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Carboxylation of terminal alkynes with CO_2 catalyzed by imidazolium-bridged bis(phenolato) rare-earth metal complexes

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Contents

Experimental section

General procedures

All manipulations involving air- and moisture-sensitive components were performed in a dry argon or carbon dioxide atmosphere using standard Schlenk techniques unless otherwise stated. All solvents were purchased and dried directly without purification prior to use. THF, toluene, and *n*-hexane were degassed and distilled from sodium benzophenone ketyl before use, while DMSO was dried using CaH_2 and $CHCl_3$ was treated by P_4O_{10}. Various liquid bases were also treated with dehydration and distilled before use. Commercial available terminal alkynes were used directly. The proligand H_2LCl and rare-earth metal precursors $RE[N(SiMe_3)_2]_3$ were prepared according to the published method[1-3]. All NMR spectra were obtained on Bruker Ascend 400 spectrometer (400 MHz for ^1H and 101 MHz for ^{13}C) or Bruker Kalsruhe 300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C). X-ray crystallographic data were obtained using a Bruker D8 QUEST CCD X-ray diffractometer or Rigaku Mercury CCD instrument. Data reduction was accomplished by the Bruker APEX program and refined by OLEX2 software. IR spectra were recorded with a VERTEX 70+HYPERION 2000 instrument. High-resolution mass spectra were obtained by Bruker ESI-TOF or Waters EI-GCT-TOF MS.

Typical procedure for the synthesis of imidazolium-bridged bis(phenolato) rare-earth metal complexes $L_3RE_2Cl_3$

To a Schlenk flask containing a THF solution of the ligand precursor H_2LCl, a THF solution of $RE[N(SiMe_3)_2]_3$ was added and the reaction was stirred for 12 h at room temperature. After removal of the THF under reduced pressure, the $HN(SiMe_3)_2$ was eliminated by washing with hexane three times. Crystals were obtained by recrystallisation in a mixture of THF-toluene or THF-hexane at room temperature.

General procedure for the reactions of terminal alkynes with CO_2 catalyzed by complex 1

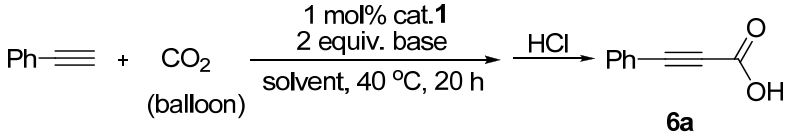
In a 5 mL Schlenk vial equipped with a magnetic stirrer, complex **1** (8.9 mg, 0.005 mmol) and Cs_2CO_3 (325 mg, 1 mmol) were added, followed by the injection of

anhydrous DMSO (1 mL) using a syringe. After stirring for about 10 min, the argon gas in the flask was discharged three times with CO_2 immediately after the addition of terminal alkyne. Thereafter, CO_2 was introduced at ambient pressure using a balloon. The reaction mixture was stirred at 40 °C for 20 h. After cooling to room temperature, the reaction system was quenched by adding 10 mL of water. It was then acidified with the aqueous solution of hydrochloric acid (6 N, 10 mL) and extracted with ethyl ether (3 x 15 mL). The combined organic layer was washed with brine, dried with anhydrous sodium sulfate and filtered, and the crude acid was obtained after the removal of organic solvent under reduced pressure. The pure target product was obtained by flash column chromatography.

General procedure for the one-pot three-component reaction of terminal alkynes, CO_2, and alkyl halide catalyzed by complex 1

In a 5 mL Schlenk vial equipped with a magnetic stirrer, complex **1** (8.9 mg, 0.005 mmol), Cs_2CO_3 (325 mg, 1 mmol) and DMSO (1 mL) were added. After stirring for about 10 min, the terminal alkyne (0.5 mmol) and alkyl bromide (0.6 mmol) were added orderly with syringes, followed by the argon gas in the flask discharging with CO_2 three times. Thereafter, CO_2 was introduced at ambient pressure using a balloon. The reaction mixture was stirred at 50 °C for 30 h. After cooling to room temperature, the reaction system was quenched by adding 10 mL of water. It was then acidified with the dilute aqueous solution of hydrochloric acid (2 N, 10 mL) and extracted with ethyl ether (3 x 15 mL). The combined organic layer was washed with brine, dried with anhydrous sodium sulfate and filtered. The crude esters were obtained by concentration in vacuum. The pure esters were finally obtained by flash column chromatography (petroleum ether as eluent).

Table S1. Screening of solvents and bases in carboxylation of phenylacetylene with CO_2[a]

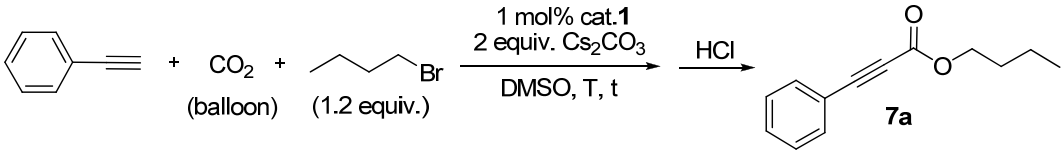


6a

Entry	Base	Solvent	Yield[b]/%
1	Cs_2CO_3	DMF	20
2	Cs_2CO_3	$CHCl_3$	12
3	Cs_2CO_3	THF	14
4	Cs_2CO_3	Tol	-
5	Cs_2CO_3	DMSO	97
6	Na_2CO_3	DMSO	-
7	K_2CO_3	DMSO	-
8	DBU	DMSO	30
9	TEA	DMSO	15

[a] Reaction conditions: phenylacetylene (0.5 mmol), base (1.0 mmol), cat.**1** (0.005 mmol), CO_2 (1 atm), solvent (1 mL), 20 h. [b] Isolated yields.

Table S2. Optimization of three-component reaction of phenylacetylene, *n*-butyl bromide and CO_2[a]



7a

Entry	t/h	T/°C	Yield[b]/%
1	20	40	60
2	20	50	72
3	20	60	75
4	20	80	76
5	24	50	80
6	30	50	96
7	36	50	99

[a]Reaction conditions: phenylacetylene (0.5 mmol), base (1.0 mmol), *n*-butyl bromide (0.6 mmol), cat.**1** (0.005 mmol), CO_2 (1 atm), DMSO (1 mL). [b] Isolated yields.

Solid state structures of complexes 1-4

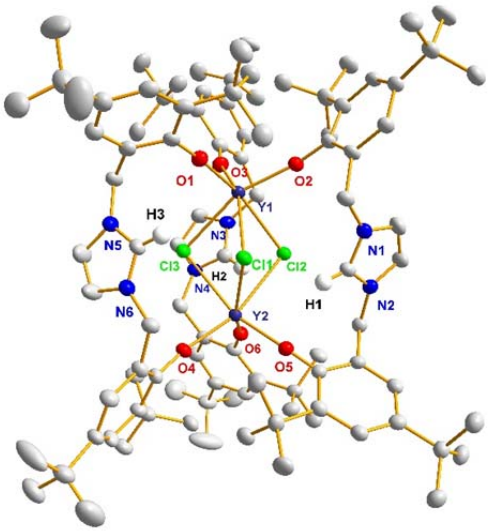


Figure S1. ORTEP view of complex **1·4**THF with ellipsoids at the 30% probability level. Hydrogen atoms, except the H1, H2, H3 atoms are omitted for clarity.

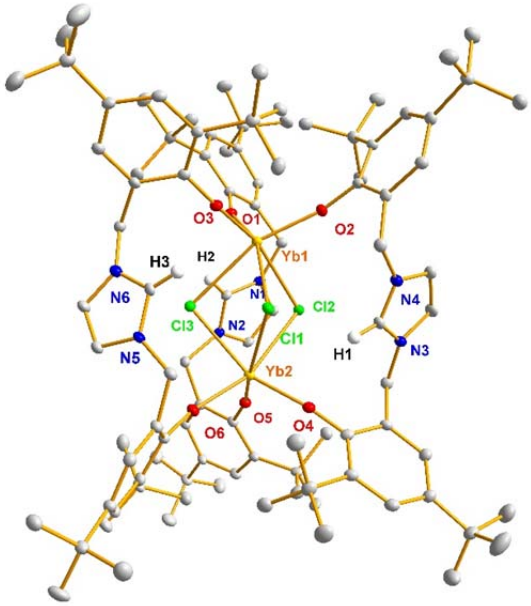


Figure S2. ORTEP view of complex **2·6**THF with ellipsoids at the 30% probability level. Hydrogen atoms, except the H1, H2, H3 atoms are omitted for clarity.

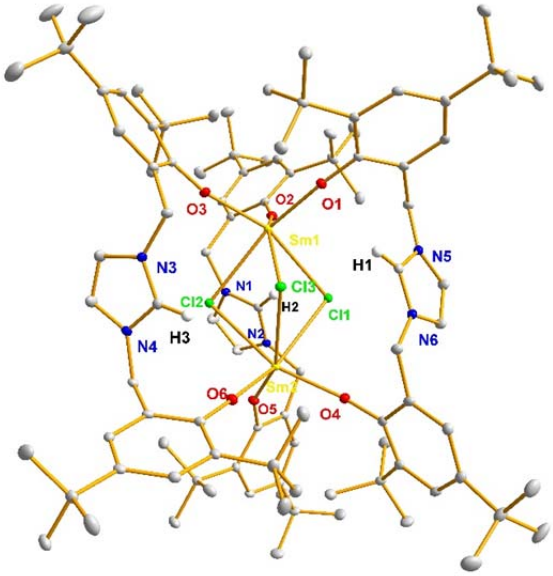


Figure S3. ORTEP view of complex **3·6**THF with ellipsoids at the 30% probability level. Hydrogen atoms, except the H1, H2, H3 atoms are omitted for clarity.

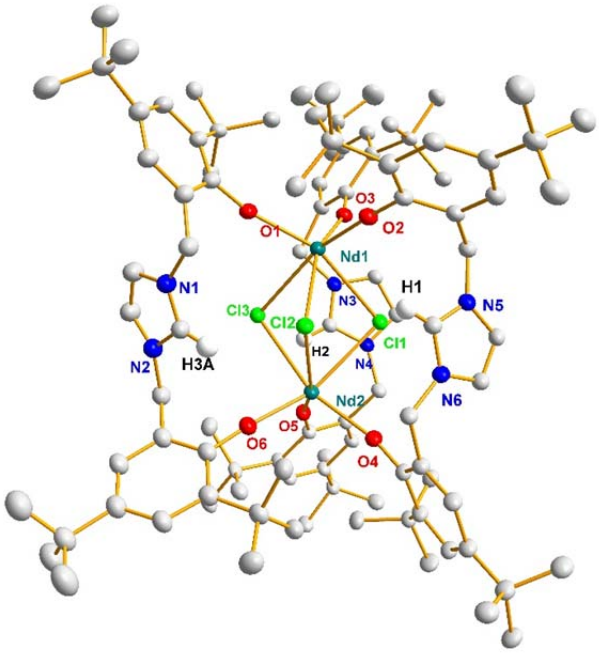


Figure S4. ORTEP view of complex **4·5.5**THF with ellipsoids at the 30% probability level. Hydrogen atoms, except the H1, H2, H3A atoms are omitted for clarity.

Crystallographic data for complexes 1-4

Table S3. Crystallographic data and structure refinement details for complexes 1-4.

	1·4THF	**2**·6THF	**3**·6THF	**4**·5.5THF
Empirical formula	$C_{115}Cl_3H_{173}N_6O_{10}Y_2$	$C_{123}Cl_3H_{189}N_6O_{12}Yb_2$	$C_{123}Cl_3H_{189}N_6O_{12}Sm_2$	$C_{121}Cl_3H_{185}N_6Nd_2O_{11.5}$
Formula weight	2083.75	2396.22	2350.84	2302.57
Temperature/K	119.96	120.05	119.99	120.0
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/n$
a/Å	14.596(9)	14.754(1)	14.662(1)	17.000(2)
b/Å	24.365(1)	16.988(1)	24.481(1)	21.841(2)
c/Å	31.832(3)	25.199(2)	31.882(1)	32.617(4)
α/°	90	98.378(2)	90	90
β/°	96.598(2)	97.840(2)	96.634(1)	96.453(4)
γ/°	90	100.313(2)	90	90
Volume/$Å^3$	11246.3(8)	6061.1(6)	11366.9(9)	12034(2)
Z	4	2	4	4
ρ_{calc} g/cm^3	1.231	1.313	1.374	1.271
μ/mm^{-1}	1.156	1.659	1.157	0.978
F(000)	4456.0	2512.0	4960.0	4864.0
Crystal size/mm^3	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.1	0.2 × 0.15 × 0.15	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.392 to 55.034	3.738 to 55.104	3.942 to 55.006	3.398 to 55.026
Index ranges	-18 ≤ h ≤ 18, -31 ≤ k ≤ 31, -41 ≤ l ≤ 41	-19 ≤ h ≤ 19, -22 ≤ k ≤ 22, -32 ≤ l ≤ 32	-19 ≤ h ≤ 19, -31 ≤ k ≤ 31, -41 ≤ l ≤ 41	-22 ≤ h ≤ 22, -28 ≤ k ≤ 28, -42 ≤ l ≤ 42
Reflections collected	234999	125271	303288	267931
Independent reflections	25827 [R_{int} = 0.1504, R_{sigma} = 0.0931]	27523 [R_{int} = 0.1224, R_{sigma} = 0.1092]	26067 [R_{int} = 0.0988, R_{sigma} = 0.0434]	27573 [R_{int} = 0.0982, R_{sigma} = 0.0490]
Data/restraints/parameters	25827/0/1081	27523/3510/1081	26067/0/1081	27573/2343/1081
Goodness-of-fit on F^2	1.032	1.038	1.037	1.026
Final R indexes [I >= 2σ (I)]	R_1 = 0.0552, wR_2 = 0.1075	R_1 = 0.0578, wR_2 = 0.1433	R_1 = 0.0337, wR_2 = 0.0838	R_1 = 0.0389, wR_2 = 0.0987
Final R indexes [all data]	R_1 = 0.1007, wR_2 = 0.1230	R_1 = 0.0954, wR_2 = 0.1606	R_1 = 0.0516, wR_2 = 0.0944	R_1 = 0.0548, wR_2 = 0.1095
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.64	2.10/-1.65	1.24/-0.94	1.32/-1.30

Table S4 Selected bond lengths (Å) and bond angles (^{o}) for complex 1·4THF.

1·4THF			
Y(1)-O(1)	2.132(2)	Y(2)-Cl(2)	2.806(8)
Y(1)-O(2)	2.132(2)	Y(2)-Cl(3)	2.781(5)
Y(1)-O(3)	2.139(2)	Cl(3)-Y(1)-Cl(2)	76.85(2)
Y(1)-Cl(1)	2.876(1)	O(2)-Y(1)-Cl(2)	82.90(6)
Y(1)-Cl(2)	2.795(2)	O(2)-Y(1)-O(1)	102.08(8)
Y(1)-Cl(3)	2.785(2)	O(1)-Y(1)-Cl(3)	96.28(6)
Y(2)-O(4)	2.111(2)	O(3)-Y(1)-Cl(1)	156.85(6)
Y(2)-O(5)	2.142(5)	Y(1)-Cl(1)-Y(2)	89.23(2)
Y(2)-O(6)	2.161(6)	Y(1)-Cl(2)-Y(2)	90.98(2)
Y(2)-Cl(1)	2.811(6)	Y(1)-Cl(3)-Y(2)	91.72(2)

Table S5 Selected bond lengths (Å) and bond angles (^{o}) for complex 2·6THF.

2·6THF			
Yb(1)-O(1)	2.125(4)	Yb(2)-Cl(2)	2.752(1)
Yb(1)-O(2)	2.097(4)	Yb(2)-Cl(3)	2.730(2)
Yb(1)-O(3)	2.110(4)	Cl(2)-Yb(1)-Cl(3)	75.06(4)
Yb(1)-Cl(1)	2.760(2)	O(2)-Yb(1)-Cl(1)	98.60(12)
Yb(1)-Cl(2)	2.738(1)	O(2)-Yb(1)-O(1)	101.90(16)
Yb(1)-Cl(3)	2.796(2)	O(1)-Yb(1)-Cl(3)	83.94(12)
Yb(2)-O(4)	2.093(4)	O(3)-Yb(1)-Cl(2)	157.42(12)
Yb(2)-O(5)	2.103(4)	Yb(1)-Cl(1)-Yb(2)	89.71(4)
Yb(2)-O(6)	2.109(4)	Yb(1)-Cl(2)-Yb(2)	91.53(4)
Yb(2)-Cl(1)	2.816(1)	Yb(1)-Cl(3)-Yb(2)	90.76(4)

Table S6 Selected bond lengths (Å) and bond angles (^{o}) for complex 3·6THF.

3·6THF			
Sm(1)-O(1)	2.205(1)	Sm(2)-Cl(2)	2.846(1)
Sm(1)-O(2)	2.216(1)	Sm(2)-Cl(3)	2.929(3)
Sm(1)-O(3)	2.170(1)	Cl(2)-Sm(1)-Cl(3)	75.39 (3)
Sm(1)-Cl(1)	2.859(1)	O(2)-Sm(1)-Cl(2)	92.80(5)
Sm(1)-Cl(2)	2.841(1)	O(1)-Sm(1)-O(2)	106.83(7)
Sm(1)-Cl(3)	2.872(1)	O(1)-Sm(1)-Cl(3)	82.82(5)
Sm(2)-O(4)	2.191(1)	O(3)-Sm(1)-Cl(1)	161.38(5)
Sm(2)-O(5)	2.199(1)	Sm(1)-Cl(1)-Sm(2)	90.19(1)
Sm(2)-O(6)	2.191(1)	Sm(1)-Cl(2)-Sm(2)	90.77 (2)
Sm(2)-Cl(1)	2.856 (4)	Sm(1)-Cl(3)-Sm(2)	88.50(1)

Table S7 Selected bond lengths (Å) and bond angles (^{o}) for complex 4·5.5THF.

4·5.5THF			
Nd(1)-O(1)	2.221(2)	Nd(2)-Cl(2)	2.915(2)
Nd(1)-O(2)	2.225(2)	Nd(2)-Cl(3)	2.877(1)
Nd(1)-O(3)	2.226(2)	Cl(2)-Nd(1)-Cl(3)	75.90(2)
Nd(1)-Cl(1)	2.908(0)	O(2)-Nd(1)-Cl(2)	85.98(6)
Nd(1)-Cl(2)	2.870(2)	O(1)-Nd(1)-O(2)	100.45(8)
Nd(1)-Cl(3)	2.889(6)	O(1)-Nd(1)-Cl(3)	95.01(6)
Nd(2)-O(4)	2.232(2)	O(3)-Nd(1)-Cl(1)	160.83(6)
Nd(2)-O(5)	2.227(2)	Nd(1)-Cl(1)-Nd(2)	89.33(2)
Nd(2)-O(6)	2.235(2)	Nd(1)-Cl(2)-Nd(2)	90.15(2)
Nd(2)-Cl(1)	2.919 (6)	Nd(1)-Cl(3)-Nd(2)	90.53(2)

Characterization data of ligand and complexes 1-5

H_2LCl: White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 1H), 8.80 (s, 2H), 7.69 (d, *J* = 1.6 Hz, 2H), 7.23 (d, *J* = 2.4 Hz, 2H), 7.08 (d, *J* = 2.4 Hz, 2H), 5.50 (s, 4H), 1.34 (s, 18H), 1.21 (s, 18H) ppm.

$L_3Y_2Cl_3$ (1): Colorless crystals. Yield: 1.58 g (88%). Mp. 342.7–344.3 °C. Anal. Calcd for $C_{99}H_{141}N_6O_6Cl_3Y_2$ (1792.81): C 66.23, H 7.92, N 4.68; Found: C 66.41, H 8.36, N 4.57. ^{1}H NMR (400 MHz, Tol-d_8): δ 9.53 (s, 3H), 7.33 (s, 6H), 6.81 (s, 6H), 6.24 (d, *J* = 13.0 Hz, 6H), 5.70 (s, 6H), 3.61 (d, *J* = 13.0 Hz, 6H), 1.28 (s, 54H), 1.22 (s, 54H) ppm. ^{13}C{^{1}H} NMR (101 MHz, Tol-d_8) δ 161.73 (d, *J* = 5.1 Hz), 139.1, 137.9, 136.7, 125.0, 124.8, 122.8, 118.2, 52.9, 35.2, 33.8, 31.7, 30.2 ppm. IR (cm^{-1}) ν 2951.3, 1467.5, 1438.3, 1359.4, 1290.9, 1274.1, 1128.4, 834.0, 794.6, 745.4, 643.3.

$L_3Yb_2Cl_3$ (2): Yellow crystals. Yield: 1.67 g (85%). Mp. 345.5–346.9 °C. Anal. Calcd for $C_{107}H_{157}N_6O_8Cl_3Yb_2$ (2034.93): C 60.77, H 7.38, N 4.13; Found: C 60.54, H 7.88, N 3.85. IR (cm^{-1}) ν 2951.0, 1465.2, 1438.5, 1359.5, 1292.6, 1275.1, 1132.5, 834.2, 792.9, 745.6, 643.3.

$L_3Sm_2Cl_3$ (3): Yellow crystals. Yield: 1.34 g (70%). Mp. 343.5–345.1 °C. Anal. Calcd for $C_{107}H_{157}N_6O_8Cl_3Sm_2$ (2062.95): C 62.31, H 7.67, N 4.07; Found: C 62.53, H 8.16, N 4.01. IR (cm^{-1}) ν 2951.7, 1464.2, 1438.4, 1359.7, 1292.9, 1275.4, 1131.3, 832.4, 792.1, 743.9, 643.7.

$L_3Nd_2Cl_3$ (4): Blue crystals. Yield: 1.23 g (65%). Mp. 347.5–349.2 °C. Anal. Calcd for $C_{103}H_{149}N_6O_7Cl_3Nd_2$ (1970.87): C 62.54, H 7.59, N 4.25; Found: C 62.22, H 7.97, N 4.20. IR (cm^{-1}) ν 2951.0, 1464.8, 1438.0, 1359.7, 1330.8, 1274.8, 1128.1, 831.2, 792.4, 743.0, 642.4.

$L_3La_2Cl_3$ (5): Colorless crystals. Yield: 1.04 g (55%). Mp. 346.3–347.8 °C. Anal. Calcd for $C_{106}H_{149}N_6O_6Cl_3La_2$ (1984.87): C 64.06, H 7.56, N 4.23; Found: C 64.32, H 7.96, N 3.96. ^{1}H NMR (400 MHz, C_6D_6): δ 9.74 (s, 3H), 7.56 (d, *J* = 2.6 Hz, 6H), 6.97 (d, *J* = 2.5 Hz, 6H), 6.33 (d, *J* = 13.2 Hz, 6H), 5.78 (d, *J* = 1.5 Hz, 6H), 3.79 (d, *J* = 13.1 Hz, 6H), 1.58 (s, 54H), 1.37 (s, 54H) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 162.8, 138.3, 137.0, 136.4, 125.3, 124.8, 122.0, 118.6, 52.0, 35.1, 33.8, 31.7, 30.2 ppm. IR (cm^{-1}) ν 2951.9, 1466.5, 1436.4, 1358.1, 1275.6, 1233.7, 830.8, 791.2, 736.0, 643.1.

NMR spectra of the complexes 1 and 5

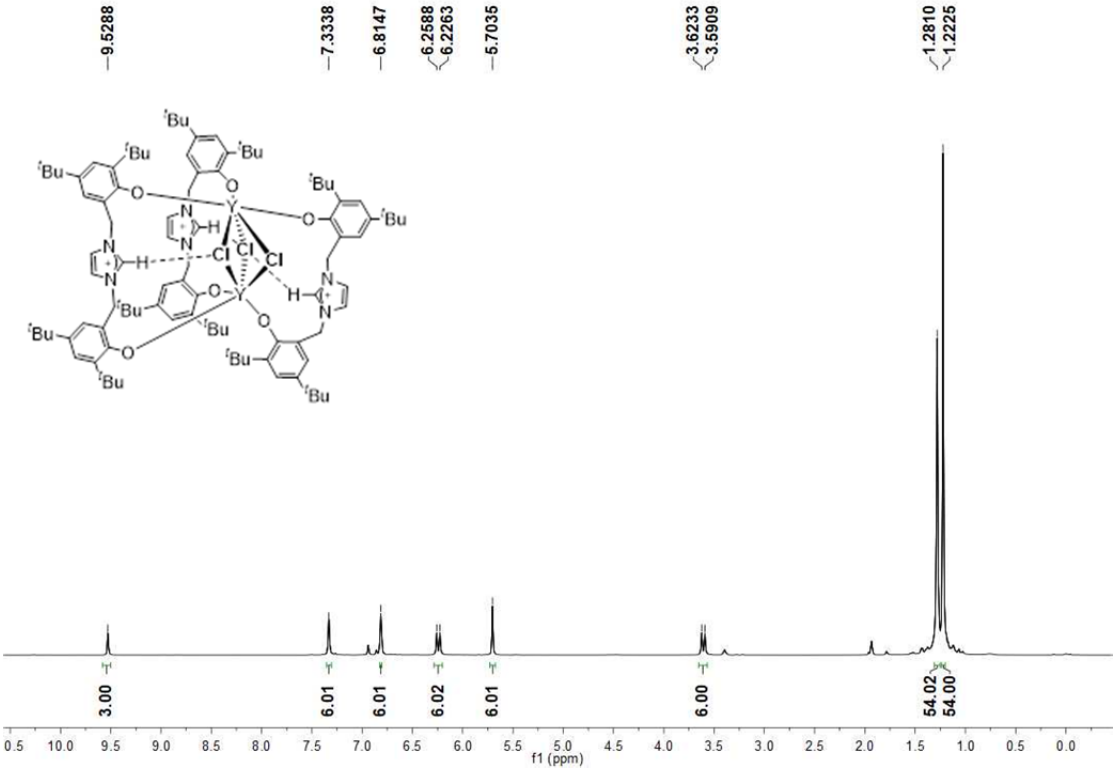


Fig. S5 ^{1}H NMR spectrum of complex 1 in Tol-d_8

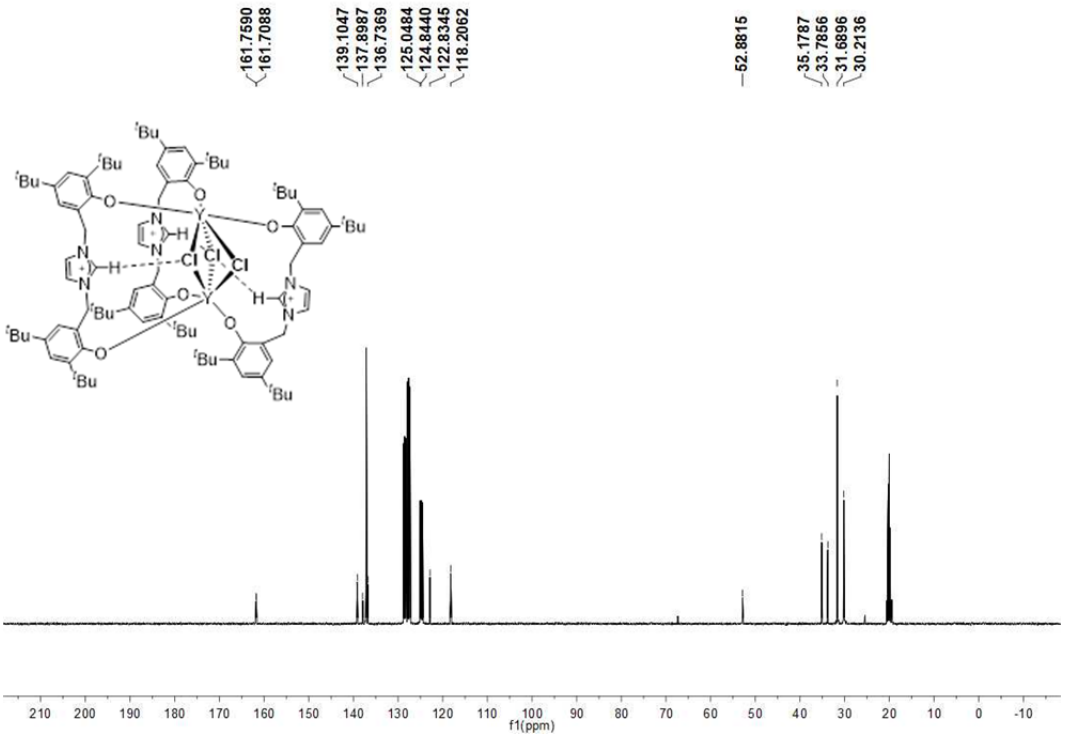


Fig. S6 ^{13}C{^{1}H} NMR spectrum of complex 1 in Tol-d_8

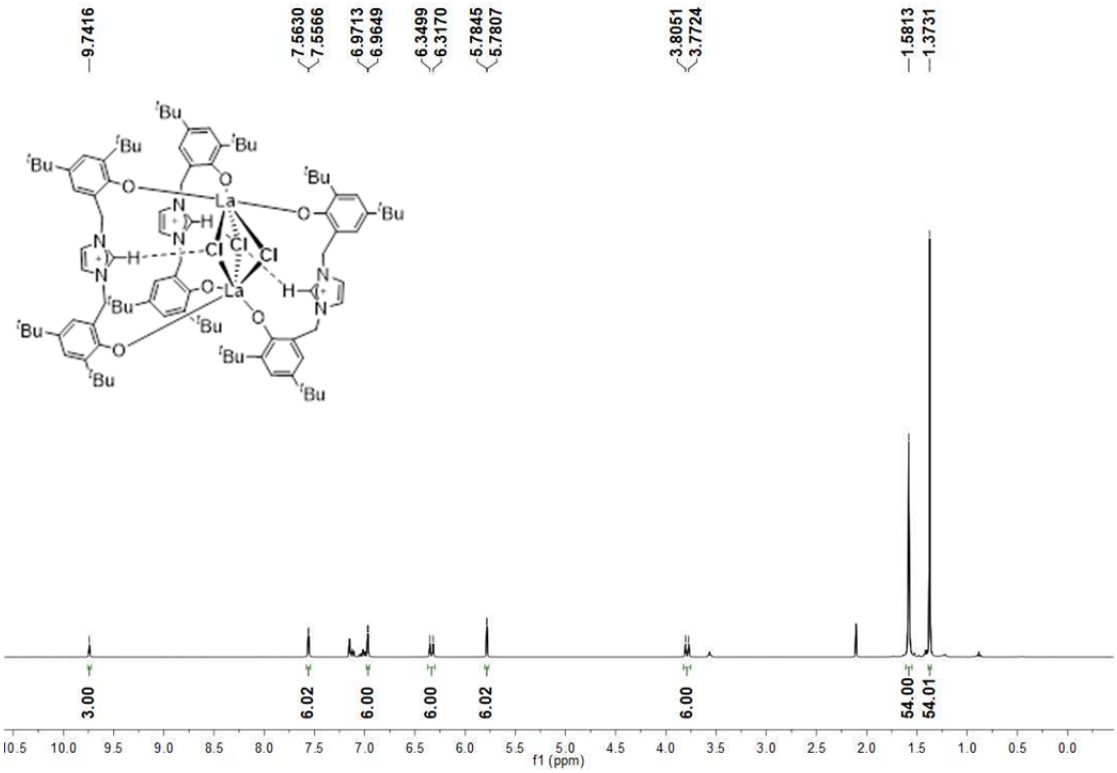


Fig. S7 ^{1}H NMR spectrum of complex 5 in C_6D_6

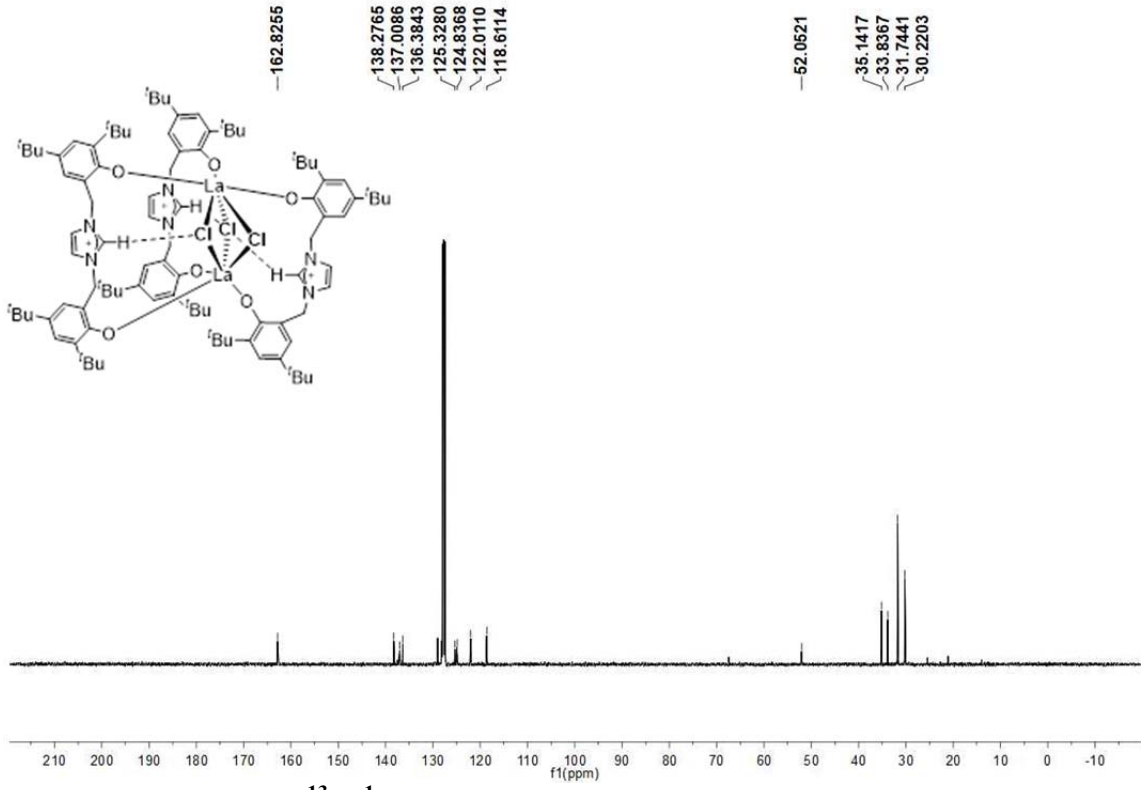


Fig. S8 ^{13}C{^{1}H} NMR spectrum of complex 5 in C_6D_6

Characterization data of the propiolic acids

Phenylpropiolic acid (6a)[4,5]. White solid, 70.8 mg, yield 97%; Mp. 141.5–142.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H, COOH), 7.61-7.59 (m, 2H, ArH); 7.49-7.45 (m, 1H, ArH); 7.40-7.36 (t, J = 7.5 Hz, 2H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.8, 133.3, 131.2, 128.7, 119.1, 89.2, 80.1 ppm. HRMS (ESI, m/z) calcd for $C_9H_7O_2^+$: 147.0440, found: 147.0452.

2-Fluorophenylpropiolic acid (6b)[4,5]**.** White solid, 76.3 mg, yield 93%; Mp. 118.7–120.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.92 (s, 1H, COOH), 7.73-7.69 (t, J = 1.7 Hz, 1H, ArH); 7.65–7.59 (m, 1H, ArH); 7.42-7.37 (t, J = 9.1 Hz, 1H, ArH); 7.34-7.30 (t, J = 7.4 Hz,1H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 163.3 (d, $^{1}J_{C–F}$ = 253.2 Hz), 154.4, 135.0, 133.9 (d, $^{3}J_{C–F}$ = 8.1 Hz), 125.6 (d, $^{4}J_{C–F}$ = 3.0 Hz), 116.5 (d, $^{2}J_{C–F}$ = 20.2 Hz), 108.1 (d, $^{2}J_{C–F}$ = 16.1 Hz), 86.8 (d, $^{3}J_{C–F}$ = 3.0 Hz), 78.1 ppm. ^{19}F NMR (377 MHz, DMSO-d_6): δ −109.0 ppm. HRMS (ESI, m/z) calcd for $C_9H_5O_2FNa^+$:187.0165, found: 187.0167.

4-Fluorophenylpropiolic acid (6c)[4,5]**.** White solid, 80.4 mg, yield 98%; Mp. 151.1–152.3 °C. ^{1}HNMR (400 MHz, DMSO-d_6): δ 13.80 (s, 1H, COOH), 7.73-7.70 (m, 2H, ArH); 7.35-7.31 (m, 2H, ArH) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.7 (d, $^{1}J_{C–F}$ = 251.5 Hz), 154.7, 135.8 (d, $^{3}J_{C–F}$ = 9.1 Hz), 116.9 (d, $^{2}J_{C–F}$ = 22.2 Hz), 115.9 ($^{4}J_{C–F}$ =3.0 Hz), 83.8, 82.1 ppm. ^{19}F NMR (377 MHz, DMSO-d_6): δ −107.0 ppm. HRMS (ESI, m/z) calcd for $C_9H_6O_2F^+$:165.0346, found: 165.0347.

4-Chlorophenylpropiolic acid (6d)[4,5]**.** White solid, 86.4 mg, yield 96%; Mp. 189.5–190.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.91 (s, 1H, COOH), 7.67-7.65 (d, J = 8.6 Hz, 2H, ArH); 7.56-7.54 (d, J = 8.6 Hz, 2H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.6, 136.3, 134.8, 129.7, 118.3, 83.6, 83.0 ppm. HRMS (ESI, m/z) calcd for $C_9H_5O_2ClNa^+$: 202.9870, found: 202.9876.

4-Bromophenylpropiolic acid (6e)[4,5]**.** Light yellow solid, 109.7 mg, yield 98%; Mp. 198.5–200.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.87 (s, 1H, COOH), 7.70-7.68 (d, J = 8.6 Hz, 2H, ArH); 7.59-7.57 (d, J = 8.6 Hz, 2H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.6, 134.9, 132.6, 125.1, 118.7, 83.6, 83.2 ppm. HRMS (ESI, m/z) calcd for $C_9H_5O_2BrNa^+$: 246.9365, found: 246.9365.

3-Bromophenylpropiolic acid (6f)[4,5]**.** White solid, 106.4 mg, yield 95%; Mp. 187.5–188.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.84 (s, 1H, ArH); 7.75-7.73 (d, J = 8.1 Hz, 1H, ArH); 7.64-7.62 (d, J = 7.8 Hz, 1H, ArH); 7.44-7.40 (t, J = 7.9 Hz, 1H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.5, 135.1, 134.3, 132.1, 131.5, 122.3, 121.7, 83.1 82.9 ppm. HRMS (ESI, m/z) calcd for $C_9H_5O_2BrNa^+$: 246.9365, found: 246.9370.

4-Trifluoromethylphenylpropiolic acid (6g)[4,5]**.** White solid, 102.7 mg, yield 96%;

Mp. 142.3–143.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.86-7.81 (m, 4H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.4, 133.8, 130.9 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 126.3 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 125.5, 123.3 (d, $^{1}J_{C\text{-}F}$ = 103.0 Hz), 83.9, 82.7 ppm. ^{19}F NMR (377 MHz, DMSO-d_6): δ -61.7 ppm. HRMS (ESI, m/z) calcd for $C_{10}H_6O_2F_3^+$: 215.0314, found: 215.03116.

3-(3,5-Bis(trifluoromethyl)phenyl)propiolic acid (6h)[4,5]. White solid, 136.7 mg, yield 97%; Mp. 135.2–136.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.35 (s, 2H, ArH); 8.24 (s, 1H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.2, 133.6 (d, $^{3}J_{C\text{–}F}$ = 3.0 Hz), 131.5 (q, $^{2}J_{C\text{–}F}$ = 33.3 Hz), 124.5, 123.1 (q, $^{1}J_{C\text{–}F}$ = 274.7 Hz), 122.4, 84.4, 80.9 ppm. ^{19}F NMR (377 MHz, DMSO-d_6): δ -61.7 ppm. HRMS (ESI, m/z) calcd for $C_{11}H_5O_2F_6^+$:283.0188, found: 283.0191.

4-Nitrophenylpropiolic acid (6i)[4,5]. Yellow solid, 91.7 mg, yield 96%; Mp. 173.5–174.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29-8.27 (d, J = 8.9 Hz, 2H, ArH); 7.92-7.90 (d, J = 8.9 Hz, 2H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.3, 148.7, 134.3, 126.1, 124.4, 85.5, 82.2 ppm. HRMS (ESI, m/z) calcd for $C_9H_5O_4NNa^+$: 214.0110, found: 214.0115.

4-Cyanophenylpropiolic acid(6j)[5]. White solid, 83.7 mg, yield 98%; Mp. 178.6–179.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94-7.92 (d, J = 8.3 Hz, 2H, ArH); 7.82-7.80 (d, J = 8.3 Hz, 2H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.3, 133.6, 133.2, 124.3, 118.5, 113.5, 85.0, 82.6 ppm. HRMS (EI, m/z) calcd for $C_{10}H_5O_2N^+$: 171.0320, found: 171.0326.

4-Formylphenylpropiolic acid (6k)[5]. White solid, 85.3 mg, yield 98%; Mp. 189.5–190.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.97 (s, 1H, COOH), 10.06 (s, 1H, CHO), 7.99-7.97 (d, J = 8.2 Hz, 2H, ArH); 7.85-7.83 (d, J = 8.1 Hz, 2H, ArH) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 193.0, 154.4, 137.4, 133.6, 130.1, 125.1, 84.6, 83.4 ppm. HRMS (EI, m/z) calcd for $C_{10}H_6O_3^+$: 174.0317, found: 174.0313.

4-(Methoxycarbonyl)phenylpropiolic acid (6l)[5]. Light yellow solid, 99.8 mg, yield 98%; Mp. 162.8–163.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.03-8.00 (d, J = 8.3 Hz, 2H, ArH); 7.78-7.76 (d, J = 8.3 Hz, 2H, ArH); 3.89 (s, 3H, OCH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 165.8, 154.4, 133.3, 131.6, 129.9, 124.1, 84.2, 83.3, 52.9 ppm. HRMS (EI, m/z) calcd for $C_{11}H_8O_4^+$: 204.0423, found: 204.0429.

4-Methylphenylpropiolic acid (6m)[4,5]. White solid, 78.4 mg, yield 98%; Mp. 151.5–152.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.51-7.49 (d, J = 8.1 Hz, 2H, ArH); 7.28-7.26 (d, J = 8.0 Hz, 2H, ArH); 2.34 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.9, 141.6, 133.1, 130.1, 116.3, 85.3, 81.9, 21.6 ppm. HRMS (ESI, m/z) calcd for $C_{10}H_9O_2^+$: 161.0597, found: 161.0596.

3-Methylphenylpropiolic acid (6n)[4,5]**.** White solid, 72.1 mg, yield 90%; Mp. 130.7–131.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.44 (s, 1H, ArH); 7.42-7.40 (m, 1H, ArH); 7.36 (s, 1H, ArH); 7.34 (s, 1H, ArH); 2.32 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.8, 139.0, 133.3, 132.1, 130.2, 129.4, 119.3, 85.0, 82.0, 21.1 ppm. HRMS (ESI, m/z) calcd for $C_{10}H_8O_2Na^+$: 183.0416, found: 183.0422.

4-tert-Butylphenylpropiolic acid (6o)[4,5]**.** White solid, 97.1 mg, yield 96%; Mp. 155.5–156.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.65 (s, 1H, COOH), 7.59-7.57 (d, *J* = 8.5 Hz, 2H, ArH); 7.44-7.42 (d, *J* = 8.5 Hz, 2H, ArH); 1.34 (s, 9H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.8, 154.9, 133.2, 125.8, 116.0, 89.6, 79.9, 35.1, 31.0 ppm. HRMS (ESI, m/z) calcd for $C_{13}H_{14}O_2Na^+$: 225.0886, found: 225.0887.

3-(Biphenyl-4-yl)propiolic acid (6p)[4,5]**.** Brown solid, 106.6 mg, yield 96%; Mp. 162.4–163.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.76 (s, 1H, COOH), 7.79-7.77 (d, *J* = 8.4 Hz, 2H, ArH); 7.73-7.71 (m, 4H, ArH); 7.52-7.48 (t, *J* = 7.5 Hz, 2H, ArH); 7.44-7.40 (t, *J* = 7.3 Hz, 1H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.8, 142.8, 139.2, 133.7, 129.6, 128.8, 127.6, 127.3, 118.3, 84.8, 82.9 ppm. HRMS (ESI, m/z) calcd For $C_{15}H_{10}O_2Na^+$: 245.0573, found: 245.0569.

4-Methoxylphenylpropiolic acid (6q)[4,5]**.** Brown solid, 57.2 mg, yield 65%; Mp. 153.6–154.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.59-7.57 (d, *J* = 8.8 Hz, 2H, ArH); 7.03-7.01 (d, *J* = 8.9 Hz, 2H, ArH); δ 3.81 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 161.7, 155.0, 135.1, 115.2, 111.0, 85.8, 81.5, 55.9 ppm. HRMS (ESI, m/z) calcd for $C_{10}H_9O_3^+$: 177.0546, found: 177.0559.

3-(Naphthalen-1-yl)propiolic acid (6r)[5]**.** White solid, 97.1 mg, yield 99%; Mp. 135.8–136.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.88 (s, 1H, COOH), 8.24-8.22 (d, *J* = 7.2 Hz, 1H, ArH); 8.13-8.11 (d, *J* = 7.2 Hz, 1H, ArH); 8.04-8.03 (d, *J* = 7.0 Hz, 1H, ArH); 7.93-7.92 (d, *J* = 5.6 Hz, 1H, ArH); 7.72-7.58 (m, 3H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.8, 133.3, 133.2, 133.1, 131.9, 129.2, 128.5, 127.6, 126.1, 125.3, 116.8, 86.9, 82.9 ppm. HRMS (EI, m/z) calcd for $C_{13}H_8O_2$: 196.0524, found: 196.0521.

3-(Phenanthren-9-yl)propiolic acid (6s)[5]**.** White solid, 121.8 mg, yield 99%; Mp. 183.8–184.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.01 (s, 1H, COOH), 8.93-8.91 (m, 1H, ArH); 8.88-8.86 (d, *J* = 8.1 Hz, 1H, ArH); 8.43 (s, 1H, ArH); 8.32-8.31 (d, *J* = 4.9 Hz, 1H, ArH); 8.10-8.08 (d, *J* = 7.6 Hz, 1H, ArH); 7.82 (s, 1H, ArH); 7.74-7.71 (t, *J* = 7.3 Hz, 1H, ArH) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 154.8, 135.6, 131.0, 130.7, 130.3, 130.0, 129.7, 128.4, 128.1, 126.1, 124.1, 123.5, 115.7, 86.5, 83.0 ppm. HRMS (ESI, m/z) calcd for $C_{17}H_9O_2$ $[M–H]^-$: 245.0608, found: 245.0612.

3-(Pyren-1-yl)propiolic acid (6t)[4,5]**.** Yellow solid, 133.7 mg, yield 99%; Mp. 172.6–173.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 14.01 (s, 1H, COOH), 8.47–8.39 (m, 4H,

ArH); 8.33–8.31 (m, 3H, ArH); 8.24 (d, J = 8.9 Hz, 1H, ArH); 8.18-8.14 (t, J = 7.6 Hz, 1H, ArH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 154.9, 133.1, 133.0, 131.3, 131.1, 130.7, 130.2, 130.0, 127.6, 127.5, 127.2, 127.1, 125.4, 124.5, 123.8, 123.5, 113.2, 87.6, 84.0 ppm. HRMS (ESI, m/z) calcd for $C_{19}H_{11}O_2^+$: 271.0753, found: 271.0768.

3-(Thiophen-2-yl)propiolic acid (6u)[4,5]**.** Brown solid, 75.2 mg, yield 99%; Mp. 153.7–154.9 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 13.85 (s, 1H, COOH), 7.88-7.87 (d, J = 5.1 Hz, 1H, ArH); 7.68-7.66 (dd, J_1 = 3.7 Hz, J_2 = 1.0 Hz, 1H, ArH); 7.21-7.18 (dd, J_1 = 5.1 Hz, J_2 = 3.7Hz, 1H, ArH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 154.6, 137.5, 133.2, 128.8, 118.7, 86.3, 78.9 ppm. HRMS (ESI, m/z) calcd for $C_7H_5O_2S^+$: 153.0005, found: 153.0010.

3,3′-(1,3-Phenylene)dipropiolic acid (6v)[4,5]**.** White solid, 101.7 mg, yield 95%; Mp. 298.7 °C (dec.). ^1H NMR (400 MHz, DMSO-d_6): δ 13.91 (s, 1H, COOH), 7.86 (s, 1H, ArH); 7.80-7.77 (dd, J = 7.8, 1.4 Hz, 2H, ArH); 7.60-7.56 (t, J = 7.8 Hz, 1H, ArH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 154.5, 136.3, 135.1, 130.3, 120.4, 83.0, 82.9 ppm. HRMS (ESI, m/z) calcd for $C_{12}H_6O_4Na^+$: 237.0158, found: 237.0150.

3,3′,3′′-(1,3,5-Phenylene)tripropiolic acid (6w)[5]**.** Light yellow solid, 121.3 mg, yield 86%; 301.3 °C (dec.). ^1H NMR (300 MHz, DMSO-d_6): δ 7.99 (s, 3H, ArH) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 154.4, 137.8, 121.6, 83.9, 81.4 ppm.

Characterization data of the esters of propiolic acids

Butyl 3-phenylpropiolate (7a)[7]**.** Light yellow liquid, 97.1 mg, yield 96%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 2H, ArH), 7.44-7.41 (t, J = 7.5 Hz, 1H, ArH), 7.37-7.33 (t, J = 7.4 Hz, 2H, ArH), 4.24-4.21 (t, J = 6.7 Hz, 2H, OCH_2), 1.72-1.65 (dd, J = 14.5, 7.4 Hz, 2H, CH_2), 1.47-1.38 (dd, J = 15.1, 7.5 Hz, 2H, CH_2), 0.97-0.93 (t, J = 7.4 Hz, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 154.1, 132.9, 130.6, 128.5, 119.6, 85.9, 80.8, 65.8, 30.5, 19.0, 13.6 ppm. HRMS (ESI, m/z) calcd for $C_{13}H_{14}O_2Na^+$: 225.0886, found: 225.0889.

Benzyl 3-phenylpropiolate (7b)[6]**.** Light yellow liquid, 94.4 mg, yield 80%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H, ArH), 7.47-7.36 (m, 8H, ArH), 5.29 (s, 2H, OCH_2) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 153.9, 135.0, 133.1, 130.8, 128.7, 128.7, 128.6, 119.6, 86.8, 80.6, 67.7 ppm. HRMS (ESI, m/z) calcd for $C_{16}H_{12}O_2Na^+$: 259.0730, found: 259.0725.

Cinnamyl 3-phenylpropiolate (7c)[6]**.** Light yellow liquid, 117.9 mg, yield 90%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 2H, ArH), 7.43-7.23 (m, 8H, ArH), 6.72-6.68 (d, J = 15.9 Hz, 1H, CH), 6.34-6.27 (dt, J = 15.9, 6.6 Hz, 1H, CH), 4.88-4.86 (dd, J = 6.6, 1.2 Hz, 2H, OCH_2) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ

153.9, 136.0, 135.4, 133.1, 130.8, 128.7, 128.6, 128.3, 126.8, 122.1, 119.6, 86.7, 80.6, 66.6 ppm. HRMS (ESI, m/z) calcd for $C_{18}H_{14}O_2Na^+$: 285.0886, found: 285.0893.

Butyl 3-(4-(trifluoromethyl)phenyl)propiolate (7d)[7]. Light yellow liquid, 121.5 mg, yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (d, *J* = 8.3 Hz, 2H, ArH), 7.61-7.59 (d, *J* = 8.4 Hz, 2H, ArH), 4.24-4.21 (t, *J* = 6.7 Hz, 2H, OCH_2), 1.71-1.63 (m, 2H, CH_2), 1.45-1.36 (dt, *J* = 14.7, 7.5 Hz, 2H, CH_2), 0.94-0.91 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.6, 133.1, 132.0 (q, $^2J_{C-F}$ = 33.3 Hz), 125.4 (q, $^3J_{C-F}$ = 4.0 Hz), 123.6 (q, $^1J_{C-F}$ = 273.7 Hz), 123.5, 83.6, 82.3, 66.1, 30.4, 19.0, 13.5 ppm. ^{19}F NMR (377 MHz, $CDCl_3$): δ -63.3 ppm. HRMS (ESI, m/z) calcd for $C_{14}H_{13}O_2F_3Na^+$: 293.0760, found: 293.0745.

Butyl 3-(*p*-tolyl)propiolate (7e)[7]. Light yellow liquid, 91.8 mg, yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (d, *J* = 8.2 Hz, 2H, ArH), 7.17-7.15 (d, *J* = 7.9 Hz, 2H, ArH), 4.24-4.20 (t, *J* = 6.7 Hz, 2H, OCH_2), 2.36 (s, 3H, $ArCH_3$), 1.71-1.65 (m, 2H, CH_2), 1.47-1.38 (dt, *J* = 14.7, 7.4 Hz, 2H, CH_2), 0.97-0.93 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.3, 141.2, 133.0, 129.3, 116.5, 86.6, 80.4, 65.8, 30.5, 21.7, 19.1, 13.7 ppm. HRMS (ESI, m/z) calcd for $C_{14}H_{16}O_2Na^+$: 239.1045, found: 239.1043.

Butyl 3-(thiophen-2-yl)propiolate (7f)[7]. Brown liquid, 72.8 mg, yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.43 (dd, *J* = 8.5, 4.4 Hz, 2H, ArH), 7.04-7.02 (dd, *J* = 5.0, 3.8 Hz, 1H, ArH), 4.24-4.20 (t, *J* = 6.7 Hz, 2H, OCH_2), 1.71-1.64 (m, *J* = 14.4, 7.4 Hz, 2H, CH_2), 1.46-1.37 (dt, *J* = 14.9, 7.4 Hz, 2H, CH_2), 0.96-0.92 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 154.1, 136.5, 131.1, 127.5, 119.4, 84.9, 80.0, 65.9, 30.5, 19.1, 13.7 ppm. HRMS (ESI,m/z) calcd for $C_{11}H_{12}O_2SNa^+$: 231.0450, found: 231.0442.

NMR spectra of the propiolic acids

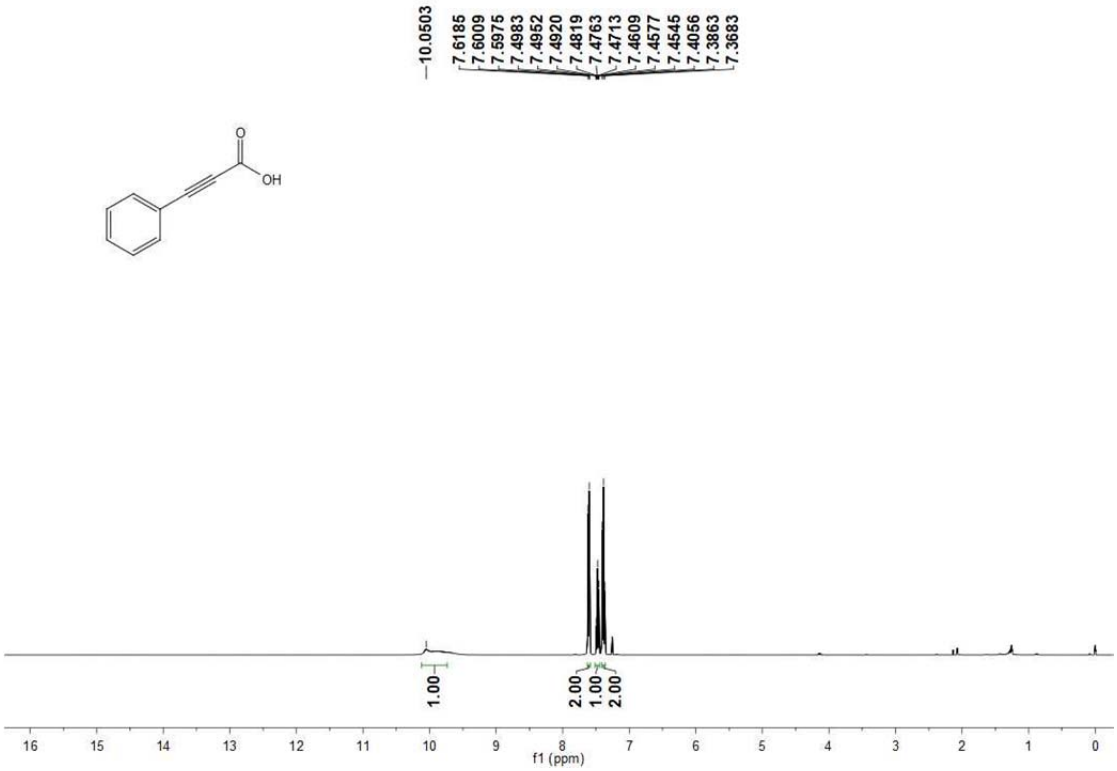


Fig. S9 ^{1}H NMR spectrum of **6a** in $CDCl_3$

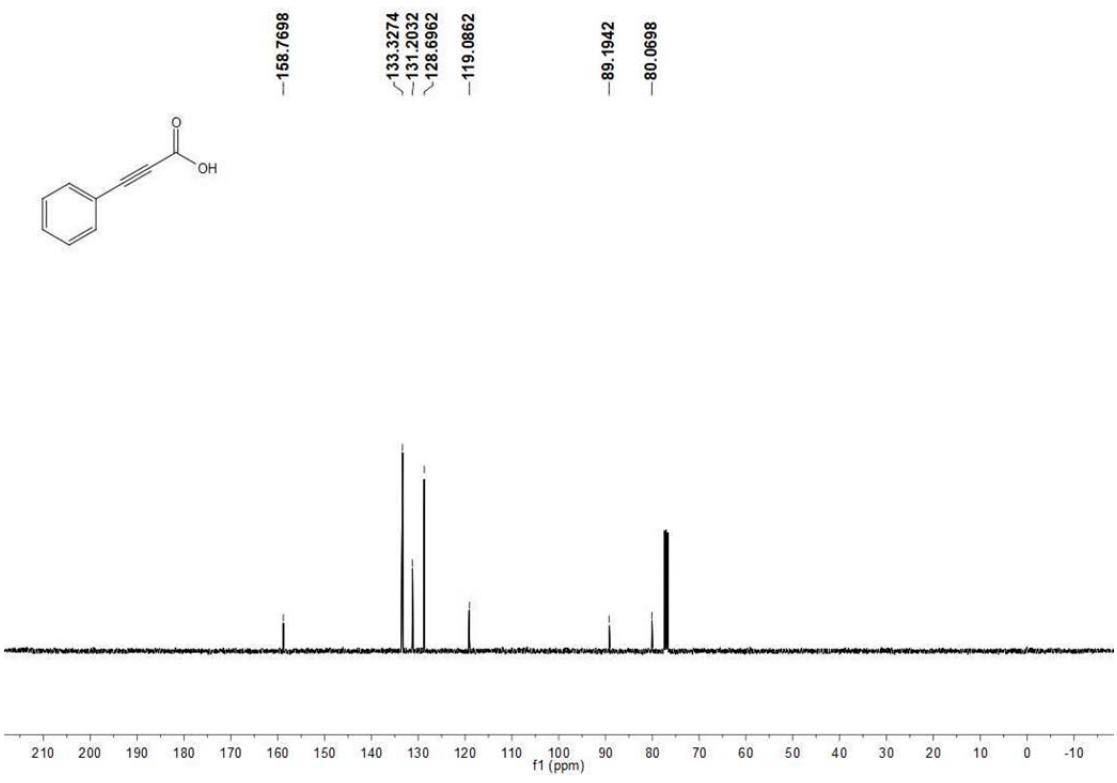


Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$

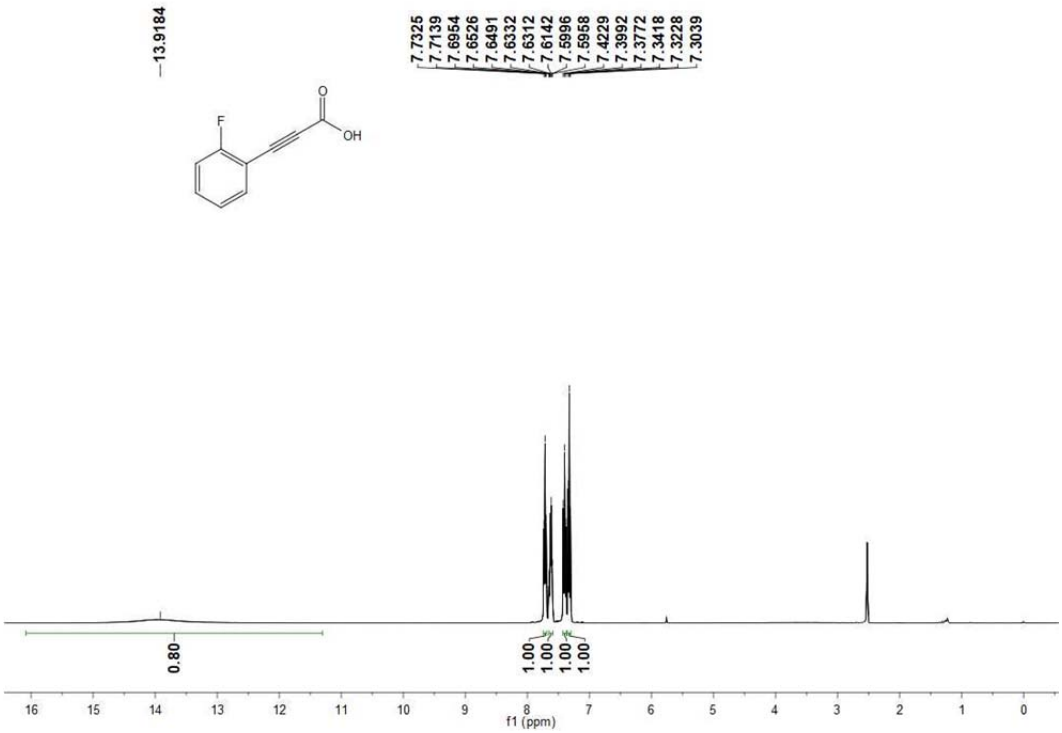


Fig. S11 ^{1}H NMR spectrum of **6b** in DMSO-d_6

Fig. S12 ^{19}F NMR spectrum of **6b** in DMSO-d_6

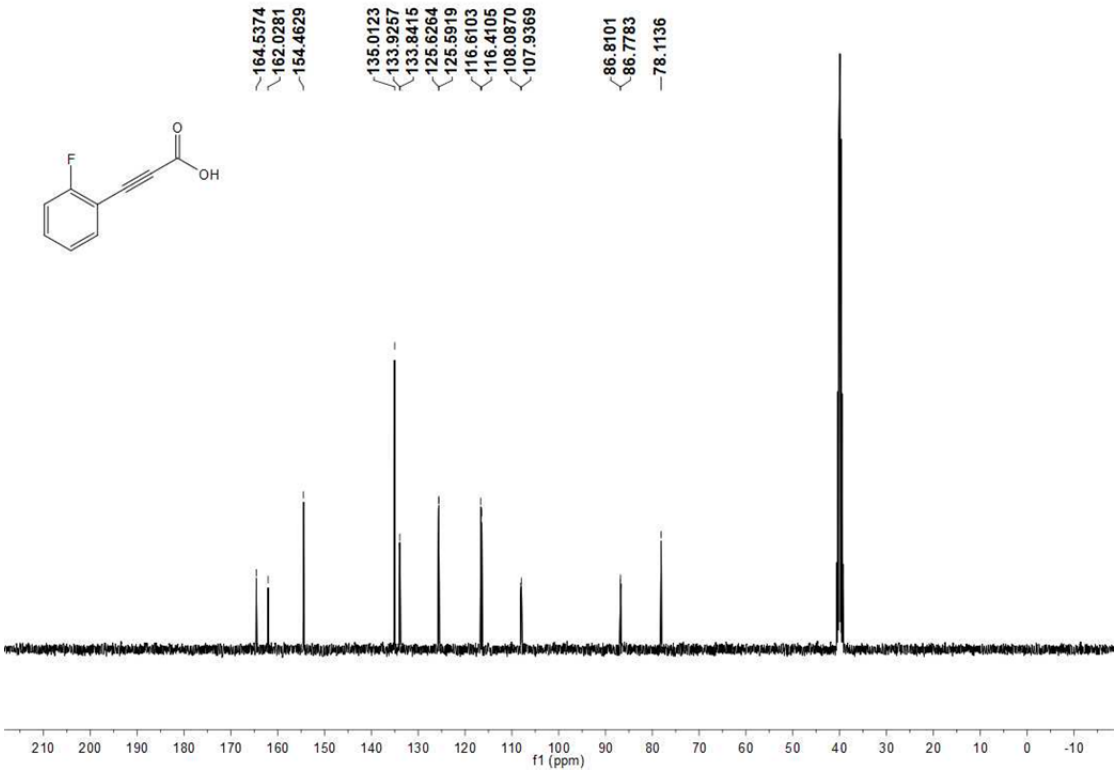


Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of **6b** in DMSO-d_6

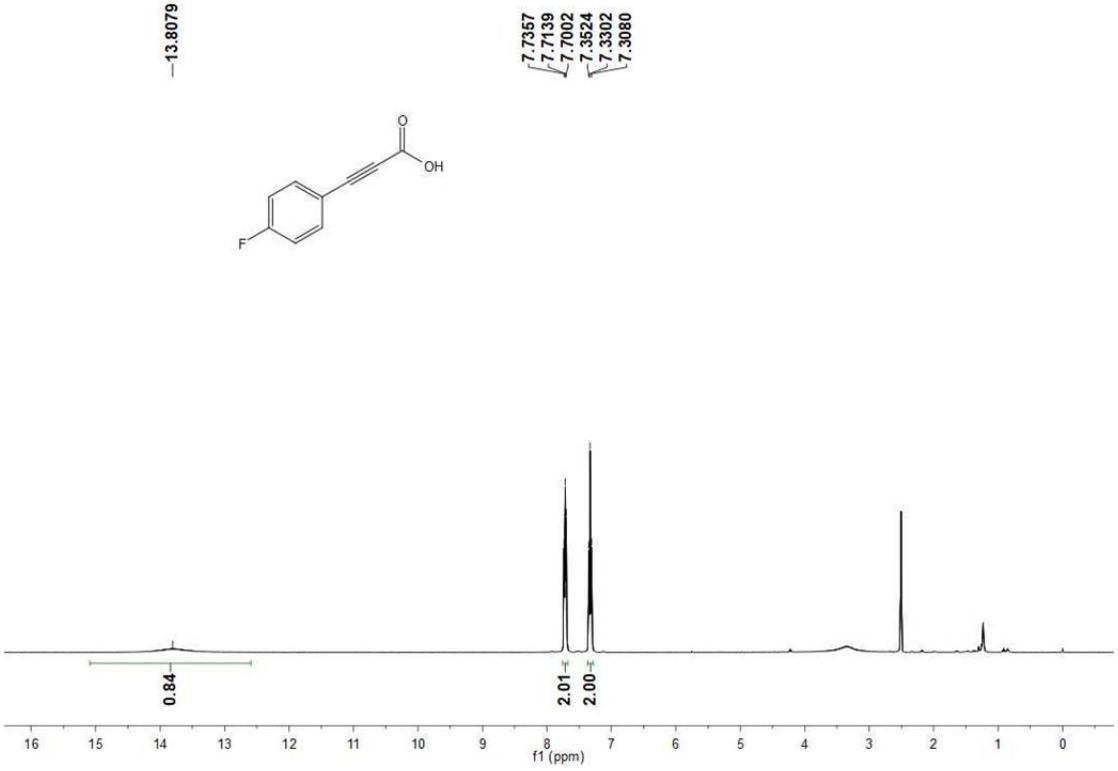


Fig. S14 ^{1}H NMR spectrum of **6c** in DMSO-d_6

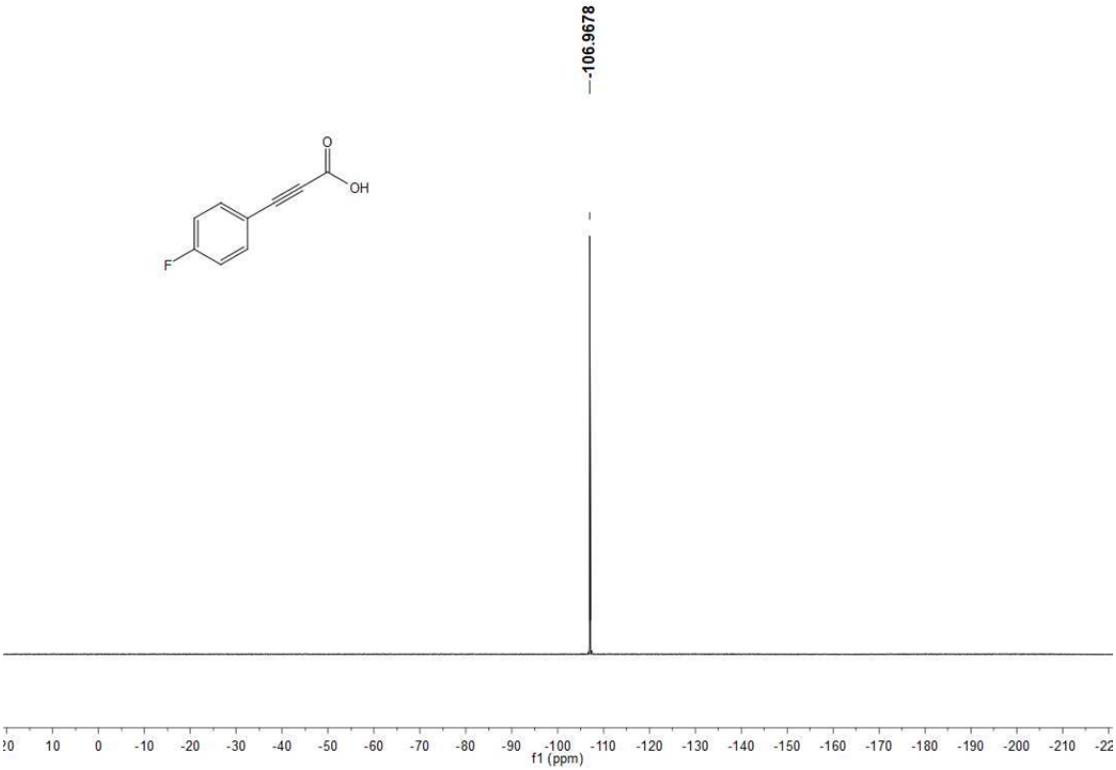


Fig. S15 ^{19}F NMR spectrum of **6c** in DMSO-d_6

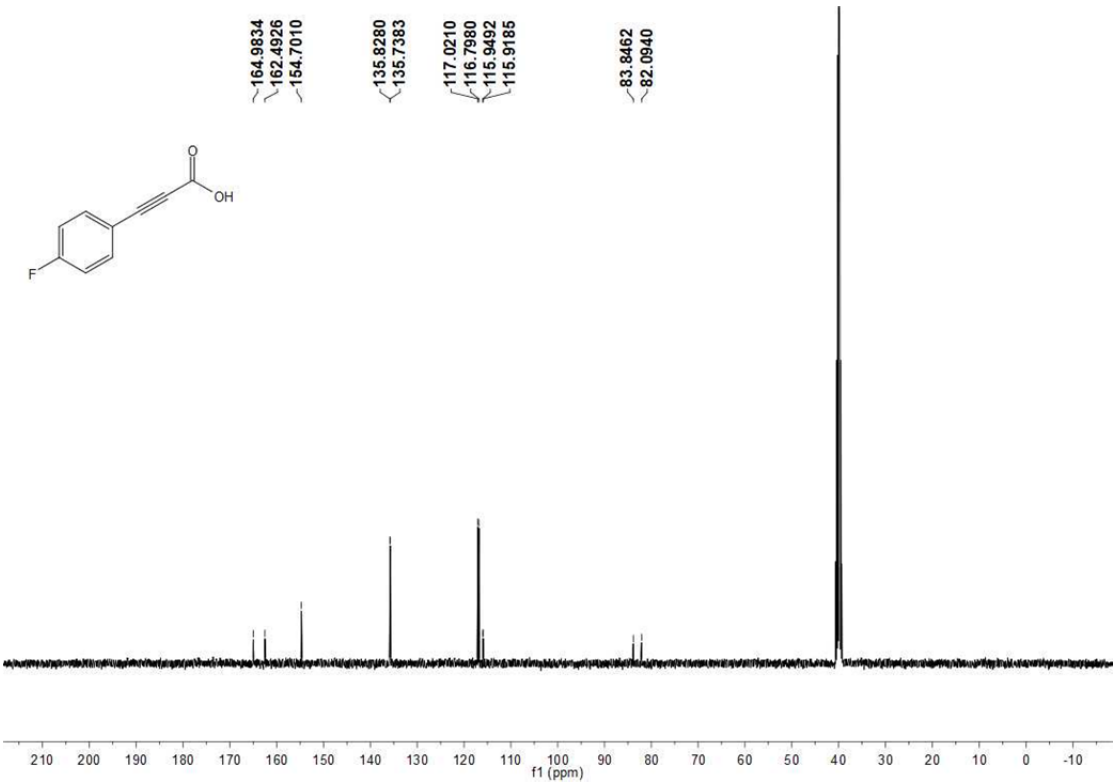


Fig. S16 ^{13}C{^{1}H} NMR spectrum of **6c** in DMSO-d_6

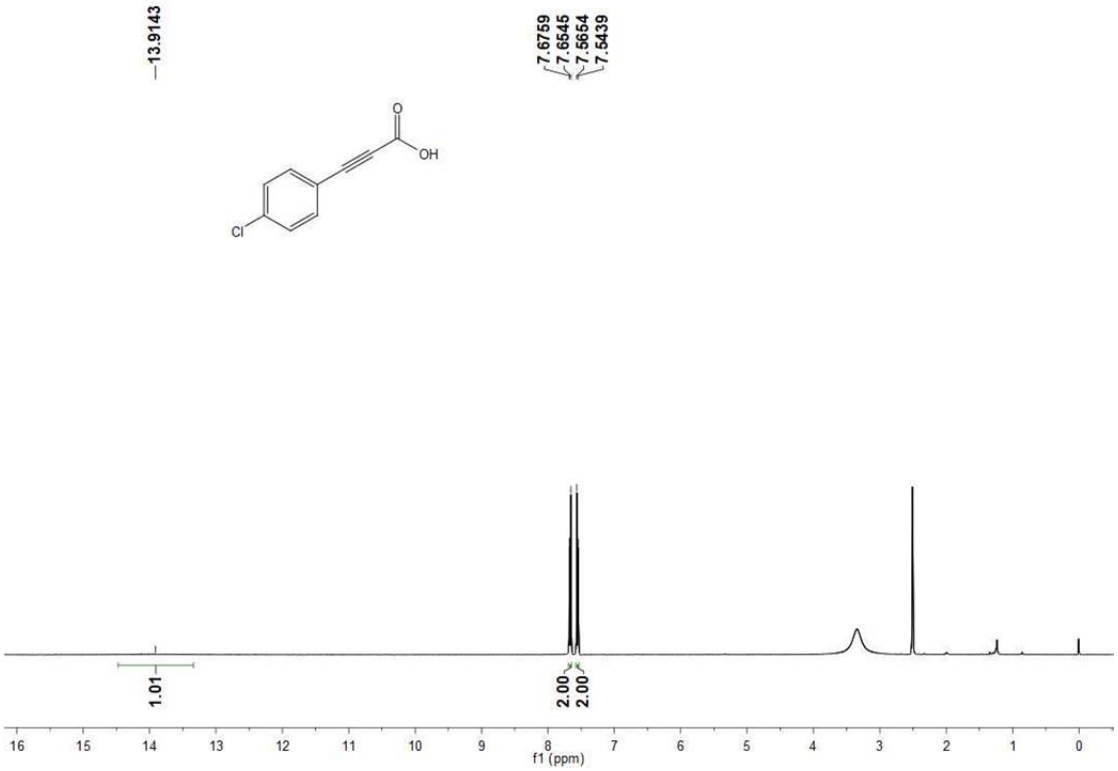


Fig. S17 ^{1}H NMR spectrum of **6d** in DMSO-d_6

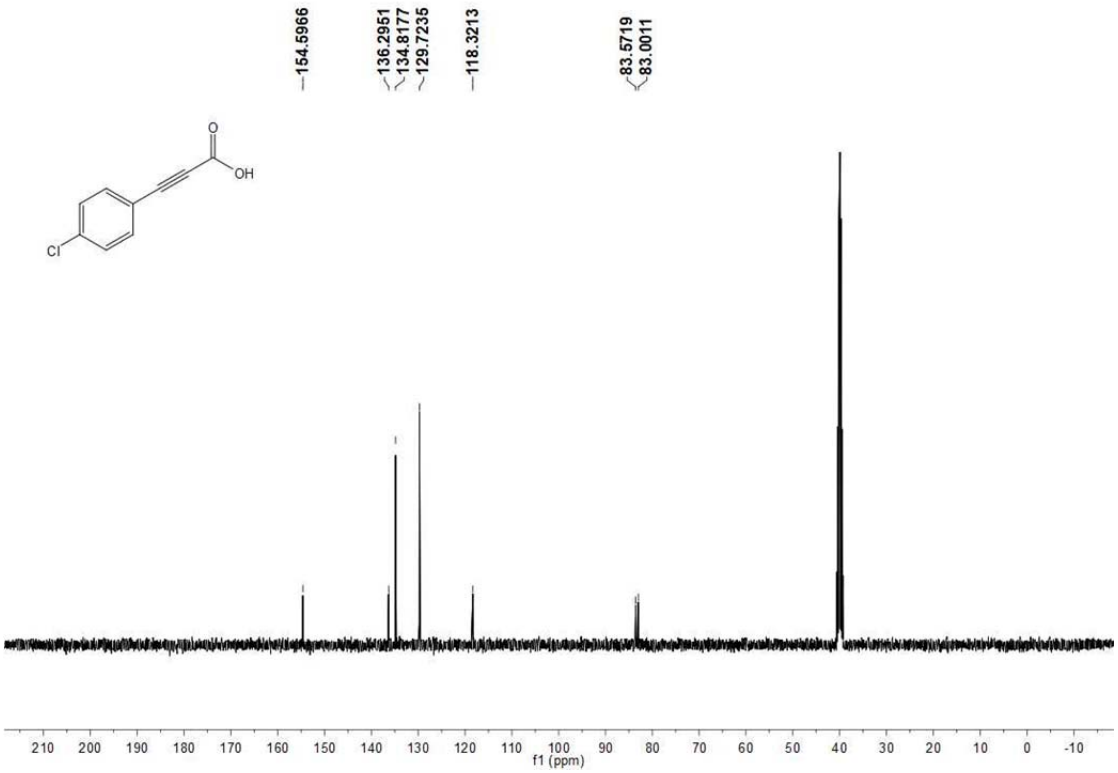


Fig. S18 ^{13}C{^{1}H} NMR spectrum of **6d** in DMSO-d_6

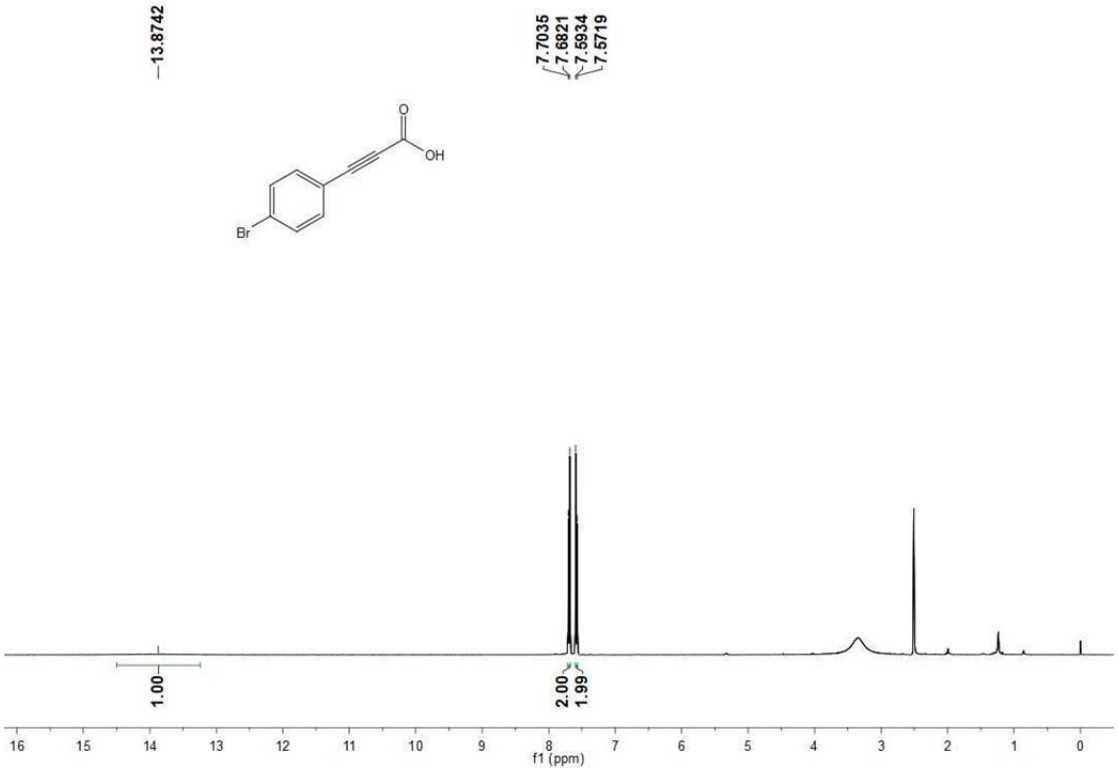


Fig. S19 ^{1}H NMR spectrum of **6e** in DMSO-d_6

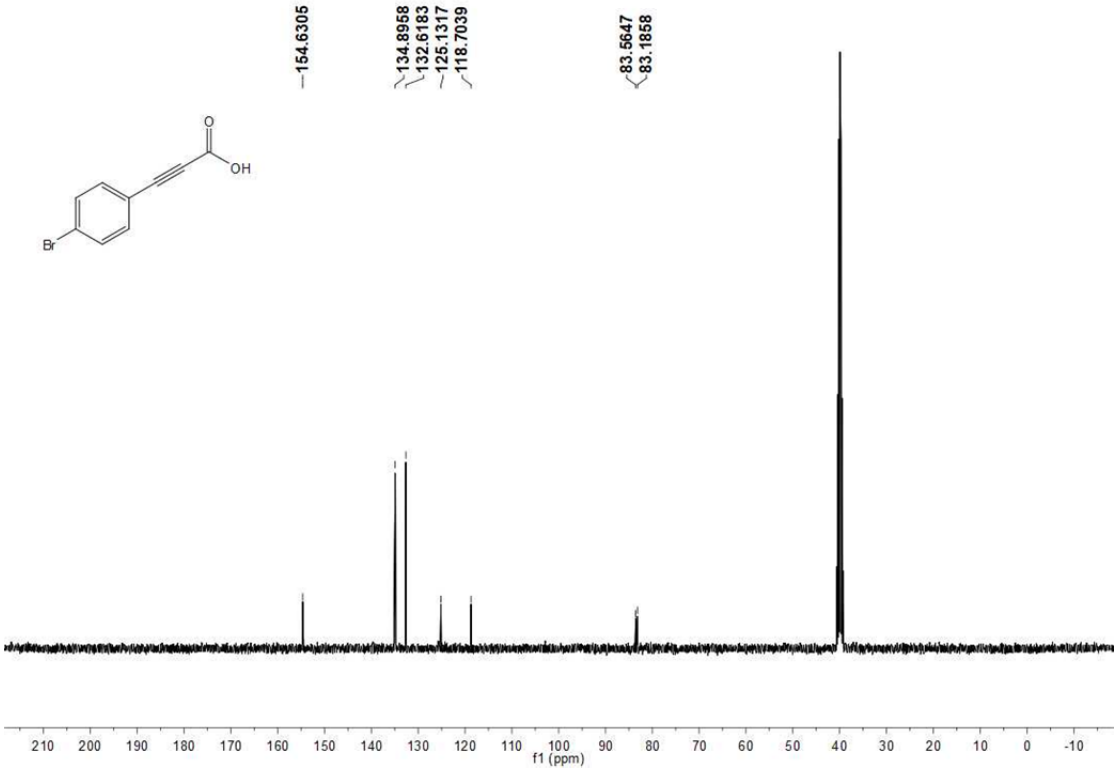


Fig. S20 ^{13}C{^{1}H} NMR spectrum of **6e** in DMSO-d_6

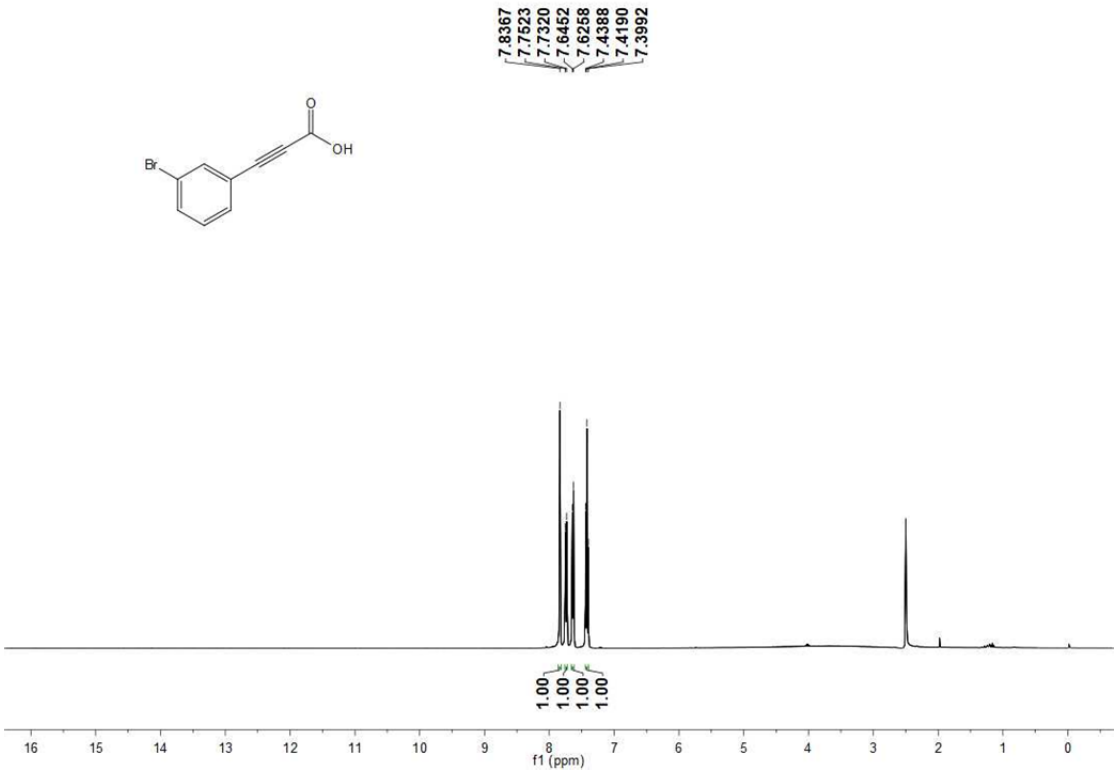


Fig. S21 ^{1}H NMR spectrum of **6f** in DMSO-d_6

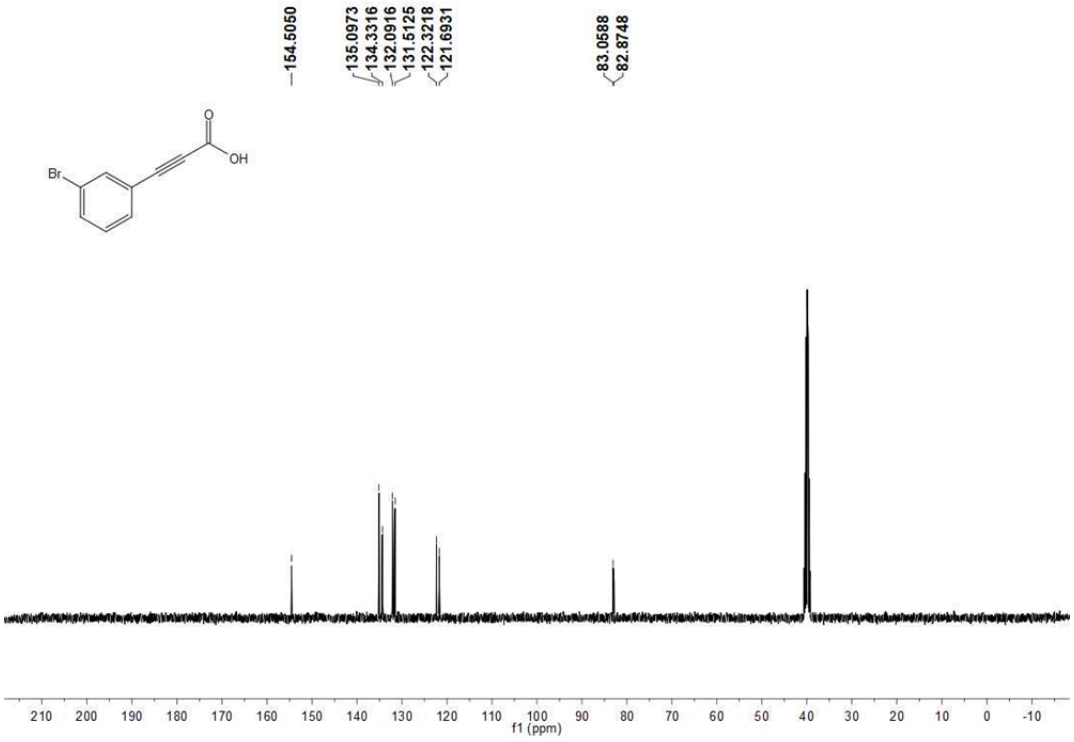


Fig. S22 ^{13}C{^{1}H} NMR spectrum of **6f** in DMSO-d_6

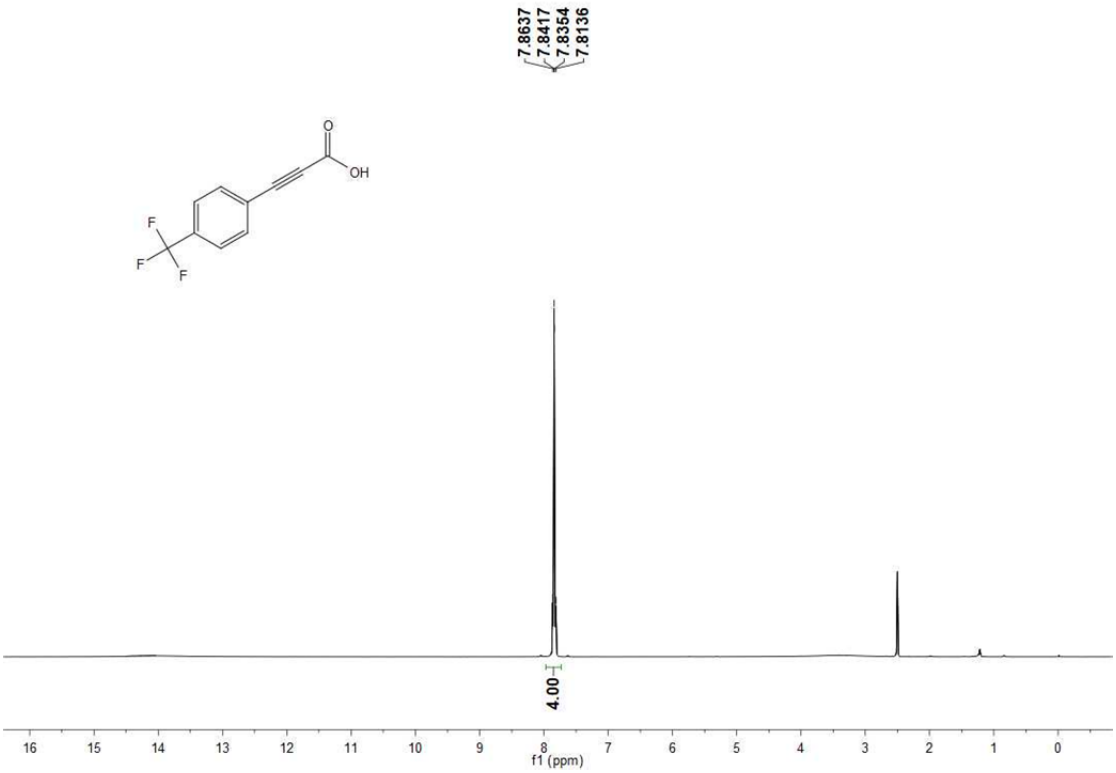


Fig. S23 ^{1}H NMR spectrum of **6g** in DMSO-d_6

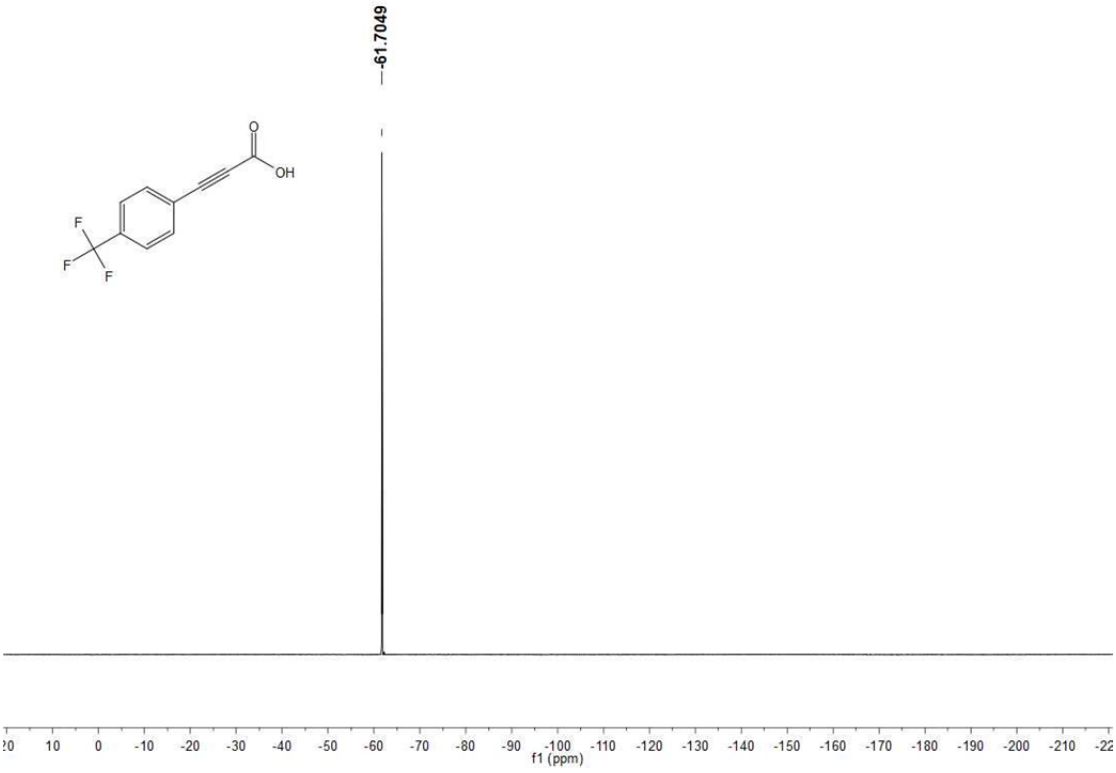


Fig. S24 ^{19}F NMR spectrum of **6g** in DMSO-d_6

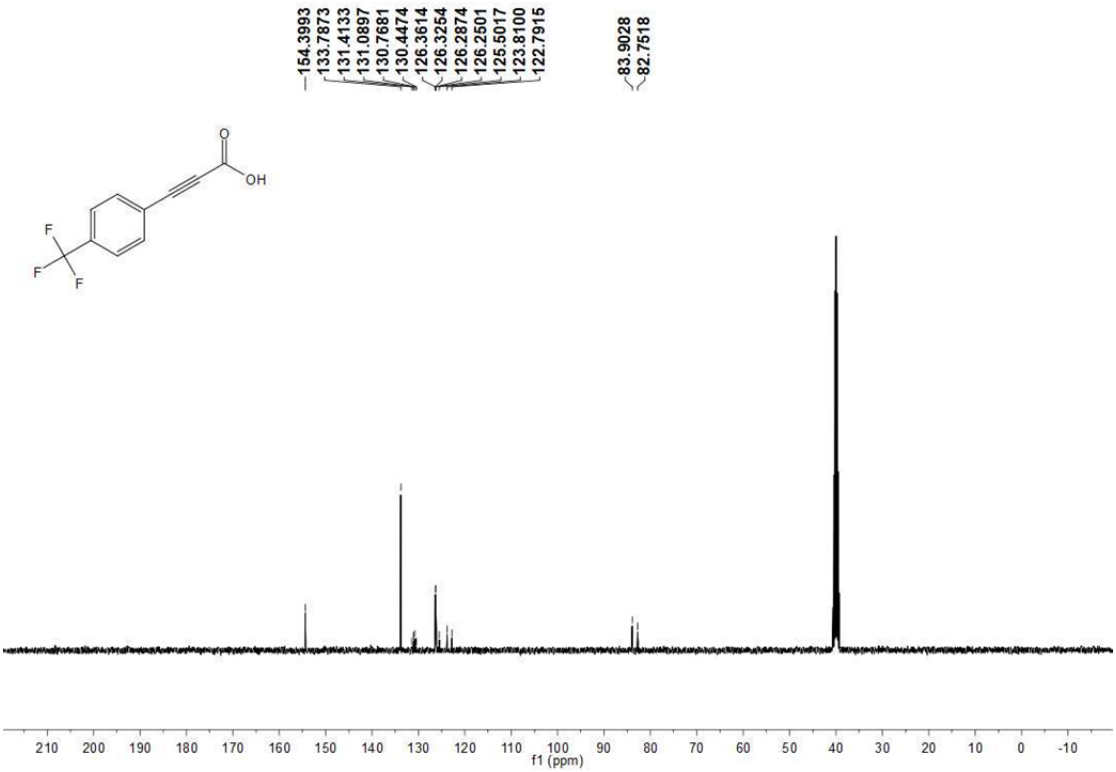


Fig. S25 $^{13}C\{^{1}H\}$ NMR spectrum of **6g** in DMSO-d_6

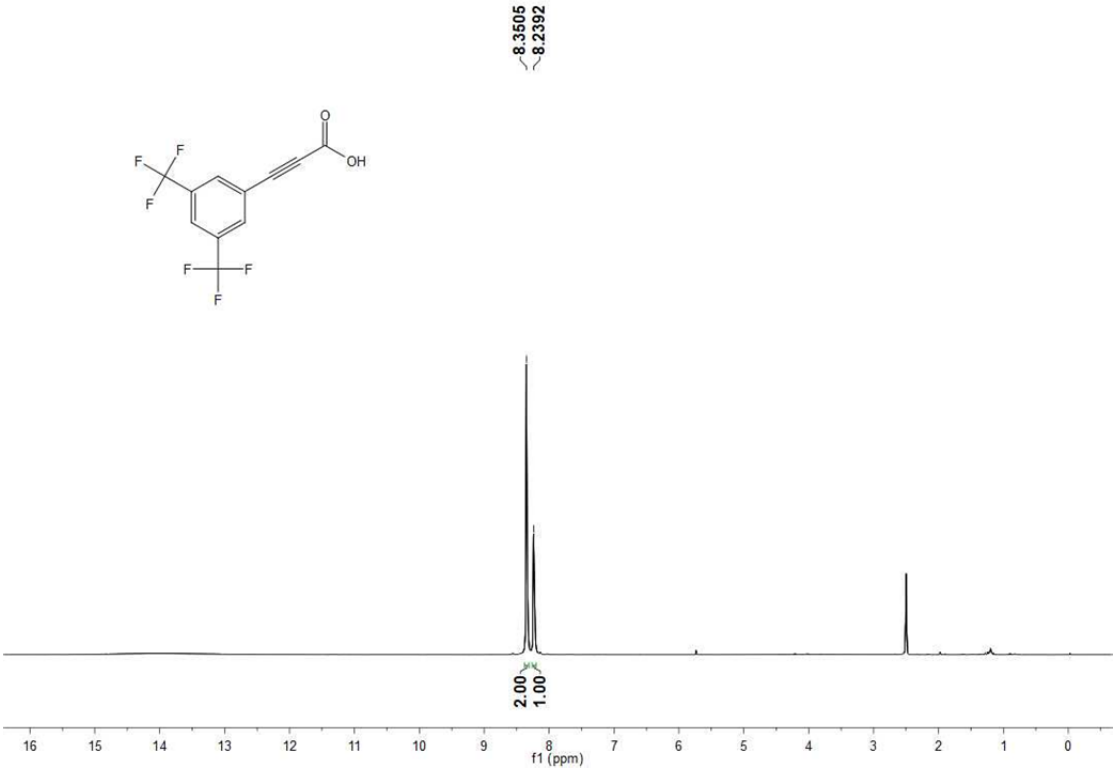


Fig. S26 ^{1}H NMR spectrum of **6h** in DMSO-d_6

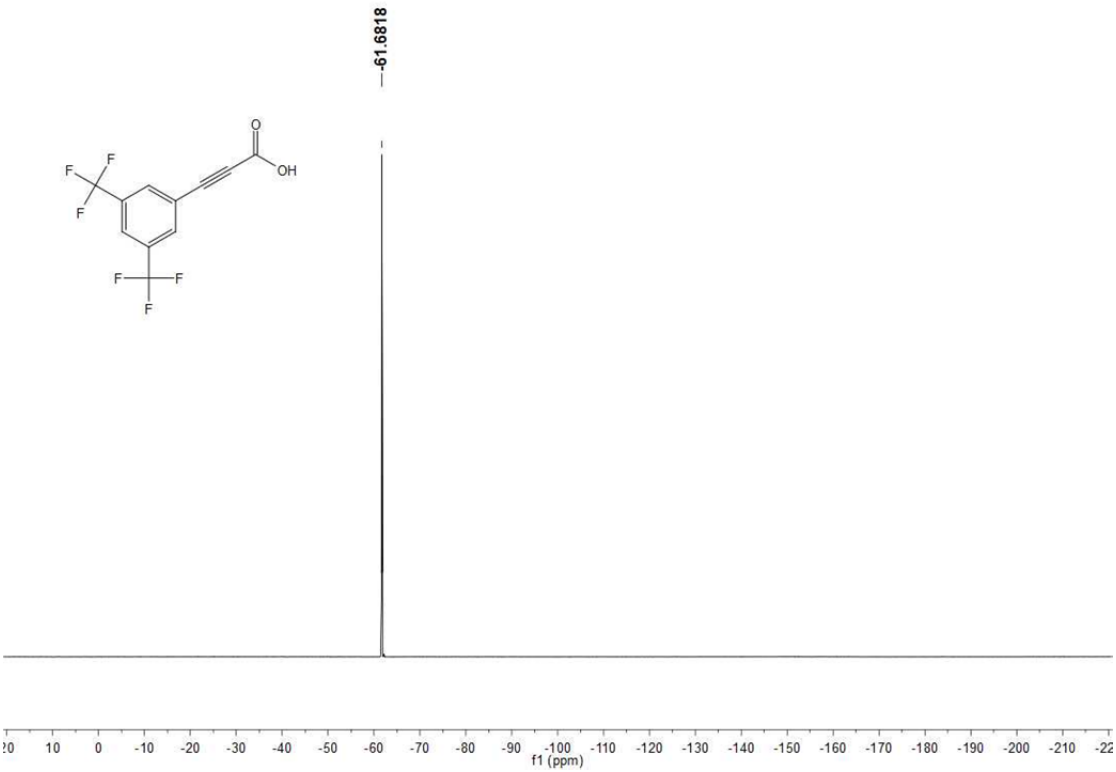


Fig. S27 ^{19}F NMR spectrum of **6h** in DMSO-d_6

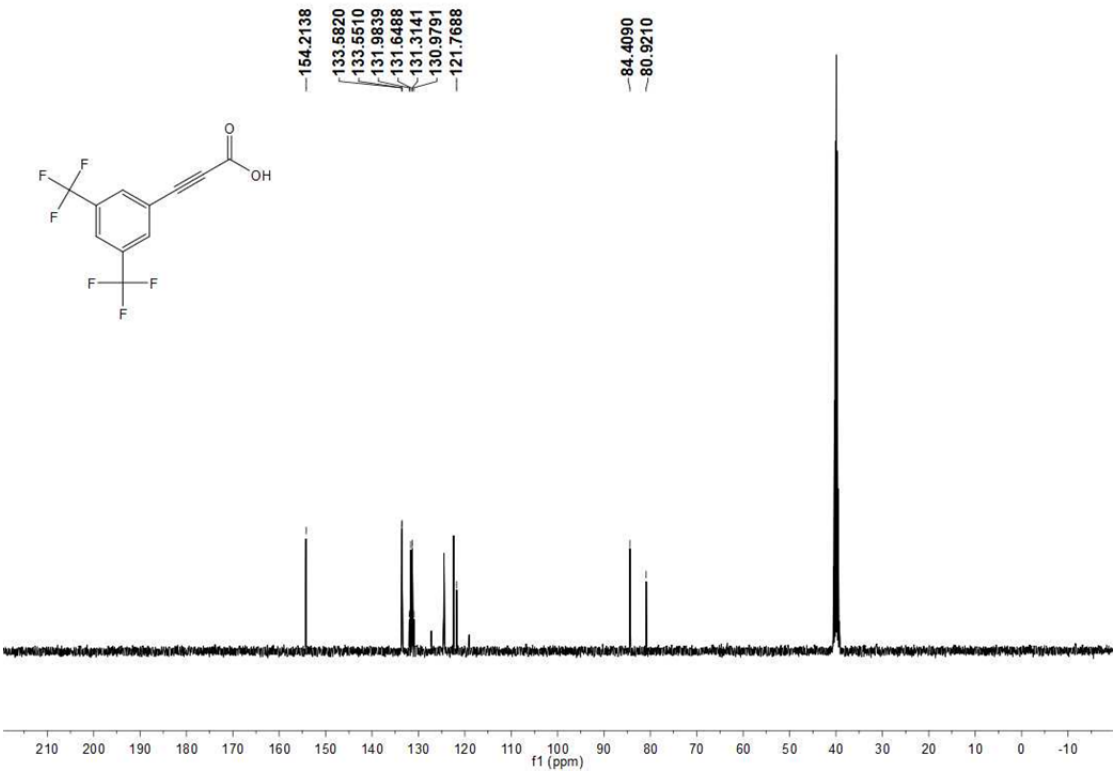


Fig. S28 ^{13}C{^{1}H} NMR spectrum of **6h** in DMSO-d_6

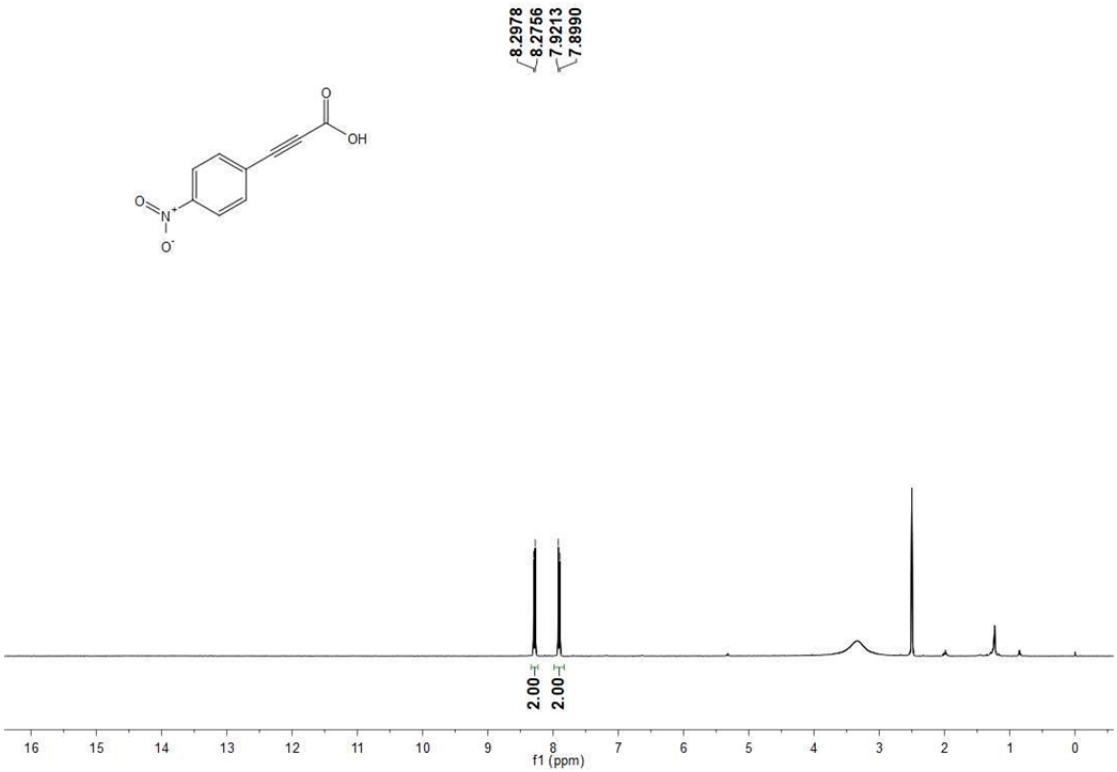


Fig. S29 ^{1}H NMR spectrum of **6i** in DMSO-d_6

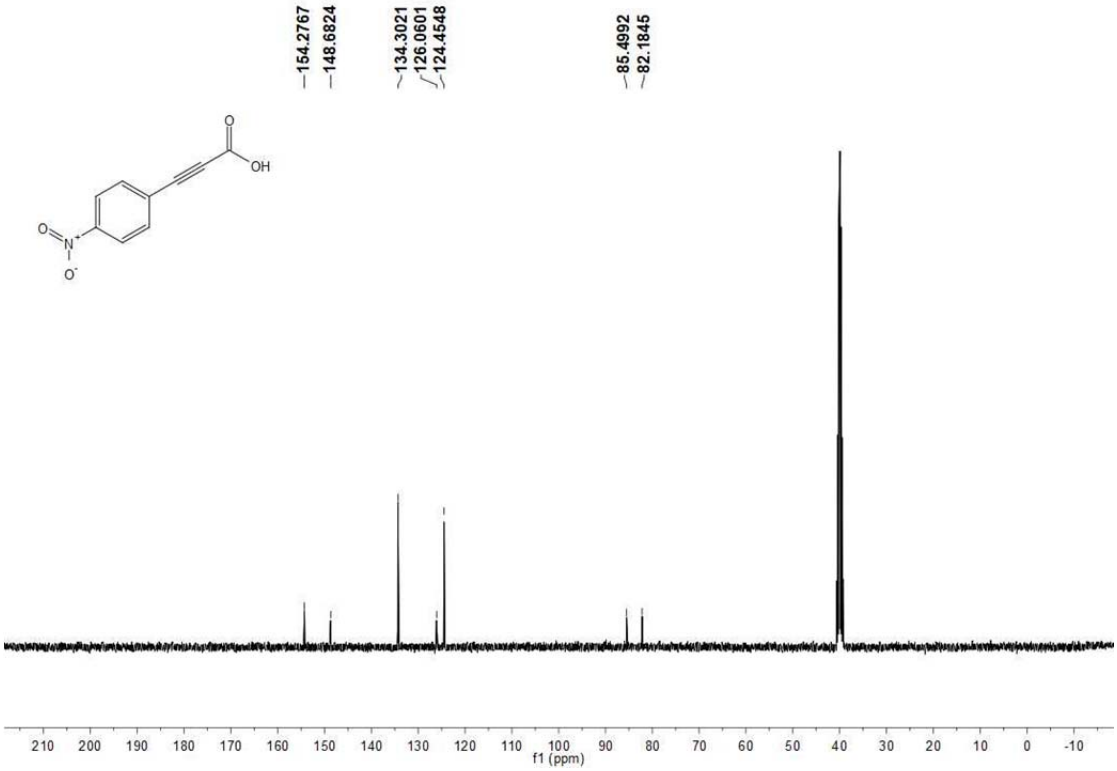


Fig. S30 ^{13}C{^{1}H} NMR spectrum of **6i** in DMSO-d_6

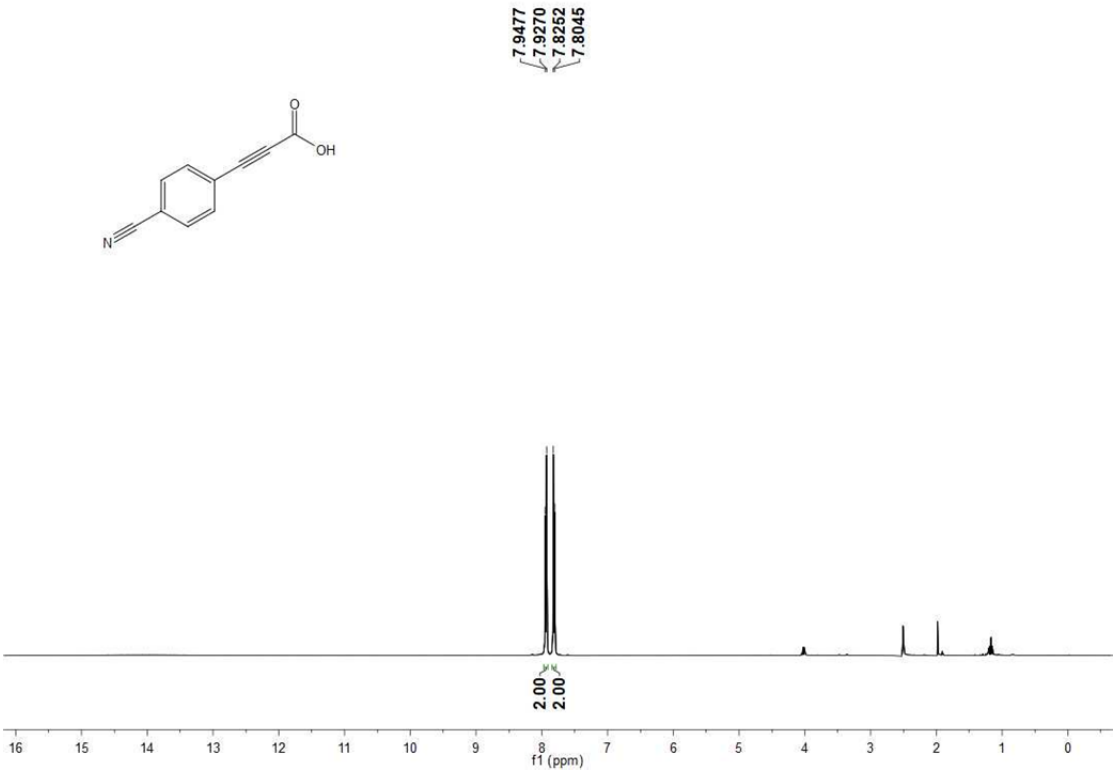


Fig. S31 ^{1}H NMR spectrum of **6j** in DMSO-d_6

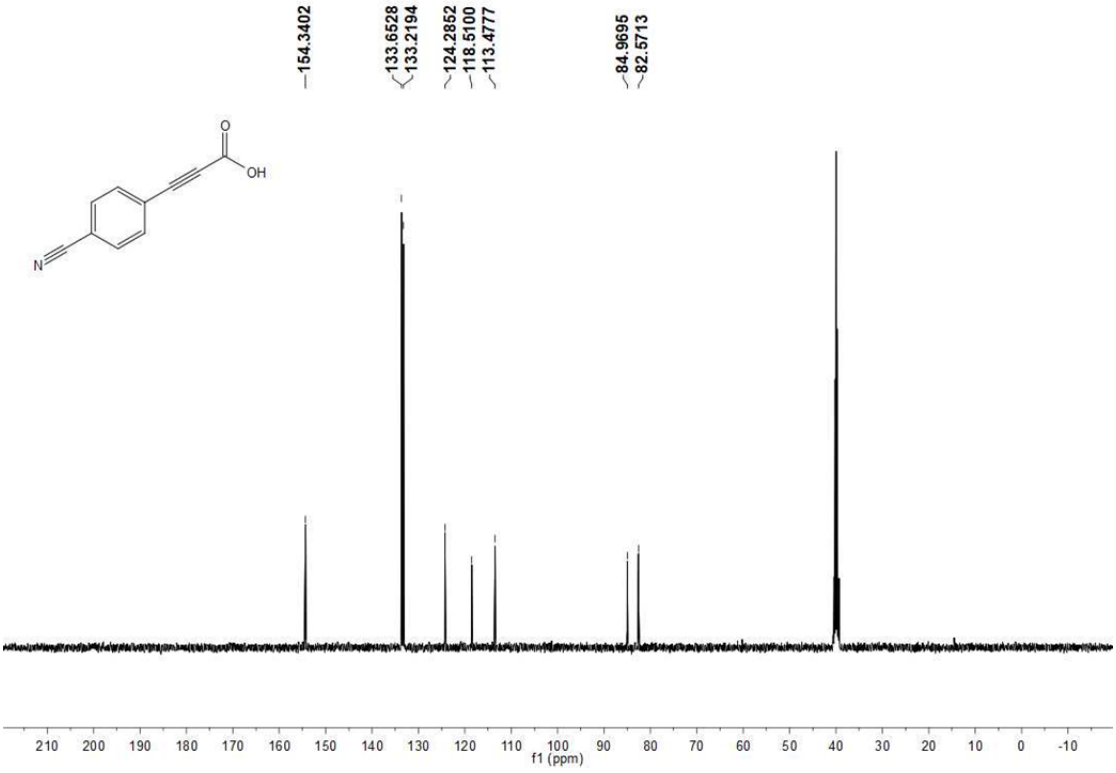


Fig. S32 ^{13}C{^{1}H} NMR spectrum of **6j** in DMSO-d_6

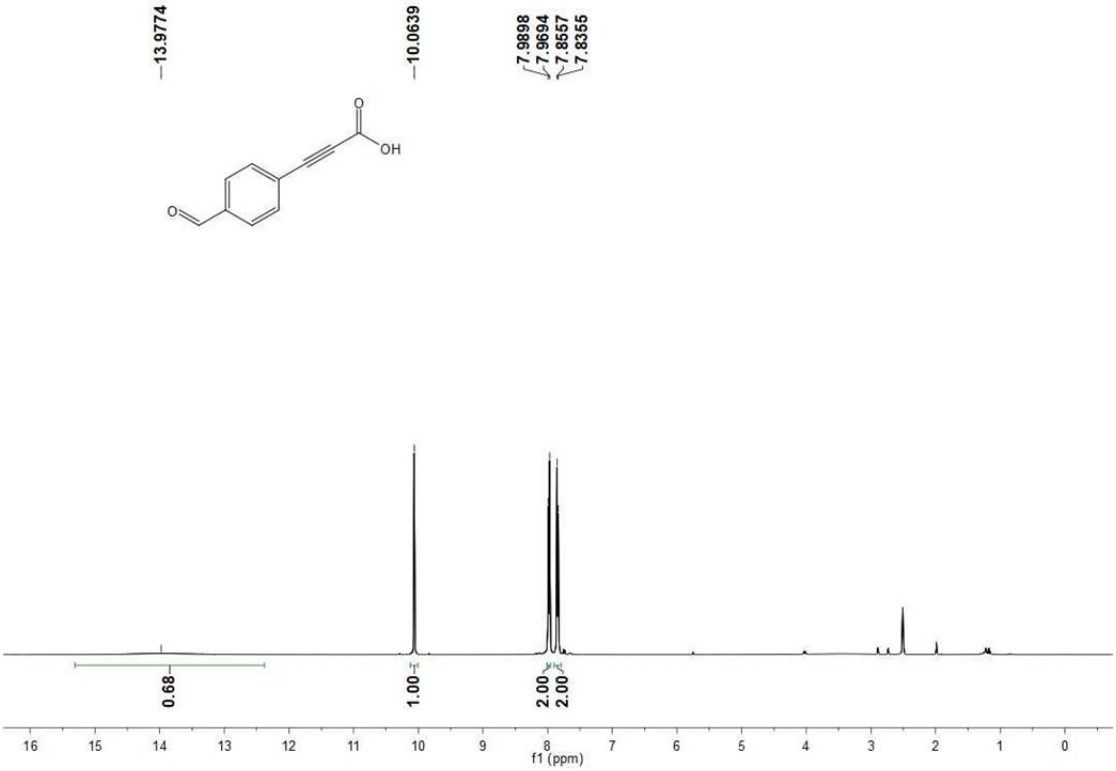


Fig. S33 ^{1}H NMR spectrum of **6k** in DMSO-d_6

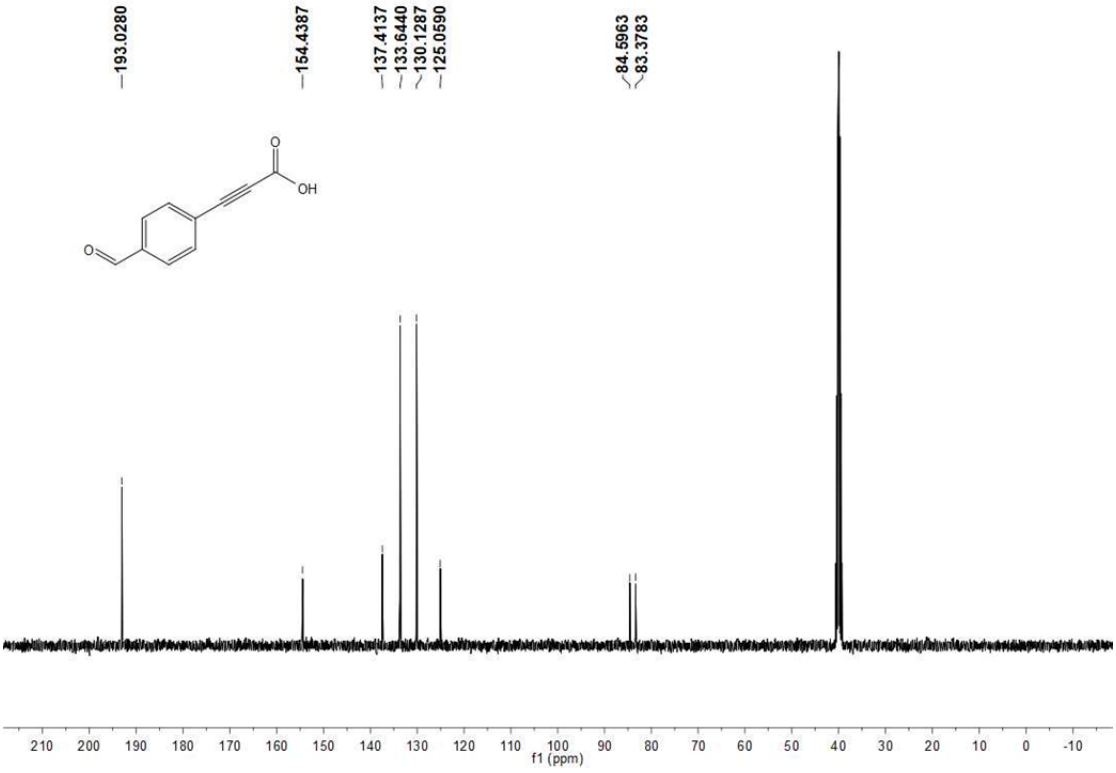


Fig. S34 ^{13}C{^{1}H} NMR spectrum of **6k** in DMSO-d_6

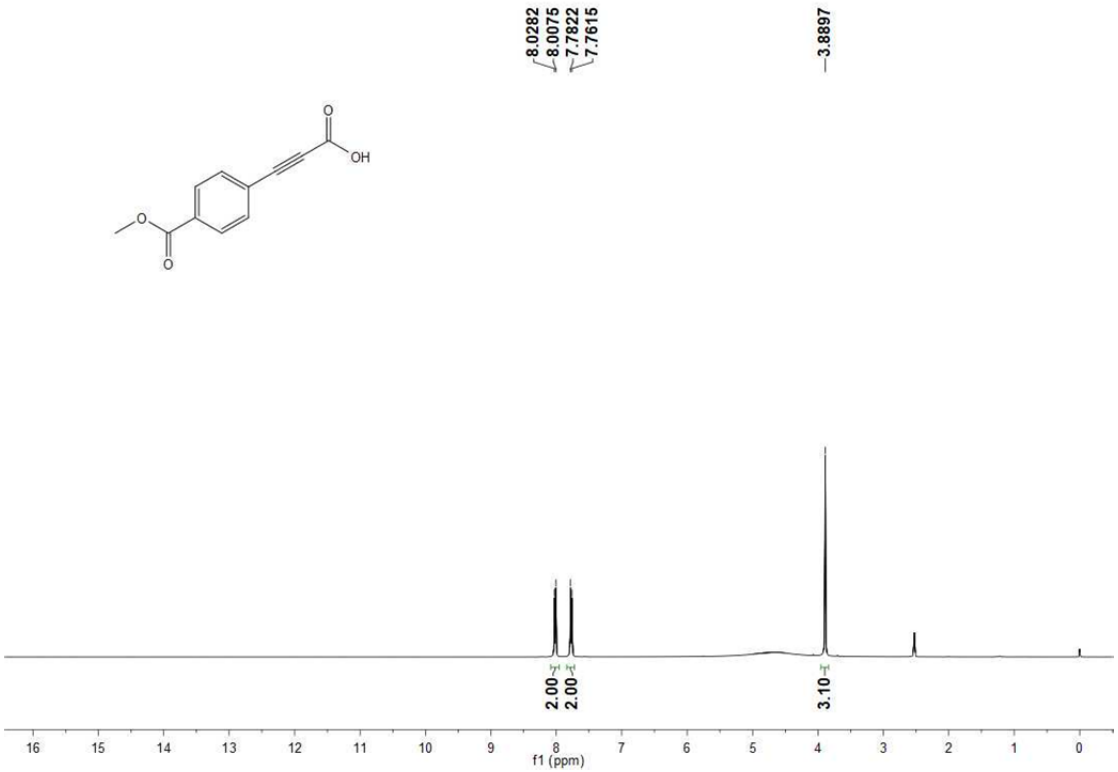


Fig. S35 ^{1}H NMR spectrum of **6l** in DMSO-d_6

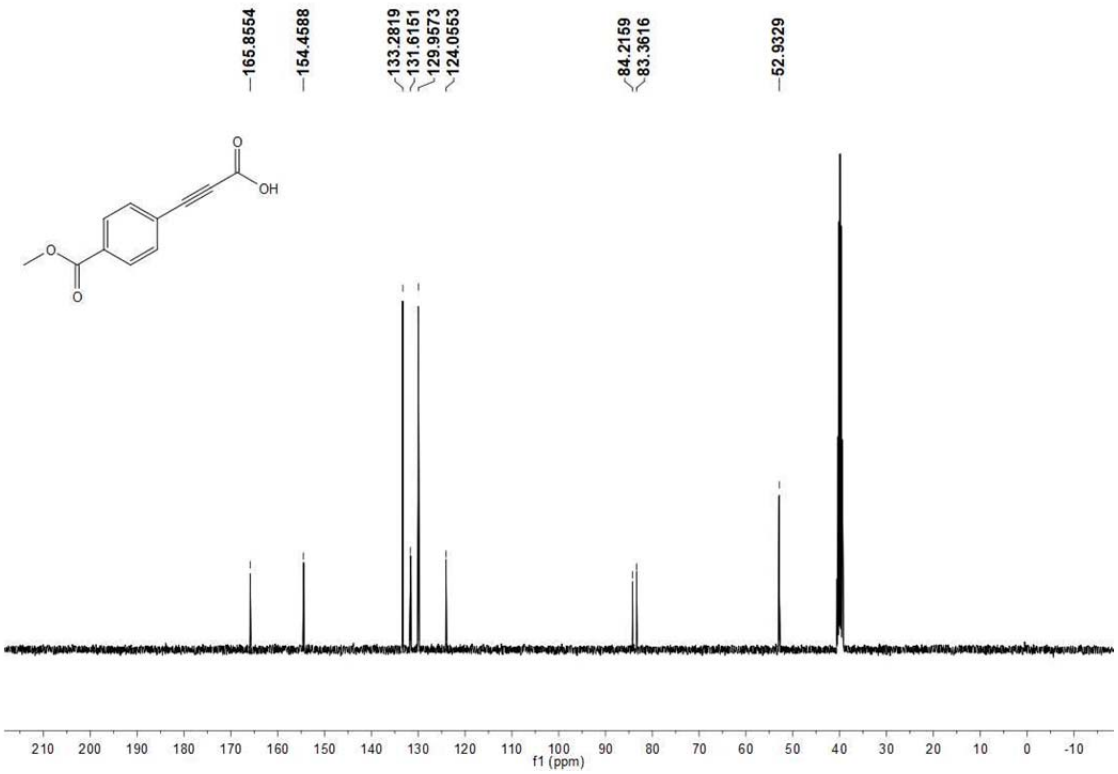


Fig. S36 ^{13}C{^{1}H} NMR spectrum of **6l** in DMSO-d_6

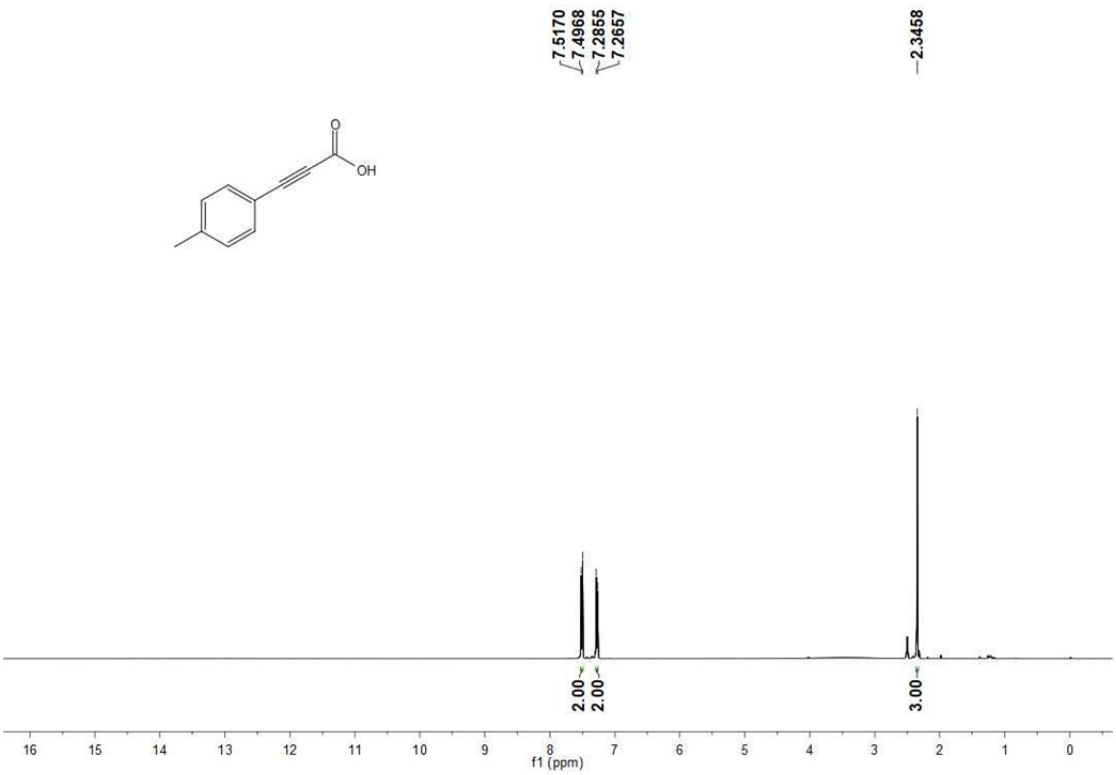


Fig. S37 ^{1}H NMR spectrum of **6m** in DMSO-d_6

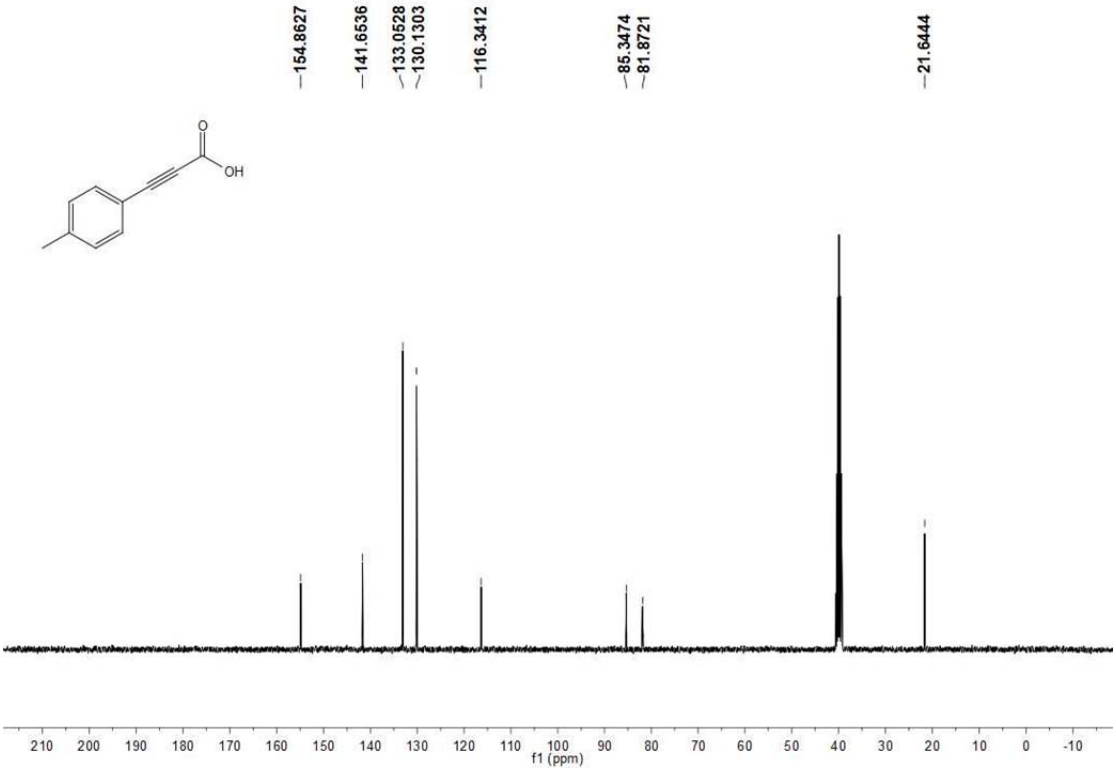


Fig. S38 ^{13}C{^{1}H} NMR spectrum of **6m** in DMSO-d_6

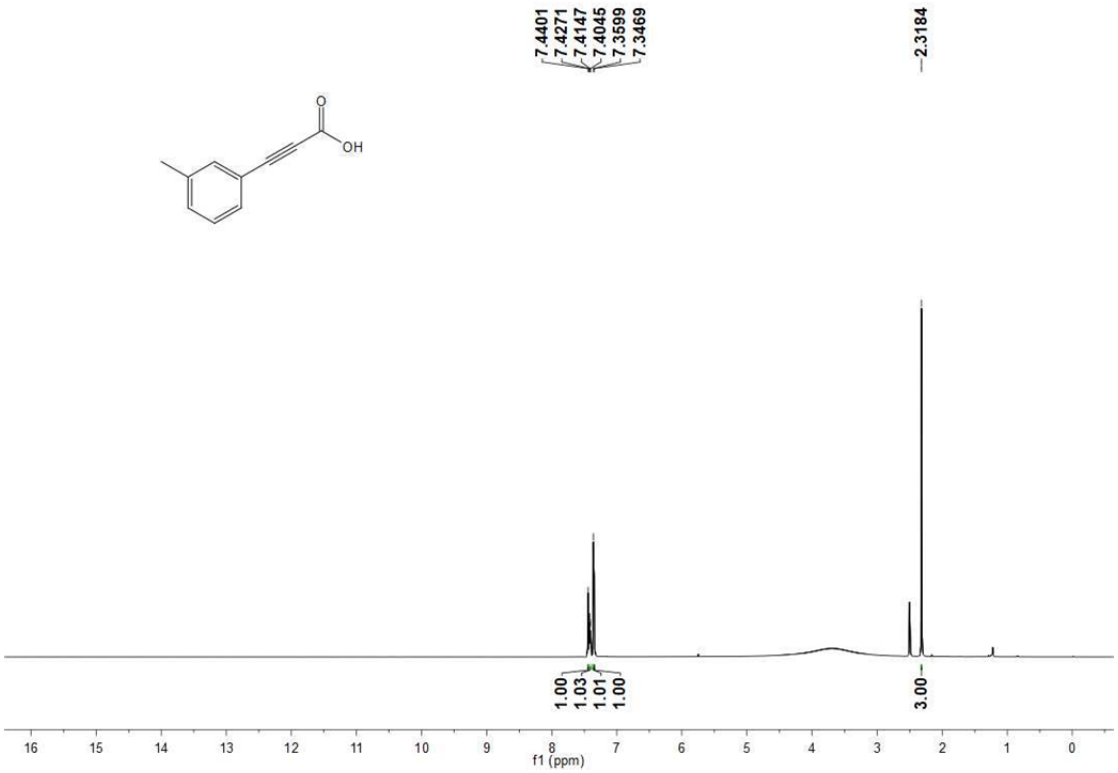


Fig. S39 ^{1}H NMR spectrum of **6n** in DMSO-d_6

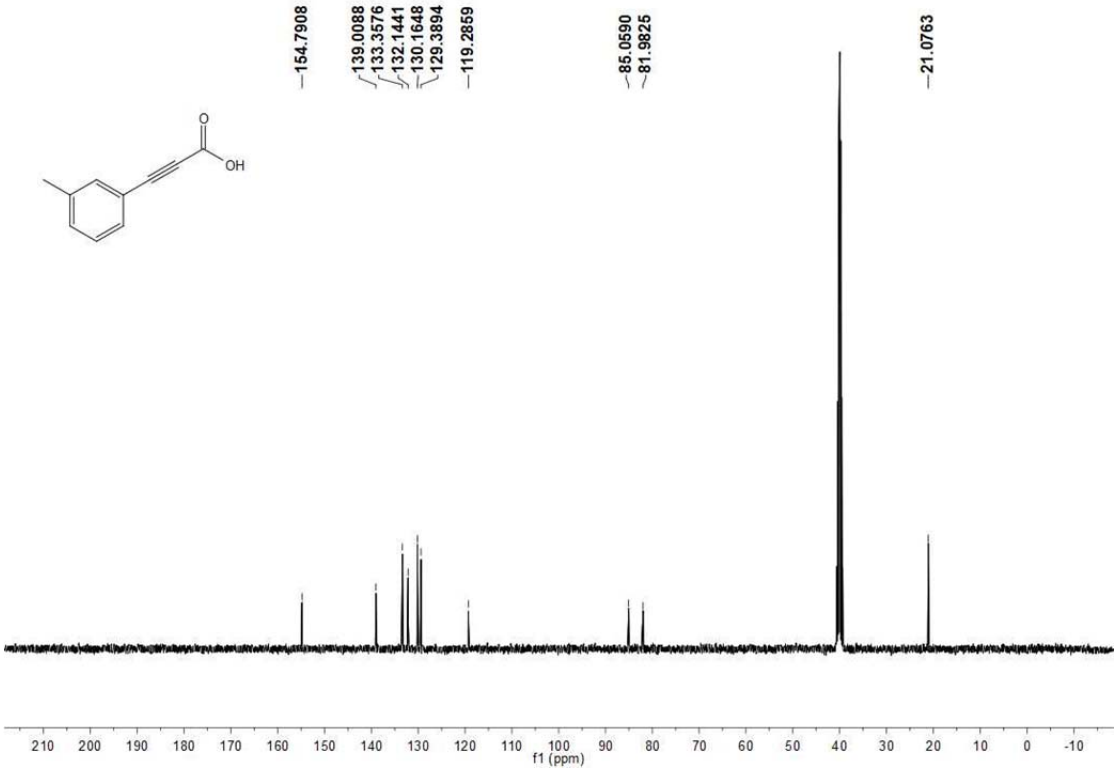


Fig. S40 ^{13}C{^{1}H} NMR spectrum of **6n** in DMSO-d_6

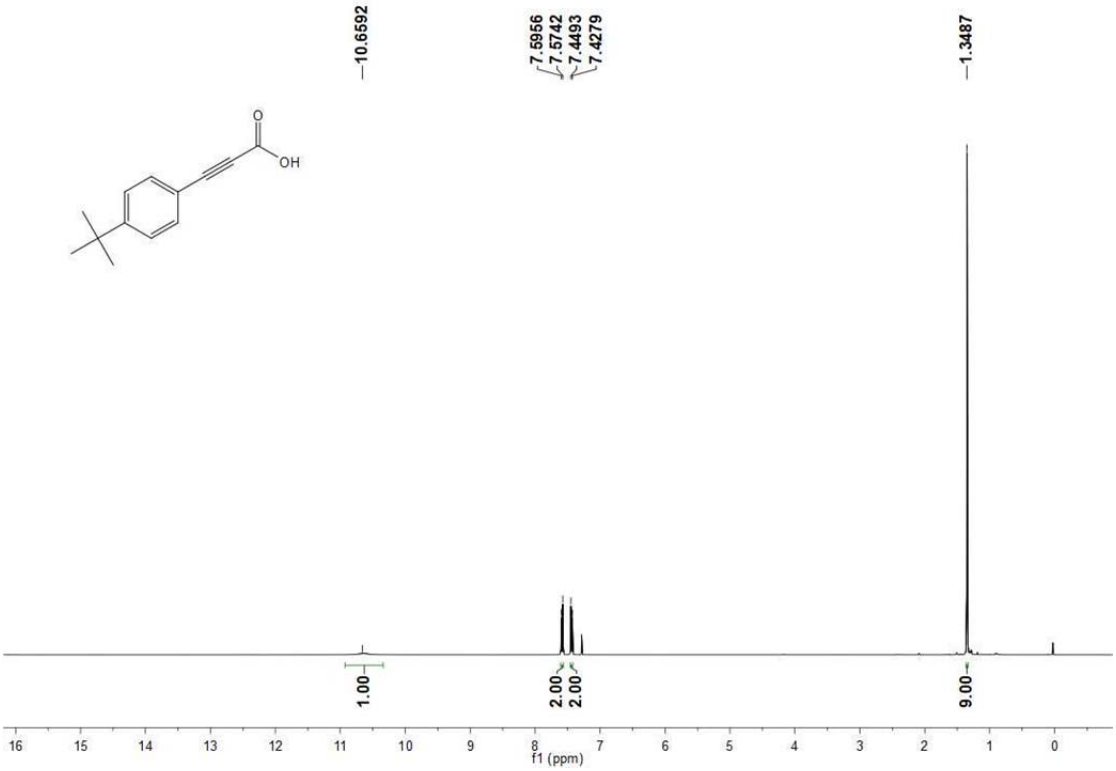


Fig. S41 ^{1}H NMR spectrum of **6o** in $CDCl_3$

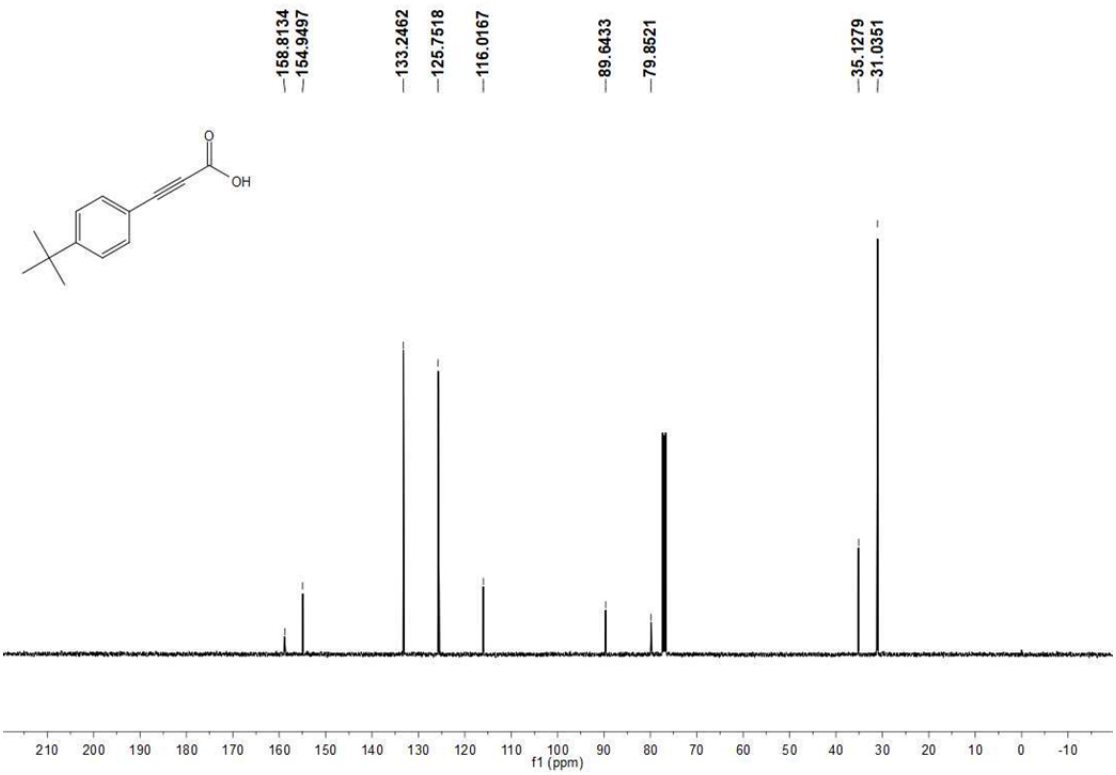


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum of **6o** in DMSO-d_6

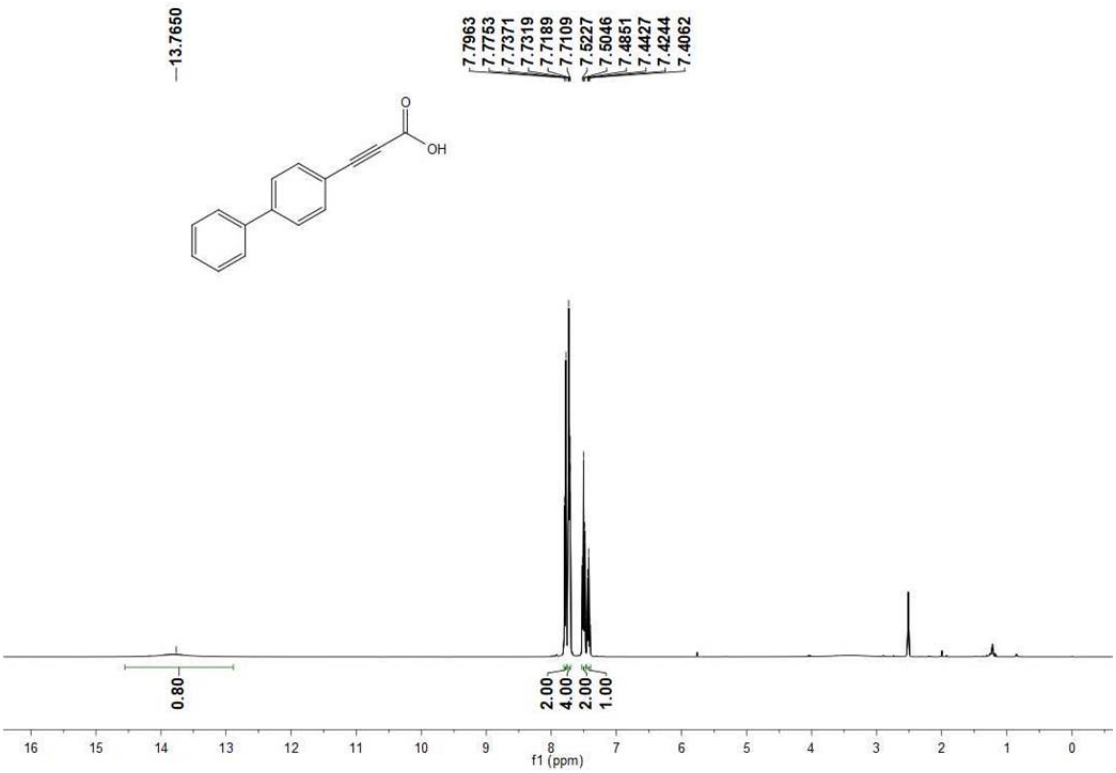


Fig. S43 ^{1}H NMR spectrum of **6p** in DMSO-d_6

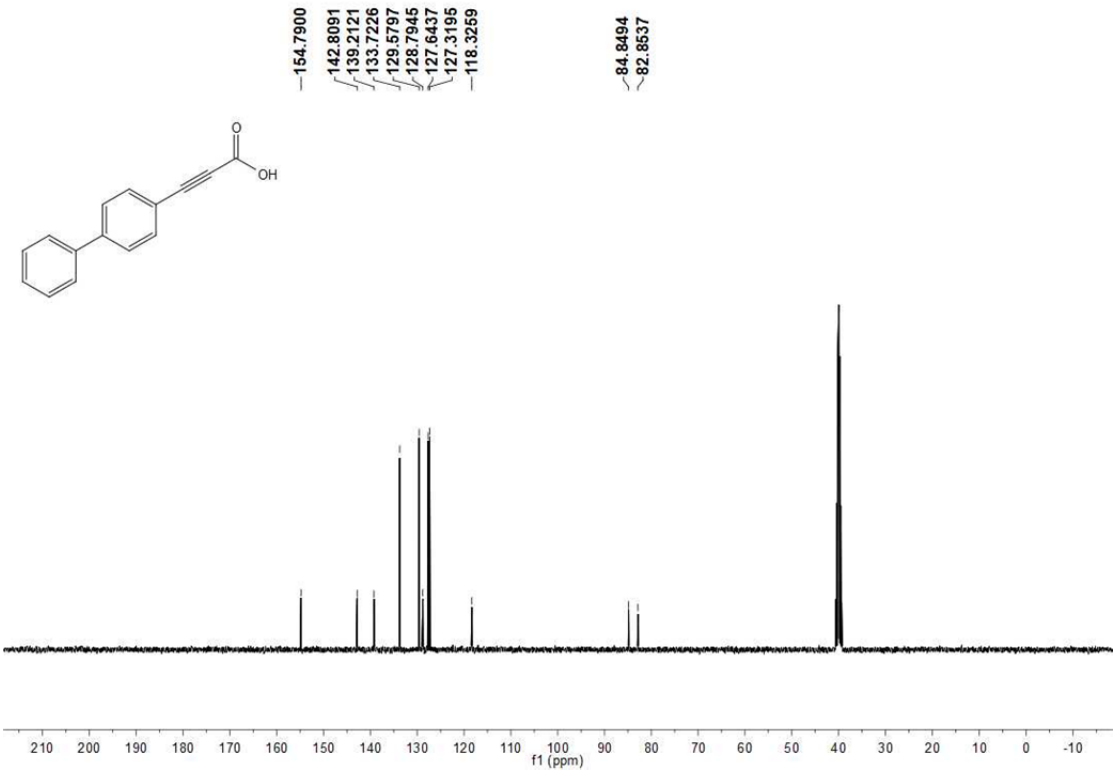


Fig. S44 ^{13}C{^{1}H} NMR spectrum of **6p** in DMSO-d_6

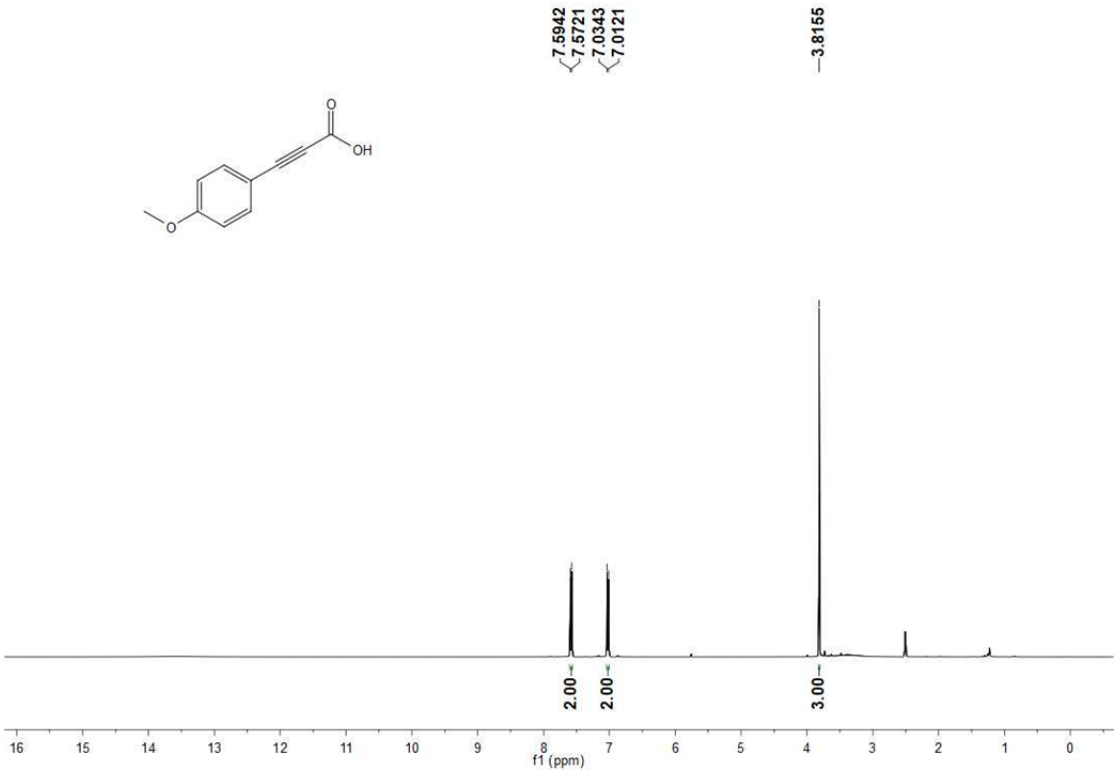


Fig. S45 ^{1}H NMR spectrum of **6q** in DMSO-d_6

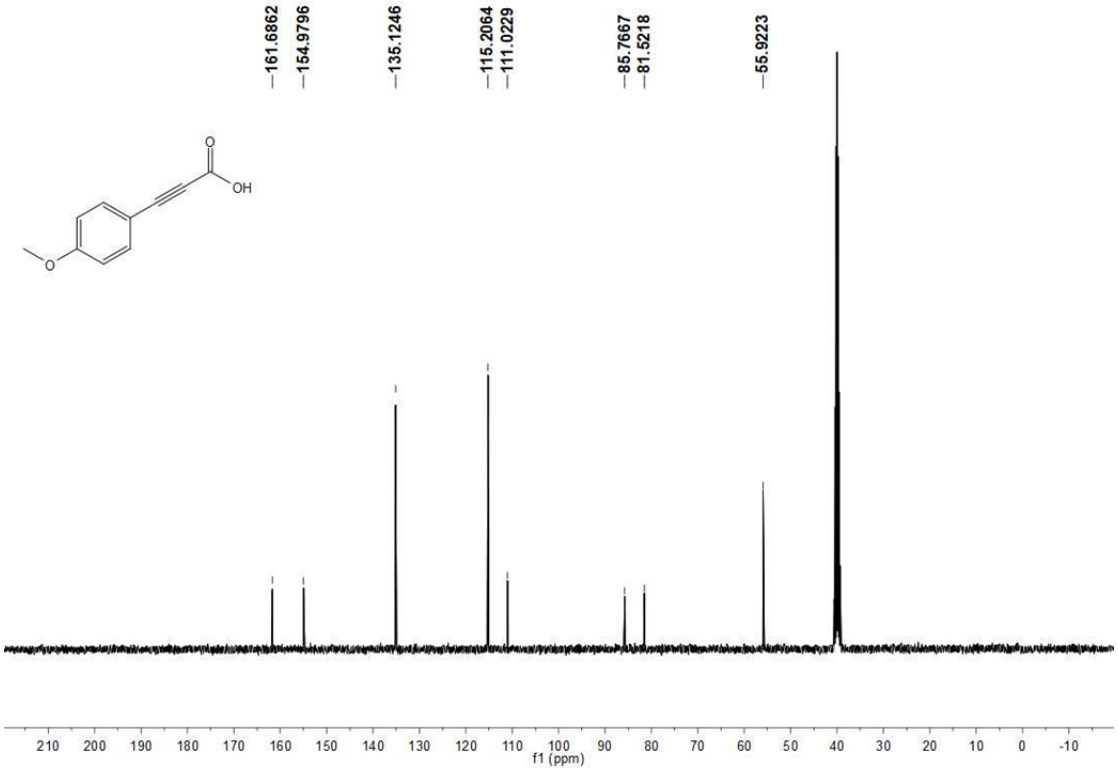


Fig. S46 ^{13}C{^{1}H} NMR spectrum of **6q** in DMSO-d_6

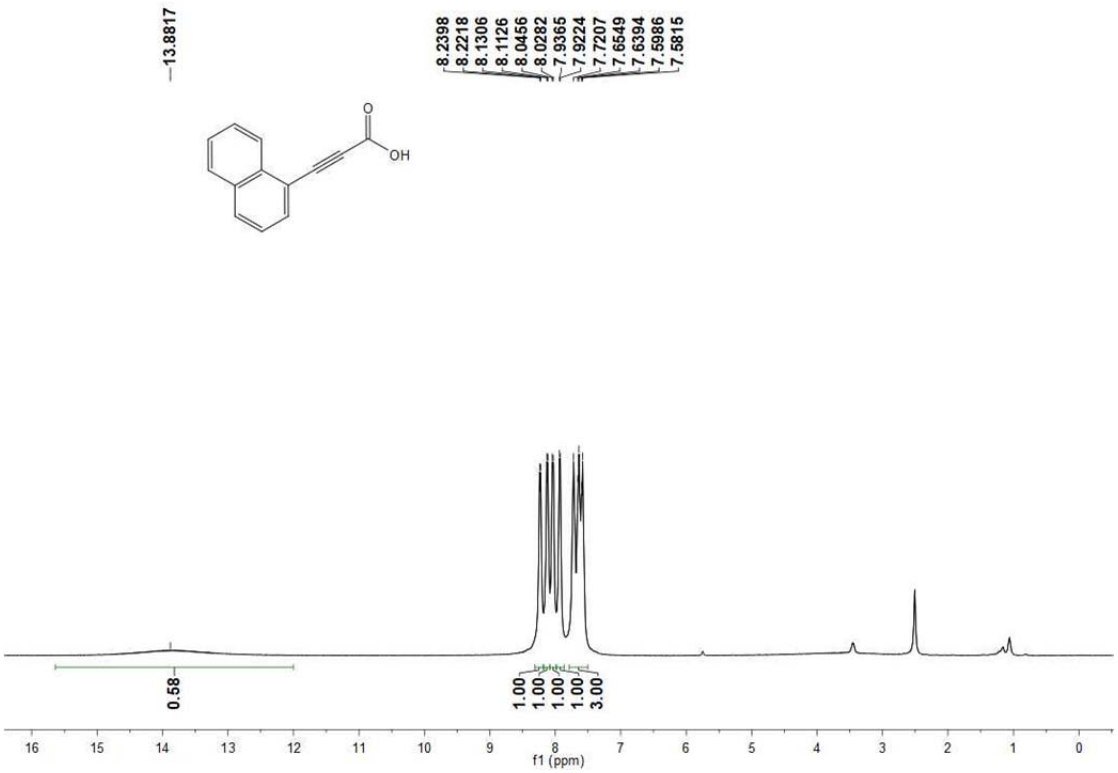


Fig. S47 ^{1}H NMR spectrum of **6r** in DMSO-d_6

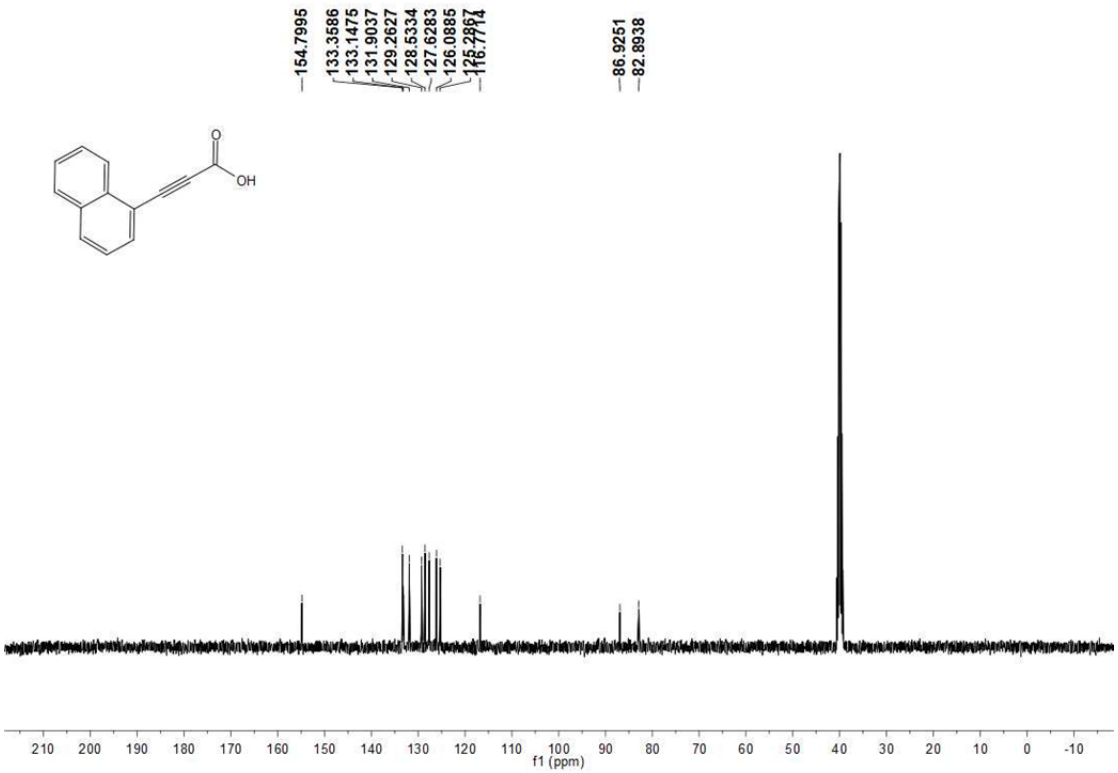


Fig. S48 ^{13}C{^{1}H} NMR spectrum of **6r** in DMSO-d_6

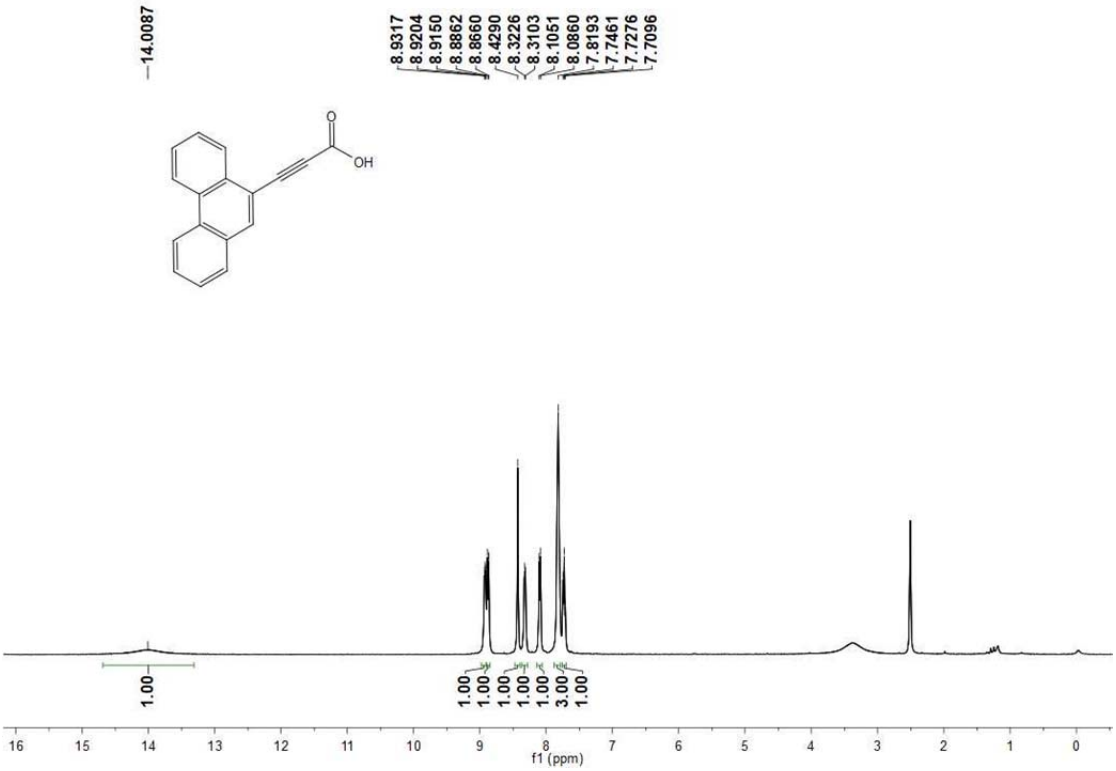


Fig. S49 ^{1}H NMR spectrum of **6s** in DMSO-d_6

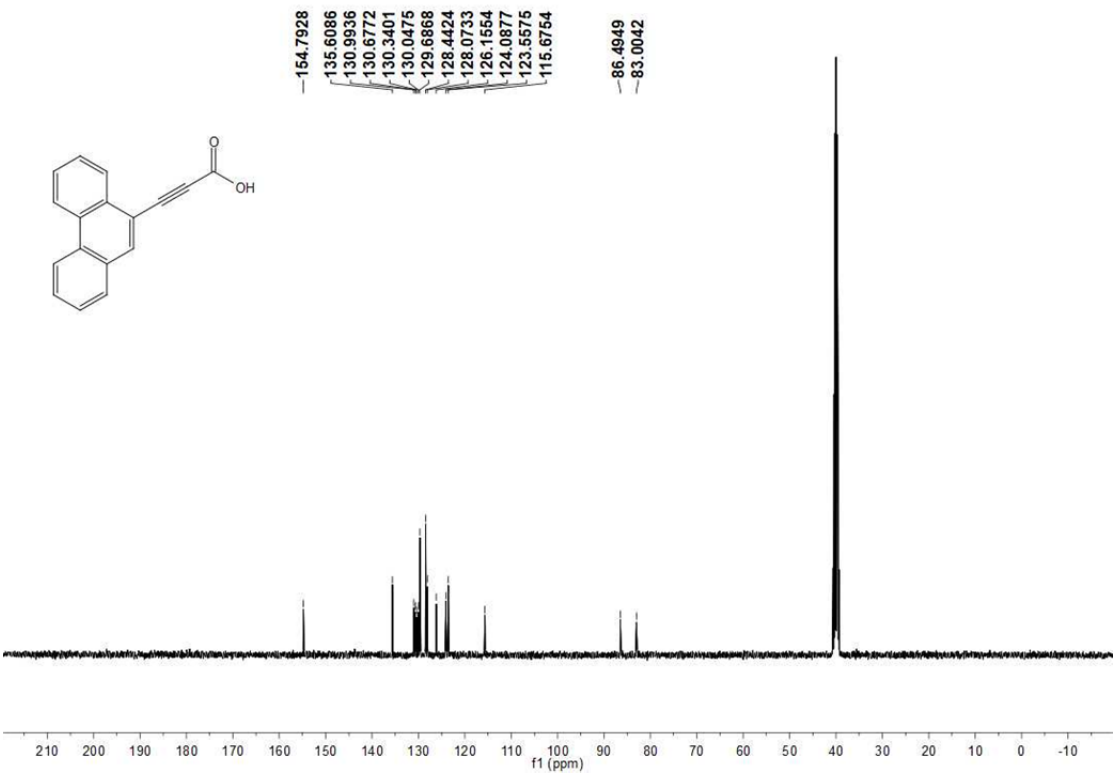


Fig. S50 ^{13}C{^{1}H} NMR spectrum of **6s** in DMSO-d_6

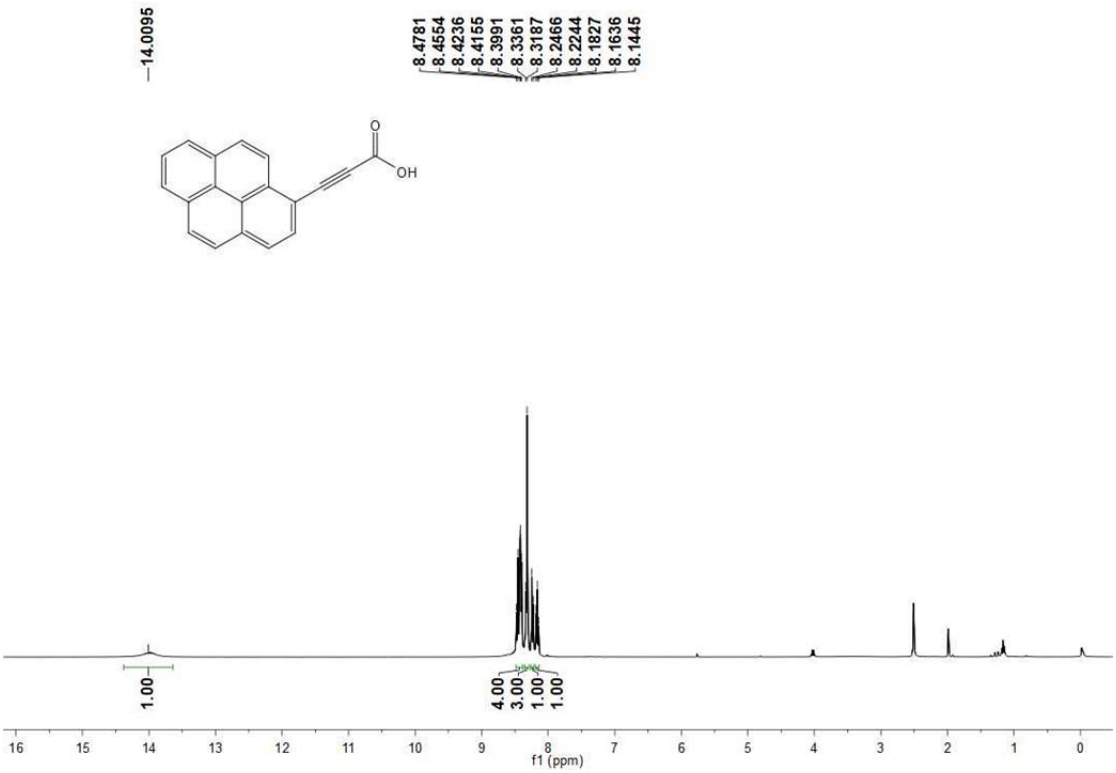


Fig. S51 ^{1}H NMR spectrum of **6t** in DMSO-d_6

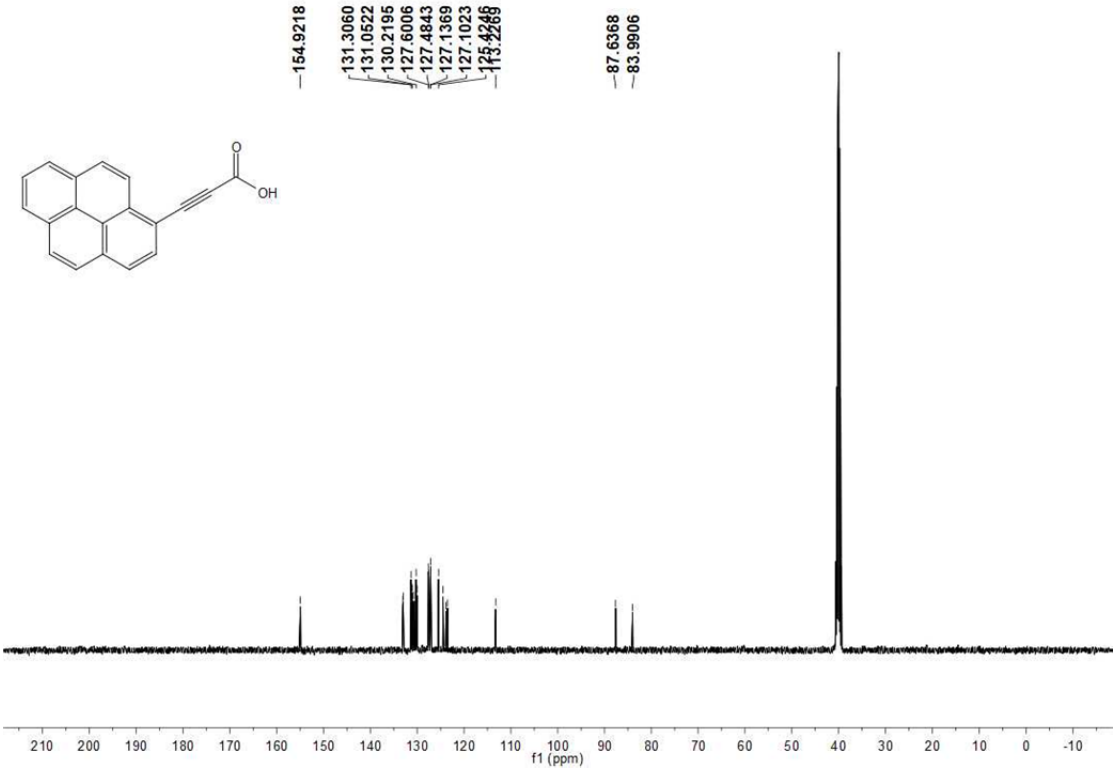


Fig. S52 ^{13}C{^{1}H} NMR spectrum of **6t** in DMSO-d_6

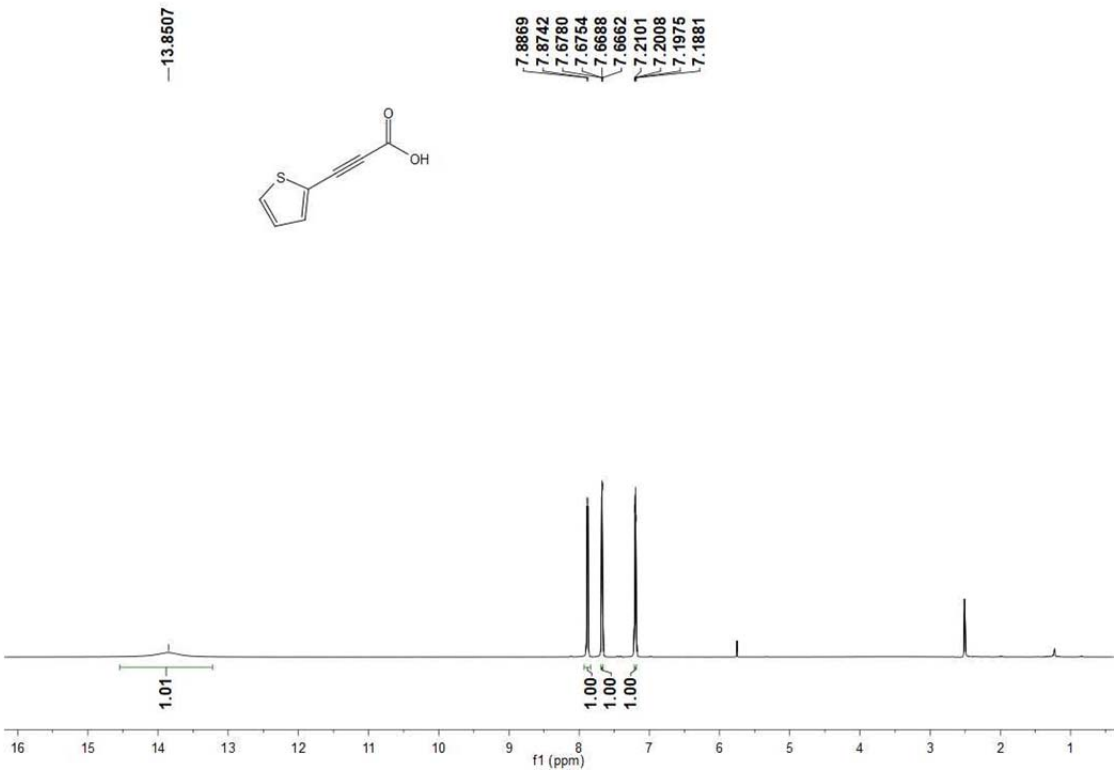


Fig. S53 ^{1}H NMR spectrum of **6u** in DMSO-d_6

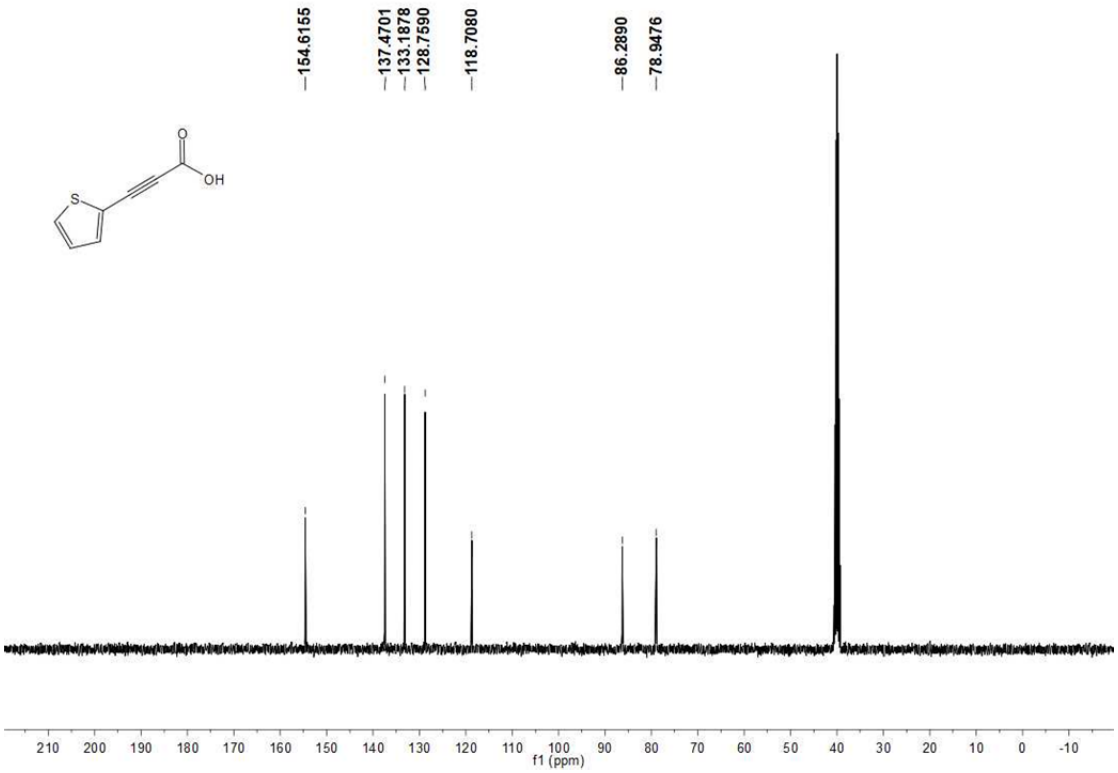


Fig. S54 ^{13}C{^{1}H} NMR spectrum of **6u** in DMSO-d_6

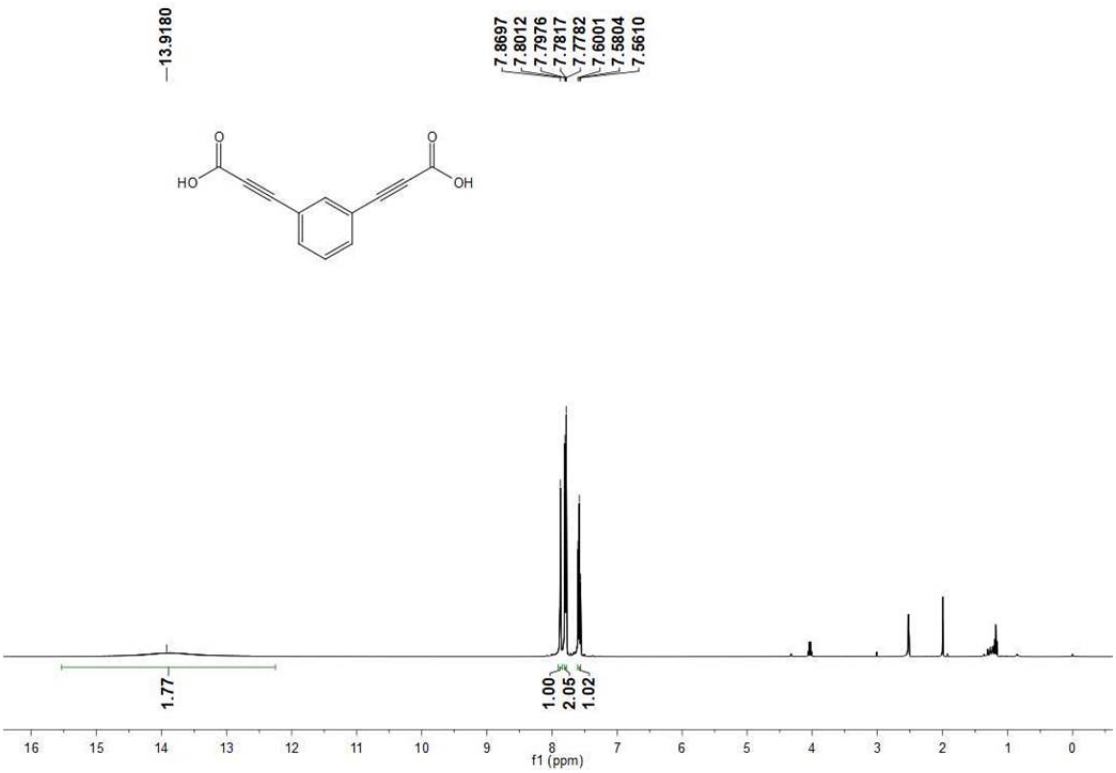


Fig. S55 ^{1}H NMR spectrum of **6v** in DMSO-d_6

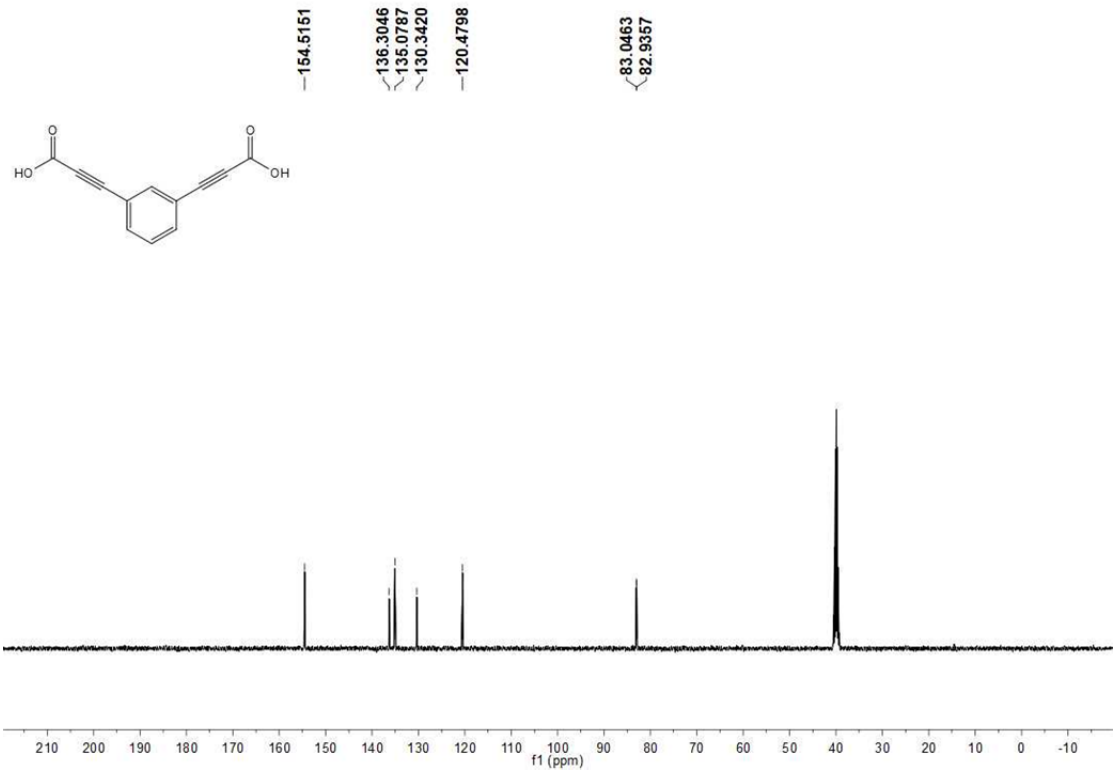


Fig. S56 ^{13}C{^{1}H} NMR spectrum of **6v** in DMSO-d_6

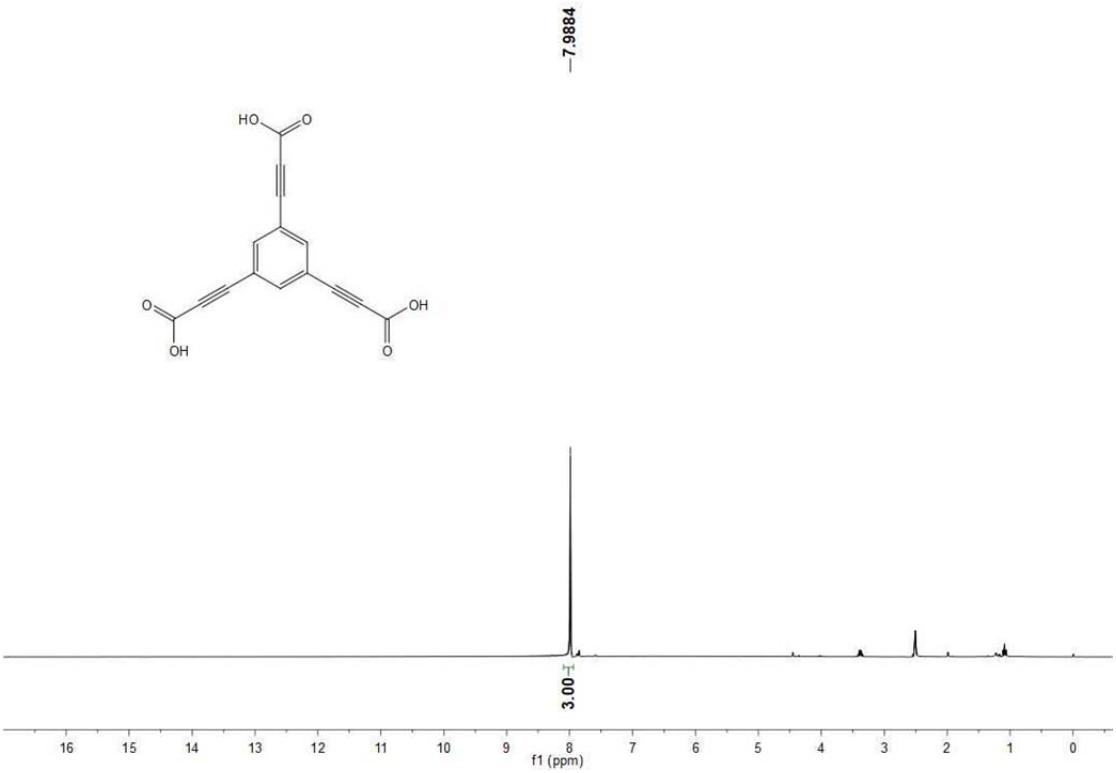


Fig. S57 ^{1}H NMR spectrum of **6w** in DMSO-d_6

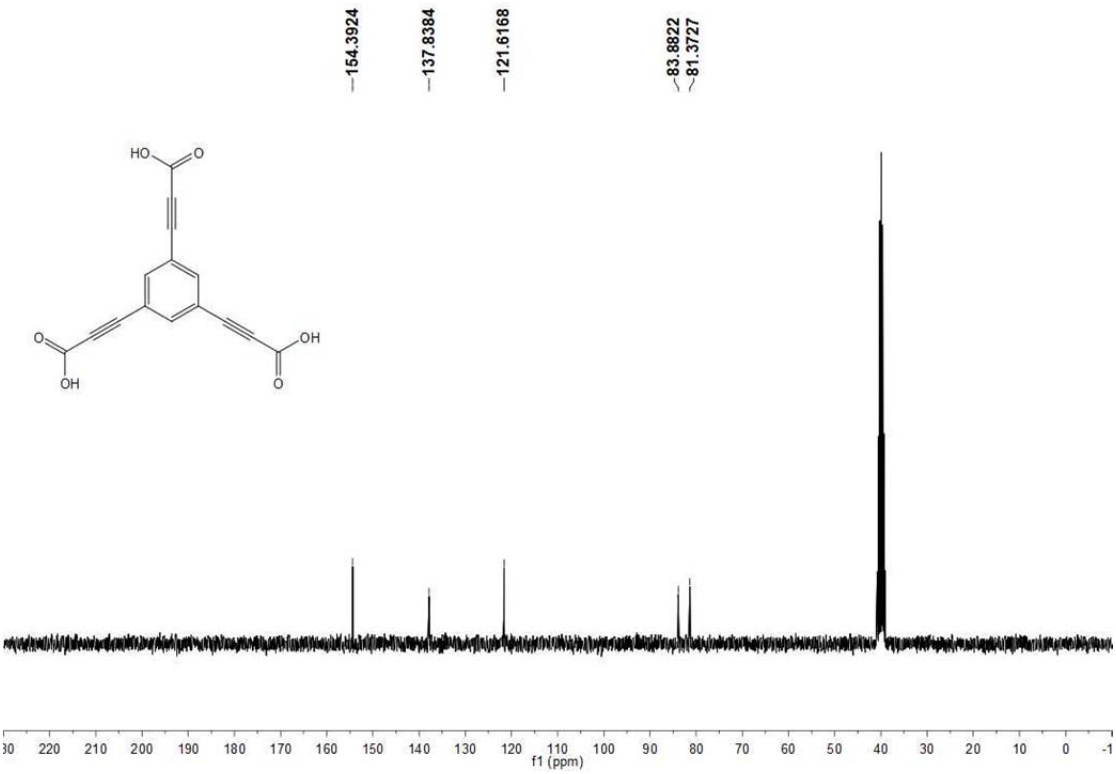


Fig. S58 ^{13}C{^{1}H} NMR spectrum of **6w** in DMSO-d_6

NMR spectra of the esters of propiolic acids

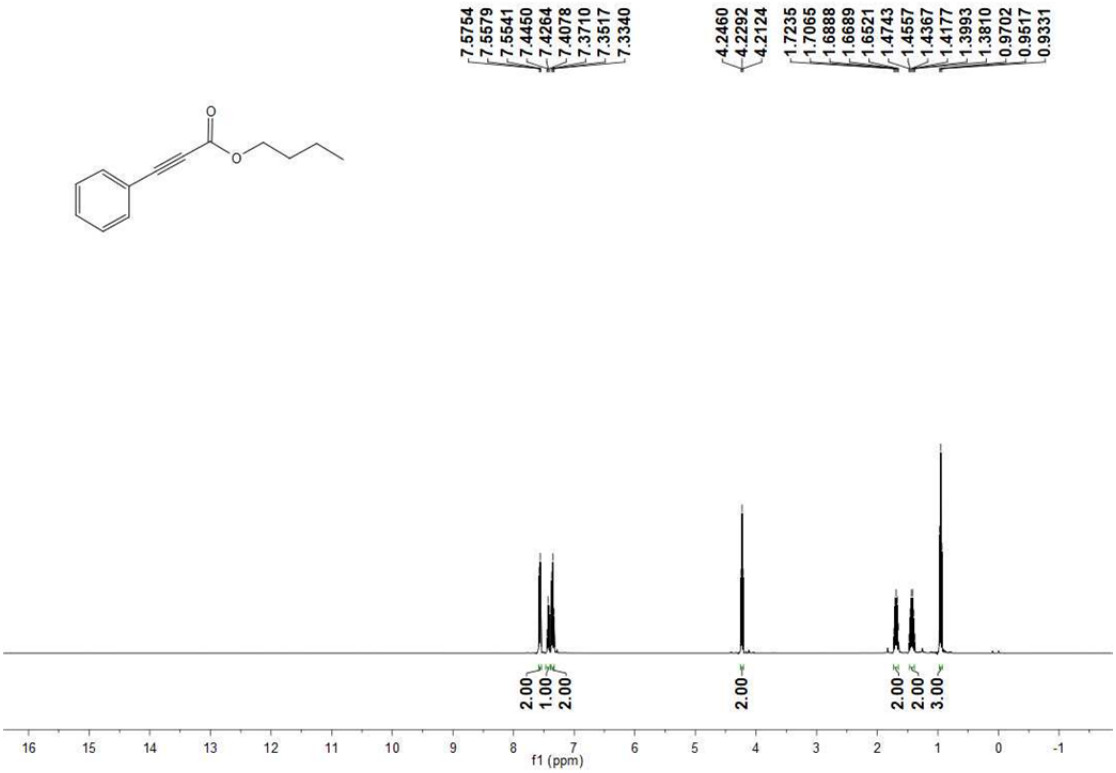


Fig. S59 ^{1}H NMR spectrum of **7a** in $CDCl_3$

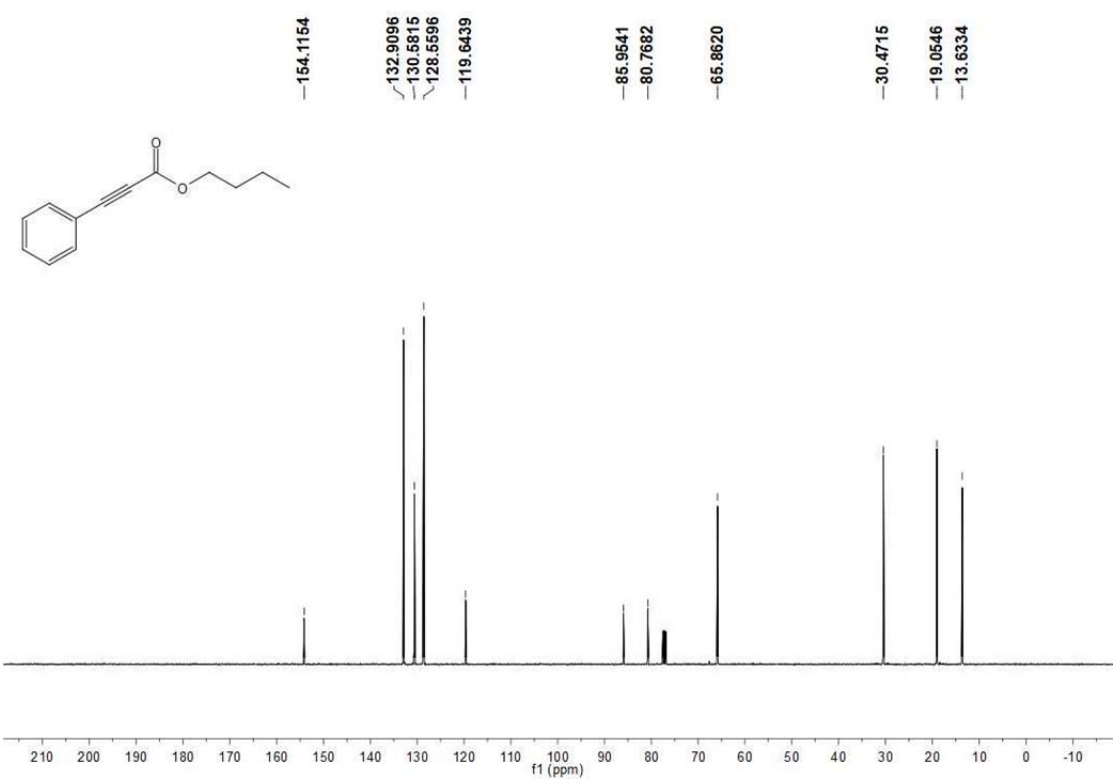


Fig. S60 $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$

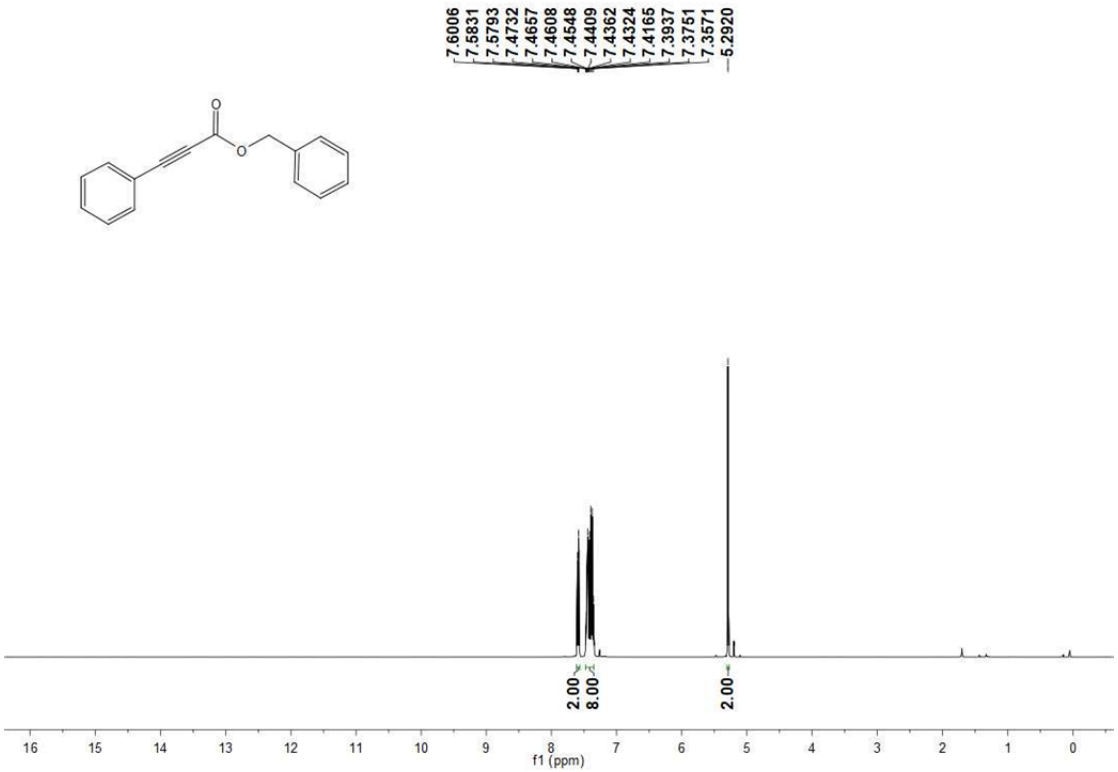


Fig. S61 ^{1}H NMR spectrum of **7b** in $CDCl_3$

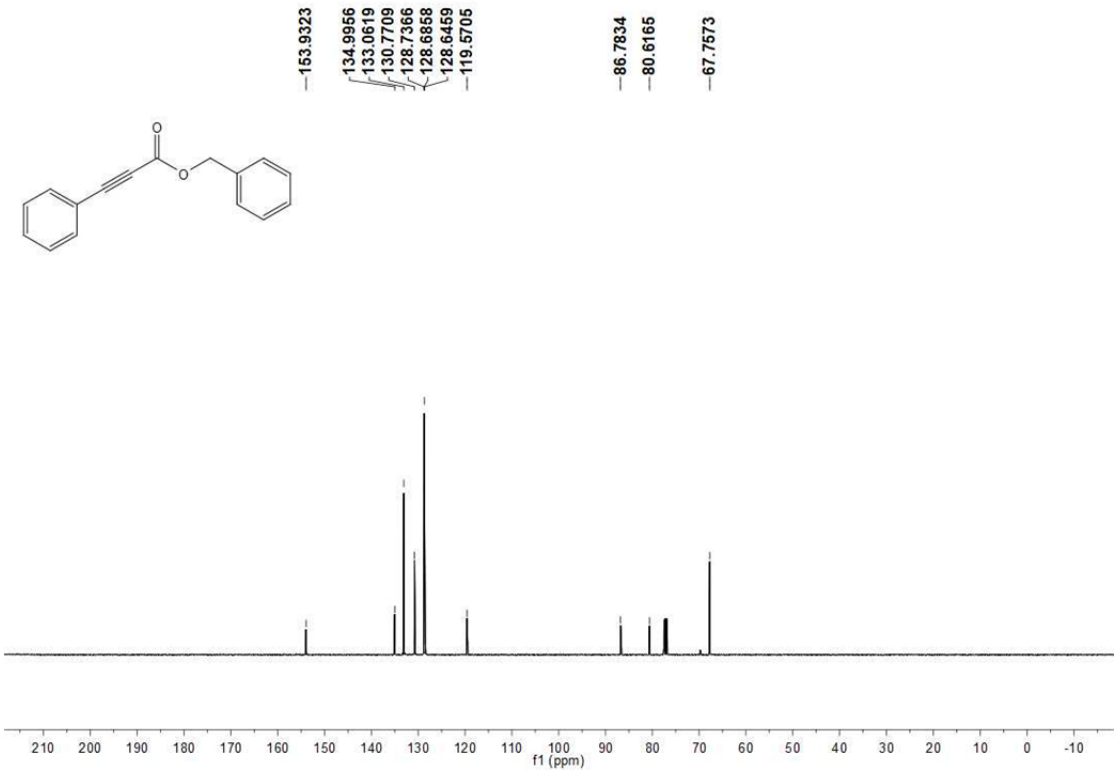


Fig. S62 $^{13}C\{^{1}H\}$ NMR spectrum of **7b** in $CDCl_3$

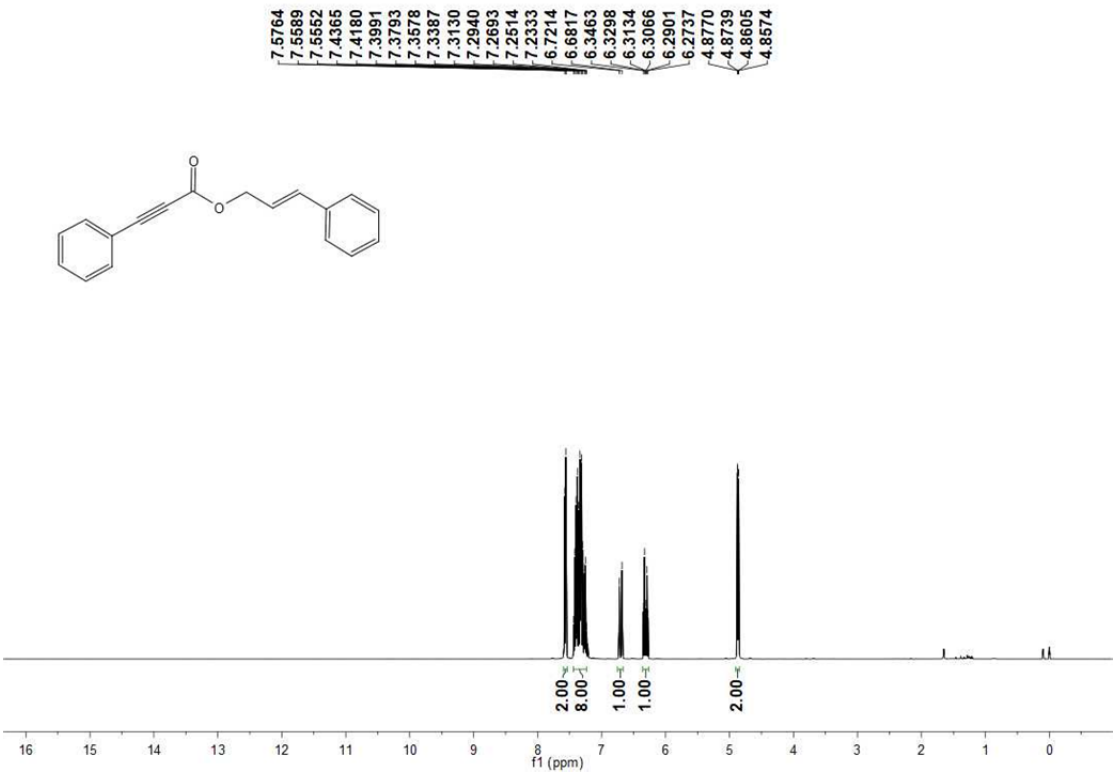


Fig. S63 ^{1}H NMR spectrum of **7c** in $CDCl_3$

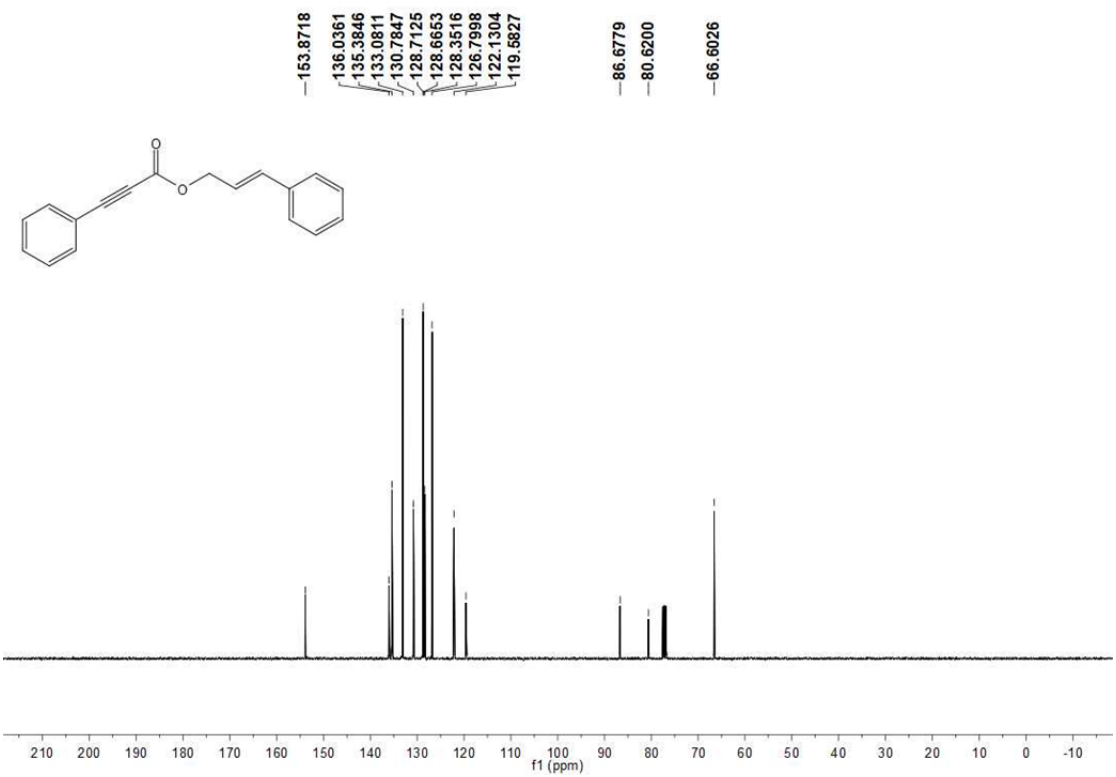


Fig. S64 $^{13}C\{^{1}H\}$ NMR spectrum of **7c** in $CDCl_3$

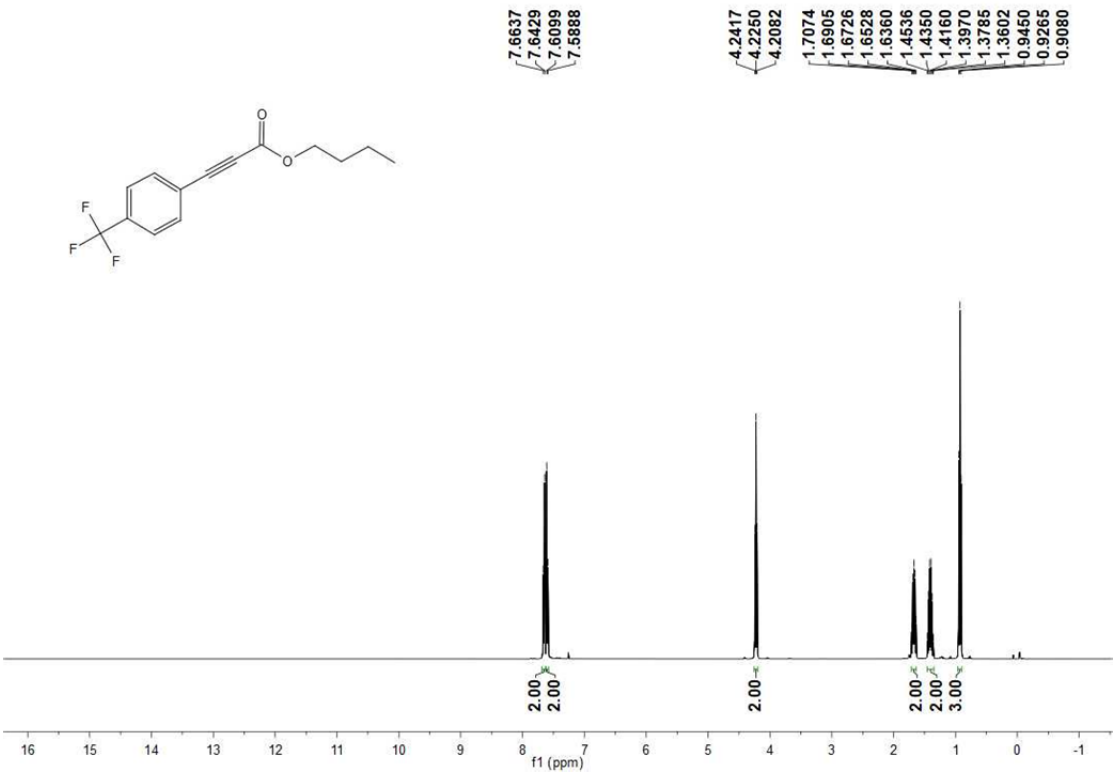


Fig. S65 ^{1}H NMR spectrum of **7d** in $CDCl_3$

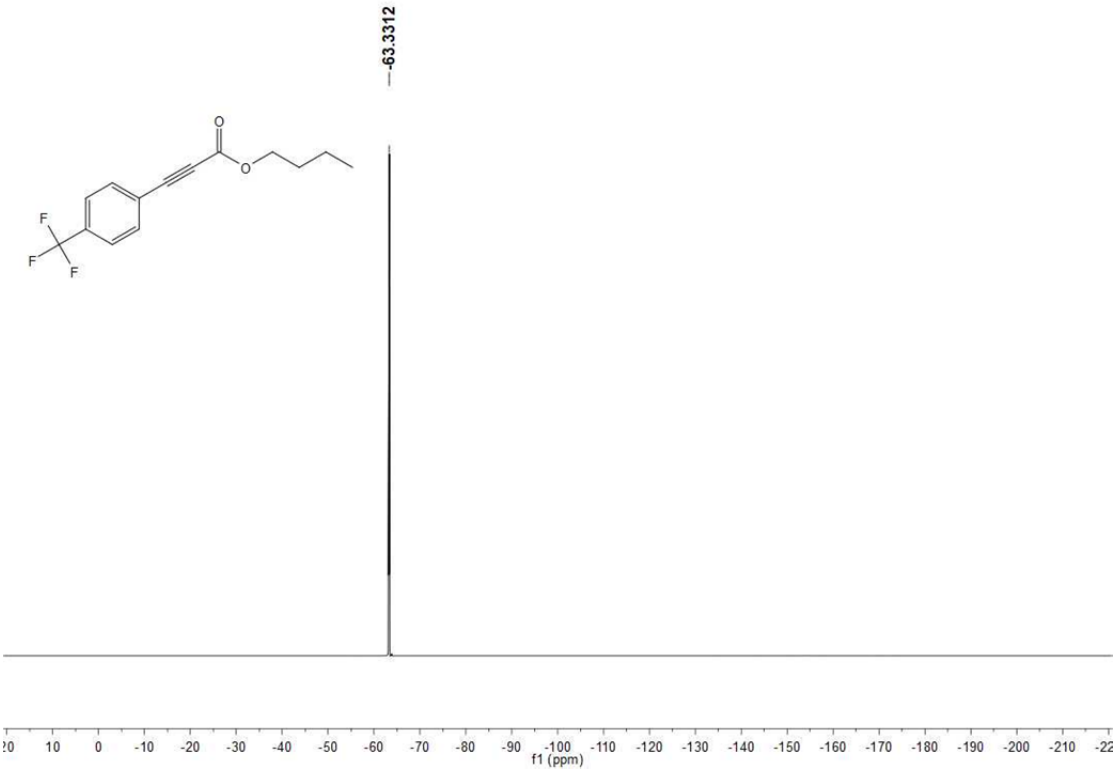


Fig. S66 ^{19}F NMR spectrum of **7d** in $CDCl_3$

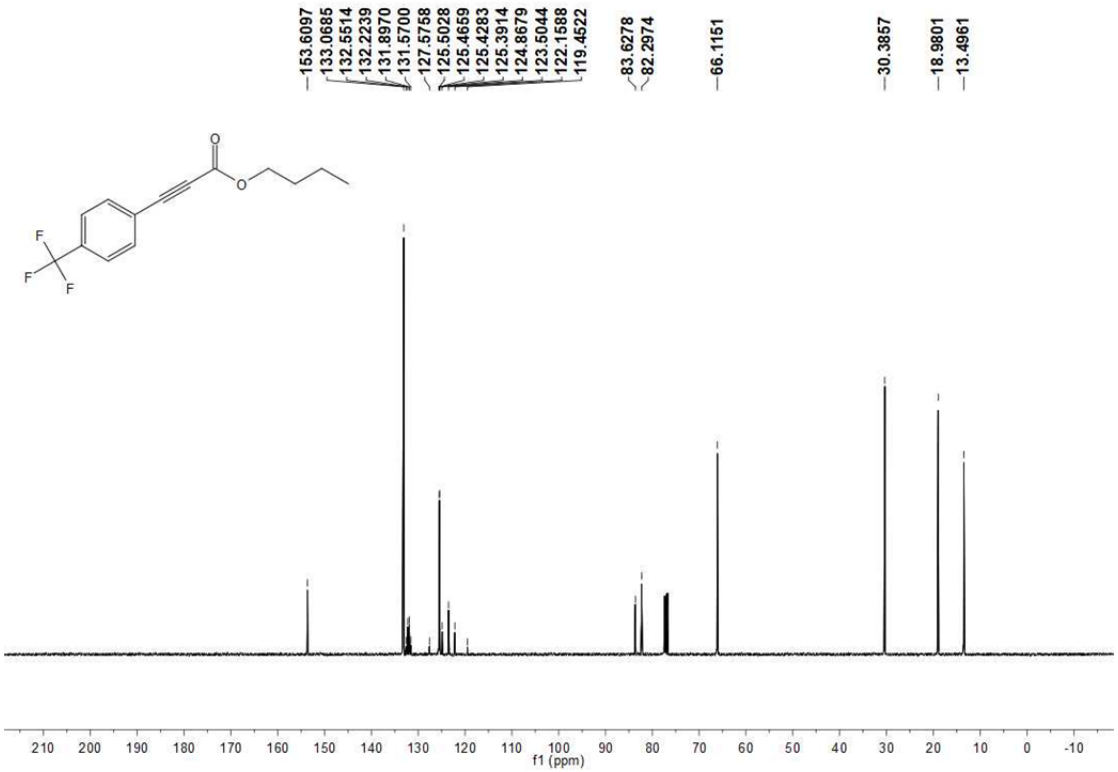


Fig. S67 $^{13}C\{^{1}H\}$ NMR spectrum of **7d** in $CDCl_3$

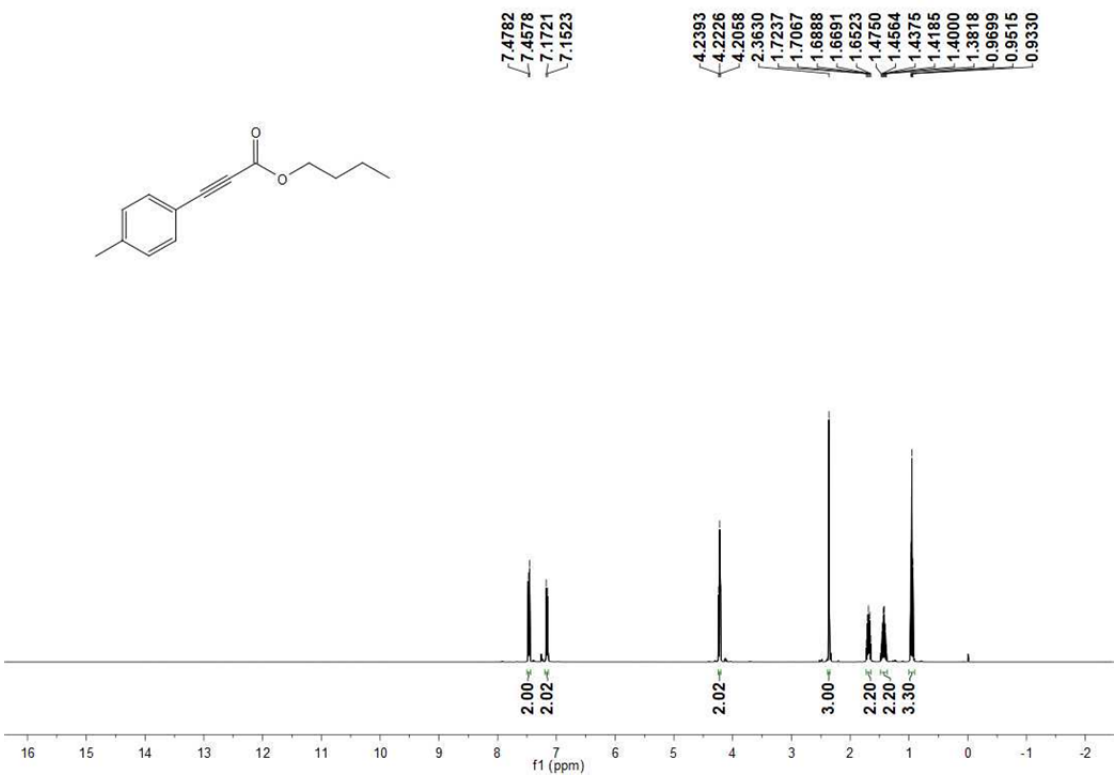


Fig. S68 ^{1}H NMR spectrum of **7e** in $CDCl_3$

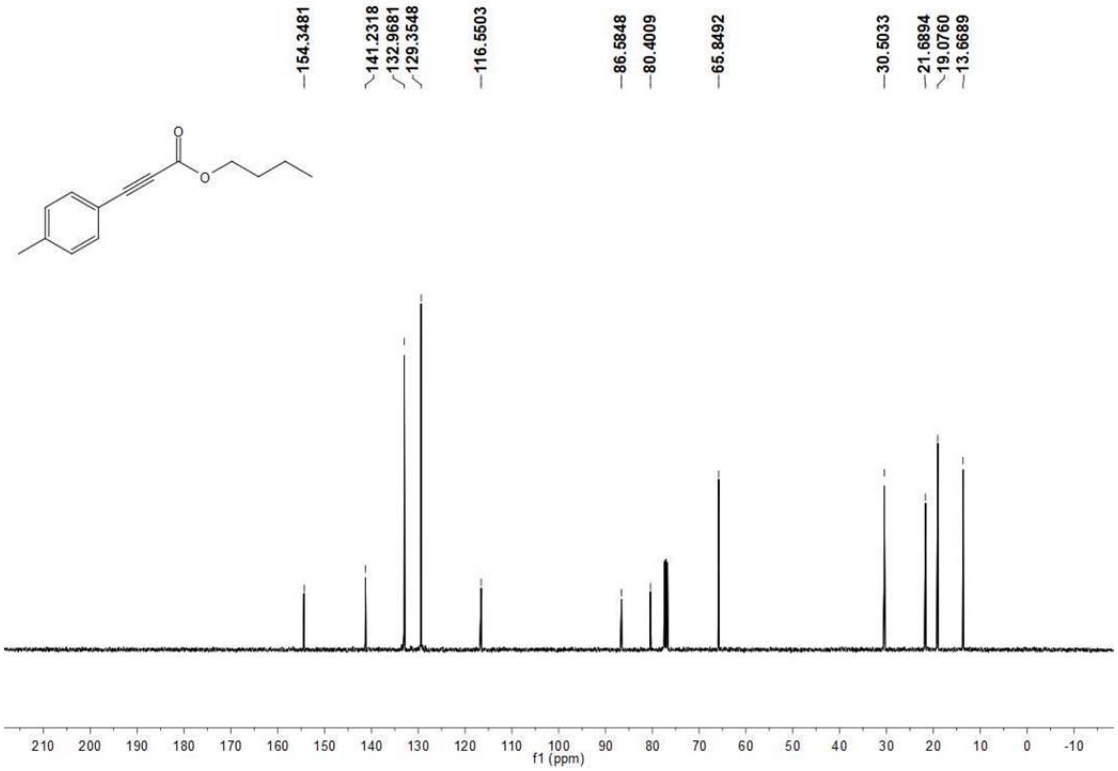


Fig. S69 $^{13}C\{^{1}H\}$ NMR spectrum of **7e** in $CDCl_3$

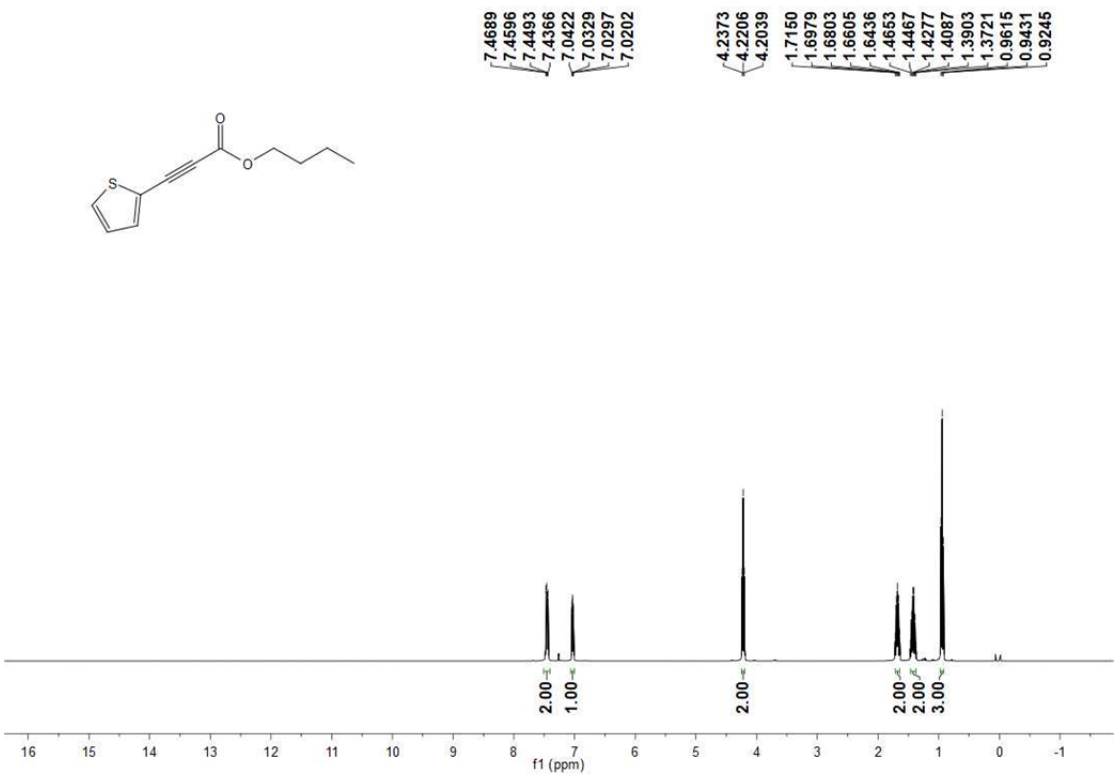


Fig. S70 ^{1}H NMR spectrum of **7f** in $CDCl_3$

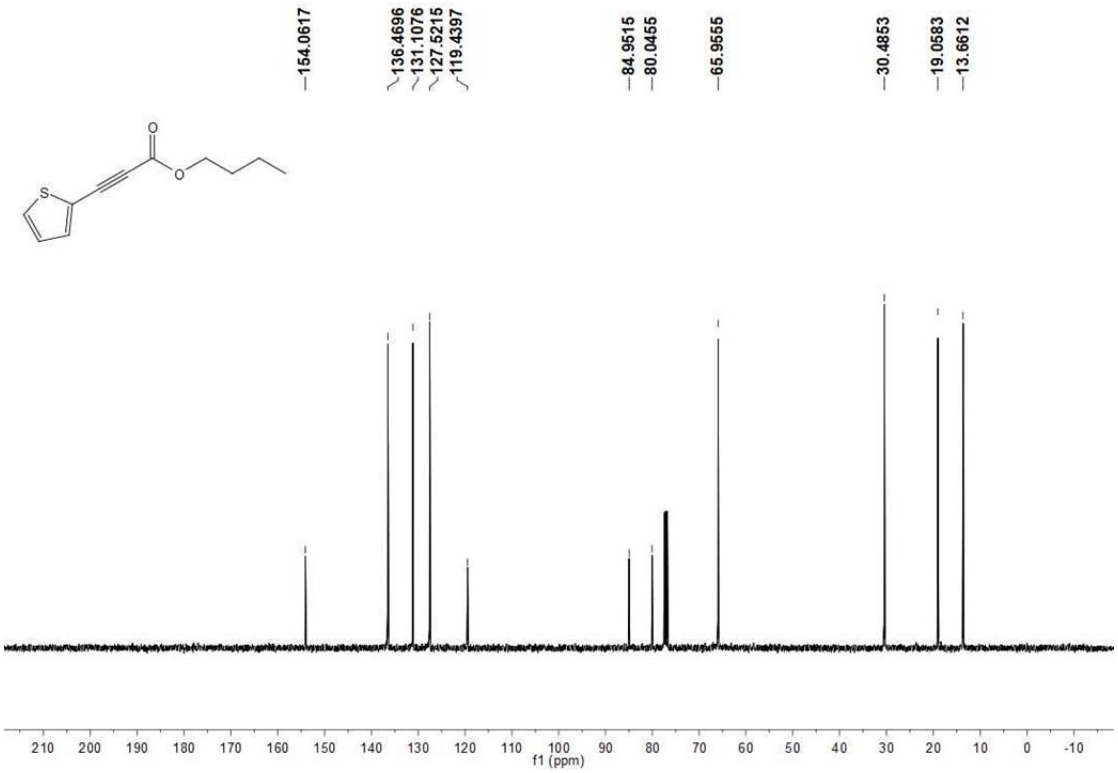


Fig. S71 $^{13}C\{^{1}H\}$ NMR spectrum of **7f** in $CDCl_3$

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