Supporting Information

Charge Transfer Complex Enabled Mechanochemical Synthesis of Chalcogenoacetylenes via Alkynyl Radicals

Fang Tan,[a,b†] Chang-Zhen Fang,[b†] Bing-Sheng Qiu,[b†] He Sheng,[b,c*] Yong-Liang Tu[b*] and Xiang-Yu Chen[b,c*]

[a]School of Chemical Engineering, Guizhou Minzu University, Guiyang 550025, China
[b]School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
[c]Binzhou Institute of Technology, Weiqiao-UCAS Science and Technology Park, Binzhou, Shandong Province 256606, China
E-mail: shenghe@ucas.ac.cn; tuyongliang@ucas.ac.cn; chenxiangyu20@ucas.ac.cn.

Contents

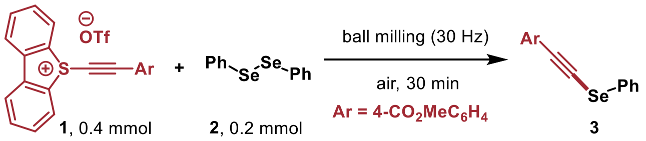
1. General Information

- Chemicals were purchased from Heowns, Innochem and Bidepharm, and they were used without further purification unless otherwise noted. Diselenides and ditellurides were prepared according to the literature methods.[1] Alkynyl sulfonium salts were prepared according to the literature methods.[2] Solvents were purified using a solvent-purification system (VSPS-8, Vigor).
- Analytical thin layer chromatography was carried out with silica gel pre-coated glass plates (TLC-Silica gel GF254, coating thickness: 0.25 mm) purchased from Xinnuo Chemical (Yantai, China). Chromatographic purification of the products was performed on silica gel 200-300 mesh. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution.
- Chromatographic purification of the products was performed on 200-300 mesh silica gel.
- IR spectra were taken on a Vertex 70 spectrophotometer and reported as wave numbers (cm^{-1}).
- The GC-MS TQ8040 was used in the detection of the reaction mixture.
- High-resolution mass spectra (HRMS) were obtained with the mass analyzer of an orbitrap. The calculated values are based on the most abundant isotope.
- The SGW X-4 was used to measure the melting point of solids.
- ^{1}H- and ^{13}C- NMR spectra were recorded at ambient temperature on a JNM-ECZ-400S/500S/600R Spectrometer. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as the internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (J) are reported in Hertz (Hz).
- All mechanochemical reactions were carried out using grinding vessels in a Retsch MM 400 mill with stainless jars (5 mL) and balls (5 mm), or PTFE-coated jars (25 mL) and balls (15 mm) (Figure S1).

Figure S1. Retsch MM 400, stainless jars and balls, and PTFE-coated jars and balls were used in this study.

2. General Procedure and the Optimization of the Reaction Conditions

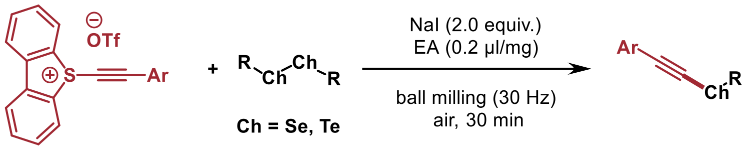
2.1 **Table S1** Optimization of the reaction conditions



Entry	Additive (2 equiv.)	LAG (0.2 µl/mg)	Yield (%)[a]
1	NaOAc	EA	59
2	Na_2CO_3	EA	14
3	NaCl	EA	33
4	NaI	EA	89
5	NaI	DMF	63
6	NaI	DCM	76
7	NaI	THF	72
8	NaI	1,4-dioxane	49
9	NaI	PhMe	45
10	NaI	MeCN	34
11	NaI	DMA	45
12	-	EA	trace
13	NaI	-	47
14	-	-	trace
15[b]	NaI	EA	trace
16[c]	NaI	EA	44
17[d]	NaI	EA	62
18[e]	NaI	EA	64
19[f]	NaI	EA	78
20[g]	NaI	EA	49
21[h]	NaI	EA	64
22[i]	NaI	EA	68
23[j]	NaI	EA	76
24[k]	NaI	EA	93

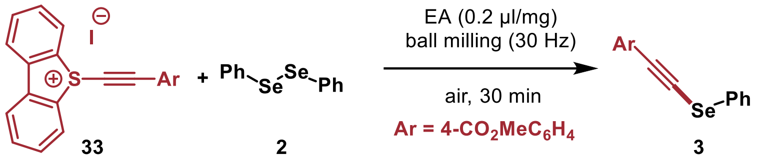
[a] Reaction conditions: **1** (0.4 mmol, 2.0 equiv.), **2** (0.2 mmol), NaI (0.4 mmol, 2.0 equiv.),and EA (0.2 µL/mg) were added into a stainless steel jar (5 mL) with nine stainless steel balls (for one stainless steel ball: diameter: 5 mm, weight: ca. 0.6 g) under air and milled at 30 Hz for 30 min. [b] NaI (0.1 mmol). [c] NaI (0.2 mmol). [d] NaI (0.3 mmol). [e] **1** (0.24 mmol). [f] **1** (0.30 mmol). [g] One stainless steel ball was used. [h] Three stainless steel balls were used. [i] Five stainless steel ball was used. [j] Seven stainless steel ball was used. [k] **1** (2.0 mmol), **2** (1.0 mmol), NaI (2.0 mmol) and EA (0.2 µL/mg) were added into a PTFE-coated jar (25 mL) with two balls (for one ball: diameter: 15 mm weight: ca. 5.3 g) under air and milled at 30 Hz for 30 min.

2.2 General procedure for the synthesis of chalcogenoacetylenes

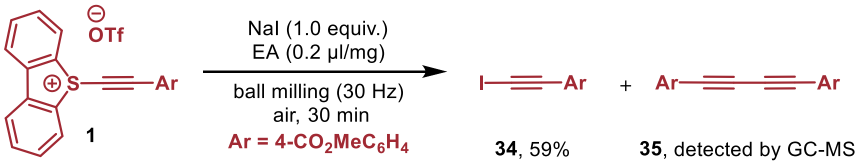


A mixture of diselenides or ditellurides (0.2 mmol, 1.0 equiv.), alkynyl sulfonium salts (0.4 mmol, 2.0 equiv.), NaI (0.4 mmol, 2.0 equiv.) and EA (0.2 µl/mg) were milled in a 5 mL stainless steel milling jar with nine milling balls made of the same material (5 mm in diameter). After 30 min of reaction at 30 Hz, the reaction mixture was recovered from the milling jar with DCM, and the product was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate) to afford the desired products.

3. Control Experiments



A mixture of diphenyl diselenide **2** (0.2 mmol, 1.0 equiv.), alkynyl sulfonium salt **33** (0.4 mmol, 2.0 equiv.), and EA (0.2 µl/mg) were milled in a 5 mL stainless steel milling jar with nine milling balls made of the same material (5 mm in diameter). After 30 min of reaction at 30 Hz, the reaction mixture was recovered from the milling jar with DCM and the product was purified by flash column chromatography on silica gel (PE/EA = 100:1) to afford the product **3** as a white solid (0.178 mmol, 56 mg, 89% yield).



A mixture of alkynyl sulfonium salt **1** (0.4 mmol, 1.0 equiv.), NaI (0.4 mmol, 1.0 equiv.) and EA (0.2 µl/mg) were milled in a 5 mL stainless steel milling jar with nine milling balls made of the same material (5 mm in diameter). After 30 min of reaction at 30 Hz, the reaction mixture was recovered from the milling jar with DCM and the product was purified by flash column chromatography on silica gel (PE/EA = 100:1) to afford the product **34** as a white solid (0.236 mmol, 68 mg, 59% yield). The dimer of phenylacetylene **35** was detected by GC-MS.

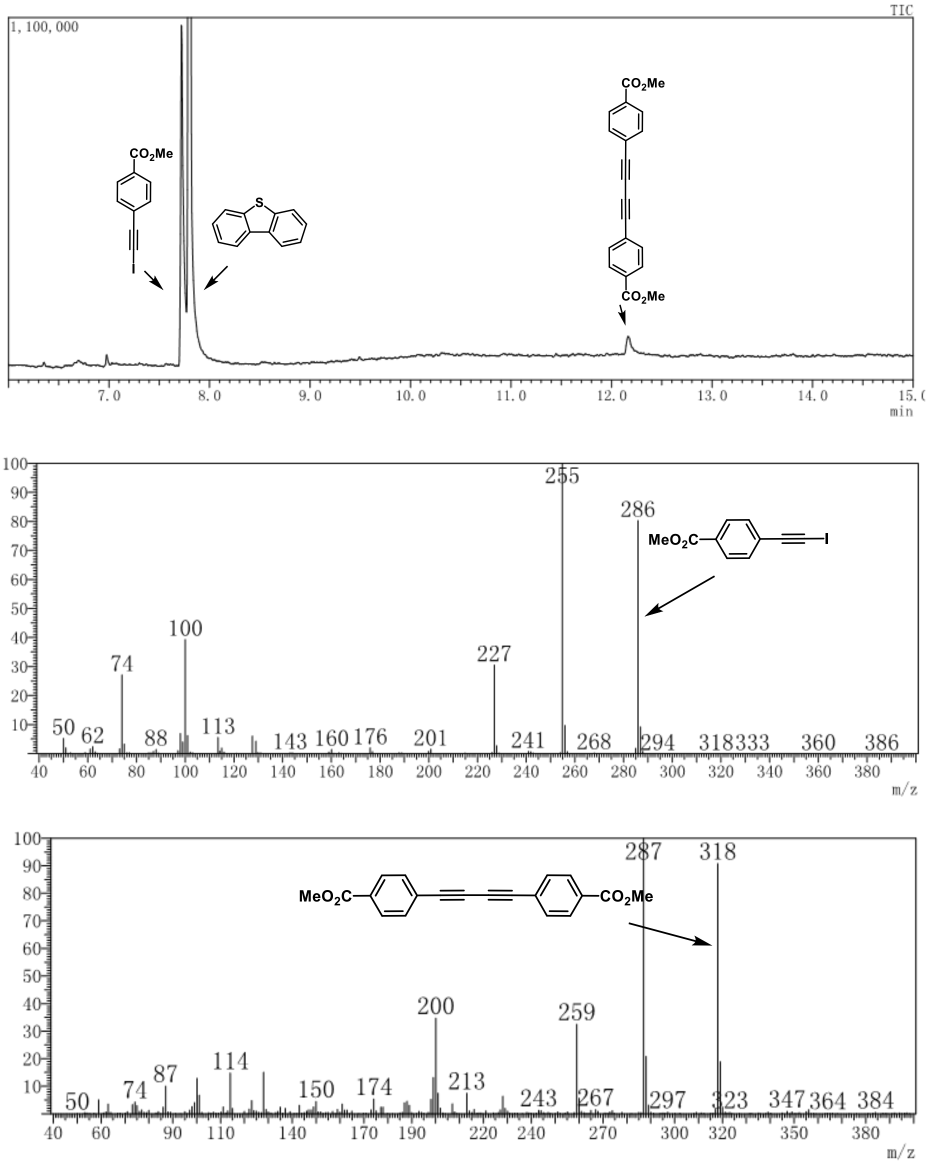
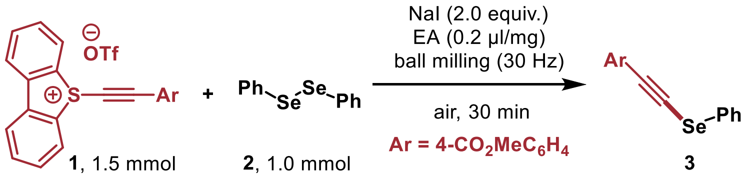


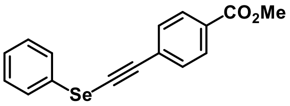
Figure S2. GC-MS spectra of the mechanochemical reaction in the presence of diphenyl diselenide

4. Scale-up Experiment



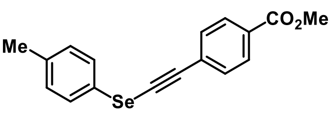
A mixture of diphenyl diselenide **2** (1.0 mmol, 1.0 equiv.), alkynyl sulfonium salt **1** (1.5 mmol, 1.5 equiv.), NaI (2.0 mmol, 2.0 equiv.) and EA (0.2 μl/mg) were milled in a 5 mL stainless steel milling jar with nine milling balls made of the same material (5 mm in diameter). After 30 min of reaction at 30 Hz, the reaction mixture was recovered from the milling jar with DCM, and the product was purified by flash column chromatography on silica gel (petroleum ether and ethyl acetate) to afford the desired products (285 mg) with 91% yield.

5. Compound Characterization Data



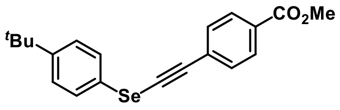
Methyl 4-((phenylselanyl)ethynyl)benzoate (3)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **3** as a white solid (0.177 mmol, 56 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 6.8 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 6.8 Hz, 2H), 7.35 (m, *J* = 7.2 Hz, 2H), 7.32 – 7.27 (m, 1H), 3.92 (s, 3H). **^{13}C NMR** (126MHz, $CDCl_3$): δ = 166.6, 131.4, 129.8, 129.7, 129.5, 128.5, 127.9, 127.6, 102.3, 73.7, 53.1. These data are in agreement with those reported previously in the literature.[3]



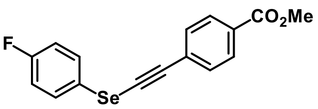
Methyl 4-((p-tolylselanyl)ethynyl)benzoate (4)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **4** as a faint yellow solid (0.174 mmol, 57 mg, 87% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.92 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.7, 137.8, 131.3, 130.6, 130.0, 129.6, 129.5, 128.0, 124.5, 101.7, 74.3, 52.4, 21.2. These data are in agreement with those reported previously in the literature.[3]



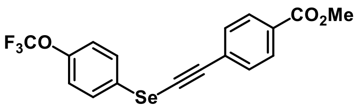
Methyl 4-(((4-(tert-butyl)phenyl)selanyl)ethynyl) benzoate (5)

Prepared according to the general procedure, the chromatographic purification using PE and EA (150 : 1) as the eluent afforded **5** as a yellow oil (0.142 mmol, 53 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.49 (m, 4H), 7.38 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.7, 151.0, 131.4, 129.6, 129.6, 129.5, 128.0, 127.0, 124.7, 101.7, 74.2, 52.4, 34.7, 31.4. These data are in agreement with those reported previously in the literature.[3]



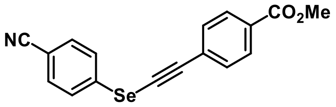
Methyl 4-(((4-fluorophenyl)selanyl)ethynyl)benzoate (6)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **6** as a white solid (0.164 mmol, 55 mg, 82% yield). **Melting Point:** 77-78 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2H), 7.59 - 7.54 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.03 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 162.7 (d, $J_{C\text{-}F}$ = 247.6 Hz), 131.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 131.4, 129.75, 129.67, 127.69, 122.7 (d, $J_{C\text{-}F}$ = 3.4 Hz), 117.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 101.9, 73.7, 52.4. **IR (ATR)**: 3062, 2958, 2154, 1710, 1601, 1487, 1278, 1107, 823, 766 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{16}H_{11}FO_2Se^+$: 333.9903, found 333.9897.



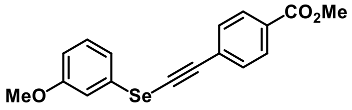
Methyl 4-(((4-(trifluoromethoxy)phenyl)selanyl) ethynyl) benzoate (7)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **7** as a yellow solid (0.168 mmol, 67 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 148.9, 131.5, 130.9, 129.9, 129.7, 127.5, 126.8, 122.4, 120.5 (q, J_{C-F} = 258.3 Hz), 102.7, 72.8, 52.4. These data are in agreement with those reported previously in the literature.[3]



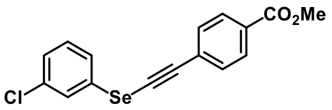
Methyl 4-(((4-cyanophenyl)selanyl)ethynyl)benzoate (8)

Prepared according to the general procedure, the chromatographic purification using PE and EA (50 : 1) as the eluent afforded **8** as a yellow solid (0.130 mmol, 44 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.5, 136.4, 133.0, 131.6, 130.3, 129.8, 128.9, 127.1, 118.5, 110.9, 104.5, 70.9, 52.5. These data are in agreement with those reported previously in the literature.[3]



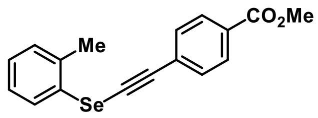
Methyl 4-(((3-methoxyphenyl)selanyl)ethynyl)benzoate (9)

Prepared according to the general procedure, the chromatographic purification using PE and EA (75 : 1) as the eluent afforded **9** as a faint yellow solid (0.166 mmol, 57 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.18 – 7.11 (m, 2H), 6.85 – 6.80 (m, 1H), 3.92 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 160.5, 131.4, 130.5, 129.7, 129.5, 127.9, 121.5, 114.8, 113.4, 102.8, 73.6, 55.5, 52.4. These data are in agreement with those reported previously in the literature.[3]



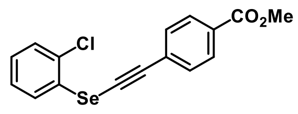
Methyl 4-(((3-chlorophenyl)selanyl)ethynyl)benzoate (10)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **10** as a faint yellow solid (0.166 mmol, 58 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.28 – 7.25 (m, 2H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 135.6, 131.5, 130.7, 130.2, 129.9, 129.7, 128.9, 127.7, 127.5, 127.2, 103.3, 72.5, 52.4. These data are in agreement with those reported previously in the literature.[3]



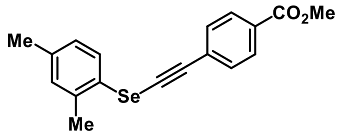
Methyl 4-((*o*-tolylselanyl)ethynyl)benzoate (11)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **11** as a faint yellow solid (0.152 mmol, 50 mg, 76% yield). **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.77 (m, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.18 (m, 3H), 3.92 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 166.6, 137.0, 131.4, 130.5, 129.8, 129.7, 129.2, 127.9, 127.7, 127.5, 102.4, 73.5, 52.4, 21.2. These data are in agreement with those reported previously in the literature.[3]



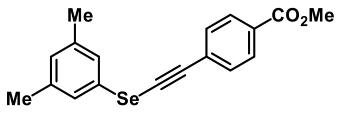
Methyl 4-(((2-chlorophenyl)selanyl)ethynyl)benzoate (12)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **12** as a yellow wax (0.122 mmol, 43 mg, 61% yield). **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 8.04 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.36– 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 166.6, 131.9, 131.6, 130.0, 129.7, 129.6, 129.5, 129.4, 128.2, 128.2, 127.5, 104.5, 72.8, 52.5. These data are in agreement with those reported previously in the literature.[3]



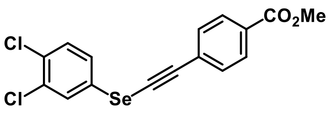
Methyl 4-(((2,4-dimethylphenyl)selanyl)ethynyl)benzoate (13)

Prepared according to the general procedure, the chromatographic purification using PE and EA (150 : 1) as the eluent afforded **13** as a faint yellow solid (0.158 mmol, 54 mg, 79% yield). **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 3.92 (s, 3H), 2.35 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 166.7, 137.1, 134.0, 131.4, 130.5, 130.3, 129.7, 129.6, 128.6, 128.6, 128.0, 102.2, 73.9, 52.4, 21.2, 20.8. These data are in agreement with those reported previously in the literature.[3]



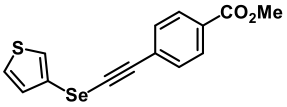
Methyl 4-(((3,5-dimethylphenyl)selanyl)ethynyl)benzoate (14)

Prepared according to the general procedure, the chromatographic purification using PE and EA (150 : 1) as the eluent afforded **14** as a yellow solid (0.154 mmol, 53 mg, 77% yield). **^{1}H NMR** (500 MHz, CDCl$_3$): δ = 8.00 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.21 (s, 2H), 6.92 (s, 1H), 3.92 (s, 3H), 2.32 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$): δ = 166.7, 139.6, 131.4, 129.7, 129.6, 129.5, 128.0, 127.8, 127.2, 102.1, 74.2, 52.4, 21.4. These data are in agreement with those reported previously in the literature.[3]



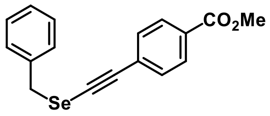
Methyl 4-(((3,4-dichlorophenyl)selanyl)ethynyl)benzoate (15)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **15** as a faint yellow solid (0.164 mmol, 63 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.67 (s, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.41 (s, 2H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.5, 133.9, 131.9, 131.5, 131.3, 130.8, 130.1, 129.7, 128.5, 128.1, 127.3, 103.6, 72.0, 52.5. These data are in agreement with those reported previously in the literature.[3]



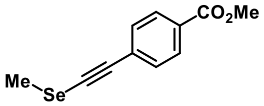
Methyl 4-((thiophen-3-ylselanyl)ethynyl)benzoate (16)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **16** as a faint yellow solid (0.140 mmol, 45 mg, 70% yield). **Melting Point:** 123-124 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.44 (m, 1H), 7.41 – 7.39 (m, 1H), 7.23 – 7.21 (m, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 131.4, 130.0, 129.6, 128.7, 127.9, 127.3, 125.8, 119.8, 100.4, 73.8, 52.4. **IR (ATR)**: 2952, 2359, 1715, 1600, 1434, 1276, 1096, 848, 765, 693, 598 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{14}H_{10}O_2SSe^+$: 321.9561, found 321.9555.



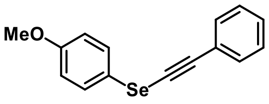
Methyl 4-((benzylselanyl)ethynyl)benzoate (17)

Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **17** as a faint yellow solid (0.136 mmol, 45 mg, 68% yield). **Melting Point:** 59-60 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.27 (m, 7H), 4.14 (s, 2H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.7, 137.4, 131.1, 129.6, 129.3, 129.2, 128.8, 128.3, 127.8, 101.0, 75.5, 52.4, 33.3. **IR (ATR)**: 2953, 2358, 2150, 1717, 1601, 1438, 1274, 1109, 859, 760, 692 cm^{-1}. **HRMS:** m/z $[M+H]^+$ calcd for $C_{17}H_{15}O_2Se^+$: 331.0232, found 331.0225.



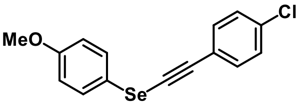
Methyl 4-((methylselanyl)ethynyl)benzoate (18)

Prepared according to the general procedure, the chromatographic purification using PE as the eluent afforded **18** as a colorless solid (0.178 mmol, 45 mg, 89% yield). **Melting Point:** 97-98 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.7, 131.2, 129.6, 129.3, 128.3, 98.1, 75.8, 52.3, 10.0. **IR (ATR)**: 2920, 2151, 1708, 1599, 1437, 1252, 1179, 1111, 853, 768, 698 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{11}H_{10}O_2Se^+$: 253.9841, found 253.9829.



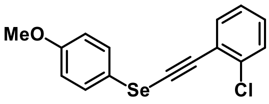
(4-Methoxyphenyl)(phenylethynyl)selane (19)

Prepared according to the general procedure, the chromatographic purification using PE and EA (200 : 1) as the eluent afforded **19** as a yellow oil (0.150 mmol, 43 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.8 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.33 – 7.29 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 159.6, 132.0, 131.8, 128.5, 128.4, 123.4, 118.5, 115.5, 101.6, 70.5, 55.5. These data are in agreement with those reported previously in the literature.[3]



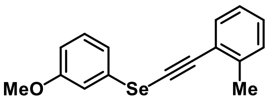
((4-chlorophenyl)ethynyl)(4-methoxyphenyl)selane (20)

Prepared according to the general procedure, the chromatographic purification using PE and EA (200 : 1) as the eluent afforded **20** as a yellow wax (0.158 mmol, 51 mg, 79% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 159.8, 134.5, 133.0, 132.3, 128.8, 121.9, 118.1, 115.5, 100.3, 72.0, 55.5. These data are in agreement with those reported previously in the literature.[3]



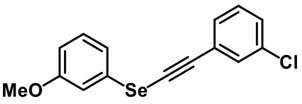
((2-chlorophenyl)ethynyl)(4-methoxyphenyl)selane (21)

Prepared according to the general procedure, the chromatographic purification using PE and EA (200 : 1) as the eluent afforded **21** as a yellow oil (0.146 mmol, 47 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 159.6, 135.8, 133.2, 131.9, 129.4, 129.3, 126.6, 123.4, 118.2, 115.5, 98.6, 76.6, 55.5. These data are in agreement with those reported previously in the literature.[3]



(3-Methoxyphenyl)(o-tolylethynyl)selane (22)

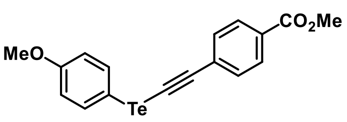
Prepared according to the general procedure, the chromatographic purification using PE and EA (200 : 1) as the eluent afforded **22** as a yellow oil (0.146 mmol, 44 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.0 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.19 – 7.13 (m, 3H), 6.83 – 6.77 (m, 1H), 3.81 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 160.5, 140.5, 132.2, 130.3, 129.6, 128.7, 125.7, 123.1, 121.1, 114.3, 113.2, 102.6, 72.6, 55.5, 21.0. These data are in agreement with those reported previously in the literature.[3]



((3-chlorophenyl)ethynyl)(3-methoxyphenyl)selane (23)

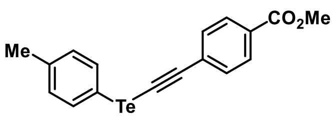
Prepared according to the general procedure, the chromatographic purification using PE and EA (200 : 1) as the eluent afforded **23** as a yellow oil (0.162 mmol, 52 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 7.36 (d, *J* =

7.6 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.15 – 7.11 (m, 2H), 6.84 – 6.80 (m, 1H), 3.82 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 160.5, 134.4, 131.5, 130.5, 129.8, 129.7, 129.6, 128.9, 124.9, 121.5, 114.8, 113.3, 101.9, 71.3, 55.5. These data are in agreement with those reported previously in the literature.[3]



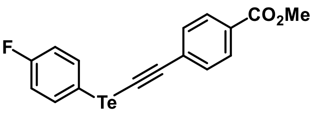
Methyl 4-(((4-methoxyphenyl)tellanyl)ethynyl)benzoate (24)

Prepared according to the general procedure, the chromatographic purification using PE and EA (50 : 1) as the eluent afforded **24** as a faint yellow solid (0.162 mmol, 64 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 160.5, 138.9, 131.6, 129.6, 129.5, 128.1, 116.0, 112.5, 101.1, 55.4, 52.6, 52.3. These data are in agreement with those reported previously in the literature.[3]



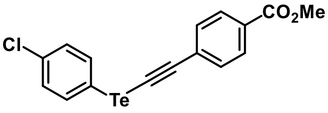
Methyl 4-((p-tolyltellanyl)ethynyl)benzoate (25)

Prepared according to the general procedure, the chromatographic purification using PE and EA (200 : 1) as the eluent afforded **25** as a faint yellow solid (0.166 mmol, 63 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.6, 138.7, 136.3, 131.6, 130.9, 129.7, 129.6, 128.1, 113.1, 108.4, 52.4, 52.4, 21.3. These data are in agreement with those reported previously in the literature.[3]



Methyl 4-(((4-fluorophenyl)tellanyl)ethynyl)benzoate (26)

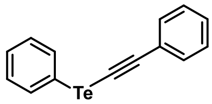
Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **26** as a yellow solid (0.168 mmol, 64 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.4 Hz, 2H), 7.79 – 7.72 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.05 – 6.98 (m, 2H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.5, 163.4(d, J_{C-F} = 248.2 Hz), 138.3 (d, J_{C-F} = 7.6 Hz), 131.7, 129.8, 129.6, 127.9, 117.4 (d, J_{C-F} = 21.4 Hz), 113.5, 106.2 (d, J_{C-F} = 3.8 Hz), 52.4, 51.9. These data are in agreement with those reported previously in the literature.[3]



Methyl 4-(((4-chlorophenyl)tellanyl)ethynyl)benzoate (27)

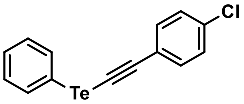
Prepared according to the general procedure, the chromatographic purification using PE and EA (100 : 1) as the eluent afforded **27** as a faint yellow solid (0.170 mmol, 68 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H). **^{13}C**

NMR (126 MHz, $CDCl_3$): δ = 166.5, 137.0, 134.9, 131.7, 130.2, 129.9, 129.6, 127.8, 114.0, 110.4, 52.4, 51.6. These data are in agreement with those reported previously in the literature.[3]



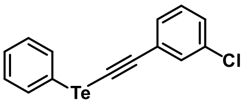
Phenyl(phenylethynyl)tellane (28)

Prepared according to the general procedure, the chromatographic purification using PE as the eluent afforded **28** as a yellow oil (0.156 mmol, 48 mg, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.26 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 135.3, 132.1, 129.9, 128.8, 128.4, 128.1, 123.5, 114.4, 113.3, 47.4. **IR (ATR)**: 4048, 3051, 2335, 2138, 1571, 1473, 1433, 1015, 725, 685 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{14}H_9ClTe^+$: 307.9839, found 307.9834.



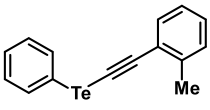
((4-chlorophenyl)ethynyl)(phenyl)tellane (29)

Prepared according to the general procedure, the chromatographic purification using PE as the eluent afforded **29** as a colorless solid (0.170 mmol, 58 mg, 85% yield). **Melting Point:** 100-101 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.76 – 7.71 (m, 2H), 7.40 – 7.36 (m, 2H), 7.31 – 7.26 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 135.5, 134.8, 133.3, 130.0, 128.8, 128.3, 122.0, 113.1, 113.0, 49.0. **IR (ATR)**: 3046, 1568, 1473, 1433, 1096, 1013, 833, 730, 690, 637, 532 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{14}H_9ClTe^+$: 341.9450, found 341.9448.



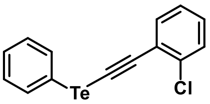
((3-chlorophenyl)ethynyl)(phenyl)tellane (30)

Prepared according to the general procedure, the chromatographic purification using PE as the eluent afforded **30** as a brown oil (0.164 mmol, 56 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.4 Hz, 2H), 7.43 (s, 1H), 7.30 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 135.6, 134.2, 131.8, 130.1, 130.0, 129.6, 129.0, 128.3, 125.2, 112.9, 112.8, 49.7. **IR (ATR)**: 4057, 3054, 2146, 1555, 1471, 1078, 870, 781, 679, 444 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{14}H_9ClTe^+$: 341.9450, found 341.9445.



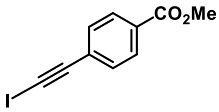
Phenyl(o-tolylethynyl)tellane (31)

Prepared according to the general procedure, the chromatographic purification using PE as the eluent afforded **31** as a yellow oil (0.168 mmol, 54 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.77 – 7.72 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.20 (d, *J* = 4.8 Hz, 2H), 7.16 – 7.11 (m, 1H), 2.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 140.8, 135.2, 132.4, 129.9, 129.5, 128.7, 128.0, 125.6, 123.4, 113.6, 113.6, 50.8, 20.9. **IR (ATR)**: 3053, 2718, 2135, 1573, 1474, 1434, 1016, 754, 727, 687 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{15}H_{12}Te^+$: 321.9996, found 321.9988.



((2-chlorophenyl)ethynyl)(phenyl)tellane (32)

Prepared according to the general procedure, the chromatographic purification using PE as the eluent afforded **32** as a yellow oil (0.146 mmol, 50 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 3.5 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.29 (s, 3H), 7.24 – 7.20 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 136.2, 135.3, 133.6, 130.0, 129.6, 129.4, 128.1, 126.5, 123.4, 113.2, 111.2, 53.9. **IR (ATR)**: 3052, 2141, 1572, 1471, 1434, 1055, 1016, 751, 727, 685, 449 cm^{-1}. **HRMS:** m/z $[M]^+$ calcd for $C_{14}H_9ClTe^+$: 341.9450, found 341.9449.

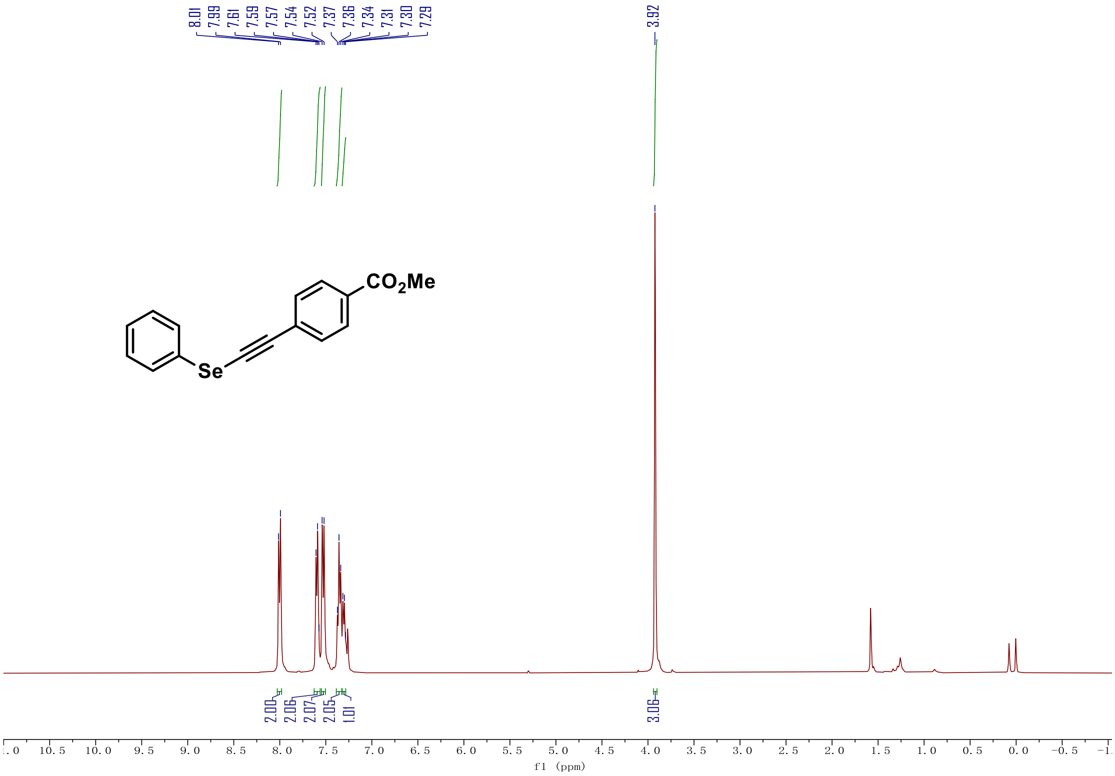


Methyl 4-(iodoethynyl)benzoate (34)

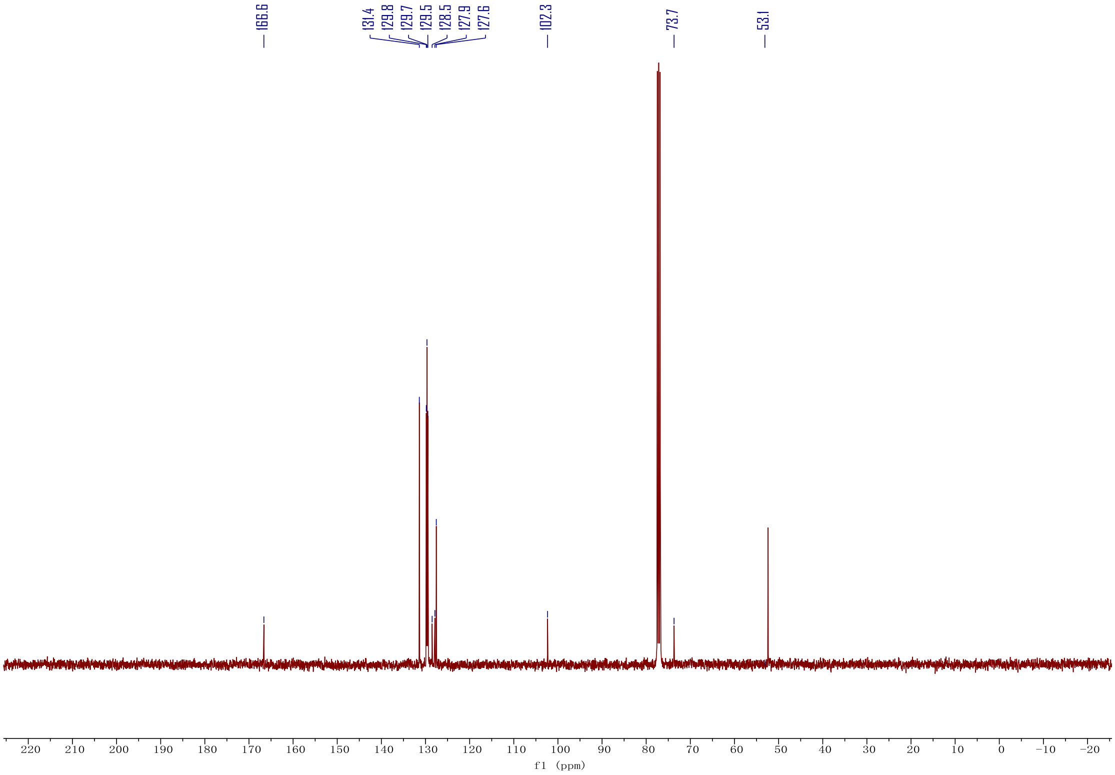
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 166.5, 132.4, 130.2, 129.5, 128.0, 93.6, 52.4, 10.6. These data are in agreement with those reported previously in the literature.[4]

6. NMR Spectra

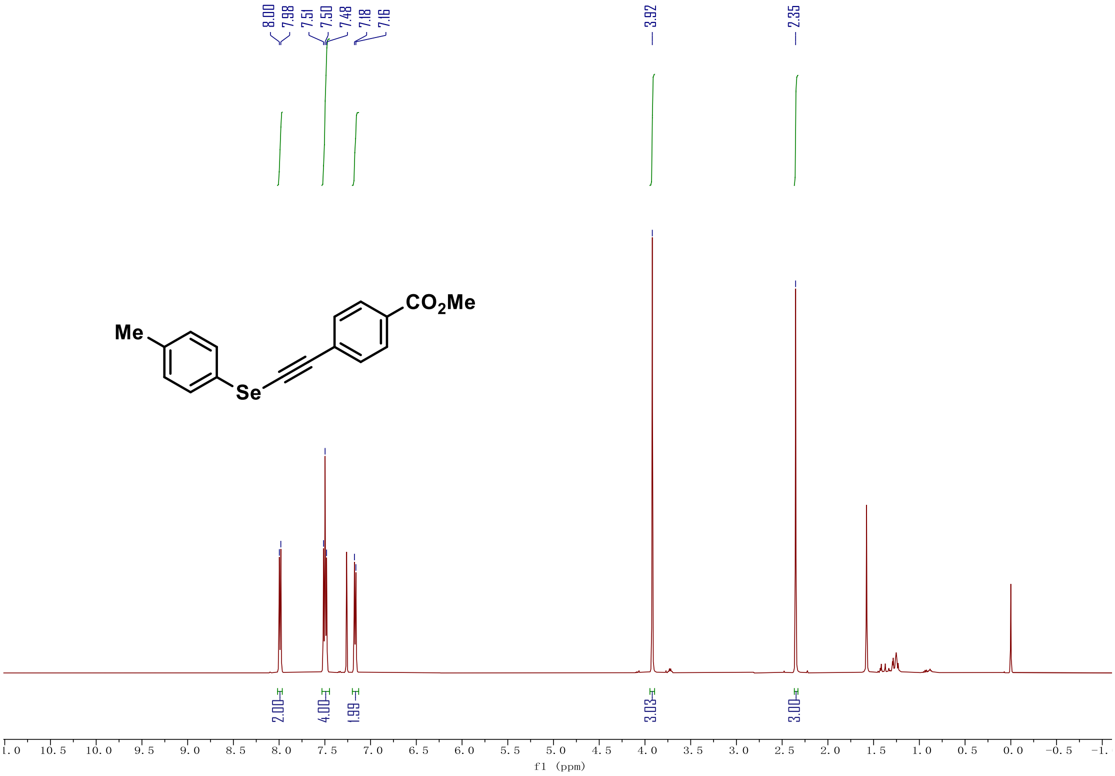
^{1}H NMR of compound 3 (500 MHz in $CDCl_3$)



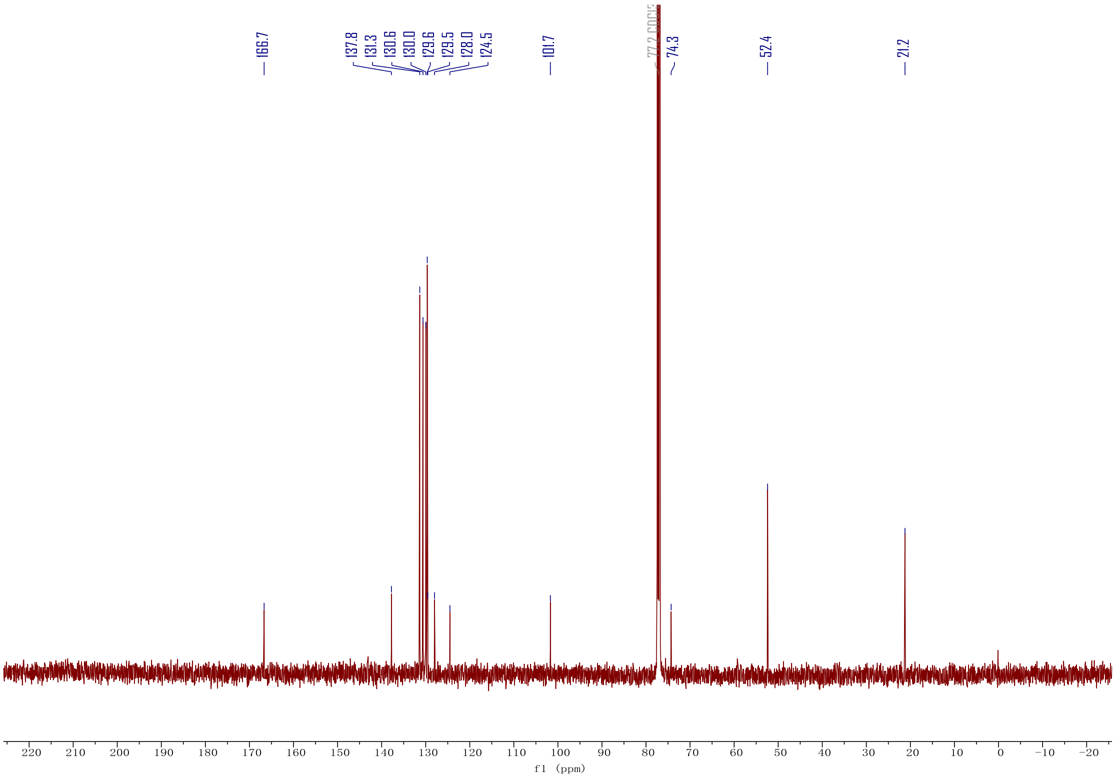
^{13}C NMR of compound 3 (126 MHz in $CDCl_3$)



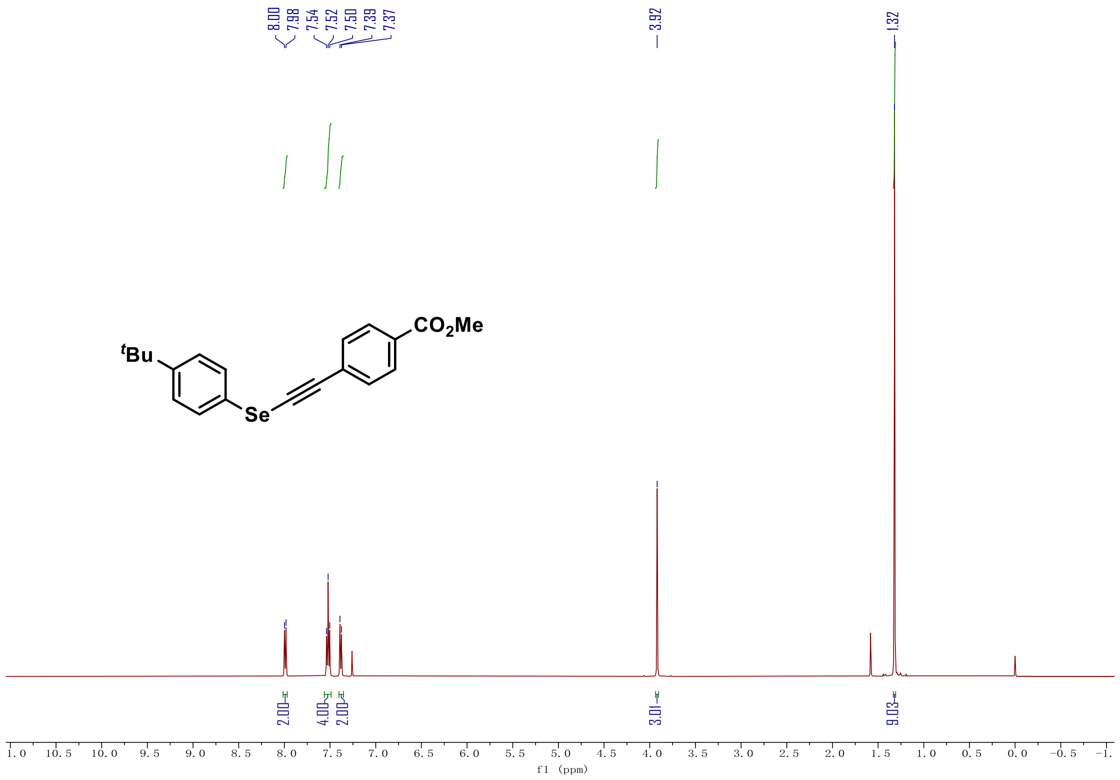
^{1}H NMR of compound 4 (500 MHz in CDCl$_3$)



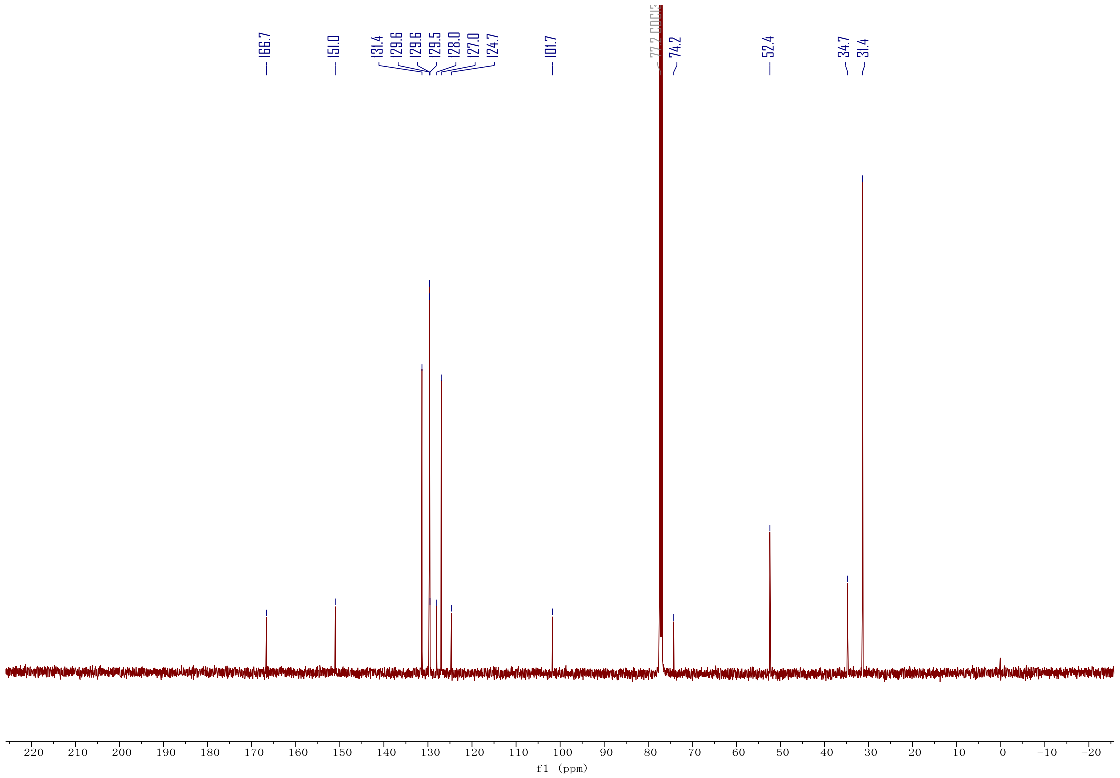
^{13}C NMR of compound 4 (126 MHz in CDCl$_3$)



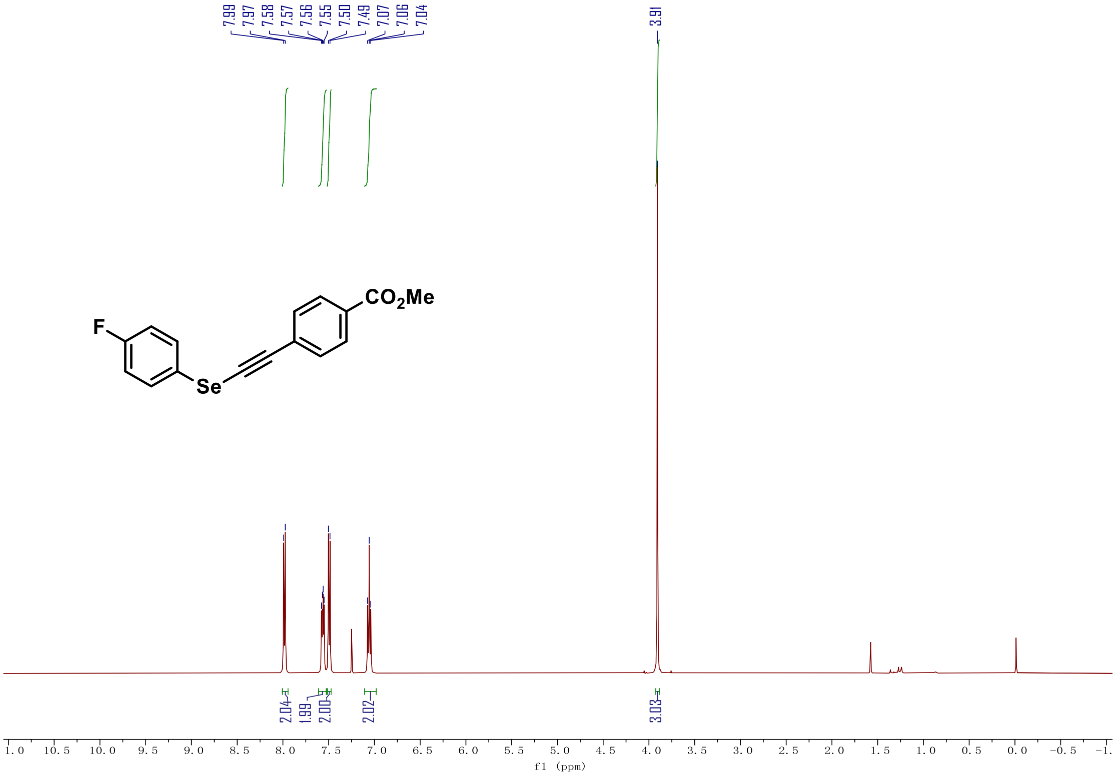
^{1}H NMR of compound 5 (500 MHz in CDCl$_3$)



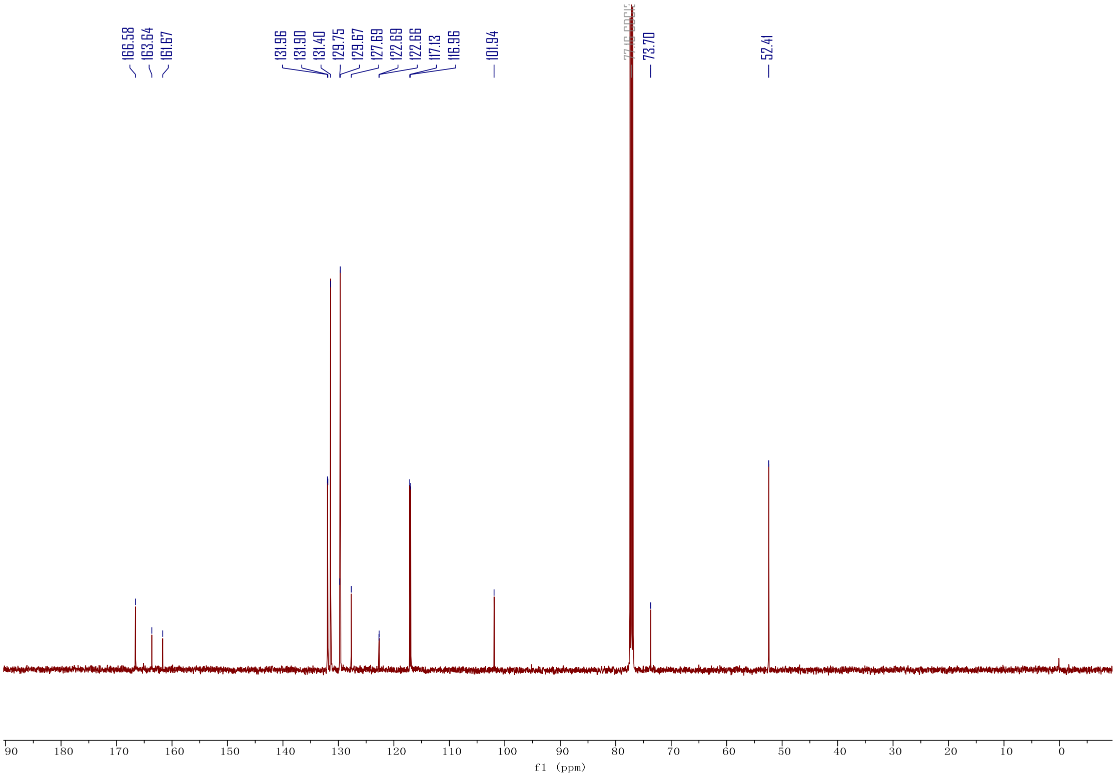
^{13}C NMR of compound 5 (126 MHz in CDCl$_3$)



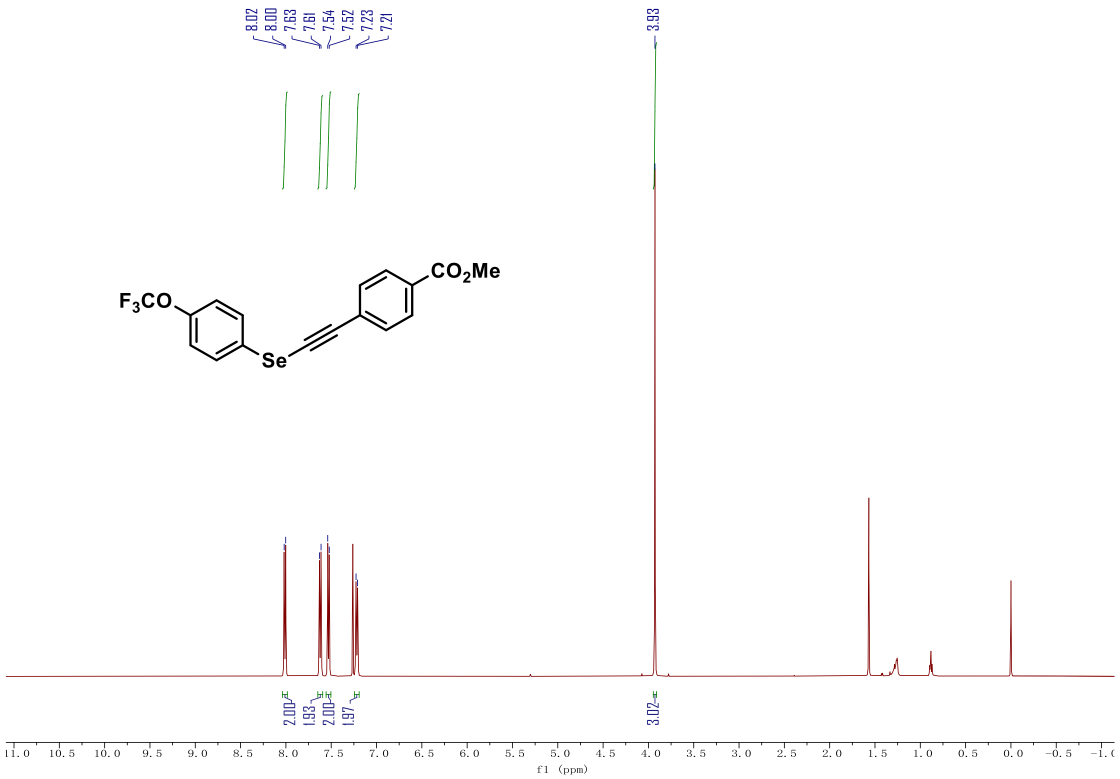
^{1}H NMR of compound 6 (500 MHz in $CDCl_3$)



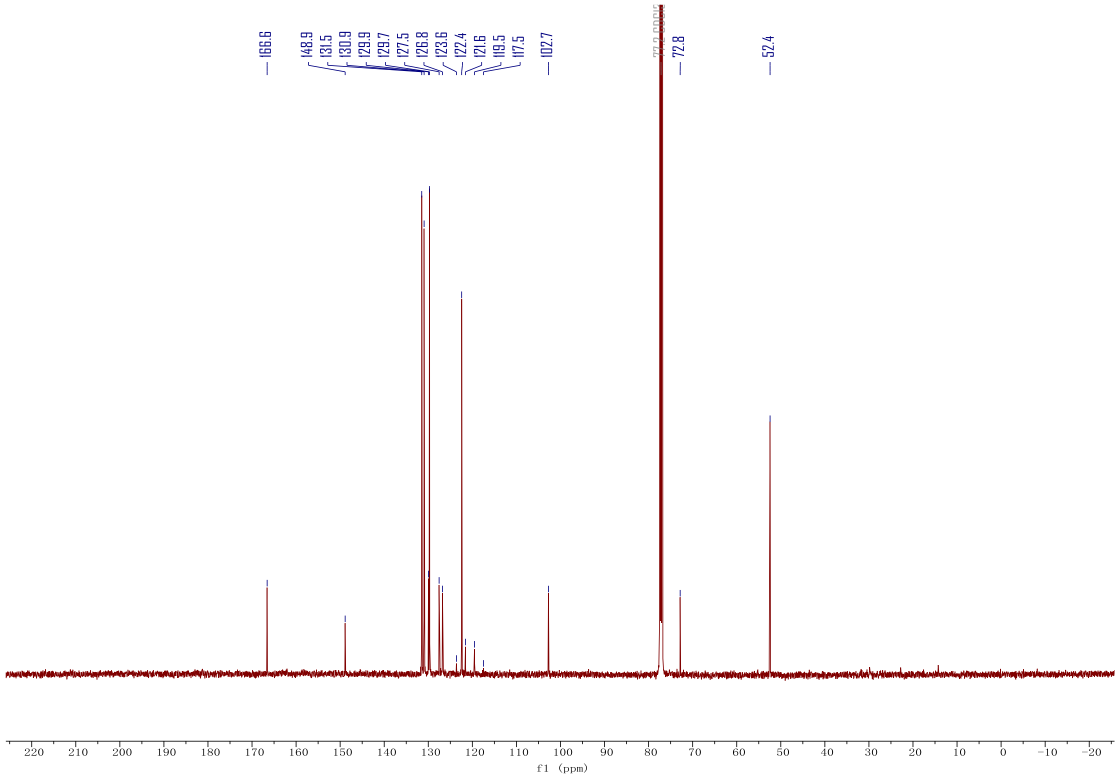
^{13}C NMR of compound 6 (126 MHz in $CDCl_3$)



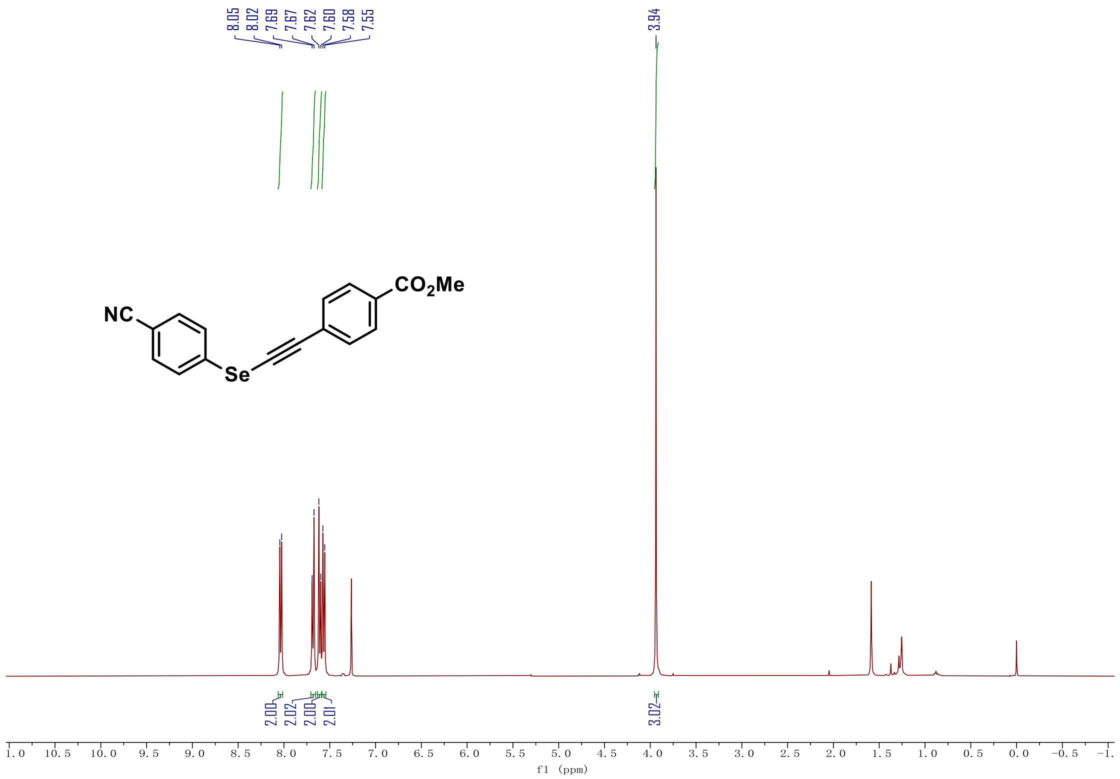
^{1}H NMR of compound 7 (500 MHz in $CDCl_3$)



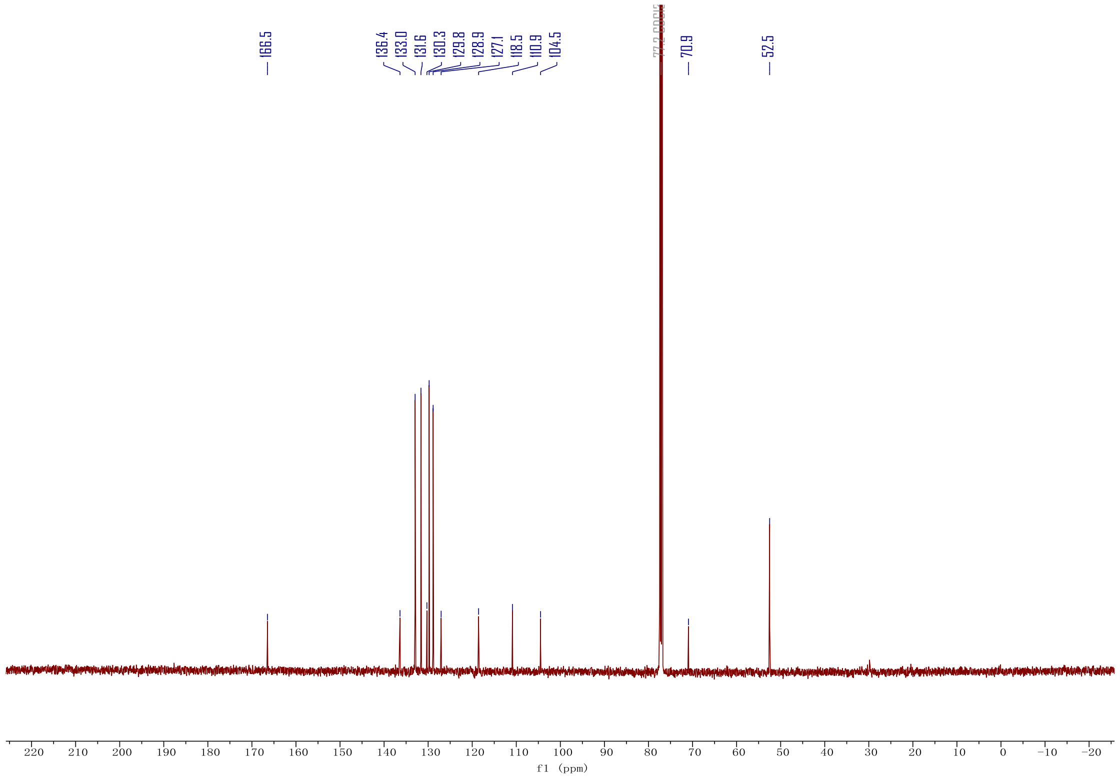
^{13}C NMR of compound 7 (126 MHz in $CDCl_3$)



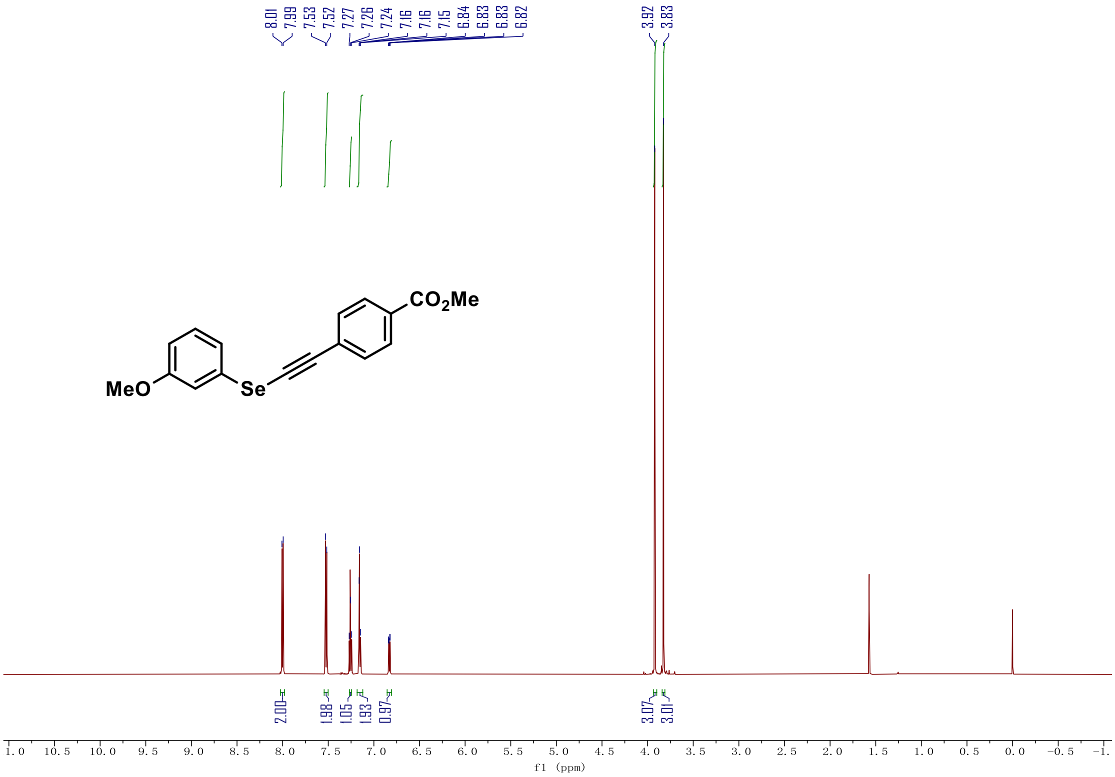
^{1}H NMR of compound 8 (500 MHz in $CDCl_3$)



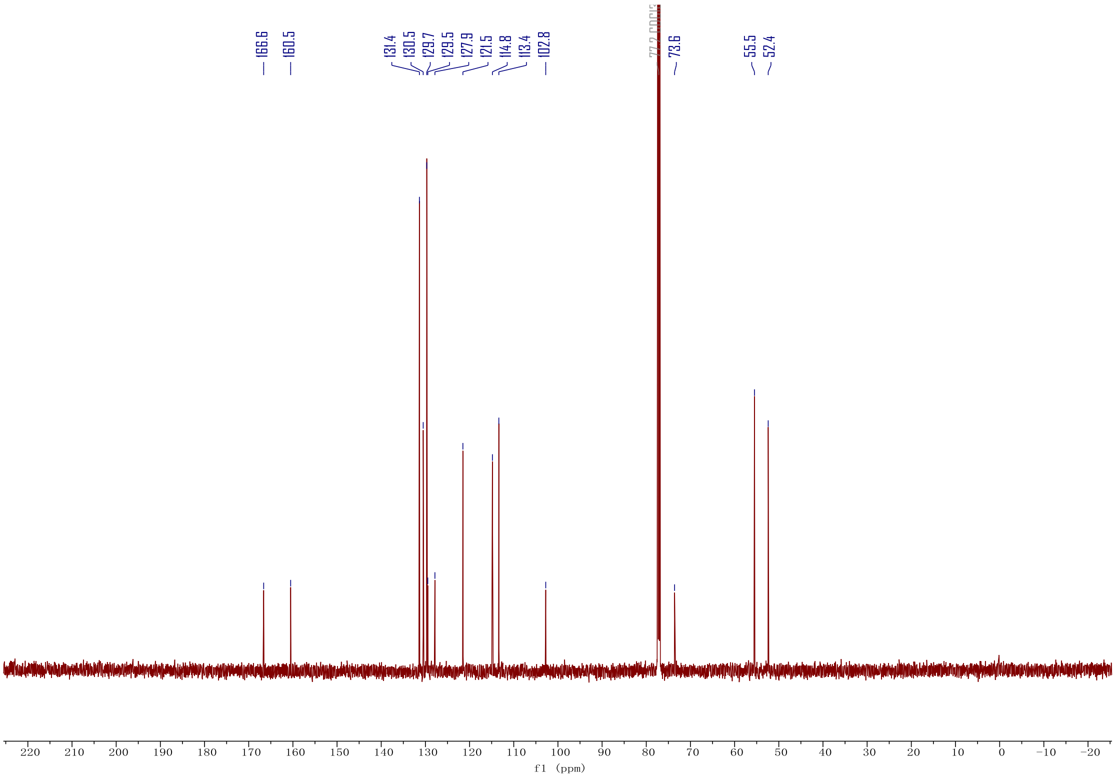
^{13}C NMR of compound 8 (126 MHz in $CDCl_3$)



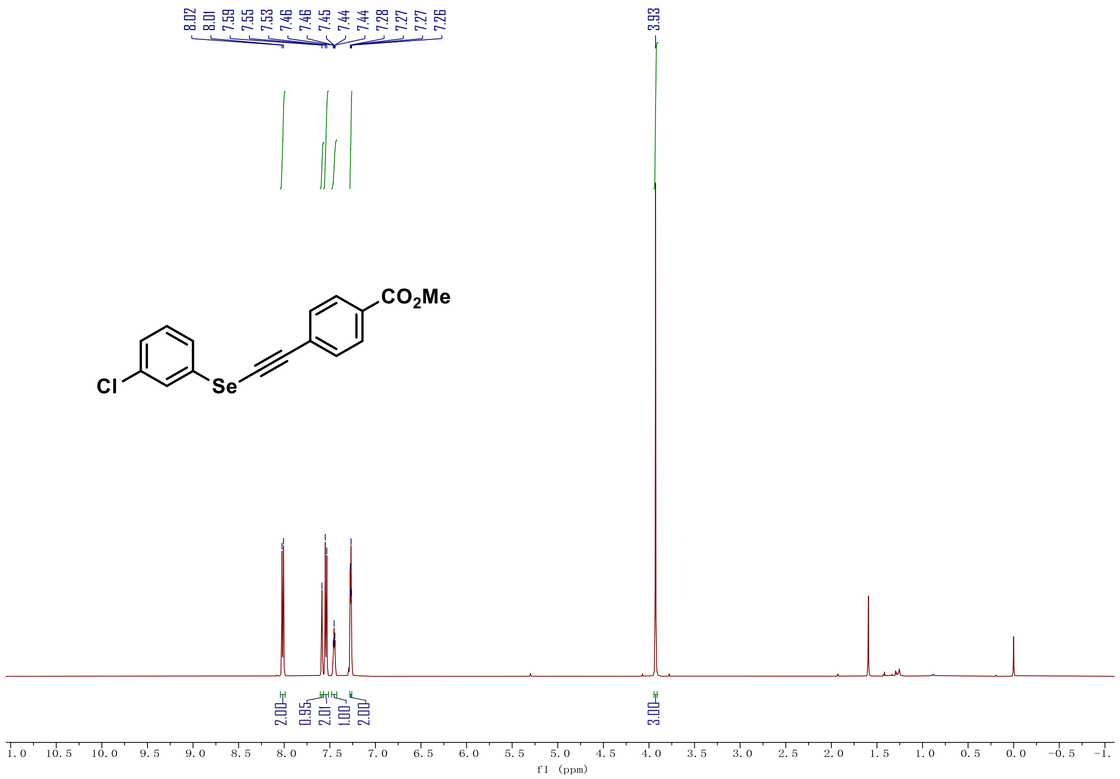
^{1}H NMR of compound 9 (500 MHz in CDCl$_3$)



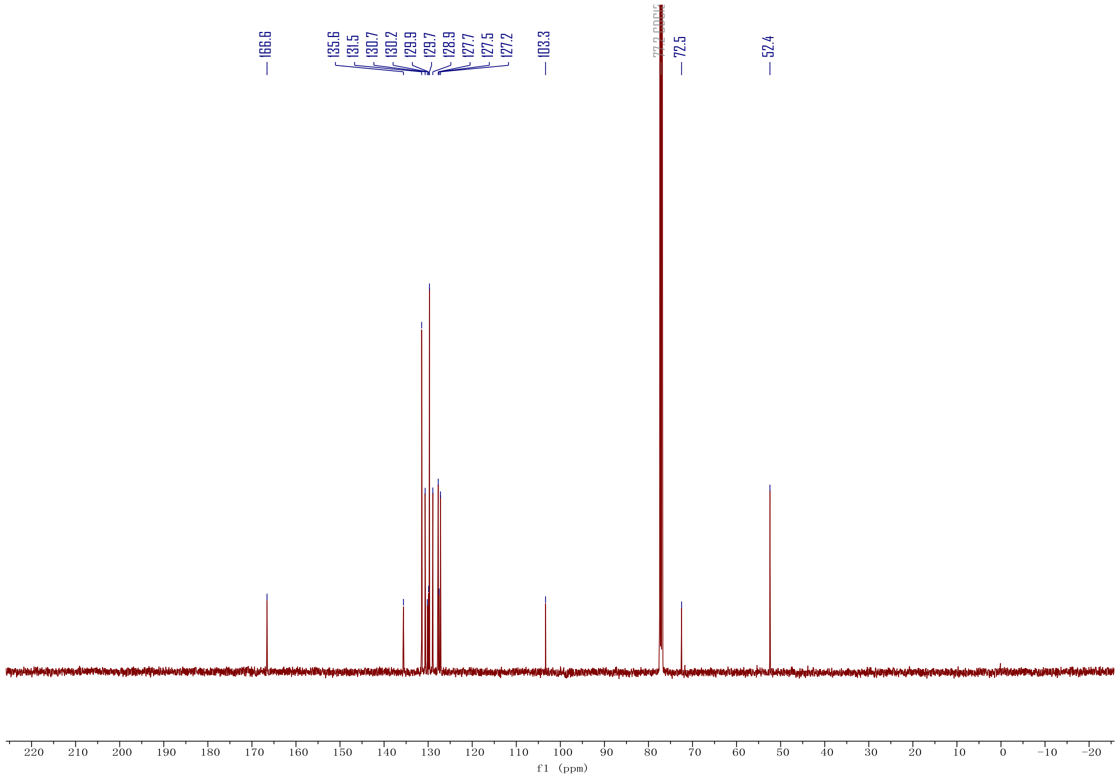
^{13}C NMR of compound 9 (126 MHz in CDCl$_3$)



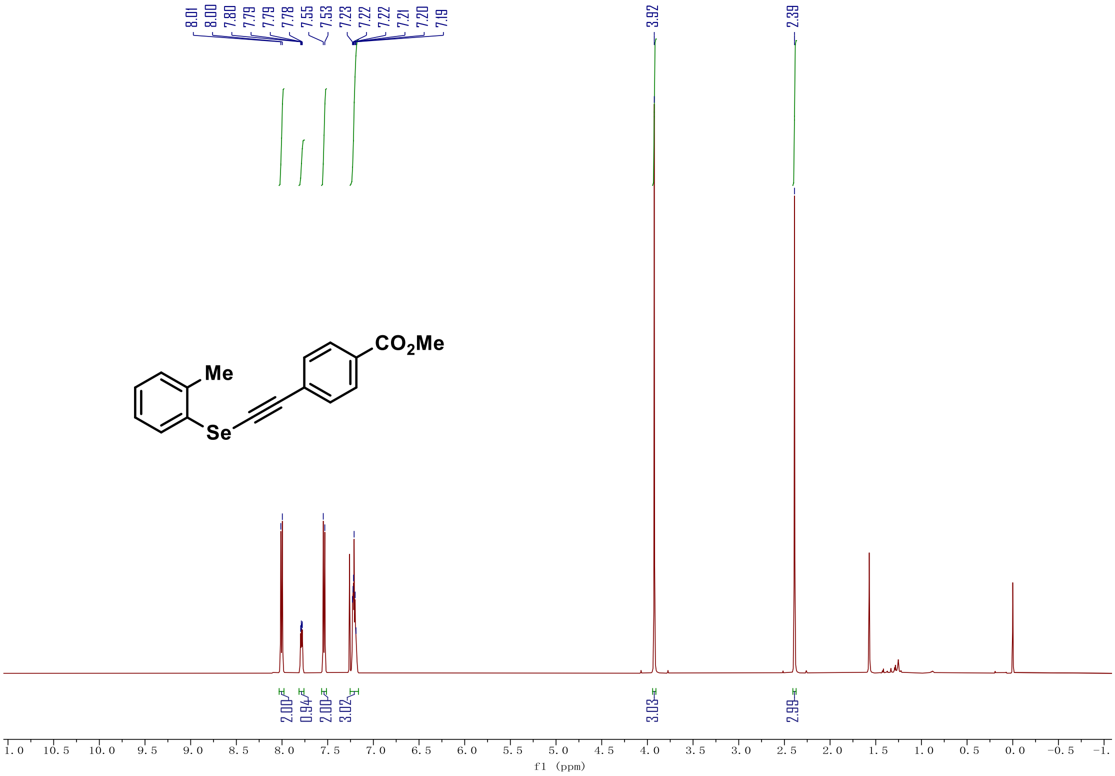
^{1}H NMR of compound 10 (500 MHz in CDCl$_3$)



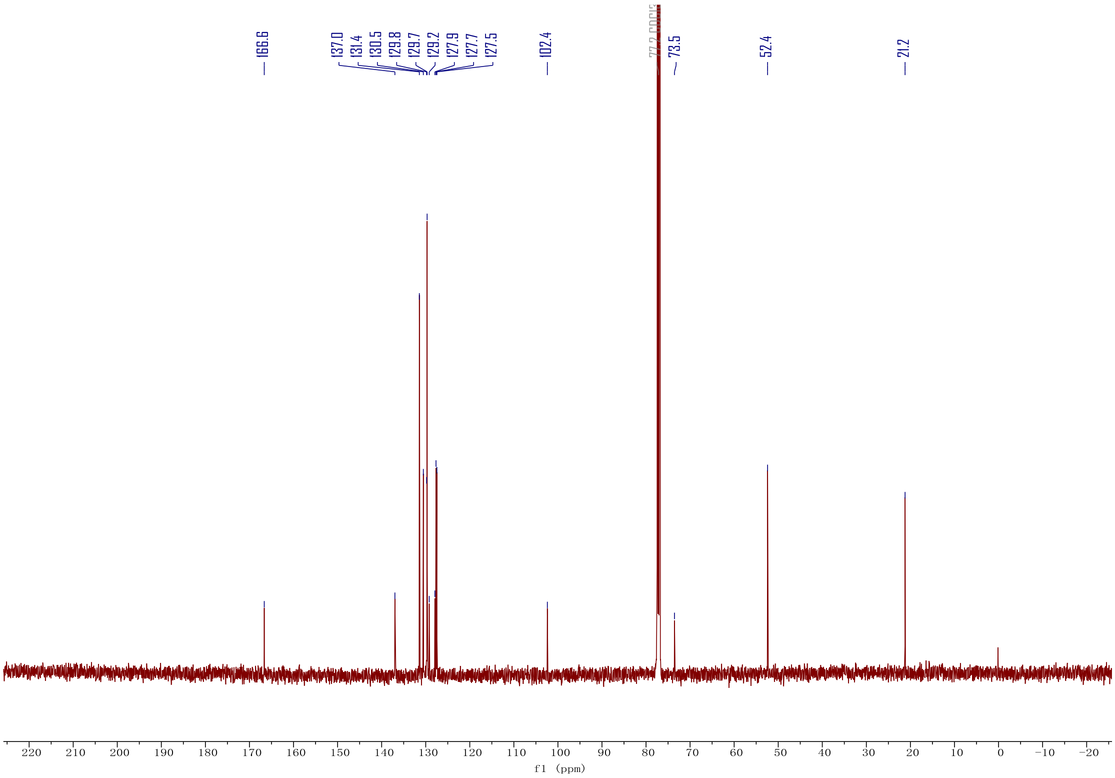
^{13}C NMR of compound 10 (126 MHz in CDCl$_3$)



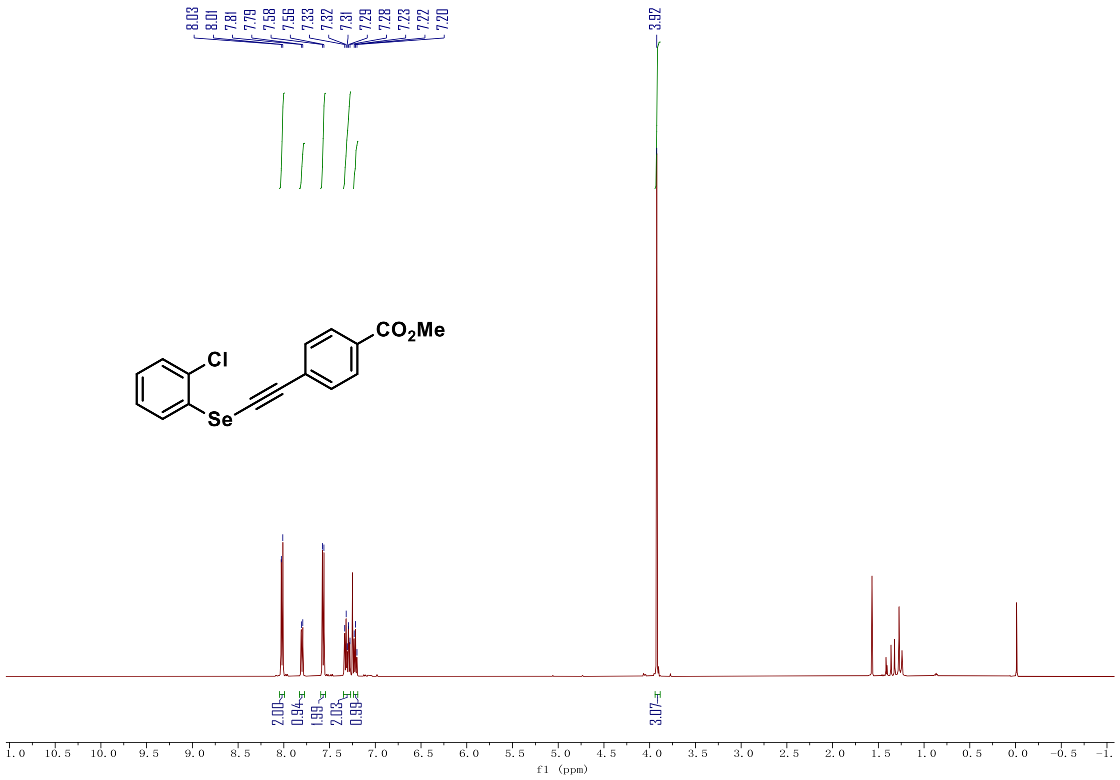
^{1}H NMR of compound 11 (500 MHz in CDCl$_3$)



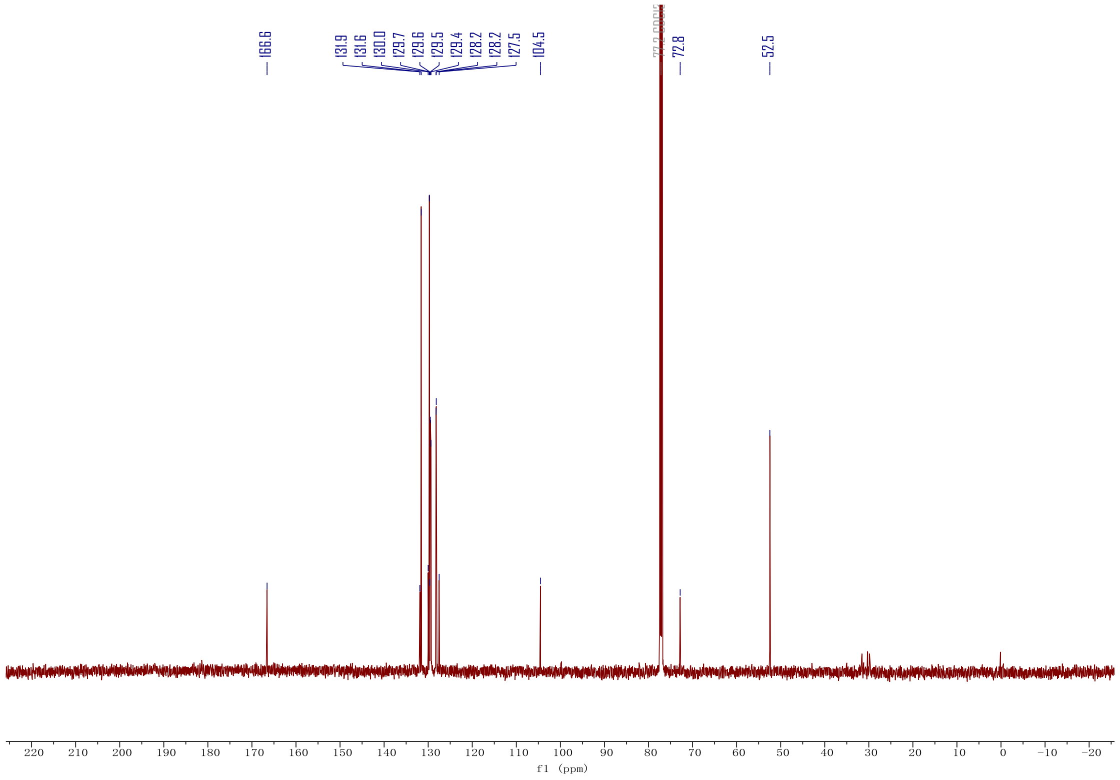
^{13}C NMR of compound 11 (126 MHz in CDCl$_3$)



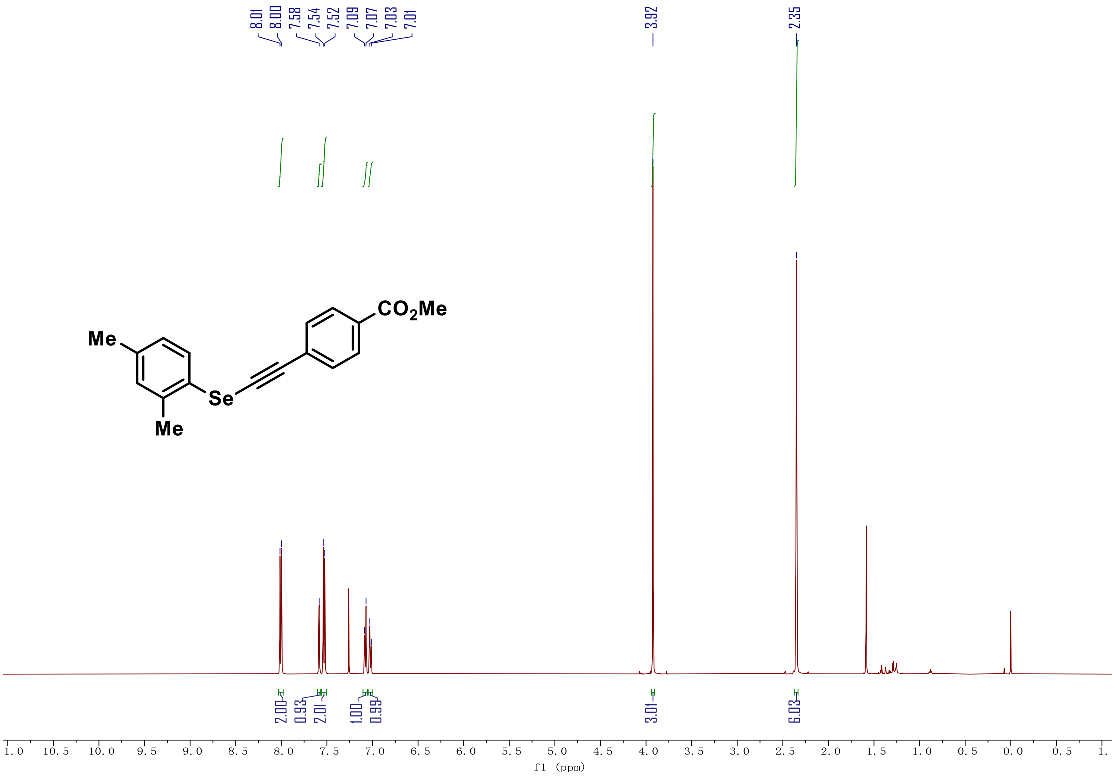
^{1}H NMR of compound 12 (500 MHz in CDCl$_3$)



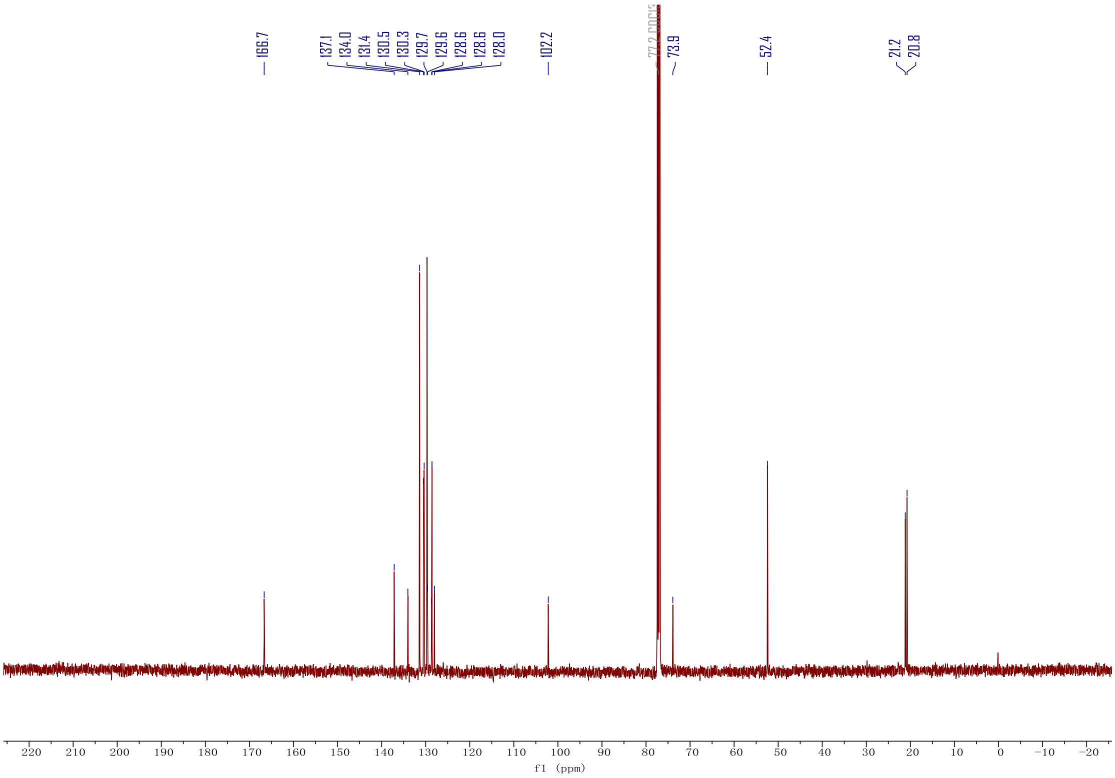
^{13}C NMR of compound 12 (126 MHz in CDCl$_3$)



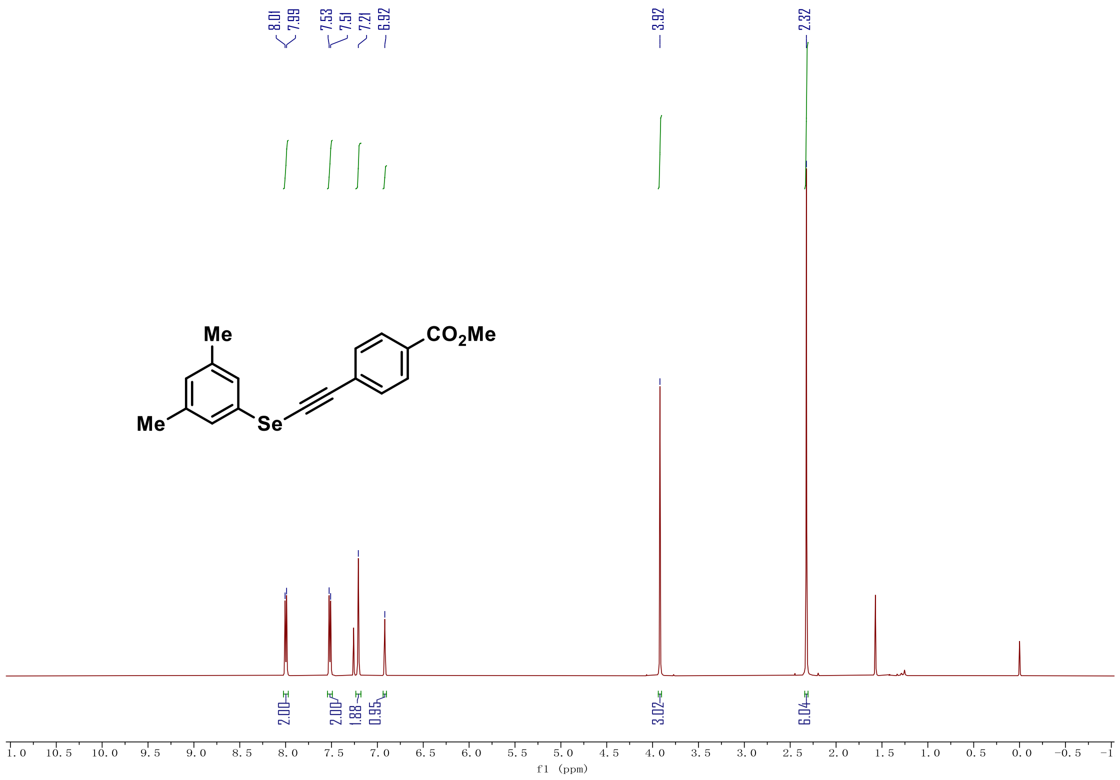
^{1}H NMR of compound 13 (500 MHz in CDCl$_3$)



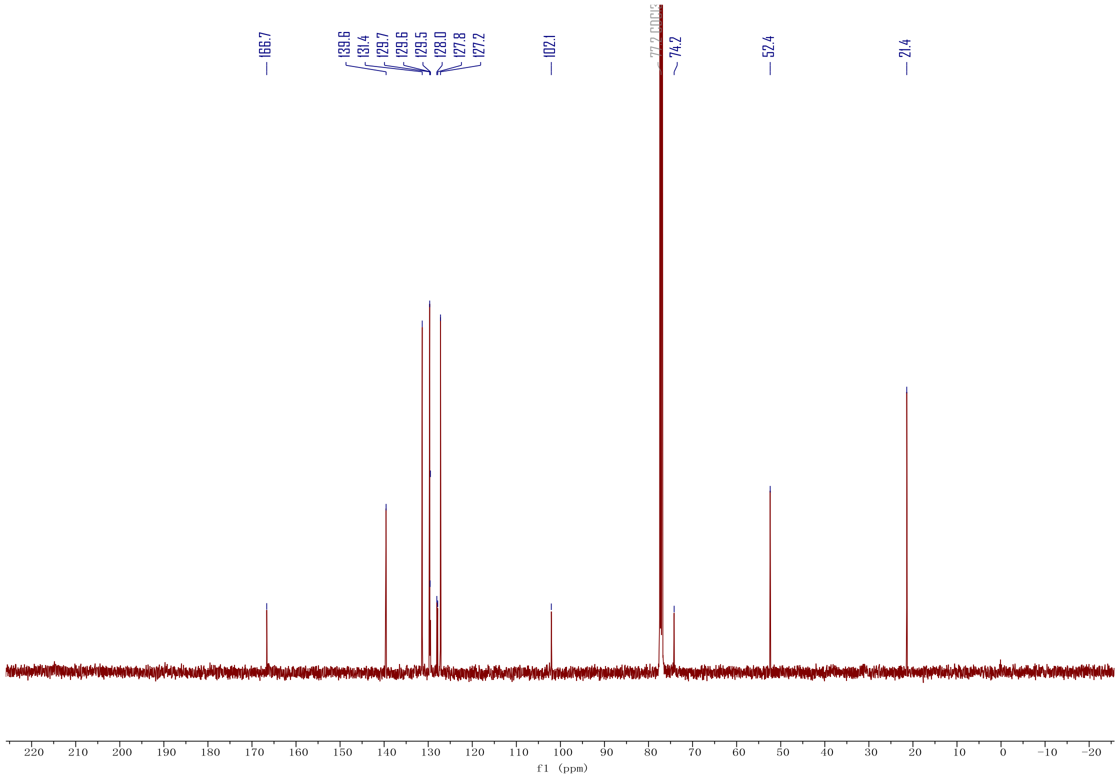
^{13}C NMR of compound 13 (126 MHz in CDCl$_3$)



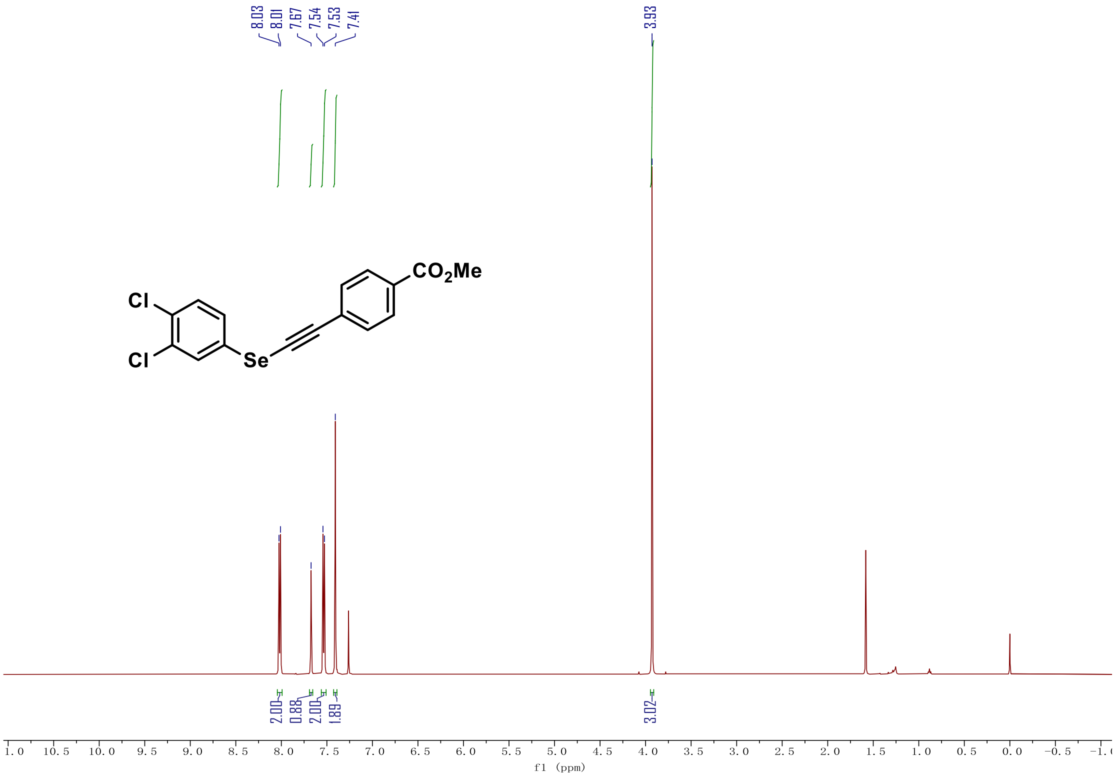
^{1}H NMR of compound 14 (500 MHz in CDCl$_3$)



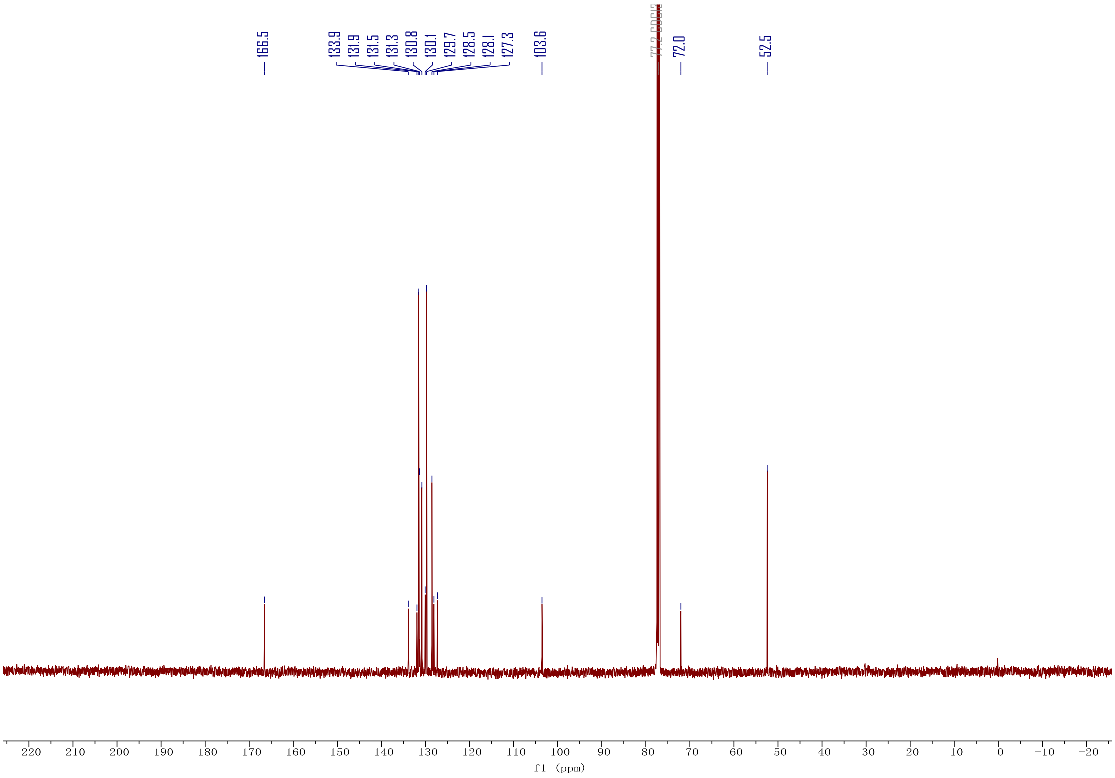
^{13}C NMR of compound 14 (126 MHz in CDCl$_3$)



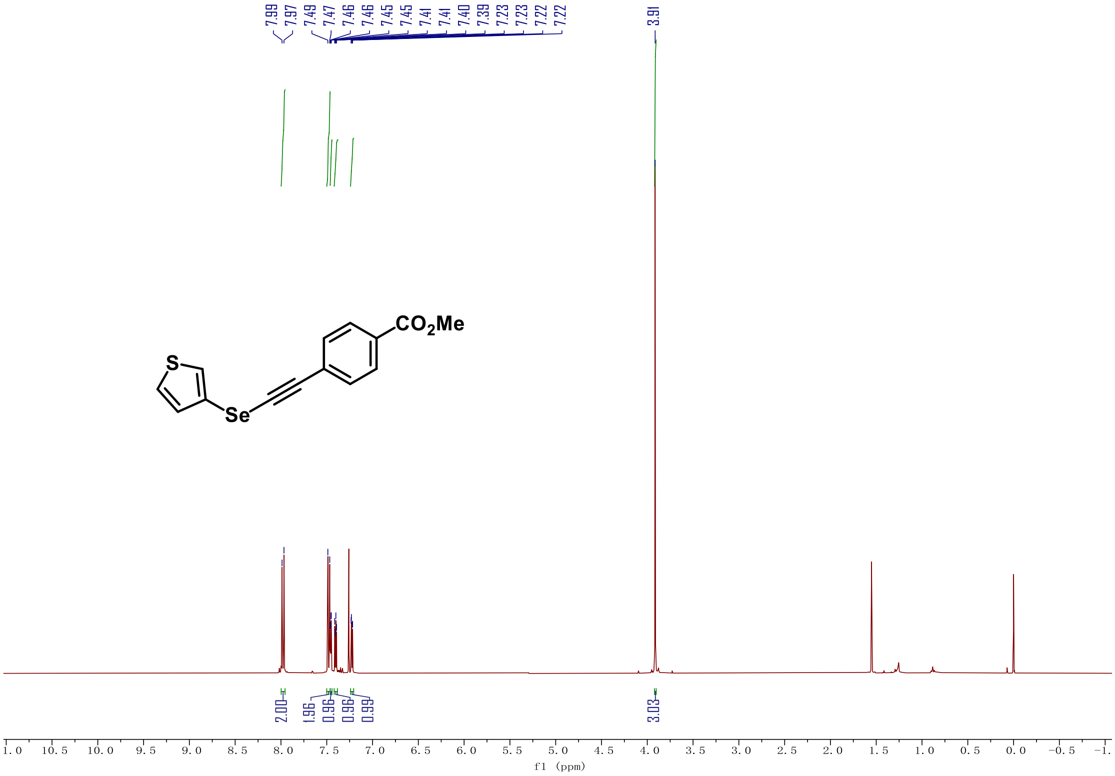
^{1}H NMR of compound 15 (500 MHz in $CDCl_3$)



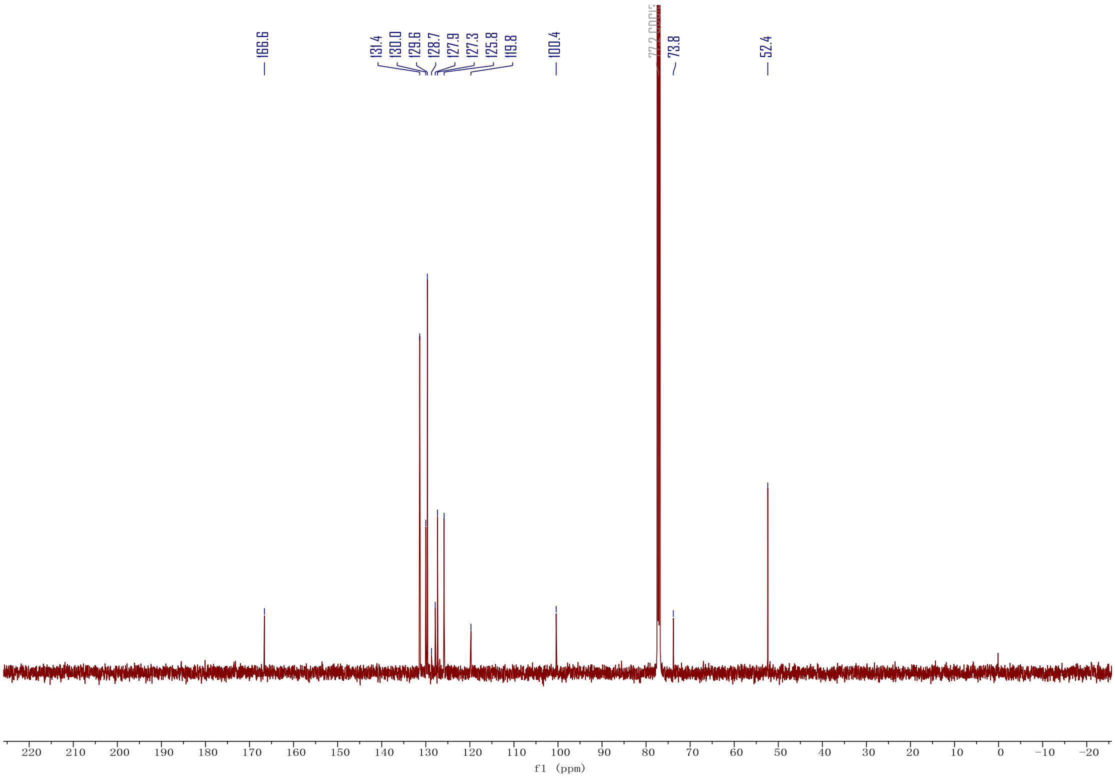
^{13}C NMR of compound 15 (126 MHz in $CDCl_3$)



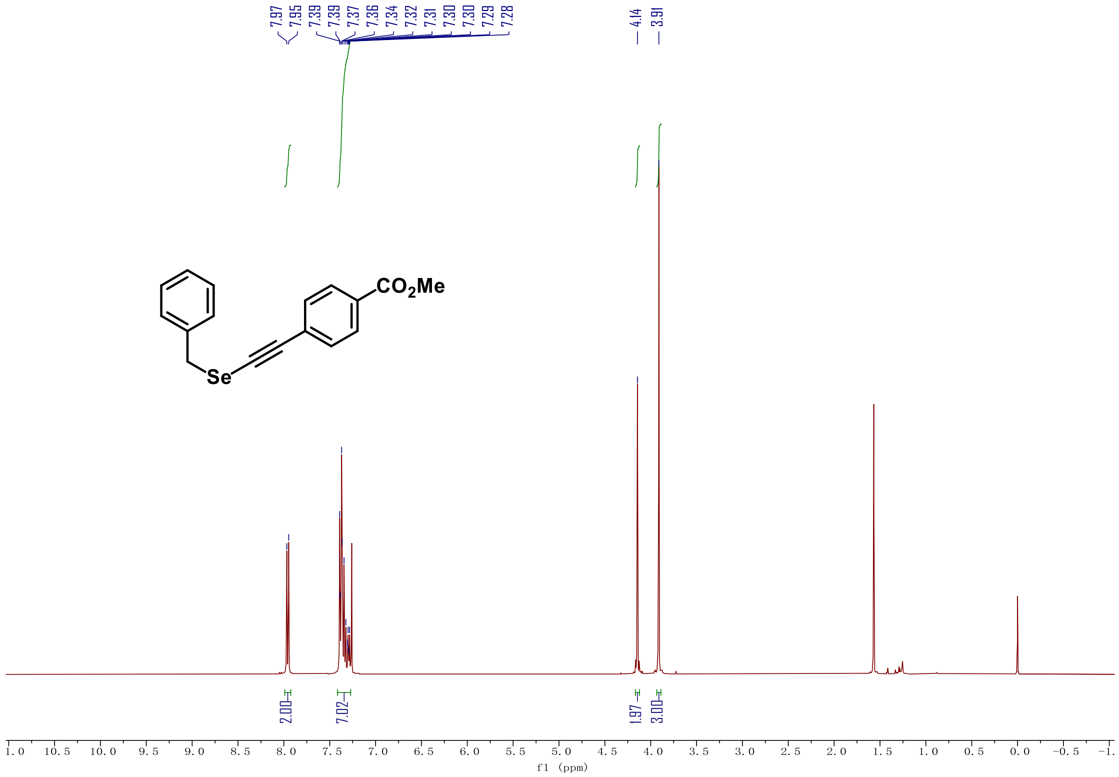
^{1}H NMR of compound 16 (500 MHz in CDCl$_3$)



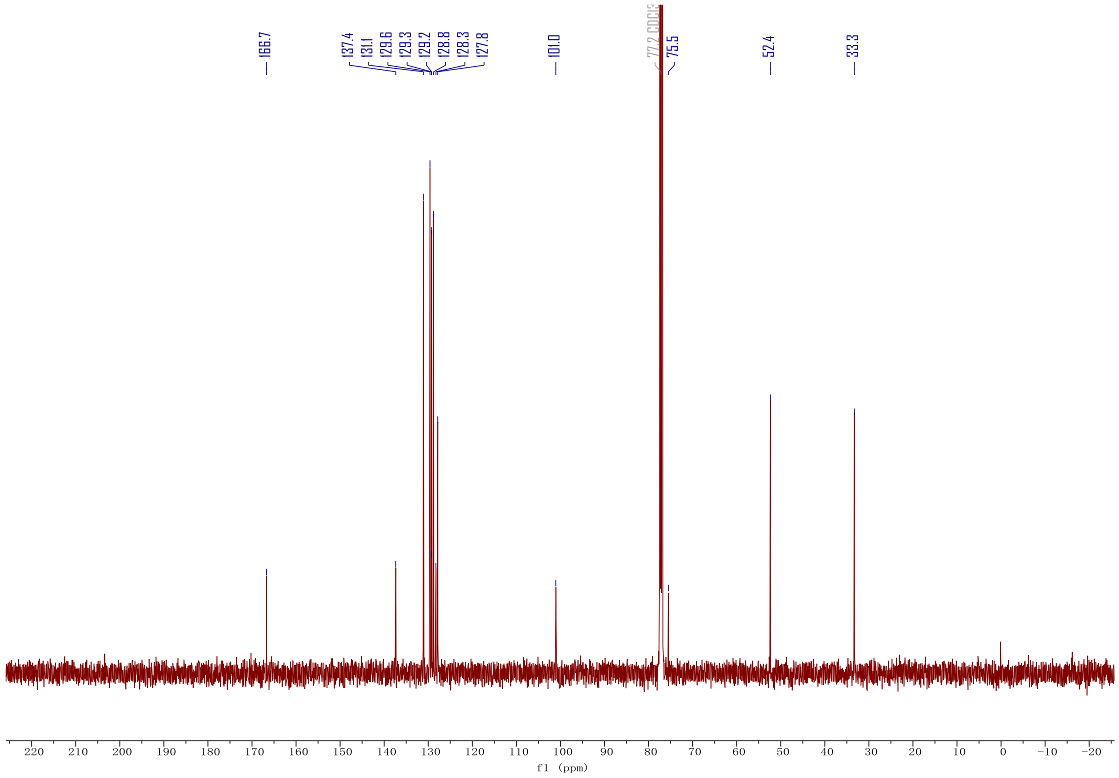
^{13}C NMR of compound 16 (126 MHz in CDCl$_3$)



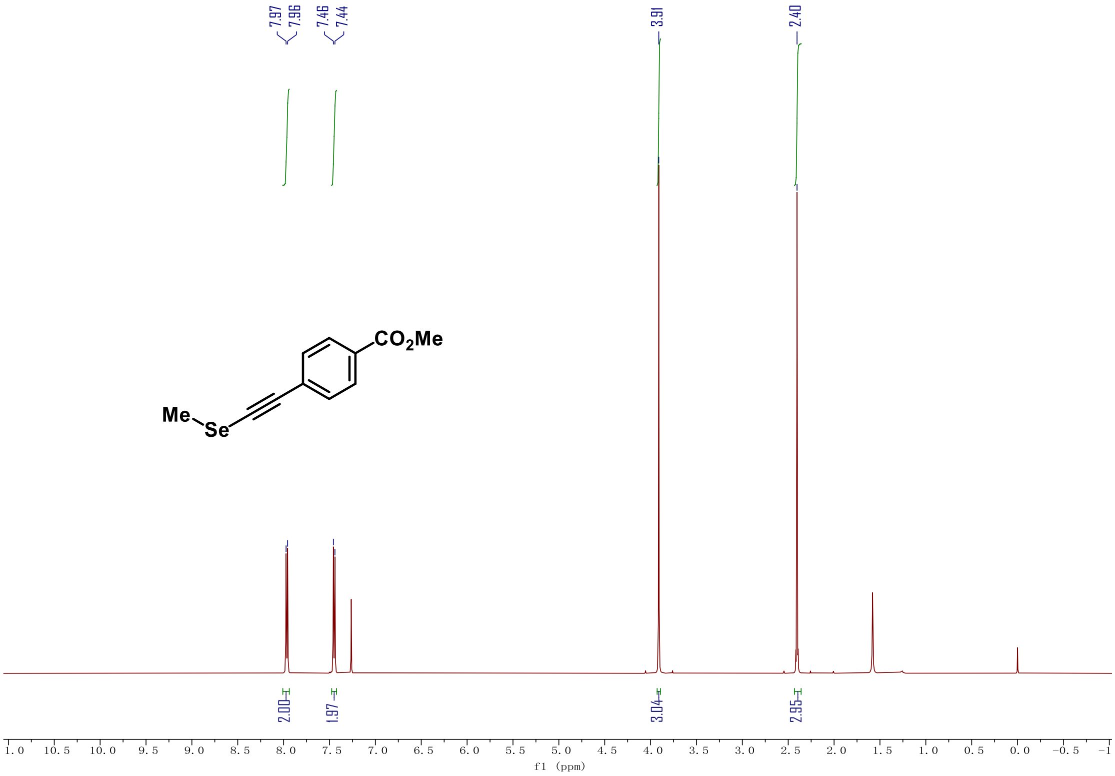
^{1}H NMR of compound 17 (500 MHz in CDCl$_3$)



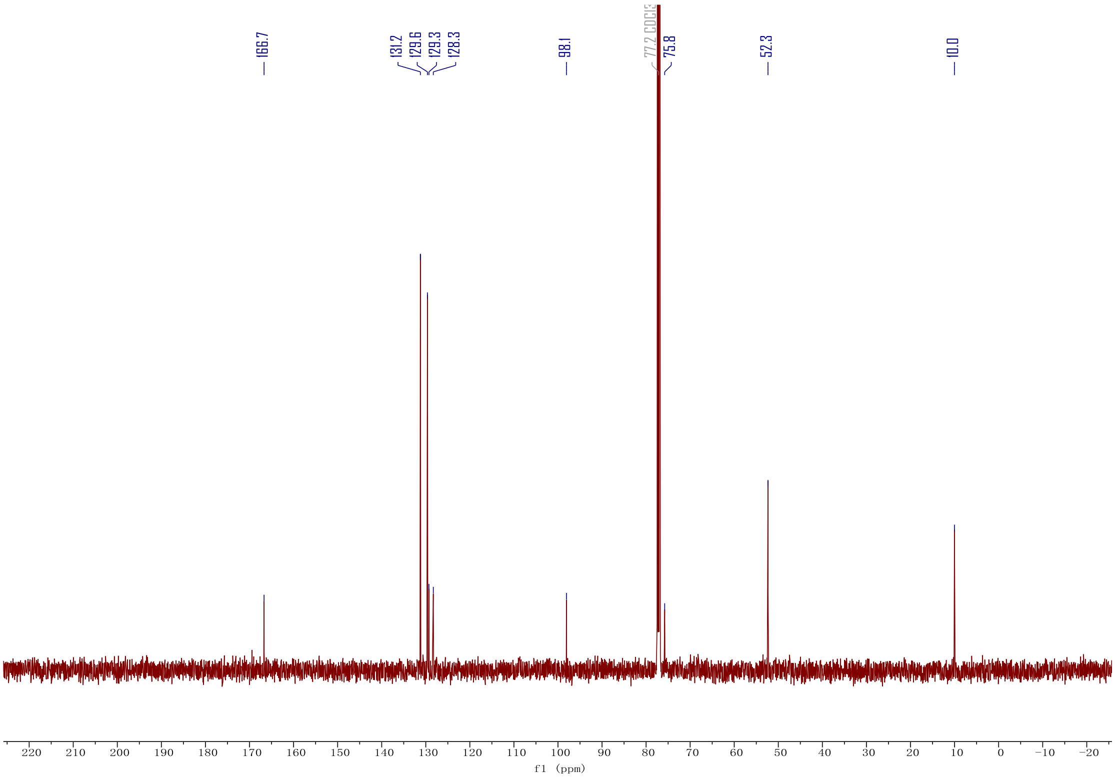
^{1}H NMR of compound 17 (500 MHz in CDCl$_3$)



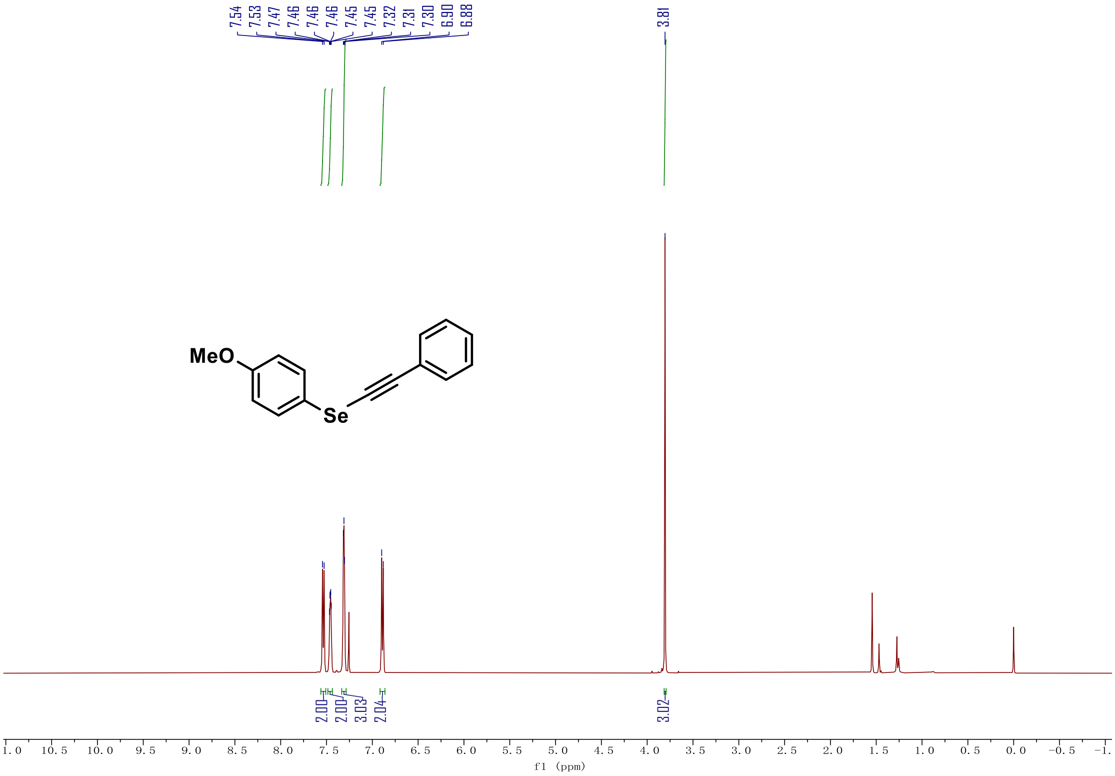
^{1}H NMR of compound 18 (500 MHz in $CDCl_3$)



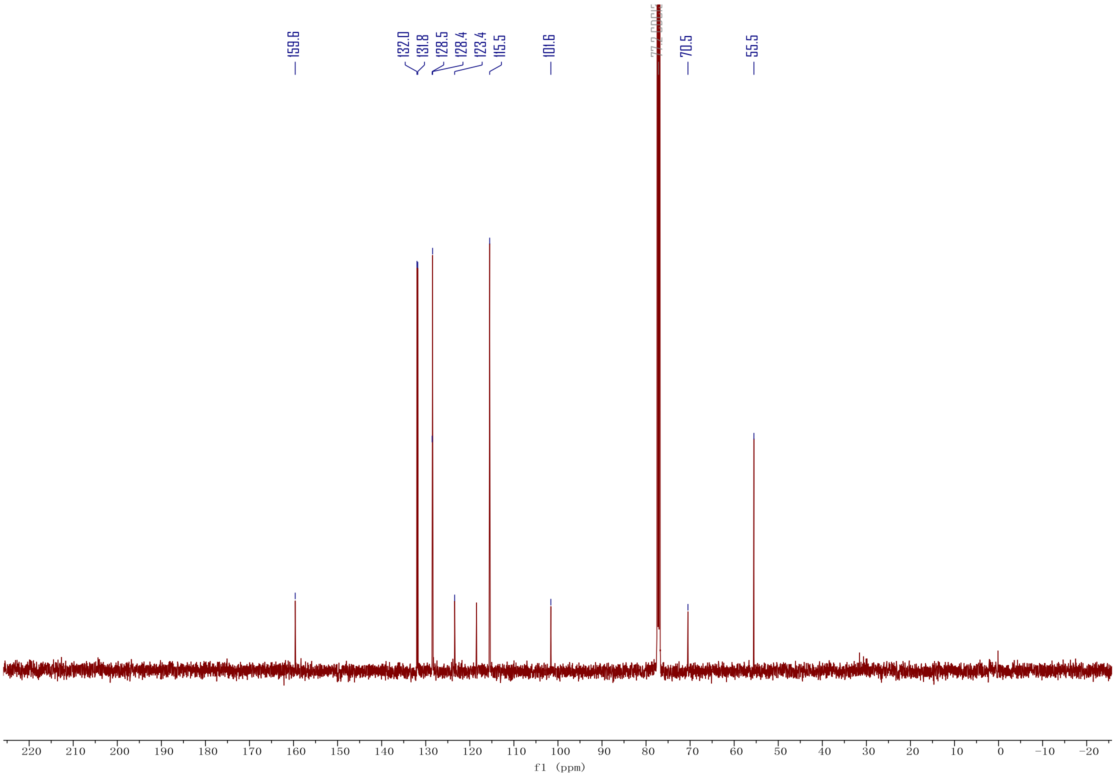
^{1}H NMR of compound 18 (500 MHz in $CDCl_3$)



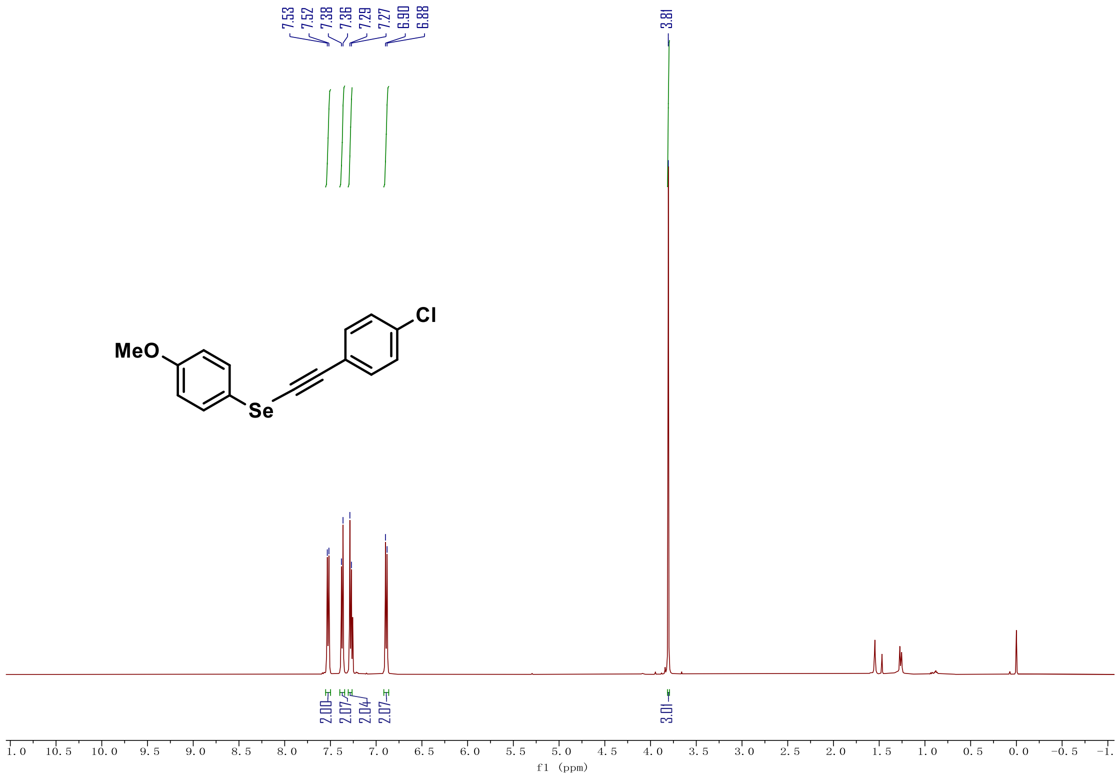
^{1}H NMR of compound 19 (500 MHz in CDCl$_3$)



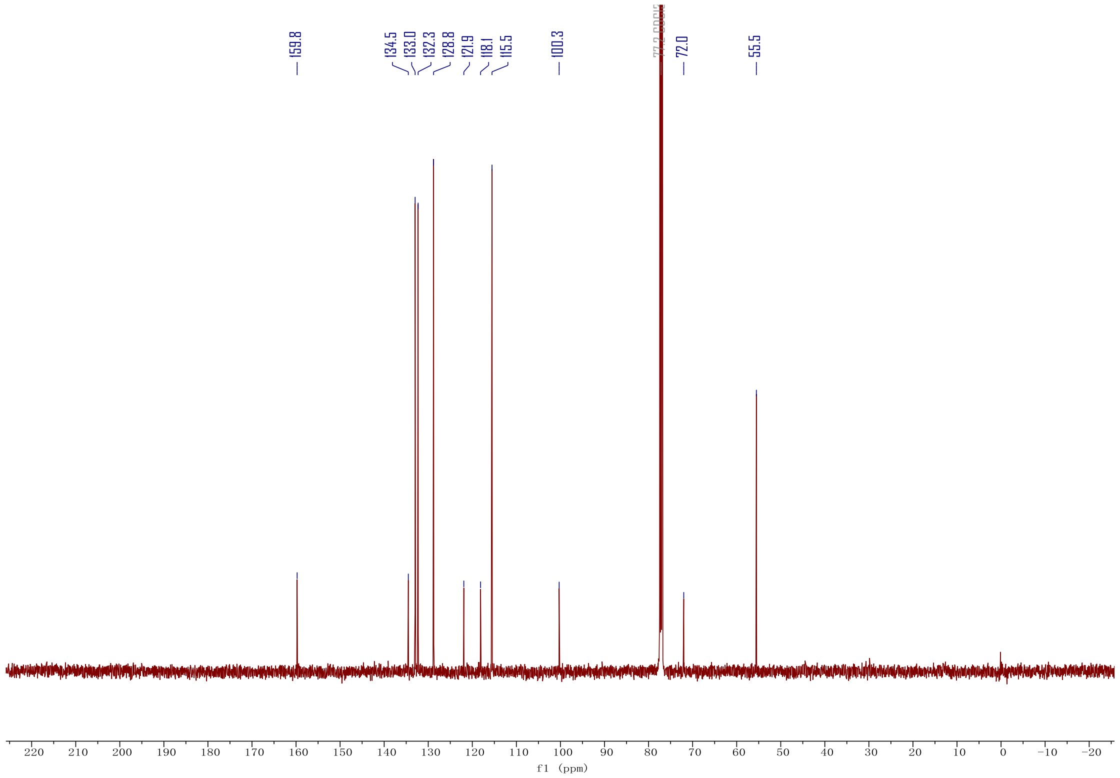
^{13}C NMR of compound 19 (126 MHz in CDCl$_3$)



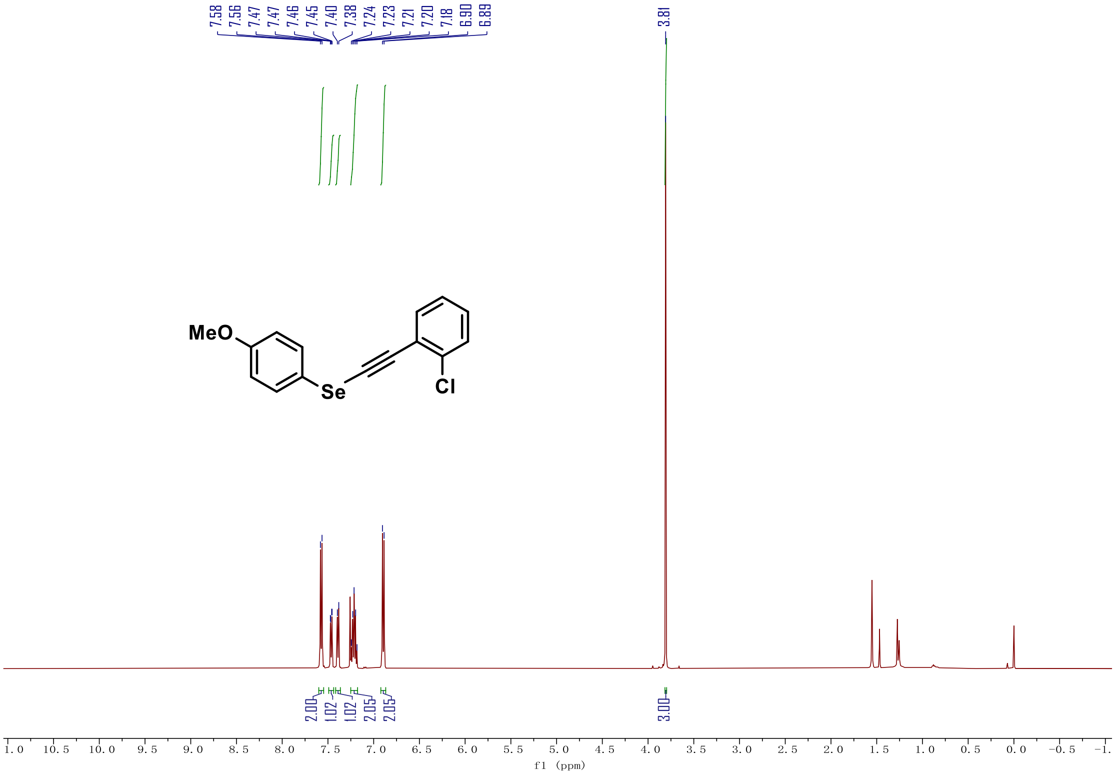
^{1}H NMR of compound 20 (500 MHz in $CDCl_3$)



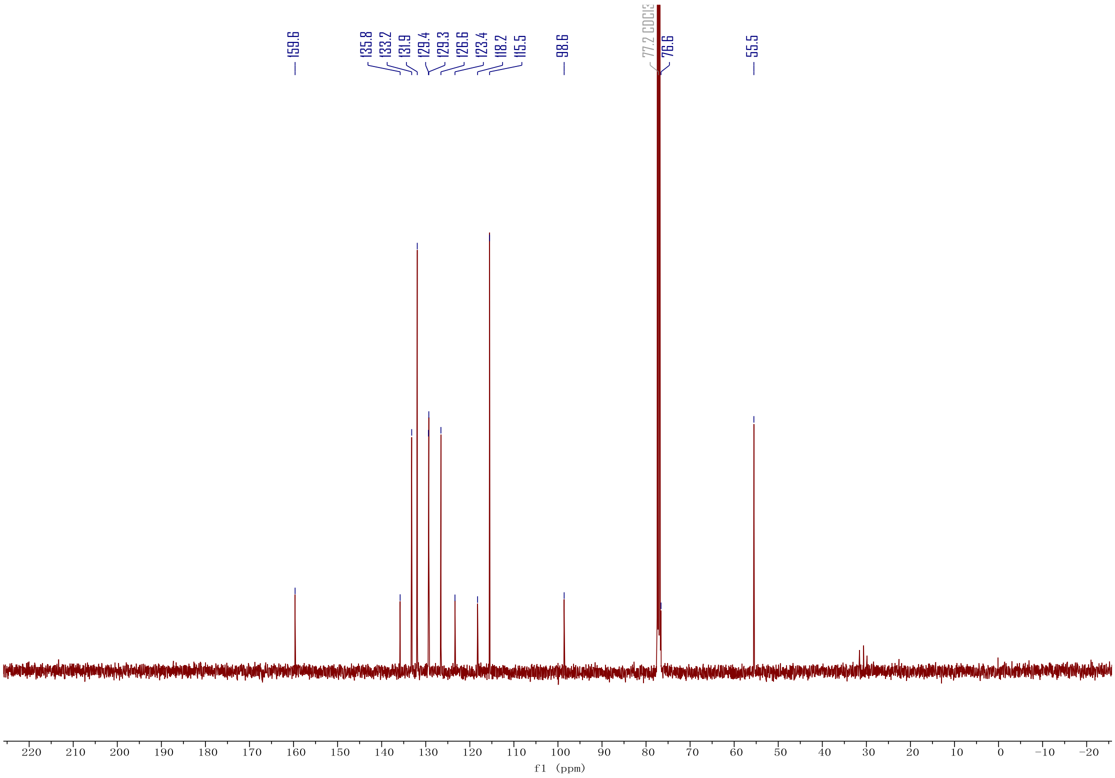
^{13}C NMR of compound 20 (126 MHz in $CDCl_3$)



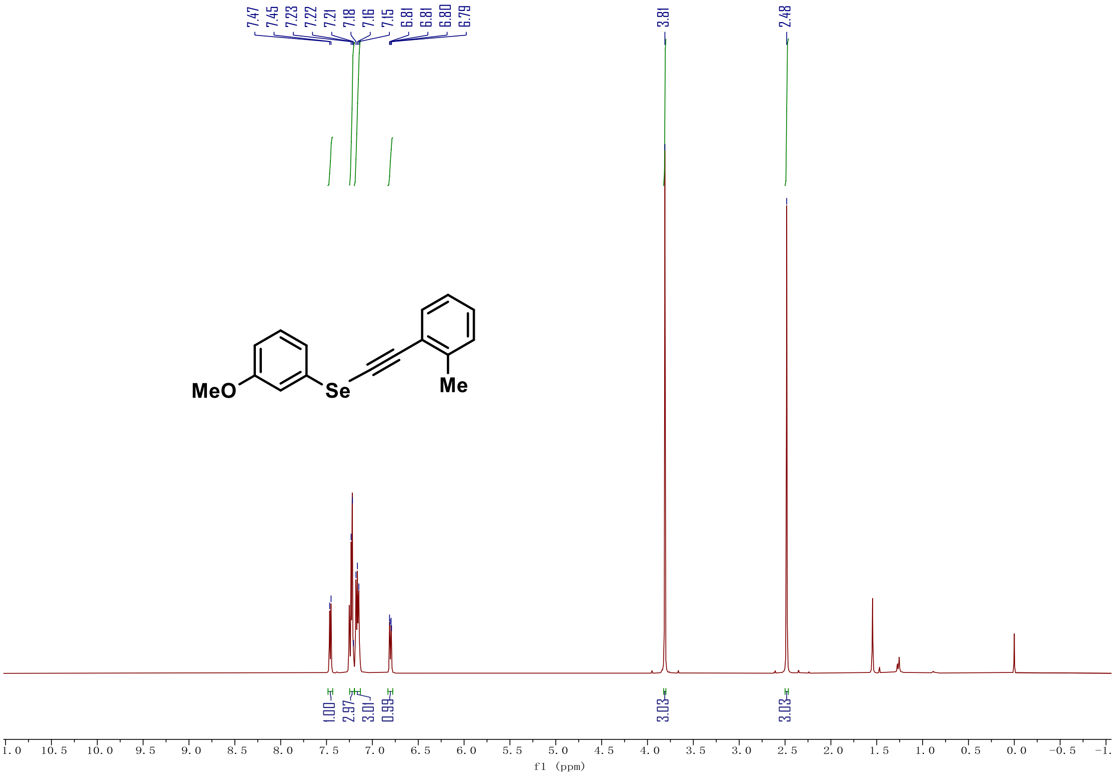
^{1}H NMR of compound 21 (500 MHz in $CDCl_3$)



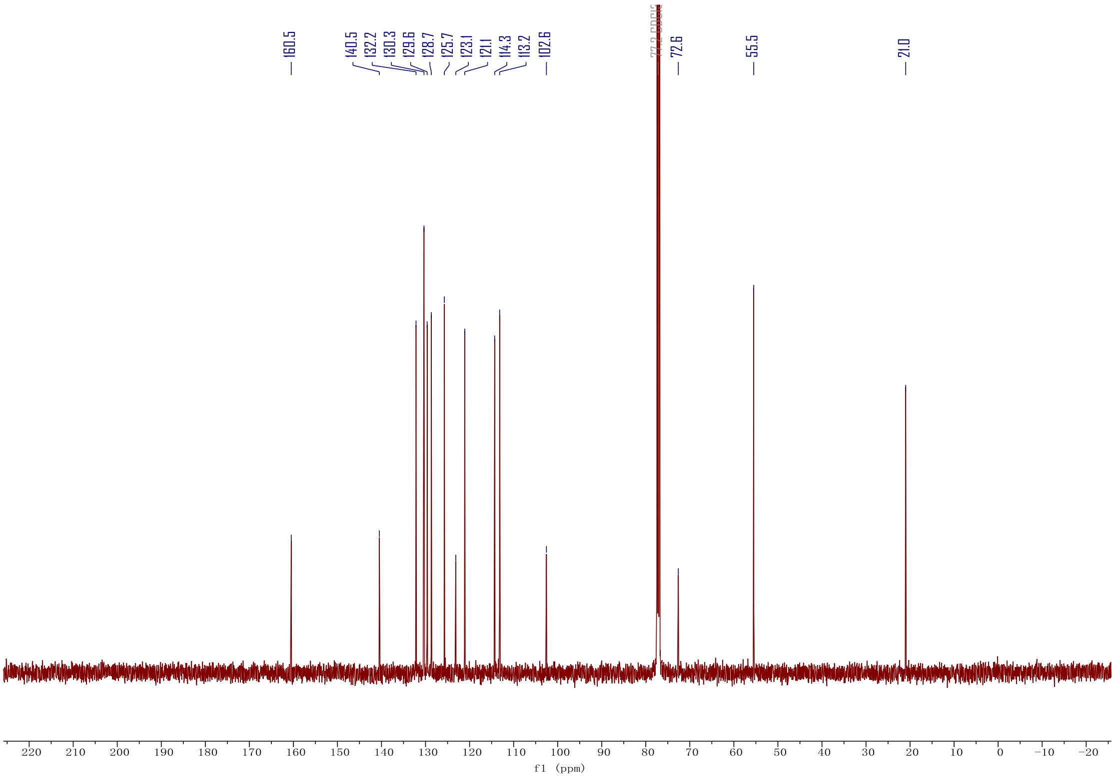
^{13}C NMR of compound 21 (126 MHz in $CDCl_3$)



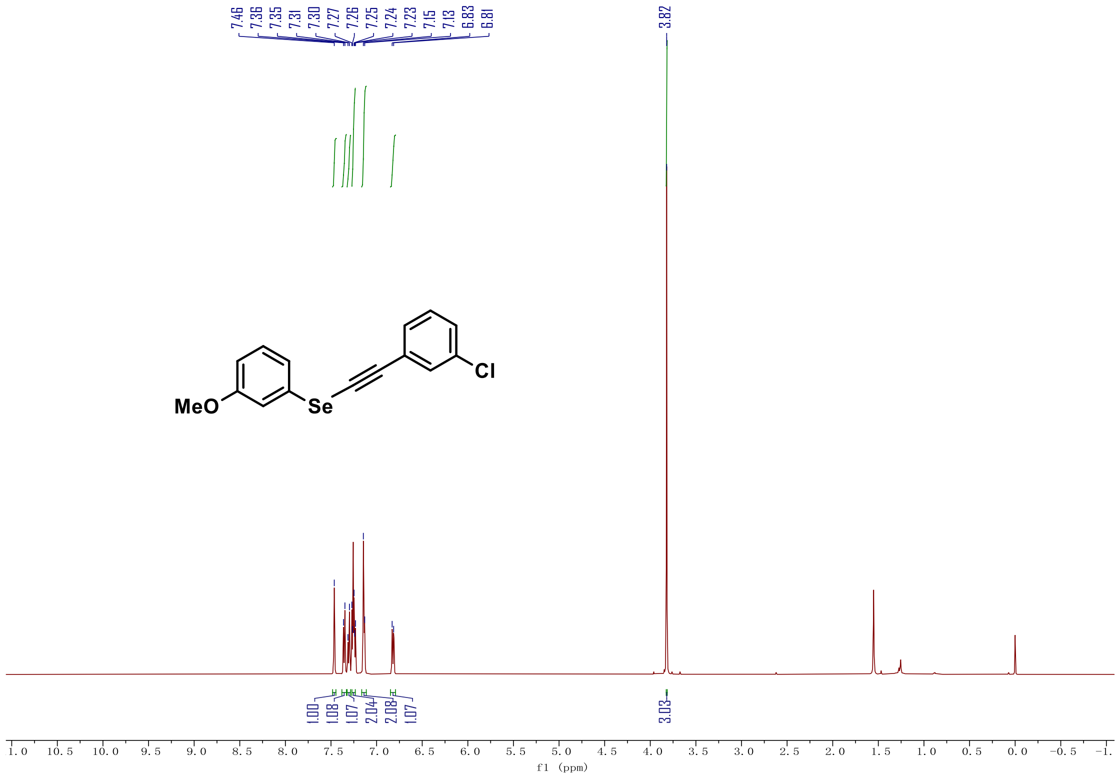
^{1}H NMR of compound 22 (500 MHz in $CDCl_3$)



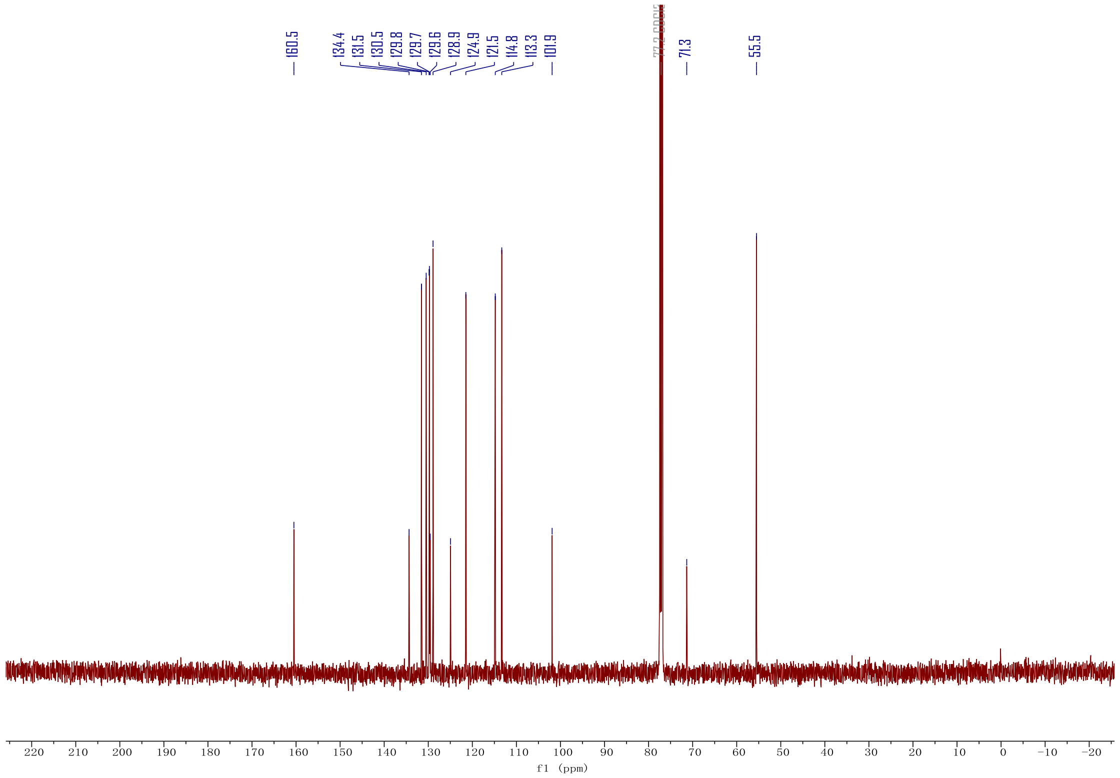
^{13}C NMR of compound 22 (126 MHz in $CDCl_3$)



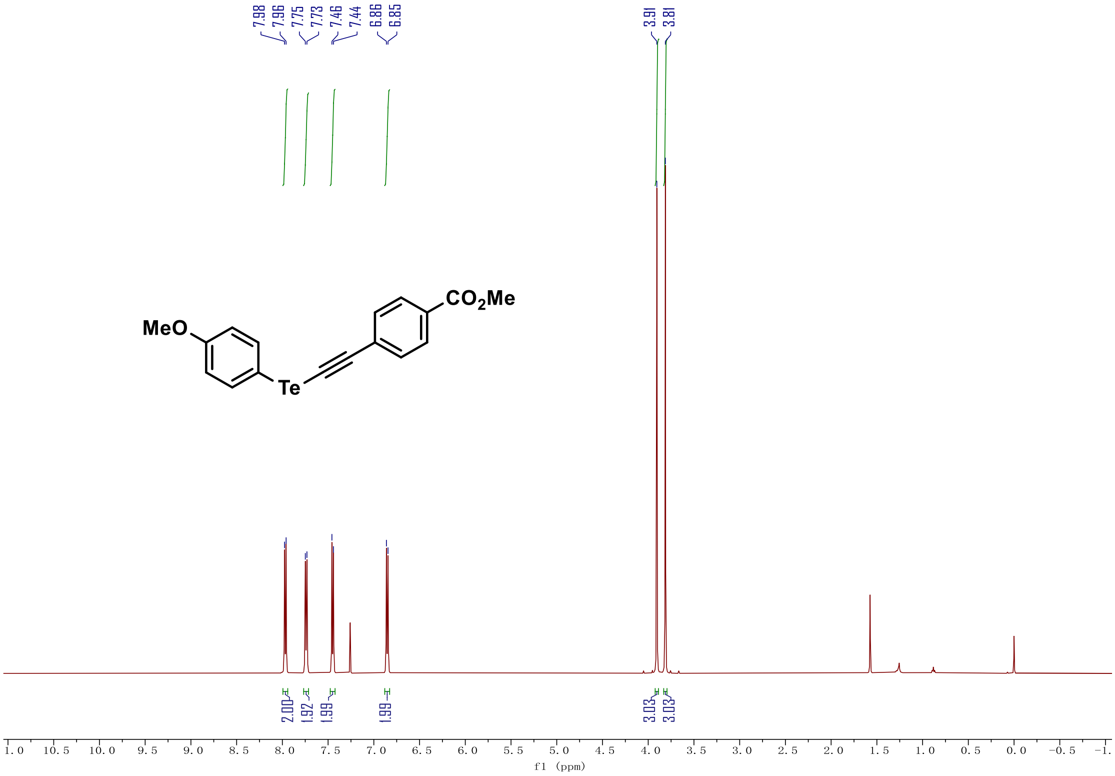
^{1}H NMR of compound 23 (500 MHz in CDCl$_3$)



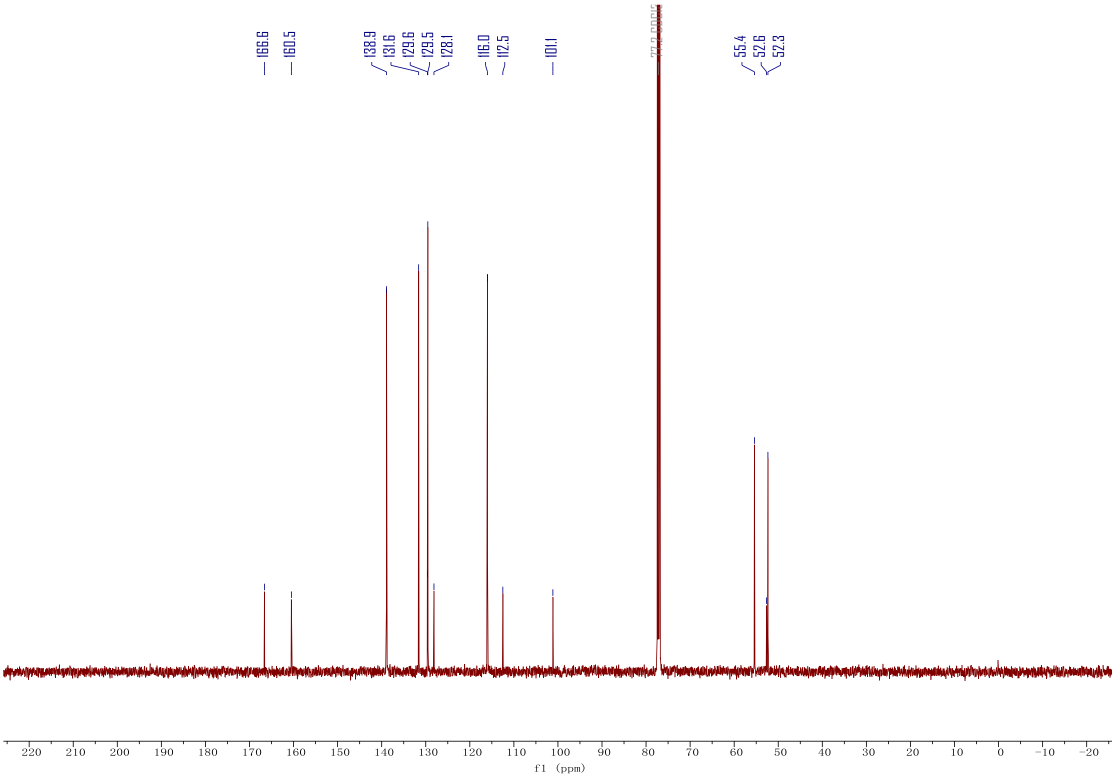
^{13}C NMR of compound 23 (126 MHz in CDCl$_3$)



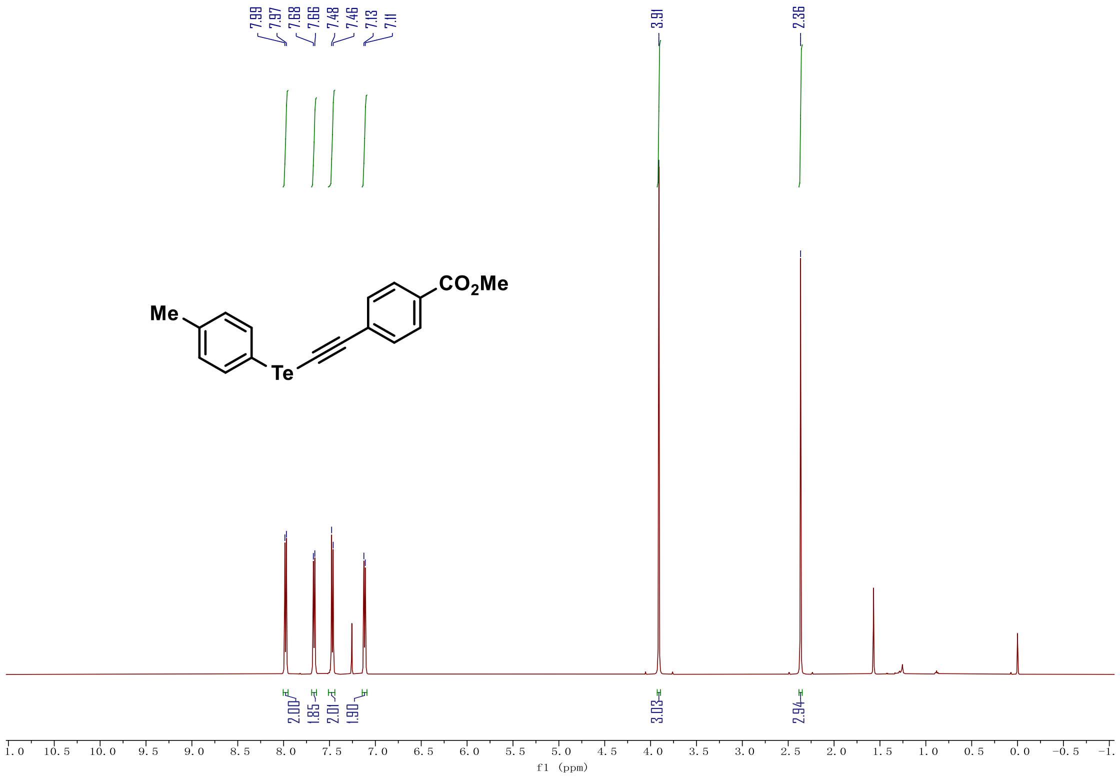
^{1}H NMR of compound 24 (500 MHz in $CDCl_3$)



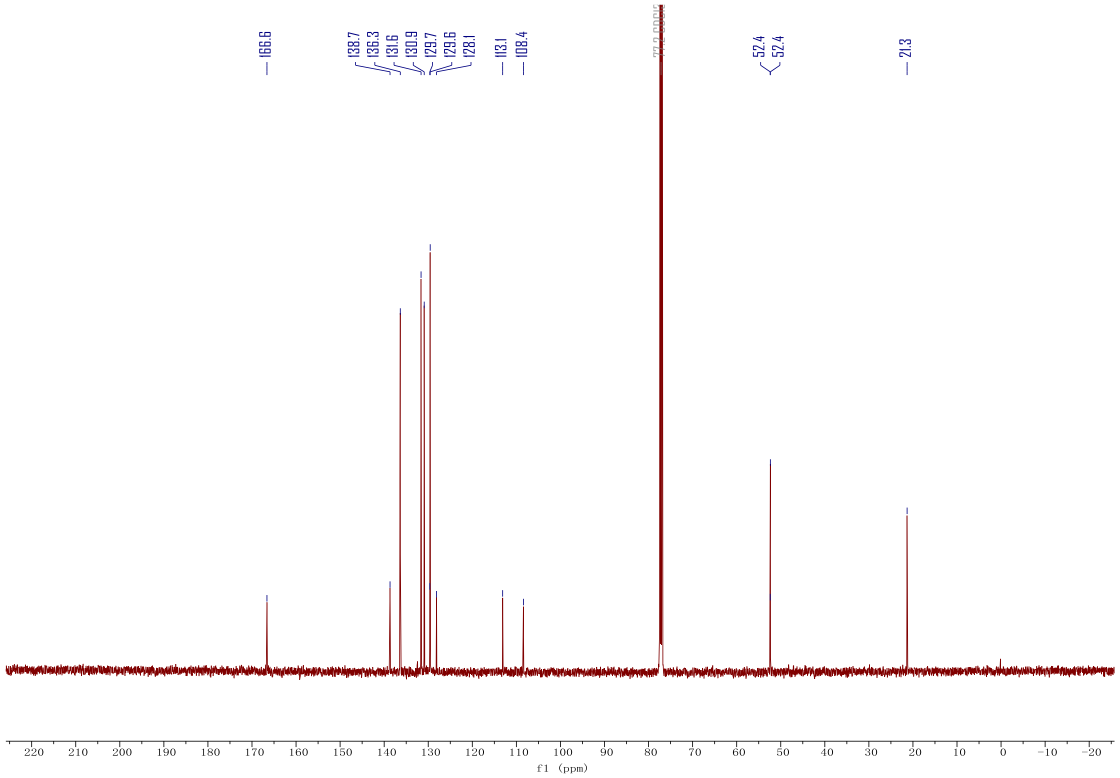
^{13}C NMR of compound 24 (126 MHz in $CDCl_3$)



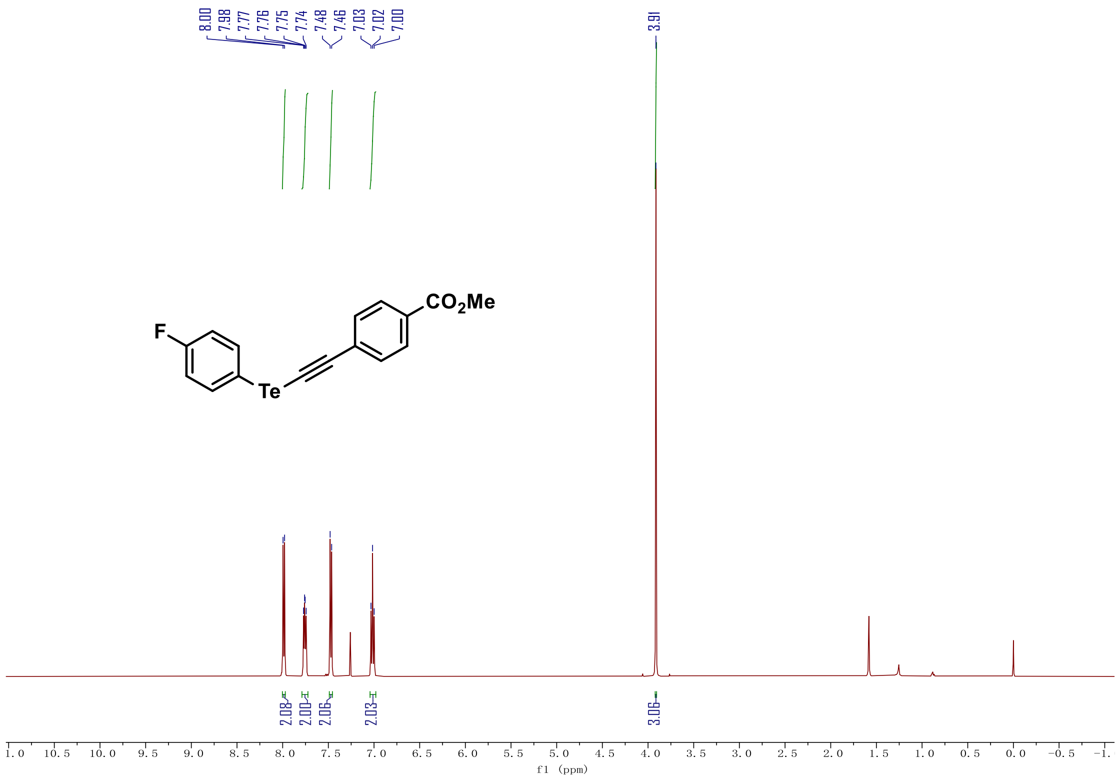
^{1}H NMR of compound 25 (500 MHz in CDCl$_3$)



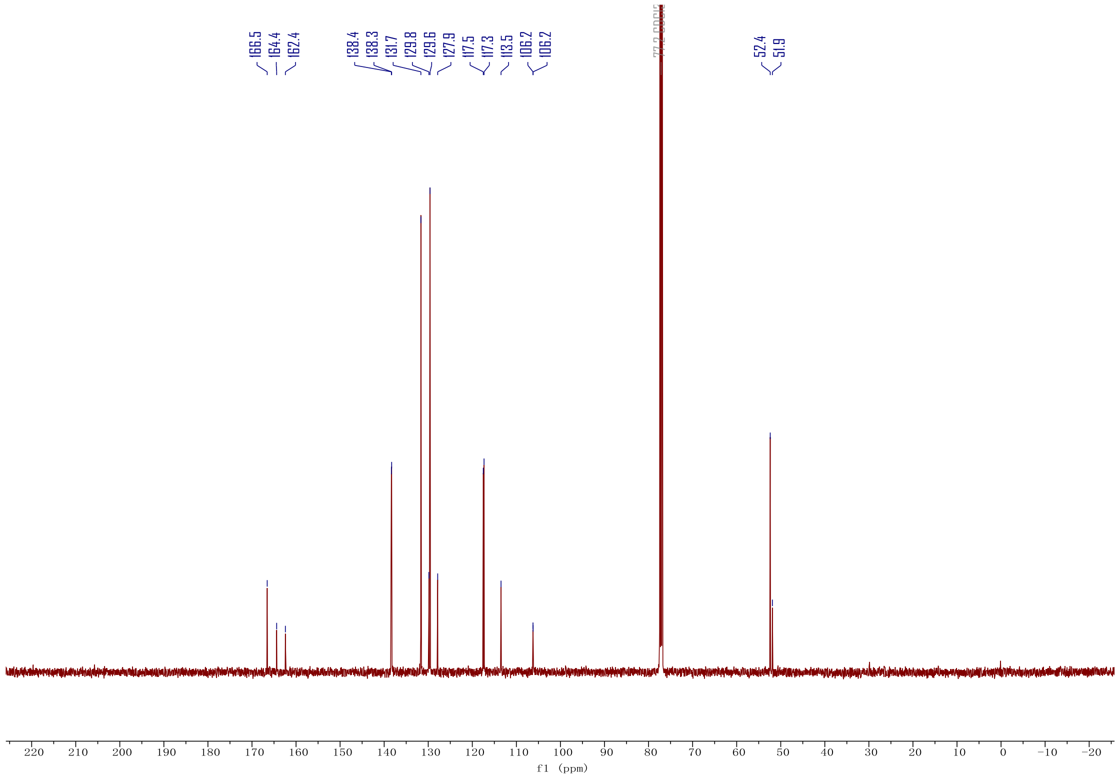
^{13}C NMR of compound 25 (126 MHz in CDCl$_3$)



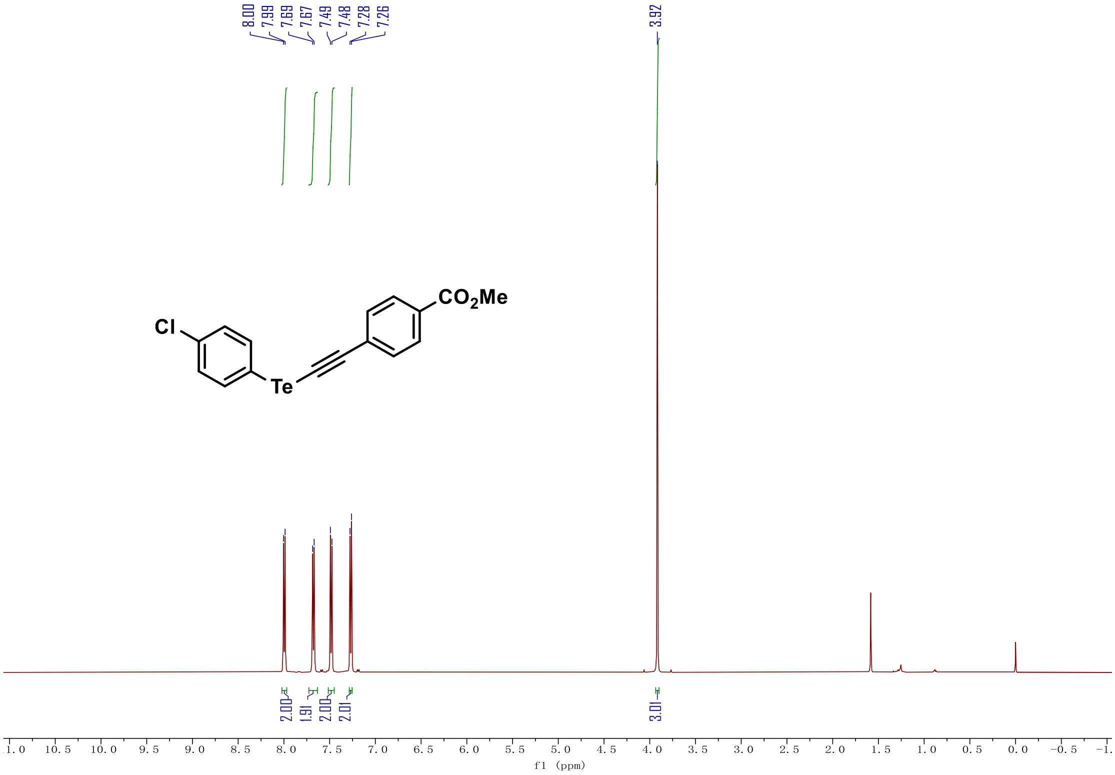
^{1}H NMR of compound 26 (500 MHz in $CDCl_3$)



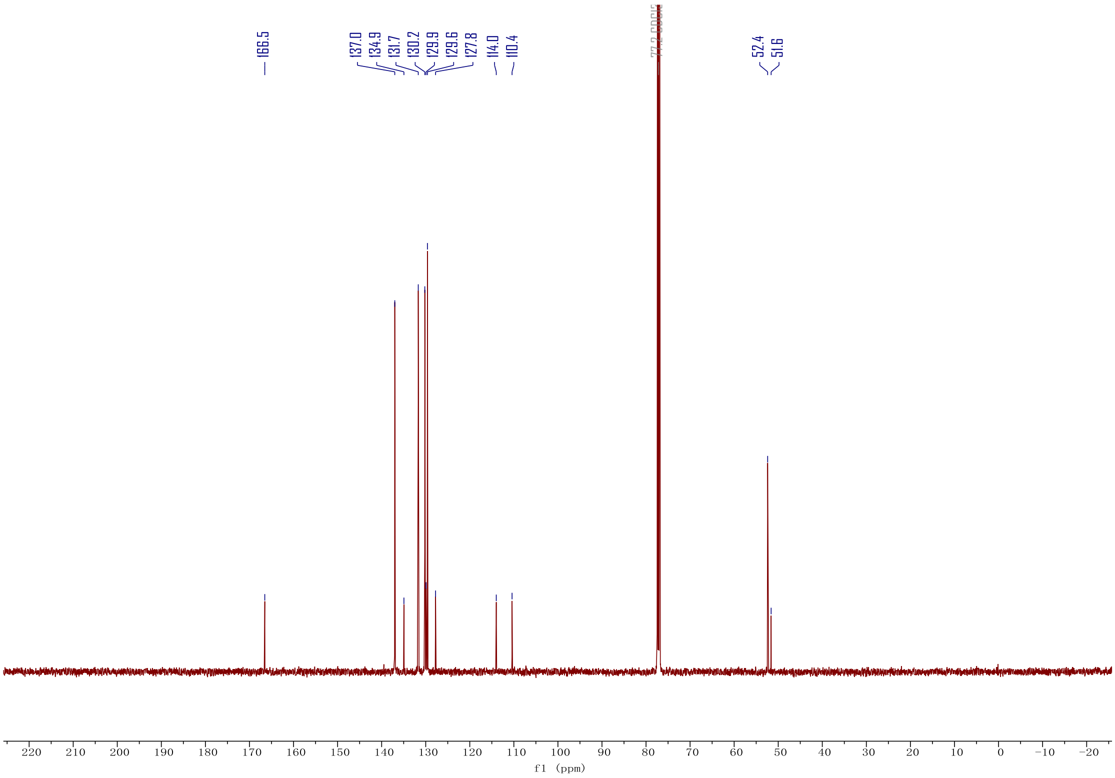
^{13}C NMR of compound 26 (126 MHz in $CDCl_3$)



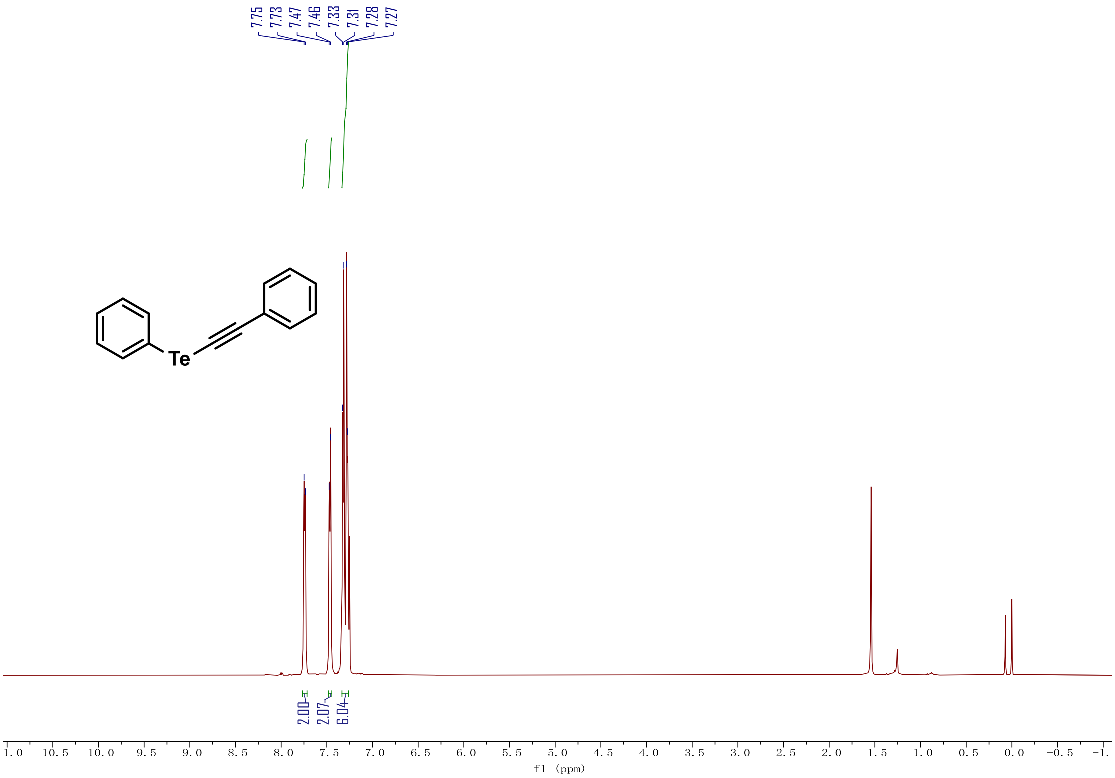
^{1}H NMR of compound 27 (500 MHz in CDCl$_3$)



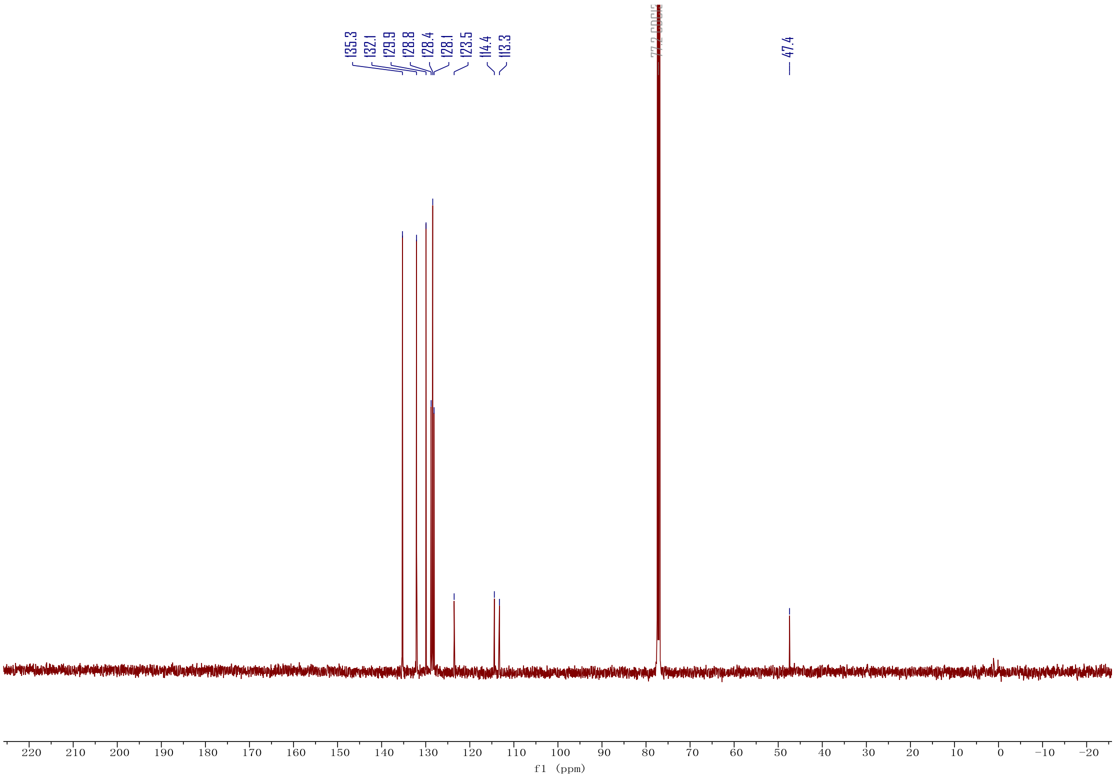
^{13}C NMR of compound 27 (126 MHz in CDCl$_3$)



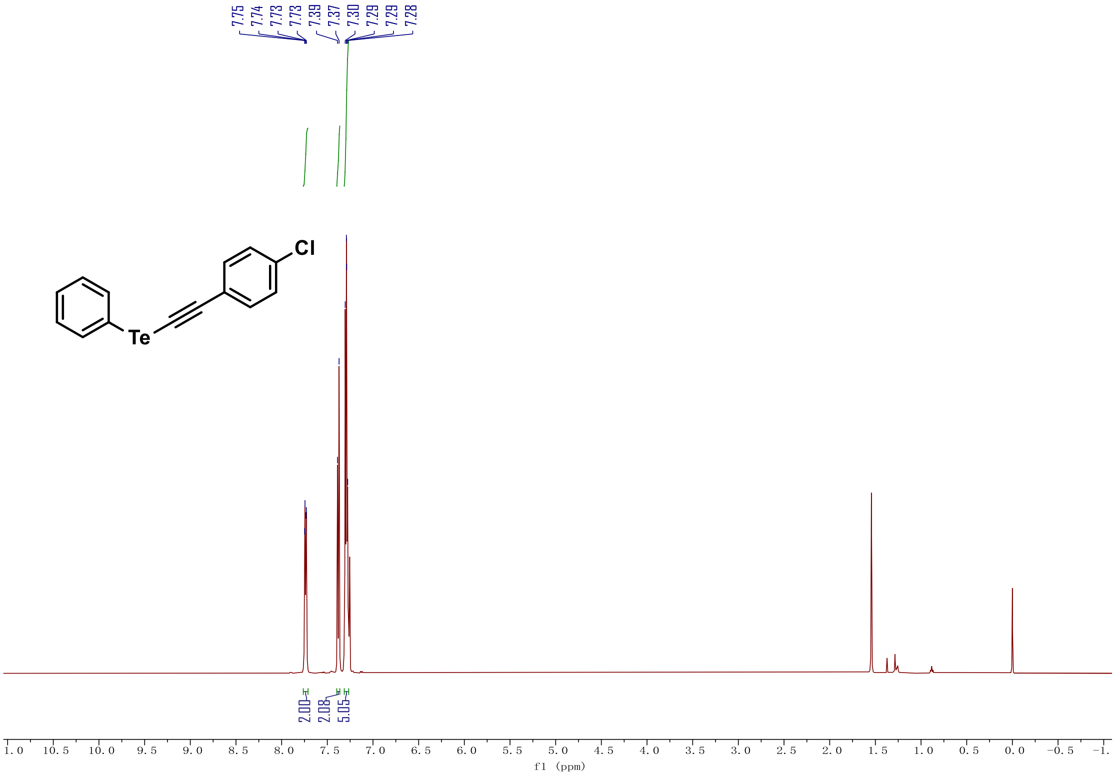
^{1}H NMR of compound 28 (500 MHz in $CDCl_3$)



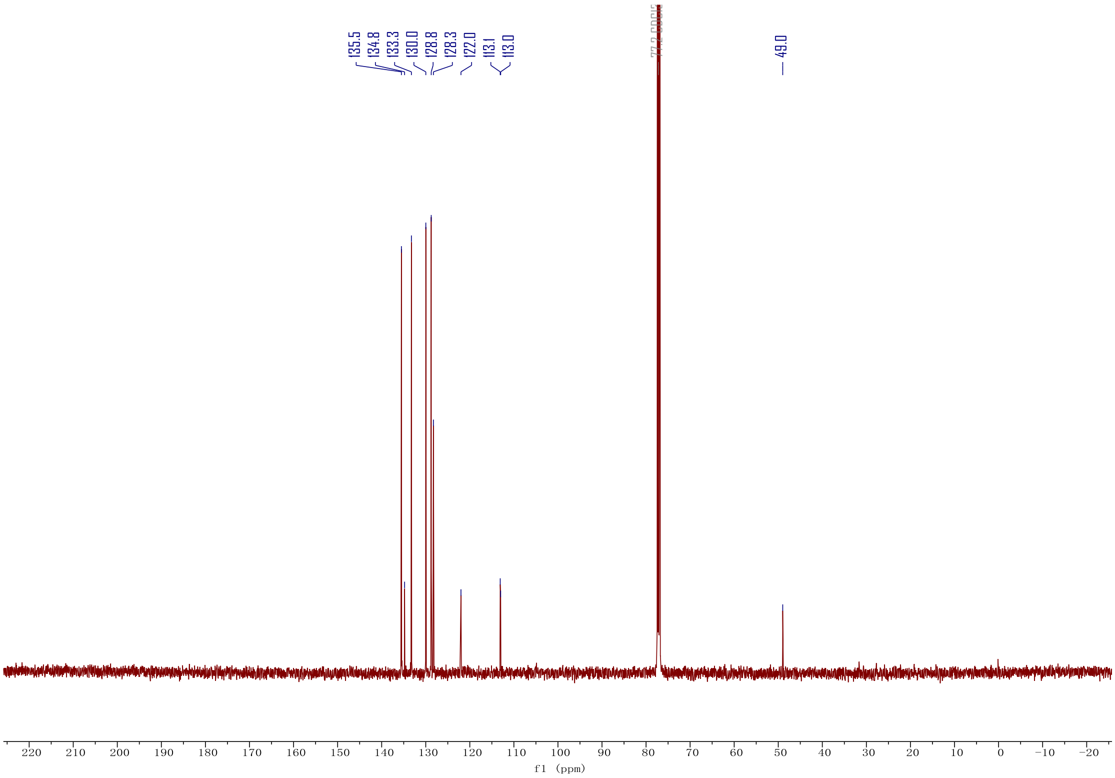
^{13}C NMR of compound 28 (126 MHz in $CDCl_3$)



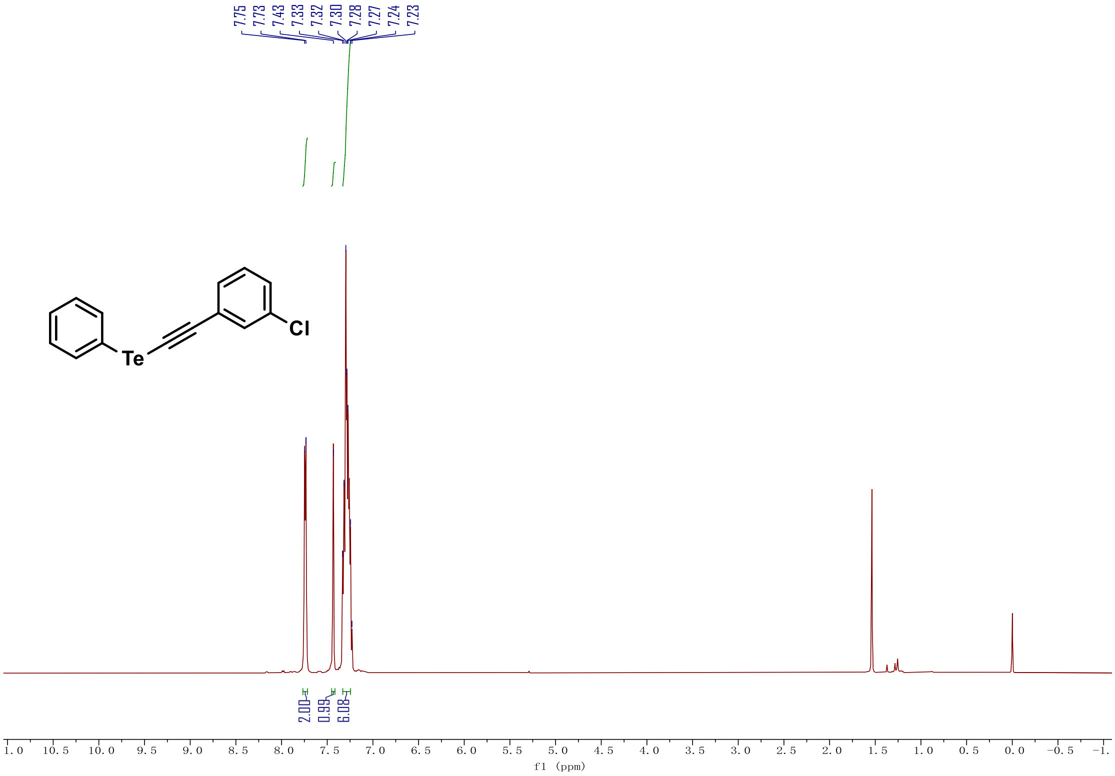
^{1}H NMR of compound 29 (500 MHz in $CDCl_3$)



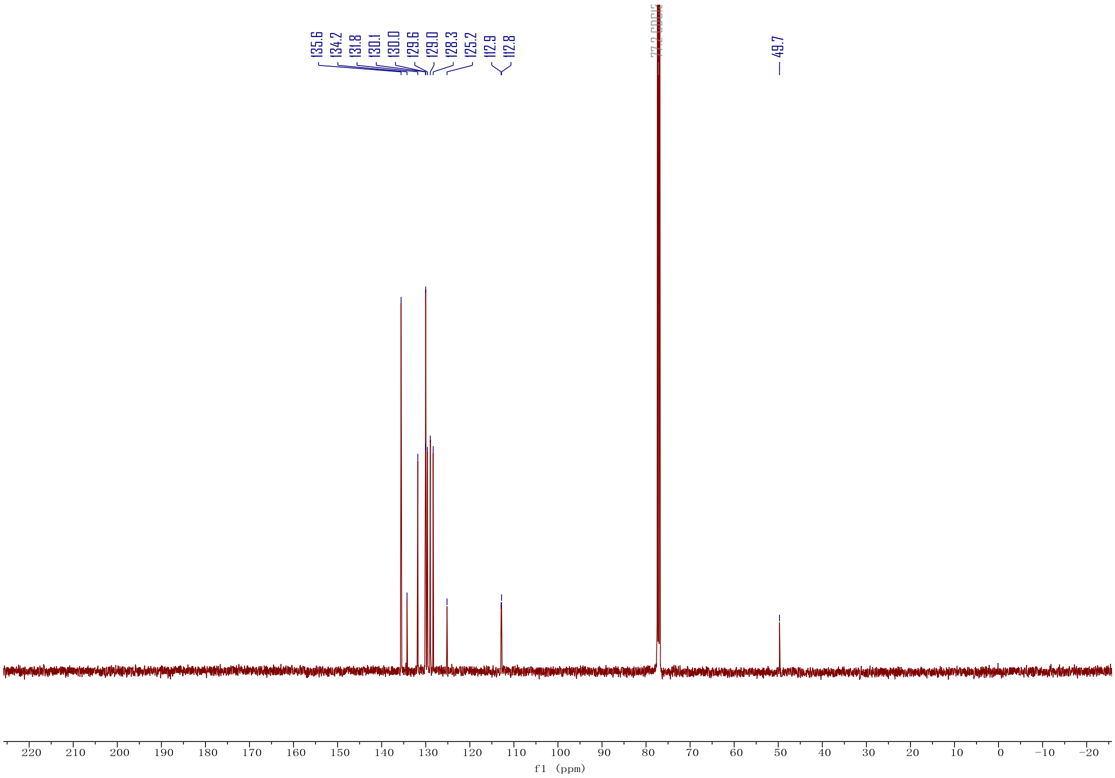
^{13}C NMR of compound 29 (126 MHz in $CDCl_3$)



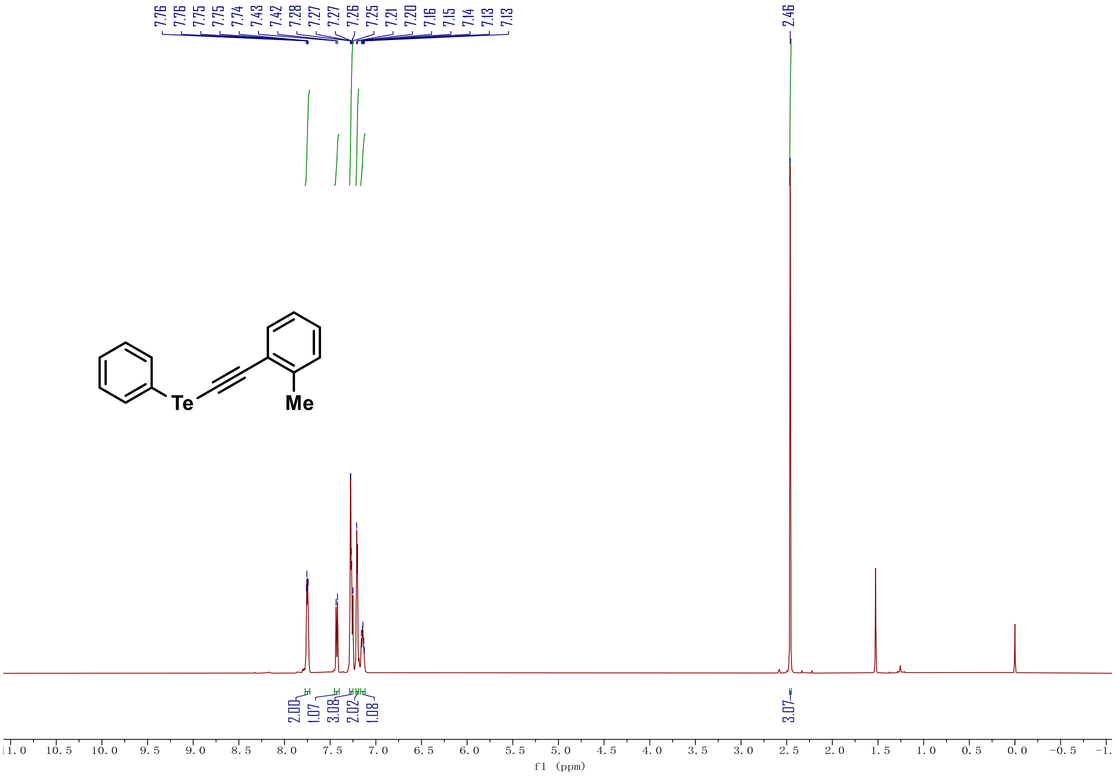
^{1}H NMR of compound 30 (500 MHz in CDCl$_3$)



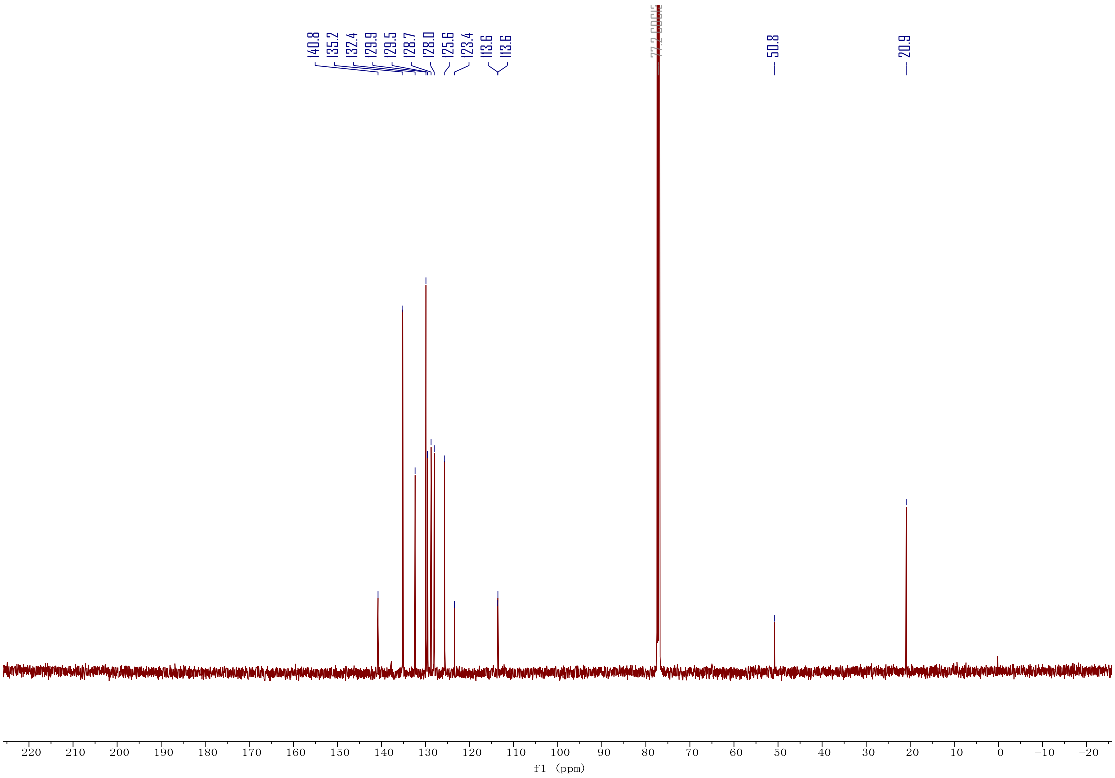
^{13}C NMR of compound 30 (126 MHz in CDCl$_3$)



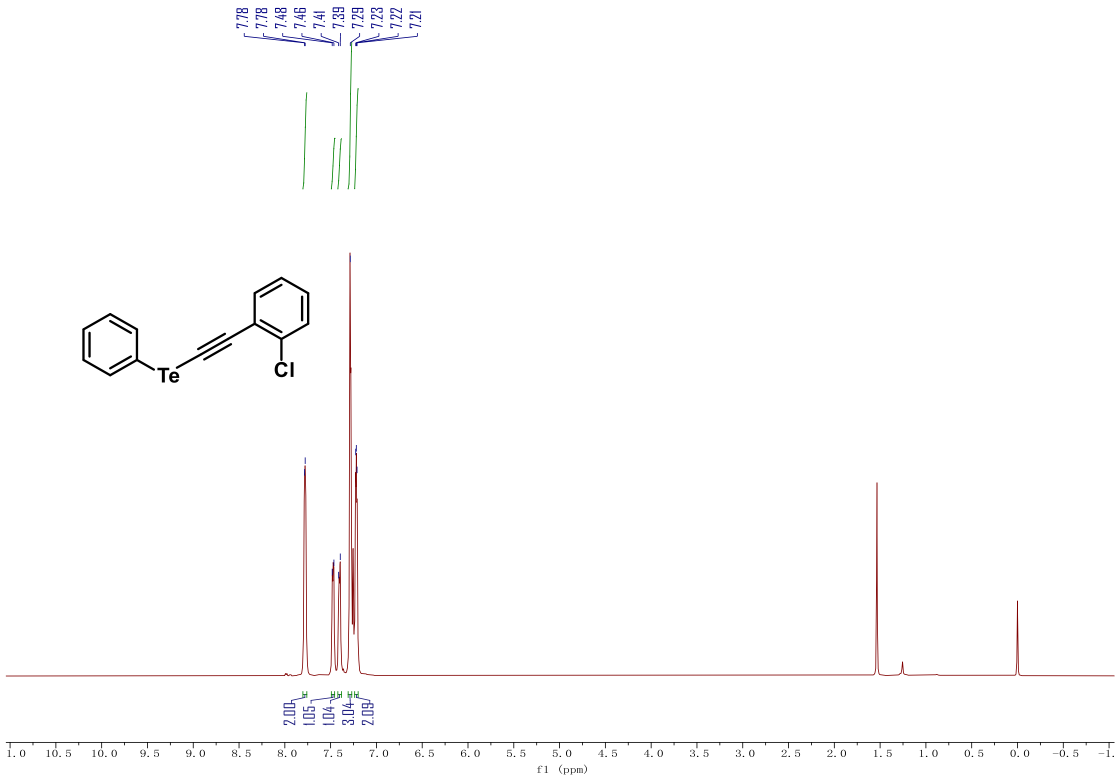
^{1}H NMR of compound 31 (500 MHz in $CDCl_3$)



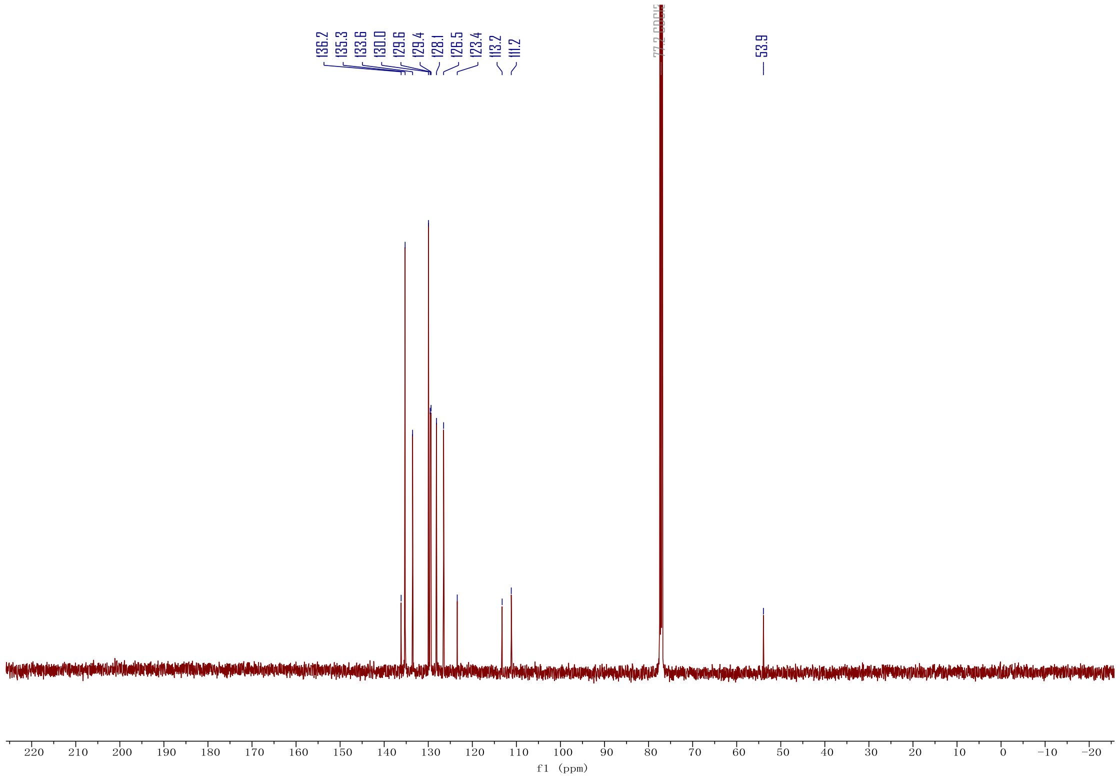
^{13}C NMR of compound 31 (126 MHz in $CDCl_3$)



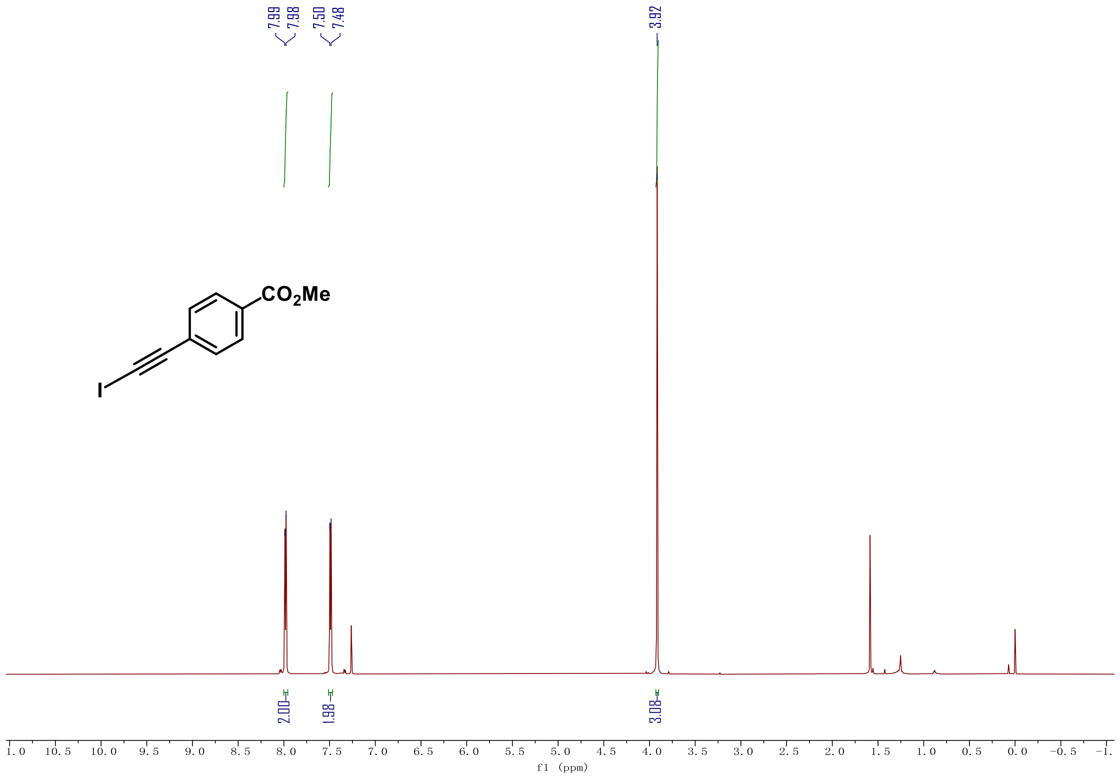
^{1}H NMR of compound 32 (500 MHz in $CDCl_3$)



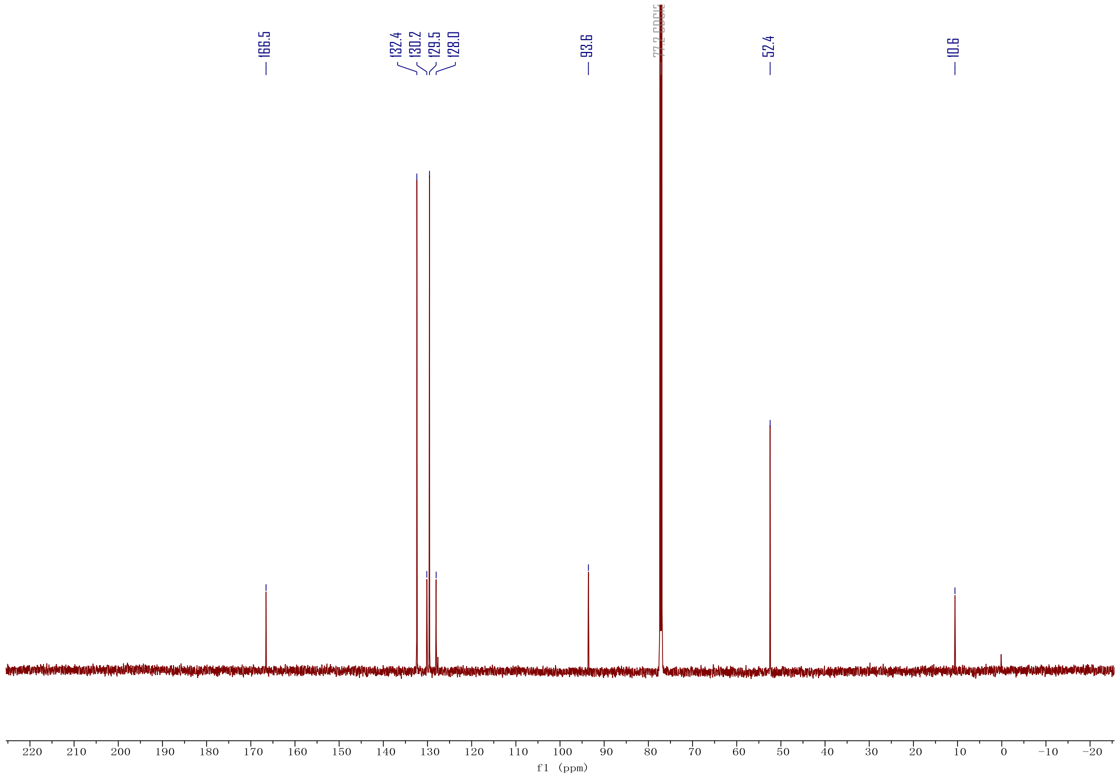
^{13}C NMR of compound 32 (126 MHz in $CDCl_3$)



^{1}H NMR of compound 34 (500 MHz in CDCl$_3$)



^{13}C NMR of compound 34 (126 MHz in CDCl$_3$)



7. References

1 X. Ren, Q. Liu, Z. Yang, Z. Wang and X. Chen, Aryldiazonium salts can serve as nitrogen-based Lewis acid catalysts and their applications in the formation of photoactive charge transfer complexes, *Chin. Chem. Lett.*, 2023, **34**, 107821.

2 B. Waldecker, F. Kraft, C. Golz and M. Alcarazo, 5-(Alkynyl)dibenzothiophenium Triflates: Sulfur-Based Reagents for Electrophilic Alkynylation, *Angew. Chem., Int. Ed.*, 2018, **57**, 12538–12542.

3 Y. Lu, Q. Liu, Z.-X. Wang and X.-Y. Chen, Alkynyl Sulfonium Salts Can Be Employed as Chalcogen-Bonding Catalysts and Generate Alkynyl Radicals under Blue-Light Irradiation, *Angew. Chem., Int. Ed.*, 2022, **61**, e202116071.

4 Y. Liu, D. Huang, J. Huang and K. Maruoka, Hypervalent Iodine Mediated Chemoselective Iodination of Alkynes, *J. Org. Chem.*, 2017, **82**, 11865–11871.