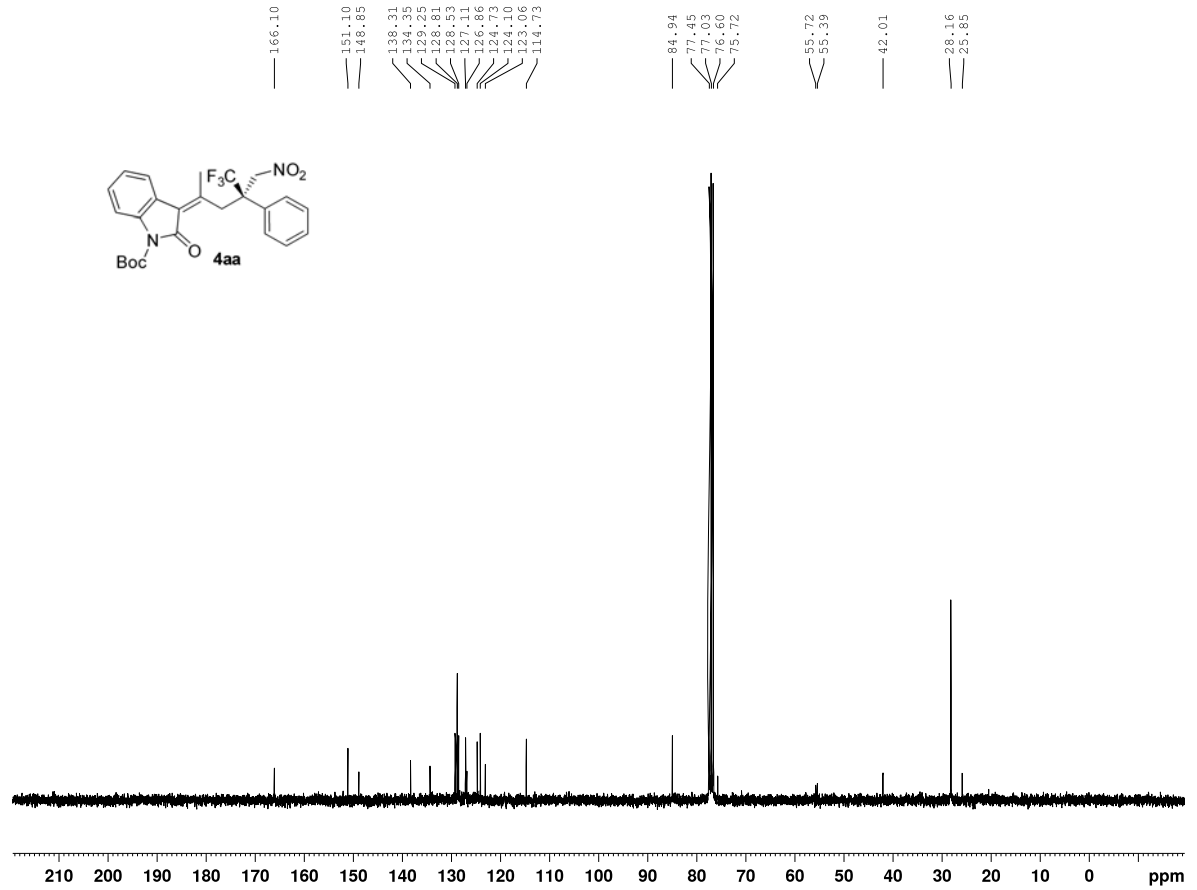
ent-**5**

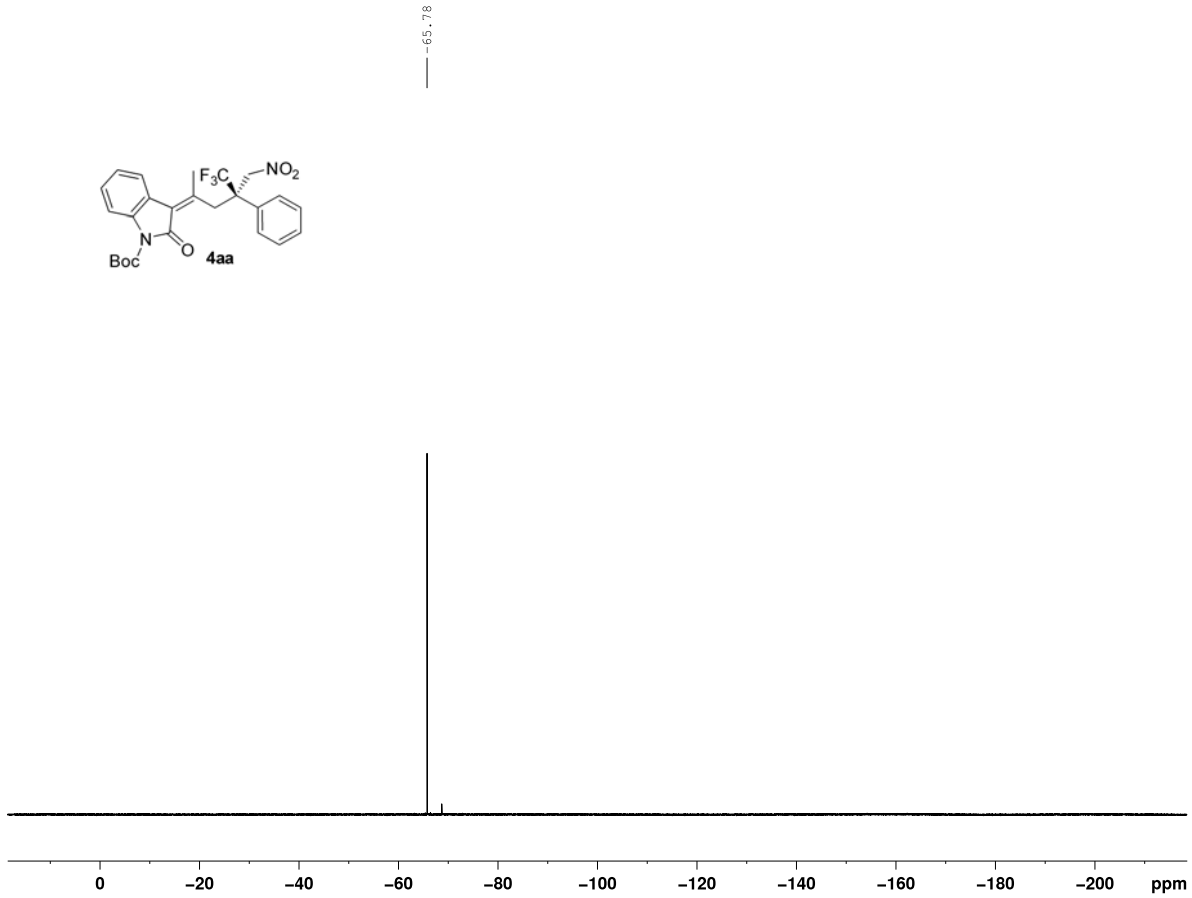


Entry	Retention Time	Area	Area (%)	Height	Int Type
1	8.905	33303601	99.50	1137619	BB
2	14.184	167789	0.50	4410	bb

8.0 Copies of NMR Spectra of Products



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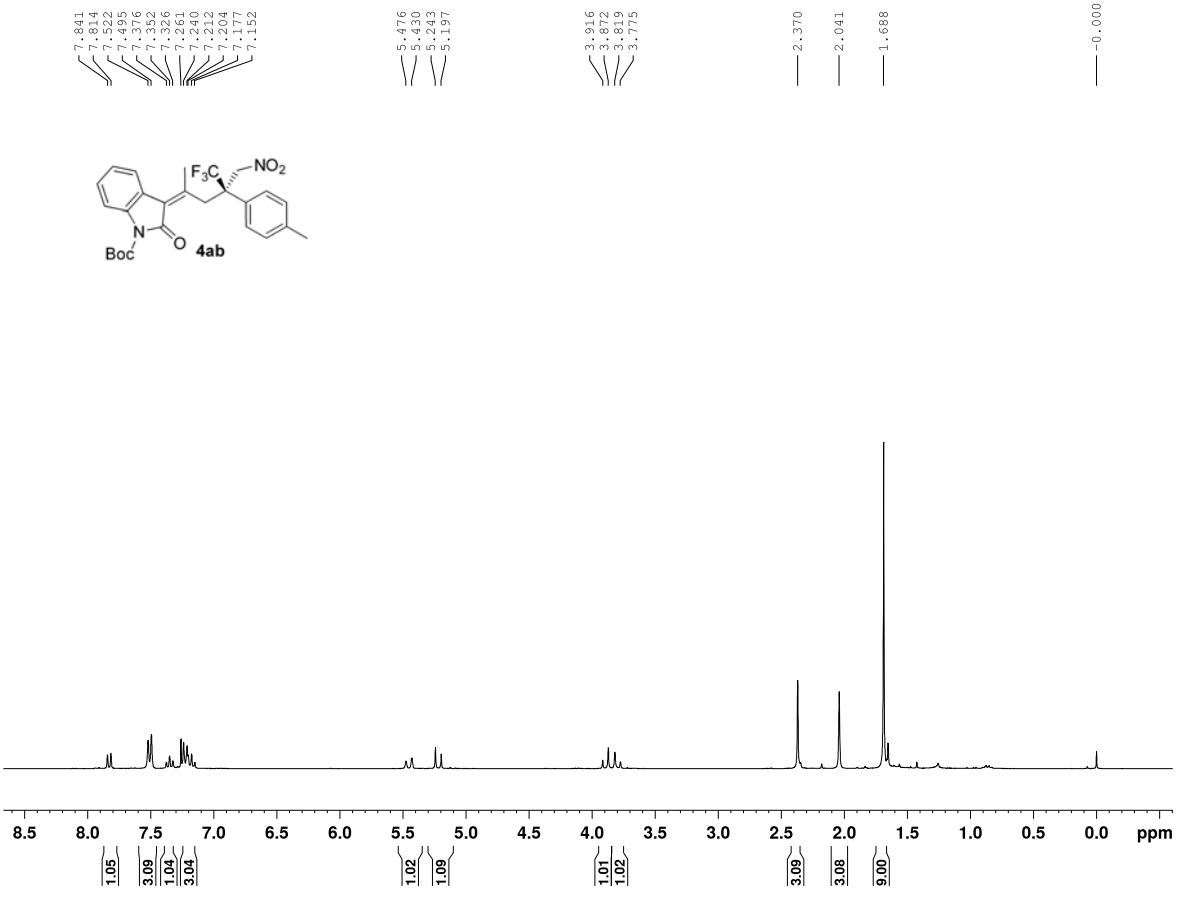
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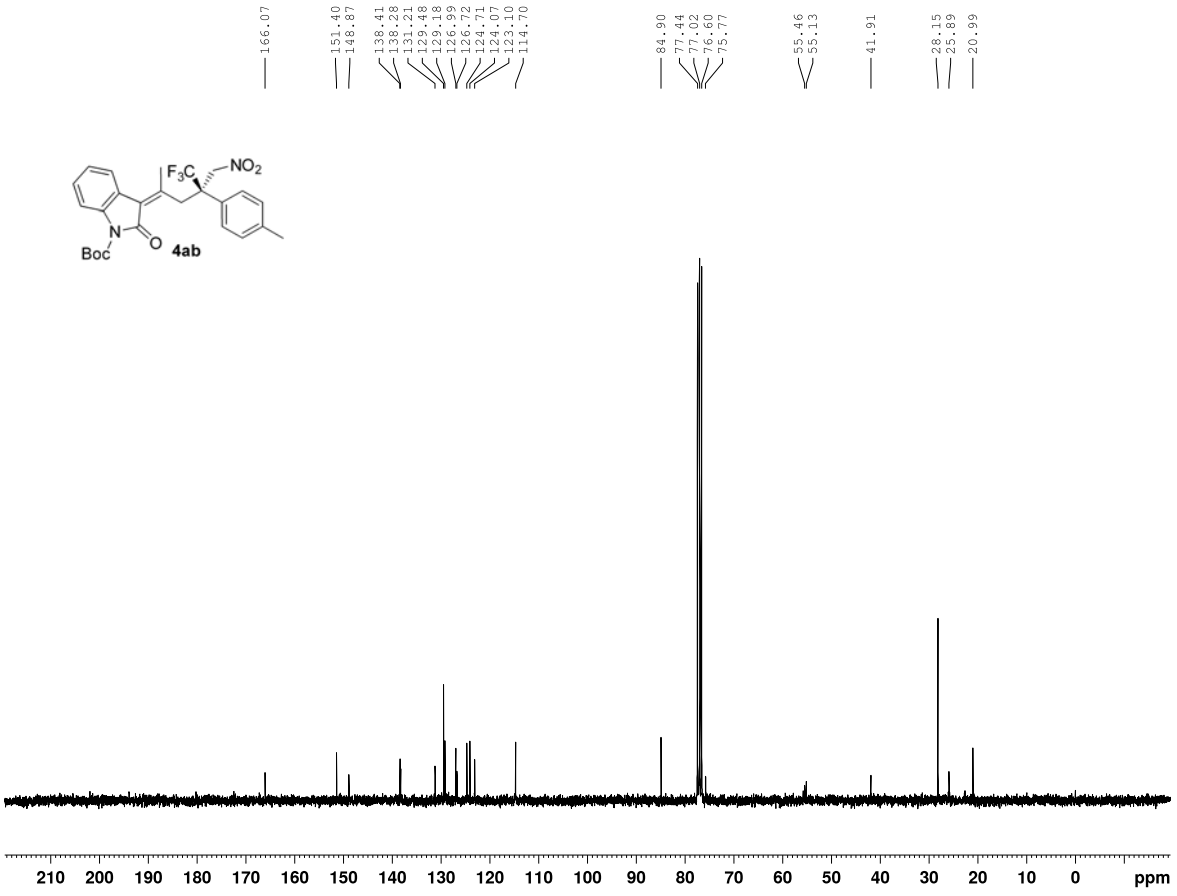
9.00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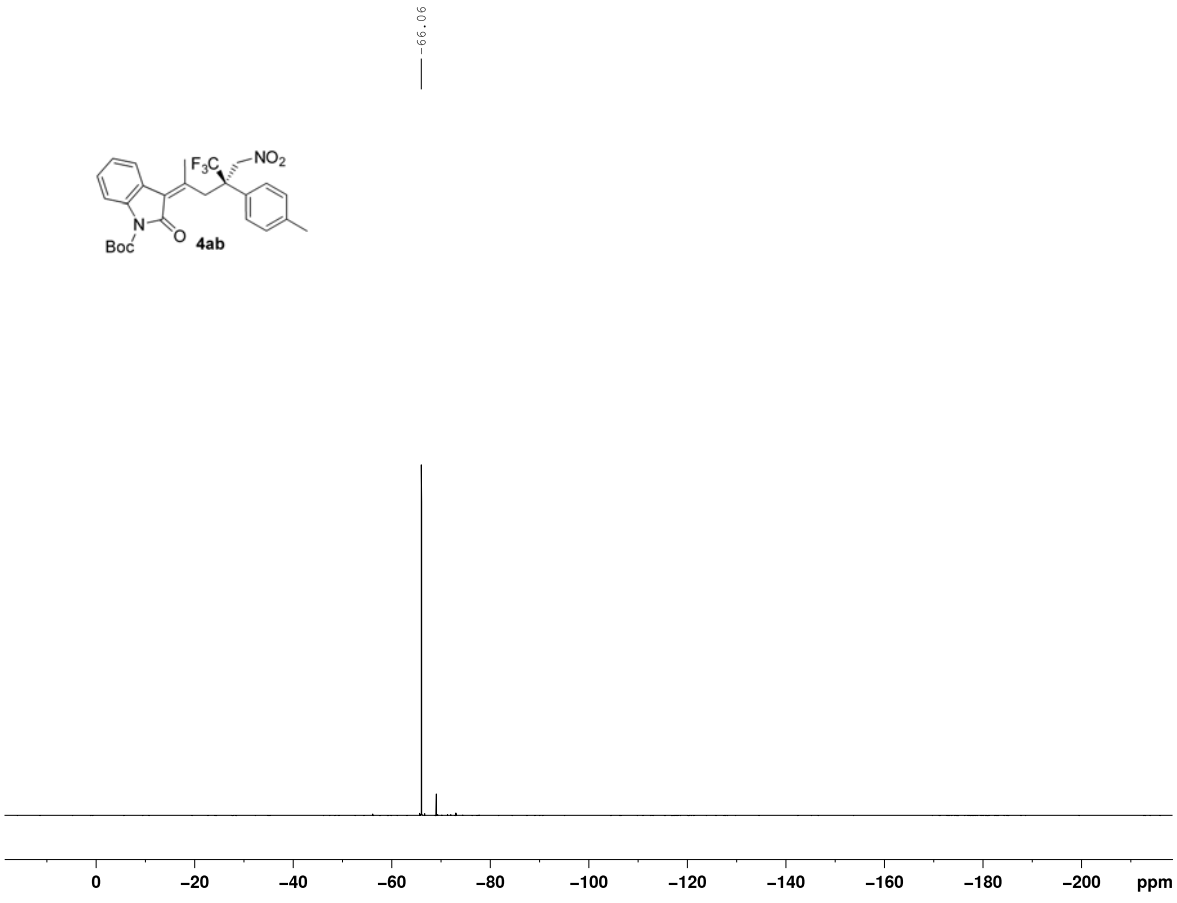
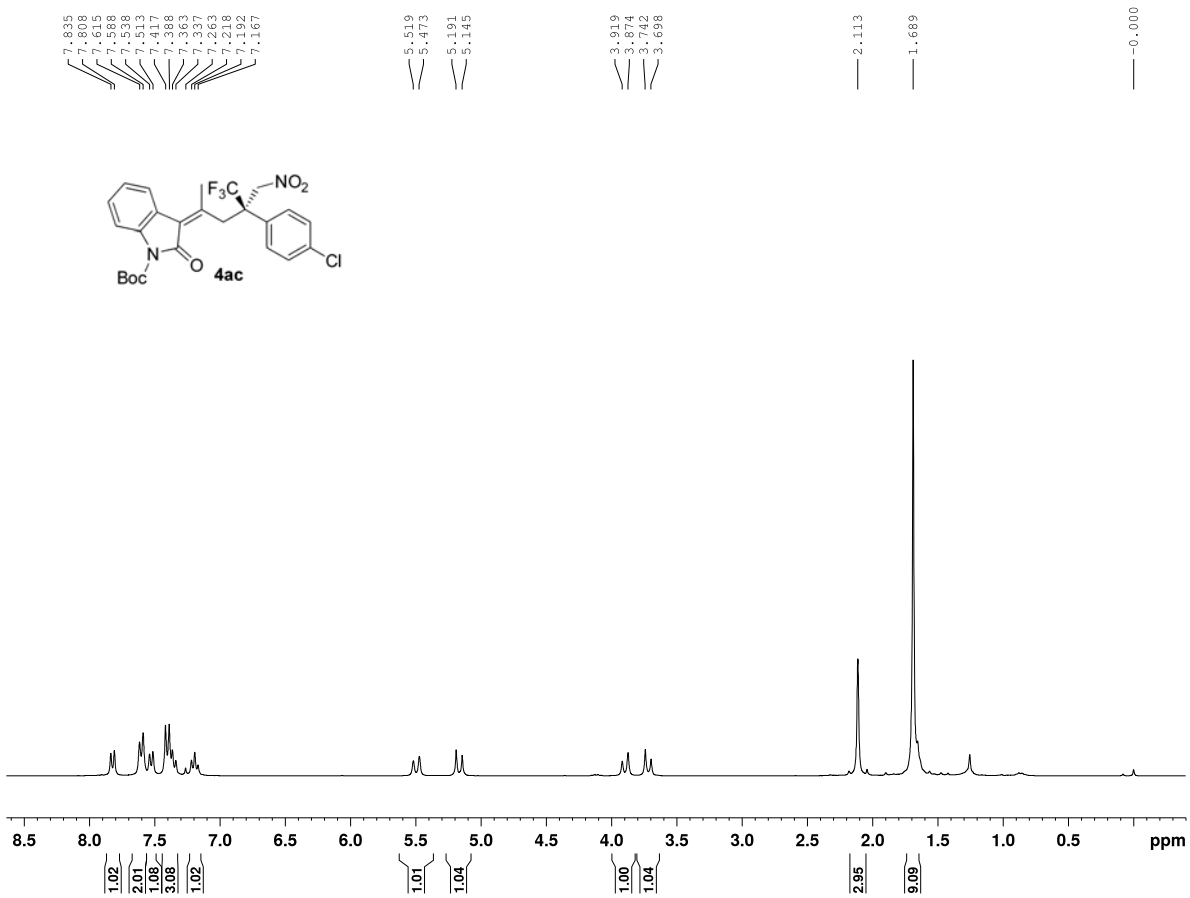
151.40
148.87
138.41
138.28
131.21
129.48
129.18
126.99
126.72
124.71
124.07
123.10
114.70
84.90
77.44
77.02
76.60
75.77
55.46
55.13
41.91
28.15
25.89
20.99
F3C
NO2
N
O
Boc
4ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-66.06
F3C
NO2
N
O
Boc
4ab
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm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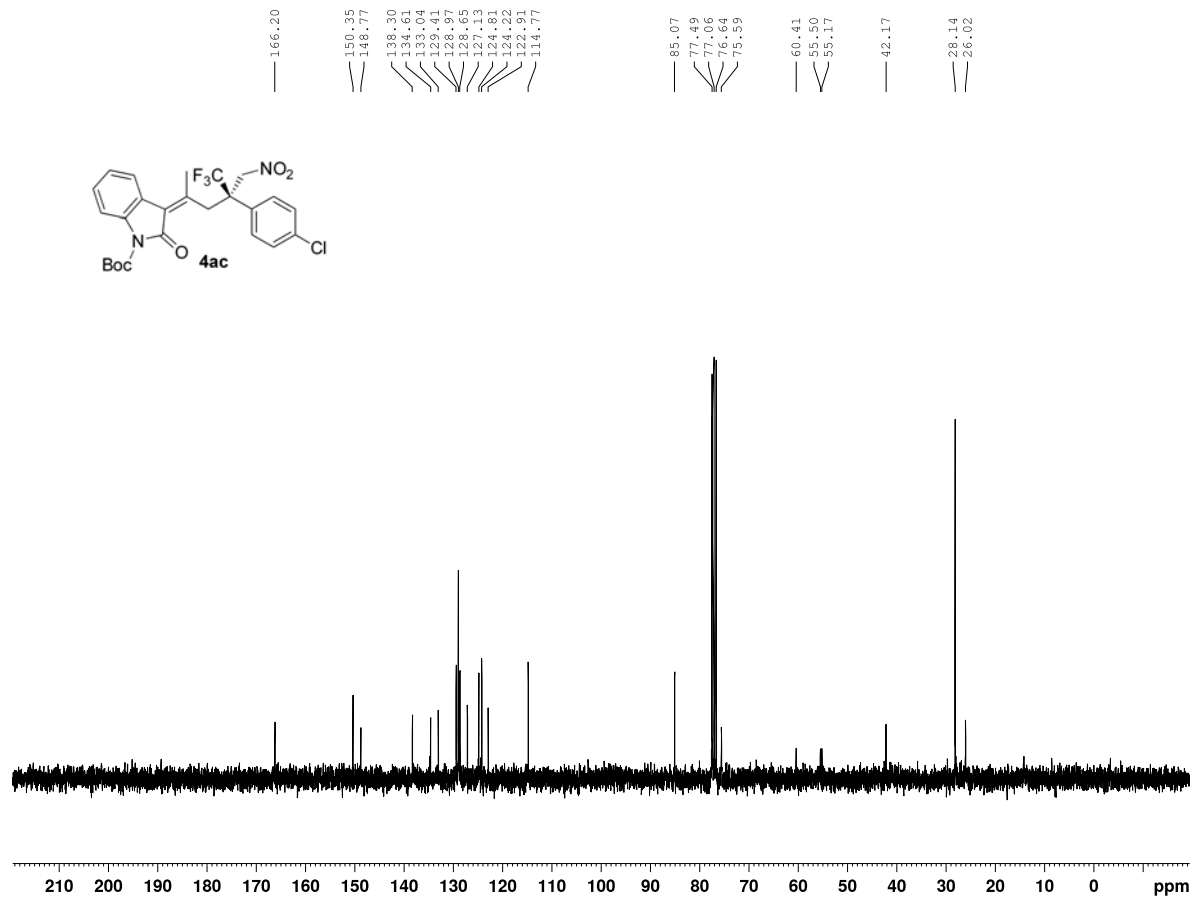
7.808
7.615
7.588
7.538
7.513
7.417
7.388
7.363
7.337
7.263
7.218
7.192
7.167
5.519
5.473
5.191
5.145
3.919
3.874
3.742
3.698
2.113
1.689
0.000
F3C
NO2
Cl
N
O
Boc
4ac
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
2.01
1.08
3.08
1.02
1.01
1.04
1.00
1.04
2.95
9.09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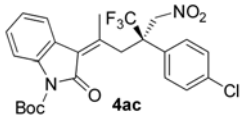
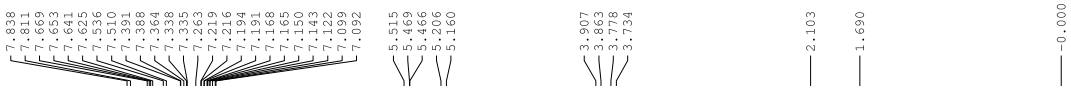
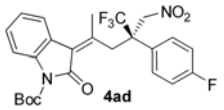
150.35
148.77
138.30
134.61
133.04
129.41
128.97
128.65
127.13
124.81
124.22
122.91
114.77
85.07
77.49
77.06
76.64
75.59
60.41
55.50
55.17
42.17
28.14
26.02
F3C
NO2
Cl
N
O
Boc
4ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F3C
NO2
N
Boc
O
Cl

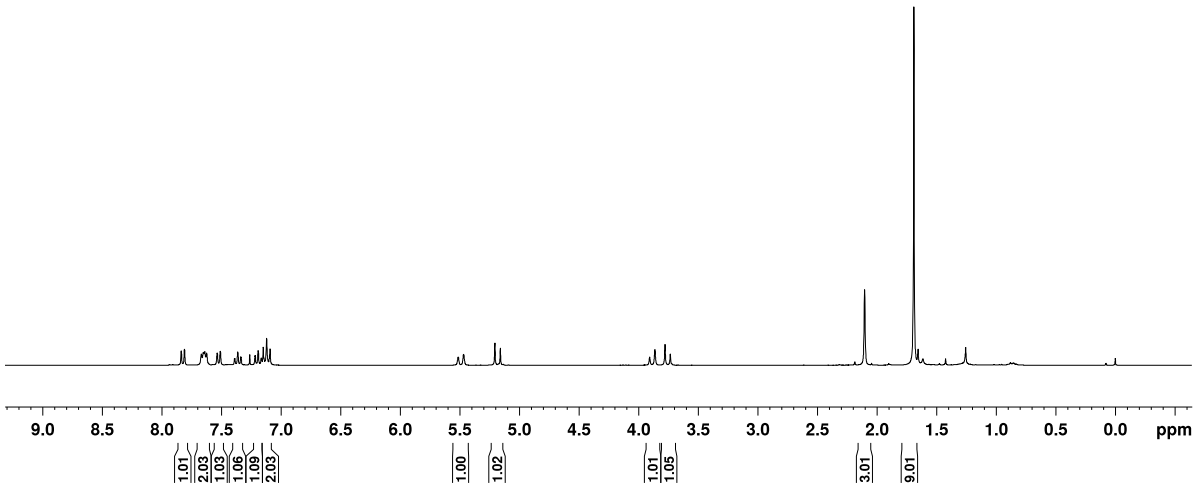
4ac

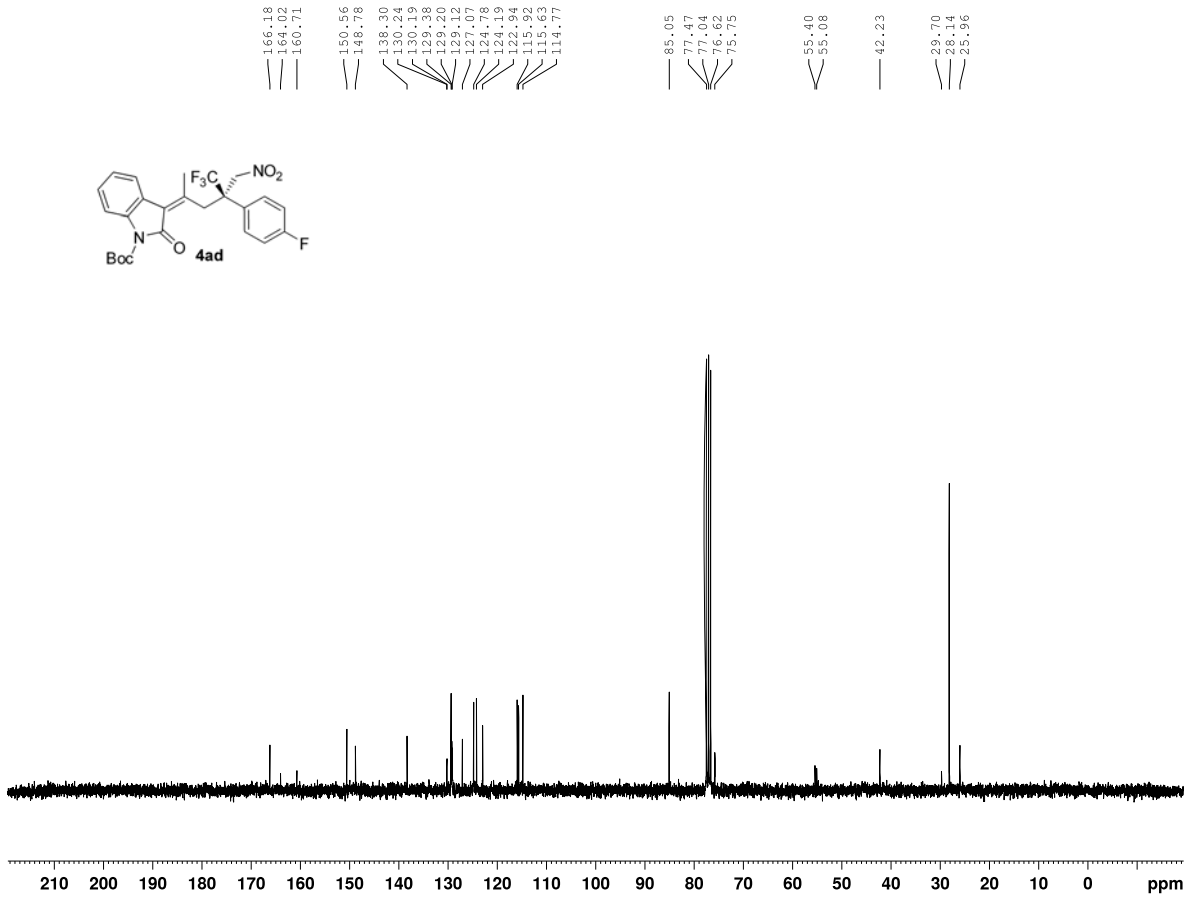
-65.85
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

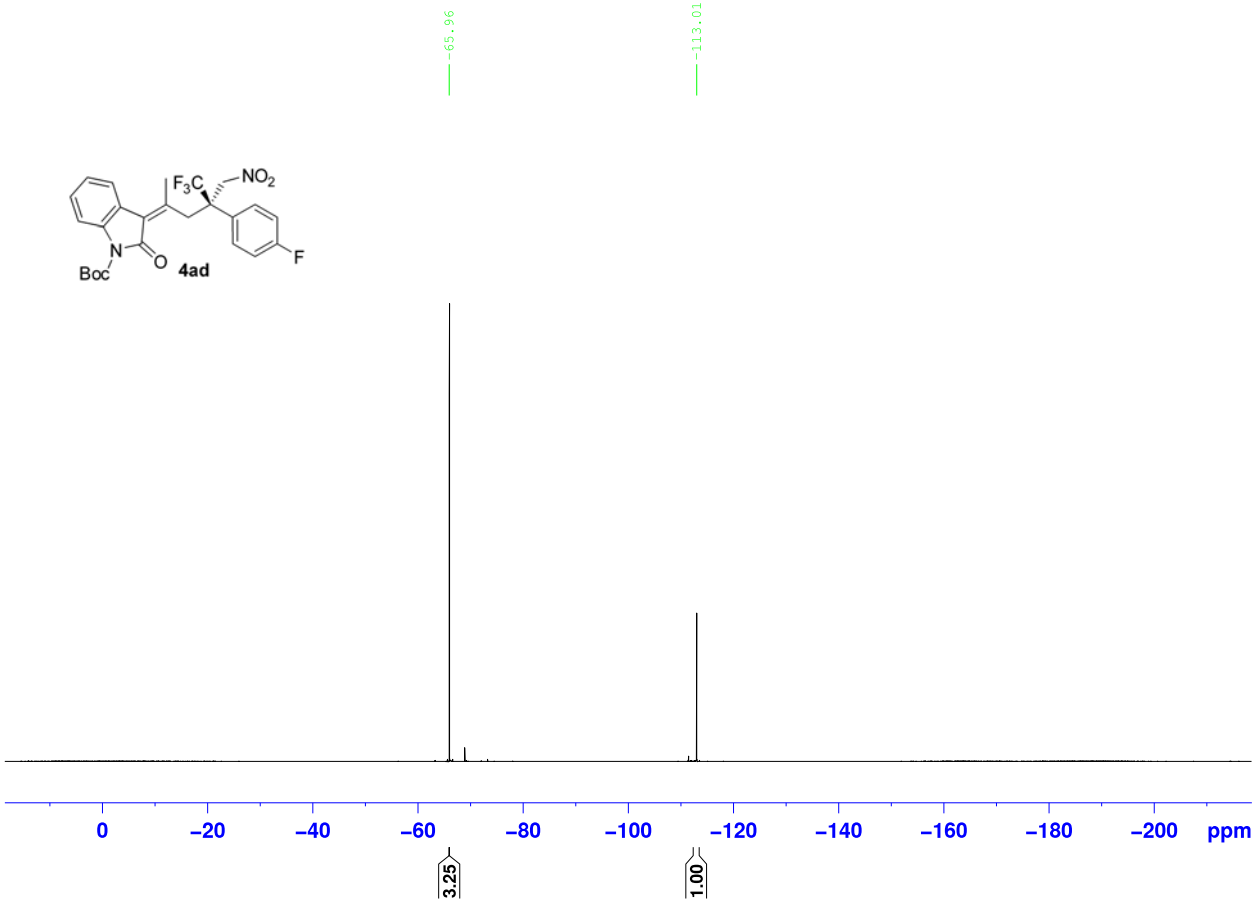

7.838
7.811
7.669
7.653
7.641
7.625
7.536
7.510
7.391
7.388
7.364
7.338
7.335
7.263
7.219
7.216
7.194
7.191
7.168
7.165
7.150
7.143
7.122
7.099
7.092
5.515
5.469
5.466
5.206
5.160
3.907
3.863
3.778
3.734
2.103
1.690
0.000

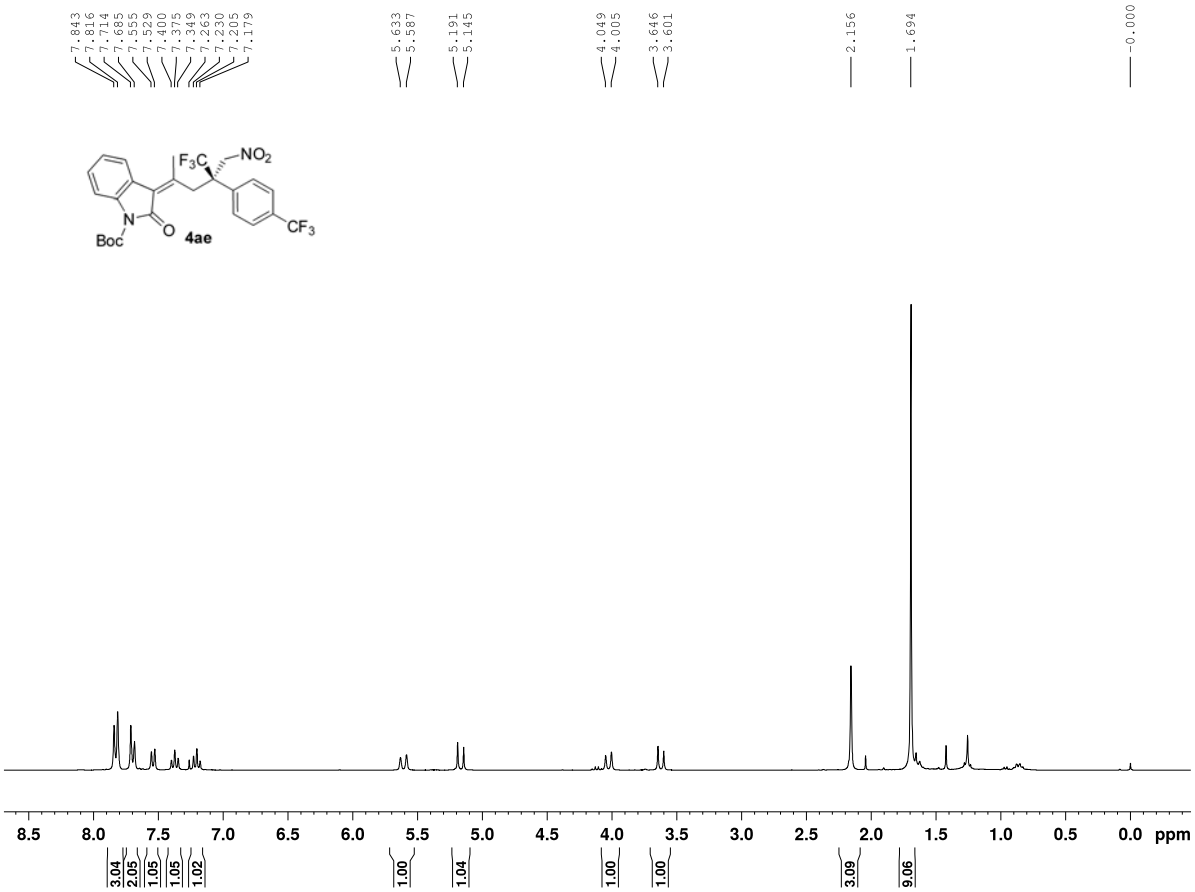

F3C
NO2
N
Boc
O
F

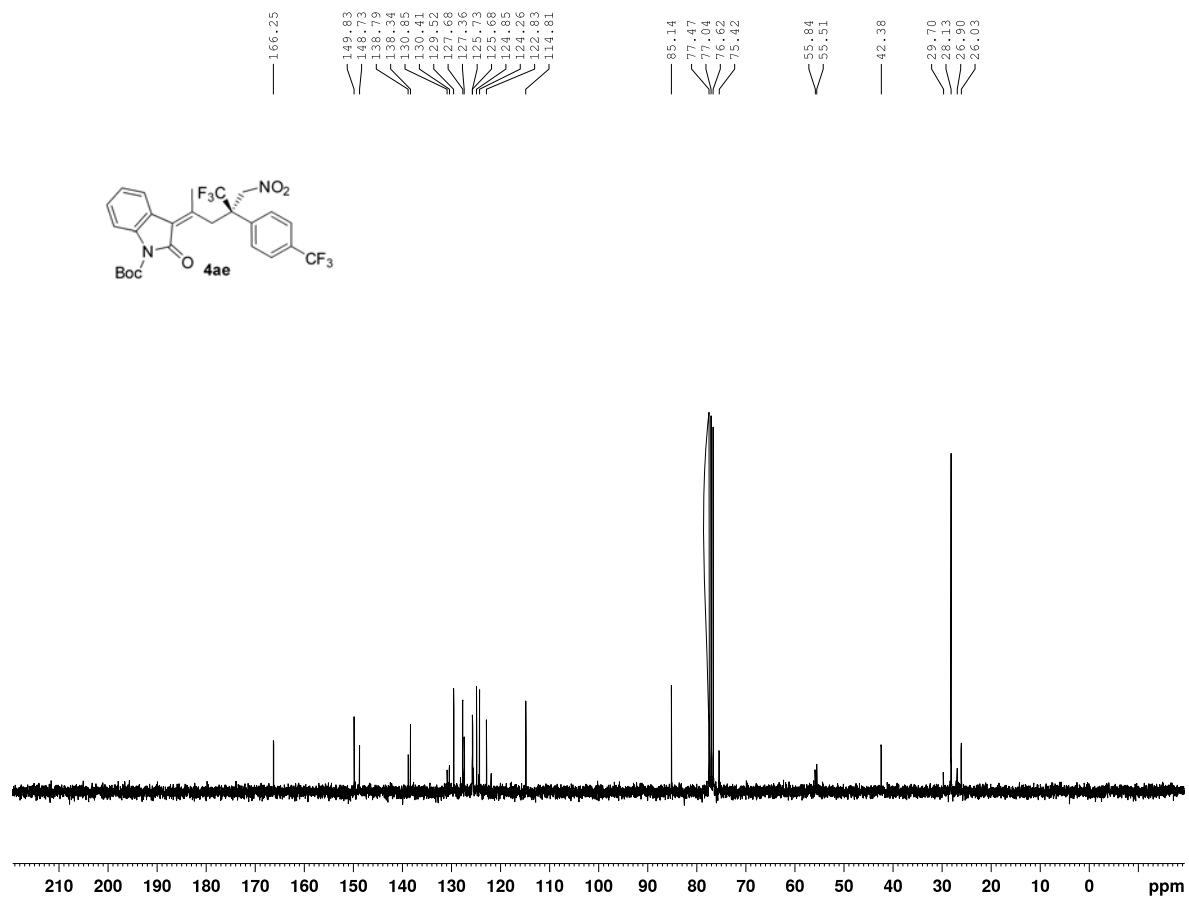
4ad

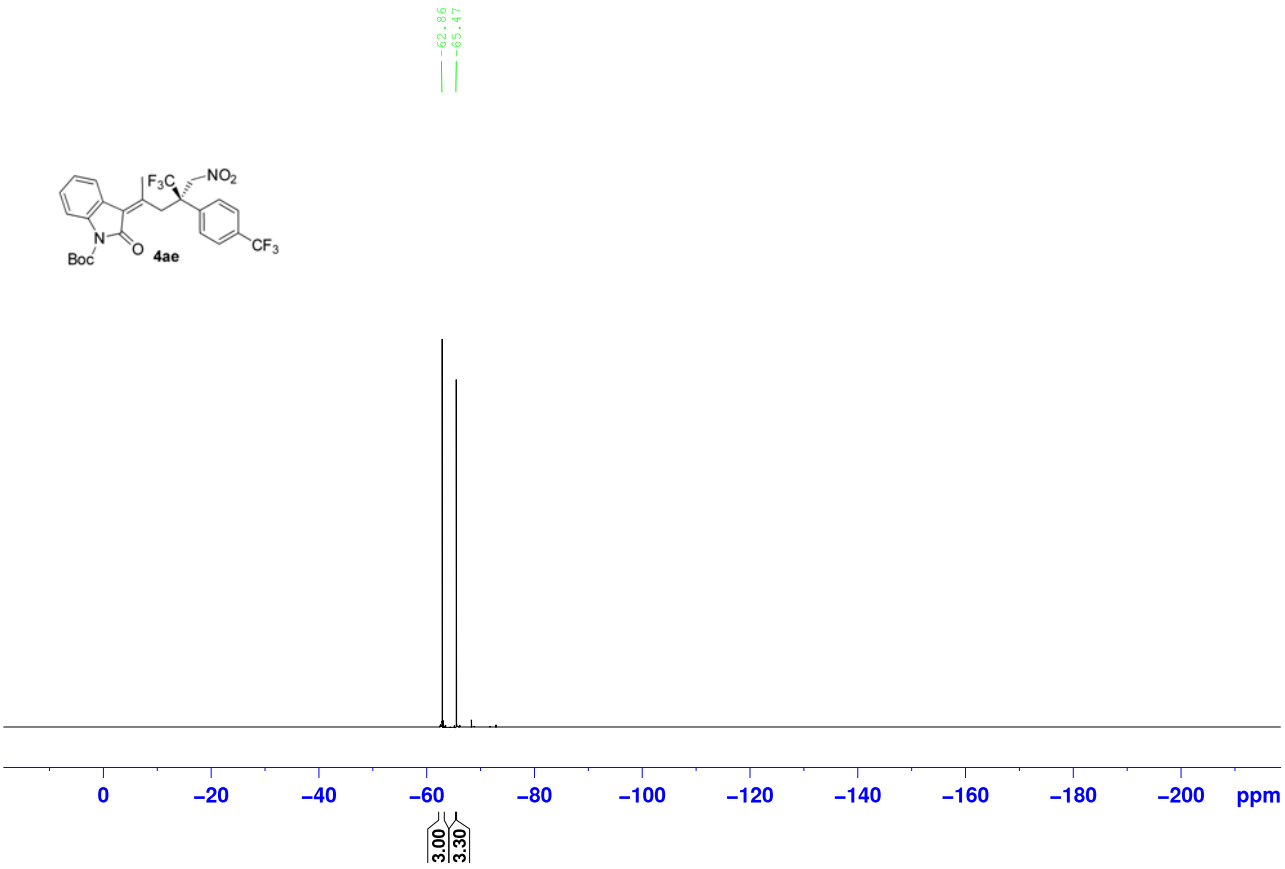

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
2.03
1.03
1.06
1.09
2.03
1.00
1.02
1.01
1.05
3.01
9.01

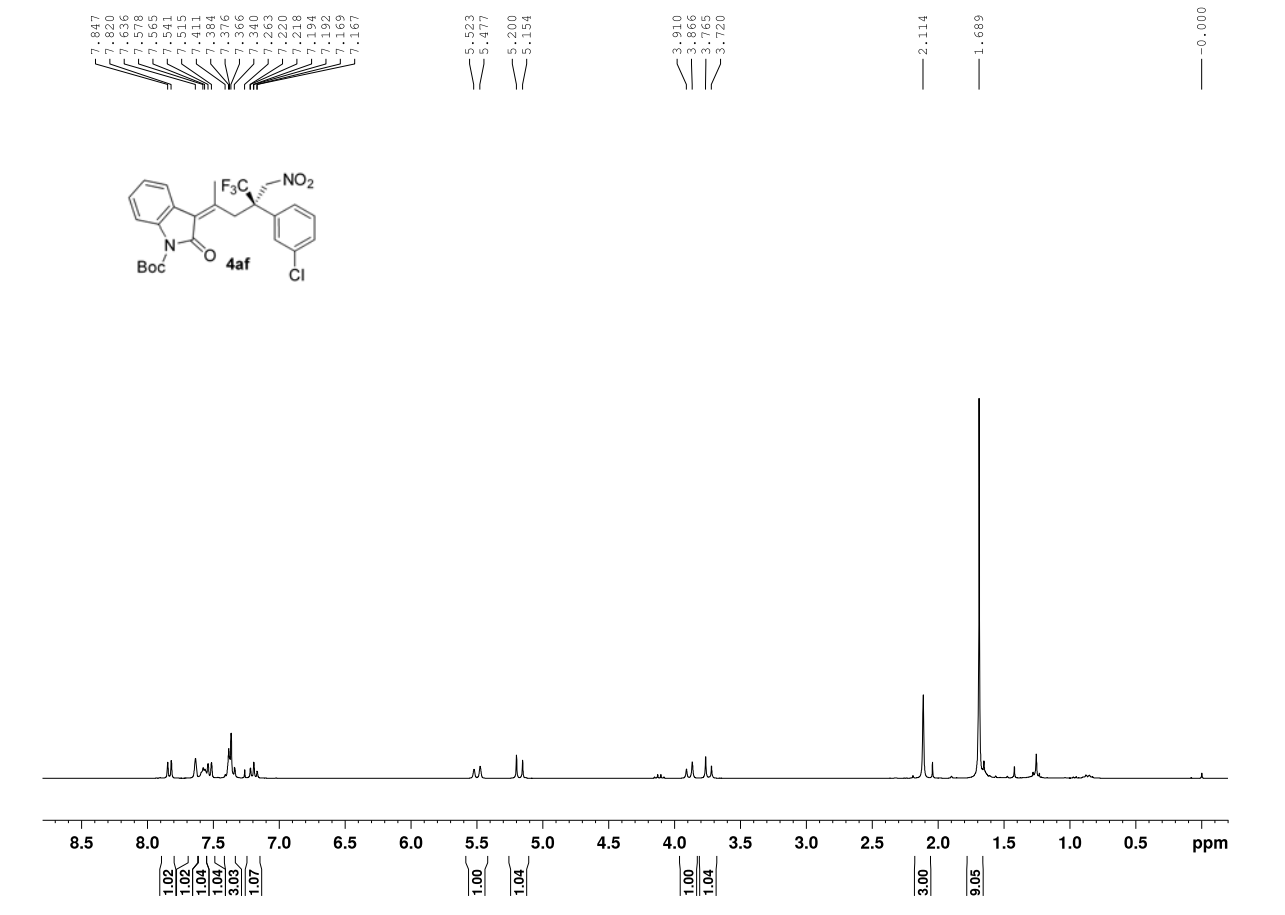

166.18
164.02
160.71
150.56
148.78
138.30
130.24
130.19
129.38
129.20
129.12
127.07
124.78
124.19
122.94
115.92
115.63
114.77
85.05
77.47
77.04
76.62
75.75
55.40
55.08
42.23
29.70
28.14
25.96
F3C
NO2
N
O
Boc
4ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-65.96
-113.01
F3C
NO2
N
O
Boc
4ad
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
3.25
1.00


7.843
7.816
7.714
7.685
7.555
7.529
7.400
7.375
7.349
7.263
7.230
7.205
7.179
5.633
5.587
5.191
5.145
4.049
4.005
3.646
3.601
2.156
1.694
0.000
F3C
NO2
N
O
Boc
CF3
4ae
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.04
2.05
1.05
1.05
1.02
1.00
1.04
1.00
1.00
3.09
9.06


166.25
149.83
148.73
138.79
138.34
130.85
130.41
129.52
127.68
127.36
125.73
125.68
124.85
124.26
122.83
114.81
85.14
77.47
77.04
76.62
75.42
55.84
55.51
42.38
29.70
28.13
26.90
26.03
F3C
NO2
N
O
Boc
CF3
4ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-62.886
-65.147
F3C
NO2
N
O
Boc
CF3
4ae
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm
3.00
3.30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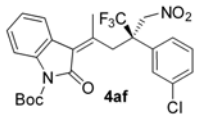
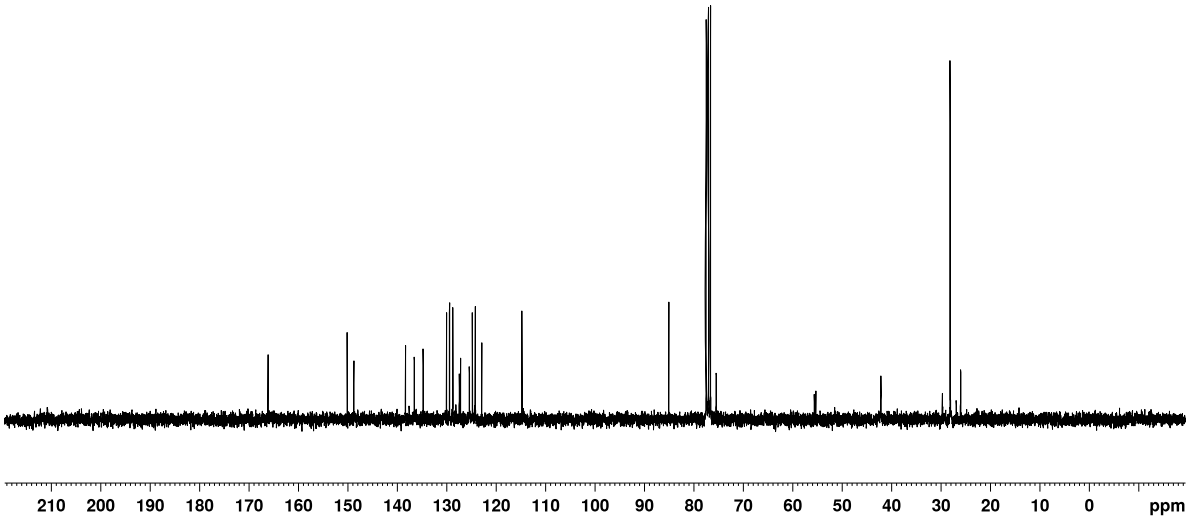
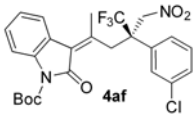
7.820
7.636
7.578
7.565
7.541
7.515
7.411
7.384
7.376
7.366
7.340
7.263
7.220
7.218
7.194
7.192
7.169
7.167
5.523
5.477
5.200
5.154
3.910
3.866
3.765
3.720
2.114
1.689
-0.000
F3C
NO2
N
O
Boc
4af
Cl
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
1.02
1.04
1.04
3.03
1.07
1.00
1.04
1.00
1.04
3.00
9.05

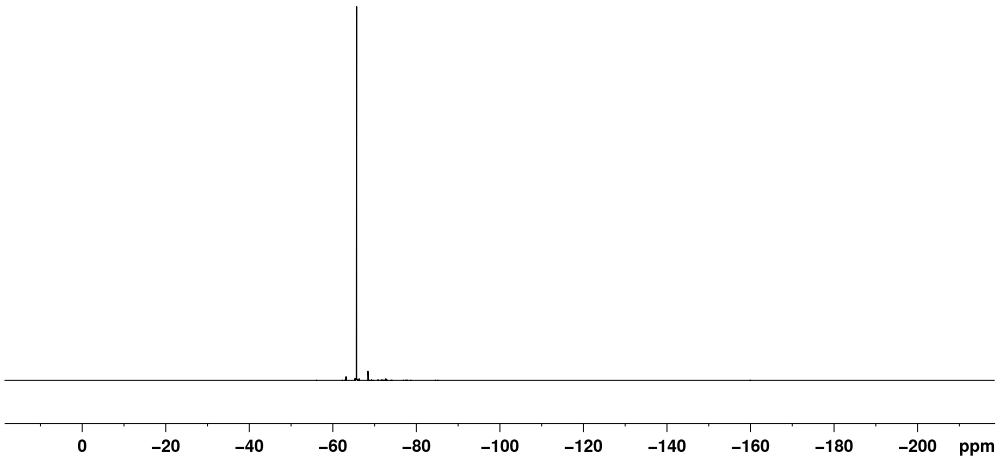
166.13
150.13
148.80
138.35
136.56
134.76
130.03
129.42
128.77
127.46
127.19
125.44
124.81
124.21
122.91
114.78
85.04
77.48
77.06
76.63
75.47
55.62
55.29
42.15
29.70
28.14
26.90
26.00

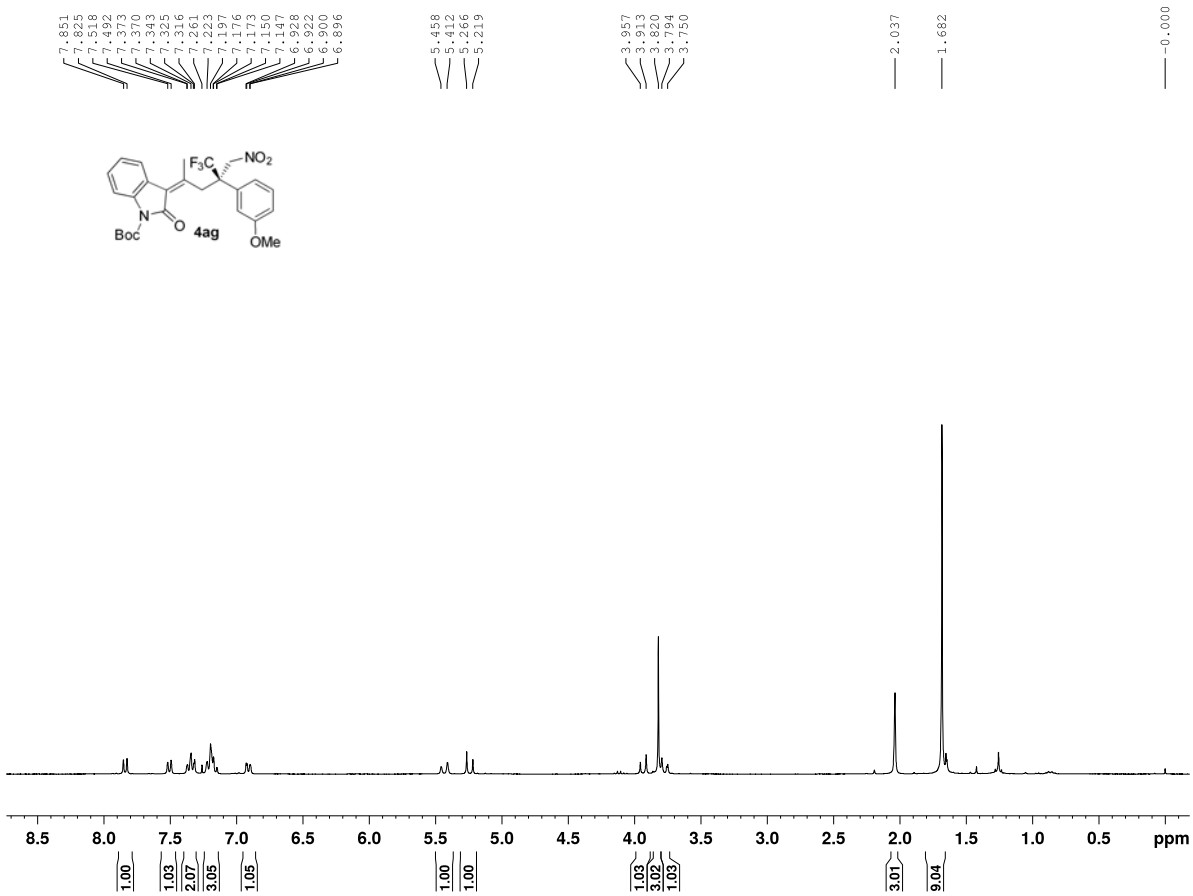




-65.70



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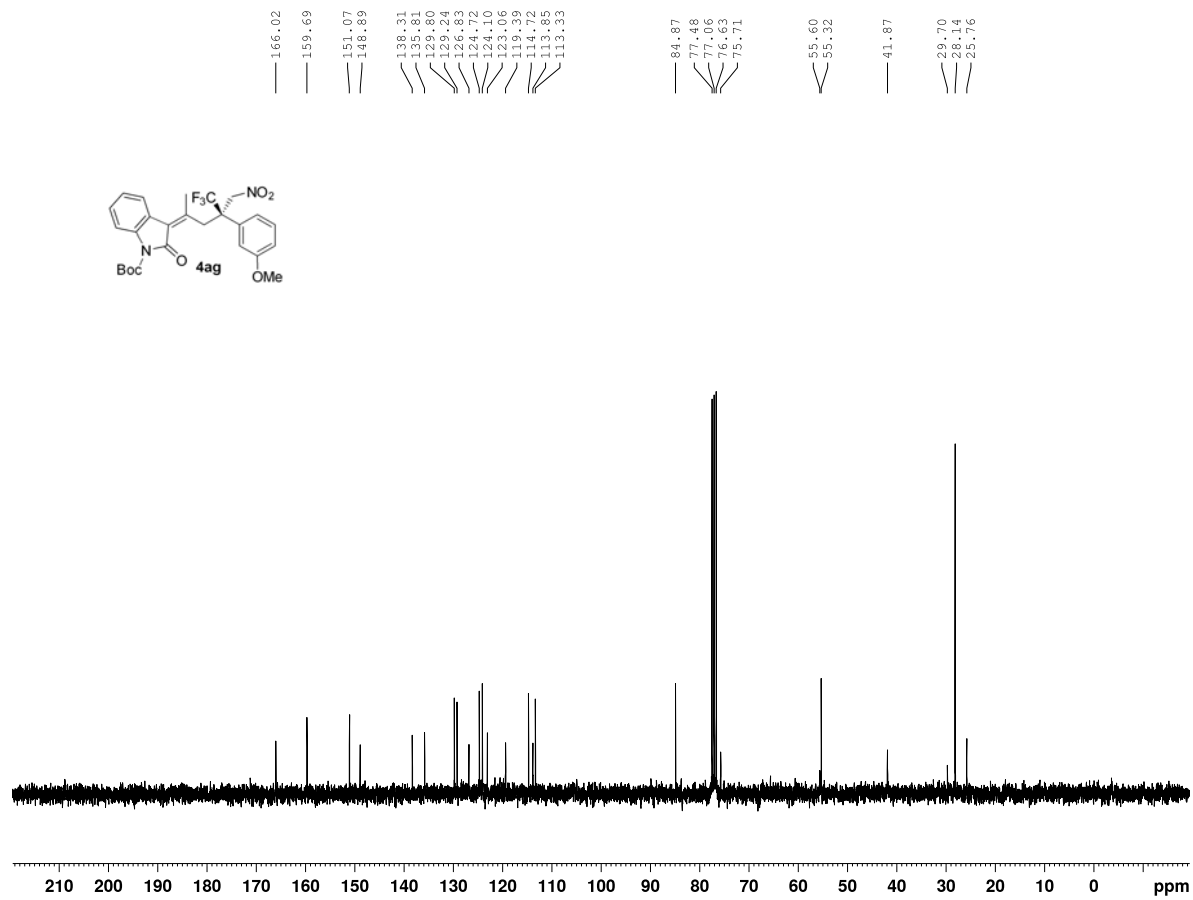
7.825
7.548
7.492
7.373
7.370
7.343
7.325
7.316
7.261
7.223
7.197
7.176
7.173
7.150
7.147
6.928
6.922
6.900
6.896
5.458
5.412
5.266
5.219
3.957
3.913
3.820
3.794
3.750
2.037
1.682
0.000
F3C
NO2
N
Boc
O
4ag
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
2.07
3.05
1.05
1.00
1.00
1.03
3.02
1.03
3.01
9.04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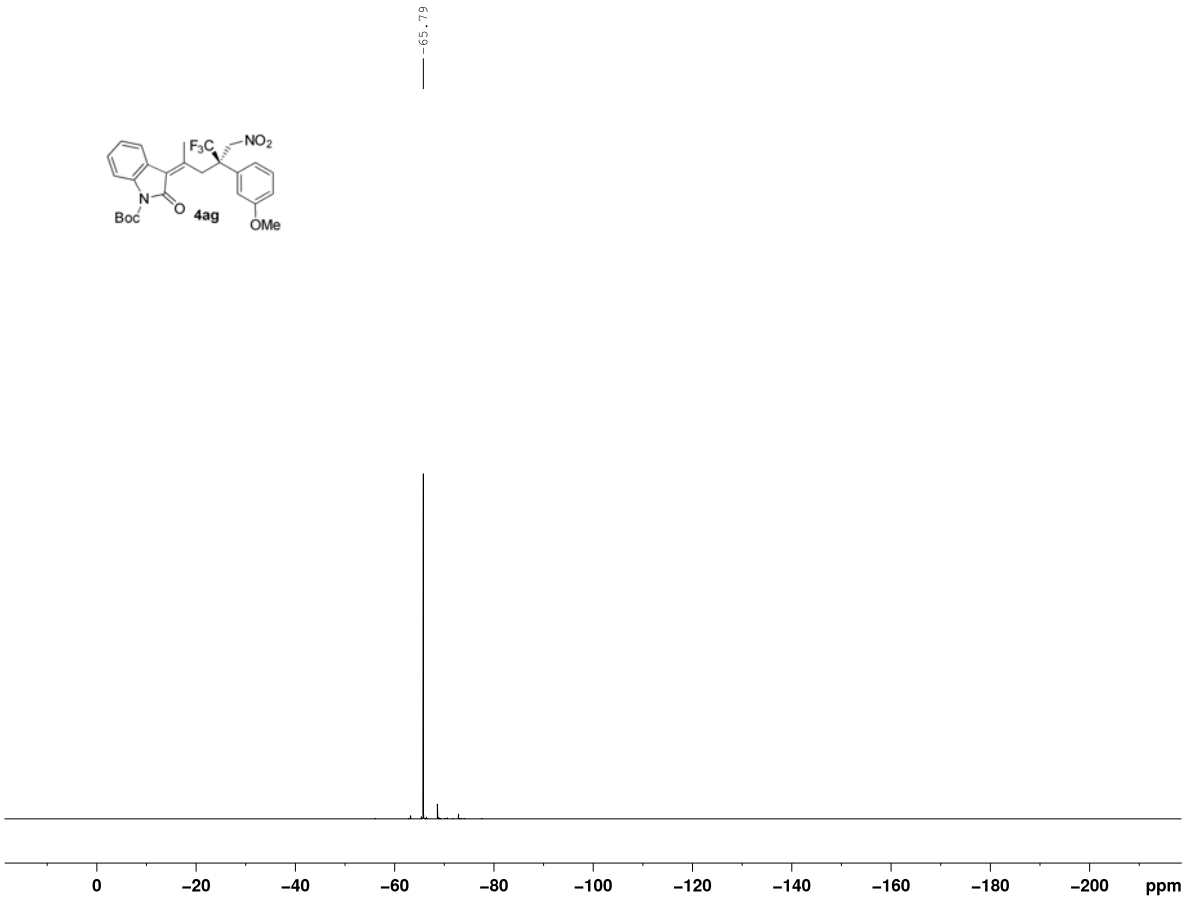
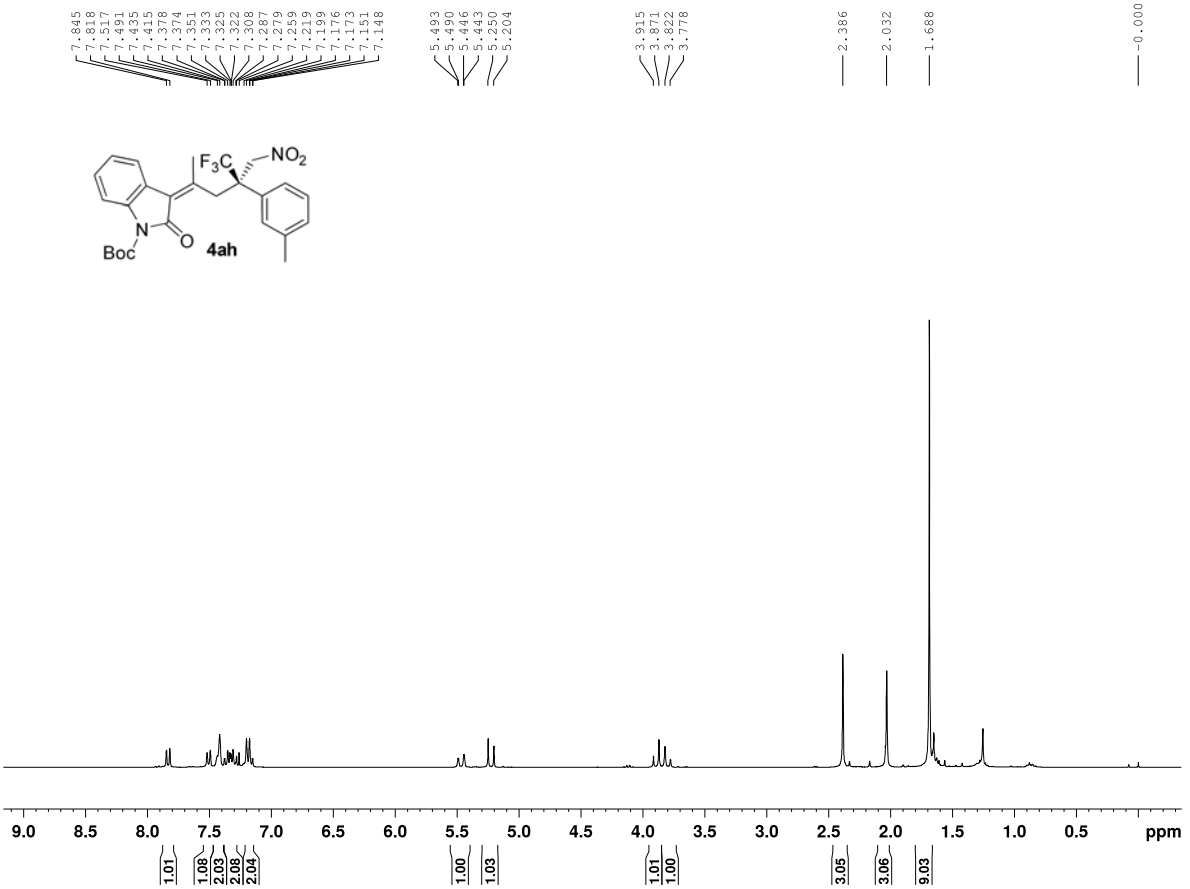
159.69
151.07
148.89
138.31
135.81
129.80
129.24
126.83
124.72
124.10
123.06
119.39
114.72
113.85
113.33
84.87
77.48
77.06
76.63
75.71
55.60
55.32
41.87
29.70
28.14
25.76
F3C
NO2
N
Boc
O
4ag
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-65.79
F3C
NO2
N
O
Boc
4ag
OMe
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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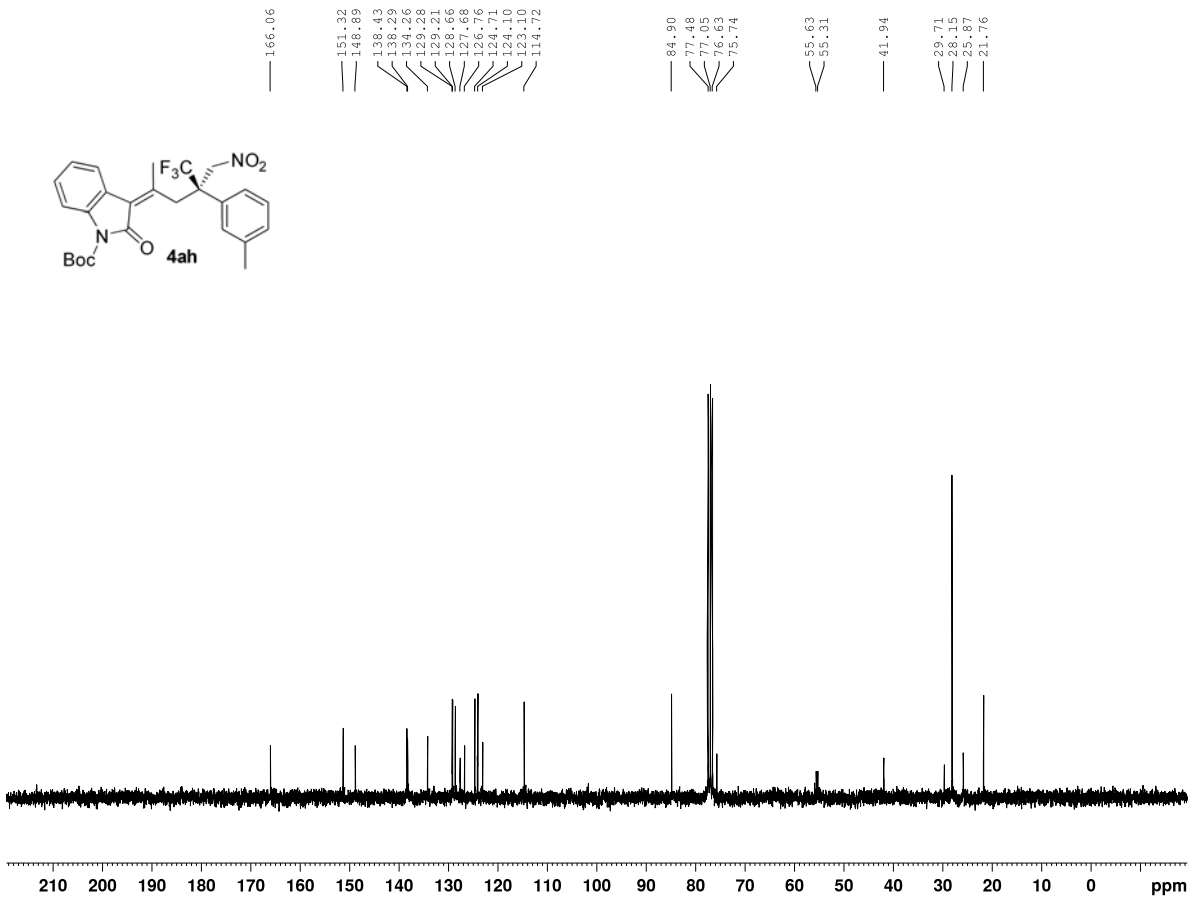
7.818
7.517
7.491
7.435
7.415
7.378
7.374
7.351
7.333
7.325
7.322
7.308
7.287
7.279
7.259
7.219
7.199
7.176
7.173
7.151
7.148
5.493
5.490
5.446
5.443
5.250
5.204
3.915
3.871
3.822
3.778
2.386
2.032
1.688
-0.000
F3C
NO2
N
O
Boc
4ah
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
1.06
2.03
2.08
2.04
1.00
1.03
1.01
1.00
3.05
3.06
9.03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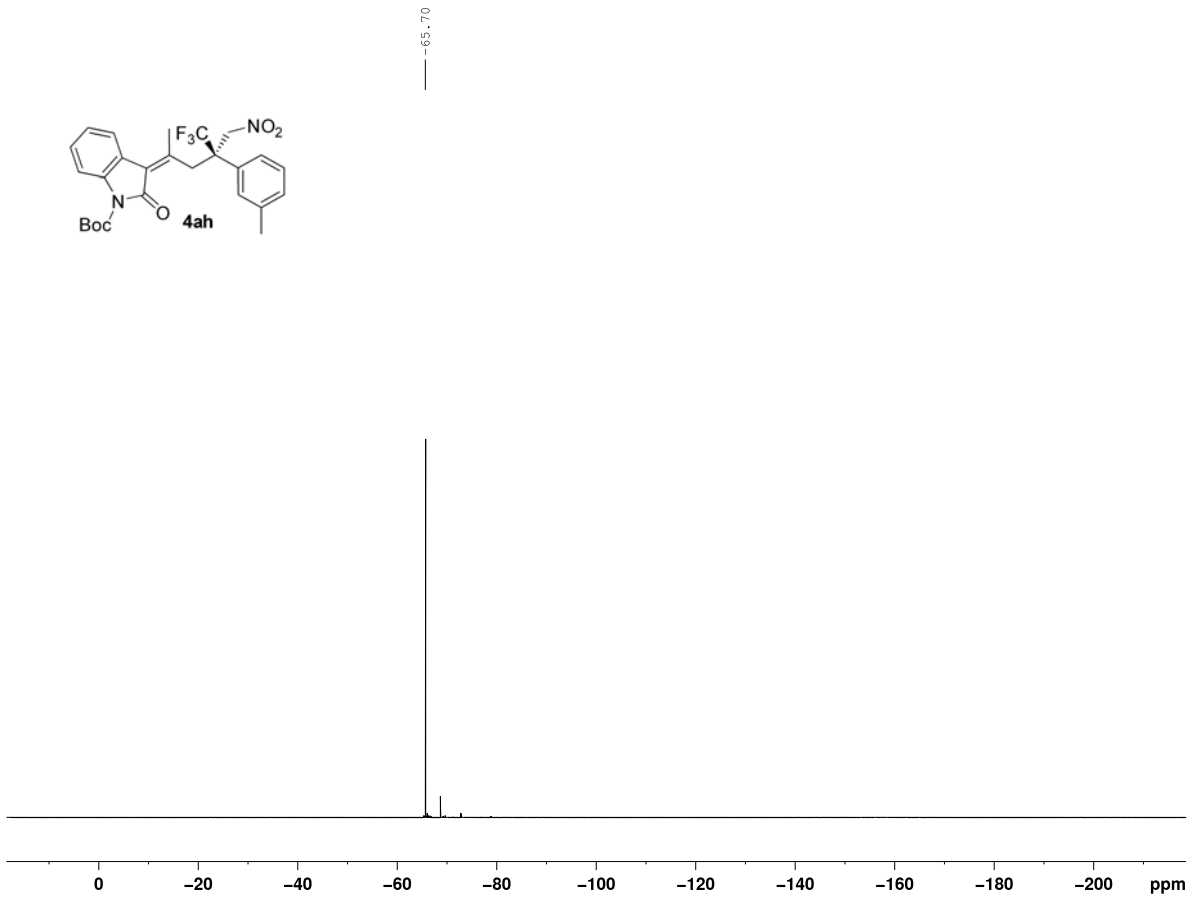
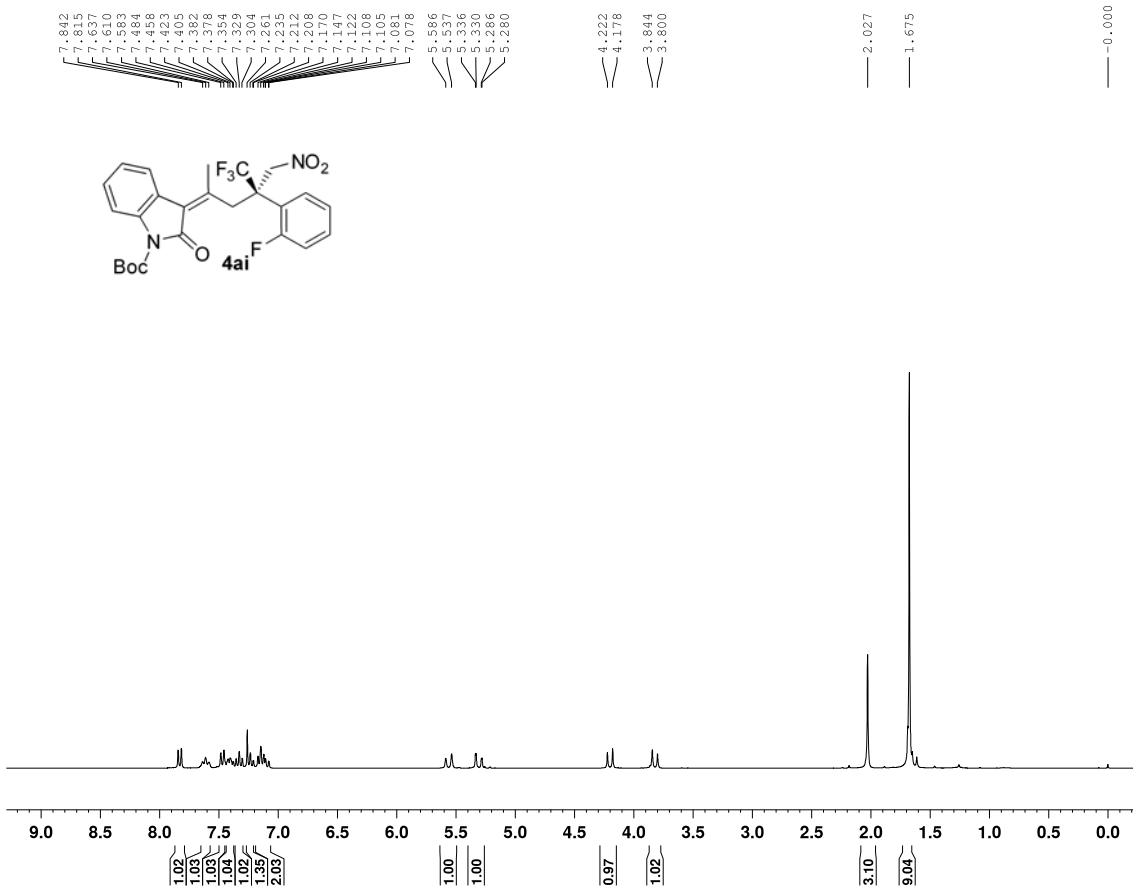
151.32
148.89
138.43
138.29
134.26
129.28
129.21
128.66
127.68
126.76
124.71
124.10
123.10
114.72
84.90
77.48
77.05
76.63
75.74
55.63
55.31
41.94
29.71
28.15
25.87
21.76
F3C
NO2
N
Boc
O
4ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-65.70
F3C
NO2
N
Boc
O
4ah
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm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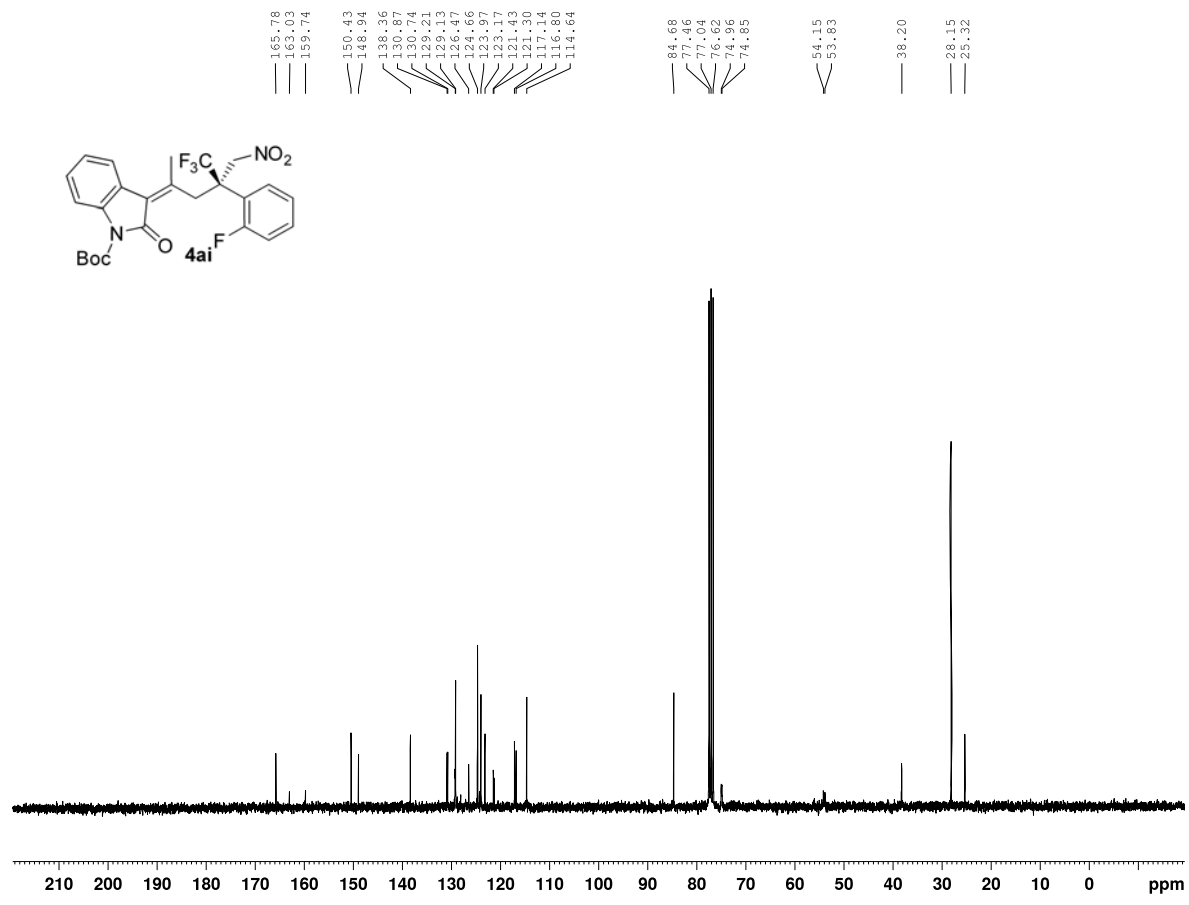
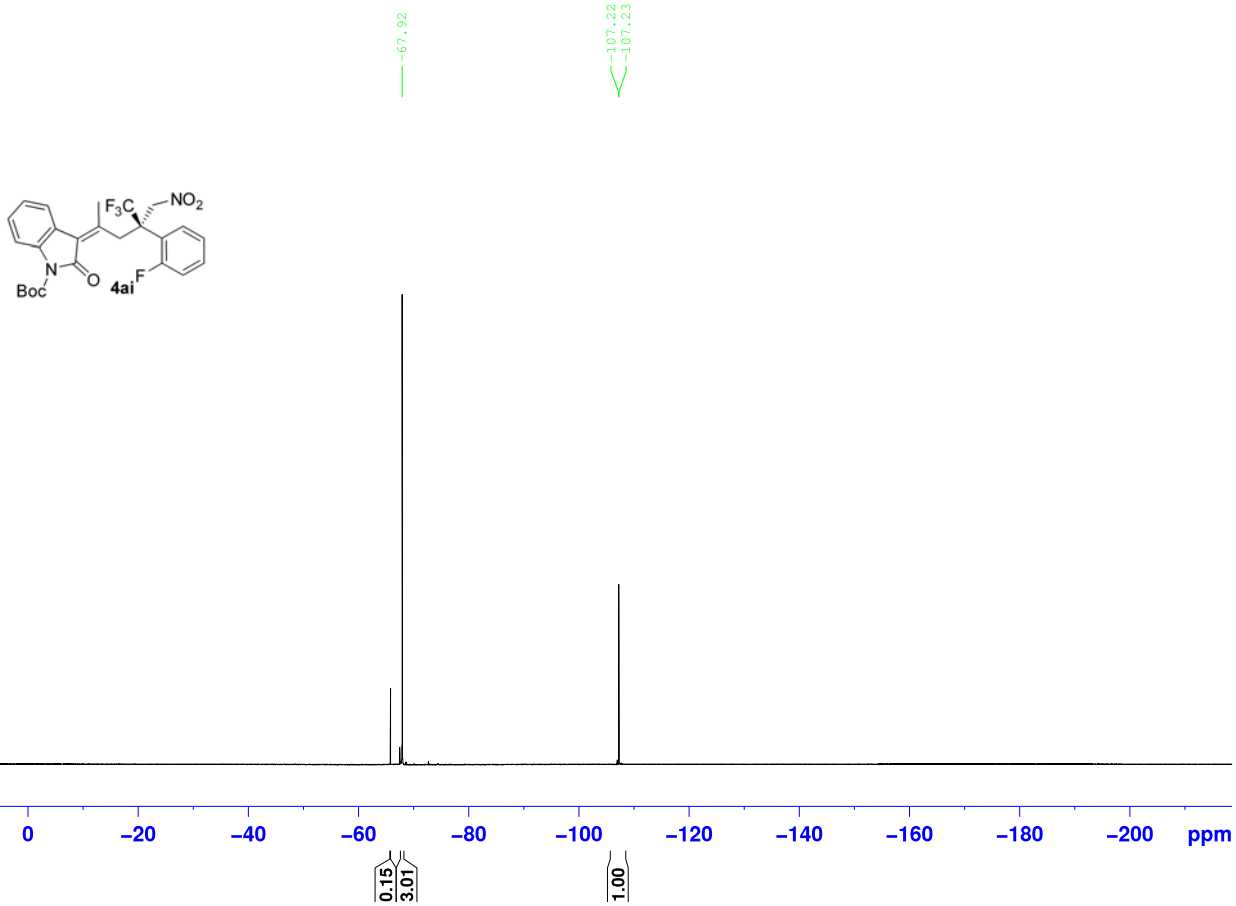
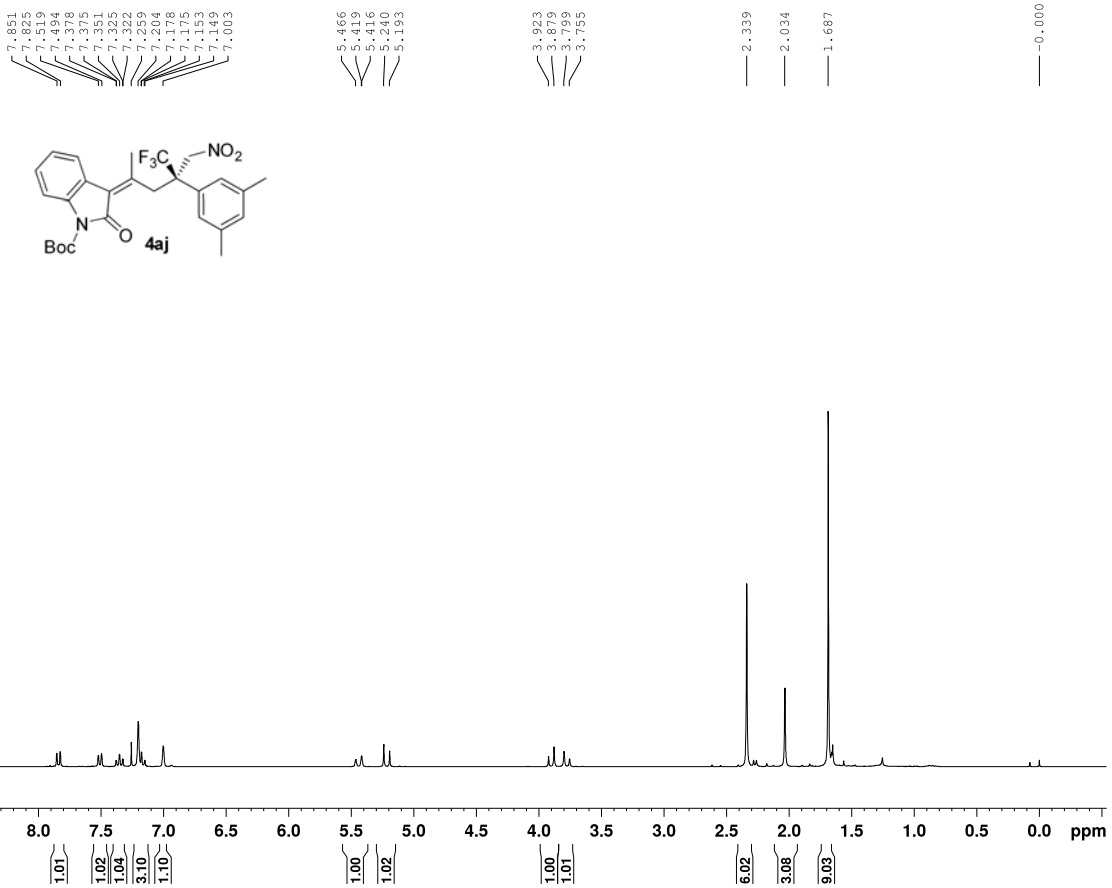
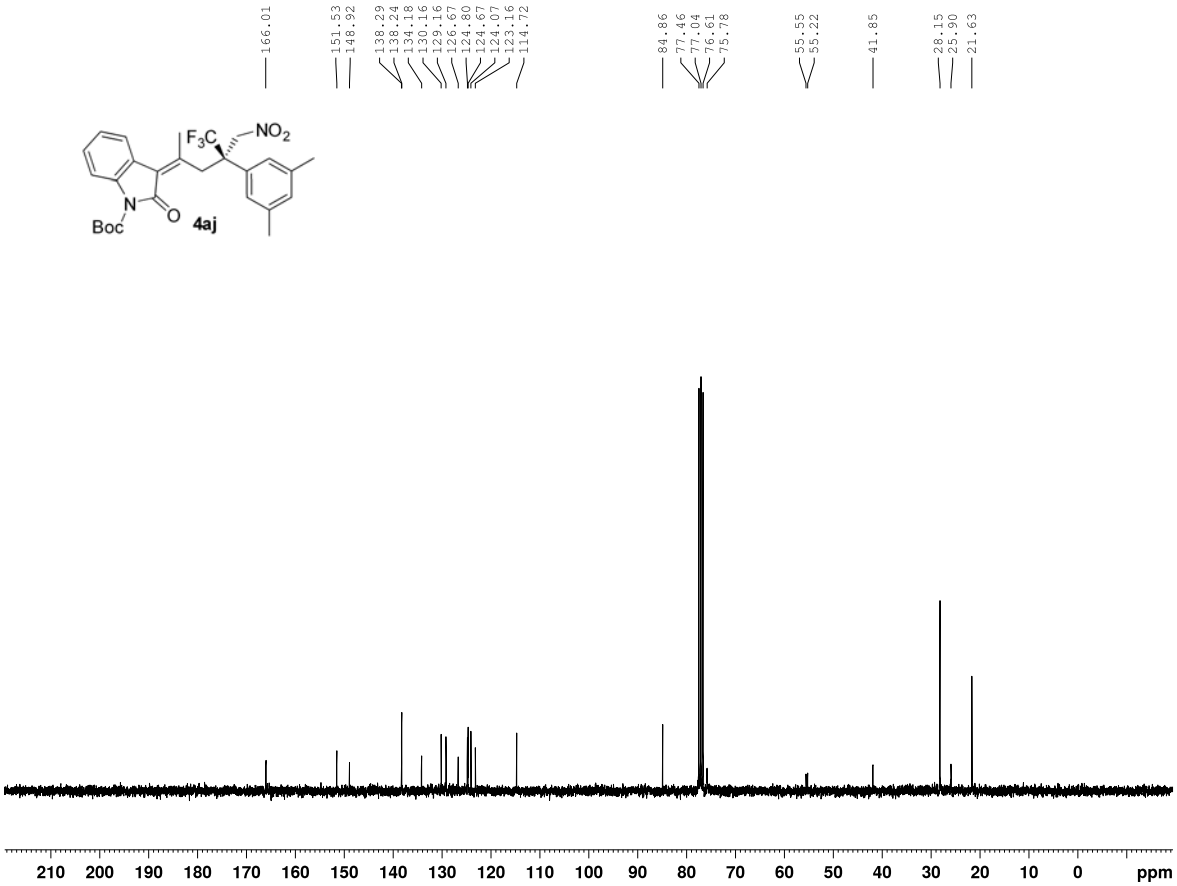
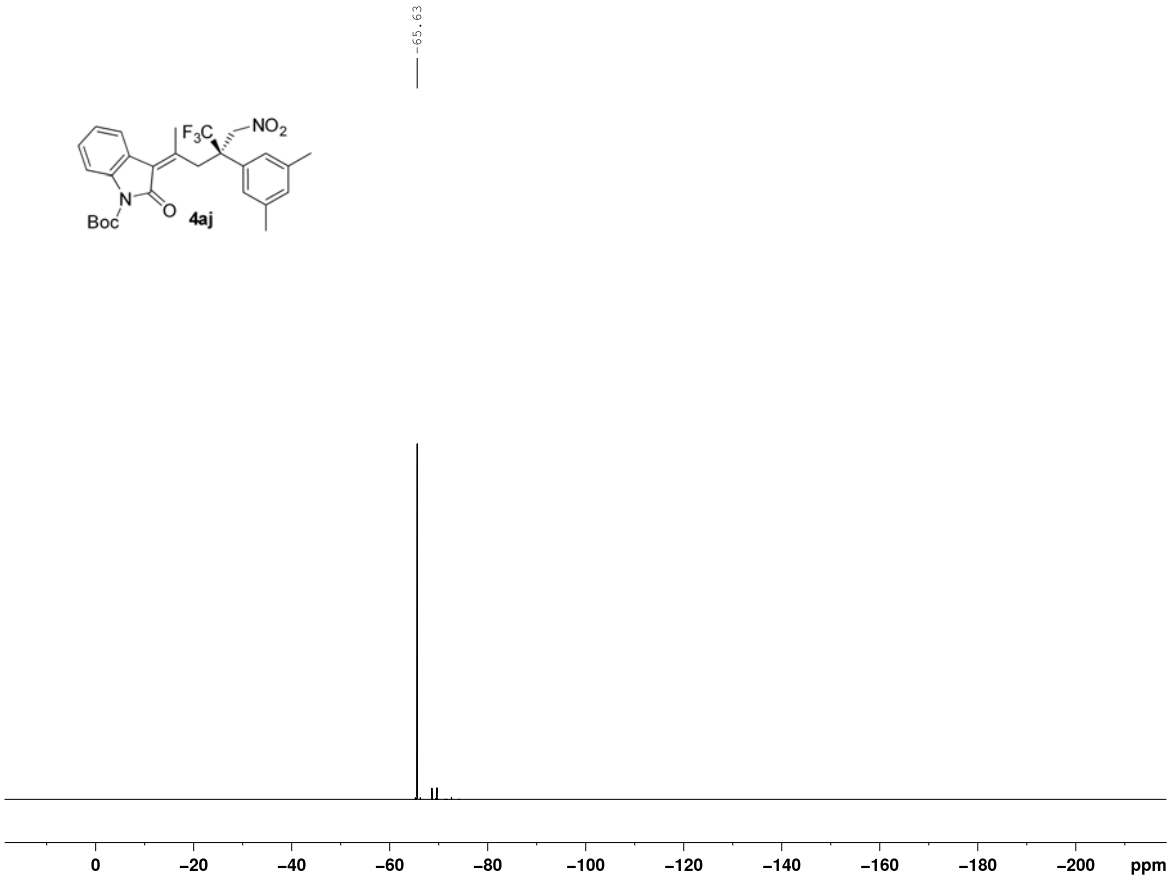
7.610
7.583
7.484
7.458
7.423
7.405
7.382
7.378
7.354
7.329
7.304
7.261
7.235
7.212
7.208
7.170
7.147
7.122
7.108
7.105
7.081
7.078
5.586
5.537
5.336
5.330
5.286
5.280
4.222
4.178
3.844
3.800
2.027
1.675
0.000
F3C
NO2
N
O
Boc
4ai
F
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02
1.03
1.03
1.04
1.02
1.35
2.03
1.00
1.00
0.97
1.02
3.10
9.04

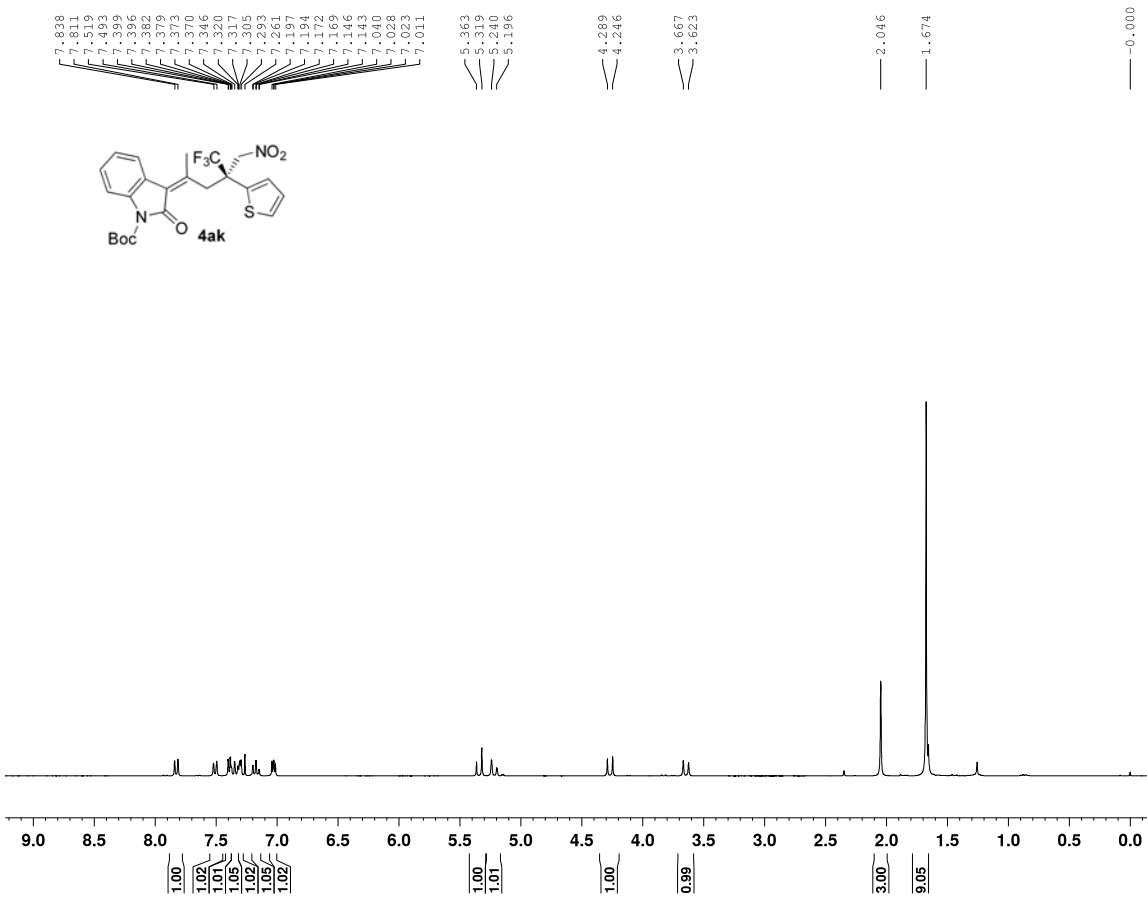

165.78
163.03
159.74
150.43
148.94
138.36
130.87
130.74
129.21
129.13
126.47
124.66
123.97
123.17
121.43
121.30
117.14
116.80
114.64
84.68
77.46
77.04
76.62
74.96
74.85
54.15
53.83
38.20
28.15
25.32
F3C
NO2
N
O
Boc
4ai
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

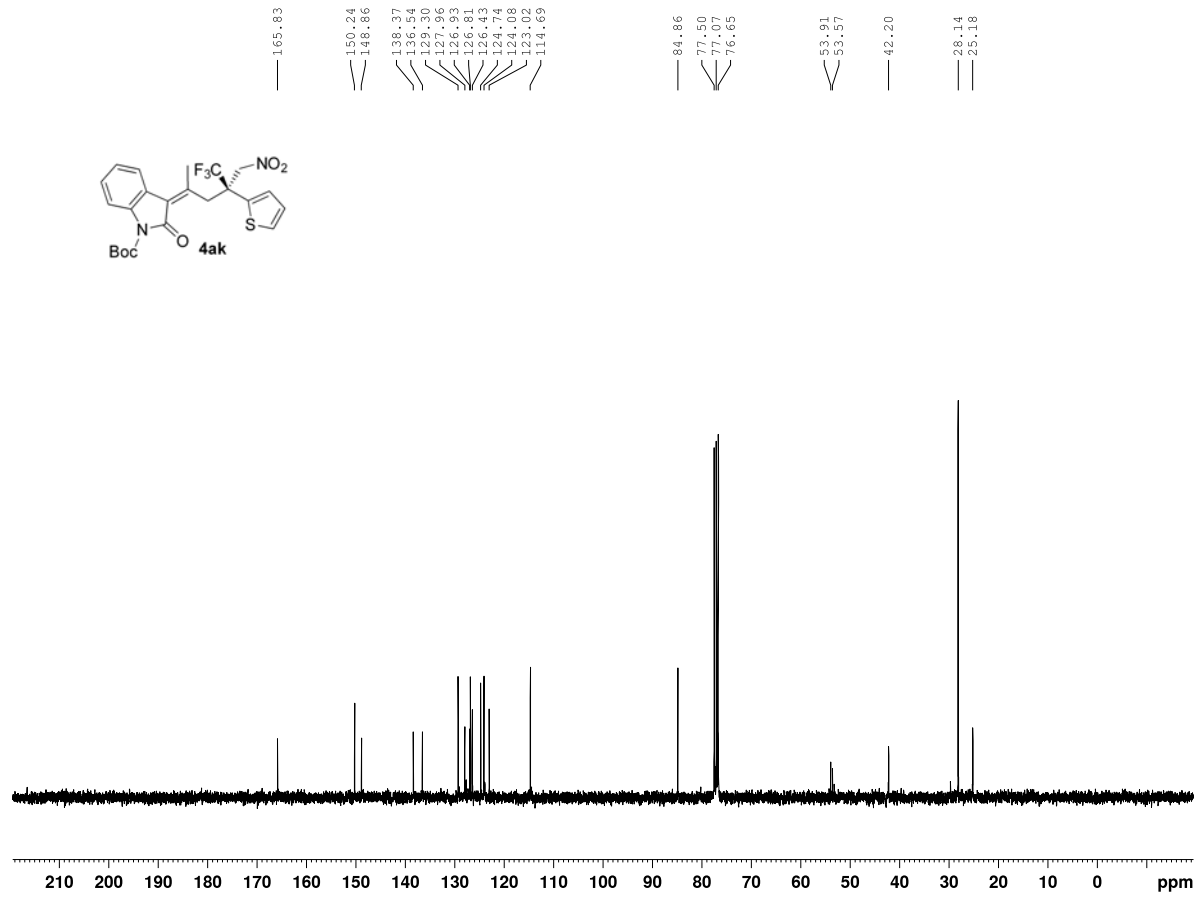

-67.92
-107.22
-107.23
F3C
NO2
N
Boc
O
F
4ai
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
0.15
3.01
1.00


7.851
7.825
7.519
7.494
7.378
7.375
7.351
7.325
7.322
7.259
7.204
7.178
7.175
7.153
7.149
7.003
5.466
5.419
5.416
5.240
5.193
3.923
3.879
3.799
3.755
2.339
2.034
1.687
-0.000
F3C
NO2
N
Boc
O
4aj
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.02
1.04
3.10
1.10
1.00
1.02
1.00
1.01
6.02
3.08
9.03


166.01
151.53
148.92
138.29
138.24
134.18
130.16
129.16
126.67
124.80
124.67
124.07
123.16
114.72
84.86
77.46
77.04
76.61
75.78
55.55
55.22
41.85
28.15
25.90
21.63
F3C
NO2
N
O
Boc
4aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-65.63
F3C
NO2
N
O
Boc
4aj
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm


7.838
7.811
7.519
7.493
7.399
7.396
7.382
7.379
7.373
7.370
7.346
7.320
7.317
7.305
7.293
7.261
7.197
7.194
7.172
7.169
7.146
7.143
7.040
7.028
7.023
7.011
5.363
5.319
5.240
5.196
4.289
4.246
3.667
3.623
2.046
1.674
0.000
F3C
NO2
N
Boc
O
S
4ak
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.02 1.01 1.05 1.02 1.05 1.02 1.00 1.01 1.00 0.99 3.00 9.05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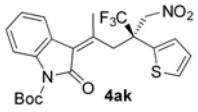
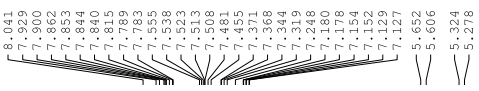
150.24
148.86
138.37
136.54
129.30
127.96
126.93
126.81
126.43
124.74
124.08
123.02
114.69
84.86
77.50
77.07
76.65
53.91
53.57
42.20
28.14
25.18
F3C
NO2
N
Boc
O
S
4ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


F3C
NO2
N
Boc
O
S

4ak

-69.22
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


8.041
7.929
7.900
7.862
7.853
7.844
7.840
7.815
7.789
7.783
7.555
7.538
7.523
7.513
7.508
7.481
7.455
7.371
7.368
7.344
7.319
7.248
7.180
7.178
7.154
7.152
7.129
7.127
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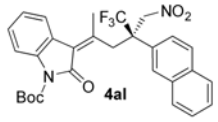
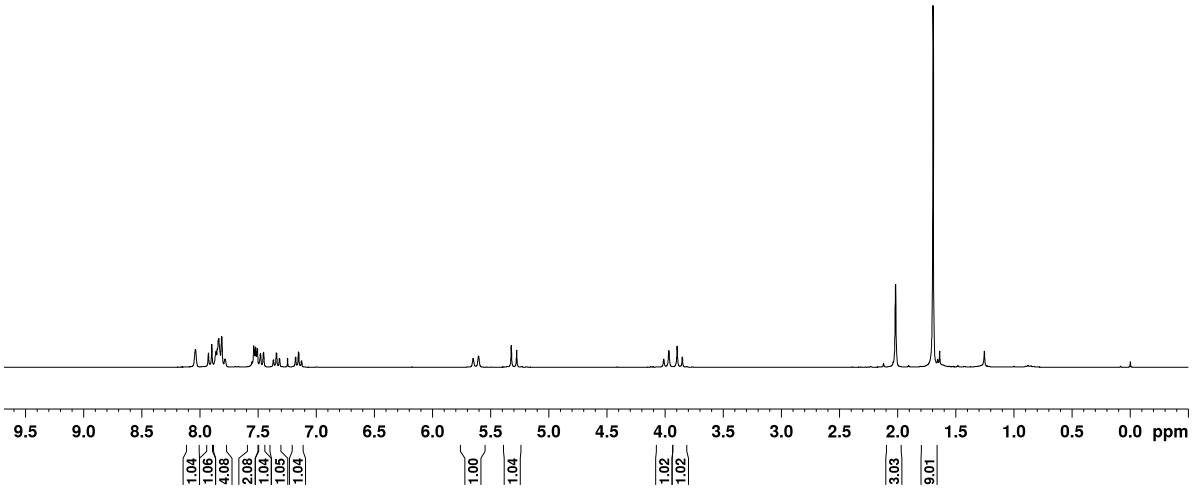
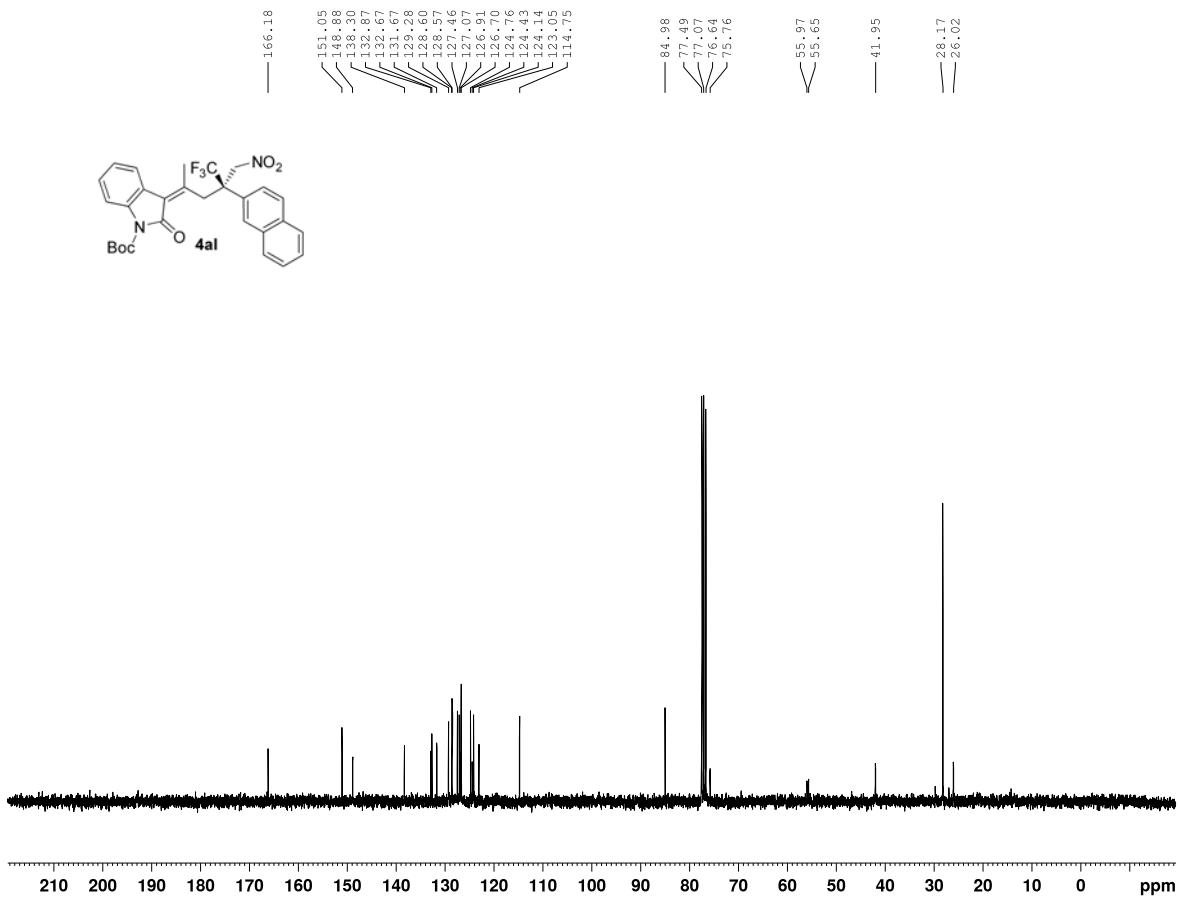
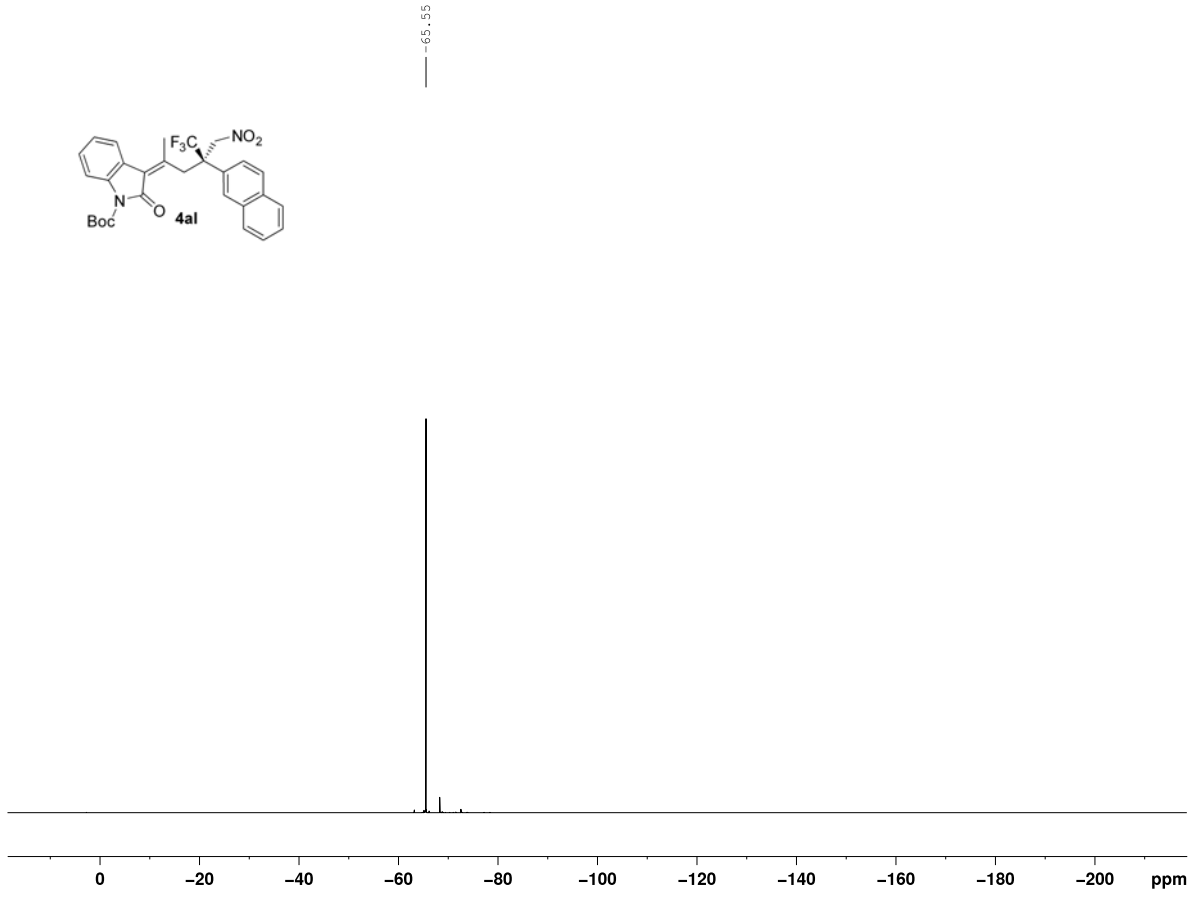
5.606
5.324
5.278
4.013
3.969
3.897
3.853
2.019
1.696
0.000

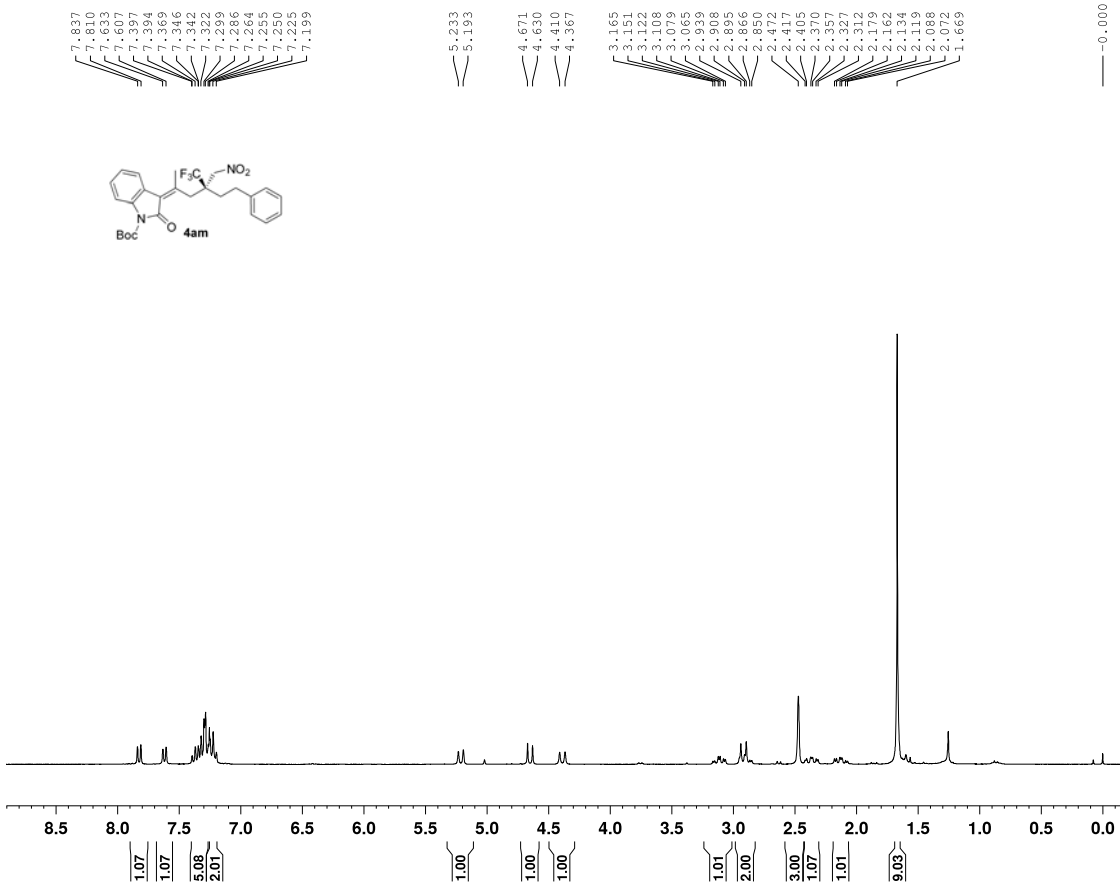

F3C
NO2
N
Boc
O

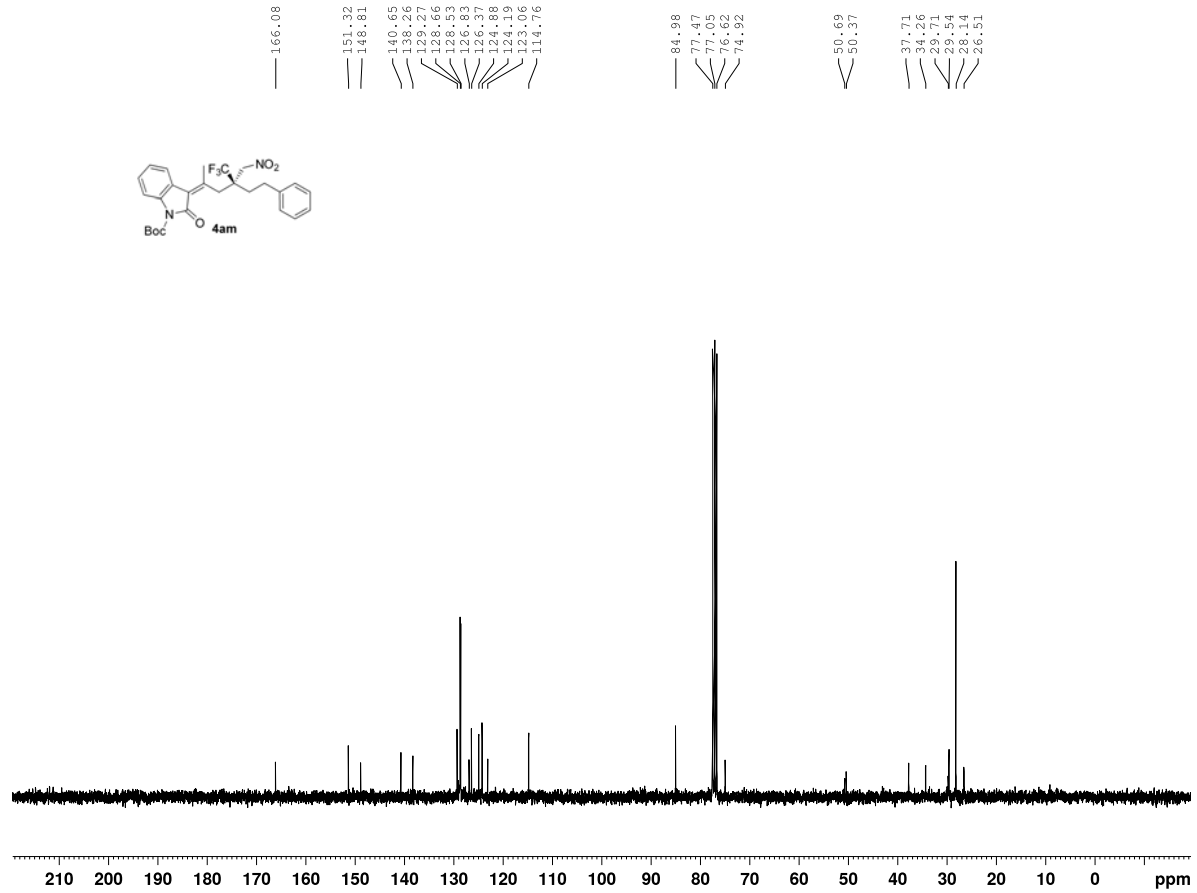
4al

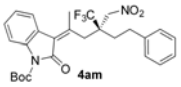

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.04
1.06
4.08
2.08
1.04
1.05
1.04
1.00
1.04
1.02
1.02
3.03
9.01


166.18
151.05
148.88
138.30
132.87
132.67
131.67
129.28
128.60
128.57
127.46
127.07
126.91
126.70
124.76
124.43
124.14
123.05
114.75
84.98
77.49
77.07
76.64
75.76
55.97
55.65
41.95
28.17
26.02
F3C
NO2
N
Boc
O
4al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-65.55
F3C
NO2
N
Boc
O
4al
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

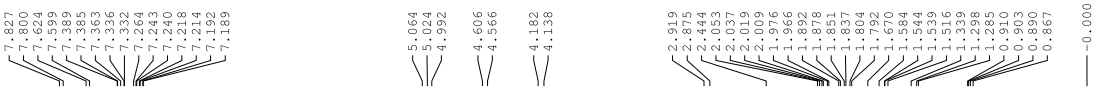

7.837
7.810
7.633
7.607
7.397
7.394
7.369
7.346
7.342
7.322
7.299
7.286
7.264
7.255
7.250
7.225
7.199
5.233
5.193
4.671
4.630
4.410
4.367
3.165
3.151
3.122
3.108
3.079
3.065
2.939
2.908
2.895
2.866
2.850
2.472
2.417
2.405
2.370
2.357
2.327
2.312
2.179
2.162
2.134
2.119
2.088
2.072
1.669
-0.000
F3C
NO2
N
Boc
O
4am
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.07
1.07
5.08
2.01
1.00
1.00
1.00
1.01
2.00
3.00
1.07
1.01
9.03

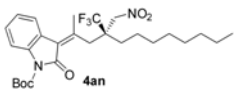

166.08
151.32
148.81
140.65
138.26
129.27
128.66
128.53
126.83
126.37
124.88
124.19
123.06
114.76
84.98
77.47
77.05
76.62
74.92
50.69
50.37
37.71
34.26
29.71
29.54
28.14
26.51
F3C
NO2
N
Boc
O
4am
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F3C
NO2
N
Boc
O

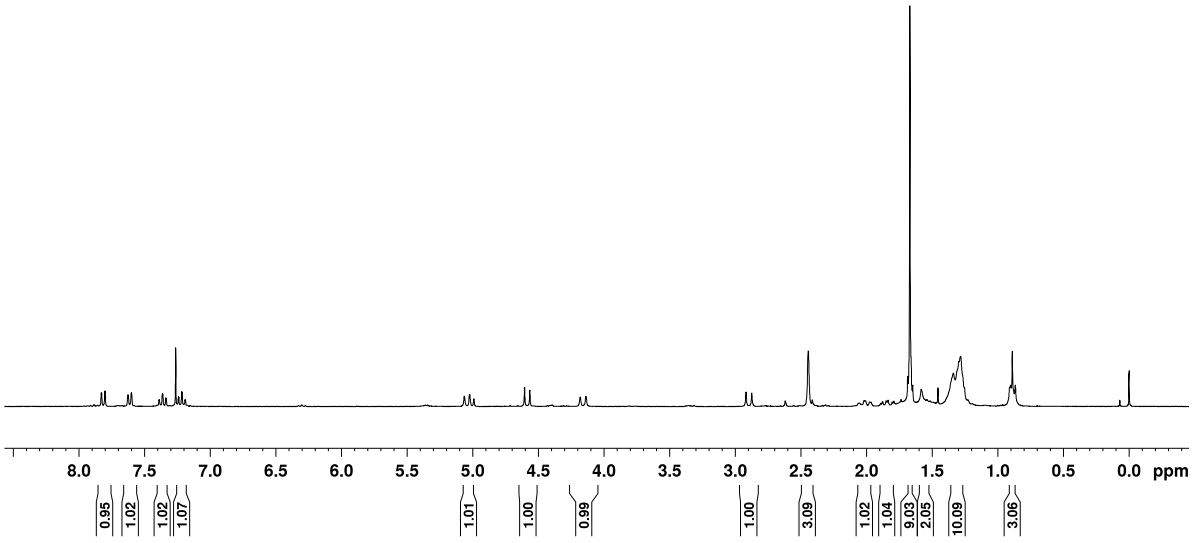
4am

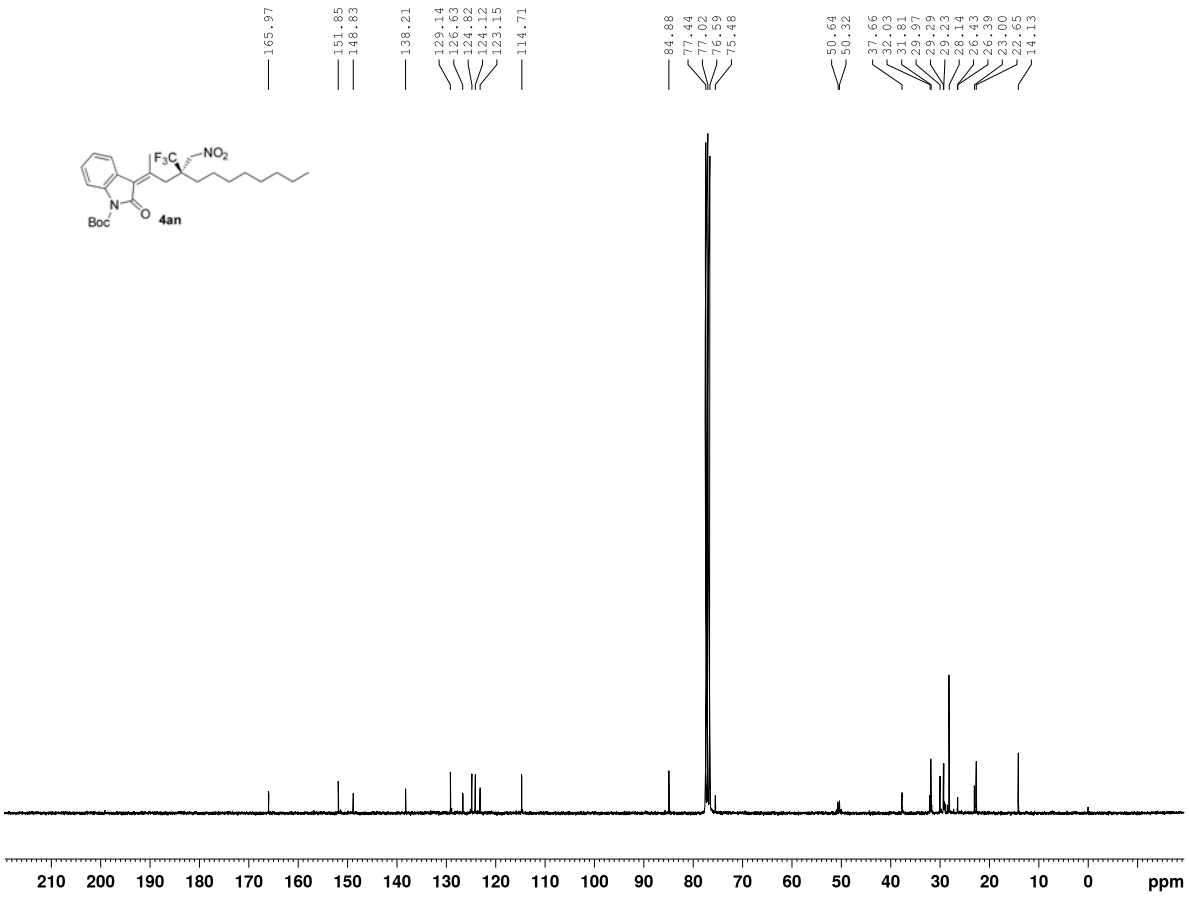
-69.76
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

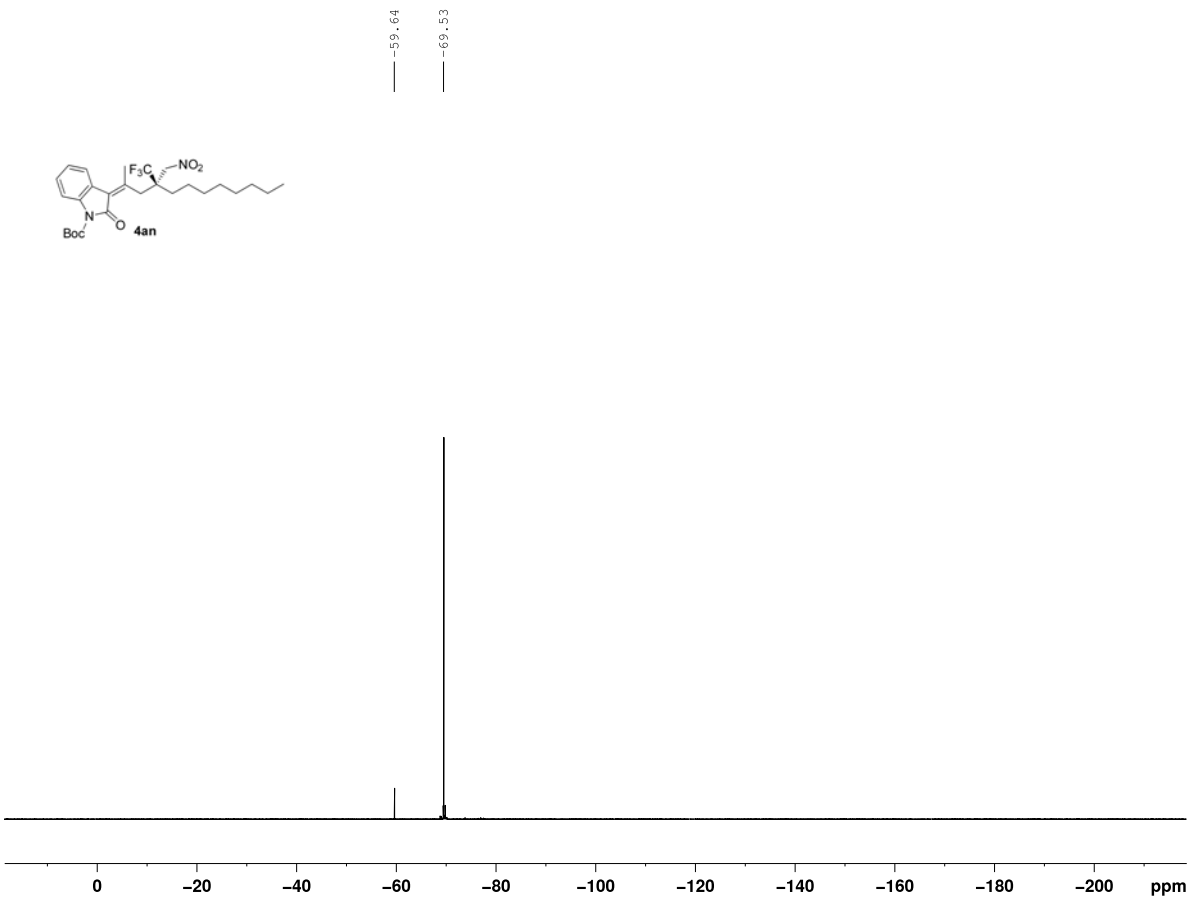

7.827
7.800
7.624
7.599
7.389
7.385
7.363
7.336
7.332
7.264
7.243
7.240
7.218
7.214
7.192
7.189
5.064
5.024
4.992
4.606
4.566
4.182
4.138
2.919
2.875
2.444
2.053
2.037
2.019
2.009
1.976
1.966
1.892
1.878
1.851
1.837
1.804
1.792
1.670
1.584
1.544
1.539
1.516
1.339
1.298
1.285
0.910
0.903
0.890
0.867
-0.000

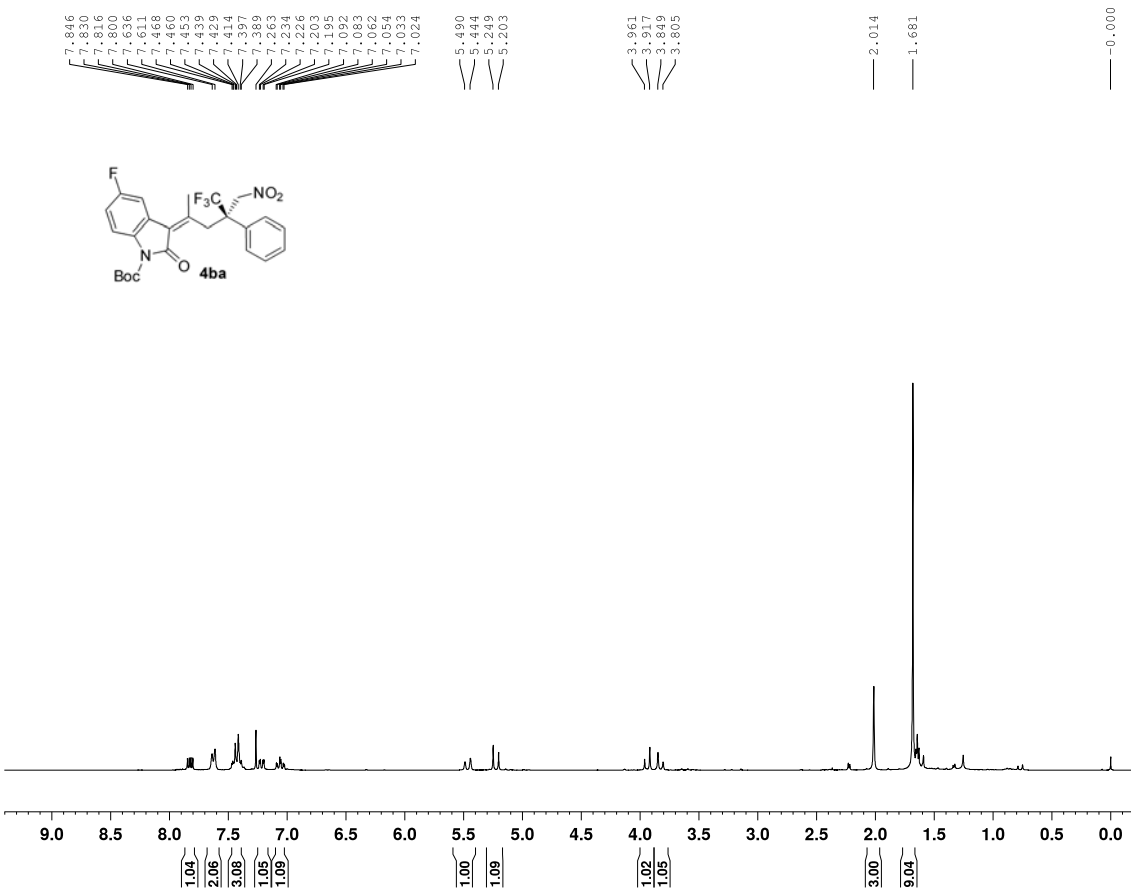

F3C
NO2
N
Boc
O

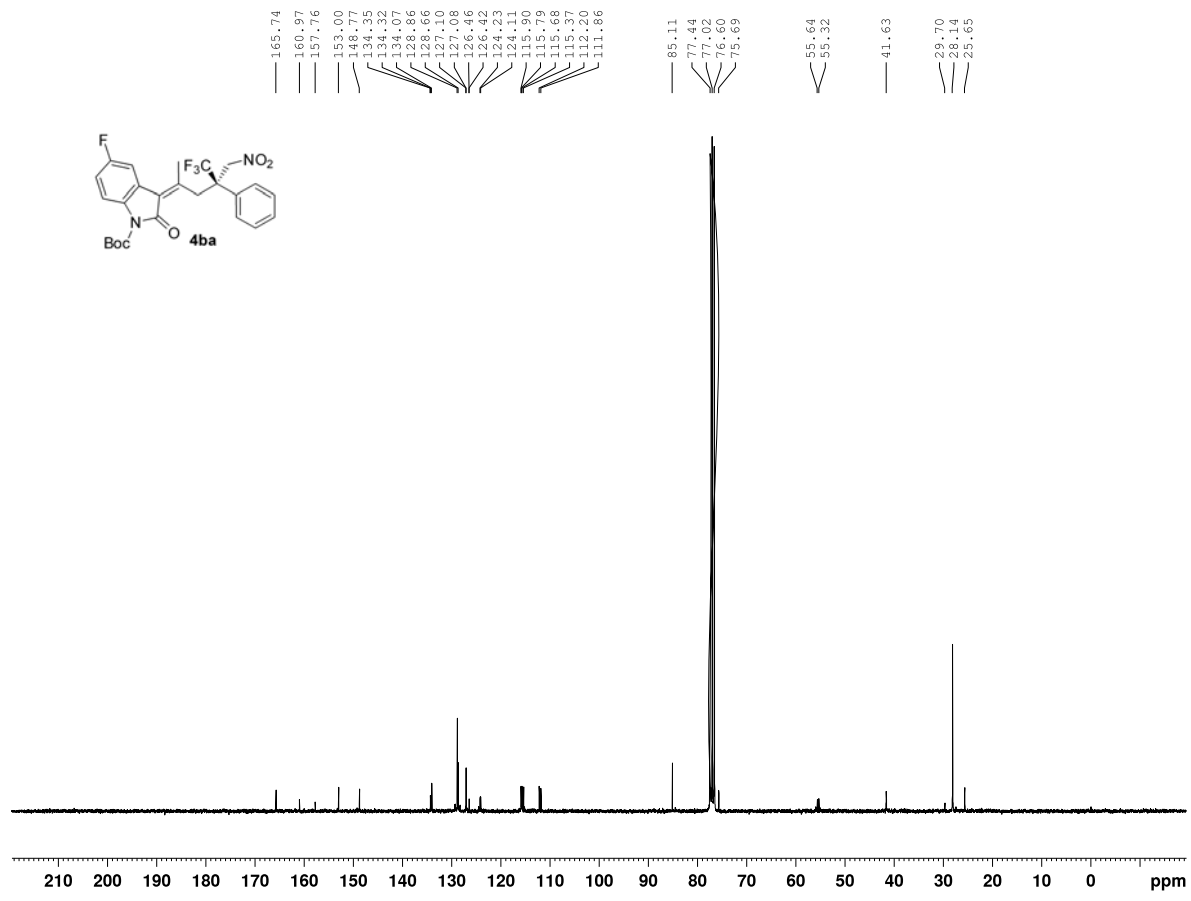
4an

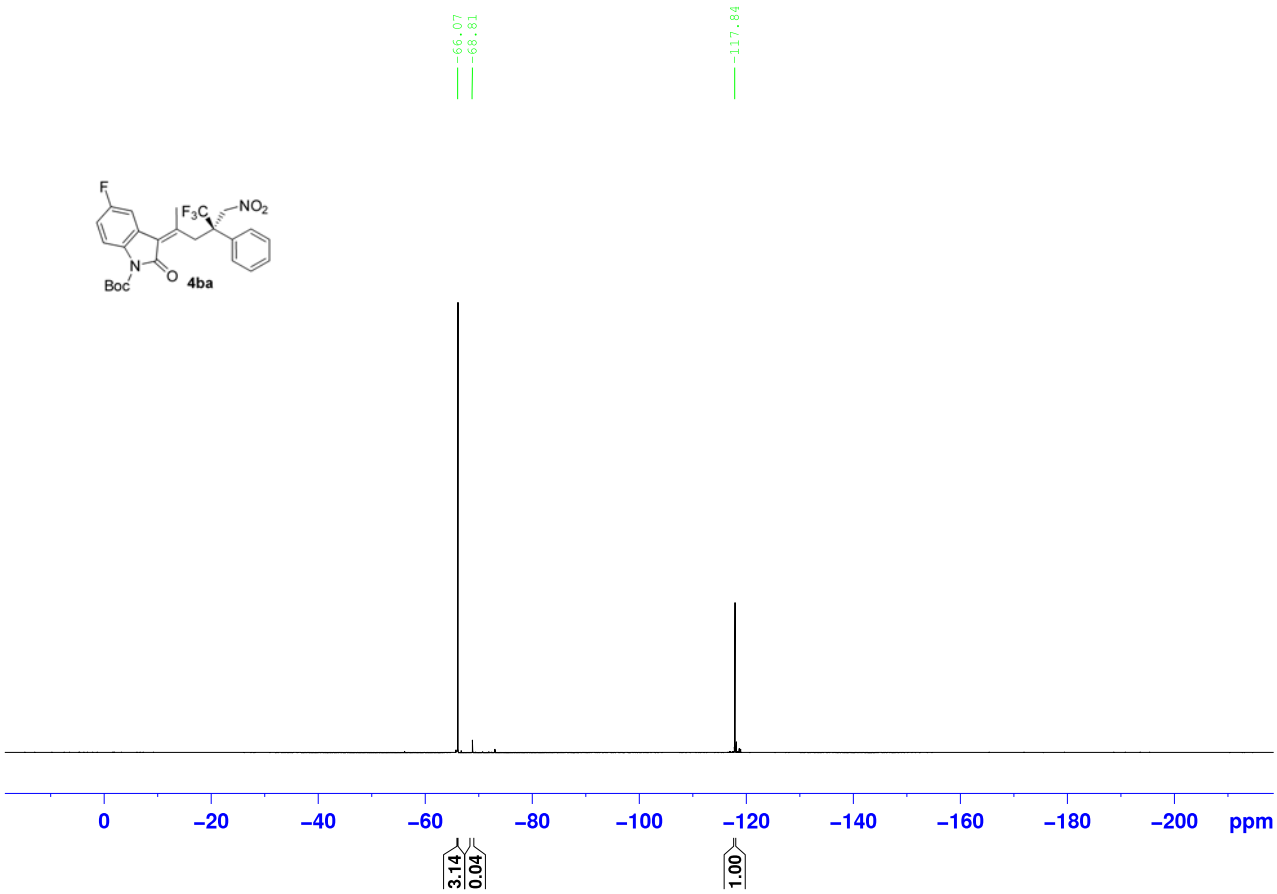

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.95
1.02
1.02
1.07
1.01
1.00
0.99
1.00
3.09
1.02
1.04
9.03
2.05
10.09
3.06

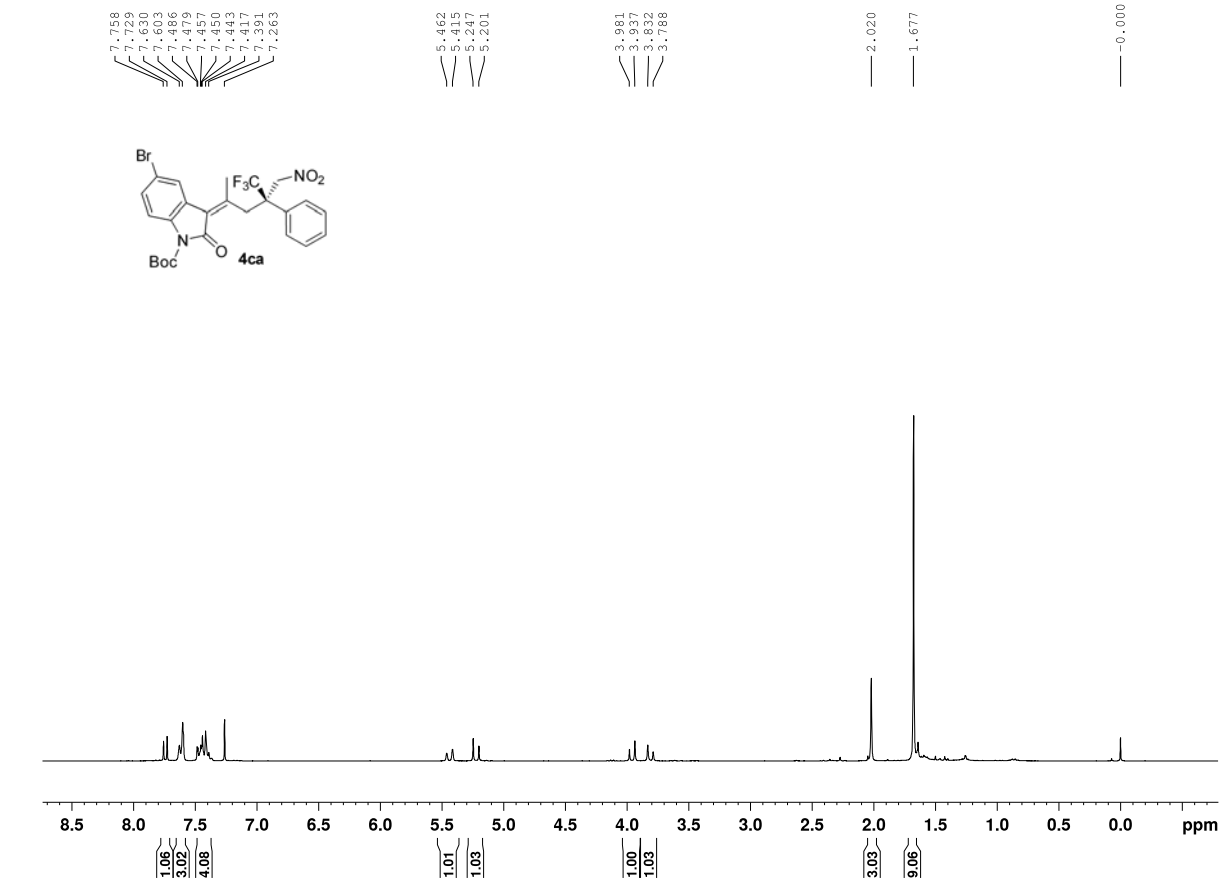

165.97
151.85
148.83
138.21
129.14
126.63
124.82
124.12
123.15
114.71
84.88
77.44
77.02
76.59
75.48
50.64
50.32
37.66
32.03
31.81
29.97
29.29
29.23
28.14
26.43
26.39
23.00
22.65
14.13
F3C
NO2
N
O
Boc
4an
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

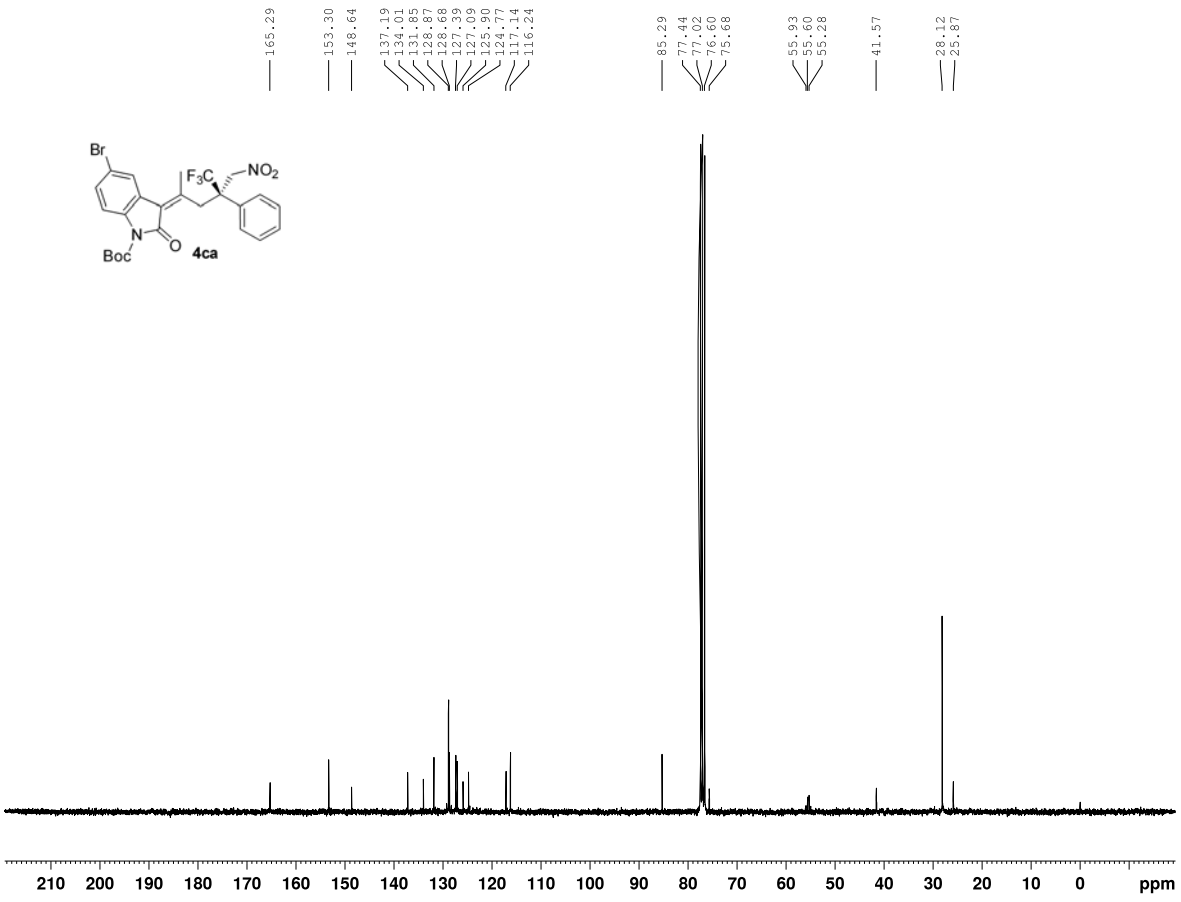

-59.64
-69.53
F3C
NO2
N
O
Boc
4an
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

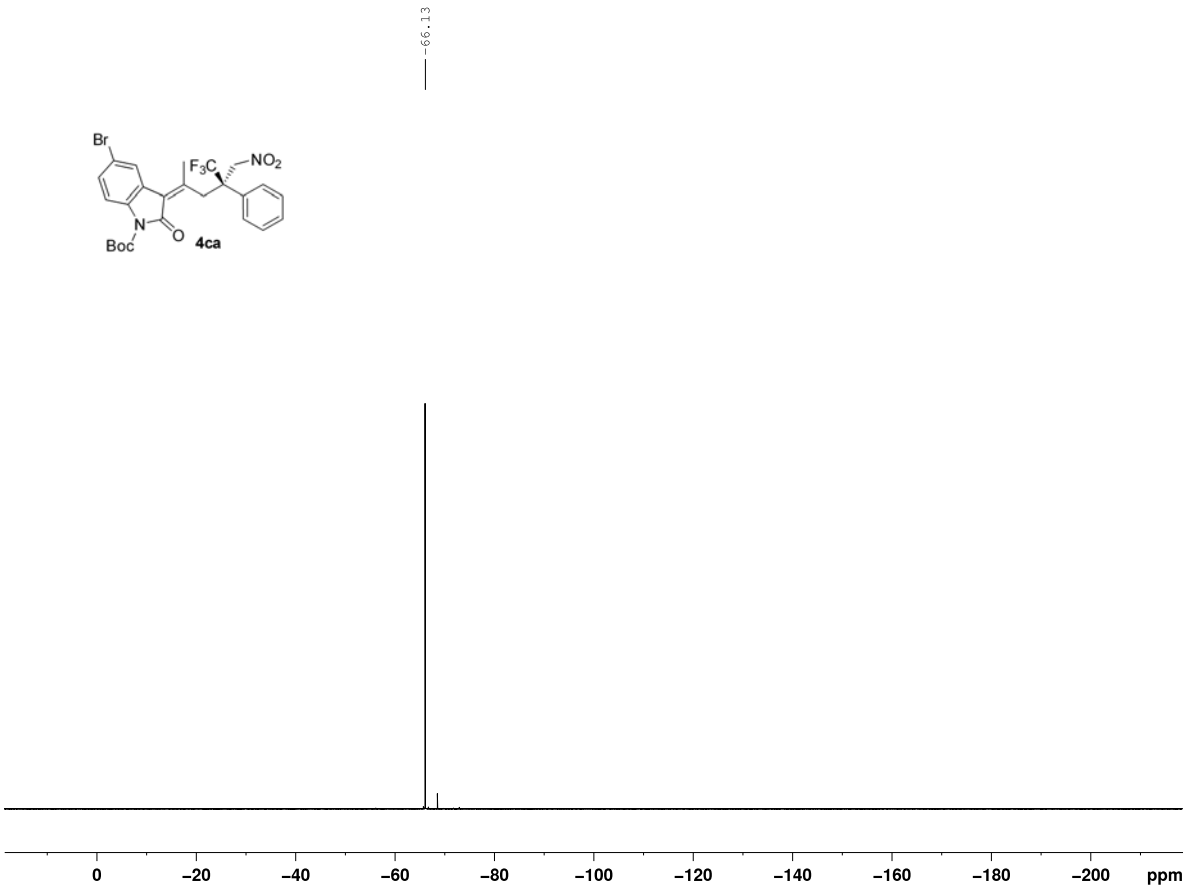

7.846
7.830
7.816
7.800
7.636
7.611
7.468
7.460
7.453
7.439
7.429
7.414
7.397
7.389
7.263
7.234
7.226
7.203
7.195
7.092
7.083
7.062
7.054
7.033
7.024
5.490
5.444
5.249
5.203
3.961
3.917
3.849
3.805
2.014
1.681
-0.000
F
F3C
NO2
N
Boc
O
4ba
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.04
2.06
3.08
1.05
1.09
1.00
1.09
1.02
1.05
3.00
9.04

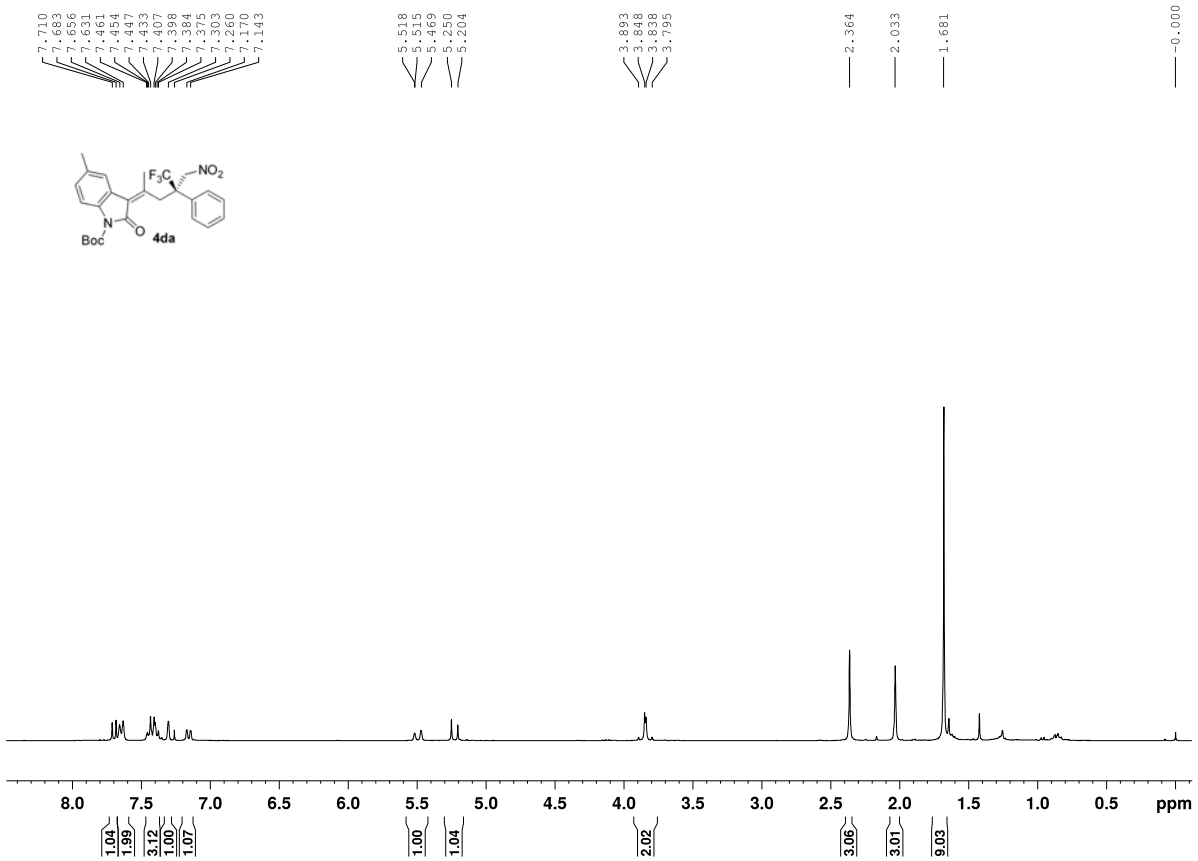

165.74
160.97
157.76
153.00
148.77
134.35
134.32
134.07
128.86
128.66
127.10
127.08
126.46
126.42
124.23
124.11
115.90
115.79
115.68
115.37
112.20
111.86
85.11
77.44
77.02
76.60
75.69
55.64
55.32
41.63
29.70
28.14
25.65
F
F3C
NO2
N
Boc
O
4ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

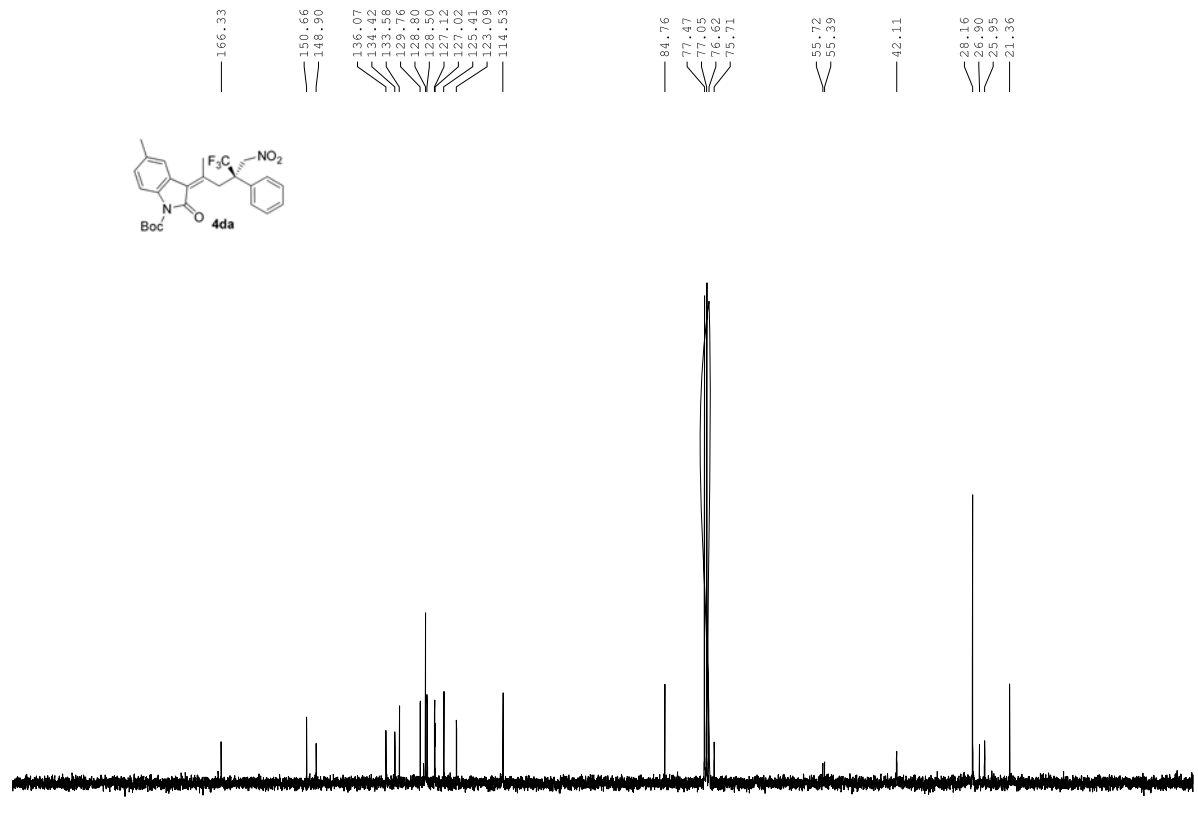

-66.07
-68.81
-117.84
F
F3C
NO2
N
Boc
O
4ba
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
3.14
0.04
1.00

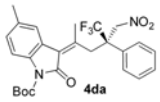

7.758
7.729
7.630
7.603
7.486
7.479
7.457
7.450
7.443
7.417
7.391
7.263
5.462
5.415
5.247
5.201
3.981
3.937
3.832
3.788
2.020
1.677
0.000
Br
F3C
NO2
N
Boc
O
4ca
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.06
3.02
4.08
1.01
1.03
1.00
1.03
3.03
9.06


165.29
153.30
148.64
137.19
134.01
131.85
128.87
128.68
127.39
127.09
125.90
124.77
117.14
116.24
85.29
77.44
77.02
76.60
75.68
55.93
55.60
55.28
41.57
28.12
25.87
Br
F3C
NO2
N
O
Boc
4ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-66.13
Br
F3C
NO2
N
O
Boc
4ca
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm


7.710
7.683
7.656
7.631
7.461
7.454
7.447
7.433
7.407
7.398
7.384
7.375
7.303
7.260
7.170
7.143
5.518
5.515
5.469
5.250
5.204
3.893
3.848
3.838
3.795
2.364
2.033
1.681
0.000
F3C
NO2
N
Boc
O
4da
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.04
1.99
3.12
1.00
1.07
1.00
1.04
2.02
3.06
3.01
9.03


166.33
150.66
148.90
136.07
134.42
133.58
129.76
128.80
128.50
127.12
127.02
125.41
123.09
114.53
84.76
77.47
77.05
76.62
75.71
55.72
55.39
42.11
28.16
26.90
25.95
21.36
F3C
NO2
N
Boc
O
4da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F3C
NO2
N
O
Boc

4da

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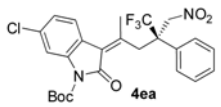
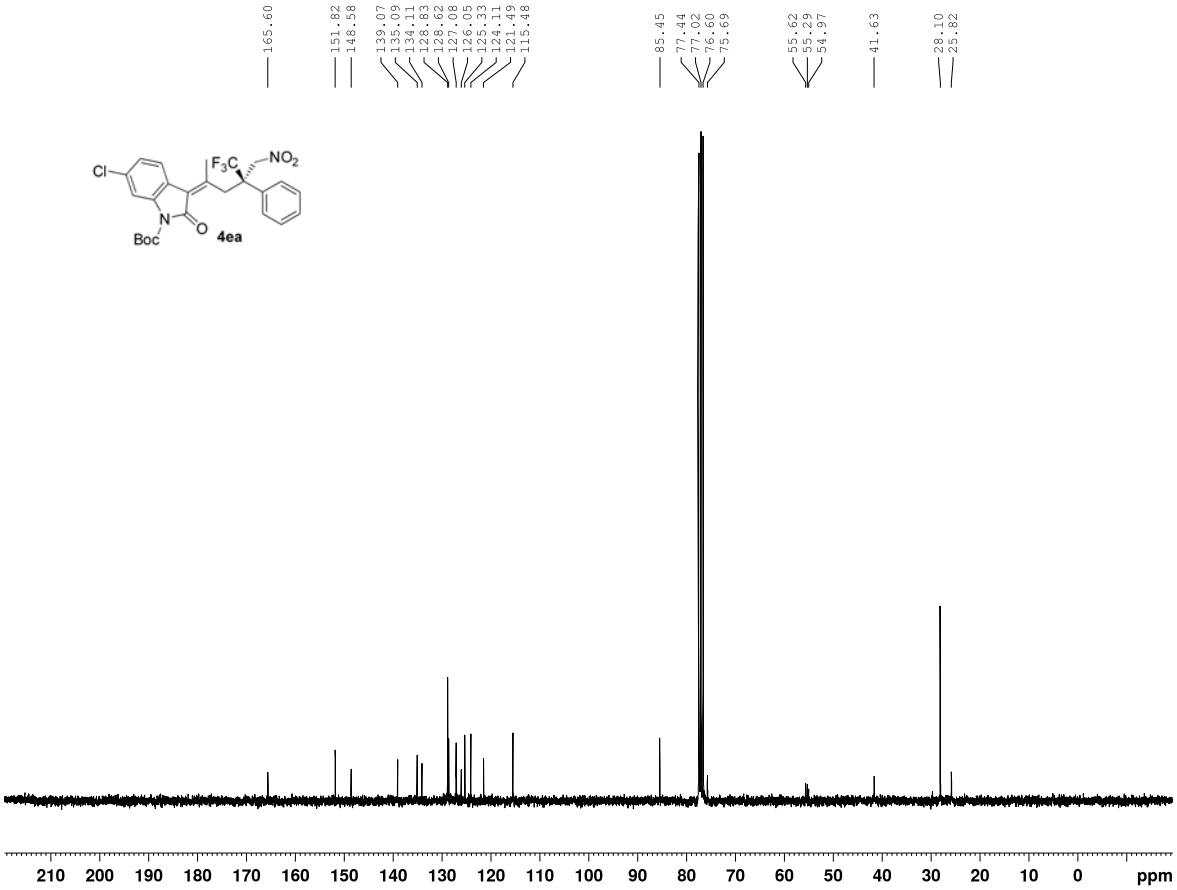
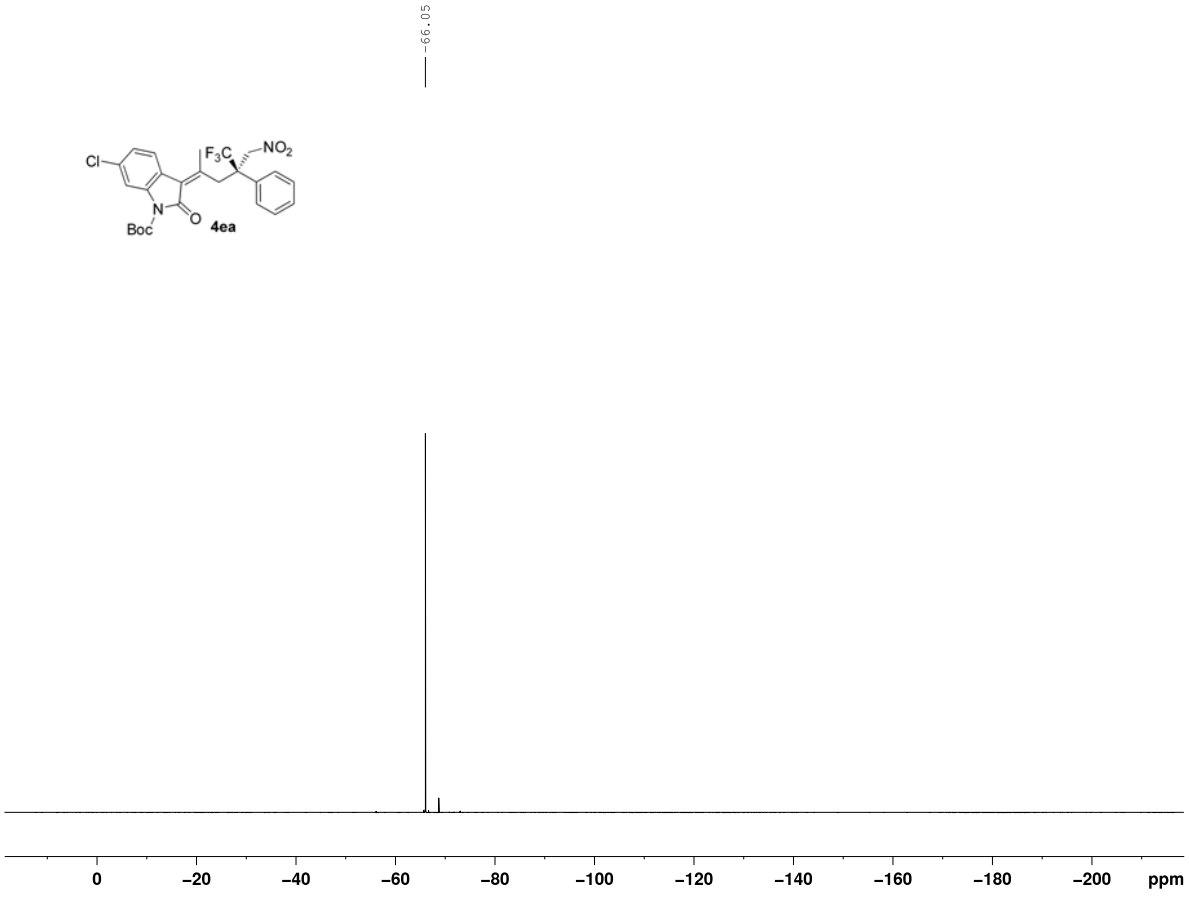
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

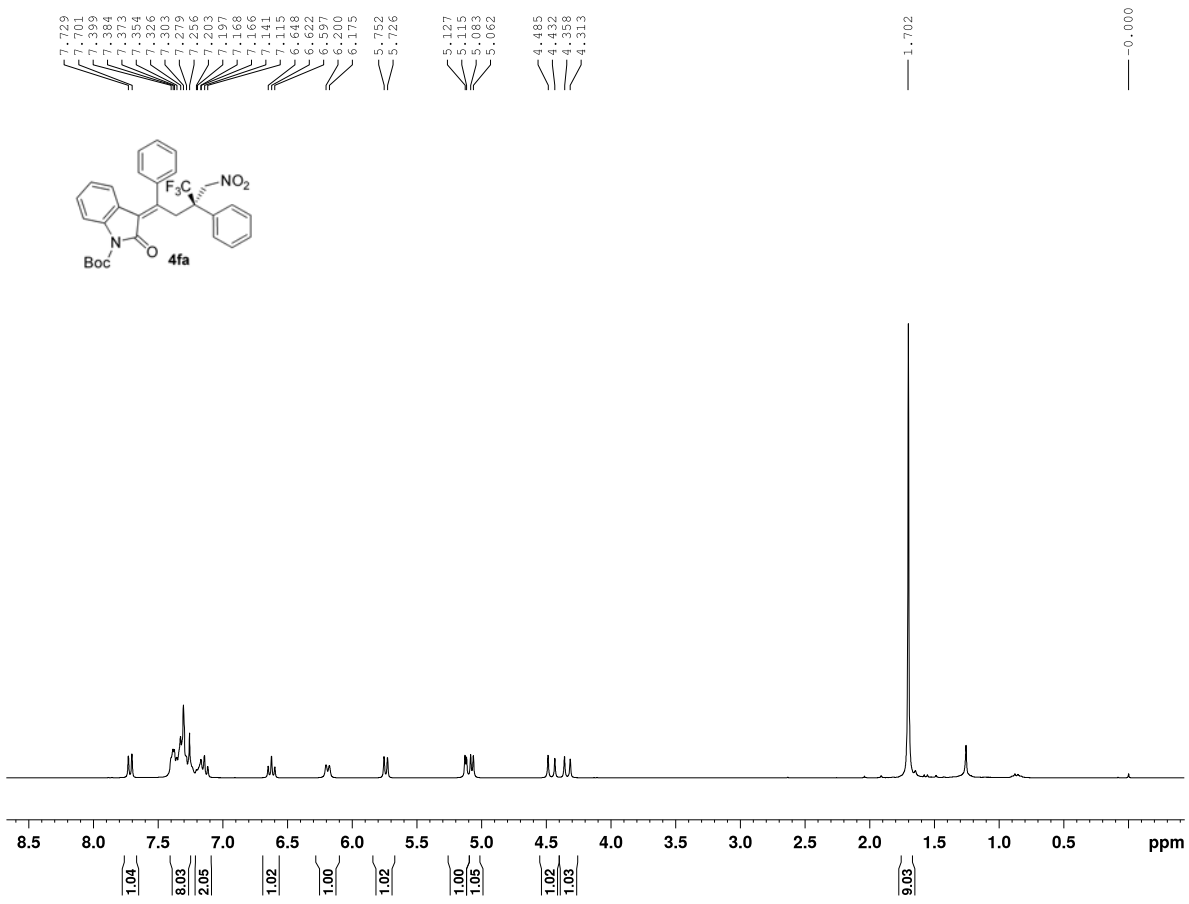

Cl
F3C
NO2
N
O
Boc

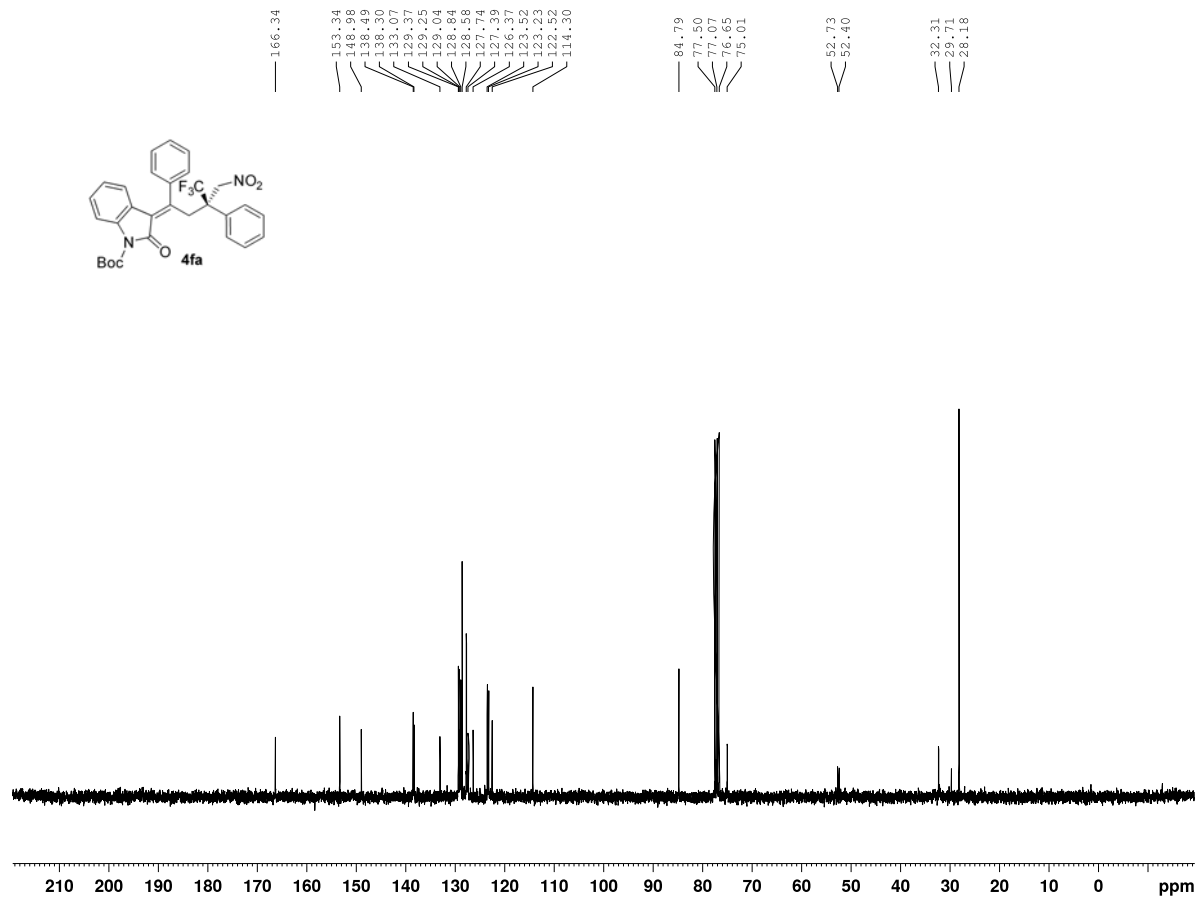
4ea

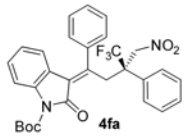
7.909
7.903
7.633
7.608
7.462
7.454
7.434
7.418
7.408
7.390
7.262
7.171
7.164
7.143
7.136
5.477
5.431
5.240
5.194
3.932
3.888
3.830
3.785
2.007
1.690
-0.000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
2.05
4.07
1.04
1.00
1.04
1.01
1.05
3.00
9.09


165.60
151.82
148.58
139.07
135.09
134.11
128.83
128.62
127.08
126.05
125.33
124.11
121.49
115.48
85.45
77.44
77.02
76.60
75.69
55.62
55.29
54.97
41.63
28.10
25.82
Cl
F3C
NO2
N
O
Boc
4ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-66.05
Cl
F3C
NO2
N
O
Boc
4ea
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

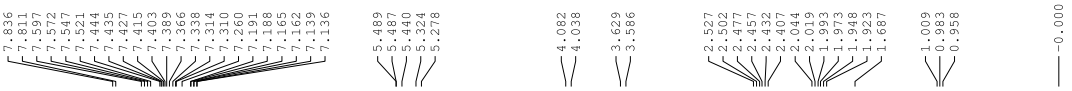

7.729
7.701
7.399
7.384
7.373
7.354
7.326
7.303
7.279
7.256
7.203
7.197
7.168
7.166
7.141
7.115
6.648
6.622
6.597
6.200
6.175
5.752
5.726
5.127
5.115
5.083
5.062
4.485
4.432
4.358
4.313
1.702
0.000
F3C
NO2
N
O
Boc
4fa
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.04
8.03
2.05
1.02
1.00
1.02
1.00
1.05
1.02
1.03
9.03

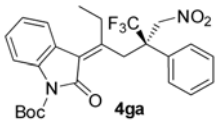

166.34
153.34
148.98
138.49
138.30
133.07
129.37
129.25
129.04
128.84
128.58
127.74
127.39
126.37
123.52
123.23
122.52
114.30
84.79
77.50
77.07
76.65
75.01
52.73
52.40
32.31
29.71
28.18
F3C
NO2
N
O
Boc
4fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F3C
NO2
N
O
Boc

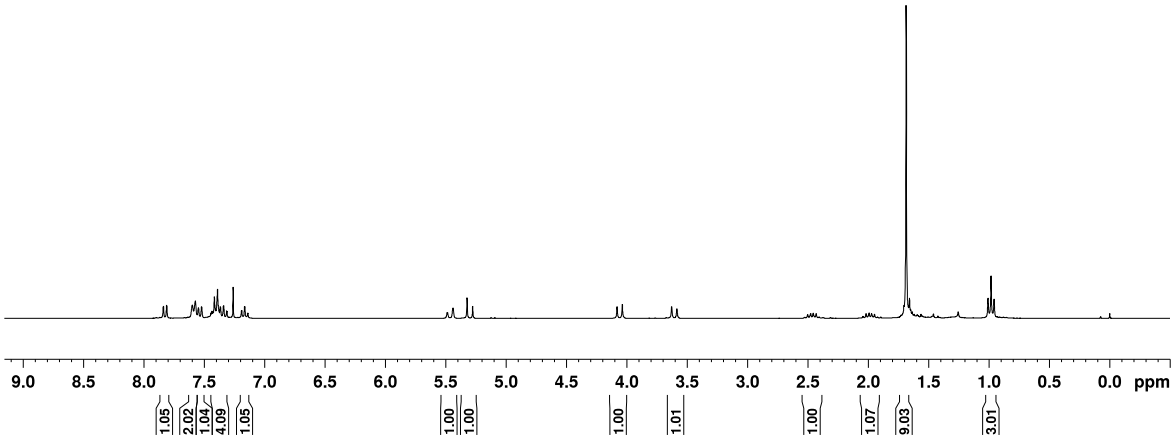
4fa

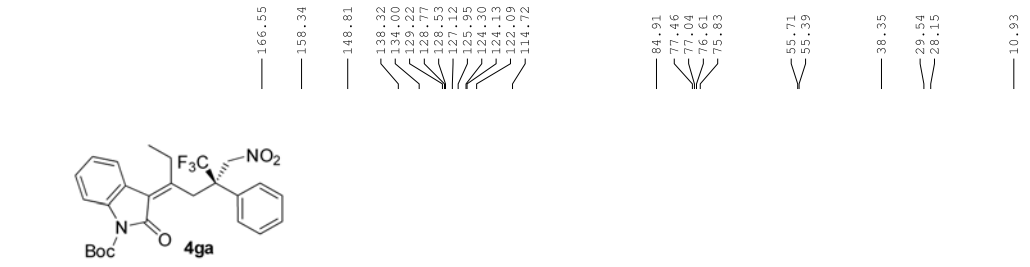
-70.84
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


7.836
7.811
7.597
7.572
7.547
7.521
7.444
7.435
7.427
7.415
7.403
7.389
7.366
7.338
7.314
7.310
7.260
7.191
7.188
7.165
7.162
7.139
7.136
5.489
5.487
5.440
5.324
5.278
4.082
4.038
3.629
3.586
2.527
2.502
2.477
2.457
2.432
2.407
2.044
2.019
1.993
1.973
1.948
1.923
1.687
1.009
0.983
0.958
-0.000

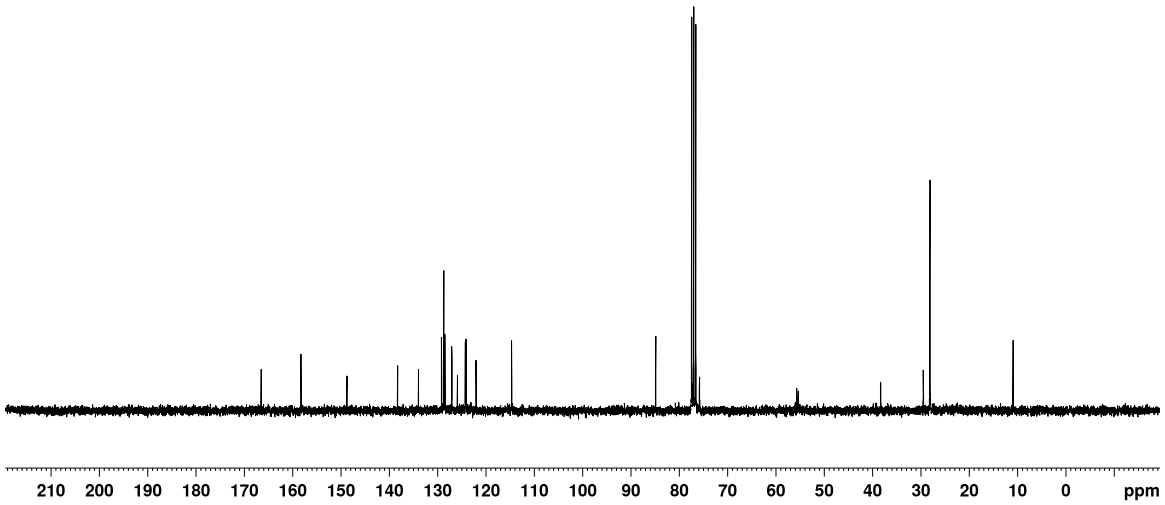

F3C
NO2
N
O
Boc

4ga

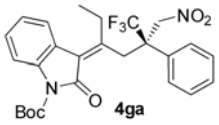

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.05
2.02
1.04
4.09
1.05
1.00
1.00
1.00
1.01
1.00
1.07
9.03
3.01

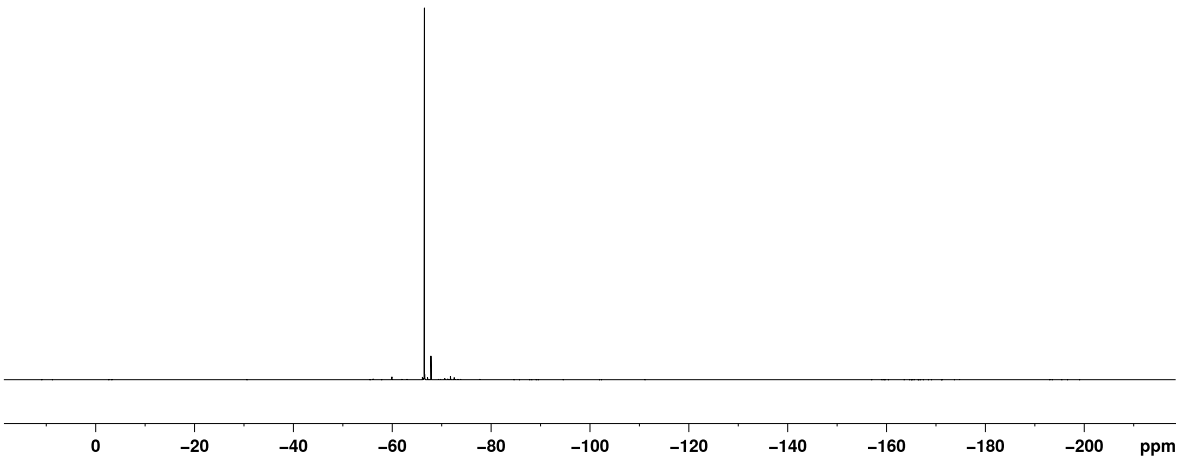

166.55
158.34
148.81
138.32
134.00
129.22
128.77
128.53
127.22
125.95
124.30
124.13
122.09
114.72
84.91
77.46
77.04
76.61
75.83
55.71
55.39
38.35
29.54
28.15
10.93

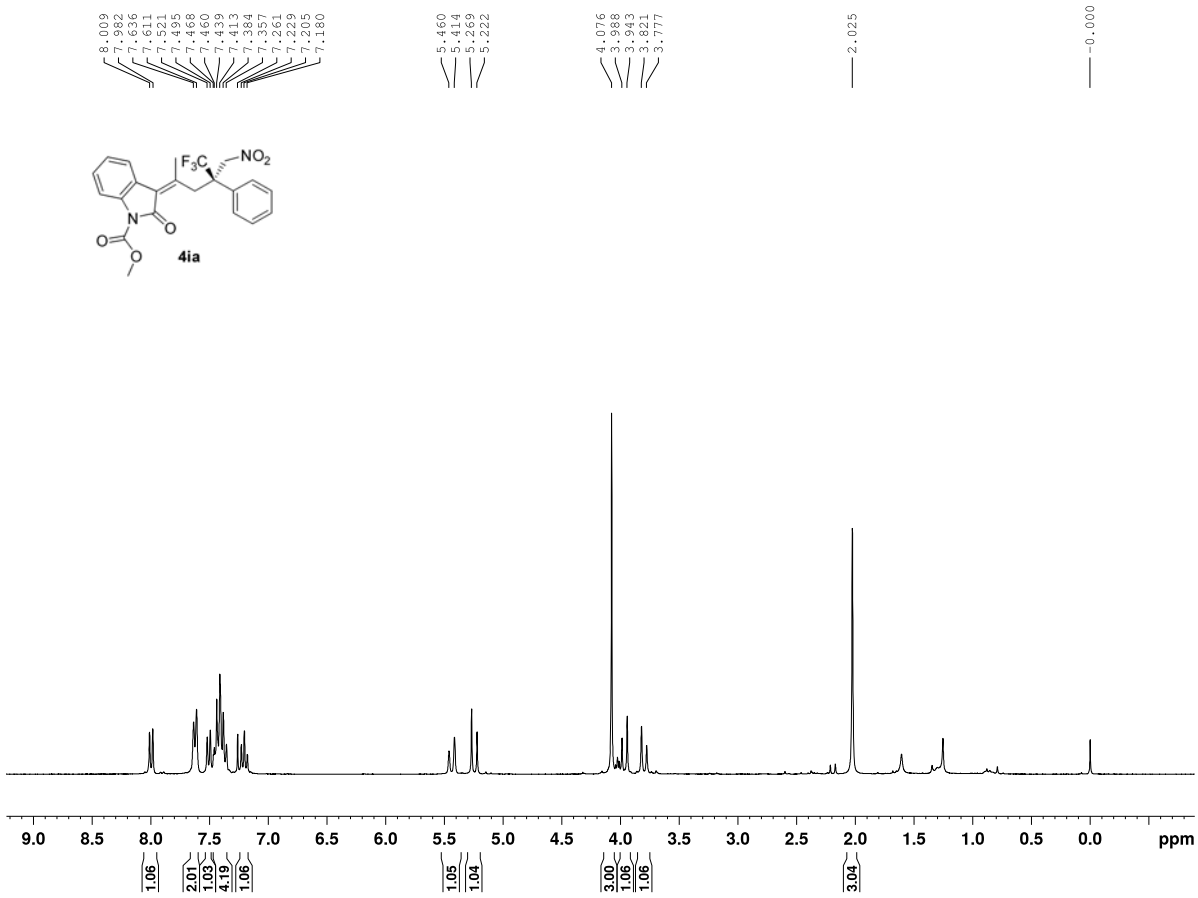
F3C
NO2
N
O
Boc
4ga

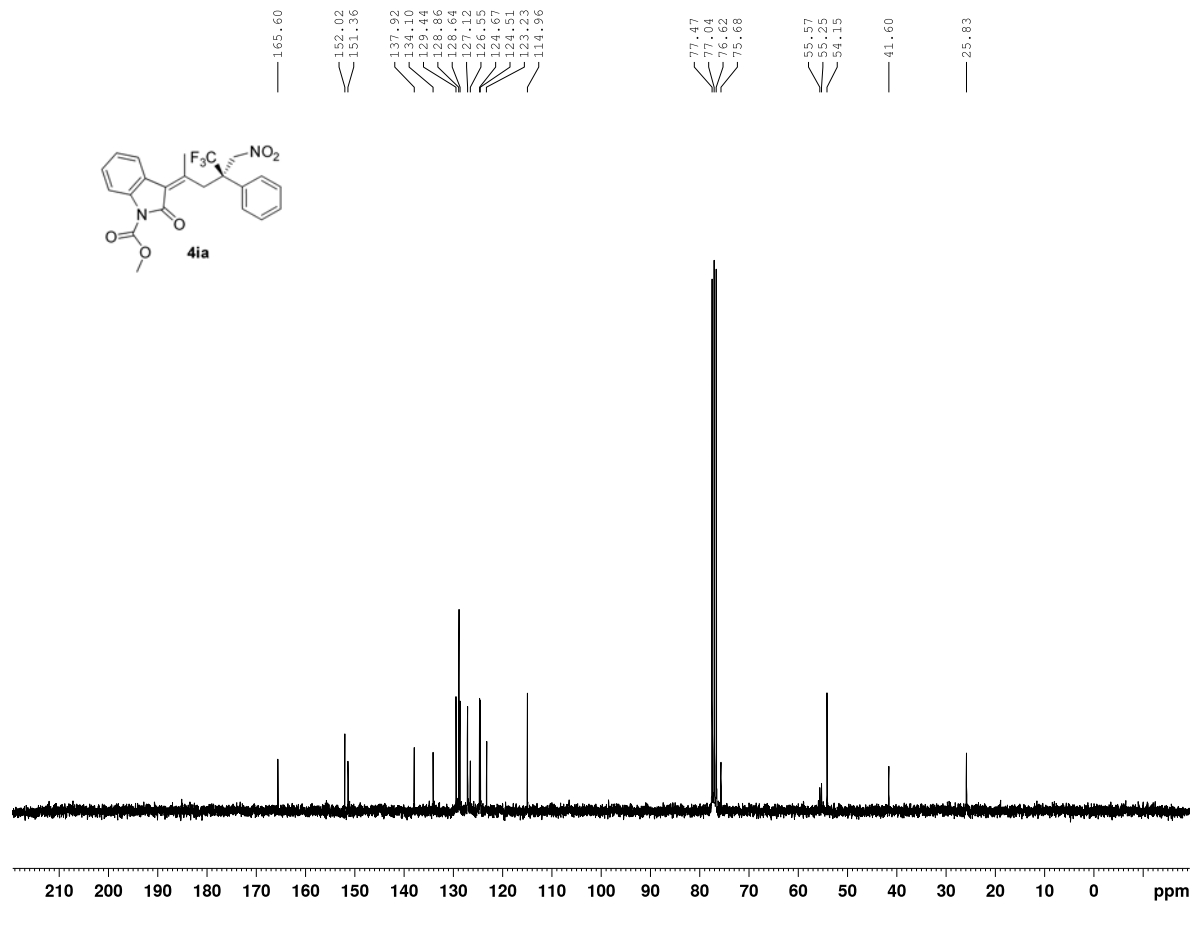

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

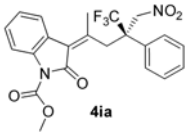
-66.51


F3C
NO2
N
O
Boc
4ga


0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 ppm

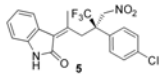

8.009
7.982
7.636
7.611
7.521
7.495
7.468
7.460
7.439
7.413
7.384
7.357
7.261
7.229
7.205
7.180
5.460
5.414
5.259
5.222
4.076
3.988
3.943
3.821
3.777
2.025
0.000
F3C
NO2
N
O
O
O
4ia
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.06
2.01
1.03
4.19
1.06
1.05
1.04
3.00
1.06
1.06
3.04


165.60
152.02
151.36
137.92
134.10
129.44
128.86
128.64
127.12
126.55
124.67
124.51
123.23
114.96
77.47
77.04
76.62
75.68
55.57
55.25
54.15
41.60
25.83
F3C
NO2
N
O
O
O
4ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



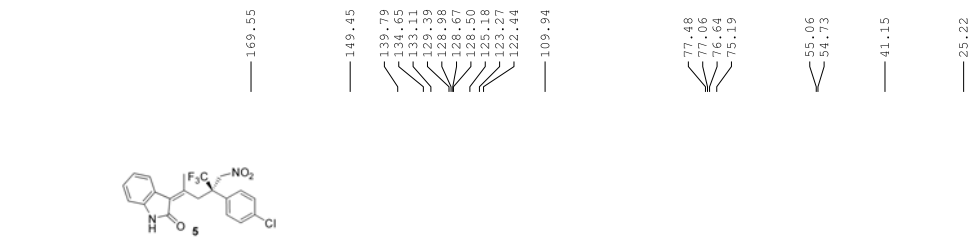
4ia

-66.03
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

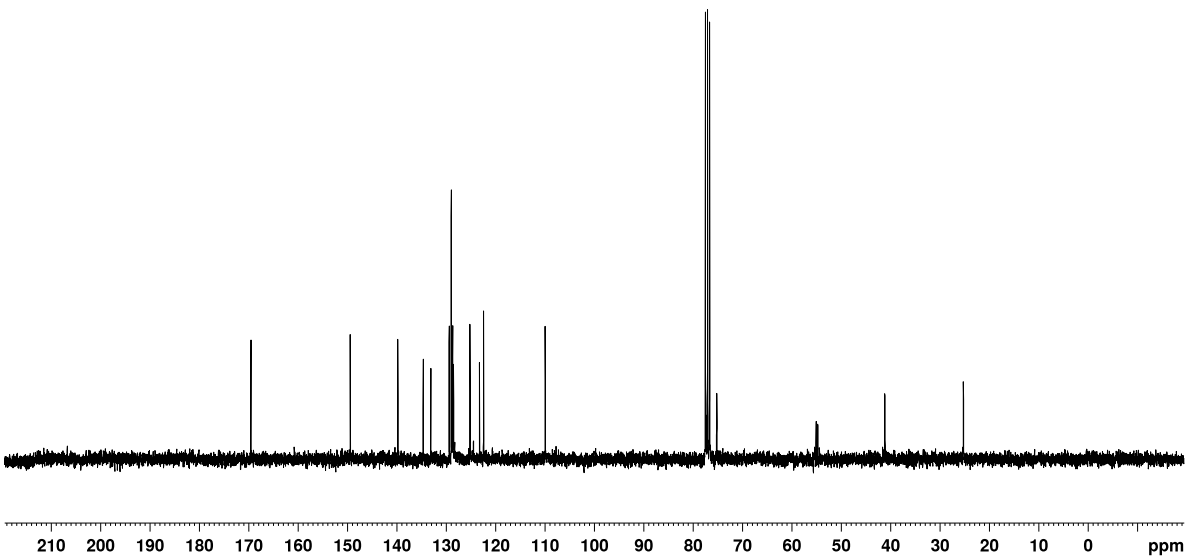


5

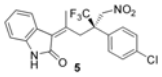
9.295
7.612
7.584
7.449
7.422
7.393
7.307
7.282
7.252
7.080
7.055
7.029
6.919
6.894
5.500
5.454
5.282
5.235
3.958
3.914
3.832
3.789
2.046
-0.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.05
3.05
1.02
1.05
1.04
1.01
1.02
1.01
1.00
3.04

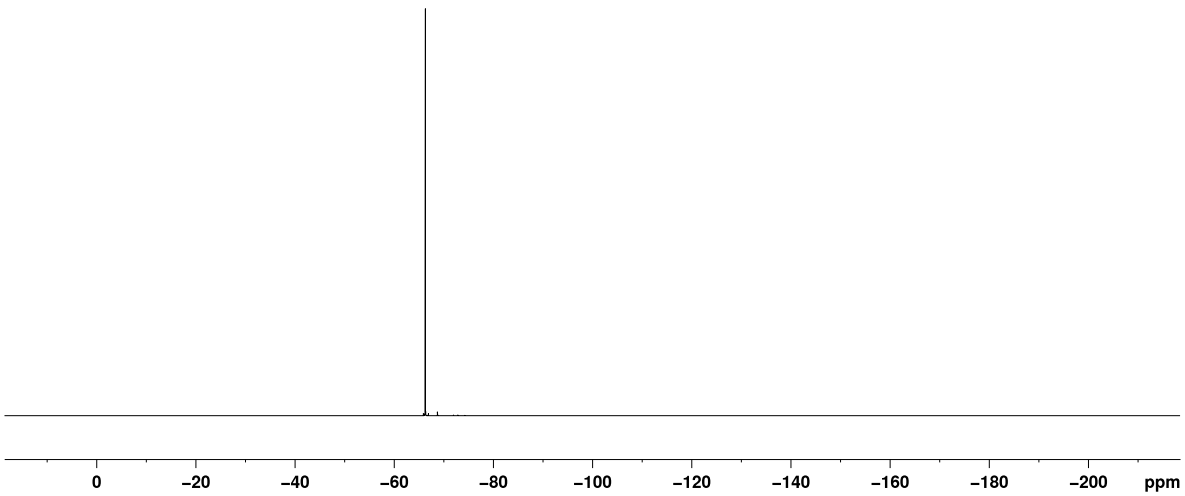

169.55
149.45
139.79
134.65
133.11
129.39
128.98
128.67
128.50
125.18
123.27
122.44
109.94
77.48
77.06
76.64
75.19
55.06
54.73
41.15
25.22

F3C
NO2
N
H
O
5
Cl


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

-66.29


F3C
NO2
N
H
O
5
Cl


0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
ppm