Cu-catalyzed Aryl-carbocyclization of Alkynes with Diaryliodonium Salts through C-C Bond Formation on Inert $C_{(sp3)}$-H Bond

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1. General Comments

All the reactions were conducted in a pre-dried screwcapped tube with a Teflon-lined septum under N_2 atmosphere. Ph_2IPF_6 was purchased from Alfa-aesar. Diaryliodonium hexafluorophosphates except Ph_2IPF_6 were prepared according to the literatues[1]. Alkynes reagents except for those commercially available were prepared referring to the literatures. All of the solvents were freshly distilled before use. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL AL-300MHz, AL-400MHz or AL-600MHz spectrometer at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, dq, q, t, d, s referred to multiplet, doublet quartet, quartet, triplet, doublet, singlet. Chemical shifts of representative products (**3b, 3l** and **3a'**) were assigned according to 2D-NMR experiments recorded at AL-600MHz spectrometer.

HRMS experimets were carried out on a on a Thermo Scientific LTQ Oribtrap XL (Bremen, Germany). The linear ion trap (LTQ) part of the hybrid MS system was equipped with Atmospheric-pressure Photoionization (APPI) probe and operated in the positive ion mode. The discharge current is 8 kV with a capillary voltage at 25 V, and a nitrogen sheath gas (30 units), a nitrogen auxiliary gas (5 units) and sweep gas (5 unites) were used to stabilize the spray. The heated capillary was set at 350 °C. The HRMS experiments were operated in the FTMS mode at a resolution of 100,000. The scan range of each full MS scan was from 50 to 2000 Da. The obtained data were processed using XCalibur (v. 2.0) software. Melting points were tested by mini-Lamp. MS data were monitored by GC-MS. The reaction progress was detected by GC-MS if applicable, with n-Dodecane as internal standard.

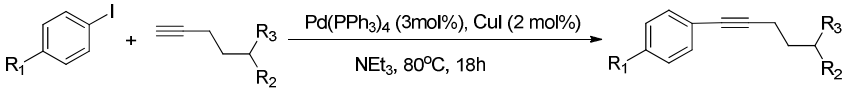
2. Experimental Section

2.1 Starting material: Diaryliodonium salts

Diaryliodonium salts with OTf^- anion were synthesized according to the literature procedures.[1] Diaryliodonium salts of OTf^- anion were converted to the ones of PF_6^- anion by stirring with KPF_6 (6.0 equiv) in acetonitrile for 24 h.

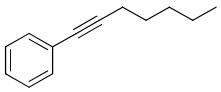
2.2 Starting material: Alkynes

2.2.1 General procedure for the preparation of 1-phenyl-1-heptyne (1b), 1-phenyl-1-octyne (1c), 1-(4-trifluoromethyl)-phenyl-1-hexyne (1e), 1-biphenyl-1-hexyne (1f), 5-methyl-1-phenyl-1-hexyne (1h), 5-methyl-1-(4-chloride)-phenyl-1-hexyne (1i) and 5-methyl-1-(4-trifluoromethoxy)-phenyl-1-hexyne (1j)



R_1=H, R_2=H, R_3=CH_2CH_3 89%
R_1=H, R_2=H, R_3=$CH_2CH_2CH_3$ 86%
R_1=Ph, R_2=H, R_3=CH_3 85%
R_1=CF_3, R_2=H R_3=CH_3 80%
R_1=H, R_2=CH_3, R_3=CH_3 88%
R_1=Cl, R_2=CH_3 R_3=CH_3 82%
R_1=OCF_3, R_2=CH_3, R_3=CH_3 78%

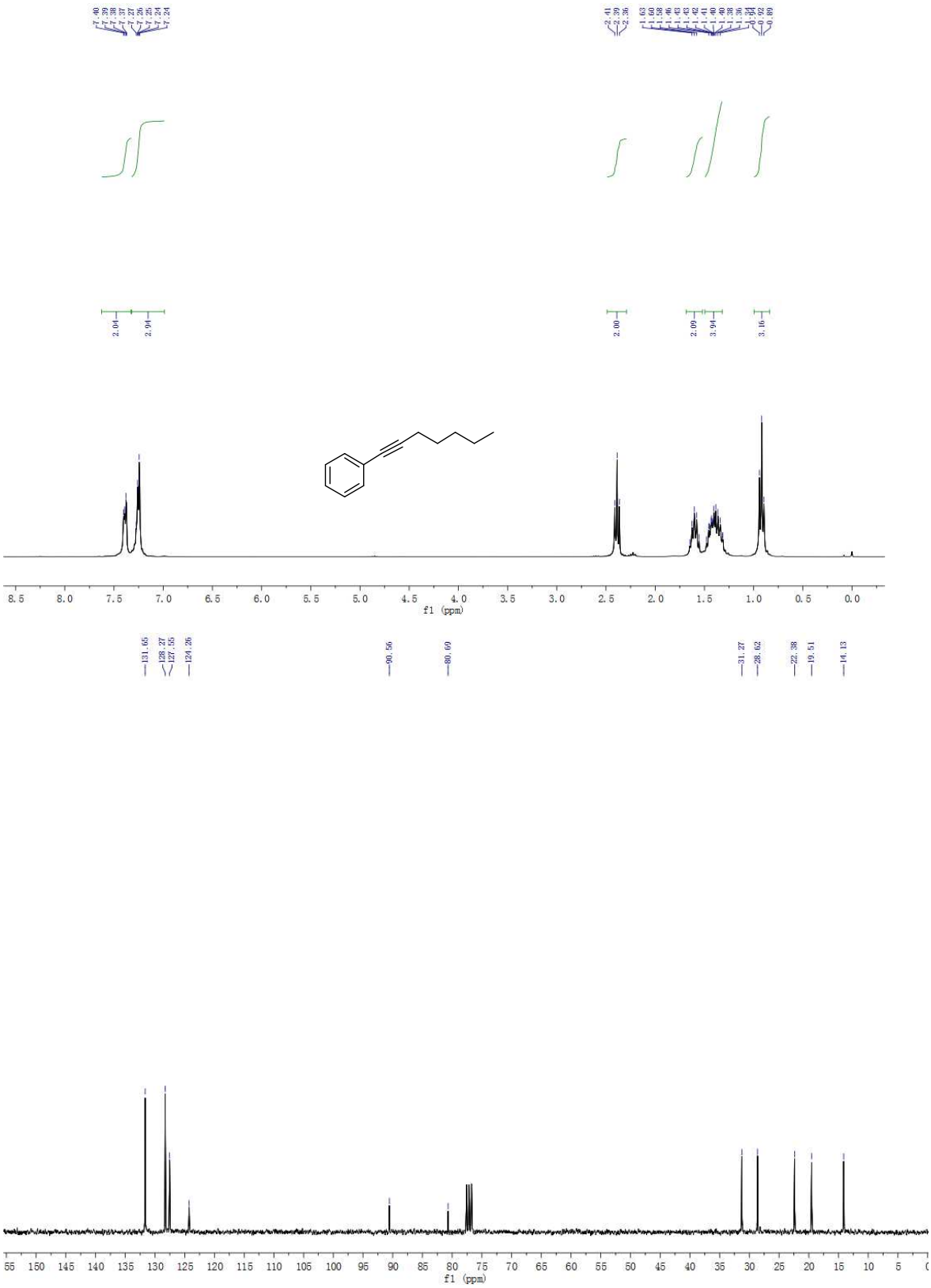
A Schlenk tube was charged with the mixture of $Pd(PPh_3)_4$ (3 mol%,) and CuI (2 mol%). The tube was evacuated and recharged with N_2 for 3 times. After the alkynes and appropriate iodobenzene were added, the tube was sealed and the mixture was allowed to stir at 80 °C for 18 h. After the starting materials were completed converted, the mixture was cooled to room temperature. Then $NaHCO_3$ solution was added and the mixture was extracted with DCM (25 mL x 3). The organic solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (pure petroleum ether) provided the corresponding products. [2]



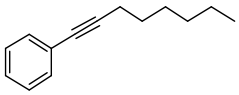
1-phenyl-1-heptyne (**1b**) :Pale yellow liquid; yield:89%

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.40-7.37 (m, 2H), 7.27 – 7.24 (m, 3H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.52 (m, 2H), 1.49 – 1.32 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.7, 128.3, 127.6, 124.3, 90.6, 80.7, 31.3, 28.6, 22.4, 19.5, 14.1



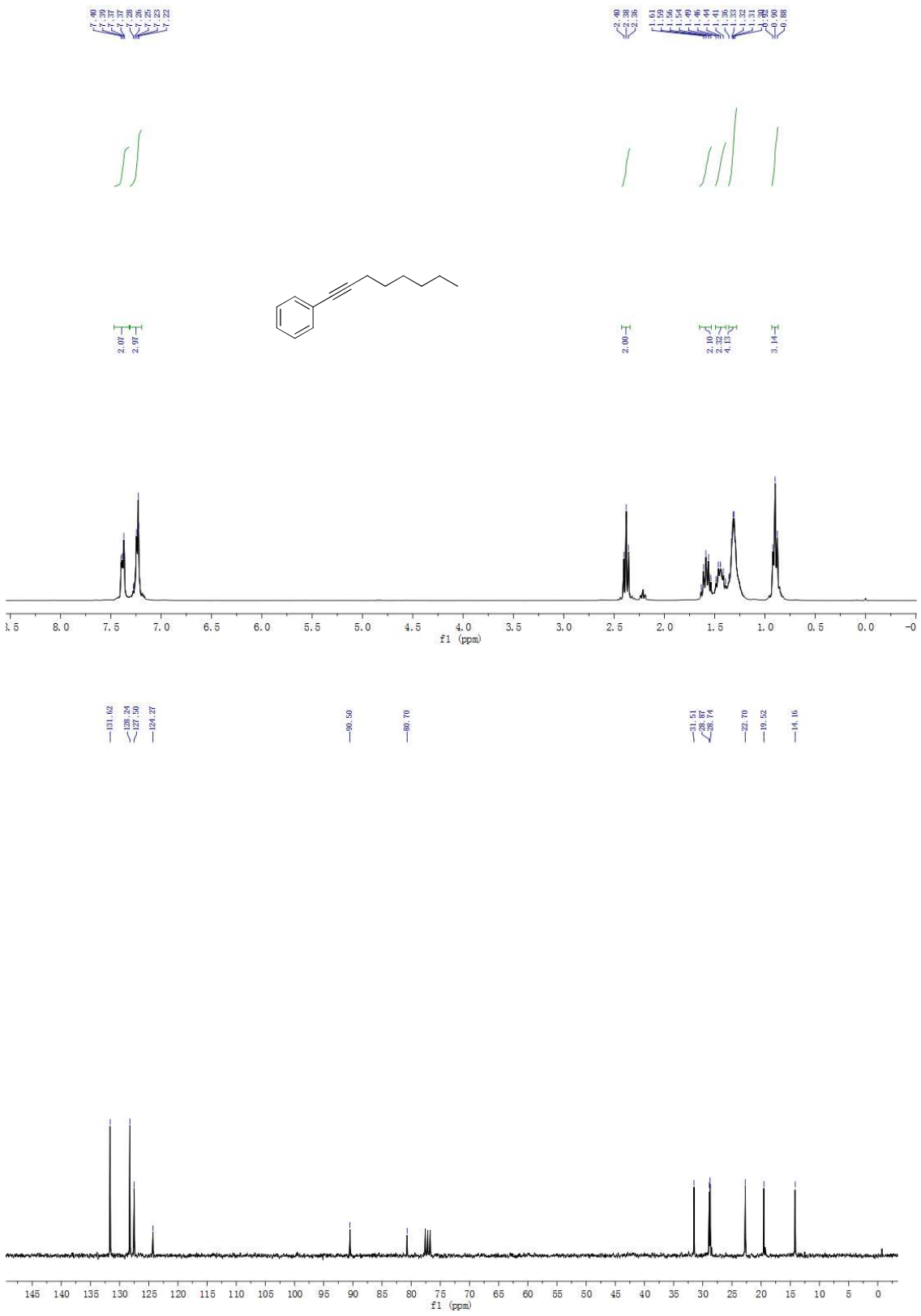
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



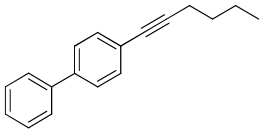
1-phenyl-1-octyne (**1c**): Pale yellow liquid; yield: 86%.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.40-7.37 (m, 2H), 7.31 – 7.19 (m, 3H), 2.38 (t, *J* = 7.0 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.49 – 1.39 (m, 2H), 1.36 – 1.28 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.62, 128.2, 127.5, 124.3, 90.5, 80.7, 31.59, 28.7, 22.7, 19.5, 14.2



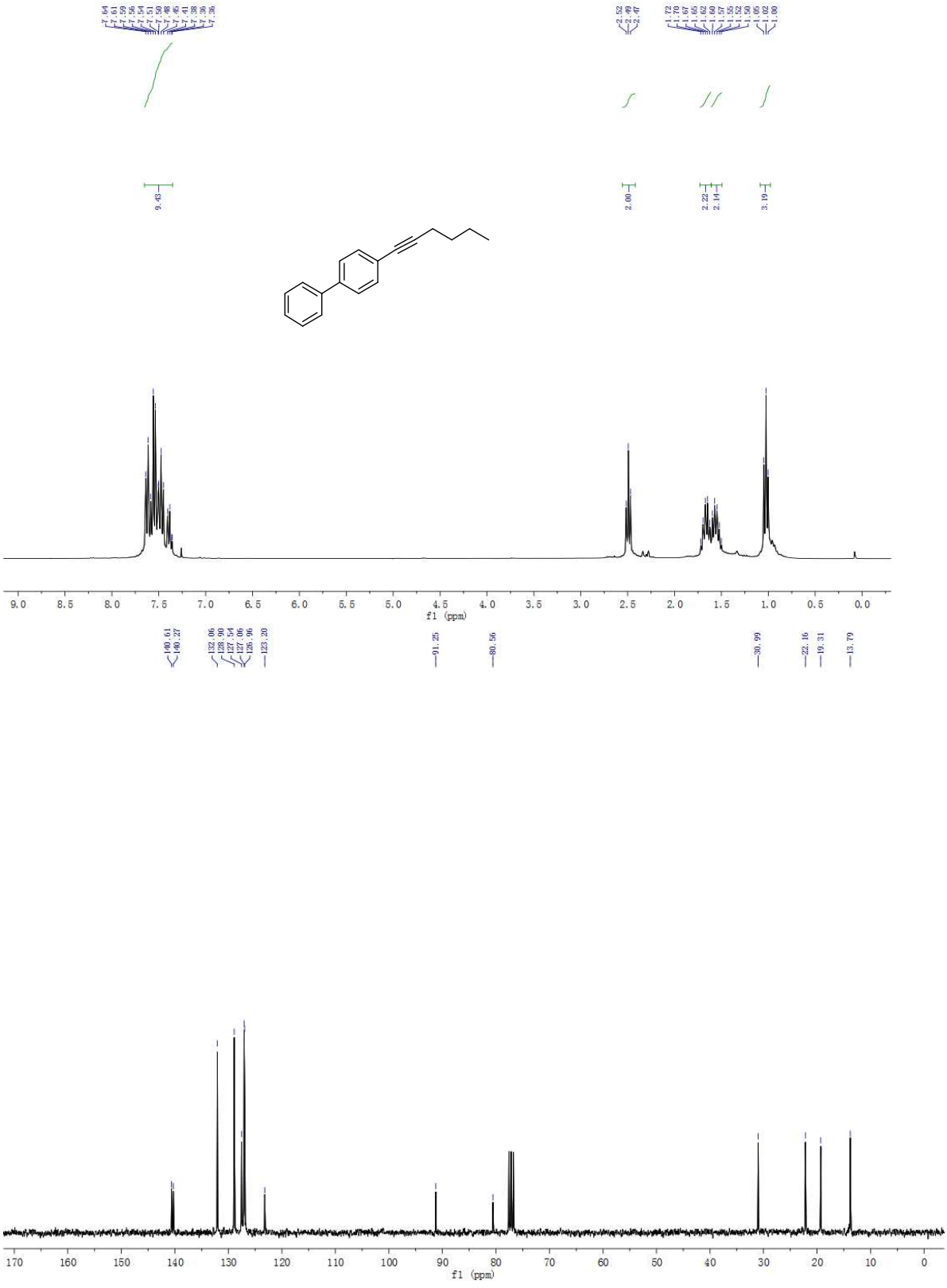
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



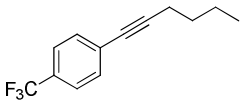
1-biphenyl-1-hexyne (**1f**): Pale yellow liquid; yield: 85%

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.65 – 7.35 (m, 9H), 2.49 (t, *J* = 6.9 Hz, 2H), 1.72-1.62 (m, 2H), 1.60-1.50 (m, 2H), 1.03 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 140.6, 140.3, 132.1, 128.9, 127.5, 127.1, 127.0, 123.2, 91.3, 80.6, 31.0, 22.2, 19.3, 13.8



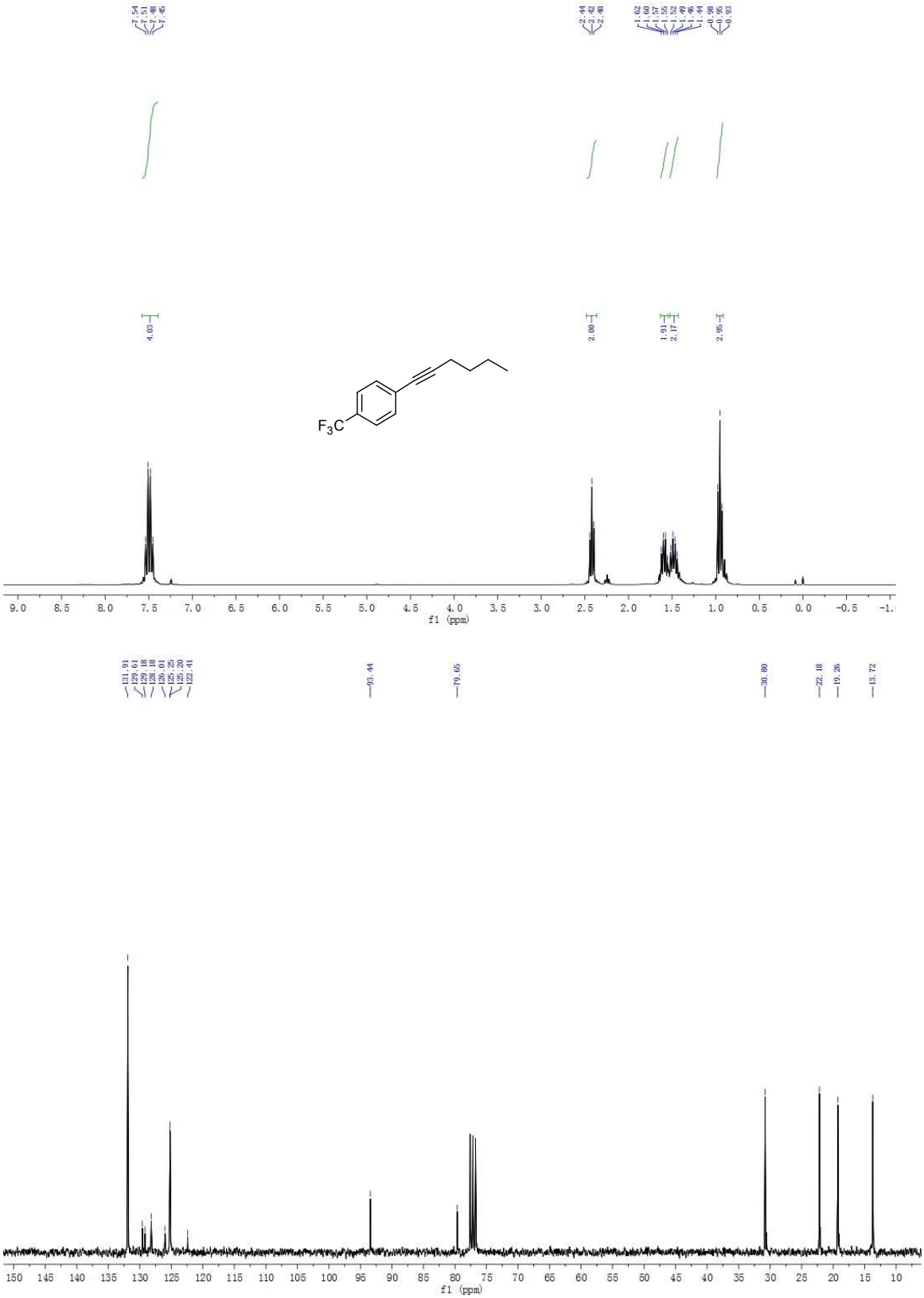
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



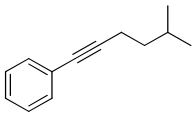
1-(4-trifluoromethyl)-1-hexyne (**1e**): Pale yellow liquid; yield: 89%

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.54-7.45 (m, 4H), 2.42 (t, *J* = 7.0 Hz, 2H), 1.62 -1.55(m, 2H), 1.52-1.44 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.9, 128.2 (dd, *J* = 173.7, 98.3 Hz), 125.2 (d, *J* = 3.8 Hz), 122.4, 93.4, 79.7, 30.8, 22.2, 19.3, 13.7



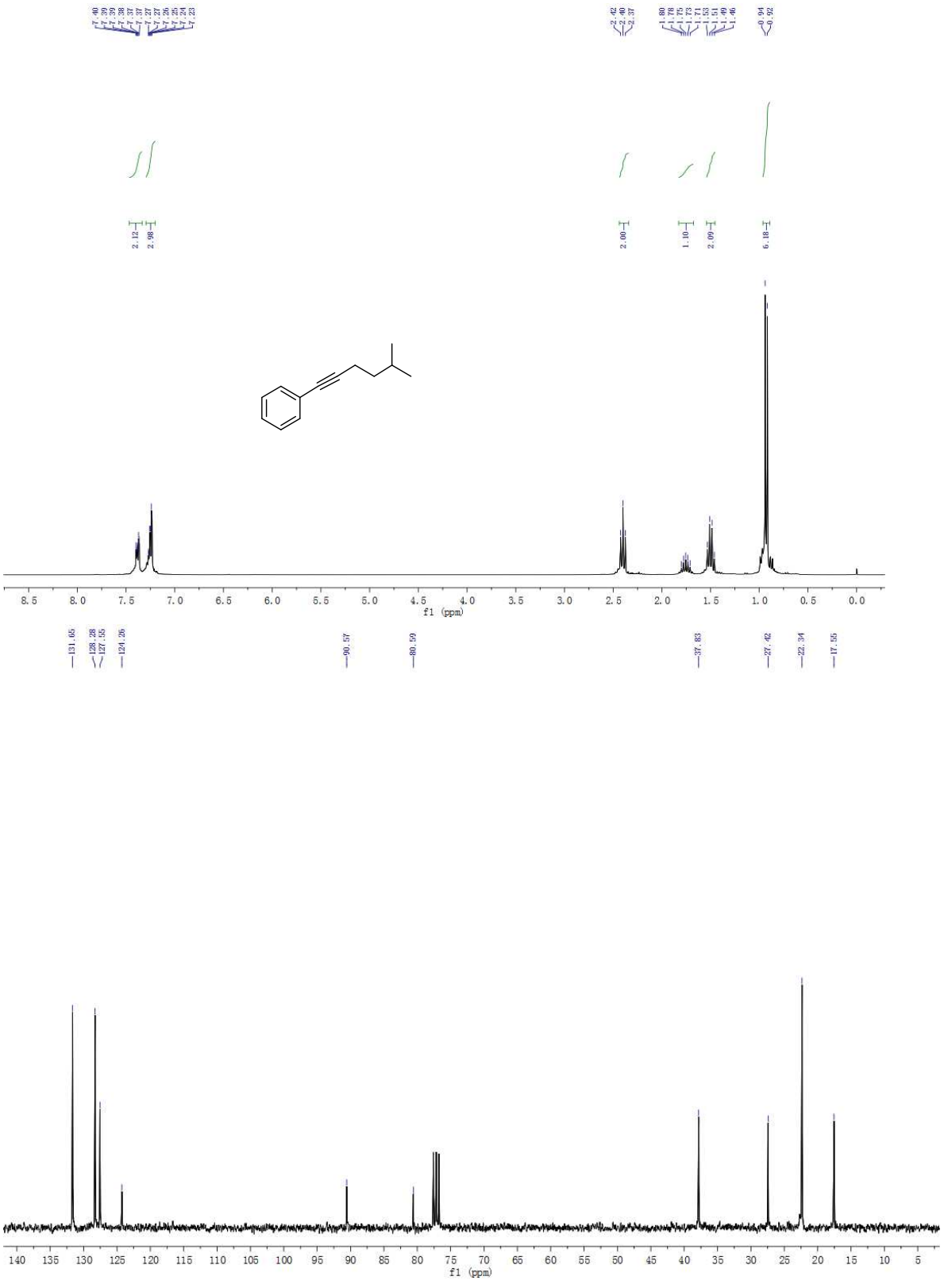
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



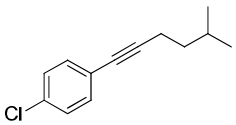
5-methyl-1-phenyl-1-hexyne (**1h**): Pale yellow liquid; yield: 88%.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.47 – 7.34 (m, 2H), 7.30 – 7.20 (m, 3H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.80-1.71 (m, 1H), 1.53-1.46 (m, 2H), 0.93 (d, *J* = 6.7 Hz, 6H).

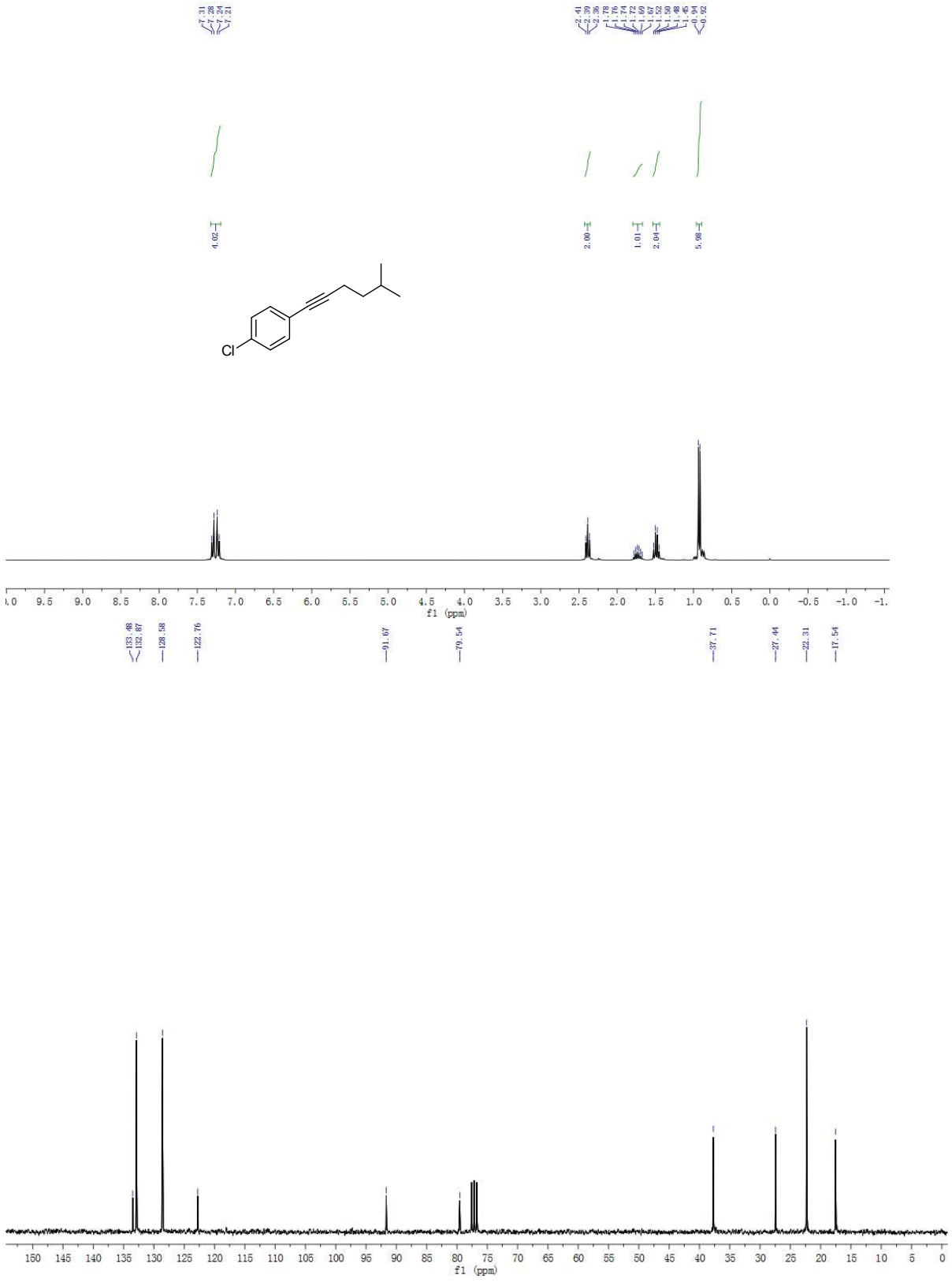
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.7, 128.3, 127.6, 124.3, 90.6, 80.6, 37.8, 27.4, 22.34 (s), 17.6



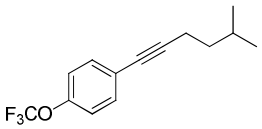
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



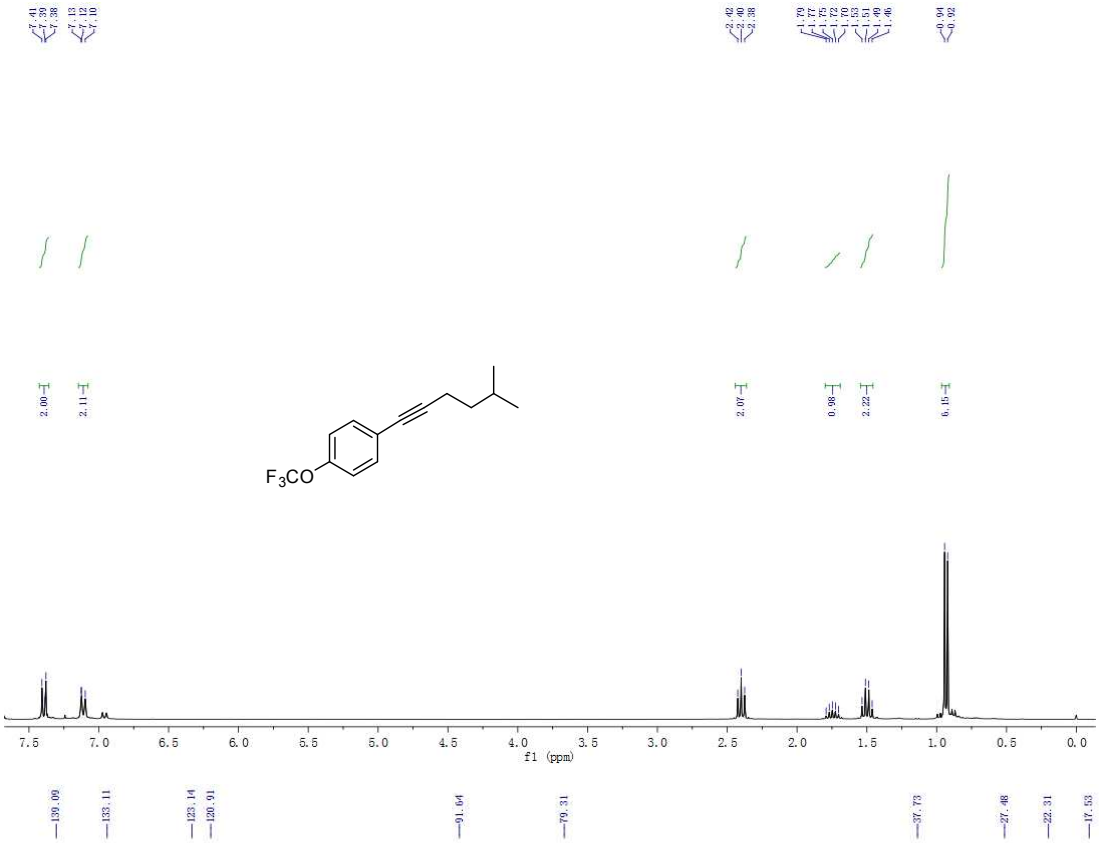
5-methyl-1-(4-chloride)-phenyl-1-hexyne (**1i**): Pale yellow liquid; yield: 82%.
^{1}H NMR (301 MHz, CHLOROFORM-D) δ7.31-7.21 (m, 4H), 2.39 (t, *J* = 7.4 Hz, 2H), 1.78-1.69 (m, 1H), 1.52-1.45 (m, 2H), 0.93 (d, *J* = 6.4 Hz, 6H).
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 133.5, 132.9, 128.6, 122.8, 91.7, 79.5, 37.7, 27.4, 22.31, 17.5

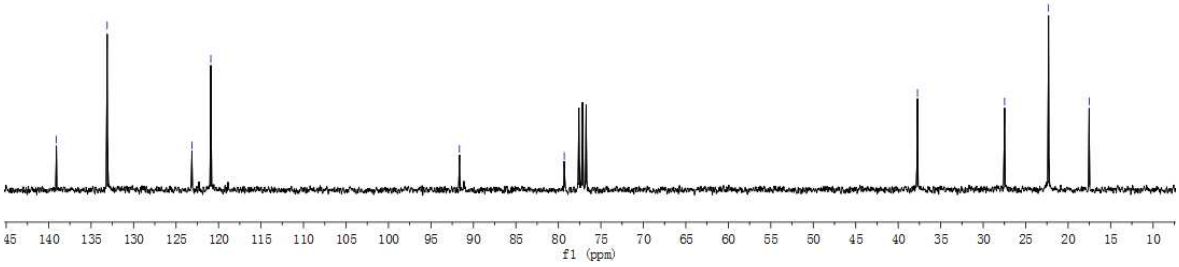


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



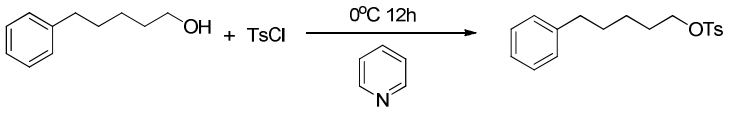
5-methyl-1-(4-trifluoromethoxy)-phenyl-1-hexyne (**1j**): Pale yellow liquid; yield: 78%
^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.42 – 7.36 (m, 2H), 7.14 – 7.07 (m, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.79-1.70 (m, 1H), 1.53-1.46 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 139.1, 133.1, 123.1, 120.9, 91.6, 79.3, 37.7, 27.5, 22.31, 17.5



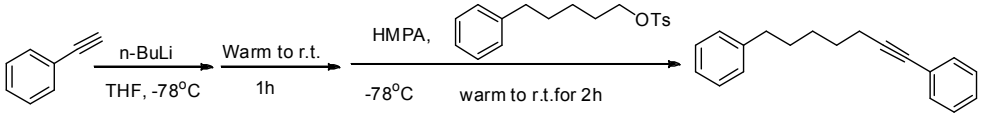


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

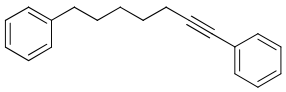
2.2.2 Procedure for the preparation of 1,7-diphenyl-1-heptyne (1d)



TsCl (24 mmol, 4.58 g) was placed in a round-bottom flask and 5-phenyl-1-pentanol (20 mmol, 3.36 mml) solution in pyridine (40 mmol, 32 mml) was added at 0°C. The mixture was stir at 0°C for 12 h. The reaction was quenched by adding 40 ml of HCl aqueous solution (1mol/L) and then extracted with DCM (50 mL x 3). The organic solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether/DCM=20:1) provided the desired product (yield: 67%).[3]



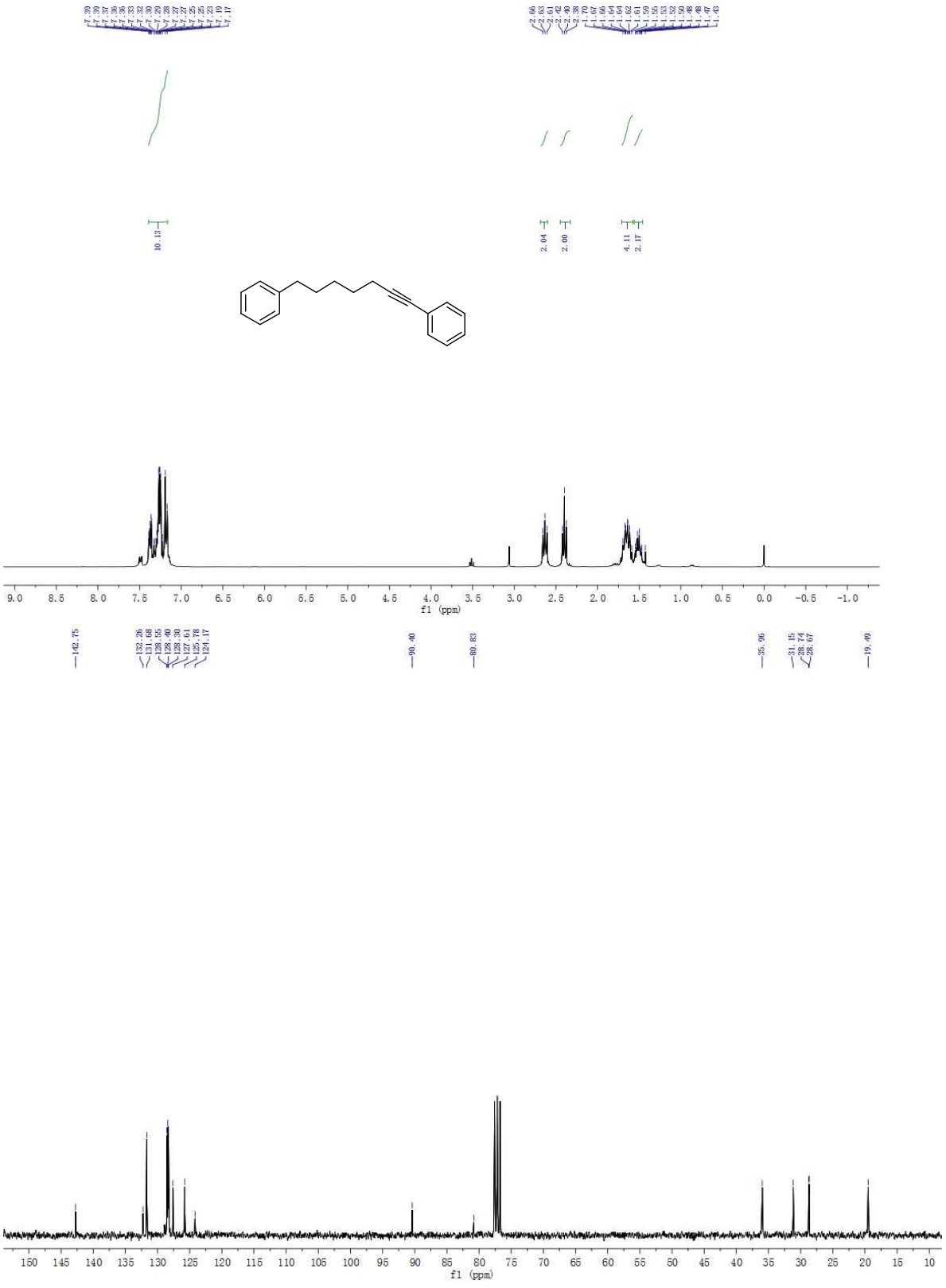
To a solution of phenyl acethylene (1.0 mL, 9 mmol) in THF (20 mL) at -78°C was added n-BuLi (6.0 mL, 1.6 M in hexane, 9.5 mmol), and the mixture was allowed to warm to rt over 0.5 h. The mixture was then cooled to -78 °C before HMPA (1.74 mL, 10 mmol) and 5-phenylpentyl-tosylate (2.86g, 9 mmol) were added. The mixture was allowed to warm to rt about 2 h and then was quenched with water, and extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether) to give 1,7-diphenyl-1-heptyne (**1d**) (yield:83%)[4]



1,7-diphenyl-1-heptyne **(1d)**: Pale yellow liquid; yield: 83%

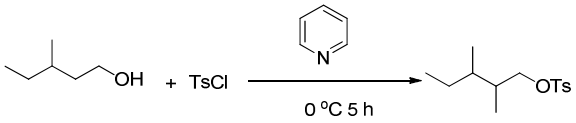
^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.39-7.17 (m, 10H), 2.66-2.61 (m, 2H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.70-1.59 (m, 4H), 1.55-1.43 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 142.8, 132.3, 131.7, 128.6, 128.4, 128.3, 127.6, 125.8, 124.2, 90.4, 80.8, 36.0, 31.2, 28.7, 28.7, 19.5

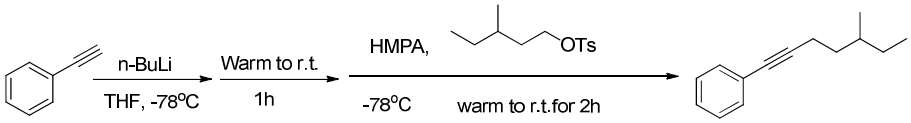


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

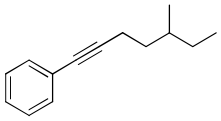
2.2.3 Procedure for the preparation of 5-methyl-1-phenyl-1-heptyne (1k)



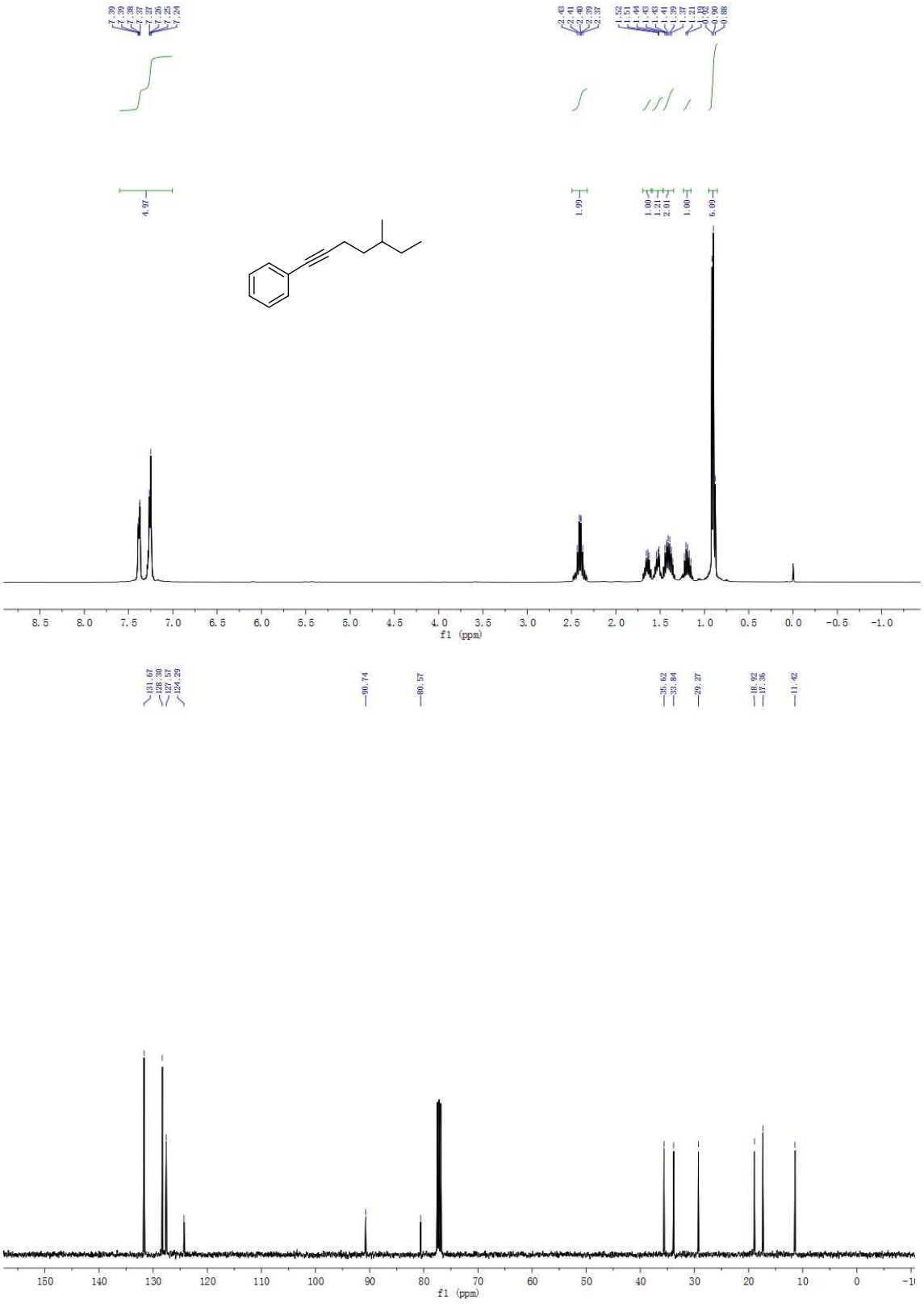
TsCl (24 mmol, 4.58 g) was placed in a round bottom flask and 3-methyl-1-pentanol (20 mmol, 2.15 ml) solution in pyridine (40 mmol, 3.2 ml) was added at 0°C. The mixture was stir at 0°C for 5 h. The reaction was quenched by adding 40 ml of HCl aqueous solution (1mol/L) and then extracted with DCM (50 mL x 3). The organic solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether/DCM=20:1) provided the desired product (yield:78%)[3]



To a solution of phenyl acethylene (1.0 mL, 9 mmol) in THF (20 mL) at -78°C was added n-BuLi (6.0 mL, 1.6 M in hexane, 9.5 mmol), and the mixture was allowed to warm to rt over 0.5 h. The mixture was then cooled to -78 °C , and HMPA (1.74 mL, 10 mmol) and 3-methyl-pentyl tosylate (2.18g, 9 mmol) were added. The mixture was allowed to warm to rt about 2 h and then was quenched with water, and extracted with ether. The organic layer was washed brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether) to give 5-methyl-1-phenyl-1-heptyne (**1k**, yield:85%)[4]



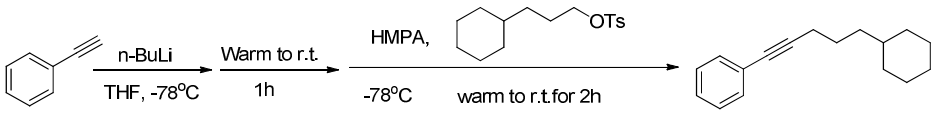
5-methyl-1-phenyl-1-heptyne**(1k)**: Pale yellow liquid; yield: 66%
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39-7.24(m,5H), 2.50-2.33 (m, 2H), 1.70-1.60 (m, 1H), 1.59-1.47 (m, 1H), 1.47-1.35 (m, 2H), 1.24-1.15 (m, 1H), 0.92-0.88 (m, 6H).
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.7, 128.37, 127.6, 124.3, 90.7, 80.6, 35.6, 33.8, 29.27 (s), 18.9, 17.4, 11.4



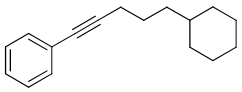
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

2.2.4 Procedure for the preparation of 5-cyclohexyl-1-phenyl-1-pentyne (1n)

TsCl (24 mmol, 4.58 g) was placed in a round bottom flask and 3-cyclohexyl-1-propanol (20 mmol, 2.84g) solution in pyridine(40 mmol, 32 mml) were added at 0°C.The mixture was stir at 0°C for 5h. The reaction was quenched by adding 40 ml HCl aqueous solution (1mol/L) and then extracted with DCM (50 mL x 3). The organic solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether/DCM=20:1) provided the desired product (yield:85%)[3]



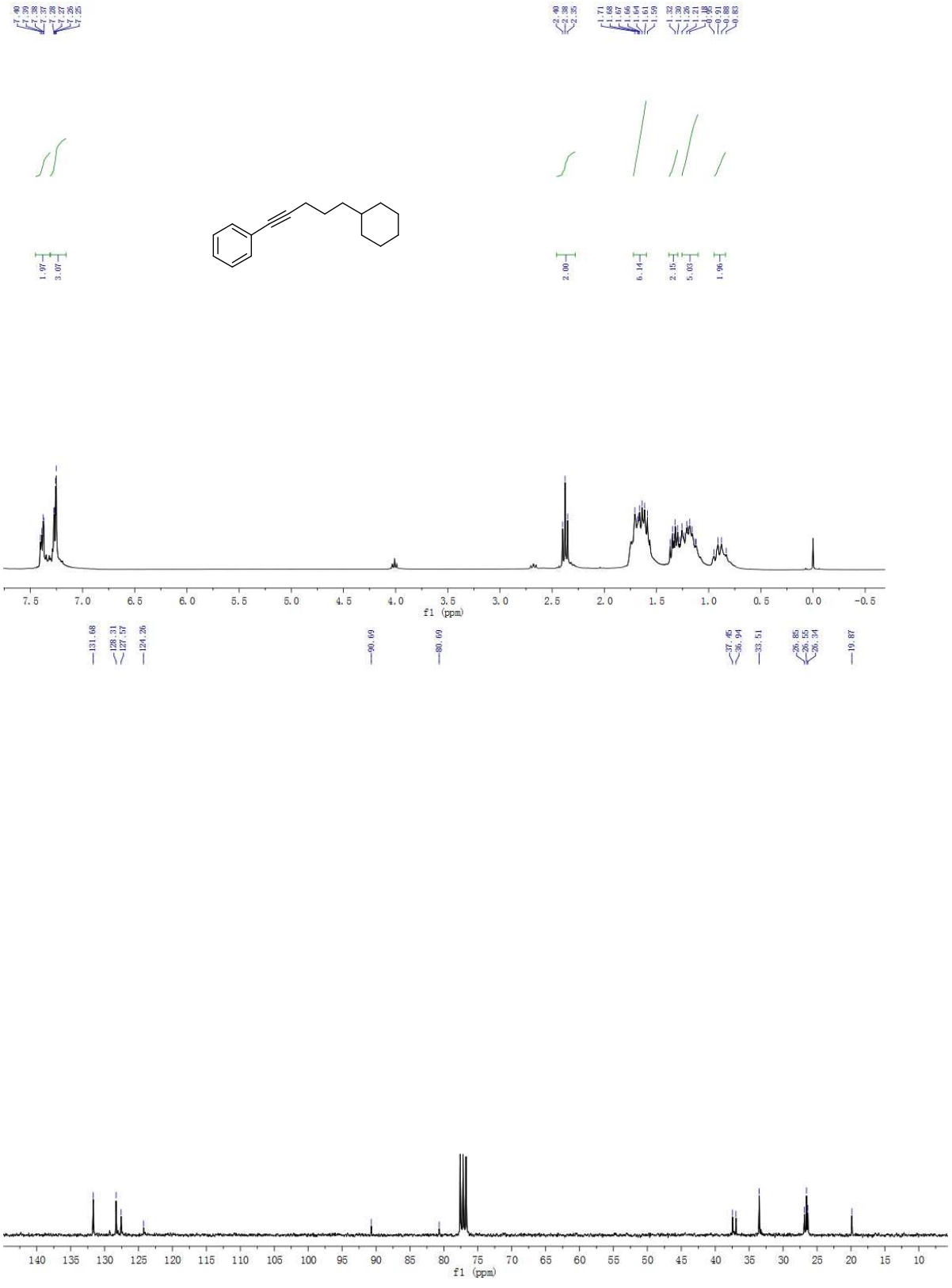
To a solution of phenyl acethylene (1.0 mL, 9 mmol) in THF (20 mL) at -78°C was added n-BuLi (6.0 mL, 1.6 M in hexane, 9.5 mmol), and the mixture was allowed to warm to rt over 0.5 h. The mixture was then cooled to -78 °C, and HMPA (1.74 mL, 10 mmol) and 3-cyclohexylpropyl tosylate (2.66g, 9 mmol) were added. The mixture was allowed to warm to rt about 2 h and then was quenched with water, and extracted with ether. The organic layer was washed brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether) to give 5-cyclohexyl-1-phenyl-1-pentyne (**1n**, yield: 82%)[4]



5-cyclohexyl-1-phenyl-1-pentyn(**1n**): Pale yellow liquid; yield: 70%

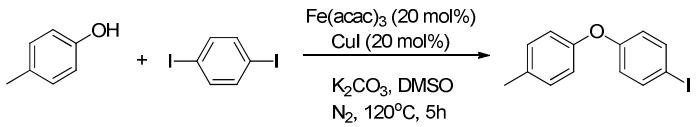
^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.40-7.37 (m, 2H), 7.28-7.25 (m, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.71-1.59 (m, 6H), 1.33-1.18 (m, 2H), 1.26-1.15 (m, 5H), 0.95-0.83 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.7, 128.37, 127.6, 124.3, 90.7, 80.7, 37.5, 37.0, 33.5, 26.9, 26.6, 26.3, 19.9



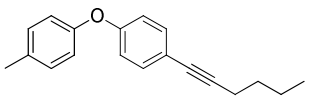
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

2.2.5 Procedure for the preparation of 1-(hex-1-yn-1-yl)-4-(p-tolyloxy)benzene (1g)



$Fe(acac)_3$ (706.34 mg, 2 mmol) ,CuI (380.9 mg, 2 mmol) and 1,4-Diiodobenzene (3.96 mg, 12 mmol) were placed into a dry a Schlenk tube. The tube was evacuated and recharged with N_2 for 3 times. After the solvent DMSO (10 ml) and 4-Cresol(1.1 ml, 10 mmol) were added, the tube was sealed and the mixture was allowed to stir at 120 °C for 5 h. After the starting materials were completed converted, the mixture was cooled to room temperature, then $NaHCO_3$ was added and the mixture was extracted with DCM (25 mL x 3). The organic solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether) provided the desired product (yield: 51%).[5]

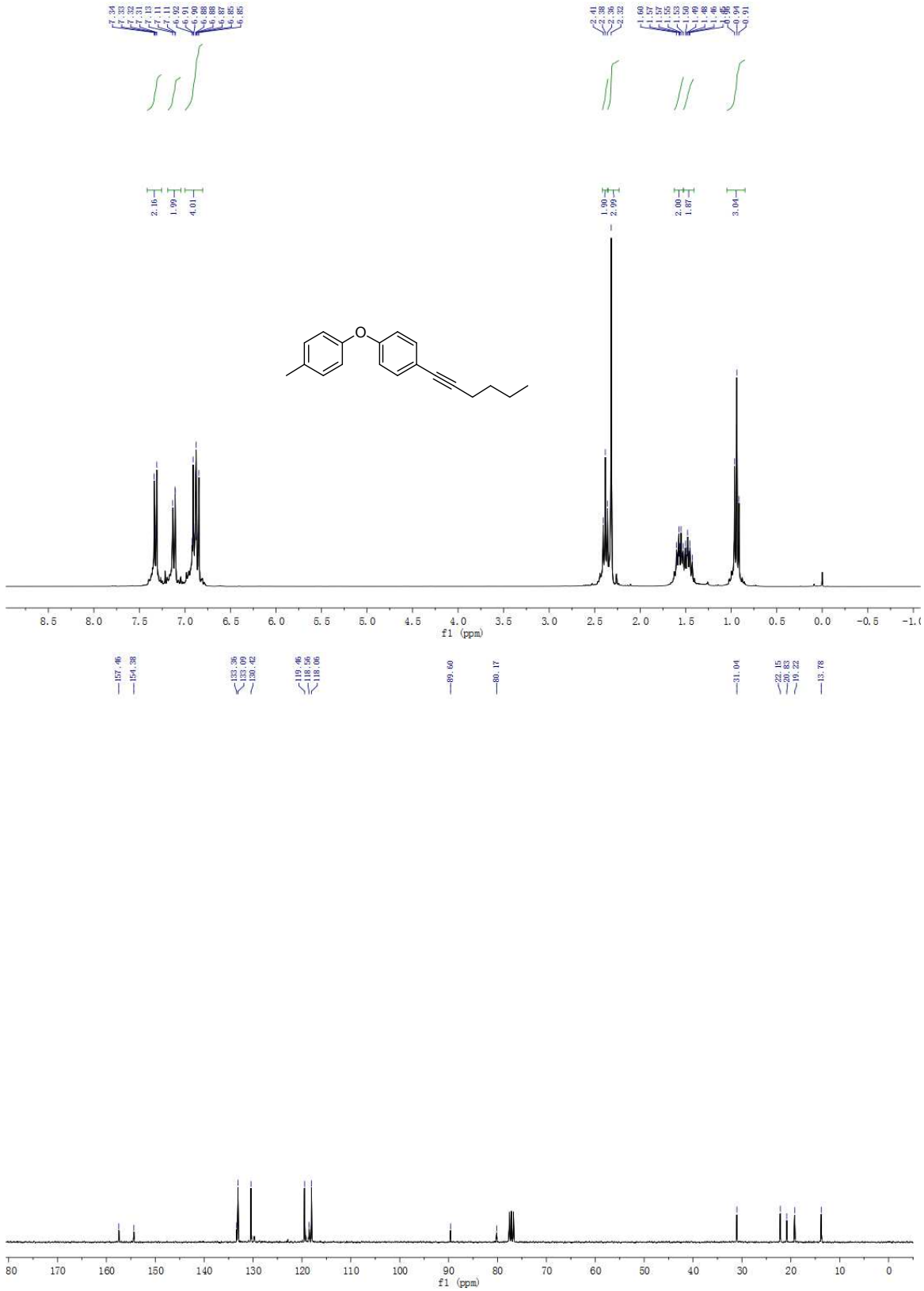
Sonogasira coupling reaction was conducted according to the procedure of **2.2.1** to get (1-hexynyl)-4-(p-tolyloxy)benzene (**1g**, yield:90%).[2]



(1-hexynyl)-4-(p-tolyloxy)benzene **(1g)**: Pale yellow liquid; yield:46%

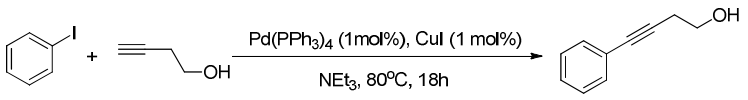
^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.42 – 7.26 (m, 2H), 7.19 – 7.05 (m, 2H), 6.92-6.85 (m, 4H), 2.38 (t, *J* = 6.9 Hz, 2H), 2.32 (s, 3H), 1.63 – 1.53 (m, 2H), 1.52 – 1.41 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.7, 128.37, 127.6, 124.3, 90.7, 80.6, 35.6, 33.8, 29.3, 18.9, 17.4, 11.4

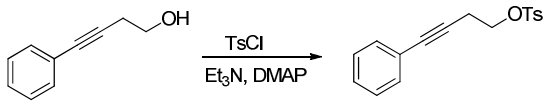


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

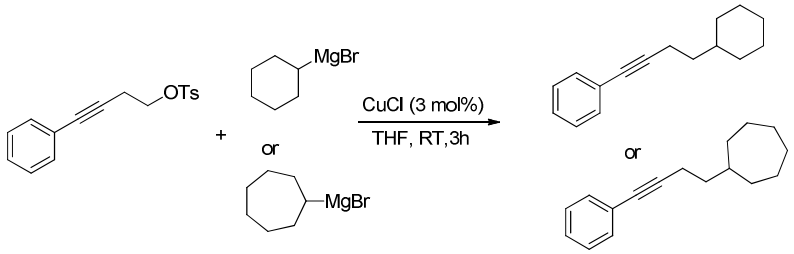
2.2.6 Procedure for the preparation of 5-cyclohexyl-1-phenyl-1-butyne (1l) and 5-cycloheptyl-1-phenyl-1-butyne (1m)



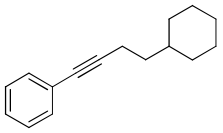
A Schlenk tube was charged with the mixture of $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) and CuI (38 mg，0.2 mmol). The tube was evacuated and recharged with N_2 for 3 times. After 3-butyn-1-ol (1.27 ml, 22 mmol) and iodobenzene (20 mmol,4.08g) were added, the tube was sealed and the mixture was allowed to stir at 80 °C for 18 h. After the starting materials were completed converted, the mixture was cooled to room temperature, then $NaHCO_3$ was added and the mixture was extracted with DCM (25 mL x 3). The organic solution was dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (pure petroleum ether) provided 4-phenylbut-3-yn-1-ol (yield:83%). [2]



4-phenylbut-3-yn-1-ol (1.46g,10 mmol) in CH_2Cl_2 (40 mL) was cooled to 0°C and then DMAP (1.22 g, 10 mmol), tosyl chloride (2.28g, 12 mmol) and Et_3N (1.67 mL, 12 mmol) were added. The reaction mixture was stirred for 30 min and then quenched with an aqueous NH_4Cl solution, extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated and chromatographed (hexanes-EtOAc, 10:1 to 2:1) to afford 4-phenylbut-3-yn-1-yl tosylate (yield: 56%).[6]



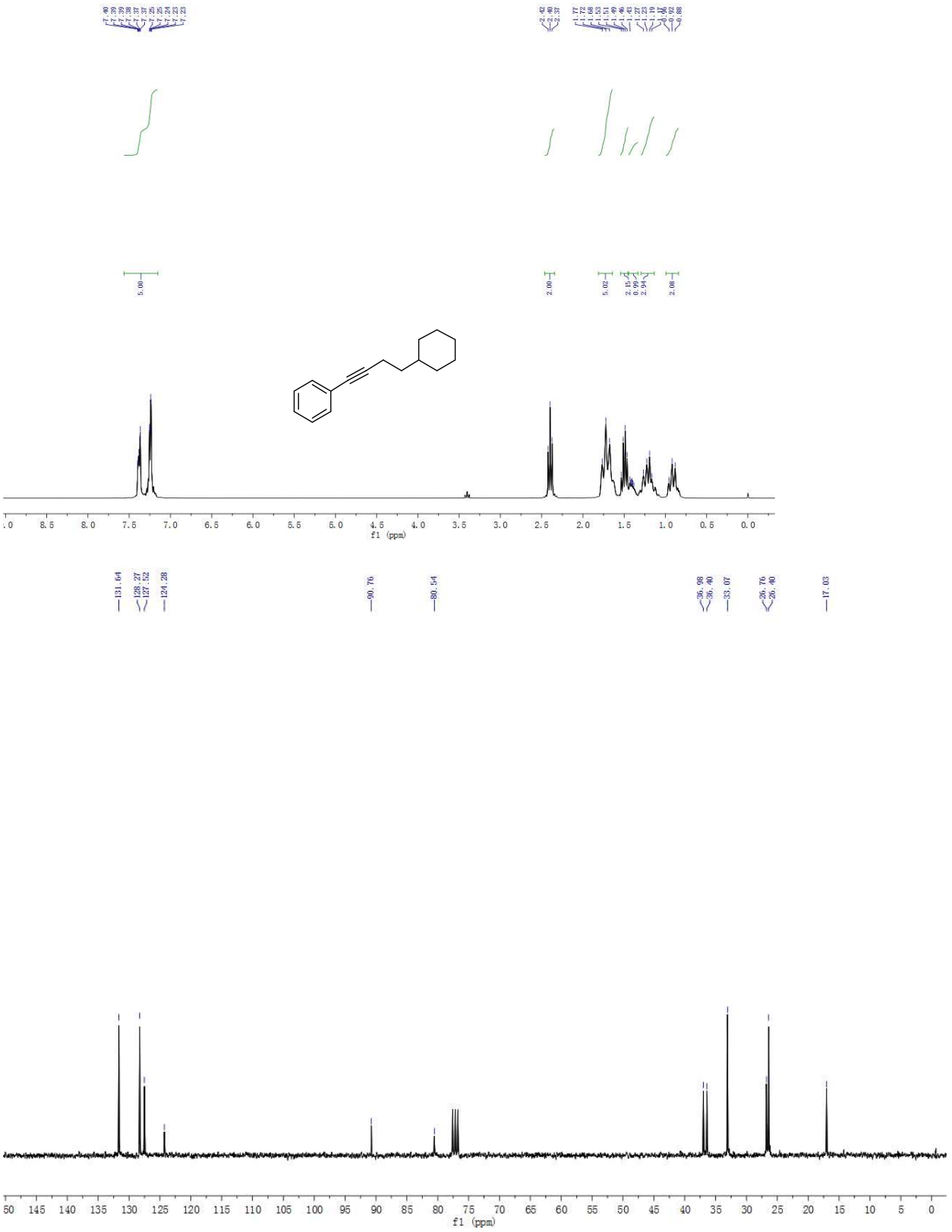
A 1.0 M solution of cyclohexylmagnesium bromide or cycloheptylmagnesium bromide (2.5mL, 2.5 mmol) in THF was added to a 15 mL of THF solution containing CuCl (7.5 mg, 0.075 mmol) and 4-phenylbut-3-yn-1-yl tosylate (624 mg, 2.08 mmol). The reaction mixture was stirred at room temperature for 3 h. It was quenched by the addition of 30 mL of saturated NH_4Cl aqueous solution.The organic phase in the resulting mixture was extracted with ether (3 times, 30 mL each), dried over Na_2SO_4, filtered, concentrated and chromatographed (hexanes-EtOAc, 10:1 to 2:1) to afford 5-cyclohexyl-1-phenyl-1-butyne (**1l**, yield: 74%) or 5-cycloheptyl-1-phenyl-1-butyne (**1m**, yield: 70%).[7]



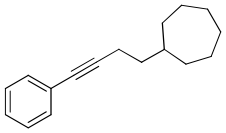
5-cyclohexyl-1-phenyl-1-butyne**(1l)**: Pale yellow liquid; yield: 74%

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.56 – 7.15 (m, 5H), 2.40 (t, *J* = 7.3 Hz, 2H), 1.77-1.68 (m, 5H), 1.53-1.46 (m, 2H), 1.44-1.33 (m, 1H), 1.27-1.17 (m, 3H), 0.96-0.88 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.6, 128.3, 127.5, 124.3, 90.8, 80.5, 37.0, 36.4, 33.1, 26.8, 26.4, 17.0



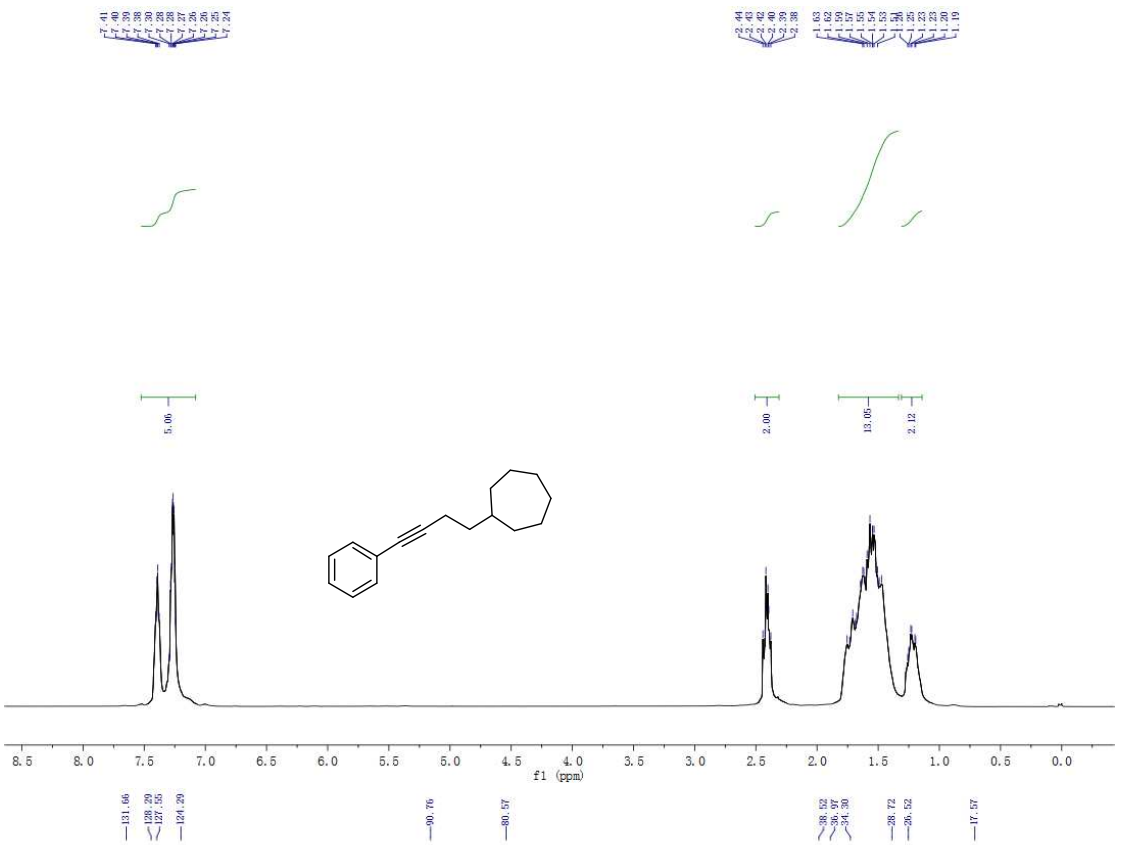
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

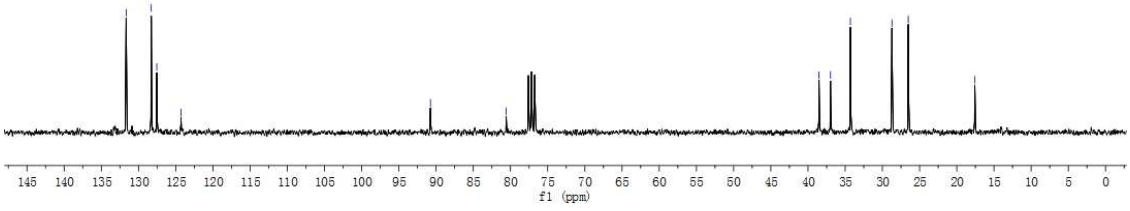


5-cycloheptyl-1-phenyl-1-butyne**(1m)**: Pale yellow liquid; yield: 70%

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.41-7.24 (m, 5H), 2.44-2.38 (m, 2H), 1.82-1.33 (m, 13H), 1.31-1.14 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.7, 128.3, 127.6, 124.3, 90.8, 80.6, 38.5, 37.0, 34.3, 28.7, 26.5, 17.6

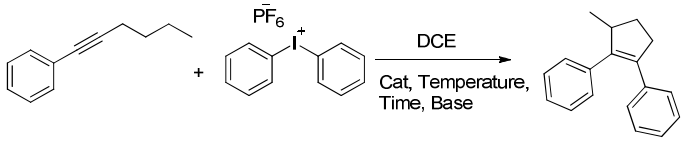




^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

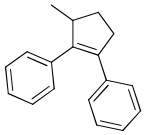
2.3 Products

General procedure: Diaryliodonium salts (0.7mmol) and $Cu(OTf)_2$ (0.025 mmol, 9 mg) were placed in a Schlenk tube. Solid mixture was heated under vacuum at 80 ^oC for 1 h to guarantee that they were free from moisture. Then the Schlenk tube was cooled to room temperature and added the corresponding acetylene and 2 mL of DCE while the tube was filled with N_2. The tube was sealed and heated at 60 ^oC for 12h. The mixture was quenched with NH_4Cl solution and extracted the solid phase with ethyl acetate and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (Hexane) provided the corresponding products.



Entry	Ratio	Catalyst (mol%)	Time	Tempreture(^oC)	Base	Yield(%)[a]
1	1:1	$Cu(OTf)_2$ (10)	12h	40	None	42
2	1:1	$AgBF_4$	12h	40	None	0
3	2:1	$Cu(OTf)_2$ (10)	12h	40	None	Alkyne Left
4	1.5:1	$Cu(OTf)_2$ (10)	12h	r.t	$^iPr_2NEt$ (1eq.)	0
5	1:2:1	$Cu(OTf)_2$ (10)	12h	30	None	23
6	1.2:1	$Cu(OTf)_2$ (10)	12h	30	DMA	Trace
7	1:1	$Cu(OTf)_2$ (10)	12h	30	None	31
8	1:1.4	$Cu(OTf)_2$ (10)	12h	30	None	42
9	1:1.4	$Cu(OTf)_2$ (10)	12h	60	None	78
10	1:1.4	$Cu(OTf)_2$ (10)	5h	60	None	39

[a] Determined by GC/MS analysis using Dodecane as an internal standard

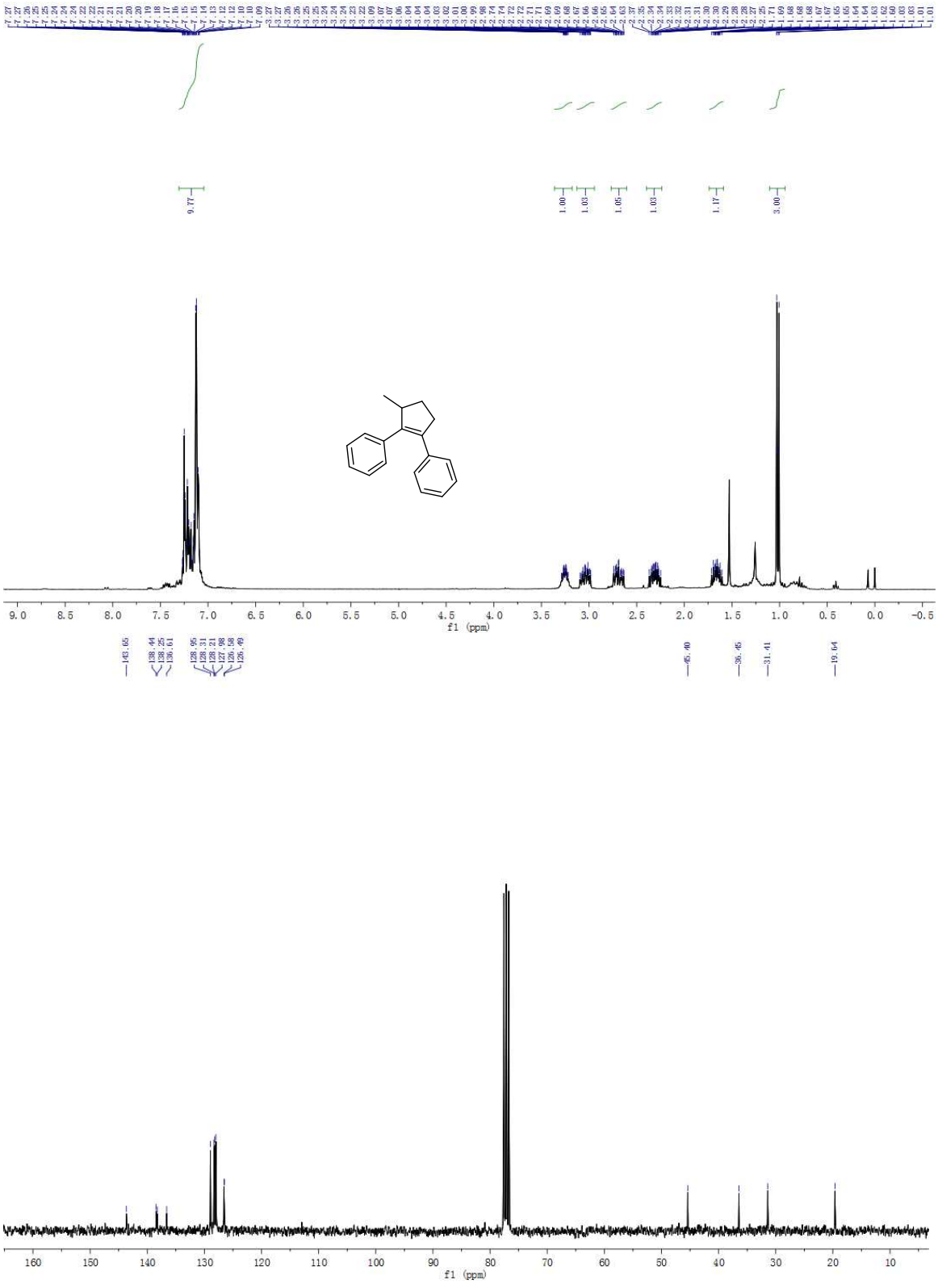


(3-methylcyclopent-1-ene-1,2-diyl)dibenzene (3a): Colorless liquid, 87 mg, yield: 75%.

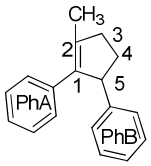
^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.30-7.04 (m, 10H), 3.36-3.18 (m, 1H), 3.13 -2.94 (m, 1H), 2.69 (dddd, *J* = 16.1, 9.0, 5.8, 1.5 Hz, 1H), 2.40-2.24 (m, 1H), 1.74-1.59 (m, 1H), 1.02 (d, *J* = 6.9, Hz, 3H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 143.7, 138.4, 138.2, 136.6, 129.0, 128.31, 128.2, 128.0, 126.6, 126.5, 45.4, 36.5, 31.4, 19.6

HRMS(APPI): cacud for $C_{18}H_{17}^{+}$[M-H]$^{+}$:233.13248, found: 233.13249



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

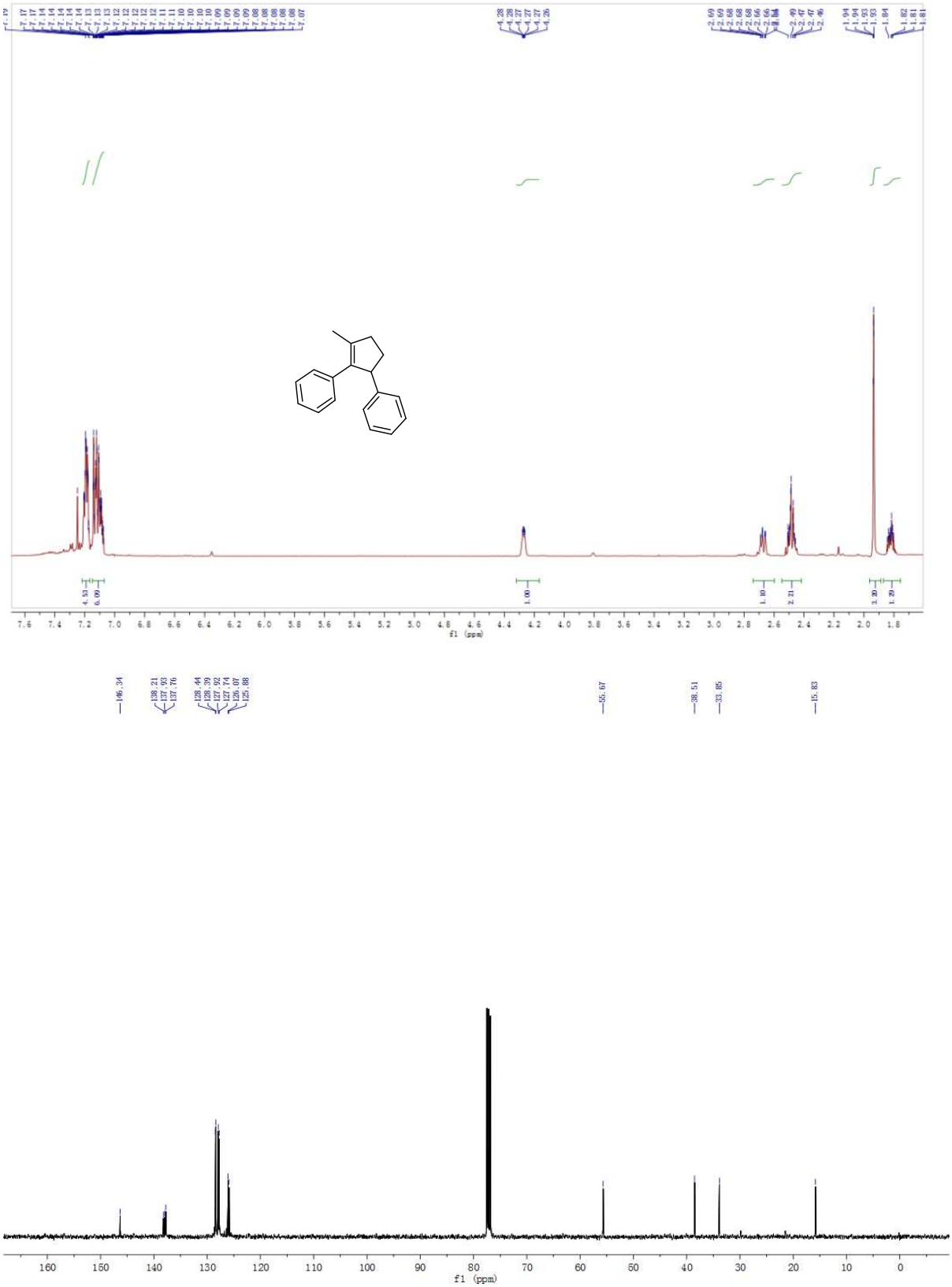


(3-methylcyclopent-2-ene-1,2-diyl)dibenzene (3a')

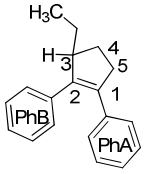
^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.22-7.17 (m, 4H, PhA & PhB), 7.14-7.07 (m, 6H, PhA & PhB) 4.30-4.22 (m, 1H, 5-CH), 2.66 (dd, *J* = 10.1, 7.7 Hz, 1H, 3-CH_2), 2.52-2.48 (m, 1H, 4-CH_2), 2.550-2.46 (m, 1H, 3-CH_2), 1.92 (b, 3H, CH_3), 1.86-1.81 (m, 1H, 4-CH_2).

^{13}C NMR (150 MHz, CHLOROFORM-D) δ 146.3 (1-C), 138.0 (2-C), 138.2, 137.8 (*ipso*-PhA & PhB), 128.4, 128.4, 127.9, 127.7 (*m, p*-PhA & PhB), 126.1, 125.9 (*p*-PhA & PhB), 55.7 (5-CH), 38.5 (3-CH_2), 33.9 (4-CH_2), 15.8 (CH_3)

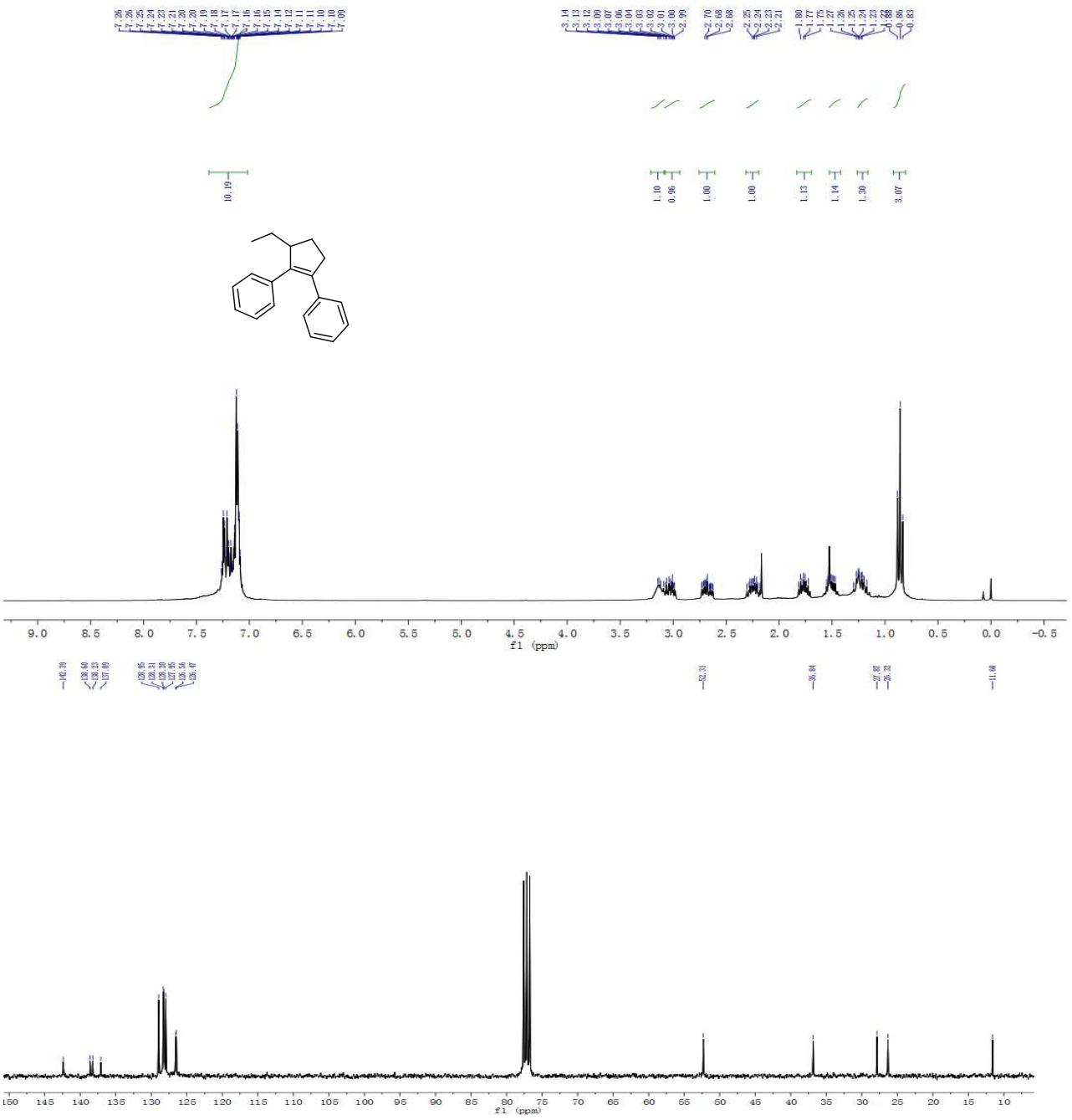
HRMS(APPI) cacud for $C_{18}H_{17}^{+}$[M-H] $^{+}$:233.13248, found: 233.13258



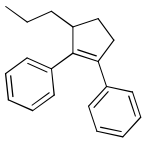
^{1}H NMR (600 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (150 MHz, $CDCl_3$) (**Down**)



(3-ethylcyclopent-1-ene-1,2-diyl)dibenzene (3b): Colorless liquid, 93mg, yield: 75%. ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.24-7.22 (m, 2H, *m*-PhB), 7.19-7.16 (m, 1H, *p*-PhB), 7.16-7.11 (m, 2H, *o*-PhA), 7.14-7.12 (m, 2H, *o*-PhB), 7.14-7.09 (m, 3H, *o*-PhA, *p*-PhA), 3.12 (dd, *J* = 10.2, 5.6 Hz, 1H, 3-H), 3.03 (ddd, *J* = 9.1, 7.9, 3.1 Hz, 1H, 5-H), 2.75-2.61 (m, 1H, 5-H), 2.31-2.19 (m, 1H, 4-H), 1.83-1.69 (m, 1H, 4-H), 1.53-1.42 (m, 1H, Et-CH_2), 1.22 (m, 1H, Et-CH_2), 0.86 (t, *J* = 7.4 Hz, 3H, Et-CH_3). ^{13}C NMR (150 MHz, CHLOROFORM-D) δ 142.4 (2-C), 138.6 (*ipso*-PhB), 138.2 (*ipso*-PhA), 137.1 (1-C), 129.0 (*o*-PhB), 128.3 (*o*-PhA), 128.2 (*m*-PhB), 128.0 (*m*-PhA), 126.6, 126.5(*p*-PhB& *p*-PhA), 52.3 (3-CH), 36.8 (5-CH_2), 27.9 (4- CH_2), 26.3 (Et- CH_2), 11.6 (Et-CH_3).
HRMS(APPI): cacud for $C_{19}H_{19}^{+}$[M-H] $^{+}$:247.14813,found:247.14794.



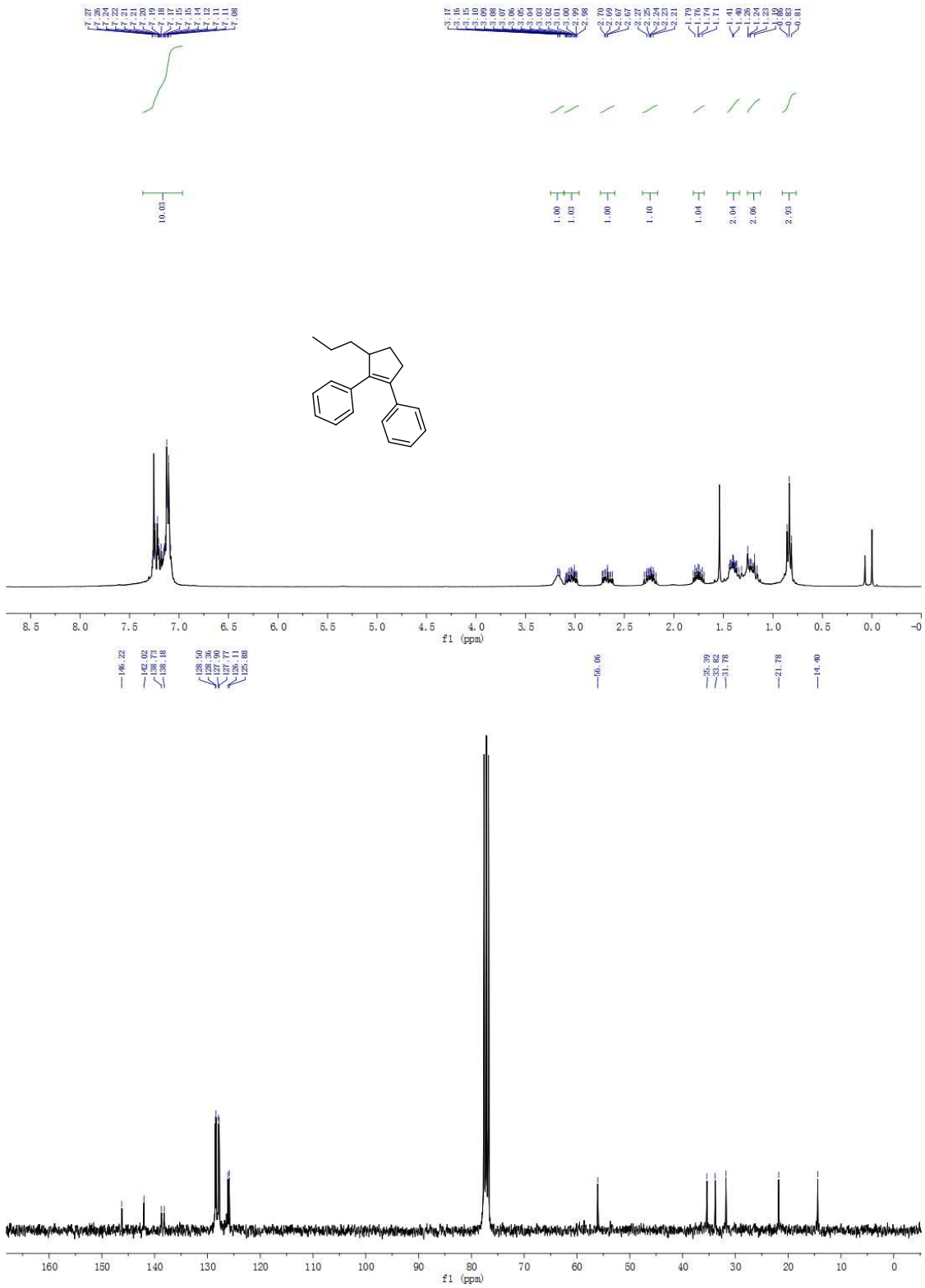
^{1}H NMR (600 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (150 MHz, $CDCl_3$) (**Down**)



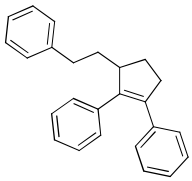
(3-propylcyclopent-1-ene-1,2-diyl)dibenzene (3c): Colorless liquid,90mg, yield: 71%.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.37 – 6.96 (m, 10H), 3.25 – 3.11 (m, 1H), 3.11 – 2.96 (m, 1H), 2.74 – 2.60 (m, 1H), 2.32 – 2.17 (m, 1H), 1.80 – 1.69 (m, 1H), 1.46 – 1.34 (m, 2H), 1.26 – 1.13 (m, 2H), 0.83 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 146.2, 142.0, 138.7, 138.2, 128.5, 128.4, 127.9, 127.8, 126.1, 125.956.1 35.4 33.8, 31.8 21.8 14.4.

HRMS(APPI): cacud for $C_{20}H_{21}^{+}$[M-H]$^{+}$:261.16378,found:261.16364



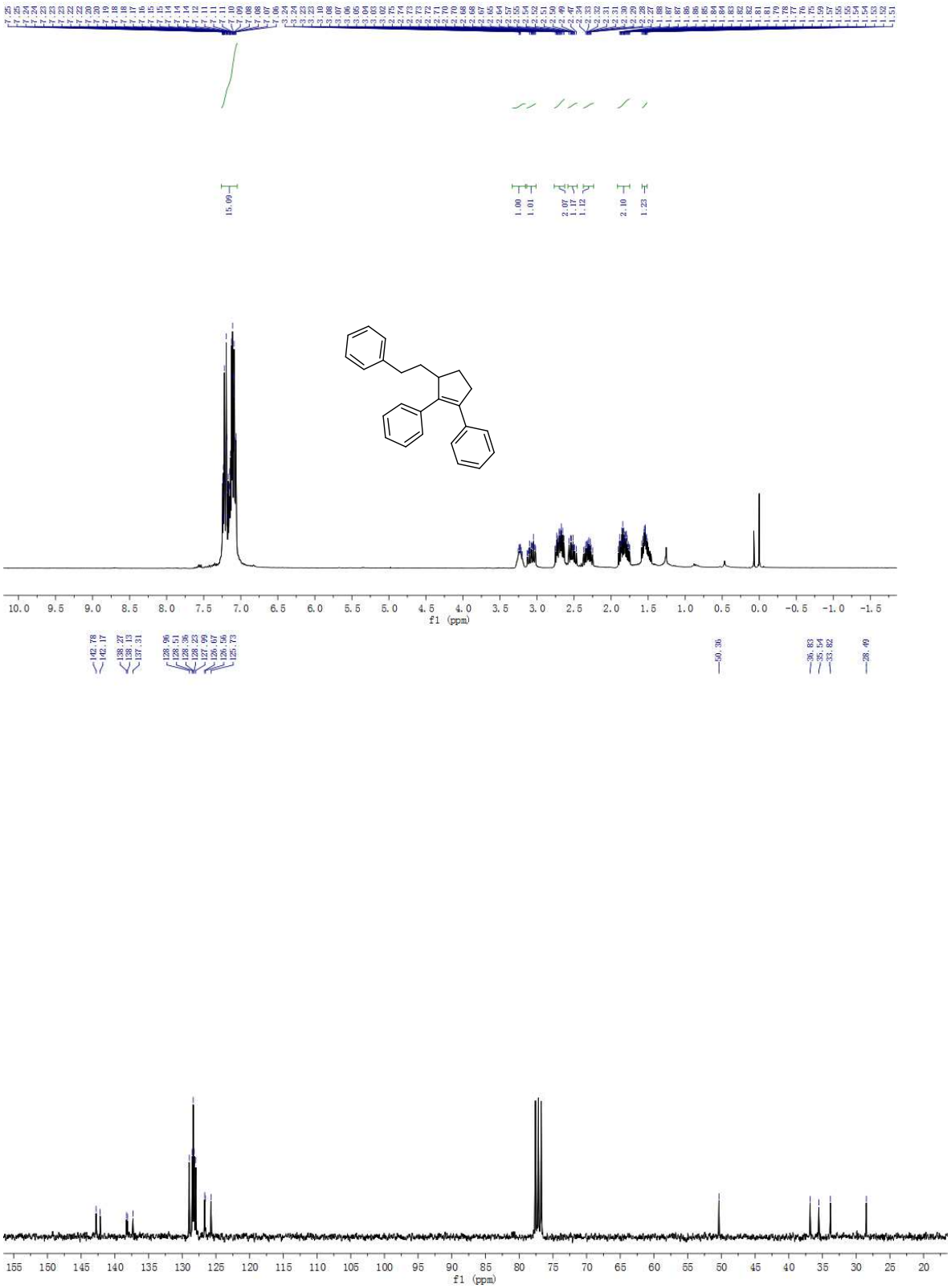
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



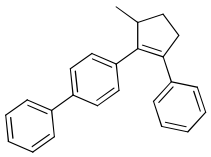
(3-phenethylcyclopent-1-ene-1,2-diyl)dibenzene (3d): Colorless liquid,97 mg, yield: 60%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.26 – 7.05 (m, 15H), 3.33 – 3.15 (m, 1H), 3.14 – 3.01 (m, 1H), 2.77 – 2.63 (m, 2H), 2.58 – 2.46 (m, 1H), 2.37 – 2.23 (m, 1H), 1.91 – 1.75 (m, 2H), 1.58 – 1.51 (m, 1H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 142.8, 142.12, 138.3, 138.1, 137.3, 129.0, 128.5, 128.4, 128.2, 128.0, 126.7, 126.6 , 125.7, 50.4, 36.8, 35.5, 33.8, 28.5

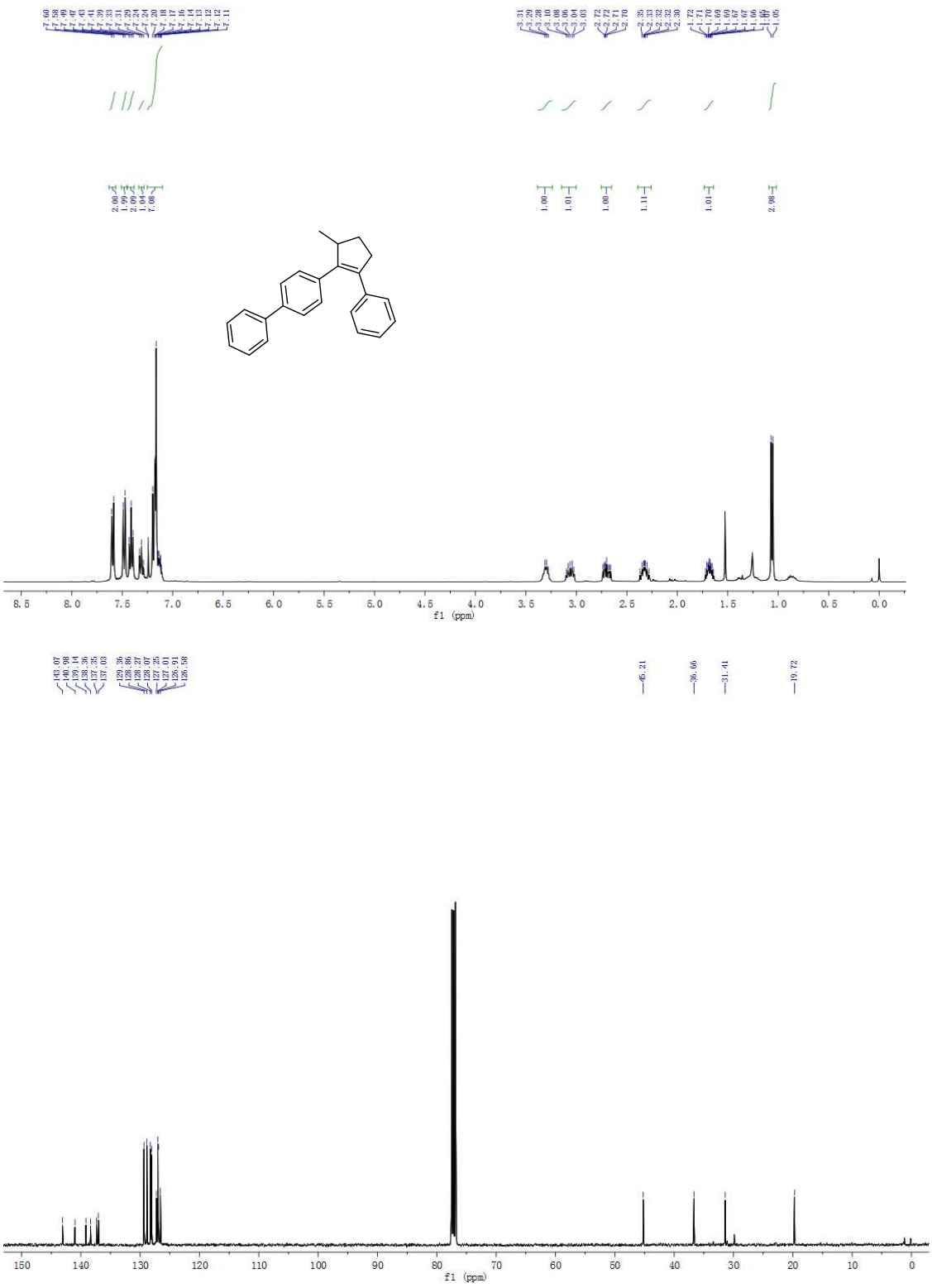
HRMS(APPI): cacud for $C_{25}H_{23}^{+}$[M-H]$^{+}$:323.17943,found:323.17935



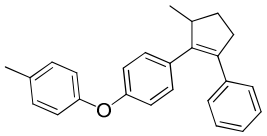
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



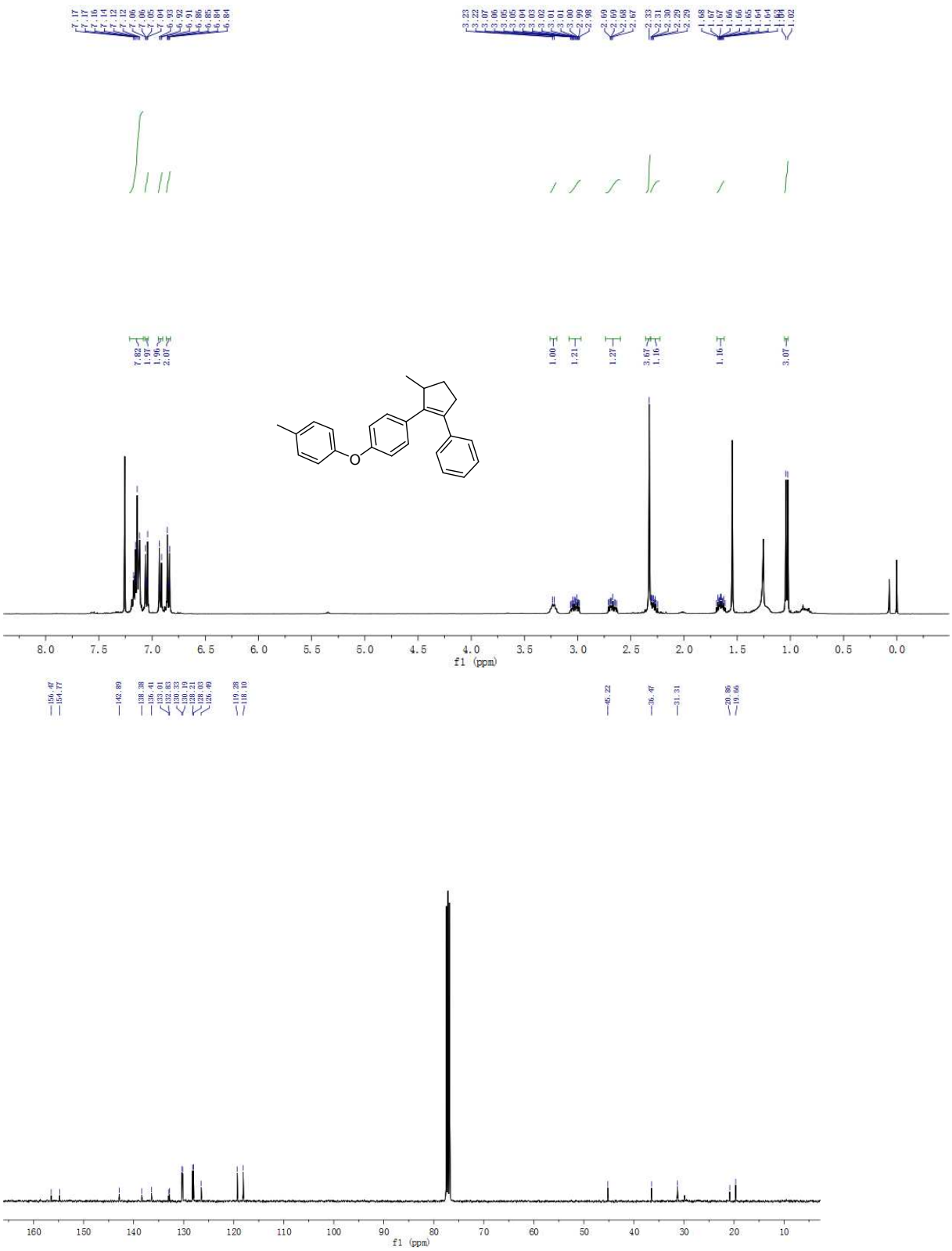
4-(5-methyl-2-phenylcyclopenten-1-yl)-1,1'-biphenyl (3f): Colorless liquid,100mg, yield: 66%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.43-7.39 (m, 2H), 7.33-7.29 (m, 1H), 7.20-7.16 (m, 7H),3.38-3.24 (m, 1H), 3.15-3.00 (m, 1H), 2.70 (ddd, *J* = 15.8, 8.2, 5.6 Hz, 1H), 2.39-2.26 (m, 1H), 1.73-1.64 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.1, 141.0, 139.1, 138.4, 137.4, 137.0, 129.4, 128.9, 128.3, 128.1, 127.3, 127.0, 126.9, 126.6, 45.2, 36.7, 31.4, 19.7
HRMS(APPI): cacud for $C_{24}H_{21}^{+}$[M-H]$^{+}$:309.16378, found: 309.16368



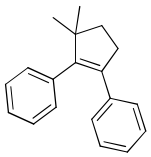
^{1}H NMR (400 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (101 MHz, $CDCl_3$) (**Down**)



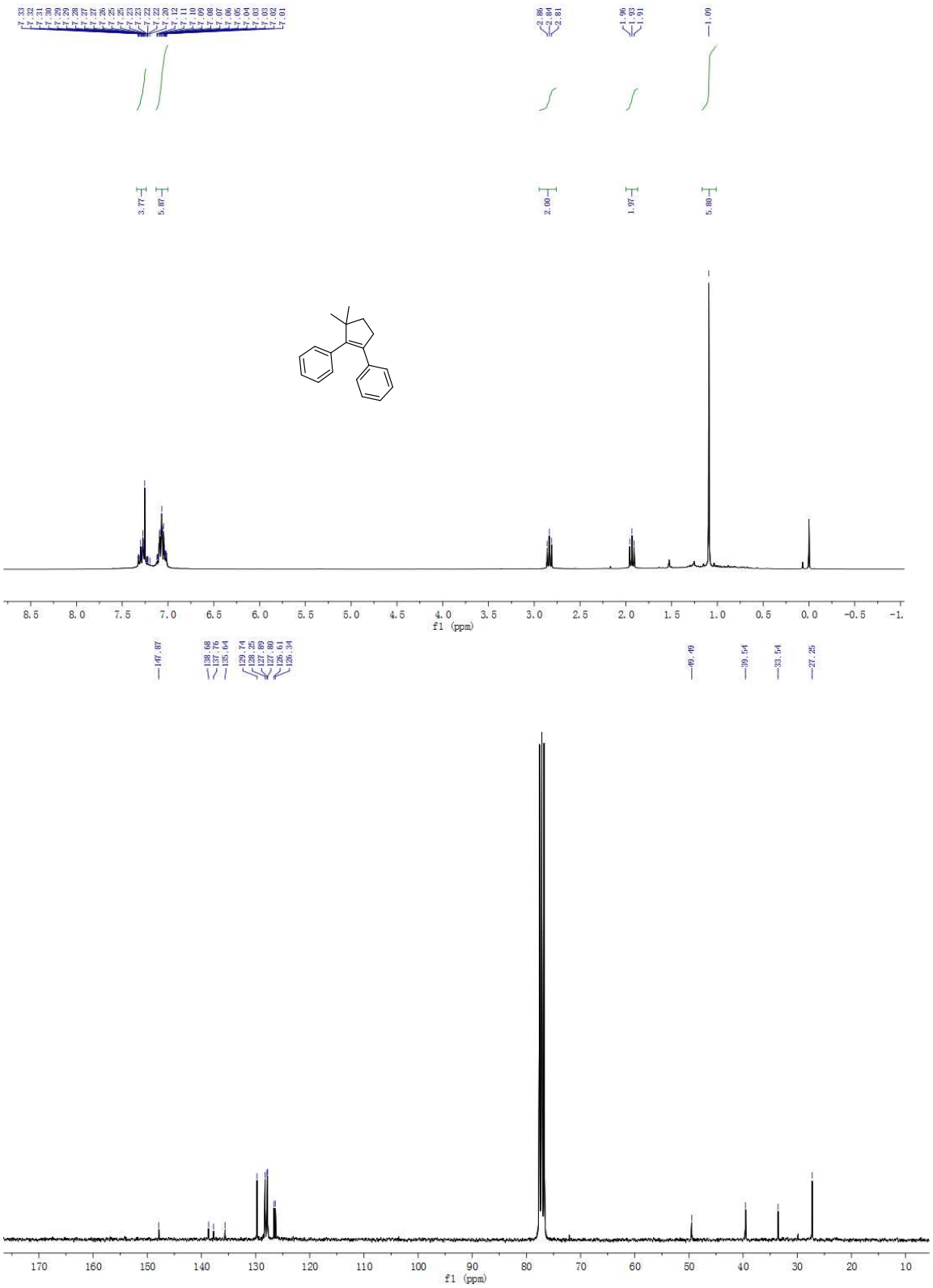
1-(5-methyl-2-phenylcyclopent-1-en-1-yl)-4-phenoxybenzene (3g): Colorless liquid, 61 mg, yield: 36%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.21 – 7.08 (m, 8H), 7.07 – 7.04 (m, 2H), 6.94 – 6.90 (m, 2H), 6.87 – 6.83 (m, 2H), 3.25-3.20 (m, 1H), 3.08 – 2.97 (m, 1H), 2.74 – 2.60 (m, 1H), 2.33 (s, 4H), 2.31-2.25 (m, 1H), 1.69 – 1.62 (m, 1H), 1.03 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 156.5, 154.8, 142.9, 138.4, 136.4, 133.0, 132.8, 130.3 130.2, 128.2, 128.0, 126.5, 119.3, 118.1, 45.2, 36.5, 31.3, 20.9, 19.7
HRMS(APPI): cacud for $C_{25}H_{23}O^{+}[M-H]^{+}$:339.17434,found:339.17421



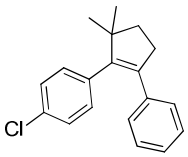
^{1}H NMR (400 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR,101 MHz, $CDCl_3$) (**Down**)



(3,3-dimethylcyclopent-1-ene-1,2-diyl)dibenzene(3h): Colorless solid, 105 mg, yield:85%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ7.34 – 7.24 (m, 4H), 7.13-7.00 (m, 6H), 2.83 (t, *J* = 7.1 Hz, 2H), 1.93 (t, *J* = 7.1 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 147.9, 138.7, 137.8, 135.6, 129.7, 128.3, 127.9, 127.8, 126.6, 126.3, 49.5, 39.5, 33.5, 27.3. HRMS(APPI): cacud for $C_{19}H_{19}^{+}$[M-H]$^{+}$:247.14813,found:247.14810

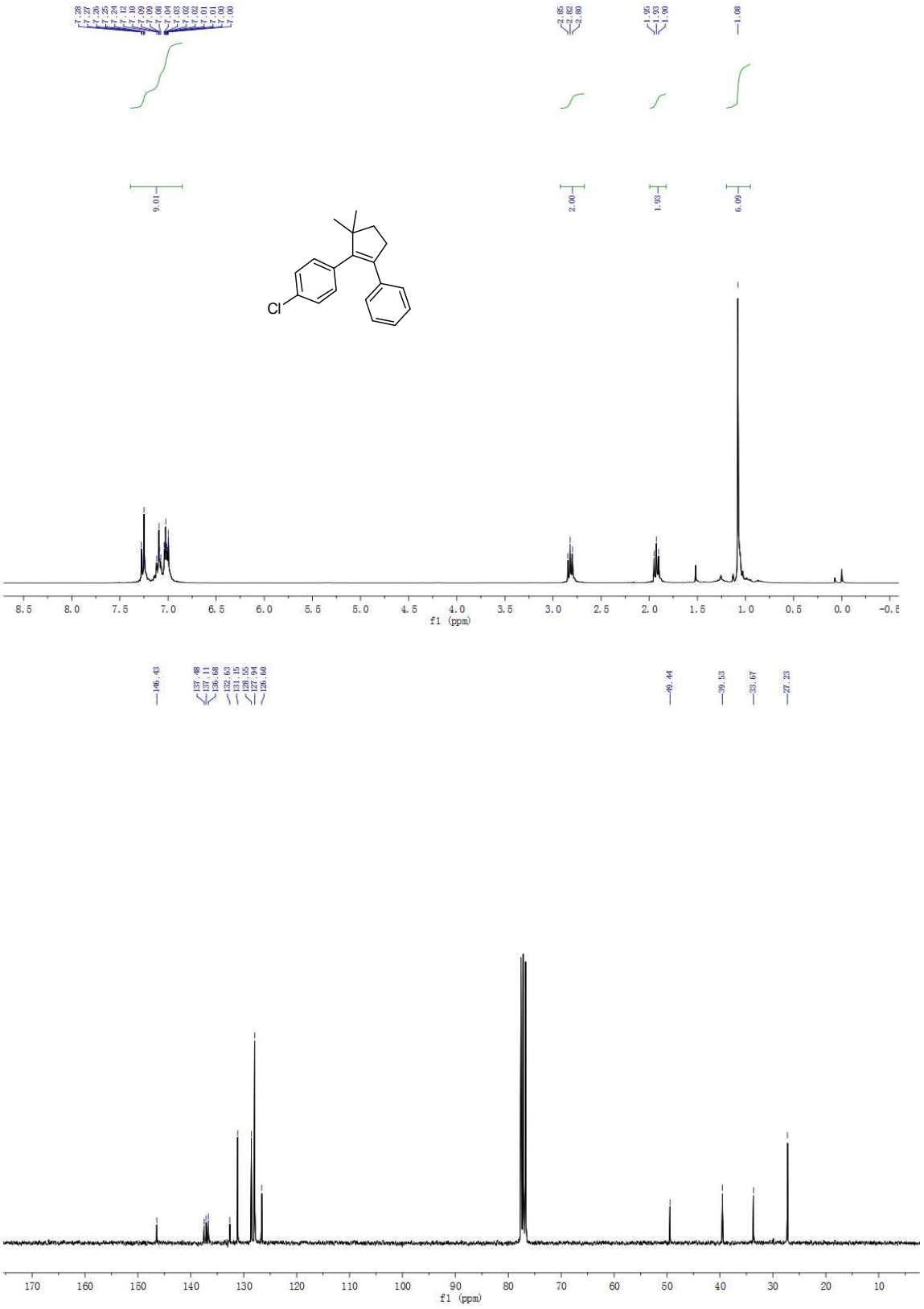


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

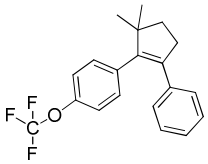


1-chloro-4-(5,5-dimethyl-2-phenylcyclopent-1-en-1-yl)benzene(3i): Colorless solid, 97 mg, yield:69%; Melting point: 109°C. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.39 – 6.85 (m, 9H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.93 (t, *J* = 7.2 Hz, 2H), 1.08 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 146.4, 137.5, 137.1, 136.7, 132.6, 131.2 128.6127.9, 126.6, 49.4, 39.5, 33.7, 27.2

HRMS(APPI): cacud for $C_{19}H_{18}Cl^{+}[M-H]^{+}$:281.10915, found:281.10878

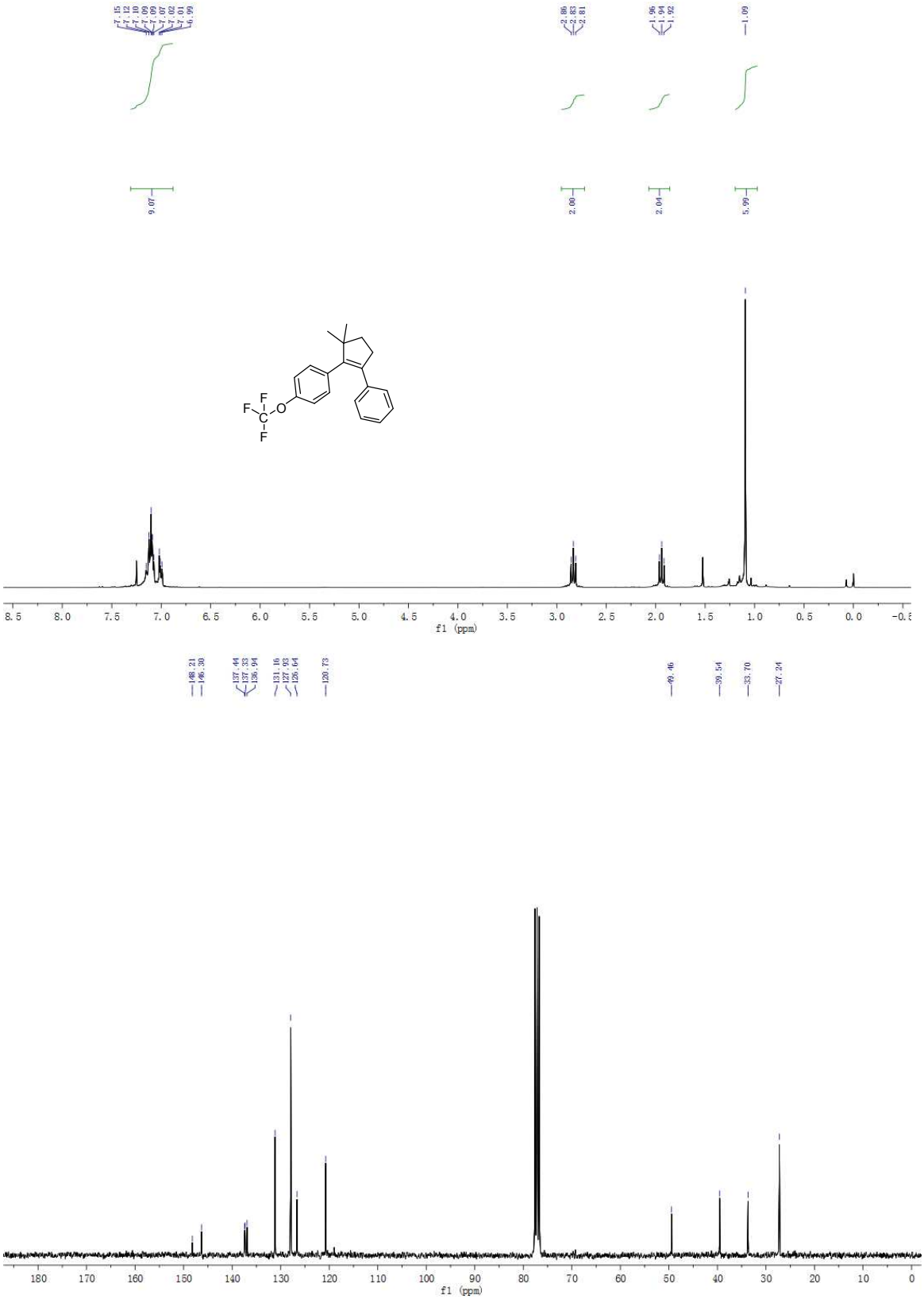


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

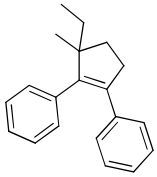


1-(5,5-dimethyl-2-phenylcyclopent-1-en-1-yl)-4-(trifluoromethoxy)benzene(3j): Colorless liquid, 120 mg, yield: 72%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.07 (m, 9H), 2.83 (t, *J* = 7.1 Hz, 2H), 1.94 (t, *J* = 7.1 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 148.2, 146.3, 137.4, 137.3, 136.9, 131.2, 127.9, 126.6, 120.7, 49.5, 39.5, 33.7, 27.2

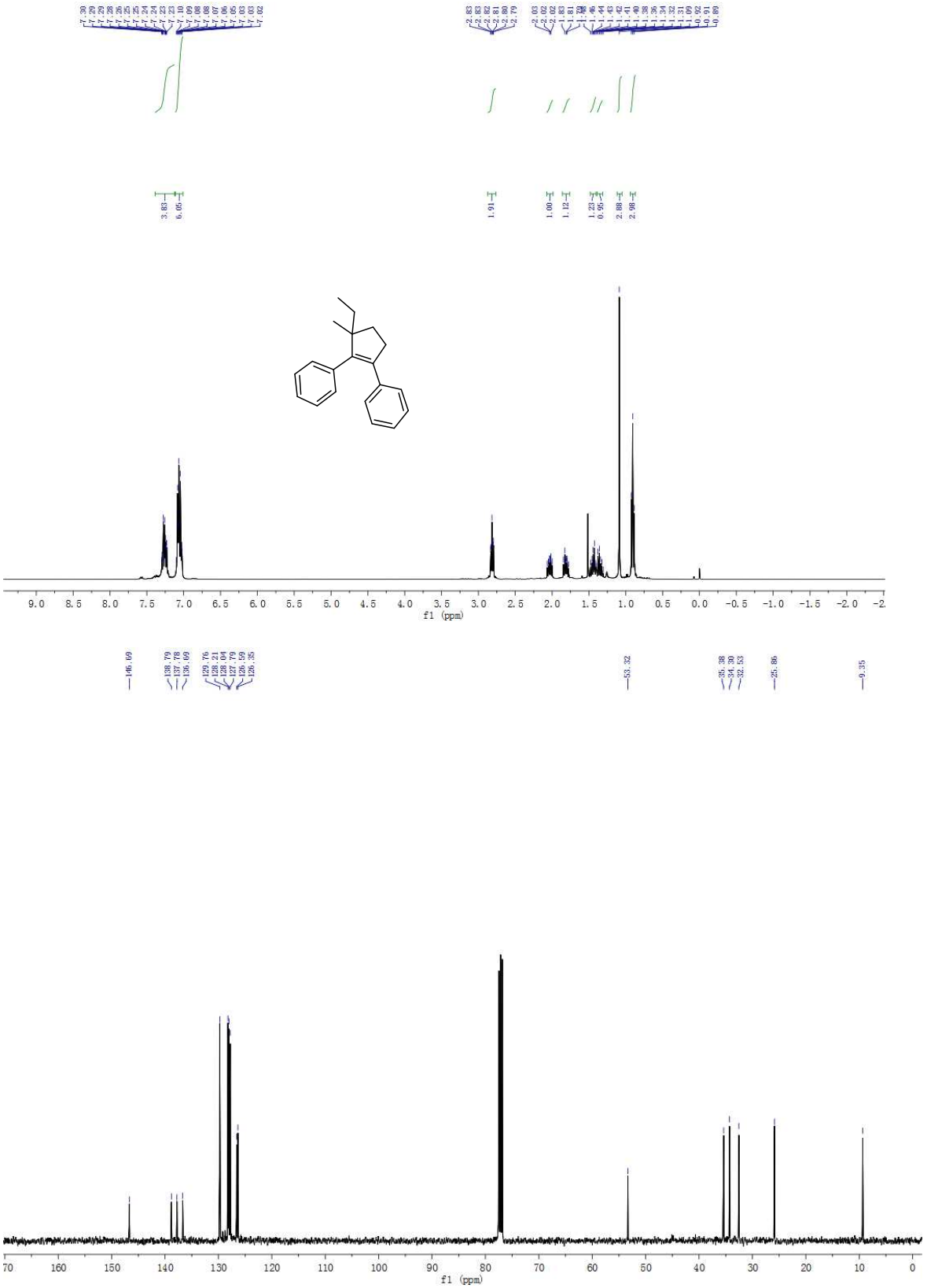
HRMS(APPI): cacud for $C_{20}H_{18}F_3O^+[M-H]^+$:331.13043,found:331.13025



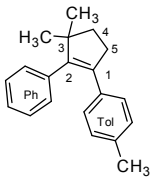
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



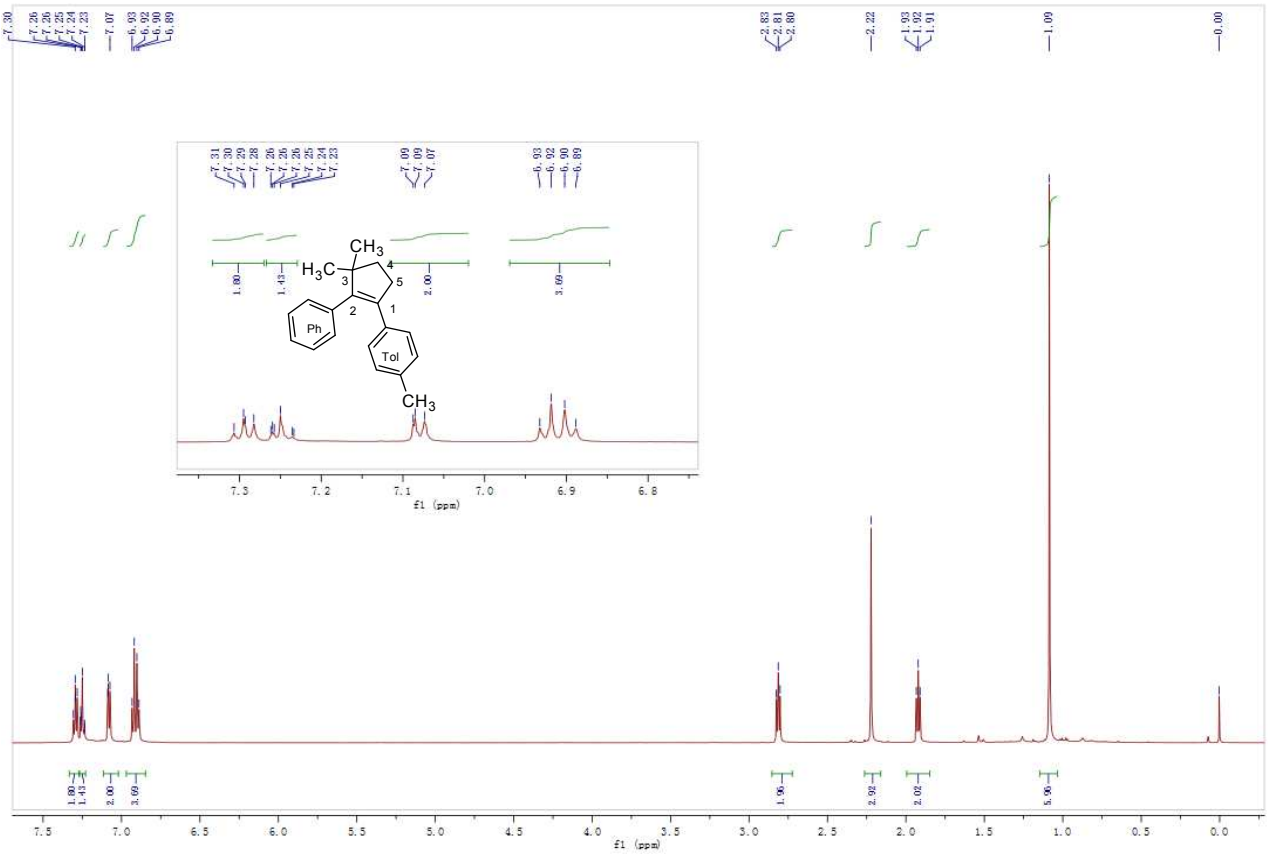
(3-ethyl-3-methylcyclopent-1-ene-1,2-diyl)dibenzene (3k): Colorless liquid, 74 mg, yield: 57%.^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 – 7.12 (m, 4H), 7.11 – 7.01 (m, 6H), 2.87 – 2.76 (m, 2H), 2.07-2.00 (m, 1H), 1.86 – 1.76 (m, 1H), 1.48-1.40 (m, 1H), 1.38-1.31 (m, 7.1 Hz, 1H), 1.09 (s, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 146.7, 138.8, 137.8, 136.7, 129.8, 128.2, 128.0, 127.8, 126.6, 126.4, 53.3, 35.4, 34.3, 32.5, 25.9, 9.4
HRMS(APPI) cacud for $C_{20}H_{21}^{+}$[M-H]$^{+}$:261.16378,found:261.16357

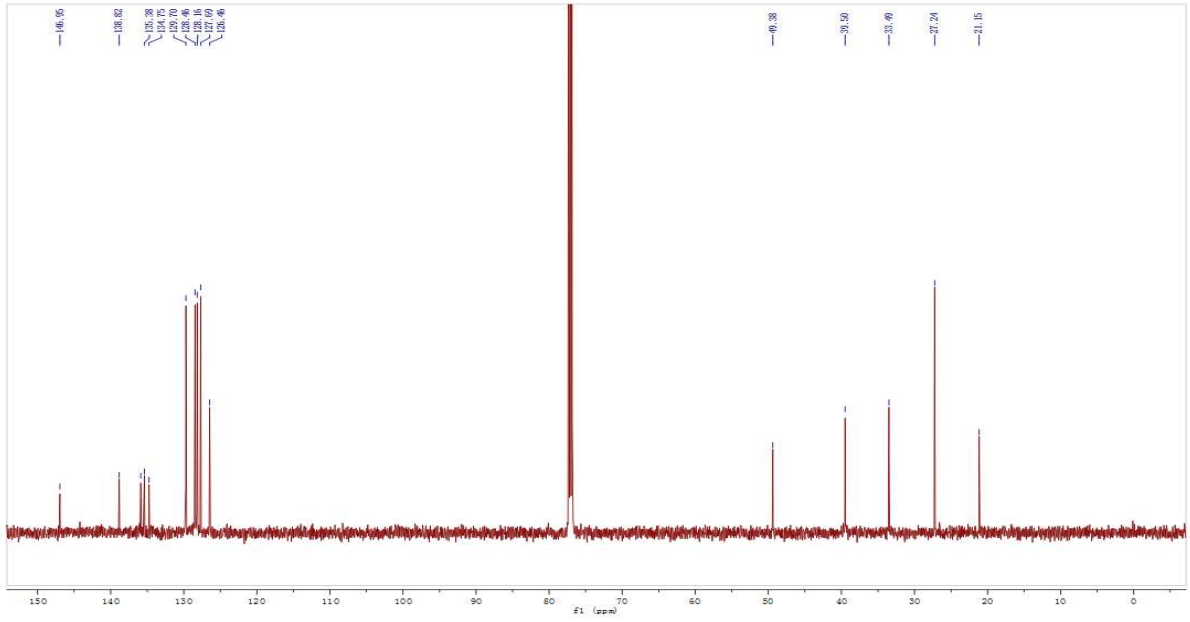


^{1}H NMR (400 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (101 MHz, $CDCl_3$) (**Down**)



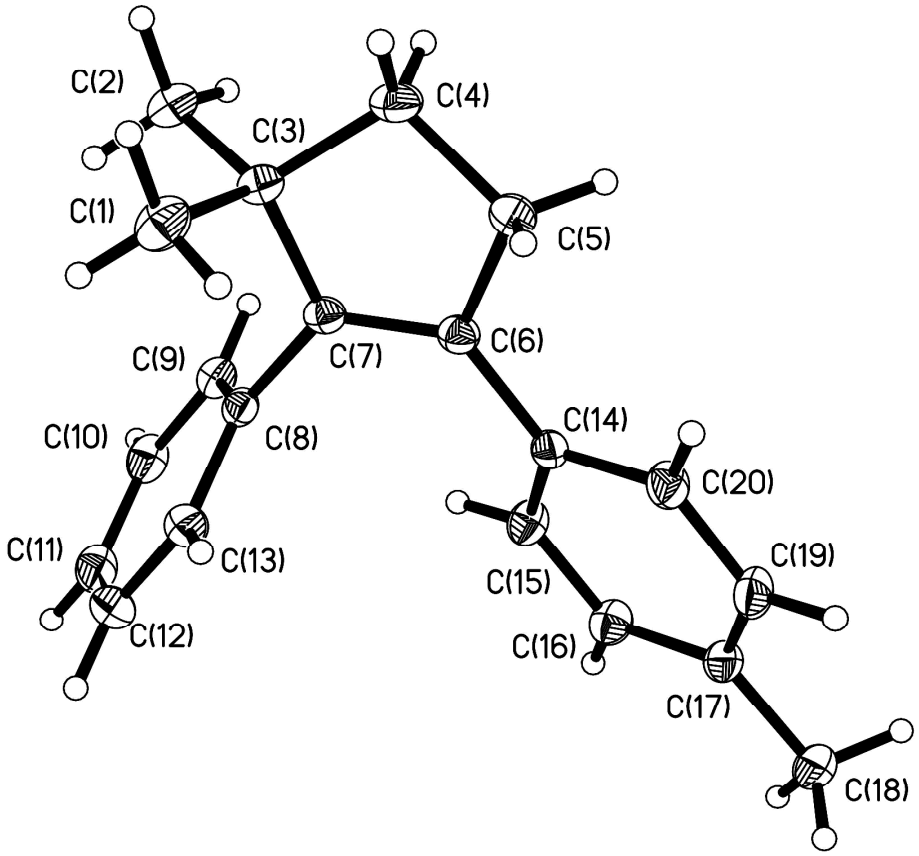
1-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)-4-methylbenzene (3l): Colorless solid, 117 mg, yield: 90%; Melting point: 90°C. ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.29 (dd, *J* = 7.9, 6.7 Hz, 2H, *m*-Ph), 7.27-7.22 (m, 1H, *p*-Ph), 7.08 (dd, *J* = 8.1, 1.2 Hz, 2H, *o*-Ph), 6.93 (d, *J* = 8.3 Hz, 2H, *o*-Tol), 6.90 (d, *J* = 8.2 Hz, 2H, *m*-Tol), 2.81 (t, *J* = 7.2 Hz, 2H, 5-CH_2), 2.22 (s, 3H, Tol-CH_3), 1.92 (t, *J* = 7.2 Hz, 2H, 4-CH_2), 1.09 (s, 6H, 3-2CH_3). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 146.9 (2-C), 138.8 (*ipso*-Ph), 135.9 (*p*-tol), 135.4 (1-C), 134.8 (*ipso*-tol), 129.7 (*o*-Ph), 128.5 (*o*-Tol), 128.2 (*m*-Ph), 127.7 (*m*-Tol), 126.5 (*p*-Ph), 49.4 (3-C), 39.5 (4-C), 33.5 (5-C), 27.2 (3-2CH_3), 21.2 (tol-CH_3).
HRMS(APPI): cacud for $C_{20}H_{21}^{+}$[M-H]$^{+}$:261.16379, found:261.16378.

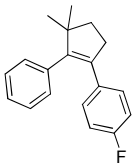




^{1}H NMR (600 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (151 MHz, $CDCl_3$) (**Down**)

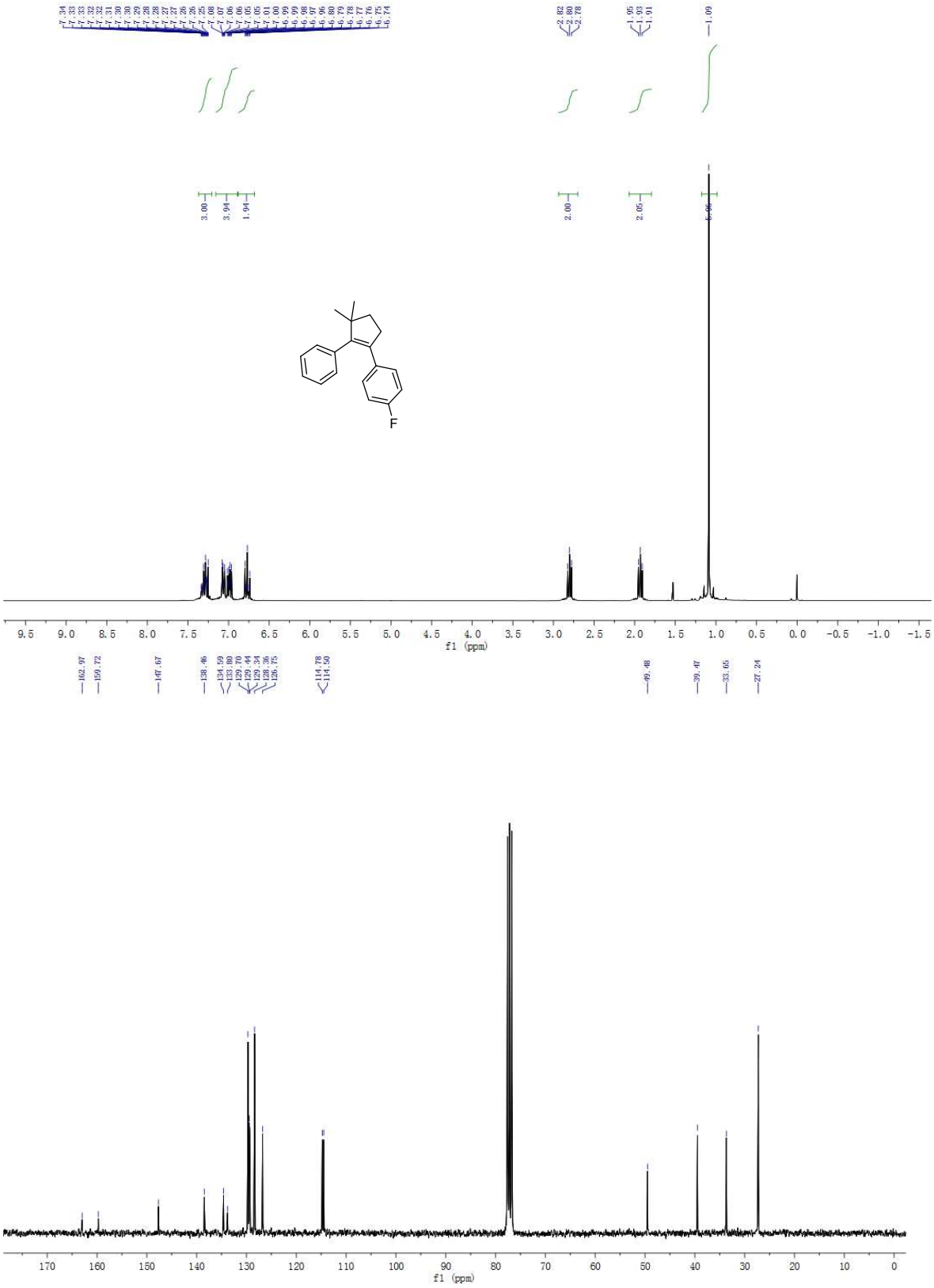
X-ray crystal structure analysis of compound 3l: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in hexane. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 970669.** Formula: C20H22, M = 262.38, colourless crystal, 0.348 x 0.333 x 0.204 mm, a = 5.9388 (12), b = 12.164 (2), c = 21.118 (4) Å, α = 90.00, β = 97.72(3), γ = 90.00 , V = 1511.7(5) Å^3, ρ_{calc} = 1.153 gcm^{-3}, μ = 0.064 mm^{-1}, Z = 4, Monoclinic, space group *p_1_21/n_1*, λ = 0.71073 Å, T = 293(2) K. Data completeness = 0.991, Theta (max) = 27.4839, R (reflections) = 0.0486(3088), wR2 (reflections) = 0.0998(3439).



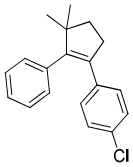


1-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)-4-fluorobenzene (3m): Colorless solid, 118 mg, yield: 88%; Melting point: 94°C. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.35 – 7.23 (m, 3H), 7.08-6.78 (m, 4H), 6.77-6.74 (m, 2H), 2.80 (t, *J* = 7.2 Hz ,2H), 1,93 (t, *J* = 7.2 Hz ,2H), 1.09 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 161.3 (d, *J* = 245.8 Hz), 147.7, 138.5, 134.6, 133.8, 129.7, 129.4 (d, *J* = 7.6 Hz), 128.4, 126.8, 114.6 (d, *J* = 21.1 Hz), 49.5, 39.5, 33.7, 27.2

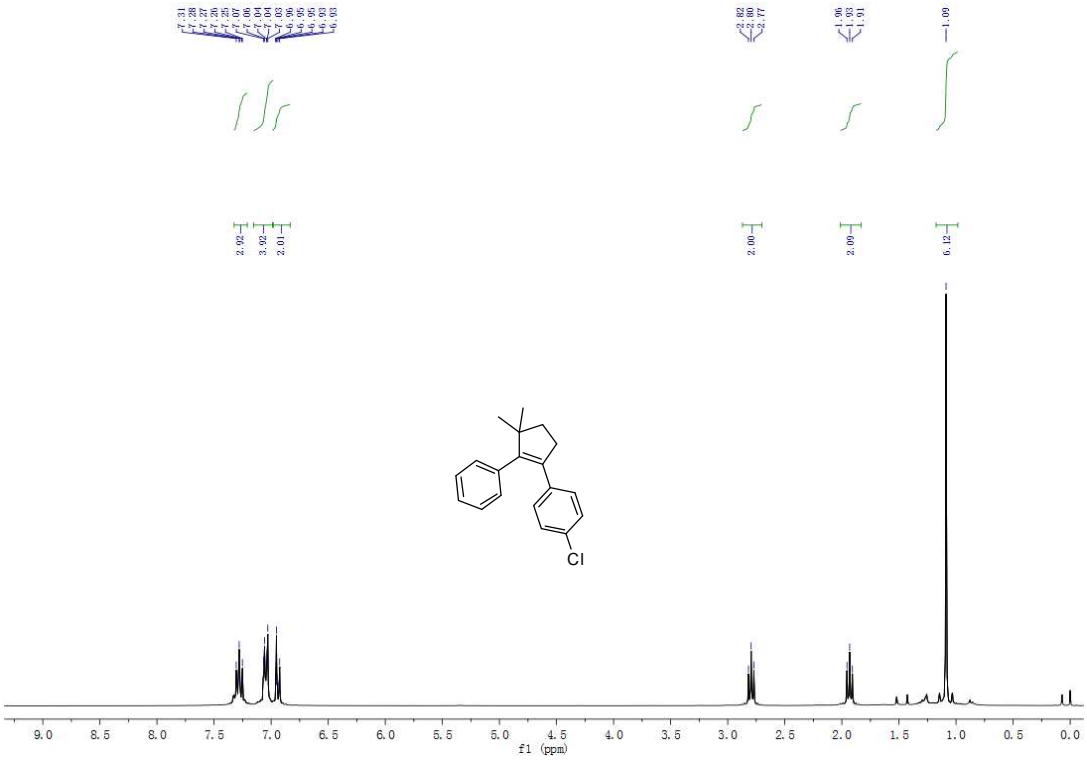
HRMS(APPI) cacud for $C_{19}H_{18}F^{+}[M-H]^{+}$:265.13871,found:265.13826



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



1-chloro-4-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)benzene(3n): Colorless solid, 125 mg, yield: 90%; Melting point: 111°C. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.32- 7.21 (m, 3H), 7.15-6.98 (m, 4H), 6.99-6.83 (m, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 1.93 (t, *J* = 7.2 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 148.67, 138.3, 136.2, 134.6, 132.0, 129.6, 129.1, 128.4, 128.0, 126.9, 49.6, 39.5, 33.5, 27.2
HRMS(APPI) cacud for $C_{19}H_{18}Cl^{+}[M-H]^{+}$:281.10915,found:281.10905



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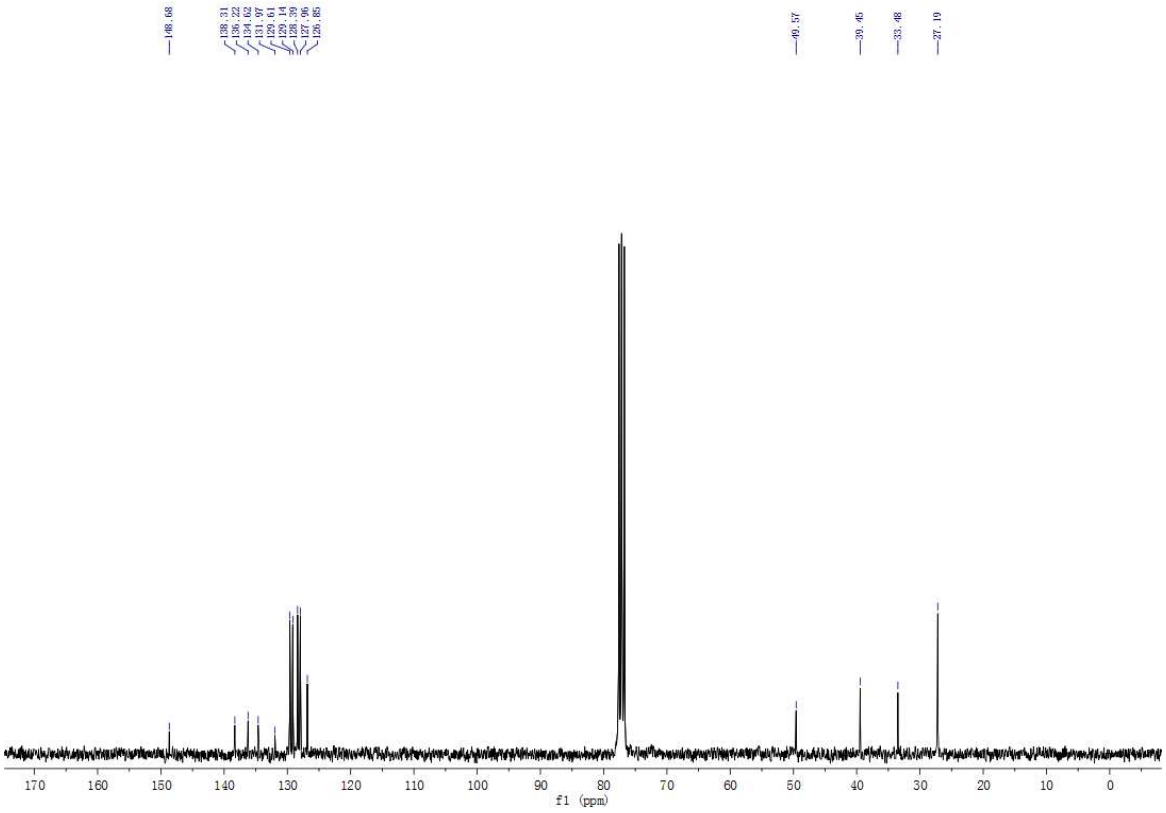
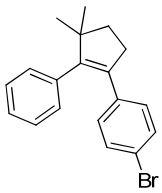
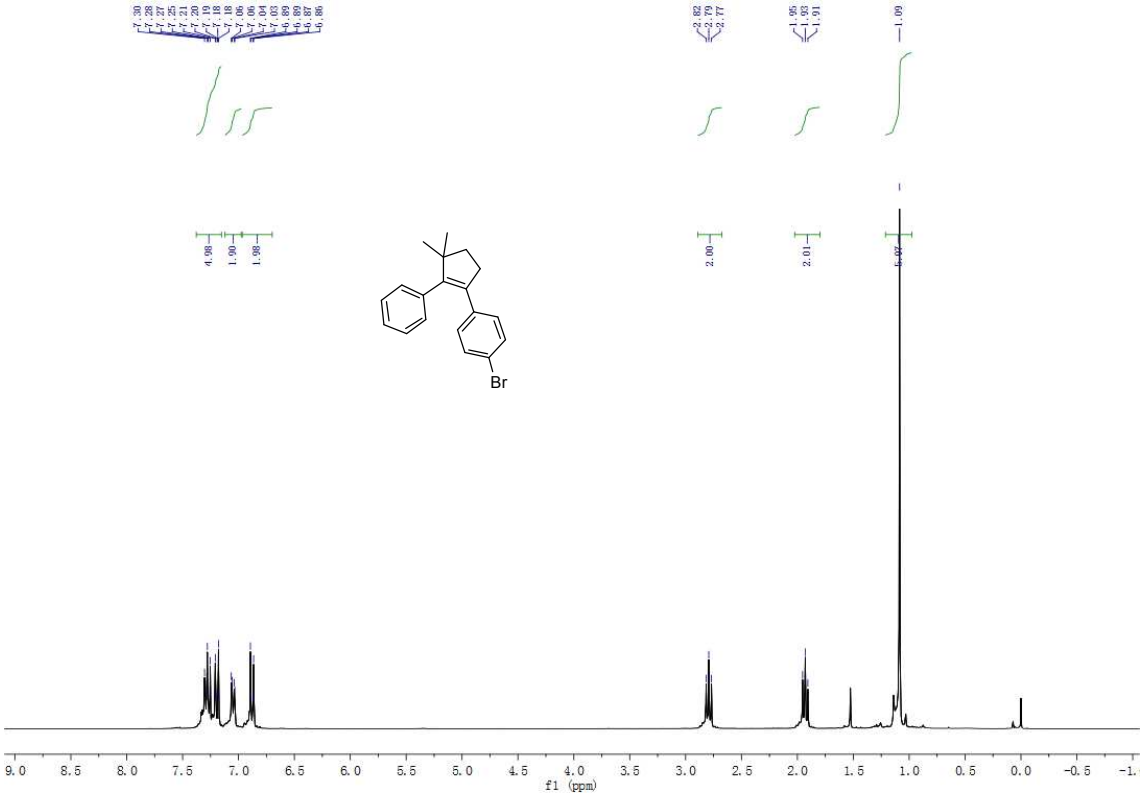


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



1-bromo-4-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)benzene (3o): Colorless solid, 144 mg, yield:88%; Melting point: 113°C. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.38- 7.15 (m, 5H), 7.08-7.03 (m, 2H), 6.97-6.70 (m, 2H), 2.79 (t, *J* = 7.1 Hz, 2H), 1.93 (t, *J* = 7.1 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 148.8, 138.3, 136.7, 134.7, 130.9, 129.6,129.5, 128.4, 126.9, 120.2, 49.6, 39.5, 33.4, 27.2

HRMS(APPI): cacud for $C_{19}H_{18}Cl^{+}[M-H]^{+}$:325.05864,found:325.05832



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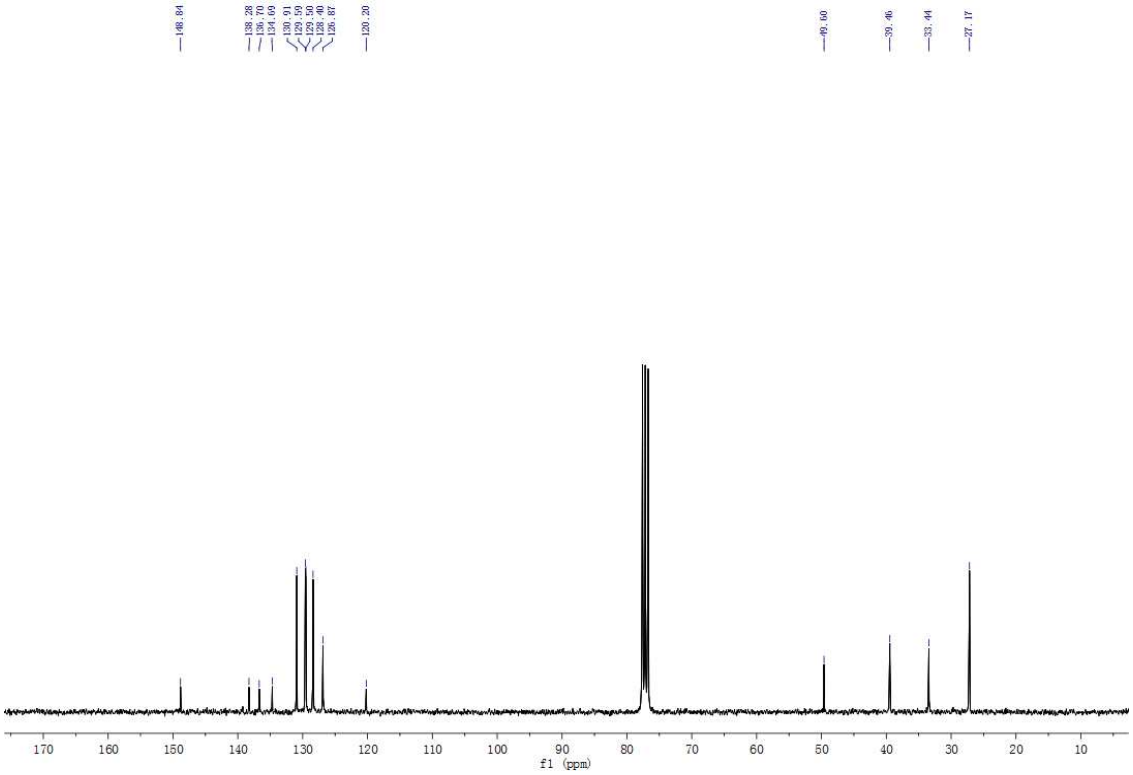
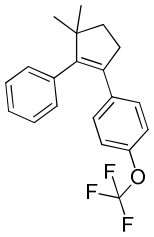
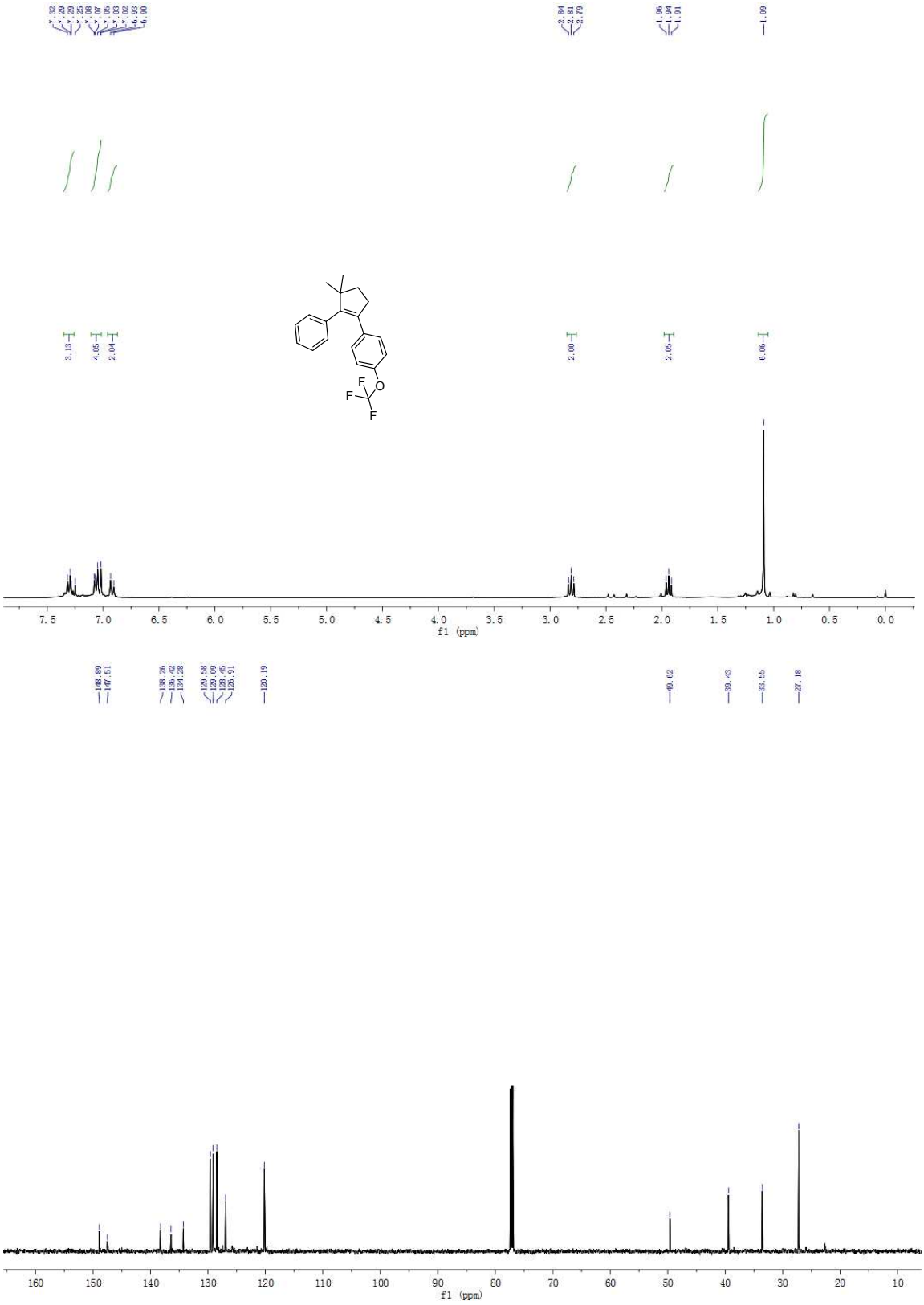


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

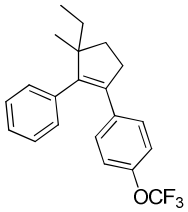


1-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)-4-(trifluoromethoxy)benzene(3p): Colorless liquid, 126 mg, yield: 76%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.32-7.27 (m, 3H), 7.08-7.01 (m, 4H), 6.93-6.90 (m, 2H), 2.81 (t, *J* = 7.1 Hz, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 148.9, 147.5, 138.3, 136.4, 134.3, 129.6, 129.1, 128.5, 126.9, 120.2, 49.6, 39.4, 33.6, 27.2.

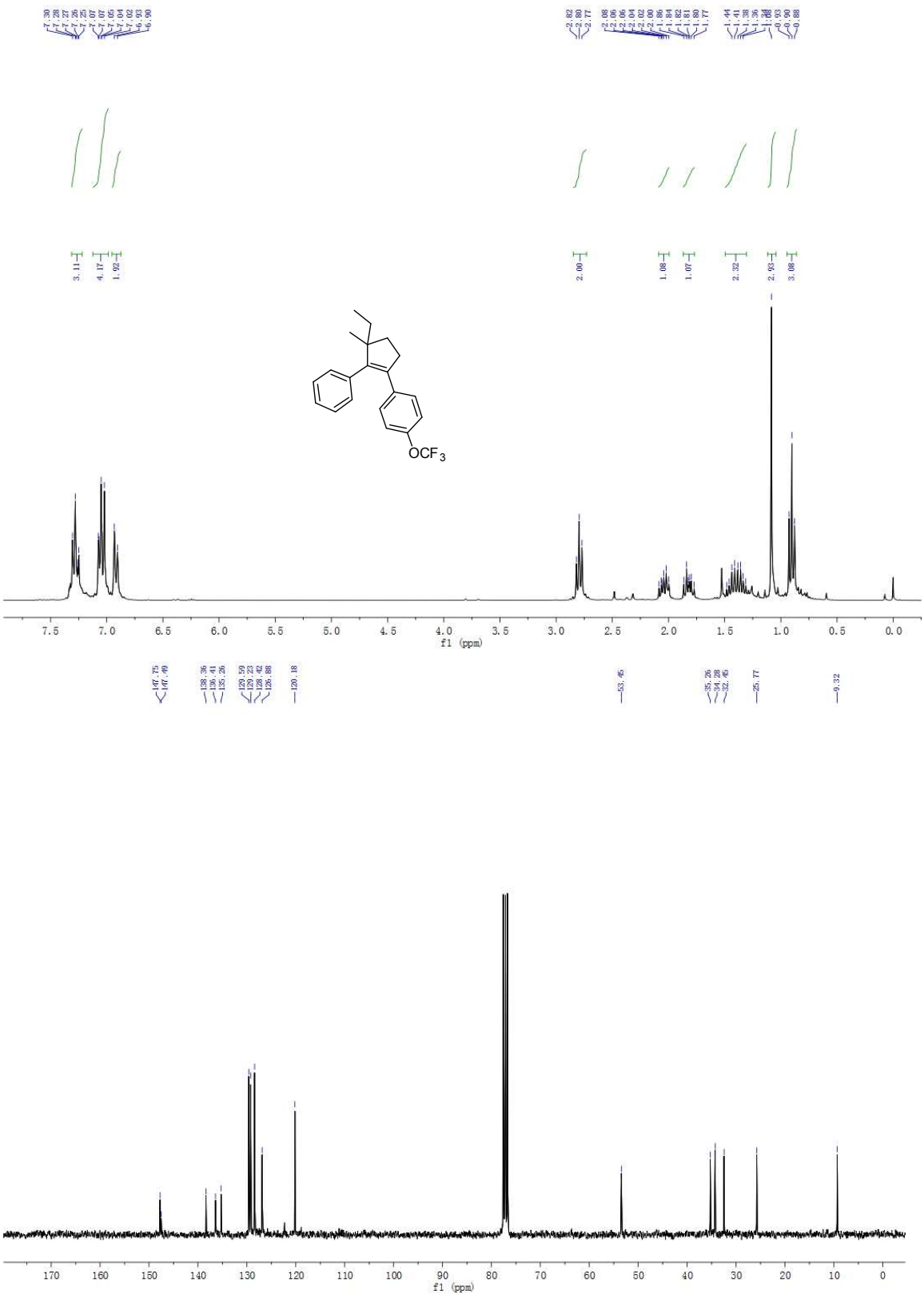
HRMS(APPI) cacud for $C_{20}H_{18}F_3O^+[M-H]^+$:331.13011,found:331.13043



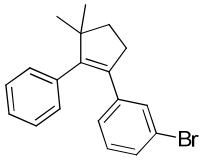
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



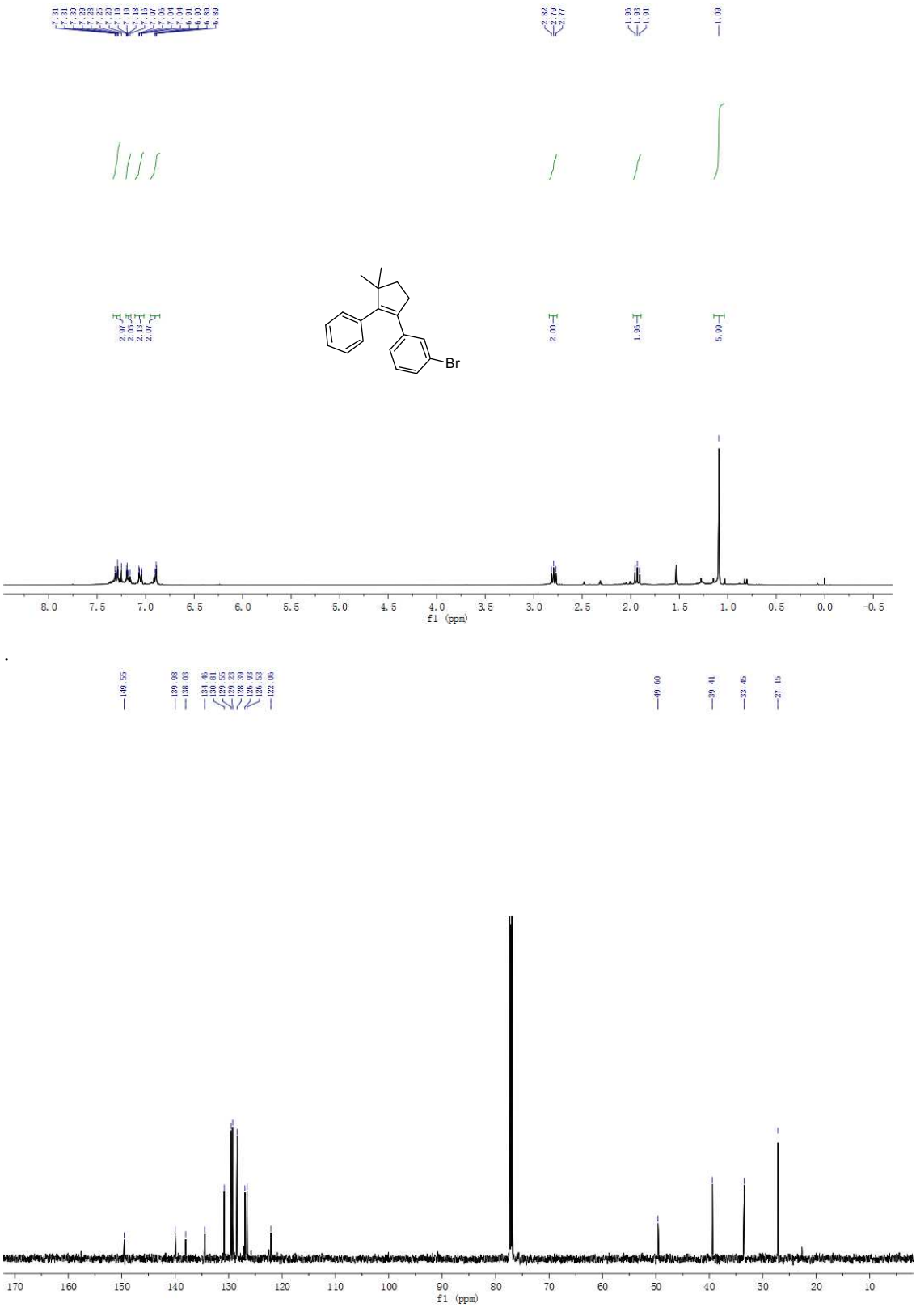
1-(3-ethyl-3-methyl-2-phenylcyclopent-1-en-1-yl)-4-(trifluoromethoxy)benzene (3q):
Colorless liquid,88mg, yield: 51%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.31-7.22 (m, 3H), 7.12-6.98 (m, 4H), 6.92 (d, *J* = 8.6 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.09 -1.99 (m, 1H), 1.88-1.77 (m, 1H), 1.44-1.34 (m, 2H), 1.08 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 147.8, 147.5, 138.4, 136.4, 135.3, 129.6, 129.2, 128.4, 126.9, 120.2, 53.5, 35.3, 34.3, 32.5, 25.8, 9.3
HRMS(APPI): cacud for $C_{21}H_{20}F_3O^+[M-H]^+$:345.14608,found:345.14593



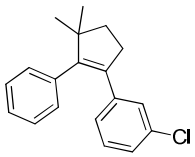
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



1-bromo-3-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)benzene(3r): Colorless liquid, 84 mg, yield:52%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.31-7.27 (m, 3H), 7.21 -7.15 (m, 2H), 7.07-7.04 (m, 2H), 6.91-6.89 (m, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 1.93 (t, *J* = 7.1 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 149.6, 140.0, 138.0, 134.5, 130.8, 129.6, 129.2, 128.4, 127.0, 126.5, 122.1, 49.6, 39.4, 33.5, 27.2
HRMS(APPI): cacud for $C_{19}H_{18}Cl^{+}[M-H]^{+}$:325.05864,found:325.05840

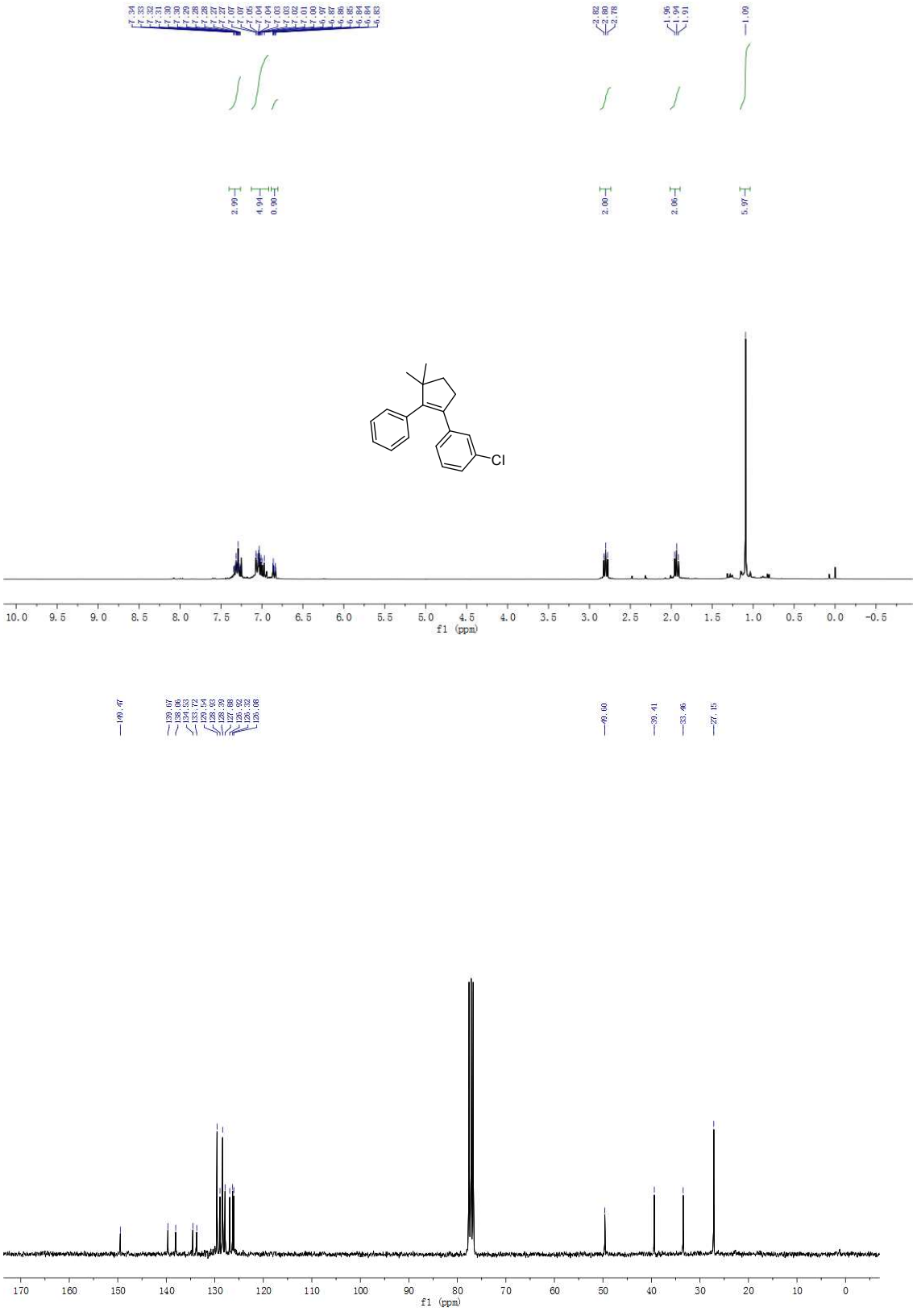


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

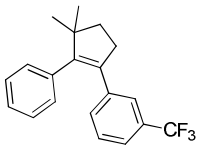


1-chloro-3-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)benzene(3s): Colorless liquid, 82 mg, yield: 59%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.34-7.27 (m, 3H), 7.07- 6.97 (m, 5H), 6.87-6.83 (m, 1H), 2.80 (t, *J* = 7.2 Hz, 2H), 1.93 (t, *J* = 7.2 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 149.5, 139.7, 138.1, 134.5, 133.7, 129.5, 128.9, 128.4, 127.9, 126.9, 126.3, 126.1, 49.6, 39.4, 33.5, 27.2

HRMS(APPI) cacud for $C_{19}H_{18}Cl^{+}$[M-H]$^{+}$:281.10915,found:281.10908

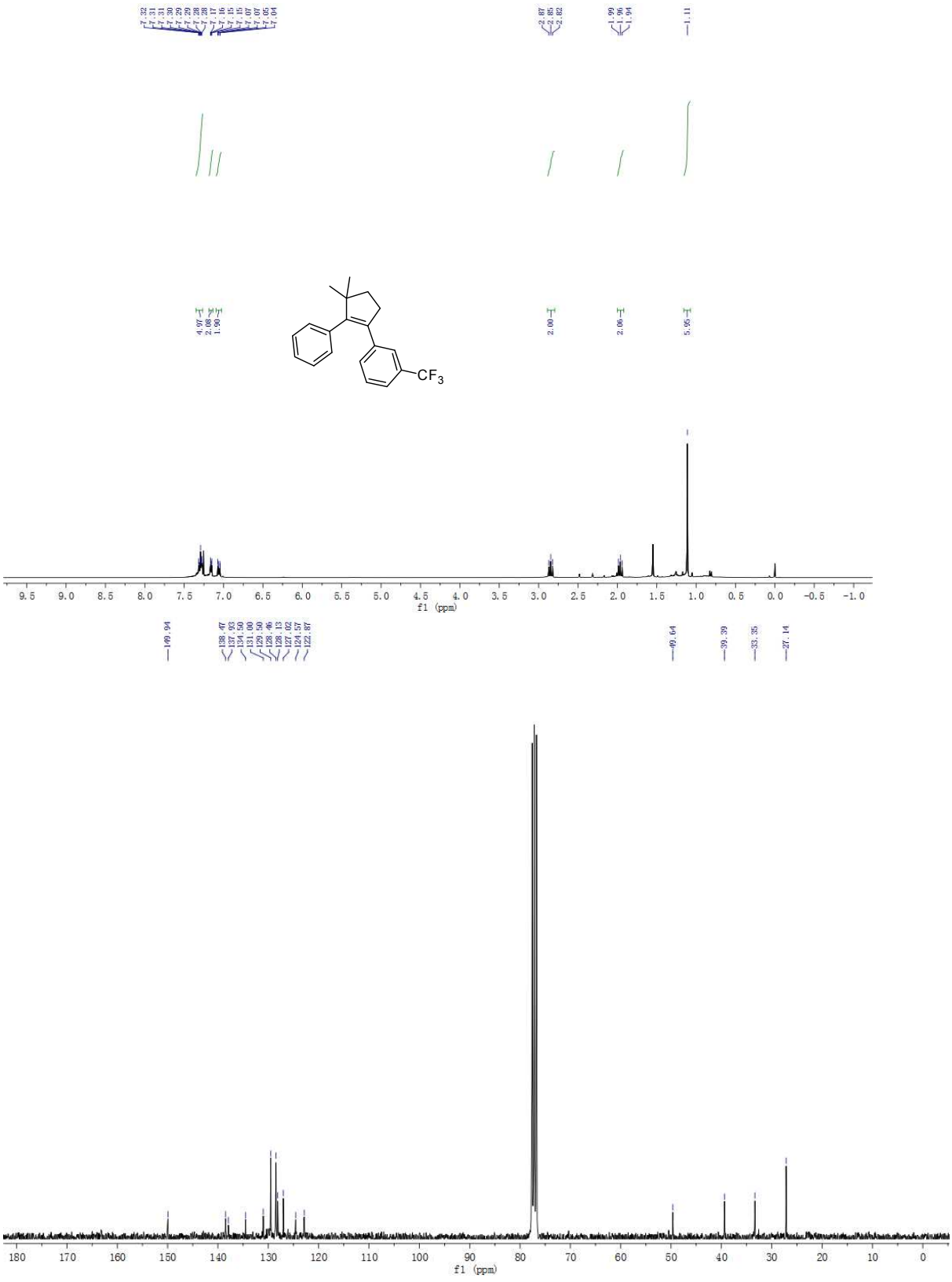


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

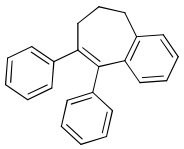


1-(3,3-dimethyl-2-phenylcyclopent-1-en-1-yl)-3-(trifluoromethyl)benzene (3t): Colorless liquid, 104 mg, yield:65%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.32 – 7.28 (m, 5H), 7.17-7.15 (m, 2H), 7.07-7.04 (m, 2H), 2.90 – 2.79 (m, 2H), 2.01 – 1.92 (m, 2H), 1.12 (s, 6H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 149.9, 138.5, 137.9, 134.5, 131.0, 129.5, 128.5, 128.1, 127.0, 124.6, 122.9, 49.6, 39.4, 33.4, 27.1

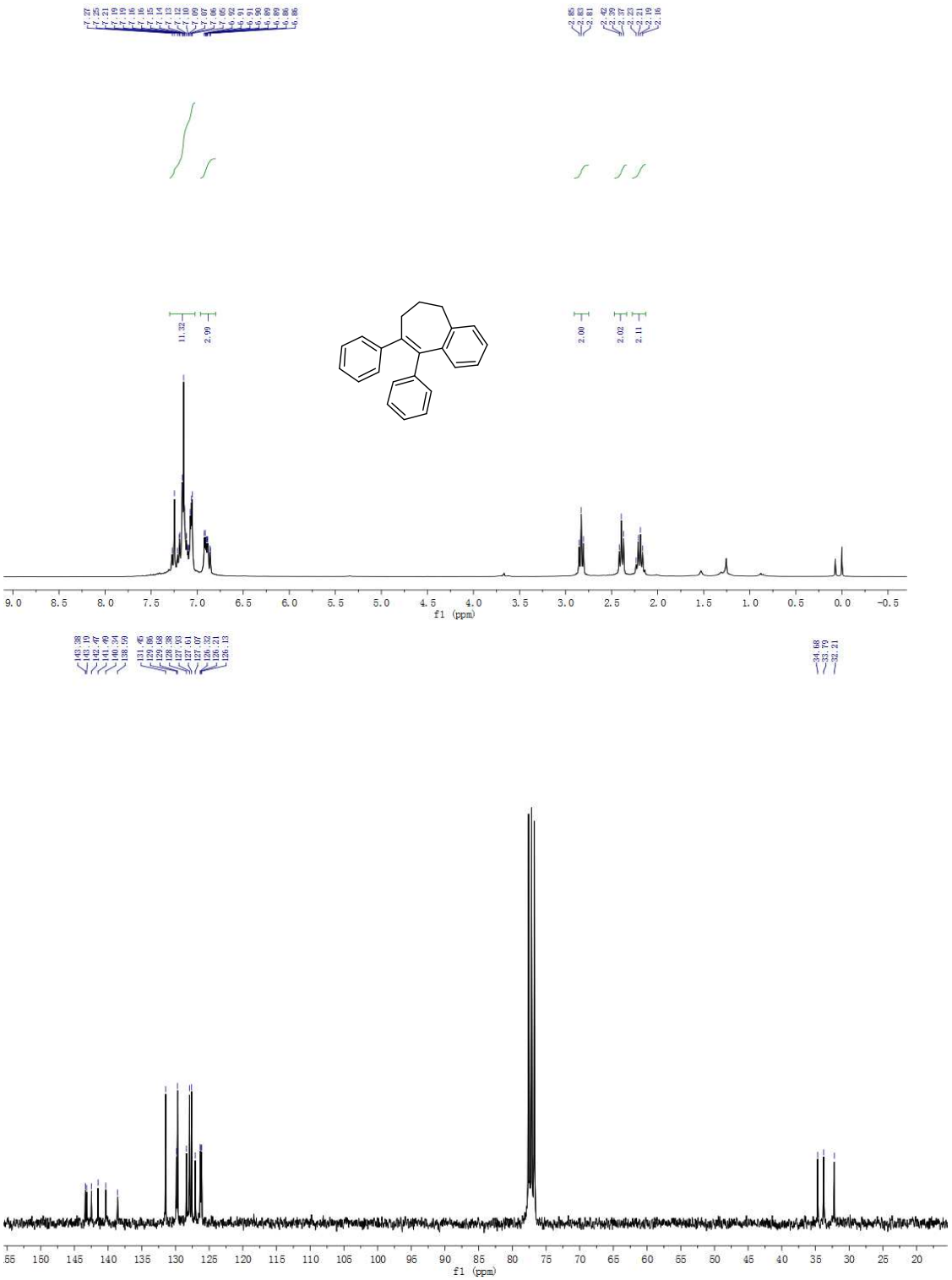
HRMS(APPI) cacud for $C_{20}H_{18}F_3^+$[M-H]$^+$:315.13551,found:315.13609



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

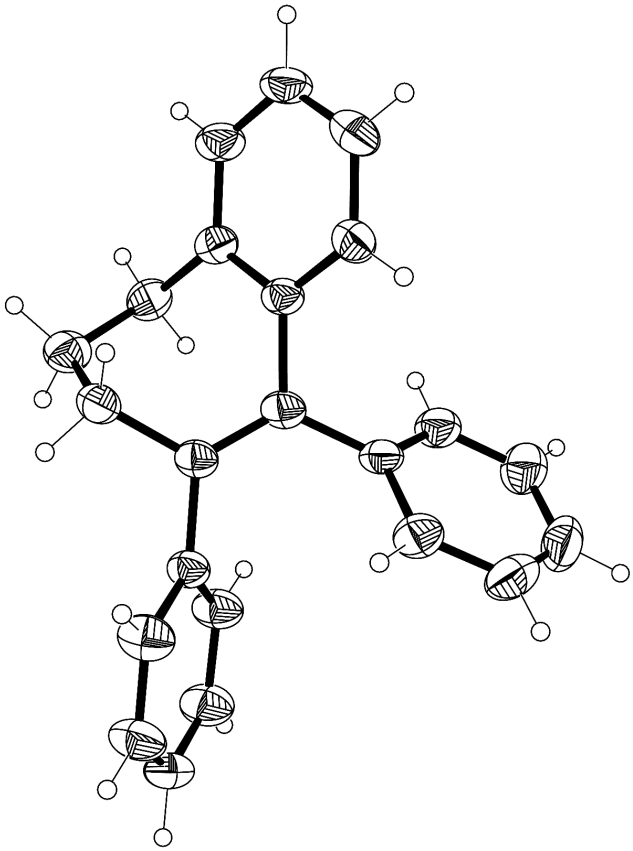


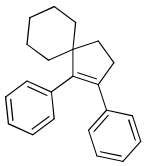
8,9-diphenyl-6,7-dihydro-5H-benzo[7]annulene (4): Colorless solid, 92 mg, yield:62%. Melting point: 120°C ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.30-7.02 (m, 11H), 6.92-6.86 (m, 3H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.39 (t, *J* = 6.9 Hz, 2H), 2.23-2,16 (m, 2H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 143.4, 143.2, 142.5, 141.5, 140.3, 138.6, 131.5, 129.9, 129.7, 128.4, 128.0 127.6, 127.1, 126.3, 126.2, 126.1, 34.7, 33.8, 32.2



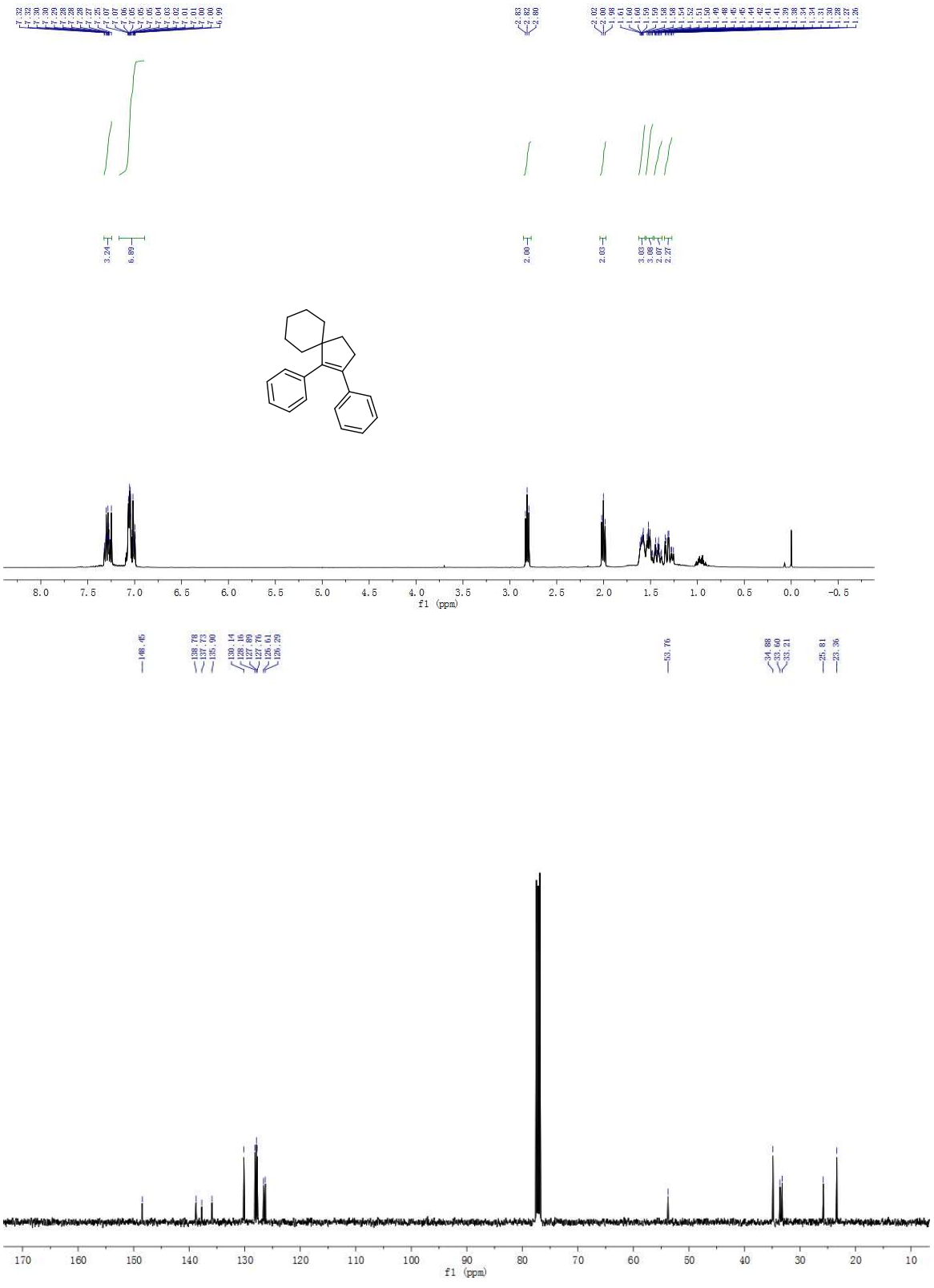
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

X-ray crystal structure analysis of compound 4: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in hexane. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 970671.** Formula: C23H20, M = 296.39, colorless prism, 0.3 × 0.4 × 0.4 mm, a = 5.606(3), b = 8.951(7), c = 17.058(11) Å, α = 81.48(5), β = 82.58(5), γ = 77.41(4) , V = 821.9(9) Å^3, ρ_{calc} = 1.198 gcm^{-3}, μ = 0.067 mm^{-1}, Z = 2, triclinic, space group *P1*, λ = 0.71073 Å, T = 295(2) K. Data completeness = 0.998, Theta (max) = 25.0500, R (reflections) = 0.1114 (1654), wR2 (reflections) = 0.2341 (1654).

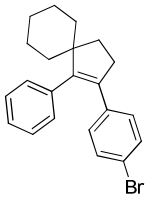




1,2-diphenylspiro[4.5]dec-1-ene (3u): Colorless liquid,96mg, yield: 67%.
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.33-7.25 (m, 3H), 7.07-6.99 (m, 7H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.00 (t, *J* = 7.2 Hz, 2H), 1.61-1.56 (m, 3H), 1.52-1.50 (m, 3H), 1.45-1.43 (m, 2H), 1.35-1.27 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.5, 138.8 , 137.7, 135.9, 130.1, 128.2, 127.9 , 127.8, 126.6, 126.3, 53.8, 34.9, 33.6, 33.2, 25.8, 23.4
HRMS(APPI): cacud for $C_{22}H_{23}^{+}$[M-H]$^{+}$:287.17943,found:287.17923

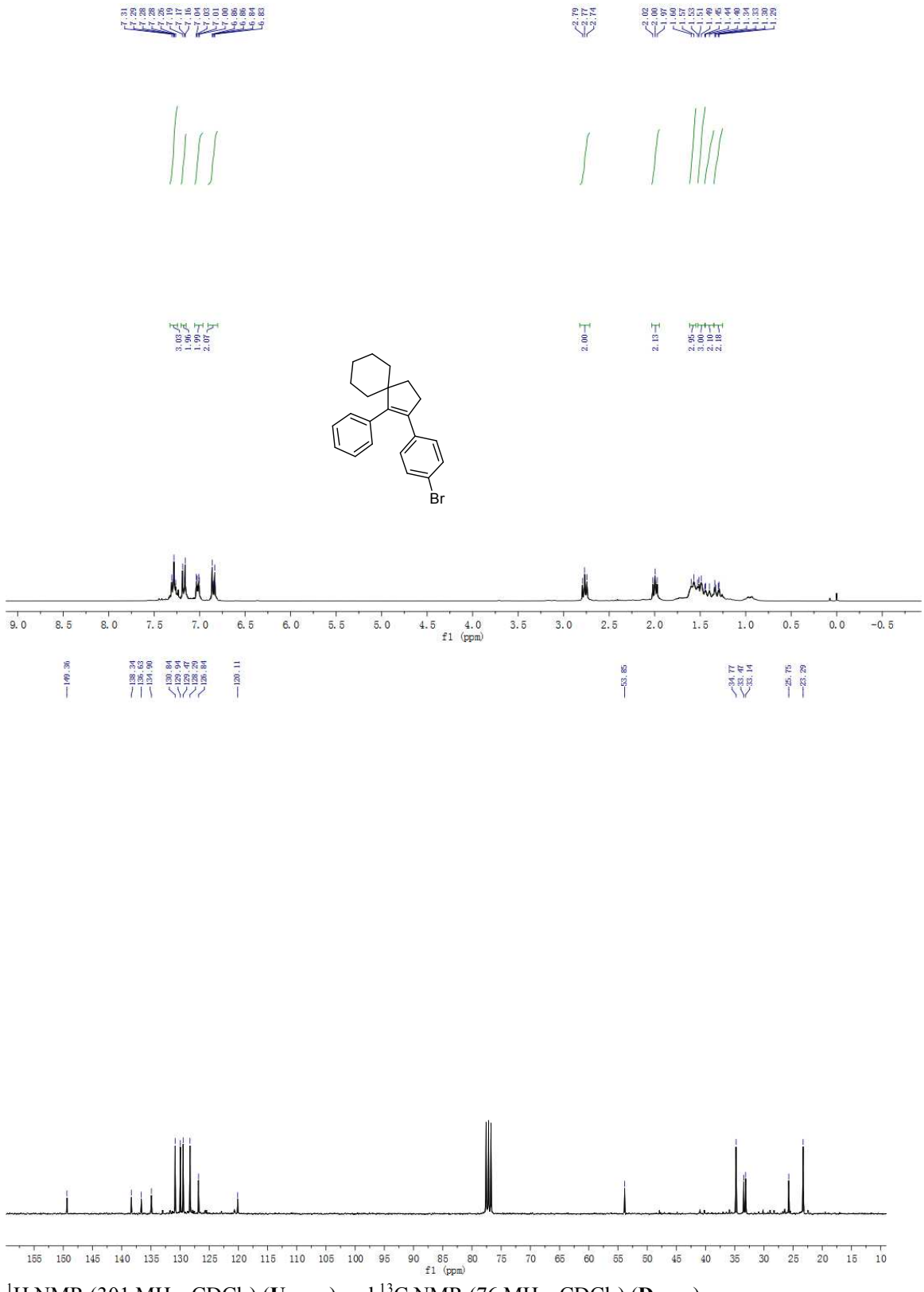


^{1}H NMR (400 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (101 MHz, $CDCl_3$) (**Down**)

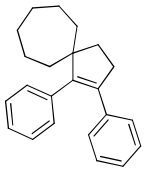


2-(4-bromophenyl)-1-phenylspiro[4.5]dec-1-ene (3v): Colorless liquid,118mg, yield:65%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.31-7.26 (m, 3H), 7.19-7.16 (m, 2H), 7.04-7.00 (m, 2H), 6.86-6.83 (m, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.00 (t, *J* = 7.2 Hz, 2H), 1.60-1.57 (m, 3H), 1.54-1.46 (m, 3H), 1.46-1.36 (m, 2H), 1.34-1.39 (m, 2H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 149.4, 138.3, 136.6 134.9, 130.8, 129.9, 129.5, 128.3, 126.8, 120.1, 53.9, 34.8, 33.5, 33.1, 25.8, 23.3

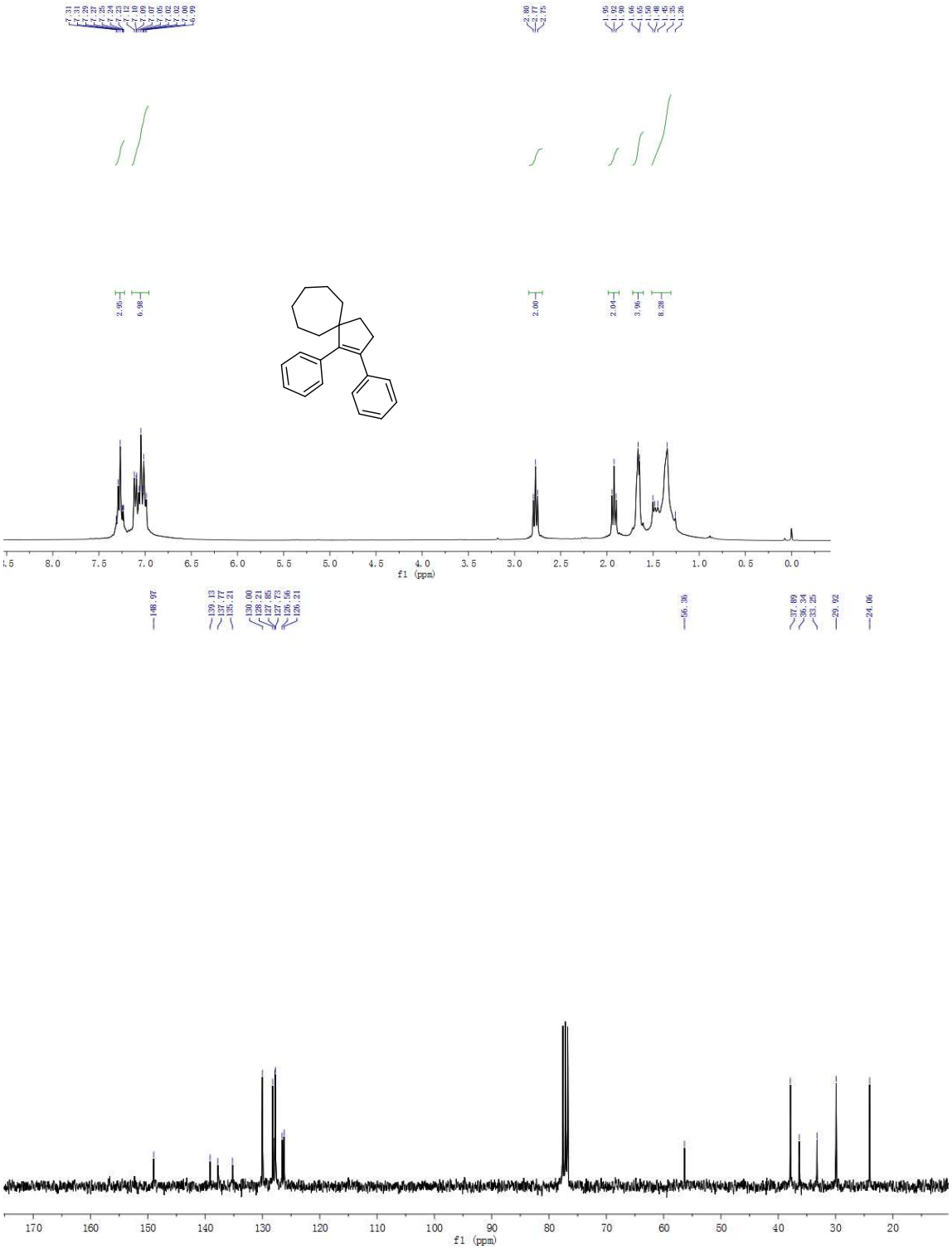
HRMS(APPI): cacud for $C_{22}H_{22}Br^{+}[M-H]^{+}$:366.09776,found:366.09756



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

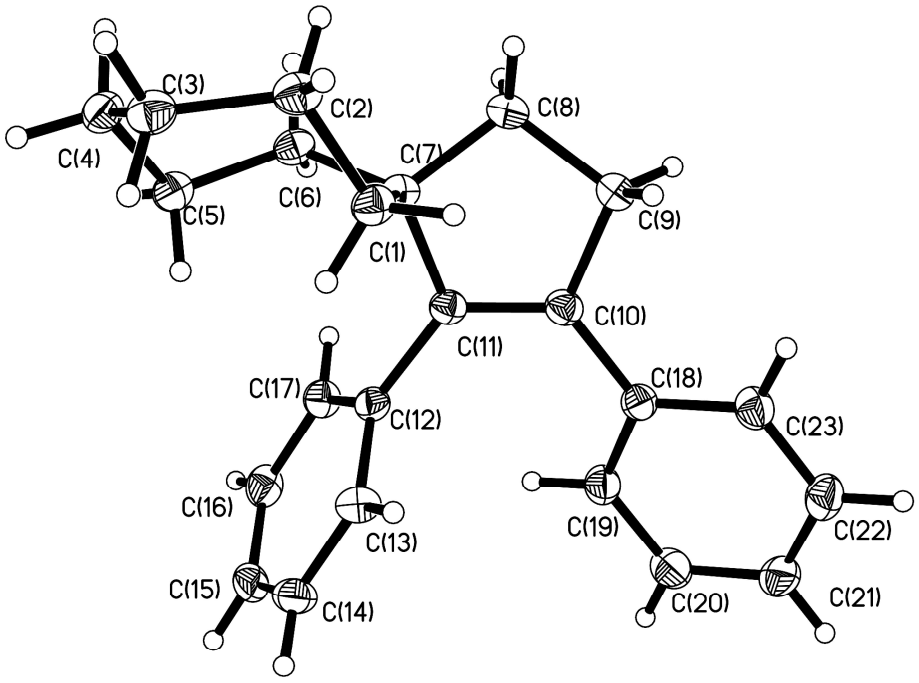


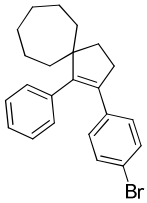
1,2-diphenylspiro[4.6]undec-1-ene (3w): Colorless solid,110 mg, yield:73%; Melting point: 83°C. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.32 – 7.22 (m, 3H), 7.14 – 6.96 (m, 7H), 2.77 (t, *J* = 7.0 Hz, 2H), 1.92 (t, *J* = 7.0 Hz, 2H), 1.66-1.65 (m, 4H), 1.50-1.26 (m, 8H).^{13}C NMR (76 MHz, CHLOROFORM-D) δ 149.0, 139.1, 137.8, 135.2, 130.0, 128.2, 127.9, 127.7, 126.6, 126.2, 56.4, 37.9, 36.3, 33.3, 29.9, 24.1
HRMS(APPI): cacud for $C_{23}H_{25}^{+}$[M-H]$^{+}$:302.20262,found:302.20290



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

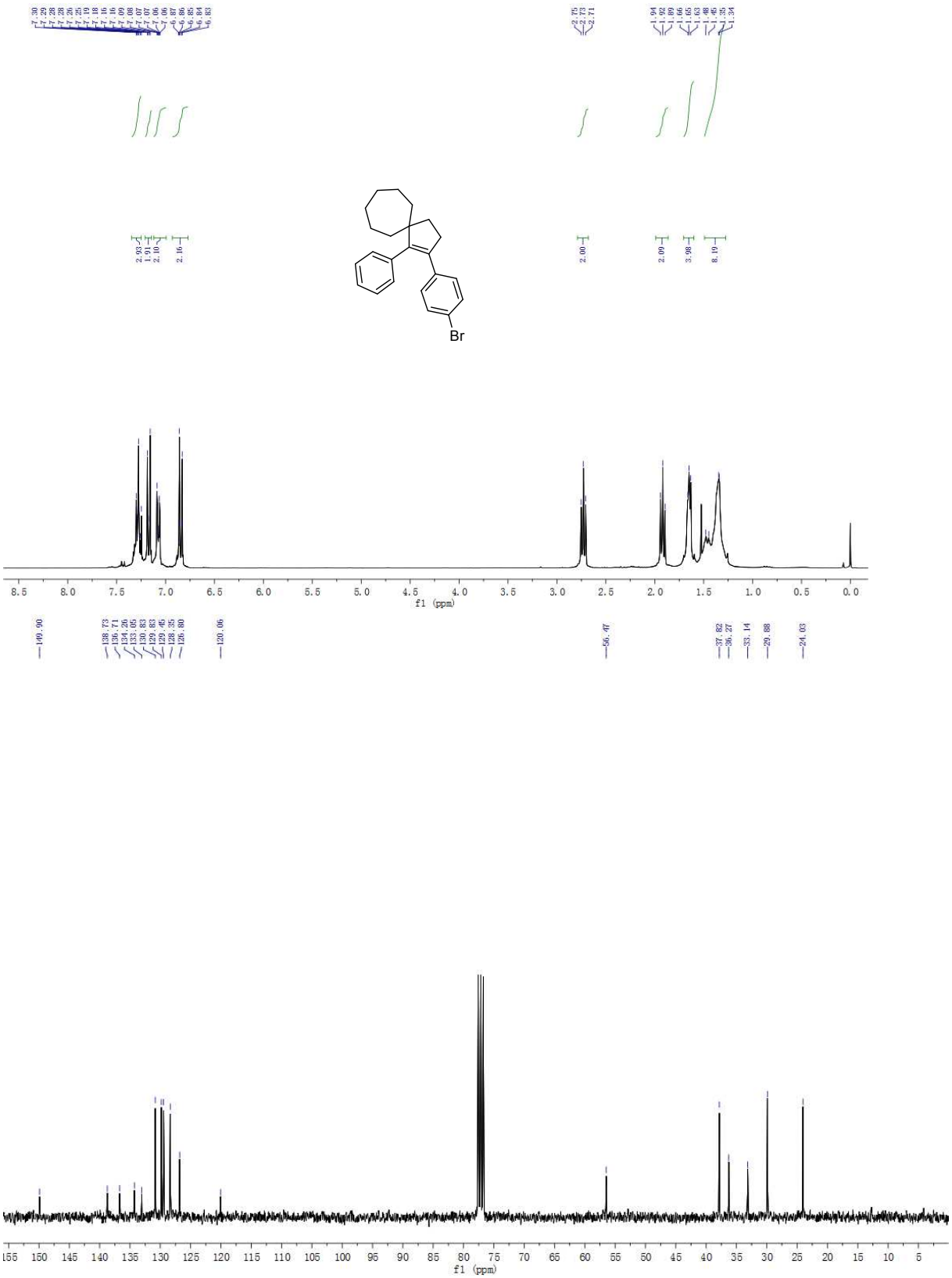
X-ray crystal structure analysis of compound 3w: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in hexane. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 970670.** Formula: C23H26, *M* = 302.44, colourless crystal, 0.391 x 0.354 x 0.159 mm, *a* = 7.7819(16), *b* = 6.1510(12), *c* = 18.029(4) Å, α = 90.00, β = 97.73(3), γ = 90.00 , *V* = 855.1(3) Å^3, ρ_{calc} = 1.175 gcm^{-3}, μ = 0.066 mm^{-1}, *Z* = 2, Monoclinic, space group *p2(1)*, λ = 0.71073 Å, *T* = 293(2) K. Data completeness = 0.0982, Theta (max) = 27.45, R (reflections) = 0.0461 (3252), wR2 (reflections) = 0.1166 (3252).



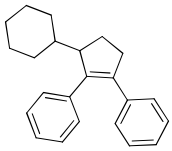


2-(4-bromophenyl)-1-phenylspiro[4.6]undec-1-ene (3x): Colorless solid,133mg, yield:70%; Melting point: 91°C. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.35-7.25 (m, 3H), 7.21-7.14 (m, 2H), 7.12-6.99 (m, 2H), 6.93-6.77 (m, 2H), 2.73 (t, *J* = 7.0 Hz, 2H), 1.92 (t, *J* = 7.0 Hz, 2H), 1.70-1.60 (m, 4H), 1.43-1.34 (m, 8H). ^{13}C NMR (76 MHz, CHLOROFORM-D) δ 149.9, 138.7, 136.7, 134.3, 133.1, 130.8, 129.8, 129.5, 128.4, 126.8, 120.1, 56.5, 37.8, 36.3, 33.1, 29.9, 24.0

HRMS(APPI): cacud for $C_{23}H_{24}Br^{+}[M-H]^{+}$:380.11310,found:380.11341



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

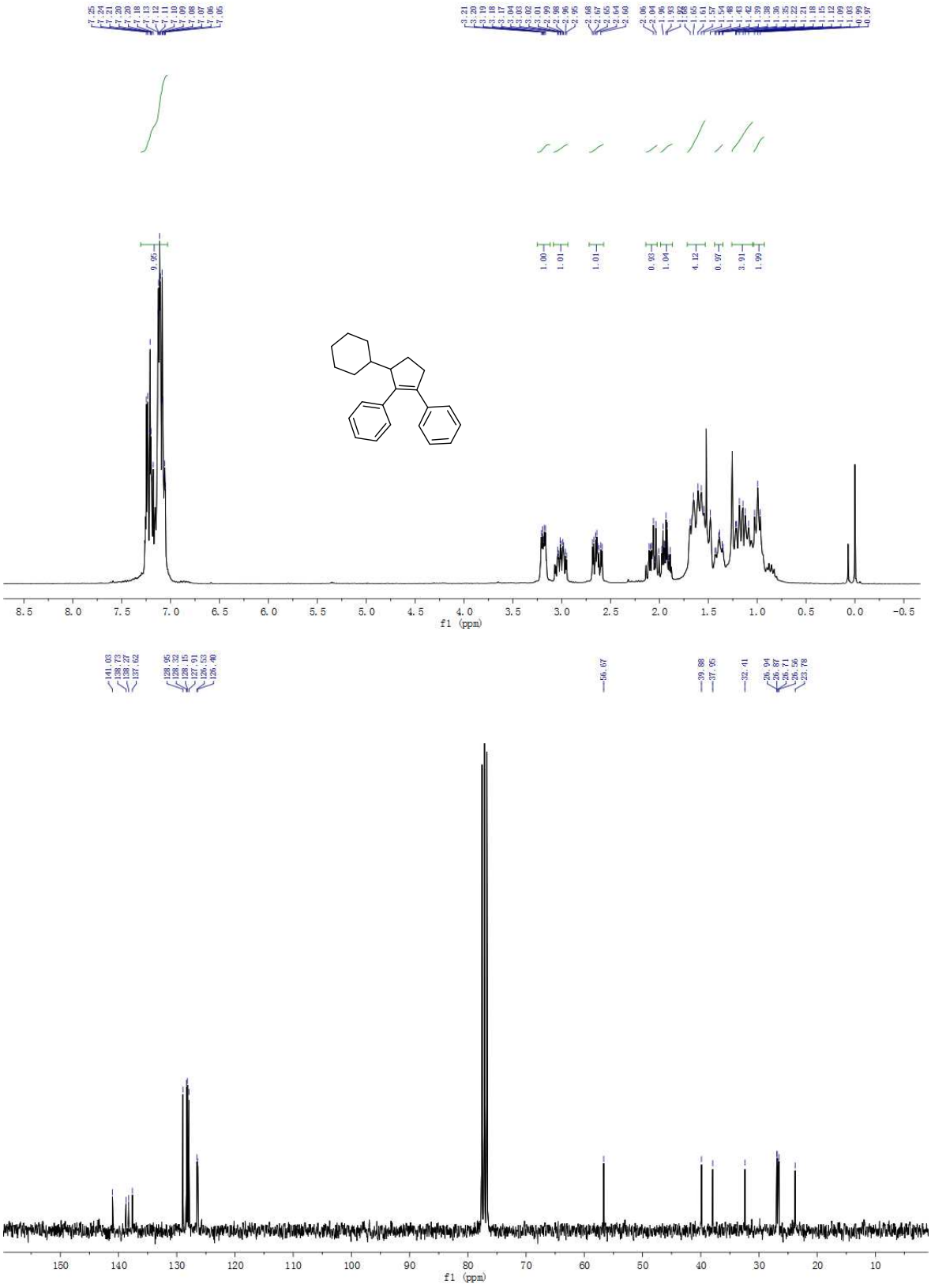


(3-cyclohexylcyclopent-1-ene-1,2-diyl)dibenzene (3e): Colorless liquid,105 mg, yield: 70%.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.31-7.03 (m, 10H), 3.25-3.12 (m, 1H), 3.00 (ddd, *J* = 16.3, 8.3, 3.0 Hz, 1H), 2.64 (ddd, *J* = 15.9, 9.6, 3.6 Hz, 1H), 2.14-2.02 (m, 1H), 1.99-1.87 (m, 1H), 1.72-1.53 (m, 4H), 1.43-1.35 (m, 1H), 1.26-1.05 (m, 4H), 1.04-0.93 (m, 2H).

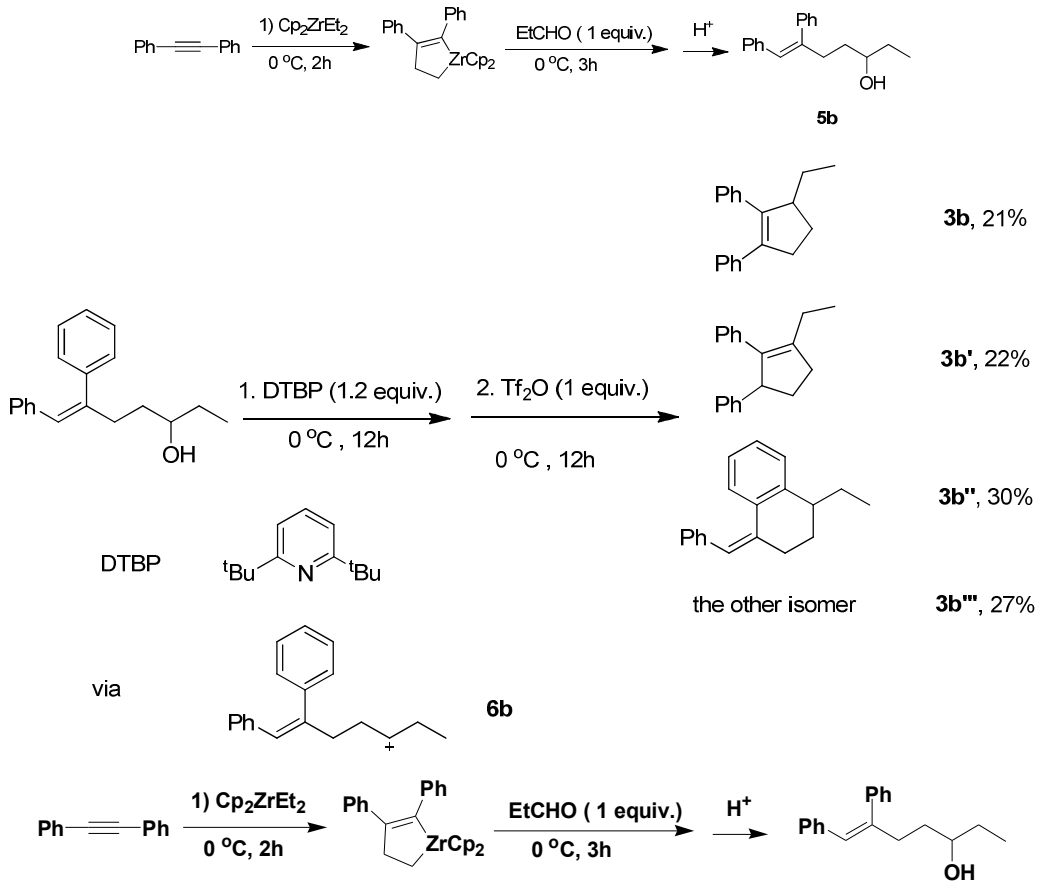
^{13}C NMR (76 MHz, CHLOROFORM-D) δ 141.0, 138.7, 138.3, 137.6, 129.0, 128.3, 128.2, 127.9, 126.5, 126.4, 56.7, 39.9, 38.0, 32.41 (s), 27.0, 26.9, 26.7, 26.6 23.8

HRMS(APPI): cacud for $C_{23}H_{25}^{+}$[M-H]$^{+}$: 301.19508,found: 301.19489

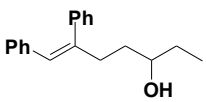


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

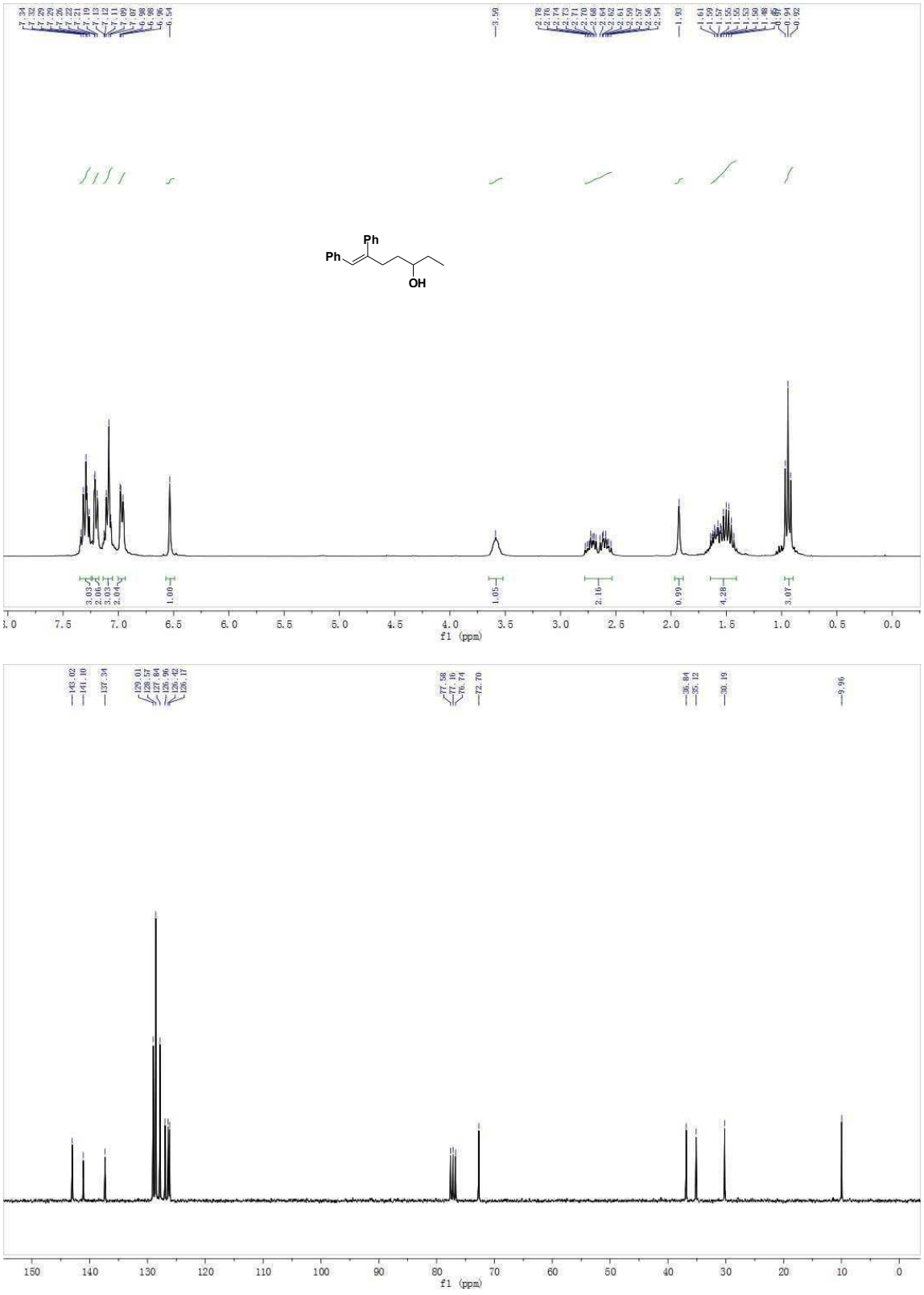
3 Mechanistic Study



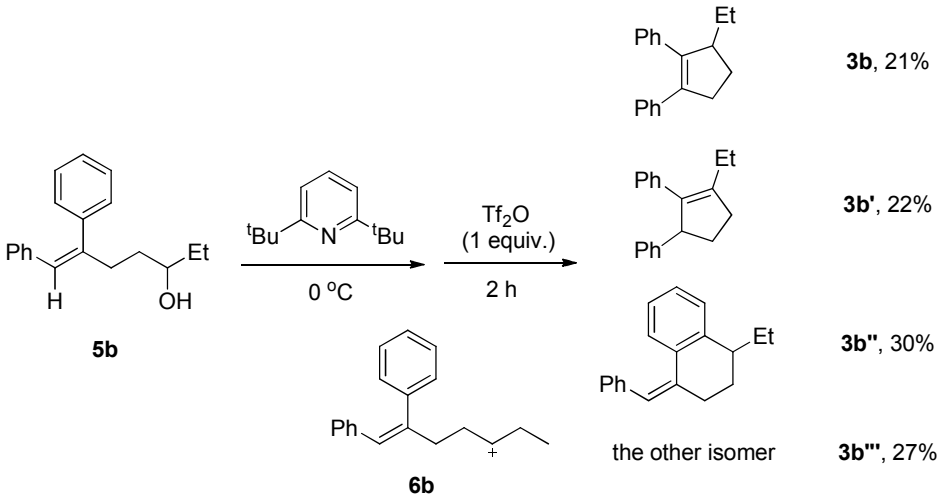
A 50-mL Schlenk tube under dried nitrogen was charged with Cp_2ZrCl_2 (2.95 g, 10 mmol) and THF (20 mL). To this mixture was added ethylmagnesium bromide (2.0 M THF solution, 20 mmol, 10 mL) at -78 °C. After 1 h of stirring, diphenylacetylene (1.78 g, 10 mmol) was added and the reaction mixture was stirred at 0 °C for 3 h. Then to the reaction mixture was added propyl aldehyde (0.717 mL, 10 mmol) and the reaction mixture was stirred at 0 °C for 3 h. The above reaction mixture was then quenched with 3 N HCl and extracted with ethyl acetate. The solvent was evaporated in vacuo to give a light yellow liquid. The liquid was subjected to silica gel column using petroleum ether and ethyl acetate (6:1) as the eluent. The final product was obtained as a colorless liquid.



(Z)-6,7-diphenylhept-6-en-3-ol: colorless oil, yield: 18%. ^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.36-7.26 (m, 3H), 7.22-7.17 (m, 2H), 7.14-7.05 (m, 3H), 7.00 -6.94 (m, 2H), 6.54 (s, 1H), 3.59 (m, 1H), 2.79-2.53 (m, 2H), 1.93 (b, 1H), 1.66-1.43 (m, 4H), 0.94 (t, J = 7.4 Hz, 3H).^{13}C NMR (76MHz, CHLOROFORM-D) δ 143.02, 141.10, 137.34, 129.01, 128.57, 127.84, 126.96, 126.42, 126.17, 72.70, 36.84, 35.12, 30.19, 9.96. GC-MS: m/z calcd for $C_{19}H_{22}O$: 266; found: 266.

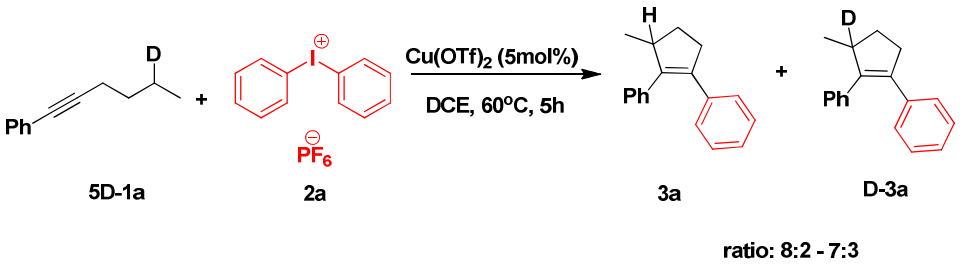


^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

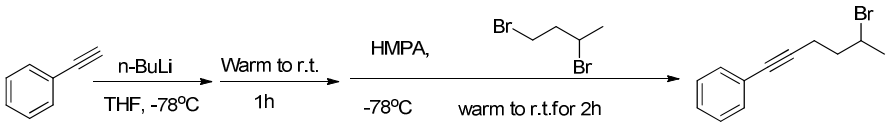


Method : A sealed tube was charged under dried nitrogen with the mixture of (Z)-6,7-diphenylhept-6-en-3-ol **5b** (0.2 mmol, 51 *u*L) and DTBP (2,6-Di-tert-Butyl pyridine, 0.24 mmol, 54 *u*L), then Tf_2O (0.2 mmol, 34 *u*L) was dropped slowly to it by strring at 0 °C. The reaction was allowed to stir at 0 °C in ice-bath tube for 12 h. Evaporation of the solvent followed by purification on silica gel using petroleum ether as the eluent to provide the final product as yellow oil. The structure might be assigned to the mixture of four isomers of **3b**.

To get insight the mechanism, the kinetic isotope effect experiment was carried out with **D-1a**. and **2a**. After major **D-1a** was converted, the mixture of undeuterated product **3a** and deuterated product **D-3a** was isolated at a radio between 8:2 and 7:3. Since that deuterium of **D-3a** locates at allylic position, it is very much likely to be exchanged by protons in the reaction system. So this kinetic isotope effect experiment provides subtle suggestion on the process of cylization.

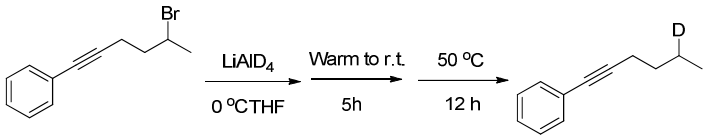


Procedure for the preparation of 5-D-1-phenyl-1-hexyne (5D-1n)

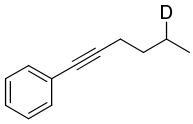


To a solution of phenyl acethylene (1.0 mL, 9 mmol) in THF (20 mL) at -78°C was added n-BuLi (6.0 mL, 1.6 M in hexane, 9.5 mmol), and the mixture was allowed to warm to rt over 0.5 h. The mixture was then cooled to -78 °C, and HMPA (1.74 mL, 10 mmol) and

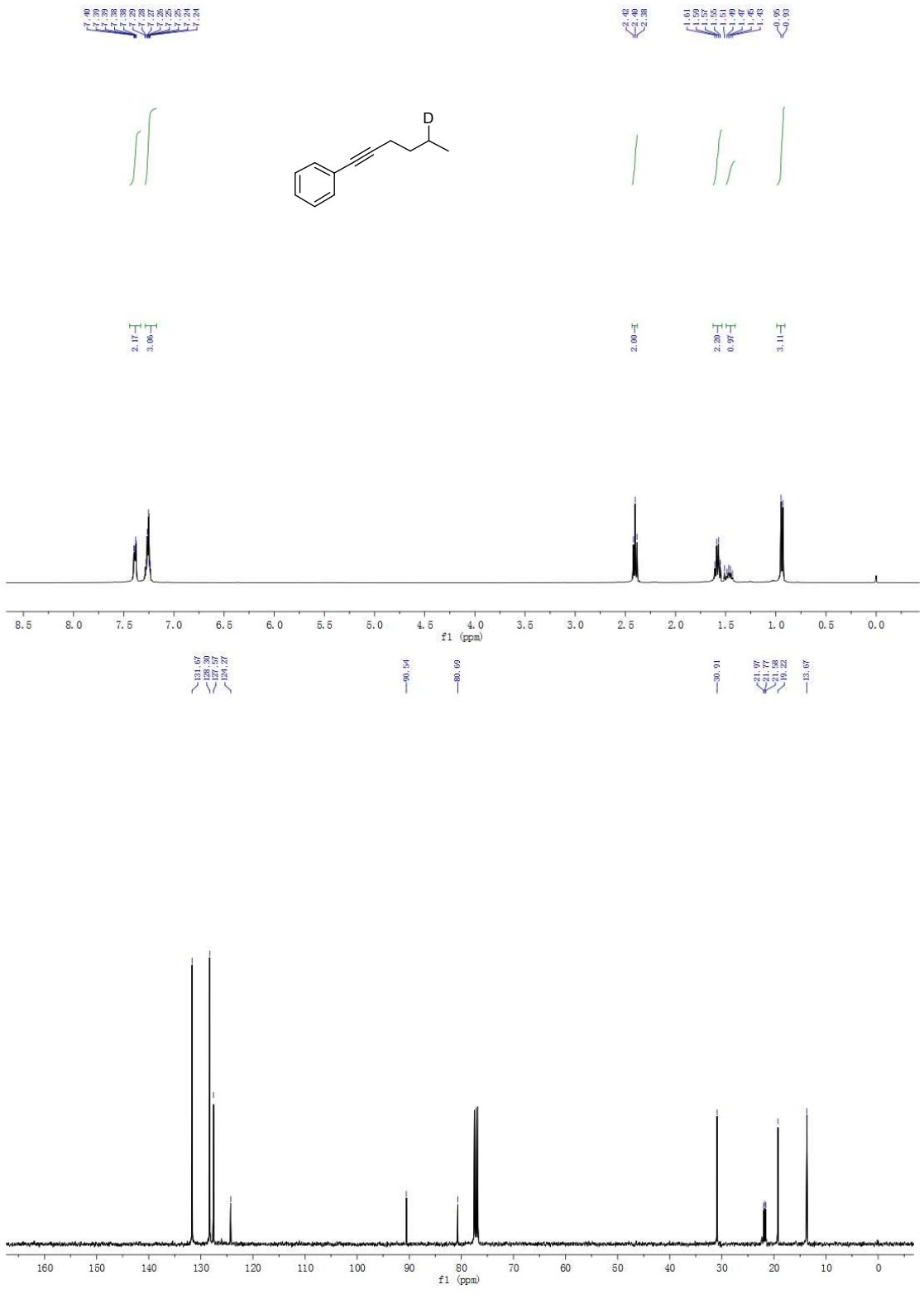
1,3-dibromobutane (1.09 ml, 9 mmol) were added. The mixture was allowed to warm to rt about 2 h and then was quenched with water, and extracted with ether. The organic layer was washed brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether) to give 5-Br-1-phenyl-1-hexyne (yield:75%)[4]



A Schlenk tube was charged with D_4AlLi (190 mg, 5 mmol). The tube was evacuated and recharged with N_2 for 3 times. Adding the solvent of THF and 5-Br-1-phenyl-1-hexyne (5 mmol, 1.18mg) at 0°C then tube was sealed and the mixture was allowed to stir at r.t. for 5 h. The mixture at 50°C for 12h .After the starting materials were completed converted, the mixture was extracted with DCM (25 mL x 3), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (pure petroleum ether) provided 5-D-1-phenyl-1-hexyne (**5D-1n**, yield: 87%).

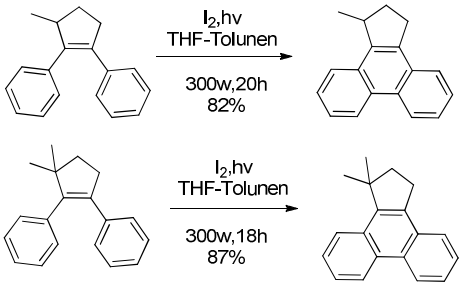


5-D-1-phenyl-1-hexyne (5D-1n): Pale yellow liquid; yield: 65%. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.44-7.33 (m, 2H), 7.29-7.17 (m, 3H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.58 (dd, *J* = 14.4, 7.1 Hz, 2H), 1.46 (dd, *J* = 14.8, 7.4 Hz, 1H), 0.94 (d, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.7, 128.3, 127.6, 124.3, 90.5, 80.7, 30.9, 22.2 (t, *J* = 20 Hz), 19.2, 13.7



^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)

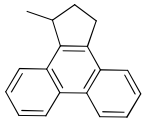
4 Procedure for the preparation of 1-methyl-2,3-dihydro-1H-cyclopenta[l]phenanthrene and 1,1-dimethyl-2,3-dihydro-1H-cyclopenta[l]phenanthrene:



A solution of (3-methylcyclopent-1-ene-1,2-diyl)dibenzene (**3a**) (100 mg, 0.43 mmol) and iodine (154mg,0.61 mmol) in toluene (1 mL) and tetrahydrofuran (2 mL) was irradiated in a standard immersion well photoreactor with 300-W high pressure mercury vapor lamp for 20 h, until no starting material was seen by TLC. The reaction mixture was then quenched by aqueous sodium thiosulfate and extracted the aimed compound with ethyl acetate. The concentrated mixture was purified on silica gel column to afford 1-methyl-2,3-dihydro-1H-cyclopenta[l]phenanthrene as with liquid (82 mg,81%) [14]

The same operation was conducted with the starting material of (3,3-dimethylcyclopent-1-ene-1,2-diyl)dibenzene(3h)

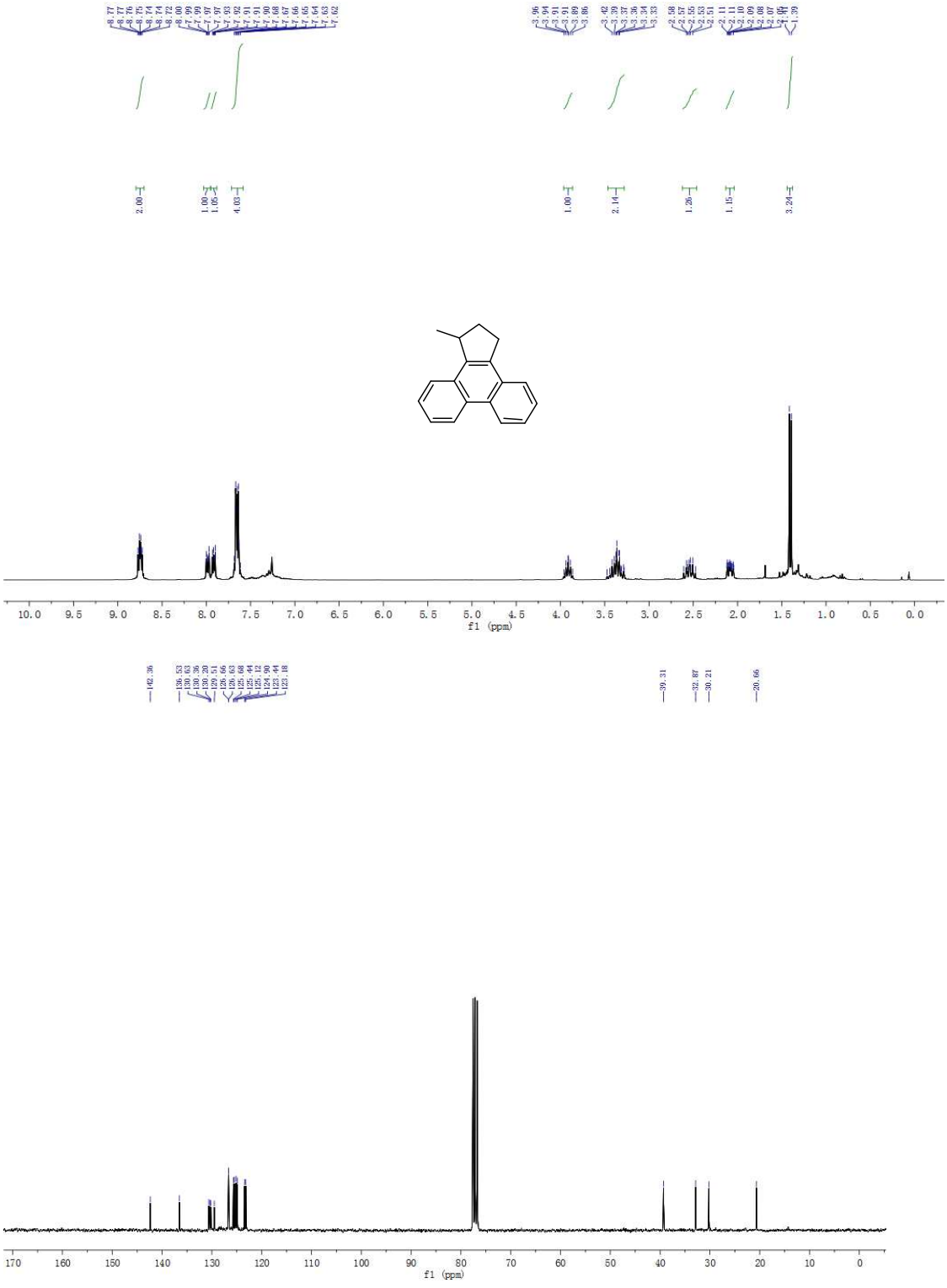
Photocatalytic experiments were conducted with under UV light (365 nm, 300 W) irradiation on an XPA photochemical reactor (Xujiang, Nanjing ,China). A 300-W high pressure mercury vapor lamp was placed in the center of the reactor which emitted UV light (365nm) without any cutofffilter. The tube filled with reactant and solvent was place on a turntable which rotated for 15second per round.



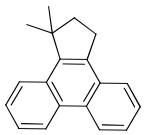
1-methyl-2,3-dihydro-1H-cyclopenta[l]phenanthrene(7a): colorless liquid, 82 mg, yield: 82%.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 8.79 – 8.70 (m, 2H), 8.03 – 7.95 (m, 1H), 7.95 – 7.88 (m, 1H), 7.71 – 7.58 (m, 4H), 3.91 (dq, *J* = 14.1, 7.0 Hz, 1H), 3.46 – 3.28 (m, 2H), 2.54 (ddd, *J* = 18.2, 12.6, 9.5 Hz, 1H), 2.13 – 2.04 (m, 1H), 1.40 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 142.4, 136.5, 130.6, 130.4, 130.2, 129.5, 126.7, 126.6, 125.7, 125.4, 125.1, 124.9, 123.4, 123.2, 39.3, 32.9, 30.2, 20.7



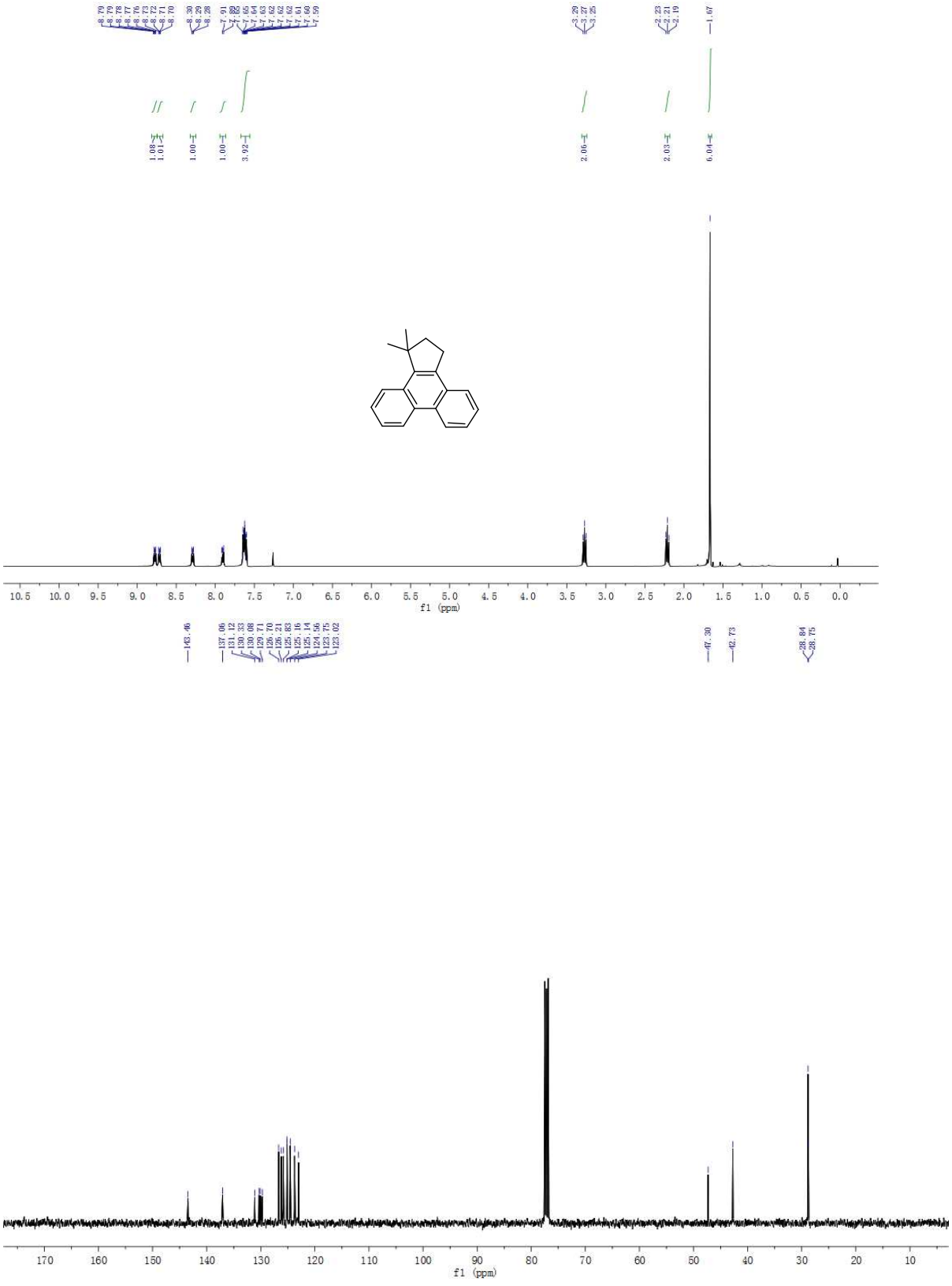
^{1}H NMR (301 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (76 MHz, $CDCl_3$) (**Down**)



1,1-dimethyl-2,3-dihydro-1H-cyclopenta[l]phenanthrene: colorless solid, mp:147°C, 87mg, yield: 87%.

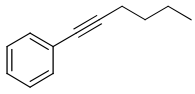
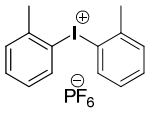
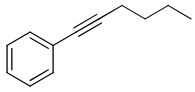
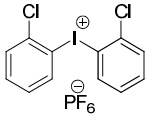
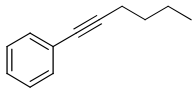
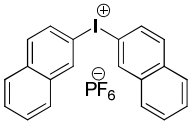
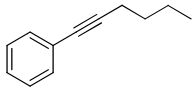
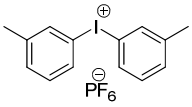
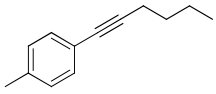
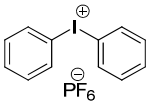
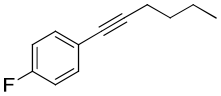
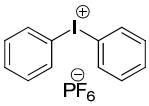
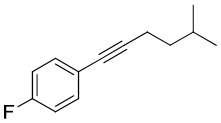
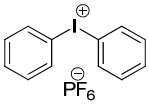
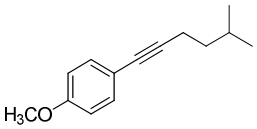
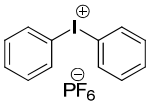
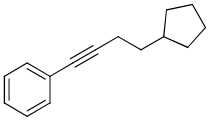
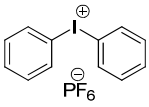
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.82 – 8.75 (m, 1H), 8.71 (dd, *J* = 6.2, 3.3 Hz, 1H), 8.29 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.90 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.67 – 7.56 (m, 4H), 3.27 (t, *J* = 7.4 Hz, 2H), 2.21 (t, *J* = 7.4 Hz, 2H), 1.67 (s, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.5, 126.7, 126.2 125.8, 125.2, 125.1, 124.6, 123.8, 123.0, 47.3, 42.7, 28.8, 28.8



^{1}H NMR (400 MHz, $CDCl_3$) (**Upper**) and ^{13}C NMR (101 MHz, $CDCl_3$) (**Down**)

5 Discussion of the negative results

Alkynes	Diaryliodonium salts	Result
		**Trace amount of the desired product**
		**Trace amount of the desired product**
		**No desired product**
		**Undefined impurities**
		**Undefined impurities**
		**Undefined impurities**
		**Undefined impurities**
		**Easily decomposed**
		**Undefined impurities**

6 Computational Details:

Density functional theory (DFT) calculations were employed to explore the reaction mechanism. For full geometry optimization in gas phase, hybrid GGA functional B3LYP[8] was used with Ahlrichs' double-ζ polarized def2-SVP basis set,[9] called B1, for all the atoms. Optimized minima and transition states are verified by vibrational analysis to have no and one imaginary frequency, respectively. The thermal correction at the experimental temperature of 60 ºC for free Gibbs energy was obtained also from these harmonic vibrational frequency calculations. To refine the calculated energy, single point calculation with larger basis set were then done on these optimized structures, by using B3LYP functional and triple-ζ multiple polarized def2-TZVP basis set,[9] called B2. Unless specified otherwise, reported energetics in this work is from the B3LYP/B2 level. In both B1 and B2 basis set, Stuttgart-Köln small-core energy-consistent relativistic pseudopotential ECP28MDF was employed for iodine atom to account for the scalar relativistic effect.[10] Solvent effect was modeled in these single point calculations with B2 basis set by employing continuum solvation model SMD,[11] with dichloroethane (DCE) as solvent. The final reported energetics also include the Grimme's DFT-D3 empirical dispersion correction for B3LYP with Becke-Johnson short-range damping scheme.[12] All calculations were performed with Gaussian 09 program.[13]

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