Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium-catalyzed denitrative Sonogashira-type cross-coupling of nitrobenzenes with terminal alkynes

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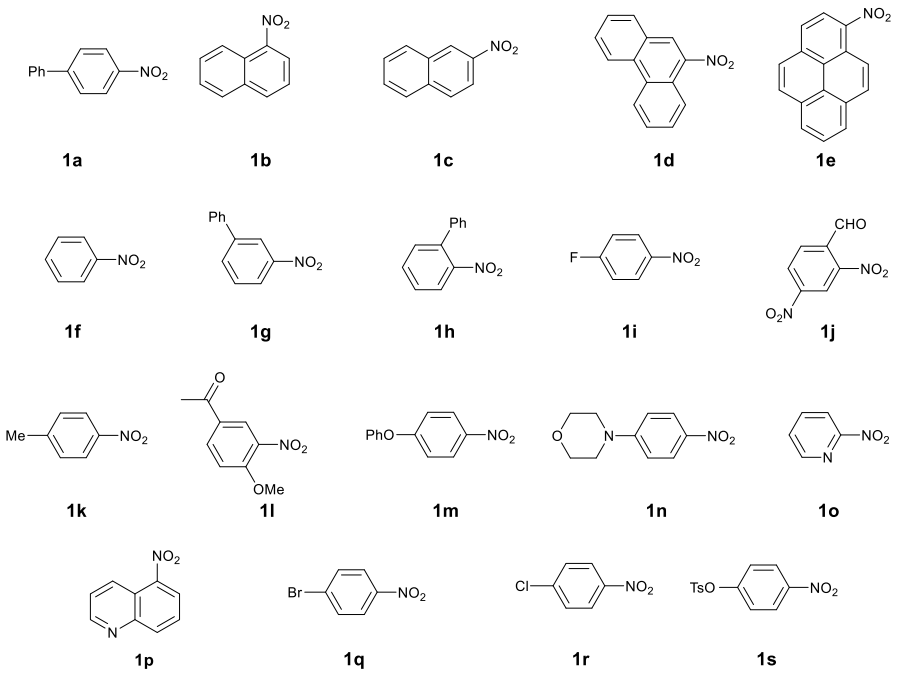
I. General remarks

NMR spectra were prepared on a Bruker AV II-400 MHz or Agilent 400-MR DD2 spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz). The ^{1}H NMR (400 MHz) chemical shifts and the ^{13}C NMR (100 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference. GC-MS spectra (EI) were recorded by Shimadzu GCMS-QP2010 SE. High resolution mass spectra (HRMS) were prepared with a Waters-Q-TOF-Premier (ESI) or a Shimadzu LCMS-IT-TOF (ESI).

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using an Innovative Technology PS-MD-5 Solvent Purification System. $Pd(acac)_2$[1] and $Pd(en)(NO_3)_2$[2] were synthesized according to the literature procedures. $PdCl_2$ and $Pd(OAc)_2$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd.. $[Pd(allyl)Cl]_2$ was purchased from Alfa Aesar. BrettPhos were purchased from Adamas-beta Ltd.. Dcype were purchased from Sigma-Aldrich. Arylboronic acids, DavePhos, XPhos and alkynes were purchased from Energy Chemical. Unless otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen in dried glassware with standard vacuum-line techniques.

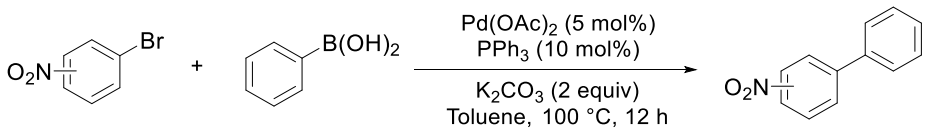
II. Preparation of nitroarenes



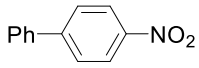
Scheme S1 Nitroaromatic substrates

Compound **1b**, **1d**, **1i**, **1j**, **1k**, **1o, 1p, 1q** and **1r** were purchased and used without

further purification. Compound **1c**,[3], **1e**,[4] **1l**,[5] **1m**,[6] **1n**,[7], **1o**[3] and **1s**[8] were prepared according to literature. 4-Nitro-1,1'-biphenyl (**1a**), 3-nitro-1,1'-biphenyl (**1g**) and 2-nitro-1,1'-biphenyl (**1h**) were synthesized by Suzuki coupling of the corresponding bromo nitroarenes with phenylboronic acid as shown below.

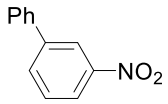


An oven-dried Schlenk tube equipped with a stirring bar was charged with aryl bromide (1 mmol, 1.0 equiv), $PhB(OH)_2$ (146 mg, 1.2 equiv), $Pd(OAc)_2$ (11 mg, 5 mol%), PPh_3 (27 mg, 10 mol%) and K_2CO_3 (275 mg, 2 equiv) under N_2. Toluene (5 ml) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 100 °C, and stirred for 12 h. The reaction mixture was then cooled down to room temperature, diluted with CH_2Cl_2 (20 mL), filtered through celite, and concentrated. The resulting crude mixture was purified by flash chromatography on silica gel (200-300 mesh, petroleum ether/CH_2Cl_2 = 6/1) to afford the corresponding product.



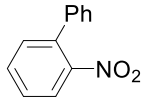
4-Nitro-1,1'-biphenyl (1a)

White solid (159 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 – 7.54 (m, 3H), 7.61 – 7.66 (m, 2H), 7.72 – 7.77 (m, 2H), 8.28 – 8.33 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 124.2, 127.5, 127.9, 129.0, 129.3, 138.9, 147.2, 147.8 ppm. The NMR spectrum data are consistent with the literature.[9]



3-Nitro-1,1'-biphenyl (1g)

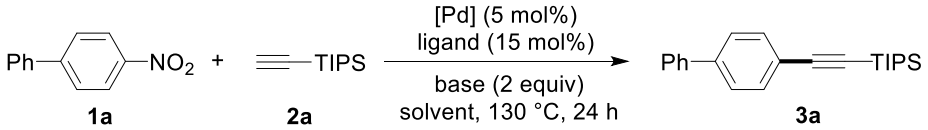
Yellow solid (168 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.45 (m, 1H), 7.45 – 7.52 (m, 2H), 7.57 – 7.64 (m, 3H), 7.88 – 7.93 (m, 1H), 8.16 – 8.22 (m, 1H), 8.44 (t, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 122.1, 122.2, 127.3, 128.7, 129.3, 129.8, 133.2, 138.8, 143.0, 148.8 ppm. The NMR spectrum data are consistent with the literature.[9]



2-Nitro-1,1'-biphenyl (1h)

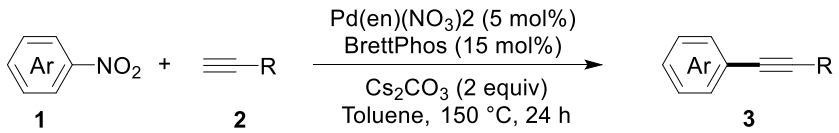
Yellow solid (143 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.31 – 7.35 (m, 2H), 7.40 – 7.52 (m, 5H), 7.62 (td, J = 7.6, 1.2 Hz, 1H), 7.86 (dd, J = 8.0, 1.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 124.2, 128.0, 128.3, 128.4, 128.8, 132.1, 132.4, 136.5, 137.5, 149.4 ppm. The NMR spectrum data are consistent with the literature.[9]

III. General procedure for the optimization study



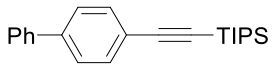
An oven-dried Schlenk tube equipped with a stirring bar was charged with 4-nitro-1,1'-biphenyl (0.2 mmol, 1.0 equiv), triisopropylsilylacetylene (0.4 mmol, 2 equiv), Pd catalyst (5 mol%), ligand (15 mol%) and base (2 equiv) under N_2. Then solvent (0.6 ml) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. Next, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered through celite, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh, petroleum ether) to afford the corresponding alkynylated product.

IV. General procedure for the denitrative Sonogashira-type alkynylation



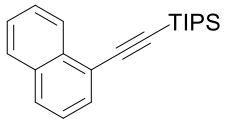
An oven-dried Schlenk tube equipped with a stirring bar was charged with nitroarene **1** (0.2 mmol, 1.0 equiv), alkyne **2** (0.4 mmol, 2 equiv), $Pd(en)(NO_3)_2$ (2.9 mg, 5 mol%), BrettPhos (16.1 mg, 15 mol%) and Cs_2CO_3 (130 mg, 2 equiv) under N_2. Then toluene (0.6 ml) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for 24 h. Next, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered through celite, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh) to afford the corresponding alkynylated product.

V. Experimental data for the described substances



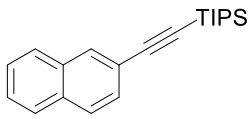
([1,1'-Biphenyl]-4-ylethynyl)triisopropylsilane (3a)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3a** as colorless oil (53 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 – 1.17 (m, 21H), 7.33 – 7.39 (m, 1H), 7.43 – 7.48 (t, 2H), 7.52 – 7.64 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 11.5, 18.8, 91.4, 107.1, 122.6, 127.0, 127.2, 127.7, 129.0, 132.6, 140.5, 141.2 ppm. HRMS (ESI^+) calcd for $C_{23}H_{31}Si$ $[M+H]^+$ 335.2190, found 335.2194. The NMR spectrum data are consistent with the literature.[10]



Triisopropyl(naphthalen-1-ylethynyl)silane (3b)

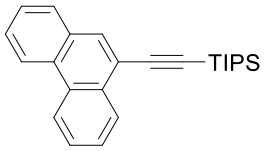
According to the general procedure for denitrative alkynylation, $Pd(acac)_2$ (3.1 mg, 5 mol%) was used as the catalyst and K_3PO_4 (85 mg, 2 equiv) was used as the base. Purification by column chromatography (petroleum ether) on silica gel afforded compound **3b** as yellowish oil (51 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 – 1.24 (m, 21H), 7.43 (dd, J = 8.0, 7.2 Hz, 1H), 7.50 – 7.56 (m, 1H), 7.57 – 7.63 (m, 1H), 7.75 (dd, J = 7.2, 1.2 Hz, 1H), 7.84 (t, J = 8.8 Hz, 2H), 8.42 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 18.9, 95.9, 105.0, 121.3, 125.3, 126.4, 126.5, 126.9, 128.4, 128.9, 131.1, 133.2, 133.6 ppm. HRMS (ESI^+) calcd for $C_{21}H_{28}NaSi$ $[M+Na]^+$ 331.1852, found 331.1852. The NMR spectrum data are consistent with the literature.[11]



Triisopropyl(naphthalen-2-ylethynyl)silane (3c)

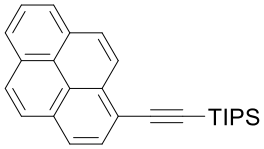
According to the general procedure for denitrative alkynylation, $Pd(acac)_2$ (3.1 mg, 5 mol%) was used as the catalyst and K_3PO_4 (85 mg, 2 equiv) was used as the base. Purification by column chromatography (petroleum ether) on silica gel afforded compound **3c** as yellowish oil (46 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (s, 21H), 7.47 – 7.54 (m, 3H), 7.76 – 7.82 (m, 3H), 8.01 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 18.9, 91.0, 107.6, 120.9, 126.6, 126.7, 127.8, 127.9, 127.9, 128.9, 132.0, 132.9, 133.0 ppm. HRMS (ESI^+) calcd for $C_{21}H_{28}NaSi$ $[M+Na]^+$

331.1852, found 331.1855. The NMR spectrum data are consistent with the literature.[10]



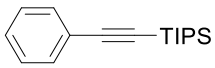
Triisopropyl(phenanthren-9-ylethynyl)silane (3d)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3d** as yellow oil (57 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, 21H), 7.55 – 7.71 (m, 4H), 7.85 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H), 8.50 – 8.53 (m, 1H), 8.63 – 8.71 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.6, 18.9, 95.7, 105.2, 120.1, 122.7, 122.9, 127.05, 127.12, 127.17, 127.2, 127.6, 128.6, 130.2, 130.4, 131.3, 131.4, 132.6 ppm. HRMS (ESI^+) calcd for $C_{25}H_{31}Si$ $[M+H]^+$ 359.2190, found 359.2191. The NMR spectrum data are consistent with the literature.[12]



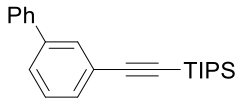
Triisopropyl(pyren-1-ylethynyl)silane (3e)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3e** as a yellow solid (65 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 – 1.28 (m, 21H), 8.00 – 8.04 (m, 2H), 8.07 – 8.10 (m, 2H), 8.16 – 8.22 (m, 4H), 8.63 (d, J = 8.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.6, 19.0, 96.8, 106.1, 118.2, 124.4, 124.48, 124.50, 125.66, 125.71, 125.72, 126.3, 127.4, 128.3, 128.5, 130.3, 131.2, 131.3, 131.4, 132.4 ppm. HRMS (ESI^+) calcd for $C_{27}H_{31}Si$ $[M+H]^+$ 383.2195, found 383.2195.



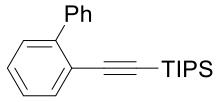
Triisopropyl(phenylethynyl)silane (3f)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3f** as yellowish oil (37 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 21H), 7.27 – 7.33 (m, 3H), 7.45 – 7.50 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 18.8, 90.6, 107.2, 123.7, 128.3, 128.4, 132.2 ppm. HRMS (ESI^+) calcd for $C_{17}H_{26}NaSi$ $[M+Na]^+$ 281.1696, found 281.1691. The NMR spectrum data are consistent with the literature.[11]



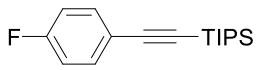
([1,1'-Biphenyl]-3-ylethynyl)triisopropylsilane (3g)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3g** as yellow oil (39 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (s, 21H), 7.35 – 7.41 (m, 2H), 7.44 – 7.49 (m, 2H), 7.53 – 7.56 (m, 1H), 7.59 – 7.61 (m, 2H), 7.70 – 7.72 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 18.8, 90.8, 107.1, 124.1, 127.29, 127.32, 127.4, 127.7, 128.8, 128.89, 128.93, 130.9, 131.0, 140.5, 141.5 ppm. HRMS (ESI^+) calcd for $C_{23}H_{30}NaSi$ $[M+Na]^+$ 357.2009, found 357.2017. The NMR spectrum data are consistent with the literature.[10]



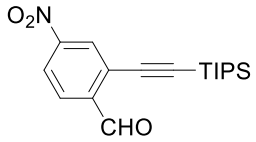
([1,1'-Biphenyl]-2-ylethynyl)triisopropylsilane (3h)

Reaction was conducted in toluene (0.6 mL) at 150 °C for 36 h. Purification by column chromatography (petroleum ether) on silica gel afforded compound **3h** as yellow oil (35 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 21H), 7.26 – 7.40 (m, 6H), 7.55 – 7.64 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 18.7, 94.0, 106.4, 122.1, 127.0, 127.3, 127.4, 128.0, 128.6, 128.9, 129.4, 129.5, 133.9, 140.6, 144.3 ppm. HRMS (ESI^+) calcd for $C_{23}H_{31}Si$ $[M+H]^+$ 335.2190, found 335.2196. The NMR spectrum data are consistent with the literature.[10]



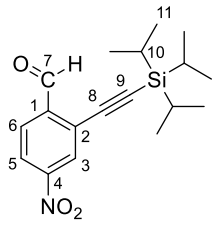
((4-fluorophenyl)ethynyl)triisopropylsilane (3i)

Reaction was conducted in toluene (0.6 mL) at 150 °C for 36 h. Purification by column chromatography (petroleum ether) on silica gel afforded compound **3i** as colorless oil (33 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 21H), 6.95 – 7.02 (m, 2H), 7.41 – 7.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 18.8, 90.3, 106.0, 115.6 (d, J = 22.1 Hz), 119.8 (d, J = 3.5 Hz), 134.1 (d, J = 8.4 Hz), 162.6 (d, J = 249.5 Hz) ppm. **MS (EI):** m/z (%) = 276.1 ($[M]^+$, 5), 232.9 (57), 190.9 (27), 163.0 (100), 146.9 (44), 123.0 (22), 95 (3). The NMR spectrum data are consistent with the literature.[12]

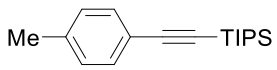


4-Nitro-2-((triisopropylsilyl)ethynyl)benzaldehyde (3j)

Triisopropylsilylacetylene (1.2 equiv) was used. Purification by column chromatography (petroleum ether/ethyl acetate = 6/1) on silica gel afforded compound **3j** as a brown solid (60 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 – 1.19 (m, 21H), 8.07 (d, J = 8.6 Hz, 1H), 8.23 (dd, J = 8.4, 2.0 Hz, 1H), 8.40 (d, J = 2.0 Hz, 1H), 10.65 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3, 18.8, 99.7, 103.3, 123.3, 128.3, 128.6, 128.9, 139.7, 150.6, 190.1 ppm. HRMS (ESI$^-$) calcd for $C_{18}H_{24}NO_3Si$ [M-H]$^-$ 330.1531, found 330.1530.

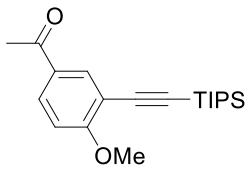


^{13}C NMR ($CDCl_3$)	HMBC	Assignment
11.3	1.15	C-10
18.8	1.14	C-11
99.7	8.40	C-8
103.3		C-9
123.3	8.40	C-2
128.3	8.07	C-5
128.6	10.65	C-6
128.9	8.23	C-3
139.7	8.23, 8.40, 10.65	C-1
150.6	8.07, 8.23, 8.40	C-4
190.1	8.07	C-7



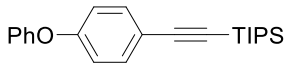
Triisopropyl(p-tolylethynyl)silane (3k)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3k** (47 mg, 86% yield) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 21H), 2.34 (s, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 18.8, 21.7, 89.7, 107.4, 120.6, 129.0, 132.0, 138.5 ppm. MS (EI): m/z (%) = 272.0 ([M]$^+$, 8.63), 228.9 (73), 187.0 (40), 159.0 (100), 143.0 (41), 115.1 (9), 9.0 (6). The NMR spectrum data are consistent with the literature.[12]



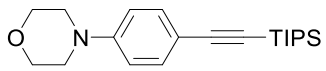
1-(4-Methoxy-3-((triisopropylsilyl)ethynyl)phenyl)ethan-1-one (3l)

Purification by column chromatography (petroleum ether/ethyl acetate = 10/1) on silica gel afforded compound **3l** as a yellow solid (33 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 21H), 2.56 (s, 3H), 3.92 (s, 3H), 6.89 (d, J = 8.8 Hz, 1H), 7.91 (dd, J = 8.8, 2.4 Hz, 1H), 8.03 (d, J = 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 18.6, 26.5, 56.2, 96.2, 101.8, 110.1, 113.0, 129.7, 130.4, 134.4, 164.2, 196.3 ppm. HRMS (ESI$^+$) calcd for $C_{20}H_{31}O_2Si$ [M+H]$^+$ 331.2088, found 331.2092.



Triisopropyl((4-phenoxyphenyl)ethynyl)silane (3m)

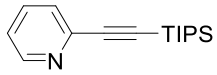
Purification by column chromatography (petroleum ether) on silica gel afforded compound **3m** (31 mg, 44% yield) as yellowish oil. ^{1}H NMR (400MHz, $CDCl_3$) δ =1.13 (s, 21H), 6.91 – 6.94 (m, 2H), 7.00 – 7.03 (m, 2H), 7.11 – 7.15 (m, 1H), 7.32 – 7.37 (m, 2H), 7.43 – 7.46 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.5, 18.8, 89.8, 106.7, 118.4, 118.5, 119.4, 123.9, 130.0, 133.8, 156.7, 157.6 ppm. HRMS (ESI$^+$) calcd for $C_{23}H_{31}OSi$ [M+H]$^+$ 351.2139, found 351.2138.



4-(4-((Triisopropylsilyl)ethynyl)phenyl)morpholine (3n)

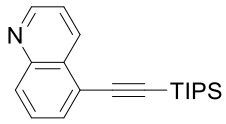
Reaction was conducted in toluene (0.6 mL) at 150 °C for 36 h. Purification by column chromatography (petroleum ether/ethyl acetate = 8/1) on silica gel afforded compound **3n** as a yellowish solid (24 mg, 35% yield). ^{1}H NMR 1.11 (s, 21H), 3.14 –

3.21 (m, 4H), 3.81 – 3.89 (m, 4H), 6.80 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.5, 18.8, 48.7, 66.9, 88.6, 107.6, 114.4, 114.9, 133.3, 151.0 ppm. HRMS (ESI^+) calcd for $C_{21}H_{34}NOSi$ $[M+H]^+$ 334.2404, found 334.2406.



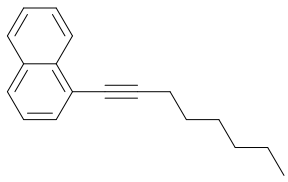
2-((Triisopropylsilyl)ethynyl)pyridine (3o)

Purification by column chromatography (petroleum ether/ethyl acetate = 20/1) on neutral Al_2O_3 afforded compound **3o** as yellow oil (46 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 – 1.14 (m, 21H), 7.16 – 7.20 (m, 1H), 7.43 (dt, J = 8.0, 1.2 Hz, 1H), 7.60 (td, J = 7.6, 2.0 Hz, 1H), 8.53 – 8.56 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3, 18.7, 91.5, 105.9, 122.9, 127.8, 136.1, 143.4, 150.0 ppm. HRMS (ESI^+) calcd for $C_{16}H_{26}Si$ $[M+H]^+$ 260.1829, found 260.1830.The NMR spectrum data are consistent with the literature.[13]



5-((Triisopropylsilyl)ethynyl)quinoline (3p)

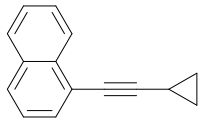
Purification by column chromatography (petroleum ether/ethyl acetate = 15/1) on neutral Al_2O_3 afforded compound **3p** as a brown solid (43 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (m, 21H), 7.49 (dd, J = 8.8, 4.0 Hz, 1H), 7.62 – 7.66 (m, 1H), 7.77 (dd, J = 7.2, 1.2 Hz, 1H), 8.08 (dt, J = 8.4, 1.2 Hz, 1H), 8.65 – 8.68 (m, 1H), 8.94 (dd, J = 4.4, 2.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 18.9, 96.9, 103.6, 121.6, 121.9, 128.91, 128.93, 130.4, 131.4, 134.7, 148.0, 150.9 ppm. HRMS (ESI^+) calcd for $C_{20}H_{28}NSi$ $[M+H]^+$ 310.1986, found 310.1987. The NMR spectrum data are consistent with the literature.[13]



1-(oct-1-yn-1-yl)naphthalene (3q)

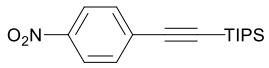
Purification by column chromatography (petroleum ether) on silica gel afforded compound **3q** as yellowish oil (48 mg, 96% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ = 0.93 – 0.97 (m, 3H), 1.36-1.41 (m, 4H), 1.53 – 1.60 (m, 2H), 1.70 – 1.77 (m 2H), 2.59

(t, J = 7.2 Hz, 2H), 7.41 (dd, J =8.0, 6.8 Hz, 1H), 7.50 – 7.59 (m, 2H), 7.64 (dd, J =7.2 Hz, 1.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.83 – 7.86 (m, 1H), 8.36 – 8.39 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.2, 19.9, 22.8, 28.9, 29.0, 31.5, 78.7, 95.7, 121.9, 125.4, 126.3, 126.4, 126.6, 128.0, 128.3, 130.1, 133.3, 133.6 ppm. **MS (EI):** m/z (%) = 236.0 ([M]$^+$, 29), 220.9 (5), 206.9 (17), 165.0 (100), 152.1 (35), 139.0 (16), 128 (5). The NMR spectrum data are consistent with the literature.[14]



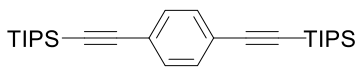
1-(cyclopropylethynyl)naphthalene (3r)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3r** as yellowish oil (35 mg, 92% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ = 0.90 – 1.00 (m, 4H), 1.62 (tt, J = 8.0, 5.2 Hz, 1H), 7.39 (dd, J = 8.4, 7.2 Hz, 1H), 7.47 – 7.59 (m, 2H), 7.62 (dd, J = 7.2, 1.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 0.6, 9.1, 73.9, 98.7, 121.7, 125.3, 126.3, 126.4, 126.6, 128.0, 128.3, 130.2, 133.3, 133.7 ppm. HRMS (ESI$^+$) calcd for $C_{15}H_{13}$ [M+H]$^+$ 193.1012, found 193.1028. The NMR spectrum data are consistent with the literature.[15]



1-(cyclopropylethynyl)naphthalene (3s)

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3s** as yellow oil (23 mg, 38% yield from **1q**, 11 mg, 18% yield from **1r**). ^{1}H NMR (400MHz, $CDCl_3$) δ = 1.11 – 1.15 (m, 21H), 7.58 – 7.63 (m, 2H), 8.15 – 8.20 (m, 2H) ppm . ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.3, 18.8, 97.7, 104.9, 123.6, 130.4, 132.9, 147.1 ppm. The NMR spectrum data are consistent with the literature.[9]

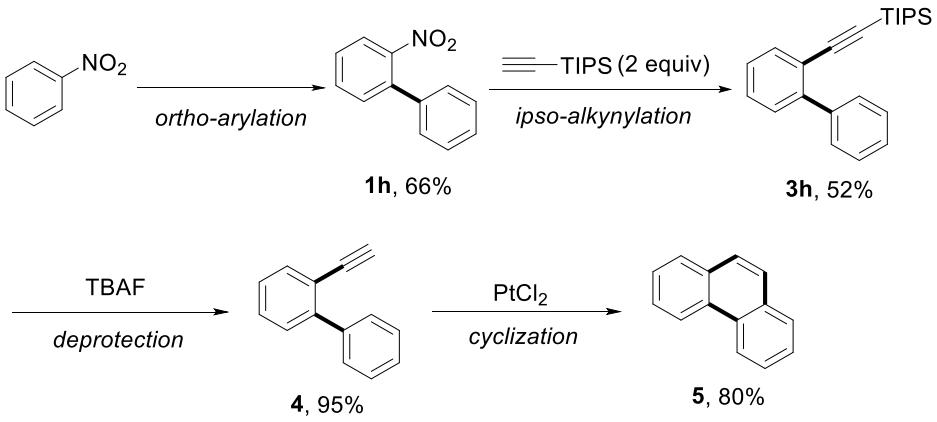


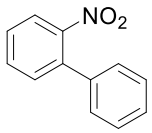
1,4-bis((triisopropylsilyl)ethynyl)benzene (3s')

Purification by column chromatography (petroleum ether) on silica gel afforded compound **3s'** as colorless oil (39 mg, 44% yield from **1q**, 28 mg, 32% yield from **1r**). ^{1}H NMR (400MHz, $CDCl_3$) δ = 1.12 (s, 42H), 7.39 (s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 11.4, 18.8, 92.8, 106.8, 123.5, 131.9 ppm. HRMS (ESI$^+$) calcd for $C_{28}H_{46}SiNa$ [M+Na]$^+$ 461.3030, found 461.3038.

VI. Synthetic Applications

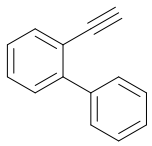
(a) The synthesis of phenanthrene





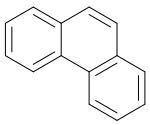
2-nitro-1,1'-biphenyl (1h)

A modified procedure of Fagnou's work was used for the synthesis of **1h**.[17] An oven-dried vial equipped with a stirring bar was charged with nitrobenzene (4 mmol, 2 equiv), 4-bromobenzene (2 mmol, 1.0 equiv), $[Pd(allyl)Cl]_2$ (19 mg, 2.5 mol%), $PCy_3 \cdot HBF_4$ (55 mg, 7.5 mol%), 2,2-dimethylbutanoic acid (75 μL, 0.3 equiv) and K_2CO_3 (550 mg, 2 equiv) under N_2. Then toluene (5 ml) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 130 °C, and stirred for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH_2Cl_2 (50 mL), filtered through celite, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh, petroleum ether/dichloromethane = 6/1) to afford the corresponding product as yellow oil (263 mg, 66%). ^{1}H NMR (400MHz, $CDCl_3$) δ =7.31 – 7.35 (m, 2H), 7.40 – 7.52 (m, 5H), 7.62 (td, J = 7.6, 1.2 Hz, 1H), 7.86 (dd, J = 8.0, 1.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 124.2, 128.0, 128.3, 128.4, 128.8, 132.1, 132.4, 136.5, 137.5, 149.4 ppm. The NMR spectrum data are consistent with the literature.[9]



2-ethynyl-1,1'-biphenyl (4)

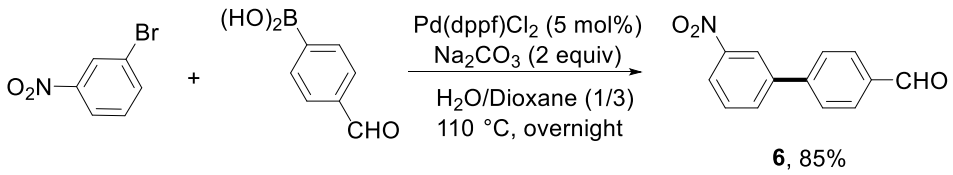
Compound **4** was prepared by the deprotection of **3c**. A mixture of **3c** (67 mg, 0.5 mmol), TBAF (1.0 M in THF, 1.5 mL, 1.5 mmol) and water (0.4 mL) were added to 25 mL-round-bottom flask and stirred at room temperature for 2 h. The mixture was then extracted with dichloromethane. The organic layer was washed with brine and water, dried over Na_2SO_4 and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh, petroleum ether) to afford the corresponding product as yellowish oil (84 mg, 95%). H NMR (400MHz, $CDCl_3$) δ = 3.03 (s, 1H), 7.28 – 7.32 (m, 1H), 7.36 – 7.45 (m, 5H), 7.57 – 7.59 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 80.3, 83.2, 120.5, 127.1, 127.7, 128.1, 129.1, 129.4, 129.7, 134.0, 140.4, 144.5 ppm. The NMR spectrum data are consistent with the literature.[18]



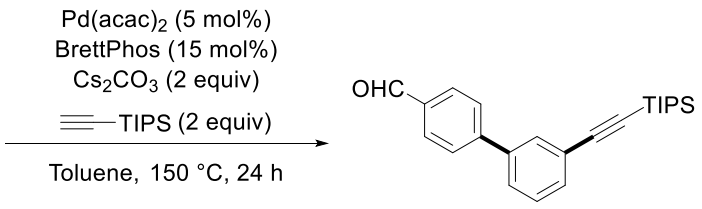
Phenanthrene (5)

Compound **5** was obtained by the cyclization of **4**. A mixture of **4** (35.6 mg, 0.2 mmol) and $PtCl_2$ (26.6 mg, 5 mol%) in toluene (1 mL) was stirred at 100 °C for 24 h. The reaction mixture was then cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered through celite, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh, petroleum ether) to afford the corresponding product as a white solid (27 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.70 (m, 4H), 7.77 (s, 2H), 7.92 (dd, J = 7.6 Hz, 1.2 Hz, 2H), 8.72 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.8, 126.7, 127.1, 128.7, 130.4, 132.2 ppm. The NMR spectrum data are consistent with the literature.[18]

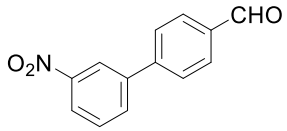
(b) Orthogonal cross-couplings



6, 85%

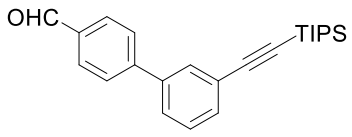


7, 55%



3'-Nitro[1,1'-biphenyl]-4-carboxaldehyde (6)

Compound **6** was obtained by Suzuki coupling. An oven-dried Schlenk tube equipped with a stirring bar was charged with 3-bromo-nitrobenzene (2 mmol, 1.0 equiv), Pd(dppf)Cl_2 (5 mol%) and Na_2CO_3 (848 mg, 2equiv) under N_2. Then a mixture of water/dioxane (1/3, 8 ml) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 110 °C, and stirred overnight. Next, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (20 mL), filtered through celite, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (200-300 mesh, petroleum ether/ethyl acetate = 12/1) to afford the biaryl product **6** as a white solid (386 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (t, J = 8.0 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.94 – 8.06 (m, 3H), 8.26 – 8.29 (m, 1H), 8.50 (t, J = 2.0 Hz, 1H), 10.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.4, 123.3, 128.0, 130.2, 130.6, 133.4, 136.2, 141.5, 144.5, 148.9, 191.8. The NMR spectrum data are consistent with the literature.[19]



3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-4-carbaldehyde (7)

Compound **7** was obtained by the general denitrative Sonogashira-type alkynylation procedure. An oven-dried Schlenk tube equipped with a stirring bar was charged with compound **6** (0.2 mmol, 1.0 equiv), triisopropylsilylacetylene (0.4 mmol, 2 equiv),

$Pd(en)(NO_3)_2$ (2.9 mg, 5 mol%), BrettPhos (16.1 mg, 15 mol%) and Cs_2CO_3 (130 mg, 2 equiv) under N_2. Then toluene (0.6 ml) was added at room temperature. The reaction mixture was placed in a preheated oil bath at 150 °C, and stirred for 24 h. Next, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered through celite, and concentrated. Purification by column chromatography (petroleum ether/dichloromethane = 3/1) on silica gel afforded compound **7** as yellowish oil (40 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 21H), 7.42 (t, J = 7.6 Hz, 1H), 7.55 (dd, J = 17.6, 7.6 Hz, 2H), 7.71 – 7.77 (m, 3H), 7.96 (d, J = 8.0 Hz, 2H), 10.06 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 18.8, 91.5, 106.6, 124.5, 127.4, 127.9, 129.1, 130.4, 131.0, 132.1, 135.5, 140.0, 146.5, 192.1 ppm. HRMS (ESI^+) calcd for $C_{24}H_{31}OSi$ $[M+H]^+$ 363.2139, found 363.2144.

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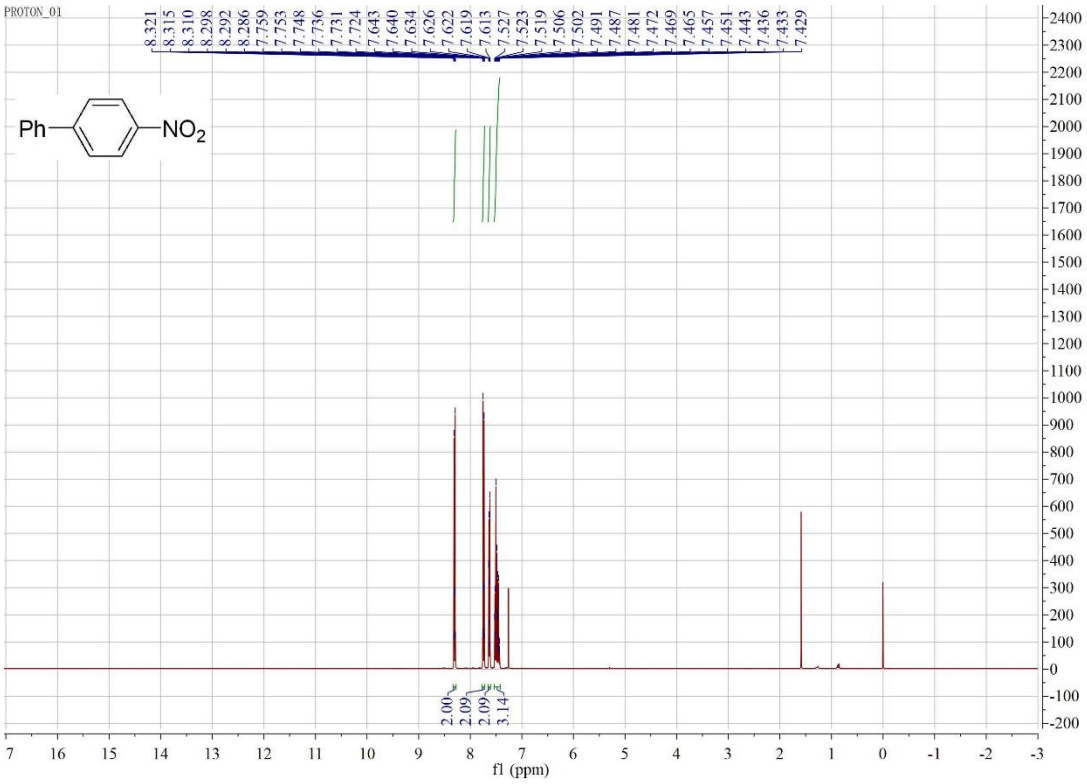
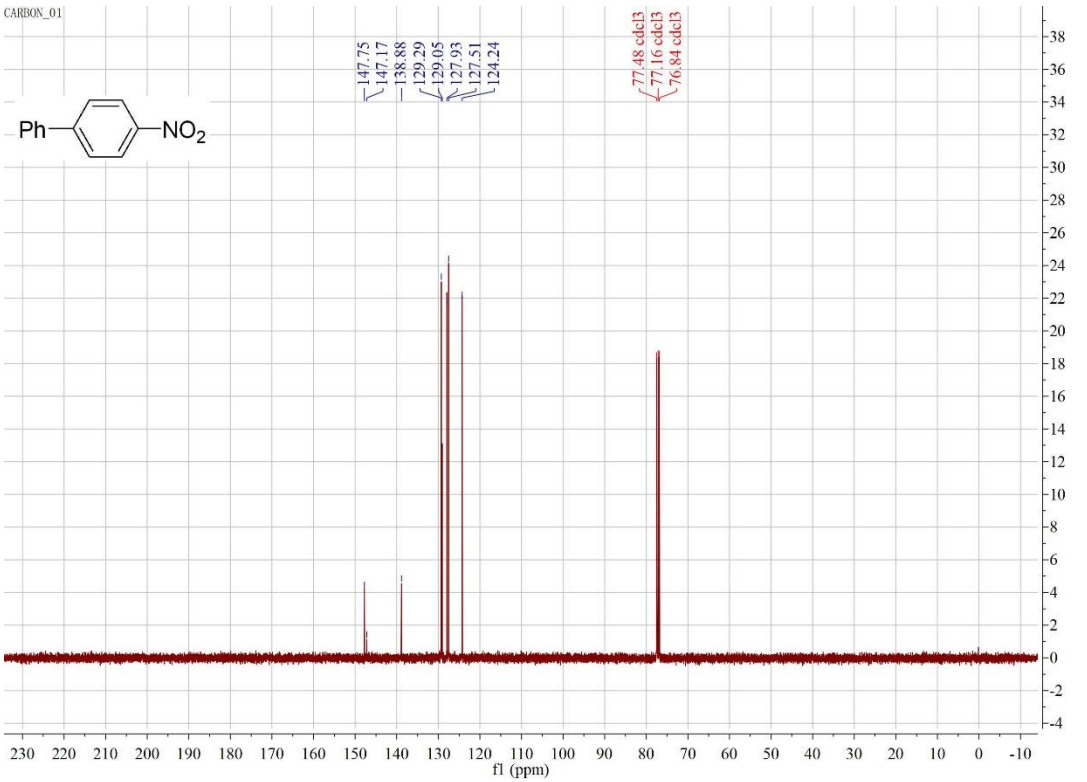
VIII. Copies of NMR spectra

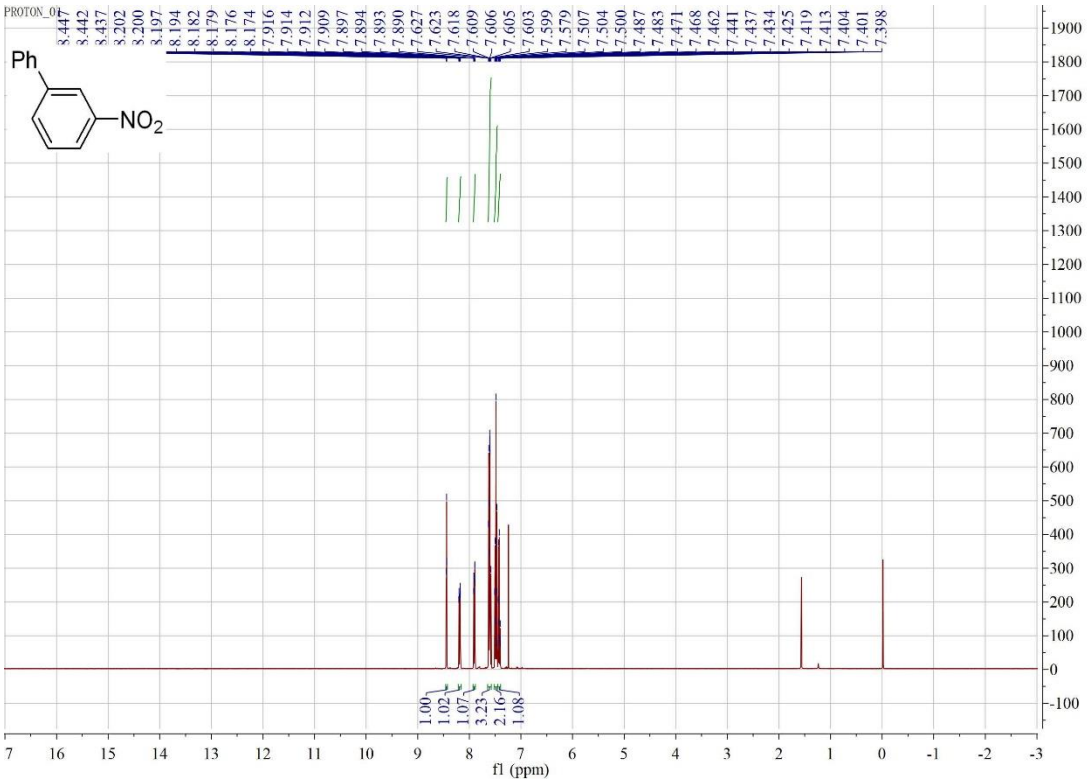
^{1}H NMR spectra of compound **1a**:



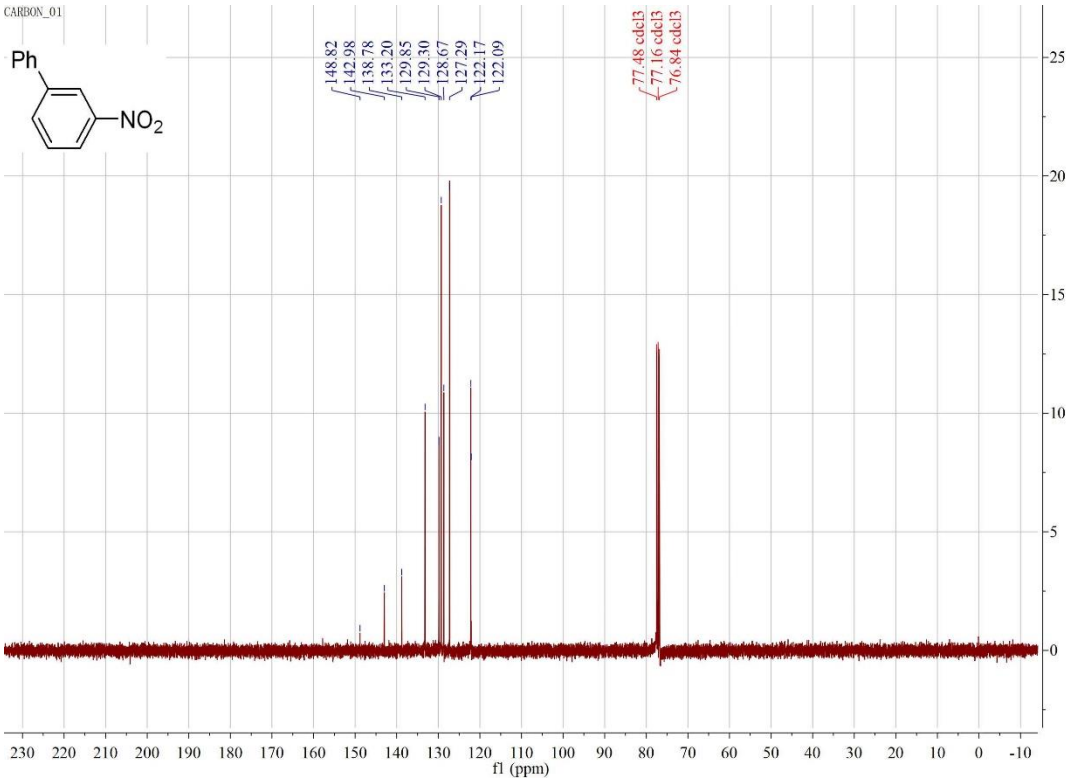
^{13}C NMR spectra of compound **1a**:



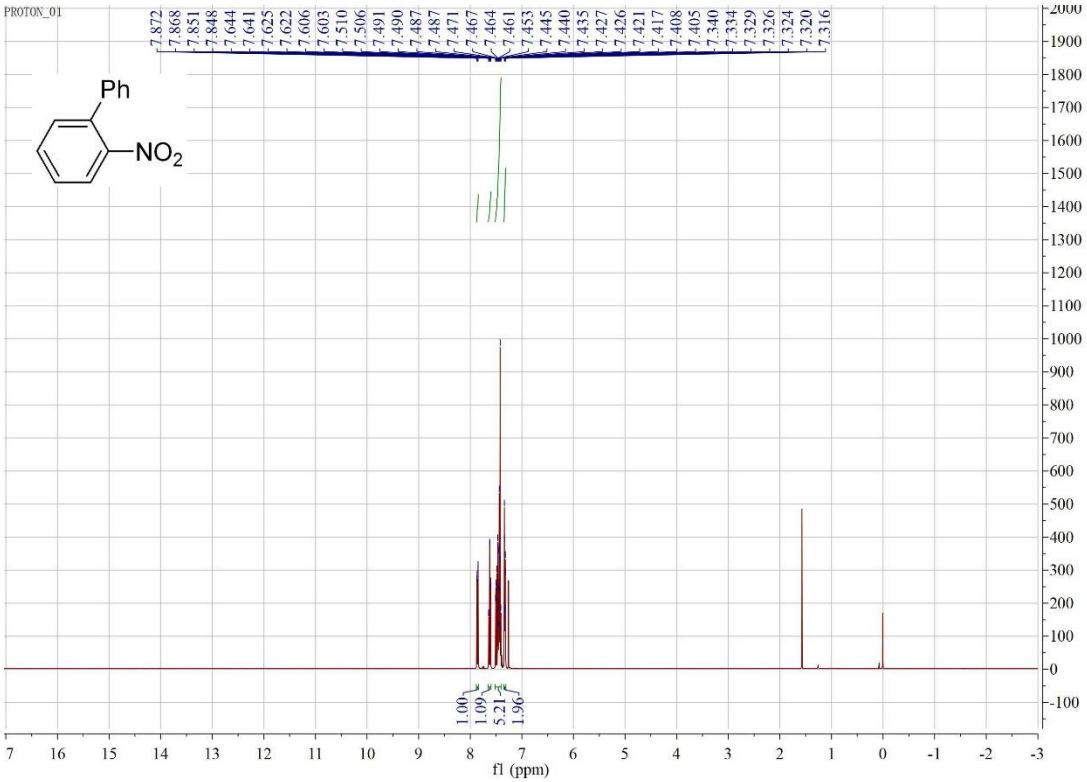
^{1}H NMR spectra of compound **1g**:



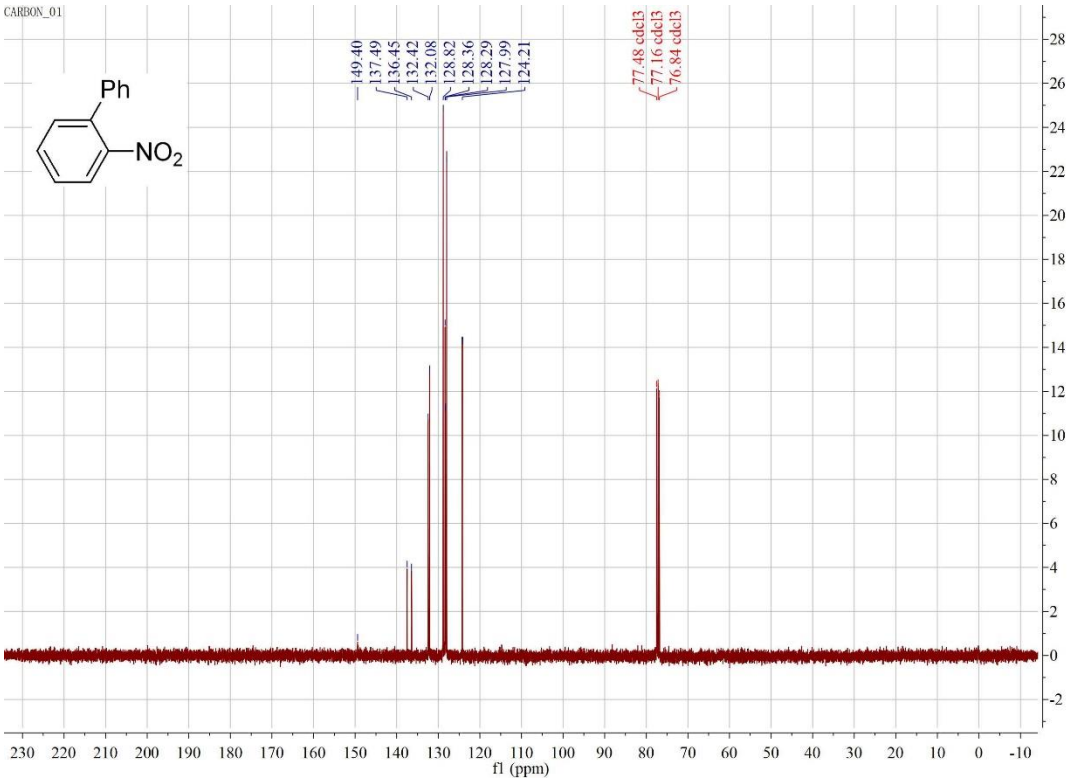
^{13}C NMR spectra of compound **1g**:



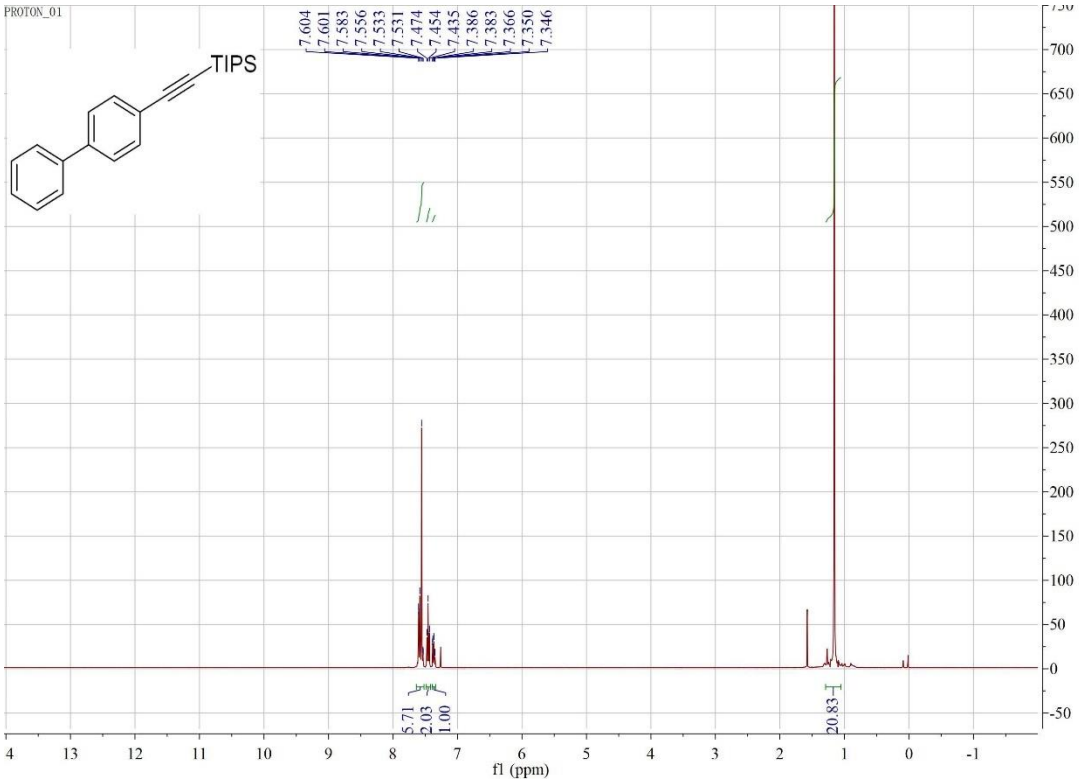
^{1}H NMR spectra of compound **1h**:



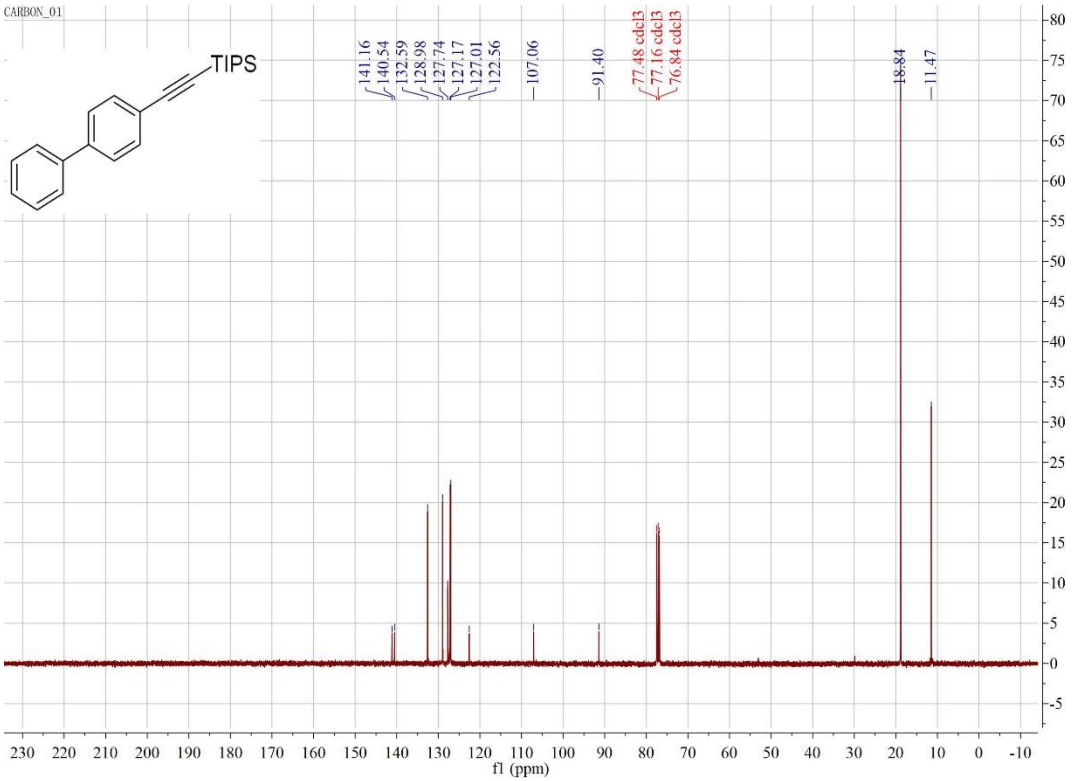
^{13}C NMR spectra of compound **1h**:



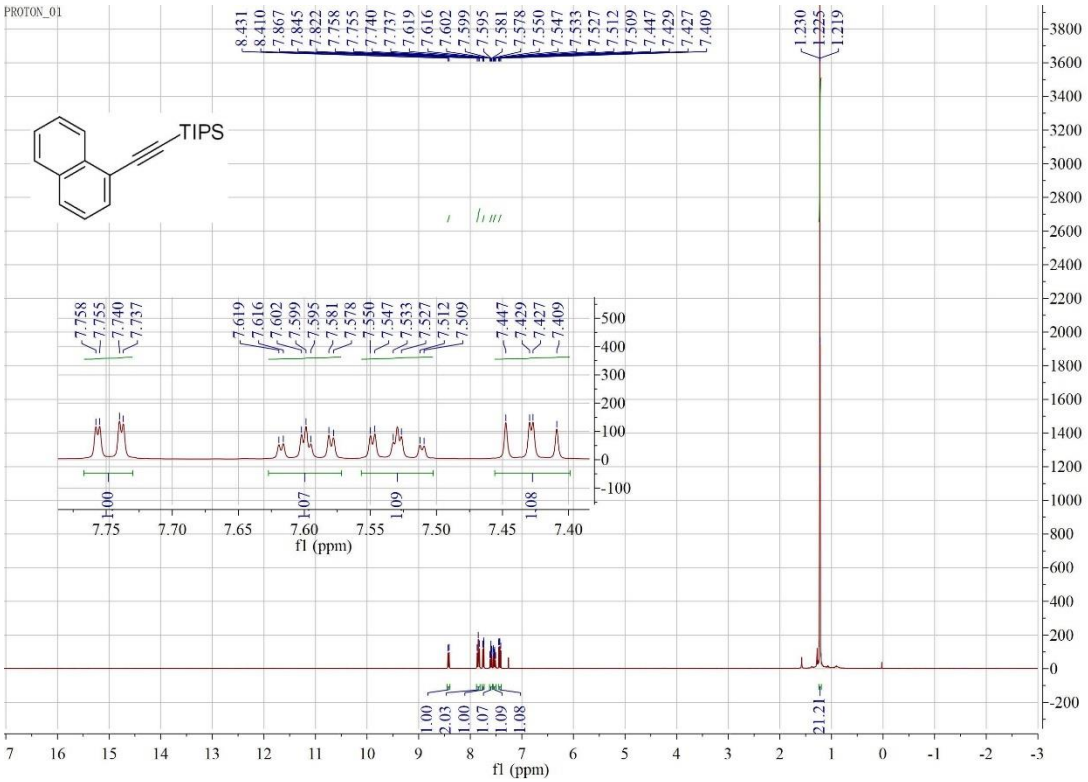
^{1}H NMR spectra of compound **3a**:



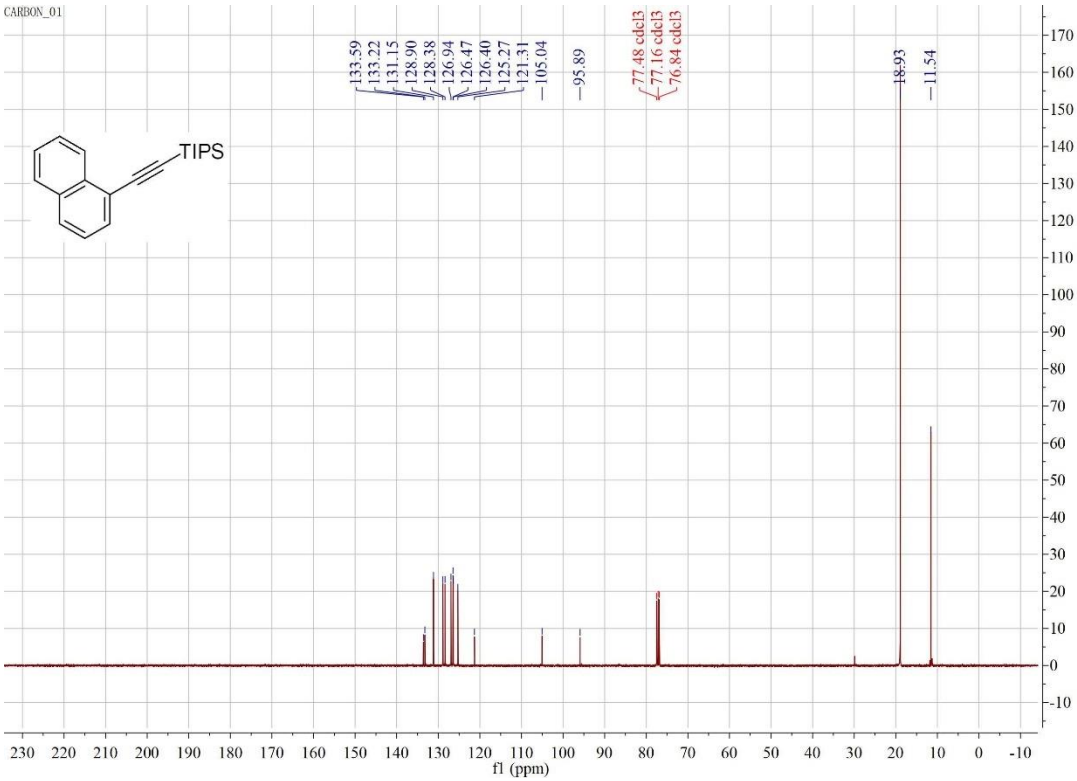
^{13}C NMR spectra of compound **3a**:



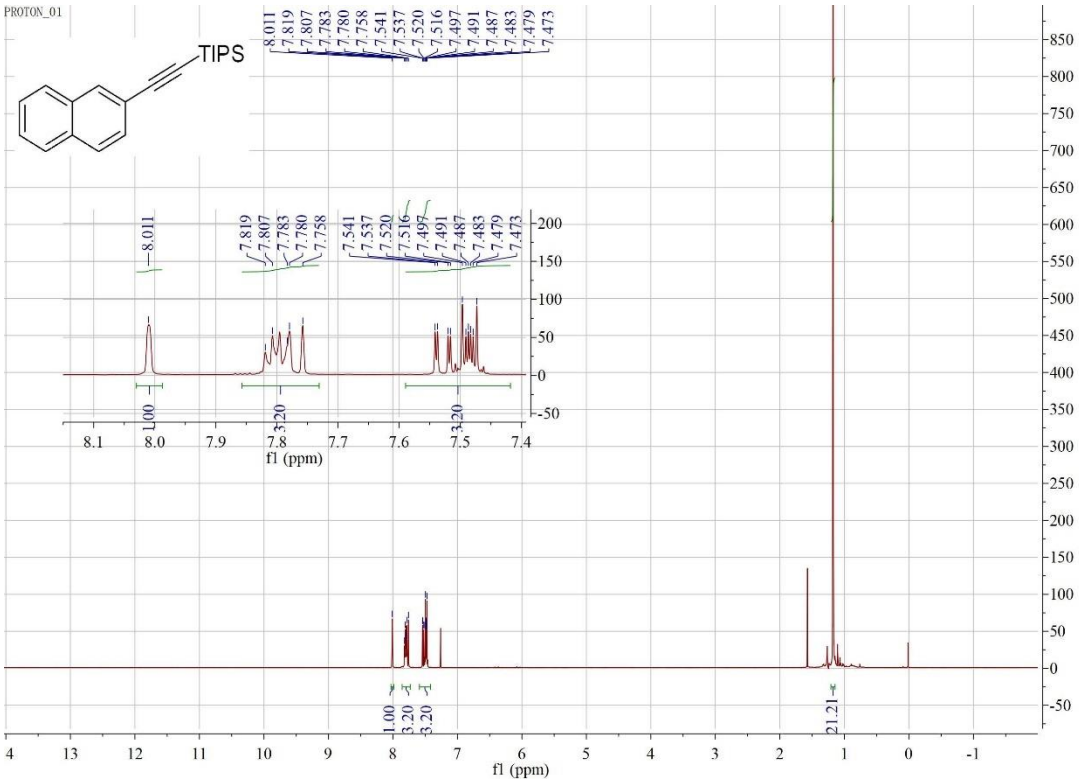
^{1}H NMR spectra of compound **3b**:



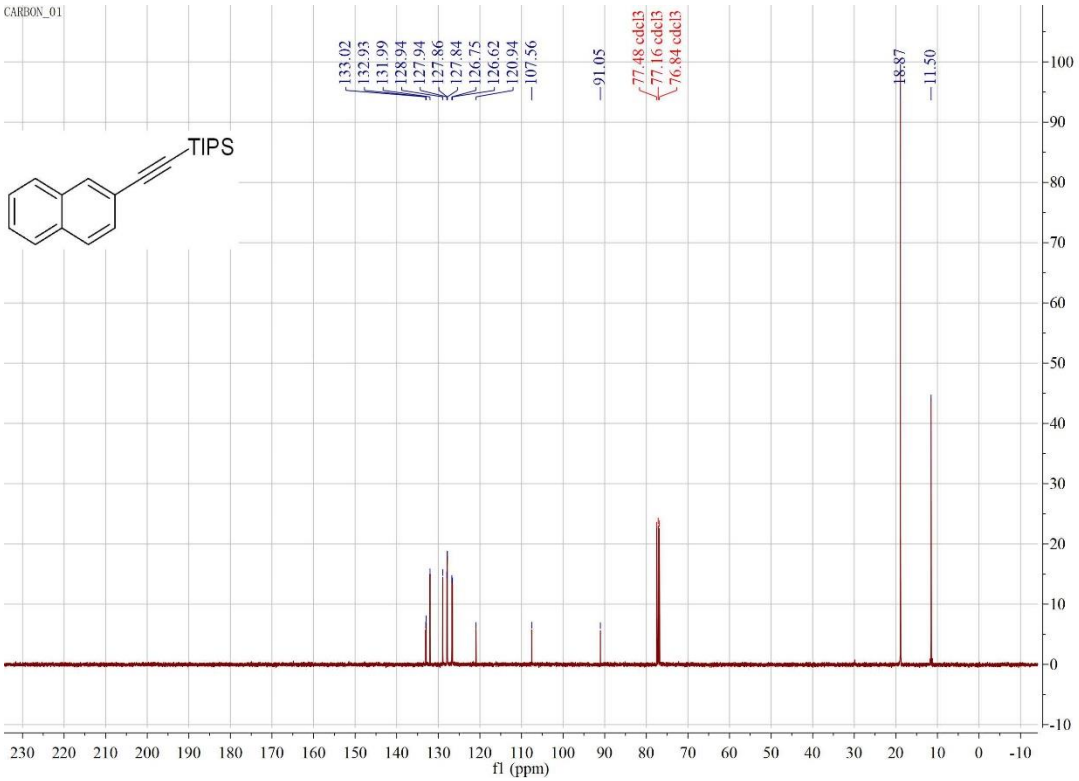
^{13}C NMR spectra of compound **3b**:



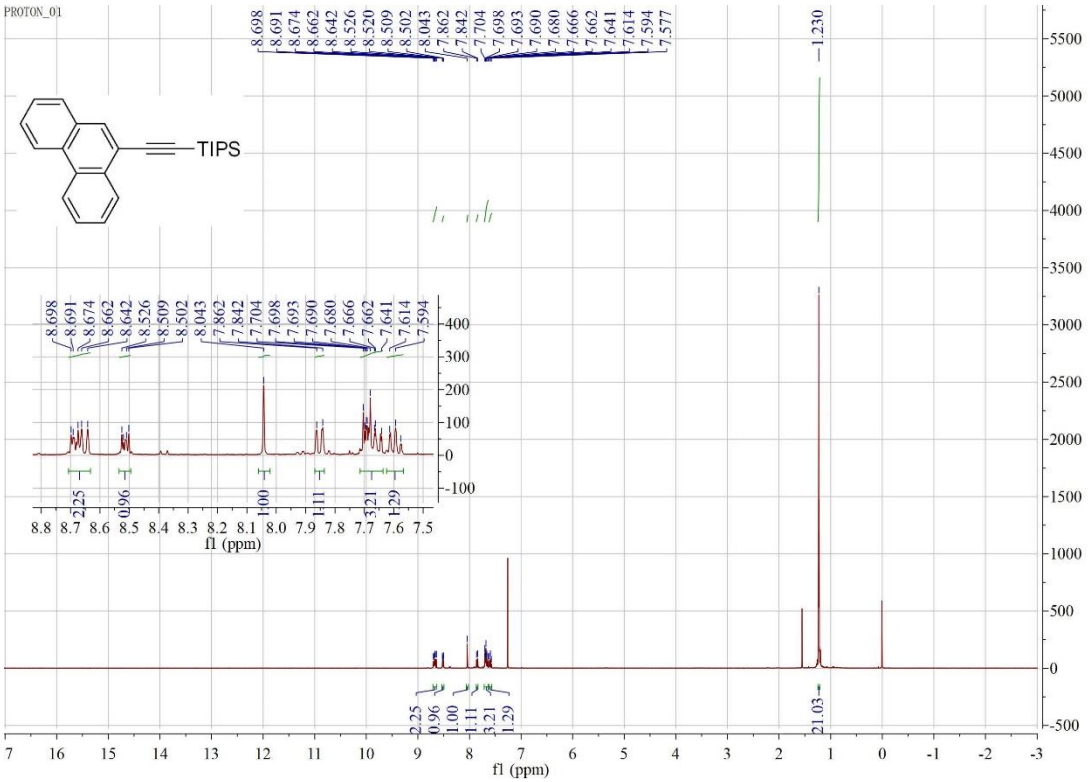
^{1}H NMR spectra of compound **3c**:



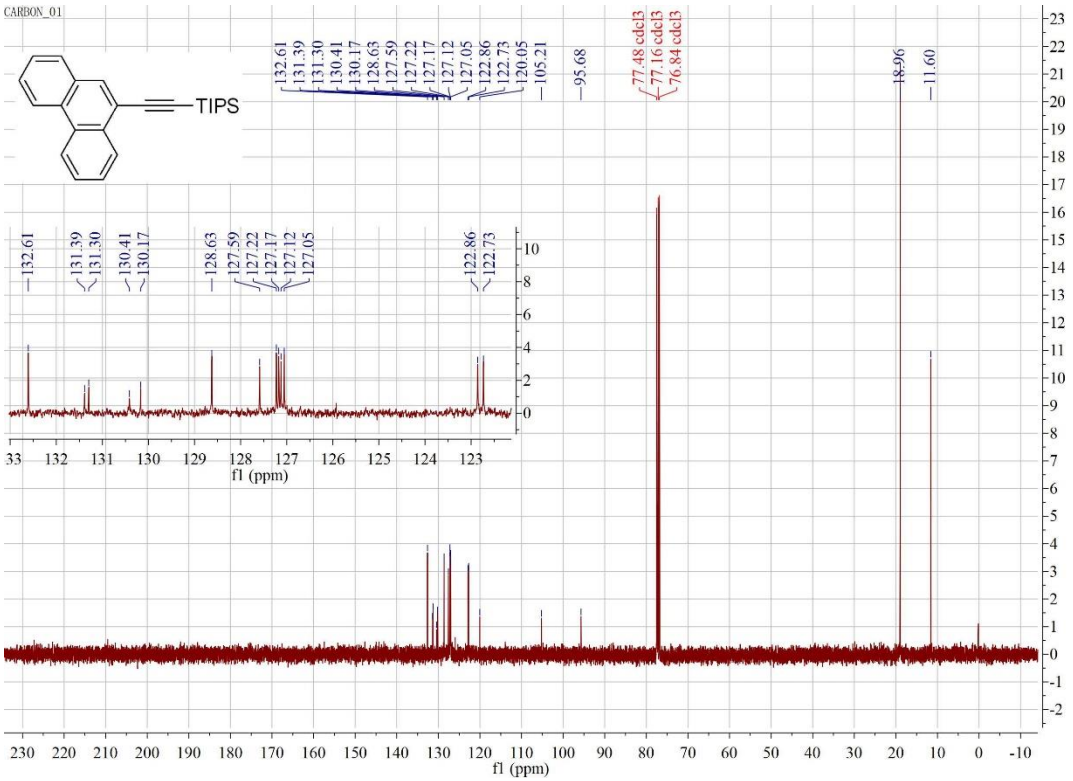
^{13}C NMR spectra of compound **3c**:



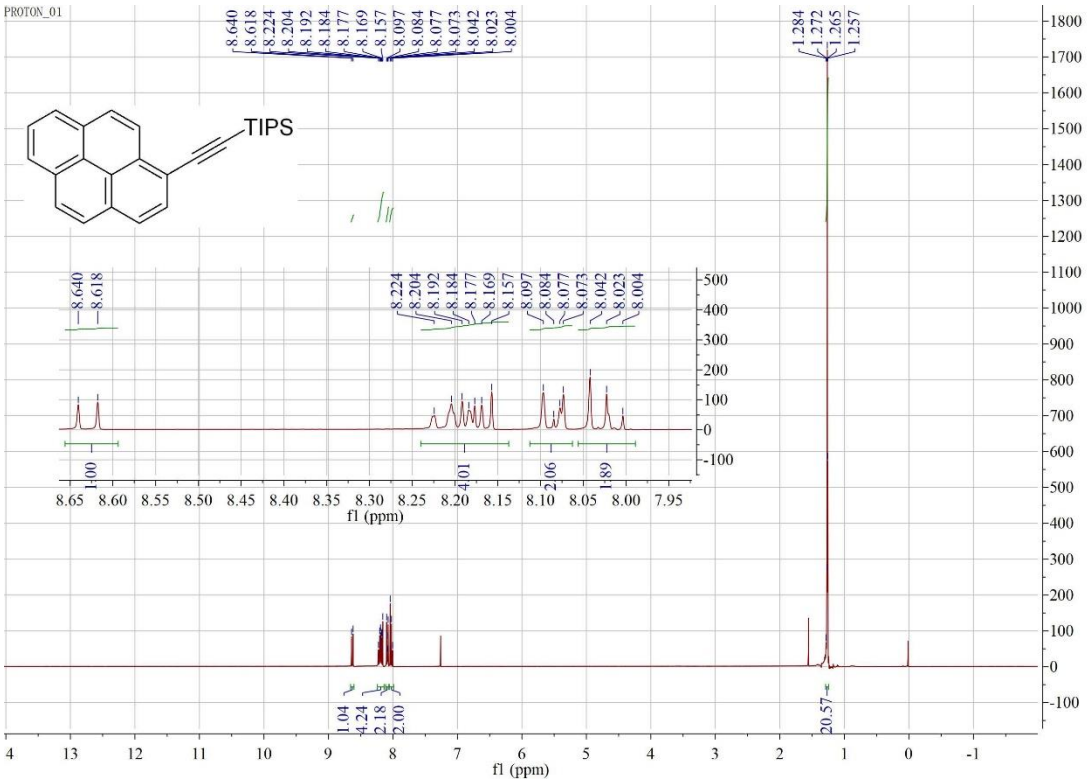
^{1}H NMR spectra of compound **3d**:



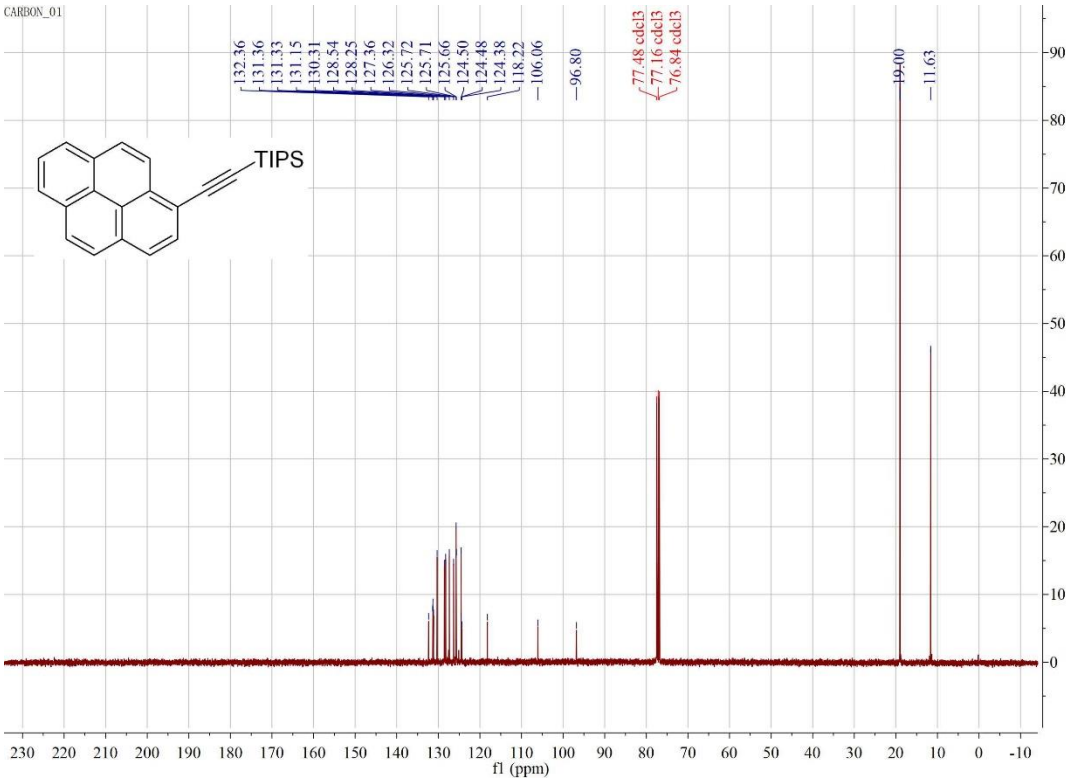
^{13}C NMR spectra of compound **3d**:



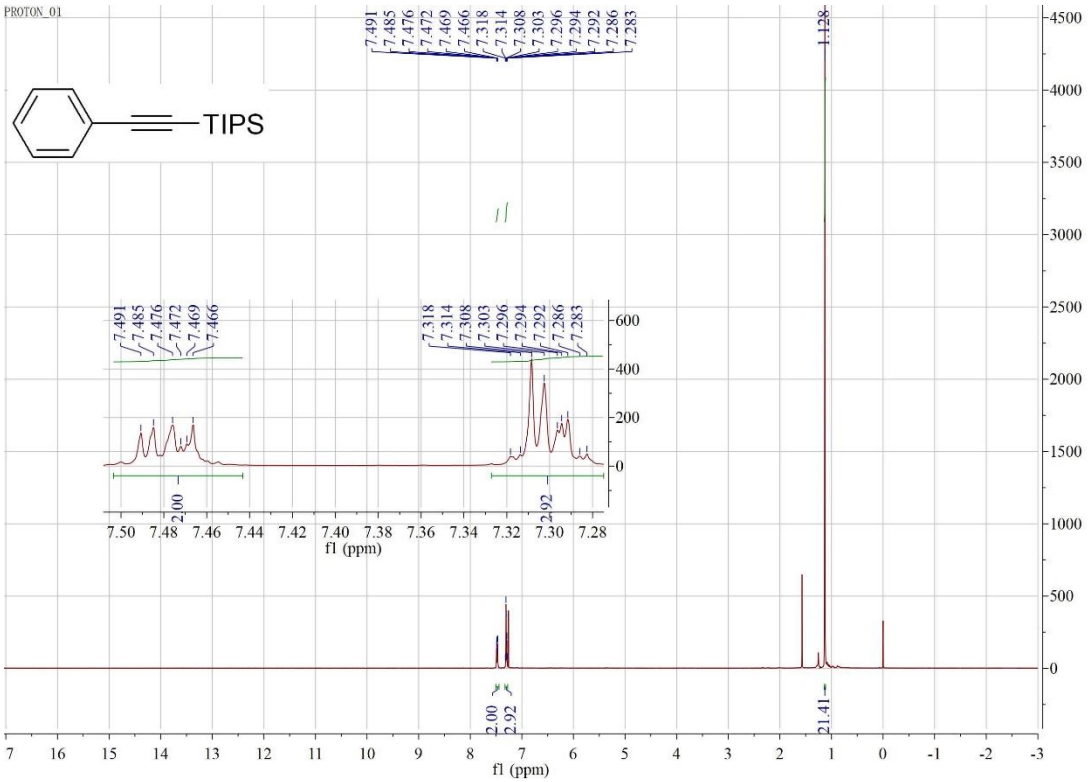
^{1}H NMR spectra of compound **3e**:



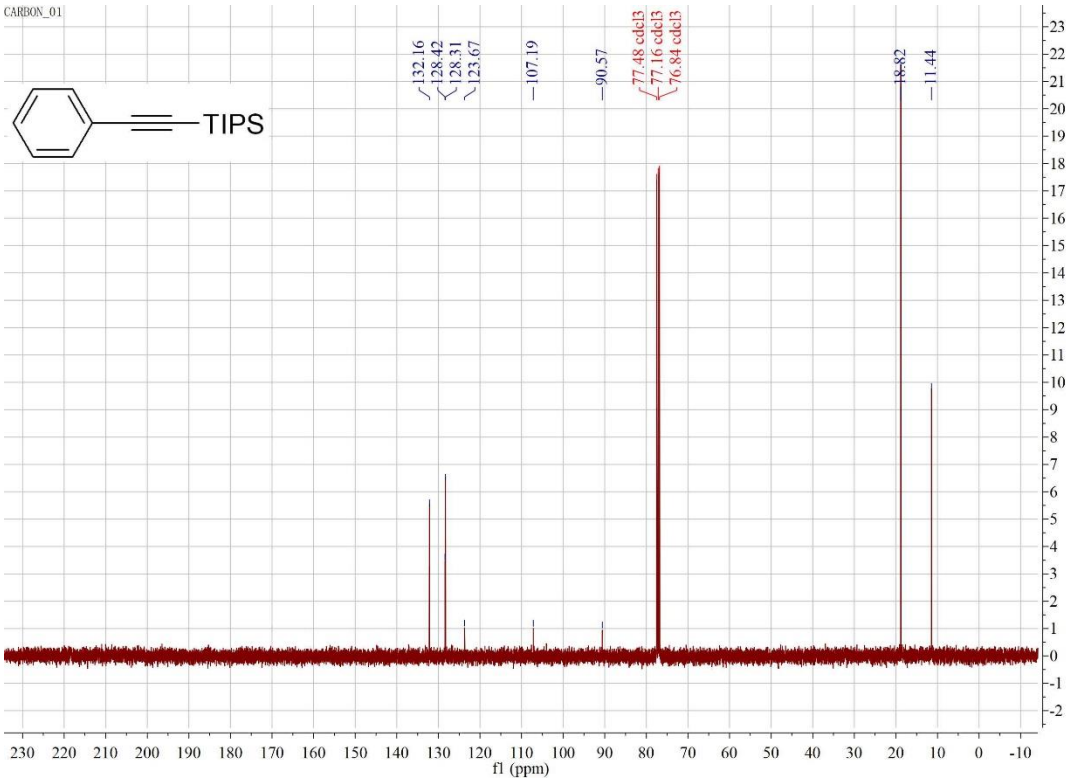
^{13}C NMR spectra of compound **3e**:



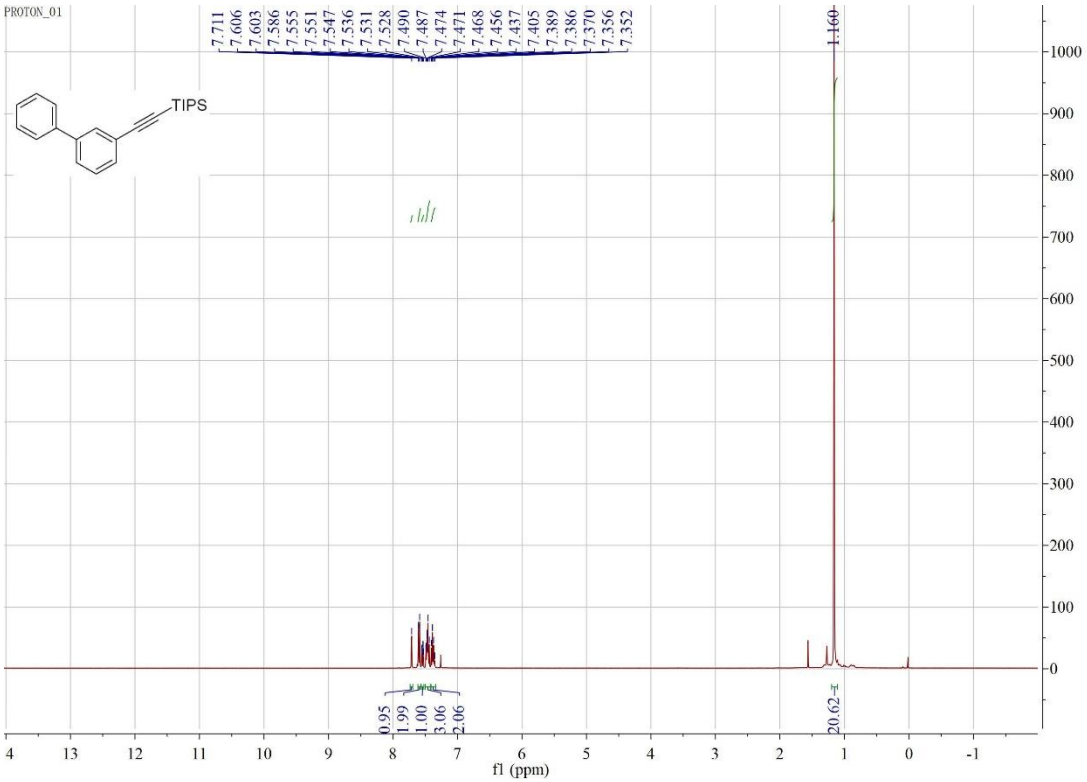
^{1}H NMR spectra of compound **3f**:



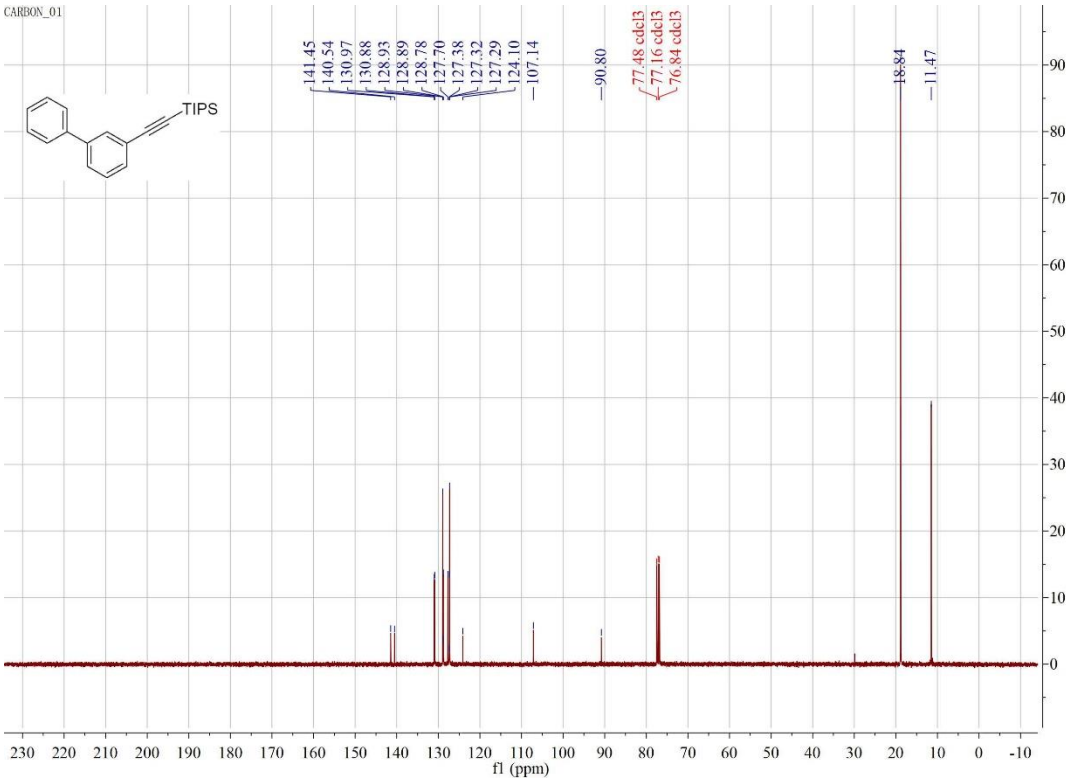
^{13}C NMR spectra of compound **3f**:



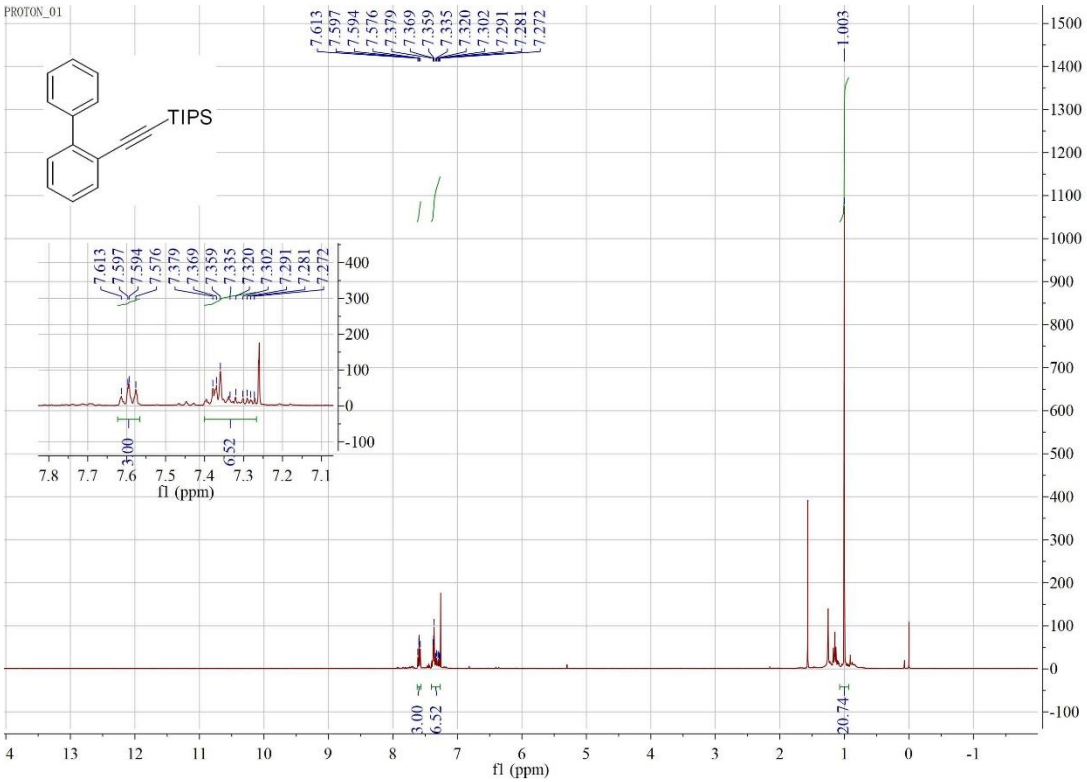
^{1}H NMR spectra of compound **3g**:



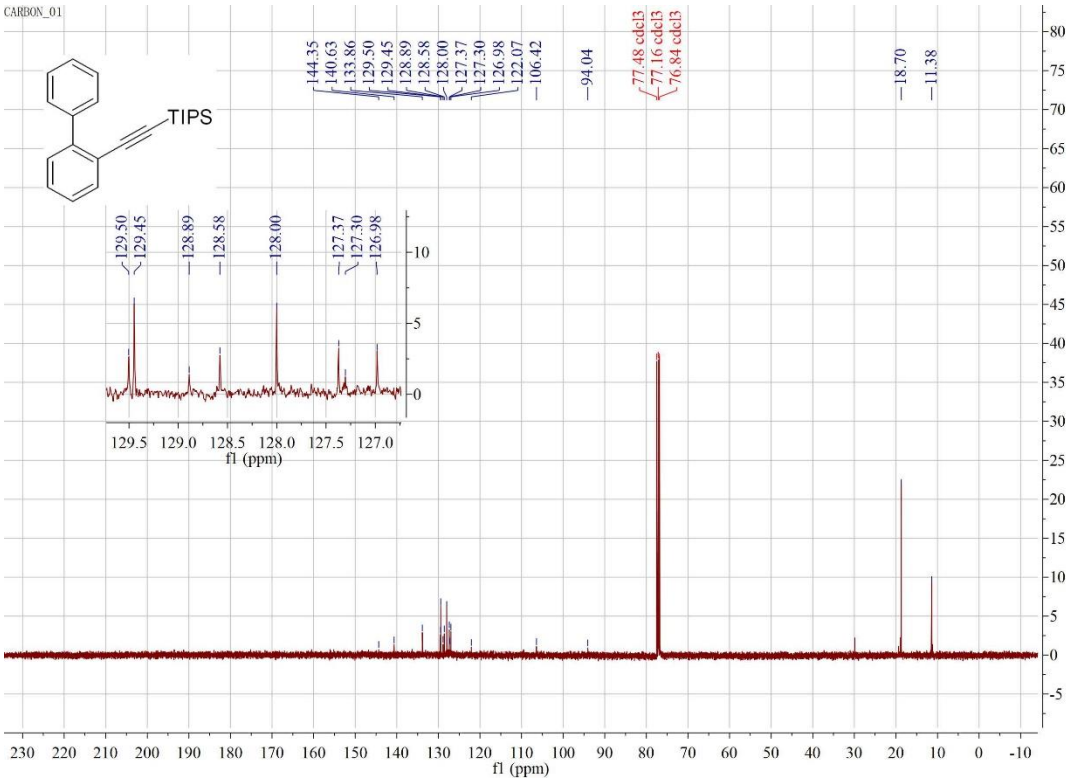
^{13}C NMR spectra of compound **3g**:



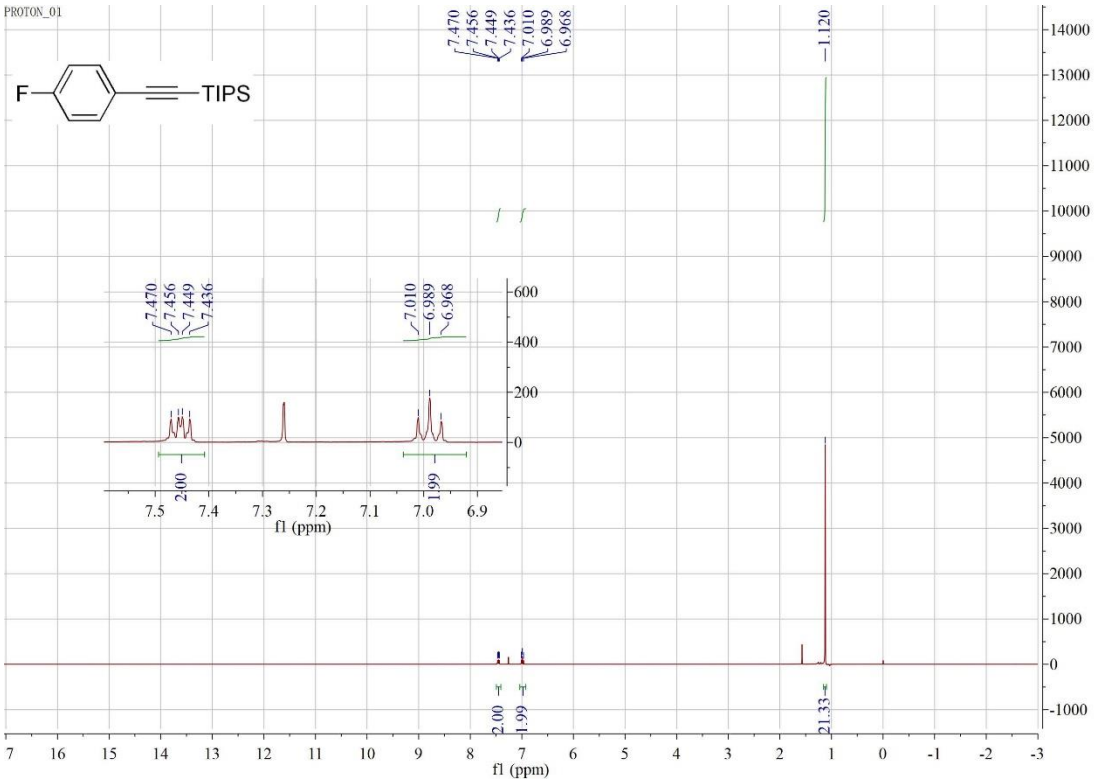
^{1}H NMR spectra of compound **3h**:



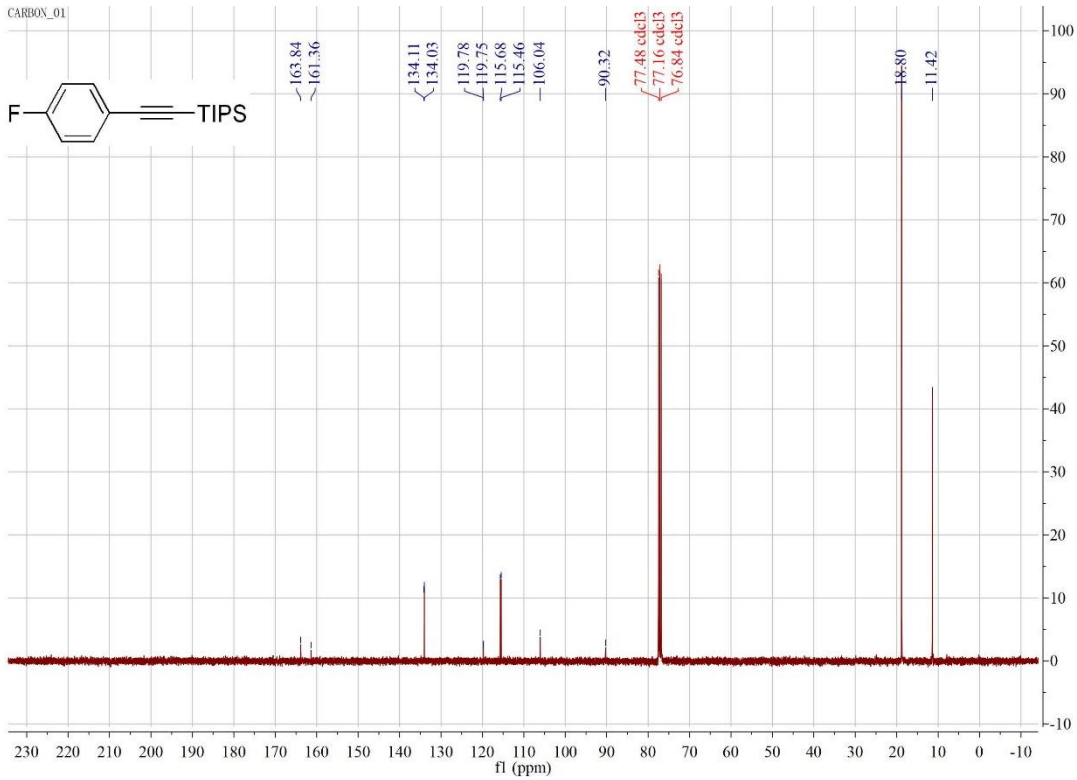
^{13}C NMR spectra of compound **3h**:



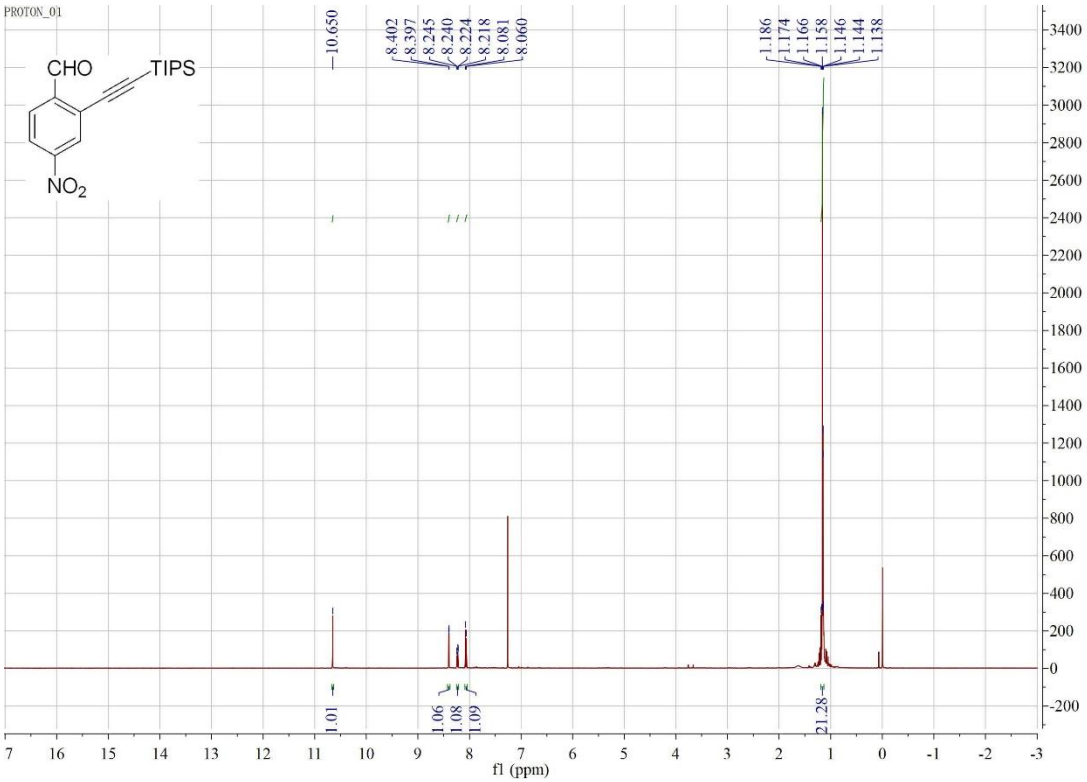
^{1}H NMR spectra of compound **3i**:



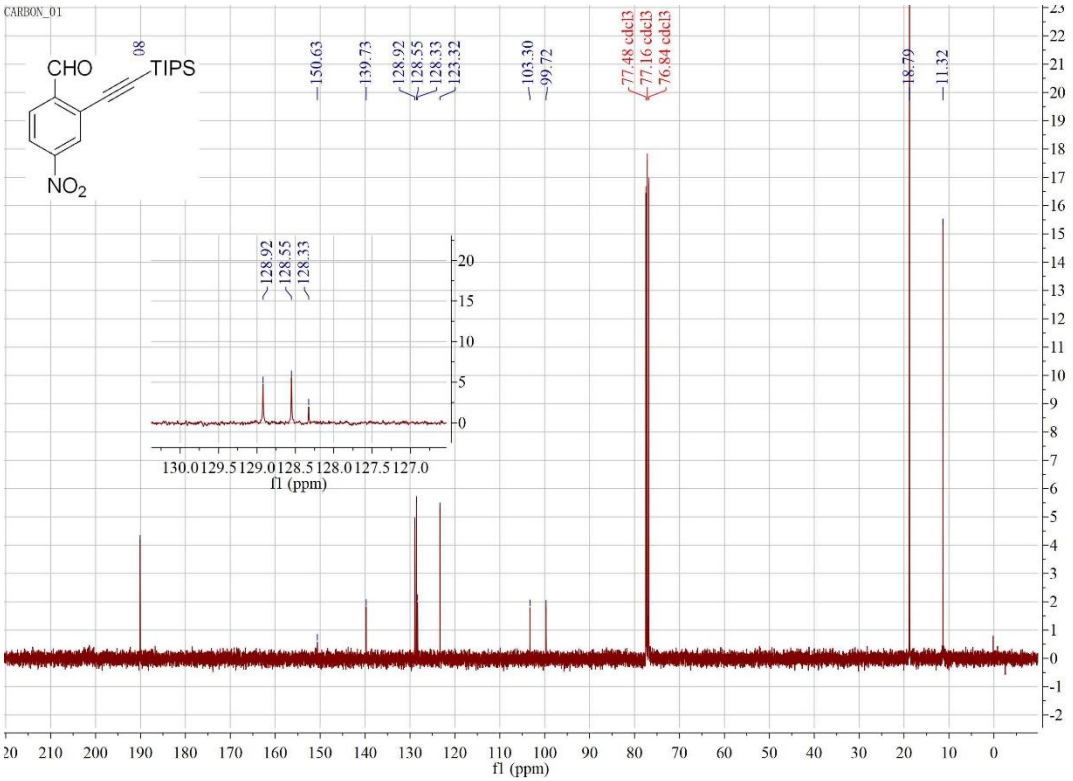
^{13}C NMR spectra of compound **3i**:



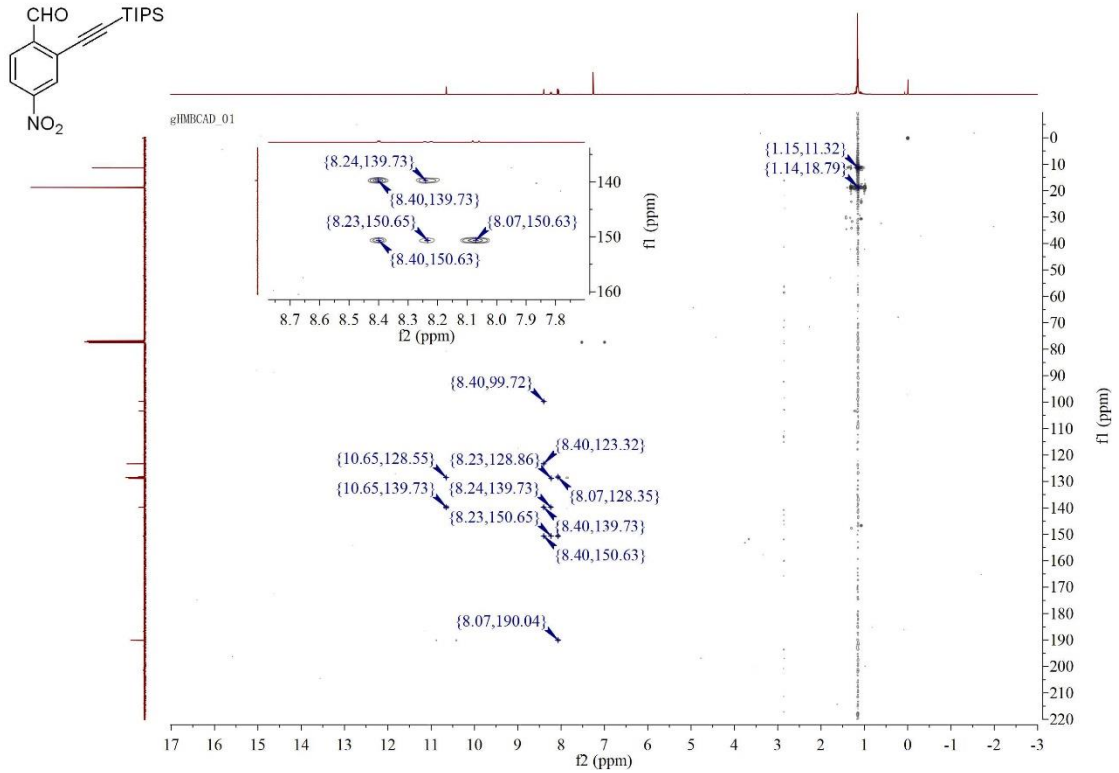
^{1}H NMR spectra of compound **3j**:



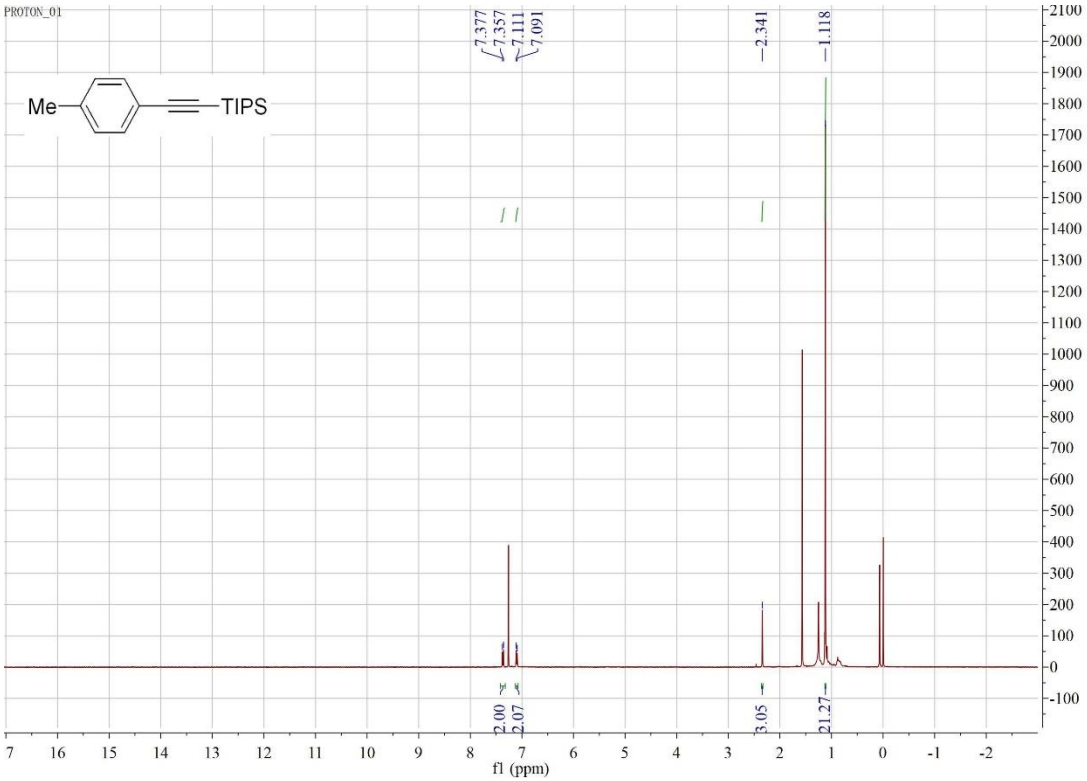
^{13}C NMR spectra of compound **3j**:



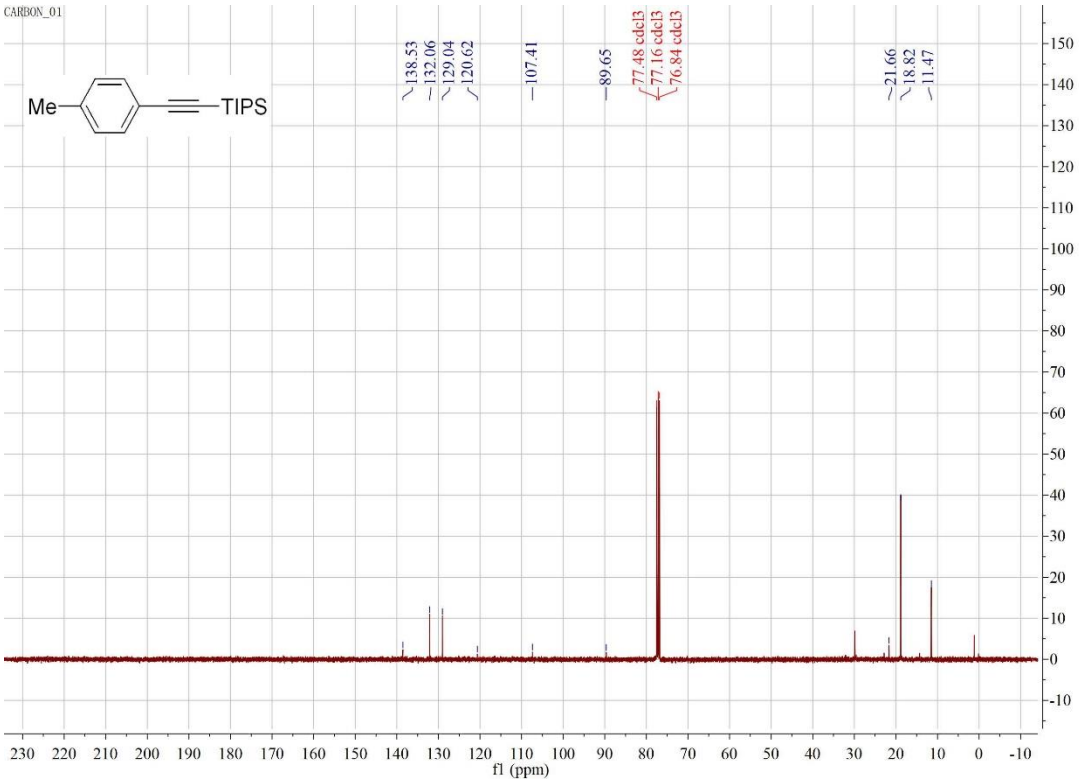
HMBC spectra of compound **3j**:



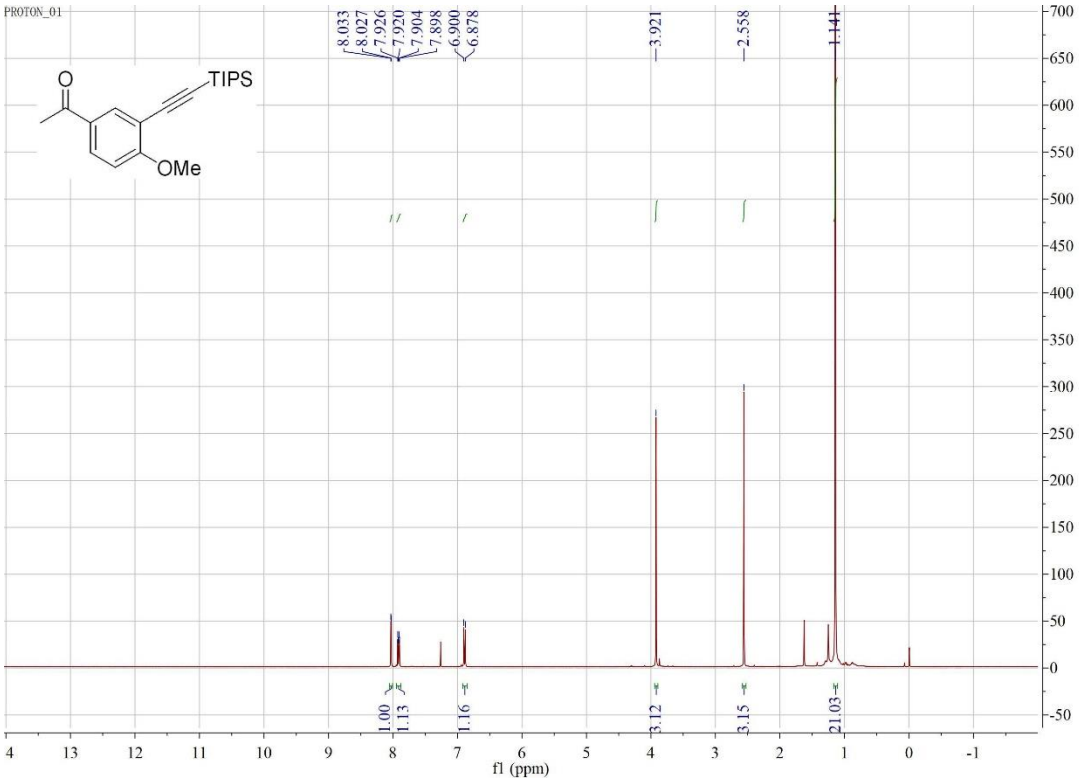
^{1}H NMR spectra of compound **3k**:



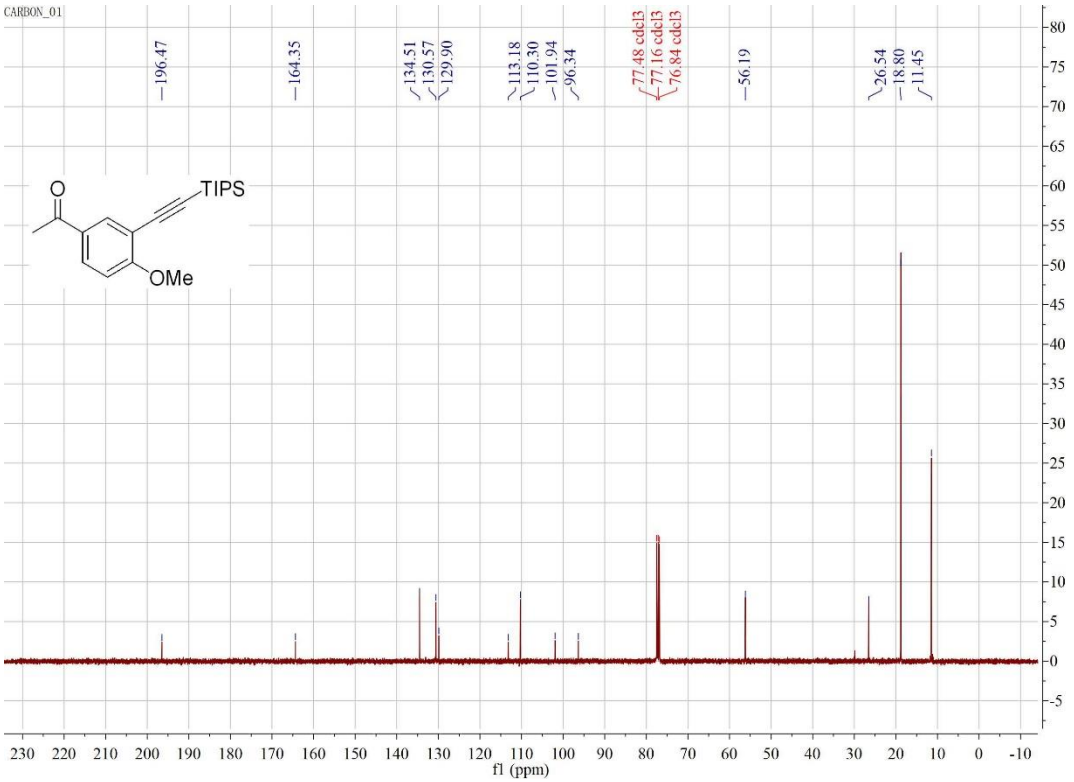
^{13}C NMR spectra of compound **3k**:



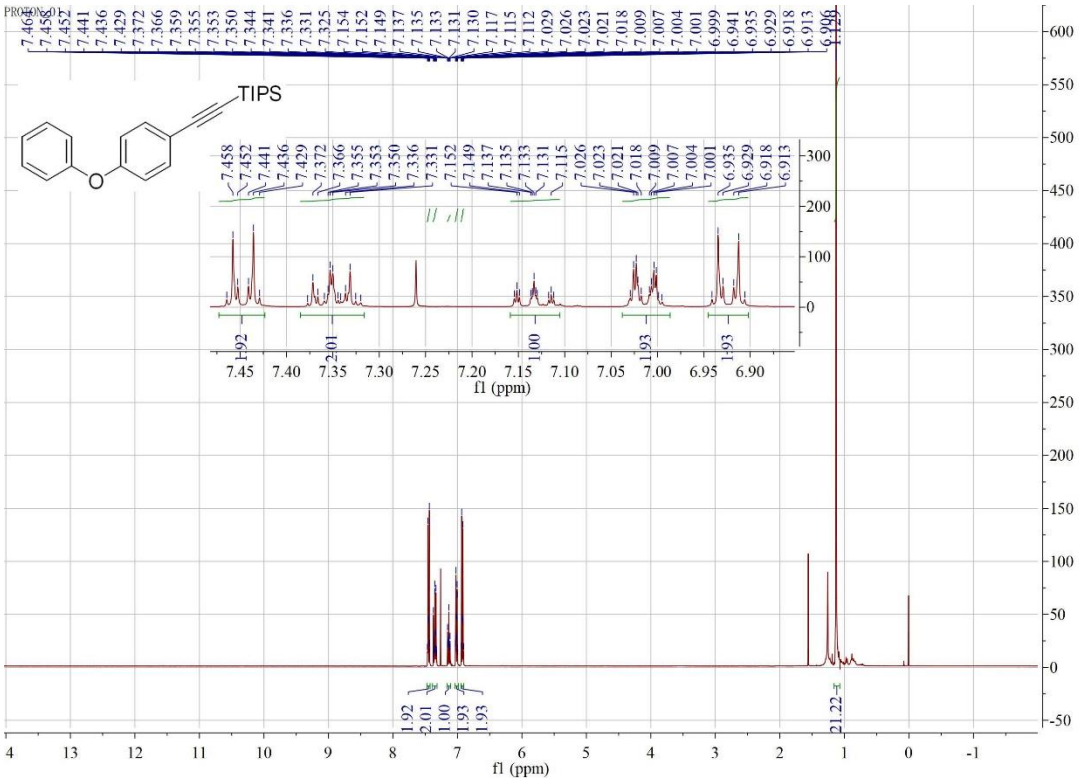
^{1}H NMR spectra of compound **3l**:



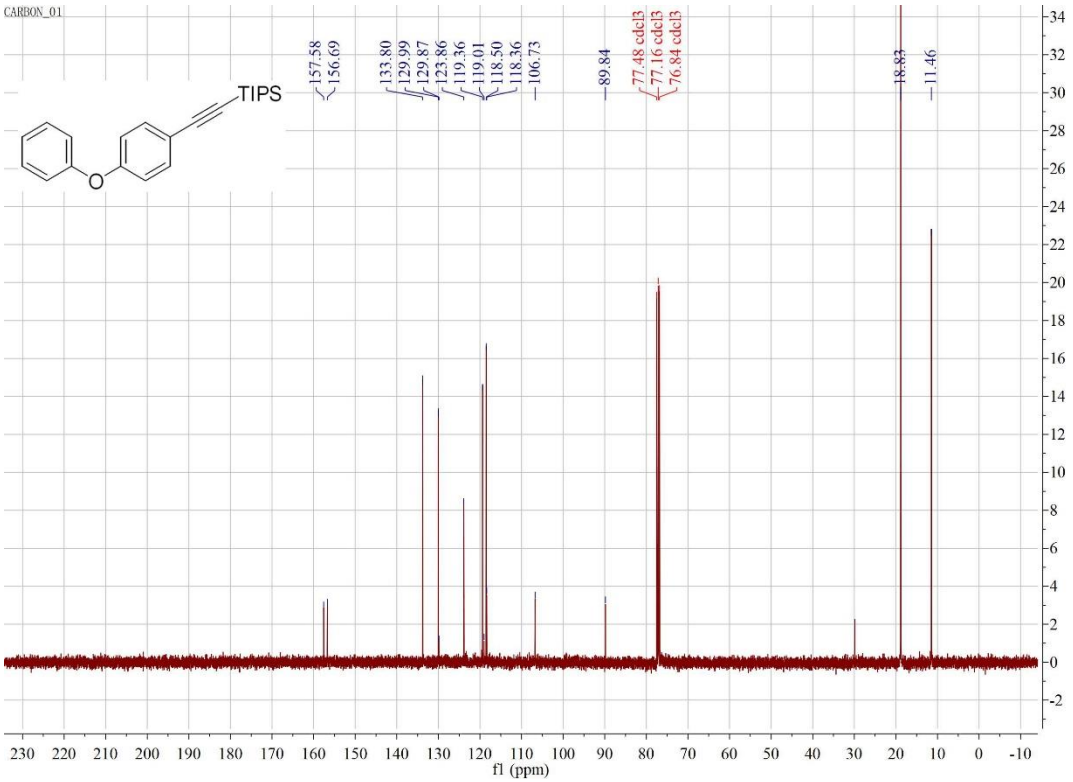
^{13}C NMR spectra of compound **3l**:



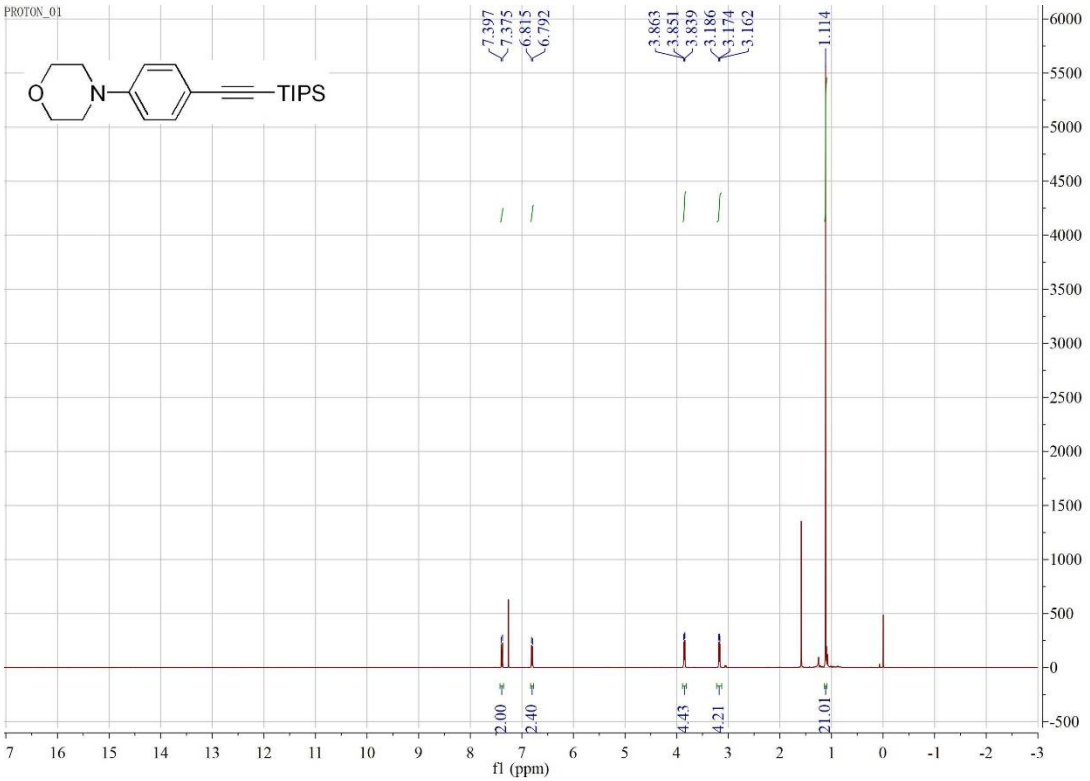
^{1}H NMR spectra of compound **3m**:



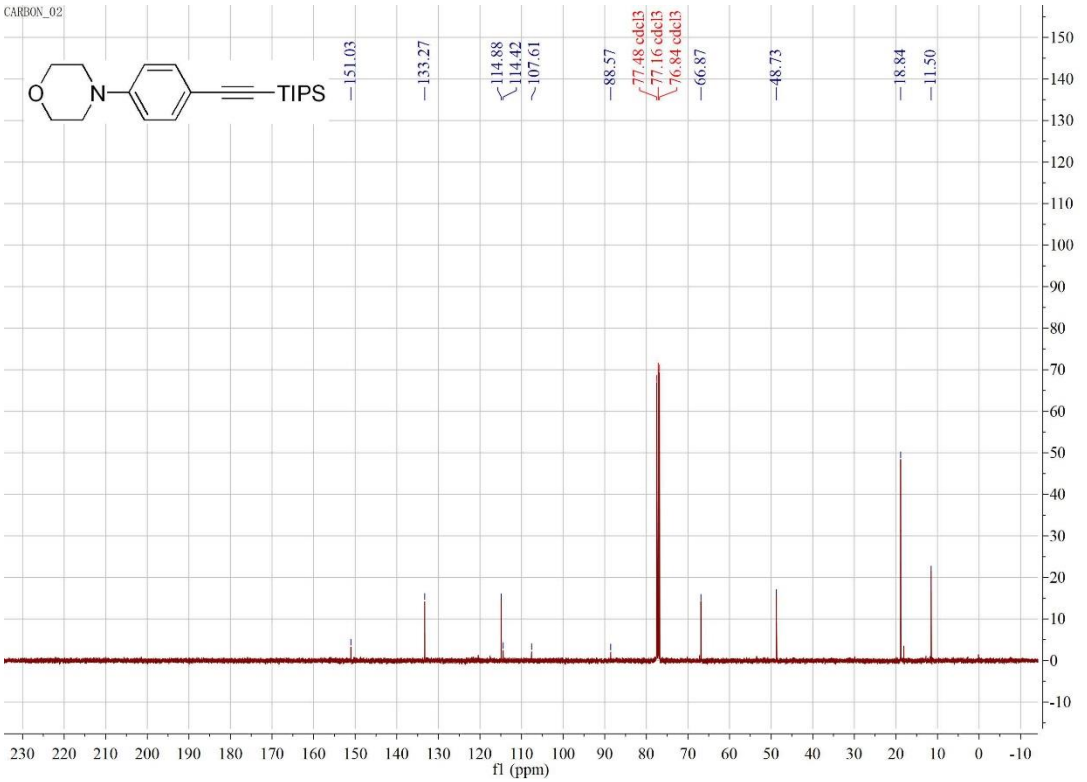
^{13}C NMR spectra of compound **3m**:



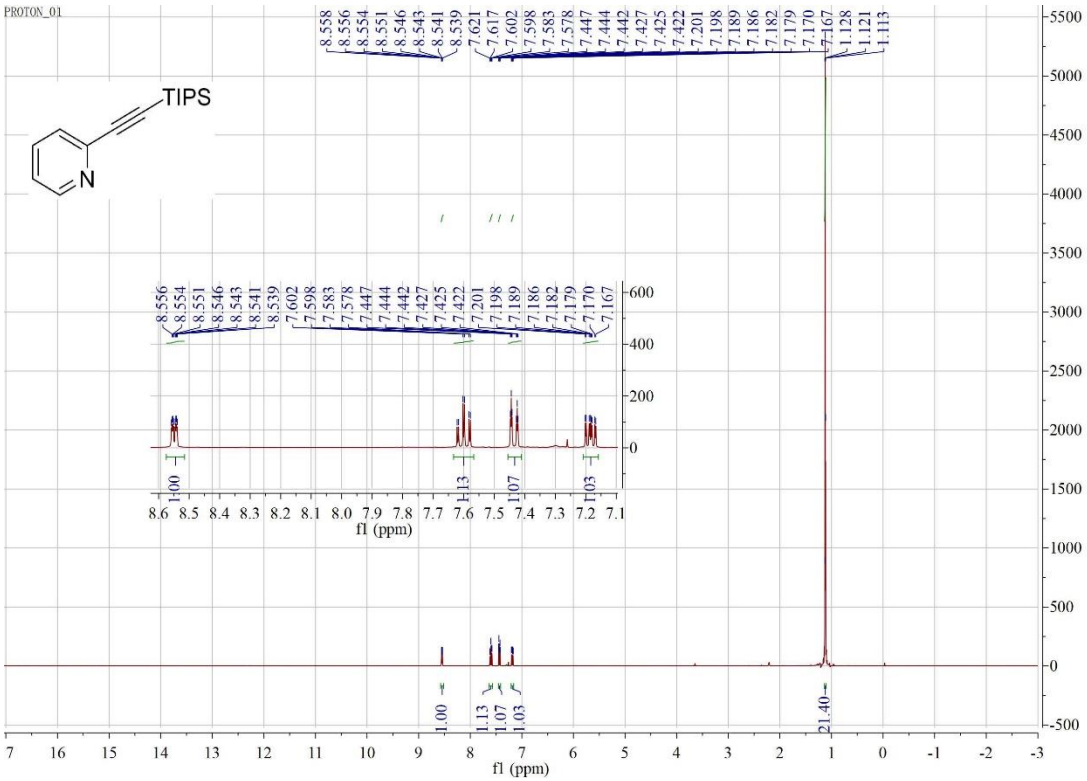
^{1}H NMR spectra of compound **3n**:



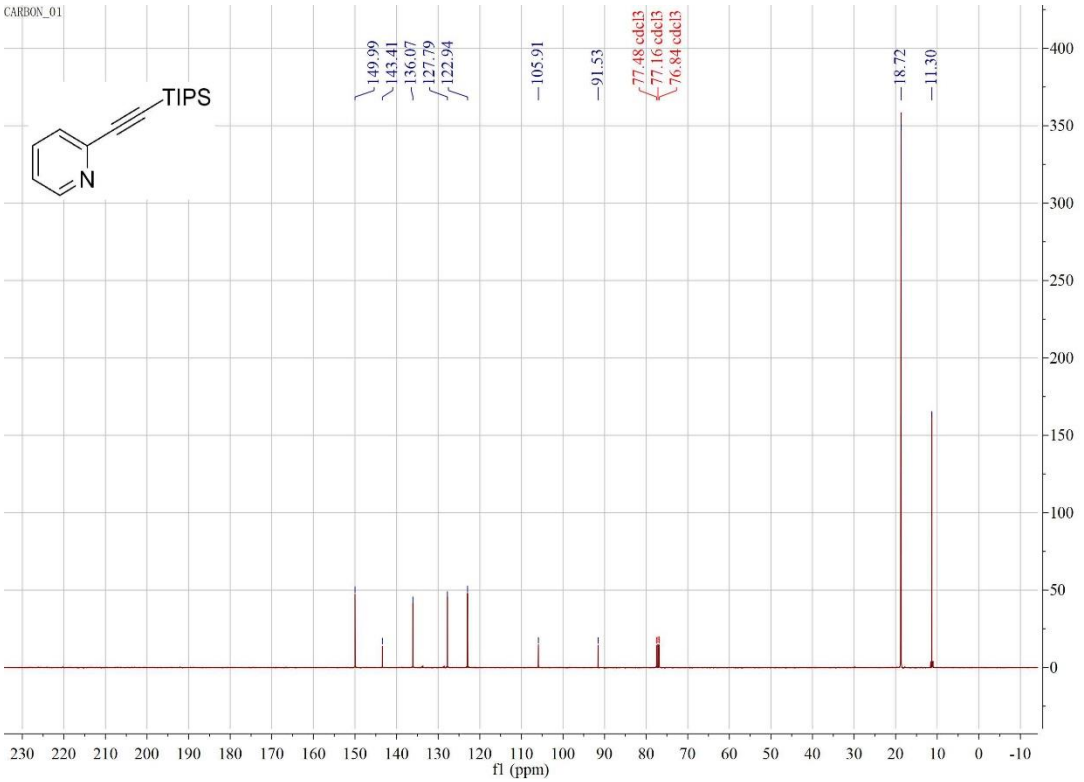
^{13}C NMR spectra of compound **3n**:



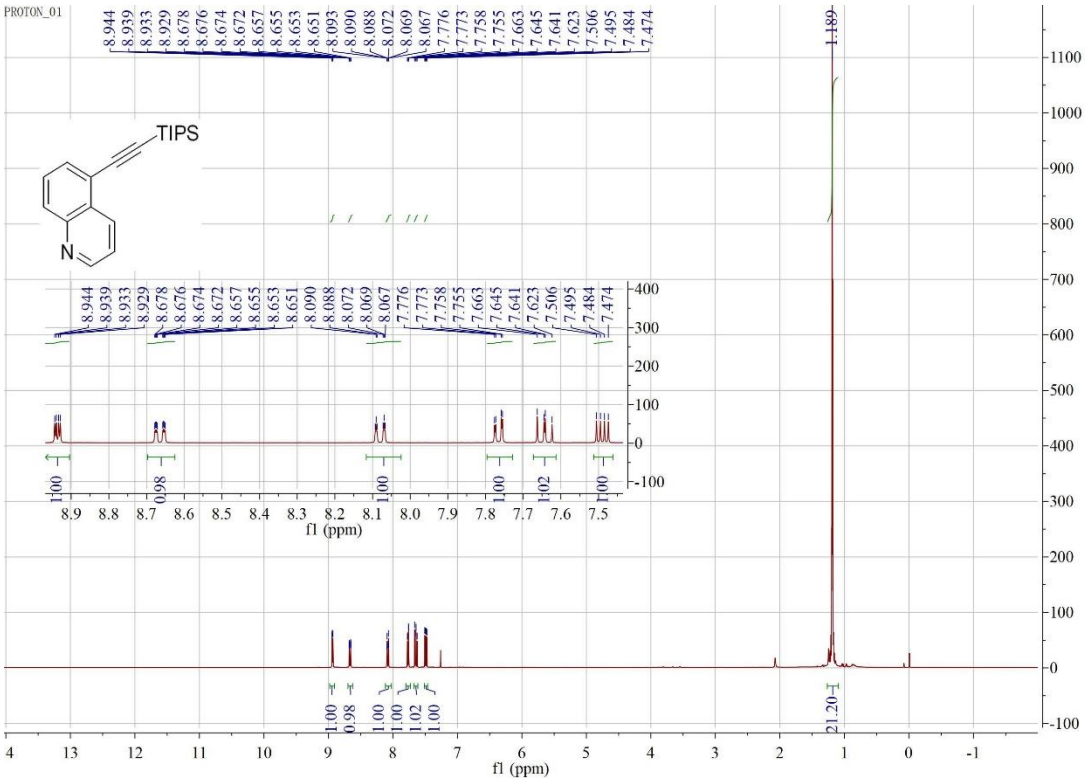
^{1}H NMR spectra of compound **3o**:



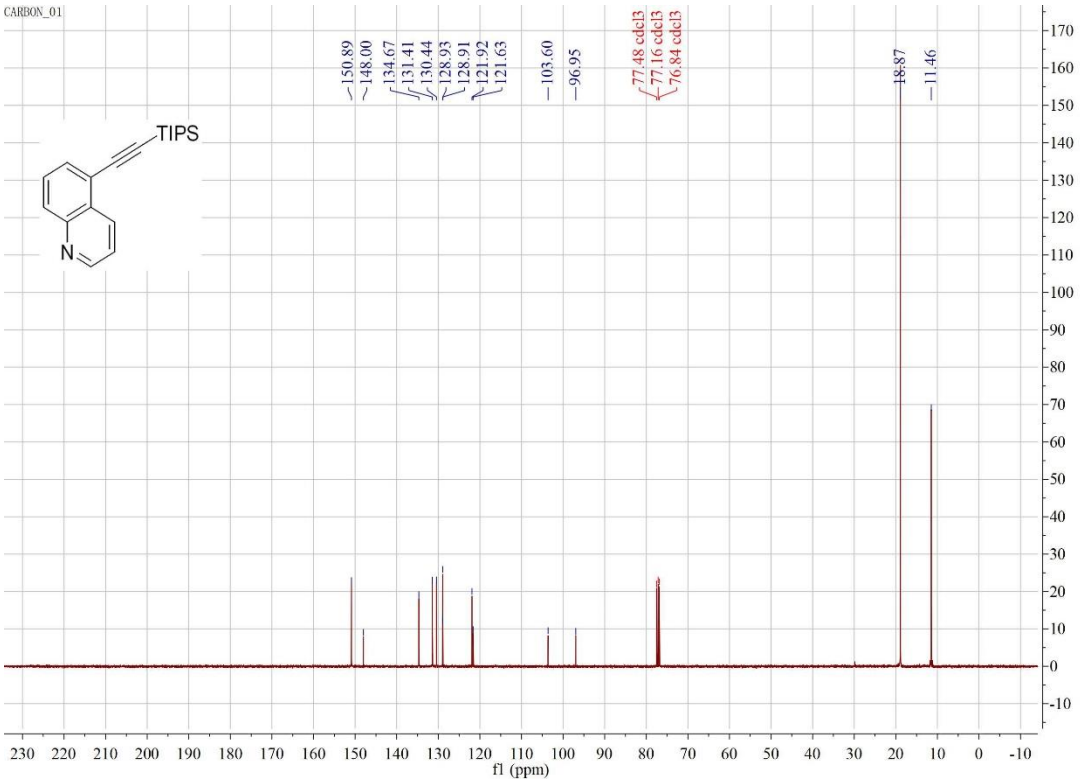
^{13}C NMR spectra of compound **3o**:



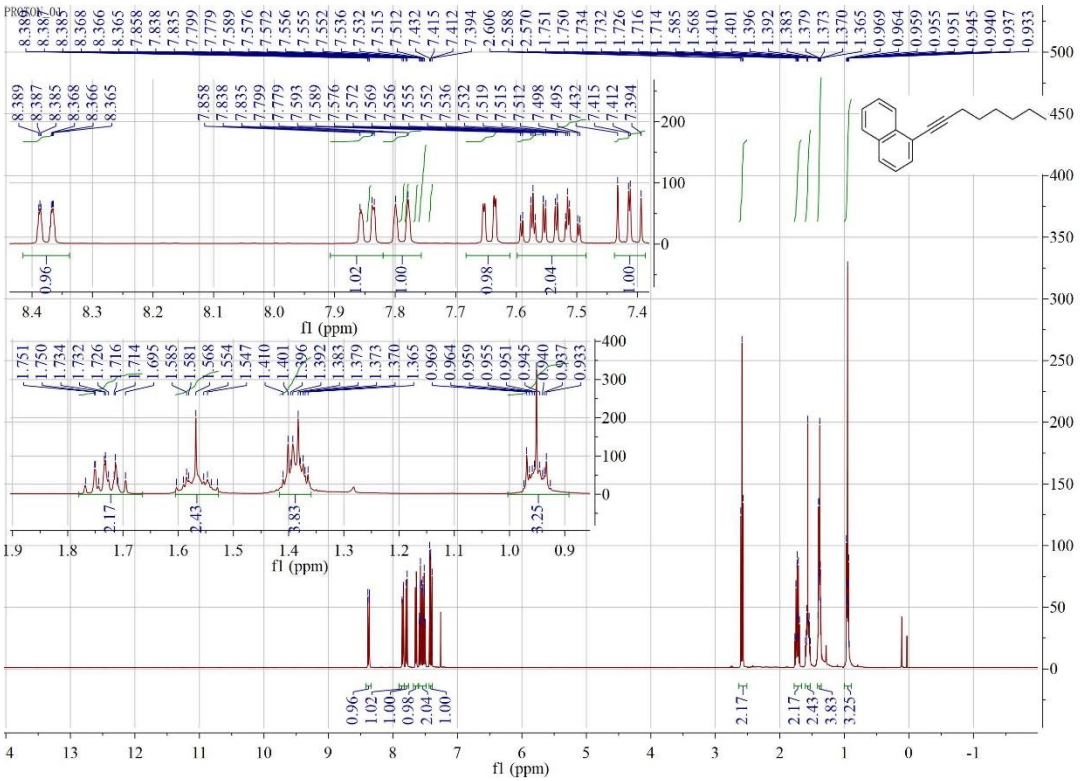
^{1}H NMR spectra of compound **3p**:



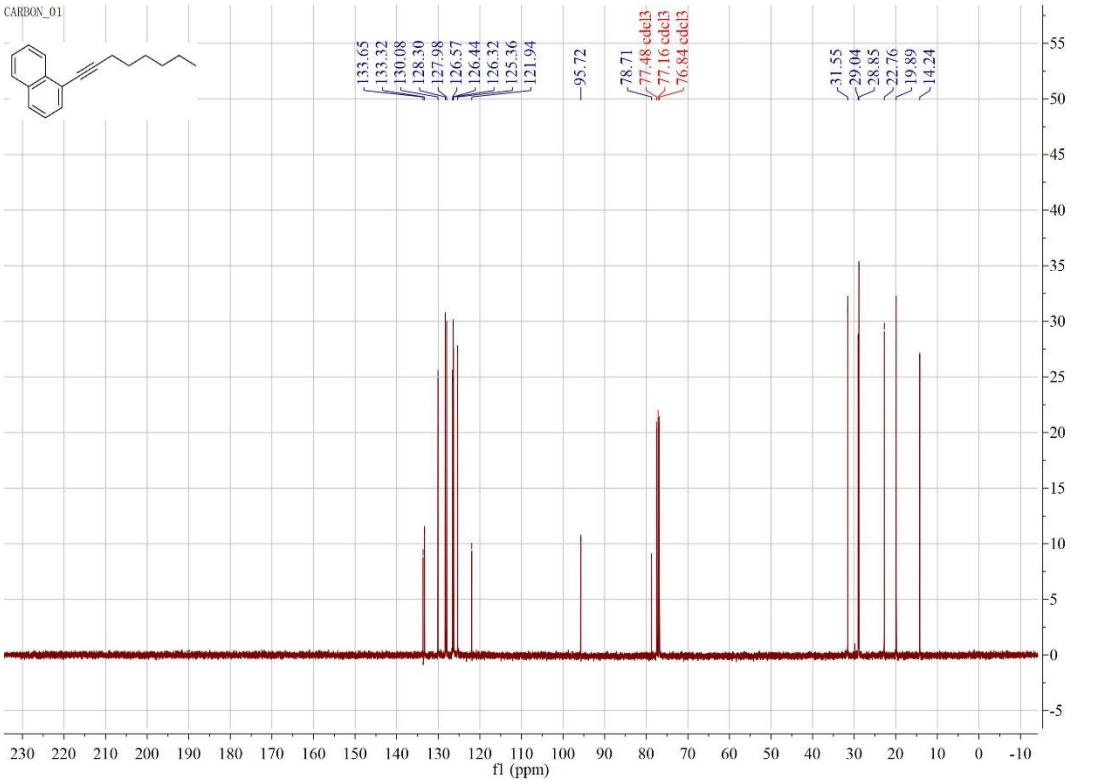
^{13}C NMR spectra of compound **3p**:



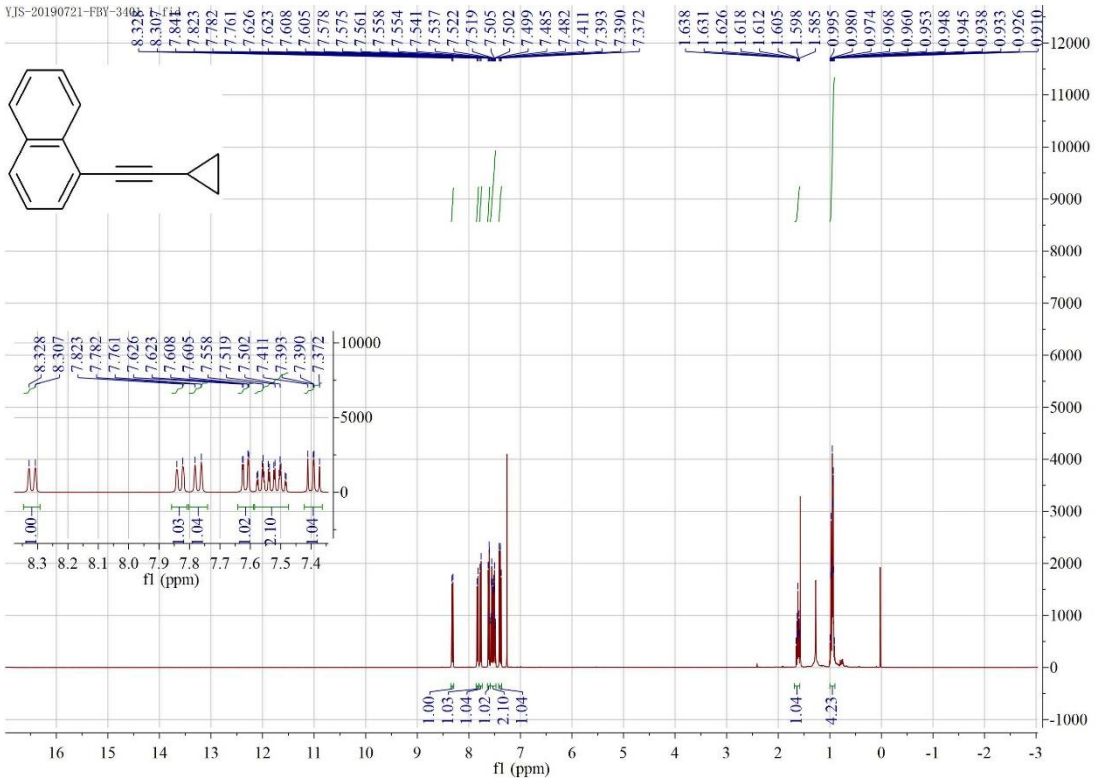
^{1}H NMR spectra of compound **3q**:



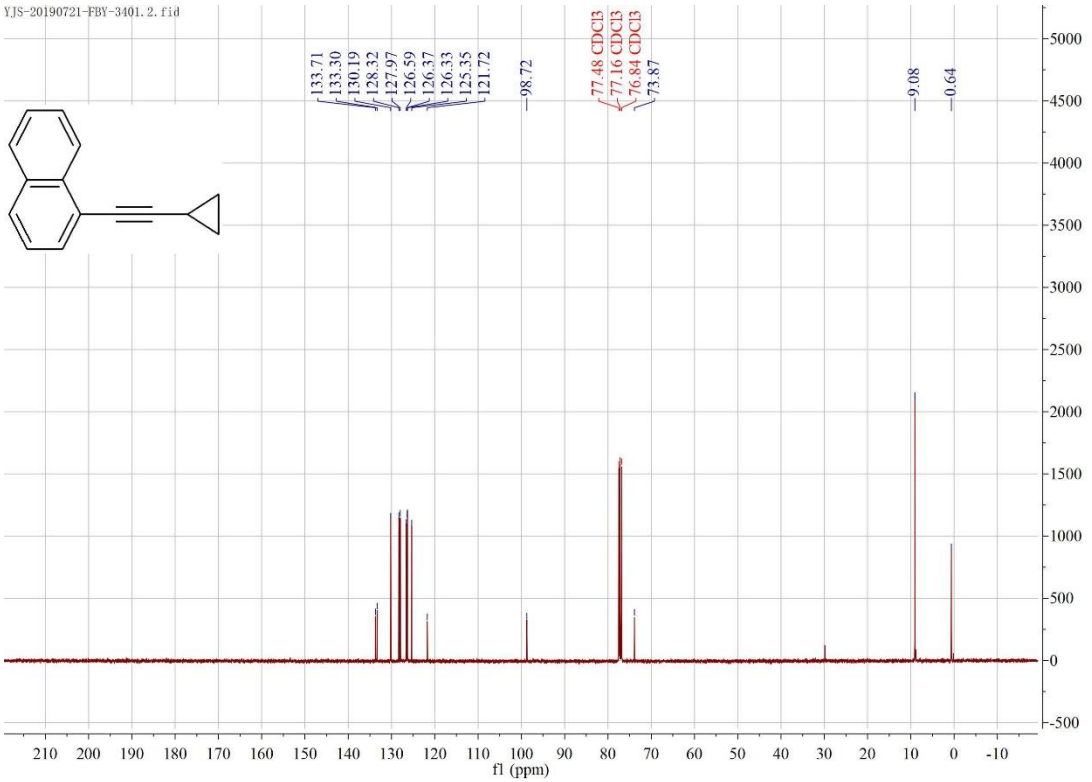
^{13}C NMR spectra of compound **3q**:



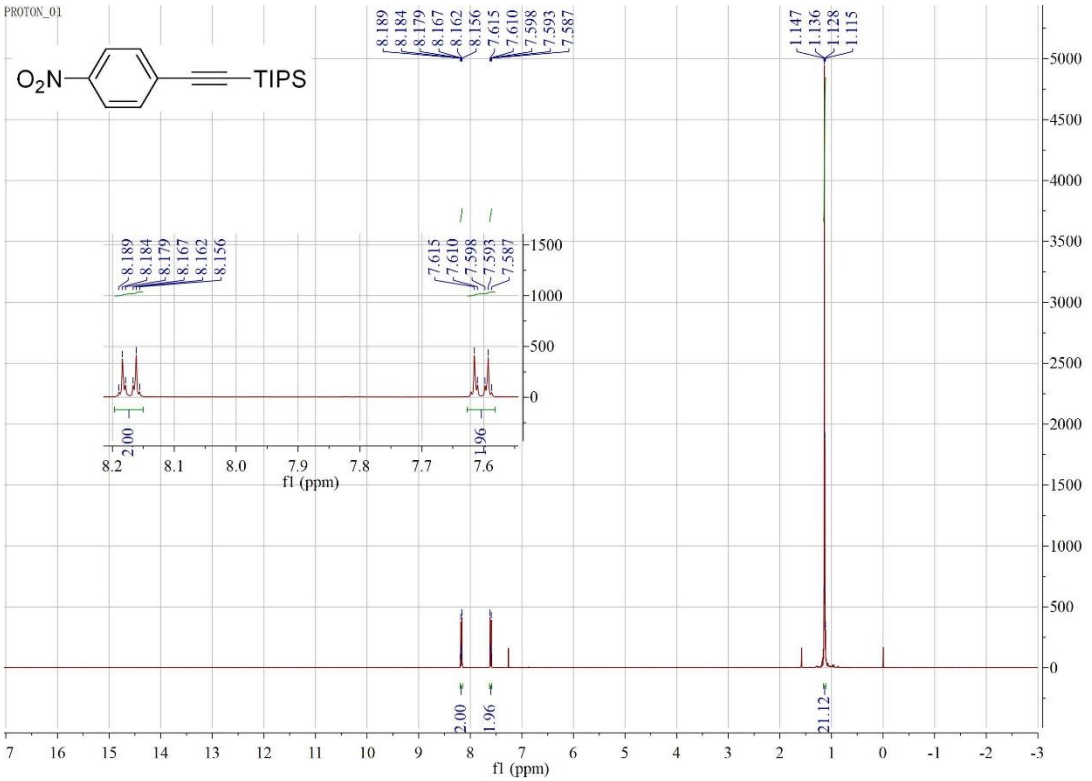
^{1}H NMR spectra of compound **3r**:



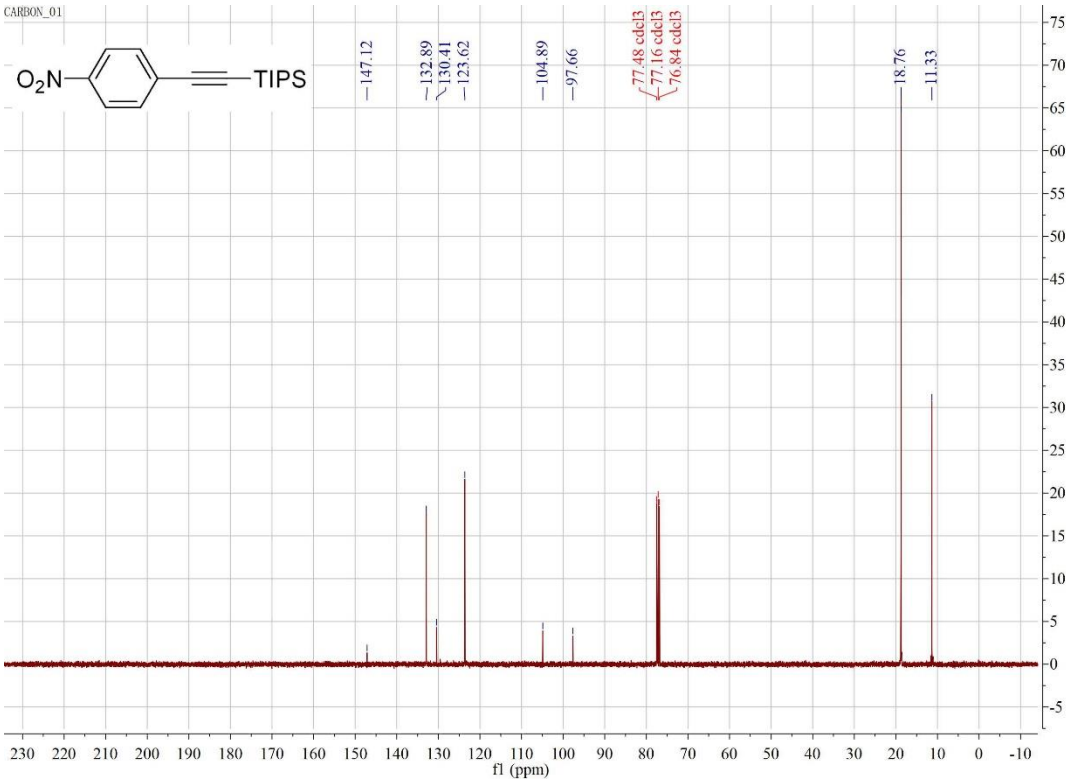
^{13}C NMR spectra of compound **3r**:



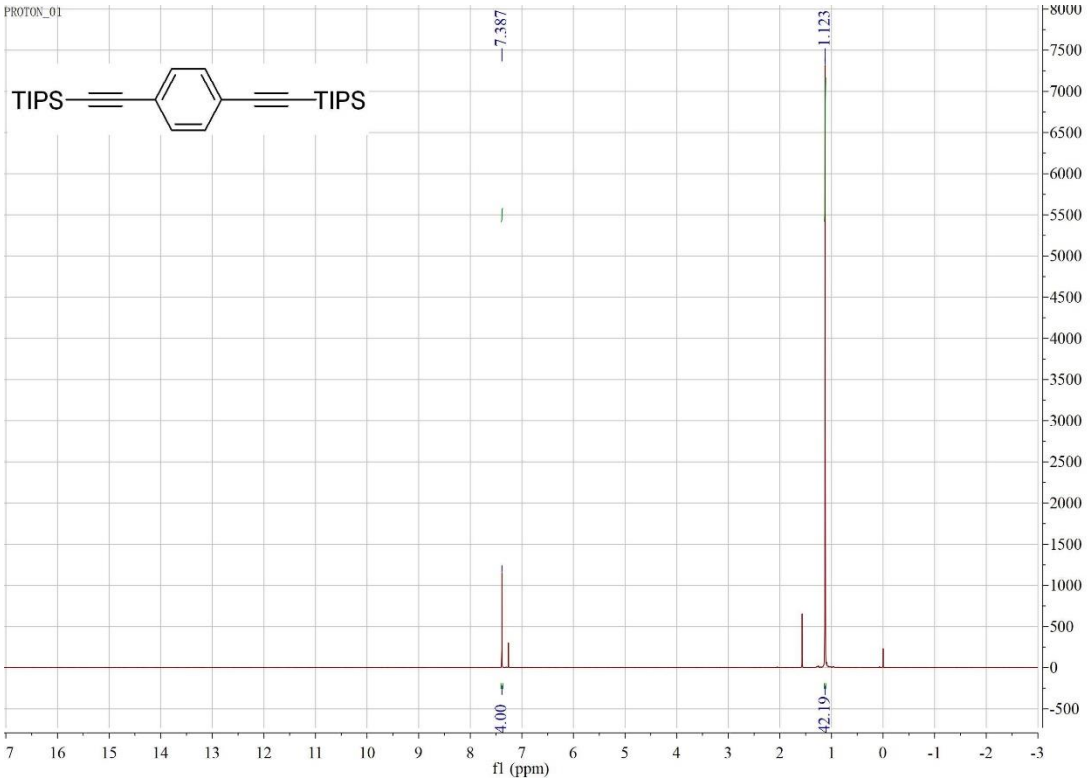
^{1}H NMR spectra of compound **3s**:



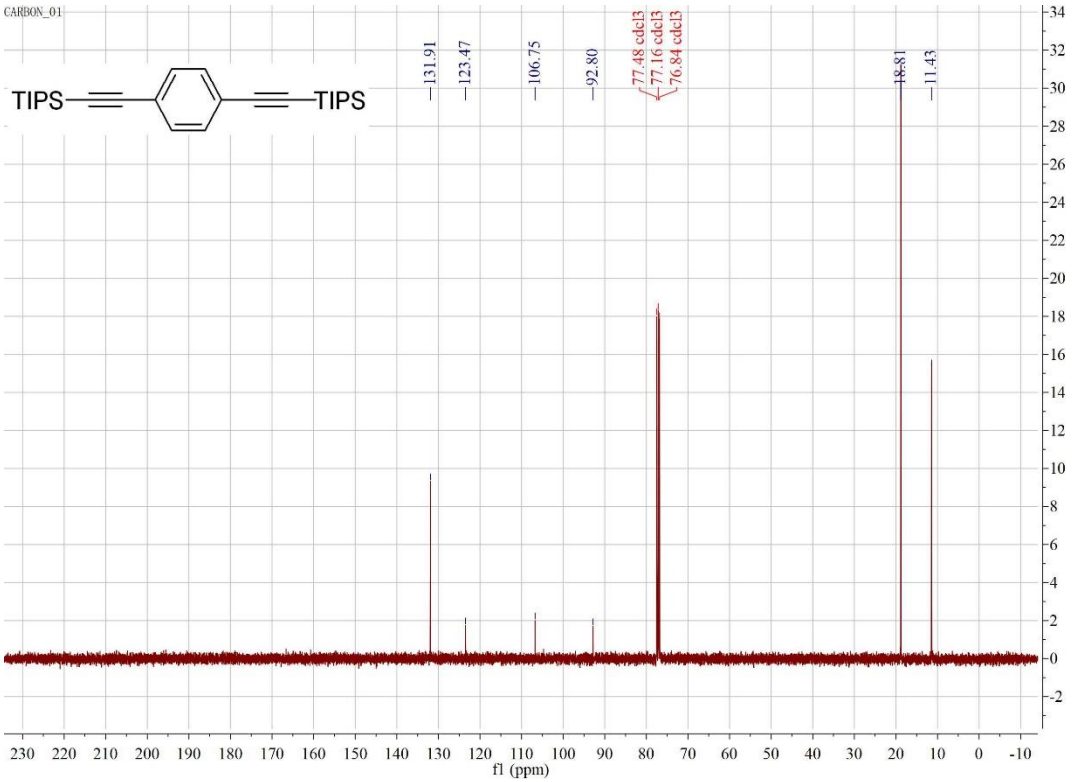
^{13}C NMR spectra of compound **3s**:



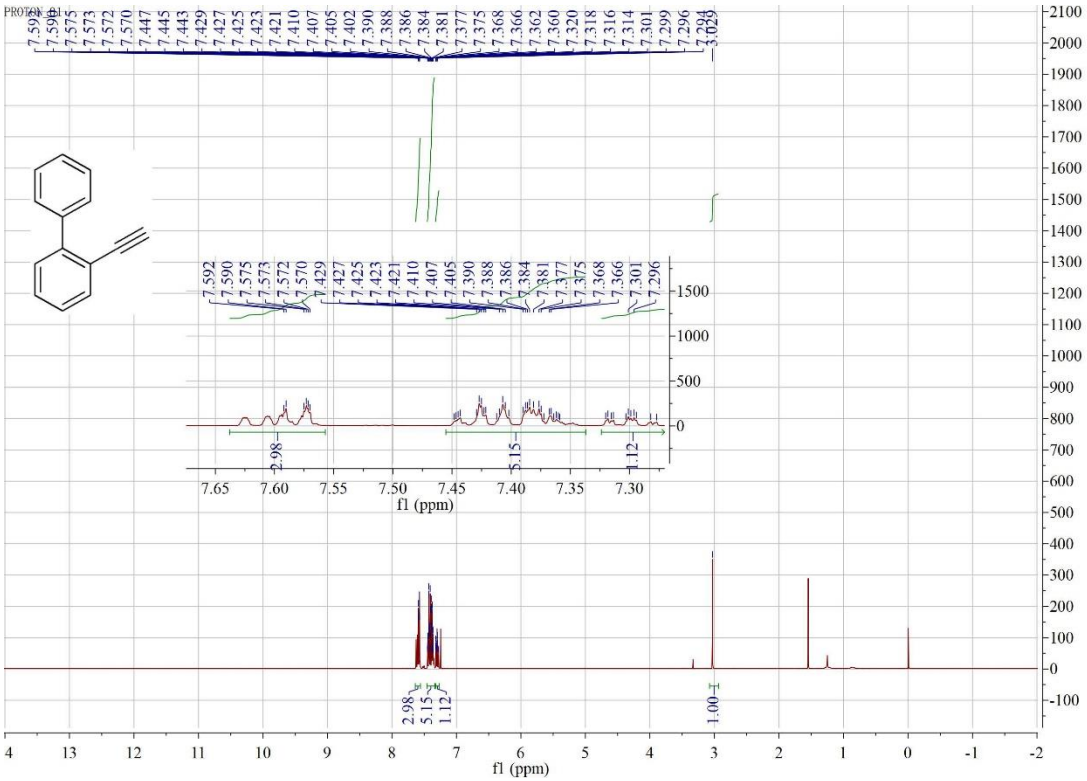
^{1}H NMR spectra of compound **3s'**:



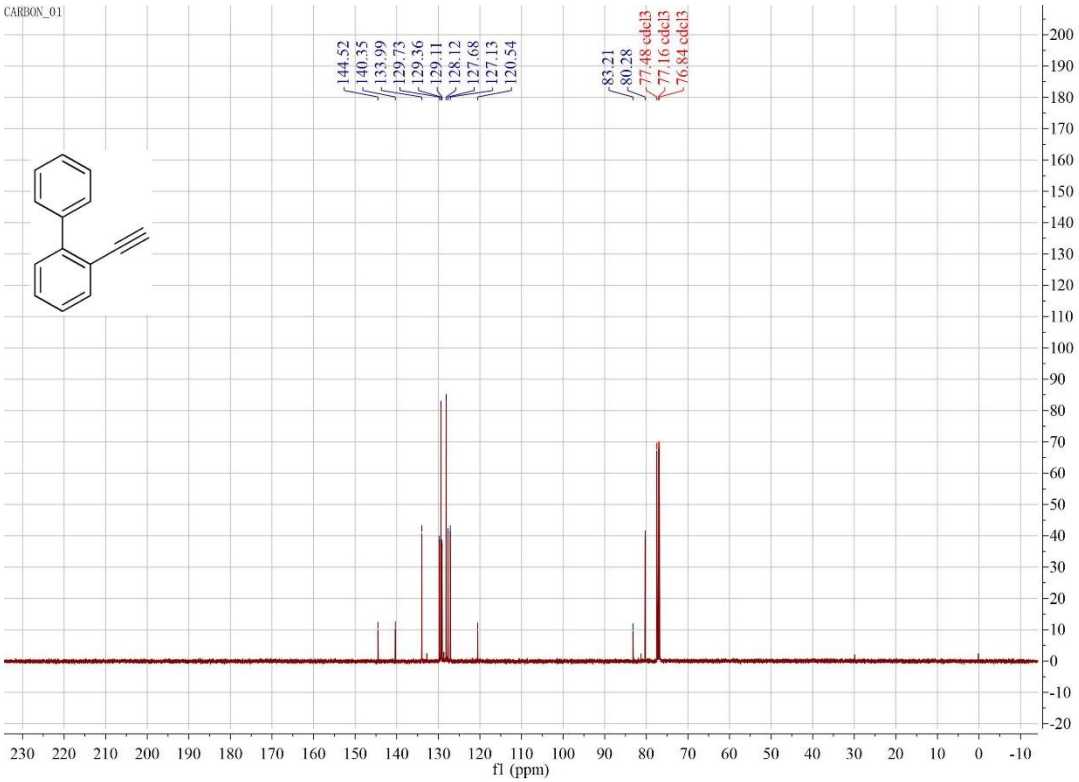
^{13}C NMR spectra of compound **3s'**:



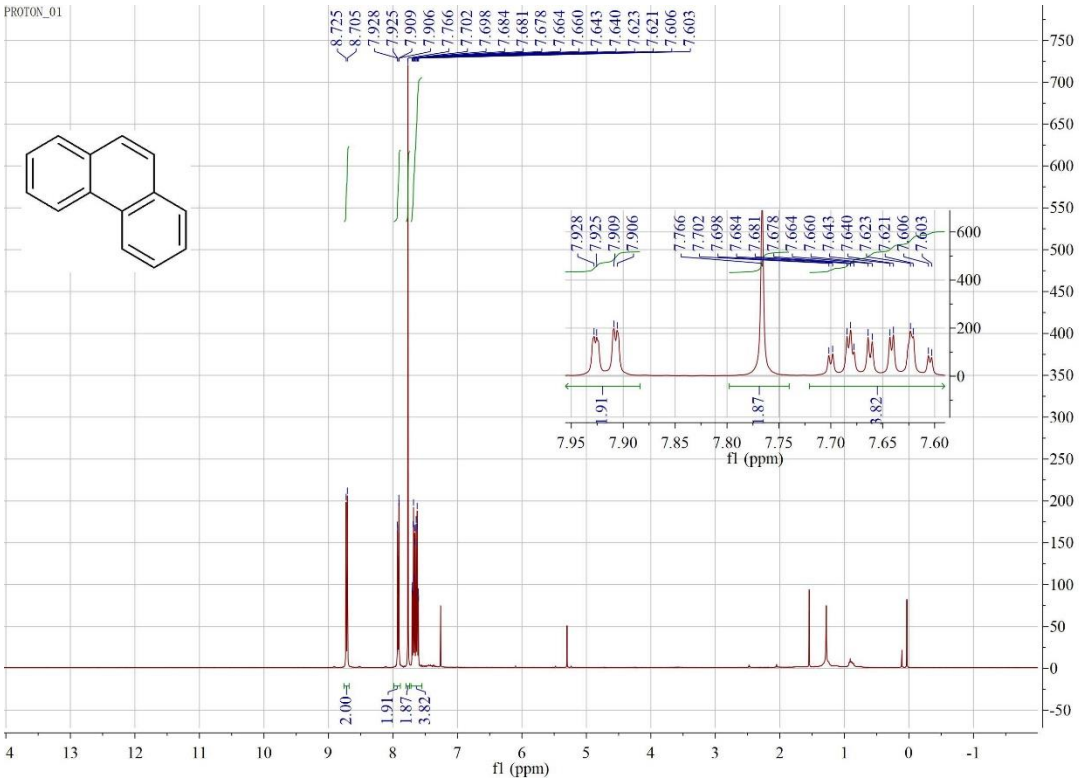
^{1}H NMR spectra of compound **4**:



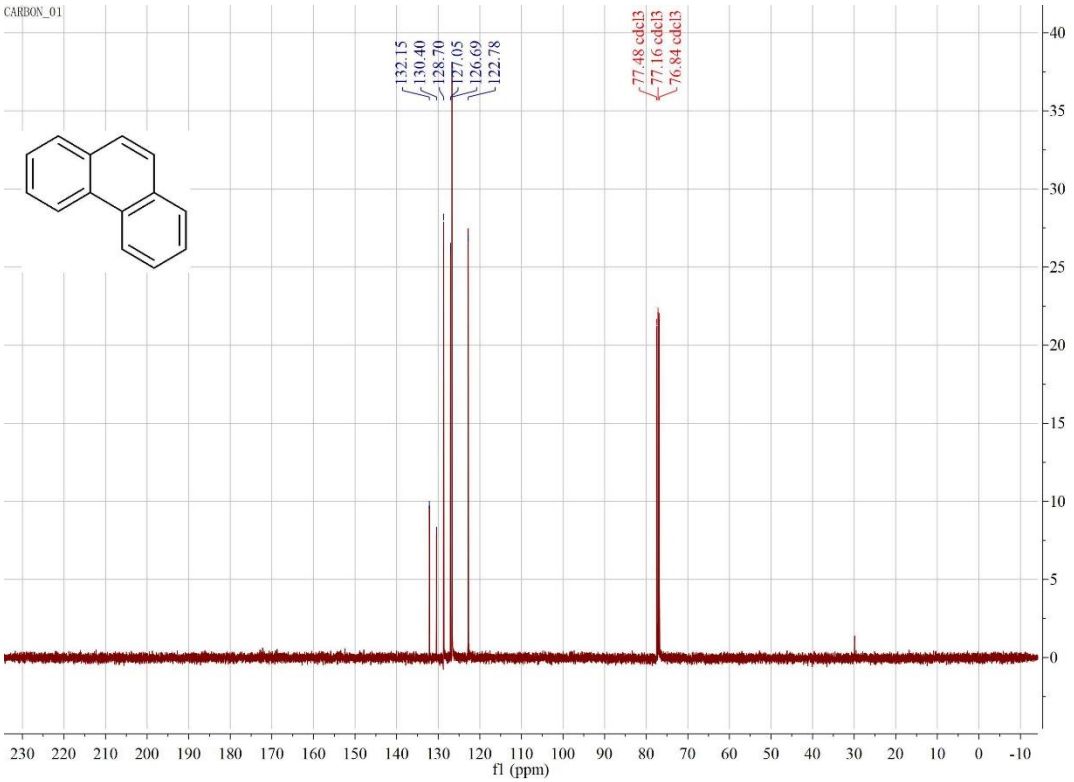
^{13}C NMR spectra of compound **4**:



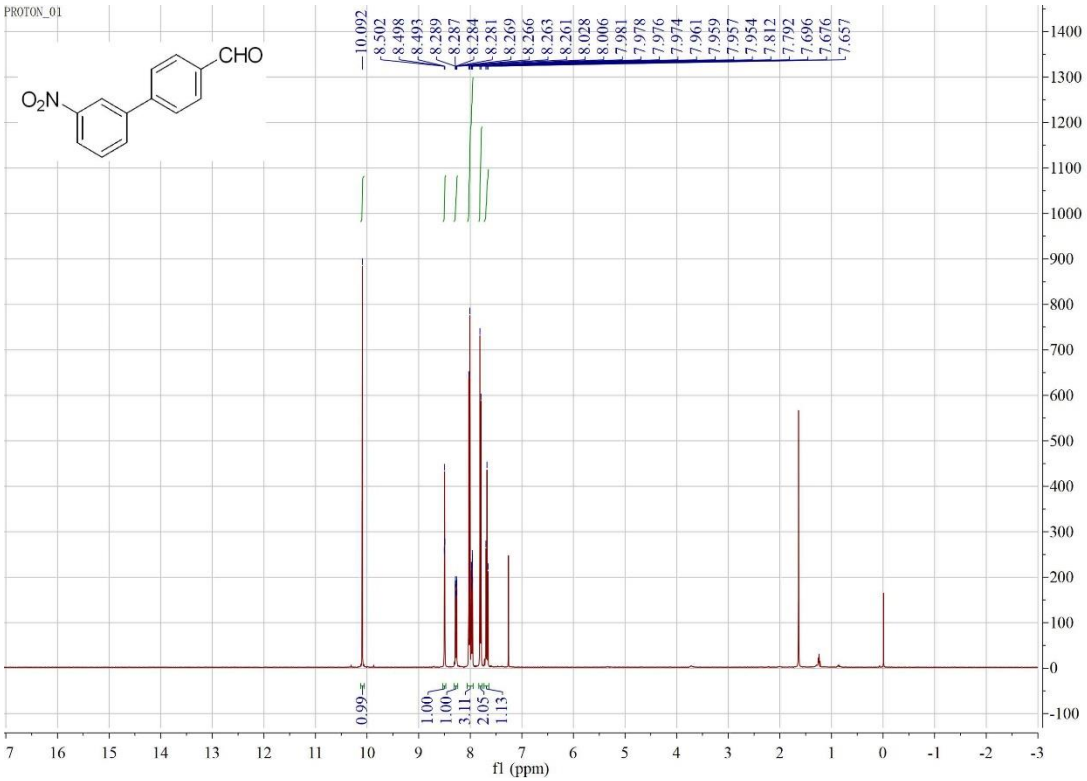
^{1}H NMR spectra of compound **5**:



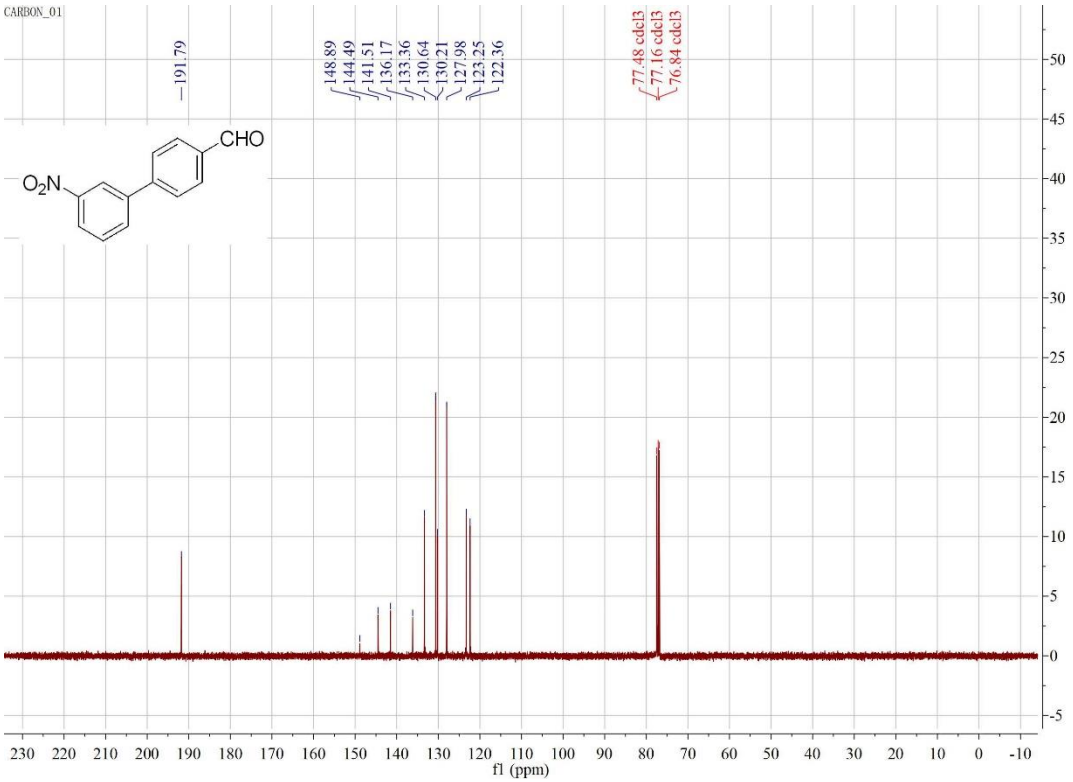
^{13}C NMR spectra of compound **5**:



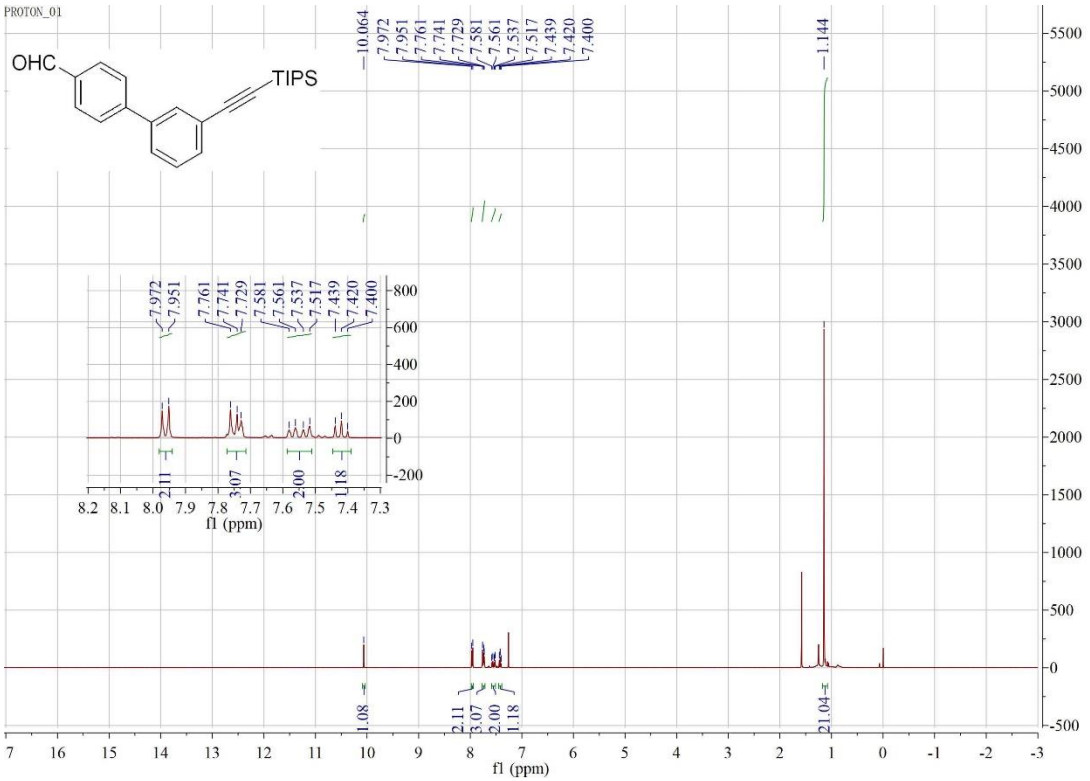
^{1}H NMR spectra of compound **6**:



^{13}C NMR spectra of compound **6**:



^{1}H NMR spectra of compound **7**:



^{13}C NMR spectra of compound **7**: