Supplementary Information

Nickel-catalysed migratory hydroalkynylation and enantioselective hydroalkynylation of olefins with bromoalkynes

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Supplementary Methods

General reagent information. Solvents were either purified and dried by passage through alumina and Q5 reactant-packed columns on a solvent purification system or bought from the commercial sources and transferred to the glovebox without exposure to air. Other commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, TCI, Aladdin, J&K, Energy Chemical, Bide Pharmatech Ltd. and were used as received. Flash chromatography was performed using glass columns with silica gel (*SiliaFlash*® P60, particle size 40-63 μm, Silicycle).

$NiBr_2$·diglyme (CAS 312696-09-6) was purchased from Sigma-Aldrich;
NiI_2·xH_2O (CAS 7790-34-3) was purchased from Strem Chemical;
Na_2CO_3 (CAS 497-19-8) was purchased from Alfa Aesar;
K_3PO_4·H_2O (CAS 27176-10-9) was purchased from Sigma-Aldrich;
NaI (CAS 7681-82-5) was purchased from Alfa Aesar (ACS, 99.0% min.);
DME (CAS 110-71-4, 99.9%, extra dry, with molecular sieves, water≤30 ppm (by K.F.), EnergySeal) was purchased from Energy Chemical;
Benzotrifluoride ($PhCF_3$, CAS 98-08-8, 99%, SuperDry, water≤10 ppm, J&K Seal) was purchased from J&K;
Diglyme (CAS 111-96-6, 99.5%, SuperDry, J&K Seal) was purchased from J&K;
Bathocuproine (CAS 4733-39-5) was purchased from Energy Chemical;
4-Phenyl-1-butene (CAS 768-56-9) was purchased from TCI;
PMHS (CAS 63148-57-2, poly(methylhydrosiloxane)) was purchased from Sigma-Aldrich and stored under nitrogen at –20 °C in glove box;
$(MeO)_3SiH$ (CAS 2487-90-3) was purchased from Energy Chemical and stored under nitrogen at –20 °C in glove box;

Safety note: MSDS indicates that $(MeO)_3SiH$ is a corrosive and flammable liquid. According to the literatures[1,2], it may form pyrophoric gas (possibly SiH_4) during the storage or reaction. Although during our reaction, we used $(MeO)_3SiH$ without incident and SiH_4 was not observed, we urge the users of these procedures to be alert to the possibility of SiH_4 formation and possible exotherms and to take suitable precautions (suitable eye protection is also required).

General analytical information. All compounds (starting materials and products) were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and high-resolution mass spectrometry. ^1H NMR spectra were recorded on Bruker 500 MHz spectrometer and are referenced relative to residual $CDCl_3$ proton signals at δ 7.26 ppm. ^{19}F NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to $CFCl_3$ (δ 0.0

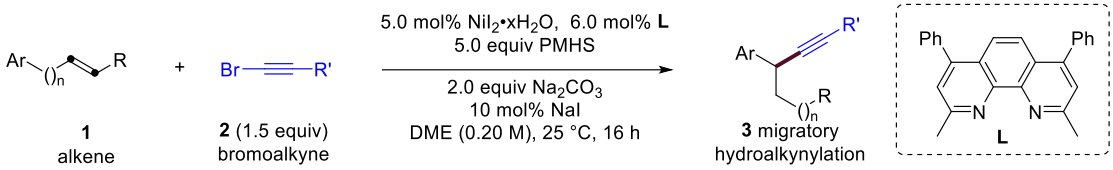
ppm). Data for ^{1}H and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant (Hz). ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer and are referenced to $CDCl_3$ at δ 77.16 ppm. The ^{13}C NMR spectra were obtained with ^{1}H decoupling. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were obtained on a Bruker Alpha and was reported in terms of frequency of absorption (cm^{-1}). GC analyses were performed on Agilent 7890 or 8890 gas chromatograph with an FID detector using a J&W DB-1 column (10 m, 0.1 mm I.D.). Low Resolution Mass spectra were obtained from on an Agilent 5977A GC-MS. r.r. refers to regioisomeric ratio, representing the ratio of the terminal coupling product to the sum of all other isomers as determined by GC and GC-MS analysis. High Resolution Mass spectra were obtained from on an Agilent 6540 Q-TOF mass spectrometer, operating electrospray ionization (ESI) mode. High pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using Daicel Chiralcel columns (250 mm). Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm pathlength cell at 589 nm with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions:
a Fisher 13×100 mm tube (Cat. No. 14-959-35C)

b Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)

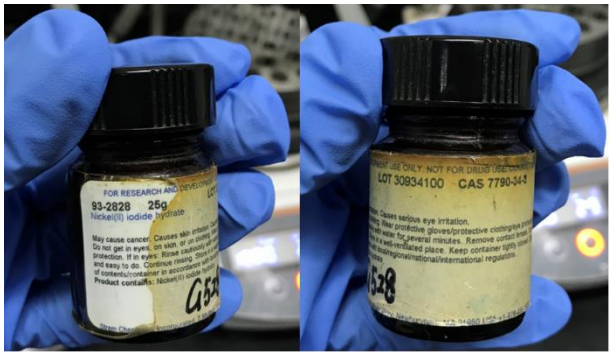
Supplementary Fig. 1. Screw-cap test tube and cap used.

NiH-Catalyzed Reductive Migratory Hydroalkynylation



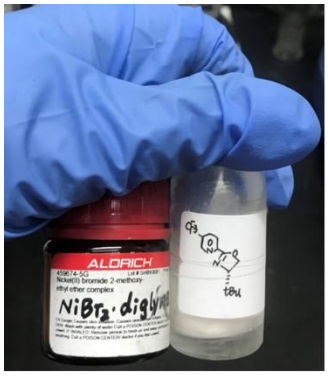
<u>General procedure (A)</u> for NiH-catalyzed reductive migratory hydroalkynylation.

In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar were added $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%) and anhydrous DME (1.0 mL). The mixture was stirred for 20 min at room temperature (stirred at 800 rpm) before the addition of PMHS (60 μL, 1.0 mmol, 5.0 equiv). Stirring was continued for an additional 5 min at room temperature before the addition of olefin **1** (0.20 mmol, 1.0 equiv) and bromoalkyne **2** (0.30 mmol, 1.5 equiv). The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 25 °C for up to 16 h (the mixture was stirred at 1000 rpm). After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with EtOAc. The organic layer was concentrated to give the crude product. Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by flash column chromatography (petroleum ether/EtOAc) for each substrate. The yields reported are the average of at least two experiments, unless otherwise indicated.

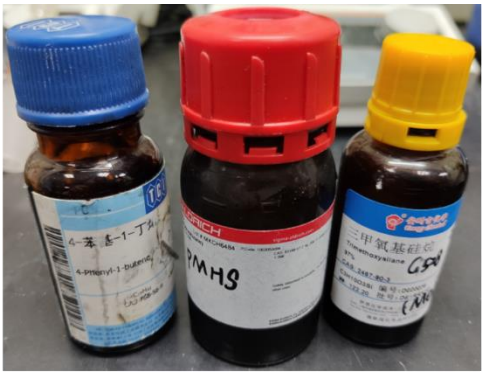


$NiI_2 \cdot xH_2O$

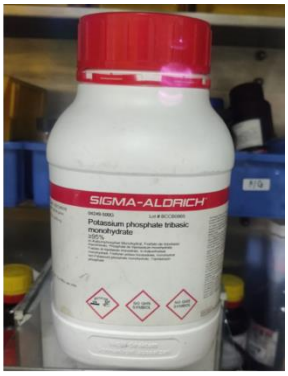
Na_2CO_3, NaI, **L**



L*, $NiBr_2 \cdot diglyme$

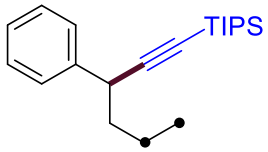


PMHS, $(MeO)_3SiH$, 4-Phenyl-1-butene



$K_3PO_4 \cdot H_2O$

Supplementary Fig. 2. Catalyst and reagents to be used.



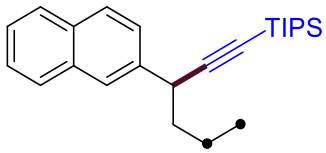
Triisopropyl(3-phenylhex-1-yn-1-yl)silane (Figure 3, **3a**). From **4-phenyl-1-butene** (**1a**) (26.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 82% yield (51.6 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.22 (m, 1H), 3.74 (dd, J = 7.9, 6.4 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.60 – 1.46 (m, 2H), 1.20 – 1.06 (m, 21H), 0.96 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 128.4, 127.6, 126.5, 110.2, 83.1, 41.4, 38.8, 20.6, 18.8, 13.9, 11.4;

HRMS (ESI) calcd. for $C_{21}H_{34}SiNa$ $[M+Na]^+$ *m/z* 337.2322, found 337.2320;

IR (neat, cm^{-1}) 2941, 2864, 2164, 1462, 1097, 663.



Triisopropyl(3-(naphthalen-2-yl)hex-1-yn-1-yl)silane (Figure 3, **3b**). From **2-(but-3-en-1-yl)naphthalene** (**1b**) (36.4 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 54% yield (39.6 mg),

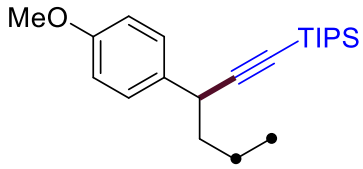
and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.84 – 7.78 (m, 3H), 7.54 – 7.42 (m, 3H), 3.88 (t, *J* = 7.1 Hz, 1H), 1.88 – 1.75 (m, 2H), 1.64 – 1.39 (m, 2H), 1.19 – 1.07 (m, 21H), 0.95 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 133.5, 132.4, 128.0, 127.8, 127.7, 126.2, 126.1 (2C), 125.5, 110.2, 83.5, 41.0, 38.9, 20.6, 18.8, 13.9, 11.5;

HRMS (ESI) calcd. for $C_{25}H_{36}SiNa$ $[M+Na]^+$ *m/z* 387.2478, found 387.2480;

IR (neat, cm^{-1}) 2956, 2891, 2167, 1462, 854, 744.



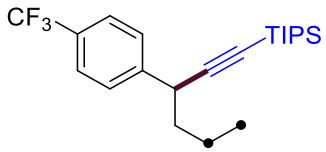
Triisopropyl(3-(4-methoxyphenyl)hex-1-yn-1-yl)silane (Figure 3, **3c**). From **1-(but-3-en-1-yl)-4-methoxybenzene** (**1c**) (32.4 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 75% yield (51.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.67 (dd, *J* = 8.0, 6.3 Hz, 1H), 1.75 – 1.64 (m, 2H), 1.59 – 1.35 (m, 2H), 1.12 – 0.97 (m, 21H), 0.93 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.6, 128.5, 113.8, 110.6, 82.8, 55.3, 41.4, 37.9, 20.5, 18.8, 13.9, 11.4;

HRMS (ESI) calcd. for $C_{22}H_{36}OSiNa$ $[M+Na]^+$ m/z 367.2428, found 367.2426;

IR (neat, cm^{-1}) 2955, 2863, 2167, 1610, 1462, 882.



Triisopropyl(3-(4-(trifluoromethyl)phenyl)hex-1-yn-1-yl)silane (Figure 3, **3d**). From **1-(but-3-en-1-yl)-4-(trifluoromethyl)benzene** (**1d**) (40.0 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 92% yield (70.0 mg), and >99:1 rr was detected by GC.

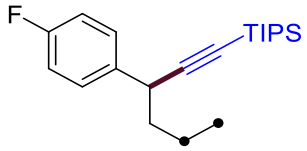
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 3.77 (dd, J = 7.9, 6.5 Hz, 1H), 1.76 – 1.67 (m, 2H), 1.58 – 1.46 (m, 2H), 1.16 – 1.04 (m, 21H), 0.94 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 128.9 (q, J = 32.4 Hz), 127.9, 125.4 (q, J = 3.9 Hz), 124.2 (q, J = 272.4 Hz), 109.0, 84.1, 41.1, 38.7, 20.5, 18.8, 13.8, 11.4;

^{19}F NMR (471 MHz, $CDCl_3$) δ –62.3;

HRMS (ESI) calcd. for $C_{22}H_{33}F_3SiNa$ $[M+Na]^+$ *m/z* 405.2196, found 405.2198;

IR (neat, cm^{-1}) 2958, 2865, 2169, 1463, 882, 675.



(3-(4-Fluorophenyl)hex-1-yn-1-yl)triisopropylsilane (Figure 3, **3e**). From **1-(but-3-en-1-yl)-4-fluorobenzene** (**1e**) (30.0 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16

h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 65% yield (43.2 mg), and >99:1 rr was detected by GC.

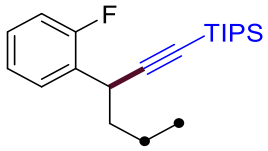
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.04 – 6.96 (m, 2H), 3.69 (dd, *J* = 8.1, 6.2 Hz, 1H), 1.74 – 1.65 (m, 2H), 1.55 – 1.38 (m, 2H), 1.12 – 1.04 (m, 21H), 0.93 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.6 Hz), 138.1 (d, *J* = 3.3 Hz), 129.0 (d, *J* = 8.8 Hz), 115.1 (d, *J* = 21.3 Hz), 110.0, 83.4, 41.3, 38.0, 20.5, 18.8, 13.8, 11.4;

^{19}F NMR (471 MHz, $CDCl_3$) δ –116.8;

HRMS (ESI) calcd. for $C_{21}H_{33}FSiNa$ $[M+Na]^+$ *m/z* 355.2228, found 355.2225;

IR (neat, cm^{-1}) 2957, 2864, 2168, 1604, 1462, 665.



(3-(2-Fluorophenyl)hex-1-yn-1-yl)triisopropylsilane (Figure 3, **3f**). From **1-(but-3-en-1-yl)-2-fluorobenzene** (**1f**) (30.0 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 75% yield (49.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.24 – 7.17 (m, 1H), 7.15 – 7.08 (m, 1H), 7.05 – 6.93 (m, 1H), 4.07 (dd, *J* = 8.2, 5.9 Hz, 1H), 1.76 – 1.64 (m, 2H), 1.58 – 1.44 (m, 2H), 1.13 – 1.07 (m, 21H), 0.94 (t, *J* = 7.3 Hz, 3H);

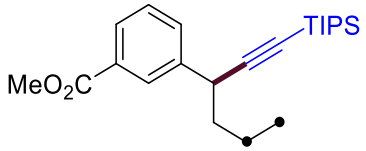
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0 (d, *J* = 246.1 Hz), 129.4 (d, *J* = 4.1 Hz), 129.3, 128.2 (d, *J* = 8.1 Hz), 124.1 (d, *J* = 3.5 Hz), 115.2 (d, *J* = 22.3 Hz), 109.1, 83.1, 39.7,

31.9 (d, J = 3.3 Hz), 20.5, 18.8, 13.8, 11.4;

^{19}F NMR (471 MHz, $CDCl_3$) δ –119.8;

HRMS (ESI) calcd. for $C_{21}H_{33}FSiNa$ $[M+Na]^+$ *m/z* 355.2228, found 355.2224;

IR (neat, cm^{-1}) 2957, 2864, 2169, 1228, 882, 675.



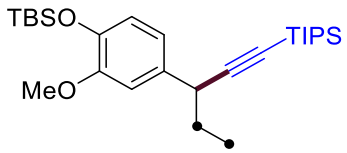
Methyl 3-(1-(triisopropylsilyl)hex-1-yn-3-yl)benzoate (Figure 3, **3g**). From **methyl 3-(but-3-en-1-yl)benzoate** (**1g**) (38.0 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 82% yield (61.0 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 1H), 7.94 – 7.87 (m, 1H), 7.61 – 7.54 (m, 1H), 7.39 (t, J = 7.7 Hz, 1H), 3.91 (s, 3H), 3.76 (t, J = 7.2 Hz, 1H), 1.80 – 1.67 (m, 2H), 1.55 – 1.36 (m, 2H), 1.13 – 1.05 (m, 21H), 0.93 (t, J = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 142.8, 132.1, 130.3, 128.8, 128.5, 127.9, 109.4, 83.9, 52.1, 41.1, 38.5, 20.5, 18.7, 13.8, 11.4;

HRMS (ESI) calcd. for $C_{23}H_{36}O_2SiNa$ $[M+Na]^+$ *m/z* 395.2377, found 395.2374;

IR (neat, cm^{-1}) 2941, 2864, 2168, 1462, 855, 675.



***tert*-Butyl(2-methoxy-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)phenoxy)dimethylsilane** (Figure 3, **3h**). From **(4-allyl-2-methoxyphenoxy)(tert-**

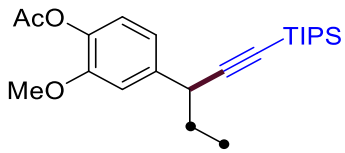
butyl)dimethylsilane (**1h**) (55.7 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 57% yield (52.4 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* = 1.8 Hz, 1H), 6.81 – 6.73 (m, 2H), 3.80 (s, 3H), 3.61 (dd, *J* = 8.2, 5.4 Hz, 1H), 1.86 – 1.65 (m, 2H), 1.13 – 1.07 (m, 21H), 1.03 – 0.96 (m, 12H), 0.16 (s, 3H), 0.16 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 143.5, 135.5, 120.5, 119.7, 111.5, 110.5, 83.2, 55.4, 40.1, 32.2, 25.8, 18.8, 18.5, 11.7, 11.4, –4.4, –4.5;

HRMS (ESI) calcd. for $C_{27}H_{48}O_2Si_2Na$ $[M+Na]^+$ *m/z* 483.3085, found 483.3082;

IR (neat, cm^{-1}) 2938, 2863, 2166, 1463, 1282, 728.



2-Methoxy-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)phenyl acetate (Figure 3, **3i**). From **4-allyl-2-methoxyphenyl acetate** (**1i**) (41.2 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 78% yield (60.8 mg), and >99:1 rr was detected by GC.

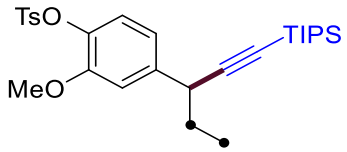
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.90 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.83 (s, 3H), 3.66 (dd, *J* = 8.5, 5.3 Hz, 1H), 2.31 (s, 3H), 1.88

– 1.78 (m, 1H), 1.77 – 1.68 (m, 1H), 1.14 – 1.07 (m, 21H), 1.05 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 150.8, 140.9, 138.2, 122.4, 119.7, 111.8, 109.5, 83.8, 55.8, 40.4, 32.2, 20.8, 18.8, 11.8, 11.4;

HRMS (ESI) calcd. for $C_{23}H_{36}O_3SiNa$ $[M+Na]^+$ *m/z* 411.2326, found 411.2322;

IR (neat, cm^{-1}) 2958, 2864, 2167, 1462, 881, 673.



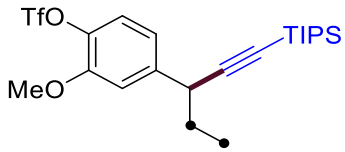
2-Methoxy-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)phenyl 4-methylbenzenesulfonate (Figure 3, **3j**). From **4-allyl-2-methoxyphenyl 4-methylbenzenesulfonate** (**1j**) (63.7 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 99% yield (98.7 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.83 (dd, J = 8.3, 2.0 Hz, 1H), 3.61 (dd, J = 8.3, 5.3 Hz, 1H), 3.52 (s, 3H), 2.43 (s, 3H), 1.83 – 1.73 (m, 1H), 1.73 – 1.63 (m, 1H), 1.08 (t, J = 2.2 Hz, 21H), 1.00 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 144.9, 142.3, 136.9, 133.3, 129.3, 128.7, 123.7, 119.6, 111.9, 109.3, 84.0, 55.4, 40.3, 32.0, 21.7, 18.7, 11.6, 11.3;

HRMS (ESI) calcd. for $C_{28}H_{40}O_4SSiNa$ $[M+Na]^+$ *m/z* 523.2309, found 523.2304;

IR (neat, cm^{-1}) 2942, 2865, 2168, 1373, 1092, 649.



2-Methoxy-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)phenyl trifluoromethanesulfonate (Figure 3, **3k**). From **4-allyl-2-methoxyphenyl trifluoromethanesulfonate** (**1k**) (59.2 mg, 0.20 mmol), and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 96% yield (91.4 mg), and >99:1 rr was detected by GC.

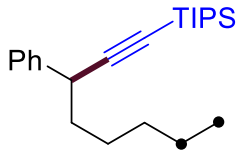
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.0 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.91 (s, 3H), 3.69 (dd, *J* = 8.4, 5.3 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.76 – 1.67 (m, 1H), 1.12 – 1.10 (m, 21H), 1.05 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 143.8, 137.3, 122.1, 119.9, 118.9 (q, *J* = 321.3 Hz), 112.5, 108.8, 84.6, 56.1, 40.4, 32.1, 18.8, 11.7, 11.4;

^{19}F NMR (471 MHz, $CDCl_3$) δ –73.9;

HRMS (ESI) calcd. for $C_{22}H_{33}F_3O_4SSiNa$ $[M+Na]^+$ *m/z* 501.1713, found 501.1709;

IR (neat, cm^{-1}) 2941, 2865, 2169, 1503, 1205, 881.



Triisopropyl(3-phenyloct-1-yn-1-yl)silane (Figure 3, **3l**). From **hex-5-en-1-ylbenzene** (**1l**) (32.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (7.6 mg, 10.0 mol%), **L** (8.6 mg, 12.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (6.0 mg, 20 mol%), PMHS (60.0 μL, 5.0 equiv) and

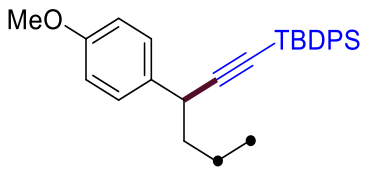
anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 44% yield (30.3 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.36 – 7.27 (m, 2H), 7.27 – 7.17 (m, 1H), 3.69 (dd, *J* = 7.8, 6.4 Hz, 1H), 1.78 – 1.64 (m, 2H), 1.53 – 1.42 (m, 2H), 1.33 – 1.26 (m, 4H), 1.13 – 1.00 (m, 21H), 0.91 – 0.85 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.4, 127.5, 126.5, 110.2, 83.2, 39.2, 39.0, 31.6, 27.0, 22.6, 18.8, 14.1, 11.4;

HRMS (ESI) calcd. for $C_{23}H_{38}SiNa$ $[M+Na]^+$ *m/z* 365.2635, found 365.2636;

IR (neat, cm^{-1}) 2939, 2863, 2167, 1462, 882, 663.



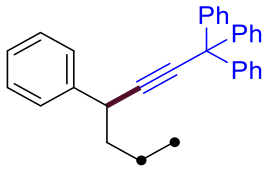
***tert*-Butyldiphenyl(3-phenylhex-1-yn-1-yl)silane** (Figure 3, **3m**). From **1-(but-3-en-1-yl)-4-methoxybenzene** (**1m**) (32.4 mg, 0.20 mmol), and **(bromoethynyl)(*tert*-butyl)diphenylsilane** (**2b**) (103.0 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10 mol%), PMHS (60.0 μL, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 95% yield (80.9 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) 8.14 – 7.62 (m, 4H), 7.43 – 7.32 (m, 8H), 6.94 – 6.85 (m, 2H), 3.87 – 3.70 (m, 4H), 1.90 – 1.71 (m, 2H), 1.63 – 1.46 (m, 2H), 1.11 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 135.7, 134.1, 134.0, 133.9, 129.4, 128.6, 127.7, 113.9, 113.3, 82.0, 55.4, 41.2, 38.1, 27.2, 20.7, 18.7, 13.9;

HRMS (ESI) calcd. for $C_{29}H_{35}OSi$ $[M+H]^+$ *m/z* 427.2452, found 427.2446;

IR (neat, cm^{-1}) 2956, 2856, 2168, 1509, 1248, 697.



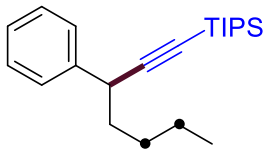
Hept-2-yne-1,1,1,4-tetrayltetrabenzene (Figure 3, **3n**). From **4-phenyl-1- butene** (**1n**) (26.4 mg, 0.20 mmol) and **(3-bromoprop-2-yne-1,1,1-triyl)tribenzene** (**2c**) (104.2 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 40% yield (31.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.33 – 7.20 (m, 18H), 3.83 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.90 – 1.74 (m, 2H), 1.54 – 1.43 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 142.8, 129.3, 128.4, 127.9, 127.6, 126.7, 126.5, 89.0, 87.0, 55.8, 41.2, 38.0, 20.7, 13.9;

HRMS (ESI) calcd. for $C_{31}H_{28}Na$ $[M+Na]^+$ m/z 423.2083, found 423.2090;

IR (neat, cm^{-1}) 2957, 2929, 1490, 1446, 756, 696;



Triisopropyl(3-phenylhept-1-yn-1-yl)silane (Figure 3, **3o**). From **pent-3-en-1-ylbenzene** (**1o**) (29.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4

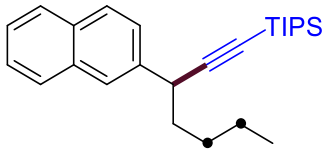
mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 71% yield (46.6 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 3.70 (dd, *J* = 8.1, 6.2 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.52 – 1.42 (m, 2H), 1.40 – 1.25 (m, 2H), 1.20 – 1.05 (m, 21 H), 0.89 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 128.4, 127.5, 126.5, 110.2, 83.2, 39.0, 38.9, 29.6, 22.4, 18.8, 14.1, 11.4;

HRMS (ESI) calcd. for $C_{22}H_{36}SiNa$ $[M+Na]^+$ m/z 351.2478, found 351.2477;

IR (neat, cm^{-1}) 2940, 2864, 2168, 1462, 738, 664.



Triisopropyl(3-(naphthalen-2-yl)hept-1-yn-1-yl)silane (Figure 3, **3p**). From **2-(pent-3-en-1-yl)naphthalene** (**1p**) (39.3 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 84% yield (63.8 mg), and >99:1 rr was detected by GC.

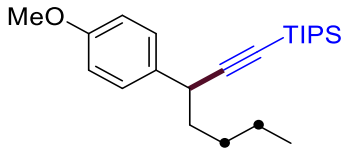
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.84 – 7.77 (m, 3H), 7.53 – 7.38 (m, 3H), 3.86 (dd, *J* = 7.9, 6.2 Hz, 1H), 1.88 – 1.77 (m, 2H), 1.54 – 1.46 (m, 2H), 1.42 – 1.29 (m, 2H), 1.17 – 1.08 (m, 21H), 0.90 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 133.5, 132.4, 128.0, 127.8, 127.7, 126.1, 126.0,

125.5, 110.2, 83.5, 39.1, 38.6, 29.6, 22.5, 18.8, 14.1, 11.5;

HRMS (ESI) calcd. for $C_{26}H_{38}SiNa$ $[M+Na]^+$ m/z 401.2635, found 401.2637;

IR (neat, cm^{-1}) 2939, 2863, 2167, 1462, 882, 674.



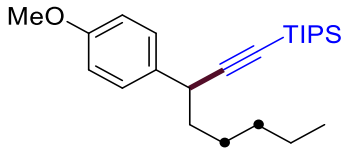
Triisopropyl(3-(4-methoxyphenyl)hept-1-yn-1-yl)silane (Figure 3, **3q**). From **1-methoxy-4-(pent-3-en-1-yl)benzene** (**1q**) (35.3 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 70% yield (50.0 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.88 – 6.79 (m, 2H), 3.80 (s, 3H), 3.64 (dd, *J* = 7.8, 6.5 Hz, 1H), 1.75 – 1.65 (m, 2H), 1.48 – 1.40 (m, 2H), 1.36 – 1.27 (m, 2H), 1.12 – 1.01 (m, 21H), 0.88 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 134.6, 128.5, 113.7, 110.6, 82.9, 55.4, 39.0, 38.1, 29.5, 22.5, 18.9, 18.8, 14.1, 11.4;

HRMS (ESI) calcd. for $C_{23}H_{38}OSiNa$ $[M+Na]^+$ m/z 381.2584, found 381.2581;

IR (neat, cm^{-1}) 2940, 2864, 2167, 1510, 1247, 677.



Triisopropyl(3-(4-methoxyphenyl)oct-1-yn-1-yl)silane (Figure 3, **3r**). From **1-(hex-3-en-1-yl)-4-methoxybenzene** (**1r**) (38.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was

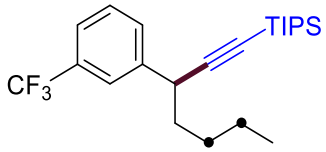
prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 77% yield (57.6 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.90 – 6.82 (m, 2H), 3.80 (s, 3H), 3.70 – 3.55 (m, 1H), 1.73 – 1.65 (m, 2H), 1.52 – 1.41 (m, 2H), 1.34 – 1.24 (m, 4H), 1.14 – 1.02 (m, 21H), 0.92 – 0.83 (m, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 134.6, 128.5, 113.7, 110.6, 82.9, 55.4, 39.3, 38.1, 31.6, 27.0, 22.7, 18.9, 18.8, 14.1, 11.4;

HRMS (ESI) calcd. for $C_{24}H_{40}OSiNa$ $[M+Na]^+$ m/z 395.2741, found 395.2743;

IR (neat, cm^{-1}) 2937, 2863, 2167, 1510, 1245, 667.



Triisopropyl(3-(3-(trifluoromethyl)phenyl)hept-1-yn-1-yl)silane (Figure 3, **3s**). From **1-(pent-3-en-1-yl)-3-(trifluoromethyl)benzene** (**1s**) (42.8 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 69% yield (54.9 mg), and >99:1 rr was detected by GC.

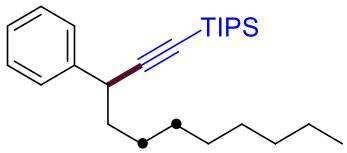
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.47 (m, 1H), 7.45 – 7.40 (m, 1H), 3.75 (dd, *J* = 8.3, 6.1 Hz, 1H), 1.80 – 1.65 (m, 2H), 1.53 – 1.43 (m, 2H), 1.40 – 1.28 (m, 2H), 1.12 – 1.07 (m, 21H), 0.90 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 130.9, 130.8 (q, *J* = 32.2 Hz), 128.8, 124.4 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 272.7 Hz), 123.5 (q, *J* = 3.9 Hz), 109.0, 84.4, 38.8, 38.7, 29.5, 22.4, 18.7, 14.1, 11.4;

^{19}F NMR (471 MHz, $CDCl_3$) δ –62.6;

HRMS (ESI) calcd. for $C_{23}H_{35}F_3SiNa$ $[M+Na]^+$ m/z 419.2352, found 419.2351;

IR (neat, cm^{-1}) 2941, 2865, 2170, 1325, 1126, 663.



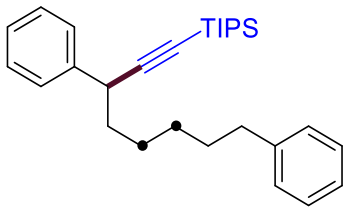
Triisopropyl(3-phenylundec-1-yn-1-yl)silane (Figure 3, **3t**). From **non-3-en-1-ylbenzene** (**1t**) (40.5 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 85% yield (65.5 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 3.69 (dd, *J* = 8.2, 6.2 Hz, 1H), 1.78 – 1.65 (m, 2H), 1.52 – 1.39 (m, 2H), 1.35 – 1.16 (m, 10H), 1.13 – 1.05 (m, 21H), 0.87 (t, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 128.4, 127.5, 126.5, 110.2, 83.2, 39.2, 39.0, 32.0, 29.6, 29.3, 27.4, 22.8, 18.8, 14.2, 11.4;

HRMS (ESI) calcd. for $C_{26}H_{44}SiNa$ $[M+Na]^+$ m/z 407.3104, found 407.3105;

IR (neat, cm^{-1}) 2924, 2856, 2168, 1454, 966, 696.



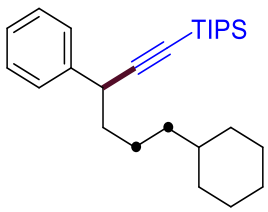
(3,8-Diphenyloct-1-yn-1-yl)triisopropylsilane (Figure 3, **3u**). From **1,6-diphenylhex-3-ene** (**1u**) (47.3 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 89% yield (74.7 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.15 (m, 3H), 3.70 (dd, *J* = 8.0, 6.2 Hz, 1H), 2.63 – 2.57 (m, 2H), 1.83 – 1.70 (m, 2H), 1.66 – 1.58 (m, 2H), 1.57 – 1.50 (m, 2H), 1.43 – 1.31 (m, 2H), 1.13 – 1.07 (m, 21H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.3, 128.5, 128.4, 128.3, 127.5, 126.5, 125.7, 110.1, 83.3, 39.1, 38.9, 35.9, 31.5, 29.0, 27.2, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{29}H_{42}SiNa$ $[M+Na]^+$ m/z 441.2948, found 441.2953;

IR (neat, cm^{-1}) 2937, 2862, 2167, 1453, 882, 697.



(6-Cyclohexyl-3-phenylhex-1-yn-1-yl)triisopropylsilane (Figure 3, **3v**). From **(4-cyclohexylbut-3-en-1-yl)benzene** (**1v**) (42.9 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was

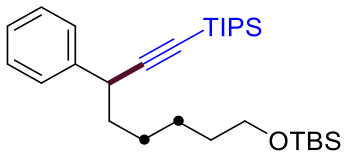
prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 83% yield (65.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 3.77 – 3.63 (m, 1H), 1.73 – 1.60 (m, 7H), 1.54 – 1.40 (m, 2H), 1.24 – 1.13 (m, 6H), 1.12 – 1.04 (m, 21H), 0.91 – 0.78 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 128.4, 127.5, 126.5, 110.2, 83.2, 39.5, 39.0, 37.6, 37.1, 33.5, 33.4, 26.8, 26.6, 26.5, 24.7, 18.9, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{27}H_{44}SiNa$ $[M+Na]^+$ m/z 419.3104, found 419.3101;

IR (neat, cm^{-1}) 2921, 2862, 2168, 1450, 882, 664.



***tert*-Butyldimethyl((6-phenyl-8-(triisopropylsilyl)oct-7-yn-1-yl)oxy)silane** (Figure 3, **3w**). From ***tert*-butyldimethyl((6-phenylhex-3-en-1-yl)oxy)silane** (**1w**) (58.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous diglyme (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 45% yield (42.5 mg), and >99:1 rr was detected by GC.

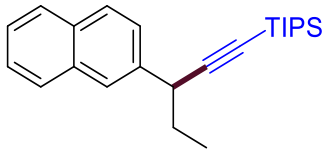
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 3.69 (dd, *J* = 8.0, 6.3 Hz, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.67 (m,2H),

1.54 – 1.42 (m, 4H), 1.38 – 1.28 (m, 2H), 1.12 – 0.98 (m, 21H), 0.89 (s, 9H), 0.04 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 128.4, 127.5, 126.5, 110.1, 83.3, 63.3, 39.2, 38.9, 32.9, 27.2, 26.1, 25.6, 18.8, 18.5, 11.4, –5.1;

HRMS (ESI) calcd. for $C_{29}H_{53}OSi_2$ $[M+H]^+$ m/z 473.3629, found 473.3633;

IR (neat, cm^{-1}) 2937, 2862, 2168, 1098, 833, 663.



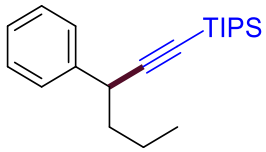
Triisopropyl(3-(naphthalen-2-yl)pent-1-yn-1-yl)silane (Figure 3, **3x**). From **2-(prop-1-en-1-yl)naphthalene** (**1x**) (33.6 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 95% yield (66.5 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 1H), 7.85 – 7.78 (m, 3H), 7.52 – 7.41 (m, 3H), 3.83 (dd, *J* = 8.1, 5.5 Hz, 1H), 1.98 – 1.80 (m, 2H), 1.16 – 1.11 (m, 21H), 1.06 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 133.5, 132.5, 128.0, 127.8, 127.7, 126.3, 126.2, 126.1, 125.6, 109.9, 83.7, 40.6, 31.9, 18.8, 11.8, 11.5;

HRMS (ESI) calcd. for $C_{24}H_{34}SiNa$ $[M+Na]^+$ m/z 373.2322, found 373.2318;

IR (neat, cm^{-1}) 2940, 2863, 2167, 882, 676.



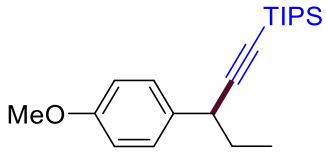
Triisopropyl(3-phenylhex-1-yn-1-yl)silane (Figure 3, **3y**). From **but-1-en-1-ylbenzene** (**1y**) (26.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%) and PMHS (60 μL, 1.0 mmol, 5.0 equiv), anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 93% yield (58.7 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.37 – 7.27 (m, 2H), 7.28 – 7.18 (m, 1H), 3.72 (t, *J* = 7.2 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.58 – 1.45 (m, 2H), 1.14 – 1.06 (m, 21H), 0.94 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.4, 127.6, 126.5, 110.2, 83.1, 41.3, 38.8, 20.6, 18.8, 13.9, 11.5;

HRMS (ESI) calcd. for $C_{21}H_{34}SiNa$ $[M+Na]^+$ m/z 337.2322, found 337.2320;

IR (neat, cm^{-1}) 2940, 2864, 2167, 1462, 882, 675.



Triisopropyl(3-(4-methoxyphenyl)pent-1-yn-1-yl)silane (Figure 3, **3z**). From **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**1z**) (29.6 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column

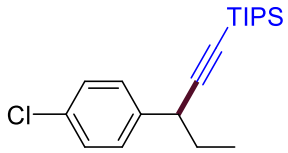
chromatography (petroleum ether) to provide the title compound as a colorless liquid in 86% yield (56.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.88 – 6.83 (m, 2H), 3.80 (s, 3H), 3.61 (dd, *J* = 8.1, 5.6 Hz, 1H), 1.82 – 1.66 (m, 2H), 1.14 – 1.05 (m, 21H), 1.01 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 134.2, 128.6, 113.7, 110.3, 83.1, 55.4, 39.7, 32.2, 18.8, 11.7, 11.5;

HRMS (ESI) calcd. for $C_{21}H_{34}OSiNa$ $[M+Na]^+$ m/z 353.2271, found 353.2268;

IR (neat, cm^{-1}) 2940, 2864, 2166, 1510, 1245, 666.



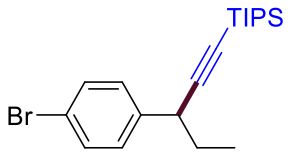
(3-(4-Chlorophenyl)pent-1-yn-1-yl)triisopropylsilane (Figure 3, **3a'**). From **1-chloro-4-(prop-1-en-1-yl)benzene** (**1a'**) (30.5 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 94% yield (62.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 3.63 (dd, *J* = 8.2, 5.6 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.75 – 1.67 (m, 1H), 1.13 – 1.05 (m, 21H), 1.01 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 132.3, 129.0, 128.5, 109.3, 83.8, 39.9, 32.0, 18.8, 11.6, 11.4;

HRMS (ESI) calcd. for $C_{20}H_{31}ClSiNa$ $[M+Na]^+$ m/z 357.1776, found 357.1779;

IR (neat, cm^{-1}) 2941, 2864, 2169, 1407, 881, 661.



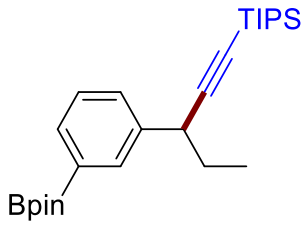
(3-(4-Bromophenyl)pent-1-yn-1-yl)triisopropylsilane (Figure 3, **3b'**). From **1-bromo-4-(prop-1-en-1-yl)benzene** (**1b'**) (39.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 96% yield (72.7 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.28 – 7.23 (m, 2H), 3.62 (dd, *J* = 8.1, 5.5 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H), 1.10 – 1.08 (m, 21H), 1.01 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 131.4, 129.4, 120.4, 109.2, 83.9, 40.0, 32.0, 18.8, 11.6, 11.4;

HRMS (ESI) calcd. for $C_{20}H_{31}BrSiNa$ $[M+Na]^+$ m/z 401.1271, found 401.1270;

IR (neat, cm^{-1}) 2940, 2864, 2169, 1461, 1101, 881.



Triisopropyl(3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-1-yn-1-yl)silane (Figure 3, **3c'**). From **4,4,5,5-tetramethyl-2-(3-(prop-1-en-1-yl)phenyl)-1,3,2-dioxaborolane** (**1c'**) (48.8 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L**

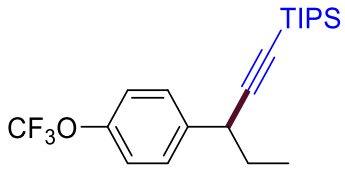
(4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 69% yield (59.1 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 3.66 (dd, *J* = 8.5, 5.3 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.76 – 1.68 (m, 1H), 1.34 (s, 12H), 1.13 – 1.07 (m, 21H), 1.02 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 134.1, 133.0, 130.5, 127.8, 110.0, 83.8, 83.4, 40.5, 32.1, 25.0, 24.9, 18.8, 11.9, 11.5;

HRMS (ESI) calcd. for $C_{26}H_{43}BO_2SiNa$ $[M+Na]^+$ m/z 449.3018, found 449.3019;

IR (neat, cm^{-1}) 2940, 2864, 2168, 1357, 1143, 673.



Triisopropyl(3-(4-(trifluoromethoxy)phenyl)pent-1-yn-1-yl)silane (Figure 3, **3d'**). From **1-(prop-1-en-1-yl)-4-(trifluoromethoxy)benzene** (**1d'**) (40.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 93% yield (71.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 3.68 (dd, *J* = 8.3, 5.4 Hz, 1H), 1.86 – 1.66 (m, 2H), 1.12 – 1.07 (m, 21H), 1.02 (t, *J* = 7.3 Hz, 3H);

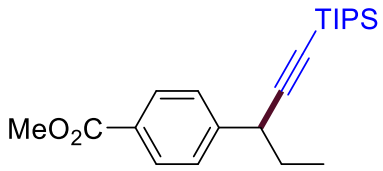
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 140.8, 128.9, 120.9, 120.7 (q, *J* = 257.2 Hz),

109.2, 84.1, 39.9, 32.1, 18.8, 11.7, 11.4;

^{19}F NMR (471 MHz, $CDCl_3$) δ –57.9;

HRMS (ESI) calcd. for $C_{21}H_{31}F_3OSiNa$ $[M+Na]^+$ m/z 407.1988, found 407.1987;

IR (neat, cm^{-1}) 2942, 2865, 2170, 1256, 1162, 673.



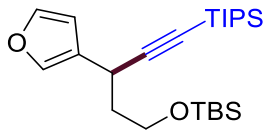
Methyl 4-(1-(triisopropylsilyl)pent-1-yn-3-yl)benzoate (Figure 3, **3e'**). From **methyl 4-(prop-1-en-1-yl)benzoate** (**1e'**) (35.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 76% yield (54.4 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.48 – 7.41 (m, 2H), 3.91 (s, 3H), 3.70 (dd, *J* = 8.1, 5.5 Hz, 1H), 1.86 – 1.69 (m, 2H), 1.15 – 1.04 (m, 21H), 1.01 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 147.4, 129.8, 128.6, 127.7, 109.0, 84.2, 52.1, 40.5, 31.9, 18.8, 11.7, 11.4;

HRMS (ESI) calcd. for $C_{22}H_{34}O_2SiNa$ $[M+Na]^+$ m/z 381.2220, found 381.2221;

IR (neat, cm^{-1}) 2941, 2864, 2169, 1725, 1276, 676.



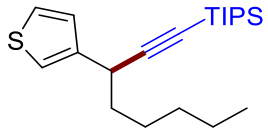
***tert*-Butyl((3-(furan-3-yl)-5-(triisopropylsilyl)pent-4-yn-1-yl)oxy)dimethylsilane** (Figure 3, **3f'**). From ***tert*-butyl((3-(furan-3-yl)allyl)oxy)dimethylsilane** (**1f'**) (47.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 200:1) to provide the title compound as a colorless liquid in 85% yield (71.9 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 1H), 7.37 – 7.35 (m, 1H), 6.40 – 6.34 (m, 1H), 3.90 – 3.83 (m, 1H), 3.81 – 3.71 (m, 2H), 2.01 – 1.91 (m, 1H), 1.89 – 1.80 (m, 1H), 1.11 – 1.02 (m, 21H), 0.91 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 139.5, 126.2, 110.0, 109.1, 82.0, 60.6, 39.9, 26.1, 25.9, 18.8, 18.4, 11.4, –5.1, –5.2;

HRMS (ESI) calcd. for $C_{24}H_{44}O_2Si_2Na$ $[M+Na]^+$ m/z 443.2772, found 443.2767;

IR (neat, cm^{-1}) 2942, 2864, 2168, 1103, 833, 775.



Triisopropyl(3-(thiophen-3-yl)oct-1-yn-1-yl)silane (Figure 3, **3g'**). From **3-(hex-1-en-1-yl)thiophene** (**1g'**) (33.3 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude

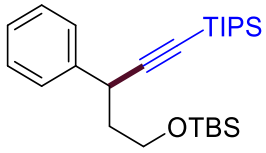
material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 91% yield (63.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.21 – 7.16 (m, 1H), 7.05 (dd, *J* = 4.9, 1.3 Hz, 1H), 3.79 (dd, *J* = 8.6, 5.3 Hz, 1H), 1.85 – 1.66 (m, 2H), 1.57 – 1.45 (m, 2H), 1.36 – 1.25 (m, 4H), 1.14 – 1.05 (m, 21H), 0.89 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 127.1, 125.5, 120.7, 110.0, 82.6, 37.7, 34.3, 31.5, 26.8, 22.7, 18.8, 14.1, 11.4;

HRMS (ESI) calcd. for $C_{21}H_{36}SSiNa$ $[M+Na]^+$ m/z 371.2199, found 371.2200;

IR (neat, cm^{-1}) 2936, 2863, 2168, 1461, 882, 664;



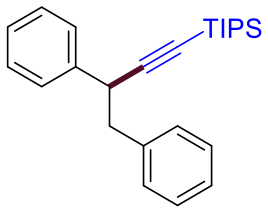
***tert*-Butyldimethyl((3-phenyl-5-(triisopropylsilyl)pent-4-yn-1-yl)oxy)silane** (Figure 3, **3h'**). From ***tert*-butyl(cinnamyloxy)dimethylsilane** (**1h'**) (49.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 65% yield (55.8 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.17 (m, 1H), 3.90 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.74 – 3.67 (m, 1H), 2.04 – 1.83 (m, 2H), 1.17 – 1.05 (m, 21H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 128.4, 127.6, 126.6, 109.7, 83.4, 60.8, 42.2, 35.2, 26.1, 18.8, 18.4, 11.4, –5.1, –5.1;

HRMS (ESI) calcd. for $C_{26}H_{46}OSi_2Na$ $[M+Na]^+$ m/z 453.2979, found 453.2977;

IR (neat, cm^{-1}) 2941, 2863, 2167, 1104, 832, 698.



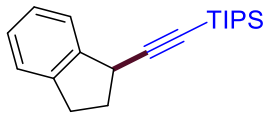
(3,4-Biphenylbut-1-yn-1-yl)triisopropylsilane (Figure 3, **3i'**). From **(*E*)-1,2-diphenylethene** (**1i'**) (36.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (2.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 91% yield (65.9 mg), and >99:1 rr was detected by GC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 4H), 7.33 – 7.26 (m, 4H), 7.24 – 7.20 (m, 2H), 4.04 (dd, *J* = 8.3, 6.2 Hz,1H), 3.18 – 3.00 (m, 2H), 1.20 – 0.76 (m, 21H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 138.9, 129.6, 128.4, 128.1, 127.8, 126.8, 126.4, 109.2, 84.5, 45.5, 41.3, 18.7, 11.4;

HRMS (ESI) calcd. for $C_{25}H_{34}SiNa$ $[M+Na]^+$ m/z 385.2322, found 385.2321;

IR (neat, cm^{-1}) 2941, 2864, 2169, 1453, 882, 697.



((2,3-Dihydro-1*H*-inden-1-yl)ethynyl)triisopropylsilane (Figure 3, **3j'**). From **1*H*-indene** (**1j'**) (23.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title

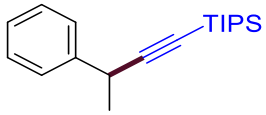
compound as a colorless liquid in 94% yield (56.3 mg), and >99:1 rr was detected by GC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 1H), 7.26 – 7.16 (m, 3H), 4.08 – 3.99 (m, 1H), 3.03 – 2.93 (m, 1H), 2.92 – 2.81 (m, 1H), 2.65 – 2.44 (m, 1H), 2.20 – 2.03 (m, 1H), 1.15 – 1.03 (m, 21H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 143.0, 127.0, 126.6, 124.4, 124.3, 110.3, 81.1, 37.4, 34.8, 31.6, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{20}H_{30}SiNa$ $[M+Na]^+$ m/z 321.2009, found 321.2009;

IR (neat, cm^{-1}) 2941, 2864, 2172, 1460, 881, 671.



Triisopropyl(3-phenylbut-1-yn-1-yl)silane (Figure 3, **3k'**). From **styrene** (**1k'**) (20.8 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), **L** (4.3 mg, 6.0 mol%), Na_2CO_3 (42.4 mg, 2.0 equiv), NaI (3.0 mg, 10.0 mol%), PMHS (60 μL, 1.0 mmol, 5.0 equiv) and anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 57% yield (32.4 mg), and >99:1 rr was detected by GC.

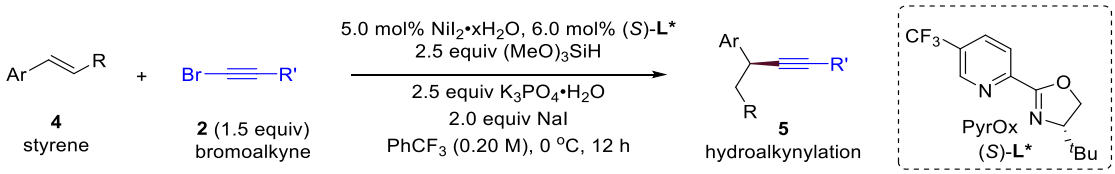
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.30 – 7.25 (m, 1H), 3.87 (q, J = 7.1 Hz, 1H), 1.56 (d, J = 7.2 Hz, 3H), 1.21 – 1.04 (m, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 128.5, 127.0, 126.6, 111.3, 82.4, 33.1, 25.2, 18.8, 11.4.

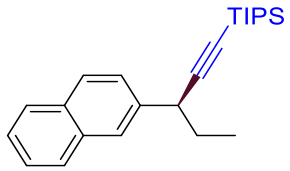
HRMS (ESI) calcd. for $C_{19}H_{30}SiNa$ $[M+Na]^+$ *m/z* 309.2009, found 309.2011;

IR (neat, cm^{-1}) 2941, 2864, 2164, 1462, 1097, 663.

Enantioselective NiH-Catalyzed Reductive Hydroalkynylation.



<u>General procedure (B)</u> for enantioselective NiH-catalyzed reductive hydroalkynylation. In a nitrogen-filled glove box, to an oven-dried 8 mL screw-cap vial equipped with a magnetic stir bar were added $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv) and anhydrous $PhCF_3$ (1.0 mL). The mixture was stirred for 20 min at room temperature (stirred at 800 rpm) before the addition of $(MeO)_3SiH$ (64 μL, 0.50 mmol, 2.5 equiv). Stirring was continued for an additional 5 min at room temperature before the addition of olefin **4** (0.20 mmol, 1.0 equiv) and bromoalkyne **2** (0.30 mmol, 1.5 equiv). The tube was sealed with a teflon-lined screw cap, removed from the glove box and the reaction was stirred at 0 °C for up to 12 h (the mixture was stirred at 800 rpm). After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with EtOAc. The organic layer was concentrated to give the crude product. Dodecane (20 μL) was added as an internal standard for GC analysis. The product was purified by flash column chromatography (petroleum ether/EtOAc) for each substrate. The yields reported are the average of at least two experiments, unless otherwise indicated. The enantiomeric excesses (% ee) of the corresponding products were determined by HPLC analysis using chiral stationary phases.



(*S*)-Triisopropyl(3-(naphthalen-2-yl)pent-1-yn-1-yl)silane (Figure 4, **5a**). From **2-(prop-1-en-1-yl)naphthalene** (**4a**) (33.6 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 71% yield (49.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.89 – 7.80 (m, 3H), 7.61 – 7.44 (m, 3H), 3.88 (dd, *J* = 8.0, 5.6 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.92 – 1.85 (m, 1H), 1.23 – 1.16 (m, 21H), 1.11 (t, *J* = 7.3 Hz, 3H);

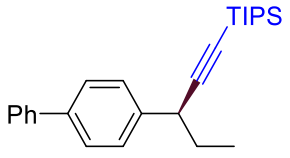
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 133.5, 132.5, 128.0, 127.8, 127.7, 126.2, 126.1, 126.0, 125.6, 109.9, 83.7, 40.6, 31.9, 18.8, 11.8, 11.5;

HRMS (ESI) calcd. for $C_{24}H_{35}Si$ $[M+H]^+$ m/z 351.2503, found 351.2504;

IR (neat, cm^{-1}) 2940, 2863, 2167, 1461, 882, 669;

$[\alpha]_D^{18}$ = –23.9 (c = 1.76, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 7.5 min, t_R (major) = 8.6 min.



(*S*)-(3-([1,1'-Biphenyl]-4-yl)pent-1-yn-1-yl)triisopropylsilane (Figure 4, **5b**). From **4-(prop-1-en-1-yl)-1,1'-biphenyl** (**4b**) (38.9 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was

prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 66% yield (49.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.62 – 7.58 (m, 2H), 7.53 – 7.44 (m, 4H), 7.41 – 7.30 (m, 1H), 3.76 (dd, *J* = 8.3, 5.4 Hz, 1H), 1.97 – 1.75 (m, 2H), 1.20 – 1.14 (m, 21H), 1.11 (t, *J* = 7.4 Hz, 3H);

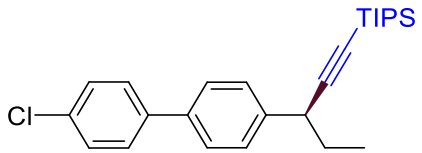
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 141.0, 139.5, 128.8, 128.0, 127.3, 127.2, 127.1, 109.8, 83.5, 40.2, 32.2, 18.8, 11.8, 11.5;

HRMS (APCI) calcd. for $C_{26}H_{36}SiNa$ $[M+Na]^+$ m/z 399.2478, found 399.2474;

IR (neat, cm^{-1}) 2958, 2863, 2167, 1486, 761, 695;

$[\alpha]_D^{18}$ = –11.9 (c = 1.46, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 10.4 min, t_R (major) = 12.4 min.



(*S*)-(3-([1,1'-Biphenyl]-4-yl)pent-1-yn-1-yl)triisopropylsilane (Figure 4, **5c**). From **4-chloro-4'-(prop-1-en-1-yl)-1,1'-biphenyl** (**4c**) (45.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 51% yield (42.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 4H), 7.51 – 7.46 (m, 2H), 7.44 – 7.39 (m, 2H), 3.74 (dd, *J* = 8.3, 5.4 Hz, 1H), 1.92 – 1.76 (m, 2H), 1.19 – 1.12 (m, 21H), 1.09 (t, *J* = 7.3 Hz, 3H);

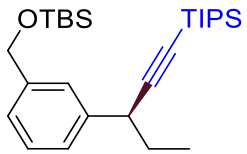
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 139.5, 138.2, 133.3, 128.9, 128.3, 128.2, 126.9, 109.7, 83.6, 40.2, 32.1, 18.8, 11.8, 11.5;

HRMS (ESI) calcd. for $C_{26}H_{35}ClSiNa$ $[M+Na]^+$ m/z 433.2089, found 433.2092

IR (neat, cm^{-1}) 2940, 2864, 2167, 1484, 814, 671;

$[\alpha]_D^{18}$ = –3.3 (c = 1.38, $CHCl_3$); 96% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 13.5 min, t_R (major) = 14.2 min.



(*S*)-*tert*-Butyldimethyl((3-(1-(triisopropylsilyl)pent-1-yn-3-yl)benzyl)oxy)silane (Figure 4, **5d**). From ***tert*-butyldimethyl((3-(prop-1-en-1-yl)benzyl)oxy)silane** (**4d**) (52.5mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 91% yield (81.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 4.78 – 4.72 (m, 2H), 3.68 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.89 – 1.72 (m, 2H), 1.17 – 1.09 (m, 21H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.98 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H);

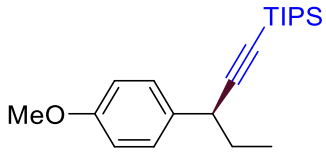
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 141.5, 128.3, 126.3, 125.5, 124.5, 110.1, 83.2, 65.2, 40.5, 32.1, 26.1, 18.8, 18.5, 11.8, 11.5, –5.0;

HRMS (ESI) calcd. for $C_{27}H_{48}OSi_2Na$ $[M+Na]^+$ m/z 467.3136, found 467.3135;

IR (neat, cm^{-1}) 2929, 2863, 2169, 1077, 835, 670;

$[\alpha]_D^{18}$ = –15.2 (c = 1.33, $CHCl_3$); 90% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 14.3 min, t_R (minor) = 14.8 min.



(*S*)-Triisopropyl(3-(4-methoxyphenyl)pent-1-yn-1-yl)silane (Figure 4, **5e**). From **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**4e**) (29.6 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 82% yield (54.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 6.91 – 6.80 (m, 2H), 3.81 (s, 3H), 3.63 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.78 – 1.67 (m, 1H), 1.15 – 1.07 (m, 21H), 1.03 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.2, 128.5, 113.7, 110.3, 83.1, 55.3, 39.7, 32.2, 18.8, 11.7, 11.4;

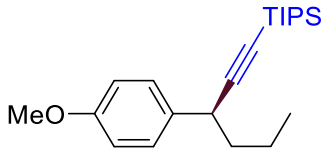
HRMS (ESI) calcd. for $C_{21}H_{35}OSi$ $[M+H]^+$ m/z 331.2452, found 331.2458;

IR (neat, cm^{-1}) 2940, 2864, 2167, 1510, 1245, 670;

$[\alpha]_D^{18}$ = –16.6 (c = 1.05, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 22.7min, t_R (minor)

= 26.5 min.



(*S*)-Triisopropyl(3-(4-methoxyphenyl)hex-1-yn-1-yl)silane (Figure 4, **5f**). From **1-(but-1-en-1-yl)-4-methoxybenzene** (**4f**) (32.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 82% yield (56.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 6.90 – 6.86 (m, 2H), 3.82 (s, 3H), 3.69 (dd, *J* = 8.0, 6.3 Hz, 1H), 1.77 – 1.68 (m, 2H), 1.58 – 1.44 (m, 2H), 1.20 – 1.06 (m, 21H), 0.96 (t, *J* = 7.4 Hz, 3H);

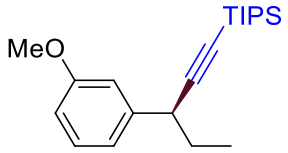
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.5, 128.5, 113.7, 110.6, 82.8, 55.3, 41.4, 37.9, 20.5, 18.8, 13.9, 11.4;

HRMS (ESI) calcd. for $C_{22}H_{37}OSi$ $[M+H]^+$ m/z 345.2608, found 345.2609;

IR (neat, cm^{-1}) 2941, 2863, 2170, 1453, 696, 674;

$[\alpha]_D^{18}$ = –24.4 (c = 1.22, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (major) = 13.4 min, t_R (minor) = 15.6 min.



(*S*)-Triisopropyl(3-(3-methoxyphenyl)pent-1-yn-1-yl)silane (Figure 4, **5g**). From **1-**

methoxy-3-(prop-1-en-1-yl)benzene (**4g**) (29.6 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 83% yield (54.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 7.05 – 7.02 (m, 1H), 6.99 – 6.94 (m, 1H), 6.80 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.83 (s, 3H), 3.68 (dd, *J* = 8.3, 5.4 Hz, 1H), 1.88 – 1.71 (m, 2H), 1.17 – 1.06 (m, 21H), 1.06 (t, *J* = 7.4 Hz, 3H);

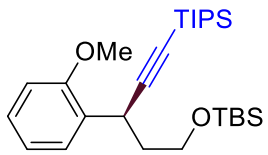
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 143.7, 129.3, 120.0, 112.9, 112.4, 109.8, 83.4, 55.2, 40.5, 32.1, 18.8, 11.8, 11.4;

HRMS (ESI) calcd. for $C_{21}H_{34}OSiNa$ $[M+Na]^+$ m/z 353.2271, found 353.2272;

IR (neat, cm^{-1}) 2940, 2864, 2168, 1487, 881, 665;

$[\alpha]_D^{20}$ = –26.5 (c = 1.59, $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (major) = 14.5 min, t_R (minor) = 16.0 min.



(*S*)-*tert*-Butyl((3-(2-methoxyphenyl)-5-(triisopropylsilyl)pent-4-yn-1-yl)oxy)dimethylsilane (Figure 4, **5h**). From ***tert*-butyl((3-(2-methoxyphenyl)allyl)oxy)dimethylsilane** (**4h**) (55.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv),

$(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 88% yield (81.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.00 – 6.92 (m, 1H), 6.84 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.30 (dd, *J* = 10.0, 4.2 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.84 – 3.78 (m, 4H), 2.06 – 1.94 (m, 1H), 1.80 – 1.67 (m, 1H), 1.15 – 1.05 (m, 21H), 0.92 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H);

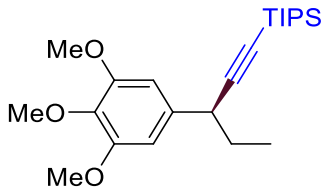
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 130.4, 128.6, 127.7, 120.6, 110.2, 110.0, 82.7, 61.5, 55.3, 40.0, 29.1, 26.0, 18.9, 18.8, 18.4, 11.4, -5.0, -5.1;

HRMS (ESI) calcd. for $C_{27}H_{48}O_2Si_2Na$ $[M+Na]^+$ m/z 483.3085, found 483.3087;

IR (neat, cm^{-1}) 2940, 2863, 2166, 1243, 831, 665;

$[\alpha]_D^{18}$ = –30.6 (c = 1.15, $CHCl_3$); 90% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 15.0 min, t_R (major) = 19.1 min.



(*S*)-Triisopropyl(3-(3,4,5-trimethoxyphenyl)pent-1-yn-1-yl)silane (Figure 4, **5i**). From **1,2,3-trimethoxy-5-(prop-1-en-1-yl)benzene** (**4i**) (41.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless liquid in 65% yield (51.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (s, 2H), 3.85 (s, 6H), 3.83 (s, 3H), 3.61 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.87 – 1.76 (m, 1H), 1.76 – 1.63 (m, 1H), 1.14 – 1.02 (m, 21H), 1.03 (t, *J* = 7.3 Hz, 3H);

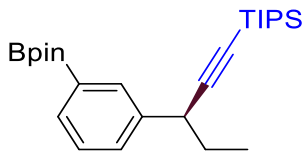
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 137.8, 136.4, 109.7, 104.4, 83.7, 60.9, 56.0, 40.7, 32.3, 18.9, 18.8, 11.8, 11.4;

HRMS (ESI) calcd. for $C_{23}H_{38}O_3SiNa$ $[M+Na]^+$ m/z 413.2482, found 413.2481;

IR (neat, cm^{-1}) 2940, 2864, 2167, 1460, 1127, 674;

$[\alpha]_D^{18}$ = –19.5 (c = 1.51, $CHCl_3$); 88% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 99/1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 10.5 min, t_R (major) = 11.1 min.



(*S*)-Triisopropyl(3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-1-yn-1-yl)silane (Figure 4, **5j**). From **4,4,5,5-tetramethyl-2-(3-(prop-1-en-1-yl)phenyl)-1,3,2-dioxaborolane** (**4j**) (48.8 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 82% yield (69.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.72 – 7.67 (m, 1H), 7.57 – 7.48 (m, 1H), 7.39 – 7.32 (m, 1H), 3.69 (dd, *J* = 8.5, 5.4 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.81 – 1.71 (m, 1H), 1.37 (s, 12H), 1.20 – 1.09 (m, 21H), 1.06 (t, *J* = 7.3 Hz, 3H);

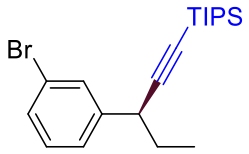
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 134.1, 133.0, 130.5, 127.8, 110.0, 83.8, 83.4, 40.5, 32.1, 25.0, 24.9, 18.8, 11.9, 11.4;

HRMS (ESI) calcd. for $C_{26}H_{43}BO_2SiNa$ $[M+Na]^+$ m/z 449.3018, found 449.3017;

IR (neat, cm^{-1}) 2940, 2864, 2168, 1357, 882, 674;

$[\alpha]_D^{18}$ = –15.7 (c = 1.59, $CHCl_3$); 90% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.3 mL/min, 220 nm UV detector, t_R (major) = 28.2 min, t_R (minor) = 29.4 min.



(*S*)-(3-(3-Bromophenyl)pent-1-yn-1-yl)triisopropylsilane (Figure 4, **5k**). From **1-bromo-3-(prop-1-en-1-yl)benzene** (**4k**) (39.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiBr_2$·diglyme (3.5 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4·H_2O$ (115.1 mg, 2.5 equiv), NaI (90.0 mg, 3.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous DCE (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 66% yield (49.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 3.63 (dd, *J* = 8.2, 5.4 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.77 – 1.65 (m, 1H), 1.13 – 1.03 (m, 21H), 1.02 (t, *J* = 7.3 Hz, 3H);

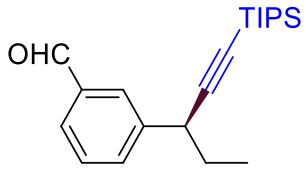
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 130.9, 129.9, 129.7, 126.3, 122.5, 108.9, 84.3, 40.1, 31.9, 18.8, 11.7, 11.4;

HRMS (ESI) calcd. for $C_{20}H_{31}BrSiNa$ $[M+Na]^+$ m/z 401.1271, found 401.1272;

IR (neat, cm^{-1}) 2940, 2864, 2169, 1462, 881, 675;

$[\alpha]_D^{18}$ = –22.9 (c = 1.26, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALPAK IE-3 column, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.3 mL/min, 220 nm UV detector, t_R (minor) = 13.3 min, t_R (major) = 13.8 min.



(*S*)-3-(1-(Triisopropylsilyl)pent-1-yn-3-yl)benzaldehyde (Figure 4, **5l**). From **3-(prop-1-en-1-yl)benzaldehyde** (**4l**) (29.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 52% yield (34.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.95 – 7.89 (m, 1H), 7.77 – 7.73 (m, 1H), 7.69 – 7.59 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 3.75 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.81 – 1.71 (m, 1H), 1.11 – 1.08 (m, 21H), 1.03 (t, *J* = 7.4 Hz, 3H);

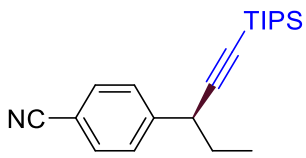
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.4, 143.3, 136.6, 133.8, 129.2, 129.1, 128.0, 108.9, 84.4, 40.2, 31.9, 18.8, 11.6, 11.4;

HRMS (ESI) calcd. for $C_{21}H_{32}OSiNa$ $[M+Na]^+$ m/z 351.2115, found 351.2113;

IR (neat, cm^{-1}) 2940, 2864, 2169, 1696, 738, 675;

$[\alpha]_D^{18}$ = –24.0 (c = 0.95, $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 38.3 min, t_R (minor) = 42.7 min.



(*S*)-4-(1-(Triisopropylsilyl)pent-1-yn-3-yl)benzonitrile (Figure 4, **5m**). From **4-(prop-1-en-1-yl)benzonitrile** (**4m**) (28.6 mg, 0.20 mmol) and

(bromoethynyl)triisopropylsilane (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiBr_2$·diglyme (3.5 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4·H_2O$ (115.1 mg, 2.5 equiv), NaI (90.0 mg, 3.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv and anhydrous DCE (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 62% yield (40.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.51 – 7.44 (m, 2H), 3.71 (dd, *J* = 8.3, 5.5 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.77 – 1.67 (m, 1H), 1.12 – 1.02 (m, 21H), 1.01 (t, *J* = 7.4 Hz, 3H);

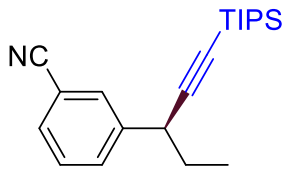
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 132.3, 128.4, 119.0, 110.6, 108.1, 84.9, 40.6, 31.8, 18.7, 11.6, 11.3;

HRMS (ESI) calcd. for $C_{21}H_{31}NSiNa$ $[M+Na]^+$ m/z 348.2118 found 348.2121;

IR (neat, cm^{-1}) 2940, 2864, 2229, 2169, 882, 665;

$[\alpha]_D^{18}$ = –14.7 (c = 0.38, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 39.4 min, t_R (major) = 41.3 min.



(*S*)-3-(1-(Triisopropylsilyl)pent-1-yn-3-yl)benzonitrile (Figure 4, **5n**). From **4-(prop-1-en-1-yl)benzonitrile** (**4n**) (28.6 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2·xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4·H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous DCE (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column

chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 65% yield (42.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 1H), 7.63 – 7.59 (m, 1H), 7.55 – 7.51 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 3.69 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.86 – 1.67 (m, 2H), 1.12 – 1.06 (m, 21H), 1.02 (t, *J* = 7.3 Hz, 3H);

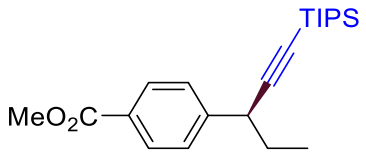
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 132.2, 131.4, 130.5, 129.2, 119.0, 112.5, 108.1, 85.0, 40.1, 31.8, 18.7, 11.6, 11.4;

HRMS (ESI) calcd. for $C_{21}H_{32}NSi$ $[M+H]^+$ m/z 326.2299 found 326.2296;

IR (neat, cm^{-1}) 2964, 2864, 2231, 2169, 882, 664;

$[\alpha]_D^{18}$ = –21.4 (c = 0.29, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALPAK AD-H column, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 13.5 min, t_R (major) = 19.3 min.



Methyl (*S*)-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)benzoate (Figure 4, **5o**). From **methyl 4-(prop-1-en-1-yl)benzoate** (**4o**) (35.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiBr_2$·diglyme (3.5 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), K_3PO_4·H_2O (115.1 mg, 2.5 equiv), NaI (90.0 mg, 3.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous DCE (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 65% yield (46.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.92 (m, 2H), 7.48 – 7.41 (m, 2H), 3.90 (s, 3H), 3.70 (dd, *J* = 8.3, 5.5 Hz, 1H), 1.86 – 1.64 (m, 2H), 1.17 – 0.98 (m, 21H), 1.02 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 147.4, 129.8, 128.6, 127.7, 108.9, 84.1, 52.1,

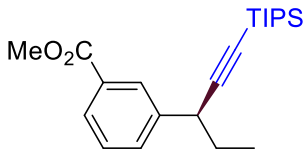
40.5, 31.9, 18.7, 11.6, 11.4;

HRMS (ESI) calcd. for $C_{22}H_{35}O_2Si$ $[M+H]^+$ m/z 359.2401, found 359.2405;

IR (neat, cm^{-1}) 2941, 2864, 2168, 1715, 1276, 663;

$[\alpha]_D^{18}$ = –15.6 (c = 1.45, $CHCl_3$); 96% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (major) = 27.8 min, t_R (minor) = 30.7 min.



Methyl (*S*)-3-(1-(triisopropylsilyl)pent-1-yn-3-yl)benzoate (Figure 4, **5p**). From **methyl 3-(prop-1-en-1-yl)benzoate** (**4p**) (35.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 83% yield (59.6mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 7.94 – 7.89 (m, 1H), 7.62 – 7.53 (m, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 3.91 (s, 3H), 3.72 (dd, *J* = 8.2, 5.4 Hz, 1H), 1.88 – 1.70 (m, 2H), 1.12 – 1.08 (m, 21H), 1.02 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 142.4, 132.2, 130.3, 128.9, 128.4, 128.0, 109.2, 84.2, 52.1, 40.3, 32.0, 18.8, 11.7, 11.4;

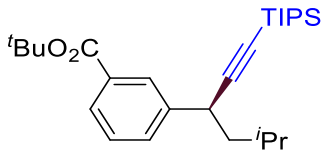
HRMS (ESI) calcd. for $C_{22}H_{35}O_2Si$ $[M+H]^+$ m/z 359.2401, found 359.2405;

IR (neat, cm^{-1}) 2941, 2864, 2169, 1726, 1281, 665;

$[\alpha]_D^{18}$ = –31.5 (c = 0.59, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 100/0, flow

rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 20.5 min, t_R (minor) = 22.2 min.



tert*-Butyl (*S*)-3-(5-methyl-1-(triisopropylsilyl)hex-1-yn-3-yl)benzoate** (Figure 4, **5q**). From ***tert*-butyl 3-(3-methylbut-1-en-1-yl)benzoate** (**4q**) (49.3 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 71% yield (60.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 1H), 7.87 – 7.82 (m, 1H), 7.57 – 7.53 (m, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 3.76 (dd, *J* = 10.1, 5.7 Hz, 1H), 1.95 – 1.84 (m, 1H), 1.74 – 1.67 (m, 1H), 1.59 (s, 9H), 1.51 – 1.40 (m, 1H), 1.12 – 0.98 (m, 21H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H);

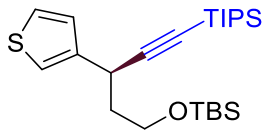
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 143.1, 132.3, 131.6, 128.5, 128.4, 127.8, 109.7, 83.4, 81.1, 48.5, 37.1, 28.3, 26.3, 23.2, 21.7, 18.9, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{27}H_{44}O_2SiNa$ $[M+Na]^+$ m/z 451.3003, found 451.3004;

IR (neat, cm^{-1}) 2941, 2865, 2168, 1715, 1291, 1159;

$[\alpha]_D^{18}$ = –26.2 (c = 1.27, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 19.2 min, t_R (major) = 19.9 min.



(*R*)-*tert*-Butyldimethyl((3-(thiophen-3-yl)-5-(triisopropylsilyl)pent-4-yn-1-yl)oxy)silane (Figure 4, **5r**). From ***tert*-butyldimethyl((3-(thiophen-3-yl)allyl)oxy)silane** (**4r**) (50.9 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 88% yield (76.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.21 – 7.17 (m, 1H), 7.07 (dd, *J* = 5.0, 1.3 Hz, 1H), 3.98 (dd, *J* = 9.6, 5.1 Hz, 1H), 3.90 – 3.83 (m, 1H), 3.77 – 3.69 (m, 1H), 2.07 – 1.97 (m, 1H), 1.96 – 1.84 (m, 1H), 1.15 – 1.03 (m, 21H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H);

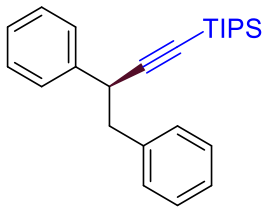
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 127.2, 125.7, 120.9, 109.5, 82.8, 60.7, 40.8, 30.6, 26.1, 18.8, 18.4, 11.4, –5.1, –5.2;

HRMS (ESI) calcd. for $C_{24}H_{44}OSSi_2Na$ $[M+Na]^+$ m/z 459.2544, found 459.2549;

IR (neat, cm^{-1}) 2941, 2863, 2168, 1103, 831, 775;

$[\alpha]_D^{18}$ = –22.0 (c = 1.10, $CHCl_3$); 82% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.3 mL/min, 220 nm UV detector, t_R (major) = 24.5 min, t_R (minor) = 25.4 min.



(*S*)-(3,4-Diphenylbut-1-yn-1-yl)triisopropylsilane (Figure 4, **5s**). From **(*E*)-1,2-diphenylethene** (**4s**) (36.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 73% yield (52.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.29 – 7.21 (m, 4H), 7.20 – 7.15 (m, 2H), 4.00 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.16 – 2.93 (m, 2H), 1.13 – 0.85 (m, 21H);

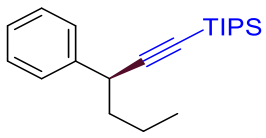
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 138.9, 129.6, 128.4, 128.0, 127.8, 126.8, 126.4, 109.2, 84.5, 45.5, 41.3, 18.7, 11.4;

HRMS (ESI) calcd. for $C_{25}H_{34}SiNa$ $[M+Na]^+$ m/z 385.2322, found 385.2325;

IR (neat, cm^{-1}) 2941, 2863, 2170, 1453, 882, 696;

$[\alpha]_D^{18}$ = –20.7 (c = 1.16, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 16.7 min, t_R (major) = 19.6 min.



(*S*)-Triisopropyl(3-phenylhex-1-yn-1-yl)silane (Figure 4, **5t**). From **but-1-en-1-ylbenzene** (**4t**) (26.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**)

(78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 81% yield (50.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.18 (m, 1H), 3.72 (dd, *J* = 7.9, 6.5 Hz, 1H), 1.78 – 1.65 (m, 2H), 1.58 – 1.41 (m, 2H), 1.10 (t, *J* = 2.8 Hz, 21H), 0.94 (t, *J* = 7.4 Hz, 3H);

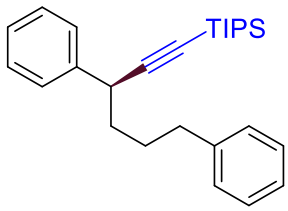
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 128.4, 127.6, 126.5, 110.2, 83.1, 41.3, 38.8, 20.6, 18.8, 13.9, 11.4;

HRMS (ESI) calcd. for $C_{21}H_{34}SiNa$ $[M+Na]^+$ m/z 337.2322, found 337.2321;

IR (neat, cm^{-1}) 2940, 2864, 2167, 1462, 882, 670;

$[\alpha]_D^{18}$ = –18.2 (c = 1.44, $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.3 mL/min, 220 nm UV detector, t_R (major) = 24.5 min, t_R (minor) = 25.2 min.



(*S*)-(3,6-Diphenylhex-1-yn-1-yl)triisopropylsilane (Figure 4, **5u**). From **but-1-ene-1,4-diyldibenzene** (**4u**) (41.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for

12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 90% yield (70.2 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.27 (m, 4H), 7.27 – 7.16 (m, 4H), 3.77 (dd, *J* = 7.8, 5.7 Hz, 1H), 2.73 – 2.56 (m, 2H), 1.96 – 1.72 (m, 4H), 1.15 – 1.10 (m, 21H);

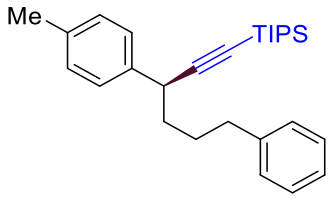
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 142.1, 128.6, 128.5, 128.4, 127.5, 126.6, 125.8, 109.9, 83.5, 38.8, 38.6, 35.6, 29.1, 18.9, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{27}H_{38}SiNa$ $[M+Na]^+$ m/z 413.2635, found 413.2637;

IR (neat, cm^{-1}) 2940, 2863, 2168, 1453, 882, 696;

$[\alpha]_D^{18}$ = –25.3 (c = 1.37, $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 16.4 min, t_R (major) = 18.0 min.



(*S*)-Triisopropyl(6-phenyl-3-(*p*-tolyl)hex-1-yn-1-yl)silane (Figure 4, **5v**). From **1-methyl-4-(4-phenylbut-1-en-1-yl)benzene** (**4v**) (44.5 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 84% yield (67.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 4H), 7.23 – 7.18 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 3.74 (dd, *J* = 7.8, 5.9 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.37 (s, 3H), 1.95 – 1.84 (m, 2H), 1.83 – 1.76 (m, 2H), 1.16 – 1.10 (m, 21H);

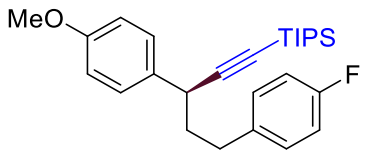
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 139.1, 136.1, 129.1, 128.5, 128.3, 127.4, 125.7, 110.1, 83.2, 38.7, 38.4, 35.6, 29.1, 21.1, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{28}H_{40}SiNa$ $[M+Na]^+$ m/z 427.2791, found 427.2791;

IR (neat, cm^{-1}) 2940, 2862, 2168, 1454, 882, 675;

$[\alpha]_D^{18}$ = –21.3 (c = 1.26, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 15.6 min, t_R (major) = 18.9 min.



(*S*)-(5-(4-Fluorophenyl)-3-(4-methoxyphenyl)pent-1-yn-1-yl)triisopropylsilane (Figure 4, **5w**). From **1-fluoro-4-(3-(4-methoxyphenyl)allyl)benzene** (**4w**) (48.5 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2{\cdot}xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4{\cdot}H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 89% yield (75.7 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.19 – 7.13 (m, 2H), 7.02 – 6.95 (m, 2H), 6.93 – 6.85 (m, 2H), 3.82 (s, 3H), 3.70 – 3.64 (m, 1H), 2.87 – 2.76 (m, 2H), 2.05 – 1.96 (m, 2H), 1.21 – 1.09 (m, 21H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.8 Hz), 158.4, 137.5 (d, *J* = 3.1 Hz), 133.9, 129.9 (d, *J* = 7.8 Hz), 128.4, 115.2 (d, *J* = 20.9 Hz), 113.9, 109.9, 83.8, 55.3, 41.1, 37.5, 32.8, 18.8, 11.4;

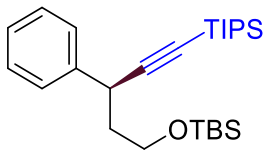
^{19}F NMR (471 MHz, $CDCl_3$) δ –117.6;

HRMS (ESI) calcd. for $C_{27}H_{37}FOSiNa$ $[M+Na]^+$ m/z 447.2490, found 447.2489;

IR (neat, cm^{-1}) 2941, 2863, 2168, 1508, 1246, 825;

$[\alpha]_D^{18}$ = –29.5 (c = 1.35, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 64.1 min, t_R (minor) = 81.1 min.



(*S*)-*tert*-Butyldimethyl((3-phenyl-5-(triisopropylsilyl)pent-4-yn-1-yl)oxy)silane (Figure 4, **5x**). From ***tert*-butyl(cinnamyloxy)dimethylsilane** (**4x**) (49.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 70% yield (60.3 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.21 (m, 1H), 3.92 (dd, *J* = 9.4, 5.4 Hz, 1H), 3.90 – 3.84 (m, 1H), 3.76 – 3.70 (m, 1H), 2.04 – 1.88 (m, 2H), 1.19 – 1.06 (m, 21H), 0.93 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H);

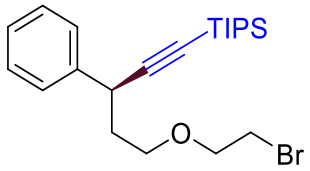
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 128.5, 127.6, 126.6, 109.7, 83.4, 60.8, 42.2, 35.2, 26.1, 18.9, 18.8, 18.4, 11.4, –5.1, –5.2;

HRMS (ESI) calcd. for $C_{26}H_{47}OSi_2$ $[M+H]^+$ m/z 431.3160, found 431.3154;

IR (neat, cm^{-1}) 2942, 2864, 2172, 1741, 1247, 665;

$[\alpha]_D^{18}$ = –24.4 (c = 1.24, $CHCl_3$); 90% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 14.3 min, t_R (major) = 15.0 min.



(*S*)-(5-(2-Bromoethoxy)-3-phenylpent-1-yn-1-yl)triisopropylsilane (Figure 4, **5y**). From **(*E*)-(3-(2-bromoethoxy)prop-1-en-1-yl)benzene** (**4y**) (48.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 81% yield (68.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 3.95 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.76 (t, *J* = 6.2 Hz, 2H), 3.74 – 3.69 (m, 1H), 3.60 – 3.53 (m, 1H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.09 – 1.90 (m, 2H), 1.22 – 0.89 (m, 21H);

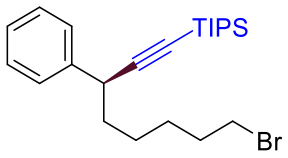
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 128.5, 127.6, 126.8, 109.4, 83.6, 70.9, 68.6, 38.9, 35.4, 30.5, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{22}H_{36}BrOSi$ $[M+H]^+$ m/z 423.1713, found 423.1712;

IR (neat, cm^{-1}) 2941, 2863, 2167, 1113, 882, 665;

$[\alpha]_D^{18}$ = –20.7 (c = 1.47, $CHCl_3$); 88% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 99/1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 7.1min, t_R (major) = 11.6 min.



(*S*)-(8-Bromo-3-phenyloct-1-yn-1-yl)triisopropylsilane (Figure 4, **5z**). From **(6-bromohex-1-en-1-yl)benzene** (**4z**) (47.8 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 62% yield (52.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 1H), 3.71 (dd, *J* = 8.2, 6.1 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.77 – 1.70 (m, 2H), 1.54 – 1.40 (m, 4H), 1.16 – 1.04 (m, 21H);

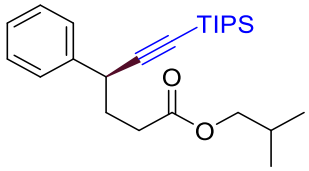
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 128.4, 127.5, 126.6, 109.8, 83.5, 38.9, 38.8, 33.9, 32.8, 27.9, 26.5, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{23}H_{38}BrSi$ $[M+H]^+$ m/z 421.1921, found 421.1922;

IR (neat, cm^{-1}) 2941, 2864, 2169, 1735, 1152, 674;

$[\alpha]_D^{18}$ = –16.8 (c = 0.57, $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 28.3 min, t_R (minor) = 36.2 min.



Isobutyl (*S*)-4-phenyl-6-(triisopropylsilyl)hex-5-ynoate (Figure 4, **5a'**). From **isobutyl (*E*)-4-phenylbut-3-enoate** (**4a'**) (43.7 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 67% yield (53.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 1H), 3.90 – 3.75 (m, 3H), 2.61 – 2.53 (m, 1H), 2.52 – 2.41 (m, 1H), 2.17 – 2.08 (m, 1H), 2.04 – 1.95 (m, 1H), 1.95 – 1.85 (m, 1H), 1.13 – 0.96 (m, 21H), 0.93 (s, 3H), 0.92 (s, 3H);

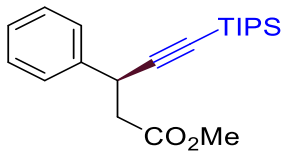
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 141.2, 128.6, 127.6, 126.9, 108.8, 84.4, 70.6, 38.1, 33.9, 31.9, 27.8, 19.2, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{25}H_{41}O_2Si$ $[M+H]^+$ m/z 401.2870, found 401.2871;

IR (neat, cm^{-1}) 2942, 2864, 2173, 1742, 1151, 664;

$[\alpha]_D^{18}$ = –12.8 (c = 0.69, $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALPAK two connected AD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 33.2 min, t_R (minor) = 38.8 min.



Methyl (*S*)-3-phenyl-5-(triisopropylsilyl)pent-4-ynoate (Figure 4, **5b'**). From **methyl (*E*)-4-phenylbut-3-enoate** (**4b'**) (32.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 50:1) to provide the title compound as a colorless liquid in 66% yield (45.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 4.24 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.67 (s, 3H), 2.80 (dd, *J* = 15.1, 8.9 Hz, 1H), 2.73 (dd, *J* = 15.1, 6.5 Hz, 1H), 1.26 – 0.64 (m, 21H);

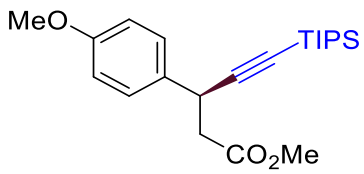
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 140.4, 128.7, 127.5, 127.2, 108.1, 84.1, 51.9, 44.0, 35.4, 18.7, 11.3;

HRMS (ESI) calcd. for $C_{21}H_{33}O_2Si$ $[M+H]^+$ m/z 345.2244, found 345.2247;

IR (neat, cm^{-1}) 2942, 2864, 2174, 1742, 882, 664;

$[\alpha]_D^{18}$ = –12.0 (c = 0.93, $CHCl_3$); 84% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 99/1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 8.1 min, t_R (major) = 20.9 min.



Methyl (*S*)-3-(4-methoxyphenyl)-5-(triisopropylsilyl)pent-4-ynoate (Figure 4, **5c'**). From **methyl (*E*)-4-(4-methoxyphenyl)but-3-enoate** (**4c'**) (38.4 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was

prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless liquid in 66% yield (49.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 6.91 – 6.81 (m, 2H), 4.18 (dd, *J* = 8.7, 6.7 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 2.77 (dd, *J* = 15.1, 8.7 Hz, 1H), 2.69 (dd, *J* = 15.1, 6.7 Hz, 1H), 1.12 – 0.90 (m, 21H);

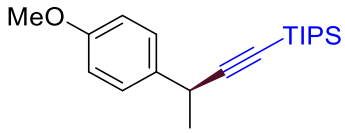
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 158.7, 132.5, 128.54, 114.0, 108.5, 83.8, 55.4, 51.8, 44.1, 34.6, 18.7, 11.3;

HRMS (ESI) calcd. for $C_{22}H_{34}O_3SiNa$ $[M+Na]^+$ m/z 397.2169, found 397.2169;

IR (neat, cm^{-1}) 2942, 2864, 2172, 1741, 1247, 665;

$[\alpha]_D^{18}$ = –5.3 (c = 0.30, $CHCl_3$); 86% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 99/1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 9.5 min, t_R (major) = 14.2 min.



(*S*)-Triisopropyl(3-(4-methoxyphenyl)but-1-yn-1-yl)silane (Figure 4, **5d'**). From **1-methoxy-4-vinylbenzene** (**4d'**) (26.8 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 87% yield (55.0 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 6.89 – 6.83 (m, 2H), 3.84 – 3.74 (m, 4H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.13 – 1.05 (m, 21H);

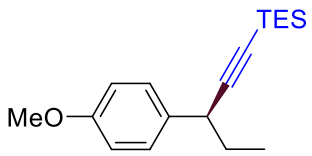
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 135.6, 127.9, 113.8, 111.7, 82.1, 55.3, 32.2, 25.3, 18.8, 11.4;

HRMS (ESI) calcd. for $C_{20}H_{33}OSi$ $[M+H]^+$ m/z 317.2295, found 317.2294;

IR (neat, cm^{-1}) 2940, 2864, 2164, 1510, 1243, 665;

$[\alpha]_D^{18}$ = –4.0 (c = 1.15 $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 24.9 min, t_R (minor) = 26.5 min.



(*S*)-Triethyl(3-(4-methoxyphenyl)pent-1-yn-1-yl)silane (Figure 4, **5e'**). From **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**4e**) (29.6 mg, 0.20 mmol) and **(bromoethynyl)triethylsilane** (**2e**) (65.8 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 40 % yield (23.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 6.88 – 6.83 (m, 2H), 3.80 (s, 3H), 3.59 (dd, *J* = 8.1, 5.7 Hz, 1H), 1.83 – 1.65 (m, 2H), 1.08 – 0.94 (m, 12H), 0.67 – 0.56 (m, 6H);

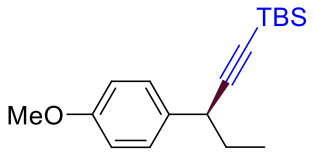
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.1, 128.5, 113.8, 109.8, 84.3, 55.3, 39.6, 32.1, 11.7, 7.6, 4.7;

HRMS (ESI) calcd. for $C_{18}H_{28}OSi$ $[M+H]^+$ m/z 289.1982, found 289.1976;

IR (neat, cm^{-1}) 2954, 2873, 2167, 1510, 1245, 722;

$[\alpha]_D^{20}$ = –13.6 (c = 0.88 $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 23.6 min, t_R (minor) = 26.8 min.



(*S*)-*tert*-Butyl(3-(4-methoxyphenyl)pent-1-yn-1-yl)dimethylsilane (Figure 4, **5f'**). From **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**4e**) (29.6 mg, 0.20 mmol) and **(bromoethynyl)(*tert*-butyl)dimethylsilane** (**2f**) (65.8 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 50 % yield (28.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 6.91 – 6.82 (m, 2H), 3.80 (s, 3H), 3.58 (dd, *J* = 8.0, 5.8 Hz, 1H), 1.82 – 1.62 (m, 2H), 1.01 – 0.95 (m, 12H), 0.13 (s, 6H);

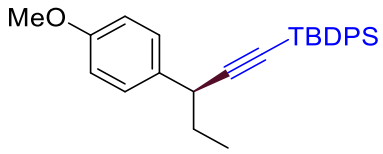
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.0, 128.5, 113.8, 109.2, 85.3, 55.3, 39.6, 32.0, 26.2, 16.7, 11.7, –4.2;

HRMS (ESI) calcd. for $C_{18}H_{28}OSi$ $[M+H]^+$ m/z 289.1982, found 289.1975;

IR (neat, cm^{-1}) 2928, 2856, 2168, 1510, 1245, 824;

$[\alpha]_D^{20}$ = –10.7 (c = 1.12 $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 23.1 min, t_R (minor) = 26.8 min.



(*S*)-*tert*-Butyl(3-(4-methoxyphenyl)pent-1-yn-1-yl)diphenylsilane (Table 3, **5g'**). From **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**4e**) (29.6 mg, 0.20 mmol) and **(bromoethynyl)(*tert*-butyl)diphenylsilane (2b)** (103.0 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 42% yield (34.6 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 4H), 7.42 – 7.34 (m, 8H), 6.93 – 6.82 (m, 2H), 3.82 (s, 3H), 3.76 (dd, *J* = 7.7, 6.1 Hz, 1H), 1.92 – 1.78 (m, 2H), 1.12 – 0.99 (m, 12H);

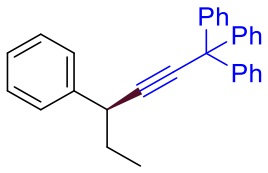
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 135.7, 134.0, 133.9, 133.7, 129.4, 128.6, 127.7, 113.9, 113.1, 82.3, 55.4, 39.9, 32.1, 27.2, 18.7, 11.9;

HRMS (ESI) calcd. for $C_{28}H_{32}OSiNa$ $[M+Na]^+$ m/z 435.2115, found 435.2115;

IR (neat, cm^{-1}) 2929, 2856, 2169, 1510, 1246, 698;

$[\alpha]_D^{18}$ = –12.9 (c = 0.65 $CHCl_3$); 96% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.8 mL/min, 220 nm UV detector, t_R (minor) = 26.9 min, t_R (major) = 28.6 min.



(*S*)-Hex-2-yne-1,1,1,4-tetrayltetrabenzene (Table 3, **5h'**). From **(*E*)-prop-1-en-1-ylbenzene** (**4h'**) (23.6 mg, 0.20 mmol) and **(3-bromoprop-2-yne-1,1,1-triyl)tribenzene (2c)** (104.2 mg, 0.30 mmol), the title compound was prepared

following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 50% yield (38.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.34 – 7.20 (m, 18H), 3.78 (dd, *J* = 7.9, 6.0 Hz, 1H), 1.98 – 1.71 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H);

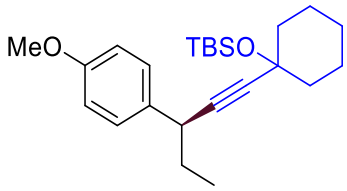
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9, 142.4, 129.3, 128.4, 128.0, 127.7, 126.7, 126.6, 89.3, 86.8, 55.8, 39.8, 32.1, 12.0;

HRMS (ESI) calcd. for $C_{30}H_{27}$ $[M+H]^+$ m/z 387.2107, found 387.2102;

IR (neat, cm^{-1}) 3285, 2921, 1489, 1446, 753, 697;

$[\alpha]_D^{18}$ = –7.5 (c = 1.02 $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 45.5 min, t_R (major) = 48.2 min.



(*S*)-*tert*-Butyl((1-(3-(4-methoxyphenyl)pent-1-yn-1-yl)cyclohexyl)oxy)dimethylsilane (Table 3, **5i'**). From **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**4e**) (29.6 mg, 0.20 mmol) and **((1-(bromoethynyl)cyclohexyl)oxy)(*tert*-butyl)dimethylsilane** (**2d**) (95.2 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc =

100:1) to provide the title compound as a colorless liquid in 66 % yield (50.9 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 6.88 – 6.79 (m, 2H), 3.80 (s, 3H), 3.55 (t, *J* = 6.9 Hz, 1H), 1.85 – 1.69 (m, 4H), 1.67 – 1.47 (m, 6H), 1.47 – 1.39 (m, 1H), 1.33 – 1.27 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.87 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H);

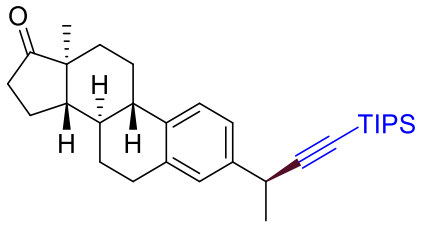
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 134.3, 128.6, 113.7, 87.4, 86.5, 69.5, 55.4, 41.7, 41.6, 38.6, 31.6, 25.9, 25.5, 23.2, 23.1, 18.2, 11.9, –2.6, –2.7;

HRMS (ESI) calcd. for $C_{24}H_{39}O_2Si$ $[M+H]^+$ m/z 387.2714, found 387.2716;

IR (neat, cm^{-1}) 2928, 2854, 1510, 1249, 836, 776;

$[\alpha]_D^{18}$ = –12.8 (c = 0.72 $CHCl_3$); 86% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 21.9 min, t_R (minor) = 24.6 min.



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((*S*)-4-(triisopropylsilyl)but-3-yn-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (Table 3, **5j'**). From **(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one** (**4j'**) (56.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2{\cdot}xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4{\cdot}H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless liquid in 74% yield (68.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.22 – 7.18 (m, 2H), 3.77 (q, *J* = 7.1 Hz, 1H), 2.98 – 2.86 (m, 2H), 2.51 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.34 – 2.26 (m, 1H), 2.20 – 2.11 (m, 1H), 2.10 – 2.00 (m, 2H), 2.00 – 1.93 (m, 1H), 1.67 – 1.58 (m, 2H), 1.58 – 1.42 (m, 7H), 1.18 – 1.06 (m, 21H), 0.92 (s, 3H);

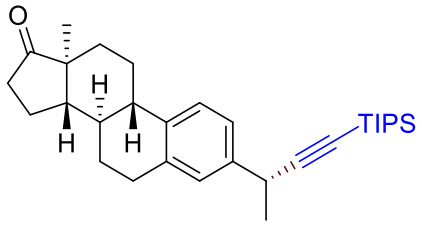
^{13}C NMR (126 MHz, $CDCl_3$) δ 221.0, 140.8, 138.0, 136.5, 127.7, 125.5, 124.4, 111.4, 82.2, 50.6, 48.1, 44.4, 38.3, 35.9, 32.5, 31.7, 29.5, 26.6, 25.8, 25.2, 21.7, 18.8, 13.9, 11.4;

HRMS (ESI) calcd. for $C_{31}H_{46}OSiNa$ $[M+Na]^+$ m/z 485.3210, found 485.3207;

IR (neat, cm^{-1}) 2928, 2863, 2165, 1738, 735, 675;

$[\alpha]_D^{18}$ = +93.4 (c = 0.91 $CHCl_3$); 97:3 *dr*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 99.5/0.5, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 27.6 min, t_R (major) = 29.1 min.



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((*R*)-4-(triisopropylsilyl)but-3-yn-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (Table 3, **5k'**). From **(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one** (**4j'**) (56.1 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*R*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 20:1) to provide the title compound as a colorless liquid in 81% yield (74.8 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.22 – 7.18 (m, 2H), 3.77 (q, *J* = 7.1 Hz, 1H), 2.92 (dd, *J* = 9.1, 4.2 Hz, 2H), 2.51 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.34 – 2.26 (m, 1H), 2.20 – 2.11 (m, 1H), 2.11 – 2.00 (m, 2H), 2.00 – 1.94 (m, 1H), 1.67 – 1.58 (m, 2H), 1.58 – 1.41 (m, 7H), 1.15 – 0.99 (m, 21H), 0.92 (s, 3H);

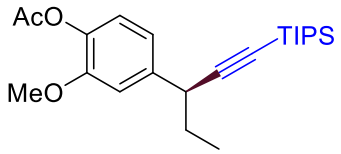
^{13}C NMR (126 MHz, $CDCl_3$) δ 221.0, 140.8, 137.9, 136.5, 127.7, 125.5, 124.4, 111.5, 82.2, 50.6, 48.1, 44.4, 38.2, 35.9, 32.5, 31.7, 29.5, 26.6, 25.8, 25.2, 21.7, 18.8, 13.9, 11.4;

HRMS (ESI) calcd. for $C_{31}H_{46}OSiNa$ $[M+Na]^+$ m/z 485.3210, found 485.3205;

IR (neat, cm^{-1}) 2926, 2863, 2165, 1740, 1009, 670;

$[\alpha]_D^{18}$ = +89.5 (c = 1.20 $CHCl_3$); 5:95 *dr*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 99.5/0.5, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 27.6 min, t_R (minor) = 29.2 min.



(*S*)-2-Methoxy-4-(1-(triisopropylsilyl)pent-1-yn-3-yl)phenyl acetate (Figure 5a, (*S*)-**3i**). From **4-allyl-2-methoxyphenyl acetate** (**1i**) (41.2 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane (2a)** (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L*** (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv) and anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound as a colorless liquid in 78 % yield (60.5 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 1.9 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.89 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, *J* = 8.5, 5.3 Hz, 1H), 2.31 (s, 3H), 1.87 – 1.77 (m, 1H), 1.76 – 1.66 (m, 1H), 1.11 – 1.06 (m, 21H), 1.04 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 150.8, 141.0, 138.2, 122.4, 119.8, 111.8, 109.6, 83.8, 55.9, 40.4, 32.2, 20.8, 18.8, 11.8, 11.4;

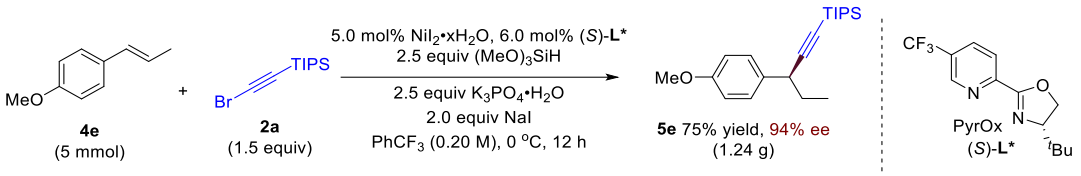
HRMS (ESI) calcd. for $C_{23}H_{36}O_3Si$ $[M+Na]^+$ m/z 411.2326, found 411.2319;

IR (neat, cm^{-1}) 2940, 2864, 2167, 1766, 1508, 1195;

$[\alpha]_D^{20}$ = –20.5 (c = 0.85 $CHCl_3$); 90% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 99/1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 17.7 min, t_R (major) = 20.6 min.

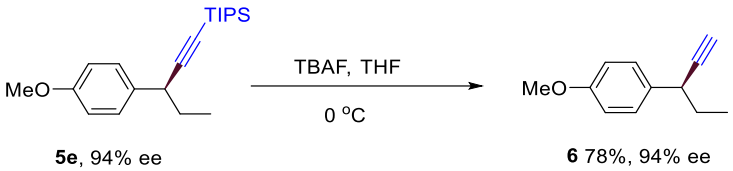
Gram-Scale Experiment



In a nitrogen-filled glove box, to an oven-dried 50 mL round bottom flask equipped with a magnetic stir bar were added $NiI_2 \cdot xH_2O$ (95.0 mg, 5.0 mol%), (*S*)-**L*** (82.5 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (2.88 g, 2.5 equiv), NaI (1.50 g, 2.0 equiv) and anhydrous $PhCF_3$ (25.0 mL, 0.20M). The mixture was stirred for 20 min at room temperature before the addition of $(MeO)_3SiH$ (1.60 mL, 12.5 mmol, 2.5 equiv). Stirring was continued for an additional 5 min at room temperature before (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene **4e** (5.0 mmol, 1.0 equiv) and (bromoethynyl)triisopropylsilane **2a** (7.5 mmol, 1.5 equiv) were added to the resulting mixture in this order. The flask was sealed with a rubber stopper, removed from the glove box and equipped with a N_2 balloon, and stirred at 0 °C for up to 12 h (the mixture was stirred at 800 rpm). After the reaction was complete, the reaction was quenched upon the addition of H_2O, and the mixture was extracted with EtOAc. The organic layer was concentrated. The crude material was purified by flash column chromatography (petroleum ether) to provide **5e** as a colorless liquid in 75% yield (1.24 g). The ee (94%) was determined via HPLC analysis (General procedure **B**).

Synthetic Transformations

Removing the TIPS Group in 5e



5e, 94% ee **6** 78%, 94% ee

A 10-mL Schlenk tube was charged with the product **5e** (66.0 mg, 0.2 mmol) and THF (2 mL), and filled with nitrogen. To the solution cooled to 0 °C was added a solution of tetrabutylammonium fluoride (1.0 mol/L solution in THF; 2.0 mL, 2.0 mmol) dropwise via syringe over 2 min. After 4 h, the reaction was quenched with water (2 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. Then the mixture was purified by silica gel column chromatography (eluted with petroleum ether) to afford the desilylation product **6** as colorless oil (27.2 mg, 78% yield, 94% ee).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.09 (m, 2H), 7.00 – 6.71 (m, 2H), 3.80 (s, 3H), 3.59 – 3.39 (m, 1H), 2.27 (d, *J* = 2.5 Hz, 1H), 1.83 – 1.72 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 133.6, 128.5, 113.9, 86.3, 70.8, 55.4, 38.4, 31.5, 11.7;

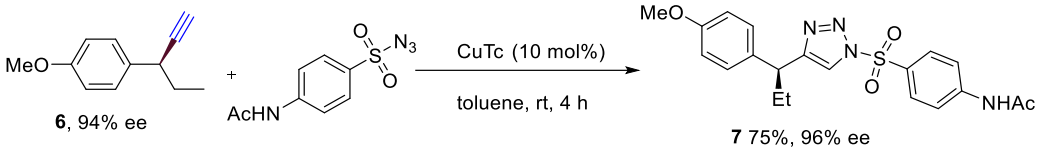
HRMS (ESI) calcd. for $C_{12}H_{14}ONa$ $[M+Na]^+$ m/z 197.0937, found 197.0934;

IR (neat, cm^{-1}) 3292, 2940, 1509, 1243, 1034, 632;

$[\alpha]_D^{18}$ = –21.0 (c = 0.59 $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL OD-H column, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 44.2 min, t_R (minor) = 51.9 min.

Click Reaction



To a solution of CuTc (3.8 mg, 0.02 mmol) and **6** (34.8 mg, 0.2 mmol) in toluene (2 mL), 4-acetamidobenzenesulfonyl azide (48.0 mg, 0.2 mmol) was added, and the mixture was stirred at room temperature for 4 h. After the reaction was completed, the organic solvent was removed under vacuum, and the residue was purified by column chromatography (DCM/EtOAc = 5:1) to give the product **7** (62.1 mg, 75% yield, 96% ee) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.57 (s, 1H), 8.65 (s, 1H), 8.05 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.92 (t, J = 7.8 Hz, 1H), 3.70 (s, 3H), 2.09 (s, 3H), 2.07 – 1.99 (m, 1H), 1.93 – 1.83 (m, 1H), 0.74 (t, J = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.5, 157.8, 151.5, 146.0, 134.5, 129.9, 128.6, 127.8, 121.5, 119.1, 113.8, 54.9, 42.9, 28.2, 24.2, 12.1;

HRMS (ESI) calcd. for $C_{20}H_{22}N_4O_4SNa$ $[M+Na]^+$ m/z 437.1254, found 437.1256;

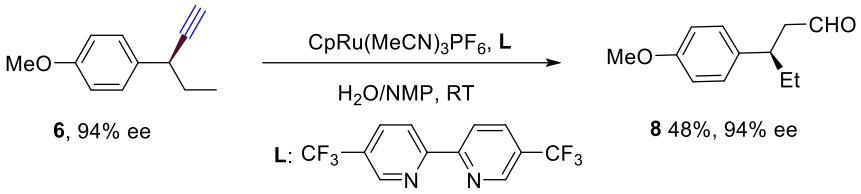
IR (neat, cm^{-1}) 3330, 3107, 2961, 1394, 1176, 577;

m.p. 135.6 – 136.7 °C;

$[\alpha]_D^{18}$ = +21.8 (c = 0.57 Acetone); 96% *ee*;

HPLC analysis CHIRALPAK IC column, *n*-hexane/*iso*-propanol = 80/20, flow rate 0.8 mL/min, 254 nm UV detector, t_R (major) = 24.7 min, t_R (minor) = 30.3 min.

Conversion of the Terminal Alkyne into Aldehyde



6, 94% ee

8 48%, 94% ee

To a Schlenk tube containing $[CpRu(MeCN)_3]PF_6$ (1.7 mg, 0.0040 mmol, 2.0 mol%) and 5,5'- bis(trifluoromethyl)-2,2'-bipyridine **L** (1.2 mg, 0.0040 mmol, 2.0 mol%) was added **6** (0.20 mmol) in a mixture of NMP (0.8 mL) and water (0.2 mL) under nitrogen atmosphere and the reaction mixture was stirred at 25 °C overnight. After completion of reaction (monitored by TLC), the reaction mixture was diluted by EtOAc, washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford **8** as a colorless oil (18.4 mg, 48%, 94% ee).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (t, *J* = 2.2 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 3.08 – 2.99 (m, 1H), 2.72 – 2.63 (m, 2H), 1.73 – 1.64 (m, 1H), 1.64 – 1.52 (m, 1H), 0.80 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.4, 158.3, 135.7, 128.5, 114.0, 55.3, 50.5, 41.1, 29.8, 12.0;

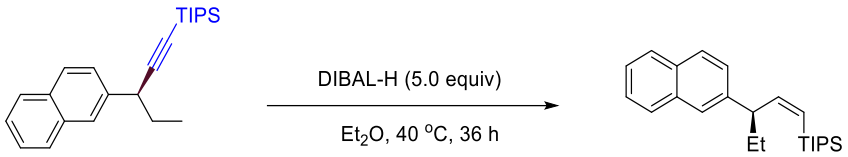
HRMS (ESI) calcd. for $C_{12}H_{17}O_2$ $[M+H]^+$ m/z 193.1223, found 193.1224;

IR (neat, cm^{-1}) 2960, 2927, 1708, 1512, 1249, 829;

$[\alpha]_D^{18}$ = –14.8 (c = 0.31 $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALPAK IC column, *n*-hexane/*iso*-propanol = 99/1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 26.1 min, t_R (major) = 27.6 min.

Semi-Reduction of the Triple Bond by DIBAL-H



5a, 94% ee

9, 98%, 94% ee

To a solution of **5a** (70.0 mg, 0.2 mmol) in Et_2O (2 mL), DIBAL-H (1.0 mL, 1.0 M solution in hexanes) was added, then the mixture was stirred at 40 °C for 36 h. After the reaction was completed, aqueous solution of NaOH was added to quench extra DIABL-H, and the solution was extracted by Et_2O. The combined organic layer was dried over $MgSO_4$, and filtered. After the removal of the solvent, the residue was purified by column chromatography (petroleum ether) to give product **9** (69.0 mg, 98% yield, 94% ee) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 3H), 7.67 – 7.63 (m, 1H), 7.52 – 7.38 (m, 3H), 6.84 (dd, *J* = 14.4, 10.7 Hz, 1H), 5.50 (d, *J* = 14.4 Hz, 1H), 3.60 – 3.32 (m, 1H), 1.91 – 1.76 (m, 2H), 1.28 – 1.17 (m, 3H), 1.12 (d, *J* = 7.4 Hz, 9H), 1.04 (d, *J* = 7.4 Hz, 9H), 0.86 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 142.2, 133.7, 132.2, 128.0, 127.8, 127.7, 126.2, 126.1, 125.9, 125.2, 123.2, 51.8, 31.1, 19.1, 19.0, 12.5, 11.9;

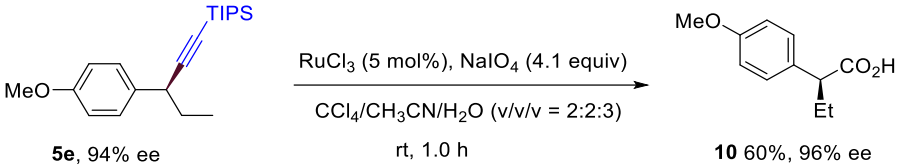
HRMS (ESI) calcd. for $C_{24}H_{36}SiNa$ $[M+Na]^+$ m/z 375.2478, found 375.2480;

IR (neat, cm^{-1}) 2939, 2863, 1460, 743, 664, 474;

$[\alpha]_D^{18}$ = –147.1 (c = 1.07 $CHCl_3$); 94% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (major) = 23.5 min, t_R (minor) = 26.8 min.

Oxidative Cleavage of the Triple Bond to Carboxylic Acid



5e, 94% ee

10 60%, 96% ee

To a solution of **5e** (66.0 mg, 0.2 mmol) in a mixed solvent of CCl_4, CH_3CN and H_2O (1.7 mL, v/v/v 2:2:3), $RuCl_3$ (2.0 mg, 5 mol%) and sodium periodate (175.4 mg, 4.1 equiv) were added, then the mixture was stirred vigorously at room temperature for 1 h. After reaction completion, the mixture was extracted with dichloromethane (3 x 5 mL). The combined organic phase was dried over Na_2SO_4. The organic solvent was removed under vacuum, and the residue was purified via a preparative plate (petroleum ether /EtOAc) to give acid **10** (23.2 mg, 60%, 96% ee) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.87 – 6.84 (m, 2H), 3.79 (s, 3H), 3.41 (t, *J* = 7.7 Hz, 1H), 2.17 – 2.00 (m, 1H), 1.85 – 1.69 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 159.0, 130.6, 129.2, 114.1, 55.4, 52.4, 26.4, 12.2;

HRMS (ESI) calcd. for $C_{11}H_{14}O_3Na$ $[M+Na]^+$ m/z 217.0835, found 217.0834;

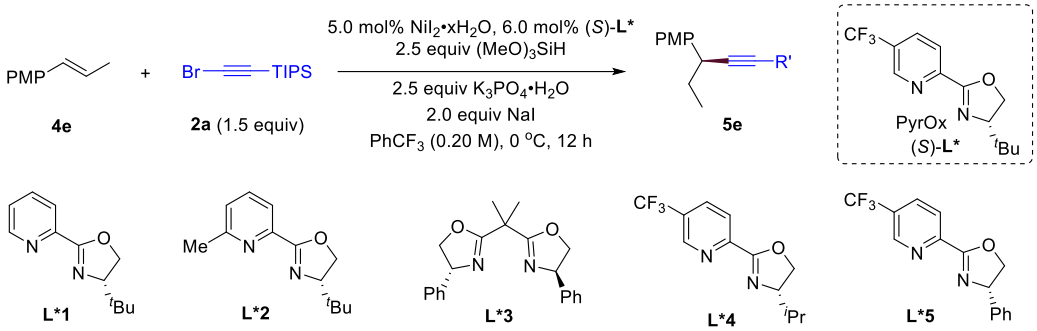
IR (neat, cm^{-1}) 2964, 2930, 1703, 1511, 1250, 1178;

$[\alpha]_D^{18}$ = +50.0 (c = 0.14 $CHCl_3$); 96% *ee*;

HPLC analysis CHIRALPAK AD-H column, *n*-hexane/*iso*-propanol/TFA = 90/10/0.1, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 17.5 min, t_R (major) = 20.3 min.

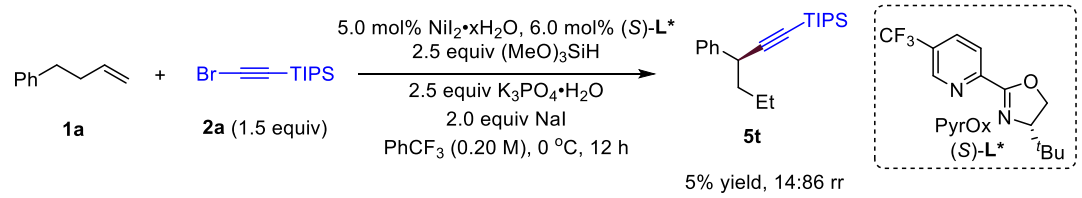
Conditions Optimization

Supplementary Table 1. The conditions optimization for enantioselective NiH-catalyzed reductive hydroalkynylation.

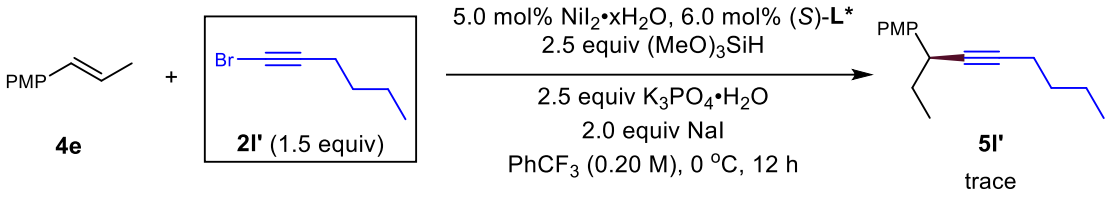


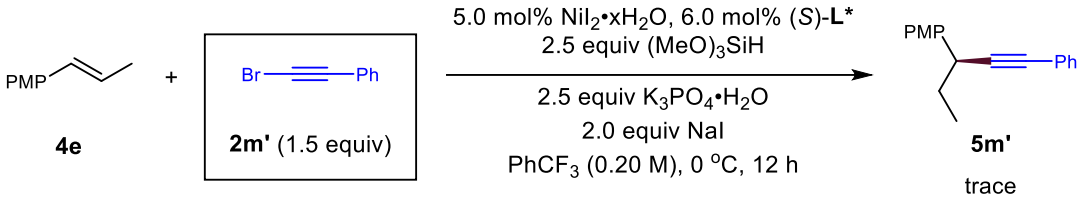
Entry	Variation from the standard conditions	Yield (%)[a]	ee (%)[b]
1	None	86	94
2	w/o $NiI_2 \cdot xH_2O$	NR	
3	w/o $K_3PO_4 \cdot H_2O$	NR	
4	w/o NaI	29	94
5	**L*1** instead of **L***	44	82
6	**L*2** instead of **L***	73	10
7	**L*3** instead of **L***	40	62
8	**L*4** instead of **L***	12	88
9	**L*5** instead of **L***	16	86
10	PMHS instead of $(MeO)_3SiH$	<5	nd
11	DMMS instead of $(MeO)_3SiH$	42	94
12	DME instead of $PhCF_3$	13	84
13	DCE instead of $PhCF_3$	82	92
14	$Ni(NO_3)_2 \cdot 6H_2O$ instead of $NiI_2 \cdot xH_2O$	79	94
15	NiI_2 instead of $NiI_2 \cdot xH_2O$	<5	nd
16	Na_2CO_3 instead of $K_3PO_4 \cdot H_2O$	6	92
17	MeOLi instead of $K_3PO_4 \cdot H_2O$	<5	nd
18	KI instead of NaI	70	94
19	TBAI instead of NaI	41	94
20	25 °C	57	90

[a]Yield were determined by GC using dodecane as internal standard; [b]The enantiomeric excesses (ee) were determined by chiral HPLC analysis.

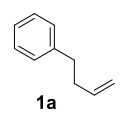


Unsuccessful Substrates





Preparation of Substrates



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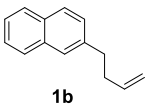

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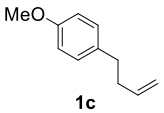

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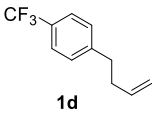

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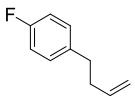

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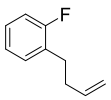

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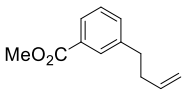

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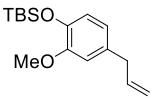

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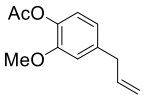

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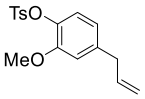

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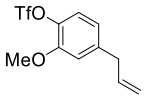

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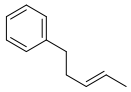

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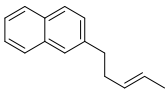

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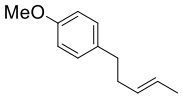

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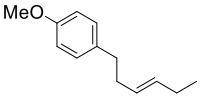

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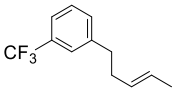

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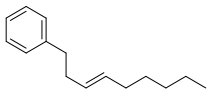

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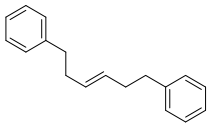

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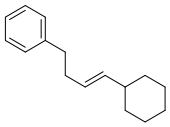

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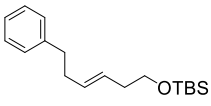
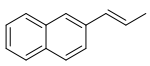


1w



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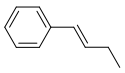
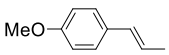
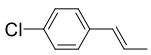


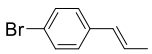
1y



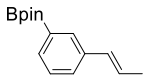
1z



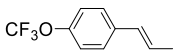
1a'



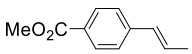
1b'



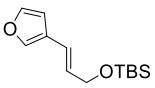
1c'



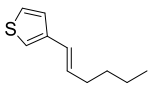
1d'



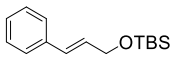
1e'



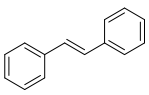
1f'



1g'



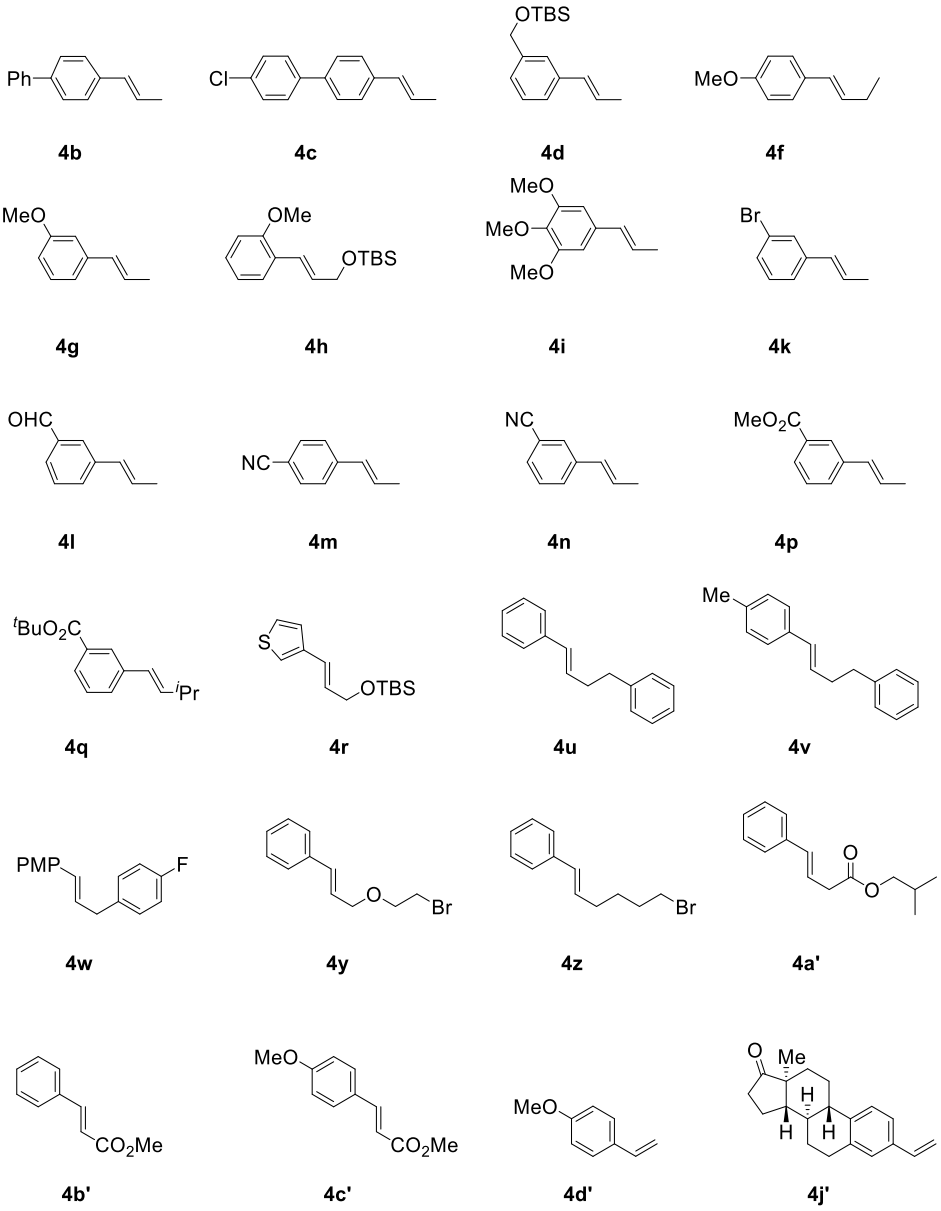
1h'



1i'

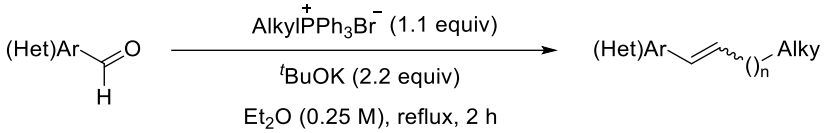
1j'

1k'



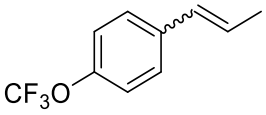
Compounds **1a**, **1z**, **1i'**, **1j'**, **1k'**, **4b'**, and **4d'** are commercially available. Compounds **1b**[7], **1c**[8], **1d**[8], **1e**[8], **1f**[9], **1n**[9], **1g**[10], **1j**[10], **1u**[10], **4u**[10], **4a'**[10], **1h**[11], **1i**[12], **1k**[13], **1p**[14], **1q**[14], **1r**[15], **1s**[16], **4j'**[16], **1t**[17], **1v**[17], **1w**[18], **1x**[19], **1a'**[19], **1b'**[19], **4b**[19], **4f**[19], **4g**[19], **4i**[19], **1y**[20], **1c'**[20], **1e'**[20], **1g'**[20], **4d**[20], **4m**[20], **1h'**[21], **4k**[22], **4l**[23], **4p**[24], **4w**[25], **4y**[26], **4z**[27], **4v**[28], **4c'**[29], and **4n**[30] were prepared according to the previously reported procedures.

General procedure (C) for the synthesis of olefins 1d', 4c, and 4q



A flame dried 250 round bottom flask was charged with alkyl triphenyl phosphonium bromide (1.1 equiv), KO^{t}Bu (2.2 equiv, ***Note: hydroscopic, stored under nitrogen. Exposure to air should be less than 5 minutes***), a stir bar, and anhydrous diethyl ether (0.25 M). A reflux condense was attached and the reaction mixture was heated to reflux for over 1 h before adding a solution of aldehyde (1.0 equiv) in anhydrous diethyl ether. The reaction was monitored by TLC and upon completion of the reaction (~ 2 h), the solvent was removed in vacuo. The resulting compound was diluted with hexanes, filtered over a thick plug of silica gel and concentrated again. The reaction was purified via column chromatography to get the desired compound.

Characterization of Substrates:



1-(Prop-1-en-1-yl)-4-(trifluoromethoxy)benzene (1d'):

Yield 78% (1.57 g, ~ 1:1.8 *E/Z*), colorless liquid;

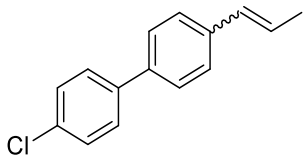
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.21 – 7.12 (m, 2H), 6.45 – 6.35 (m, 1H), [6.28 – 6.17 (m, 0.35H) & 5.88 – 5.79 (m, 0.65H), *due to Z/E*], 1.94 – 1.80 (m, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ (147.9 & 147.5, *due to Z/E*), (136.7, 136.3 & *due to Z/E*), (130.0 & 129.6, *due to Z/E*), (128.5 & 127.6, *due to Z/E*), (126.9 & 126.8, *due to Z/E*), (121.0 & 120.6, *due to Z/E*), 120.5 (q, J = 257.4), (18.4 & 14.4, *due to Z/E*);

^{19}F NMR (471 MHz, CDCl3) δ –57.8;

HRMS (ESI) calcd. for $C_{10}H_{10}F_3O$ $[M+H]^+$ m/z 203.0678, found 203.0676;

IR (neat, cm^{-1}) 2921, 1507, 1253, 1155, 814, 526.



4-Chloro-4'-(prop-1-en-1-yl)-1,1'-biphenyl (4c):

Yield 65% (~ 1:3 *E/Z*), white solid;

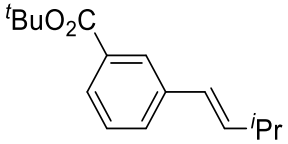
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 4H), 7.44 – 7.36 (m, 4H), 6.52 – 6.41 (m, 1H), [6.36 – 6.26 (m, 0.24H) & 5.92 – 5.80 (m, 0.76H), *due to Z/E*], [1.97 (dd, *J* = 7.2, 1.8 Hz, 2.32H) & 1.93 (dd, *J* = 6.6, 1.7 Hz, 0.75H), *due to Z/E*];

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.41, (138.2 & 137.9, *due to Z/E*), (137.4 & 137.1, *due to Z/E*), (133.4 & 133.3, *due to Z/E*), 130.58, (129.5 & 129.42, *due to Z/E*), (129.1 & 129.0, *due to Z/E*), (128.3 & 128.2, *due to Z/E*), (127.4 & 127.1, *due to Z/E*), (126.7 & 126.4, *due to Z/E*), (18.72 & 14.92, *due to Z/E*);

HRMS (ESI) calcd. for $C_{15}H_{13}ClNa$ $[M+Na]^+$ m/z 251.0598, found 251.0598;

IR (neat, cm^{-1}) 2913, 1473, 1093, 821, 787, 504;

m.p. 93.3 – 94.4 °C.



***tert*-Butyl (*E*)-3-(3-methylbut-1-en-1-yl)benzoate (4q)**:

Yield 60% (> 95:5 *Z/E*), colorless liquid;

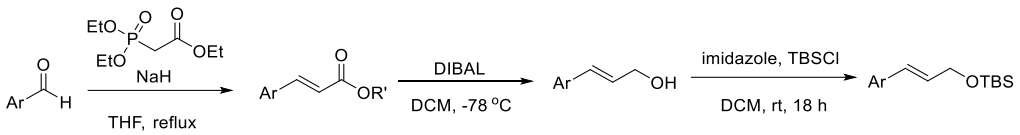
^{1}H NMR (500 MHz, $CHCl_3$) δ 7.94 – 7.89 (m, 1H), 7.88 – 7.82 (m, 1H), 7.44 – 7.33 (m, 2H), 6.32 (d, *J* = 11.6 Hz, 1H), 5.53 (dd, *J* = 11.6, 10.2 Hz, 1H), 2.94 – 2.80 (m, 1H), 1.60 (s, 9H), 1.07 (s, 3H), 1.06 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 141.3, 137.9, 132.6, 132.0, 129.7, 128.1, 127.5, 125.7, 81.0, 28.3, 27.3, 23.2;

HRMS (ESI) calcd. for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ m/z 269.1512, found 269.1513;

IR (neat, cm^{-1}) 2963, 1713, 1367, 1293, 1156, 773.

General procedure (D) for the preparation of olefins 1f', 4h and **4r**[3,4]



Step 1:

Phosphonoacetate (1.2 equiv) was added dropwise under argon over a period of 5 minutes to a stirred suspension of sodium hydride (55% dispersion in oil, 1.2 equiv) in dry THF (1.3 mL per 1.2 mmol of sodium hydride), and the resulting mixture was stirred at 0 °C for additional 15 min. A solution of aldehyde (1.0 equiv) in dry THF (1.0 M) was slowly added to the resulting mixture, and it was stirred at 0 °C for additional 0.5 h. Subsequently, the reaction mixture was refluxed overnight and then cooled to ambient temperature, and the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was used without further purification.

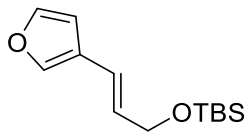
Step 2:

To a stirred solution of ethyl acrylates (1.0 equiv) in anhydrous CH_2Cl_2 (0.71 M) was added dropwise diisobutylaluminum hydride (1.0 M in toluene, 2.2 equiv) under argon at −78 °C. The mixture was stirred at −78 °C for 1.5 h, and the reaction was quenched with 10% aqueous NaOH (1.0 mL per 1.0 mL of diisobutylaluminum hydride solution). The resulting mixture was allowed to warm to ambient temperature and stirred for additional 1 h. The aqueous layer was extracted with CH_2Cl_2 (30 mL × 3), and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using petroleum ether/EtOAc (v/v = 5:1–3:1) as an eluent gave the corresponding allylic alcohols.

Step 3:

In a flame-dried 25 mL round bottom flask was added allylic alcohols (1 equiv) in dry CH_2Cl_2 (0.3 M). Then imidazole (1.5 equiv) and trialkylsilyl chloride (1.3 equiv) were added. The reaction was stirred at room temperature for 18 h. The reaction was

quenched with water. The reaction was extracted with ether (2 x 15 mL). Organic layers were combined, washed with brine (20 mL), dried over magnesium sulfate, filtered and concentrated in vacuum to provide a crude oil which was purified by flash chromatography to provide the desired product.



***tert*-Butyl((3-(furan-3-yl)allyl)oxy)dimethylsilane (1f')**:

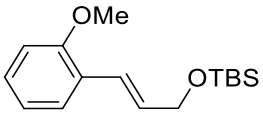
Yield 90% (> 95:5 *E/Z*), colorless liquid;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.33 (m, 2H), 6.54 – 6.51 (m, 1H), 6.48 – 6.42 (m, 1H), 6.08 – 5.95 (m, 1H), 4.30 (dd, *J* = 5.2, 1.8 Hz, 2H), 0.95 (s, 9H), 0.11 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 140.3, 128.8, 124.0, 119.4, 107.7, 63.8, 26.1, 18.5, -5.0;

HRMS (ESI) calcd. for $C_{13}H_{22}O_2SiNa$ $[M+Na]^+$ m/z 261.1281, found 261.1282;

IR (neat, cm^{-1}) 2956, 2856, 1254, 1071, 836, 776.



***tert*-Butyl((3-(2-methoxyphenyl)allyl)oxy)dimethylsilane (4h)**:

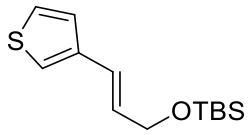
Yield 80% (~ 5:1 *E/Z*), colorless liquid;

^{1}H NMR (500 MHz, $CDCl_3$) δ [7.45 (dd, *J* = 7.6, 1.7 Hz, 0.83H) & 7.14 (dd, *J* = 7.5, 1.7 Hz, 0.16H), *due to Z/E*], [7.29 – 7.26 (m, 0.13H) & 7.25 – 7.19 (m, 0.86H), *due to Z/E*], 6.96 – 6.89 (m, 2H), [6.87 (d, *J* = 8.2 Hz, 1H) & 6.66 (d, *J* = 11.7 Hz, 0.16H), *due to Z/E*], [6.36 – 6.25 (m, 0.82H) & 5.92 – 5.84 (m, 0.16H), *due to Z/E*], [4.39 – 4.37 (m, 1.81H) & 4.37 – 4.36 (m, 0.18H), *due to Z/E*], [3.85 (s, 2.44H) & 3.84 (s, 0.55H), *due to Z/E*], [0.97 (s, 7.40H) & 0.91 (s, 1.60H), *due to Z/E*], [0.13 (s, 4.96H) & 0.06 (s, 1.04H), *due to Z/E*];

^{13}C NMR (126 MHz, $CDCl_3$) δ (157.0 & 156.8, *due to Z/E*), 132.0, (130.3 & 129.9, *due to Z/E*), (128.7 & 128.4, *due to Z/E*), (127.0 & 126.3, *due to Z/E*), (125.4 & 124.7, *due to Z/E*), (120.7 & 120.1, *due to Z/E*), (110.9 &110.4, *due to Z/E*), (64.5 & 60.5, *due to Z/E*), (55.5 & 55.5, *due to Z/E*), (26.1 & 26.0, *due to Z/E*), (18.5 & 18.4, *due to Z/E*), (–4.9 & –5.0, *due to Z/E*);

HRMS (ESI) calcd. for $C_{16}H_{26}O_2SiNa$ $[M+Na]^+$ m/z 301.1594, found 301.1592;

IR (neat, cm^{-1}) 2929, 2855, 1437, 1241, 830, 747.



***tert*-Butyldimethyl((3-(thiophen-3-yl)allyl)oxy)silane (4r)**:

Yield 85% (> 95:5 *E/Z*), colorless liquid;

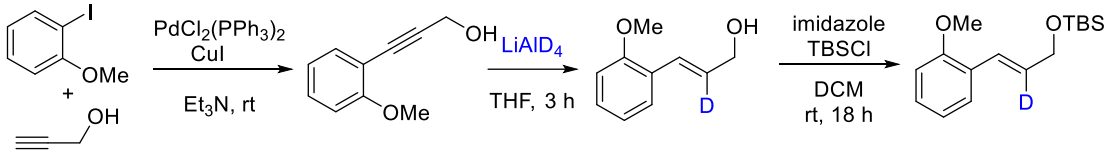
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.23 – 7.20 (m, 1H), 7.15 – 7.13 (m, 1H), 6.64 – 6.57 (m, 1H), 6.19 – 6.12 (m, 1H), 4.33 (dd, *J* = 5.1, 1.8 Hz, 2H), 0.96 (s, 9H), 0.13 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 129.1, 125.9, 125.2, 123.9, 121.7, 63.8, 26.1, 18.6, –5.0;

HRMS (ESI) calcd. for $C_{13}H_{22}OSSiNa$ $[M+Na]^+$ m/z 277.1053, found 277.1050;

IR (neat, cm^{-1}) 2953, 2855, 1252, 1061, 831, 771.

General procedure (E) for the preparation of olefin (*E*)-4h-D[4,5,6]



Step 1:

To a stirred solution of substituted iodobenzene (10 mmol, 1.0 equiv) in triethylamine (50 mL) under nitrogen were sequentially added $Pd(PPh_3)_2Cl_2$ (2 mol %) and CuI (4 mol %) at room temperature. The mixture was allowed to stir for 10 min. Then propargyl alcohol (11 mmol, 1.1 equiv) was added. The mixture was allowed to stir overnight. After the reaction was finished, water was added and the solution was extracted with ethyl acetate; The combined extract was dried with anhydrous $MgSO_4$. Solvent was removed, and the residue was separated by column chromatography to give the aryl substituted propargyl alcohol.

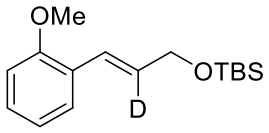
Step 2:

To a flame dried round-bottomed flask charged with $LiAlD_4$ (210 mg, 5 mmol, 100 mol%) under nitrogen was added THF (15 mL, 0.33 M with respect to propargylic alcohol). The reaction vessel was placed in an ice batch. After 5 minutes a solution of aryl substituted propargyl alcohol (5 mmol, 100 mol%) in dry THF (5 mL, 1.0 M with respect to propargylic alcohol) was added slowly and the mixture was stirred at room temperature for 3 hours. After the reaction vessel was placed in an ice batch, water (1 mL), NaOH (1 mL, 10% aqueous solution) and water (3 mL) were added to the reaction mixture. After 10 minutes, $MgSO_4$ was added and the reaction mixture was filtered (celite) with the aid of CH_2Cl_2 (10 mL) and the filtrate was concentrated under reduced pressure. The resulting oily residue was subjected to the next step without further purification.

Step 3:

To a flame-dried 25 mL round bottom flask was added allylic alcohol (1 equiv) in dry DCM (0.3 M). Then imidazole (1.5 equiv) and trialkylsilyl chloride (1.3 equiv) were added. The reaction was stirred at room temperature for 18 h. The reaction was quenched with water and was extracted with ether (2 x 15 mL). Organic layers were

combined, washed with brine (20 mL), dried over magnesium sulfate, filtered and concentrated in vacuum to provide a crude oil which was purified by flash chromatography to provide the desired product.



(*E*)-*tert*-Butyl((3-(2-methoxyphenyl)allyl-2-*d*)oxy)dimethylsilane (4h-D):

Yield 65%, colorless liquid;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.94 – 6.83 (m, 3H), 4.36 (d, *J* = 1.8 Hz, 2H), 3.84 (s, 3H), 0.95 (s, 9H), 0.12 (s, 6H);

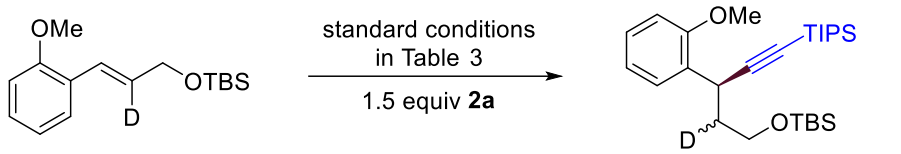
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 129.6 (t, *J* = 23.6 Hz), 128.4, 127.1, 126.3, 124.6, 120.7, 110.9, 64.5, 55.6, 26.1, 18.6, –4.9;

HRMS (ESI) calcd. for $C_{16}H_{25}DO_2SiNa$ $[M+Na]^+$ m/z 302.1657, found 302.1658;

IR (neat, cm^{-1}) 2928, 2855, 1462, 1244, 833, 747.

Isotopic Labelling Experiments

a) NiD experiment: NiD *syn*-hydrometallation is not the enantio-determining step



(*E*)-**4h-D** **5h-D** 81% yield, 0.55:0.45 dr, 92% ee

tert*-Butyl(((2*S*,3*S*)-3-(2-methoxyphenyl)-5-(triisopropylsilyl)pent-4-yn-1-yl-2-*d*)oxy)dimethylsilane** (Figure 5, **5h-D**). From **(*E*)-*tert*-butyl((3-(2-methoxyphenyl)allyl-2-*d*)oxy)dimethylsilane** (**4h-D**) (55.9 mg, 0.20 mmol) and **(bromoethynyl)triisopropylsilane** (**2a**) (78.4 mg, 0.30 mmol), the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 5.0 mol%), (*S*)-**L (3.3 mg, 6.0 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 2.5 equiv), NaI (60.0 mg, 2.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 2.5 equiv), anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 100:1) to provide the title compound as a colorless liquid in 81% yield (74.4 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.25 – 7.17 (m, 1H), 6.99 – 6.91 (m, 1H), 6.84 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.32 – 4.26 (m, 1H), 3.92 – 3.86 (m, 1H), 3.83 – 3.78 (m, 4H), [2.03 – 1.95 (m, 0.45H) & 1.77 – 1.68 (m, 0.55H), *due to dr*], 1.15 – 1.05 (m, 21H), 0.92 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 130.4, 128.6, 127.7, 120.6, 110.3, 110.1, 82.7, 61.5, 55.3, 39.8 – 39.4 (m, 1C), 29.1, 26.0, 18.9, 18.8, 18.4, 11.4, –5.0, –5.1;

^{2}H NMR (92 MHz, $CDCl_3$) δ 2.00 (0.55D), 1.74 (0.45D);

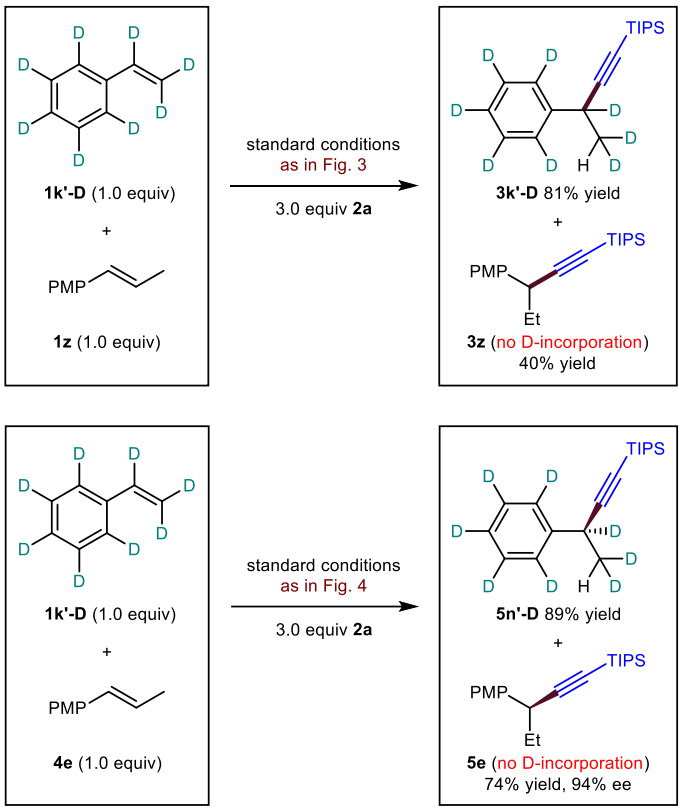
HRMS (ESI) calcd. for $C_{27}H_{47}DO_2Si_2Na$ $[M+Na]^+$ m/z 484.3148, found 484.3147;

IR (neat, cm^{-1}) 2943, 2864, 2164, 1244, 1090, 835;

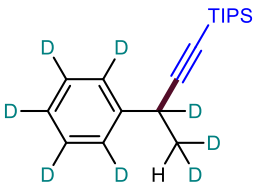
$[\alpha]_D^{18}$ = –31.2 (c = 1.24, $CHCl_3$); 92% *ee*;

HPLC analysis CHIRALCEL two connected OD-H columns, *n*-hexane/*iso*-propanol = 100/0, flow rate 0.5 mL/min, 220 nm UV detector, t_R (minor) = 14.5 min, t_R (major) = 18.0 min.

b) Crossover experiment: no intermolecular H/D scrambled crossover products



From **styrene-d_8 (1k'-D)** (11.2 mg, 0.1 mmol) and **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**1z**) (14.8 mg, 0.1 mmol). the title compound was prepared following the general procedure **A** using $NiI_2 \cdot xH_2O$ (3.8 mg, 10 mol%), **L** (3.3 mg, 12 mol%), Na_2CO_3 (42.4 mg, 4.0 equiv), NaI (3.0 mg, 0.2 equiv), PMHS (60 μL, 1.0 mmol, 10.0 equiv), anhydrous DME (1.0 mL). The reaction mixture was stirred for 16 h at 25 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound.



Triisopropyl(3-(phenyl-d_5)but-1-yn-1-yl-4,4-d_3)silane (Figure 5, **3k'-D**):

Yield 81%, colorless liquid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 1H), 1.15 – 1.06 (m, 21H);

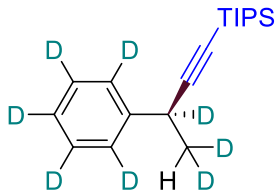
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, [128.2 & 128.0 & 127.7] (1C), [126.8 & 126.6 & 126.3] (1C), [126.0 & 125.8] (1C), 111.4, 82.3, 24.9 – 24.1, 18.8, 11.4;

^{2}H NMR (92 MHz, $CDCl_3$) [7.44 & 7.35, (5D)], 3.78 (1D), 1.47 (2D);

HRMS (ESI) calcd. for $C_{19}H_{22}D_8SiNa$ $[M+H]^+$ m/z 295.2692, found 295.2686;

IR (neat, cm^{-1}) 2942, 2864, 2167, 1462, 996, 882;

From **styrene-*d*$_8$ (1k'-D)** (11.2 mg, 0.1 mmol) and **(*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene** (**4e**) (14.8 mg, 0.1 mmol). the title compound was prepared following the general procedure **B** using $NiI_2 \cdot xH_2O$ (3.8 mg, 10 mol%), (*S*)-**L*** (3.3 mg, 12 mol%), $K_3PO_4 \cdot H_2O$ (115.1 mg, 5.0 equiv), NaI (60.0 mg, 4.0 equiv), $(MeO)_3SiH$ (64 μL, 0.5 mmol, 5.0 equiv), anhydrous $PhCF_3$ (1.0 mL). The reaction mixture was stirred for 12 h at 0 °C. The crude material was purified by flash column chromatography (petroleum ether) to provide the title compound.



(*S*)-Triisopropyl(3-(phenyl-*d*$_5$)but-1-yn-1-yl-3,4,4-*d*$_3$)silane (Figure 5, **5n'-D**):

Yield 89%, colorless liquid;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 1H), 1.15 – 0.77 (m, 21H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, [128.2 & 128.0 & 127.8] (1C), [126.8 & 126.6 & 126.4] (1C), [126.2 & 126.0 & 125.9] (1C), 111.4, 82.3, 24.9 – 24.2 (m, 1C), 18.8, 11.4;

^{2}H NMR (92 MHz, $CDCl_3$) δ [7.46 & 7.36, (5D)], 3.79 (1D), 1.48 (2D);

HRMS (ESI) calcd. for $C_{19}H_{22}D_8SiNa$ $[M+Na]^+$ m/z 317.2511, found 317.2507;

IR (neat, cm^{-1}) 2942, 2864, 2168, 1462, 882, 659;

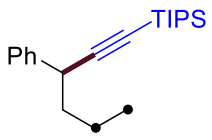
Supplementary Note 1. Spectroscopic Data (GC Traces)

1) *n*-Dodecane (t_R = 2.0 min) was used as internal standard for GC yield.

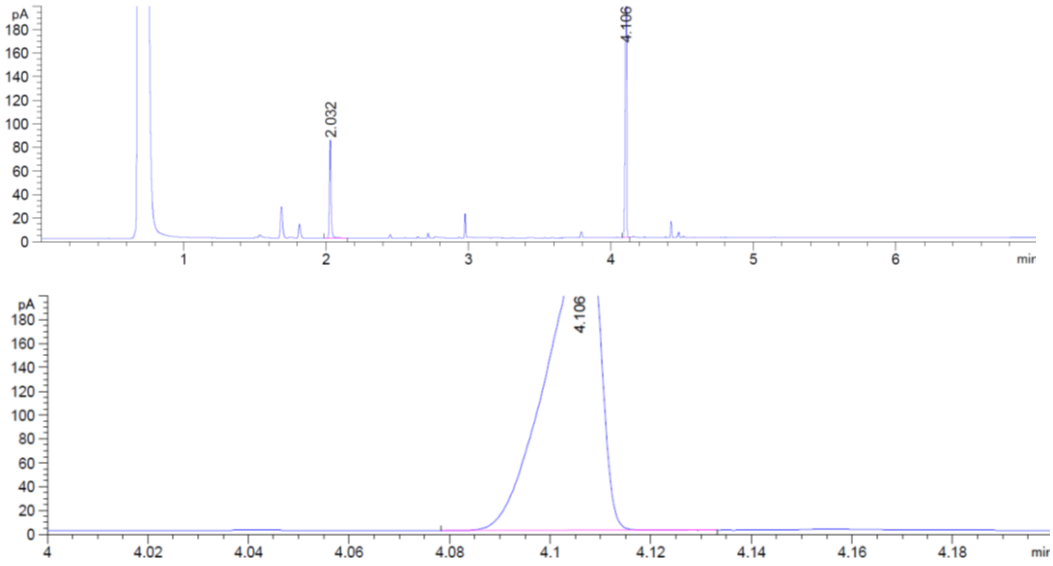
2) GC analysis was performed on Agilent 7890B gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). GC-MS analysis was performed on an Agilent 7890B gas chromatograph with 5977A MSD mass spectrum using an HP-5 MS column (30 m, 0.25 mm I.D.).

3) GC method: 100 method starts at 100 °C holds the oven at this temperature for 1 minute, then ramp of 50 °C/min till 250 °C and hold the oven at this temperature for 3 minutes (or 5 minutes for 100B method, or 16 minutes for 100C method).

4) rr refers to regioisomeric ratio, represents the ratio of major product to the sum of all other isomers as determined by GC, all isomers' peaks were confirmed by GC-MS analysis.

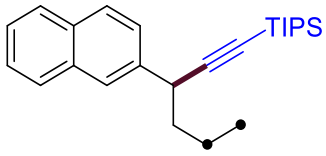


3a

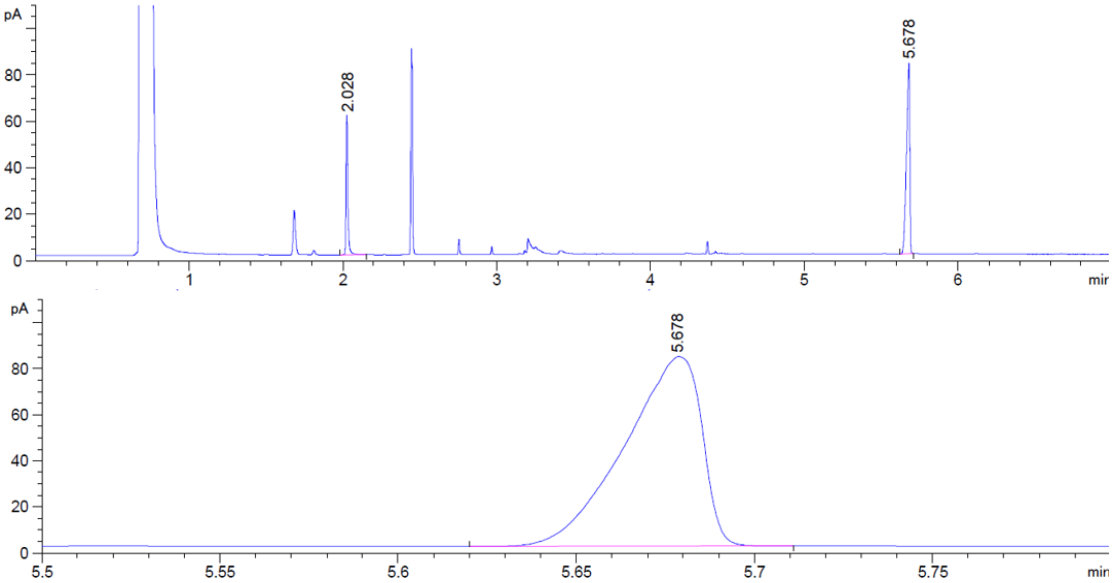


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.106	BB	0.0113	186.16582	244.35548	1.000e2

Supplementary Fig. 3. GC spectra of compound **3a**, Related to Figure 3.

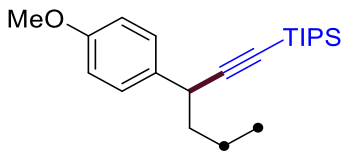


3b

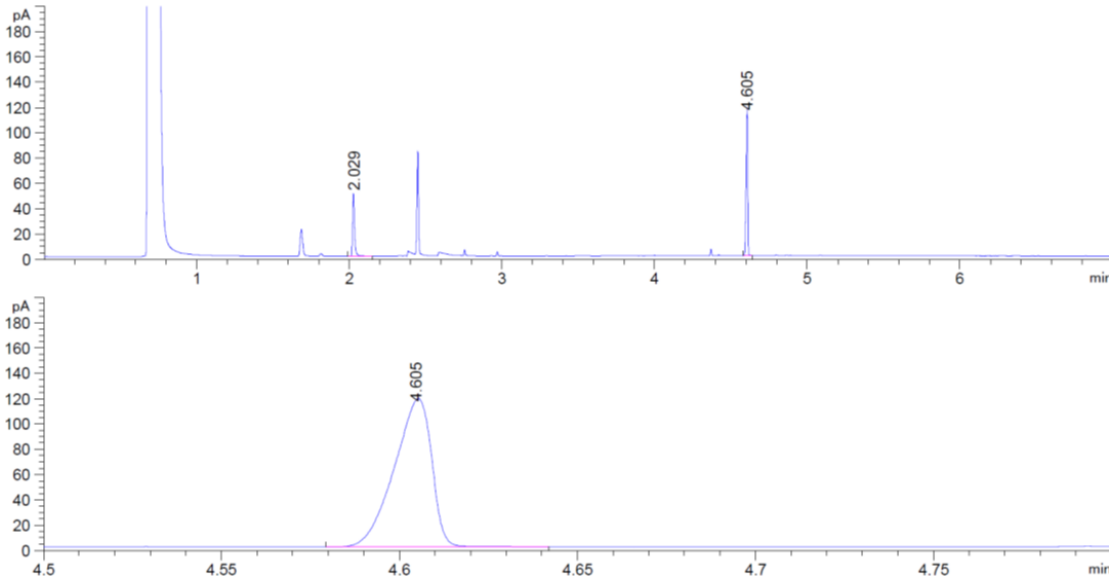


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.678	BB	0.0232	123.87083	82.12784	1.000e2

Supplementary Fig. 4. GC spectra of compound **3b**, Related to Figure 3.

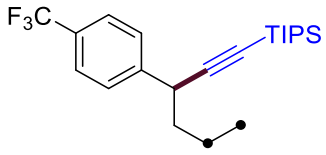


3c

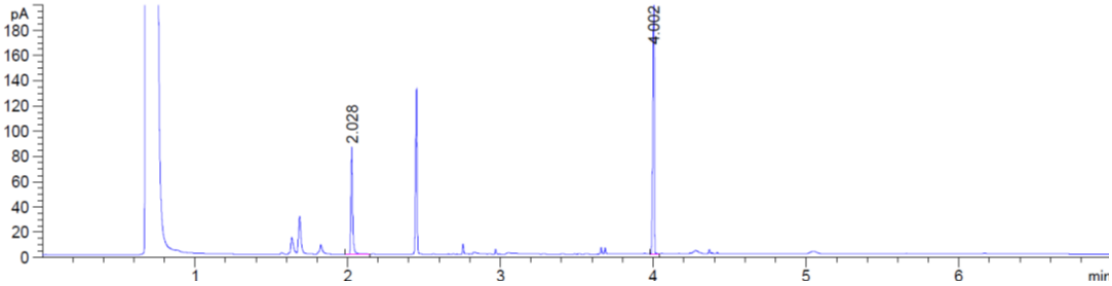


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.605	BB	0.0121	85.66869	111.75015	1.000e2

Supplementary Fig. 5. GC spectra of compound **3c**, Related to Figure 3.

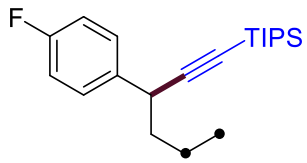


3d

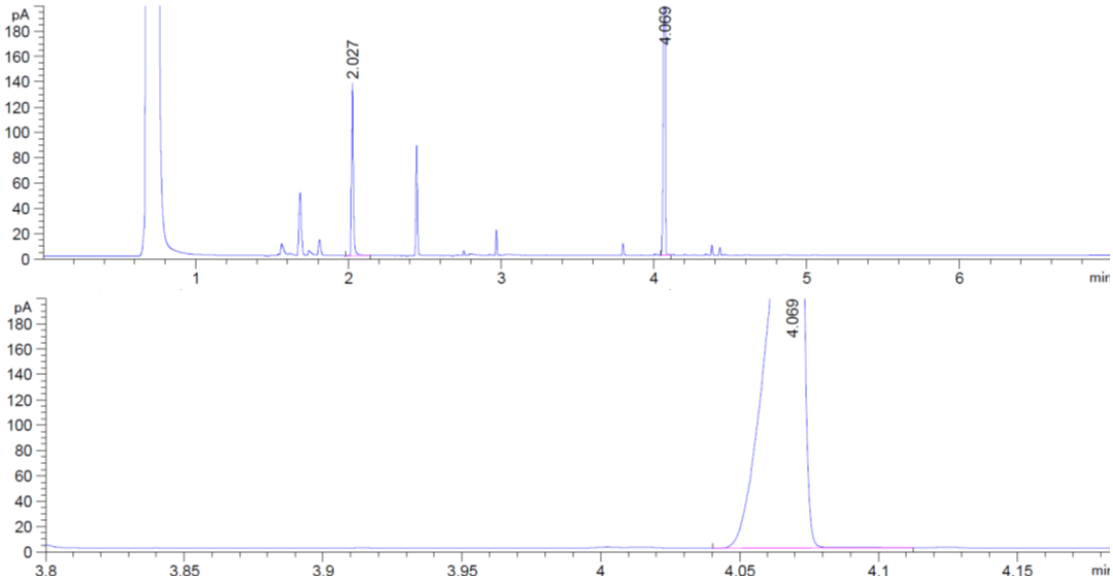


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.002	BB	0.0114	154.49745	219.06358	1.000e2

Supplementary Fig. 6. GC spectra of compound **3d**, Related to Figure 3.

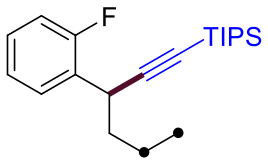


3e

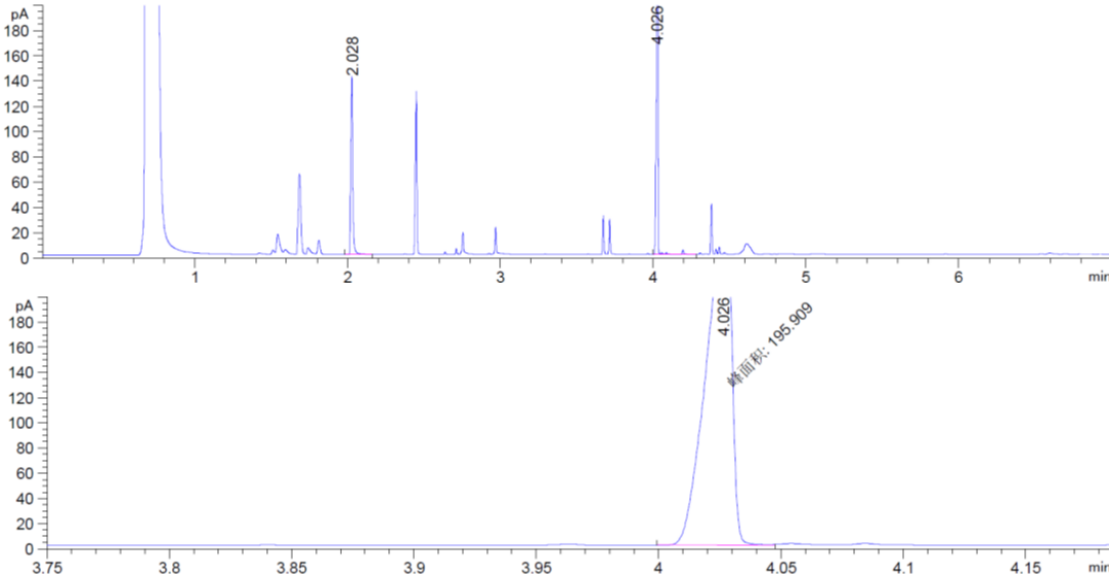


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.069	BB	0.0132	306.20294	355.76334	1.000e2

Supplementary Fig. 7. GC spectra of compound **3e**, Related to Figure 3.

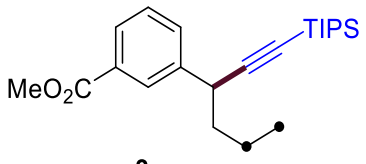


3f

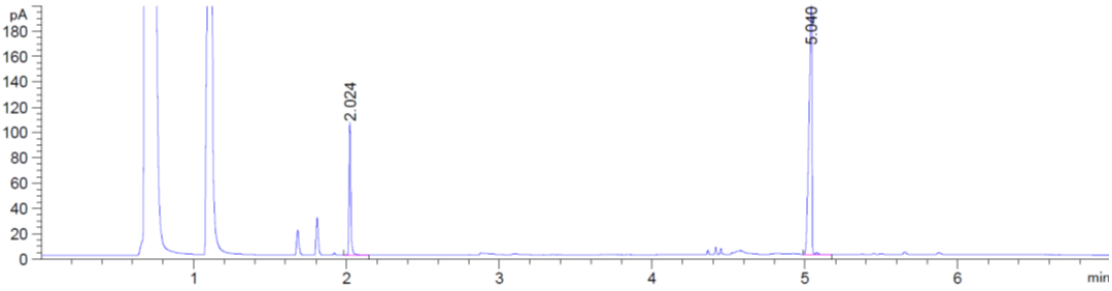


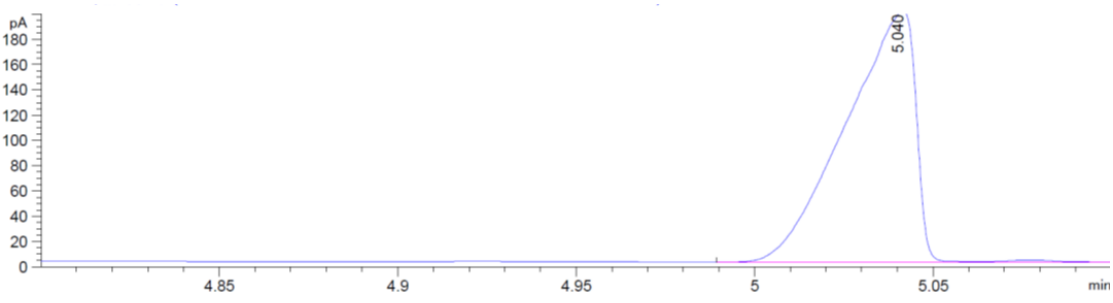
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.026	MM	0.0113	195.90855	290.07196	1.000e2

Supplementary Fig. 8. GC spectra of compound **3f**, Related to Figure 3.



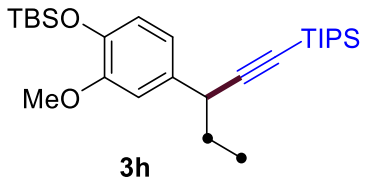
3g



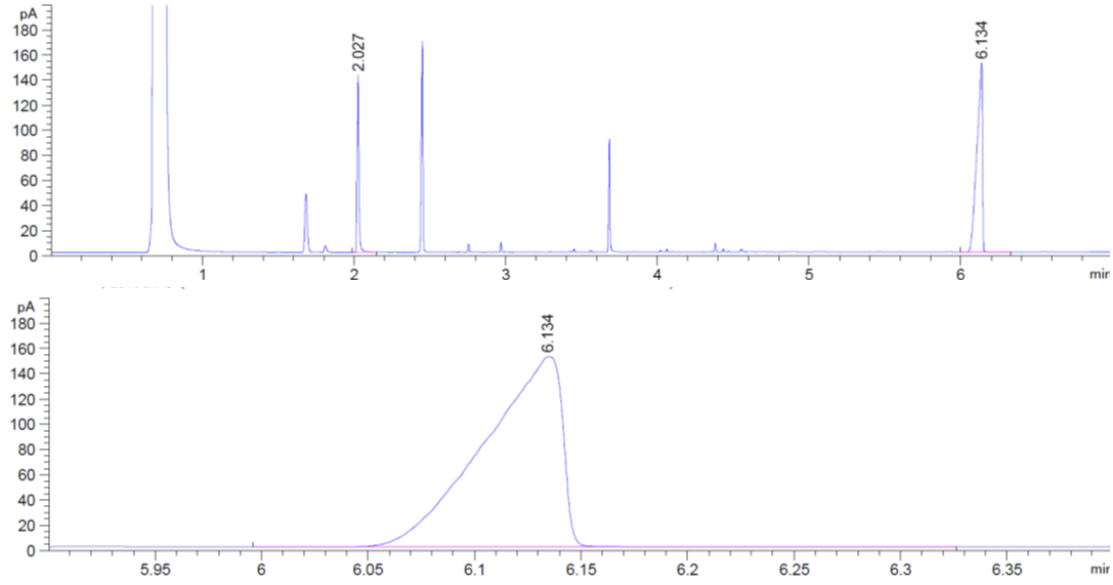


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.040	BV R	0.0188	271.26648	201.11446	1.000e2

Supplementary Fig. 9. GC spectra of compound **3g**, Related to Figure 3.

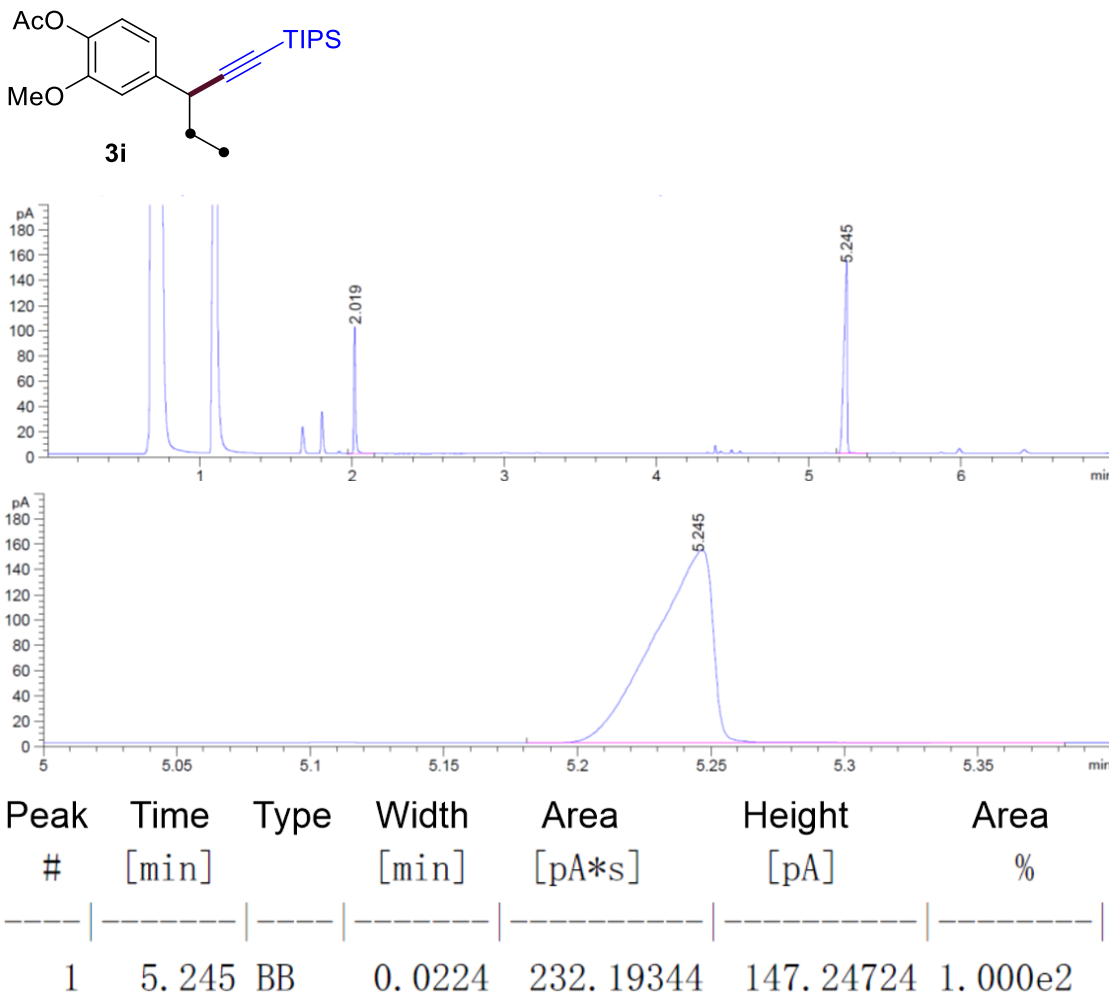


3h



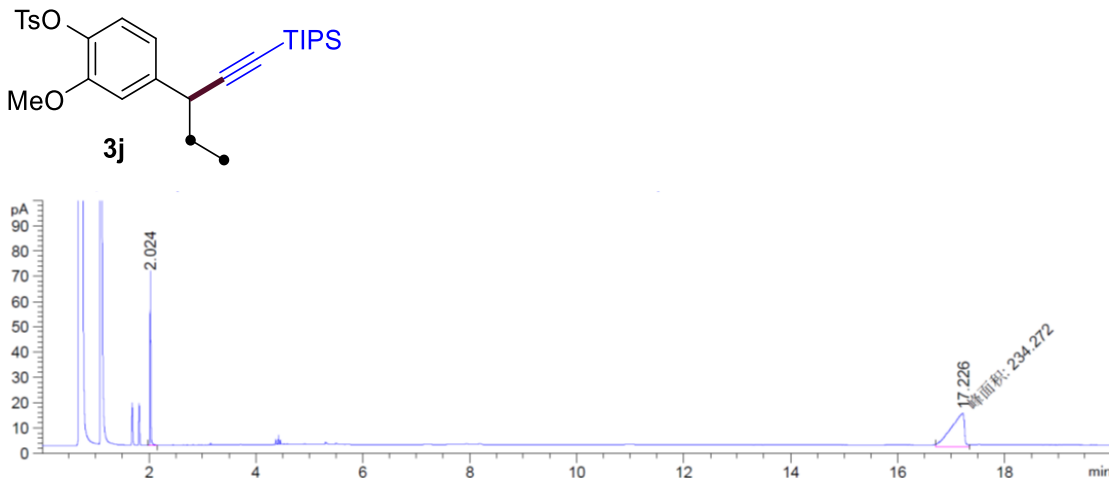
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.134	BB	0.0337	383.35068	150.40926	1.000e2

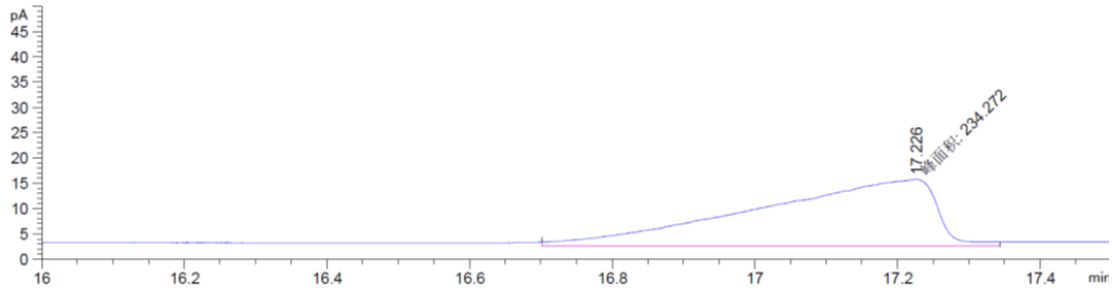
Supplementary Fig. 10. GC spectra of compound **3h**, Related to Figure 3.



Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.245	BB	0.0224	232.19344	147.24724	1.000e2

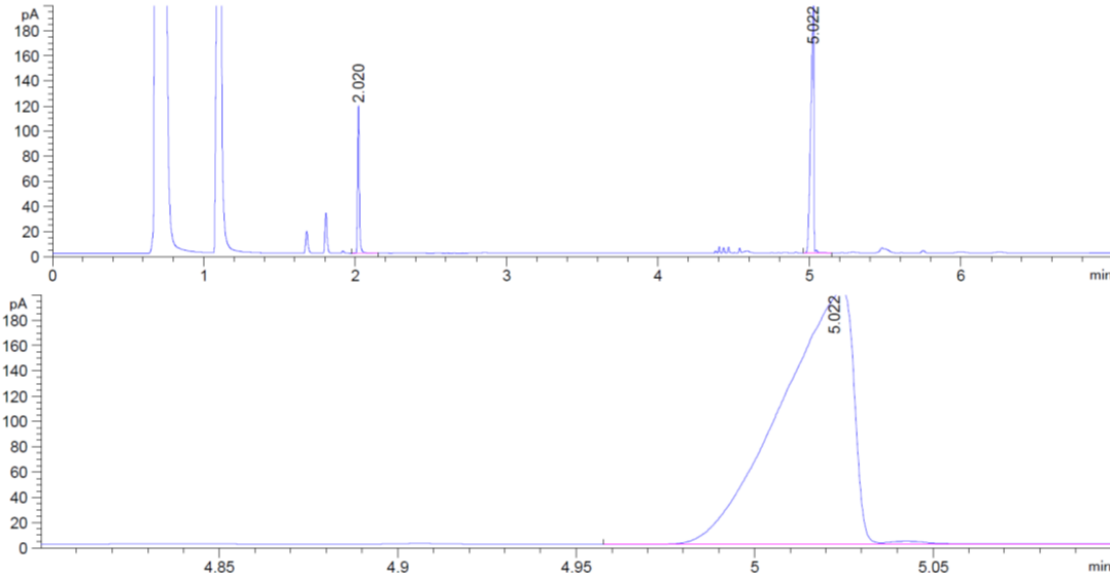
Supplementary Fig. 11. GC spectra of compound **3i**, Related to Figure 3.





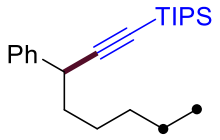
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	17.226	MM	0.2940	234.27243	13.28021	1.000e2

Supplementary Fig. 12. GC spectra of compound **3j**, Related to Figure 3.

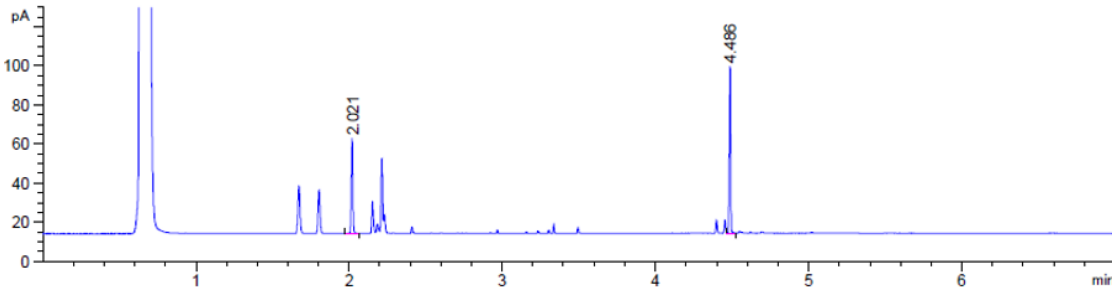


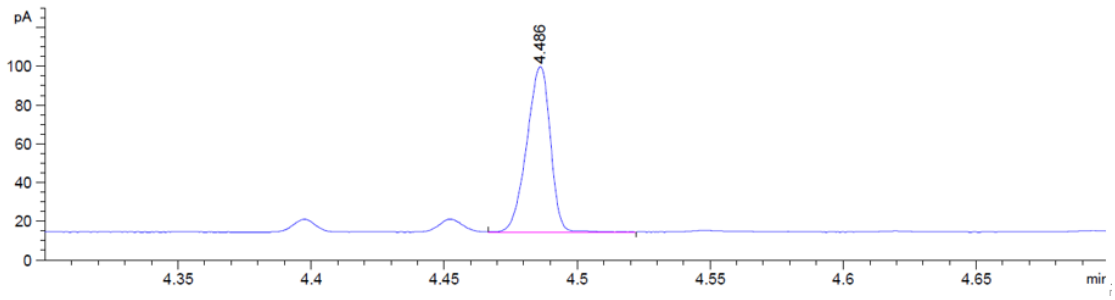
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.022	BB	0.0218	285.20779	195.70508	1.000e2

Supplementary Fig. 13. GC spectra of compound **3k**, Related to Figure 3.



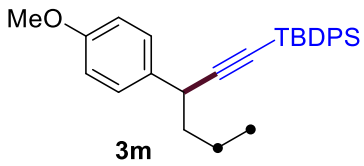
3l



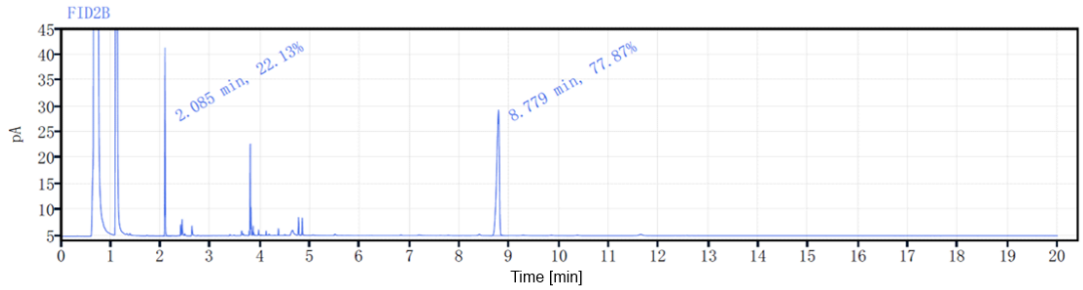


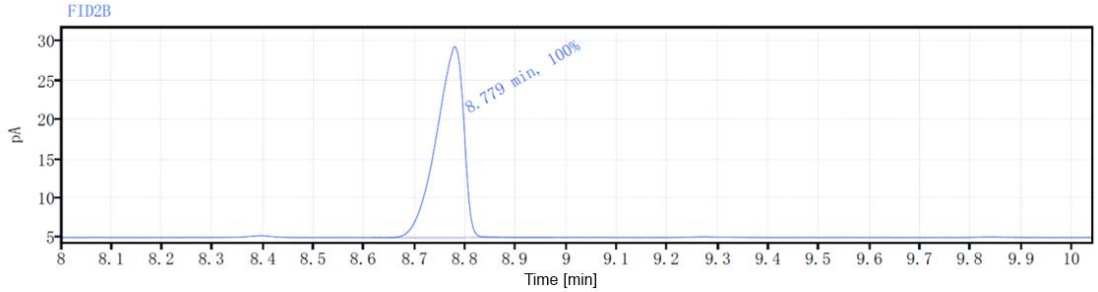
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.486	VB	0.0105	52.76726	84.63114	1.000e2

Supplementary Fig. 14. GC spectra of compound **3l**, Related to Figure 3.



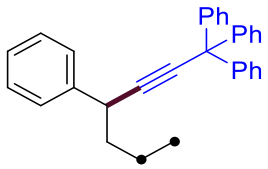
3m



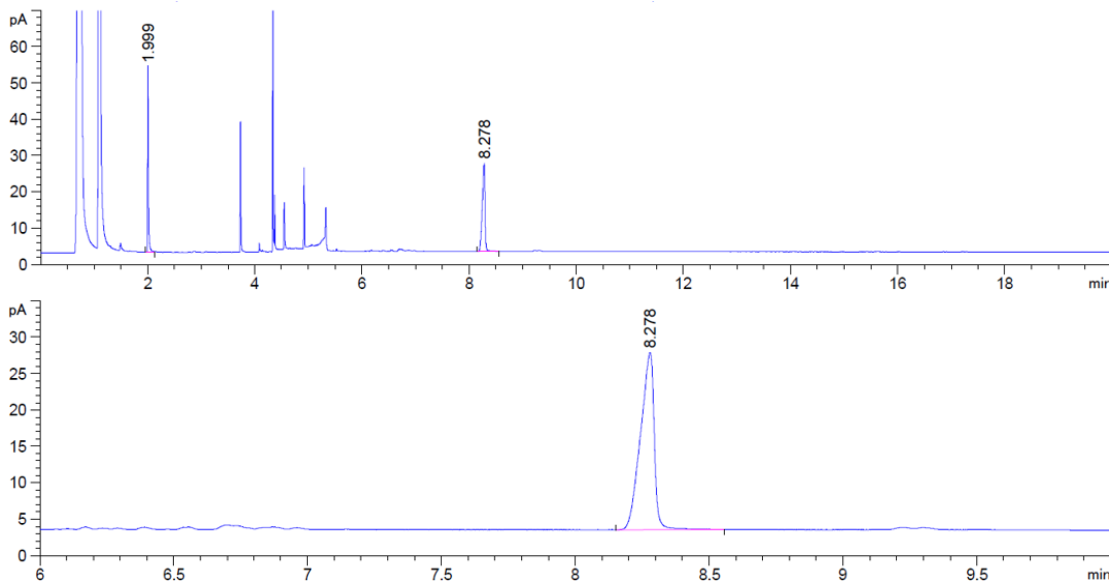


RetTime (min)	Signal	Width (time)	Area	Height	Area%
8.779	FID2B	0.359	91.9	24.4	100.00

Supplementary Fig. 15. GC spectra of compound **3m**, Related to Figure 3.

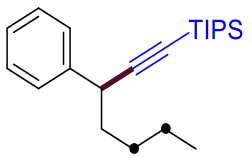


3n

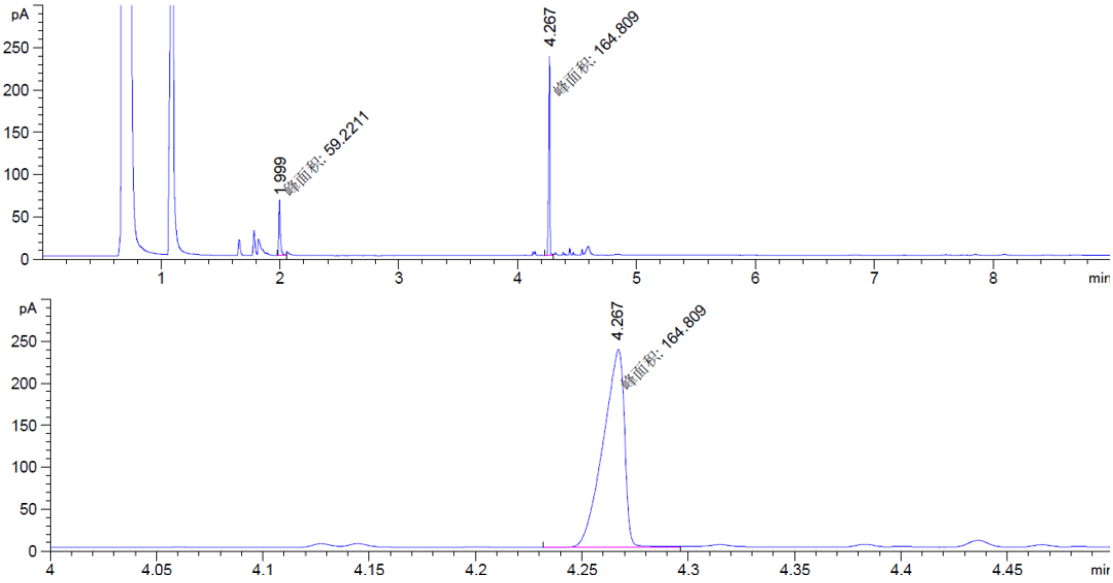


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.278	BB	0.0515	87.30582	24.33629	1.000e2

Supplementary Fig. 16. GC spectra of compound **3n**, Related to Figure 3.

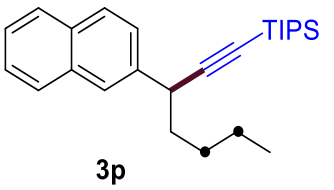


3o

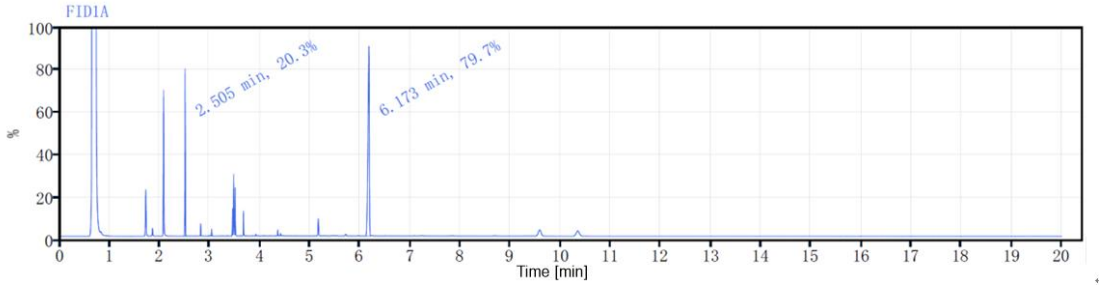


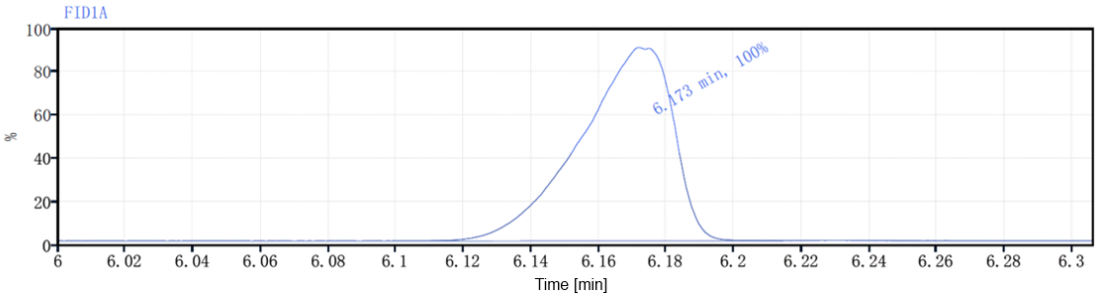
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.267	MF	0.0114	164.80936	241.84032	1.000e2

Supplementary Fig. 17. GC spectra of compound **3o**, Related to Figure 3.



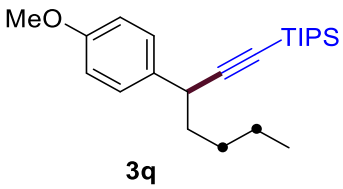
3p



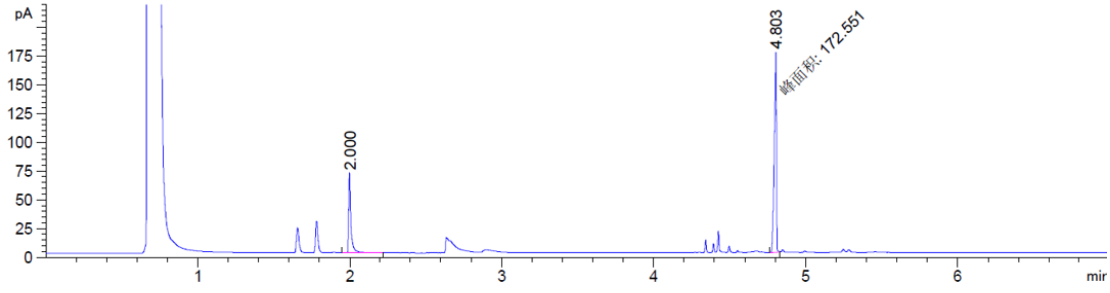


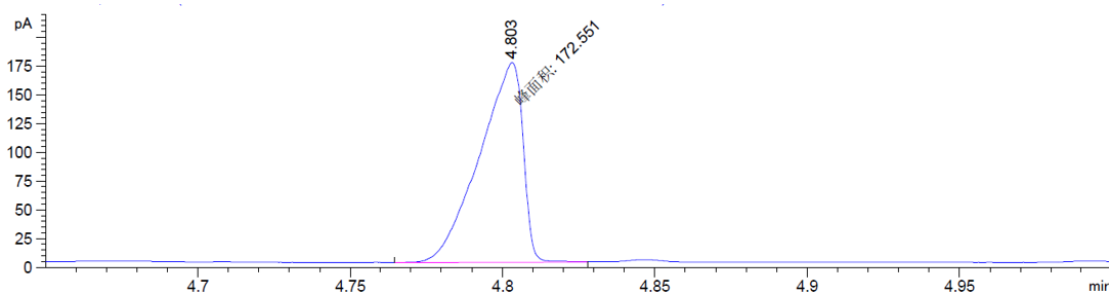
RetTime (min)	Signal	Width (min)	Area	Height	Area%
6.173	FID1A	0.118	116.5	60.7	100.00

Supplementary Fig. 18. GC spectra of compound **3p**, Related to Figure 3.



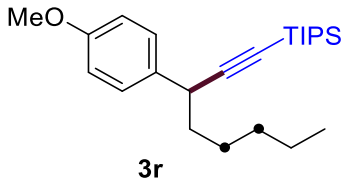
3q



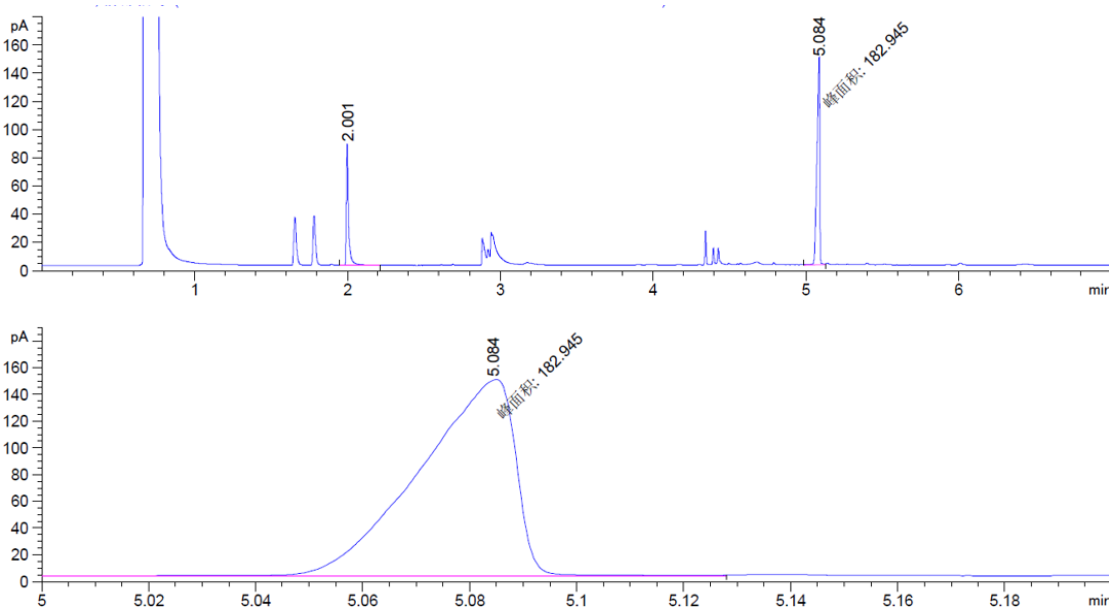


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.803	MF	0.0166	172.55072	173.33826	1.000e2

Supplementary Fig. 19. GC spectra of compound **3q**, Related to Figure 3.

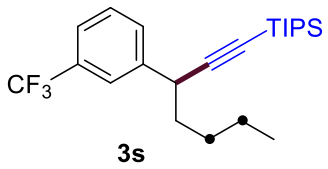


3r

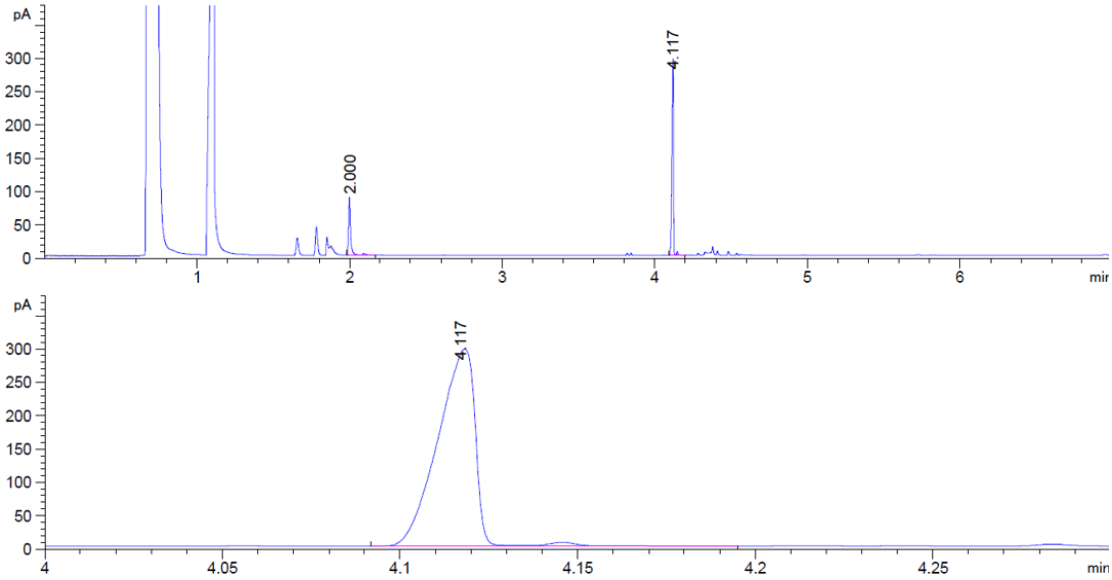


Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.084	MF	0.0209	182.94456	146.10146	1.000e2

Supplementary Fig. 20. GC spectra of compound **3r**, Related to Figure 3.

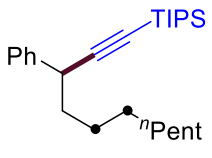


3s

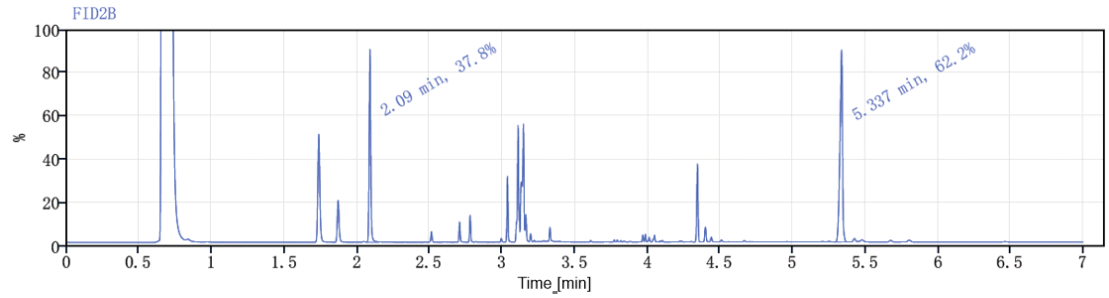


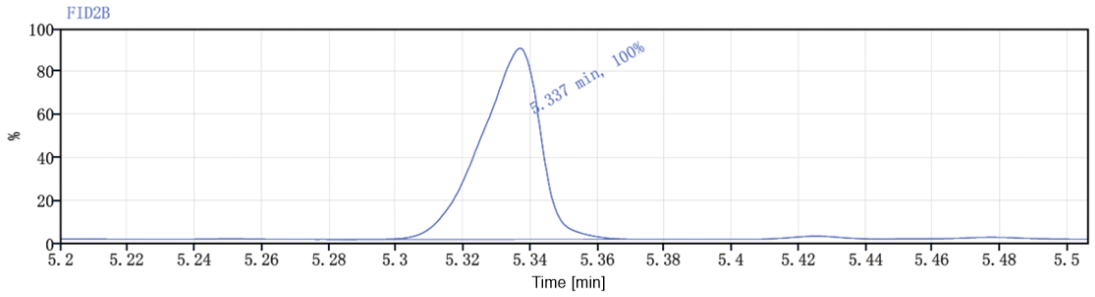
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	4.117	BV R	0.0123	218.62238	273.70059	1.000e2

Supplementary Fig. 21. GC spectra of compound **3s**, Related to Figure 3.



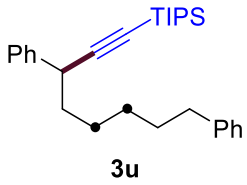
3t



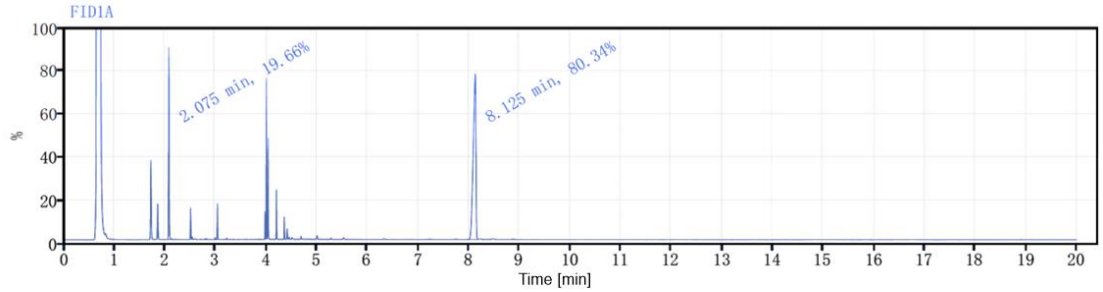


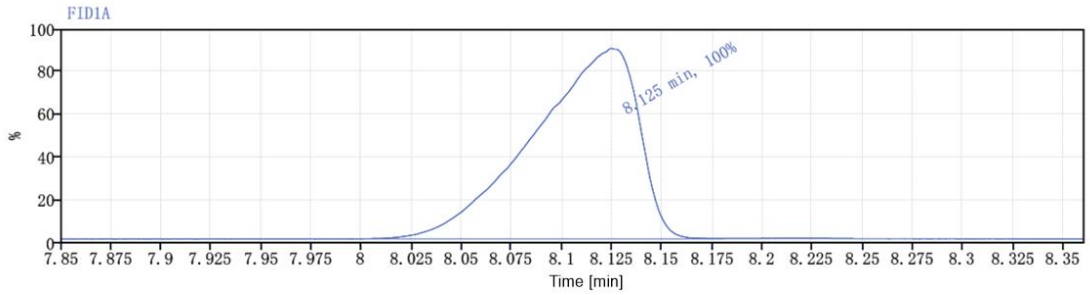
RetTime (min)	Signal	Width (min)	Area	Height	Area%
5.337	FID2B	0.114	118.5	95.6	100.00

Supplementary Fig. 22. GC spectra of compound **3t**, Related to Figure 3.



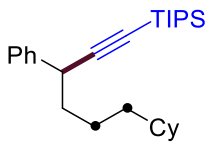
3u



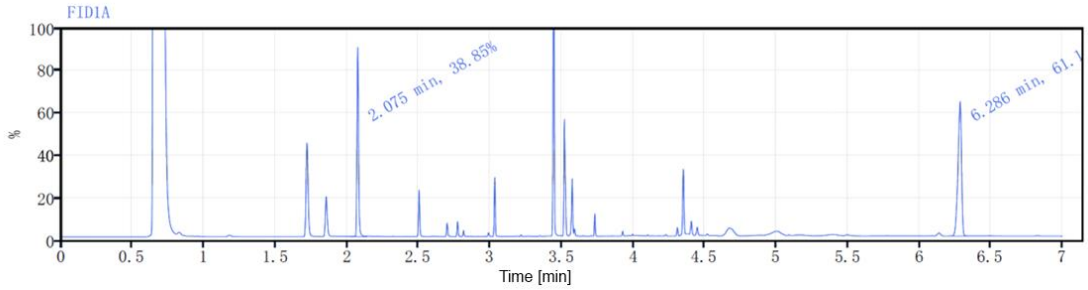


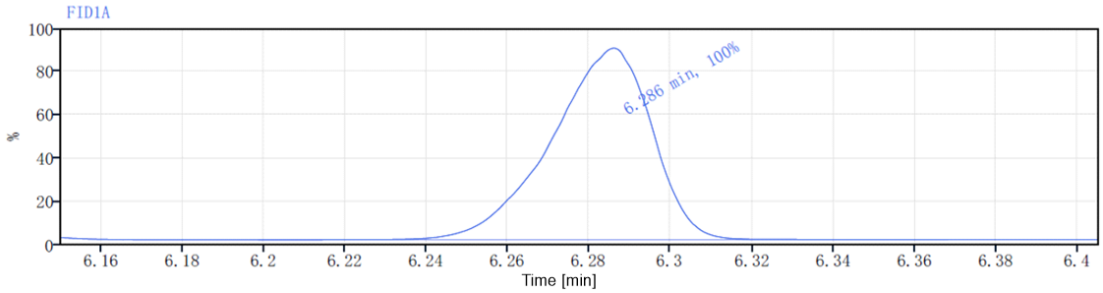
RetTime (min)	Signal	Width (min)	Area	Height	Area%
8.125	FID1A	0.188	147.4	40.2	100.00

Supplementary Fig. 23. GC spectra of compound **3u**, Related to Figure 3.



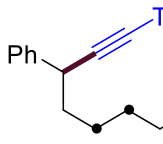
3v



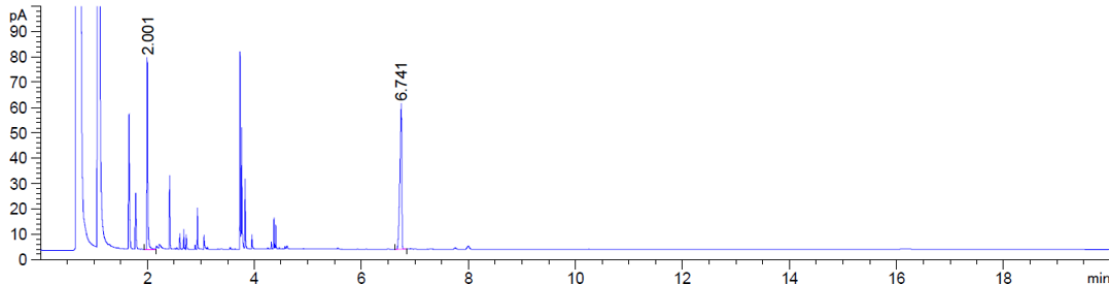


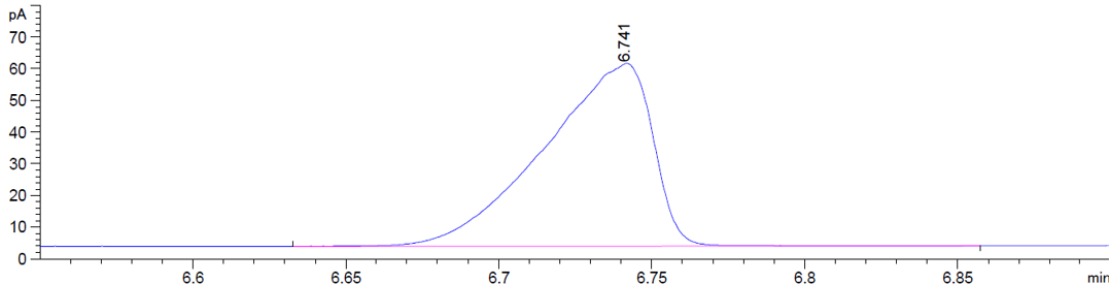
RetTime (min)	Signal	Width (min)	Area	Height	Area%
6.286	FID1A	0.170	62.0	35.9	100.00

Supplementary Fig. 24. GC spectra of compound **3v**, Related to Figure 3.



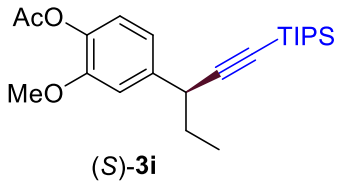
3w



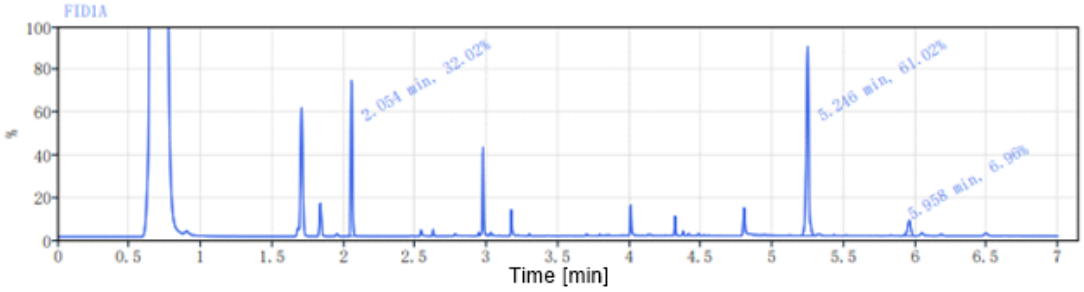


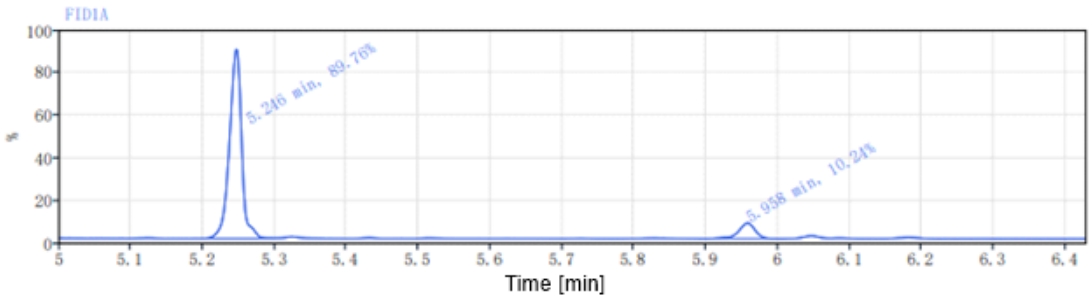
Peak #	Time [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.741	BB	0.0356	142.18549	56.85785	1.000e2

Supplementary Fig. 25. GC spectra of compound **3w**, Related to Figure 3.



(*S*)-**3i**

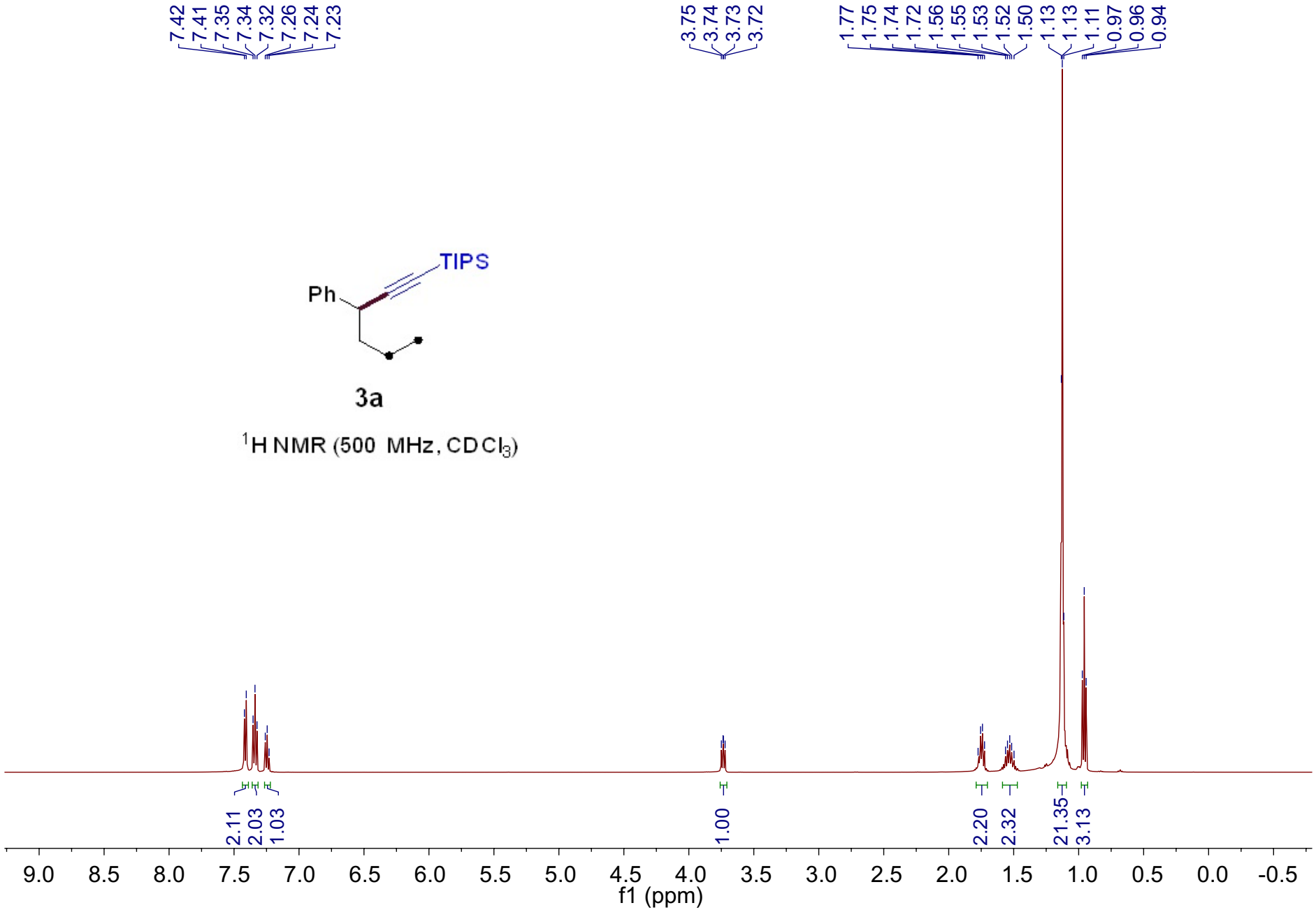




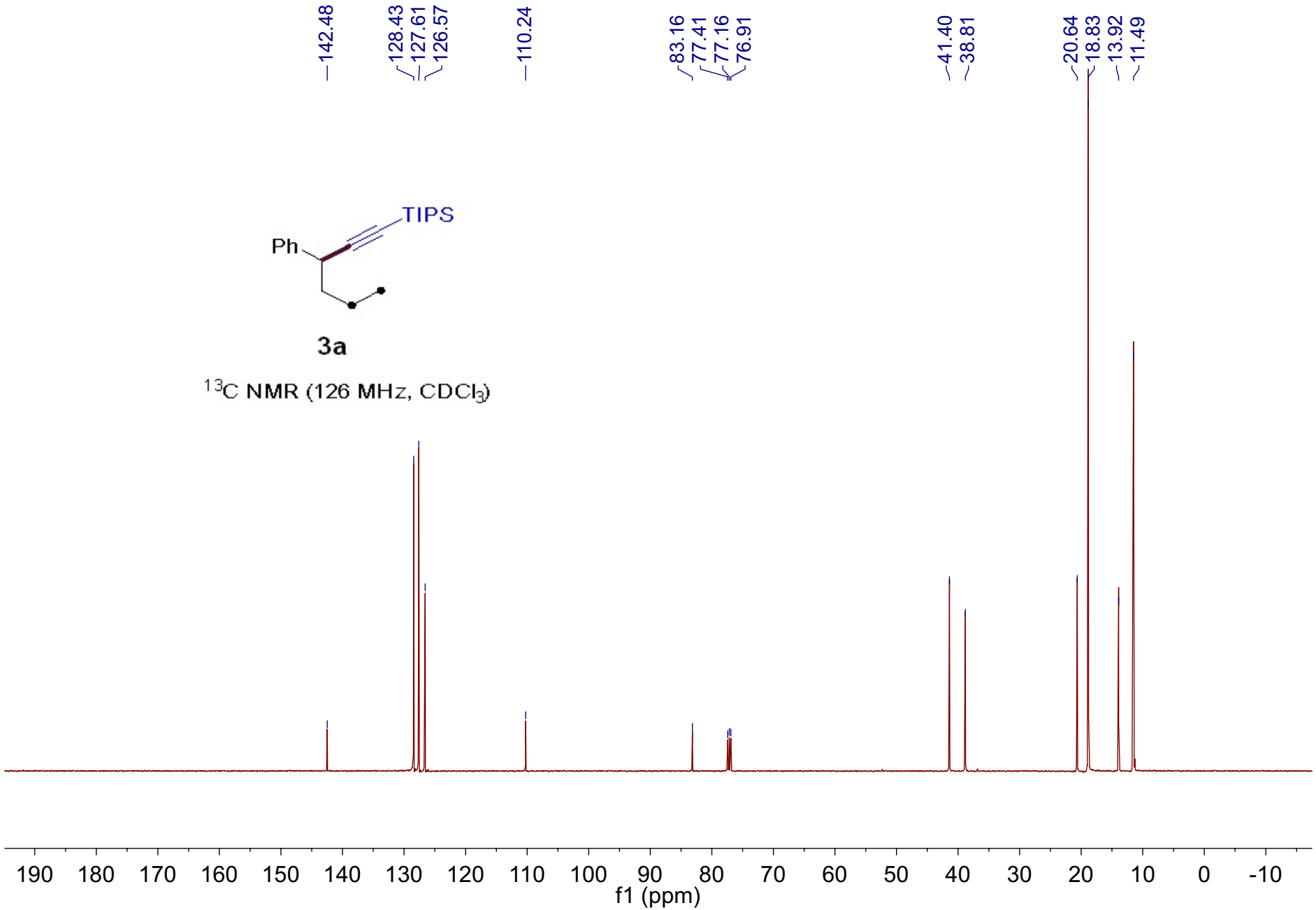
RetTime	Signal	Width (min)	Area	Height	Area%
5.246	FID1A	0.116	37.6	31.7	89.76
5.958	FID1A	0.120	4.3	2.6	10.24

Supplementary Fig. 26. GC spectra of compound (*S*)-**3i**, Related to Figure 5a.

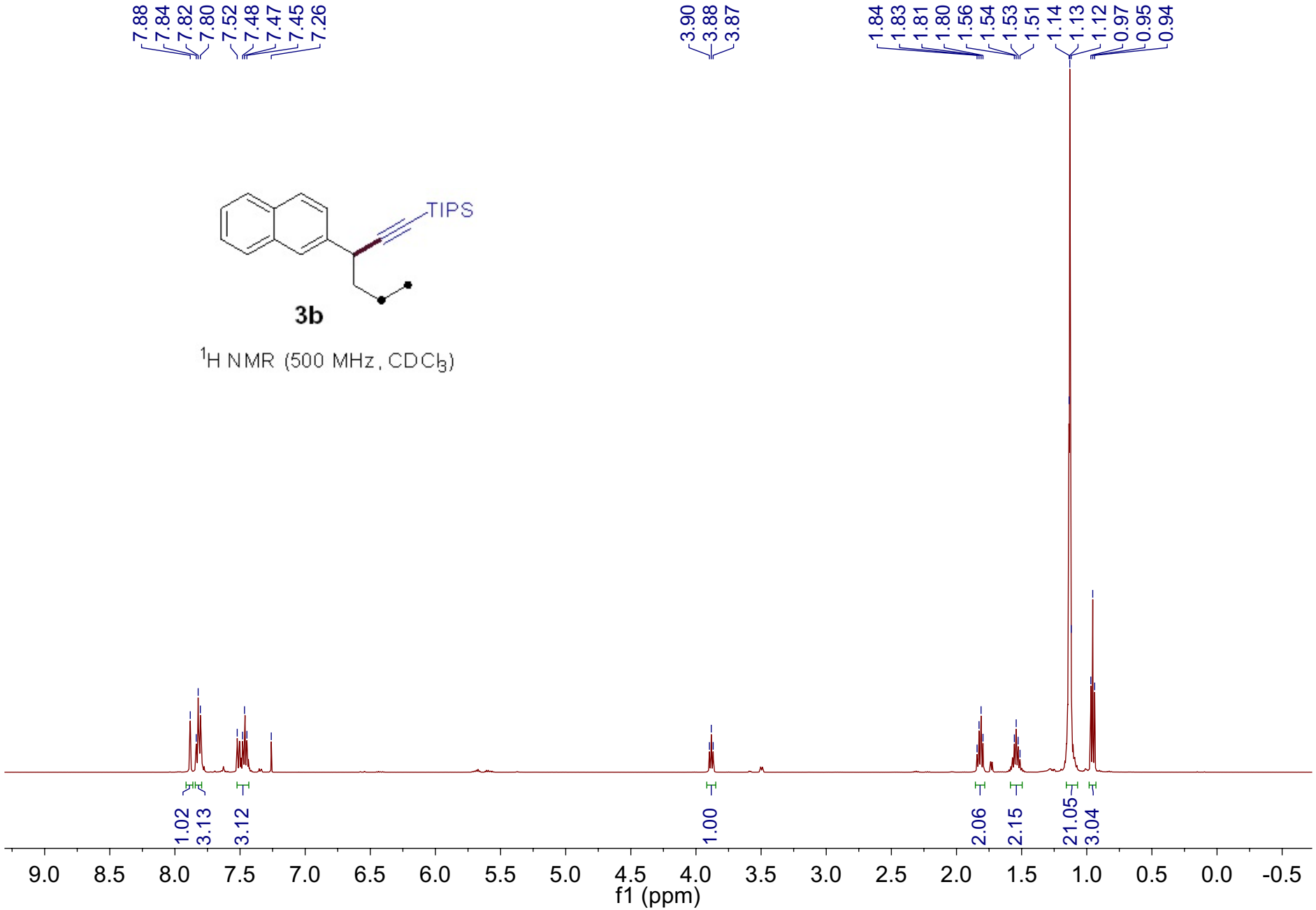
Spectroscopic Data (NMR Spectrum)



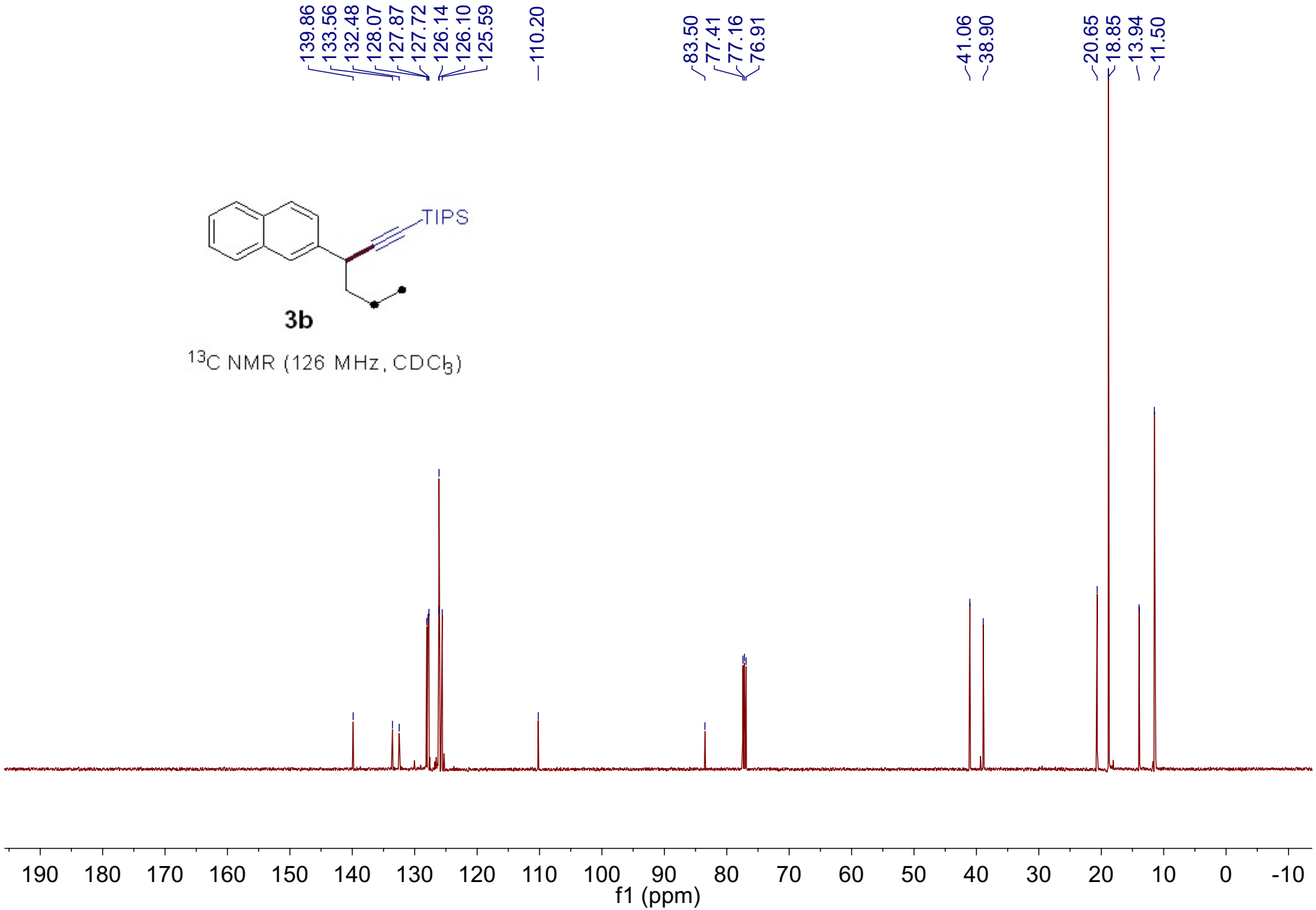
Supplementary Fig. 27. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3a**



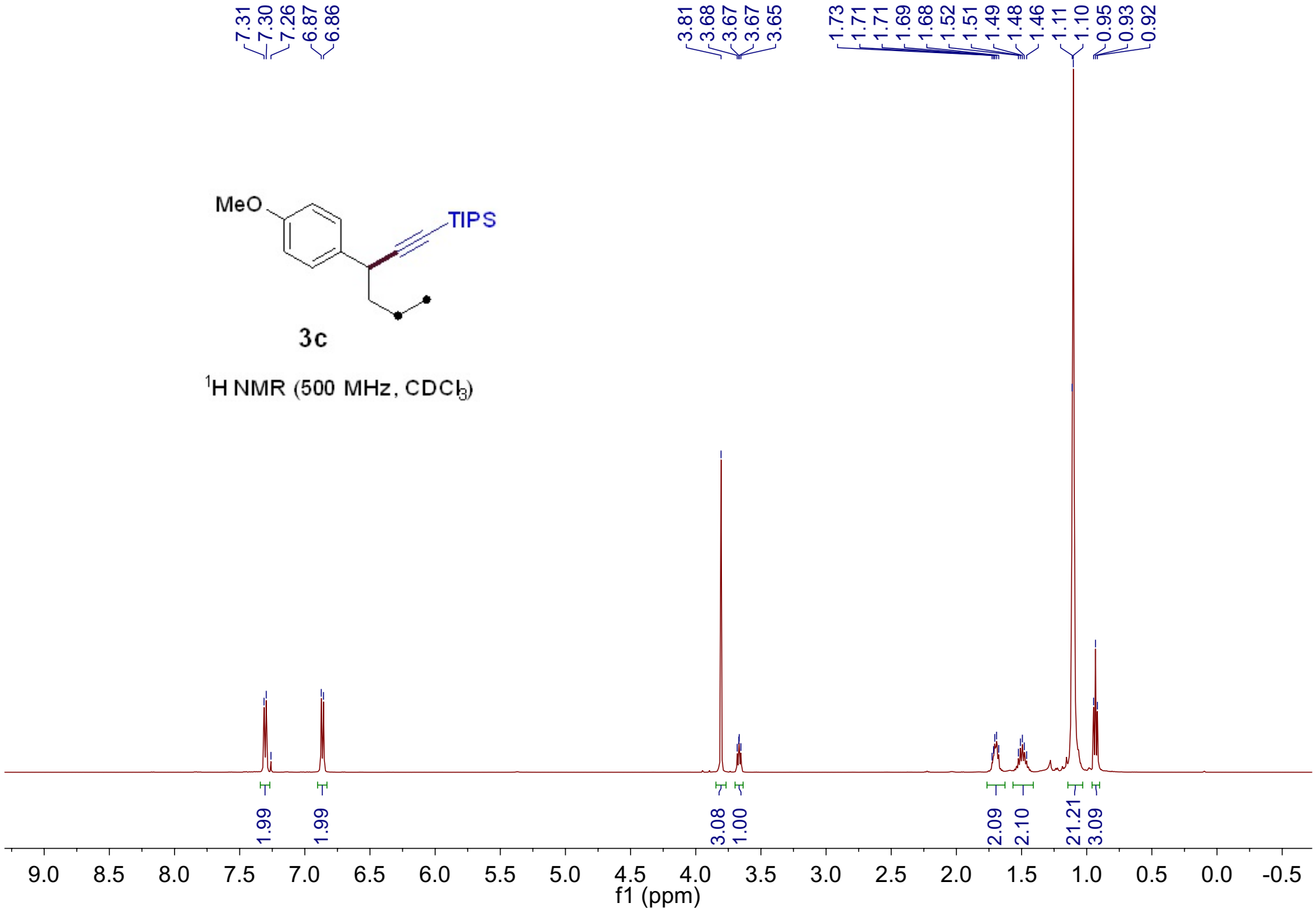
Supplementary Fig. 28. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3a**



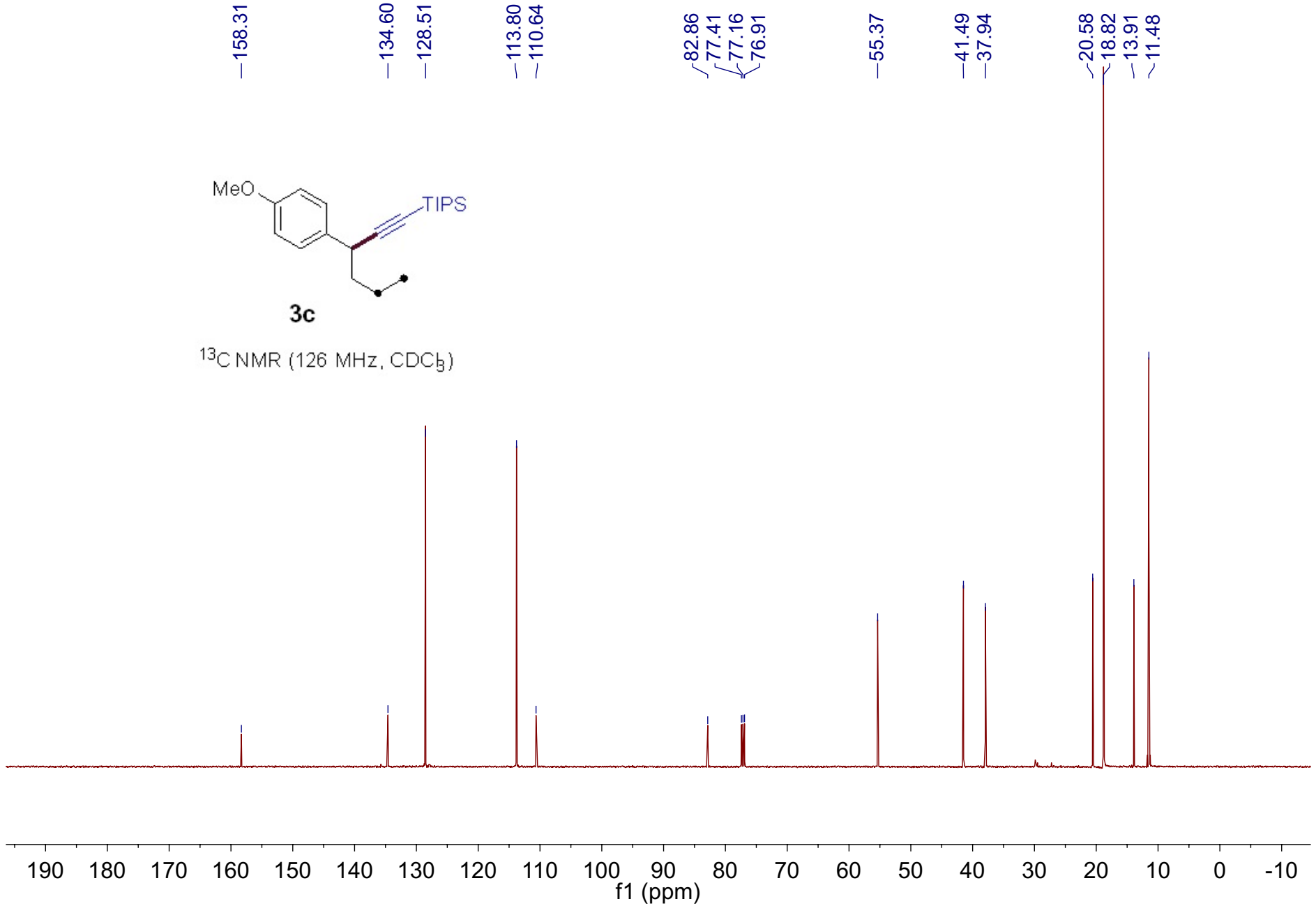
Supplementary Fig. 29. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3b**



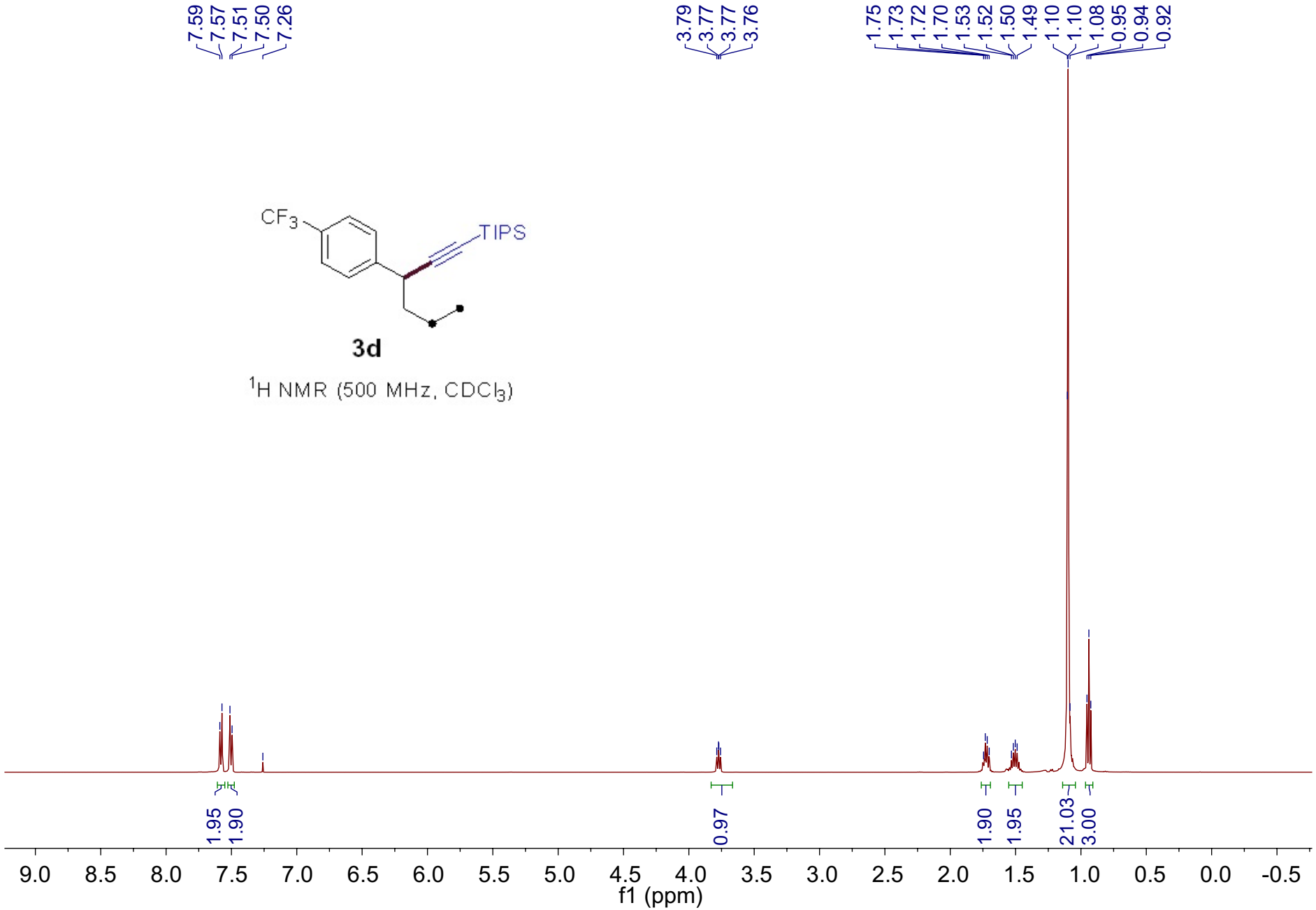
Supplementary Fig. 30. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3b**



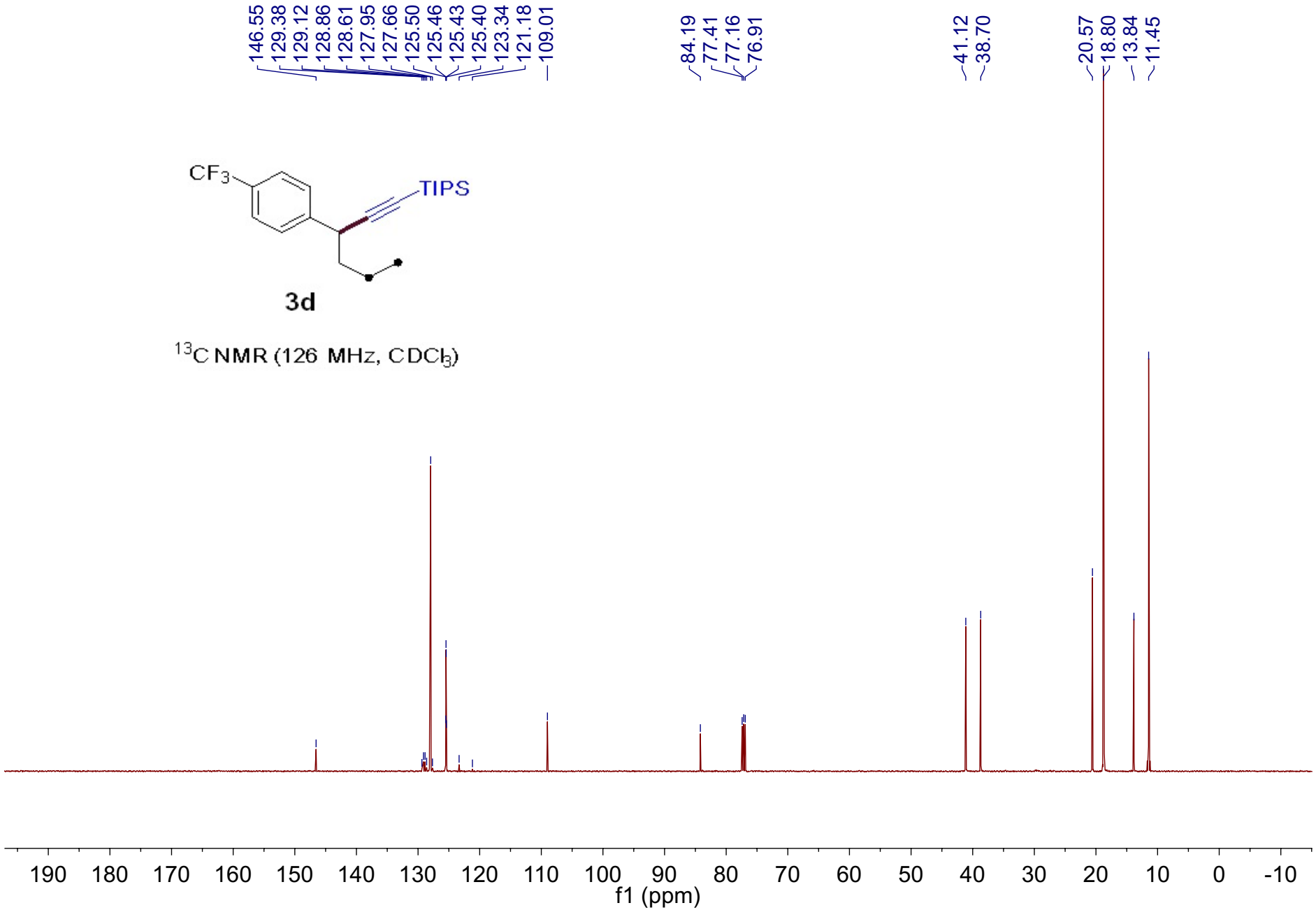
Supplementary Fig. 31. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3c**



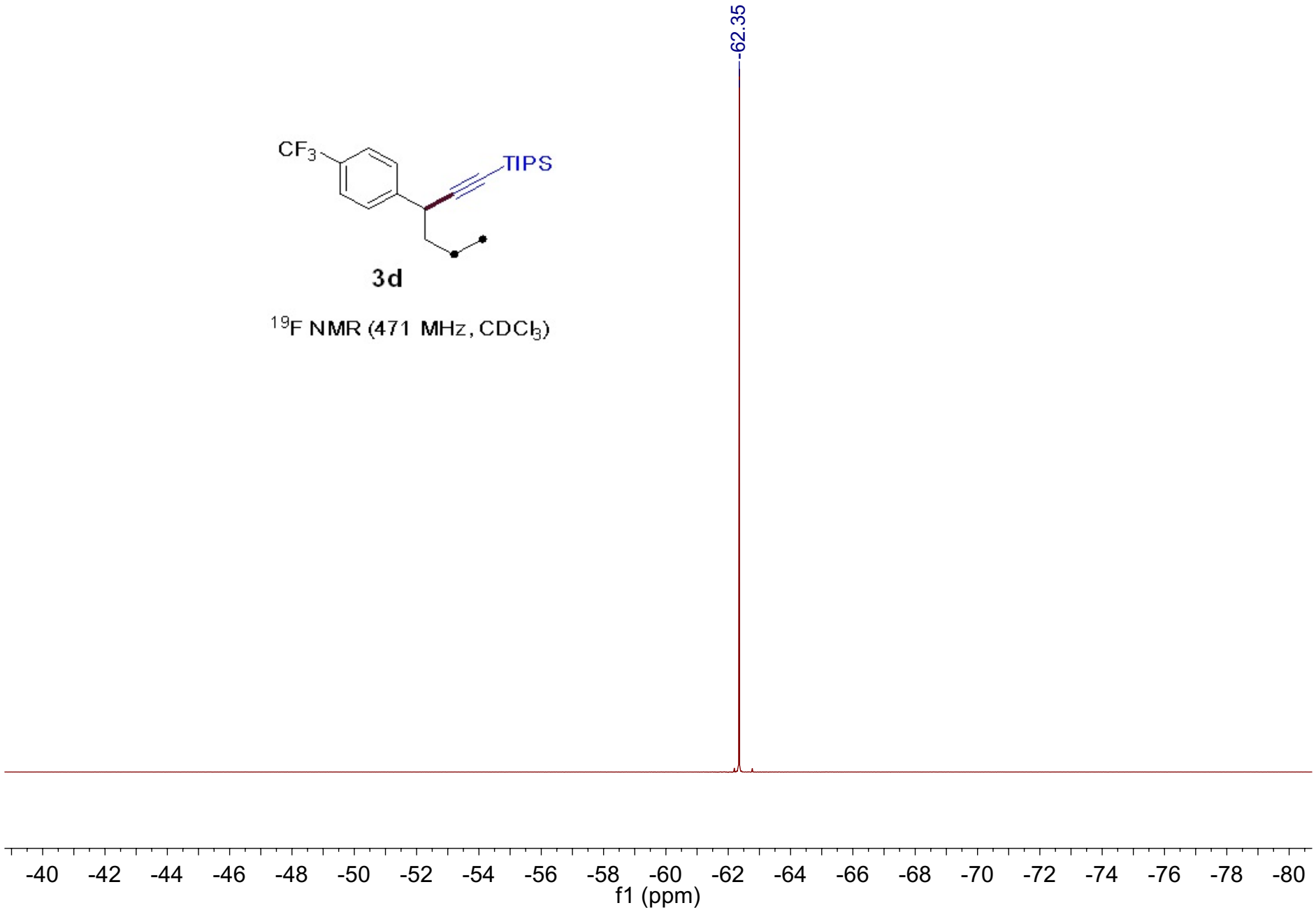
Supplementary Fig. 32. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3c**



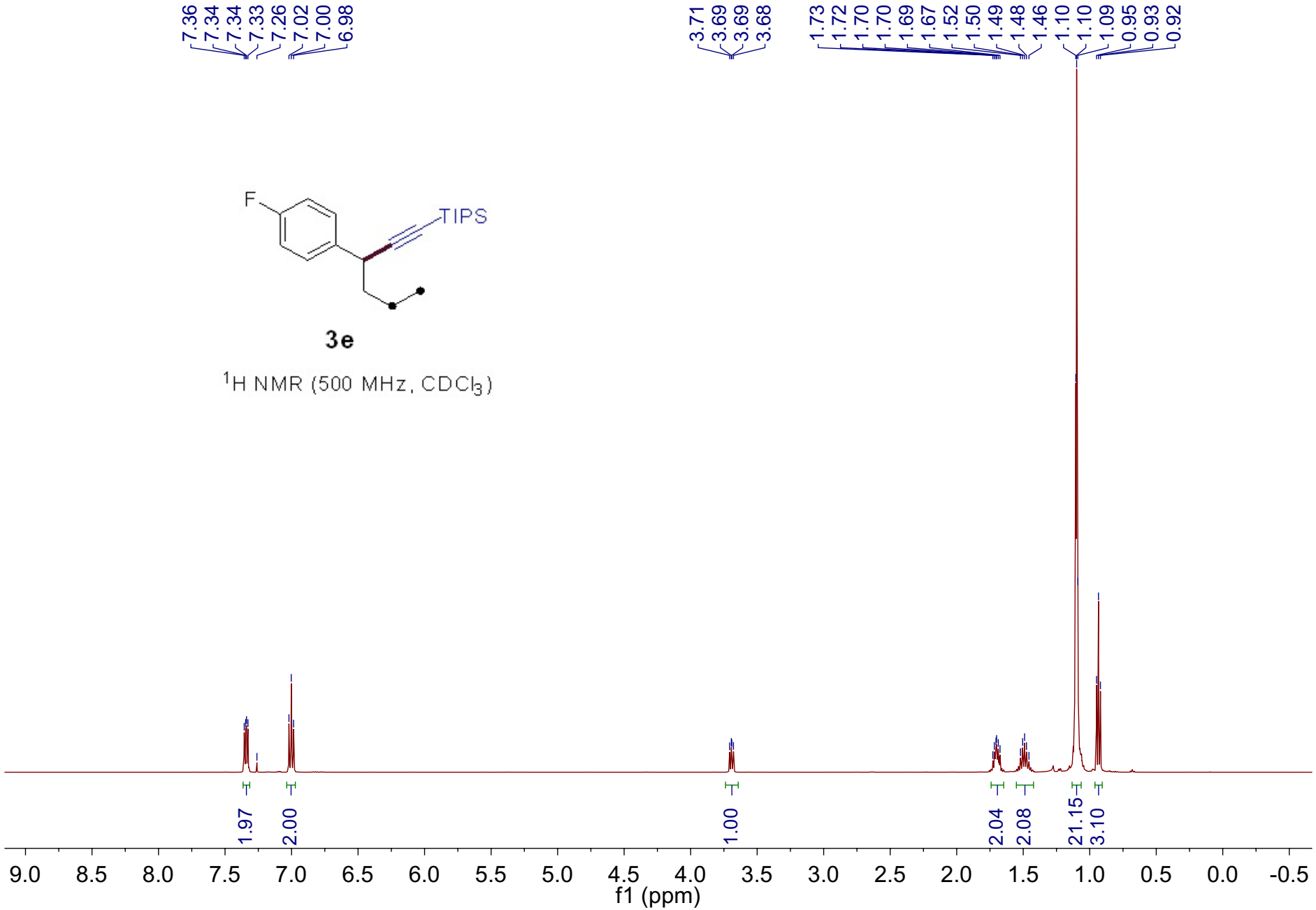
Supplementary Fig. 33. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3d**



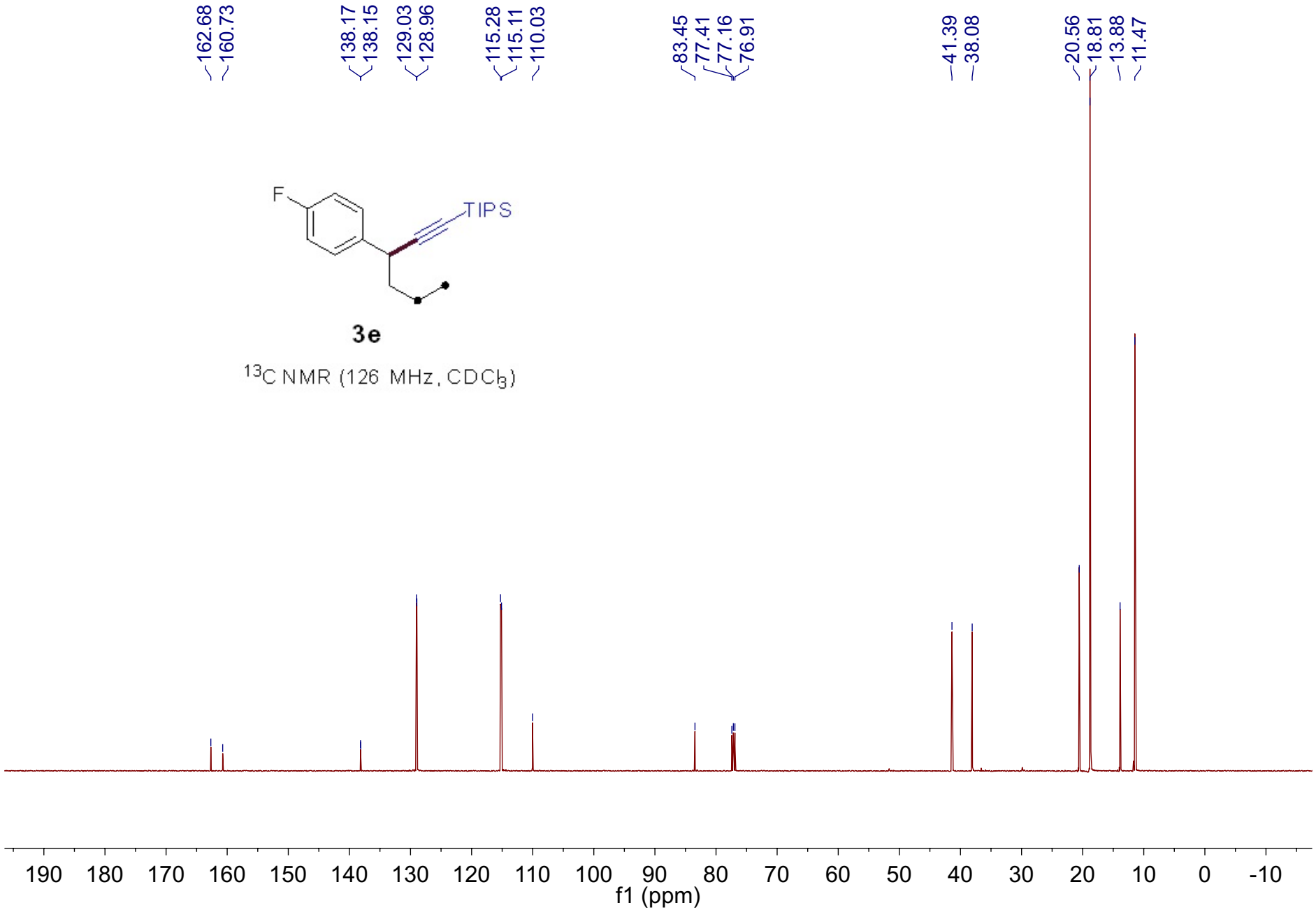
Supplementary Fig. 34. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3d**



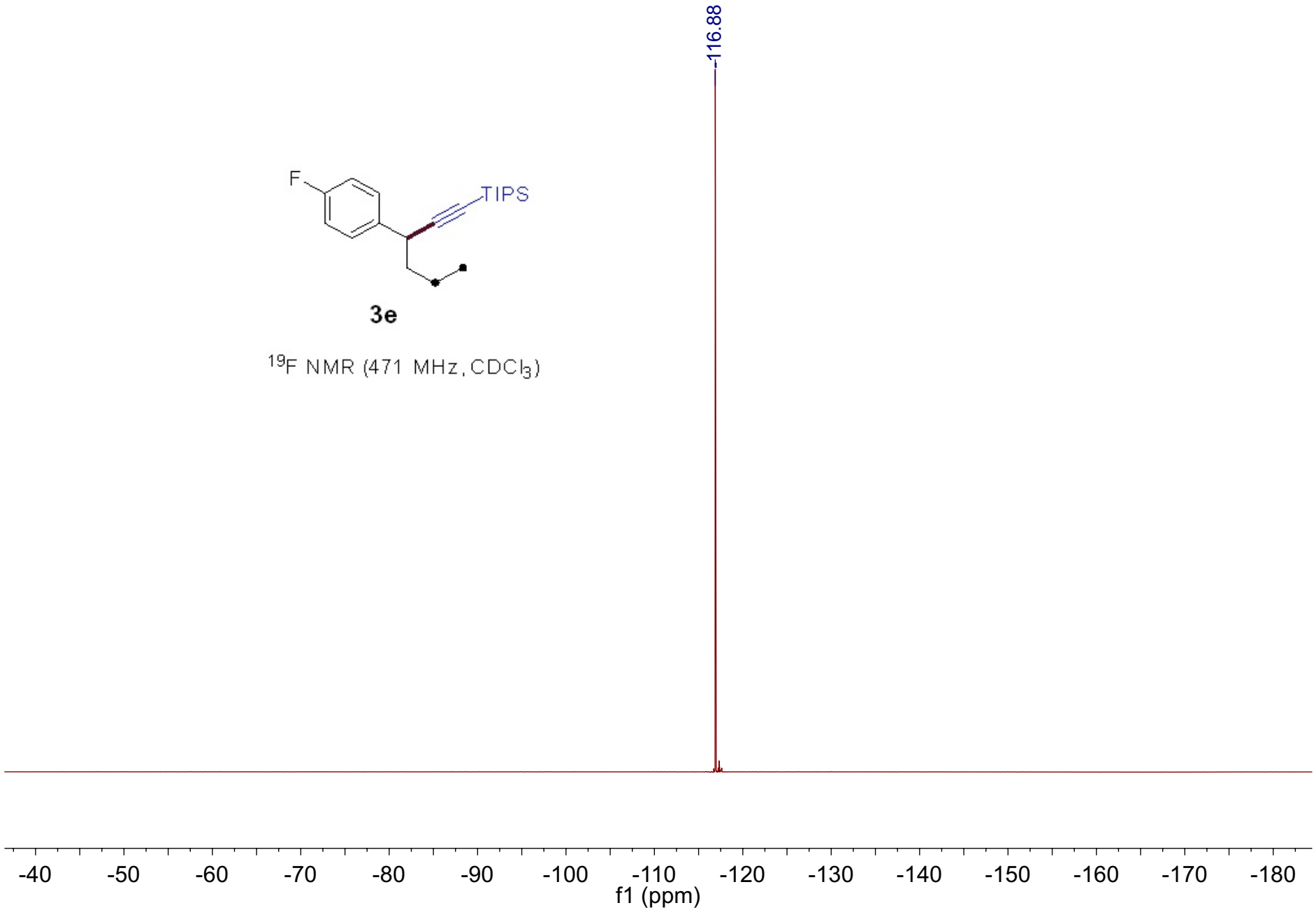
Supplementary Fig. 35. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **3d**



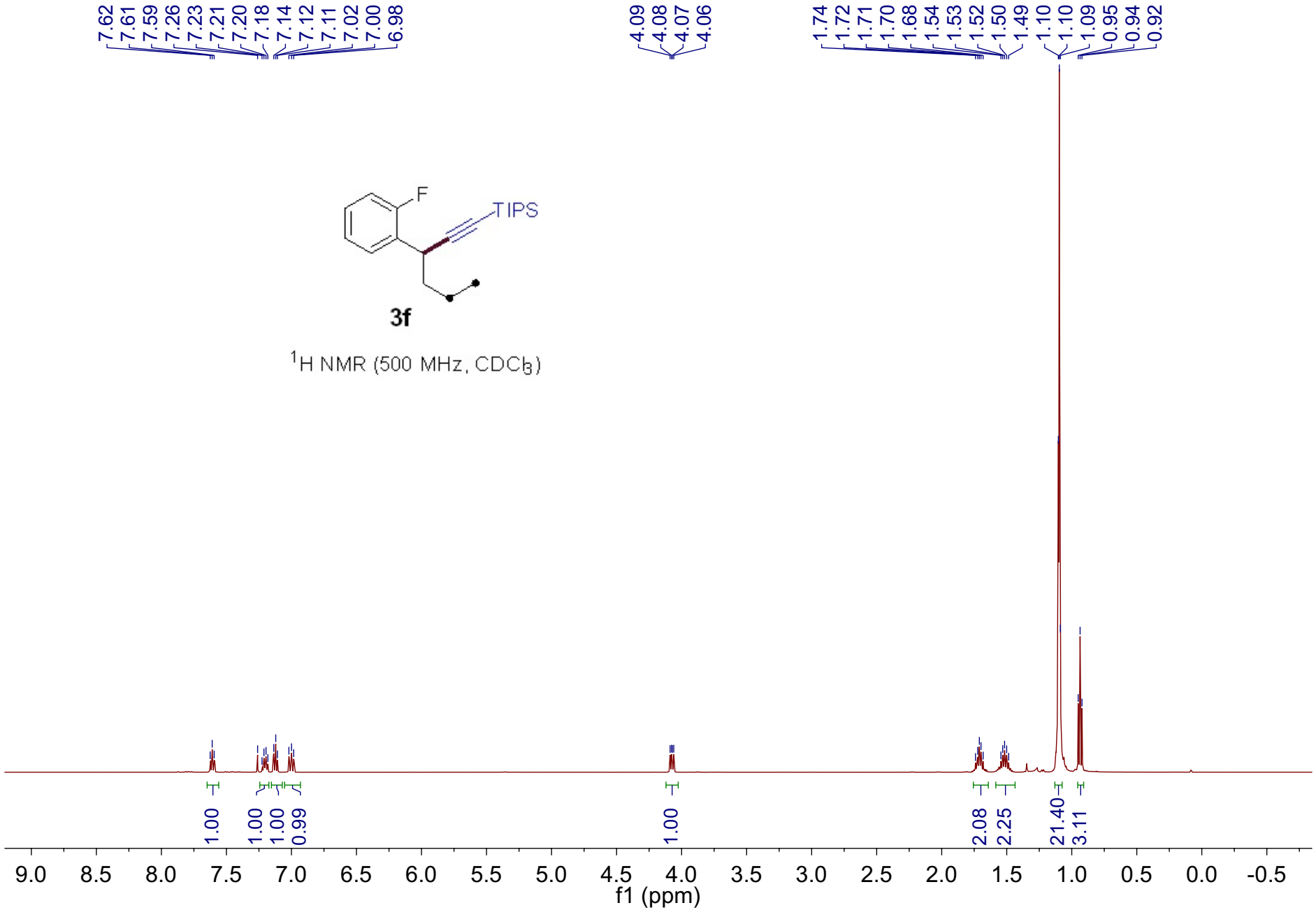
Supplementary Fig. 36. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3e**



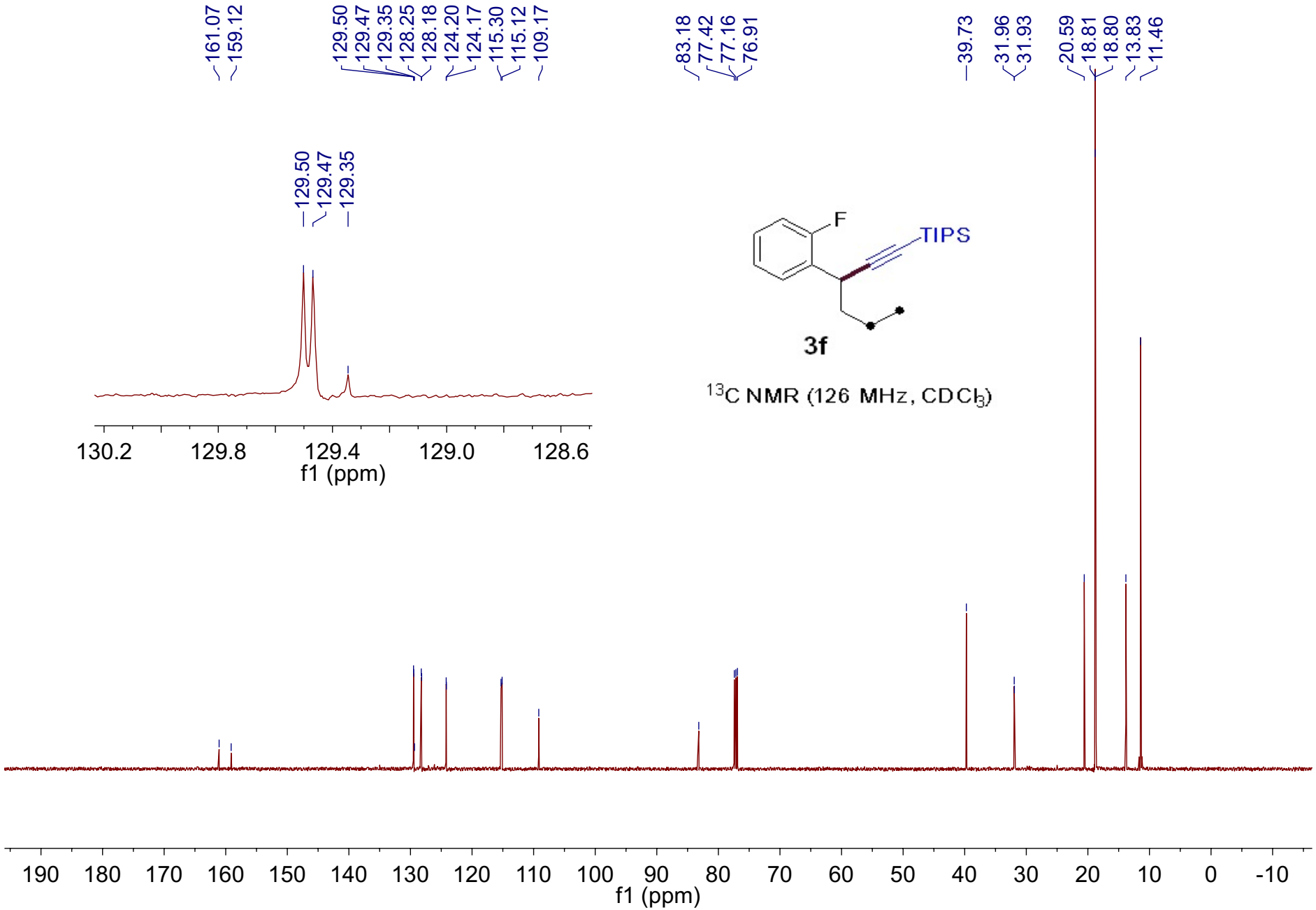
Supplementary Fig. 37. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3e**



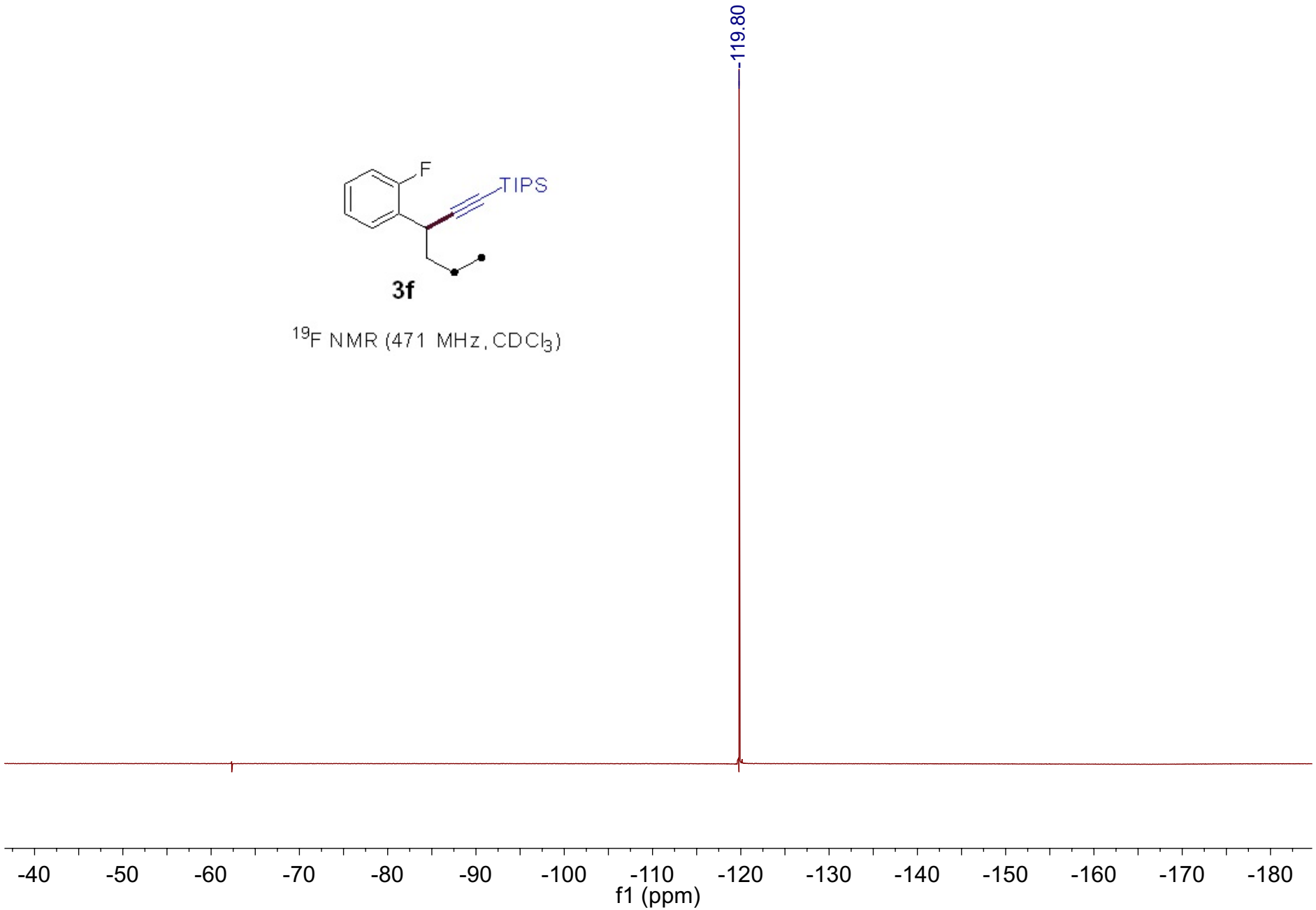
Supplementary Fig. 38. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **3e**



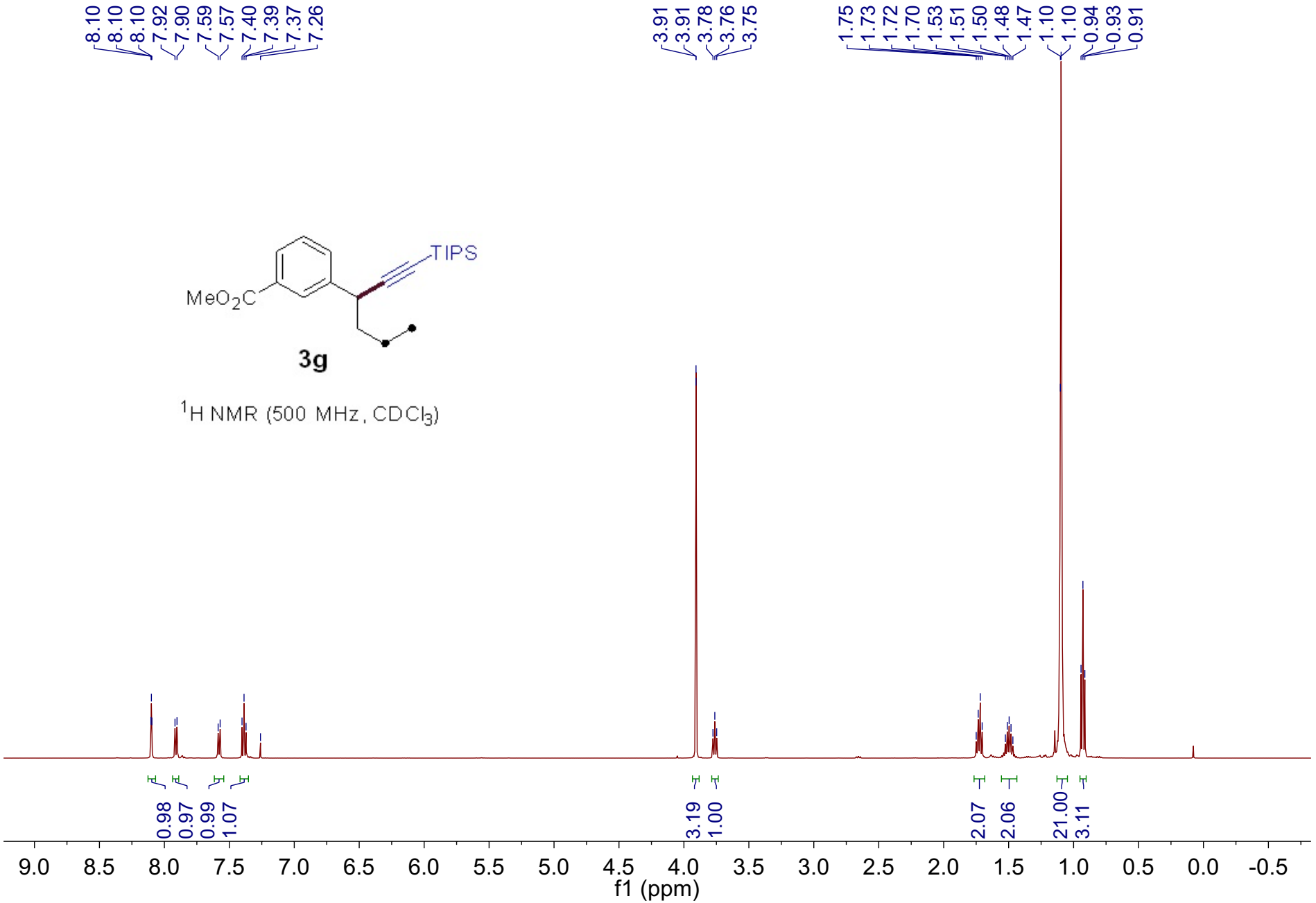
Supplementary Fig. 39. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3f**



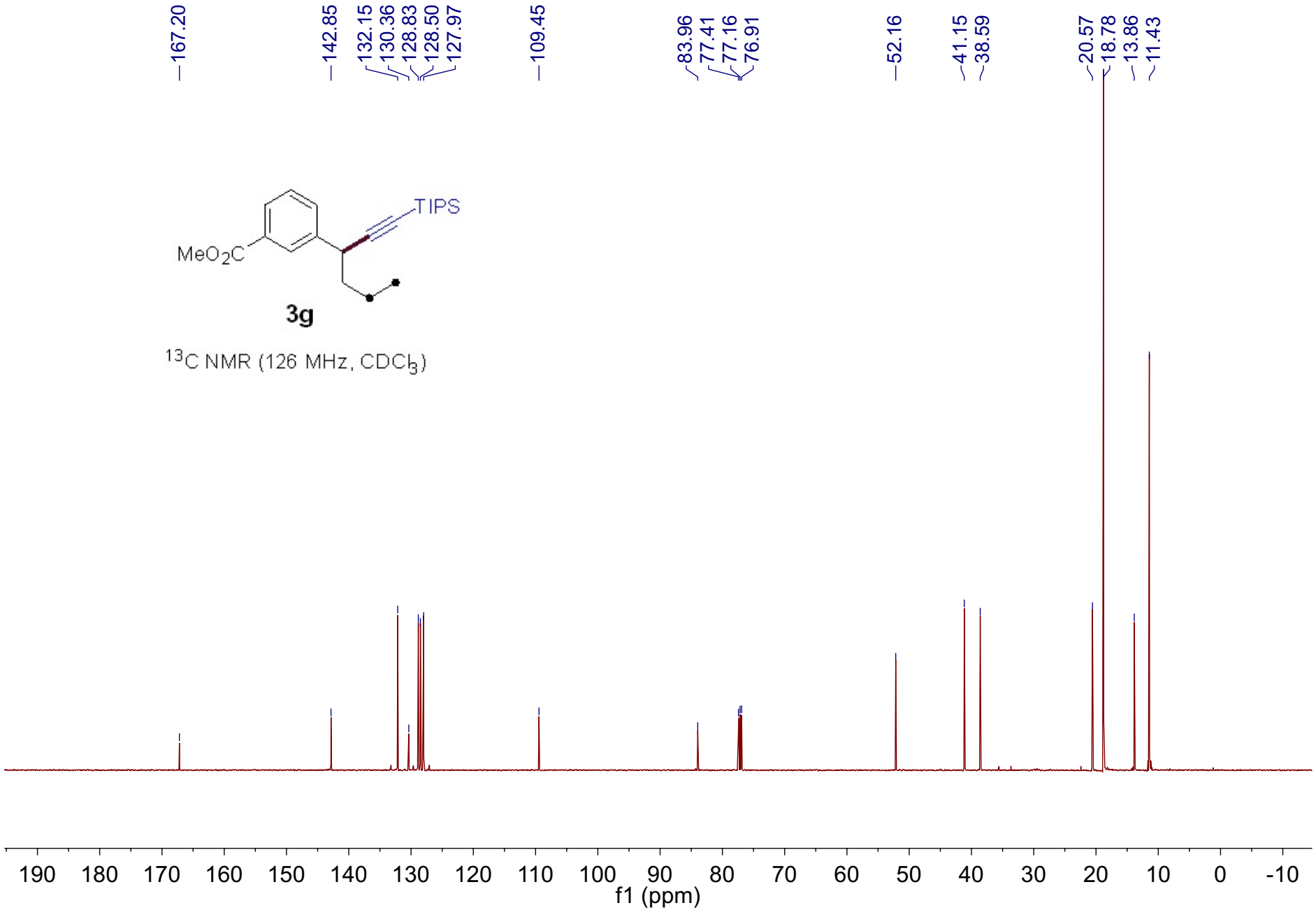
Supplementary Fig. 40. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3f**



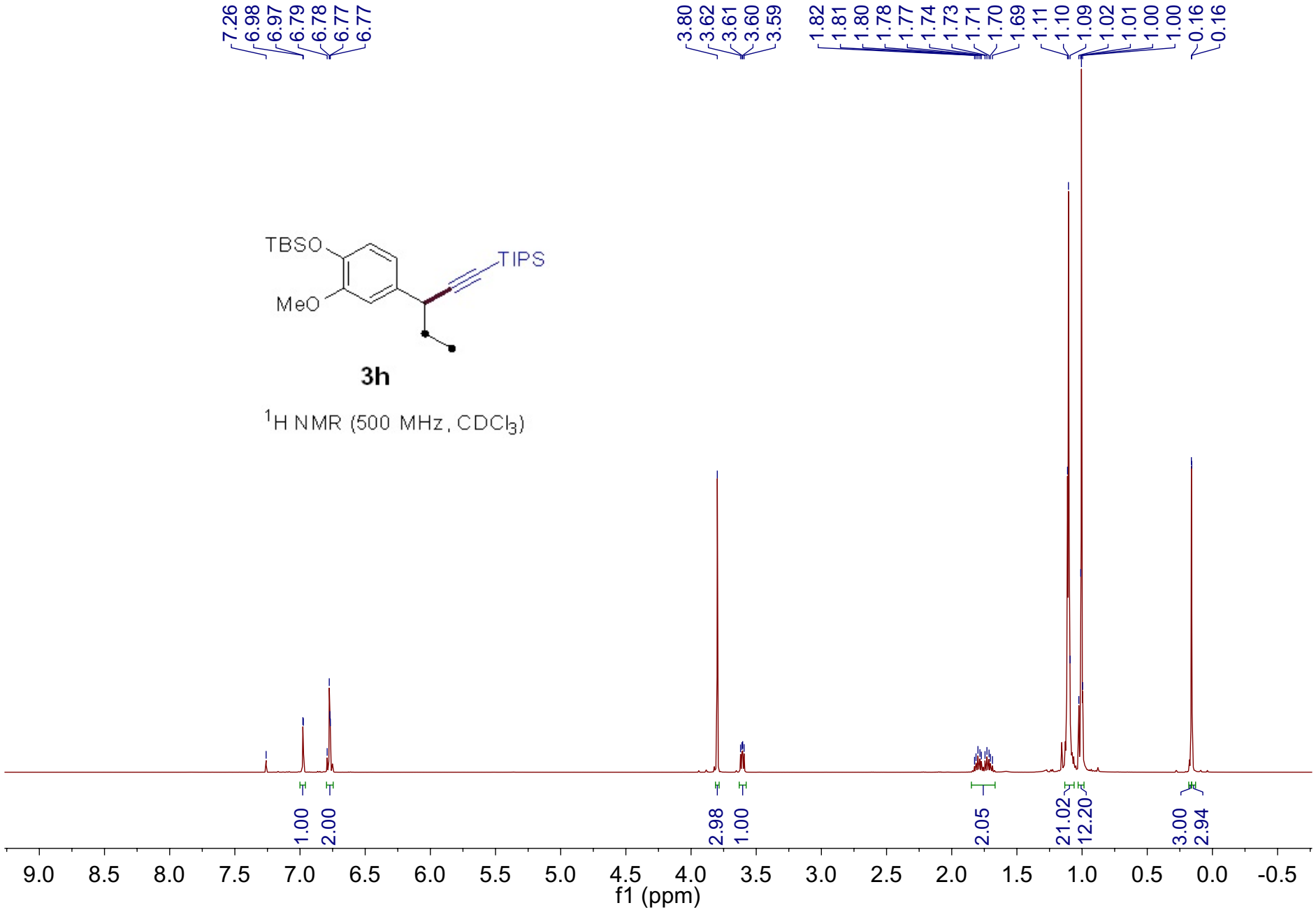
Supplementary Fig. 41. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **3f**



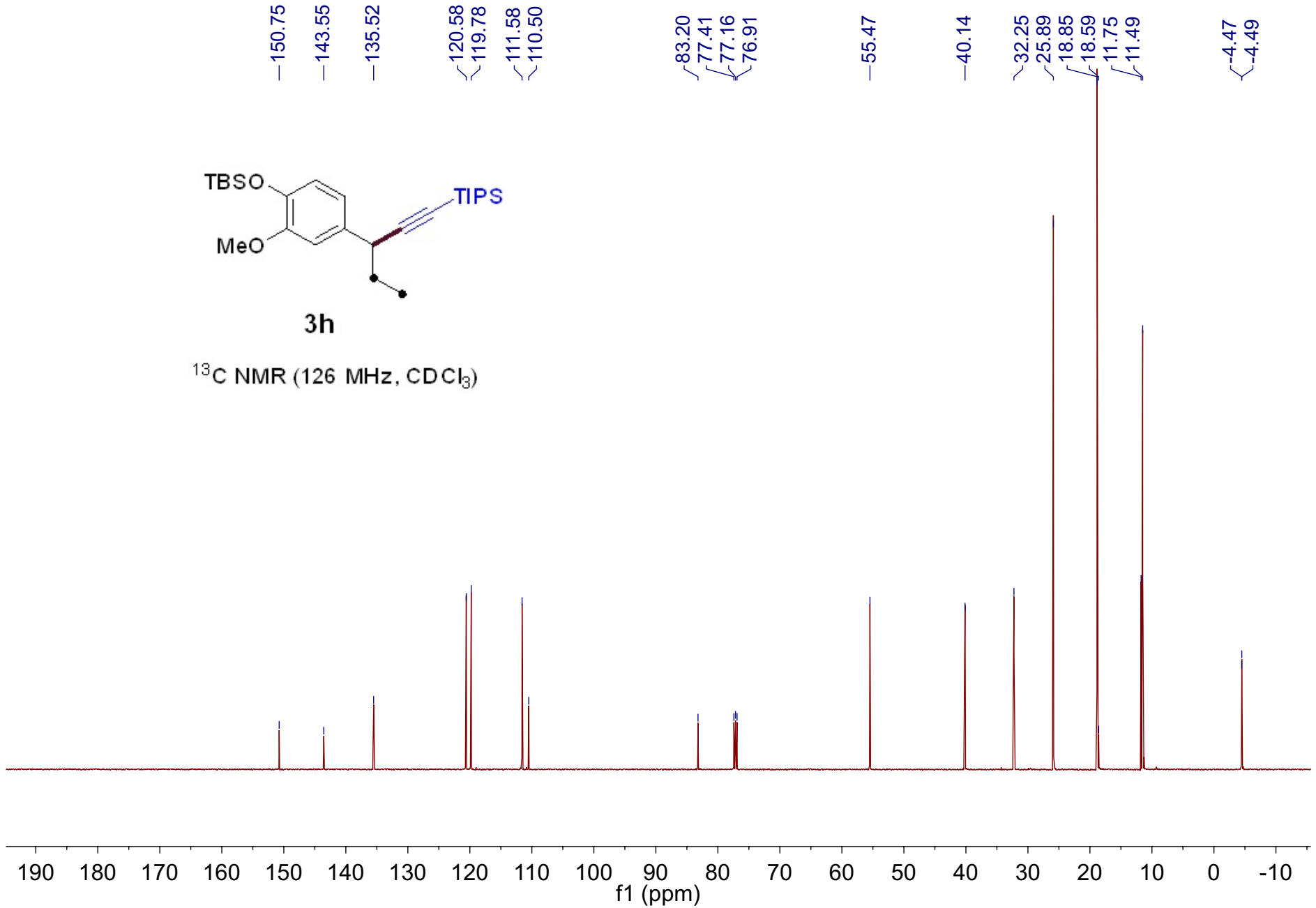
Supplementary Fig. 42. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3g**



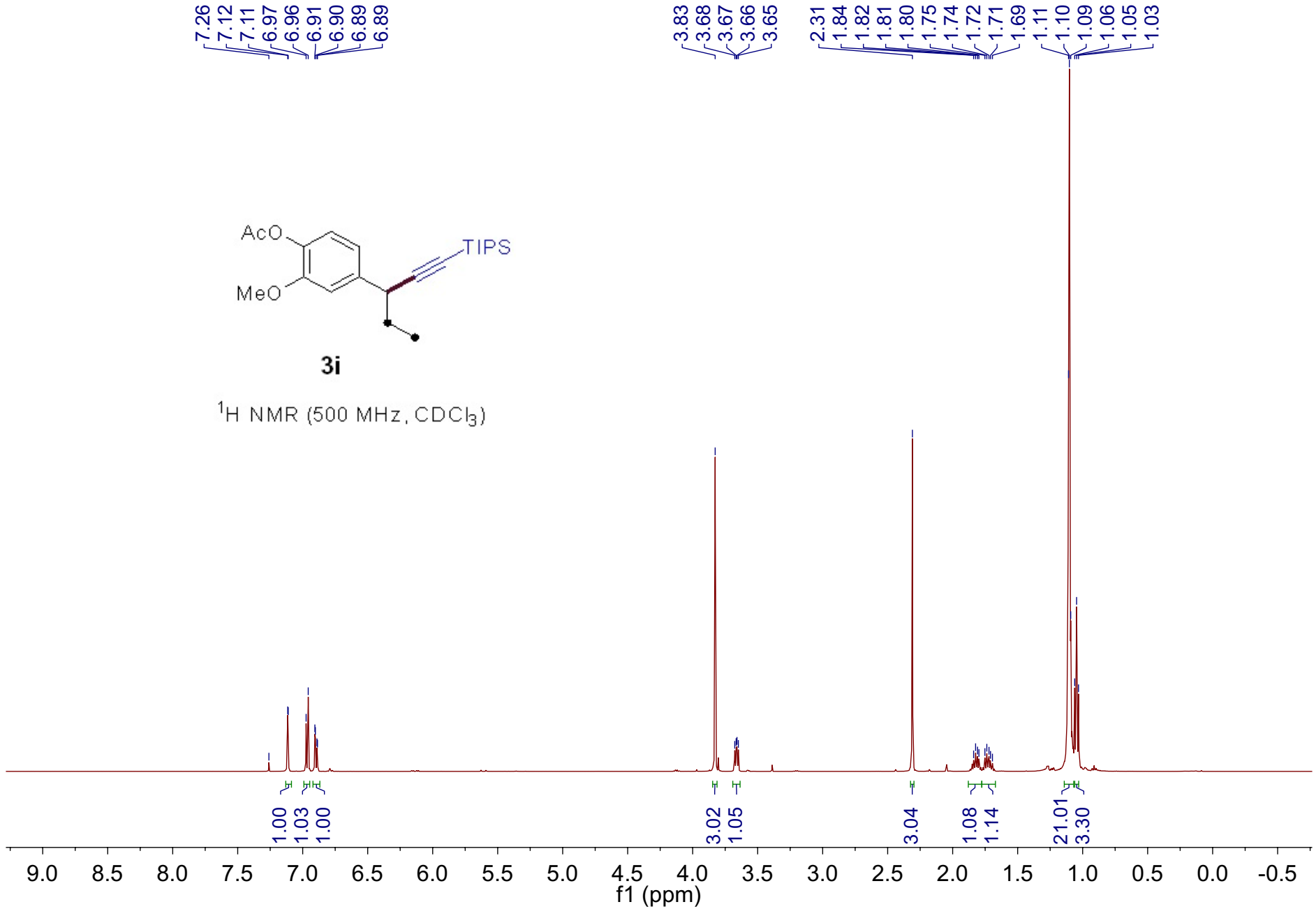
Supplementary Fig. 43. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3g**



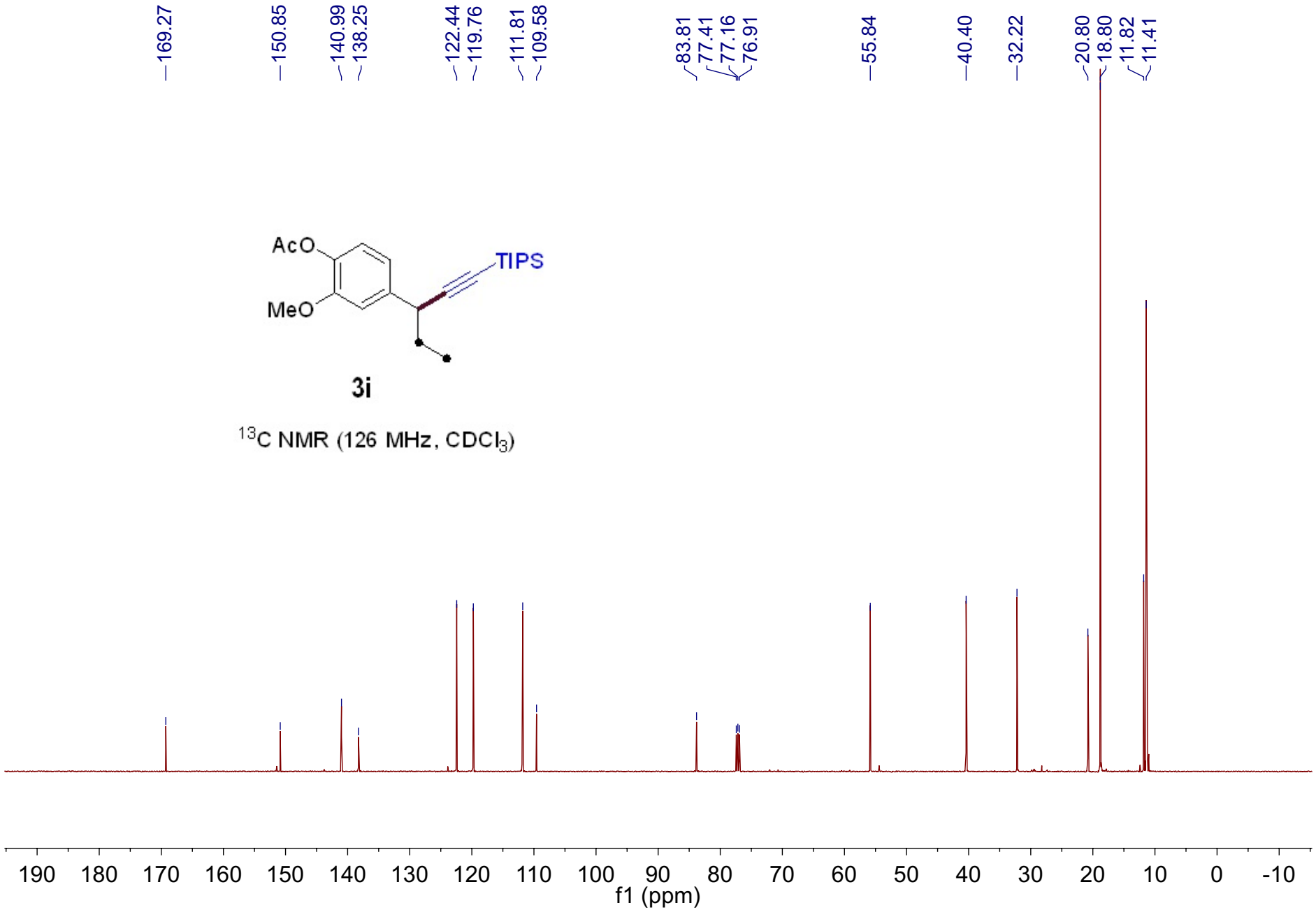
Supplementary Fig. 44. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3h**



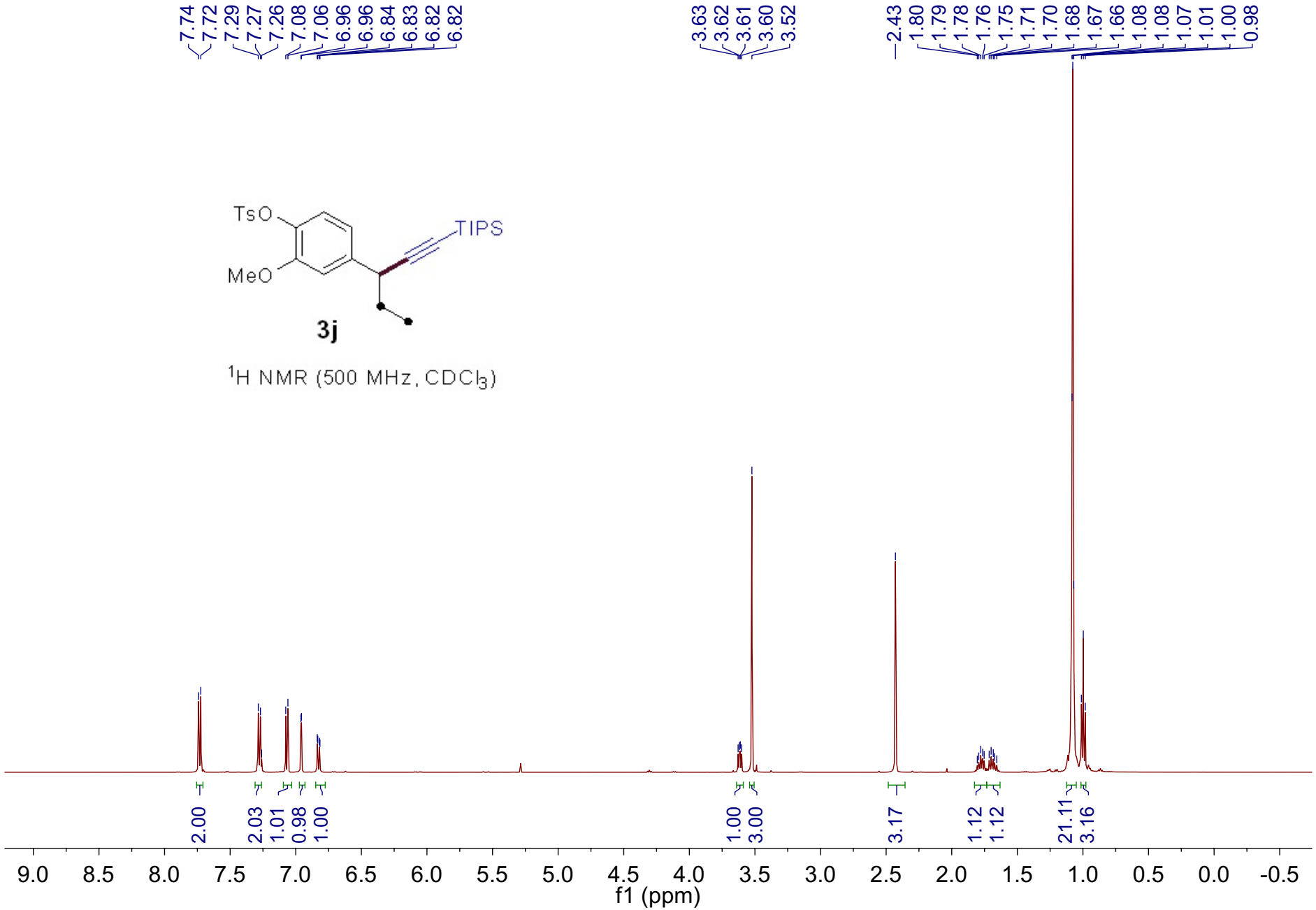
Supplementary Fig. 45. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3h**



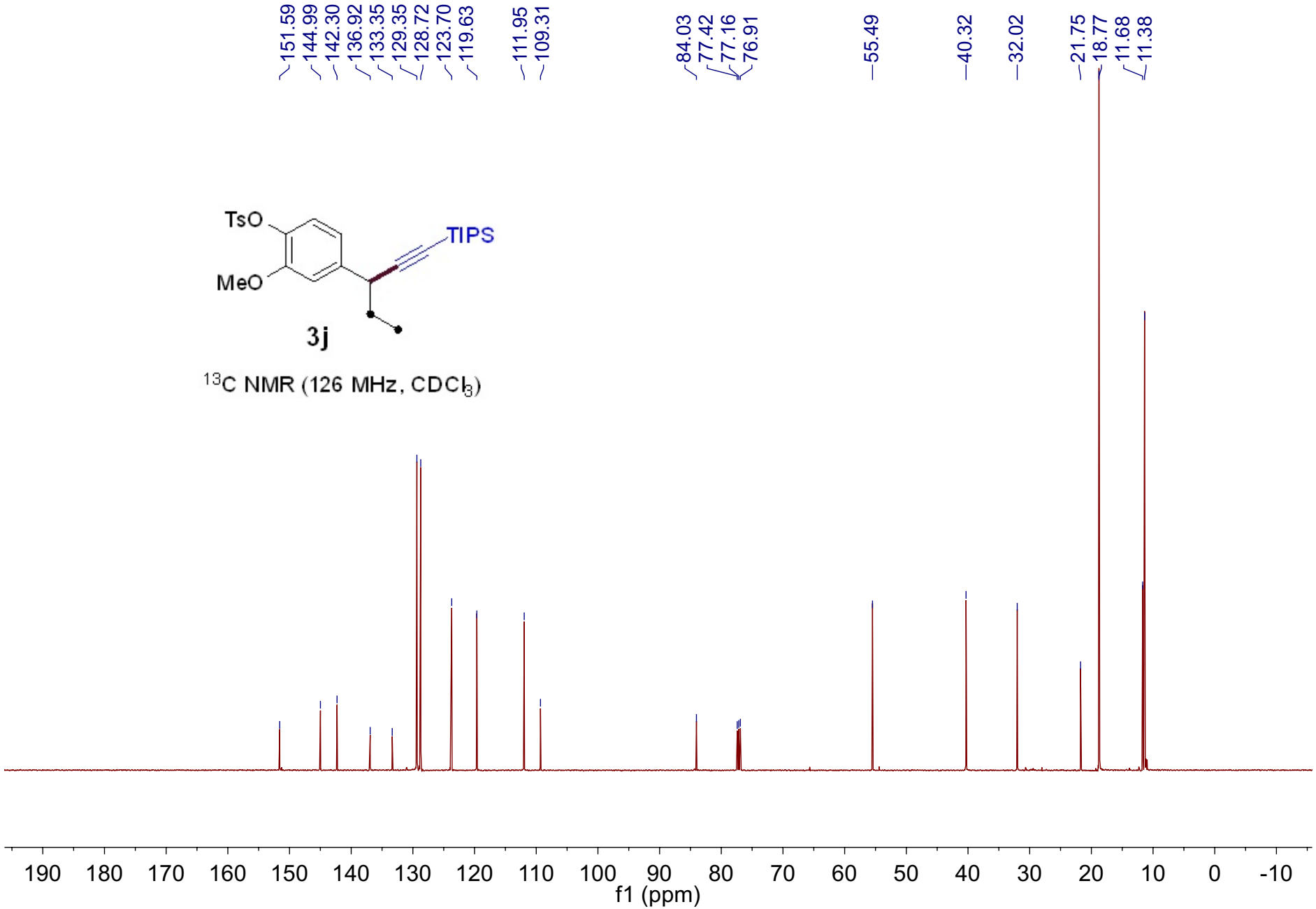
Supplementary Fig. 46. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3i**



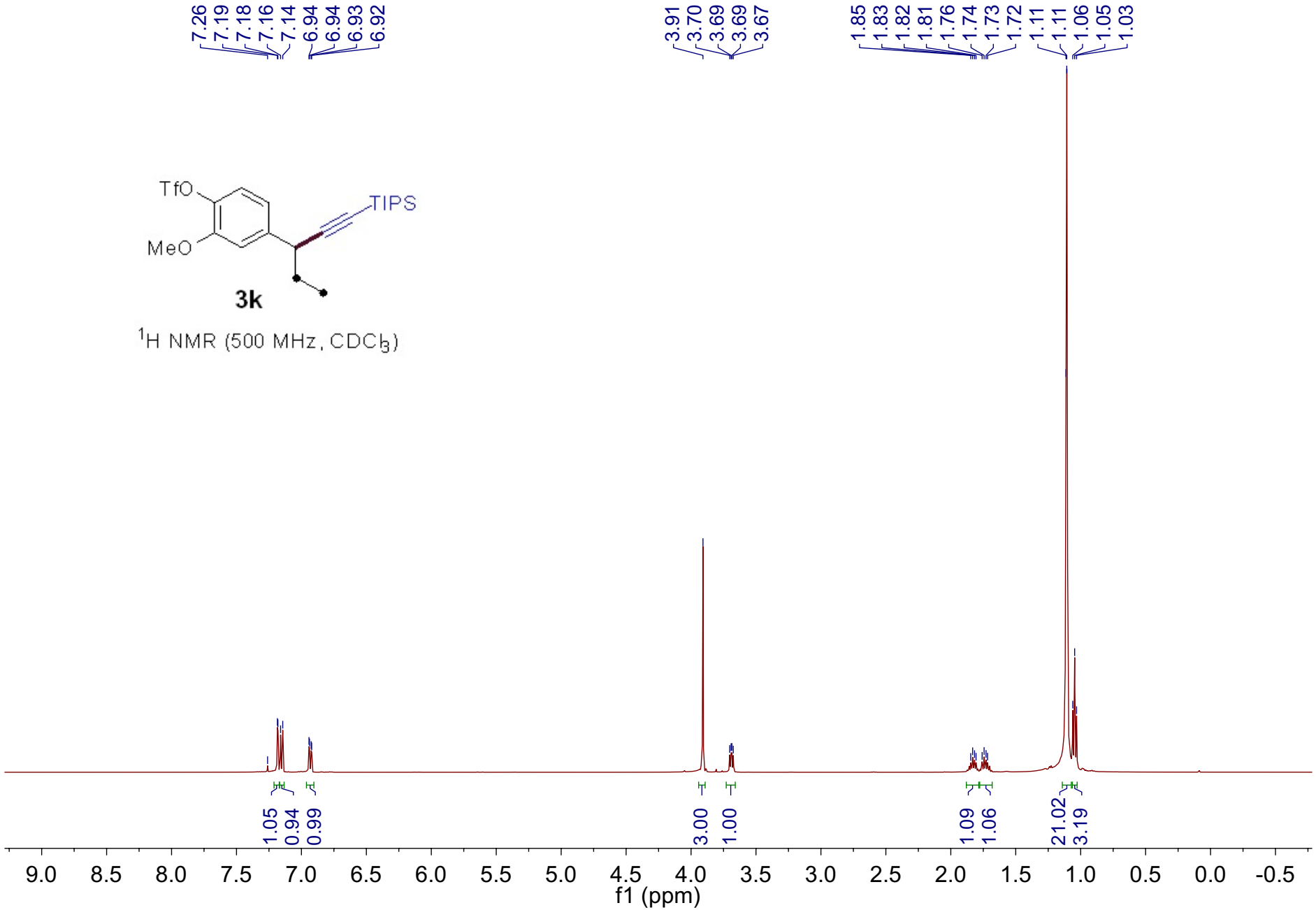
Supplementary Fig. 47. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3i**



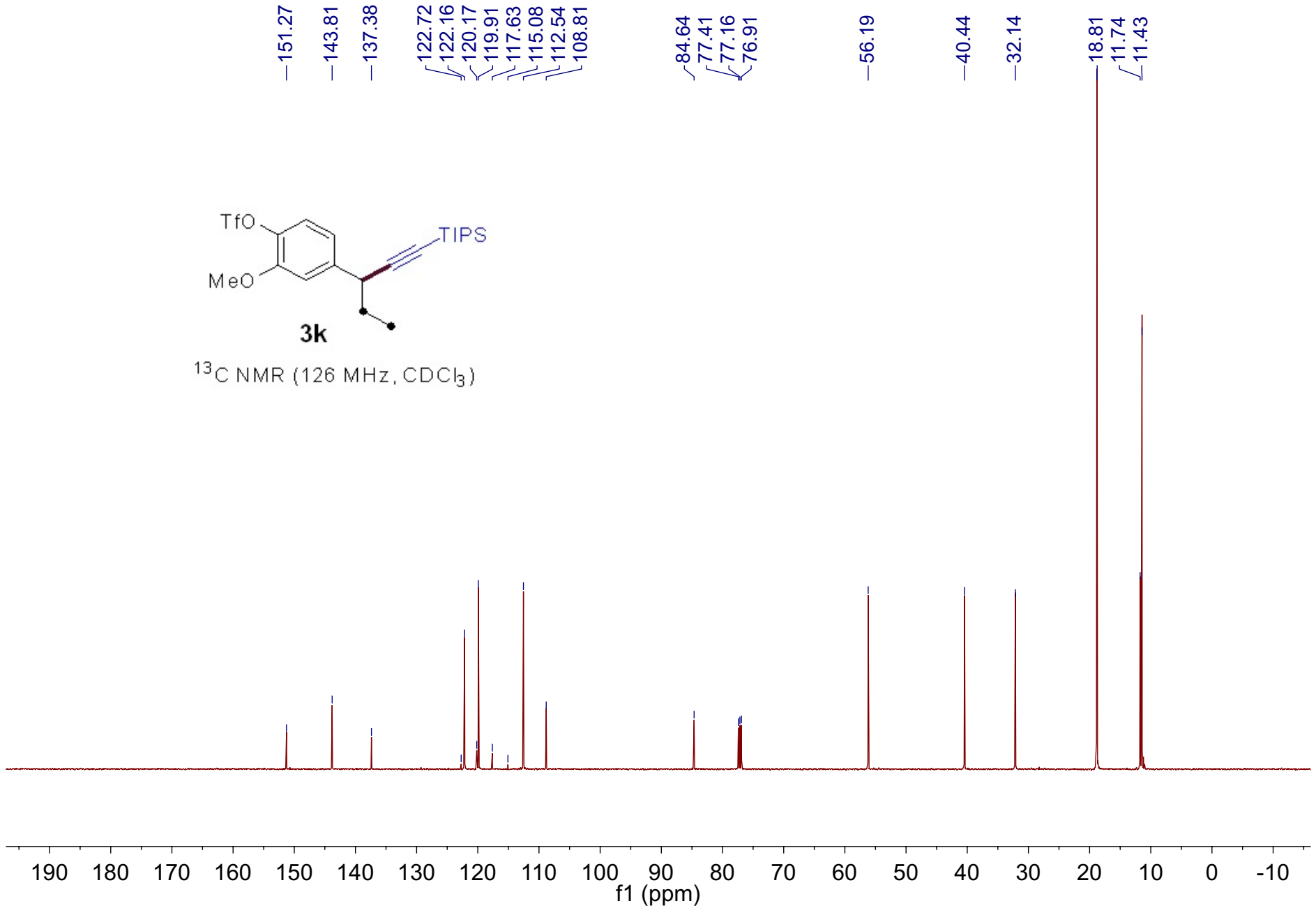
Supplementary Fig. 48. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3j**



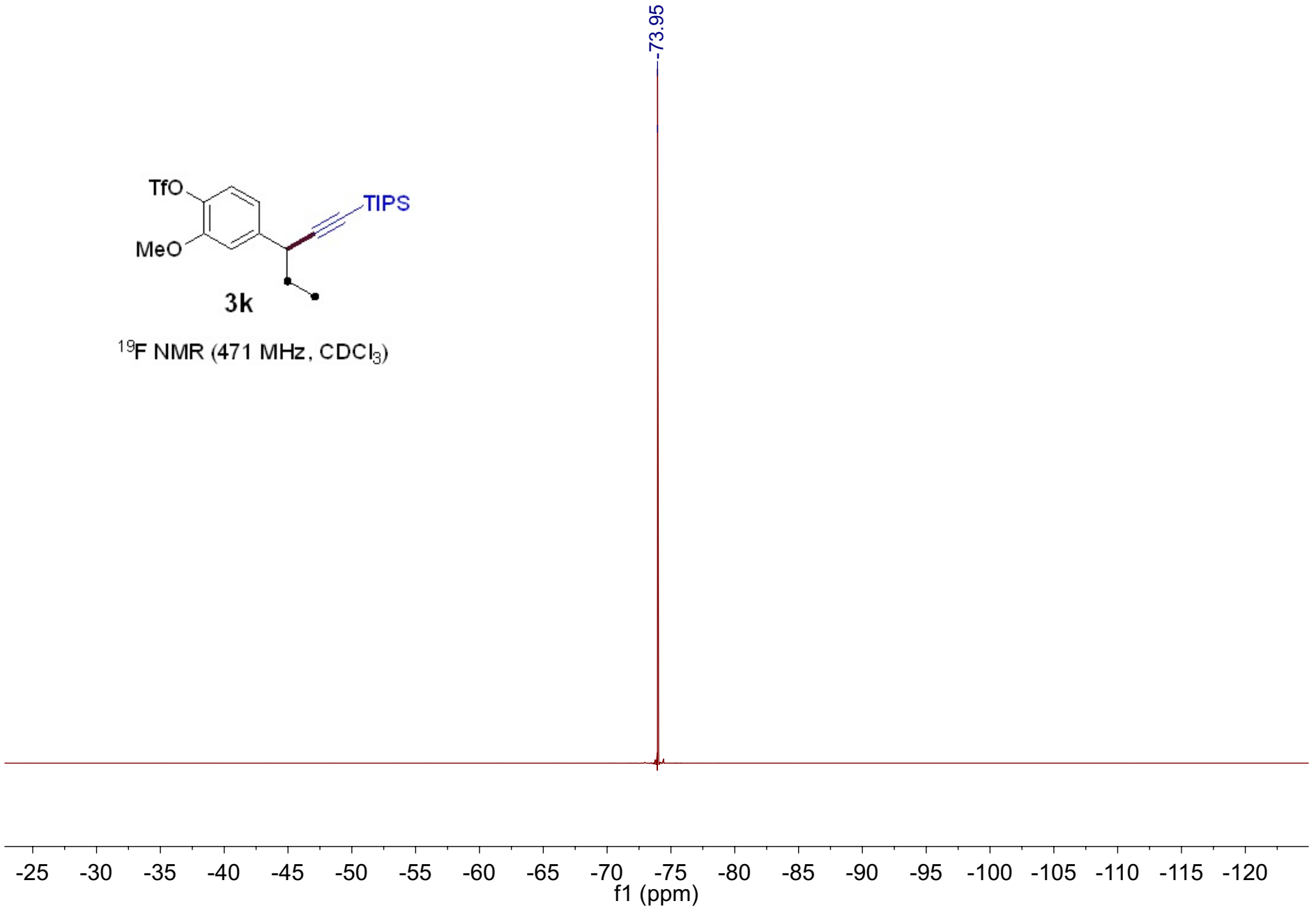
Supplementary Fig. 49. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound 3j



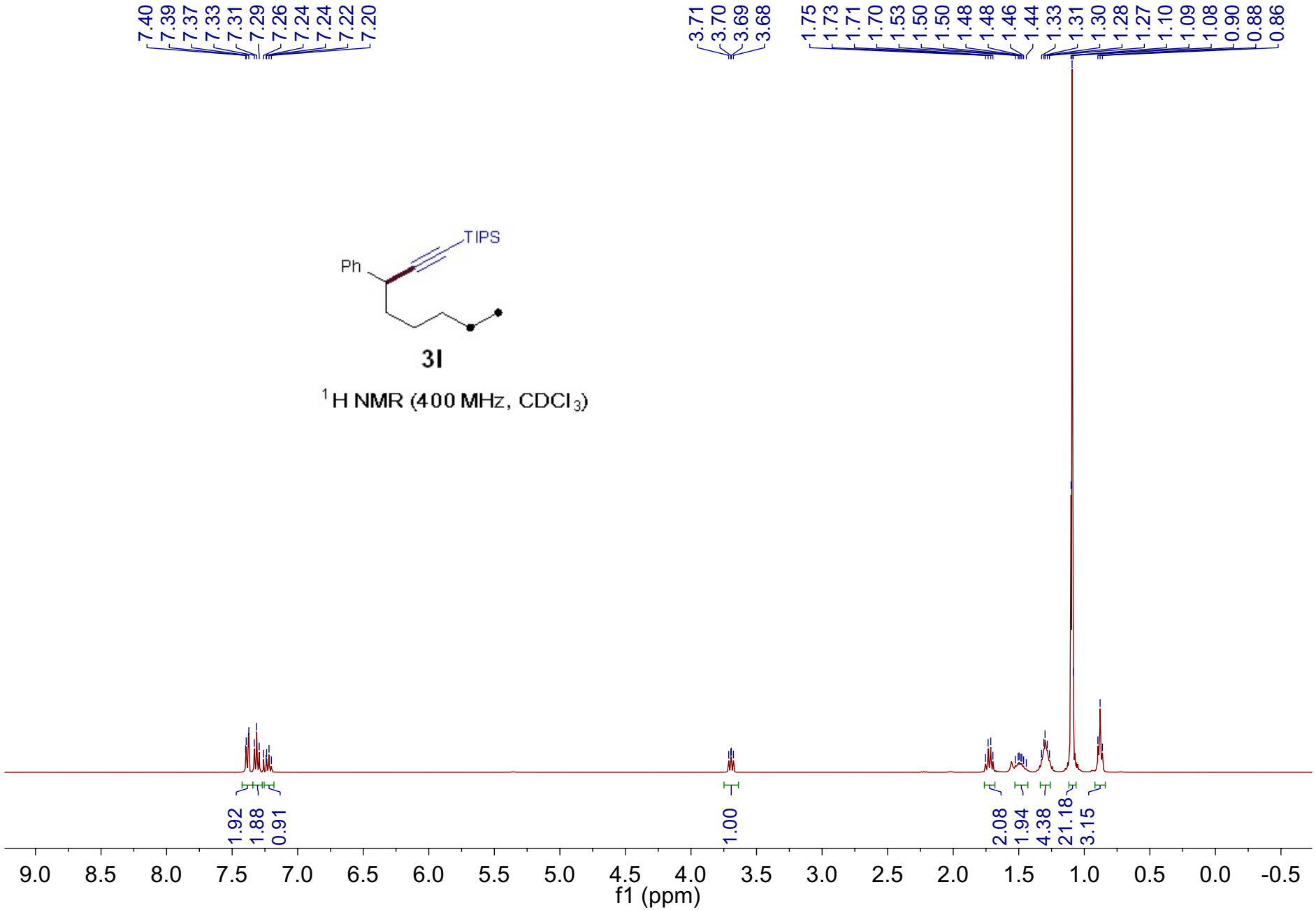
Supplementary Fig. 50. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3k**



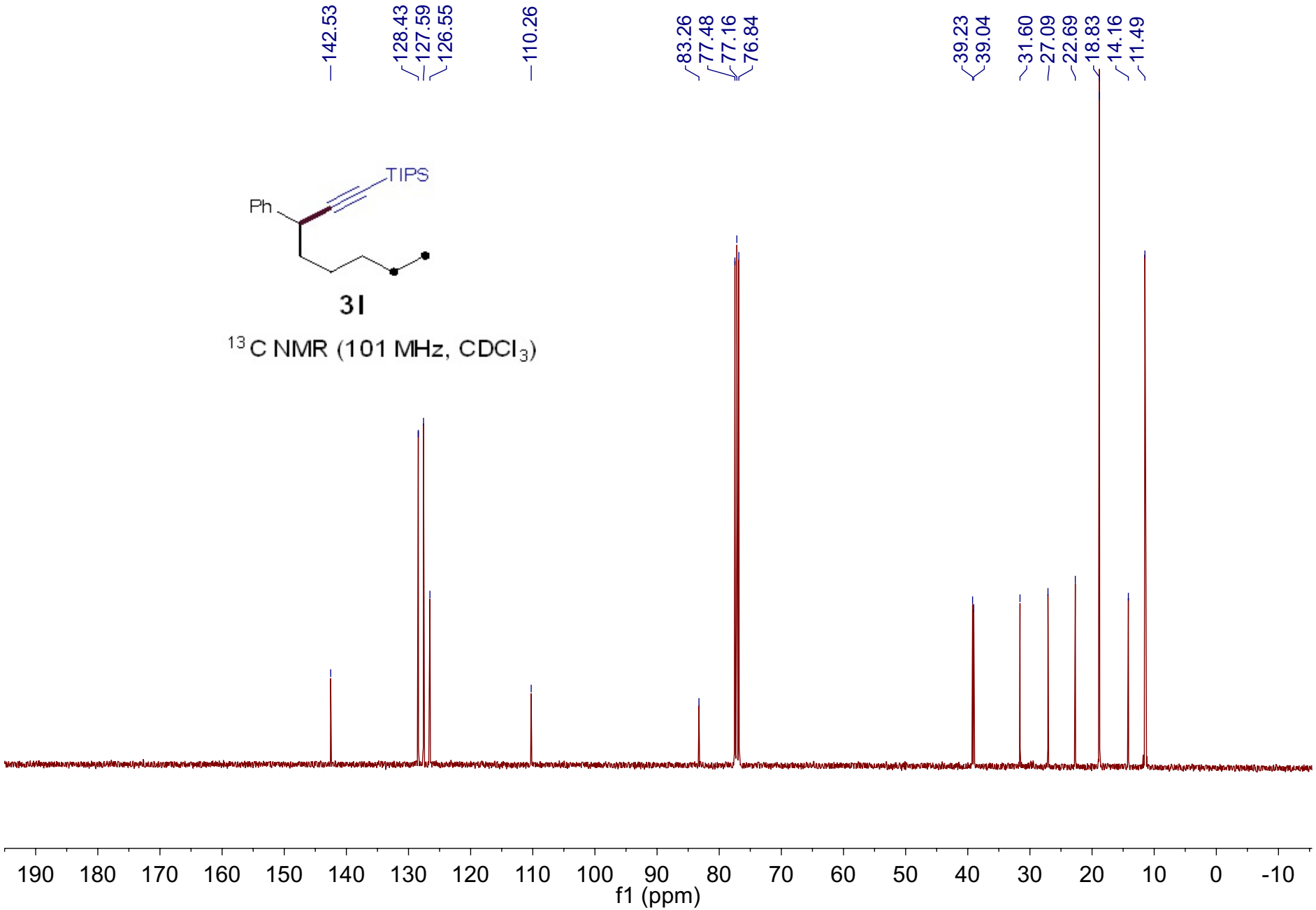
Supplementary Fig. 51. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3k**



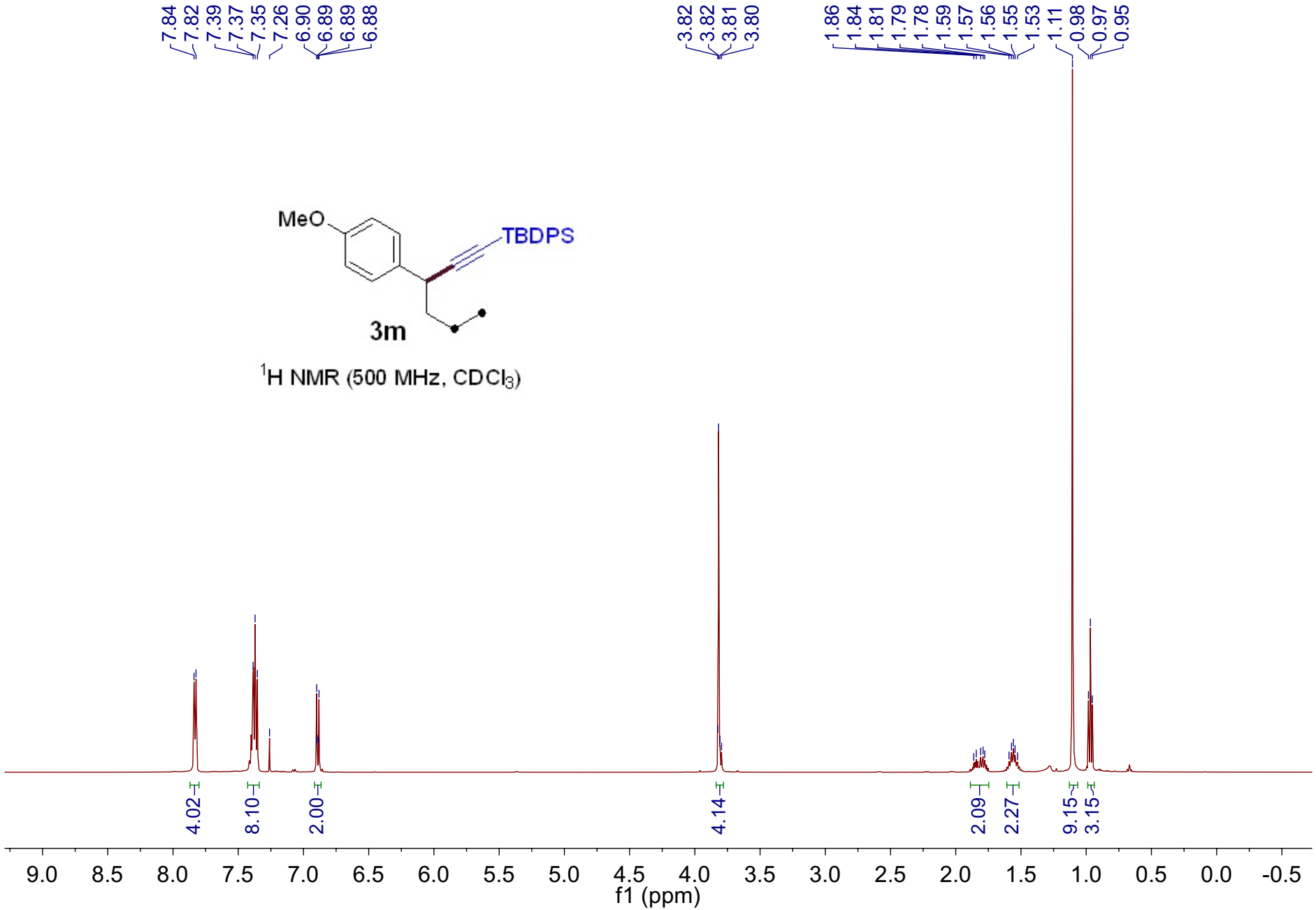
Supplementary Fig. 52. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **3k**



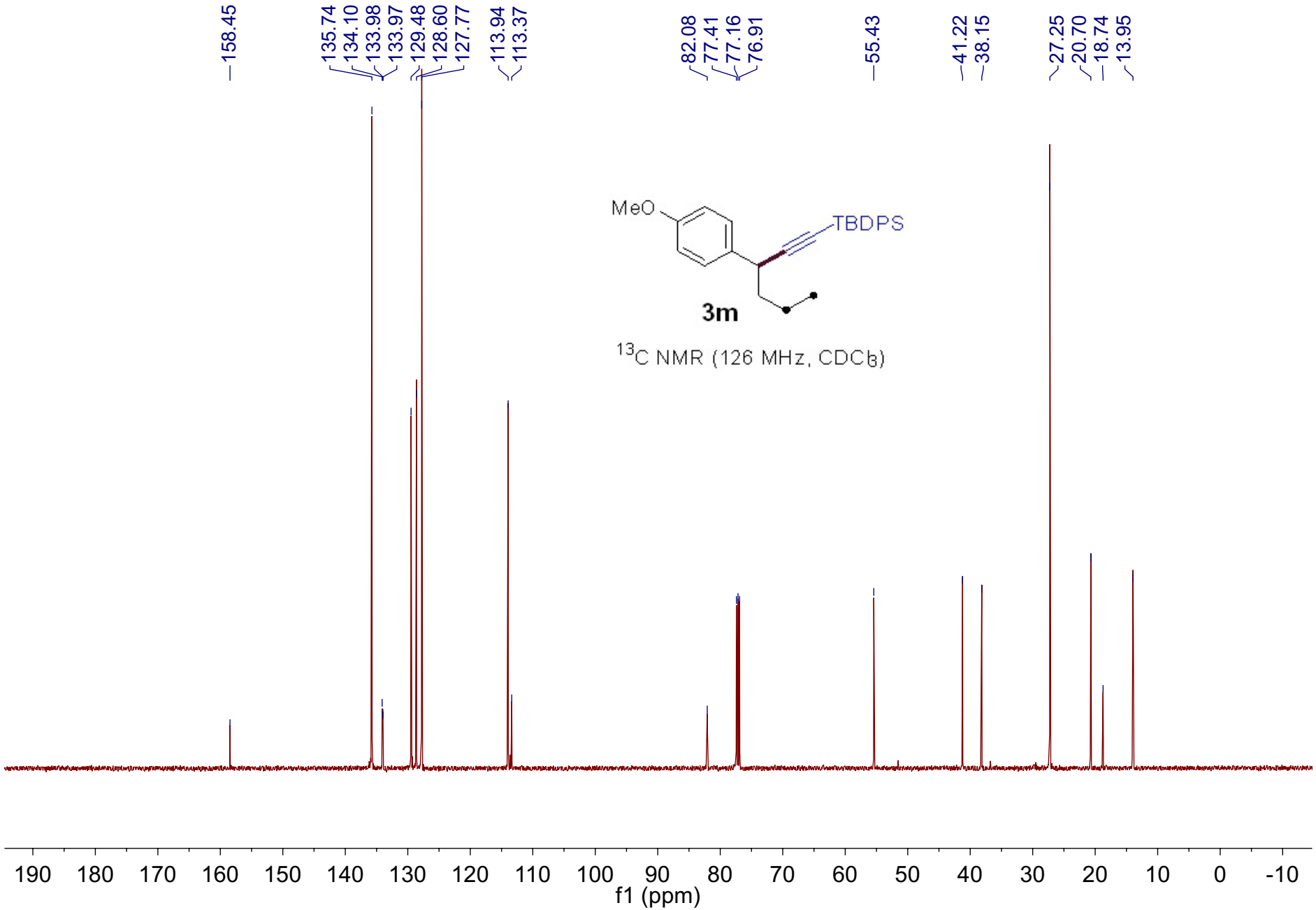
Supplementary Fig. 53. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3l**



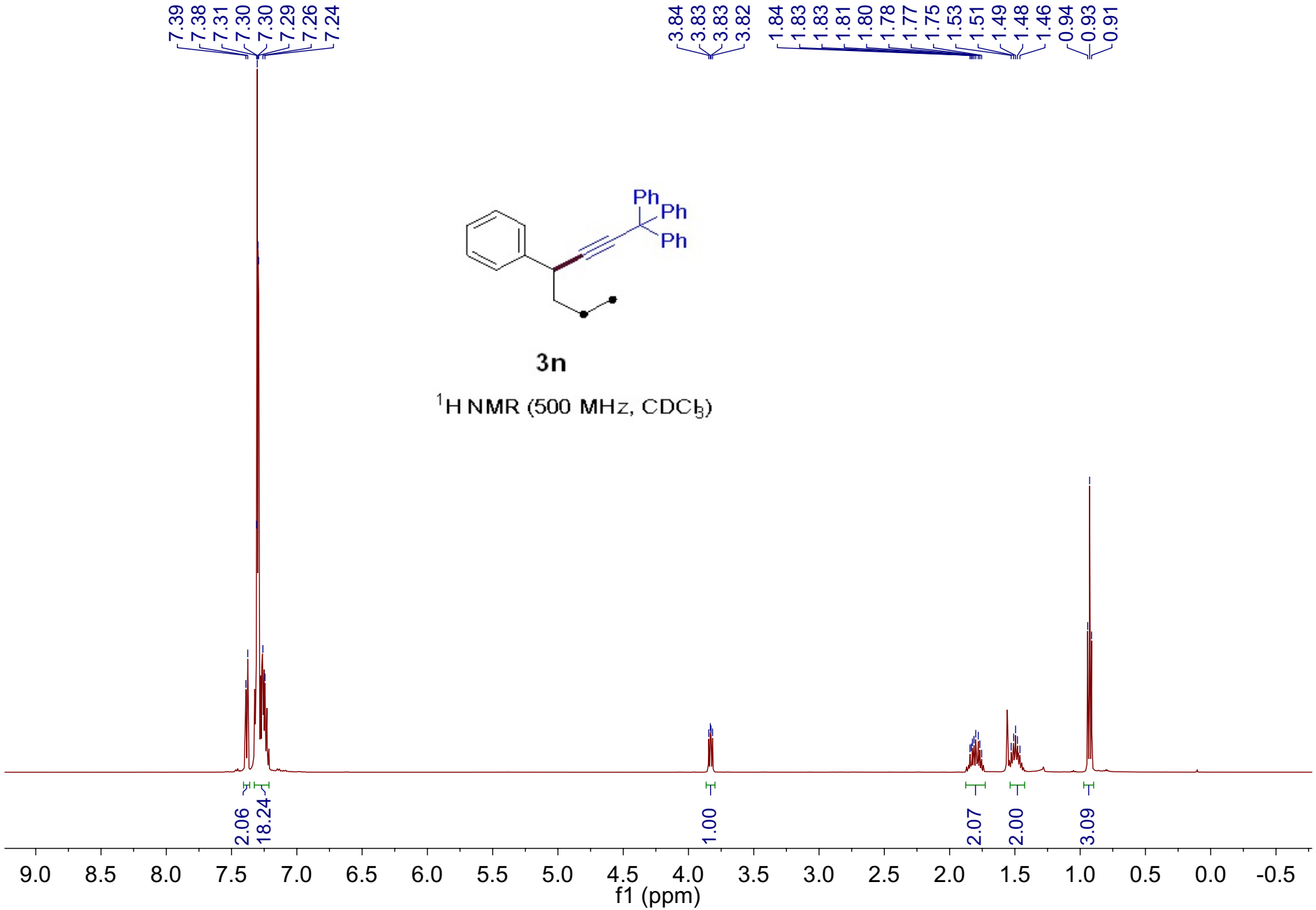
Supplementary Fig. 54. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3l**



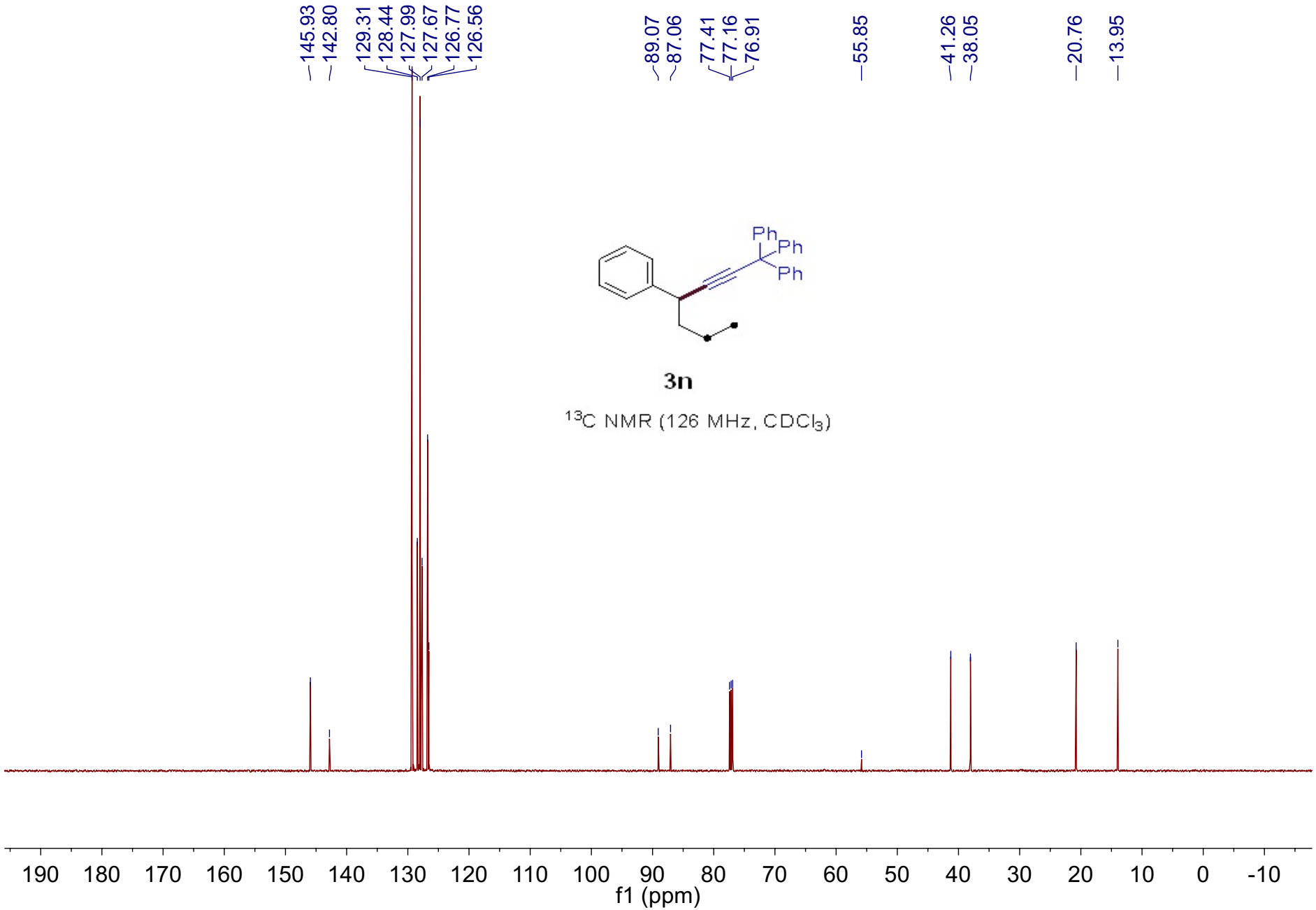
Supplementary Fig. 55. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3m**



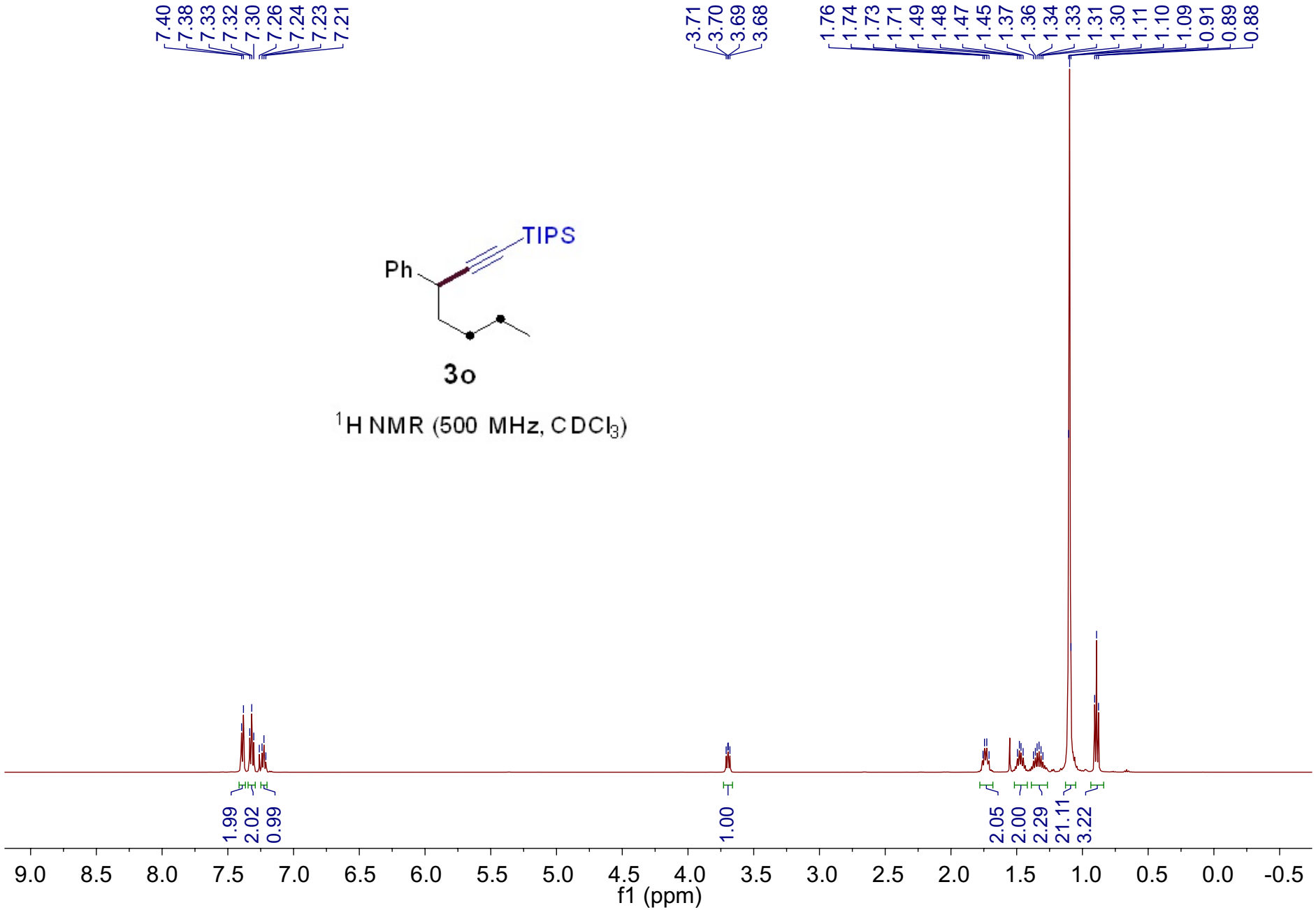
Supplementary Fig. 56. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3m**



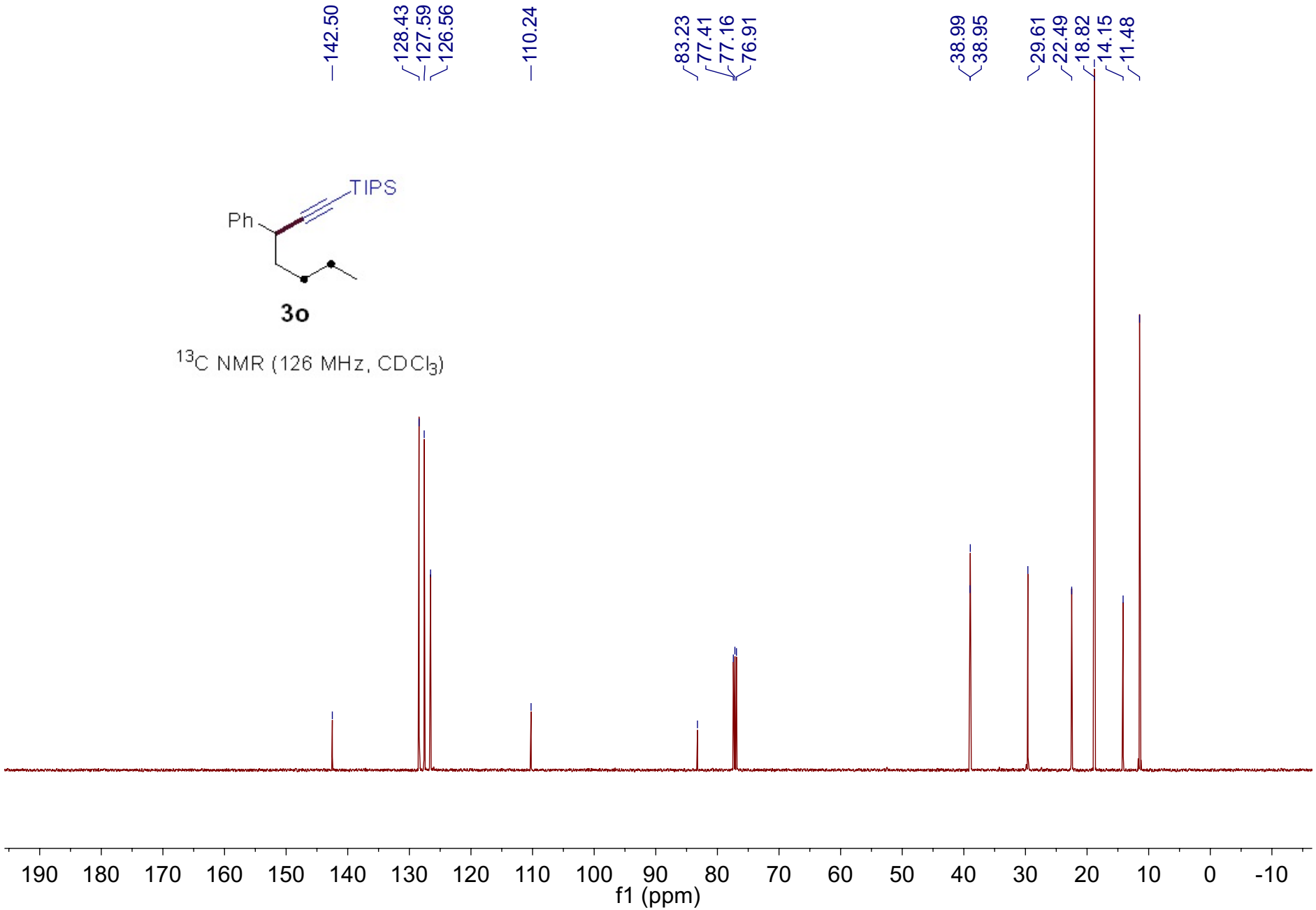
Supplementary Fig. 57. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3n**



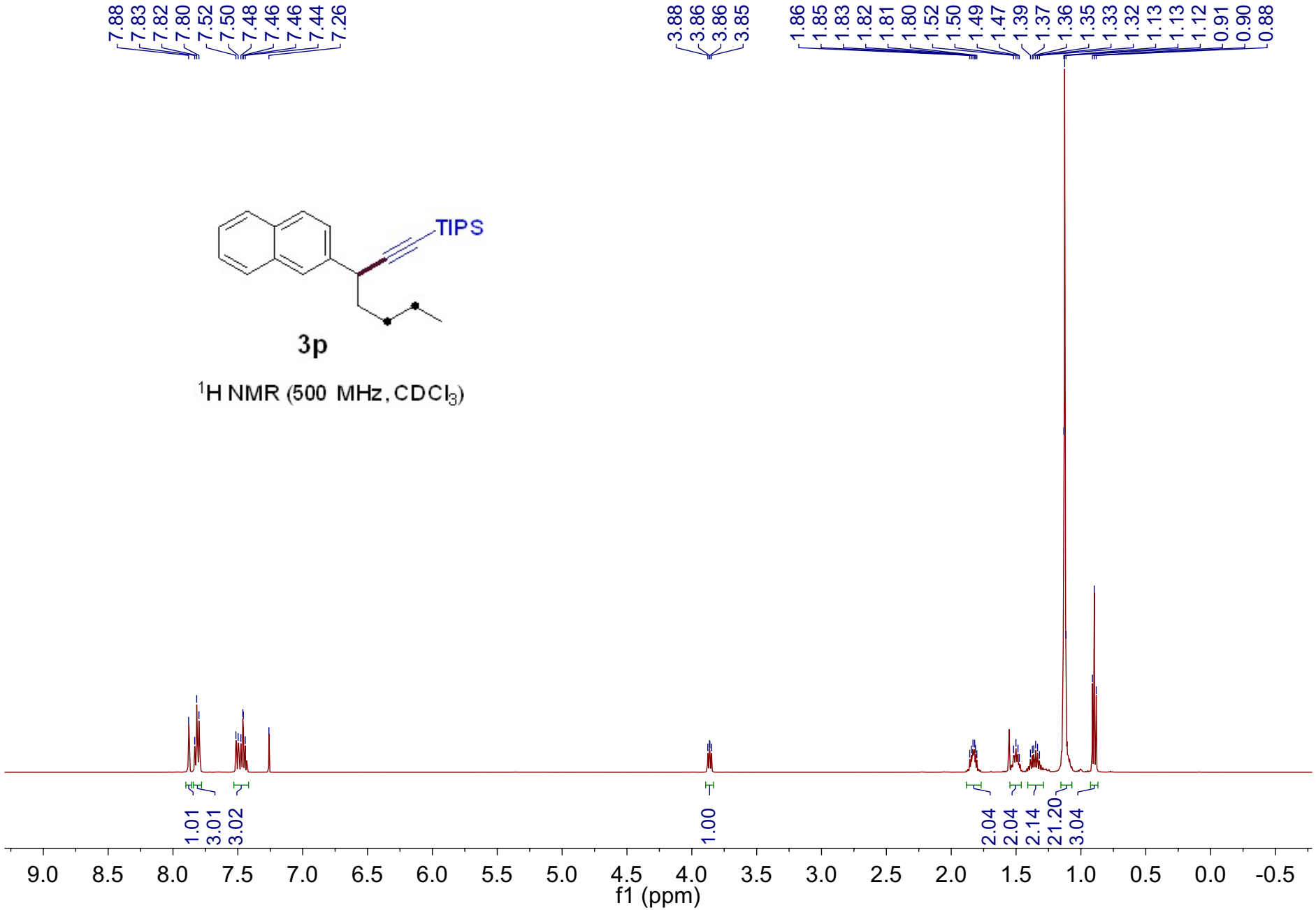
Supplementary Fig. 58. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3n**



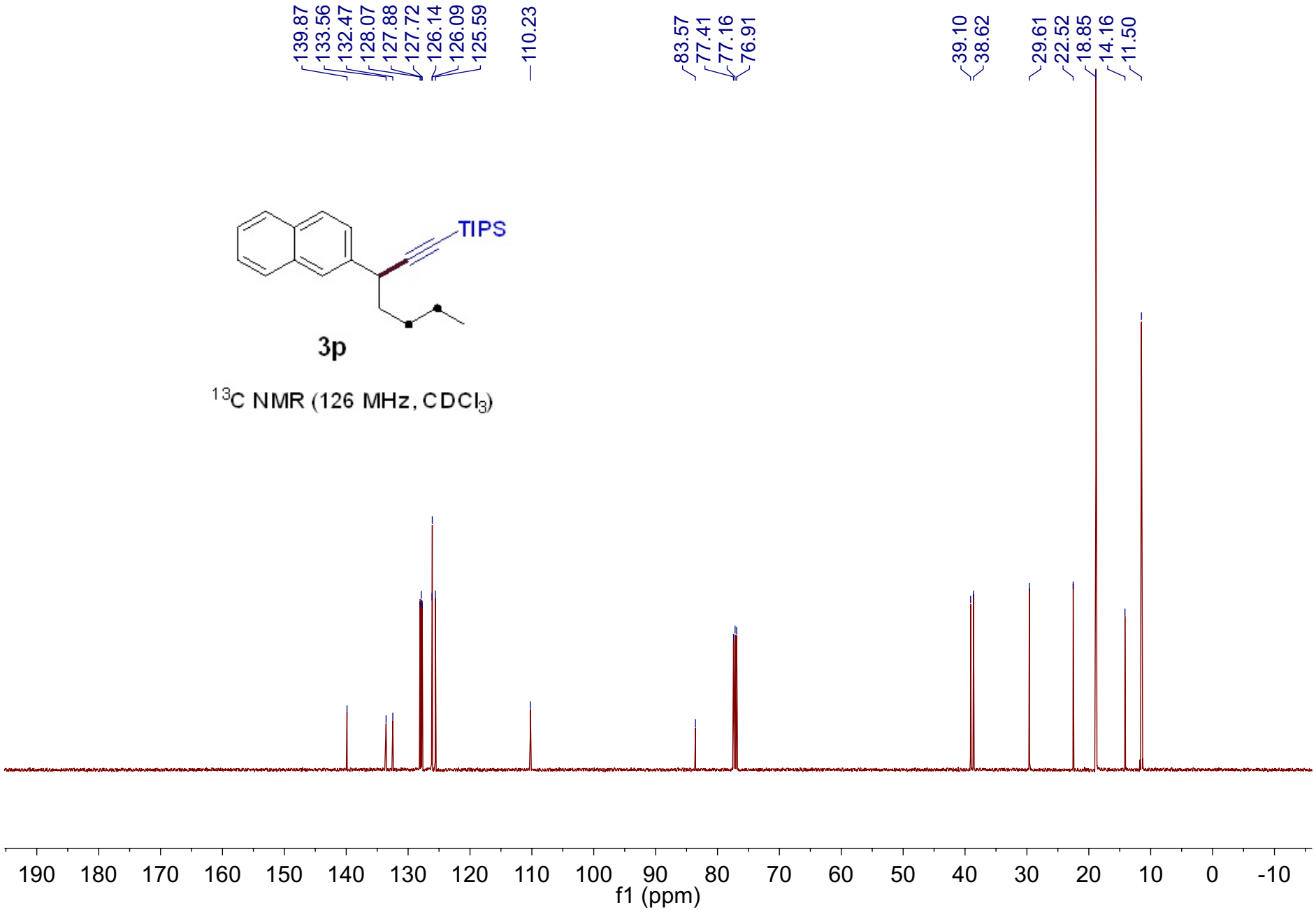
Supplementary Fig. 59. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3o**



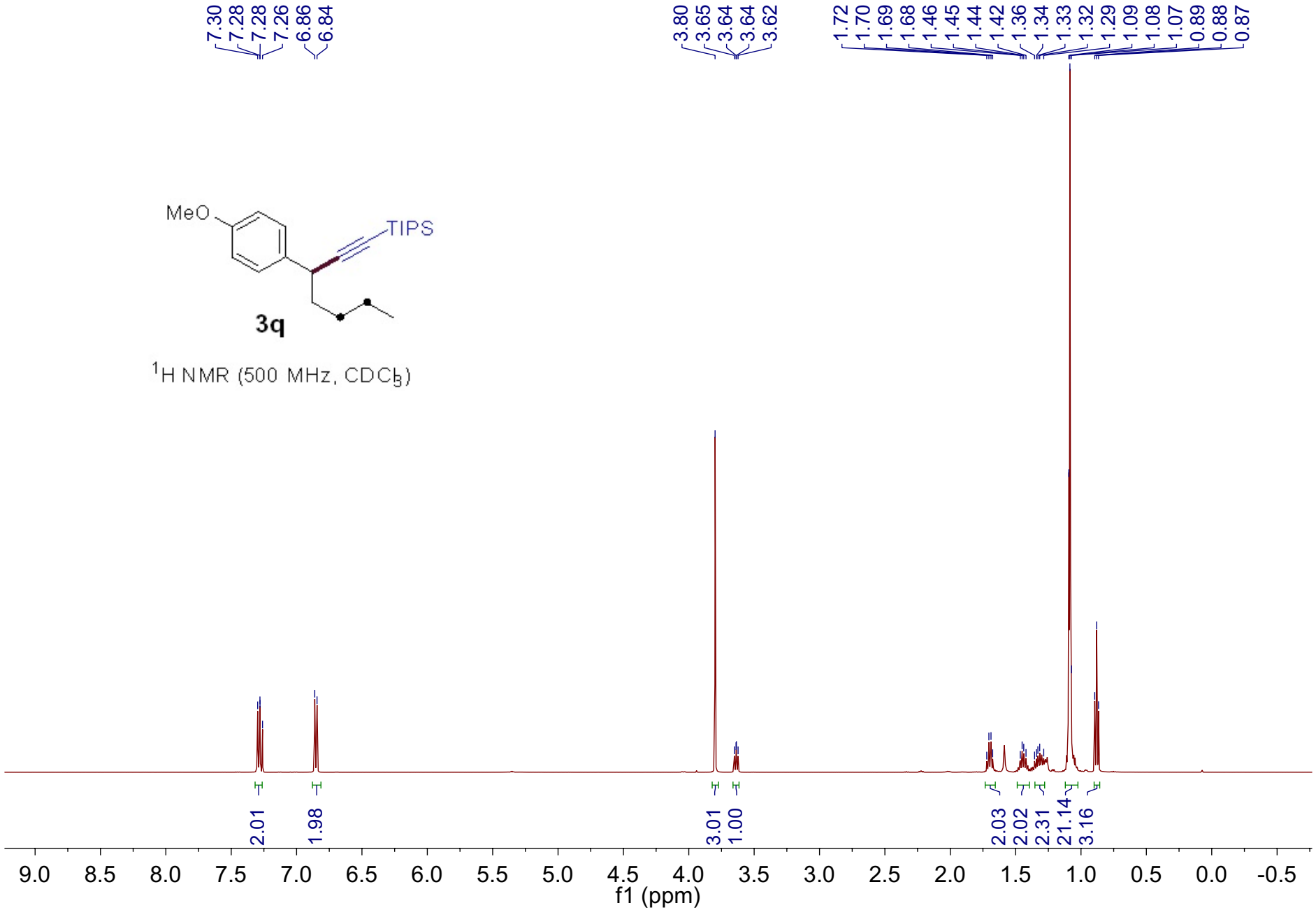
Supplementary Fig. 60. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3o**



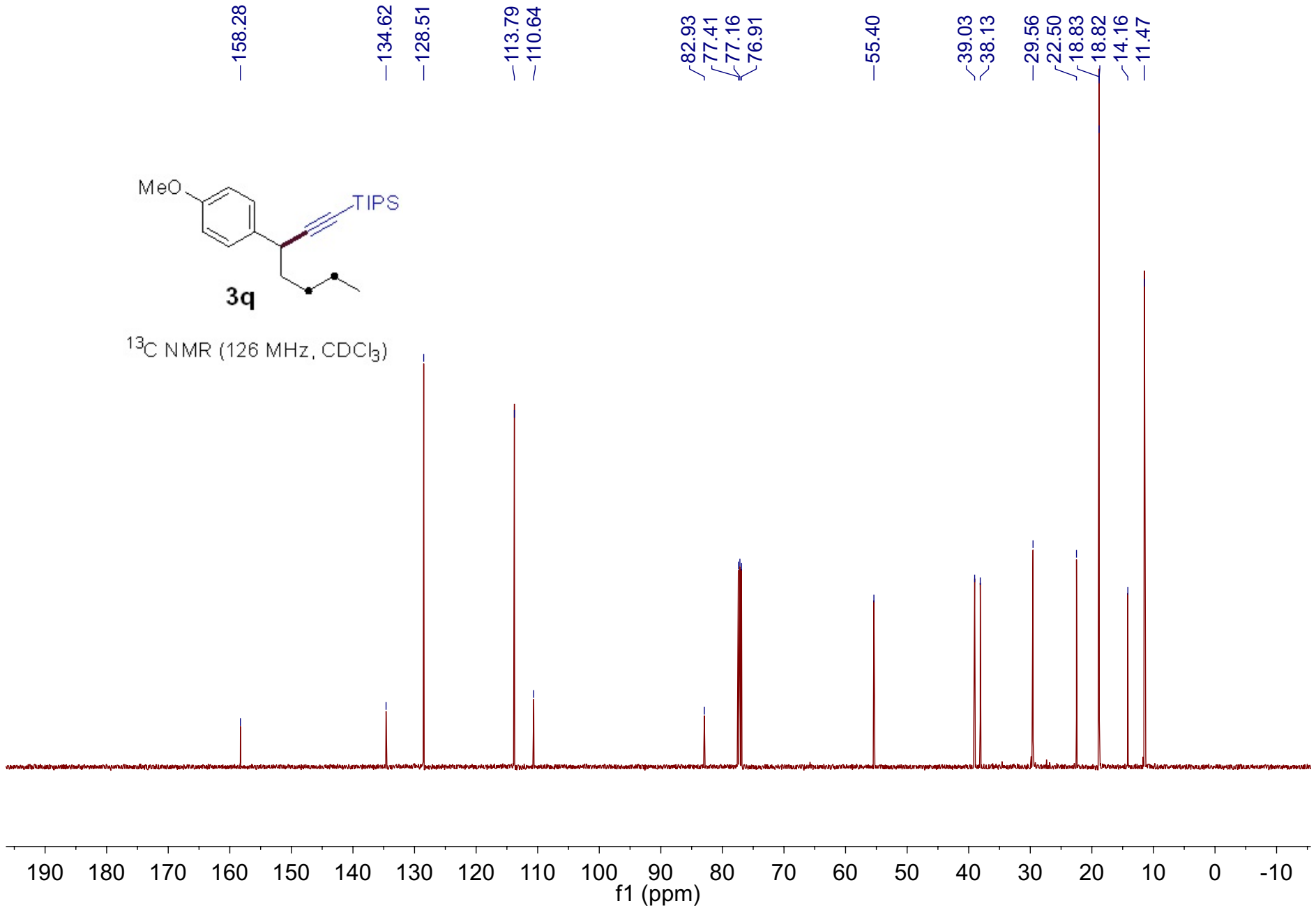
Supplementary Fig. 61. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3p**



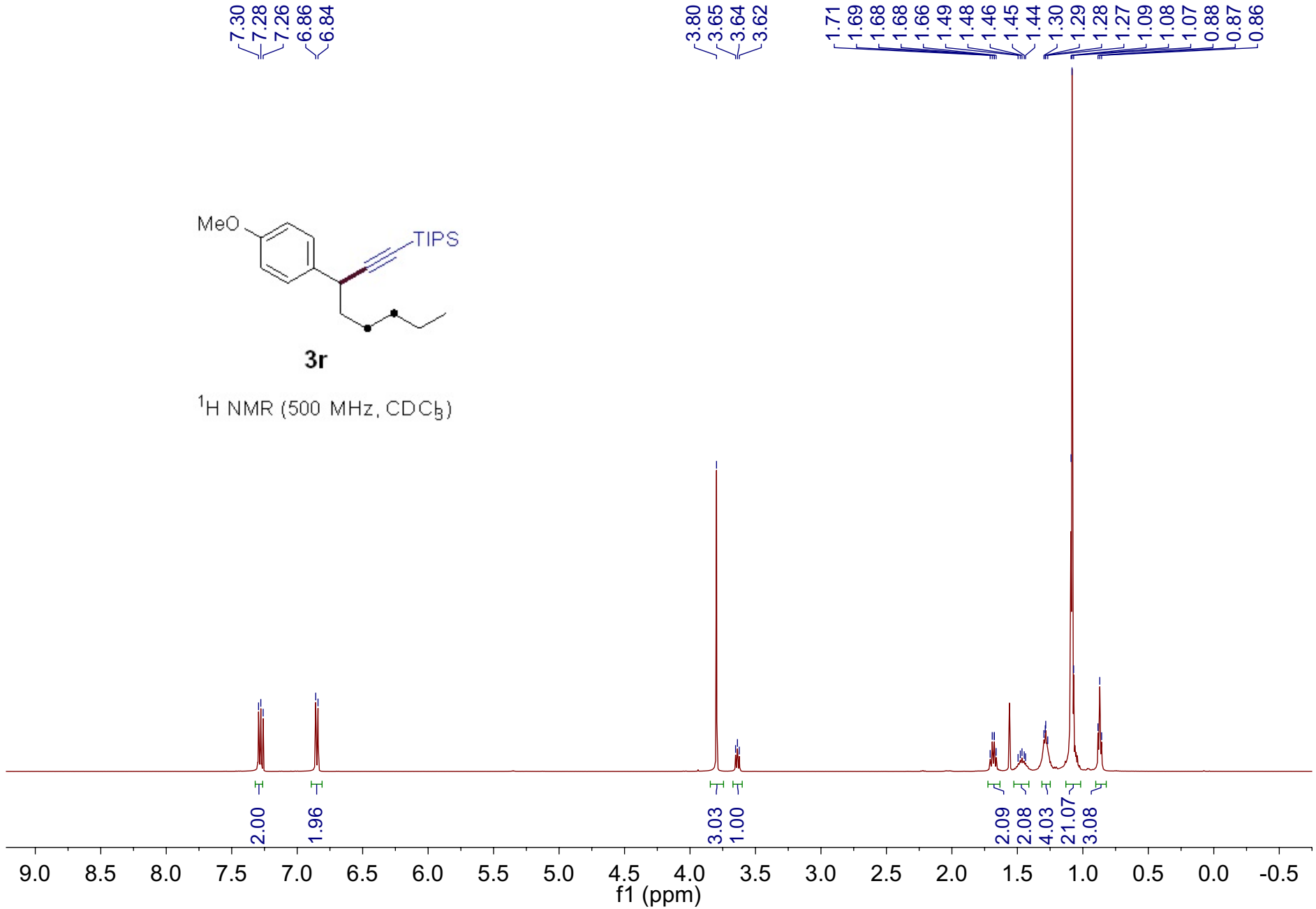
Supplementary Fig. 62. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3p**



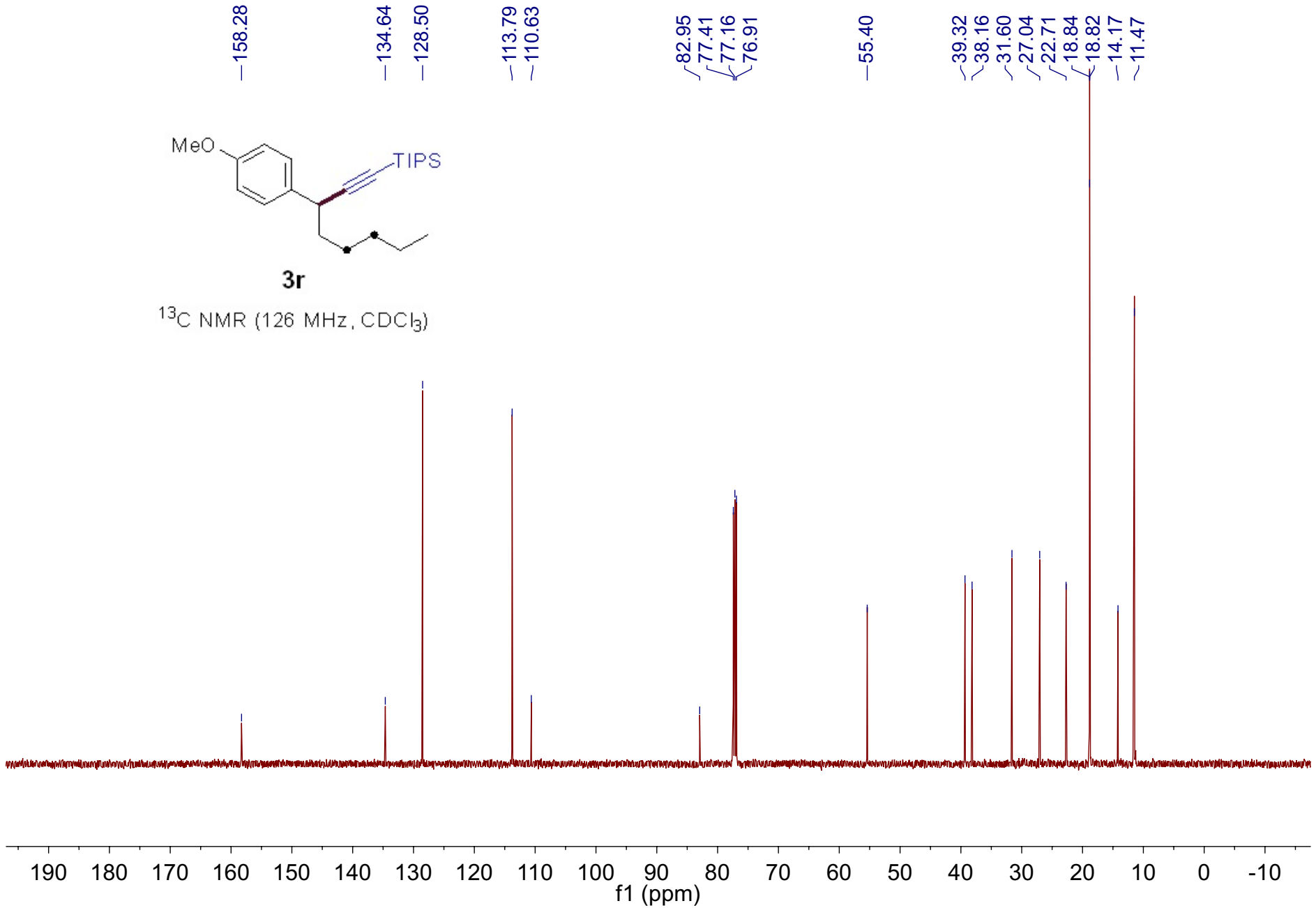
Supplementary Fig. 63. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3q**



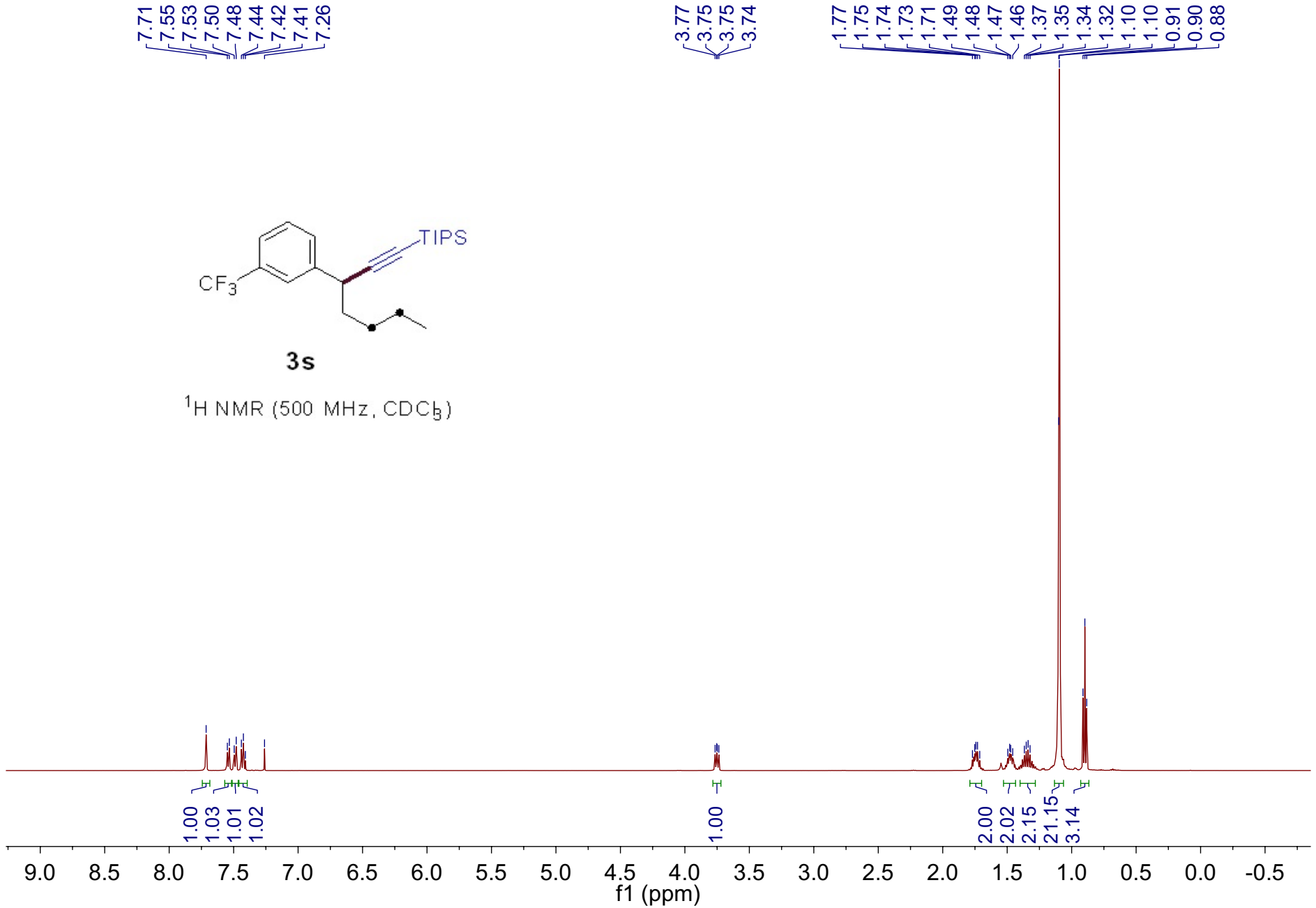
Supplementary Fig. 64. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3q**



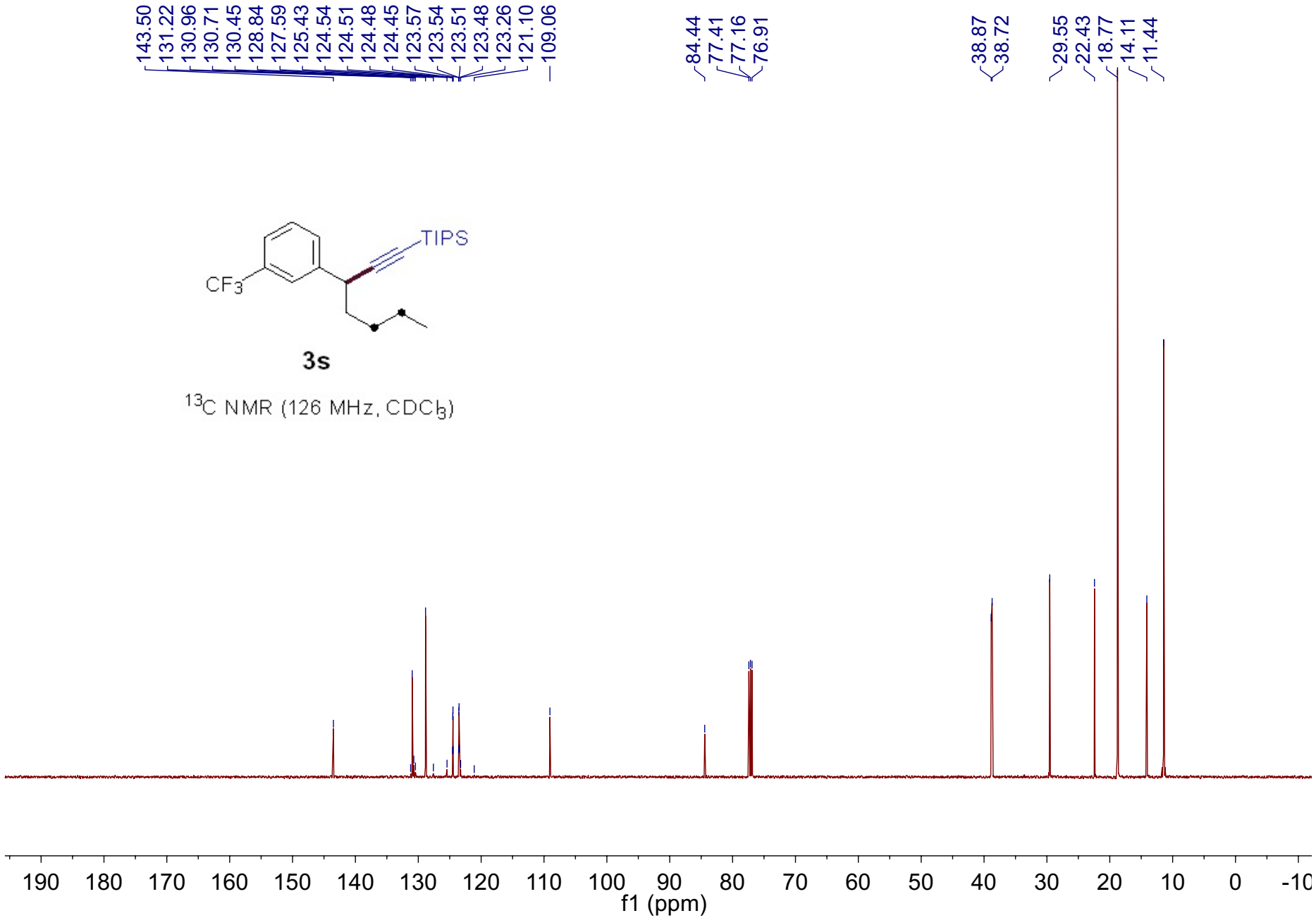
Supplementary Fig. 65. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3r**



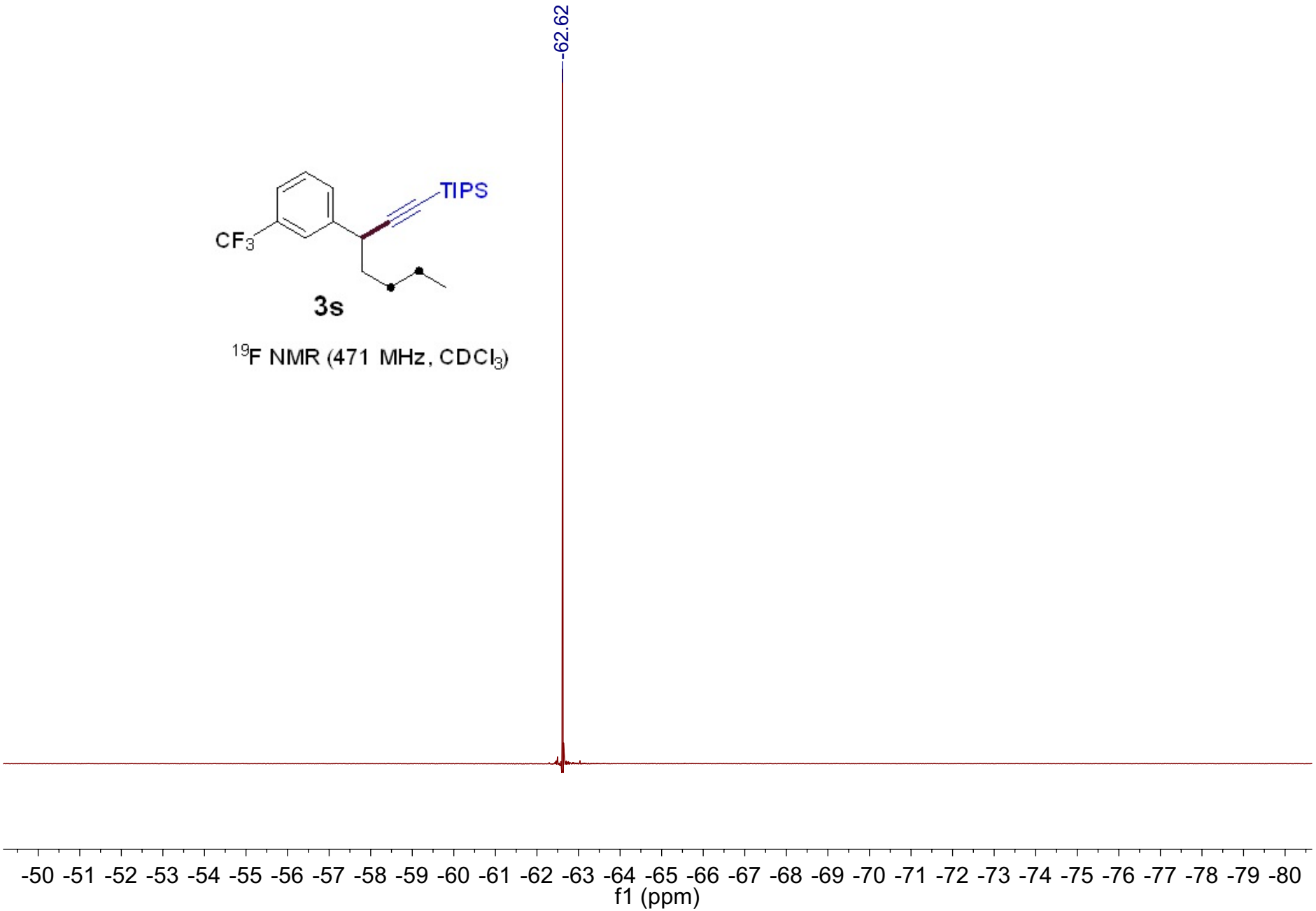
Supplementary Fig. 66. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3r**



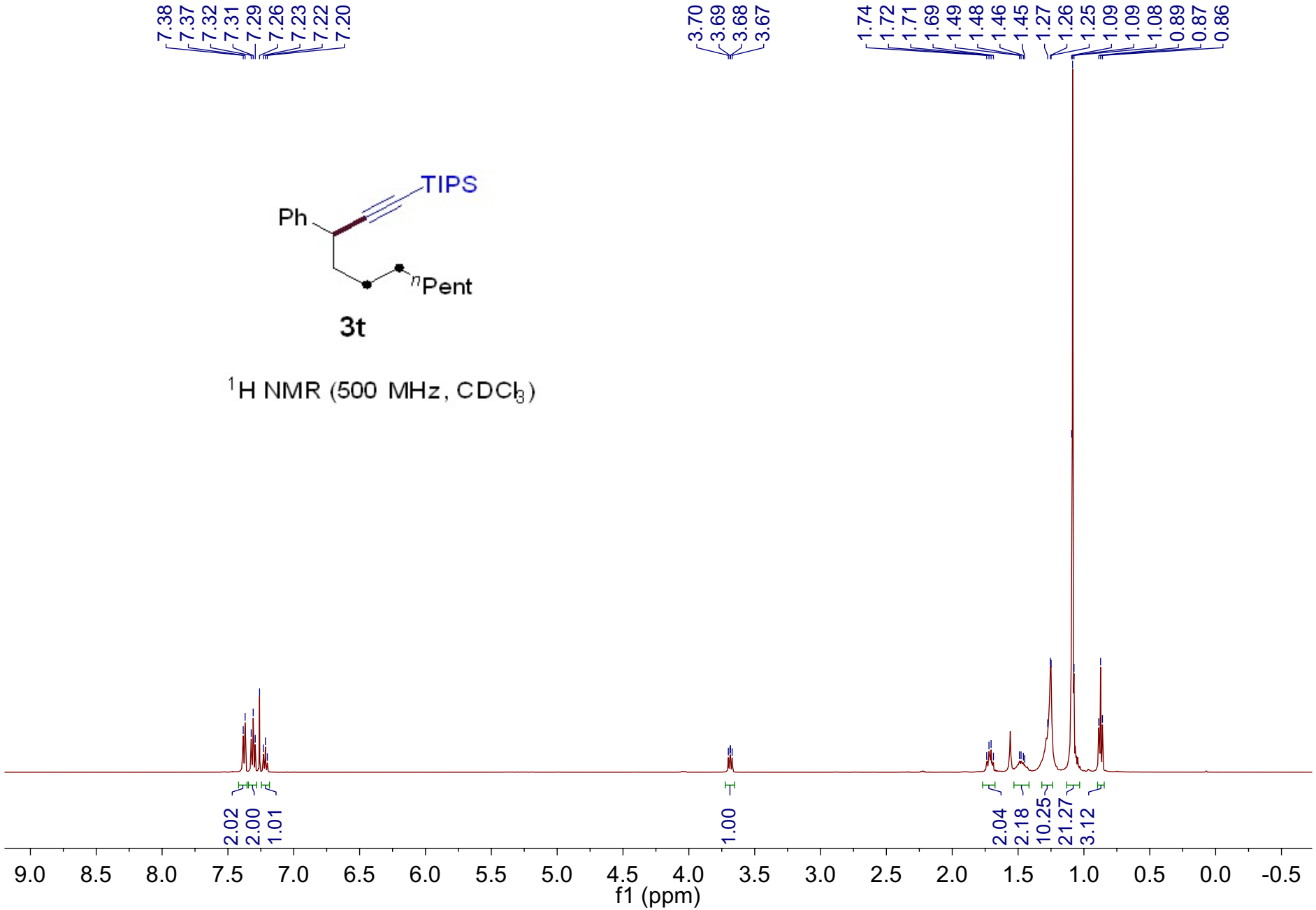
Supplementary Fig. 67. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3s**



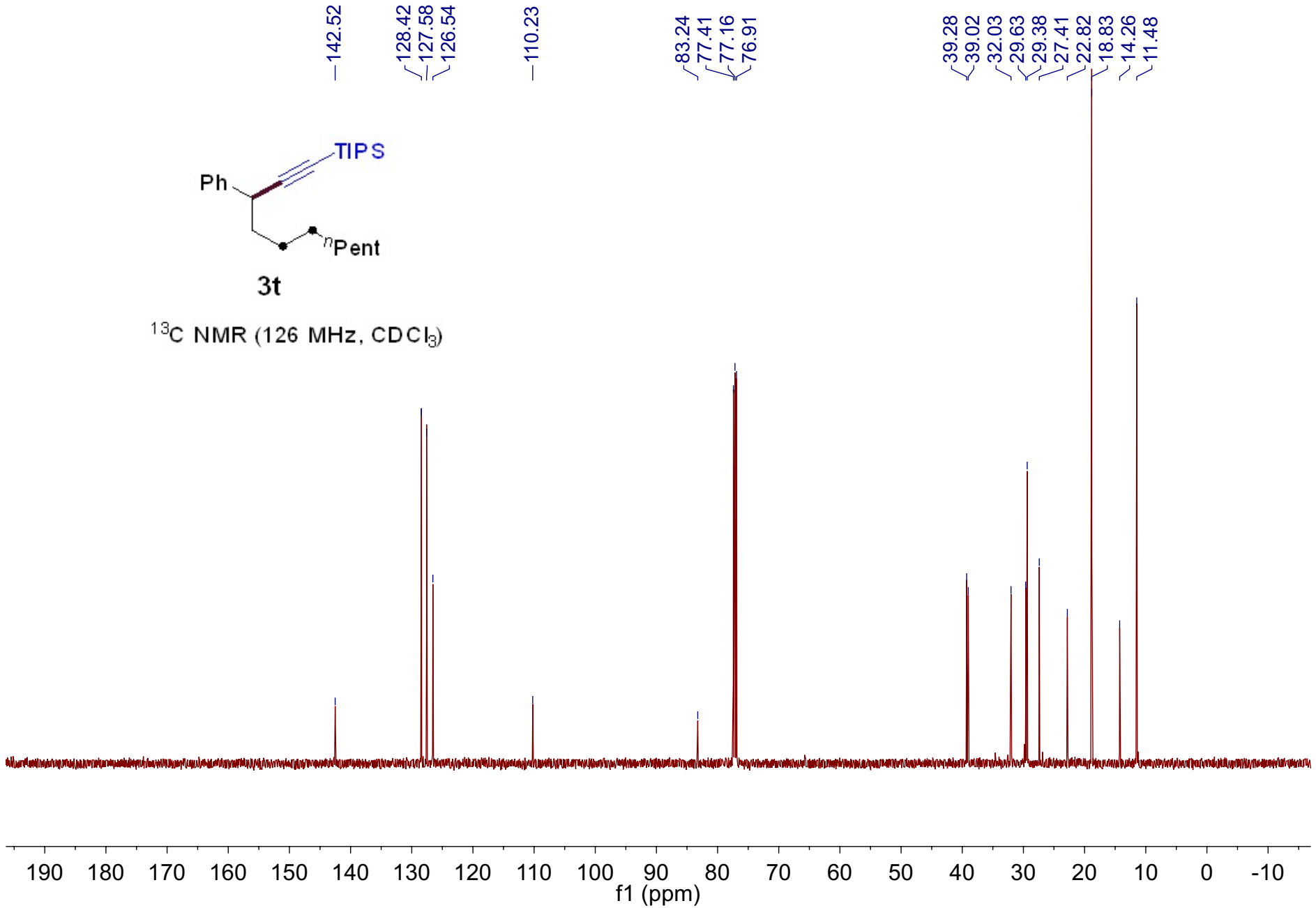
Supplementary Fig. 68. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3s**



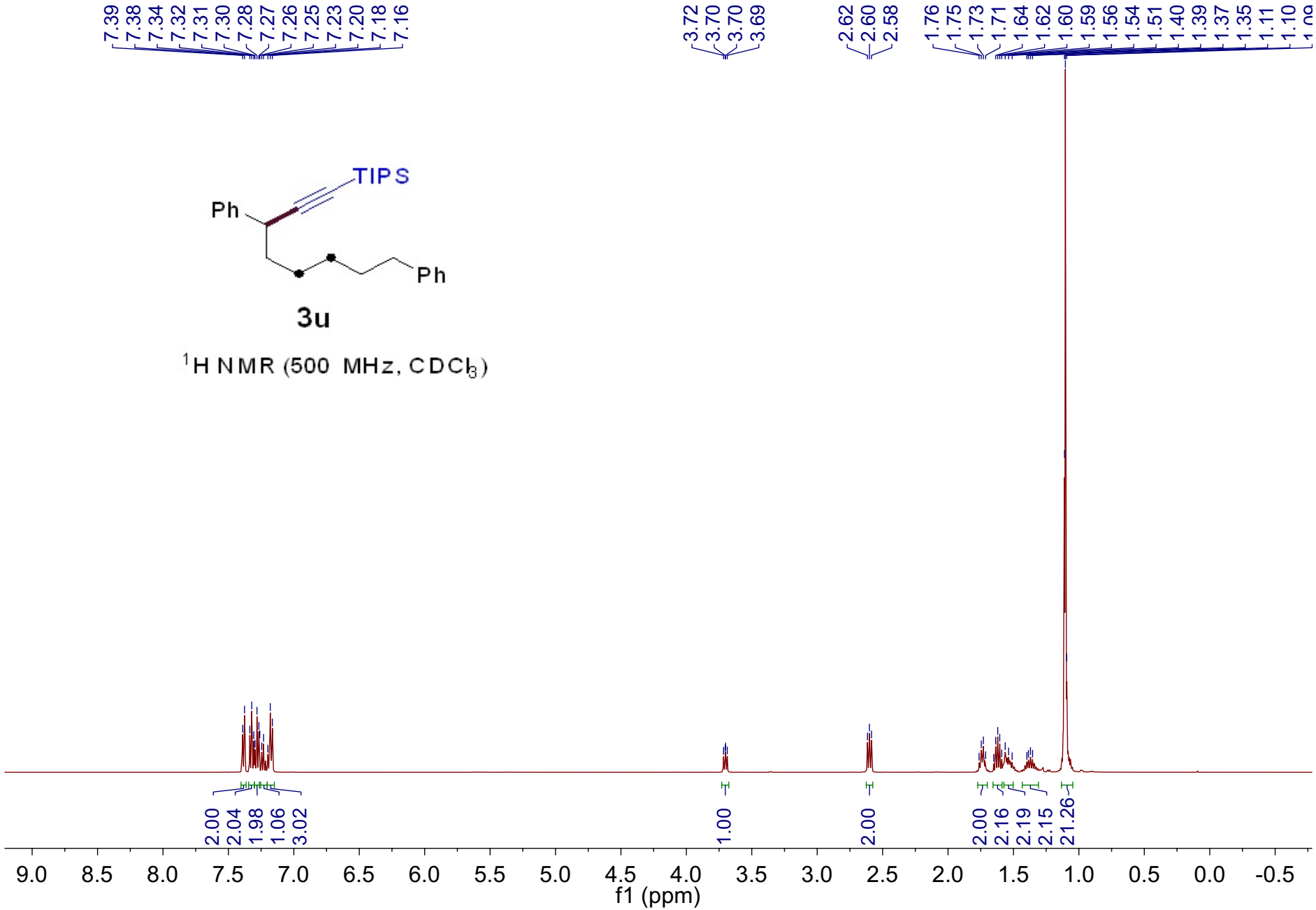
Supplementary Fig. 69. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **3s**



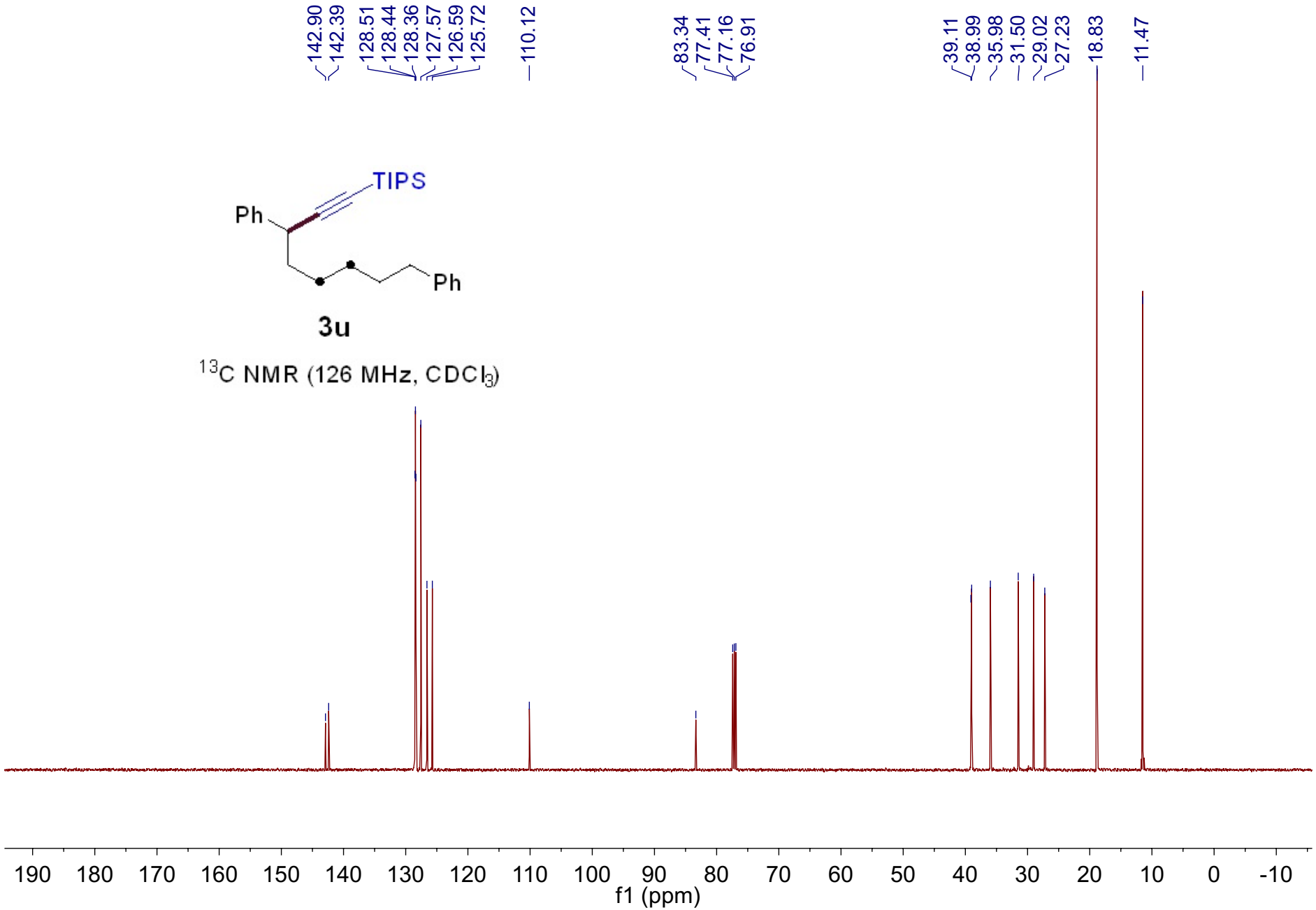
Supplementary Fig. 70. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3t**



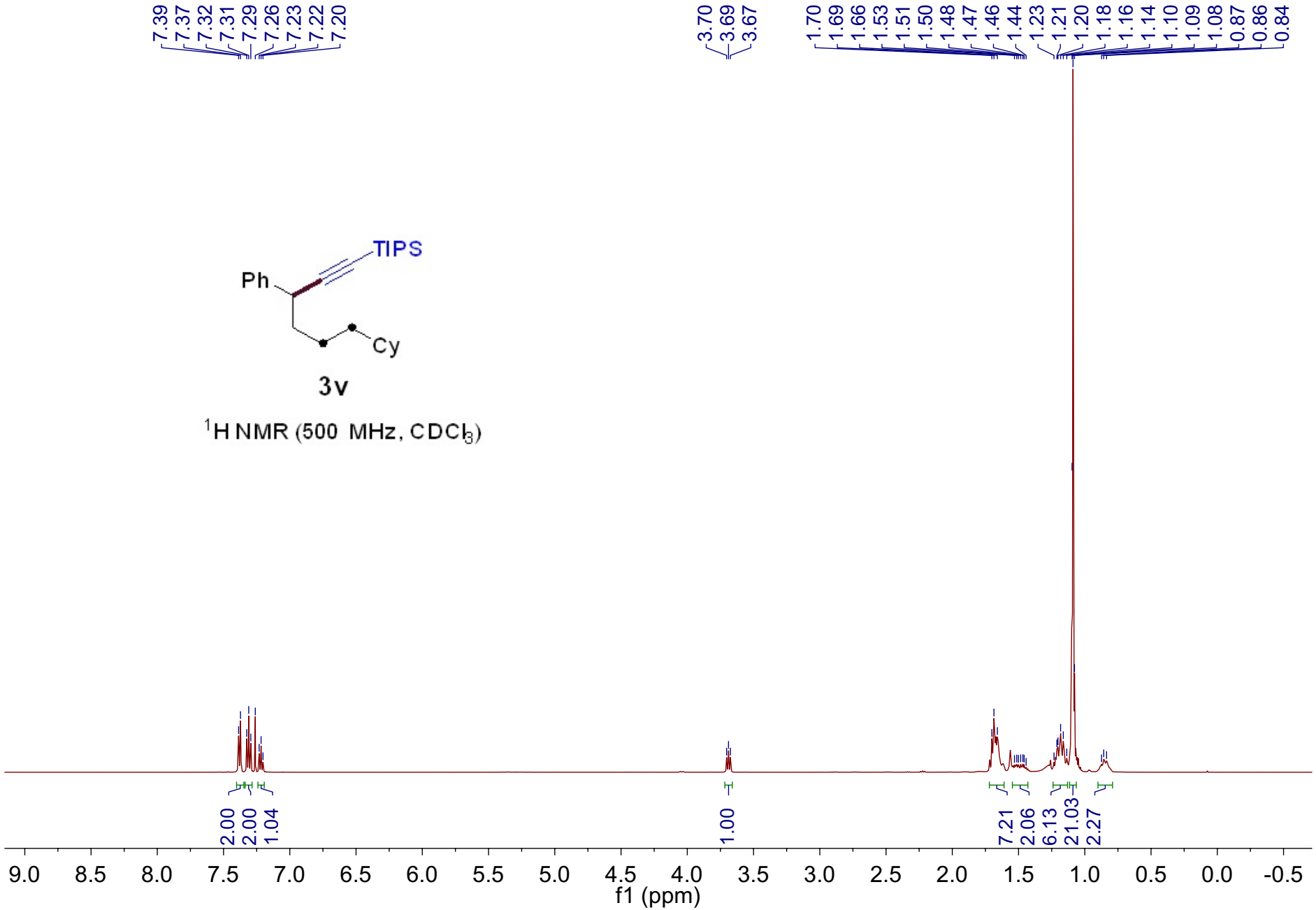
Supplementary Fig. 71. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3t**



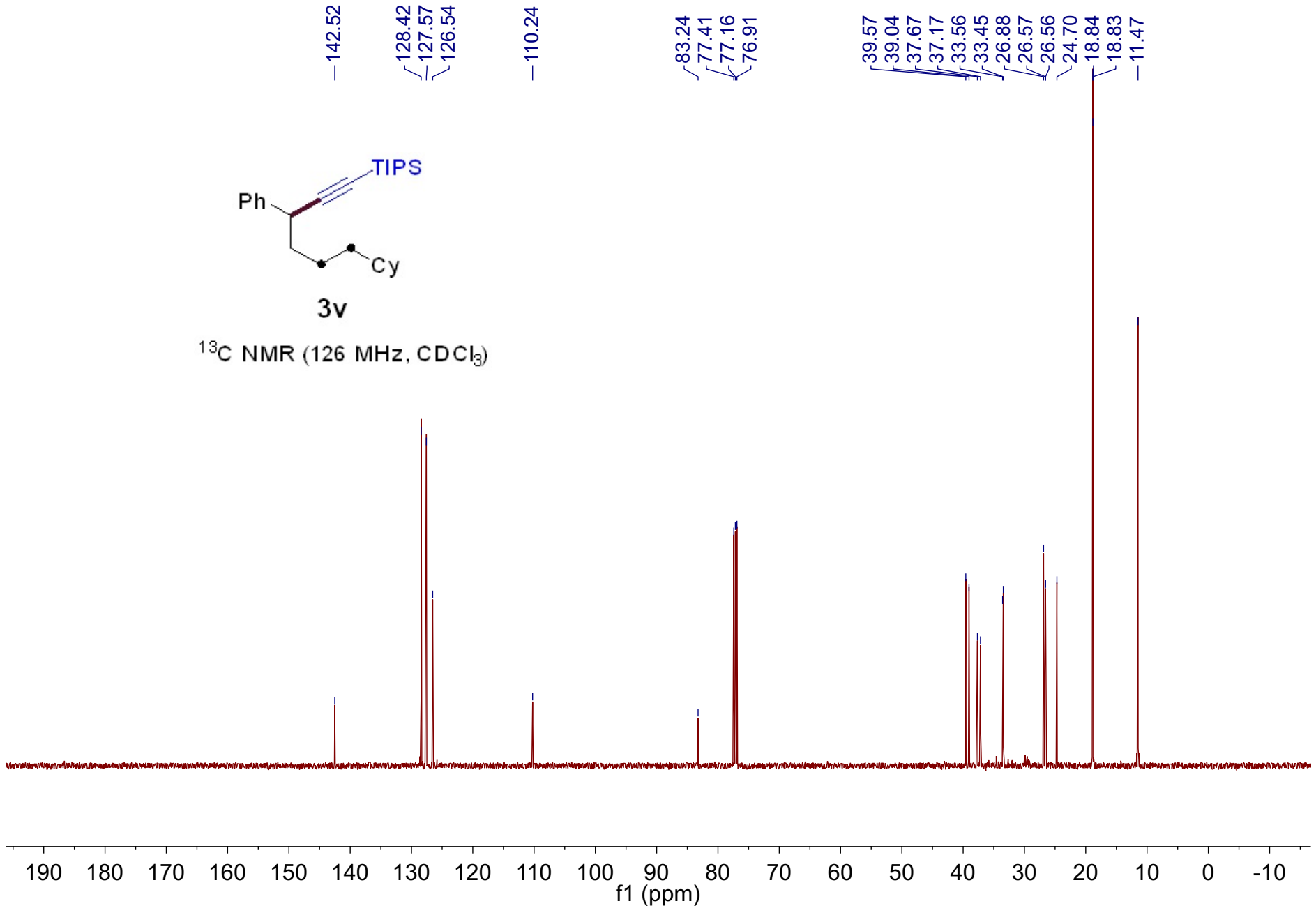
Supplementary Fig. 72. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3u**



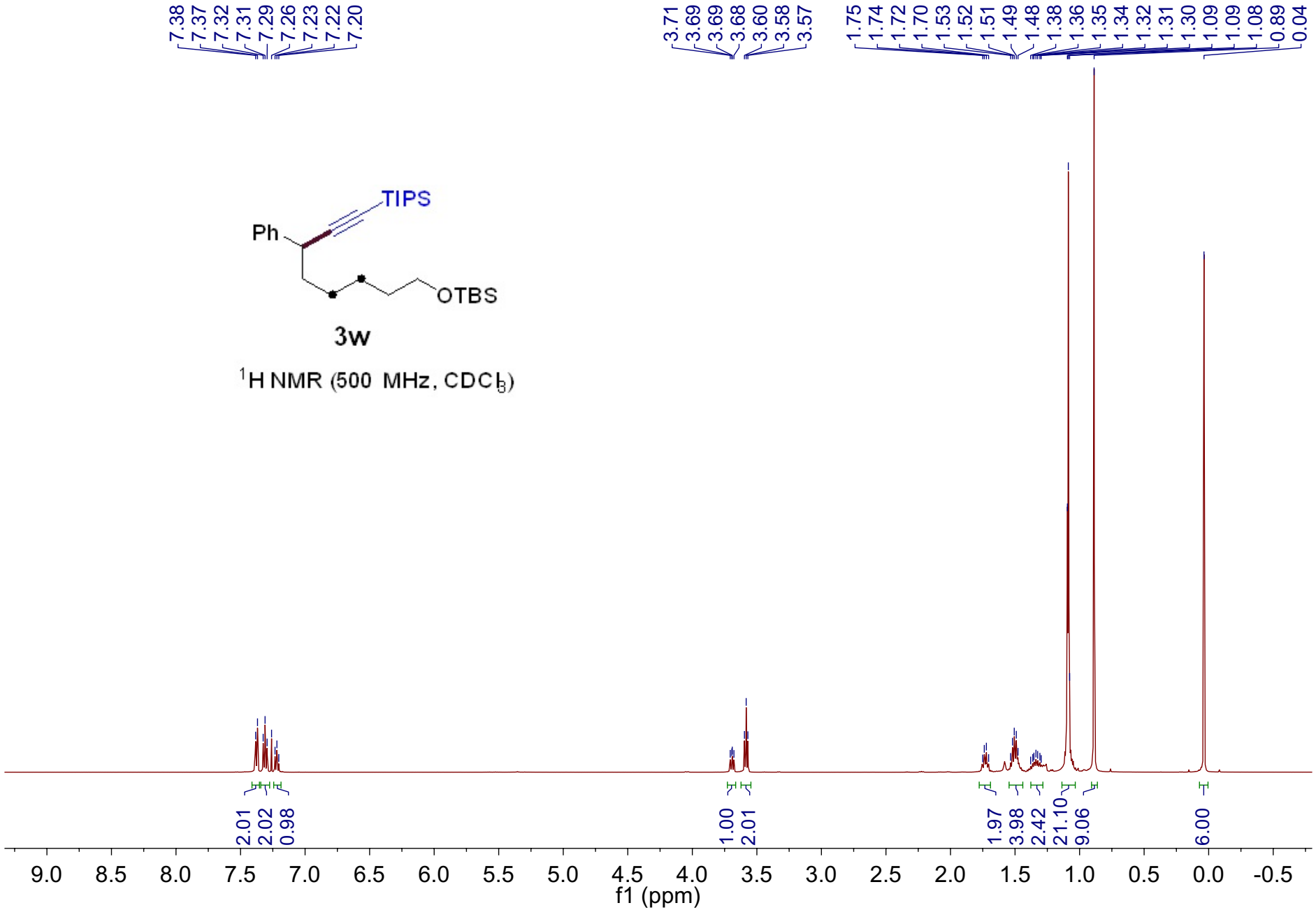
Supplementary Fig. 73. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3u**



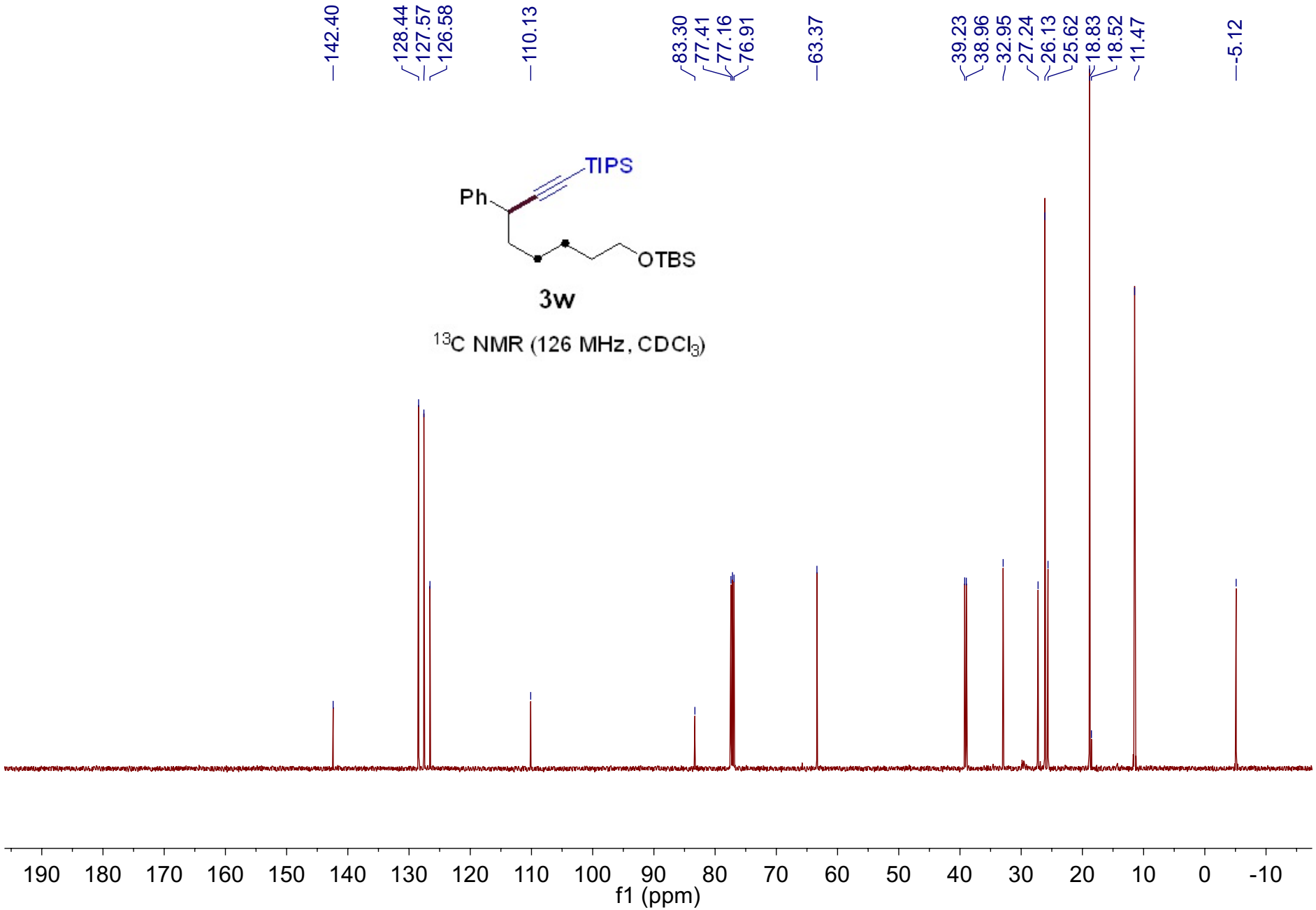
Supplementary Fig. 74. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3v**



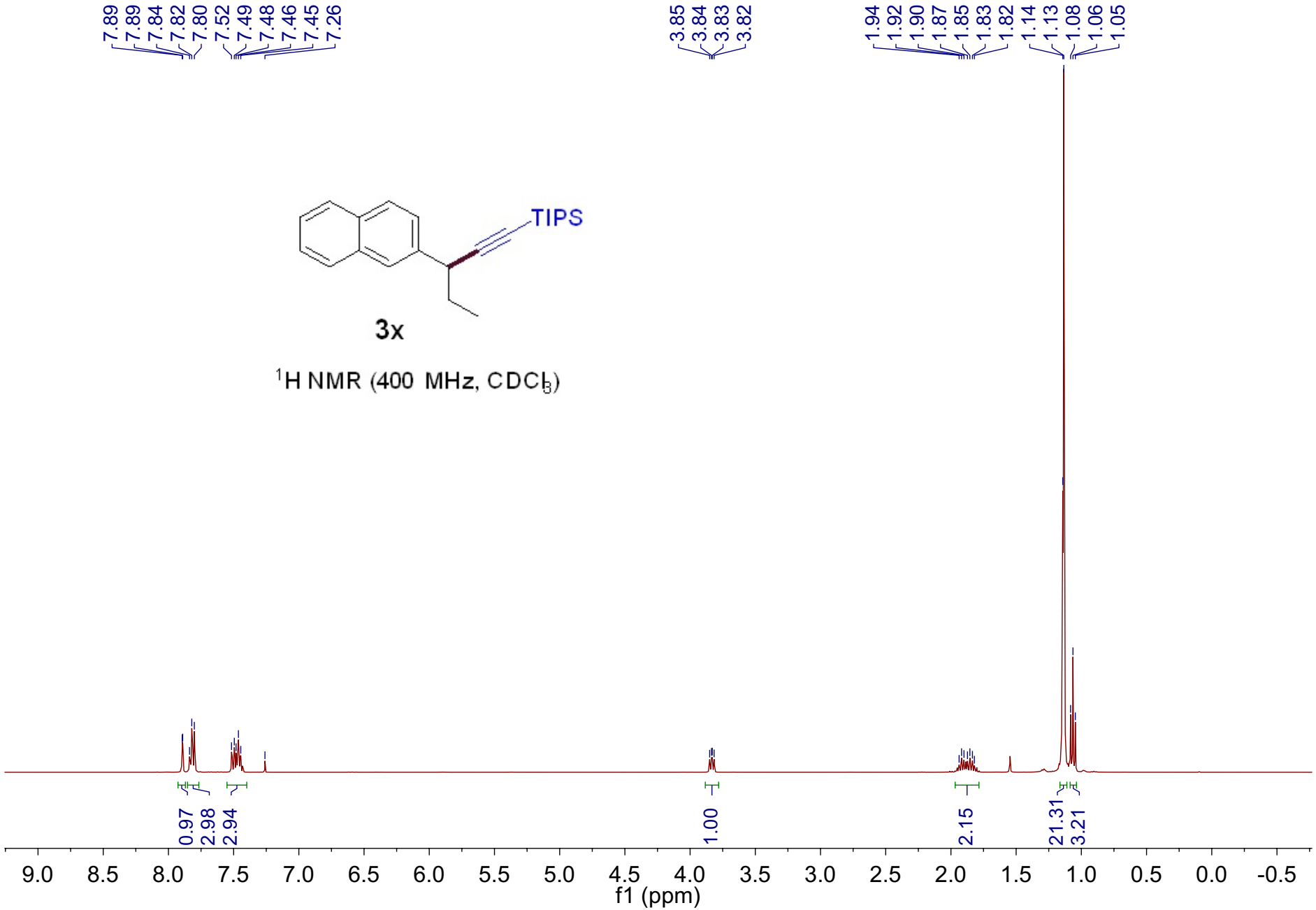
Supplementary Fig. 75. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3v**



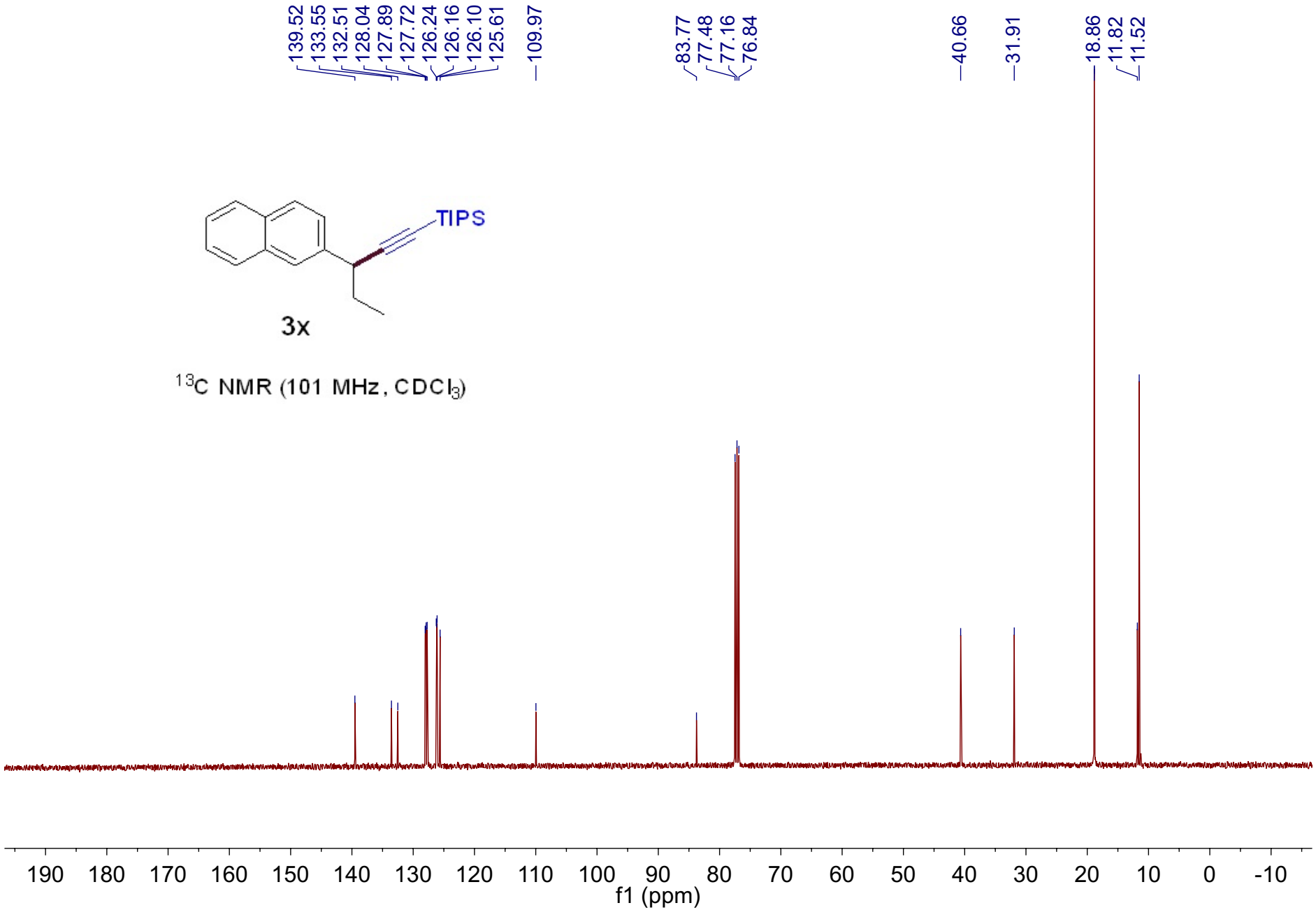
Supplementary Fig. 76. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3w**



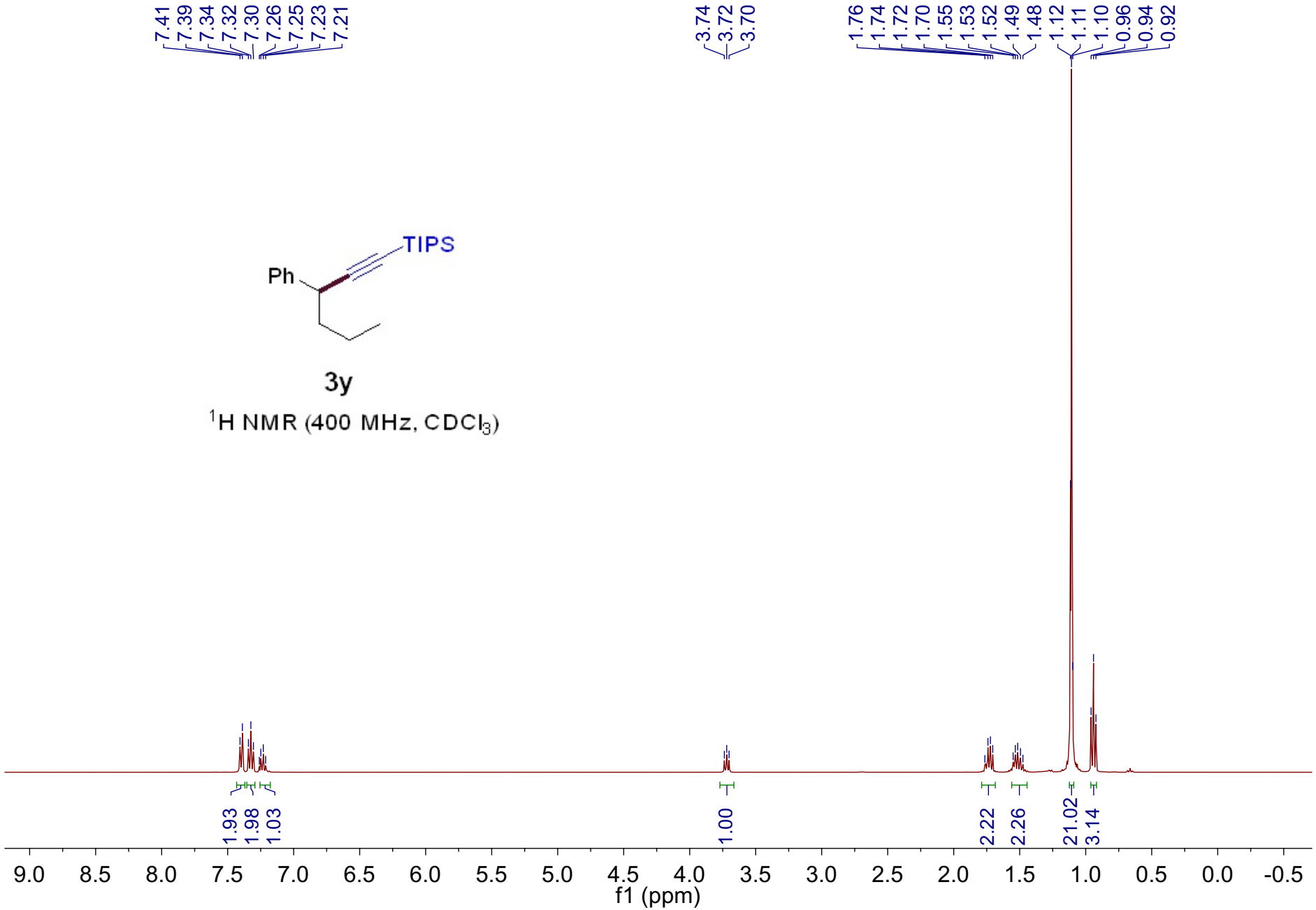
Supplementary Fig. 77. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3w**



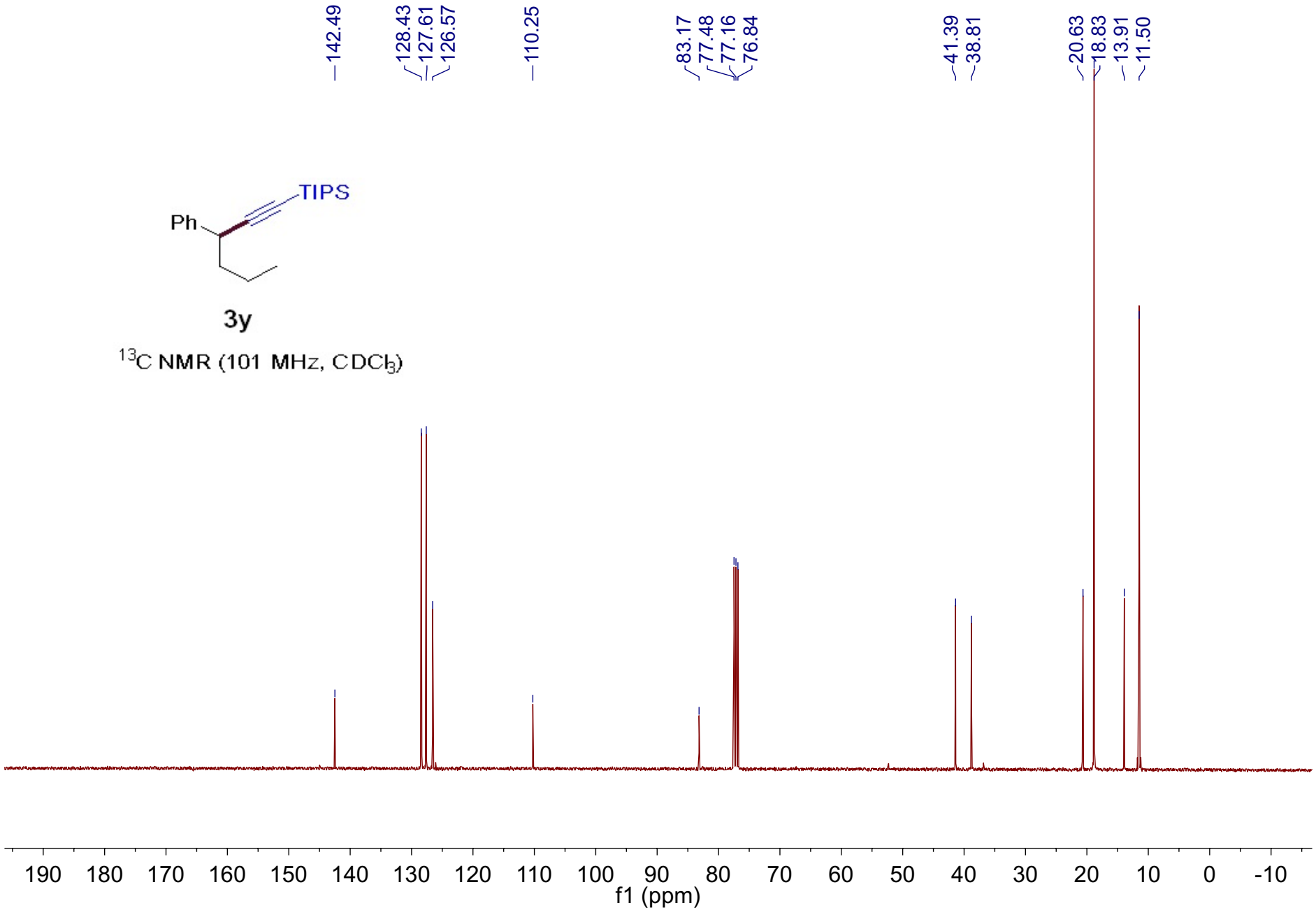
Supplementary Fig. 78. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3x**



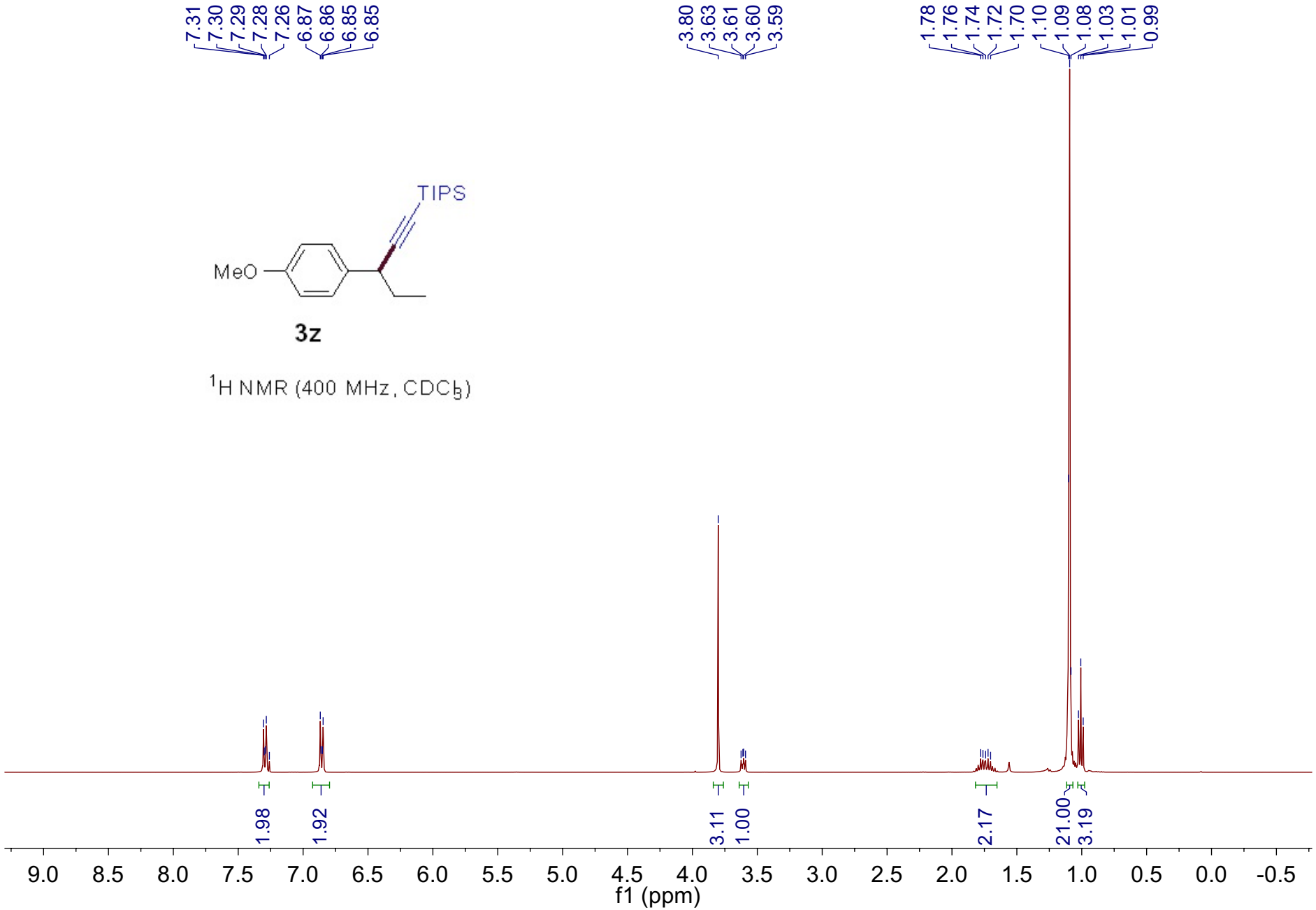
Supplementary Fig. 79. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3x**



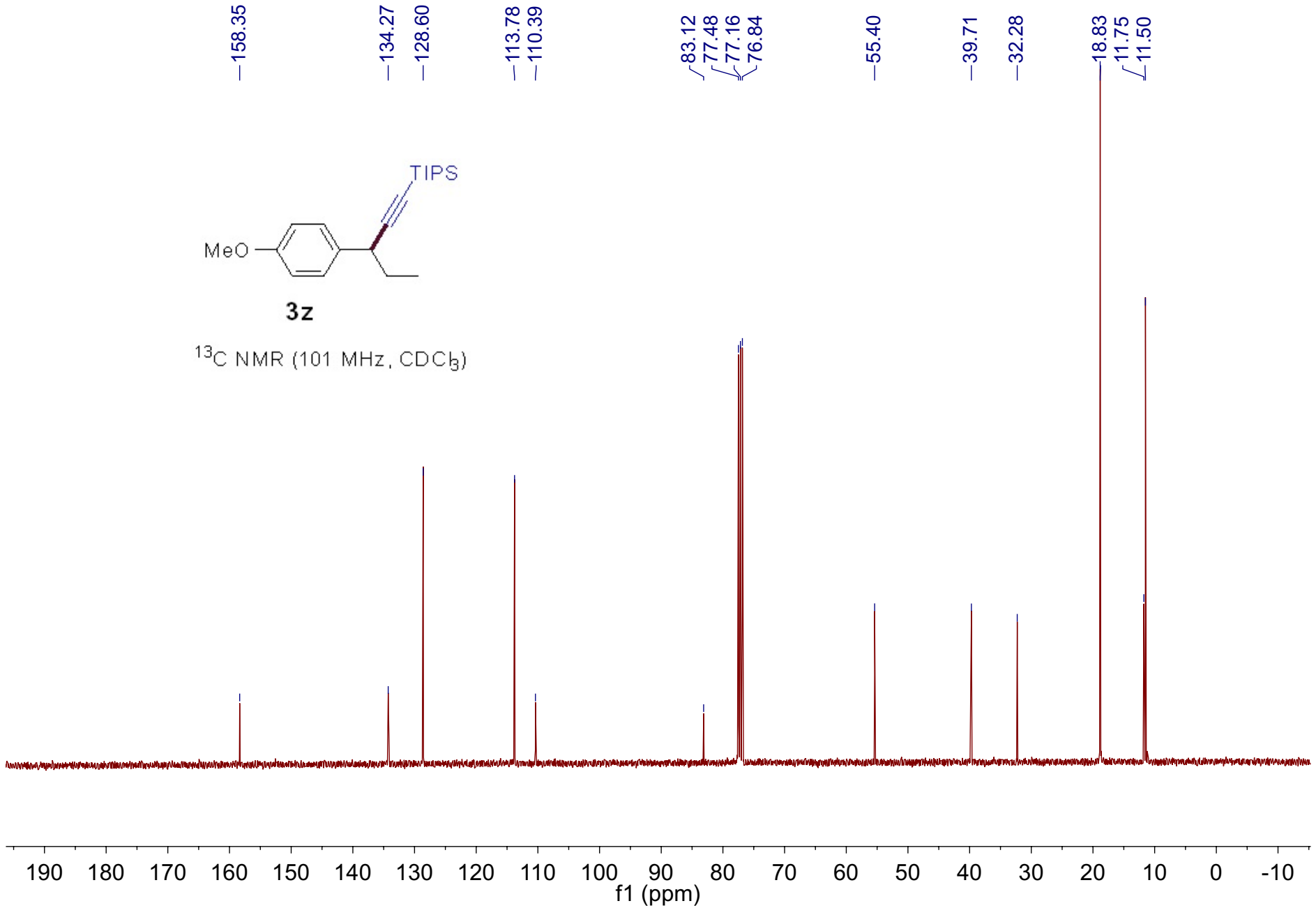
Supplementary Fig. 80. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3y**



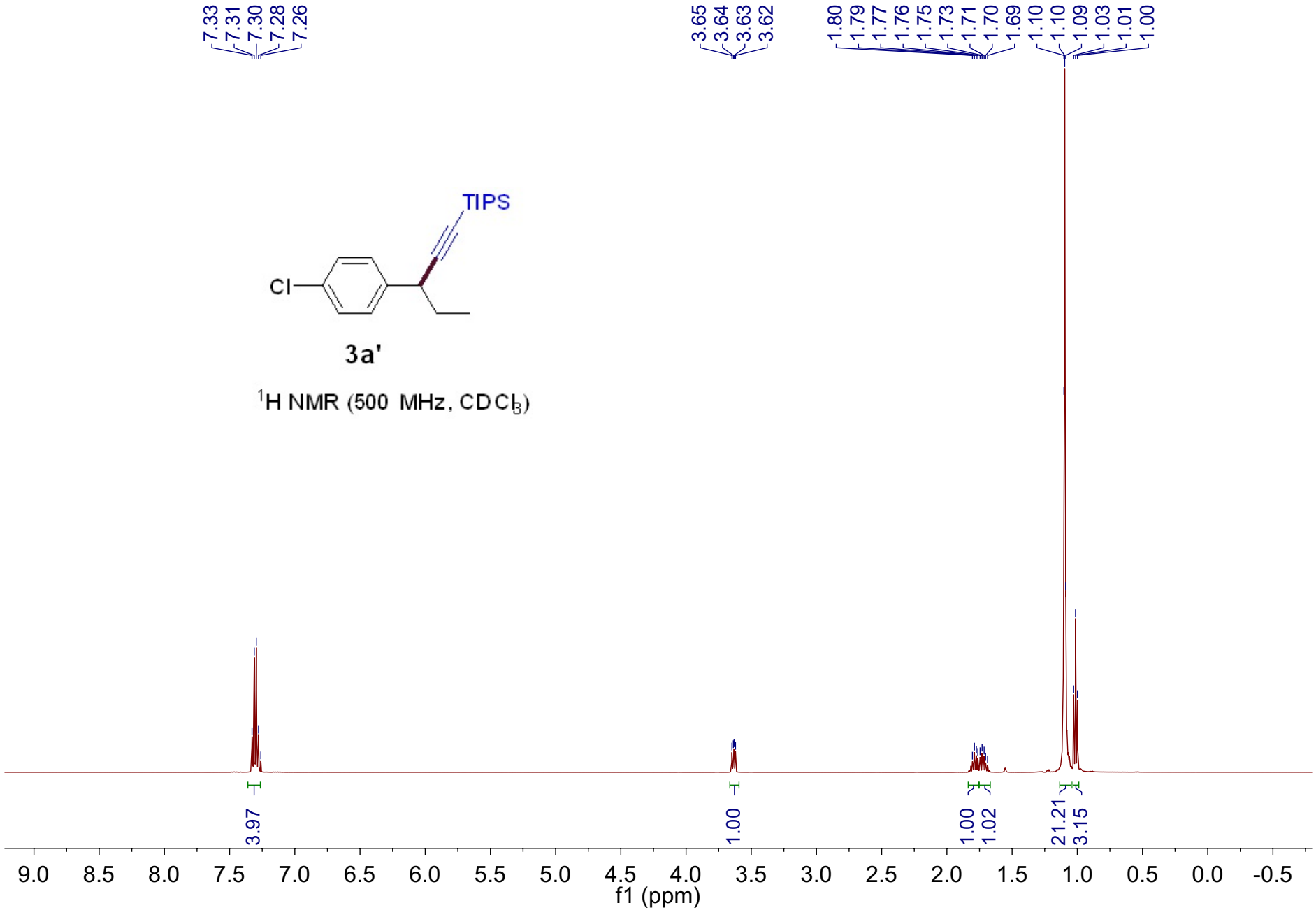
Supplementary Fig. 81. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3y**



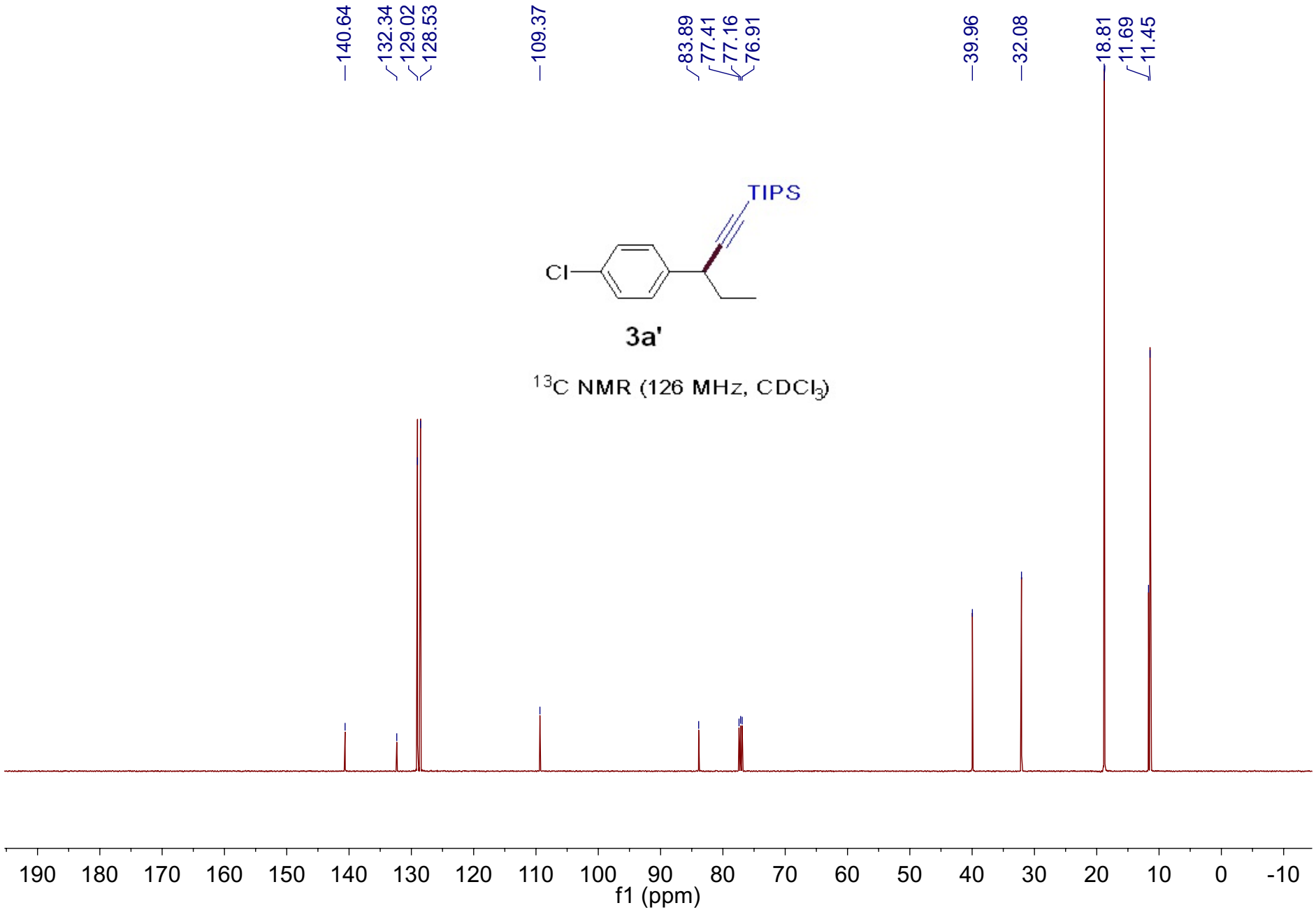
Supplementary Fig. 82. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3z**



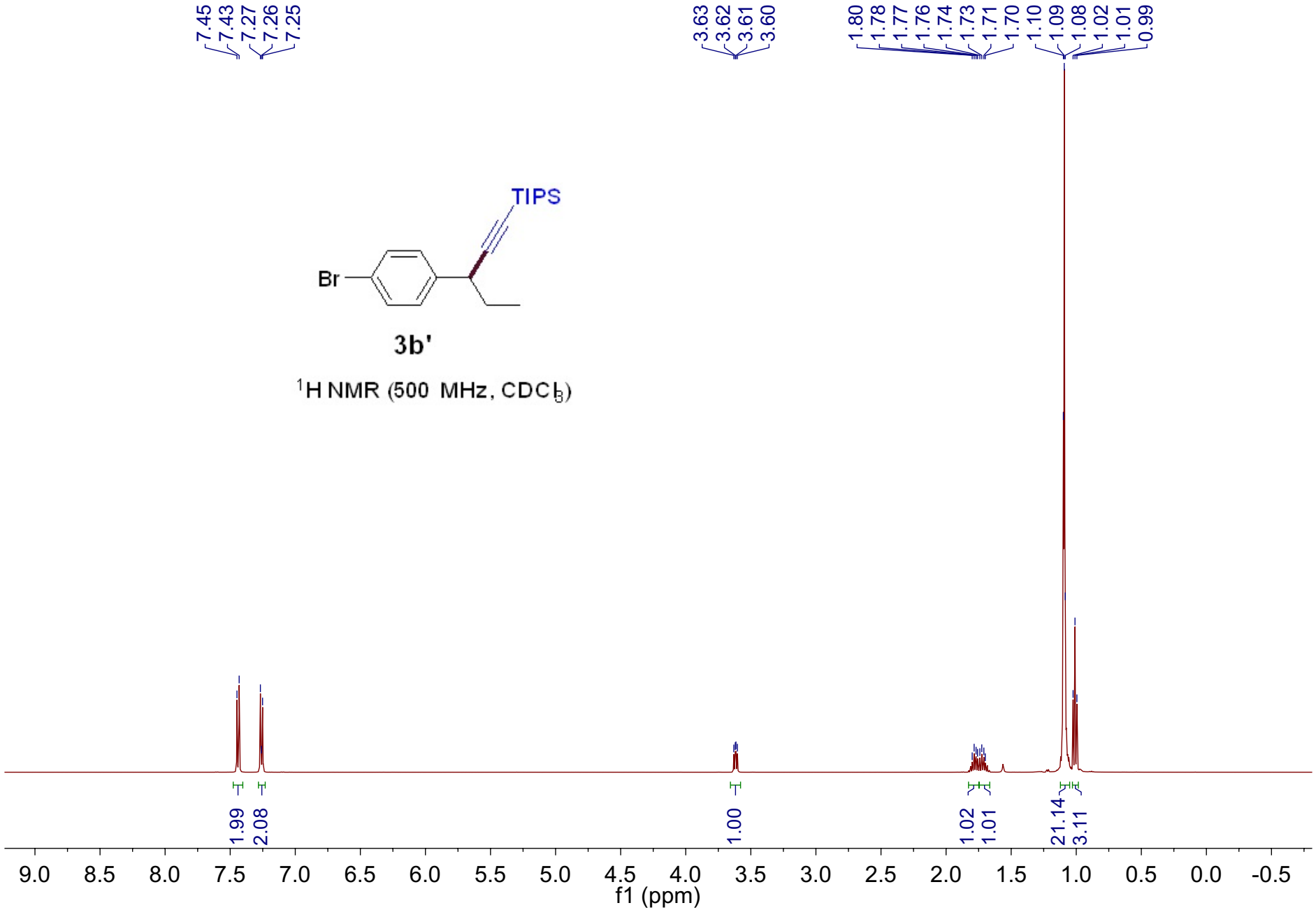
Supplementary Fig. 83. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3z**



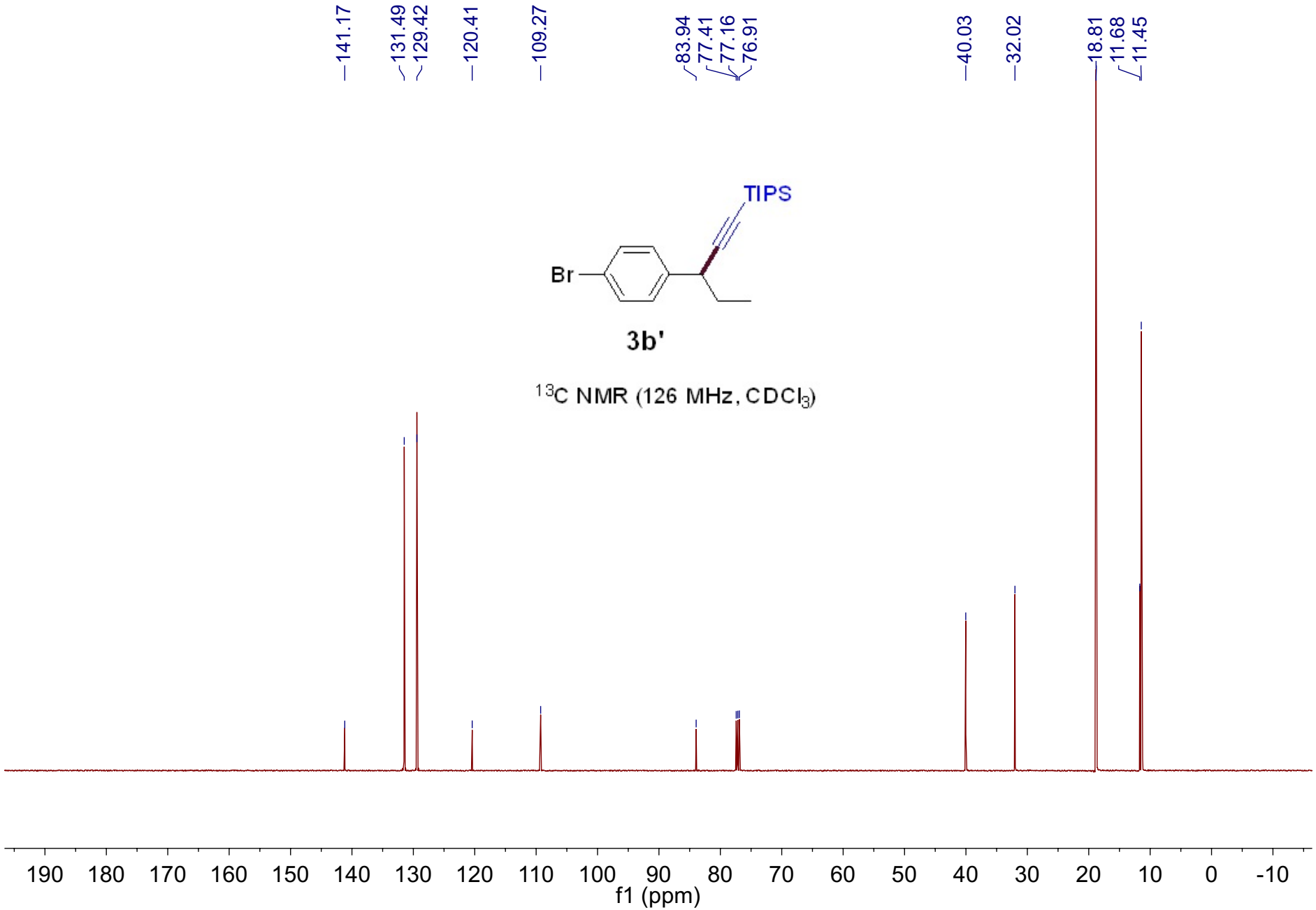
Supplementary Fig. 84. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3a'**



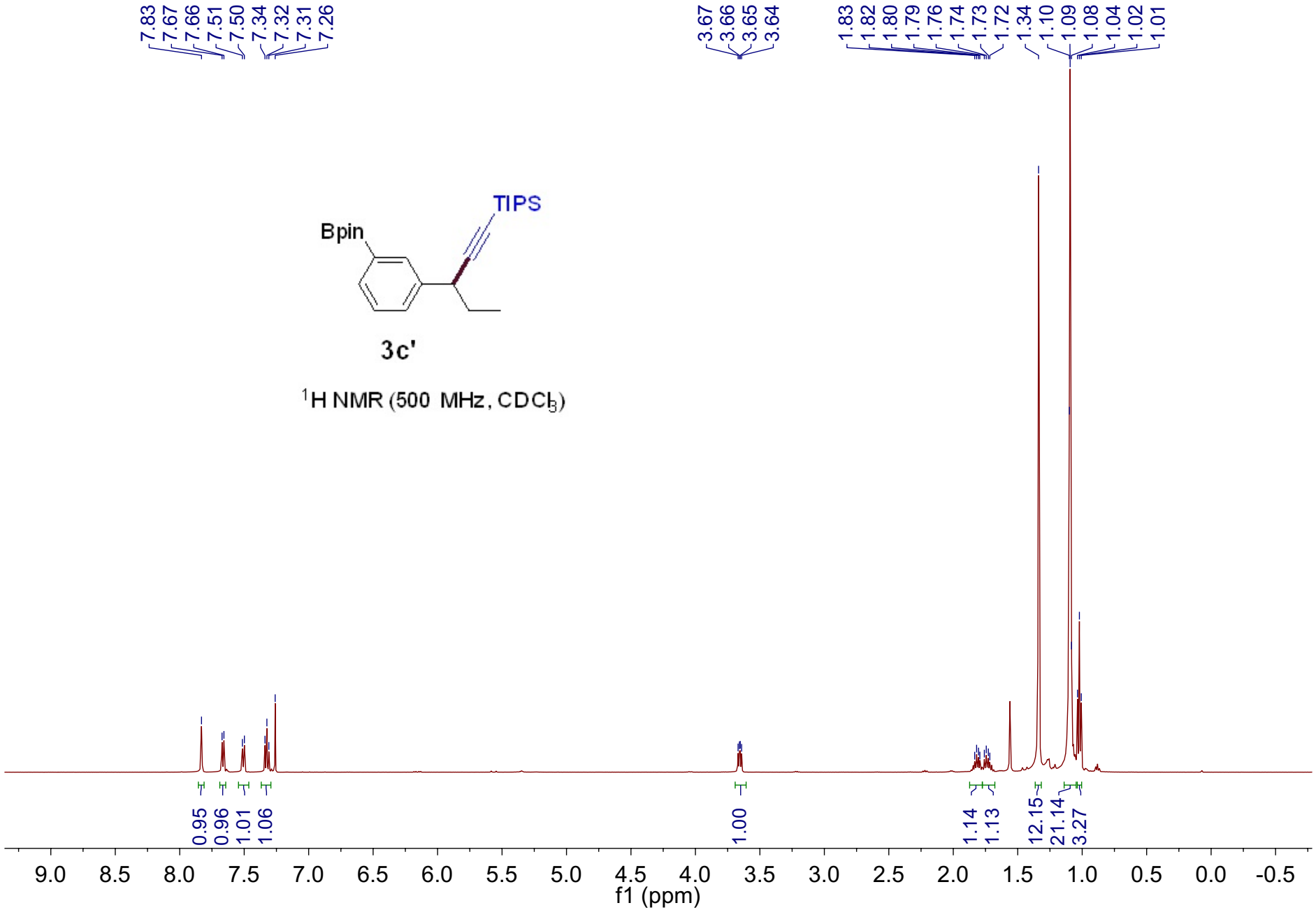
Supplementary Fig. 85. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3a'**



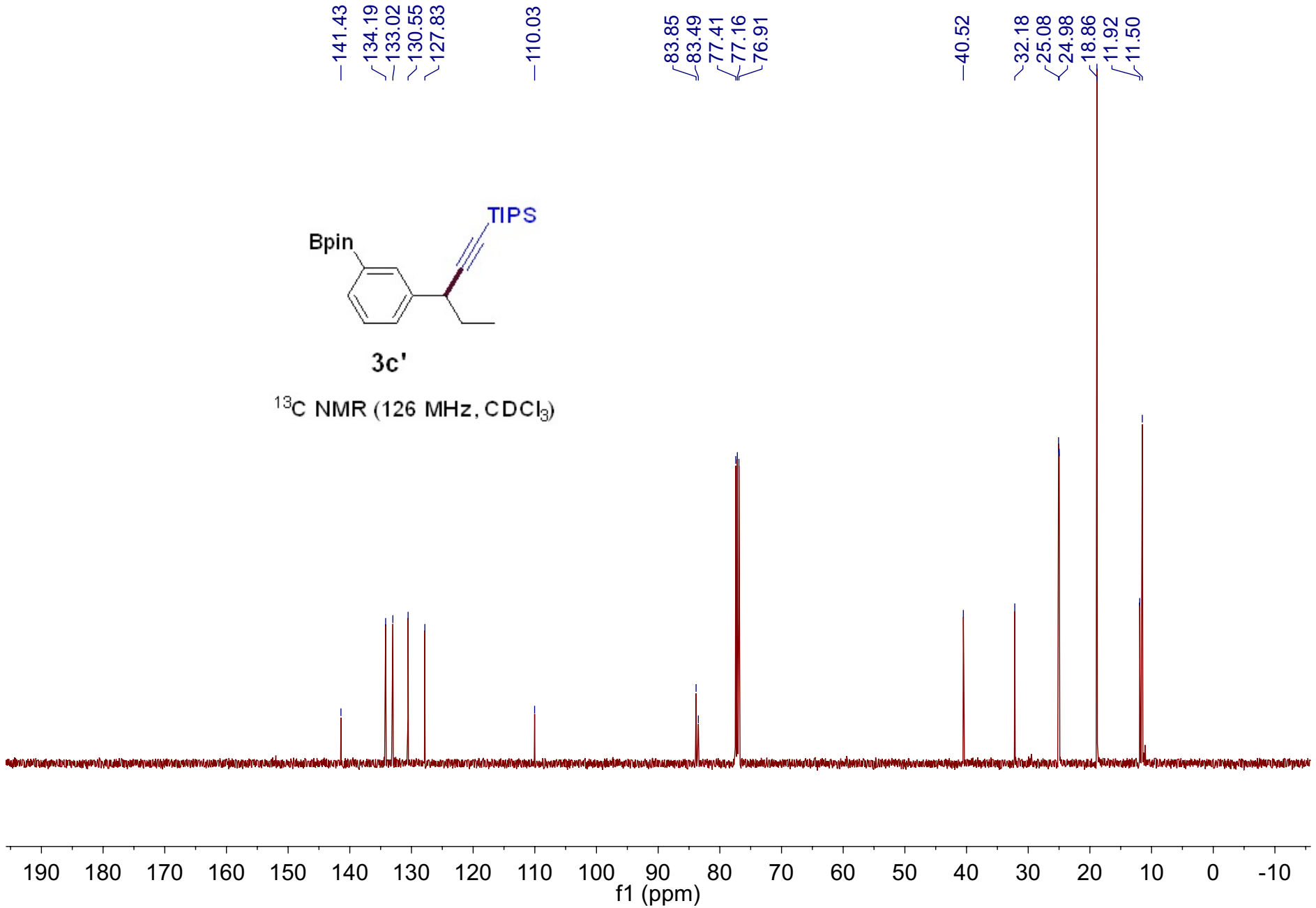
Supplementary Fig. 86. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3b'**



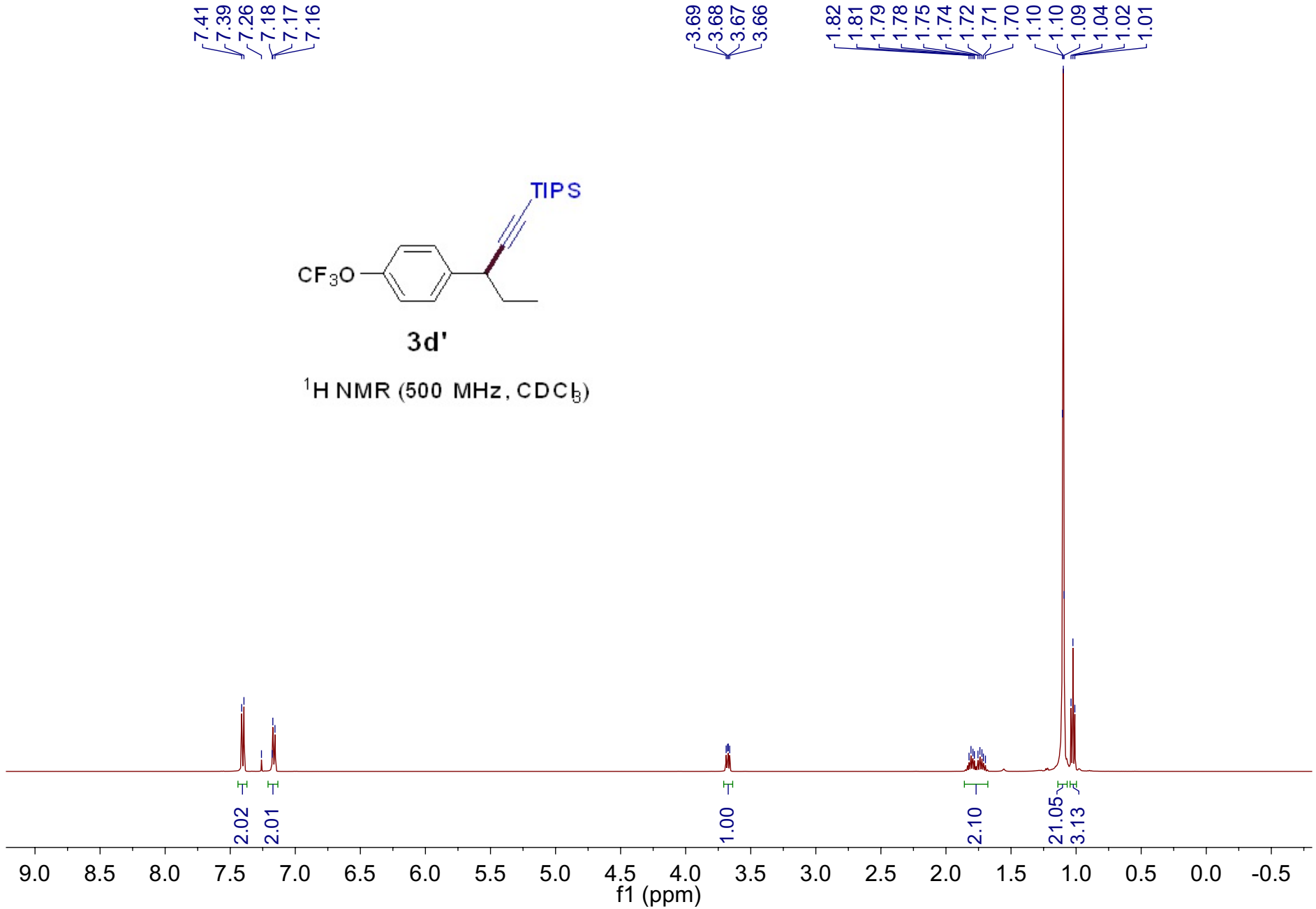
Supplementary Fig. 87. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3b'**



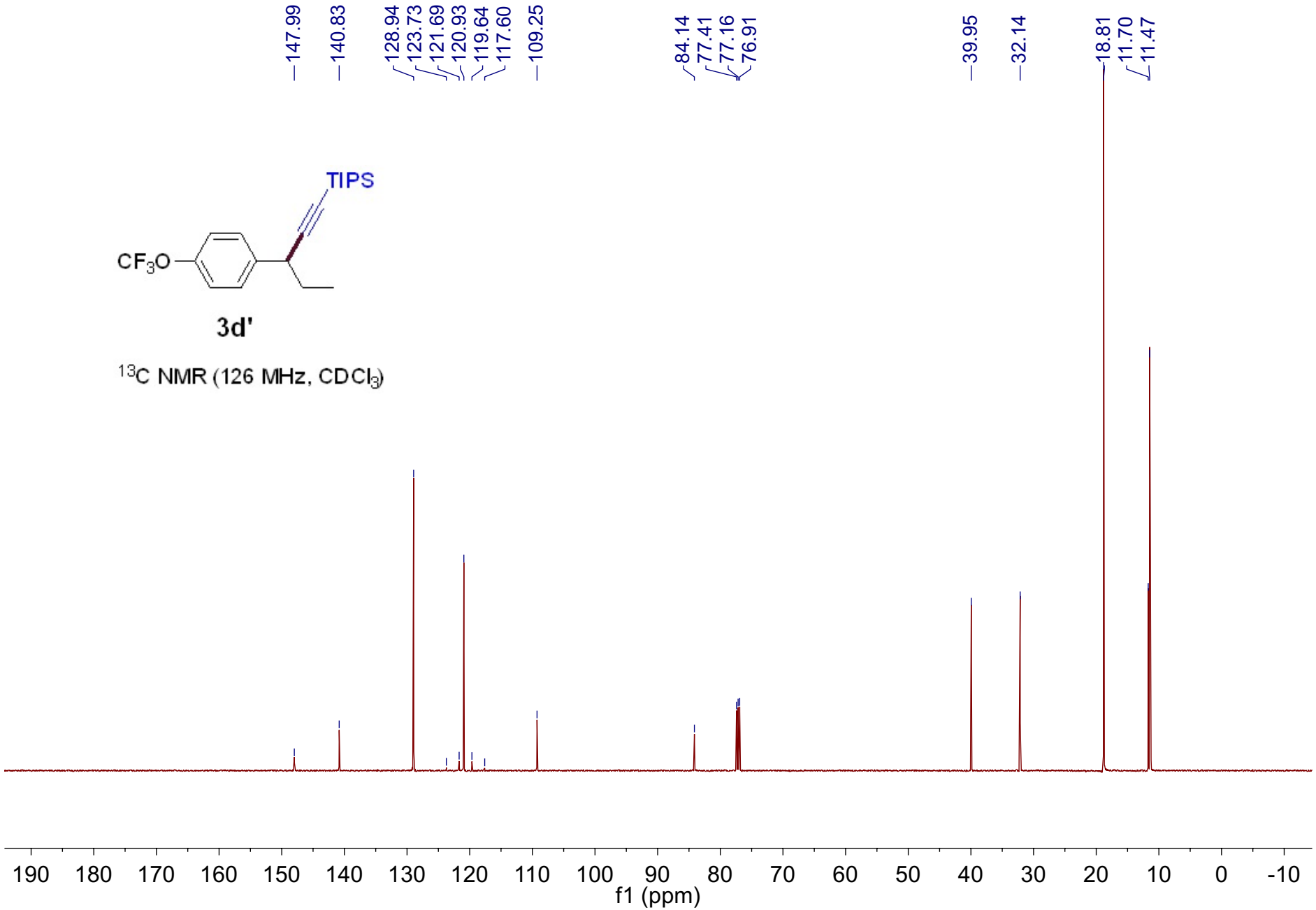
Supplementary Fig. 88. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3c'**



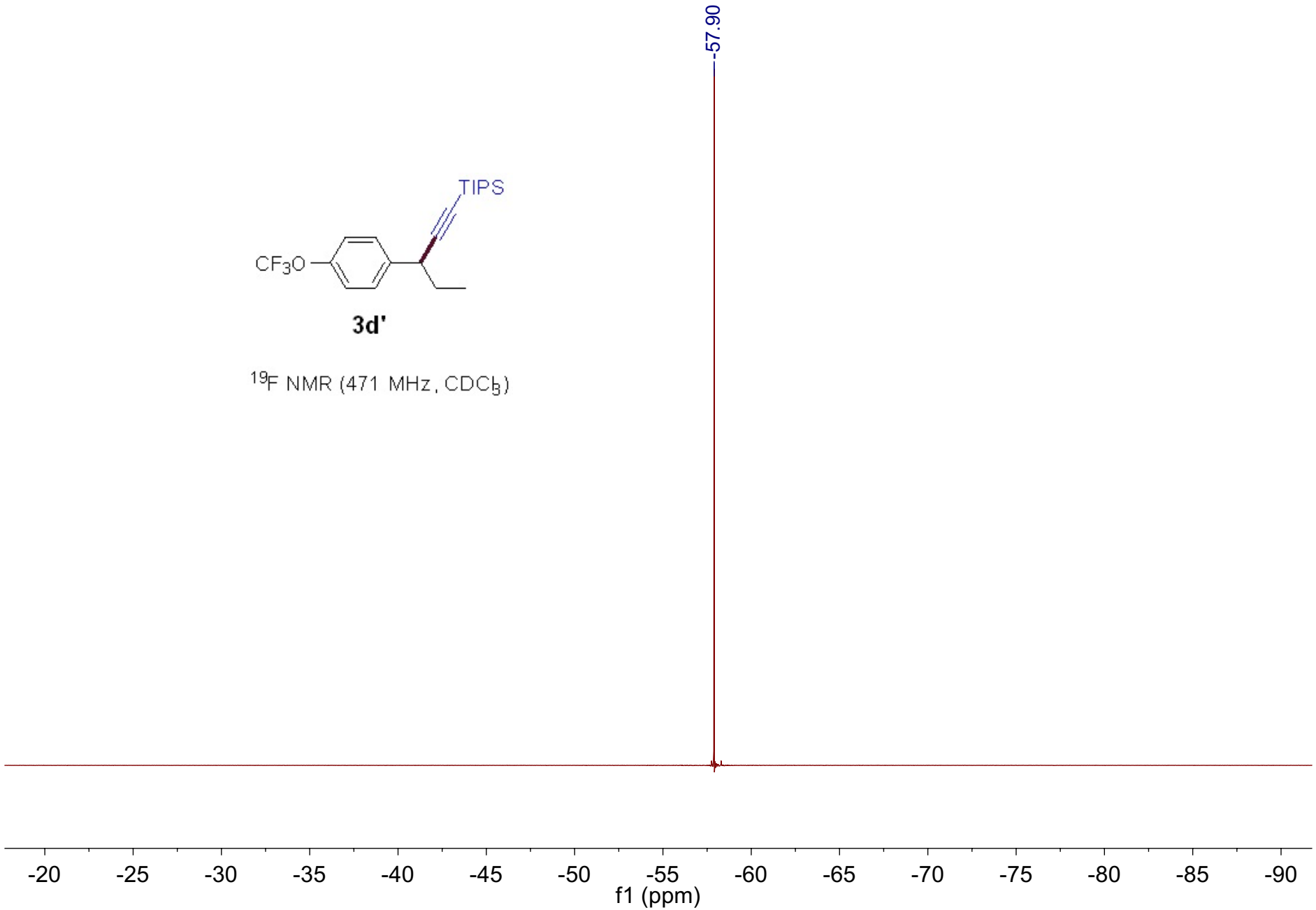
Supplementary Fig. 89. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3c'**



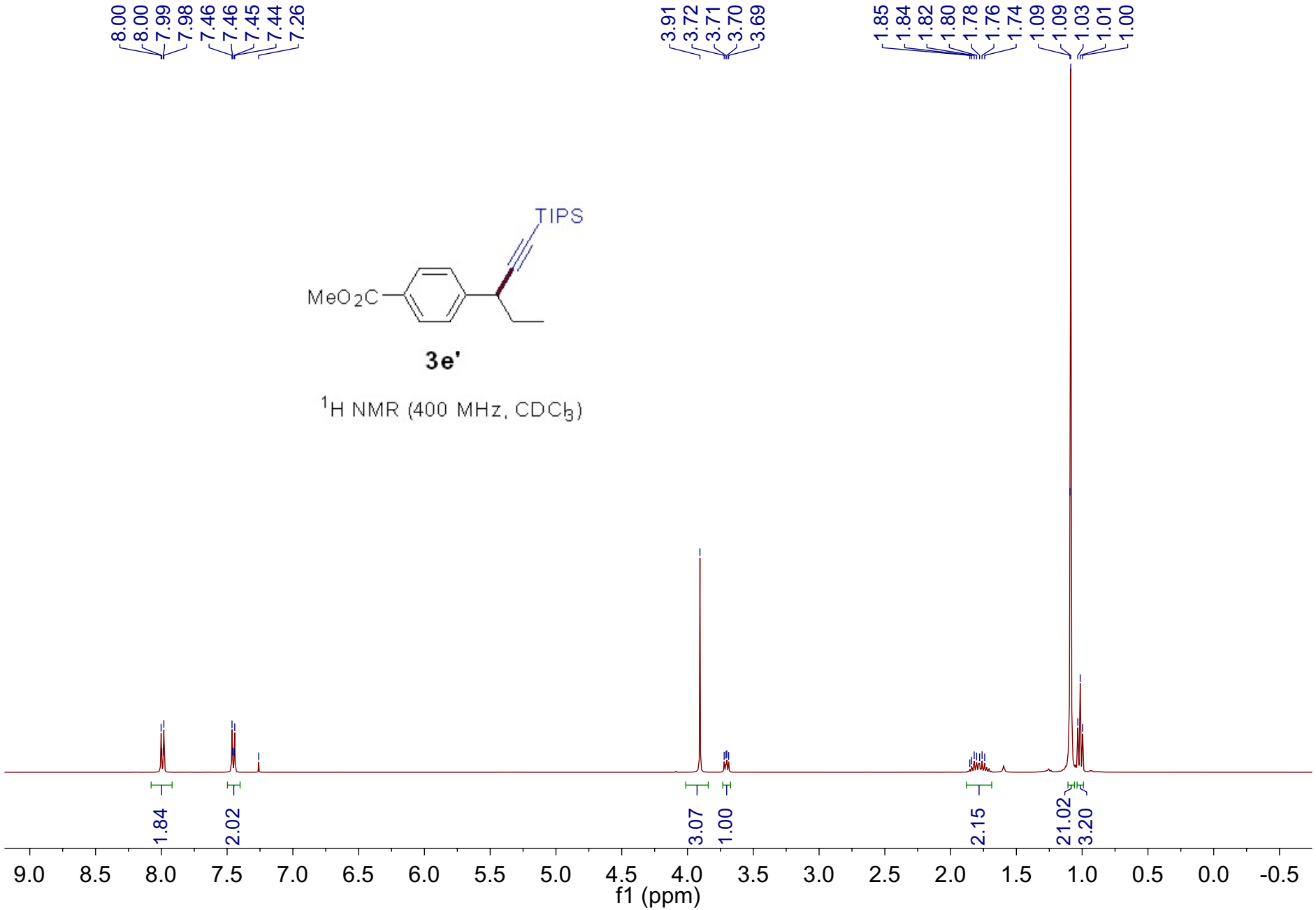
Supplementary Fig. 90. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3d'**



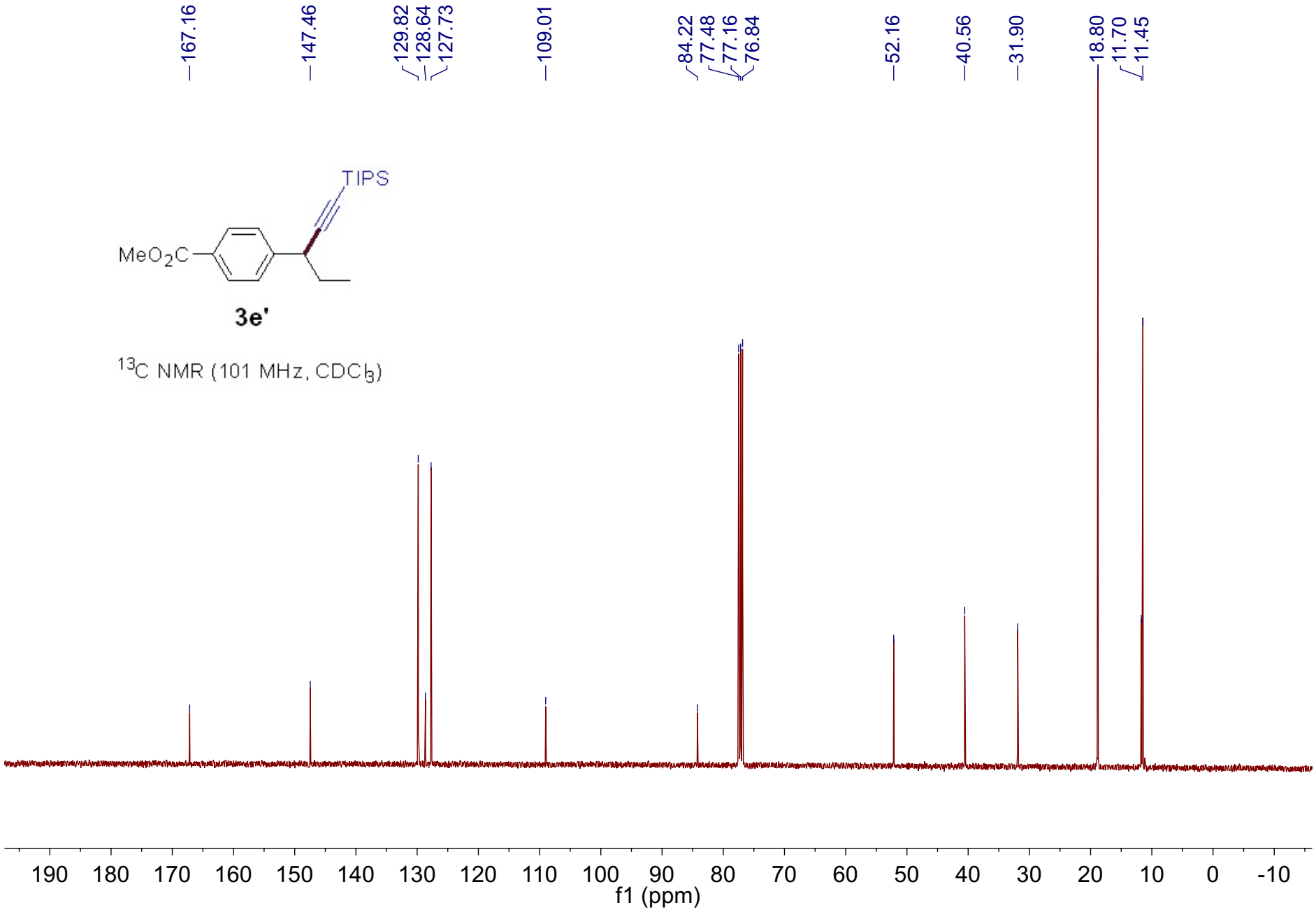
Supplementary Fig. 91. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3d'**



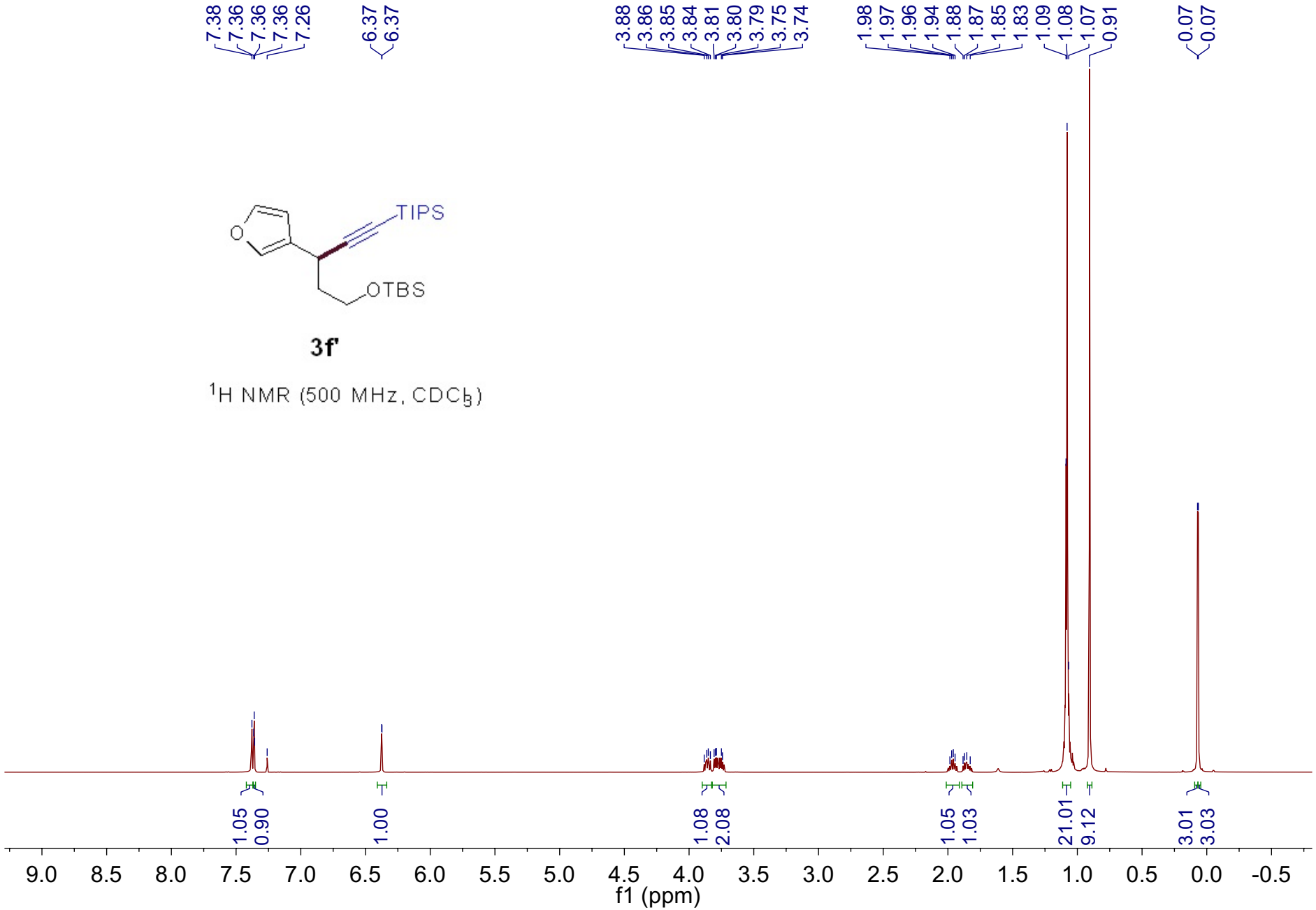
Supplementary Fig. 92. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **3d'**



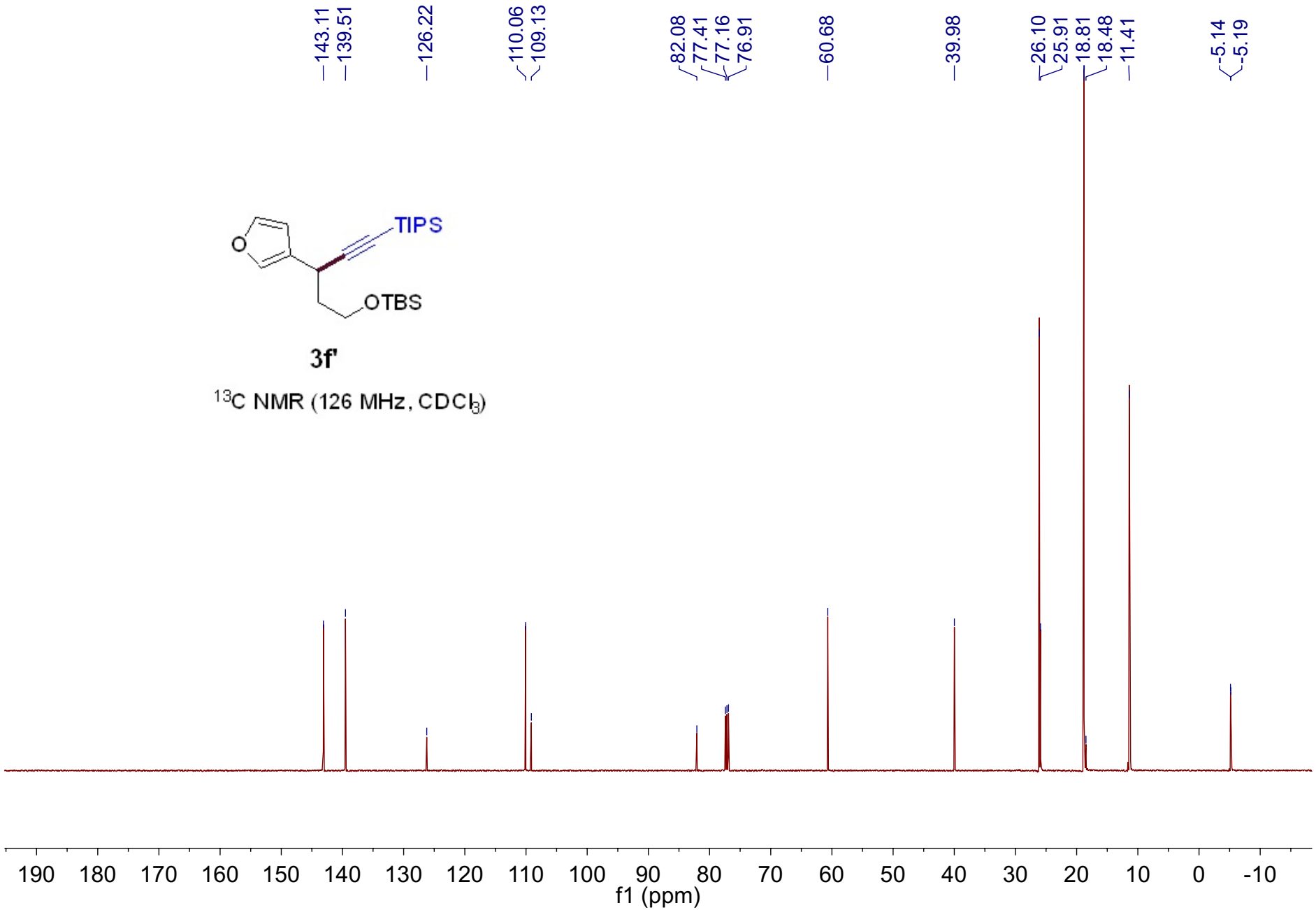
Supplementary Fig. 93. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3e'**



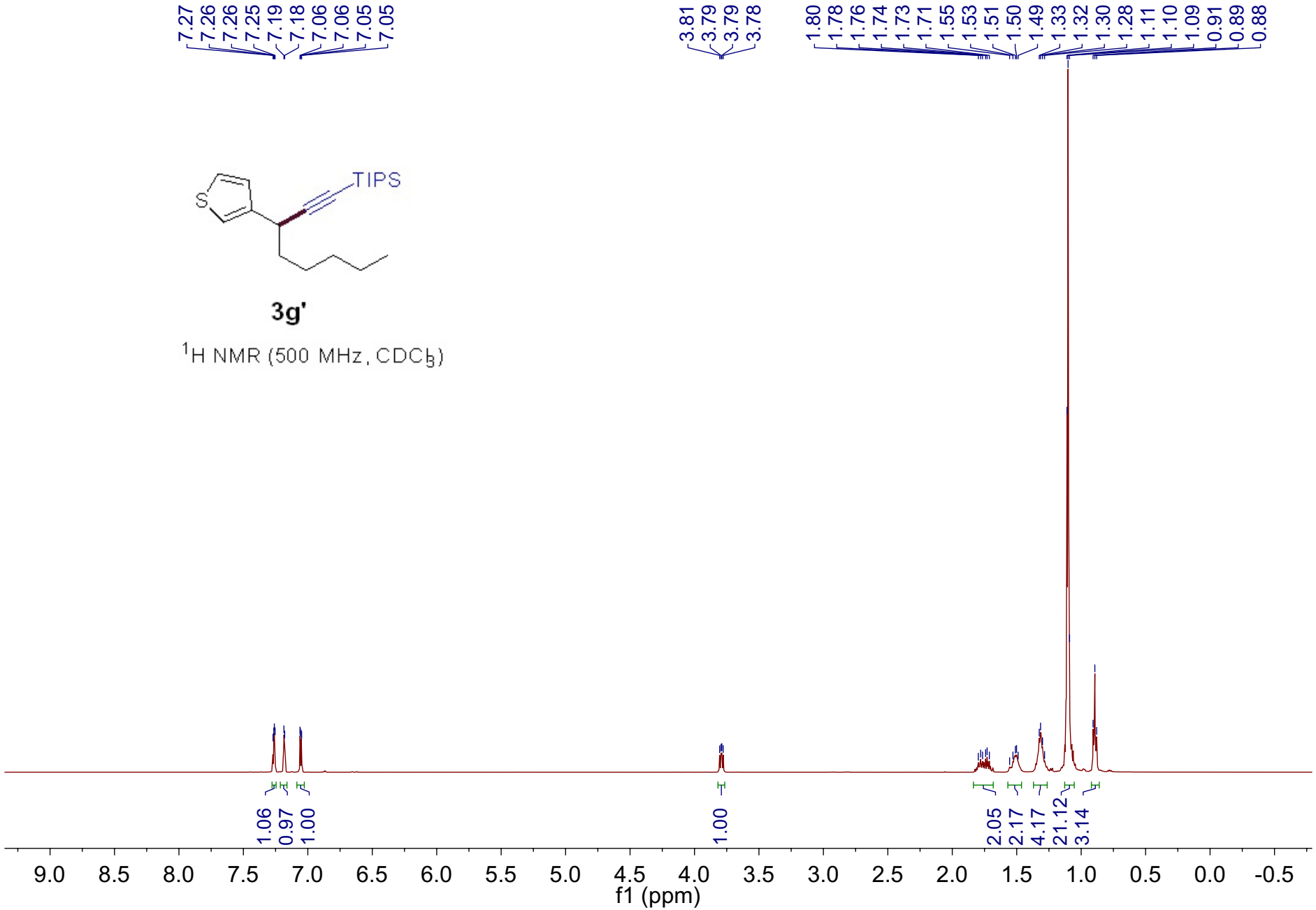
Supplementary Fig. 94. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3e'**



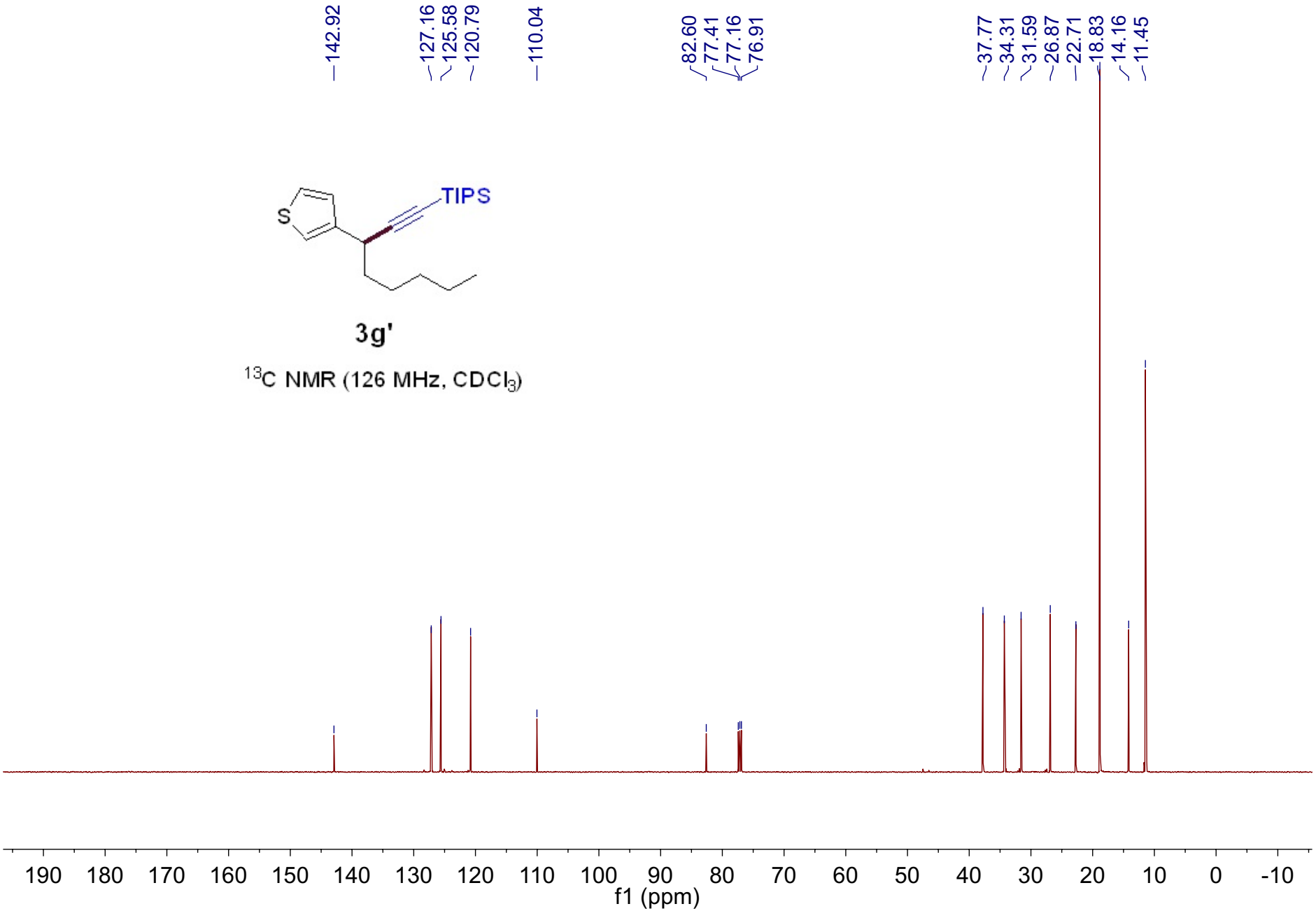
Supplementary Fig. 95. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3f'**



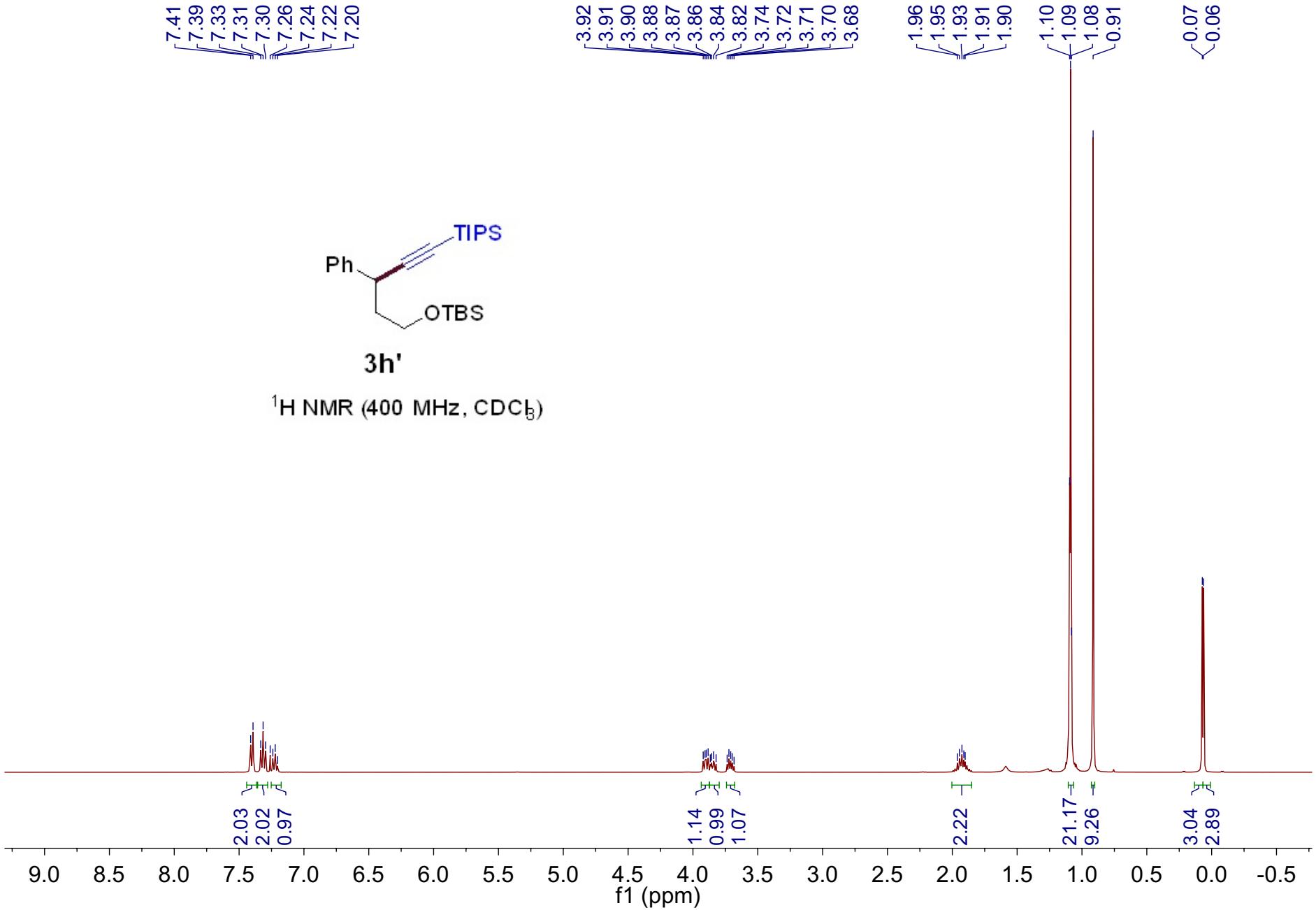
Supplementary Fig. 96. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3f'**



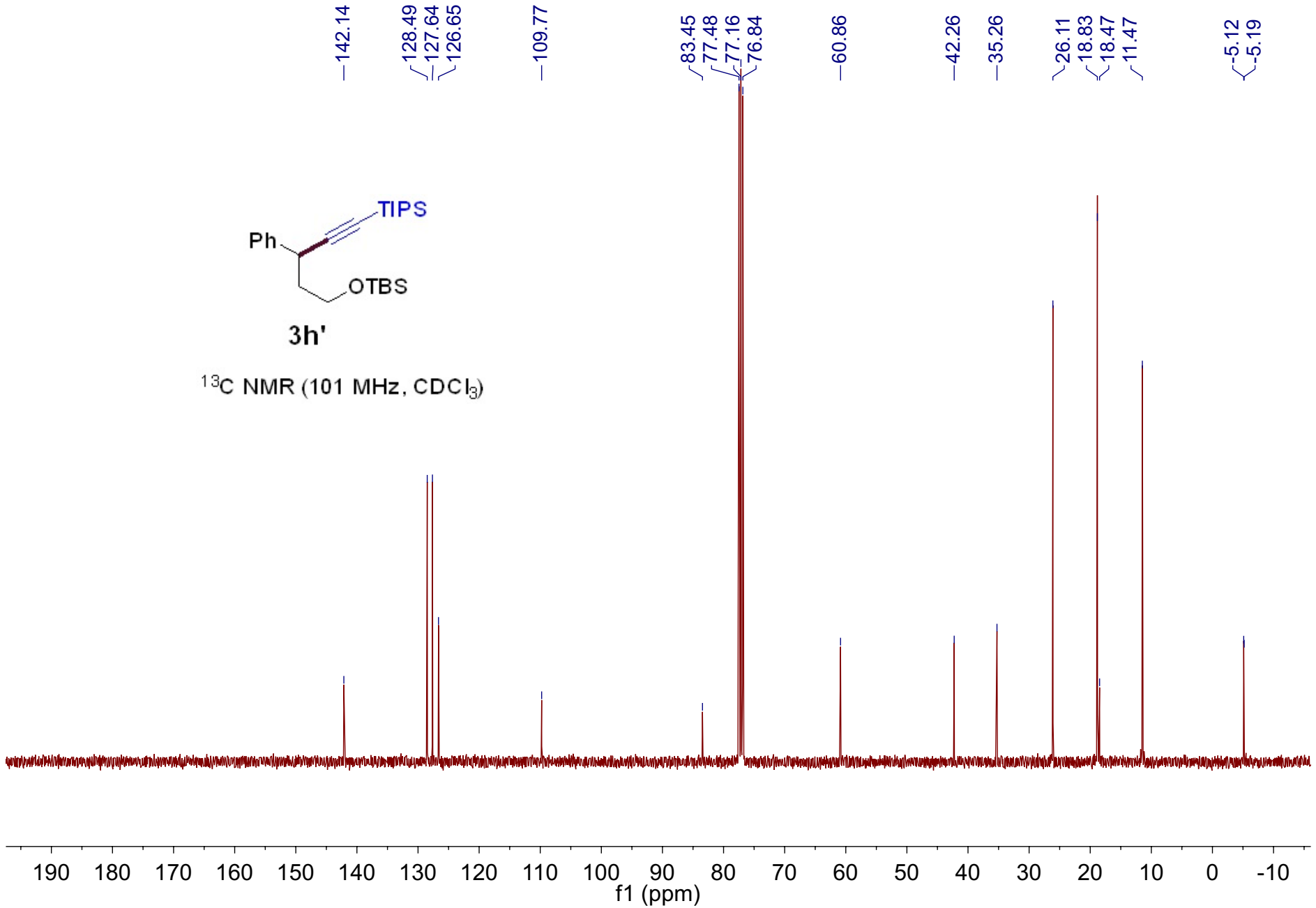
Supplementary Fig. 97. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3g'**



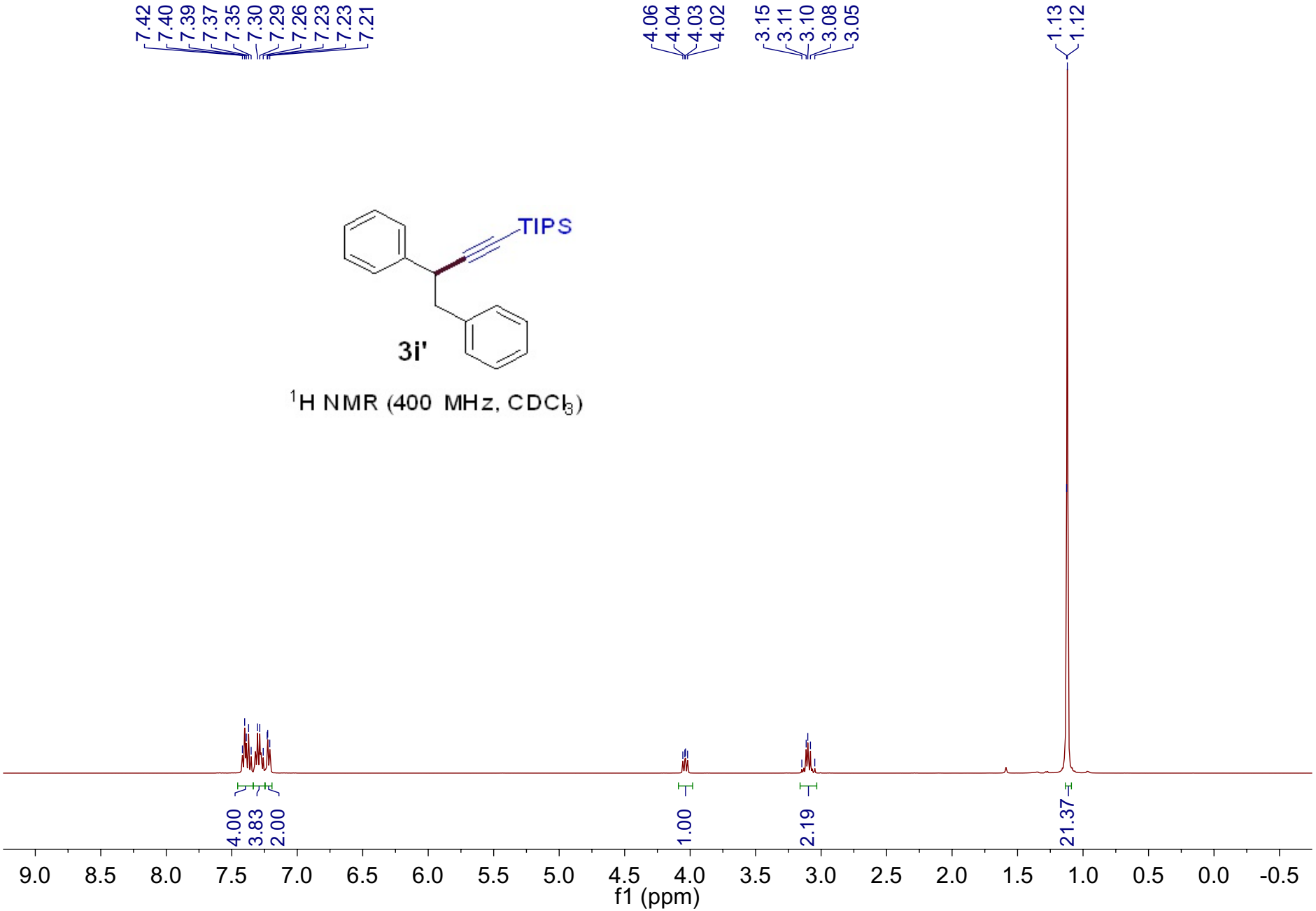
Supplementary Fig. 98. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3g'**



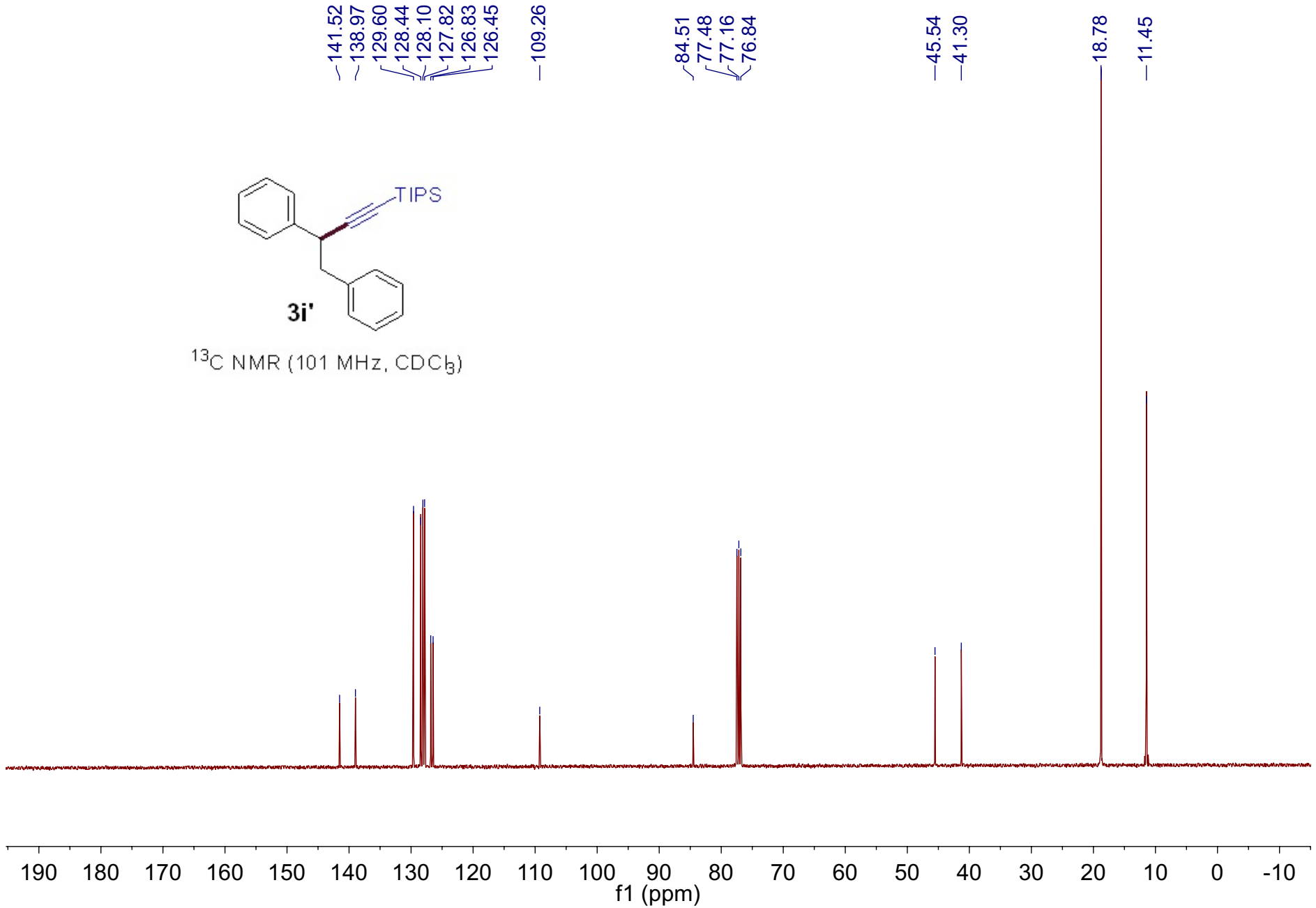
Supplementary Fig. 99. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3h'**



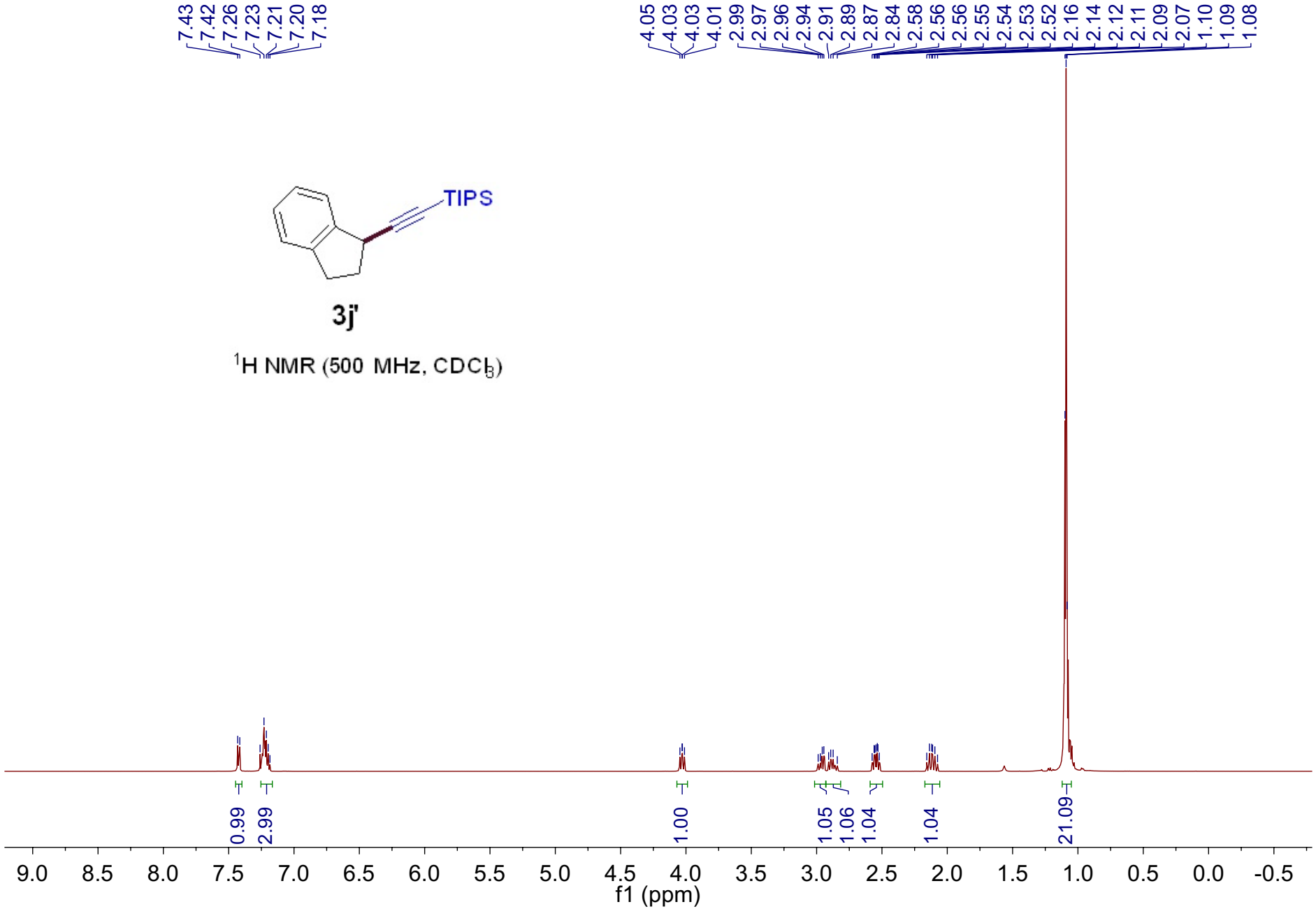
Supplementary Fig. 100. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3h'**



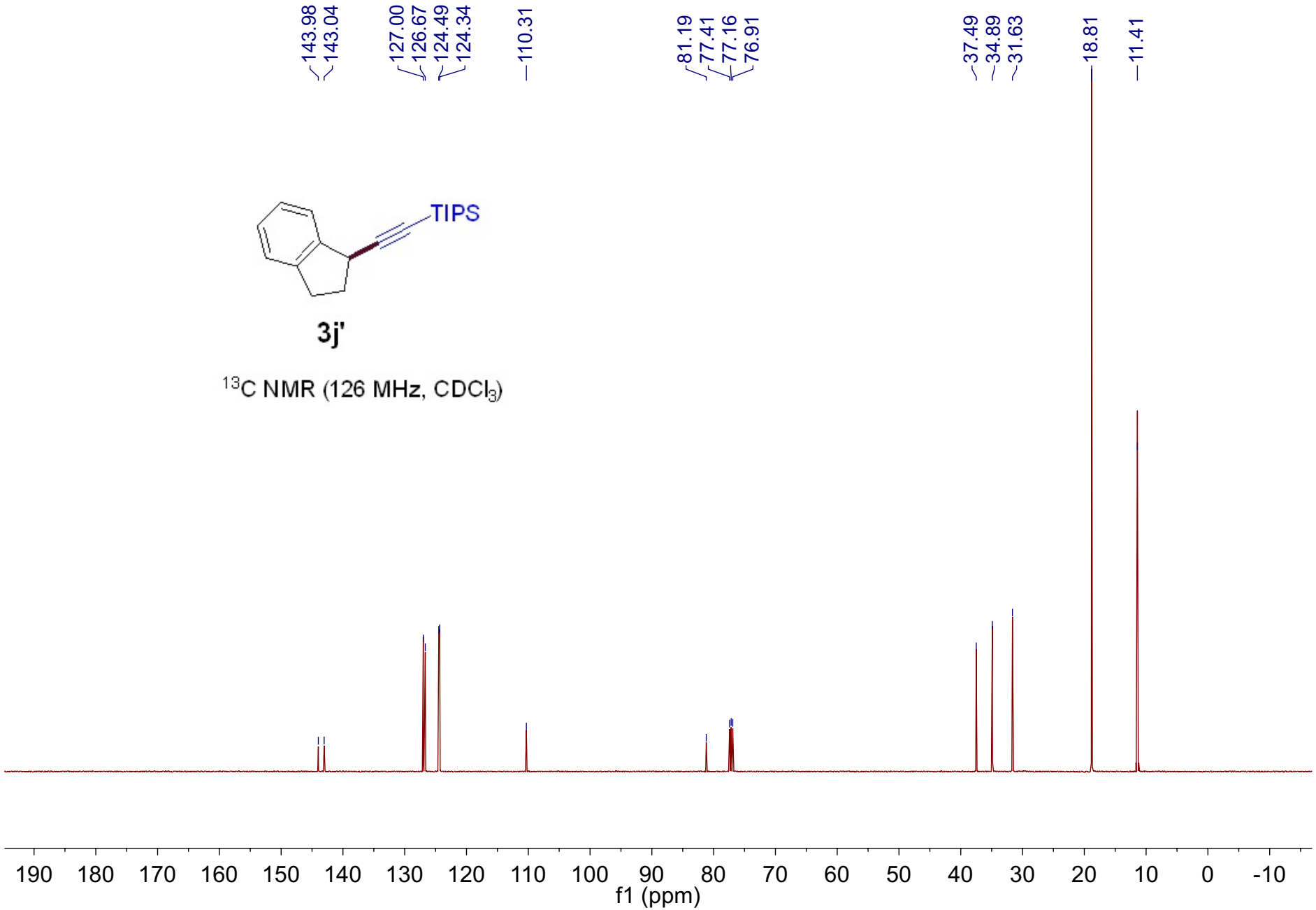
Supplementary Fig. 101. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3i'**



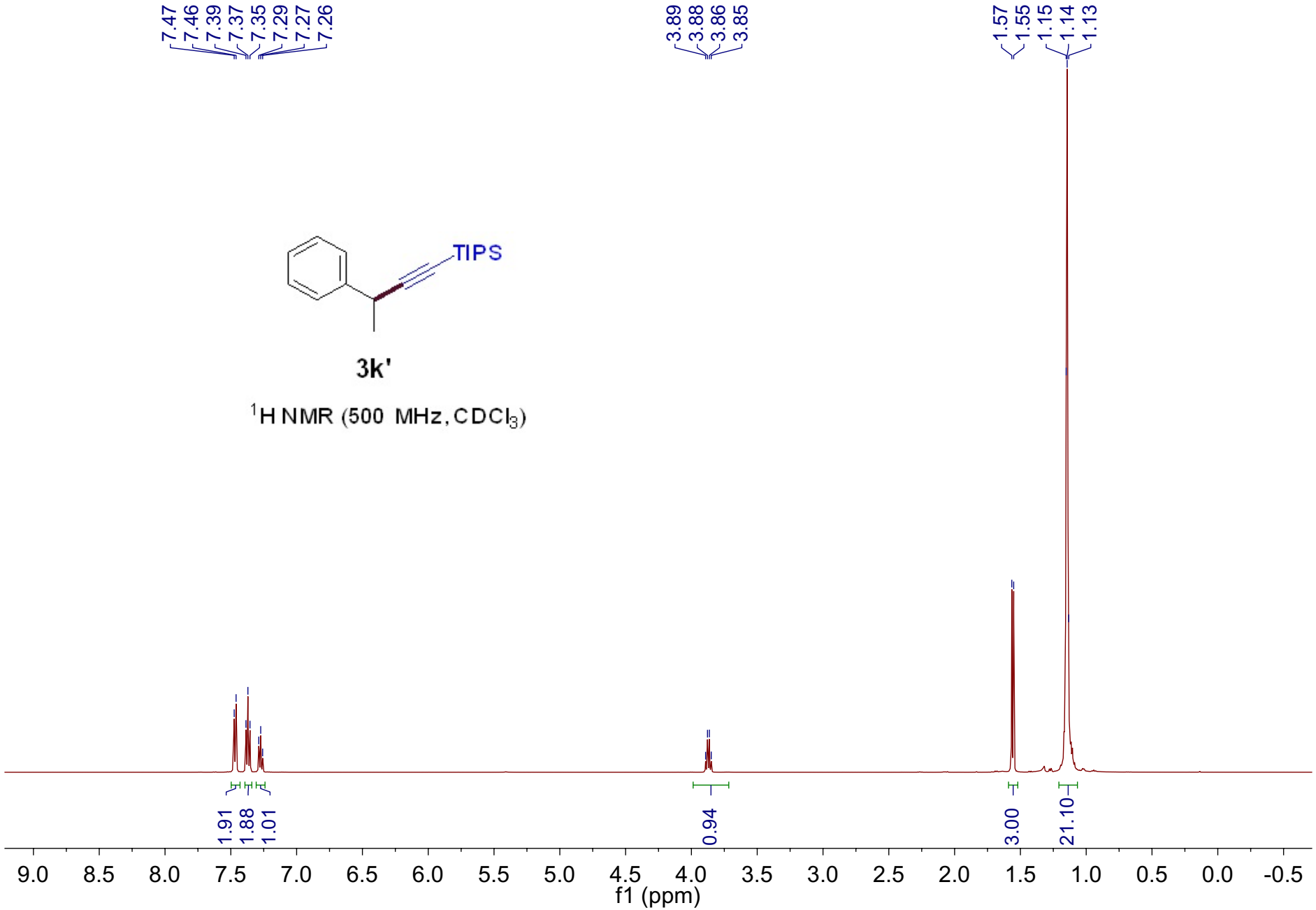
Supplementary Fig. 102. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3i'**



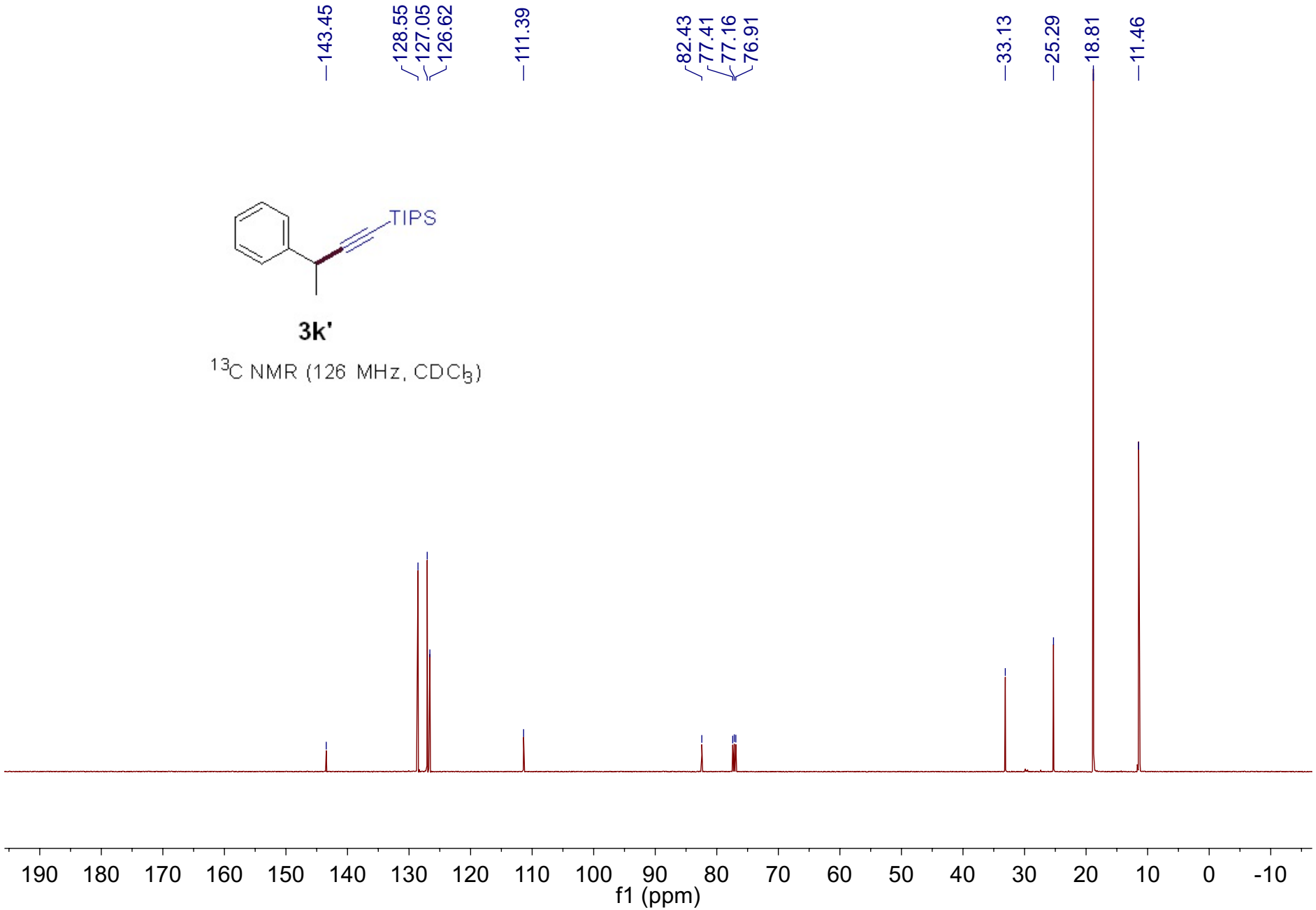
Supplementary Fig. 103. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3j'**



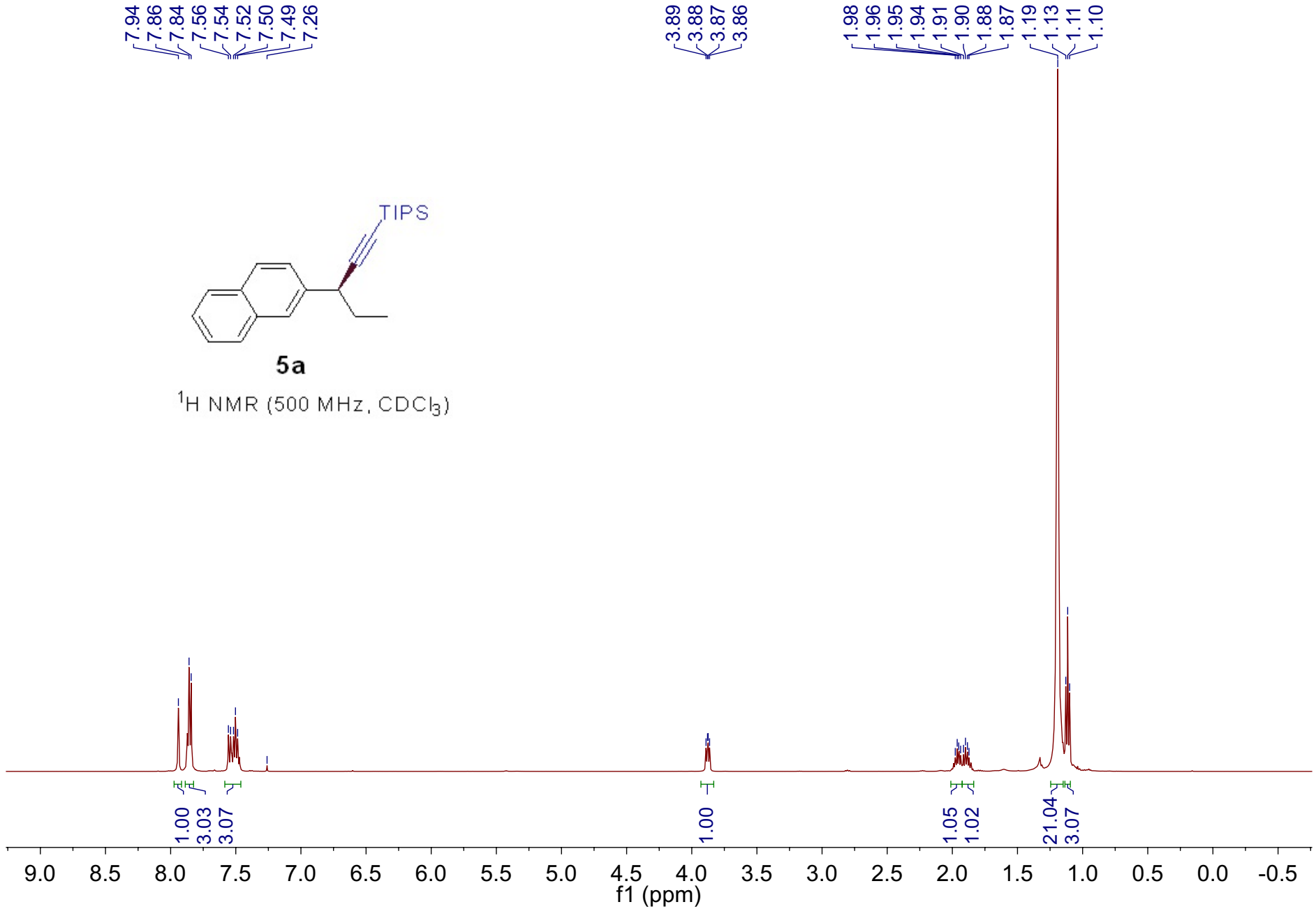
Supplementary Fig. 104. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3j'**



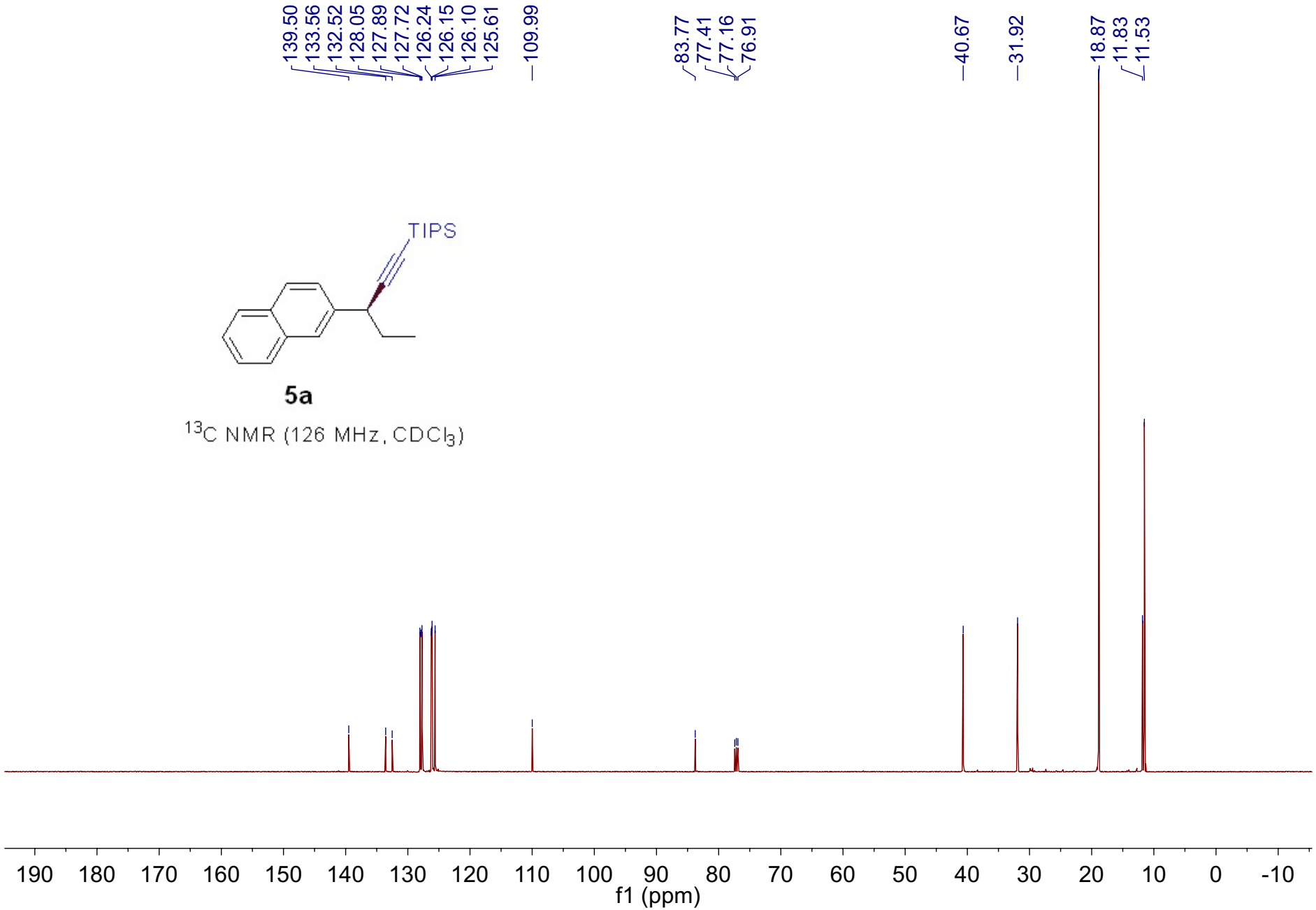
Supplementary Fig. 105. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3k'**



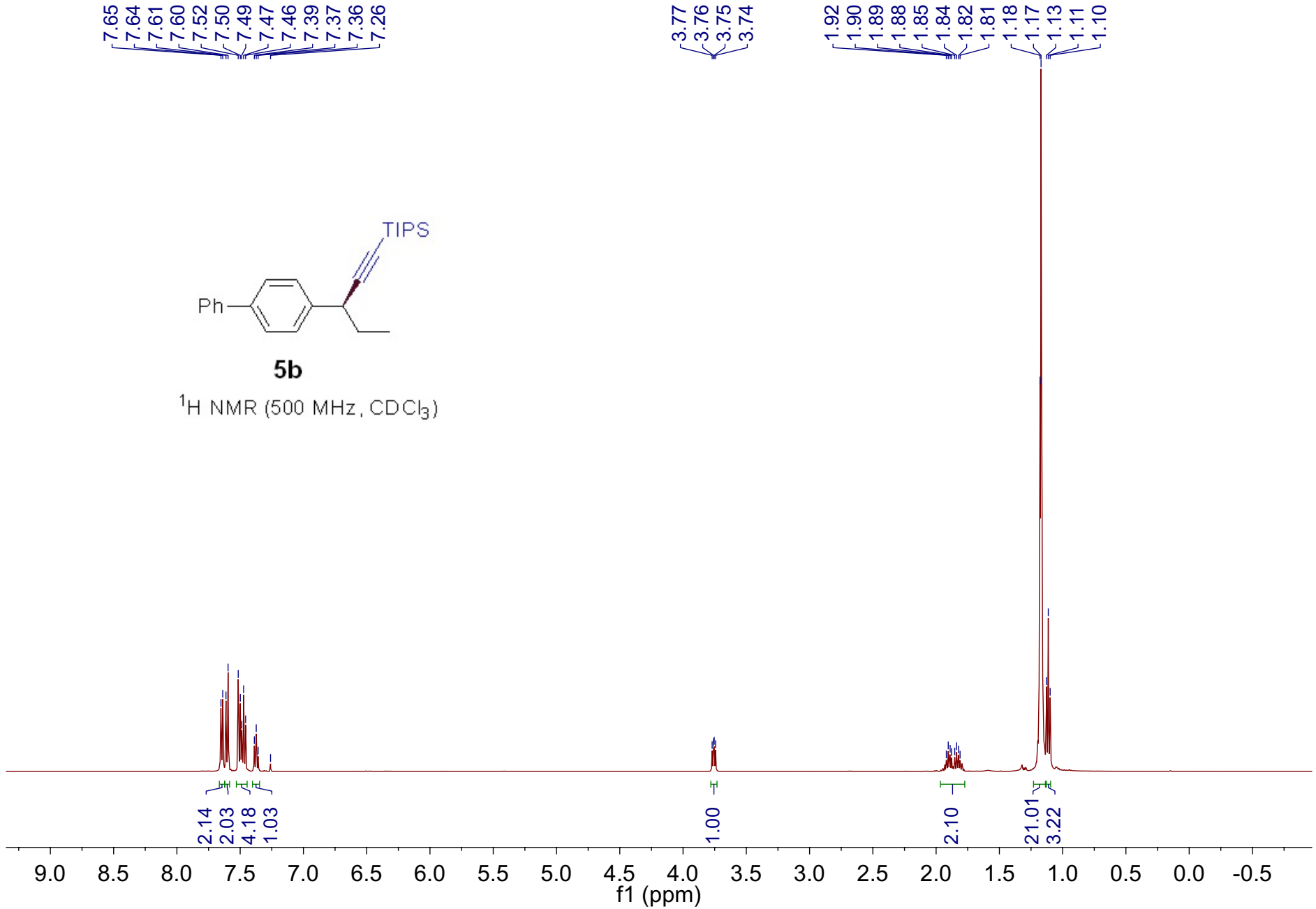
Supplementary Fig. 106. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3k'**



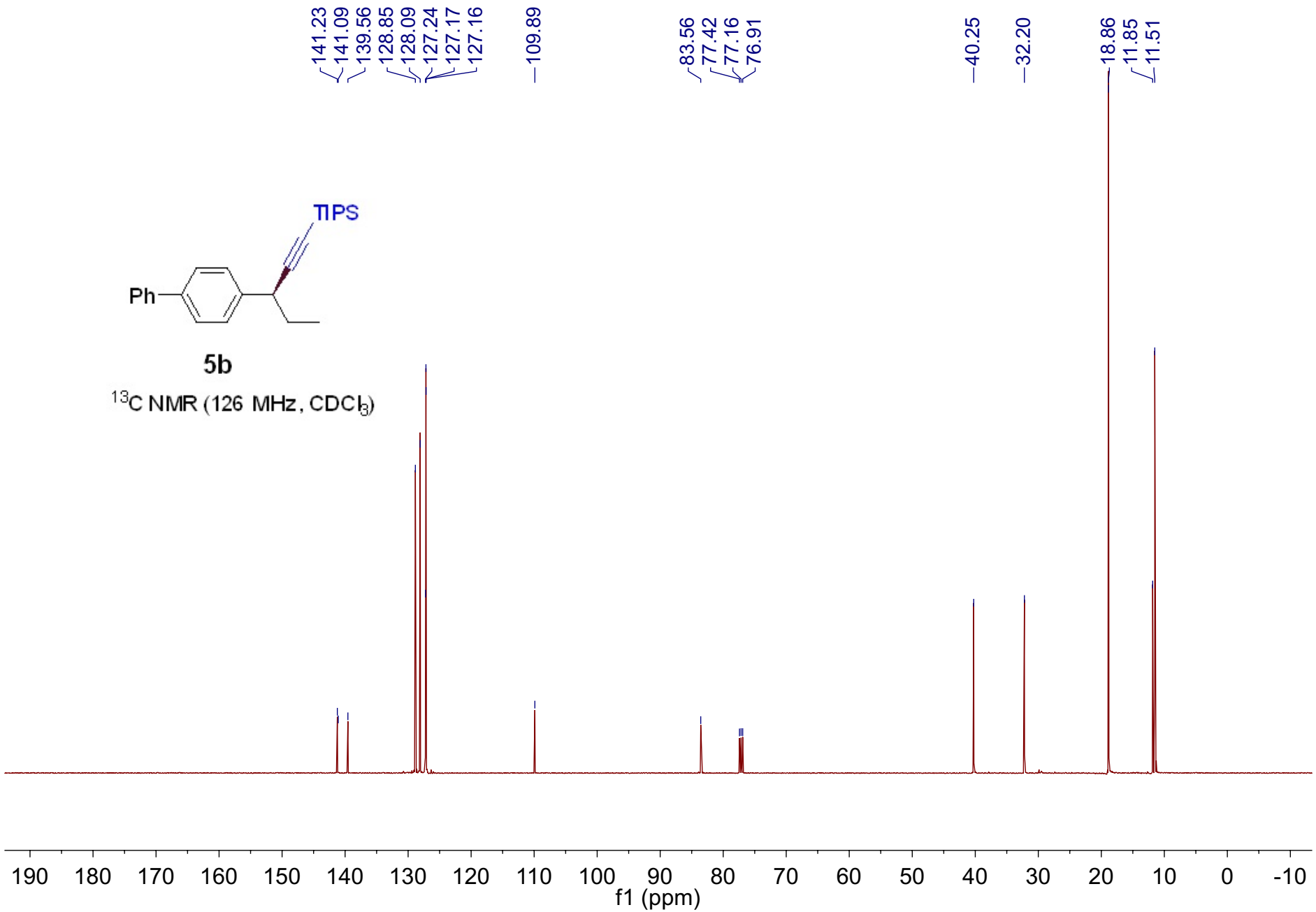
Supplementary Fig. 107. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5a**



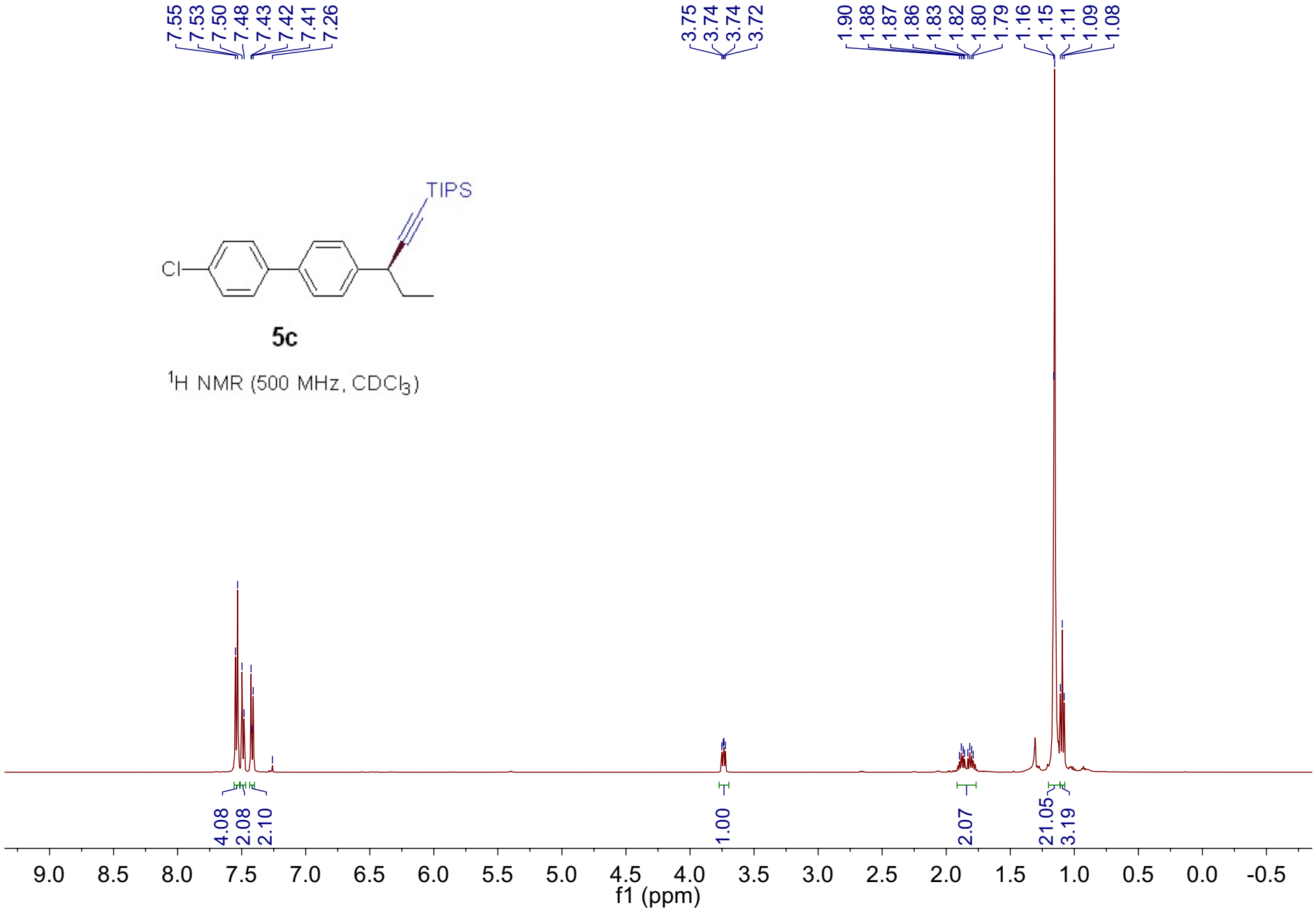
Supplementary Fig. 108. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5a**



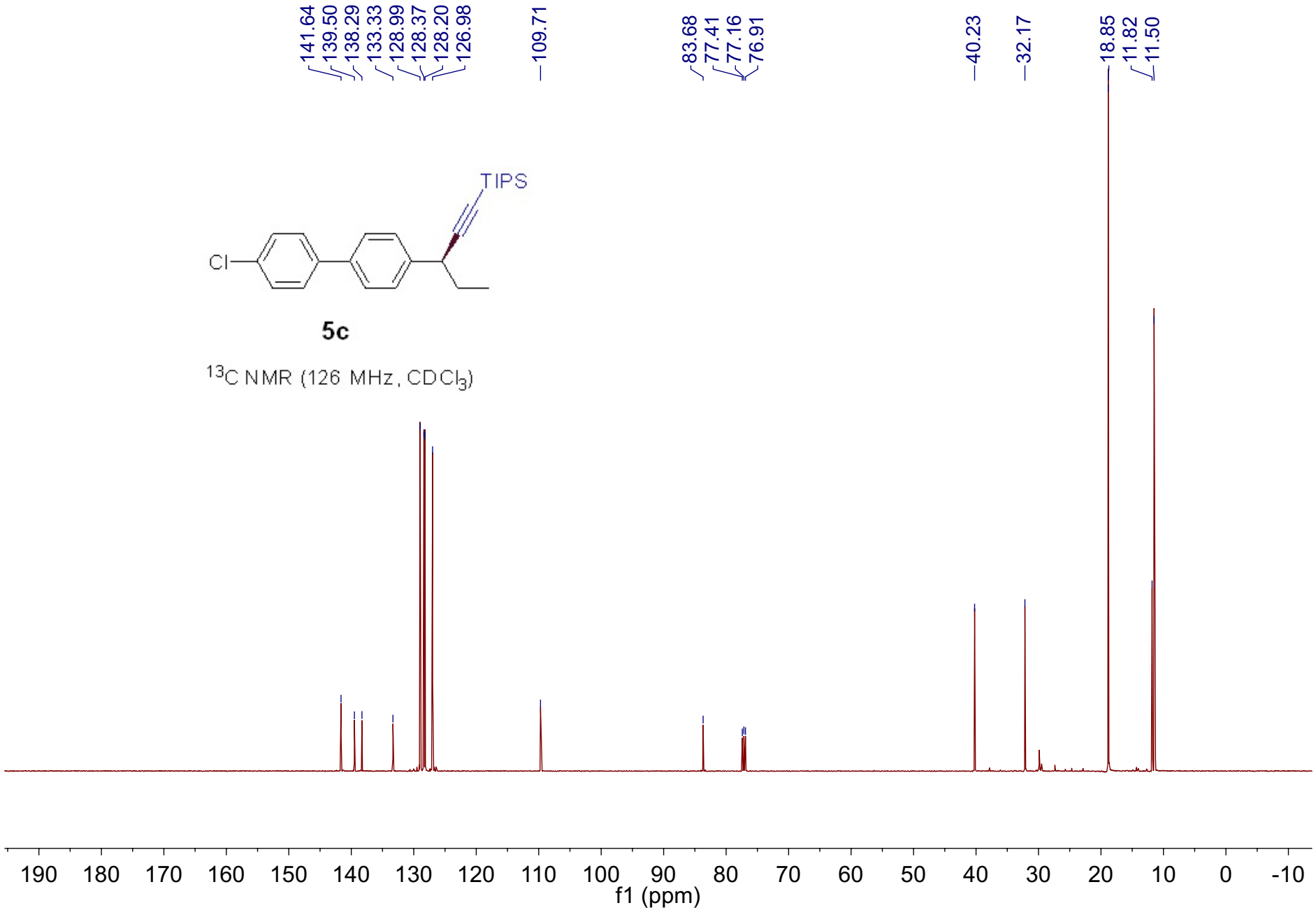
Supplementary Fig. 109. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5b**



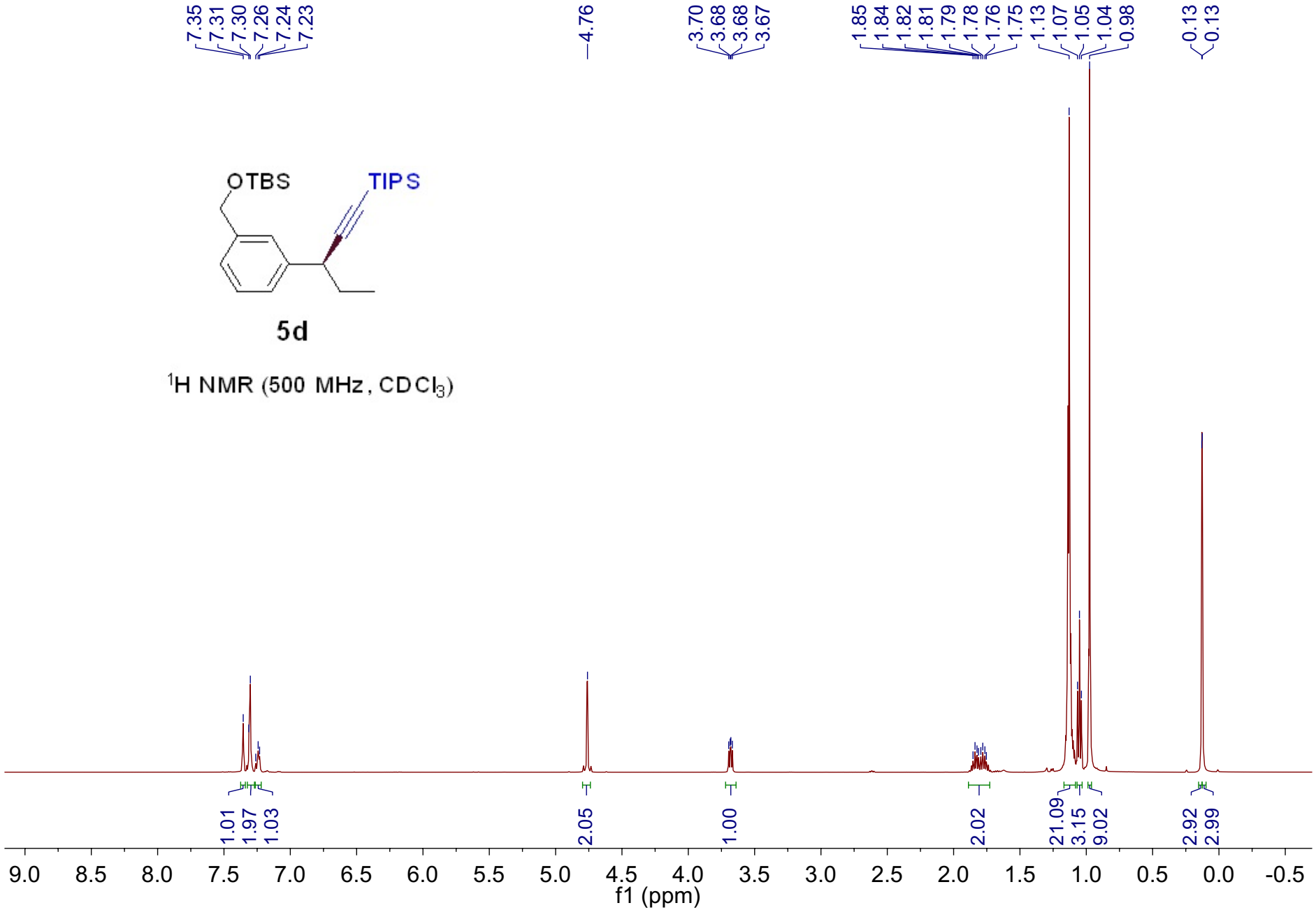
Supplementary Fig. 110. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5b**



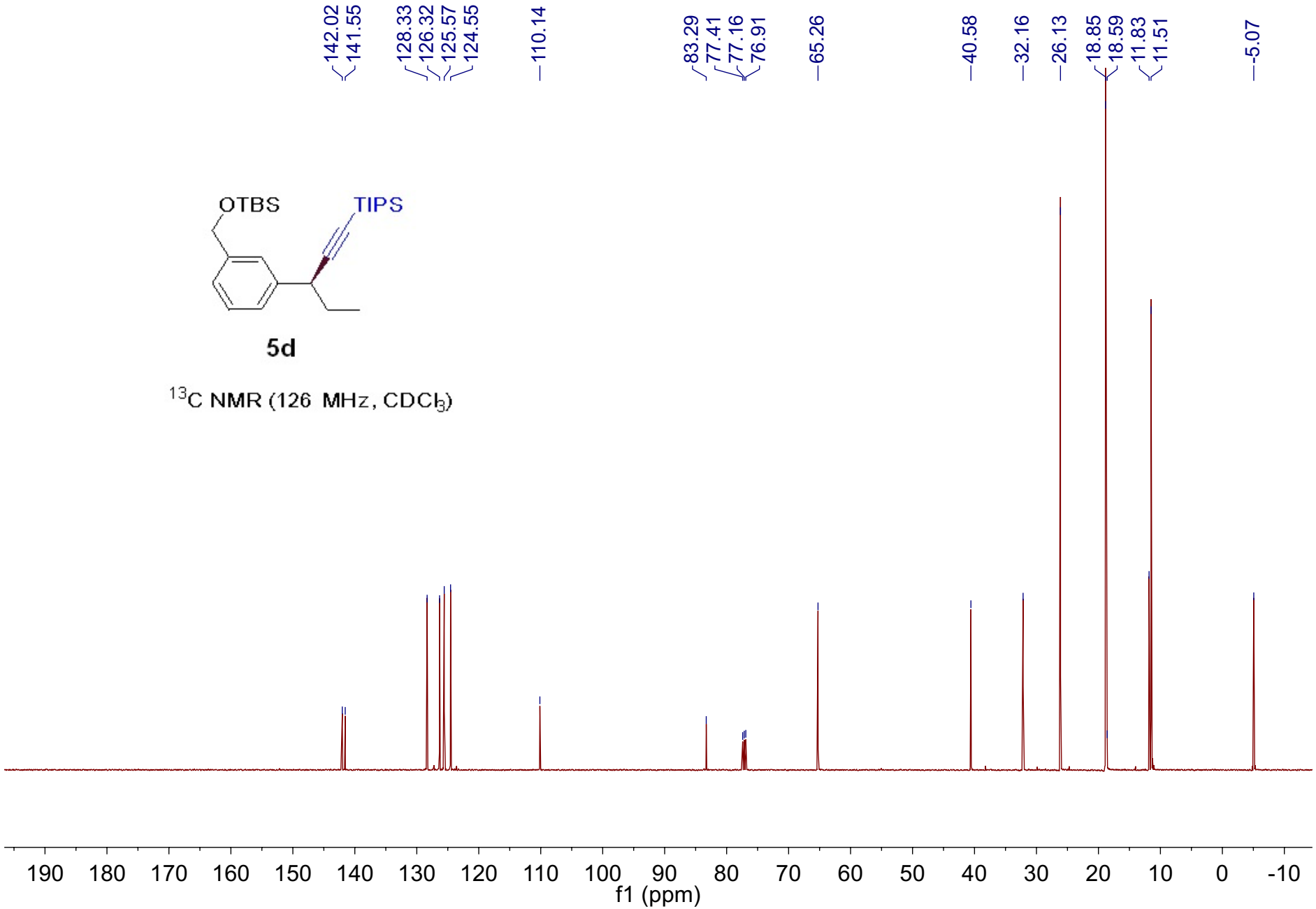
Supplementary Fig. 111. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5c**



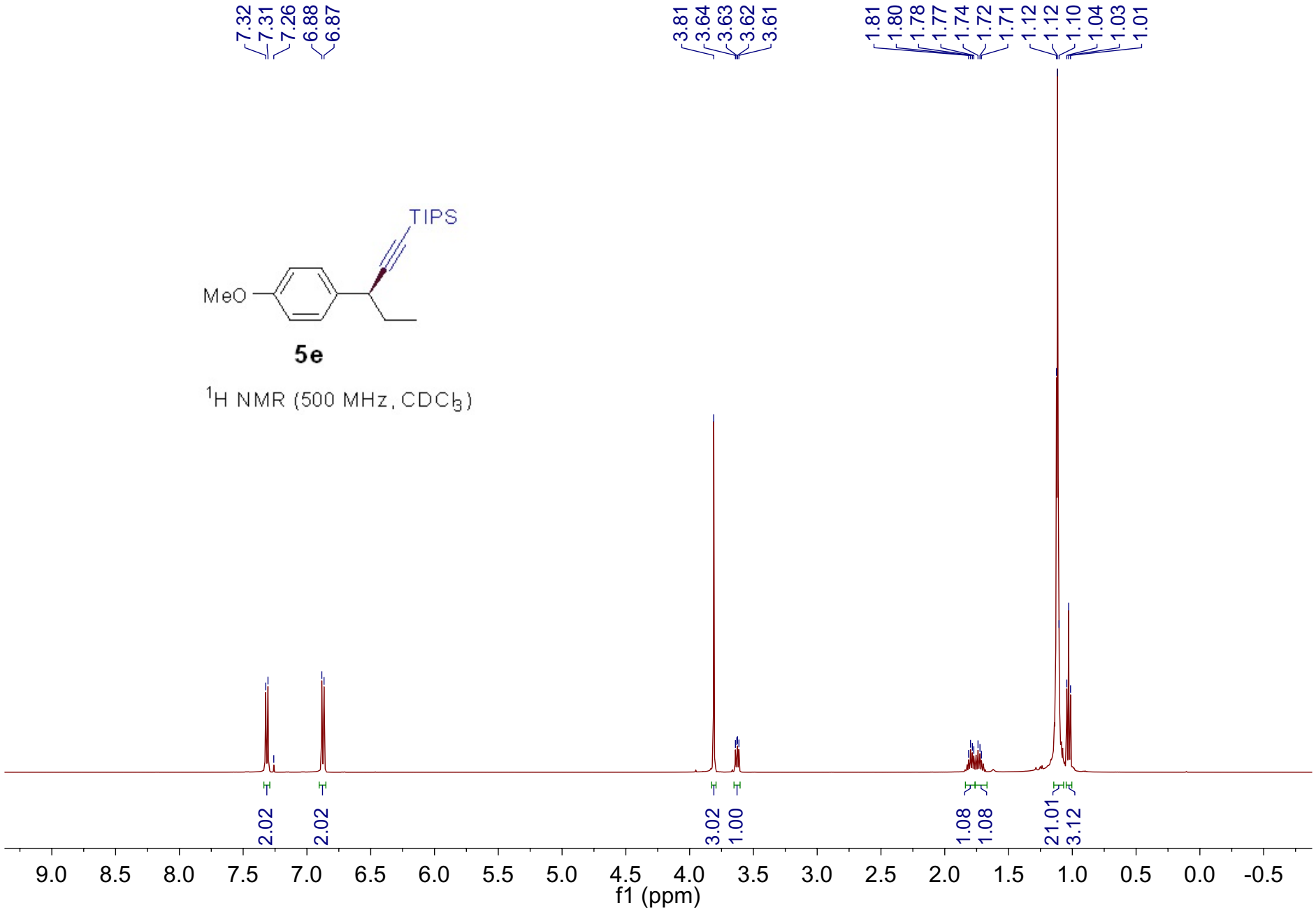
Supplementary Fig. 112. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5c**



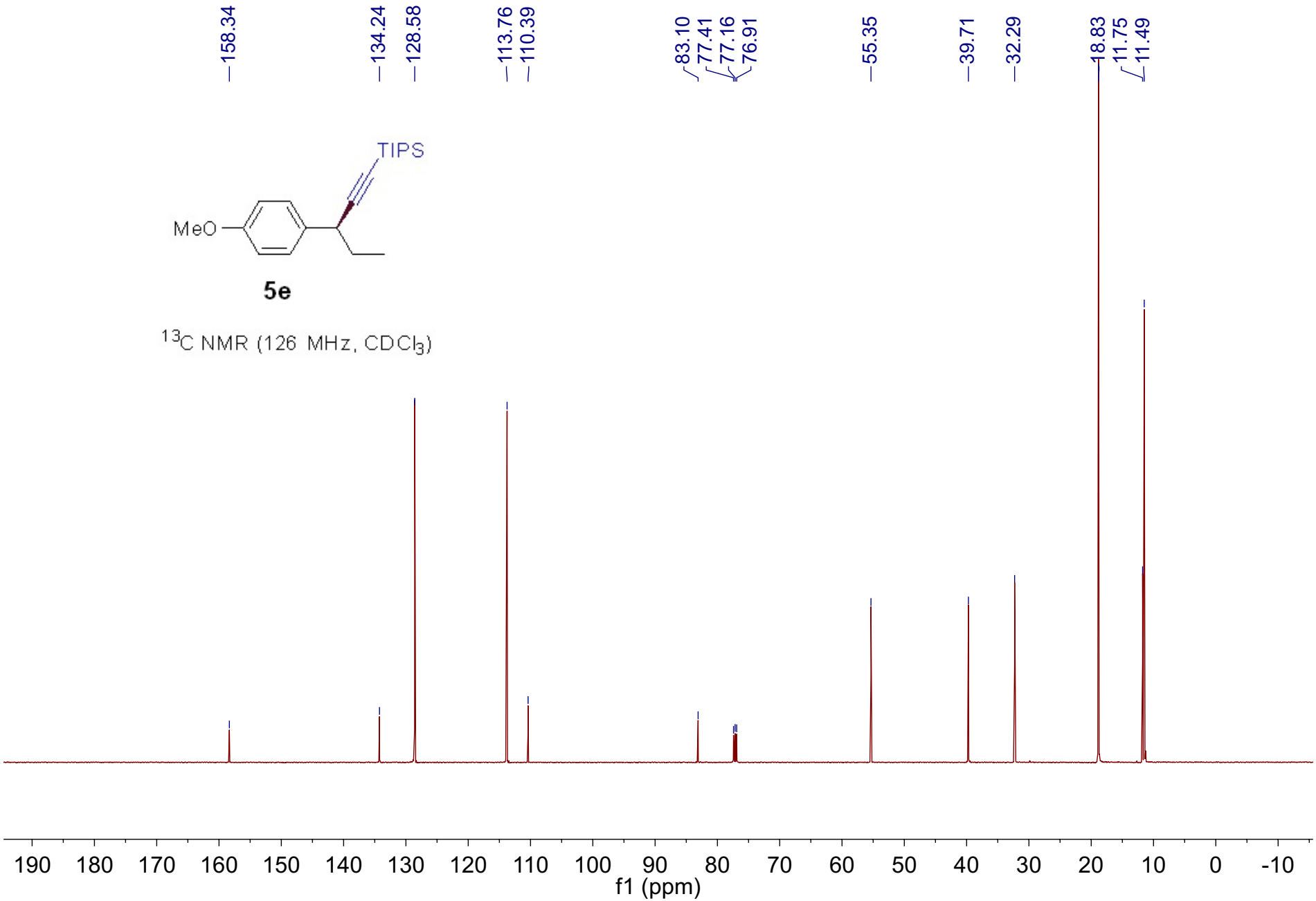
Supplementary Fig. 113. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5d**



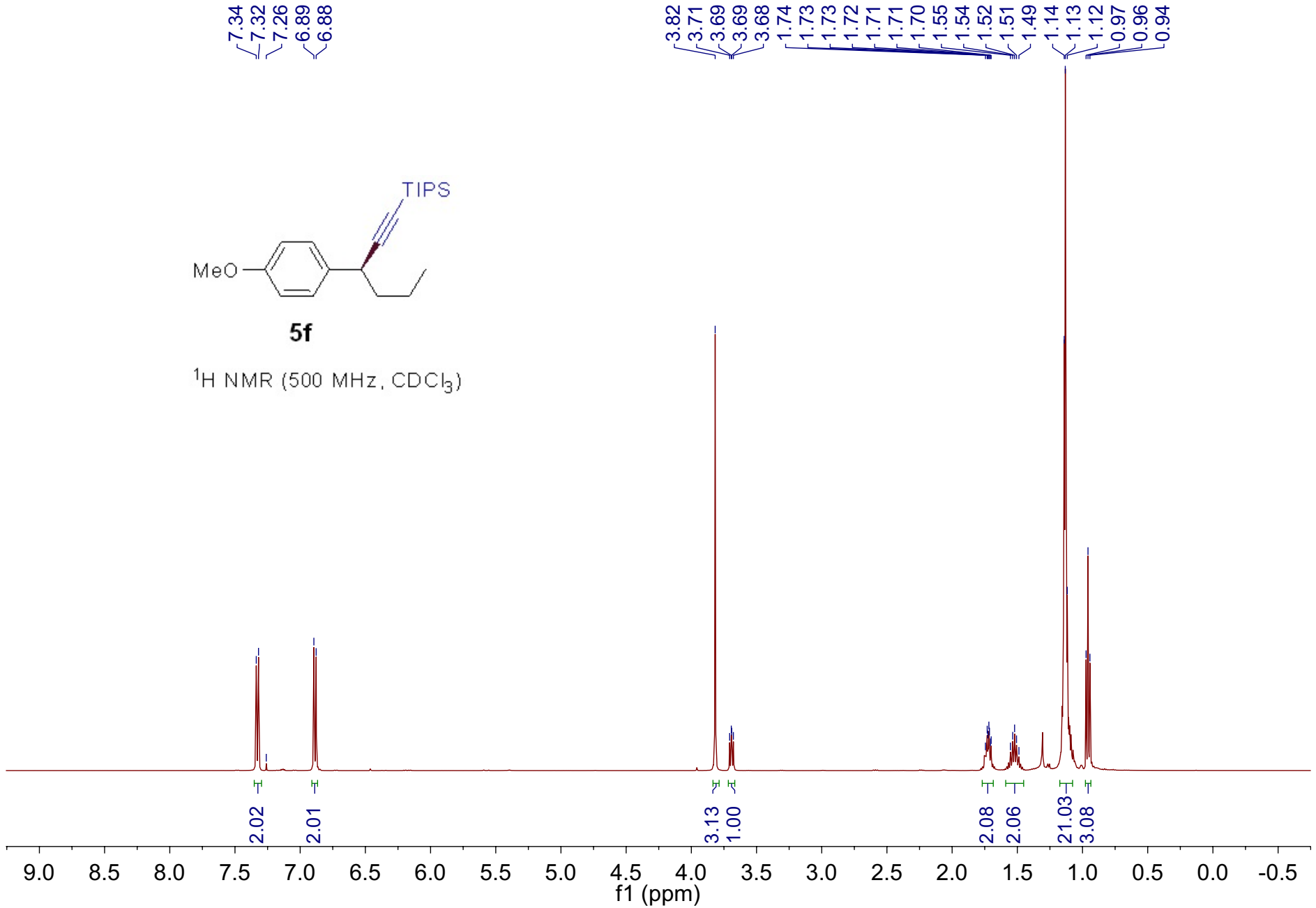
Supplementary Fig. 114. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5d**



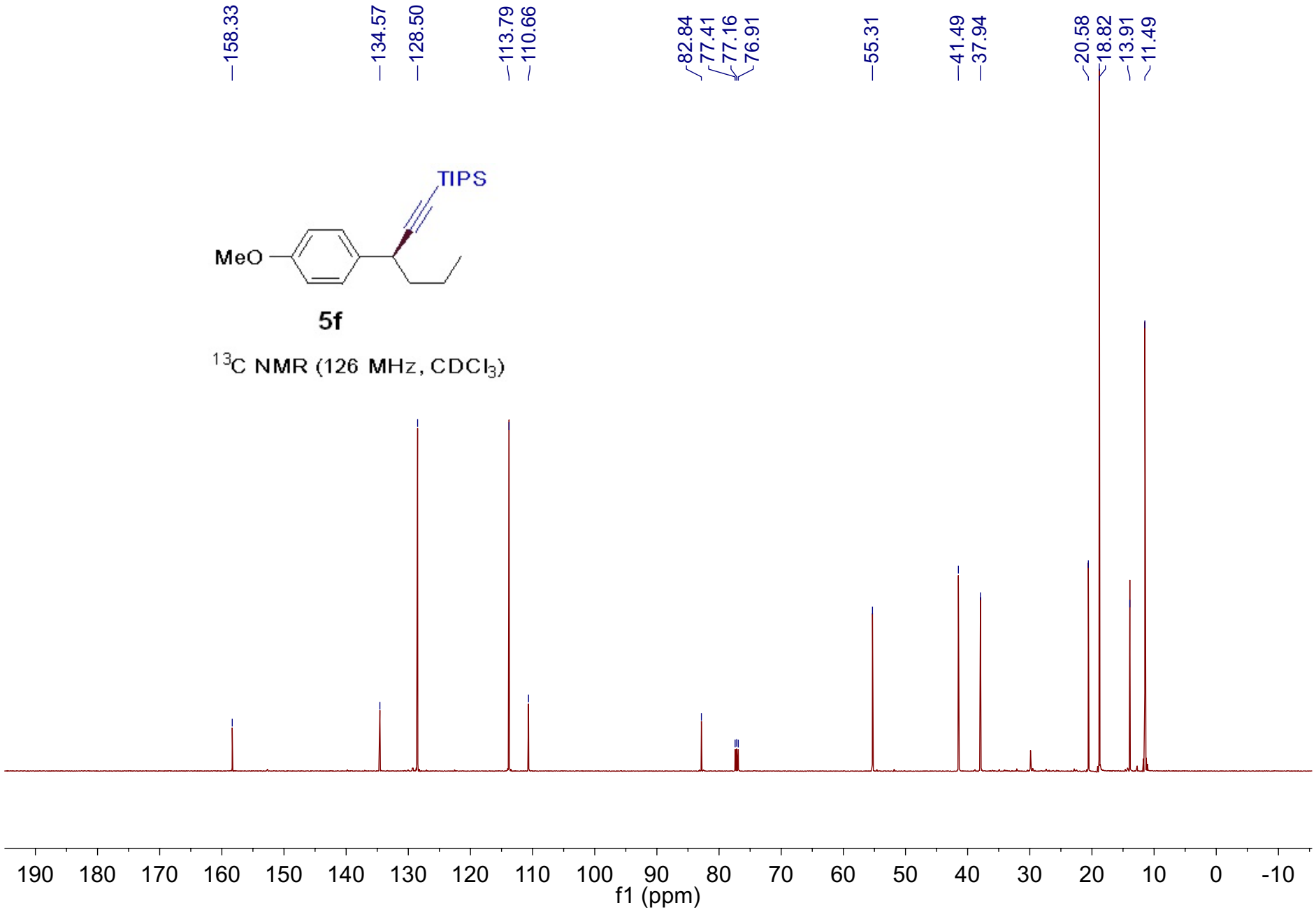
Supplementary Fig. 115. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5e**



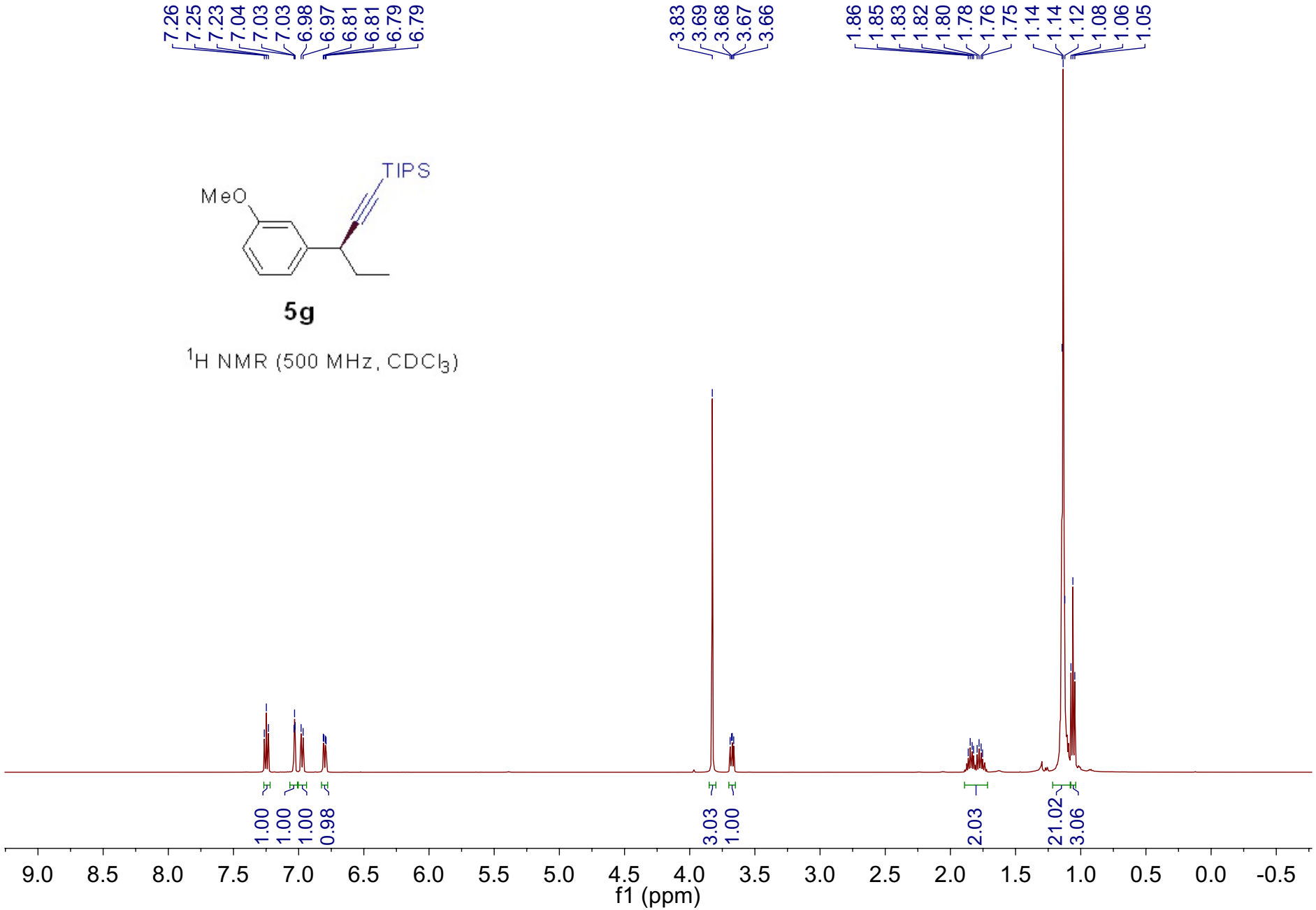
Supplementary Fig. 116. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5e**



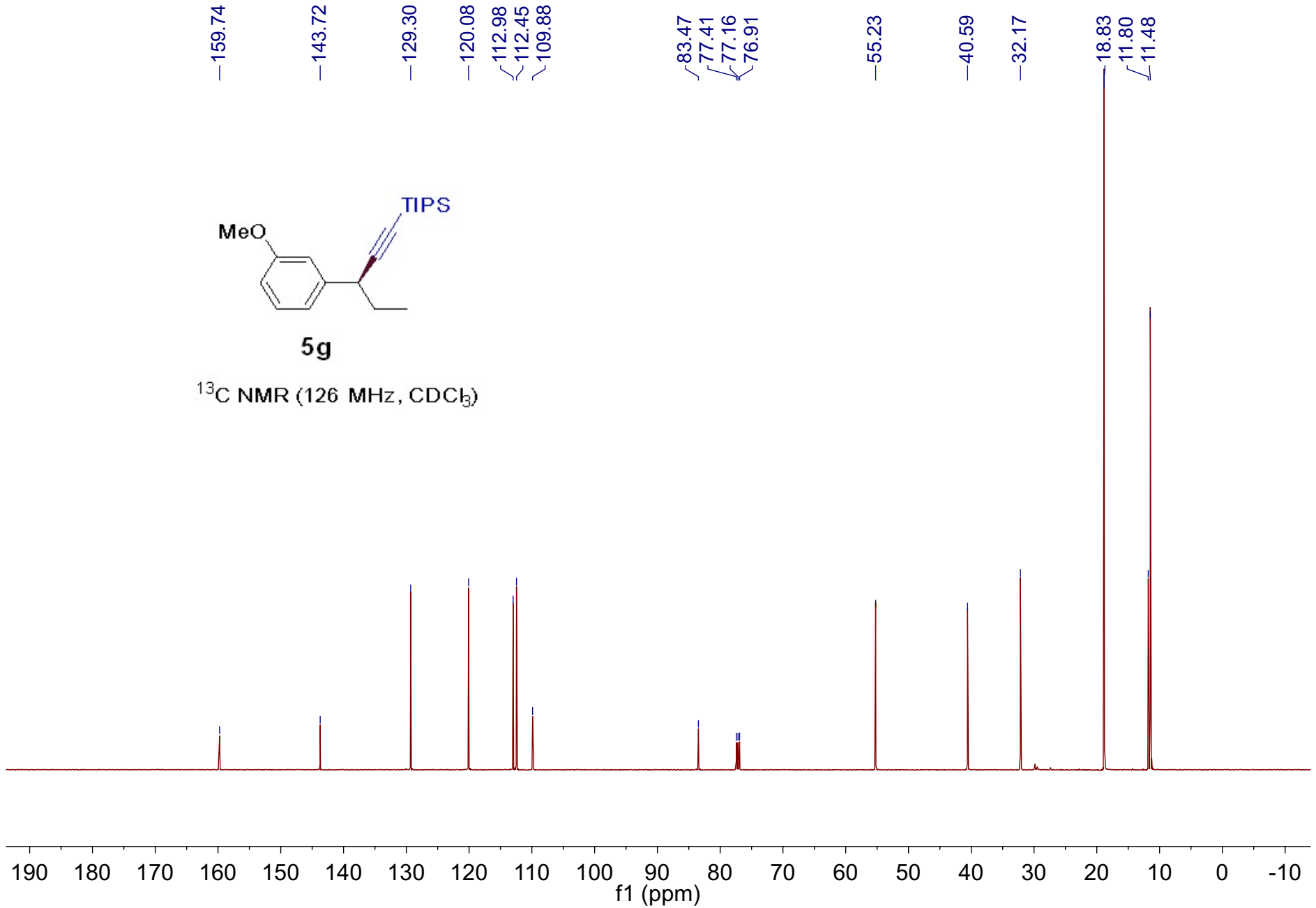
Supplementary Fig. 117. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5f**



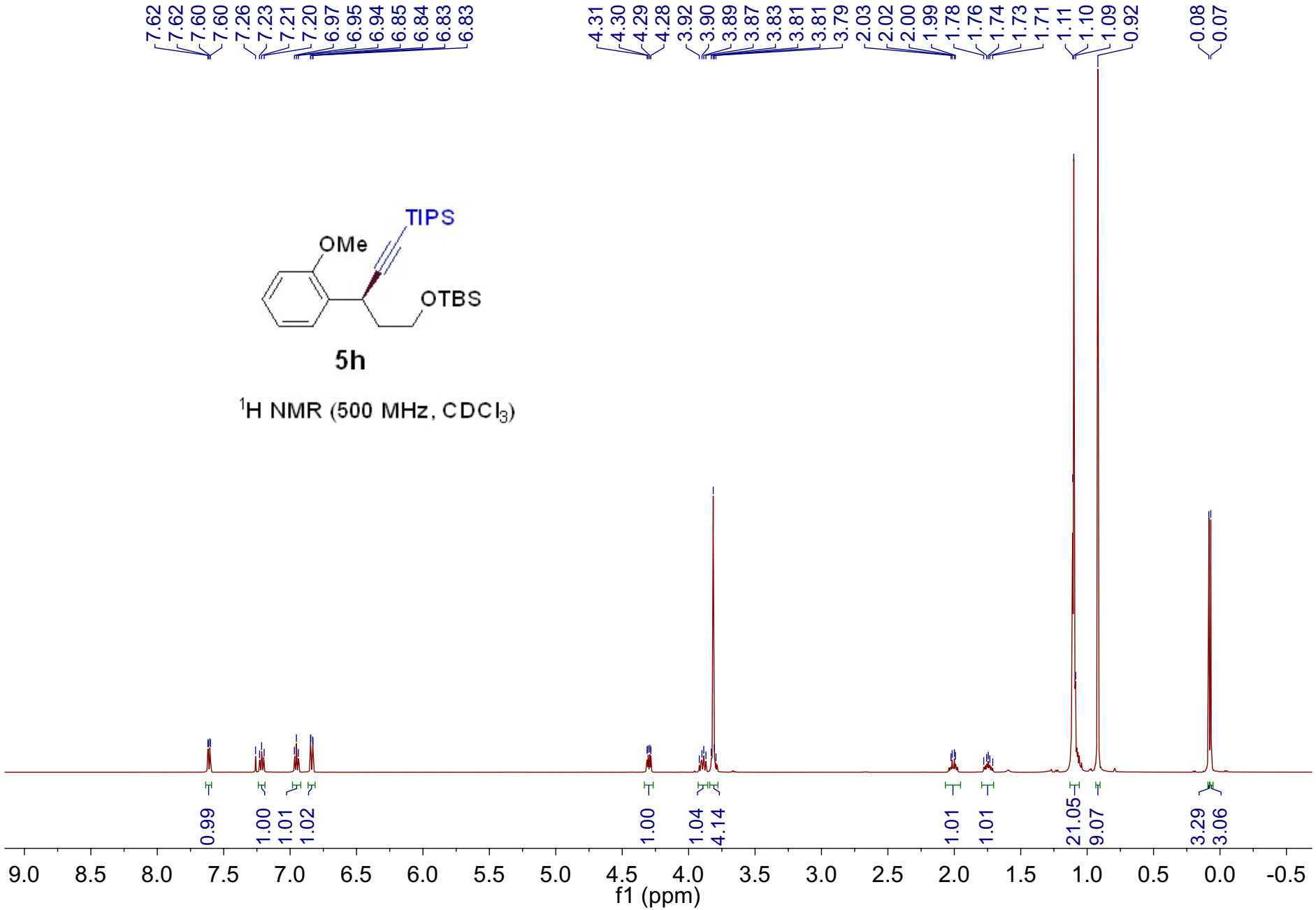
Supplementary Fig. 118. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5f**



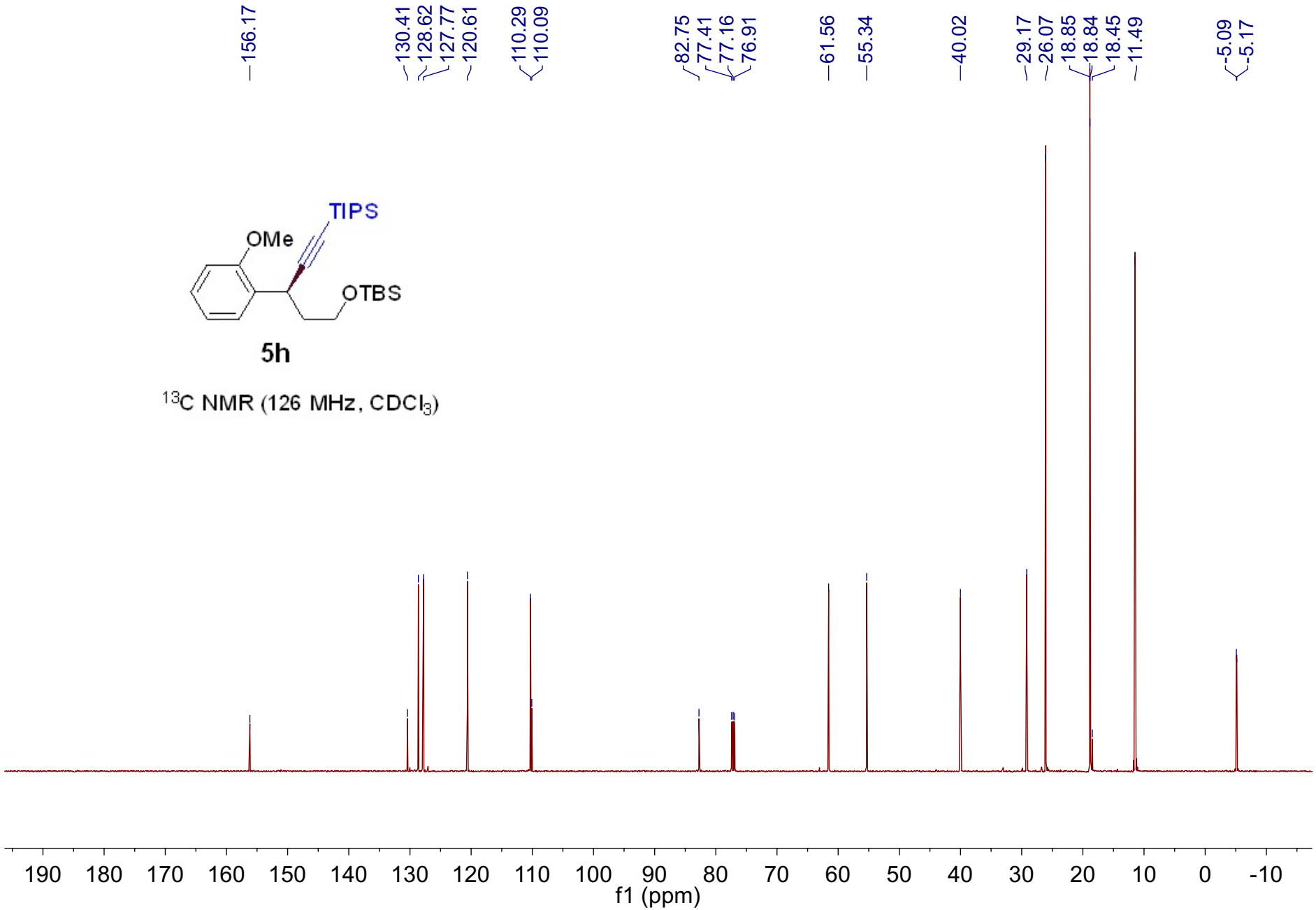
Supplementary Fig. 119. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5g**



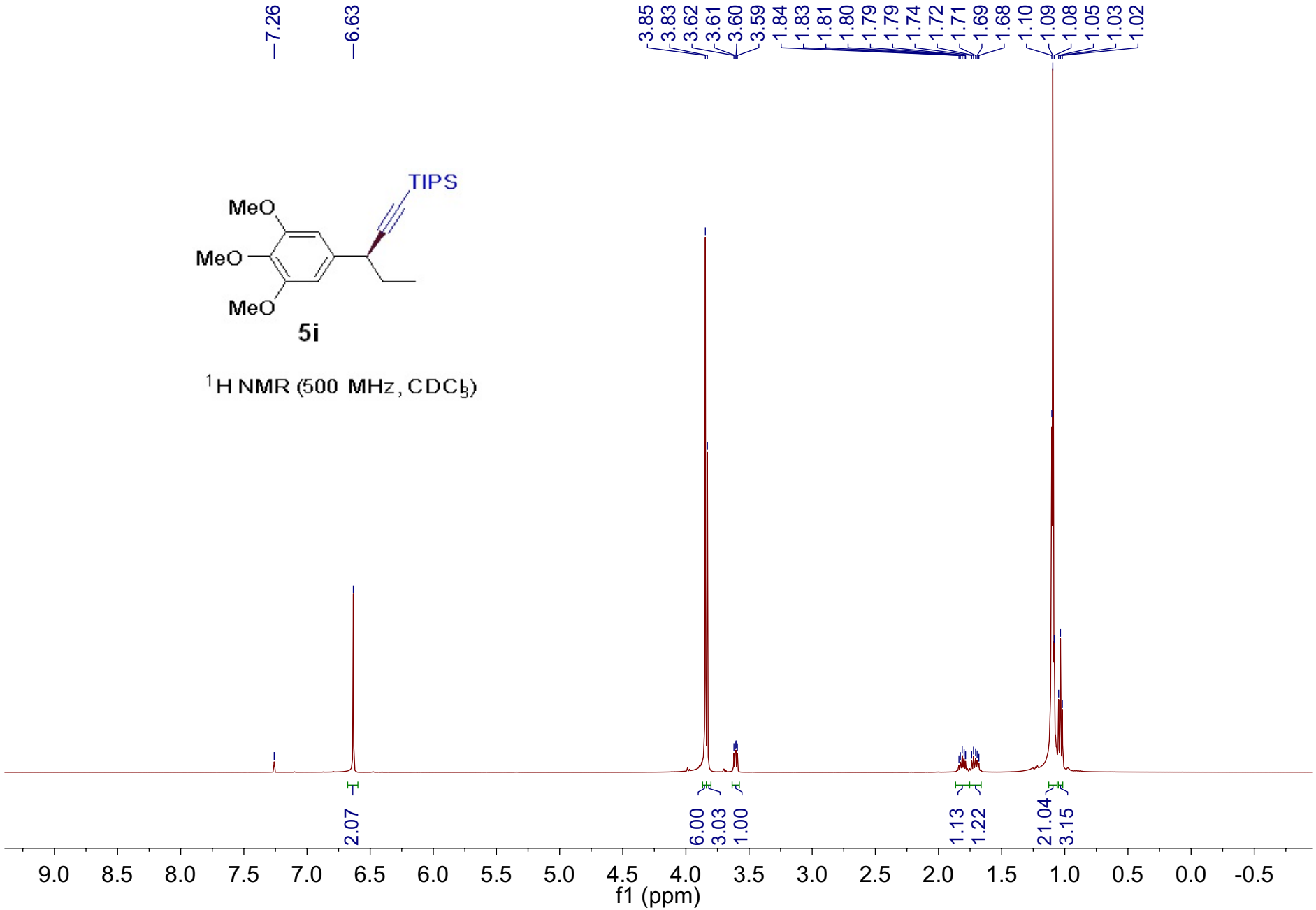
Supplementary Fig. 120. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5g**



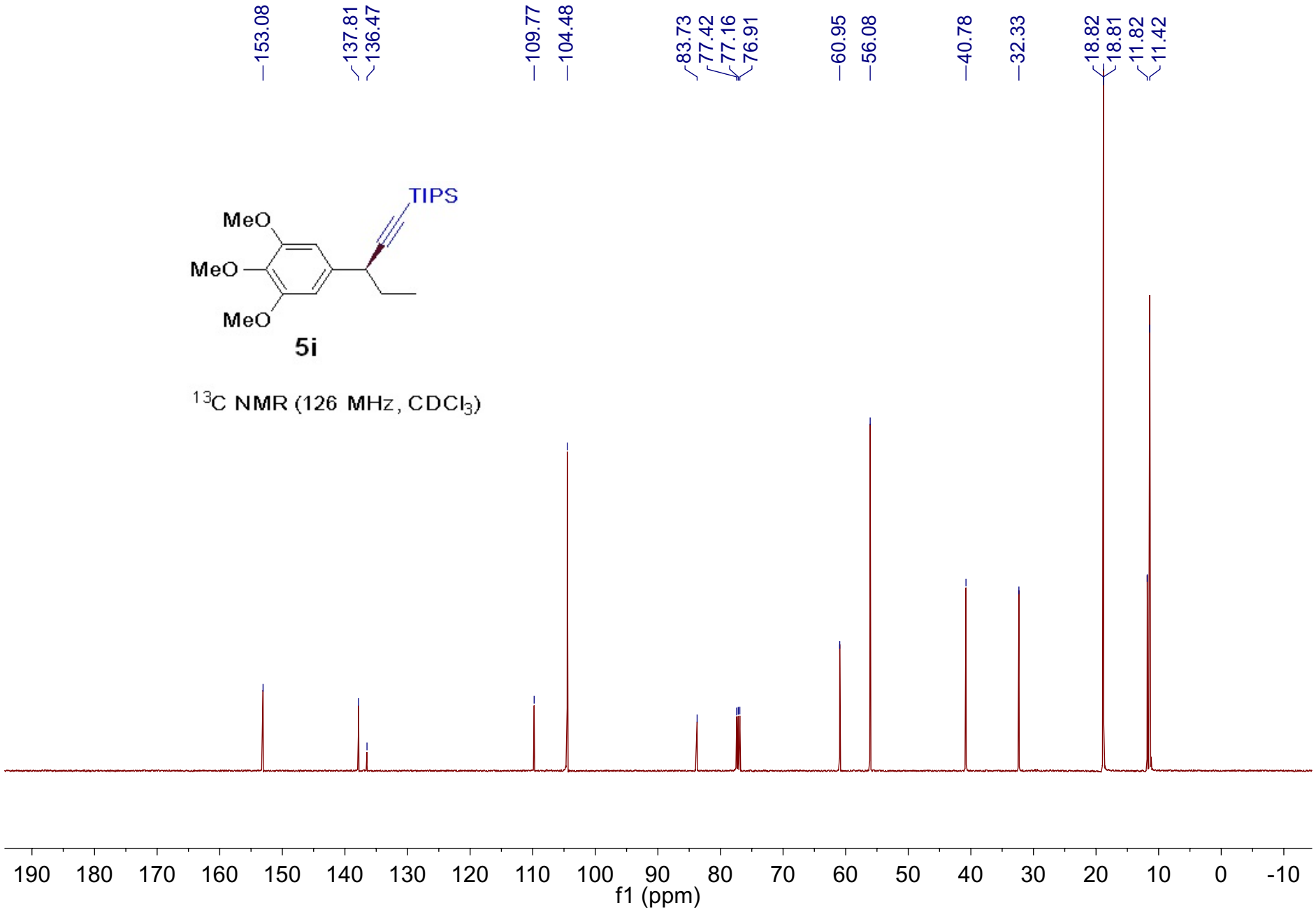
Supplementary Fig. 121. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5h**



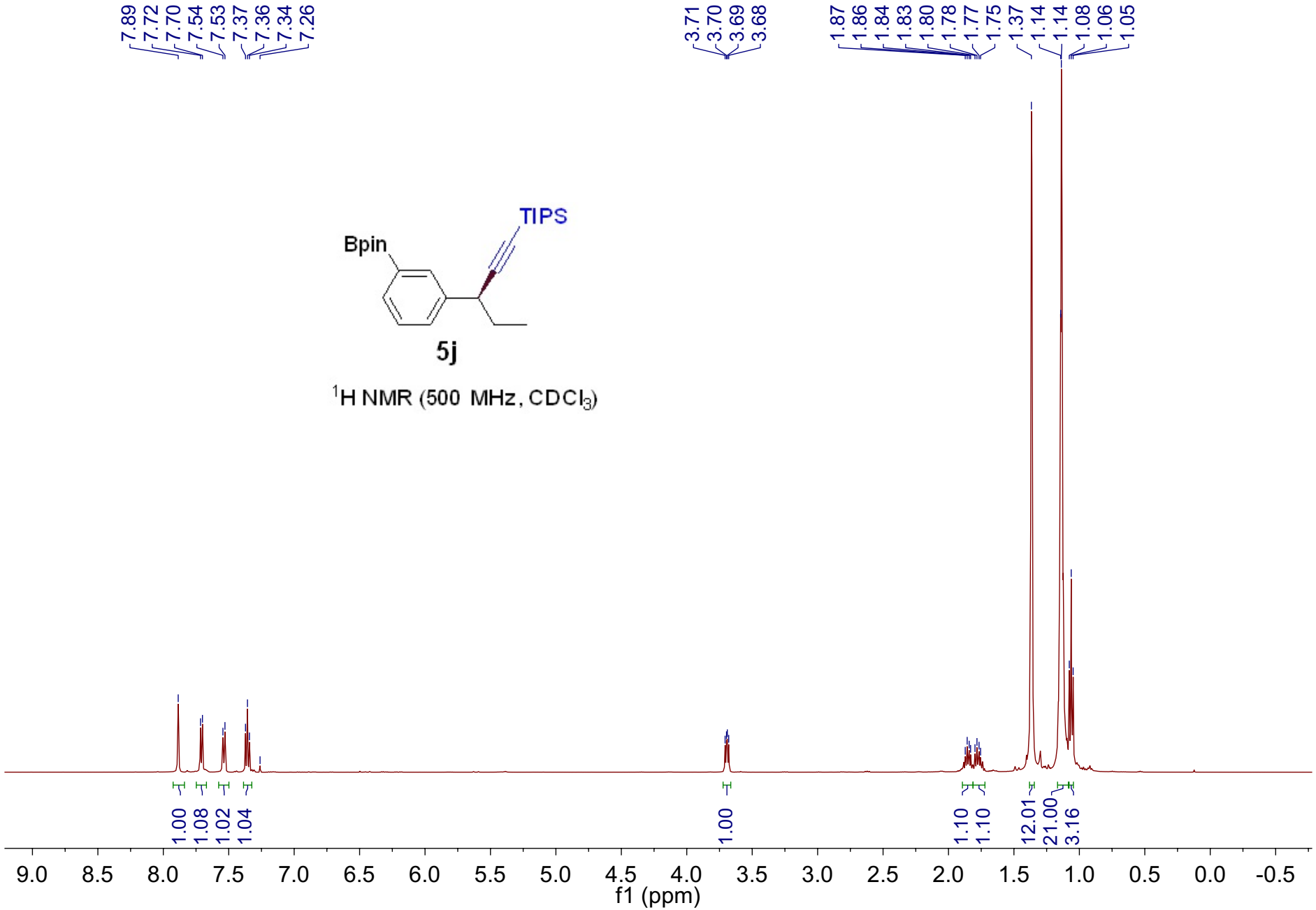
Supplementary Fig. 122. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5h**



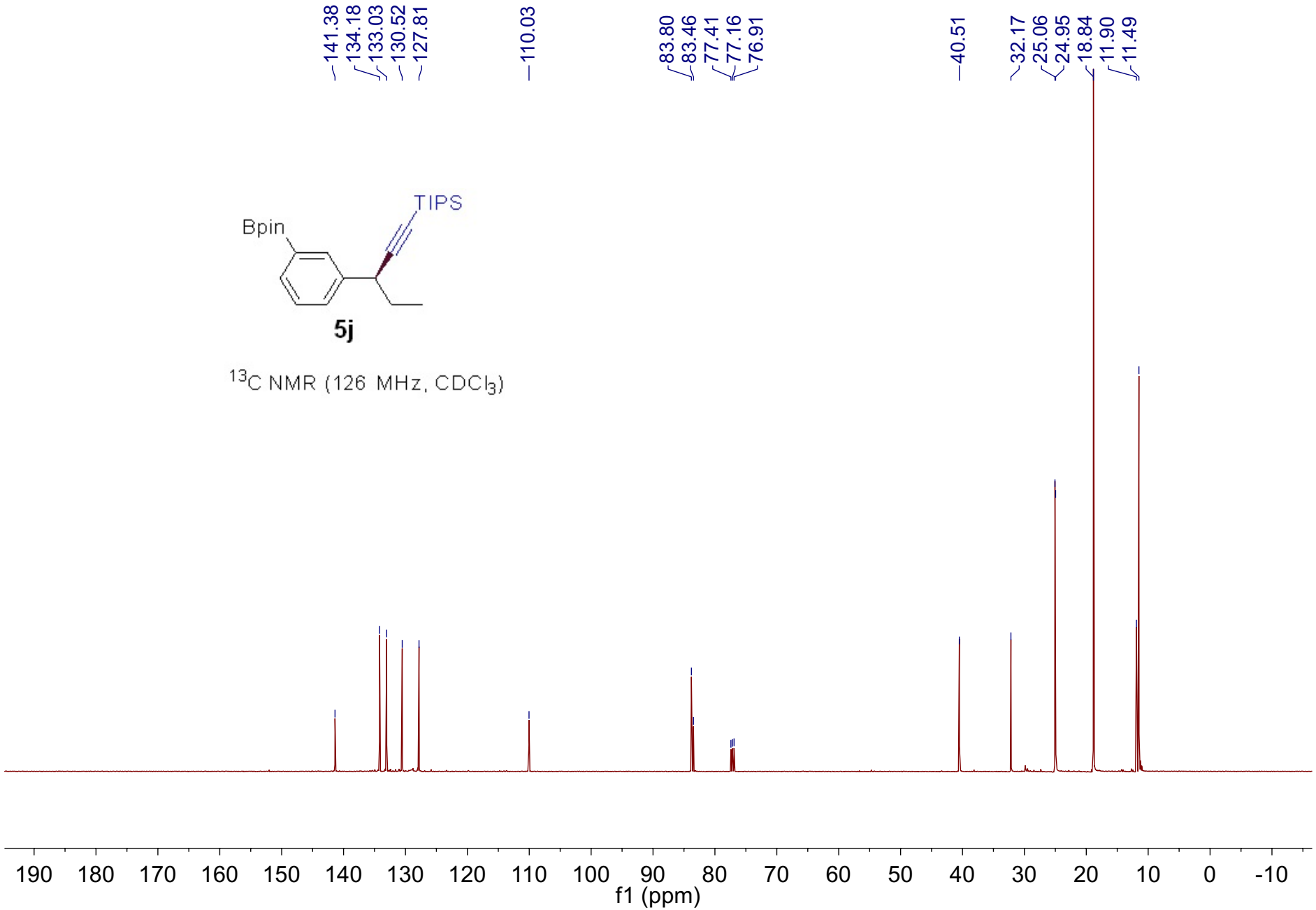
Supplementary Fig. 123. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5i**



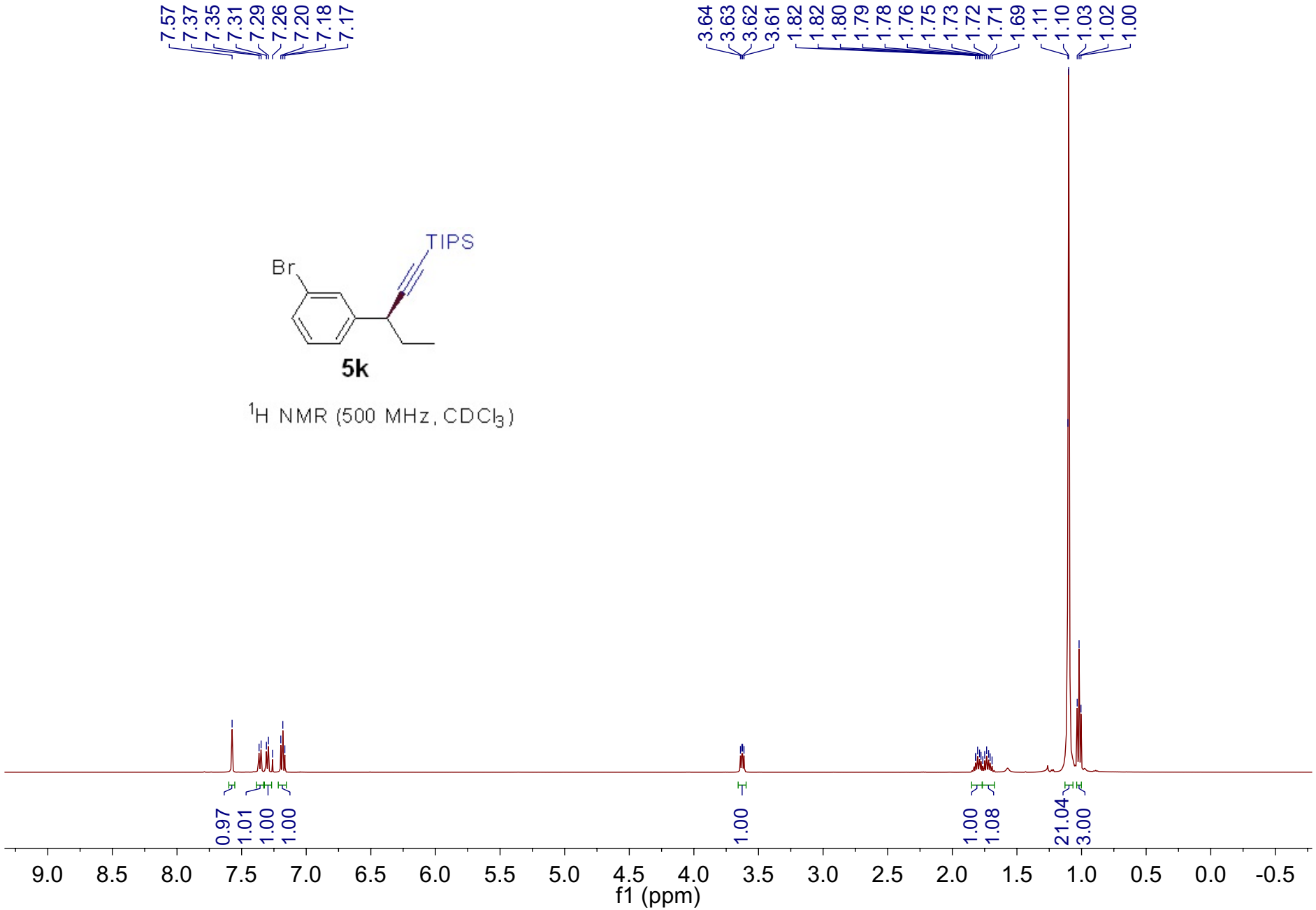
Supplementary Fig. 124. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5i**



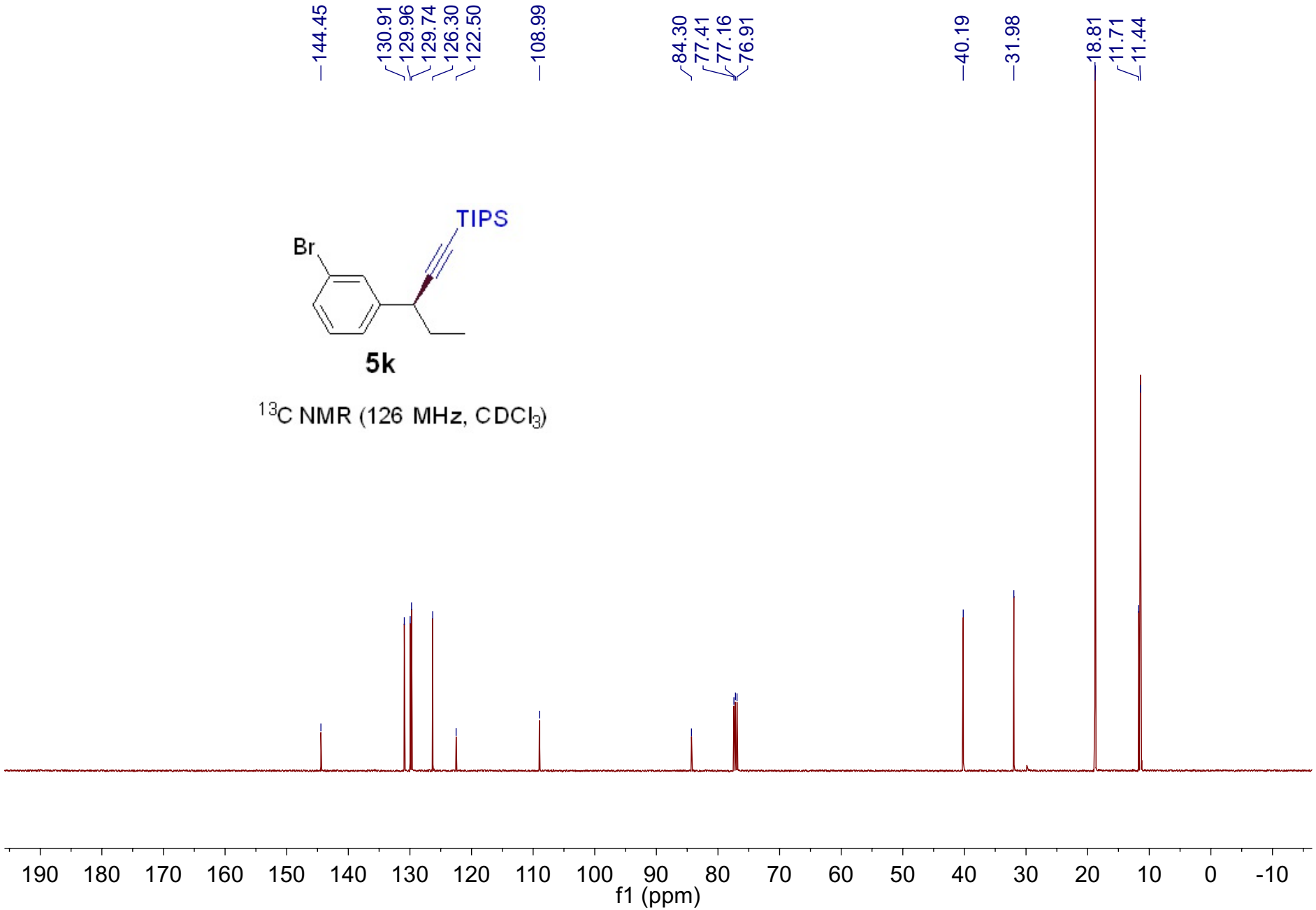
Supplementary Fig. 125. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5j**



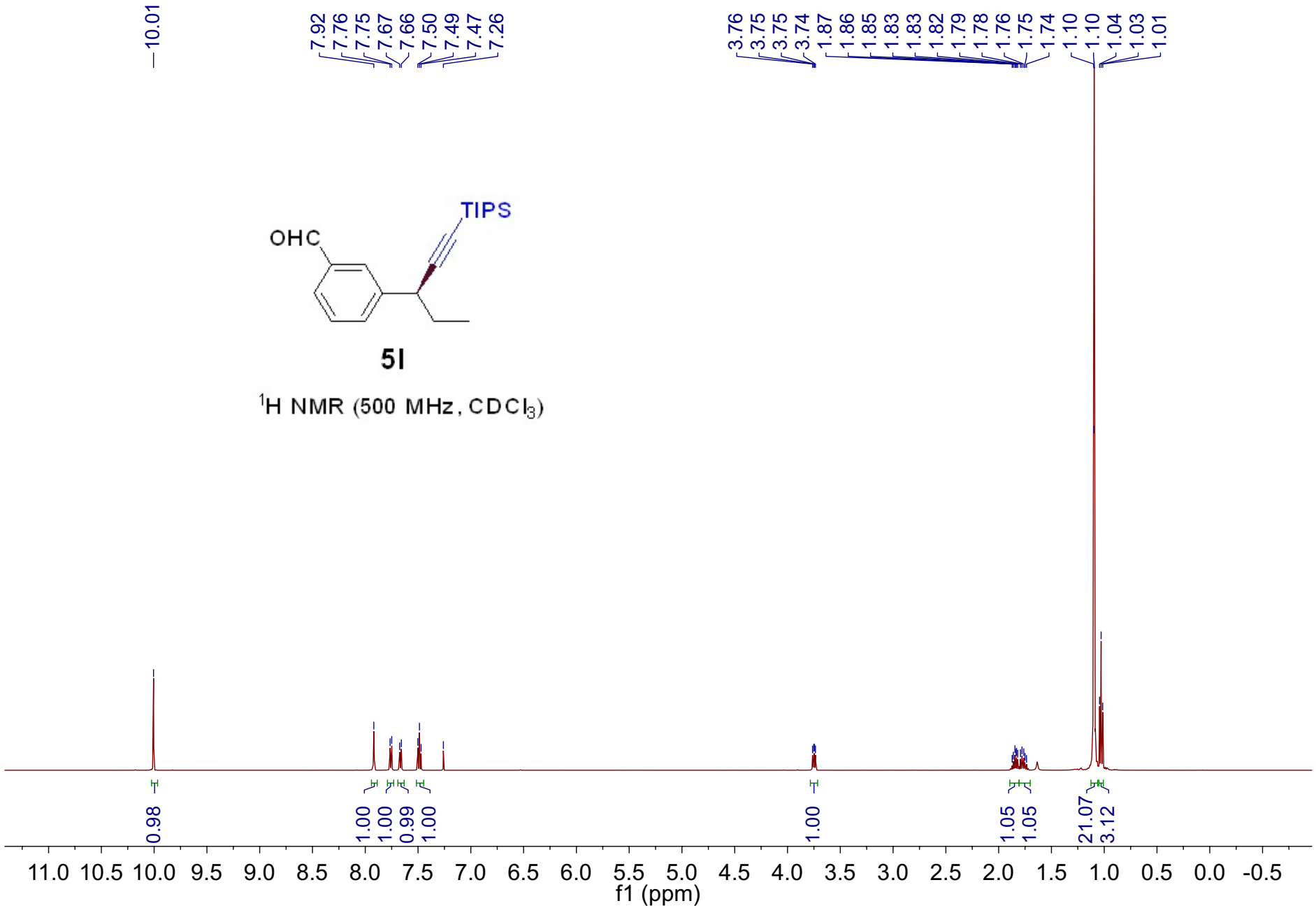
Supplementary Fig. 126. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5j**



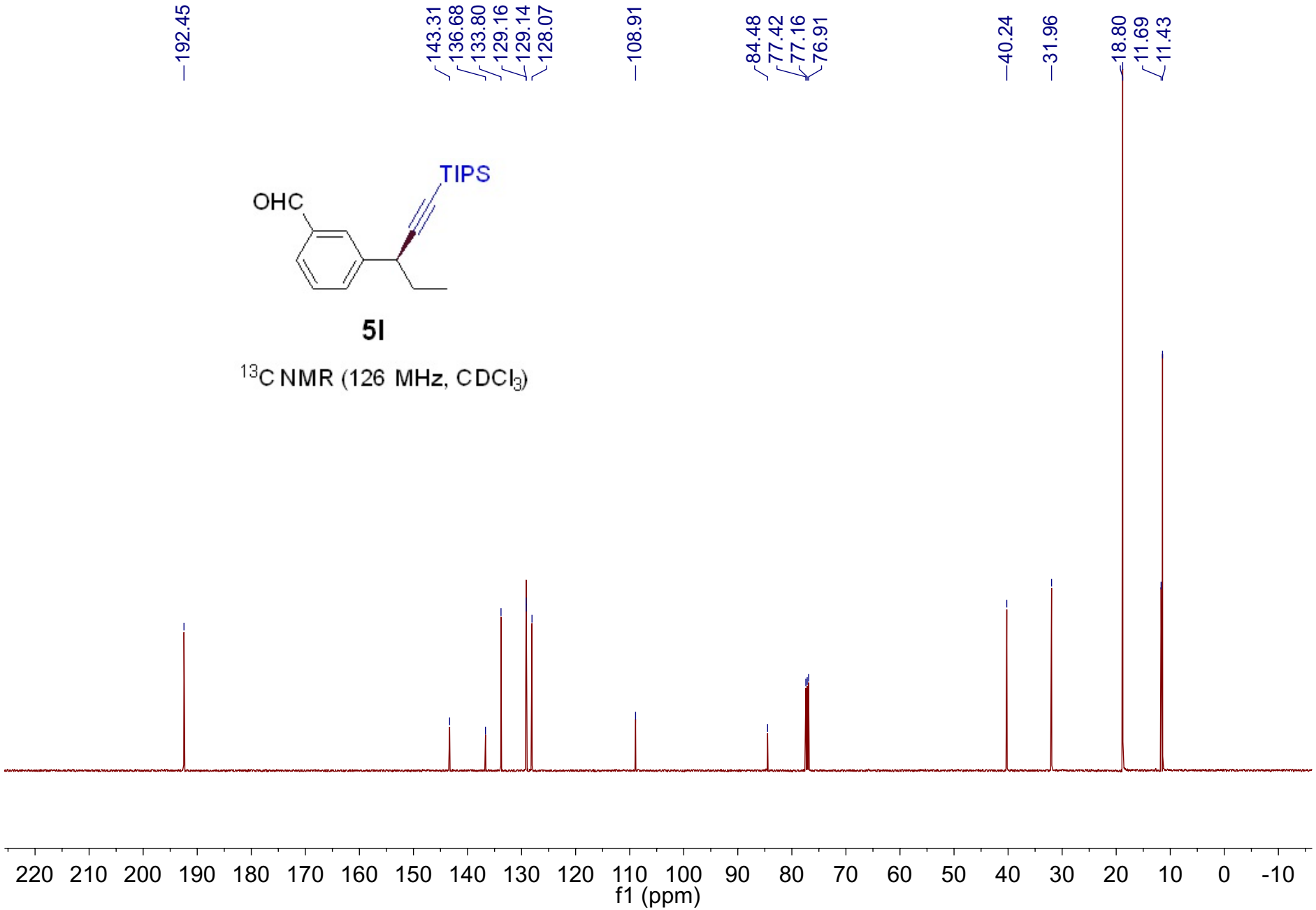
Supplementary Fig. 127. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5k**



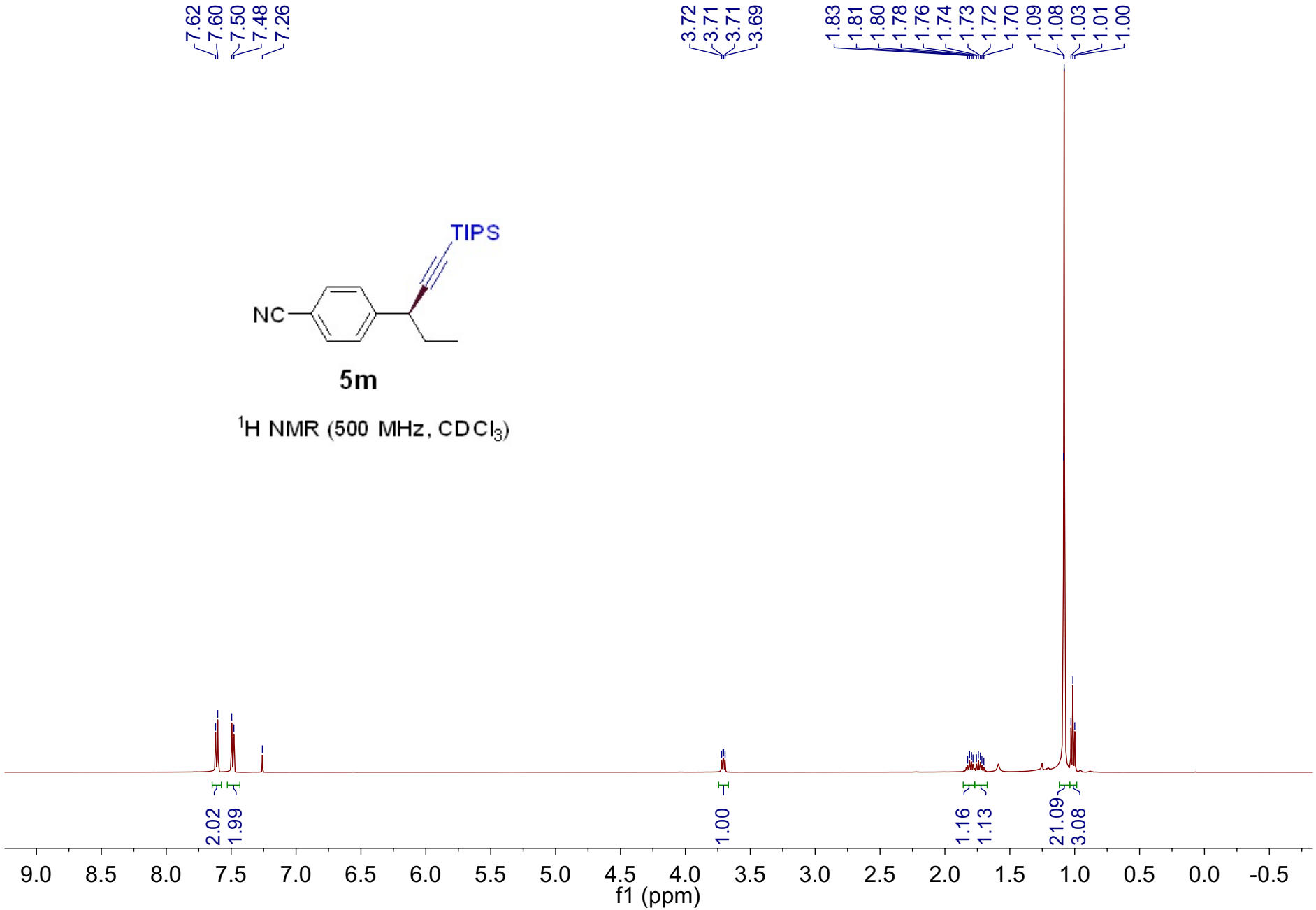
Supplementary Fig. 128. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5k**



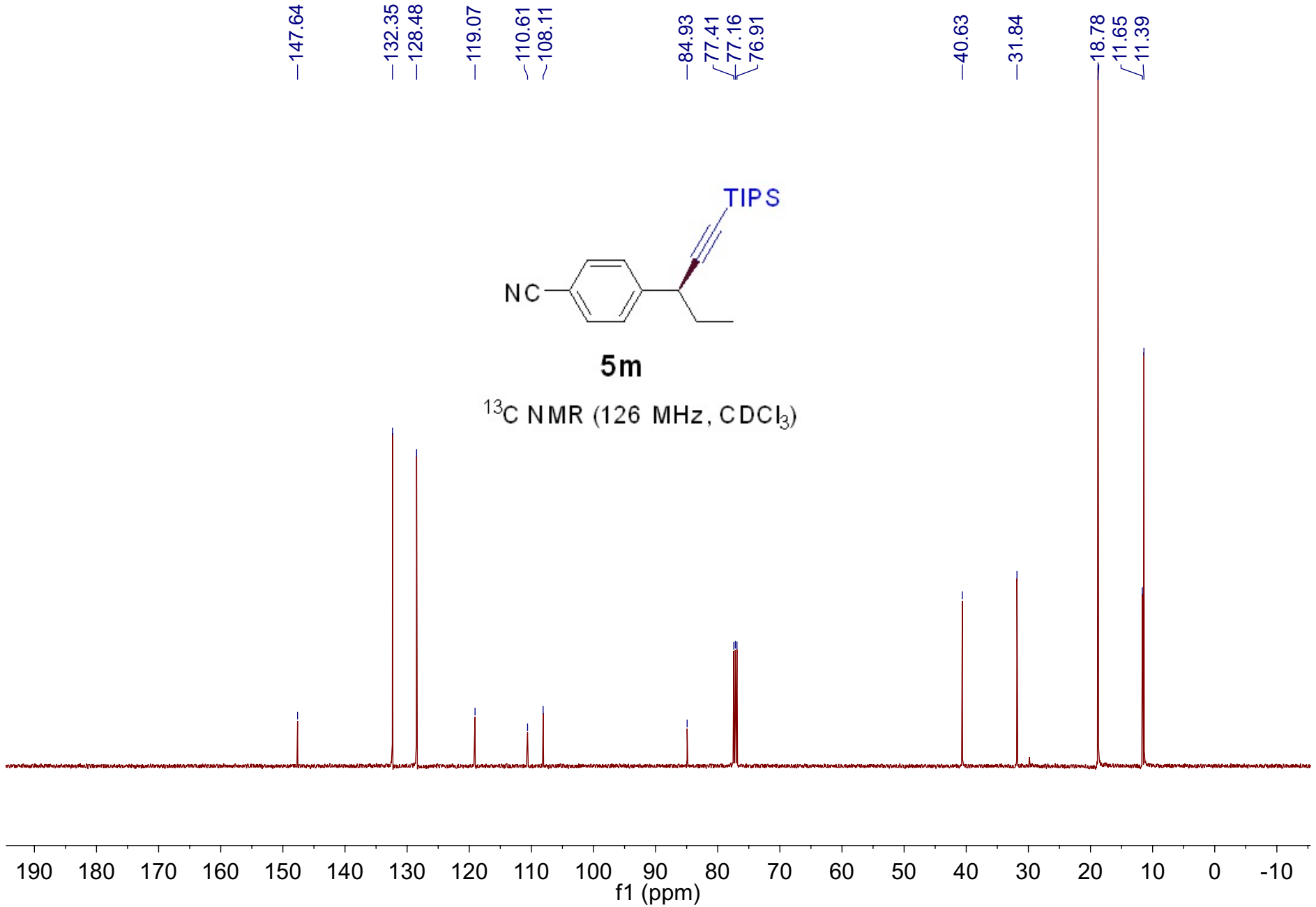
Supplementary Fig. 129. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5l**



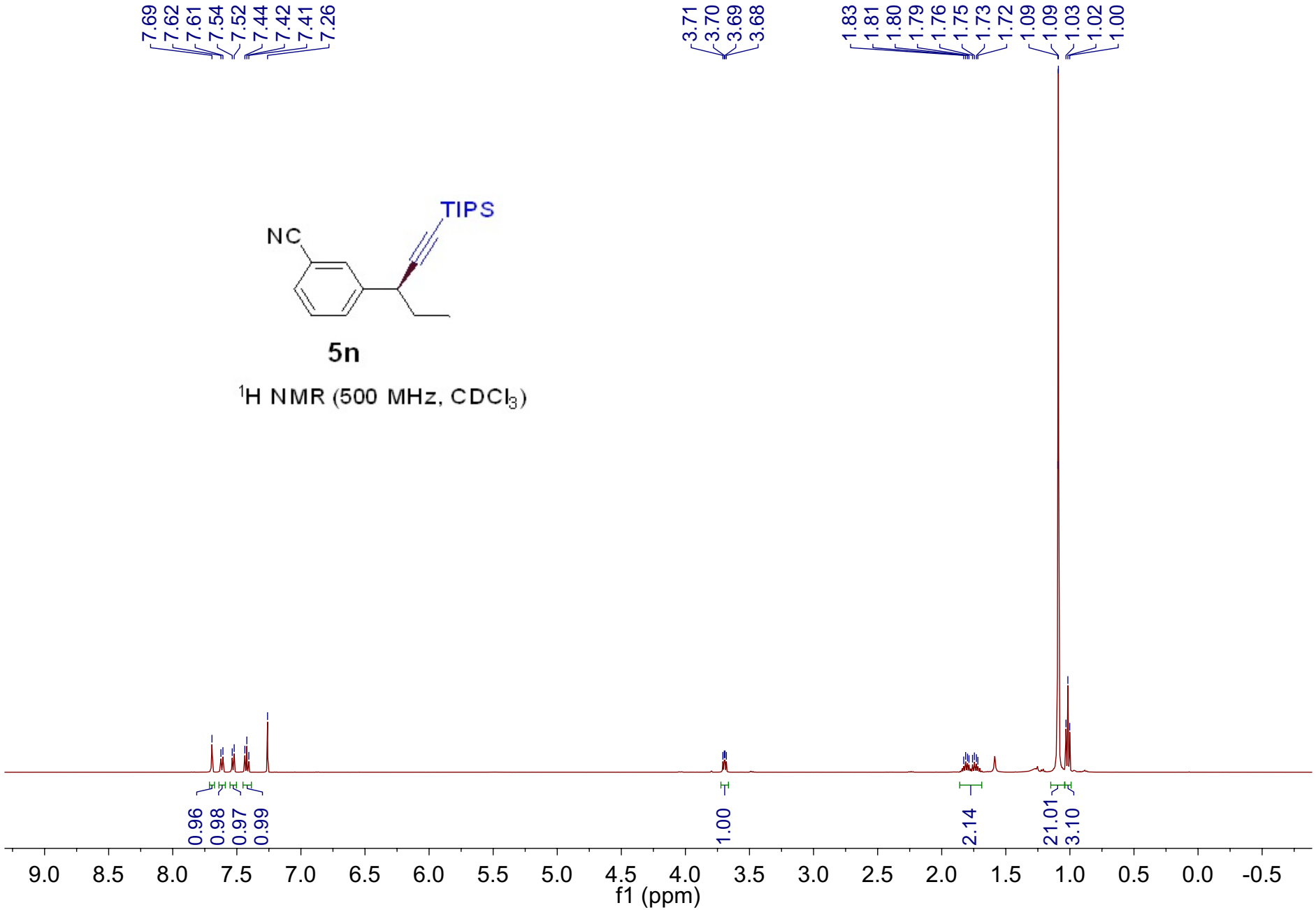
Supplementary Fig. 130. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5l**



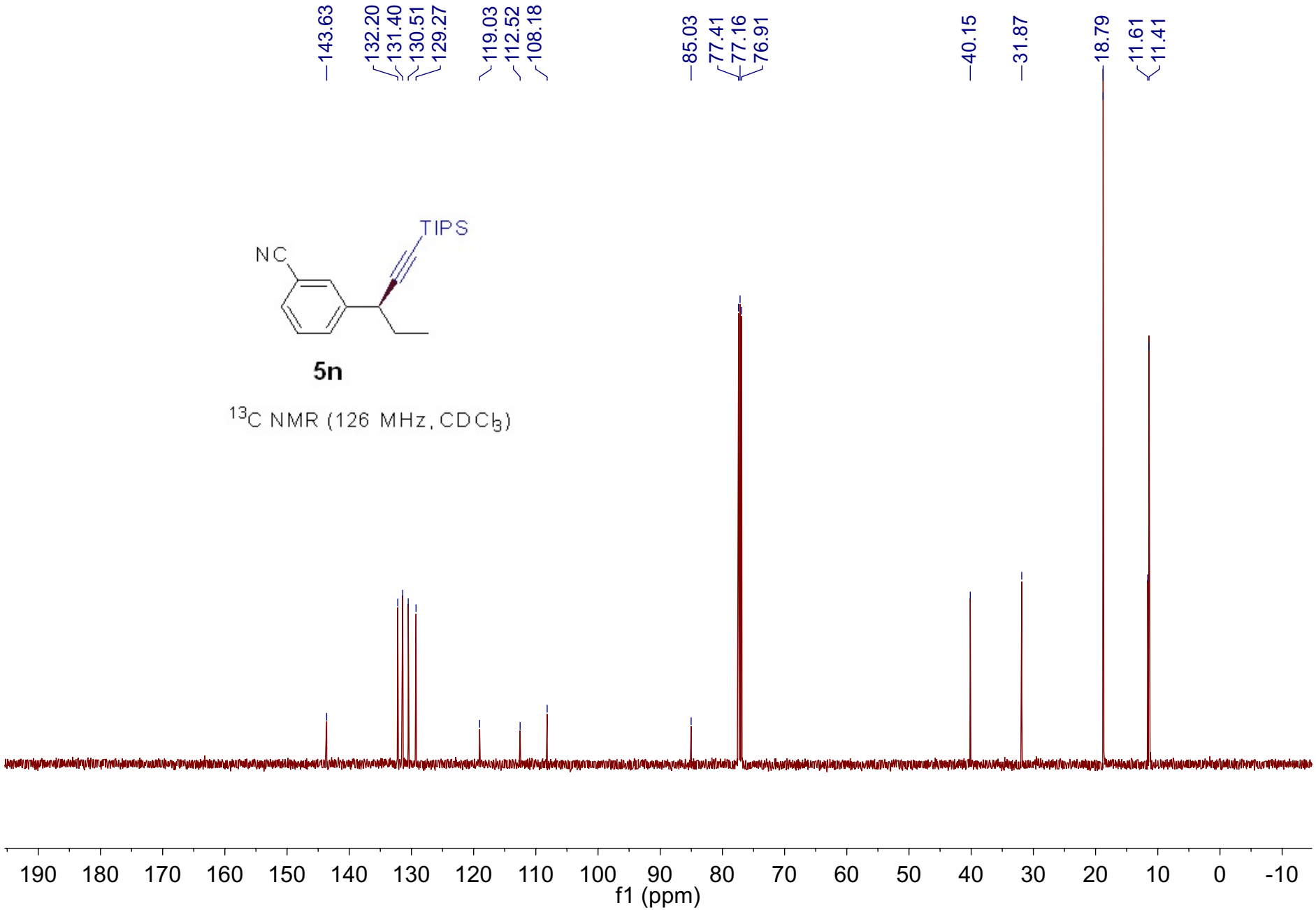
Supplementary Fig. 131. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5m**



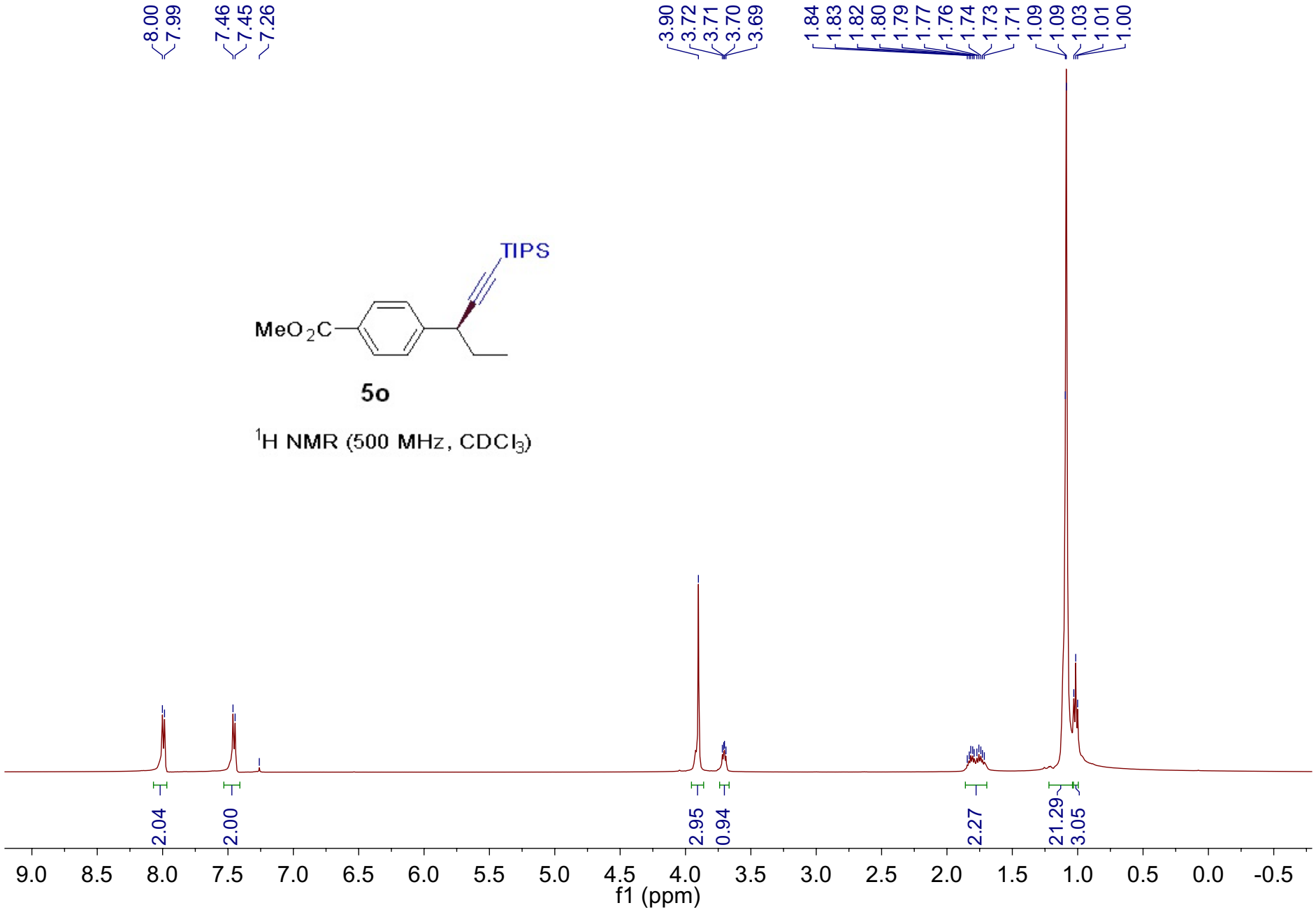
Supplementary Fig. 132. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5m**



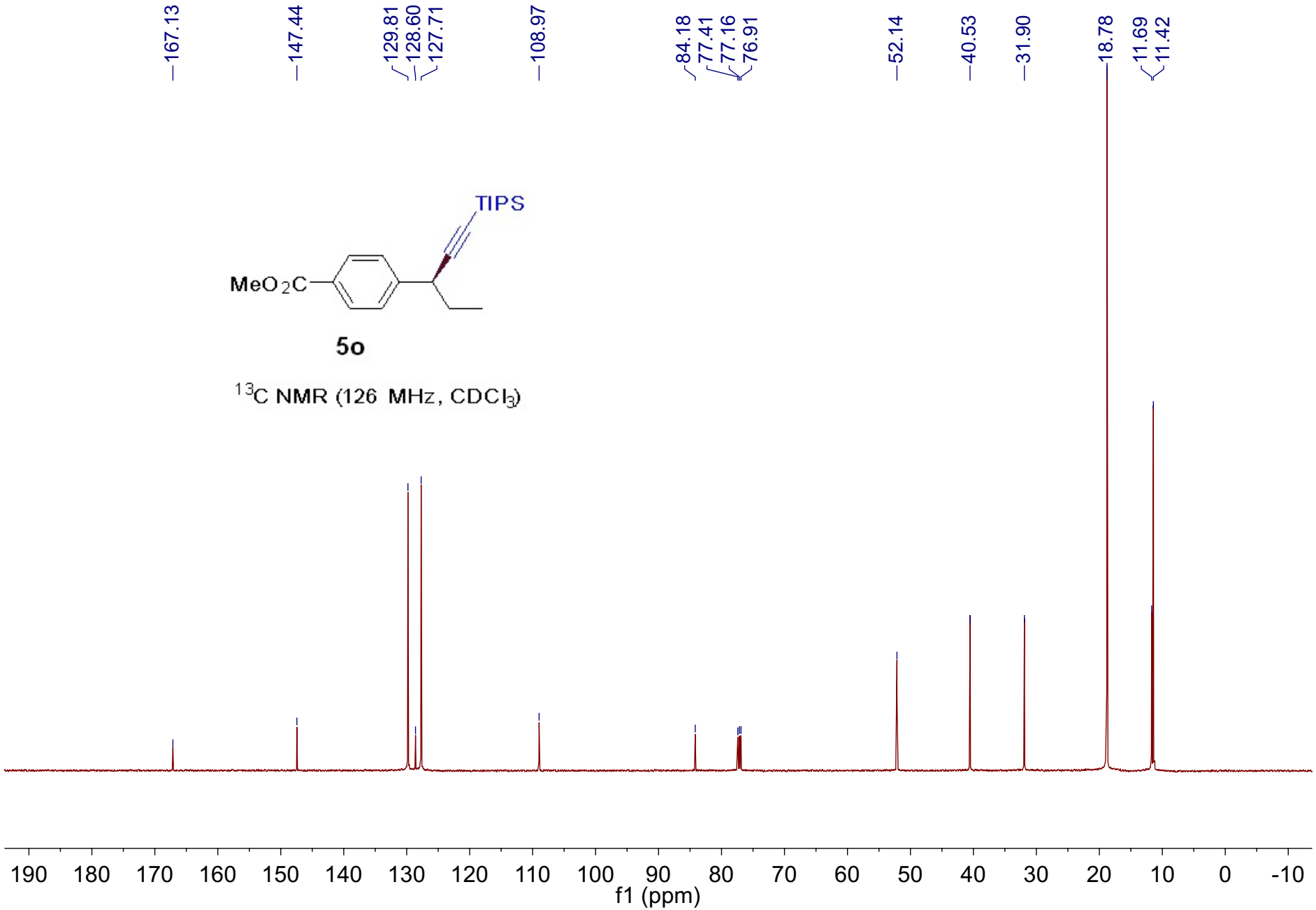
Supplementary Fig. 133. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5n**



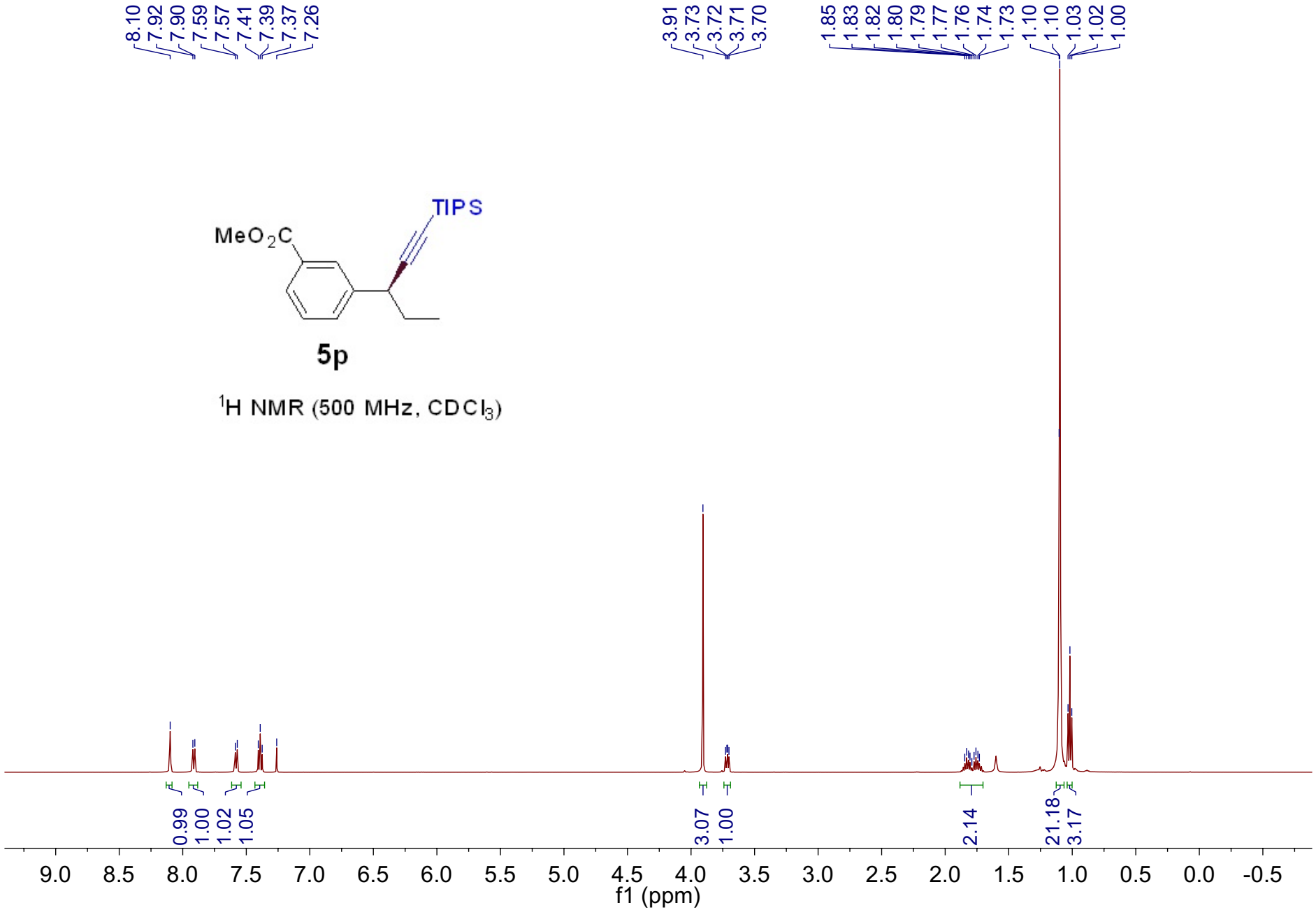
Supplementary Fig. 134. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5n**



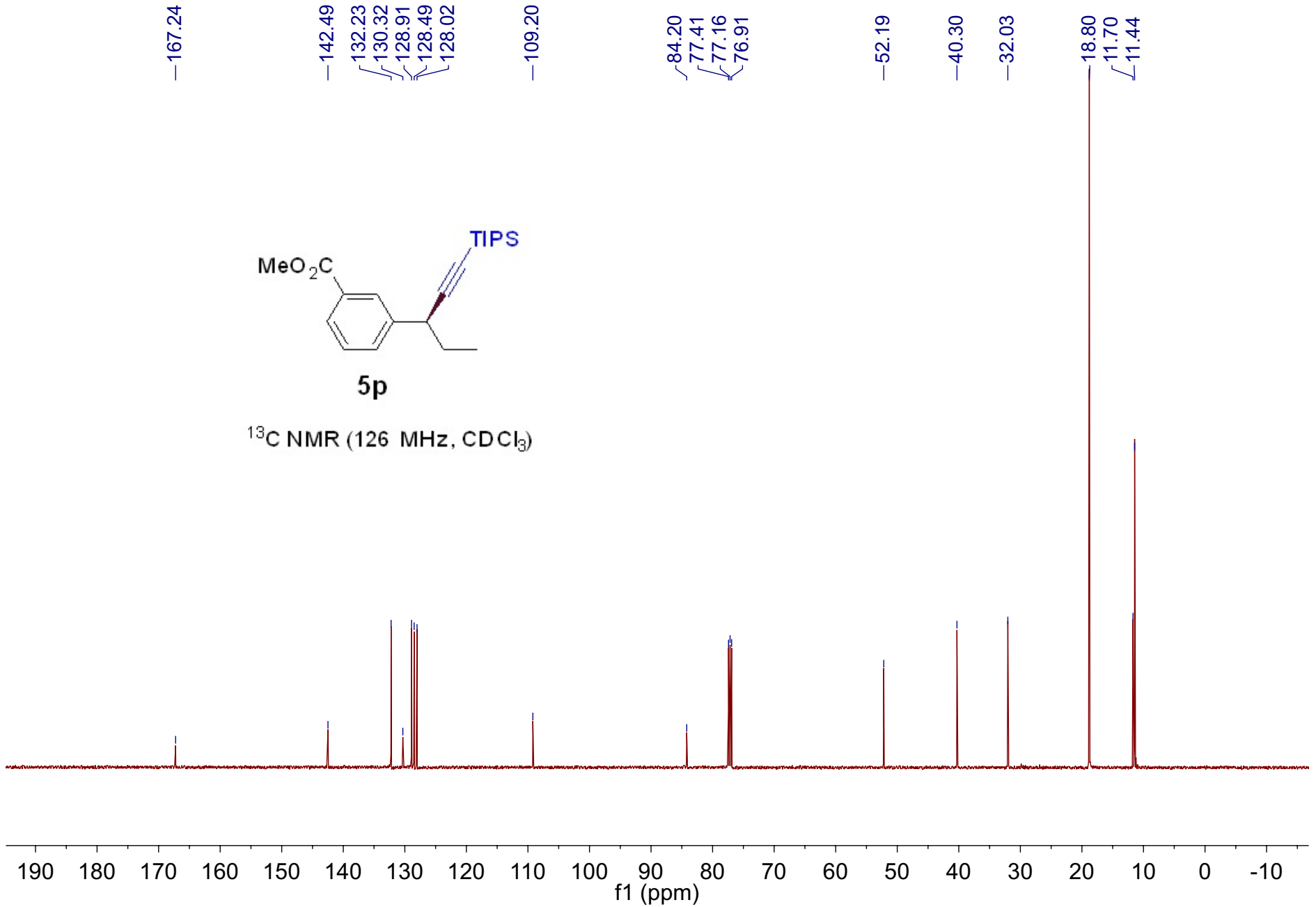
Supplementary Fig. 135. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5o**



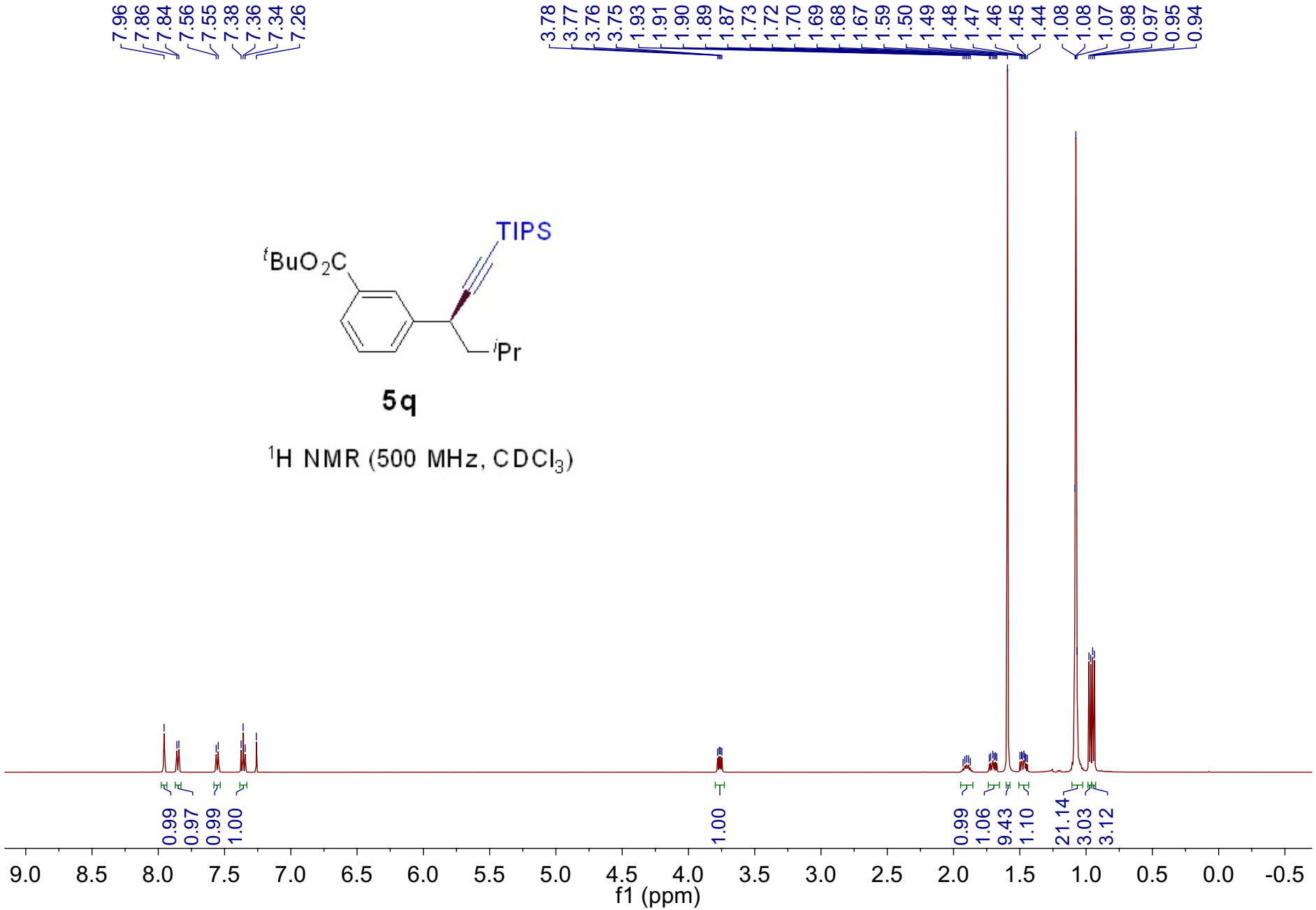
Supplementary Fig. 136. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5o**



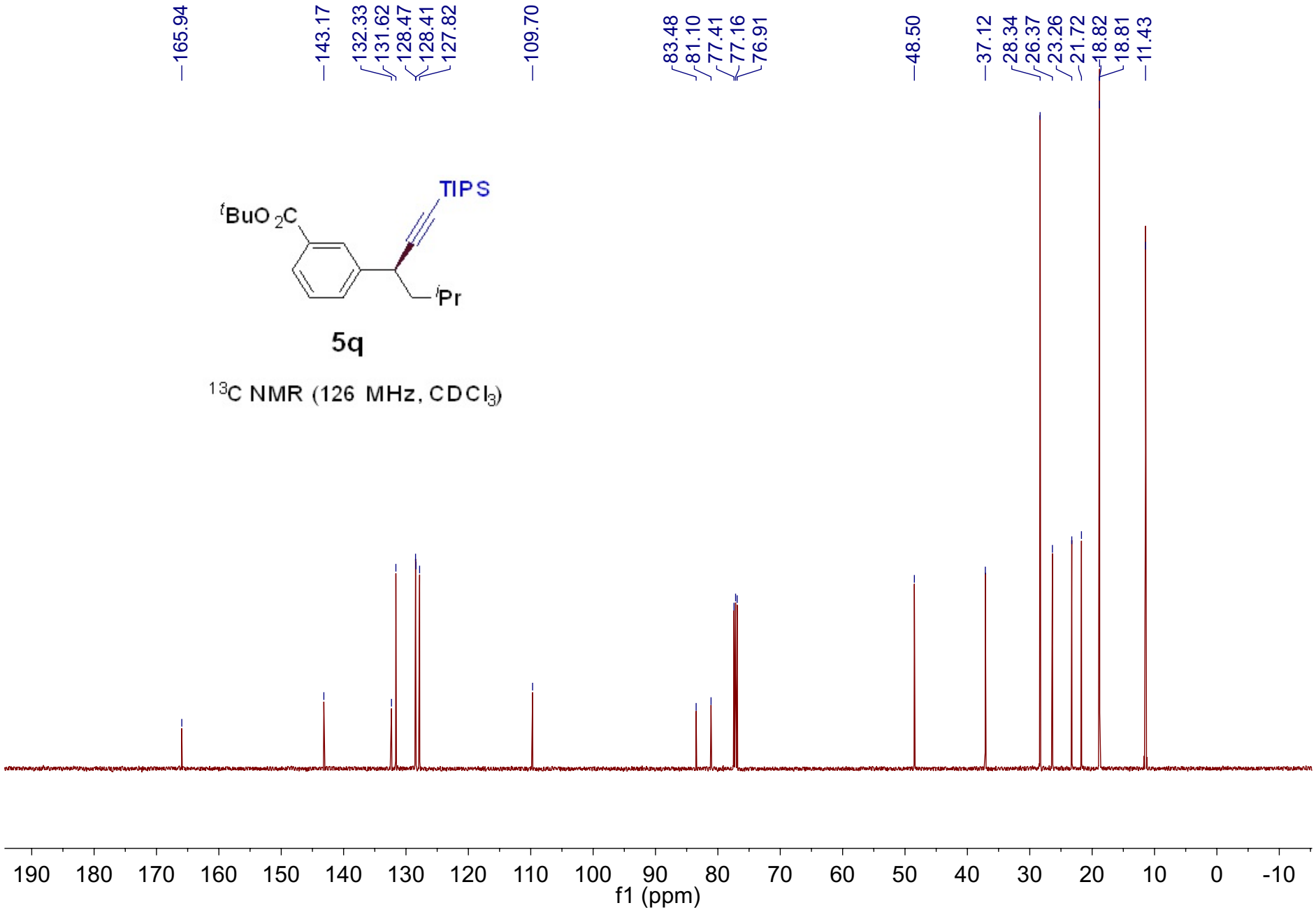
Supplementary Fig. 137. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5p**



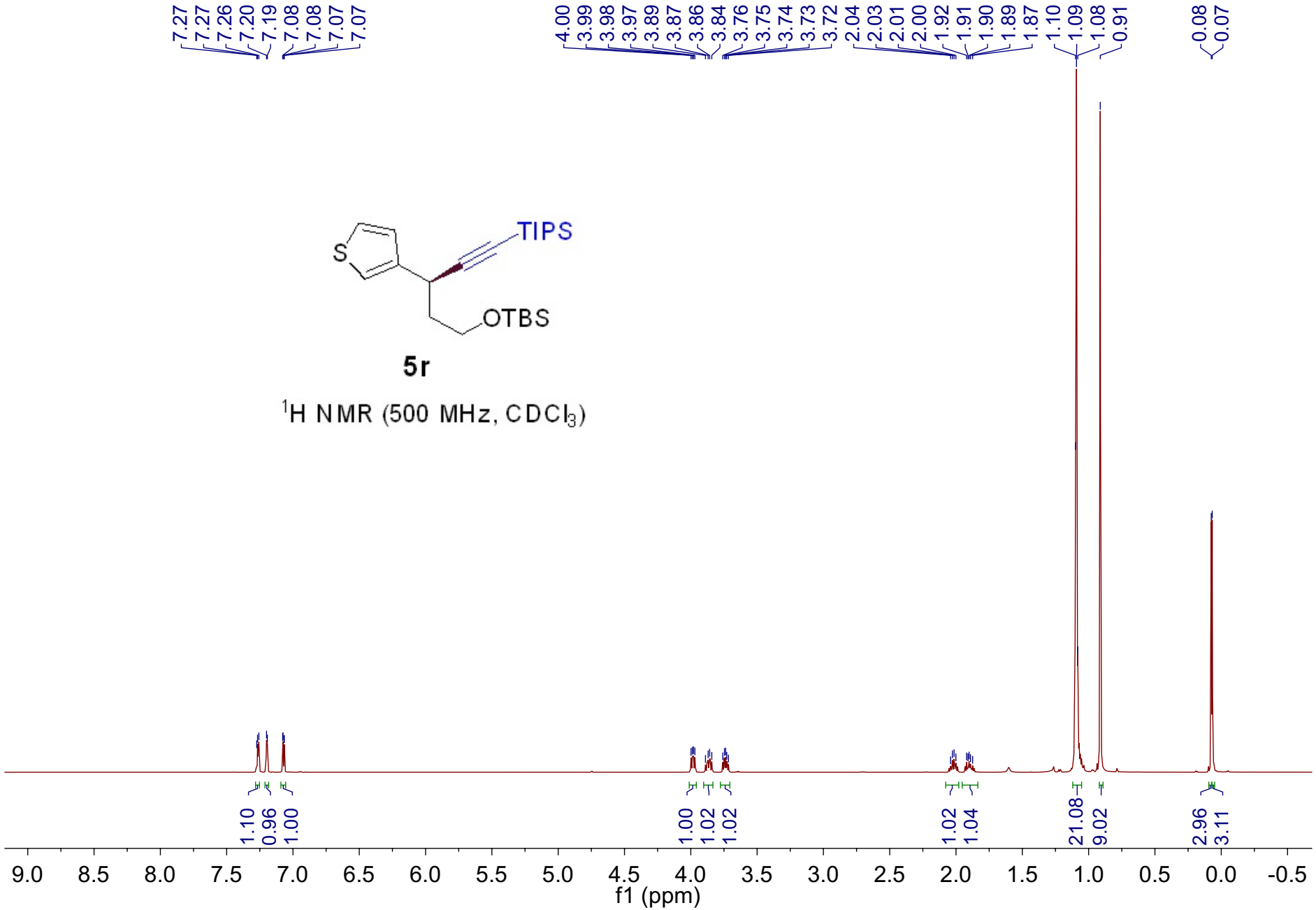
Supplementary Fig. 138. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5p**



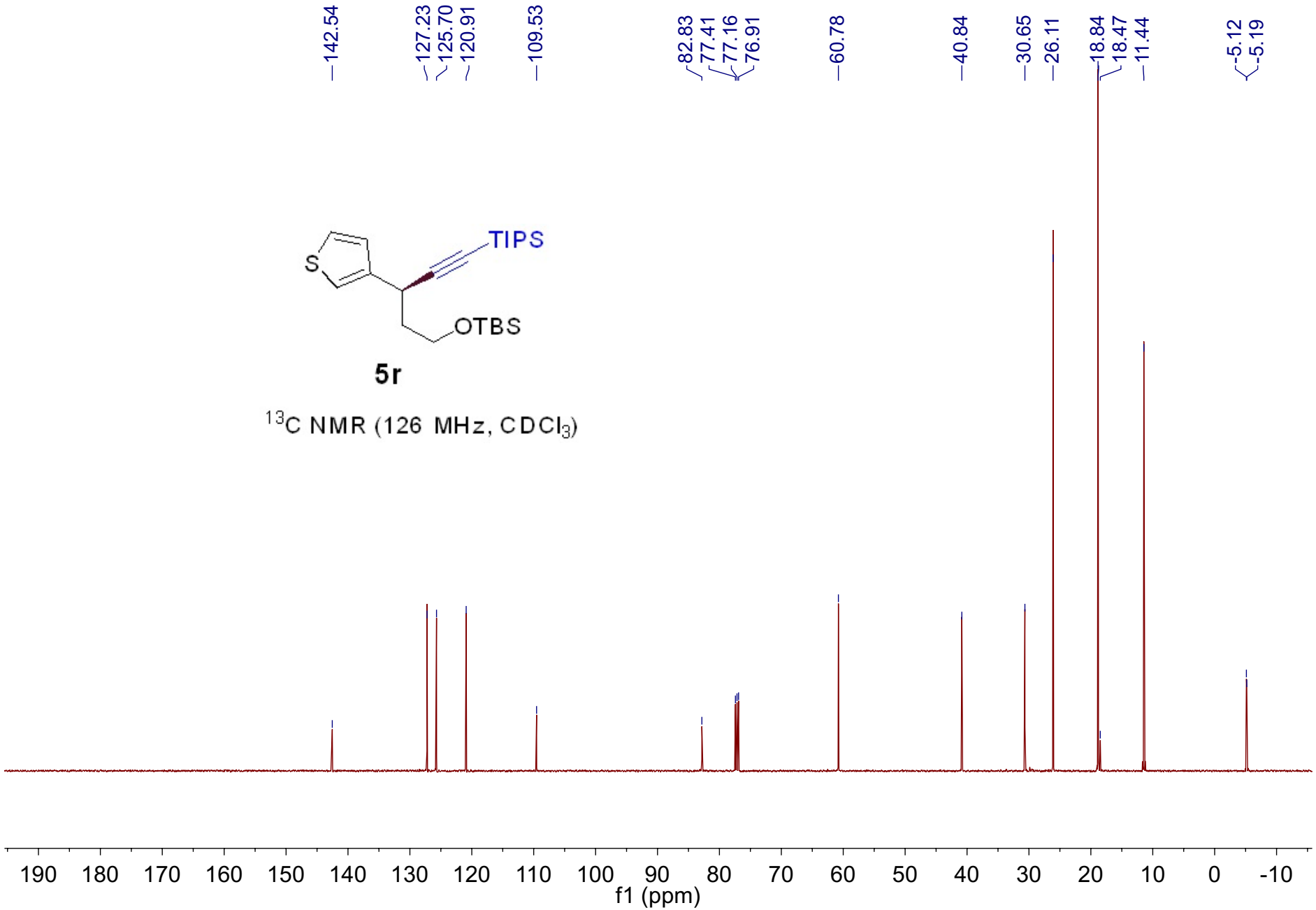
Supplementary Fig. 139. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5q**



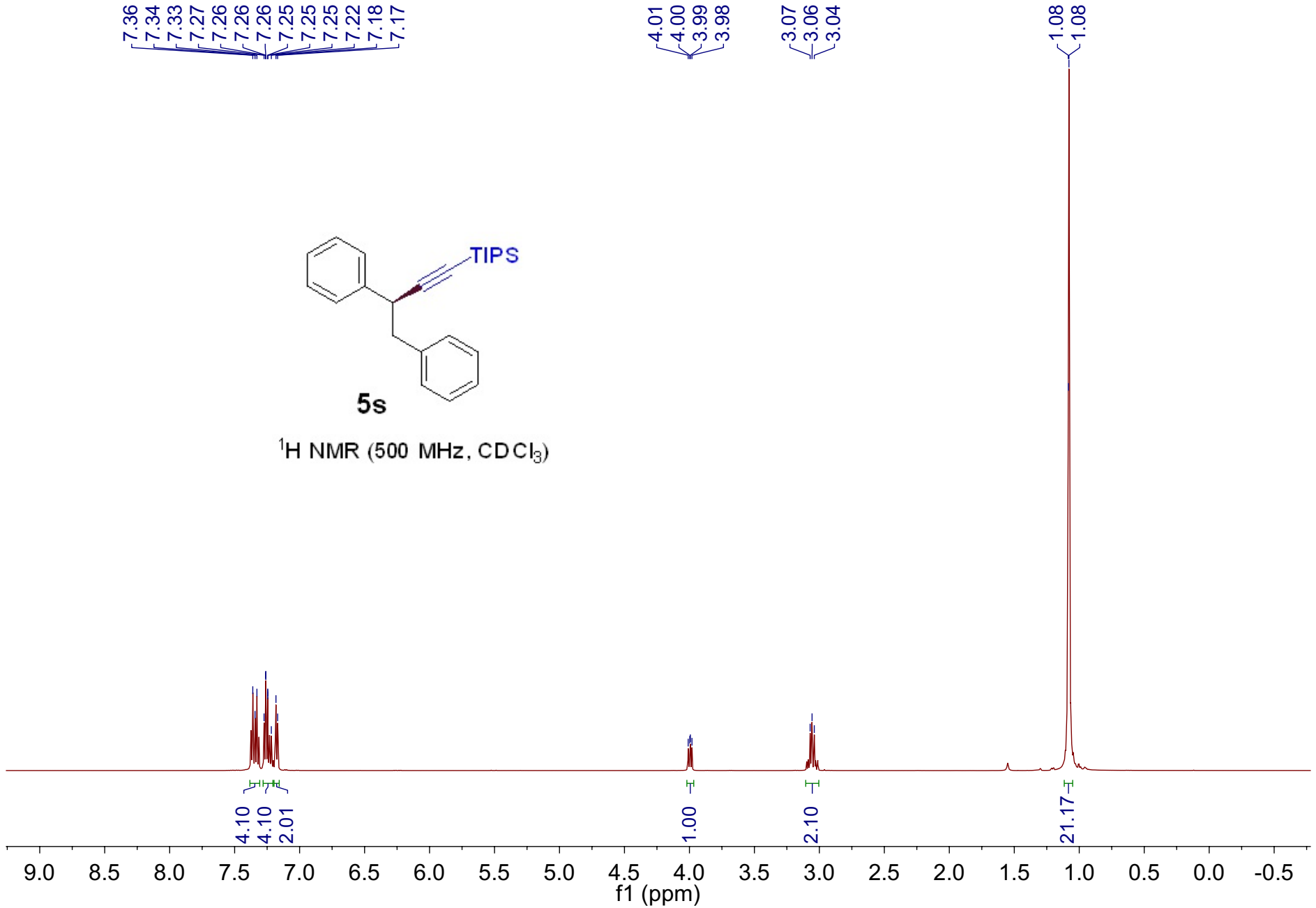
Supplementary Fig. 140. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5q**



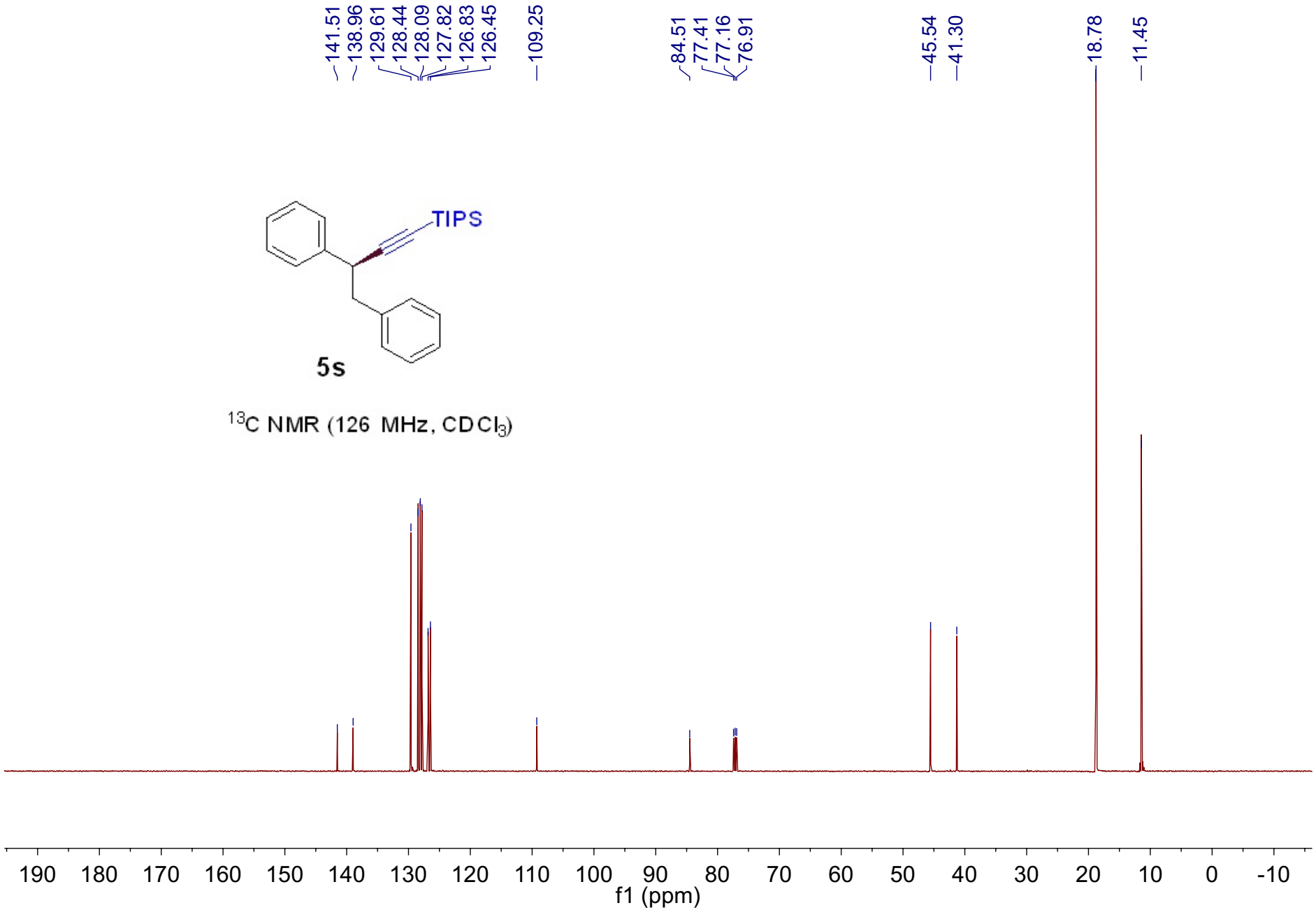
Supplementary Fig. 141. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5r**



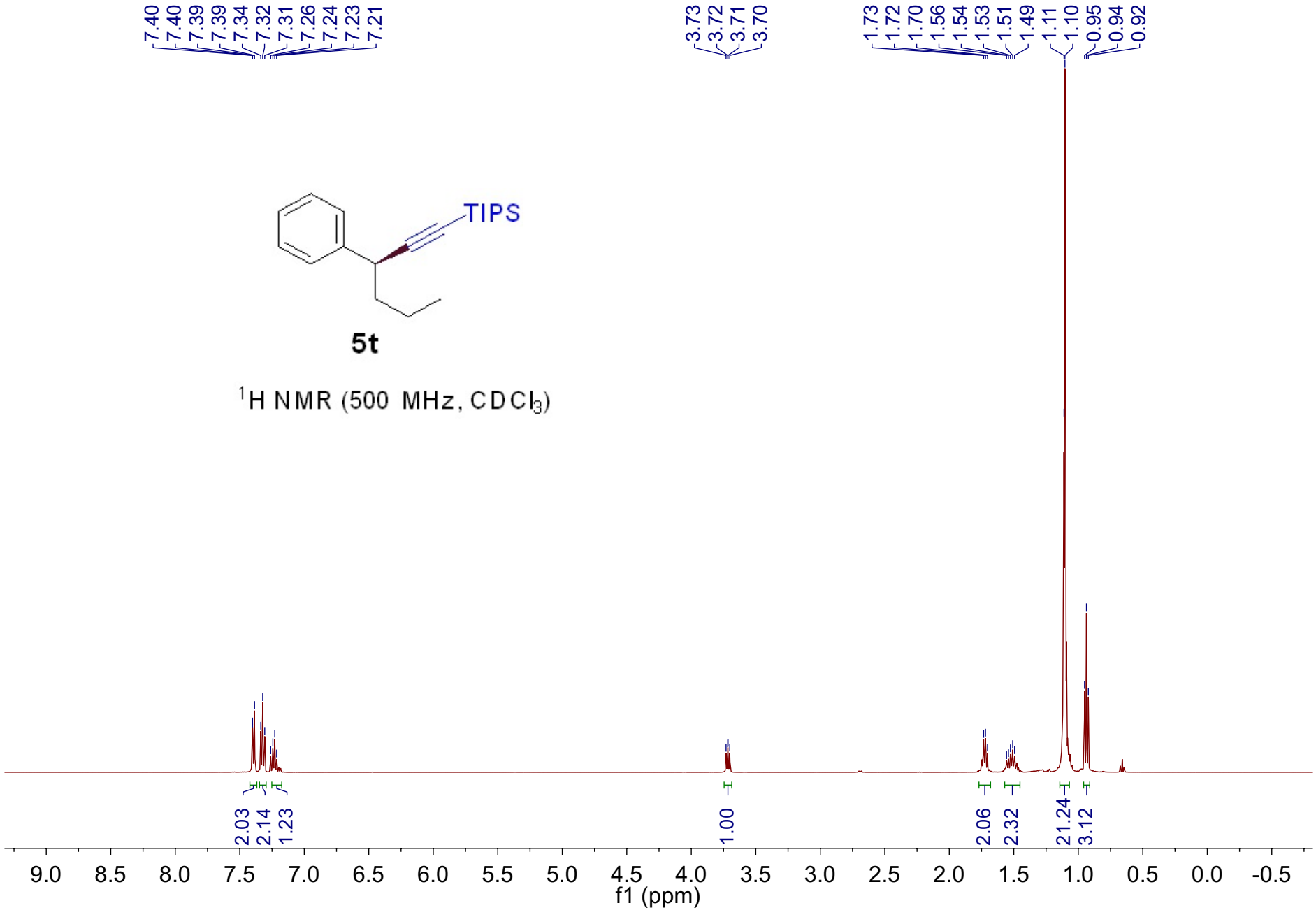
Supplementary Fig. 142. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5r**



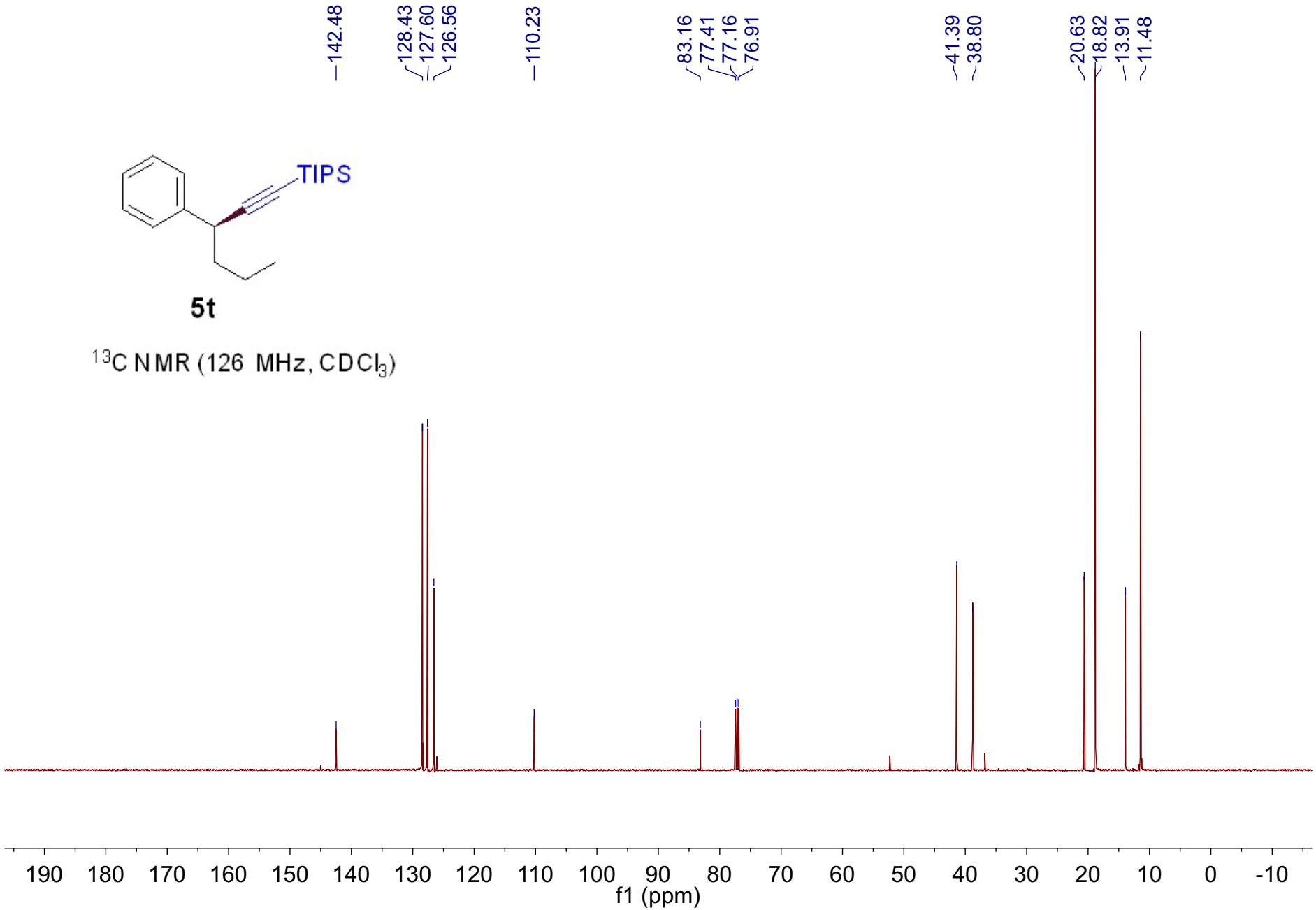
Supplementary Fig. 143. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5s**



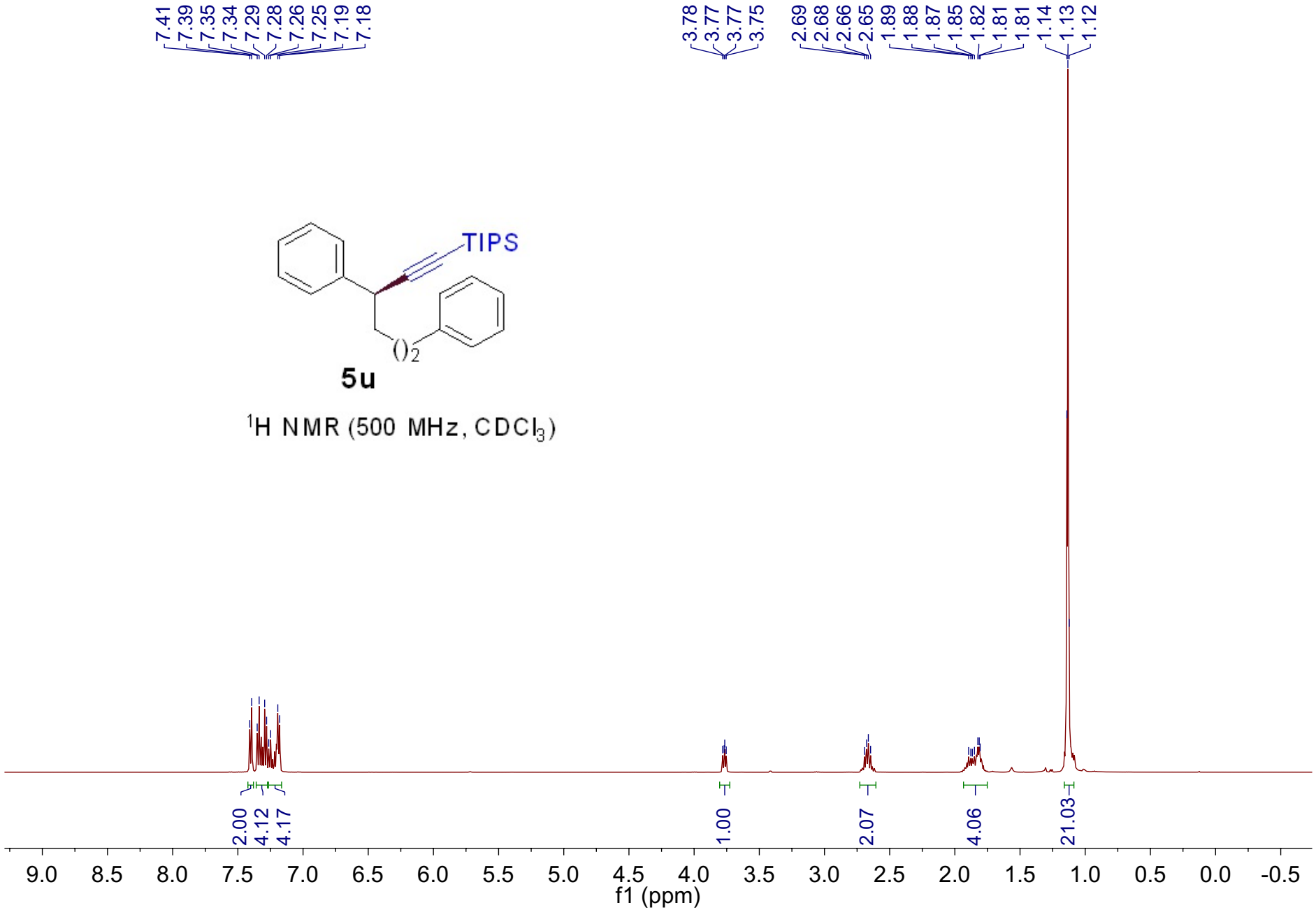
Supplementary Fig. 144. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5s**



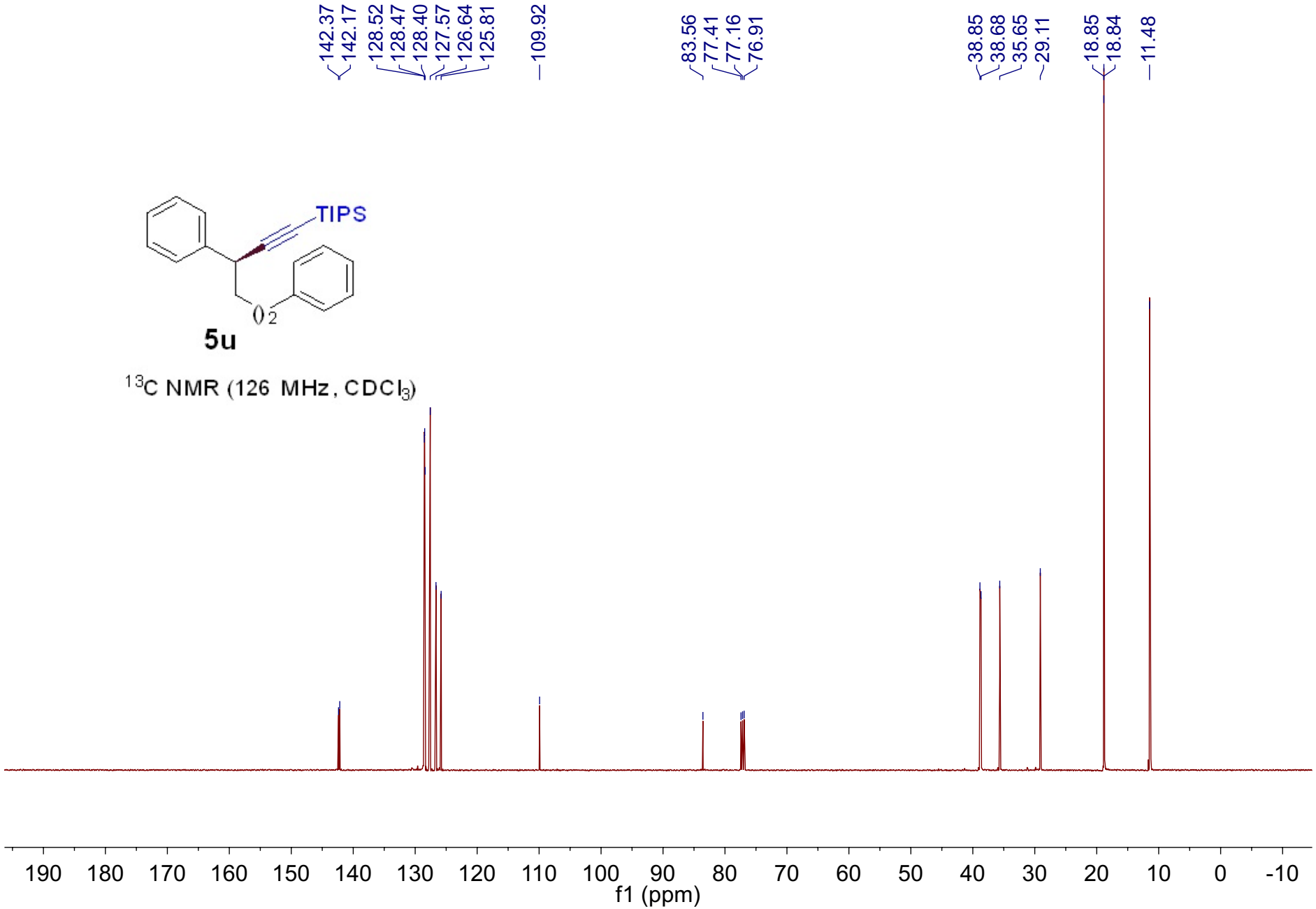
Supplementary Fig. 145. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5t**



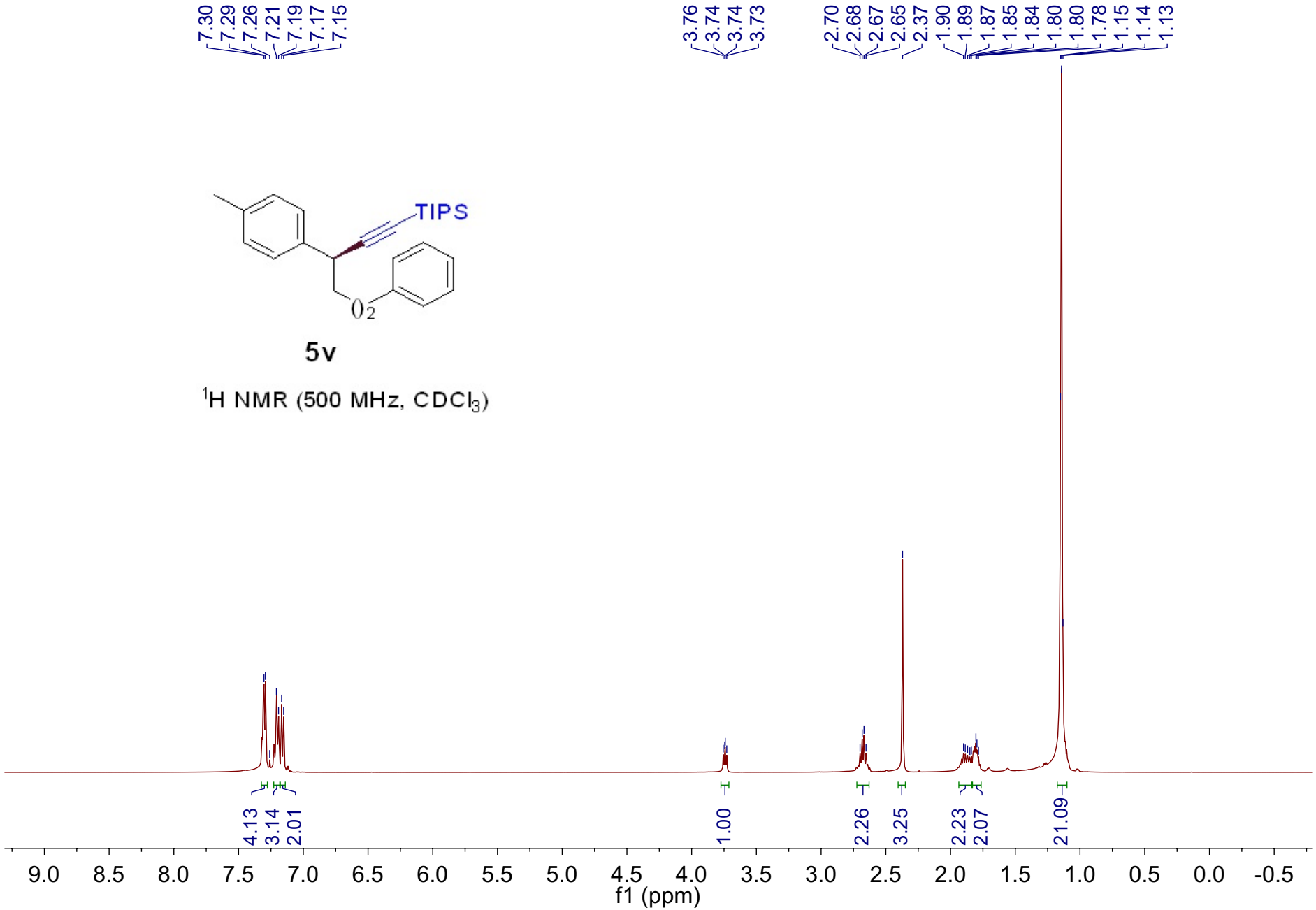
Supplementary Fig. 146. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5t**



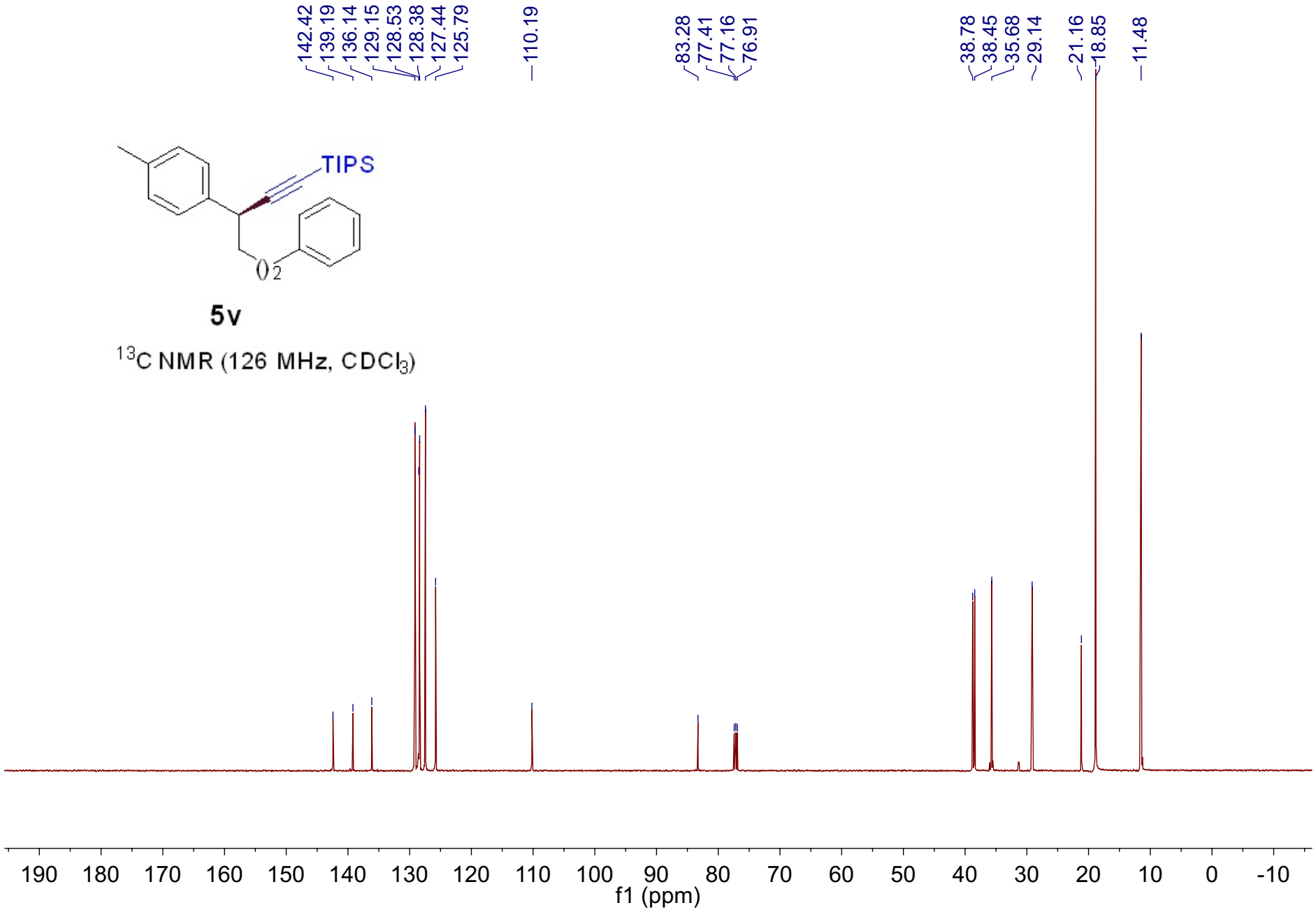
Supplementary Fig. 147. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5u**



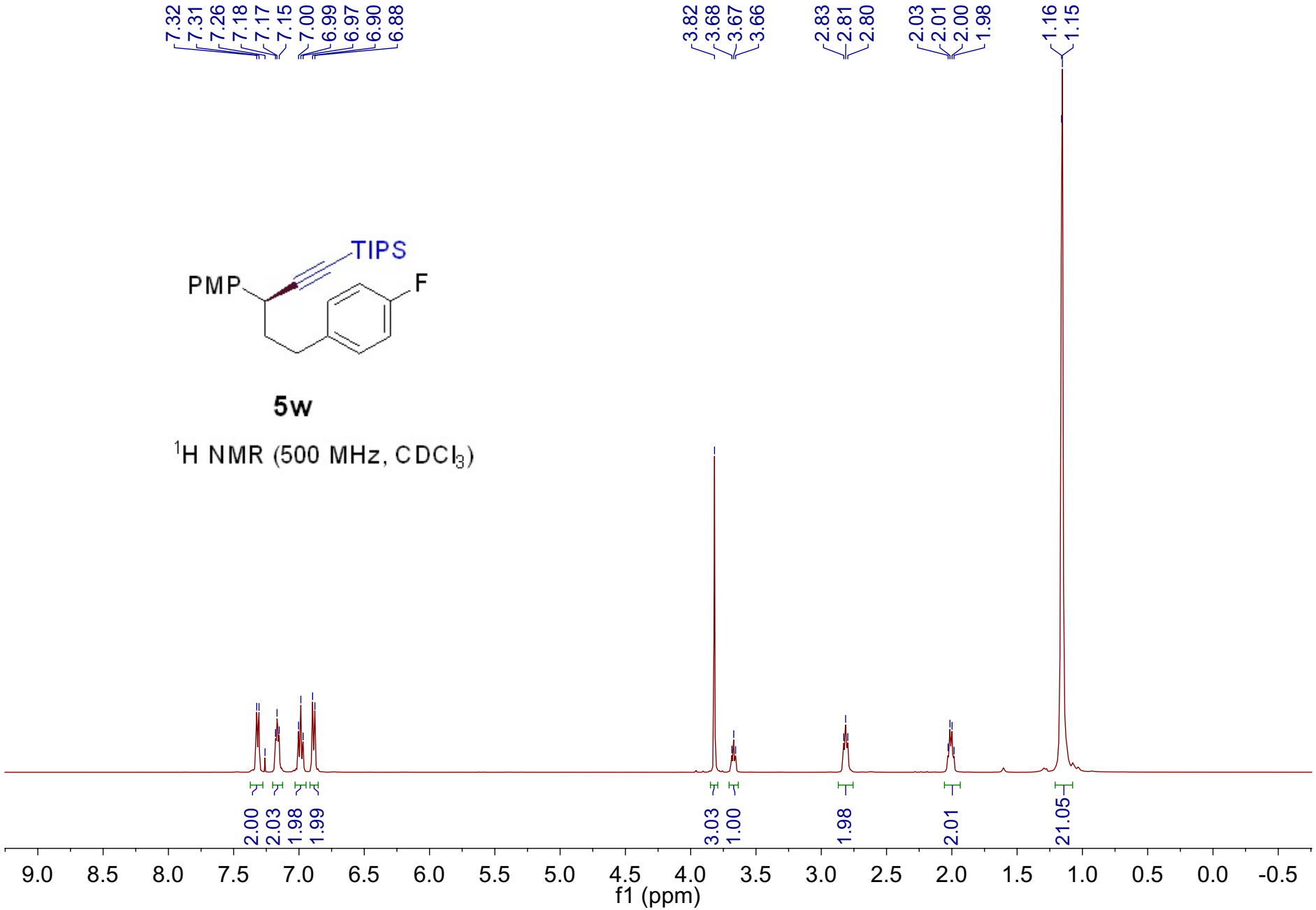
Supplementary Fig. 148. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5u**



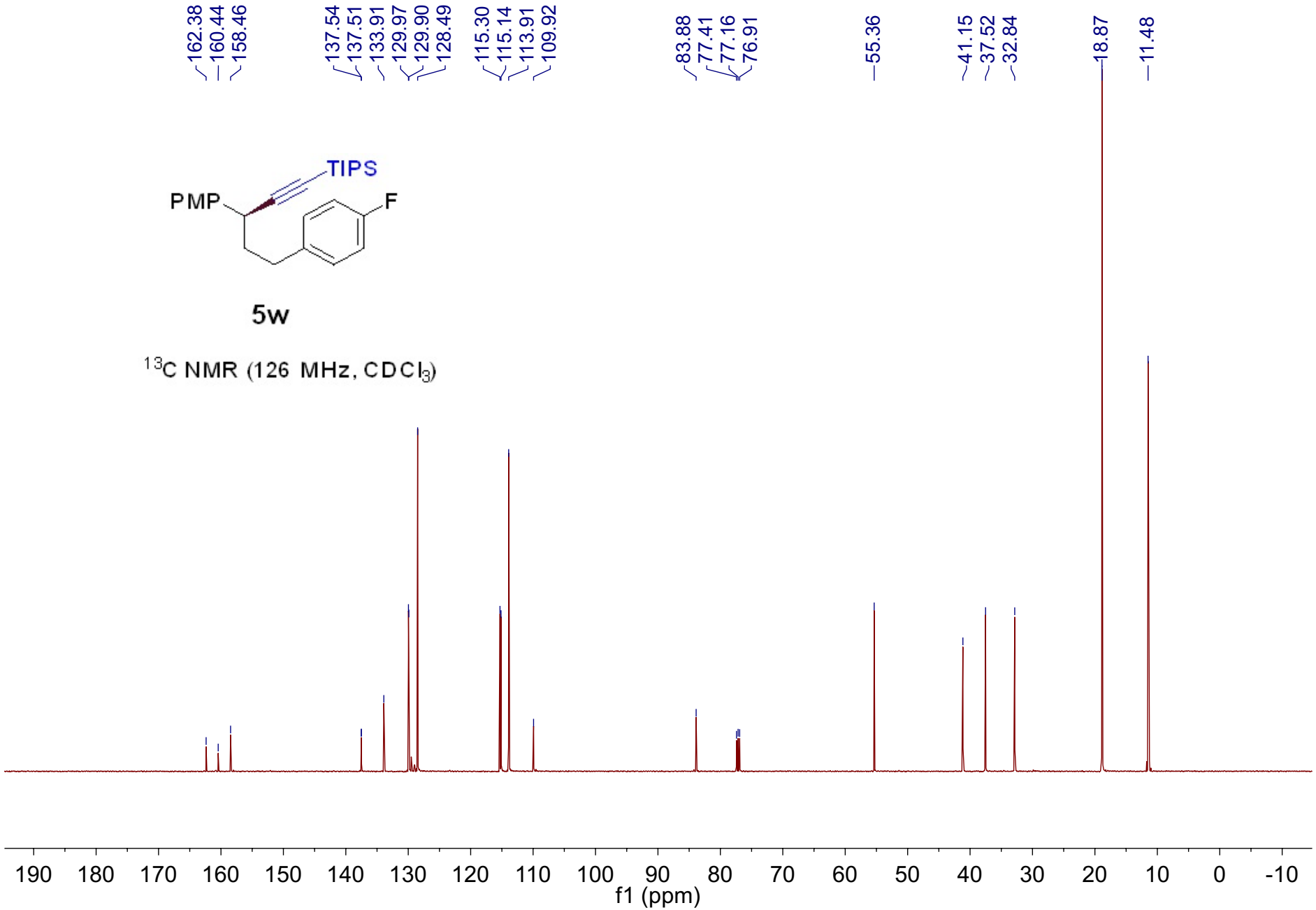
Supplementary Fig. 149. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5v**



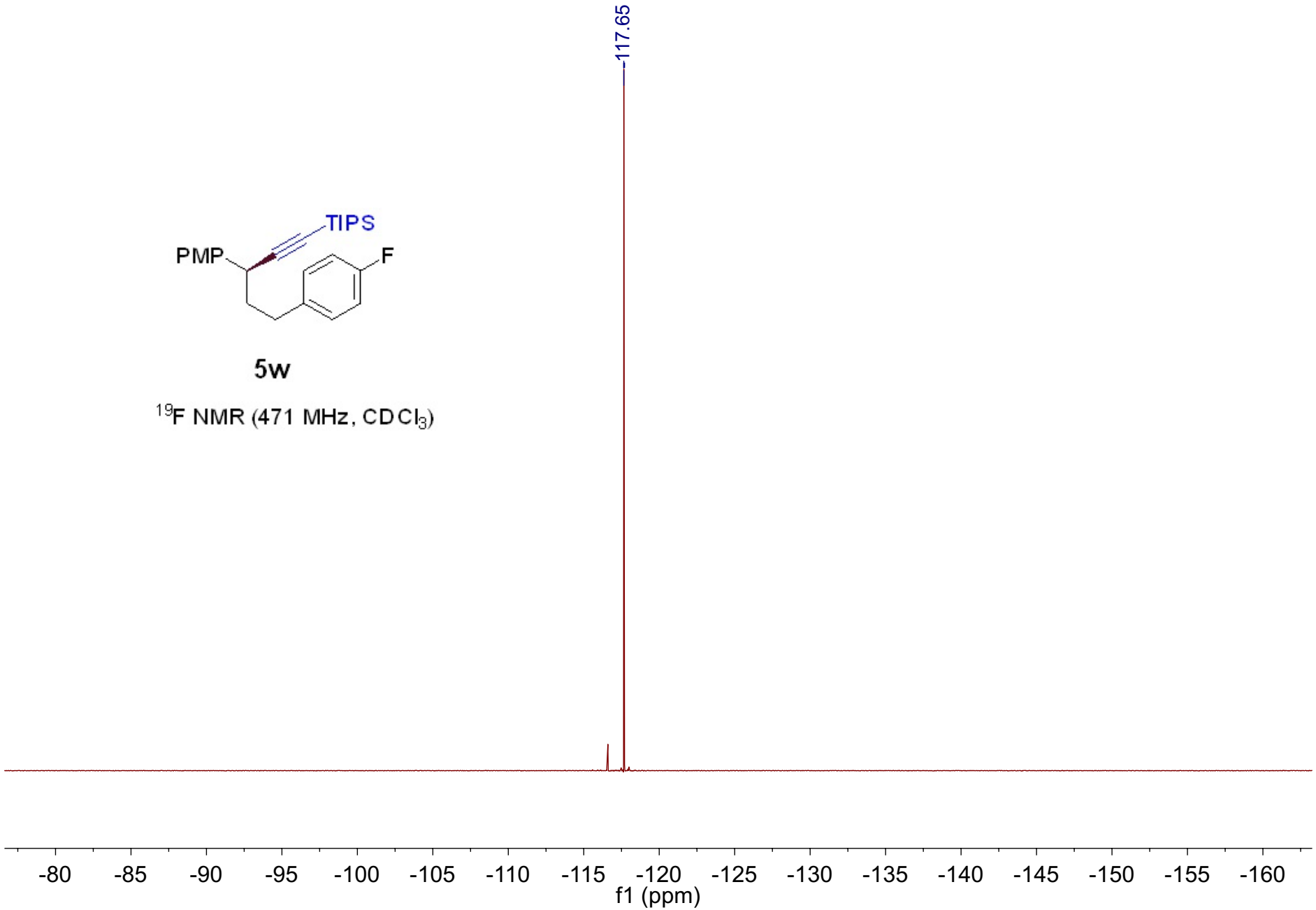
Supplementary Fig. 150. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5v**



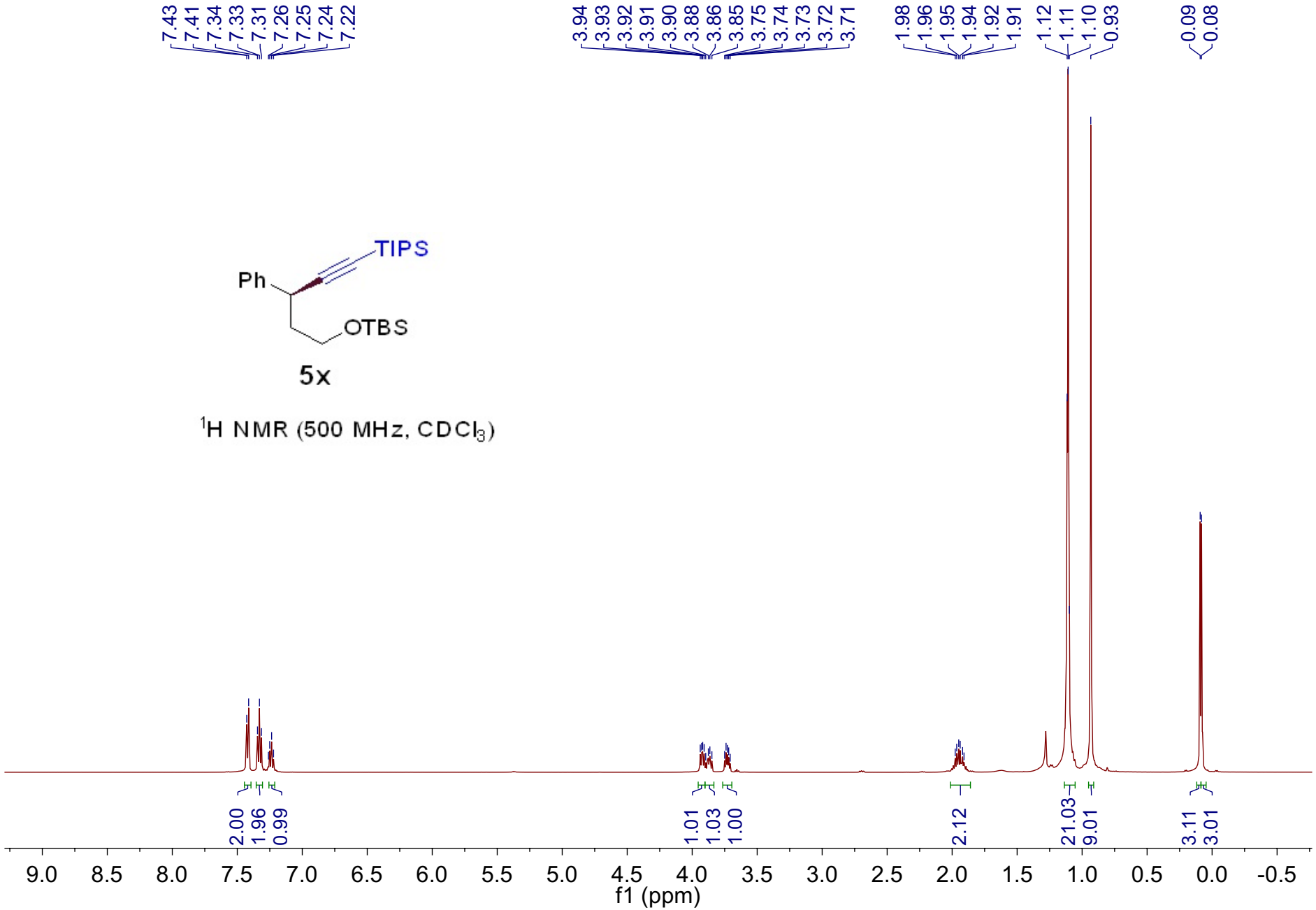
Supplementary Fig. 151. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5w**



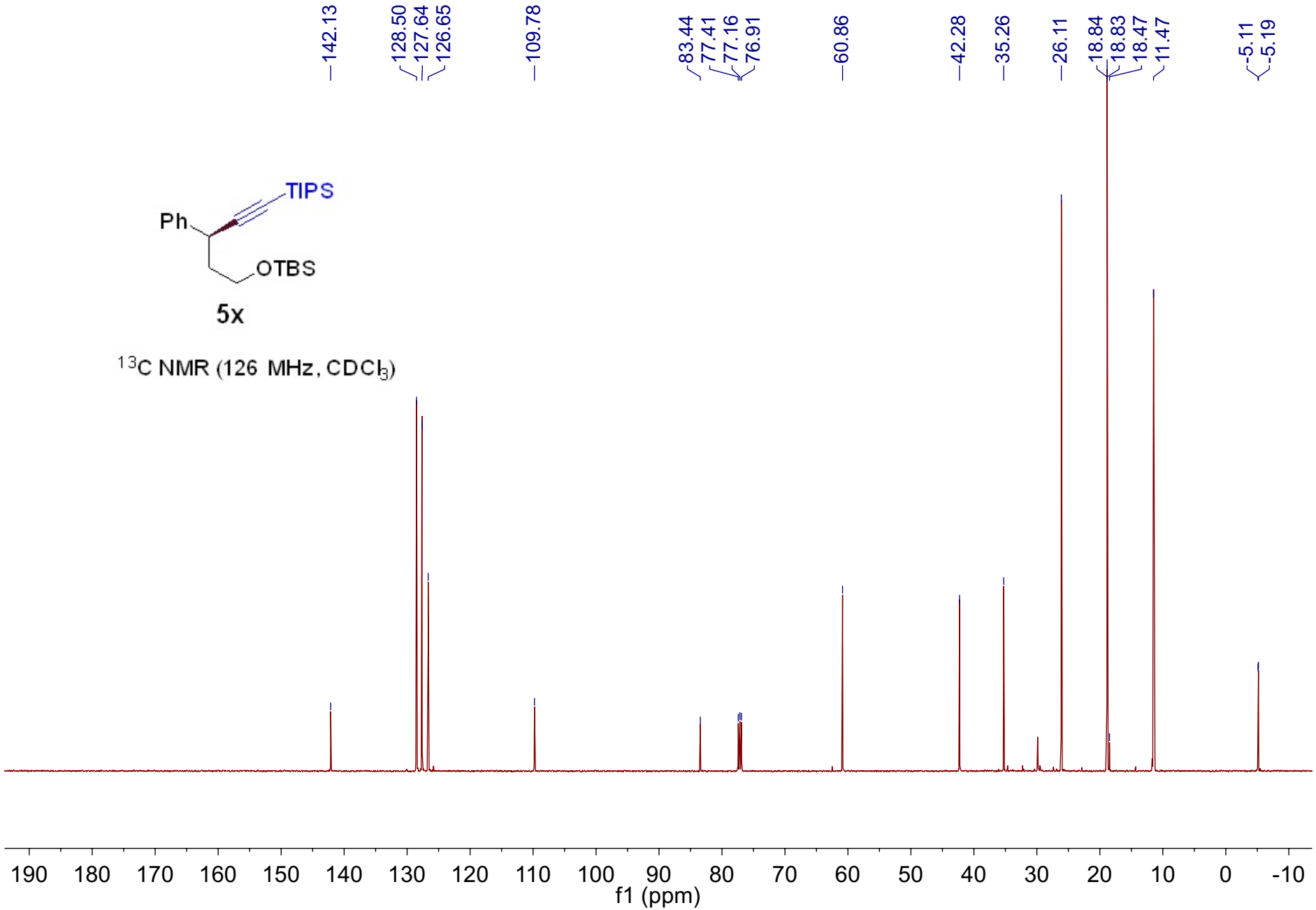
Supplementary Fig. 152. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5w**



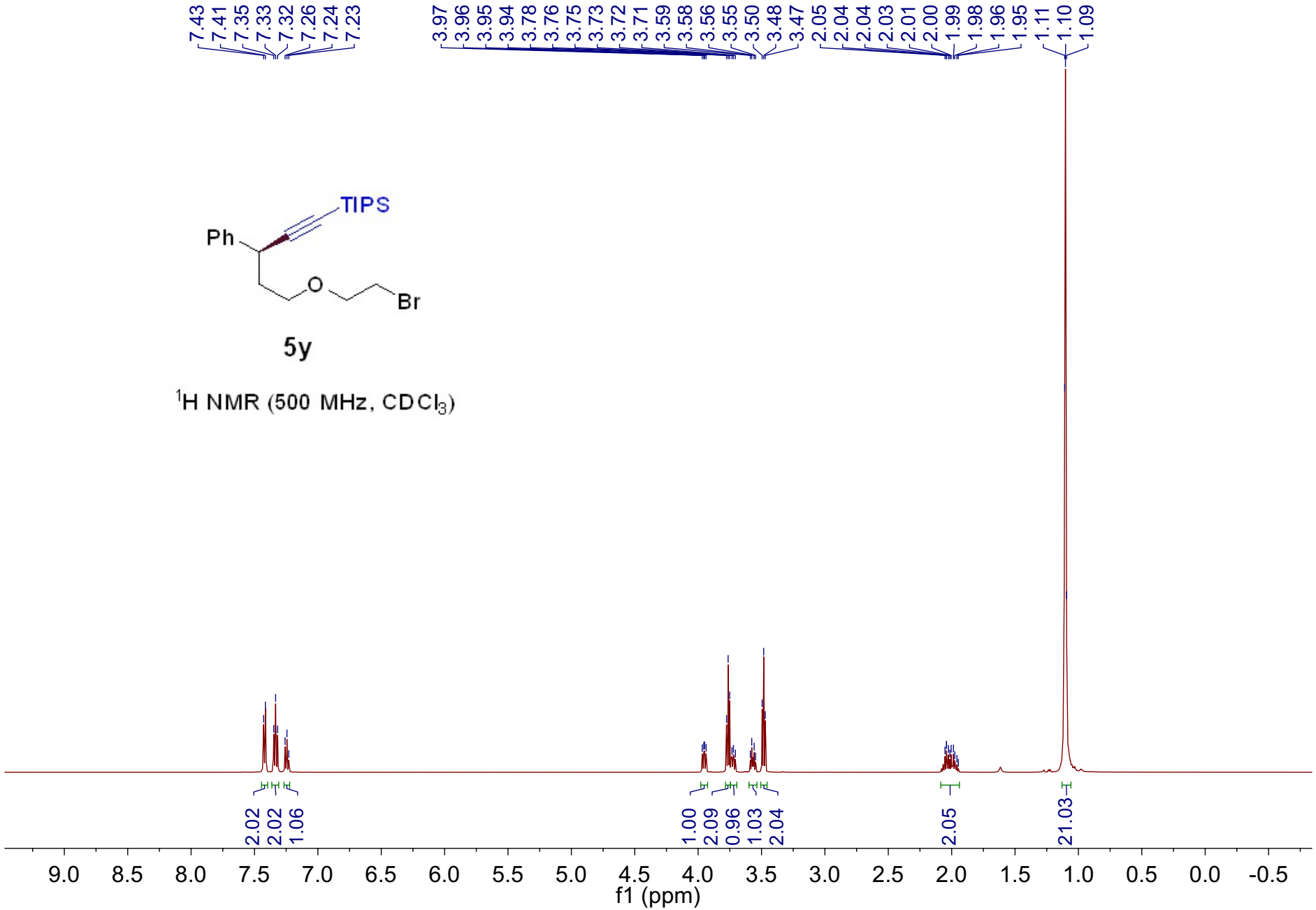
Supplementary Fig. 153. ^{19}F NMR (471 MHz, $CDCl_3$) spectra for compound **5w**



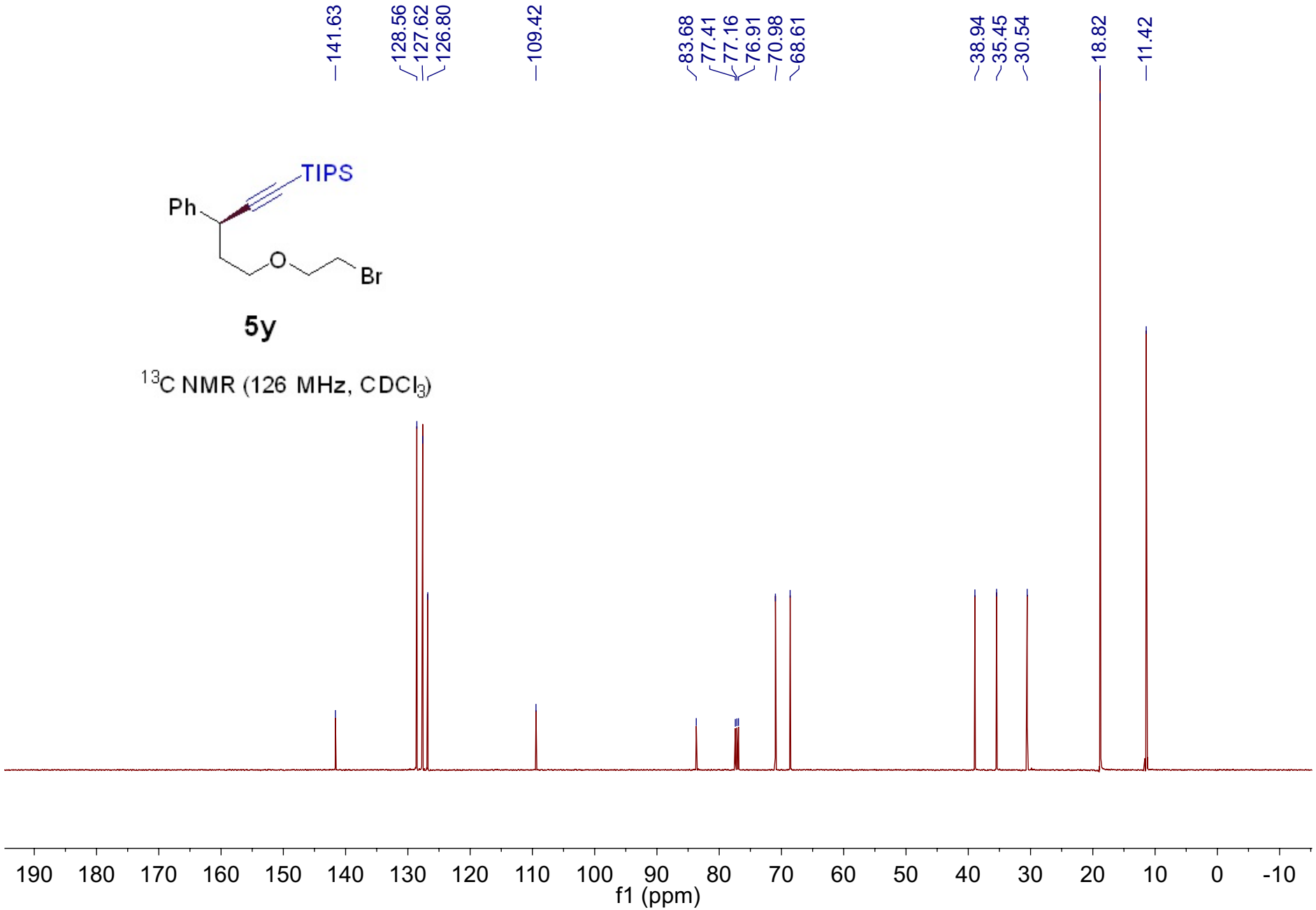
Supplementary Fig. 154. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5x**



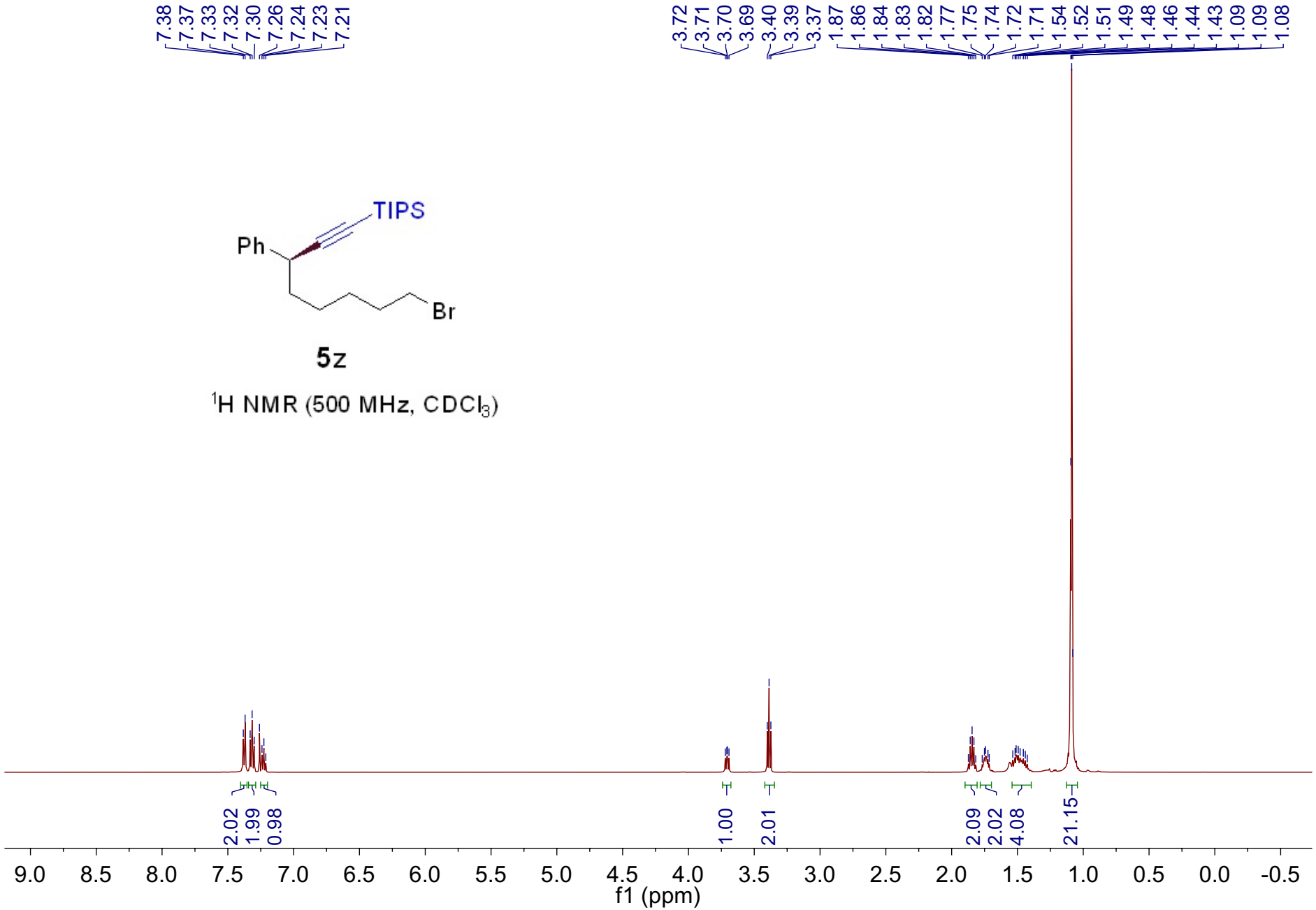
Supplementary Fig. 155. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5x**



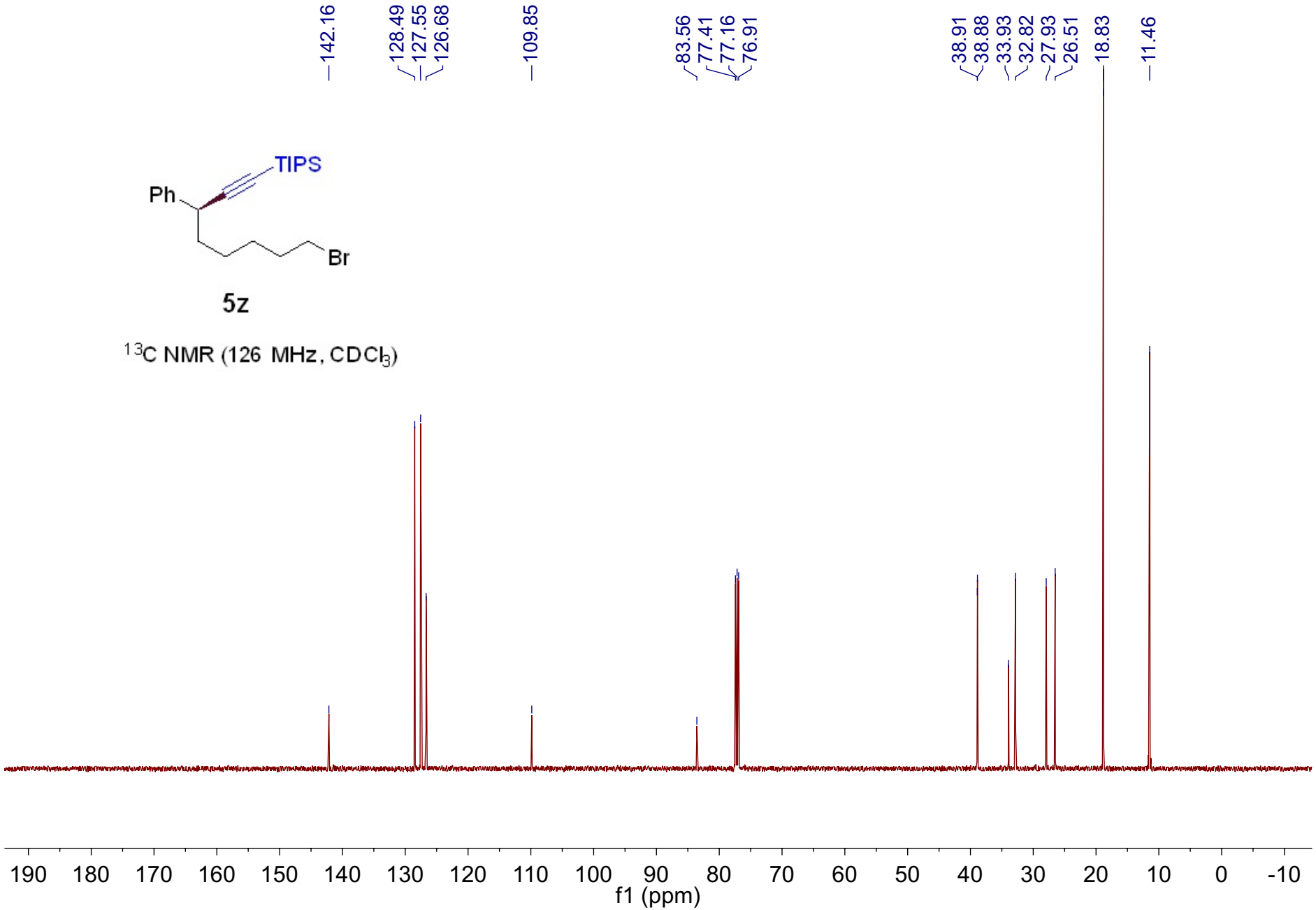
Supplementary Fig. 156. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5y**



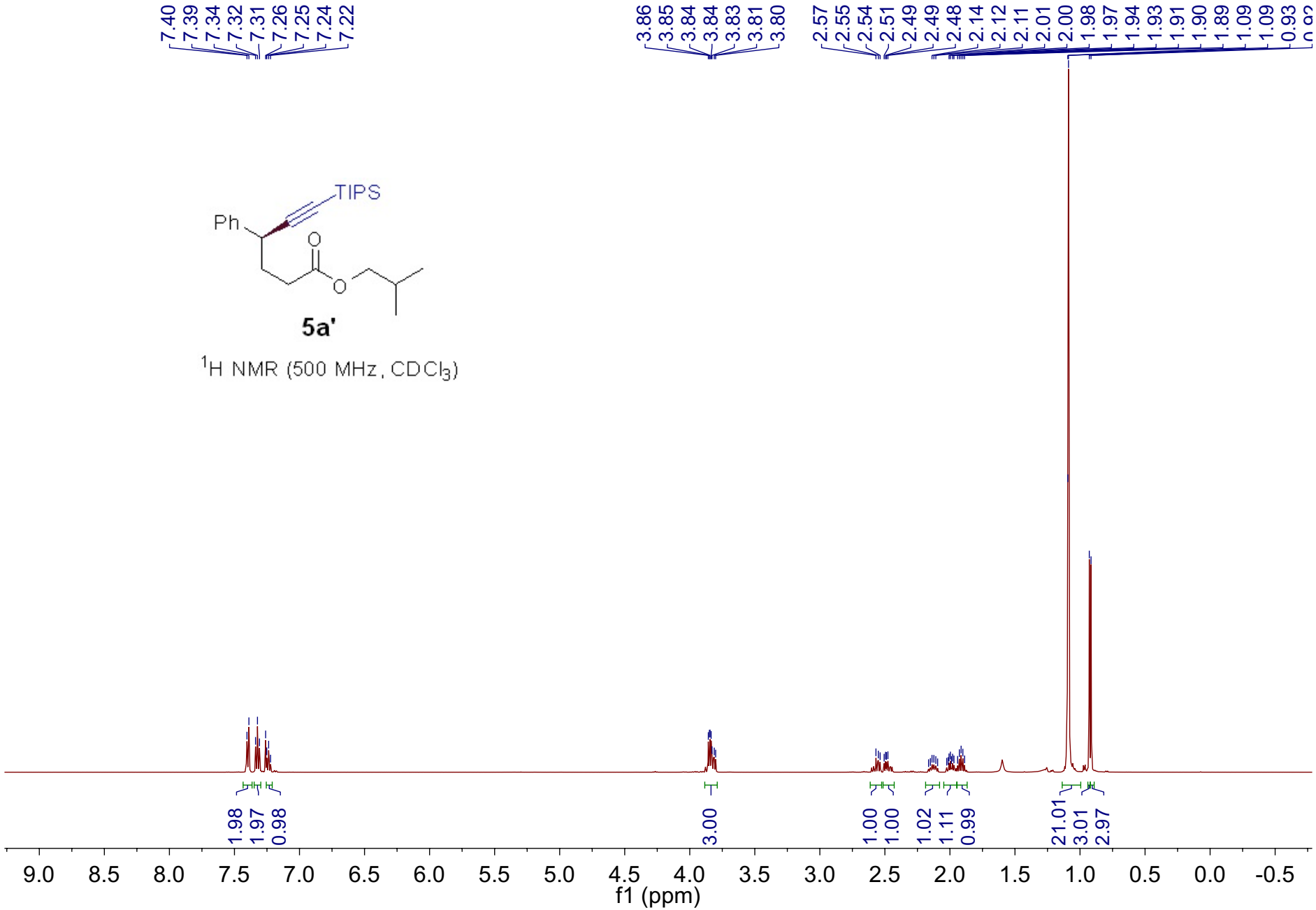
Supplementary Fig. 157. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5y**



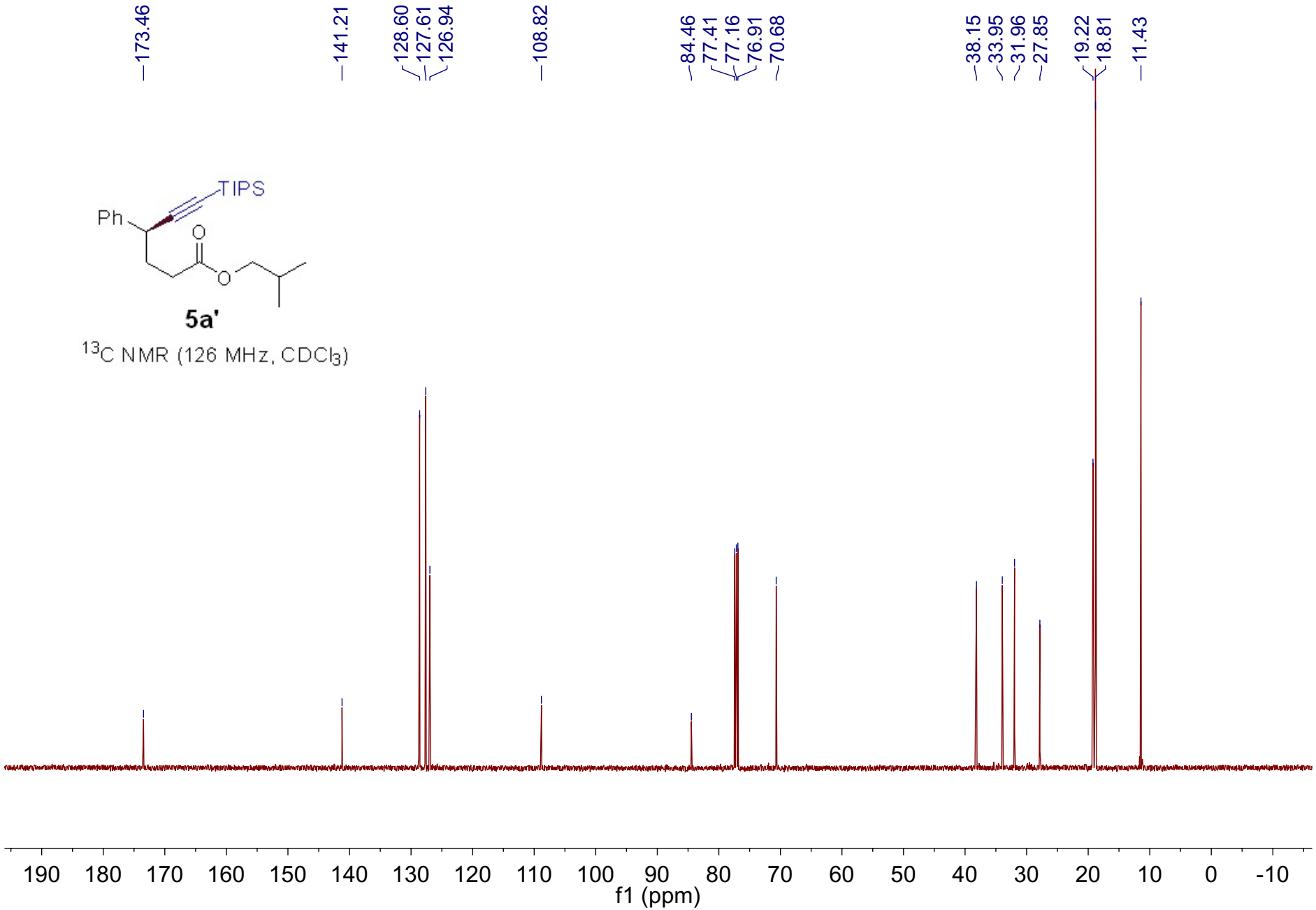
Supplementary Fig. 158. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5z**



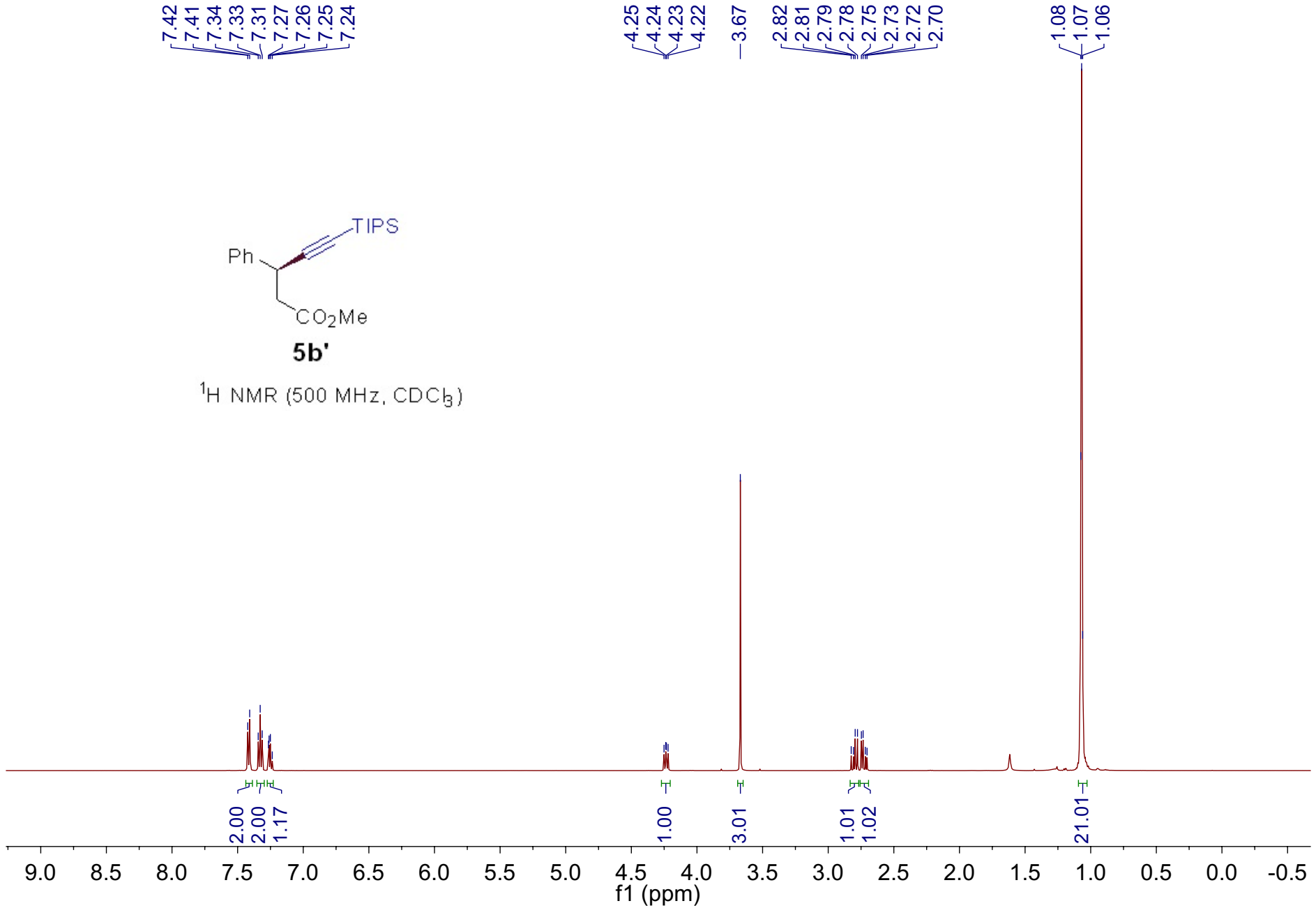
Supplementary Fig. 159. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5z**



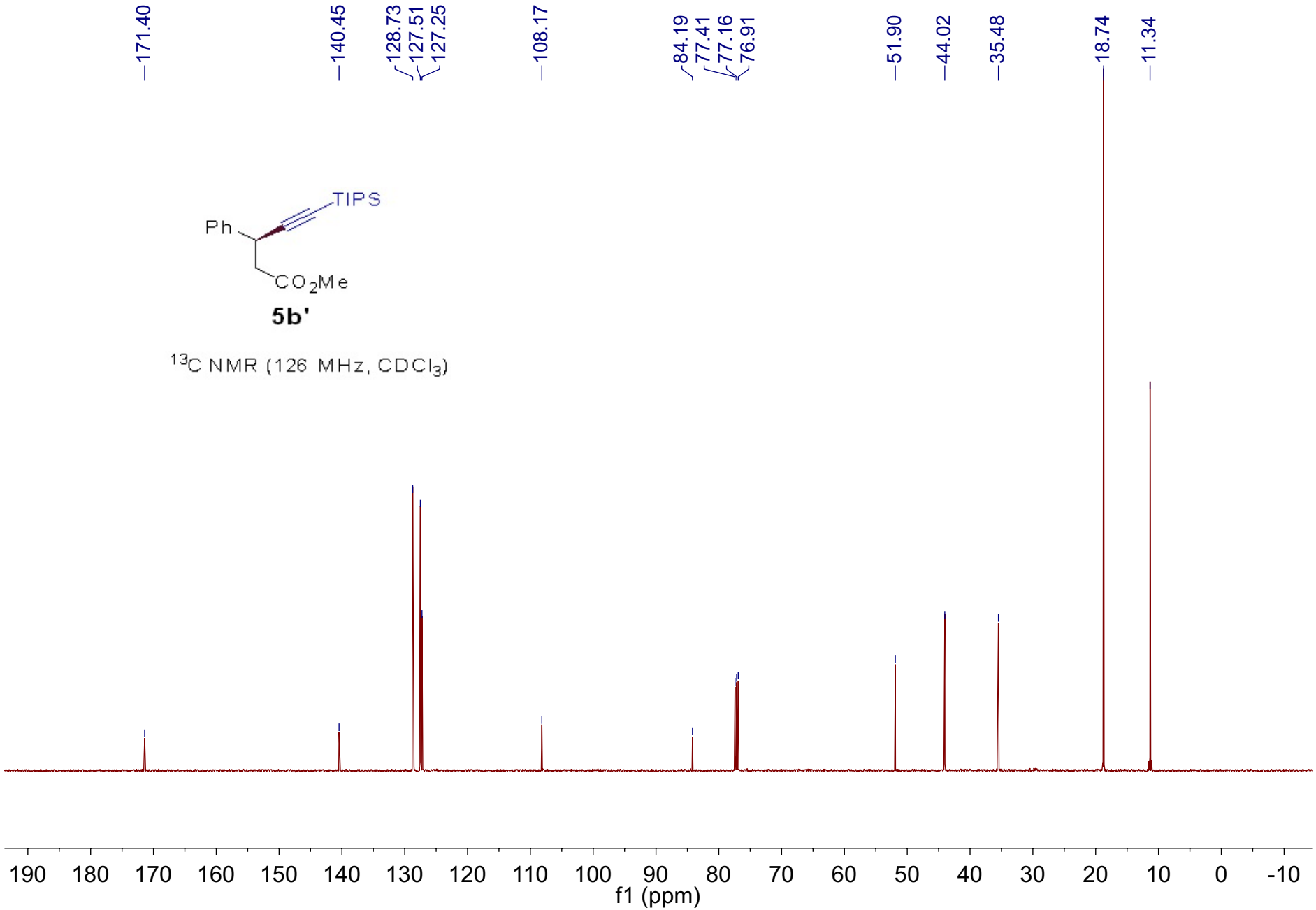
Supplementary Fig. 160. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5a'**



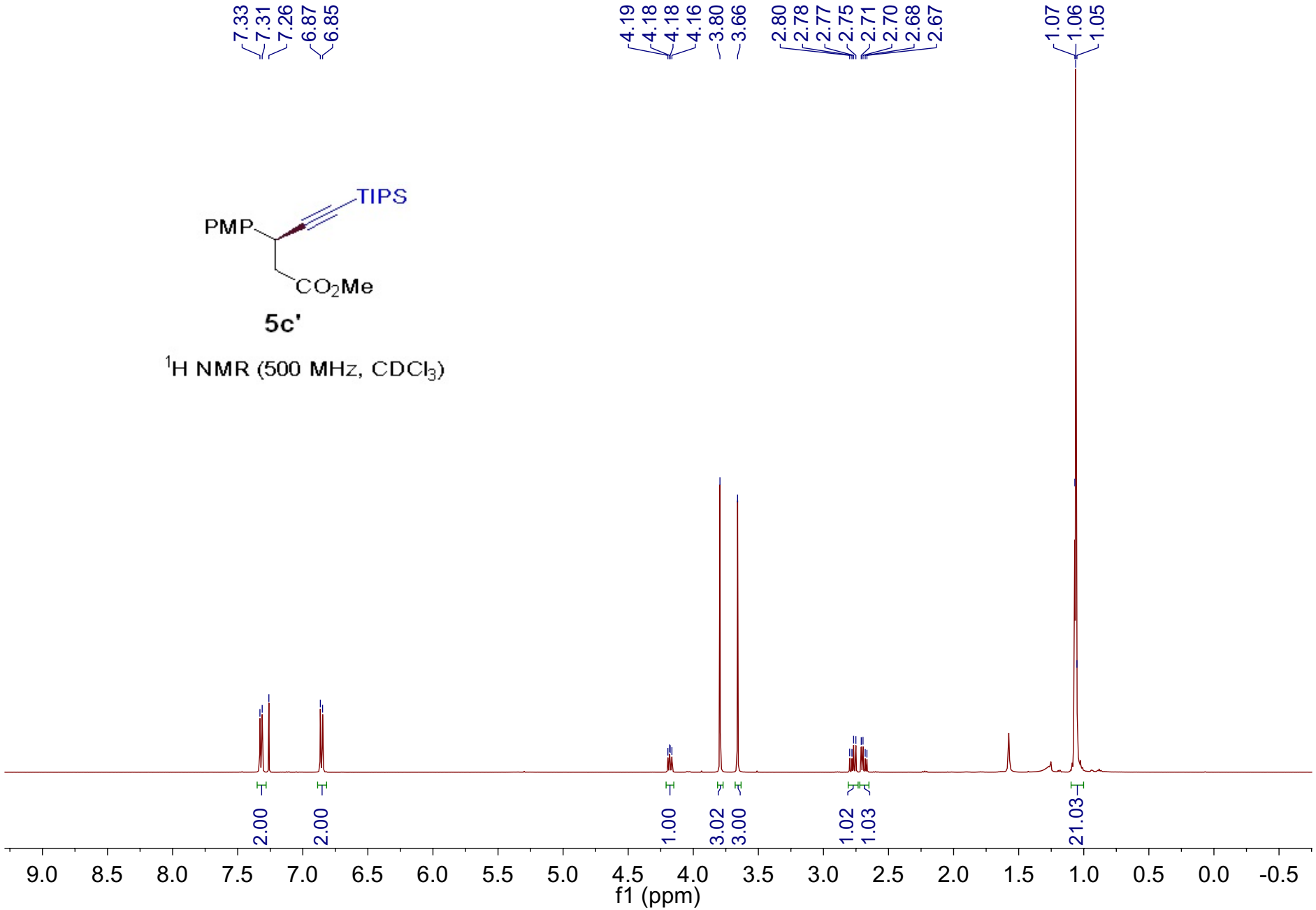
Supplementary Fig. 161. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5a'**



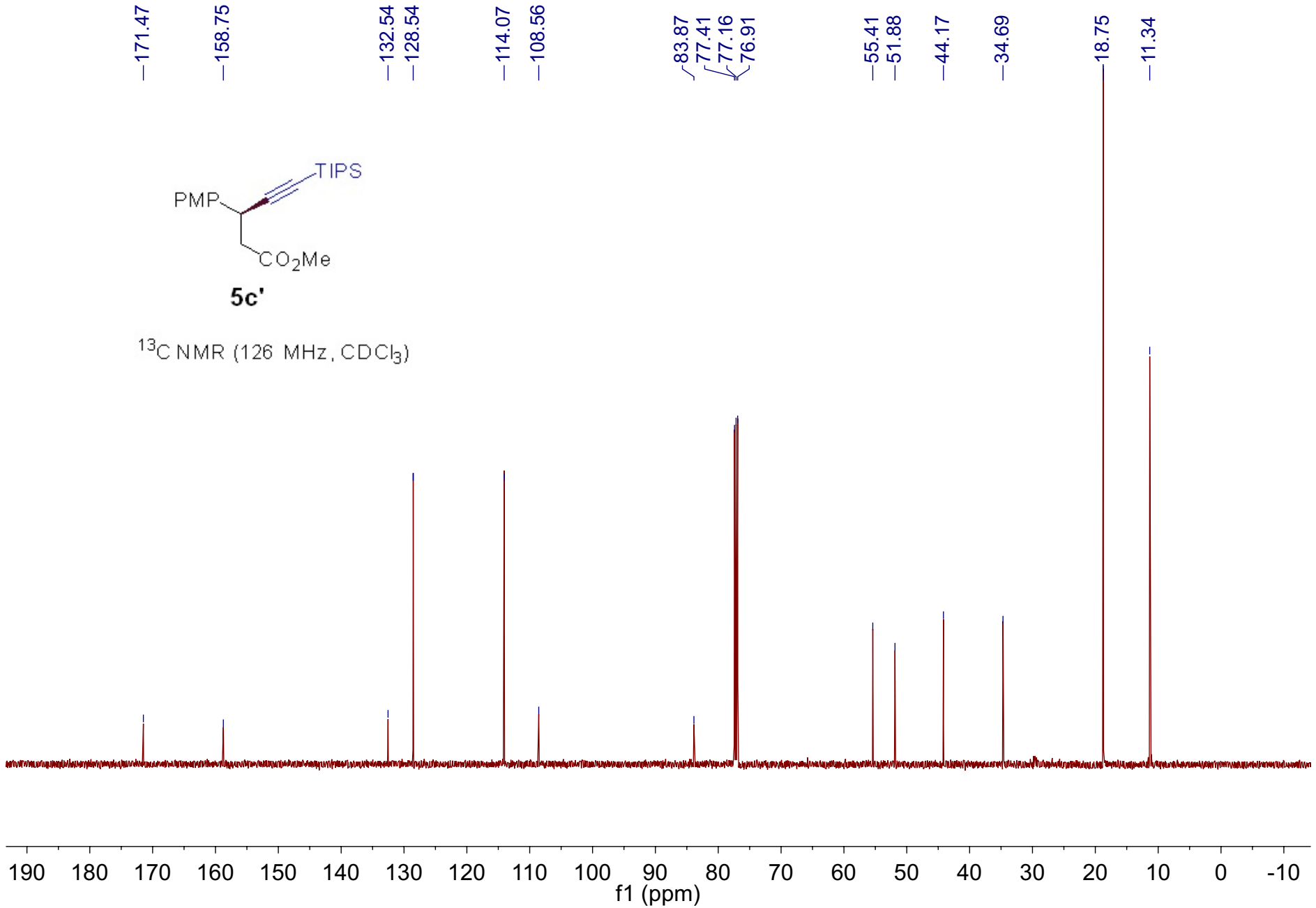
Supplementary Fig. 162. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5b'**



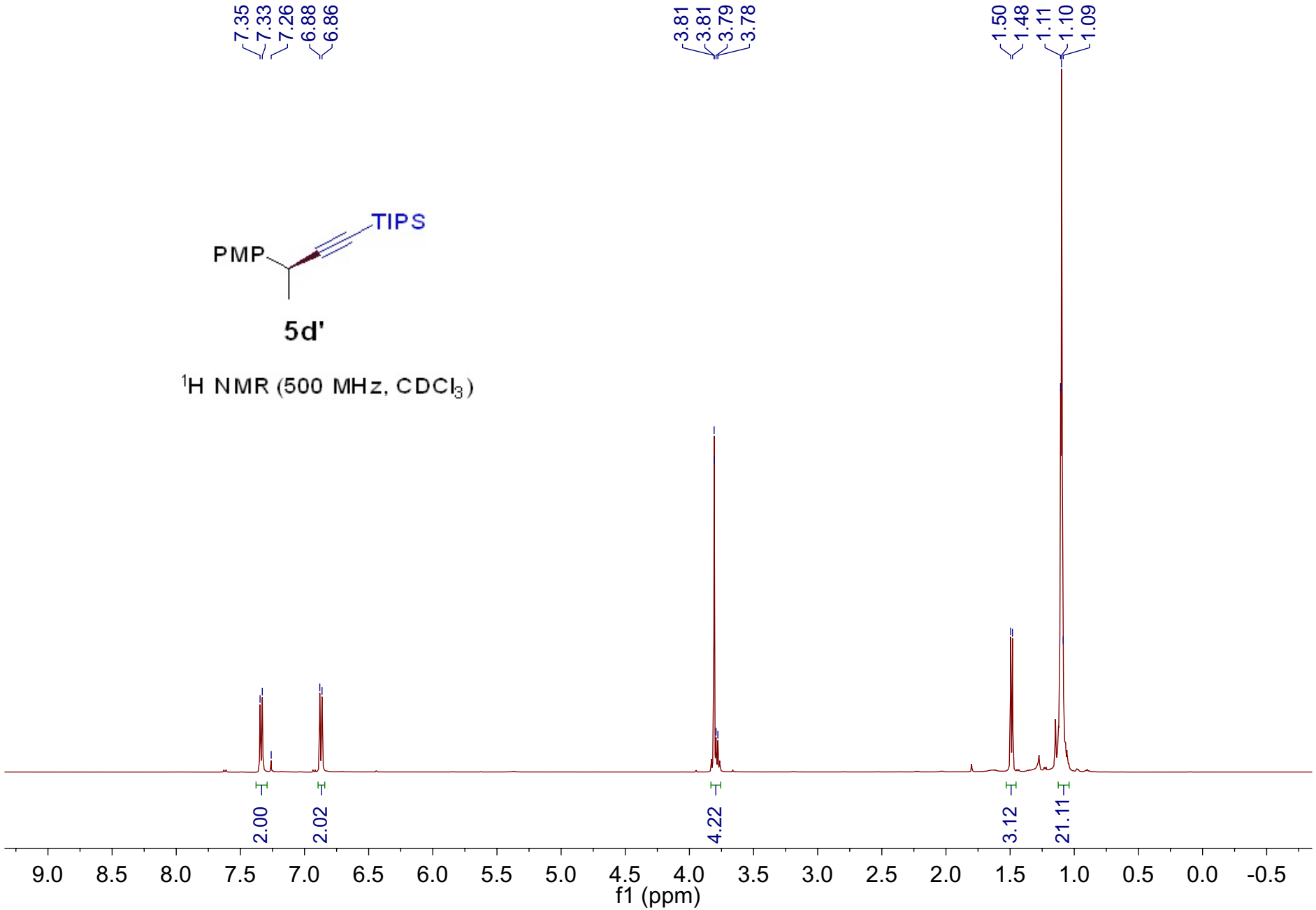
Supplementary Fig. 163. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5b'**



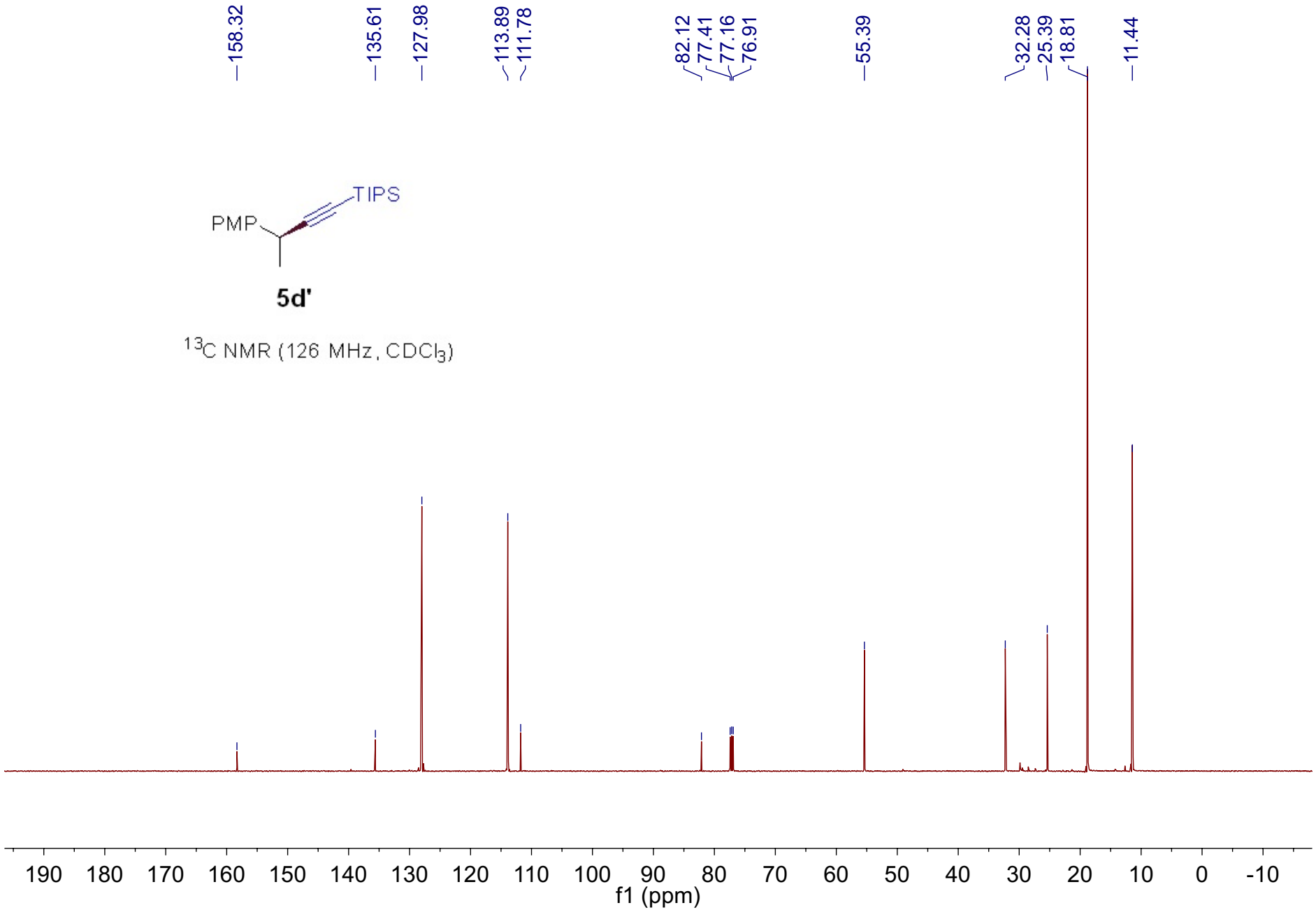
Supplementary Fig. 164. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5c'**



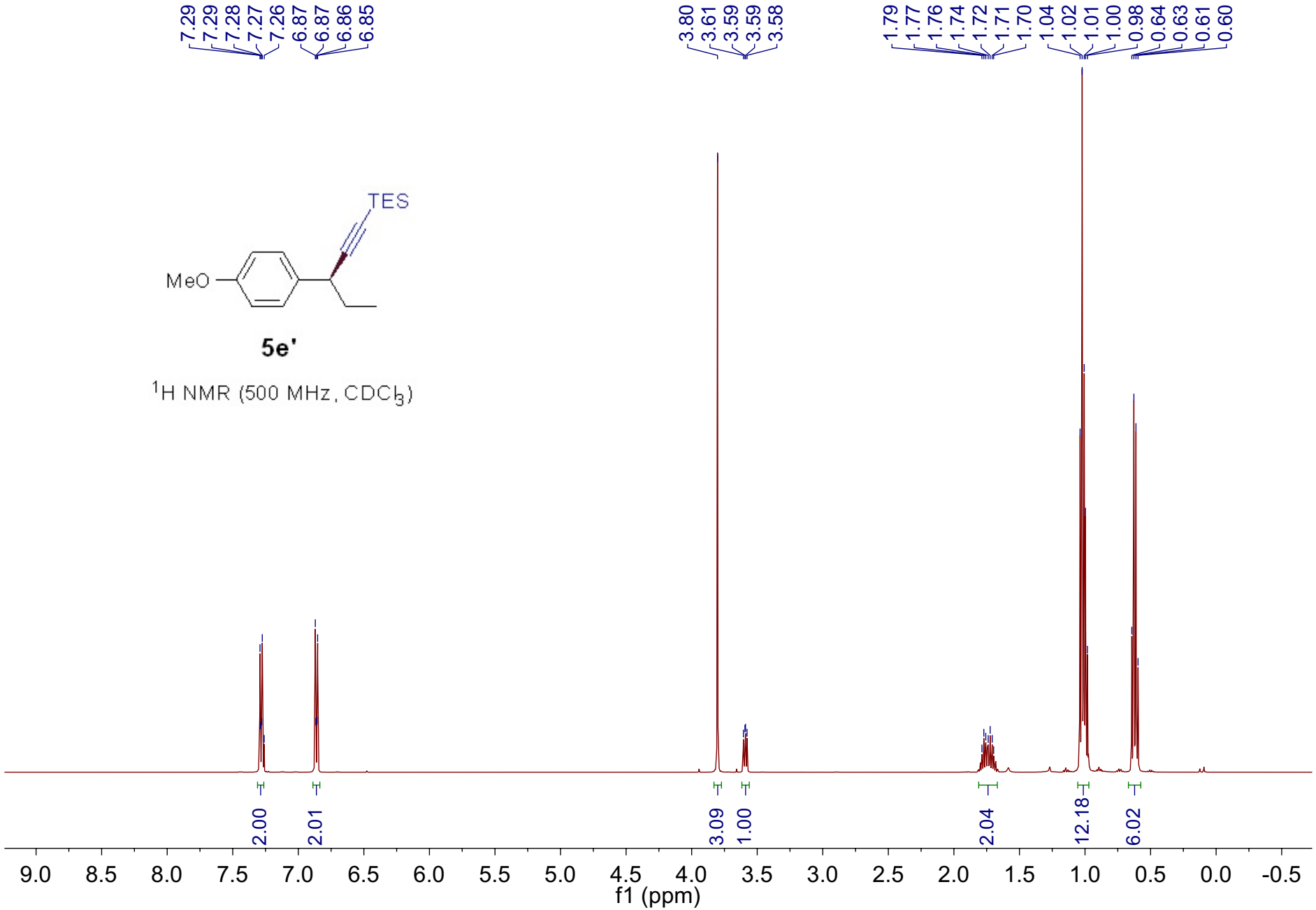
Supplementary Fig. 165. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5c'**



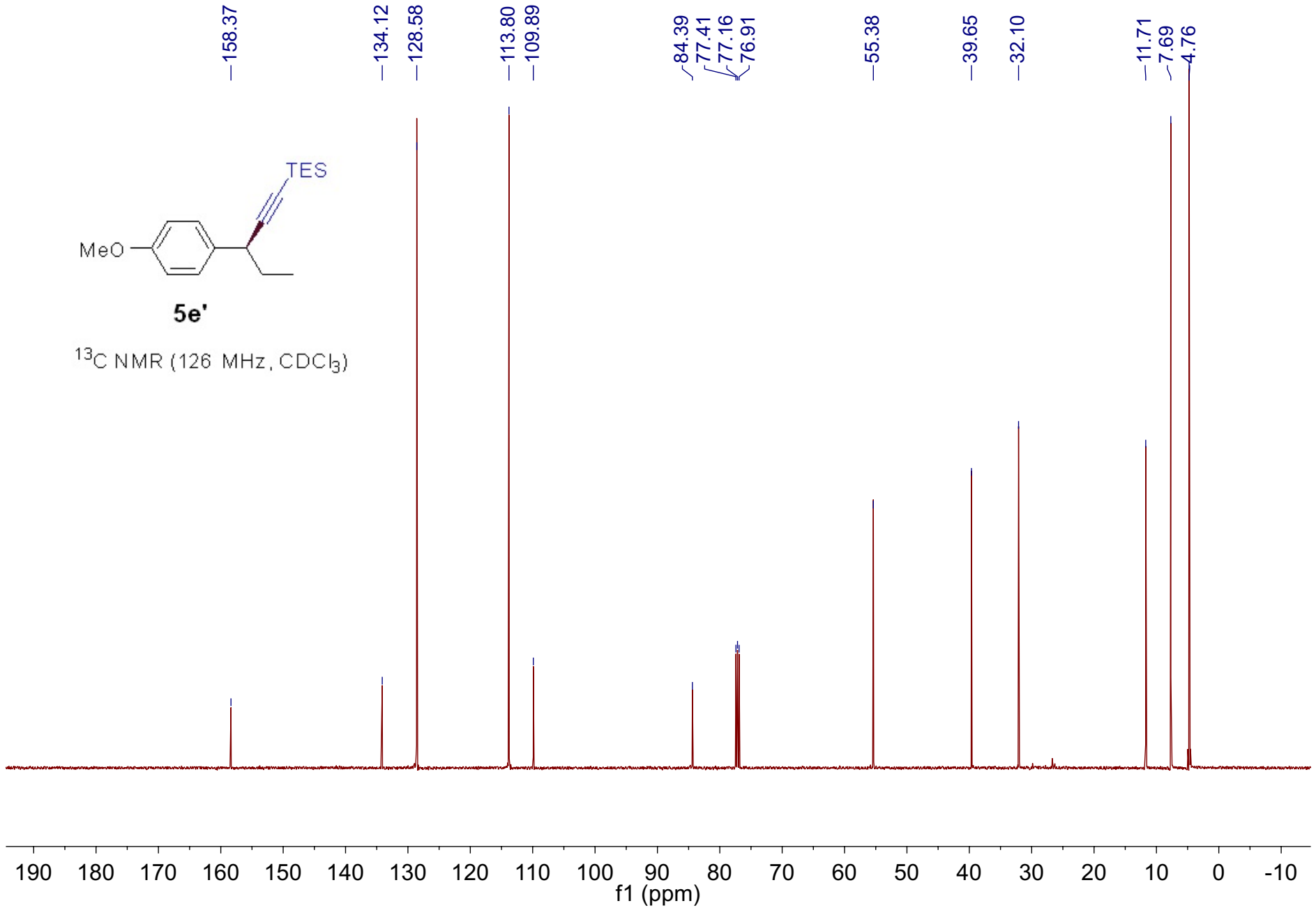
Supplementary Fig. 166. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5d'**



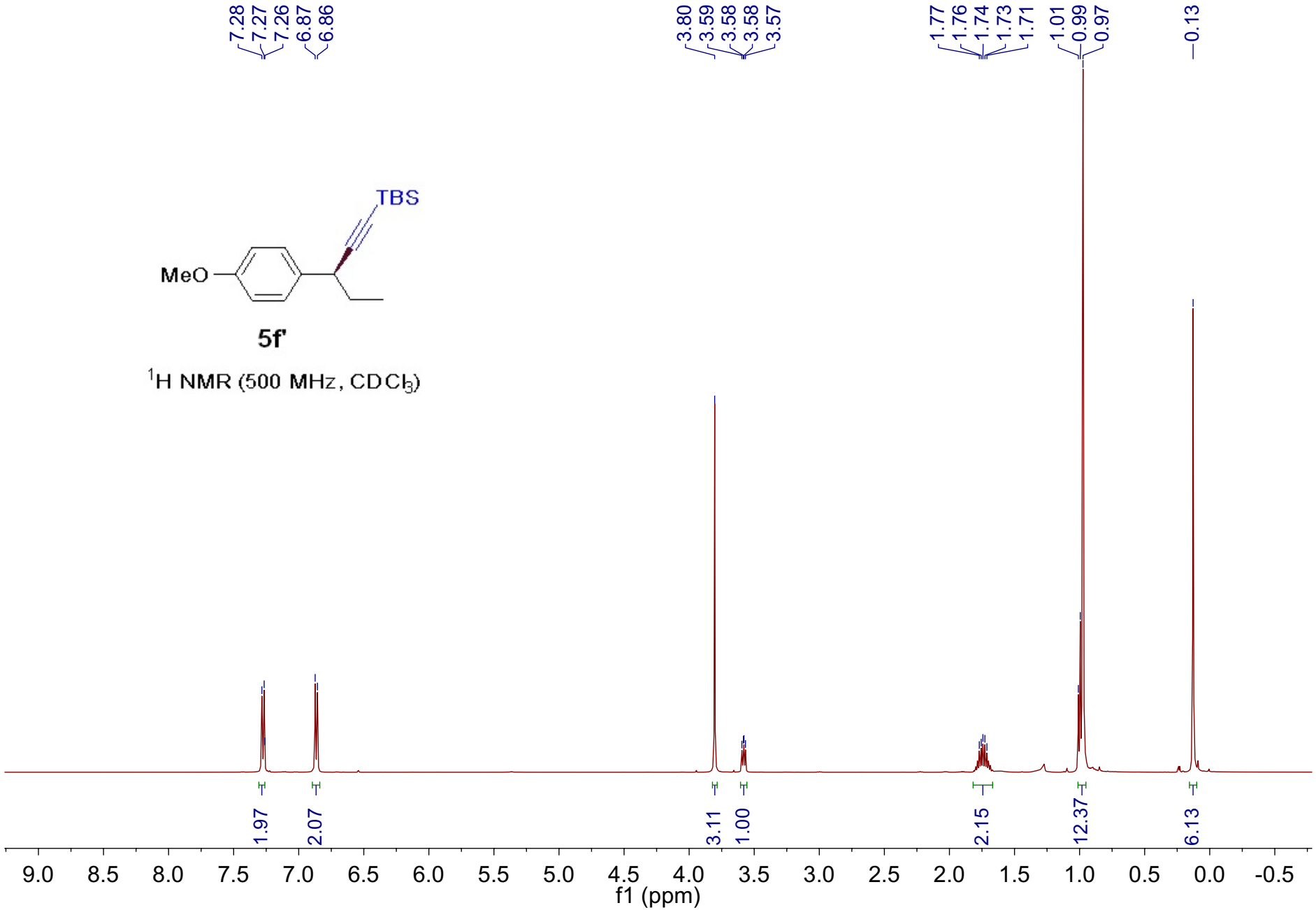
Supplementary Fig. 167. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5d'**



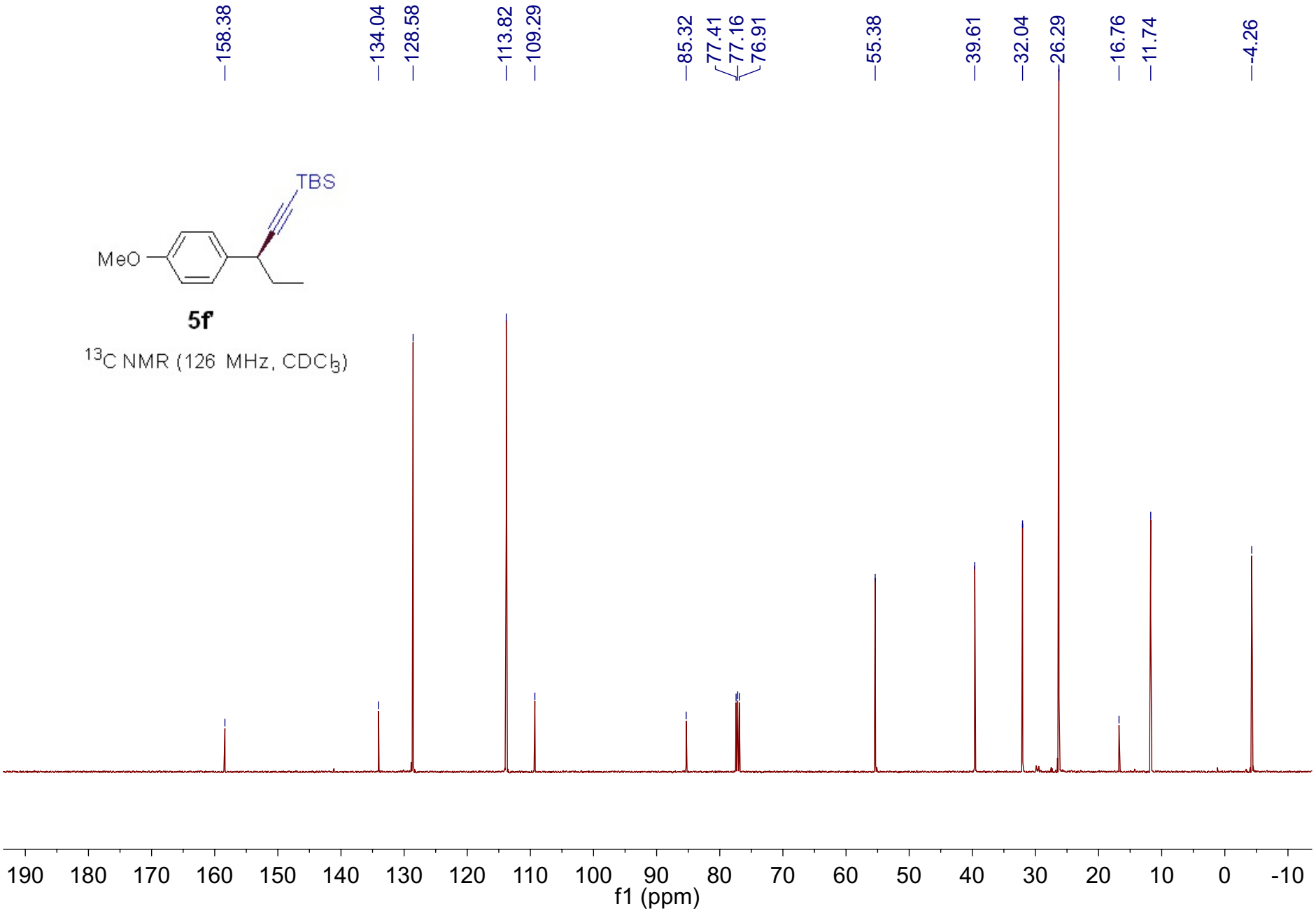
Supplementary Fig. 168. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5e'**



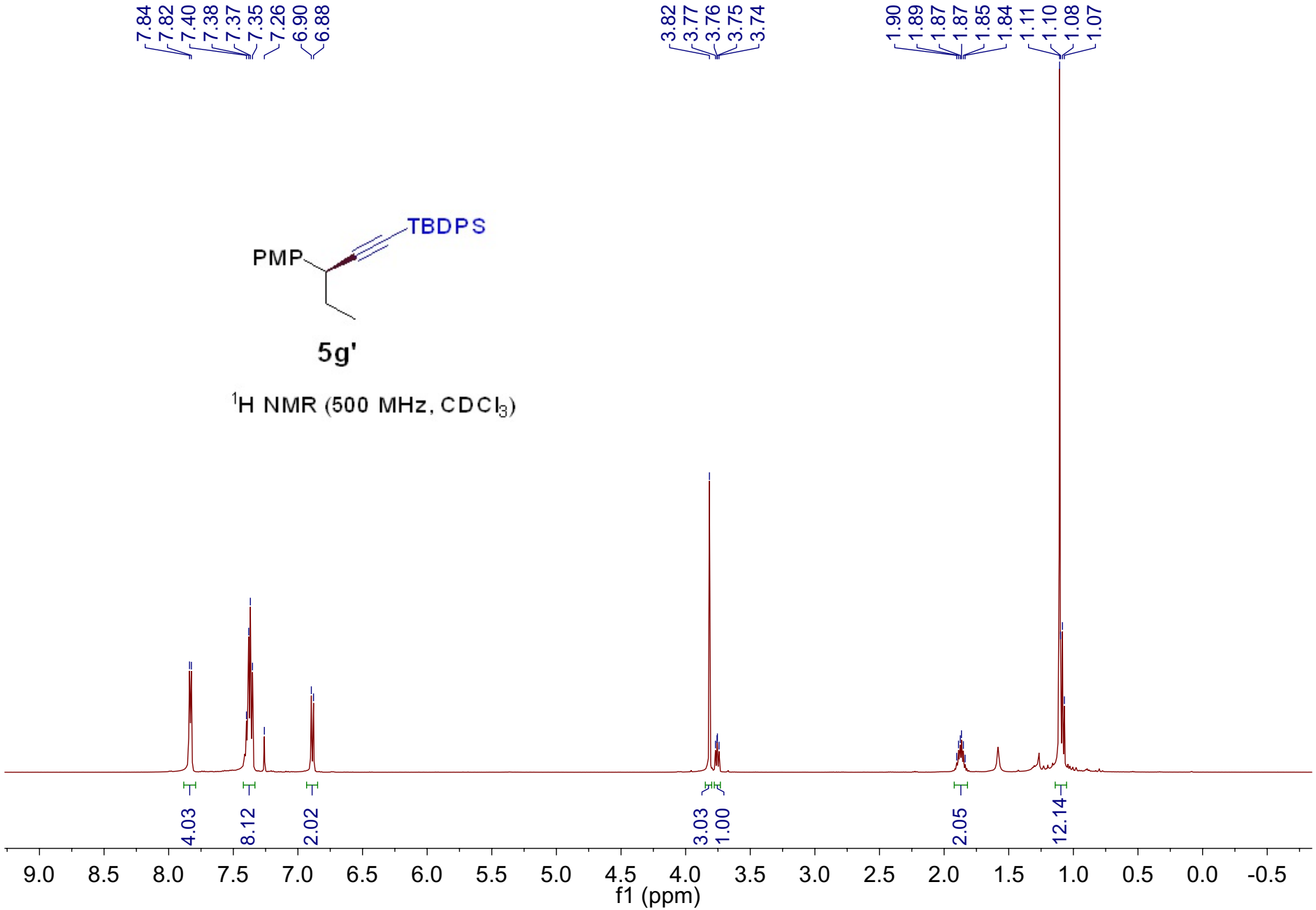
Supplementary Fig. 169. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5e'**



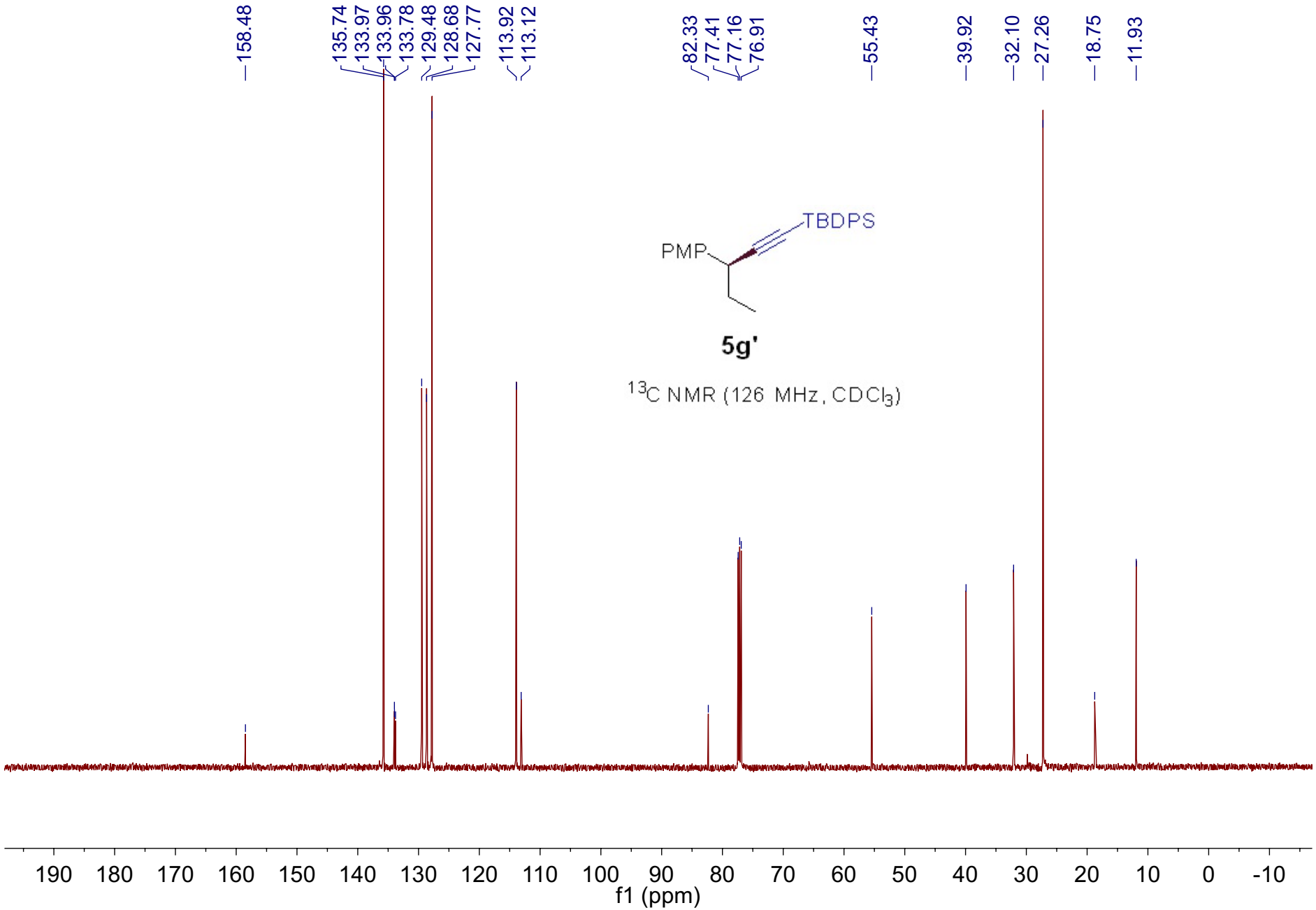
Supplementary Fig. 170. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5f'**



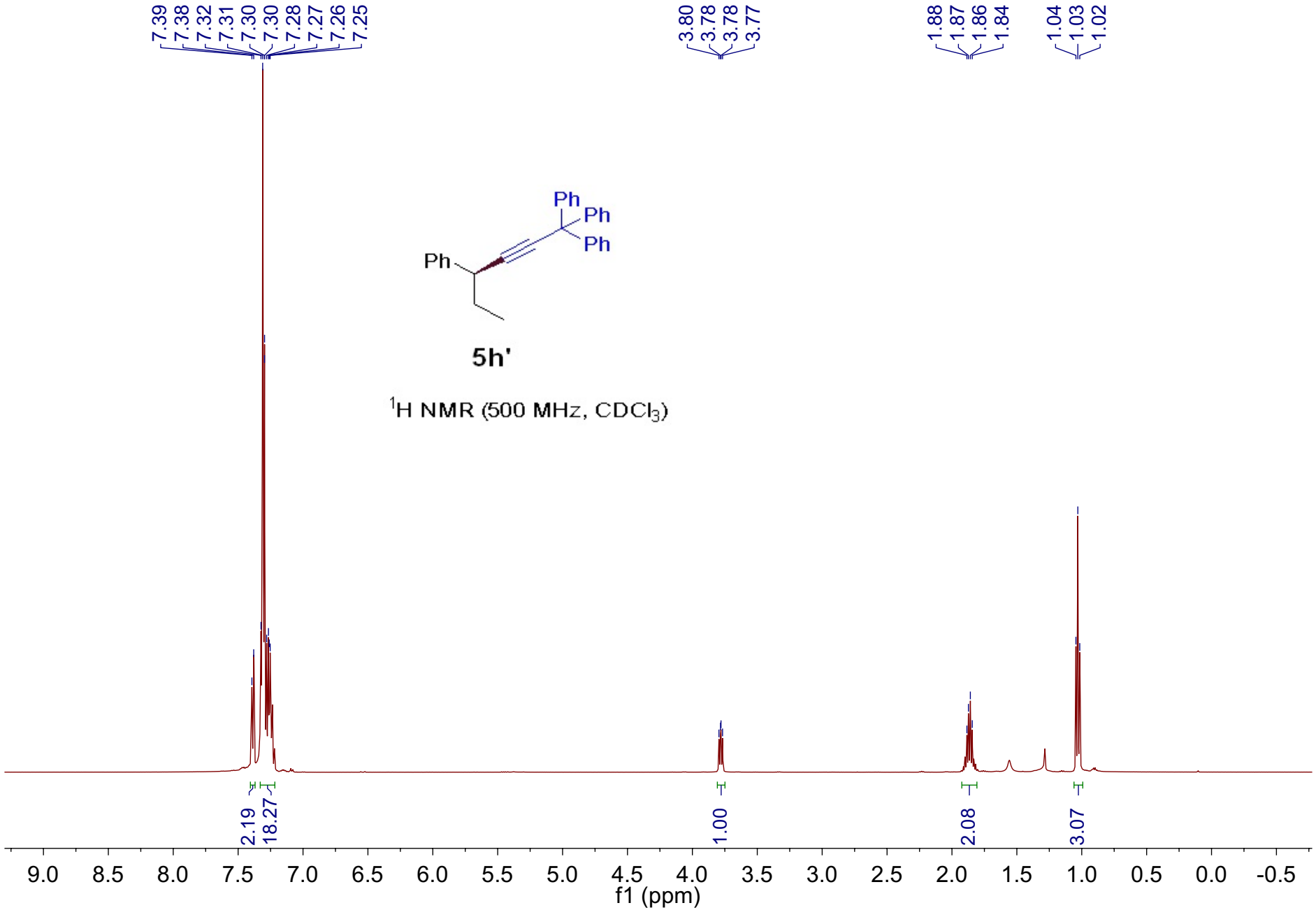
Supplementary Fig. 171. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5f'**



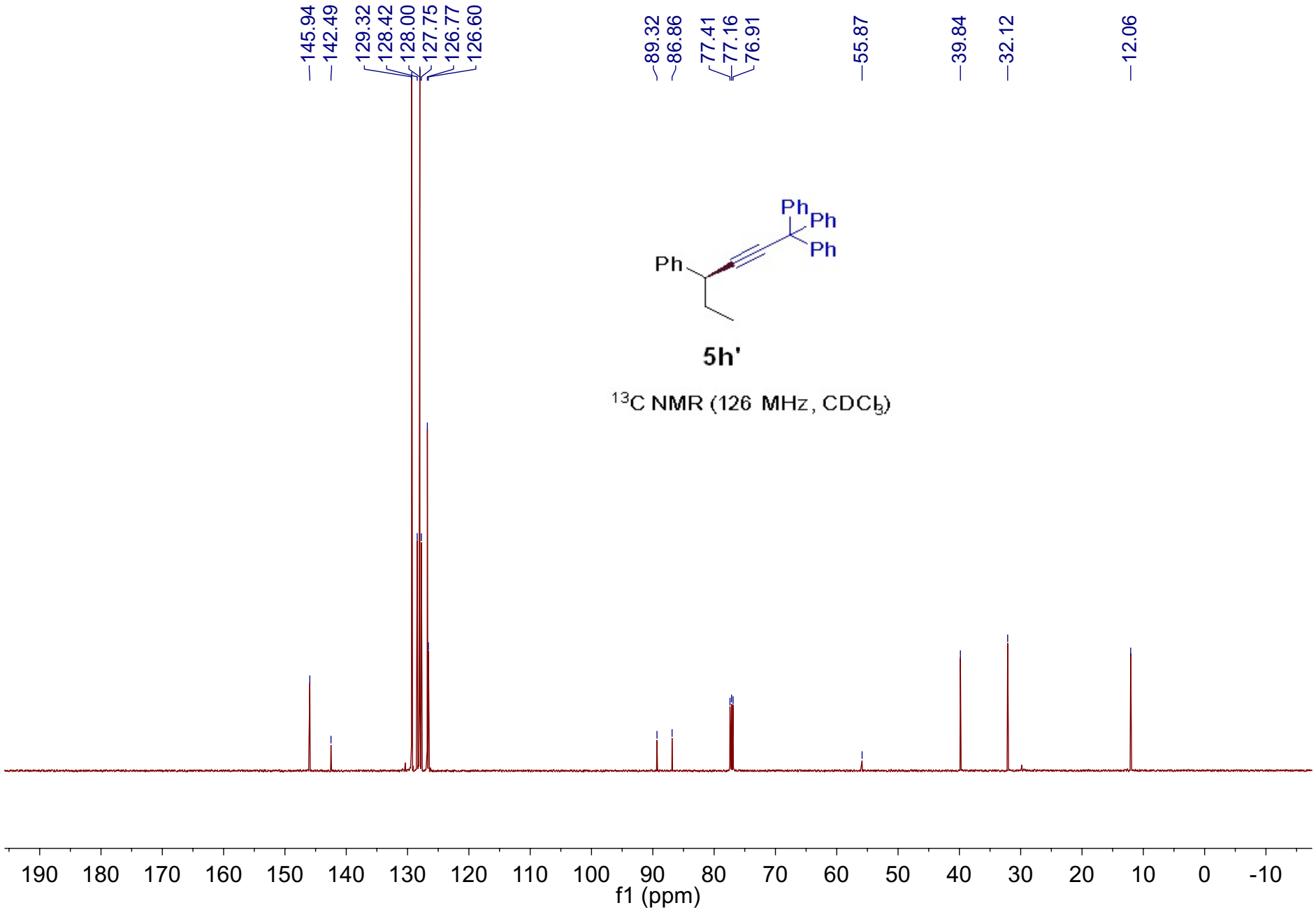
Supplementary Fig. 172. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5g'**



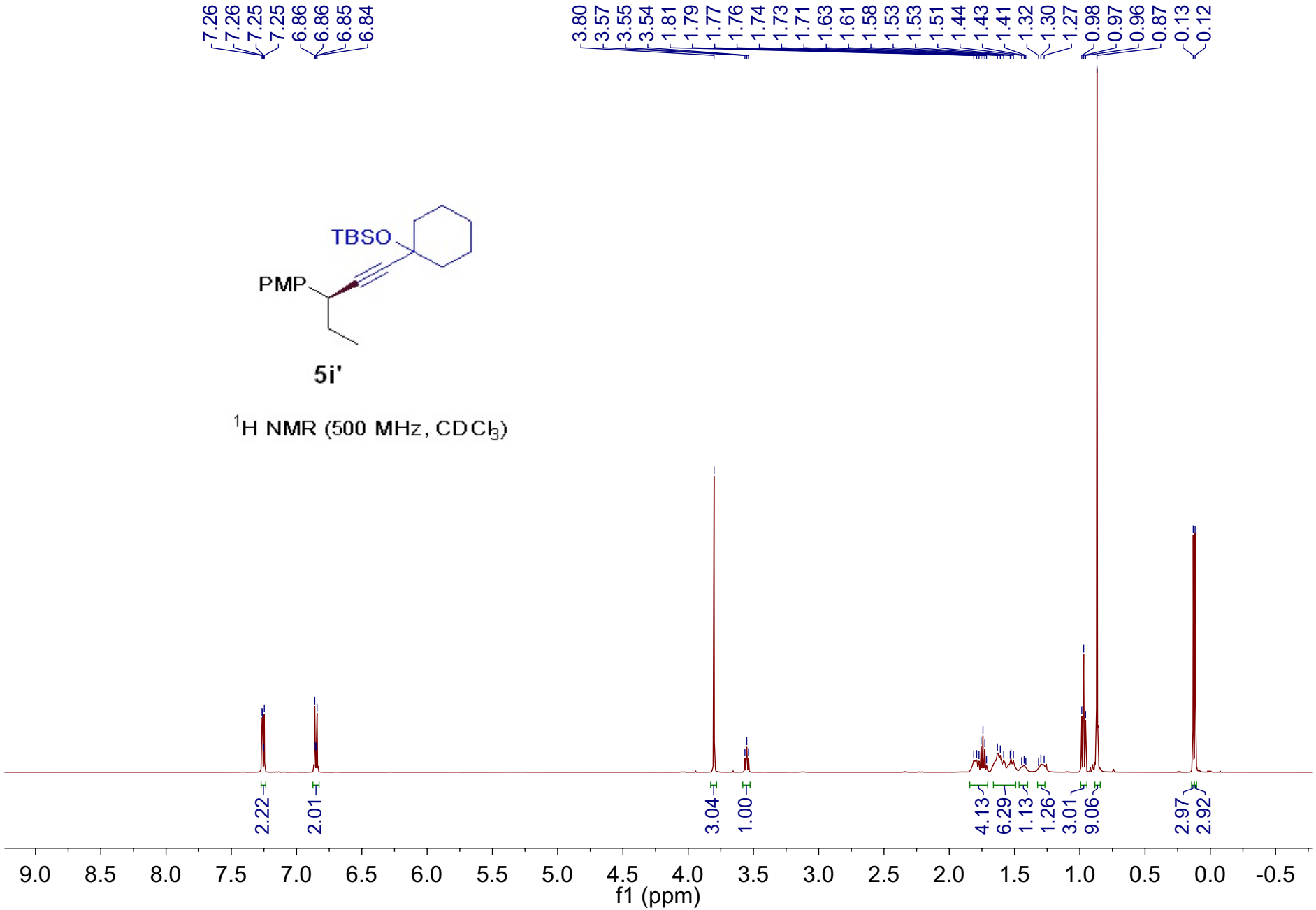
Supplementary Fig. 173. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5g'**



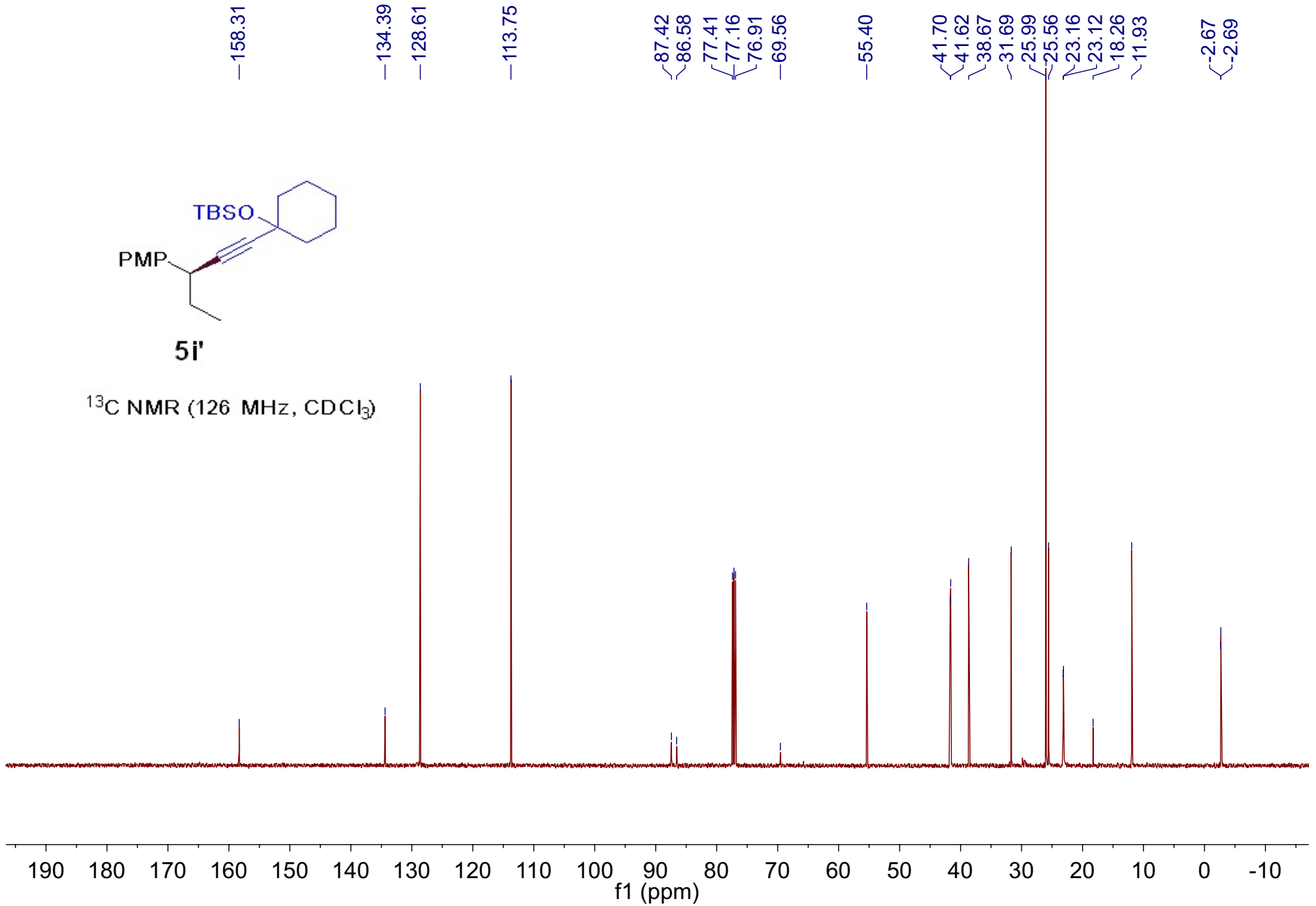
Supplementary Fig. 174. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5h'**



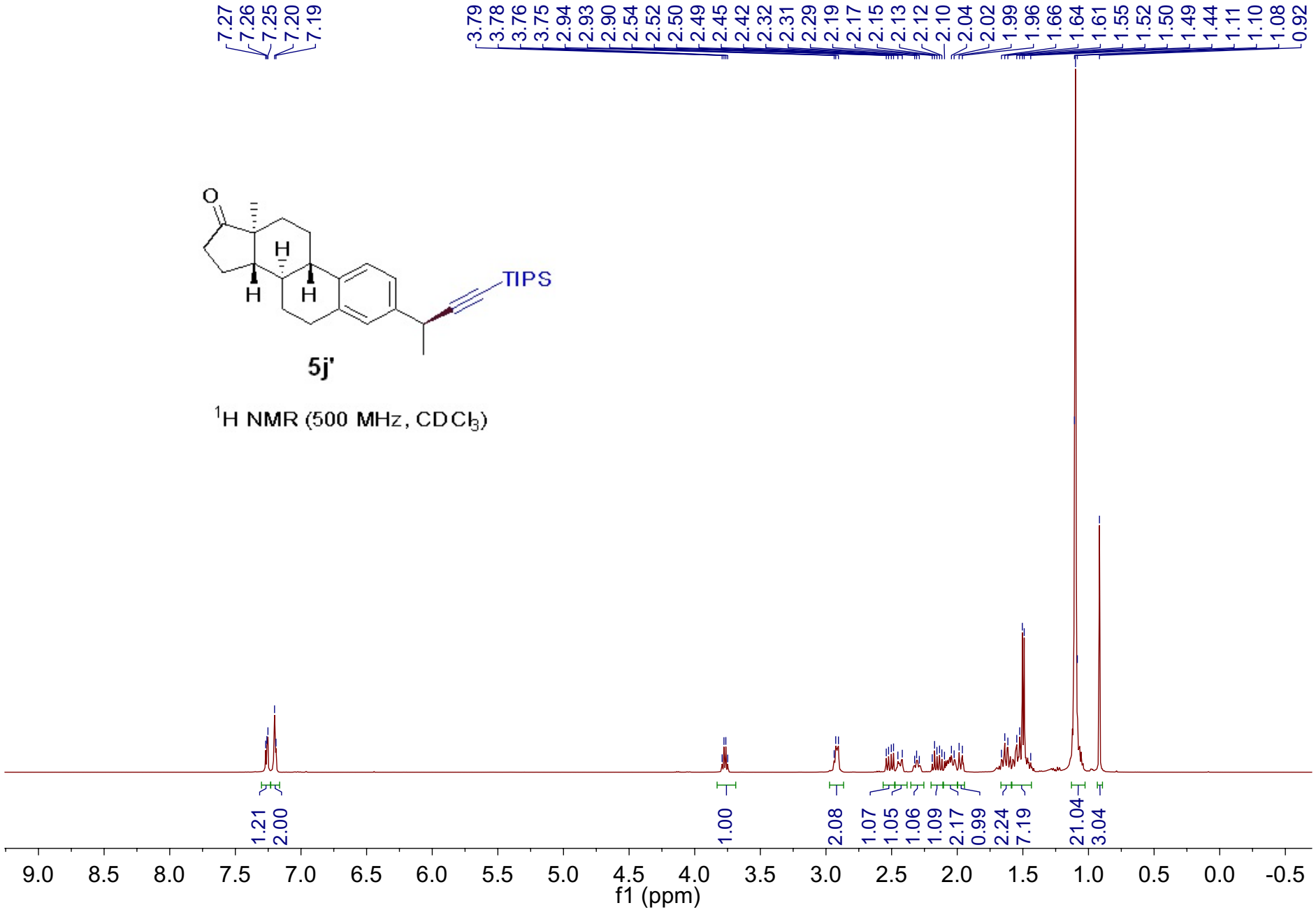
Supplementary Fig. 175. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5h'**



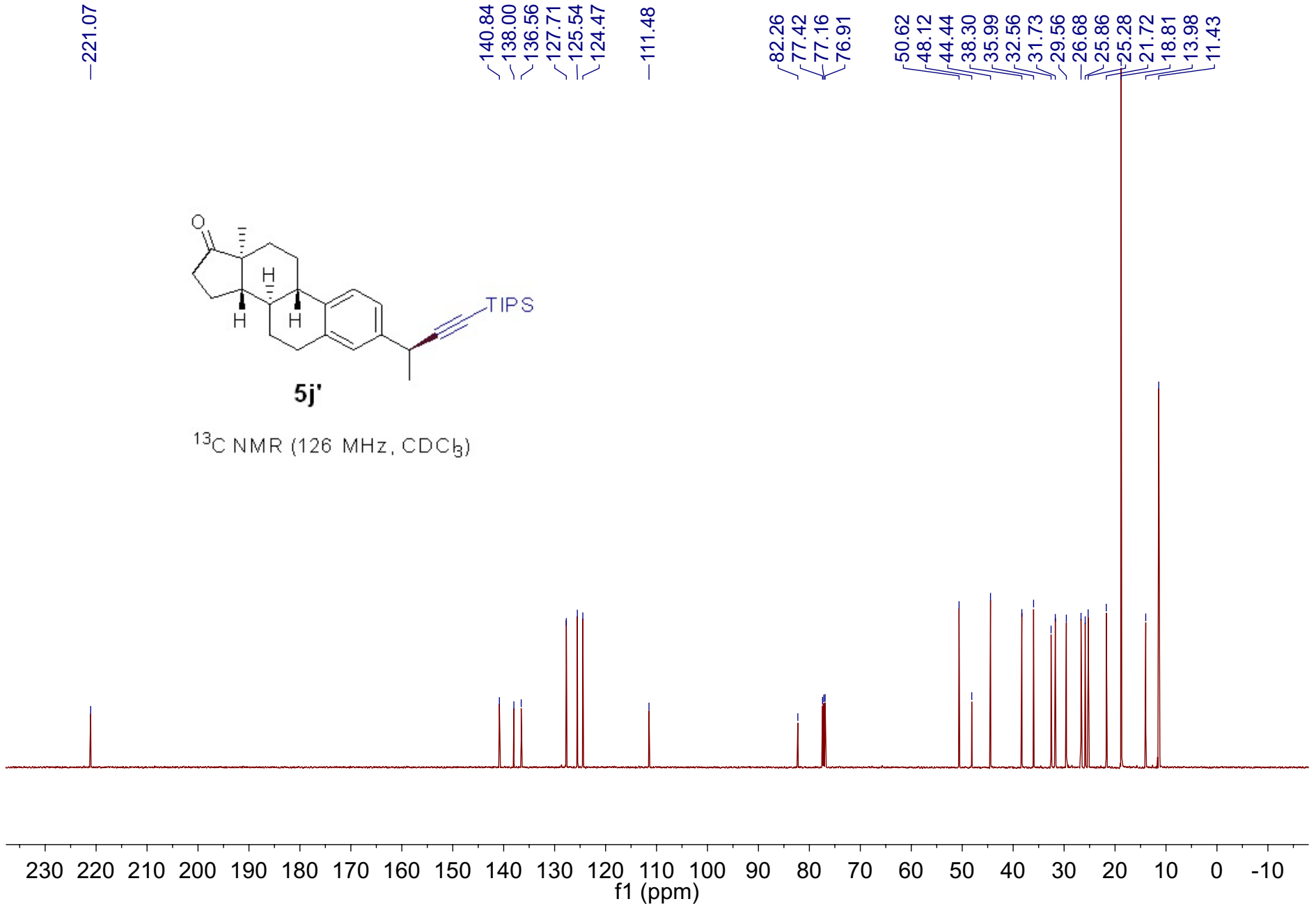
Supplementary Fig. 176. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5i'**



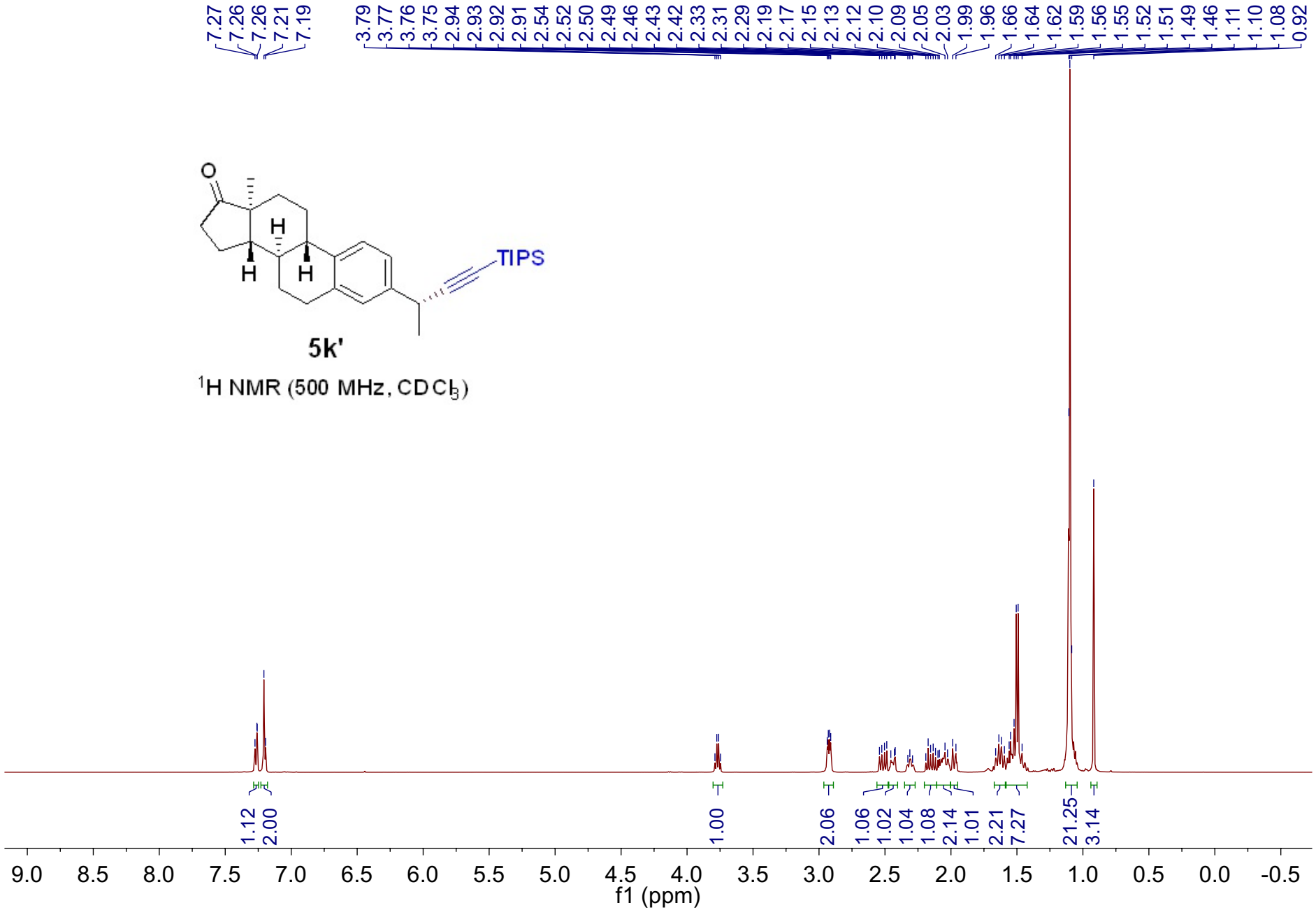
Supplementary Fig. 177. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5i'**



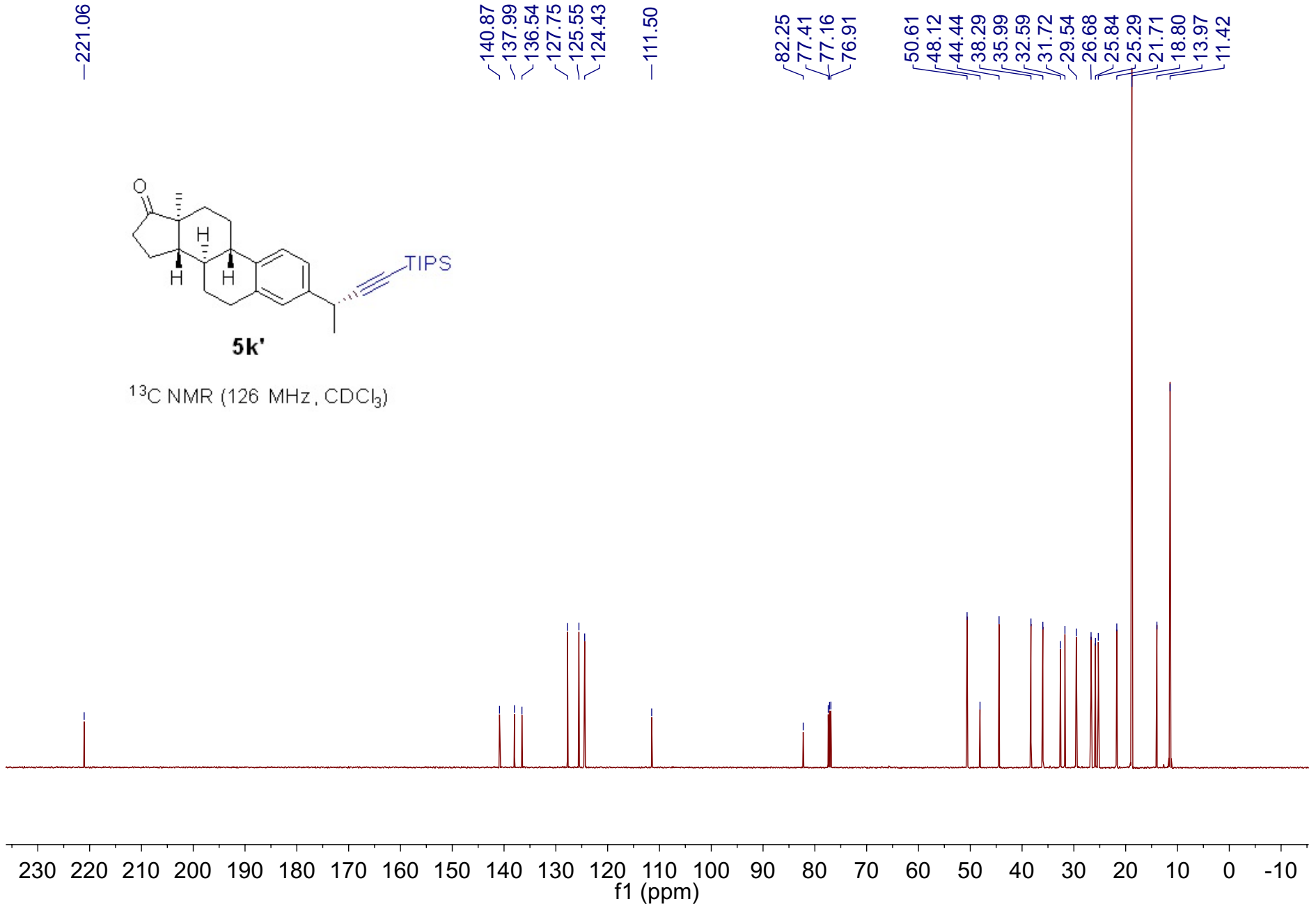
Supplementary Fig. 178. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5j'**



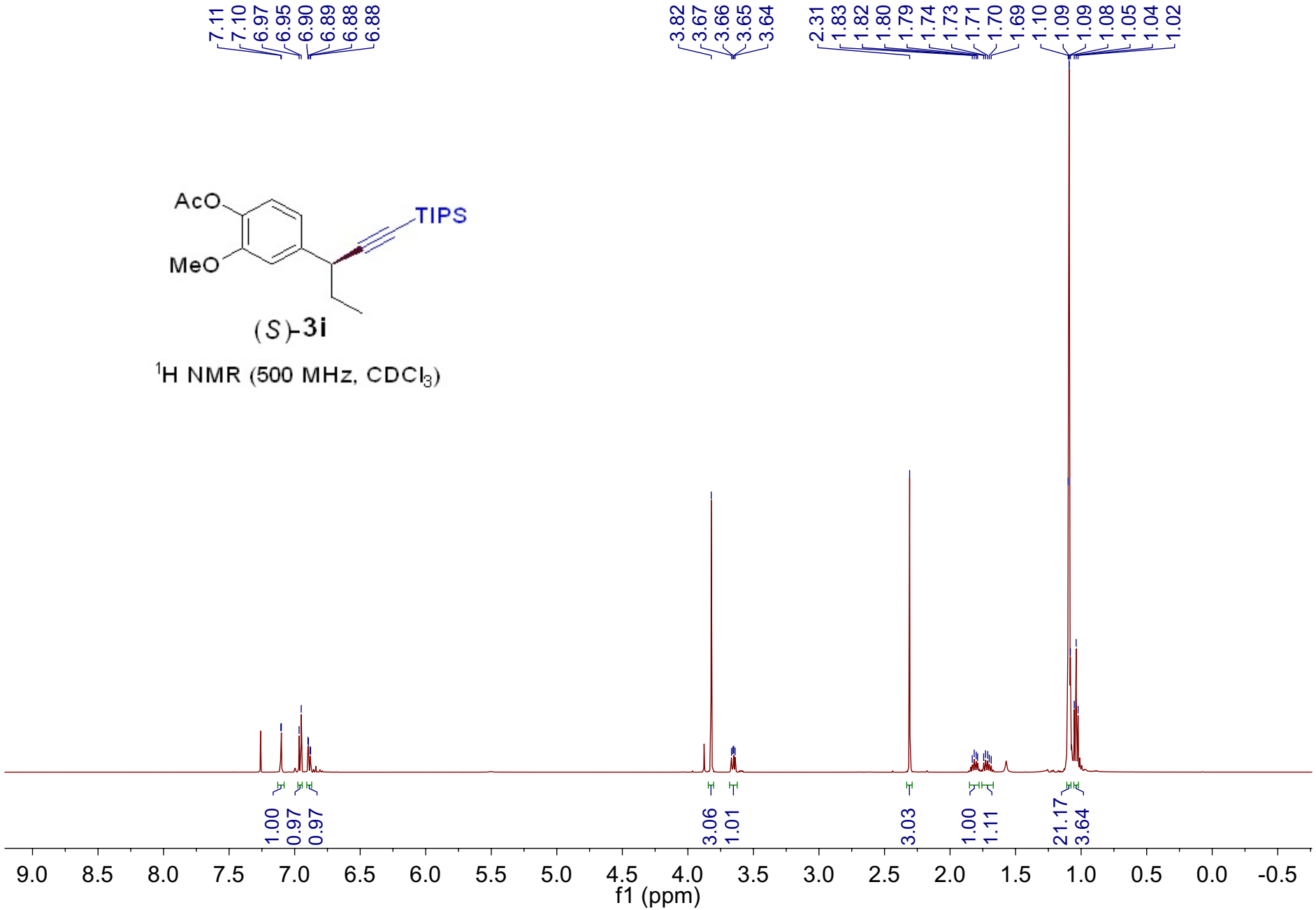
Supplementary Fig. 179. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5j'**



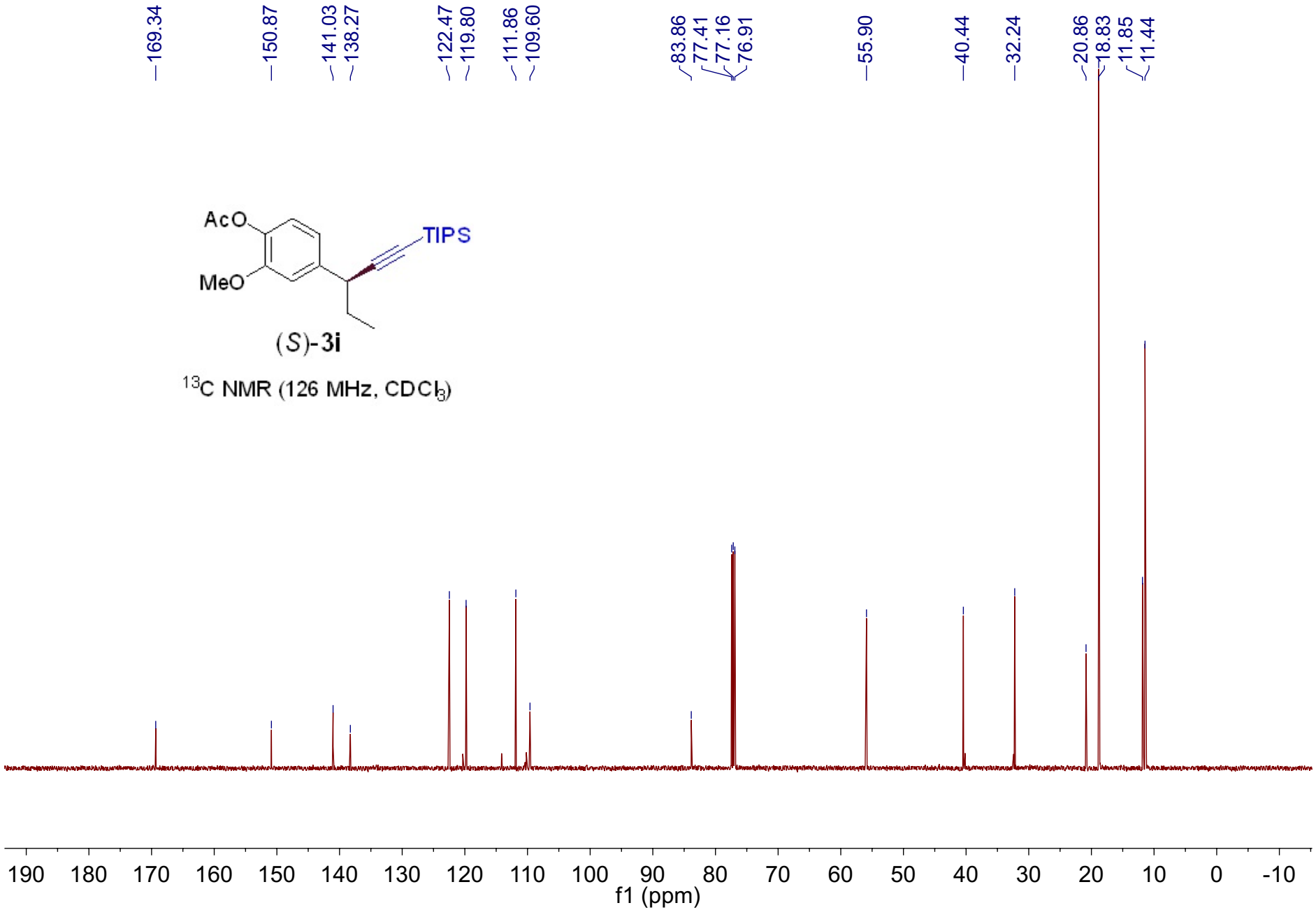
Supplementary Fig. 180. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5k'**



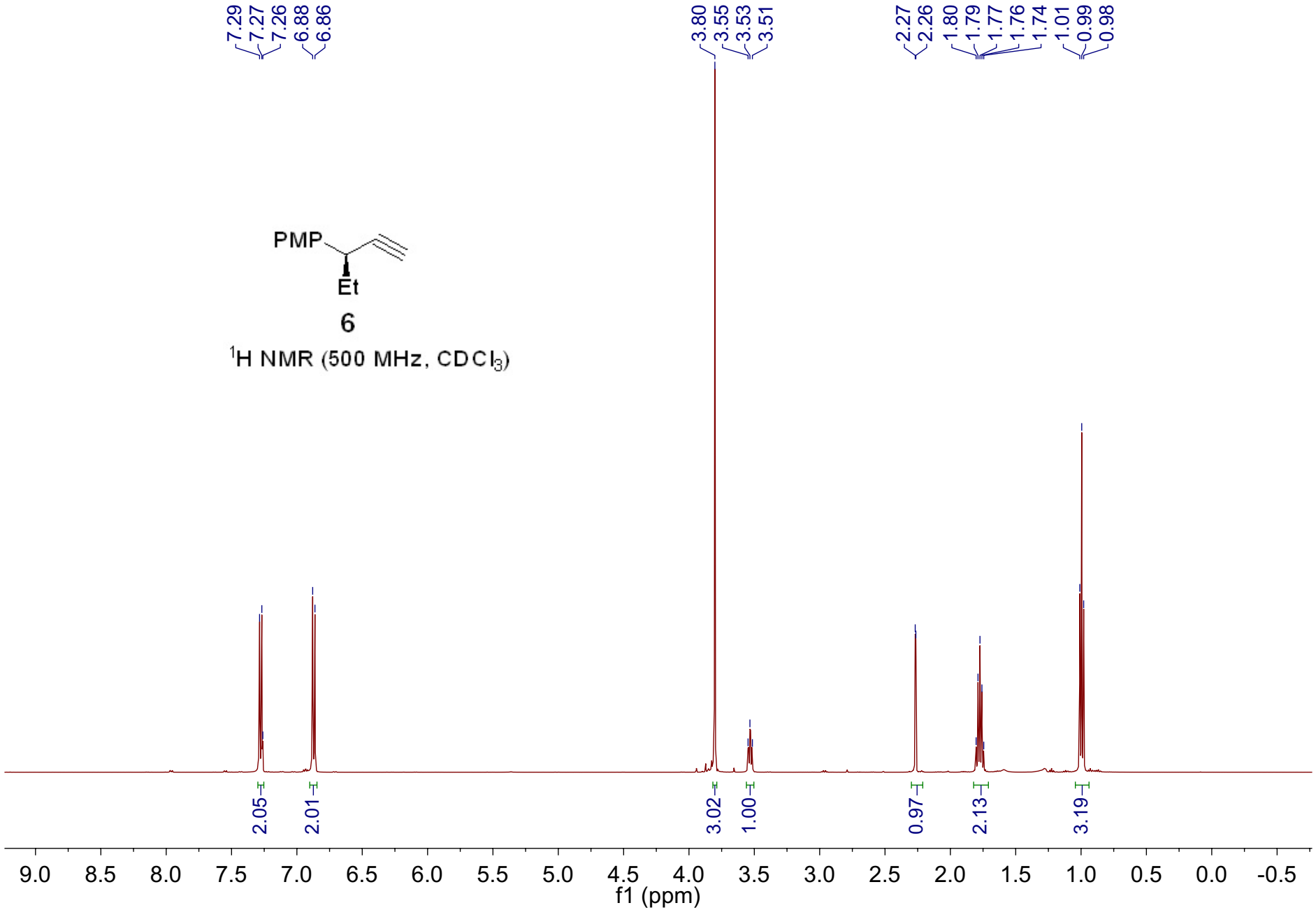
Supplementary Fig. 181. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5k'**



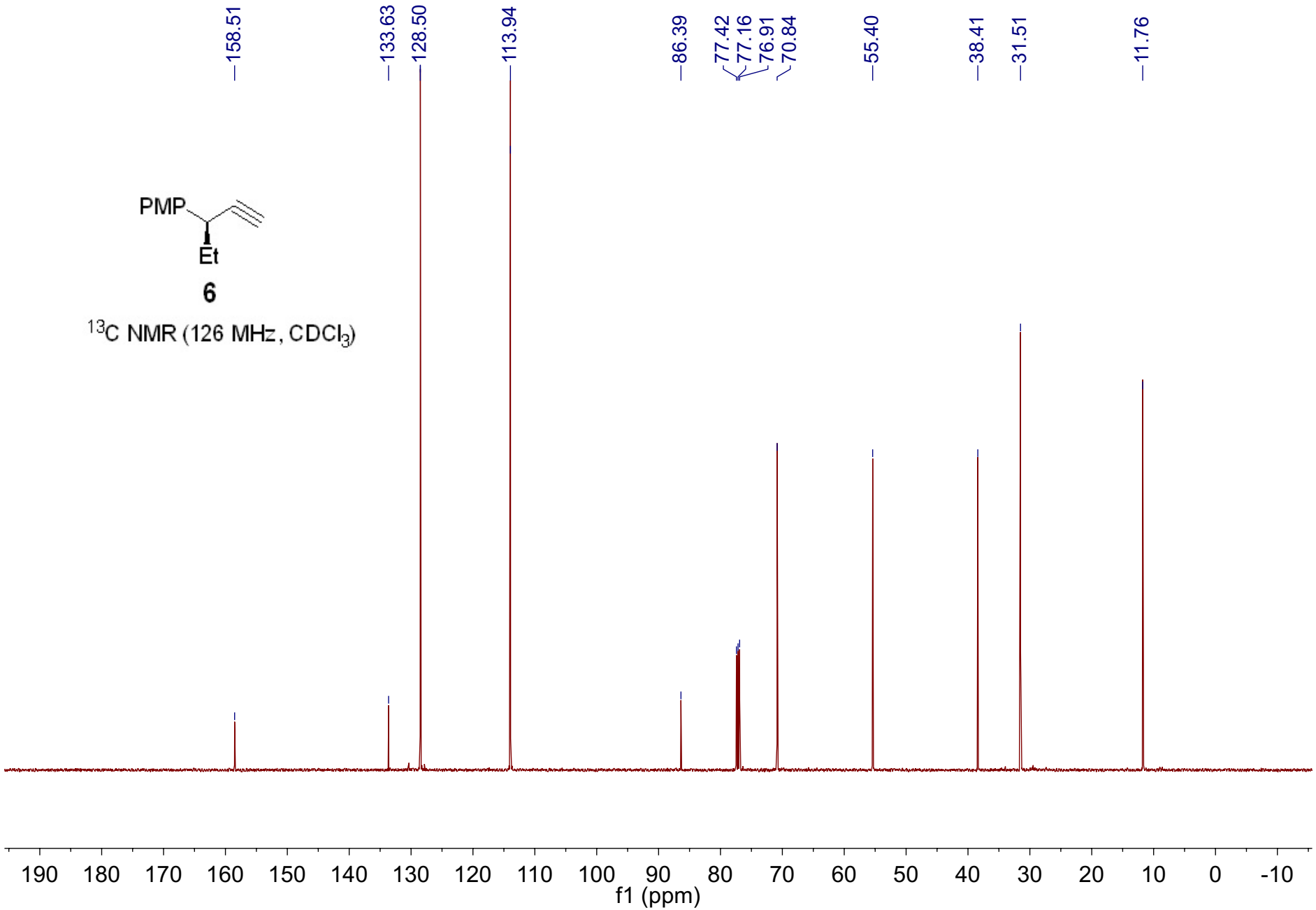
Supplementary Fig. 182. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound (*S*)-**3i**



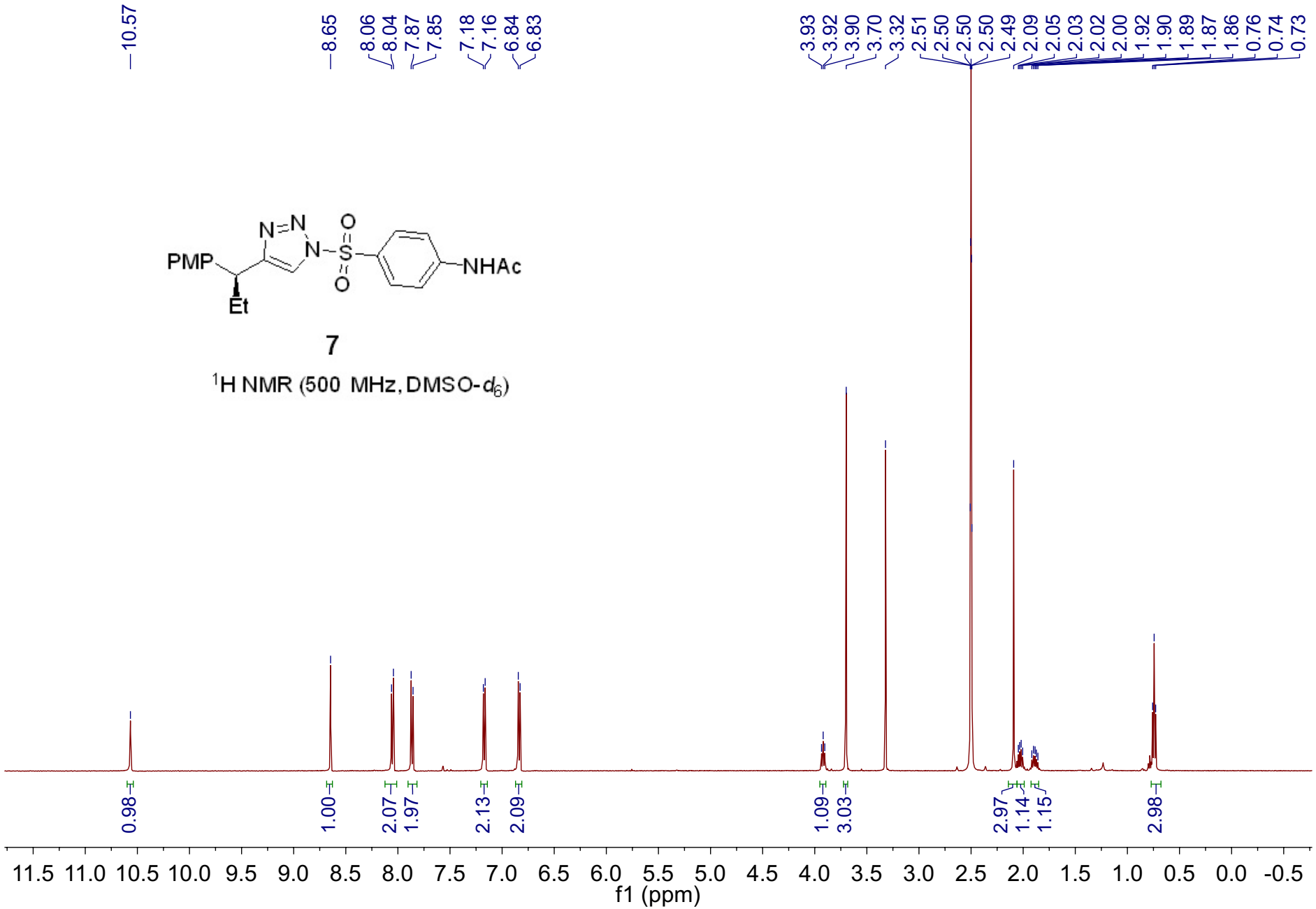
Supplementary Fig. 183. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound (*S*)-**3i**



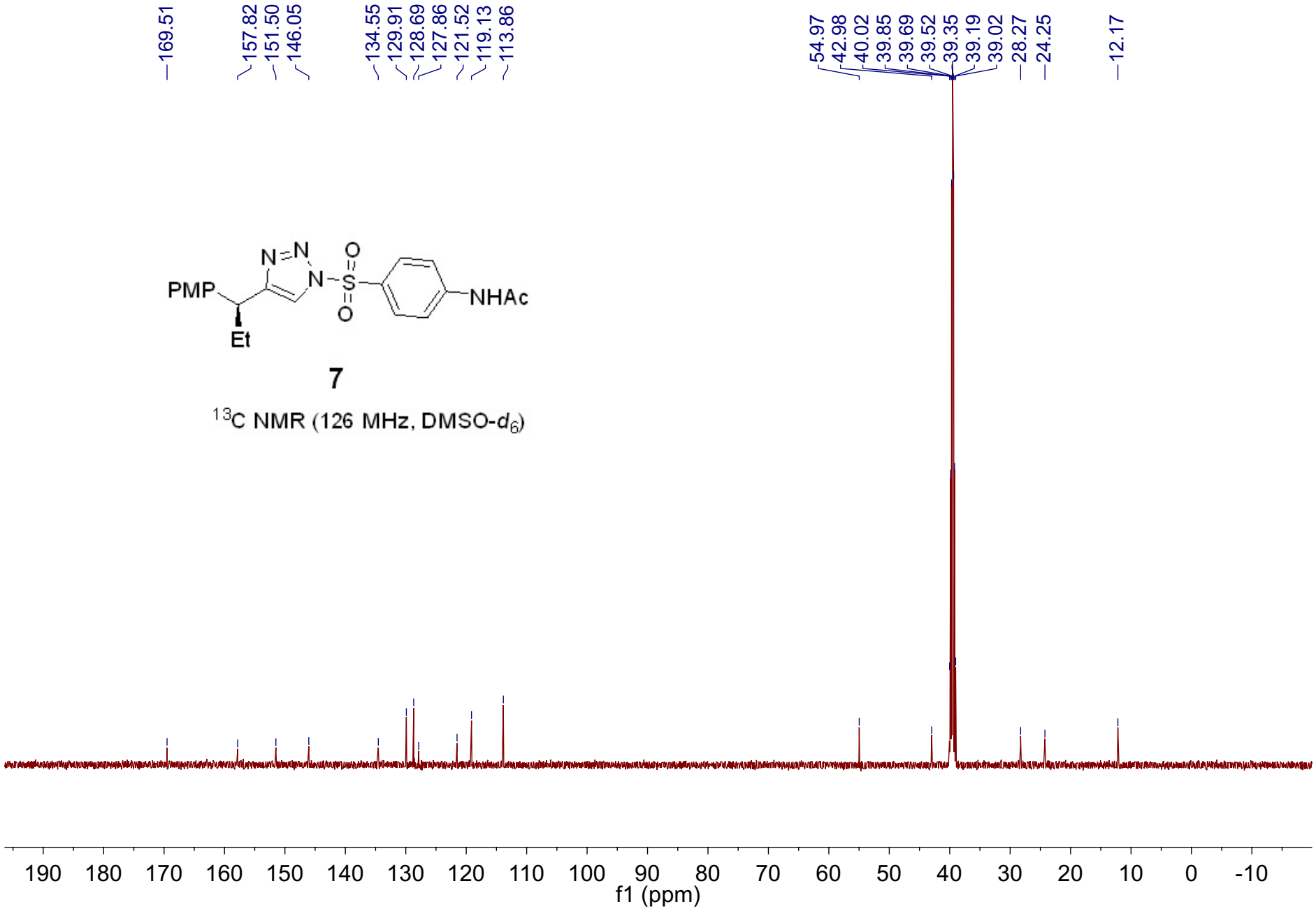
Supplementary Fig. 184. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **6**



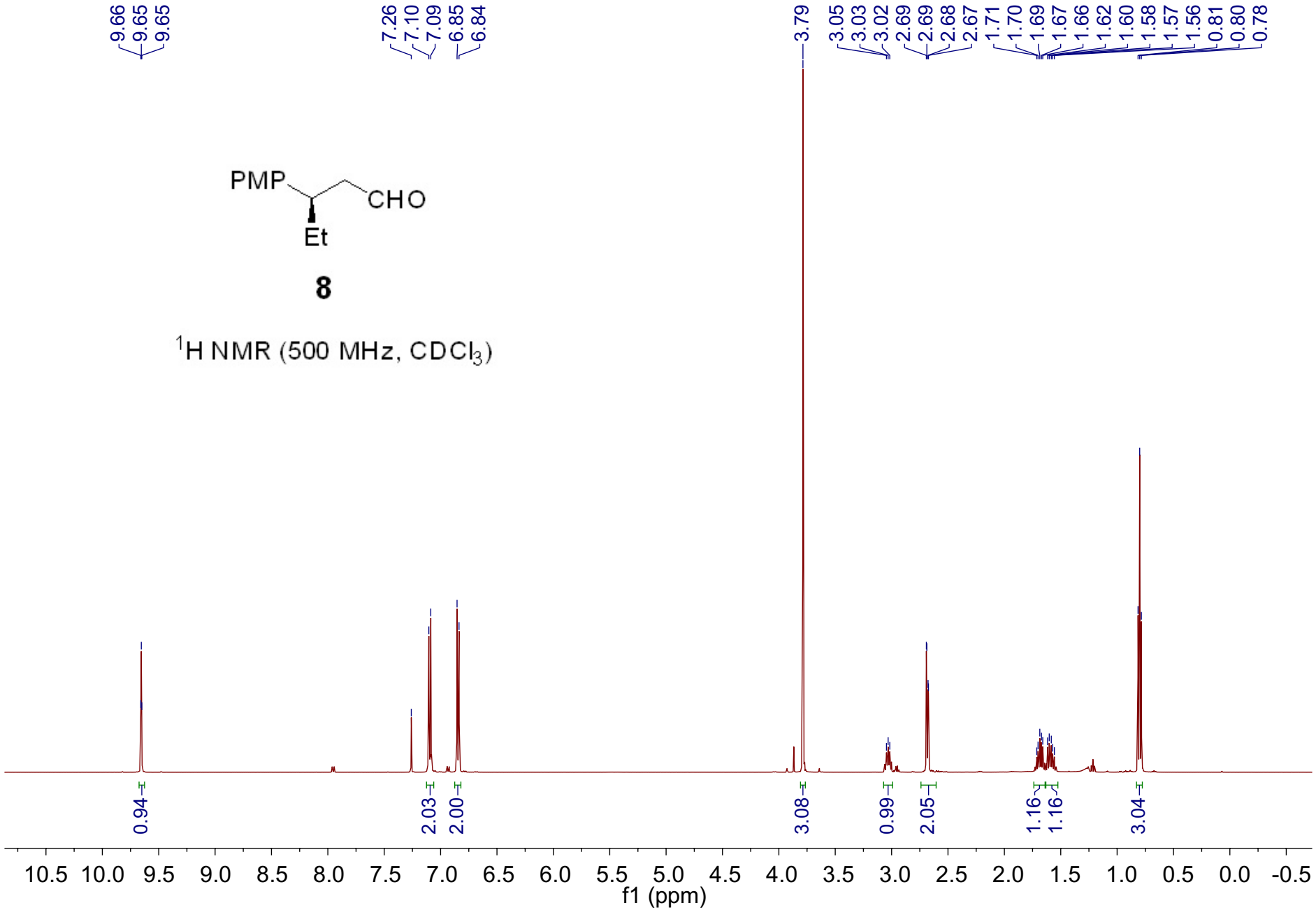
Supplementary Fig. 185. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **6**



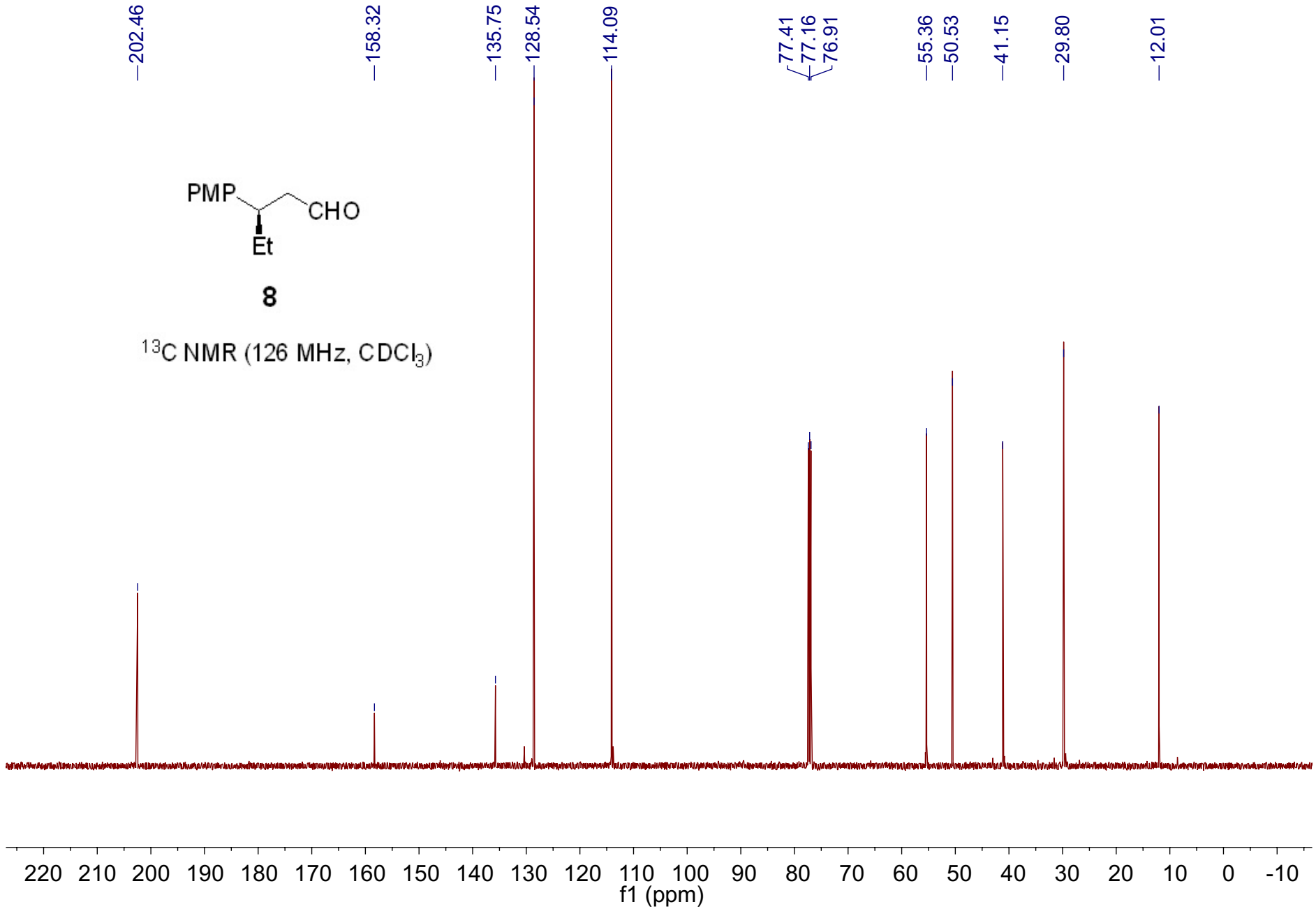
Supplementary Fig. 186. ^{1}H NMR (500 MHz, DMSO-d_6) spectra for compound **7**



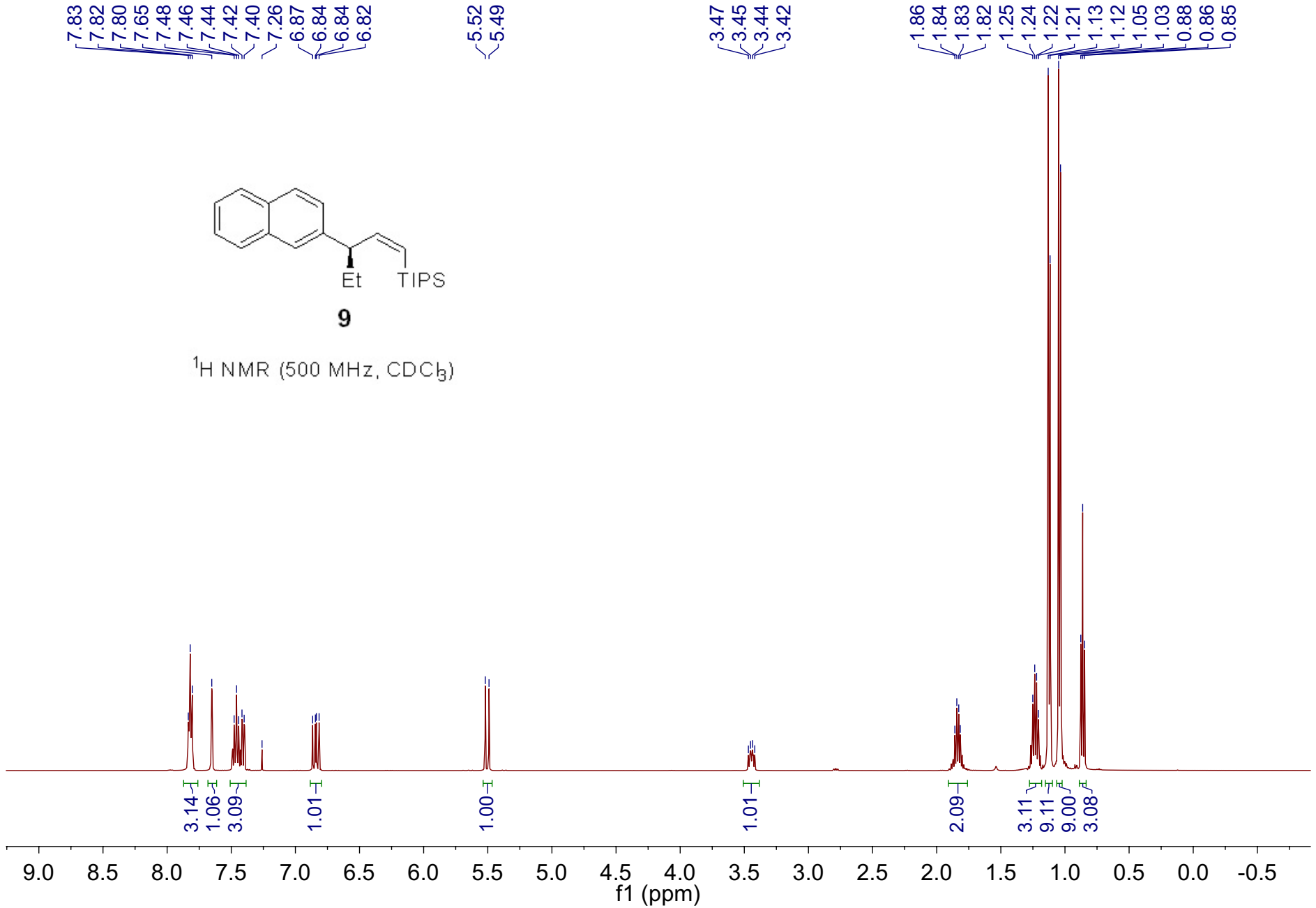
Supplementary Fig. 187. ^{13}C NMR (126 MHz, DMSO-d_6) spectra for compound **7**



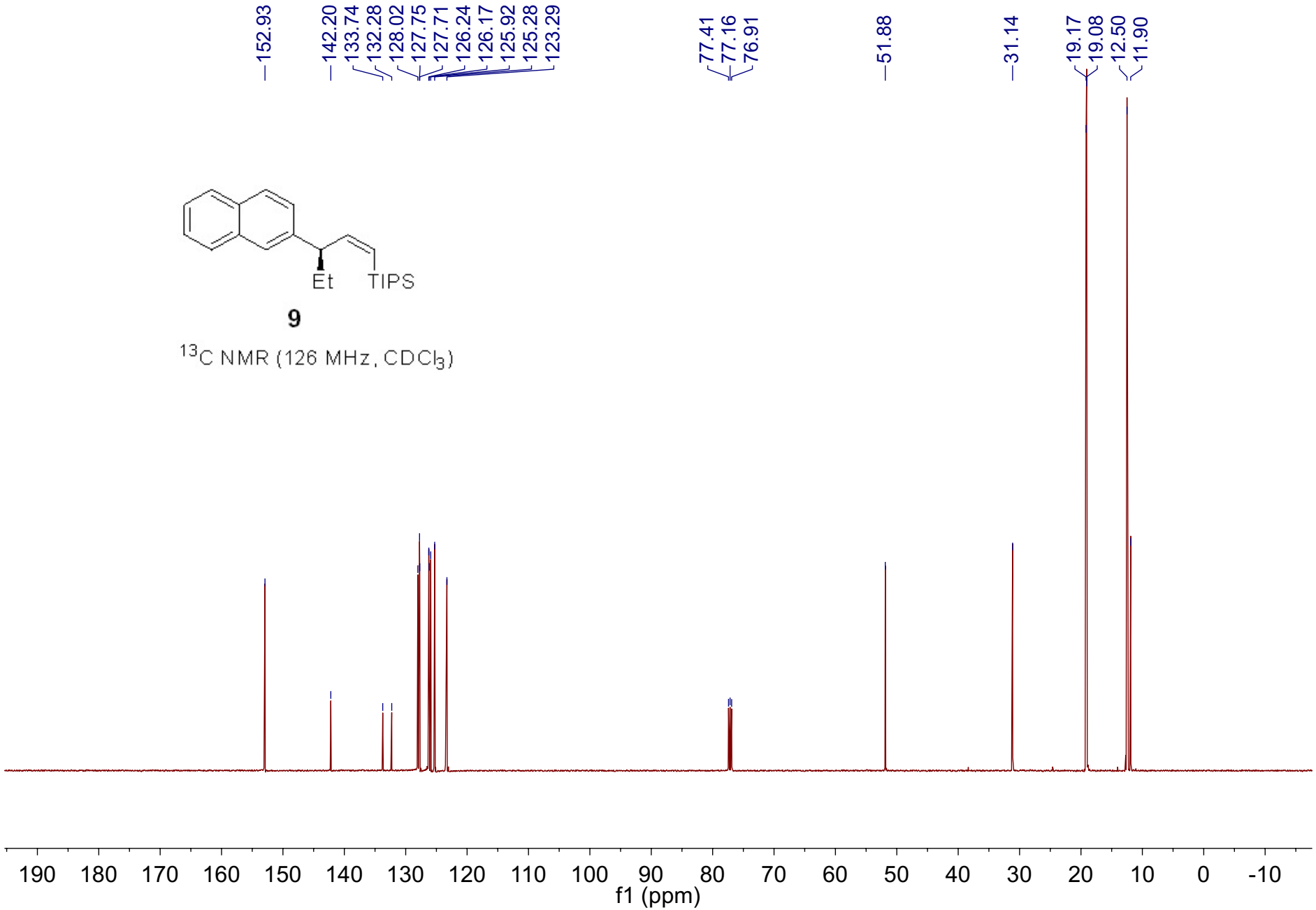
Supplementary Fig. 188. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **8**



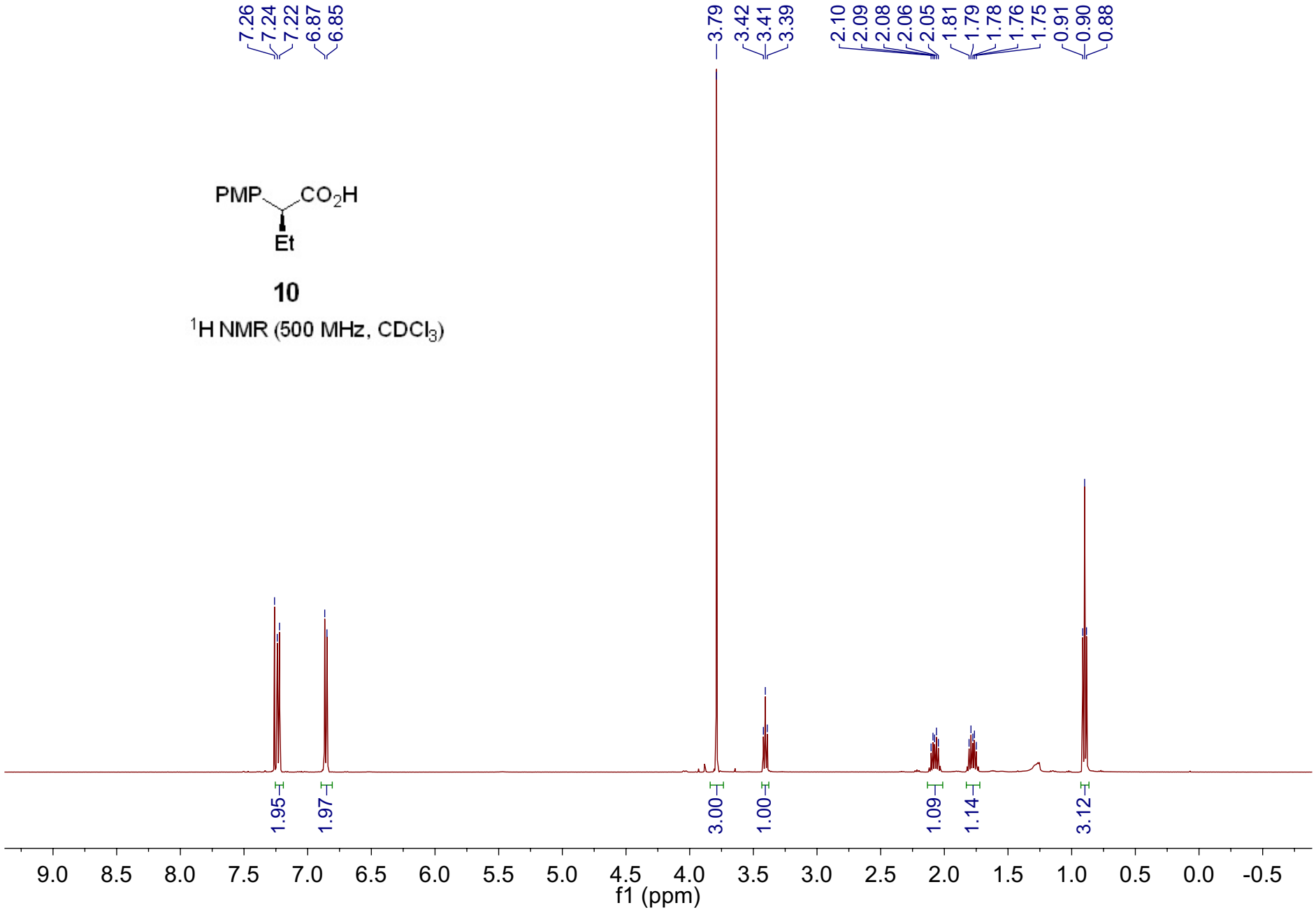
Supplementary Fig. 189. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **8**



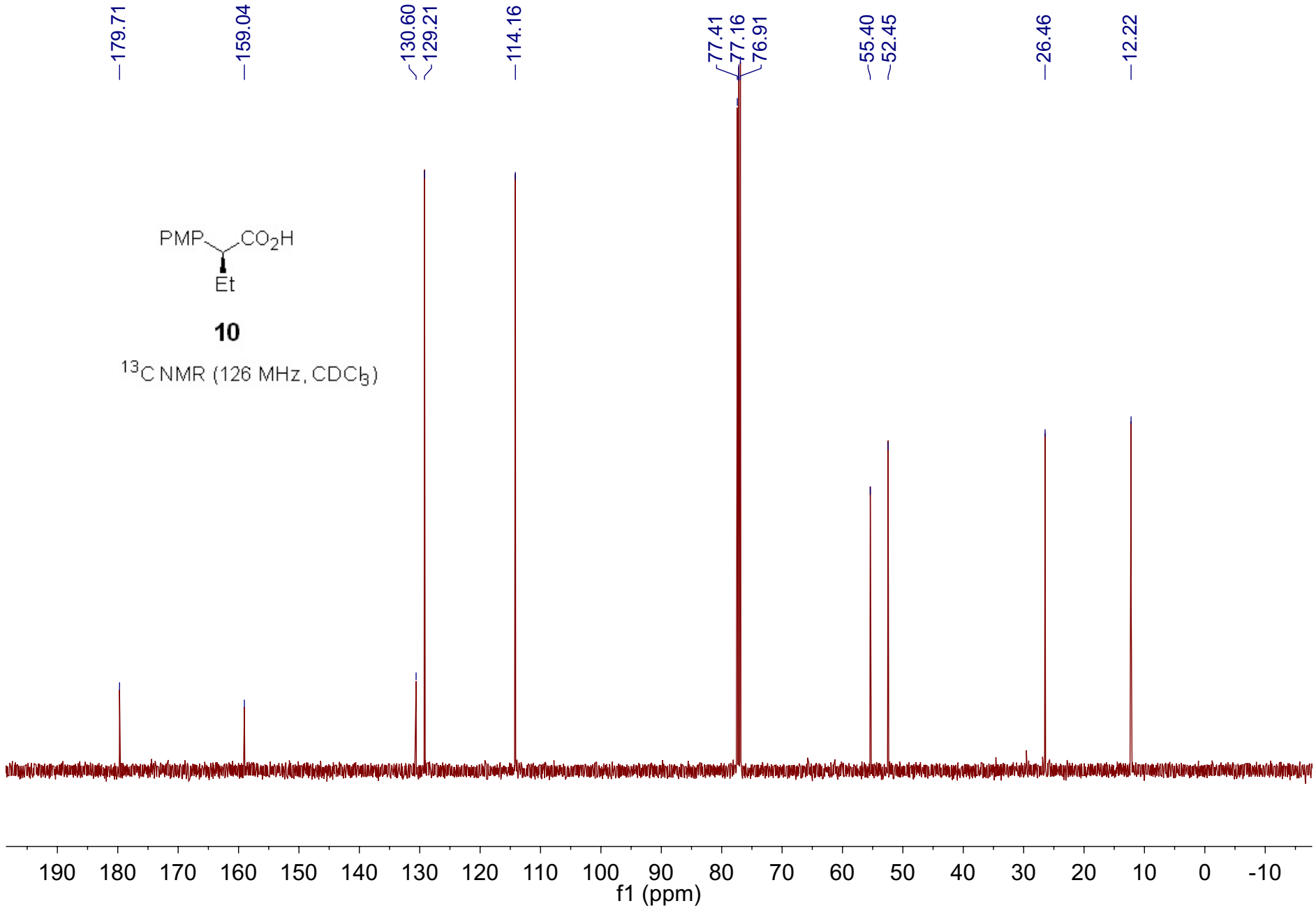
Supplementary Fig. 190. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **9**



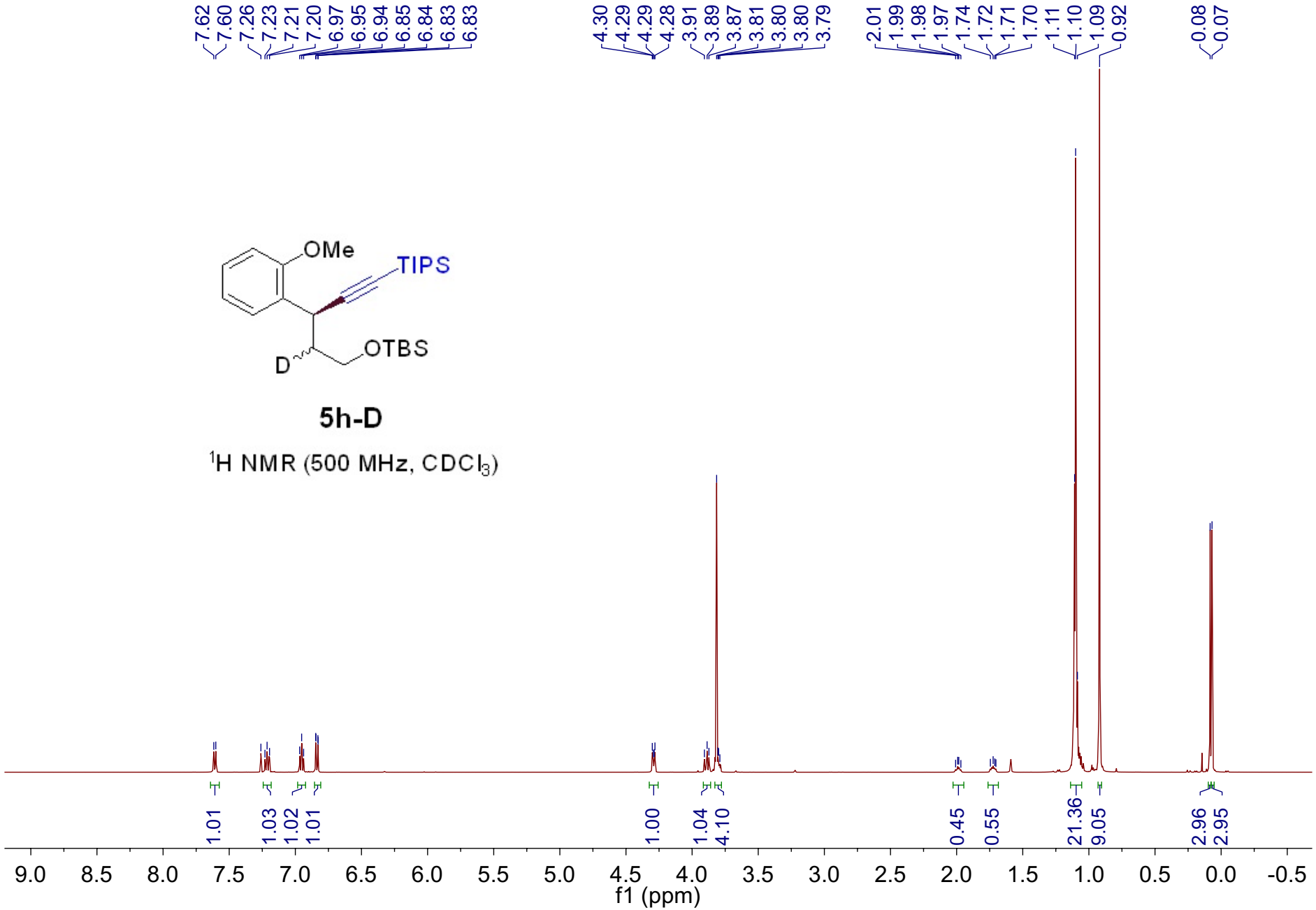
Supplementary Fig. 191. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **9**



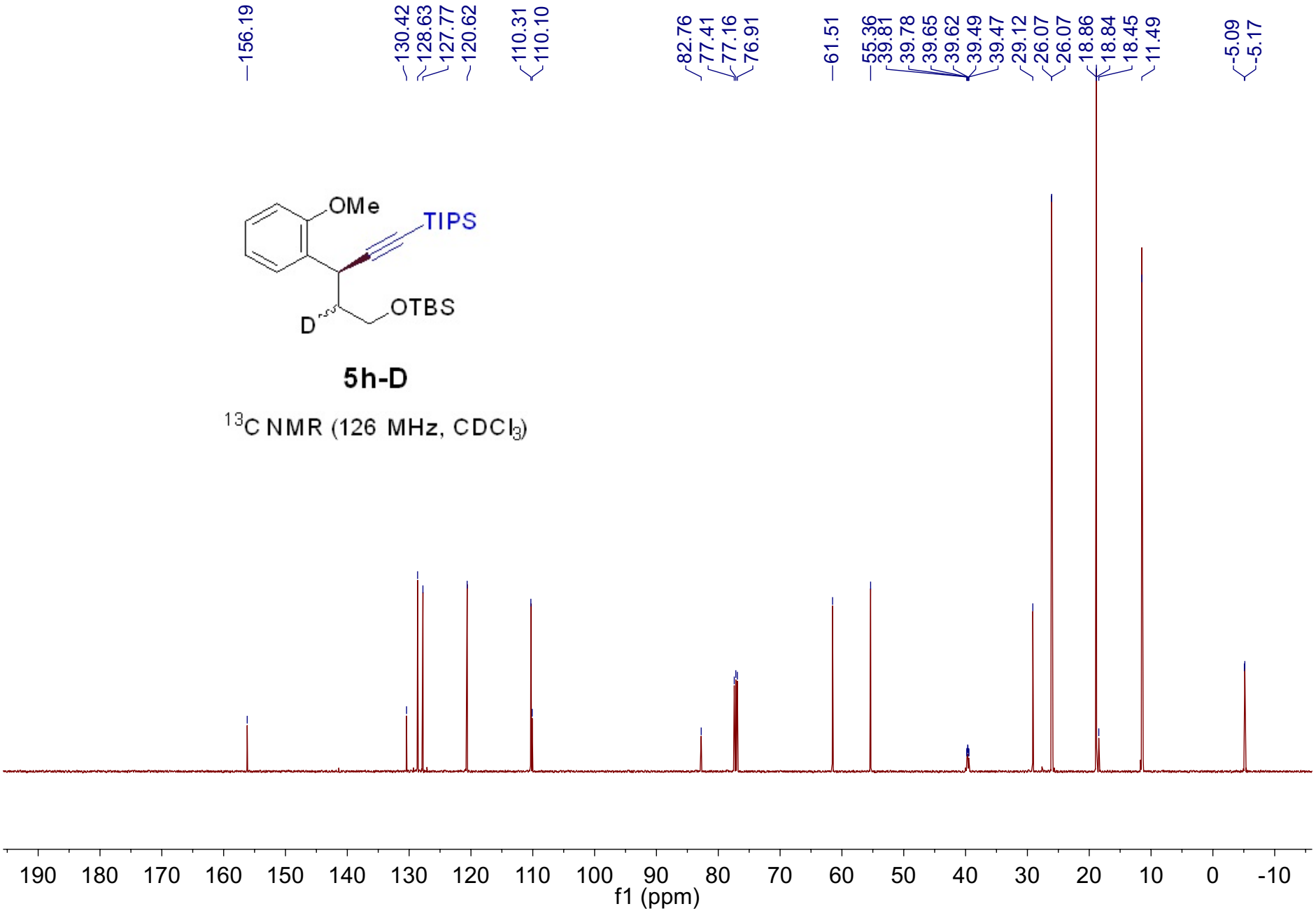
Supplementary Fig. 192. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **10**



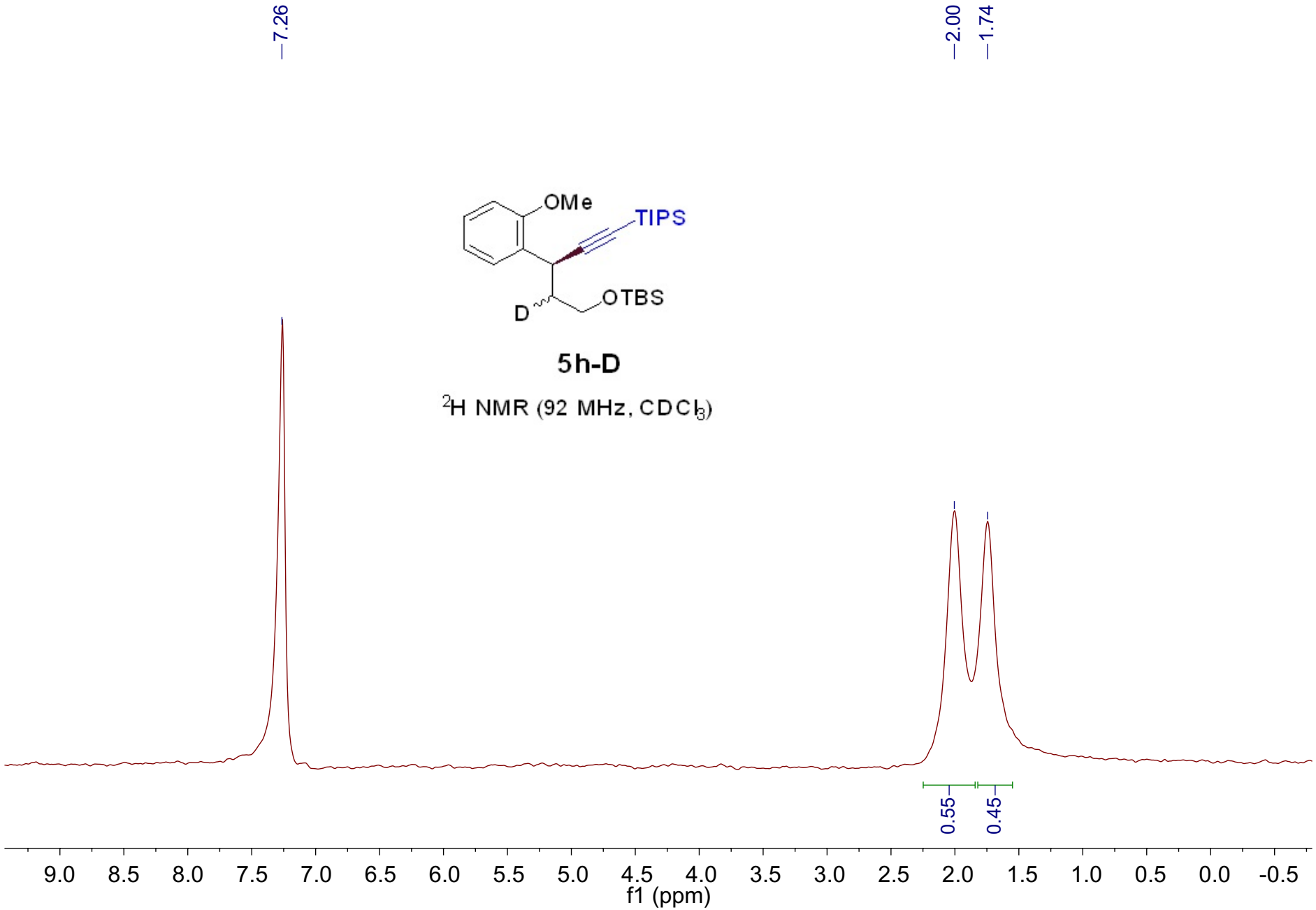
Supplementary Fig. 193. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **10**



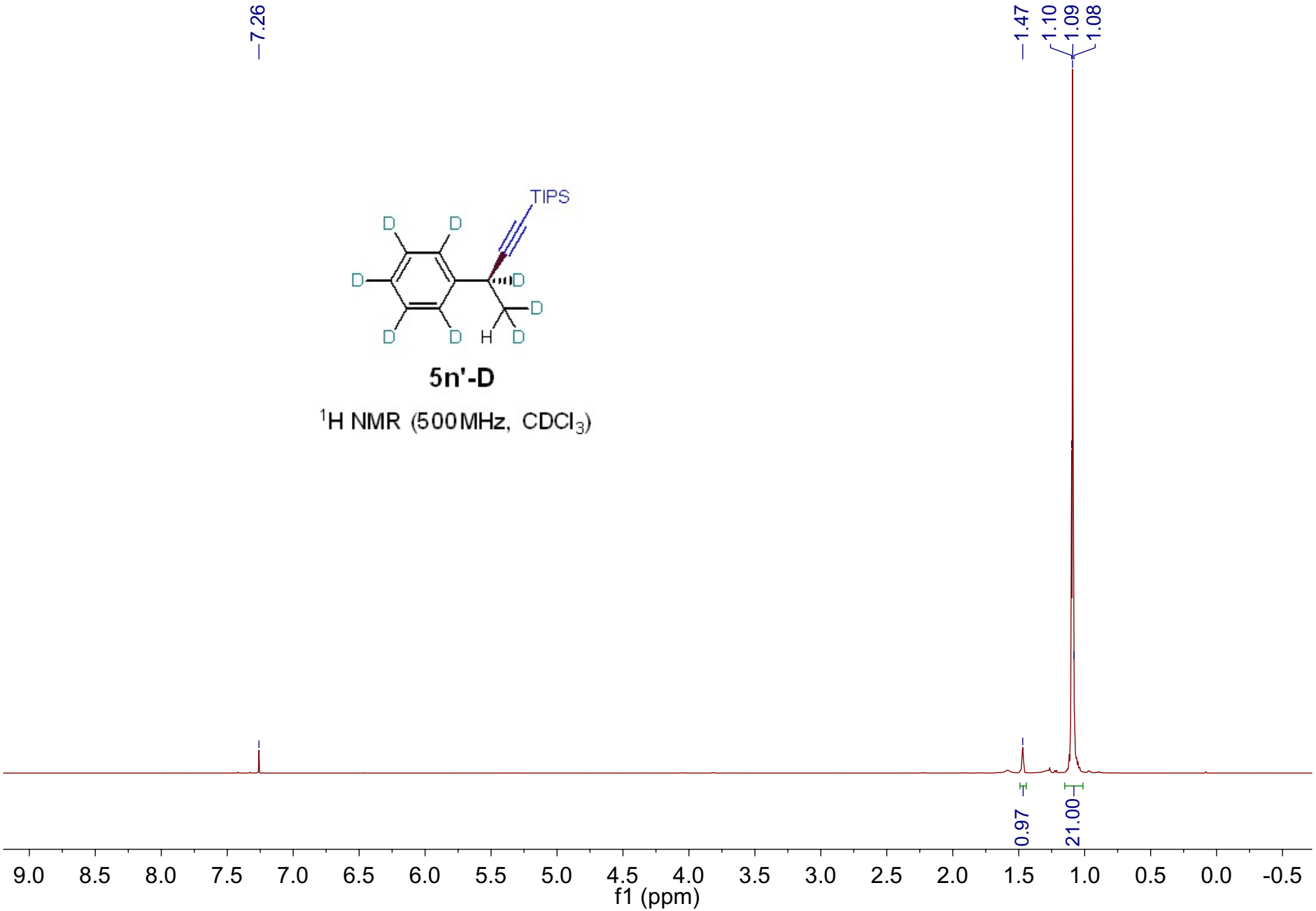
Supplementary Fig. 194. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5h-D**



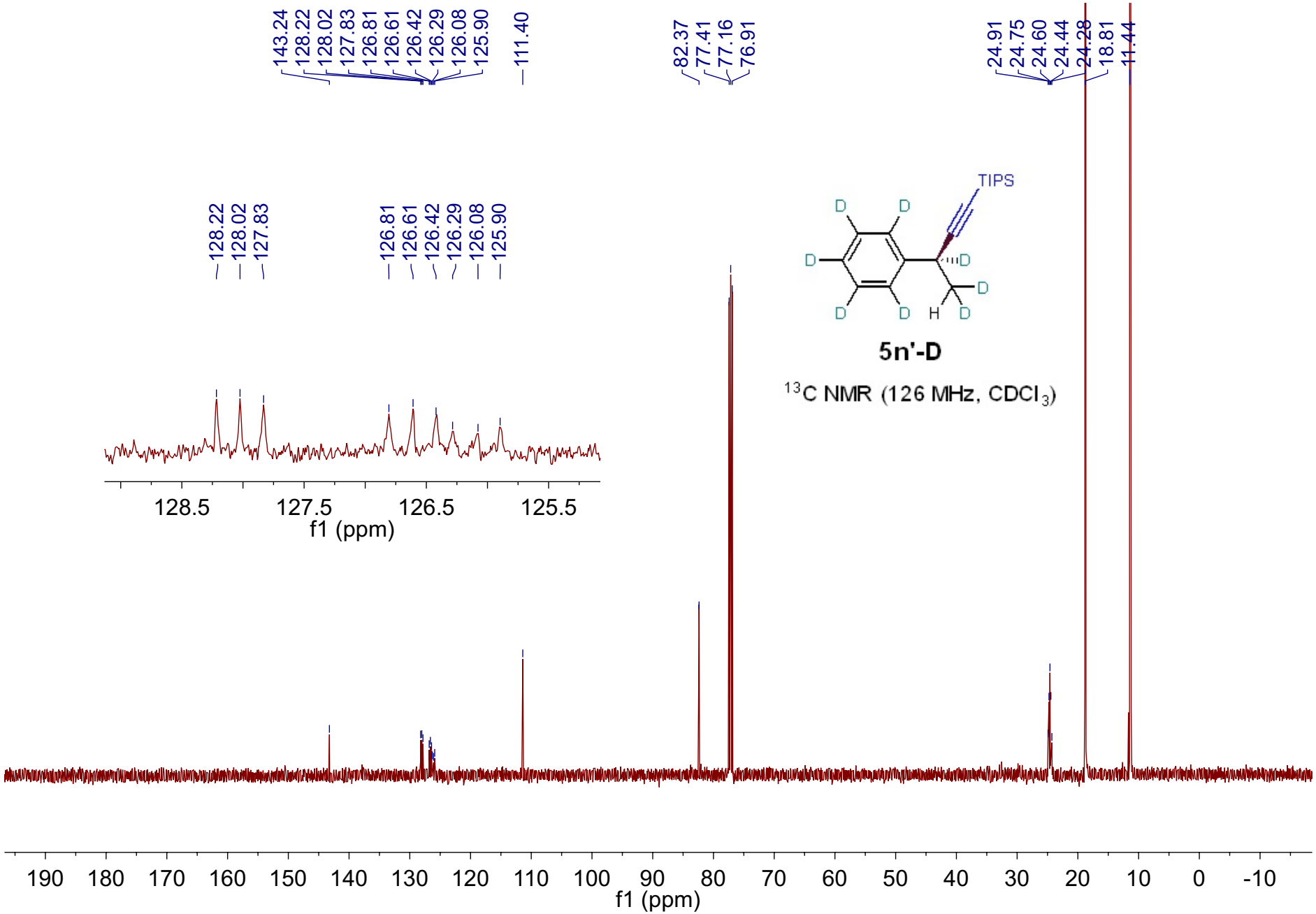
Supplementary Fig. 195. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5h-D**



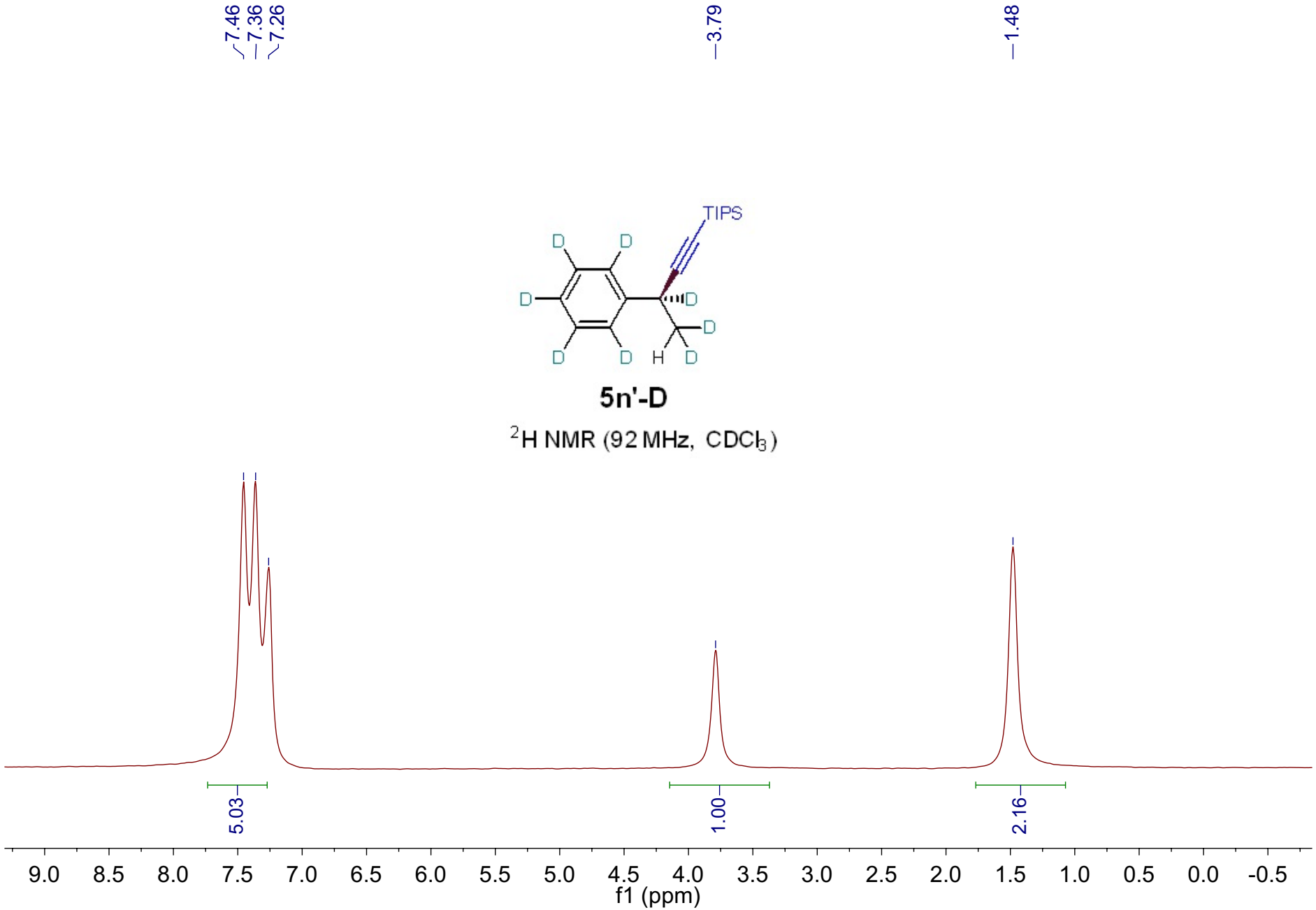
Supplementary Fig. 196. ^{2}H NMR (92 MHz, $CDCl_3$) spectra for compound **5h-D**



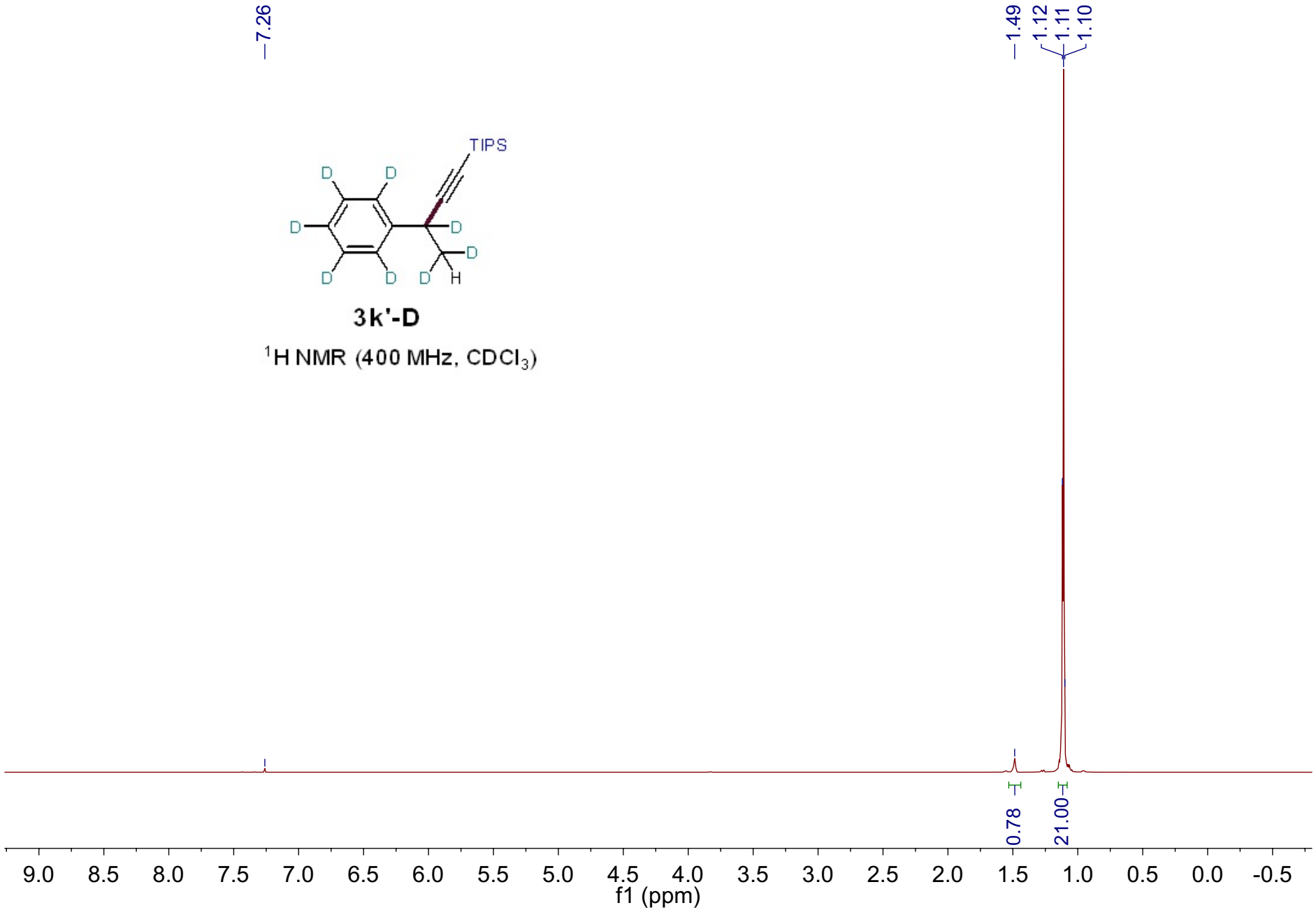
Supplementary Fig. 197. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **5n'-D**



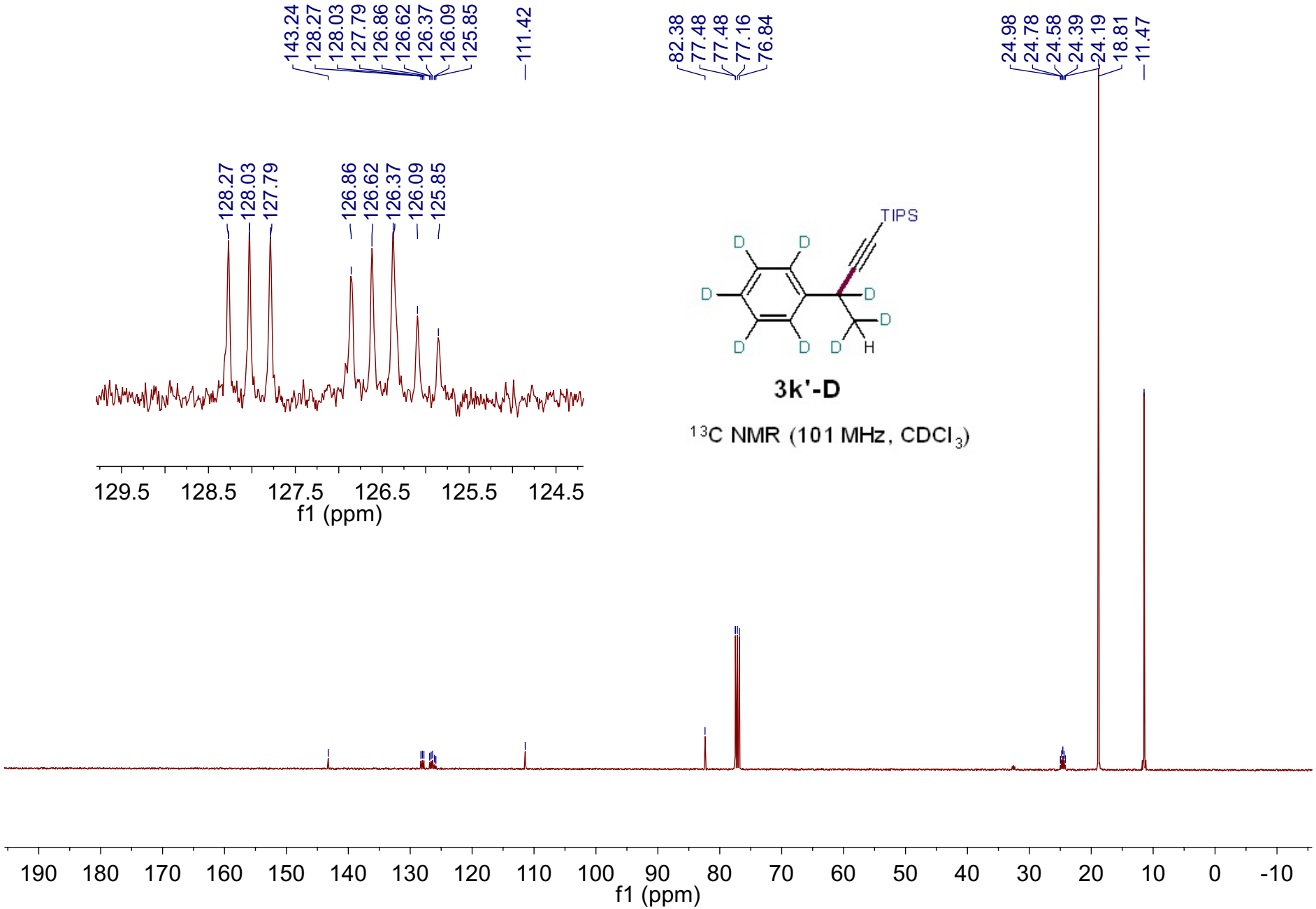
Supplementary Fig. 198. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **5n'-D**



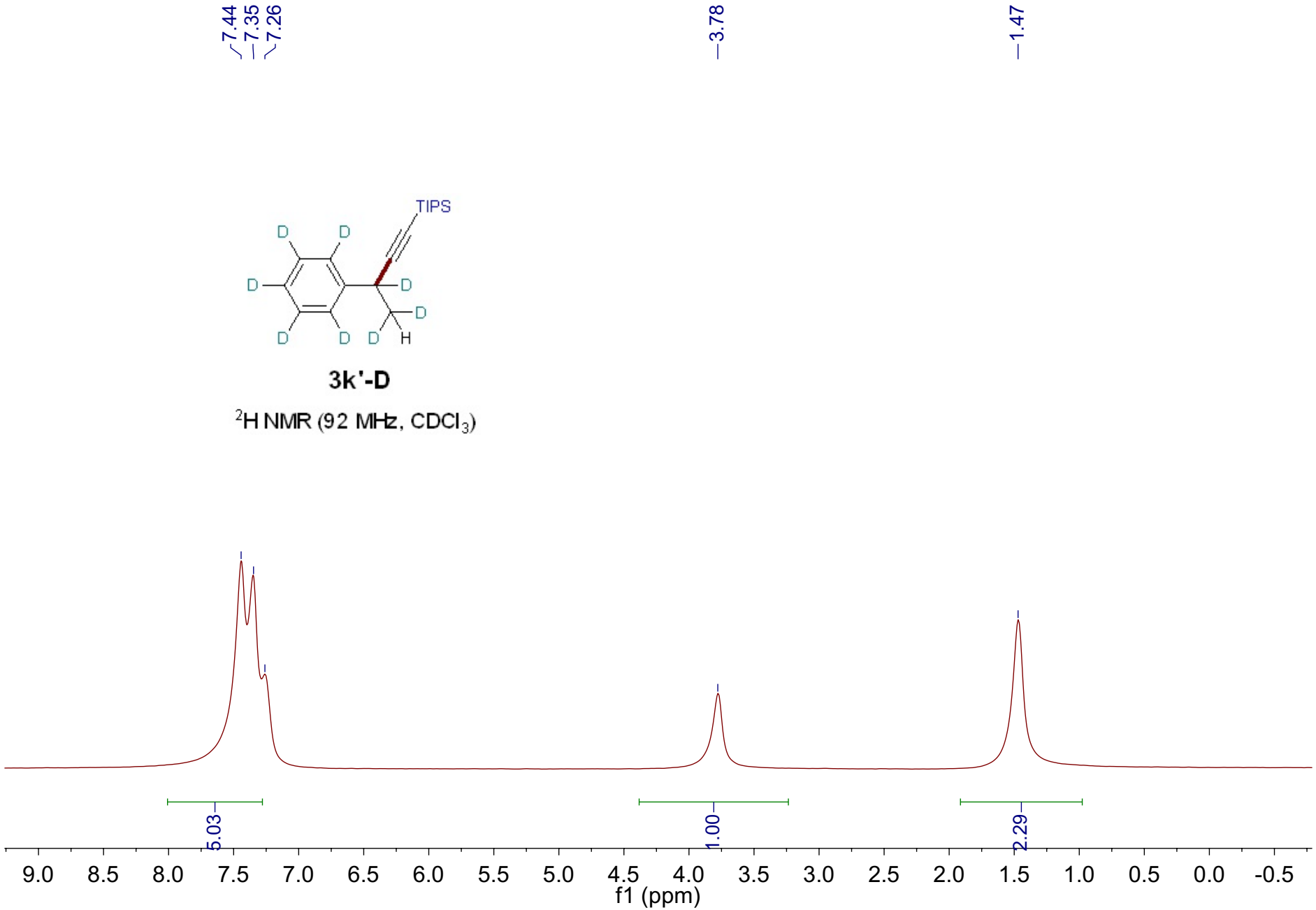
Supplementary Fig. 199. ^{2}H NMR (92 MHz, $CDCl_3$) spectra for compound **5n'-D**



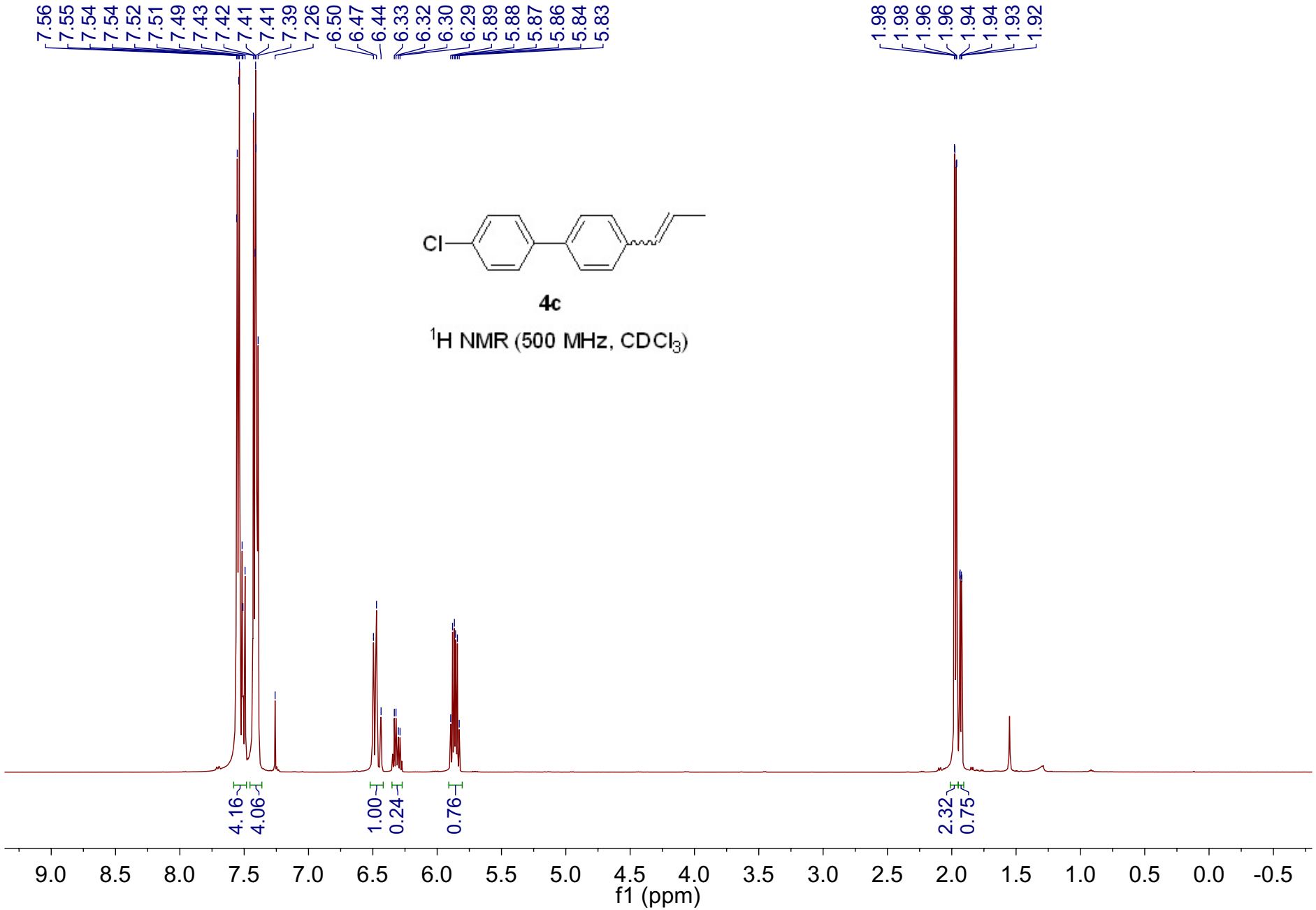
Supplementary Fig. 200. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3k'-D**



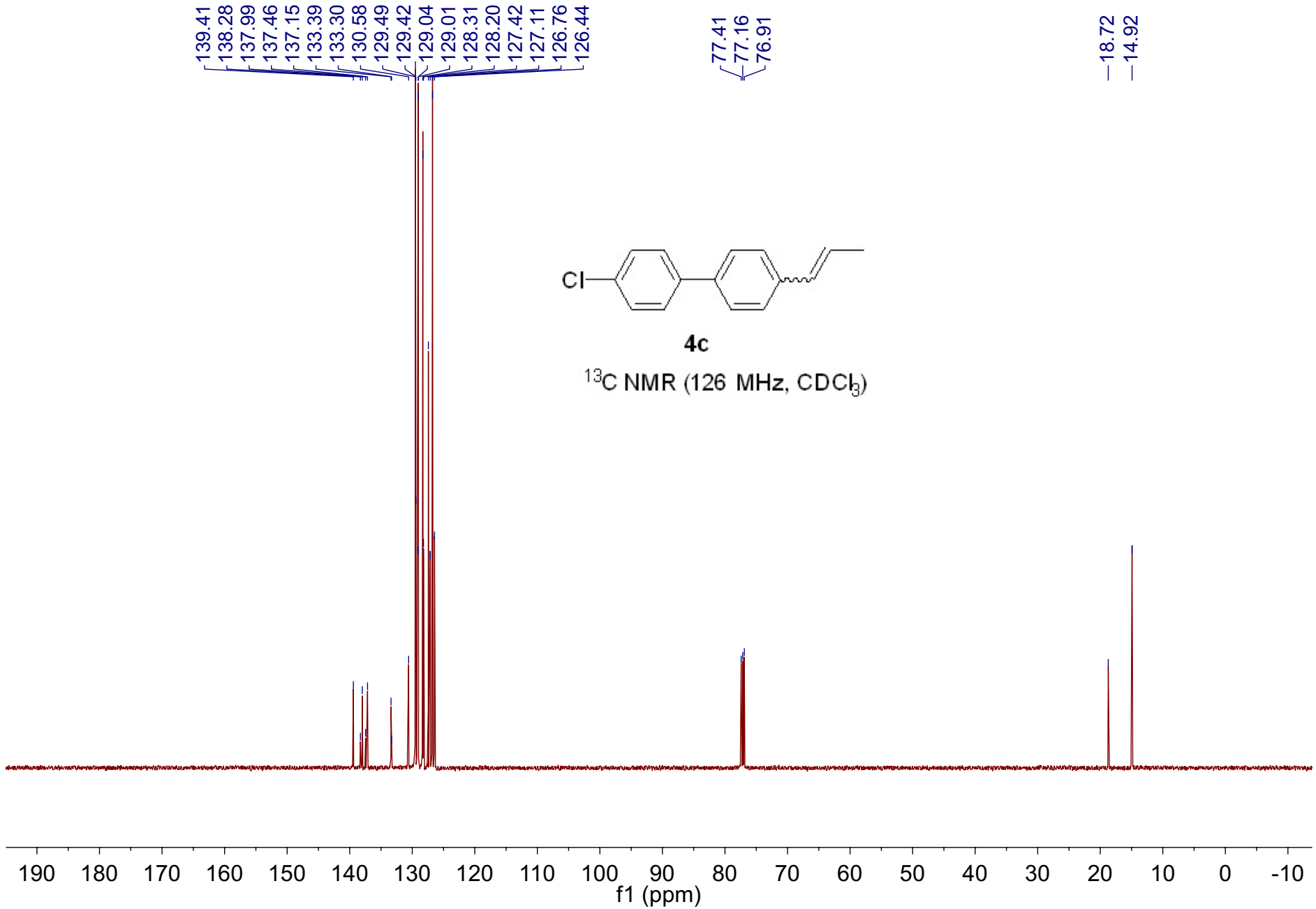
Supplementary Fig. 201. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3k'-D**



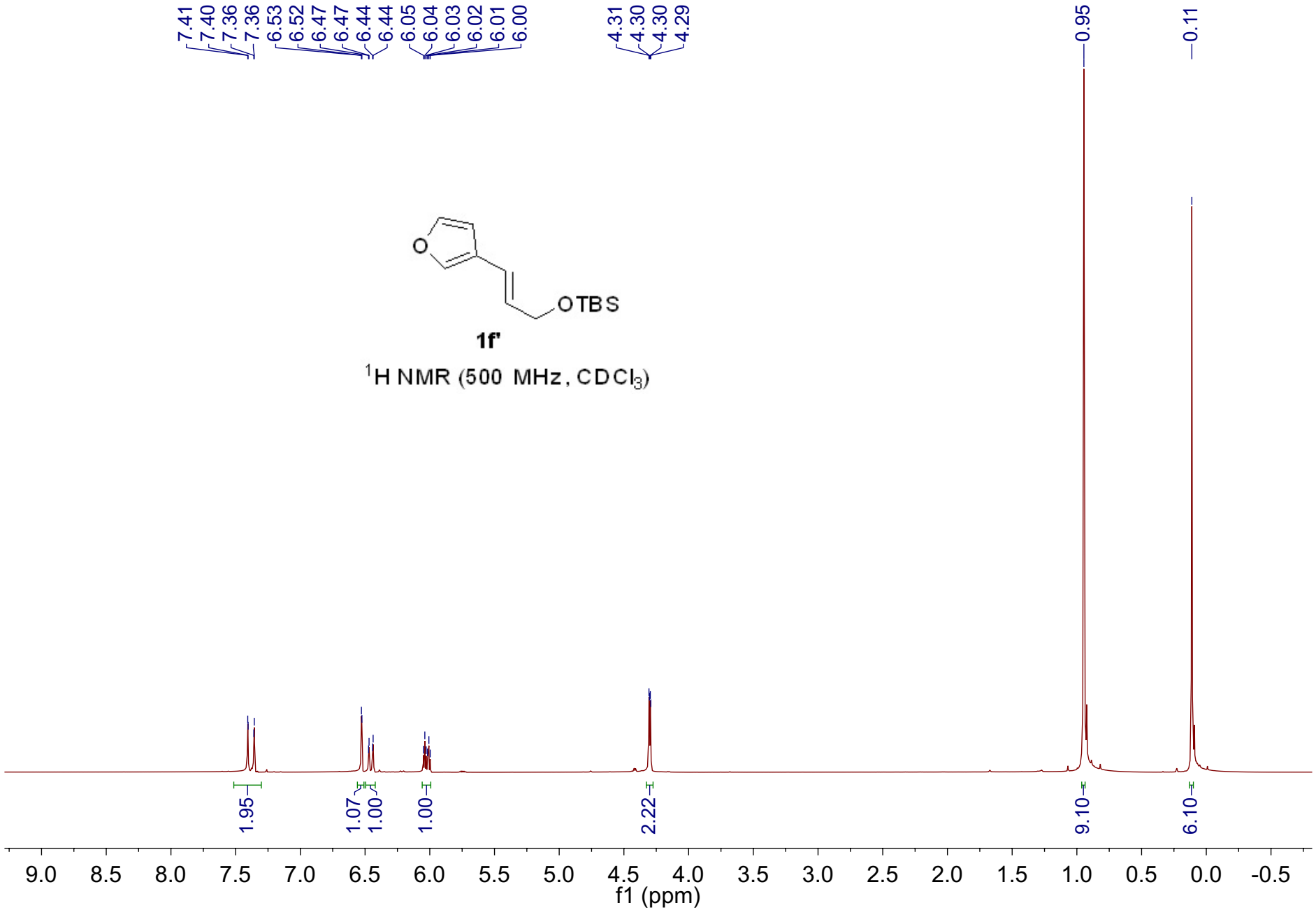
Supplementary Fig. 202. ^{2}H NMR (92 MHz, $CDCl_3$) spectra for compound **3k'-D**



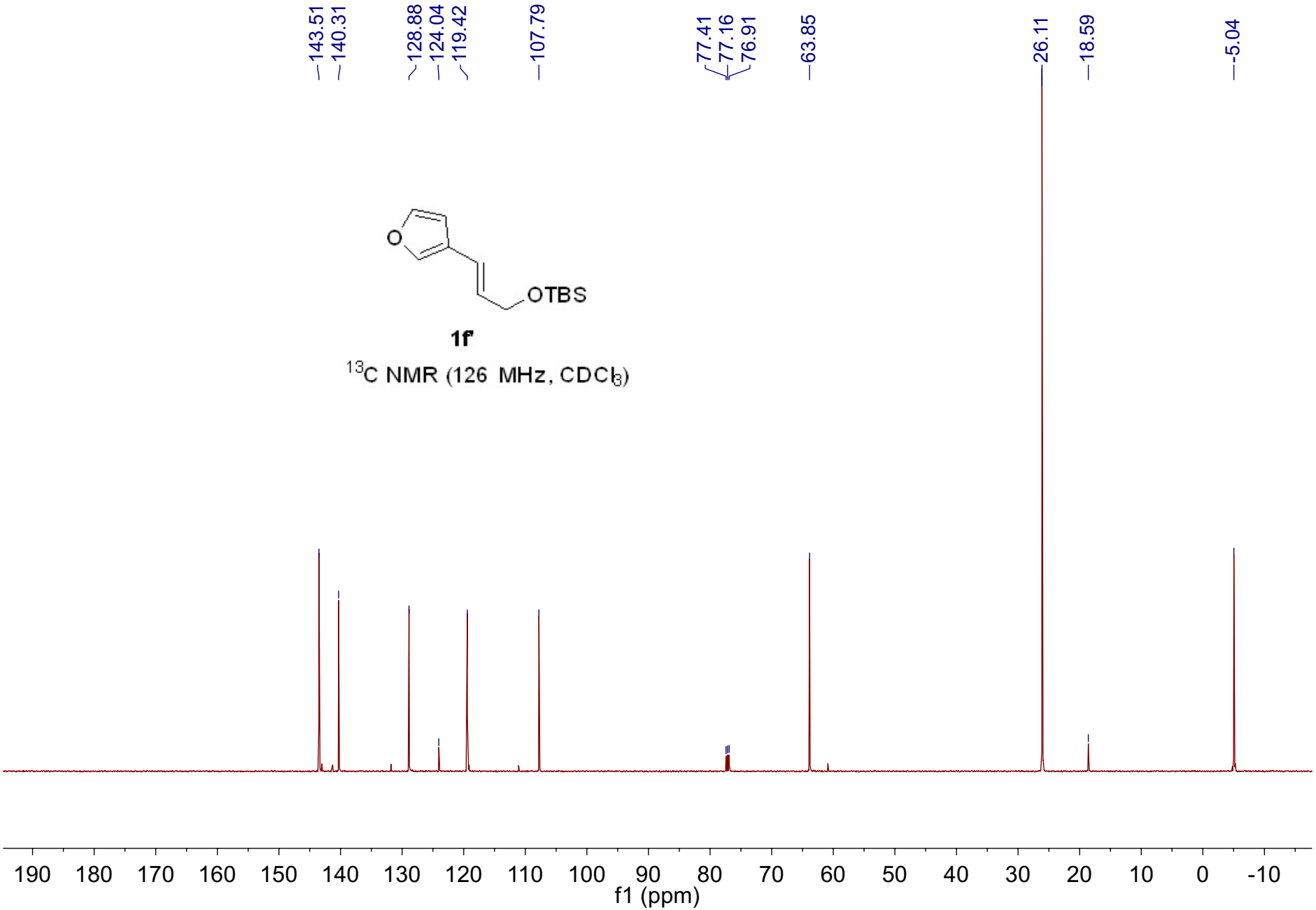
Supplementary Fig. 203. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **4c**



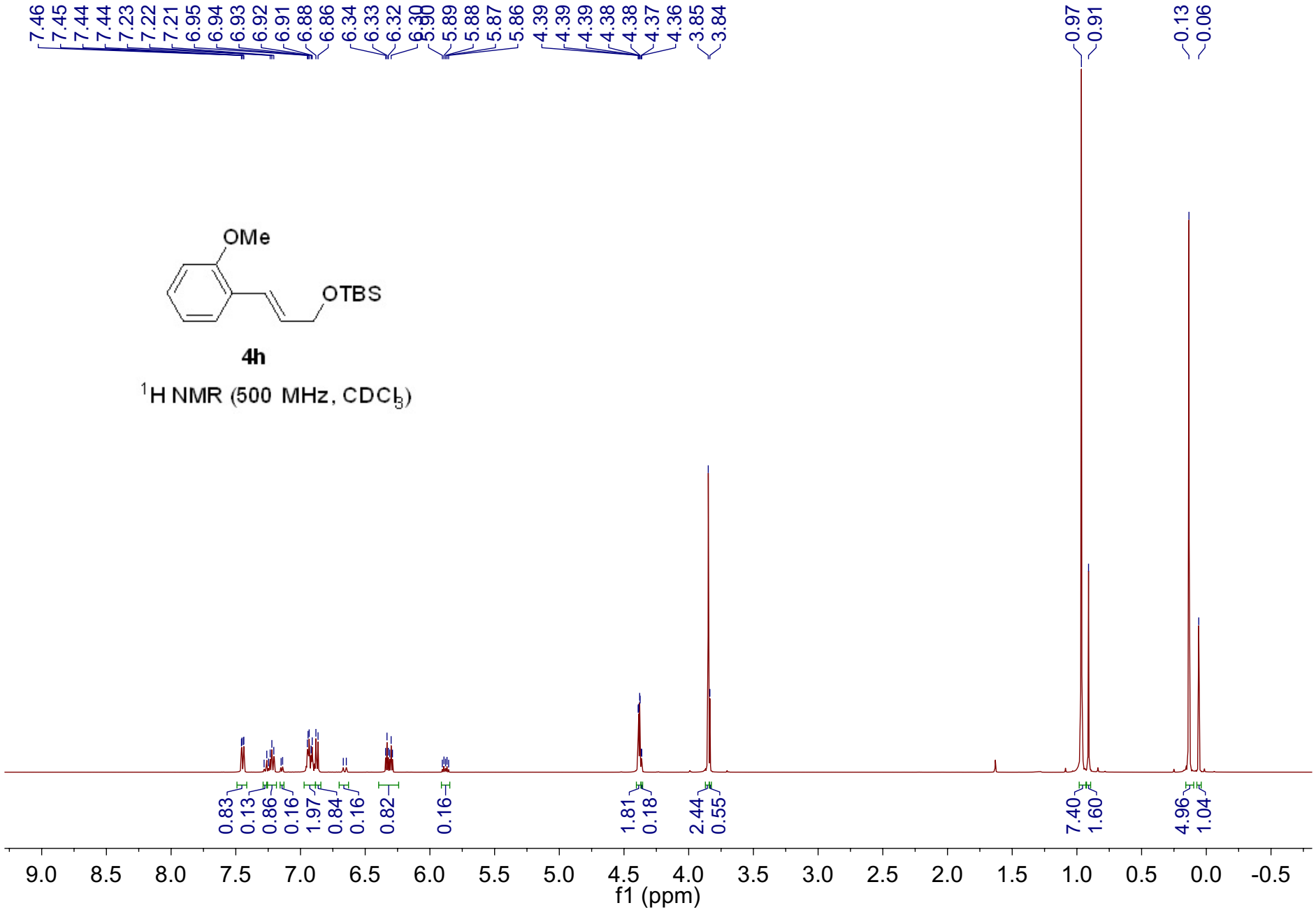
Supplementary Fig. 204. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **4c**



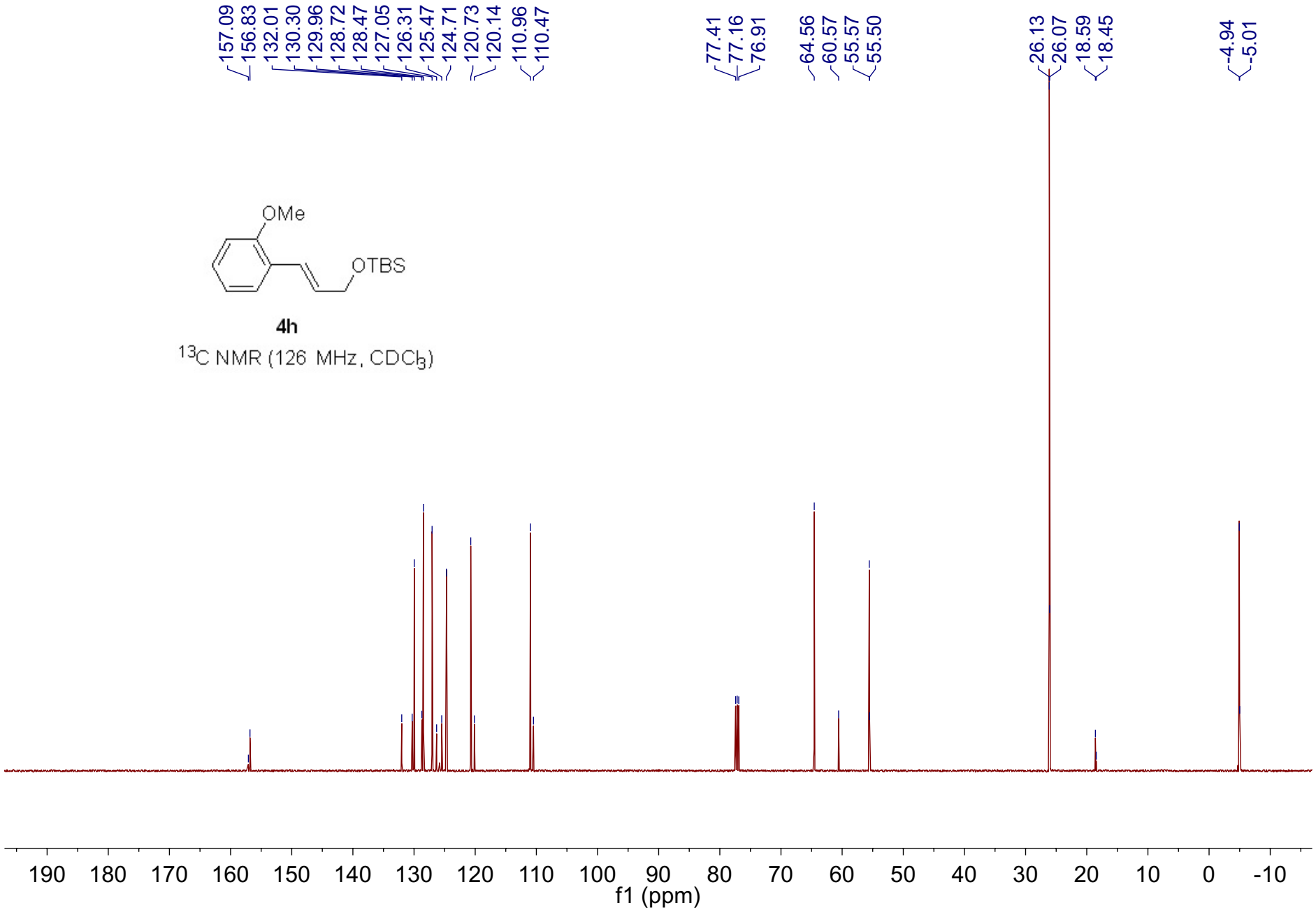
Supplementary Fig. 205. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **1f'**



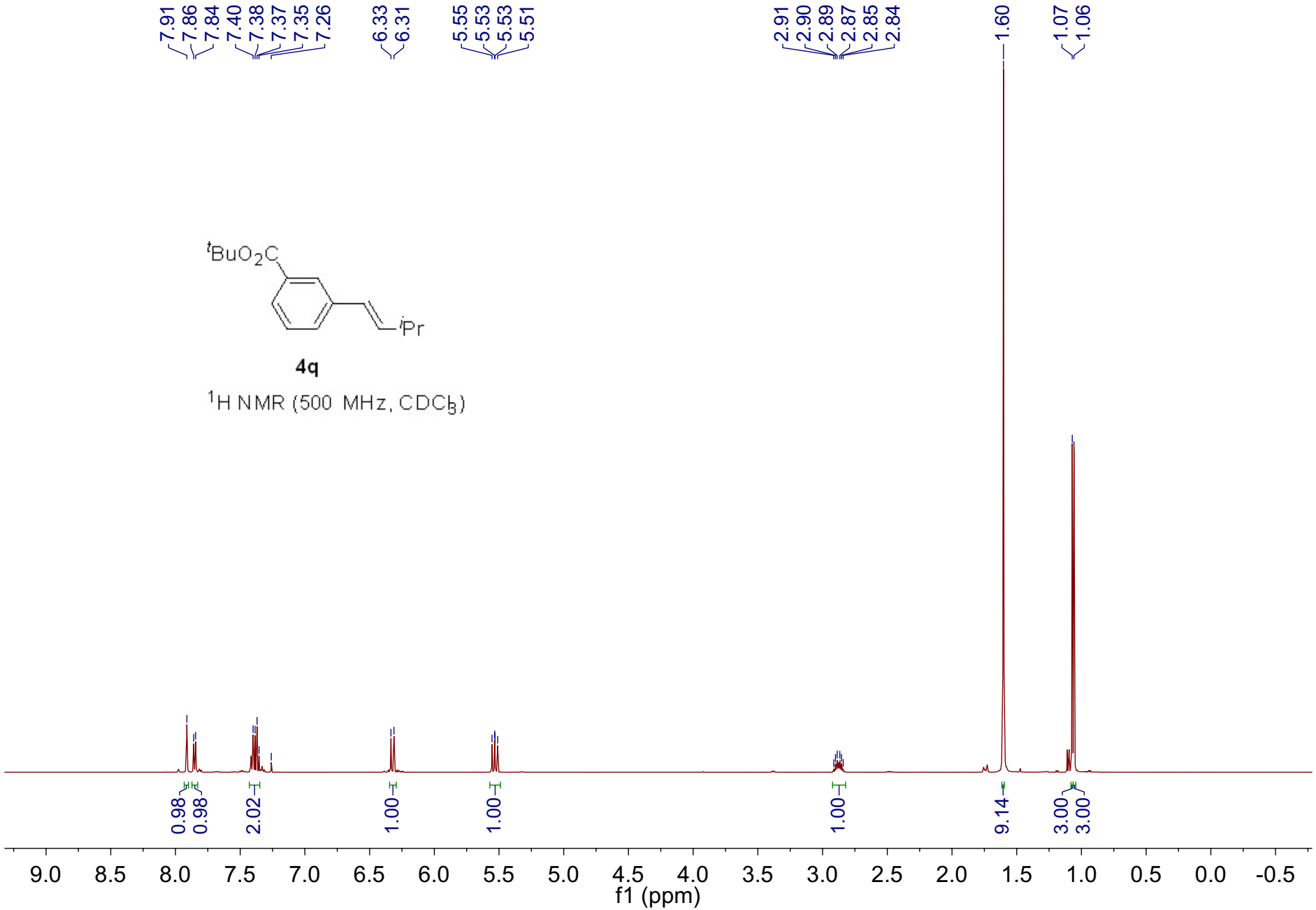
Supplementary Fig. 206. ^{1}H NMR (126 MHz, $CDCl_3$) spectra for compound **1f'**



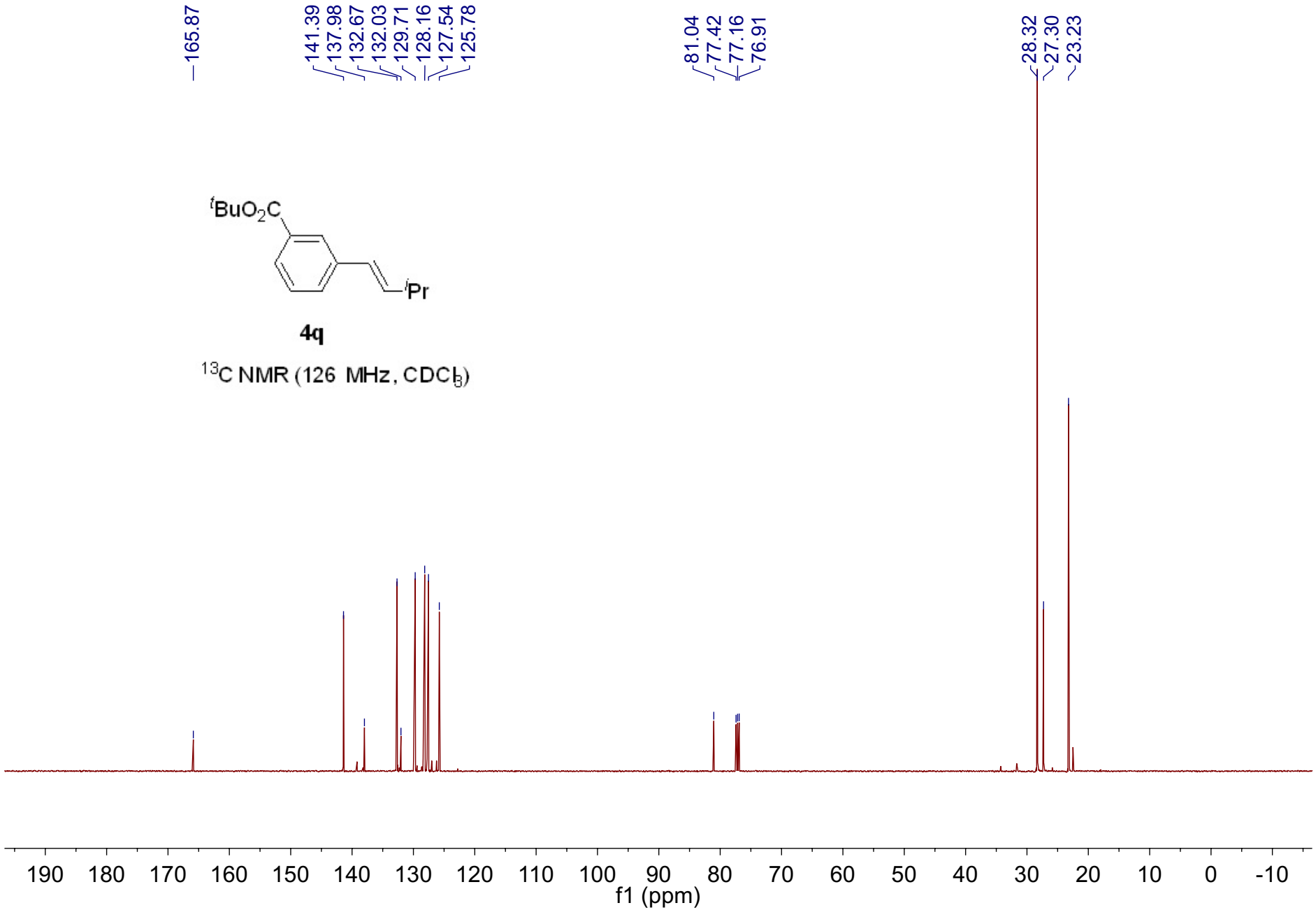
Supplementary Fig. 207. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **4h**



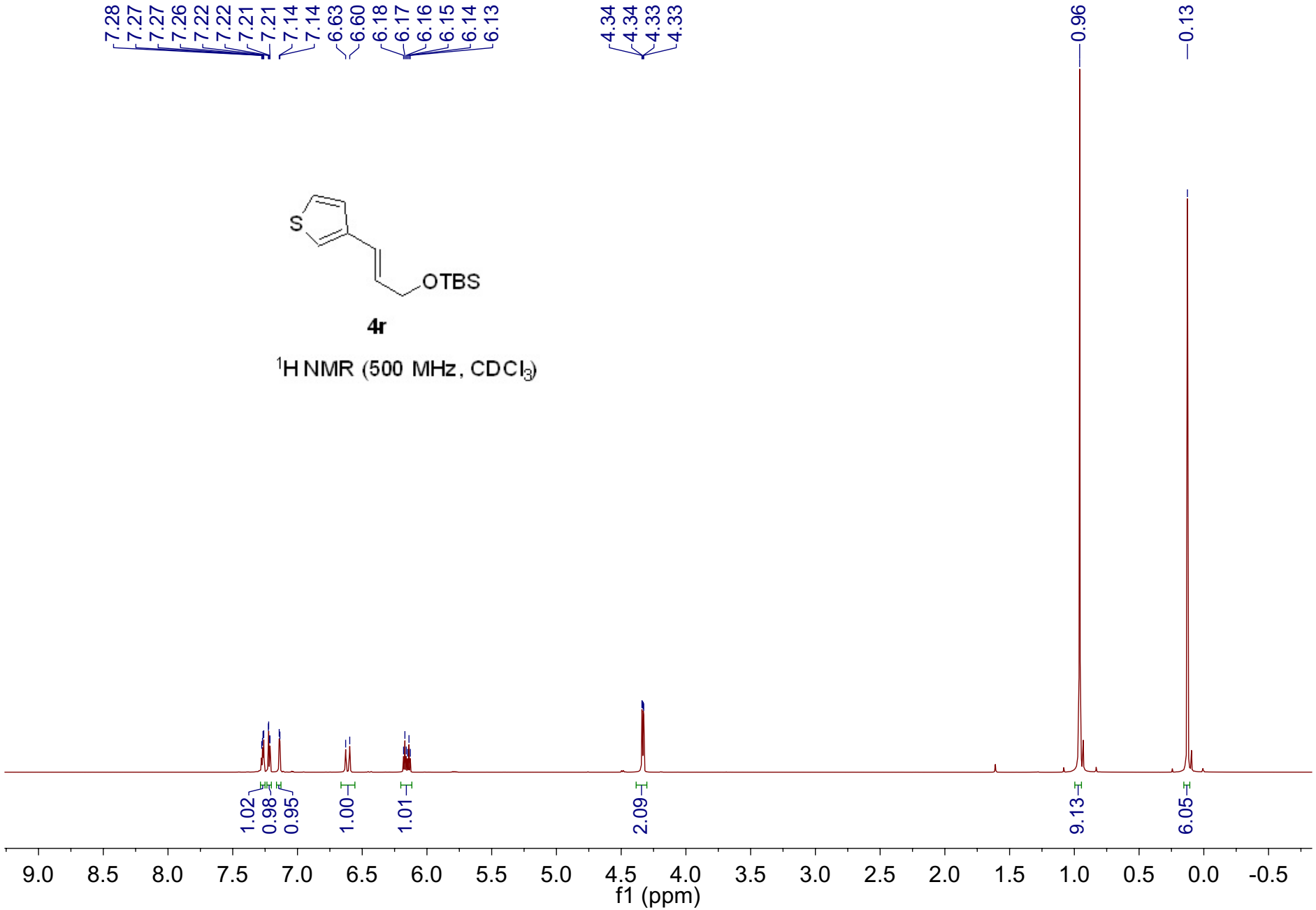
Supplementary Fig. 208. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **4h**



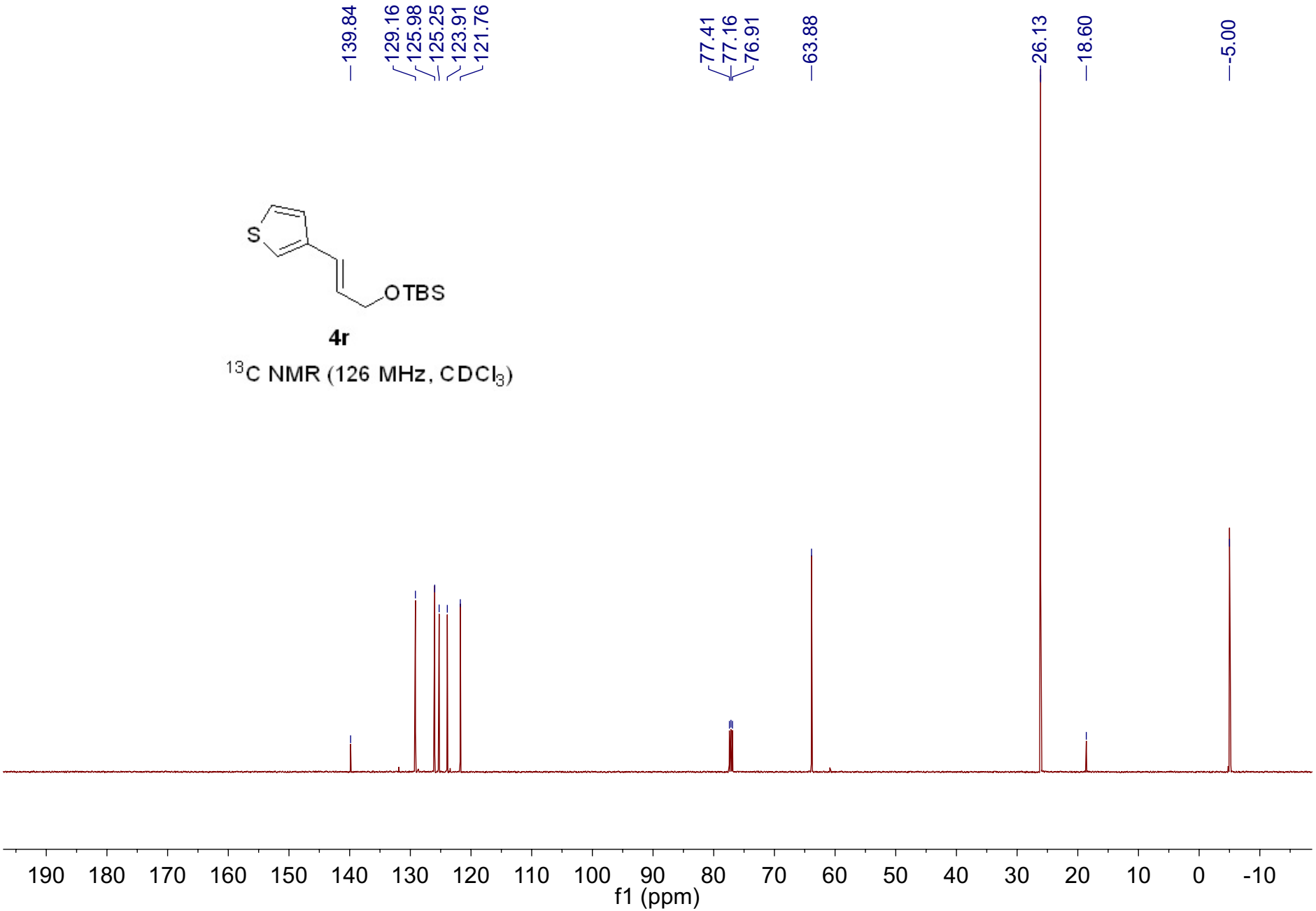
Supplementary Fig. 209. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **4q**



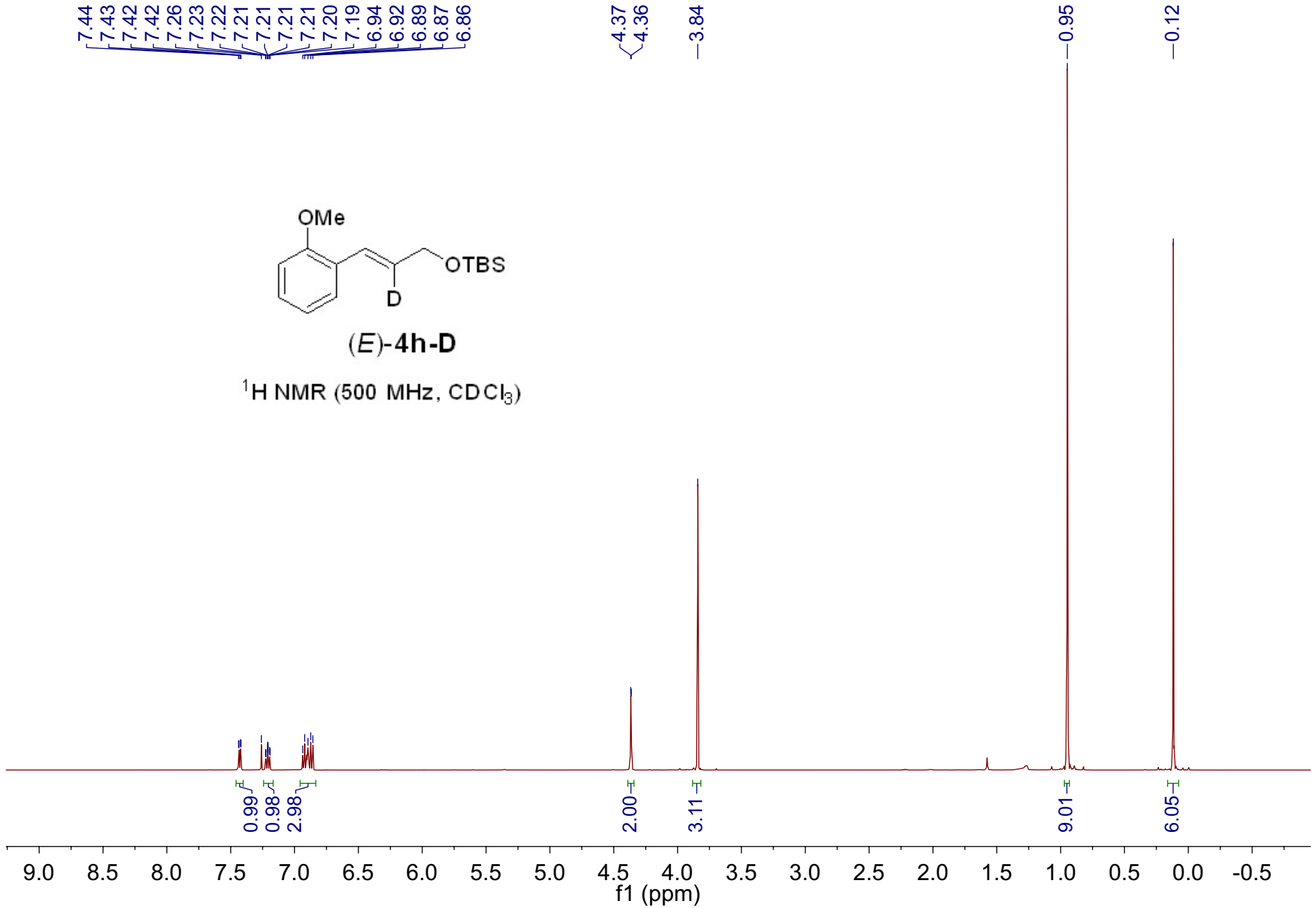
Supplementary Fig. 210. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **4q**



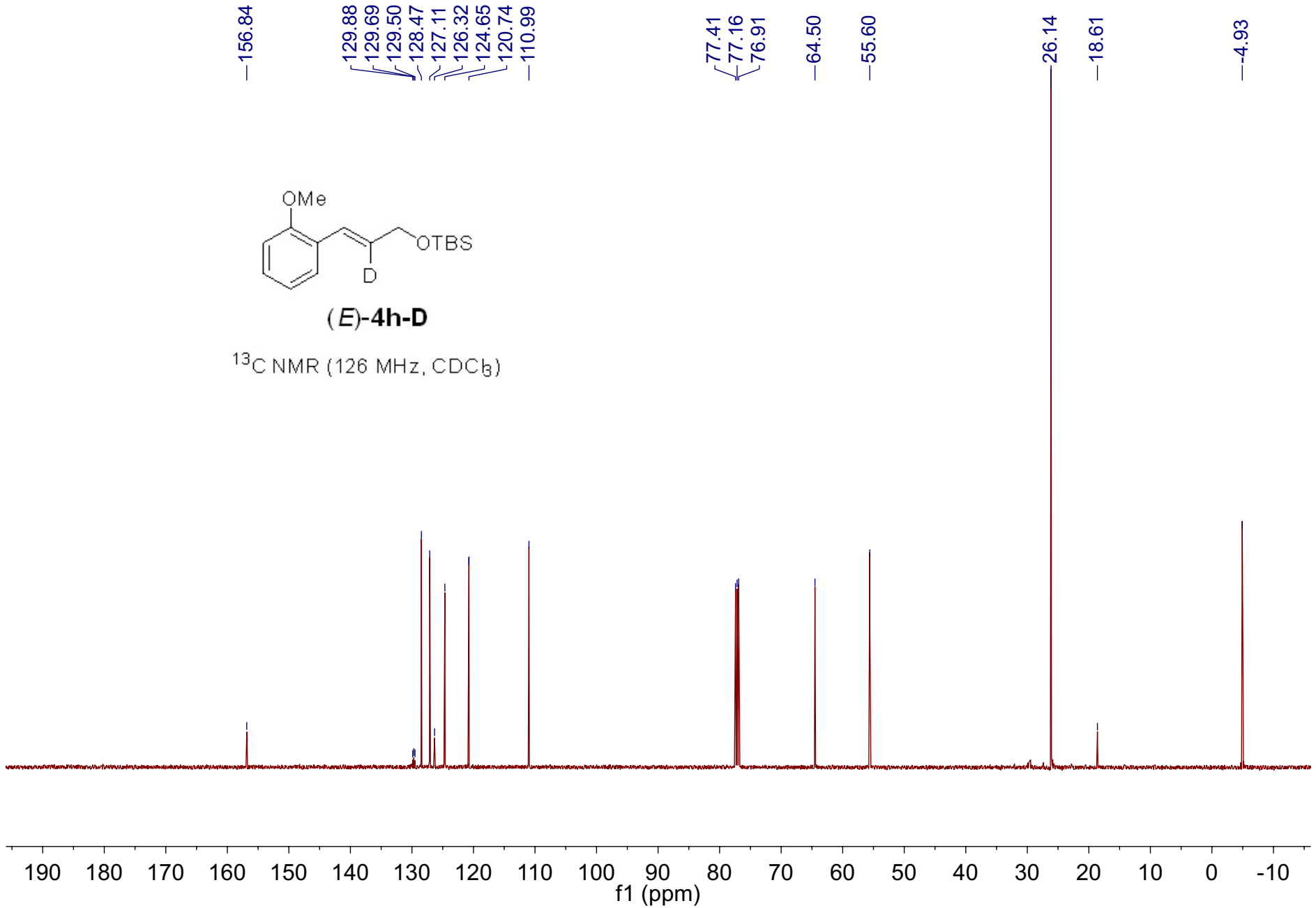
Supplementary Fig. 211. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **4r**



Supplementary Fig. 212. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **4r**



Supplementary Fig. 213. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound (*E*)-**4h-D**



Supplementary Fig. 214. ^{1}H NMR (126 MHz, $CDCl_3$) spectra for compound (*E*)-**4h-D**

Data File H:\JXL HPLC\JXL-03-67-1-OD(1)-RAC.D
Sample Name: JXL-03-67-1-OD(1)

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                      Location :   93
Injection Date  : 7/30/2020 7:51:24 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\JXL\20200730\YH 2020-07-30 16-30-45\0IPA-35-0.8-1-2-220-JXL.M
Last changed    : 7/30/2020 7:54:31 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-13 20-54-13\8IPA_40_0.8_4.M (Sequence Method)
Last changed    : 12/18/2020 8:28:46 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

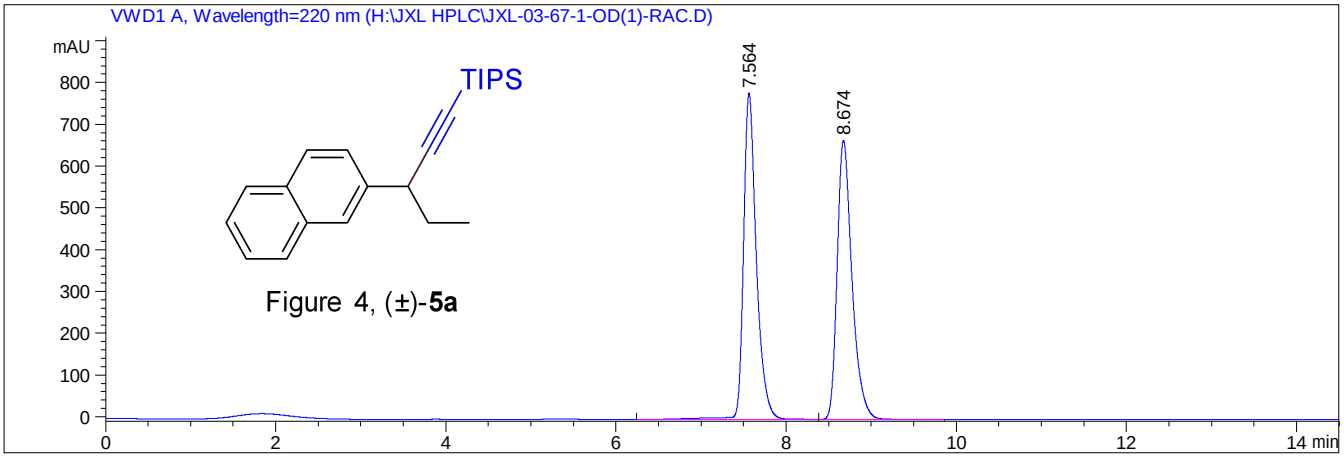


Figure 4, (±)-**5a**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.564 VB R  0.1577 8214.19043  781.32666  50.3793
   2   8.674 BB    0.1833 8090.48779  667.96808  49.6207

Totals :                  1.63047e4  1449.29474

======================================================================
                        *** End of Report ***
```


Supplementary Fig. 215. HPLC spectra for compound (±)-**5a**

Data File H:\JXL HPLC\JXL-03-87-1-OD(1)-EE.D
Sample Name: JXL-03-87-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  14
Acq. Instrument : HPLC-1260                     Location :   71
Injection Date  : 8/13/2020 12:53:42 AM             Inj :   2
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\JXL\20200812\YH 2020-08-12 19-08-25\0IPA-15-0.8-1-2-220-JXL.M
Last changed    : 8/12/2020 11:00:47 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 7:33:03 PM by SYSTEM
                  (modified after loading)
```

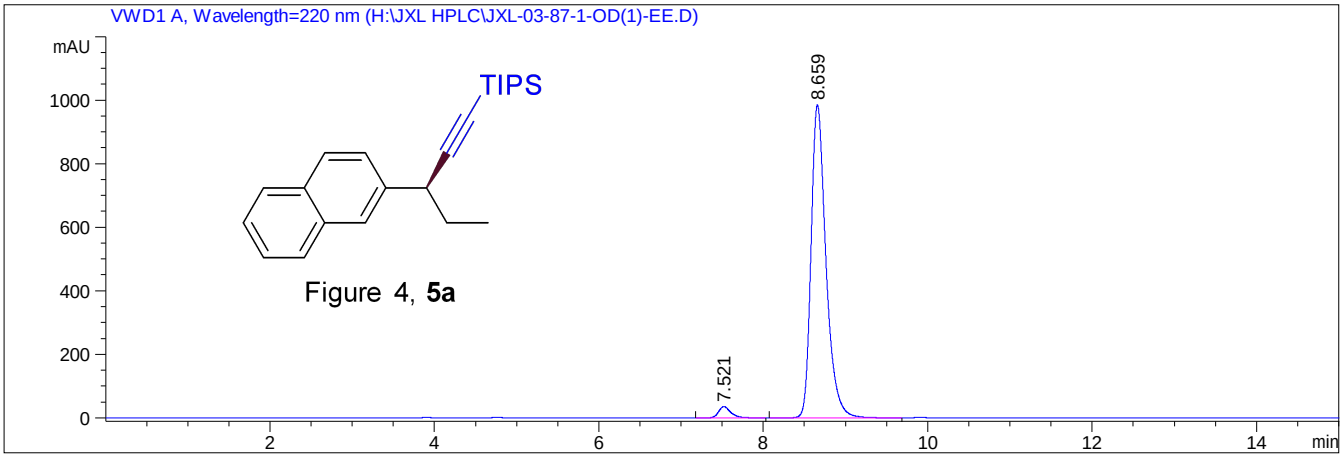


Figure 4, **5a**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.521 BB    0.1554  368.12753   35.80718   2.8803
   2   8.659 BB    0.1909 1.24129e4   985.56152  97.1197

Totals :                  1.27811e4  1021.36870


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 216. HPLC spectra for compound **5a**

Data File H:\JXL HPLC\JXL-03-52-1-OD(1)-RAC.D
Sample Name: JXL-03-52-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                     Location :   91
Injection Date  : 7/29/2020 2:43:42 PM               Inj :   2
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\JXL\20200729\YH 2020-07-29 13-10-22\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 7/29/2020 3:00:14 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 7:34:31 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

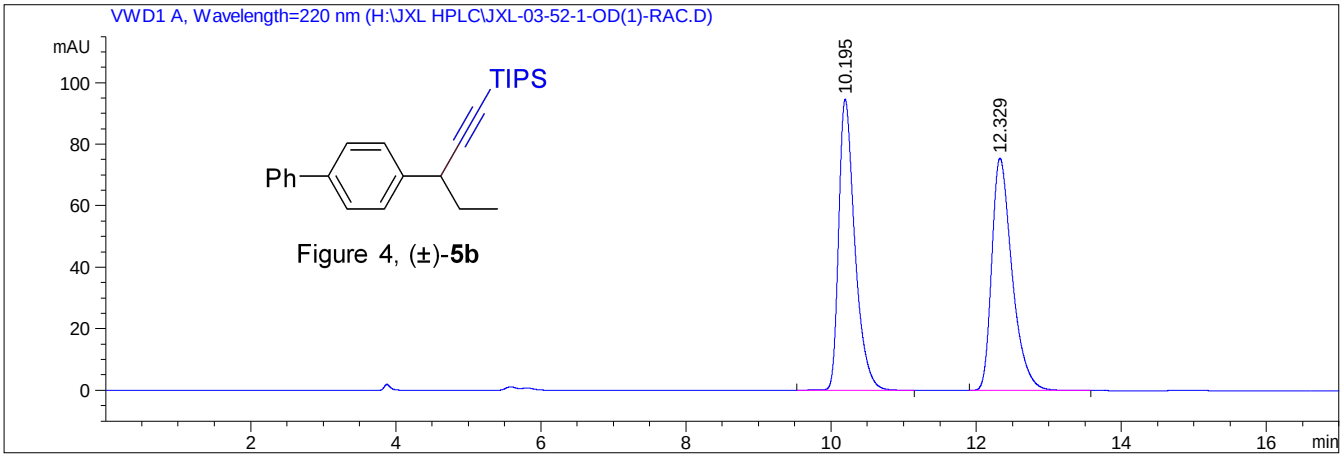


Figure 4, (±)-**5b**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.195 BB    0.2340 1469.57141   94.70167  49.9464
   2  12.329 BB    0.2973 1472.72339   75.57758  50.0536

Totals :                  2942.29480  170.27924


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 217. HPLC spectra for compound (±)-**5b**

Data File H:\JXL HPLC\JXL-03-90-1-OD(1)-EE.D
Sample Name: JXL-03-90-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                     Location :   81
Injection Date  : 8/14/2020 1:17:53 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\JXL\20200813\YH 2020-08-13 23-35-04\0IPA-20-0.8-1-6-220-JXL.M
Last changed    : 8/13/2020 11:36:14 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 7:42:23 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

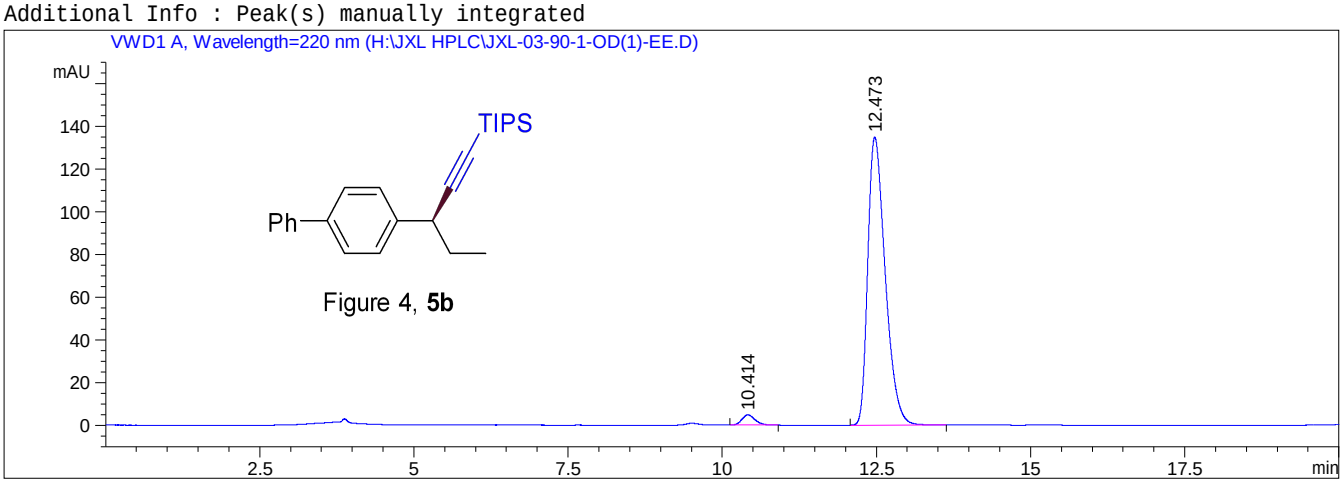


Figure 4, **5b**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.414 BB    0.2247   71.15249    4.80578   2.6157
   2  12.473 BB    0.3011 2649.05762  134.92877  97.3843

Totals :                  2720.21011  139.73455


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 218. HPLC spectra for compound **5b**

Data File H:\JXL HPLC\JXL-03-92-1-OD(2)-RAC.D
Sample Name: JXL-03-92-1-OD(2)

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :  11
Acq. Instrument : HPLC-1260                     Location :   85
Injection Date  : 8/17/2020 3:32:40 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\JXL\20200817\YH 2020-08-17 08-55-41\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 8/17/2020 3:53:54 PM by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\15IPA_30_8_4.M
Last changed    : 12/18/2020 9:34:33 PM by SYSTEM
                  (modified after loading)
```

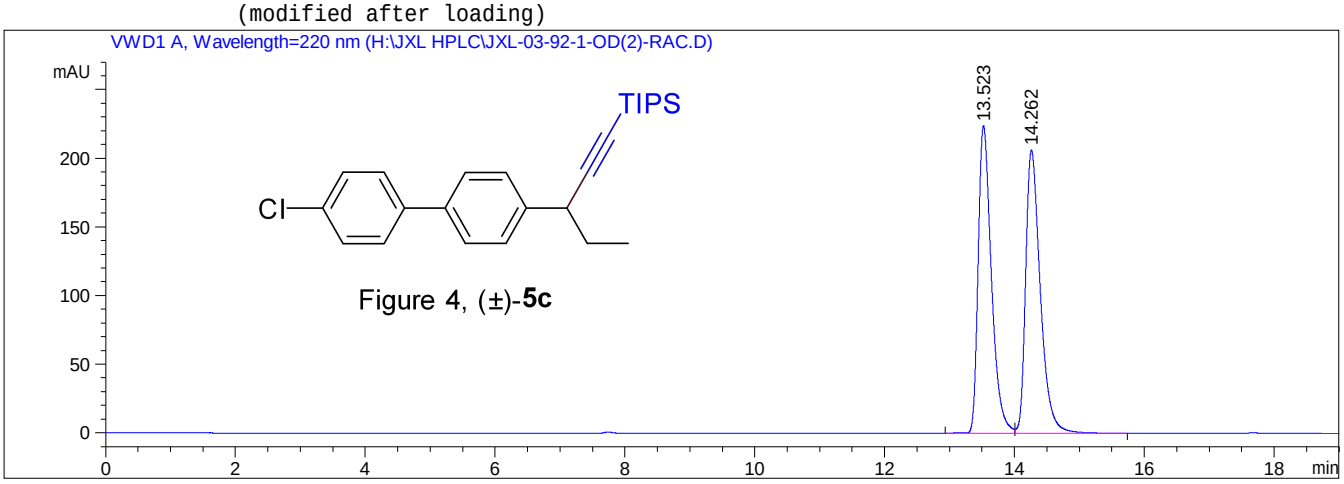


Figure 4, (±)-**5c**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.523 VV R  0.2158 3176.07349  224.10931  49.4844
   2  14.262 VB    0.2387 3242.26465  206.43098  50.5156

Totals :                  6418.33813  430.54030


======================================================================
                        *** End of Report ***
```


Supplementary Fig. 219. HPLC spectra for compound (±)-**5c**

Data File H:\JXL HPLC\JXL-03-118-1-OD(2)-EE.D
Sample Name: JXL-03-118-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  11
Acq. Instrument : HPLC-1260                     Location :   83
Injection Date  : 8/26/2020 1:43:16 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\JXL\20200826\YH 2020-08-26 09-02-52\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 8/26/2020 1:59:25 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 7:29:52 PM by SYSTEM
                  (modified after loading)
```

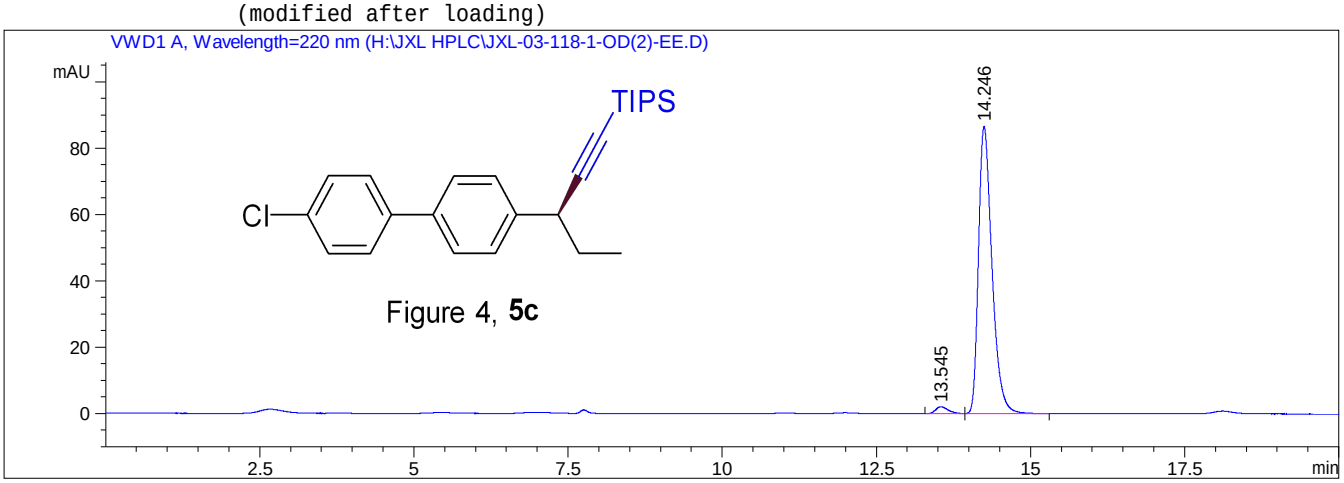


Figure 4, **5c**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.545 BB    0.1861   29.73621    2.10822   2.2080
   2  14.246 BB    0.2312 1317.04065   86.69881  97.7920

Totals :                  1346.77686   88.80703


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 220. HPLC spectra for compound **5c**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--042.D
Sample Name: JXL-02-157-8-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  42
Acq. Instrument : HPLC-1260                      Location :   77
Injection Date  : 12/13/2020 8:10:48 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 12/13/2020 8:31:37 PM by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\15IPA_30_8_4.M
Last changed    : 12/18/2020 9:36:51 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

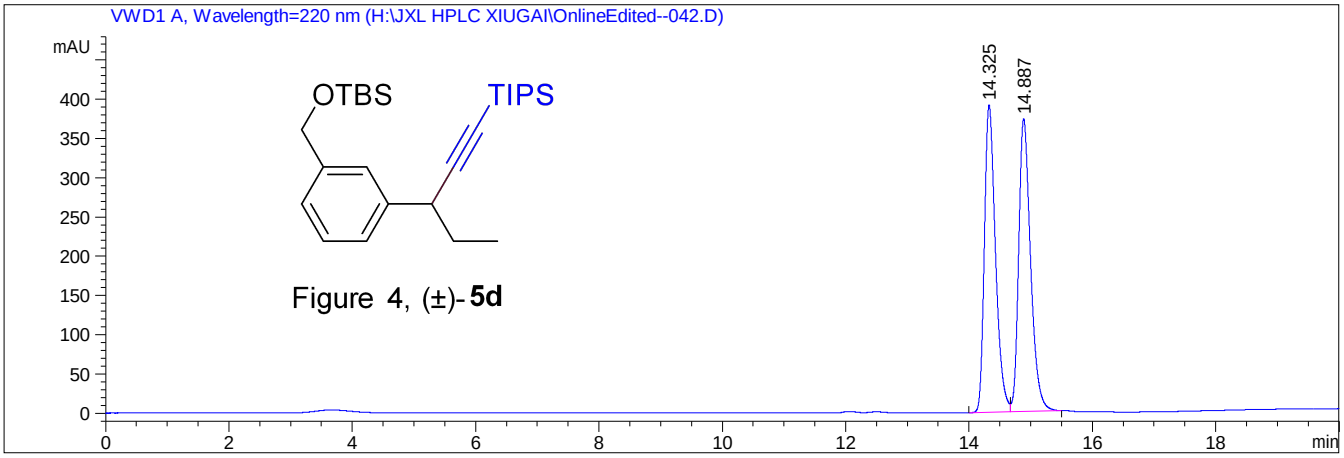


Figure 4, (±)-**5d**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.325 BV    0.1908 4898.95654  392.01218  49.5196
   2  14.887 VB    0.2036 4994.00635  373.24091  50.4804

Totals :                  9892.96289  765.25308


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 221. HPLC spectra for compound (±)-**5d**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--043.D
Sample Name: JXL-03-102-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  43
Acq. Instrument : HPLC-1260                      Location :   78
Injection Date  : 12/13/2020 8:33:02 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.700 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 12/13/2020 8:31:37 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-16 12-53-00\8IPA_38_0.8_3.M (Sequence Method)
Last changed    : 12/16/2020 9:48:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

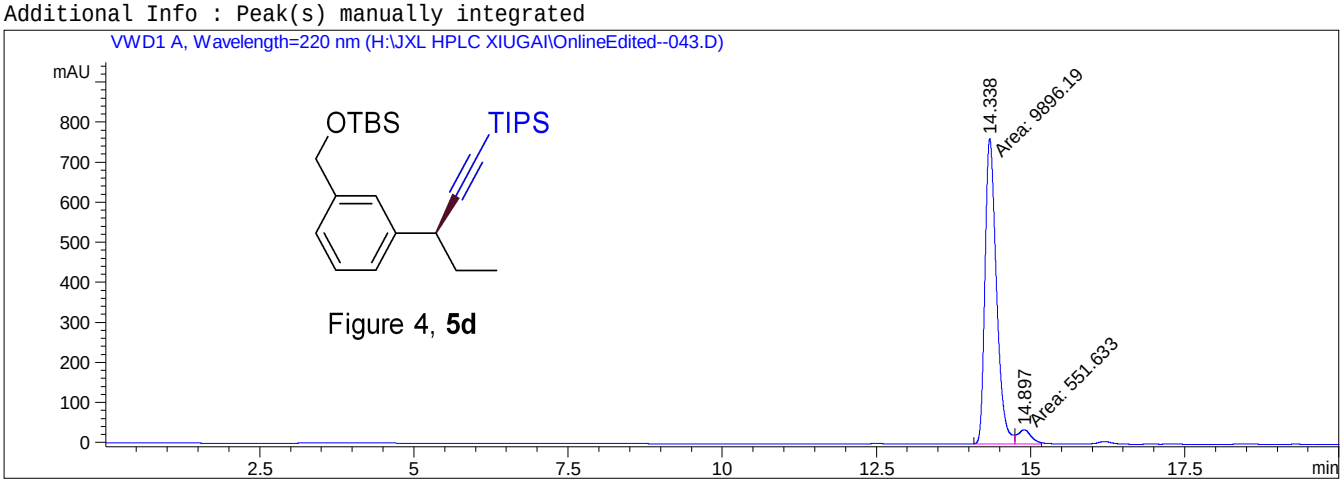


Figure 4, **5d**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.338 FM    0.2162 9896.19434  763.04950  94.7201
   2  14.897 MF    0.2551  551.63306   36.04580   5.2799

Totals :                  1.04478e4   799.09530


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 222. HPLC spectra for compound **5d**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--223.D
Sample Name: JXL-02-132-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line : 223
Acq. Instrument : HPLC-1260                      Location :  81
Injection Date  : 12/17/2020 10:38:06 AM             Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 12/14/2020 9:39:45 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-27 14-40-53\1EtOH-40-0.8-3-220-XYH.M (Sequence
                  Method)
Last changed    : 12/17/2020 11:25:28 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

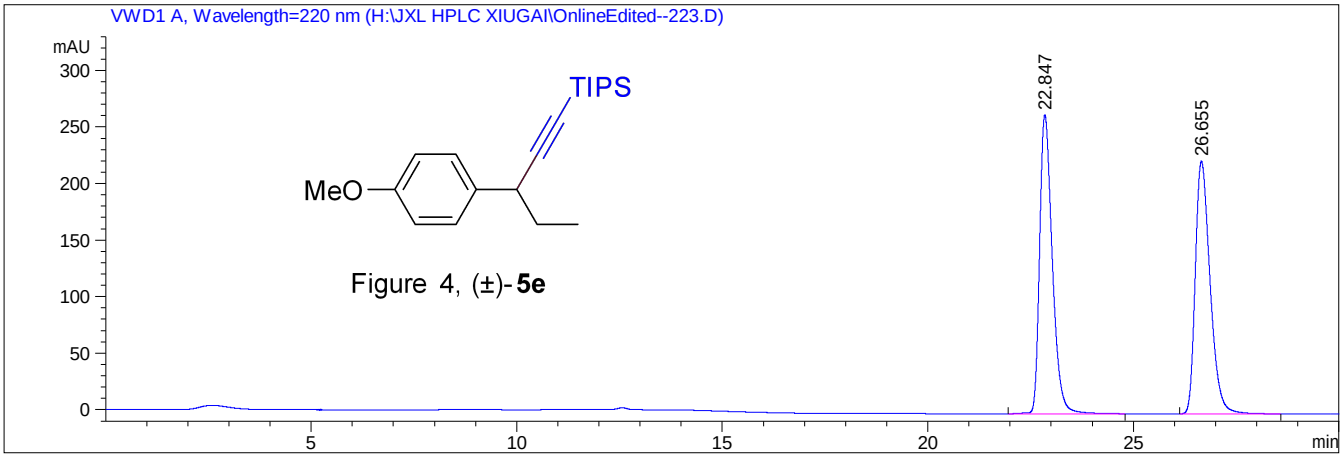


Figure 4, (±)-**5e**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.847 BB    0.3280 5665.40869  264.39789  50.3487
   2  26.655 BB    0.3807 5586.92920  223.48183  49.6513

Totals :                  1.12523e4   487.87971

=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 223. HPLC spectra for compound (±)-**5e**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--224.D
Sample Name: JXL-03-127-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 224
Acq. Instrument : HPLC-1260                      Location :  79
Injection Date  : 12/17/2020 11:09:29 AM            Inj :  1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 12/14/2020 9:39:45 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-27 14-40-53\1EtOH-40-0.8-3-220-XYH.M (Sequence
                  Method)
Last changed    : 12/17/2020 11:26:08 PM by SYSTEM
                  (modified after loading)
```

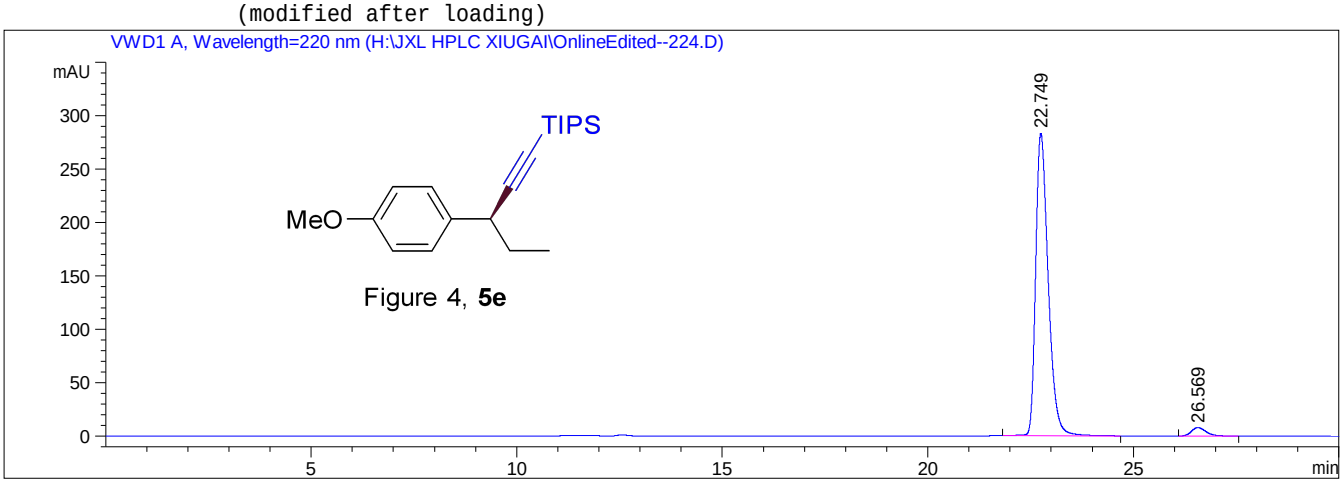


Figure 4, **5e**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.749 BB    0.3245 5984.18018  283.18457  96.8689
   2  26.569 BB    0.3349  193.42569    7.92140   3.1311

Totals :                  6177.60587  291.10598


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 224. HPLC spectra for compound **5e**

Data File H:\JXL HPLC\JXL-03-92-2-OD(2)-RAC.D
Sample Name: JXL-03-92-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                     Location :   81
Injection Date  : 8/17/2020 10:26:59 AM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\JXL\20200817\YH 2020-08-17 08-55-41\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 8/17/2020 10:49:51 AM by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\15IPA_30_8_4.M
Last changed    : 12/18/2020 9:38:07 PM by SYSTEM
                  (modified after loading)
```

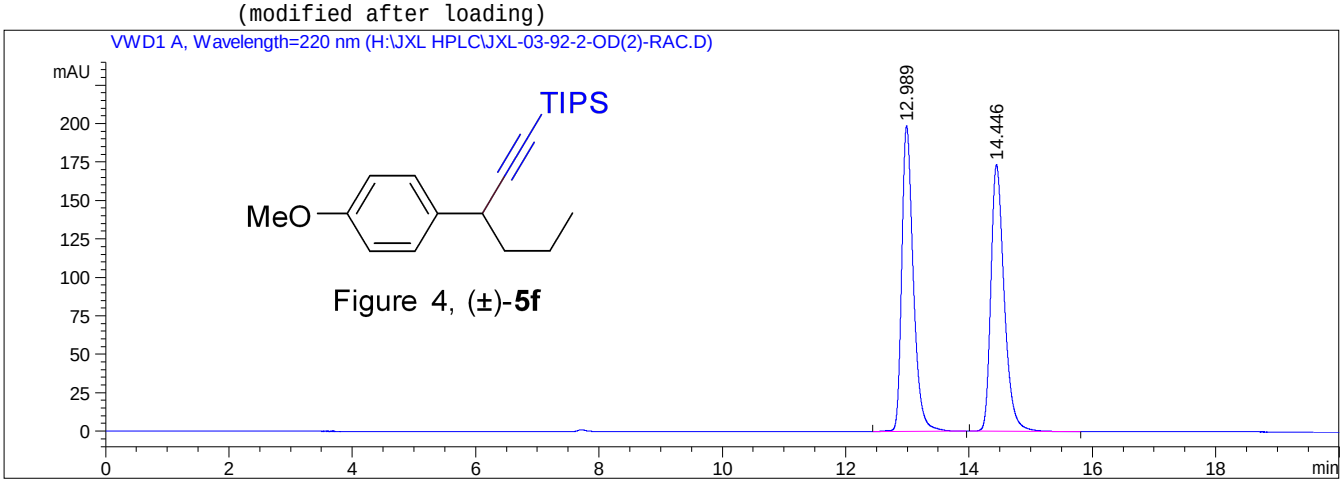


Figure 4, (±)-**5f**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.989 BB    0.1981 2590.69507  198.68257  49.8213
   2  14.446 BB    0.2291 2609.28149  173.36870  50.1787

Totals :                  5199.97656  372.05127


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 225. HPLC spectra for compound (±)-**5f**

Data File H:\JXL HPLC\JXL-03-105-1-OD(2)-EE.D
Sample Name: JXL-03-105-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  28
Acq. Instrument : HPLC-1260                     Location :   95
Injection Date  : 8/22/2020 12:54:36 AM              Inj :   2
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\YH\20200820\YH 2020-08-21 08-21-12\0IPA-20-0.8-1-6-220-JXL.M
Last changed    : 8/21/2020 11:21:53 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:19:17 PM by SYSTEM
                  (modified after loading)
```

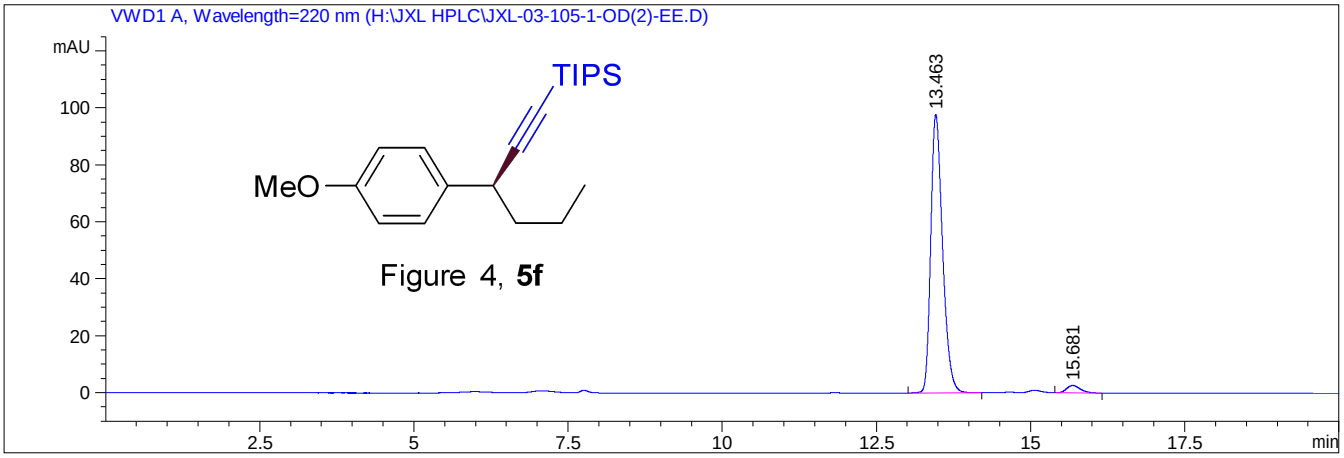


Figure 4, **5f**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.463 BB    0.2036 1303.97400   97.74081  96.9901
   2  15.681 BB    0.2027   40.46679    2.62005   3.0099

Totals :                  1344.44079  100.36086


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 226. HPLC spectra for compound **5f**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--022.D
Sample Name: JXL-03-5-4-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  22
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 12/13/2020 5:23:48 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.500 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.8-1-6-220-JXL.M
Last changed    : 12/13/2020 4:39:41 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:20:01 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

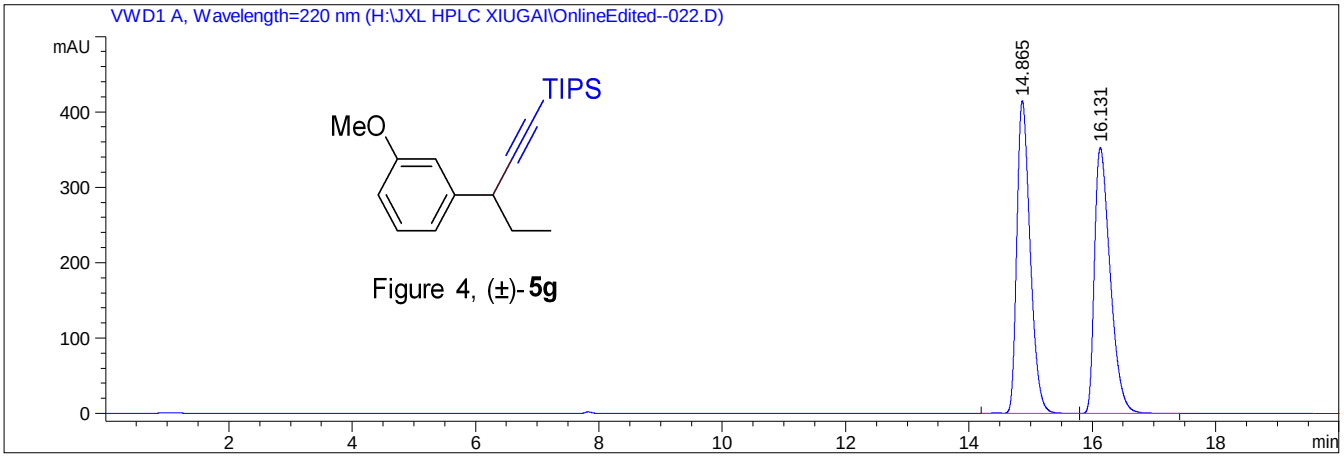


Figure 4, (±)-**5g**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.865 VB R  0.2318 6233.67725  414.96182  49.9749
   2  16.131 BB    0.2736 6239.94482  352.28775  50.0251

Totals :                  1.24736e4   767.24957


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 227. HPLC spectra for compound (±)-**5g**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--021.D
Sample Name: JXL-03-93-3-OD(2)

```
==================================================================
Acq. Operator   : 系统                          Seq. Line :  21
Acq. Instrument : HPLC-1260                      Location :  82
Injection Date  : 12/13/2020 5:02:26 AM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.8-1-6-220-JXL.M
Last changed    : 12/13/2020 4:39:41 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:27:48 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

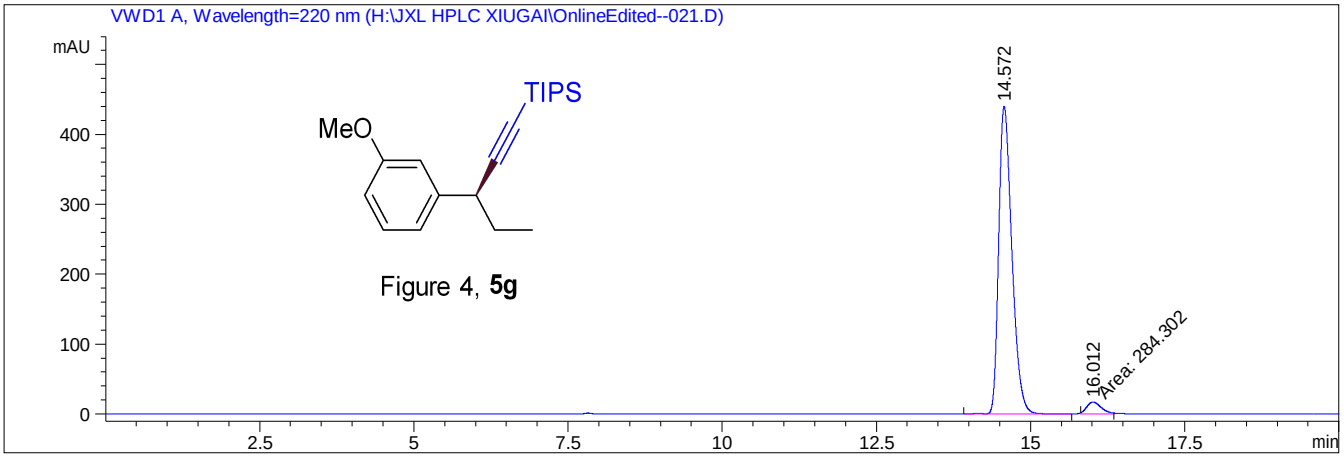


Figure 4, **5g**

```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.572 VB R  0.2298 6559.40625  440.30060  95.8458
   2  16.012 FM    0.2754  284.30161   17.20478   4.1542

Totals :                  6843.70786  457.50538


==================================================================
                        *** End of Report ***
```


Supplementary Fig. 228. HPLC spectra for compound **5g**

Data File H:\JXL HPLC\JXL-03-157-1-OD(2)-RAC.D
Sample Name: JXL-03-157-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 165
Acq. Instrument : HPLC-1260                     Location :  96
Injection Date  : 9/18/2020 3:32:54 AM               Inj :  2
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-15 11-31-01\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 9/17/2020 11:59:29 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:25:11 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

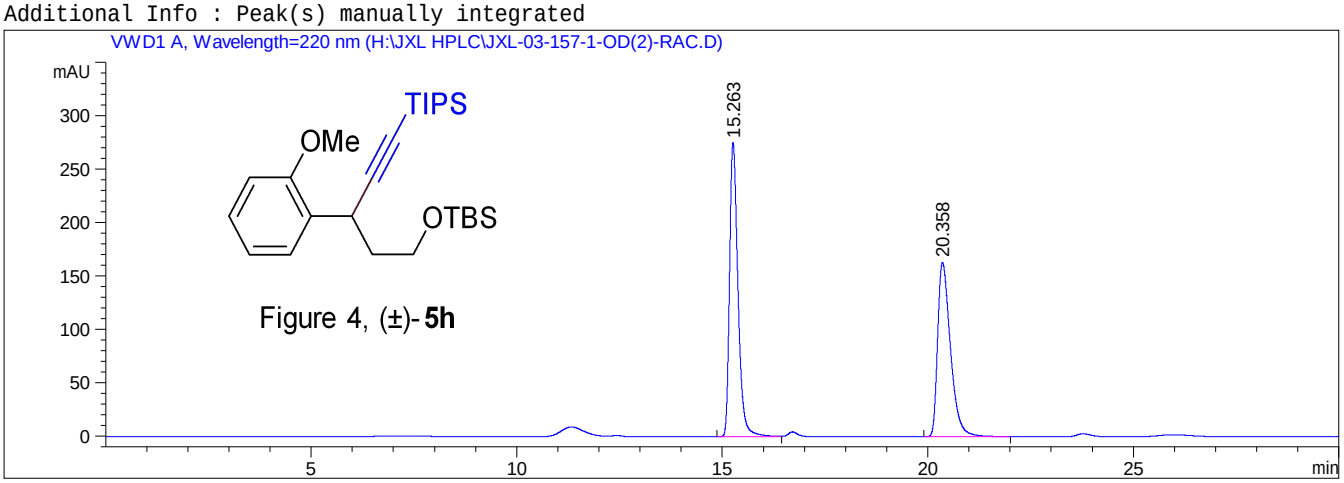


Figure 4, (±)-**5h**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.263 BB    0.2178 3914.83374  275.44077  52.5555
   2  20.358 BB    0.3282 3534.11255  163.15683  47.4445

Totals :                  7448.94629  438.59760


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 229. HPLC spectra for compound (±)-**5h**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--039.D
Sample Name: JXL-04-22-5-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  39
Acq. Instrument : HPLC-1260                      Location :   73
Injection Date  : 10/30/2020 5:15:41 AM              Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 10/29/2020 6:19:06 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-16 12-53-00\15IPA_30_0.8_4.M (Sequence Method)
Last changed    : 12/16/2020 3:05:37 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

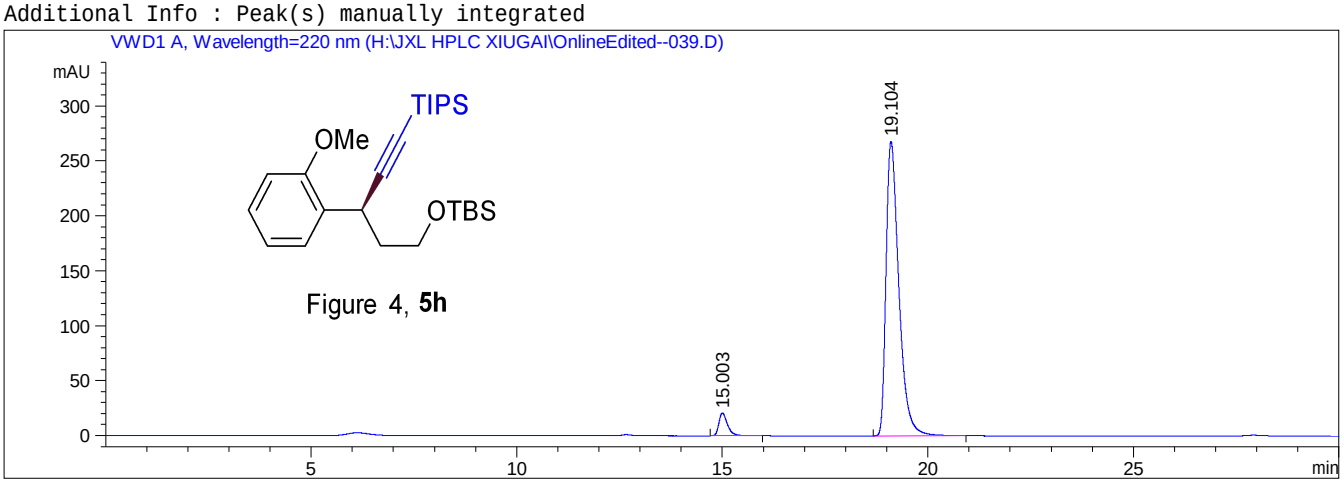


Figure 4, **5h**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.003 BB    0.2210  303.79639   20.79279   4.9837
   2  19.104 BB    0.3307 5791.94336  267.88892  95.0163

Totals :                  6095.73975  288.68170


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 230. HPLC spectra for compound **5h**

Data File H:\JXL HPLC XIUGAI\091-0402.D
Sample Name: JXL-03-44-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                     Location :   91
Injection Date  : 12/12/2020 9:23:04 PM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\1IPA-20-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 9:21:20 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:38:05 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

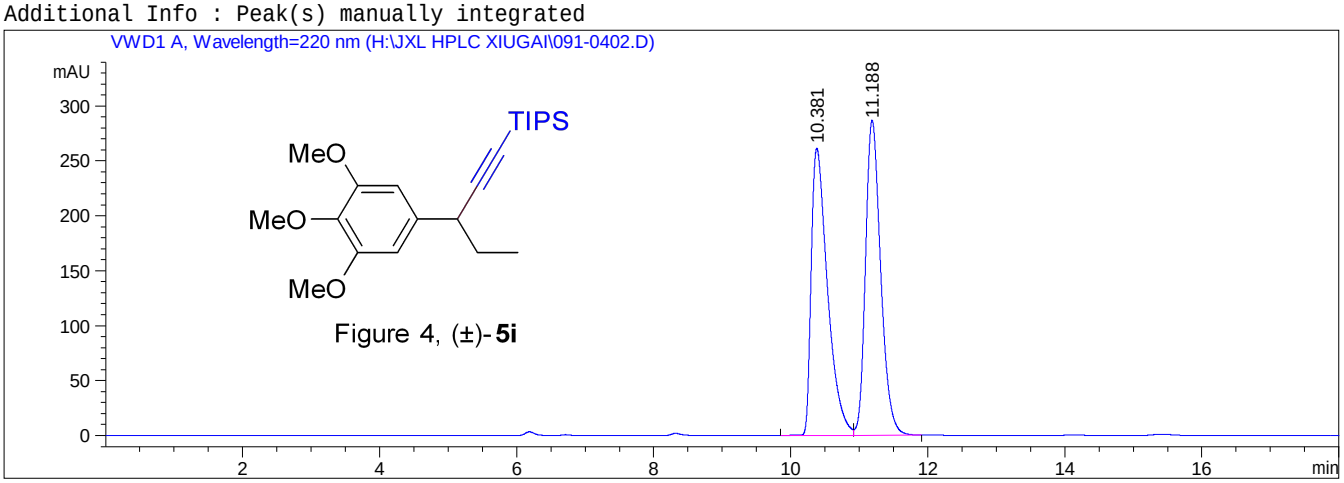


Figure 4, (±)-**5i**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.381 VV R  0.2500 4336.35254  261.50546  49.5476
   2  11.188 VB    0.2371 4415.54150  286.78824  50.4524

Totals :                  8751.89404  548.29370


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 231. HPLC spectra for compound (±)-**5i**

Data File H:\JXL HPLC XIUGAI\092-0501.D
Sample Name: JXL-03-96-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                     Location :   92
Injection Date  : 12/12/2020 9:42:29 PM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\1IPA-20-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 10:04:54 PM by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\15IPA_30_8_4.M
Last changed    : 12/18/2020 9:40:44 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

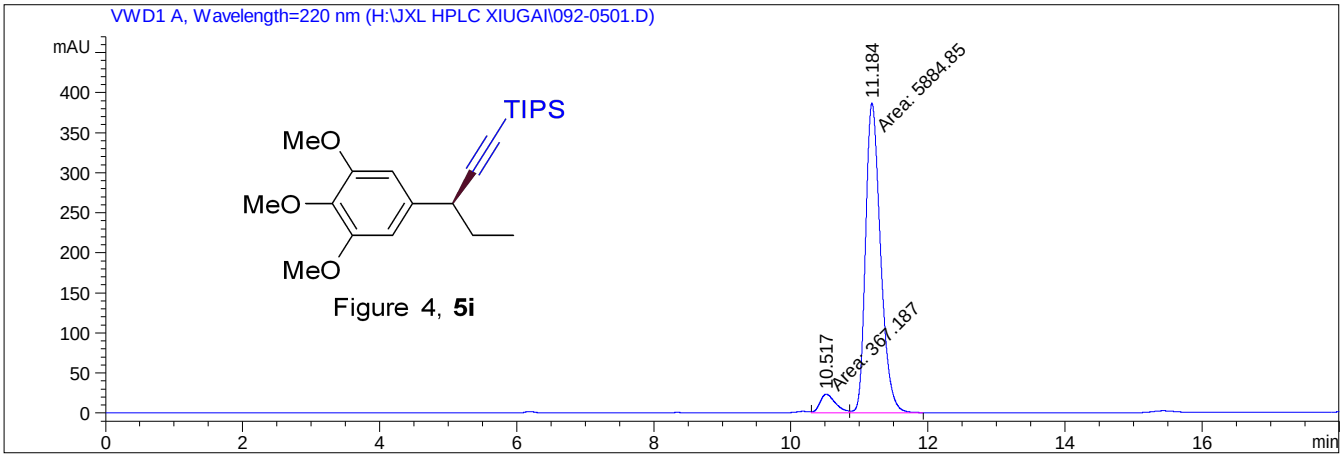


Figure 4, **5i**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.517 MF    0.2625  367.18674   23.31229   5.8731
   2  11.184 FM    0.2538 5884.84668  386.49524  94.1269

Totals :                  6252.03342  409.80753


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 232. HPLC spectra for compound **5i**

Data File H:\JXL HPLC\JXL-02-164-9-OD(2)-RAC.D
Sample Name: JXL-02-164-9-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  34
Acq. Instrument : HPLC-1260                     Location :   81
Injection Date  : 8/16/2020 6:01:09 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20200814\YH 2020-08-15 15-49-29\0IPA-40-0.3-1-2-220-JXL.M
Last changed    : 8/15/2020 10:39:12 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:43:43 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

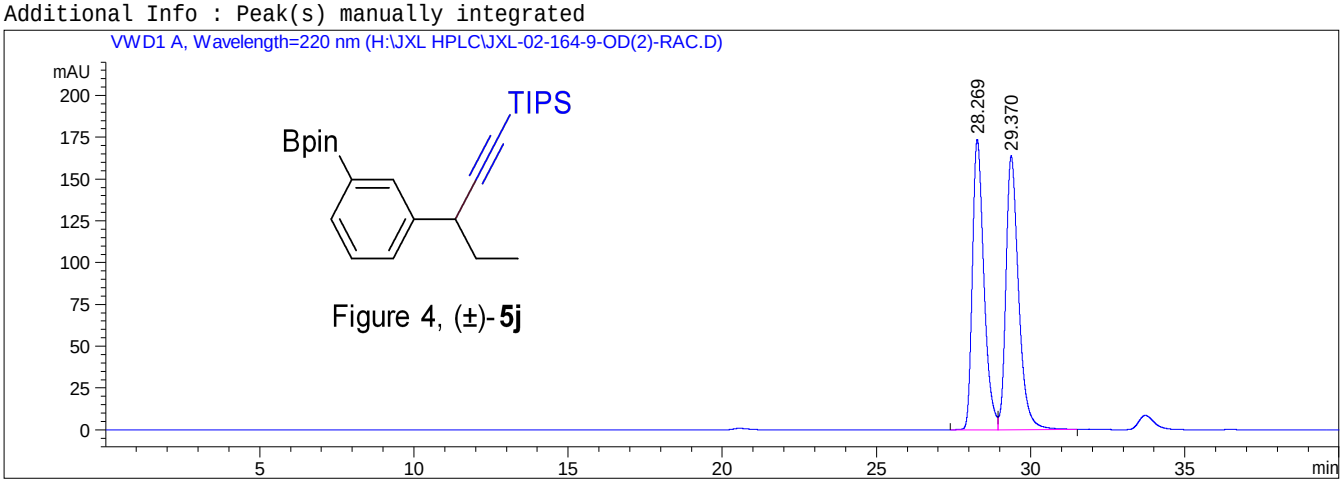


Figure 4, (±)-**5j**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.269 BV    0.3981 4526.81055  173.69307  49.1311
   2  29.370 VB    0.4353 4686.92578  163.81421  50.8689

Totals :                  9213.73633  337.50728


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 233. HPLC spectra for compound (±)-**5j**

Data File H:\JXL HPLC\JXL-03-95-1-OD(2)-EE.D
Sample Name: JXL-03-95-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  35
Acq. Instrument : HPLC-1260                     Location :   85
Injection Date  : 8/16/2020 6:42:35 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20200814\YH 2020-08-15 15-49-29\0IPA-40-0.3-1-2-220-JXL.M
Last changed    : 8/15/2020 10:39:12 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:44:39 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

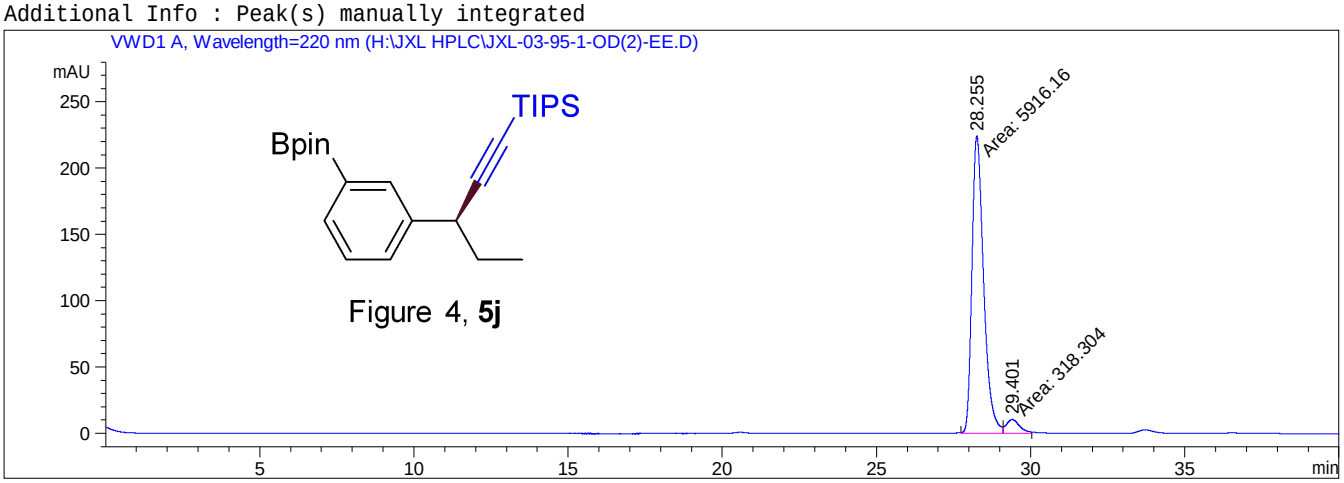


Figure 4, **5j**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.255 MF    0.4394 5916.15869  224.40263  94.8945
   2  29.401 MF    0.5088  318.30356   10.42563   5.1055

Totals :                  6234.46225  234.82827


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 234. HPLC spectra for compound **5j**

Data File H:\JXL HPLC\JXL-03-167-3-IE(1)-RAC.D
Sample Name: JXL-03-167-3-IE(1)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  59
Acq. Instrument : HPLC-1260                      Location :   84
Injection Date  : 9/22/2020 6:09:20 PM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-21 18-04-54\0IPA-35-0.3-1-6-220-JXL.M
Last changed    : 9/22/2020 5:03:45 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:47:09 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

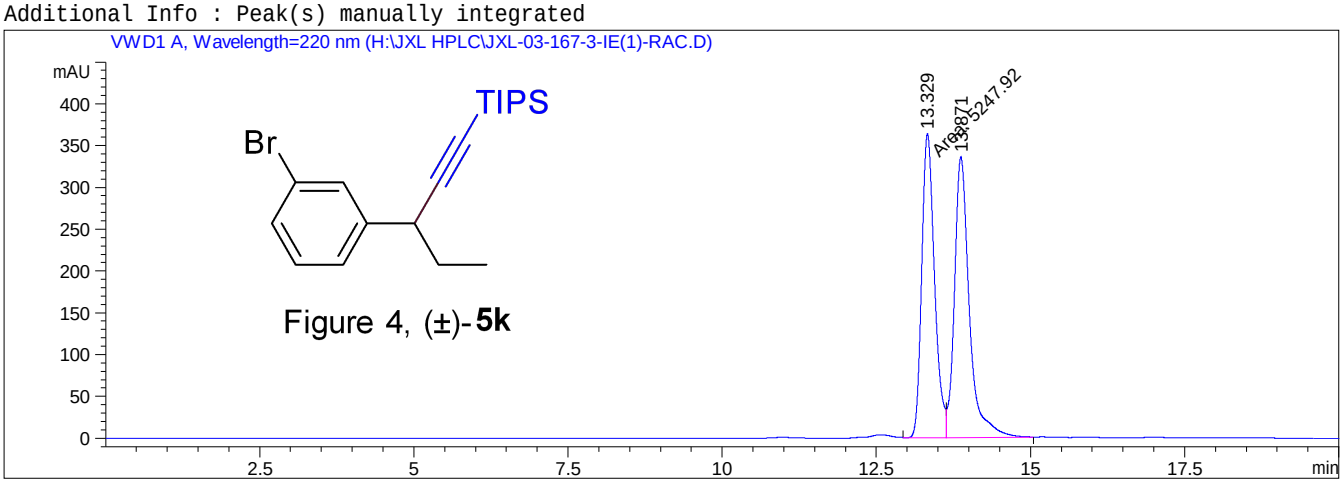


Figure 4, (±)-**5k**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.329 FM    0.2407 5247.91748  363.43359  48.2757
   2  13.871 VB    0.2509 5622.79443  335.64539  51.7243

Totals :                  1.08707e4   699.07898


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 235. HPLC spectra for compound (±)-**5k**

Data File H:\JXL HPLC\JXL-03-167-1-IE(1)-EE.D
Sample Name: JXL-03-167-1-IE(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  56
Acq. Instrument : HPLC-1260                      Location :   85
Injection Date  : 9/22/2020 5:05:09 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-21 18-04-54\0IPA-35-0.3-1-6-220-JXL.M
Last changed    : 9/22/2020 5:03:45 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:48:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

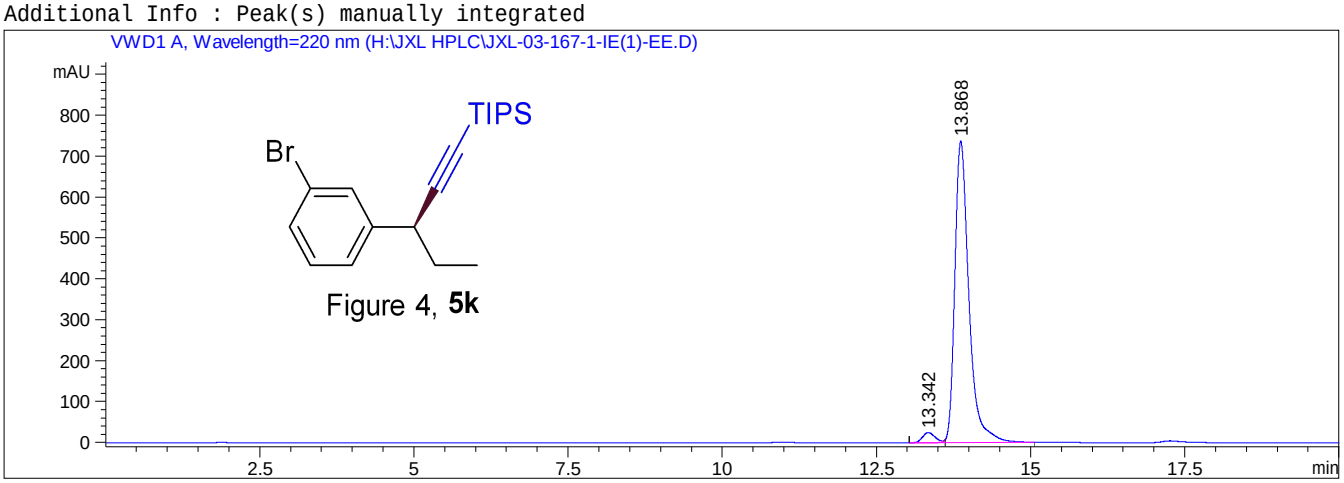


Figure 4, **5k**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.342 BV E  0.2140  345.04163   24.92293   2.8670
   2  13.868 VB R  0.2396 1.16897e4   736.77887  97.1330

Totals :                  1.20347e4   761.70180


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 236. HPLC spectra for compound **5k**

Data File H:\JXL HPLC XIUGAI\084-0301--004.D
Sample Name: JXL-03-92-5-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   4
Acq. Instrument : HPLC-1260                      Location :   84
Injection Date  : 8/17/2020 8:42:43 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.500 µl
Acq. Method     : D:\JXL\20200817\YH 2020-08-17 19-27-56\0IPA-40-0.5-1-2-220-JXL.M
Last changed    : 8/17/2020 9:37:40 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-28 19-00-53\20IPA_20_10_3.M (Sequence Method)
Last changed    : 12/29/2020 3:26:14 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

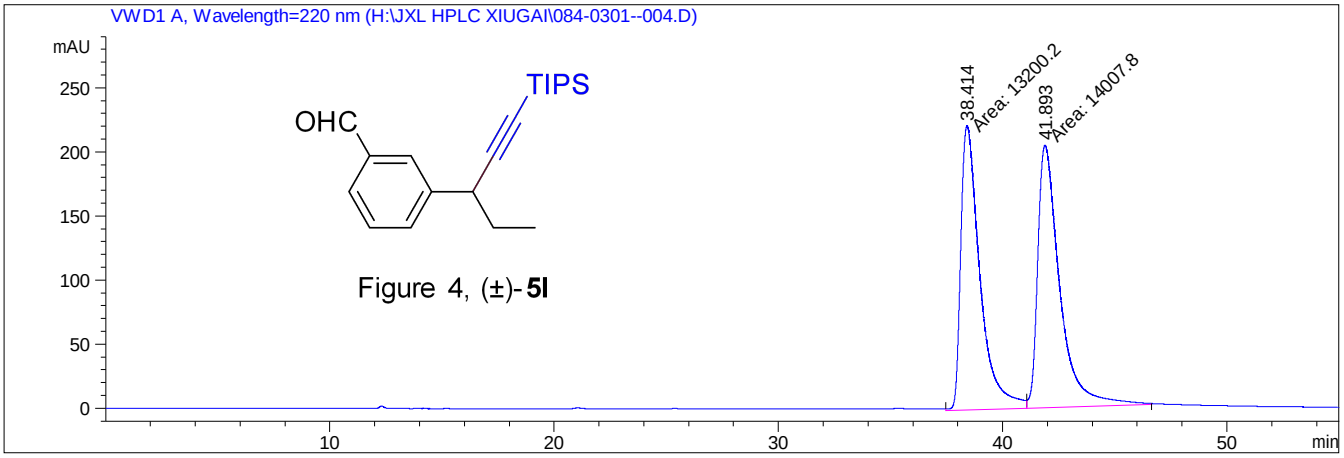


Figure 4, (±)-**5l**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  38.414 MF    0.9917 1.32002e4   221.85463  48.5158
   2  41.893 FM    1.1406 1.40078e4   204.67603  51.4842

Totals :                  2.72080e4   426.53065


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 237. HPLC spectra for compound (±)-**5l**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--228.D
Sample Name: JXL-04-13-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 228
Acq. Instrument : HPLC-1260                      Location :  65
Injection Date  : 12/17/2020 12:59:39 PM            Inj :  1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 4.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-75-0.5-1-6-220-JXL.M
Last changed    : 12/16/2020 10:14:40 PM by 系统
Analysis Method : C:\CHEM32\1\METHODS\10IPA_35_0.8_254_1.M
Last changed    : 12/29/2020 3:32:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

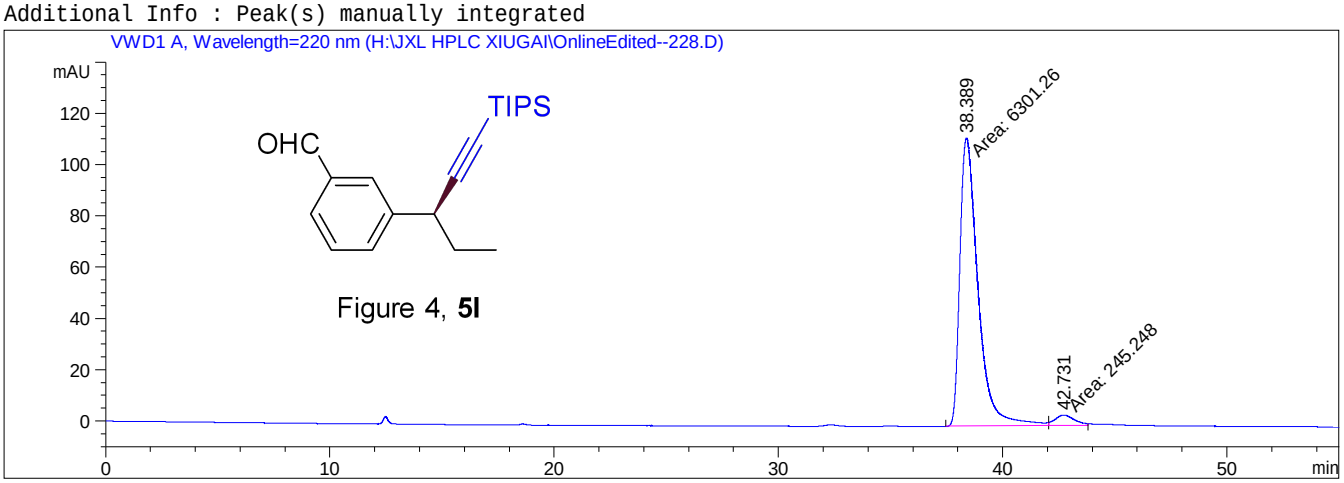


Figure 4, **5l**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  38.389 MF    0.9346 6301.26416  112.37509  96.2538
   2  42.731 MF    1.0123  245.24841    4.03794   3.7462

Totals :                  6546.51257  116.41303


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 238. HPLC spectra for compound **5l**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--008.D
Sample Name: JXL-03-156-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   8
Acq. Instrument : HPLC-1260                      Location :   93
Injection Date  : 9/5/2020 12:26:45 PM               Inj :   2
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\JXL\20200905\YH 2020-09-05 08-53-26\0IPA-50-0.5-1-6-220-JXL.M
Last changed    : 9/5/2020 11:44:07 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-16 12-53-00\15IPA_30_0.8_4.M (Sequence Method)
Last changed    : 12/16/2020 3:20:04 PM by SYSTEM
                  (modified after loading)
```

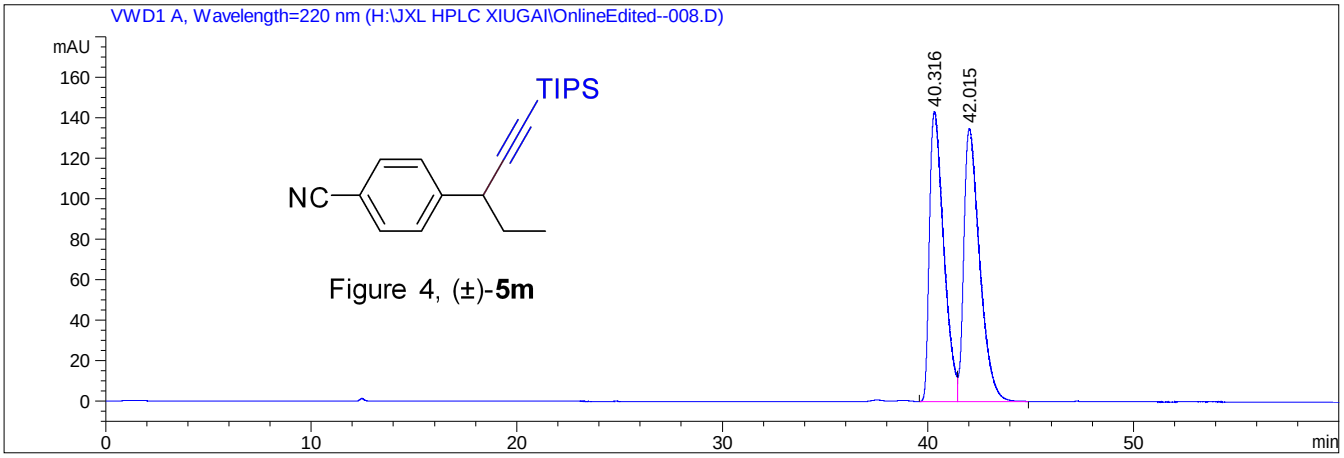


Figure 4, (±)-**5m**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  40.316 BV    0.7029 6916.47607  143.22227  48.8690
   2  42.015 VB    0.7842 7236.61133  134.82007  51.1310

Totals :                  1.41531e4   278.04234


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 239. HPLC spectra for compound (±)-**5m**

Data File H:\JXL HPLC\JXL-03-140-3-OD(2)-EE.D
Sample Name: JXL-03-140-3-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  77
Acq. Instrument : HPLC-1260                     Location :   97
Injection Date  : 9/7/2020 3:28:25 PM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20200906\YH 2020-09-06 12-21-16\0IPA-50-0.5-1-6-220-JXL.M
Last changed    : 9/7/2020 4:35:33 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-16 12-53-00\15IPA_30_0.8_4.M (Sequence Method)
Last changed    : 12/16/2020 3:14:40 PM by SYSTEM
                  (modified after loading)
```

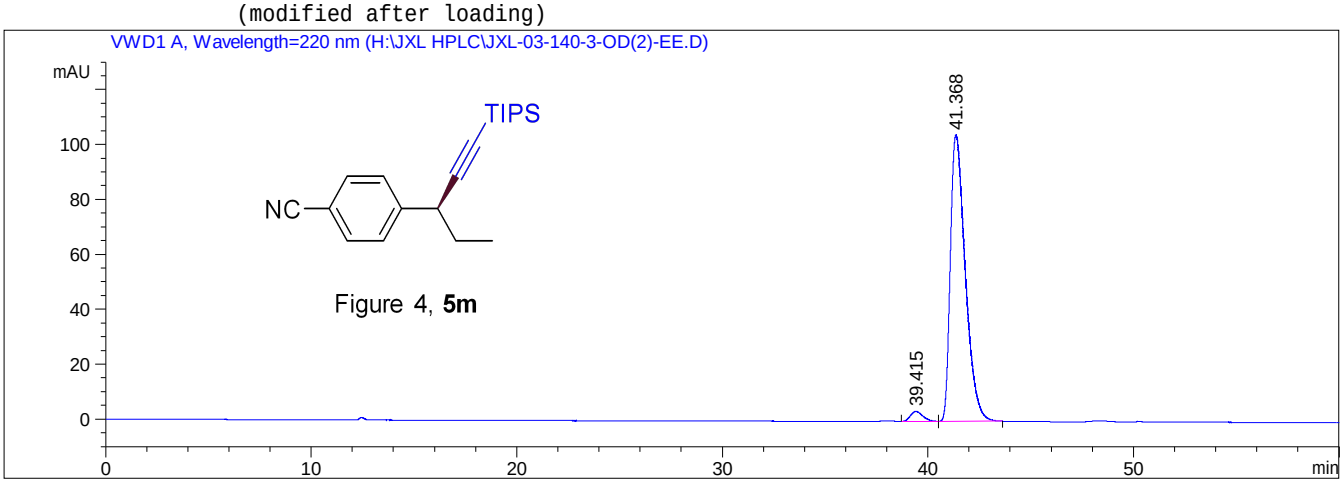


Figure 4, **5m**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  39.415 BB    0.4882  151.74007    3.64863   2.8049
   2  41.368 BB    0.7510 5258.08691  104.41154  97.1951

Totals :                  5409.82698  108.06016


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 240. HPLC spectra for compound **5m**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--020.D
Sample Name: JXL-03-44-2-AD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  20
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 12/12/2020 4:57:42 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 09-12-36\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 12/12/2020 5:33:13 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:50:28 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

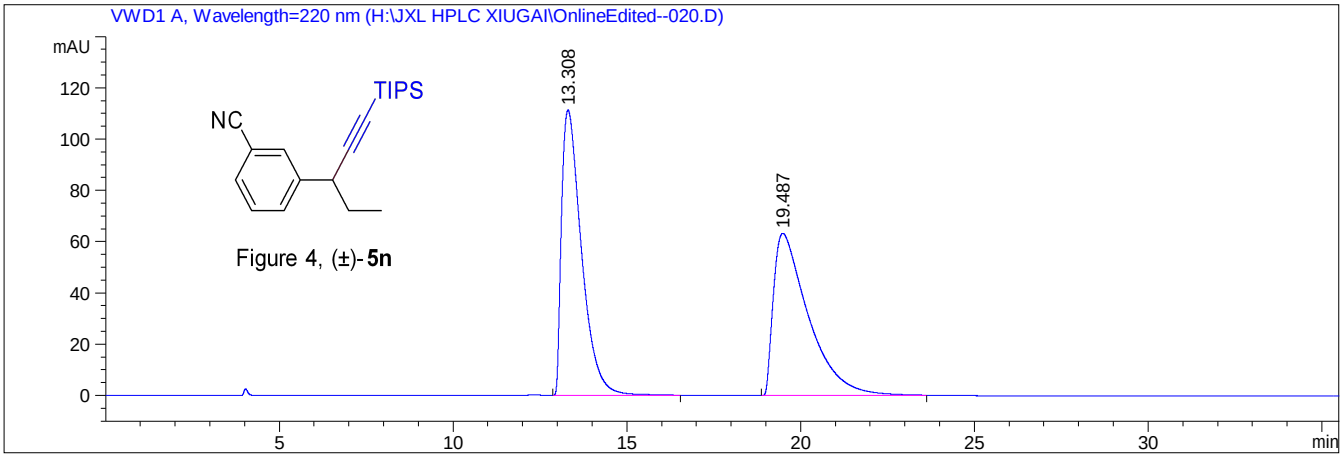


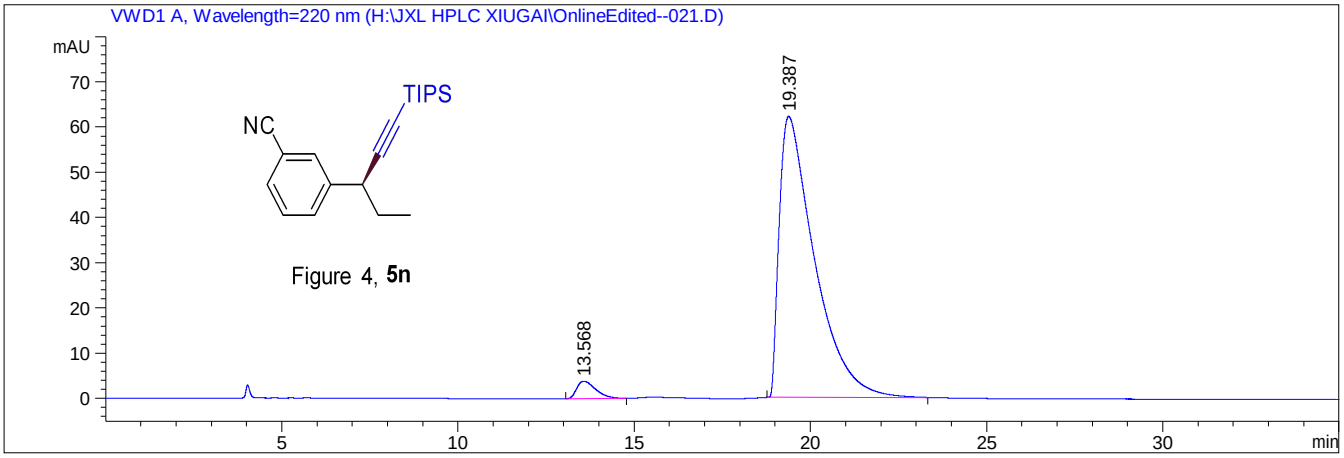
Figure 4, (±)-**5n**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.308 BB    0.6101 4459.22852  111.38471  50.2351
   2  19.487 BB    0.9239 4417.49512   63.20845  49.7649

Totals :                  8876.72363  174.59316

==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 241. HPLC spectra for compound (±)-**5n**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--021.D
Sample Name: JXL-03-119-AD(1)

```
==================================================================
Acq. Operator   : 系统                          Seq. Line :  21
Acq. Instrument : HPLC-1260                      Location :  82
Injection Date  : 12/12/2020 5:34:37 PM              Inj :  1
                                                Inj Volume : 3.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 09-12-36\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 12/12/2020 5:33:13 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:53:09 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.568 BB    0.4392  144.75229    3.87164   3.2444
   2  19.387 BB    0.9460 4316.88574   62.13744  96.7556

Totals :                  4461.63803   66.00907


==================================================================
                        *** End of Report ***
```


Supplementary Fig. 242. HPLC spectra for compound **5n**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--110.D
Sample Name: JXL-02-149-5-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line : 110
Acq. Instrument : HPLC-1260                      Location :  61
Injection Date  : 12/15/2020 1:31:57 AM               Inj :  2
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 5.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-40-0.8-1-6-220-JXL.M
Last changed    : 12/14/2020 9:36:57 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 9:00:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

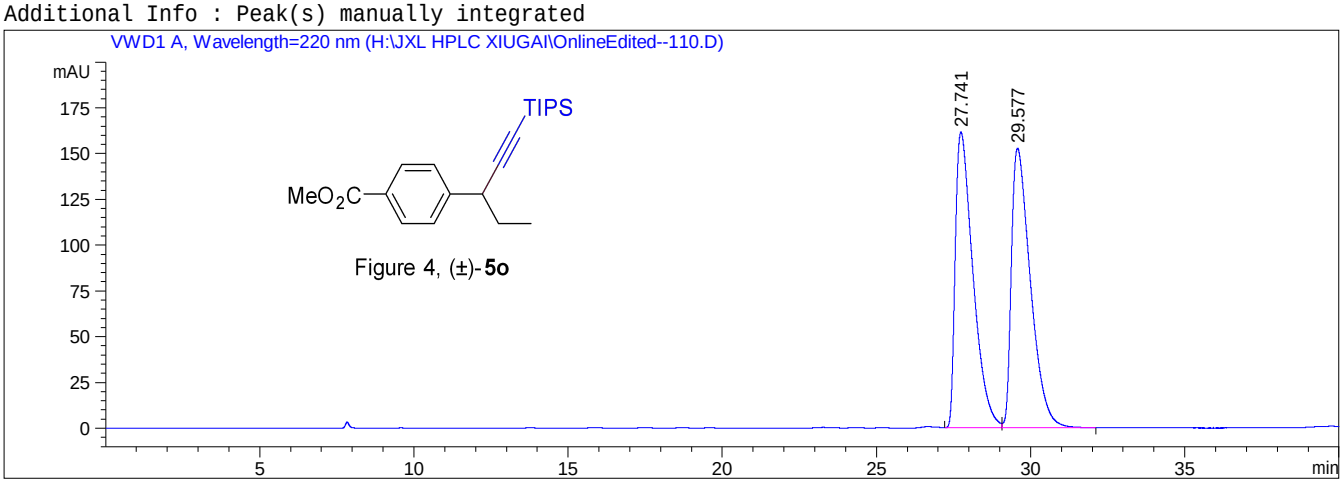


Figure 4, (±)-**5o**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.741 BV    0.5997 6440.34473  161.52284  49.5692
   2  29.577 VB    0.6333 6552.29932  152.65790  50.4308

Totals :                  1.29926e4   314.18074


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 243. HPLC spectra for compound (±)-**5o**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--111.D
Sample Name: JXL-DB-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 111
Acq. Instrument : HPLC-1260                      Location :  62
Injection Date  : 12/15/2020 2:13:22 AM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-40-0.8-1-6-220-JXL.M
Last changed    : 12/14/2020 9:36:57 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 8:59:06 PM by SYSTEM
                  (modified after loading)
```

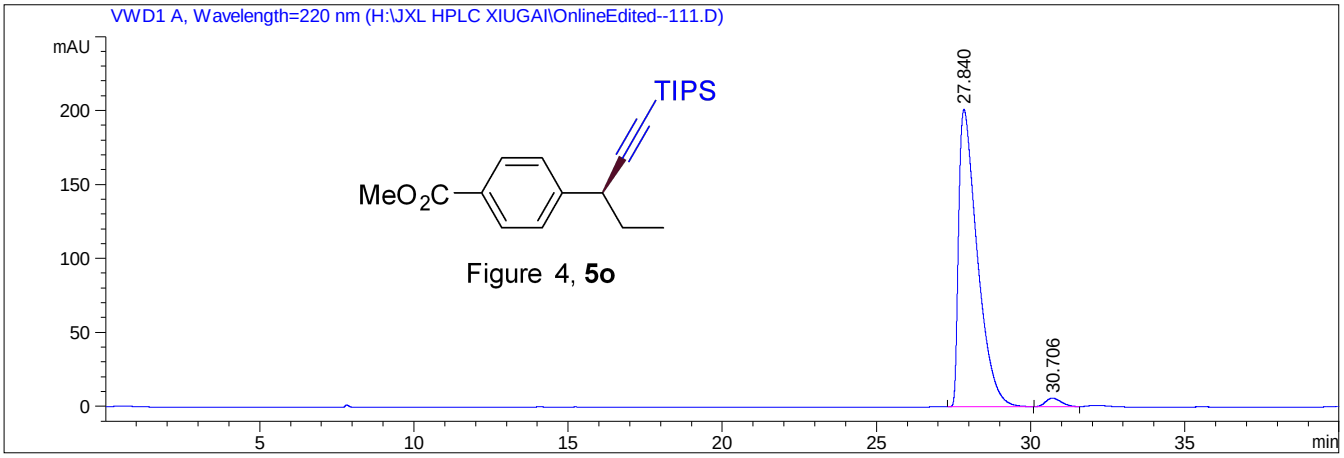


Figure 4, **5o**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.840 BB    0.6234 8452.31738  201.06433  97.6544
   2  30.706 BB    0.4168  203.01605    5.77937   2.3456

Totals :                  8655.33344  206.84370


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 244. HPLC spectra for compound **5o**

Data File H:\JXL HPLC\JXL-02-149-6-OD(1)-RAC.D
Sample Name: JXL-02-149-6-OD

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :  31
Acq. Instrument : HPLC-1260                      Location :  95
Injection Date  : 6/15/2020 8:54:24 PM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20200615\YH 2020-06-15 08-21-52\0IPA-30-0.5-1-2-220-JXL.M
Last changed    : 6/15/2020 8:52:56 PM by 系统
Analysis Method : C:\CHEM32\1\METHODS\15IPA_30_8_4.M
Last changed    : 12/18/2020 9:43:32 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

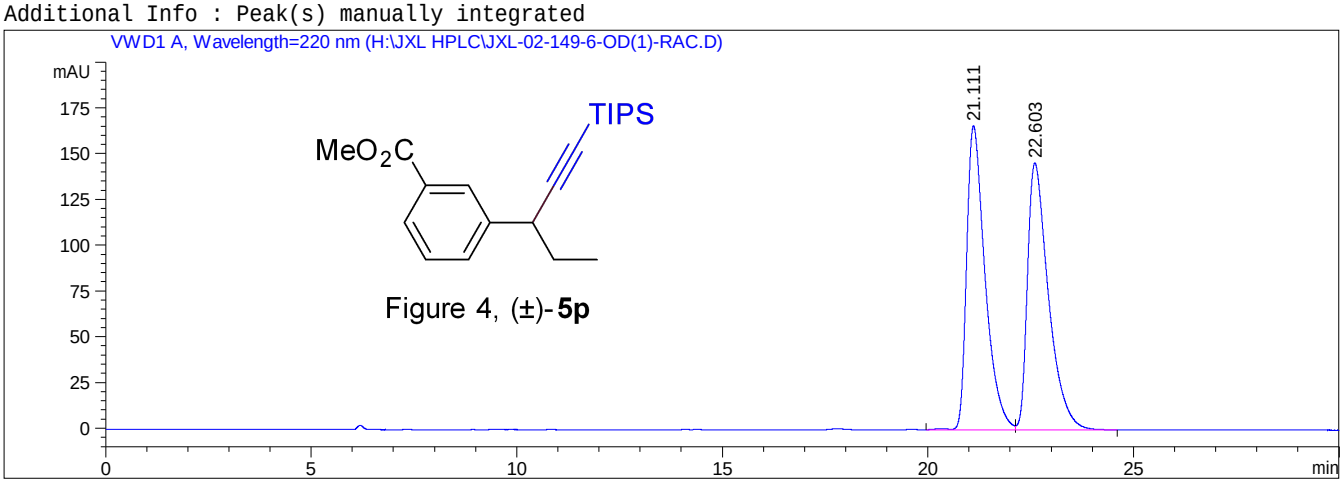


Figure 4, (±)-**5p**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.111 VV R  0.4701 5171.46680  165.94023  50.0069
   2  22.603 VB    0.5322 5170.04248  145.63780  49.9931

Totals :                  1.03415e4   311.57803


======================================================================
                        *** End of Report ***
```


Supplementary Fig. 245. HPLC spectra for compound (±)-**5p**

Data File H:\JXL HPLC\JXL-02-149-2-OD-EE.D
Sample Name: JXL-02-149-2-OD

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  49
Acq. Instrument : HPLC-1260                      Location :   96
Injection Date  : 6/16/2020 4:59:14 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.400 µl
Acq. Method     : D:\G527\FZ\20200611\YH 2020-06-15 23-14-24\0IPA-30-0.5-1-2-220-JXL.M
Last changed    : 6/16/2020 8:53:54 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:40:15 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

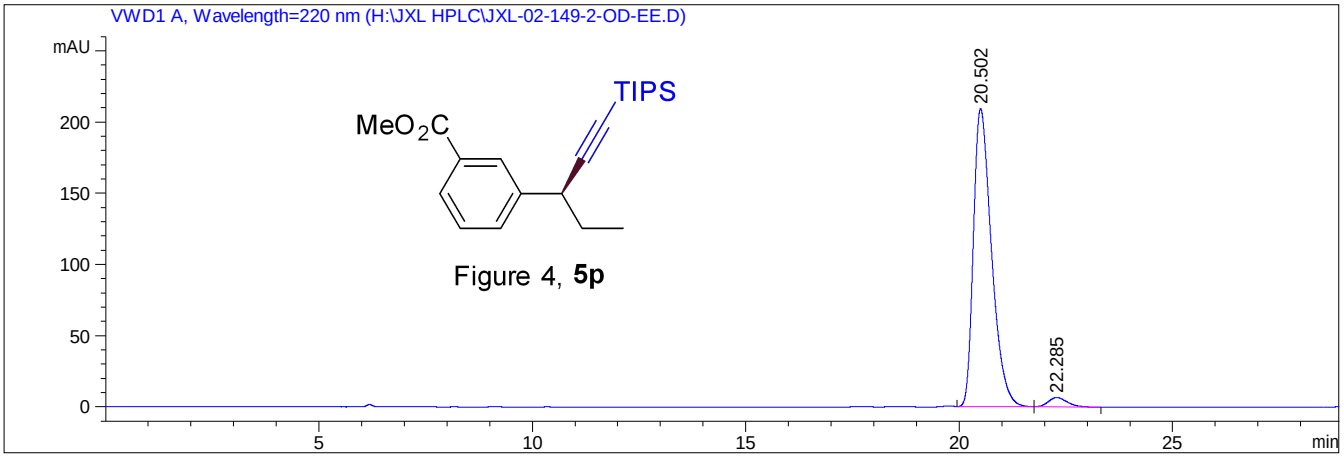


Figure 4, **5p**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.502 BB    0.4508 6165.68359  209.24425  96.8537
   2  22.285 BB    0.3691  200.29059    6.55361   3.1463

Totals :                  6365.97418  215.79785

==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 246. HPLC spectra for compound **5p**

Data File H:\JXL HPLC\JXL-02-157-2-OD(2)-RAC.D
Sample Name: JXL-02-157-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  87
Acq. Instrument : HPLC-1260                     Location :   62
Injection Date  : 6/21/2020 8:45:38 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20200619\YH 2020-06-19 10-26-40\0IPA-60-0.5-1-2-220-JXL.M
Last changed    : 6/20/2020 11:08:48 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-19 17-11-35\0.6IPA_15_0.8_3.CJ.M (Sequence
                  Method)
Last changed    : 12/20/2020 3:24:03 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

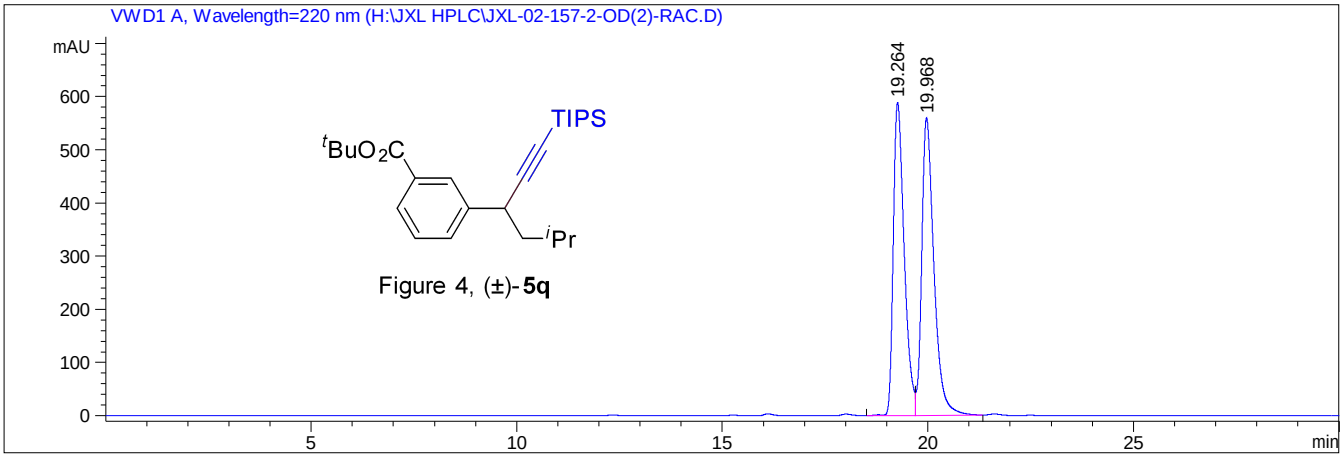


Figure 4, (±)-**5q**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.264 VV R  0.2823 1.08682e4   588.87714  48.5491
   2  19.968 VB    0.3102 1.15178e4   559.51123  51.4509

Totals :                  2.23860e4  1148.38837

==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 247. HPLC spectra for compound (±)-**5q**

Data File H:\JXL HPLC\JXL-03-115-OD(2)-EE.D
Sample Name: JXL-115-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line : 124
Acq. Instrument : HPLC-1260                      Location :  86
Injection Date  : 11/1/2020 6:47:32 AM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\0IPA-40-0.5-1-6-220-JXL.M
Last changed    : 10/31/2020 10:15:10 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 9:24:30 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

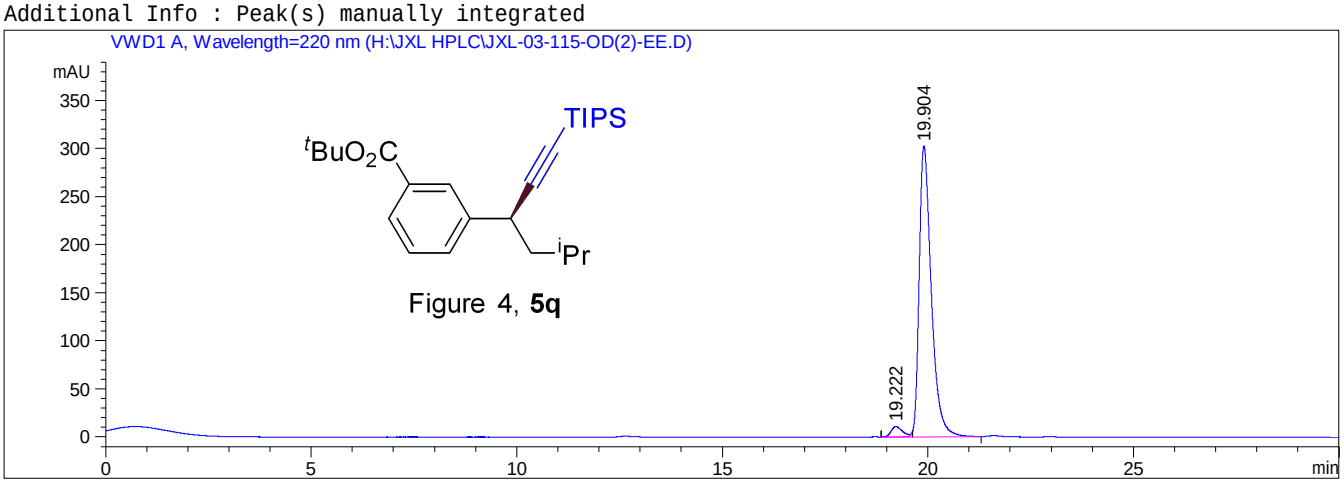


Figure 4, **5q**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.222 BV E  0.2773  208.75603   10.95368   3.2626
   2  19.904 VB R  0.3090 6189.72070  302.73431  96.7374

Totals :                  6398.47673  313.68800


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 248. HPLC spectra for compound **5q**

Data File H:\JXL HPLC\JXL-03-157-2-OD(2)-RAC.D
Sample Name: JXL-03-157-2-OD(2)

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :  35
Acq. Instrument : HPLC-1260                      Location :  94
Injection Date  : 9/22/2020 8:11:49 AM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-21 18-04-54\0IPA-35-0.3-1-6-220-JXL.M
Last changed    : 9/21/2020 10:01:05 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 9:26:51 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

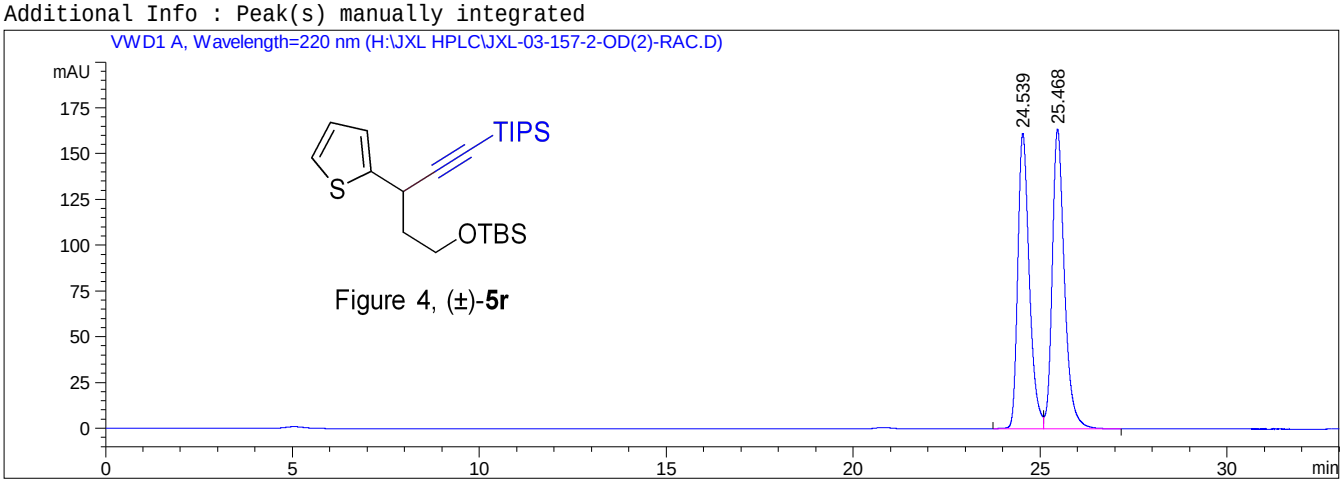


Figure 4, (±)-**5r**

```
======================================================================
                          Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.539 BV    0.3261 3451.30762  161.34341  48.1006
   2  25.468 VB    0.3434 3723.87671  163.69365  51.8994

Totals :                  7175.18433  325.03706


======================================================================
                          *** End of Report ***
```


Supplementary Fig. 249. HPLC spectra for compound (±)-**5r**

Data File H:\JXL HPLC\JXL-03-166-1-OD(2)-EE.D
Sample Name: JXL-03-166-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  38
Acq. Instrument : HPLC-1260                     Location :   95
Injection Date  : 9/22/2020 9:58:01 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-21 18-04-54\0IPA-35-0.3-1-6-220-JXL.M
Last changed    : 9/22/2020 9:56:24 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 9:28:34 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

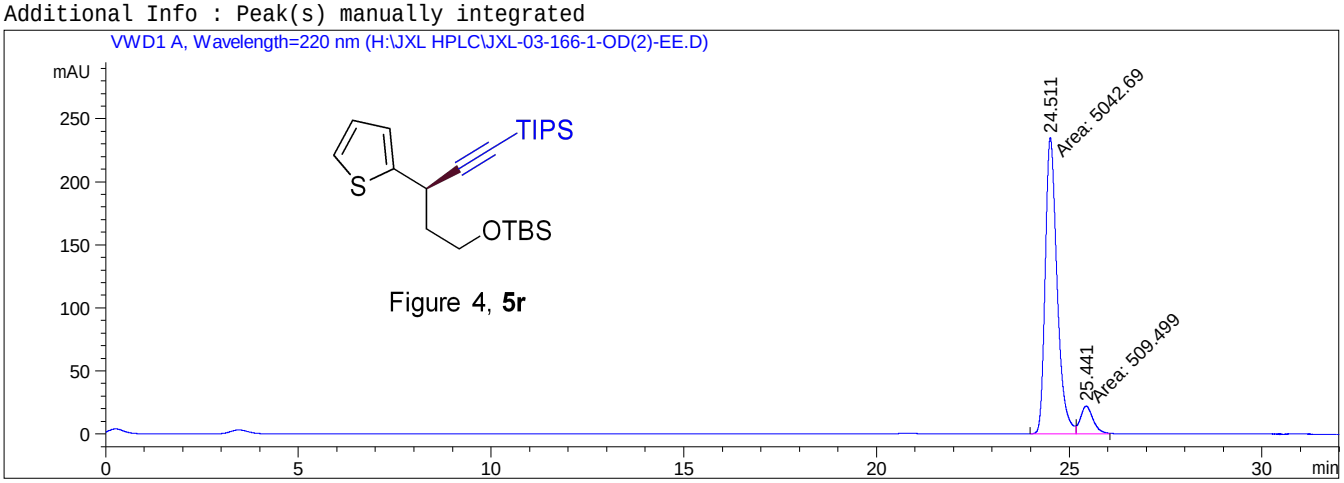


Figure 4, **5r**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.511 FM    0.3576 5042.69092  235.04404  90.8235
   2  25.441 MF    0.3822  509.49850   22.21989   9.1765

Totals :                  5552.18942  257.26392


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 250. HPLC spectra for compound **5r**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--116.D
Sample Name: JXL-02-157-3-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 116
Acq. Instrument : HPLC-1260                      Location :  83
Injection Date  : 12/15/2020 5:00:41 AM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.8-1-6-220-JXL.M
Last changed    : 12/14/2020 9:37:57 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:43:39 AM by SYSTEM
                  (modified after loading)
```

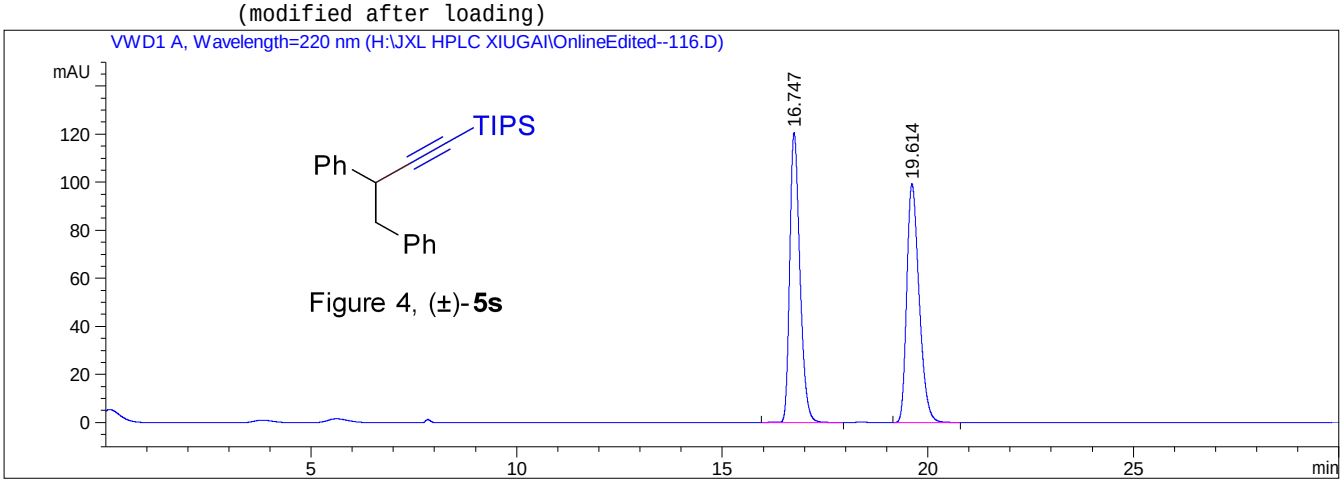


Figure 4, (±)-**5s**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.747 VB R  0.2644 2085.05396  120.80421  50.0368
   2  19.614 BB    0.3213 2081.99048   99.44037  49.9632

Totals :                  4167.04443  220.24458


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 251. HPLC spectra for compound (±)-**5s**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--117.D
Sample Name: JXL-02-167-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 117
Acq. Instrument : HPLC-1260                      Location :  84
Injection Date  : 12/15/2020 5:32:11 AM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-30-0.8-1-6-220-JXL.M
Last changed    : 12/14/2020 9:37:57 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:45:08 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

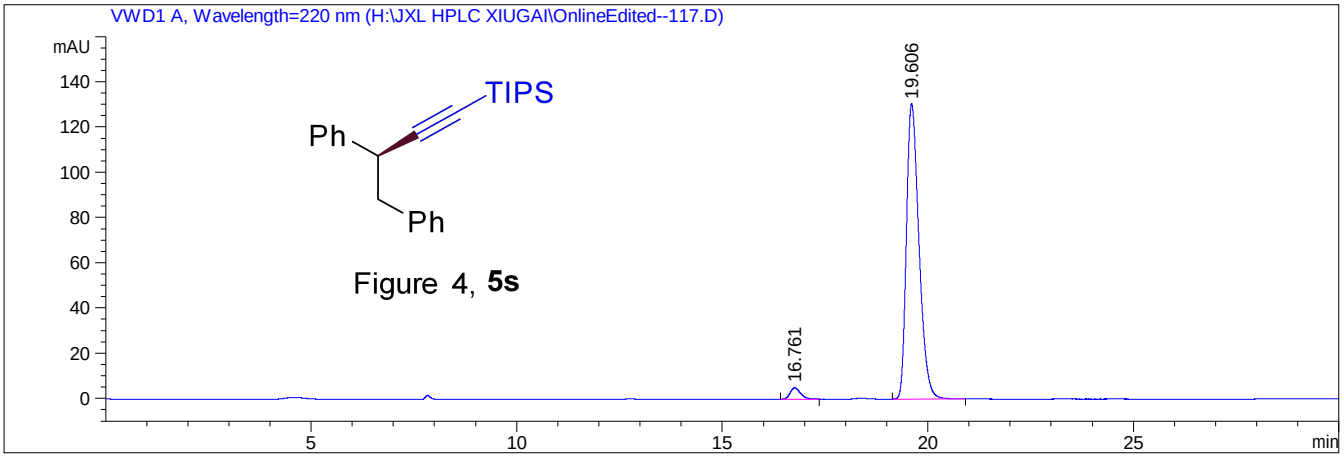


Figure 4, **5s**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.761 BB    0.2505   86.25835    5.04446   3.0187
   2  19.606 BB    0.3264 2771.22437  130.70523  96.9813

Totals :                  2857.48272  135.74969


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 252. HPLC spectra for compound **5s**

Data File H:\JXL HPLC XIUGAI\091-0802--010.D
Sample Name: JXL-03-31-1-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  10
Acq. Instrument : HPLC-1260                      Location :   91
Injection Date  : 8/8/2020 8:42:21 PM                 Inj :   2
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\JXL\20200808\YH 2020-08-08 16-05-24\0IPA-40-0.3-1-2-220-JXL.M
Last changed    : 8/8/2020 9:16:15 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-19 17-11-35\10IPA_45_0.8_4.M (Sequence Method)
Last changed    : 12/20/2020 1:16:54 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

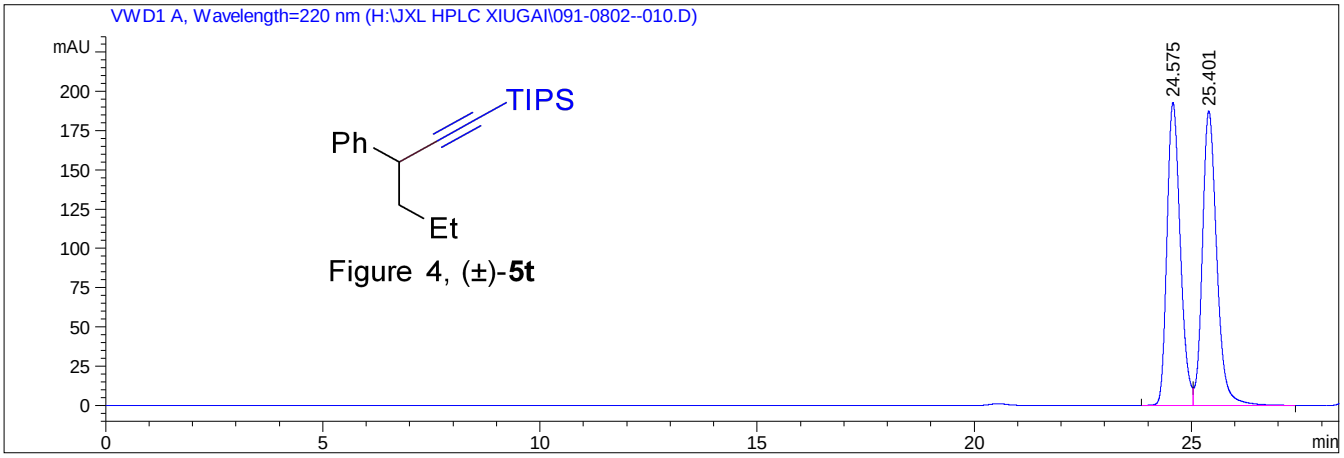


Figure 4, (±)-**5t**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.575 BV    0.3294 4100.78613  193.01289  48.7329
   2  25.401 VB    0.3520 4314.04102  187.80188  51.2671

Totals :                  8414.82715  380.81477


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 253. HPLC spectra for compound (±)-**5t**

Data File H:\JXL HPLC\JXL-03-101-1-OD(2).D
Sample Name: JXL-03-101-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  13
Acq. Instrument : HPLC-1260                     Location :   95
Injection Date  : 8/20/2020 3:34:30 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\JXL\20200819\YH 2020-08-19 21-39-43\0IPA-30-0.3-1-6-220-JXL.M
Last changed    : 8/19/2020 9:39:43 PM by 系统
Analysis Method : C:\CHEM32\1\METHODS\1IPA_20_1.0_3.CJM.M
Last changed    : 12/16/2020 2:45:22 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

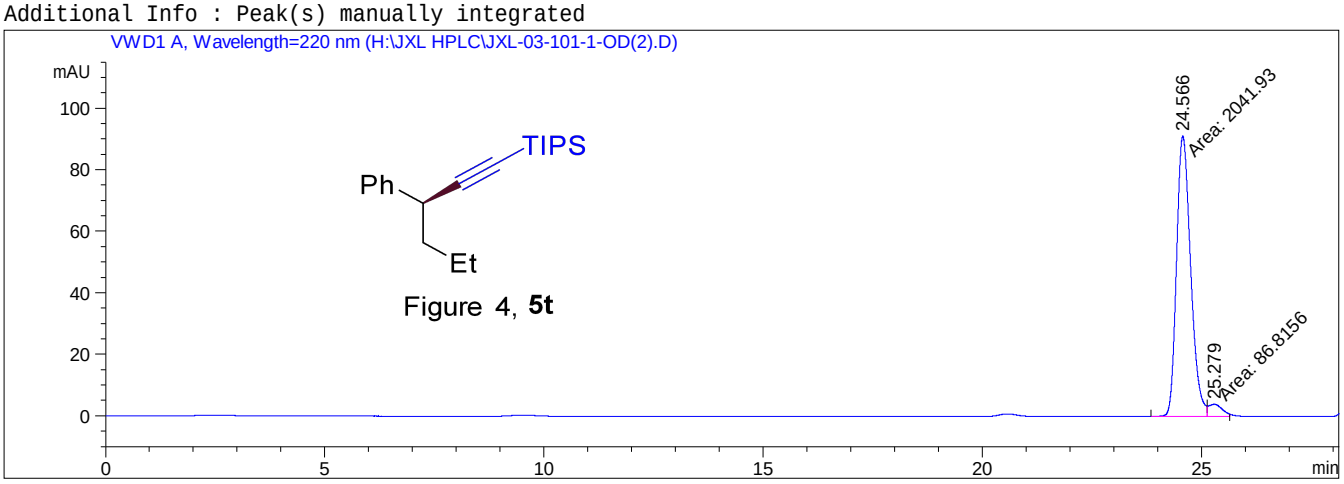


Figure 4, **5t**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.566 MF    0.3732 2041.93396   91.18871  95.9218
   2  25.279 MF    0.3618   86.81557    3.99962   4.0782

Totals :                  2128.74953   95.18834


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 254. HPLC spectra for compound **5t**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--019.D
Sample Name: JXL-02-164-6-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  19
Acq. Instrument : HPLC-1260                      Location :   91
Injection Date  : 8/23/2020 1:24:20 AM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-08-22 18-57-44\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 8/22/2020 9:23:07 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\20IPA_15_10_3.M (Sequence Method)
Last changed    : 12/18/2020 3:03:04 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

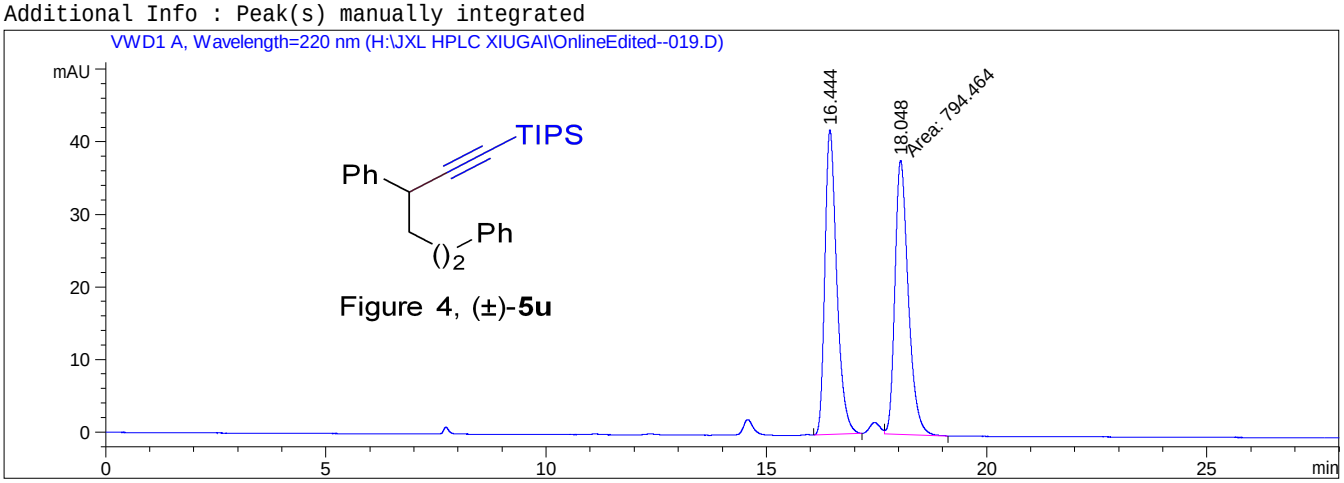


Figure 4, (±)-**5u**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.444 BB    0.2856  786.78638   41.99541  49.7572
   2  18.048 FM    0.3504  794.46375   37.78609  50.2428

Totals :                  1581.25012   79.78150


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 255. HPLC spectra for compound (±)-**5u**

Data File H:\JXL HPLC\JXL-03-108-1-OD(2)-EE.D
Sample Name: JXL-03-108-1

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :   3
Acq. Instrument : HPLC-1260                      Location :   92
Injection Date  : 8/23/2020 8:08:34 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\JXL\20200823\YH 2020-08-23 19-08-47\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 8/23/2020 8:45:56 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\20IPA_15_10_3.M (Sequence Method)
Last changed    : 12/18/2020 3:05:03 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

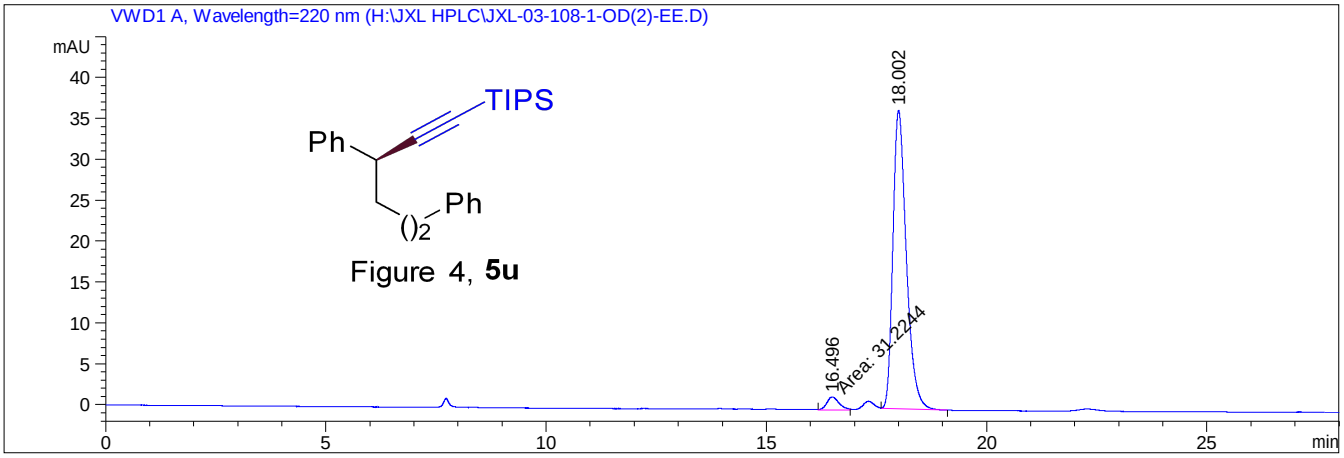


Figure 4, **5u**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.496 MM    0.3235   31.22440    1.60860   3.8895
   2  18.002 BB    0.3203  771.57056   36.47853  96.1105

Totals :                   802.79495   38.08713

======================================================================
                        *** End of Report ***
```


Supplementary Fig. 256. HPLC spectra for compound **5u**

Data File H:\JXL HPLC\JXL-03-117-2-OD(2)-RAC.D
Sample Name: JXL-03-117-2-OD(2)

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :   5
Acq. Instrument : HPLC-1260                      Location :   92
Injection Date  : 8/28/2020 1:12:31 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\JXL\20200827\YH 2020-08-27 23-15-17\0IPA-40-0.8-1-2-220-JXL.M
Last changed    : 8/27/2020 11:27:50 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:07:12 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

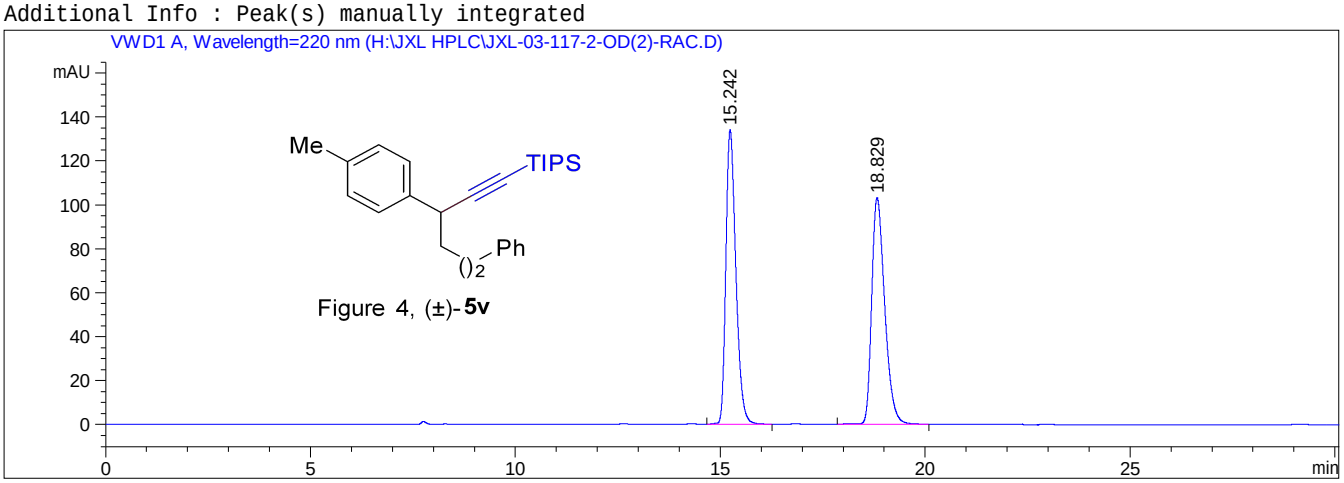


Figure 4, (±)-**5v**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.242 BB    0.2599 2274.47729  134.07082  49.9280
   2  18.829 BB    0.3388 2281.03564  103.21310  50.0720

Totals :                  4555.51294  237.28392


======================================================================
                        *** End of Report ***
```


Supplementary Fig. 257. HPLC spectra for compound (±)-**5v**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--067.D
Sample Name: JXL-03-133-1-XIA-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  67
Acq. Instrument : HPLC-1260                      Location :   88
Injection Date  : 9/2/2020 10:39:15 AM                Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\zy\20200901\YH 2020-09-01 09-59-23\0IPA-40-0.8-1-6-220-JXL.M
Last changed    : 9/1/2020 10:11:54 PM by 系统
Analysis Method : C:\CHEM32\1\METHODS\1IPA_20_1.0_3.CJM.M
Last changed    : 12/16/2020 2:48:23 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

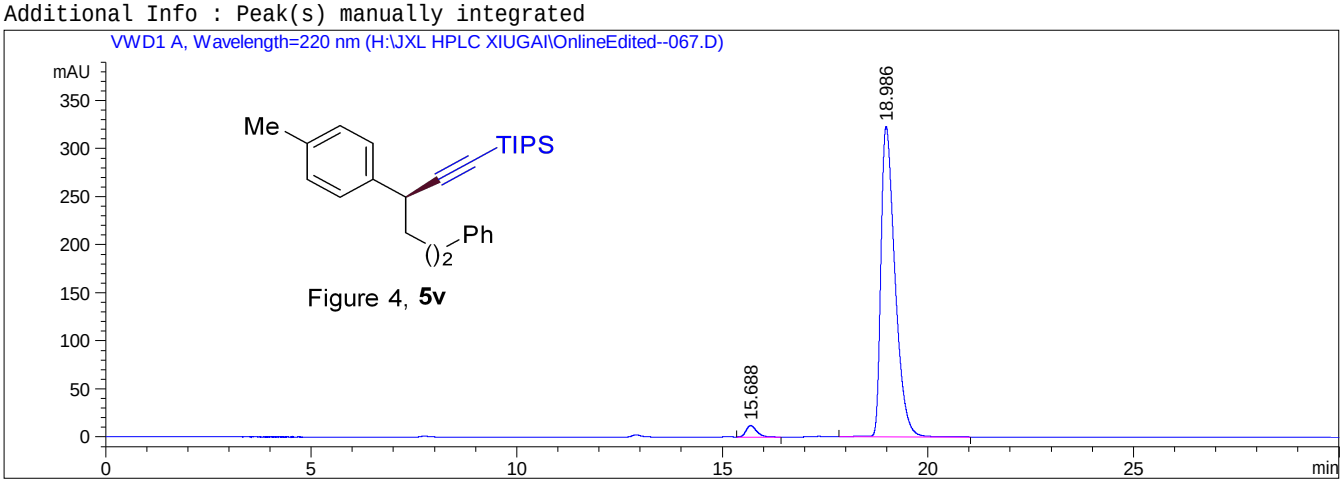


Figure 4, **5v**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.688 BB    0.2716  211.30690   11.79120   2.6762
   2  18.986 VB R  0.3611 7684.48779  322.94391  97.3238

Totals :                  7895.79469  334.73511


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 258. HPLC spectra for compound **5v**

Data File H:\JXL HPLC\JXL-03-131-4-OD(2)-1.D
Sample Name: JXL-03-131-4-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  36
Acq. Instrument : HPLC-1260                     Location :   89
Injection Date  : 9/3/2020 11:05:09 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\JXL\20200902\YH 2020-09-02 16-57-48\0IPA-90-0.5-1-6-220-JXL.M
Last changed    : 9/3/2020 11:09:41 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:10:58 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

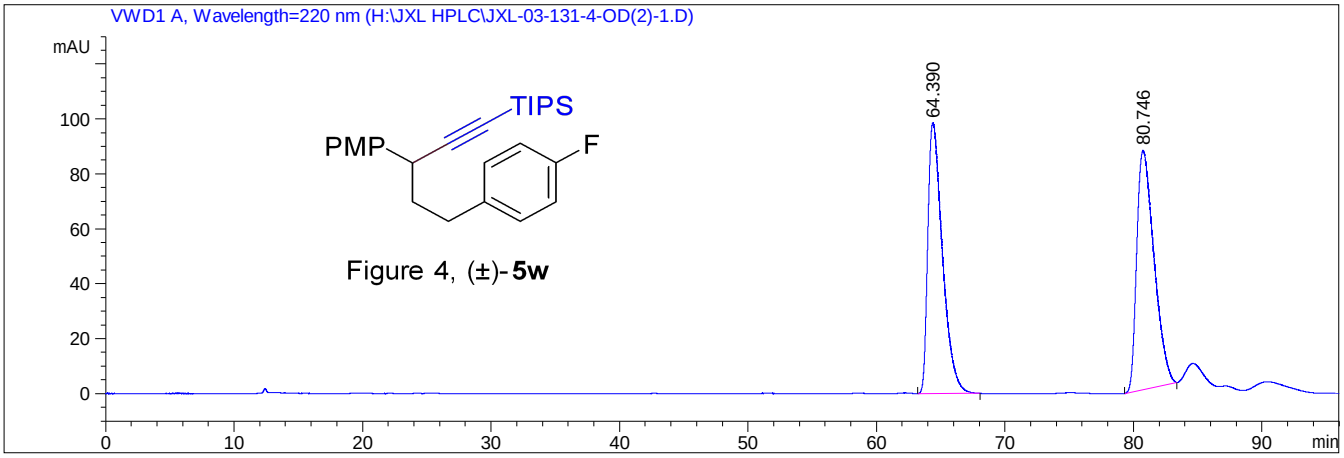


Figure 4, (±)-**5w**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  64.390 BB    1.0778 7801.03662   98.67648  48.9508
   2  80.746 BB    1.2471 8135.43311   87.11023  51.0492

Totals :                  1.59365e4   185.78671

==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 259. HPLC spectra for compound (±)-**5w**

Data File H:\JXL HPLC\JXL-03-123-1-XIA-OD(2).D
Sample Name: JXL-03-123-1-XIA-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  35
Acq. Instrument : HPLC-1260                      Location :  72
Injection Date  : 9/3/2020 9:33:43 PM                Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\JXL\20200902\YH 2020-09-02 16-57-48\0IPA-90-0.5-1-6-220-JXL.M
Last changed    : 9/3/2020 11:02:41 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:12:40 PM by SYSTEM
                  (modified after loading)
```

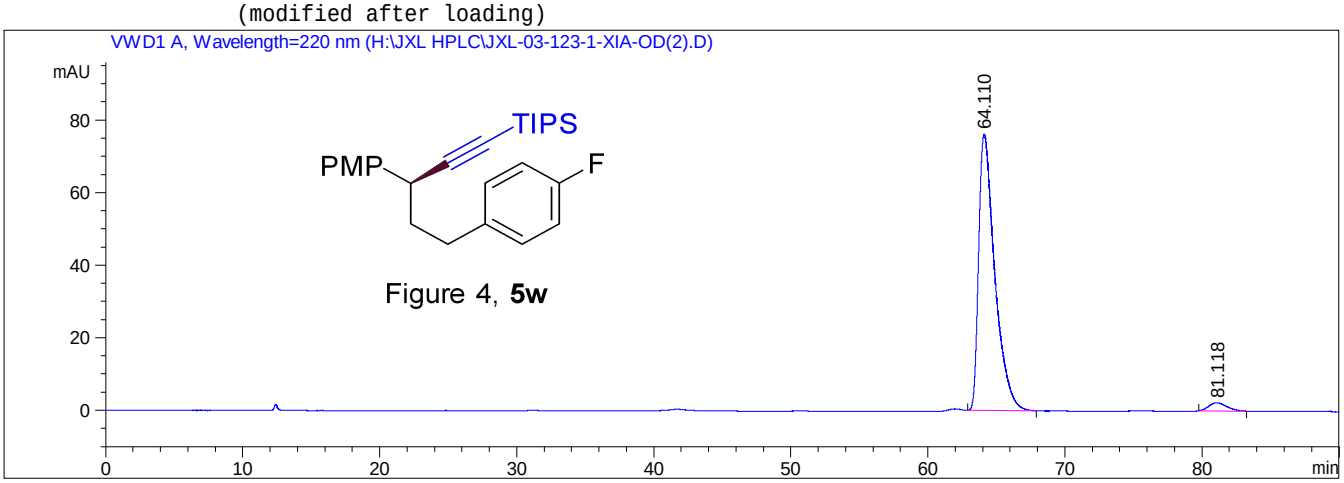


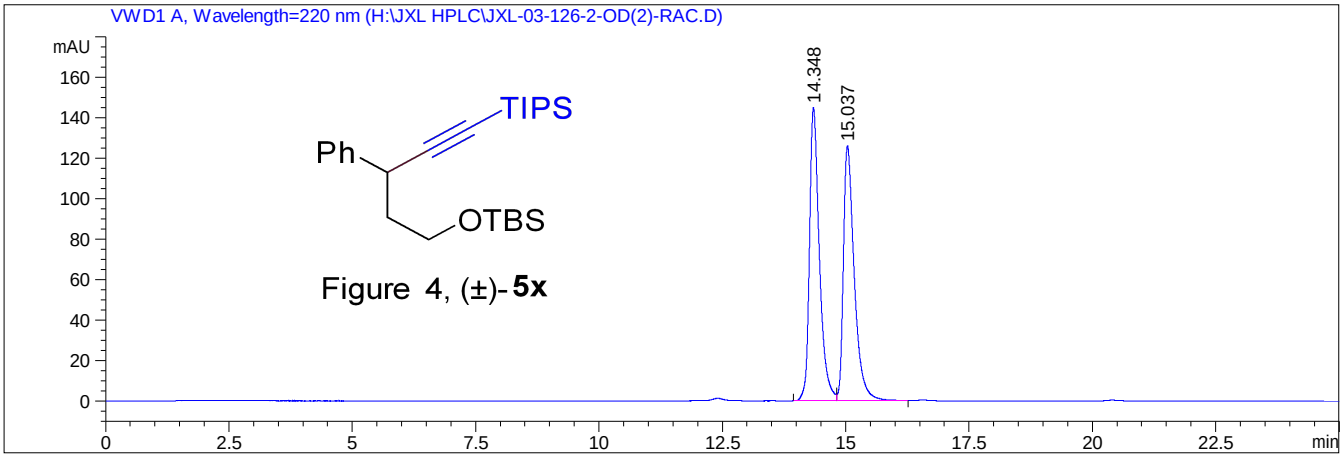
Figure 4, **5w**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  64.110 BB    1.1146 6215.83203   76.20796  96.8170
   2  81.118 BB    1.0648  204.35680    2.24434   3.1830

Totals :                  6420.18883   78.45230


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 260. HPLC spectra for compound **5w**

Data File H:\JXL HPLC\JXL-03-126-2-OD(2)-RAC.D
Sample Name: JXL-03-126-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   9
Acq. Instrument : HPLC-1260                     Location :   81
Injection Date  : 9/3/2020 1:06:15 AM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\JXL\20200902\YH 2020-09-02 16-57-48\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 9/2/2020 11:43:41 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:13:54 PM by SYSTEM
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.348 BV    0.2091 2025.82507  144.89226  51.1203
   2  15.037 VB    0.2303 1937.03552  126.01382  48.8797

Totals :                  3962.86060  270.90607


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 261. HPLC spectra for compound (±)-**5x**

Data File H:\JXL HPLC\JXL-03-135-1-OD(2)-EE.D
Sample Name: JXL-03-135-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  10
Acq. Instrument : HPLC-1260                     Location :   82
Injection Date  : 9/3/2020 1:37:40 AM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\JXL\20200902\YH 2020-09-02 16-57-48\0IPA-30-0.5-1-6-220-JXL.M
Last changed    : 9/2/2020 11:43:41 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:15:20 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

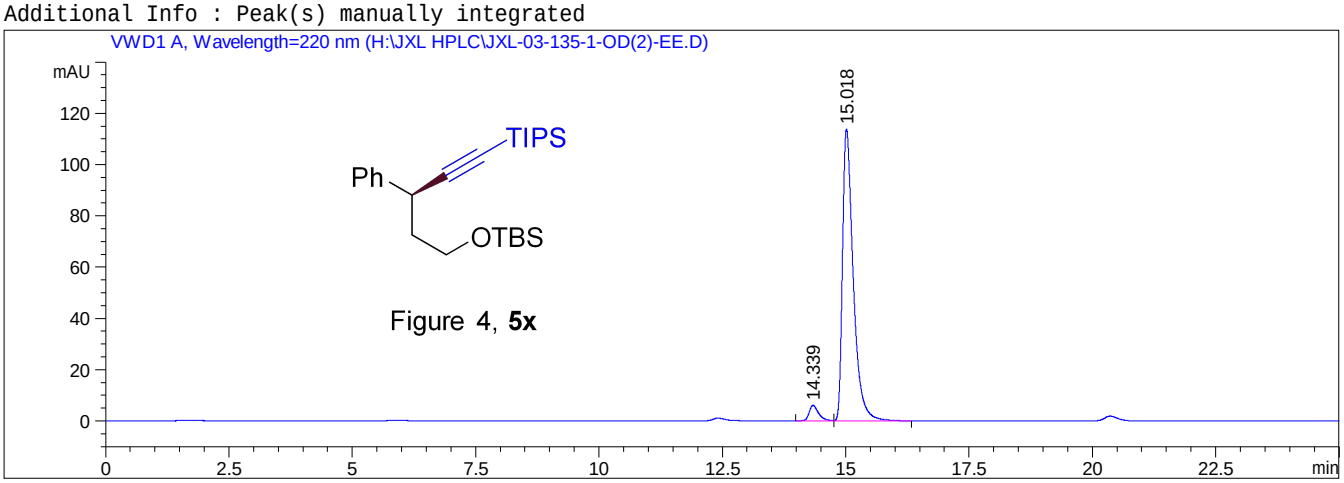


Figure 4, **5x**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.339 BV    0.1966   81.53291    6.11455   4.5107
   2  15.018 VB    0.2278 1726.00415  113.87477  95.4893

Totals :                  1807.53706  119.98932


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 262. HPLC spectra for compound **5x**

Data File H:\JXL HPLC\JXL-03-150-4-OD(1)-RAC.D
Sample Name: JXL-03-150-4-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 192
Acq. Instrument : HPLC-1260                     Location :   95
Injection Date  : 9/15/2020 9:49:37 AM               Inj :   3
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-11 23-16-57\1IPA-30-0.5-1-2-220-JXL.M
Last changed    : 9/15/2020 9:11:51 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:17:14 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

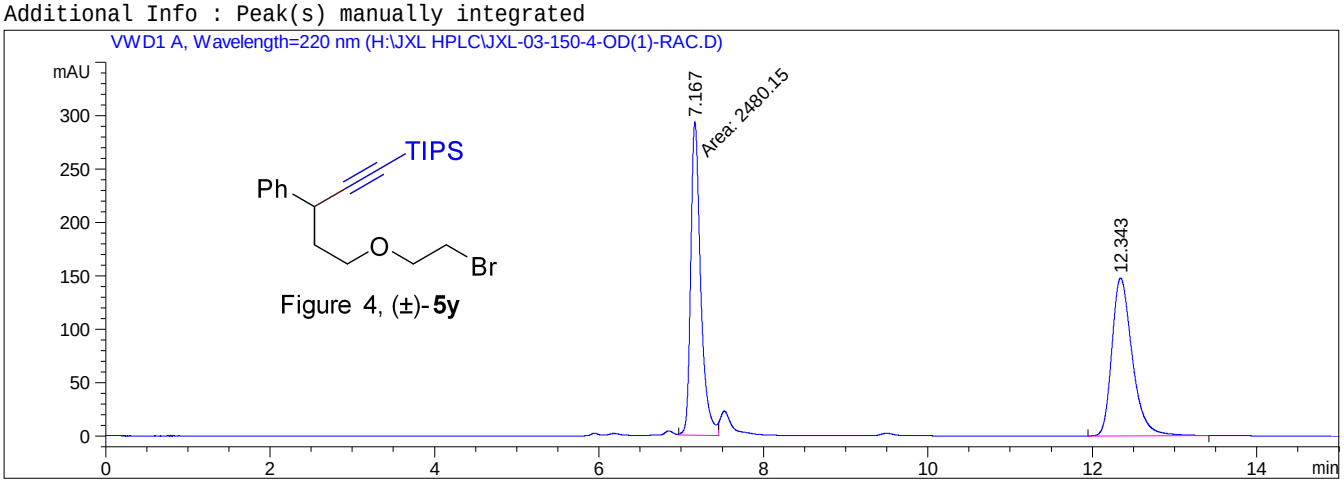


Figure 4, (±)-**5y**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.167 FM    0.1409 2480.15137  293.46741  49.4393
   2  12.343 BB    0.2629 2536.40210  147.66779  50.5607

Totals :                  5016.55347  441.13519


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 263. HPLC spectra for compound (±)-**5y**

Data File H:\JXL HPLC\JXL-03-153-1-OD(1)-EE.D
Sample Name: JXL-03-153-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 102
Acq. Instrument : HPLC-1260                      Location :  96
Injection Date  : 9/13/2020 8:02:04 PM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20200822\YH 2020-09-11 23-16-57\1IPA-30-0.5-1-2-220-JXL.M
Last changed    : 9/13/2020 7:58:29 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:19:23 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

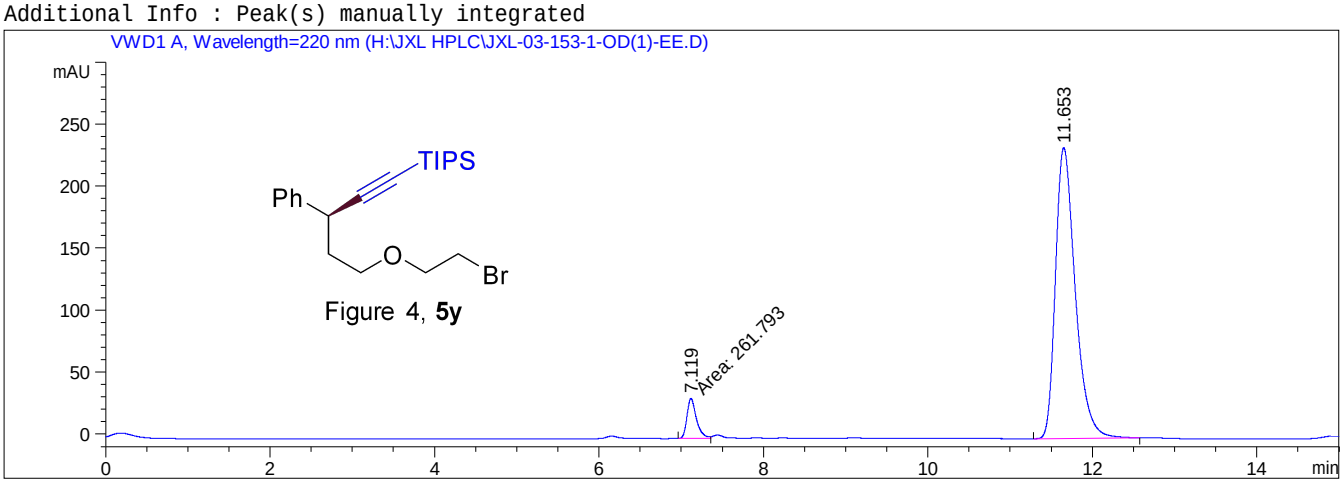


Figure 4, **5y**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.119 FM    0.1345  261.79251   32.42925   6.2619
   2  11.653 BB    0.2565 3918.89722  234.48160  93.7381

Totals :                  4180.68973  266.91085


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 264. HPLC spectra for compound **5y**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--029.D
Sample Name: JXL-03-126-3-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  29
Acq. Instrument : HPLC-1260                      Location :   89
Injection Date  : 12/13/2020 11:16:29 AM             Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 4.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-45-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 9:24:33 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\15IPA_30_8_4.M (Sequence Method)
Last changed    : 12/18/2020 3:13:02 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

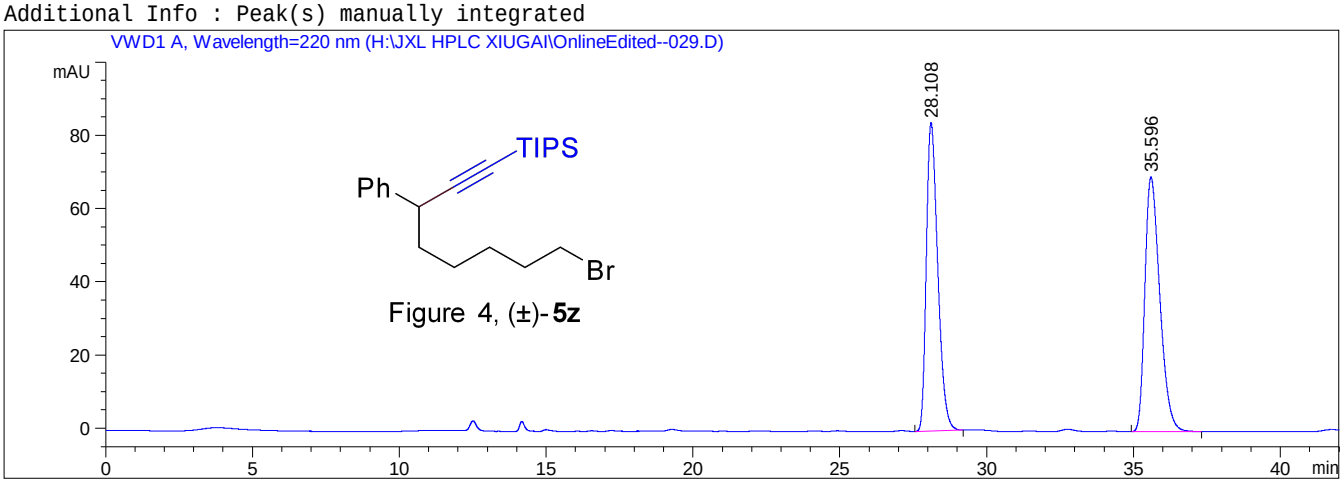


Figure 4, (±)-**5z**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.108 BB    0.4169 2276.74316   84.21875  48.0828
   2  35.596 BB    0.5323 2458.30249   69.55943  51.9172

Totals :                  4735.04565  153.77818


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 265. HPLC spectra for compound (±)-**5z**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--044.D
Sample Name: JXL-03-138-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  44
Acq. Instrument : HPLC-1260                      Location :   90
Injection Date  : 12/13/2020 8:54:29 PM              Inj :   1
                                                Inj Volume : 3.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-45-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 9:24:33 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:22:57 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

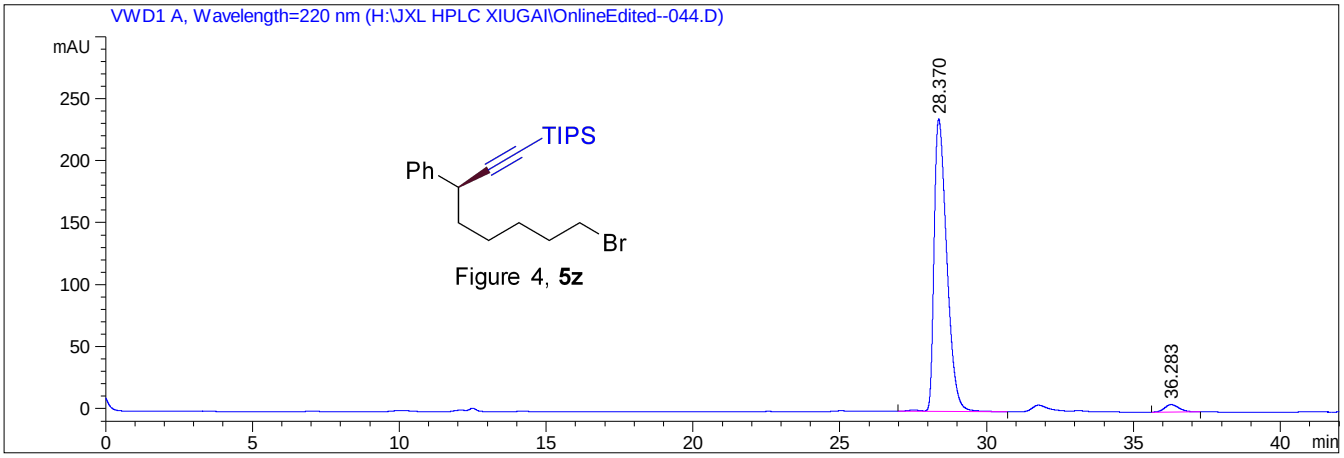


Figure 4, **5z**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.370 VB R  0.4587 7076.32129  236.06902  97.1948
   2  36.283 BB    0.4036  204.23074    5.95462   2.8052

Totals :                  7280.55203  242.02364


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 266. HPLC spectra for compound **5z**

Data File H:\JXL HPLC\JXL-02-164-4-AD(2)-RAC.D
Sample Name: JXL-02-164-4-AD(2)

```
======================================================================
Acq. Operator   : 系统                          Seq. Line :   6
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 9/20/2020 5:35:17 PM               Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\JXL\20200920\YH 2020-09-20 14-51-06\0IPA-45-0.5-1-6-220-JXL.M
Last changed    : 9/20/2020 3:40:59 PM by 系统
Analysis Method : E:\DATA\20210127\LC 2021-01-27 19-42-16\10IPA_20_1.0_3.MZWJ.M (Sequence
                  Method)
Last changed    : 1/29/2021 4:34:03 PM by SYSTEM
                  (modified after loading)
```

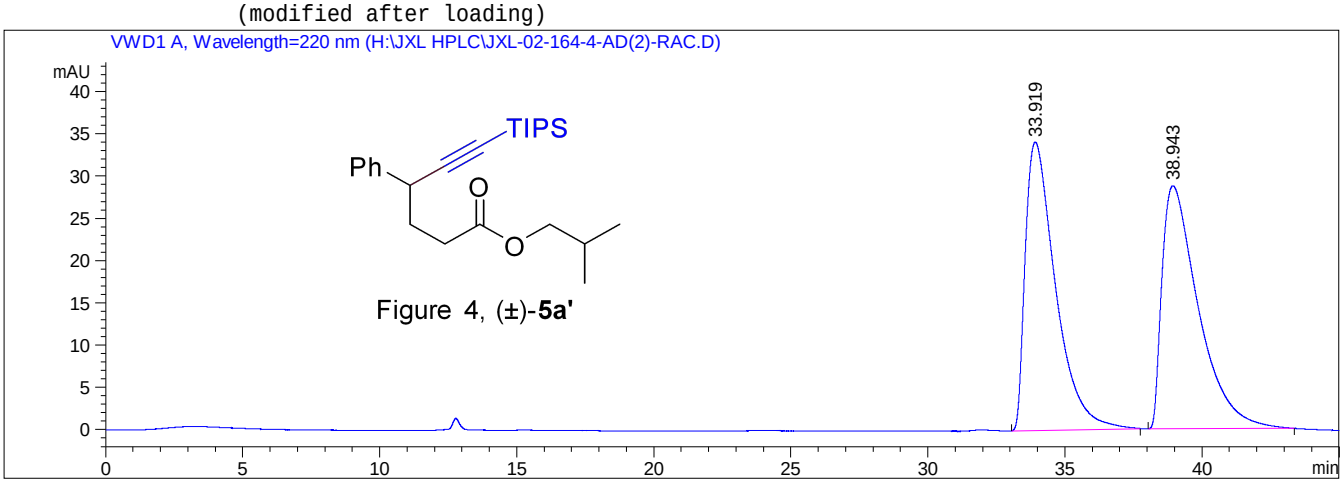


Figure 4, (±)-**5a'**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  33.919 BB    0.9033 2623.93433   34.13412  49.6876
   2  38.943 BB    1.0816 2656.93164   28.77937  50.3124

Totals :                  5280.86597   62.91348


======================================================================
                        *** End of Report ***
```


Supplementary Fig. 267. HPLC spectra for compound (±)-**5a'**

Data File H:\JXL HPLC\OnlineEdited--008.D
Sample Name: JXL-03-116-1-AD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   8
Acq. Instrument : HPLC-1260                      Location :   92
Injection Date  : 1/23/2021 1:14:05 PM              Inj :   1
                                                 Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 4.000 µl
Acq. Method     : D:\JXL\20210123\YH 2021-01-23 09-26-26\0IPA-45-0.5-1-2-220-JXL.M
Last changed    : 1/23/2021 9:58:41 AM by 系统
Analysis Method : E:\DATA\20210127\LC 2021-01-27 19-42-16\10IPA_20_1.0_3.MZWJ.M (Sequence
                  Method)
Last changed    : 1/29/2021 4:32:32 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

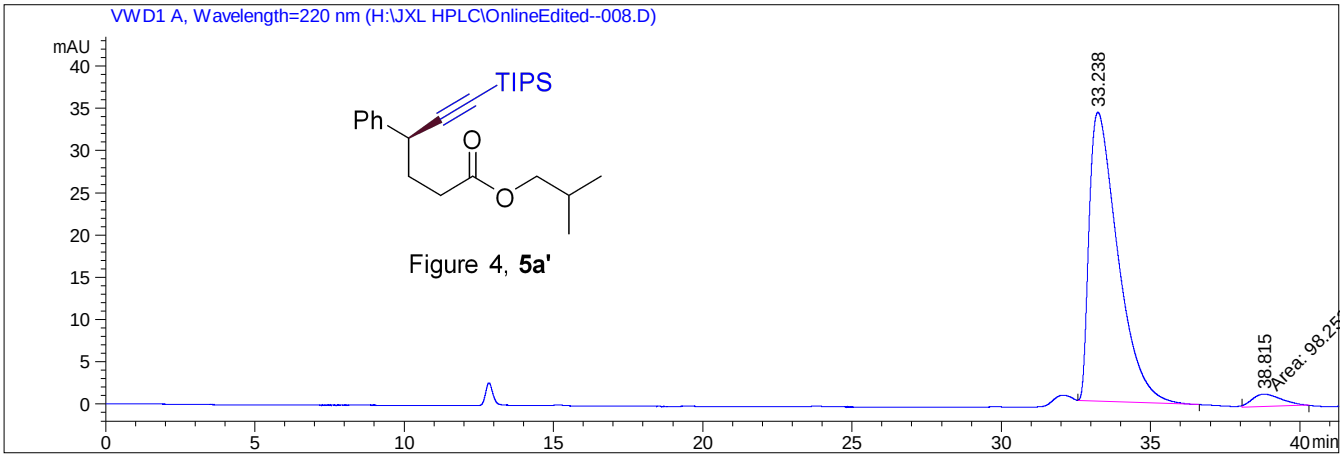


Figure 4, **5a'**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  33.238 BB    0.7824 2280.43457   34.18036  95.8695
   2  38.815 MM    1.1224   98.25251    1.45902   4.1305

Totals :                  2378.68708   35.63938

==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 268. HPLC spectra for compound **5a'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--010.D
Sample Name: JXL-03-153-5-OD(1)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  10
Acq. Instrument : HPLC-1260                      Location :  95
Injection Date  : 12/12/2020 11:47:56 PM            Inj :   1
                                                Inj Volume : 3.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\1IPA-20-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 11:16:10 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:41:58 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

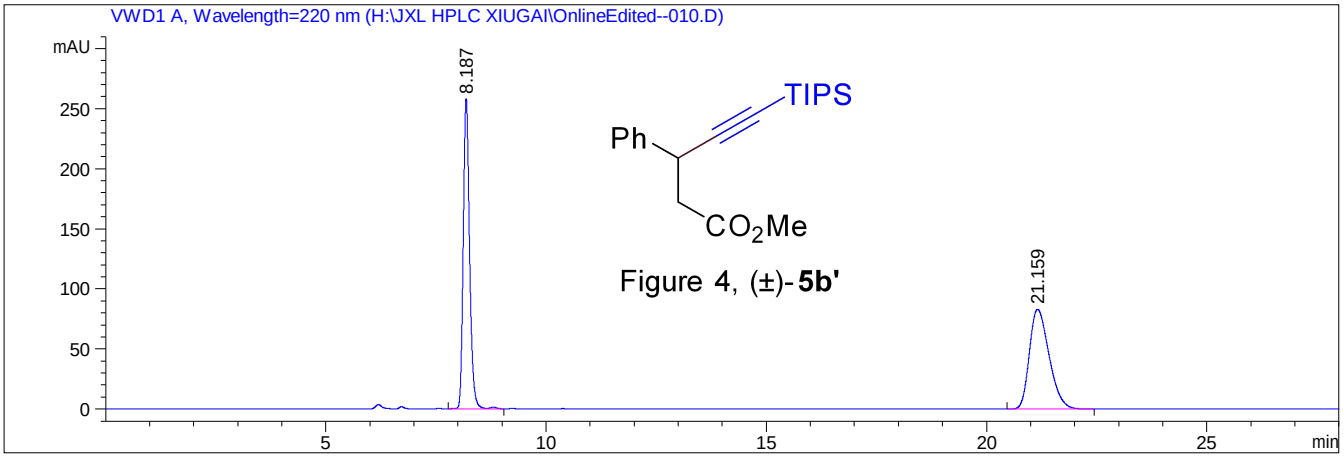


Figure 4, (±)-**5b'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.187 BV R  0.1524 2576.23950  258.17044  49.9962
   2  21.159 BB    0.4717 2576.62598   83.11460  50.0038

Totals :                  5152.86548  341.28504


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 269. HPLC spectra for compound (±)-**5b'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--011.D
Sample Name: JXL-03-158-3-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  11
Acq. Instrument : HPLC-1260                     Location :   96
Injection Date  : 12/13/2020 12:17:20 AM            Inj :   1
                                               Inj Volume : 3.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\1IPA-20-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 11:16:10 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:42:45 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

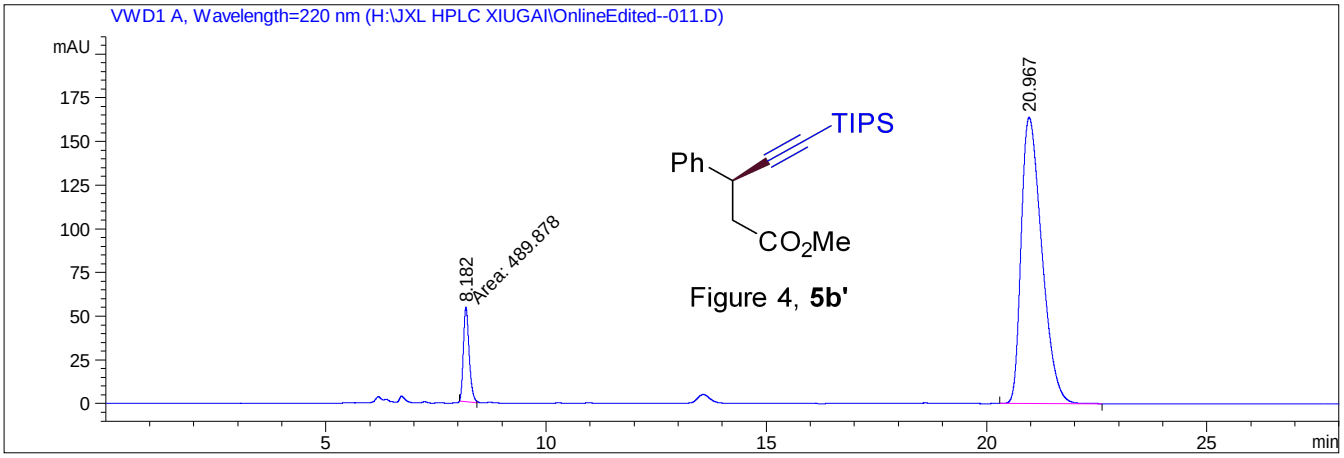


Figure 4, **5b'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.182 PM    0.1516  489.87790   53.86531   8.4159
   2  20.967 BB    0.4982 5331.00342  163.80722  91.5841

Totals :                  5820.88132  217.67253


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 270. HPLC spectra for compound **5b'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--006.D
Sample Name: JXL-03-131-5-OD(1)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :   6
Acq. Instrument : HPLC-1260                      Location :   93
Injection Date  : 12/12/2020 10:06:17 PM             Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\1IPA-20-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 10:25:23 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:50:20 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

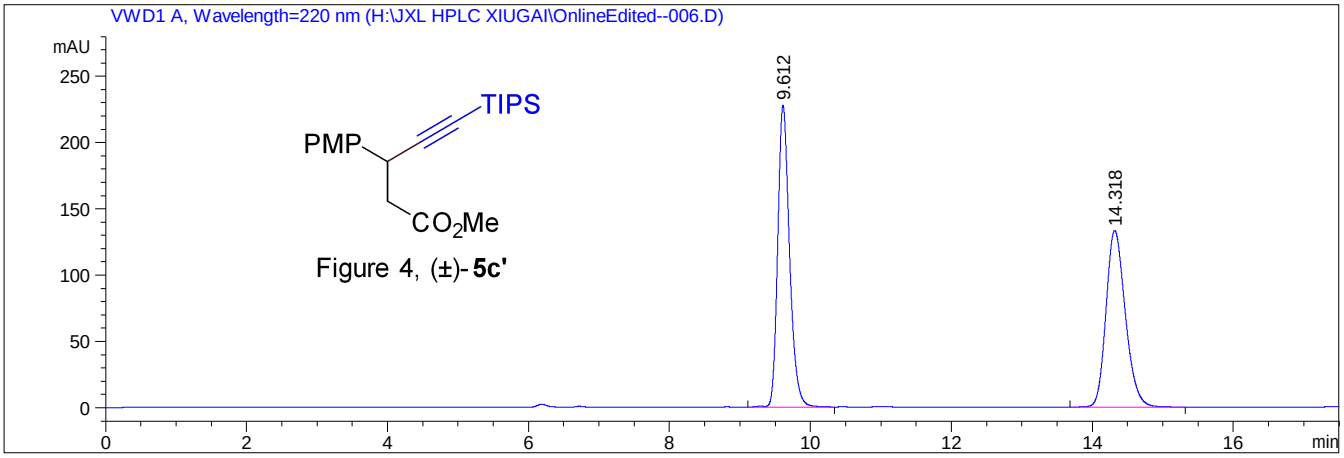


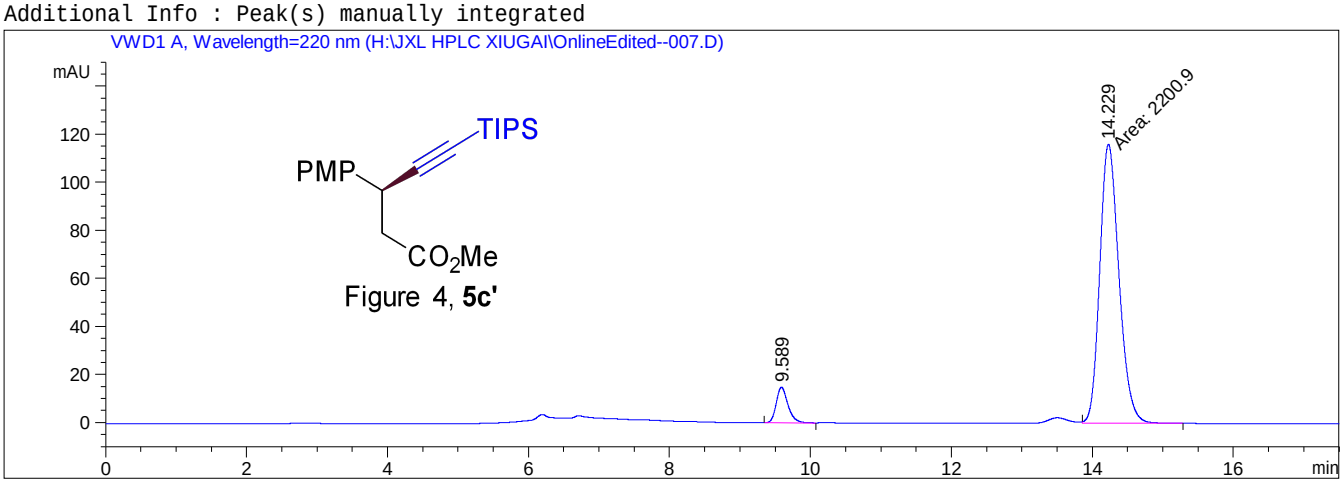
Figure 4, (±)-**5c'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.612 VB R  0.1765 2641.20361  227.43277  51.0177
   2  14.318 BB    0.2906 2535.82764  133.21794  48.9823

Totals :                  5177.03125  360.65071


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 271. HPLC spectra for compound (±)-**5c'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--007.D
Sample Name: JXL-03-137-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :   7
Acq. Instrument : HPLC-1260                     Location :   94
Injection Date  : 12/12/2020 10:27:40 PM            Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\1IPA-20-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 10:25:23 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:51:28 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.589 BB    0.1754  170.47371   14.79596   7.1888
   2  14.229 FM    0.3158 2200.89990  116.16302  92.8112

Totals :                  2371.37361  130.95898


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 272. HPLC spectra for compound **5c'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--032.D
Sample Name: JXL-02-95-3-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  32
Acq. Instrument : HPLC-1260                      Location :   71
Injection Date  : 12/13/2020 1:51:07 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-40-0.5-1-6-220-JXL.M
Last changed    : 12/12/2020 9:26:27 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\15IPA_30_8_4.M (Sequence Method)
Last changed    : 12/18/2020 3:18:06 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

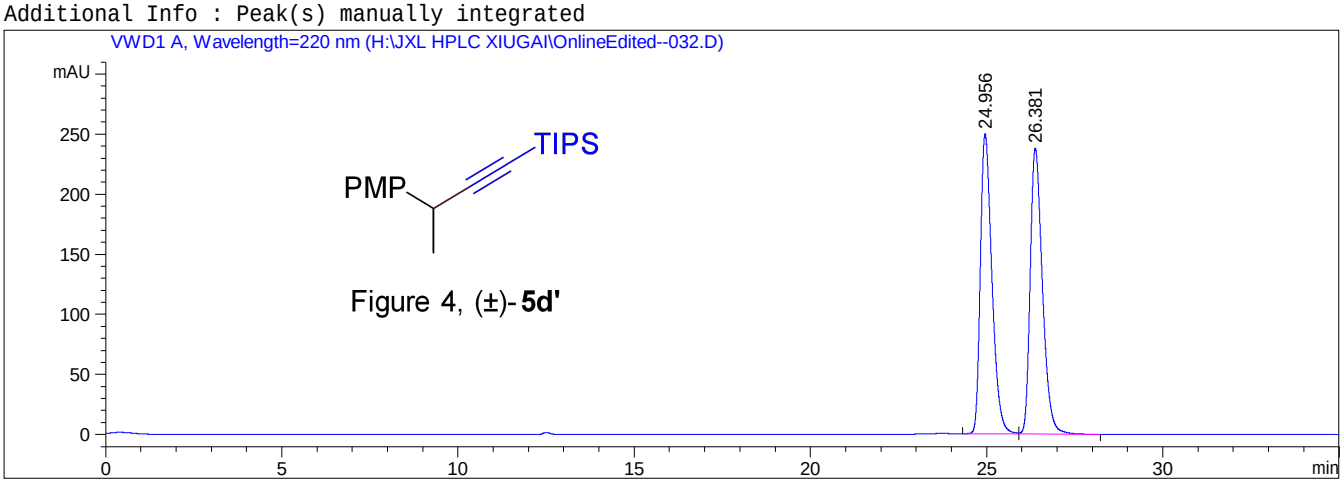


Figure 4, (±)-**5d'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.956 BV    0.3465 5686.15039  249.83354  49.7768
   2  26.381 VB    0.3651 5737.15039  238.07536  50.2232

Totals :                  1.14233e4   487.90891


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 273. HPLC spectra for compound (±)-**5d'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--041.D
Sample Name: JXL-03-132-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  41
Acq. Instrument : HPLC-1260                     Location :   72
Injection Date  : 12/13/2020 7:34:17 PM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-40-0.5-1-6-220-JXL.M
Last changed    : 12/13/2020 8:07:11 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 10:54:24 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

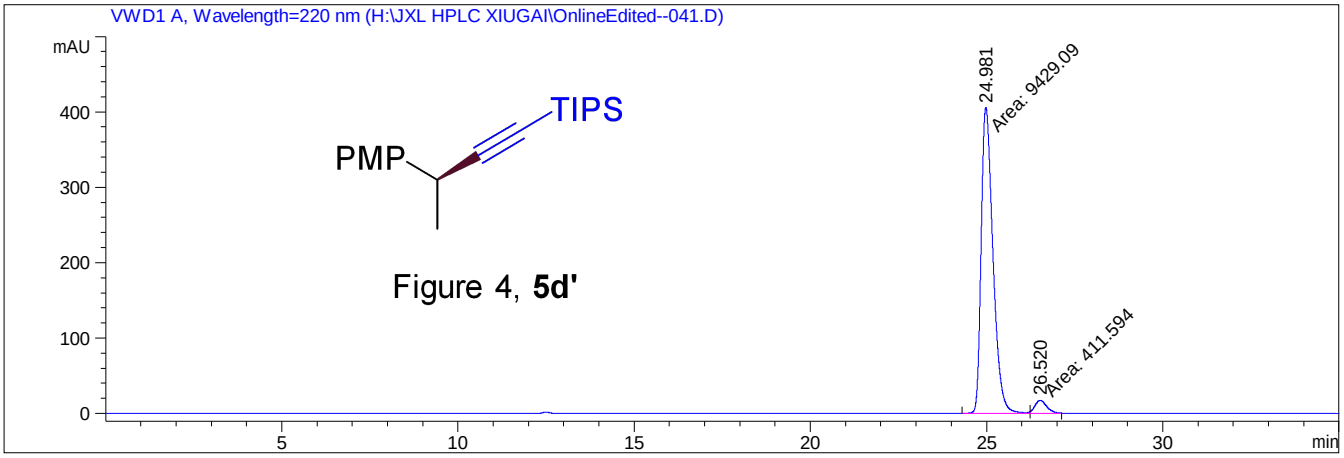


Figure 4, **5d'**

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.981 MF    0.3870 9429.09473  406.02753  95.8174
   2  26.520 FM    0.3954  411.59427   17.34928   4.1826

Totals :                  9840.68900  423.37681

==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 274. HPLC spectra for compound **5d'**

Data File H:\HPLC20210310\OnlineEdited--027.D
Sample Name: JXL-04-125-3-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  27
Acq. Instrument : HPLC-1260                      Location :   81
Injection Date  : 3/5/2021 8:58:56 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\ZHH\20210304\YH 2021-03-05 08-58-35\0IPA-45-0.5-1-2-220-JXL.M
Last changed    : 3/5/2021 9:34:52 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20210310\LC 2021-03-10 20-00-42\0IPA_30_0.5_2 H.M (Sequence Method)
Last changed    : 3/10/2021 10:33:44 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

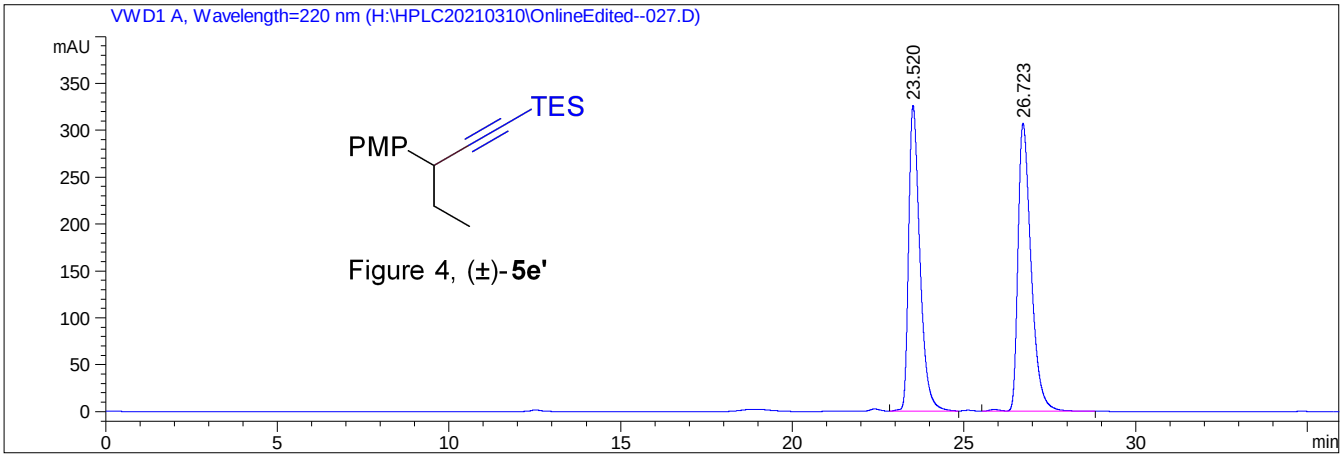


Figure 4, (±)-**5e'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.520 BB    0.3475 7443.00439  325.79547  47.6595
   2  26.723 VB R  0.3985 8174.02979  307.09445  52.3405

Totals :                  1.56170e4   632.88992


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 275. HPLC spectra for compound (±)-**5e'**

Data File H:\HPLC20210310\OnlineEdited--024.D
Sample Name: JXL-04-124-3-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  24
Acq. Instrument : HPLC-1260                      Location :  93
Injection Date  : 3/5/2021 7:09:43 PM                 Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\ZHH\20210304\YH 2021-03-05 08-58-35\0IPA-45-0.5-1-2-220-JXL.M
Last changed    : 3/5/2021 7:39:28 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20210310\LC 2021-03-10 20-00-42\0IPA_30_0.5_2 H.M (Sequence Method)
Last changed    : 3/10/2021 10:35:06 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

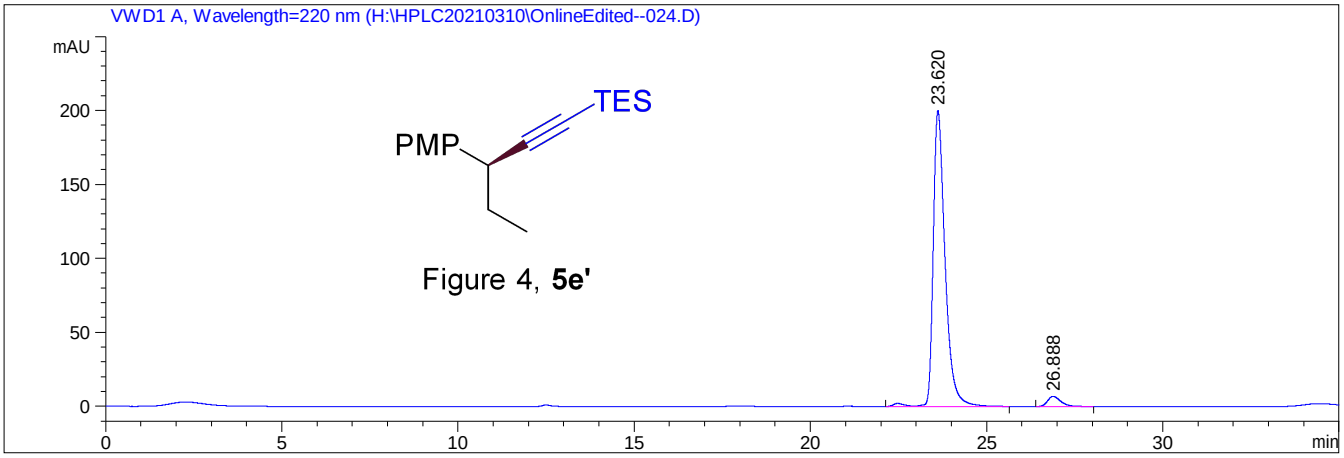


Figure 4, **5e'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.620 VB R  0.3499 4690.87891  200.07715  96.2894
   2  26.888 BB    0.3508  180.76852    6.95428   3.7106

Totals :                  4871.64743  207.03143


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 276. HPLC spectra for compound **5e'**

Data File H:\HPLC20210310\OnlineEdited--025.D
Sample Name: JXL-04-125-5-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  25
Acq. Instrument : HPLC-1260                      Location :   82
Injection Date  : 3/5/2021 7:46:06 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.700 µl
Acq. Method     : D:\ZHH\20210304\YH 2021-03-05 08-58-35\0IPA-45-0.5-1-2-220-JXL.M
Last changed    : 3/5/2021 7:39:28 PM by 系统
Analysis Method : E:\DATA\20210310\LC 2021-03-10 20-00-42\0IPA_30_0.5_2 H.M (Sequence Method)
Last changed    : 3/10/2021 10:36:25 PM by SYSTEM
                  (modified after loading)
```

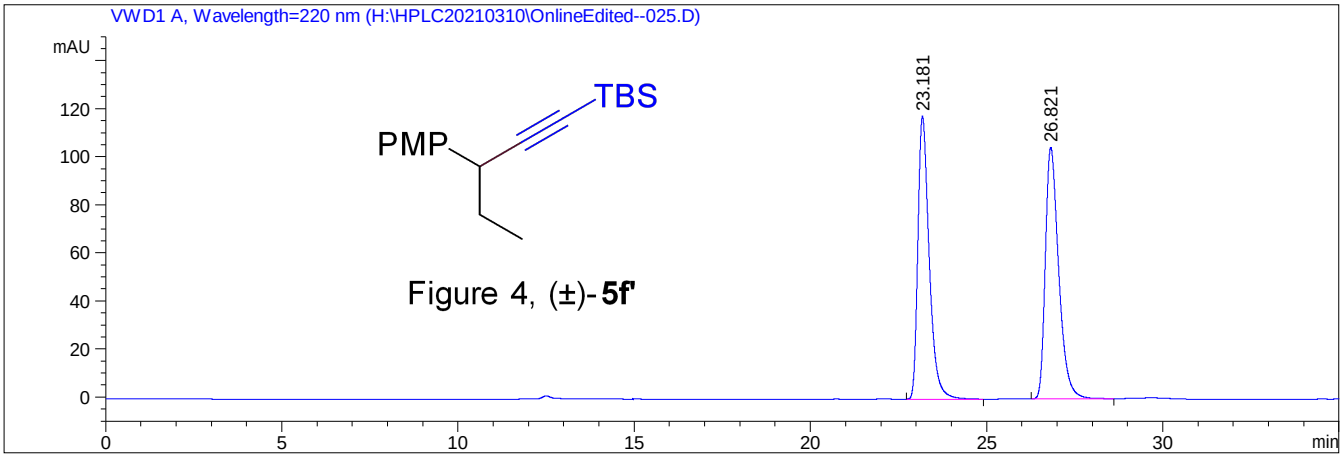


Figure 4, (±)-**5f'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.181 BB    0.3379 2628.45190  117.75947  48.7145
   2  26.821 BB    0.4016 2767.17554  104.77796  51.2855

Totals :                  5395.62744  222.53743


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 277. HPLC spectra for compound (±)-**5f'**

Data File H:\HPLC20210310\OnlineEdited--026.D
Sample Name: JXL-04-124-7-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  26
Acq. Instrument : HPLC-1260                      Location :   94
Injection Date  : 3/5/2021 8:22:32 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\ZHH\20210304\YH 2021-03-05 08-58-35\0IPA-45-0.5-1-2-220-JXL.M
Last changed    : 3/5/2021 7:39:28 PM by 系统
Analysis Method : E:\DATA\20210310\LC 2021-03-10 20-00-42\0IPA_30_0.5_2 H.M (Sequence Method)
Last changed    : 3/10/2021 10:37:09 PM by SYSTEM
                  (modified after loading)
```

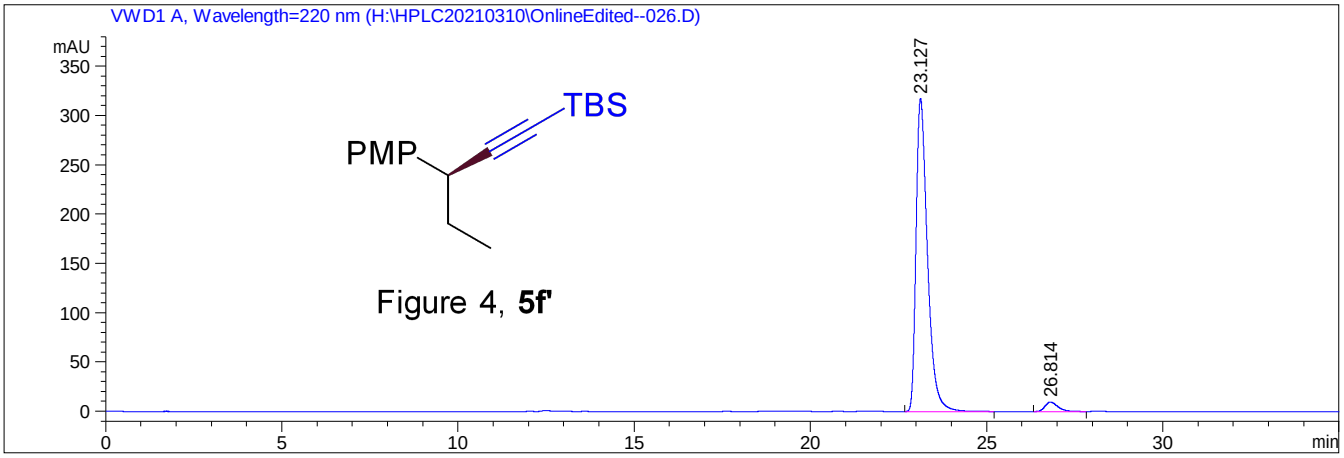


Figure 4, **5f'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.127 BB    0.3407 7151.65332  317.55710  96.6746
   2  26.814 BB    0.3599  245.99886    9.61679   3.3254

Totals :                  7397.65218  327.17389


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 278. HPLC spectra for compound **5f'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--015.D
Sample Name: JXL-03-148-1-OD(1)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  15
Acq. Instrument : HPLC-1260                      Location :   97
Injection Date  : 12/13/2020 2:21:41 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 8.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-40-0.8-1-6-220-JXL.M
Last changed    : 12/13/2020 1:42:46 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\15IPA_30_8_4.M (Sequence Method)
Last changed    : 12/18/2020 3:22:43 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

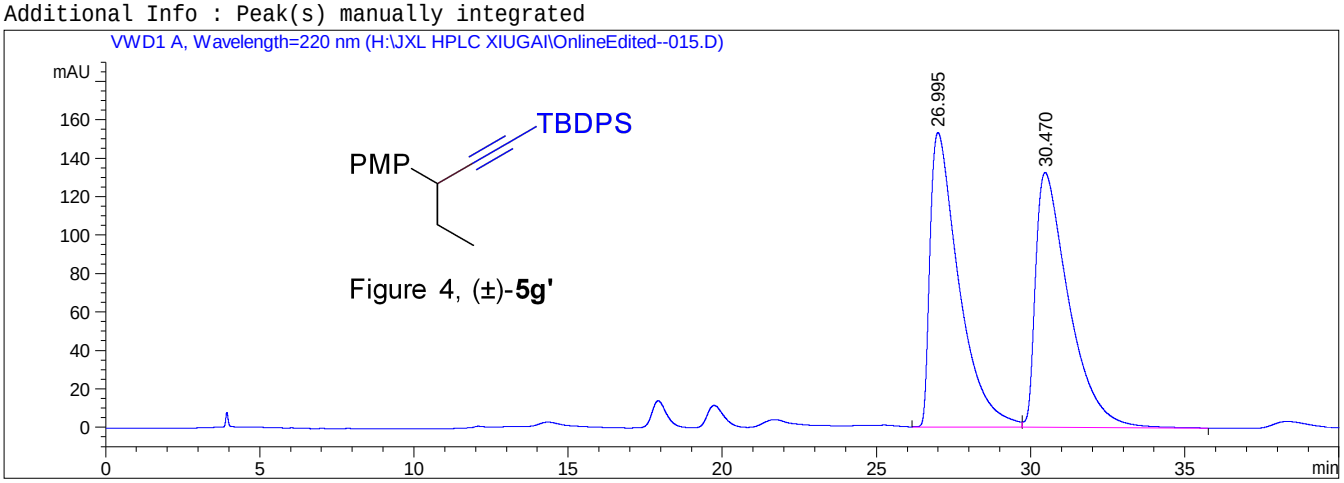


Figure 4, (±)-**5g'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.995 BV    0.9186 9964.35254  153.24321  50.1070
   2  30.470 VB    1.0340 9921.79297  132.51718  49.8930

Totals :                  1.98861e4   285.76039


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 279. HPLC spectra for compound (±)-**5g'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--014.D
Sample Name: JXL-03-154-2-OD(1)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  14
Acq. Instrument : HPLC-1260                      Location :   98
Injection Date  : 12/13/2020 1:40:07 AM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 5.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-40-0.8-1-6-220-JXL.M
Last changed    : 12/13/2020 1:42:46 AM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\6IPA_10_0.8_3.M (Sequence Method)
Last changed    : 12/15/2020 11:00:35 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

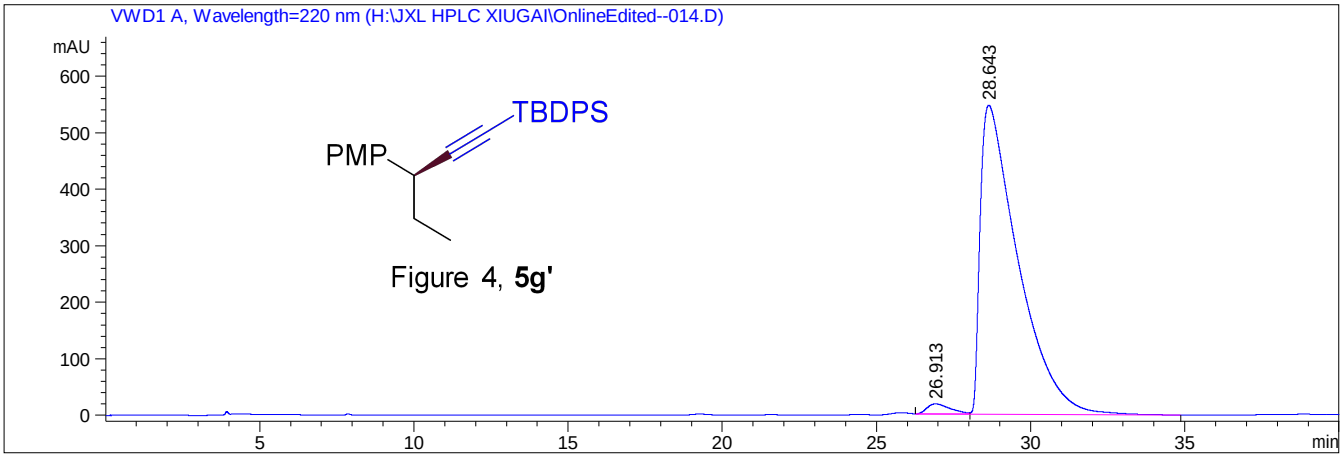


Figure 4, **5g'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.913 BV E  0.6800  925.29993   17.77107   1.9496
   2  28.643 VB R  1.1901 4.65365e4   546.39746  98.0504

Totals :                  4.74618e4   564.16853


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 280. HPLC spectra for compound **5g'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--027.D
Sample Name: JXL-03-126-7-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  27
Acq. Instrument : HPLC-1260                      Location :   75
Injection Date  : 12/13/2020 9:15:35 AM              Inj :   1
                                                Inj Volume : 3.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-60-0.5-1-6-220-JXL.M
Last changed    : 12/13/2020 10:16:07 AM by 系统
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\15IPA_30_8_4.M
Last changed    : 12/19/2020 9:38:39 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

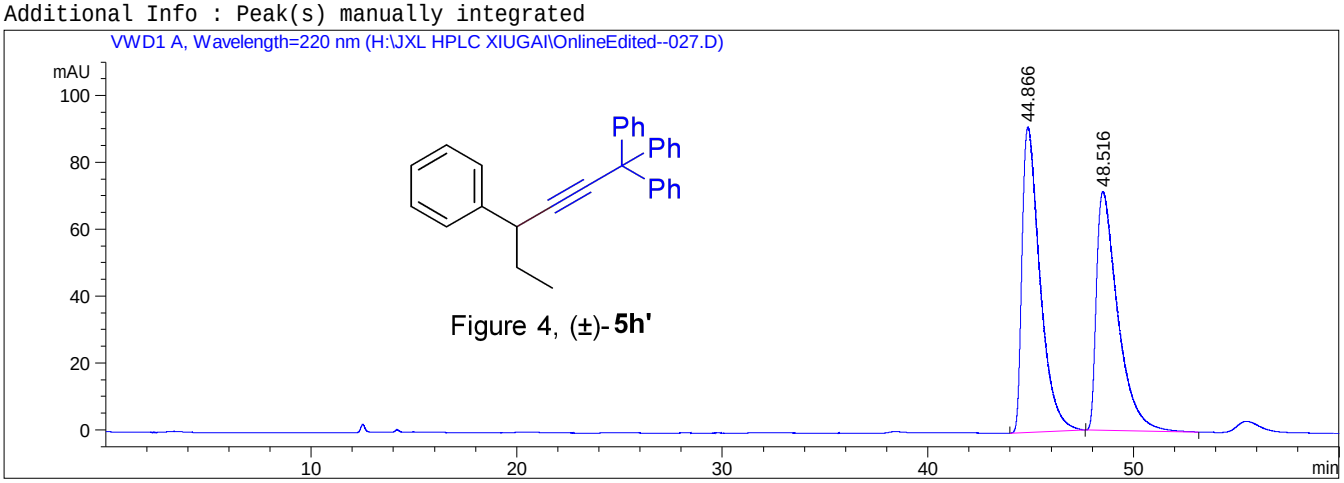


Figure 4, (±)-**5h'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  44.866 BB    0.8906 5530.87402   91.31907  51.8735
   2  48.516 BB    1.0003 5131.35156   71.41467  48.1265

Totals :                  1.06622e4   162.73374


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 281. HPLC spectra for compound (±)-**5h'**

Data File H:\JXL HPLC XIUGAI\OnlineEdited--038.D
Sample Name: JXL-03-145-1-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  38
Acq. Instrument : HPLC-1260                      Location :  76
Injection Date  : 12/13/2020 5:29:55 PM               Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 6.000 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-12 20-24-28\0IPA-60-0.5-1-6-220-JXL.M
Last changed    : 12/13/2020 11:18:35 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\10IPA_20_1.0_4.ZWJ.M (Sequence
                  Method)
Last changed    : 12/16/2020 10:24:22 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

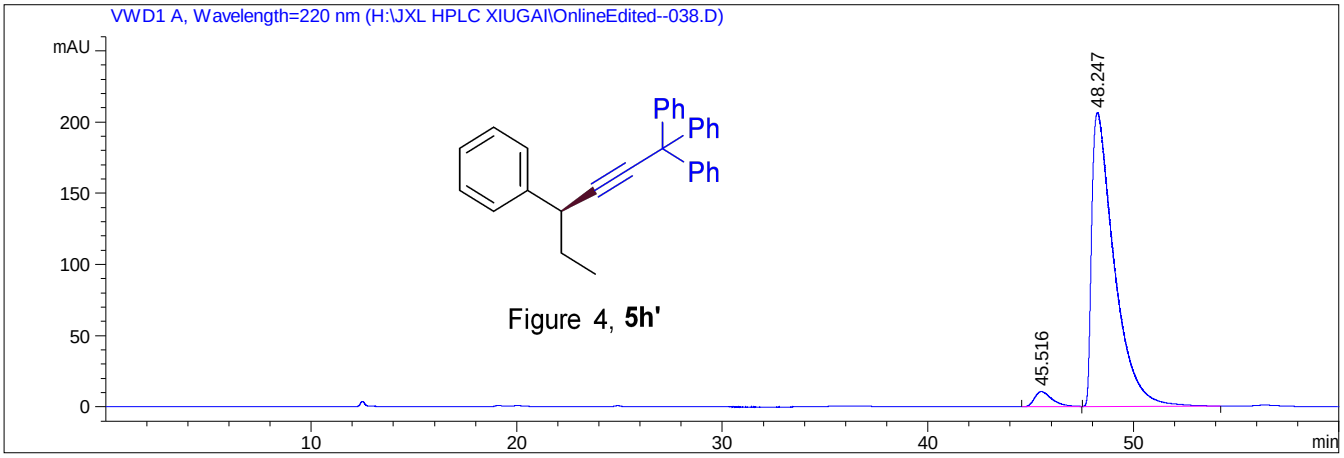


Figure 4, **5h'**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  45.516 BB    0.6972  631.42139   10.64241   3.8816
   2  48.247 BB    1.0764 1.56356e4   206.36812  96.1184

Totals :                  1.62670e4   217.01053

=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 282. HPLC spectra for compound **5h'**

Data File H:\JXL HPLC\JXL-03-136-2-OD(2)-RAC.D
Sample Name: JXL-03-136-2-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  51
Acq. Instrument : HPLC-1260                     Location :   76
Injection Date  : 9/4/2020 10:05:01 AM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.600 µl
Acq. Method     : D:\JXL\20200902\YH 2020-09-02 16-57-48\0IPA-50-0.5-1-6-220-JXL.M
Last changed    : 9/4/2020 10:33:34 AM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\10IPA_20_1.0_4.ZWJ.M (Sequence
                  Method)
Last changed    : 12/16/2020 10:29:15 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

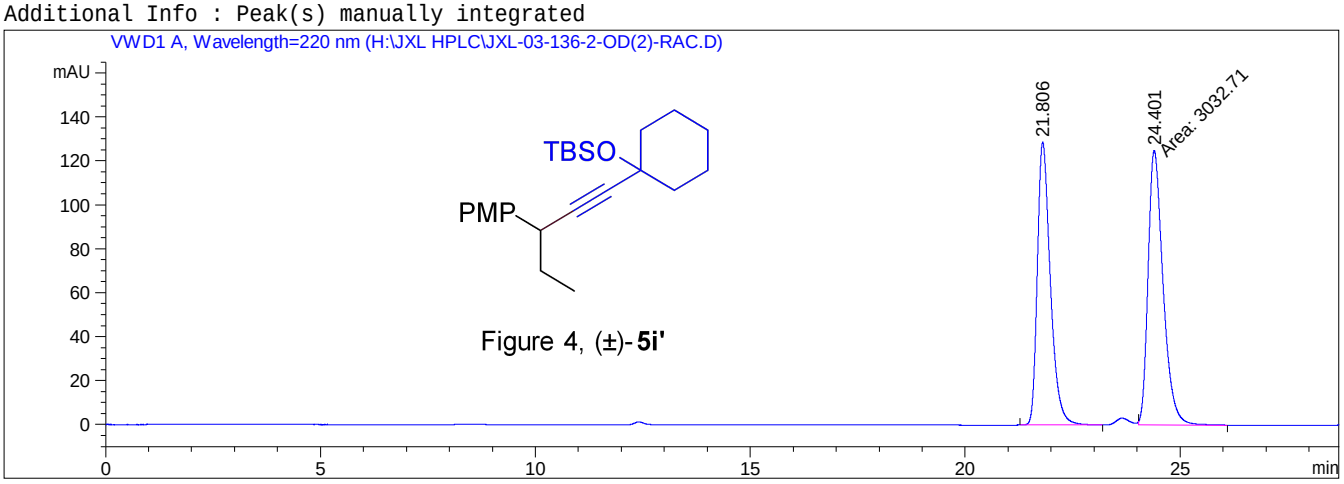


Figure 4, (±)-**5i'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.806 BB    0.3197 2708.47876  128.85146  47.1763
   2  24.401 FM    0.4045 3032.70752  124.94582  52.8237

Totals :                  5741.18628  253.79727


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 283. HPLC spectra for compound (±)-**5i'**

Data File H:\JXL HPLC\JXL-03-146-1-OD(2)-EE.D
Sample Name: JXL-03-146-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  90
Acq. Instrument : HPLC-1260                     Location :   81
Injection Date  : 9/8/2020 1:06:59 AM                Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\zy\20200906\YH 2020-09-06 12-21-16\0IPA-50-0.5-1-6-220-JXL.M
Last changed    : 9/8/2020 12:10:11 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\15IPA_30_8_4.M (Sequence Method)
Last changed    : 12/18/2020 3:26:55 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

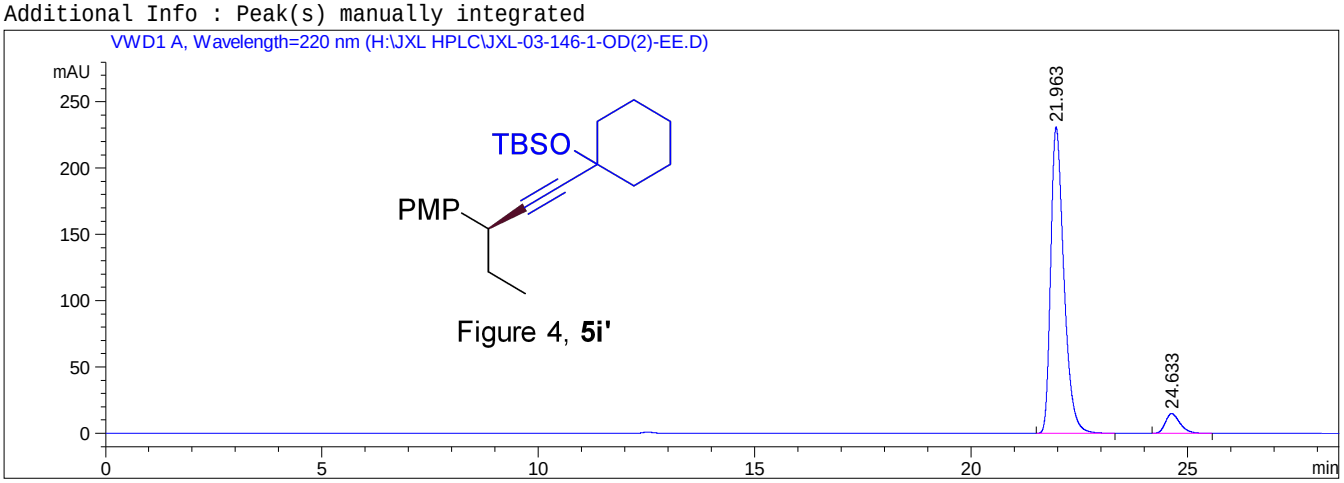


Figure 4, **5i'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.963 BB    0.3228 4895.04541  230.91272  93.3120
   2  24.633 BB    0.3485  350.84473   14.96423   6.6880

Totals :                  5245.89014  245.87695


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 284. HPLC spectra for compound **5i'**

Data File H:\JXL HPLC\JXL-03-183-2-CHUNHUA-RAC-OD(2).D
Sample Name: JXL-03-183-2-CHUNHUA-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  69
Acq. Instrument : HPLC-1260                     Location :   73
Injection Date  : 10/31/2020 4:30:26 AM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\0.5IPA-60-0.5-1-6-220-JXL.M
Last changed    : 10/30/2020 11:25:02 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-18 10-52-42\15IPA_30_8_4.M (Sequence Method)
Last changed    : 12/18/2020 3:29:11 PM by SYSTEM
                  (modified after loading)
```

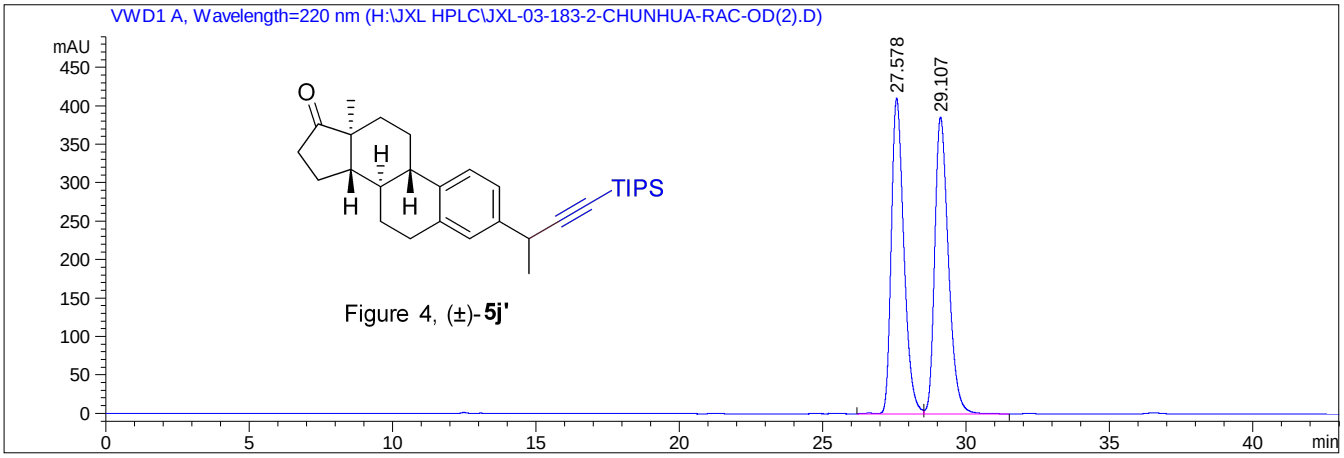


Figure 4, (±)-**5j'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.578 VV R  0.4689 1.25377e4   410.39276  49.5354
   2  29.107 VB    0.5077 1.27729e4   385.89130  50.4646

Totals :                  2.53106e4   796.28406


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 285. HPLC spectra for compound (±)-**5j'**

Data File H:\JXL HPLC\JXL-03-186-1-OD(2)-dr.D
Sample Name: JXL-03-186-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  70
Acq. Instrument : HPLC-1260                     Location :   71
Injection Date  : 10/31/2020 5:31:56 AM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\0.5IPA-60-0.5-1-6-220-JXL.M
Last changed    : 10/30/2020 11:25:02 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\10IPA_20_1.0_4.ZWJ.M (Sequence
                  Method)
Last changed    : 12/16/2020 10:35:31 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

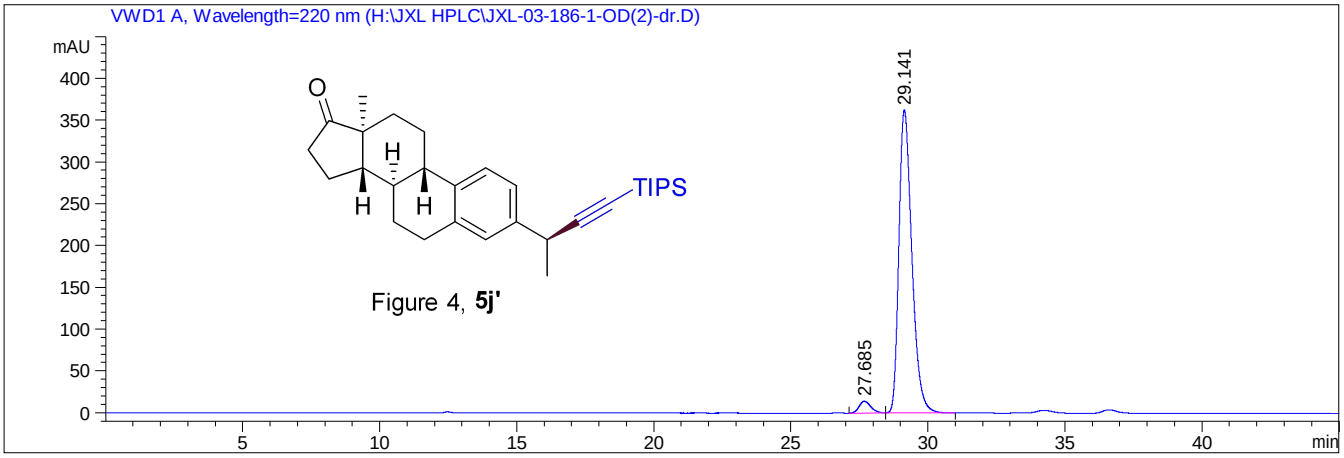


Figure 4, **5j'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.685 BB    0.4149  415.06985   14.10046   3.3649
   2  29.141 BB    0.5068 1.19203e4   362.34137  96.6351

Totals :                  1.23354e4   376.44183

==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 286. HPLC spectra for compound **5j'**

Data File H:\JXL HPLC\JXL-03-189-1-OD(2)-dr.D
Sample Name: JXL-03-189-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  71
Acq. Instrument : HPLC-1260                     Location :   72
Injection Date  : 10/31/2020 6:33:24 AM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.500 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\0.5IPA-60-0.5-1-6-220-JXL.M
Last changed    : 10/30/2020 11:25:02 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\10IPA_20_1.0_4.ZWJ.M (Sequence
                  Method)
Last changed    : 12/16/2020 10:38:02 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

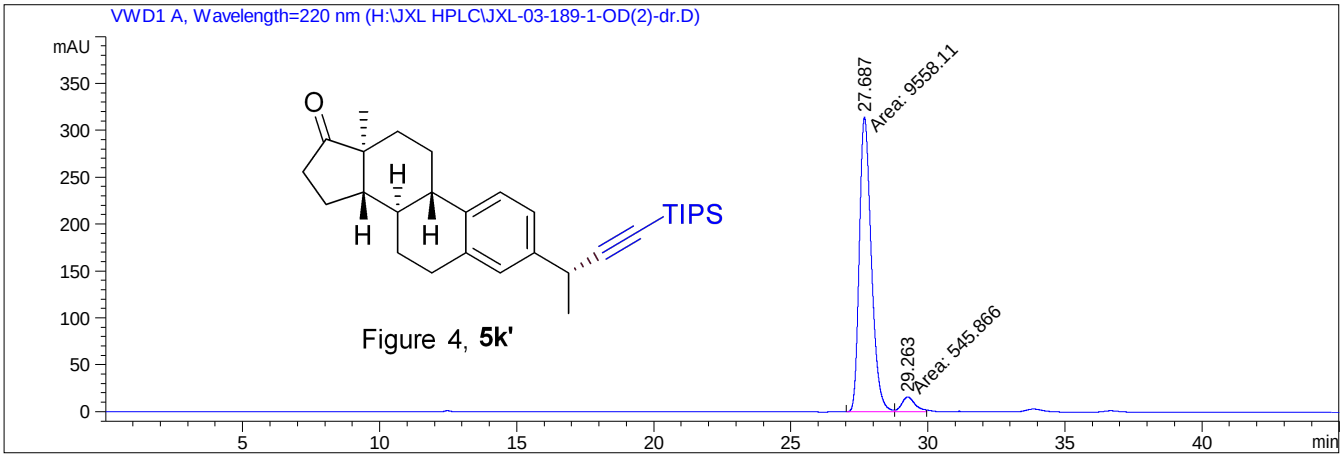


Figure 4, **5k'**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.687 MF    0.5074 9558.11328  313.93344  94.5975
   2  29.263 MF    0.5734  545.86591   15.86660   5.4025

Totals :                  1.01040e4   329.80004


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 287. HPLC spectra for compound (±)-**5k'**

Data File H:\HPLC20210310\OnlineEdited--020.D
Sample Name: HB-04-48-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  20
Acq. Instrument : HPLC-1260                     Location :   91
Injection Date  : 3/9/2021 4:31:46 PM           Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\ZHH\20210309\YH 2021-03-09 10-26-38\1IPA-30-0.5-1-2-220-JXL .M
Last changed    : 3/9/2021 4:13:51 PM by 系统
Analysis Method : E:\DATA\20210310\LC 2021-03-10 20-00-42\0IPA_30_0.5_2 H.M (Sequence Method)
Last changed    : 3/10/2021 10:29:41 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

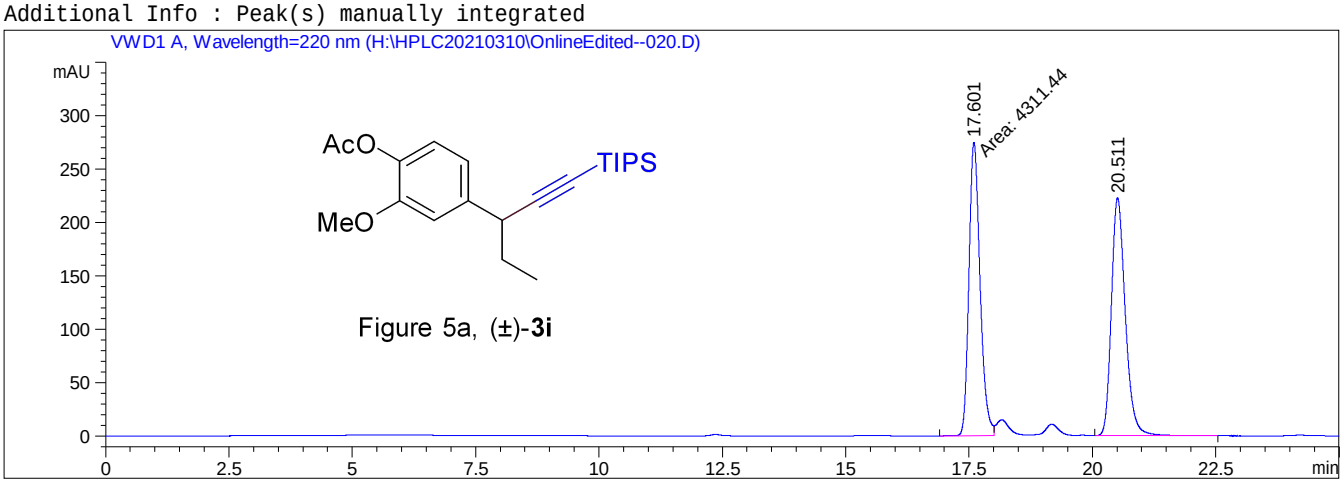


Figure 5a, (±)-**3i**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.601 MF    0.2615 4311.43701  274.81775  49.6585
   2  20.511 BB    0.3011 4370.74121  222.61029  50.3415

Totals :                  8682.17822  497.42804


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 288. HPLC spectra for compound (±)-**3i**

Data File H:\HPLC20210310\OnlineEdited--022.D
Sample Name: JXL-04-128-5-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  22
Acq. Instrument : HPLC-1260                      Location :   92
Injection Date  : 3/9/2021 5:34:34 PM                 Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.800 µl
Acq. Method     : D:\ZHH\20210309\YH 2021-03-09 10-26-38\1IPA-30-0.5-1-2-220-JXL .M
Last changed    : 3/9/2021 4:13:51 PM by 系统
Analysis Method : E:\DATA\20210310\LC 2021-03-10 20-00-42\0IPA_30_0.5_2 H.M (Sequence Method)
Last changed    : 3/10/2021 10:31:15 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

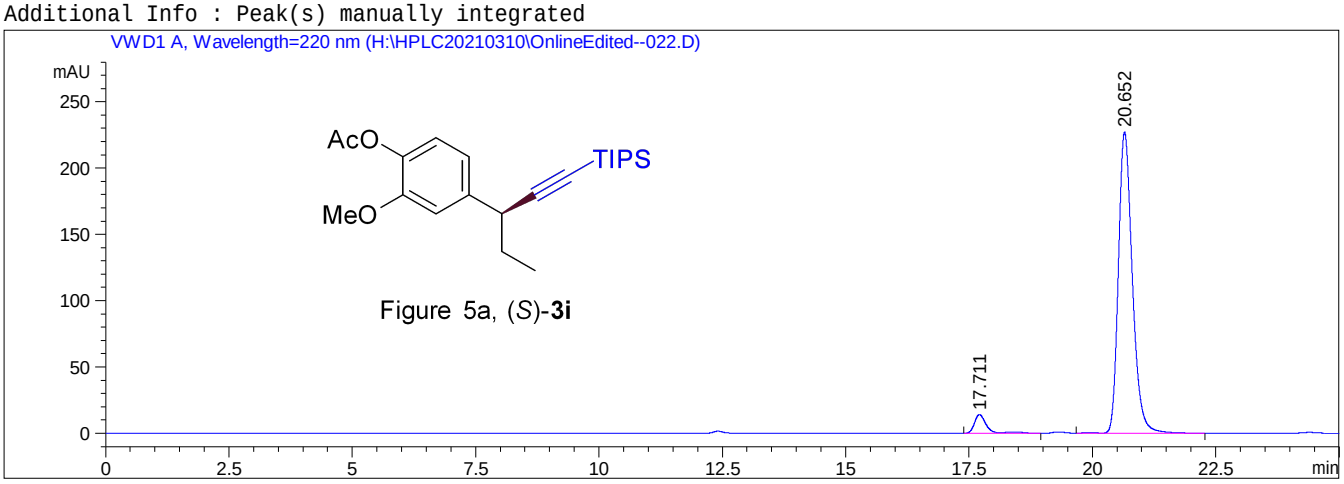


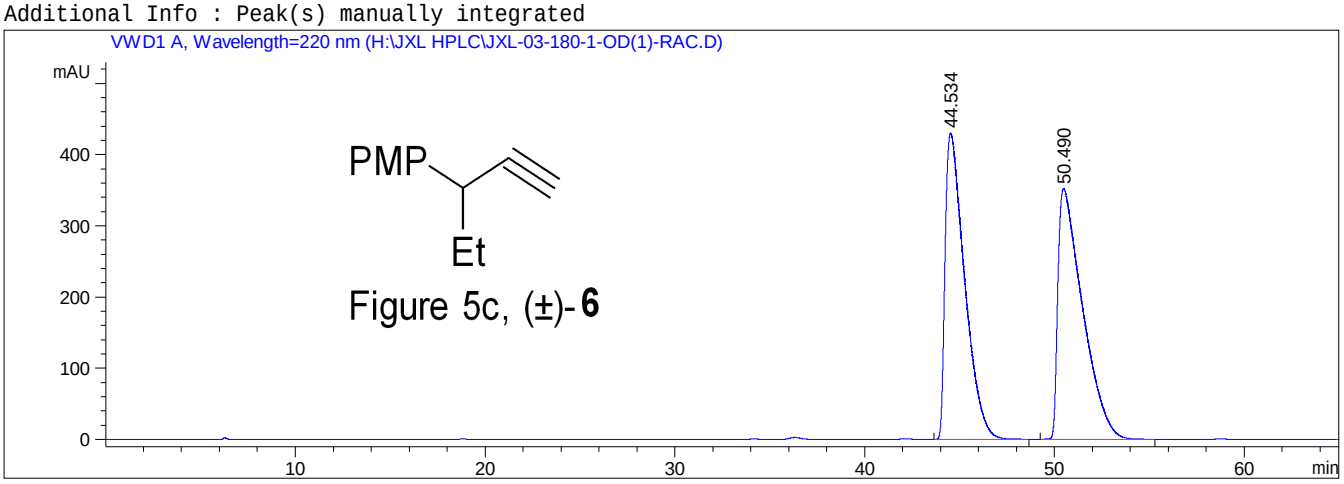
Figure 5a, (*S*)-**3i**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.711 BV R  0.2603  247.38464   14.19770   5.2441
   2  20.652 VB R  0.3020 4470.03857  227.23535  94.7559

Totals :                  4717.42322  241.43305


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 289. HPLC spectra for compound (*S*)-**3i**

Data File H:\JXL HPLC\JXL-03-180-1-OD(1)-RAC.D
Sample Name: JXL-03-180-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  13
Acq. Instrument : HPLC-1260                     Location :   82
Injection Date  : 10/1/2020 7:46:18 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : D:\zy\20200930\YH 2020-10-01 14-39-42\0IPA-80-0.5-1-6-220-JXL.M
Last changed    : 10/1/2020 8:42:50 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M (
                  Sequence Method)
Last changed    : 12/16/2020 10:51:17 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

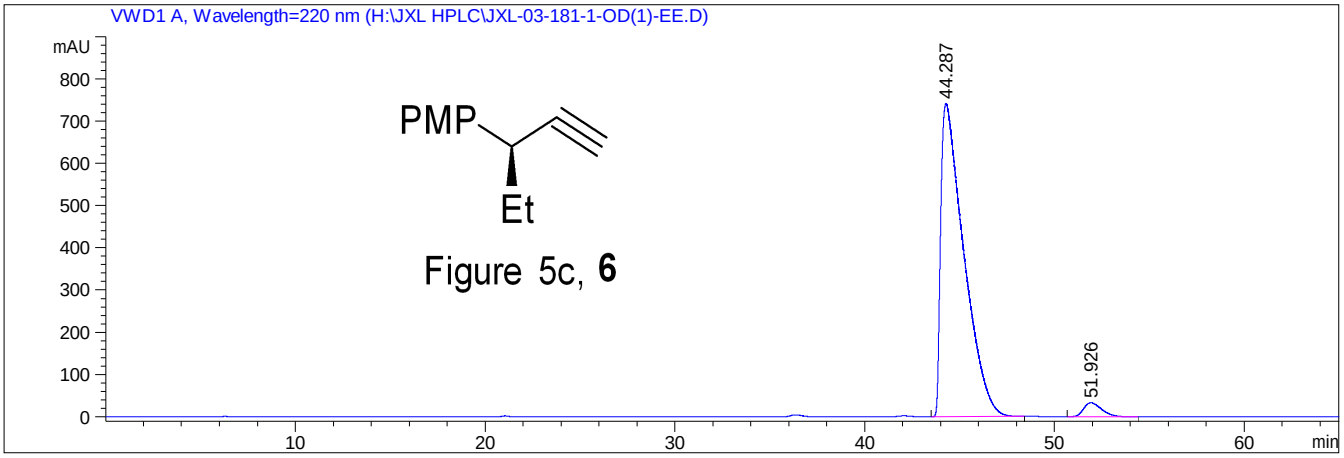



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  44.534 BB    1.0287 3.06876e4   430.47202  49.1524
   2  50.490 BB    1.2161 3.17460e4   352.04309  50.8476

Totals :                  6.24336e4   782.51511


==========================================================================
                        *** End of Report ***
```


Supplementary Fig. 290. HPLC spectra for compound (±)-**6**

Data File H:\JXL HPLC\JXL-03-181-1-OD(1)-EE.D
Sample Name: JXL-03-181-1-OD(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  14
Acq. Instrument : HPLC-1260                     Location :   83
Injection Date  : 10/1/2020 8:52:42 PM               Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 1.500 µl
Acq. Method     : D:\zy\20200930\YH 2020-10-01 14-39-42\0IPA-80-0.5-1-6-220-JXL.M
Last changed    : 10/1/2020 8:42:50 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M (
                  Sequence Method)
Last changed    : 12/16/2020 10:54:09 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  44.287 BB    1.1729 6.26115e4   741.29761  96.5824
   2  51.926 BB    0.7805 2215.55591   33.26823   3.4176

Totals :                  6.48271e4   774.56584

==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 291. HPLC spectra for compound **6**

Data File H:\JXL HPLC\JXL-04-20-1-Click-RAC-IC(1).D
Sample Name: JXL-04-20-1-Click-RAC-IC(1)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 157
Acq. Instrument : HPLC-1260                      Location :  93
Injection Date  : 11/1/2020 10:51:34 PM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 8.000 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\20IPA-60-0.8-1-2-254-JXL.M
Last changed    : 10/30/2020 11:10:37 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M (
                  Sequence Method)
Last changed    : 12/16/2020 10:55:36 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

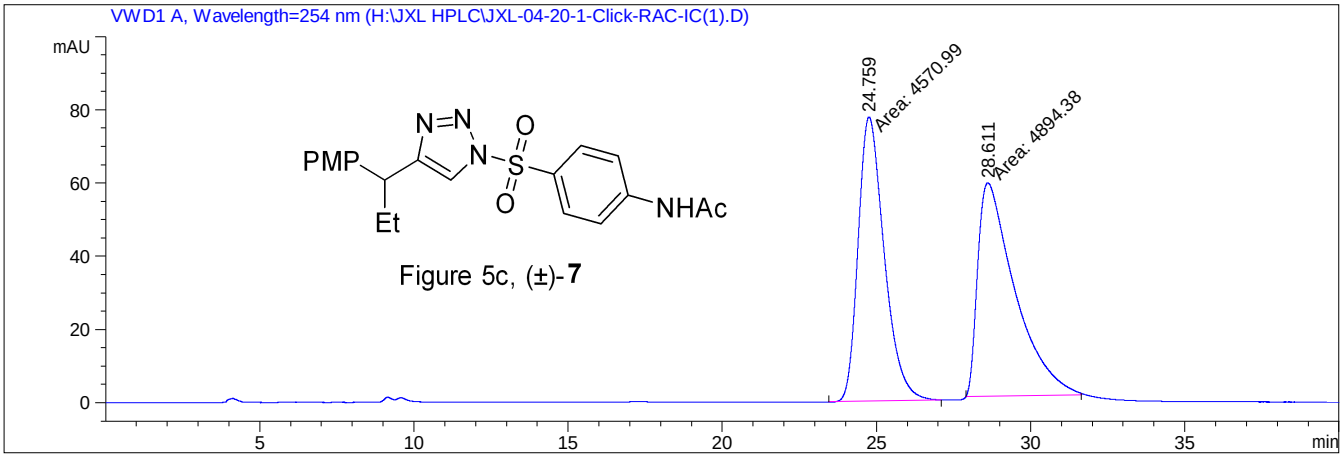


Figure 5c, (±)-**7**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.759 MM    0.9815 4570.99170   77.61681  48.2917
   2  28.611 MM    1.3984 4894.38379   58.33504  51.7083

Totals :                  9465.37549  135.95186


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 292. HPLC spectra for compound (±)-**7**

Data File H:\JXL HPLC\JXL-04-20-1-Click-EE-IC(1).D
Sample Name: JXL-04-20-1-Click-EE-IC(1)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line : 158
Acq. Instrument : HPLC-1260                      Location :  94
Injection Date  : 11/1/2020 11:33:06 PM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 8.000 µl
Acq. Method     : D:\G527\FZ\20201026\YH 2020-10-29 08-35-49\20IPA-60-0.8-1-2-254-JXL.M
Last changed    : 10/30/2020 11:10:37 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-29 20-00-48\15IPA_20_8_4.M (Sequence Method)
Last changed    : 12/31/2020 11:53:19 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

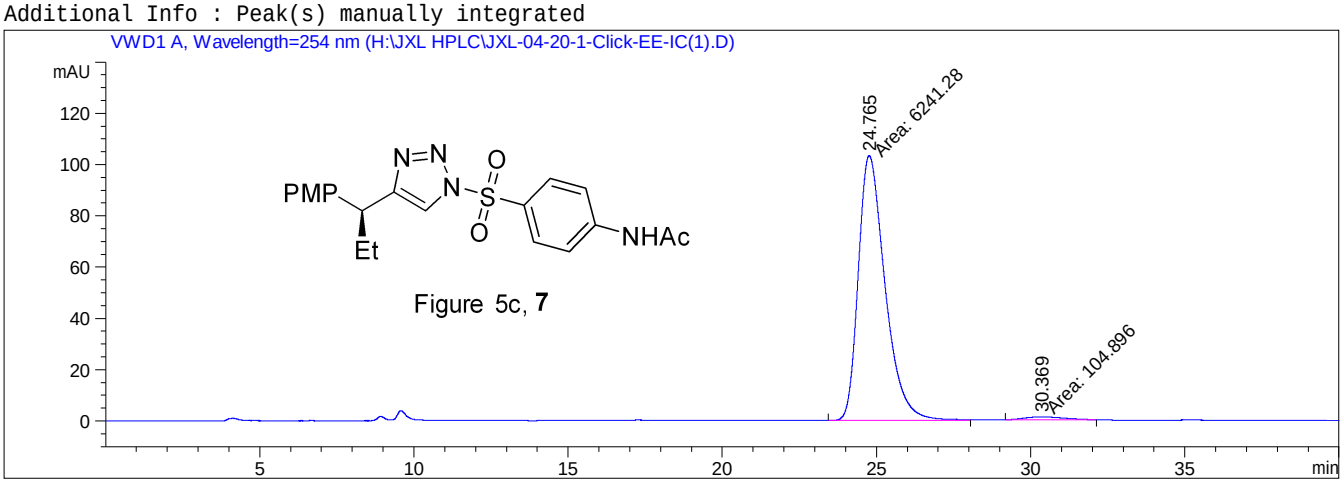


Figure 5c, **7**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.765 MF    1.0067 6241.28369  103.32697  98.3471
   2  30.369 MM    1.4662  104.89571    1.19238   1.6529

Totals :                  6346.17941  104.51934


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 293. HPLC spectra for compound **7**

Data File E:\DATA\20201027\LC 2020-11-24 17-29-49\OnlineEdited--059.D
Sample Name: JXL-04-47-1-IC(1)-RAC

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  59
Acq. Instrument : HPLC1260                       Location :   P2-B1
Injection Date  : 11/25/2020 4:28:55 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M
Last changed    : 11/25/2020 5:10:38 PM by SYSTEM
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:01:36 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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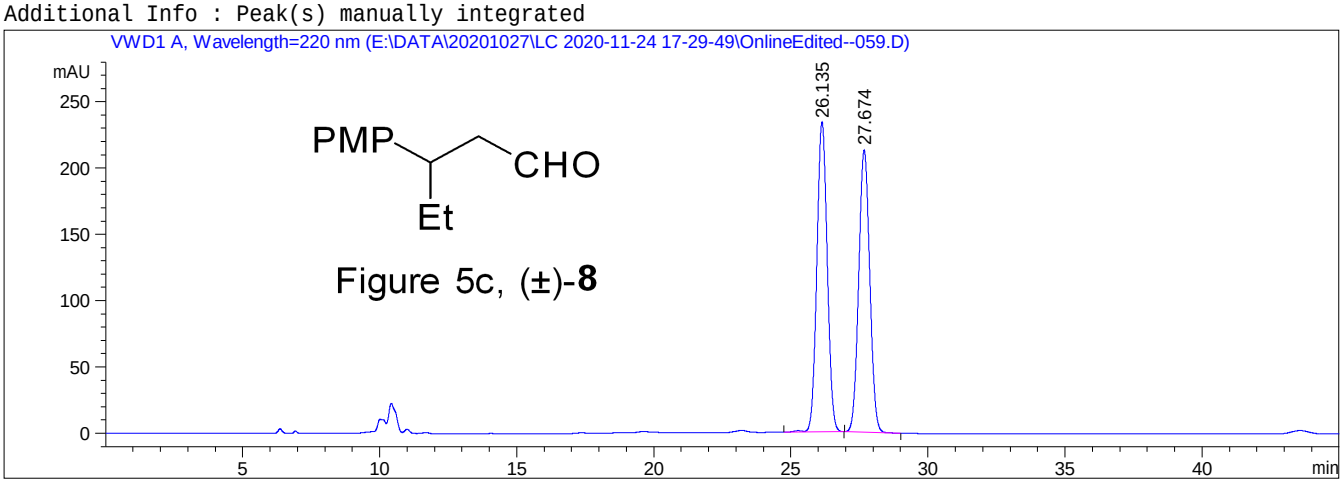

Figure 5c, (±)-**8**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.135 VB R  0.4109 6170.07764  233.78003  50.8392
   2  27.674 BB    0.4379 5966.36768  212.94882  49.1608

Totals :                  1.21364e4   446.72885


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 294. HPLC spectra for compound (±)-**8**

Data File E:\DATA\20201027\LC 2020-11-24 17-29-49\OnlineEdited--060.D
Sample Name: JXL-04-47-2-IC(1)-EE

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  60
Acq. Instrument : HPLC1260                       Location :   P2-B2
Injection Date  : 11/25/2020 5:14:38 PM               Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M
Last changed    : 11/25/2020 5:10:38 PM by SYSTEM
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:01:36 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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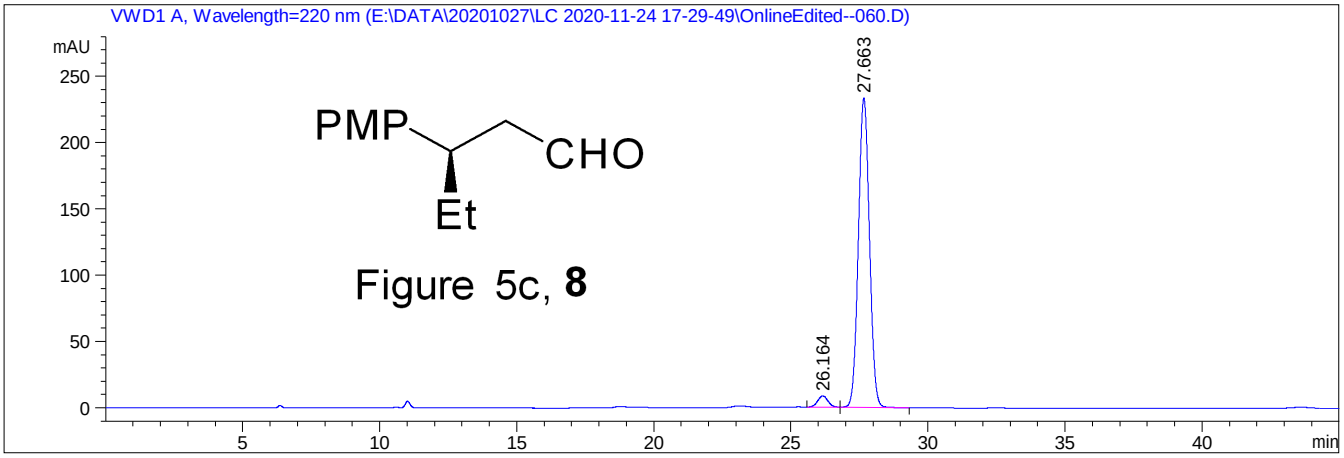

Figure 5c, **8**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.164 BB    0.4043  217.16803    8.40917   3.2146
   2  27.663 BB    0.4369 6538.50342  233.36398  96.7854

Totals :                  6755.67145  241.77315


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 295. HPLC spectra for compound **8**

Data File H:\JXL HPLC\JXL-DIBAL-OD(2)-RAC.D
Sample Name: JXL-DIBAL-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line : 111
Acq. Instrument : HPLC-1260                     Location :  91
Injection Date  : 10/16/2020 2:02:41 AM              Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\G527\FZ\20201013\YH 2020-10-13 08-36-19\0IPA-40-0.5-1-2-220-JXL.M
Last changed    : 10/15/2020 11:27:15 PM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\10IPA_20_1.0_4.ZWJ.M (Sequence
                  Method)
Last changed    : 12/16/2020 10:39:43 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

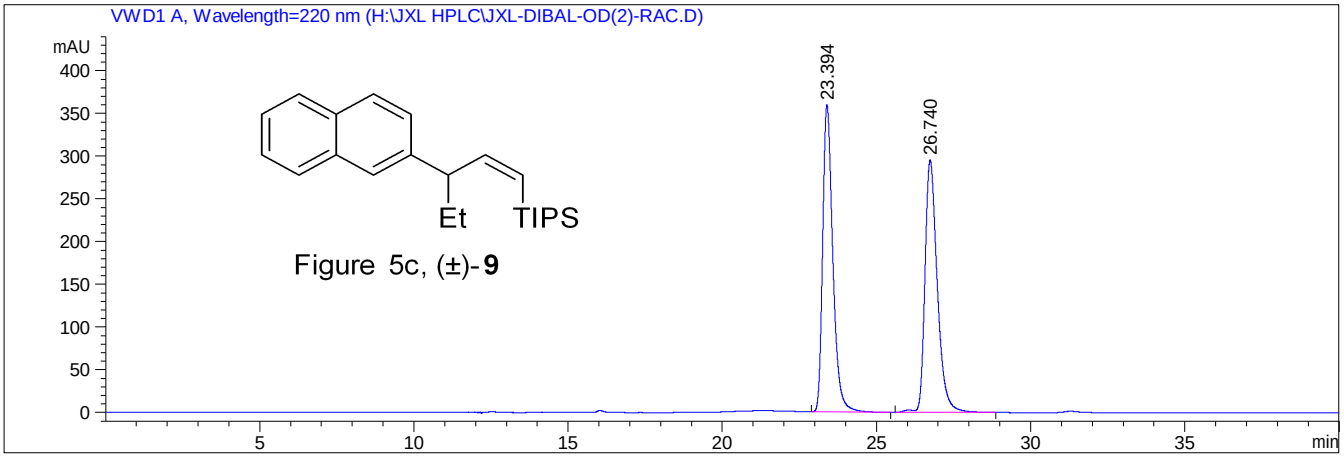

Figure 5c, (±)-**9**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.394 BB    0.3493 8235.24219  359.38779  50.0443
   2  26.740 VB R  0.4200 8220.66504  295.71948  49.9557

Totals :                  1.64559e4   655.10727


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 296. HPLC spectra for compound (±)-**9**

Data File H:\JXL HPLC\DIBAL-H(XIN)-OD(2).D
Sample Name: DIBAL-H(XIN)-OD(2)

```
==================================================================
Acq. Operator   : 系统                          Seq. Line :  26
Acq. Instrument : HPLC-1260                      Location :  93
Injection Date  : 11/6/2020 10:32:36 PM             Inj :  1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.200 µl
Acq. Method     : D:\G527\FZ\20201106\YH 2020-11-06 09-03-38\0IPA-40-0.5-1-6-220-JXL.M
Last changed    : 11/6/2020 11:03:43 PM by 系统
                  (modified after loading)
Analysis Method : E:\DATA\20201027\LC 2020-12-15 14-02-17\10IPA_20_1.0_4.ZWJ.M (Sequence
                  Method)
Last changed    : 12/16/2020 10:41:24 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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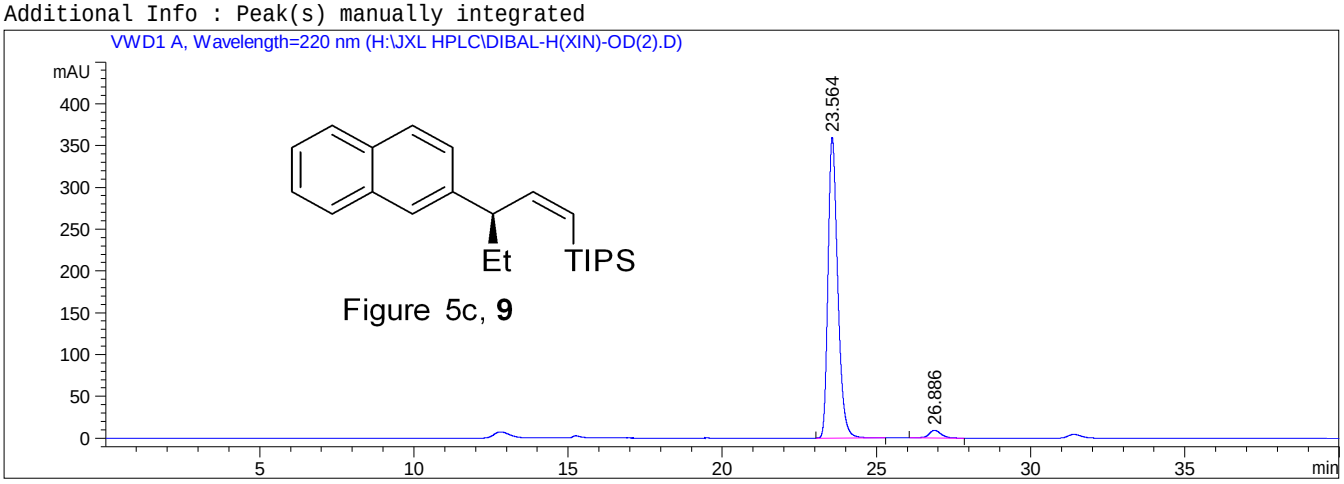

Figure 5c, **9**

```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.564 BB    0.3336 7883.77832  359.83118  96.8967
   2  26.886 BB    0.3775  252.49660    9.36688   3.1033

Totals :                  8136.27492  369.19806


==================================================================
                        *** End of Report ***
```


Supplementary Fig. 297. HPLC spectra for compound **9**

Data File E:\DATA\20201027\LC 2020-11-25 23-35-05\OnlineEdited--009.D
Sample Name: JXL-XYH-02-24-1-AD(1)-RAC

```
======================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   9
Acq. Instrument : HPLC1260                          Location :   P2-B5
Injection Date  : 11/26/2020 4:53:04 AM                Inj :   1
                                                  Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 6.000 µl
Acq. Method     : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M
Last changed    : 11/26/2020 12:35:05 AM by SYSTEM
Analysis Method : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M (
                  Sequence Method)
Last changed    : 12/18/2020 3:32:57 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

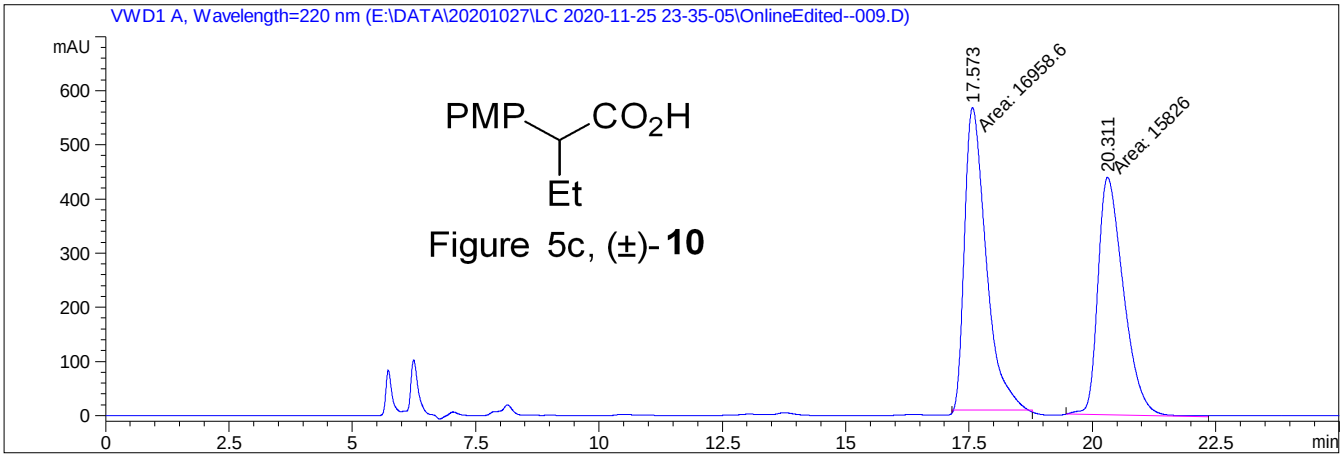

Figure 5c, (±)-**10**

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.573 MM    0.5064 1.69586e4   558.18024  51.7273
   2  20.311 PM    0.6016 1.58260e4   438.45648  48.2727

Totals :                  3.27845e4   996.63672

======================================================================
                        *** End of Report ***
```


Supplementary Fig. 298. HPLC spectra for compound (±)-**10**

Data File E:\DATA\20201027\LC 2020-11-25 23-35-05\OnlineEdited--003.D
Sample Name: JXL-XYH-02-27-AD(1)-EE

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : HPLC1260                       Location :   P2-B1
Injection Date  : 11/26/2020 12:48:22 AM              Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 2.000 µl
Acq. Method     : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M
Last changed    : 11/26/2020 12:35:05 AM by SYSTEM
Analysis Method : E:\DATA\20201027\LC 2020-11-25 23-35-05\10IPA-60-0.5-220-4-JXL TFA.M (
                  Sequence Method)
Last changed    : 12/16/2020 10:49:52 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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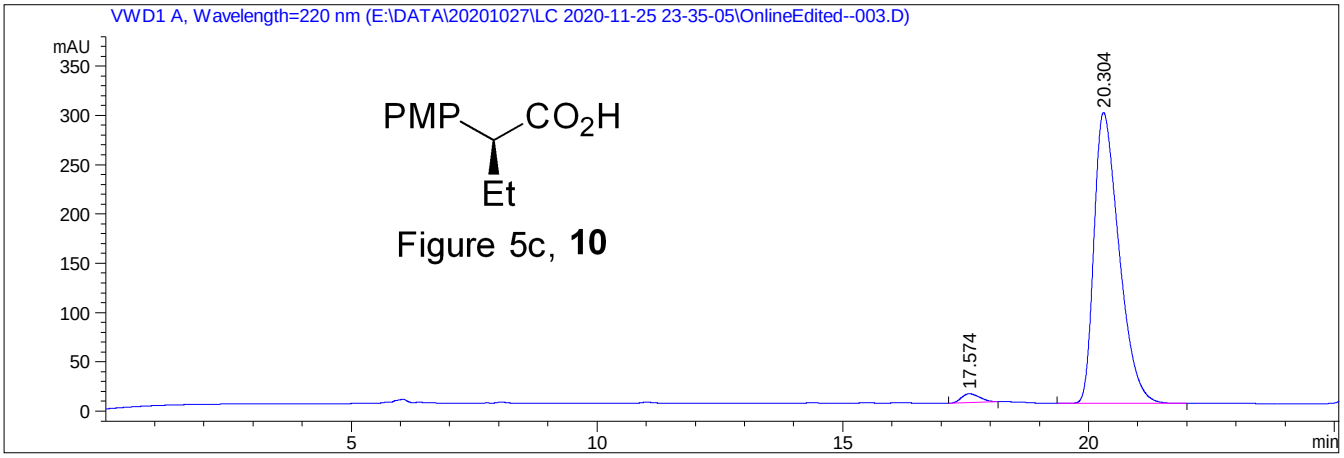

Figure 5c, **10**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.574 BB    0.4057  230.44807    9.00215   2.1554
   2  20.304 BB    0.5433 1.04610e4   295.26358  97.8446

Totals :                  1.06914e4   304.26573

=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 299. HPLC spectra for compound **10**

Data File H:\JXL HPLC\JXL-04-55-2-OD(2)-RAC.D
Sample Name: JXL--04-55-2-OD(2)

```
=====================================================================
Acq. Operator   : 系统                          Seq. Line :  62
Acq. Instrument : HPLC-1260                      Location :   91
Injection Date  : 12/11/2020 6:39:59 AM              Inj :   1
                                                Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20201127\YH 2020-12-10 10-05-55\0IPA-40-0.5-1-6-220-JXL.M
Last changed    : 12/11/2020 12:15:19 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:05:22 AM by SYSTEM
                  (modified after loading)
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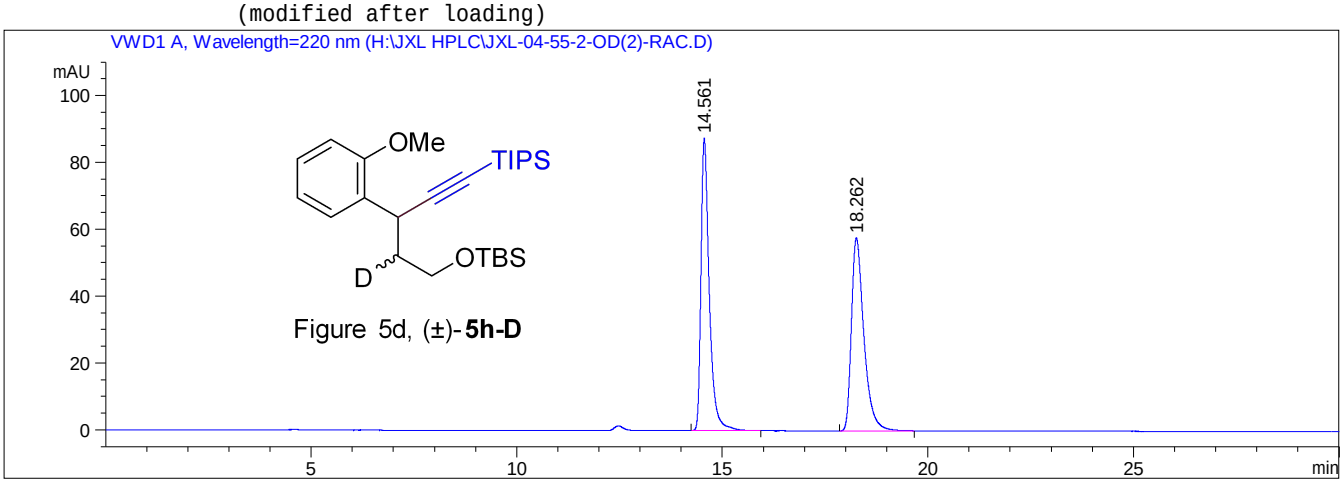

Figure 5d, (±)-**5h-D**

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.561 BB    0.2087 1226.21692   87.40794  50.1898
   2  18.262 BB    0.3189 1216.94397   57.72718  49.8102

Totals :                  2443.16089  145.13512


=====================================================================
                        *** End of Report ***
```


Supplementary Fig. 300. HPLC spectra for compound (±)-**5h-D**

Data File H:\JXL HPLC\JXL-04-49-1-OD(2)-EE-DAODAIDIWU.D
Sample Name: JXL-04-49-1-OD(2)

```
==========================================================================
Acq. Operator   : 系统                          Seq. Line :  54
Acq. Instrument : HPLC-1260                     Location :   91
Injection Date  : 11/25/2020 3:53:25 AM              Inj :   1
                                               Inj Volume : 3.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 0.300 µl
Acq. Method     : D:\G527\FZ\20201124\YH 2020-11-24 08-36-13\0IPA-40-0.5-1-6-220-JXL.M
Last changed    : 11/25/2020 12:09:48 AM by 系统
Analysis Method : E:\DATA\20201027\LC 2020-11-24 17-29-49\1IPA-40-0.5-220-3-JXL.M (Sequence
                  Method)
Last changed    : 12/16/2020 11:06:48 AM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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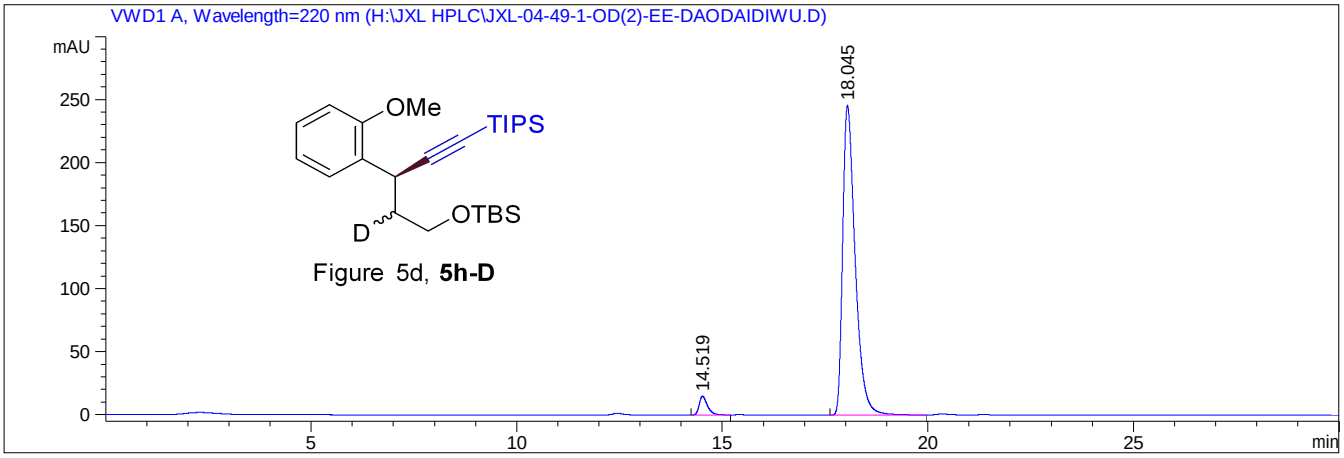

Figure 5d, **5h-D**

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.519 BB    0.2058  205.12283   14.88075   3.8076
   2  18.045 BB    0.3213 5182.03369  245.47847  96.1924

Totals :                  5387.15652  260.35922


==========================================================================
                          *** End of Report ***
```


Supplementary Fig. 301. HPLC spectra for compound (±)-**5h-D**

Supplementary References

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