Radical 1,2,3-Tricarbofunctionalization of *α*-Vinyl-*β*-Ketoesters Enabled by Carbon Shift from All-carbon Quaternary Center

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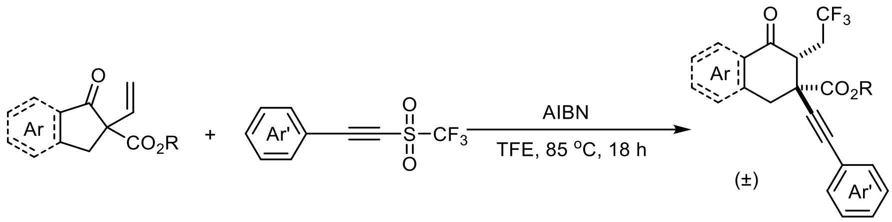
Materials and methods

All reactions were carried out under an atmosphere of nitrogen in glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Inert PureSolv MD5. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. Melting points were measured on a Melt-Temp apparatus and were uncorrected. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for ^{1}H NMR spectra are reported relative to TMS as an internal standard (0 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to $CDCl_3$ as an internal standard (77.0 ppm) and are reported in terms of chemical shift (ppm). IR spectra were obtained with a Vertex70 spectrophotometer. GC-MS data were recorded on Thermo ISQ QD. HRMS data were recorded on Bruker Impact II UHR-TOF, Waters Micromass GCT Premier, or Thermo Fisher Scientific LTQ FT Ultra.

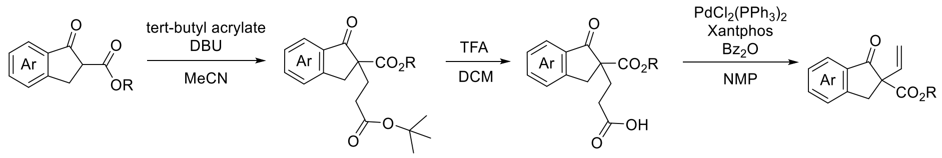
General procedure



General procedure: In a flame-dried sealed tube, *α*-vinyl-*β*-ketoester (0.2 mmol, 1.0 equiv), AIBN (0.06 mmol, 30 mol %) and an alkynyl triflone (0.3 mmol, 1.5 equiv) were dissolved in TFE (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 85 ^{o}C (oil bath) for 9 h. Then, another addition of the alkynyl triflone (0.3 mmol, 1.5 equiv) and AIBN (0.06 mmol, 30 mol %) was performed and the mixture was stirred at the same temperature for additional 9 h. After the complete consumption of the *α*-vinyl-*β*-ketoester as monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether / ethyl acetate) to afford the corresponding product.

A gram scale reaction: In a flame-dried sealed tube, *α*-vinyl-*β*-ketoester **1a** (972 mg, 4.5 mmol, 1.0 equiv), AIBN (221 mg, 1.35 mmol, 30 mol %) and phenylethynyl triflone **2b** (1.6 g, 6.75 mmol, 1.5 equiv) were dissolved in TFE (67.5 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 85 ^{o}C (oil bath) for 9 h. Then, another addition of phenylethynyl triflone **2b** (1.6 g, 6.75 mmol, 1.5 equiv) and AIBN (221 mg, 1.35 mmol, 30 mol %) was performed and the mixture was stirred at the same temperature for 9 h. After the complete consumption of **1a** as monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether / ethyl acetate 10:1) to afford product **4a** (1.2 g, 69% yield, dr > 20:1).

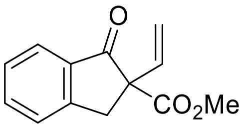
Synthesis of *α*-vinyl-*β*-ketoesters



S1 **S2** **S3** **1**

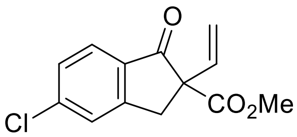
To a MeCN (10 mL) solution of ketyl ester **S1** (5 mmol, 1.0 equiv) at rt were added tert-butyl acrylate (5.1 mmol, 1.02 equiv) and DBU (0.25 mmol, 5 mol %) sequentially. The reaction was stirred at rt for 8 h, as monitored by TLC for completion. Concentration of the solvent under reduced pressure would afford the crude material **S2**. To a DCM (5 mL) solution of the crude material **S2** was added trifluoroacetic acid (5 mL) and the mixture was stirred at rt for 3 h. After removal of the remaining trifluoroacetic acid, the crude material was purified by flash chromatography to yield **S3**. In a flame-dried Schlenk tube, $PdCl_2(PPh_3)_2$ (0.01 mmol, 1 mol %), Xantphos (0.012 mmol, 1.2 mol %), **S3** (1 mmol, 1 equiv) and benzoic anhydride (1.2 mmol, 1.2 equiv) were dissolved in NMP (1 mL) under a nitrogen atmosphere, and the mixture was stirred at 132 °C (oil bath) for 3 h. After cooling to ambient temperature, Et_3N (0.3 mL) was added, and the mixture was purified by flash column chromatography on silica gel to afford the corresponding *α*-vinyl-*β*-ketoester **1**.[1]

Characterization data for *α*-vinyl-*β*-ketoesters



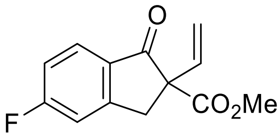
1a

Compound **1a** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 65.4 – 66.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz,1H), 6.39 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.28 – 5.17 (m, 2H), 3.83 (d, *J* = 17.3 Hz, 1H), 3.73 (s, 3H), 3.39 (d, *J* = 17.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 170.6, 152.5, 135.5, 135.0, 134.1, 127.9, 126.3, 125.2, 116.2, 63.3, 53.1, 36.8. IR (film): *ν* 1735, 1711 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{13}H_{12}O_3Na]^+$ ($[M+Na]^+$): 239.0679, found: 239.0679.



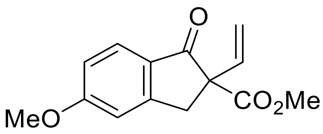
1b

Compound **1b** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 73.9 – 74.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.51 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 6.38 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.33 – 5.16 (m, 2H), 3.81 (d, *J* = 17.4 Hz, 1H), 3.75 (s, 3H), 3.36 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 170.2, 153.9, 142.1, 134.7, 132.6, 128.8, 126.6, 126.3, 116.5, 63.5, 53.2, 36.4. IR (film): *ν* 1742, 1717 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{13}H_{11}ClO_3Na]^+$ ($[M+Na]^+$): 273.0289, found: 273.0290.



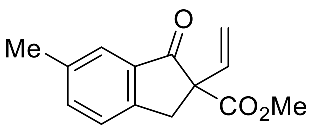
1c

Compound **1c** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 76.0 – 76.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.20 – 7.08 (m, 2H), 6.38 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.31 – 5.18 (m, 2H), 3.82 (d, *J* = 17.5 Hz, 1H), 3.75 (s, 3H), 3.37 (d, *J* = 17.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.18 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 170.3, 167.6 (d, *J* = 257.8 Hz), 155.4 (d, *J* = 10.4 Hz), 134.8, 130.5 (d, *J* = 1.7 Hz), 127.6 (d, *J* = 10.7 Hz), 116.4 (d, *J* = 23.9 Hz), 116.4, 113.1 (d, *J* = 22.7 Hz), 63.6, 53.2, 36.6. IR (film): *ν* 1744, 1717 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{13}H_{11}FO_3Na]^+$ ($[M+Na]^+$): 257.0584, found: 257.0585.



1d

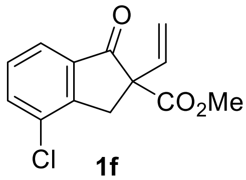
Compound **1d** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 1H), 6.96 – 6.90 (m, 2H), 6.40 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.29 – 5.16 (m, 2H), 3.90 (s, 3H), 3.80 – 3.72 (m, 4H), 3.33 (d, *J* = 17.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 170.9, 166.0, 155.6, 135.4, 127.2, 126.9, 116.0, 115.9, 109.4, 63.5, 55.8, 53.0, 36.7. IR (film): ν 1735, 1701 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{14}H_{14}O_4Na]^+$ ($[M+Na]^+$): 269.0784, found: 269.0785.



1e

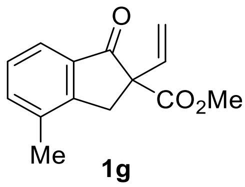
Compound **1e** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 44.6 – 45.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 6.39 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.29 – 5.16 (m, 2H), 3.76 (d, *J* = 17.2 Hz, 1H), 3.73 (s, 3H), 3.33 (d, *J* = 17.1 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 200.0, 170.8, 149.9, 138.0, 136.8, 135.1, 134.3, 126.0, 125.0, 116.1, 63.6, 53.0, 36.5, 21.0. IR (film): *v* 1744, 1715 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{14}H_{14}O_3Na]^+$ ($[M+Na]^+$): 253.0835, found: 253.0835.



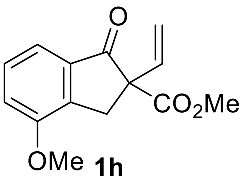
1f

Compound **1f** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 79.5 – 80.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.29 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.32 – 5.08 (m, 2H), 3.75 – 3.62 (m, 4H), 3.29 (d, *J* = 17.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 170.1, 150.0, 136.1, 135.1, 134.4, 132.6, 129.5, 123.4, 116.6, 63.2, 53.2, 35.8. IR (film): *v* 1748, 1719 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{13}H_{11}ClO_3Na]^+$ ($[M+Na]^+$): 273.0289, found: 273.0289.



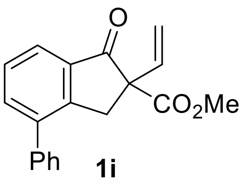
1g

Compound **1g** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 67.8 – 68.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.40 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.29 – 5.18 (m, 2H), 3.74 (s, 3H), 3.71 (d, *J* = 17.4 Hz, 1H), 3.26 (d, *J* = 17.3 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 170.8, 151.4, 136.0, 135.6, 135.2, 134.0, 128.2, 122.6, 116.2, 63.2, 53.1, 35.9, 17.8. IR (film): *v* 1743, 1713 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{14}H_{14}O_3Na]^+$ ($[M+Na]^+$): 253.0835, found: 253.0836.



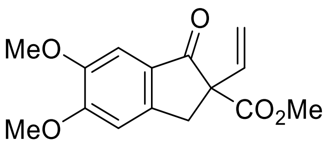
1h

Compound **1h** was purified with silica gel chromatography (PE/EA = 5:1) as a white solid. Mp 61.1 – 61.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.08 (dd, *J* = 6.4, 2.4 Hz, 1H), 6.38 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.28 – 5.19 (m, 2H), 3.92 (s, 3H), 3.72 (s, 3H), 3.68 (d, *J* = 17.7 Hz, 1H), 3.31 (d, *J* = 17.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 170.7, 156.7, 141.4, 135.6, 135.0, 129.5, 116.5, 116.2, 115.6, 63.0, 55.5, 53.0, 33.7. IR (film): *v* 1744, 1716 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{14}H_{14}O_4Na]^+$ ($[M+Na]^+$): 269.0784, found: 269.0784.



1i

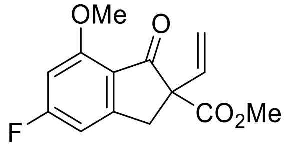
Compound **1i** was purified with silica gel chromatography (PE/EA = 10:1) as a white solid. Mp 79.0 – 79.8 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 6.7 Hz, 1H), 7.52 – 7.45 (m, 5H), 7.45 – 7.39 (m, 1H), 6.36 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.28 – 5.11 (m, 2H), 3.89 (d, *J* = 17.4 Hz, 1H), 3.74 (s, 3H), 3.36 (d, *J* = 17.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 170.6, 149.9, 140.2, 138.7, 135.7, 134.9, 134.7, 128.8, 128.6, 128.5, 128.0, 124.2, 116.4, 63.5, 53.1, 36.8. IR (film): *v* 1744, 1716 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{19}H_{16}O_3Na]^+$ ($[M+Na]^+$): 315.0992, found: 315.0992.



1j

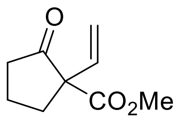
Compound **1j** was purified with silica gel chromatography (PE/EA = 3:1) as a white solid. Mp 96.0 – 96.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.95 (s, 1H), 6.40 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.27 – 5.17 (m, 2H), 3.99 (s, 3H), 3.90 (s, 3H), 3.76 – 3.69

(m, 4H), 3.30 (d, *J* = 17.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 170.9, 156.1, 149.8, 148.1, 135.4, 126.7, 115.8, 107.2, 105.1, 63.5, 56.3, 56.1, 52.9, 36.6. IR (film): *v* 1735, 1701 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{15}H_{16}O_5Na]^+$ ($[M+Na]^+$): 299.0890, found: 299.0893.



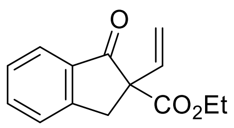
1k

Compound **1k** was purified with silica gel chromatography (PE/EA = 5:1) as a white solid. Note: compound **1k** is synthesized from 5,7-difluoro-1-indanone. Mp 53.4 – 54.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.70 (m, 1H), 6.58 – 6.50 (m, 1H), 6.39 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.35 – 5.09 (m, 2H), 3.93 (s, 3H), 3.79 – 3.69 (m, 4H), 3.30 (d, *J* = 17.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.1. (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 170.5, 168.9 (d, *J* = 257.5 Hz), 160.7 (d, *J* = 12.4 Hz), 157.4 (d, *J* = 12.5 Hz), 135.1, 118.9, 116.0, 105.0 (d, *J* = 22.9 Hz), 98.5 (d, *J* = 27.3 Hz), 63.8, 56.2, 53.1, 36.3. IR (film): *v* 1741, 1712 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{14}H_{13}FO_4Na]^+$ ($[M+Na]^+$): 287.0690, found: 287.0690.



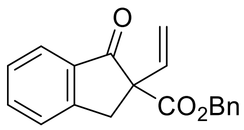
1l

Compound **1l** was purified with silica gel chromatography (PE/EA = 10:1) as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.34 – 5.14 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.66 – 2.52 (m, 1H), 2.48 – 2.27 (m, 2H), 2.26 – 2.14 (m, 1H), 2.11 – 1.87 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). The data matches previously reported values.[1]



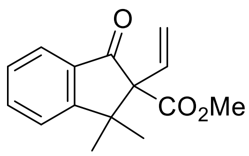
1m

Compound **1m** was purified with silica gel chromatography (PE/EA = 10:1) as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 6.40 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.51 – 5.02 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.82 (d, *J* = 17.2 Hz, 1H), 3.38 (d, *J* = 17.2 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 170.2, 152.6, 135.4, 135.1, 134.2, 127.9, 126.3, 125.2, 116.1, 63.3, 62.0, 36.8, 14.0. The data matches previously reported values.[2]



1n

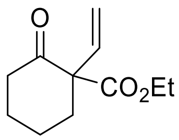
Compound **1n** was purified with silica gel chromatography (PE/EA = 10:1) as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.24 (m, 5H), 6.42 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.29 – 5.12 (m, 4H), 3.80 (d, *J* = 17.2 Hz, 1H), 3.38 (d, *J* = 17.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 170.0, 152.5, 135.5, 135.5, 134.9, 134.2, 128.5, 128.2, 128.0, 127.8, 126.3, 125.2, 116.4, 67.4, 63.4, 36.8. IR (film): *v* 1734, 1717 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{19}H_{16}O_3Na]^+$ ($[M+Na]^+$): 315.0992, found: 315.0992.



1o

Compound **1o** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5

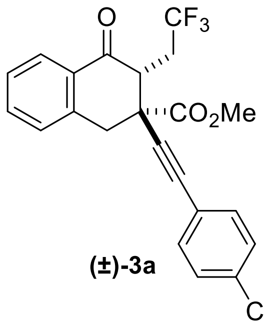
Hz, 1H), 7.48 – 7.38 (m, 2H), 6.21 (dd, *J* = 17.8, 11.1 Hz, 1H), 5.30 (d, *J* = 11.1 Hz, 1H), 5.17 (d, *J* = 17.8 Hz, 1H), 3.69 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.8, 170.9, 160.8, 135.7, 134.6, 133.8, 128.0, 124.3, 123.4, 118.2, 70.2, 52.2, 47.4, 27.7, 27.2. MS (EI): 244.2 [M^+].



1p

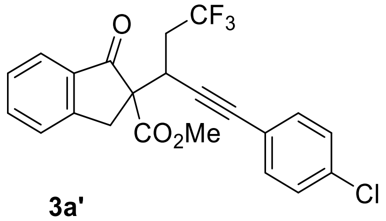
Compound **1p** was purified with silica gel chromatography (PE/EA = 10:1) as a pale-yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (dd, *J* = 17.7, 10.8 Hz, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 5.05 (d, *J* = 17.7 Hz, 1H), 4.25 – 4.06 (m, 2H), 2.59 – 2.50 (m, 1H), 2.46 – 2.31 (m, 2H), 1.98 – 1.89 (m, 1H), 1.80 – 1.54 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.1, 135.7, 116.4, 63.3, 61.6, 40.8, 35.6, 27.2, 22.4, 14.0. The spectra data matches previously reported values.[3]

Characterization data for products



(±)-3a

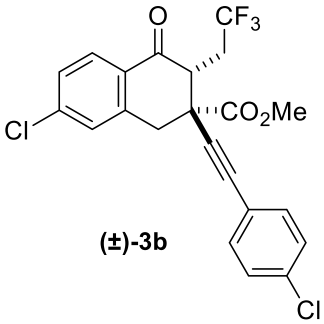
Following the general procedure, **(±)-3a** was obtained as a pale-yellow solid (55 mg, 65% yield, dr > 20:1, R$_f$ = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 165.7 – 166.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.42 – 7.24 (m, 6H), 3.78 (d, *J* = 16.6 Hz, 1H), 3.70 – 3.55 (m, 4H), 3.55 – 3.41 (m, 1H), 3.10 – 2.99 (m, 1H), 2.73 – 2.56 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.73 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 170.1, 138.1, 134.2, 131.8, 131.1, 128.9, 128.6, 128.4, 127.8, 127.8, 126.9 (q, *J* = 276.5 Hz), 121.8, 86.1, 85.7, 53.4, 49.8, 49.6 (q, *J* = 1.7 Hz), 41.1, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1733, 1695 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{16}ClF_3O_3Na]^+$ ($[M+Na]^+$): 443.0632, found: 443.0632.



3a'

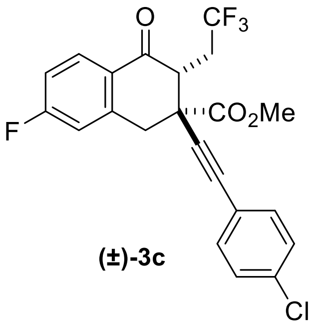
Only one isomer was isolated as pure compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.06 (dd, *J* = 11.0, 2.4 Hz, 1H), 3.79 (d, *J* = 17.1 Hz, 1H), 3.74 (s, 3H), 3.41 (d, *J* = 17.1 Hz, 1H), 2.68 – 2.38 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.08 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 168.9, 153.6, 135.8, 134.8, 134.3, 132.6, 128.3, 128.0, 126.3, 126.0 (q, *J* = 277.6

Hz), 125.1, 120.6, 86.1, 83.2, 63.2, 53.3, 35.8 (q, J = 28.7 Hz), 33.7, 31.1 (q, J = 2.8 Hz). IR (film): ν 1745, 1717 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{22}H_{16}ClF_3O_3Na]^+$ ($[M+Na]^+$): 443.0632, found: 443.0631.



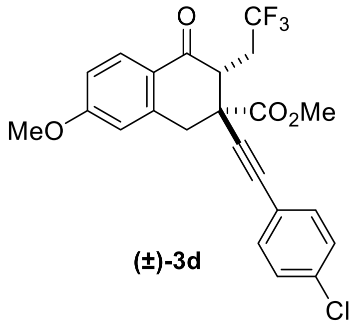
(±)-3b

Following the general procedure, **(±)-3b** was obtained as a pale-yellow solid (66 mg, 73% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 157.6 – 158.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.43 – 7.21 (m, 6H), 3.73 (d, J = 16.9 Hz, 1H), 3.64 (s, 3H), 3.61 (d, J = 16.9 Hz, 1H), 3.55 – 3.35 (m, 1H), 3.07 – 3.01 (m, 1H), 2.73 – 2.52 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.75 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 169.6, 140.6, 139.5, 135.2, 133.1, 129.5 (q, J = 1.4 Hz), 128.8, 128.5, 128.4, 126.8 (q, J = 276.5 Hz), 120.1, 86.6, 84.8, 53.6, 49.6, 49.4 (q, J = 1.9 Hz), 40.6, 31.8 (q, J = 29.8 Hz). IR (film): ν 1735, 1701 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{22}H_{15}Cl_2F_3O_3Na]^+$ ($[M+Na]^+$): 477.0243, found: 477.0240.



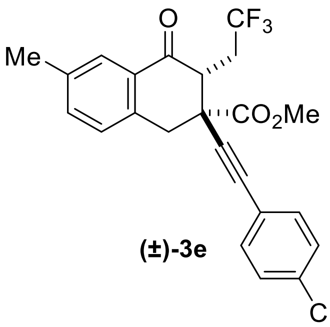
(±)-3c

Following the general procedure, **(±)-3c** was obtained as a pale-yellow solid (58 mg, 66% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 174.8 – 175.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.7, 5.9 Hz, 1H), 7.41 – 7.29 (m, 4H), 7.10 – 7.02 (m, 1H), 6.98 – 6.92 (m, 1H), 3.76 (d, J = 16.8 Hz, 1H), 3.68 – 3.57 (m, 4H), 3.55 – 3.39 (m, 1H), 3.07 – 3.01 (m, 1H), 2.72 – 2.56 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.78 (s, 3F), -102.91 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 169.6, 166.1 (d, J = 257.0 Hz), 141.0 (d, J = 9.3 Hz), 135.2, 133.1, 131.1 (d, J = 9.9 Hz), 128.8, 127.7 (d, J = 2.7 Hz), 126.8 (q, J = 276.5 Hz), 120.1, 115.5 (d, J = 46.2 Hz), 115.3 (d, J = 46.3 Hz), 86.7, 84.8, 53.5, 49.6, 49.3 (q, J = 2.1 Hz), 40.8, 31.7 (q, J = 29.7 Hz). IR (film): v 1734, 1696 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{22}H_{15}ClF_4O_3Na]^+$ ($[M+Na]^+$): 461.0538, found: 461.0536.



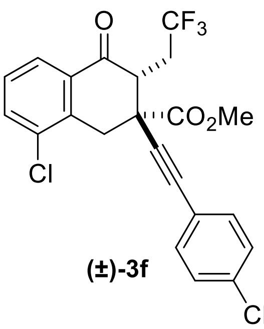
(±)-3d

Following the general procedure, **(±)-3d** was obtained as a pale-yellow solid (54 mg, 60% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 5:1)). Mp 143.7 – 144.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 1H), 7.38 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 6.87 (dd, J = 8.8, 2.4 Hz, 1H), 6.72 – 6.67 (m, 1H), 3.87 (s, 3H), 3.73 (d, J = 16.6 Hz, 1H), 3.66 – 3.55 (m, 4H), 3.54 – 3.40 (m, 1H), 3.06 – 2.97 (m, 1H), 2.71 – 2.55 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.73 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 169.8, 164.2, 140.5, 135.0, 133.1, 130.4, 128.8, 127.0 (q, J = 276.4 Hz), 124.5, 120.3, 114.0, 112.8, 87.2, 84.4, 55.5, 53.4, 49.7, 49.1 (q, J = 2.2 Hz), 41.2, 31.8 (q, J = 29.5 Hz). IR (film): v 1740, 1685 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{23}H_{18}ClF_3O_4Na]^+$ ($[M+Na]^+$): 473.0738, found: 473.0740.



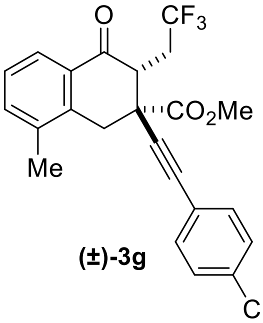
(±)-3e

Following the general procedure, **(±)-3e** was obtained as a pale-yellow solid (49 mg, 57% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 160.9 – 161.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.45 – 7.28 (m, 5H), 7.15 (d, *J* = 7.8 Hz, 1H), 3.73 (d, *J* = 16.6 Hz, 1H), 3.63 – 3.55 (m, 4H), 3.54 – 3.39 (m, 1H), 3.06 – 2.99 (m, 1H), 2.70 – 2.52 (m, 1H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.73 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 170.0, 137.7, 135.2, 135.0, 133.1, 130.8, 128.8, 128.5, 127.9, 126.9 (q, *J* = 276.5 Hz), 120.3, 87.2, 84.4, 53.4, 49.9, 49.5 (q, *J* = 1.7 Hz), 40.7, 31.9 (q, *J* = 29.6 Hz), 21.0. IR (film): *v* 1735, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{18}ClF_3O_3Na]^+$ ($[M+Na]^+$): 457.0789, found: 457.0789.



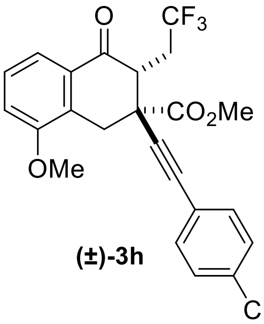
(±)-3f

Following the general procedure, **(±)-3f** was obtained as a pale-yellow solid (51 mg, 56% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 139.1 – 140.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.67 – 7.57 (m, 1H), 7.46 – 7.28 (m, 5H), 4.08 (d, *J* = 17.7 Hz, 1H), 3.66 (s, 3H), 3.55 – 3.30 (m, 2H), 3.15 – 2.99 (m, 1H), 2.76 – 2.52 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.72 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 169.7, 135.7, 135.2, 134.7, 133.9, 133.1, 132.8, 128.8, 128.5, 126.7 (q, *J* = 276.6 Hz), 126.4, 120.1, 86.8, 84.9, 53.6, 48.9, 48.6 (q, *J* = 1.8 Hz), 38.1, 31.6 (q, J = 29.8 Hz). IR (film): v 1740, 1705 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{22}H_{15}Cl_2F_3O_3Na]^+$ ($[M+Na]^+$): 477.0243, found: 477.0245.



(±)-3g

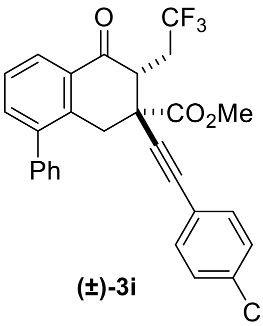
Following the general procedure, **(±)-3g** was obtained as a pale-yellow solid (43 mg, 50% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 135.9 – 136.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.8 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.34 – 7.24 (m, 3H), 3.84 (d, J = 17.1 Hz, 1H), 3.62 (s, 3H), 3.56 – 3.43 (m, 1H), 3.38 (d, J = 17.1 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.76 – 2.57 (m, 1H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.73 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 170.0, 136.5, 136.4, 135.7, 135.1, 133.1, 131.2, 128.8, 127.3, 126.9 (q, J = 276.4 Hz), 125.7, 120.3, 87.4, 84.5, 53.4, 49.1, 48.7 (q, J = 2.3 Hz), 38.1, 31.7 (q, J = 29.6 Hz), 19.4. IR (film): v 1740, 1697 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{23}H_{18}ClF_3O_3Na]^+$ ($[M+Na]^+$): 457.0789, found: 457.0791.



(±)-3h

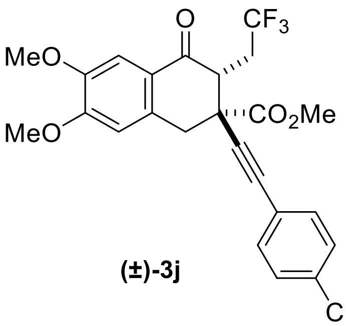
Following the general procedure, **(±)-3h** was obtained as a pale-yellow solid (44 mg, 49% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 5:1)). Mp 131.9 – 132.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 1H), 7.42 – 7.27 (m, 5H), 7.06 (d, J = 8.1 Hz, 1H), 4.01 (d, J = 17.7 Hz, 1H), 3.89 (s, 3H), 3.63 (s, 3H), 3.54 – 3.36 (m, 1H), 3.29 (d, J = 17.7 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.70 – 2.54 (m, 1H). ^{19}F NMR

(376 MHz, $CDCl_3$) δ -65.68 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 170.1, 156.6, 135.0, 133.1, 132.0, 128.7, 128.1, 126.9, 126.9 (q, J = 276.5 Hz), 120.4, 119.2, 115.0, 87.5, 84.4, 55.8, 53.4, 49.2, 48.8 (q, J = 2.1 Hz), 34.7, 31.7 (q, J = 29.6 Hz). IR (film): v 1735, 1700 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{23}H_{18}ClF_3O_4Na]^+$ ($[M+Na]^+$): 473.0738, found: 473.0739.



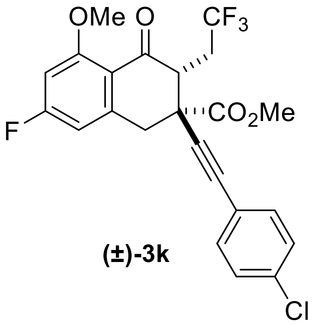
(±)-3i

Following the general procedure, **(±)-3i** was obtained as a pale-yellow solid (50 mg, 50% yield, dr = 11:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 128.6 – 129.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 1H), 7.55 – 7.19 (m, 11H), 3.73 (d, J = 16.9 Hz, 1H), 3.58 (s, 3H), 3.55 – 3.45 (m, 1H), 3.42 (d, J = 17.0 Hz, 1H), 3.10 – 3.03 (m, 1H), 2.74 – 2.58 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.77 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 169.8, 142.2, 139.6, 135.6, 135.5, 135.0, 133.1, 131.4, 129.0, 128.7, 128.7, 127.8, 127.5, 127.2, 126.9 (q, J = 276.5 Hz), 120.2, 87.1, 84.5, 53.3, 49.6, 49.4 (q, J = 2.3 Hz), 39.2, 31.9 (q, J = 29.7 Hz). IR (film): v 1735, 1697 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{28}H_{20}ClF_3O_3Na]^+$ ($[M+Na]^+$): 519.0945, found: 519.0945.



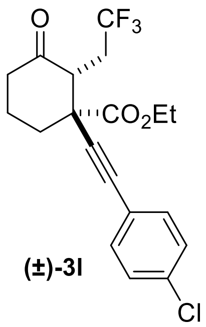
(±)-3j

Following the general procedure, **(±)-3j** was obtained as a pale-yellow solid (50 mg, 52% yield, dr > 20:1, R_f = 0.6 (petroleum ether/ ethyl acetate = 3:1)). Mp 184.6 – 185.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.42 – 7.28 (m, 4H), 6.65 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.70 (d, *J* = 16.5 Hz, 1H), 3.64 (s, 3H), 3.56 (d, *J* = 16.4 Hz, 1H), 3.54 – 3.40 (m, 1H), 3.05 – 2.97 (m, 1H), 2.72 – 2.56 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.76 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 169.9, 154.1, 148.7, 135.0, 133.1, 132.7, 128.8, 127.0 (q, *J* = 276.5 Hz), 124.3, 120.3, 109.9, 109.0, 87.2, 84.4, 56.2, 56.0, 53.4, 50.0, 48.9 (q, *J* = 2.1 Hz), 40.7, 31.9 (q, *J* = 29.4 Hz). IR (film): *v* 1735, 1685 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{24}H_{20}ClF_3O_5Na]^+$ ($[M+Na]^+$): 503.0844, found: 503.0843.



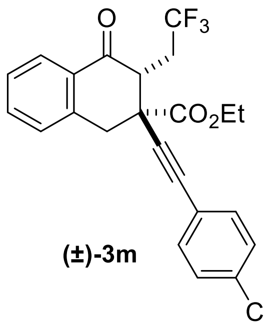
(±)-3k

Following the general procedure, **(±)-3k** was obtained as a pale-yellow solid (52 mg, 56% yield, dr = 11:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 5:1)). Mp 192.2 – 192.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 6.64 – 6.51 (m, 2H), 3.91 (s, 3H), 3.74 (d, *J* = 16.9 Hz, 1H), 3.66 (s, 3H), 3.57 (d, *J* = 16.9 Hz, 1H), 3.53 – 3.35 (m, 1H), 3.10 – 2.97 (m, 1H), 2.73 – 2.52 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.61 (s, 3F), -100.21 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 169.5, 166.2 (d, *J* = 256.0 Hz), 163.3 (d, *J* = 11.3 Hz), 143.6 (d, *J* = 11.1 Hz), 135.1, 133.1, 128.8, 126.9 (q, *J* = 276.5 Hz), 120.2, 117.2, 107.2 (d, *J* = 21.9 Hz), 99.1 (d, *J* = 25.3 Hz), 86.9, 84.6, 56.4, 53.5, 50.4 (q, *J* = 2.0 Hz), 48.6, 41.4, 31.6 (q, *J* = 29.5 Hz). IR (film): *v* 1740, 1696 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{23}H_{17}ClF_4O_4Na]^+$ ($[M+Na]^+$): 491.0644, found: 491.0644.



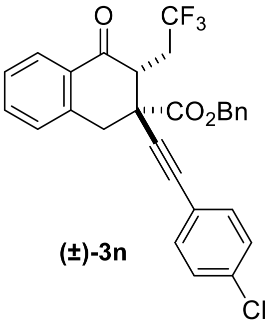
(±)-3l

Following the general procedure, **(±)-3l** was obtained as a pale-yellow liquid (37 mg, 48% yield, dr = 5:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 4H), 4.40 – 4.11 (m, 2H), 3.49 – 3.28 (m, 1H), 2.79 – 2.69 (m, 1H), 2.63 – 2.52 (m, 2H), 2.45 – 2.20 (m, 3H), 2.12 – 2.00 (m, 1H), 1.80 – 1.65 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.05 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 169.9, 134.8, 133.0, 128.7, 126.7 (q, J = 276.4 Hz), 120.6, 88.1, 83.9, 62.5, 52.5, 51.0 (q, J = 2.0 Hz), 40.0, 36.6, 30.5 (q, J = 29.6 Hz), 22.1, 14.0. IR (film): ν 1735 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{19}H_{18}ClF_3O_3Na]^+$ ($[M+Na]^+$): 409.0789, found: 409.0789.



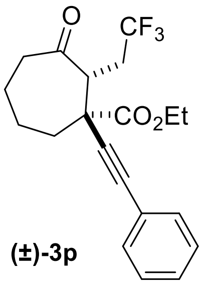
(±)-3m

Following the general procedure, **(±)-3m** was obtained as a pale-yellow solid (58 mg, 67% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 123.6 – 123.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.7 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.42 – 7.35 (m, 3H), 7.34 – 7.24 (m, 3H), 4.05 (q, J = 7.1 Hz, 2H), 3.78 (d, J = 16.6 Hz, 1H), 3.62 (d, J = 16.6 Hz, 1H), 3.57 – 3.37 (m, 1H), 3.11 – 3.00 (m, 1H), 2.74 – 2.57 (m, 1H), 1.05 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.76 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 169.3, 138.1, 135.0, 134.2, 133.1, 131.1, 128.8, 128.6, 127.8, 127.8, 126.9 (q, *J* = 276.5 Hz), 120.3, 87.2, 84.5, 62.5, 49.8, 49.5 (q, *J* = 2.0 Hz), 41.1, 31.9 (q, *J* = 29.7 Hz), 13.7. IR (film): *ν* 1734, 1701 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{18}ClF_3O_3Na]^+$ ($[M+Na]^+$): 457.0789, found: 457.0788.



(±)-3n

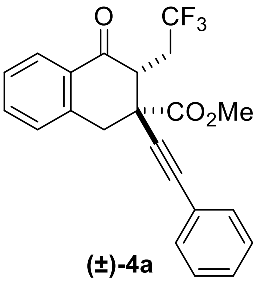
Following the general procedure, **(±)-3n** was obtained as a pale-yellow solid (59 mg, 60% yield, dr = 19:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 84.8 – 85.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.39 – 7.14 (m, 9H), 7.08 (d, *J* = 6.6 Hz, 2H), 5.08 – 4.98 (m, 2H), 3.77 (d, *J* = 16.6 Hz, 1H), 3.61 (d, *J* = 16.6 Hz, 1H), 3.56 – 3.39 (m, 1H), 3.09 – 2.99 (m, 1H), 2.71 – 2.53 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.72 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 169.2, 137.9, 135.1, 134.7, 134.2, 133.0, 131.1, 128.8, 128.6, 128.5, 128.4, 127.9, 127.8, 127.8, 126.9 (q, *J* = 276.4 Hz), 120.3, 87.0, 84.7, 67.9, 49.9, 49.5 (q, *J* = 2.2 Hz), 40.9, 31.9 (q, *J* = 29.6 Hz). IR (film): *ν* 1735, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{28}H_{20}ClF_3O_3Na]^+$ ($[M+Na]^+$): 519.0945, found: 519.0944.



(±)-3p

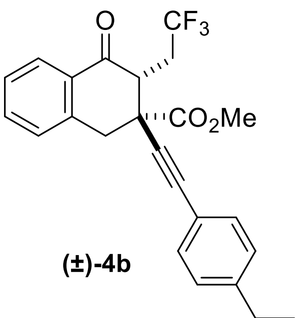
Following the general procedure, **(±)-3p** was obtained as a pale-yellow liquid (41 mg, 22% yield of 0.5 mmol scale, dr = 2.5:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 4.29 – 4.15 (m, 2H), 3.38 (d, *J* = 10.1 Hz, 1H), 3.28 – 3.11 (m, 1H), 2.89 – 2.74 (m, 1H), 2.70 – 2.59 (m, 1H), 2.58 – 2.46 (m, 2H), 2.16 – 1.96 (m, 2H), 1.96 – 1.74 (m, 3H), 1.32 (t, *J*

= 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.48 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 169.6, 131.7, 128.6, 128.3, 126.7 (q, *J* = 276.9 Hz), 122.2, 88.3, 85.6, 62.1, 50.5 (q, *J* = 2.1 Hz), 48.3, 43.2, 39.6, 33.4 (q, *J* = 28.7 Hz), 23.9, 22.4, 14.0. IR (film): *v* 1736, 1717 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{20}H_{21}F_3O_3Na]^+$ ($[M+Na]^+$): 389.1335, found: 389.1335.



(±)-4a

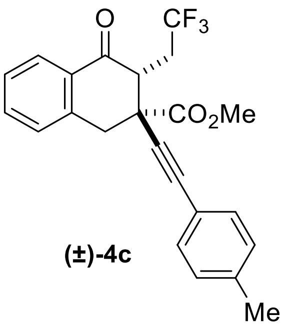
Following the general procedure, **(±)-4a** was obtained as a pale-yellow solid (46 mg, 59% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 175.3 – 175.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.23 (m, 8H), 3.79 (d, *J* = 16.7 Hz, 1H), 3.69 – 3.58 (m, 4H), 3.56 – 3.39 (m, 1H), 3.12 – 3.01 (m, 1H), 2.78 – 2.60 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.74 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 170.1, 138.1, 134.2, 131.8, 128.9, 128.6, 128.4, 127.8, 127.8, 126.9 (q, *J* = 276.5 Hz), 121.8, 86.1, 85.7, 53.4, 49.8, 49.6 (q, *J* = 1.7 Hz), 41.1, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1732, 1693 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{17}F_3O_3Na]^+$ ($[M+Na]^+$): 409.1022, found: 409.1021.



(±)-4b

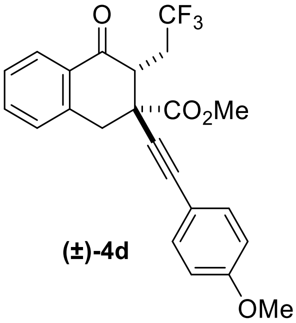
Following the general procedure, **(±)-4b** was obtained as a pale-yellow solid (57 mg, 65% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 117.0 – 117.8

°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.44 – 7.31 (m, 5H), 7.29 – 7.24 (m, 1H), 3.79 (d, *J* = 16.7 Hz, 1H), 3.71 – 3.58 (m, 4H), 3.56 – 3.39 (m, 1H), 3.12 – 3.01 (m, 1H), 2.80 – 2.60 (m, 1H), 1.31 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.72 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 170.2, 152.3, 138.2, 134.2, 131.6, 131.1, 128.6, 127.8, 127.7, 126.9 (q, *J* = 276.5 Hz), 125.4, 118.8, 85.8, 85.4, 53.3, 49.8, 49.7 (q, *J* = 1.8 Hz), 41.1, 34.8, 31.8 (q, *J* = 29.5 Hz), 31.1. IR (film): *v* 1739, 1701 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{26}H_{25}F_3O_3Na]^+$ ($[M+Na]^+$): 465.1648, found: 465.1649.



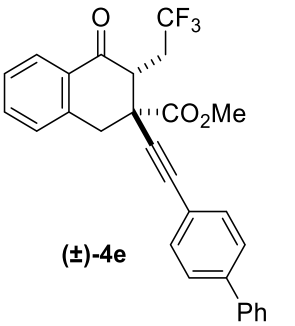
(±)-4c

Following the general procedure, **(±)-4c** was obtained as a pale-yellow solid (50 mg, 63% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 171.4 – 172.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.40 – 7.33 (m, 3H), 7.30 – 7.23 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.78 (d, *J* = 16.7 Hz, 1H), 3.68 – 3.58 (m, 4H), 3.56 – 3.39 (m, 1H), 3.09 – 3.02 (m, 1H), 2.80 – 2.59 (m, 1H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.73 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 170.1, 139.2, 138.2, 134.2, 131.7, 131.1, 129.1, 128.6, 127.8, 127.7, 126.9 (q, *J* = 276.6 Hz), 118.7, 85.8, 85.4, 53.3, 49.8, 49.7 (q *J* = 1.8 Hz), 41.1, 31.8 (q, *J* = 29.6 Hz), 21.5. IR (film): *v* 1735, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{19}F_3O_3Na]^+$ ($[M+Na]^+$): 423.1178, found: 423.1182.



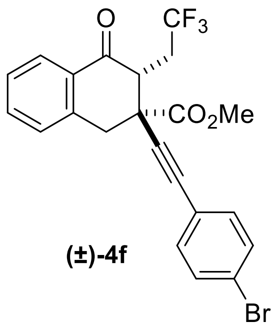
(±)-4d

Following the general procedure, **(±)-4d** was obtained as a pale-yellow solid (54 mg, 65% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 5:1)). Mp 170.1 – 171.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.44 – 7.33 (m, 3H), 7.29 – 7.22 (m, 1H), 6.92 – 6.81 (m, 2H), 3.86 – 3.74 (m, 4H), 3.67 – 3.57 (m, 4H), 3.56 – 3.38 (m, 1H), 3.10 – 3.01 (m, 1H), 2.79 – 2.61 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.71 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 170.1, 139.2, 138.2, 134.2, 131.7, 131.1, 129.1, 128.6, 127.8, 127.7, 126.9 (q, *J* = 276.5 Hz), 118.7, 85.8, 85.4, 53.3, 49.8, 49.7 (q, *J* = 1.8 Hz), 41.1, 31.8 (q, *J* = 29.6 Hz), 21.5. IR (film): *v* 1735, 1697 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{23}H_{19}F_3O_4Na]^+$ ($[M+Na]^+$): 439.1128, found: 439.1132.



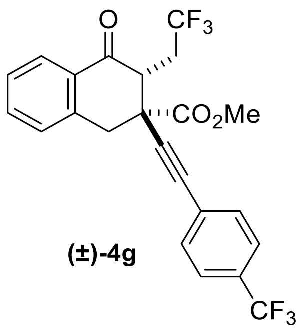
(±)-4e

Following the general procedure, **(±)-4e** was obtained as a pale-yellow solid (51 mg, 55% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 137.7 – 138.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.22 (m, 12H), 3.81 (d, *J* = 16.7 Hz, 1H), 3.71 – 3.60 (m, 4H), 3.58 – 3.42 (m, 1H), 3.13 – 3.05 (m, 1H), 2.82 – 2.61 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.68 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 170.0, 141.7, 140.2, 138.1, 134.2, 132.3, 131.1, 128.9, 128.6, 127.8, 127.8, 127.1, 127.0, 126.9 (q, *J* = 276.5 Hz), 120.6, 86.7, 85.5, 53.4, 49.9, 49.6 (q, *J* = 1.8 Hz), 41.1, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1736, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{28}H_{21}F_3O_3Na]^+$ ($[M+Na]^+$): 485.1335, found: 485.1336.



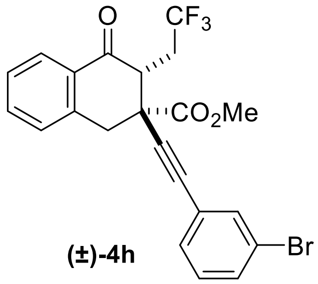
(±)-4f

Following the general procedure, **(±)-4f** was obtained as a pale-yellow solid (58 mg, 63% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 167.1 – 168.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.60 – 7.21 (m, 7H), 3.78 (d, *J* = 16.7 Hz, 1H), 3.68 – 3.58 (m, 4H), 3.56 – 3.38 (m, 1H), 3.12 – 3.00 (m, 1H), 2.75 – 2.50 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.74 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 169.8, 137.9, 134.3, 133.3, 131.7, 131.0, 128.6, 127.8, 126.9 (q, *J* = 276.6 Hz), 123.3, 120.7, 87.3, 84.6, 53.4, 49.8, 49.5 (q, *J* = 1.7 Hz), 40.9, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1735, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{16}BrF_3O_3Na]^+$ ($[M+Na]^+$): 487.0127, found: 487.0128.



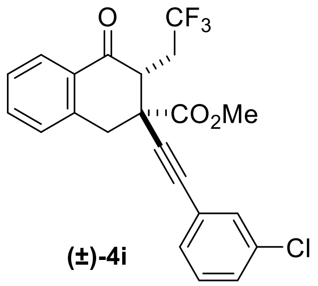
(±)-4g

Following the general procedure, **(±)-4g** was obtained as a pale-yellow solid (57 mg, 63% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 168.0 – 168.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.46 (m, 5H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 3.80 (d, *J* = 16.7 Hz, 1H), 3.70 – 3.59 (m, 4H), 3.59 – 3.43 (m, 1H), 3.12 – 3.03 (m, 1H), 2.73 – 2.54 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94 (s, 3F), -65.76 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 169.7, 137.8, 134.3, 132.1, 131.0, 130.7 (q, *J* = 32.8 Hz), 128.6, 127.9, 127.8, 126.9 (q, *J* = 276.5 Hz), 125.6 (q, *J* = 1.2 Hz), 125.3 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.3 Hz), 88.5, 84.2, 53.5, 49.8, 49.4 (q, *J* = 1.7 Hz), 40.9, 31.9 (q, *J* = 29.7 Hz). IR (film): *v* 1735, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{23}H_{16}F_6O_3Na]^+$ ($[M+Na]^+$): 477.0896, found: 477.0895.



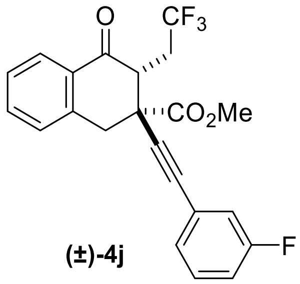
(±)-4h

Following the general procedure, **(±)-4h** was obtained as a pale-yellow solid (50 mg, 54% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 162.5 – 163.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 1H), 7.67 – 7.44 (m, 3H), 7.43 – 7.32 (m, 2H), 7.29 – 7.18 (m, 2H), 3.77 (d, *J* = 16.7 Hz, 1H), 3.69 – 3.58 (m, 4H), 3.57 – 3.38 (m, 1H), 3.10 – 3.03 (m, 1H), 2.71 – 2.54 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.74 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 169.8, 137.9, 134.5, 134.3, 132.2, 131.0, 130.4, 129.9, 128.6, 127.8, 126.9 (q, *J* = 276.6 Hz), 123.8, 122.2, 87.4, 84.1, 53.4, 49.8, 49.4 (q, *J* = 1.8 Hz)), 40.9, 31.9 (q, *J* = 29.6 Hz). IR (film): *v* 1735, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{16}BrF_3O_3Na]^+$ ($[M+Na]^+$): 487.0127, found: 487.0126.



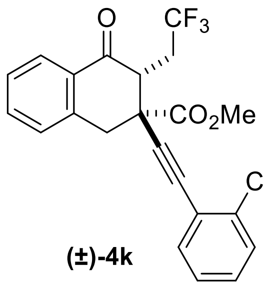
(±)-4i

Following the general procedure, **(±)-4i** was obtained as a pale-yellow solid (46 mg, 55% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 137.6 – 138.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.20 (m, 7H), 3.78 (d, *J* = 16.7 Hz, 1H), 3.71 – 3.57 (m, 4H), 3.57 – 3.37 (m, 1H), 3.12 – 2.99 (m, 1H), 2.72 – 2.53 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.74 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 169.8, 137.9, 134.3, 131.7, 131.0, 130.0, 129.7, 129.3, 128.6, 127.8, 126.9 (q, *J* = 276.5 Hz), 123.5, 87.3, 84.2, 53.4, 49.8, 49.4 (q, *J* = 1.7 Hz), 40.9, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1734, 1697 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{16}ClF_3O_3Na]^+$ ($[M+Na]^+$): 443.0632, found: 443.0630.



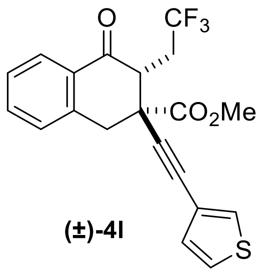
(±)-4j

Following the general procedure, **(±)-4j** was obtained as a pale-yellow solid (44 mg, 54% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 130.6 – 131.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.49 (m, 1H), 7.42 – 7.21 (m, 4H), 7.19 – 7.03 (m, 2H), 3.78 (d, *J* = 16.7 Hz, 1H), 3.70 – 3.58 (m, 4H), 3.57 – 3.40 (m, 1H), 3.11 – 3.03 (m, 1H), 2.73 – 2.56 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.75 (s, 3F), -112.56 (s, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 169.8, 162.3 (d, *J* = 247.0 Hz), 137.9, 134.3, 131.0, 130.1 (d, *J* = 8.6 Hz), 128.6, 127.8, 127.8, 127.8 (d, *J* = 3.1 Hz), 126.9 (q, *J* = 276.5 Hz), 123.6 (d, *J* = 9.4 Hz), 118.7 (d, *J* = 23.0 Hz), 116.4 (d, *J* = 21.1 Hz), 87.0, 84.4, 53.4, 49.8, 49.4 (q, *J* = 1.8 Hz), 40.9, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1730, 1696 cm^{-1}. HRMS (ESI) *m*/*z* calcd for $[C_{22}H_{16}F_4O_3Na]^+$ ($[M+Na]^+$): 427.0928, found: 427.0930.



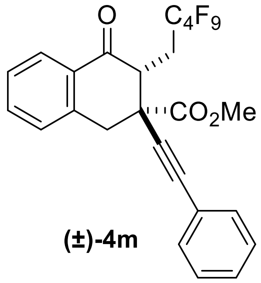
(±)-4k

Following the general procedure, **(±)-4k** was obtained as a pale-yellow solid (52 mg, 62% yield, dr = 19:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 153.1 – 154.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.45 (m, 2H), 7.44 – 7.35 (m, 2H), 7.33 – 7.18 (m, 3H), 3.83 (d, *J* = 16.7 Hz, 1H), 3.69 (d, *J* = 16.7 Hz, 1H), 3.63 (s, 3H), 3.56 – 3.36 (m, 1H), 3.16 – 3.04 (m, 1H), 2.93 – 2.62 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.56 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 169.8, 138.0, 136.4, 134.2, 133.5, 131.1, 130.0, 129.4, 128.6, 127.8, 127.8, 126.8 (q, *J* = 276.6 Hz), 126.5, 121.8, 91.2, 82.6, 53.4, 50.0, 49.3 (q, *J* = 1.8 Hz), 40.9, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1739, 1697 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{16}ClF_3O_3Na]^+$ ($[M+Na]^+$): 443.0632, found: 443.0634.



(±)-4l

Following the general procedure, **(±)-4l** was obtained as a pale brown solid (34 mg, 43% yield, dr > 20:1, R_f = 0.2 (petroleum ether/ ethyl acetate = 10:1)). Mp 158.3 – 159.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.16 – 7.09 (m, 1H), 3.77 (d, *J* = 16.7 Hz, 1H), 3.66 – 3.59 (m, 4H), 3.57 – 3.39 (m, 1H), 3.11 – 3.01 (m, 1H), 2.76 – 2.58 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.73 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 170.0, 138.1, 134.2, 131.1, 129.8, 129.8, 128.6, 127.8, 127.8, 126.9 (q, *J* = 276.4 Hz), 125.6, 120.8, 85.8, 80.9, 53.4, 49.8, 49.6 (q, *J* = 1.9 Hz), 41.0, 31.8 (q, *J* = 29.7 Hz). IR (film): *v* 1740, 1701 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{20}H_{15}F_3O_3SNa]^+$ ($[M+Na]^+$): 415.0586, found: 415.0585.

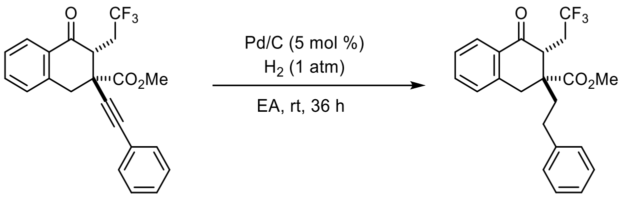


(±)-4m

Following the general procedure, **(±)-4m** was obtained as a pale-yellow solid (29 mg, 55% yield of 0.1 mmol scale, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)). Mp 69.5 – 70.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.4 Hz, 1H), 7.60 – 7.49 (m, 1H), 7.48 – 7.22 (m, 7H), 3.82 (d, *J* = 16.7 Hz, 1H), 3.68 (d, *J* = 16.7 Hz, 1H), 3.64 – 3.40 (m, 4H), 3.28 – 3.15 (m, 1H), 2.79 – 2.56 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.0 – -82.5 (m, 3F), -110.6 – -115.9 (m, 2F), -122.8 – -125.2 (m, 2F), -125.3 – -126.9 (m, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 170.1, 138.1, 134.2, 131.8, 131.1, 128.9, 128.6, 128.4, 127.8, 121.7, 86.0, 85.7, 53.4, 50.1, 48.4, 41.3, 28.7 (t, *J* = 21.3 Hz). IR (film): *v* 1740, 1701 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{25}H_{17}F_9O_3Na]^+$ ($[M+Na]^+$): 559.0926, found: 559.0924.

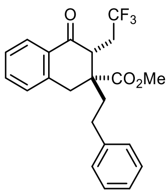
Synthetic transformations

1. Reduction of the C-C triple bond into a CH_2CH_2 unit



(±)-4a **(±)-5**

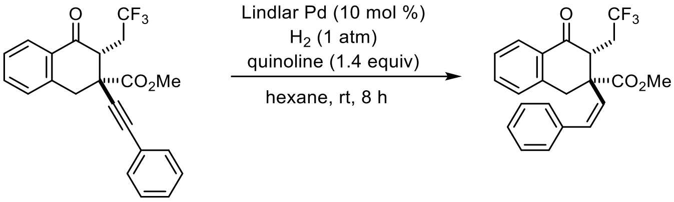
In a flame-dried sealed tube, to a solution of **(±)-4a** (0.1 mmol, 38.6 mg) and 10 wt% Pd/C (0.005 mmol, 5 mol %) in EA (1 mL), the hydrogenation with a hydrogen balloon was performed at rt for 36 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA, 10:1) to afford the product **(±)-5** as a white solid (33 mg, dr > 20:1, 84% yield, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)).[4]



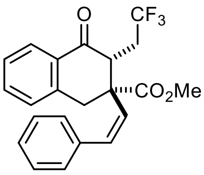
(±)-5

Mp 95.9 – 96.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 1H), 7.57 – 7.49 (m, 1H), 7.39 – 7.24 (m, 5H), 7.22 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 3.59 (s, 3H), 3.49 (d, J = 17.1 Hz, 1H), 3.25 (d, J = 17.1 Hz, 1H), 3.15 – 2.98 (m, 2H), 2.78 – 2.62 (m, 2H), 2.50 – 2.33 (m, 1H), 2.26 – 2.13 (m, 1H), 2.03 – 1.91 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.52 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 173.0, 139.5, 138.4, 133.2, 129.6, 127.9, 127.6, 127.2, 126.7, 126.3, 125.6 (q, J = 276.9 Hz) 125.3, 51.4, 50.8, 47.5 (q, J = 1.7 Hz), 37.0, 34.6, 29.6 (q, J = 29.4 Hz), 29.2. IR (film): ν 1730, 1696 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{21}F_3O_3Na]^+$ ($[M+Na]^+$): 413.1335, found: 413.1335.

2. Reduction of the C-C triple bond by Lindlar catalyst



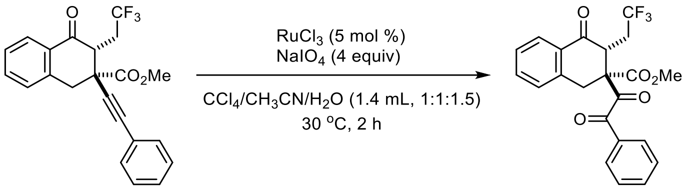
In a flame-dried sealed tube, a hexane (4 mL) solution of **(±)-4a** (0.1 mmol, 38.6 mg), Lindlar Pd (0.01 mmol, 10 mol %) and quinoline (0.14 mmol, 1.4 equiv) was stirred at rt with a hydrogen balloon for 8 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA, 10:1) to afford the product **(±)-6** as a white solid (36 mg, 92% yield, dr > 20:1, R_f = 0.3 (petroleum ether/ ethyl acetate = 10:1)).[5]



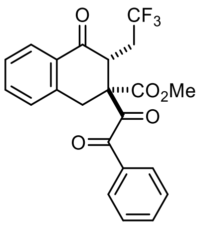
(±)-6

Mp 106.0 – 106.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 12.4 Hz, 1H), 5.66 (d, *J* = 12.5 Hz, 1H), 3.51 (d, *J* = 16.7 Hz, 1H), 3.31 – 3.16 (m, 2H), 2.99 (d, *J* = 7.0 Hz, 1H), 2.87 (s, 3H), 2.63 – 2.52 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.35 (s, 3F). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 172.0, 139.9, 135.7, 134.2, 133.0, 131.1, 128.8, 128.3, 128.1, 127.6, 127.4, 127.2, 126.9 (q, *J* = 276.1 Hz), 54.8, 51.9, 50.1, 39.7, 31.1 (q, *J* = 29.5 Hz). IR (film): *v* 1732, 1696 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{19}F_3O_3Na]^+$ ($[M+Na]^+$): 411.1178, found: 411.1174.

3. Transformation into a trifluoromethylated triketone



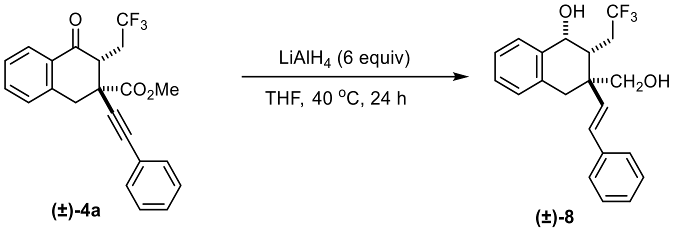
In a flame-dried sealed tube, $RuCl_3$ (0.01 mmol, 5 mol %) and $NaIO_4$ (0.8 mmol, 4 equiv) were dissolved in a mix solvent of CCl_4 (0.4 mL), MeCN (0.4 mL) and H_2O (0.6 mL) under a N_2 atmosphere, then, **(±)-4a** (0.2 mmol, 1 equiv) was sequentially added. The reaction mixture was stirred at 30 ^oC for 2 h. After completion of the reaction as detected by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product **(±)-7** as a pale-yellow liquid (54 mg, 65% yield, dr > 20:1, R_f = 0.2 (petroleum ether/ ethyl acetate = 10:1)). [6]



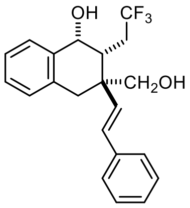
(±)-7

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 3.78 (d, *J* = 16.5 Hz, 1H), 3.62 (d, *J* = 16.8 Hz, 1H), 3.55 (s, 3H), 3.50 – 3.41 (m, 1H), 3.31 – 3.14 (m, 1H), 2.73 – 2.57 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.08 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 192.5, 190.7, 169.9, 136.9, 135.3, 134.5, 131.7, 130.4, 130.2, 129.0, 128.6, 128.1, 128.0, 126.4 (q, *J* = 276.5 Hz), 63.8, 53.0, 45.5 (q, *J* = 1.9 Hz), 36.3, 31.2 (q, *J* = 30.1 Hz). IR (film): *v* 1735, 1704, 1671 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{22}H_{17}F_3O_5Na]^+$ ($[M+Na]^+$): 441.0920, found: 441.0924.

4. Reduction to an alkenyl diol



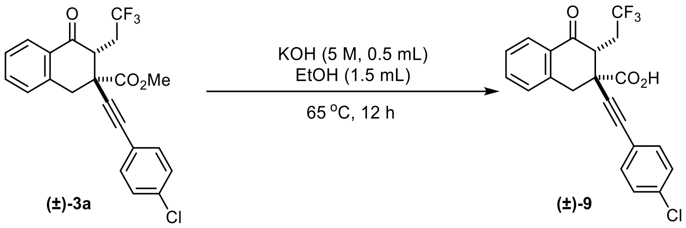
In a flame-dried sealed tube, a THF (2 mL) solution of **(±)-4a** (0.1 mmol, 38.6 mg) and $LiAlH_4$ (0.6 mmol, 6 equiv) at 40 °C was stirred for 24 h. After completion of the reaction as detected by TLC, the reaction was quenched with saturated aqueous NH_4Cl (4 mL). The aqueous layer was extracted with EA and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and filtered. The residue was purified by column chromatography on silica gel to afford the product **(±)-8** as a colorless liquid (26 mg, 72% yield, dr > 20:1, R_f = 0.3 (petroleum ether / ethyl acetate / MeOH = 90:10:4)).



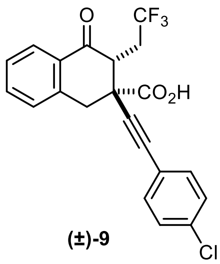
(±)-8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.35 – 7.22 (m, 7H), 7.19 –7.14 (m, 1H), 6.44 (d, *J* = 16.6 Hz, 1H), 6.34 (d, *J* = 16.6 Hz, 1H), 4.68 (s, 1H), 3.75 – 3.66 (m, 2H), 3.10 (d, *J* = 17.3 Hz, 1H), 2.76 (d, *J* = 17.3 Hz, 1H), 2.68 – 2.50 (m, 1H), 2.46 – 2.39 (m, 1H), 2.19 – 1.94 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.14 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 135.4, 132.7, 132.5, 129.4, 128.7, 127.8, 127.7, 127.4, 126.8, 126.2 (q, *J* = 276.8 Hz), 126.0, 125.2, 71.3, 65.2, 42.9, 41.2 (q, J = 1.4 Hz), 33.3, 31.8 (q, J = 28.2 Hz). IR (film): *v* 3367 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{21}F_3O_2Na]^+$ ($[M+Na]^+$): 385.1386, found: 385.1392.

5. Hydrolysis to an acid



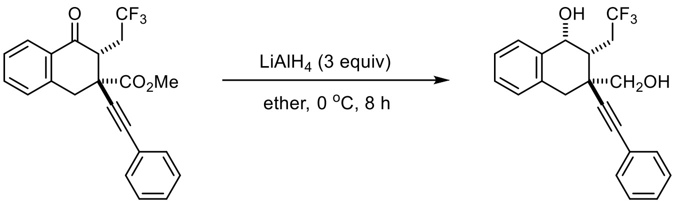
In a flame-dried sealed tube, a EtOH (1.5 mL) and aqueous KOH (5 M, 0.5 mL) solution of **(±)-3a** (0.2 mmol, 77.6 mg) was stirred at 65 °C for 12 h. After completion of the reaction as detected by TLC, the reaction was acidified with HCl (1 M, 10 mL). The aqueous layer was extracted with EA and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and filtered. The residue was purified by column chromatography on silica get to afford the product **(±)-9** as a white solid (72 mg, 89% yield, dr = 1:1, R_f = 0.6 (petroleum ether/ ethyl acetate = 1:1)).



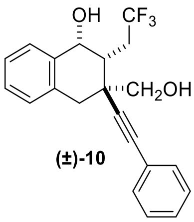
(±)-9

Mp 166.2 – 167.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.49 (m, 1H), 7.43 – 7.22 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.34 (br, 1H), 3.85 – 3.61 (m, 1.5H), 3.54 – 3.20 (m, 2H), 3.05 (d, *J* = 5.4 Hz, 0.5H), 2.74 – 2.31 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.42, -65.77. ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 192.2, 174.9, 174.3, 138.5, 137.9, 135.2, 135.0, 134.5, 134.4, 133.1, 133.0, 131.0, 130.7, 128.8, 128.7, 128.5, 127.8, 127.8, 127.6, 126.8 (q, *J* = 276.4 Hz), 126.5 (q, *J* = 276.4 Hz), 120.1, 119.9, 86.7, 85.6, 84.9, 84.8, 50.6, 49.8, 49.2, 48.2, 40.9, 38.9, 31.7 (q, *J* = 29.7 Hz), 31.2 (q, *J* = 30.3 Hz). IR (film): *v* 1717, 1698 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{13}ClF_3O_3]^+$ ($[M-H]^+$): 405.0511, found: 405.0512.

6. Reduction to an alkynyl diol

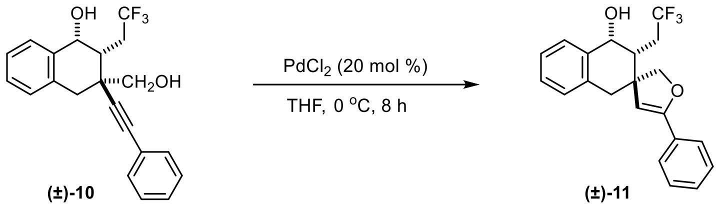


In a flame-dried sealed tube, an ether (2 mL) solution of **(±)-4a** (0.1 mmol, 38.6 mg) and $LiAlH_4$ (0.3 mmol, 3 equiv) at 0 °C was stirred for 8 h. After completion of the reaction as detected by TLC, the reaction was quenched with saturated aqueous NH_4Cl (4 mL). The aqueous layer was extracted with EA and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and filtered. The residue was purified by column chromatography on silica gel to afford the product **(±)-10** as a white solid (27 mg, 76% yield, dr > 20:1, R_f = 0.3 (petroleum ether / ethyl acetate / MeOH = 90:10:4)).[7]

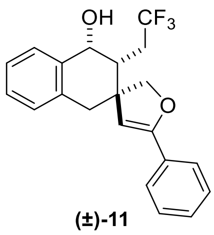


Mp 47.7 – 48.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.0 Hz, 1H), 7.39 – 7.22 (m, 7H), 7.12 (d, *J* = 7.0 Hz, 1H), 4.64 (s, 1H), 3.69 (q, *J* = 11.1 Hz, 2H), 3.15 (d, *J* = 16.9 Hz, 1H), 2.98 (d, *J* = 16.9 Hz, 1H), 2.79 – 2.56 (m, 3H), 2.25 – 1.97 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.95 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 132.6, 131.7, 129.5, 128.8, 128.7, 128.4, 128.3, 127.2, 127.1 (q, *J* = 276.7 Hz), 121.9, 91.2, 85.8, 71.7, 65.7, 41.9 (q, *J* = 2.0 Hz), 41.2, 36.4, 33.5 (q, *J* = 28.7 Hz). IR (film): *v* 3627 cm^{-1}. HRMS (ESI) *m/z* calcd for $[C_{21}H_{19}F_3O_2Na]^+$ ($[M+Na]^+$): 383.1229, found: 383.1230.

7. Cyclization into a spiro compound



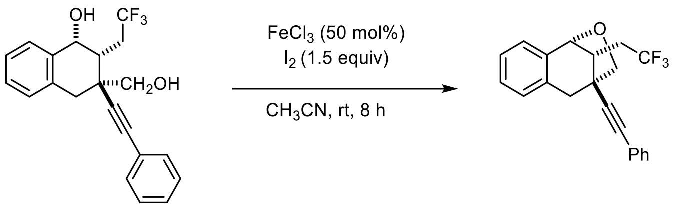
In a flame-dried sealed tube, a THF (4 mL) solution of **(±)-10** (0.1 mmol, 36 mg) and $PdCl_2$ (0.02 mmol, 20 mol %) was stirred at 0 °C for 8 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA, 3:1) to afford the product **(±)-11** as a white solid (29 mg, 81% yield, dr > 20:1, R_f = 0.4 (petroleum ether/ ethyl acetate = 3:1)).[8]



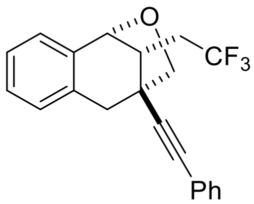
(±)-11

Mp 161.4 – 162.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.7 Hz, 2H), 7.31 – 7.18 (m, 5H), 7.13 – 7.05 (m, 2H), 5.32 (d, J = 4.8 Hz, 1H), 5.26 (s, 1H), 3.95 (d, J = 12.1 Hz, 1H), 3.84 – 3.73 (m, 1H), 3.06 – 2.99 (m, 1H), 2.88 – 2.73 (m, 2H), 2.53 – 2.37 (m, 1H), 1.90 – 1.74 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.46 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 135.5, 133.9, 133.2, 129.4, 129.2, 129.1, 128.2, 127.7, 127.0, 126.9 (q, J = 274.9 Hz), 125.6, 97.3, 81.1, 63.3, 50.4, 37.3 (q, J = 2.4 Hz), 34.8, 29.7 (q, J = 29.3 Hz). IR (film): ν 3365 cm^{-1}. HRMS (ESI) m/z calcd for $[C_{21}H_{19}F_3O_2Na]^+$ ($[M+Na]^+$): 383.1229, found: 383.1233.

8. Cyclodehydration into an endocyclic compound



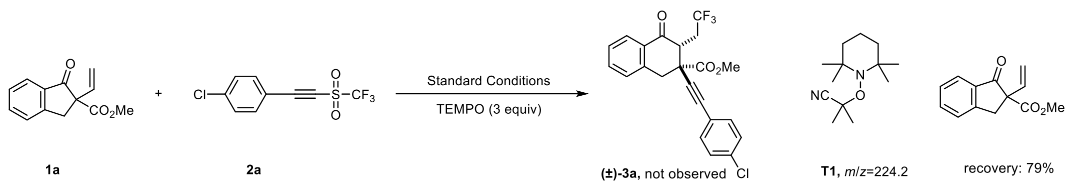
In a flame-dried sealed tube, a MeCN (3 mL) solution of **(±)-10** (0.1 mmol, 36 mg), $FeCl_3$ (0.02 mmol, 50 mol %) and I_2 (1.5 equiv) was stirred at rt for 8 h. After filtration through a short pad of celite, the organic solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA, 10:1) to afford the product **(±)-12** as a colorless liquid (27 mg, dr > 20:1, 79% yield, R_f = 0.6 (petroleum ether/ ethyl acetate = 10:1)).[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.37 – 7.31 (m, 3H), 7.31 – 7.26 (m, 1H), 7.23 – 7.14 (m, 3H), 4.93 (s, 1H), 4.07 – 4.02 (m, 1H), 3.99 (d, J = 8.6 Hz, 1H), 3.56 – 3.48 (m, 1H), 3.32 (d, J = 17.1 Hz, 1H), 2.9 – 2.8 (m, 1H), 2.6 (d, J = 12.0 Hz, 1H), 2.5 – 2.4 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.83 (s, 3F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 132.7, 131.7, 128.9, 128.7, 128.5, 128.4, 127.6, 127.1 (q, J = 276.8 Hz), 126.7, 88.1, 85.8, 80.8, 75.8, 44.8 (q, J = 2.3 Hz), 44.4, 43.2, 33.3 (q, J = 28.2 Hz). HRMS (FI) m/z calcd for $[C_{21}H_{17}F_3O_2]^+$ ($[M]^+$): 342.1226, found: 342.1223.

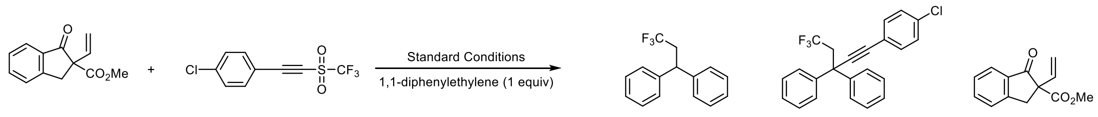
Mechanism studies

1. Radical trapping with TEMPO



In a flame-dried Schlenk tube, *α*-vinyl-*β*-ketoester **1a** (0.2 mmol, 1.0 equiv), TEMPO (0.6 mmol, 3.0 equiv), AIBN (0.06 mmol, 30 mol%) and alkynyl triflone (0.3 mmol, 1.5 equiv) were dissolved in TFE (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 85 ^{o}C (oil bath) for 9 h. Then, another addition of phenylethynyl triflone **2a** (0.3 mmol, 1.5 equiv) and AIBN (0.06 mmol, 30 mol%) was performed and the mixture was stirred at the same temperature for 9 h. The reaction mixture was detected by GC-MS analysis. An adduct of **T1** was detected. The *α*-vinyl-*β*-ketoester **1a** was recovered in 79% yield.

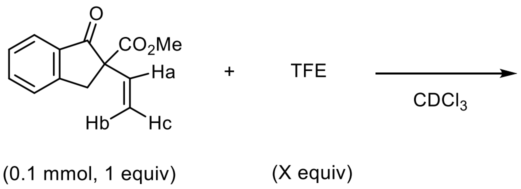
2. Radical trapping with 1,1-diphenylethylene



1a **2a** **T2**, *m/z*=250.3 **T3**, *m/z*=384.3 recovery: 81%

In a flame-dried Schlenk tube, *α*-vinyl-*β*-ketoester **1a** (0.2 mmol, 1.0 equiv), 1,1-diphenylethylene (0.2 mmol, 1.0 equiv), AIBN (0.06 mmol, 30 mol%) and alkynyltriflone **2a** (0.3 mmol, 1.5 equiv) were dissolved in TFE (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 85 °C (oil bath) for 9 h. Then, another addition of phenylethynyl triflone **2a** (0.3 mmol, 1.5 equiv) and AIBN (0.06 mmol, 30 mol%) was performed and the mixture was stirred at the same temperature for 9 h. The reaction mixture was analyzed by GC-MS study, **T2** and **T3** were detected by GC-MS. The *α*-vinyl-*β*-ketoester **1a** was recovered in 81% yield.

3. ^{1}H NMR titration experiments



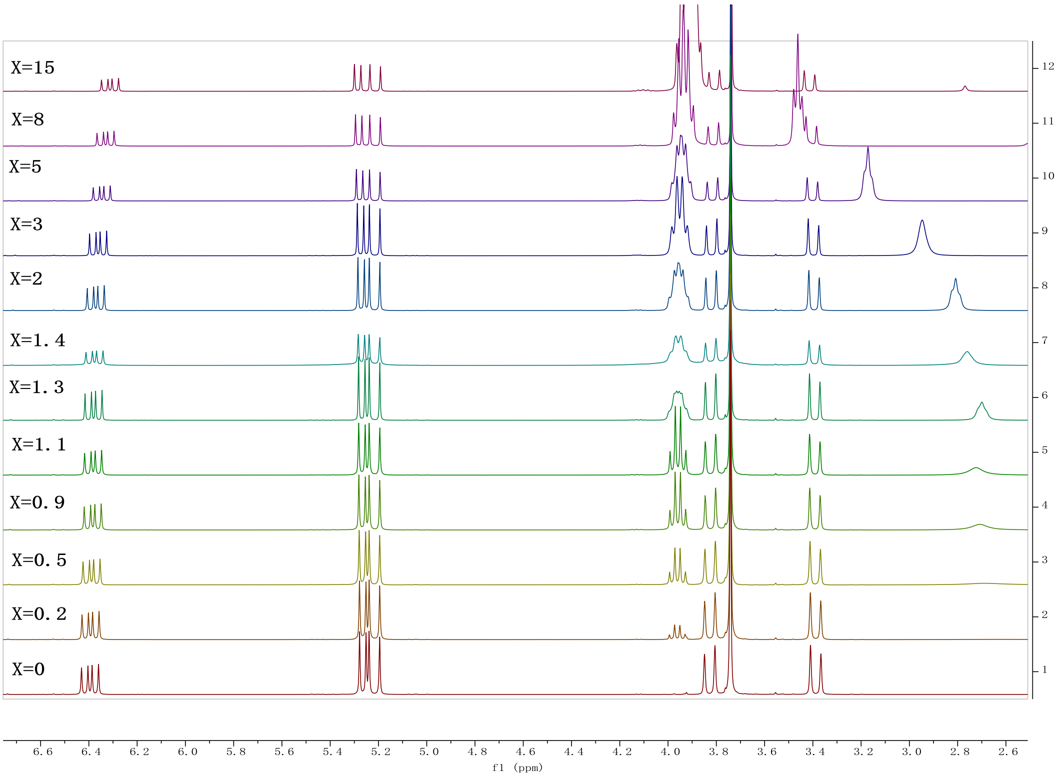


Figure S1. ^{1}H NMR titration of **1a** with increasing amounts of TFE.

Result and discussion: α-Vinyl-β-ketoester (**1a**, 0.1 mmol) was dissolved in 0.6 mL of $CDCl_3$, then TFE (0, 0.2, 0.5, 0.9, 1.1, 1.3, 1.4, 2.0, 3.0, 5.0, 8.0, 15.0 equiv.) was added to give a mixture and the ^{1}H NMR of the obtained mixture was recorded at 298 K on a Bruker-BioSpin AVANCE III HD 400 MHz spectrometer, respectively. As outlined in Figure S1, Ha of compound **1a** shows a upfield shift, with the increasing concentration of TFE. The coupling constants of Hb and Hc were enlarged with the increasing concentration of TFE. This observation might indicate the existence of hydrogen-bonding interaction between **1a** and TFE.

4. 2D NOESY experiment

(0.1 mmol, 1 equiv)   (1.5 equiv)

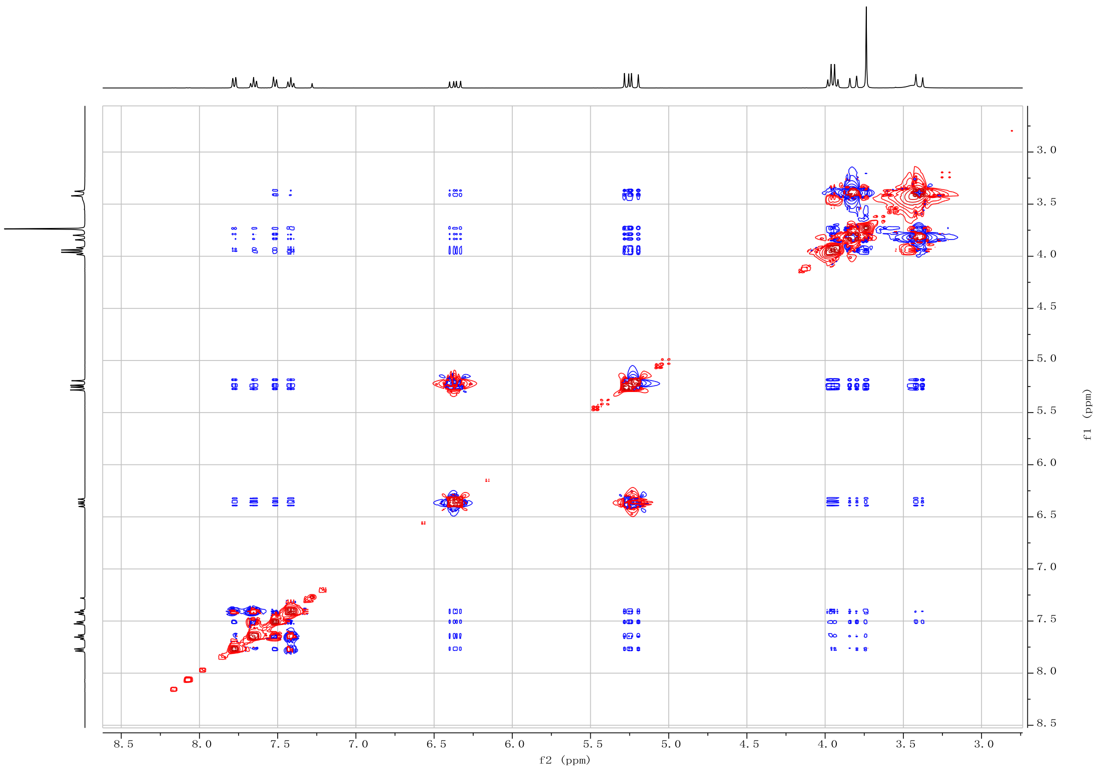


Figure S2. 2D NOESY experiment of **1a** with TFE.

Result and discussion: *α*-Vinyl-*β*-ketoester (**1a**, 0.1 mmol) and TFE (1.5 equiv) were dissolved in 0.6 mL of $CDCl_3$ to give a mixture and the 2D NOESY spectrum of the obtained mixture was recorded at 298 K on a Bruker-BioSpin AVANCE III HD 400 MHz spectrometer. As shown in Figure S2, interaction between **1a** and TFE was observed, which further support the existence of hydrogen-bonding.

5. Job-plot analysis

Job plot studies with ^{1}H NMR data of 1a

Mole fraction (**1a**) χ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Shift of Ha (ppm)	6.3410	6.3511	6.36095	6.36805	6.37475	6.38155	6.38605	6.3902	6.3936	6.3980
Δδ= δ − δmin (ppm)	0.0570	0.0469	0.03705	0.02995	0.02325	0.01645	0.01195	0.0078	0.0044	0.0000
χ ×Δδ	0.0057	0.0094	0.0111	0.0120	0.0116	0.0099	0.0084	0.0062	0.0040	0.0000

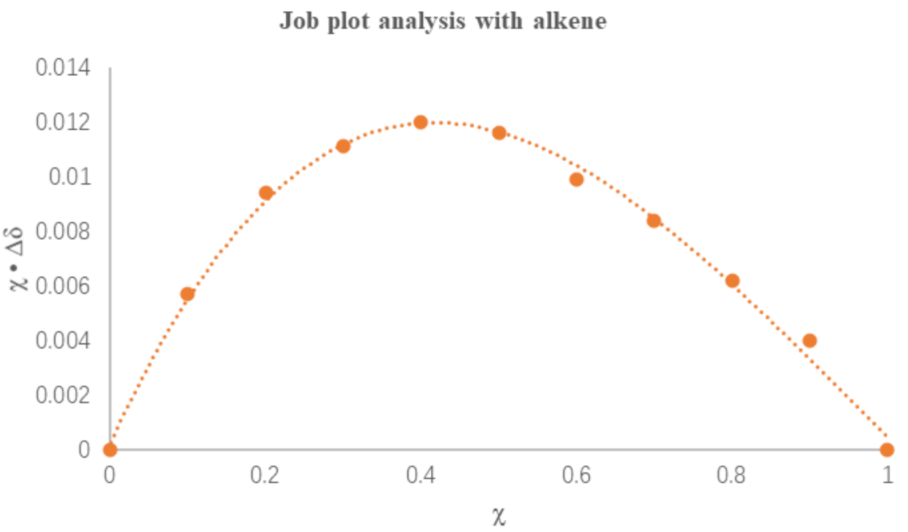


Figure S3. Job plot analysis χ ×Δδ as a function of χ. χ is the molar fraction of **1a**.

Job plot studies with ^{19}F NMR data of TFE

Mole fraction (TFE) χ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Shift of CF_3 (ppm)	-76.9383	-76.968	-77.004	-77.0471	-77.0908	-77.1414	-77.1886	-77.2551	-77.3225	-77.4128
$\Delta\delta = \delta - \delta min$ (ppm)	0.4745	0.4448	0.4088	0.3696	0.3220	0.2714	0.2242	0.1577	0.0903	0.0000
$\chi \times \Delta\delta$	0.04745	0.0889	0.12264	0.14786	0.1610	0.16284	0.15694	0.12616	0.08127	0.0000

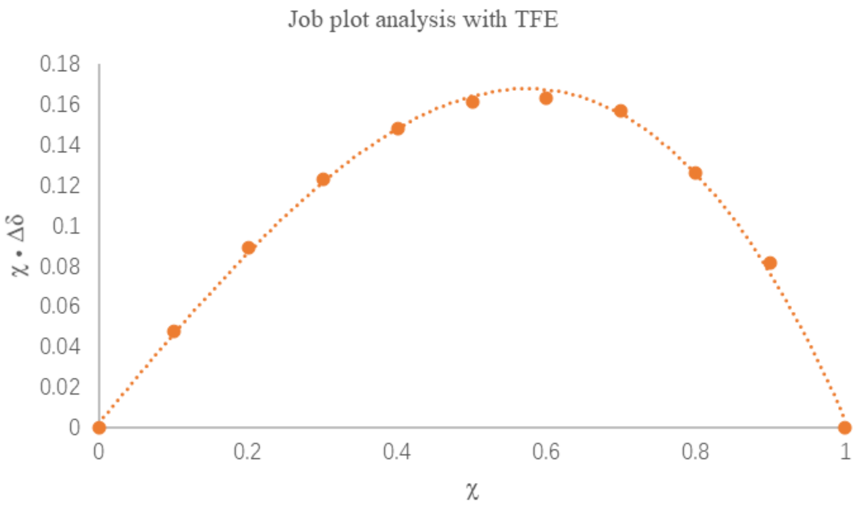
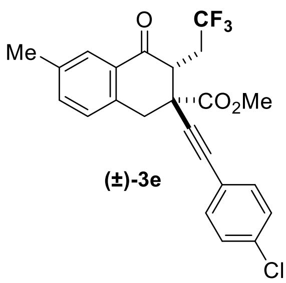


Figure S4. Job plot analysis $\chi \times \Delta\delta$ as a function of χ. χ is the molar fraction of TFE.

Result and discussion: *α*-Vinyl-*β*-ketoester (**1a**) (0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 mmol) and TFE (0.5, 0.45, 0.4, 0.35, 0.3, 0.25, 0.2, 0.15, 0.1, 0.05, 0 mmol) in $CDCl_3$ (0.5 mL) were prepared, with the sum of both concentrations at a constant value of c_{tot} = 1 mol/L. ^{1}H NMR and ^{19}F NMR of the solutions was recorded at 298 K on a Bruker-BioSpin AVANCE III HD 400 MHz spectrometer, respectively. The result outlined in Figure S3 shows a well-defined, in the Job plot studies of ^{1}H NMR, maximum at $\chi = 0.4$, while the result outlined in Figure S4 shows, in the Job plot studies of ^{19}F NMR, maximum at $\chi = 0.6$. Which indicates the 1.5:1 stoichiometry of the complex adduct resulting from TFE and *α*-vinyl-*β*-ketoester (**1a**) in $CDCl_3$. This observation also indicates a hydrogen-bonding interaction.

Single crystal data

CCDC 2108433 **(±)-3e**, 2108434 **(±)-3h**, 2108432 **(±)-4a**, and 2108435 **(±)-6** contain the supplementary crystallographic data. Crystal data and structure refinements of **(±)-3e**, **(±)-3h**, **(±)-4a** and **(±)-6** are listed in **Table S1**, **Table S2**, **Table S3**, and Table **S4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/



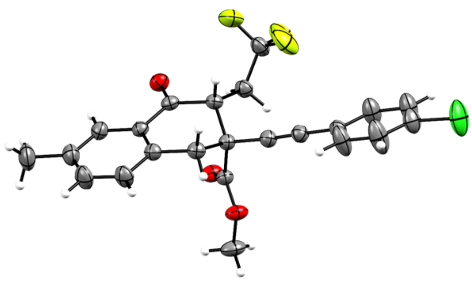
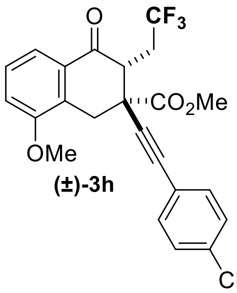


Table S1 Crystal data and structure refinement for (±)-3e.

Identification code	**(±)-3e**
Empirical formula	$C_{23}H_{18}ClF_3O_3$
Formula weight	434.82
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.5234(6)
b/Å	9.7432(5)
c/Å	17.5168(9)
α/°	90
β/°	97.018(5)
γ/°	90
Volume/Å^3	2121.35(19)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	1.324
F(000)	896.0
Crystal size/mm^3	0.03 × 0.022 × 0.02
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	9.046 to 121.556
Index ranges	$-16 \le h \le 16$, $-12 \le k \le 10$, $-22 \le l \le 22$
Reflections collected	15318
Independent reflections	4752 [R_{int} = 0.0286, R_{sigma} = 0.0270]
Data/restraints/parameters	4752/0/273
Goodness-of-fit on F^2	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0626, wR_2 = 0.1826
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1974
Largest diff. peak/hole / e Å^{-3}	0.45/-0.59



(±)-3h

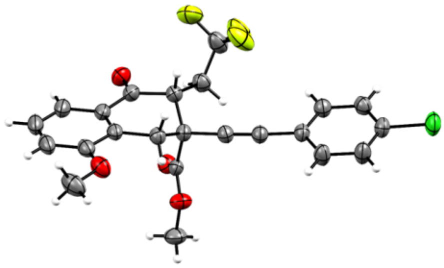
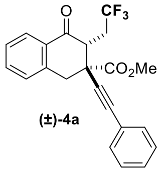


Table S2 Crystal data and structure refinement for (±)-3h.

Identification code	**(±)-3h**
Empirical formula	$C_{23}H_{18}ClF_3O_4$
Formula weight	450.82
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.9925(11)
b/Å	15.5533(14)
c/Å	16.006(2)
α/°	90
β/°	105.451(14)
γ/°	90
Volume/Å^3	2157.8(5)
Z	4
ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	1.337
F(000)	928.0
Crystal size/mm^3	0.026 × 0.025 × 0.011
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	7.016 to 123.388
Index ranges	$-11 \le h \le 11$, $-20 \le k \le 16$, $-19 \le l \le 21$
Reflections collected	18027
Independent reflections	4880 [R_{int} = 0.0346, R_{sigma} = 0.0280]
Data/restraints/parameters	4880/0/282
Goodness-of-fit on F^2	1.141
Final R indexes [I>=2σ (I)]	R_1 = 0.0720, wR_2 = 0.2027
Final R indexes [all data]	R_1 = 0.0968, wR_2 = 0.2622
Largest diff. peak/hole / e Å^{-3}	0.24/-0.59



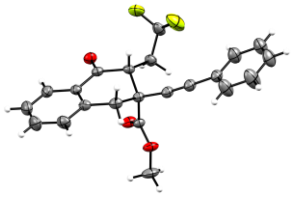
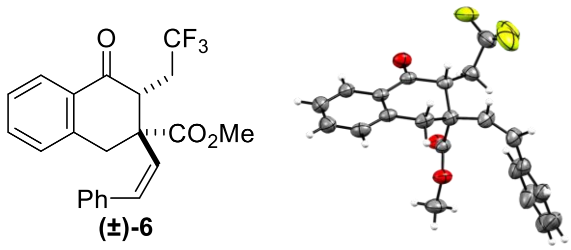


Table S3 Crystal data and structure refinement for (±)-4a.

Identification code	**(±)-4a**	
Empirical formula	C22 H17 F3 O3	
Formula weight	386.35	
Temperature	290.00(14) K	
Wavelength	1.3405 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.6118(11) Å	α= 90°.
	b = 9.7486(8) Å	β= 102.403(9)°.
	c = 17.4474(16) Å	γ = 90°.
Volume	1928.9(3) $Å^3$	
Z	4	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.583 mm^{-1}	
F(000)	800	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	4.512 to 61.591°.	
Index ranges	-15<=h<=14, -12<=k<=12, -22<=l<=21	
Reflections collected	28814	
Independent reflections	4396 [R(int) = 0.0395]	
Completeness to theta = 53.543°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81513	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4396 / 0 / 255	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1530	
R indices (all data)	R1 = 0.0730, wR2 = 0.1733	
Extinction coefficient	0.0033(8)	
Largest diff. peak and hole	0.300 and -0.269 e.$Å^{-3}$	



(±)-6

Table S4 Crystal data and structure refinement for (±)-6.

Identification code	**(±)-6**
Empirical formula	$C_{22}H_{19}F_3O_3$
Formula weight	388.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.1282(19)
b/Å	11.8989(10)
c/Å	11.6230(15)
α/°	90
β/°	111.112(15)
γ/°	90
Volume/Å^3	1951.8(4)
Z	4
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	0.574
F(000)	808.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	8.45 to 121.394
Index ranges	$-19 \leq h \leq 19$, $-14 \leq k \leq 15$, $-15 \leq l \leq 14$
Reflections collected	13341
Independent reflections	4310 [R_{int} = 0.0438, R_{sigma} = 0.0445]
Data/restraints/parameters	4310/0/254
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0647, wR_2 = 0.1926
Final R indexes [all data]	R_1 = 0.0966, wR_2 = 0.2132
Largest diff. peak/hole / e Å^{-3}	0.52/-0.29

Computational methods and details

Density functional theory (DFT) computational studies were carried out at B3LYP[10]-D3[11](SMD[12])/Def2-TZVP[13]//B3LYP-D3(SMD)/Def2-SVP level of theory, in which the D3 dispersion correction is the original D3 damping function. All of structures were optimized with SMD[12] solvation model calculation to analyze the frequencies and the thermal energies at 358 K. Transition state structures were searched by simply performing a crude relaxed potential energy surface (RPES) scan connecting reactants and products, and then optimized by the rational function optimization (RFO) method of TS.[14] The integration grid option were required at ultrafine for all of calculations. The presented Gibbs free energies were the single point electronic energy at B3LYP-D3/Def2-TZVP level with the free energy correction at B3LYP-D3/Def2-SVP level. All calculations were performed by the Gaussian 09 package.[15]

Since some amount of the 1,2-alkynyltrifluoromethylation product (without ring-expansion) was detected for all the cases, the **2b** addition pathway from **int1** has also been considered in this study (Figure S5 and Table S5). Transition state of **int1** directly adding onto **2b**, **TS2'**, was located with a barrier of 13.0 kcal/mol which is ~2 kcal/mol higher than that of **TS2**. Subsequently, TS of a SO_2 molecule with a CF_3 radical dissociation with a very low barrier (~2 kcal/mol) was found to conduct **int2'** resulting in **4a'**. This result indicates that the concerted 1,2-shift mechanism for ring-expansion is favorable but the 1,2-addition of alkene pathway may be competing with it to form the byproduct.

On the other hand, the conformations of transition state corresponding to the direct migration/ring-opening, **TS2**, have been systematically searched, and no transition state for formation the previously proposed strained alkoxyl radical was found. All of transition states corresponding to the direct ring-opening have been confirmed by IRC (intrinsic reaction coordinate) calculations (Figure S6). The spin densities of transition states and maximum force points (MFP) in the path have also been calculated, and the results indicate that the spin on oxygen atom is unstable and will transfer to C3 immediately.

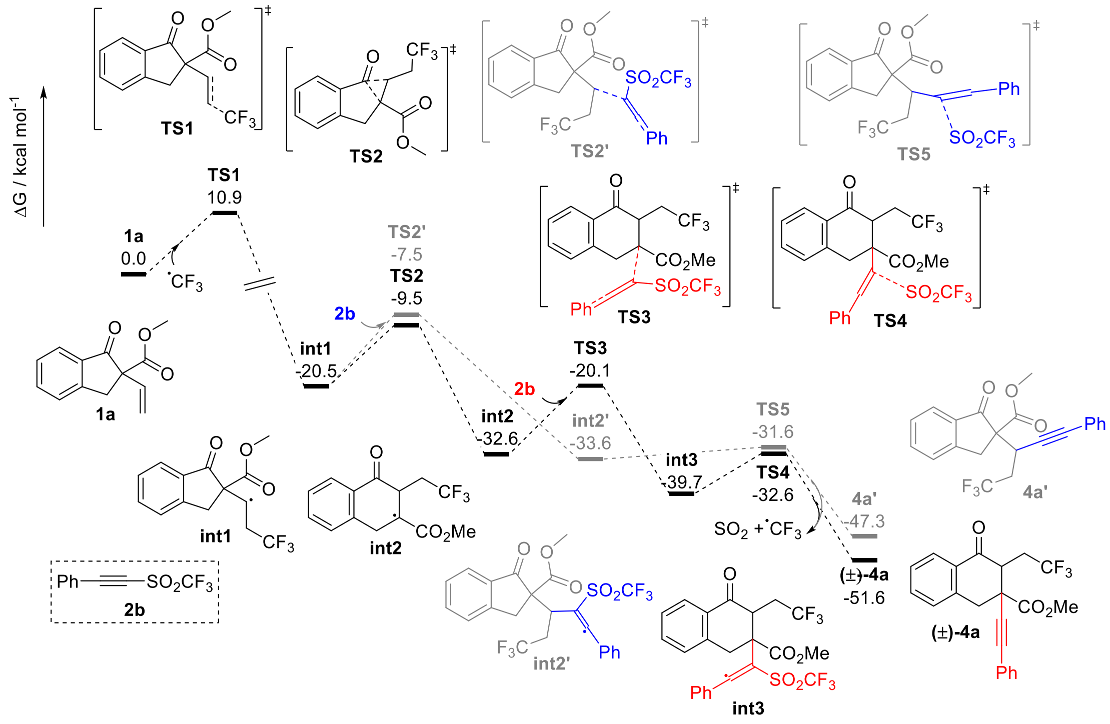


Figure S5. Energy profile for the formations of (±)-**4a** and **4a’**.

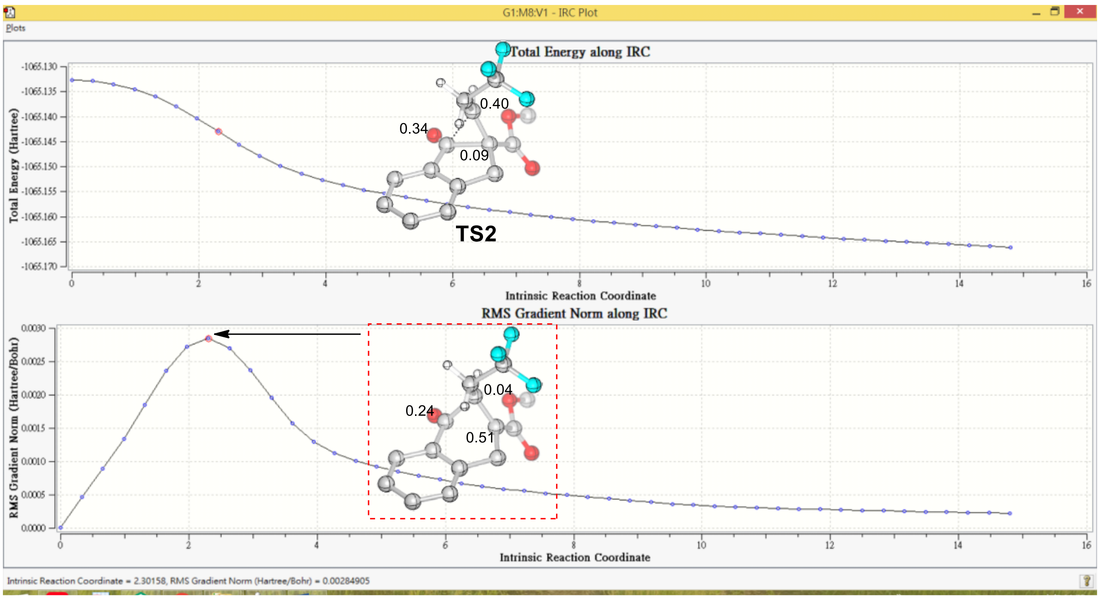


Figure S6. The IRC path and the root mean square (RMS) gradient of **TS2**. The **TS2** and MFP structures are attached with spin densities on O, C2 and C3.

Table S5. Electronic potential energies and correction to zero point energies, thermal energies, enthalpies, free energies (in Hartree) and imaginary frequencies (cm^{-1}) of optimized structures calculated at the B3LYP-D3(SMD)/Def2-TZVP//B3LYP-D3(SMD)/Def2-SVP.

Entry	Structure	$E_{el,Def2-TZVP}$	$E_{el, Def2-SVP}$	cZPE	cU_{358}	cH_{358}	cG_{358}	Imaginary Frequency
1	**1a**	-728.587131	-727.777234	0.220686	0.240571	0.241705	0.166326	
2	$\cdot CF_3$	-337.714109	-337.298951	0.012105	0.016540	0.017675	-0.020960	
3	**TS1**	-1066.307423	-1065.087828	0.233251	0.258921	0.260055	0.168968	-125.3738
4	**int1**	-1066.362464	-1065.149043	0.236018	0.261020	0.262155	0.173894	
5	**TS2**	-1066.346928	-1065.132642	0.235969	0.259955	0.261089	0.175912	-330.4427
6	**int2**	-1066.383597	-1065.169612	0.237731	0.262294	0.263428	0.175796	
7	**2b**	-1194.403443	-1193.283065	0.125230	0.138700	0.139644	0.081935	
8	**TS3**	-2260.797098	-2258.474146	0.364037	0.408298	0.409432	0.275637	-261.5328
9	**int3**	-2260.831244	-2258.519304	0.366284	0.410293	0.411427	0.278562	
10	**TS3'**	-2260.790439	-2258.467438	0.365300	0.409211	0.410345	0.276773	-221.1962
11	**TS4**	-2260.819190	-2258.509318	0.365706	0.409500	0.410634	0.277843	-162.6909
12	**(±)-4a**	-1374.359375	-1372.816838	0.342285	0.376319	0.377454	0.266259	
13	SO_2	-548.719511	-548.356817	0.006745	0.010581	0.011716	-0.024055	
14	**TS2'**	-2260.775005	-2258.453294	0.363110	0.407521	0.408655	0.273540	-188.3597
15	**int2'**	-2260.822415	-2258.509793	0.366056	0.409998	0.411132	0.279324	
16	**TS5**	-2260.815976	-2258.505577	0.364590	0.408713	0.409847	0.276099	-151.8508
17	**4a'**	-1374.354064	-1372.813116	0.341920	0.375845	0.376979	0.267913	

18	**TS3$_{DCE}$**	-2260.803243	-2258.478957	0.364022	0.408448	0.409582	0.273442	-247.3494
19	**TS3'$_{DCE}$**	-2260.799012	-2258.474202	0.364726	0.408956	0.410091	0.274995	-204.8664
20	**TS3$_{EA}$**	-2260.802801	-2258.478921	0.364217	0.408570	0.409705	0.274659	-244.0109
21	**TS3'$_{EA}$**	-2260.798550	-2258.474143	0.364839	0.409066	0.410200	0.275131	-204.6814

Coordinate of optimized structures

Structure S1. **1a**

E(B3LYP)$_{tzvp}$ = -728.587131252

E(B3LYP)$_{svp}$ = -727.777233675

6	-1.616406	-0.696385	0.469301
6	-1.431777	0.362971	-0.429105
6	-2.496994	0.942900	-1.131996
6	-3.777551	0.441398	-0.910204
6	-3.973558	-0.618487	-0.003428
6	-2.903233	-1.194237	0.690503
6	-0.013397	0.731141	-0.491516
1	-2.311750	1.766932	-1.825833
1	-4.634980	0.868916	-1.435868
1	-4.985540	-0.999152	0.160445
1	-3.072716	-2.018446	1.388133
8	0.507604	1.558489	-1.214967
6	0.743838	-0.126844	0.573225
6	-0.308951	-1.160556	1.058567
1	-0.352982	-1.218234	2.156818
1	-0.060057	-2.167315	0.689487
6	1.227376	0.744808	1.724211
6	1.135269	2.072030	1.827850
1	0.708251	2.702404	1.042904
1	1.504091	2.581054	2.723491
1	1.677690	0.168708	2.541387
6	1.929925	-0.785103	-0.137090
8	1.957841	-1.932296	-0.530273
8	2.921247	0.082102	-0.325469
6	4.053906	-0.370367	-1.083798
1	3.739058	-0.690559	-2.088675
1	4.733122	0.488082	-1.153324
1	4.551583	-1.208370	-0.572405

Structure S2. ·CF_3

E(B3LYP)$_{tzvp}$ = -337.714108563

E(B3LYP)$_{svp}$ = -337.298951081

6	0.000047	-0.000119	0.321013
9	-0.177841	1.246321	-0.071319
9	-0.990745	-0.777080	-0.071341
9	1.168555	-0.469161	-0.071348

Structure S3. **TS1**

E(B3LYP)$_{tzvp}$ = -1066.30742279

E(B3LYP)$_{svp}$ = -1065.08782840

6	-0.747621	-1.217166	0.824695
6	-0.506985	-1.356965	-0.548892
6	-1.406027	-2.009901	-1.402929
6	-2.580368	-2.517047	-0.851731
6	-2.836165	-2.368586	0.525277
6	-1.928631	-1.722743	1.371924
6	0.744808	-0.684733	-0.910876
1	-1.185733	-2.096001	-2.470017
1	-3.312223	-3.023663	-1.485779
1	-3.767226	-2.764808	0.939930
1	-2.143868	-1.612797	2.437739
8	1.294588	-0.659778	-1.995199
6	1.248527	0.074466	0.359449
6	0.381172	-0.497764	1.516020
1	0.016595	0.289679	2.191285
1	0.972454	-1.203746	2.119630
6	1.001962	1.564896	0.204988
6	0.299888	2.160526	-0.778762
1	-0.024597	1.629685	-1.677299
1	0.166871	3.245480	-0.775607
1	1.362384	2.163646	1.049066

6	2.737111	-0.222927	0.527273
8	3.200771	-1.063836	1.268074
8	3.475546	0.526274	-0.288176
6	4.892035	0.285001	-0.291034
1	5.103128	-0.752621	-0.591391
1	5.317130	0.986762	-1.018966
1	5.315779	0.467202	0.708202
6	-2.079822	1.934731	-0.011237
9	-2.059790	1.658056	1.286588
9	-2.715404	0.979994	-0.676187
9	-2.658945	3.108524	-0.222553

Frequencies -- -125.3738

Red. masses -- 7.5649

Frc consts -- 0.0701

IR Inten -- 9.6491

Structure S4. int1

E(B3LYP)$_{tzvp}$ = -1066.36246354

E(B3LYP)$_{svp}$ = -1065.14904328

6	1.540330	0.807425	-0.796719
6	1.461261	0.643432	0.593230
6	2.331751	1.299026	1.474127
6	3.309947	2.129502	0.931042
6	3.400892	2.294564	-0.464433
6	2.522226	1.641477	-1.336448
6	0.370152	-0.276515	0.932604
1	2.237258	1.147823	2.552485
1	4.011710	2.653712	1.584501
1	4.174712	2.949296	-0.874750
1	2.602538	1.785605	-2.416900
8	-0.032289	-0.583597	2.038020
6	-0.190137	-0.859963	-0.411096
6	0.457310	0.038856	-1.509950
1	-0.290878	0.734628	-1.918997
1	0.846797	-0.556386	-2.347158
6	-1.687840	-0.946899	-0.467875

6	-2.614455	-0.104928	0.344912
1	-2.371546	-0.155247	1.419469
1	-3.653786	-0.438683	0.214681
1	-2.110691	-1.599714	-1.235023
6	0.432824	-2.268167	-0.460616
8	1.457205	-2.550276	-1.043011
8	-0.267925	-3.133080	0.268264
6	0.254412	-4.467239	0.381608
1	1.243306	-4.449808	0.864478
1	-0.462419	-5.019976	1.000920
1	0.341292	-4.933393	-0.611462
6	-2.595845	1.368309	-0.013730
9	-2.910838	1.586378	-1.306508
9	-1.375279	1.922806	0.184545
9	-3.467348	2.071315	0.731034

Structure S5. TS2

E(B3LYP)$_{tzvp}$ = -1066.34692813

E(B3LYP)$_{svp}$ = -1065.13264248

6	-1.839875	-0.272968	0.833387
6	-1.816370	-0.692392	-0.504327
6	-2.982983	-0.765614	-1.271743
6	-4.189928	-0.381148	-0.681641
6	-4.218312	0.059385	0.651675
6	-3.046053	0.115048	1.417586
6	-0.451104	-1.069933	-0.941898
1	-2.939106	-1.109992	-2.307973
1	-5.116781	-0.419309	-1.259849
1	-5.169486	0.358709	1.100087
1	-3.077565	0.446956	2.458694
8	-0.135015	-1.839865	-1.866834
6	0.497560	-0.691813	0.348354
6	-0.471153	-0.338103	1.473871
1	-0.192946	0.608362	1.962036
1	-0.439472	-1.127250	2.239470
6	0.710755	0.282884	-0.718482

6	0.214910	1.698793	-0.714042
1	-0.711877	1.834400	-0.142076
1	0.034617	2.043366	-1.743056
1	1.522256	0.062485	-1.413291
6	1.541533	-1.726839	0.644605
8	1.556979	-2.387710	1.664365
8	2.427060	-1.868540	-0.339011
6	3.425846	-2.887709	-0.169453
1	2.952014	-3.871752	-0.034649
1	4.026726	-2.877489	-1.086869
1	4.057341	-2.664137	0.703716
6	1.240967	2.639834	-0.113723
9	2.407727	2.616234	-0.786254
9	1.522788	2.326452	1.169076
9	0.799189	3.909317	-0.123868

Frequencies -- -330.4427

Red. masses -- 10.8369

Frc consts -- 0.6972

IR Inten -- 12.4732

Structure S6. int2

E(B3LYP)$_{tzvp}$ = -1066.38359711

E(B3LYP)$_{svp}$ = -1065.16961209

6	1.922429	1.162946	0.358469
6	1.958097	0.018748	-0.465324
6	3.190877	-0.581186	-0.793795
6	4.380936	-0.063327	-0.297449
6	4.347936	1.071390	0.528251
6	3.132878	1.676607	0.848594
6	0.710291	-0.576880	-0.998119
1	3.187755	-1.463605	-1.437317
1	5.334400	-0.535482	-0.546759
1	5.279703	1.487323	0.920880
1	3.116995	2.567523	1.482471
8	0.710734	-1.434415	-1.868562
6	-0.581386	1.312358	0.030671

6	0.628629	1.860875	0.699623
1	0.478095	1.810701	1.799559
1	0.711830	2.940589	0.490715
6	-0.619259	-0.122049	-0.391270
6	-1.020927	-0.996709	0.830836
1	-1.974548	-0.615465	1.222830
1	-0.270435	-0.934012	1.632457
1	-1.384843	-0.271820	-1.164379
6	-1.772033	2.148731	-0.020227
8	-1.811155	3.312580	0.363845
8	-2.848567	1.512468	-0.521500
6	-4.069376	2.257877	-0.581381
1	-3.943909	3.164421	-1.193649
1	-4.811036	1.591130	-1.038945
1	-4.396557	2.550112	0.429017
6	-1.238429	-2.460979	0.529253
9	-0.088551	-3.122688	0.288584
9	-2.037253	-2.654445	-0.538757
9	-1.825254	-3.074742	1.577291

Structure S7. 2b

E(B3LYP)$_{tzvp}$ = -1194.40344275

E(B3LYP)$_{svp}$ = -1193.28306483

6	0.944072	-0.330876	0.250277
6	2.343128	-0.134532	0.105354
6	3.018085	0.779707	0.944667
6	3.057124	-0.849370	-0.882234
6	4.389300	0.972563	0.790457
1	2.460052	1.328292	1.706296
6	4.428340	-0.646108	-1.022521
1	2.529253	-1.554653	-1.527487
6	5.093921	0.262495	-0.189896
1	4.912604	1.680482	1.437620
1	4.982138	-1.197681	-1.786023
1	6.169513	0.418924	-0.306059
6	-0.259129	-0.496564	0.369604

16	-1.935848	-0.711019	0.516005
8	-2.348332	-1.933580	-0.175330
8	-2.364904	-0.432248	1.887656
6	-2.608367	0.714324	-0.524527
9	-2.206080	1.868921	-0.012645
9	-2.174906	0.599713	-1.771925
9	-3.931564	0.642225	-0.496111

Structure S8. TS3

E(B3LYP)$_{tzvp}$ = -2260.79709753

E(B3LYP)$_{svp}$ = -2258.47414642

6	0.409126	-2.191287	0.904307
6	0.066192	-2.206625	-0.463304
6	0.708572	-3.095388	-1.346389
6	1.671863	-3.980486	-0.876569
6	2.014750	-3.969055	0.484246
6	1.392582	-3.081107	1.361283
6	-0.943017	-1.261857	-1.001229
1	0.430501	-3.074870	-2.402252
1	2.165896	-4.672877	-1.562434
1	2.782594	-4.650769	0.859064
1	1.681332	-3.061230	2.415423
8	-1.073865	-1.048594	-2.196288
6	-1.078696	-0.173112	1.233628
6	-0.217803	-1.214634	1.868867
1	-0.848542	-1.776487	2.588679
1	0.555999	-0.737877	2.490518
6	-1.857127	-0.561309	0.006676
6	-3.056864	-1.455319	0.420220
1	-3.648747	-0.920865	1.177348
1	-2.721981	-2.408032	0.855331
1	-2.257349	0.328345	-0.491784
6	-1.569104	0.898205	2.115315
8	-1.128227	1.120468	3.232778
8	-2.551595	1.616453	1.553735
6	-3.056202	2.731733	2.298488
1	-2.242959	3.432172	2.536666
1	-3.796777	3.214921	1.649400
1	-3.532251	2.388850	3.229982
6	-4.004567	-1.783230	-0.708323
9	-3.457301	-2.609252	-1.624226
9	-4.418147	-0.682769	-1.367398
9	-5.106694	-2.401282	-0.239051
6	1.777086	0.612995	0.228238
6	2.969686	-0.126917	0.270593
6	3.731111	-0.193739	1.464267
6	3.391765	-0.838207	-0.880102
6	4.885056	-0.969044	1.499030
1	3.397784	0.355089	2.347255
6	4.551002	-1.605284	-0.826041
1	2.796652	-0.783301	-1.793058
6	5.295994	-1.675195	0.358908
1	5.470009	-1.028470	2.419897
1	4.873997	-2.160095	-1.709990
1	6.202892	-2.284065	0.395322
6	0.648658	1.136645	0.226431
16	-0.086507	2.608636	-0.286393
8	-1.189309	2.345622	-1.214054
8	-0.266664	3.509212	0.856176
6	1.273678	3.393129	-1.346855
9	2.353300	3.607085	-0.608257
9	1.570879	2.587886	-2.356921
9	0.805729	4.543956	-1.807700

Frequencies -- -261.5328

Red. masses -- 9.3941

Frc consts -- 0.3786

IR Inten -- 70.2988

Structure S9. int3

E(B3LYP)$_{tzvp}$ = -2260.83124407

E(B3LYP)$_{svp}$ = -2258.51930379

6	-0.408476	2.038948	1.302434

6	-0.204290	2.258802	-0.077317
6	-0.926110	3.261257	-0.749886
6	-1.835010	4.057769	-0.061210
6	-2.038863	3.843276	1.309513
6	-1.335512	2.841516	1.981022
6	0.714175	1.389383	-0.856543
1	-0.758751	3.395699	-1.820712
1	-2.392216	4.837982	-0.585255
1	-2.761214	4.455361	1.856054
1	-1.517591	2.666194	3.044616
8	0.728247	1.384234	-2.077101
6	0.874307	-0.158538	1.103315
6	0.320730	0.941357	2.041415
1	1.168681	1.374024	2.598522
1	-0.342345	0.483504	2.789612
6	1.676592	0.499900	-0.062169
6	2.902839	1.323548	0.389097
1	3.541058	0.703155	1.027690
1	2.615965	2.218980	0.958958
1	2.025160	-0.287708	-0.742685
6	1.710036	-1.117430	1.971275
8	2.896651	-1.037910	2.186141
8	0.922929	-2.048508	2.511965
6	1.551091	-3.088338	3.279727
1	2.049550	-2.665351	4.164210
1	0.743727	-3.766867	3.579004
1	2.285882	-3.619218	2.656270
6	3.773153	1.794253	-0.750541
9	3.189327	2.750430	-1.504570
9	4.115193	0.792068	-1.585901
9	4.920107	2.324180	-0.279877
6	-1.551813	-0.611697	0.380842
6	-2.839260	-0.161142	0.193257
6	-3.853582	-0.355898	1.181687
6	-3.163649	0.547396	-1.008779
6	-5.128528	0.147915	0.968322
1	-3.608435	-0.896170	2.098198
6	-4.447085	1.039497	-1.193188
1	-2.388187	0.693761	-1.762783
6	-5.434599	0.847086	-0.212053
1	-5.899807	0.000439	1.728621
1	-4.687254	1.584167	-2.109810
1	-6.442024	1.240971	-0.366883
6	-0.304436	-0.947312	0.495388
16	0.116416	-2.599042	-0.197972
8	1.579952	-2.754455	-0.296908
8	-0.713112	-3.653455	0.396641
6	-0.474509	-2.471869	-1.997055
9	-1.800873	-2.479510	-2.043424
9	-0.013540	-1.358112	-2.551428
9	0.003633	-3.525896	-2.644058

Structure S10. TS3'

E(B3LYP)$_{tzvp}$ = -2260.79043877

E(B3LYP)$_{svp}$ = -2258.46743782

6	-2.627700	1.721633	0.093625
6	-3.537093	0.642836	0.160277
6	-4.924052	0.882537	0.115058
6	-5.410673	2.179513	-0.008267
6	-4.508635	3.251815	-0.077721
6	-3.132310	3.023679	-0.022607
6	-3.057635	-0.757769	0.292882
1	-5.604122	0.029884	0.176229
1	-6.487221	2.363051	-0.046439
1	-4.883363	4.274949	-0.168421
1	-2.435696	3.865259	-0.063085
8	-3.799663	-1.692247	0.537893
6	-0.833766	0.145810	0.739938
6	-1.126354	1.490643	0.155403
1	-0.719864	1.557649	-0.868501
1	-0.646695	2.285565	0.740794
6	-1.543370	-1.003358	0.086759
6	-1.206021	-1.138985	-1.414010
1	-0.115519	-1.171750	-1.534199

1	-1.590288	-0.295771	-2.005465
1	-1.309359	-1.947931	0.587699
6	-0.489188	0.099071	2.172079
8	-0.147328	1.074323	2.825123
8	-0.538458	-1.140546	2.680218
6	-0.109691	-1.305066	4.038023
1	-0.805133	-0.797624	4.724193
1	-0.112273	-2.385673	4.226274
1	0.903173	-0.898931	4.172694
6	-1.733342	-2.398710	-2.056095
9	-3.077794	-2.402438	-2.174213
9	-1.395361	-3.510173	-1.373577
9	-1.234988	-2.534887	-3.302016
6	1.961799	1.091728	-0.153951
6	2.290551	2.411257	-0.510649
6	2.583517	2.748719	-1.854441
6	2.307334	3.412051	0.493723
6	2.887937	4.067232	-2.179216
1	2.569339	1.970920	-2.620839
6	2.612387	4.724779	0.148098
1	2.066894	3.139711	1.523733
6	2.902937	5.054206	-1.183493
1	3.115241	4.331284	-3.214819
1	2.621949	5.499431	0.918686
1	3.141843	6.087619	-1.447327
6	1.507177	-0.006885	0.200810
16	2.007423	-1.581588	0.686836
8	2.405573	-1.574739	2.097041
8	1.095817	-2.607751	0.175371
6	3.599517	-1.801516	-0.312136
9	3.317415	-1.732405	-1.606370
9	4.470777	-0.857179	0.011658
9	4.093822	-2.994679	-0.017736

Frequencies -- -221.1962

Red. masses -- 11.2780

Frc consts -- 0.3251

IR Inten -- 30.2409

Structure S11. TS4

E(B3LYP)$_{tzvp}$ = -2260.81918959

E(B3LYP)$_{svp}$ = -2258.50931831

6	0.422971	2.516235	0.993384
6	0.683991	2.402566	-0.391142
6	0.336171	3.448081	-1.266584
6	-0.251659	4.610628	-0.778540
6	-0.506094	4.729398	0.595251
6	-0.176733	3.690383	1.468328
6	1.288329	1.169082	-0.955816
1	0.538453	3.325842	-2.332889
1	-0.516231	5.422769	-1.460023
1	-0.974803	5.636040	0.987106
1	-0.397275	3.784642	2.535005
8	1.387229	0.974758	-2.156617
6	0.839799	0.024779	1.246152
6	0.756841	1.397309	1.949712
1	1.726554	1.591783	2.434979
1	0.013460	1.352681	2.758487
6	1.822999	0.127044	0.031681
6	3.265280	0.460925	0.463639
1	3.569241	-0.180462	1.302286
1	3.370619	1.505196	0.790676
1	1.843225	-0.832020	-0.499909
6	1.346554	-1.037035	2.238316
8	2.015765	-0.791798	3.215909
8	0.987774	-2.255991	1.863989
6	1.411689	-3.380228	2.650883
1	1.011627	-3.300504	3.672341
1	1.002301	-4.261643	2.143419
1	2.510327	-3.426143	2.682919
6	4.295266	0.235840	-0.618367
9	4.197746	1.120260	-1.630888
9	4.210127	-0.996019	-1.160036
9	5.539150	0.359512	-0.113834
6	-1.733659	0.013002	0.769728

6	-3.096073	0.297177	0.626752
6	-4.047943	-0.237264	1.535958
6	-3.534121	1.123121	-0.444965
6	-5.397164	0.052745	1.371029
1	-3.706900	-0.877081	2.352377
6	-4.886988	1.402943	-0.591089
1	-2.799125	1.523790	-1.145696
6	-5.820112	0.871271	0.312529
1	-6.130096	-0.360379	2.068232
1	-5.223694	2.037020	-1.414826
1	-6.882991	1.094761	0.190088
6	-0.533417	-0.339769	0.764813
16	-0.501044	-2.344320	-0.396764
8	0.756371	-2.892236	-0.973787
8	-1.420736	-3.258861	0.318807
6	-1.488476	-1.814635	-1.962349
9	-2.788967	-1.799132	-1.691116
9	-1.100681	-0.599296	-2.341572
9	-1.250031	-2.675962	-2.942394

Frequencies -- -162.6909
Red. masses -- 10.0747
Frc consts -- 0.1571
IR Inten -- 2.7578

Structure S12. (±)-4a

E(B3LYP)$_{tzvp}$ = -1374.35937513
E(B3LYP)$_{svp}$ = -1372.81683819

6	0.551109	1.822693	1.440189
6	0.717635	2.094812	0.063636
6	0.634310	3.416771	-0.413690
6	0.404697	4.470656	0.464097
6	0.243934	4.205216	1.832047
6	0.311341	2.895566	2.310601
6	0.962121	0.998554	-0.908660
1	0.757743	3.593658	-1.484519
1	0.346736	5.496364	0.091607
1	0.056618	5.026604	2.528904
1	0.168788	2.696291	3.376130
8	0.951357	1.180788	-2.116540
6	0.358860	-0.651740	0.896552
6	0.625291	0.415733	1.980875
1	1.623952	0.235655	2.412626
1	-0.087606	0.286989	2.807000
6	1.266150	-0.391139	-0.347154
6	2.762428	-0.558671	-0.016556
1	2.926938	-1.519749	0.492745
1	3.134883	0.239164	0.641866
1	1.002449	-1.111717	-1.131761
6	0.611454	-2.055271	1.482607
8	0.726040	-2.285774	2.665068
8	0.676202	-2.979750	0.530758
6	0.894972	-4.338034	0.949585
1	0.060333	-4.683095	1.578032
1	0.950742	-4.931858	0.029447
1	1.836543	-4.415590	1.513790
6	3.665974	-0.579432	-1.227127
9	3.752111	0.620029	-1.836838
9	3.260218	-1.466740	-2.157320
9	4.920427	-0.924961	-0.873611
6	-2.207339	-0.557727	0.105116
6	-3.568089	-0.474391	-0.332123
6	-4.598635	-1.097434	0.403412
6	-3.892937	0.237399	-1.506942
6	-5.921957	-1.008349	-0.030667
1	-4.352072	-1.649116	1.313563
6	-5.219663	0.321178	-1.931276
1	-3.097346	0.721343	-2.078399
6	-6.236651	-0.300170	-1.196504
1	-6.713507	-1.494961	0.545285
1	-5.461863	0.875549	-2.841815
1	-7.274734	-0.232610	-1.532412
6	-1.048706	-0.617887	0.467575

Structure S13. SO_2

E(B3LYP)$_{tzvp}$ = -548.719510573

E(B3LYP)$_{svp}$ = -548.356816805

16	0.000000	0.381093	0.000000
8	1.251551	-0.381094	0.000000
8	-1.251551	-0.381092	0.000000

Structure S14. TS2'

E(B3LYP)$_{tzvp}$ = -2260.77500473

E(B3LYP)$_{svp}$ = -2258.45329364

6	-3.859028	-0.583994	-0.841025
6	-3.384911	0.706705	-0.567517
6	-4.221377	1.830200	-0.596622
6	-5.561822	1.640634	-0.927766
6	-6.043887	0.348521	-1.211735
6	-5.204233	-0.770571	-1.167407
6	-1.954967	0.657300	-0.234723
1	-3.818693	2.820533	-0.369069
1	-6.244413	2.493076	-0.969268
1	-7.098339	0.217367	-1.469951
1	-5.595061	-1.768431	-1.382008
8	-1.272714	1.560198	0.212428
6	-1.455307	-0.781630	-0.539155
6	-2.774303	-1.618428	-0.685858
1	-2.955688	-2.228567	0.210733
1	-2.714545	-2.313328	-1.534100
6	-0.506098	-1.354956	0.487947
6	-0.535276	-0.978987	1.938669
1	-0.447747	0.108551	2.076485
1	0.305840	-1.462495	2.455845
1	-0.158379	-2.364330	0.249195
6	-0.713359	-0.810977	-1.896692
8	-0.632718	-1.803259	-2.584424
8	-0.138589	0.347259	-2.197300
6	0.730685	0.369344	-3.344367
1	0.201325	0.010541	-4.238869
1	1.035883	1.414444	-3.473256
1	1.608649	-0.264832	-3.150795
6	-1.791724	-1.392589	2.677945
9	-2.062233	-2.707778	2.546733
9	-2.882995	-0.725951	2.231591
9	-1.690688	-1.137132	3.993311
6	1.812983	0.973808	0.318751
6	1.812729	2.372944	0.488432
6	1.376085	3.212021	-0.565215
6	2.241097	2.941368	1.711676
6	1.374277	4.592474	-0.389446
1	1.032382	2.765275	-1.499234
6	2.231622	4.324840	1.869915
1	2.575717	2.289092	2.521081
6	1.800112	5.151106	0.823783
1	1.034300	5.240609	-1.200868
1	2.561921	4.763749	2.814514
1	1.794021	6.236182	0.955129
6	1.704305	-0.249098	0.172763
16	2.517070	-1.715771	-0.137515
8	2.519092	-2.554332	1.065267
8	2.107459	-2.281716	-1.426906
6	4.306700	-1.158118	-0.387266
9	4.367981	-0.323674	-1.417010
9	4.747760	-0.556085	0.707915
9	5.036135	-2.236247	-0.635690

Frequencies -- -188.3597

Red. masses -- 9.4212

Frc consts -- 0.1969

IR Inten -- 28.9053

Structure S15. int2'

E(B3LYP)$_{tzvp}$ = -2260.82241505

E(B3LYP)$_{svp}$ = -2258.50979298

6	-3.807998	-0.307306	-0.740964

6	-3.228721	0.958951	-0.905103
6	-3.978415	2.081289	-1.281906
6	-5.341244	1.909519	-1.514869
6	-5.929158	0.638906	-1.362081
6	-5.174854	-0.474125	-0.972970
6	-1.793958	0.898242	-0.607112
1	-3.492270	3.054139	-1.390546
1	-5.959248	2.758356	-1.817780
1	-6.999980	0.521047	-1.549786
1	-5.648560	-1.451491	-0.850624
8	-1.015139	1.829945	-0.525159
6	-1.424893	-0.602433	-0.394819
6	-2.796413	-1.325152	-0.281606
1	-3.014471	-1.648634	0.742618
1	-2.814621	-2.232879	-0.897559
6	-0.489544	-0.816074	0.855746
6	-0.841043	-0.010622	2.129446
1	-0.784794	1.069954	1.938536
1	-0.077467	-0.249858	2.882314
1	-0.558272	-1.887299	1.103003
6	-0.748114	-1.094658	-1.703898
8	-1.067640	-2.097092	-2.301531
8	0.210617	-0.275522	-2.124138
6	0.917968	-0.660055	-3.316343
1	0.217748	-0.753033	-4.159584
1	1.644291	0.138236	-3.506451
1	1.431069	-1.618924	-3.157236
6	-2.160374	-0.260065	2.816196
9	-2.421147	-1.573981	2.989191
9	-3.212206	0.268373	2.153227
9	-2.158956	0.303394	4.038392
6	1.574175	0.664986	0.535213
6	2.287510	1.833887	0.391381
6	2.296584	2.505791	-0.873456
6	3.027769	2.393032	1.479859
6	3.021772	3.678225	-1.025681
1	1.720896	2.086290	-1.699863
6	3.743385	3.567818	1.297569
1	3.026125	1.880045	2.443670
6	3.747788	4.216913	0.051012
1	3.024562	4.187473	-1.992868
1	4.309682	3.988661	2.132403
1	4.314972	5.141545	-0.081123
6	0.980159	-0.485515	0.576869
16	1.980549	-1.995712	0.339235
8	2.321537	-2.587934	1.640651
8	1.387900	-2.845733	-0.707513
6	3.628190	-1.374852	-0.377837
9	3.421834	-0.618876	-1.449885
9	4.297555	-0.687627	0.537351
9	4.318465	-2.453700	-0.720859

Structure S16. TS5

E(B3LYP)$_{tzvp}$ = -2260.81597605

E(B3LYP)$_{svp}$ = -2258.50557659

6	-3.897769	0.081460	-0.746117
6	-3.491890	1.164349	0.047661
6	-4.391446	2.142948	0.490439
6	-5.726068	2.027903	0.106619
6	-6.139771	0.948231	-0.697122
6	-5.236580	-0.031220	-1.126437
6	-2.052763	1.074258	0.321265
1	-4.039600	2.968929	1.113872
1	-6.456900	2.774966	0.425975
1	-7.190589	0.873648	-0.990259
1	-5.574425	-0.867125	-1.744244
8	-1.396361	1.763993	1.081427
6	-1.490871	-0.093983	-0.528414
6	-2.751496	-0.850089	-1.047540
1	-2.889952	-1.813784	-0.540673
1	-2.670993	-1.080885	-2.119206
6	-0.444596	-0.971610	0.254511
6	-0.754428	-1.305248	1.731442
1	-0.824550	-0.389235	2.333428

1	0.085868	-1.898579	2.119001
1	-0.350840	-1.915122	-0.304700
6	-0.740908	0.444078	-1.761419
8	-0.342820	-0.286486	-2.643639
8	-0.544524	1.754622	-1.744373
6	0.249349	2.302693	-2.816325
1	-0.230737	2.103932	-3.785705
1	0.301925	3.381472	-2.629839
1	1.252744	1.852959	-2.799560
6	-1.995758	-2.113126	2.010674
9	-2.093148	-3.207392	1.225590
9	-3.130997	-1.400185	1.833562
9	-2.004216	-2.539703	3.285694
6	1.568328	0.679711	0.653962
6	2.432640	1.736397	0.974794
6	2.215952	3.011976	0.388929
6	3.509129	1.552435	1.881053
6	3.067041	4.066757	0.698588
1	1.373217	3.148837	-0.290331
6	4.352277	2.618366	2.174603
1	3.670917	0.570895	2.330097
6	4.136178	3.873532	1.586234
1	2.900317	5.048319	0.248270
1	5.185374	2.476000	2.867168
1	4.802918	4.706608	1.823149
6	0.868768	-0.268782	0.251707
16	2.150800	-1.344035	-1.411136
8	1.550845	-2.583931	-1.974954
8	2.867754	-0.389821	-2.294997
6	3.517866	-2.015841	-0.255200
9	4.277274	-1.010279	0.167844
9	2.943221	-2.607872	0.788683
9	4.268339	-2.896286	-0.904639

Frequencies -- -151.8508
Red. masses -- 12.2794
Frc consts -- 0.1668
IR Inten -- 0.4096

Structure S17. 4a'

E(B3LYP)$_{tzvp}$ = -1374.35406445

E(B3LYP)$_{svp}$ = -1372.81311631

6	-3.050236	-0.947581	0.495617
6	-2.453839	-1.182604	-0.751844
6	-3.123238	-1.849579	-1.785738
6	-4.418809	-2.302286	-1.542855
6	-5.021835	-2.077996	-0.290493
6	-4.349786	-1.399968	0.733463
6	-1.099495	-0.615633	-0.774600
1	-2.627762	-2.006280	-2.747428
1	-4.971449	-2.833596	-2.321725
1	-6.038999	-2.439388	-0.115733
1	-4.835840	-1.227076	1.697113
8	-0.354697	-0.512383	-1.733056
6	-0.773893	-0.131007	0.659544
6	-2.138452	-0.168750	1.410316
1	-2.535795	0.838767	1.589050
1	-2.040546	-0.636506	2.400170
6	-0.024469	1.255356	0.676984
6	-0.521382	2.337317	-0.312983
1	-0.399054	2.000128	-1.351097
1	0.110026	3.226829	-0.177292
1	-0.130338	1.644032	1.703410
6	0.167890	-1.127748	1.363394
8	0.396925	-1.081816	2.552052
8	0.704697	-2.020428	0.539418
6	1.645309	-2.949821	1.106591
1	1.176354	-3.517757	1.923670
1	1.933808	-3.622301	0.290229
1	2.525930	-2.412363	1.487873
6	-1.941784	2.821149	-0.173289
9	-2.259100	3.155130	1.096608
9	-2.849620	1.902739	-0.574959
9	-2.144430	3.915549	-0.929417
6	2.565232	0.788809	0.164469

6	3.903718	0.392917	-0.153410
6	4.118682	-0.836517	-0.814563
6	5.011605	1.197170	0.184180
6	5.415082	-1.247464	-1.126096
1	3.258565	-1.456035	-1.079011
6	6.304422	0.777693	-0.134712
1	4.849973	2.148450	0.696514
6	6.510408	-0.442931	-0.788360
1	5.572021	-2.200741	-1.637781
1	7.157910	1.407725	0.129511
1	7.524854	-0.766839	-1.035522
6	1.403754	1.044341	0.412829

Structure S18. TS3$_{DCE}$

E(B3LYP)$_{tzvp}$ = -2260.80324330

E(B3LYP)$_{svp}$ = -2258.47895667

6	0.360344	-2.216506	0.929936
6	0.011486	-2.260111	-0.434410
6	0.621355	-3.194792	-1.292304
6	1.560144	-4.095192	-0.801428
6	1.910754	-4.054270	0.556859
6	1.319140	-3.122433	1.409062
6	-0.974470	-1.301278	-1.003258
1	0.336626	-3.192417	-2.346522
1	2.028340	-4.822761	-1.468759
1	2.658890	-4.748055	0.948788
1	1.611491	-3.081537	2.461711
8	-1.109450	-1.139727	-2.201436
6	-1.081163	-0.153202	1.218623
6	-0.245469	-1.204911	1.871468
1	-0.889531	-1.738941	2.600758
1	0.534662	-0.734342	2.489561
6	-1.856216	-0.531412	-0.014024
6	-3.101147	-1.357334	0.408289
1	-3.674788	-0.773623	1.142249
1	-2.815250	-2.310913	0.875868
1	-2.207585	0.367466	-0.533352
6	-1.564698	0.925648	2.100358
8	-1.135361	1.135972	3.219749
8	-2.542570	1.649574	1.529115
6	-3.023850	2.779401	2.262971
1	-2.201643	3.480374	2.464998
1	-3.778682	3.255674	1.624809
1	-3.477734	2.461333	3.214341
6	-4.057349	-1.677926	-0.716234
9	-3.561474	-2.585712	-1.580294
9	-4.391500	-0.587327	-1.432092
9	-5.203237	-2.195825	-0.226519
6	1.799710	0.576491	0.203572
6	2.983704	-0.182054	0.238779
6	3.794088	-0.198251	1.401227
6	3.354567	-0.952801	-0.890551
6	4.945169	-0.979396	1.426467
1	3.502117	0.396800	2.268853
6	4.510507	-1.726134	-0.847362
1	2.721934	-0.938818	-1.779349
6	5.305031	-1.743410	0.306879
1	5.568164	-0.996614	2.323784
1	4.791858	-2.326009	-1.715879
1	6.209685	-2.355826	0.335152
6	0.688433	1.131854	0.205583
16	-0.035135	2.620871	-0.294390
8	-1.112708	2.381136	-1.253009
8	-0.221368	3.502430	0.858971
6	1.362151	3.403844	-1.307566
9	2.427407	3.598007	-0.540343
9	1.682974	2.613489	-2.323826
9	0.921598	4.567841	-1.765982

Frequencies -- -247.3494

Red. masses -- 9.4704

Frc consts -- 0.3414

IR Inten -- 57.4969

Structure S19. TS3'DCE

E(B3LYP)tzvp = -2260.79901217

E(B3LYP)svp = -2258.47420180

6	-2.644814	1.640665	0.416695
6	-3.534299	0.557976	0.248723
6	-4.918276	0.789225	0.137073
6	-5.420777	2.085964	0.173567
6	-4.538035	3.164349	0.335263
6	-3.165559	2.941423	0.460723
6	-3.034383	-0.845082	0.197310
1	-5.580941	-0.070582	0.016847
1	-6.494839	2.263807	0.080349
1	-4.925344	4.186055	0.370517
1	-2.484130	3.784697	0.601814
8	-3.759120	-1.812727	0.302972
6	-0.845563	-0.012245	0.872622
6	-1.146716	1.418106	0.555646
1	-0.667974	1.705207	-0.396243
1	-0.736351	2.078502	1.330787
6	-1.506739	-1.023628	-0.016309
6	-1.123638	-0.864139	-1.501727
1	-0.035910	-0.972634	-1.598120
1	-1.410324	0.115945	-1.908423
1	-1.260421	-2.041894	0.298609
6	-0.556747	-0.338688	2.285273
8	-0.275544	0.487884	3.133897
8	-0.606509	-1.658871	2.527563
6	-0.226055	-2.088740	3.838172
1	-0.922362	-1.694943	4.594644
1	-0.266349	-3.185133	3.821513
1	0.795221	-1.753869	4.069032
6	-1.730445	-1.903639	-2.412478
9	-3.060753	-1.739370	-2.573681
9	-1.538808	-3.159197	-1.967745
9	-1.180485	-1.830383	-3.642348
6	1.943224	1.111368	0.013808
6	2.267048	2.438089	-0.329450
6	2.390811	2.811423	-1.690942
6	2.457402	3.406320	0.687953
6	2.696215	4.129064	-2.018729
1	2.247958	2.059494	-2.469698
6	2.759622	4.719650	0.340230
1	2.356978	3.111620	1.734529
6	2.879601	5.083533	-1.008316
1	2.792262	4.417499	-3.068149
1	2.902056	5.467604	1.123768
1	3.117662	6.116640	-1.273497
6	1.517277	-0.010178	0.327264
16	2.042205	-1.632117	0.604669
8	2.396345	-1.817003	2.011615
8	1.181389	-2.585722	-0.096065
6	3.673108	-1.656492	-0.358785
9	3.440983	-1.353309	-1.631192
9	4.525376	-0.782682	0.159066
9	4.174959	-2.880454	-0.273474

Frequencies -- -204.8664

Red. masses -- 10.9921

Frc consts -- 0.2718

IR Inten -- 34.5494

Structure S20. TS3EA

E(B3LYP)tzvp = -2260.80280097

E(B3LYP)svp = -2258.47892119

6	0.353138	-2.211631	0.931797
6	0.007844	-2.259360	-0.432948
6	0.614645	-3.201513	-1.284380
6	1.547460	-4.104437	-0.786893
6	1.895867	-4.058318	0.571545
6	1.306798	-3.119476	1.417519
6	-0.969557	-1.295084	-1.010846
1	0.332462	-3.201790	-2.339285
1	2.012826	-4.838149	-1.449564
1	2.639830	-4.753710	0.968617

1	1.597255	-3.075066	2.470640
8	-1.090252	-1.132106	-2.209072
6	-1.084258	-0.142206	1.209043
6	-0.251416	-1.193573	1.867266
1	-0.895448	-1.722593	2.600211
1	0.528544	-0.720987	2.484081
6	-1.855821	-0.523322	-0.025460
6	-3.097230	-1.353285	0.399537
1	-3.670866	-0.773704	1.136821
1	-2.806257	-2.306704	0.864741
1	-2.208072	0.373897	-0.547376
6	-1.571457	0.935789	2.091042
8	-1.148093	1.141555	3.212737
8	-2.548786	1.659135	1.516750
6	-3.029879	2.789798	2.248970
1	-2.204760	3.482237	2.466746
1	-3.771159	3.276422	1.602628
1	-3.500730	2.471703	3.192265
6	-4.058489	-1.677666	-0.720145
9	-3.557030	-2.571546	-1.594209
9	-4.414259	-0.586091	-1.421860
9	-5.192036	-2.215752	-0.222438
6	1.798808	0.574521	0.198002
6	2.974072	-0.198702	0.234591
6	3.782045	-0.226905	1.398101
6	3.337128	-0.973397	-0.894144
6	4.922084	-1.023973	1.425501
1	3.497140	0.372025	2.265494
6	4.481781	-1.763181	-0.848967
1	2.706947	-0.950169	-1.784526
6	5.273496	-1.792542	0.306613
1	5.543030	-1.049862	2.324104
1	4.756306	-2.366387	-1.717418
1	6.169406	-2.417727	0.336452
6	0.693534	1.140479	0.199370
16	-0.027934	2.631421	-0.305188
8	-1.085614	2.391388	-1.284421
8	-0.234099	3.507628	0.848009
6	1.391866	3.418945	-1.283276
9	2.429736	3.631433	-0.483446
9	1.756622	2.624579	-2.281843
9	0.954799	4.574183	-1.766722

Frequencies -- -244.0109
Red. masses -- 9.5090
Frc consts -- 0.3336
IR Inten -- 49.6217

Structure S21. TS3'$_{EA}$

E(B3LYP)$_{tzvp}$ = -2260.79854998
E(B3LYP)$_{svp}$ = -2258.47414267

6	-2.649032	1.620829	0.427395
6	-3.532554	0.534378	0.255896
6	-4.917043	0.759127	0.141559
6	-5.425785	2.053384	0.177690
6	-4.548925	3.135831	0.342373
6	-3.175925	2.919109	0.471221
6	-3.026028	-0.867522	0.206626
1	-5.574747	-0.104241	0.020335
1	-6.500566	2.225965	0.082416
1	-4.941245	4.155657	0.377914
1	-2.499089	3.765605	0.615876
8	-3.745228	-1.836900	0.320752
6	-0.841613	-0.025897	0.882324
6	-1.150526	1.404865	0.573395
1	-0.666783	1.703590	-0.372496
1	-0.749361	2.060802	1.357104
6	-1.496610	-1.036118	-0.012702
6	-1.115417	-0.860853	-1.496717
1	-0.028479	-0.976011	-1.595677
1	-1.395297	0.127041	-1.889348
1	-1.242859	-2.055010	0.293776
6	-0.549858	-0.356506	2.294370
8	-0.281762	0.468701	3.147612
8	-0.583125	-1.679053	2.527367

6	-0.192340	-2.112918	3.833149
1	-0.887042	-1.729188	4.596249
1	-0.223478	-3.209533	3.811048
1	0.827378	-1.771200	4.060243
6	-1.731116	-1.881465	-2.423473
9	-3.060317	-1.704527	-2.576863
9	-1.544306	-3.144478	-2.003007
9	-1.184073	-1.786708	-3.653706
6	1.938821	1.116319	0.021295
6	2.249467	2.447609	-0.318503
6	2.361093	2.828650	-1.678722
6	2.439287	3.412920	0.701484
6	2.653443	4.150166	-2.002757
1	2.219488	2.079396	-2.460391
6	2.728662	4.730216	0.357809
1	2.349071	3.112808	1.747508
6	2.836241	5.101494	-0.989561
1	2.739944	4.443918	-3.051585
1	2.870869	5.475525	1.143974
1	3.064215	6.137727	-1.251558
6	1.522860	-0.009216	0.332732
16	2.059892	-1.630706	0.603517
8	2.435104	-1.813252	2.004644
8	1.196790	-2.586970	-0.089148
6	3.676327	-1.639777	-0.384927
9	3.421667	-1.336759	-1.653757
9	4.530696	-0.759336	0.119074
9	4.190210	-2.859248	-0.309875

Frequencies -- -204.6814

Red. masses -- 10.9794

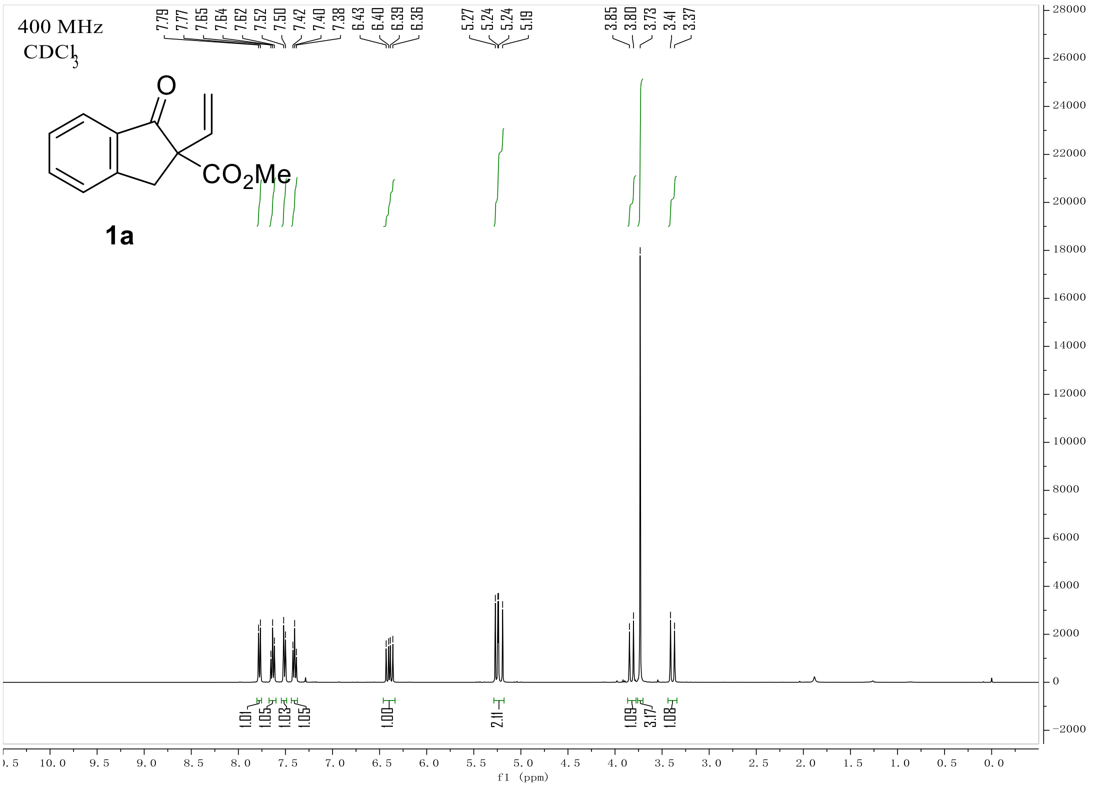
Frc consts -- 0.2710

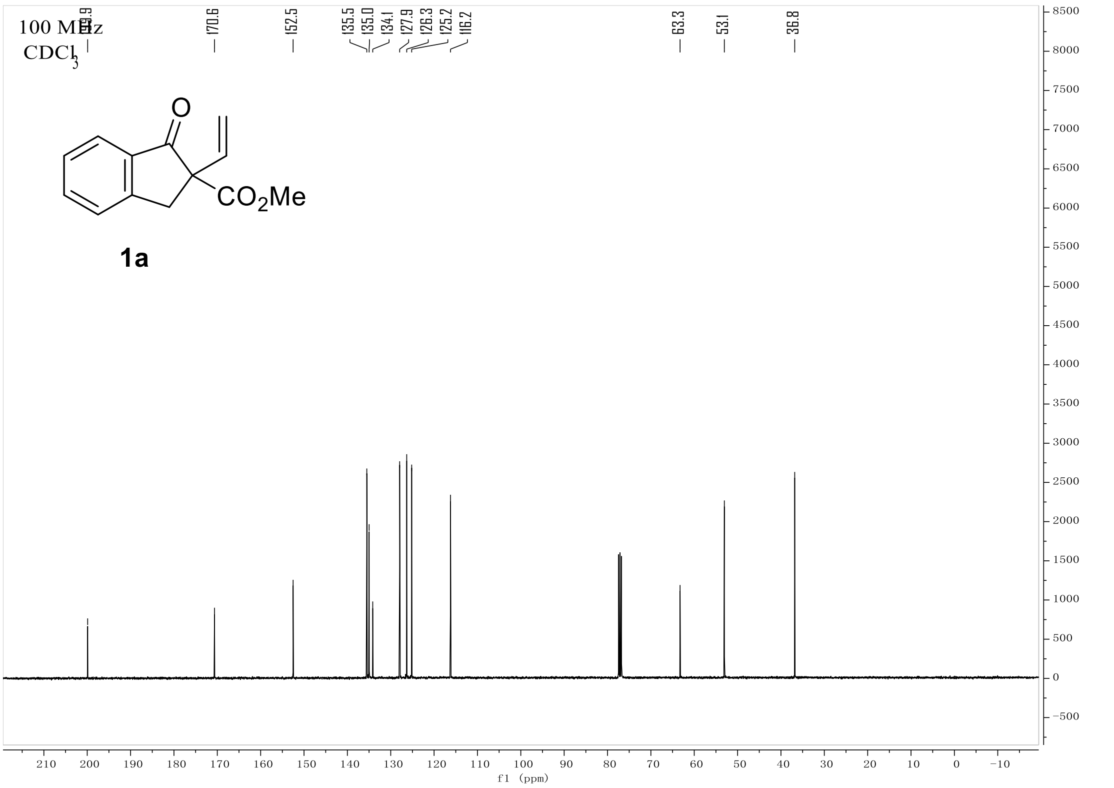
IR Inten -- 35.1108

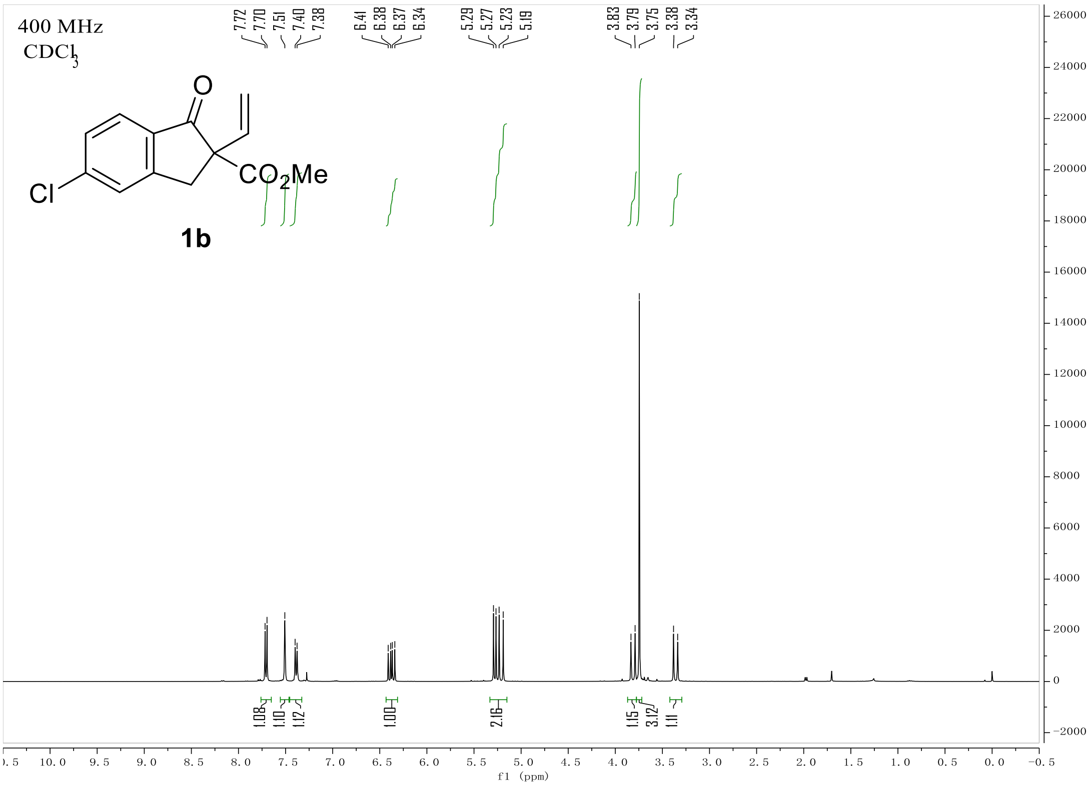
References

1. Y. Liu, S. C. Virgil, R. H. Grubbs and B. M. Stoltz, *Angew. Chem. Int. Ed.*, 2015, **54**, 11800-11803.
2. M. Nakamura, K. Endo and E. Nakamura, *Org. Lett.*, 2005, **7**, 3279-3281.
3. G. A. Koppel and M. D. Kinnick, *J. Chem. Soc., Chem. Commun.*, 1975, 473.
4. Y. Yang, C. G. Daniliuc and A. Studer, *Angew. Chem. Int. Ed.*, 2021, **60**, 2145-2148.
5. X. Gao, R. Cheng, Y.-L. Xiao, X.-L. Wan and X. Zhang, *Chem*, 2019, **5**, 2987-2999.
6. X. Y. Dong, J. T. Cheng, Y. F. Zhang, Z. L. Li, T. Y. Zhan, J. J. Chen, F. L. Wang, N. Y. Yang, L. Ye, Q. S. Gu and X. Y. Liu, *J. Am. Chem. Soc.*, 2020, **142**, 9501-9509.
7. M. Q. Tian, Z. Y. Shen, X. Zhao, P. J. Walsh and X. H. Hu, *Angew. Chem. Int. Ed.*, 2021, **60**, 9706-9711.
8. T. Saito, T. Suzuki, M. Morimoto, C. Akiyama, T. Ochiai, K. Takeuchi, T. Matsumoto and K. Suzuki, *J. Am. Chem. Soc.*, 1998, **120**, 11633-11644.
9. L. Su, C.-Y. Lei, W.-Y. Fan and L.-X. Liu, *Synthetic Commun.*, 2011, **41**, 1200-1207.
10. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
11. (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
12. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
13. (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305; (b) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
14. E. Besalú and J. M. Bofill, *Theor. Chem. Acc.*, 1998, **100**, 265-274.
15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2013.

NMR spectra for the data



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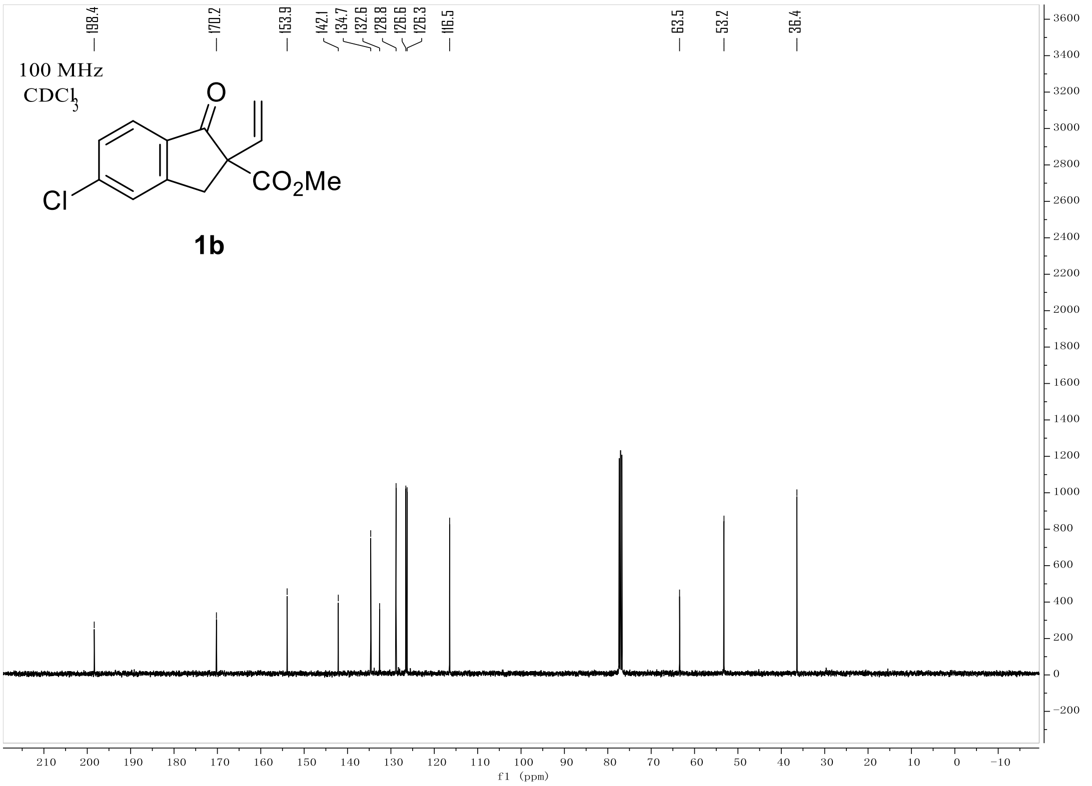
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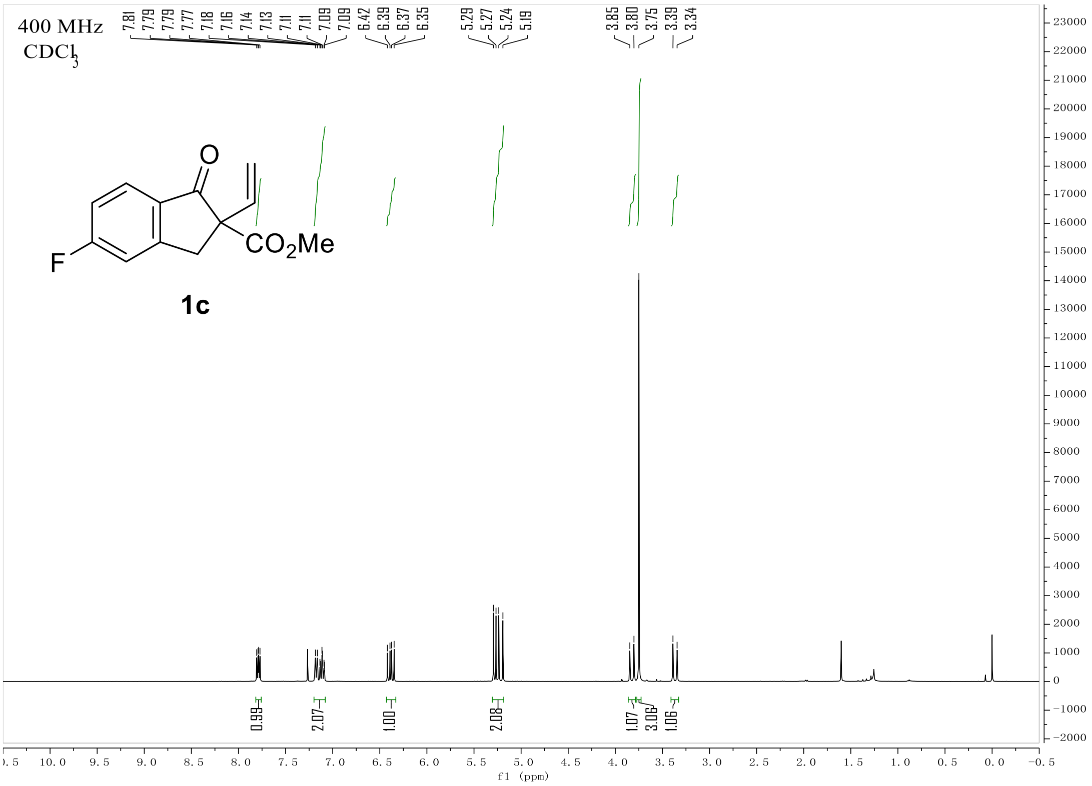
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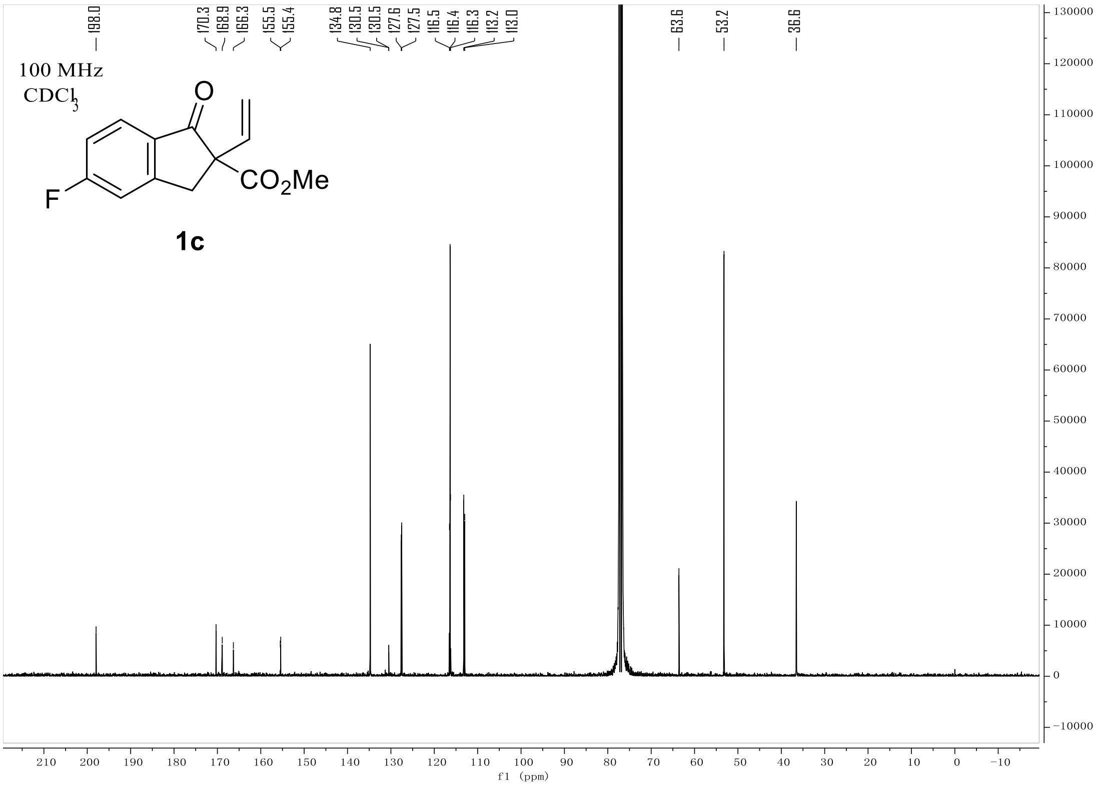
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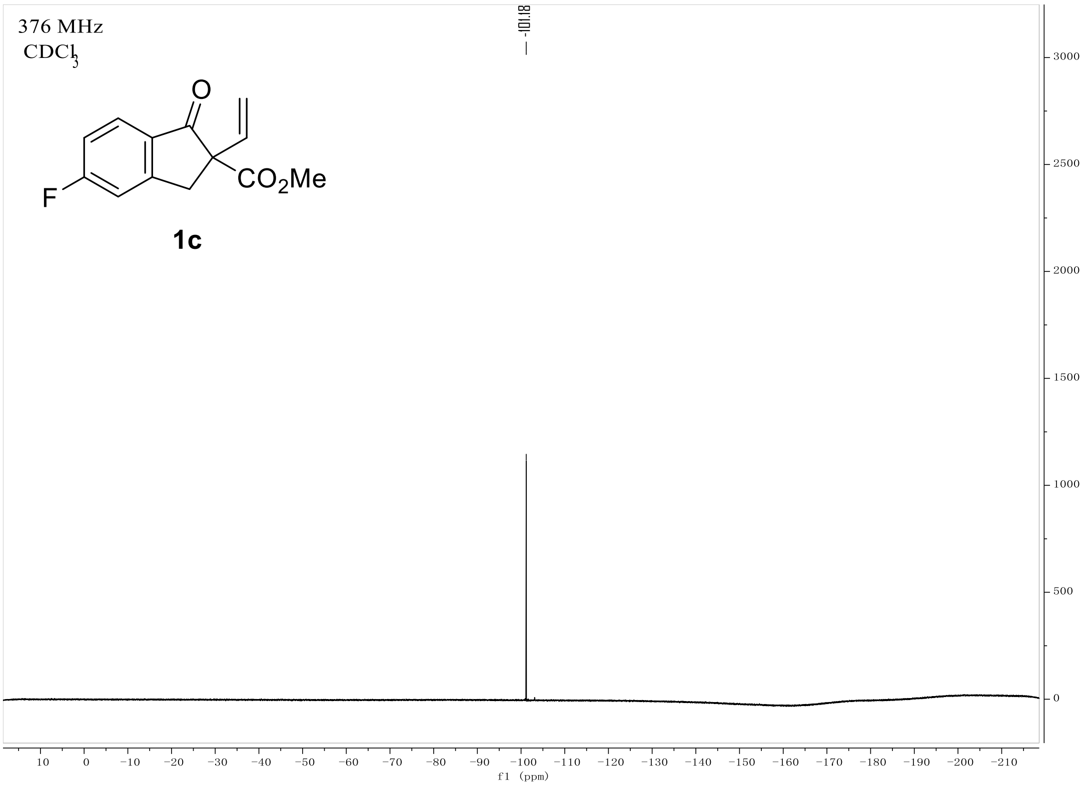

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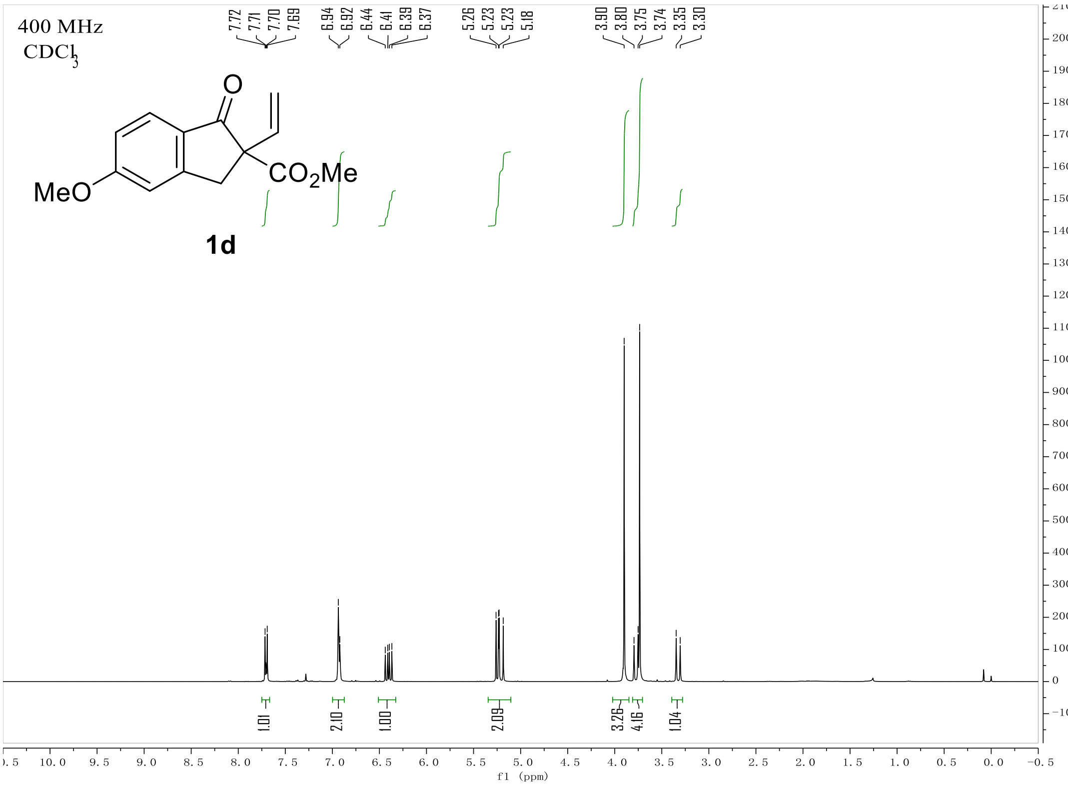
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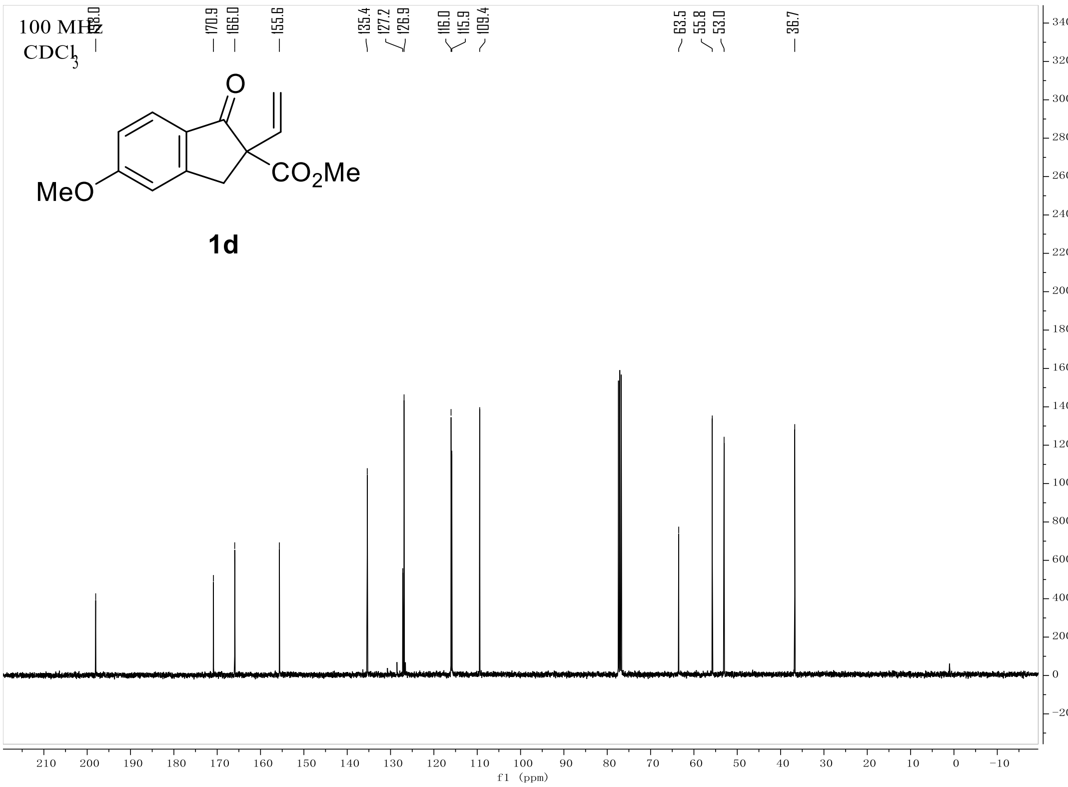
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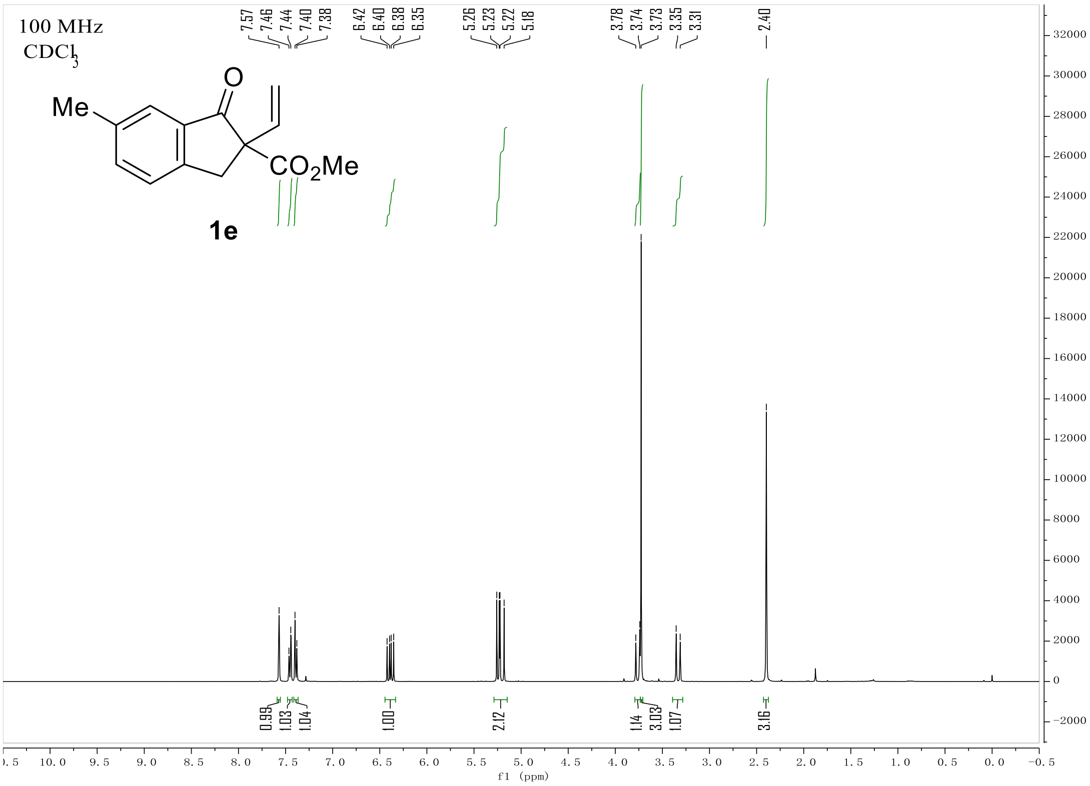

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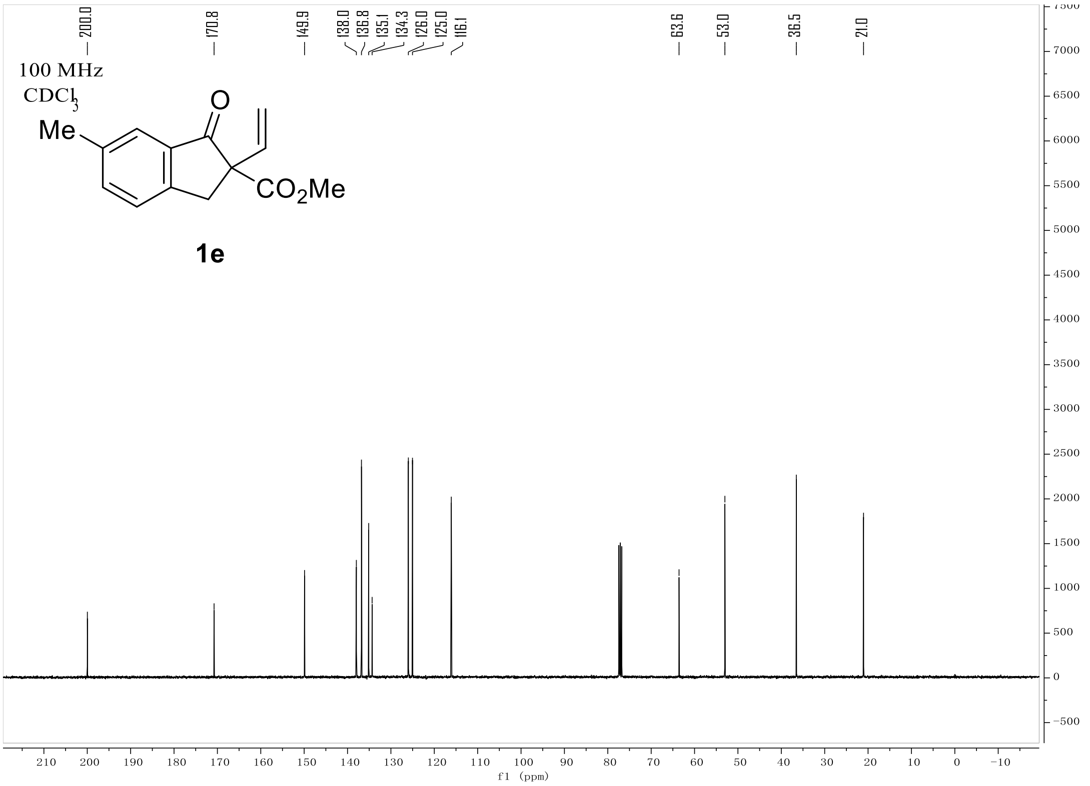

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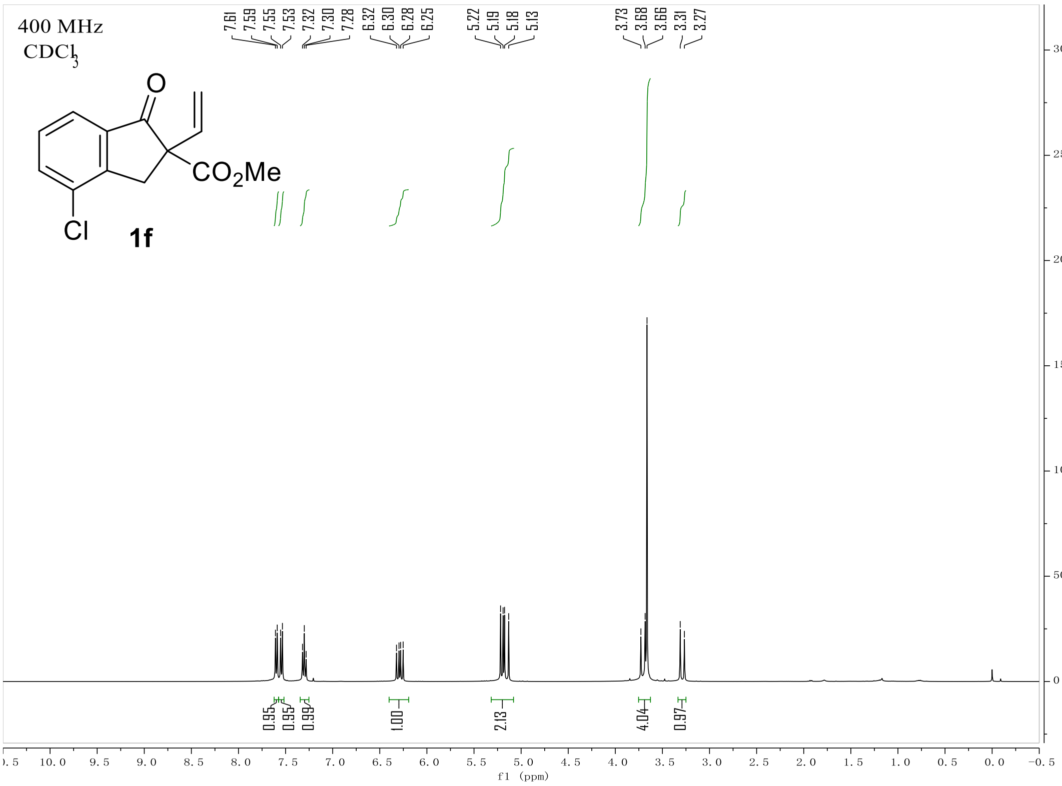
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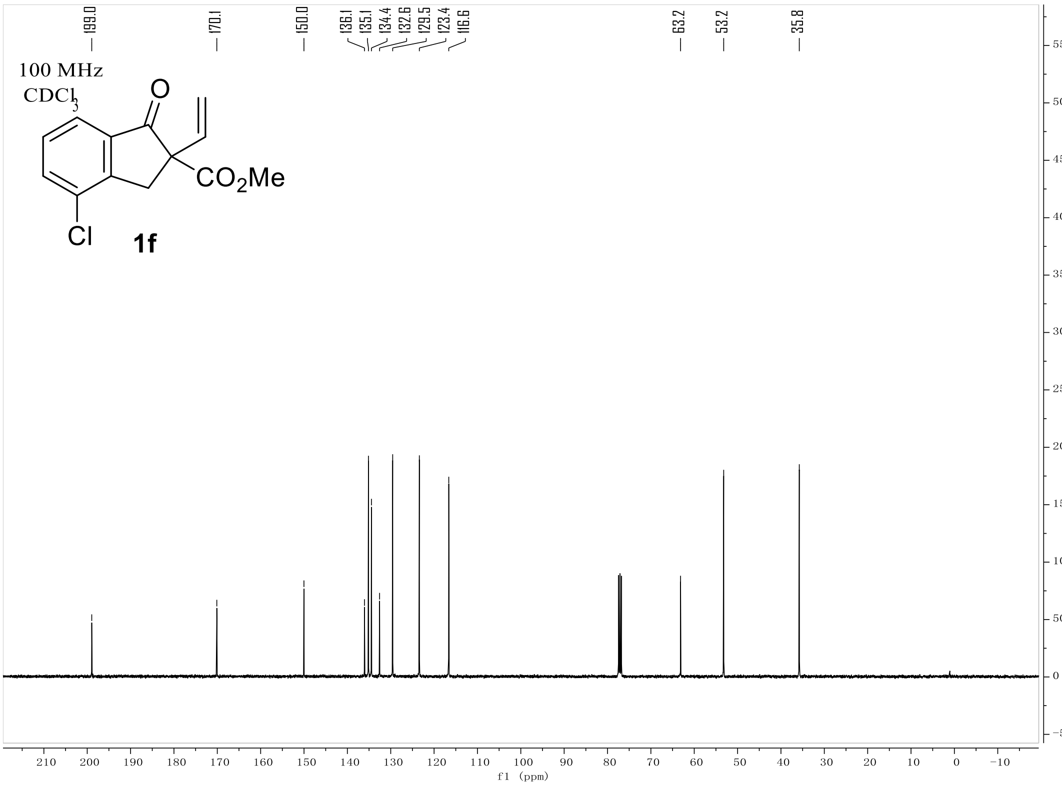
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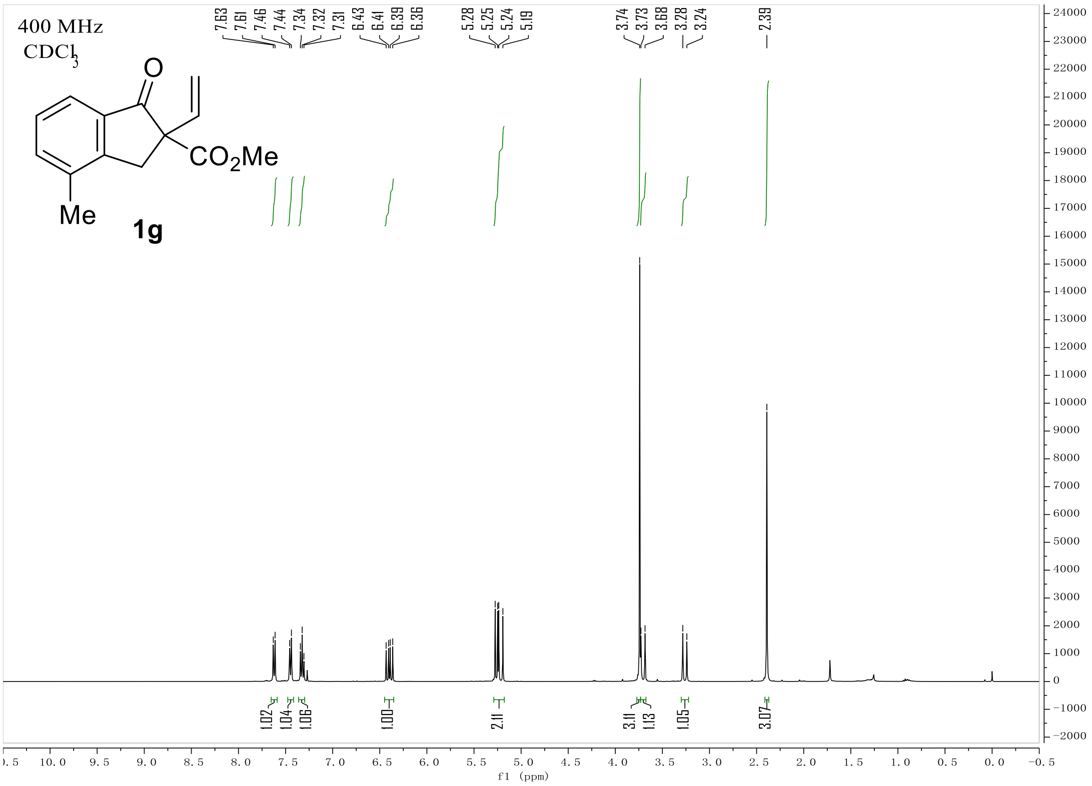
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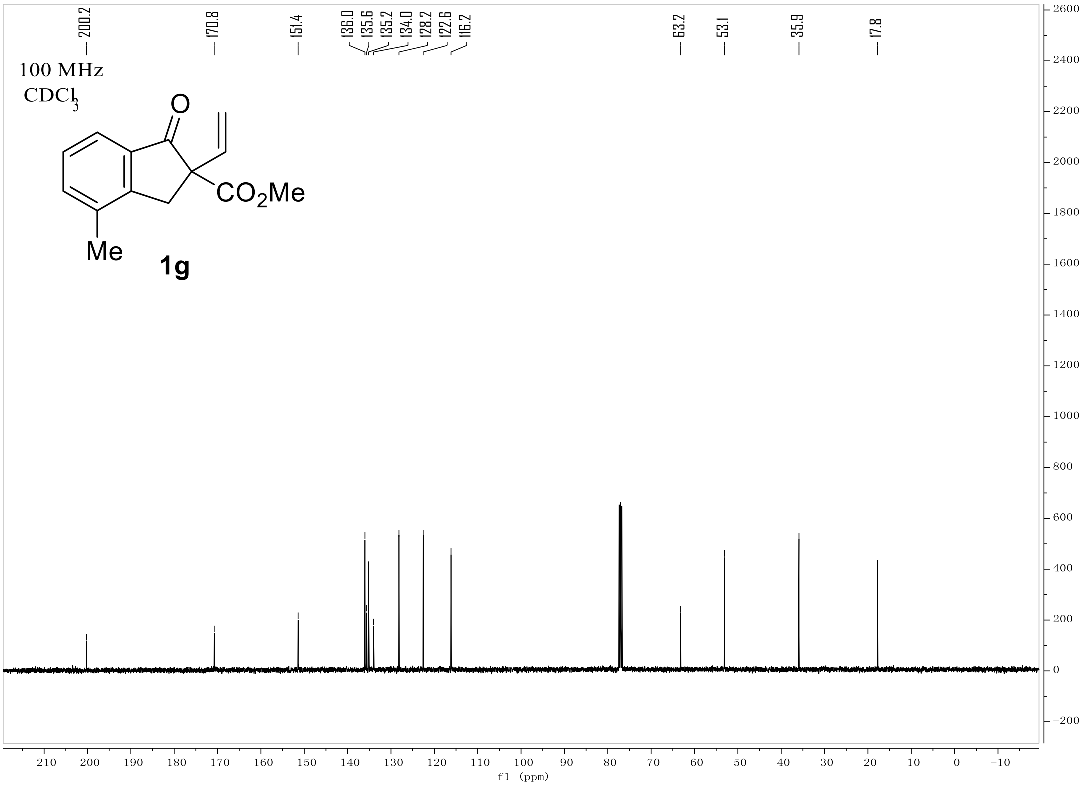
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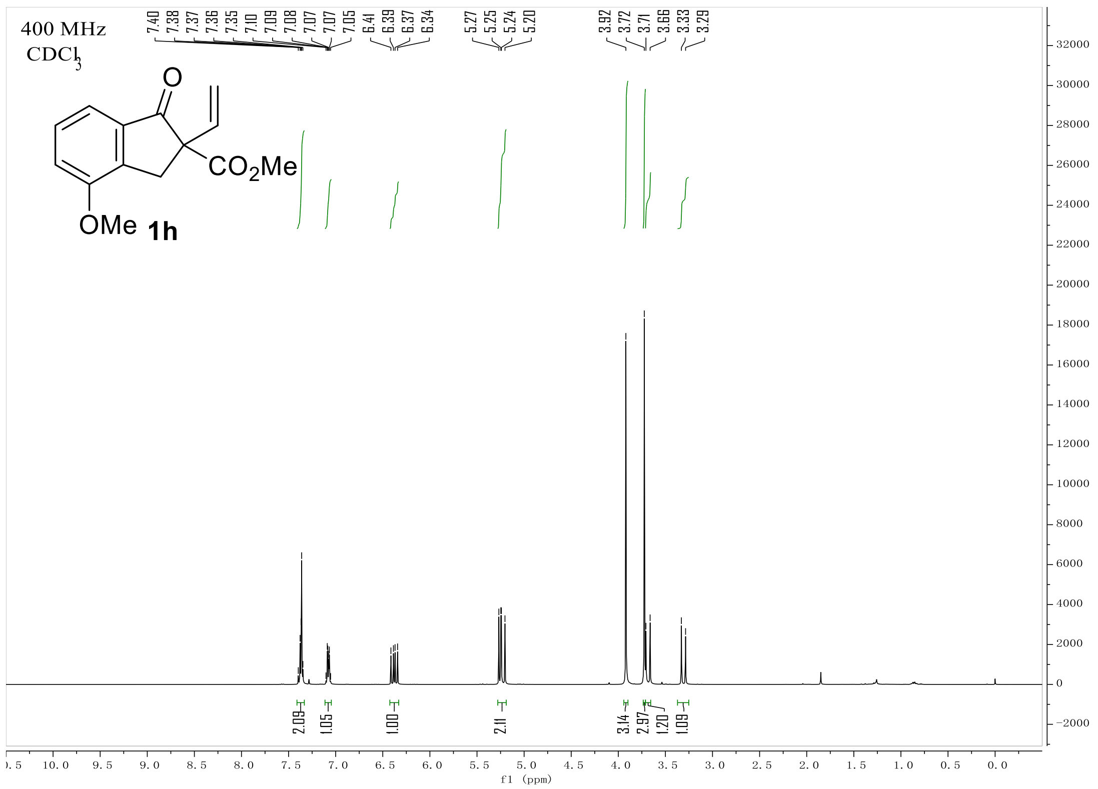
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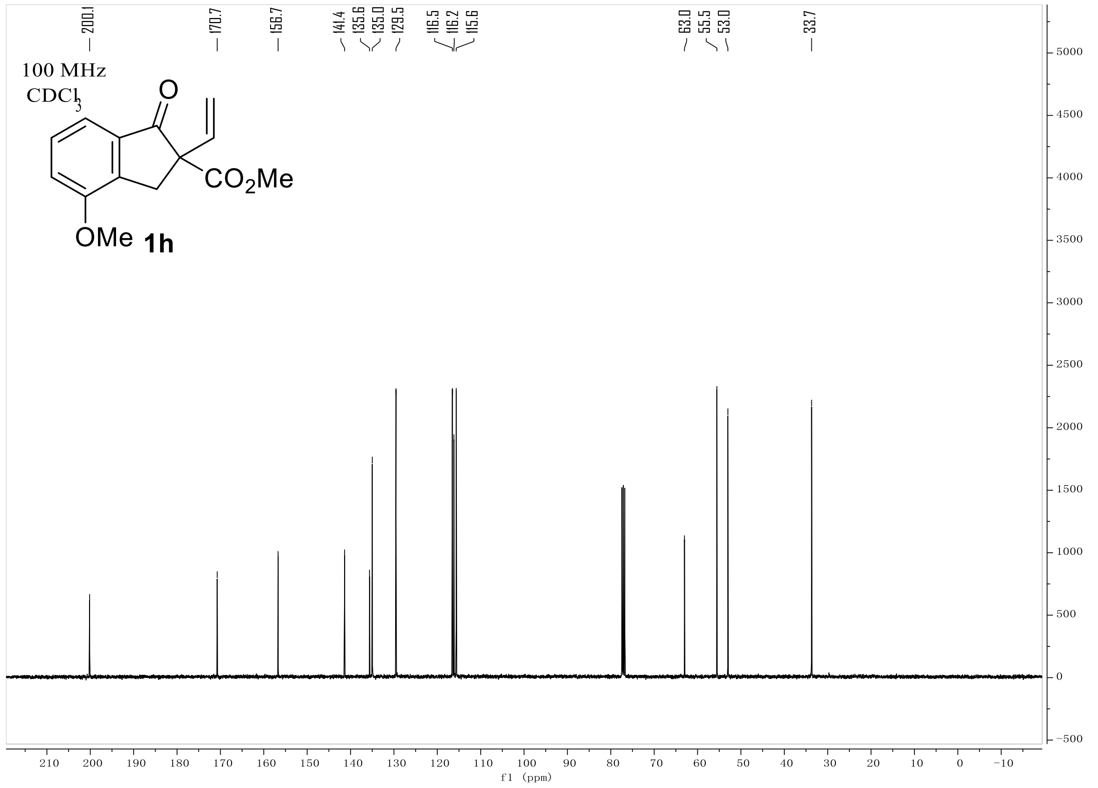
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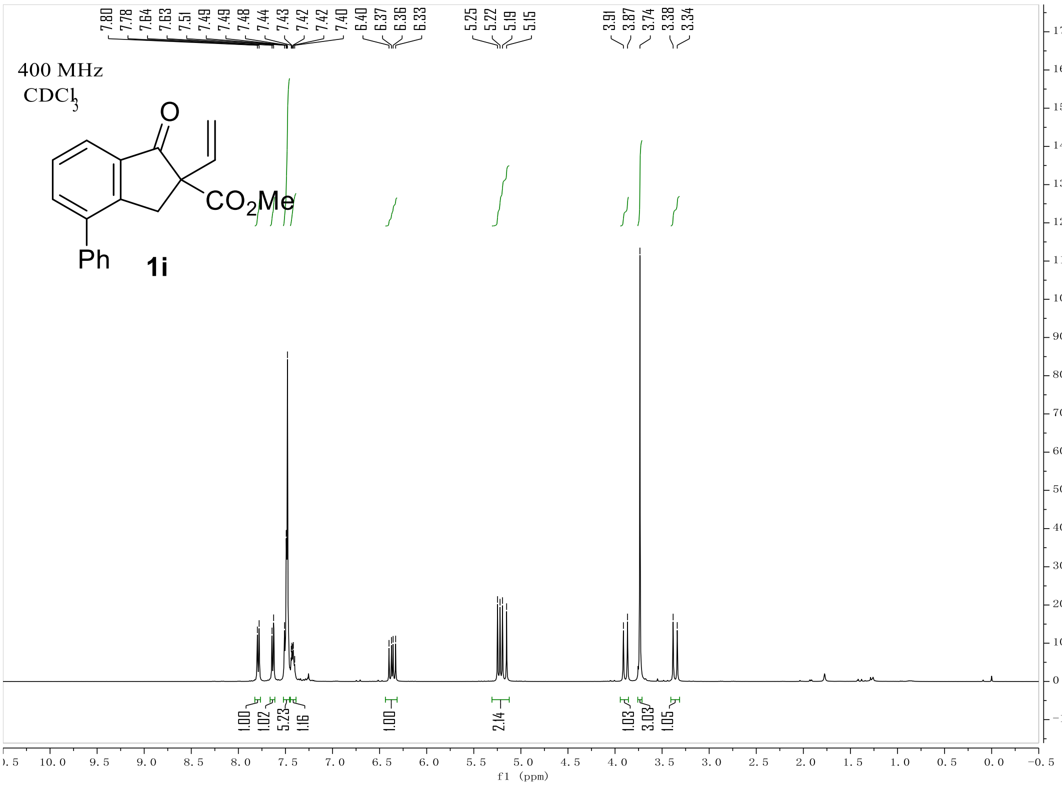
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6.40 6.37 6.36 6.33
5.25 5.22 5.19 5.15
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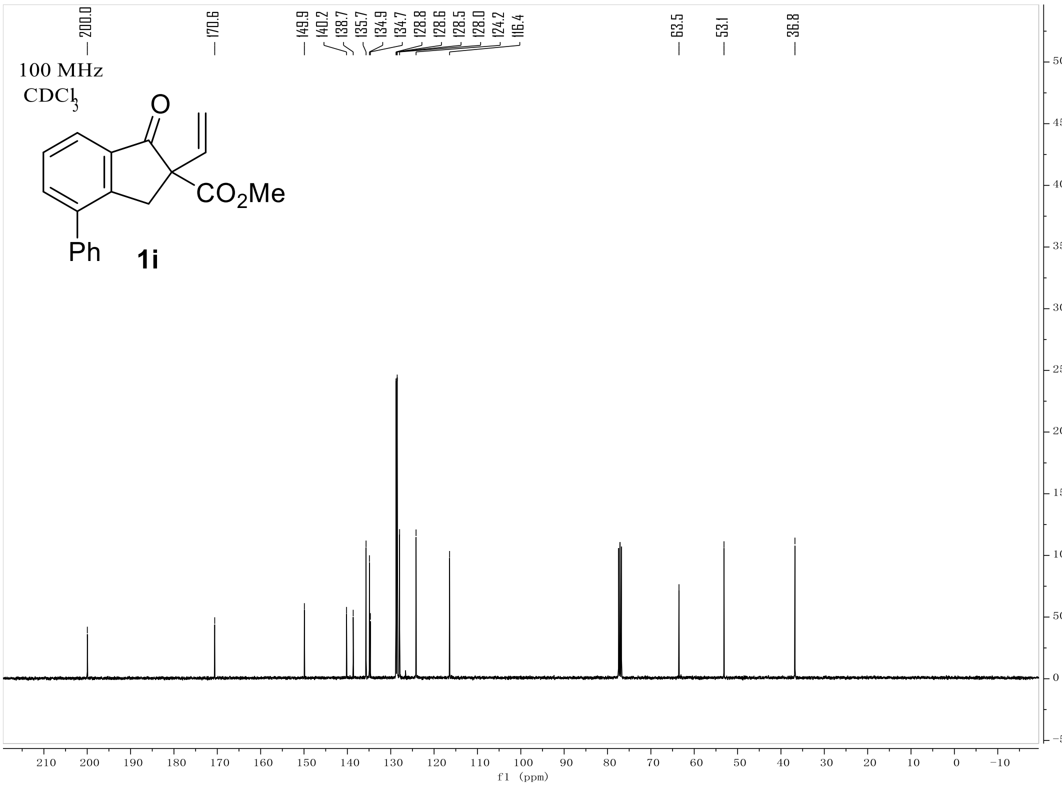
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63.5
53.1
36.8
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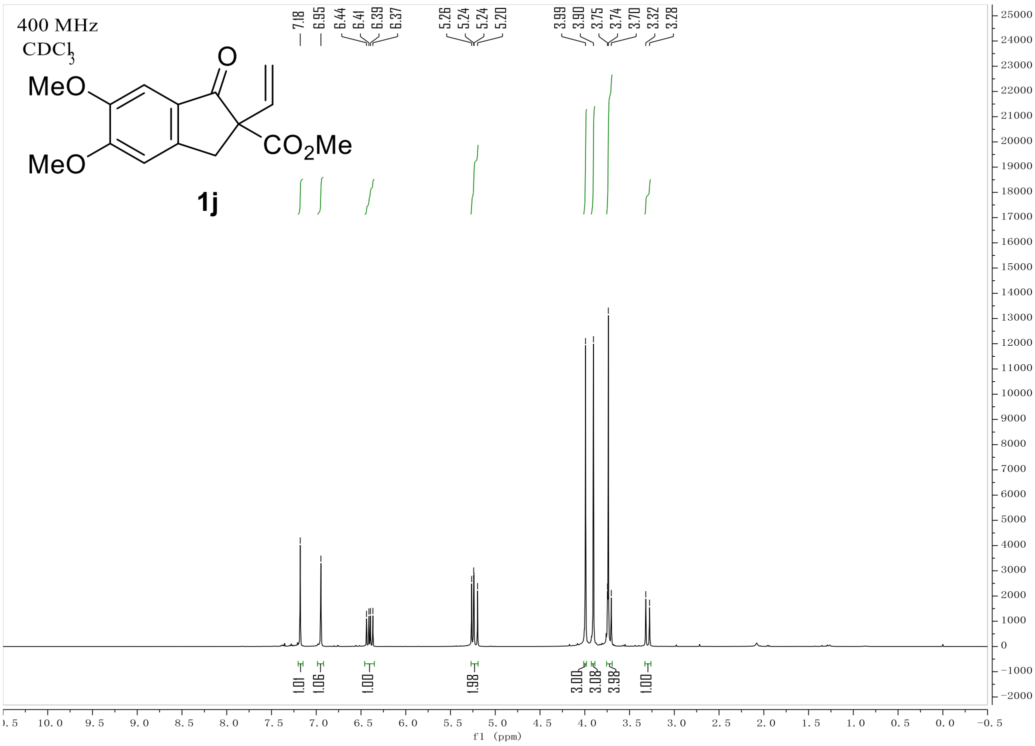
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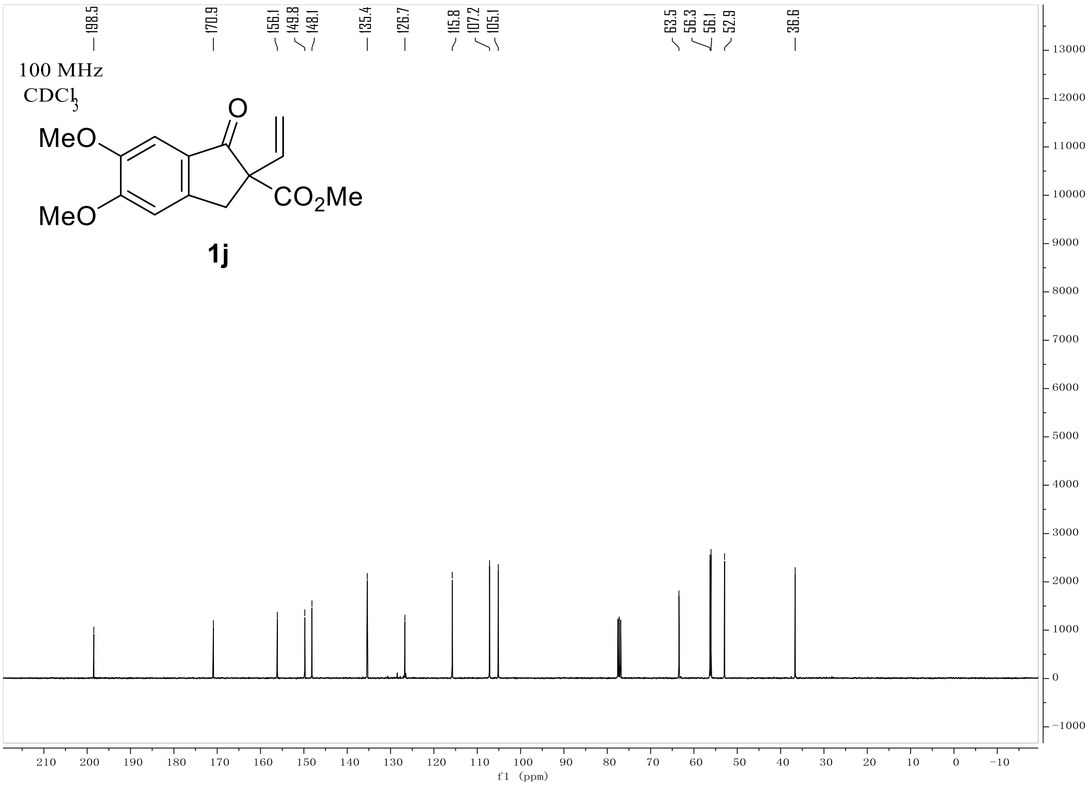
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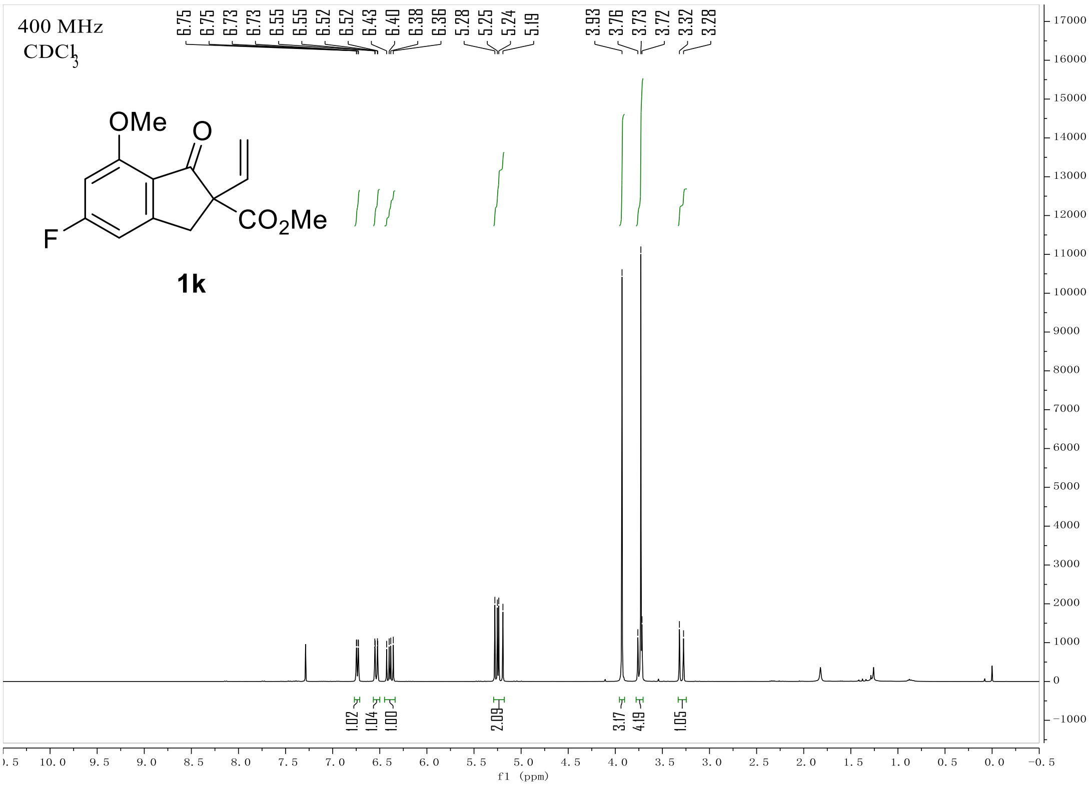
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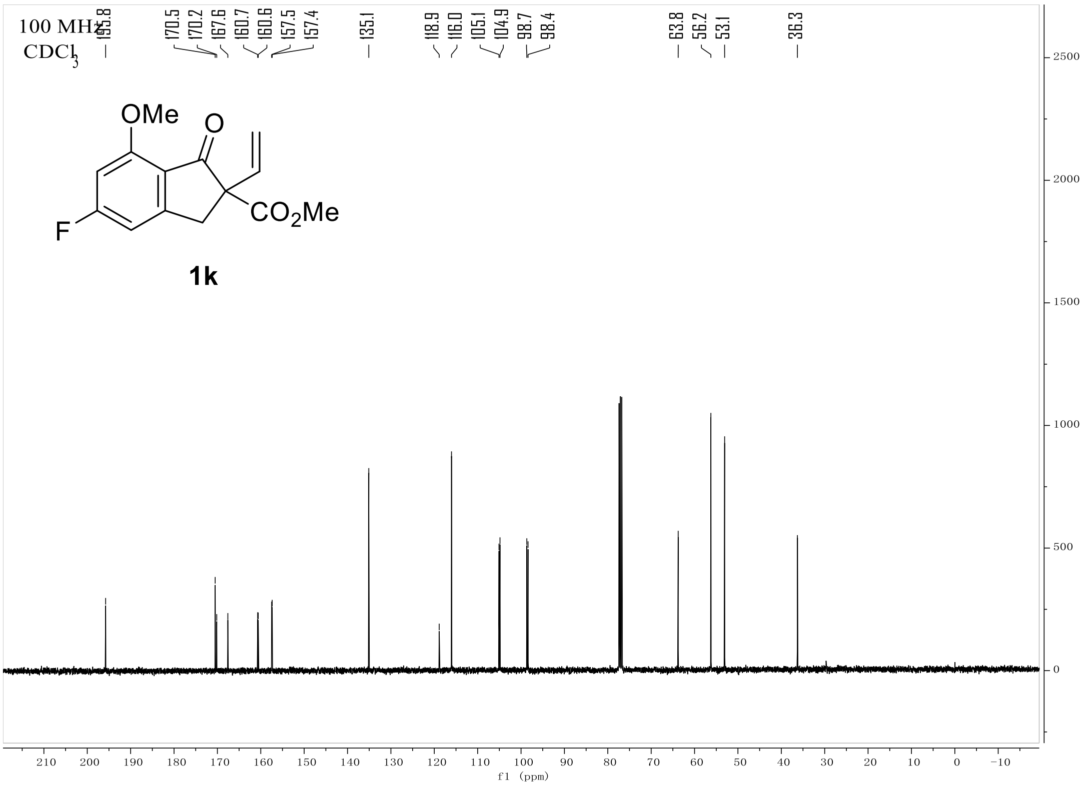
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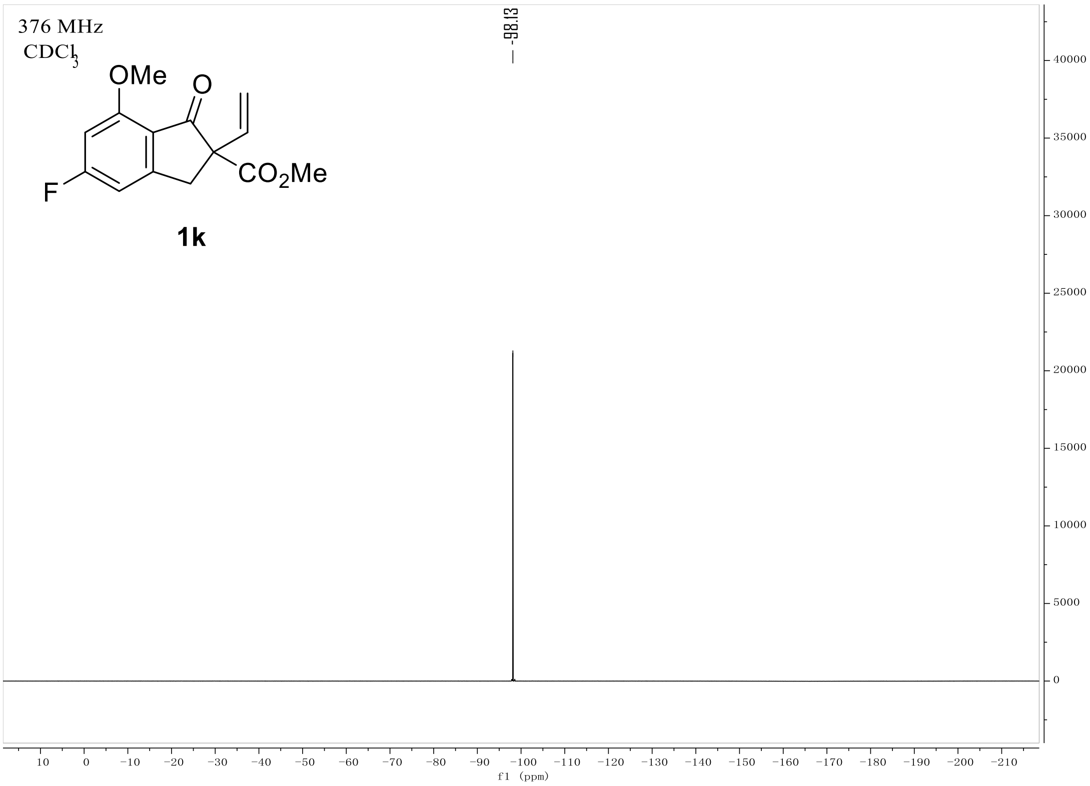
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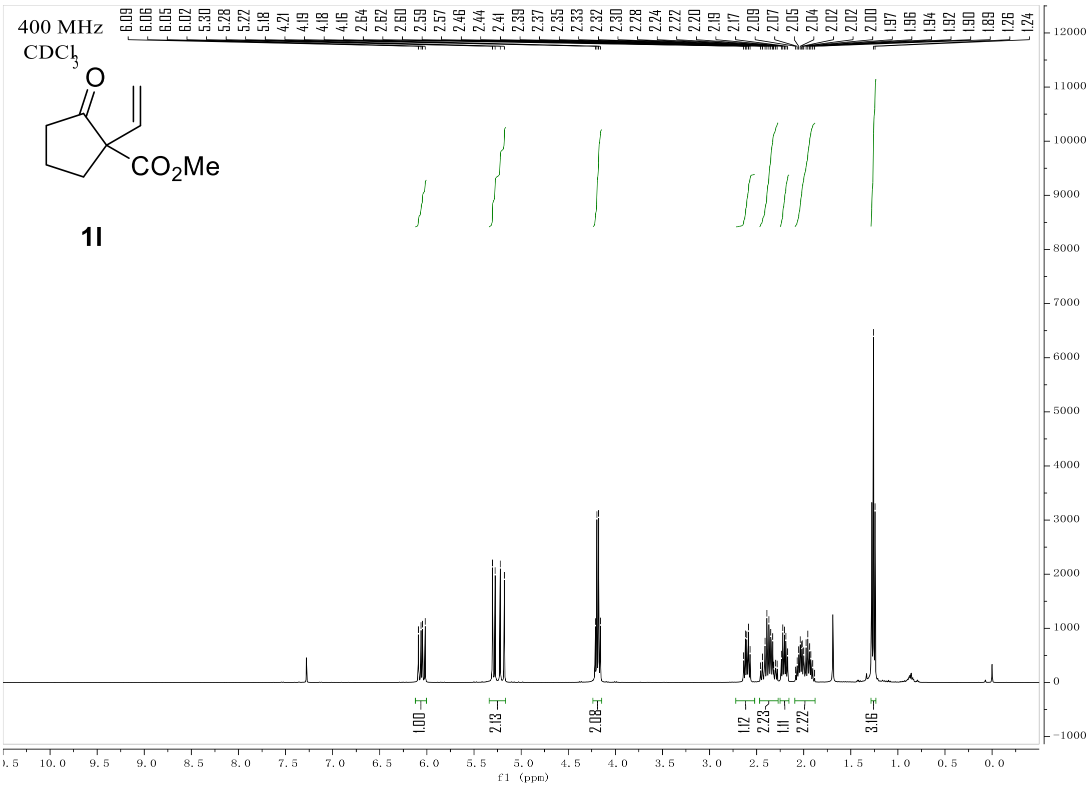
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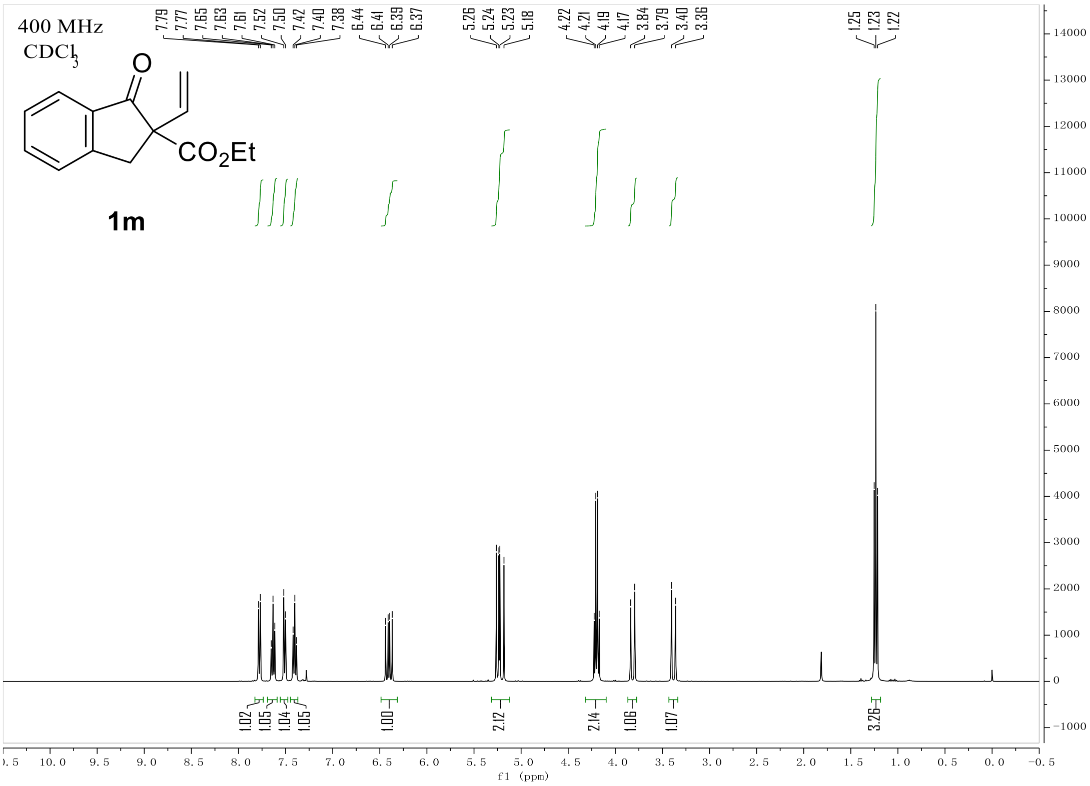
1l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1.02 1.05 1.04 1.05 1.00 2.12 2.14 1.06 1.07 3.26
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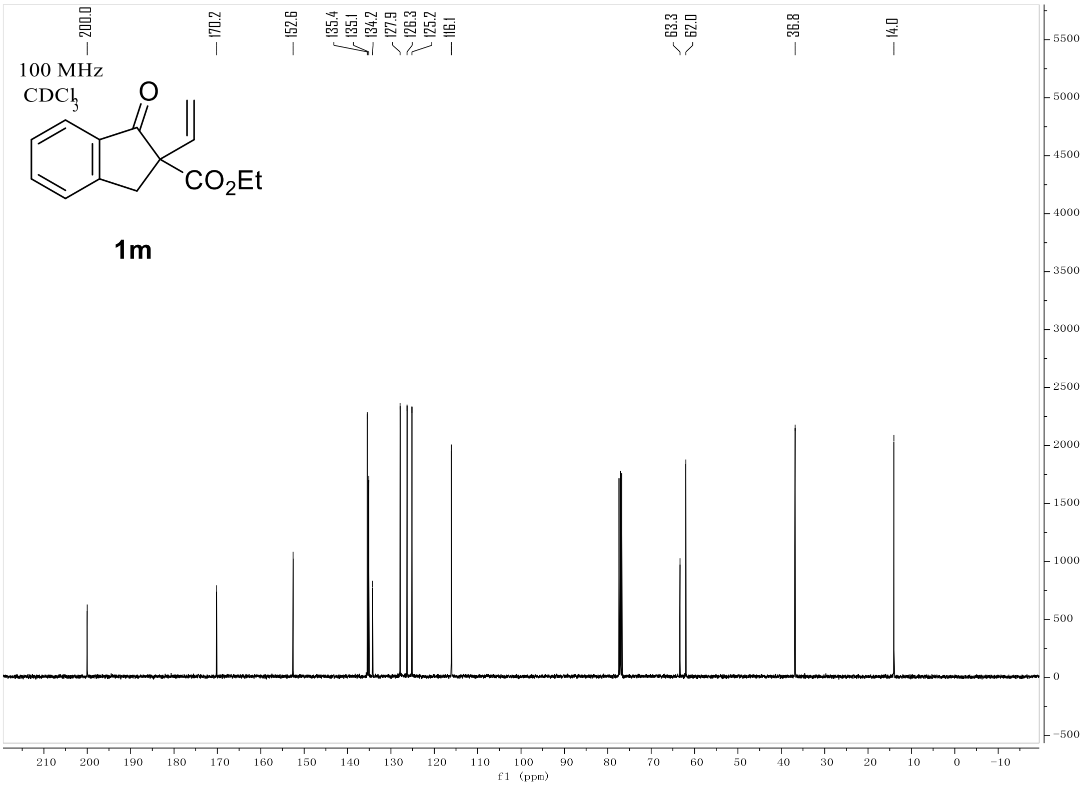
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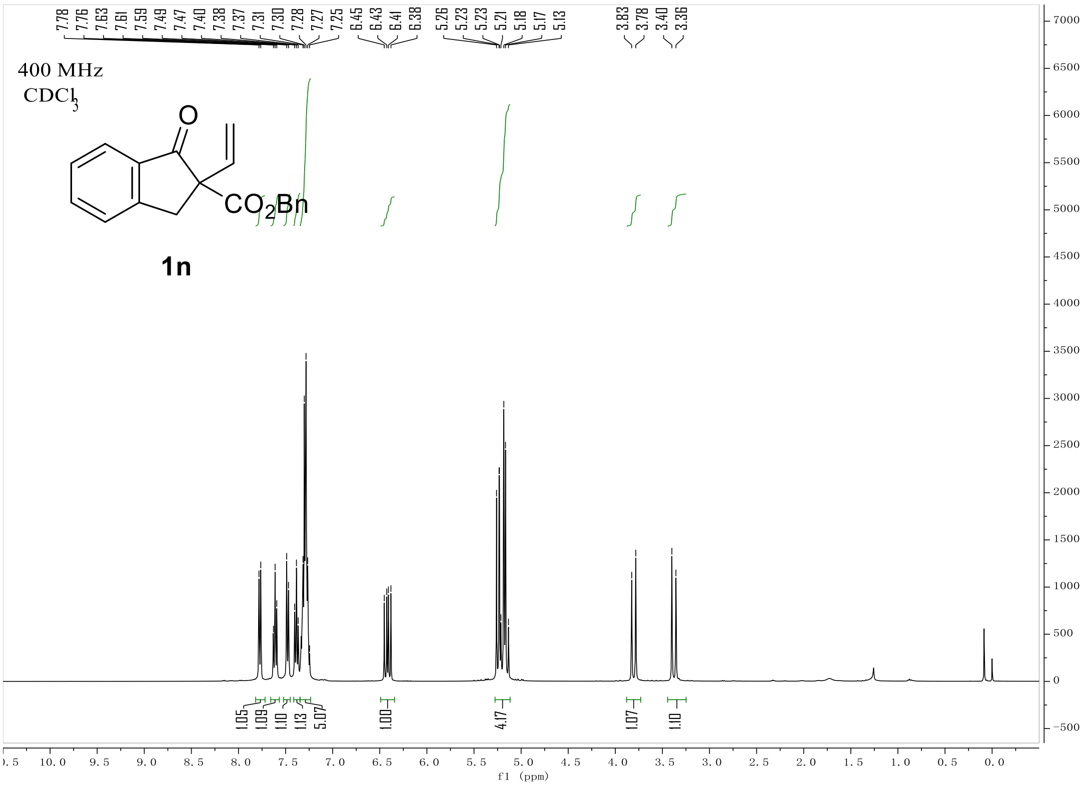
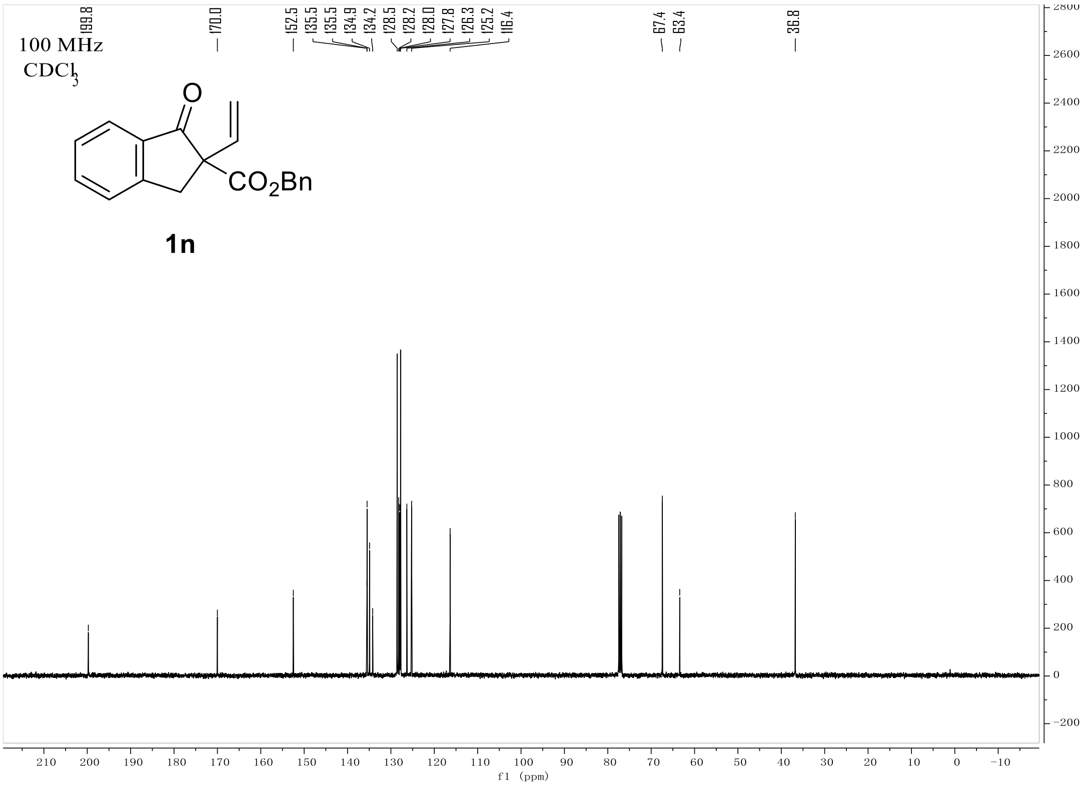
f1 (ppm)



7.78 7.76 7.63 7.61 7.59 7.49 7.47 7.40 7.38 7.37 7.31 7.30 7.28 7.27 7.25 6.45 6.43 6.41 6.38 5.26 5.23 5.23 5.21 5.18 5.17 5.13 3.83 3.78 3.40 3.36
400 MHz
CDCl3
O
CO2Bn
1n
1.05 1.09 1.10 1.13 5.07 1.00 4.17 1.07 1.10
f1 (ppm)



199.8 170.0 152.5 135.5 135.5 134.9 134.2 128.5 128.2 128.0 127.8 126.3 125.2 116.4 67.4 63.4 36.8
100 MHz
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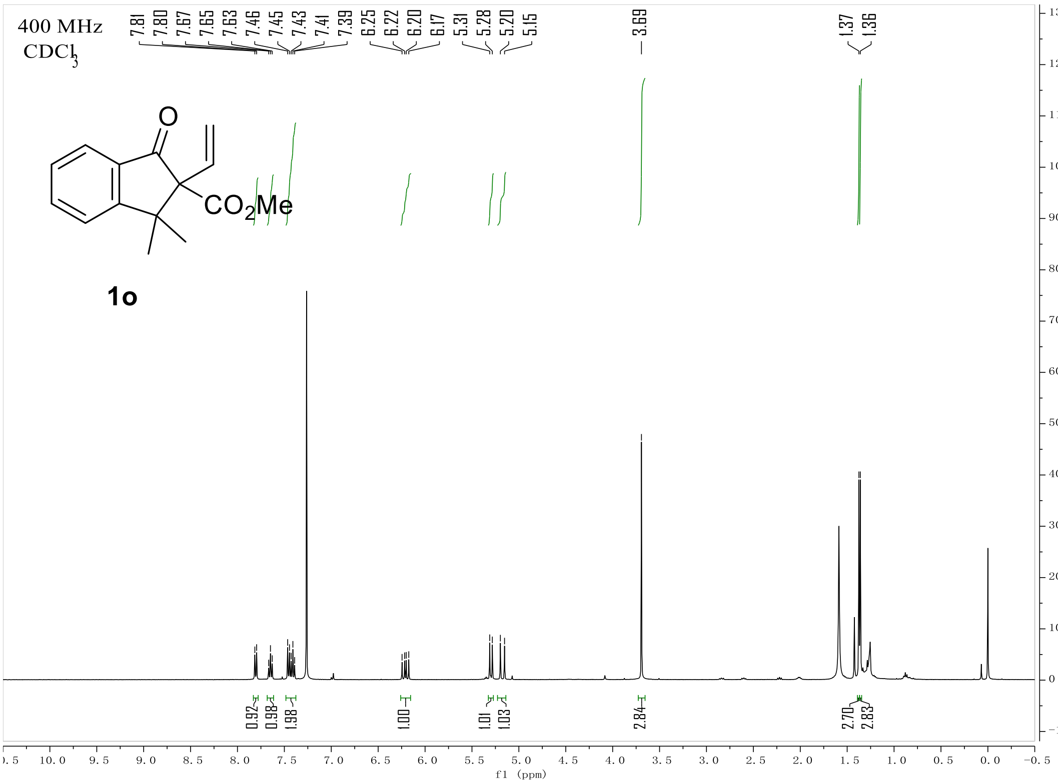
O
CO2Bn
1n
f1 (ppm)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7.46
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7.43
7.41
7.39
6.25
6.22
6.20
6.17
5.31
5.28
5.20
5.15
3.69
1.37
1.36
CO2Me
0.92
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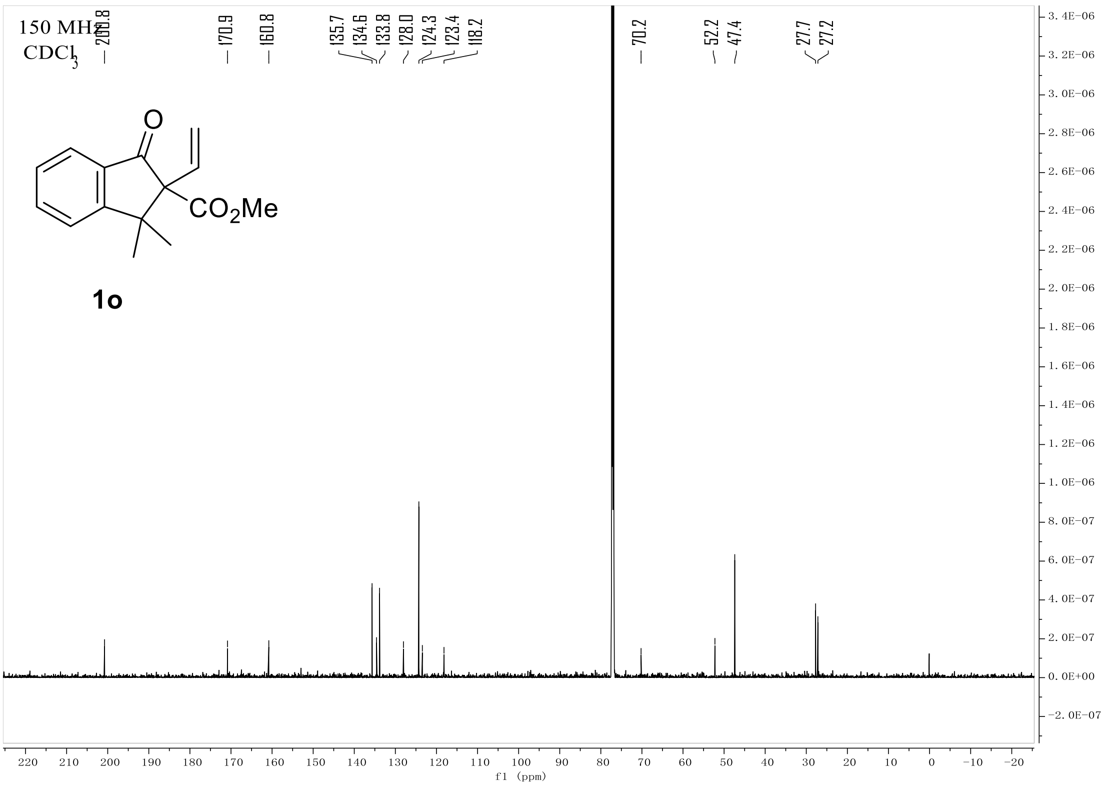
1.98
1.00
1.01
1.03
2.84
2.70
2.83
f1 (ppm)

1o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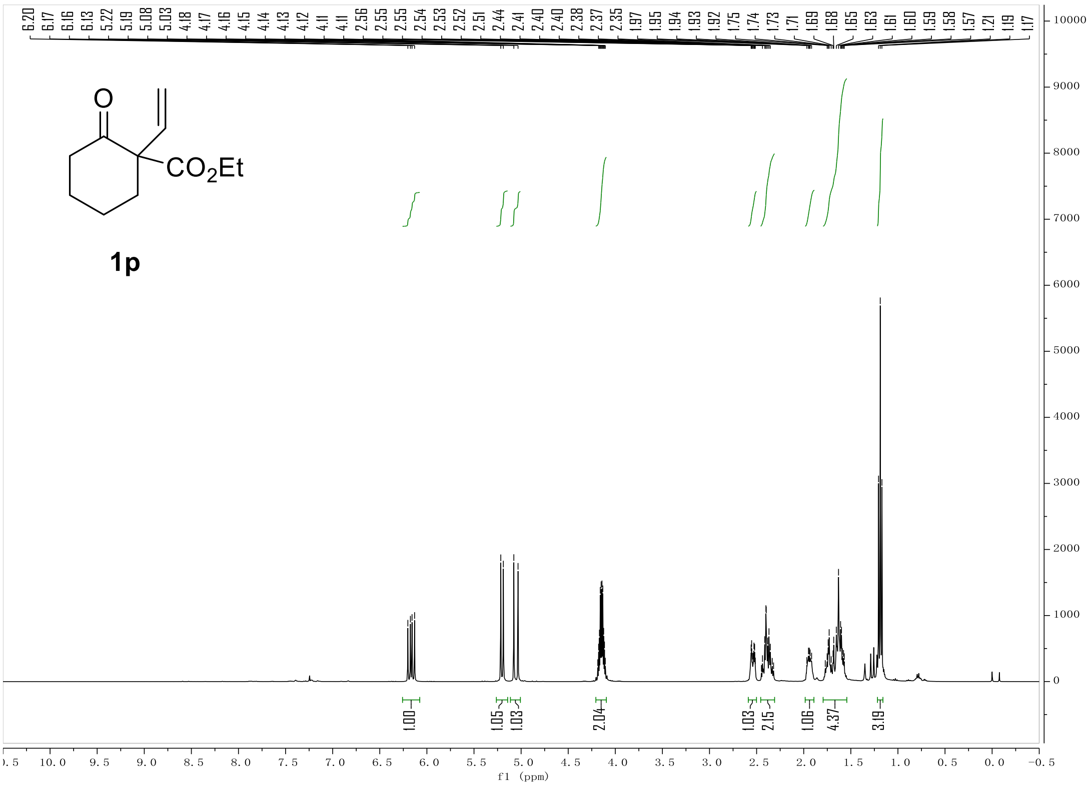
52.2
47.4
27.7
27.2
CO2Me
f1 (ppm)

1o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O
CO2Et
1p
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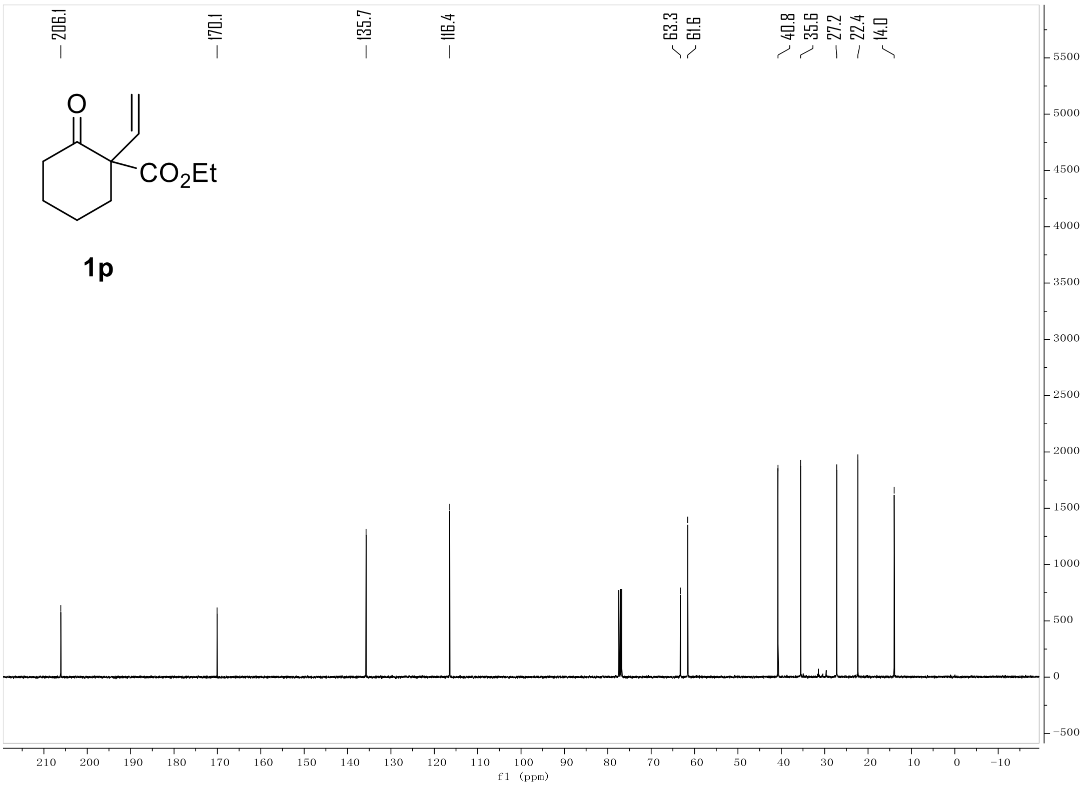
1.05
1.03
2.04
1.03
2.15
1.06
4.37
3.19
f1 (ppm)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40.8
35.6
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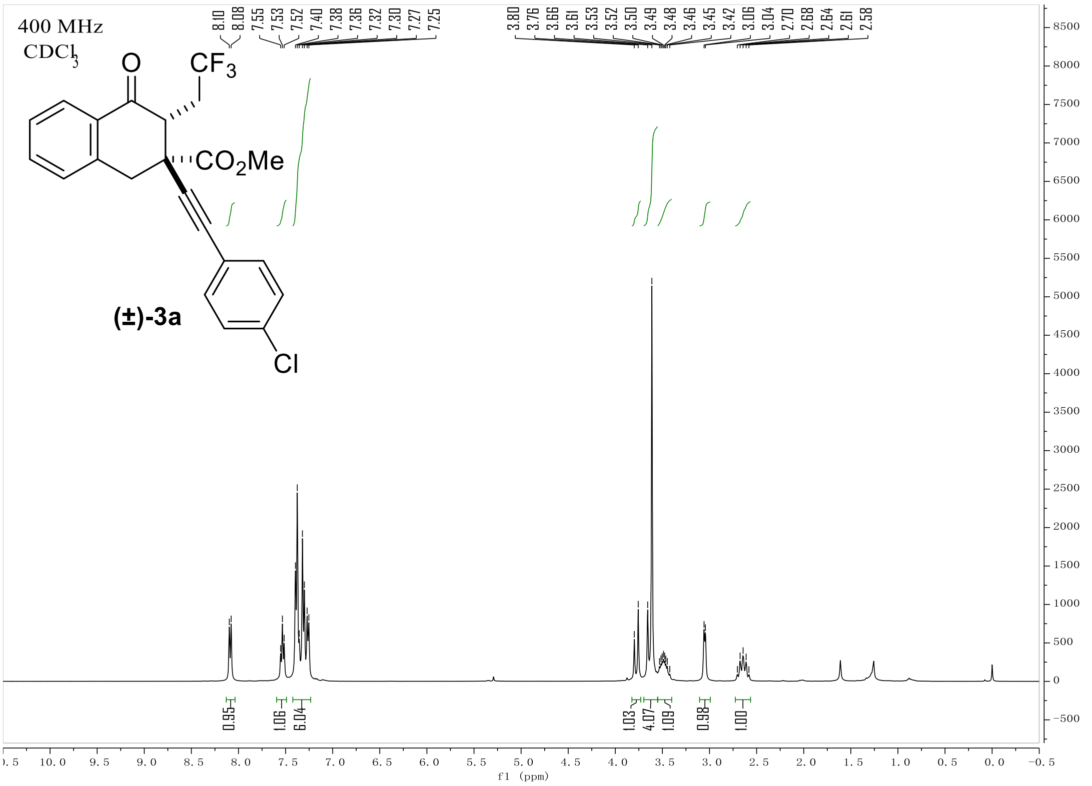
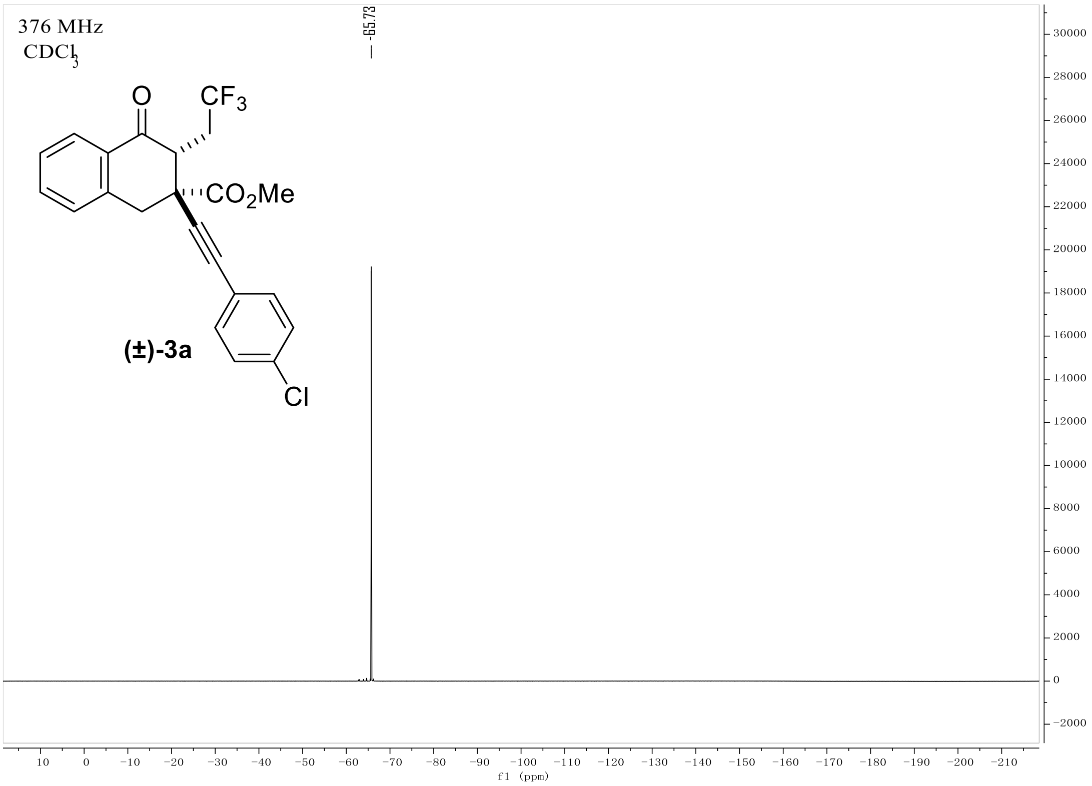
22.4
14.0
O
CO2Et
1p
f1 (ppm)


400 MHz
CDCl3
(±)-3a
f1 (ppm)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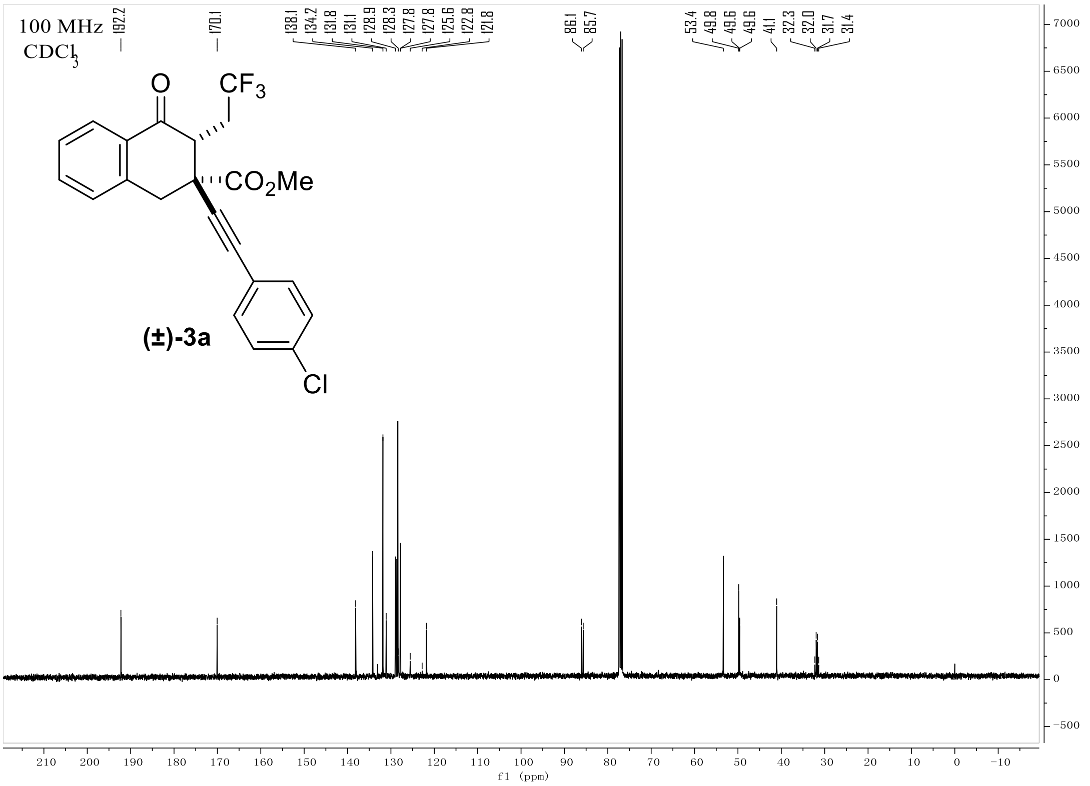
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128.3
127.8
127.8
125.6
122.8
121.8
86.1
85.7
53.4
49.8
49.6
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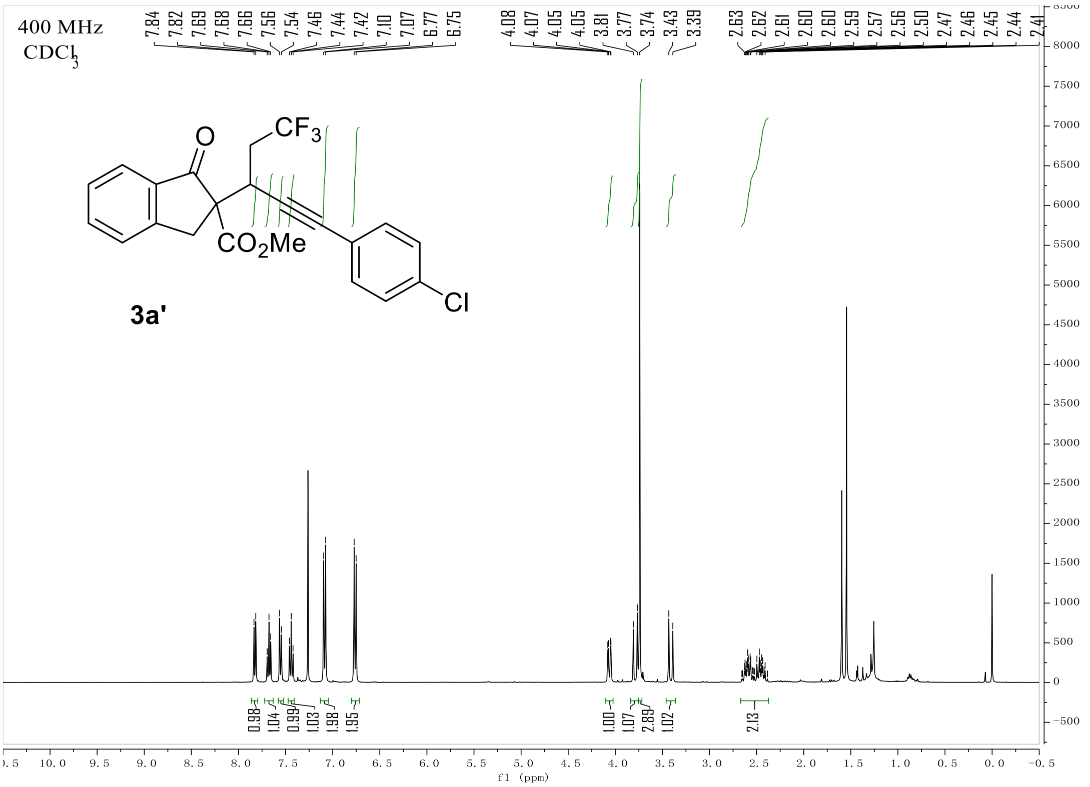
32.3
32.0
31.7
31.4
O
CF3
CO2Me
Cl
(±)-3a
f1 (ppm)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7.46
7.44
7.42
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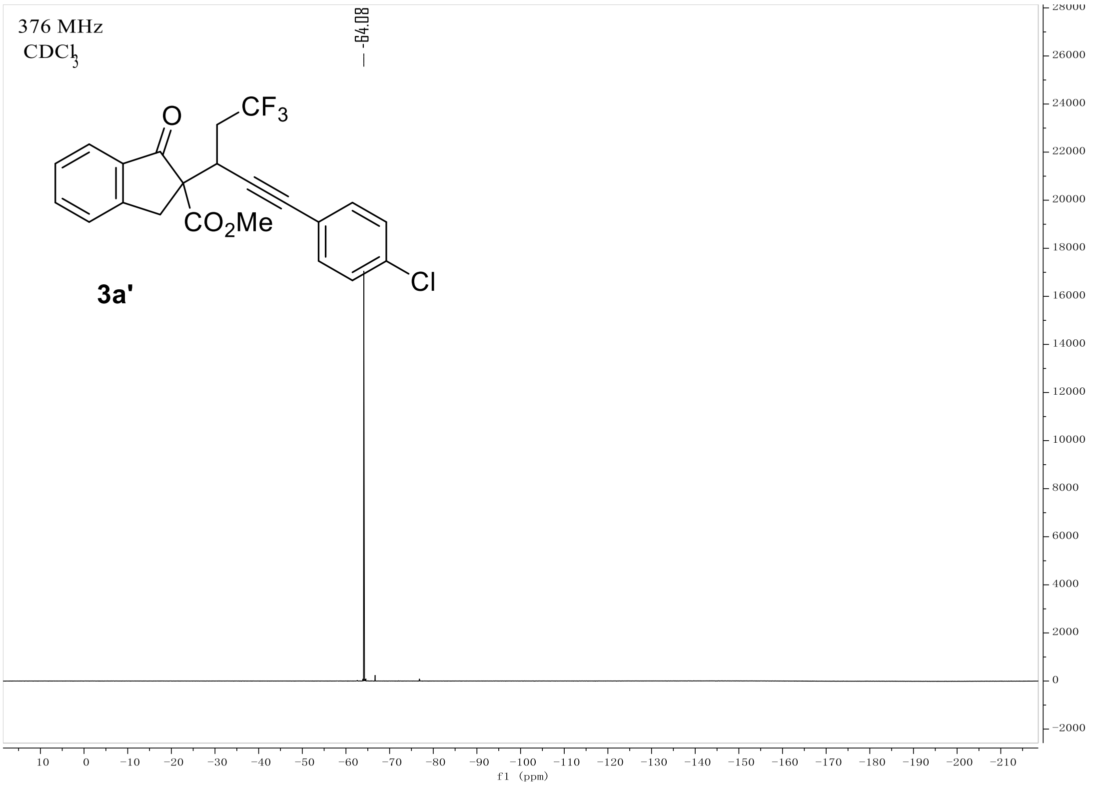
7.07
6.77
6.75
4.08
4.07
4.05
4.05
3.81
3.77
3.74
3.43
3.39
2.63
2.62
2.61
2.60
2.60
2.59
2.57
2.56
2.50
2.47
2.46
2.45
2.44
2.41
O
CF3
CO2Me
Cl
3a'
0.98
1.04
0.99
1.03
1.98
1.95
1.00
1.07
2.89
1.02
2.13
f1 (ppm)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CF3
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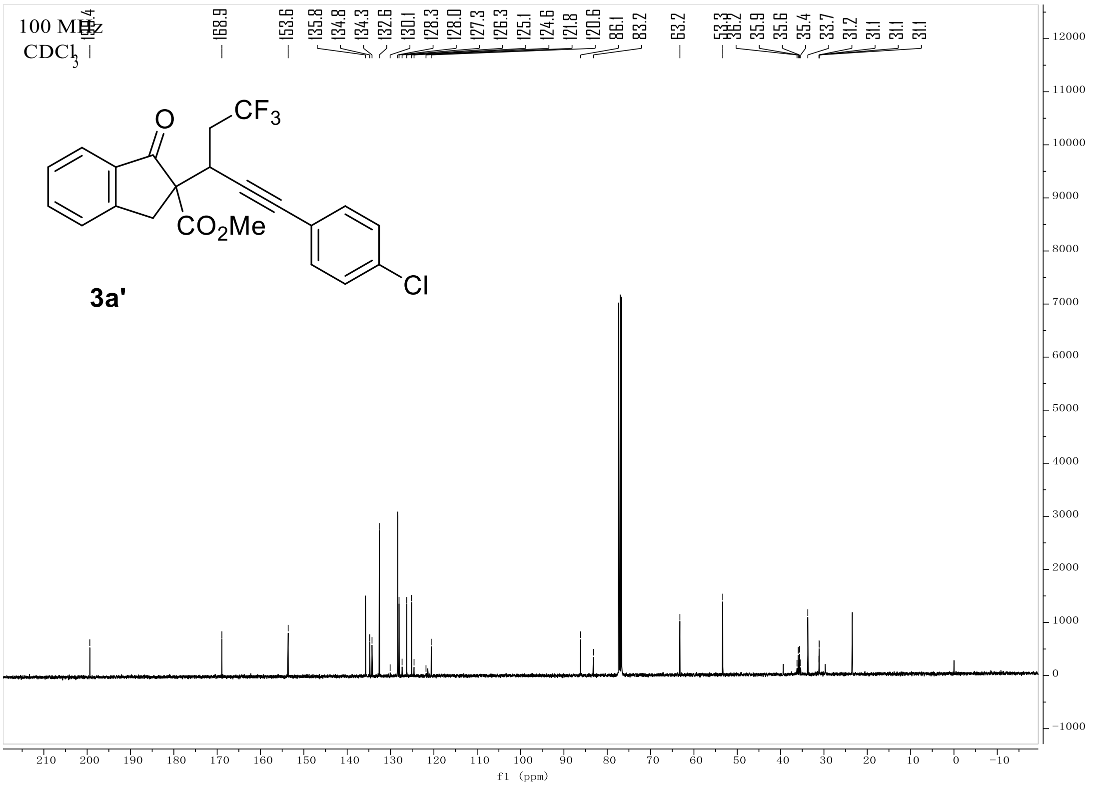
Cl
3a'
f1 (ppm)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134.8
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128.3
128.0
127.3
126.3
125.1
124.6
121.8
120.6
86.1
83.2
63.2
35.9
35.6
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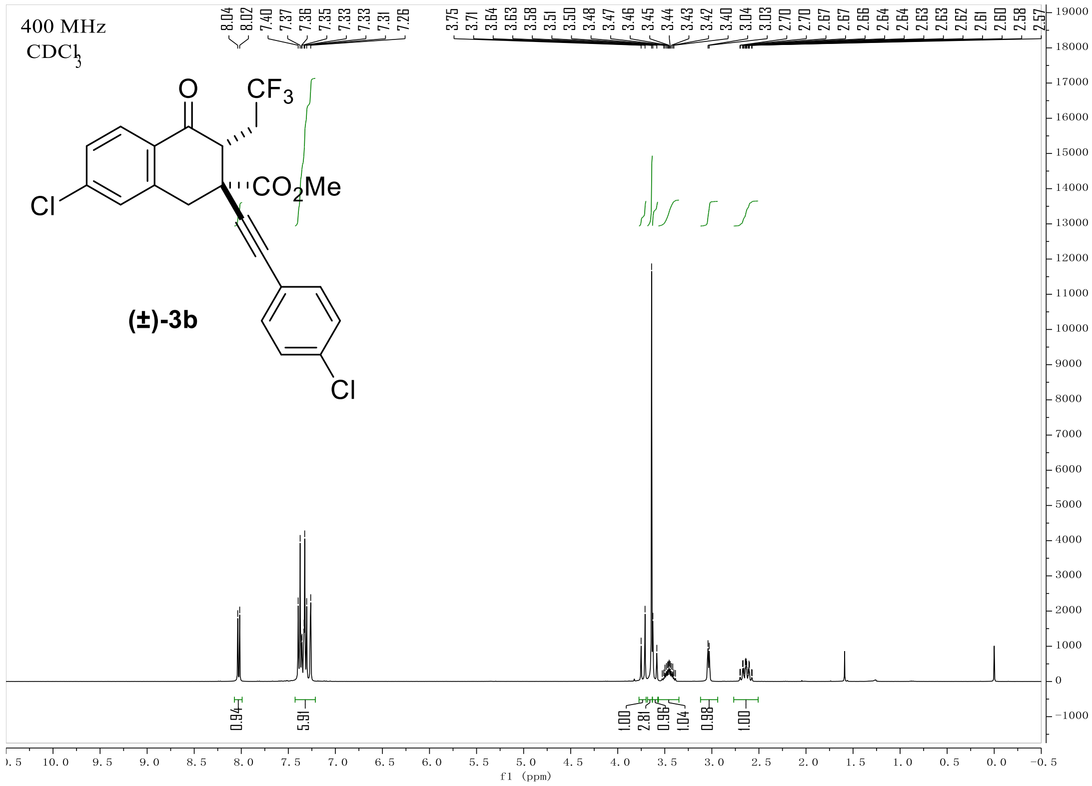
33.7
31.2
31.1
31.1
31.1
CF3
O
CO2Me
Cl
3a'
f1 (ppm)


400 MHz
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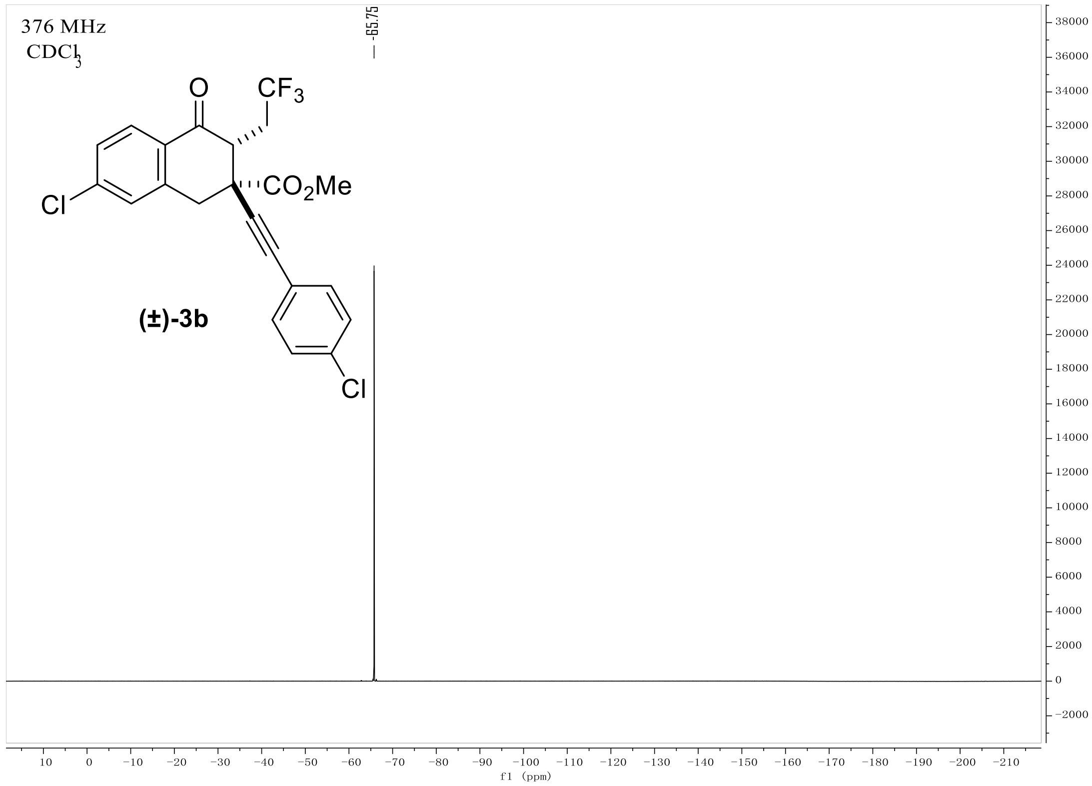
(±)-3b
f1 (ppm)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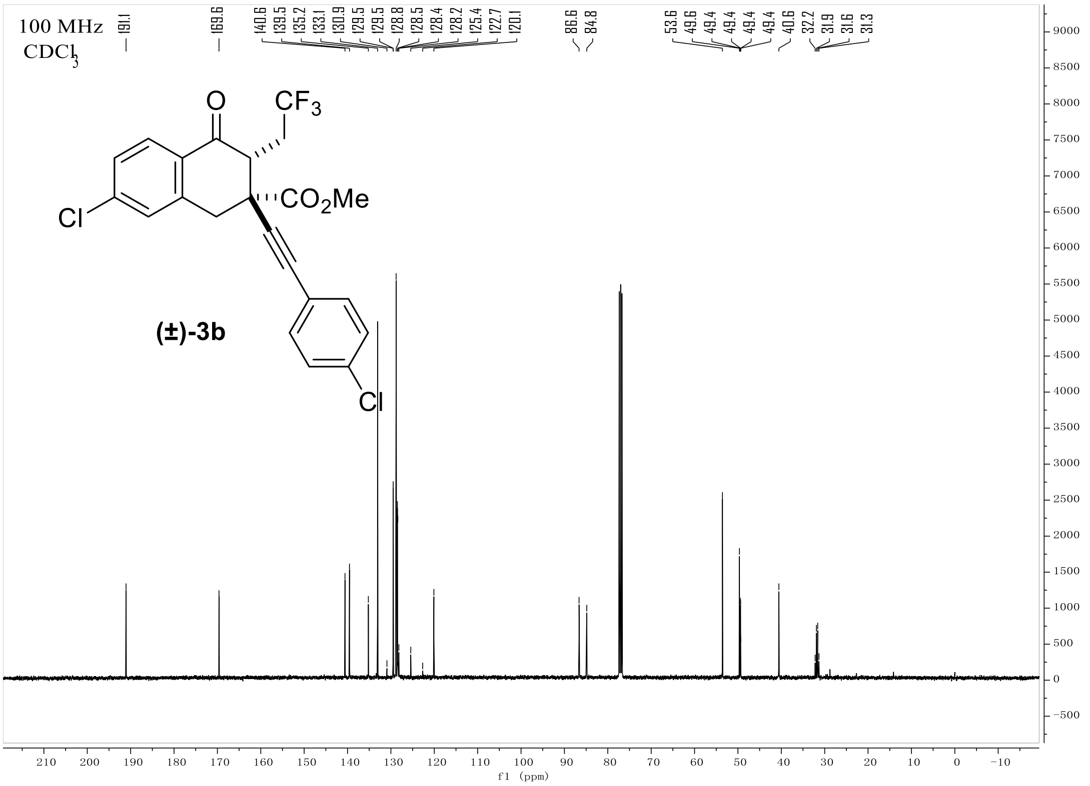
f1 (ppm)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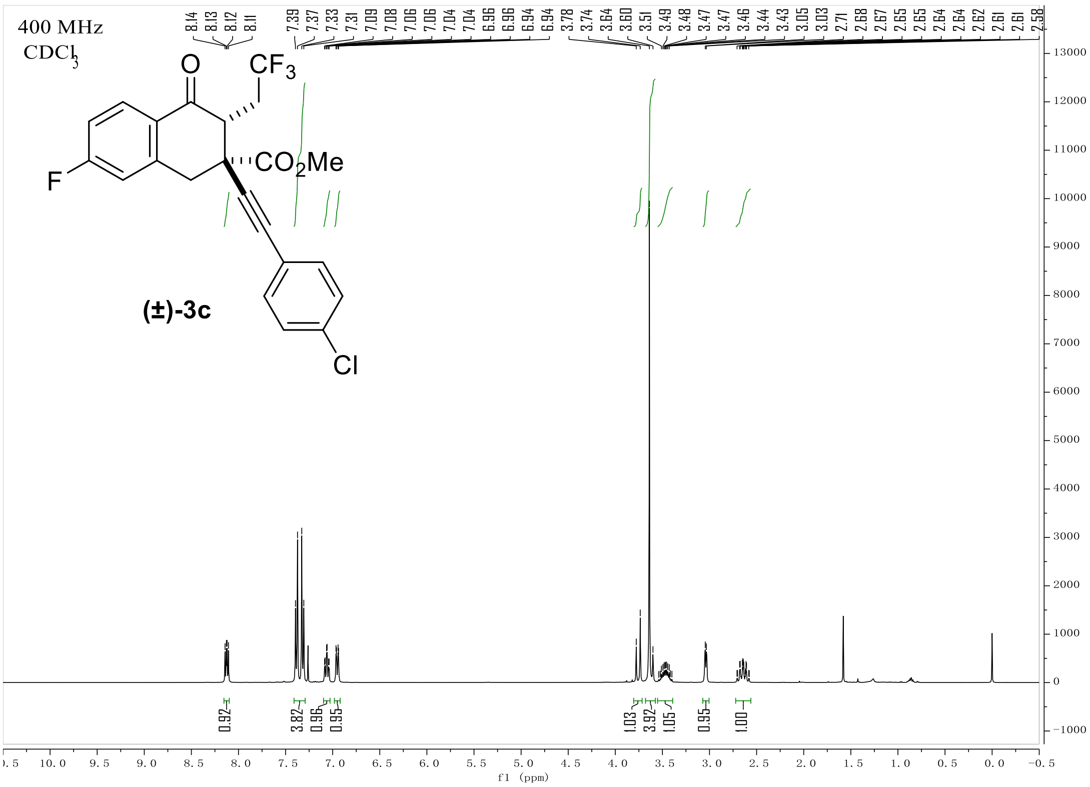
(±)-3b
f1 (ppm)


400 MHz
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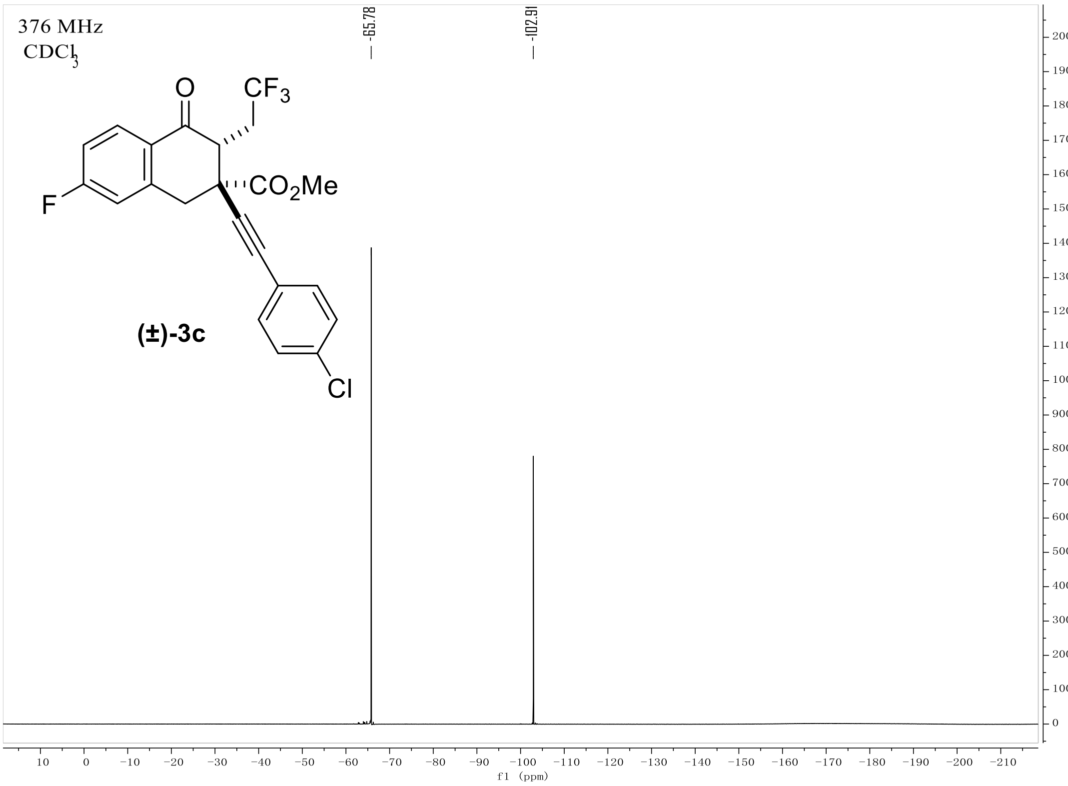
(±)-3c
f1 (ppm)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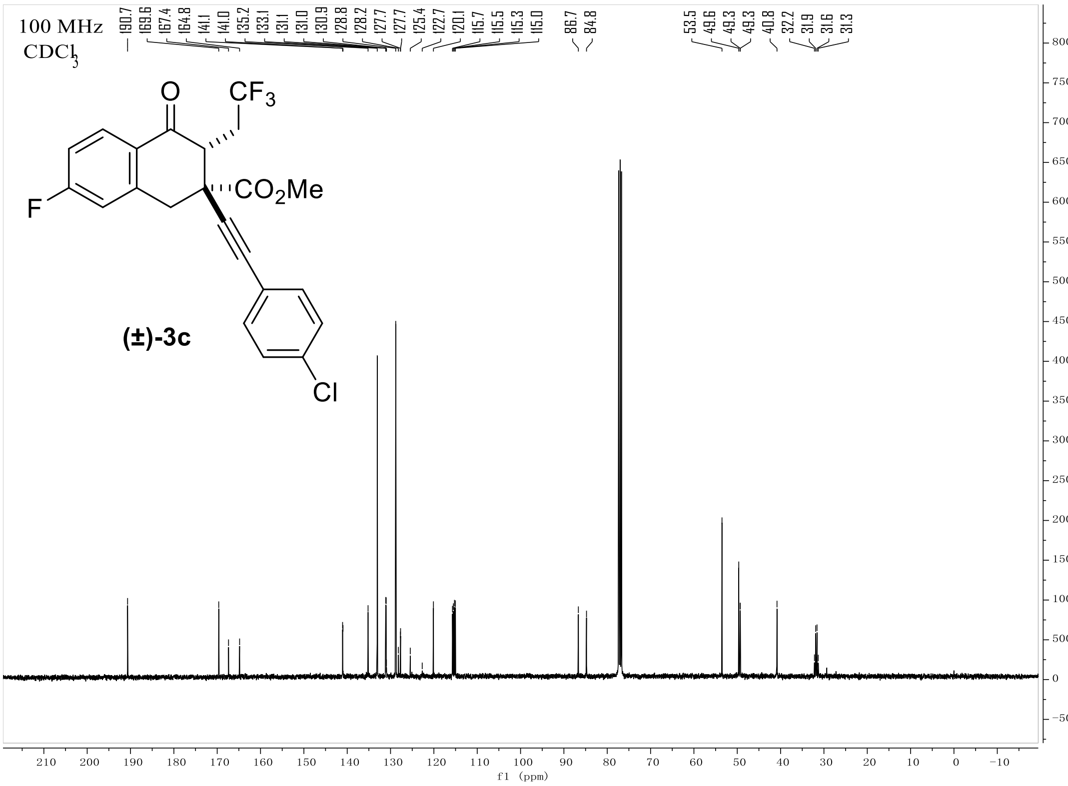
f1 (ppm)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164.8
141.1
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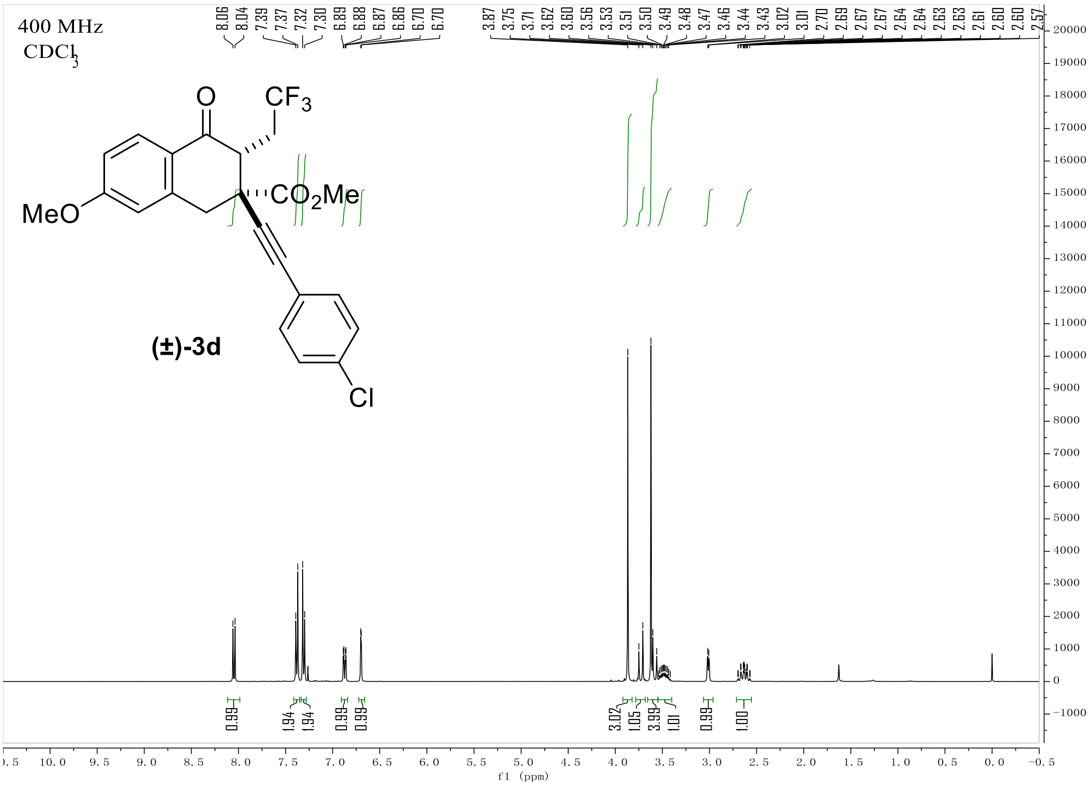
133.1
131.1
131.0
130.9
128.8
128.2
127.7
127.7
125.4
122.7
120.1
115.7
115.5
115.3
115.0
86.7
84.8
53.5
49.6
49.3
49.3
40.8
32.2
31.9
31.6
31.3
(±)-3c
f1 (ppm)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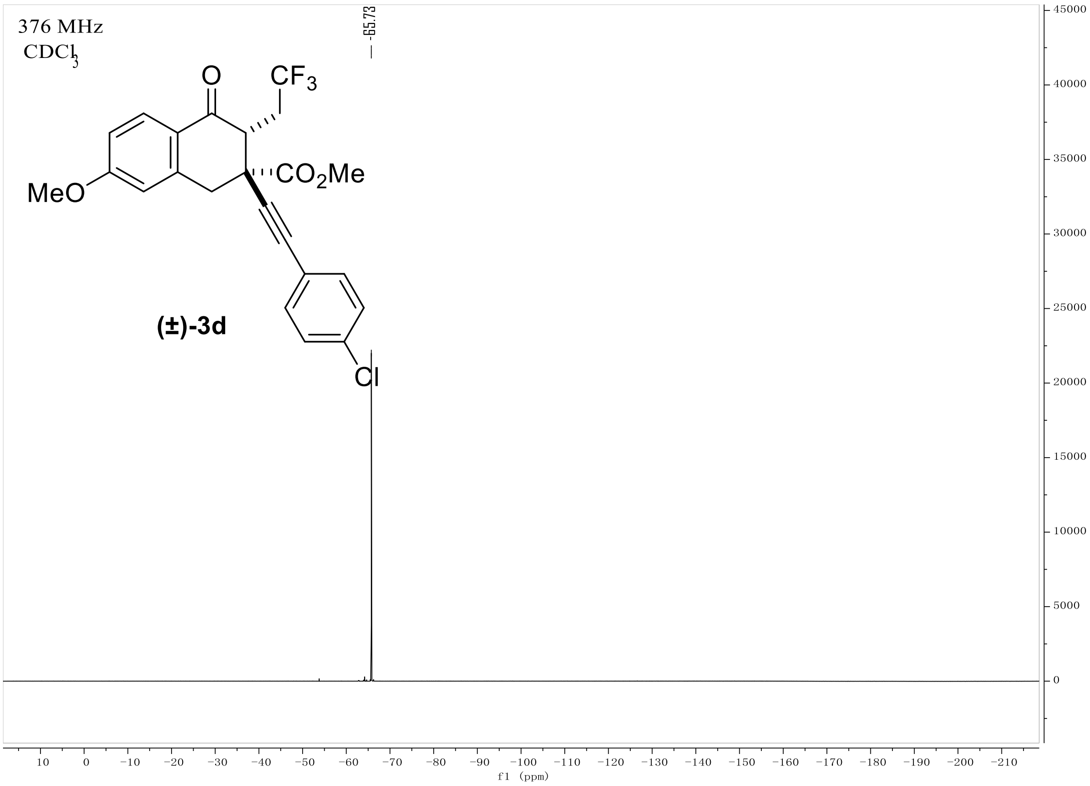
(±)-3d
MeO
O
CF3
CO2Me
Cl
f1 (ppm)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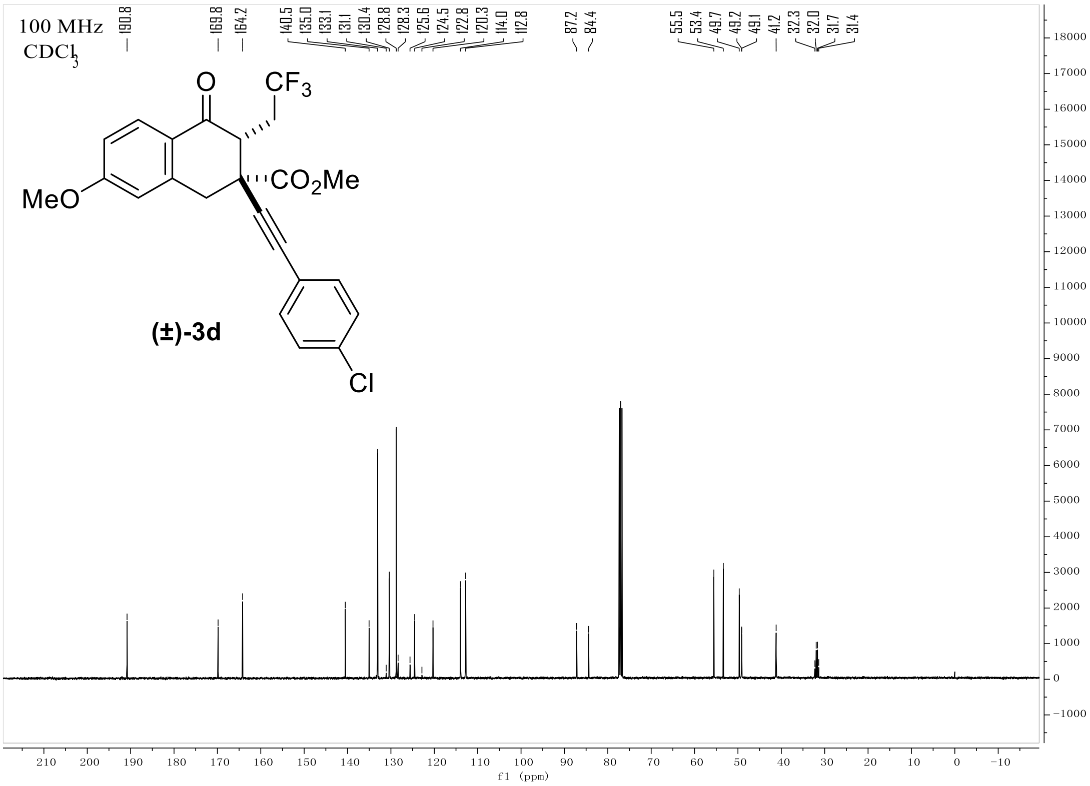
CF3
CO2Me
Cl
f1 (ppm)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130.4
128.8
128.3
125.6
124.5
122.8
120.3
114.0
112.8
87.2
84.4
55.5
53.4
49.7
49.2
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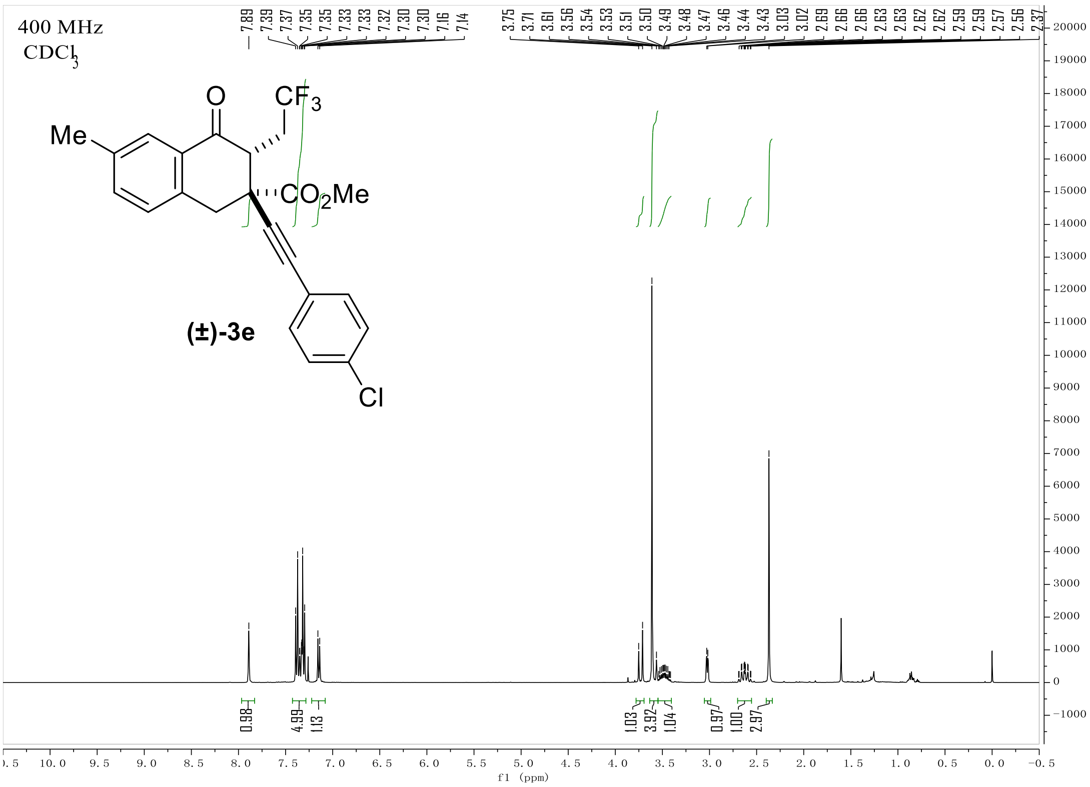
32.0
31.7
31.4
O
CF3
CO2Me
MeO
(±)-3d
Cl
f1 (ppm)


400 MHz
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7.33
7.33
7.32
7.30
7.30
7.16
7.14
3.75
3.71
3.61
3.56
3.54
3.53
3.51
3.50
3.49
3.48
3.47
3.46
3.44
3.43
3.03
3.02
2.69
2.66
2.66
2.63
2.62
2.62
2.59
2.59
2.57
2.56
2.37
O
CF3
Me
CO2Me
(±)-3e
Cl
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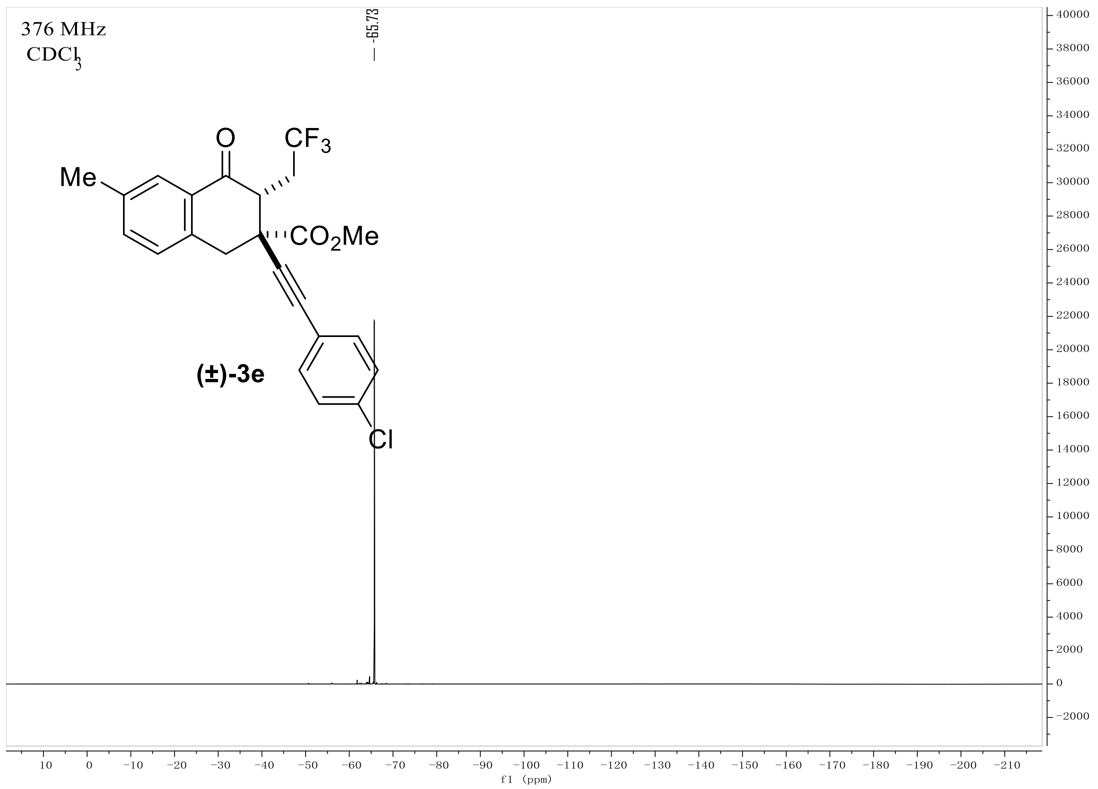
4.99
1.13
1.03
3.92
1.04
0.97
1.00
2.97
f1 (ppm)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O
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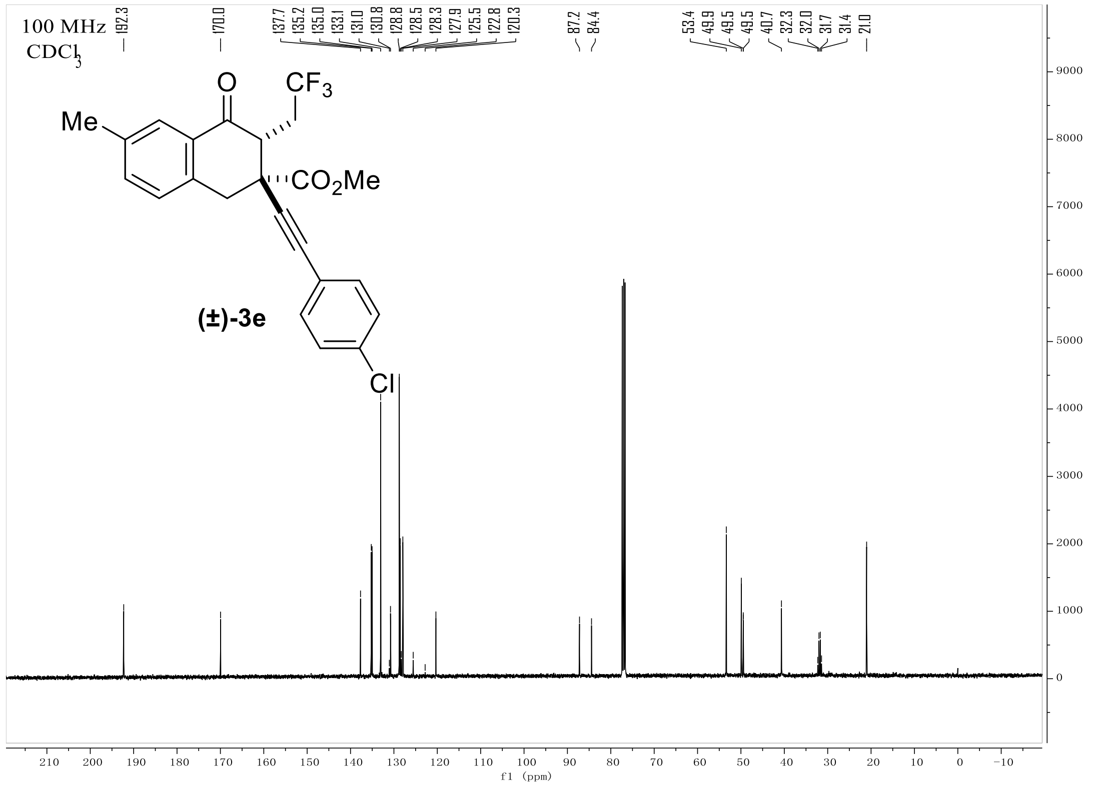
Me
CO2Me
(±)-3e
Cl
f1 (ppm)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128.8
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128.3
127.9
125.5
122.8
120.3
87.2
84.4
53.4
49.9
49.5
49.5
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31.4
21.0
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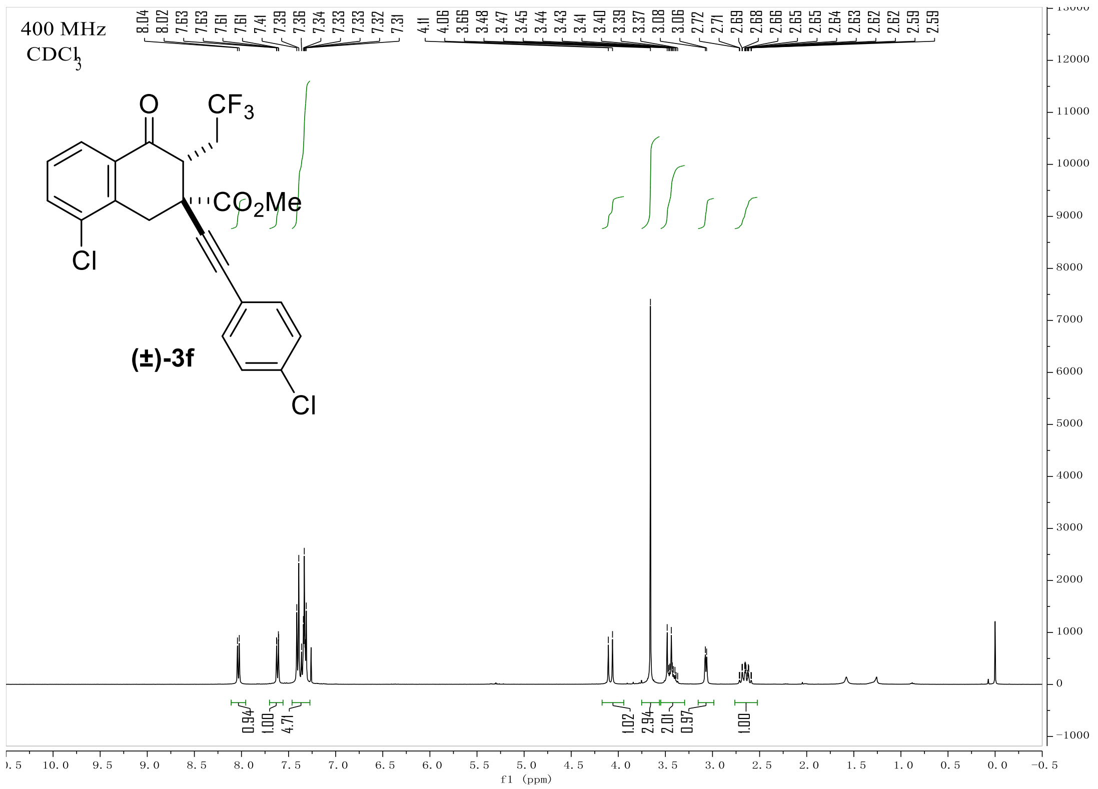
CF3
Me
CO2Me
(±)-3e
Cl
f1 (ppm)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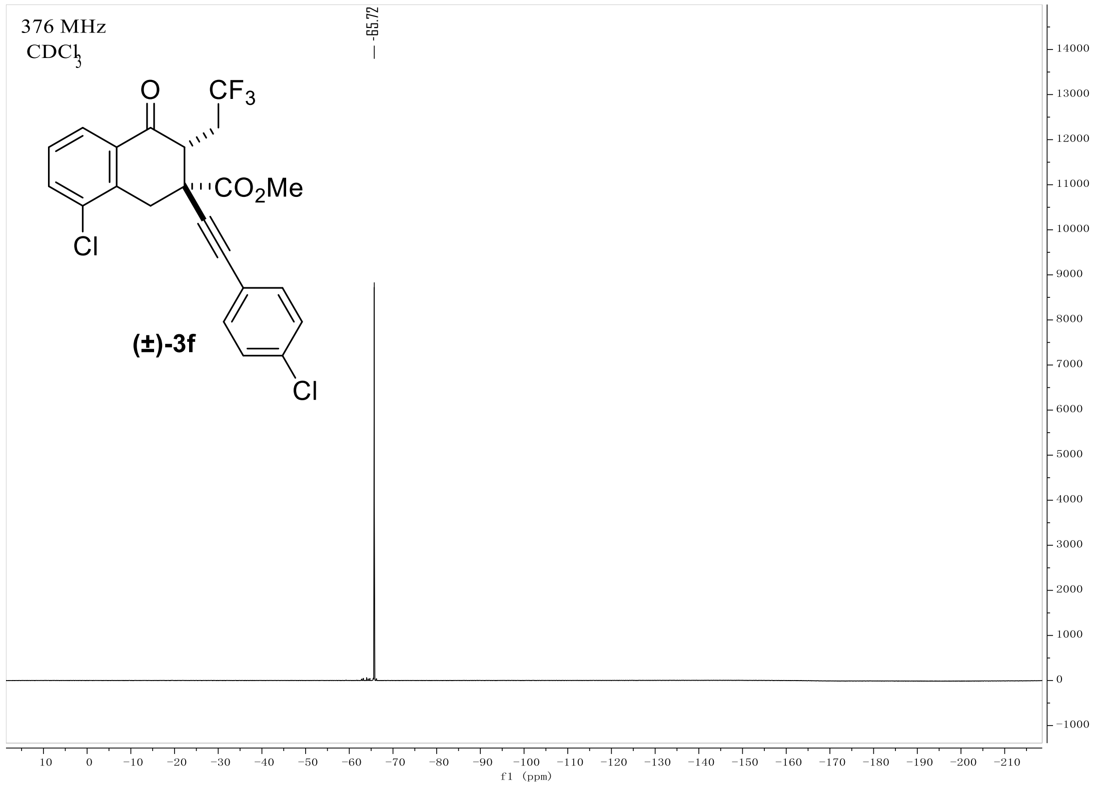
f1 (ppm)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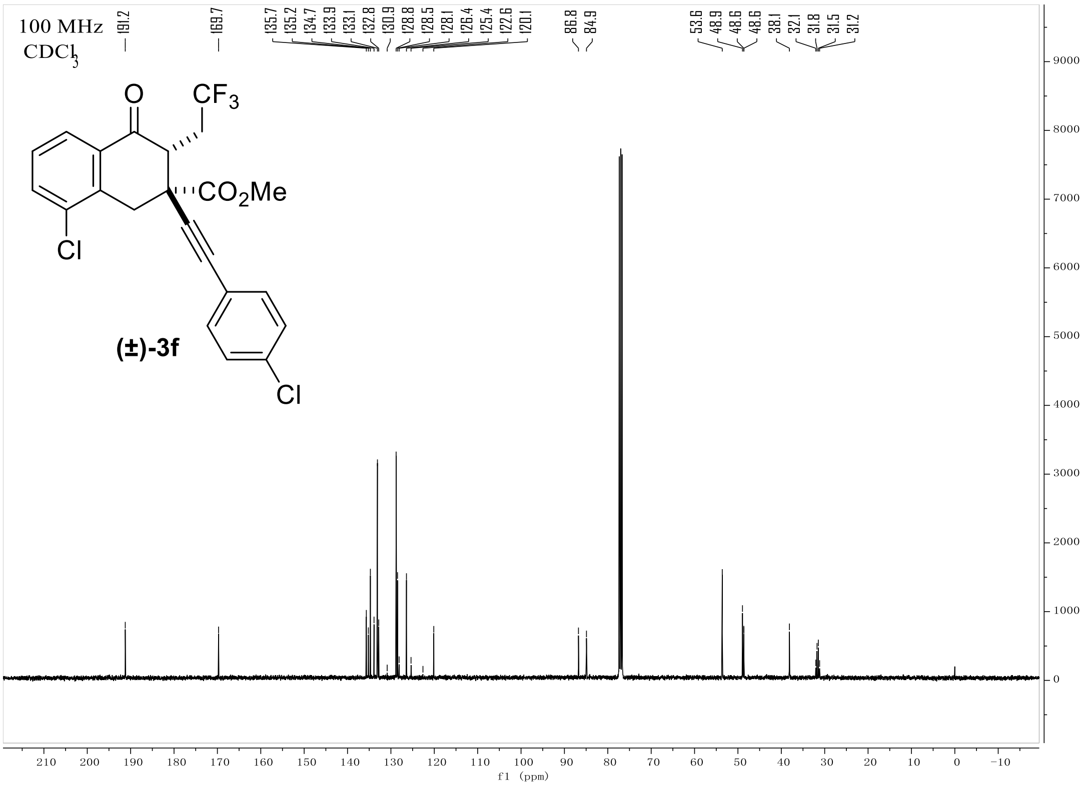
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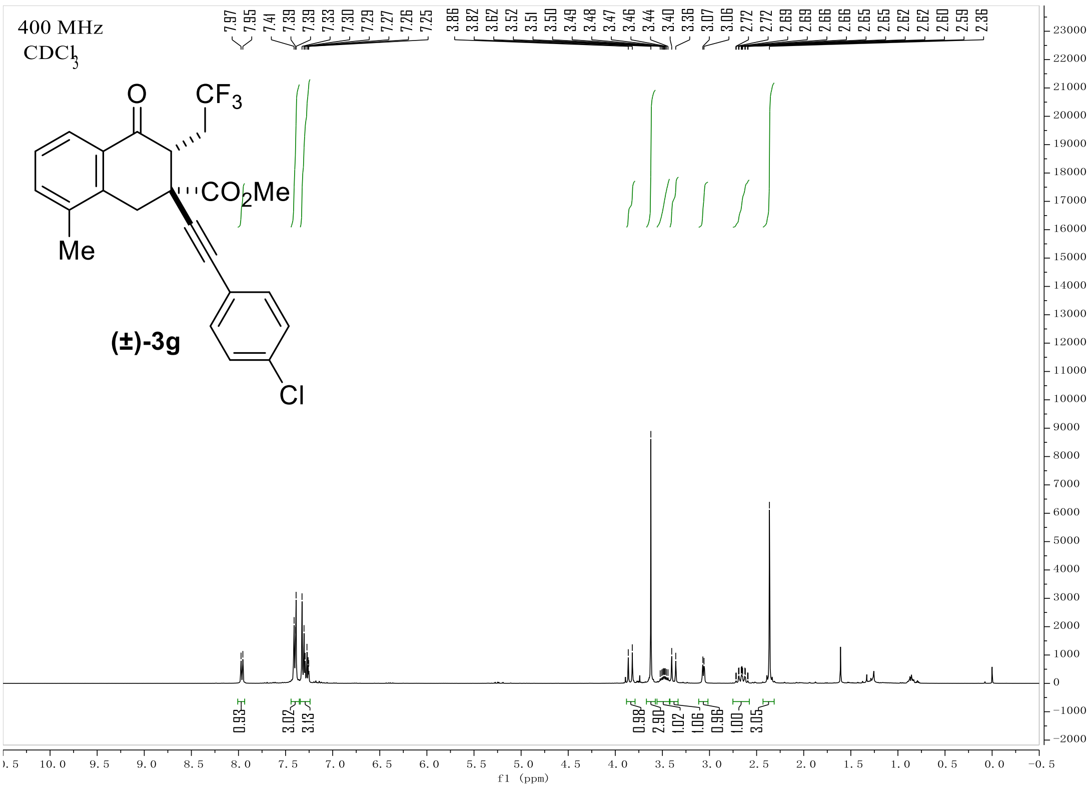
169.7
135.7 135.2 134.7 133.9 133.1 132.8 130.9 128.8 128.5 128.1 126.4 125.4 122.6 120.1
86.8 84.9
53.6 48.9 48.6 48.6 38.1 32.1 31.8 31.5 31.2
O
CF3
CO2Me
Cl
(±)-3f
Cl
f1 (ppm)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3.86 3.82 3.62 3.52 3.51 3.50 3.49 3.48 3.47 3.46 3.44 3.40 3.36 3.07 3.06 2.72 2.72 2.69 2.69 2.66 2.66 2.65 2.65 2.62 2.62 2.60 2.59 2.36
O
CF3
CO2Me
Me
(±)-3g
Cl
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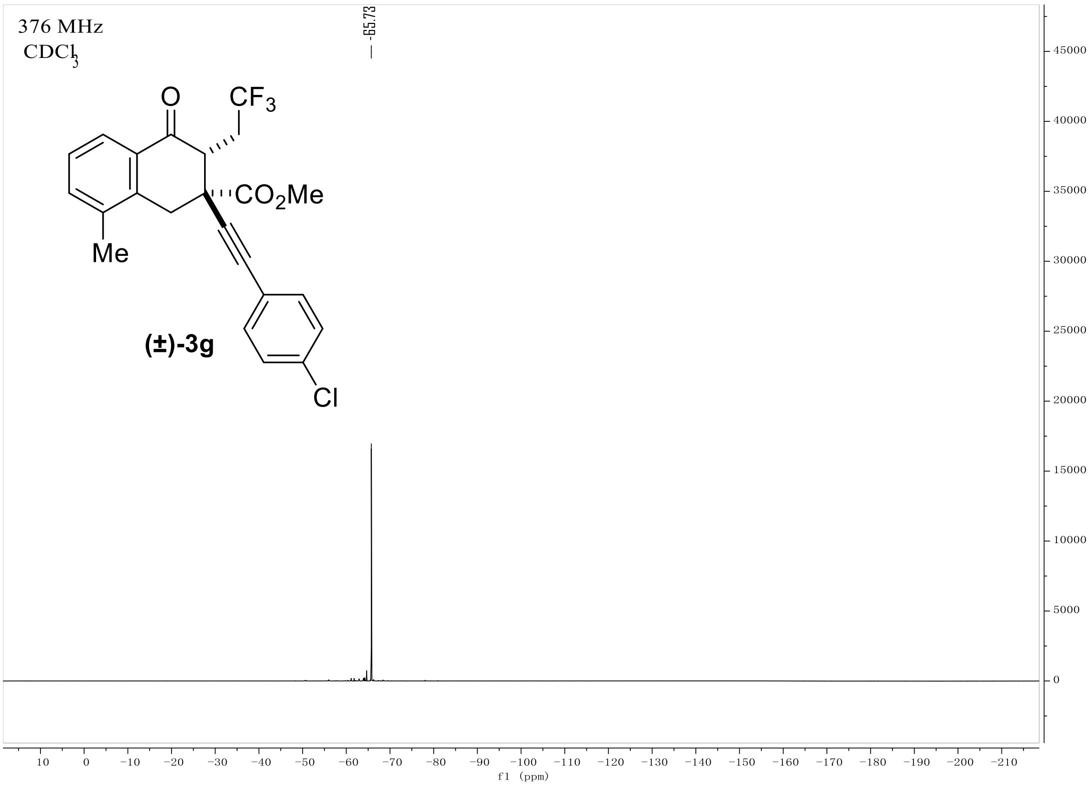
f1 (ppm)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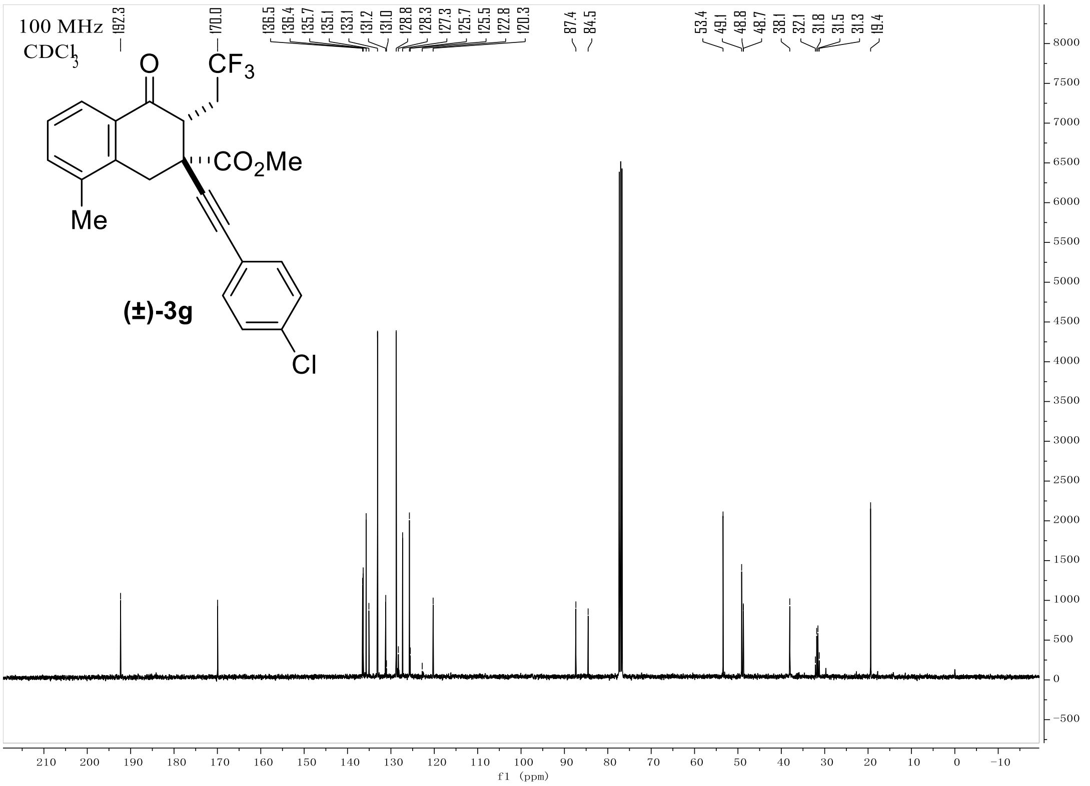
(±)-3g
f1 (ppm)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128.3
127.3
125.7
125.5
122.8
120.3
87.4
84.5
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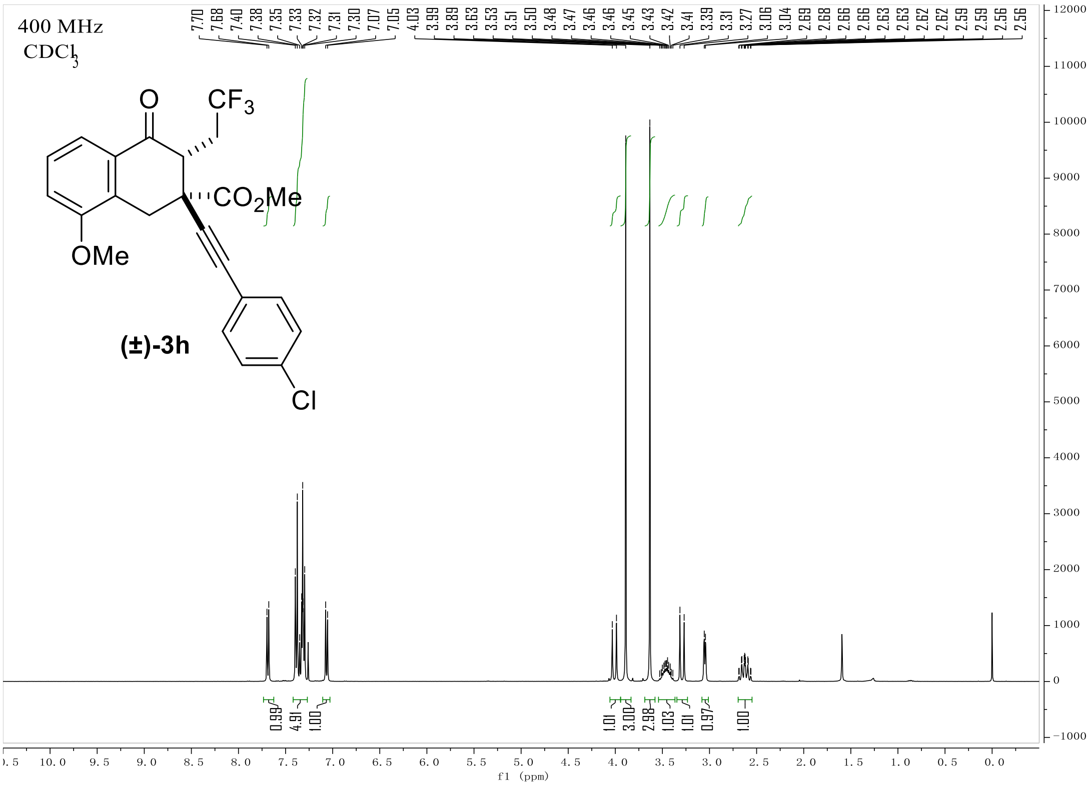
(±)-3g
f1 (ppm)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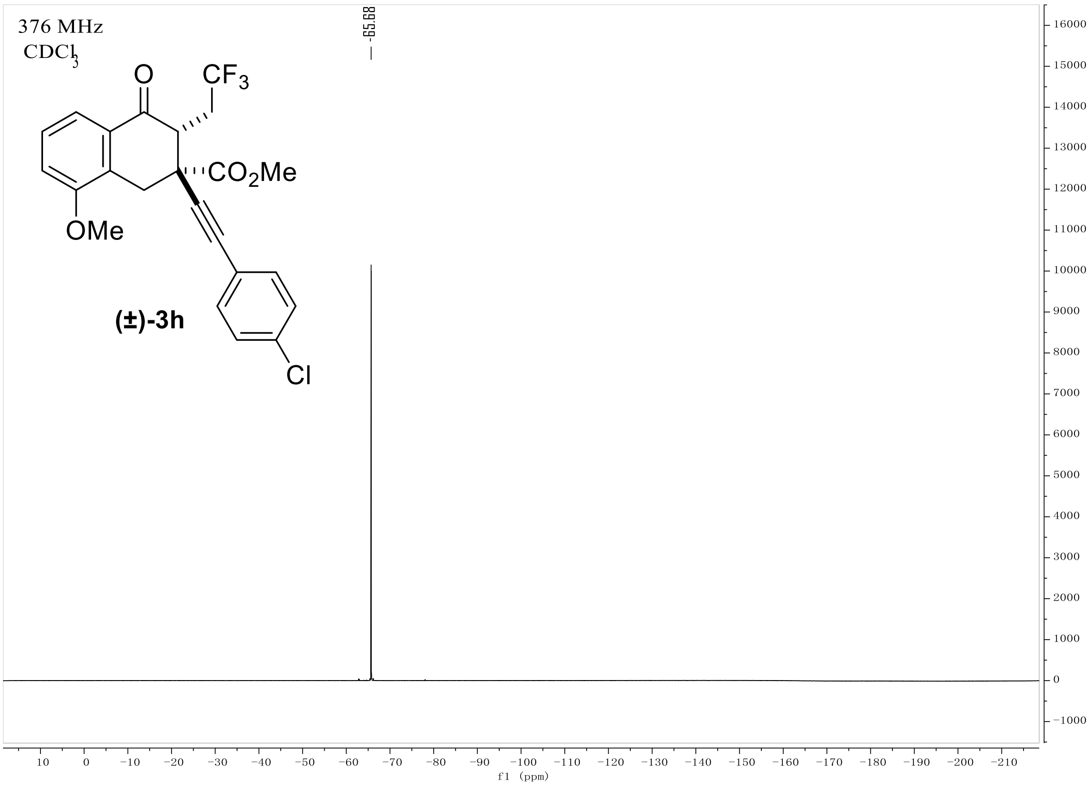
O
CF3
CO2Me
OMe
(±)-3h
Cl
0.99 4.91 1.00 1.01 3.00 2.98 1.03 1.01 0.97 1.00
f1 (ppm)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(±)-3h
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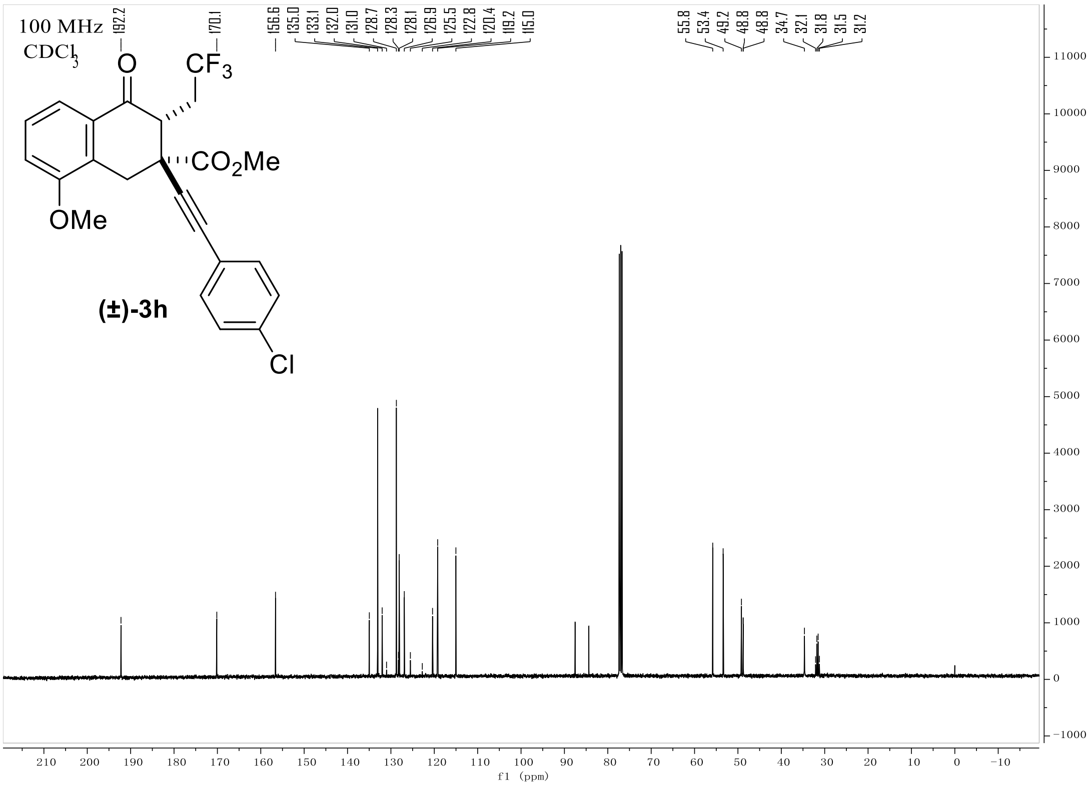
f1 (ppm)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128.7
128.3
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126.9
125.5
122.8
120.4
119.2
115.0
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53.4
49.2
48.8
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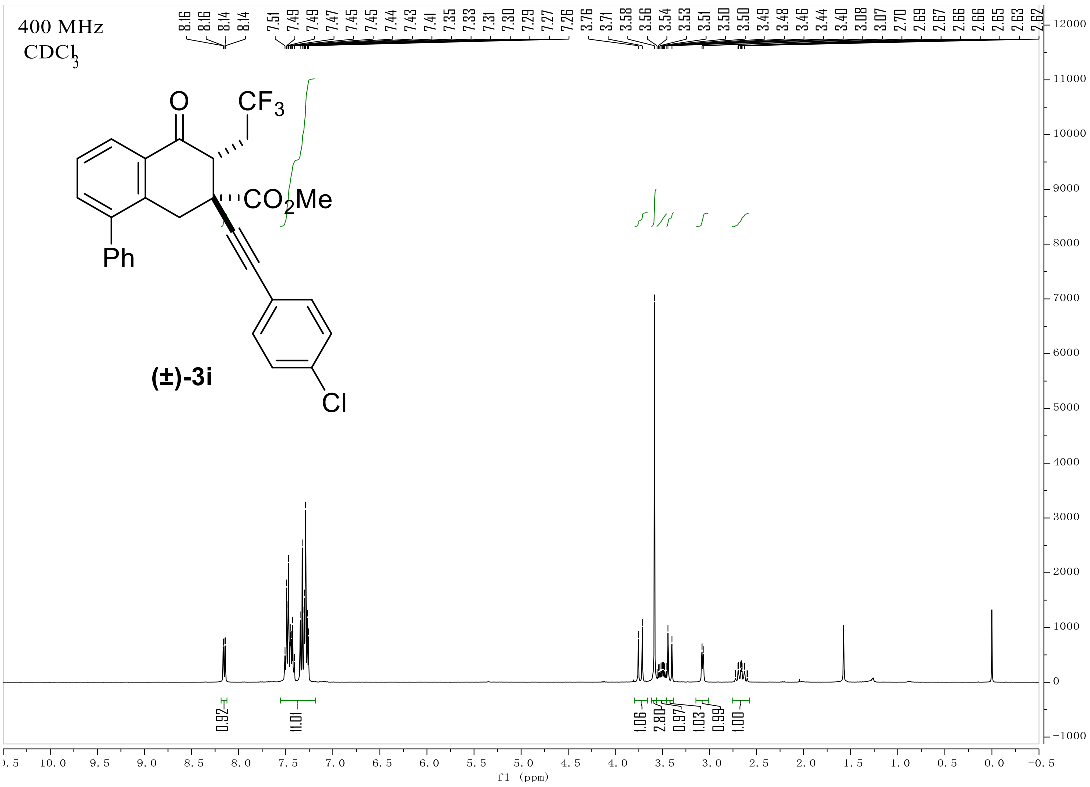
31.8
31.5
31.2
O
CF3
CO2Me
OMe
(±)-3h
Cl
f1 (ppm)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2.69
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2.66
2.66
2.65
2.63
2.62
O
CF3
CO2Me
Ph
(±)-3i
Cl
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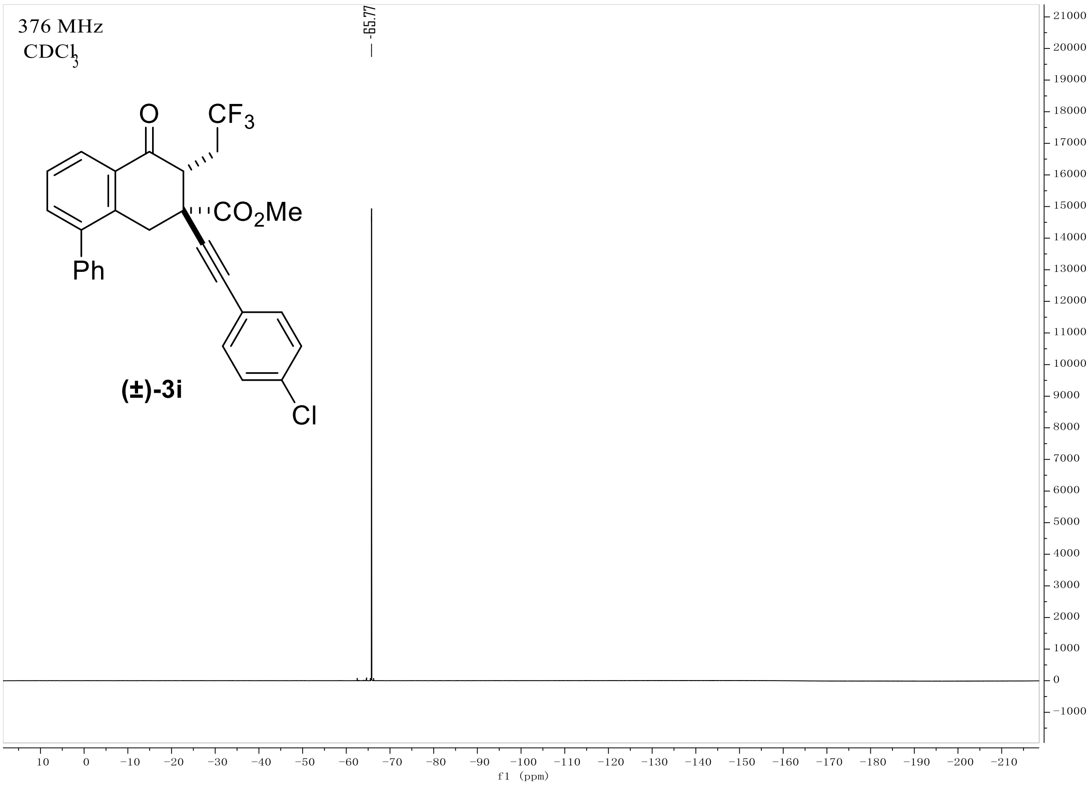
1.06
2.80
0.97
1.03
0.99
1.00
f1 (ppm)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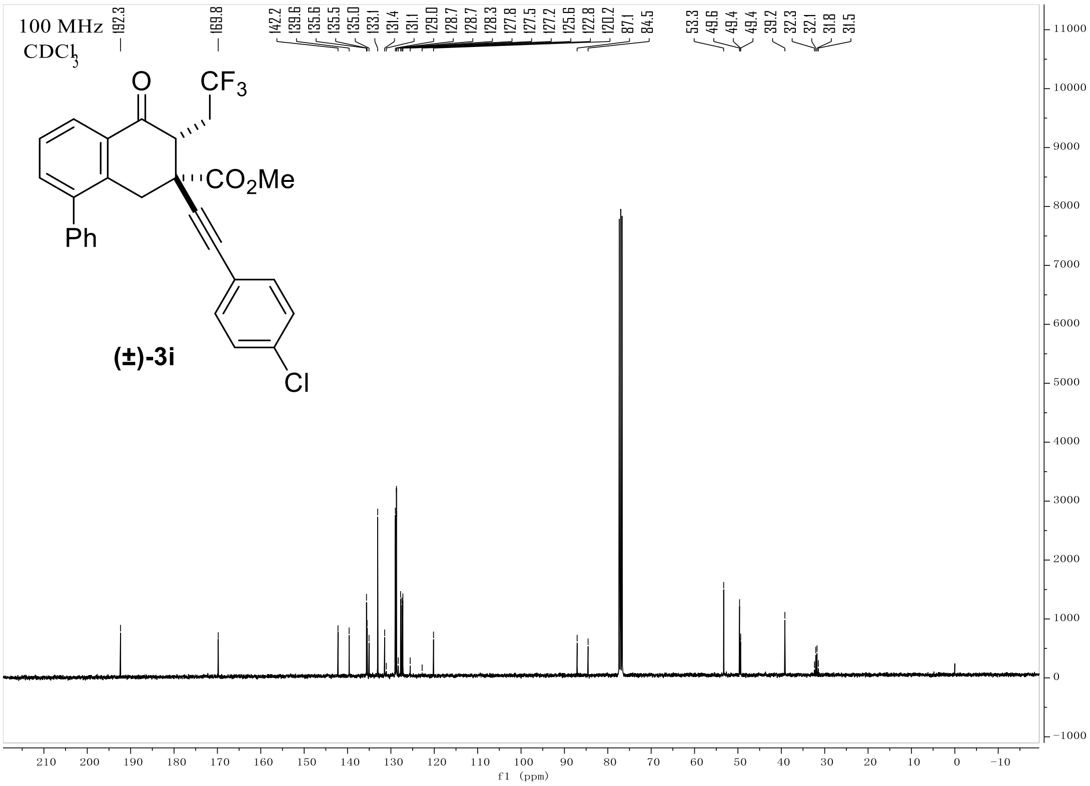
(±)-3i
f1 (ppm)


100 MHz
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127.5
127.2
125.6
122.8
120.2
87.1
84.5
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31.8
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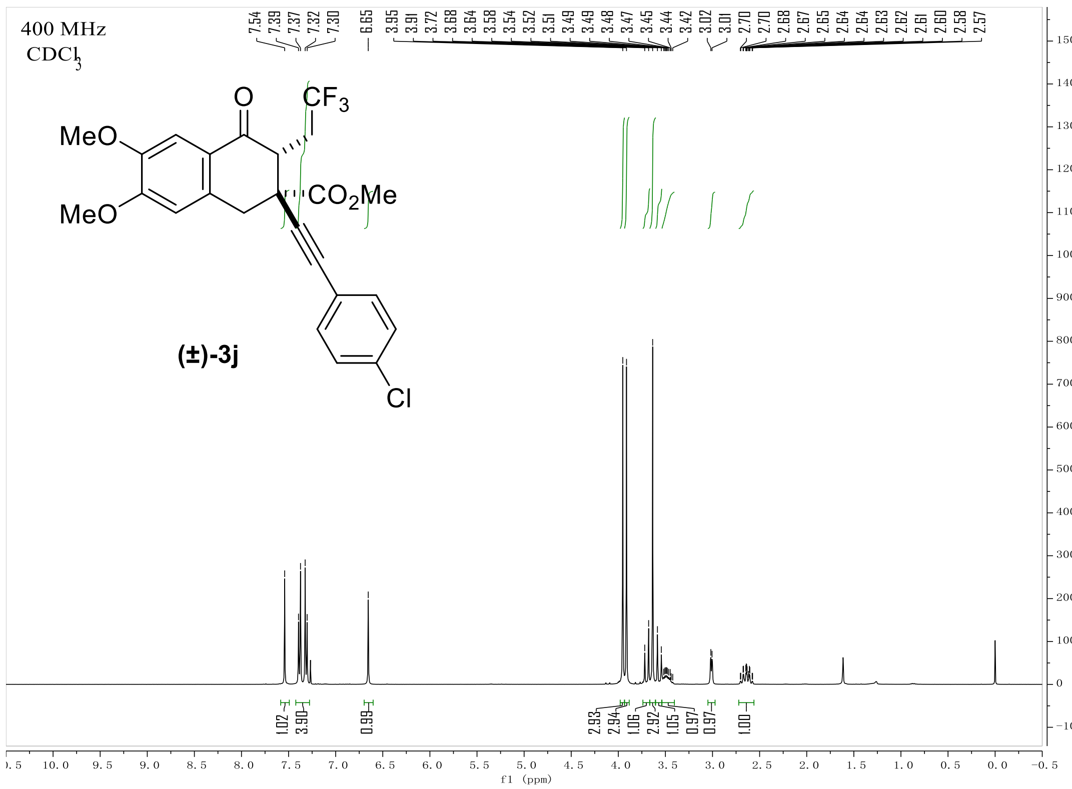
(±)-3i
f1 (ppm)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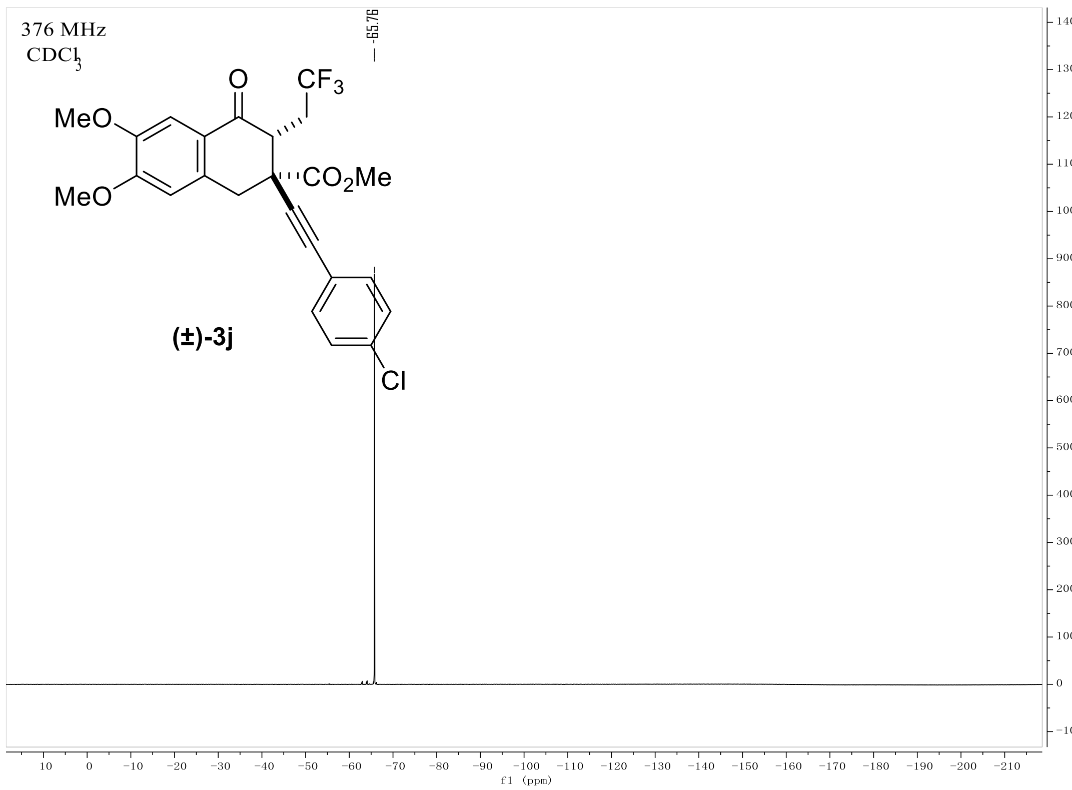
MeO
MeO
O
CF3
CO2Me
Cl
f1 (ppm)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-65.76
(±)-3j
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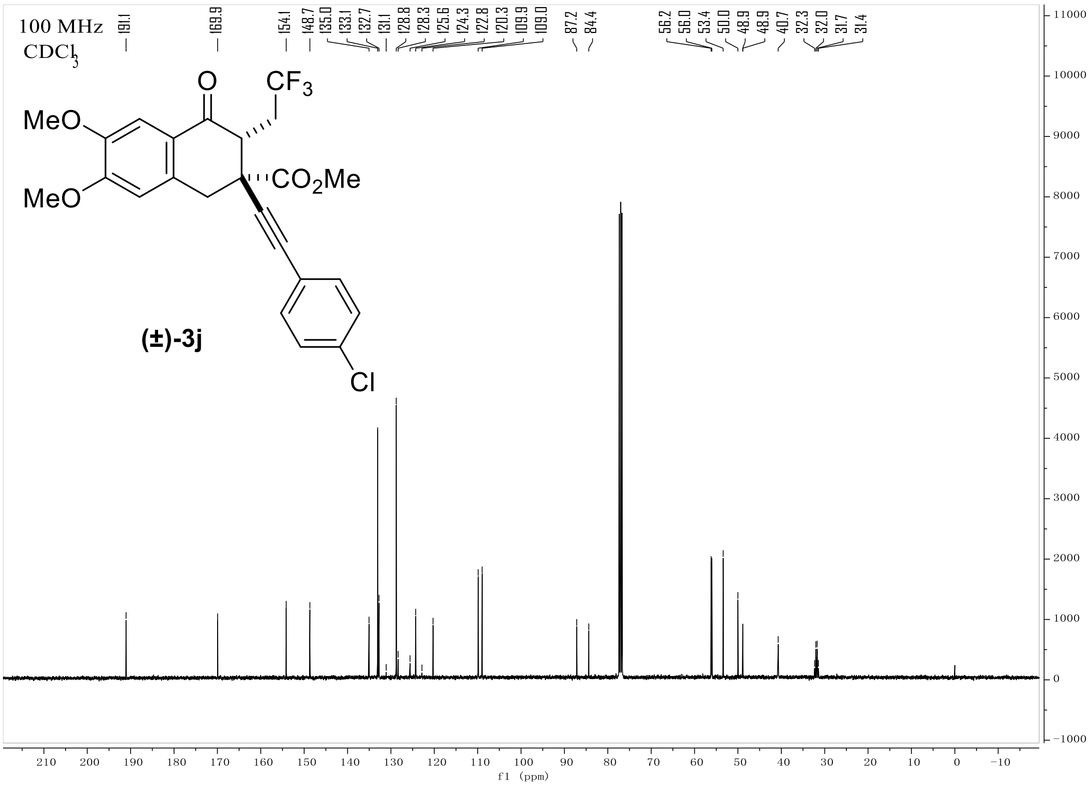
MeO
O
CF3
CO2Me
Cl
f1 (ppm)


100 MHz
CDCl3
(±)-3j
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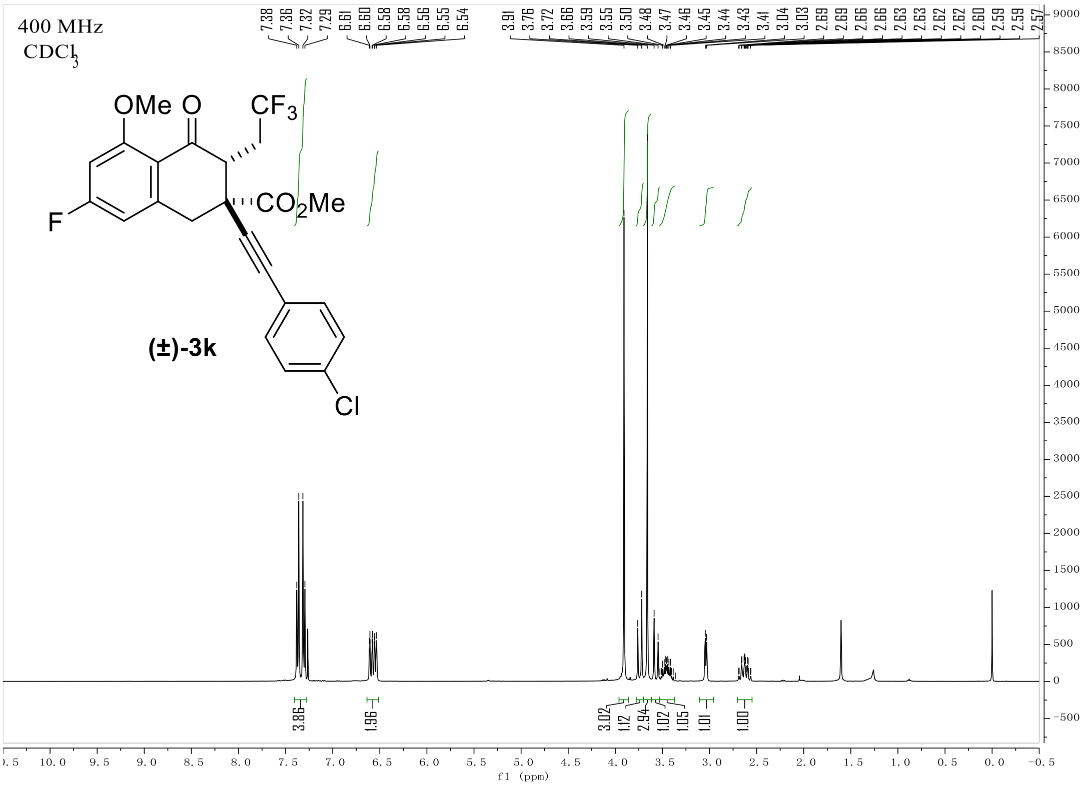
169.9
154.1
148.7
135.0
133.1
132.7
131.1
128.8
128.3
125.6
124.3
122.8
120.3
109.9
109.0
87.2
84.4
56.2
56.0
53.4
50.0
48.9
48.9
40.7
32.3
32.0
31.7
31.4
f1 (ppm)


400 MHz
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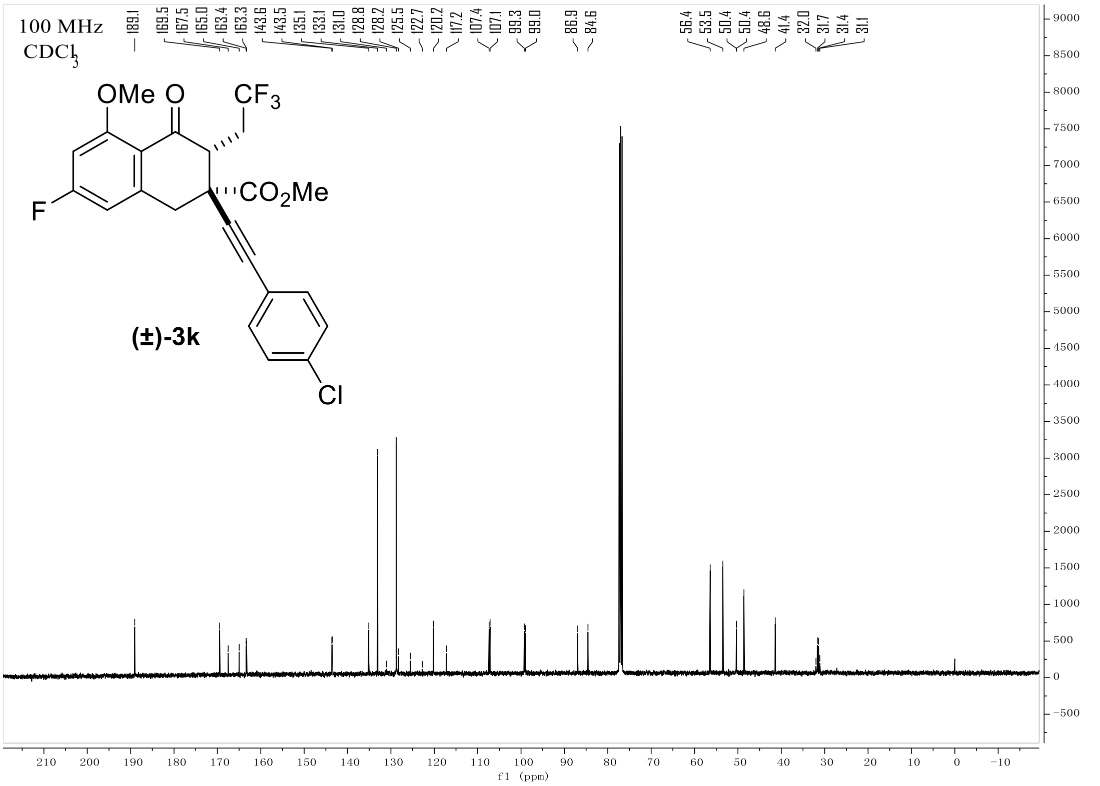
(±)-3k
7.38
7.36
7.32
7.29
6.61
6.60
6.58
6.58
6.56
6.55
6.54
3.91
3.76
3.72
3.66
3.59
3.55
3.50
3.48
3.47
3.46
3.45
3.44
3.43
3.41
3.04
3.03
2.69
2.69
2.66
2.66
2.63
2.63
2.62
2.62
2.60
2.59
2.59
2.57
3.86
1.96
3.02
1.12
2.94
1.02
1.05
1.01
1.00
f1 (ppm)

376 MHz
CDCl3
OMe O CF3
CO2Me
F
(±)-3k
Cl
-65.61
-100.21
f1 (ppm)



100 MHz
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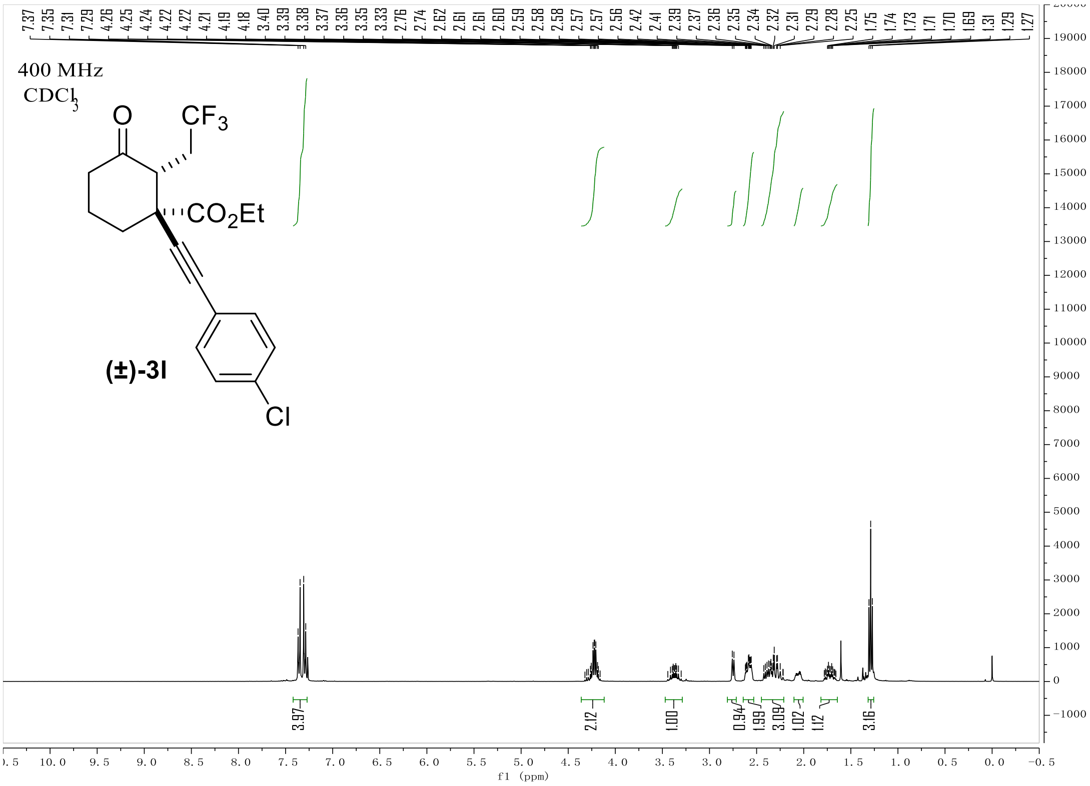
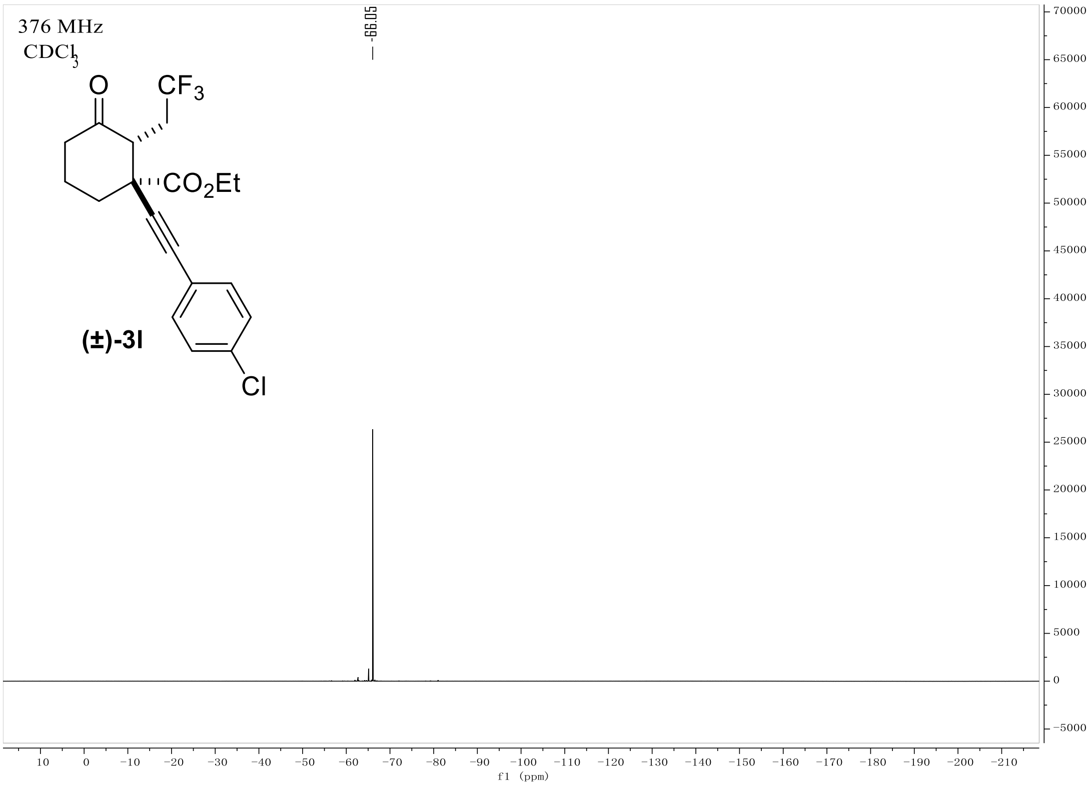
OMe O CF3
CO2Me
F
(±)-3k
Cl
189.1
169.5
167.5
165.0
163.4
163.3
143.6
143.5
135.1
133.1
131.0
128.8
128.2
125.5
122.7
120.2
117.2
107.4
107.1
99.3
99.0
86.9
84.6
56.4
53.5
50.4
50.4
48.6
41.4
32.0
31.7
31.4
31.1
f1 (ppm)


400 MHz
CDCl3
(±)-3l
f1 (ppm)


376 MHz
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(±)-3l
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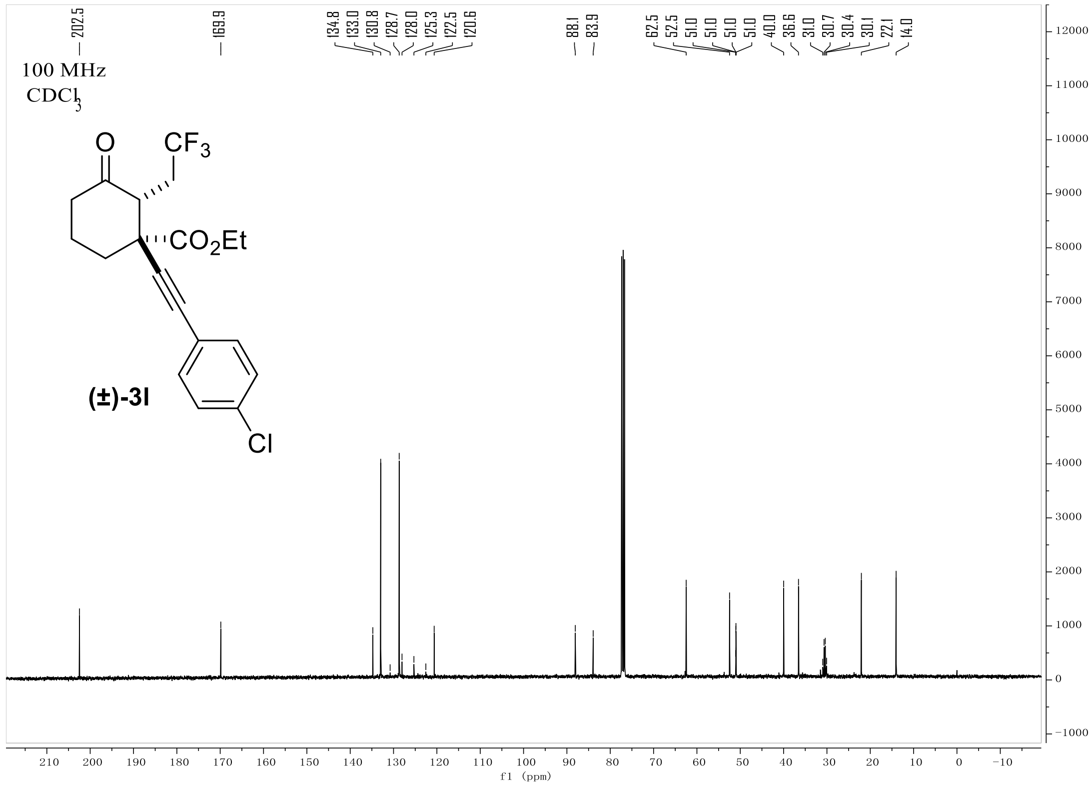
f1 (ppm)


100 MHz
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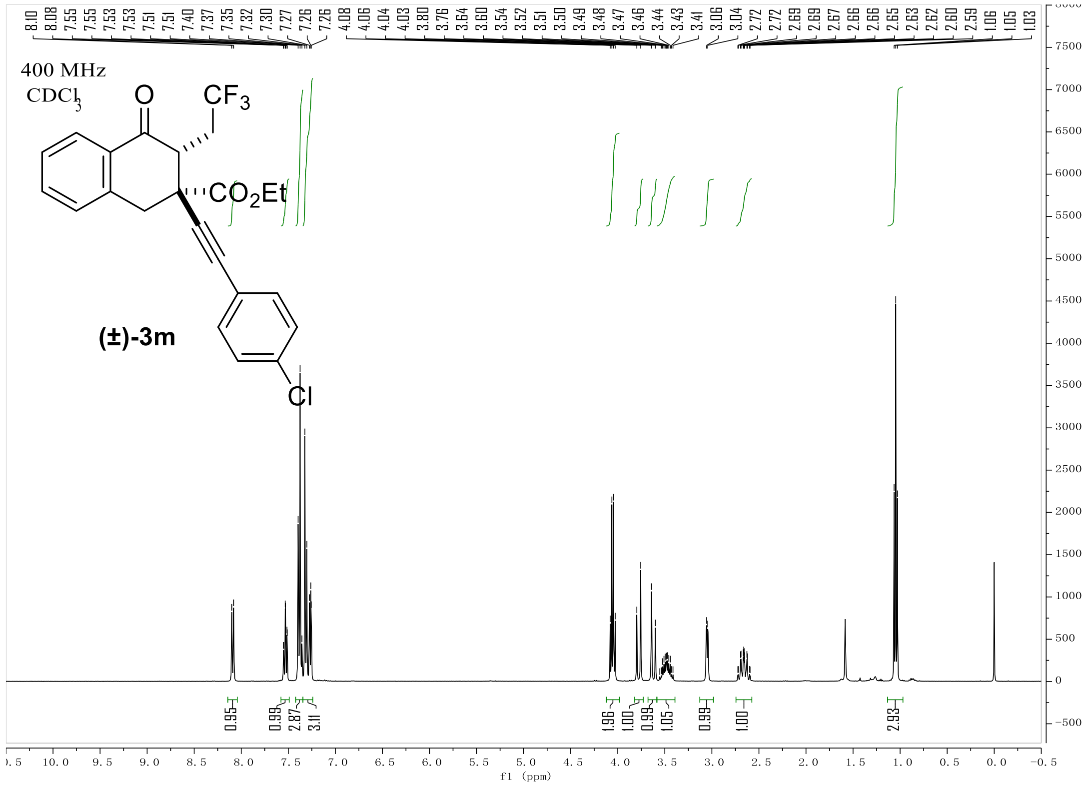
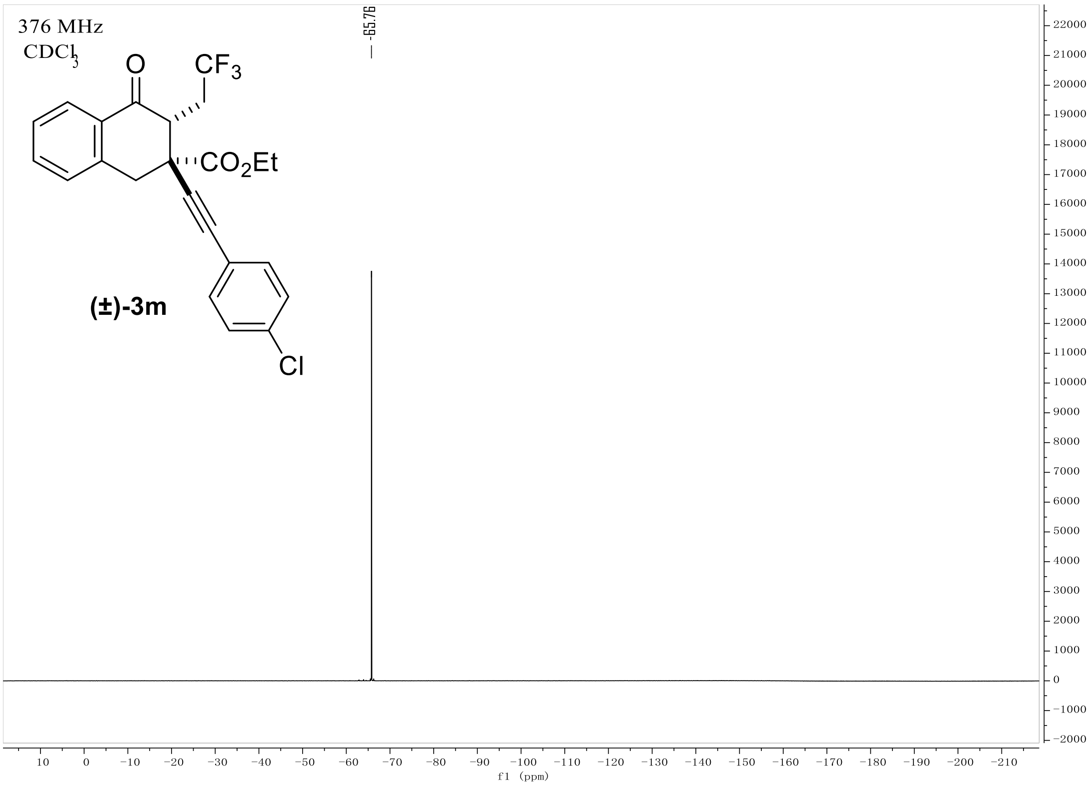
(±)-3l
f1 (ppm)


400 MHz
CDCl3
(±)-3m
f1 (ppm)


376 MHz
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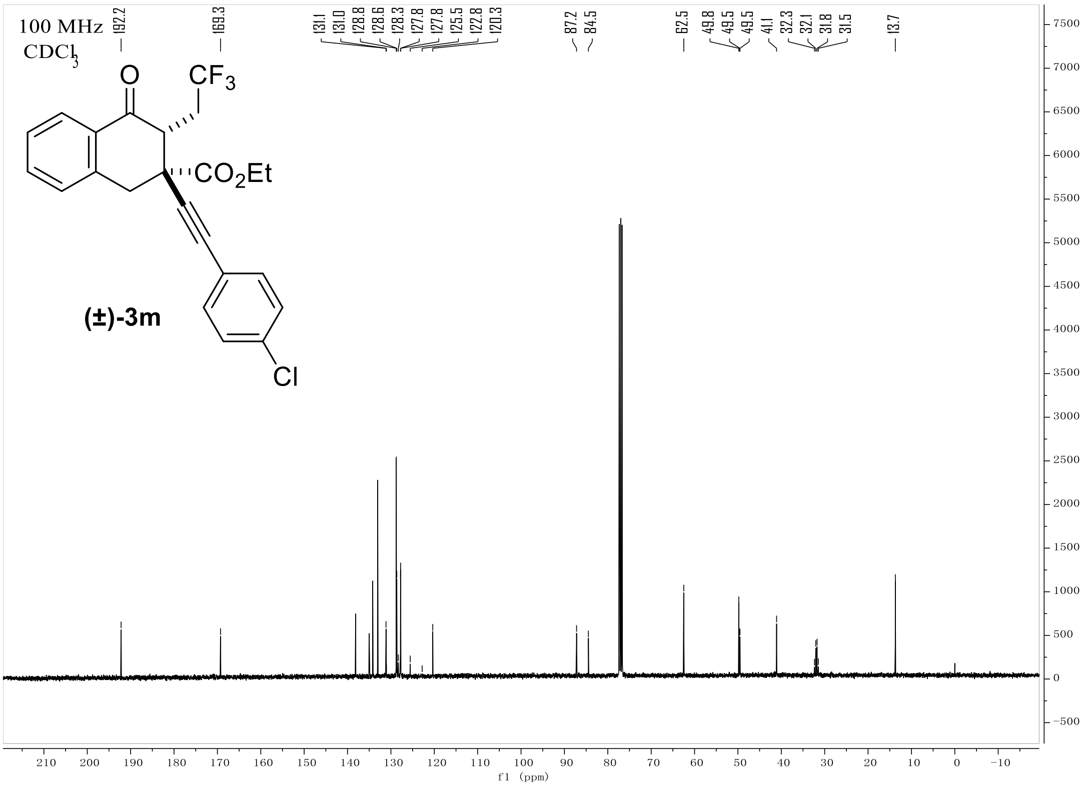
f1 (ppm)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(±)-3m
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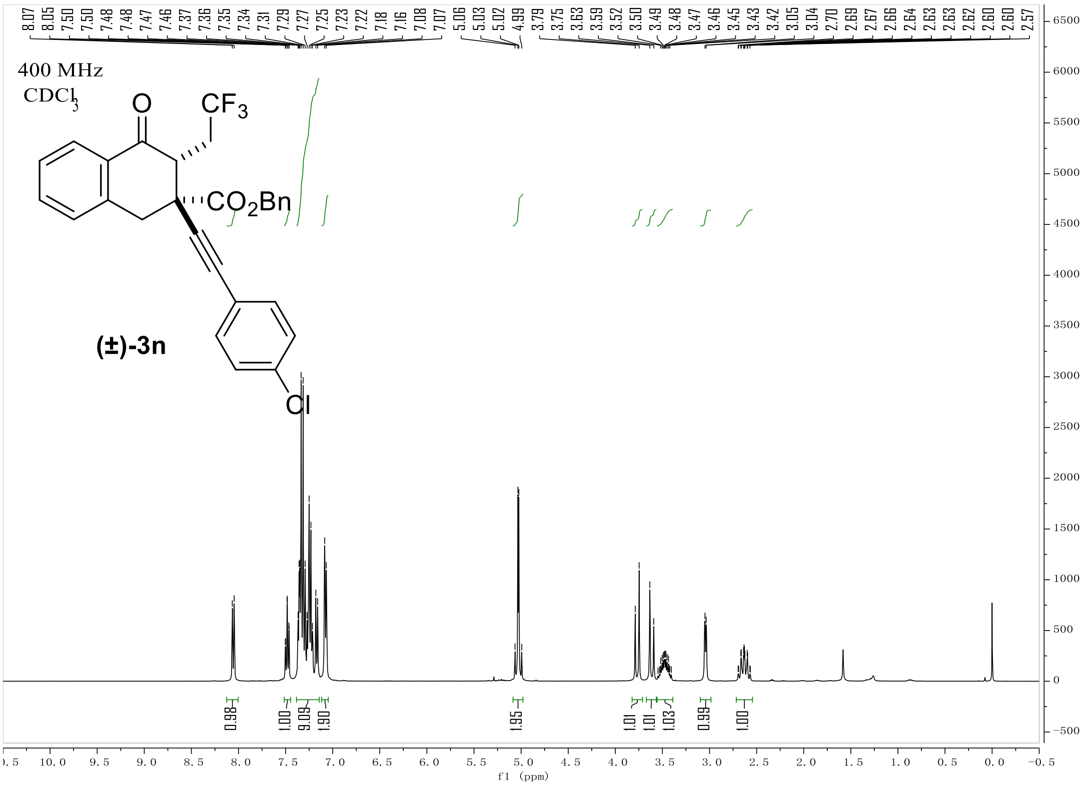
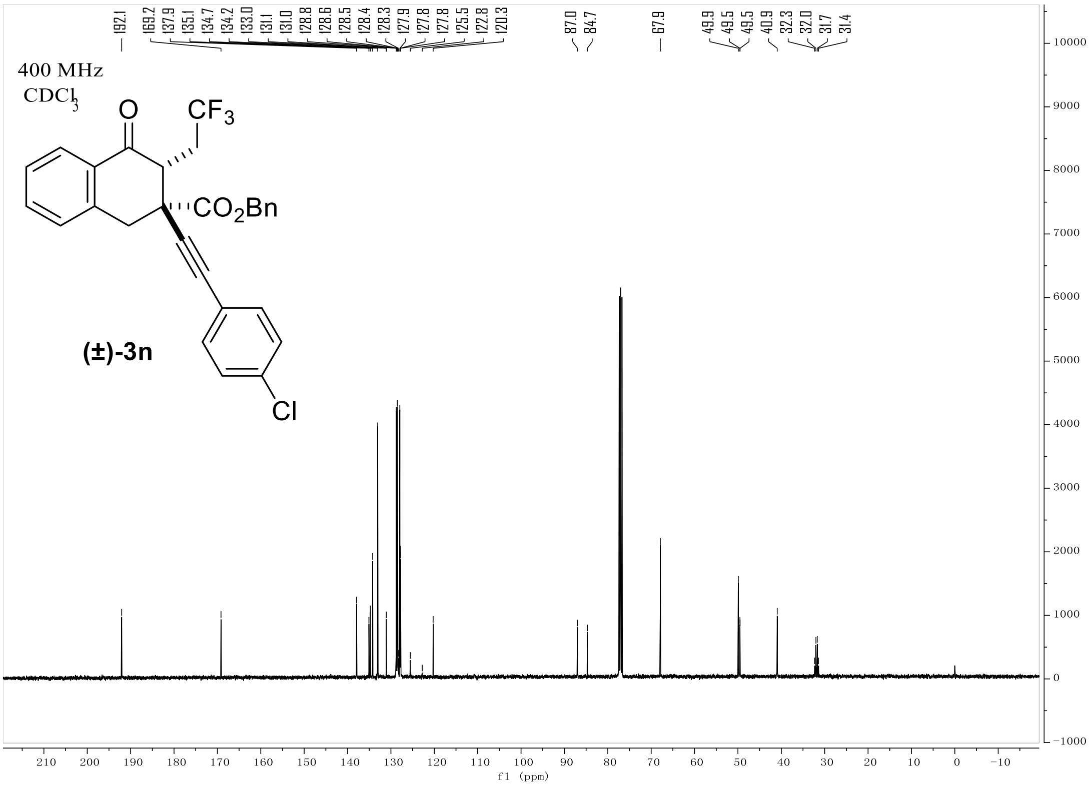
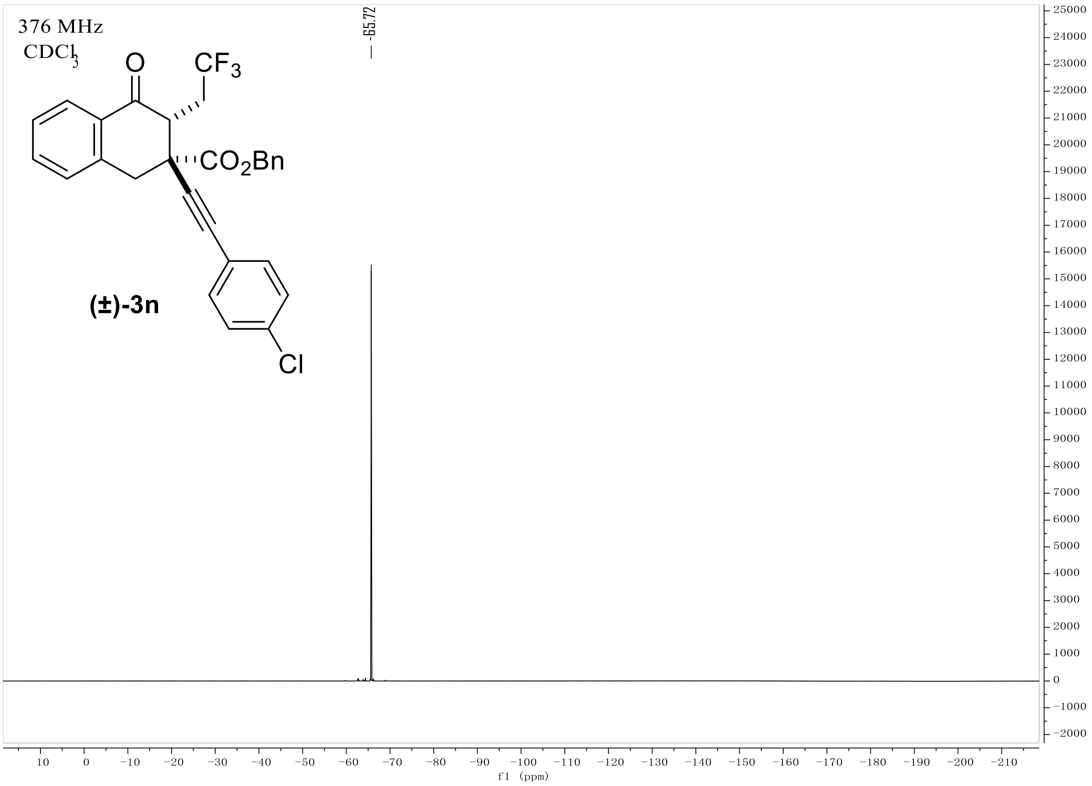
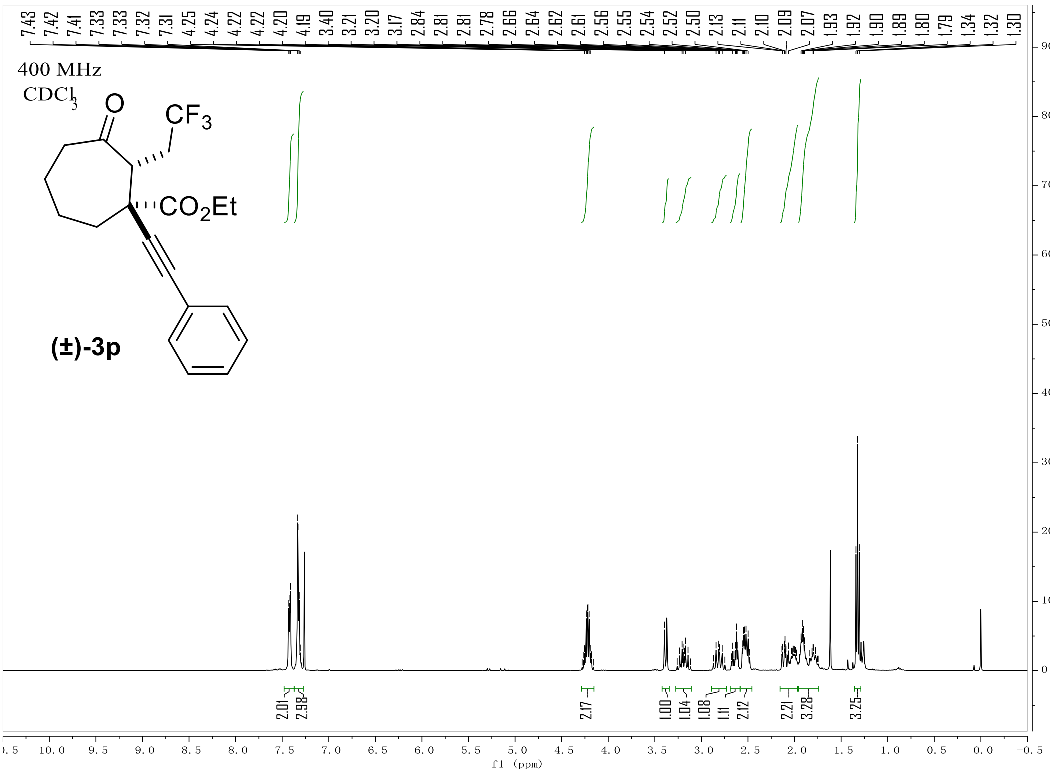
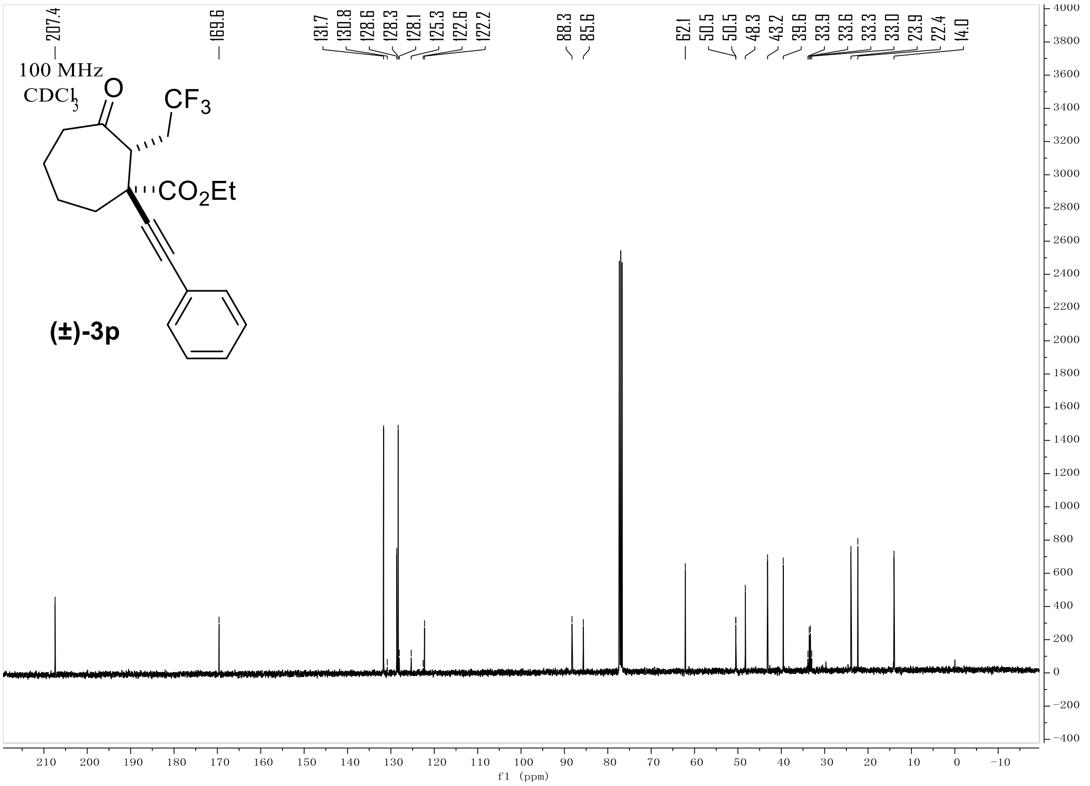
169.3
131.1
131.0
128.8
128.6
128.3
127.8
127.8
125.5
122.8
120.3
87.2
84.5
62.5
49.8
49.5
49.5
41.1
32.3
32.1
31.8
31.5
13.7
f1 (ppm)


400 MHz
CDCl3
(±)-3n
CO2Bn
CF3
Cl
f1 (ppm)

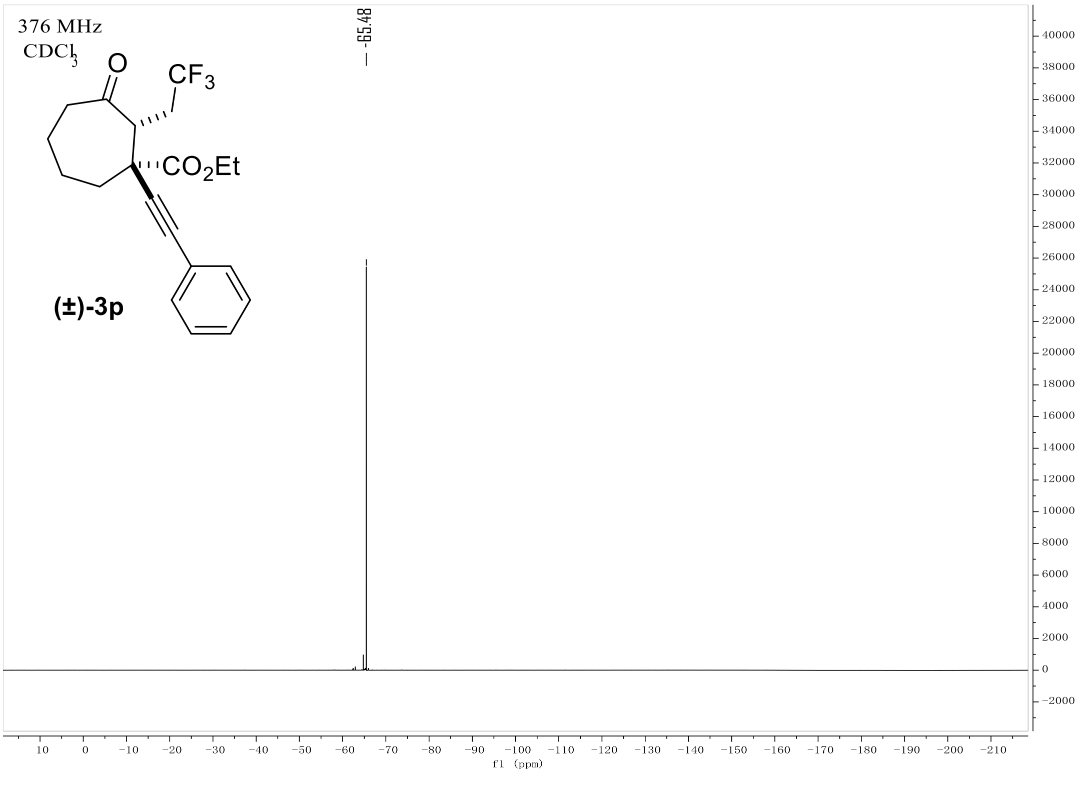

400 MHz
CDCl3
(±)-3n
CO2Bn
CF3
Cl
f1 (ppm)


376 MHz
CDCl3
-65.72
(±)-3n
f1 (ppm)


400 MHz
CDCl3
(±)-3p
f1 (ppm)



207.4
169.6
131.7
130.8
128.6
128.3
128.1
125.3
122.6
122.2
88.3
85.6
62.1
50.5
50.5
48.3
43.2
39.6
33.9
33.6
33.3
33.0
23.9
22.4
14.0
100 MHz
CDCl3
O
CF3
CO2Et
(±)-3p
f1 (ppm)



-65.48
376 MHz
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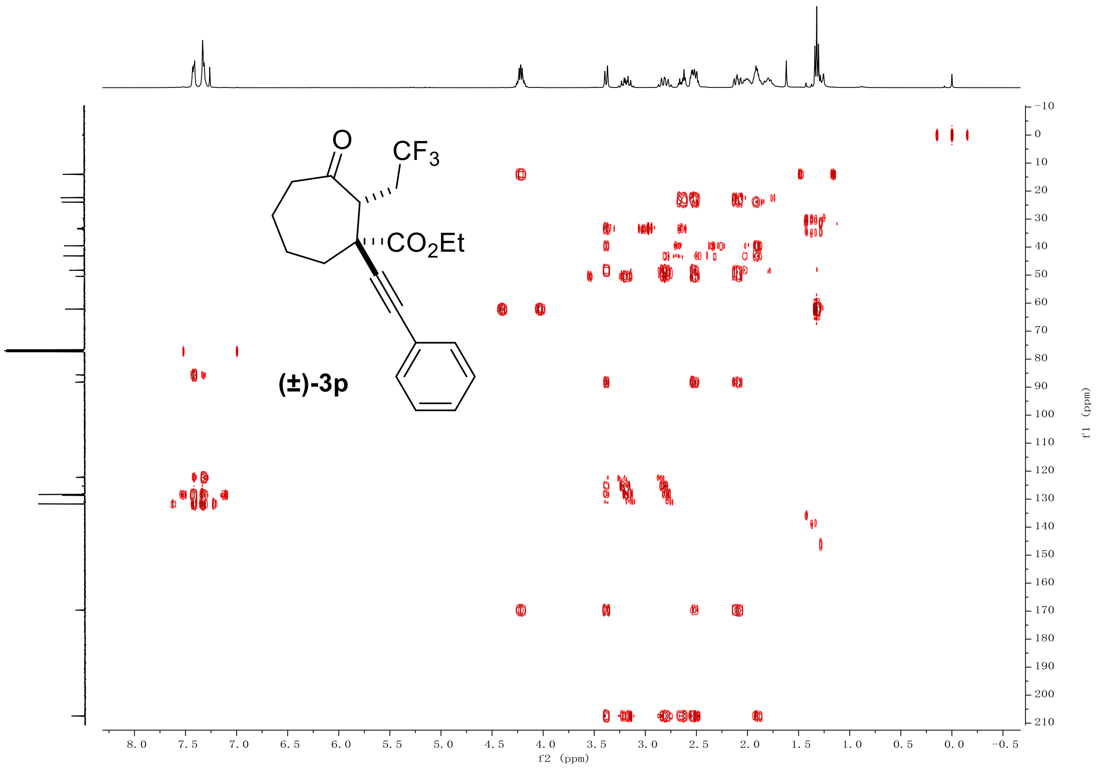
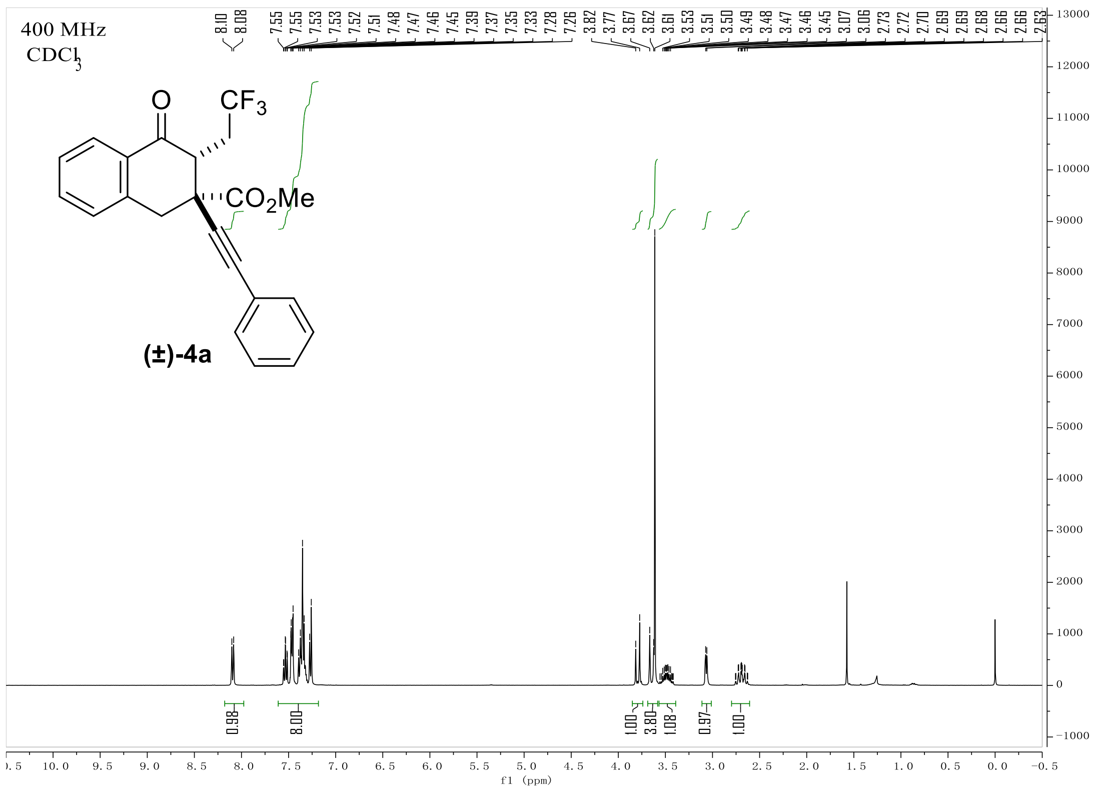
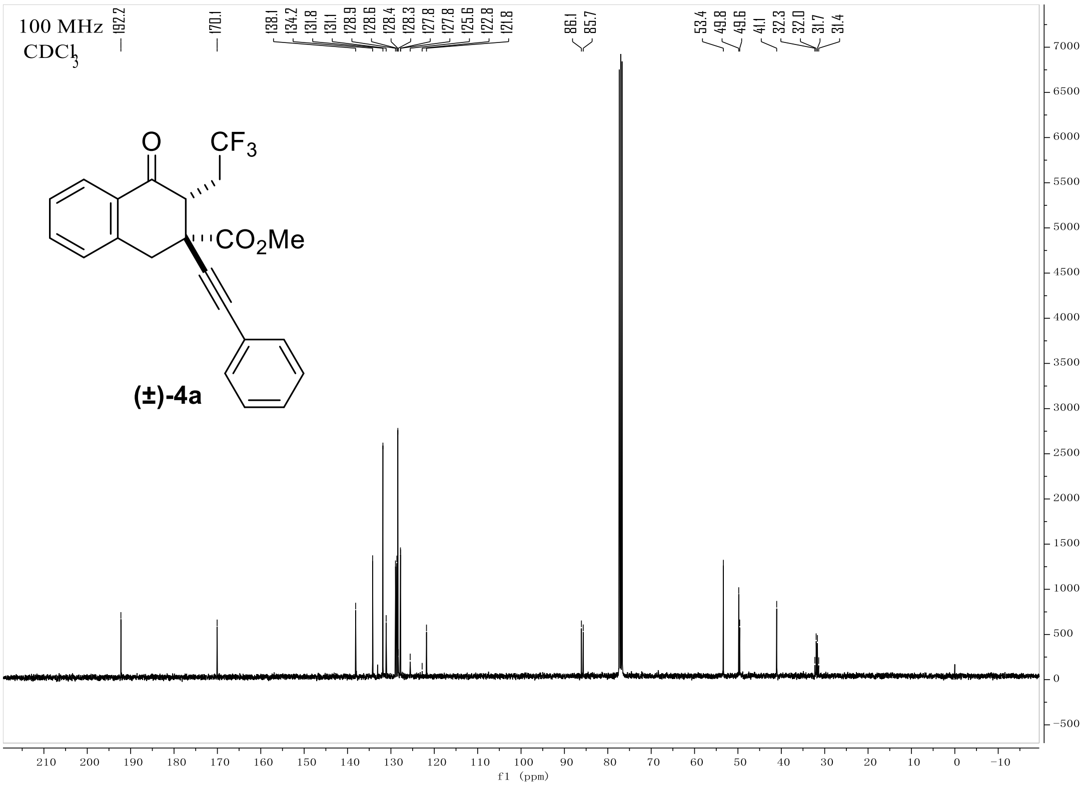
O
CF3
CO2Et
(±)-3p
f1 (ppm)



(±)-3p



400 MHz
CDCl3
(±)-4a


100 MHz
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192.2
170.1
138.1
134.2
131.8
131.1
128.9
128.6
128.4
128.3
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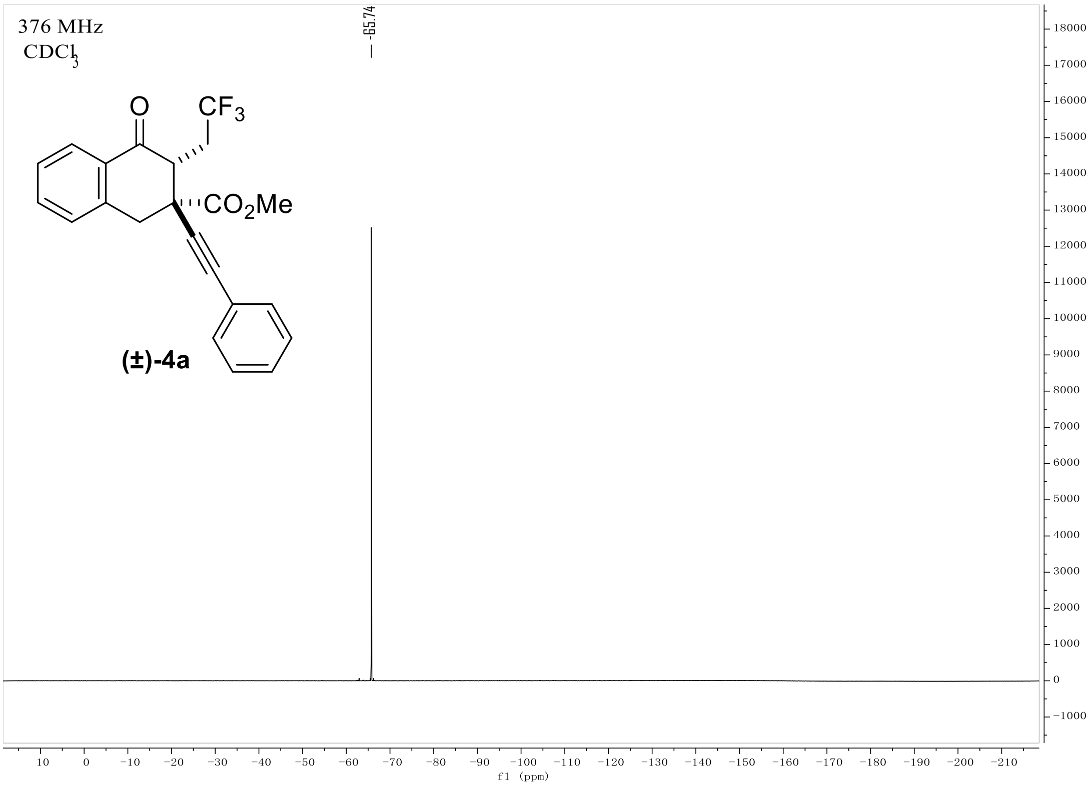
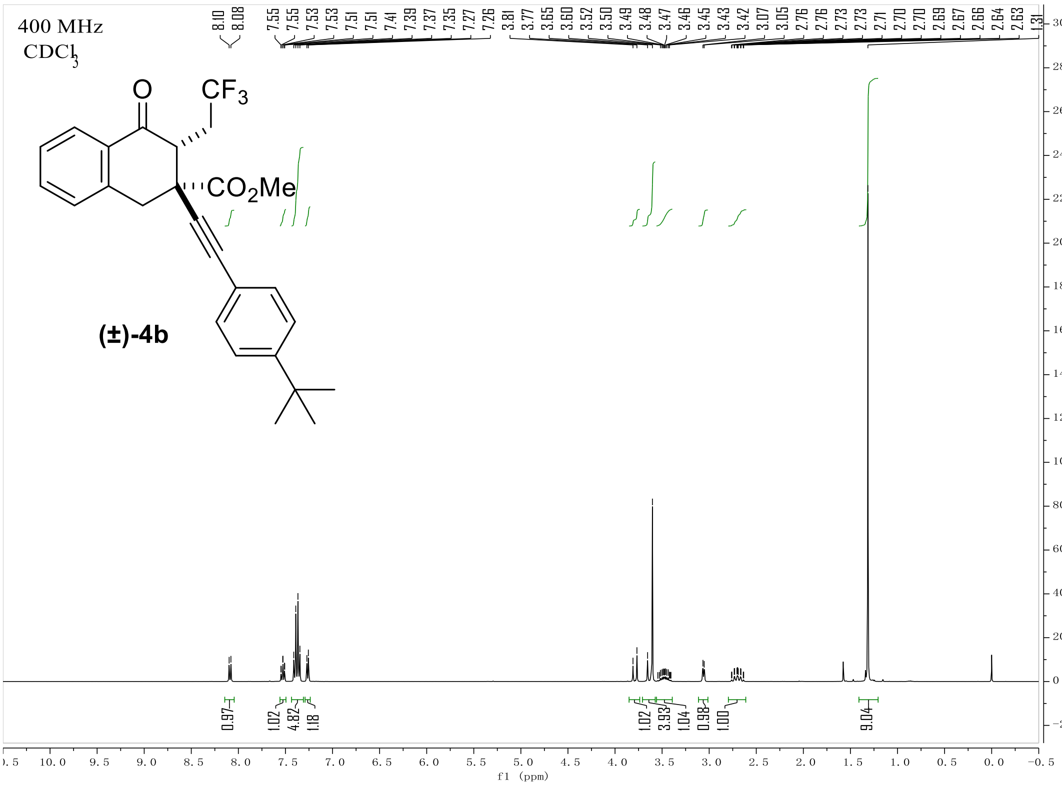
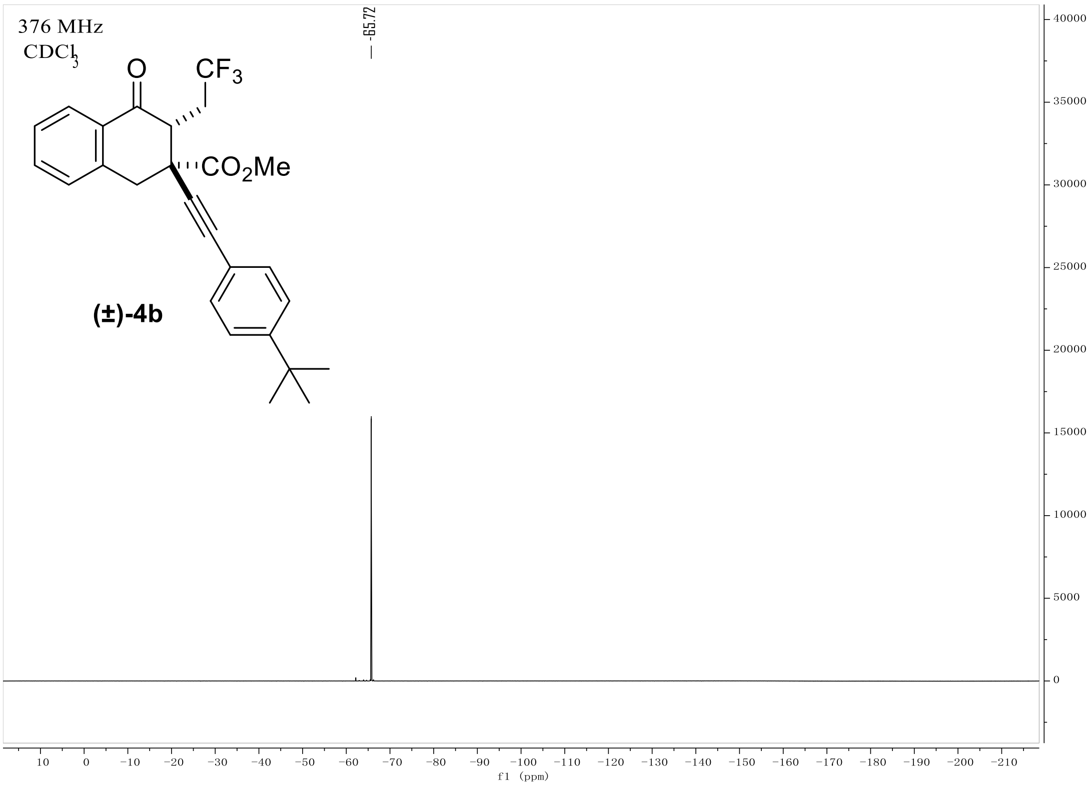
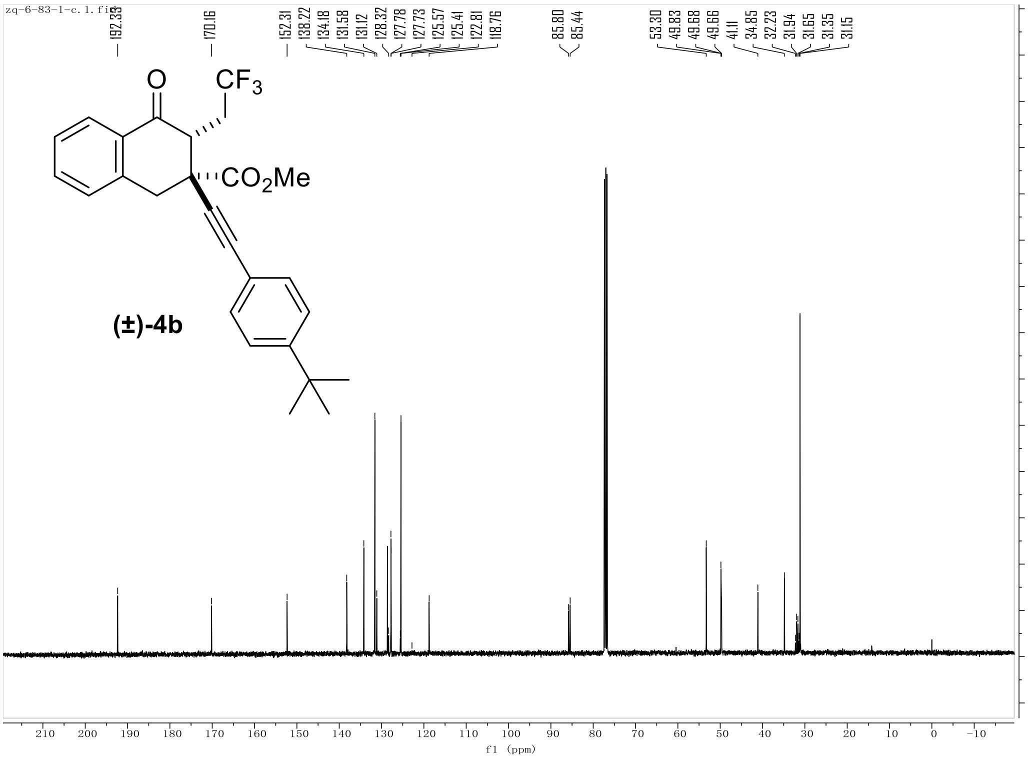
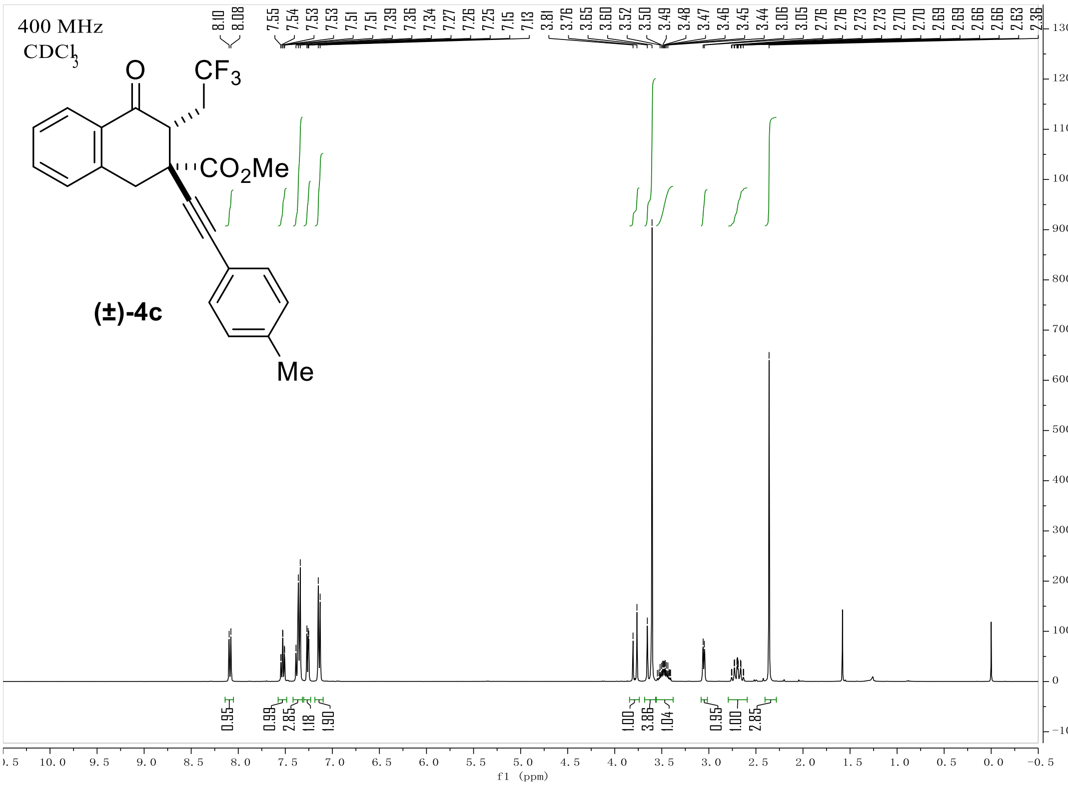
127.8
125.6
122.8
121.8
86.1
85.7
53.4
49.8
49.6
41.1
32.3
32.0
31.7
31.4
O
CF3
CO2Me
(±)-4a
f1 (ppm)


376 MHz
CDCl3
-65.74
O
CF3
CO2Me
(±)-4a
f1 (ppm)






zq-6-83-1-c.1.fid
CF3
CO2Me
(±)-4b
f1 (ppm)


400 MHz
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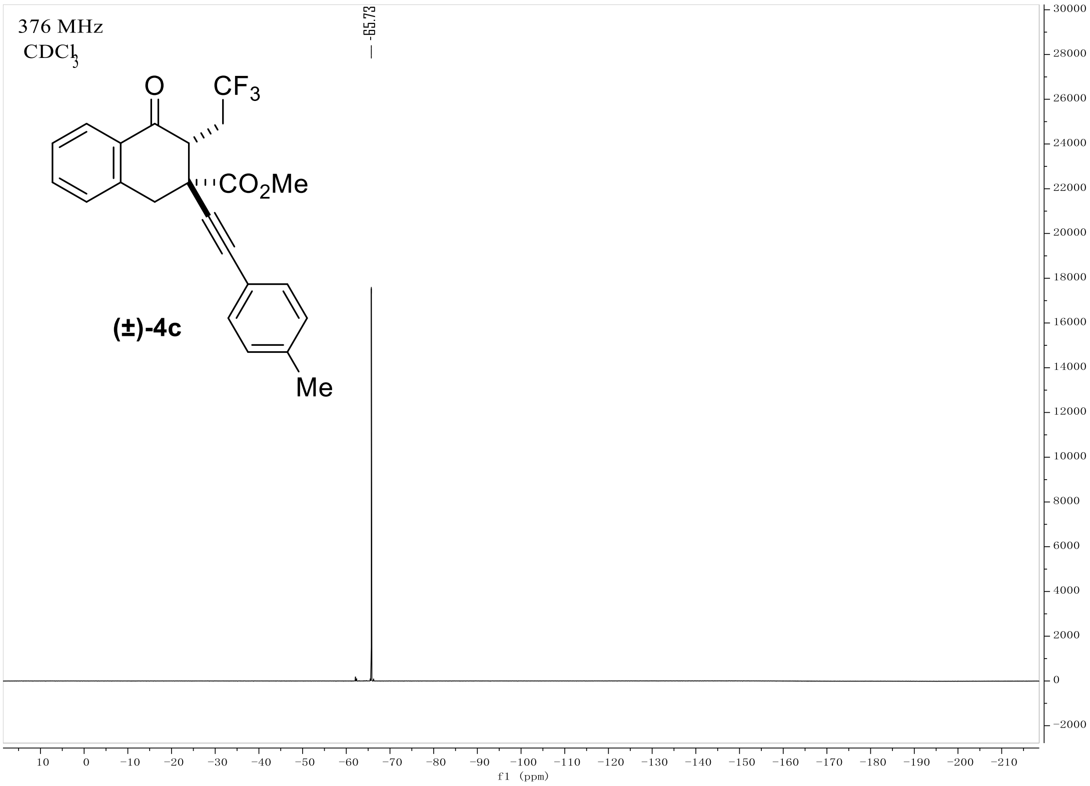
CF3
CO2Me
(±)-4c
Me
f1 (ppm)


376 MHz
CDCl3
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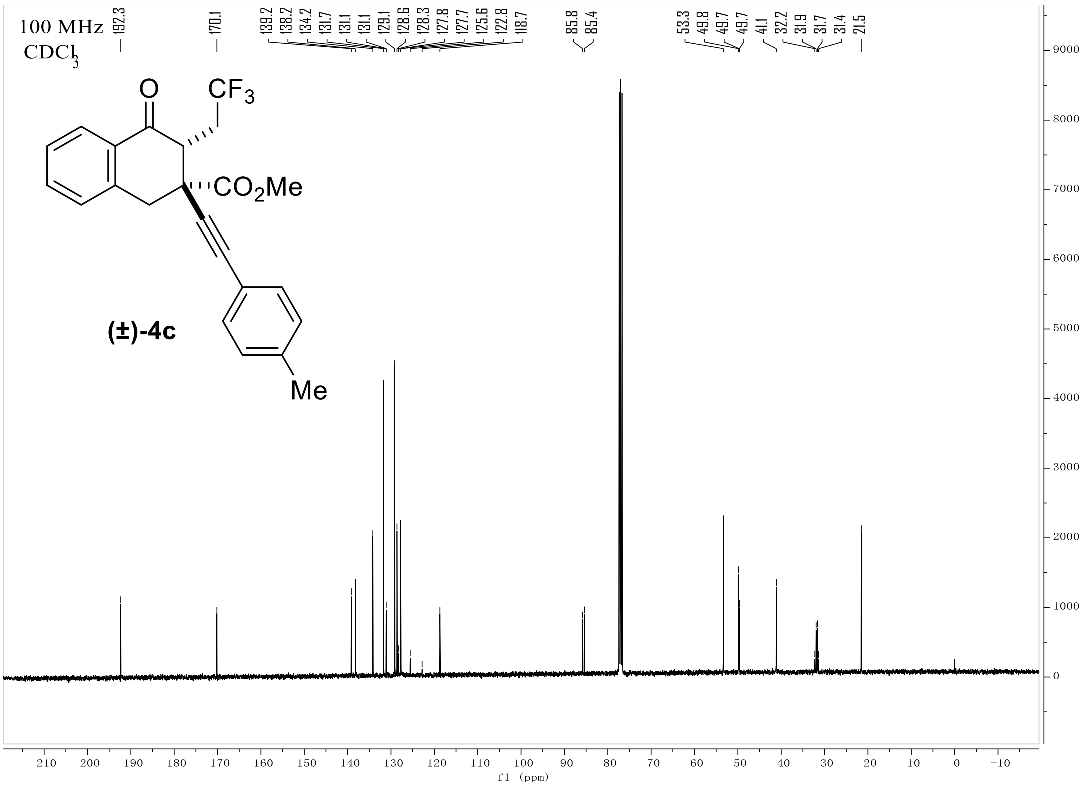
(±)-4c
Me
f1 (ppm)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134.2
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131.1
129.1
128.6
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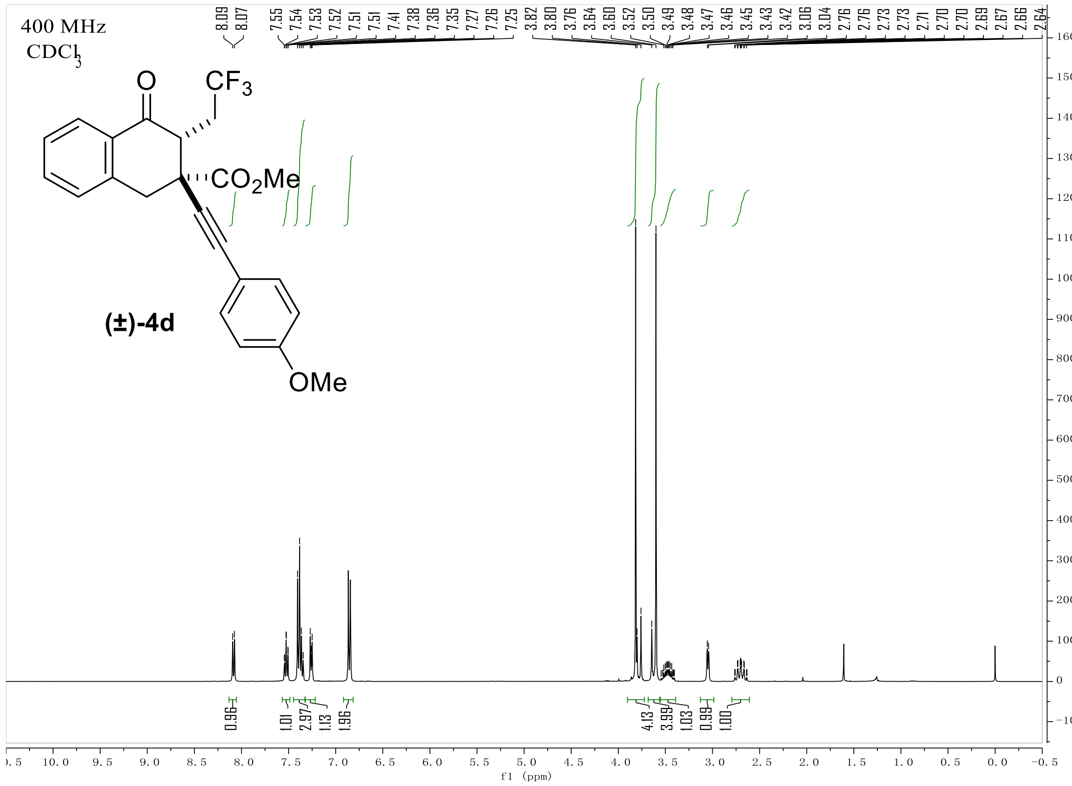
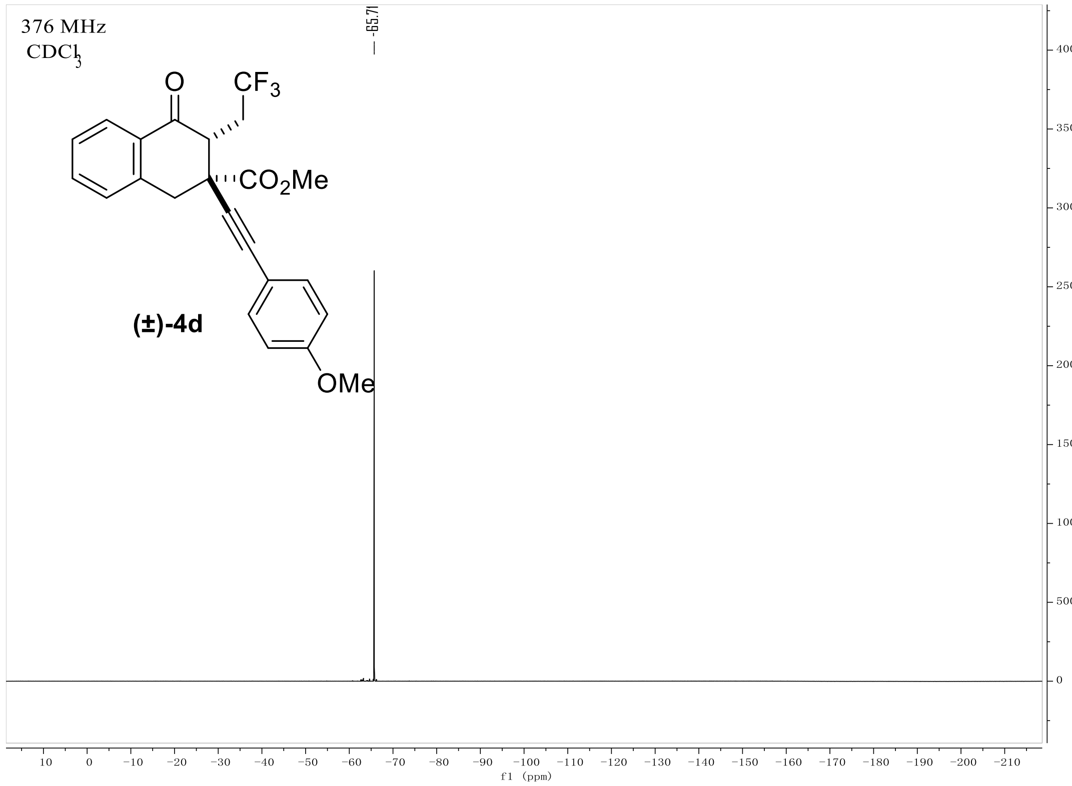
125.6
122.8
118.7
85.8
85.4
53.3
49.8
49.7
49.7
41.1
32.2
31.9
31.7
31.4
21.5
O
CF3
CO2Me
(±)-4c
Me
f1 (ppm)


400 MHz
CDCl3
(±)-4d
OMe


376 MHz
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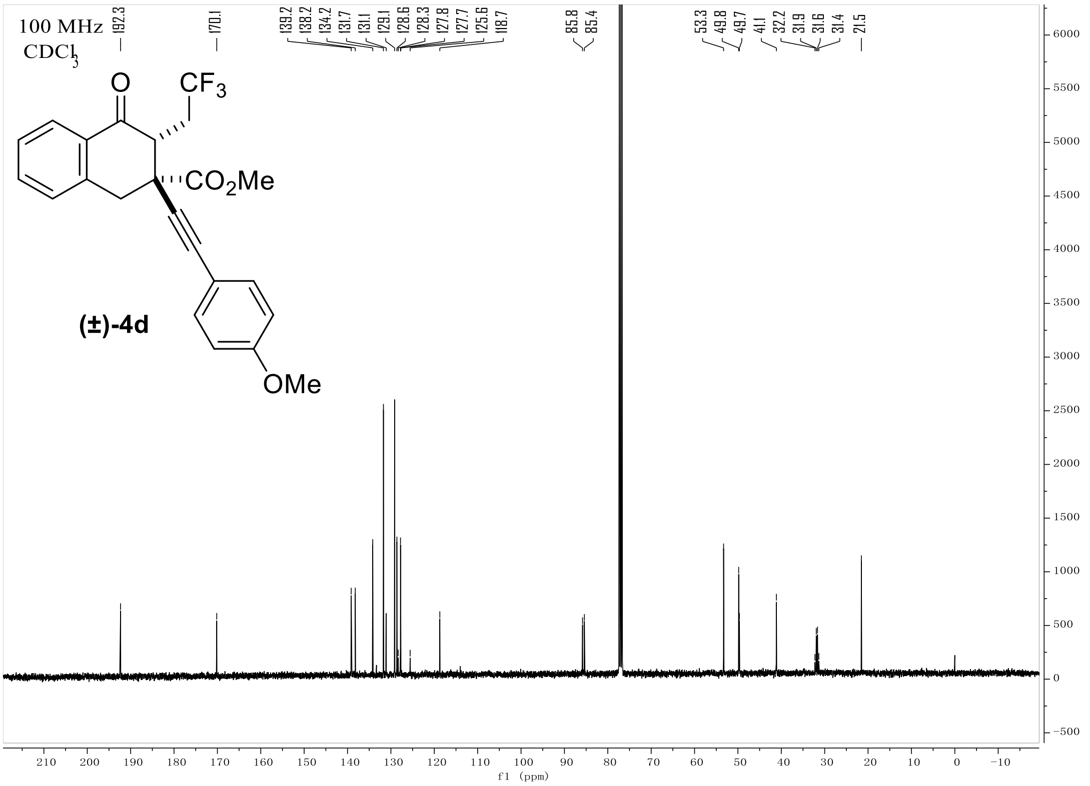
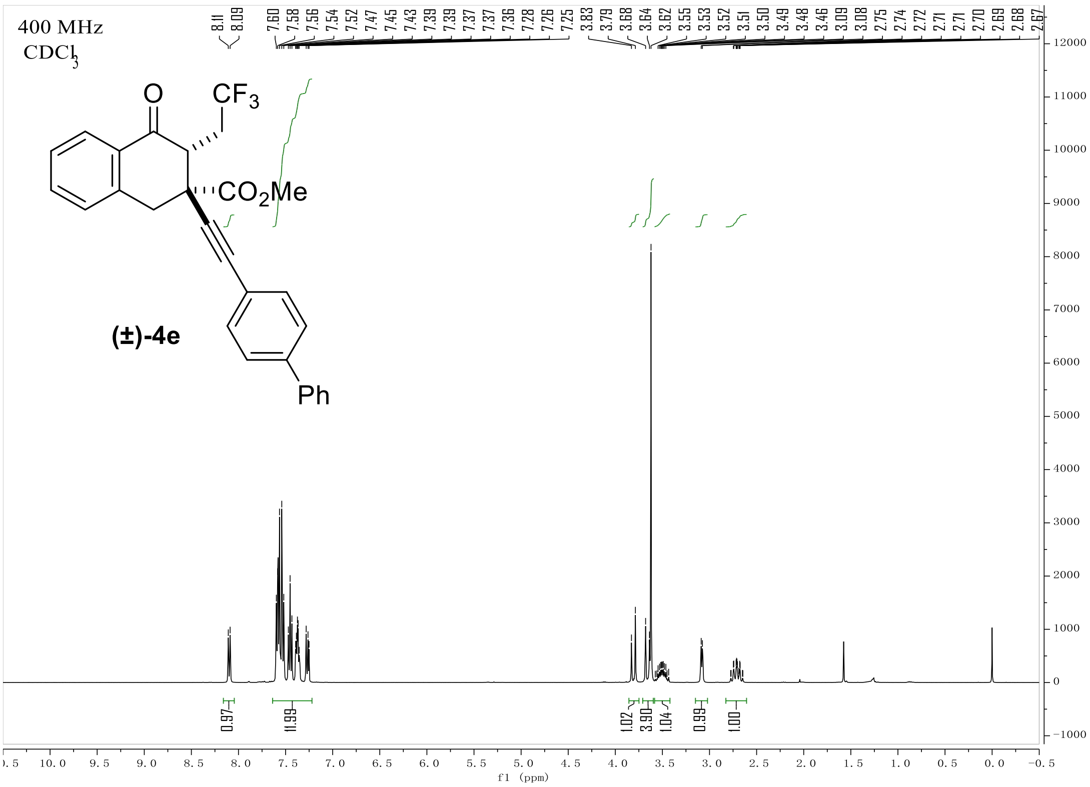
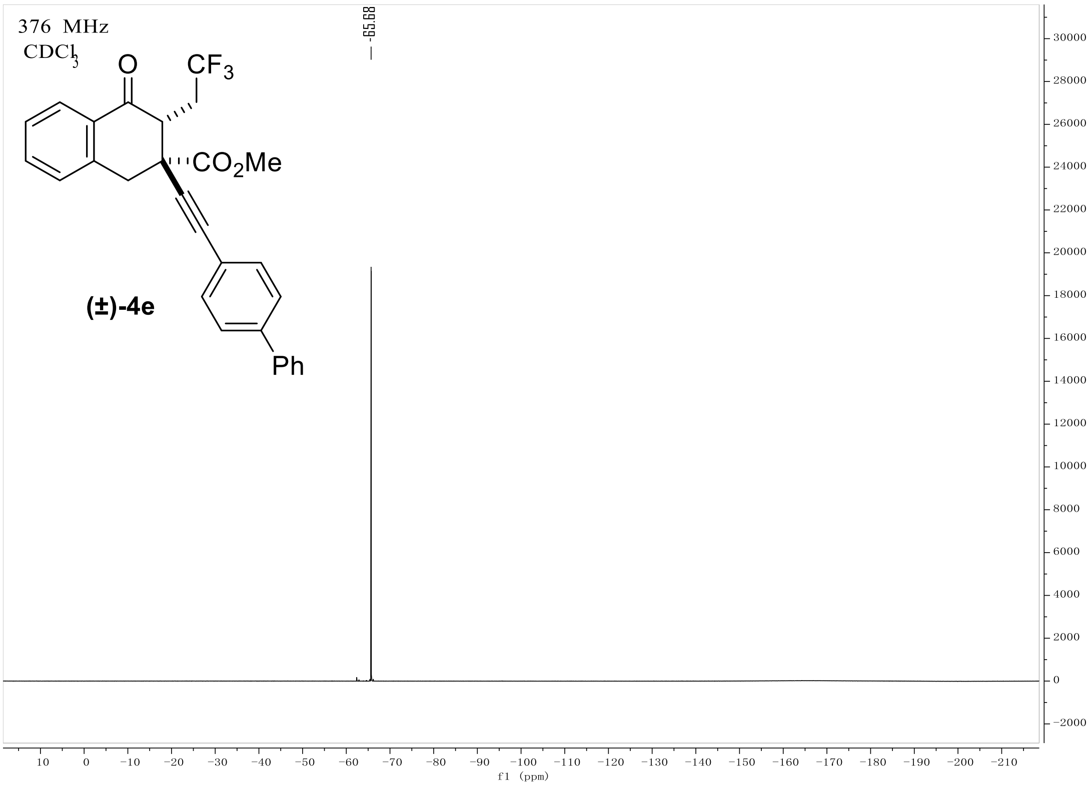
(±)-4d
OMe


100 MHz
CDCl3
(±)-4d
f1 (ppm)


400 MHz
CDCl3
(±)-4e
f1 (ppm)


376 MHz
CDCl3
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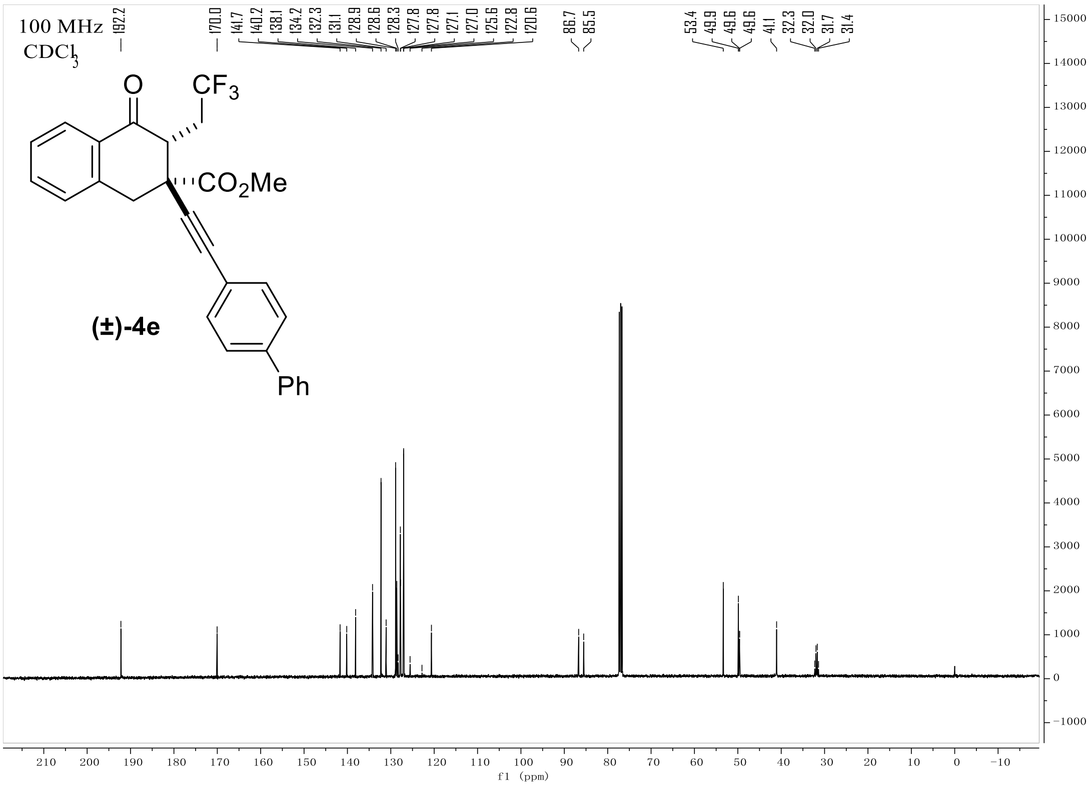
(±)-4e
f1 (ppm)


100 MHz
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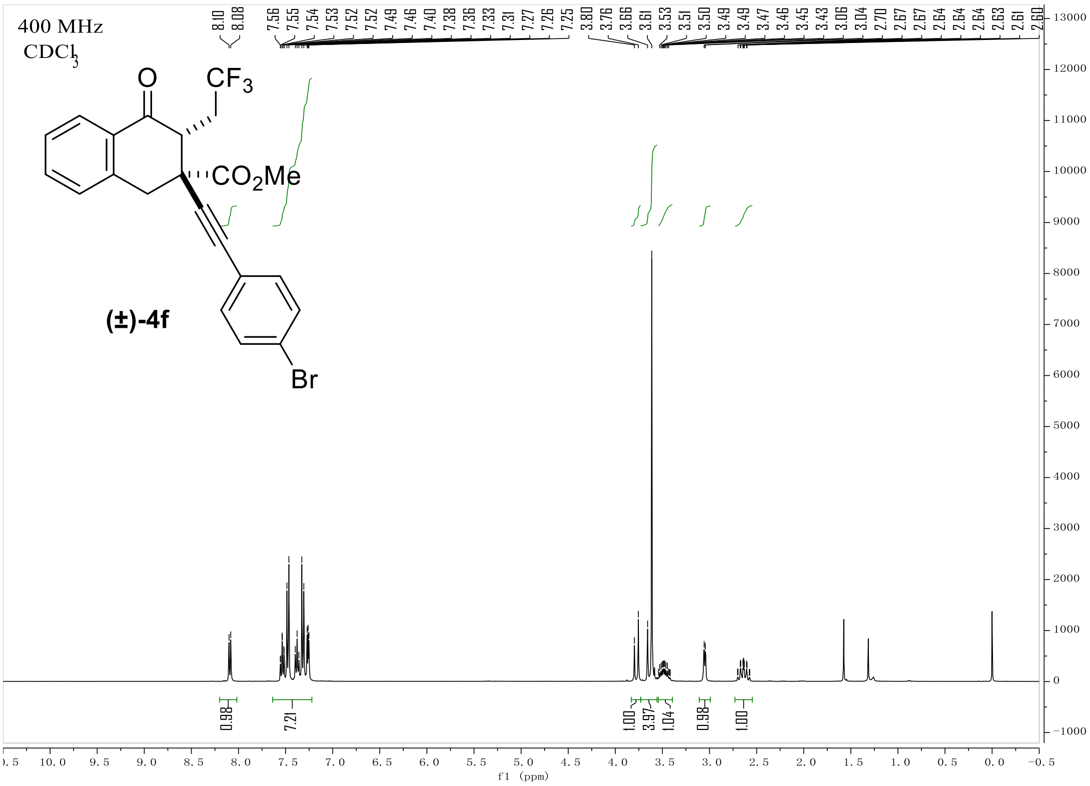
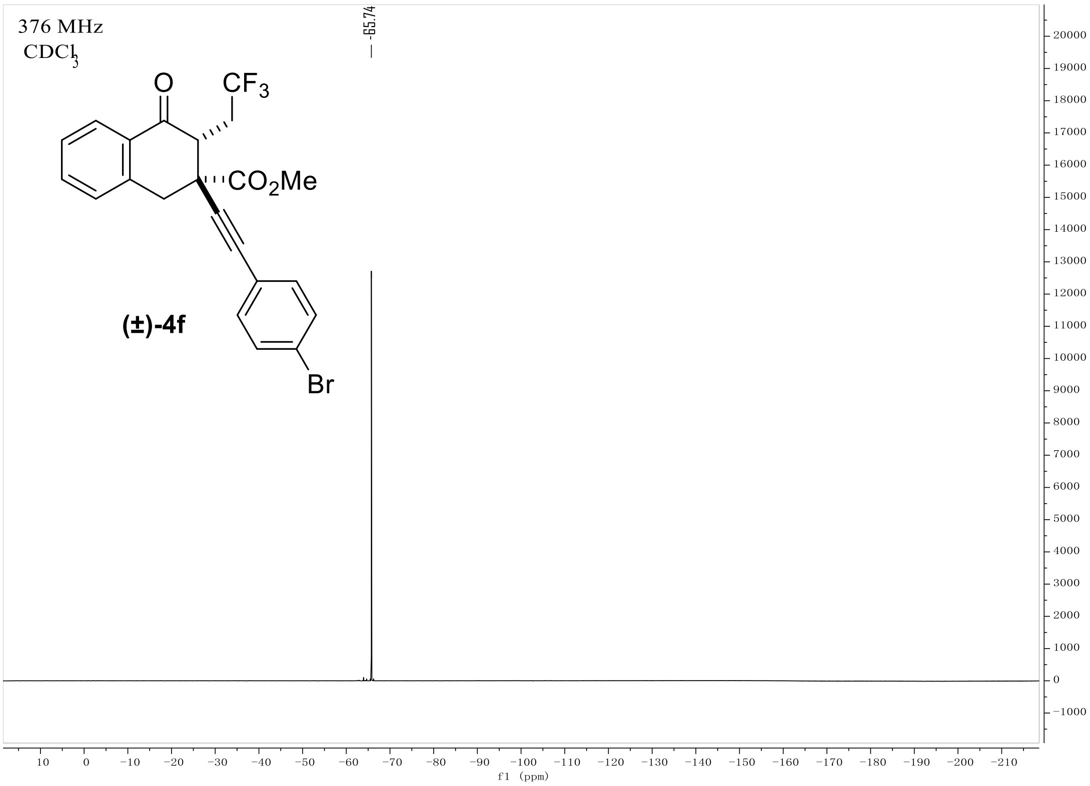
140.2
138.1
134.2
132.3
131.1
128.9
128.6
128.3
127.8
127.8
127.1
127.0
125.6
122.8
120.6
86.7
85.5
53.4
49.9
49.6
49.6
41.1
32.3
32.0
31.7
31.4
(±)-4e
f1 (ppm)


400 MHz
CDCl3
(±)-4f
f1 (ppm)


376 MHz
CDCl3
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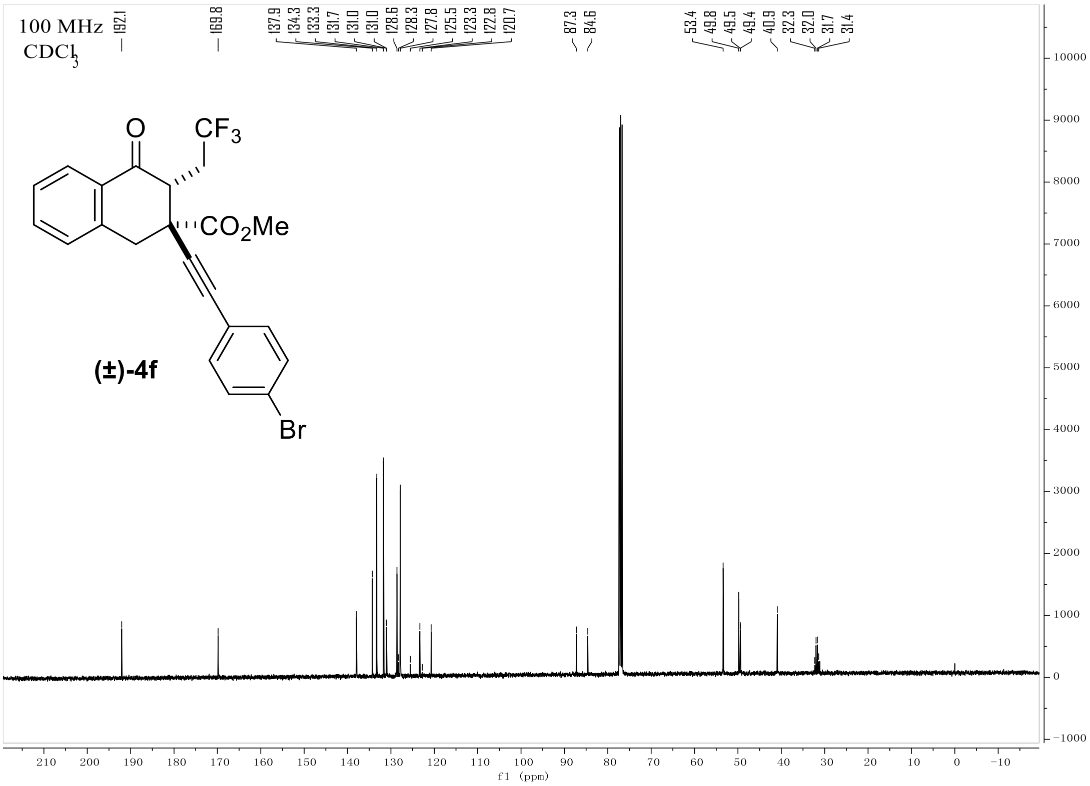
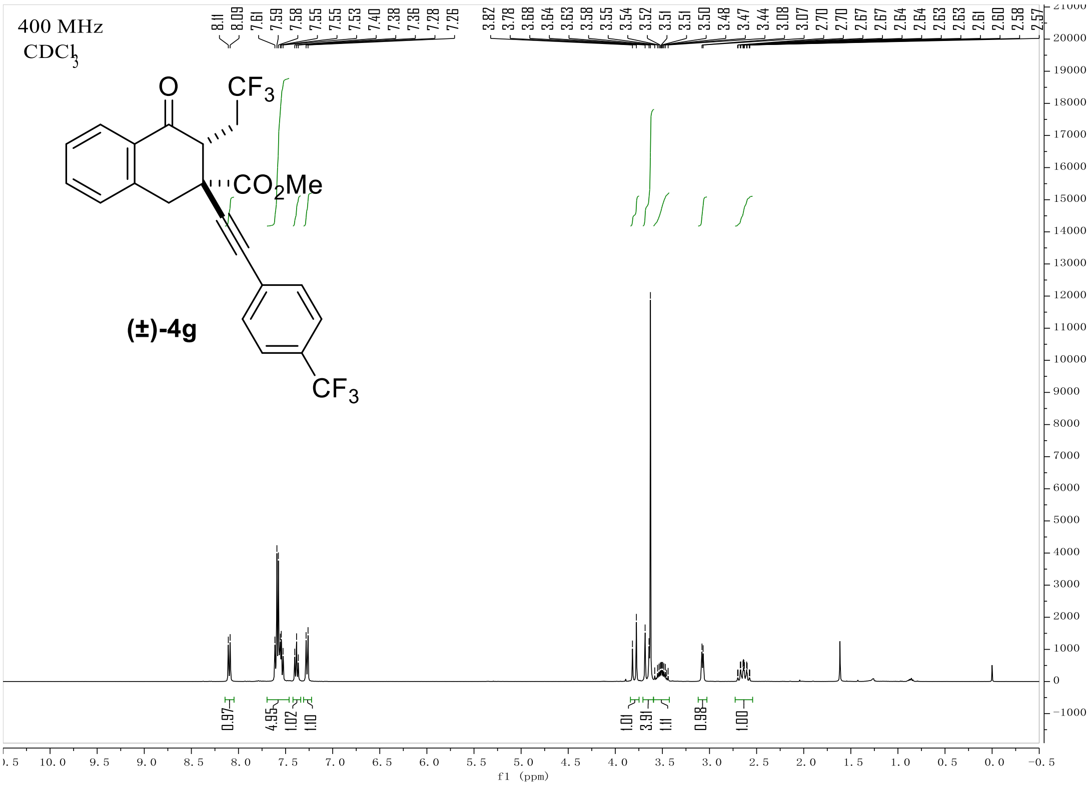
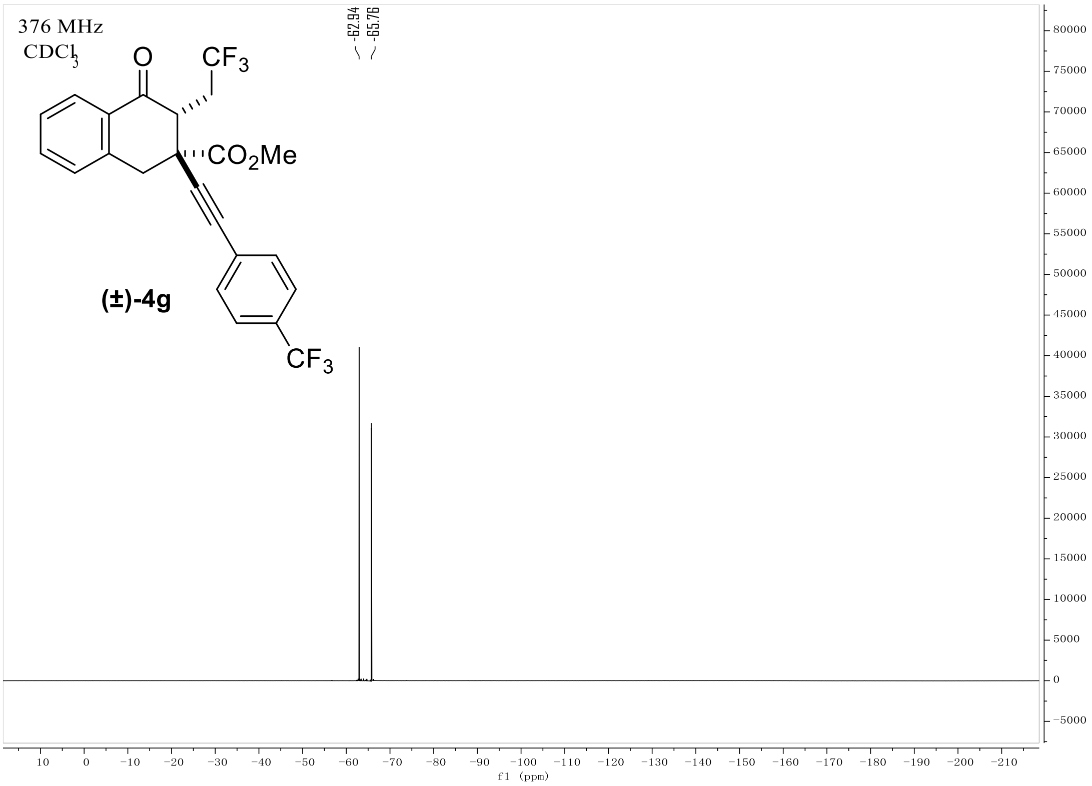
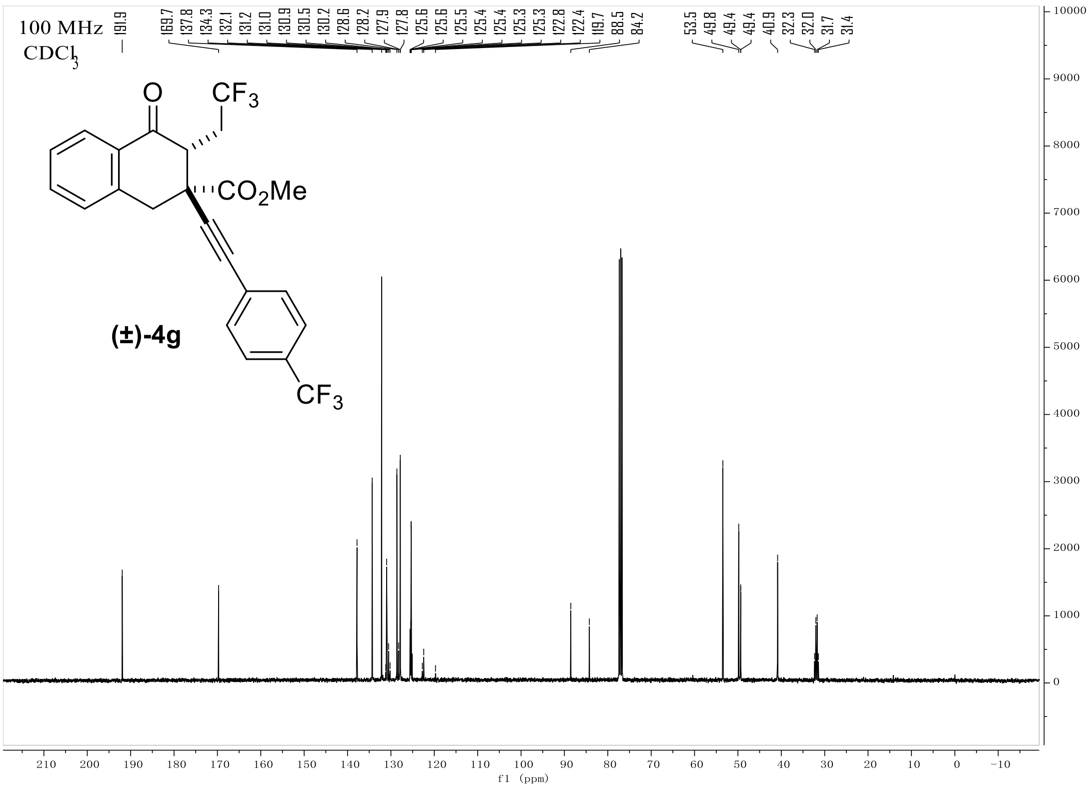
(±)-4f
f1 (ppm)


100 MHz
CDCl3
(±)-4f
192.1
169.8
137.9 134.3 133.3 131.7 131.0 131.0 128.6 128.3 127.8 125.5 123.3 122.8 120.7
87.3 84.6
53.4 49.8 49.5 49.4 40.9 32.3 32.0 31.7 31.4
f1 (ppm)


400 MHz
CDCl3
(±)-4g
8.11 8.09 7.61 7.59 7.58 7.55 7.55 7.53 7.40 7.38 7.36 7.28 7.26
3.82 3.78 3.68 3.64 3.63 3.58 3.55 3.54 3.52 3.51 3.50 3.48 3.47 3.44 3.08 3.07 2.70 2.70 2.67 2.64 2.64 2.63 2.63 2.61 2.60 2.58 2.57
0.97 4.95 1.02 1.10 1.01 3.91 1.11 0.98 1.00
f1 (ppm)


376 MHz
CDCl3
(±)-4g
CO2Me
CF3
-62.94
-65.76
f1 (ppm)


100 MHz
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(±)-4g
CO2Me
CF3
191.9
169.7
137.8
134.3
132.1
131.2
131.0
130.9
130.5
130.2
128.6
128.2
127.9
127.8
125.6
125.6
125.5
125.4
125.4
125.3
125.3
122.8
122.4
119.7
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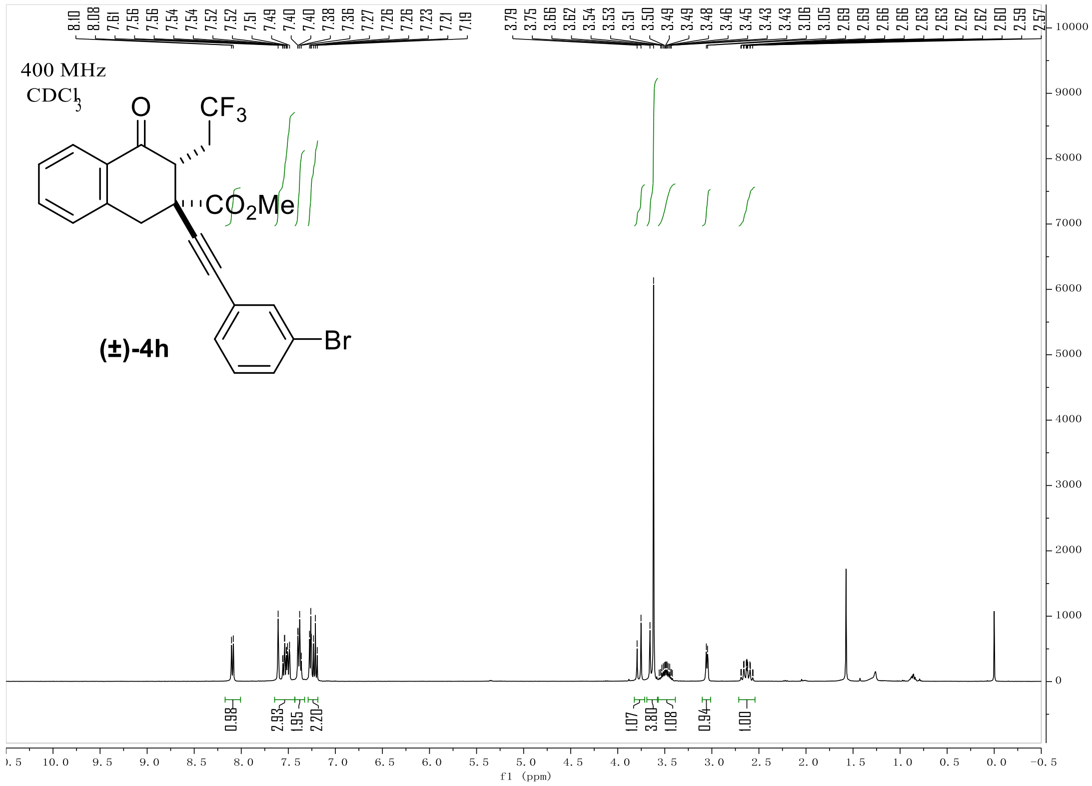
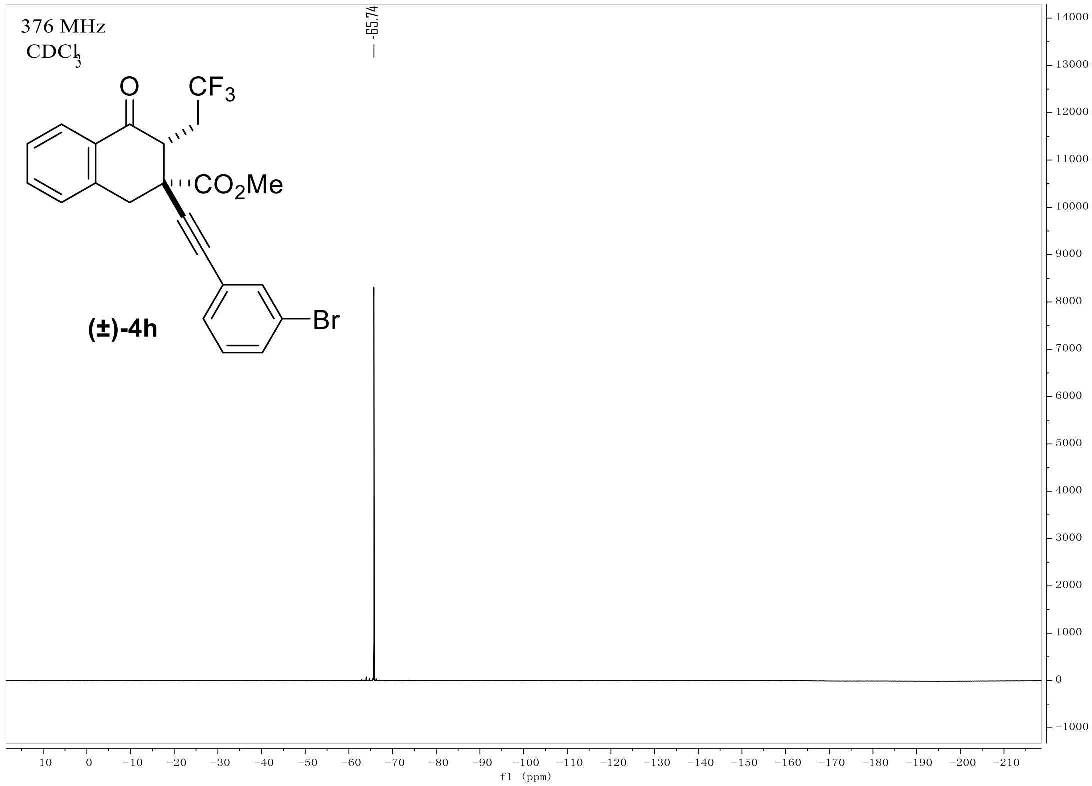
49.8
49.4
49.4
40.9
32.3
32.0
31.7
31.4
f1 (ppm)


400 MHz
CDCl3
(±)-4h
CF3
CO2Me
Br
O
f1 (ppm)


376 MHz
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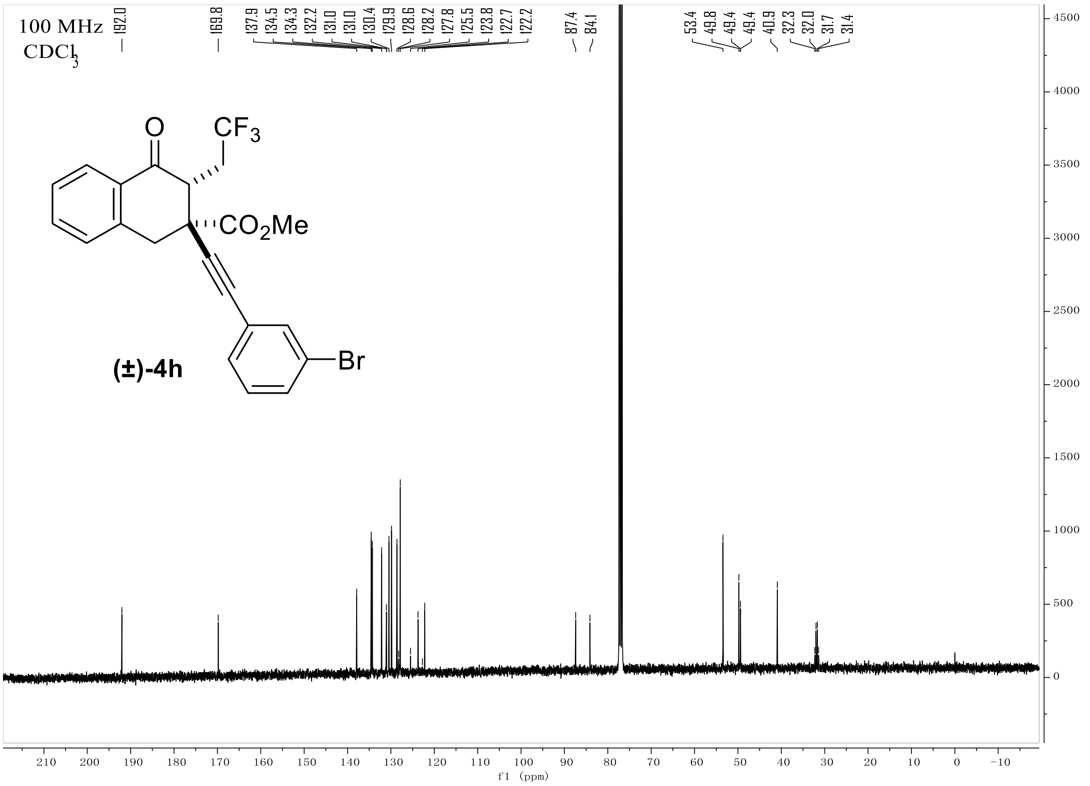
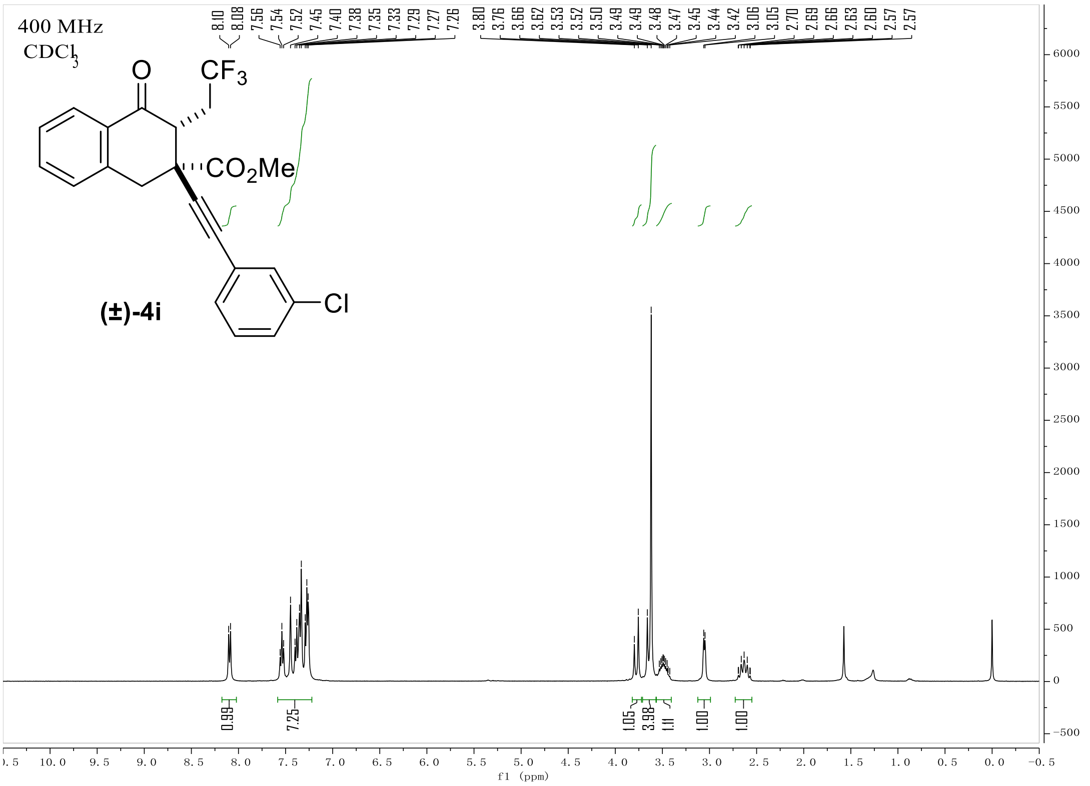
-65.74
f1 (ppm)



100 MHz
CDCl3
192.0
169.8
137.9
134.5
134.3
132.2
131.0
131.0
130.4
129.9
128.6
128.2
127.8
125.5
123.8
122.7
122.2
87.4
84.1
53.4
49.8
49.4
49.4
40.9
32.3
32.0
31.7
31.4
O
CF3
CO2Me
Br
(±)-4h
f1 (ppm)



400 MHz
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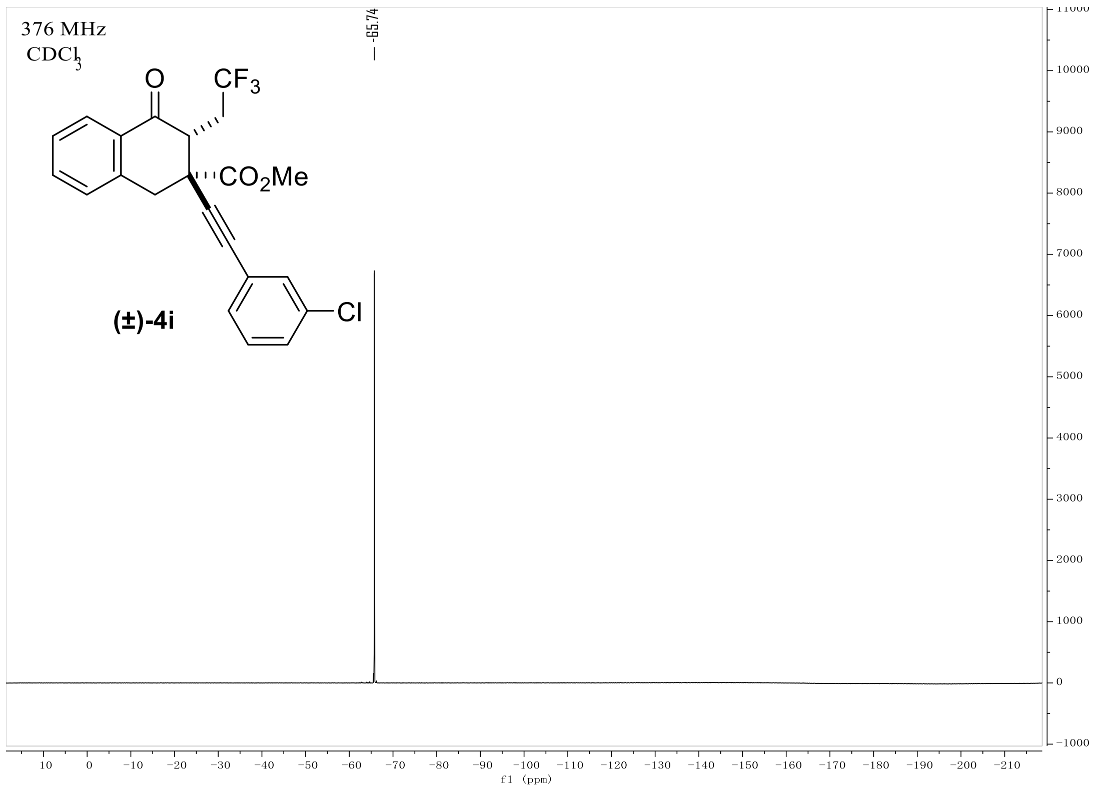
8.10
8.08
7.56
7.54
7.52
7.45
7.40
7.38
7.35
7.33
7.29
7.27
7.26
3.80
3.76
3.66
3.62
3.53
3.52
3.50
3.49
3.48
3.47
3.45
3.44
3.42
3.06
3.05
2.70
2.69
2.66
2.63
2.60
2.57
2.57
O
CF3
CO2Me
Cl
(±)-4i
0.99
7.25
1.05
3.98
1.11
1.00
1.00
f1 (ppm)


376 MHz
CDCl3
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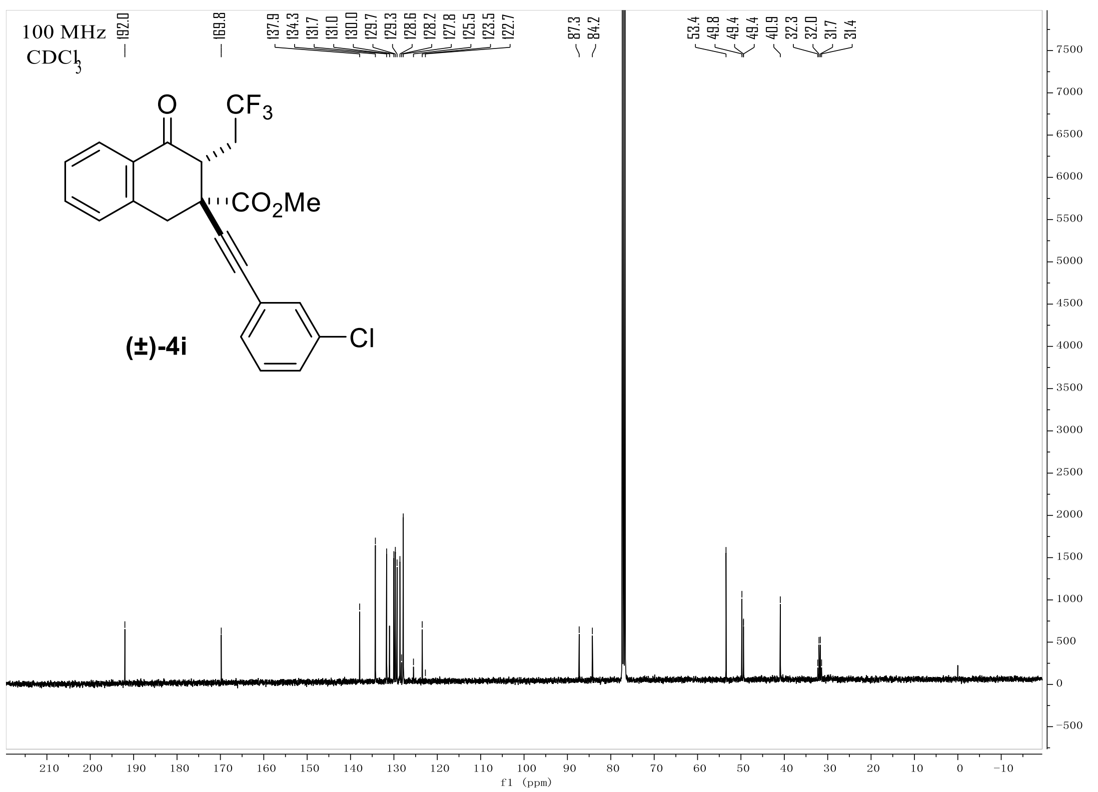
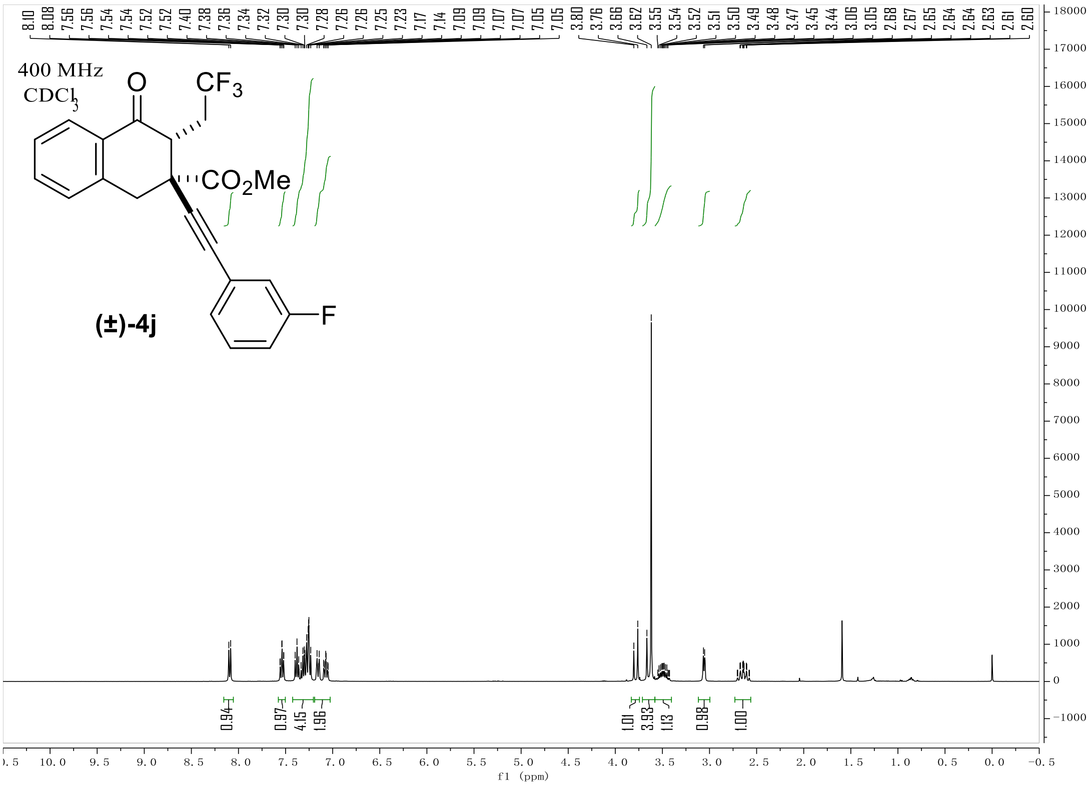
(±)-4i
f1 (ppm)


100 MHz
CDCl3
192.0
169.8
137.9
134.3
131.7
131.0
130.0
129.7
129.3
128.6
128.2
127.8
125.5
123.5
122.7
87.3
84.2
53.4
49.8
49.4
49.4
40.9
32.3
32.0
31.7
31.4
(±)-4i
f1 (ppm)


400 MHz
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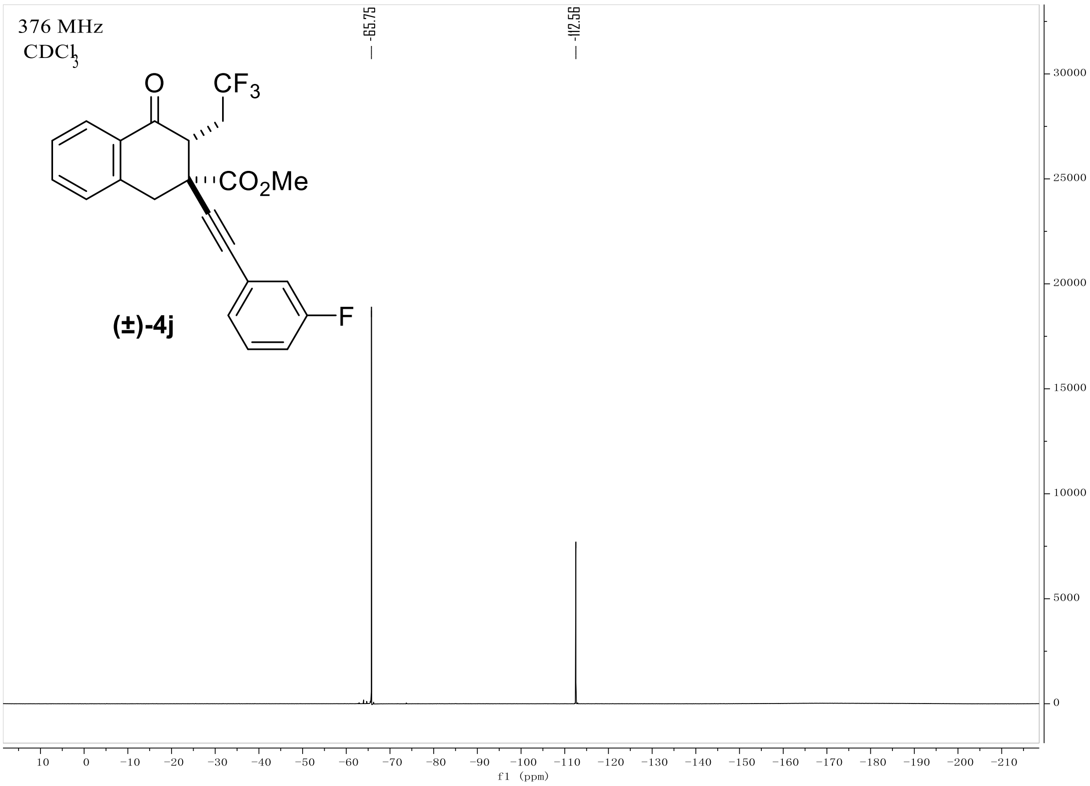
(±)-4j
f1 (ppm)


376 MHz
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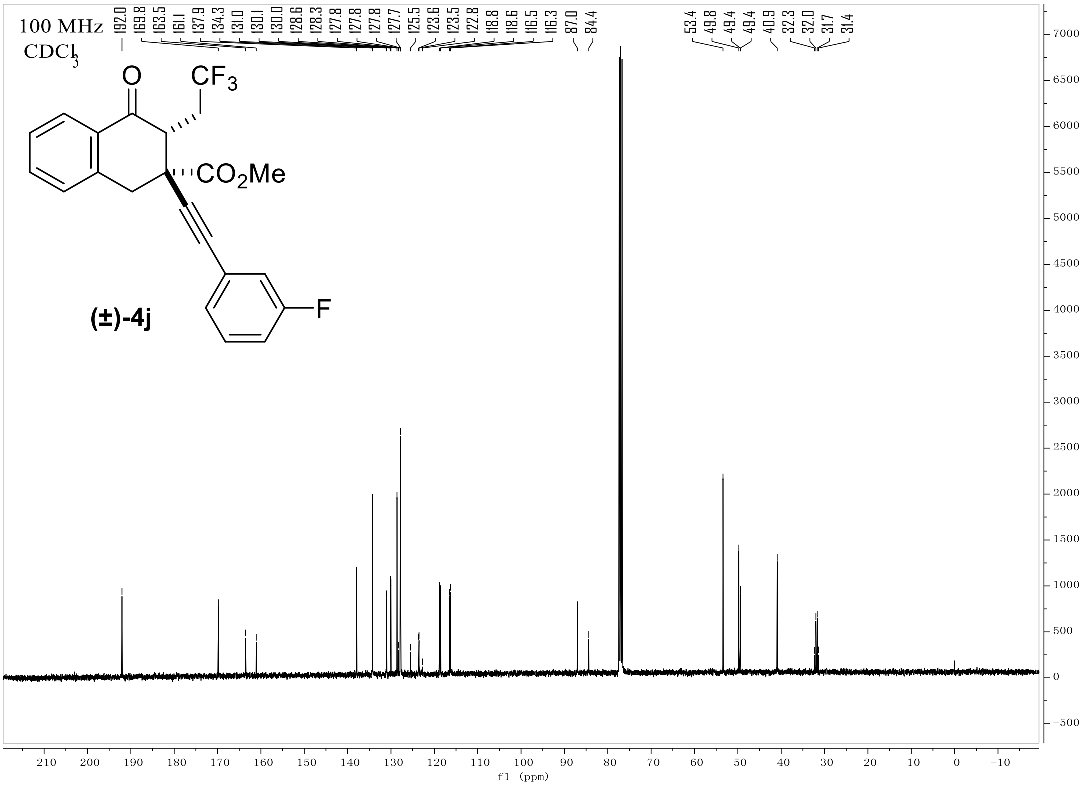
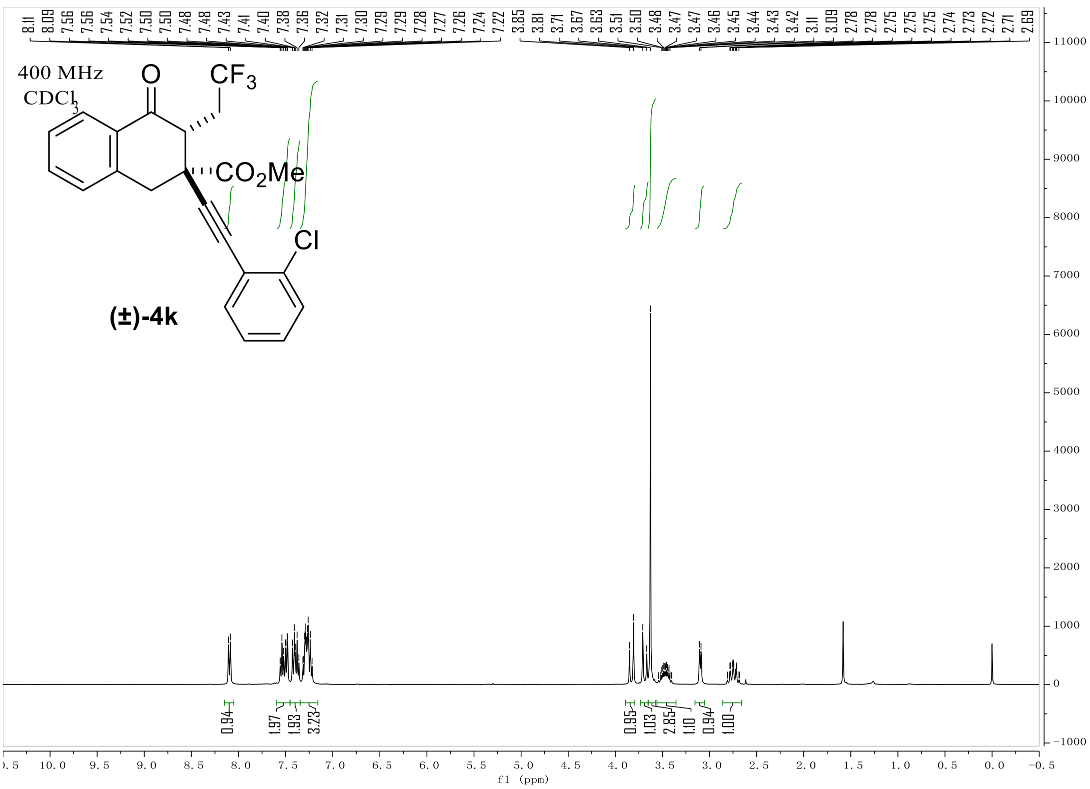
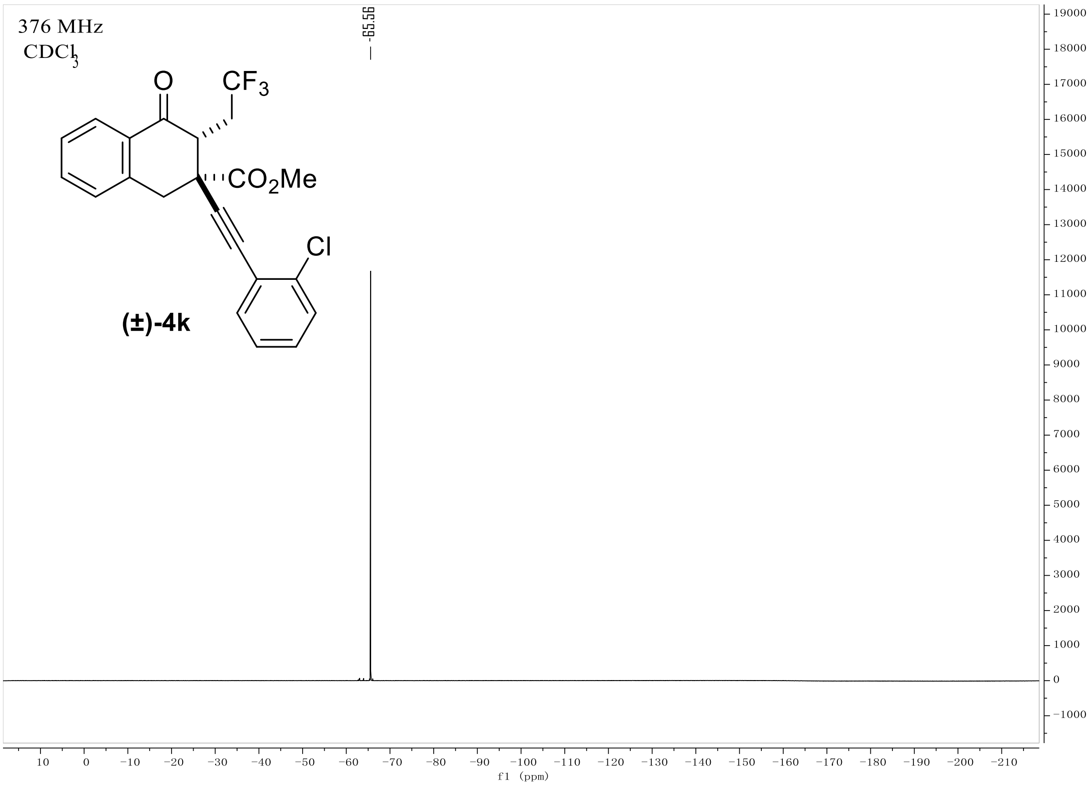
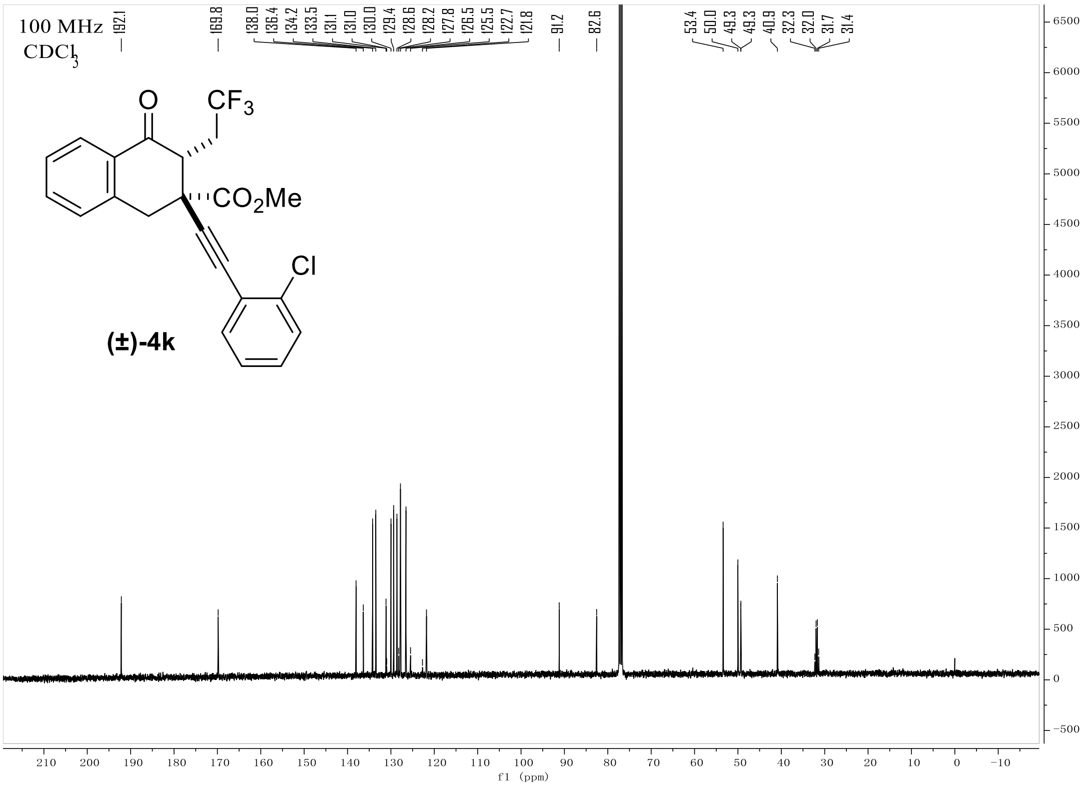
(±)-4j
-65.75
-112.56
f1 (ppm)


100 MHz
CDCl3
192.0 169.8 163.5 161.1 137.9 134.3 131.0 130.1 130.0 128.6 128.3 127.8 127.8 127.8 127.7 125.5 123.6 123.5 122.8 118.8 118.6 116.5 116.3 87.0 84.4
53.4 49.8 49.4 49.4 40.9 32.3 32.0 31.7 31.4
O
CF3
CO2Me
F
(±)-4j
f1 (ppm)


8.11 8.09 7.56 7.56 7.54 7.52 7.50 7.50 7.48 7.48 7.43 7.41 7.40 7.38 7.36 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.26 7.24 7.22 3.85 3.81 3.71 3.67 3.63 3.51 3.50 3.48 3.47 3.47 3.46 3.45 3.44 3.43 3.42 3.11 3.09 2.78 2.78 2.75 2.75 2.75 2.74 2.73 2.72 2.71 2.69
400 MHz
CDCl3
O
CF3
CO2Me
Cl
(±)-4k
0.94
1.97
1.93
3.23
0.95
1.03
2.85
1.10
0.94
1.00
f1 (ppm)


376 MHz
CDCl3
-65.56
(±)-4k
f1 (ppm)


100 MHz
CDCl3
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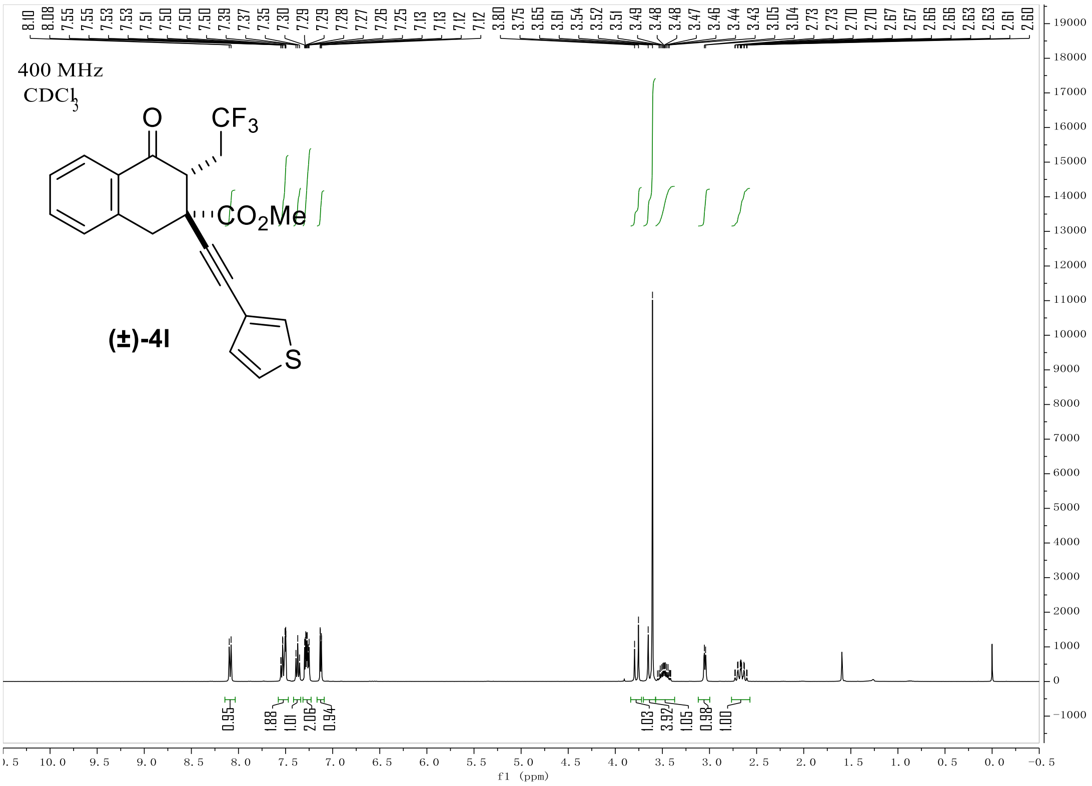
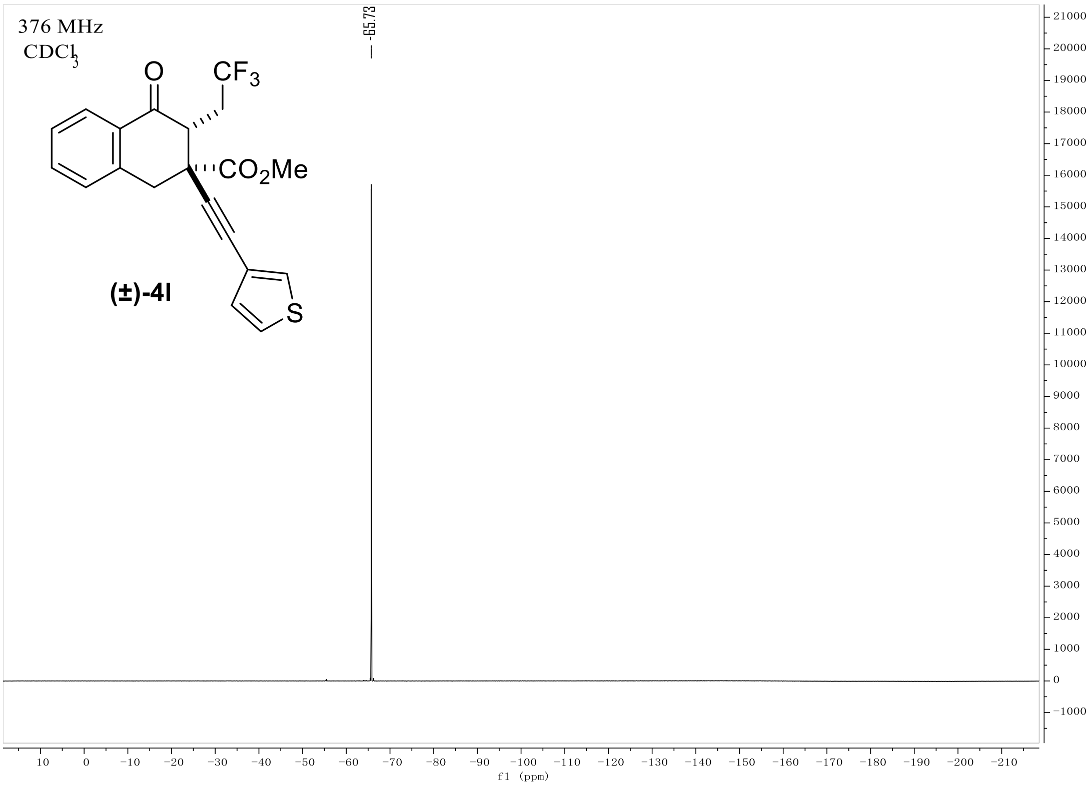
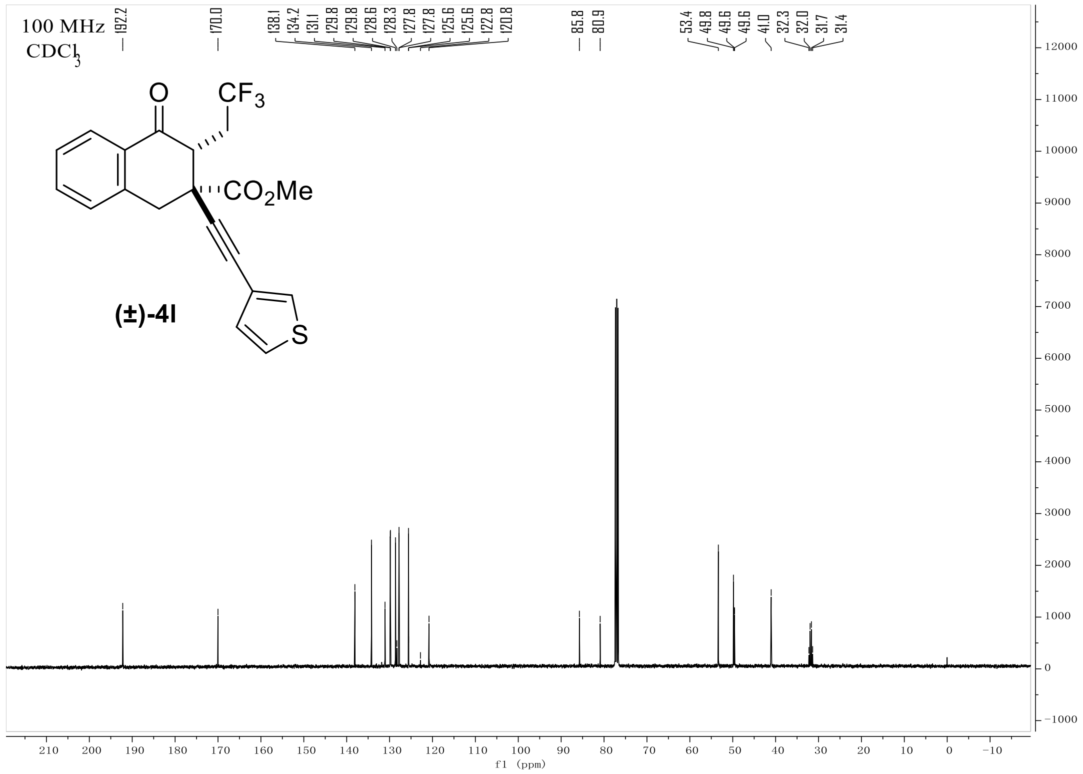
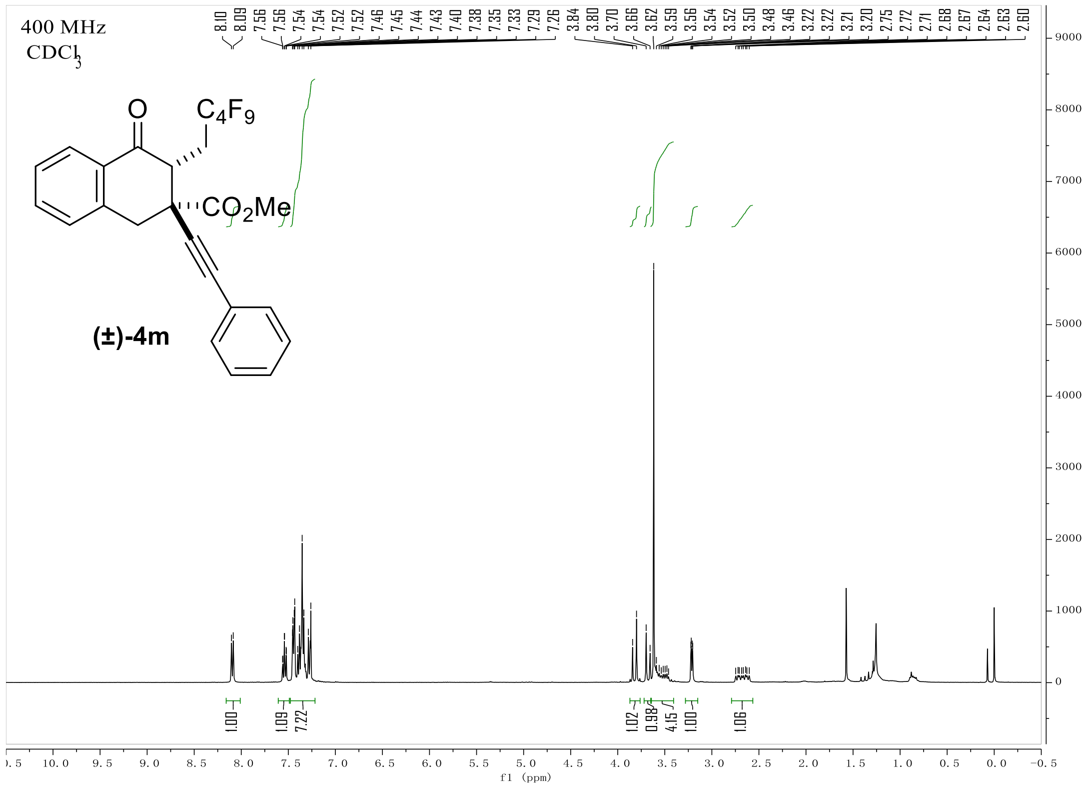
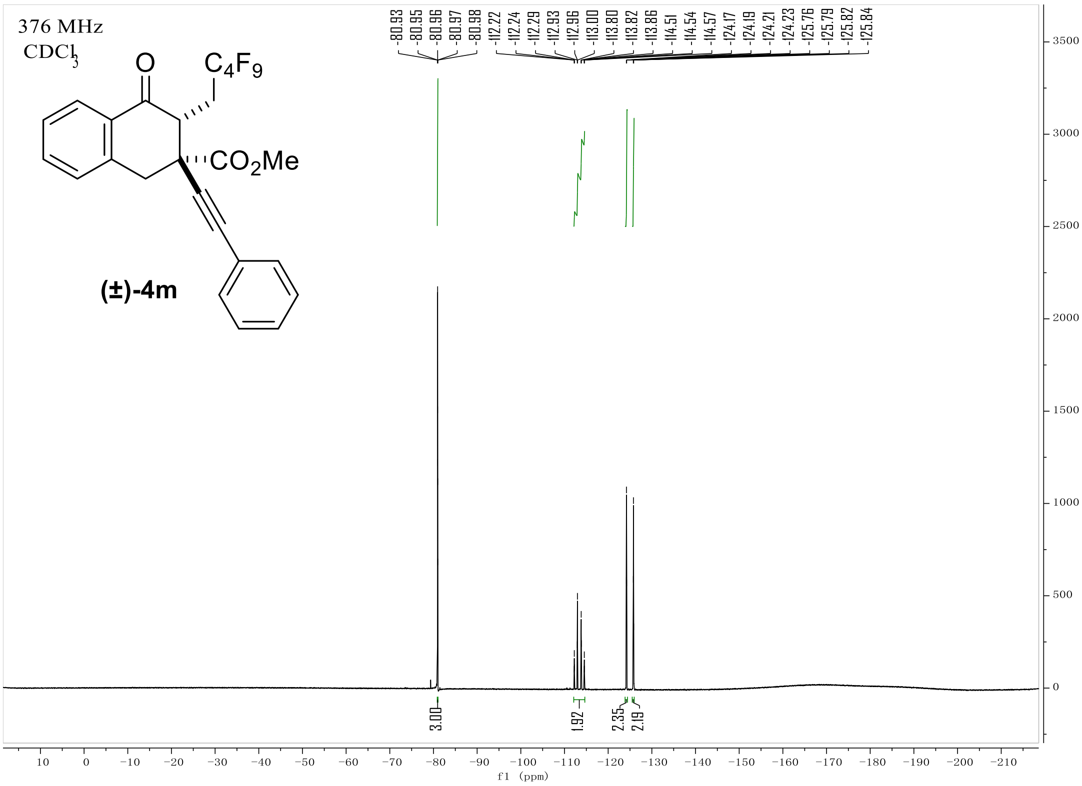
169.8
138.0
136.4
134.2
133.5
131.1
131.0
130.0
129.4
128.6
128.2
127.8
126.5
125.5
122.7
121.8
91.2
82.6
53.4
50.0
49.3
49.3
40.9
32.3
32.0
31.7
31.4
(±)-4k
f1 (ppm)

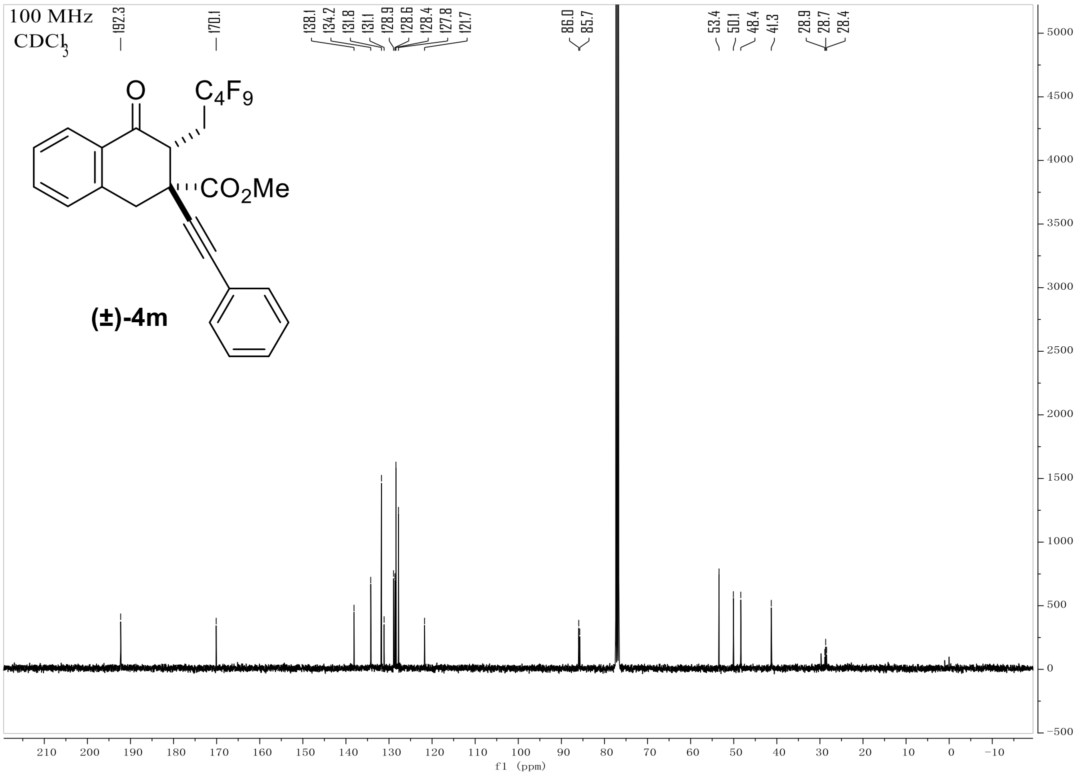

400 MHz
CDCl3
(±)-4l
8.10 8.08 7.55 7.53 7.53 7.51 7.50 7.50 7.50 7.39 7.37 7.35 7.30 7.29 7.29 7.28 7.27 7.26 7.25 7.13 7.13 7.12 7.12 3.80 3.75 3.65 3.61 3.54 3.52 3.51 3.49 3.48 3.48 3.47 3.46 3.44 3.43 3.05 3.04 2.73 2.73 2.73 2.70 2.70 2.67 2.67 2.66 2.66 2.63 2.61 2.60
0.95 1.88 1.01 2.06 0.94 1.03 3.92 1.05 0.98 1.00
f1 (ppm)

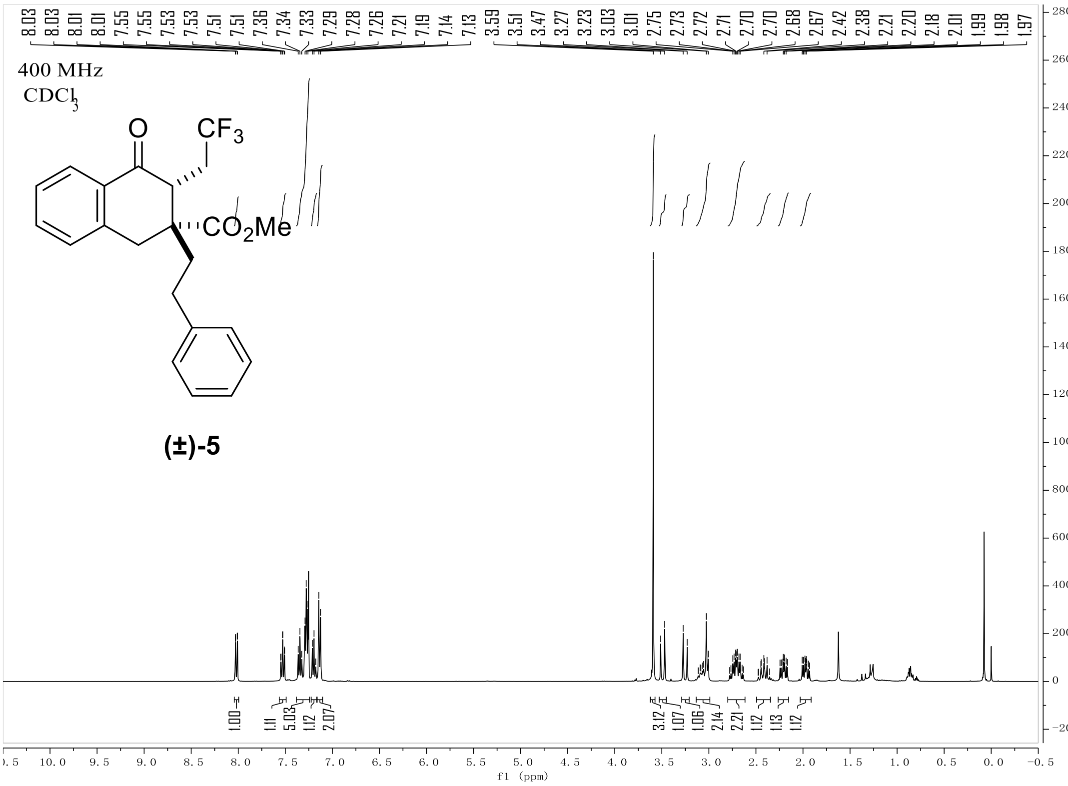

376 MHz
CDCl3
(±)-4l
-65.73
f1 (ppm)


100 MHz
CDCl3
(±)-4l
f1 (ppm)

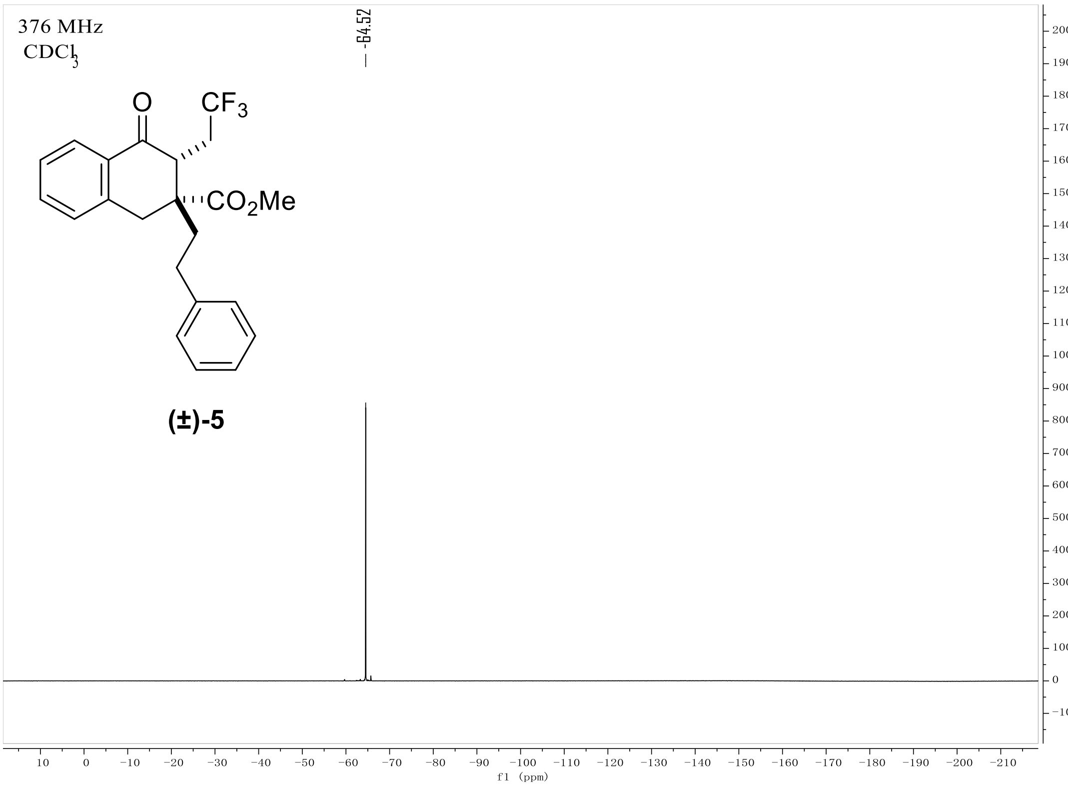

400 MHz
CDCl3
(±)-4m
f1 (ppm)


376 MHz
CDCl3
C4F9
CO2Me
(±)-4m
-80.93
-80.95
-80.96
-80.97
-80.98
-112.22
-112.24
-112.29
-112.93
-112.96
-113.00
-113.80
-113.82
-113.86
-114.51
-114.54
-114.57
-124.17
-124.19
-124.21
-124.23
-125.76
-125.79
-125.82
-125.84
3.00
1.92
2.35
2.19
f1 (ppm)

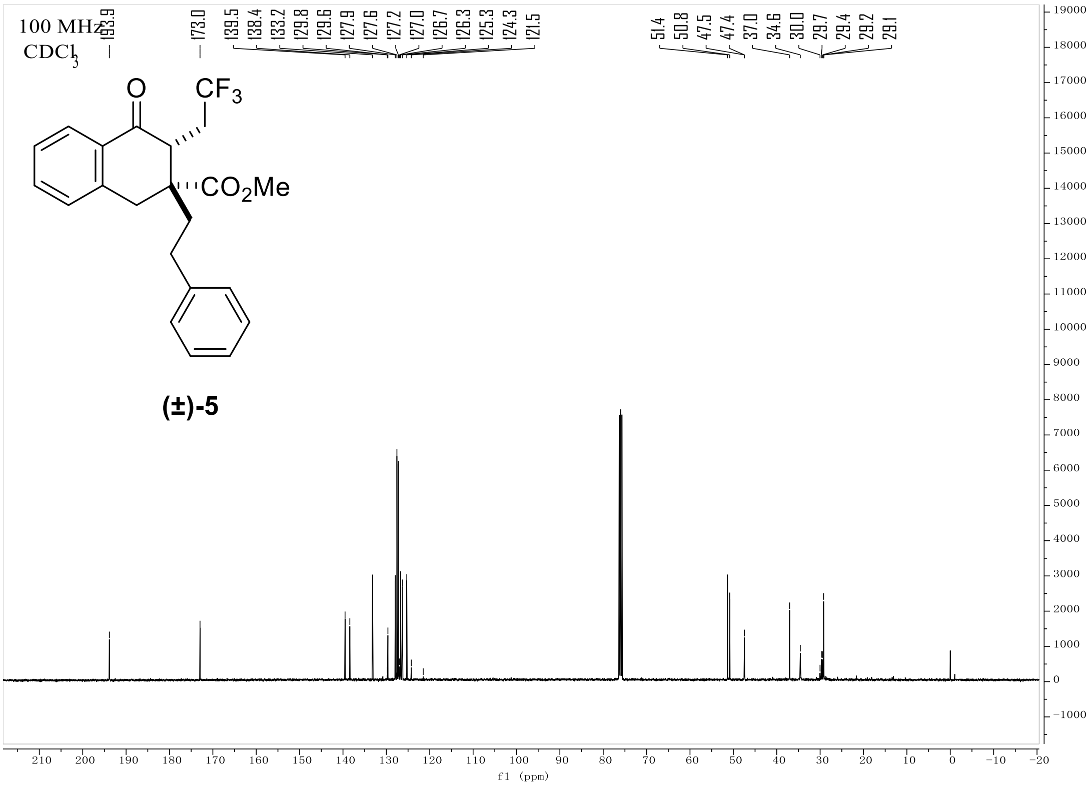

100 MHz
CDCl3
192.3
170.1
138.1
134.2
131.8
131.1
128.9
128.6
128.4
127.8
121.7
86.0
85.7
53.4
50.1
48.4
41.3
28.9
28.7
28.4
C4F9
CO2Me
(±)-4m
f1 (ppm)

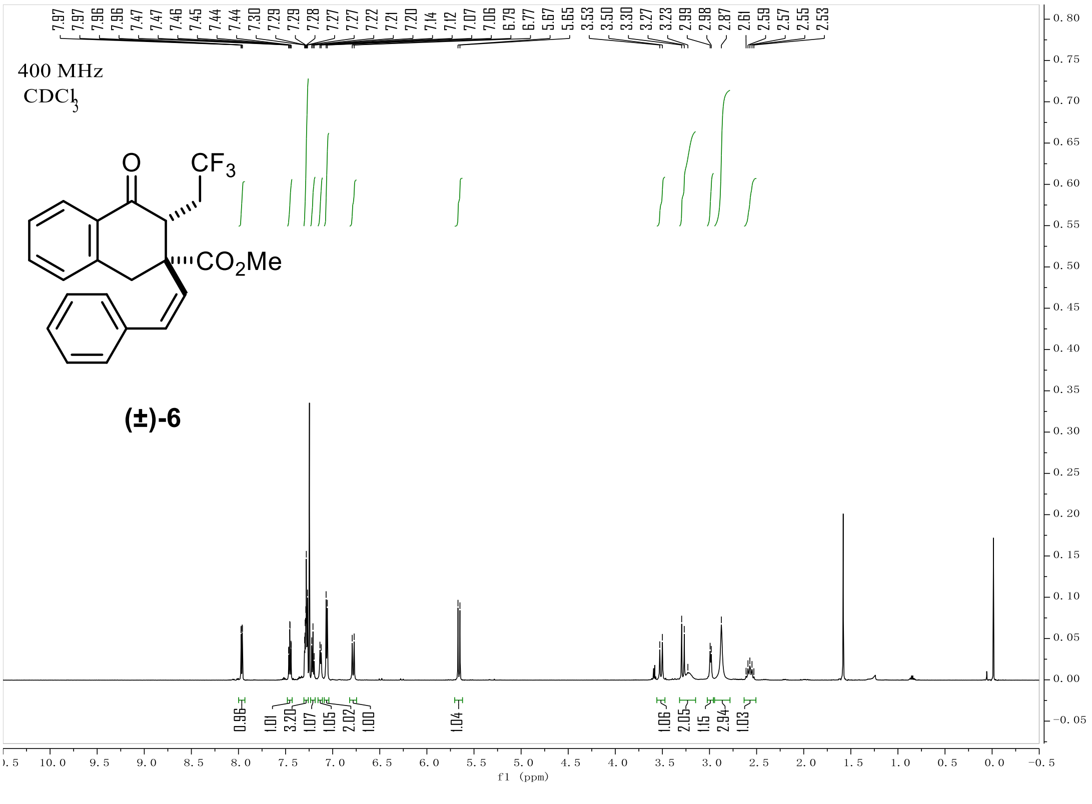

400 MHz
CDCl3
O
CF3
CO2Me
f1 (ppm)

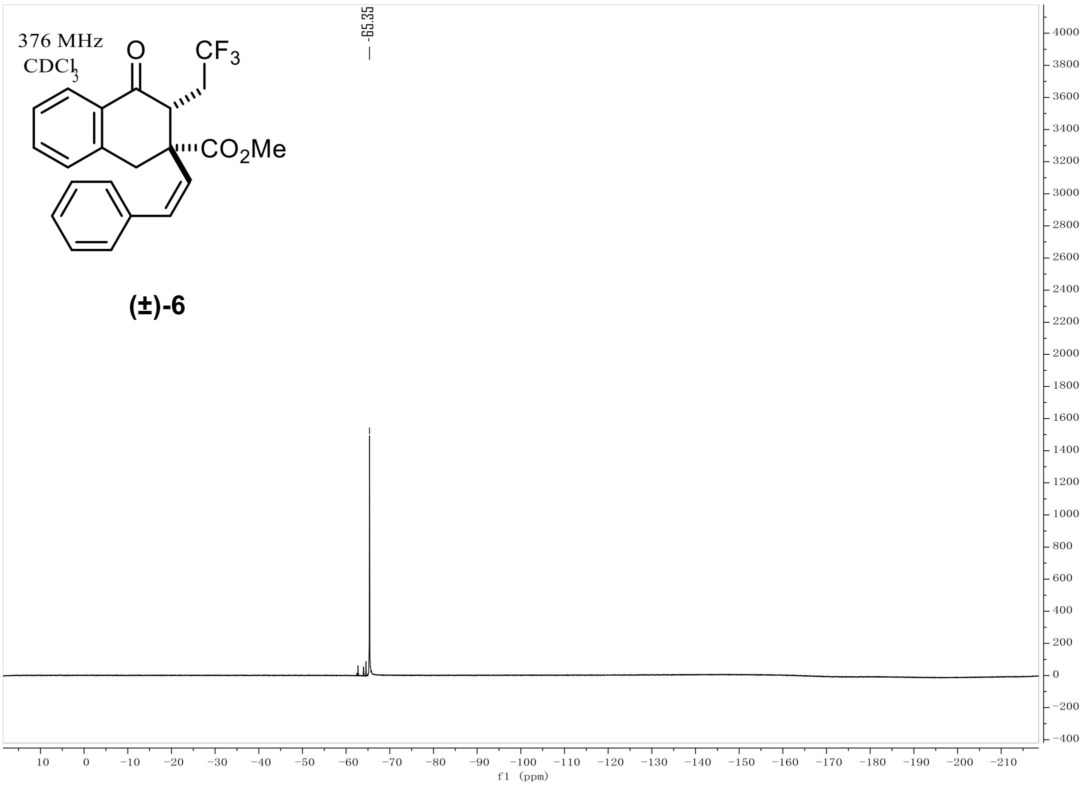
(±)-5

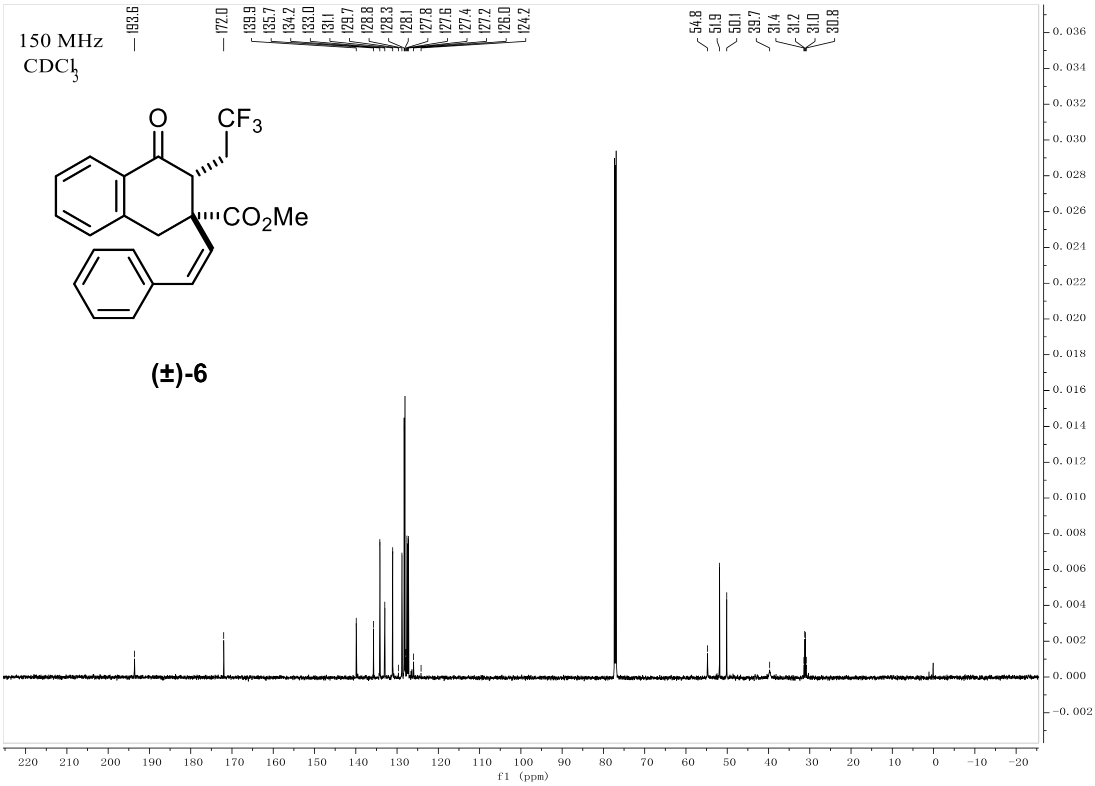

376 MHz
CDCl3
-64.52
O
CF3
CO2Me
f1 (ppm)

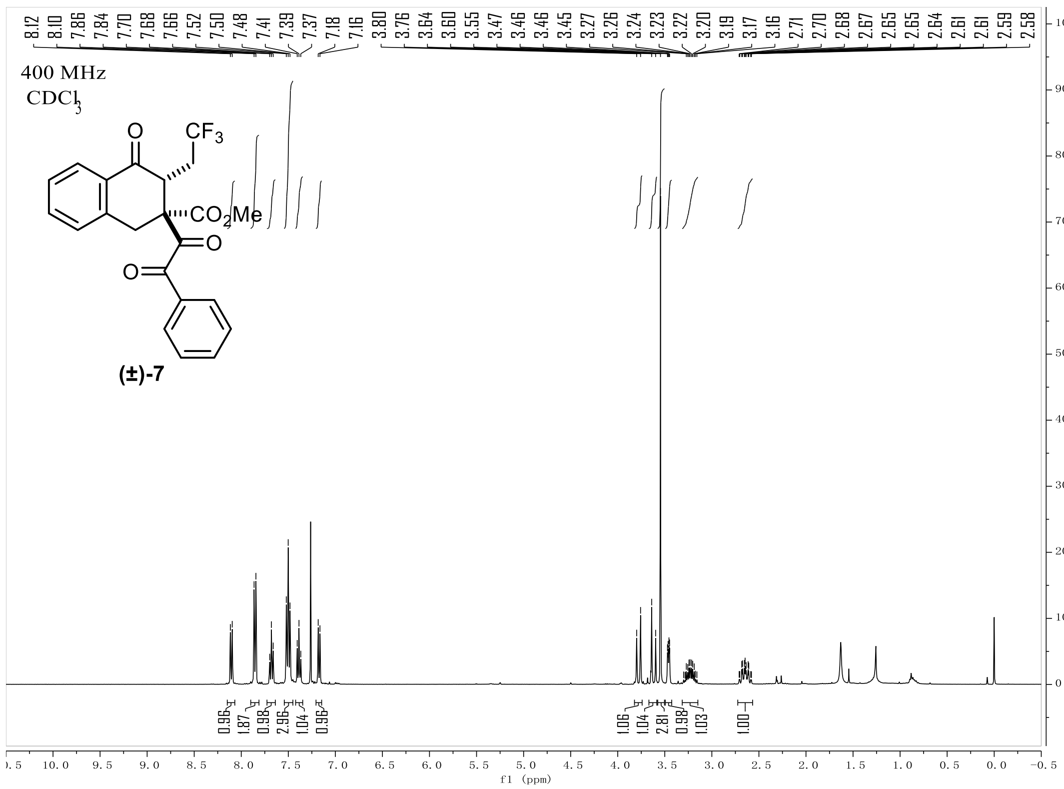
(±)-5


100 MHz
CDCl3
193.9
173.0
139.5
138.4
133.2
129.8
129.6
127.9
127.6
127.2
127.0
126.7
126.3
125.3
124.3
121.5
51.4
50.8
47.5
47.4
37.0
34.6
30.0
29.7
29.4
29.2
29.1
O
CF3
CO2Me
(±)-5
f1 (ppm)

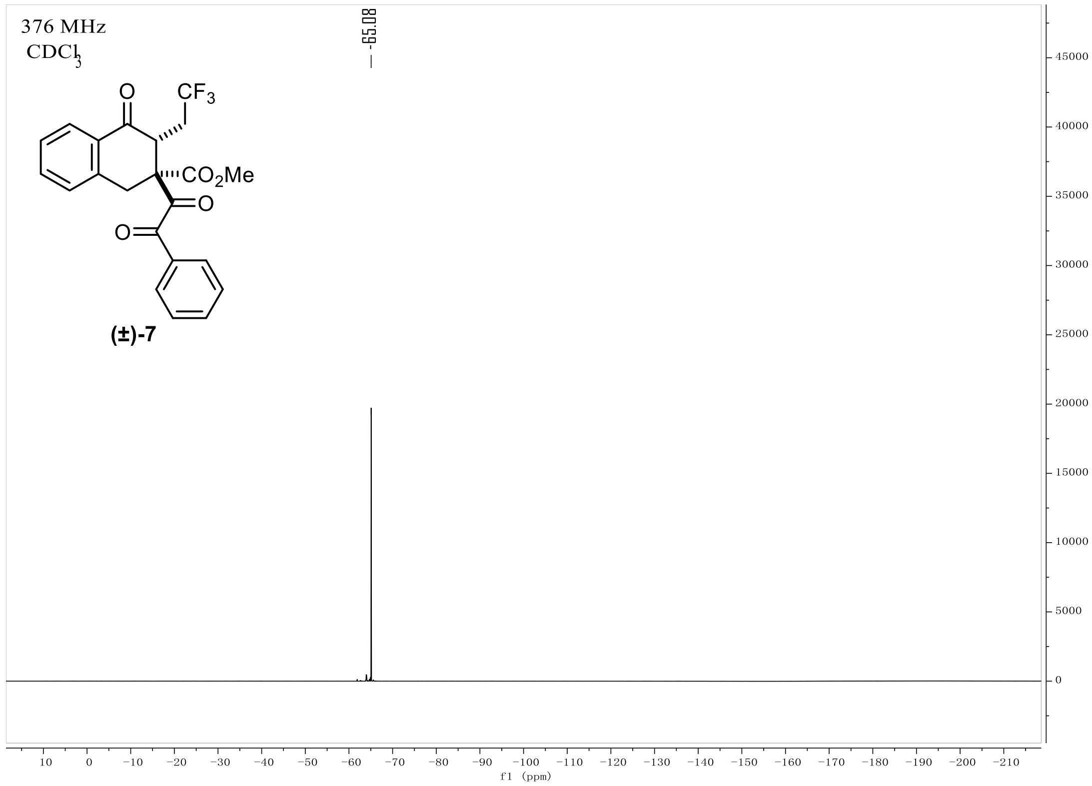

7.97
7.97
7.96
7.47
7.47
7.46
7.45
7.44
7.44
7.30
7.29
7.29
7.28
7.27
7.27
7.22
7.21
7.20
7.14
7.12
7.07
7.06
6.79
6.77
5.67
5.65
3.53
3.50
3.30
3.27
3.23
2.99
2.98
2.87
2.61
2.59
2.57
2.55
2.53
400 MHz
CDCl3
O
CF3
CO2Me
(±)-6
0.96
1.01
3.20
1.07
1.05
2.02
1.00
1.04
1.06
2.05
1.15
2.94
1.03
f1 (ppm)


376 MHz
CDCl3
CF3
CO2Me
(±)-6
-65.35
f1 (ppm)

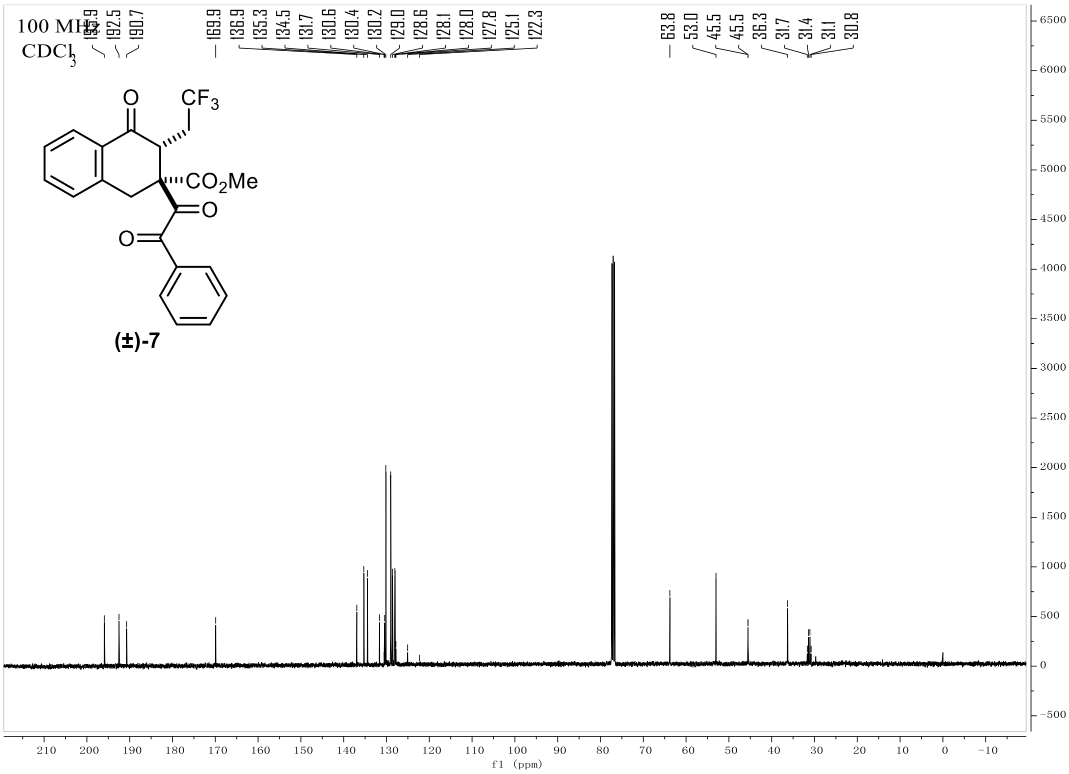

150 MHz
CDCl3
CF3
CO2Me
(±)-6
193.6
172.0
139.9 135.7 134.2 133.0 131.1 129.7 128.8 128.3 128.1 127.8 127.6 127.4 127.2 126.0 124.2
54.8 51.9 50.1 39.7 31.4 31.2 31.0 30.8
f1 (ppm)

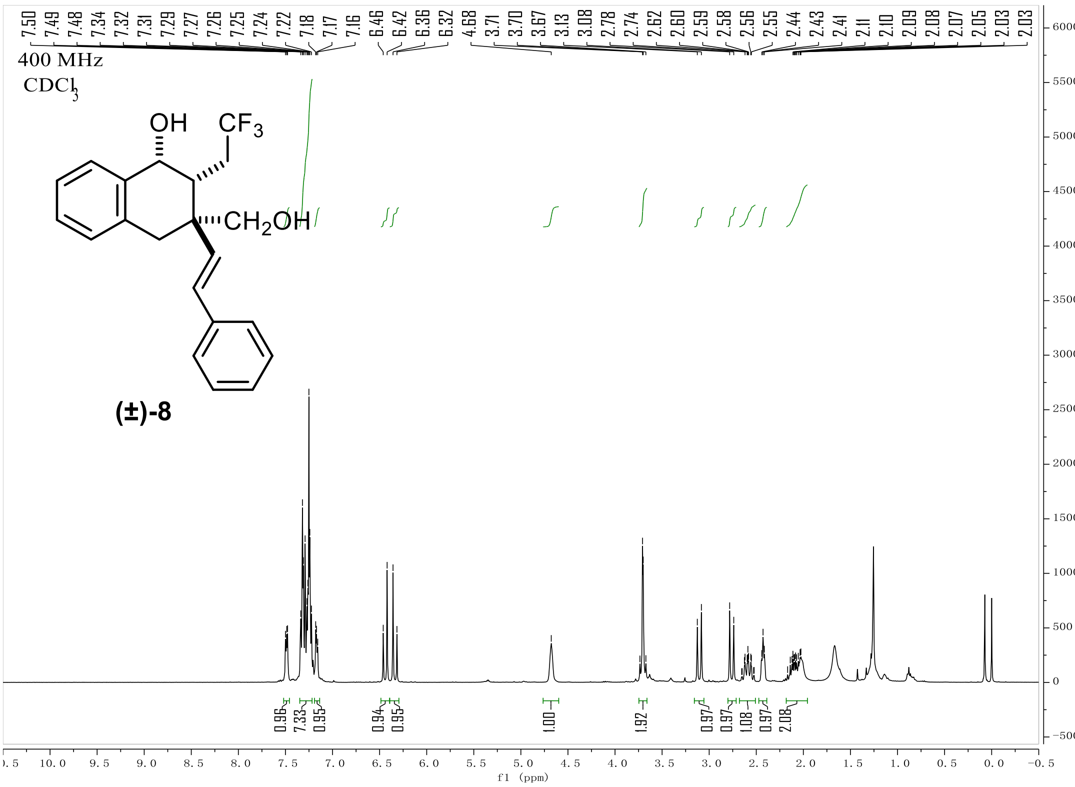


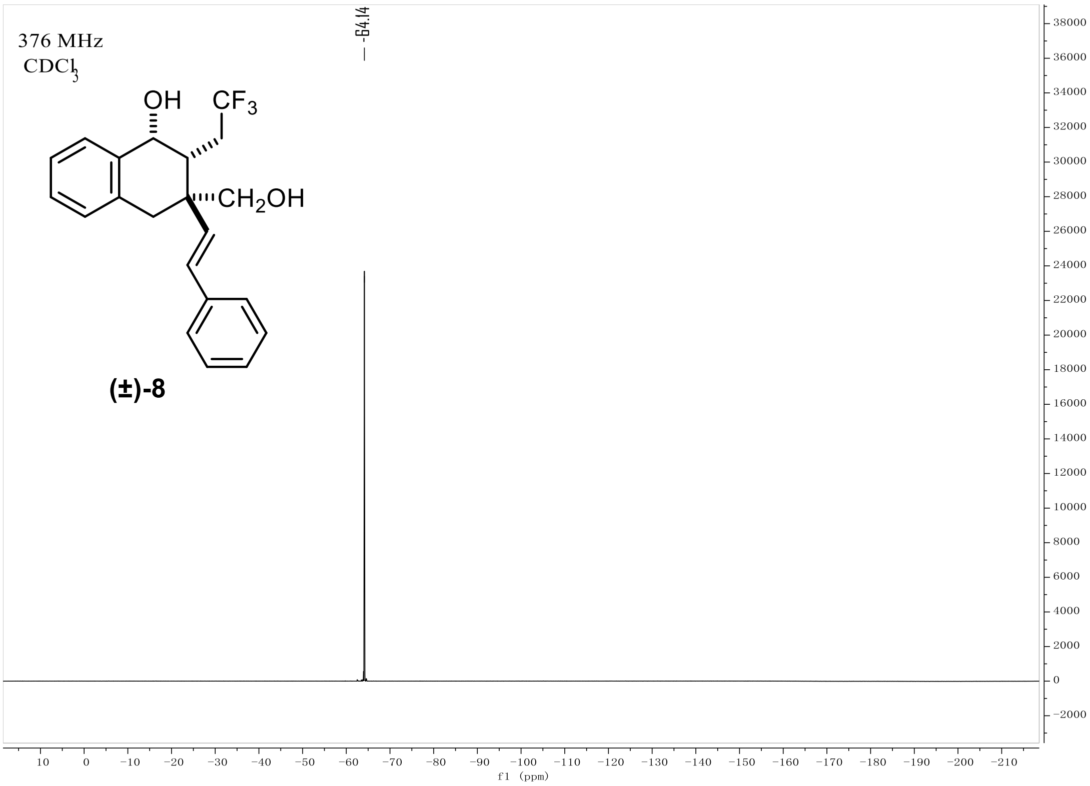
400 MHz
CDCl3
CF3
CO2Me
(±)-7
f1 (ppm)

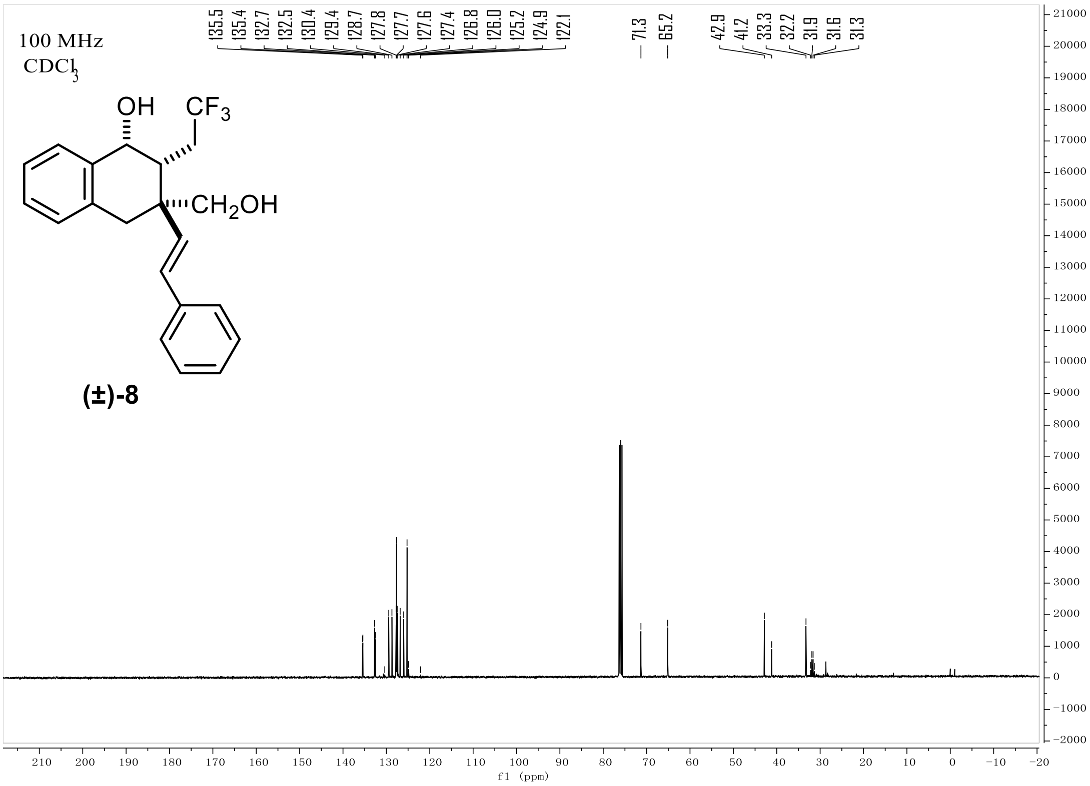


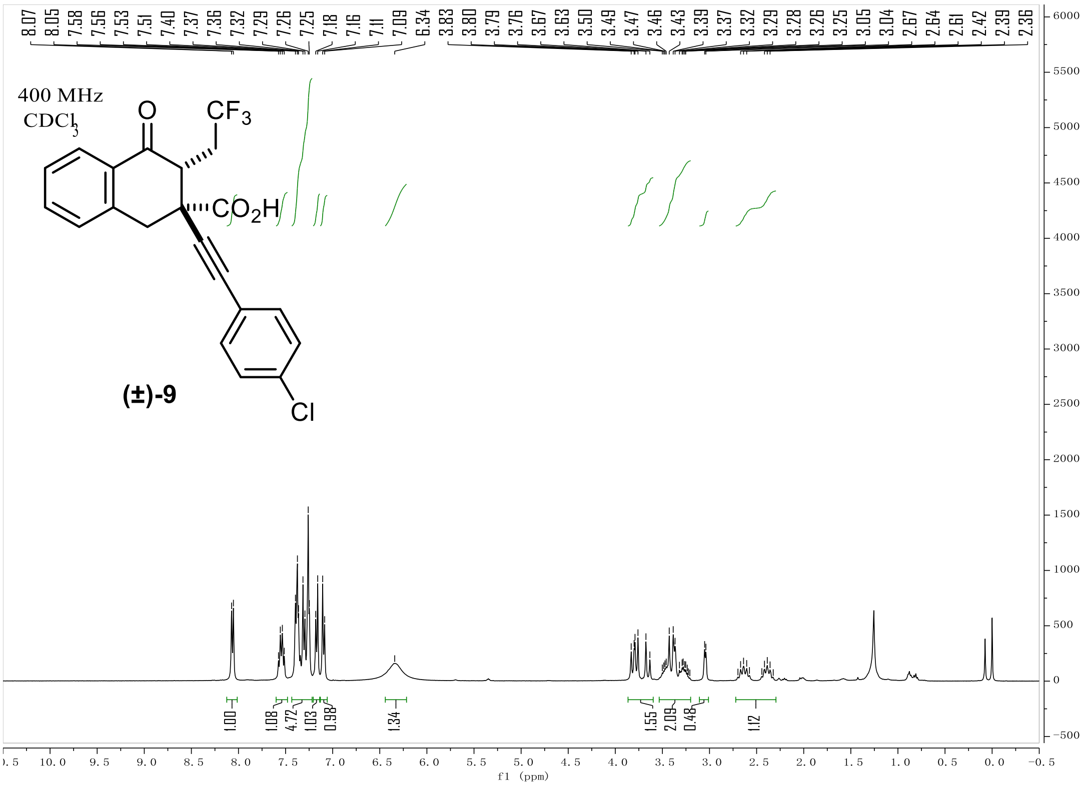
376 MHz
CDCl3
-65.08
CF3
CO2Me
(±)-7
f1 (ppm)

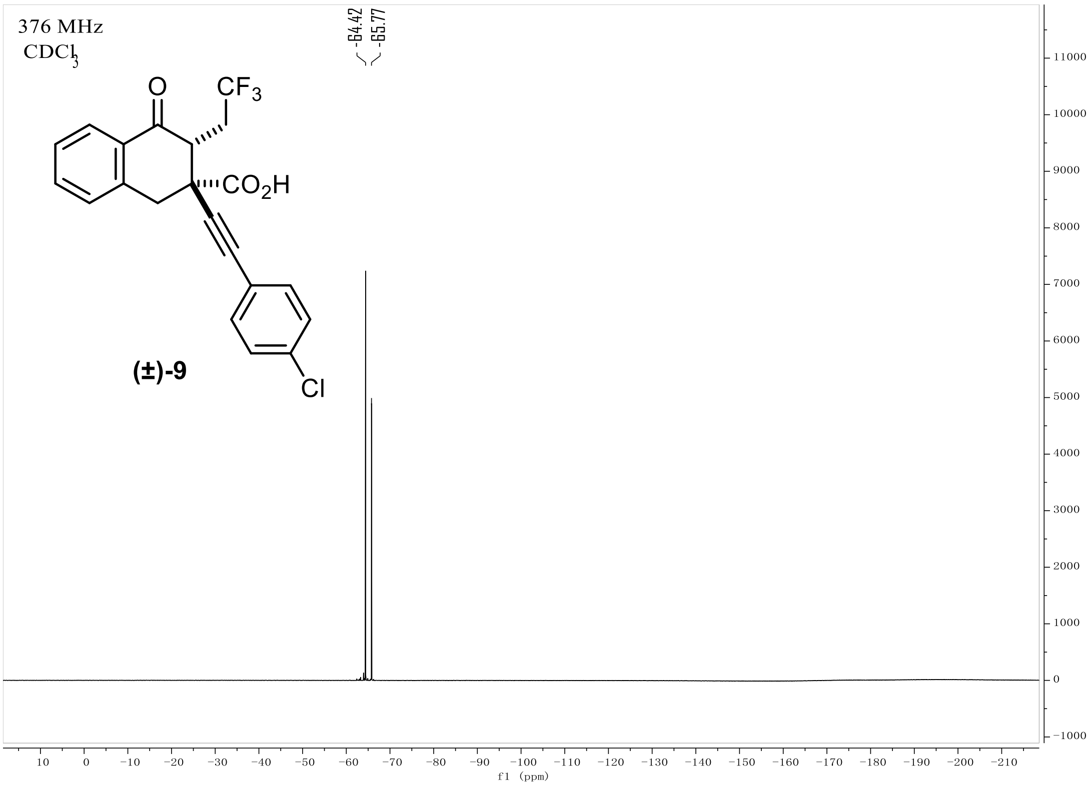

100 MHz
CDCl3
(±)-7
f1 (ppm)

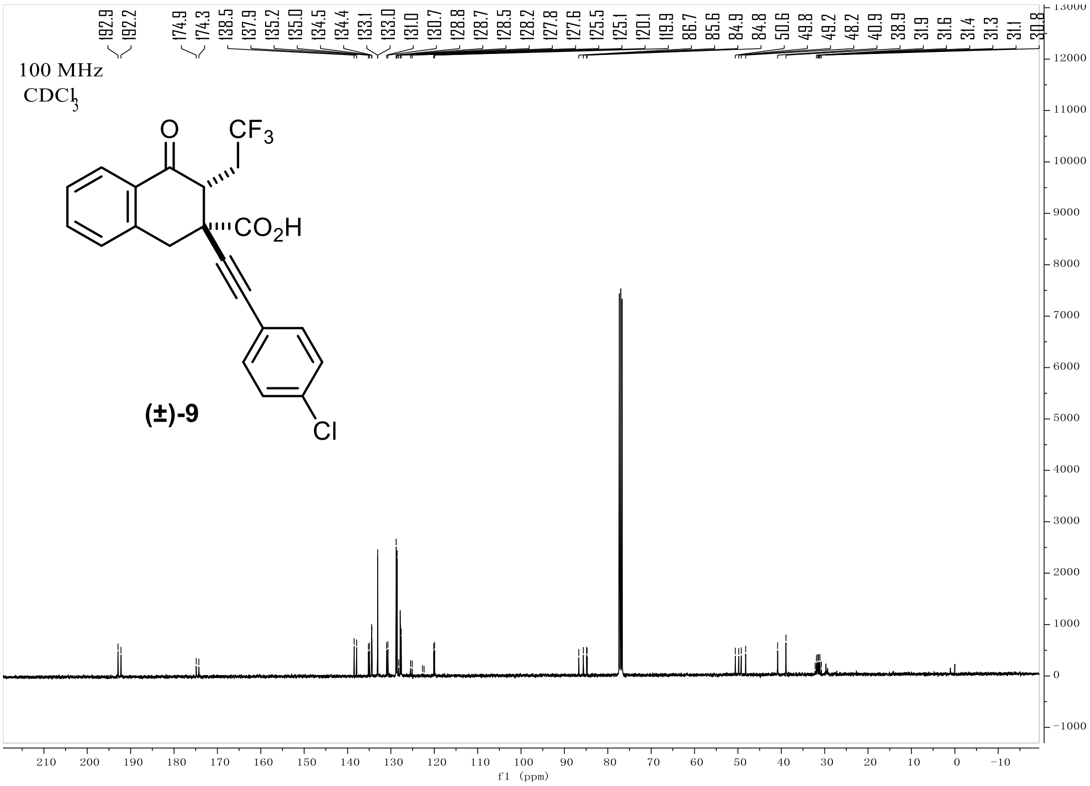

400 MHz
CDCl3
(±)-8
f1 (ppm)

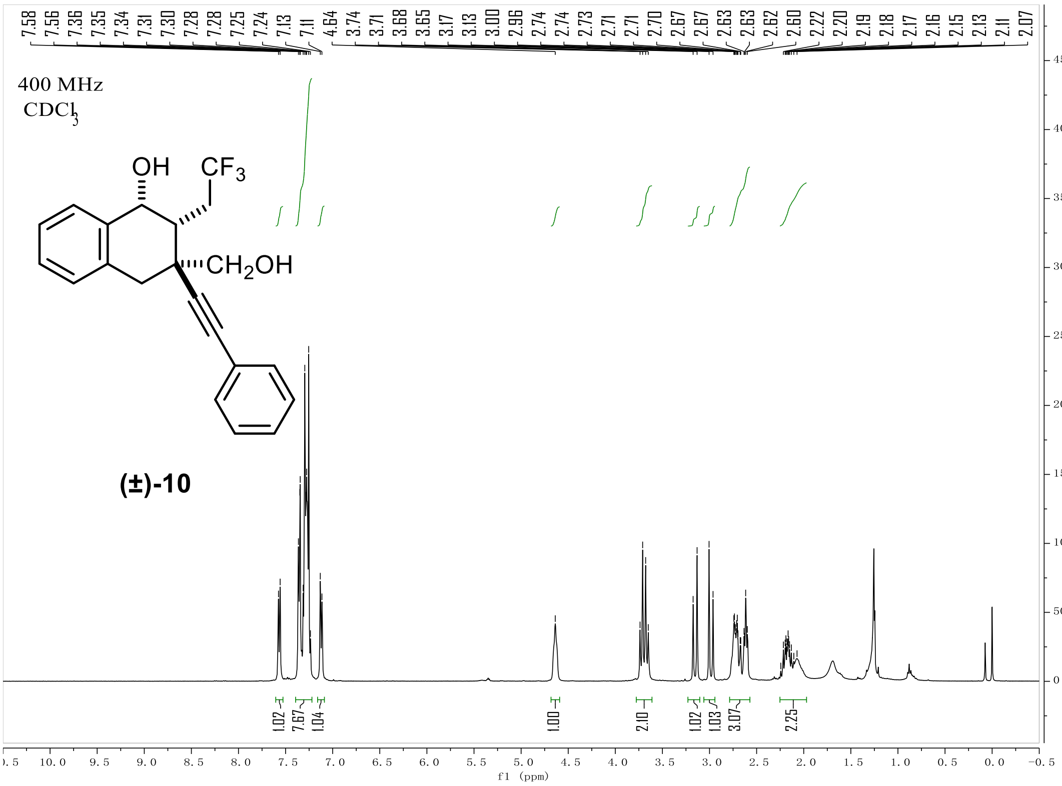

376 MHz
CDCl3
OH
CF3
CH2OH
(±)-8
-64.14
f1 (ppm)

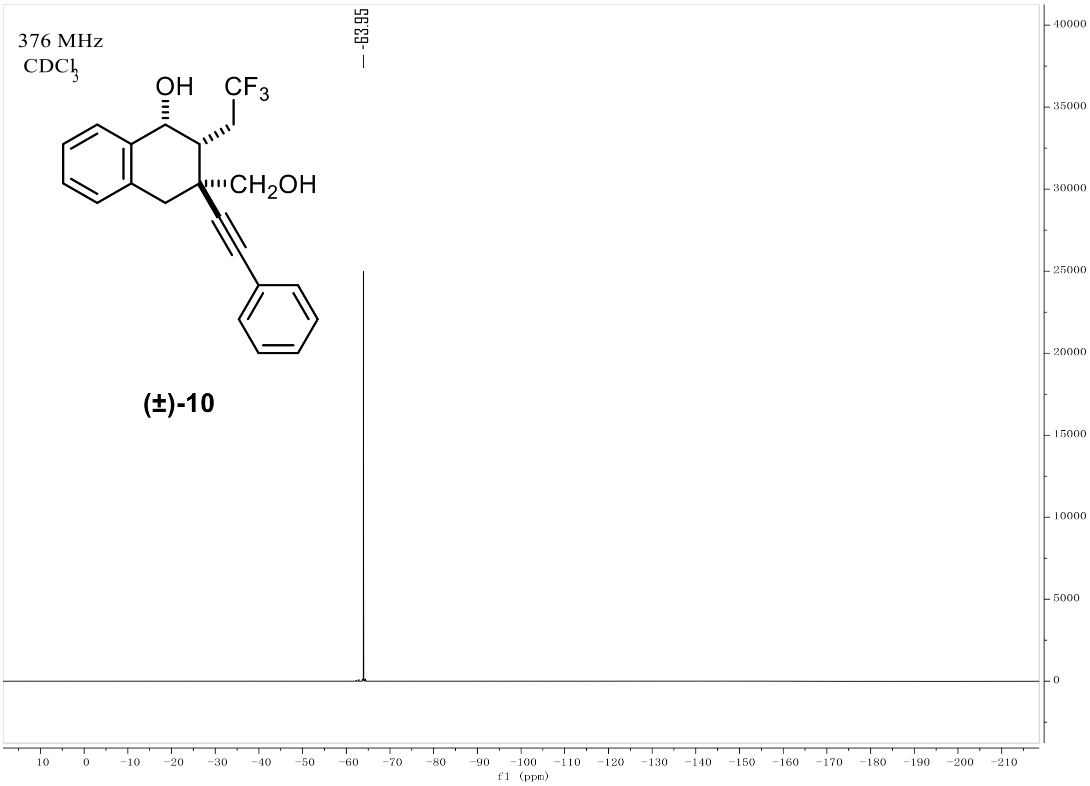

100 MHz
CDCl3
OH
CF3
CH2OH
(±)-8
135.5
135.4
132.7
132.5
130.4
129.4
128.7
127.8
127.7
127.6
127.4
126.8
126.0
125.2
124.9
122.1
71.3
65.2
42.9
41.2
33.3
32.2
31.9
31.6
31.3
f1 (ppm)

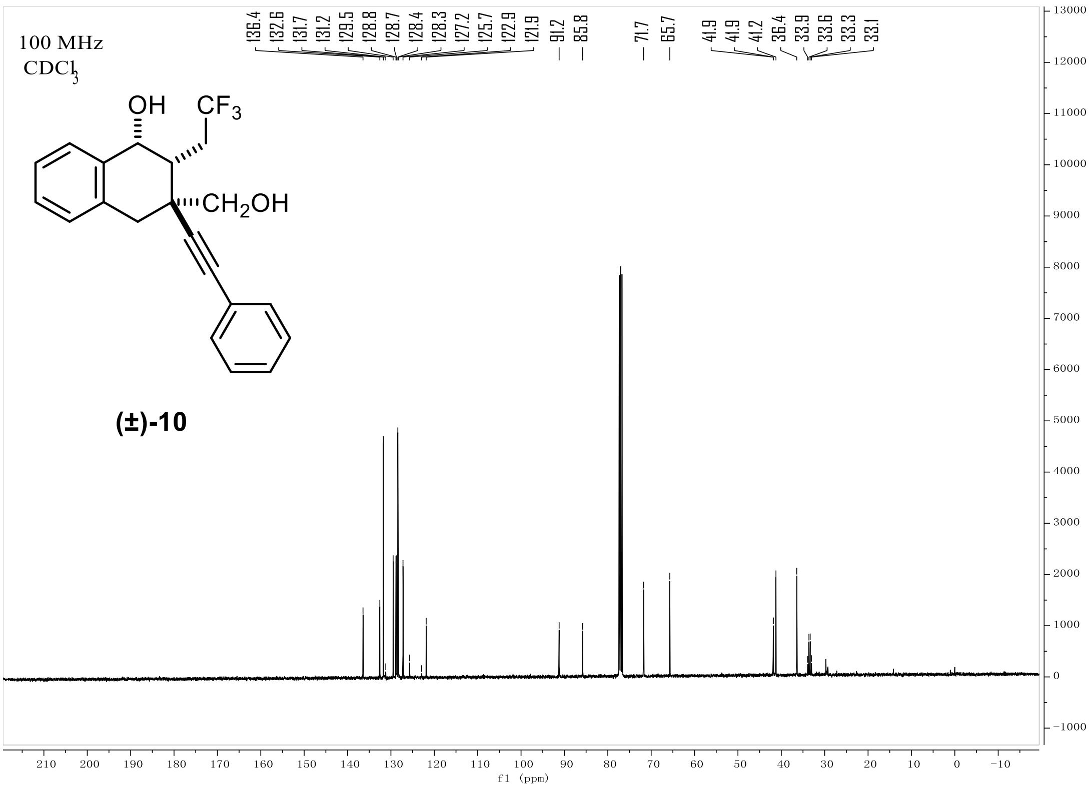

8.07 8.05 7.58 7.56 7.53 7.51 7.40 7.37 7.36 7.32 7.29 7.26 7.25 7.18 7.16 7.11 7.09 6.34 3.83 3.80 3.79 3.76 3.67 3.63 3.50 3.49 3.47 3.46 3.43 3.39 3.37 3.32 3.29 3.28 3.26 3.25 3.05 3.04 2.67 2.64 2.61 2.42 2.39 2.36
400 MHz
CDCl3
(±)-9
1.00 1.08 4.72 1.03 0.98 1.34 1.55 2.09 0.48 1.12
f1 (ppm)

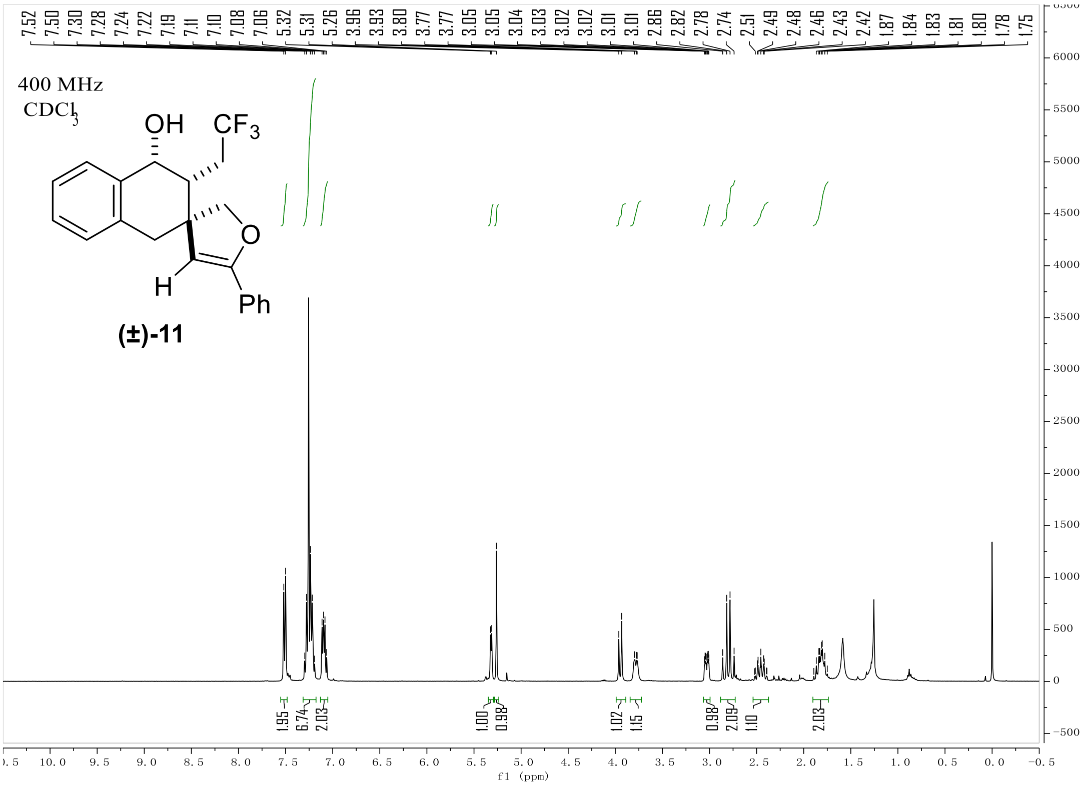

-64.42 -65.77
376 MHz
CDCl3
(±)-9
f1 (ppm)

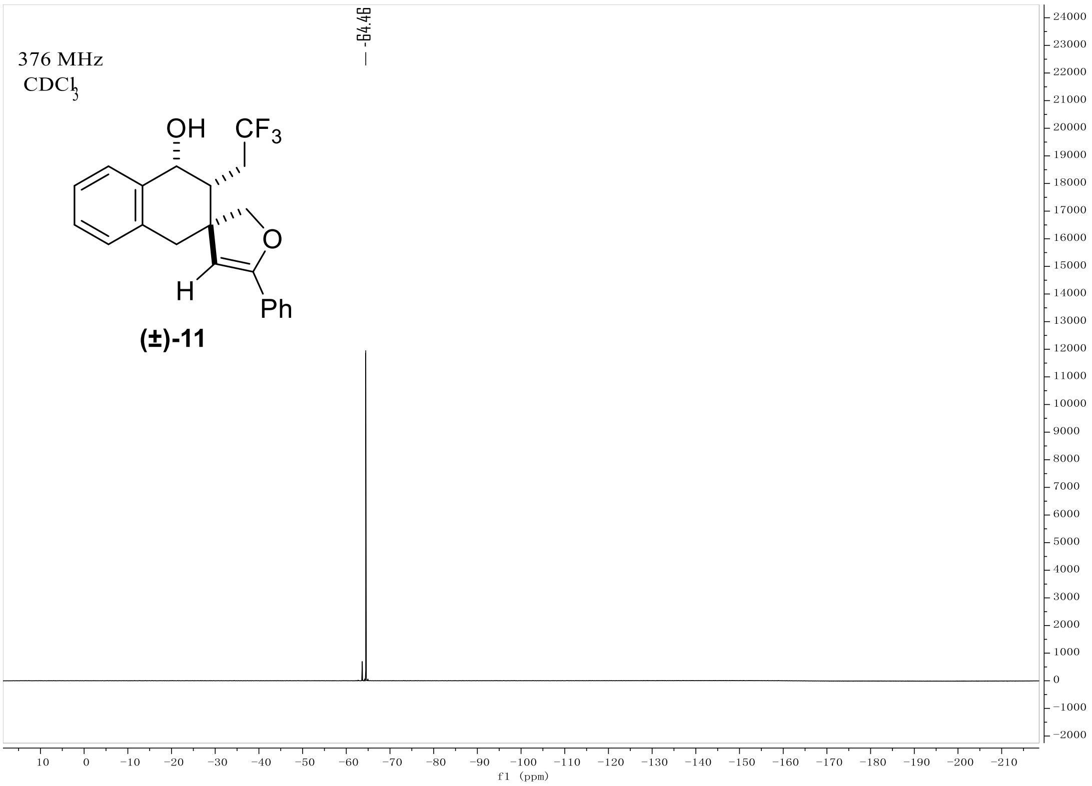

192.9 192.2 174.9 174.3 138.5 137.9 135.2 135.0 134.5 134.4 133.1 133.0 131.0 130.7 128.8 128.7 128.5 128.2 127.8 127.6 125.5 125.1 120.1 119.9 86.7 85.6 84.9 84.8 50.6 49.8 49.2 48.2 40.9 38.9 31.9 31.6 31.4 31.3 31.1 30.8
100 MHz
CDCl3
O
CF3
CO2H
Cl
(±)-9
f1 (ppm)


7.58 7.56 7.36 7.35 7.34 7.31 7.30 7.28 7.28 7.25 7.24 7.13 7.11 4.64 3.74 3.71 3.68 3.65 3.17 3.13 3.00 2.96 2.74 2.74 2.73 2.71 2.71 2.70 2.67 2.67 2.63 2.63 2.62 2.60 2.22 2.20 2.19 2.18 2.17 2.16 2.15 2.13 2.11 2.07
400 MHz
CDCl3
OH
CF3
CH2OH
(±)-10
1.02 7.67 1.04 1.00 2.10 1.02 1.03 3.07 2.25
f1 (ppm)


376 MHz
CDCl3
OH
CF3
CH2OH
(±)-10
-63.95
f1 (ppm)


100 MHz
CDCl3
OH
CF3
CH2OH
(±)-10
136.4
132.6
131.7
131.2
129.5
128.8
128.7
128.4
128.3
127.2
125.7
122.9
121.9
91.2
85.8
71.7
65.7
41.9
41.9
41.2
36.4
33.9
33.6
33.3
33.1
f1 (ppm)


400 MHz
CDCl3
OH
CF3
O
H
Ph
(±)-11
f1 (ppm)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376 MHz
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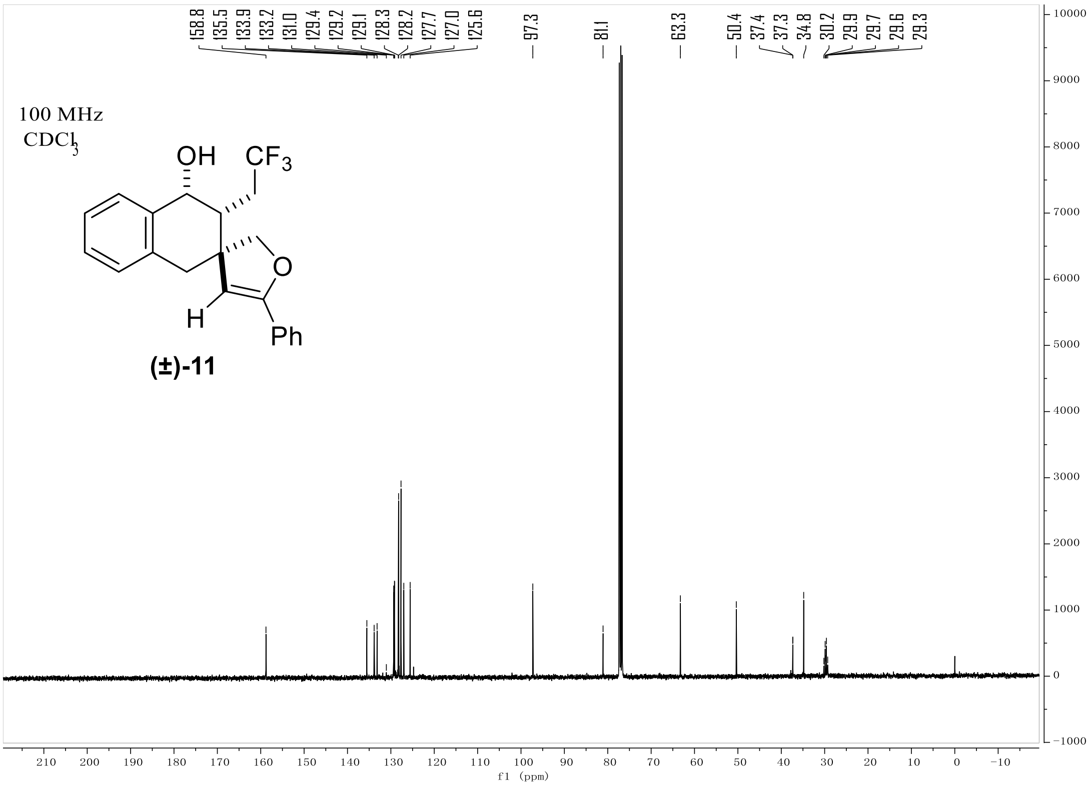
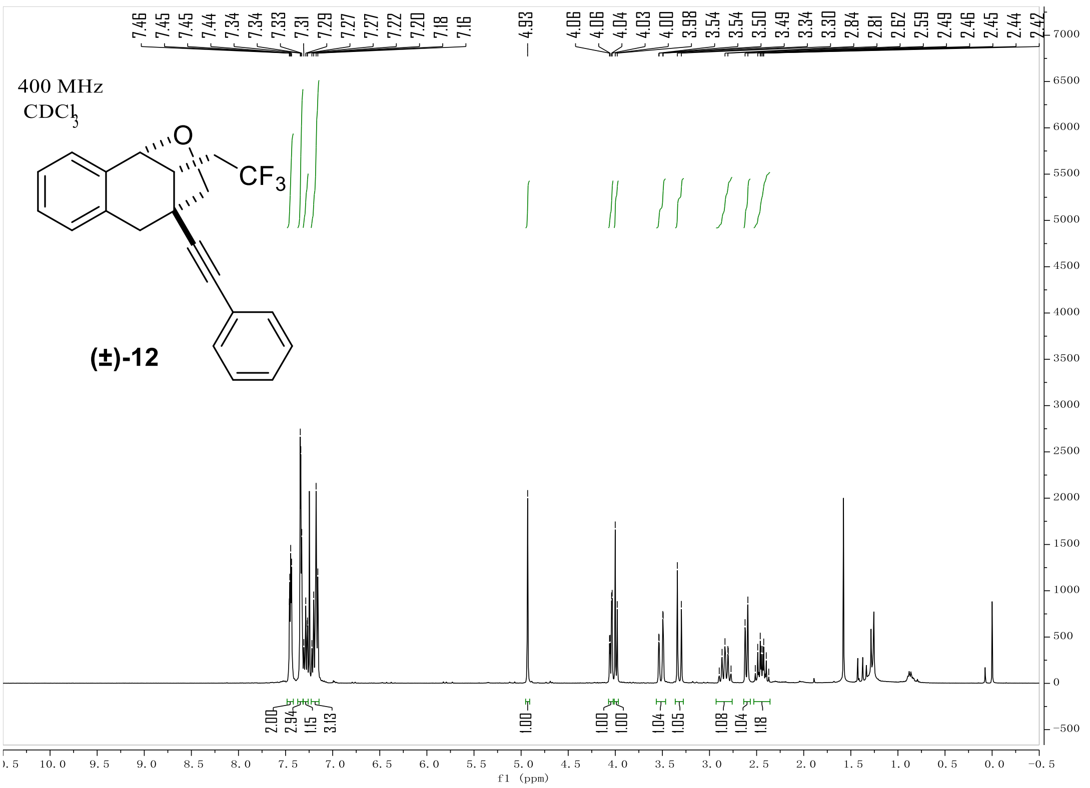
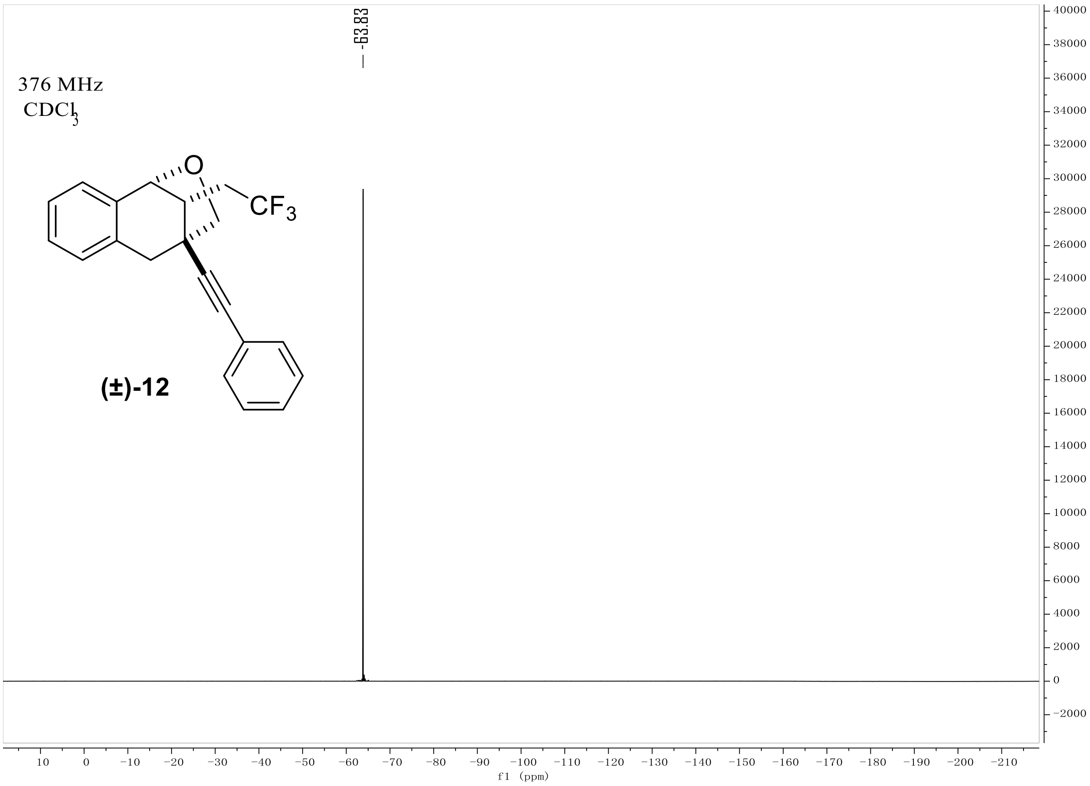
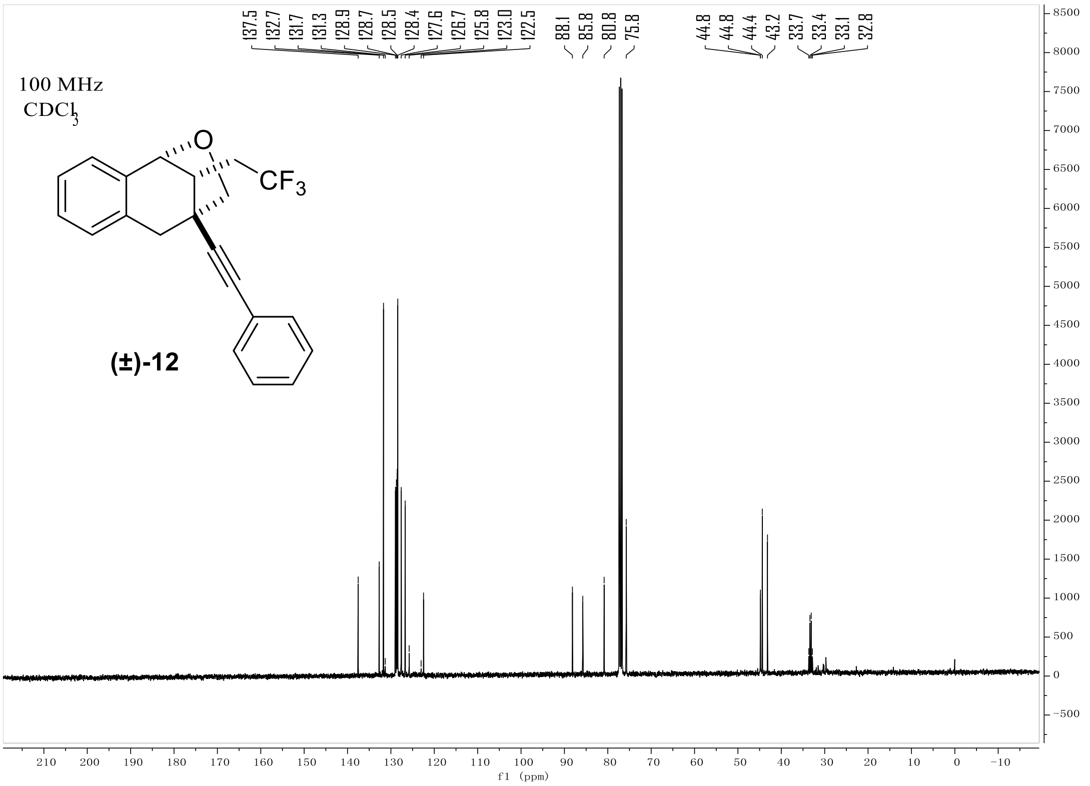
OH
CF3
O
H
Ph
(±)-11
f1 (ppm)


158.8
135.5
133.9
133.2
131.0
129.4
129.2
129.1
128.3
128.2
127.7
127.0
125.6
97.3
81.1
63.3
50.4
37.4
37.3
34.8
30.2
29.9
29.7
29.6
29.3
100 MHz
CDCl3
OH
CF3
O
H
Ph
(±)-11
f1 (ppm)


400 MHz
CDCl3
O
CF3
(±)-12
f1 (ppm)


-63.83
376 MHz
CDCl3
O
CF3
(±)-12
f1 (ppm)


137.5
132.7
131.7
131.3
128.9
128.7
128.5
128.4
127.6
126.7
125.8
123.0
122.5
88.1
85.8
80.8
75.8
44.8
44.8
44.4
43.2
33.7
33.4
33.1
32.8
100 MHz
CDCl3
O
CF3
(±)-12
f1 (ppm)