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Acid-promoted Bicyclization of Arylacetylenes to Benzobicyclo[3.2.1] Octanes through Cationic Rearrangements

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List of the contents:

1. General information

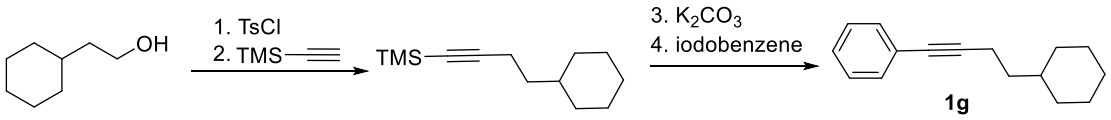
All the reactions were carried out in oven-dried screw-capped tube with a Teflon-lined septum under N_2 atmosphere. Alkynes reagents were prepared according to the literatures. Trifluoromethanesulfonic acid (TfOH) was purchased from Acros (99%) or Adamas (99%+) and used as supplied. All of the solvents were washed with H_2SO_4(c) and freshly distilled over CaH_2 to remove H_2O and ethanol before use. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^{1}H 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. ^{1}HNMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra are reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77.16 ppm. ^{2}H NMR spectra were recorded at 77 MHz using $CDCl_3$ (δ(D) = 7.26 ppm) as external reference. HRMS experiments were carried out on a Thermo Scientific LTQ Oribtrap XL (Bremen, Germany) equipped with Atmospheric-pressure Photoionization (APPI) probe and operated in the positive ion mode. The reaction progress was monitored by GC using n-Dodecane as internal standard.

2. Experimental section

2.1 Preparation of starting materials

1) Preparation of compound 1a-1o

Procedure A: Take the preparation of (4-cyclohexylbut-1-yn-1-yl)benzene (**1g**) as example

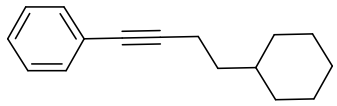


p-Toluenesulfonyl chloride (11.4 g, 60 mmol) was slowly added to a stirred solution of 2-cyclohexylethanol (50 mmol, 6.4 g) in pyridine (30 mL) maintained at 0 °C. The reaction mixture was allowed to stir an additional 12 h and then quenched with H_2O (75 mL) and extracted with EtOAc (3×30 mL), and the combined organic layers were washed with 10% HCl (3× 60 mL) followed by brine (1×50 mL). The organic layer was dried over $MgSO_4$ and concentrated under vacuum to provide the corresponding tosylate as pale yellow liquid (13.2 g, 94%) without further purification[1].

To a solution of ethynyltrimethylsilane (2.95 g, 30 mmol) in THF (20 mL) at -78^oC under N_2 atmosphere was dropwise added n-BuLi (20.6 mL, 1.6 M in hexane, 33 mmol) and was allowed to warm to r.t. for 1.0 h. The mixture was then cooled to -78 ^oC, then HMPA (5.91 g, 33 mmol) and 2-cyclohexylethyl 4-methylbenzenesulfonate (9.31 g, 33 mmol) were added. It was allowed to warm to r.t. for overnight and then was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash silica gel column chromatography with petroleum ether as eluent to give crude (4-cyclohexylbut-1-yn-1-yl)trimethylsilane (4.18 g, 67%) as colorless liquid.[2]

To a solution of (4-cyclohexylbut-1-yn-1-yl)trimethylsilane (4.16 g, 20 mmol, 1.0 eq.) in MeOH (40 ml) was added K_2CO_3 (2.76 g, 20 mmol, 1.0 eq.) under N_2 atmosphere. The originally cloudy mixture became clear upon stirring for 10 h at room temperature. Then the mixture was quenched with water and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and carefully concentrated under reduced pressure to give the but-3-yn-1-ylcyclohexane (2.01 g, 74%), which was directly used in next step without further purification.[3]

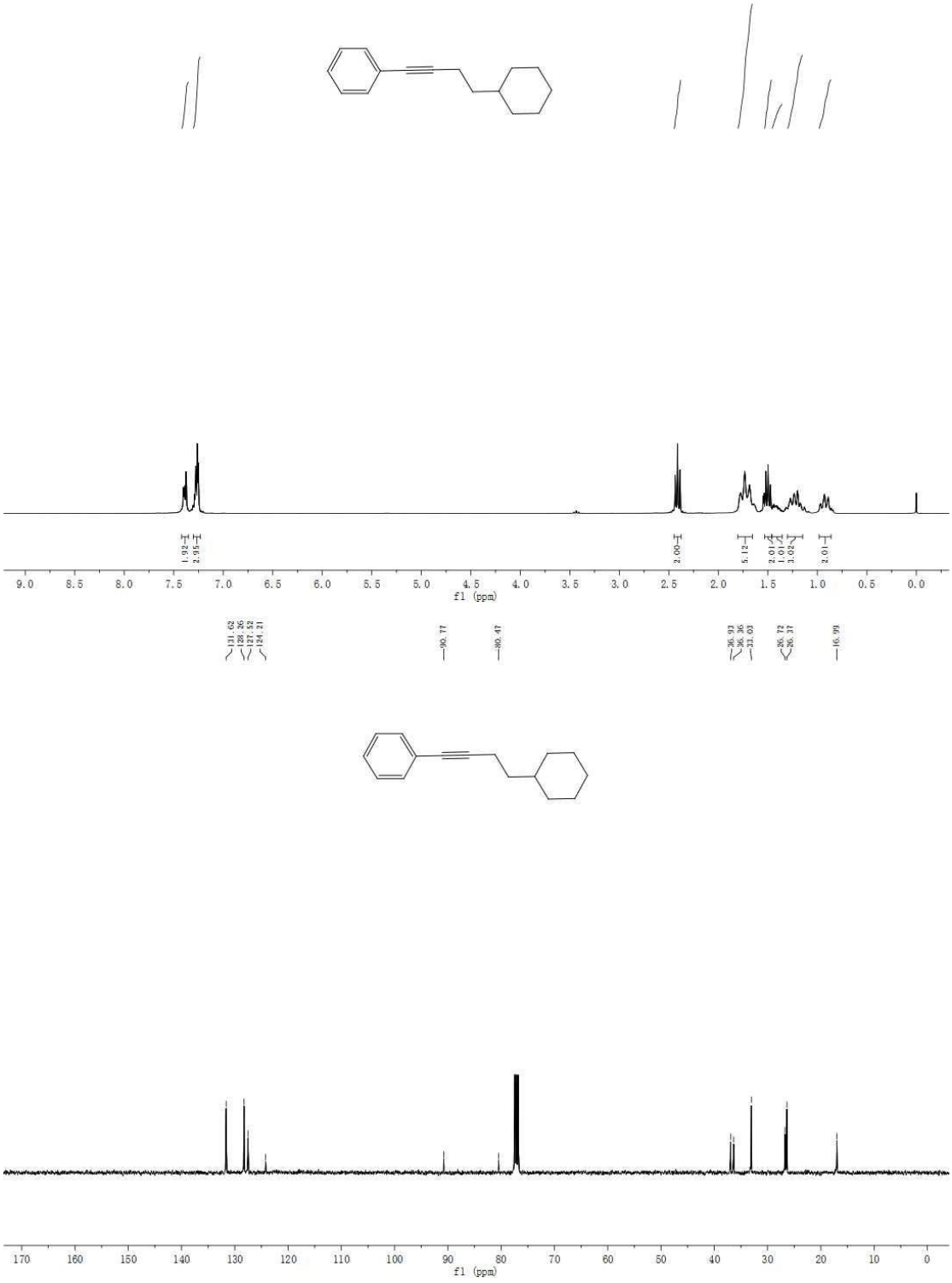
A sealed tube was charged with the mixture of $PdCl_2(PPh_3)_2$ (2 mol%, 70 mg) and CuI (1 mol%, 10 mg). The tube was evacuated and recharged with N_2 for 3 times. After the but-3-yn-1-ylcyclohexane(5.5 mmol, 748 mg), iodobenzene (5 mmol, 1.02 g) and Et_3N (10 ml) were added, the tube was allowed to stir at 65 ^oC for 12 h. After the reaction was completed, the mixture was cooled to room temperature and extracted with DCM (10 mL× 3). The organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by purification on silica gel (pure petroleum ether) provided the corresponding product (4-cyclohexylbut-1-yn-1-yl)benzene (**1g**, colorless liquid, 943 mg, 89%).[4]



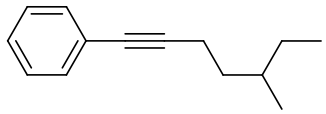
GC-MS: m/z calcd for $C_{16}H_{20}$: 212, found: 212.

^1H NMR (301 MHz, CHLOROFORM-D) δ 7.42 - 7.35 (m, 2H), 7.30 - 7.23 (m, 3H), 2.41 (t, J = 7.4 Hz, 2H), 1.80 - 1.66 (m, 5H), 1.53 - 1.46 (m, 2H), 1.46 - 1.35 (m, 1H), 1.30 - 1.15 (m, 3H), 0.98 - 0.86 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.66 (CH×2), 128.31 (CH×2), 127.56, 124.25, 90.82, 80.52, 36.98, 36.40, 33.08 (CH_2×2), 26.77, 26.41 (CH_2×2), 17.04.



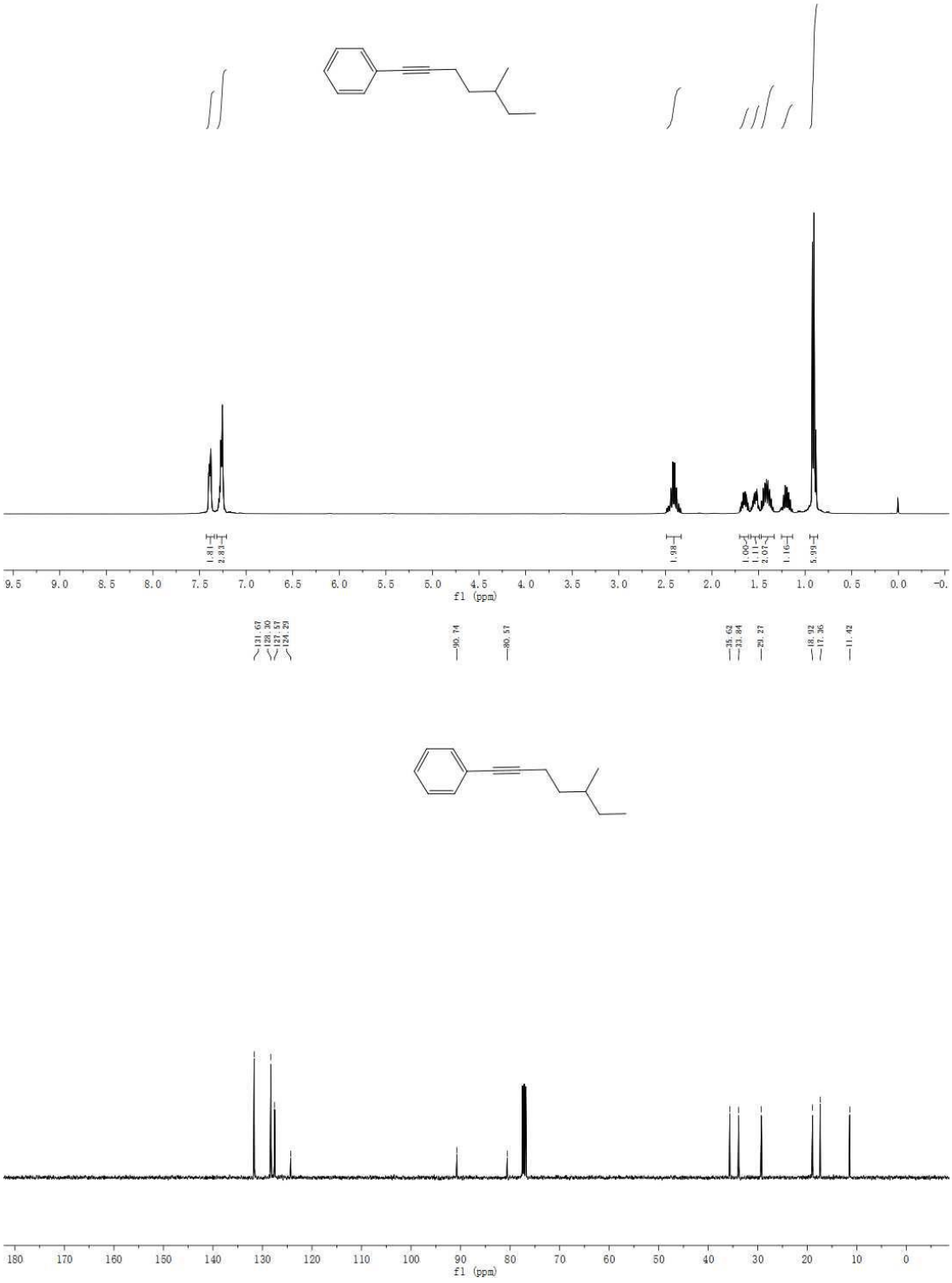
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



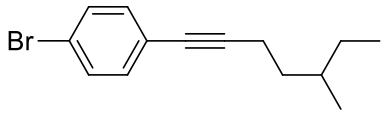
(5-methylhept-1-yn-1-yl)benzene (**1a**, prepared according to procedure A) : pale yellow liquid, isolated yield (single step): 84%. GC-MS: m/z calcd for $C_{14}H_{18}$: 186, found: 186.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (dd, J = 6.5, 1.7 Hz, 2H), 7.31 - 7.21 (m, 3H), 2.49 - 2.33 (m, 2H), 1.70 - 1.61 (m, 1H), 1.58 - 1.49 (m, 1H), 1.47 - 1.33 (m, 2H), 1.25 - 1.13 (m, 1H), 0.95 - 0.86 (m, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.67 (CH×2), 128.30 (CH×2), 127.57, 124.29, 90.74, 80.57, 35.62, 33.84, 29.27, 18.92, 17.36, 11.42.



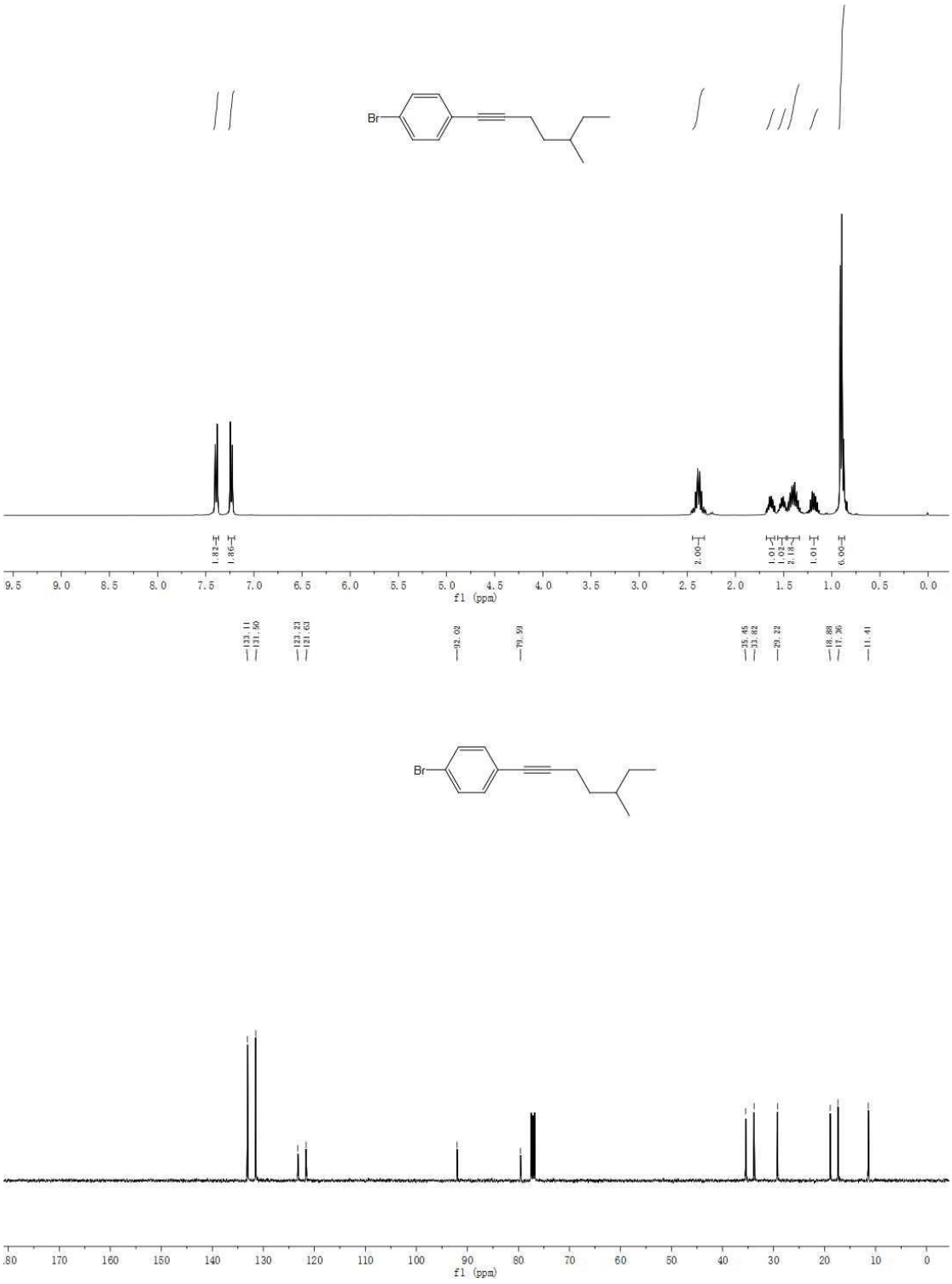
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



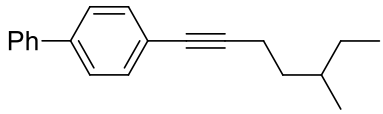
1-bromo-4-(5-methylhept-1-yn-1-yl)benzene (**1b**, prepared according to procedure A) : pale yellow liquid, isolated yield (single step): 78%. GC-MS: m/z calcd for $C_{14}H_{17}Br$: 264, found: 264.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 2.45 - 2.32 (m, 2H), 1.64 (dt, J = 13.2, 7.6 Hz, 1H), 1.56 - 1.47 (m, 1H), 1.46 - 1.34 (m, 2H), 1.23 - 1.14 (m, 1H), 0.93 - 0.87 (m, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 133.11 (CH×2), 131.50 (CH×2), 123.23, 121.63, 92.02, 79.59, 35.45, 33.82, 29.22, 18.88, 17.36, 11.41.



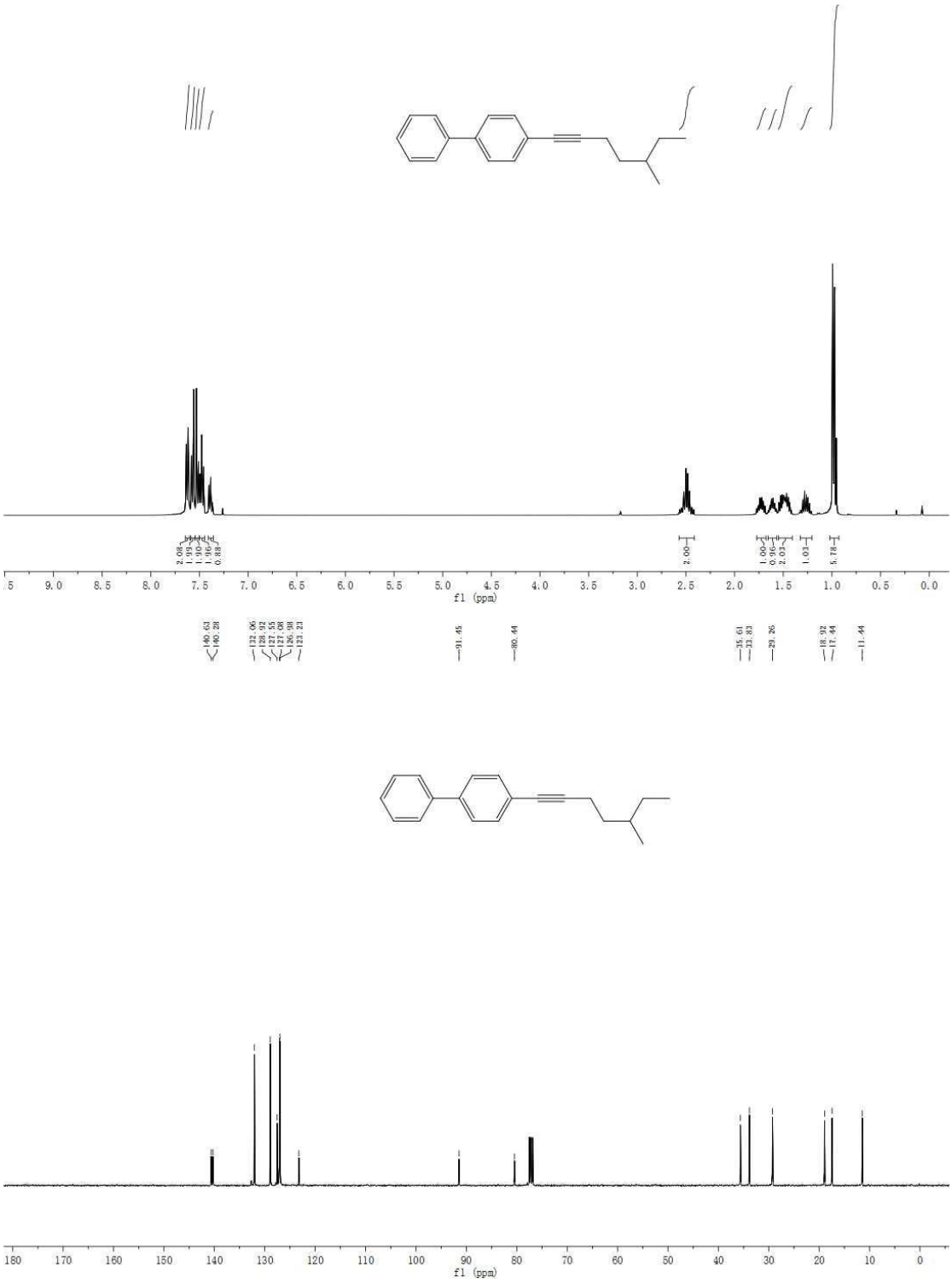
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



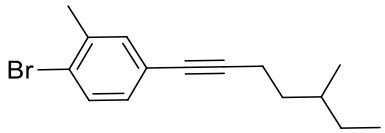
4-(5-methylhept-1-yn-1-yl)-1,1'-biphenyl (**1c**, prepared according to procedure A) : white solid, isolated yield (single step): 79%. GC-MS: m/z calcd for $C_{20}H_{22}$: 262, found: 262.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.62 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 2.57 - 2.41 (m, 2H), 1.73 (ddd, J = 13.2, 7.7, 4.5 Hz, 1H), 1.61 (td, J = 12.7, 6.3 Hz, 1H), 1.55 - 1.41 (m, 2H), 1.32 - 1.20 (m, 1H), 1.02 - 0.93 (m, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.63, 140.28, 132.06 (CH×2), 128.92 (CH×2), 127.55, 127.08 (CH×2), 126.98 (CH×2), 123.23, 91.45, 80.44, 35.61, 33.83, 29.26, 18.92, 17.44, 11.44.



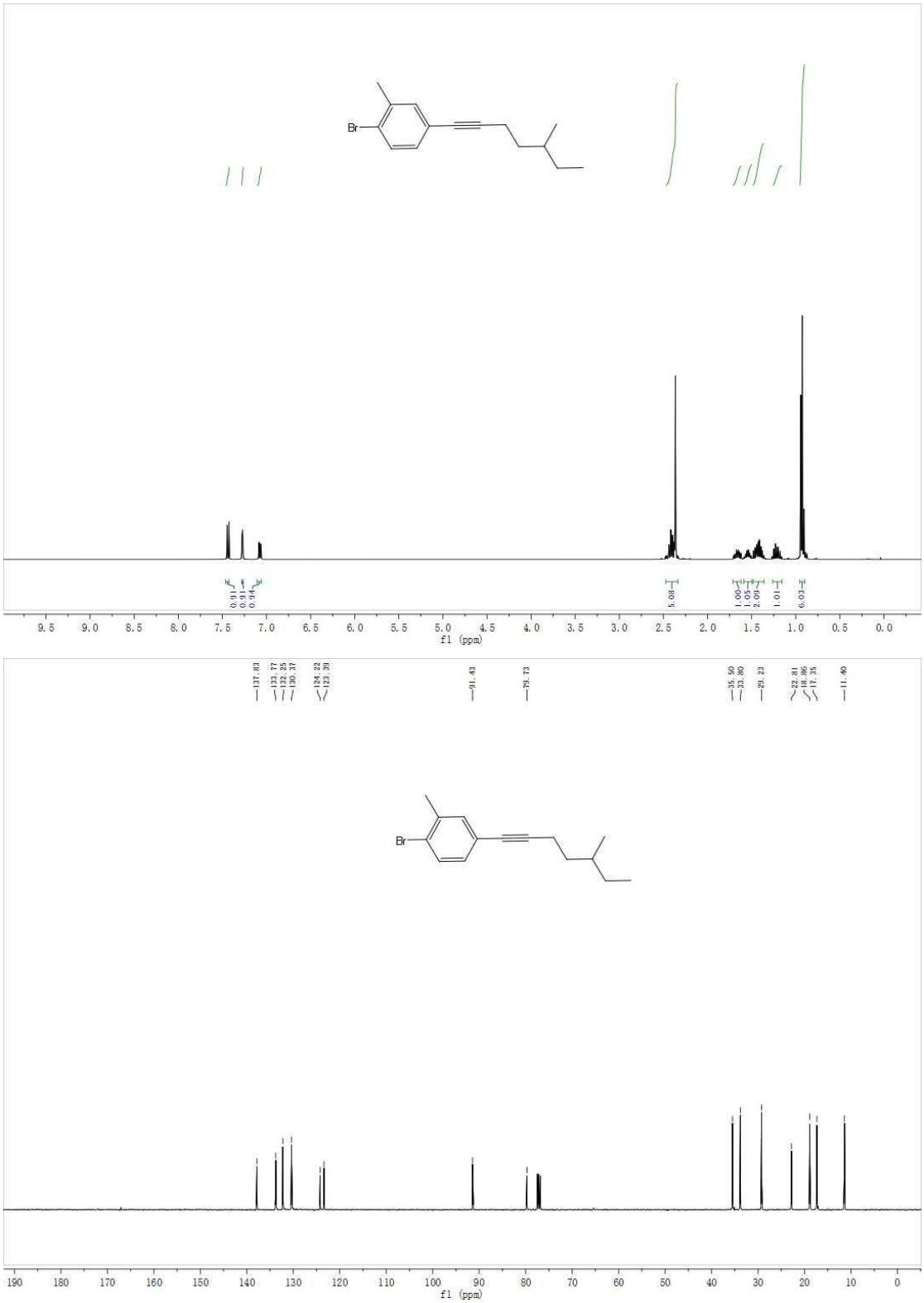
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



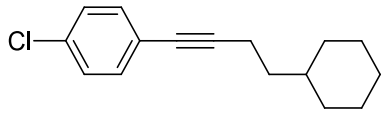
1-bromo-2-methyl-4-(5-methylhept-1-yn-1-yl)benzene (**1d**, prepared according to procedure A), pale yellow liquid, isolated yield (single step): 80%. GC-MS: m/z calcd for $C_{15}H_{19}Br$: 278, found: 278.

1H NMR (400 MHz, CHLOROFORM-D) δ 7.44 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 1.6 Hz, 1H), 7.07 (dd, J = 8.2, 1.9 Hz, 1H), 2.47 - 2.34 (m, 5H), 1.71 - 1.62 (m, 1H), 1.59 - 1.50 (m, 1H), 1.42 (m, 2H), 1.20 (m, 1H), 0.92 (m, 6H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.83, 133.77, 132.25, 130.37, 124.22, 123.39, 91.43, 79.73, 35.50, 33.80, 29.23, 22.81, 18.86, 17.35, 11.40.



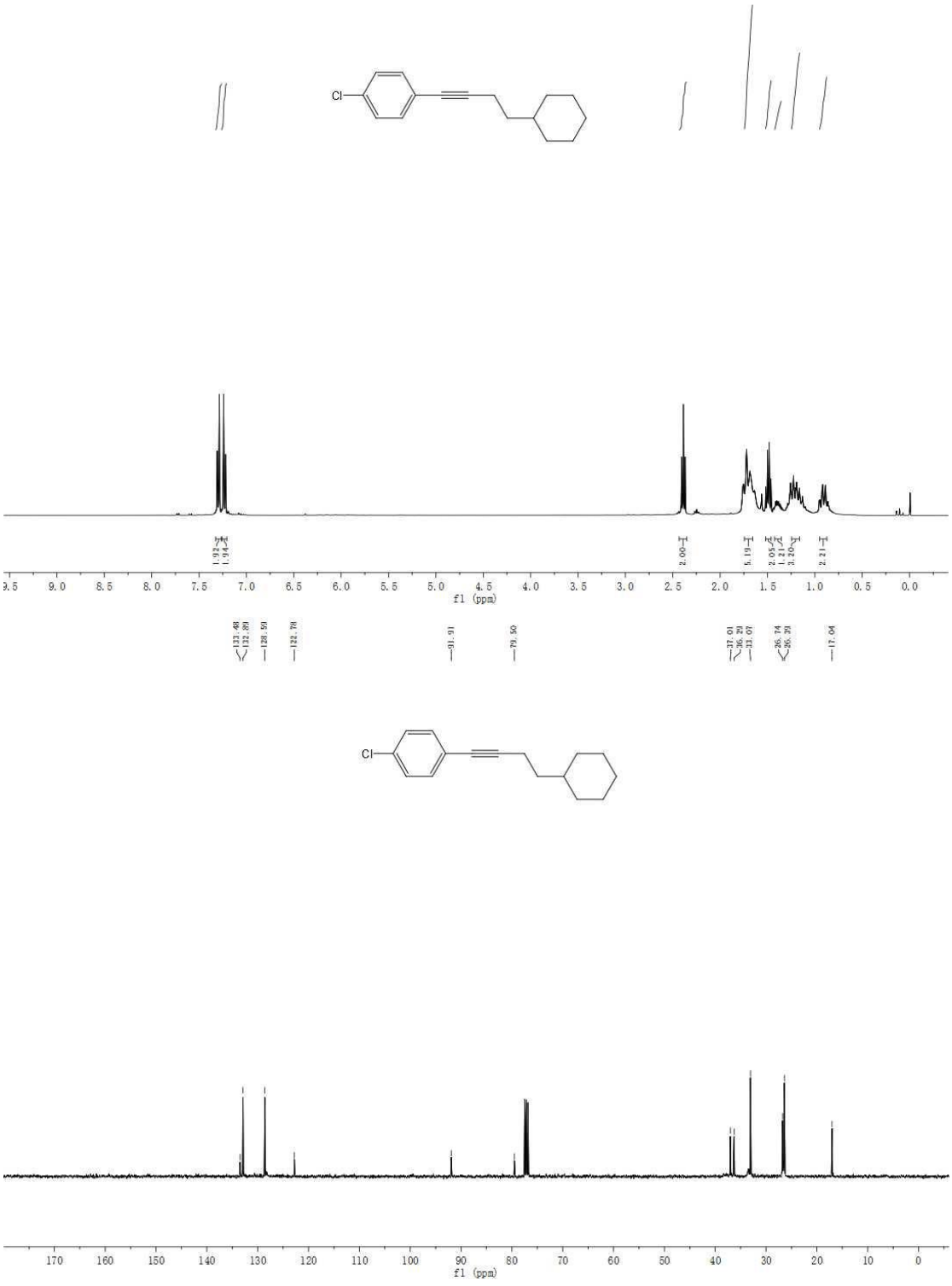
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



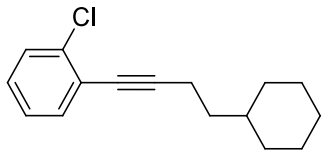
1-chloro-4-(4-cyclohexylbut-1-yn-1-yl)benzene (**1h**, prepared according to procedure A) : colorless liquid, isolated yield (single step): 84%. GC-MS: m/z calcd for $C_{16}H_{19}Cl$: 246, found: 246.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, J = 8.6 Hz, 1H), 7.23 (d, J = 8.5 Hz, 2H), 2.39 (t, J = 7.4 Hz, 1H), 1.78 - 1.63 (m, 5H), 1.49 (d, J = 7.1 Hz, 2H), 1.43 - 1.36 (m, 1H), 1.29 - 1.13 (m, 3H), 0.86 - 0.86 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 133.48, 132.89 (CH×2), 128.59 (CH×2), 122.78, 91.91, 79.50, 37.01, 36.29, 33.07 (CH_2×2), 26.74, 26.39 (CH_2×2), 17.04.



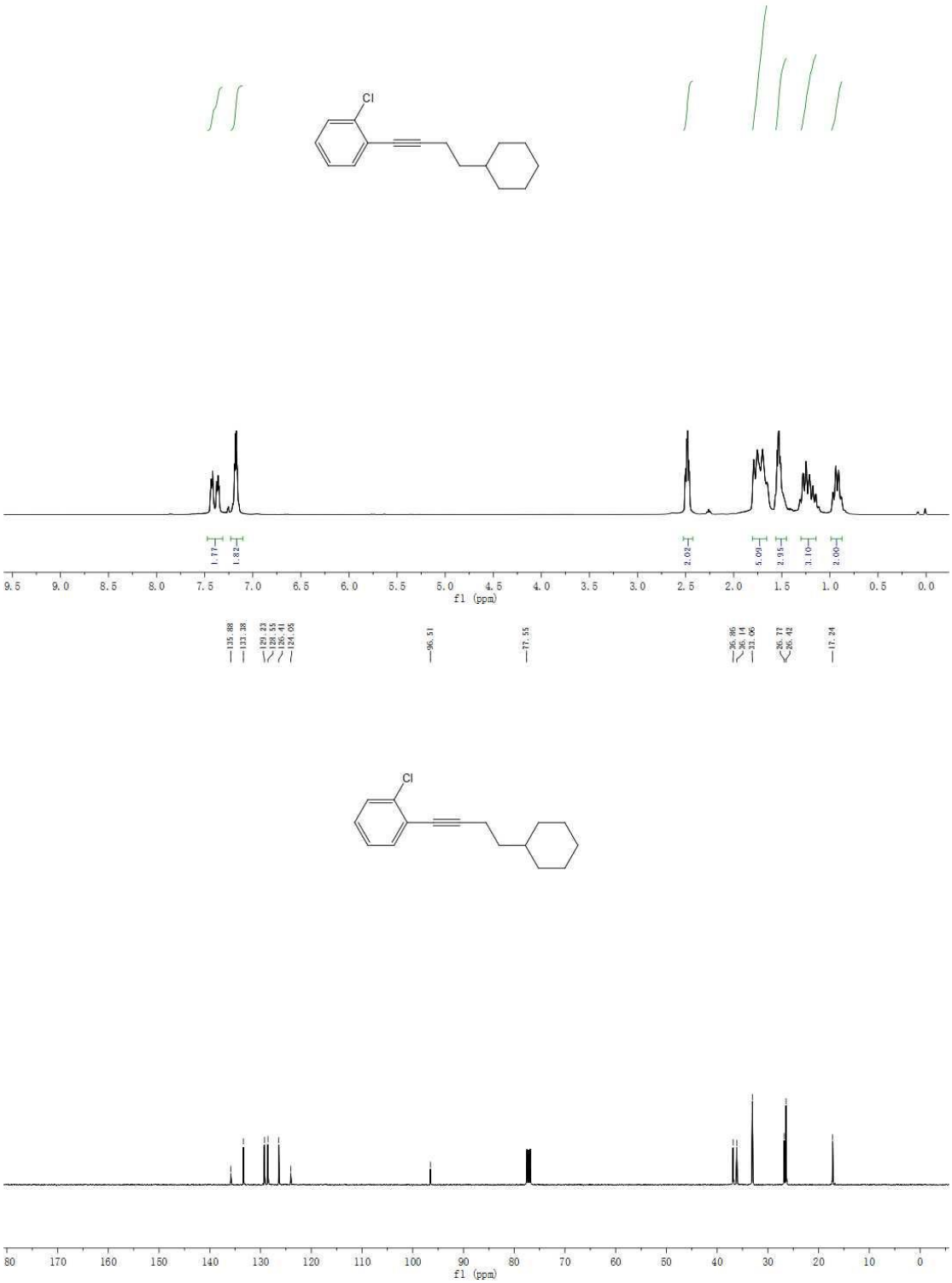
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



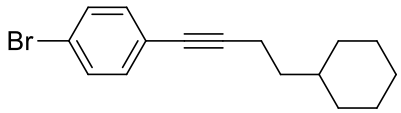
1-chloro-2-(4-cyclohexylbut-1-yn-1-yl)benzene (**1i**, prepared according to procedure A) : colorless liquid, isolated yield (single step): 91%. GC-MS: m/z calcd for $C_{16}H_{19}Cl$: 246, found: 246.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 - 7.31 (m, 2H), 7.23 - 7.10 (m, 2H), 2.48 (t, J = 7.0 Hz, 2H), 1.80 - 1.66 (m, 5H), 1.55 - 1.45 (m, 3H), 1.30 - 1.14 (m, 3H), 0.92 (dd, J = 23.0, 11.8 Hz, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 135.88, 133.38, 129.23, 128.55, 126.41, 124.05, 96.51, 77.55, 36.86, 36.14, 33.06 (CH_2×2), 26.77, 26.42 (CH_2×2), 17.24.



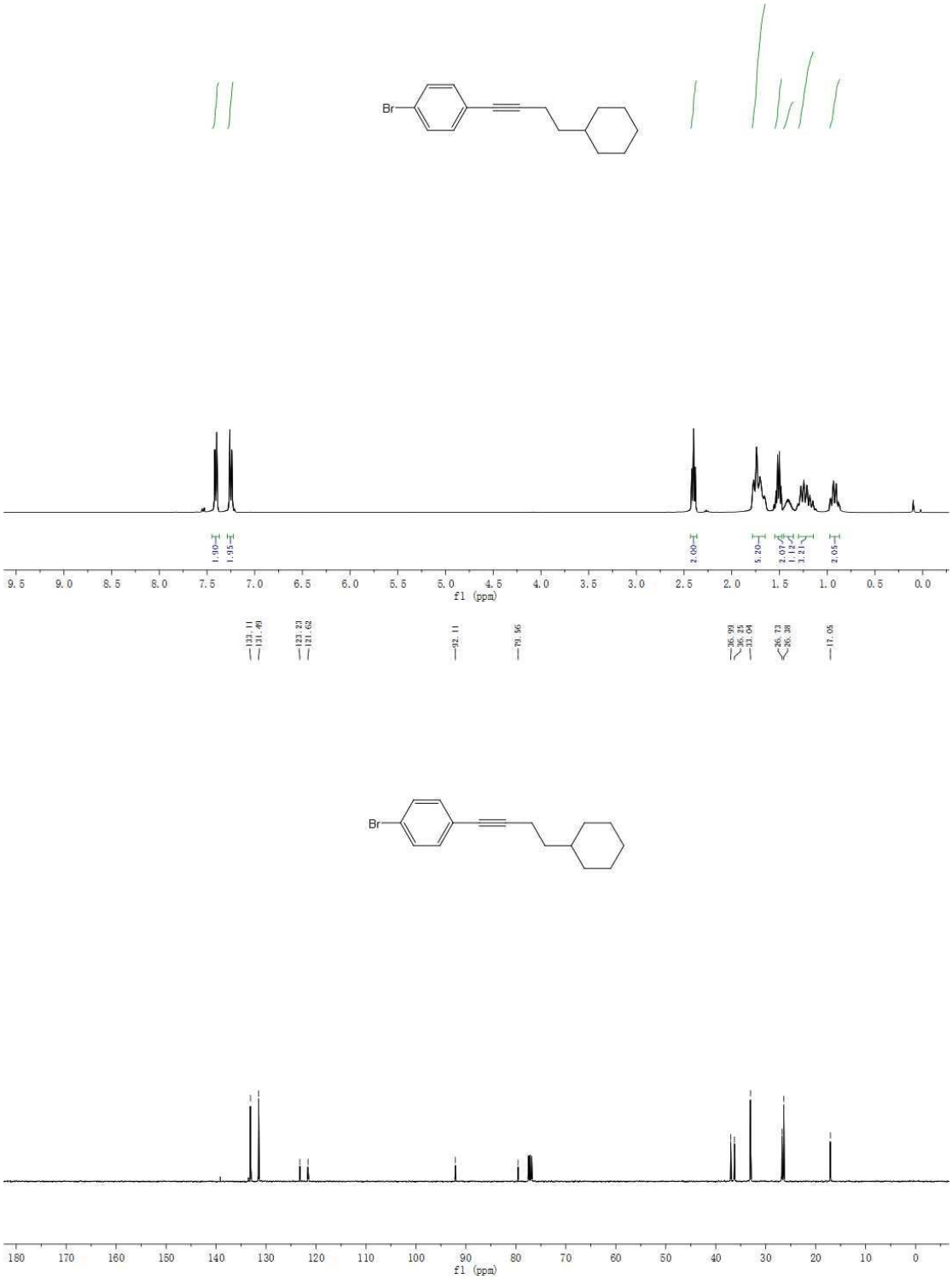
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



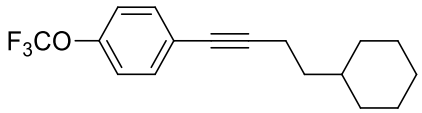
1-bromo-4-(4-cyclohexylbut-1-yn-1-yl)benzene (**1j**, prepared according to procedure A) : white solid, isolated yield (single step): 87%. GC-MS: m/z calcd for $C_{16}H_{19}Br$: 290, found: 290.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.41 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 2.40 (t, J = 7.4 Hz, 2H), 1.78 - 1.65 (m, 5H), 1.51 (q, J = 7.2 Hz, 1H), 1.46 - 1.35 (m, 1H), 1.30 - 1.15 (m, 3H), 0.97 - 0.87 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 133.11 (CH×2), 131.49 (CH×2), 123.23, 121.62, 92.11, 79.56, 36.99, 36.25, 33.04 (CH_2×2), 26.73, 26.38 (CH_2×2), 17.05.



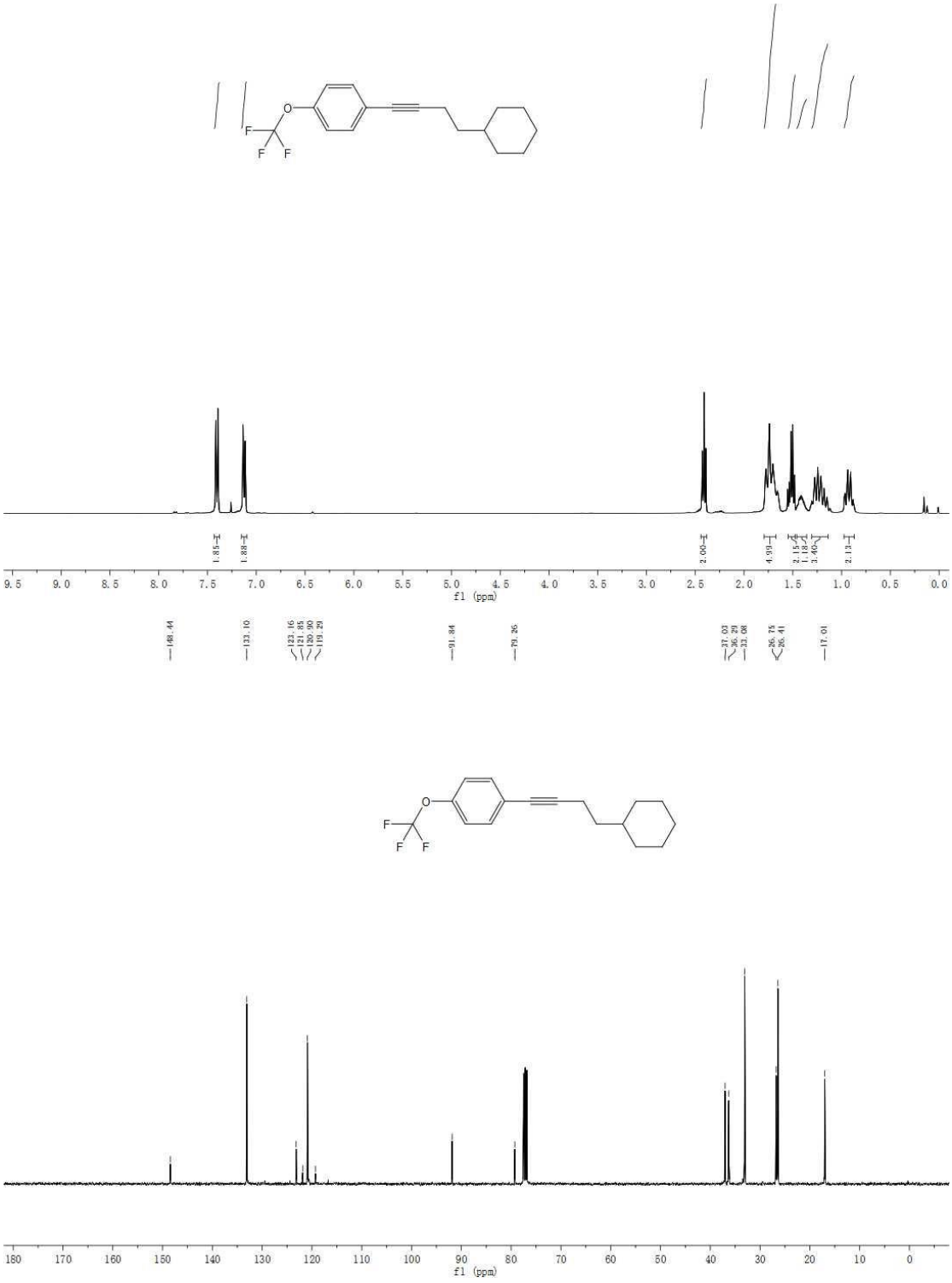
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



1-(4-cyclohexylbut-1-yn-1-yl)-4-(trifluoromethoxy)benzene (**1k**, prepared according to procedure A) : colorless liquid, isolated yield: 88%. GC-MS: m/z calcd for $C_{17}H_{19}F_3O$: 296, found: 296.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.40 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 1.79 - 1.64 (m, 5H), 1.51 (q, J = 7.2 Hz, 2H), 1.46 - 1.36 (m, 1H), 1.31 - 1.14 (m, 3H), 0.97 - 0.87 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.44, 133.10 (CH×2), 123.16, 120.90 (CH×2), 120.57 (q, J = 257.4 Hz), 91.84, 79.26, 37.03, 36.29, 33.08 (CH_2×2), 26.75, 26.41 (CH_2×2), 17.01.



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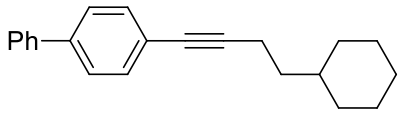
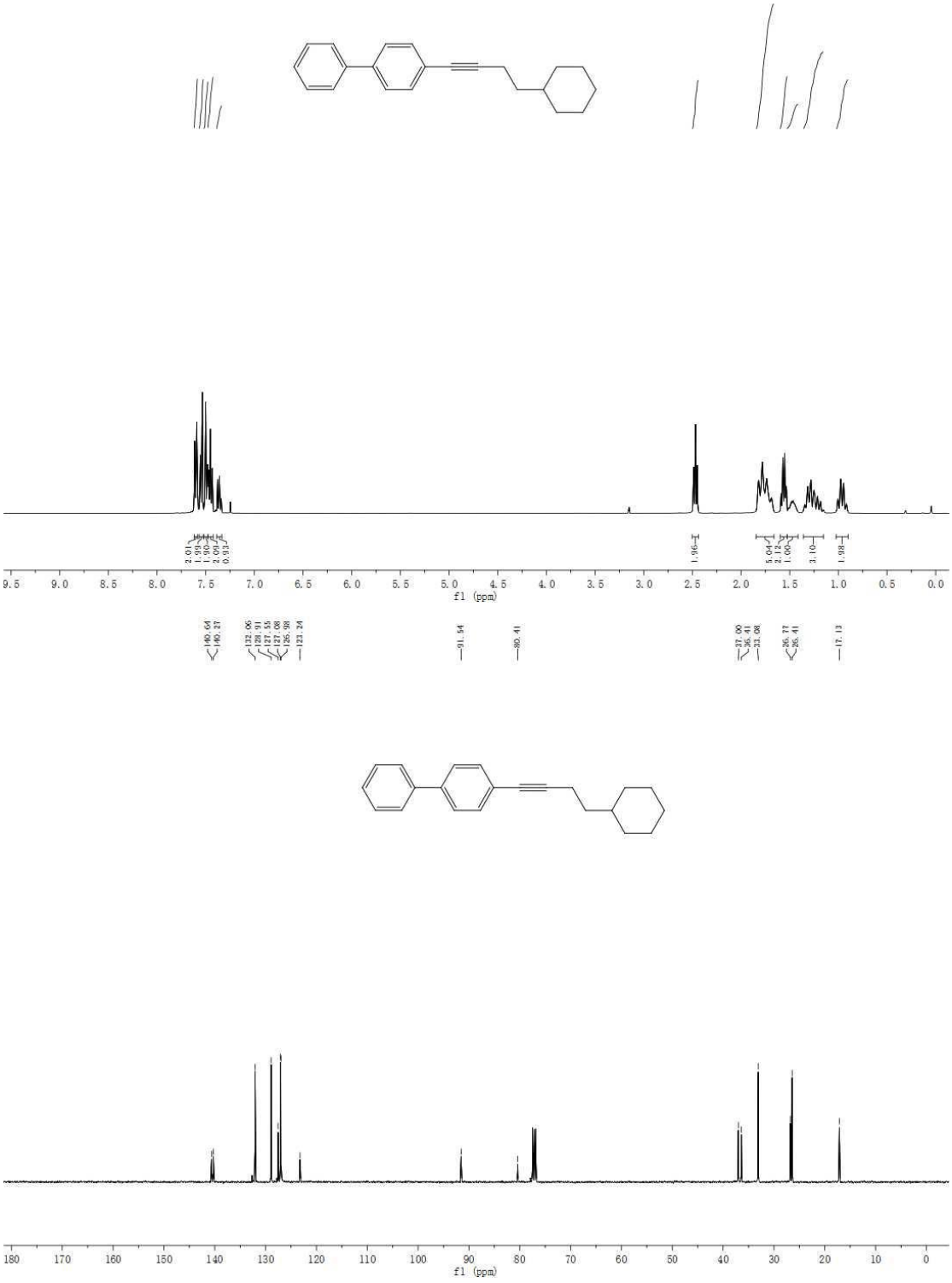


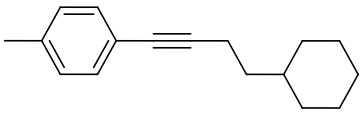
4-(4-cyclohexylbut-1-yn-1-yl)-1,1'-biphenyl (**1l**, prepared according to procedure A) : white solid, isolated yield (single step): 79%. GC-MS: m/z calcd for $C_{22}H_{24}$: 288, found: 288.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.62 - 7.58 (m, 2H), 7.57 - 7.52 (m, 2H), 7.49 (dd, J = 8.4, 1.9 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.39 - 7.33 (m, 1H), 2.47 (t, J = 7.4 Hz, 1H), 1.84 - 1.66 (m, 5H), 1.60 - 1.53 (m, 2H), 1.53 - 1.41 (m, 1H), 1.36 - 1.15 (m, 3H), 1.02 - 0.90 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.64, 140.27, 132.06 (CH×2), 128.91 (CH×2), 127.55, 127.08 (CH×2), 126.98 (CH×2), 123.24, 91.54, 80.41, 37.00, 36.41, 33.08 (CH_2×2), 26.77, 26.41 (CH_2×2), 17.13.



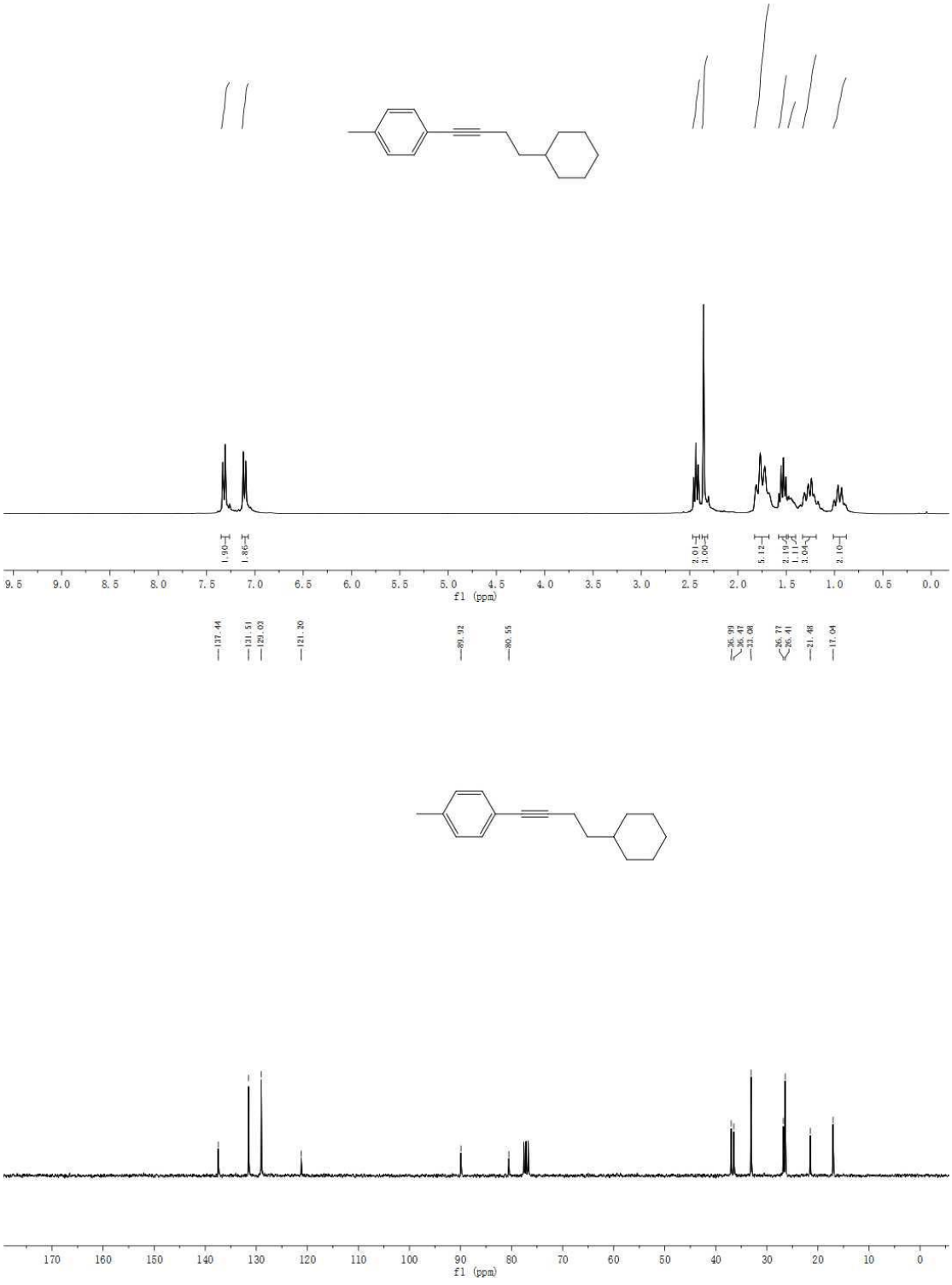
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



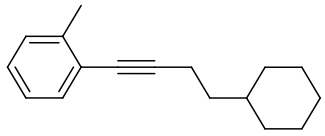
1-(4-cyclohexylbut-1-yn-1-yl)-4-methylbenzene (**1m**, prepared according to procedure A) : colorless liquid, isolated yield (single step): 88%. GC-MS: m/z calcd for $C_{17}H_{22}$: 226, found: 226.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ7.32 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 2.43 (t, J = 7.4 Hz, 2H), 2.36 (s, 1H), 1.83 - 1.68 (m, 5H), 1.54 (q, J = 7.1 Hz, 2H), 1.49 - 1.40 (m, 1H), 1.33 - 1.19 (m, 3H), 1.01 - 0.88 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 137.44, 131.51 (CH×2), 129.03 (CH×2), 121.20, 89.92, 80.55, 36.99, 36.47, 33.08 (CH_2×2), 26.77, 26.41 (CH_2×2), 21.48, 17.04.



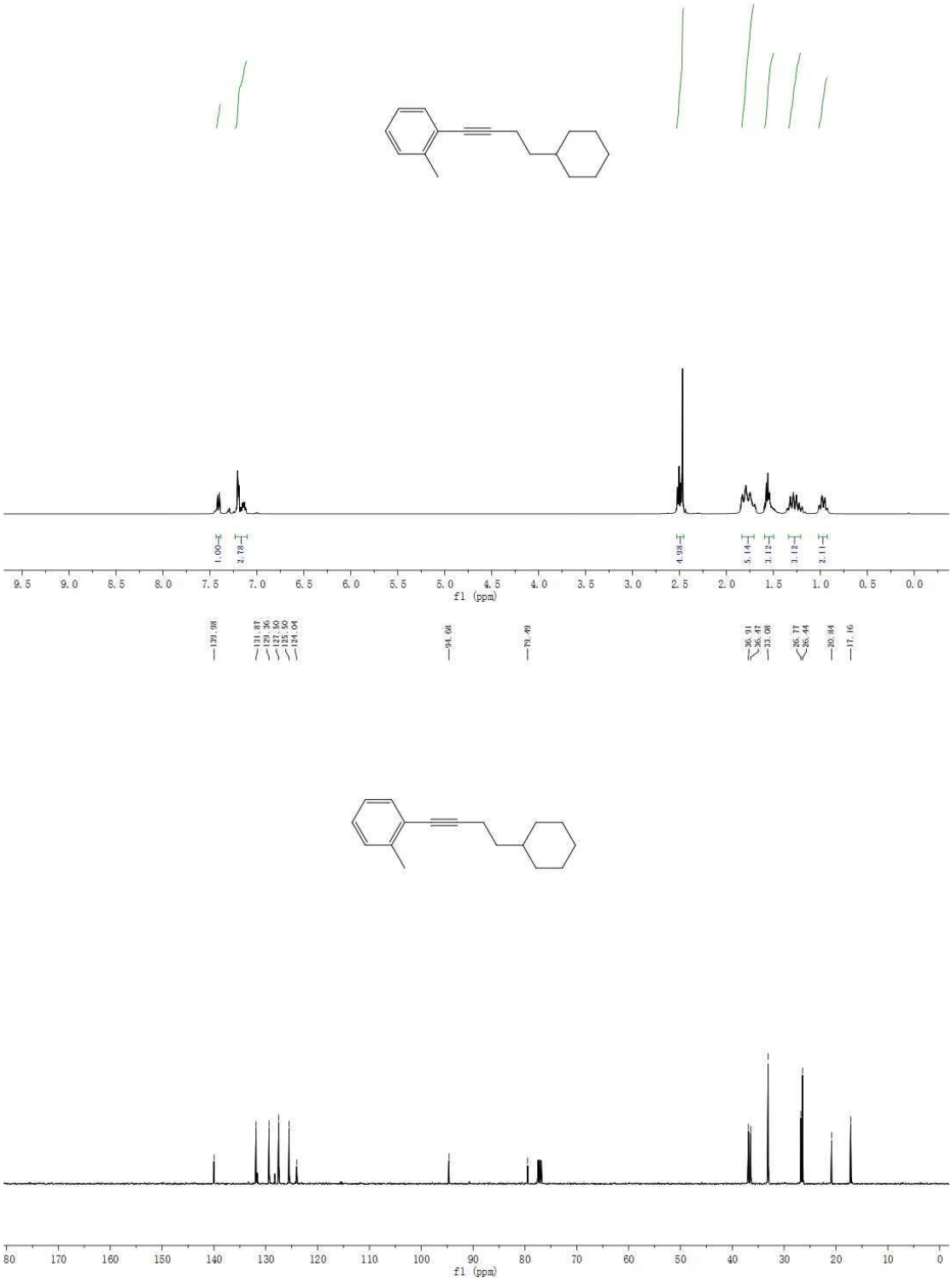
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)



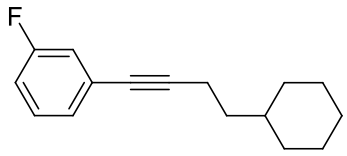
1-(4-cyclohexylbut-1-yn-1-yl)-2-methylbenzene (**1n**, prepared according to procedure A) : colorless liquid, isolated yield (single step): 85%. GC-MS: m/z calcd for $C_{17}H_{22}$: 226, found: 226.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.43- 7.38 (m, 1H), 7.23 - 7.10 (m, 3H), 2.53 - 2.45 (m, 5H), 1.83 - 1.71 (m, 5H), 1.59 - 1.50 (m, 3H), 1.26 (ddd, J = 17.6, 8.8, 6.3 Hz, 3H), 0.97 (dd, J = 22.5, 10.2 Hz, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 139.98, 131.87, 129.36, 127.50, 125.50, 124.04, 94.68, 79.49, 36.91, 36.47, 33.08 (CH_2×2), 26.77, 26.44 (CH_2×2), 20.84, 17.16.



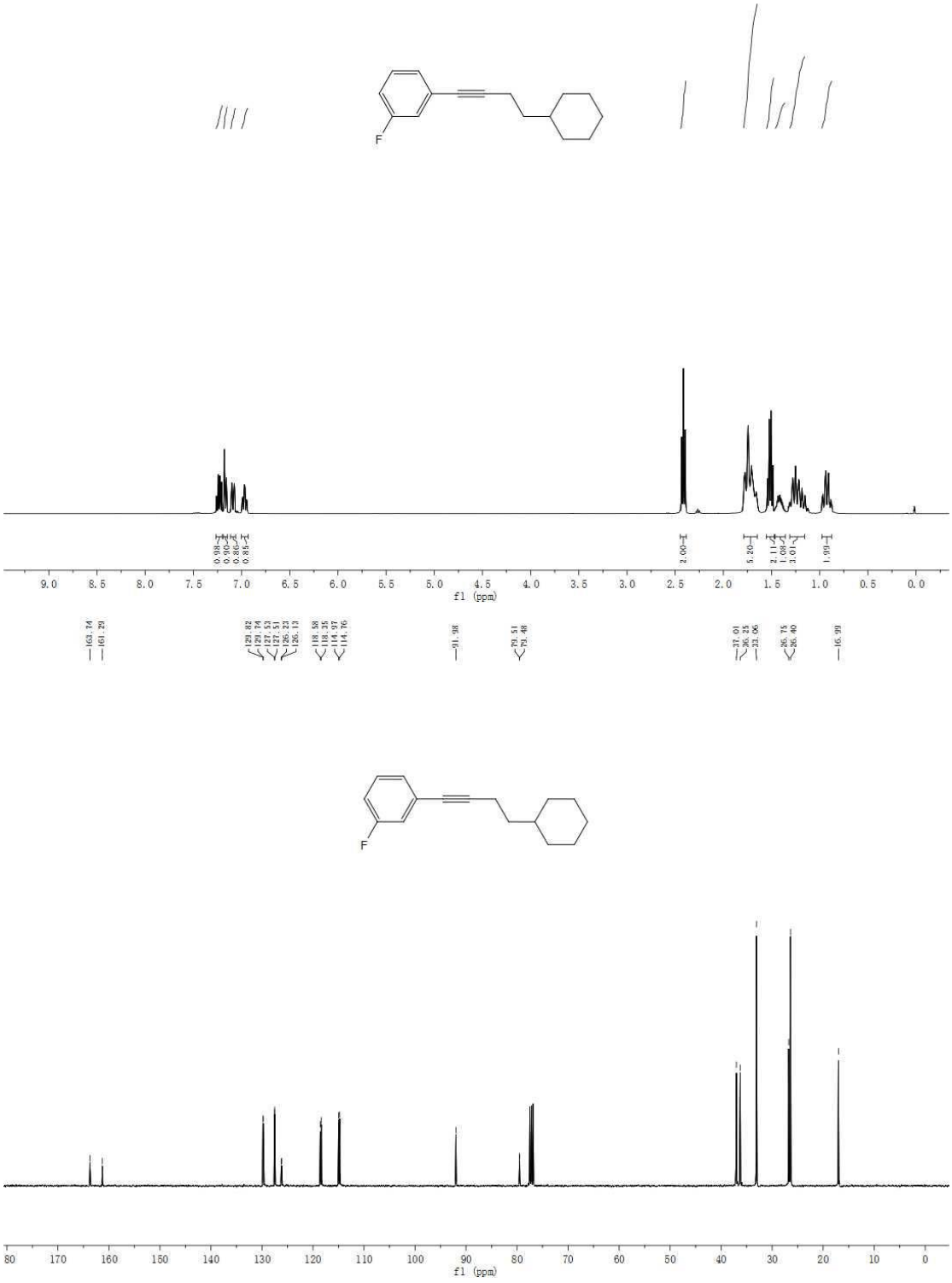
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



1-(4-cyclohexylbut-1-yn-1-yl)-3-fluorobenzene (**1o**, prepared according to procedure A) : colorless liquid, isolated yield (single step): 82%. GC-MS: m/z calcd for $C_{16}H_{19}F$: 230, found: 230.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.23 (td, J = 7.8, 5.9 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.12 - 7.06 (m, 1H), 7.00 - 6.93 (m, 1H), 2.41 (t, J = 7.4 Hz, 2H), 1.79 - 1.65 (m, 5H), 1.51 (q, J = 7.2 Hz, 2H), 1.46 - 1.36 (m, 1H), 1.31 - 1.15 (m, 3H), 0.98 - 0.88 (m, 2H).

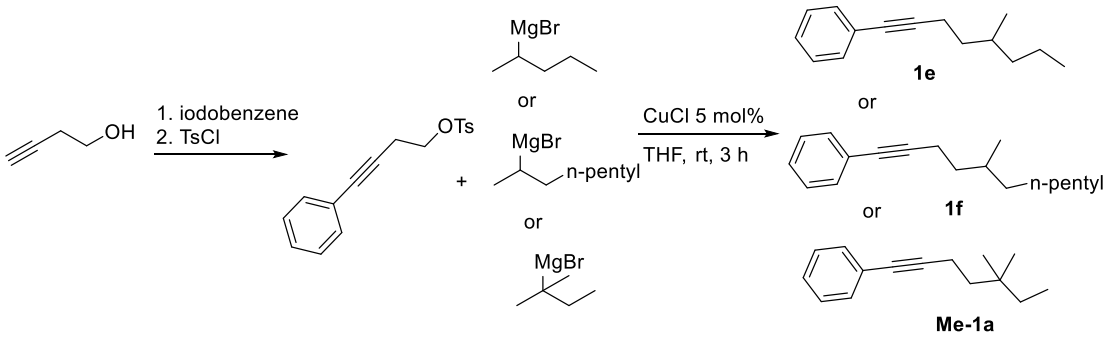
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 162.52 (d, J = 245.8 Hz), 129.78 (d, J = 8.7 Hz), 127.52 (d, J = 2.7 Hz), 126.18 (d, J = 9.5 Hz), 118.47 (d, J = 22.5 Hz), 114.87 (d, J = 21.1 Hz), 91.98, 79.50 (d, J = 3.0 Hz), 37.01, 36.25, 33.06 (CH_2×2), 26.75, 26.40 (CH_2×2), 16.99.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

2) Preparation of compound 1e, 1f and Me-1a

Procedure B:

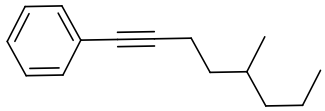


A sealed tube was charged with the mixture of $PdCl_2(PPh_3)_2$ (0.5 mol%, 105 mg) and CuI (1 mol%, 59.7 mg). The tube was evacuated and recharged with N_2 for 3 times. After the 3-butyn-1-ol (33mmol, 2.10 g), iodobenzene (30 mmol, 6.12 g) and Et_3N (50 mL) were added, the tube was allowed to stir at 65 ^oC for 12 h. After the reaction was completed, the mixture was cooled to room temperature, and extracted with DCM (40 mL× 3). The organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by flash column chromatography on silica gel (petroleum ether / EtOAc = 8/1) provided the crude product 4-phenylbut-3-yn-1-ol (3.85 g, 88%).

4-phenylbut-3-yn-1-ol (1.46g, 10 mmol) in DCM (10 mL) was cooled to 0 ^oC and then tosyl chloride (2.28g, 12 mmol), Et_3N (2.78 mL, 20 mmol) and DMAP (1 mmol, 122 mg) were added. The reaction mixture was stirred for 1.0 h and then quenched with water, extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated and chromatographed (petroleum ether / EtOAc = 15/1) to afford crude 4-phenylbut-3-yn-1-yl tosylate (2.67 g, 89%).[5]

A solution of Grignard reagent (6 mmol, prepared from corresponding alkyl bromide by reacting with magnesium (2.0 eq.) in anhydrous THF using 1,2-Dibromoethane as activation at room temperature for stirring 8 h) was added to a 10 mL of THF solution containing CuCl (24.75 mg, 0.25 mmol) and 4-phenylbut-3-yn-1-yl tosylate (5 mmol, 1.5 g) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 3 h and then quenched by saturated NH_4Cl aqueous solution. The organic phase in the resulting solution mixture was extracted with ether (3 × 10 mL), dried over $MgSO_4$, filtered, and finally evaporated under a reduced pressure. The residue was purified by

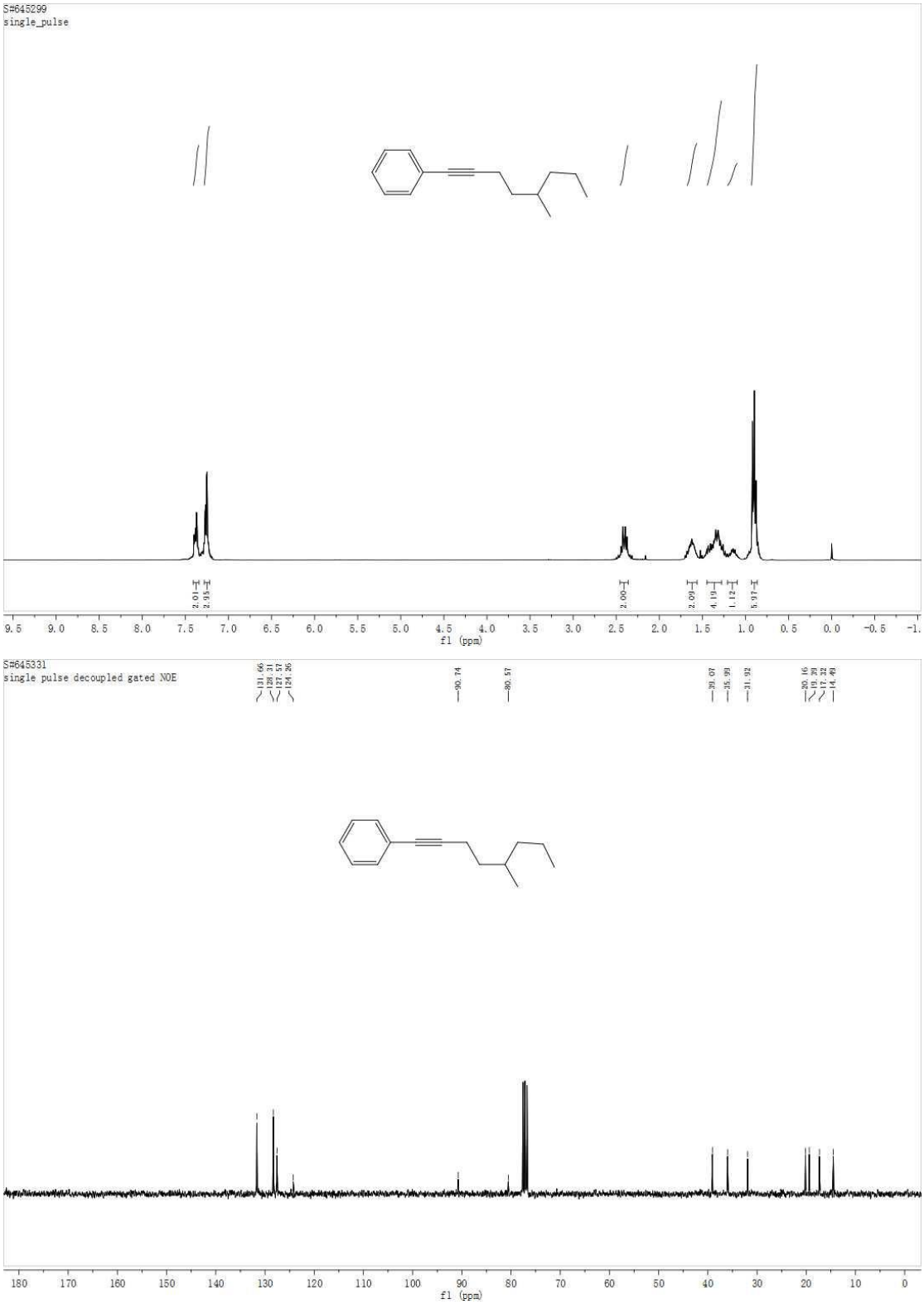
silica-gel chromatography (hexane) to afford the product **1e** and **1f**.[6]



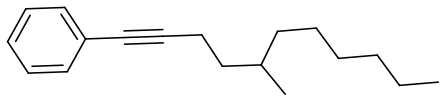
(5-methyloct-1-yn-1-yl)benzene (**1e**, prepared according to procedure B): colorless liquid, isolated yield (single step): 75%, GC-MS: m/z calcd for $C_{15}H_{20}$: 200, found: 200.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.41 - 7.34 (m, 2H), 7.26 (dt, *J* = 6.3, 2.5 Hz, 3H), 2.41 (ddd, *J* = 12.7, 8.2, 4.4 Hz, 2H), 1.68 - 1.56 (m, 2H), 1.45 - 1.28 (m, 4H), 1.21 - 1.09 (m, 1H), 0.93 - 0.86 (m, 6H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.66 (CH×2), 128.31 (CH×2), 127.57, 124.26, 90.74, 80.57, 77.58, 77.16, 76.74, 39.07, 35.99, 31.92, 20.16, 19.39, 17.32, 14.49.



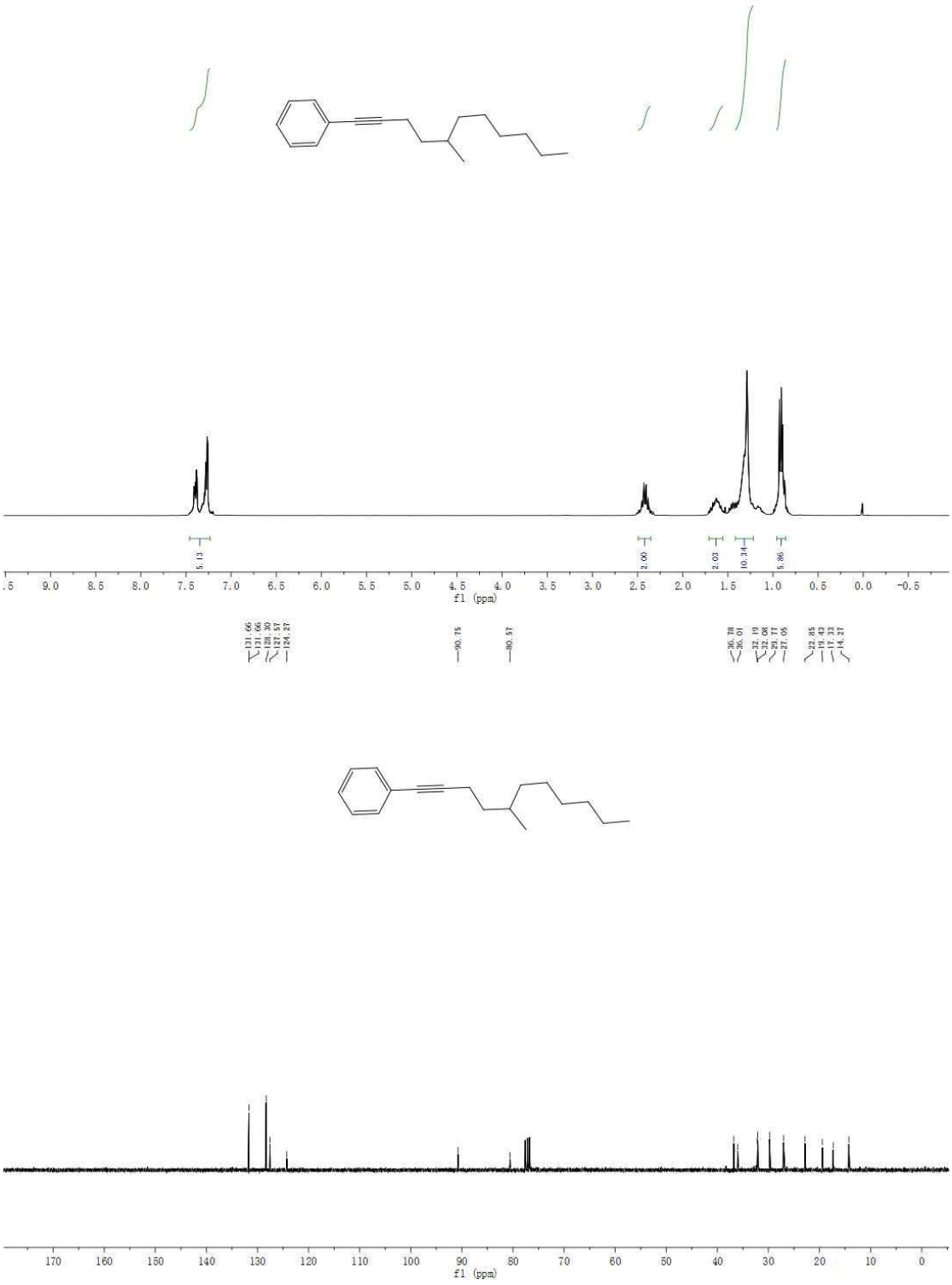
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)



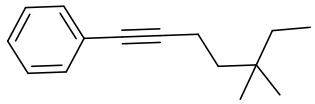
(5-methylundec-1-yn-1-yl)benzene (**1f**, prepared according to procedure B): colorless liquid, isolated yield: 80%, GC-MS: m/z calcd for $C_{18}H_{26}$: 242, found: 242.

^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.46 - 7.23 (m, 5H), 2.49 - 2.35 (m, 2H), 1.71 - 1.55 (m, 2H), 1.42 - 1.22 (m, 10H), 0.96 - 0.86 (m, 6H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 131.66 (CH×2), 128.30 (CH×2), 127.57, 124.27, 90.75, 80.57, 36.78, 36.01, 32.19, 32.08, 29.77, 27.05, 22.85, 19.43, 17.33, 14.27.



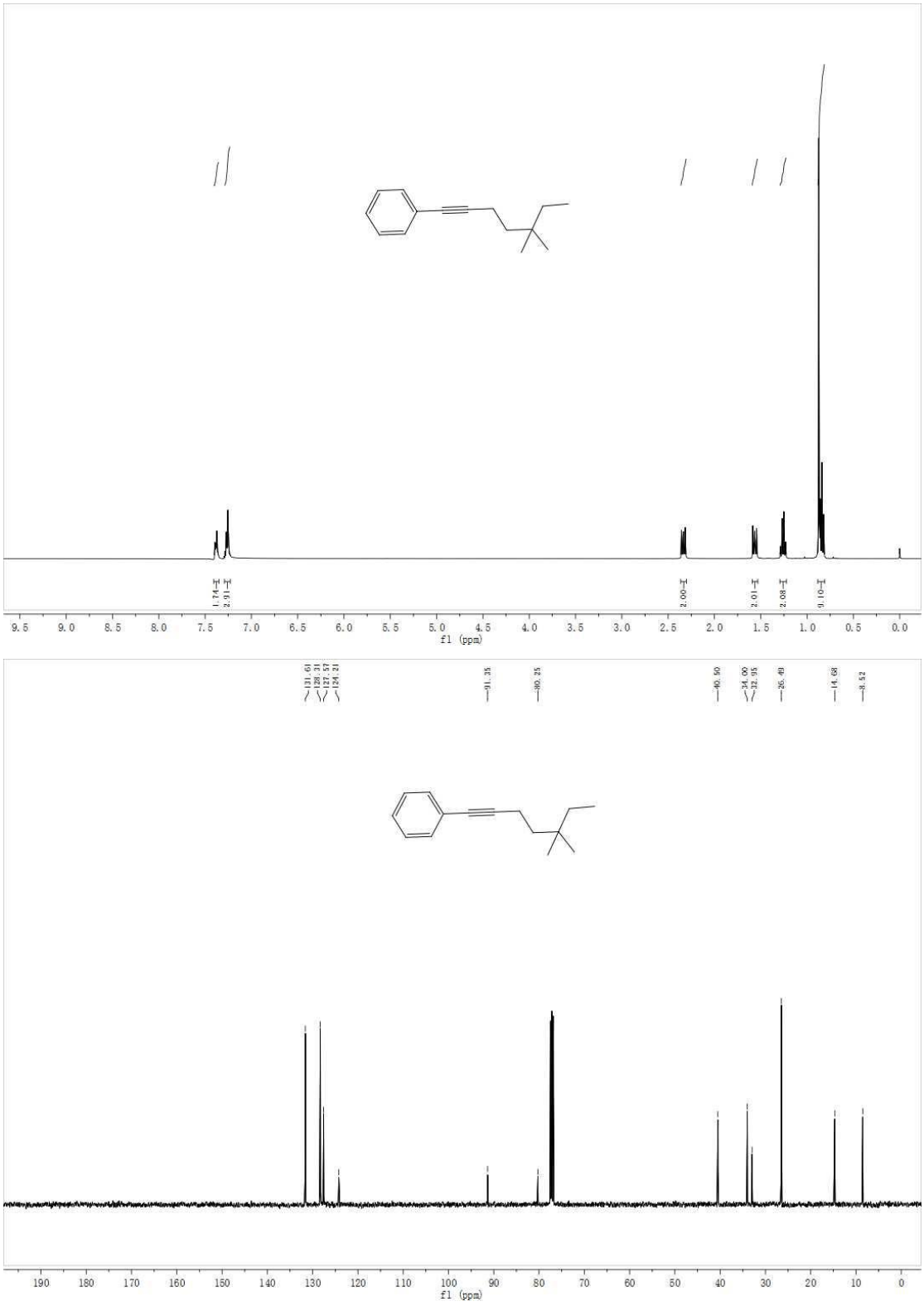
^{1}H NMR (301 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)



(5,5-dimethylhept-1-yn-1-yl)benzene (**Me-1a**, prepared according to procedure B): colorless liquid, isolated yield: 56%, GC-MS: m/z calcd for $C_{15}H_{20}$: 200, found: 200.

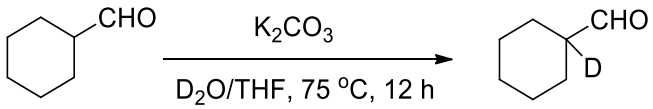
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.41 - 7.35 (m, 2H), 7.29 - 7.23 (m, 3H), 2.36 - 2.30 (m, 2H), 1.56 (ddd, *J* = 11.3, 6.5, 3.2 Hz, 2H), 1.26 (q, *J* = 7.5 Hz, 2H), 0.88 - 0.81 (m, 9H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.61(CH×2), 128.31(CH×2), 127.57, 124.21, 91.35, 80.25, 40.50, 34.00, 32.95, 26.49(CH_3×2), 14.68, 8.52.

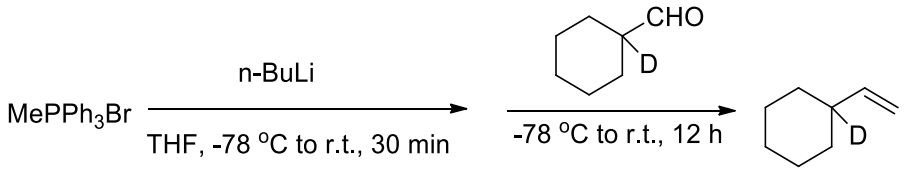


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

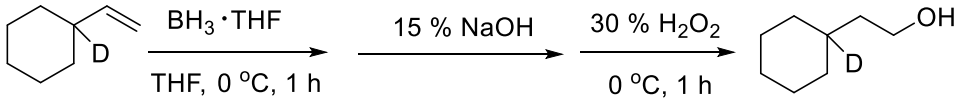
3) Preparation of compound D-1g:



A solution of Cyclohexanecarboxaldehyde (6.0 mL, 50 mmol) and K_2CO_3 (500 mg) in D_2O (10 mL) and anhydrous THF (3 mL) was stirred for 5 h at 75 °C and then extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated to give the crude product (4.97 g, 88%, D% > 95%) without further purification.[7]



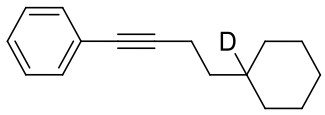
To a solution of $MePPh_3Br$(11.74 g, 33 mmol) in 15 mL THF under N_2 atmosphere was added n-BuLi (21.8 mL, 1.6 M in hexane, 35 mmol) at -78 °C. The mixture was allowed to warm to room temperature for 30 min, and then was cooled to -78 °C before D-Cyclohexanecarboxaldehyde (3.73 g, 33 mmol) was added. After stirring for 12 h at room temperature, the mixture was quenched with water and extracted with ether. The organic layer was dried over $MgSO_4$, and carefully concentrated to obtain the crude product (2.56 g, 70%).[8]



To a stirring solution of D-vinylcyclohexane (1.66g, 15 mmol) in THF (10 mL), BH_3·THF (1M in THF, 8 mL, 8 mmol) was added dropwise at 0 °C and remain for 1 h. The reaction solution was quenched with aqueous NaOH (15%, 2 mL) and followed by addition of H_2O_2 (30%, 3 mL) and stirred at 0 °C for 1 h. The reaction mixture was quenched with water (10 mL) and extracted with ether. The combined organic layers were dried over $MgSO_4$, filtered and evaporated at low temperature to give the crude product (1.26 g, 65%) as a colorless oil used without further purification.[8]

To a solution of phenylacetylene (306 mg, 3 mmol) in THF (3 mL) at -78°C under N_2

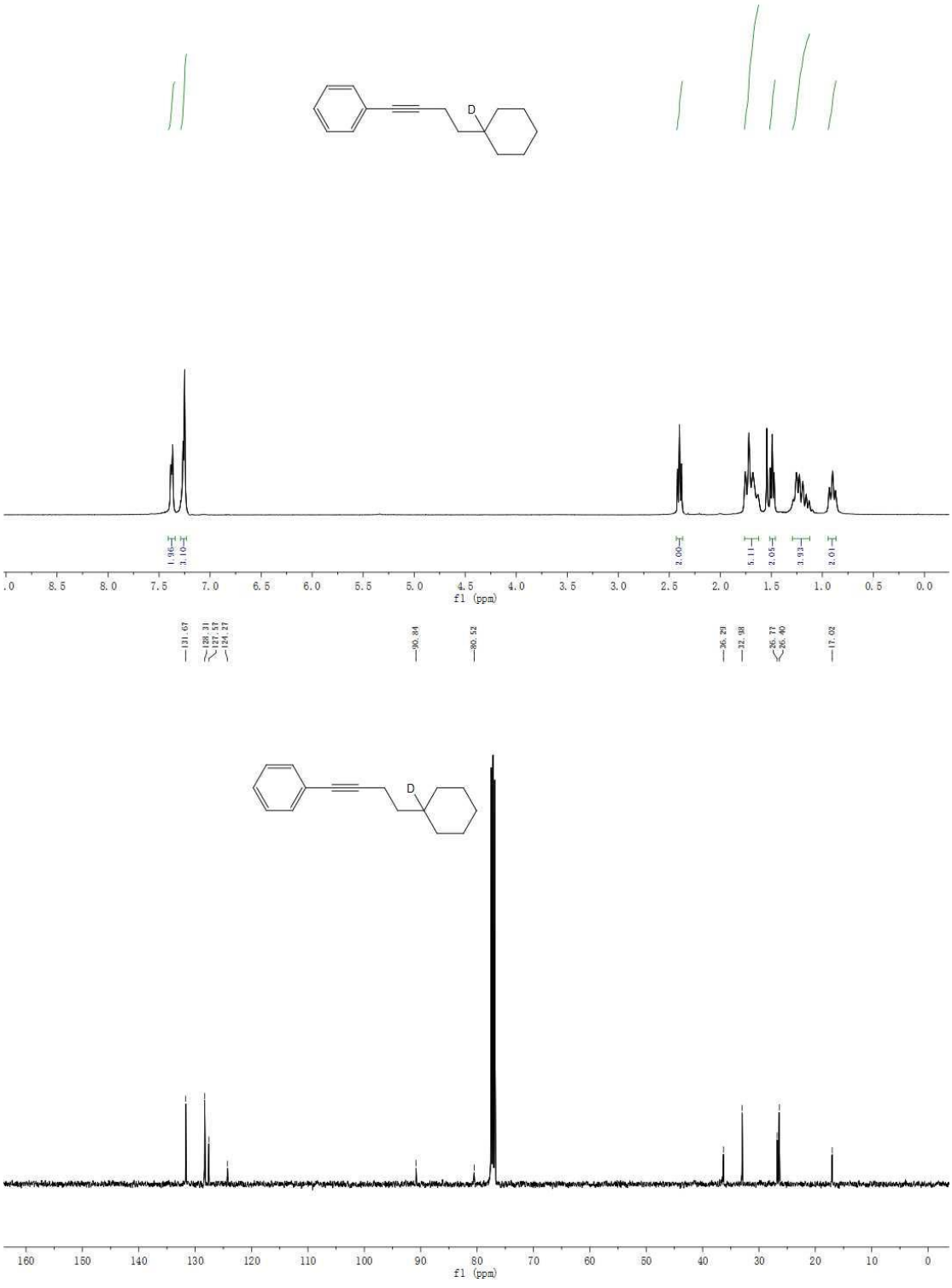
atmosphere was added n-BuLi (2.0 mL, 1.6 M in hexane, 3.3 mmol) and then was allowed to warm to r.t. for 1.0 h. The mixture was then cooled to -78 ^{o}C, HMPA (0.591 g, 3.3 mmol) and D-[2-cyclohexylethyl 4-methylbenzenesulfonate] (849 mg, 3 mmol) were added. It was allowed to warm to r.t. for 36 h and then was quenched with water, extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography with hexane as eluent to give **D-1g** (441 mg, 69%) as colorless liquid.[2]



GC-MS: m/z calced for $C_{16}H_{19}D$: 213, found: 213.

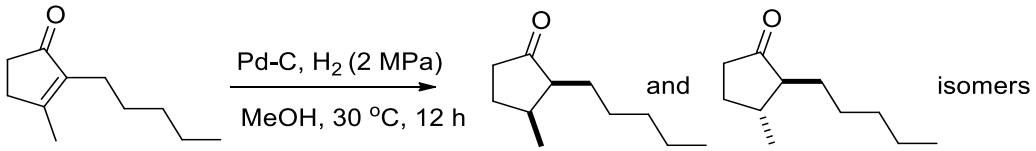
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.37 (dd, J = 7.6, 1.9 Hz, 2H), 7.29 - 7.23 (m, 3H), 2.40 (t, J = 7.5 Hz, 2H), 1.76 - 1.62 (m, 5H), 1.49 (t, J = 7.4 Hz, 2H), 1.29 - 1.12 (m, 4H), 0.94 - 0.87 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 131.67, 128.31, 127.57, 124.27, 90.84, 80.52, 36.29, 32.98 (CH_2×2), 26.77, 26.40 (CH_2×2), 17.02.

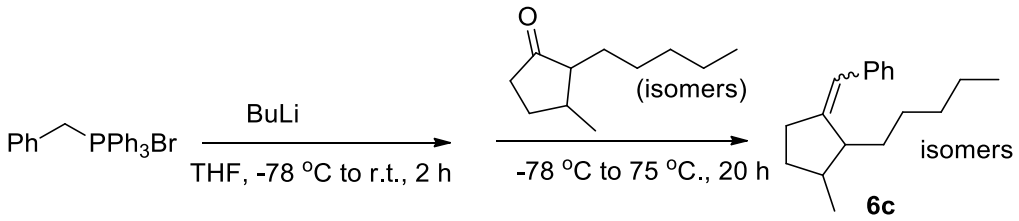


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

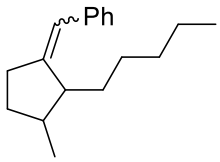
4) Preparation of compound 6c:



A mixture of 2-Pentyl-3-methyl-2-cyclopenten-1-one (2.49 g, 15 mmol), 10 wt% Pd-C (150 mg), and MeOH (15 mL) was stirred under H_2 (2 MPa) at 30 °C for 12 h. After filtering off the catalyst, the solvent was evaporated to yield the product as two isomers.[9]



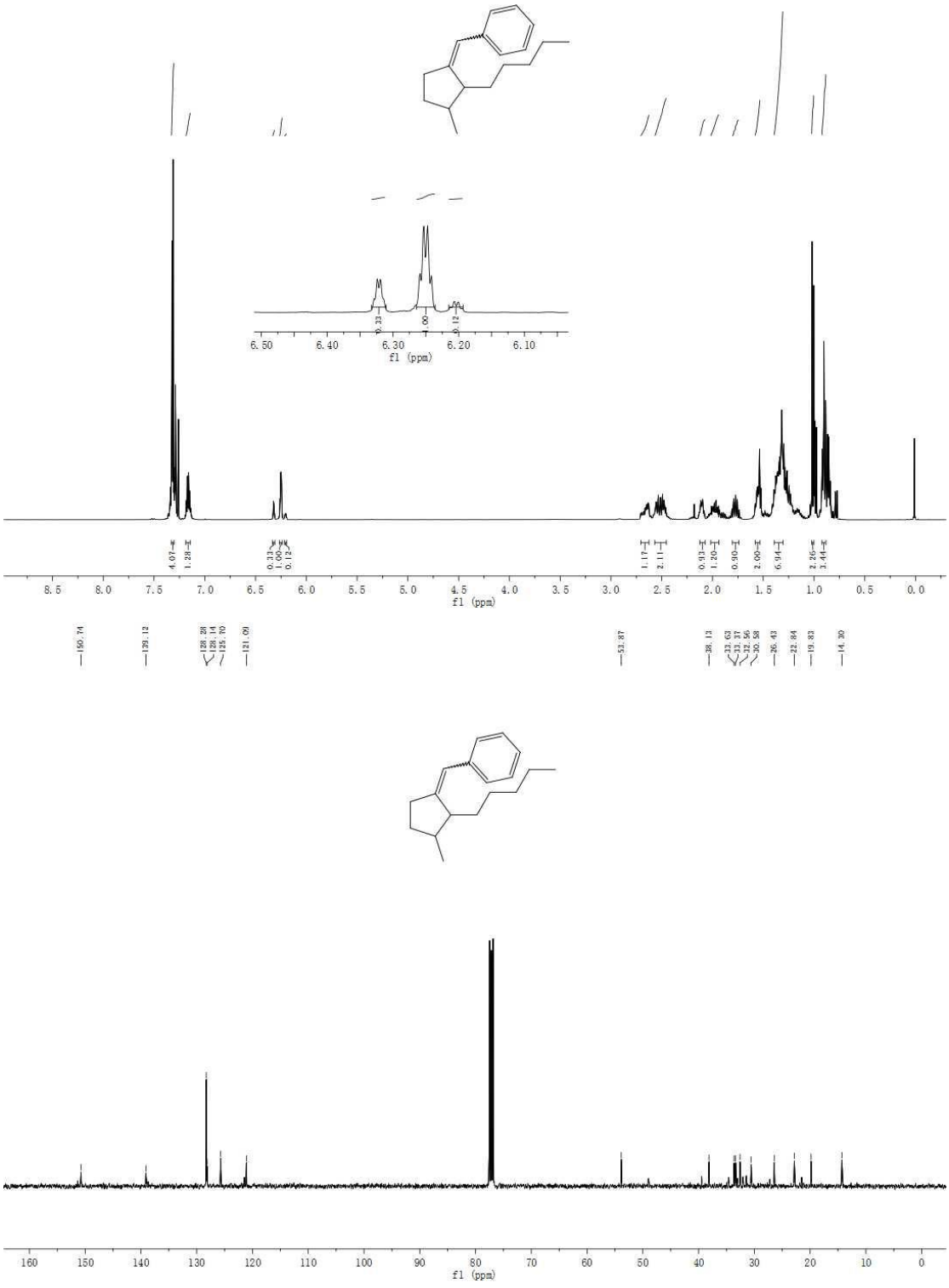
To a solution of benzylbromotriphenylphosphorane (2.16 g, 5 mmol) in THF (3 mL) at -78°C under N_2 atmosphere was added n-BuLi (3.4 mL, 1.6 M in hexane, 5.5 mmol) and was allowed to warm to r.t. for 2.0 h. The mixture was then cooled to -78 °C, then the corresponding ketone (840 mg, 5 mmol) were added. It was allowed to heat to 75 °C for 20 h and then was quenched with water, extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography with hexane as eluent to give mixed compound **6c** (726 mg, 60%) as colorless liquid.[8]



Compound 6c, GC-MS: m/z calced for $C_{18}H_{26}$: 242, found: 242.

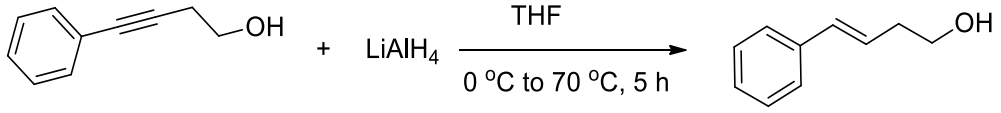
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.33 - 7.30 (m, 4H), 7.17 (dd, *J* = 8.7, 4.3 Hz, 1H), 6.32 (d, *J* = 1.9 Hz, 1H), 6.25 (dd, *J* = 4.6, 2.3 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 2.71 - 2.63 (m, 1H), 2.51 (qdd, *J* = 10.6, 5.5, 2.2 Hz, 2H), 2.12 - 2.07 (m, 1H), 2.02 - 1.94 (m, 1H), 1.77 (dd, *J* = 13.4, 6.3 Hz, 1H), 1.58 - 1.53 (m, 2H), 1.39 - 1.31 (m, 7H), 1.01 (d, *J* = 6.4 Hz, 2H), 0.90 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.74, 139.12, 128.28 (CH×4), 125.70, 121.09, 53.87, 38.13, 33.63, 33.37, 32.56, 30.58, 26.43, 22.84, 19.83, 14.30.

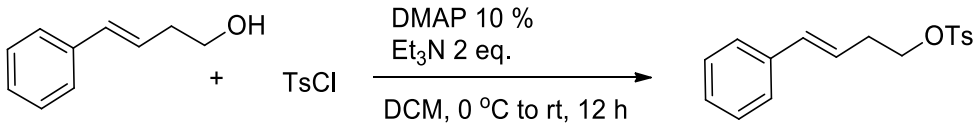


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

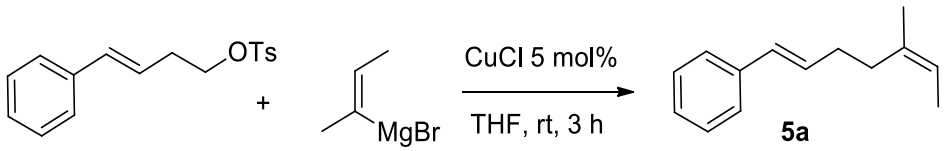
5) Preparation of compound 5a:



To a solution of 4-phenylbut-3-yn-1-ol (2.92 g, 20 mmol) in THF (50 mL) was slowly added $LiAlH_4$ (1.14 g, 30 mmol) at 0 °C and then the reaction was refluxed at 70 °C for 5 h. After cooling to 0 °C, 20% NaOH (2 mL) was added to this solution and extracted with Et_2O. The organic solvent was removed and then the residue was purified by chromatography on silica (EtOAc/hexanes:1/5) to give separable E product (2.37 g, 80%) and Z product (15%).[10]

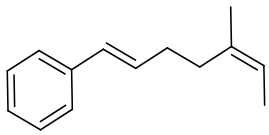


To a sealed tube under N_2 atmosphere were added TsCl (5.56 g, 14.5 mmol, 1.10 equiv), DMAP (163 mg, 1.35 mmol, 0.1 equiv), Et_3N (27.0 mmol, 2.00 equiv), and 30 mL DCM. The resulting mixture was cooled to 0 °C and a solution of (E)-4-phenylbut-3-en-1-ol (2.00 g, 13.5 mmol, 1.00 equiv) in 10 mL DCM was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The solution was then washed with saturated aqueous $NaHCO_3$ (1 × 30mL) and extracted with DCM (1 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuum. The residue was purified by flash column chromatography (EtOAc/hexanes:1/10) to give the crude tosylate (3.67 g, 90%).[11]



A solution of (Z)-but-2-en-2-ylmagnesium bromide (6 mmol, prepared from 2-bromo2-butene by reacting with magnesium (3.0 eq.) in anhydrous THF using 1,2-Dibromoethane as activation at 50 °C for stirring 12 h) was added to a THF (6 mL) solution containing CuCl (24.75 mg, 0.25 mmol) and tosylate (5 mmol, 1.5 g). The reaction mixture was stirred at room temperature for 3 h and then was quenched by the addition of 10 mL saturated NH_4Cl aqueous solution. The organic phase in the

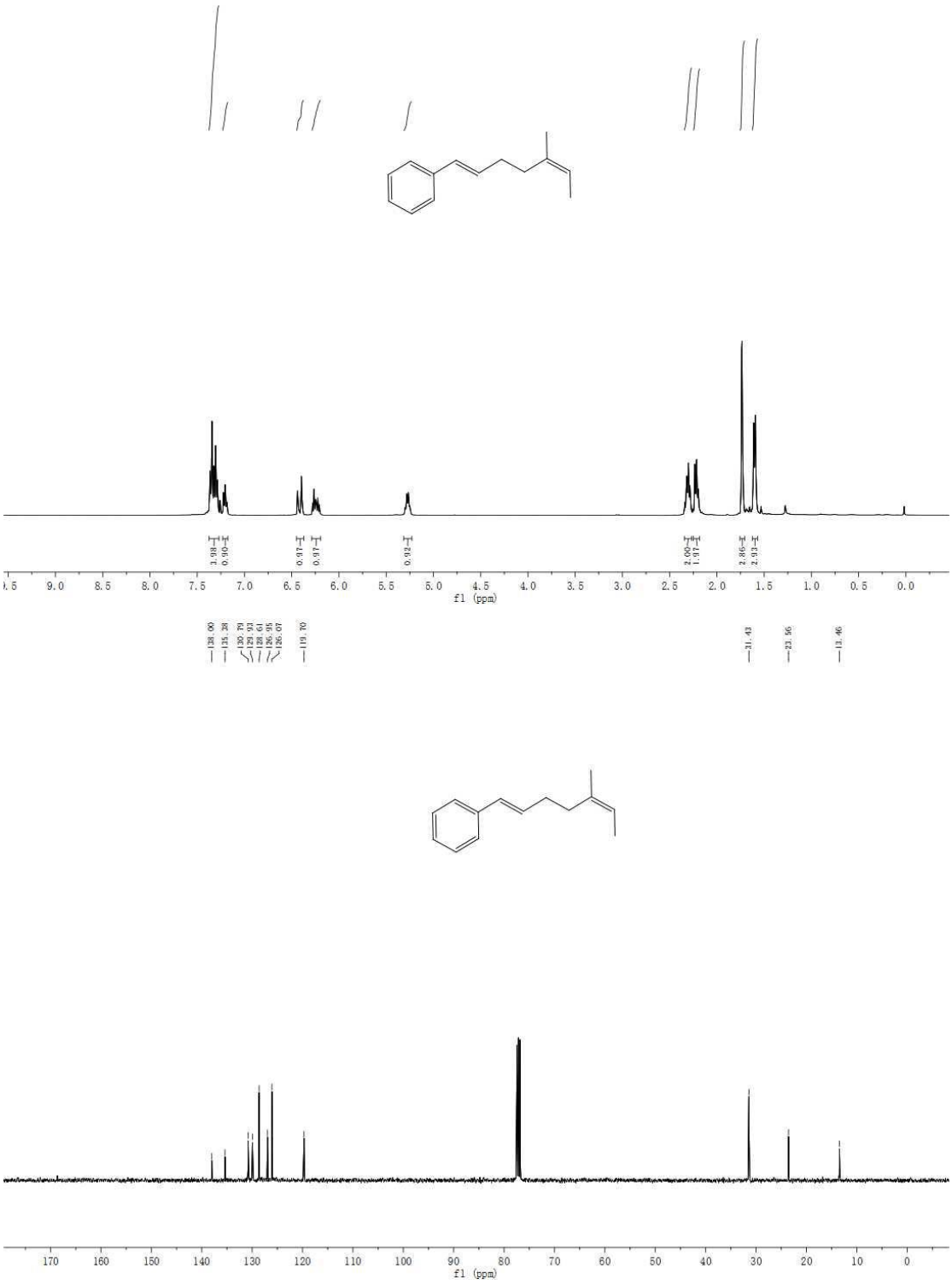
resulting solution mixture was extracted with ether (3 × 10 mL), dried over $MgSO_4$, filtered and finally evaporated under a reduced pressure. The residue was purified by silica-gel chromatography (hexane) to afford the product ((*1E,5Z*)-5-methylhepta-1,5-dien-1-yl)benzene **5a** (493 mg, 53%, *Z* configuration of the other double bond was identified by 1D-NOE).[6]



Compound 5a, GC-MS: m/z calced for $C_{14}H_{18}$: 186, found: 186.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 - 7.27 (m, 4H), 7.23 - 7.18 (m, 1H), 6.42 (d, J = 15.9 Hz, 1H), 6.29 - 6.19 (m, 1H), 5.27 (q, J = 6.6 Hz, 1H), 2.34 - 2.27 (m, 2H), 2.25 - 2.18 (m, 2H), 1.74 (s, 3H), 1.61 (d, J = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 138.00, 135.38, 130.79, 129.93, 128.61 (CH×2), 126.95, 126.07 (CH×2), 119.70, 31.43 (CH_2×2), 23.56, 13.46.

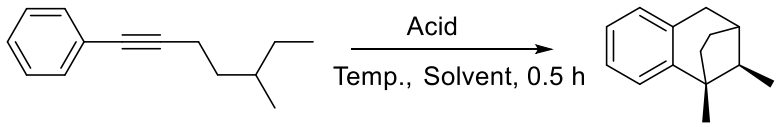


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

2.2 General procedure for the preparation of desired product

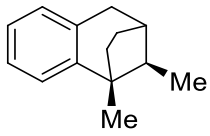
To a solution of the appropriate alkyne (0.3 mmol) in freshly distilled $CHCl_3$ (3 mL) under N_2 atmosphere was added trifluoromethanesulfonic acid (26.5 μL, 0.3 mmol) at 0 °C. The resulting dark brown reaction mixture was then stirred at 0 °C for 30 min and was quenched with water, extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude residue was finally purified by column chromatography over silica gel using n-hexane or n-pentane as eluent to yield the desired polycyclic compound.

Table 1 Condition optimization of cascade cyclization of alkyne



Entry	Acid	Acid / eq.	Temp. / °C	Solvent	Yield[a]
1	TfOH	0.2	80	DCE	10%
2	TfOH	0.2	60	DCE	15%
3	TfOH	0.2	25	DCE	<5%
4	TfOH	0.4	25	DCE	25%
5	TfOH	1.0	25	DCE	64%
6	TfOH	1.0	0	DCE	74%
7	TfOH	1.0	0	CCl_4	81%
8	TfOH	1.0	0	$CHCl_3$	88% (80%[b])
9	TfOH	1.0	-15	$CHCl_3$	80%
10	Tf_2NH	1.0	0	$CHCl_3$	<5%
11	$C_4F_9SO_3H$	1.0	0	$CHCl_3$	75%
12	$PhSO_3H$	1.0	0	$CHCl_3$	ND
13	TfOH	1.0	0	$PhCH_3$	<5%
14	TfOH	1.0	0	MesH	ND
15	TfOH	1.0	0	$PhCF_3$	74%

[a] yields were based on the GC using n-dodecane as internal standard.
[b] isolated yield. ND: no desired product.

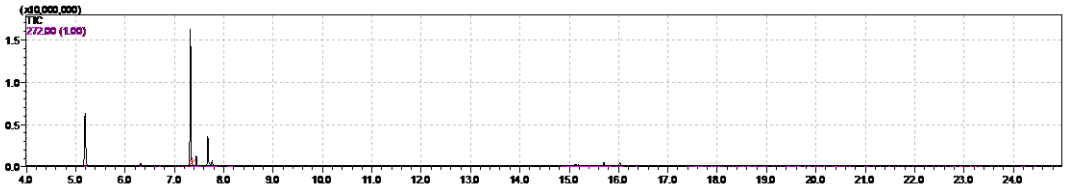


5,10-dimethyl-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene (**2a**): colorless liquid, 44 mg, isolated yield: 80%.

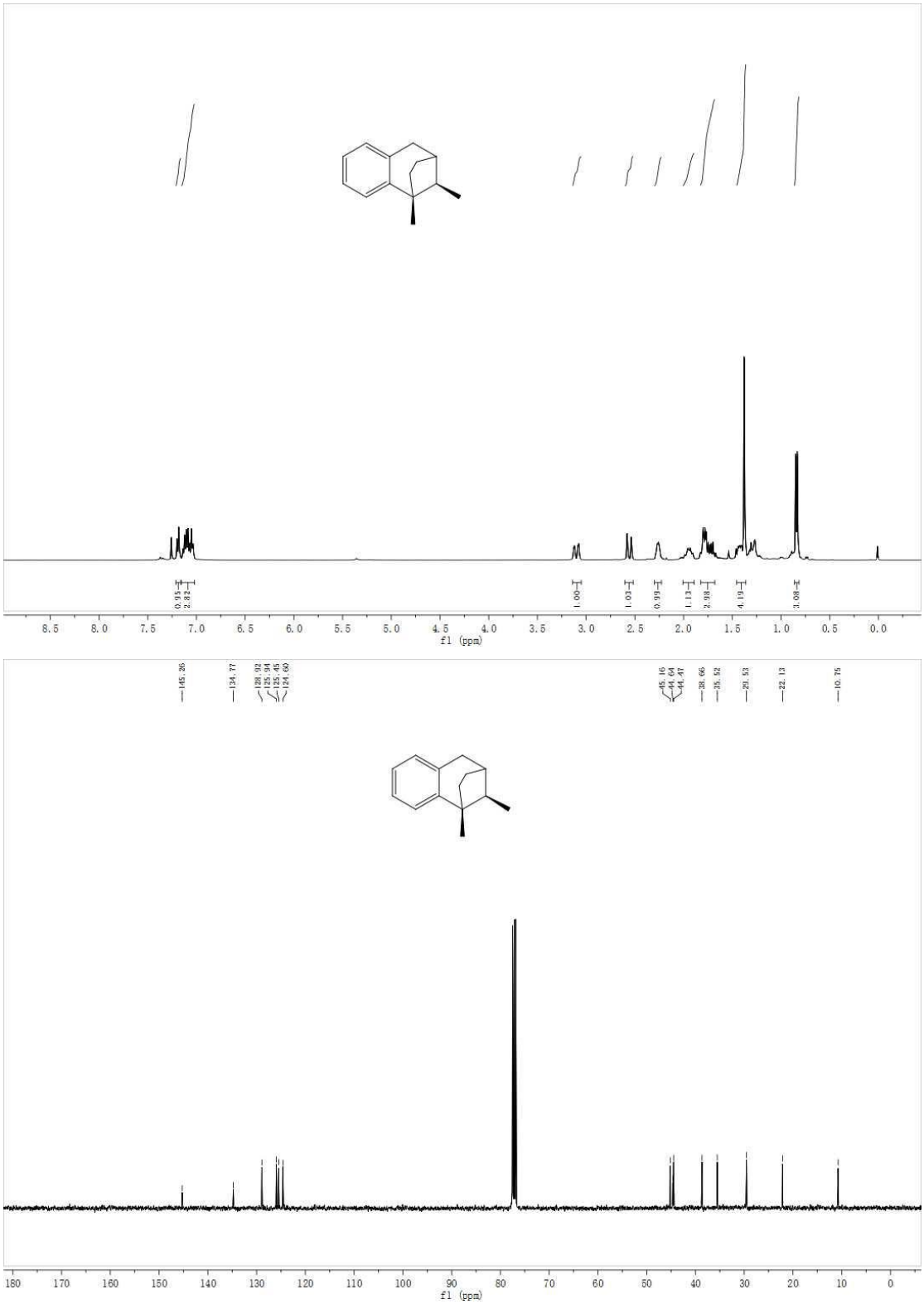
1H NMR (400 MHz, CHLOROFORM-D) δ 7.19 (d, J = 7.4 Hz, 1H), 7.15 - 7.02 (m, 3H), 3.10 (d, J = 17.1 Hz, 1H), 2.56 (d, J = 17.0 Hz, 1H), 2.30 - 2.22 (m, 1H), 2.00 - 1.89 (m, 1H), 1.83 - 1.68 (m, 3H), 1.46 - 1.36 (m, 4H), 0.84 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 145.26, 134.77, 128.92, 125.94, 125.45, 124.60, 45.16, 44.64, 44.47, 38.66, 35.52, 29.53, 22.13, 10.75.

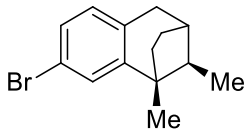
HRMS(APPI): cacud for $C_{14}H_{18}$ [M-H]$^+$: 185.1330, found: 185.1326.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

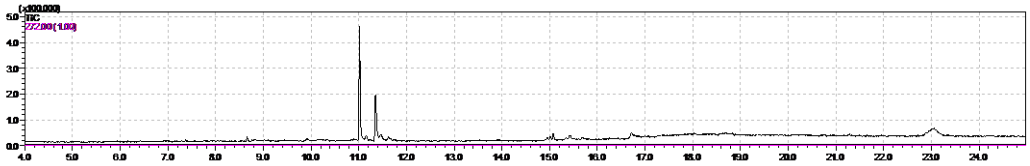


3-bromo-5,10-dimethyl-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene (**2b**): colorless liquid, 55 mg, isolated yield: 70%.

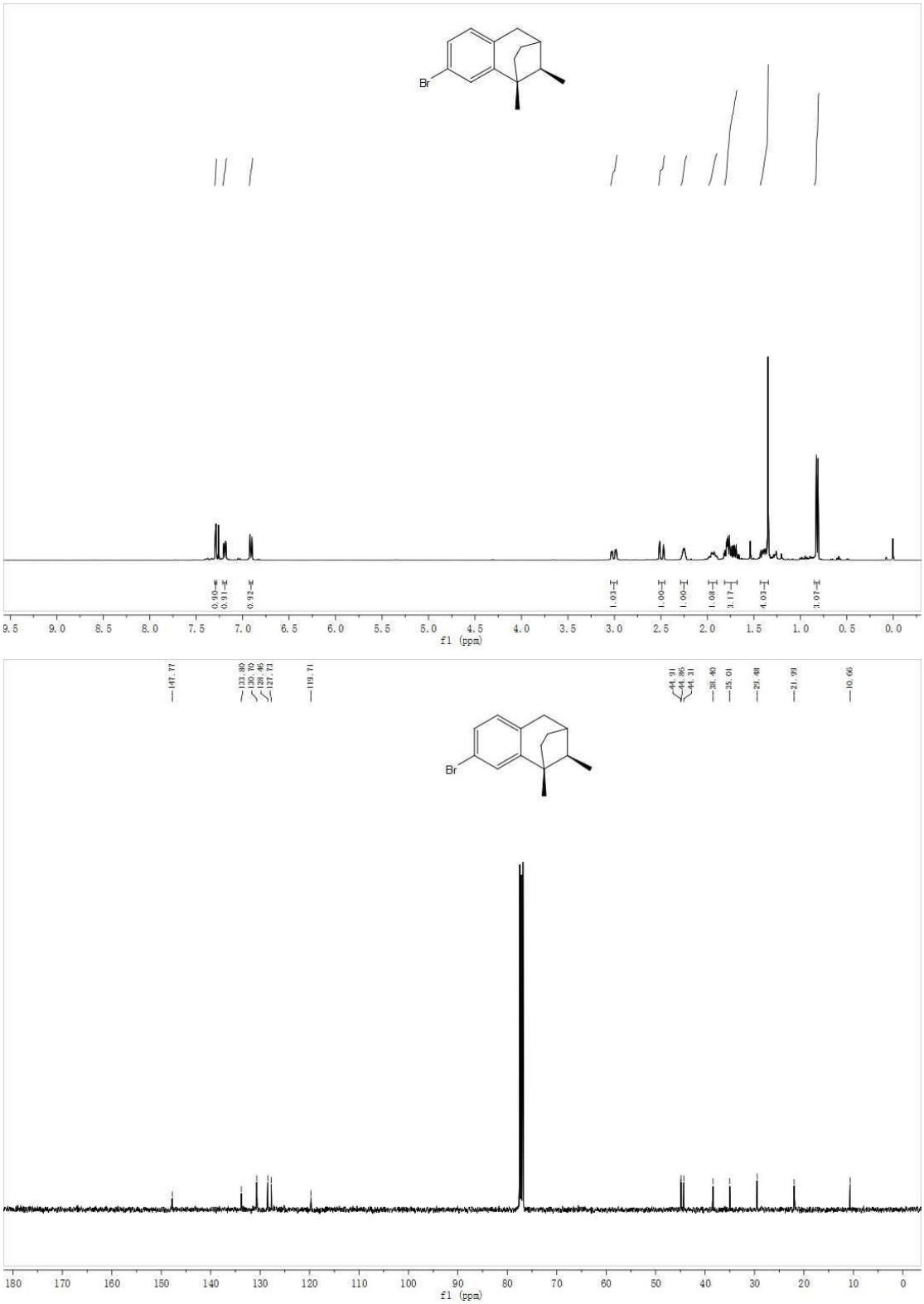
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.29 (d, J = 1.7 Hz, 1H), 7.19 (dd, J = 8.0, 1.9 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.01 (dd, J = 17.2, 4.1 Hz, 1H), 2.49 (d, J = 17.1 Hz, 1H), 2.29 - 2.21 (m, 1H), 1.99 - 1.90 (m, 1H), 1.81 - 1.68 (m, 3H), 1.43 - 1.34 (m, 4H), 0.82 (d, J = 6.9 Hz, 3H)

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 147.77, 133.80, 130.70, 128.46, 127.73, 119.71, 44.91, 44.86, 44.31, 38.40, 35.01, 29.48, 21.99, 10.66.

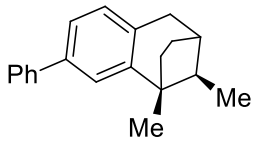
HRMS(APPI): cacud for $C_{14}H_{17}Br$ $[M-H]^+$: 263.0435, found: 263.0432.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

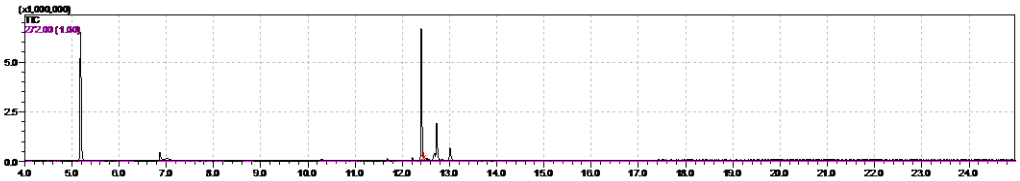


5,10-dimethyl-3-phenyl-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene (**2c**): colorless liquid, 41 mg, isolated yield: 53%.

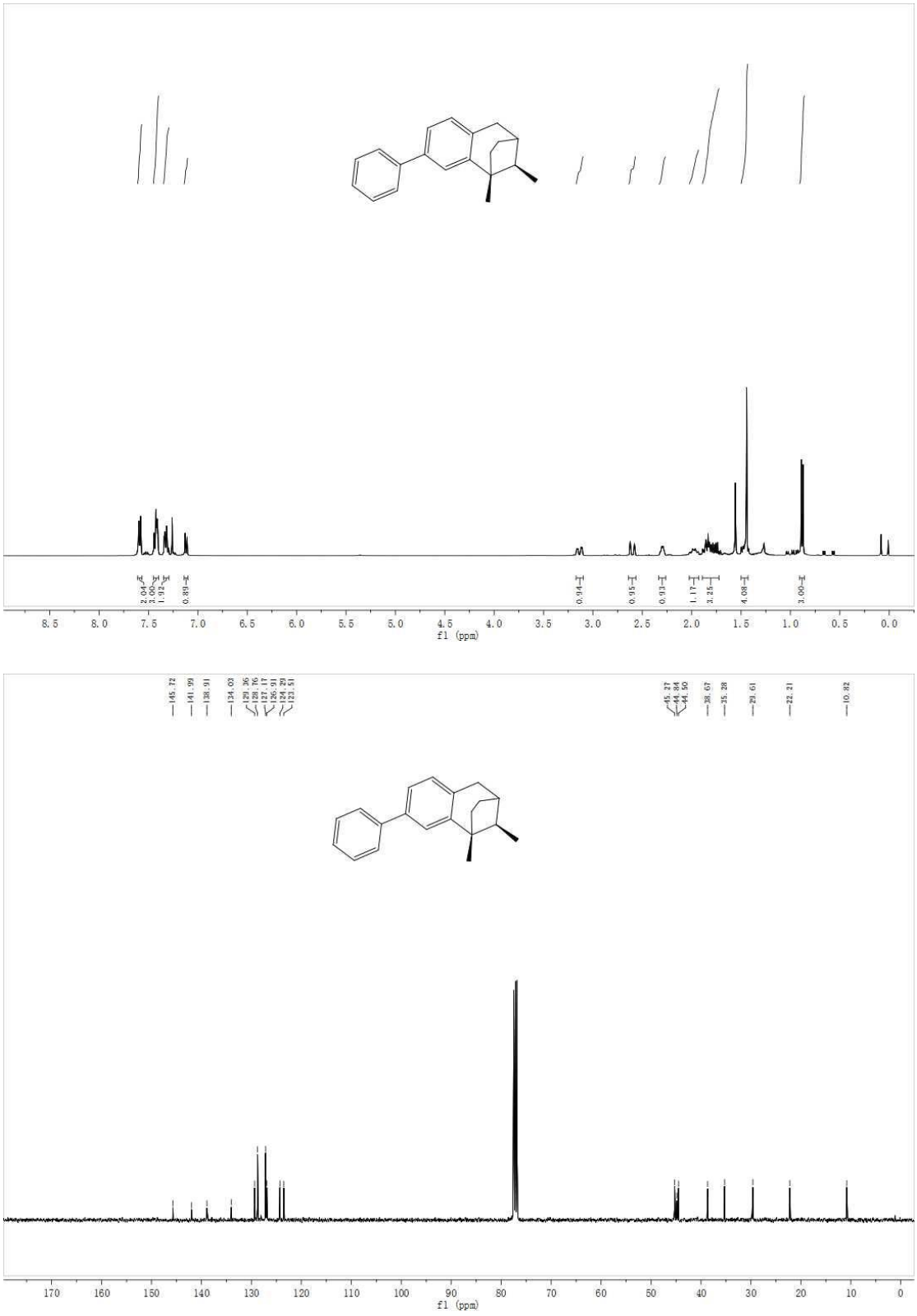
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.59 (d, J = 7.3 Hz, 2H), 7.45 - 7.40 (m, 3H), 7.35 - 7.29 (m, 2H), 7.12 (d, J = 7.8 Hz, 1H), 3.14 (dd, J = 17.2, 4.2 Hz, 1H), 2.60 (d, J = 17.1 Hz, 1H), 2.33 - 2.26 (m, 1H), 2.02 - 1.93 (m, 1H), 1.89 - 1.72 (m, 3H), 1.50 - 1.43 (m, 4H), 0.88 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 145.72, 141.99, 138.91, 134.03, 129.36, 128.76 (CH×2), 127.17 (CH×2), 126.91, 124.29, 123.51, 45.27, 44.84, 44.50, 38.67, 35.28, 29.61, 22.21, 10.82.

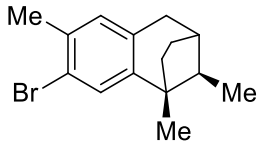
HRMS(APPI): cacud for $C_{20}H_{22}$ $[M-H]^{+}$: 261.1643, found: 261.1640.



GC-MS spectra of the reaction mixture: the highest peak at 12.4min indicated the formation of the product.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

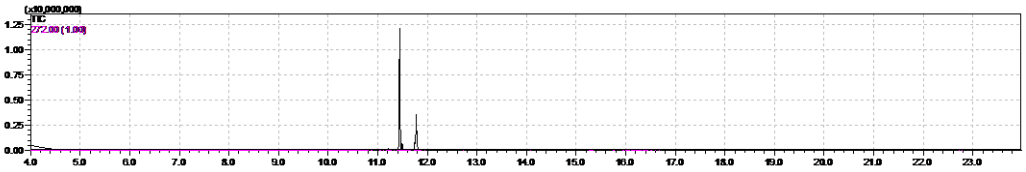


(5R,10R)-3-bromo-2,5,10-trimethyl-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene (**2d**): colorless liquid, 64 mg, isolated yield: 77%.

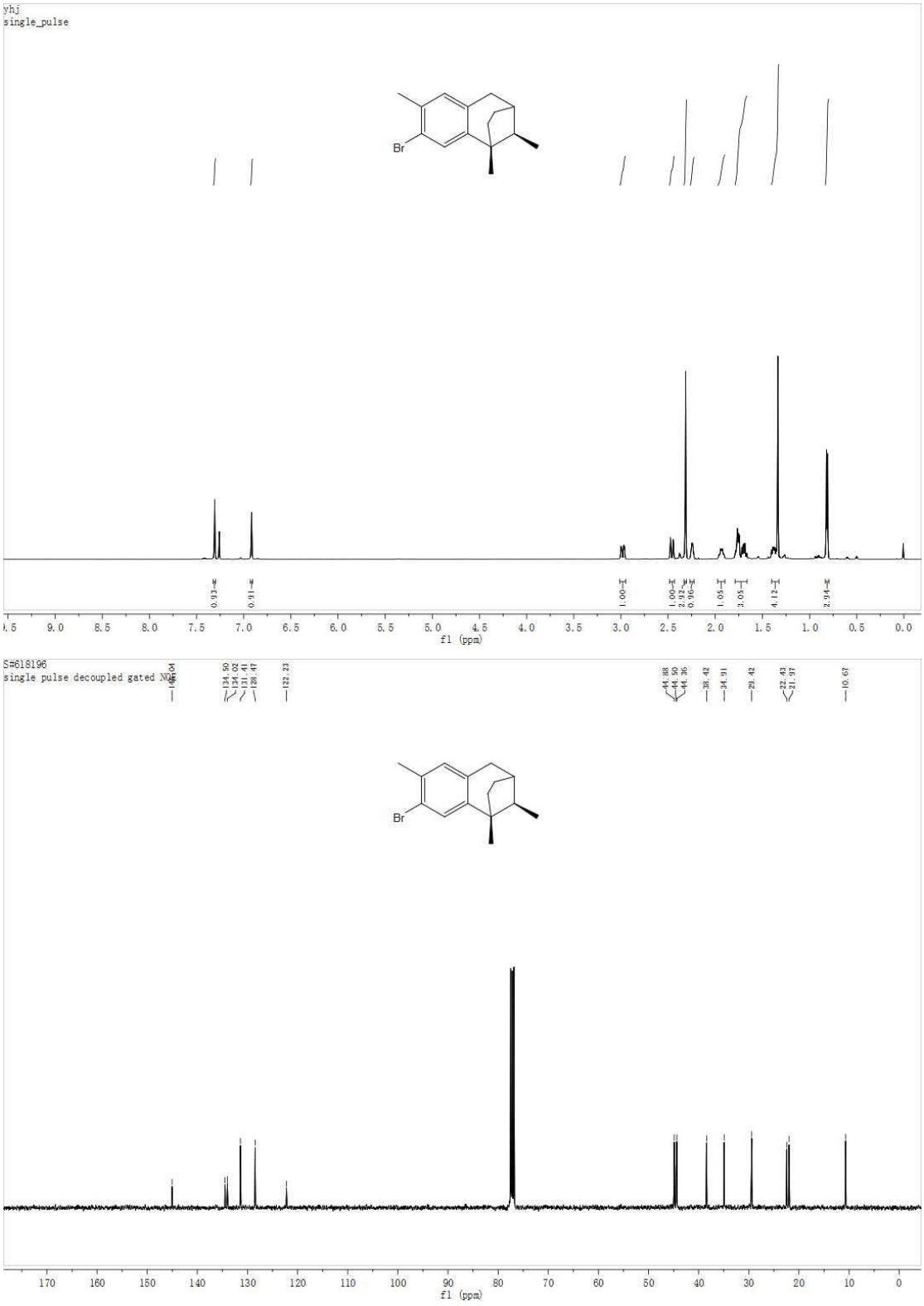
^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.31 (s, 1H), 6.92 (s, 1H), 2.98 (d, *J* = 17.1 Hz, 1H), 2.46 (d, *J* = 17.0 Hz, 1H), 2.31 (s, 3H), 2.24 (d, *J* = 4.8 Hz, 1H), 1.98 - 1.90 (m, 1H), 1.79 - 1.66 (m, 3H), 1.40 - 1.32 (m, 4H), 0.81 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 145.04, 134.50, 134.02, 131.41, 128.47, 122.23, 44.88, 44.50, 44.36, 38.42, 34.91, 29.42, 22.43, 21.97, 10.67.

HRMS(APPI): cacud for $C_{15}H_{19}Br$ [M-H]$^{+}$: 277.0592, found: 277.0591.



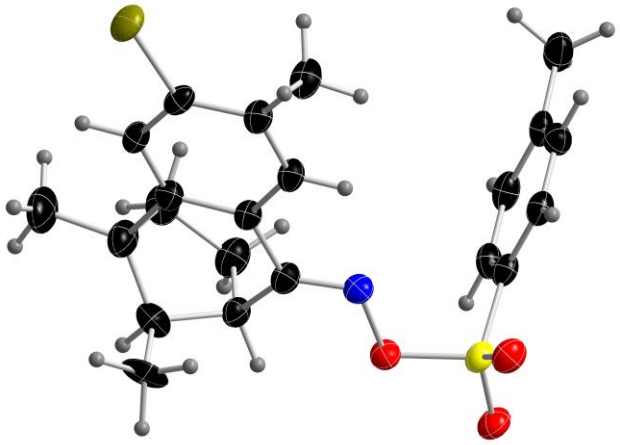
GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product.

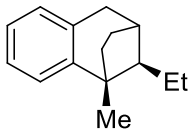


^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

X-ray crystal structure analysis of tosylate 2d: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in Et_2O. Formula: $C_{22}H_{24}BrNO_3S$, M = 462.39, colorless crystal, 0.14 x 0.25 x 0.30 mm, a = 6.9163(14), b = 13.670(3), c = 22.369(5) Å, α = 90.00°, β = 92.64(3)°, γ = 90.00°, V = 2112.7(7) $Å^3$, ρ(calcd) = 1.454 g/cm^3, μ = 2.067 mm^{-1}, Z = 4, monoclinic, space group *P2(1)/n*, λ =0.71073 Å, T = 173±2 K. Theta (max) = 27.5°, R (reflections) = 0.0576 (4216), wR2 (reflections) = 0.1442 (4802).

CCDC number: 1431439



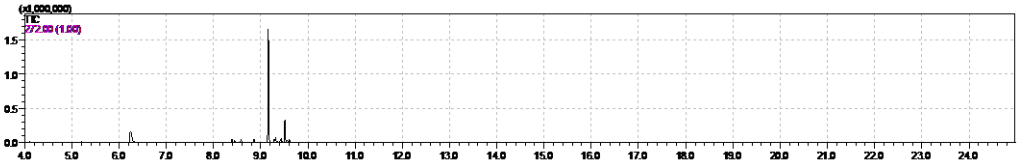


(5R,10R)-10-ethyl-5-methyl-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene (**2e**): colorless liquid, 49 mg, isolated yield: 82%.

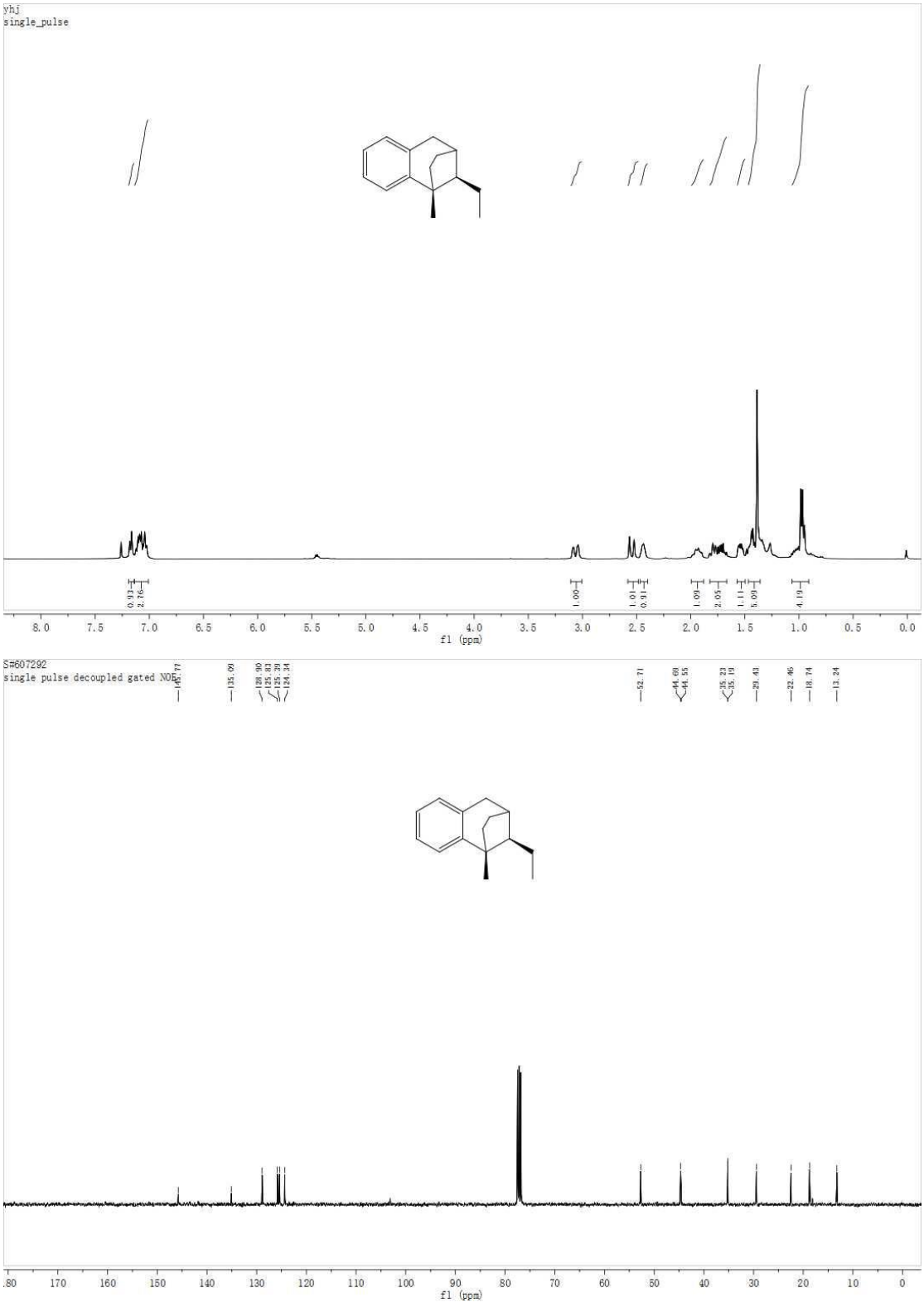
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.17 (d, *J* = 7.2 Hz, 1H), 7.14 - 7.00 (m, 3H), 3.06 (d, *J* = 17.0 Hz, 1H), 2.54 (d, *J* = 17.1 Hz, 1H), 2.44 (d, *J* = 3.0 Hz, 1H), 1.99 - 1.88 (m, 1H), 1.82 - 1.67 (m, 2H), 1.54 (dd, *J* = 10.0, 4.9 Hz, 1H), 1.47 - 1.36 (m, 5H), 1.06 - 0.95 (m, 4H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 145.77, 135.09, 128.90, 125.83, 125.39, 124.34, 52.71, 44.69, 44.55, 35.23, 35.19, 29.43, 22.46, 18.74, 13.24.

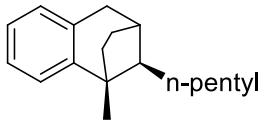
HRMS(APPI): cacud for $C_{15}H_{20}$ [M-H]$^{+}$: 199.1487, found: 199.1484.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

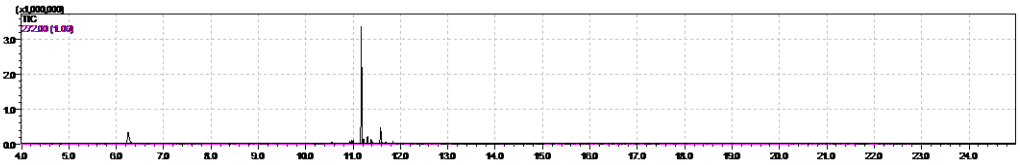


5-methyl-10-pentyl-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene (**2f**): colorless liquid, 61 mg, isolated yield: 84%.

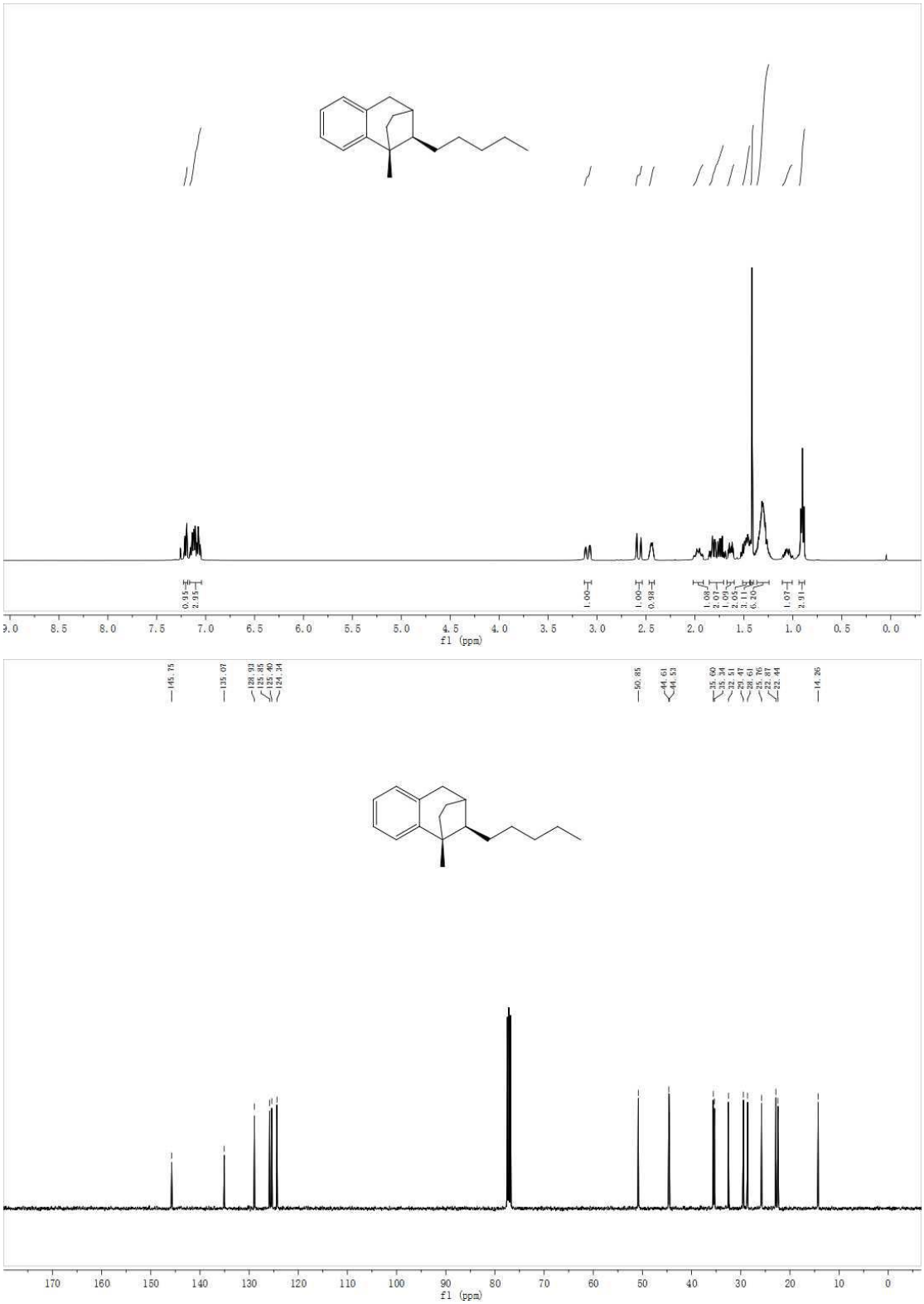
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.23 - 7.18 (m, 1H), 7.16 - 7.04 (m, 3H), 3.10 (dd, J = 17.1, 4.0 Hz, 1H), 2.57 (d, J = 17.1 Hz, 1H), 2.47 - 2.41 (m, 1H), 2.02 - 1.91 (m, 1H), 1.85 - 1.71 (m, 2H), 1.63 (dt, J = 11.1, 4.2 Hz, 1H), 1.47 (ddd, J = 11.9, 8.8, 6.1 Hz, 2H), 1.42 (s, 3H), 1.37 - 1.24 (m, 6H), 1.11 - 1.00 (m, 1H), 0.90 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 145.75, 135.07, 128.93, 125.85, 125.40, 124.34, 50.85, 44.61, 44.53, 35.60, 35.34, 32.51, 29.47, 28.61, 25.76, 22.87, 22.44, 14.26.

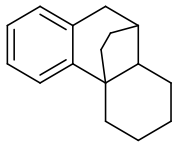
HRMS(APPI): cacud for $C_{18}H_{26}$ $[M-H]^{+}$: 241.1956, found: 241.1952.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

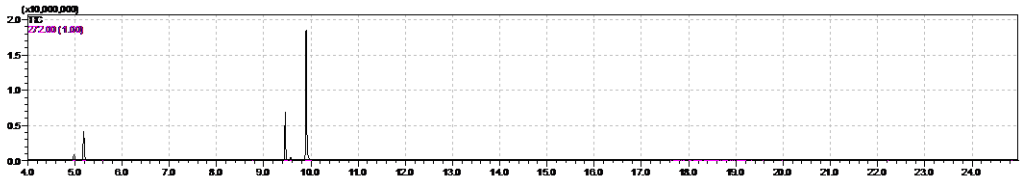


2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2g**): colorless liquid, 49 mg, isolated yield: 78%.

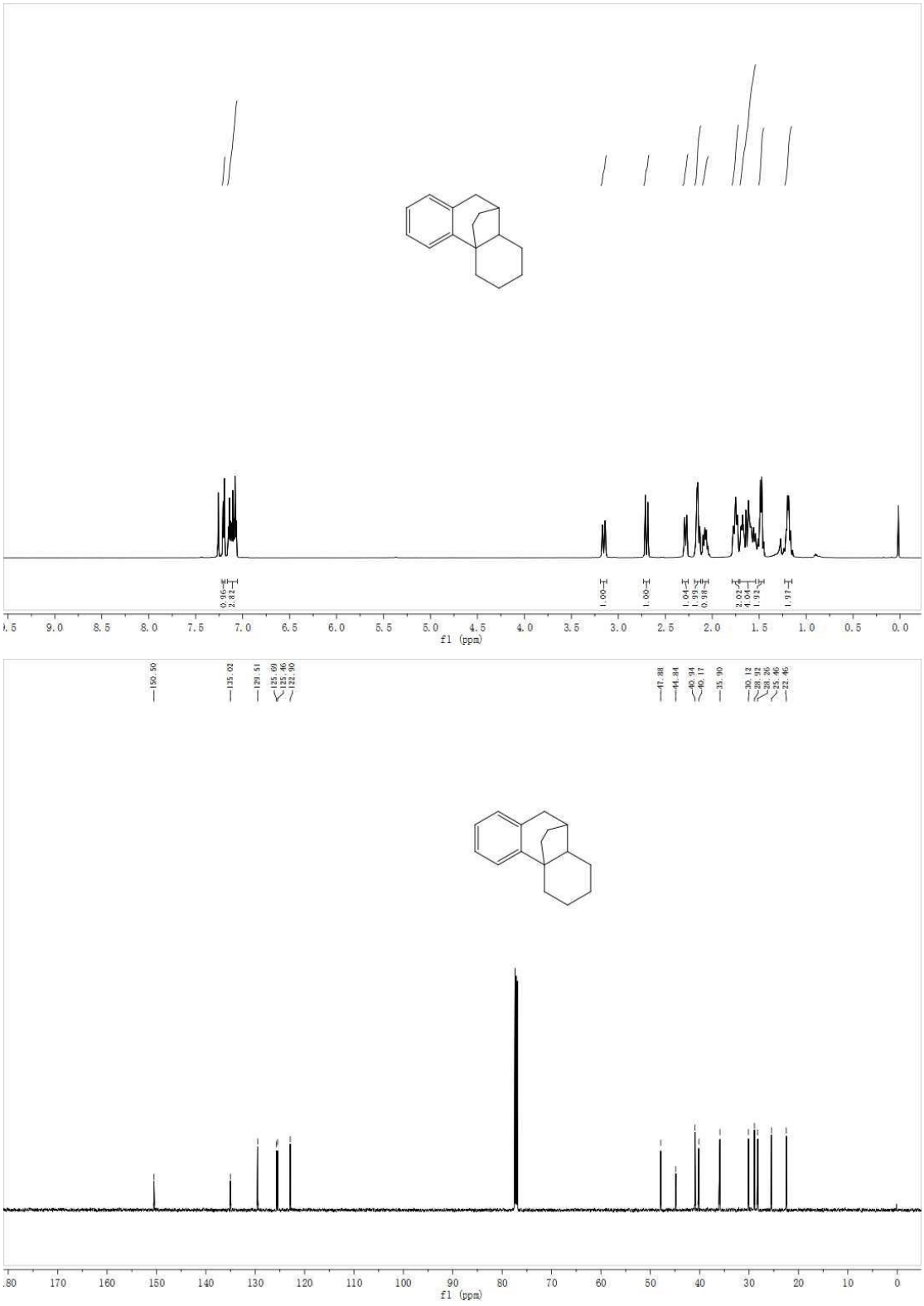
^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.20 (d, J = 7.6 Hz, 1H), 7.16 - 7.05 (m, 3H), 3.15 (dd, J = 16.5, 3.2 Hz, 1H), 2.70 (d, J = 16.5 Hz, 1H), 2.28 (d, J = 12.9 Hz, 1H), 2.19 - 2.12 (m, 2H), 2.07 (dd, J = 18.8, 11.0 Hz, 1H), 1.75 (t, J = 12.9 Hz, 2H), 1.71 - 1.54 (m, 4H), 1.51 - 1.45 (m, 2H), 1.23 - 1.15 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 150.50, 135.02, 129.51, 125.69, 125.46, 122.90, 47.88, 44.84, 40.94, 40.17, 35.90, 30.12, 28.92, 28.26, 25.46, 22.46.

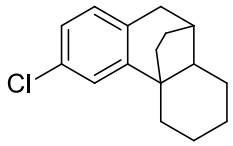
HRMS(APPI): cacud for $C_{16}H_{20}$ $[M-H]^{+}$: 211.14813, found: 211.14816.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product.



^{1}H NMR (600 MHz, $CDCl_3$) (up) and ^{13}C NMR (151 MHz, $CDCl_3$) (down)

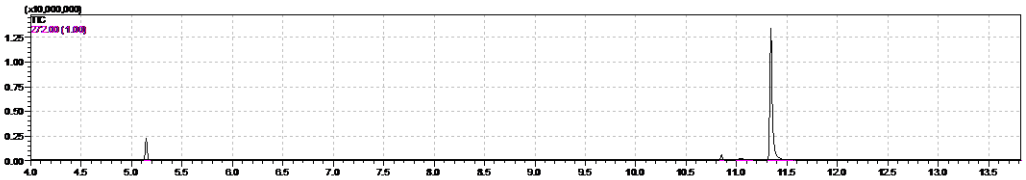


6-chloro-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2h**): colorless liquid, 62 mg, isolated yield: 85%.

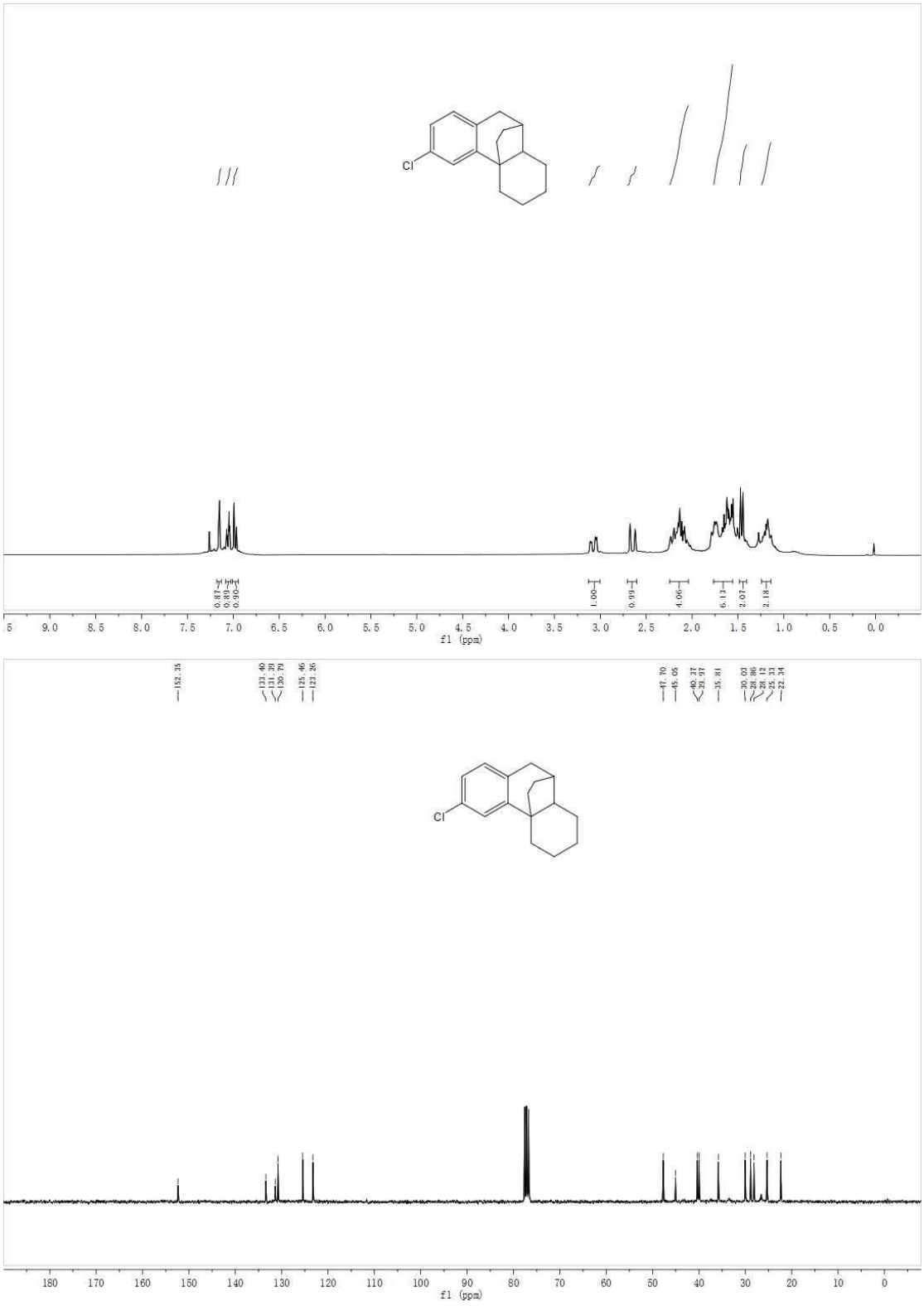
^{1}H NMR (301 MHz, CHLOROFORM-D) δ 7.15 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.1, 2.1 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 3.07 (dd, J = 16.9, 4.0 Hz, 1H), 2.65 (d, J = 16.6 Hz, 1H), 2.24 - 2.04 (m, 4H), 1.78 - 1.55 (m, 6H), 1.44 (dd, J = 13.8, 6.1 Hz, 2H), 1.24 - 1.14 (m, 2H).

^{13}C NMR (76 MHz, CHLOROFORM-D) δ 152.35, 133.40, 131.39, 130.79, 125.46, 123.26, 47.70, 45.05, 40.37, 39.97, 35.81, 30.03, 28.86, 28.12, 25.33, 22.34.

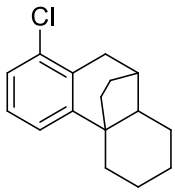
HRMS(APPI): cacud for $C_{16}H_{19}Cl$ $[M-H]^{+}$: 245.10915, found: 245.10916.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (300 MHz, $CDCl_3$) (up) and ^{13}C NMR (76 MHz, $CDCl_3$) (down)

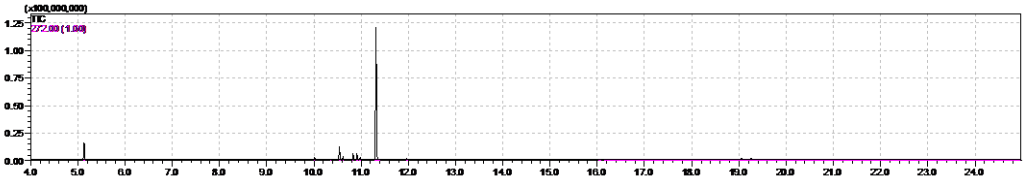


8-chloro-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2i**): colorless liquid, 60 mg, isolated yield: 82%.

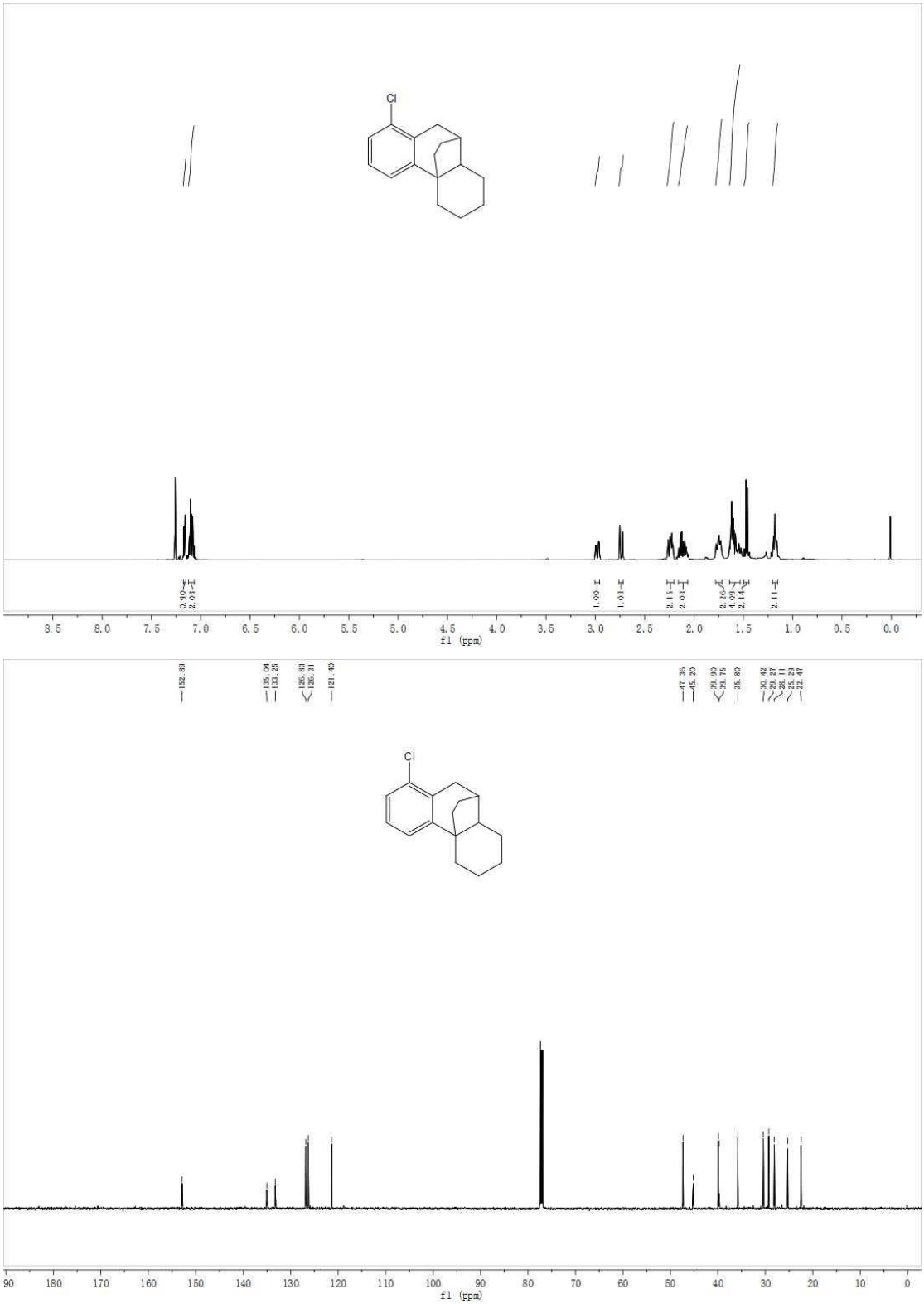
^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.16 (dd, J = 7.5, 1.5 Hz, 1H), 7.12 - 7.07 (m, 2H), 2.98 (dd, J = 17.4, 4.0 Hz, 1H), 2.74 (dd, J = 17.4, 1.7 Hz, 1H), 2.27 - 2.20 (m, 2H), 2.16 - 2.06 (m, 2H), 1.78 - 1.72 (m, 2H), 1.64 - 1.53 (m, 4H), 1.49 - 1.44 (m, 2H), 1.20 - 1.15 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 152.83, 134.99, 133.19, 126.79, 126.27, 121.35, 47.31, 45.15, 39.86, 39.71, 35.76, 30.38, 29.23, 28.07, 25.25, 22.43.

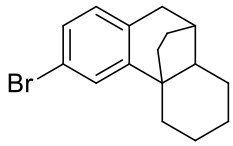
HRMS(APPI): cacud for $C_{16}H_{19}Cl$ [M-H]$^{+}$: 245.10915, found: 245.10913.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (600 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

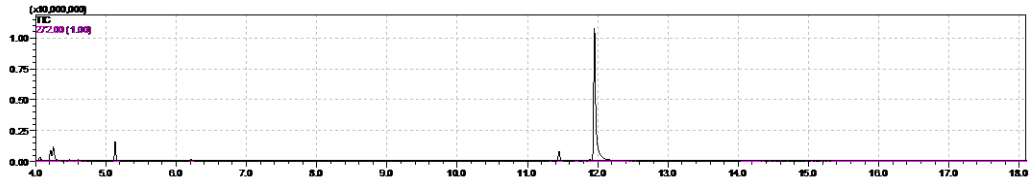


6-bromo-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2j**): white solid, 78 mg, isolated yield: 90%.

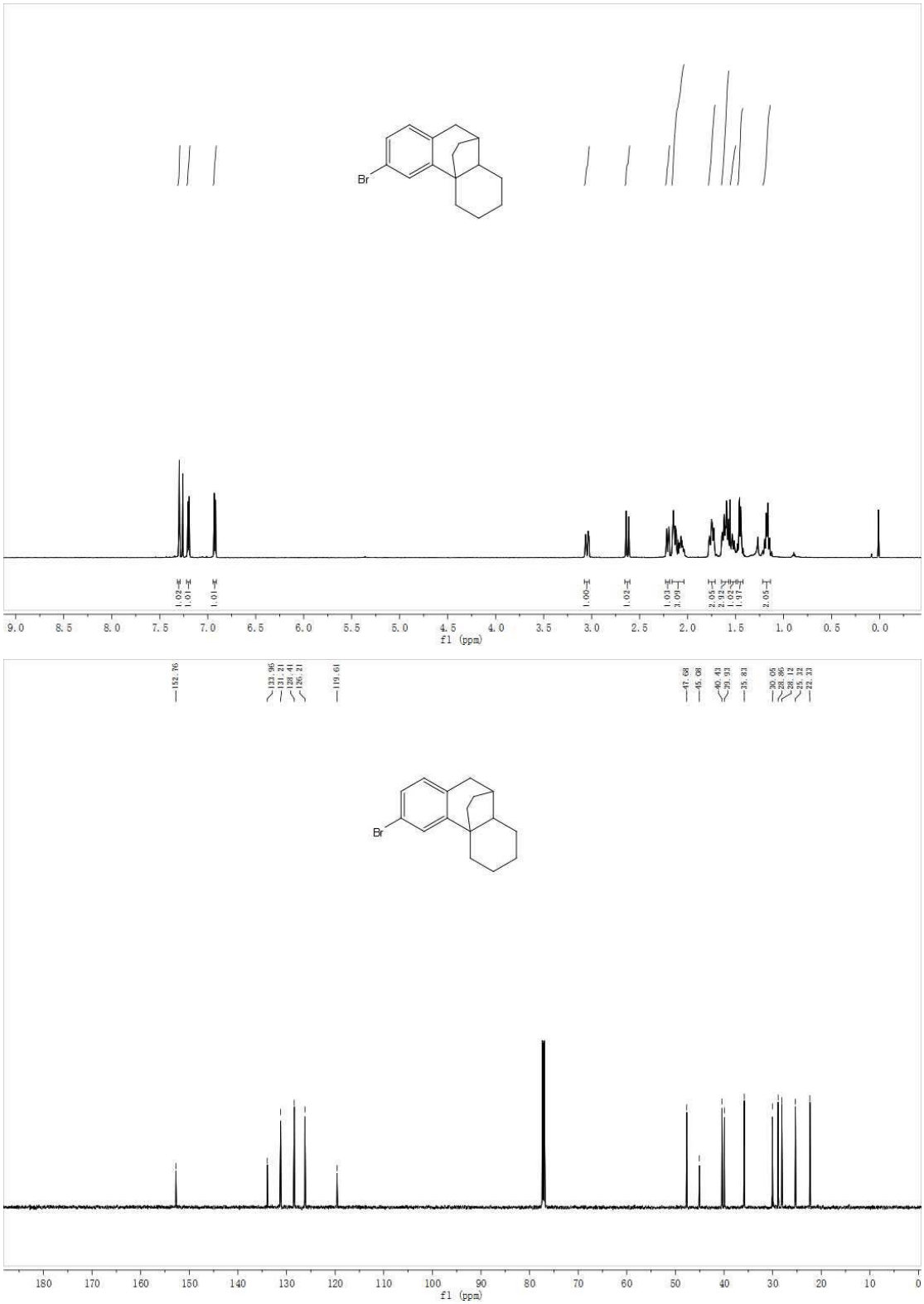
^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.30 (d, J = 1.9 Hz, 1H), 7.20 (dd, J = 8.1, 2.1 Hz, 1H), 6.92 (dd, J = 8.1, 0.8 Hz, 1H), 3.05 (dd, J = 16.7, 3.8 Hz, 1H), 2.63 (d, J = 16.7 Hz, 1H), 2.21 (d, J = 12.5 Hz, 1H), 2.16 - 2.04 (m, 3H), 1.78 - 1.71 (m, 2H), 1.65 - 1.57 (m, 3H), 1.56 - 1.50 (m, 1H), 1.48 - 1.42 (m, 2H), 1.17 (dt, J = 13.6, 10.3 Hz, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 152.76, 133.96, 131.21, 128.41, 126.21, 119.61, 47.68, 45.08, 40.43, 39.93, 35.83, 30.05, 28.86, 28.12, 25.32, 22.33

HRMS(APPI): cacud for $C_{16}H_{19}Br$ $[M-H]^{+}$: 289.05864, found: 289.05859.



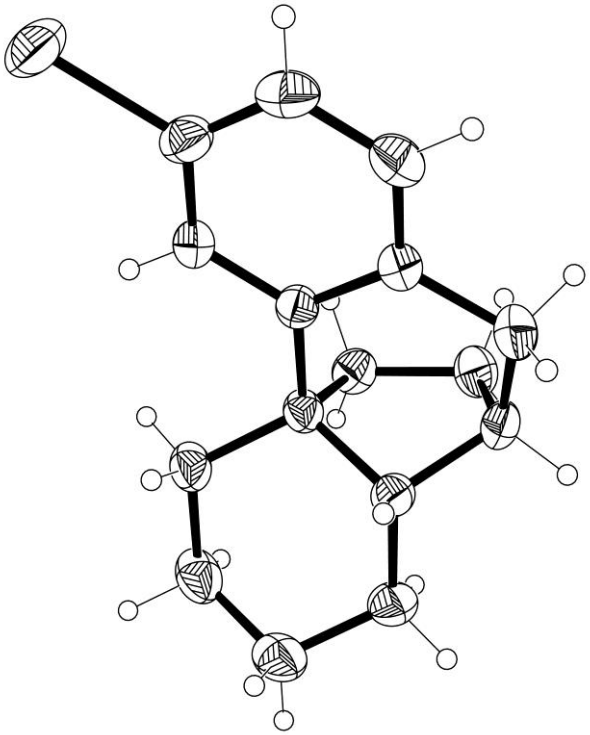
GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product

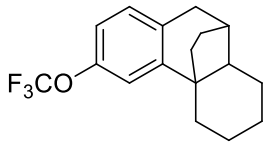


^{1}H NMR (600 MHz, $CDCl_3$) (up) and ^{13}C NMR (151 MHz, $CDCl_3$) (down)

X-ray crystal structure analysis of compound 2j: Single crystals suitable for X-ray analysis were obtained by slow evaporation of its solution in hexane. Formula: $C_{16}H_{19}Br$, M = 291.22, colorless prism, 0.4 x 0.4 x 0.5 mm, a = 18.281(3), b = 7.3569(12), c = 19.925(4) Å, α = 90.00°, β = 104.092(12)°, γ = 90.00° , V = 2599.1(8)Å^3, ρ(calcd) = 1.488 g/cm^3, μ = 3.138 mm^{-1}, Z = 8, monoclinic, space group *C*2/*c* (No. 15), λ =0.71073 Å, T = 295±2K. Theta (max) = 25.5°, R (reflections) = 0.0434 (1737), wR2 (reflections) = 0.0995 (2394).

CCDC number: 1431438



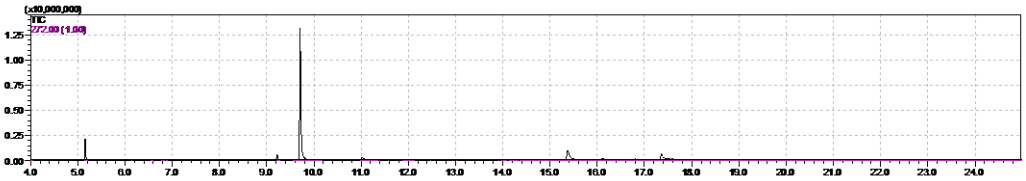


6-(trifluoromethoxy)-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2k**): colorless liquid, 77 mg, isolated yield: 87%.

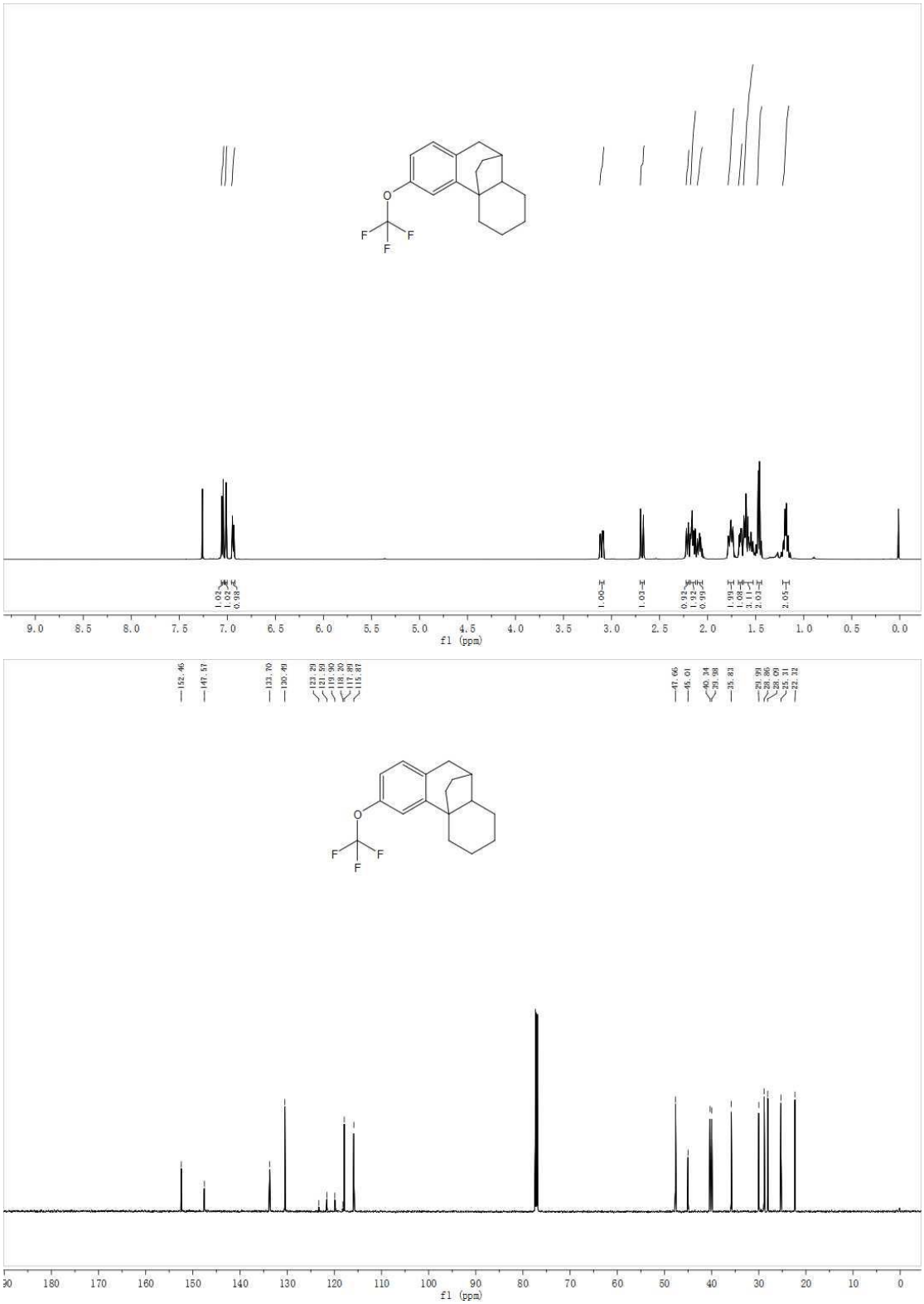
^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.05 (d, J = 8.3 Hz, 1H), 7.01 (s, 1H), 6.94 (dd, J = 8.3, 1.2 Hz, 1H), 3.10 (dd, J = 16.6, 4.4 Hz, 1H), 2.68 (dd, J = 16.7, 1.2 Hz, 1H), 2.21 (d, J = 12.0 Hz, 1H), 2.18 - 2.13 (m, 2H), 2.11 - 2.05 (m, 1H), 1.79 - 1.73 (m, 2H), 1.66 (dd, J = 11.6, 5.0 Hz, 1H), 1.63 - 1.53 (m, 3H), 1.49 - 1.44 (m, 2H), 1.22 - 1.15 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 152.46, 147.57, 133.70, 130.49, 120.75 (q, J = 255.8 Hz), 117.89, 115.87, 47.66, 45.01, 40.34, 39.98, 35.83, 29.99, 28.86, 28.09, 25.31, 22.32.

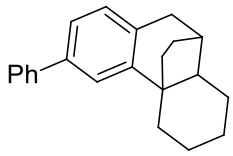
HRMS(APPI): cacud for $C_{17}H_{19}F_3O$ $[M-H]^+$: 295.13043, found: 295.13037.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (600 MHz, $CDCl_3$) (up) and ^{13}C NMR (151 MHz, $CDCl_3$) (down)

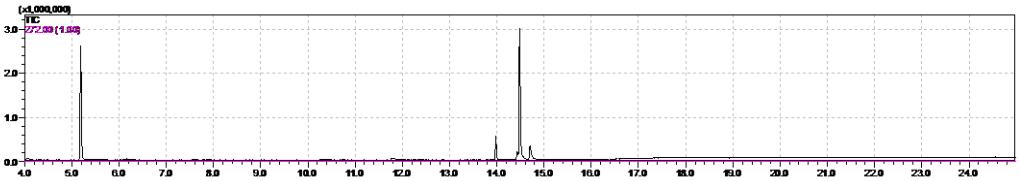


6-phenyl-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2l**): colorless liquid, 53 mg, isolated yield: 61%.

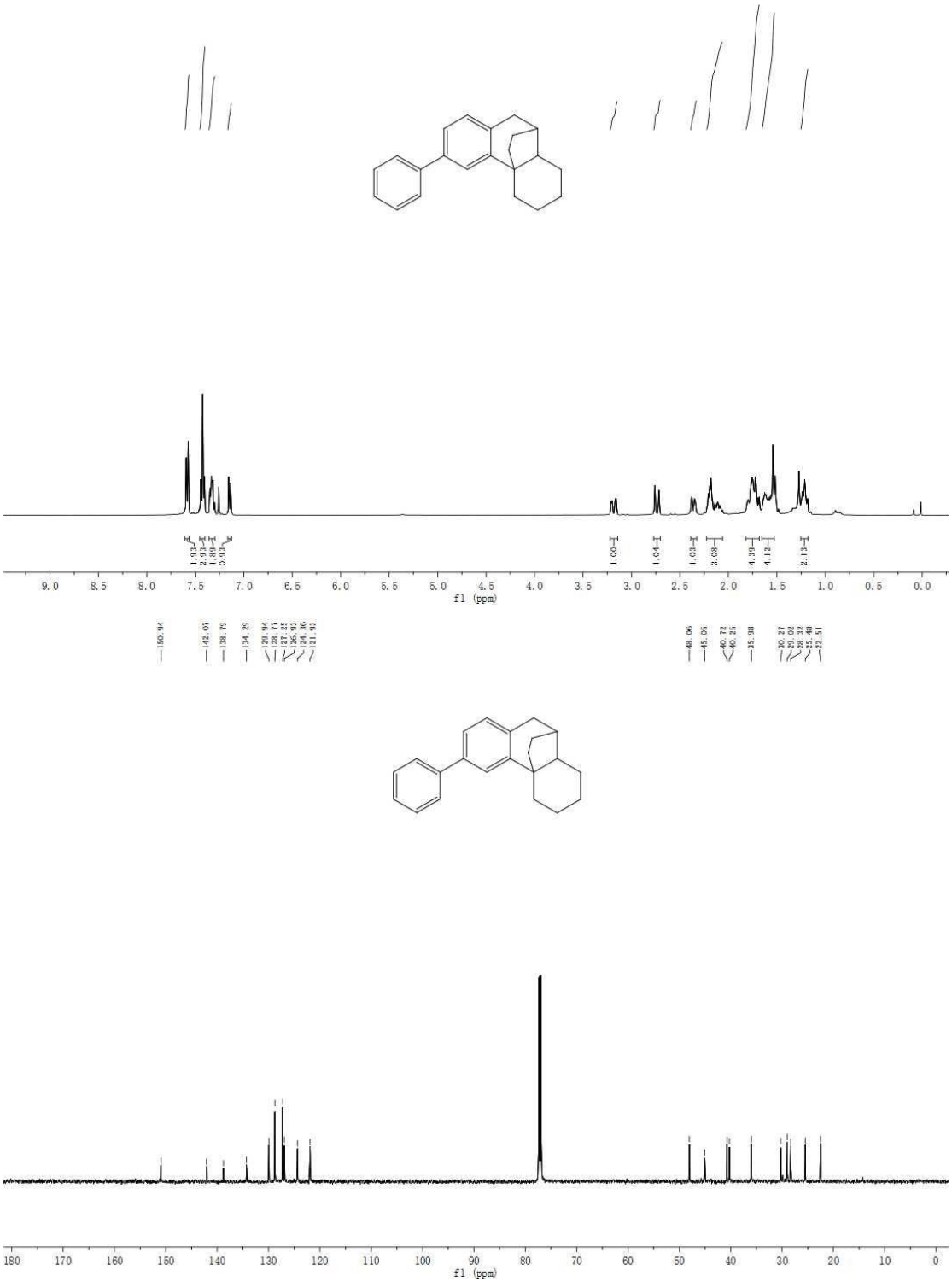
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.58 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.5 Hz, 3H), 7.36 - 7.30 (m, 2H), 7.15 (d, J = 7.8 Hz, 1H), 3.18 (dd, J = 16.7, 4.0 Hz, 1H), 2.74 (d, J = 16.7 Hz, 1H), 2.37 (d, J = 10.9 Hz, 1H), 2.22 - 2.06 (m, 3H), 1.82 - 1.68 (m, 4H), 1.66 - 1.53 (m, 4H), 1.25 - 1.18 (m, 2H).

^{13}C NMR (151 MHz, CHLOROFORM-D) δ 150.94, 142.07, 138.79, 134.29, 129.94, 128.77 (CH×2), 127.25 (CH×2), 126.93, 124.36, 121.93, 48.06, 45.05, 40.72, 40.25, 35.98, 30.27, 29.02, 28.32, 25.48, 22.51.

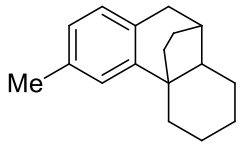
HRMS(APPI): cacud for $C_{22}H_{24}$ [M-H]$^{+}$: 287.17943, found: 287.17923.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (151 MHz, $CDCl_3$) (down)

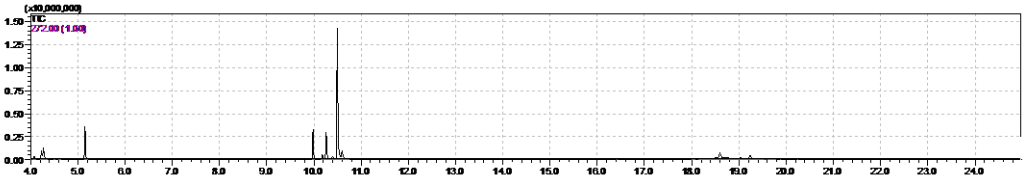


6-methyl-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2n**): colorless liquid, 50 mg, isolated yield: 74%.

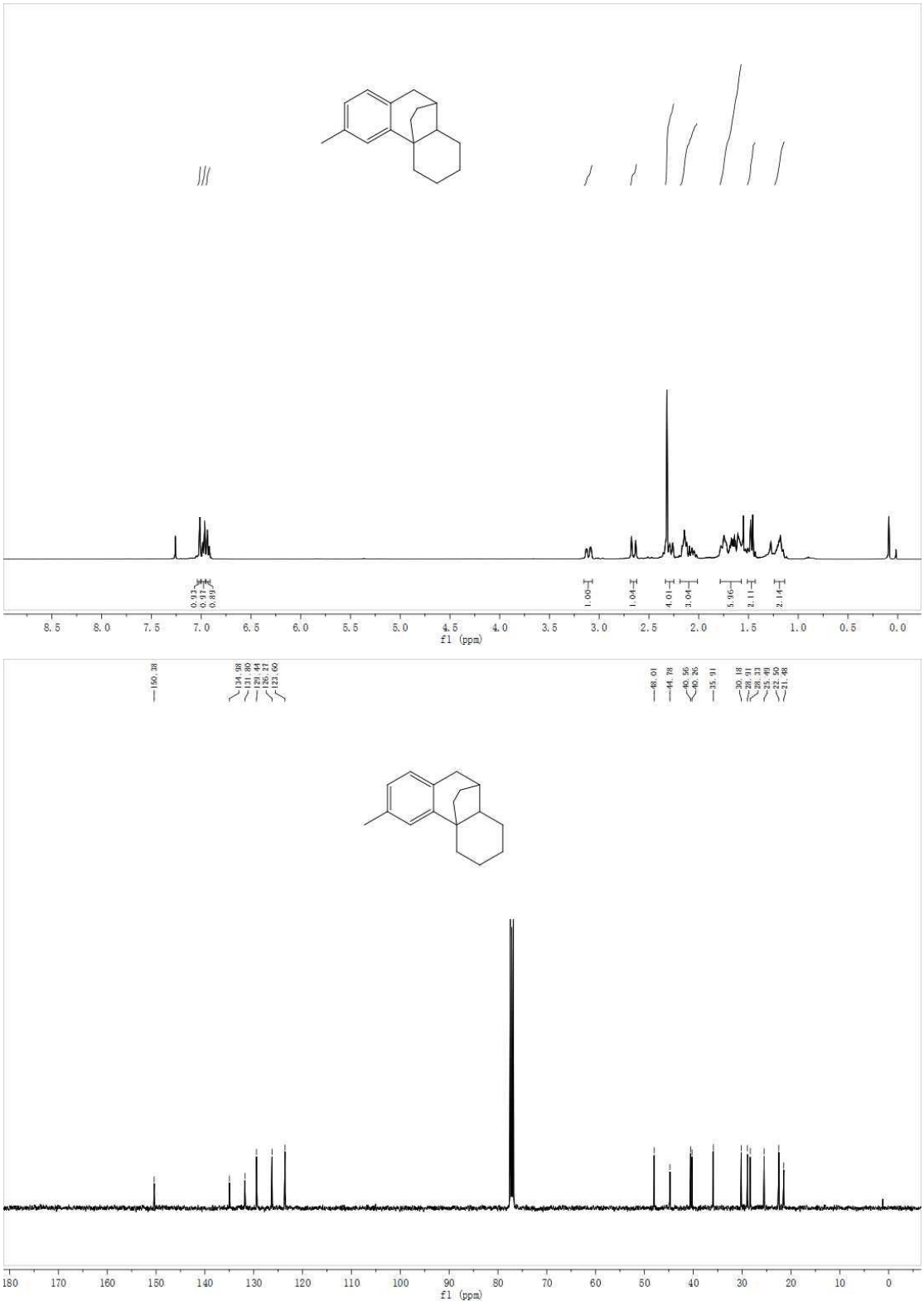
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.01 (s, 1H), 6.97 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 3.11 (dd, J = 16.3, 3.6 Hz, 1H), 2.65 (d, J = 16.4 Hz, 1H), 2.33 - 2.25 (m, 4H), 2.19 - 2.01 (m, 3H), 1.78 - 1.57 (m, 6H), 1.51 - 1.43 (m, 2H), 1.24 - 1.14 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.38, 134.98, 131.80, 129.44, 126.27, 123.60, 48.01, 44.78, 40.56, 40.26, 35.91, 30.18, 28.91, 28.33, 25.49, 22.50, 21.48.

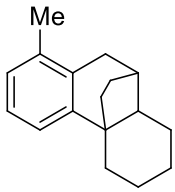
HRMS(APPI): cacud for $C_{17}H_{22}^{+}$[M-H]$^{+}$: 225.16378, found: 225.16364.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

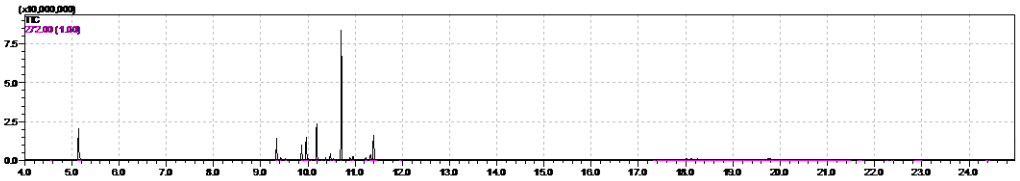


8-methyl-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2n**): colorless liquid, 42 mg, isolated yield: 62%.

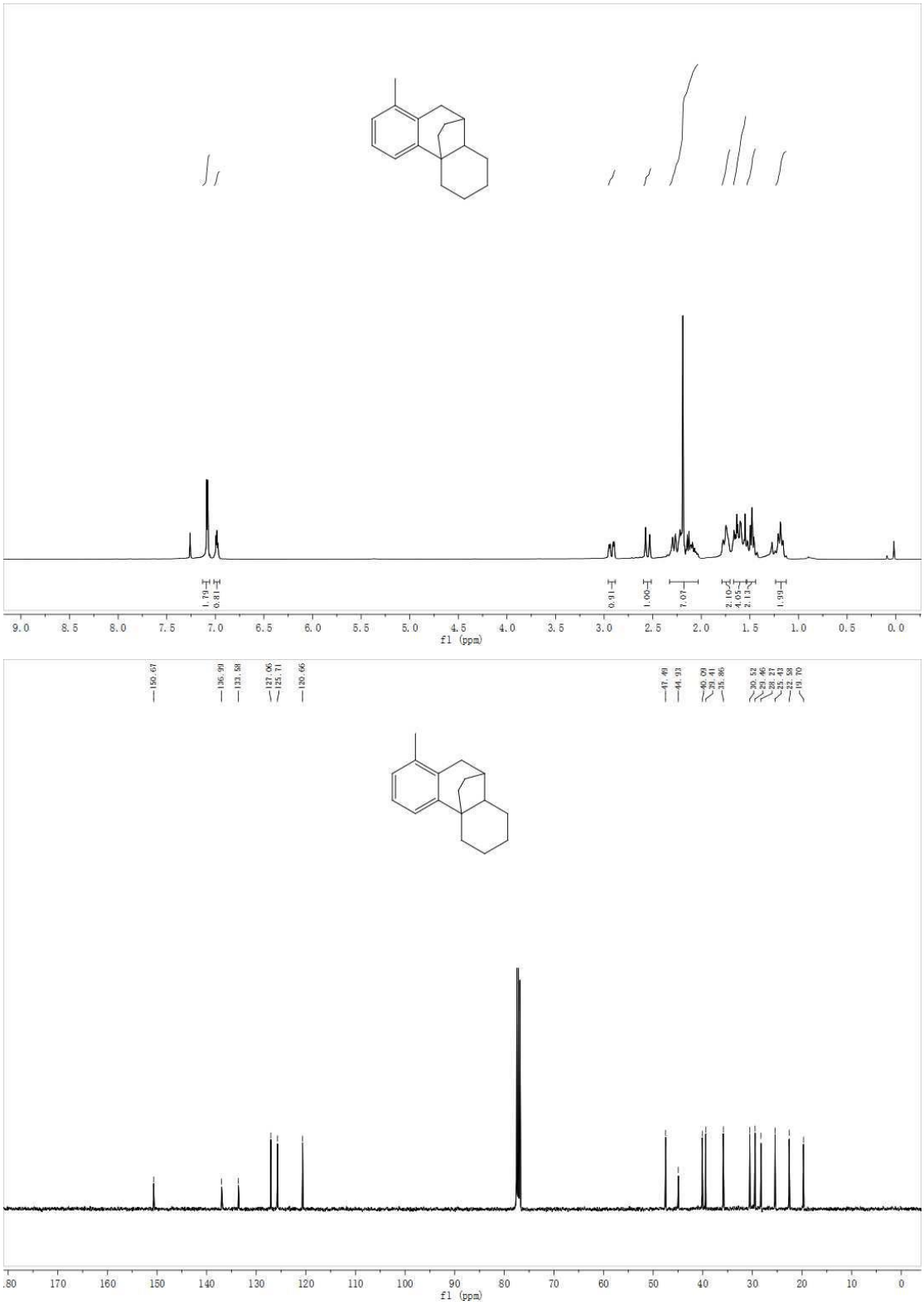
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.12 - 7.06 (m, 2H), 7.01 - 6.95 (m, 1H), 2.92 (dd, J = 16.8, 4.5 Hz, 1H), 2.55 (d, J = 16.8 Hz, 1H), 2.33 - 2.03 (m, 7H), 1.79 - 1.70 (m, 2H), 1.67 - 1.54 (m, 4H), 1.53 - 1.44 (m, 2H), 1.24 - 1.12 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.67, 136.99, 133.58, 127.06, 125.71, 120.66, 47.49, 44.93, 40.09, 39.41, 35.86, 30.52, 29.46, 28.27, 25.43, 22.58, 19.70.

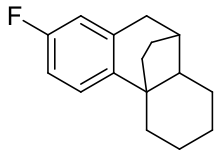
HRMS(APPI): cacud for $C_{17}H_{22}^{+}$ [M-H]$^{+}$: 225.16378, found: 225.16370.



GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

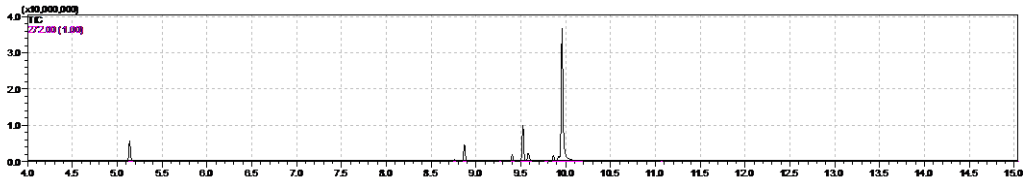


7-fluoro-2,3,4,9,10,10a-hexahydro-1H-4a,10-ethanophenanthrene (**2o**): colorless liquid, 50 mg, isolated yield: 73%.

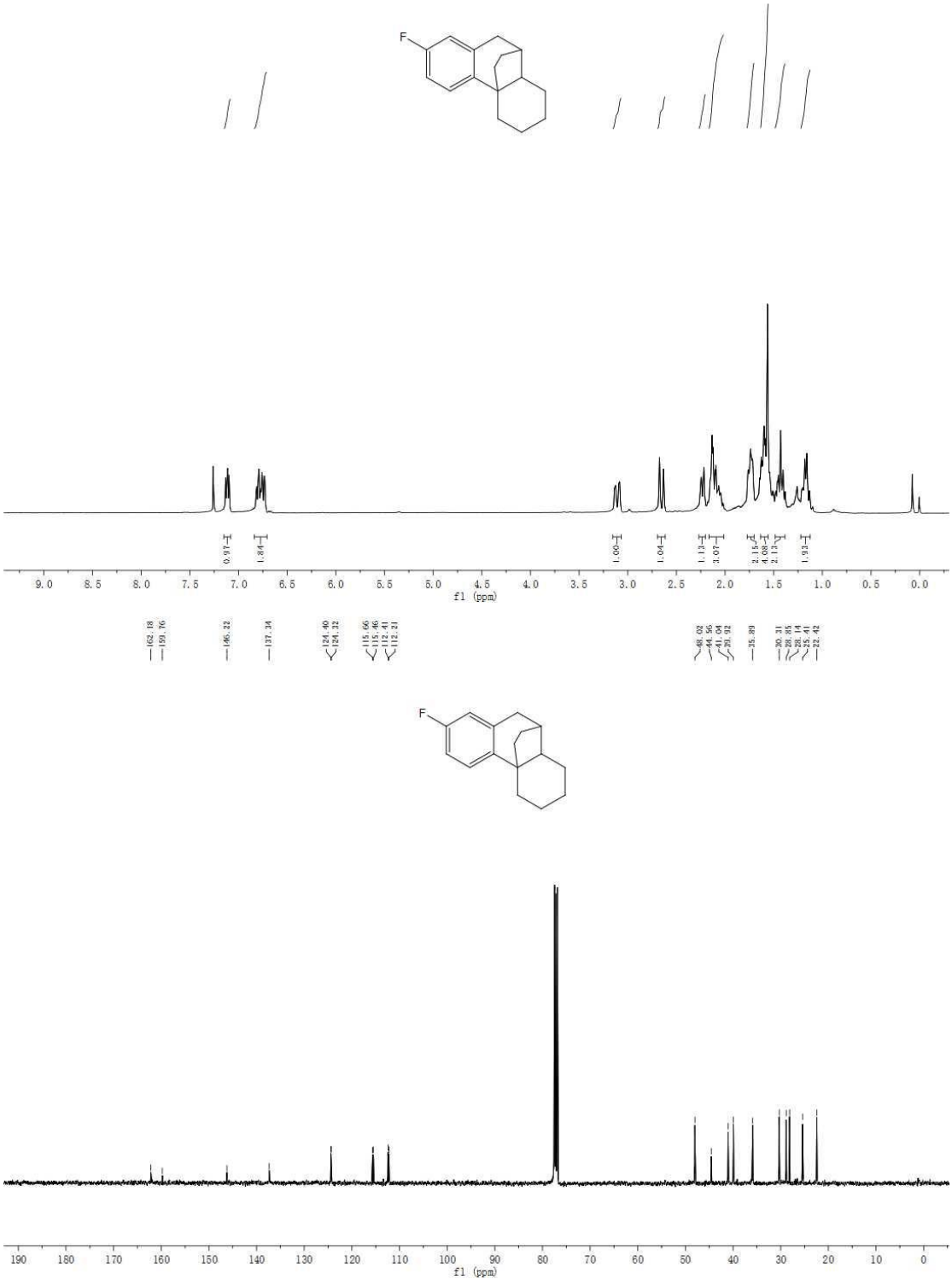
^{1}H NMR (400 MHz, CHLOROFORM-D) δ7.11 (dd, J = 8.1, 6.2 Hz, 1H), 6.84 - 6.71 (m, 2H), 3.10 (d, J = 16.8 Hz, 1H), 2.65 (d, J = 16.8 Hz, 1H), 2.23 (d, J = 11.4 Hz, 1H), 2.16 - 2.01 (m, 3H), 1.77 - 1.70 (m, 2H), 1.63 - 1.56 (m, 4H), 1.48 - 1.38 (m, 2H), 1.22 - 1.13 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ160.97 (d, J = 242.9 Hz), 146.22, 137.34, 124.36 (d, J = 7.9 Hz), 115.56 (d, J = 20.1 Hz), 112.31 (d, J = 20.7 Hz), 48.02, 44.56, 41.04, 39.92, 35.89, 30.31, 28.85, 28.14, 25.41, 22.42.

HRMS(APPI): cacud for $C_{16}H_{19}F^{+}$ $[M-H]^{+}$: 229.13871, found: 229.13873.



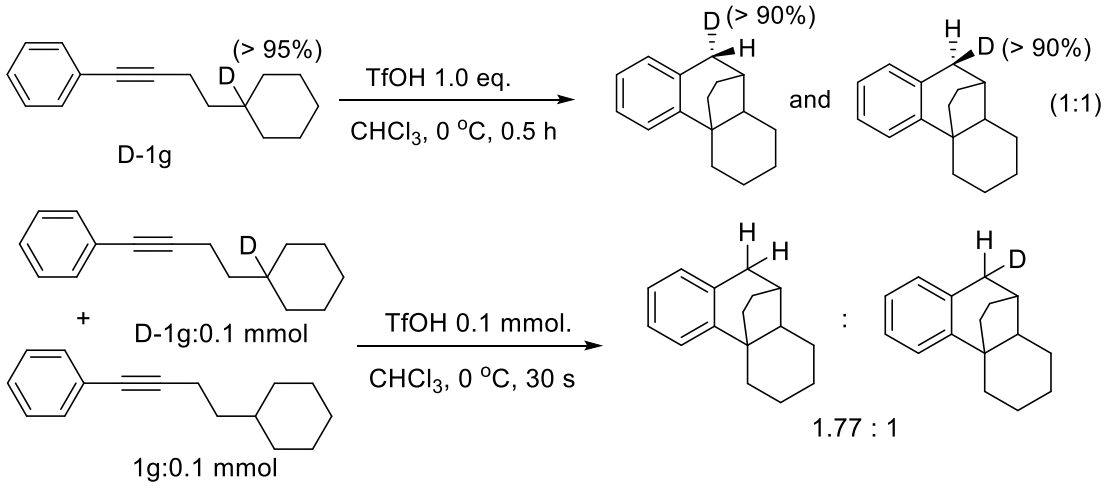
GC-MS spectra of the reaction mixture: the highest peak indicated the formation of the product



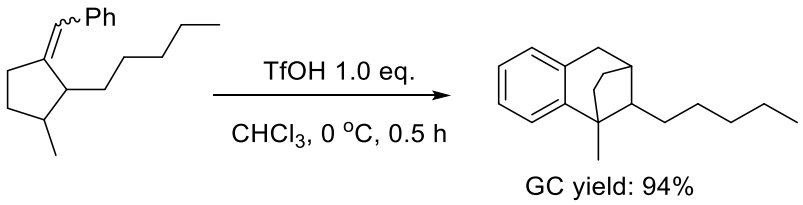
^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

3. Mechanistic study

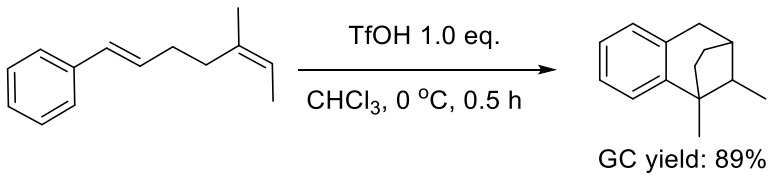
1)

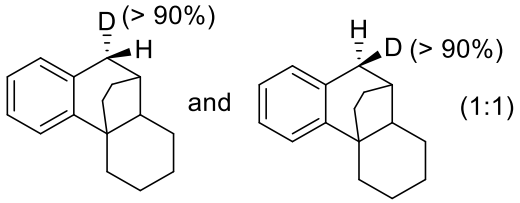


2)



3)

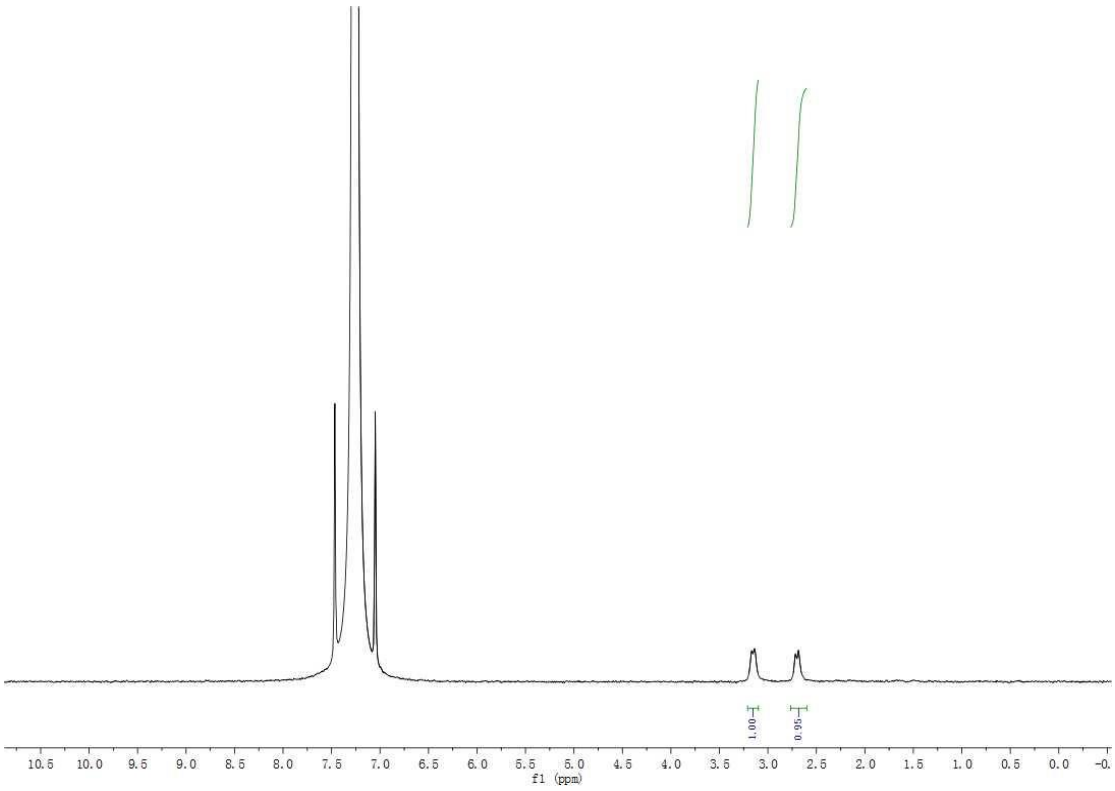




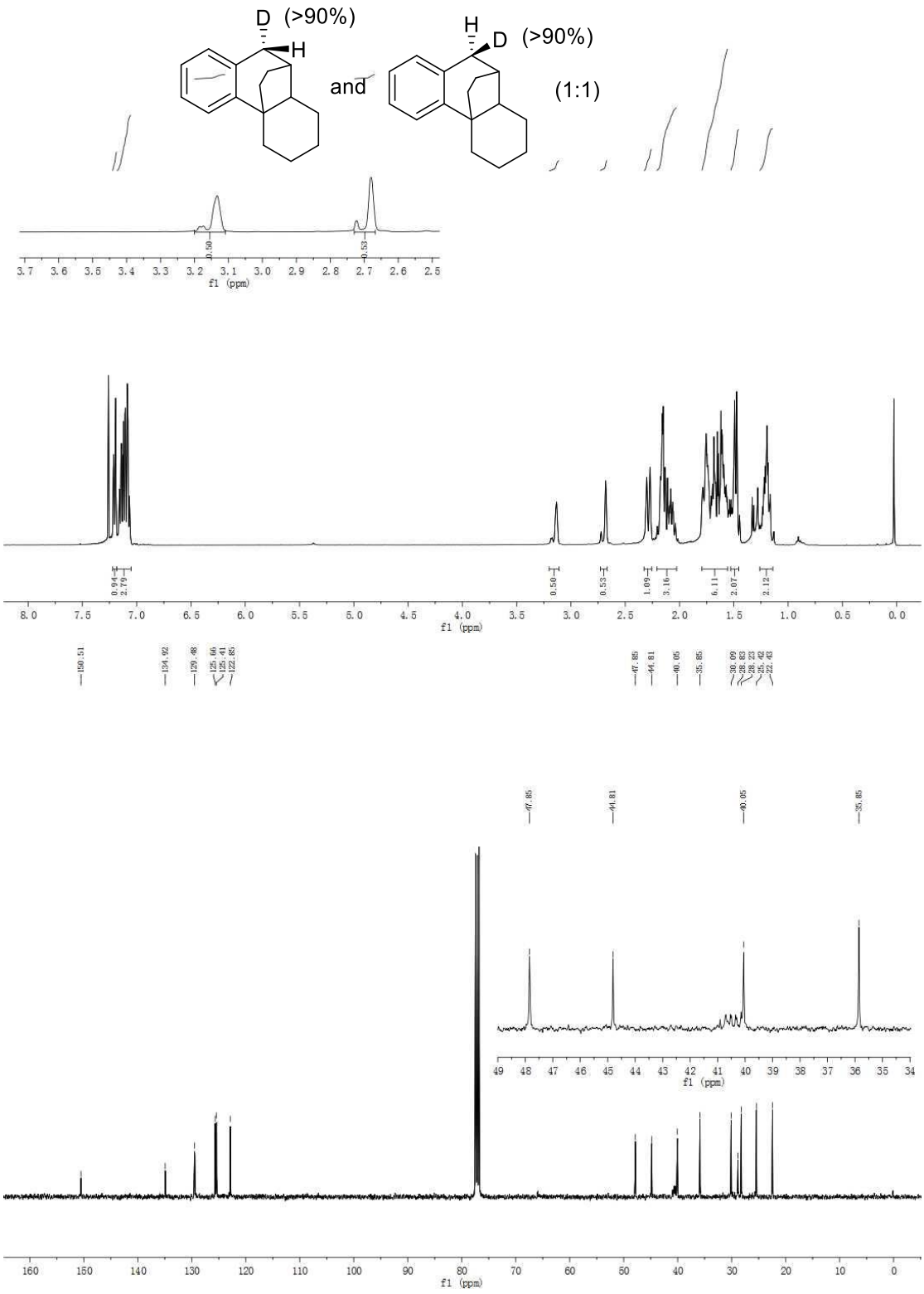
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.22 - 7.18 (m, 1H), 7.18 - 7.05 (m, 3H), 3.13 (s, 0.5 H), 2.68 (s, 0.5 H), 2.29 (d, J = 12.3 Hz, 1H), 2.21 - 2.03 (m, 3H), 1.79 - 1.56 (m, 6H), 1.53 - 1.45 (m, 2H), 1.26 - 1.14 (m, 2H).

^{2}H NMR (77 MHz, $CDCl_3$) δ 3.14 (d, J = 2.1 Hz, 1H), 2.69 (d, J = 2.5 Hz, 1H).

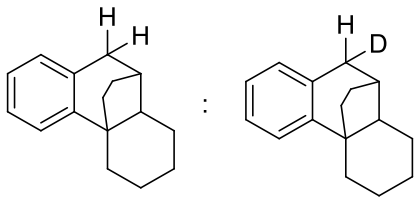
^{13}C NMR (101 MHz, CHLOROFORM-D) δ 150.51, 134.92, 129.48, 125.66, 125.41, 122.85, 47.85, 44.81, 40.05, 35.85, 30.09, 28.83, 28.23, 25.42, 22.43.



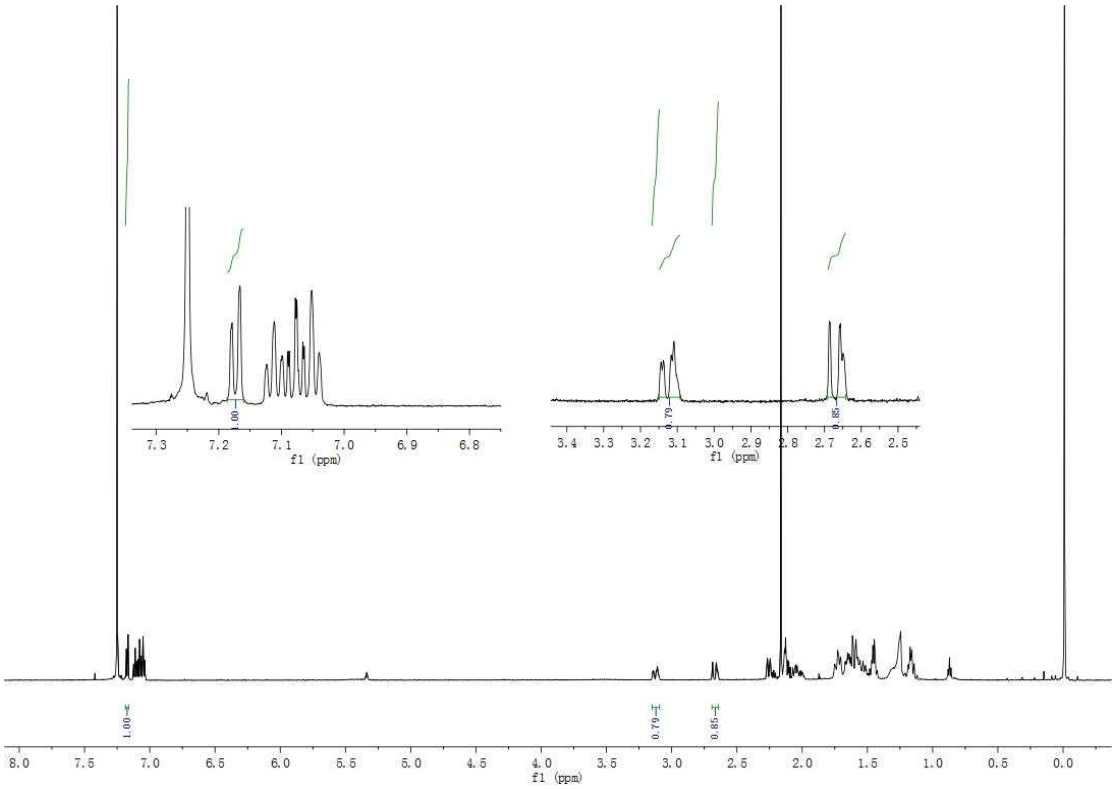
^{2}H NMR (77 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

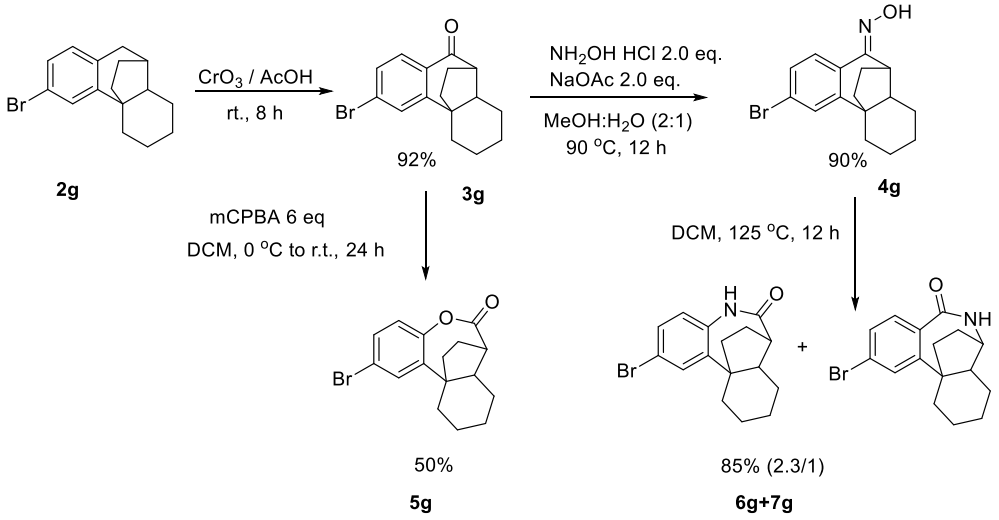


1.77 : 1



^{1}H NMR (600 MHz, $CDCl_3$)

4. Transformation of product 2g into functional compounds



Ketone 7g: To a magnetically stirred solution of 1 mmol of **2g** in 1 mL acetic acid was added dropwise 4 mL of 10% aqueous CrO_3 acetic acid solution (The chromic acid solution was prepared by dissolving 21 g (0.21 mol) of CrO_3 in 190 ml of acetic acid and 10 ml of water) over a period of 3 min. The reaction was maintained between 17 °C and 21 °C for 8 h and then quenched with water, extracted with EtOAc. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography (hexane/ EtOAc = 30/1) to give ketone **3g** as white solid (92%, 280 mg).[12]

GC-MS: m/z calced for $C_{16}H_{17}BrO$: 304, found: 304.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.8 Hz, 1H), 2.81 (d, *J* = 6.9 Hz, 1H), 2.36 - 2.29 (m, 3H), 1.96 (dd, *J* = 11.6, 5.0 Hz, 1H), 1.85 - 1.75 (m, 2H), 1.69 (dd, *J* = 12.9, 4.1 Hz, 1H), 1.61 - 1.53 (m, 3H), 1.42 - 1.35 (m 1H), 1.24 - 1.18 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 200.72, 157.40, 129.72, 129.63, 129.40, 129.14, 126.65, 55.95, 50.94, 47.51, 31.51, 29.66, 27.30, 24.85, 24.05, 21.89.

Ester 5g: To a solution of **3g** (152 mg, 0.5 mmol) in DCM (2 mL) was added m-CPBA (609 mg, 3 mmol, 85% purity) and heated at 40 °C for 48 h. The reaction was quenched with aqueous Na_2SO_4 and extracted with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (hexane) to give ester **5g** as white solid (80 mg, 50%).

GC-MS: m/z calced for $C_{16}H_{17}BrO_2$: 320, found: 320.

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.55 (d, *J* = 1.7 Hz, 1H), 7.28 (dd, *J* = 8.7, 1.7 Hz, 1H, 1H), 6.93 (dd, *J* = 8.7, 0.7 Hz, 1H), 2.93 (dd, *J* = 10.3, 5.4 Hz, 1H), 2.49 (d, *J* = 13.3 Hz, 1H), 2.45 - 2.39 (m, 1H), 2.29 (dd, *J* = 15.9, 6.5 Hz, 1H), 2.17 (dt, *J* = 14.1, 9.8 Hz, 1H), 1.85 - 1.74 (m, 4H), 1.65 (dd, *J* = 13.4, 4.3 Hz, 1H), 1.57 - 1.46 (m, 2H), 1.25 - 1.19 (m, 2H).

^{13}C NMR (101 MHz, CHLOROFORM-D) δ 172.27, 149.34, 138.91, 130.93, 130.59, 123.63, 118.13, 50.73, 50.11, 43.84, 36.65, 32.41, 30.21, 25.16, 24.21, 22.20.

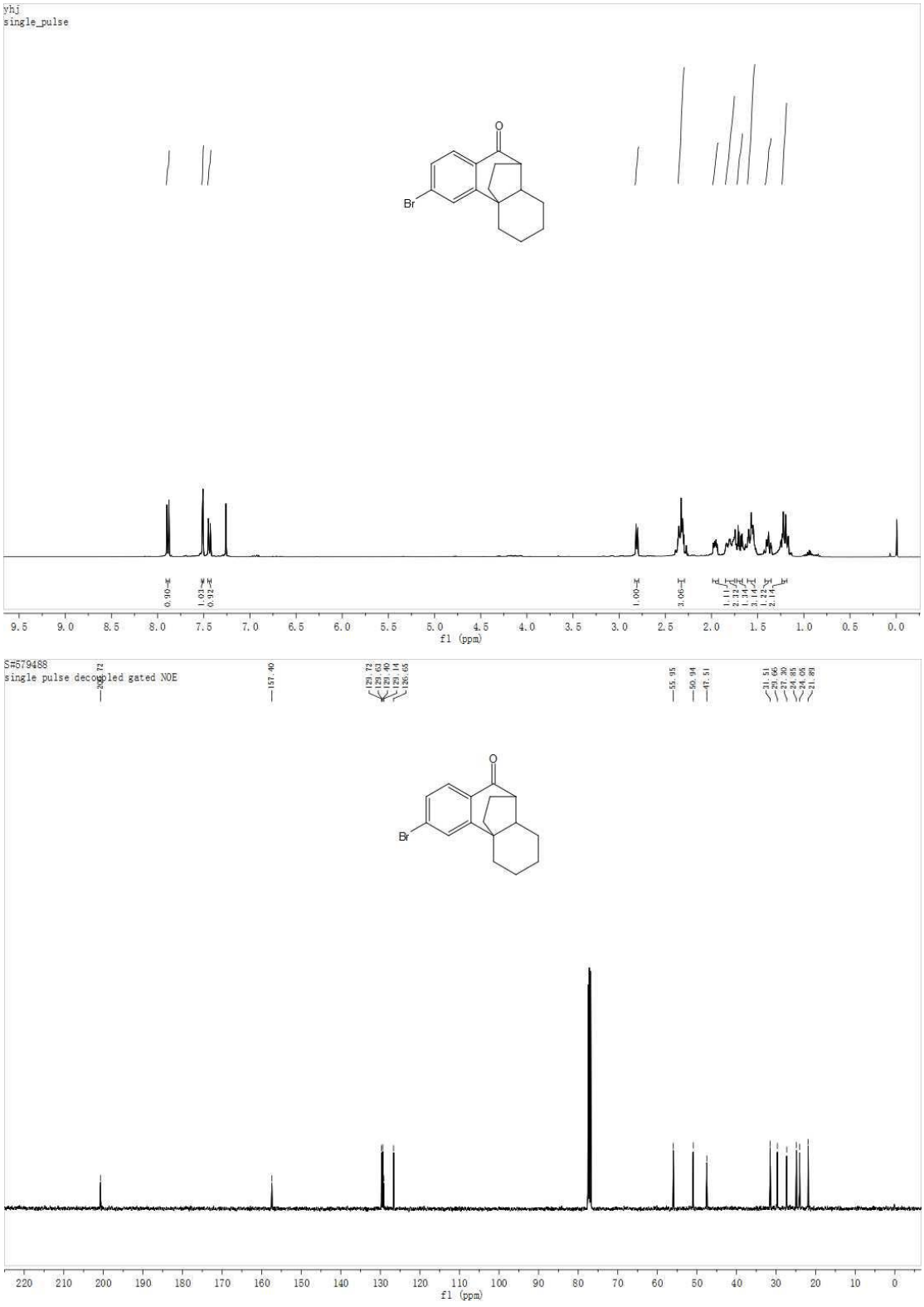
Lactam 6g and **7g**: The mixture of ketone **3g** (304 mg, 1 mmol), sodium acetate (164 mg, 2 mmol) and hydroxylamine hydrochloride (140 mg, 2 mmol) in MeOH /H_2O (2:1, 6 mL) was heated at 90 ºC for 12 h. then the reaction was allowed to cool to room temperature and was extracted with EtOAc. The combined organic layers were concentrated and purified by flash column chromatography (hexane/ EtOAc = 30/1) to give crude oxime **4g** as white solid (90%, 287mg).[13]

The oxime **4g** (0.5 mmol, 160 mg) dissolved in DCM (2 mL) was treated with PPA 1.5 g at N_2 atmosphere, and then the reaction mixture was heated to 125 ºC for 12 h. After the reaction was cooled to room temperature, ice water (5 mL) was added. The product was extracted with EtOAc and the combined organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (hexane/ EtOAc = 5/1) to give lactam **6g** and **7g** as white solid (85%, 2.3:1).[14]

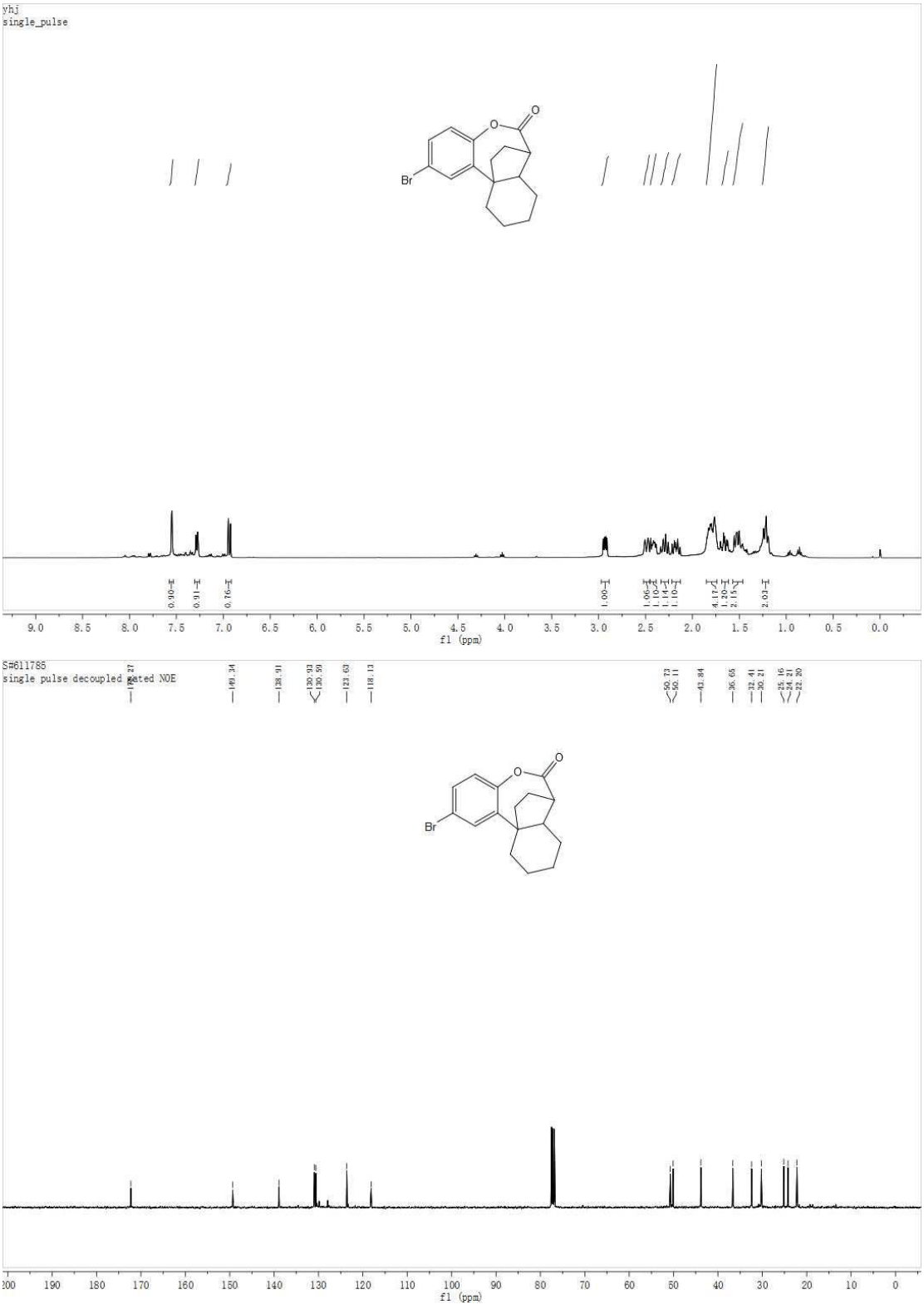
Lactam **6g**: GC-MS: m/z calced for $C_{16}H_{18}BrNO$: 319, found: 319. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.90 (s, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 2.75 - 2.68 (m, 1H), 2.48 (d, *J* = 13.2 Hz, 1H), 2.38 (dd, *J* = 11.7, 5.7 Hz, 1H), 2.34 - 2.25 (m, 1H), 2.15 (dt, *J* = 13.8, 9.8 Hz, 1H), 1.80 - 1.82 (m, 2H), 1.79 - 1.70 (m, 2H), 1.68 - 1.56 (m, 2H), 1.53 - 1.41 (m, 1H), 1.27 - 1.17 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 178.52, 139.88, 135.12, 131.10, 130.14, 122.38, 116.41, 51.93, 50.70, 43.70, 38.40, 33.45, 31.05, 25.75, 25.29, 22.65.

Lactam **7g**: GC-MS: m/z calced for $C_{16}H_{18}BrNO$: 319, found: 319. ^{1}H NMR (400

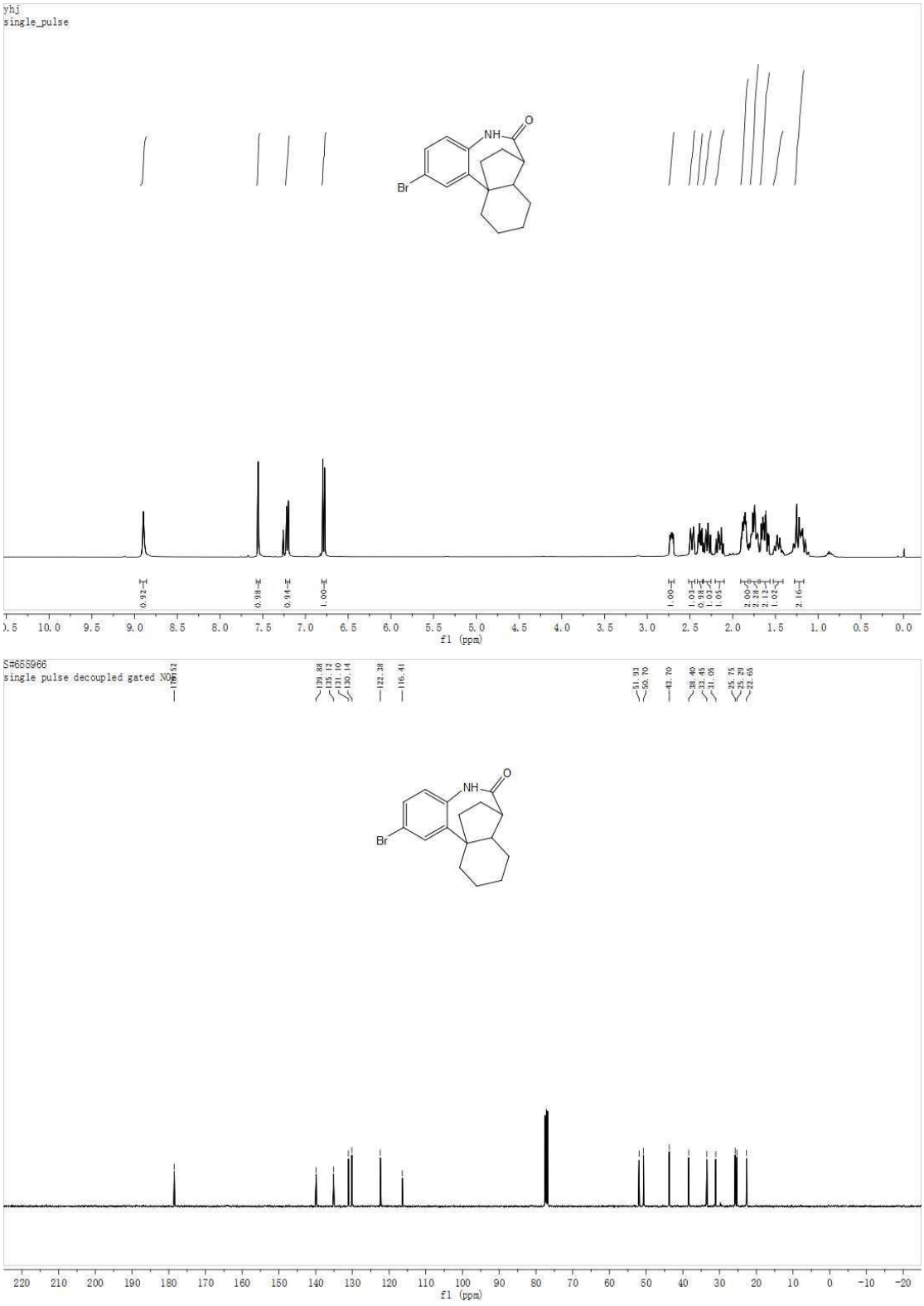
MHz, CHLOROFORM-D) δ 8.25 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 3.31 (td, *J* = 8.3, 2.6 Hz, 1H), 2.45 (d, *J* = 13.0 Hz, 1H), 2.32 – 2.15 (m, 4H), 1.88 - 1.81 (m, 1H), 1.73 (dt, *J* = 7.9, 5.1 Hz, 3H), 1.63 - 1.55 (m, 1H), 1.53 - 1.44 (m, 1H), 1.19 - 1.12 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 169.49, 153.34, 134.69, 131.06, 130.12, 129.25, 126.79, 58.05, 52.17, 51.37, 38.74, 33.20, 31.85, 29.40, 24.65, 22.44.



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)



^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

^{1}H NMR (400 MHz, $CDCl_3$) (up) and ^{13}C NMR (101 MHz, $CDCl_3$) (down)

5. Computational details

All DFT calculations were carried out with Gaussian 09 program[15] using B3LYP[16] hybrid functional. Geometries were fully optimized in gas phase using polarized double-ζ def2-SVP[17] basis set on all atoms, with Grimme's DFT-D3[18] empirical dispersion correction (with zero short range damping). Vibrational analyses were performed on all optimized geometries to verify the identities of minima, transition state. Larger polarized triple-ζ def2-TZVP[17] basis set was utilized in single point calculations to refine the calculated electronic energies of these optimized structures. The solvent effect was accounted for in these single point calculations with SMD continuum solvation model[19], employing experimentally used chloroform as the solvent. Thermal correction to Gibbs free energy was computed at 273.15 K for all the optimized geometries. Reported energies (in kcal/mol) are Gibbs free energies, including thermal free energy correction, solvent effect correction, and DFT-D3 empirical dispersion correction.

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7. Cartesian coordinates of DFT-optimized structures

A

C	-1.09013800	3.44560800	0.37694600
C	-0.16892700	3.09052700	-0.59292200
C	0.39424900	1.77168100	-0.58420300
C	0.00484200	0.83414500	0.42950900
C	-0.91676900	1.21119900	1.38913000
C	-1.46038000	2.51022600	1.36096700
H	-1.52890000	4.44529500	0.38128200
H	0.13779700	3.79595500	-1.36784100
H	0.44695300	-0.16428600	0.42907400
H	-1.22356500	0.50813800	2.16597800
H	-2.18845100	2.79946200	2.12383600
C	1.30648900	1.40764200	-1.54331200
C	2.07883000	1.04105700	-2.50988400
H	1.51360800	0.61472500	-3.35982400
C	3.58951500	1.07781200	-2.66807500
H	3.91367800	0.02270500	-2.69050200
H	3.78729300	1.47071600	-3.67885200
C	4.35230700	1.87952700	-1.61376000
H	5.42514500	1.79851900	-1.86035600
H	4.09403000	2.94742100	-1.71567200
C	4.13657400	1.43500400	-0.16174500
C	4.98479400	2.28435300	0.82338600
C	4.39401200	-0.07765300	0.03894200
C	6.30664900	1.58706300	1.16424100
H	5.16500200	3.28573600	0.39966300
C	4.72933800	-0.40050300	1.49831900
H	3.52277300	-0.66362000	-0.30087300
C	6.05882400	0.26403800	1.92183300
H	6.85892600	1.39079000	0.22881600
H	3.90404700	-0.03819400	2.13703500
H	6.04517600	0.44694900	3.00846000
H	5.23885100	-0.39416100	-0.59990300
H	4.77673900	-1.48976800	1.65167800
H	6.89831100	-0.42576300	1.73805600
H	6.94991500	2.25585200	1.75660200
H	4.41845700	2.44463300	1.75597200
H	3.07324800	1.62823500	0.08945000

TS_{A-B}

C	-0.76178200	3.35821400	0.74090700
C	0.18962200	3.08894000	-0.23101300
C	0.66134600	1.75303100	-0.40428900
C	0.16920200	0.70861400	0.43579100
C	-0.77916000	0.99871400	1.40380800
C	-1.24220600	2.31788000	1.55465000
H	-1.13699700	4.37472600	0.87503200
H	0.57965700	3.88190200	-0.87233400
H	0.54459500	-0.30790200	0.30154000
H	-1.16806300	0.20644200	2.04654100
H	-1.99058700	2.53867300	2.32025900
C	1.60133400	1.46762700	-1.38980300
C	2.16480700	1.13907600	-2.51336200
H	1.42810900	0.91855500	-3.30518000
C	3.62851100	0.98257800	-2.86802800
H	3.83185700	-0.10297800	-2.89081600
H	3.77456300	1.33878900	-3.89909900
C	4.54934300	1.71193300	-1.88692300
H	5.59189700	1.41125900	-2.08722700
H	4.48975800	2.79637900	-2.07530600
C	4.19408300	1.42702100	-0.43327800
C	4.85918700	2.37373200	0.59069000
C	4.34177200	-0.05509300	-0.03570100
C	6.06838000	1.69535200	1.25111400
H	5.14634100	3.31755900	0.10118400
C	4.39343700	-0.22656600	1.48548000
H	3.52724100	-0.65591600	-0.47251600
C	5.63727300	0.46901000	2.08369000
H	6.77859800	1.39278800	0.46283500
H	3.47273800	0.20398400	1.91885900
H	5.42130800	0.77299000	3.12047500
H	5.27496200	-0.44603200	-0.48005500
H	4.38248200	-1.29466200	1.75104200
H	6.47515000	-0.24379600	2.14195000
H	6.60574200	2.42118700	1.88050700
H	4.13398500	2.64227300	1.37815400
H	3.07989800	1.66712300	-0.37758200

B

C	-1.37522500	4.08405800	0.66410100

C	-0.37533900	3.75533700	-0.25117100
C	0.37460600	2.56799000	-0.11087600
C	0.08555000	1.71549800	0.97879400
C	-0.91257500	2.04394700	1.89040100
C	-1.64609700	3.22986900	1.73708800
H	-1.94656900	5.00649000	0.53916000
H	-0.17014600	4.42446800	-1.09131600
H	0.63963500	0.78342100	1.11042700
H	-1.12848300	1.37378700	2.72564300
H	-2.43035200	3.48296100	2.45435700
C	1.40870700	2.27458900	-1.09884300
C	2.24771200	1.21050100	-1.13781700
H	2.18918300	0.44556200	-0.35666400
C	3.24735200	0.99975000	-2.21604700
H	3.40887400	-0.06804800	-2.42336500
H	2.93173400	1.48164300	-3.15351900
C	4.71747400	1.66874000	-1.96419700
H	5.30267700	1.43996700	-2.86662800
H	4.56107900	2.75030400	-1.85671600
C	5.27659000	1.05838400	-0.77741500
C	5.02873200	1.66555600	0.53526400
C	5.98307600	-0.22909900	-0.81631000
C	5.47637600	0.82496400	1.72832800
H	5.43869000	2.69553200	0.52935000
C	5.51765800	-1.26297600	0.25764700
H	6.02223400	-0.65847500	-1.82750100
C	4.97413400	-0.61408800	1.54947700
H	6.57708900	0.84139800	1.80880400
H	4.74956500	-1.90270800	-0.20214600
H	3.87089000	-0.59148000	1.51897000
H	7.02641300	0.06772800	-0.56204300
H	6.37548300	-1.91525500	0.47473400
H	5.24342100	-1.22761900	2.42096800
H	5.09079100	1.26712600	2.65823800
H	3.92521000	1.86164200	0.54239100
H	1.49758200	3.01455800	-1.90518300

TS_{B-C}

C	-0.66904900	3.86386400	1.15997100
C	0.24758700	3.60266300	0.13907700
C	0.76413600	2.30684800	-0.05897600
C	0.32635700	1.27486300	0.79913000
C	-0.58840600	1.53535200	1.81676100
C	-1.08854700	2.83161200	2.00290000
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H	0.56501600	4.41463200	-0.52161700
H	0.68950700	0.25353000	0.66174300
H	-0.92245300	0.72340400	2.46708600
H	-1.80817700	3.03147200	2.80015900
C	1.74223700	2.09240600	-1.13297300
C	2.37868500	0.94658700	-1.45406800
H	2.15160700	0.03402900	-0.89459500
C	3.43648000	0.83859300	-2.52074200
H	3.68768600	-0.21690000	-2.70297500
H	3.07835400	1.24408100	-3.48139000
C	4.75022300	1.62759100	-2.18655500
H	5.52874100	1.38902600	-2.92576800
H	4.54254100	2.70714800	-2.23836600
C	5.18677500	1.24915500	-0.80190500
C	4.68605400	1.94711600	0.31544100
C	5.79728600	-0.10180200	-0.49808100
C	4.78685800	1.32459900	1.66979400
H	5.90616500	2.18487000	-0.29482100
C	4.85096900	-0.93777900	0.40722800
H	6.02892500	-0.63139800	-1.43210100
C	4.25828800	-0.13480500	1.59211300
H	5.84076200	1.31780100	1.99918700
H	4.03847300	-1.33896800	-0.21586500
H	3.16292000	-0.08492600	1.50722900
H	6.75735100	0.04320700	0.02360300
H	5.41950400	-1.80737500	0.76653700
H	4.47630800	-0.62481800	2.55165500
H	4.23278000	1.92280800	2.40552500
H	4.16535000	2.89695900	0.15300300
H	1.97532600	2.98867900	-1.72432200

C

C	-0.80953900	3.99759100	1.02605400
C	0.21789500	3.74773400	0.13067800
C	0.89957500	2.49100800	0.14172200
C	0.50011000	1.49518000	1.08706500
C	-0.52448600	1.75800900	1.97991600
C	-1.17776300	3.00469100	1.94926300
H	-1.33043100	4.95693300	1.01651800

H	0.51709200	4.51194500	-0.59127300
H	0.99671700	0.52428200	1.10101600
H	-0.83265600	0.99992300	2.70256200
H	-1.98975600	3.20147800	2.65441200
C	1.94652700	2.28460200	-0.77740200
C	2.84878200	1.15757500	-0.86689800
H	2.43354500	0.25628700	-0.40231800
C	3.43468500	0.87932200	-2.27642100
H	3.48093300	-0.20965500	-2.41871400
H	2.79208300	1.26939200	-3.08104200
C	4.83845700	1.50123600	-2.27973200
H	5.50738700	1.02908500	-3.01463200
H	4.77260600	2.56804900	-2.55472500
C	5.35411700	1.38760400	-0.83790400
C	4.10383800	1.67278800	0.04417300
C	6.01165600	0.03935000	-0.44799800
C	4.13979300	1.00678800	1.41574900
H	6.09070500	2.18532600	-0.65359800
C	5.03043400	-1.01265000	0.08481100
H	6.56750500	-0.35746400	-1.31227500
C	4.28511000	-0.52883100	1.35074100
H	5.00586000	1.44557300	1.94015300
H	4.30897200	-1.27891200	-0.70410700
H	3.29595700	-1.01474300	1.40442500
H	6.76486400	0.23627600	0.33307400
H	5.57189400	-1.94494300	0.30551500
H	4.81865700	-0.86073300	2.25507800
H	3.26199500	1.29643100	2.01838800
H	4.02430600	2.76463300	0.18167100
H	2.15687500	3.11736200	-1.46272000

C'

C	-1.13933000	3.84015300	1.29554300
C	-0.56492500	3.22773100	0.19608900
C	0.66686500	2.49767800	0.31816300
C	1.27457800	2.39708300	1.61399200
C	0.68440900	3.00633600	2.70630000
C	-0.51346800	3.72981700	2.54916800
H	-2.07089200	4.40014300	1.19431000
H	-1.04304100	3.30310900	-0.78388900
H	2.18887800	1.82544700	1.74624200
H	1.14352200	2.92391600	3.69333900
H	-0.96847400	4.20848800	3.42071800
C	1.18264000	1.92893800	-0.85604900
C	2.39933500	1.18691500	-1.18321800
H	1.98095400	0.17787600	-1.42495400
C	3.01969800	1.66257400	-2.54648000
H	2.35924400	1.45911100	-3.40256800
H	3.20205600	2.74901100	-2.50387900
C	4.33925700	0.89279300	-2.56839400
H	4.14219200	-0.16269700	-2.82510400
H	5.04642200	1.28728400	-3.31258300
C	4.86629300	0.99802600	-1.12784100
C	3.58932700	1.00481600	-0.21203000
C	5.88353900	-0.07211400	-0.71388600
C	3.50326700	-0.26665000	0.64288900
H	5.34955600	1.98367400	-1.01646600
C	6.06066800	-0.08438300	0.80975200
H	5.55085600	-1.06521600	-1.06250600
C	4.73734000	-0.42166200	1.54826200
H	2.57866700	-0.28328400	1.24559000
H	6.84868700	-0.79674800	1.09608900
H	4.76039400	-1.45195800	1.93620200
H	6.84587100	0.11902000	-1.21425400
H	6.42285900	0.90963700	1.12399900
H	4.62762500	0.23095900	2.43098300
H	3.42433600	-1.13415900	-0.03406100
H	3.65787000	1.88143900	0.45113300
H	0.53237700	2.05992800	-1.73253700

$TS_{C'-D}$

C	-1.30116500	3.23903900	1.45111300
C	-0.61559300	2.86414000	0.29875800
C	0.77365300	2.60362300	0.34030100
C	1.46220400	2.74707200	1.56597900
C	0.77288300	3.13244600	2.71182100
C	-0.60737500	3.37165900	2.65924500
H	-2.37451300	3.43451700	1.40836600
H	-1.15806900	2.77192400	-0.64604300
H	2.53608500	2.58224600	1.62672200
H	1.31259900	3.25203000	3.65348400
H	-1.14167100	3.67009100	3.56434800
C	1.41084300	2.24704200	-0.92715600
C	2.69315800	1.73152600	-1.23387500

H	1.60420600	0.95656900	-1.11176900
C	3.20351300	1.66247300	-2.65710500
H	2.42024200	1.46041700	-3.40337800
H	3.59514800	2.67537400	-2.87236400
C	4.35249500	0.65172300	-2.59217500
H	3.95289600	-0.37609000	-2.63837000
H	5.06309000	0.76242800	-3.42287000
C	4.98892100	0.91509800	-1.21616400
C	3.77699800	1.26051300	-0.28570200
C	5.85232800	-0.22613600	-0.65292200
C	3.37809300	0.03142900	0.56395300
H	5.61271000	1.82245000	-1.28999100
C	5.91883100	-0.14228500	0.87660100
H	5.43007800	-1.20166700	-0.95050300
C	4.52654300	-0.35956800	1.51446000
H	2.45357800	0.21857200	1.13182700
H	6.63618400	-0.87476100	1.27500200
H	4.39295200	-1.41507300	1.79875400
H	6.85927100	-0.18074300	-1.09454500
H	6.31143100	0.85051600	1.15762900
H	4.44720200	0.22240000	2.44711600
H	3.15762500	-0.79876700	-0.12794500
H	4.03237400	2.08815000	0.39610200
H	0.81364100	2.48410700	-1.81771800

D

C	-2.29213100	1.80929000	2.24713400
C	-2.00691600	0.73790200	1.40349000
C	-1.86258000	0.95086000	0.01971100
C	-1.96722400	2.25336500	-0.50073400
C	-2.25231600	3.32346100	0.34836400
C	-2.41110300	3.10344800	1.72116800
H	-2.42861900	1.63743200	3.31697800
H	-1.92279900	-0.27153400	1.81506700
H	-1.85626600	2.42901900	-1.57377200
H	-2.35399900	4.33018600	-0.06238200
H	-2.62897400	3.94267600	2.38572400
C	-1.60095400	-0.24932400	-0.91933900
C	-0.14298900	-0.16691900	-0.87654500
H	-2.00470100	-1.17549100	-0.49260600
C	0.67488900	0.59490600	-1.83583500
H	0.77235300	-0.13958600	-2.67218800
H	0.18075300	1.47068200	-2.27860800
C	2.03388800	0.79694900	-1.14977600
H	2.85275800	0.93675100	-1.86888000
H	1.98672400	1.69857500	-0.51855600
C	2.19725600	-0.47165800	-0.28606500
C	0.73147500	-0.84744300	0.11402500
C	2.86218000	-1.64843600	-1.01366700
C	0.46424400	-2.37880200	0.22036300
H	2.78219000	-0.24851100	0.61859400
C	2.94217900	-2.90192500	-0.11927400
H	2.29272500	-1.88059900	-1.93179600
C	1.71037900	-3.05374200	0.80436400
H	-0.42173700	-2.56593000	0.84575400
H	3.04917000	-3.79139800	-0.75937600
H	1.49665600	-4.11705400	0.99106600
H	3.86729600	-1.35401100	-1.35201300
H	3.85245700	-2.85932600	0.49896000
H	1.91431400	-2.60440000	1.79102900
H	0.24545200	-2.79532900	-0.77715300
H	0.49847900	-0.39927300	1.09715300
H	-2.01674200	-0.06189100	-1.91792200

$TS_{D\text{-}E}$

C	-0.52783900	1.91858900	2.07597300
C	-0.06824900	1.53277200	0.81263700
C	0.77536200	2.37575600	0.07806700
C	1.13849900	3.62022200	0.61756100
C	0.68735900	4.00314400	1.88359200
C	-0.14460300	3.14941000	2.61672200
H	-1.18937600	1.25531100	2.63789100
H	-0.37176200	0.56731200	0.39771200
H	1.76403400	4.30990100	0.03985700
H	0.97379800	4.97470200	2.29282800
H	-0.50312400	3.44980200	3.60381600
C	1.31766200	1.96308600	-1.27552800
C	2.80009400	1.71558400	-1.34244200
H	0.85723400	1.01379100	-1.60821200
C	3.56472700	1.76796800	-2.64098100
H	3.18701200	0.90537100	-3.22227200
H	3.33682600	2.66373700	-3.23721500
C	5.04824200	1.60755400	-2.25044100
H	5.61449800	1.01307300	-2.98004300

H	5.52629000	2.59849300	-2.20142000
C	5.03210700	0.96128100	-0.84745800
C	3.64402600	1.25002500	-0.30751300
C	5.18412300	-0.57817900	-0.80232800
C	3.27142200	0.72355600	1.05861400
H	5.79823000	1.40045200	-0.19151400
C	4.92019800	-1.16424300	0.61640100
H	4.49287600	-1.02161300	-1.53912500
C	4.43084600	-0.11032500	1.62588100
H	2.98794700	1.54709700	1.73273100
H	4.16854200	-1.96653700	0.54435400
H	4.09825100	-0.59740300	2.55430800
H	6.19787400	-0.82210700	-1.15259600
H	5.83236000	-1.63773400	1.00784100
H	5.25797200	0.55850300	1.91399100
H	2.36123600	0.11266000	0.94996300
H	3.45666200	2.52833200	-0.45605200
H	1.05977700	2.70432100	-2.04989800

E

C	-2.85154600	-0.24362700	1.89887000
C	-2.15765700	-0.38594000	0.69228400
C	-1.67270200	0.74211800	0.00334900
C	-1.89667700	2.01717900	0.55416600
C	-2.58370800	2.15944900	1.75976600
C	-3.06165800	1.02876400	2.43593200
H	-3.23184200	-1.12795300	2.41517200
H	-2.00724000	-1.38435600	0.27017500
H	-1.54144100	2.90847900	0.02824400
H	-2.75678200	3.15601900	2.17245000
H	-3.60326400	1.14343100	3.37762600
C	-0.92462700	0.58934400	-1.28812700
C	0.62052400	1.03618100	-1.25248400
H	-0.99852700	-0.43990700	-1.66816700
C	1.26886600	0.88793800	-2.65062100
H	0.58491200	1.17644100	-3.46076500
H	2.15018600	1.54662200	-2.71422700
C	1.69858600	-0.58895500	-2.70528300
H	0.85938800	-1.24245800	-2.99398700
H	2.51670500	-0.78165000	-3.41206300
C	2.09203800	-0.88899800	-1.24558600
C	1.32144200	0.05076200	-0.42375200
C	2.22340200	-2.34256000	-0.73254300
C	1.28346200	-0.06335700	1.02593700
H	3.08447700	-0.38595700	-1.06690300
C	1.76958000	-2.50205200	0.73170900
H	1.62085700	-2.98771100	-1.39093000
C	2.07198500	-1.25495100	1.57473500
H	1.51528900	0.91258600	1.49307600
H	0.67993000	-2.68204700	0.76241000
H	1.80448400	-1.41619600	2.62874200
H	3.26664100	-2.66839100	-0.85480000
H	2.24143600	-3.39165000	1.17267900
H	3.15307800	-1.03130700	1.55579500
H	0.18754300	-0.15711200	1.24559100
H	0.63552800	2.05061200	-0.82860700
H	-1.34550600	1.24803800	-2.06386200

$TS_{E\text{-}F}$

C	-3.03209100	-0.15541300	1.75491000
C	-2.38774100	-0.26007300	0.51724800
C	-1.72939000	0.84450500	-0.04522000
C	-1.74151400	2.06298400	0.65283400
C	-2.38186900	2.16998700	1.88982800
C	-3.02549700	1.05902100	2.44663600
H	-3.54604900	-1.02315000	2.17531400
H	-2.40449500	-1.21283100	-0.02092400
H	-1.25546400	2.94396400	0.22276300
H	-2.38676500	3.12648000	2.41795200
H	-3.52995000	1.14399100	3.41183800
C	-1.00063500	0.72095400	-1.36452700
C	0.53243200	0.98157400	-1.30881900
H	-1.18402300	-0.27473400	-1.80142800
C	1.21138300	0.76944800	-2.68731700
H	0.55170600	1.03049800	-3.52495200
H	2.10829400	1.40596500	-2.76807600
C	1.63328100	-0.71573500	-2.70067600
H	0.82089900	-1.37555400	-3.05857700
H	2.51668900	-0.94671600	-3.31417500
C	1.81379000	-1.05541300	-1.24806500
C	1.22933800	-0.05358200	-0.43492100
C	2.41155400	-2.31373600	-0.69876100
C	1.14380100	-0.19254100	1.05701900
H	2.47478800	0.04025200	-0.73526200

C	2.04182400	-2.54655300	0.77690200
H	2.06909700	-3.13803500	-1.34772400
C	2.11953100	-1.24993200	1.59413900
H	1.27741000	0.79083800	1.53317000
H	1.01518400	-2.94742600	0.83106900
H	1.89258800	-1.44874500	2.65123200
H	3.50554800	-2.27722400	-0.85185600
H	2.70138400	-3.31646800	1.20192300
H	3.15092700	-0.85236000	1.57039700
H	0.09718100	-0.47400500	1.26840200
H	0.70102100	1.99420300	-0.91492800
H	-1.40220400	1.45279200	-2.08496900

F

C	0.80298900	3.74342900	2.17228700
C	1.21362600	3.57896800	0.84446500
C	0.77643800	2.48021200	0.08915800
C	-0.09792000	1.55748300	0.68513700
C	-0.51036300	1.71868000	2.01002000
C	-0.05553300	2.80979700	2.75979900
H	1.14779500	4.60766500	2.74521100
H	1.87679700	4.32060500	0.38856100
H	-0.46394100	0.70437700	0.10566400
H	-1.19515100	0.99484100	2.45852100
H	-0.38105700	2.93812800	3.79468600
C	1.29641700	2.25151800	-1.31142500
C	2.30139800	1.09095500	-1.41394600
H	1.78422700	0.14964200	-1.15348800
C	2.93560200	0.94598600	-2.81371000
H	2.28429200	0.43512900	-3.53511000
H	3.17487400	1.93874500	-3.23025000
C	4.24140100	0.18285300	-2.54501100
H	4.03014600	-0.91101100	-2.41794900
H	5.05678600	0.22096500	-3.28641200
C	4.63330400	0.53056400	-1.18074300
C	3.53499800	1.19643700	-0.47085900
C	5.91952800	0.23669900	-0.54879900
C	3.43064600	0.77979300	1.01931500
H	3.88308300	2.26249000	-0.49109800
C	5.78065900	-0.17203400	0.94194000
H	6.52147500	-0.46061100	-1.15151400
C	4.80689500	0.74243200	1.68806900
H	2.75086200	1.47014100	1.53329200
H	5.42579500	-1.21548700	0.97887500
H	4.69955200	0.39468300	2.72718700
H	6.45017200	1.21589700	-0.59764500
H	6.77961900	-0.16149700	1.40083200
H	5.22149900	1.76457100	1.74733300
H	2.95678200	-0.21578100	1.05237400
H	1.77996100	3.17087000	-1.68298900
H	0.46317100	2.03687600	-2.00096100

B_{TfO}

C	-1.51175500	3.75567300	0.62627500
C	-0.44215100	3.63088700	-0.26323900
C	0.49137000	2.58319600	-0.14217700
C	0.31573300	1.66439600	0.91377000
C	-0.75126000	1.78719700	1.80193100
C	-1.67251200	2.83315000	1.66328000
H	-2.22172400	4.57847100	0.50902300
H	-0.32340000	4.35845100	-1.07121400
H	1.02617600	0.84550600	1.04824600
H	-0.86524100	1.06338900	2.61323900
H	-2.50710400	2.92806500	2.36238700
C	1.60116200	2.49907600	-1.10525800
C	2.52917800	1.53111500	-1.19659600
H	2.47645600	0.67868100	-0.51179900
C	3.67096400	1.54377900	-2.17952600
H	3.91886300	0.51157100	-2.47690900
H	3.34038900	2.05363700	-3.09953900
C	4.95195600	2.27986300	-1.72295900
H	5.63877900	2.32764600	-2.58435800
H	4.69004300	3.31498000	-1.46127800
C	5.75812100	1.66976900	-0.56458600
C	5.14437700	1.89208300	0.82606700
C	6.12616700	0.18432400	-0.78348000
C	5.75089500	0.94647400	1.86424200
H	5.26069400	2.94637500	1.10649500
C	5.23769000	-0.76177500	0.03144300
H	6.09758300	-0.05476800	-1.85762600
C	5.40502100	-0.52533600	1.54897200
H	6.84358200	1.08623100	1.86790000
H	4.18527900	-0.61820700	-0.25946000
H	4.47666100	-0.81766400	2.06718400

H	7.17166400	0.05222500	-0.46650800
H	5.47755800	-1.80514900	-0.22646500
H	6.19764800	-1.18047700	1.94621800
H	5.40811900	1.21972700	2.87404500
H	4.05983500	1.72538500	0.75286100
H	1.66153900	3.33442800	-1.81468000
S	7.45334000	3.88029300	-0.48219400
O	7.12260200	2.31353100	-0.60295400
O	8.44651800	4.20645600	-1.48609200
O	6.26143800	4.69354100	-0.27344300
C	8.36622700	3.83583700	1.16106300
F	7.51004400	3.57780700	2.14903200
F	9.30425800	2.89837000	1.14161100
F	8.92404500	5.02168100	1.36426300

$TS_{B\text{-}B'}$

C	-1.99583100	3.06075800	0.43520100
C	-0.94961700	3.01839900	-0.48924900
C	0.23807100	2.31329500	-0.21540200
C	0.34448900	1.65715700	1.02876900
C	-0.69816900	1.69900000	1.95232300
C	-1.87530400	2.39994200	1.66026400
H	-2.90811000	3.61367600	0.19744300
H	-1.05220300	3.53923500	-1.44548900
H	1.25738500	1.11361200	1.28278100
H	-0.59251200	1.18474400	2.91104300
H	-2.69059700	2.43238400	2.38715900
C	1.30886500	2.29662000	-1.22527200
C	2.44806400	1.58492100	-1.18867900
H	2.64050000	0.92897500	-0.33310000
C	3.52504900	1.63638100	-2.23166600
H	3.82287900	0.61208500	-2.51694700
H	3.15410200	2.12587000	-3.14585800
C	4.80229200	2.41690100	-1.78410200
H	5.55879200	2.35891200	-2.57998100
H	4.54704600	3.47418400	-1.62071000
C	5.37369200	1.83517200	-0.54451200
C	5.15001700	2.42923800	0.72822600
C	6.01950100	0.49899500	-0.55078400
C	5.39781800	1.52438500	1.93351600
H	5.99206000	3.27640900	0.71747400
C	5.24391000	-0.49631800	0.36509400
H	6.14355700	0.10696300	-1.56949500
C	4.77195500	0.13863000	1.69768000
H	6.48247000	1.42444800	2.09479600
H	4.38369000	-0.89836900	-0.19262200
H	3.67474200	0.25292600	1.68876800
H	7.02837600	0.64696000	-0.13692900
H	5.91394700	-1.34871400	0.55283200
H	5.00378800	-0.52840800	2.54220600
H	4.99152800	1.99187700	2.84227100
H	4.24371800	3.05706100	0.75333300
H	1.13448600	2.93978700	-2.09717500
S	8.15877600	3.84365100	-0.30350800
O	7.54575500	2.87098800	-1.25099600
O	8.95997000	4.91939500	-0.86898800
O	7.17803100	4.25786200	0.76453400
C	9.36856400	2.78321300	0.65843900
F	8.72784600	1.70580600	1.17029700
F	10.34063300	2.34043300	-0.13390900
F	9.90303600	3.46074200	1.66800400

B'_{TfOH}

C	-2.37957500	2.76997700	0.11194300
C	-1.25209600	2.87206300	-0.70626600
C	-0.01895700	2.30709900	-0.32698900
C	0.04520700	1.64246000	0.91568100
C	-1.07885800	1.53981600	1.73342200
C	-2.29907300	2.10136700	1.33618800
H	-3.32485000	3.21572900	-0.20854100
H	-1.32482900	3.39732200	-1.66295100
H	0.98962500	1.20819000	1.25149500
H	-1.00373100	1.02081300	2.69272500
H	-3.17827300	2.02033500	1.98025700
C	1.13681900	2.43649800	-1.23036400
C	2.33718600	1.84649900	-1.10354500
H	2.52593000	1.18834700	-0.24789400
C	3.49266600	2.03339000	-2.04188200
H	3.80985500	1.04980100	-2.43437100
H	3.18495300	2.63163500	-2.91495800
C	4.71214700	2.71741400	-1.37631400
H	5.52296600	2.80305900	-2.11953100
H	4.42981000	3.73912700	-1.07329800
C	5.23322900	1.95848300	-0.18374700

C	5.14386400	2.40422000	1.08872100
C	5.84736600	0.58934300	-0.37696700
C	5.62675000	1.51998100	2.21066300
H	6.71461700	3.35727300	0.29228100
C	5.23150100	-0.44874100	0.58919100
H	5.75516700	0.25492700	-1.42057300
C	5.07454300	0.08567300	2.03818300
H	6.73158700	1.48242100	2.20239700
H	4.24556800	-0.74677300	0.19757500
H	4.00727600	0.09772800	2.31255700
H	6.93006900	0.66811500	-0.18818700
H	5.85366700	-1.35747000	0.57404200
H	5.57123300	-0.58441500	2.75770500
H	5.33976300	1.92802800	3.19135500
H	4.66541000	3.36449100	1.31307100
H	0.97279300	3.08363800	-2.10144200
S	8.56502800	3.51037700	-0.84863000
O	8.00939000	2.50873700	-1.74989100
O	9.32019500	4.65501300	-1.30759200
O	7.44938500	4.03038300	0.17369700
C	9.66316600	2.57517300	0.35363500
F	8.93473200	1.64196200	0.98085200
F	10.63999000	1.98406000	-0.31817200
F	10.17164800	3.40307100	1.25185900

five-five-ring

C	0.70366200	3.41357500	2.42438500
C	1.16613900	3.43432000	1.10270000
C	0.85964000	2.38655400	0.22087600
C	0.06915800	1.32198500	0.68433200
C	-0.38778100	1.29535400	2.00458800
C	-0.06719600	2.34073500	2.87956000
H	0.94341600	4.24083600	3.09656300
H	1.76588000	4.28003000	0.75327600
H	-0.20678300	0.50939800	0.00406400
H	-1.00581900	0.46316600	2.34999600
H	-0.42847900	2.32259400	3.91026700
C	1.42122600	2.36465600	-1.18249500
C	2.45655400	1.23750900	-1.40337700
H	1.92924700	0.26615600	-1.20469800
C	3.14157000	1.10196200	-2.78879600
H	2.45415300	0.72321000	-3.55709600
H	3.48466500	2.09799300	-3.11701200
C	4.34644900	0.17437700	-2.51909400
H	4.03247700	-0.88255400	-2.48699900
H	5.14803300	0.26457300	-3.26337800
C	4.77597100	0.61437500	-1.10573800
C	3.54761100	1.04841700	-0.44785500
H	5.27850400	1.61691400	-1.20756600
H	1.90883900	3.32214200	-1.42311400
H	0.62436500	2.21951600	-1.92864800
C	5.53862200	-0.18234300	-0.02970400
C	5.12431400	0.54738800	1.27258300
C	3.66779900	1.00880600	1.00877300
H	6.62404300	-0.20173800	-0.19239300
H	5.17944100	-1.22518400	-0.03460500
H	5.21079700	-0.08188900	2.16817200
H	5.76409800	1.43025200	1.43263600
H	2.90180400	0.27901500	1.35170600
H	3.31907000	1.94466000	1.48668100

five-five-ring-ts

C	0.76697100	3.45870400	2.40221800
C	1.25814900	3.42405900	1.09257500
C	0.88737300	2.39442800	0.21431000
C	0.00156800	1.40498000	0.67136000
C	-0.48900400	1.43544600	1.97948300
C	-0.10316000	2.46063300	2.85031500
H	1.05938500	4.27178000	3.07104400
H	1.93285600	4.21362100	0.74795000
H	-0.32137600	0.60681800	-0.00445000
H	-1.18305300	0.66238400	2.31797900
H	-0.49015100	2.48749500	3.87153000
C	1.46879100	2.32278800	-1.18163500
C	2.37687800	1.09967600	-1.39900300
H	1.77006200	0.18241300	-1.26528300
C	3.10661000	1.04363100	-2.77295500
H	2.47633500	0.62394700	-3.56756100
H	3.37264100	2.06961500	-3.07986800
C	4.40279000	0.22382500	-2.53873800
H	4.23411300	-0.86071000	-2.68127800
H	5.25255800	0.49904900	-3.17967700
C	4.65053500	0.39387500	-1.07183500
C	3.51118200	0.90401900	-0.42164200

H	4.45800300	1.71929600	-0.80757400	H	6.70808700	0.14886400	-0.34964300
H	2.04756700	3.23631200	-1.39623400	H	5.57756000	-1.18638400	-0.07925800
H	0.66670300	2.27896600	-1.93680100	H	5.40379900	-0.09517000	2.12328000
C	5.66750700	-0.08301600	-0.08121200	H	5.68769300	1.50248100	1.41979300
C	5.17766600	0.53858300	1.25631300	H	3.04782900	-0.09305900	1.35992100
C	3.65548300	0.78390200	1.07075900	H	3.24940100	1.63822300	1.62734000