Supporting Information

Phosphine-Catalyzed [3+2] Cycloadditions of 2-Trifluoromethyl Enynes/Enediynes with Allenoates: Access to Cyclopentenes Containing CF_3-Substituted Quaternary Carbon Center

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Table of Contents

1. General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on an Bruker spectrometer operating at 500 (400) MHz, 125 (100) MHz, and 470 (376) MHz respectively. Chemical shifts are reported in parts per million (ppm), and the residual solvent or tetramethylsilane (TMS) peak was used as internal standard. High-resolution mass spectrometry (HRMS) were measured with an electrospray ionization (ESI) method. Flash chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was carried out using commercial silica gel-precoated glass plates, and compounds were visualized under UV light (254 nm).

Trifluoromethyl enynes/enediynes were synthesized *via* Sonogashira reactions from corresponding alkyne/diynes[1] and 2-bromo-3,3,3-trifluoropropene.[2] Allenoates were purchased from Energy Chemical, or prepared following the literature method.[3]

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1. (a) Trost, B. M.; Chan, V. S.; Yamamoto, D. *J. Am. Chem. Soc.* **2010**, 132, 5186-5192. (b) Cho, E. J.; Lee, D. *Org. Lett.* **2008**, 10, 257-259. (c) Karmakar, R.; Yun, S. Y.; Chen, J.; Xia, Y.; Lee, D. *Angew. Chem. Int. Ed.* **2015**, 54, 6582-6586.

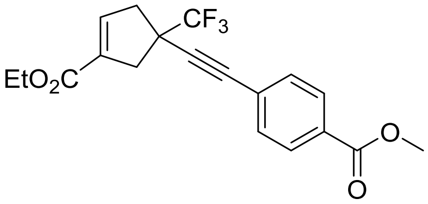
2. (a) Hu, C.-M.; Hong, F.; Xu, Y.-Y. *J. Fluorine Chem.* **1993**, 64, 1-4. (b) Trost, B. M.; Debien, L. *J. Am. Chem. Soc.* **2015**, 137, 11606-11609.

3. (a) Wang, G.; Liu, X.; Chen, Y.; Yang, J.; Li, J.; Lin, L.; Feng, X. *ACS Catal.* **2016**, 6, 2482-2486. (b) Bang, J.; Kim, H.; Kim, J.; Yu, C.-M. *Org. Lett.* **2015**, 17, 1573-1576.

2. Experimental Procedures and Spectroscopic Data

General Procedure A: Phosphine-Catalyzed [3+2] Cycloaddition of 2-Trifluoromethyl Enynes with Allenoates. Under nitrogen atmosphere, to a stirred solution of 2-trifluoromethyl enyne **2** (0.2 mmol, 1.0 equiv) and PPh_3 (0.02 mmol, 0.1 equiv) in 2 mL of EtOAc was added allenoate **1** (0.4 mmol, 2.0 equiv), and the resulting mixture was stirred room temperature for 24 h. After the reaction was complete, the mixture was concentrated *in vacuo*, and the residue was directly subjected to column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the corresponding product **3**.

Methyl 4-((3-(ethoxycarbonyl)-1-(trifluoromethyl)cyclopent-3-en-1-yl)ethynyl)benzoate (3aa).



2-Trifluoromethyl enyne **2a** (51 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 20:1), the desired cycloadduct **3aa** was obtained (65 mg, 89%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.43 (hexane/ethyl acetate = 10:1), [UV light].

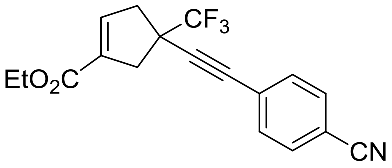
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.51-7.47 (m, 2H), 6.69 (d, *J* = 2.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.29-3.17 (m, 2H), 3.17-3.03 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 163.7, 138.6, 133.8, 131.8, 130.0, 129.4, 126.7, 126.3 (q, *J* = 278.8 Hz), 90.2 (d, *J* = 2.5 Hz), 82.9, 60.7, 52.2, 46.7 (q, *J* = 30 Hz), 42.9, 41.4, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{17}F_3NaO_4$ 389.0971, Found 389.0957.

Ethyl 4-((4-cyanophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ab).



2-Trifluoromethyl enyne **2b** (44 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 20:1), the desired cycloadduct **3ab** was obtained (47 mg, 70%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.45 (hexane/ethyl acetate = 9:1), [UV light].

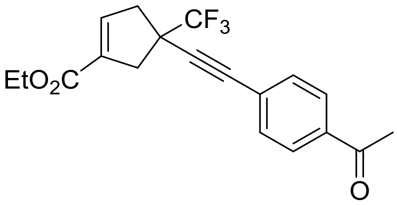
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.69 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.29-3.17 (m, 2H), 3.16-3.03 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 138.5, 133.8, 132.4, 132.0, 126.9, 126.2 (q, *J* = 278.8 Hz), 118.2, 112.2, 91.7 (d, *J* = 2.5 Hz), 82.1, 60.8, 46.7 (q, *J* = 30 Hz), 42.8, 41.3, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{14}F_3NNaO_2$ 356.0869, Found 356.0861.

Ethyl 4-((4-acetylphenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ac).



2-Trifluoromethyl enyne **2c** (48 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 10:1), the desired cycloadduct **3ac** was obtained (43 mg, 62%) as a colorless oil.

TLC (SiO_2) ***R*$_f$** = 0.31 (hexane/ethyl acetate = 9:1), [UV light].

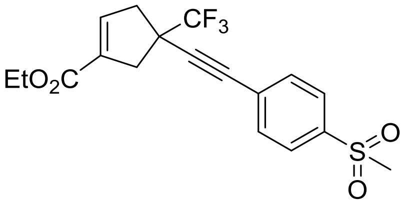
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 2.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.30-3.17 (m, 2H), 3.17-3.03 (m, 2H), 2.60 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 163.7, 138.6, 136.7, 133.8, 132.0, 128.2, 126.9, 126.3 (q, *J* = 278.8 Hz), 90.5 (d, *J* = 2.5 Hz), 82.9, 60.7, 46.7 (q, *J* = 30 Hz), 42.9, 41.4, 26.6, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{17}F_3NaO_3$ 373.1022, Found 373.1016.

Ethyl 4-((4-(methylsulfonyl)phenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ad).



2-Trifluoromethyl enyne **2d** (55 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 20:1), the desired cycloadduct **3ad** was obtained (65 mg, 84%) as a pale yellow oil.

TLC (SiO_2) ***R*$_f$** = 0.47 (hexane/ethyl acetate = 7:3), [UV light].

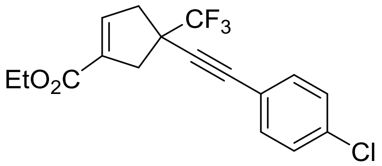
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 6.70 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.30-3.18 (m, 2H), 3.17-3.08 (m, 2H),3.05 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 140.3, 138.5, 133.8, 132.6, 127.9, 127.4, 126.2 (q, *J* = 278.8 Hz), 91.4, 82.0, 60.78, 46.7 (q, *J* = 30 Hz), 44.4, 42.8, 41.3, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{17}F_3NaO_4S$ 409.0692, Found 409.0684.

Ethyl 4-((4-chlorophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ae).



2-Trifluoromethyl enyne **2e** (46 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 30:1), the desired cycloadduct **3ae** was obtained (60 mg, 88%) as a colorless oil.

TLC (SiO_2) ***R*****f** = 0.70 (hexane/ethyl acetate = 9:1), [UV light].

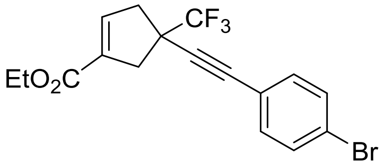
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.22-7.18 (m, 2H), 6.60 (d, *J* = 2.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.20-3.08 (m, 2H), 3.07-2.94 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 162.8, 137.7, 133.8, 132.8, 132.1, 127.6, 125.3 (q, *J* = 278.8 Hz), 119.6, 87.3 (d, *J* = 2.5 Hz), 81.6, 59.7, 45.6 (q, *J* = 28.8 Hz), 42.0, 40.4, 13.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{14}ClF_3NaO_2$ 365.0527, Found 365.0519.

Ethyl 4-((4-bromophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3af).



2-Trifluoromethyl enyne **2f** (55 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 30:1), the desired cycloadduct **3af** was obtained (62 mg, 80%) as a colorless oil.

TLC (SiO_2) ***R*****f** = 0.71 (hexane/ethyl acetate = 9:1), [UV light].

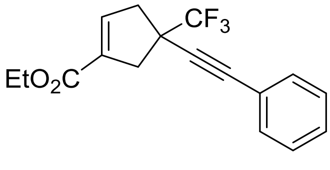
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2H), 7.31-7.25 (m, 2H), 6.68 (d, *J* = 2.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.28-3.15 (m, 2H), 3.15-3.01 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 163.8, 138.7, 133.8, 133.3, 131.6, 126.3 (q, *J* = 278.8 Hz), 123.0, 121.0, 88.5 (d, *J* = 2.5 Hz), 82.6, 60.7, 46.6 (q, *J* = 28.8 Hz), 43.0, 41.4, 14.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{14}BrF_3NaO_2$ 409.0021, Found 409.0015.

Ethyl 4-(phenylethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ag).



According to a modified procedure A, to a solution of 2-trifluoromethyl enyne **2g** (39 mg, 0.2 mmol) in EtOAc, allenoate **1a** (68 mg, 0.6 mmol) was added in two portions (2×0.3 mmol) every 10 hours, and the resulting mixture was stirred at room temperature for 48 h. After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ag** was obtained (34 mg, 56%) as a colorless oil.

TLC (SiO_2) ***R*$_f$** = 0.6 (hexane/ethyl acetate = 10:1), [UV light].

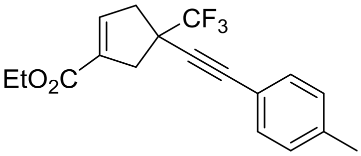
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.35-7.28 (m, 3H), 6.68 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.28-3.16 (m, 2H), 3.15-3.02 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 138.8, 133.8, 131.8, 128.7, 128.3, 126.4 (q, *J* = 278.8 Hz), 122.1, 87.3 (d, *J* = 3.8 Hz), 83.7, 60.7, 46.6 (q, *J* = 28.8 Hz), 43.1, 41.5, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.1.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{15}F_3NaO_2$ 331.0916, Found 331.0910.

Ethyl 4-(p-tolylethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ah).



According to a modified procedure A, to a solution of 2-trifluoromethyl enyne **2h** (42 mg, 0.2 mmol) in EtOAc, allenoate **1a** (68 mg, 0.6 mmol) was added in two portions (2×0.3 mmol) every 10 hours, and the resulting mixture was stirred at room temperature for 48 h. After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ah** was obtained (32 mg, 50%) as a colorless oil.

TLC (SiO_2) ***R*$_f$** = 0.68 (hexane/ethyl acetate = 9:1), [UV light].

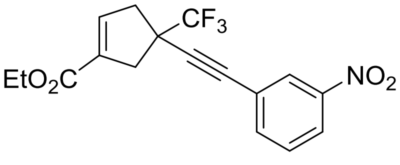
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.68 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.27-3.15 (m, 2H), 3.14-3.00 (m, 2H), 2.34 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 138.8, 133.8, 131.7, 129.0, 126.5 (q, *J* = 278.8 Hz), 119.0, 86.6 (d, *J* = 2.5 Hz), 83.8, 60.7, 46.6 (q, *J* = 28.8 Hz), 43.1, 41.6, 21.5, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.2.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{17}F_3NaO_2$ 345.1073, Found 345.1084.

Ethyl 4-((3-nitrophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ai).



2-Trifluoromethyl enyne **2i** (48 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 20:1), the desired cycloadduct **3ai** was obtained (42 mg, 60%) as a colorless oil.

TLC (SiO_2) ***R*$_f$** = 0.41 (hexane/ethyl acetate = 9:1), [UV light].

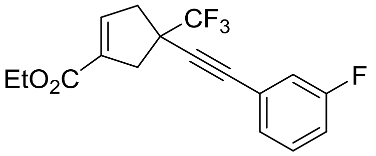
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-8.26 (m, 1H), 8.19 (m, 1H), 7.75-7.72 (m, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.30-3.18 (m, 2H), 3.18-3.05 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 148.1, 138.5, 137.5, 133.8, 129.4, 126.7, 123.9, 123.5, 126.2 (q, *J* = 278.8 Hz), 90.0 (d, *J* = 2.5 Hz), 81.3, 60.8, 46.7 (q, *J* = 28.8 Hz), 42.8, 41.3, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.8.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{14}F_3NNaO_4$ 376.0767, Found 376.0749.

Ethyl 4-((3-fluorophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3aj).



2-Trifluoromethyl enyne **2j** (43 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3aj** was obtained (42 mg, 65%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.57 (hexane/ethyl acetate = 10:1), [UV light].

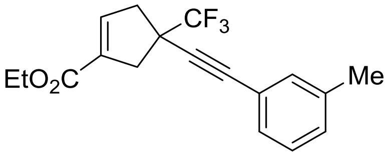
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 1H), 7.22-7.18 (m, 1H), 7.12 (m, 1H), 7.06-7.00 (m, 1H), 6.68 (d, *J* = 2.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.29-3.16 (m, 2H), 3.15-3.01 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 162.3 (d, *J* = 245 Hz), 138.6, 133.8, 129.9 (d, *J* = 7.5 Hz), 127.7 (d, *J* = 2.5 Hz), 126.3 (q, *J* = 278.8 Hz), 123.9 (d, *J* = 10 Hz), 118.7 (d, *J* = 22.5 Hz), 116.1 (d, *J* = 21.3 Hz), 88.3 (d, *J* = 2.5 Hz), 82.5 (d, *J* = 3.8 Hz), 60.7, 46.6 (q, *J* = 28.8 Hz), 43.0, 41.4, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.1, -112.8.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{14}F_4NaO_2$ 349.0822, Found 349.0812.

Ethyl 4-(m-tolylethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ak).



2-Trifluoromethyl enyne **2k** (42 mg, 0.2 mmol) was transformed according to a modified procedure A using allenoate **1a** (45 mg, 0.4 mmol) for 48 h. After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ak** was obtained (47 mg, 73%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.68 (hexane/ethyl acetate = 9:1), [UV light].

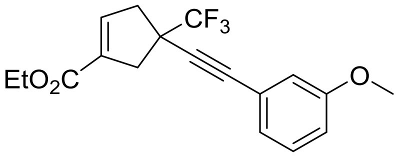
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.16 (m, 3H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.28-3.15 (m, 2H), 3.14-3.00 (m, 2H), 2.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 138.8, 138.0, 133.8, 132.4, 129.6, 128.9, 128.2, 126.5 (q, *J* = 278.8 Hz), 121.9, 87.0 (d, *J* = 2.5 Hz), 83.8, 60.7, 46.6 (q, *J* = 28.8 Hz), 43.1, 41.5, 21.1, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.1.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{17}F_3NaO_2$ 345.1073, Found 345.1063.

Ethyl 4-((3-methoxyphenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3al).



2-Trifluoromethyl enyne **2l** (45 mg, 0.2 mmol) was transformed according to a modified procedure A using allenoate **1a** (45 mg, 0.4 mmol) for 48 h. After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3al** was obtained (43 mg, 64%) as a colorless oil.

TLC (SiO_2) ***R*$_f$** = 0.5 (hexane/ethyl acetate = 10:1), [UV light].

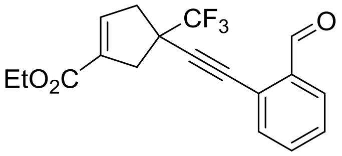
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.18 (m, 1H), 7.03-7.00 (m, 1H), 6.94 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.88 (m, 1H), 6.68 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.28-3.16 (m, 2H), 3.15-3.02 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 159.3, 138.8, 133.8, 129.4, 126.4 (q, *J* = 278.8 Hz), 124.4, 123.1, 116.6, 115.4, 87.1 (d, *J* = 2.5 Hz), 83.6, 60.7, 55.3, 46.6 (q, *J* = 30 Hz), 43.1, 41.5, 14.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.1.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{17}F_3NaO_3$ 361.1027, Found 361.1022.

Ethyl 4-((2-formylphenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3am).



2-Trifluoromethyl enyne **2m** (45 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 20:1), the desired cycloadduct **3am** was obtained (50 mg, 75%) as a pale yellow oil.

TLC (SiO_2) ***R*$_f$** = 0.44 (hexane/ethyl acetate = 9:1), [UV light].

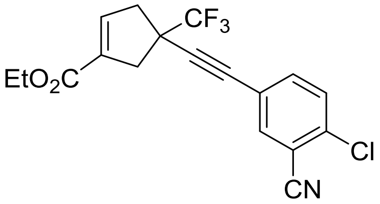
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (d, *J* = 0.6 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.58-7.54 (m, 2H), 7.49-7.45 (m, 1H), 6.71 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.32-3.20 (m, 2H), 3.20-3.06 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1, 163.6, 138.5, 136.3, 133.9, 133.7, 133.5, 129.2, 127.4, 126.2 (q, *J* = 278.8 Hz), 125.3, 94.3 (d, *J* = 2.5 Hz), 79.6, 60.8, 46.9 (q, *J* = 28.8 Hz), 42.8, 41.3, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{15}F_3NaO_3$ 359.0865, Found 359.0859.

Ethyl 4-((4-chloro-3-cyanophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3an).



2-Trifluoromethyl enyne **2n** (51 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3an** was obtained (46 mg, 62%) as a colorless oil.

TLC (SiO_2) ***R*$_f$** = 0.46 (hexane/ethyl acetate = 9:1), [UV light].

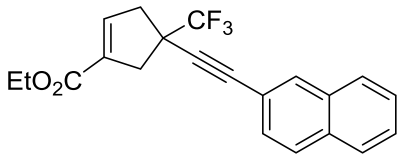
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.9 Hz, 1H), 7.57 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.28-3.16 (m, 2H), 3.14-3.02 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 138.5, 136.9, 136.9, 136.7, 133.8, 130.2, 126.1 (q, *J* = 278.8 Hz), 121.9, 115.0, 113.9, 90.8 (d, *J* = 3.8 Hz), 80.5, 60.8, 46.7 (q, *J* = 28.8 Hz), 42.8, 41.3, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.8.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{13}ClF_3NNaO_2$ 390.0479, Found 390.0473.

Ethyl 4-(naphthalen-2-ylethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ao).



2-Trifluoromethyl enyne **2o** (49 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ao** was obtained (54 mg, 75%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R}_f$ = 0.59 (hexane/ethyl acetate = 9:1), [UV light].

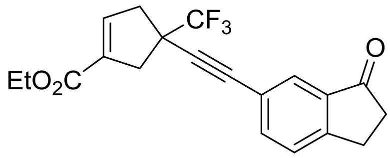
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.80-7.74 (m, 3H), 7.50-7.43 (m, 3H), 6.70 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.32-3.19 (m, 2H), 3.19-3.06 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 138.8, 133.9, 133.0, 132.9, 131.9, 128.3, 128.0, 127.8, 126.9, 126.6, 126.5 (q, *J* = 278.8 Hz), 119.4, 87.6 (d, *J* = 2.5 Hz), 84.0, 60.7, 46.7 (q, *J* = 28.8 Hz), 43.2, 41.6, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{21}H_{17}F_3NaO_2$ 381.1073, Found 381.1066.

Ethyl 4-((3-oxo-2,3-dihydro-1H-inden-5-yl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ap).



2-Trifluoromethyl enyne **2p** (50 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 8:1), the desired cycloadduct **3ap** was obtained (37 mg, 51%) as a pale yellow oil.

TLC (SiO_2) $\boldsymbol{R}_f$ = 0.17 (hexane/ethyl acetate = 10:1), [UV light].

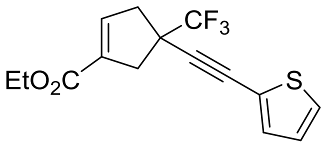
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.29-3.04 (m, 6H), 2.74-2.67 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 163.7, 154.8, 138.6, 136.9, 133.8, 130.9, 130.0, 128.3, 126.2 (q, *J* = 278.8 Hz), 123.5, 90.6 (d, *J* = 2.5 Hz), 83.2, 60.7, 46.7 (q, *J* = 28.8 Hz), 42.9, 41.4, 36.3, 25.5, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{20}H_{17}F_3NaO_3$ 385.1022, Found 385.1012.

Ethyl 4-(thiophen-2-ylethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3aq).



2-Trifluoromethyl enyne **2q** (40 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 30:1), the desired cycloadduct **3aq** was obtained (44 mg, 70%) as a pale yellow oil.

TLC (SiO_2) ***R***$_f$ = 0.72 (hexane/ethyl acetate = 9:1), [UV light].

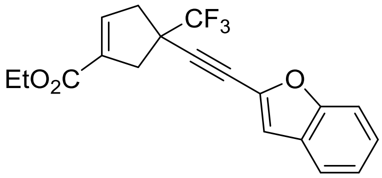
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.21 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.67 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.28-3.15 (m, 2H), 3.15-3.02 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 163.8, 138.7, 133.8, 132.7, 127.6, 126.9, 126.3 (q, *J* = 278.8 Hz), 121.9, 91.0 (d, *J* = 3.8 Hz), 77.1, 60.7, 46.8 (q, *J* = 28.8 Hz), 42.9, 41.4, 14.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{13}F_3NaO_2S$ 337.0481, Found 337.0472.

Ethyl 4-(benzofuran-2-ylethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3ar).



2-Trifluoromethyl enyne **2r** (47 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ar** was obtained (45 mg, 65%) as a colorless oil.

TLC (SiO_2) ***R***$_f$ = 0.54 (hexane/ethyl acetate = 10:1), [UV light].

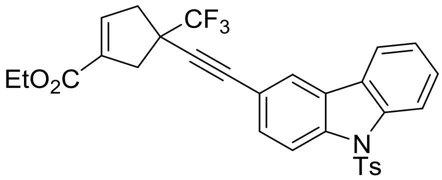
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.56-7.53 (m, 1H), 7.44 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.33 (m, 1H), 7.26-7.22 (m, 1H), 6.96 (d, *J* = 0.9 Hz, 1H), 6.69 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.31-3.07 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 163.6, 154.8, 138.5, 137.5, 133.8, 127.3, 126.1 (q, *J* = 278.8 Hz), 125.9, 123.4, 121.4, 112.4, 111.3, 93.2 (d, *J* = 2.5 Hz), 74.5, 60.8, 46.9 (q, *J* = 30 Hz), 42.8, 41.2, 14.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{15}F_3NaO_3$ 371.0871, Found 371.0866.

Ethyl 4-((9-tosyl-9H-carbazol-3-yl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3as).



2-Trifluoromethyl enyne **2s** (88 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate 20:1), the desired cycloadduct **3at** was obtained (88 mg, 80%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.43 (hexane/ethyl acetate = 9:1), [UV light].

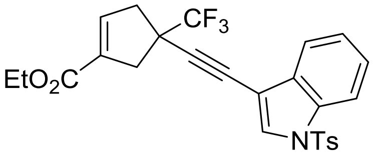
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.33–8.25 (m, 2H), 7.97 (d, *J* = 1.1 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.69-7.63 (m, 2H), 7.56-7.47 (m, 2H), 7.39-7.34 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.71 (s, 1H), 4.26-4.21 (m, 2H), 3.31-3.05 (m, 4H), 2.25 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 163.8, 145.2, 138.8, 138.2, 134.7, 133.9, 130.9, 129.7, 127.9, 126.5, 126.5, 126.4 (q, *J* = 278.8 Hz), 125.6, 124.2, 123.7, 120.2, 117.6, 115.2, 115.1, 87.2, 83.5, 60.7, 46.7 (q, *J* = 28.8 Hz), 43.1, 41.6, 21.5, 14.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{30}H_{24}F_3NNaO_4S$ 574.1270, Found 574.1276.

Ethyl 4-((1-tosyl-1H-indol-3-yl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (3at).



2-Trifluoromethyl enyne **2t** (78 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1a** (45 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 20:1 to 10:1), the desired cycloadduct **3as** was obtained (66 mg, 66%) as a pale yellow oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.36 (hexane/ethyl acetate = 9:1), [UV light].

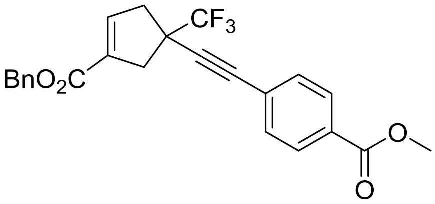
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.79-7.72 (m, 3H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.38-7.32 (m, 1H), 7.30-7.26 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 1.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.31-3.05 (m, 4H), 2.33 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 163.8, 145.4, 138.7, 134.9, 134.1, 133.9, 130.7, 130.0, 129.3, 127.0, 126.4 (q, *J* = 278.8 Hz), 125.6, 123.8, 120.3, 113.6, 104.0, 91.8 (d, *J* = 2.5 Hz), 75.0, 60.7, 46.9 (q, *J* = 28.8 Hz), 43.1, 41.6, 21.6, 14.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{22}F_3NNaO_4S$ 524.1114, Found 524.1107.

Methyl 4-((3-((benzyloxy)carbonyl)-1-(trifluoromethyl)cyclopent-3-en-1-yl)ethynyl)benzoate (3ba).



2-Trifluoromethyl enyne **2a** (51 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1b** (70 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ba** was obtained (78 mg, 91%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.48 (hexane/ethyl acetate = 9:1), [UV light].

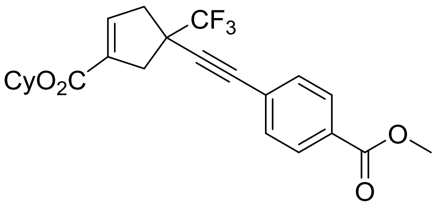
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.49-7.46 (m, 2H), 7.39-7.34 (m, 5H), 6.74 (s, 1H), 5.21 (s, 2H), 3.91 (s, 3H), 3.31-3.03 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 163.5, 139.4, 135.7, 133.5, 131.8, 130.1, 129.5, 128.6, 128.4, 128.3, 126.7, 126.3 (q, *J* = 278.8 Hz), 90.1 (d, *J* = 2.5 Hz), 83.0, 66.5, 52.3, 46.7 (q, *J* = 28.8 Hz), 43.0, 41.4.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{19}F_3NaO_4$ 451.1128, Found 451.1119.

Methyl 4-((3-((cyclohexyloxy)carbonyl)-1-(trifluoromethyl)cyclopent-3-en-1-yl)ethynyl)benzoate (3ca).



2-Trifluoromethyl enyne **2a** (51 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1c** (66 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3ca** was obtained (78 mg, 93%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R}_\mathbf{f}$ = 0.57 (hexane/ethyl acetate = 9:1), [UV light].

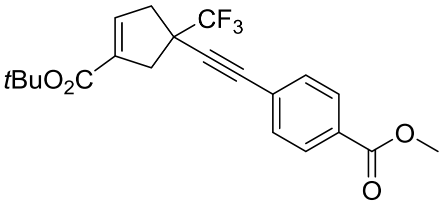
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 2.1 Hz, 1H), 4.91-4.82 (m, 1H), 3.91 (s, 3H), 3.31-3.03 (m, 4H), 1.91-1.71 (m, 4H), 1.55-1.27 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 163.1, 138.3, 134.3, 131.8, 130.0, 129.4, 126.7, 126.3 (q, *J* = 278.8 Hz), 90.3 (d, *J* = 2.5 Hz), 82.0, 72.9, 52.2, 46.6 (q, *J* = 30 Hz), 42.9, 41.4, 31.6, 25.4, 23.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{23}F_3NaO_4$ 443.1441, Found 443.1426.

Methyl 4-((3-(tert-butoxycarbonyl)-1-(trifluoromethyl)cyclopent-3-en-1-yl)ethynyl)benzoate (3da).



2-Trifluoromethyl enyne **2a** (51 mg, 0.2 mmol) was transformed according to the general procedure A using allenoate **1d** (56 mg, 0.4 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 30:1 to 20:1), the desired cycloadduct **3da** was obtained (68 mg, 86%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R}_\mathbf{f}$ = 0.60 (hexane/ethyl acetate = 9:1), [UV light].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.50 (s, 1H), 3.83 (s, 3H), 3.16-3.05 (m, 2H), 3.05-2.92 (m, 2H), 1.42 (s, 9H).

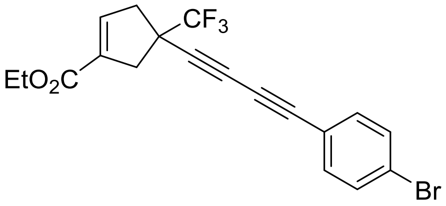
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 163.1, 137.6, 135.3, 131.8, 130.0, 129.4, 126.8, 126.3 (q, *J* = 278.8 Hz), 90.4 (d, *J* = 2.5 Hz), 82.8, 81.1, 52.2, 46.6 (q, *J* = 28.8 Hz), 42.9, 41.5, 28.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{21}H_{21}F_3NaO_4$ 417.1284, Found 417.1268.

General Procedure B: Phosphine-Catalyzed [3+2] Cycloaddition of Trifluoromethyl Enediynes with Allenoates. Under nitrogen atmosphere, to a stirred solution of trifluoromethyl enediyne **5** (0.1 mmol, 1.0 equiv) and PPh_3 (0.01 mmol, 0.1 equiv) in 1 mL of EtOAc was added allenoate **1** (0.2 mmol, 2.0 equiv), and the resulting mixture was stirred room temperature for 48 h. After the reaction was complete, the mixture was concentrated *in vacuo*, and the residue was directly subjected to column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the corresponding product **6**.

Ethyl 4-((4-bromophenyl)buta-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (6a).



Trifluoromethyl enediyne **5a** (30 mg, 0.1 mmol) was transformed according to the general procedure B using allenoate **1a** (22 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 40:1), the desired cycloadduct **6a** was obtained (31 mg, 75%) as a pale yellow oily liquid.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.70 (hexane/ethyl acetate = 10:1), [UV light].

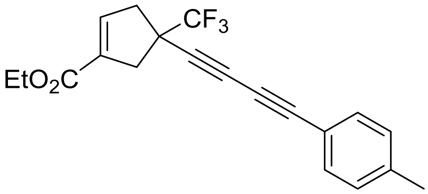
^{1}H NMR (500 MHz, D6-Acetone) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.58 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.13-3.05 (m, 2H), 3.01-2.95 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, D6-Acetone) δ 162.9, 138.5, 134.3, 133.3, 132.0, 126.1 (q, *J* = 273.8 Hz), 124.0, 119.8, 80.9, 77.3, 73.4, 68.0, 60.3, 47.0 (q, *J* = 28.8 Hz), 42.4, 40.9, 13.6.

^{19}F NMR (470 MHz, D6-Acetone) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{14}BrF_3O_2Na$ 433.0021, Found 433.0017.

Ethyl 4-(p-tolylbuta-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (6b).



Trifluoromethyl enediyne **5b** (23 mg, 0.1 mmol) was transformed according to the general procedure B using allenoate **1a** (22 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 40:1), the desired cycloadduct **6b** was obtained (32 mg, 92%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.70 (hexane/ethyl acetate = 10:1), [UV light].

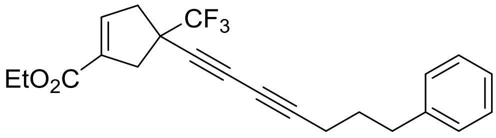
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.58 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.12-2.95 (m, 4H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 140.0, 138.5, 133.8, 132.6, 129.3, 126.0 (q, *J* = 278.8 Hz), 118.0, 79.9, 78.8, 72.4, 68.9, 60.8, 47.1 (q, *J* = 28.8 Hz), 42.8, 41.2, 21.6, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.5.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{20}H_{17}F_3NaO_2$ 369.1073, Found 369.1071.

Ethyl 4-(7-phenylhepta-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (6c).



Trifluoromethyl enediyne **5c** (26 mg, 0.1 mmol) was transformed according to the general procedure B using allenoate **1a** (22 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 40:1), the desired cycloadduct **6c** was obtained (29 mg, 78%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R}_f$ = 0.68 (hexane/ethyl acetate = 10:1), [UV light].

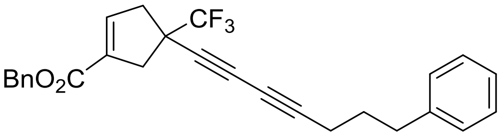
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.23-7.19 (m, 2H), 7.14-7.08 (m, 3H), 6.56 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.12-2.87 (m, 4H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.20 (t, *J* = 7.0 Hz, 2H), 1.82-1.74 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 162.6, 140.0, 137.5, 132.8, 127.5, 127.4, 125.1, 125.0 (q, *J* = 278.8 Hz), 80.1, 72.58, 68.0, 63.7, 59.7, 45.7 (q, *J* = 28.8 Hz), 41.7, 40.2, 33.7, 28.6, 17.6, 13.2.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{21}F_3NaO_2$ 397.1386, Found 397.1391.

Benzyl 4-(7-phenylhepta-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (6d).



Trifluoromethyl enediyne **5c** (26 mg, 0.1 mmol) was transformed according to the general procedure B using allenoate **1b** (35 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 40:1), the desired cycloadduct **6d** was obtained (32 mg, 73%) as a colorless oil.

TLC (SiO_2) $\boldsymbol{R}_f$ = 0.66 (hexane/ethyl acetate = 10:1), [UV light].

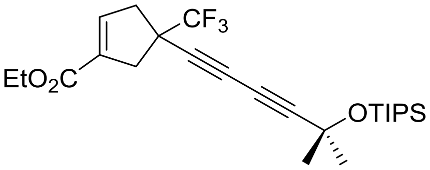
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.24 (m, 5H), 7.23-7.18 (m, 2H), 7.14-7.08 (m, 3H), 6.61 (s, 1H), 5.12 (s, 2H), 3.13-2.87 (m, 4H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.20 (t, *J* = 7.0 Hz, 2H), 1.81-1.73 (m, 2H).

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 163.4, 141.1, 139.3, 135.7, 133.4, 128.6, 128.5, 128.4, 128.4, 128.3, 126.1, 126.0 (q, *J* = 278.8 Hz), 81.2, 73.5, 69.1, 66.5, 64.7, 46.7 (q, *J* = 28.8 Hz), 42.8, 41.2, 34.7, 29.6, 18.6.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{27}H_{23}F_3NaO_2$ 459.1542, Found 459.1543.

Ethyl 4-(5-methyl-5-((triisopropylsilyl)oxy)hexa-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (**6e**).



Trifluoromethyl enediyne **5e** (36 mg, 0.1 mmol) was transformed according to the general procedure B using allenoate **1a** (22 mg, 0.2 mmol). After purification over silica gel (petroleum ether), the desired cycloadduct **6e** was obtained (36 mg, 77%) as a colorless oil.

TLC (SiO_2) ***R*** R_f = 0.31 (hexane), [UV light].

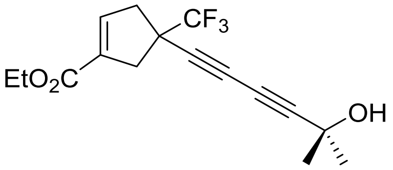
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.12-2.90 (m, 4H), 1.45 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.05-0.98 (m, 21H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 138.4, 133.8, 126.0 (q, *J* = 278.8 Hz), 84.9, 68.2, 66.5, 66.5, 60.7, 46.7 (q, *J* = 28.8 Hz), 42.7, 41.2, 32.8, 18.2, 14.2, 13.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.9.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{37}F_3NaO_3Si$ 493.2356, Found 493.2367.

Ethyl 4-(5-hydroxy-5-methylhexa-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (6f).



Trifluoromethyl enediyne **5f** (20 mg, 0.1 mmol) was transformed according to the general procedure B using allenoate **1a** (22 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 9:1 to 6:1), the desired cycloadduct **6f** was obtained (26 mg, 84%) as a pale yellow oily liquid.

TLC (SiO_2) R_f = 0.26 (hexane/ethyl acetate = 9:1), [UV light].

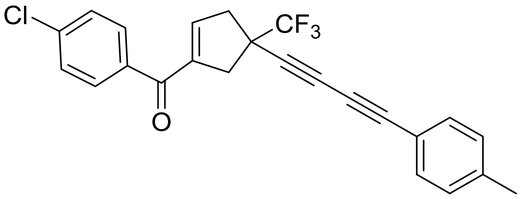
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.13-2.88 (m, 4H), 2.15 (s, 1H), 1.46 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 138.4, 133.7, 125.9 (q, *J* = 278.8 Hz), 83.8, 77.5 (q, *J* = 2.5 Hz), 68.0, 66.1, 65.5, 60.8, 46.8 (q, *J* = 28.8 Hz), 42.6, 41.1, 30.9, 14.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ -75.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{17}F_3NaO_3$ 337.1022, Found 337.1028.

(4-Chlorophenyl)(4-(*p*-tolylbuta-1,3-diyn-1-yl)-4-(trifluoromethyl)cyclopent-1-en-1-yl)methanone (6h).



p-Tolyl-substituted CF_3-enediyne **5b** (24 mg, 0.1 mmol) was transformed according to the general procedure B using α-trimethylsilyl-substituted aryl allenone **1e** (50 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 100:1 to 50:1), the desired α-cycloadduct **6h** was obtained (20 mg, 48%) as a yellowish oil.

TLC (SiO_2) R_f = 0.52 (hexane/ethyl acetate = 20:1), [UV light].

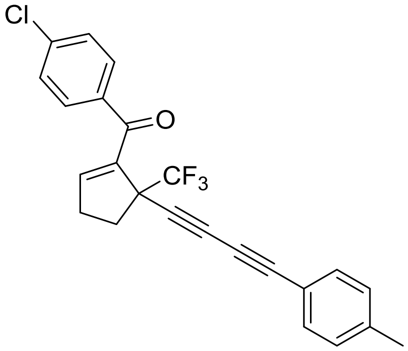
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 2H), 7.46-7.42 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.40 (s, 1H), 3.42-3.11 (m, 4H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 140.9, 140.6, 140.1, 138.9, 136.1, 132.6, 130.3, 129.3, 128.8, 126.0 (q, *J* = 279 Hz), 117.9, 79.7 (q, *J* = 3 Hz), 78.9, 72.4, 69.0, 46.5 (q, *J* = 29 Hz), 43.5, 41.7, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.3.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{16}ClF_3NaO$ 435.0734, Found 435.0736.

(4-Chlorophenyl)(5-(*p*-tolylbuta-1,3-diyn-1-yl)-5-(trifluoromethyl)cyclopent-1-en-1-yl)methanone (6i).



p-Tolyl-substituted CF_3-enediyne **5b** (24 mg, 0.1 mmol) was transformed according to the general procedure B using α-trimethylsilyl-substituted aryl allenone **1e** (50 mg, 0.2 mmol). After purification over silica gel (petroleum ether/ethyl acetate from 100:1 to 50:1), the desired γ-cycloadduct **6i** was obtained (13 mg, 32%) as a yellowish oil.

TLC (SiO_2) $\boldsymbol{R_f}$ = 0.37 (hexane/ethyl acetate = 20:1), [UV light].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.70 (m, 2H), 7.46-7.42 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.67 (t, *J* = 2.4 Hz, 1H), 2.80-2.51 (m, 4H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 149.8, 139.8, 139.3, 138.8, 136.4, 132.6, 130.7, 129.2, 128.8, 125.6 (q, *J* = 280 Hz), 118.2, 79.2, 72.8, 70.7, 54.9 (q, *J* = 30 Hz), 35.57, 31.53, 21.64.

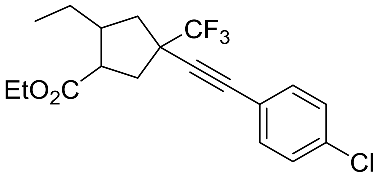
^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{16}ClF_3NaO$ 435.0734, Found 435.0734.

Procedure for Gram-Scale Synthesis of Cyclopentene 3ae. Under nitrogen atmosphere, to a stirred solution of 2-trifluoromethyl enyne **2e** (920 mg, 4 mmol, 1.0 equiv) and PPh_3 (105 mg, 0.4 mmol, 0.1 equiv) in 20 mL of EtOAc was added allenoate **1a** (672 mg, 6 mmol, 1.5 equiv) in two portions (2×3 mmol) every 5 hours, and the resulting mixture was stirred at room temperature. After the full consumption of **2e** (monitored by TLC), the mixture was concentrated *in vacuo*, and the residue was directly subjected to column chromatography on silica gel using petroleum ether/EtOAc (20:1) as eluent to afford the corresponding product **3ae** (1.18 g, 86 %) as a colorless oil.

Procedure for Preparing Compound 7. Under nitrogen atmosphere, to the suspension of CuBr•SMe_2 (4 mg, 0.04 mmol, 0.1 equiv) in THF (1 mL) at -78 °C was added HMPA (72 mg, 0.4 mmol, 2.0 equiv), EtMgBr (1.0 M in THF, 0.6 mL, 0.6 mmol, 3.0 equiv) in sequence. After 5 min, a solution of cyclopentene **3ae** (69 mg, 0.2 mmol, 1.0 equiv) and TMSCl (43 mg, 0.4 mmol, 2.0 equiv) in 1 mL of THF was added dropwise. After stirring for 4 h at the same temperature, saturated aqueous NH_4Cl was added, and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and filtered. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford the Michael addition product **7** (46 mg, 62% yield, 2:1 dr) as a colorless oil.

Ethyl 4-((4-chlorophenyl)ethynyl)-2-ethyl-4-(trifluoromethyl)cyclopentane-1-carboxylate (7).



TLC (SiO_2) ***R*** R_f = 0.59 (hexane/ethyl acetate = 10:1), [UV light].

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.30-7.26 (m, 2H), 4.20-4.13 (m, 2H), 3.07-3.02 (m, 0.3H), 2.82-2.77 (m, 0.7H), 2.56-2.24 (m, 4H), 2.18 (dd, *J* = 13.3, 7.1 Hz, 0.3H), 1.84 (dd, *J* = 13.8, 8.3 Hz, 0.7H), 2.20-2.16 (dd, 0.3H), 1.74-1.66 (m, 0.7H), 1.49-1.39 (m, 1.3H), 1.30-1.24 (m, 3H), 0.99-0.90 (m, 3H).

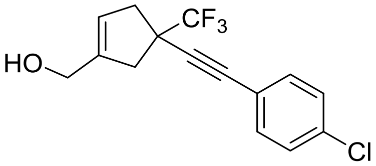
^{13}**C NMR** (125 MHz, $CDCl_3$) δ 173.8, (173.1), 134.7, (134.4), 133.0, 128.6, (128.6), 126.3 (q, *J* = 278.8 Hz), (121.2), 120.78, (89.6), 88.9, 83.0, (81.7), 60.7, (60.5), 49.6, (47.9), 47.2 (q, *J* = 28.8 Hz), (44.7), 44.6, 40.3, (40.1), 39.2, (37.4), 27.7, (23.2), (14.3), 14.2, (12.5), 12.1.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -75.0 (-75.4).

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{19}H_{20}ClF_3NaO_2$ 395.0996, Found 395.0990.

Procedure for Preparing Compound 8. Under nitrogen atmosphere, to a stirred solution of cyclopentene **3ae** (138 mg, 0.4 mmol, 1.0 equiv) in THF (4 mL) at -78 °C was added slowly DIBAL-H (1.5 M in THF, 0.8 mL, 1.2 mmol, 3.0 equiv), and the resulting mixture was stirred overnight at -78 °C. Then, a small spoon of silica gel was added to quench the reaction. The slurry was concentrated up to dryness by rotary evaporation and directly subjected to column chromatography on silica gel using petroleum ether/EtOAc (6:1 to 1:1) as eluent to afford the reduction product **8** (107 mg, 89 %) as colorless syrupy oil.

(4-((4-Chlorophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-en-1-yl)methanol (8).



TLC (SiO_2) R_f = 0.30 (hexane/ethyl acetate = 5:1), [UV light].

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.32 (m, 2H), 7.30-7.27 (m, 2H), 5.59 (s, 1H), 4.21 (s, 2H), 3.07-2.99 (m, 2H), 2.88 (t, *J* = 16.8 Hz, 2H), 1.60 (s, 1H).

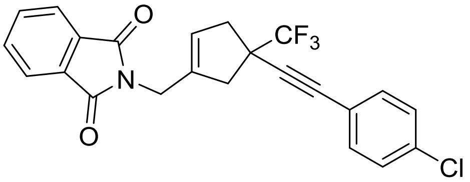
^{13}**C NMR** (125 MHz, $CDCl_3$) δ 141.2, 134.6, 133.1, 128.6, 126.7 (q, *J* = 278.8 Hz), 122.2, 120.9, 89.4 (q, *J* = 3.8 Hz), 81.9, 61.2, 46.7 (q, *J* = 30 Hz), 42.5, 42.4.

^{19}**F NMR** (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{12}ClF_3NaO$ 323.0421, Found 323.0429.

Procedure for Preparing Compound 9. Under nitrogen atmosphere, to a stirred solution of allylic alcohol **8** (30 mg, 0.1 mmol, 1.0 equiv), phthalimide (19 mg, 0.13 mmol, 1.3 equiv), and PPh_3 (34 mg, 0.13 mmol, 1.3 equiv) in 2 mL of THF at room temperature was added diethyl azodicarboxylate (DEAD) (20 μL, 0.13 mmol, 1.3 equiv) dropwise. The resulting mixture was stirred at room temperature overnight. Then, 5 mL of H_2O was added, and the aqueous phase was extracted with EtOAc (3×5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and filtered. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to give the product **9** (38 mg, 88 %) as white powder.

2-((4-((4-Chlorophenyl)ethynyl)-4-(trifluoromethyl)cyclopent-1-en-1-yl)methyl)isoindoline-1,3-dione (9).



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.68-7.63 (m, 2H), 7.24-7.20 (m, 2H), 7.18-7.16 (m, 2H), 5.50 (s, 1H), 4.28 (s, 2H), 2.93-2.90 (m, 2H), 2.80-2.73 (m, 2H).

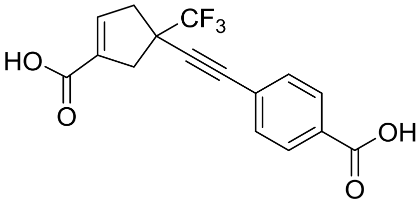
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 134.8, 133.5, 133.1, 132.0, 130.9, 127.5, 125.5 (q, *J* = 278.8 Hz), 123.8, 122.1, 119.8, 88.0 (q, *J* = 3.8 Hz), 81.0, 45.8 (q, *J* = 28.8 Hz), 42.3, 41.2, 36.3.

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.0.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{15}ClF_3NNaO_2$ 452.0636, Found 452.0640.

Procedure for Preparing Compound 10. A solution of **3ba** (224 mg, 0.5 mmol) in MeOH (0.3 mL) was added 20% NaOH solution (2.5 mL) The resulting mixture was then heated to 100 °C for 1 h. After being cooled to room temperature, 10 mL of H_2O was added and the mixture was washed with diethyl ether (2×5 mL). Then the aqueous layer was acidified with aqueous HCl (1 N) at 0 ^{o}C and extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered. Removal of the solvent gave the corresponding dicarboxylic acid **10** (154 mg, 95 %) as a white solid.

4-((3-Carboxy-1-(trifluoromethyl)cyclopent-3-en-1-yl)ethynyl)benzoic acid (10).



M.p. 196-197 ^{o}C

^{1}H NMR (500 MHz, D6-Acetone) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 6.75 (s, 1H), 3.31-3.14 (m, 4H).

^{13}C NMR (125 MHz, D6-Acetone) δ 166.0, 163.9, 139.0, 133.6, 131.8, 130.8, 129.7, 126.7 (q, *J* = 277.5 Hz), 126.4, 89.9, 82.81, 46.7 (q, *J* = 28.8 Hz), 42.8, 41.3.

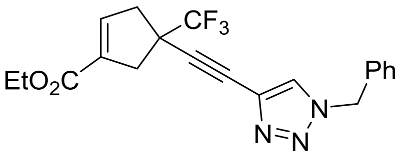
^{19}F NMR (470 MHz, D6-Acetone) δ -76.6.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{11}F_3NaO_4$ 347.0502, Found 347.0511.

Procedure for Preparing Compound 11. To a solution of **6f** (63 mg, 0.20 mmol, 1.0 equiv) in toluene (4 mL) was added grainy NaOH (18 mg, 0.44 mmol, 2.2 equiv) in one portion under a nitrogen atmosphere. After being stirred at 90 °C for 2 h, the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel eluting with ethyl acetate. Upon removal of solvent, the residue was subjected to column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as the eluent to afford the desired terminal alkyne as a colorless oil (40 mg, 78 %).

A Schlenk tube equipped with a magnetic stir bar was added CuI (15 mg, 0.078 mmol, 0.50 equiv) and purged with nitrogen. Then a solution of the resulting terminal alkyne (40 mg, 0.156 mmol, 1 equiv) in MeOH (2 mL) was added *via* syringe, followed by benzyl azide (42 mg, 0.312 mmol, 2 equiv). The mixture was allowed to stir at 80 °C in an oil bath. After 24 h, the solvent was removed *in vacuo*, and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (4:1) as the eluent to give product **11** as a colorless oil (44 mg, 73 %).

Ethyl 4-((1-benzyl-1H-1,2,3-triazol-4-yl)ethynyl)-4-(trifluoromethyl)cyclopent-1-ene-1-carboxylate (11).



TLC (SiO_2) ***R*****f** = 0.40 (hexane/ethyl acetate = 4:1), [UV light].

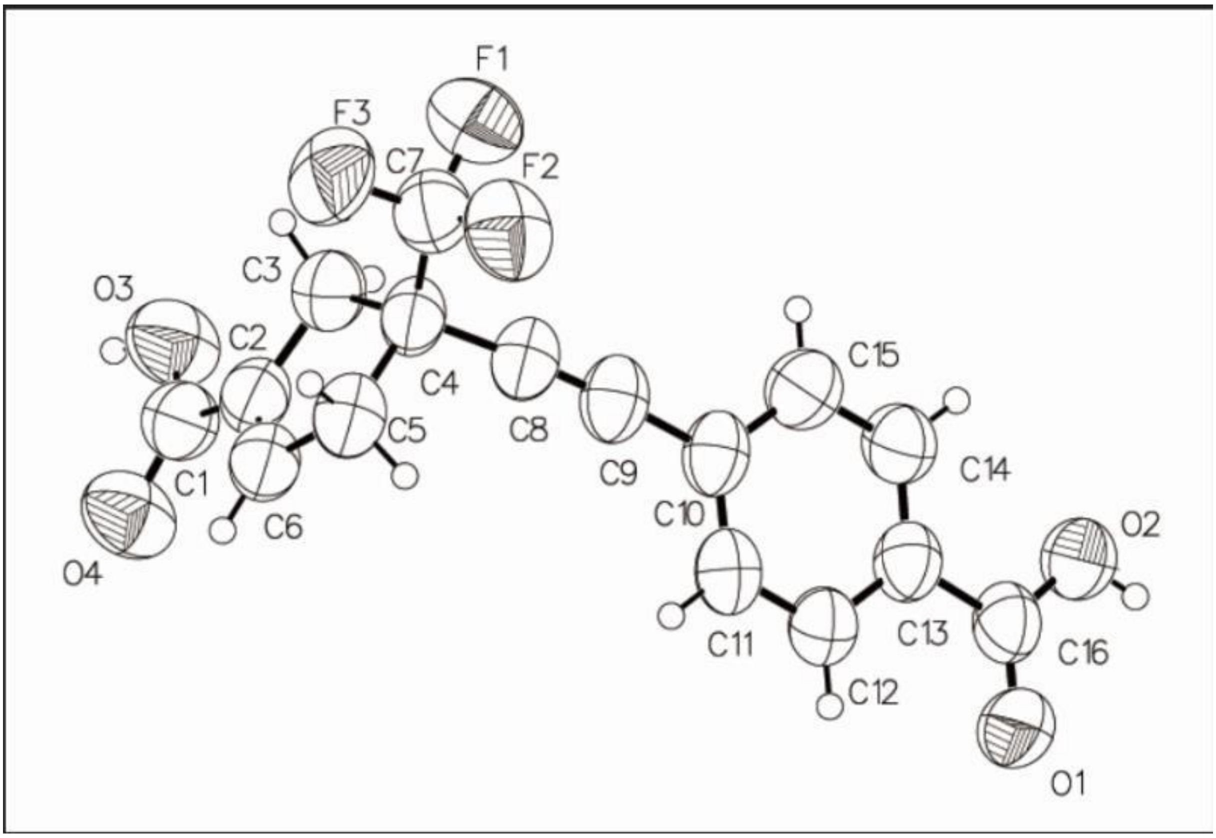
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.42-7.36 (m, 3H), 7.28-7.25 (m, 2H), 6.65 (s, 1H), 5.52 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.25-3.02 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 138.6, 133.9, 133.8, 130.4, 129.3, 129.1, 128.2, 126.4, 126.1 (q, *J* = 278 Hz), 90.9, 73.4, 60.7, 54.4, 46.7 (q, *J* = 30 Hz), 42.7, 41.2, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.7.

HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{20}H_{18}F_3N_3NaO_2$ 412.1243, Found 412.1242.

Crystal structure of 10.



A view of the molecular structure of compound **10** (thermal ellipsoids are shown with a 50% probability level). Single crystals of compound **10** suitable for the X-ray crystal structure analysis were obtained by the slow evaporation of a solution of compound **10** in EtOAc/Hexane/$CDCl_3$ at room temperature. Data intensity of **10** was collected using a Bruker 'Bruker APEX-II CCD' diffractometer at 100.01(10) K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXS structure solution program using direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. CCDC deposition number 2004999 (**10**).

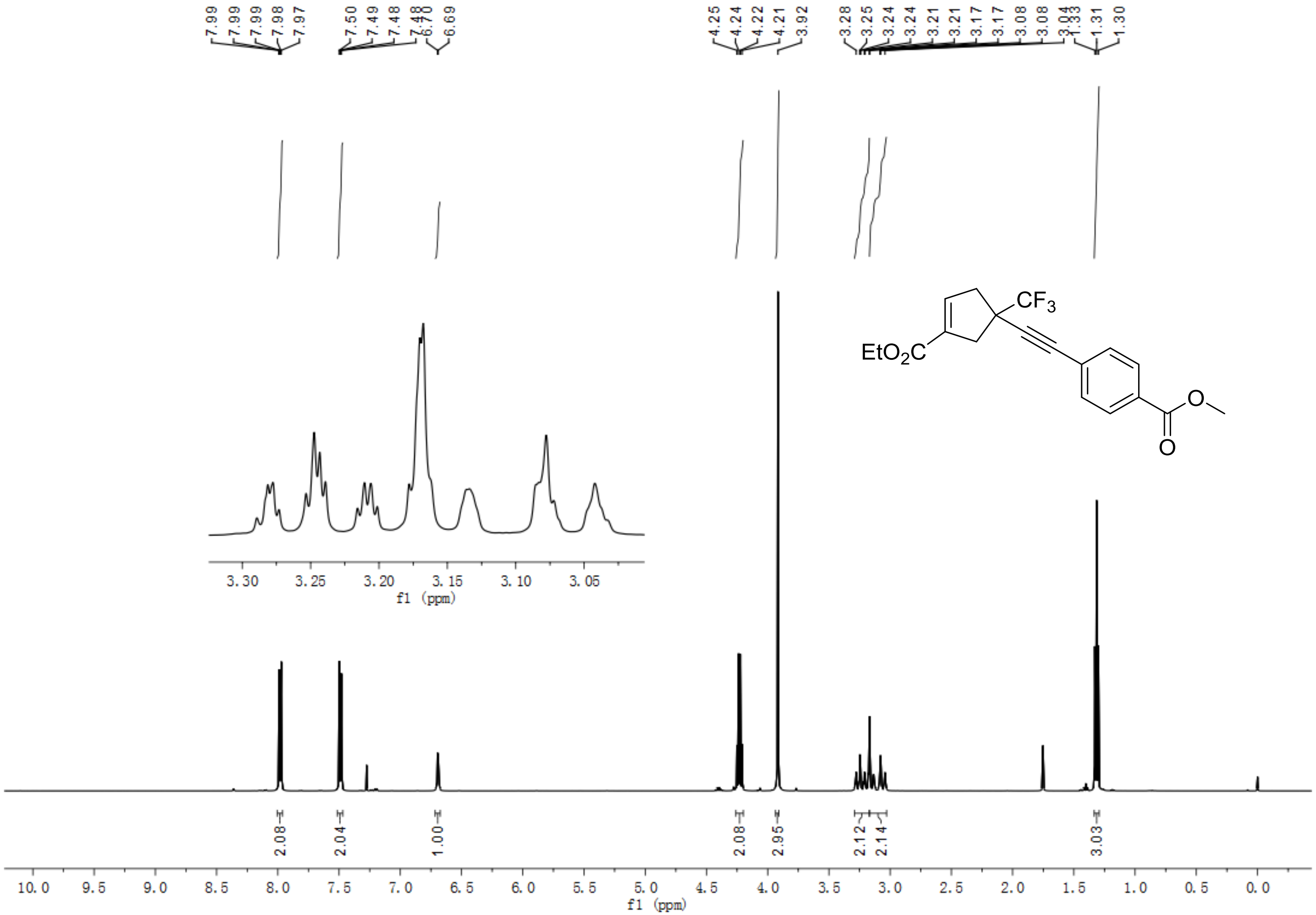
X-ray crystallographic data of 10.

Empirical formula	$C_{16}H_{11}F_3O_4$
Formula weight	324.25
Temperature/K	302.1(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.53494(10)
b/Å	17.8693(2)
c/Å	19.2521(2)
α/°	79.7570(10)

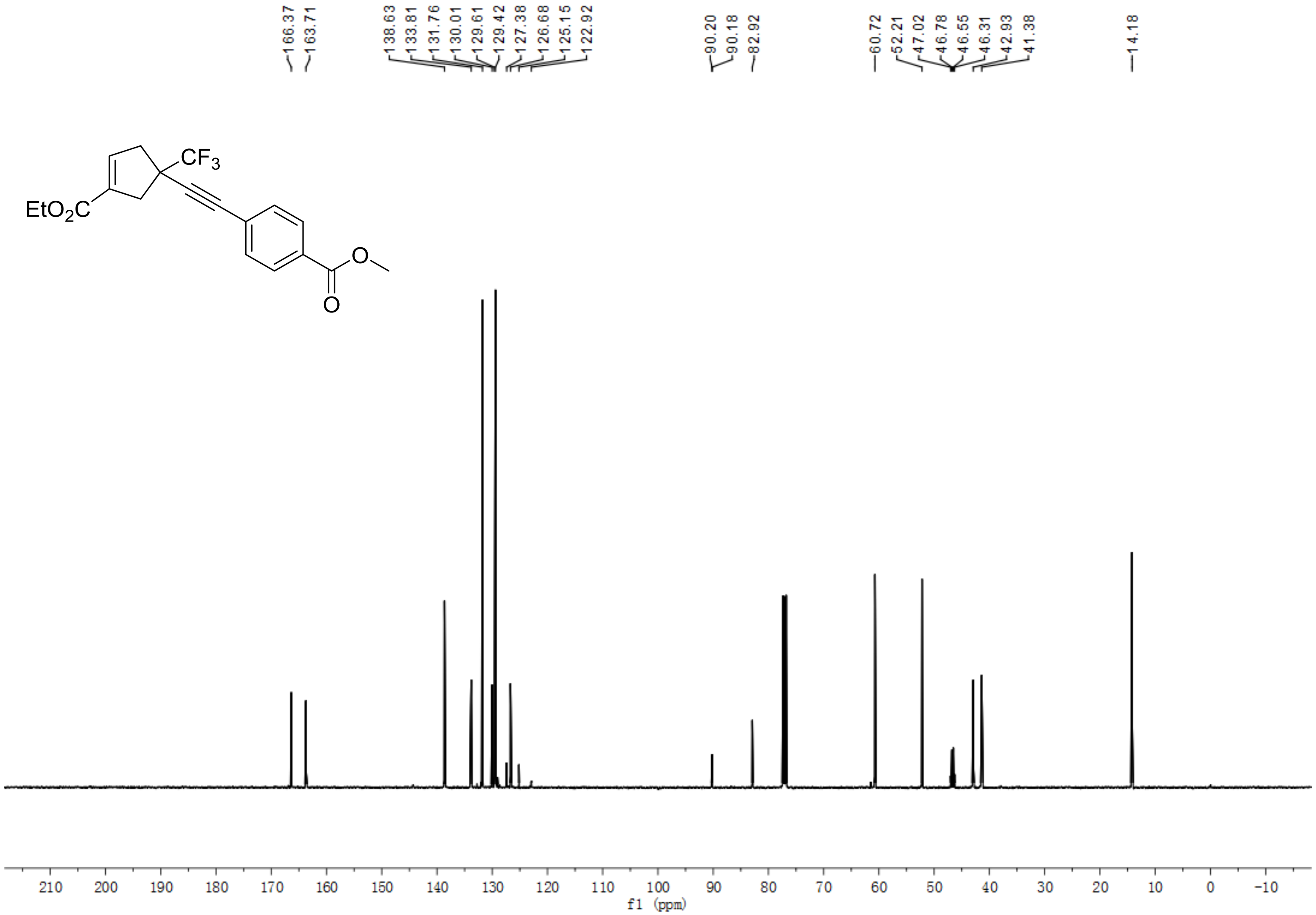
β/°	88.3822(11)
γ/°	82.9770(10)
Volume/Å^3	2195.69(5)
Z	4
ρ_{calc}g/cm^3	0.981
μ/mm^{-1}	0.757
F(000)	664.0
Crystal size/mm^3	0.31 × 0.201 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.664 to 153.95
Index ranges	$-7 \leq h \leq 8$, $-22 \leq k \leq 22$, $-23 \leq l \leq 24$
Reflections collected	26076
Independent reflections	9291 [R_{int} = 0.0495, R_{sigma} = 0.0541]
Data/restraints/parameters	9291/2/419
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0735, wR_2 = 0.2495
Final R indexes [all data]	R_1 = 0.0837, wR_2 = 0.2625
Largest diff. peak/hole / e Å^{-3}	0.38/-0.23

3. Copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR Spectra

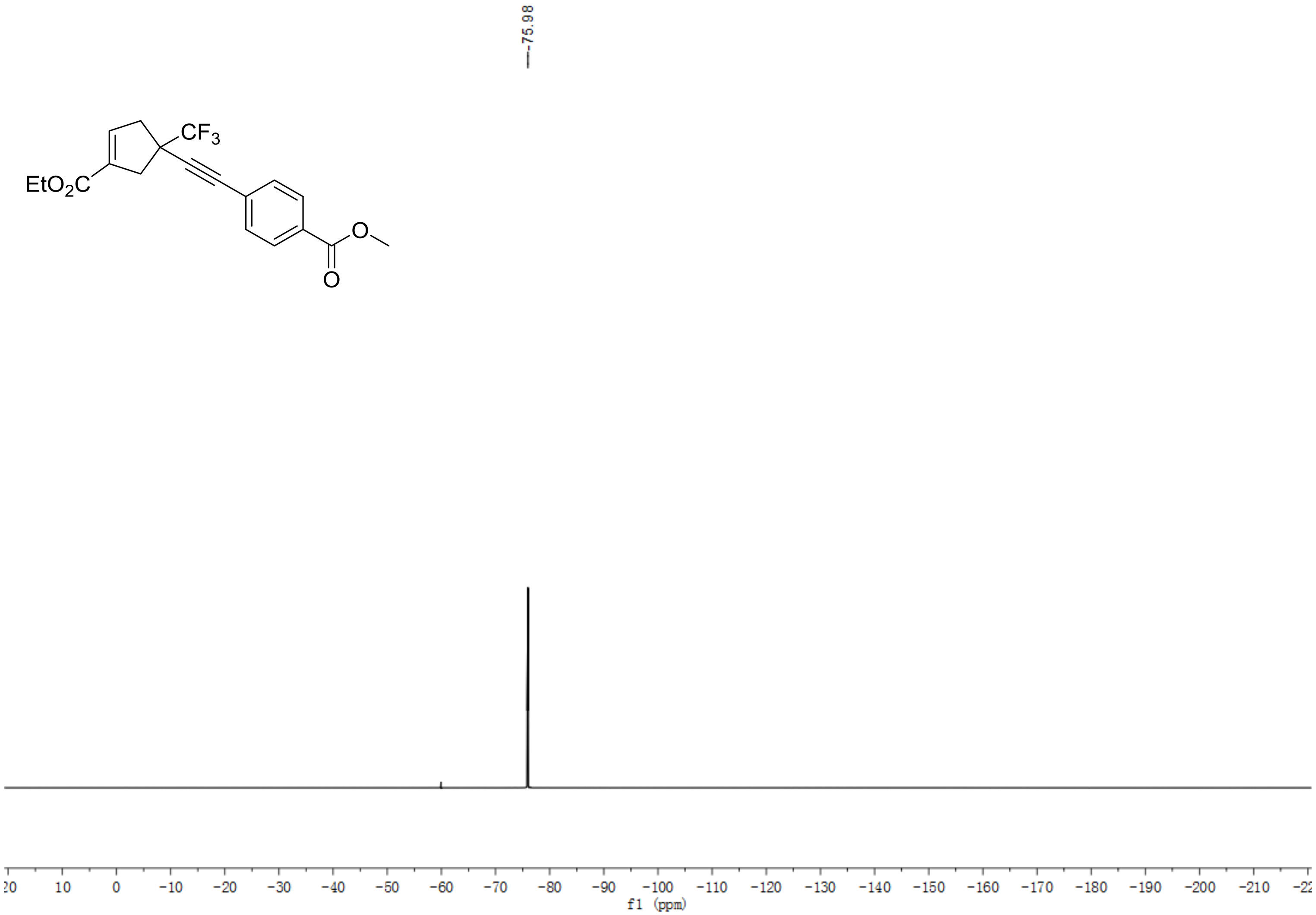
^{1}H NMR spectrum of product 3aa (500 MHz, $CDCl_3$)



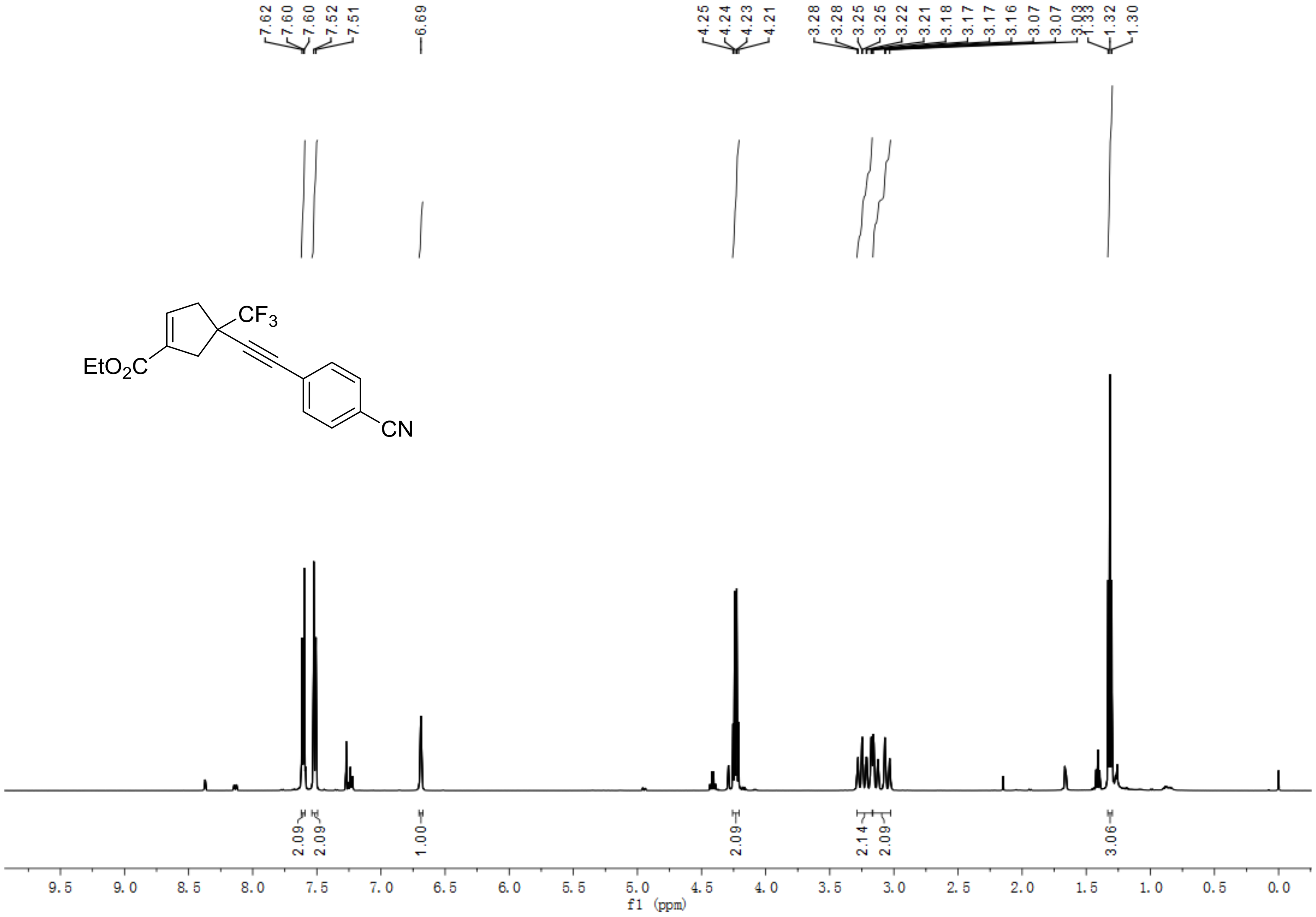
^{13}C NMR spectrum of product 3aa (125 MHz, $CDCl_3$)



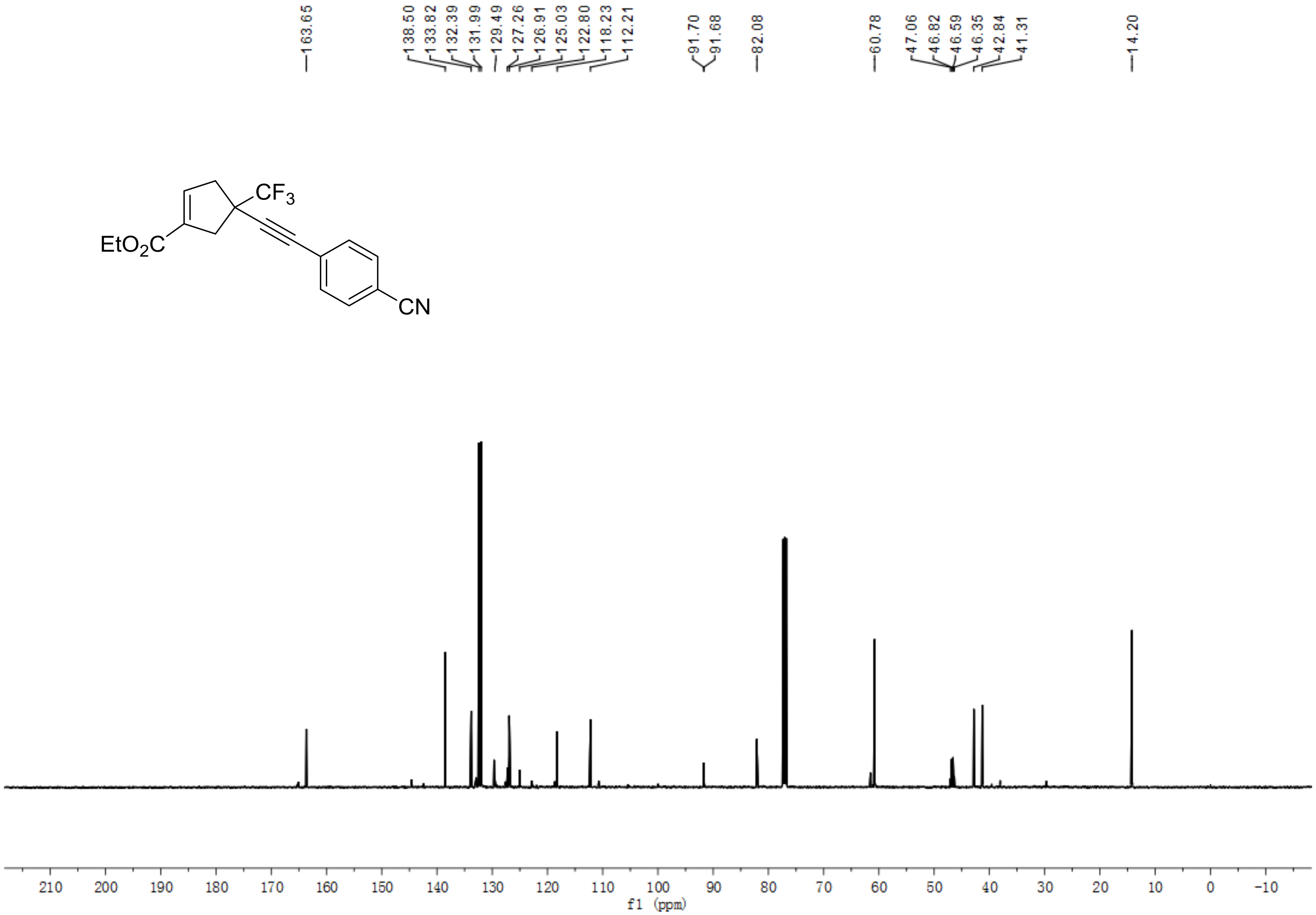
^{19}F NMR spectrum of product 3aa (470 MHz, $CDCl_3$)



^{1}H NMR spectrum of product 3ab (500 MHz, $CDCl_3$)

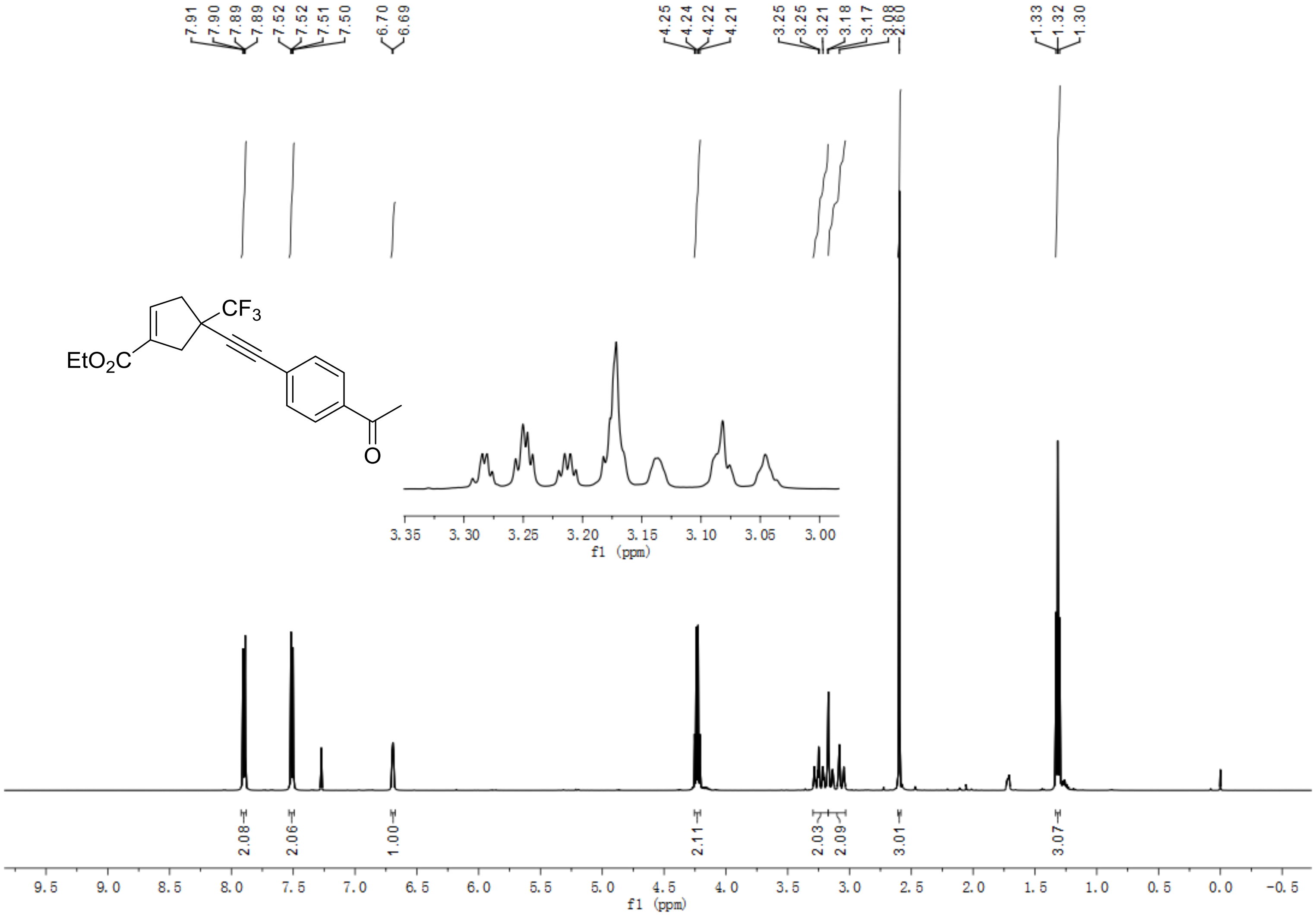


^{13}C NMR spectrum of product 3ab (125 MHz, $CDCl_3$)

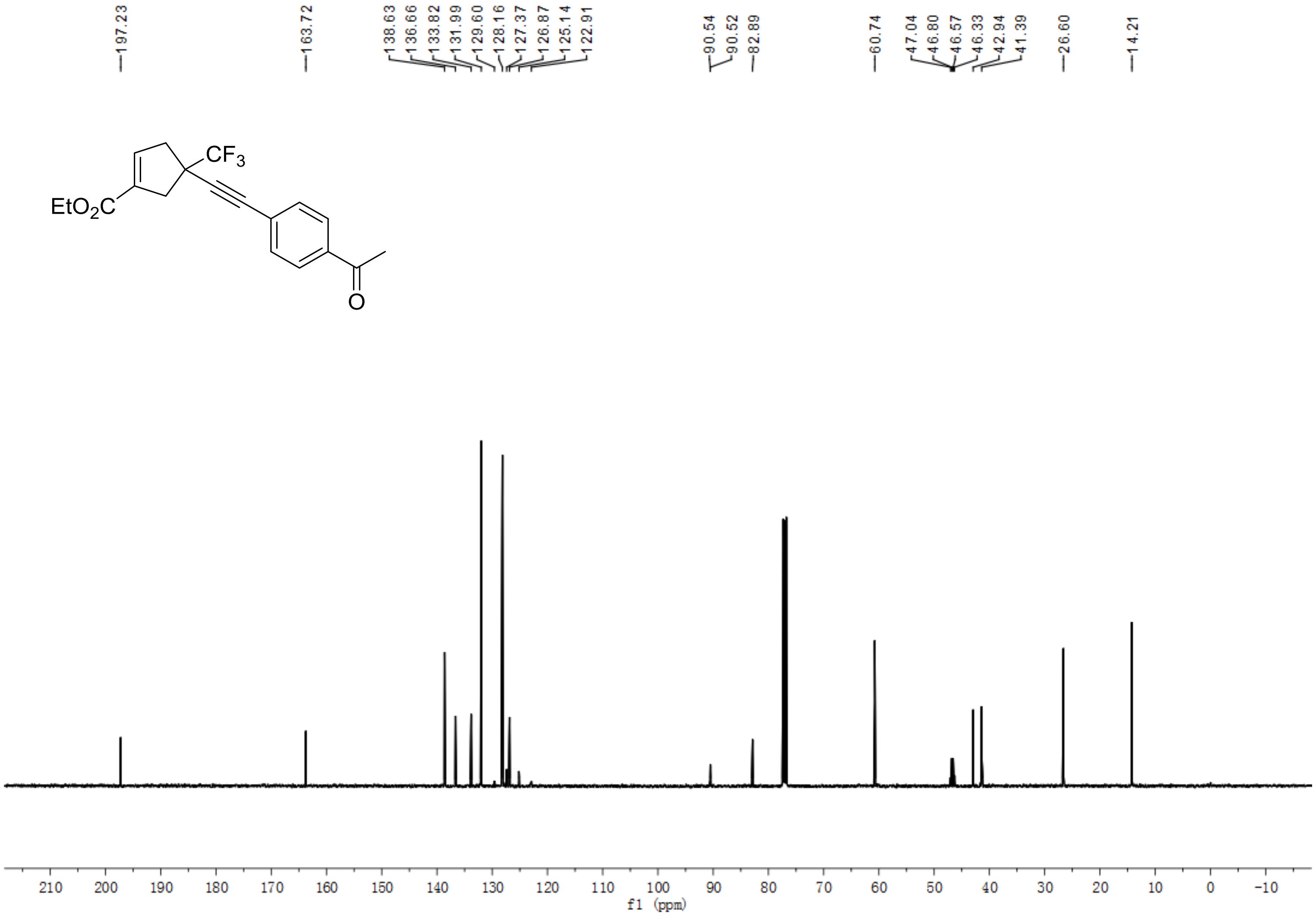


^{19}F NMR spectrum of product 3ab (470 MHz, CDCl$_3$)

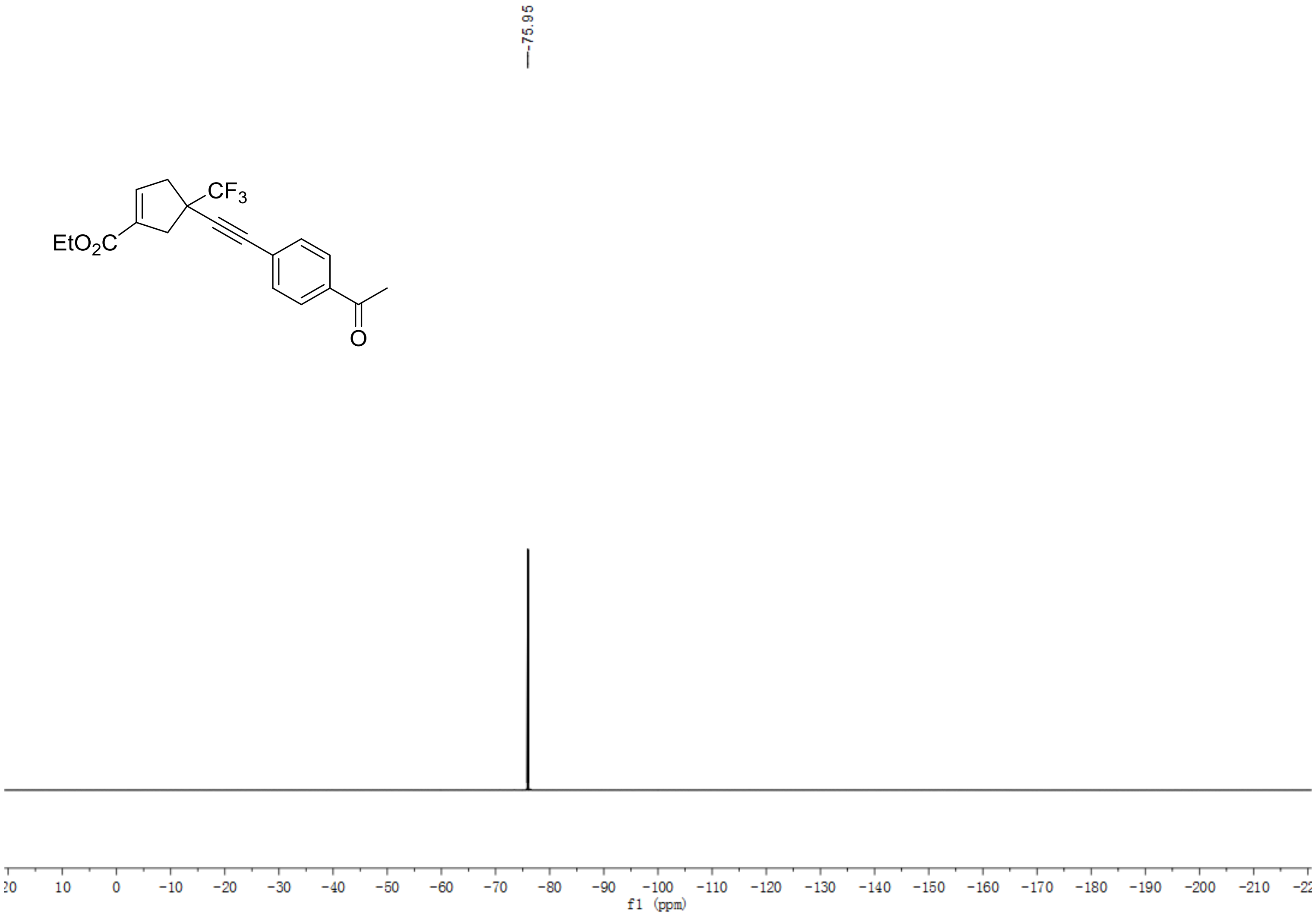
^{1}H NMR spectrum of product 3ac (500 MHz, $CDCl_3$)



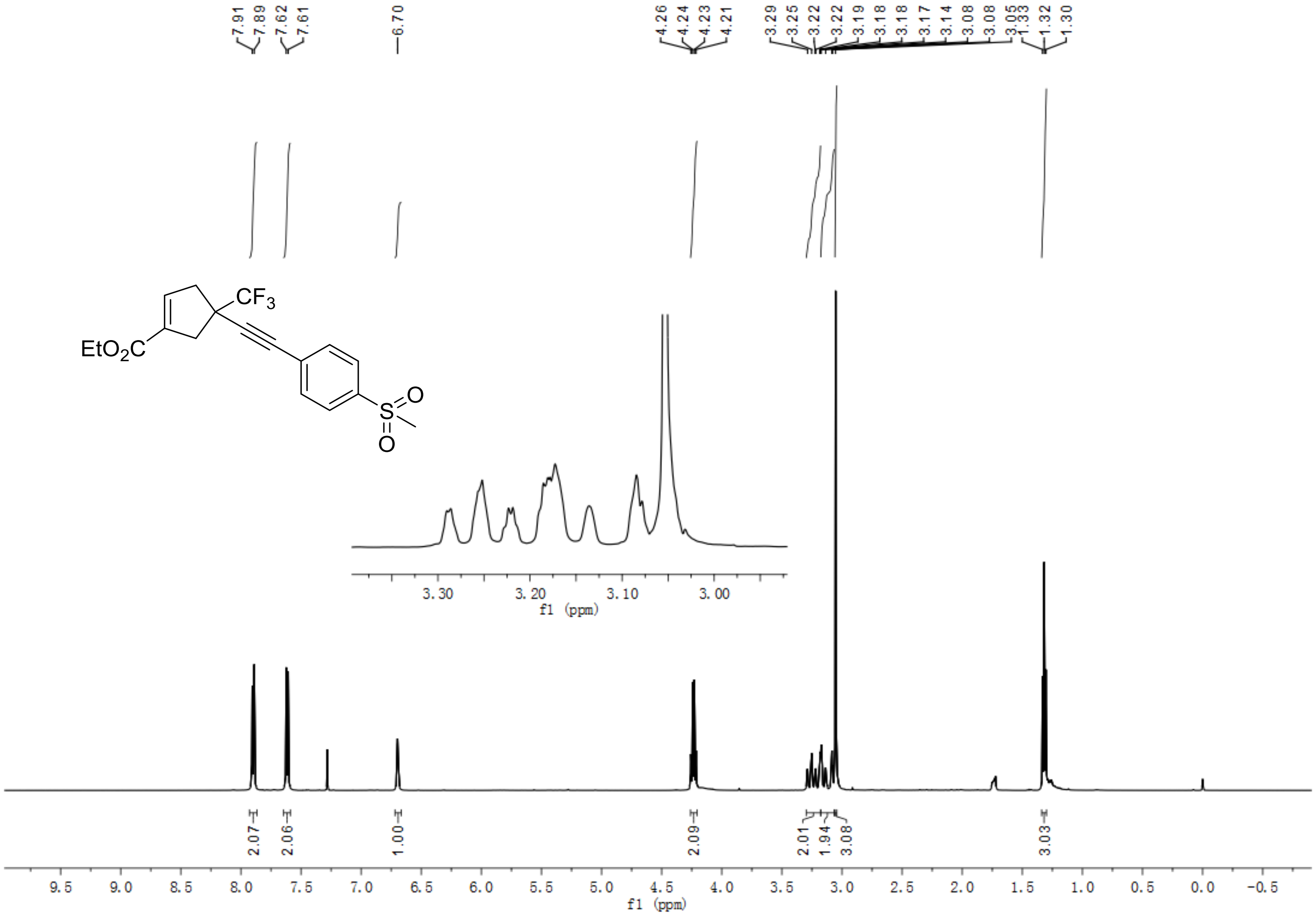
^{13}C NMR spectrum of product 3ac (125 MHz, $CDCl_3$)



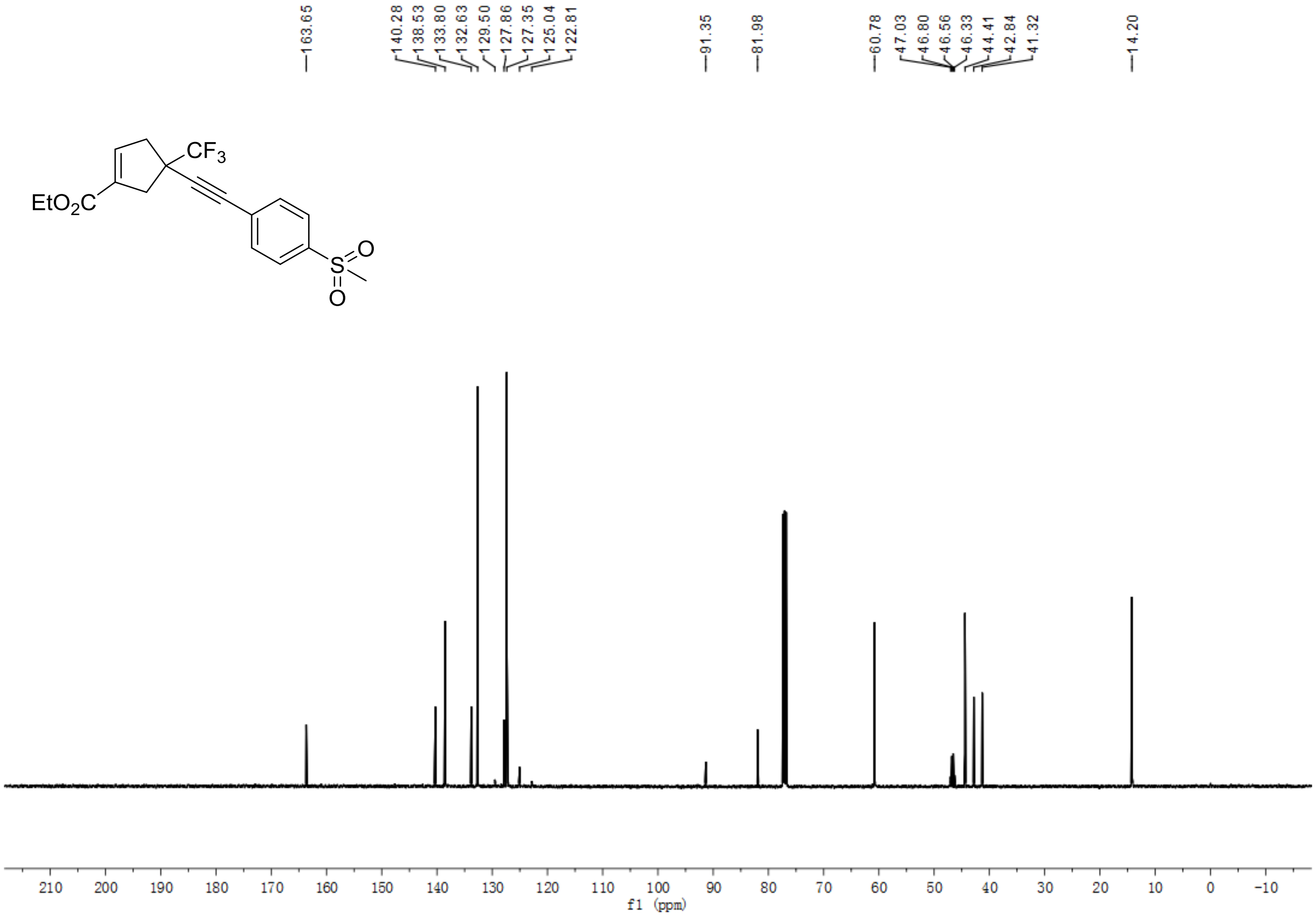
^{19}F NMR spectrum of product 3ac (470 MHz, $CDCl_3$)



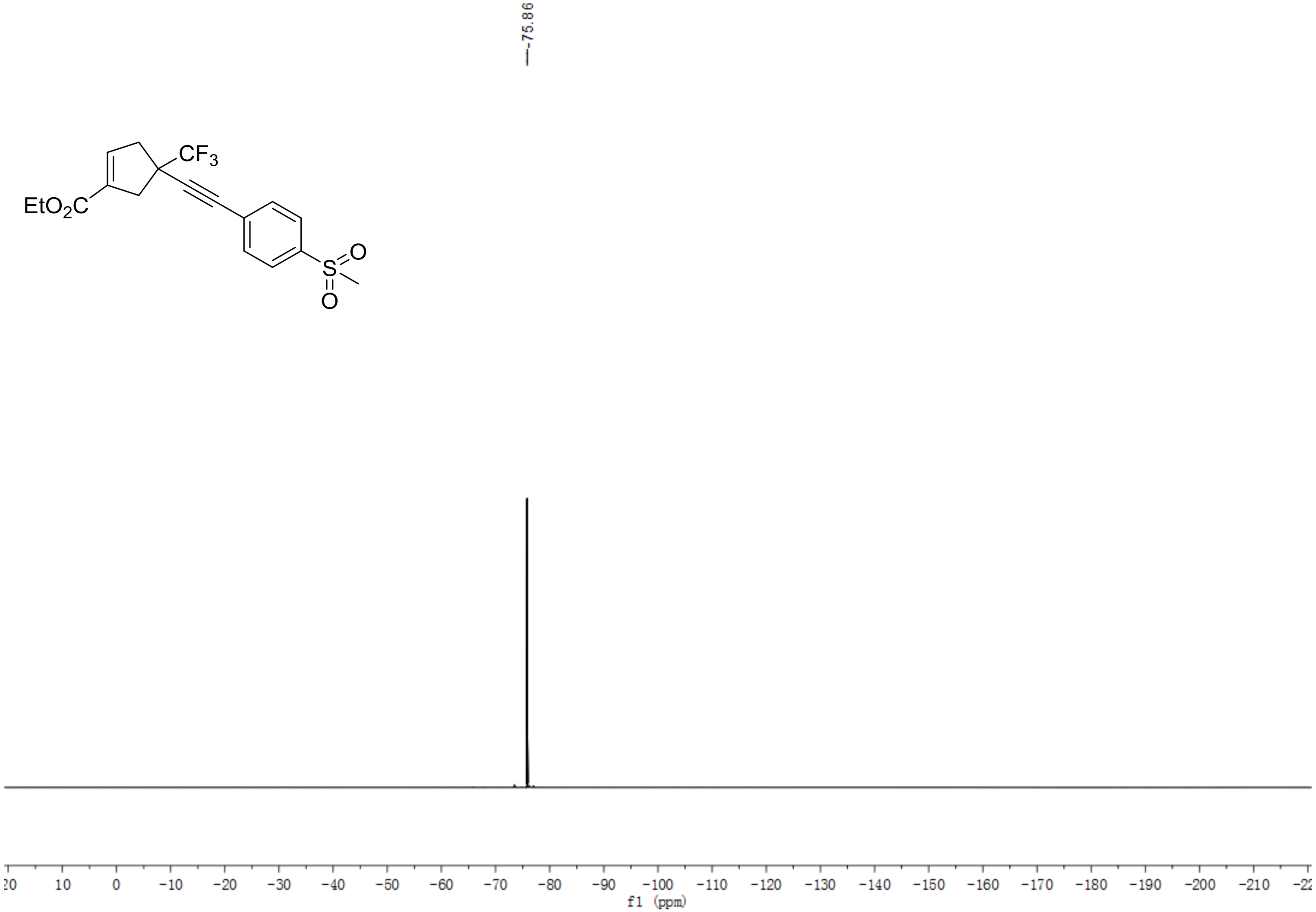
^{1}H NMR spectrum of product 3ad (500 MHz, $CDCl_3$)



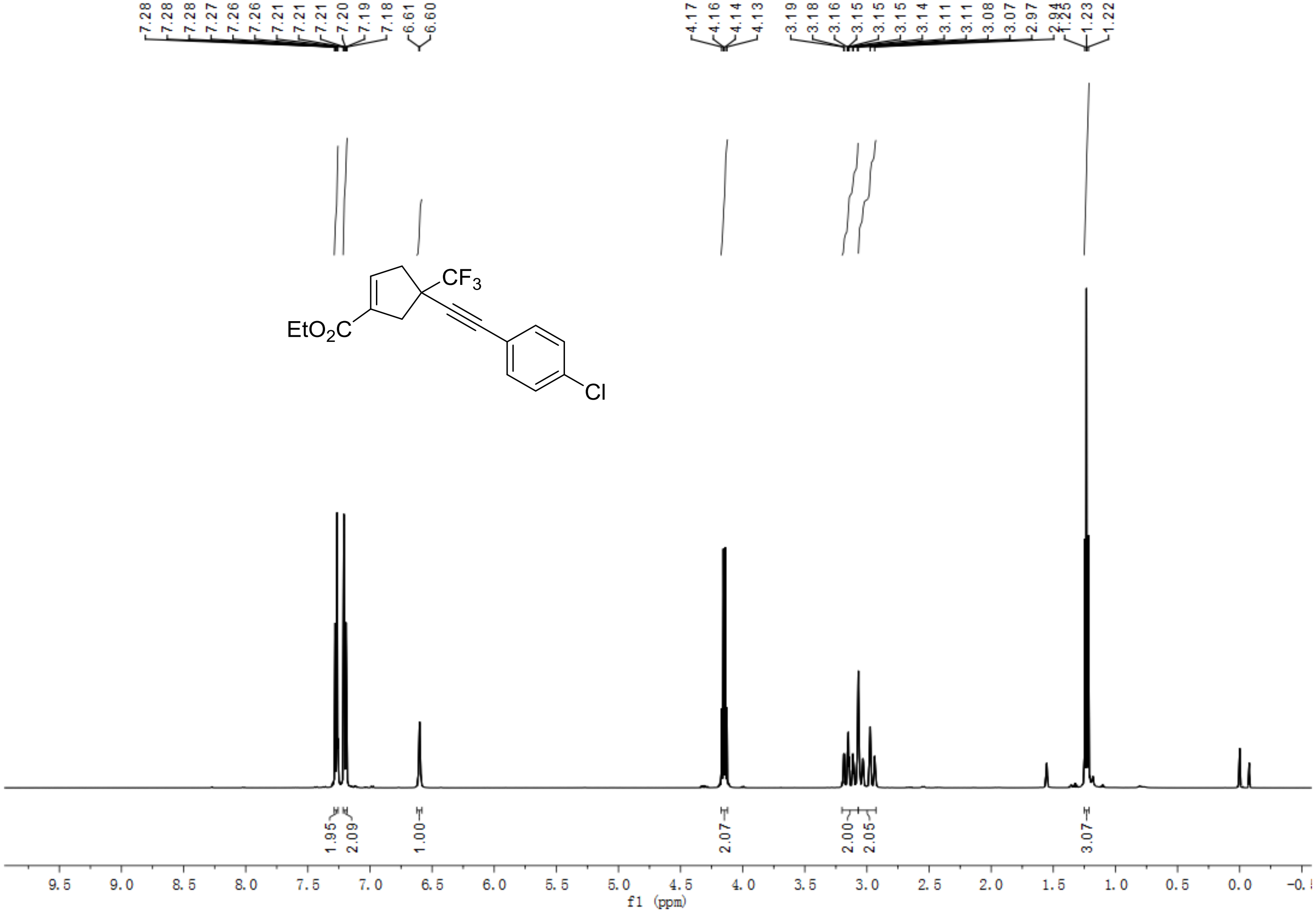
^{13}C NMR spectrum of product 3ad (125 MHz, $CDCl_3$)



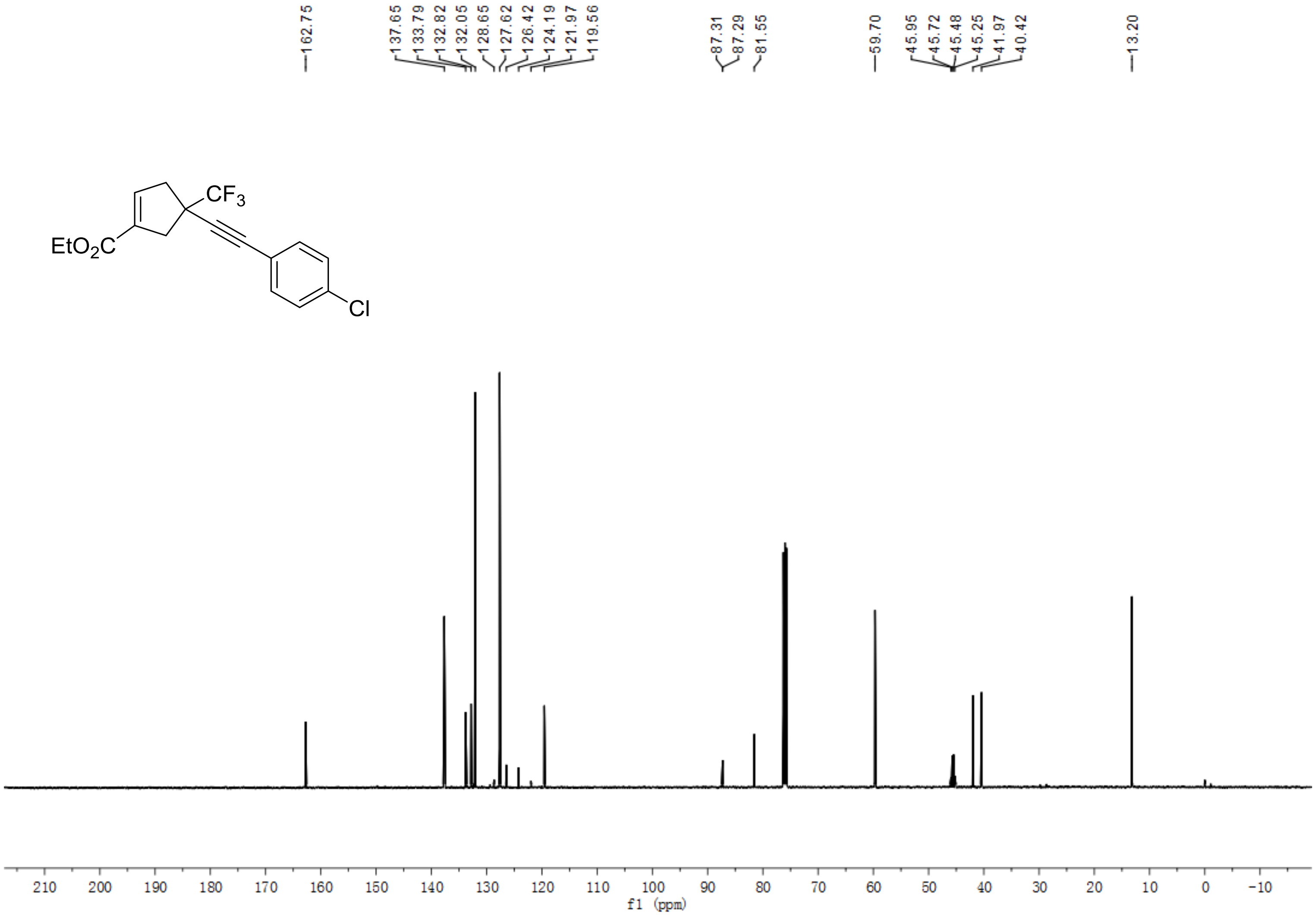
^{19}F NMR spectrum of product 3ad (470 MHz, $CDCl_3$)



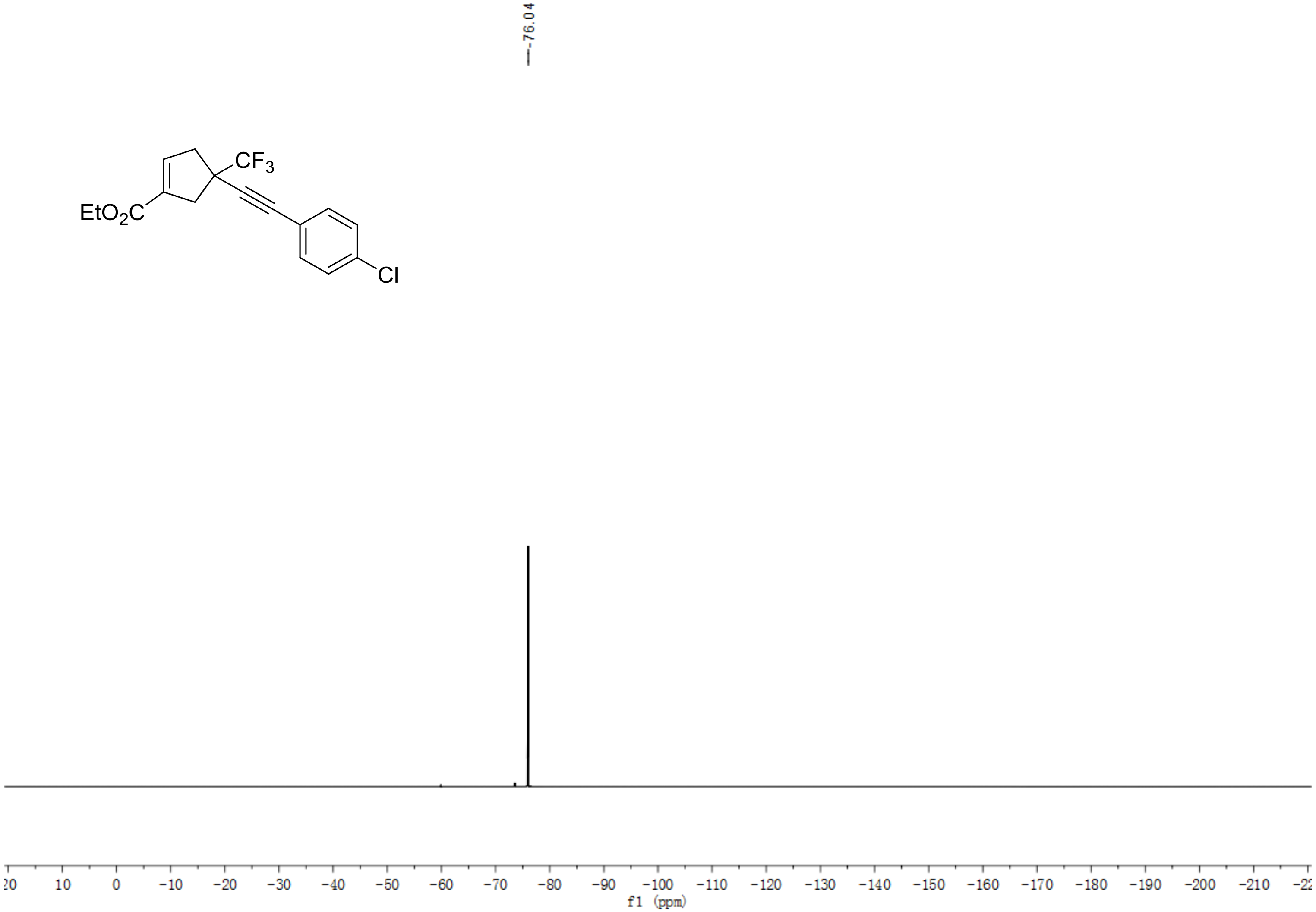
^{1}H NMR spectrum of product 3ae (500 MHz, $CDCl_3$)



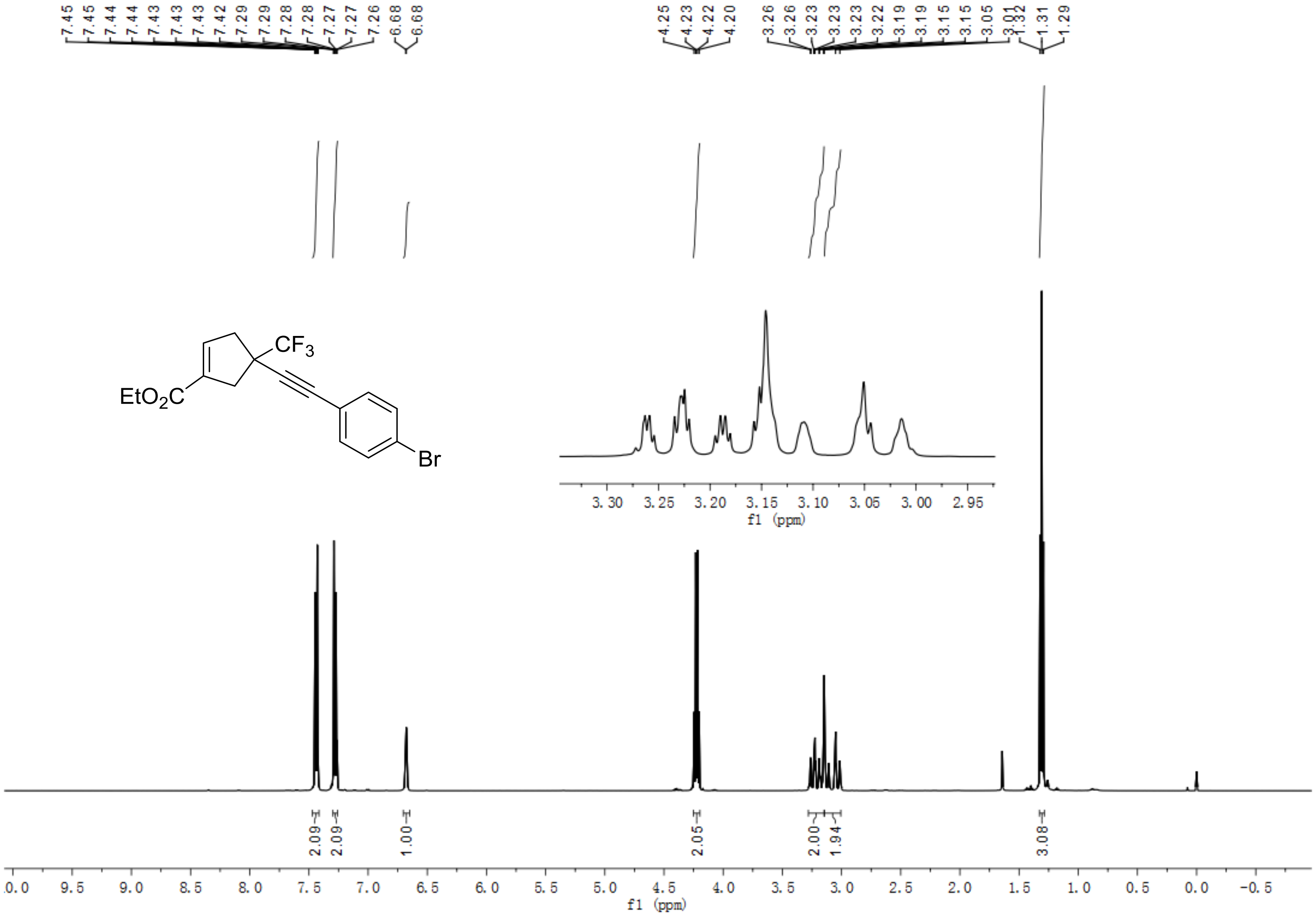
^{13}C NMR spectrum of product 3ae (125 MHz, CDCl$_3$)



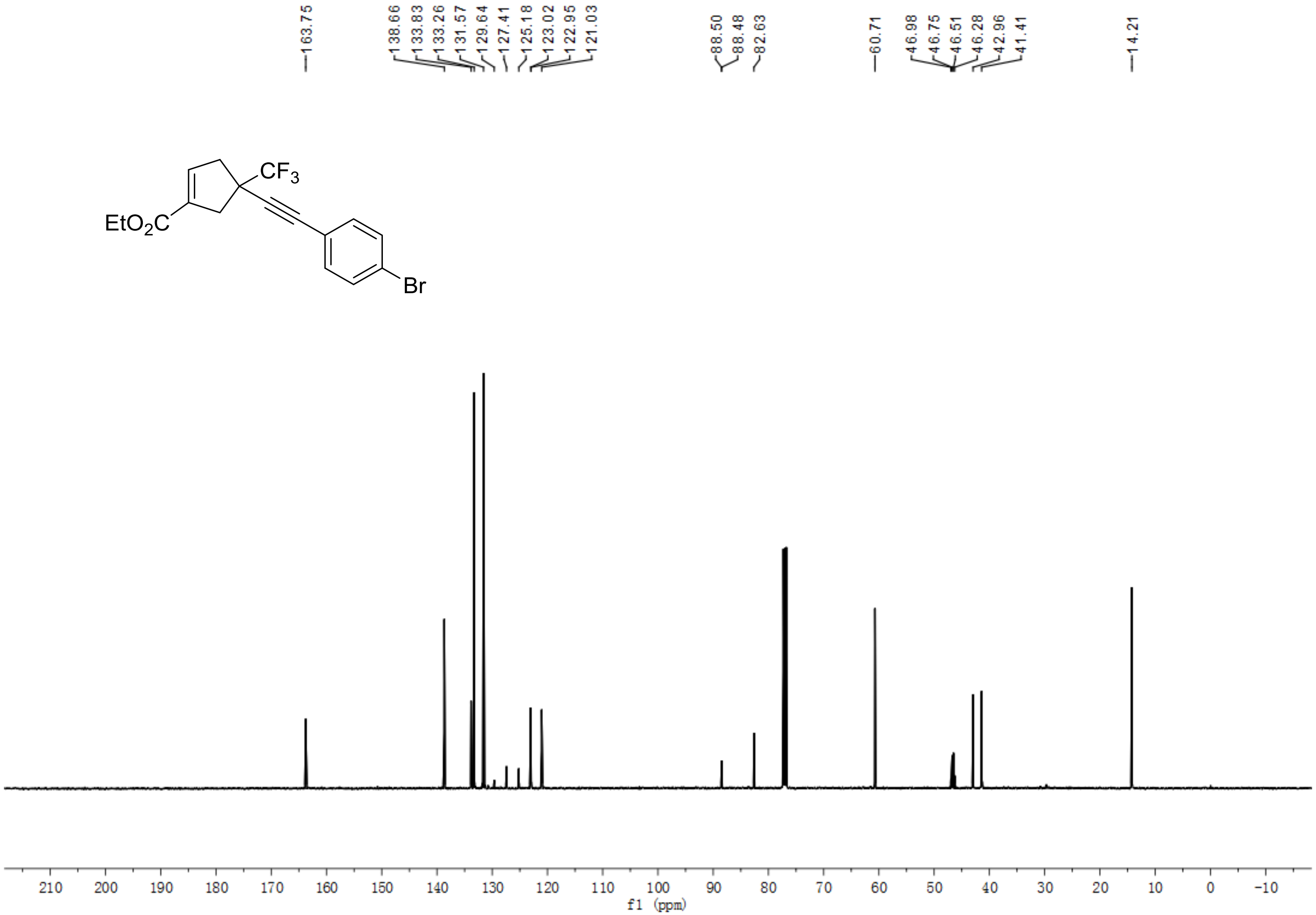
^{19}F NMR spectrum of product 3ae (470 MHz, $CDCl_3$)



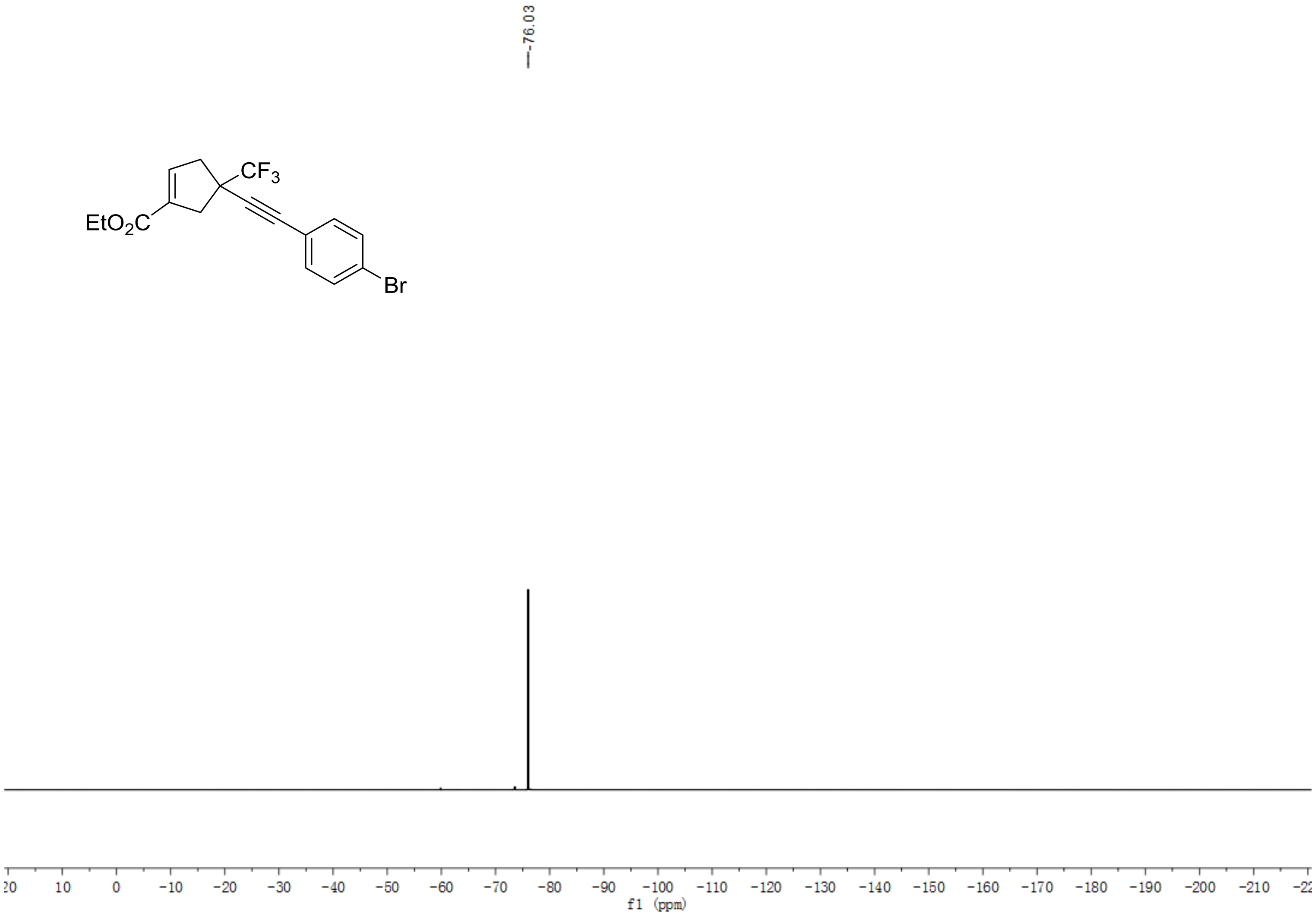
^{1}H NMR spectrum of product 3af (500 MHz, $CDCl_3$)



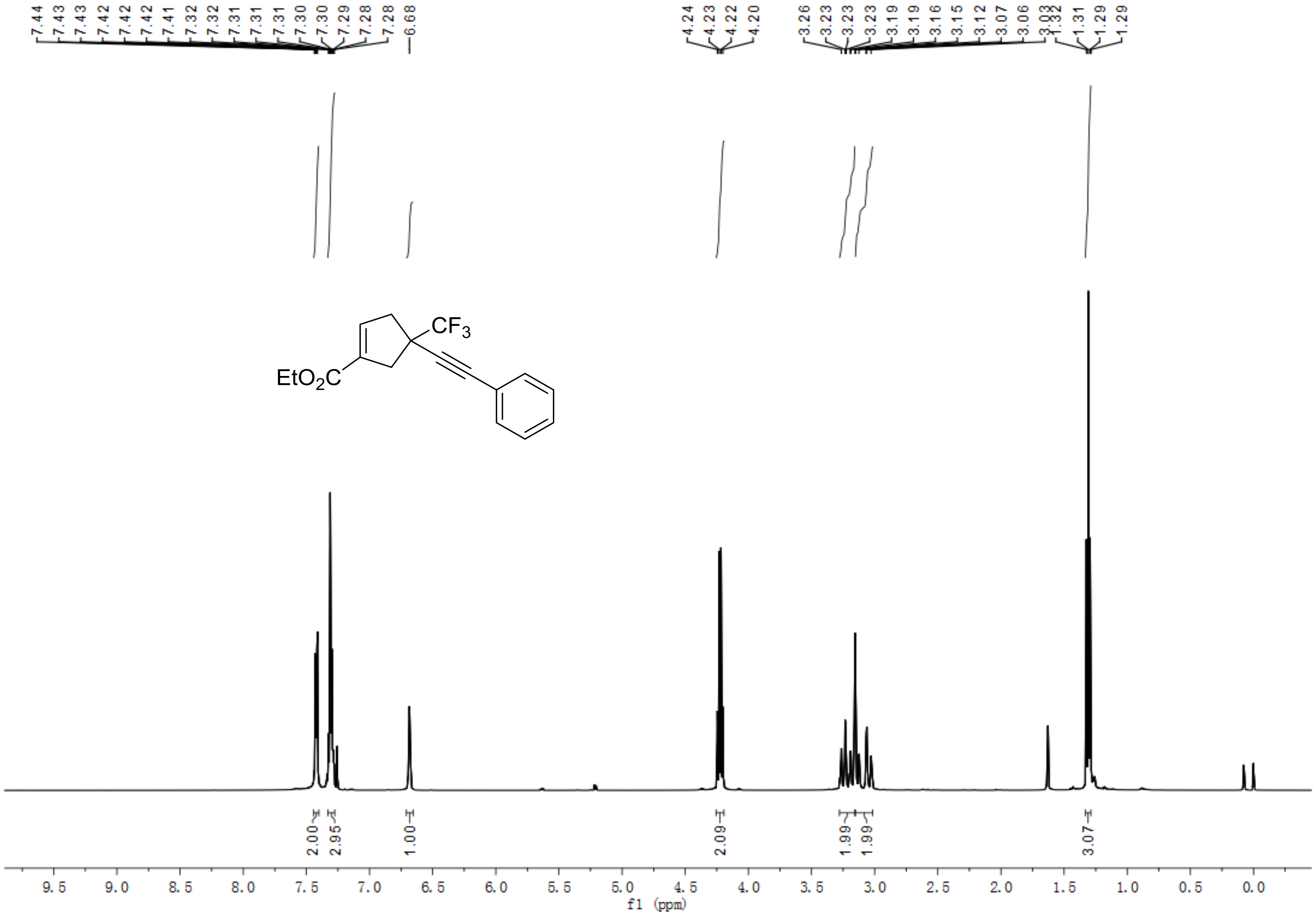
^{13}C NMR spectrum of product 3af (125 MHz, CDCl$_3$)



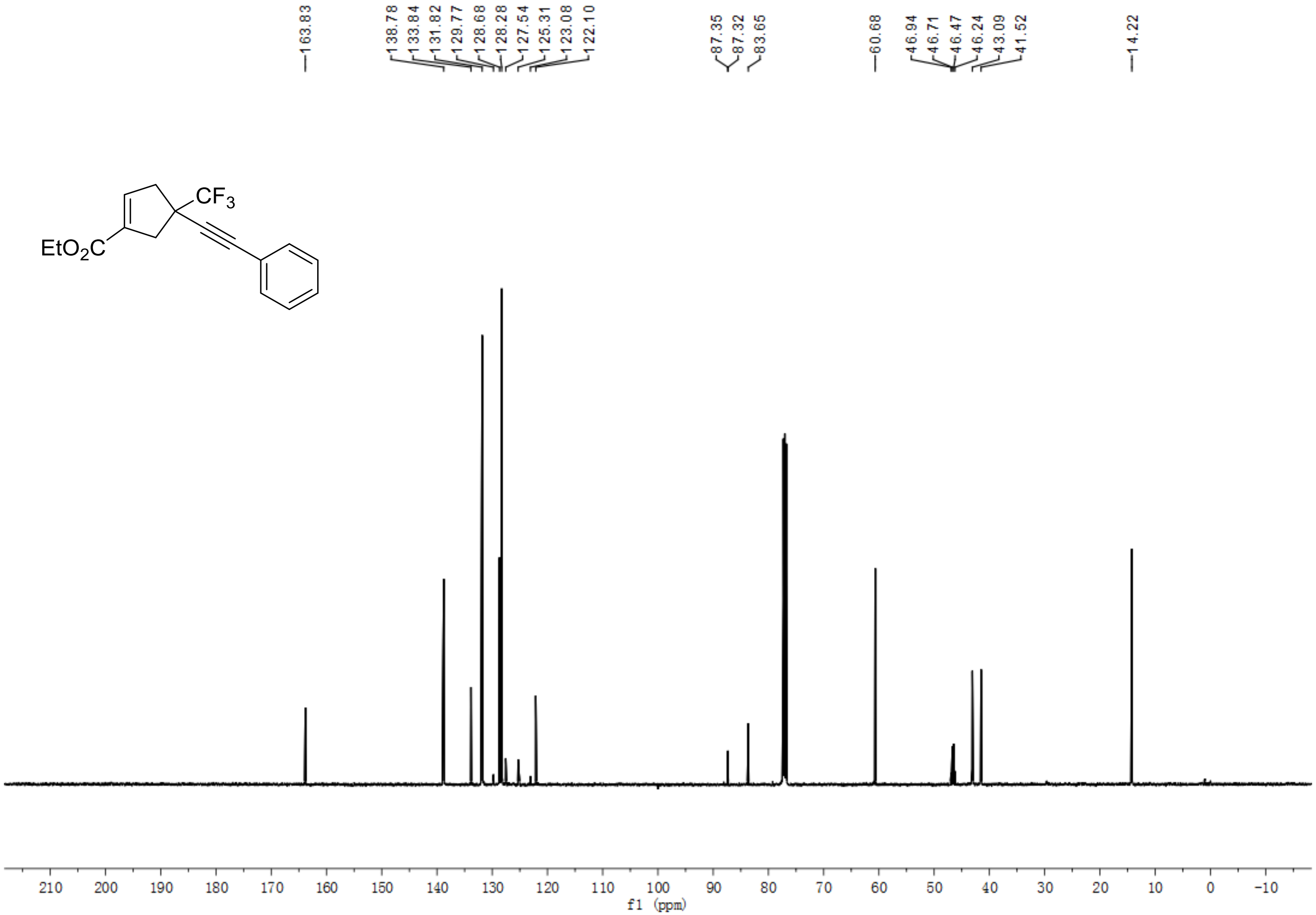
^{19}F NMR spectrum of product 3af (470 MHz, $CDCl_3$)



^{1}H NMR spectrum of product 3ag (500 MHz, $CDCl_3$)

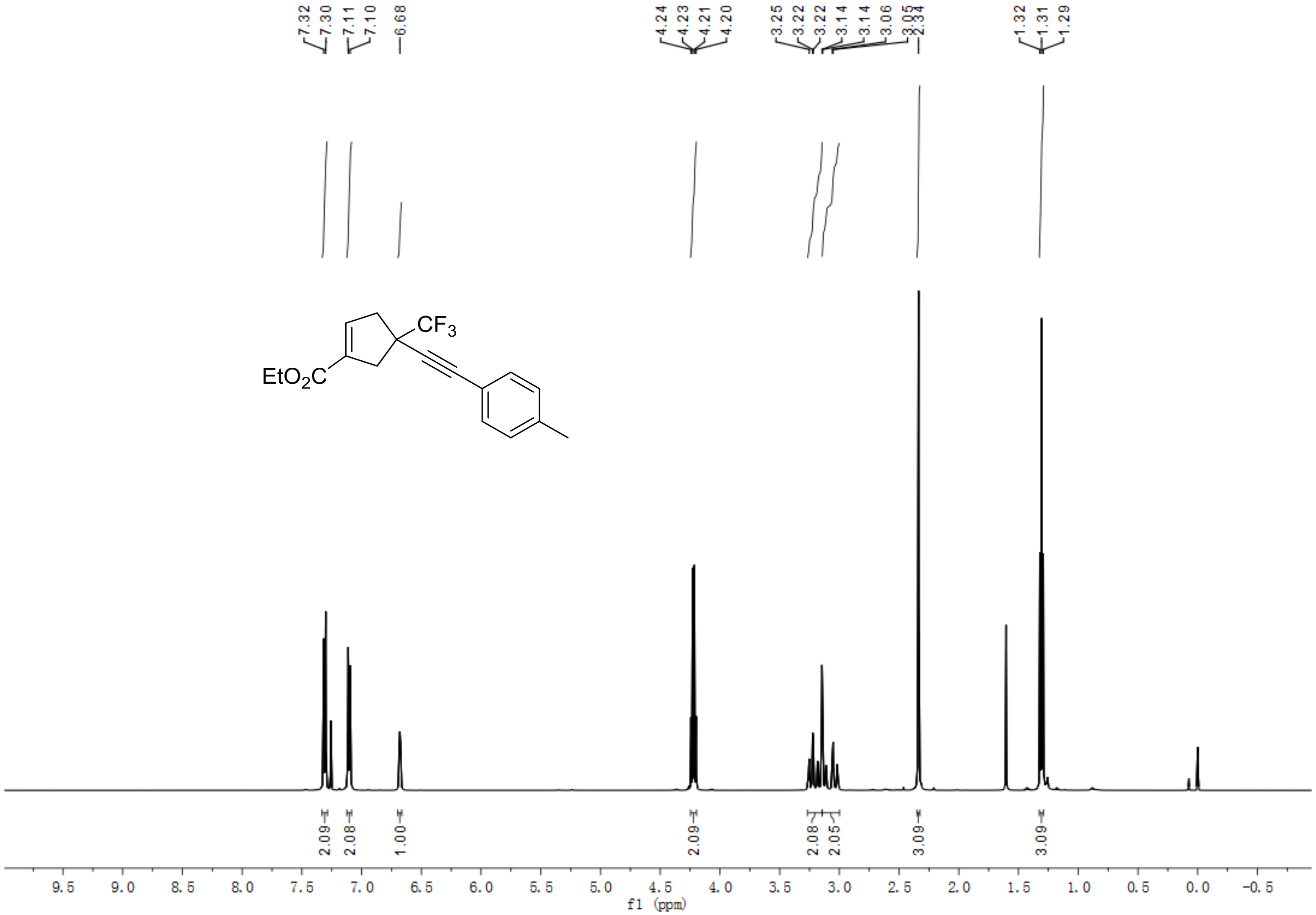


^{13}C NMR spectrum of product 3ag (125 MHz, $CDCl_3$)

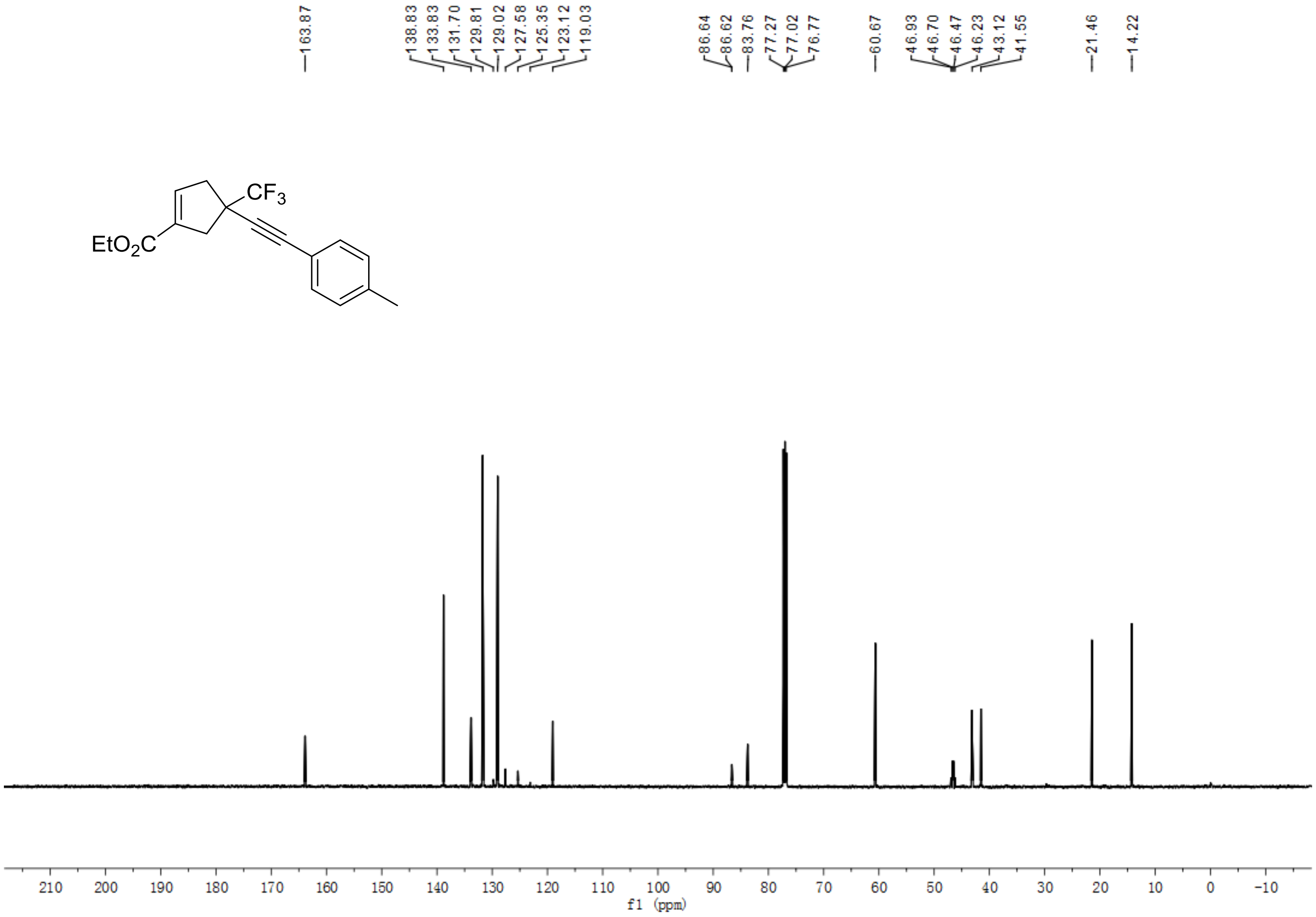


^{19}F NMR spectrum of product 3ag (470 MHz, $CDCl_3$)

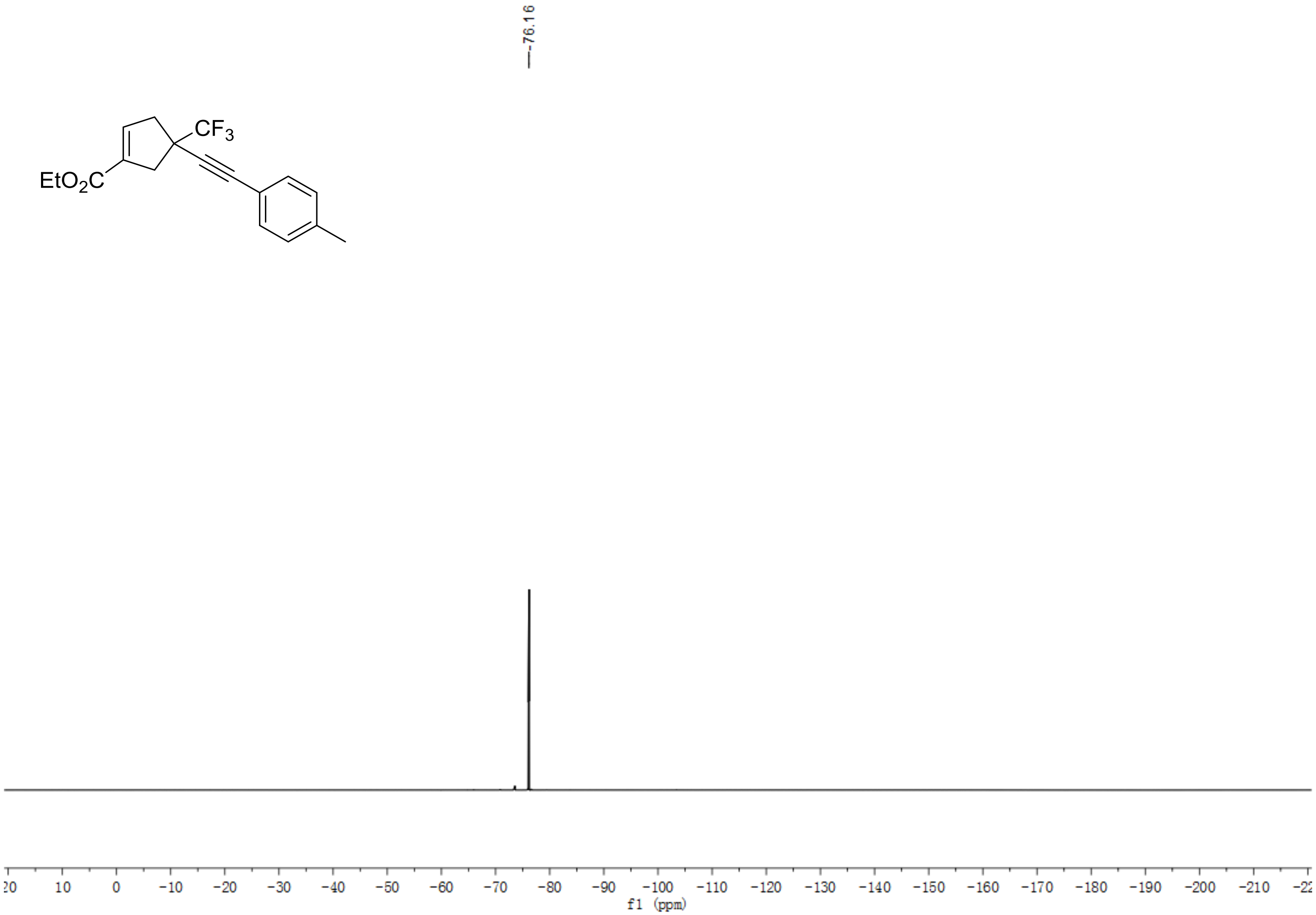
^{1}H NMR spectrum of product 3ah (500 MHz, $CDCl_3$)



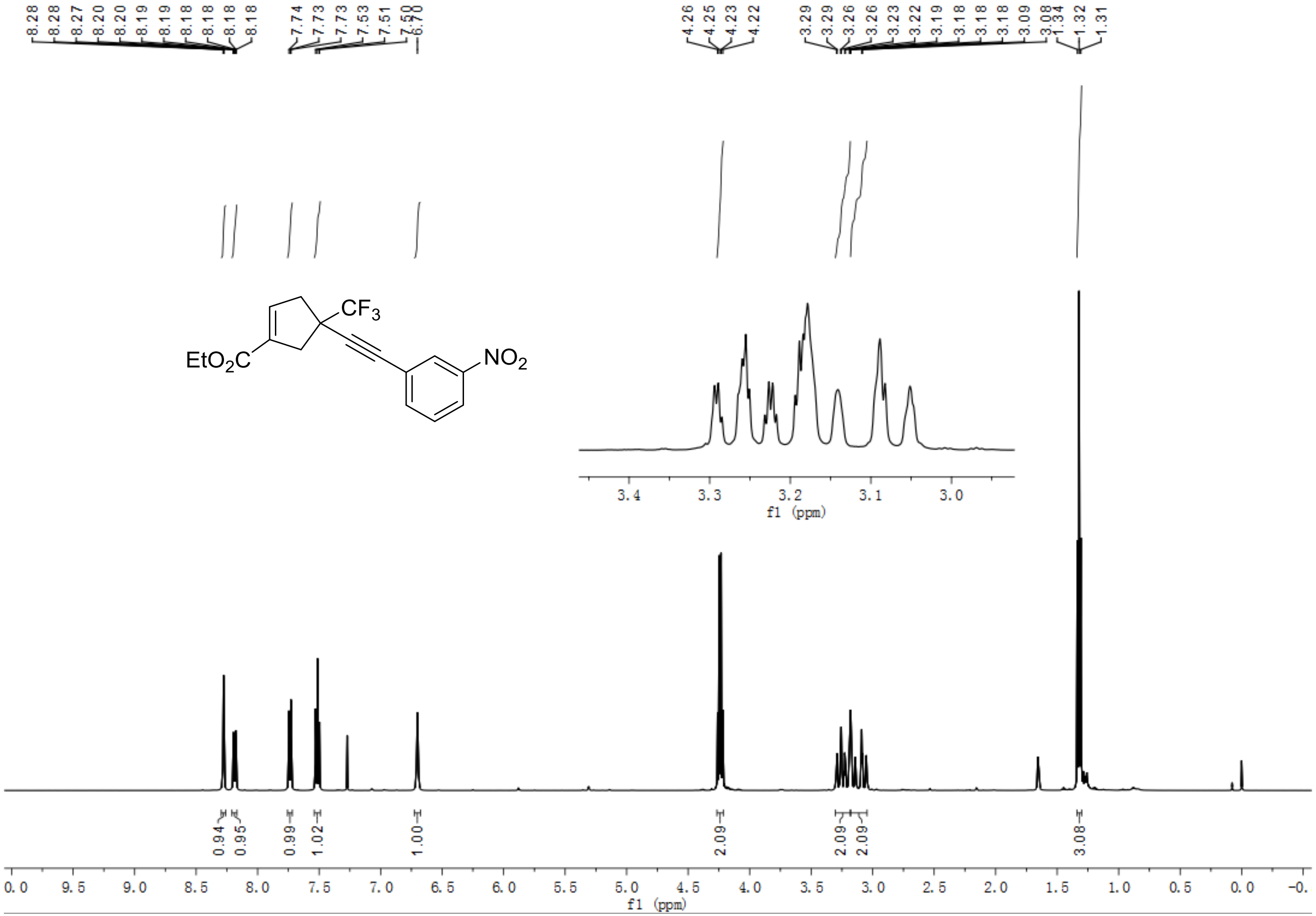
^{13}C NMR spectrum of product 3ah (125 MHz, $CDCl_3$)



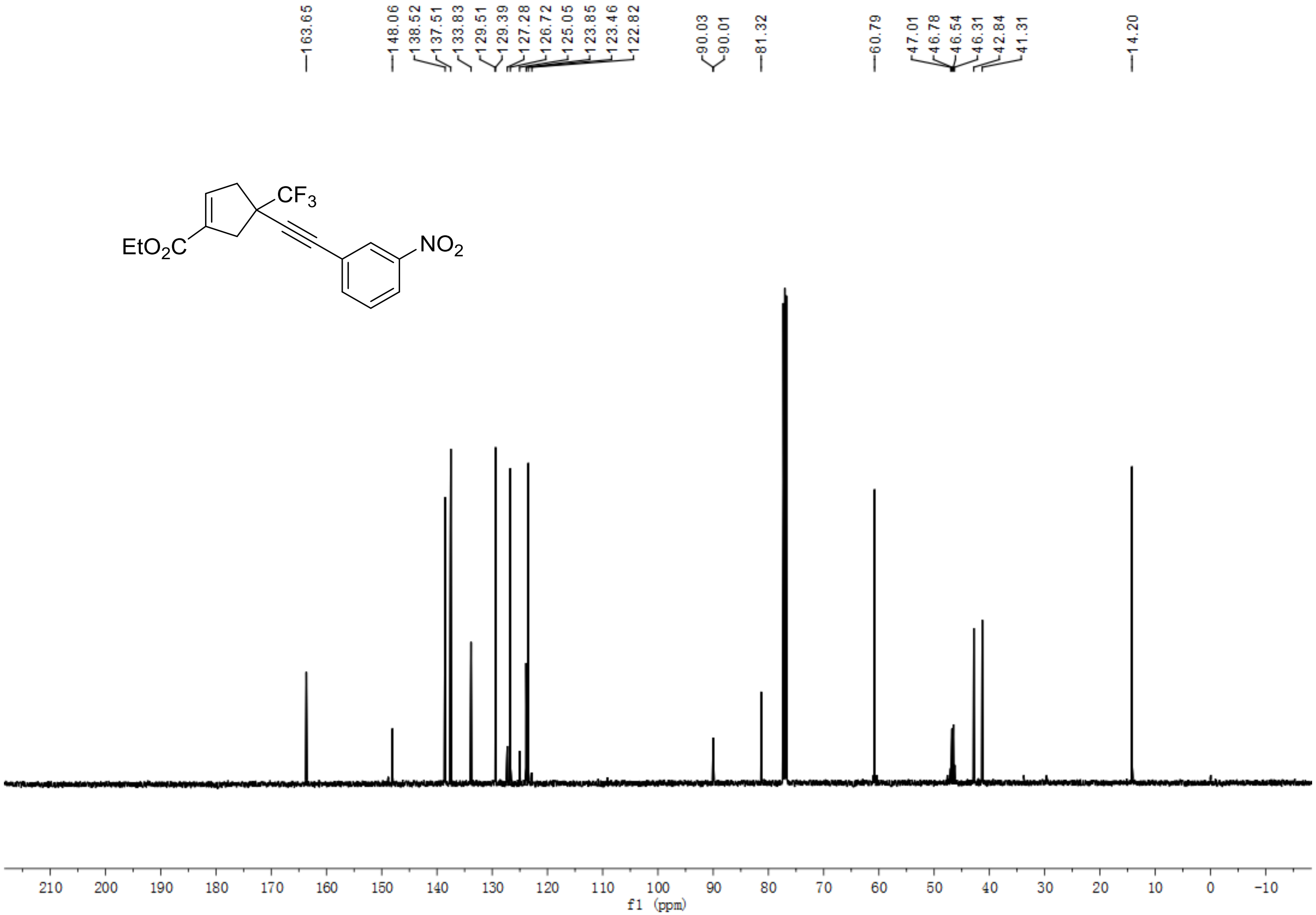
^{19}F NMR spectrum of product 3ah (470 MHz, $CDCl_3$)



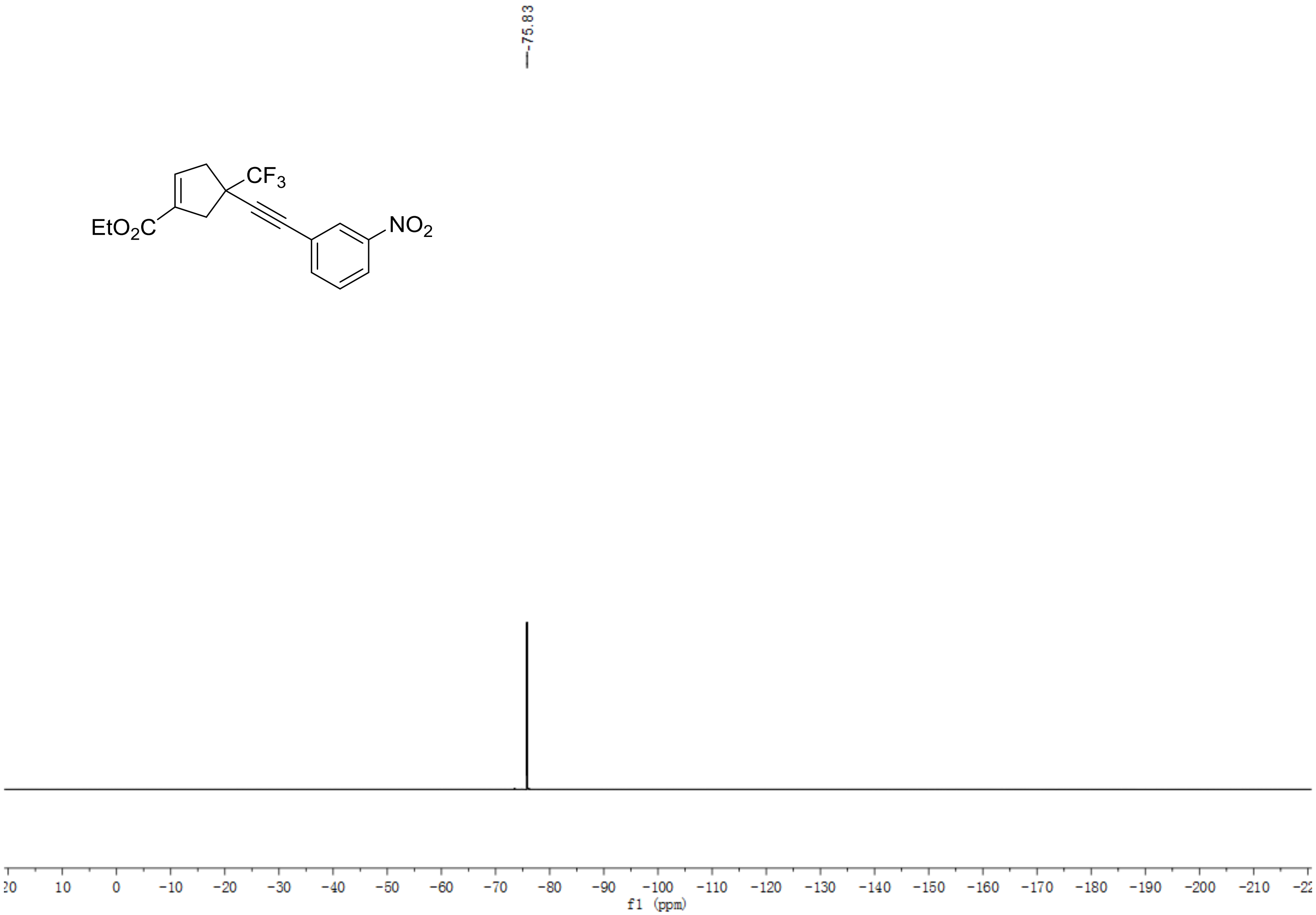
^{1}H NMR spectrum of product 3ai (500 MHz, CDCl$_3$)



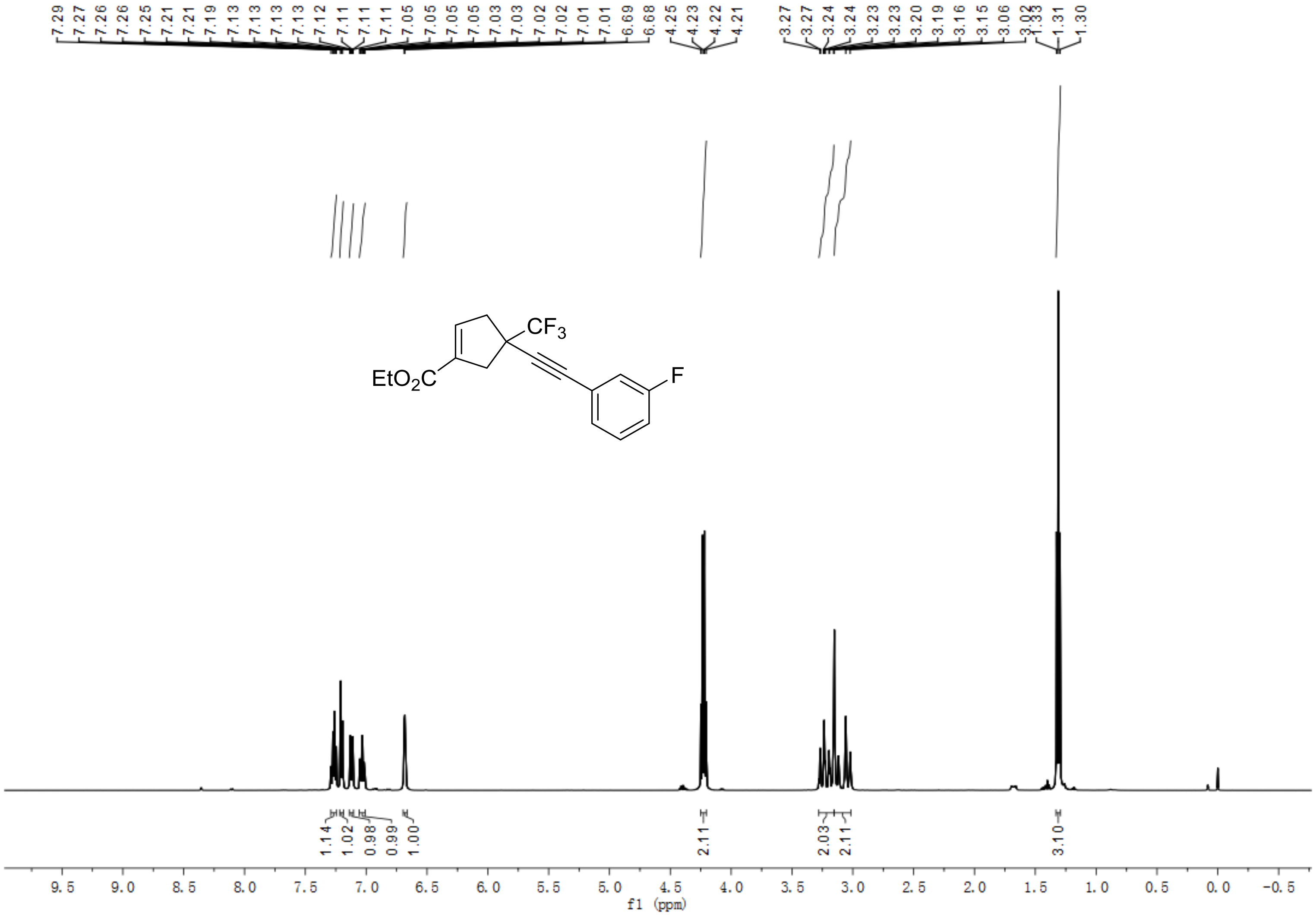
^{13}C NMR spectrum of product 3ai (125 MHz, $CDCl_3$)



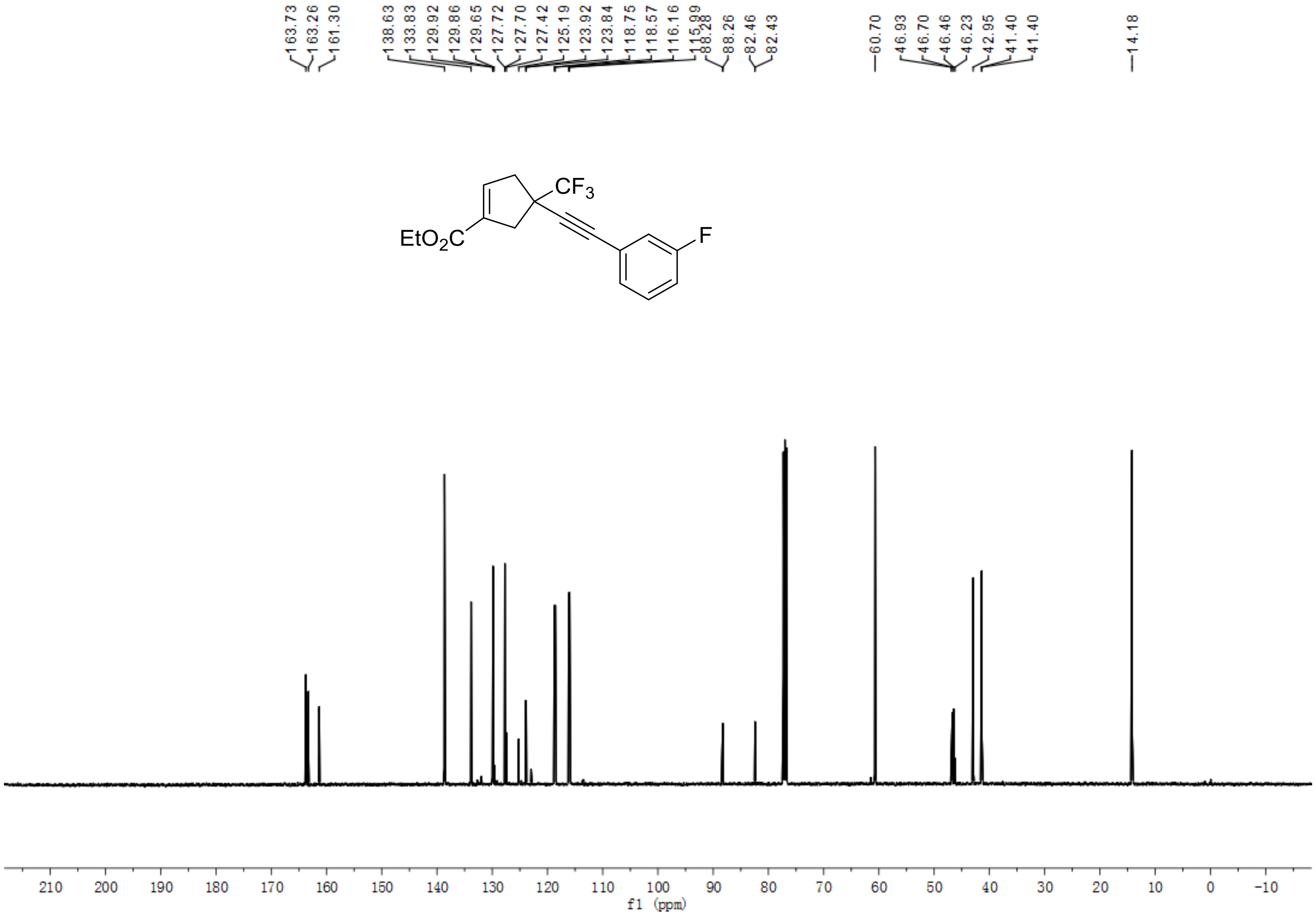
^{19}F NMR spectrum of product 3ai (470 MHz, CDCl$_3$)



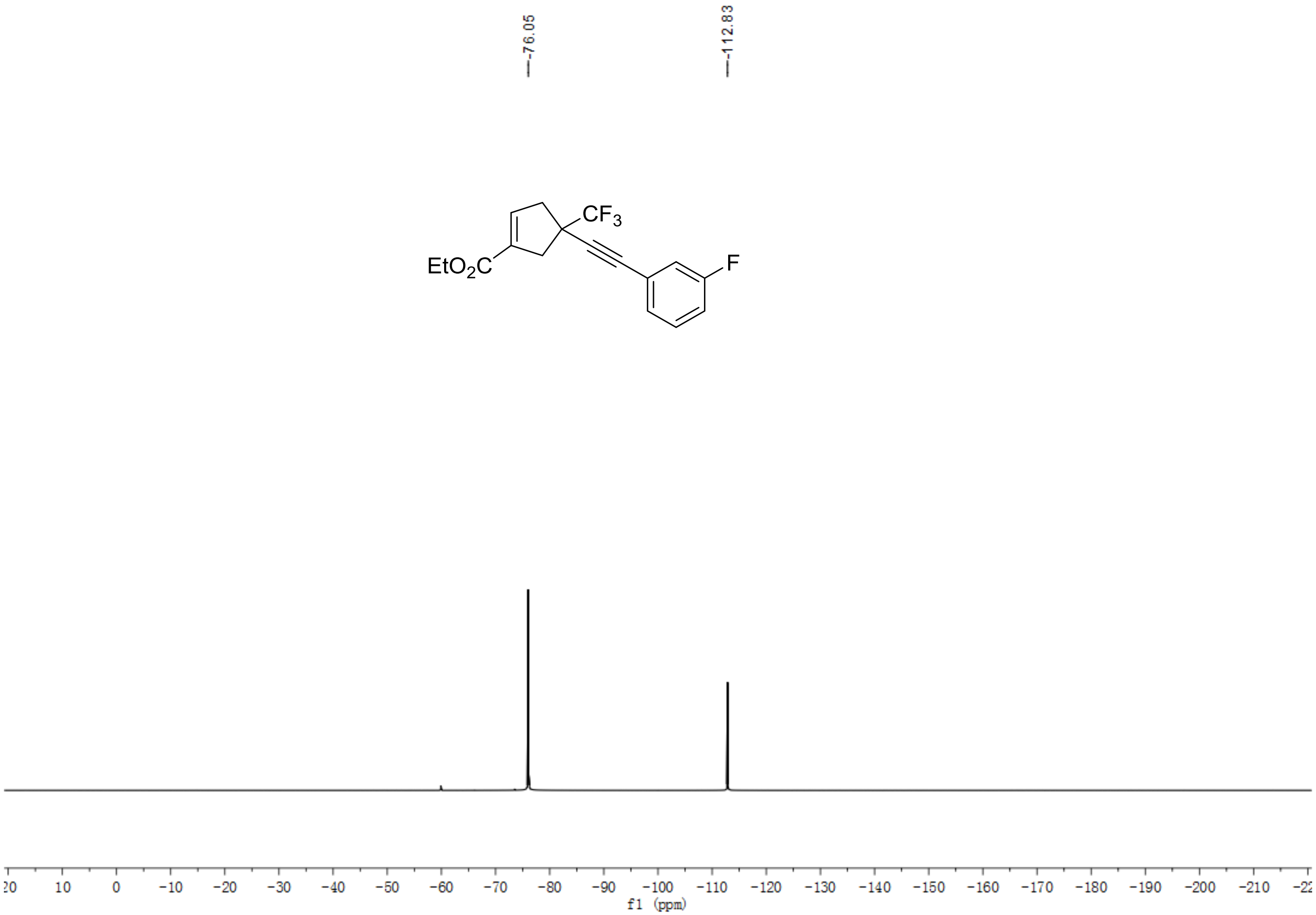
^{1}H NMR spectrum of product 3aj (500 MHz, CDCl$_3$)



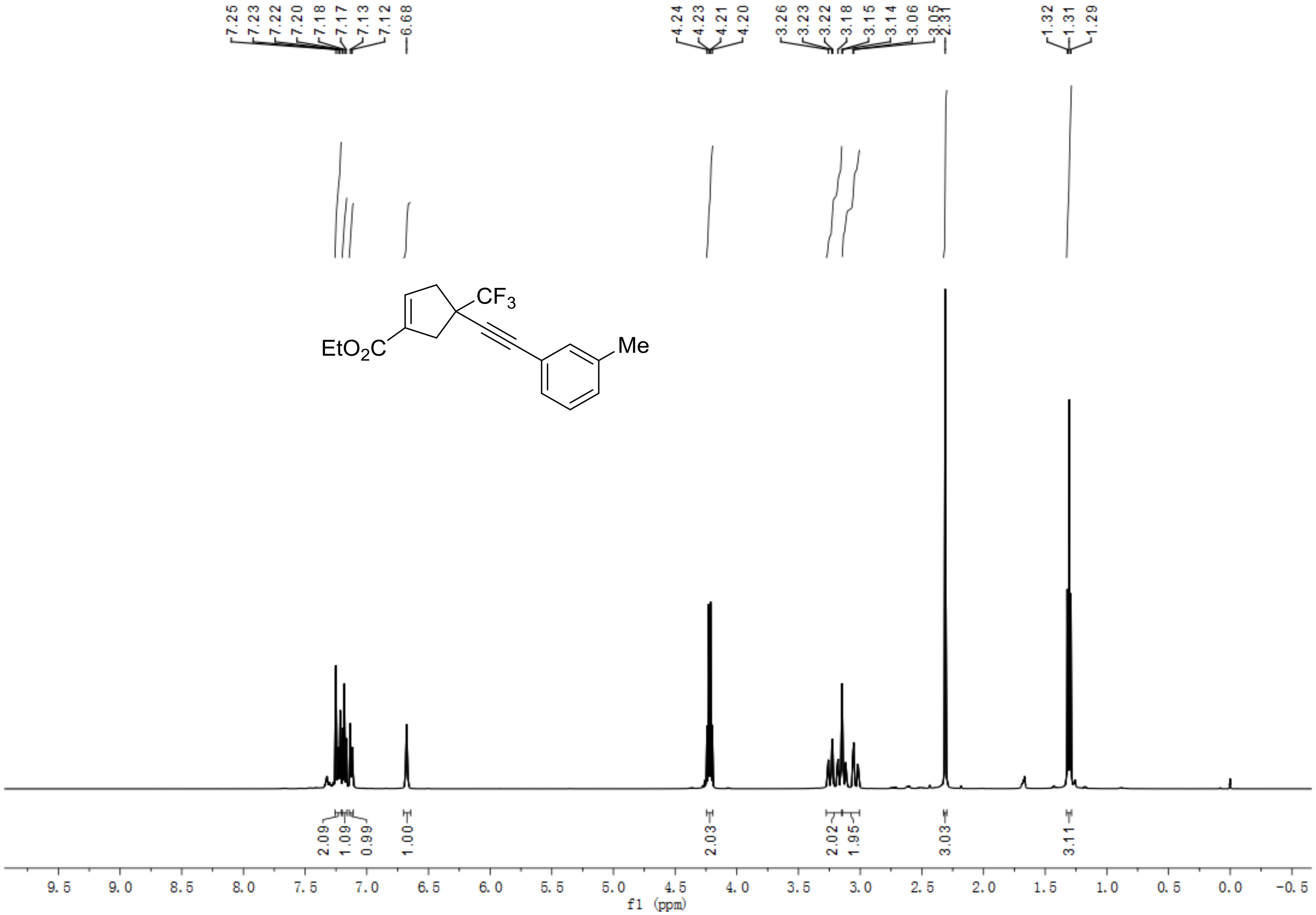
^{13}C NMR spectrum of product 3aj (125 MHz, $CDCl_3$)



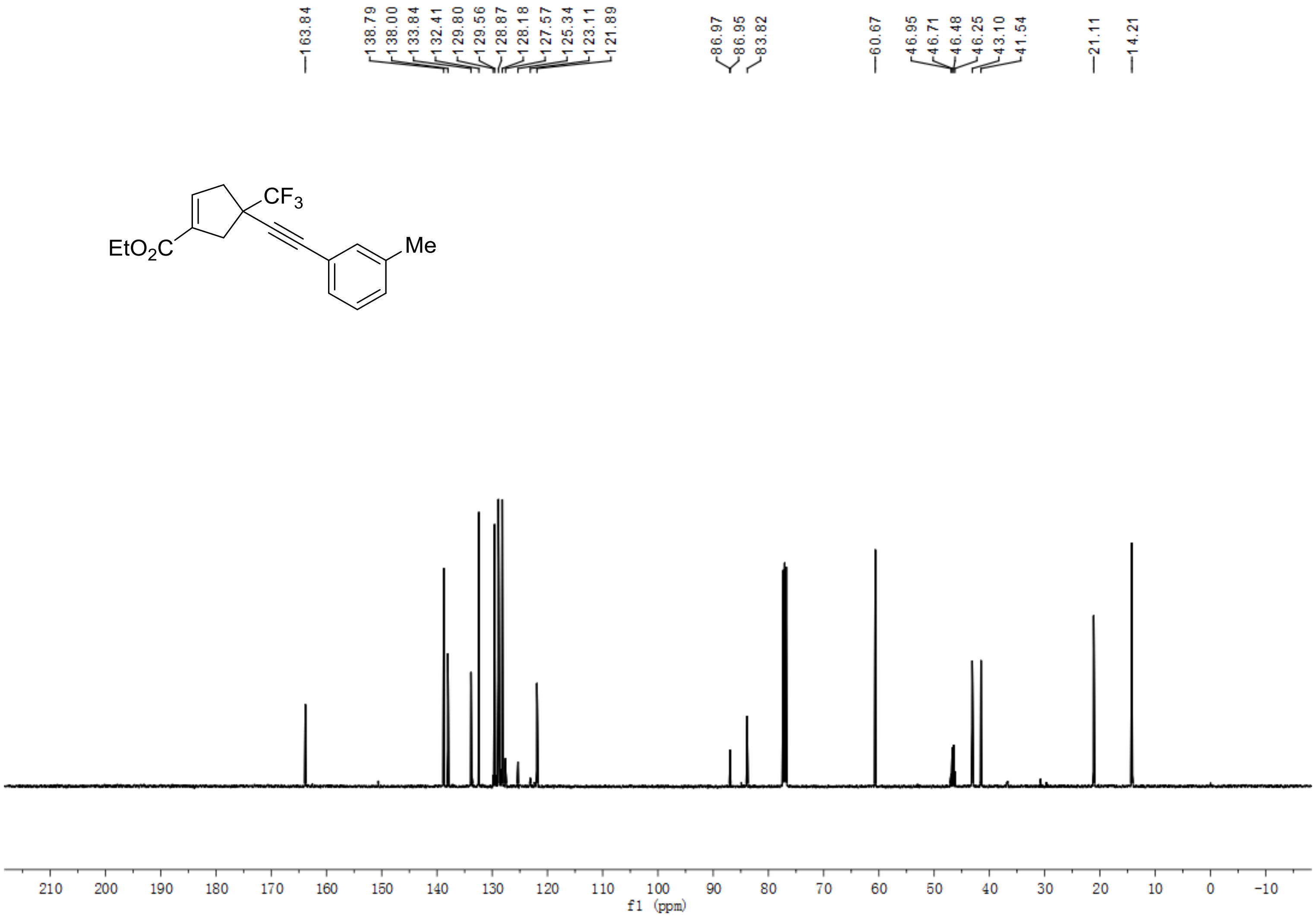
^{19}F NMR spectrum of product 3aj (470 MHz, $CDCl_3$)



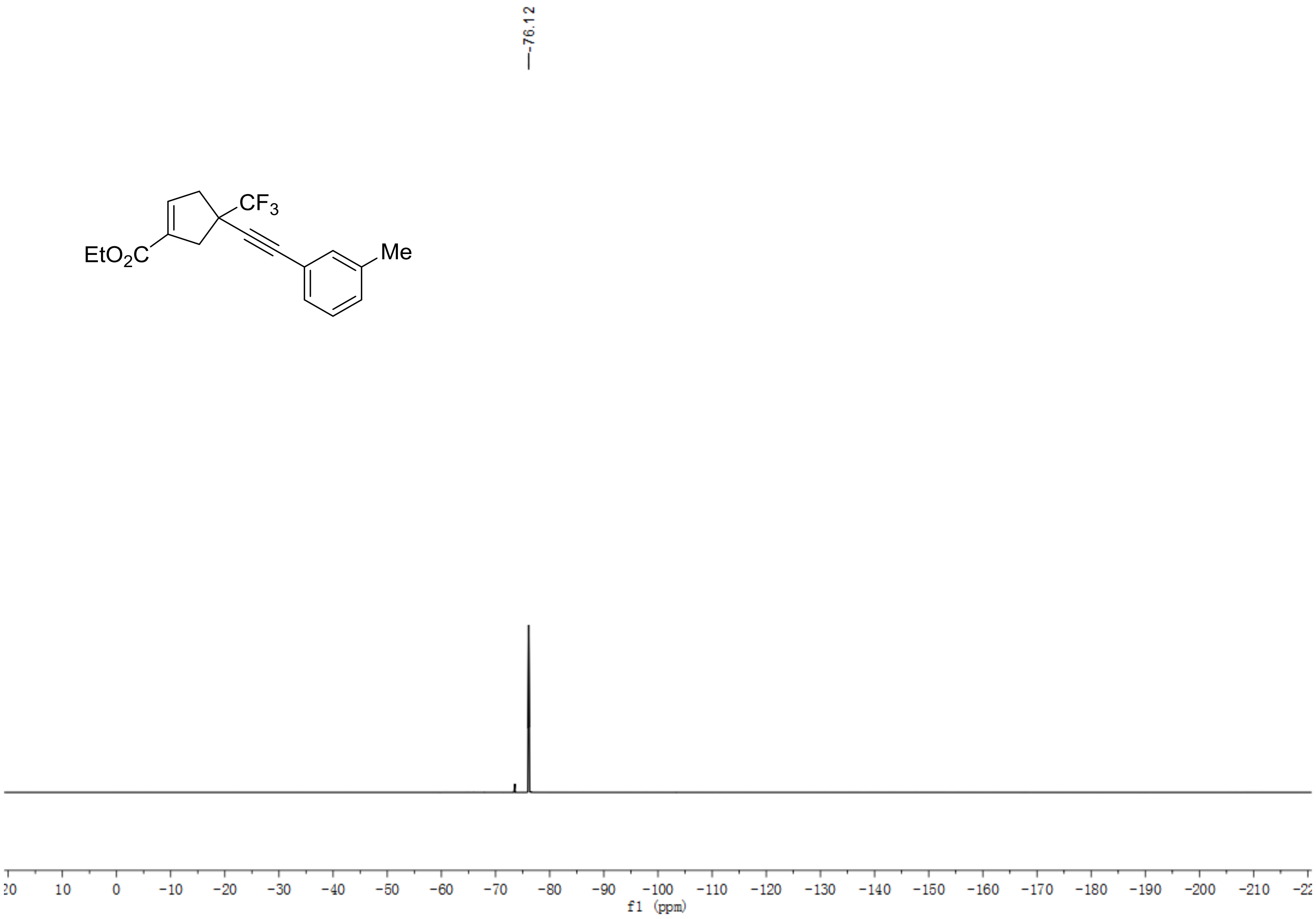
^{1}H NMR spectrum of product 3ak (500 MHz, $CDCl_3$)



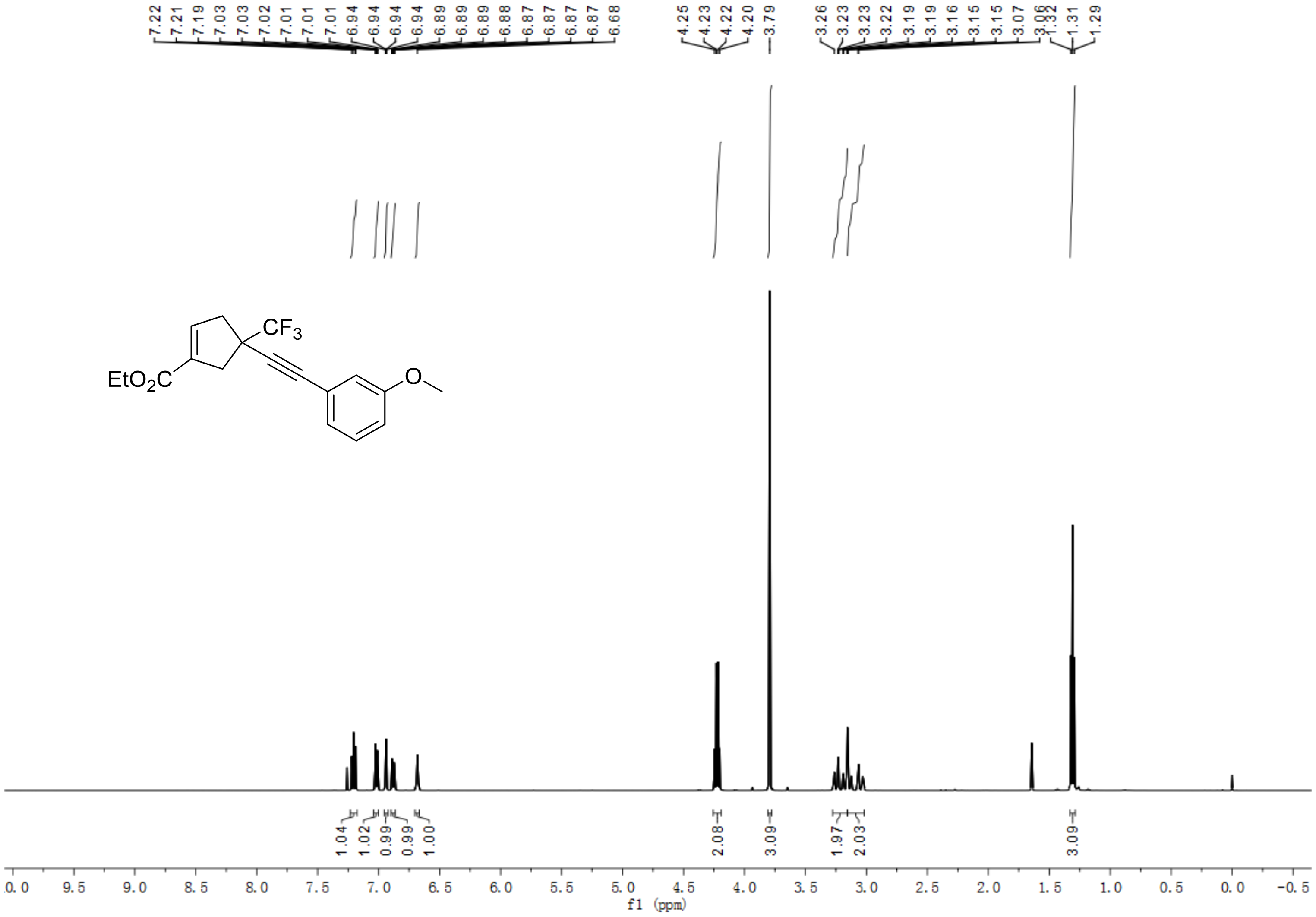
^{13}C NMR spectrum of product 3ak (125 MHz, $CDCl_3$)



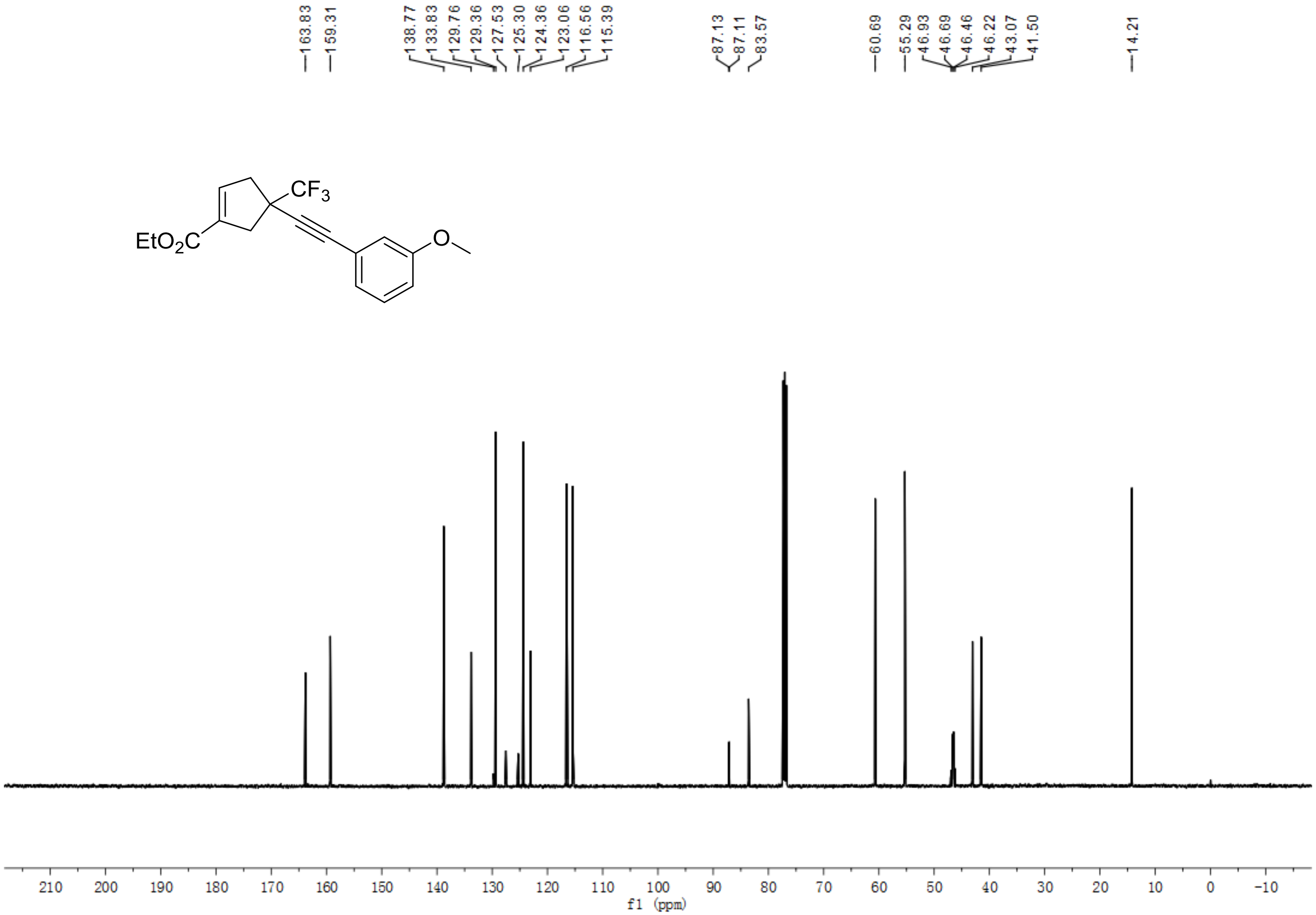
^{19}**F NMR spectrum of product 3ak (470 MHz, $CDCl_3$)**



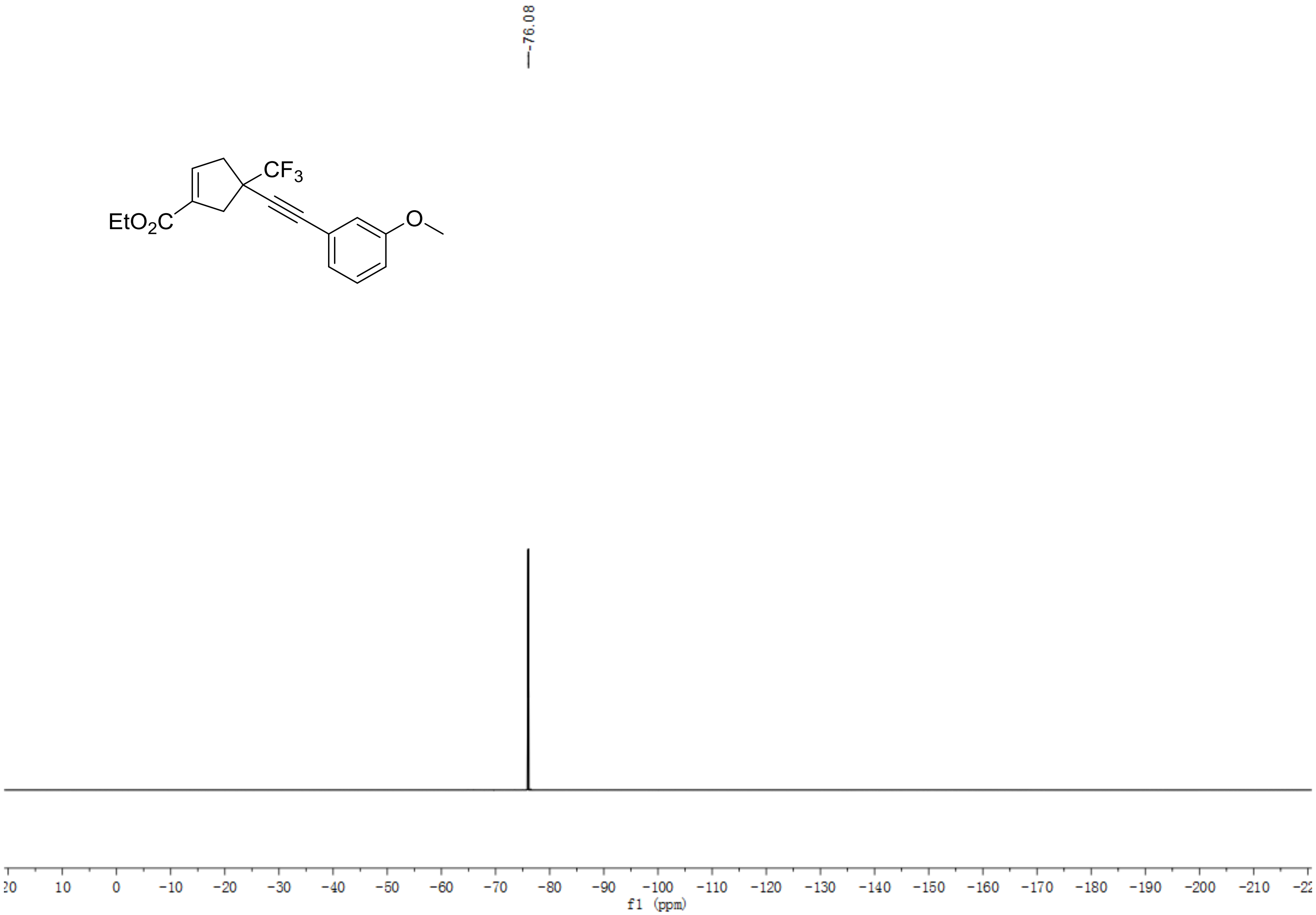
^{1}H NMR spectrum of product 3al (500 MHz, $CDCl_3$)



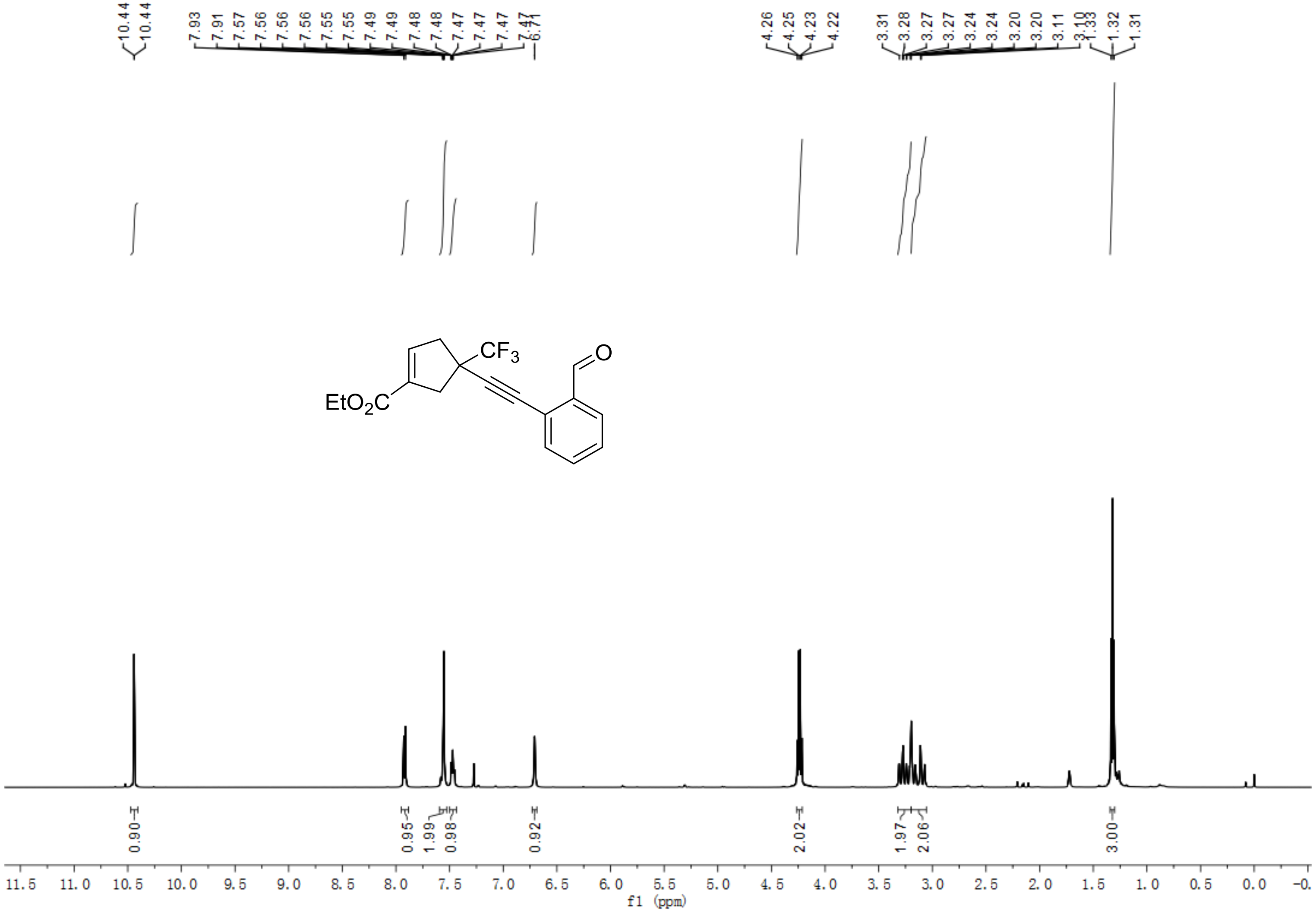
^{13}C NMR spectrum of product 3al (125 MHz, $CDCl_3$)



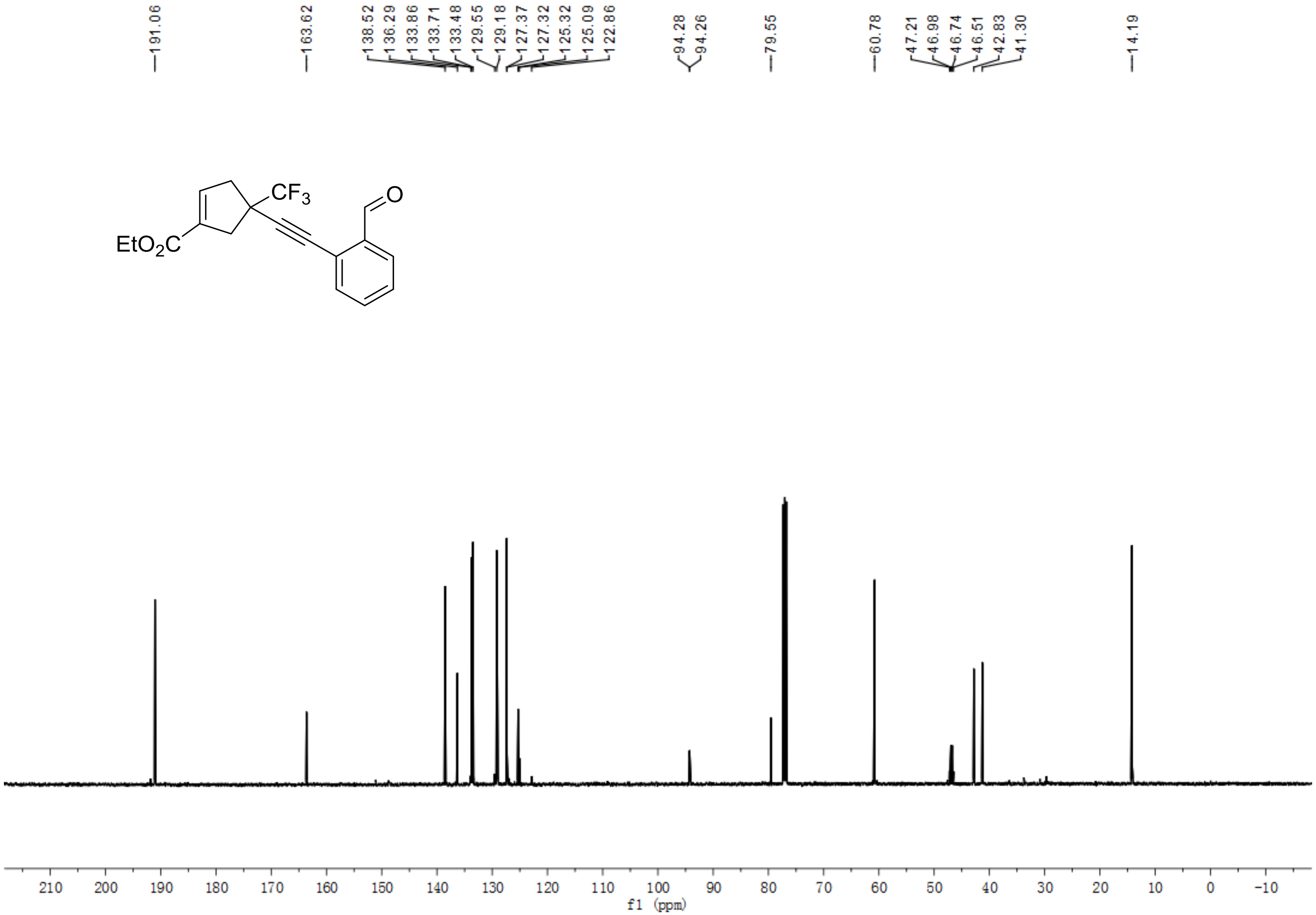
^{19}F NMR spectrum of product 3al (470 MHz, $CDCl_3$)



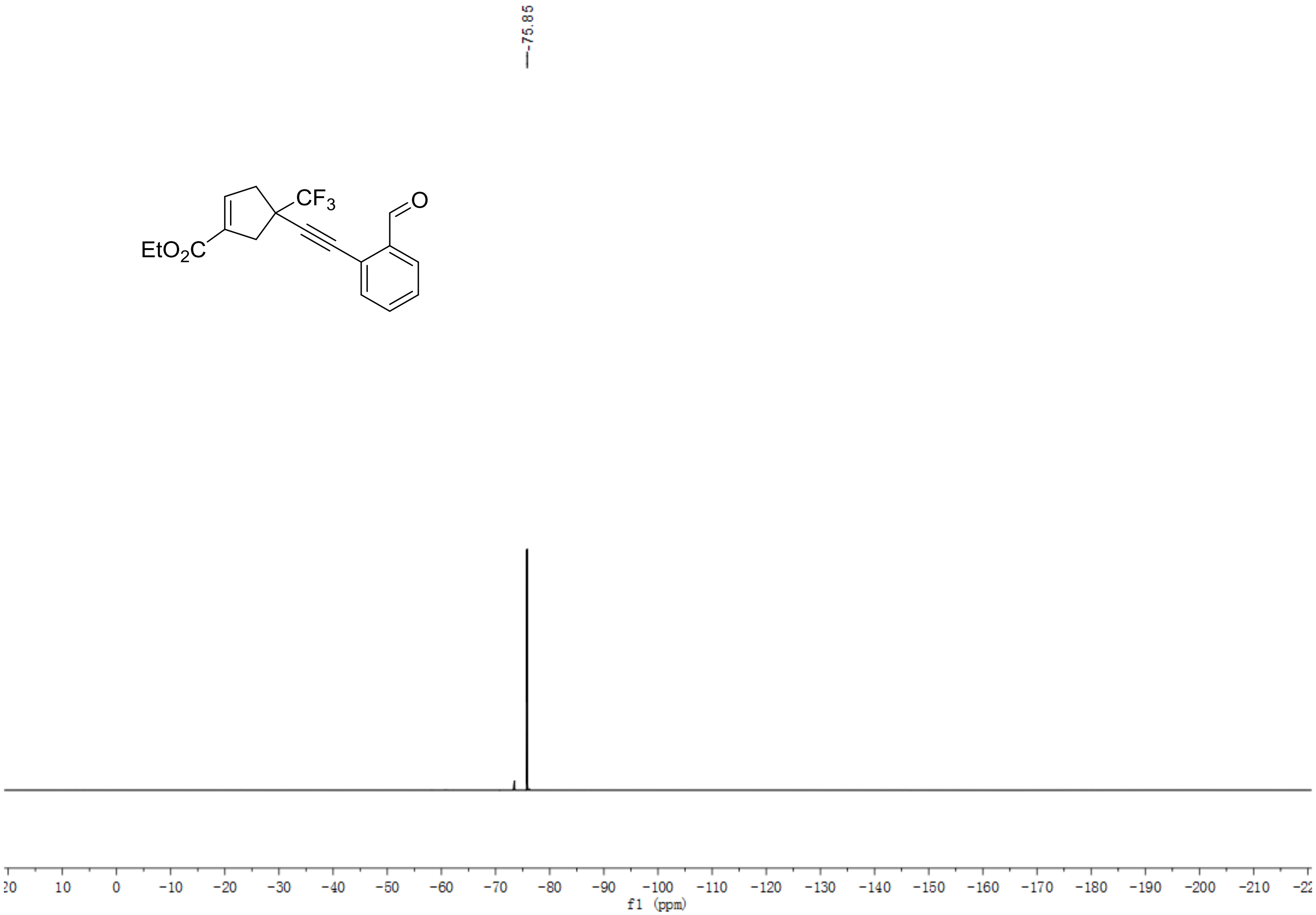
^{1}H NMR spectrum of product 3am (500 MHz, $CDCl_3$)



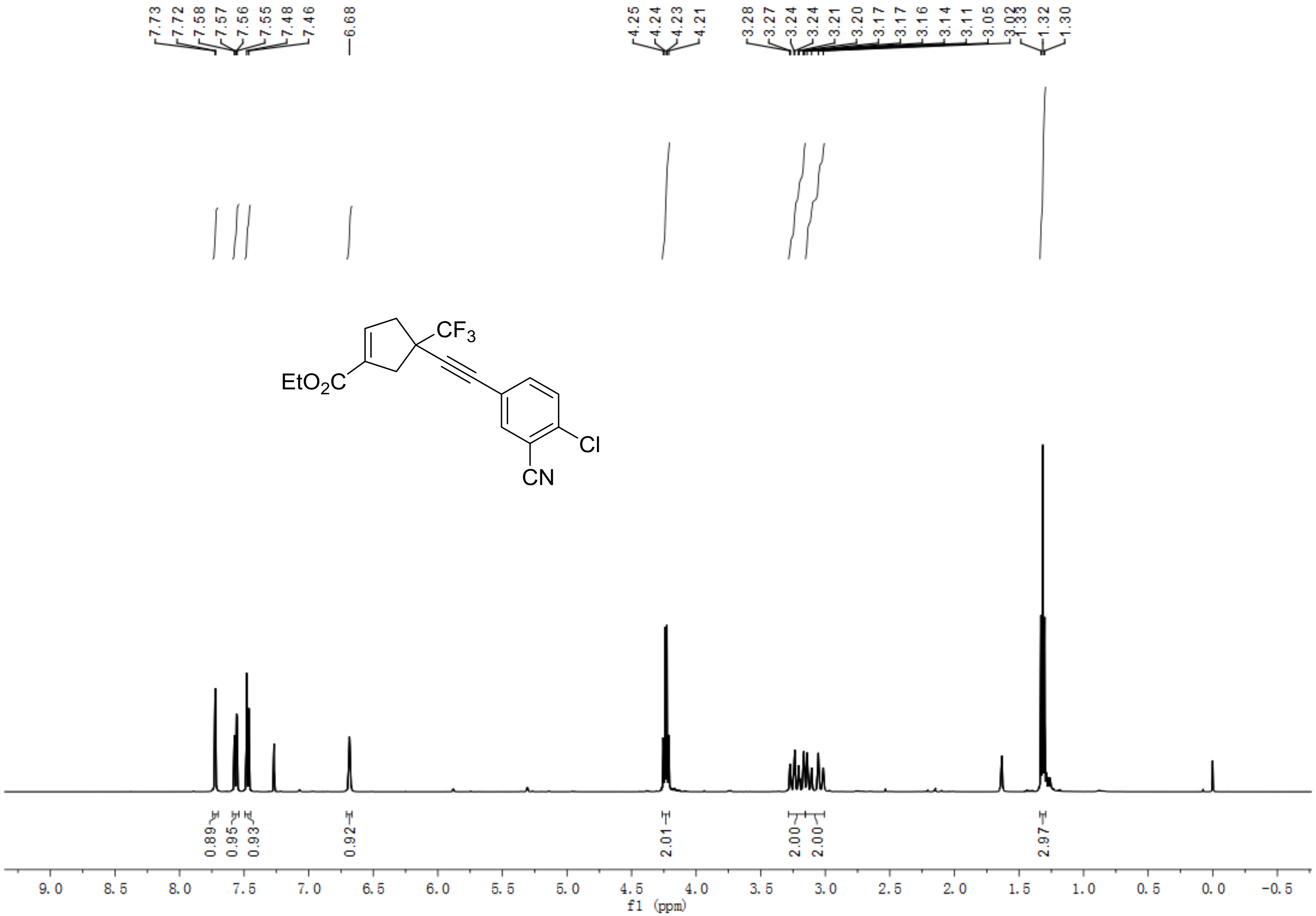
^{13}C NMR spectrum of product 3am (125 MHz, $CDCl_3$)



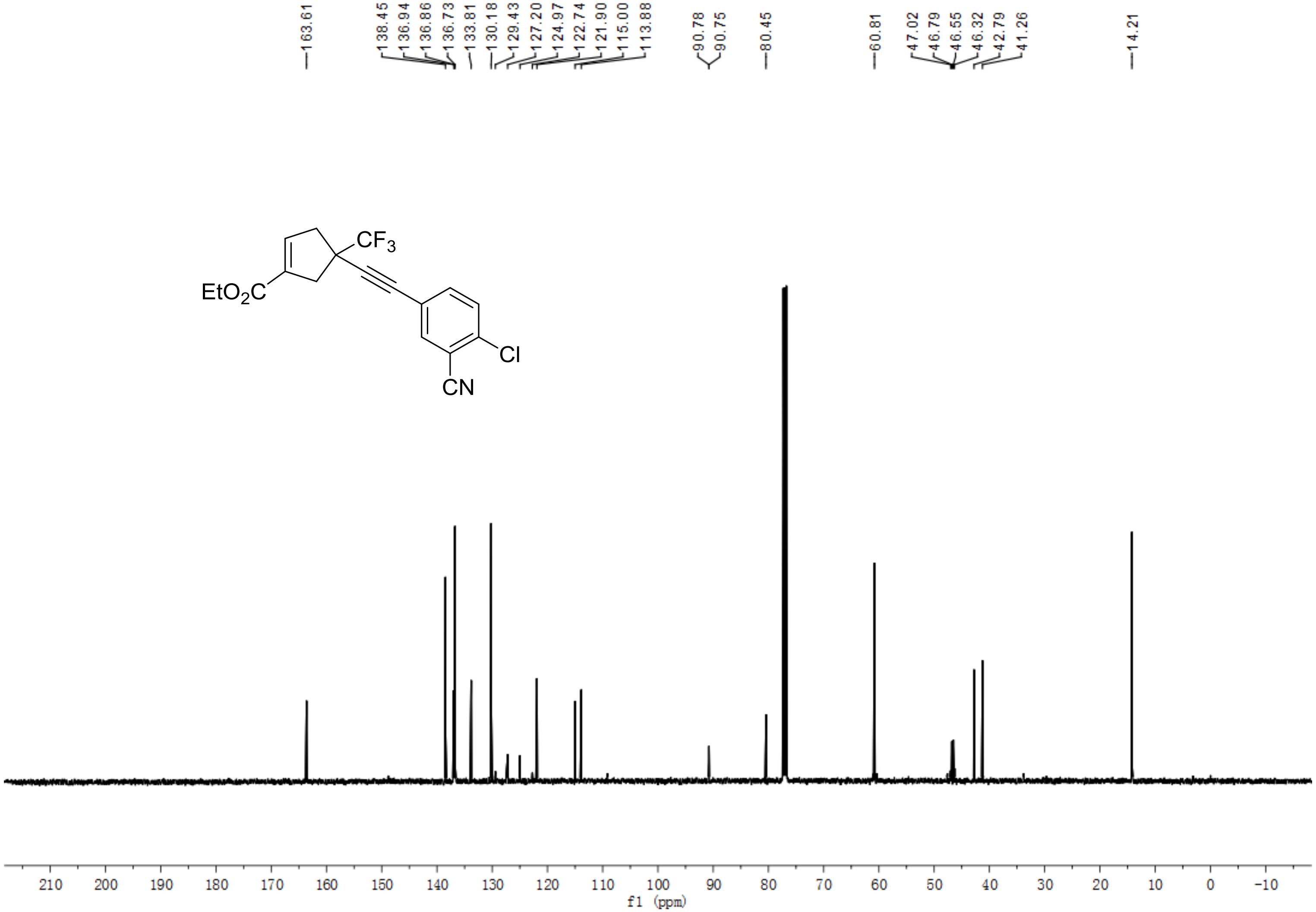
^{19}F NMR spectrum of product 3am (470 MHz, CDCl$_3$)



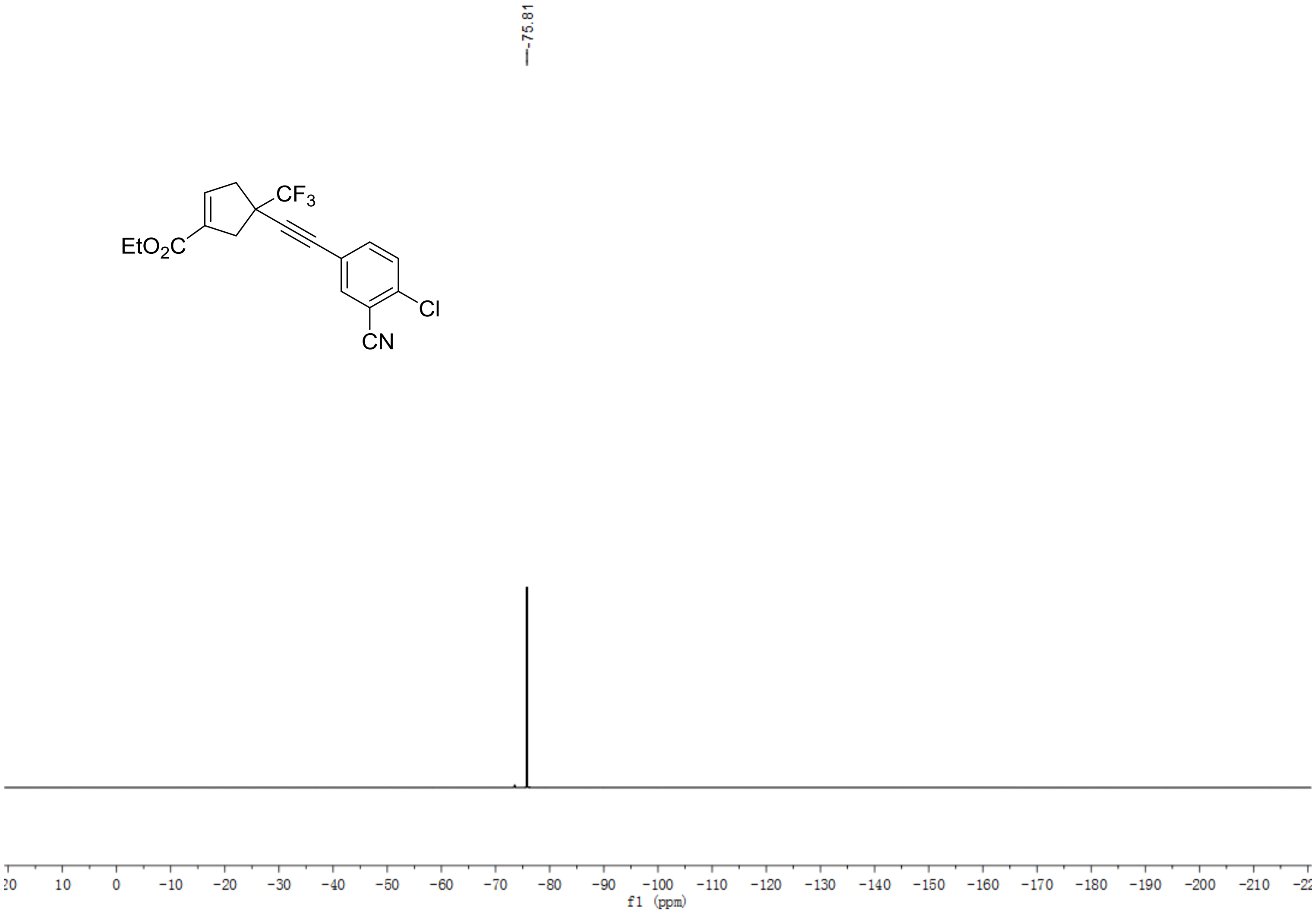
^{1}H NMR spectrum of product 3an (500 MHz, $CDCl_3$)



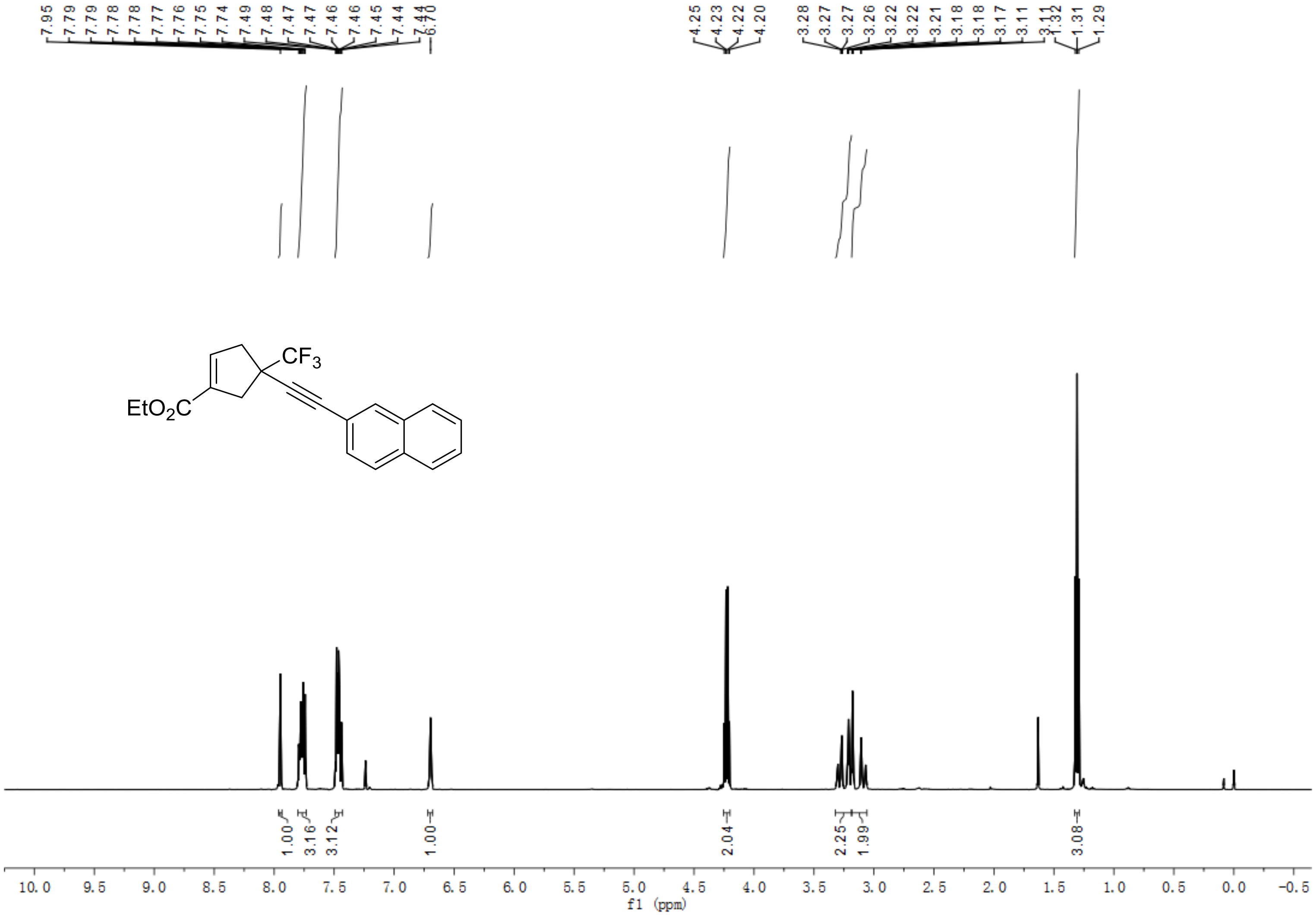
^{13}C NMR spectrum of product 3an (125 MHz, $CDCl_3$)



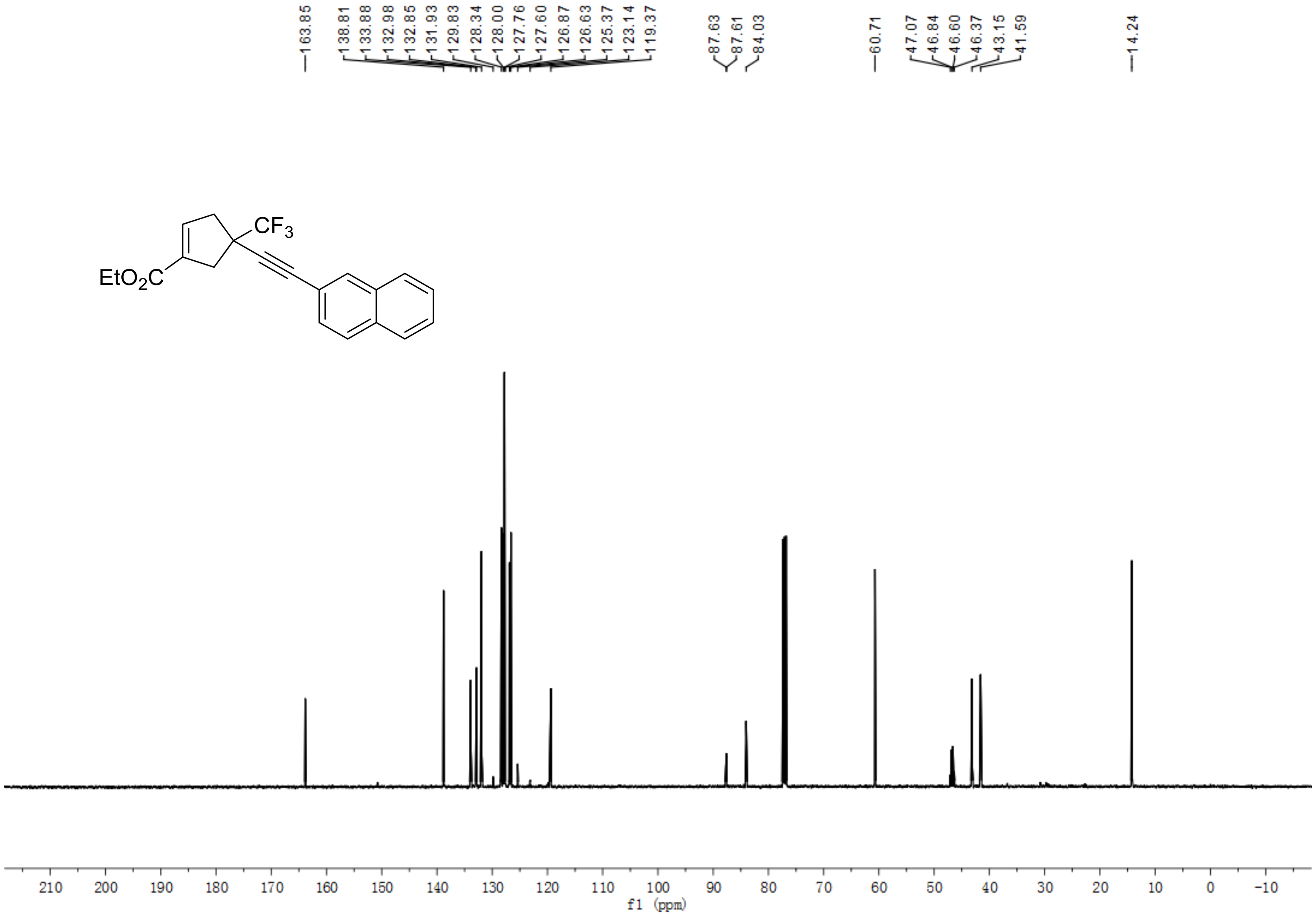
^{19}F NMR spectrum of product 3an (470 MHz, $CDCl_3$)



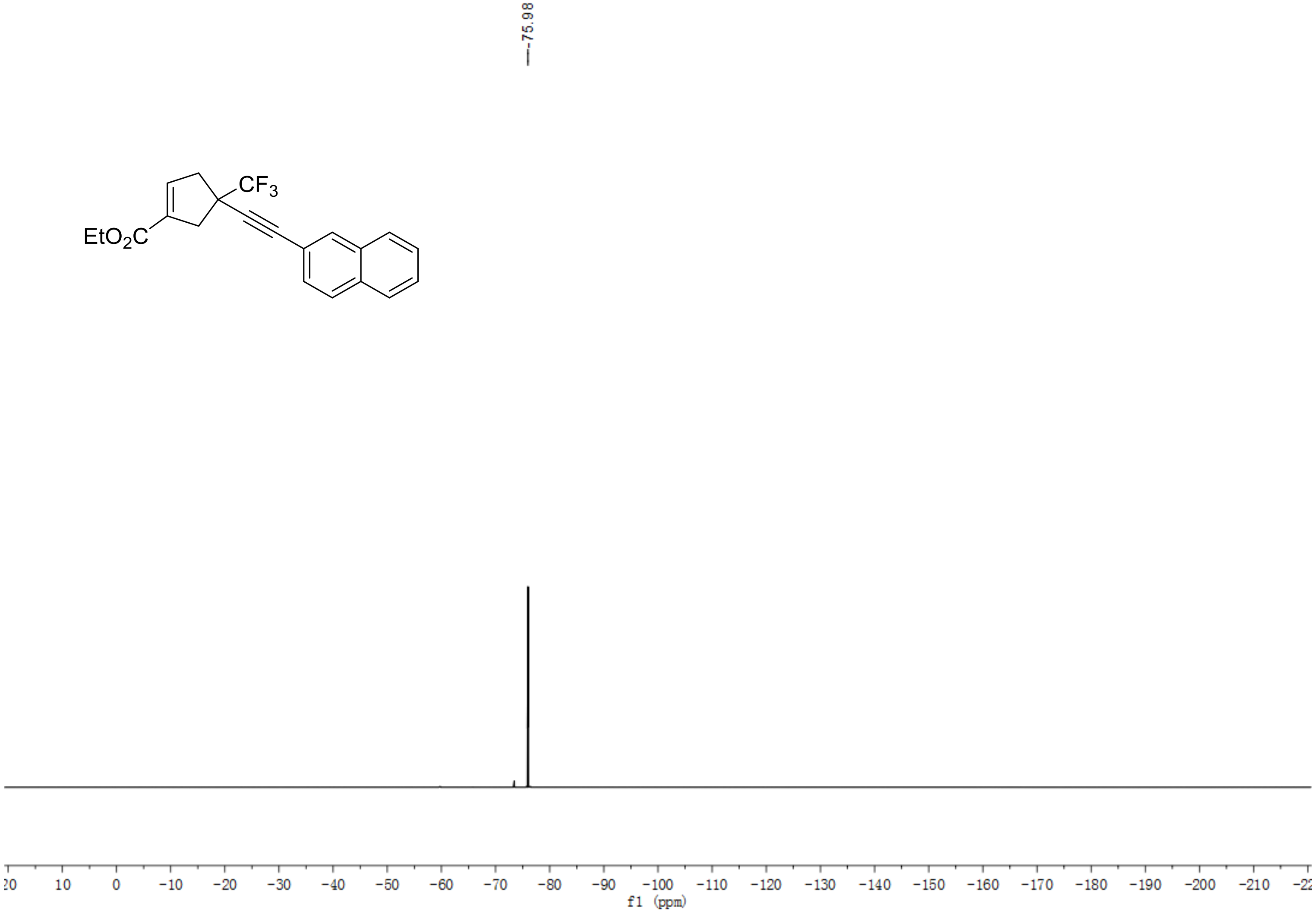
^{1}H NMR spectrum of product 3ao (500 MHz, CDCl$_3$)



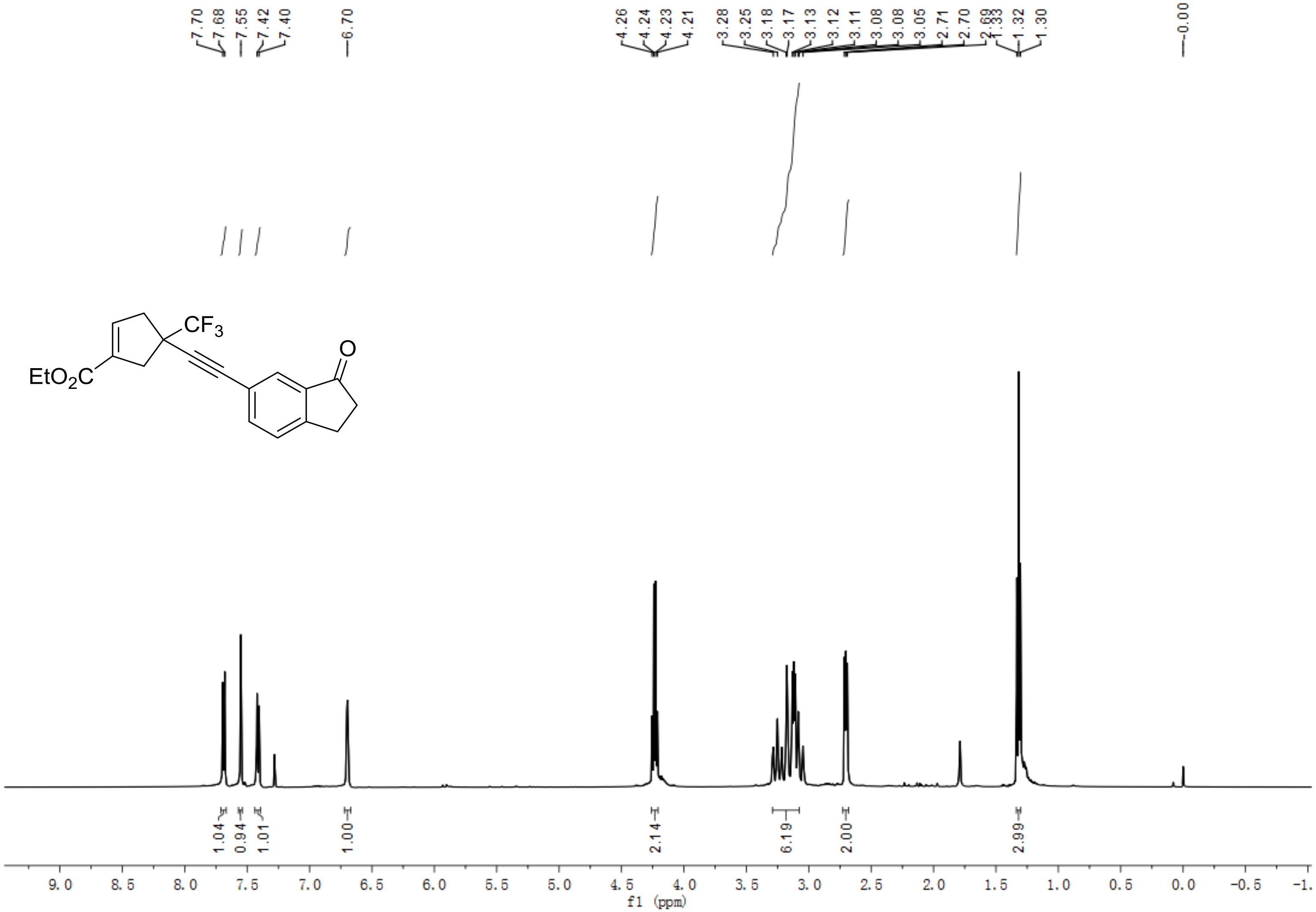
^{13}C NMR spectrum of product 3ao (125 MHz, $CDCl_3$)



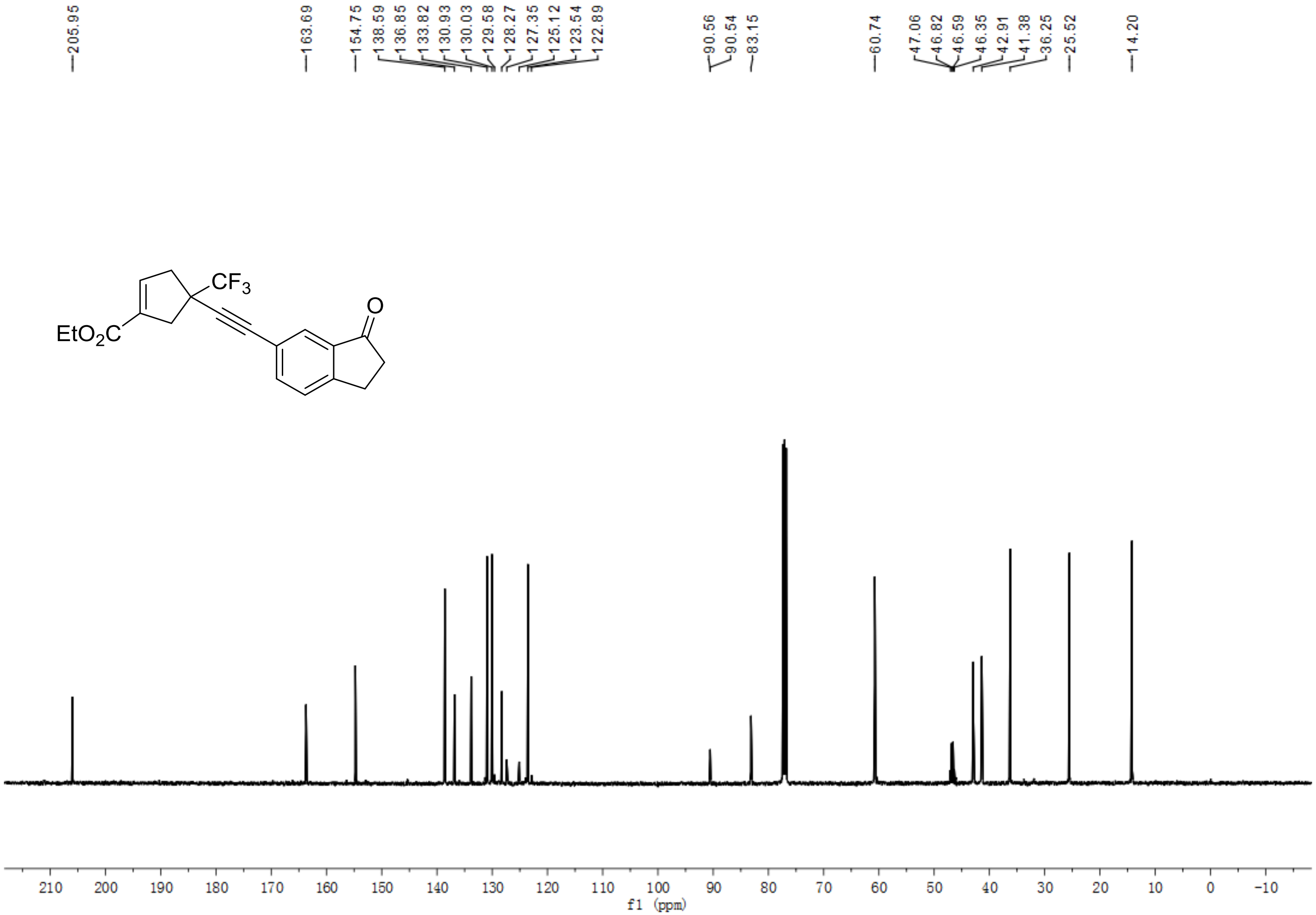
^{19}**F NMR spectrum of product 3ao (470 MHz, CDCl$_3$)**



^{1}H NMR spectrum of product 3ap (500 MHz, $CDCl_3$)

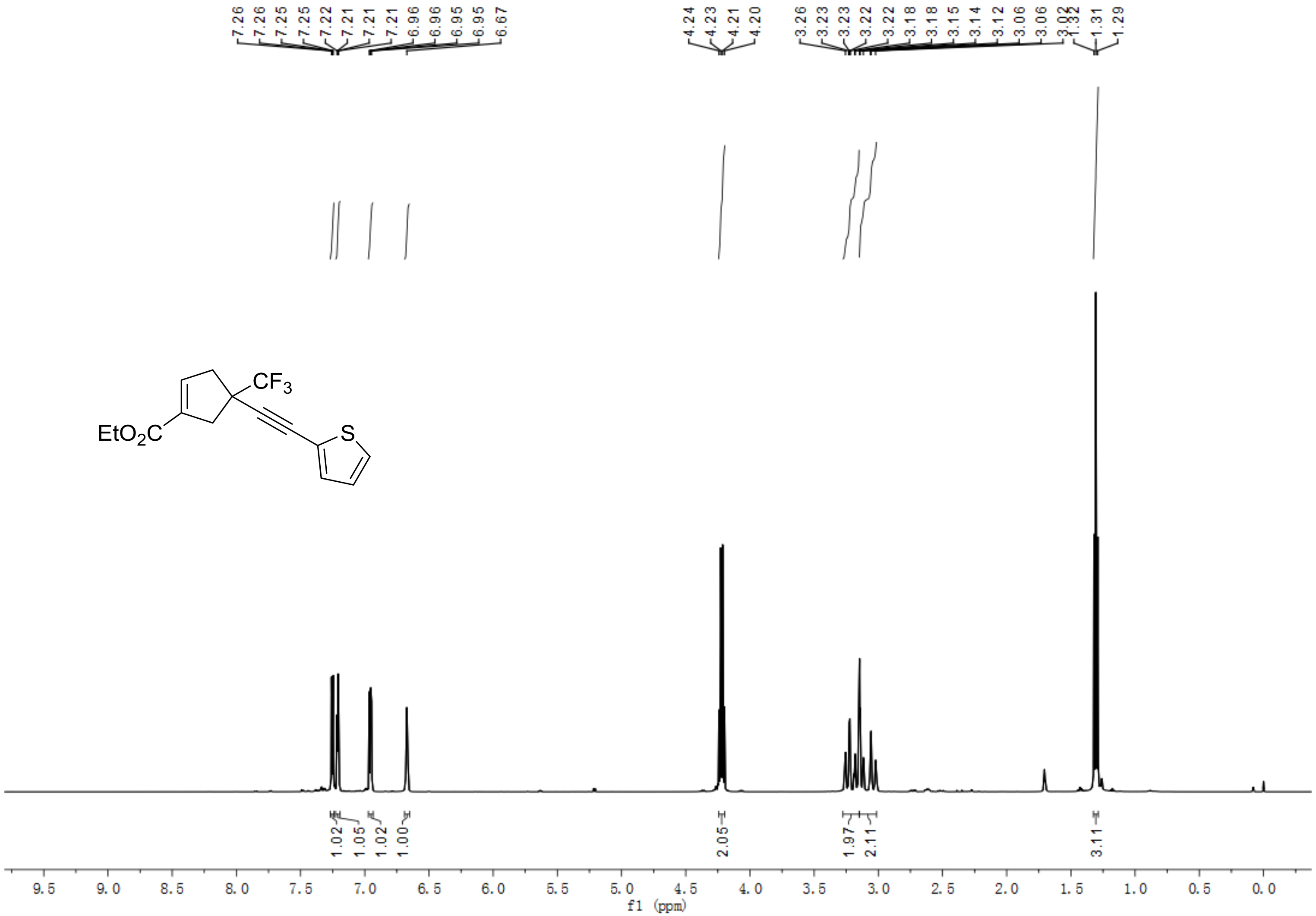


^{13}C NMR spectrum of product 3ap (125 MHz, CDCl$_3$)

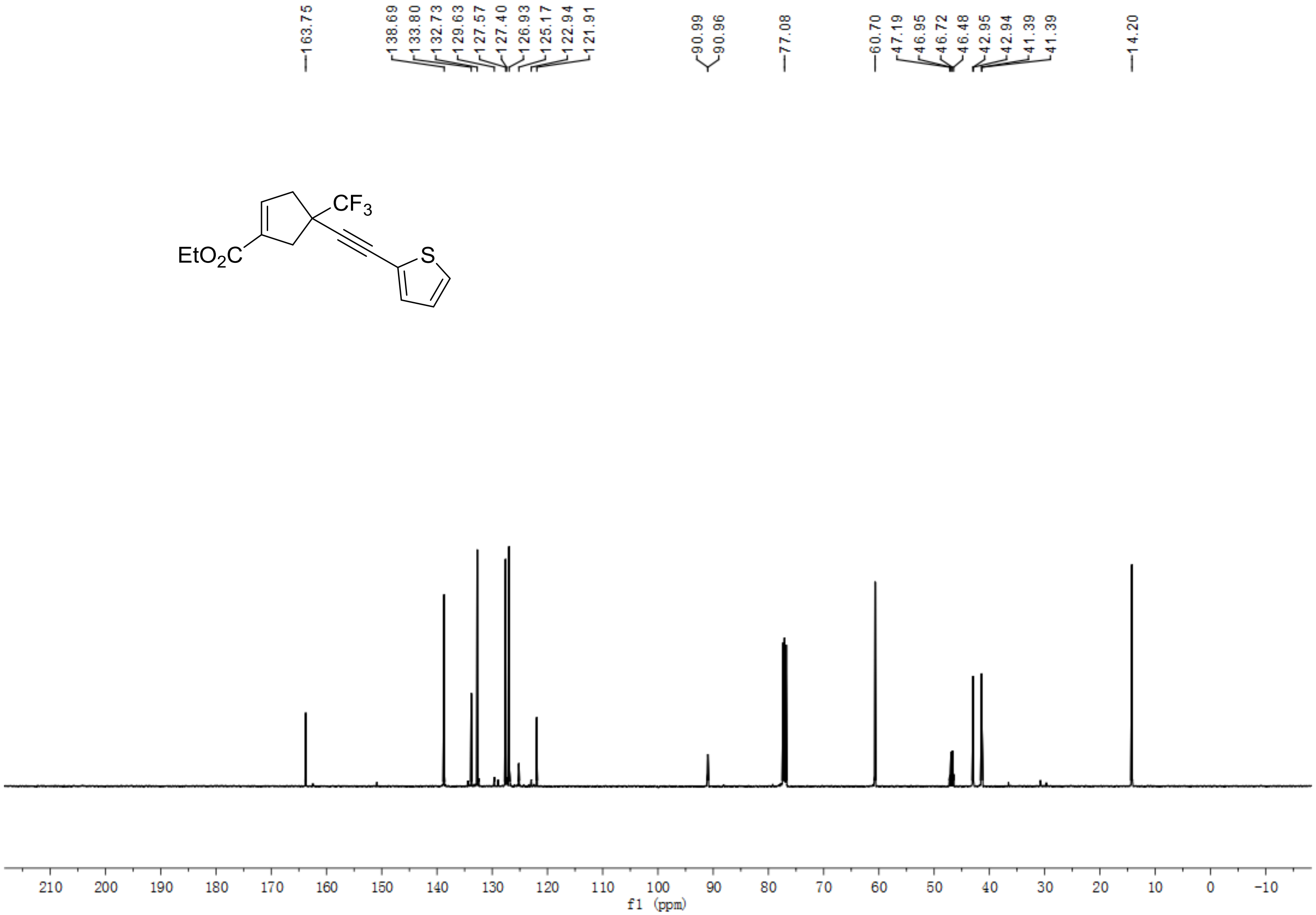


^{19}F NMR spectrum of product 3ap (470 MHz, $CDCl_3$)

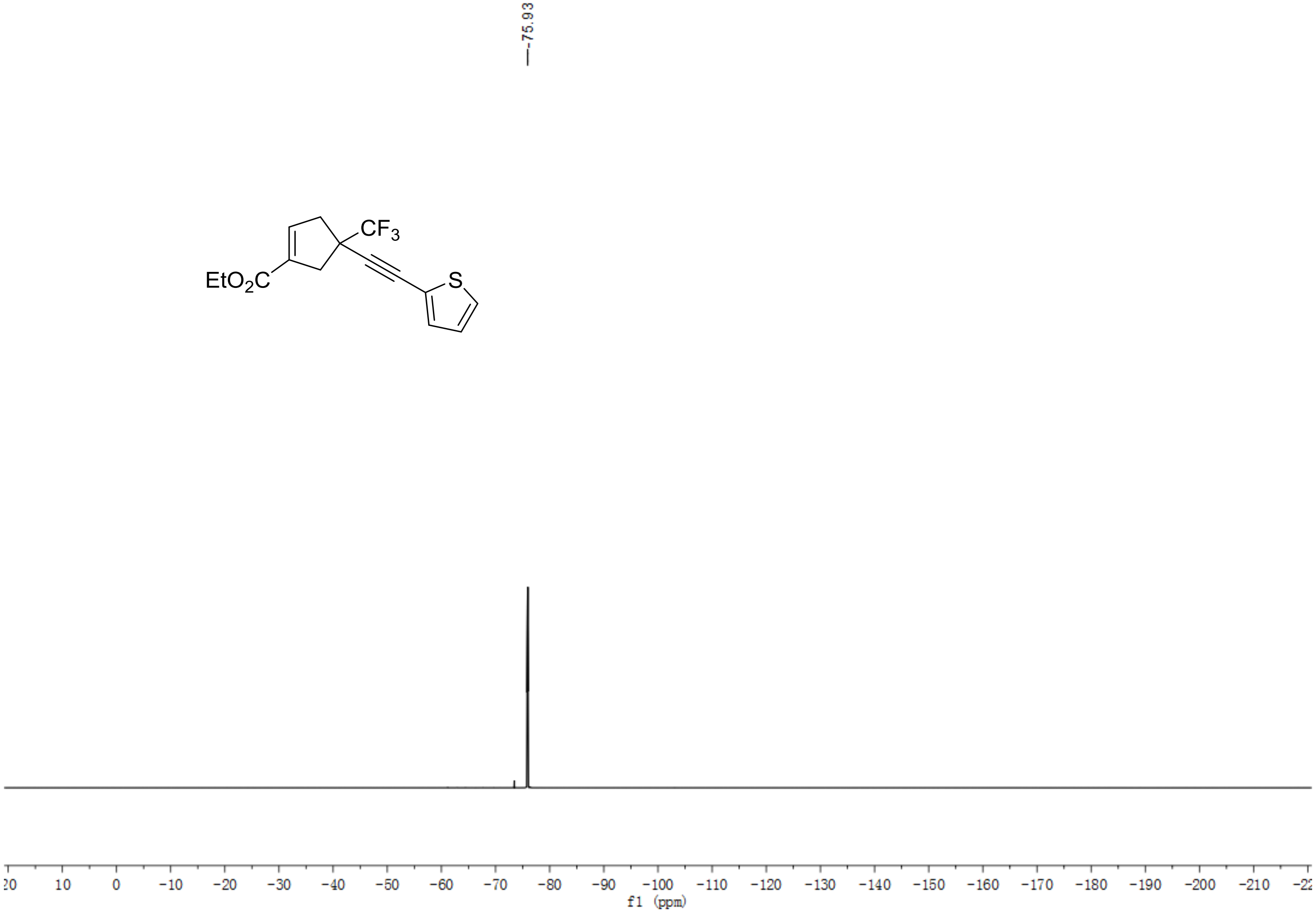
^{1}H NMR spectrum of product 3aq (500 MHz, $CDCl_3$)



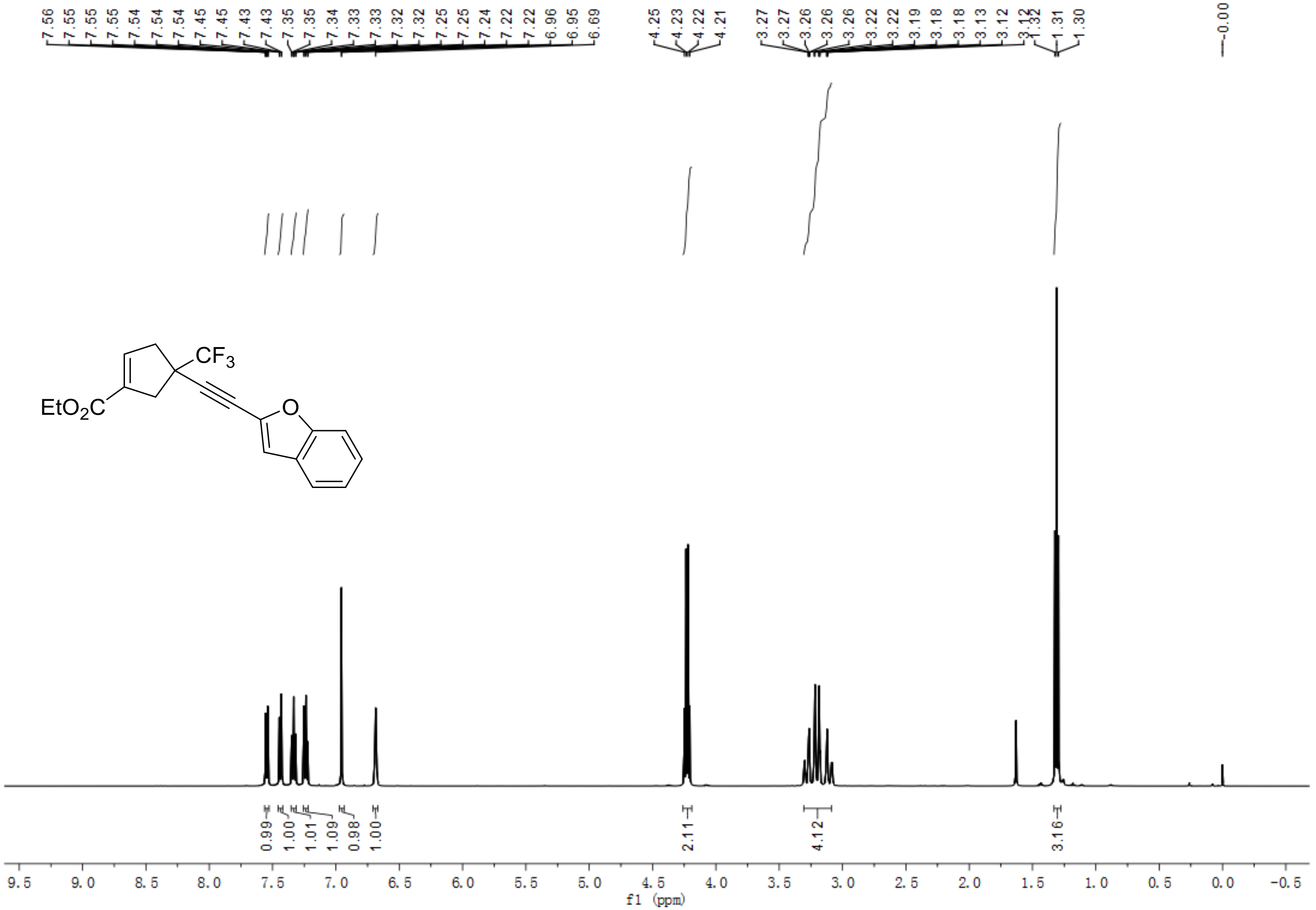
^{13}C NMR spectrum of product 3aq (125 MHz, $CDCl_3$)



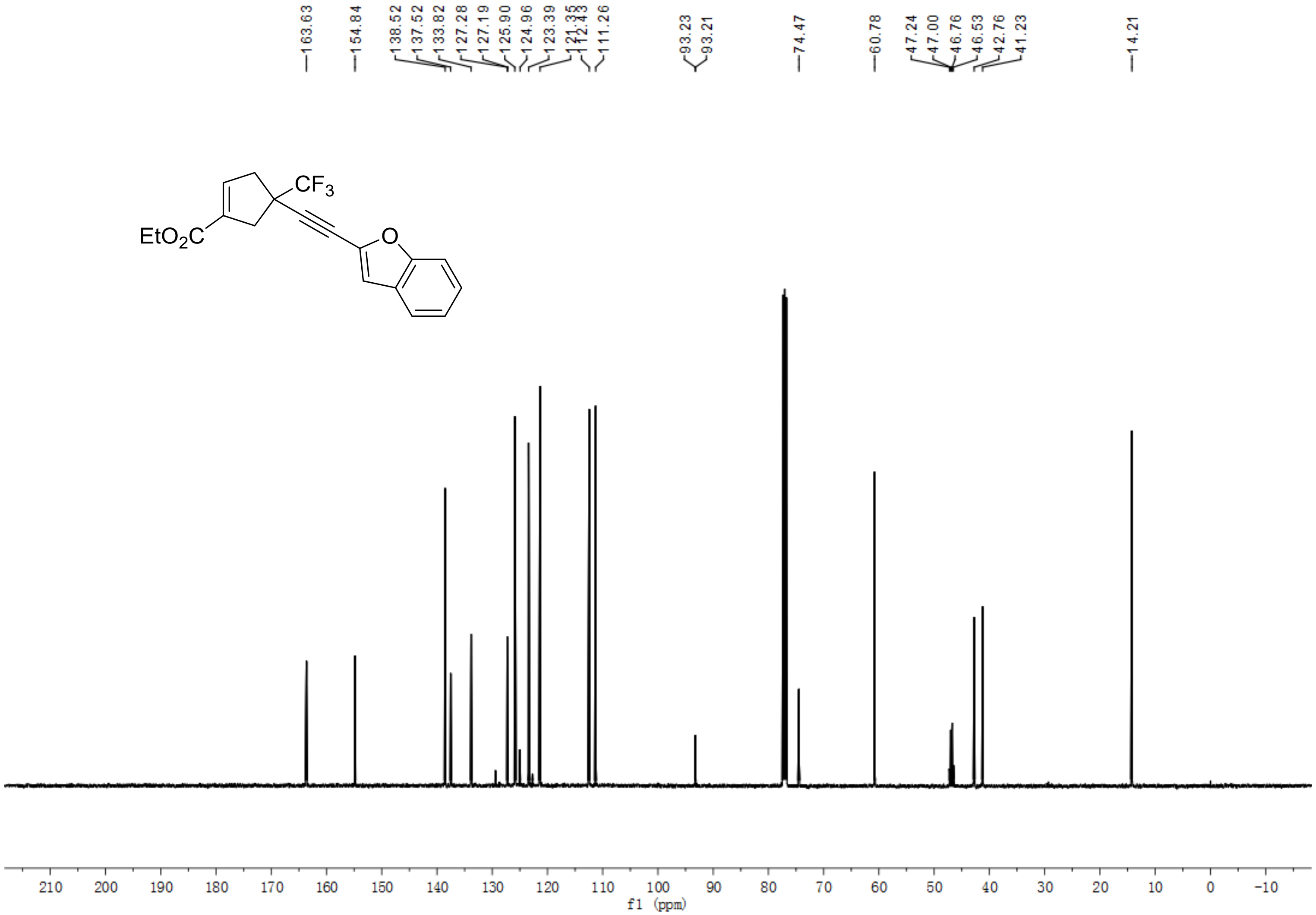
^{19}F NMR spectrum of product 3aq (470 MHz, $CDCl_3$)



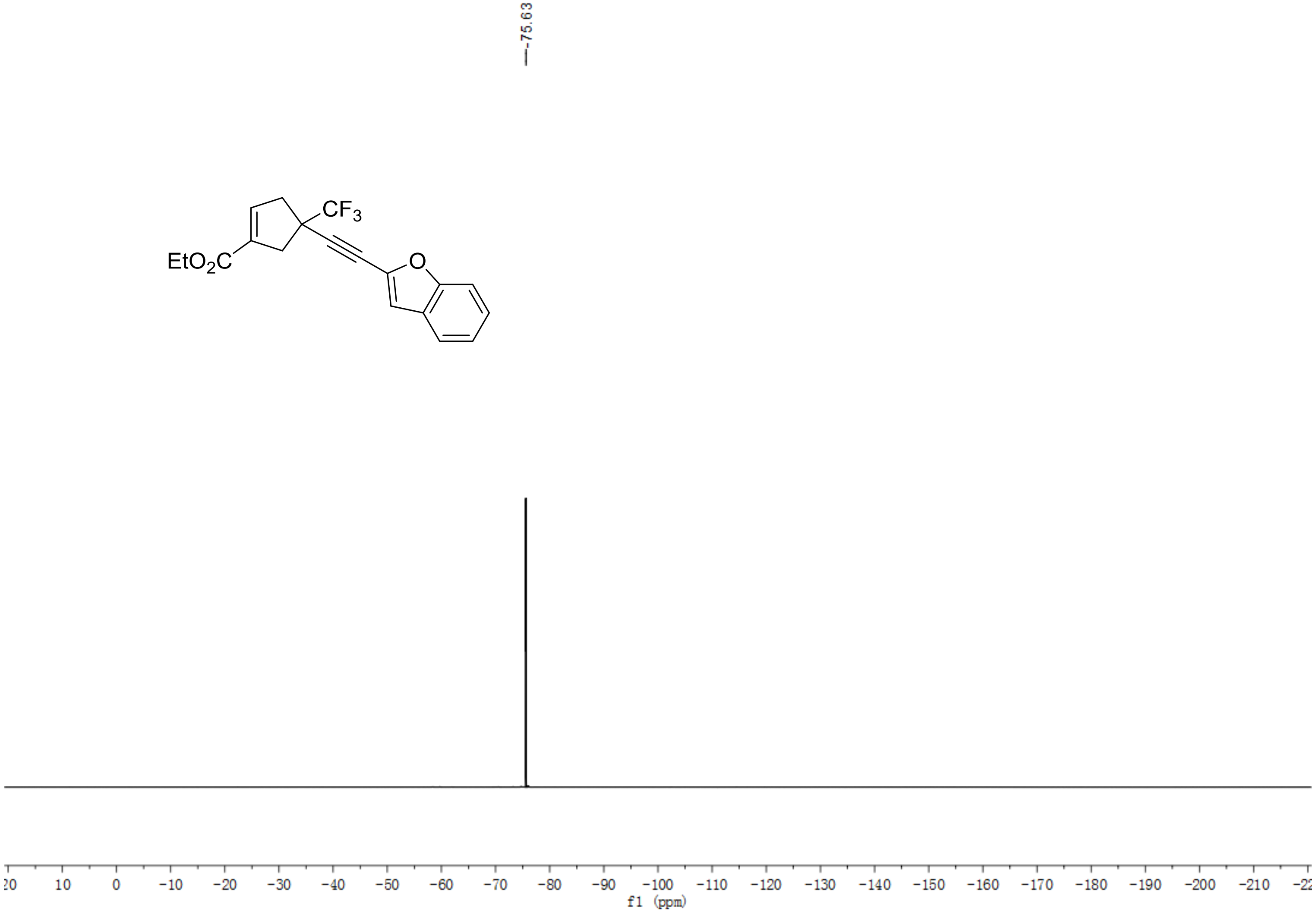
^{1}H NMR spectrum of product 3ar (500 MHz, $CDCl_3$)



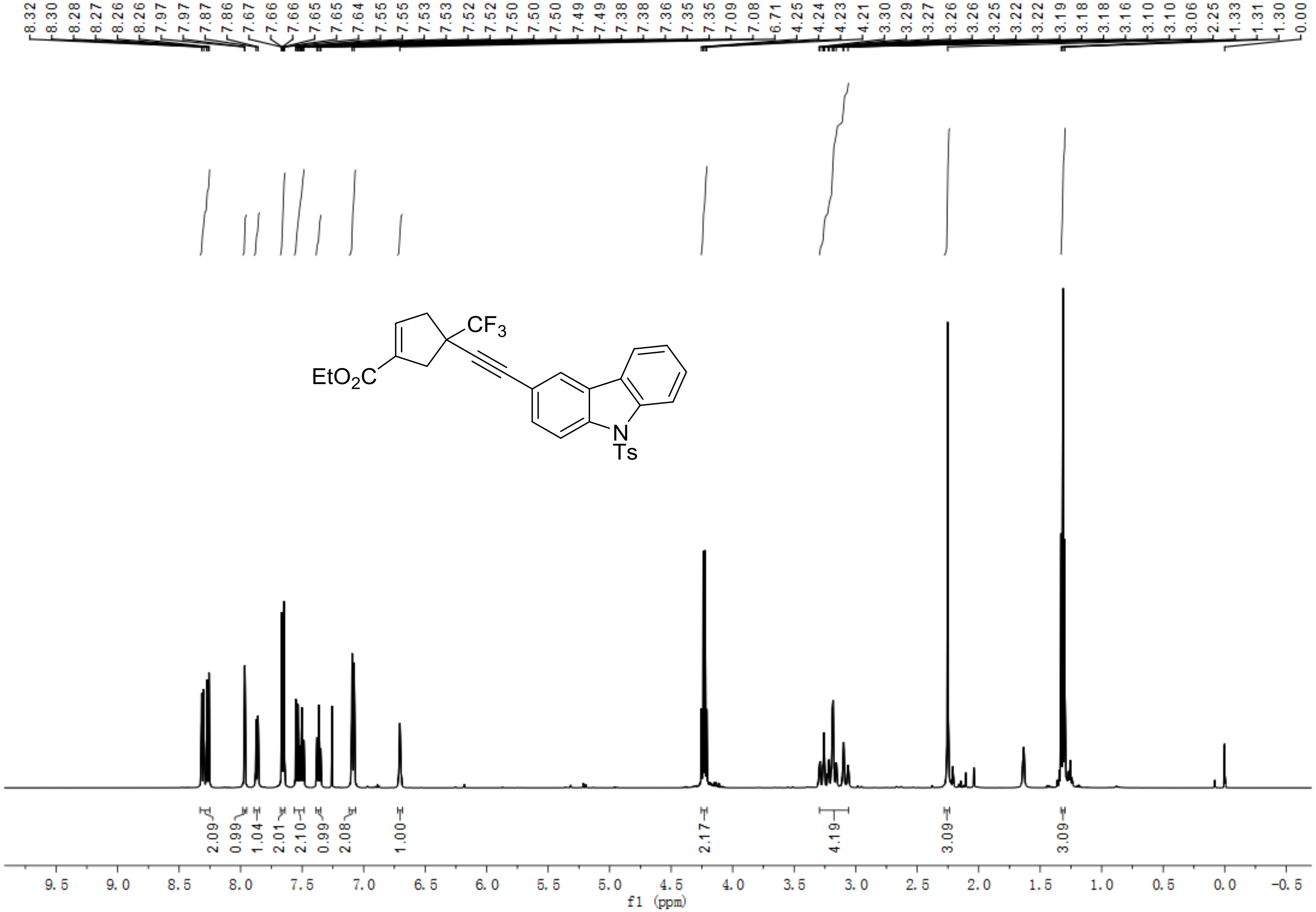
^{13}C NMR spectrum of product 3ar (125 MHz, $CDCl_3$)



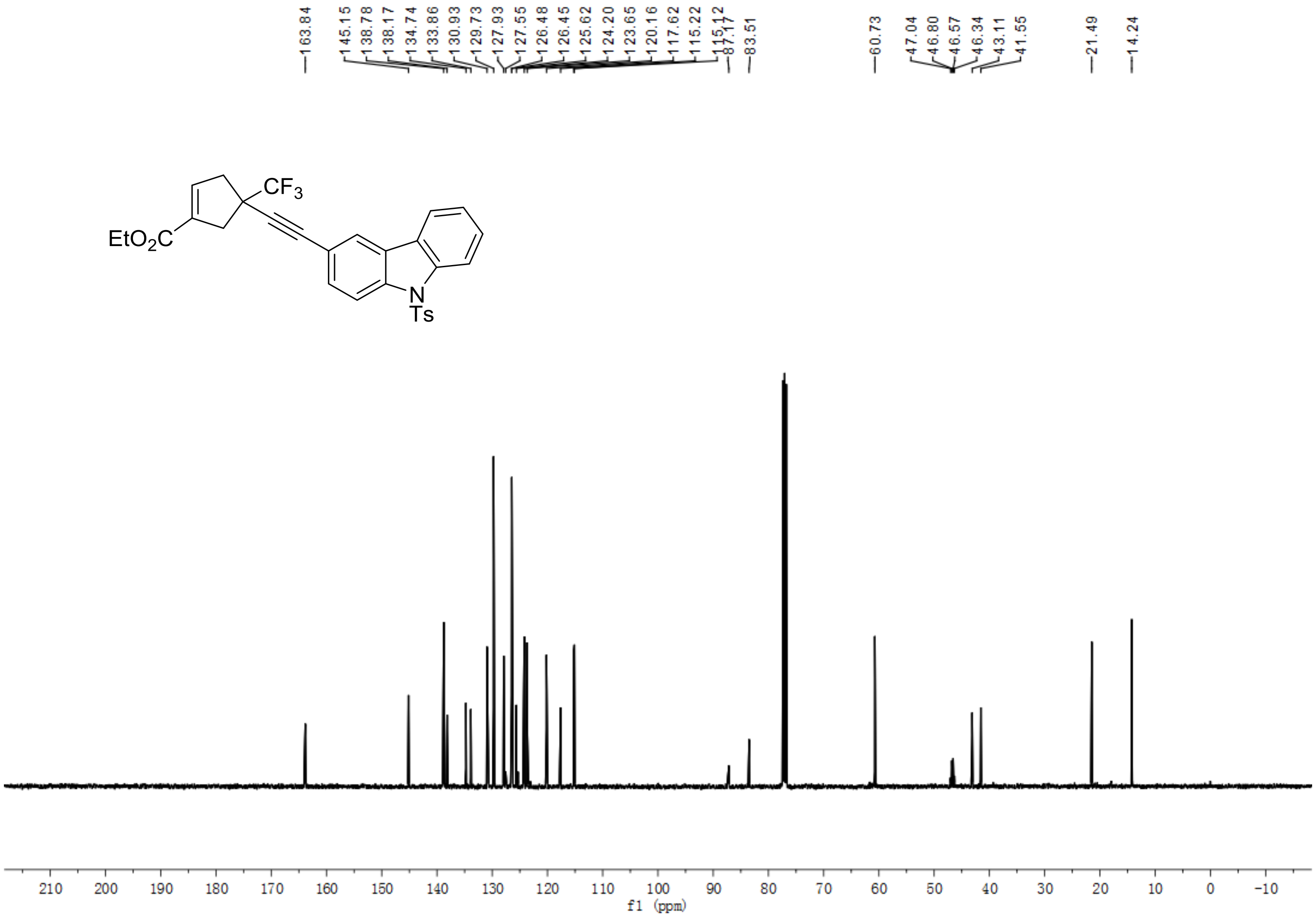
^{19}F NMR spectrum of product 3ar (470 MHz, $CDCl_3$)



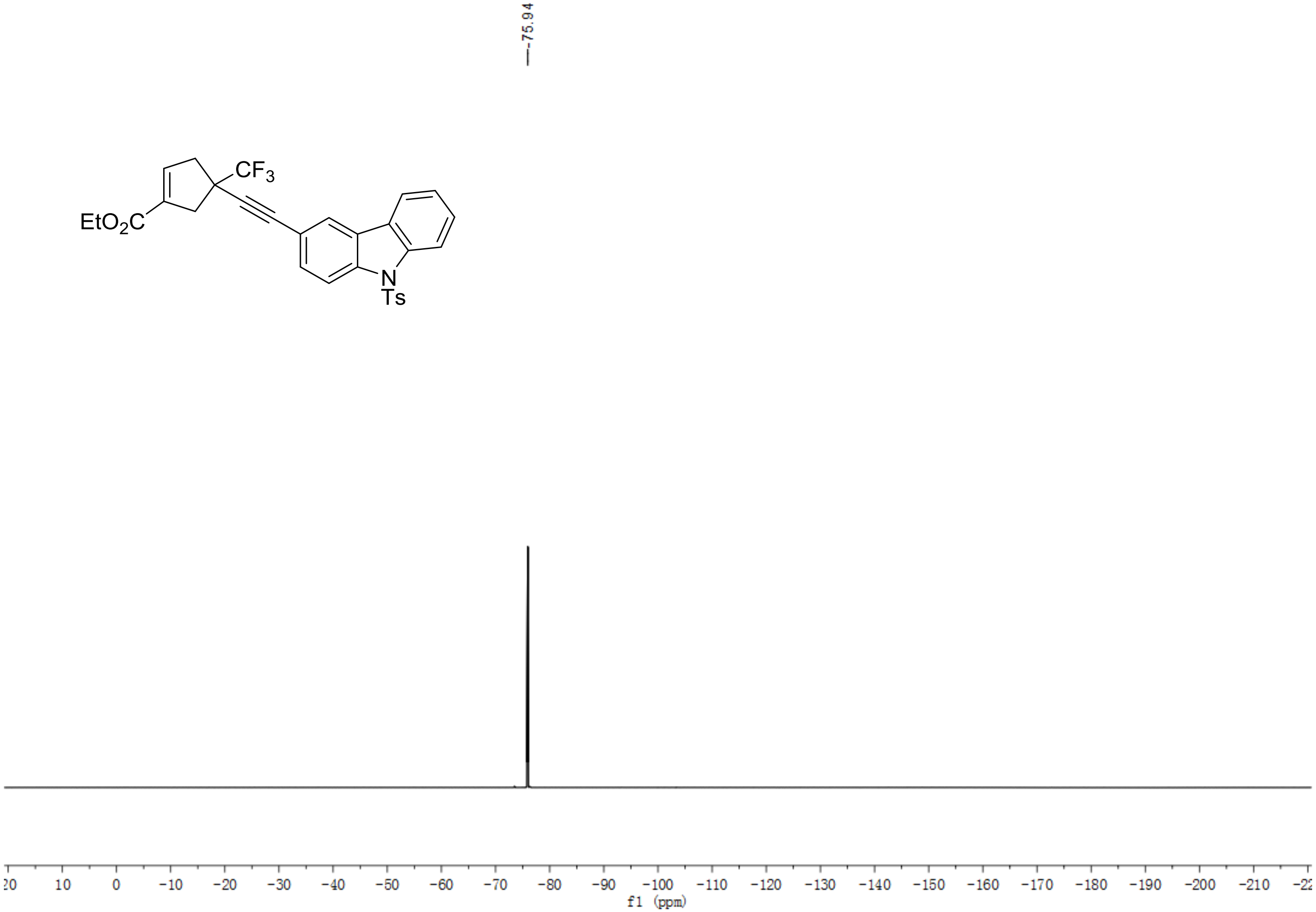
^{1}H NMR spectrum of product 3as (500 MHz, $CDCl_3$)



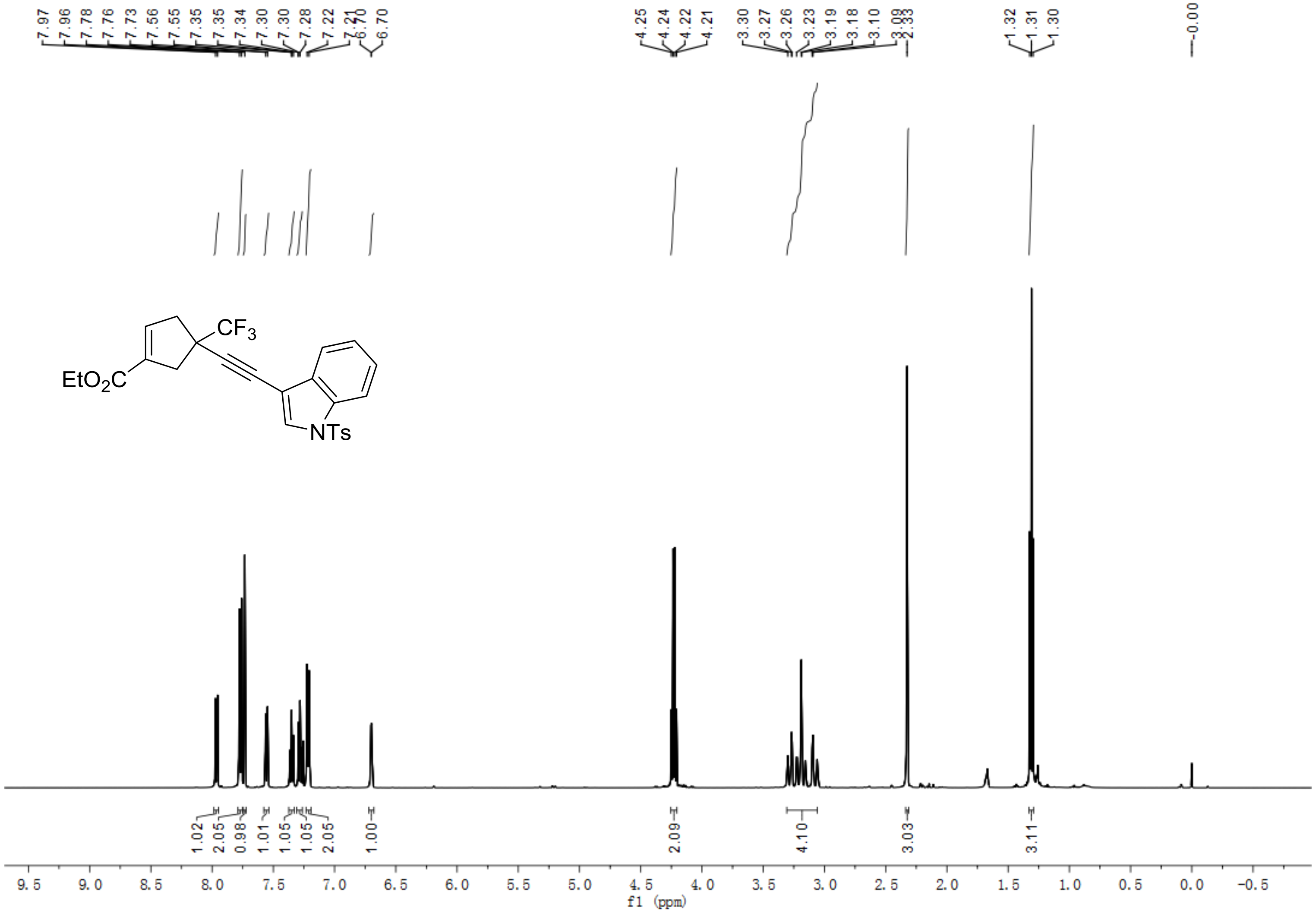
^{13}C NMR spectrum of product 3as (125 MHz, CDCl$_3$)



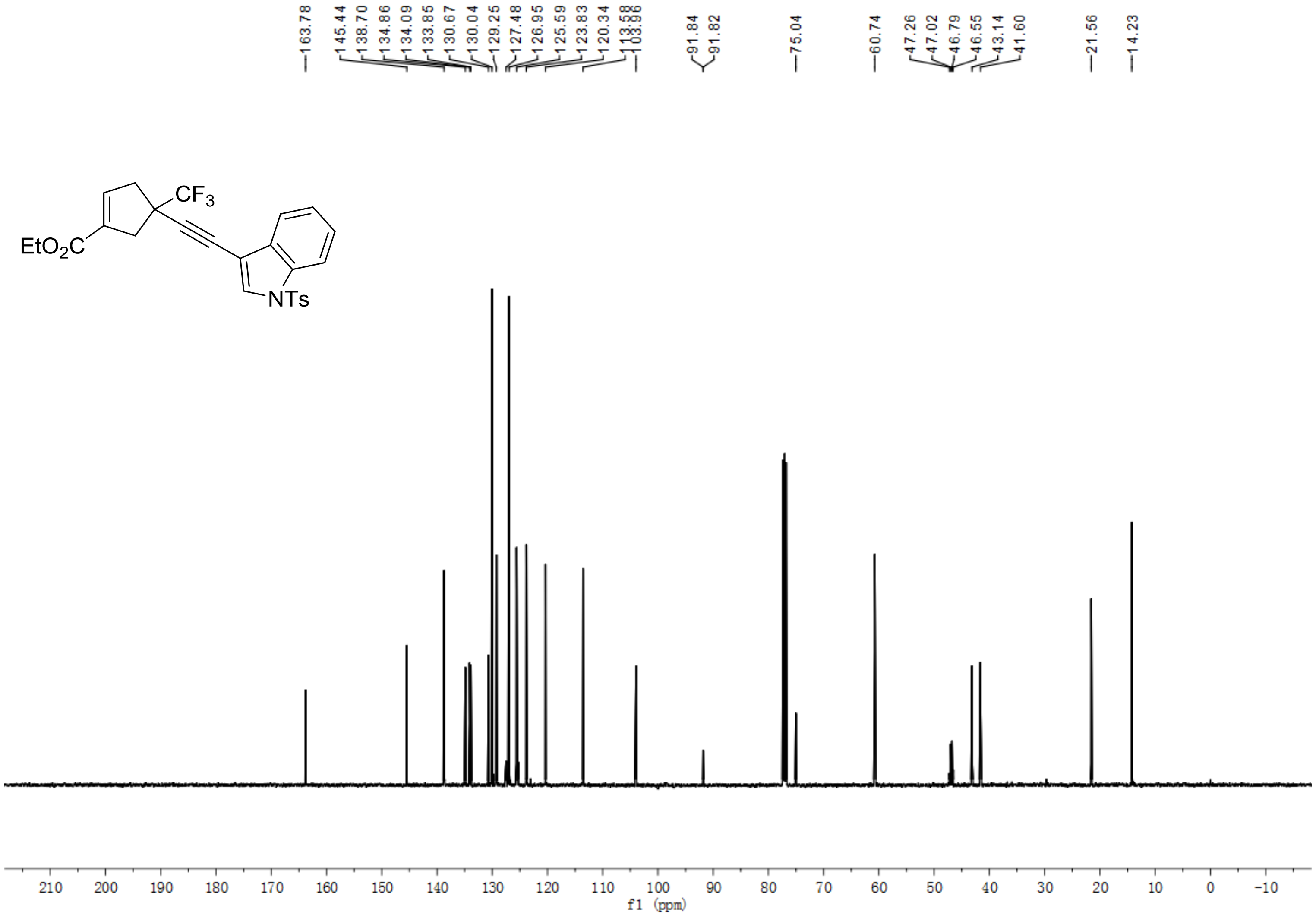
^{19}F NMR spectrum of product 3as (470 MHz, $CDCl_3$)



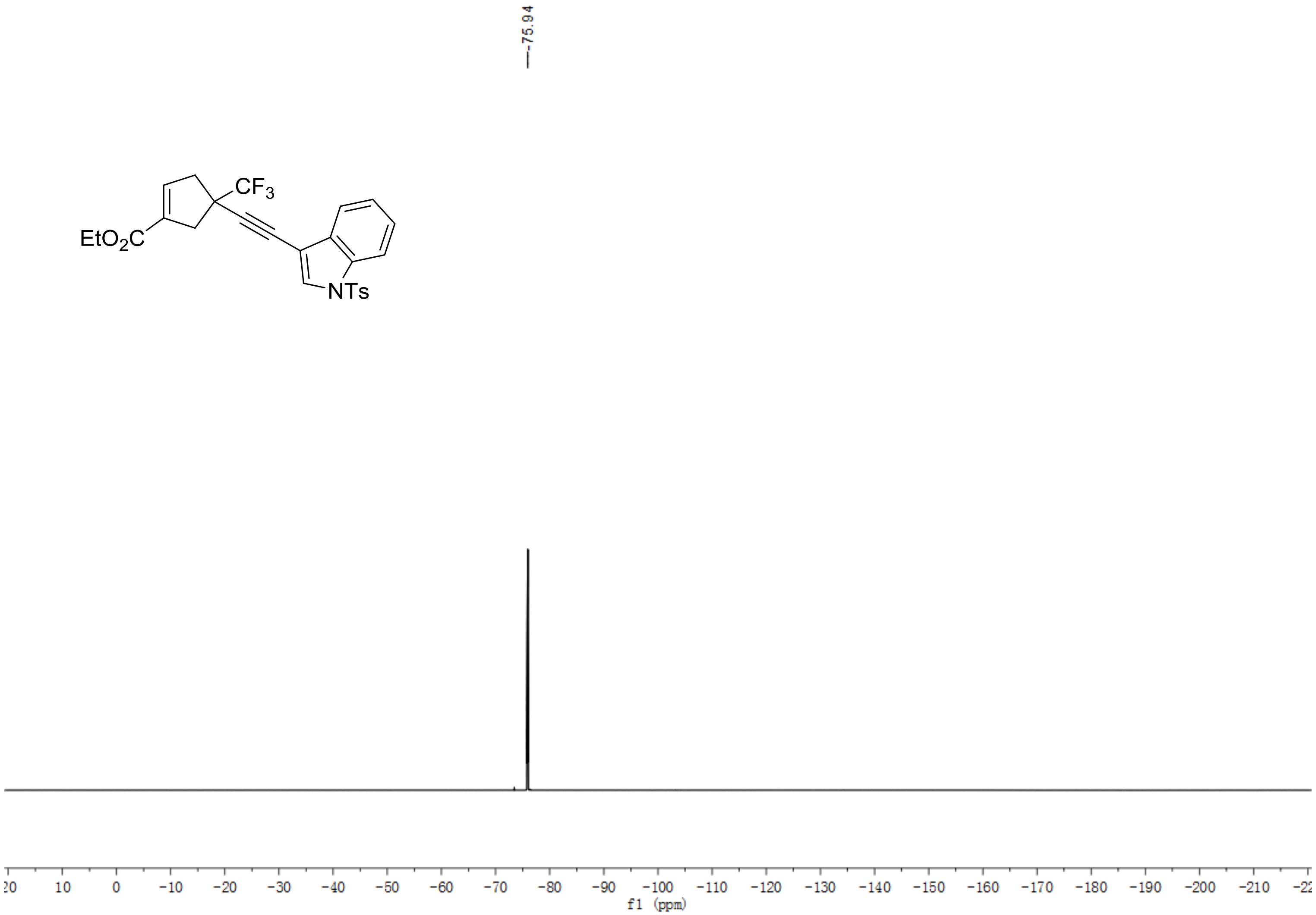
^{1}H NMR spectrum of product 3at (500 MHz, $CDCl_3$)



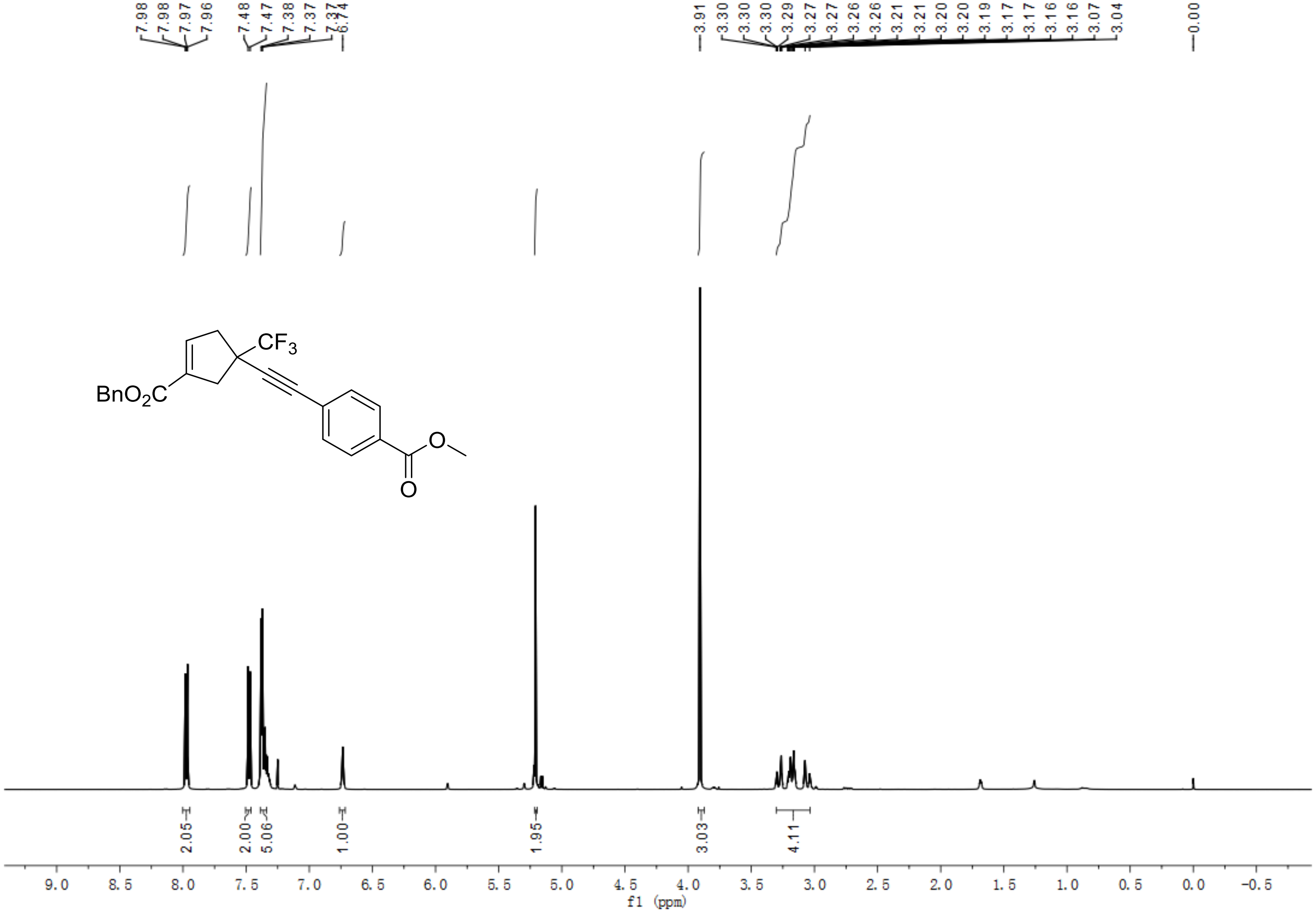
^{13}C NMR spectrum of product 3at (125 MHz, CDCl$_3$)



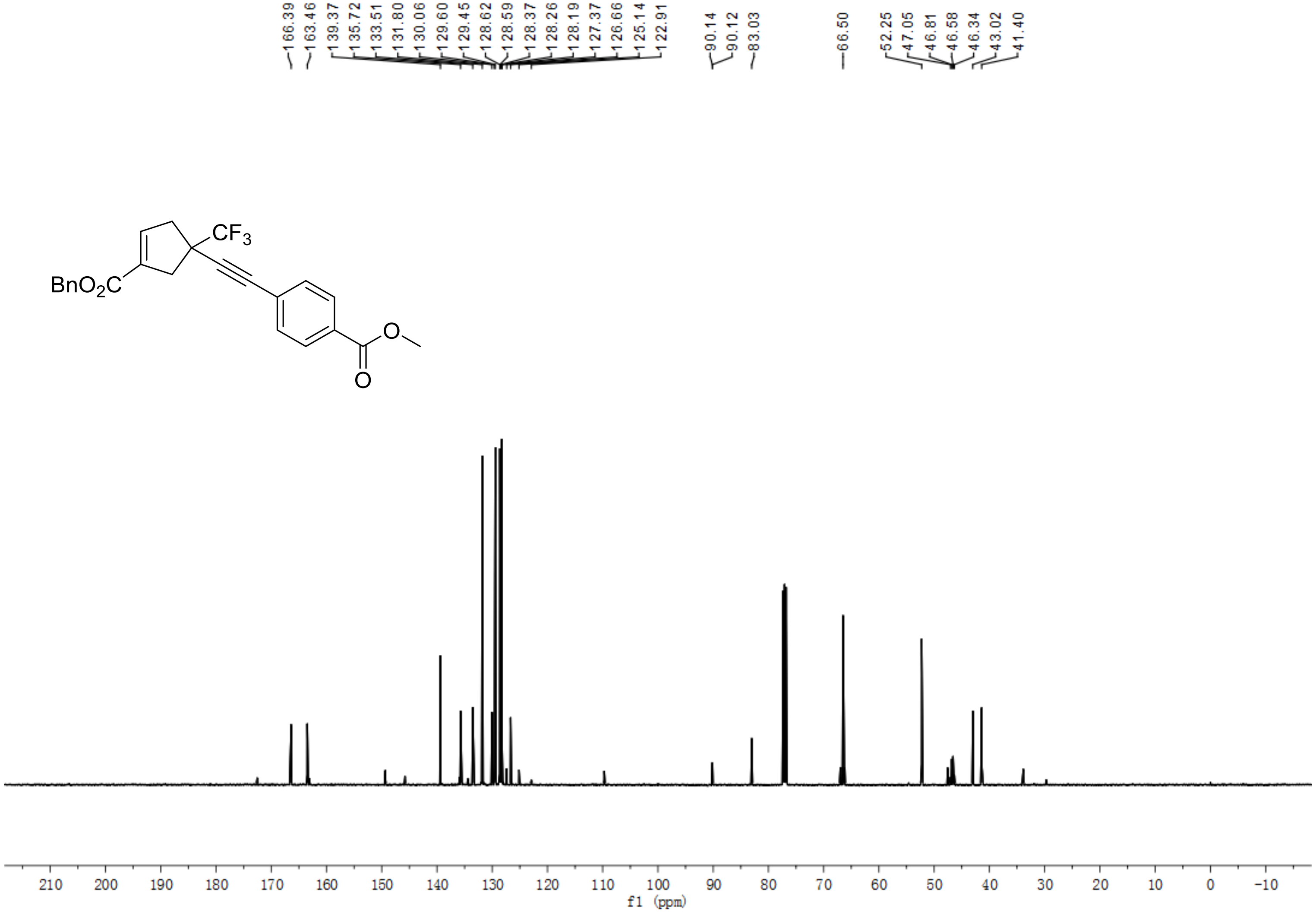
^{19}**F NMR spectrum of product 3at (470 MHz, CDCl$_3$)**



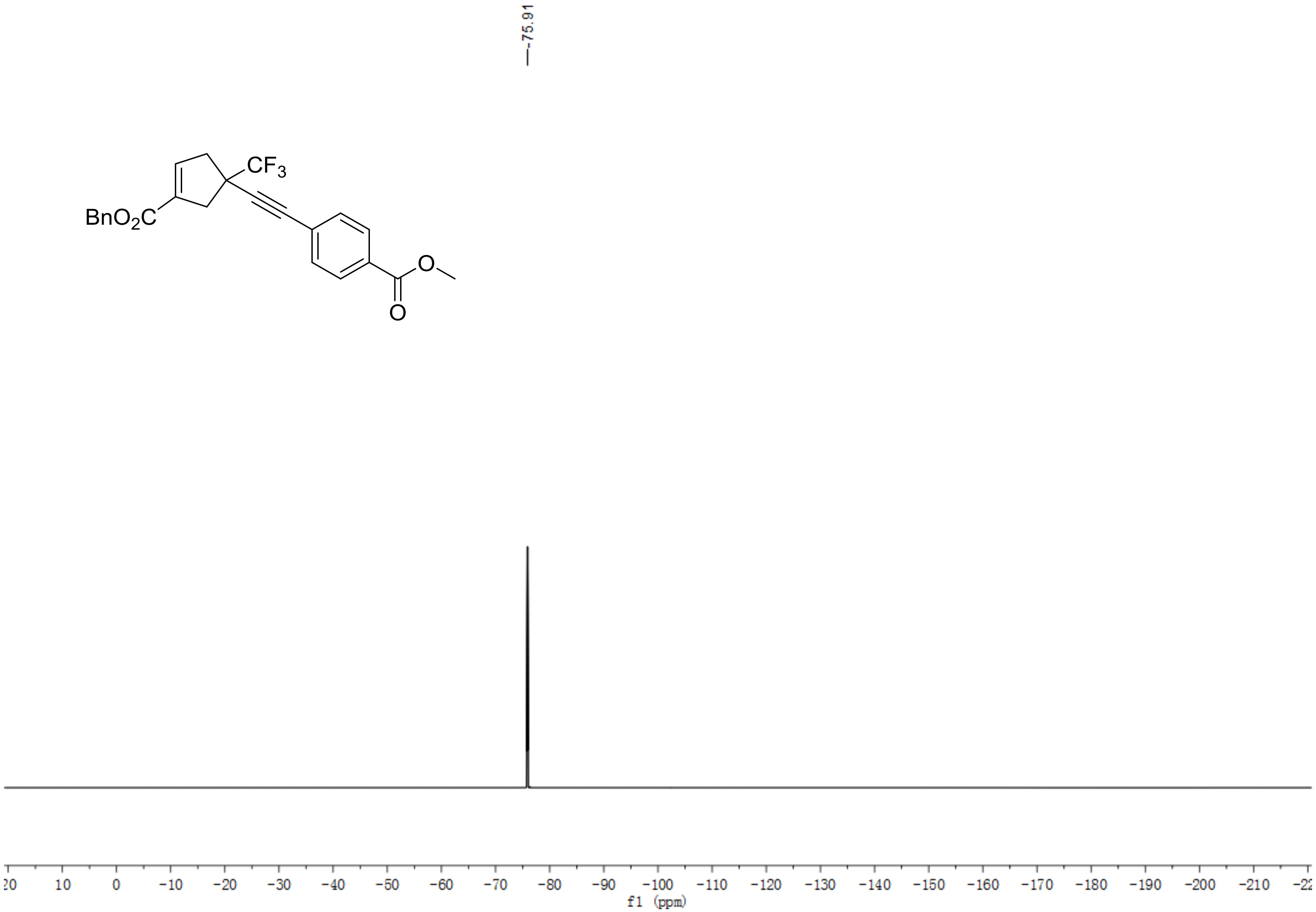
^{1}H NMR spectrum of product 3ba (500 MHz, CDCl$_3$)



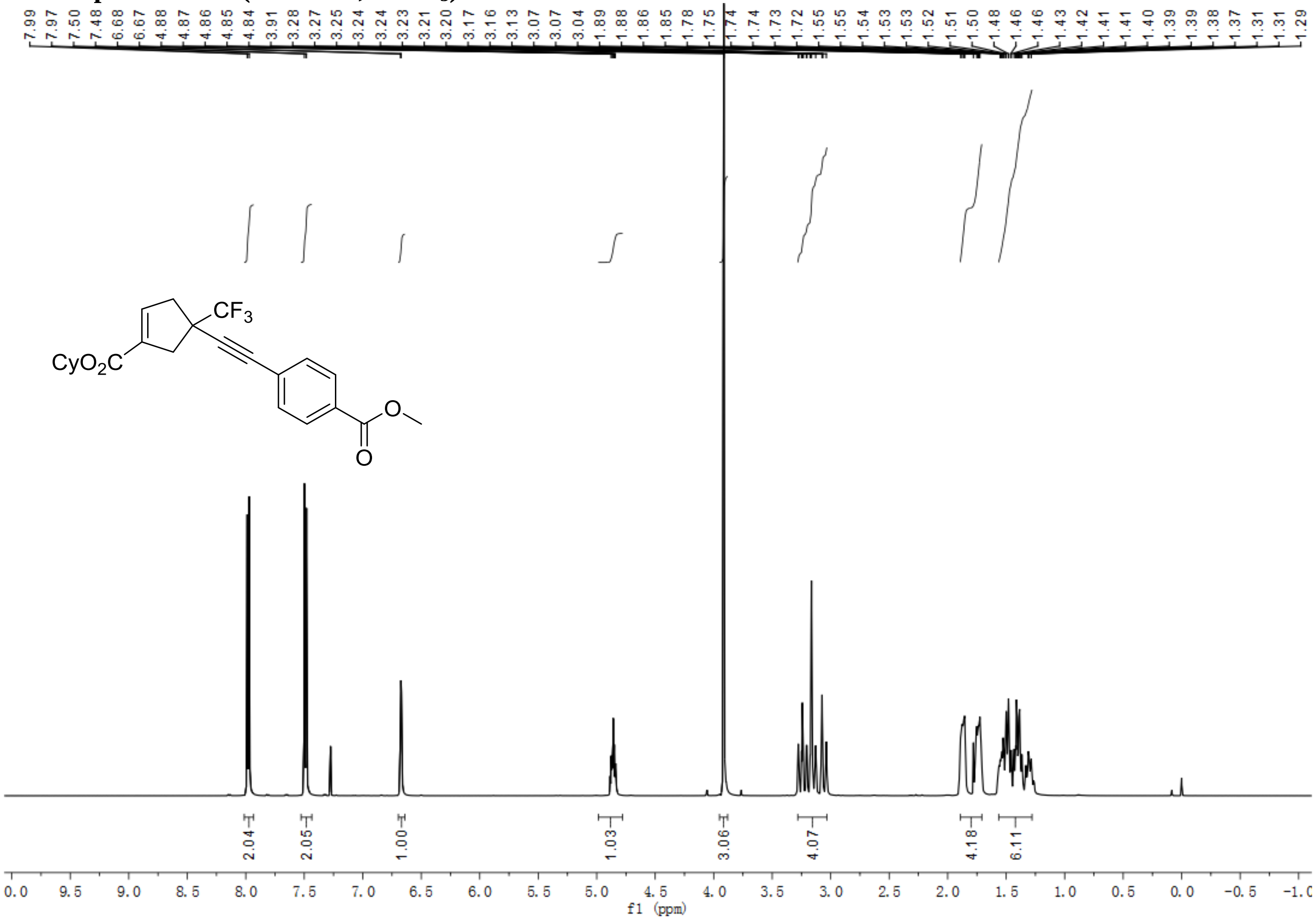
^{13}C NMR spectrum of product 3ba (125 MHz, $CDCl_3$)



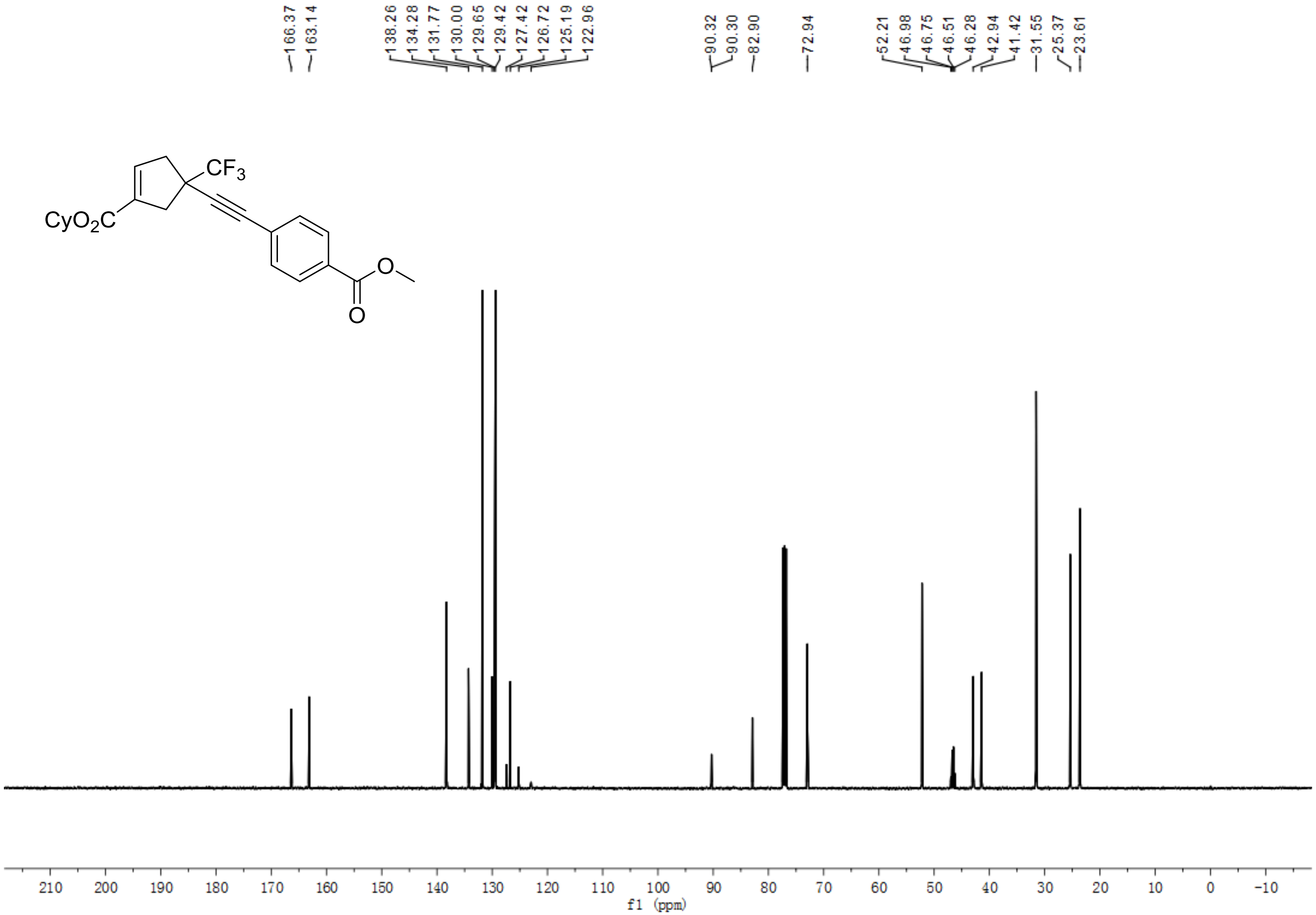
^{19}F NMR spectrum of product 3ba (470 MHz, $CDCl_3$)



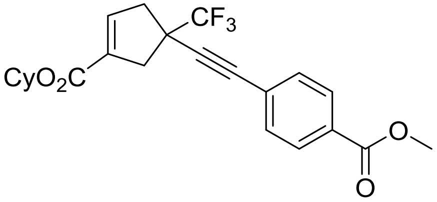
^{1}H NMR spectrum of product 3ca (500 MHz, $CDCl_3$)

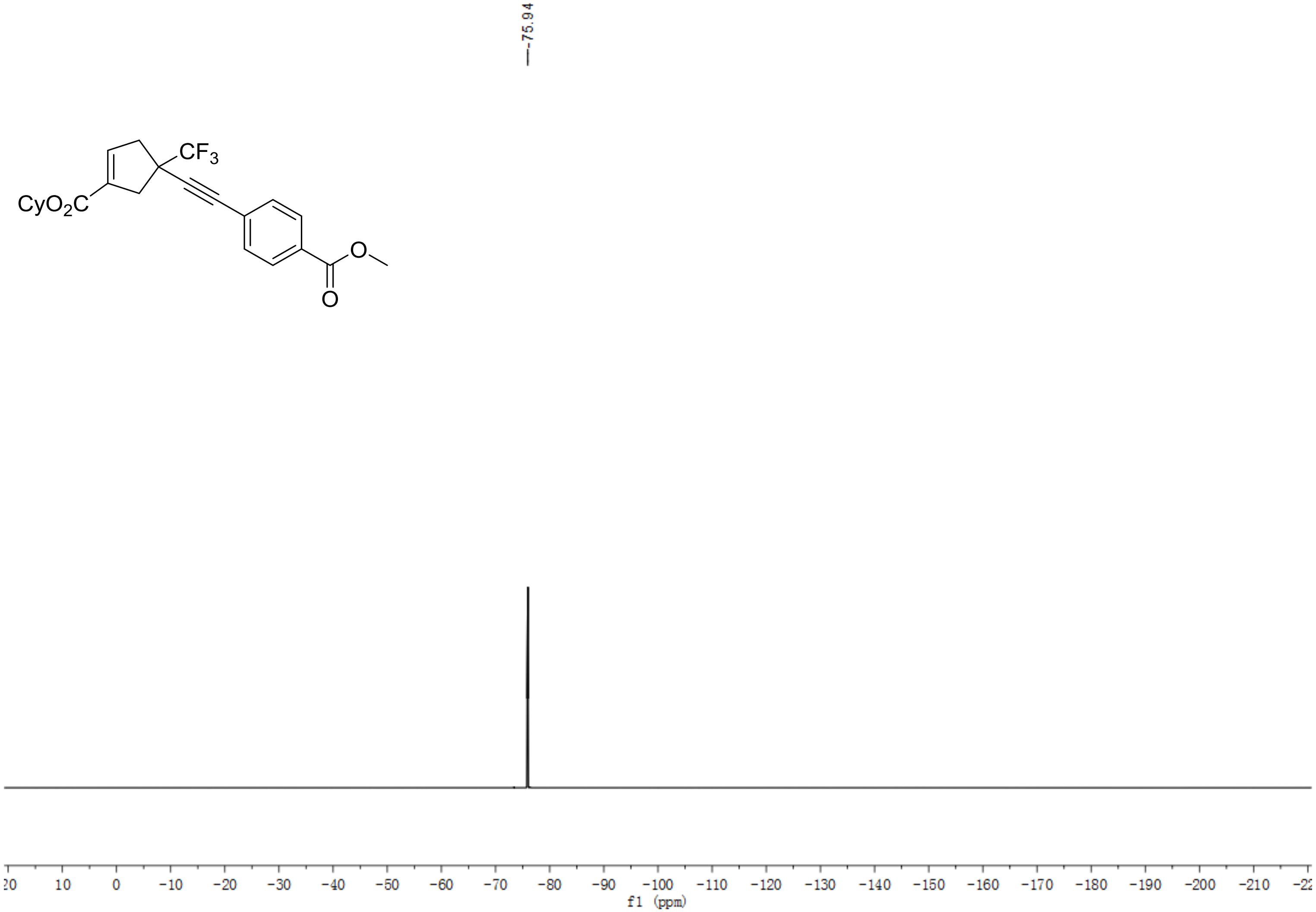


^{13}C NMR spectrum of product 3ca (125 MHz, CDCl$_3$)

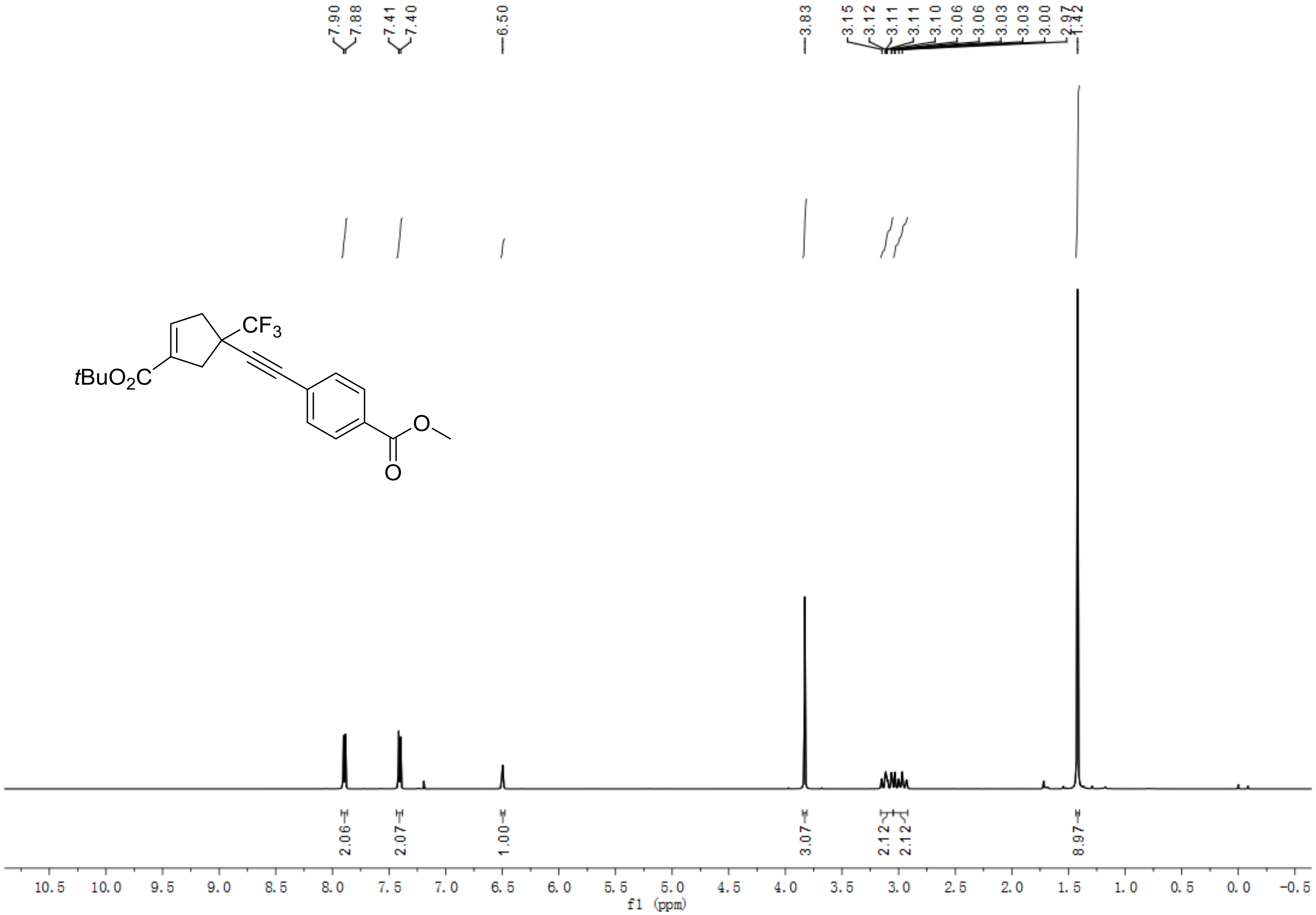


^{19}F NMR spectrum of product 3ca (470 MHz, $CDCl_3$)

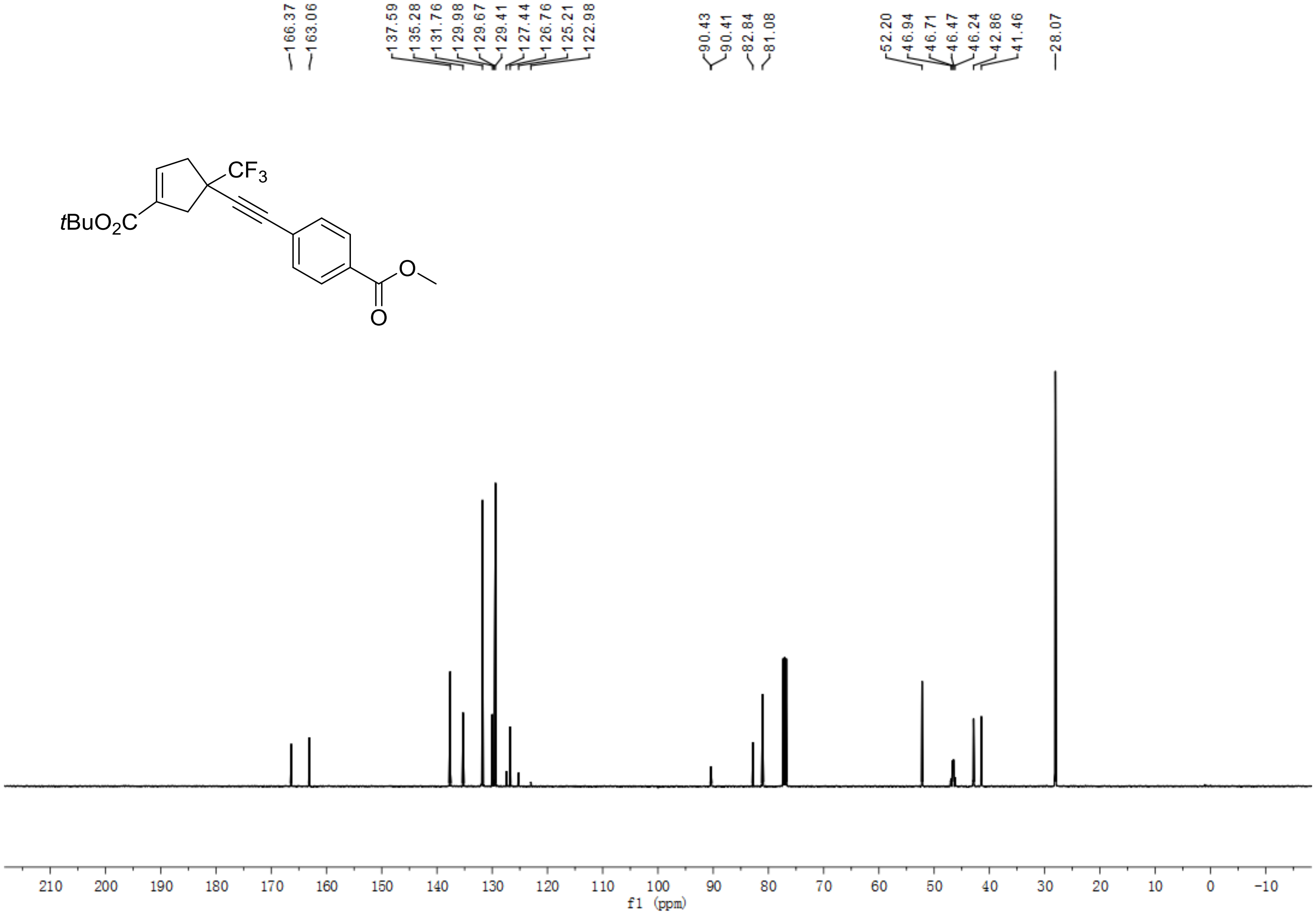




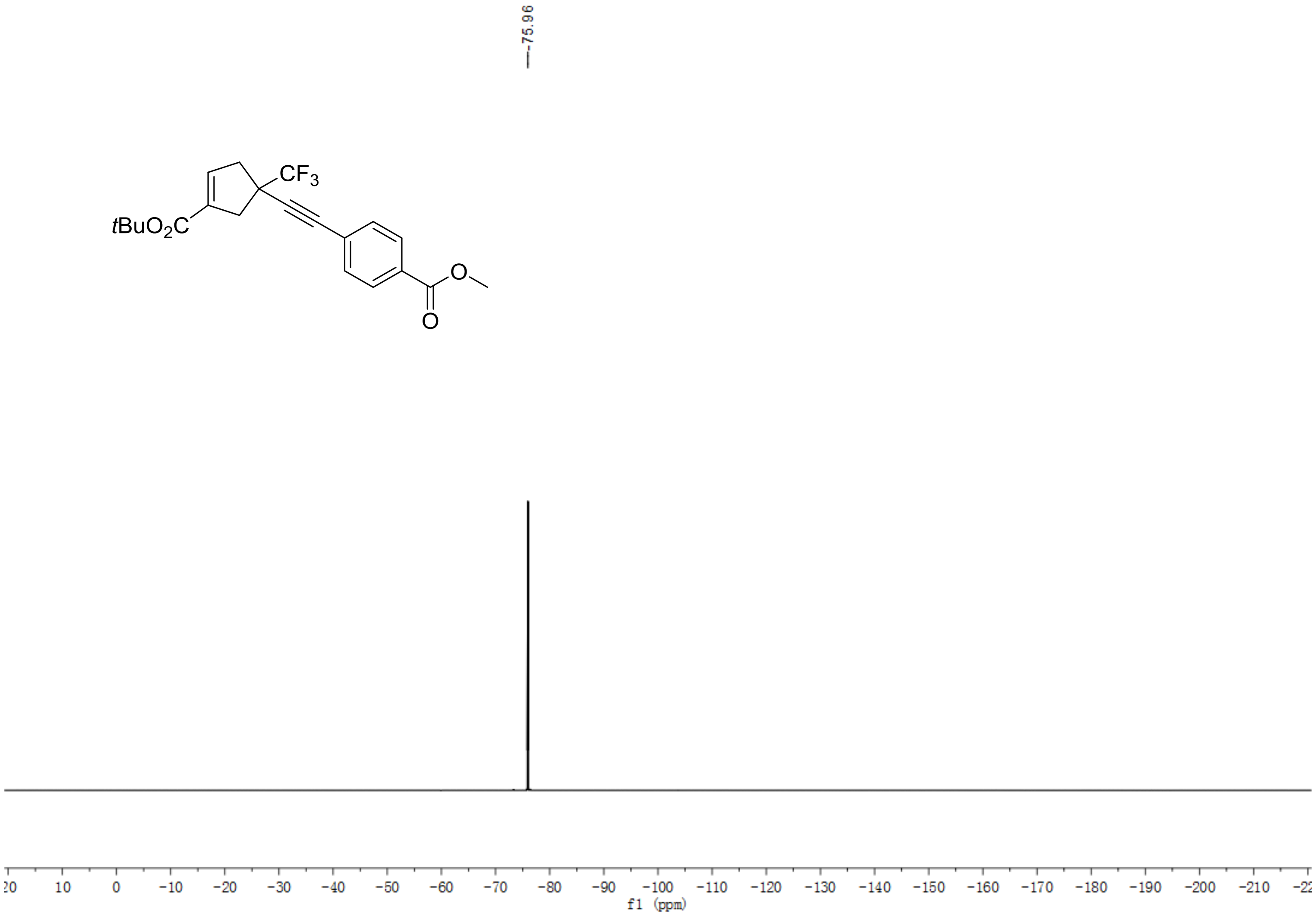
^{1}H NMR spectrum of product 3da (500 MHz, $CDCl_3$)



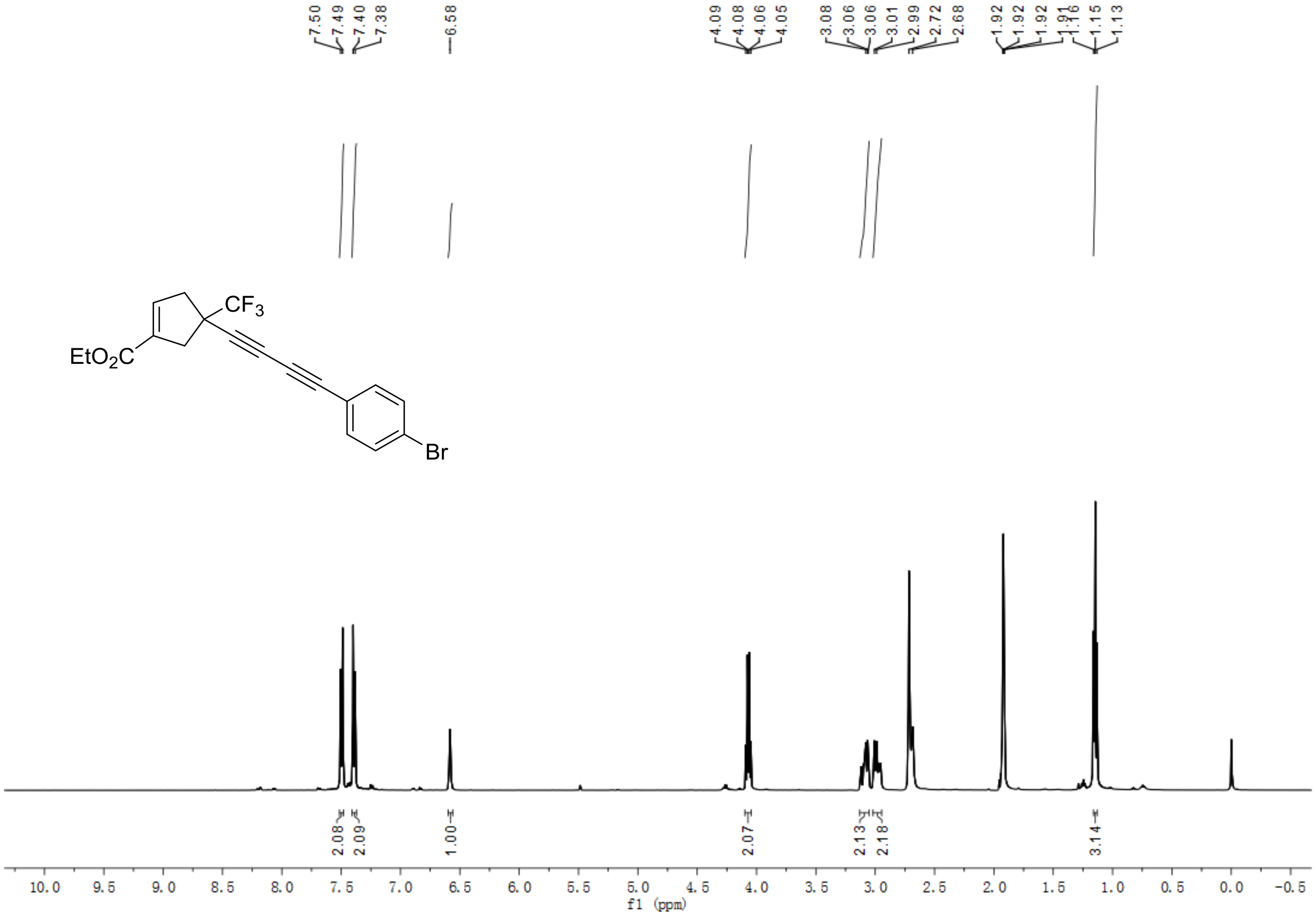
^{13}C NMR spectrum of product 3da (125 MHz, CDCl$_3$)



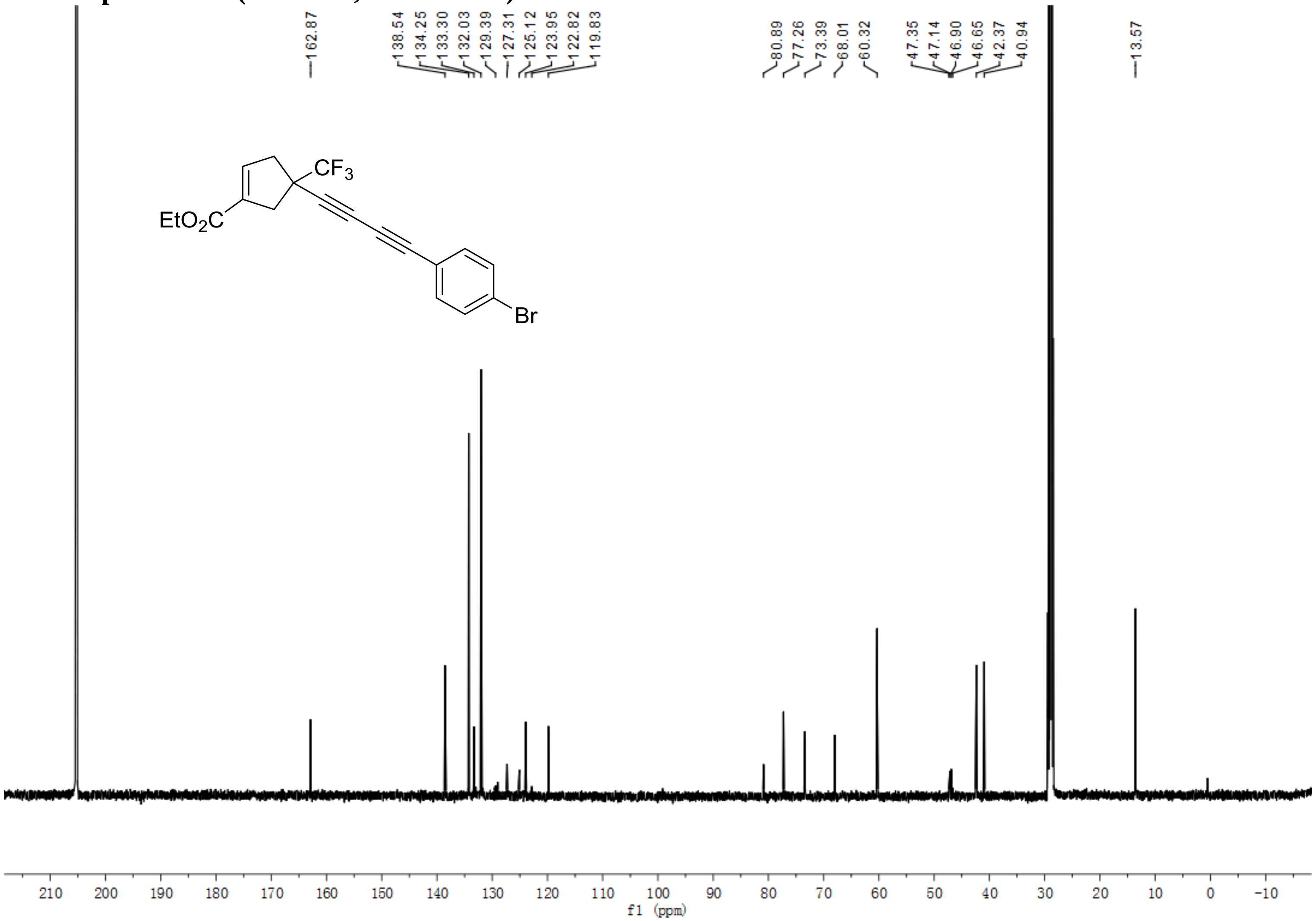
^{19}F NMR spectrum of product 3da (470 MHz, $CDCl_3$)



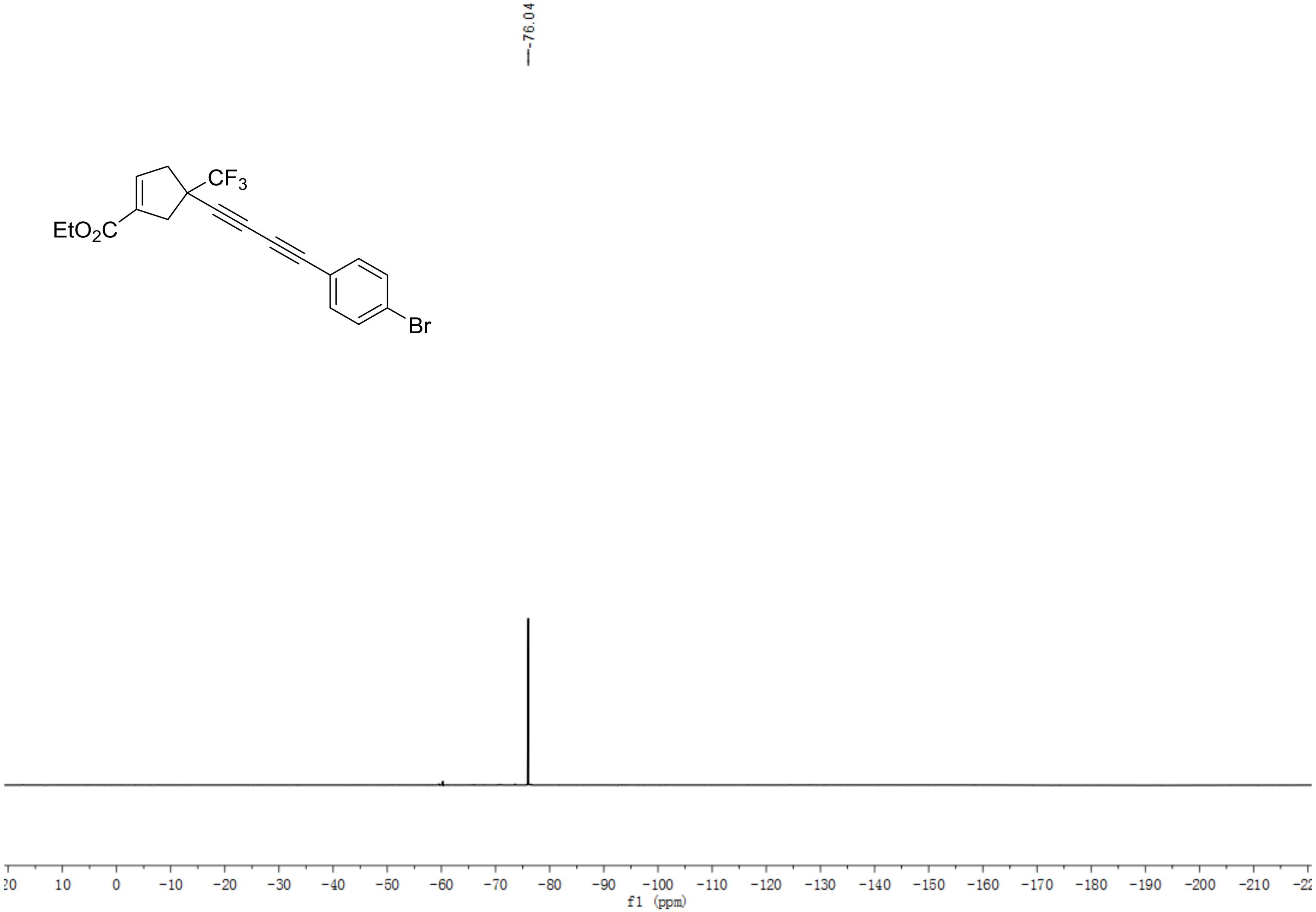
^{1}H NMR spectrum of product 6a (500 MHz, D6-Acetone)



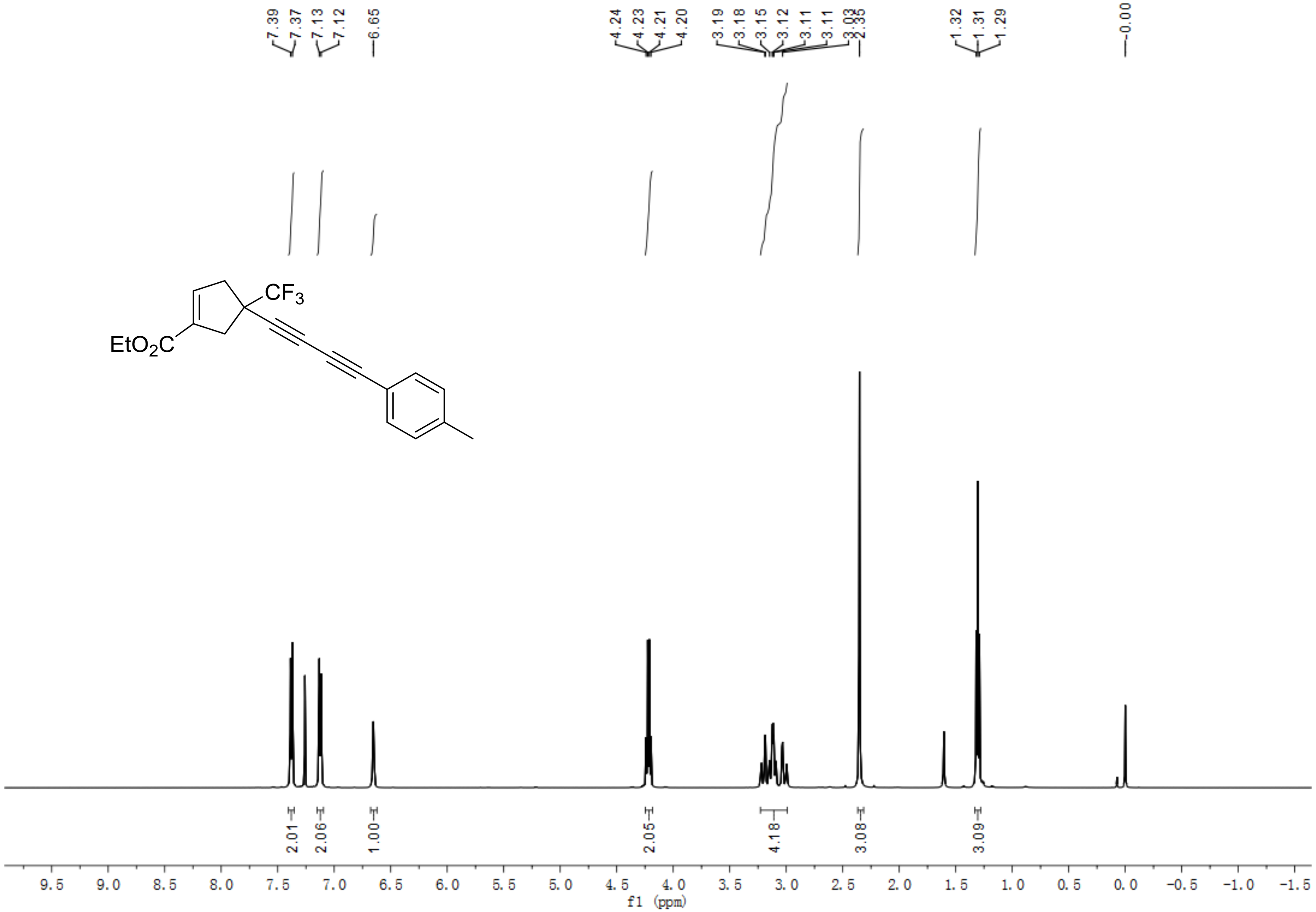
^{13}C NMR spectrum of product 6a (125 MHz, D6-Acetone)



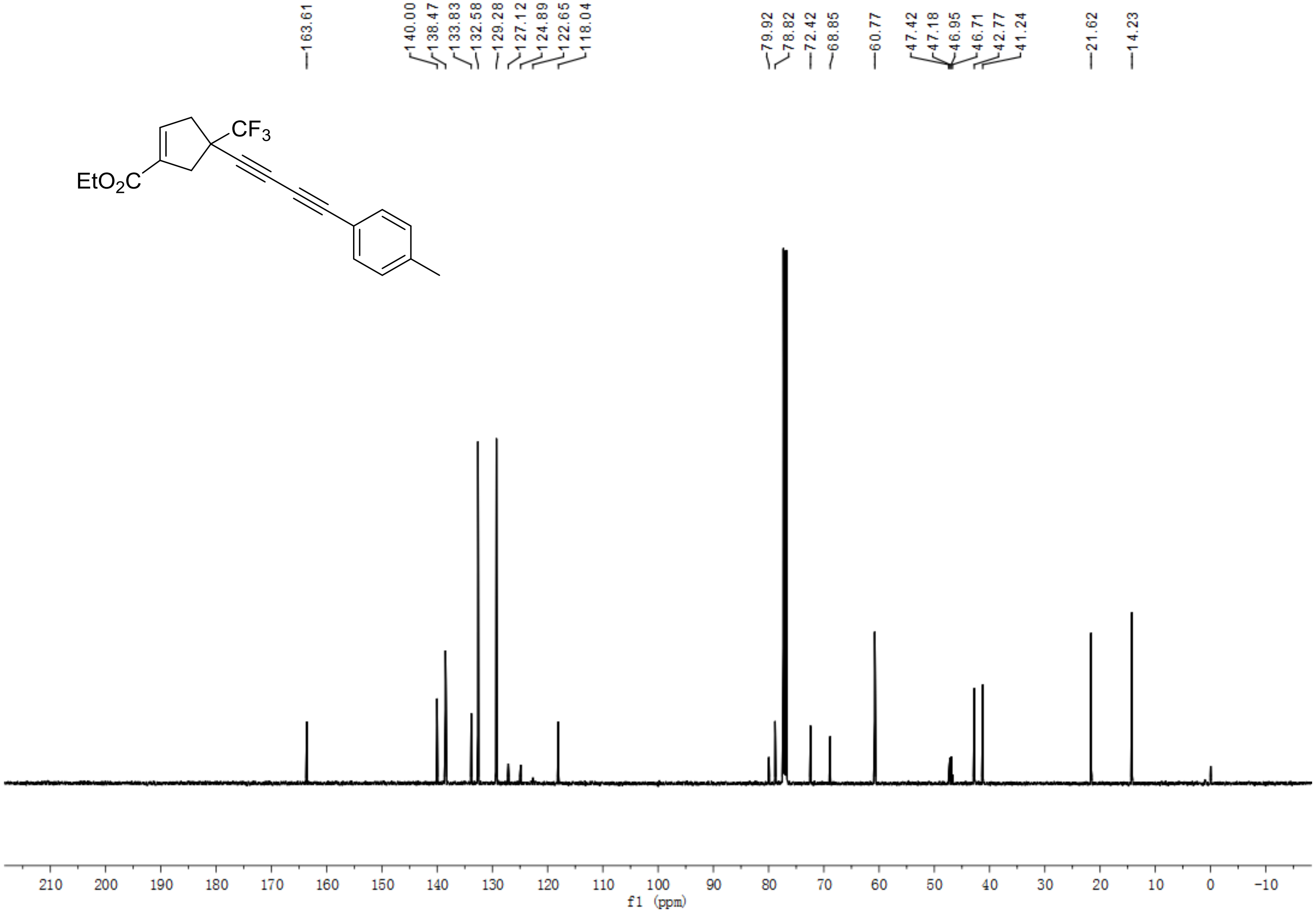
^{19}F NMR spectrum of product 6a (470 MHz, D6-Acetone)



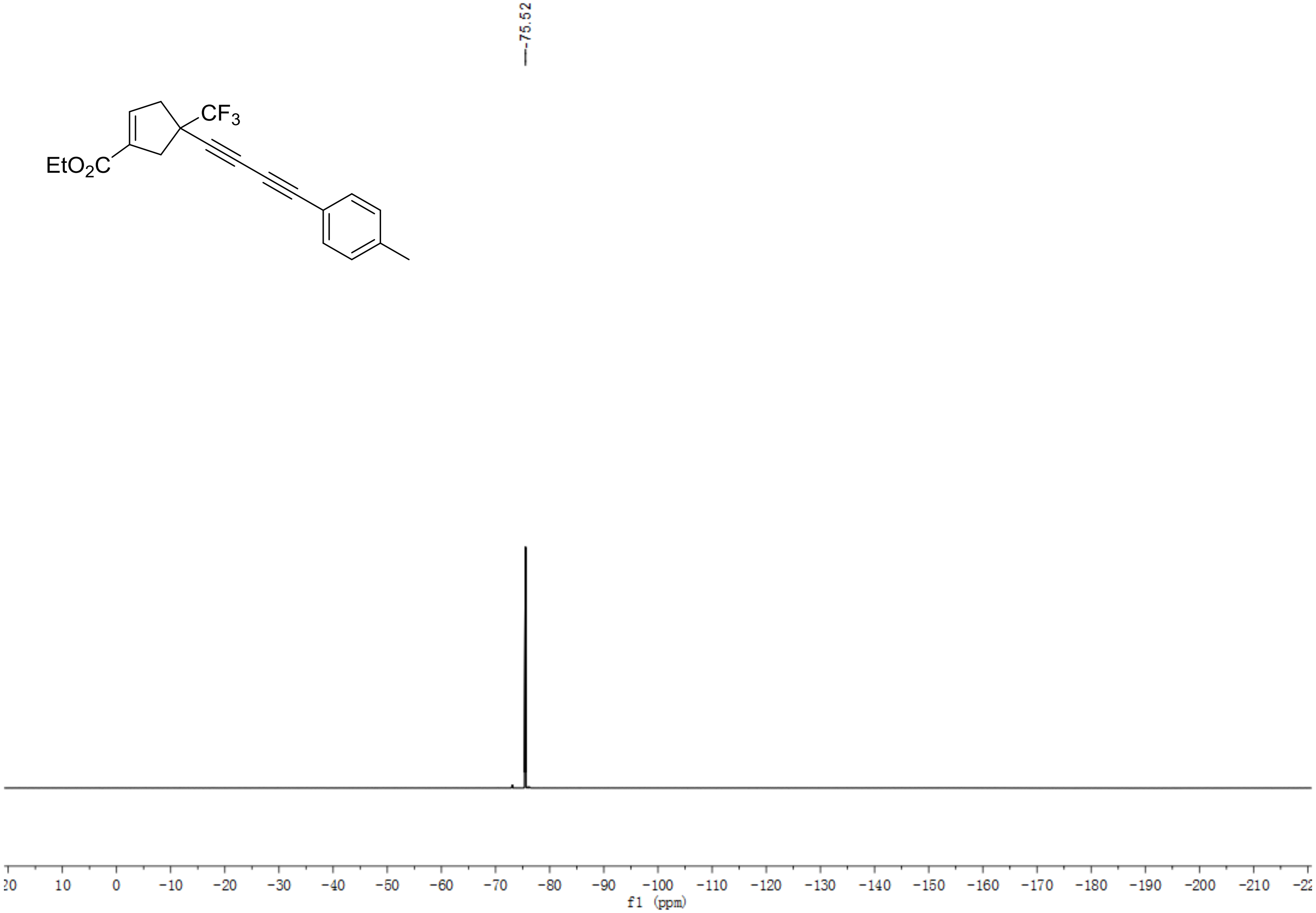
^{1}H NMR spectrum of product 6b (500 MHz, $CDCl_3$)



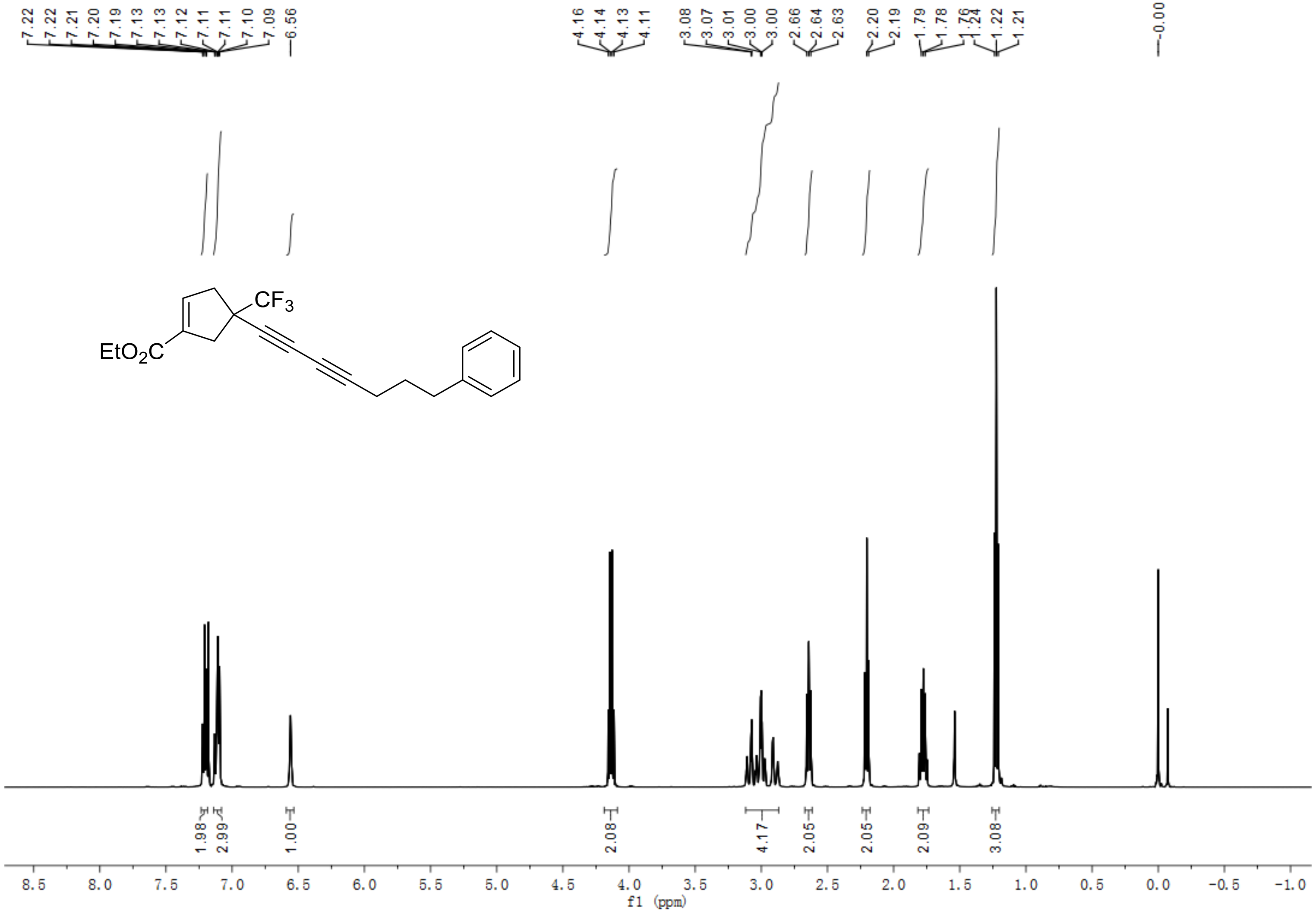
^{13}C NMR spectrum of product 6b (125 MHz, $CDCl_3$)



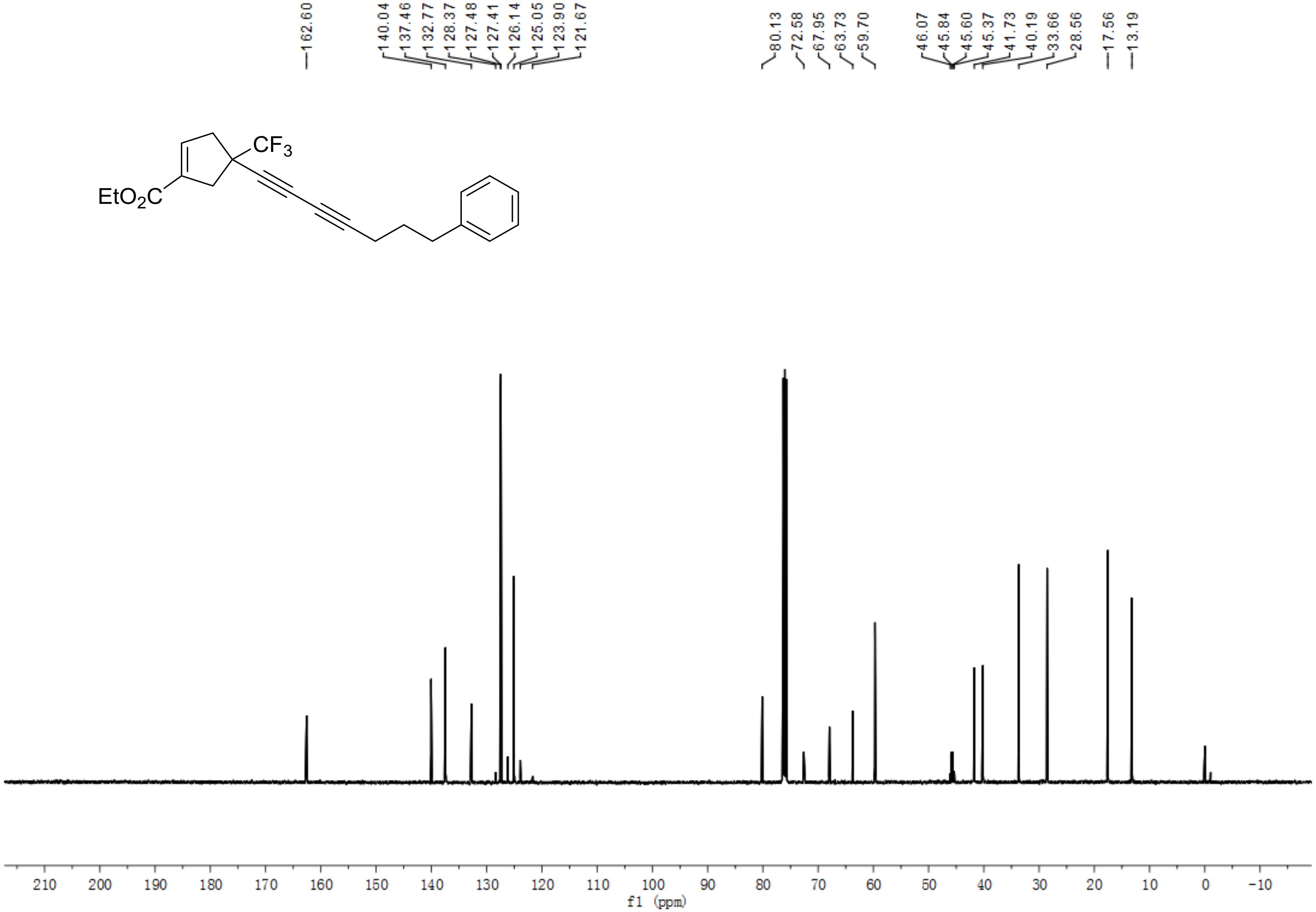
^{19}F NMR spectrum of product 6b (470 MHz, $CDCl_3$)



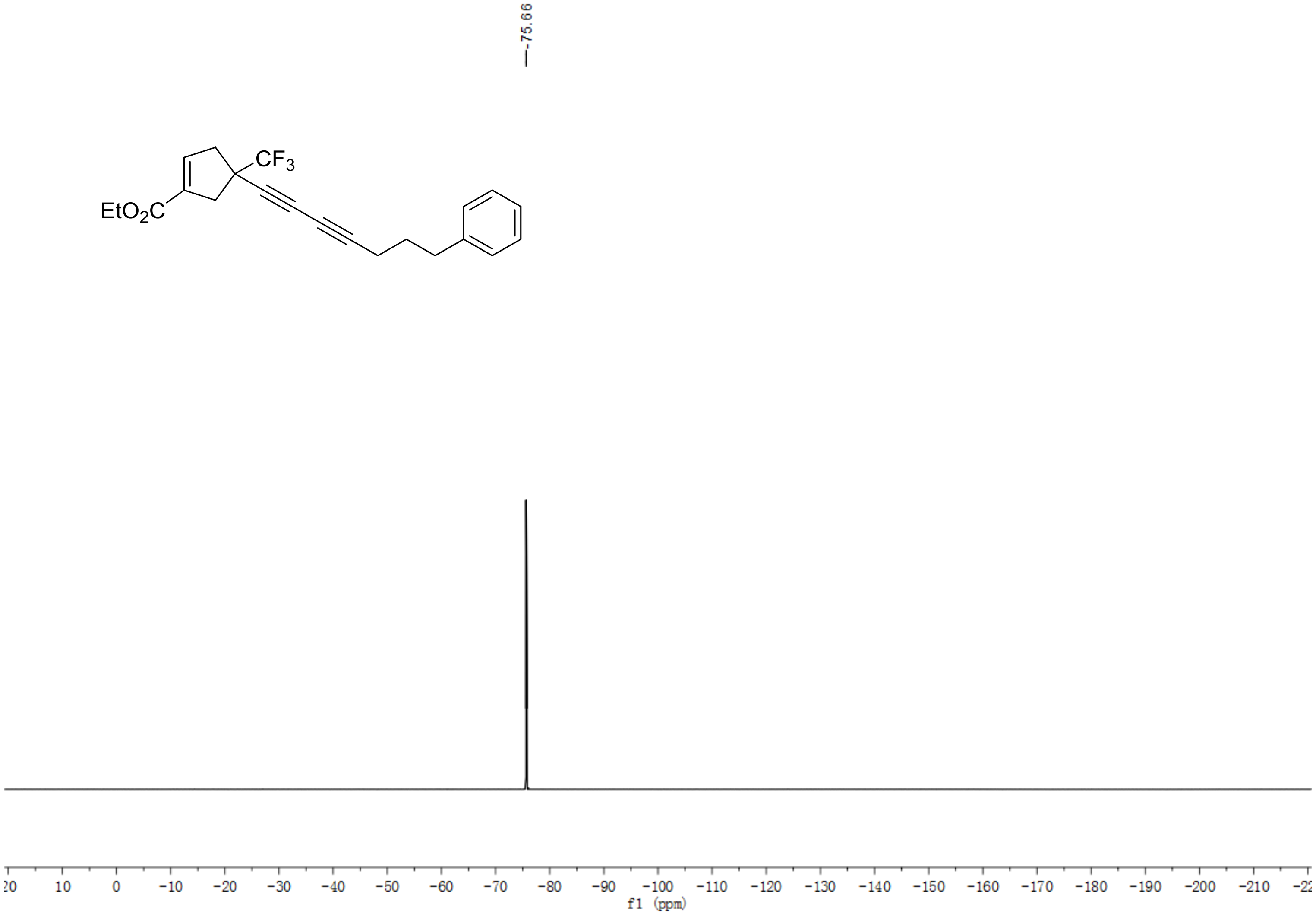
^{1}**H NMR spectrum of product 6c (500 MHz, $CDCl_3$)**



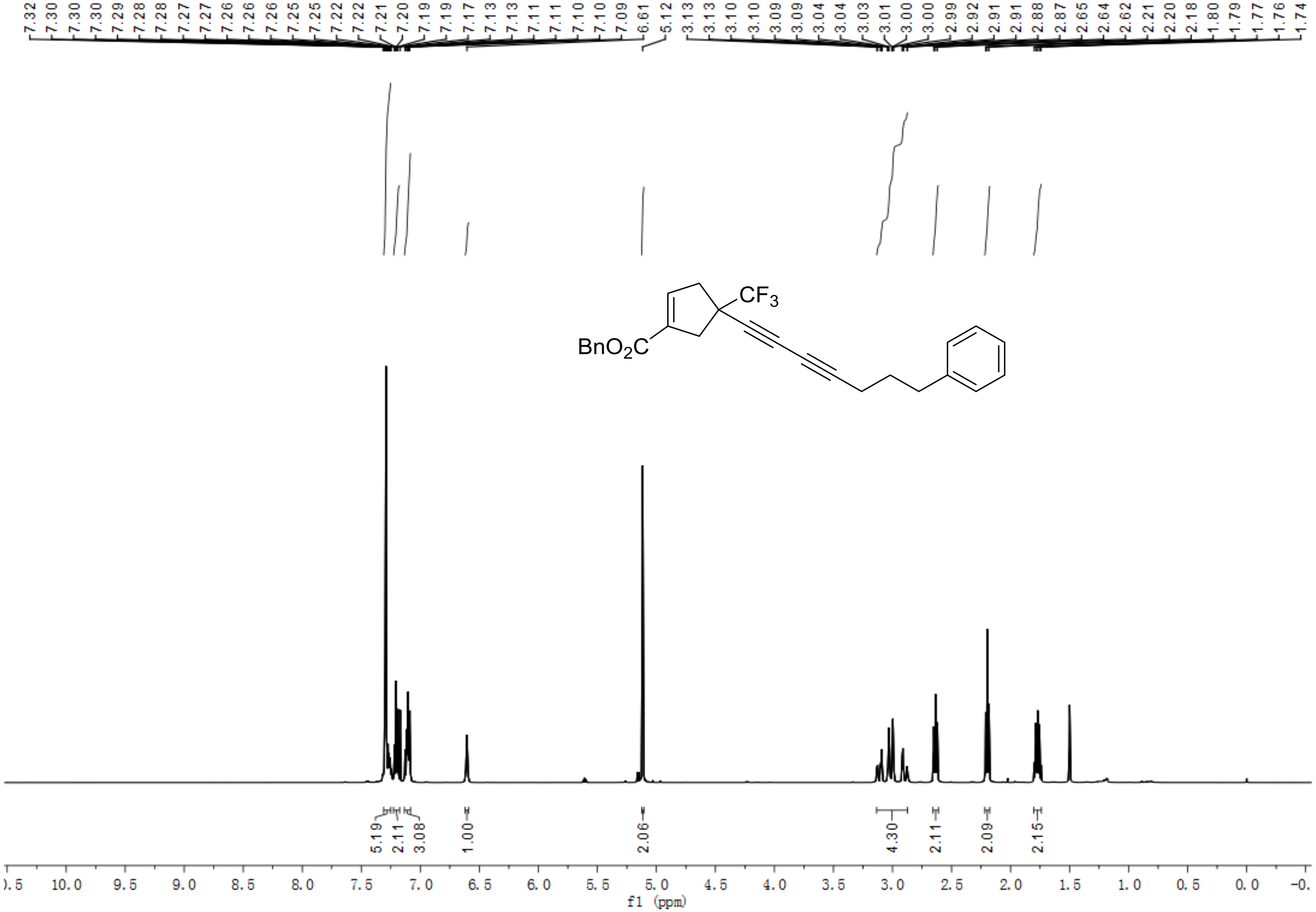
^{13}C NMR spectrum of product 6c (125 MHz, $CDCl_3$)



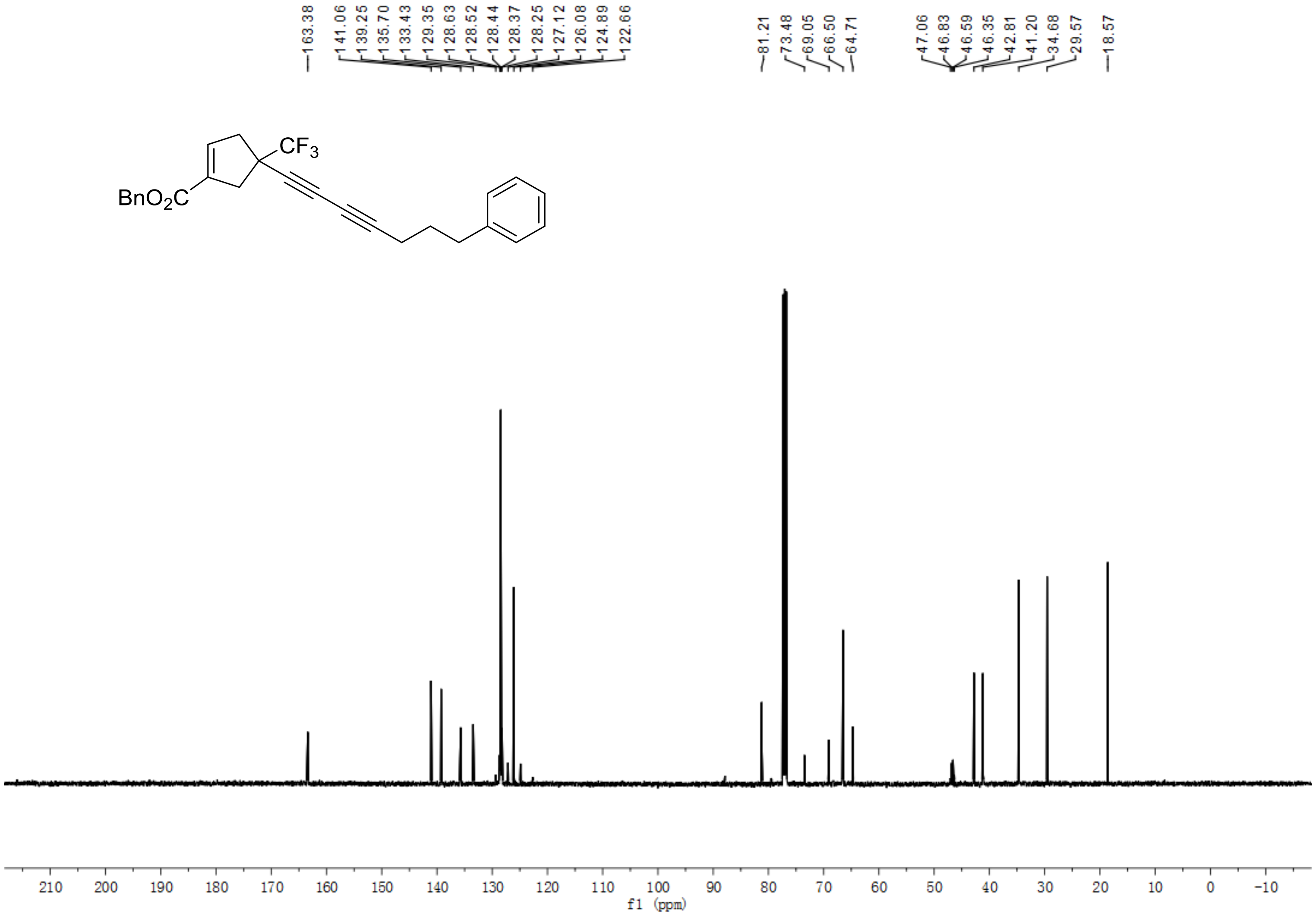
^{19}**F NMR spectrum of product 6c (470 MHz, $CDCl_3$)**



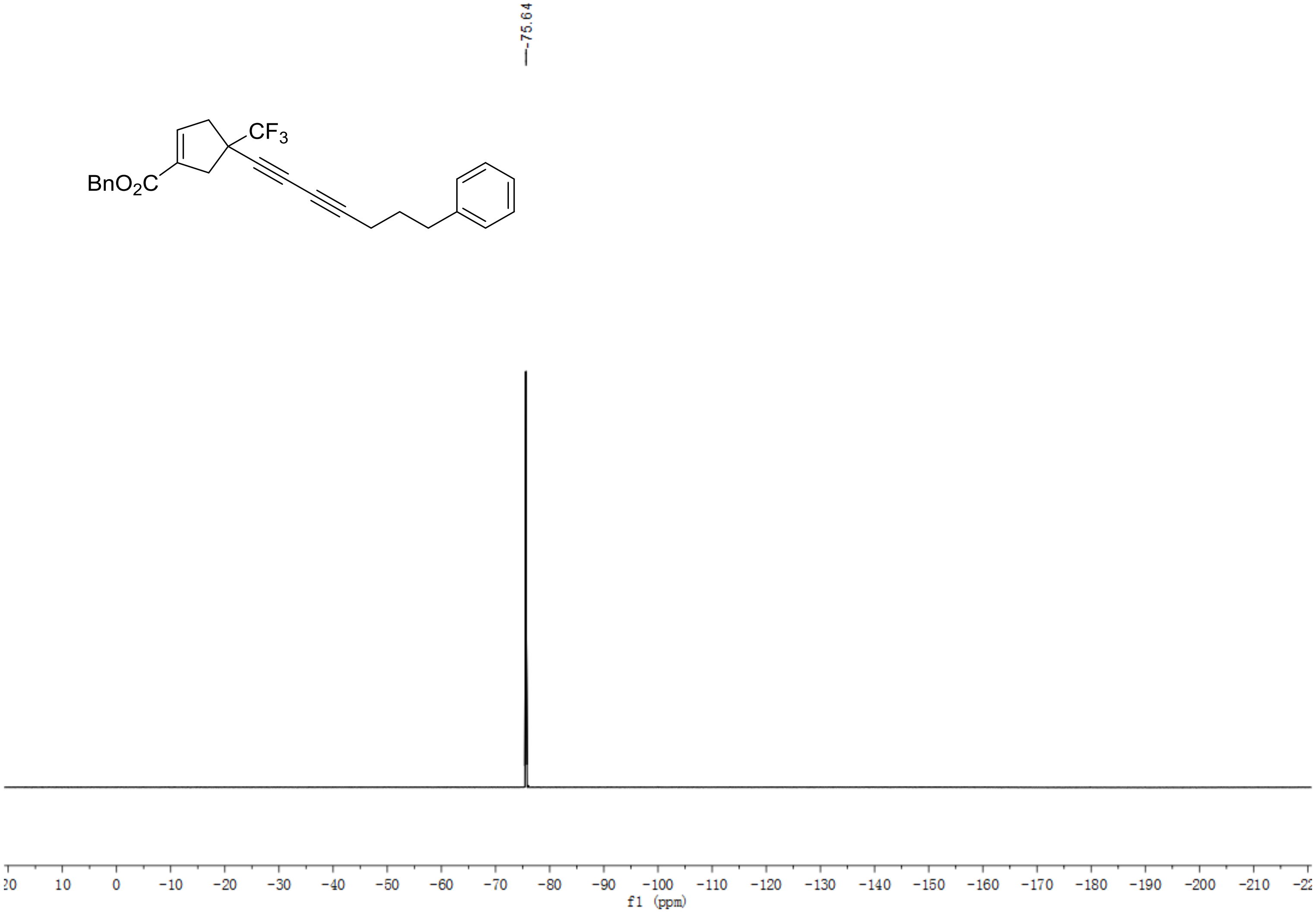
^{1}H NMR spectrum of product 6d (500 MHz, $CDCl_3$)



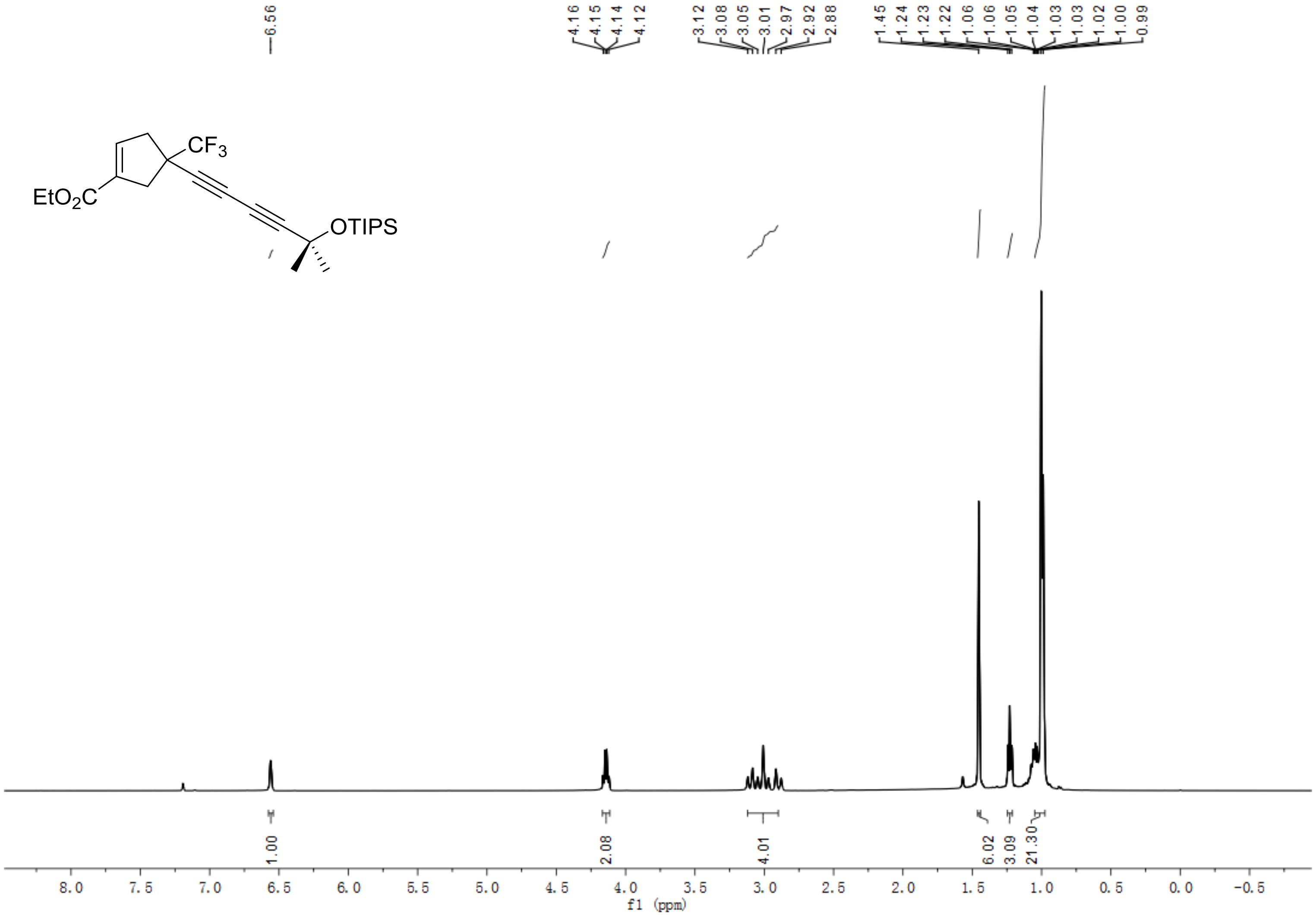
^{13}C NMR spectrum of product 6d (125 MHz, $CDCl_3$)



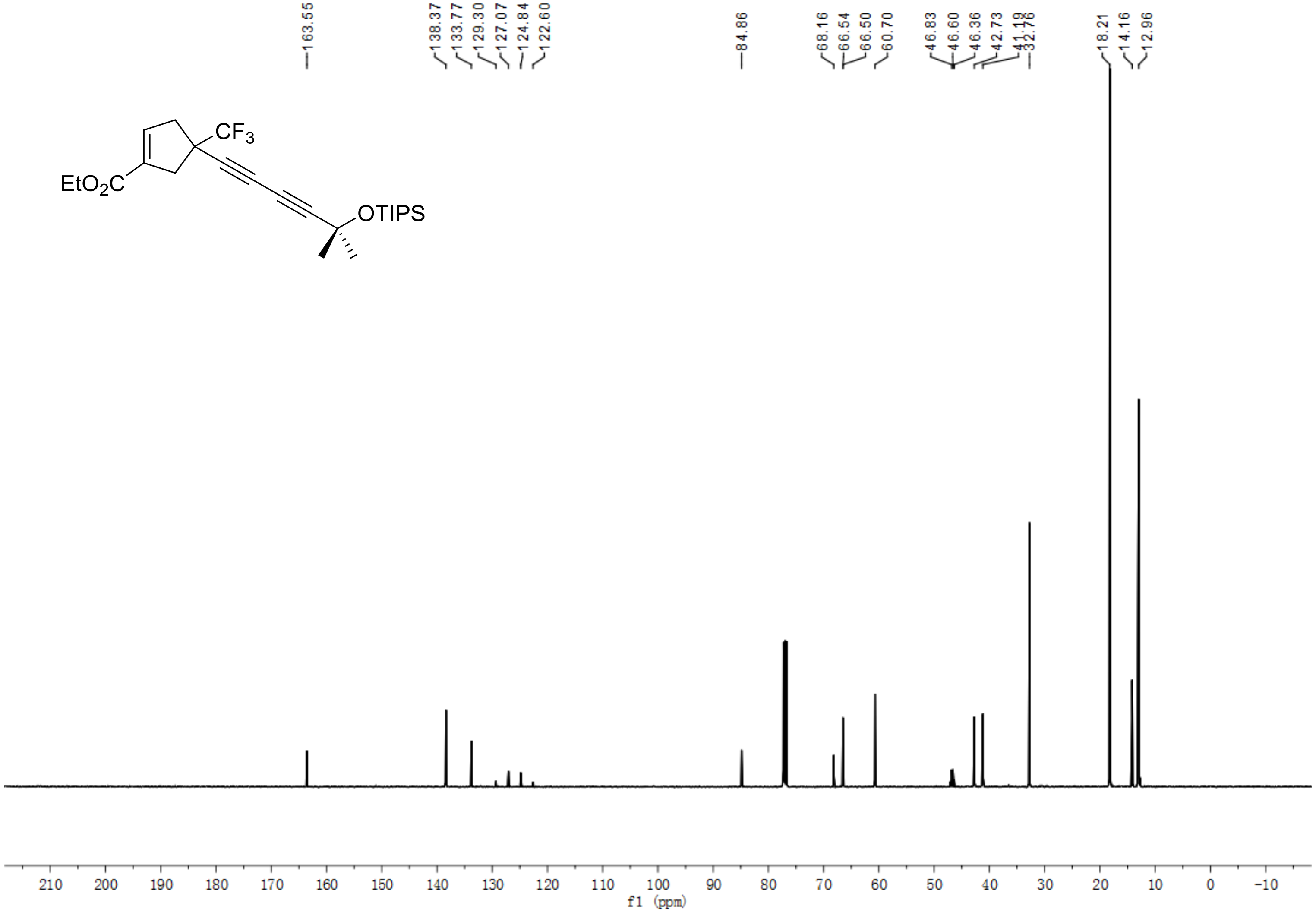
^{19}F NMR spectrum of product 6d (470 MHz, $CDCl_3$)



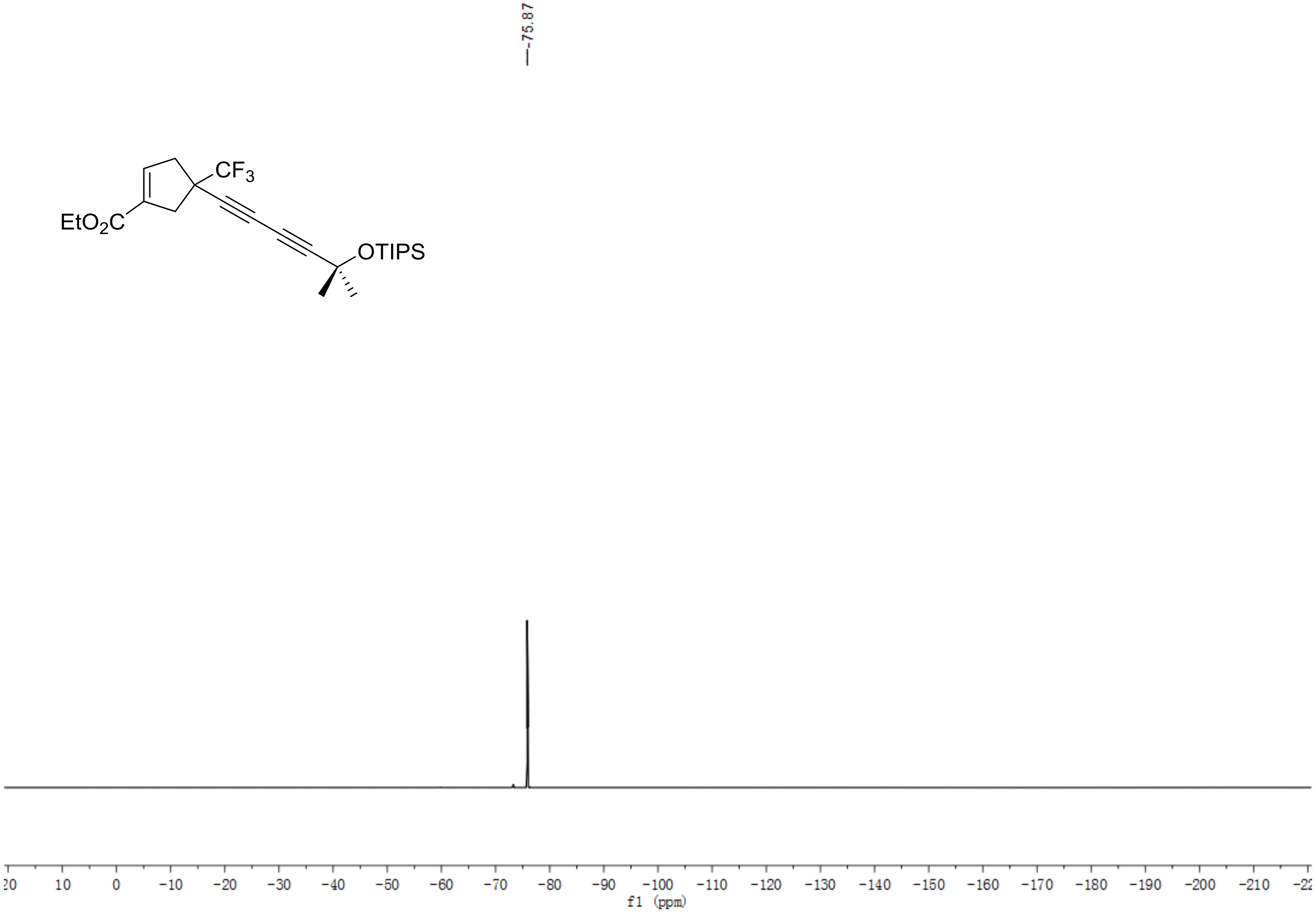
^{1}H NMR spectrum of product 6e (500 MHz, CDCl$_3$)



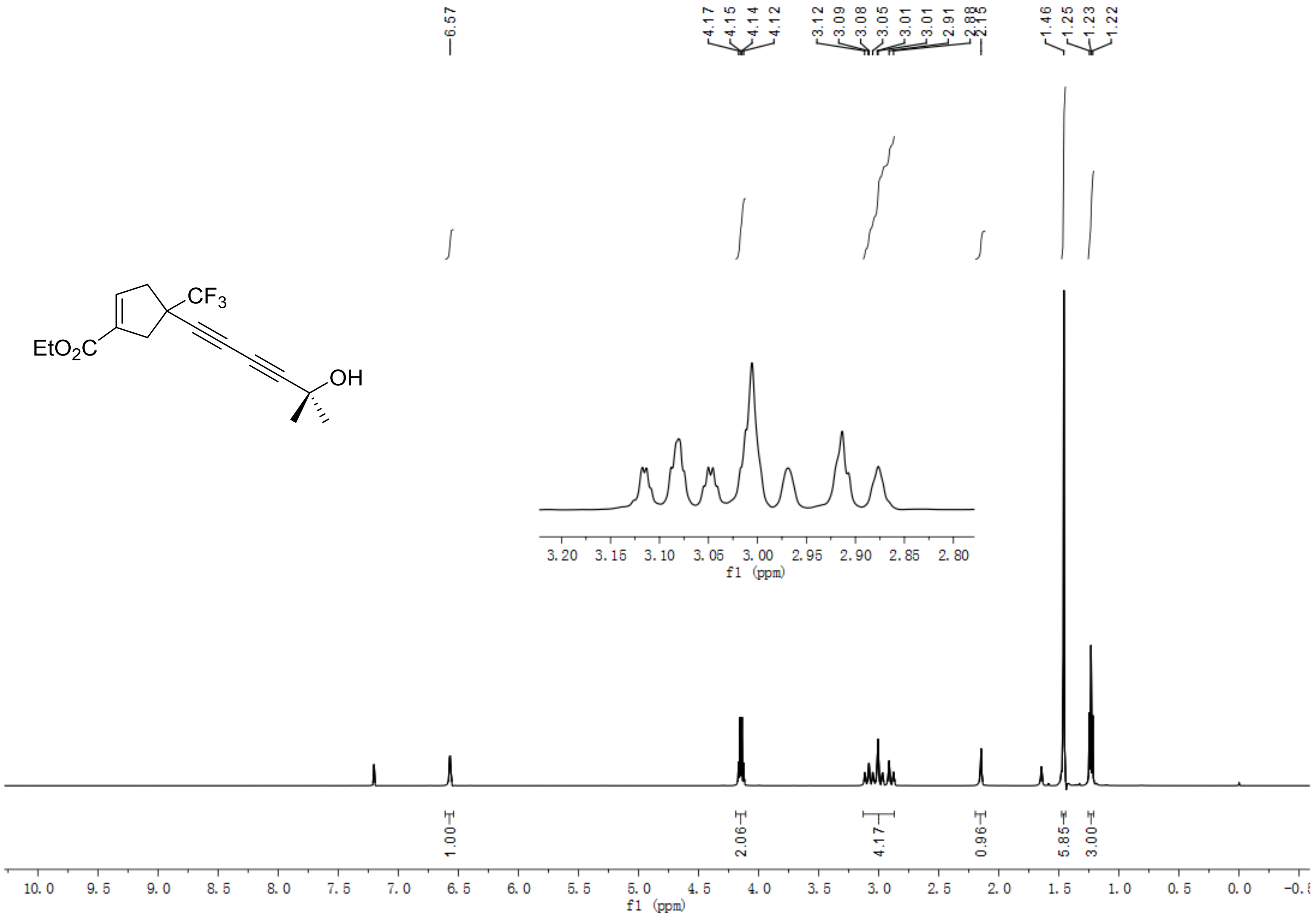
^{13}C NMR spectrum of product 6e (125 MHz, CDCl$_3$)



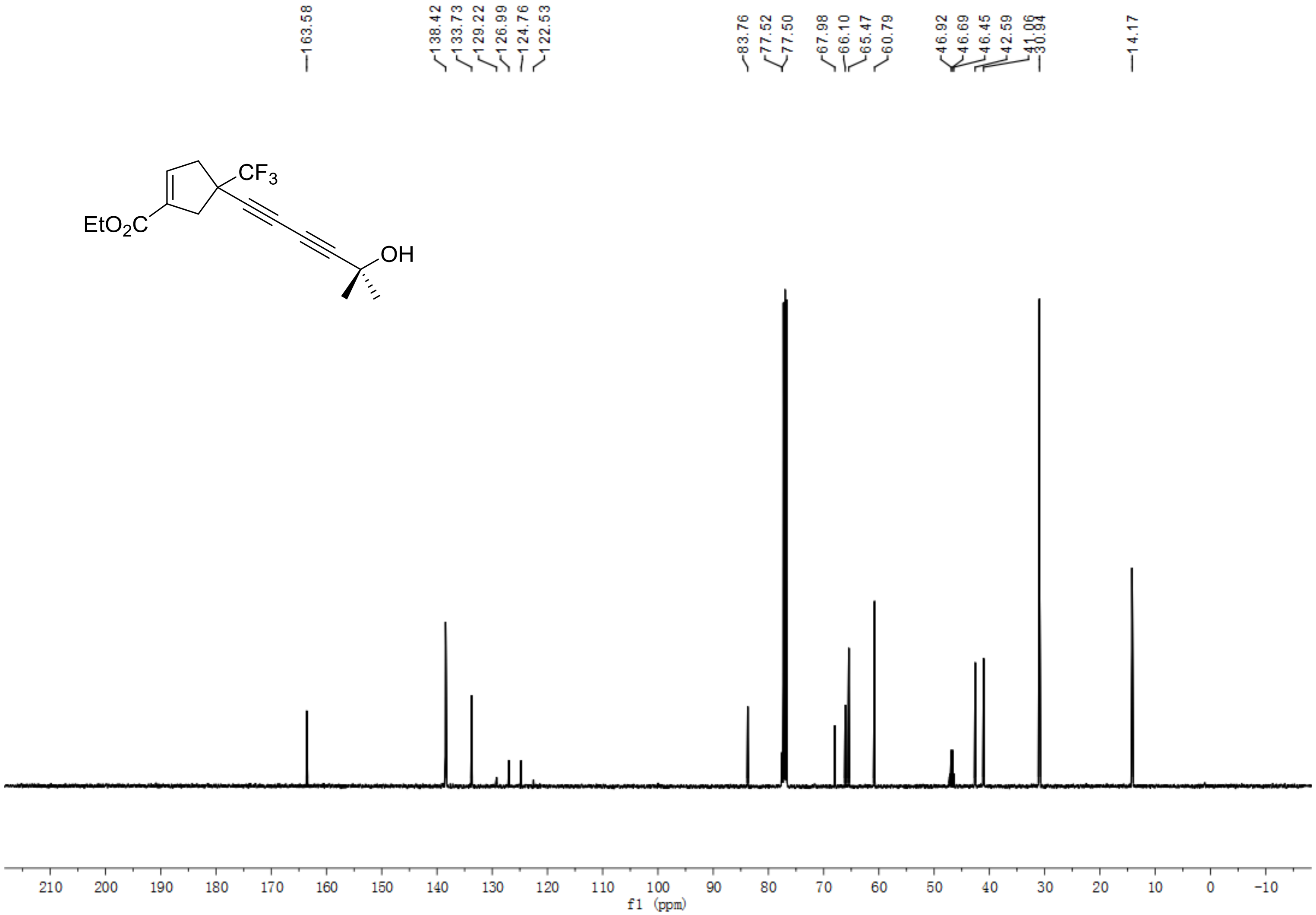
^{19}F NMR spectrum of product 6e (470 MHz, $CDCl_3$)



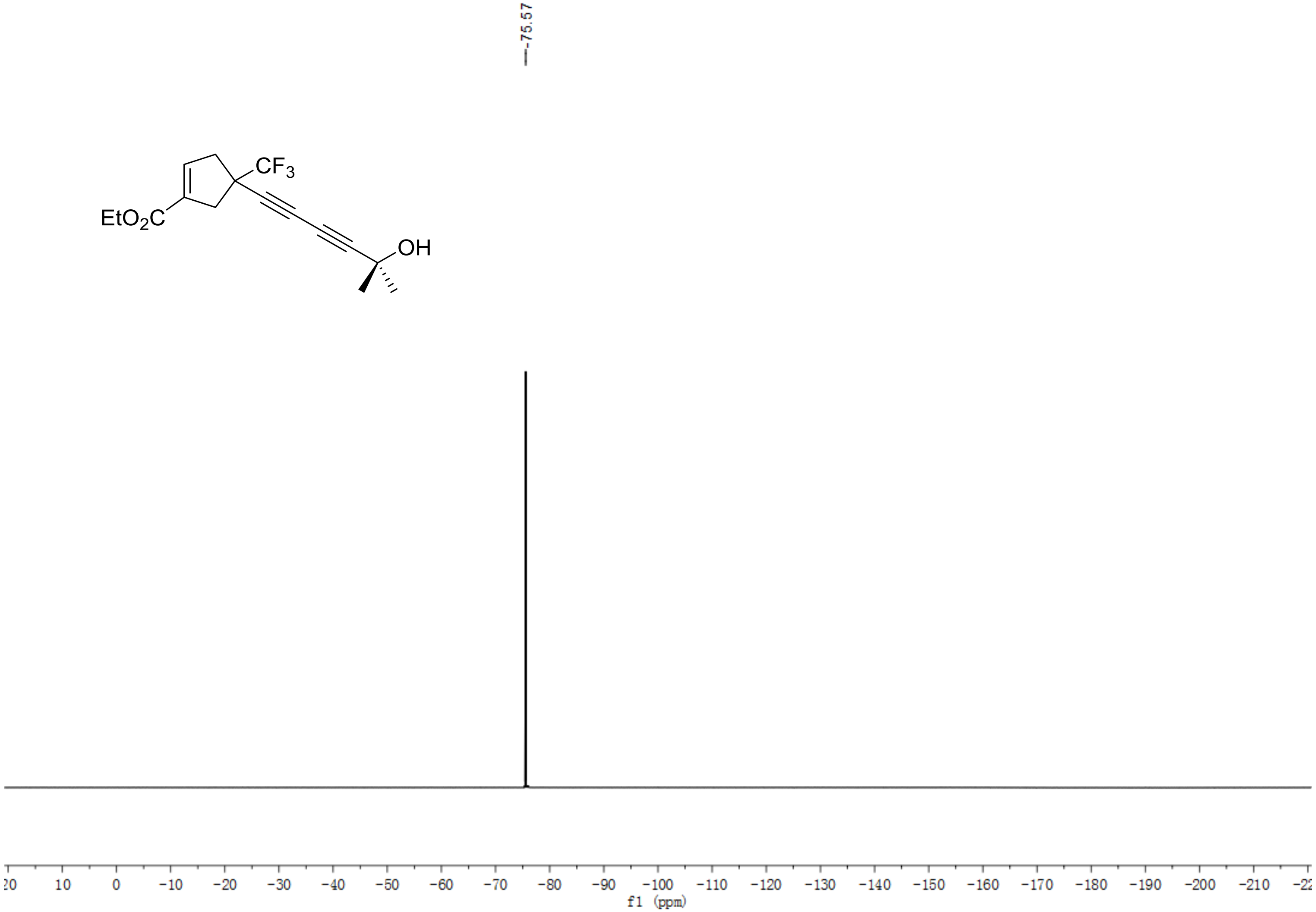
^{1}H NMR spectrum of product 6f (500 MHz, $CDCl_3$)



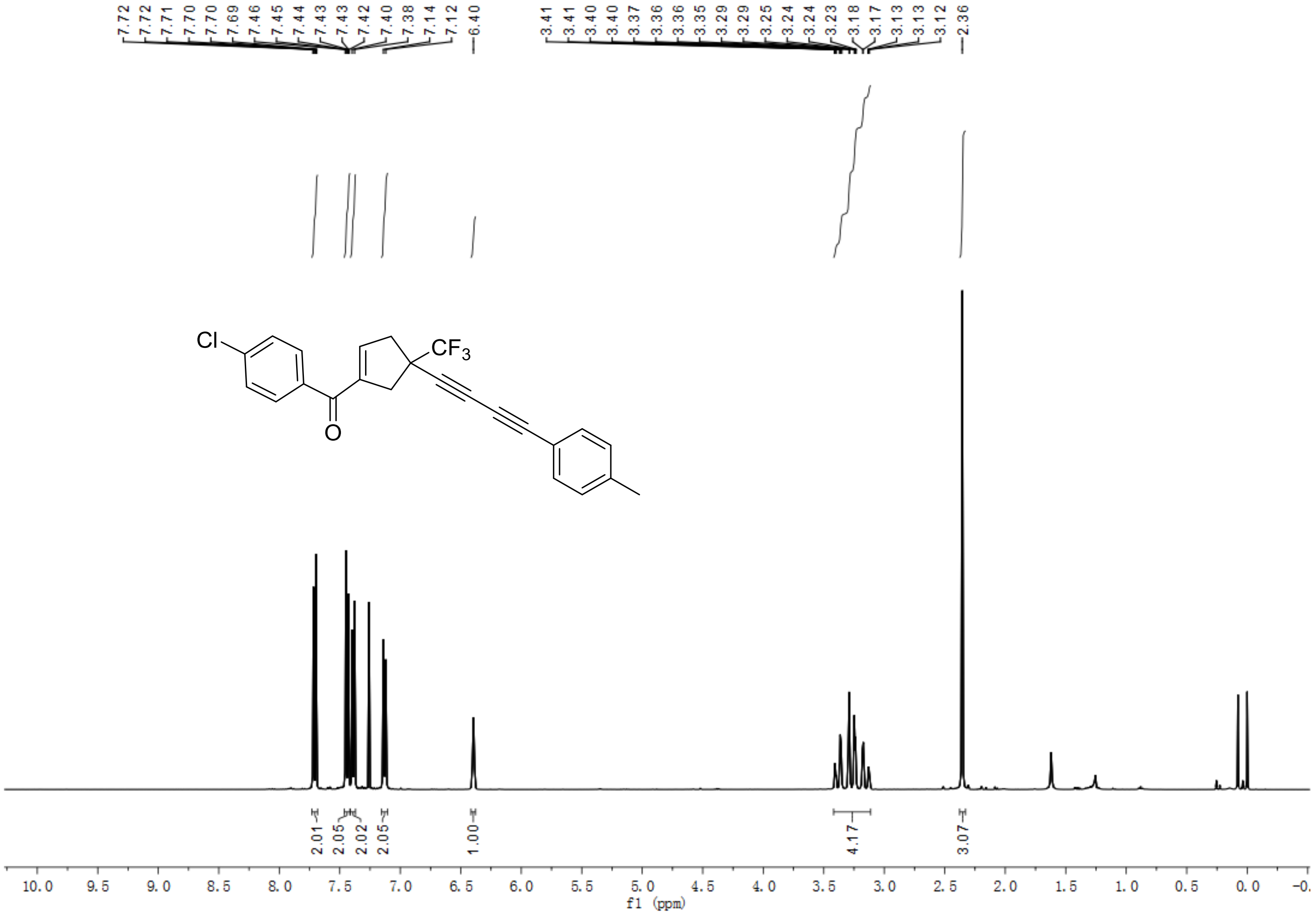
^{13}C NMR spectrum of product 6f (125 MHz, $CDCl_3$)



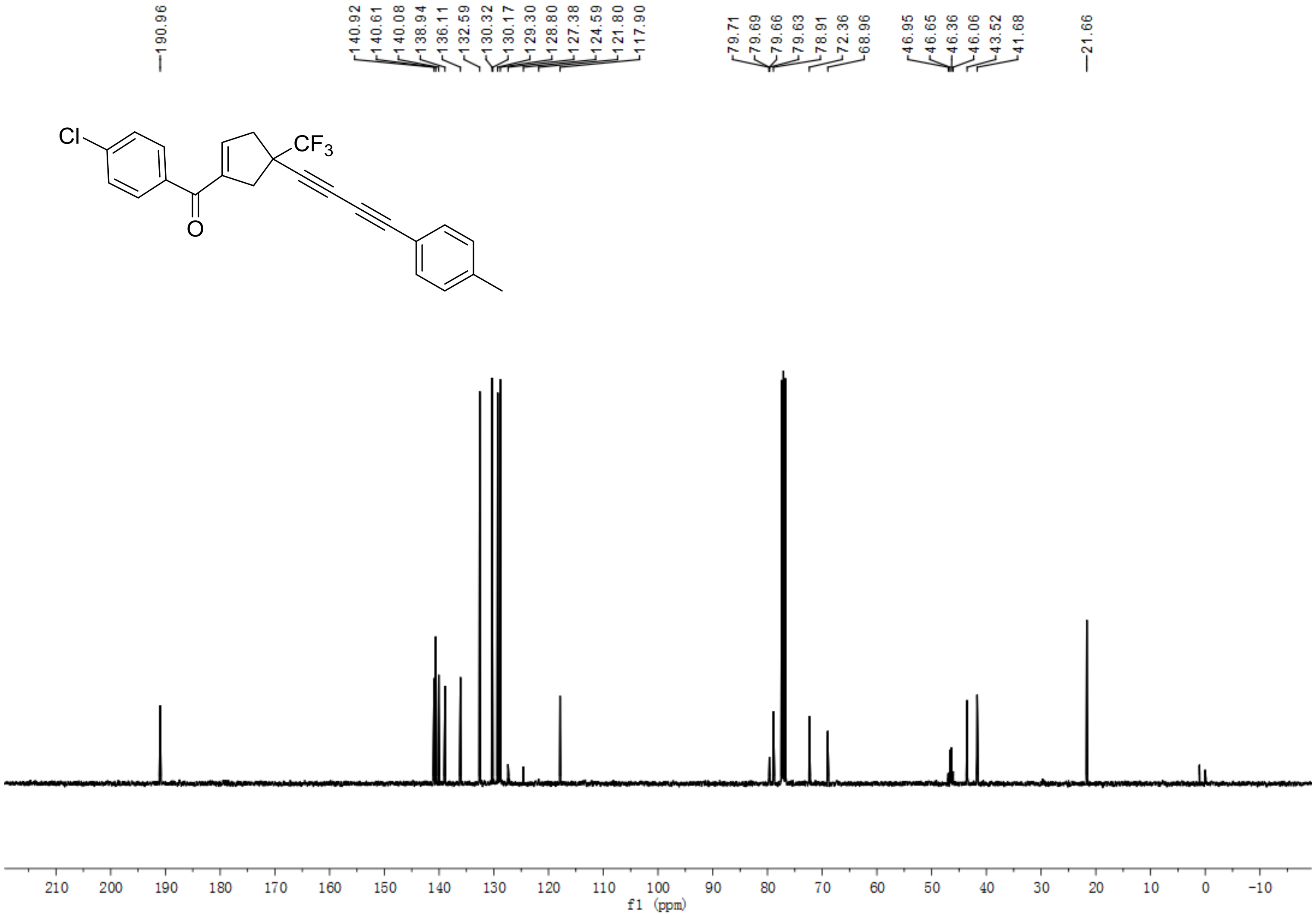
^{19}F NMR spectrum of product 6f (470 MHz, CDCl$_3$)



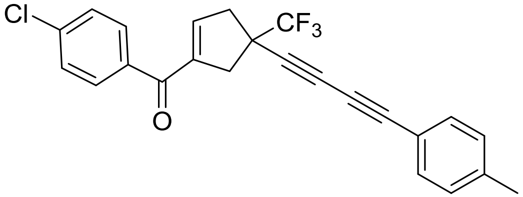
^{1}H NMR spectrum of product 6h (400 MHz, CDCl$_3$)

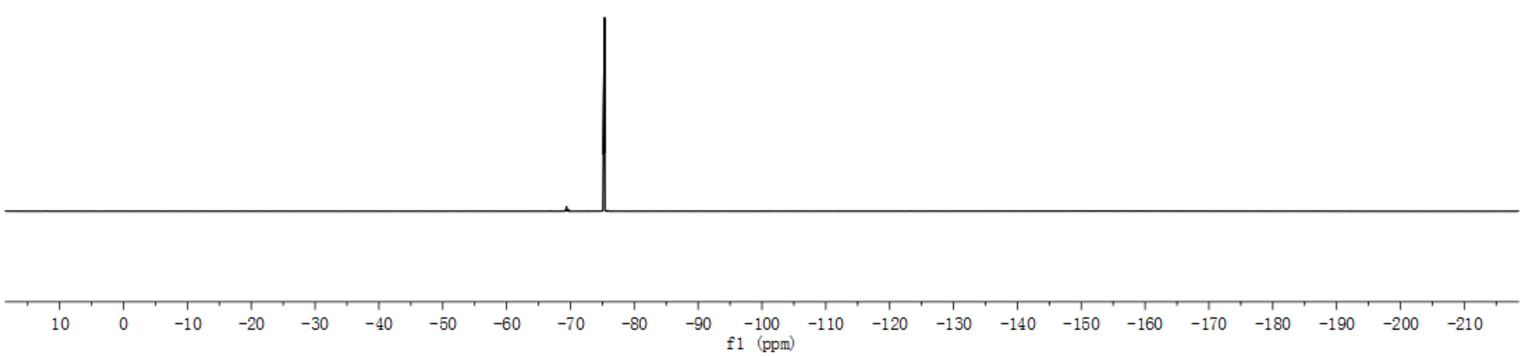


^{13}C NMR spectrum of product 6h (100 MHz, CDCl$_3$)

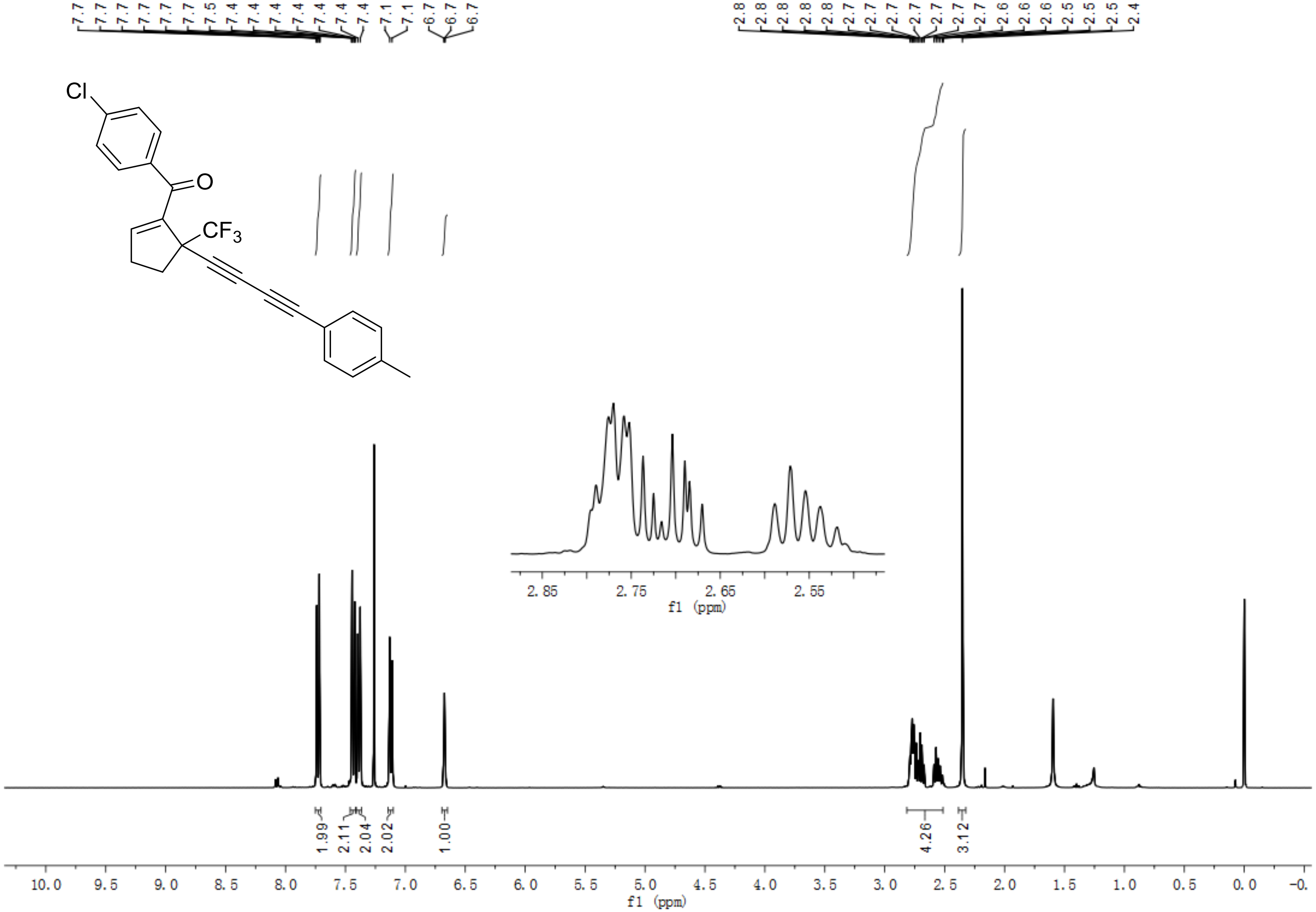


^{19}F NMR spectrum of product 6h (376 MHz, $CDCl_3$)

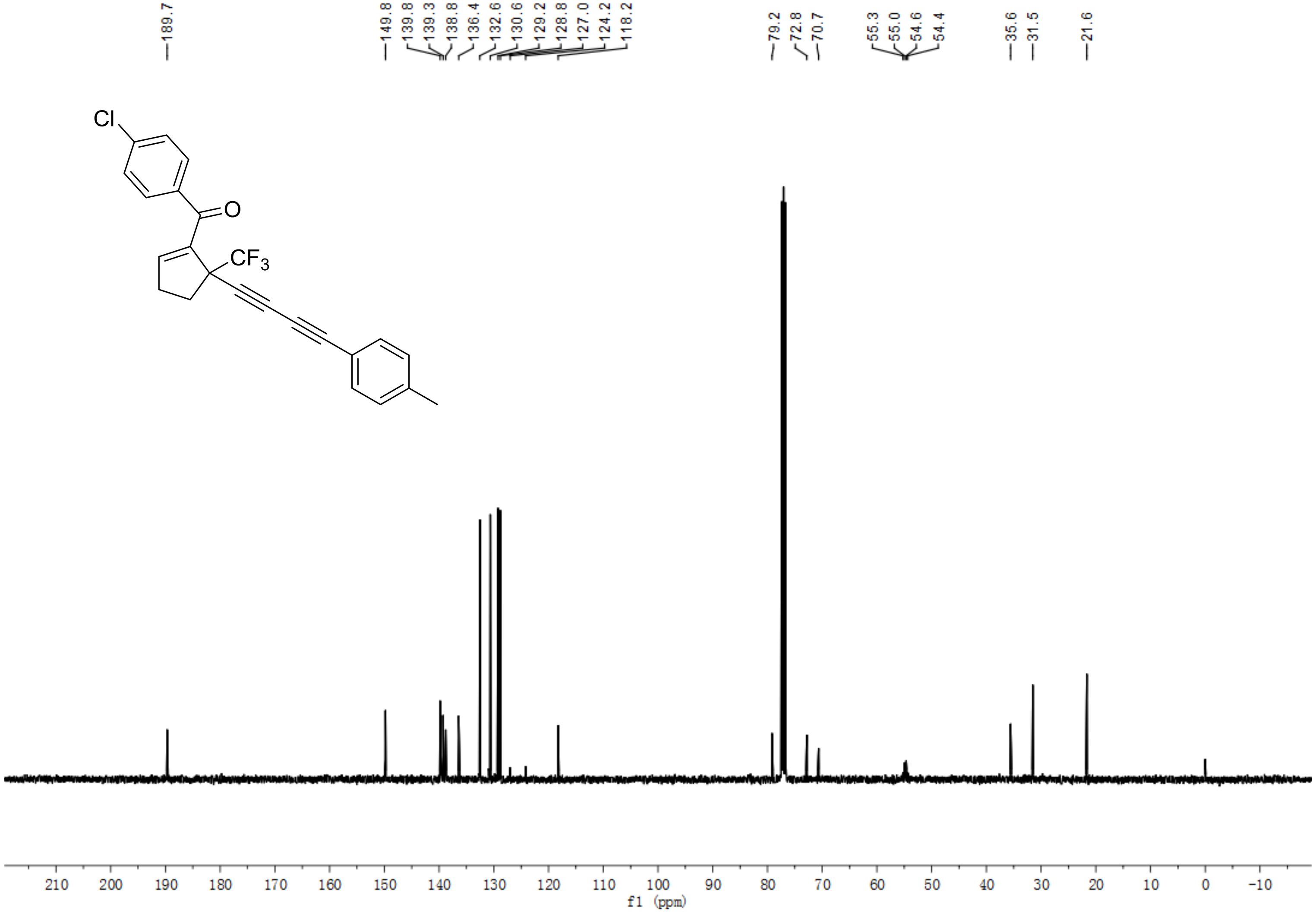




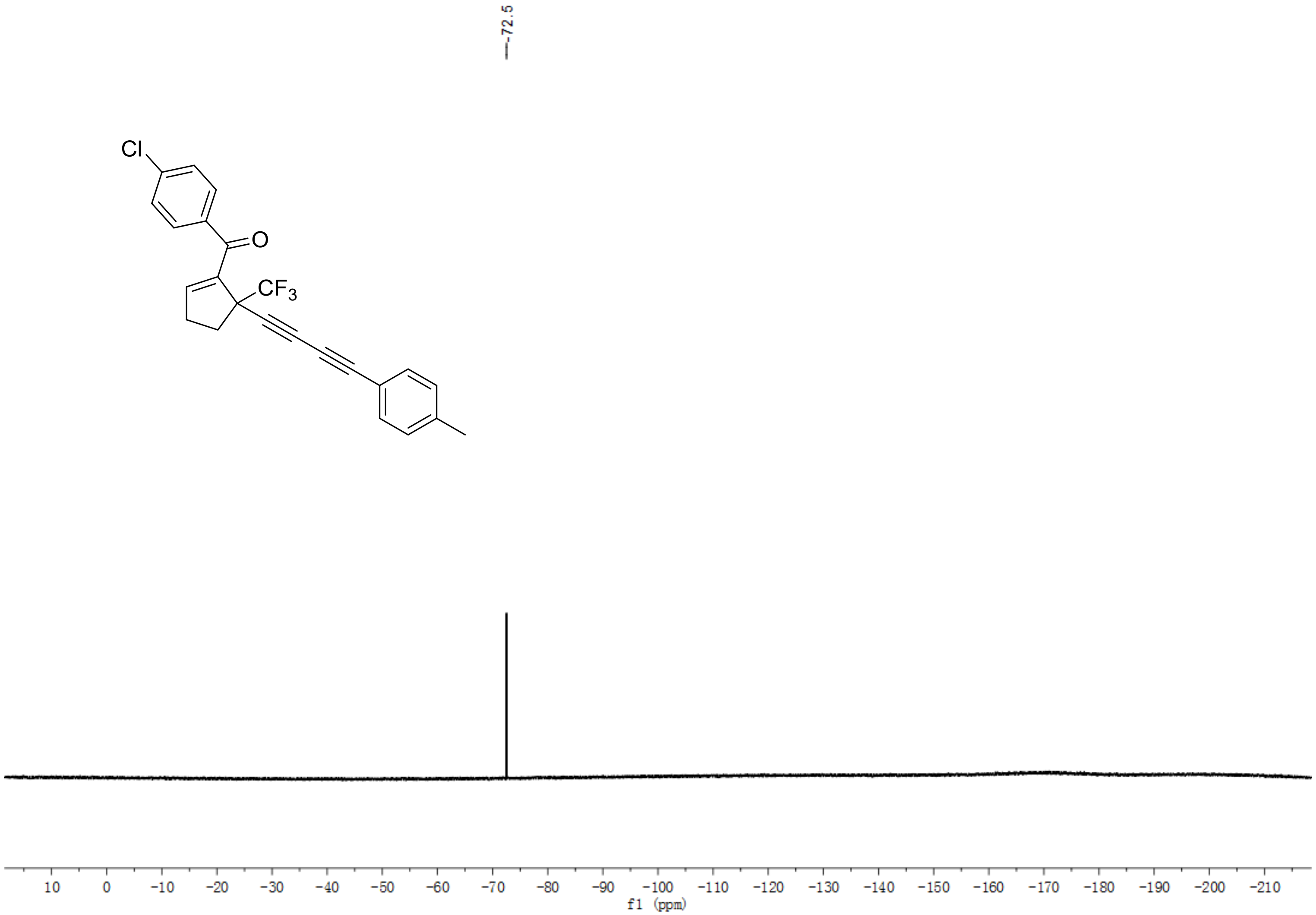
^{1}H NMR spectrum of product 6i (400 MHz, $CDCl_3$)



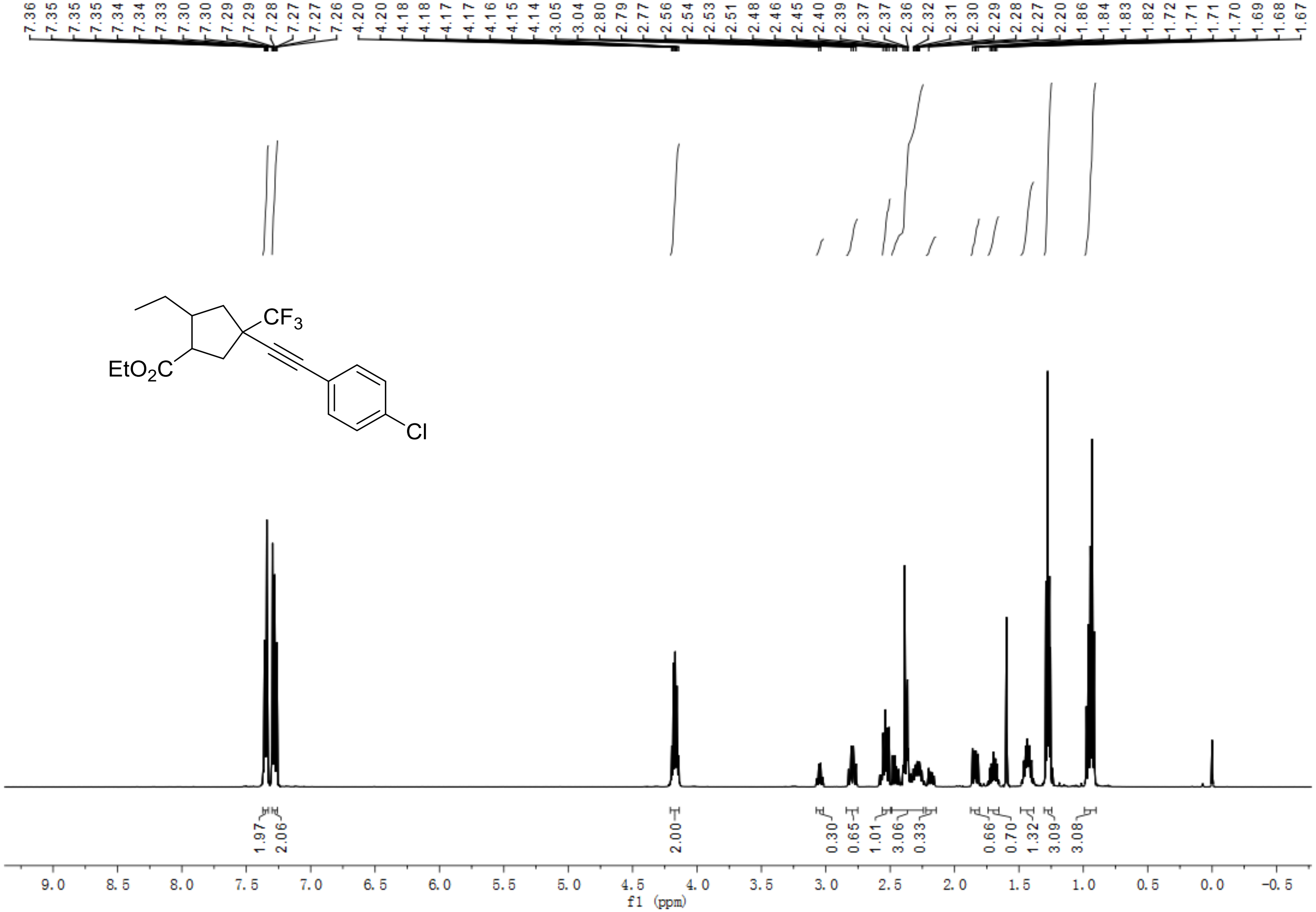
^{13}C NMR spectrum of product 6i (100 MHz, $CDCl_3$)



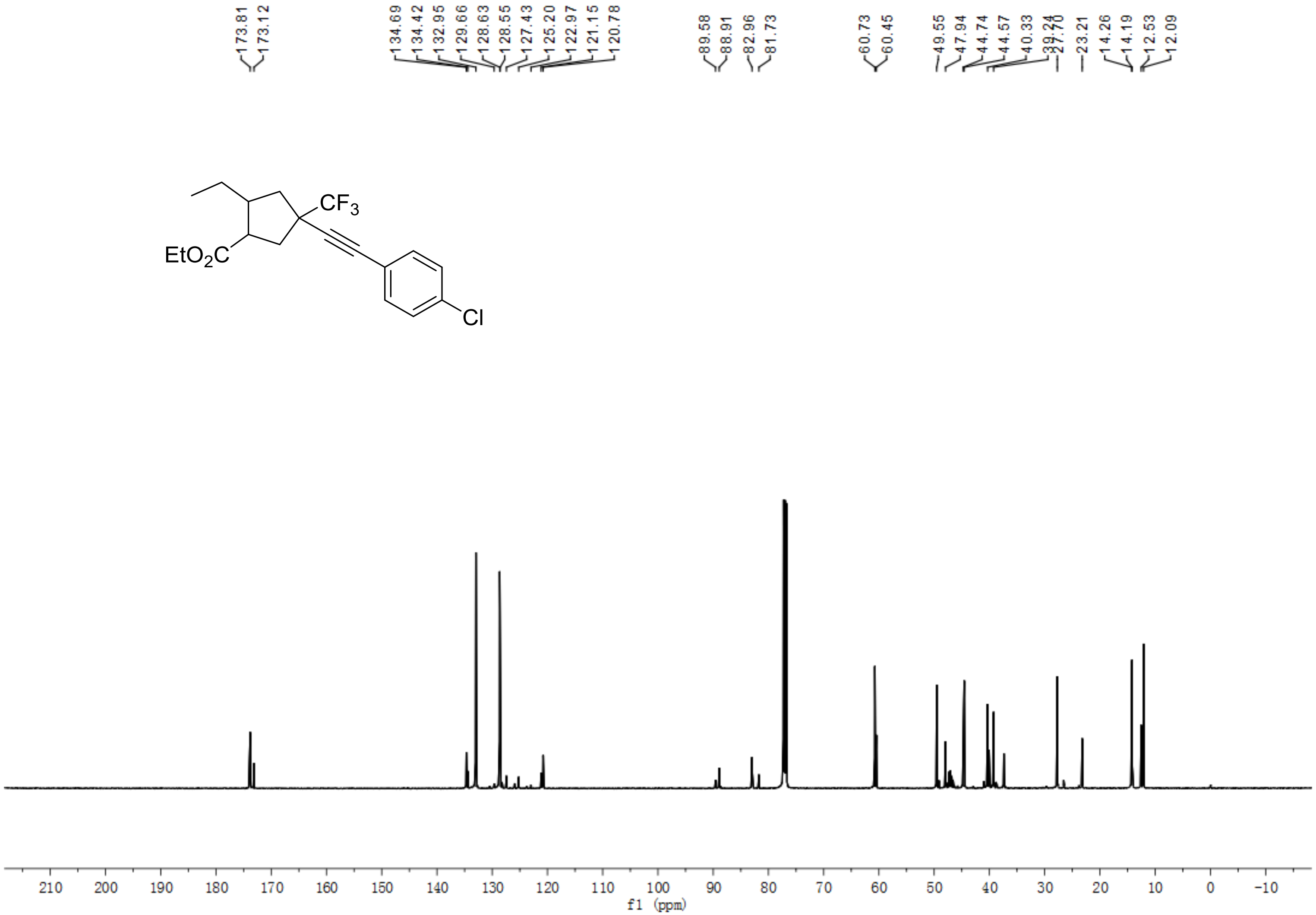
^{19}**F NMR spectrum of product 6i (376 MHz, CDCl$_3$)**



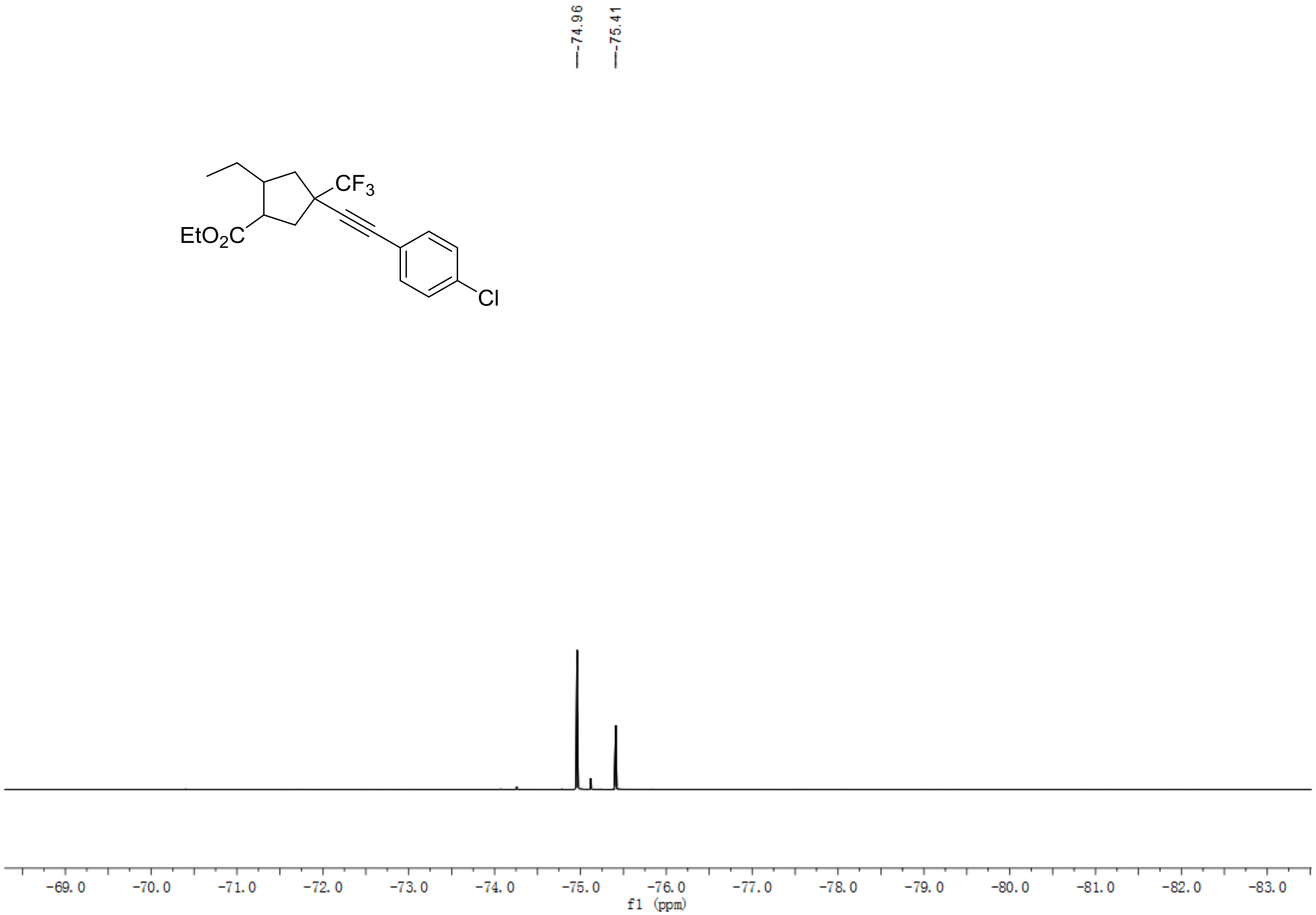
^{1}H NMR spectrum of product 7 (500 MHz, $CDCl_3$)



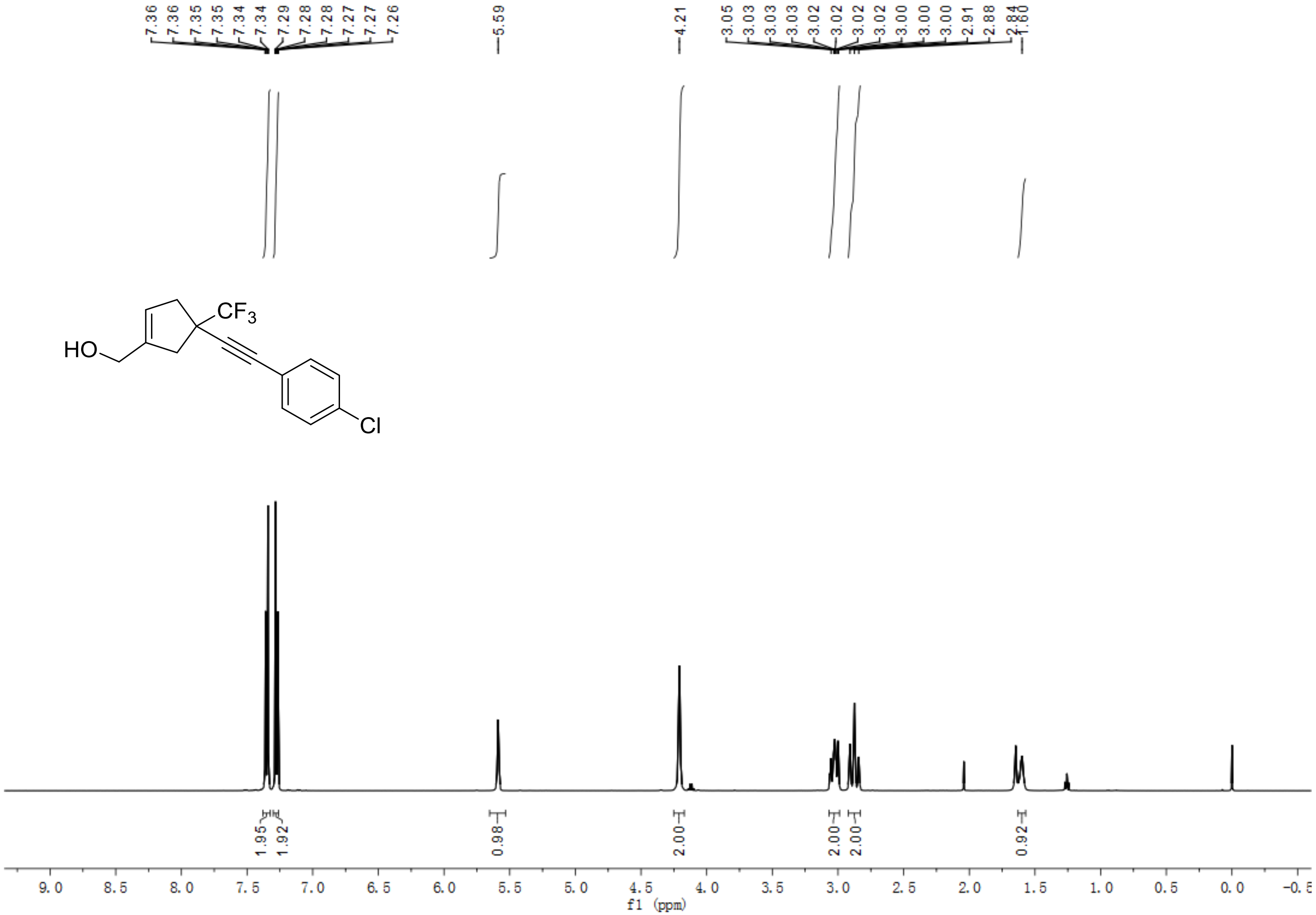
^{13}C NMR spectrum of product 7 (125 MHz, $CDCl_3$)



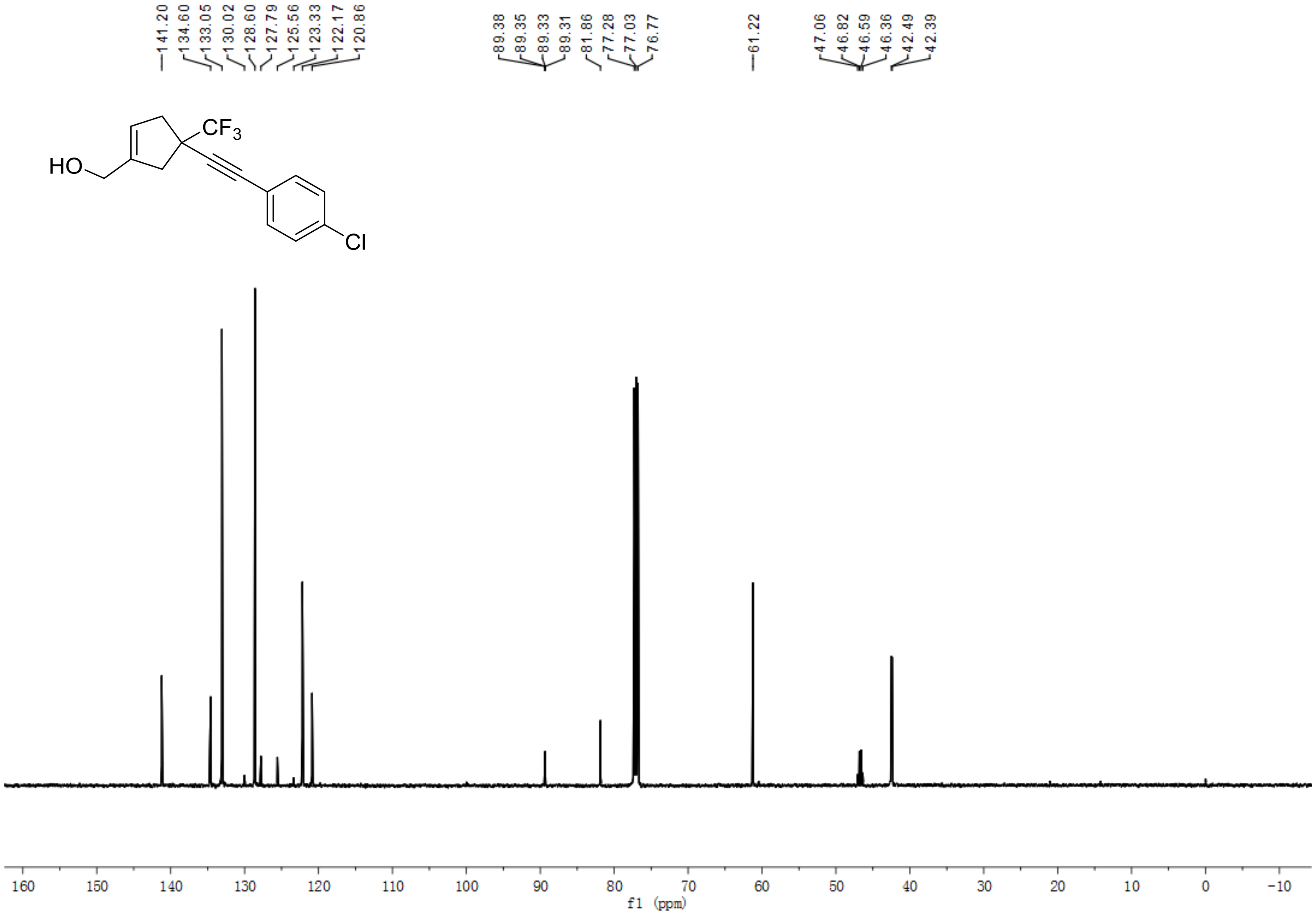
^{19}F NMR spectrum of product 7 (470 MHz, $CDCl_3$)



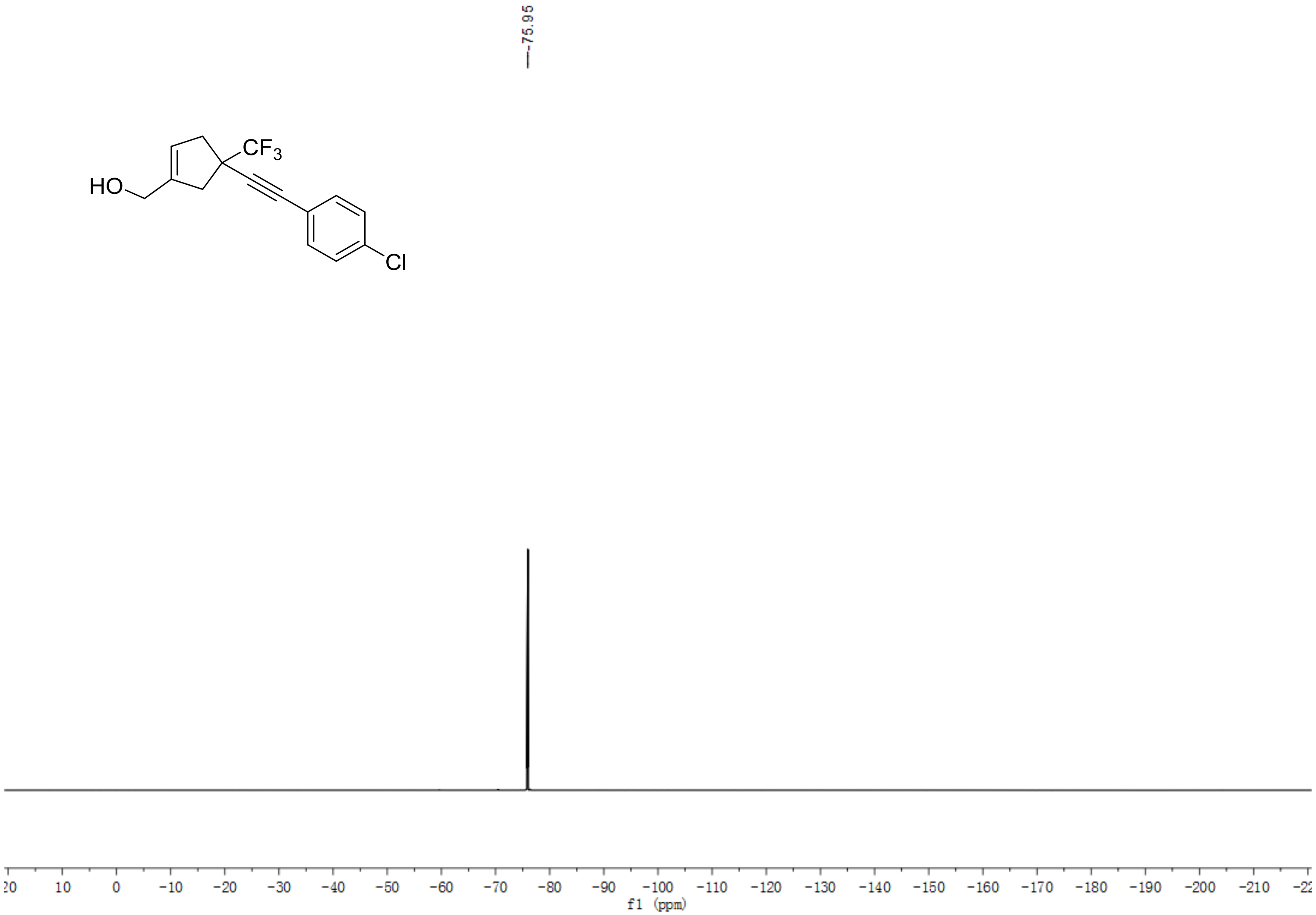
^{1}H NMR spectrum of product 8 (500 MHz, CDCl$_3$)



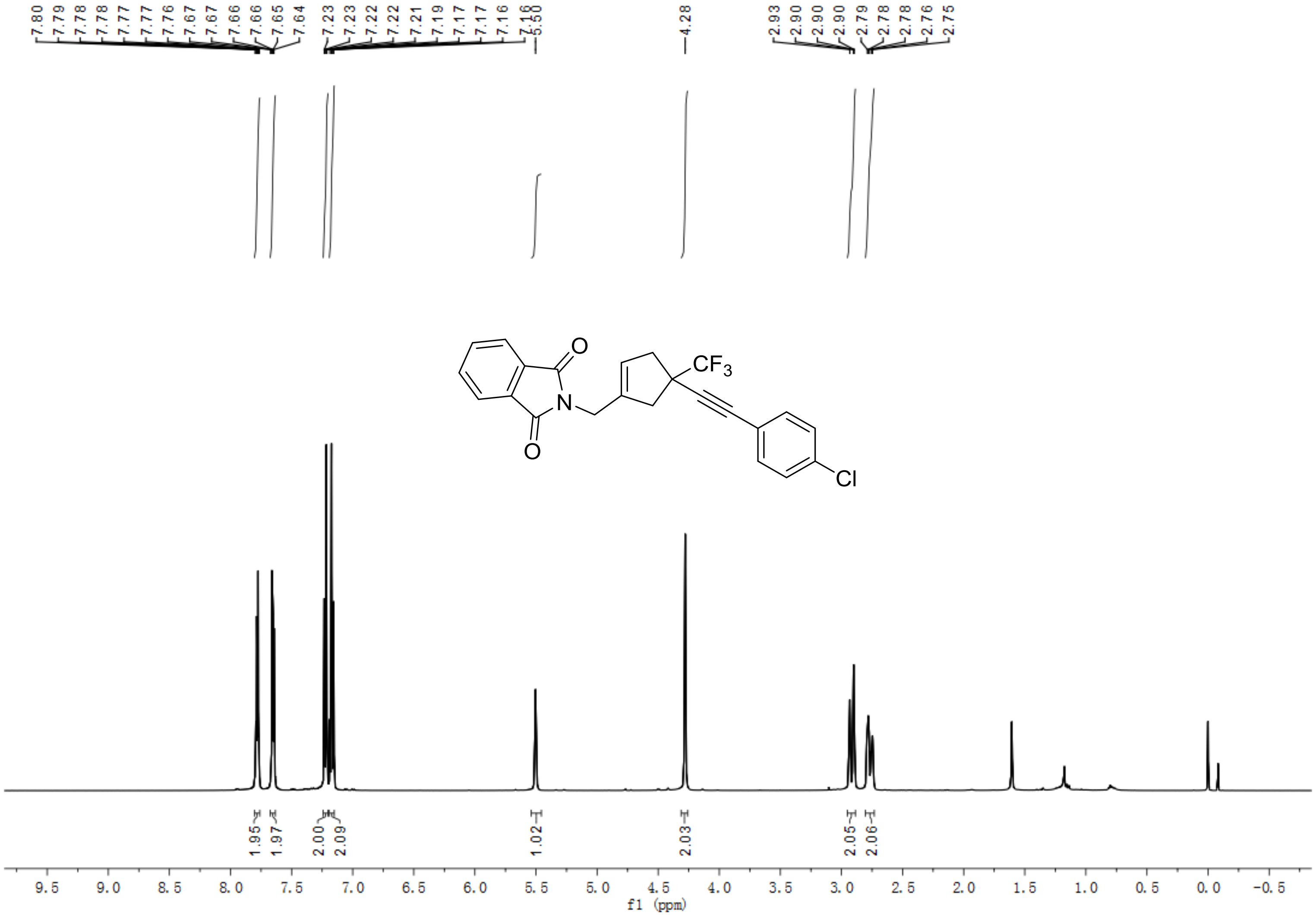
^{13}C NMR spectrum of product 8 (125 MHz, $CDCl_3$)



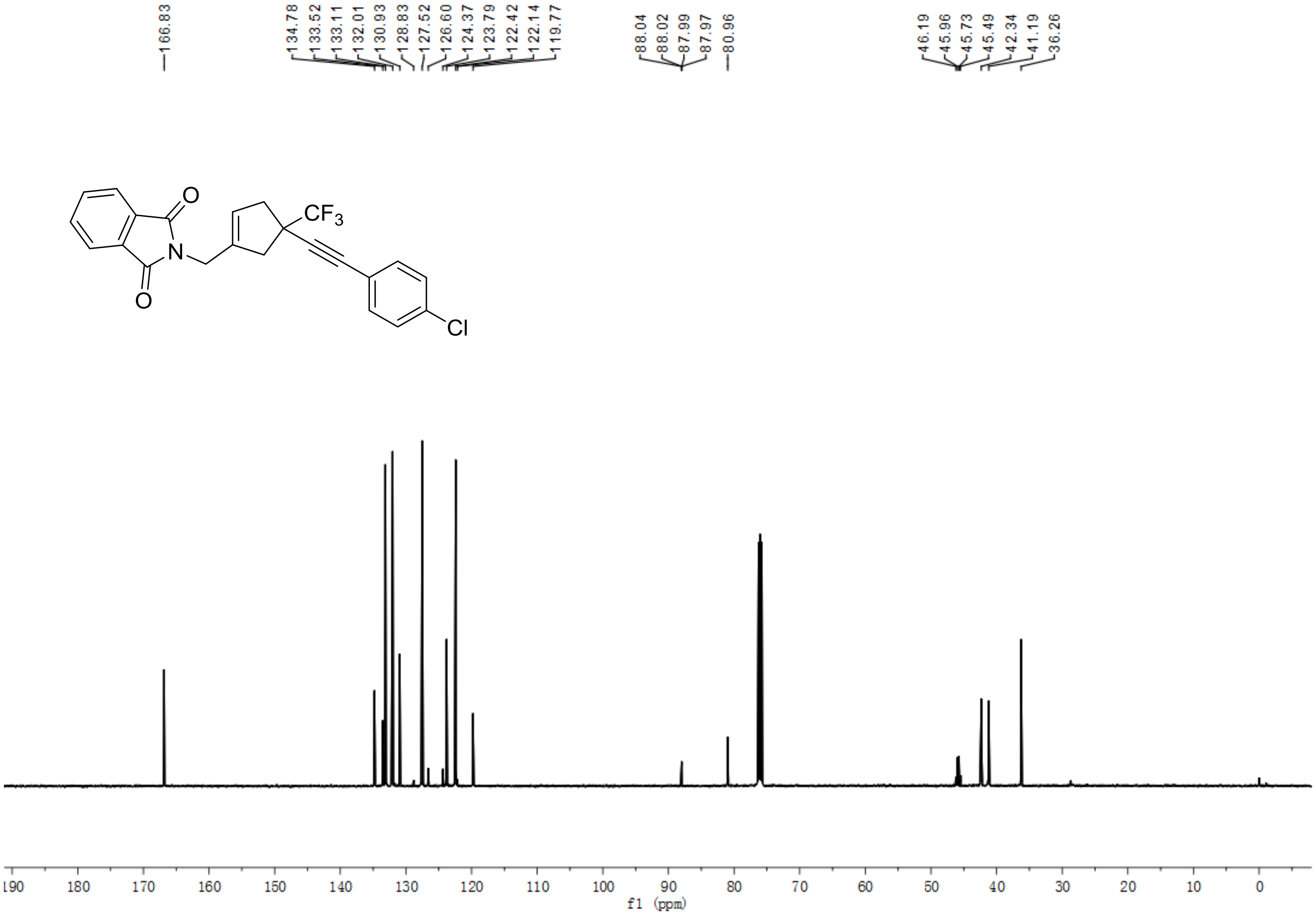
^{19}F NMR spectrum of product 8 (470 MHz, $CDCl_3$)



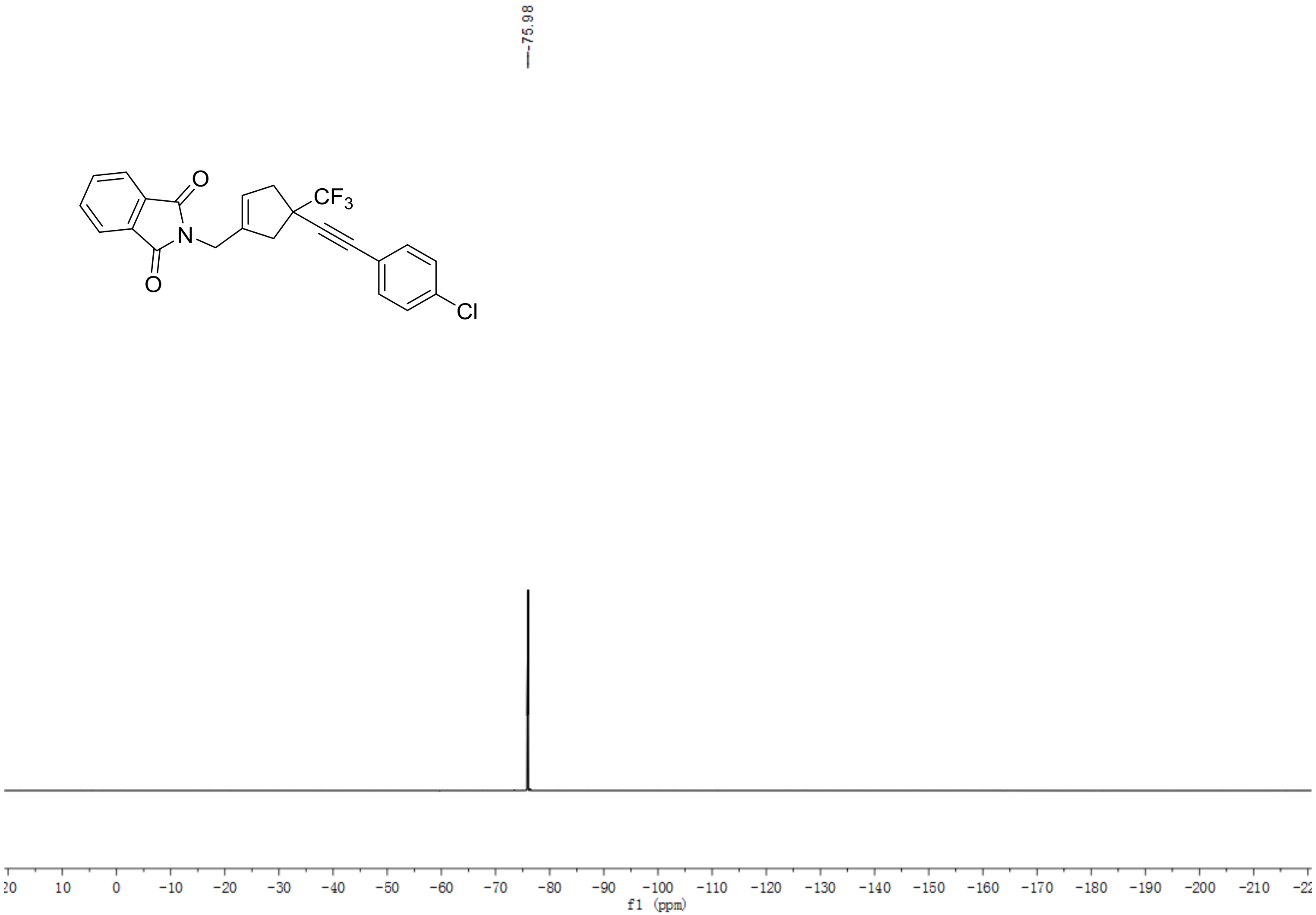
^{1}H NMR spectrum of product 9 (500 MHz, CDCl$_3$)



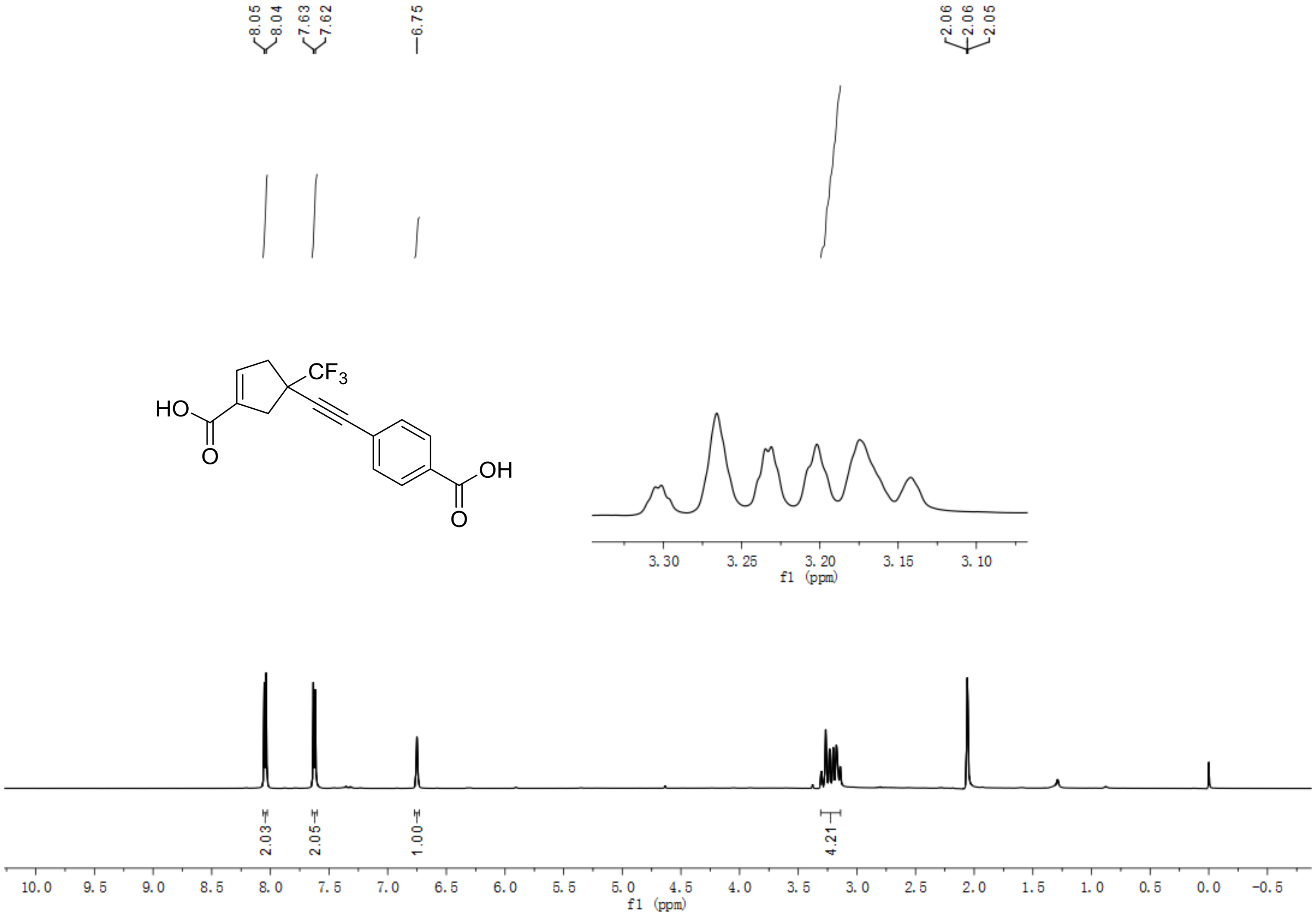
^{13}C NMR spectrum of product 9 (125 MHz, $CDCl_3$)



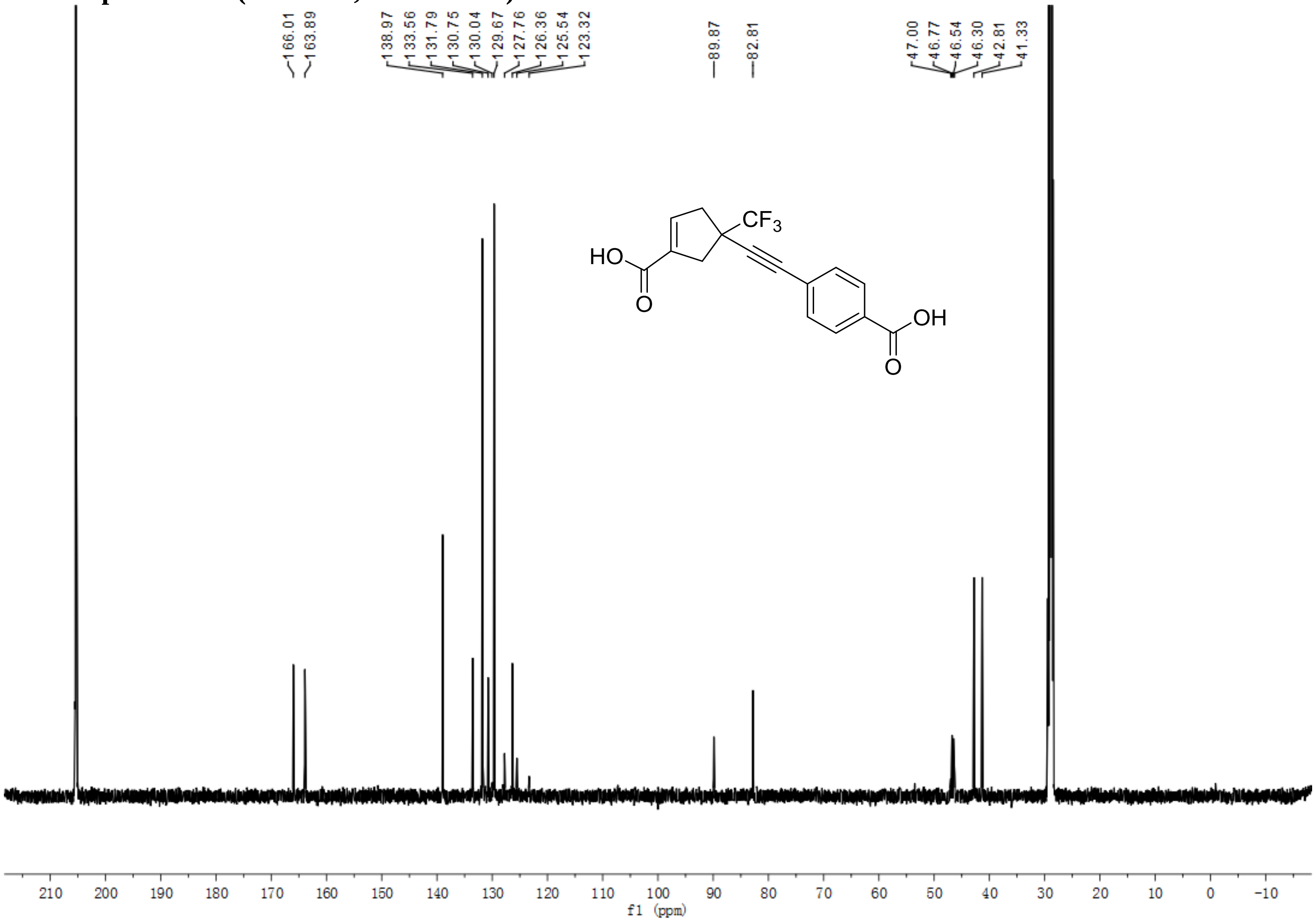
^{19}F NMR spectrum of product 9 (470 MHz, $CDCl_3$)



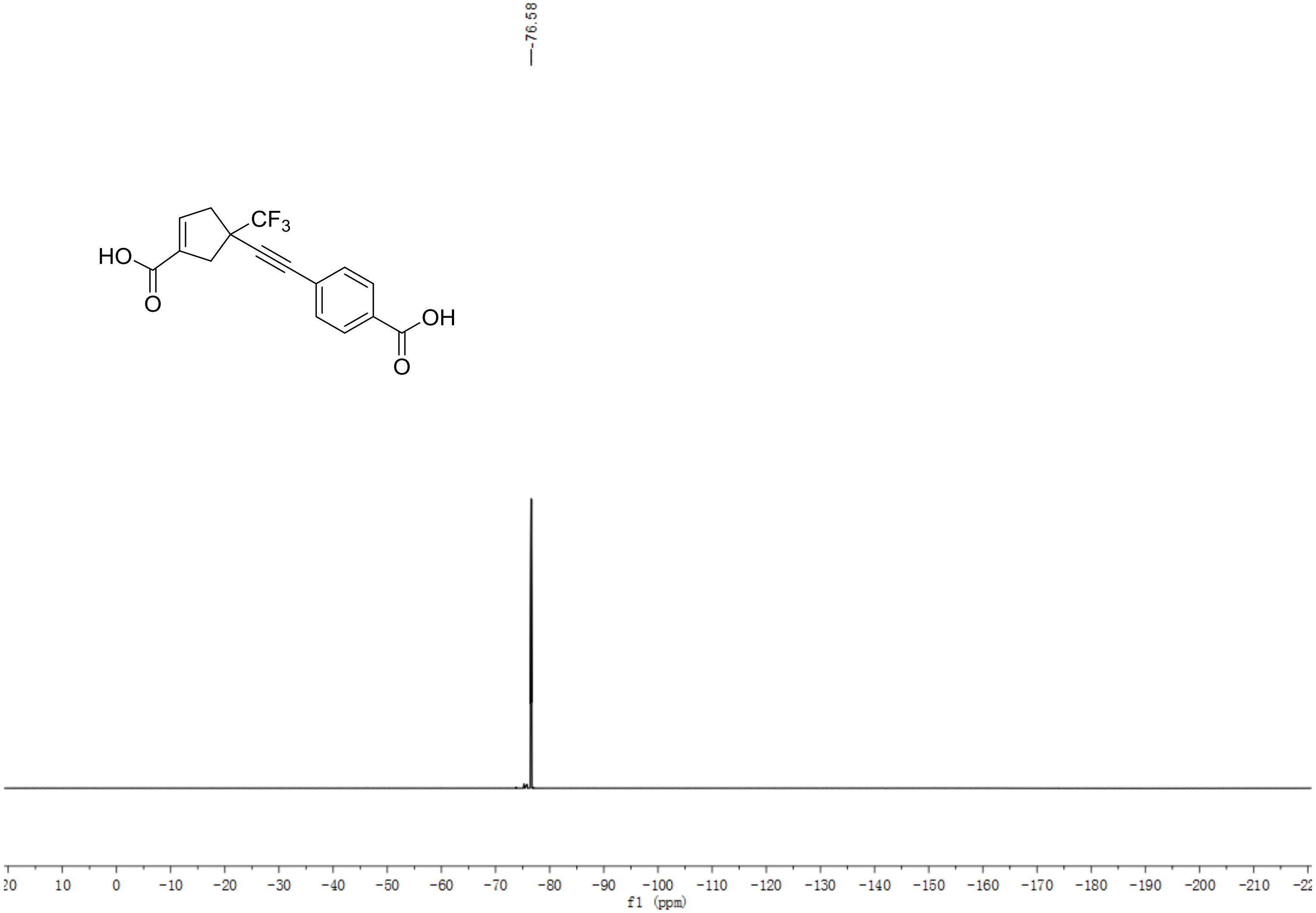
^{1}H NMR spectrum of product 10 (500 MHz, D6-Acetone)



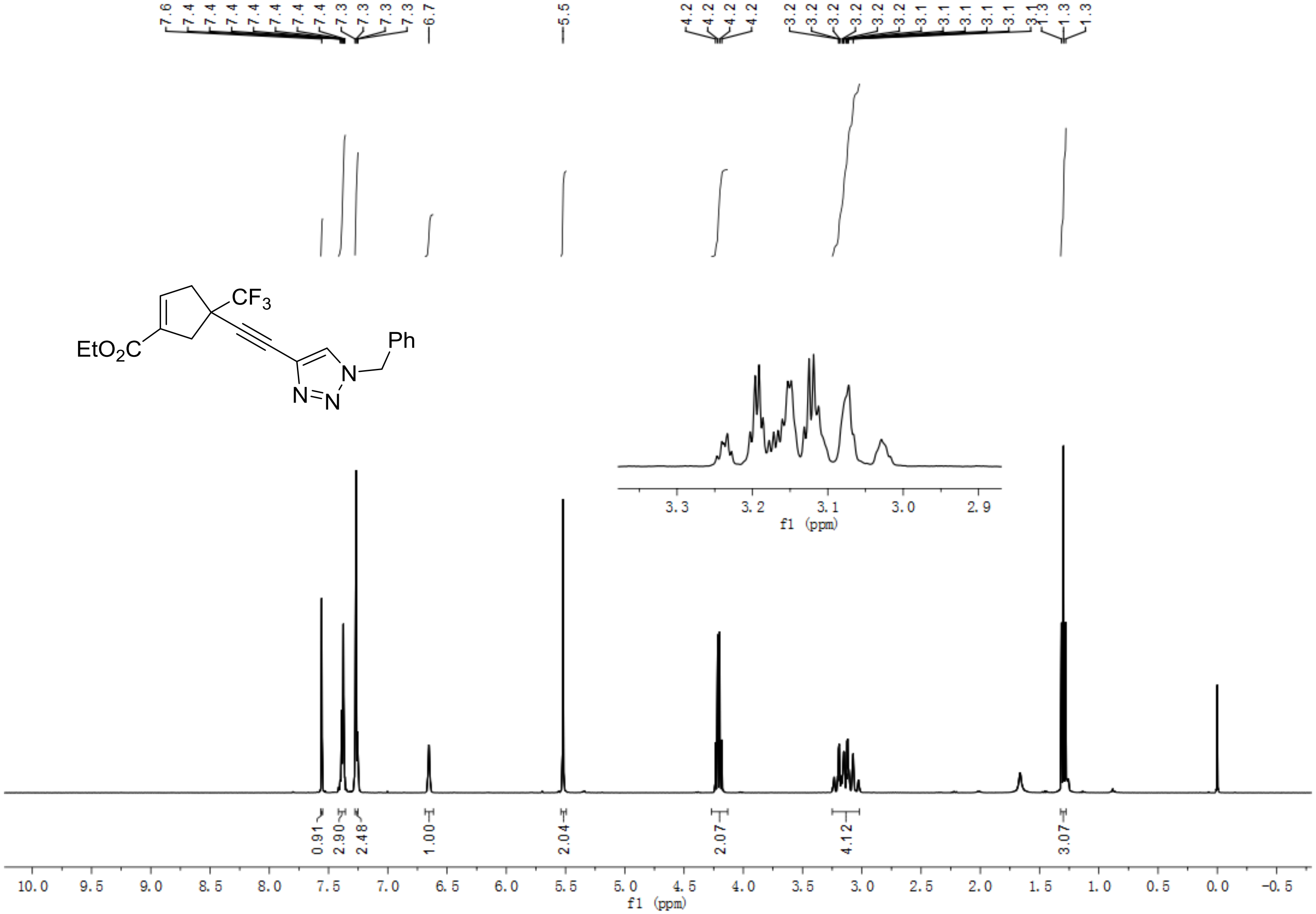
^{13}C NMR spectrum of product 10 (125 MHz, D6-Acetone)



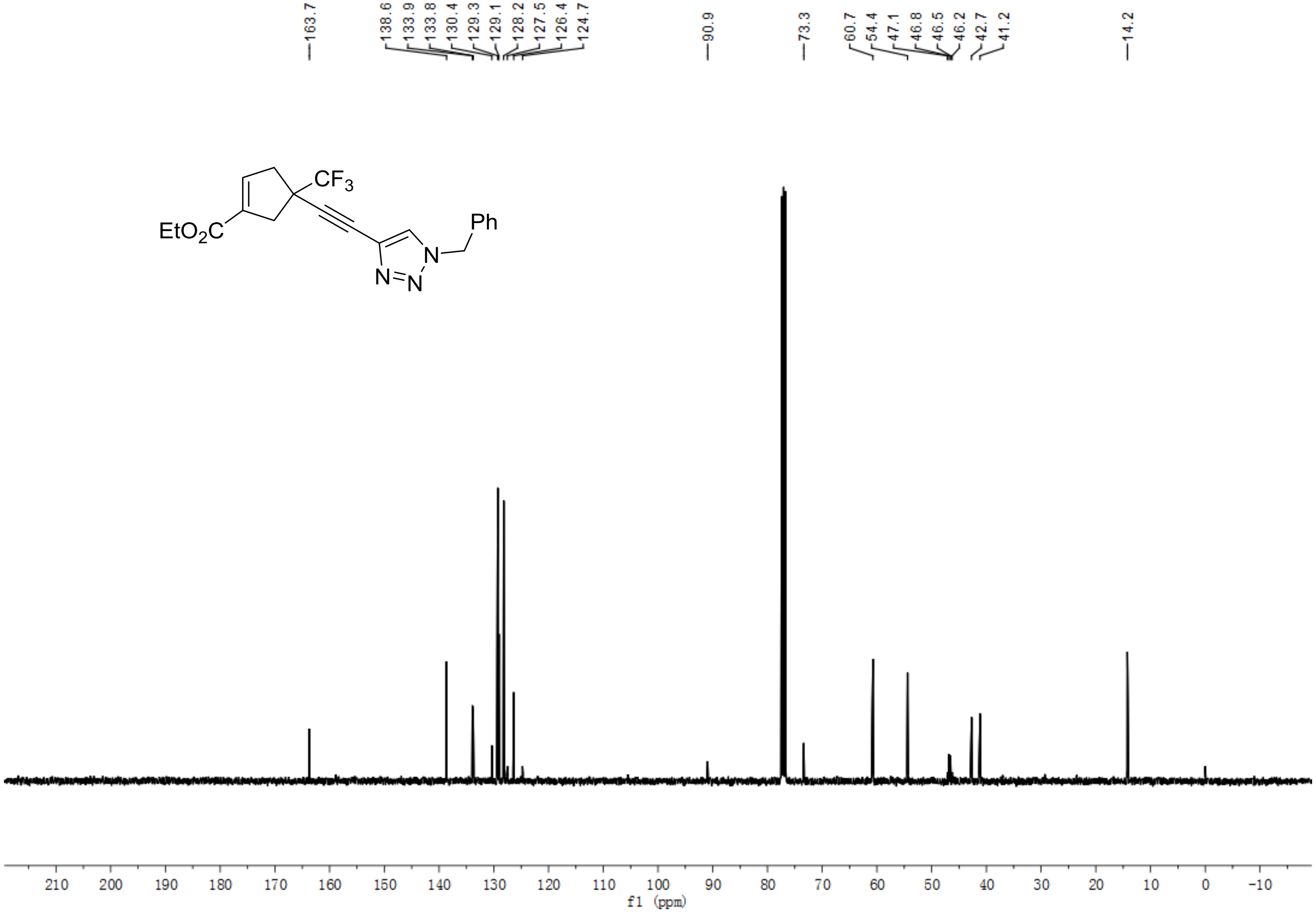
^{19}F NMR spectrum of product 10 (470 MHz, D6-Acetone)



^{1}H NMR spectrum of product 11 (400 MHz, CDCl$_3$)



^{13}C NMR spectrum of product 11 (100 MHz, $CDCl_3$)



^{19}F NMR spectrum of product 11 (376 MHz, $CDCl_3$)