Supporting Information

Gold(I)-Catalyzed Dehydrogenative Cycloisomerization of 1,5-enynes

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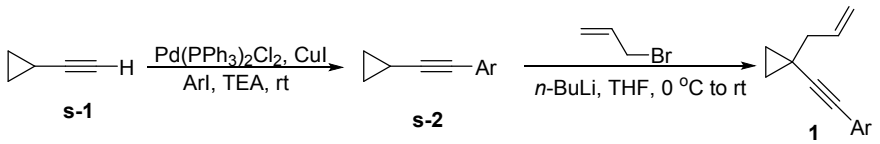
CONTENTS

1. General Remarks. ^{1}H and ^{13}C NMR spectra were recorded at the 300 and 75 MHz or the 400 and 100 MHz, respectively. Mass and HRMS spectra were recorded by EI or ESI method. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used.

2. General or Representative Reaction Procedure.

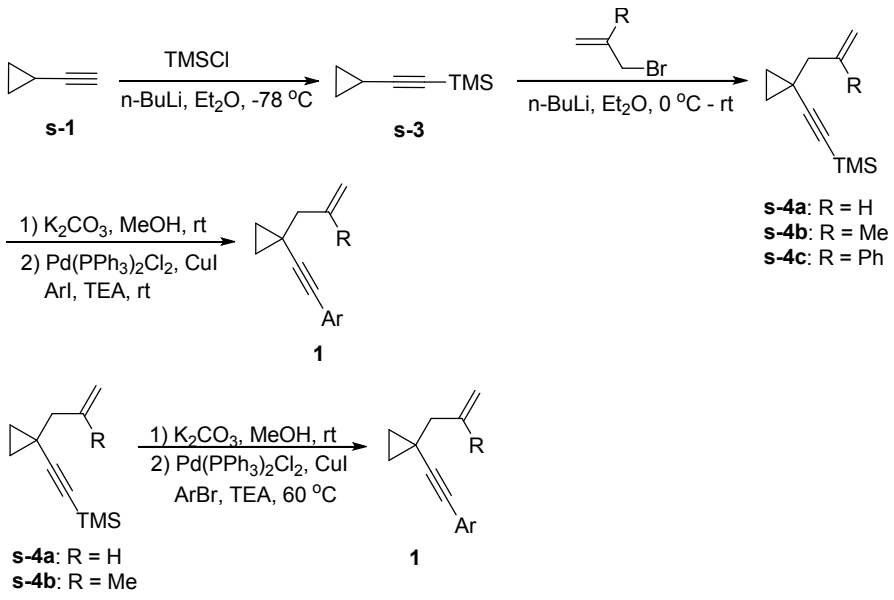
Representative procedures for the preparation of substrates:



Scheme S1

The substrates **1** were synthesized according to Scheme S1. The compound **s-2** was synthesized according to the reported procedure.[1]

Synthesis of substrate **1a**: To a 100 mL flame and vacuum dried flask was added cyclopropylphenylacetylene **s-2** (4.33 g, 31.16 mmol), and then the flask was evacuated and backfilled with Ar. *n*-BuLi (2.5M, 15 mL, 37.5 mmol) was added slowly at 0 °C. The reaction mixture was warmed to rt gradually and allowed to stir at rt for 1 h, then allyl bromide (3.0 mL, 37.4 mmol) was added slowly at 0 °C. The reaction mixture was allowed to stir overnight. The reaction was quenched with water, and then extracted with ethyl acetate (30 mL*3). The combined organic phase was dried over Na_2SO_4 (anhydrous) and evaporated at reduced pressure. The crude product was purified by column chromatography using PE as eluent. The product was afforded as colorless oil (3.12 g, yield = 58%).



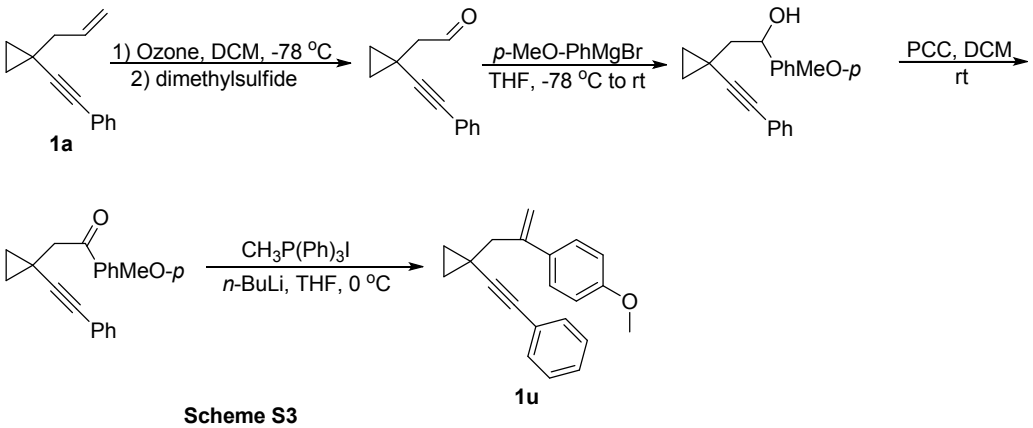
Scheme S2

The substrates **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1o**, **1p**, **1q**, **1r** and **1s** were synthesized according to Scheme S2. The corresponding iodide was synthesized according to the reported procedures.[2]

The compound **s-3** was synthesized according to the reported procedure:[3] To a 500 mL flame and vacuum dried three-neck flask was added compound **s-1** (20.3 mL, 240 mmol) and 100 mL THF under Ar, then *n*-BuLi (2.5 M, 97 mL, 240 mmol) was added slowly at -78 ^{o}C. After the addition was complete, the reaction mixture was allowed to stir at -78 ^{o}C for 2 h. TMSCl (33 mL, 240 mmol) was added to the flask slowly at -78 ^{o}C. The reaction mixture was allowed to stir at -78 ^{o}C for 2 h then warmed to rt gradually. 5 h later, the reaction was quenched with water. The reaction mixture was extracted with Et_2O, and the combined organic phase was dried over anhydrous sodium sulfate. The crude product was purified by vacuum distillation, and the product **s-3** (100 mbar, 80 ^{o}C fraction) was obtained as colorless oil (23g, yield = 69%).

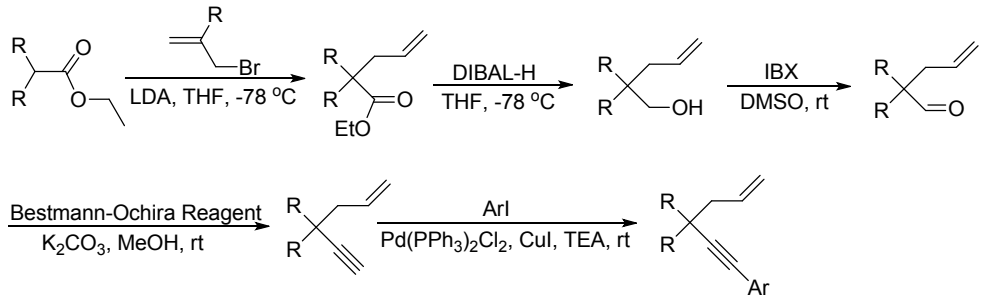
Synthesis of compound **s-4**: To a 250 mL flame and vacuum dried three-neck flask was added compound **s-3** (21.36 g, 154.5 mmol) and 100 mL Et_2O under Ar. *n*-BuLi (1.6 M, 100 mL, 160 mmol). After the addition was complete, the reaction mixture was allowed to stir at rt for 14 h. Allyl bromide (14 mL, 160 mmol) was added slowly to the reaction mixture to maintain gentle reflux. After the addition was complete, the reaction mixture was warmed to rt. The reaction was quenched with water. The reaction mixture was extracted with Et_2O, and the combined organic phase was dried over anhydrous sodium sulfate. The product **s-4** was purified by vacuum distillation (50 mbar, 90-100 ^{o}C). The product was afforded as colorless oil (17.2 g, yield = 63%).

Synthesis of compound **1h**: To a 50 mL flask was added **s-4a** (850 mg, 4.5 mmol) and K_2CO_3 (700 mg, 5 mmol) and 2.5 mL methanol, the reaction mixture was allowed to stir at rt for 2 hours. Then *p*-Ph-PhI (1.12 g, 4 mmol) and 10 mL TEA (triethylamine) were added into the reaction mixture. The reaction mixture was solidified by liquid N_2, and then evacuated and backfilled with Ar for 3 times. $Pd(PPh_3)_2Cl_2$ (70 mg, 0.01 mmol) and CuI (38 mg, 0.02 mmol) were added under Ar. The reaction mixture was allowed to stir at rt overnight. The product was purified by column chromatography using PE as eluent. The product **1h** was afforded as colorless oil (1.053 g, yield = 91%).



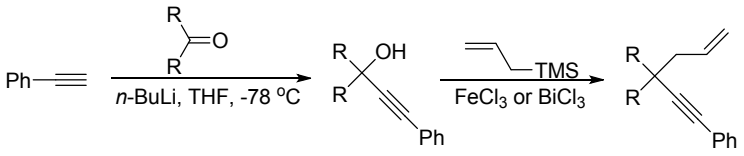
Scheme S3

The substrates **1u** were synthesized according to Scheme S3.[1b, 5]



Scheme S4

The substrates **2b**, **2c**, and **2d** were synthesized according to the procedures shown in Scheme S4.[1b, 5]



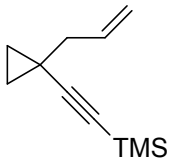
Scheme S5

The substrates **2a** and **2f** were synthesized according to Scheme S5 and the reported procedure.[4]

Representative procedure for the gold(I) catalyzed dehydrogenative cycloisomerization of substrates 1 (Condition A): To a 25 mL flame and vacuum dried Schlenk tube was added the substrate **1a** (37 mg, 0.2 mmol), DDQ (69 mg, 0.3 mmol), PPh_3AuCl (5 mg, 5 mol%) and $AgSbF_6$ (3 mg, 5 mol%), the tube was evacuated and backfilled with Ar. Then DCE (2 mL) was added. The reaction mixture was allowed to stir at rt for 30 min. The product was purified by column chromatography using PE as eluent. The product **3a** was afforded as colorless solid (27 mg, yield = 75%).

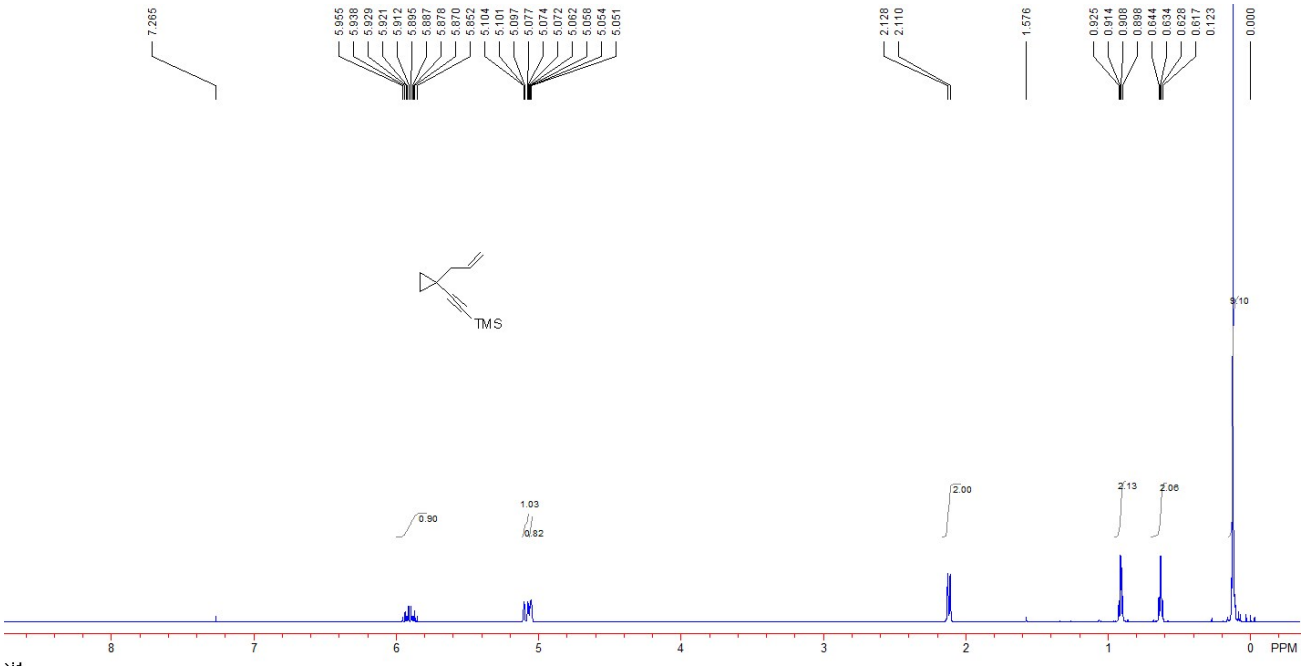
Representative procedure for the gold(I) catalyzed dehydrogenative cycloisomerization of substrates 1 (Condition B: a stepwise method): To a 25 mL flame and vacuum dried Schlenk tube was added the substrate **1a** (37 mg, 0.2 mmol) and $JohnPhosAuSbF_6$ (4 mg, 3 mol%), then the tube was evacuated and backfilled with Ar. 2 mL dry DCM was added to the tube, and the reaction mixture was allowed to stir at 0 ^oC until the disappearance of **1a** indicated by TLC. DDQ (69 mg, 0.3 mmol) was added. After 30 min, the product was purified by column chromatography using PE as eluent. The product **3a** was afforded as white solid (33 mg, yield = 89%).

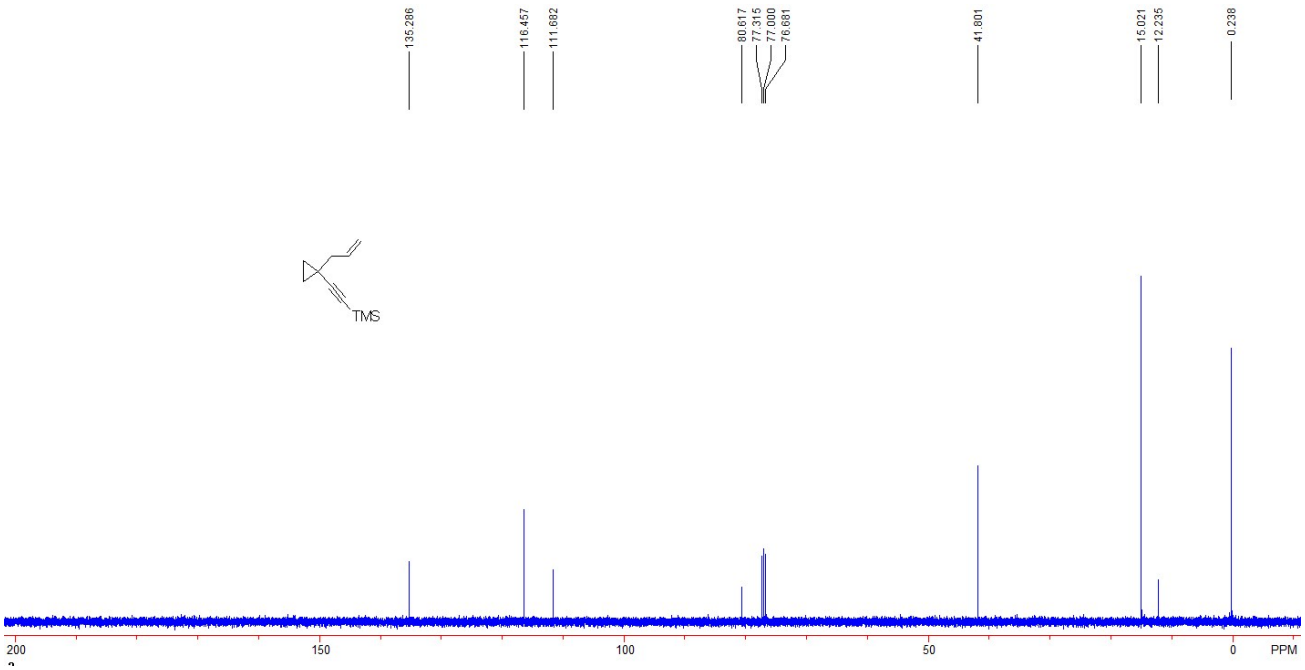
3. Spectroscopic Data.

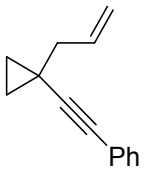


((1-Allylcyclopropyl)ethynyl)trimethylsilane s-4a:

This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.12 (s, 9H, CH_3), 0.63 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.91 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.12 (d, J = 7.2 Hz, 2H, CH_2), 5.05-5.10 (m, 2H, =CH_2), 5.85-5.96 (m, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 0.24, 12.2, 15.0, 41.8, 80.6, 111.7, 116.5, 135.3.

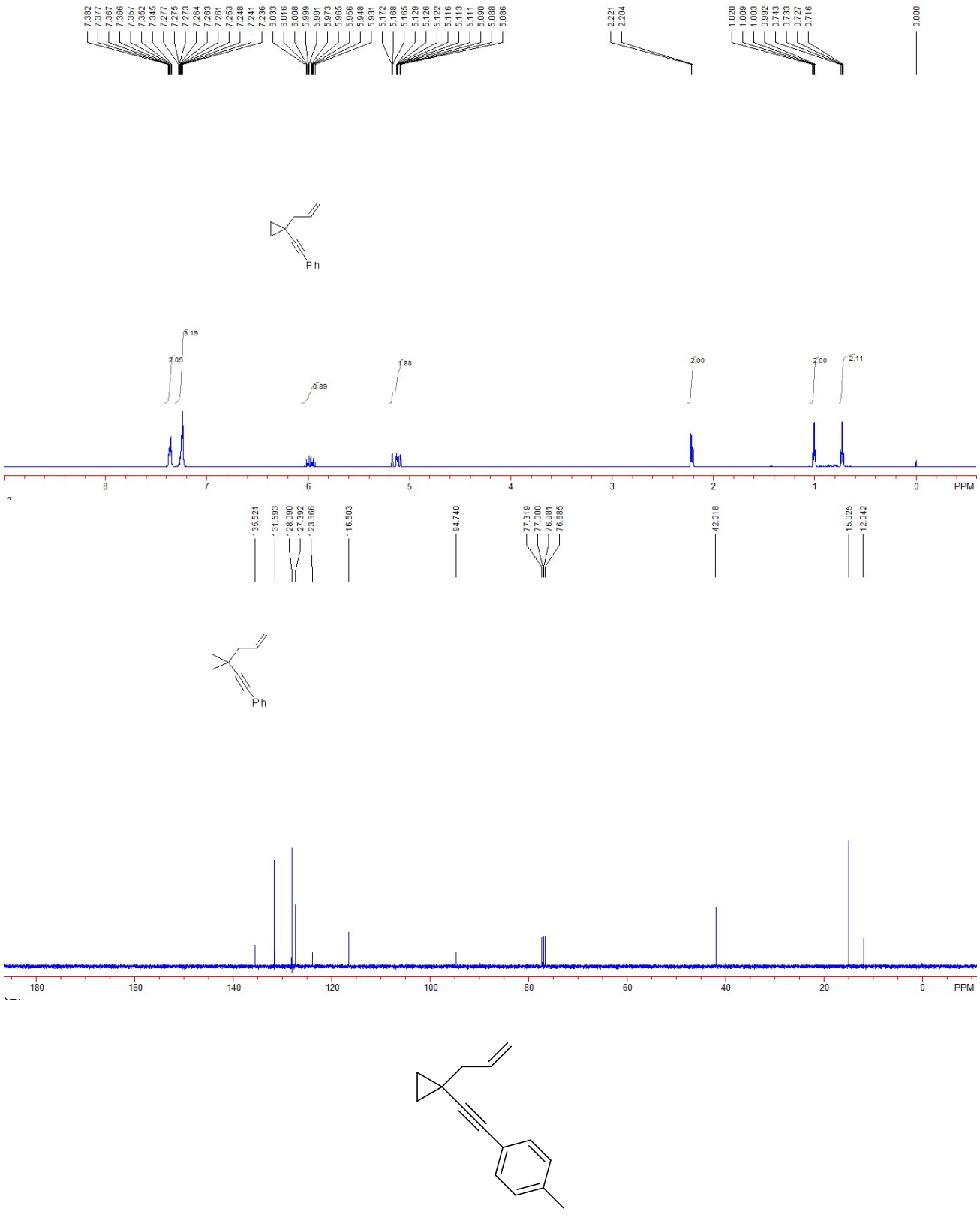






((1-allylcyclopropyl)ethynyl)benzene 1a:

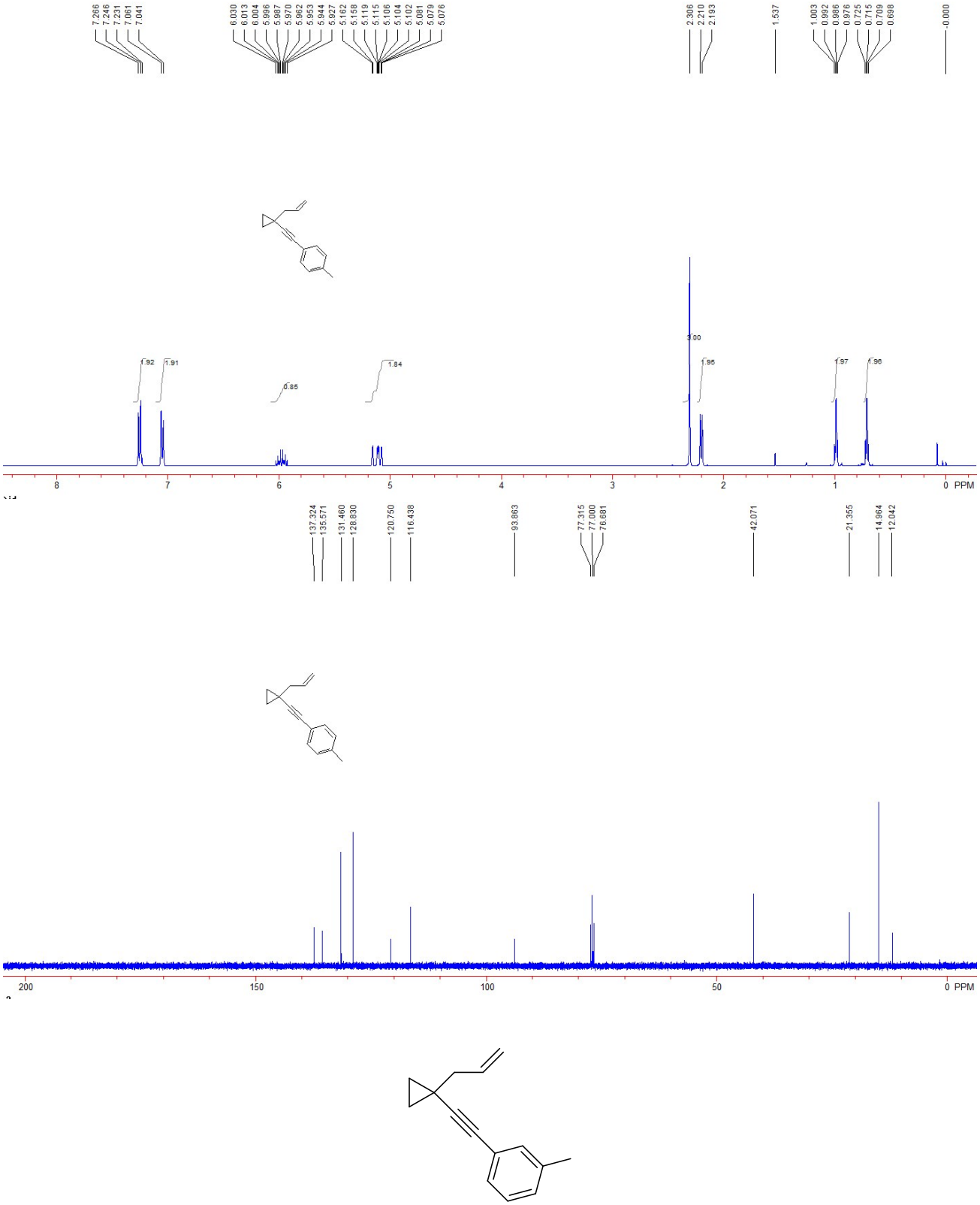
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.73 (dd, J_1 = 6.4 Hz, J_2 = 4.0 Hz, 2H, CH_2), 1.01 (dd, J_1 = 6.4 Hz, J_2 = 4.0 Hz, 2H, CH_2), 2.21 (d, J = 6.8 Hz, 2H, CH_2), 5.09-5.17 (m, 2H, =CH_2), 5.93-6.03 (m, 1H, CH_2), 7.24-7.28 (m, 3H, Ar), 7.35-7.38 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.0, 42.0, 77.0, 94.7, 116.5, 123.9, 127.4, 128.1, 131.6, 135.5.



1-((1-Allylcyclopropyl)ethynyl)-4-methylbenzene 1b:

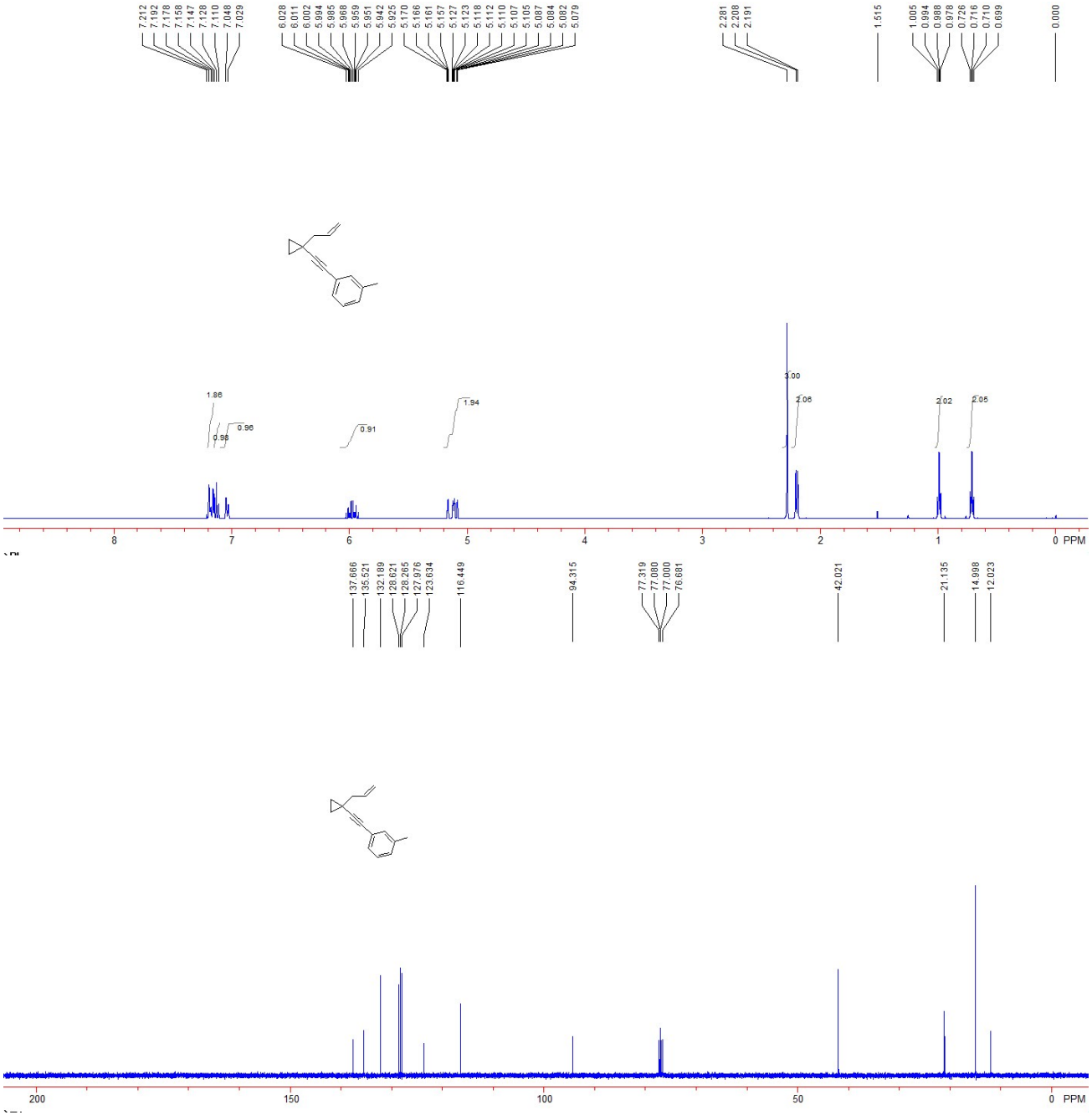
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.99 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.20 (d, J = 6.8 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 5.09 (dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H, =CH_2), 5.14 (dd, J_1 = 17.2 Hz, J_2 =

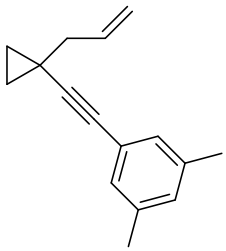
1.6 Hz, 1H, =CH_2), 5.93-6.03 (m, 1H, =CH), 7.05 (d, *J* = 8.0 Hz, 2H, Ar), 7.26 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.0, 21.4, 42.1, 93.9, 116.4, 120.8, 128.8, 131.5, 135.6, 137.3.



1-((1-Allylcyclopropyl)ethynyl)-3-methylbenzene 1c:

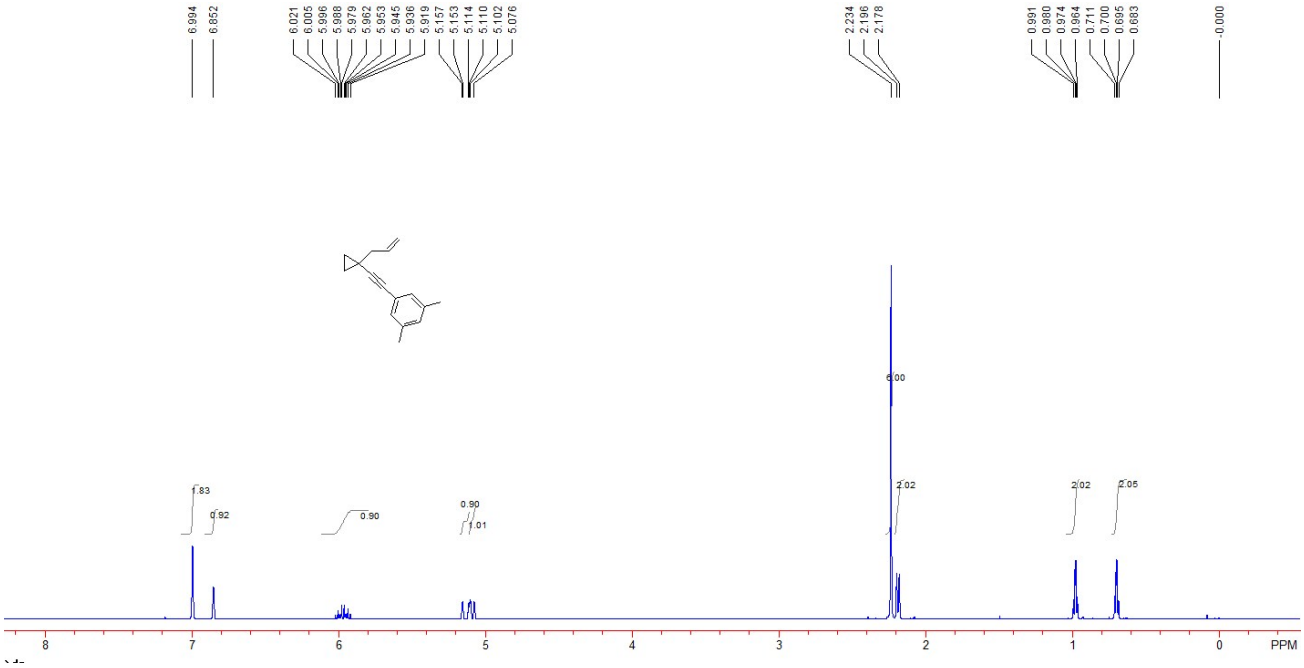
0.196 g, yield = 71%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.99 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.20 (d, J = 6.8 Hz, 2H, CH_2), 2.28 (s, 3H, CH_3), 5.08-5.17 (m, 2H, =CH_2), 5.93-6.03 (m, 1H, =CH), 7.04 (d, J = 7.6 Hz, 1H, Ar), 7.20 (d, J = 7.6 Hz, 1H, Ar), 7.15-7.21 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.0, 21.1, 42.0, 77.1, 94.3, 116.4, 123.6, 128.0, 128.6, 132.2, 135.5, 137.7. IR (CH_2Cl_2) ν 3077, 3006, 2922, 1603, 1423, 781, 690 cm^{-1}. MS (%) m/e 196 (M^+, 63.04), 181 (100.00), 155 (85.19), 128 (61.65), 115 (80.55), 105 (40.86), 89 (20.73), 77 (31.07), 63 (19.48). HRMS (EI) calcd. for $C_{15}H_{16}$: 196.1252, found: 196.1254.

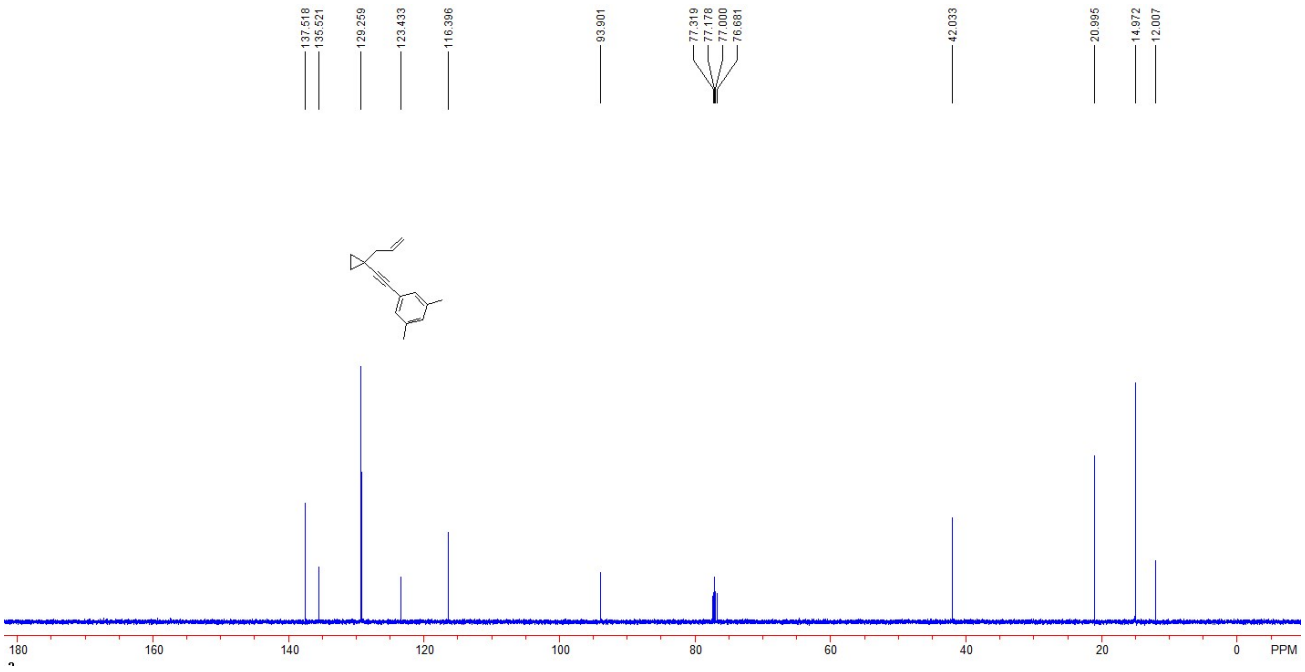


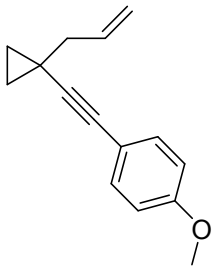


1-((1-Allylcyclopropyl)ethynyl)-3,5-dimethylbenzene 1d:

This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.70 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.98 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.19 (d, J = 6.8 Hz, 2H, CH_2), 2.23 (s, 6H, CH_3), 5.09 (d, J = 10.4 Hz, 1H, =CH_2), 5.14 (d, J = 17.2 Hz, 1H, =CH_2), 5.92-6.02 (m, 1H, =CH), 6.85 (s, 1H, Ar), 6.99 (s, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.0, 21.0, 42.0, 76.7, 93.9, 116.4, 123.4, 129.3, 135.5, 137.5.

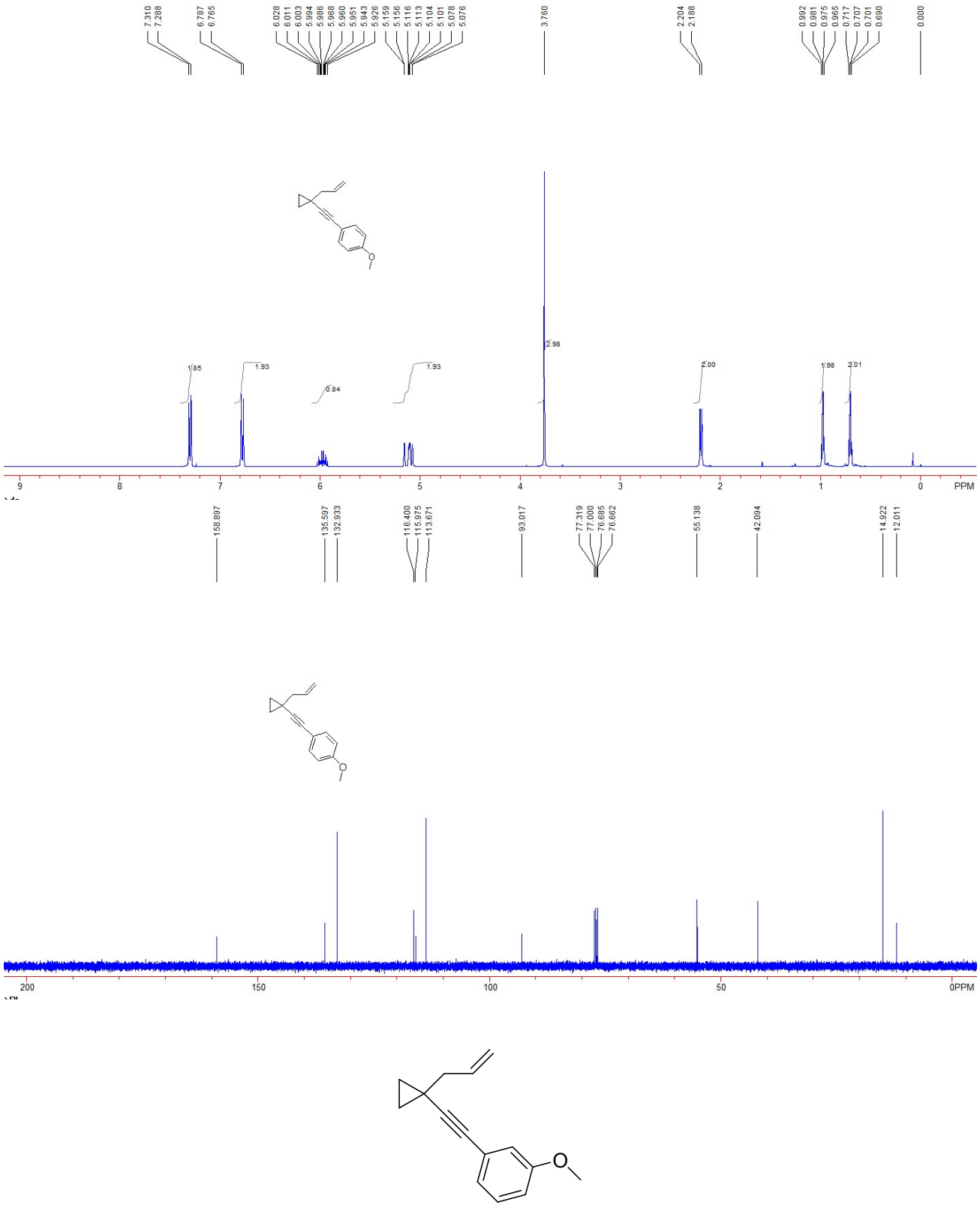






1-((1-Allylcyclopropyl)ethynyl)-4-methoxybenzene 1e:

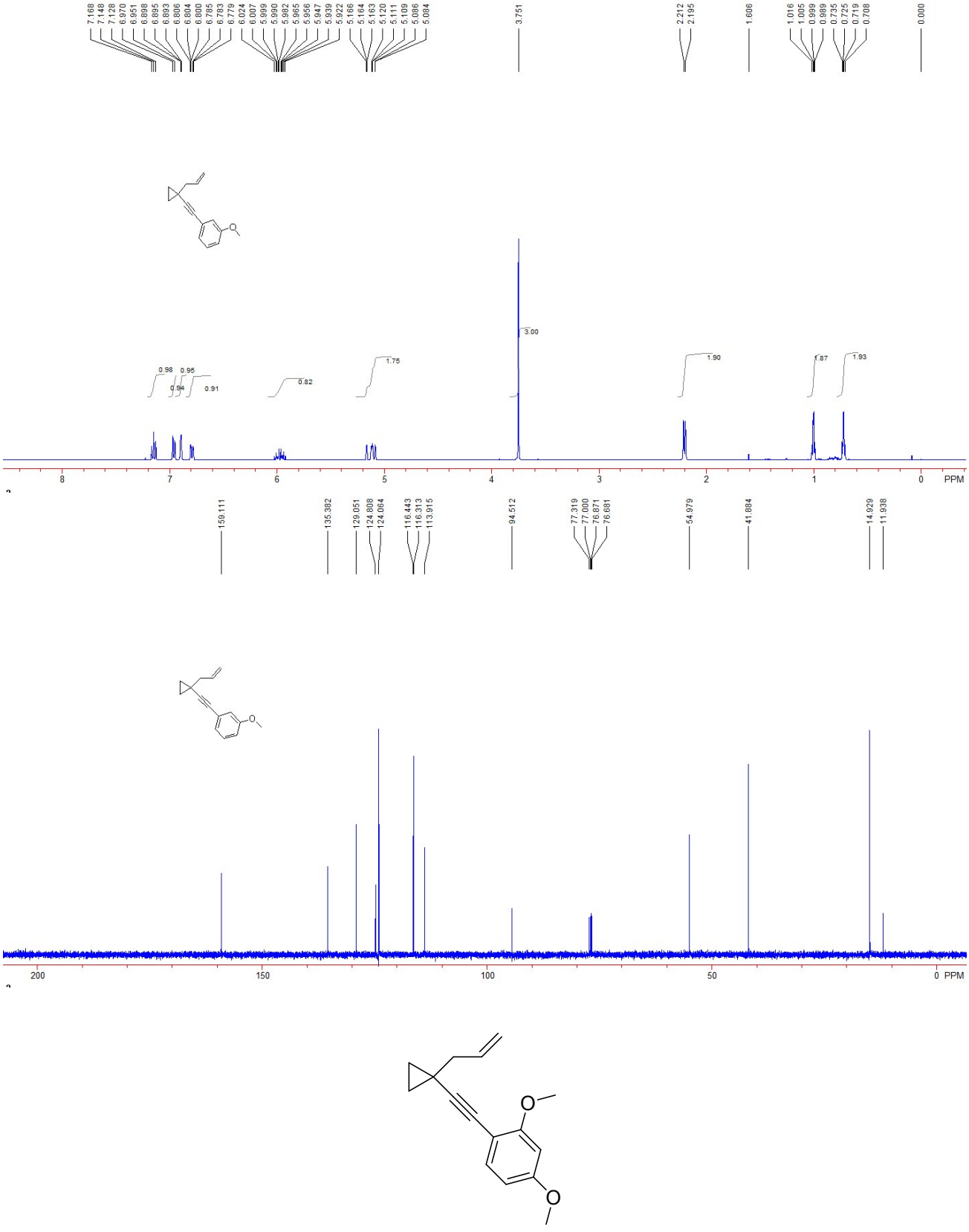
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.70 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.98 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.20 (d, J = 6.8 Hz, 2H, CH_2), 5.09 (d, J = 10.4 Hz, 1H, =CH_2), 5.14 (d, J = 17.2 Hz, 1H, =CH_2), 5.93-6.03 (m, 1H, =CH), 6.77 (d, J = 8.8 Hz, 2H, Ar), 7.30 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 14.9, 42.1, 55.1, 76.7, 93.0, 113.7, 116.0, 116.4, 132.9, 135.6, 158.9.



1-((1-Allylcyclopropyl)ethynyl)-3-methoxybenzene 1f:

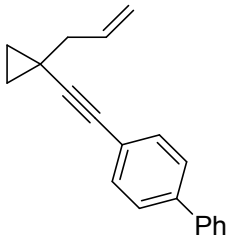
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.77 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.00 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.19 (d, J = 6.8 Hz, 2H, CH_2), 3.72 (s, 3H, CH_3), 5.07-5.17 (m, 2H, =CH_2), 5.93-6.00 (m, 1H, =CH), 6.77-6.79 (m, 1H, Ar),

6.89-6.90 (m, 1H, Ar), 6.94-6.97 (m, 1H, Ar), 7.11-7.20 (m, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.9, 14.9, 41.9, 55.0, 76.9, 94.5, 113.9, 116.3, 116.4, 124.1, 124.8, 129.1, 135.4, 159.1.



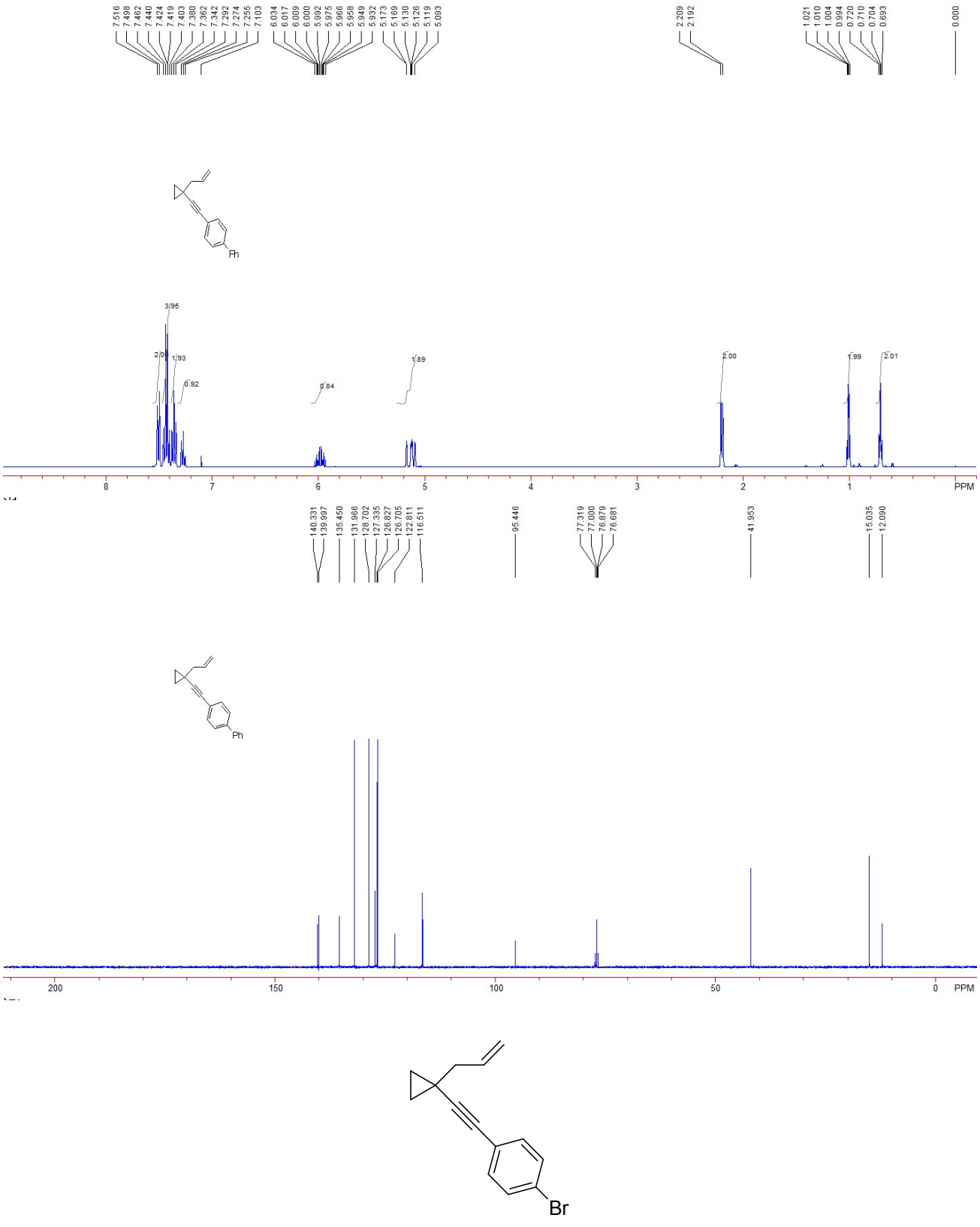
1-((1-Allylcyclopropyl)ethynyl)-2,4-dimethoxybenzene 1g:

0.530 g, yield = 73%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.0 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.01 (dd, J_1 = 6.0 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.20 (d, J = 6.8 Hz, 2H, CH_2), 3.77 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 5.09 (d, J = 10.4 Hz, 1H, =CH_2), 5.14 (d, J = 17.2 Hz, 1H, =CH_2), 5.96-6.10 (m, 1H, =CH), 6.38-6.39 (m, 2H, Ar), 7.25-7.27 (m, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.3, 15.0, 42.1, 55.2, 55.7, 72.8, 97.1, 98.3, 104.4, 105.5, 116.3, 134.2, 135.7, 160.3, 161.0. IR (CH_2Cl_2) ν 3076, 3003, 2936, 1606, 1505, 1301, 1208, 1031, 823 cm^{-1}. MS (%) m/e 242 (M^+, 100.00), 227 (41.05), 211 (33.37), 201 (24.94), 158 (26.54), 141 (23.90), 115 (65.24), 91 (22.65), 77 (22.08). HRMS (EI) calcd. for $C_{15}H_{18}O_2$: 242.1307, found: 242.1305.



4-((1-Allylcyclopropyl)ethynyl)-1,1'-biphenyl 1h:

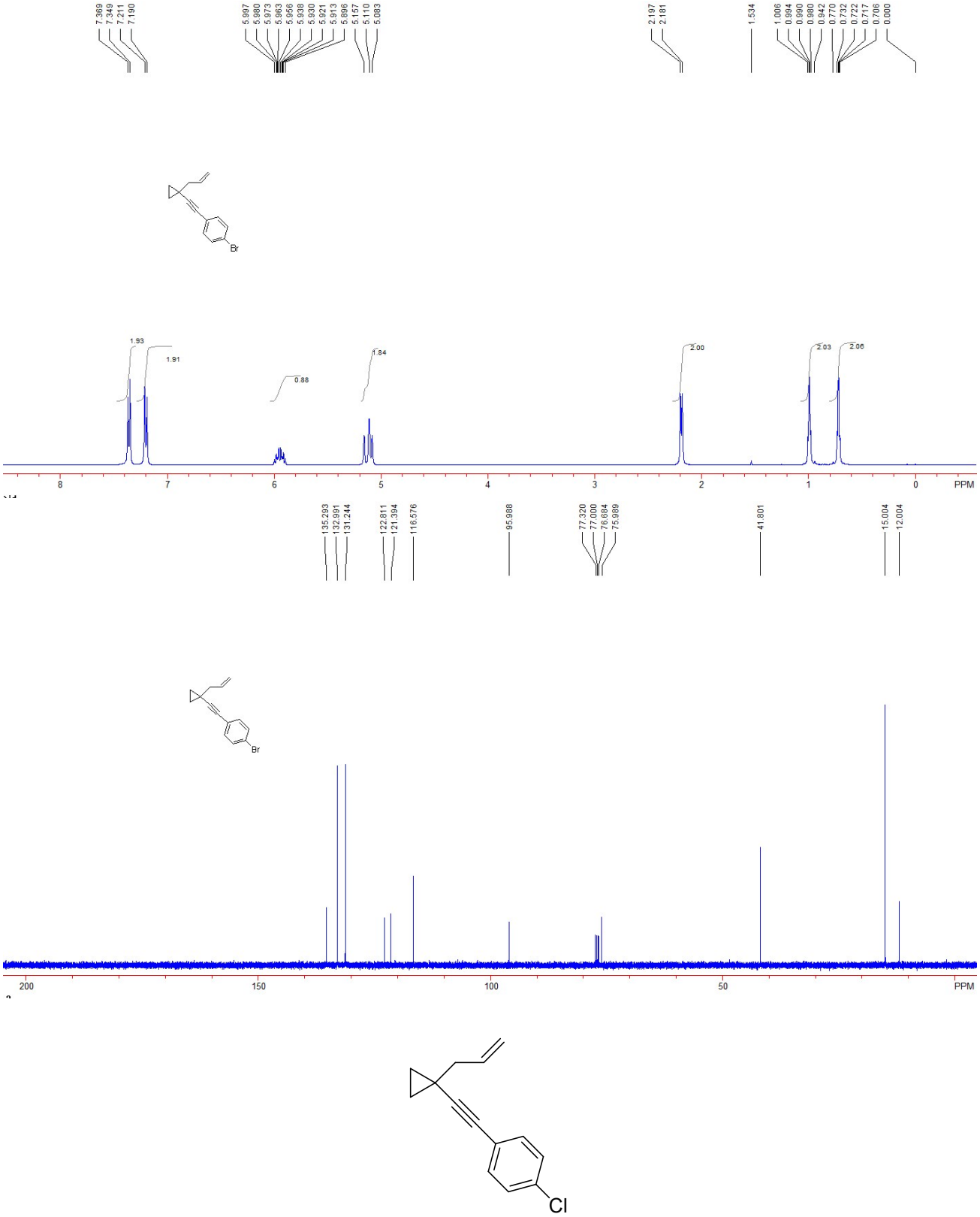
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.01 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.20 (d, J = 6.8 Hz, 2H, CH_2), 5.11 (d, J = 10.8 Hz, 1H, =CH_2), 5.13 (dd, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H, =CH_2), 5.93-6.03 (m, 1H, =CH), 7.27 (dd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 1H, Ar), 7.35 (d, J = 8.0 Hz, 1H, Ar), 7.38-7.46 (m, 4H, Ar), 7.51 (d, J = 7.2 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 15.0, 42.0, 76.9, 95.4, 116.5, 122.8, 126.7, 126.8, 127.3, 128.7, 132.0, 135.5, 140.0, 140.3.



1-((1-Allylcyclopropyl)ethynyl)-4-bromobenzene 1i:

This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.72 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.99 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.19 (d, J = 6.4 Hz, 2H, CH_2), 5.10 (d, J = 10.8 Hz, 1H, =CH_2), 5.13 (d, J = 18.8 Hz, 1H, =CH_2), 5.90-6.00 (m, 1H, =CH),

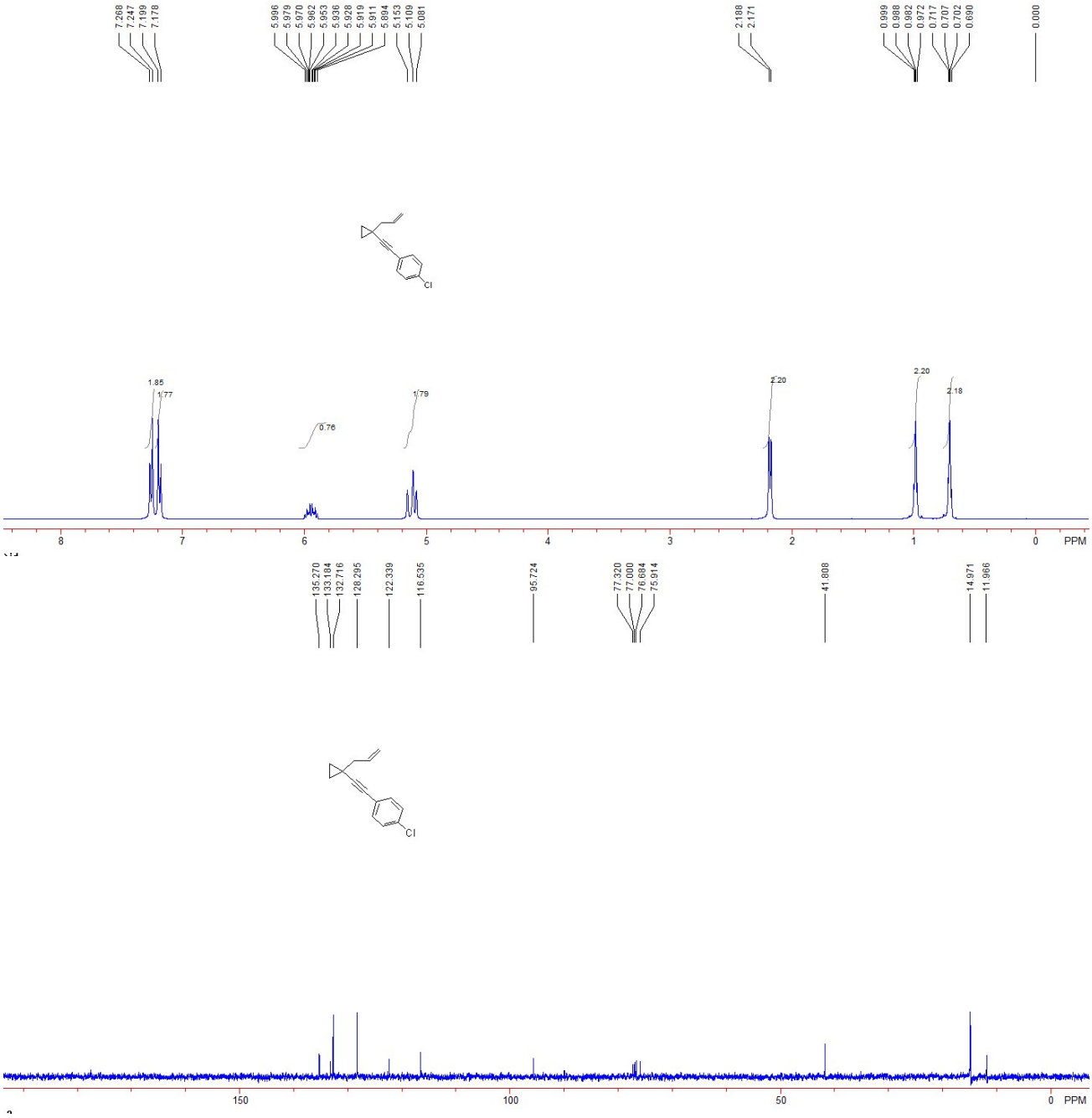
7.20 (d, J = 7.6 Hz, 2H, Ar), 7.36 (d, J = 7.6 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.0, 41.8, 76.0, 96.0, 116.6, 121.4, 122.8, 131.2, 133.0, 135.3.

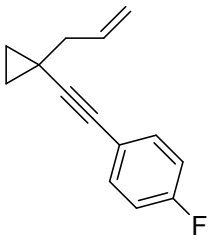


1-((1-Allylcyclopropyl)ethynyl)-4-chlorobenzene 1j:

This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.70 (dd, J_1 = 6.4

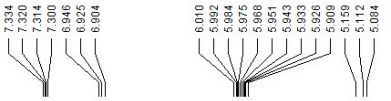
Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.99 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.18 (d, J = 6.8 Hz, 2H, CH_2), 5.09 (d, J = 11.2 Hz, 1H, =CH_2), 5.13 (d, J = 17.6 Hz, 1H, =CH_2), 5.89-5.97 (m, 1H, =CH), 7.19 (d, J = 8.4 Hz, 2H, Ar), 7.26 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.0, 41.8, 75.9, 95.7, 116.5, 122.3, 128.3, 132.7, 133.2, 135.3.

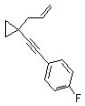


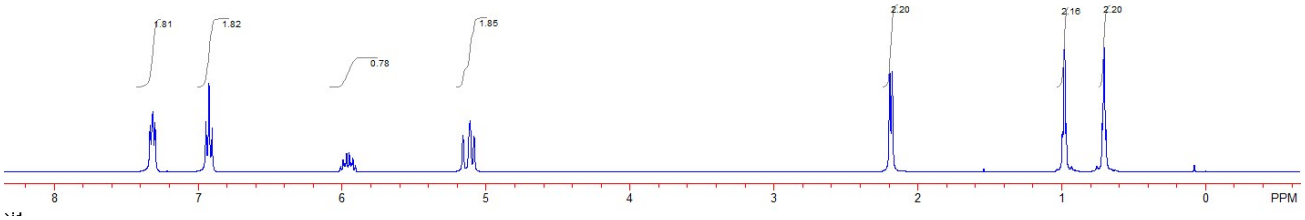


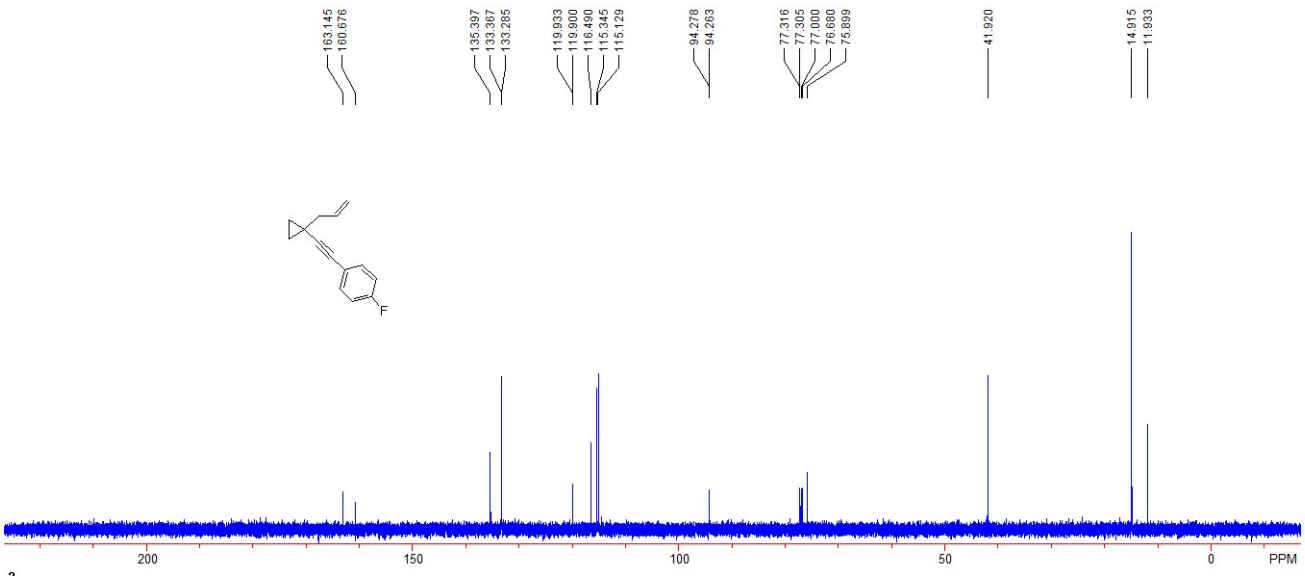
1-((1-Allylcyclopropyl)ethynyl)-4-fluorobenzene 1k:

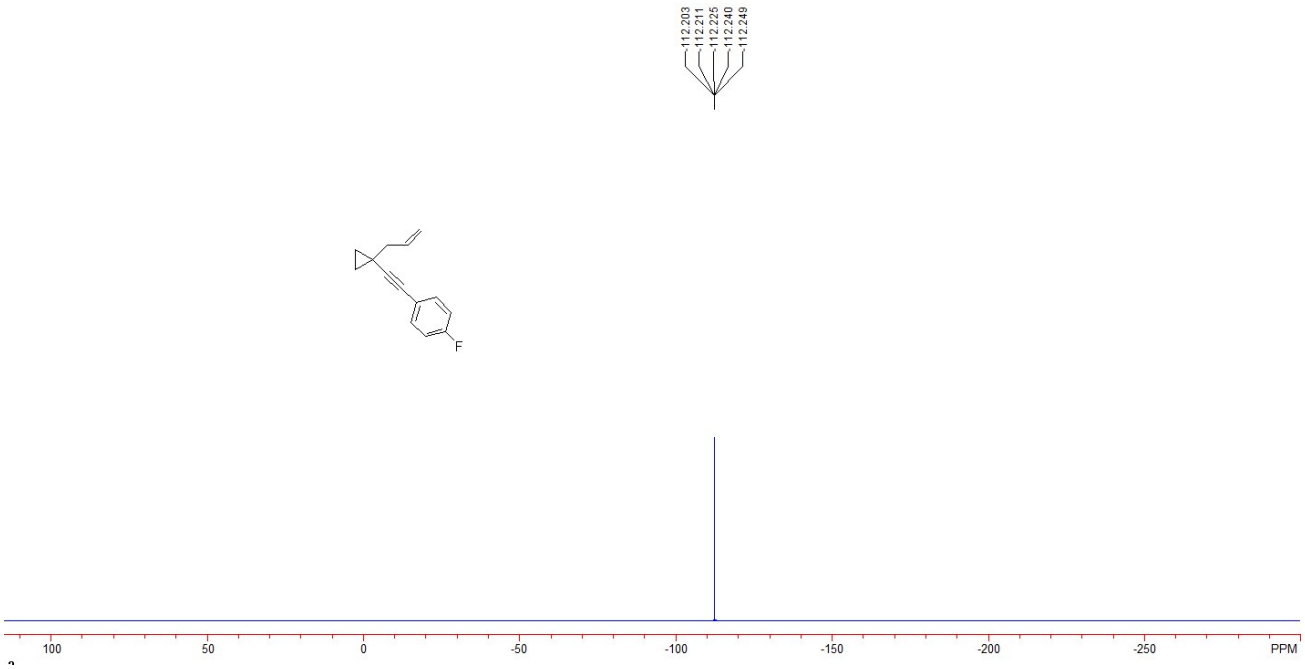
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 0.98 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.19 (d, J = 6.8 Hz, 2H, CH_2), 5.10 (d, J = 11.2 Hz, 1H, =CH_2), 5.14 (d, J = 18.8 Hz, 1H, =CH_2), 5.91-6.01 (m, 1H, =CH), 6.90-6.95 (m, 2H, Ar), 7.30-7.33 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.9, 14.9, 41.9, 75.9, 94.3 (d, J = 1.5 Hz), 115.2 (d, J = 21.6 Hz), 116.5, 119.9 (d, J = 3.3 Hz), 133.3 (d, J = 8.2 Hz), 135.4, 161.9, (d, J = 246.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -112.2.

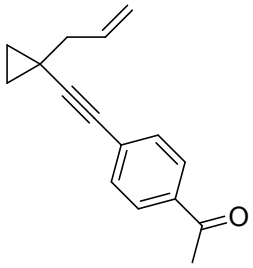








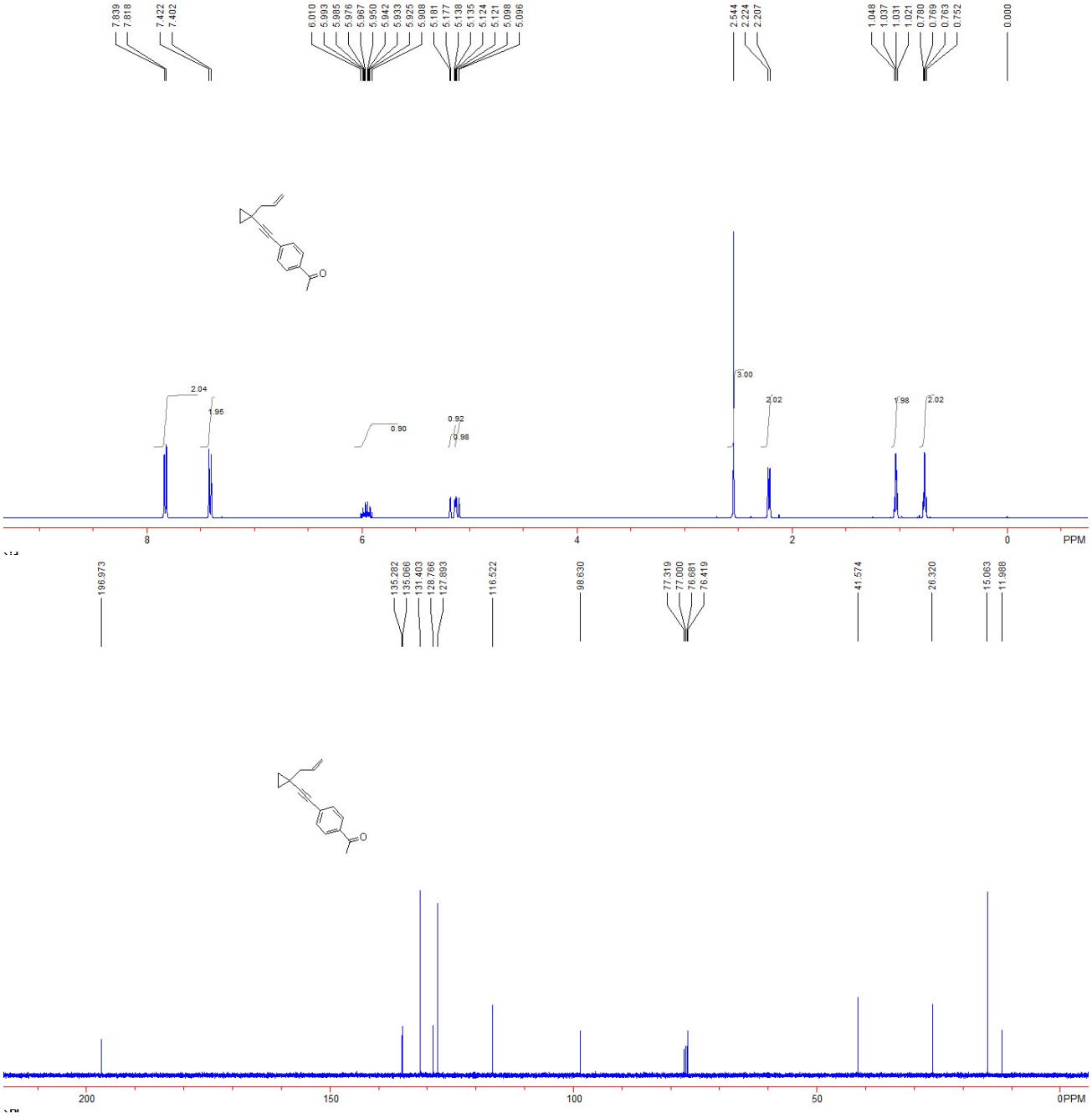


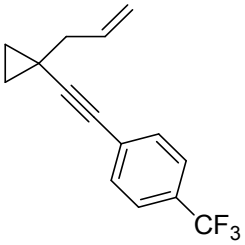


1-(4-((1-Allylcyclopropyl)ethynyl)phenyl)ethanone 1l:

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.77 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.03 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.22 (d, J = 6.8 Hz, 2H, CH_2), 2.54 (s, 3H, CH_3), 5.11 (dd, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H, =CH_2), 5.16 (dd, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H, =CH_2), 5.91-6.01

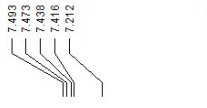
(m, 1H, =CH), 7.41 (d, J = 8.0 Hz, 2H, Ar), 7.83 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.0, 15.1, 26.3, 41.6, 76.4, 98.6, 116.5, 127.9, 128.8, 131.4, 135.1, 135.3, 197.0. IR (CH_2Cl_2) ν 3078, 3004, 1682, 1600, 1357, 1262, 1015, 916, 830 cm^{-1}. MS (%) m/e 224 (M^+, 40.12), 209 (41.11), 181 (88.83), 165 (60.82), 152 (39.96), 139 (42.30), 115 (22.57), 76 (21.15), 43 (100.00). HRMS (EI) calcd. for $C_{16}H_{16}O$: 224.1201, found: 224.1202.

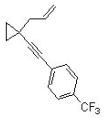


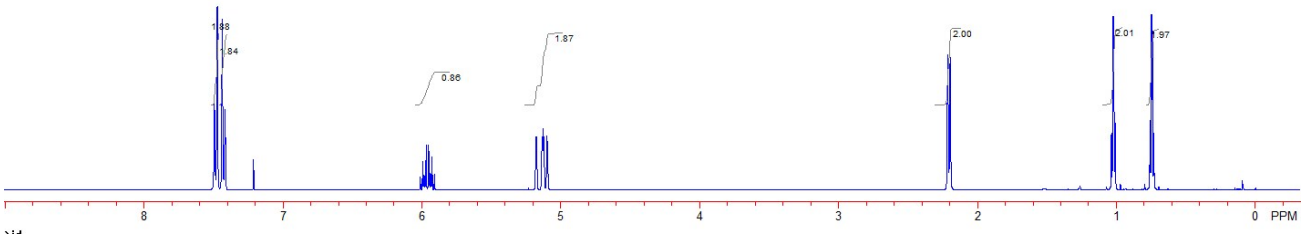


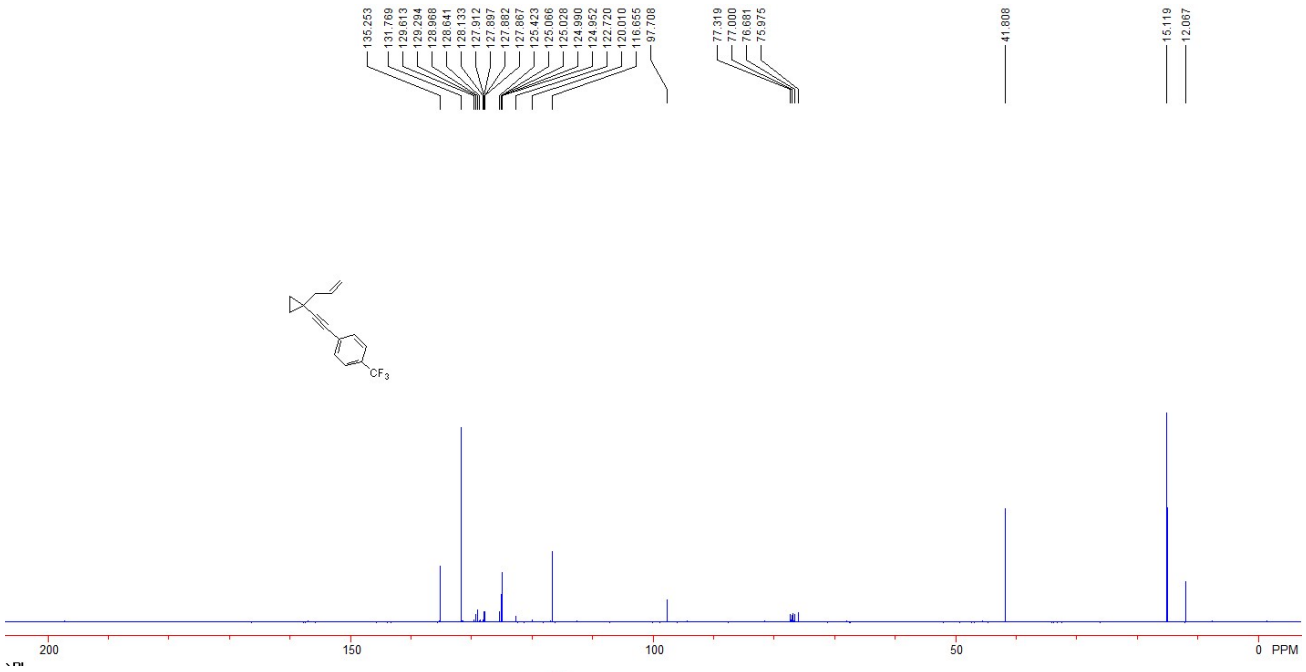
1-((1-Allylcyclopropyl)ethynyl)-4-(trifluoromethyl)benzene 1m:

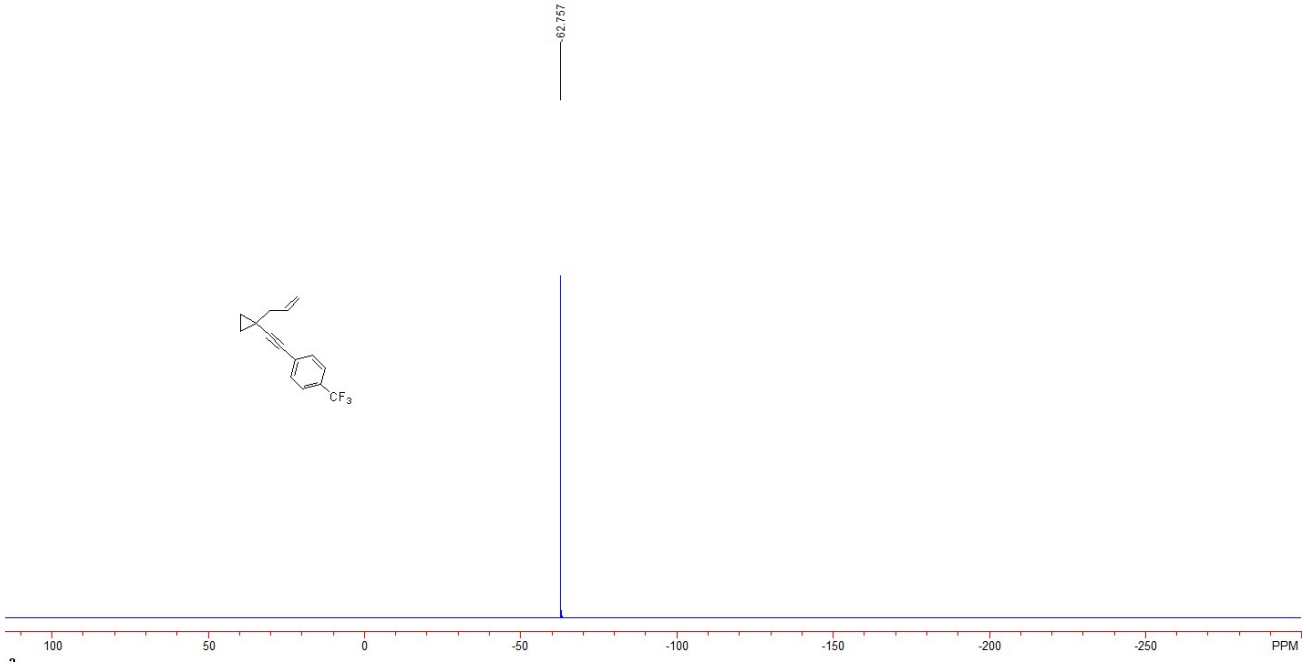
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.75 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.02 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.21 (d, J = 6.8 Hz, 2H, CH_2), 5.10-5.13 (m, 1H, =CH_2), 5.16 (dd, J_1 = 15.6 Hz, J_2 =1.6 Hz, 1H, =CH_2), 5.91-6.01 (m, 1H, =CH), 7.43 (d, J = 8.4 Hz, 2H, Ar), 7.48 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 15.1, 41.8, 76.0, 97.7, 120.0, 124.1 (q, J = 270.3 Hz), 125.1 (q, J = 3.8 Hz), 127.9 (q, J = 1.5 Hz), 129.1 (q, J = 32.6 Hz), 131.8, 135.3. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.8.

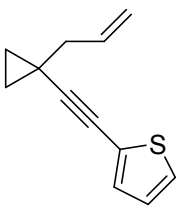








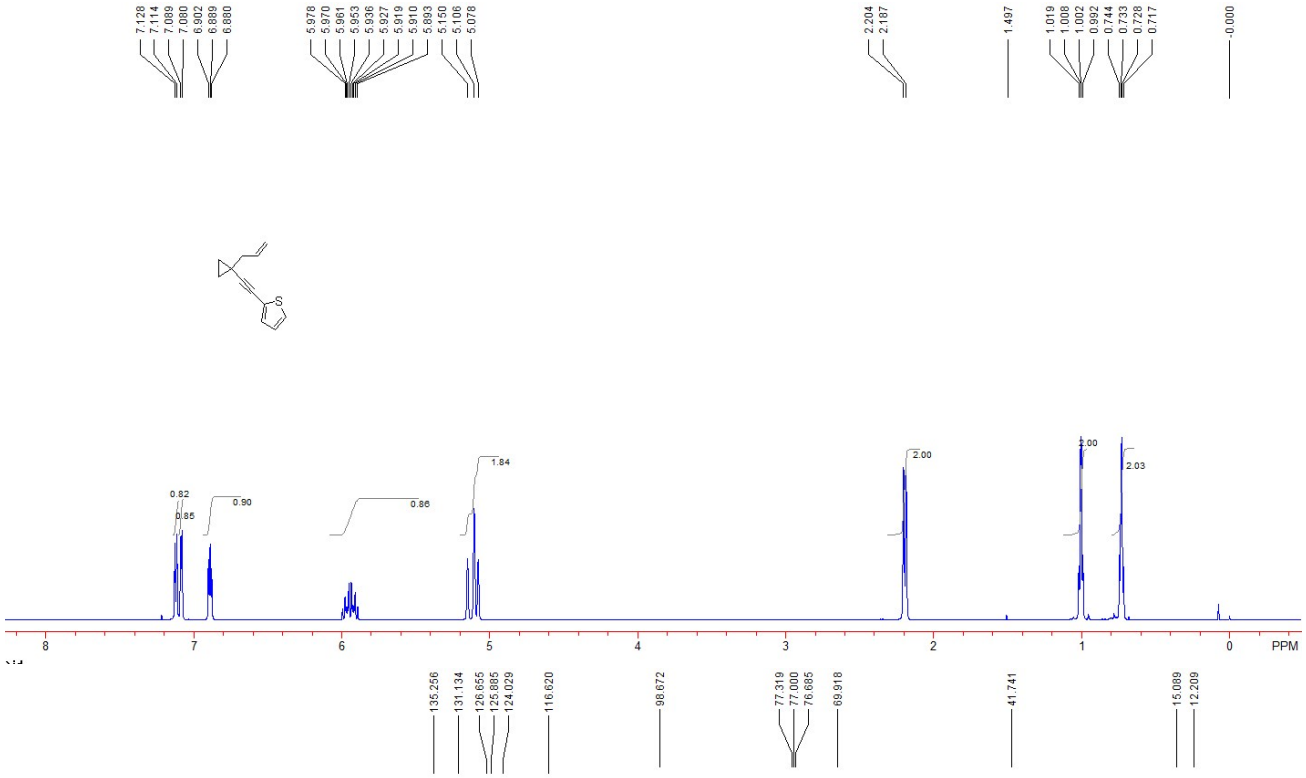


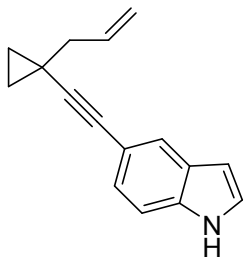


2-((1-Allylcyclopropyl)ethynyl)thiophene 1n:

This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.73 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.01 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.20 (d, J = 6.8 Hz, 2H, CH_2), 5.09 (d, J = 11.2 Hz, 1H, =CH_2), 5.13 (d, J = 17.6 Hz, 1H, =CH_2), 5.89-5.98 (m, 1H, =CH),

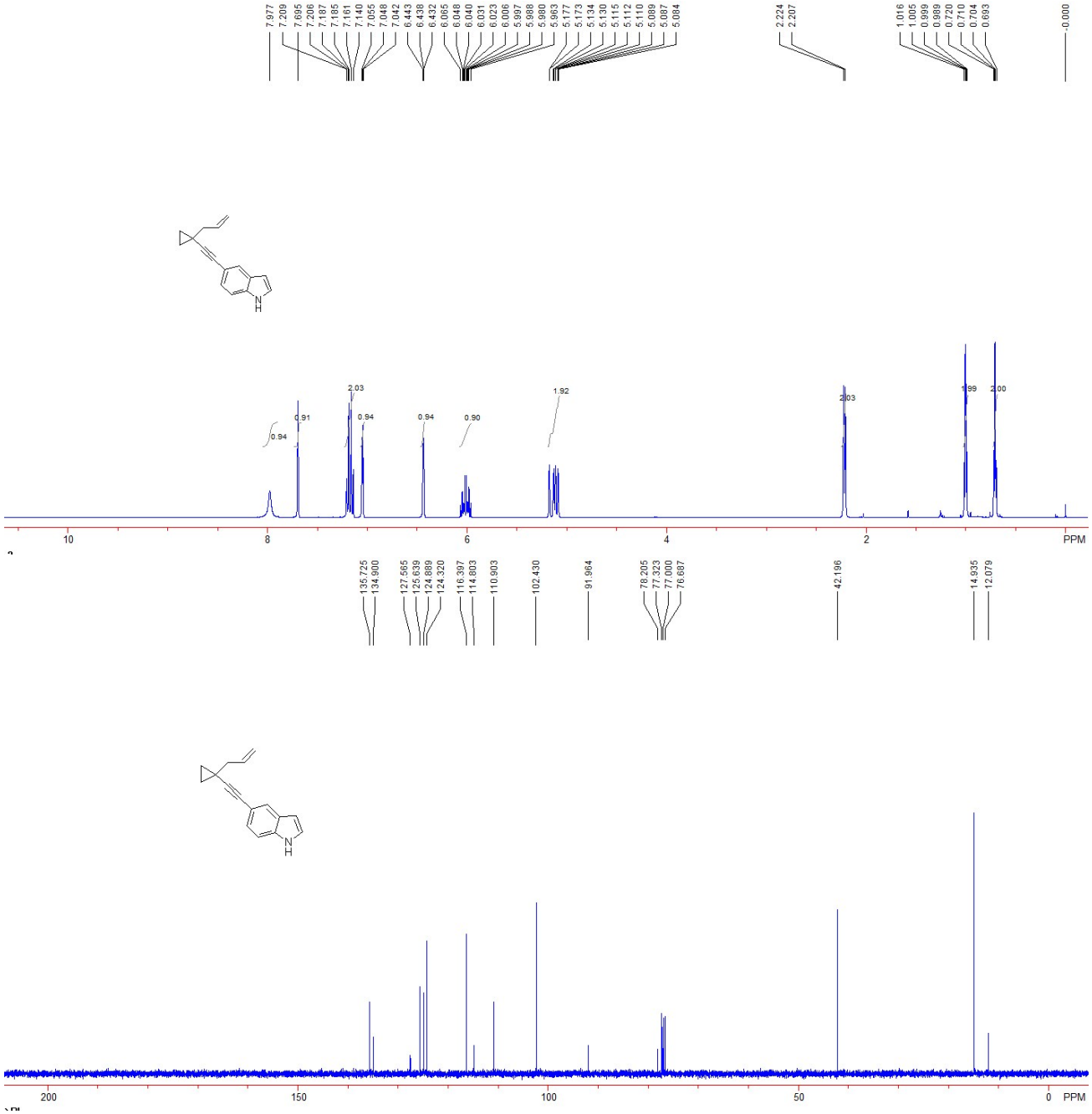
6.89 (dd, J_1 = 5.6 Hz, J_2 = 3.6 Hz, 1H, Ar), 7.08 (d, J = 3.6 Hz, 1H, Ar), 7.12 (d, J = 5.6 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 15.1, 41.7, 69.9, 98.7, 116.6, 124.0, 125.9, 126.7, 131.1, 135.3.

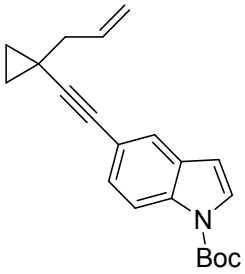




5-((1-Allylcyclopropyl)ethynyl)-1*H*-indole 1o':

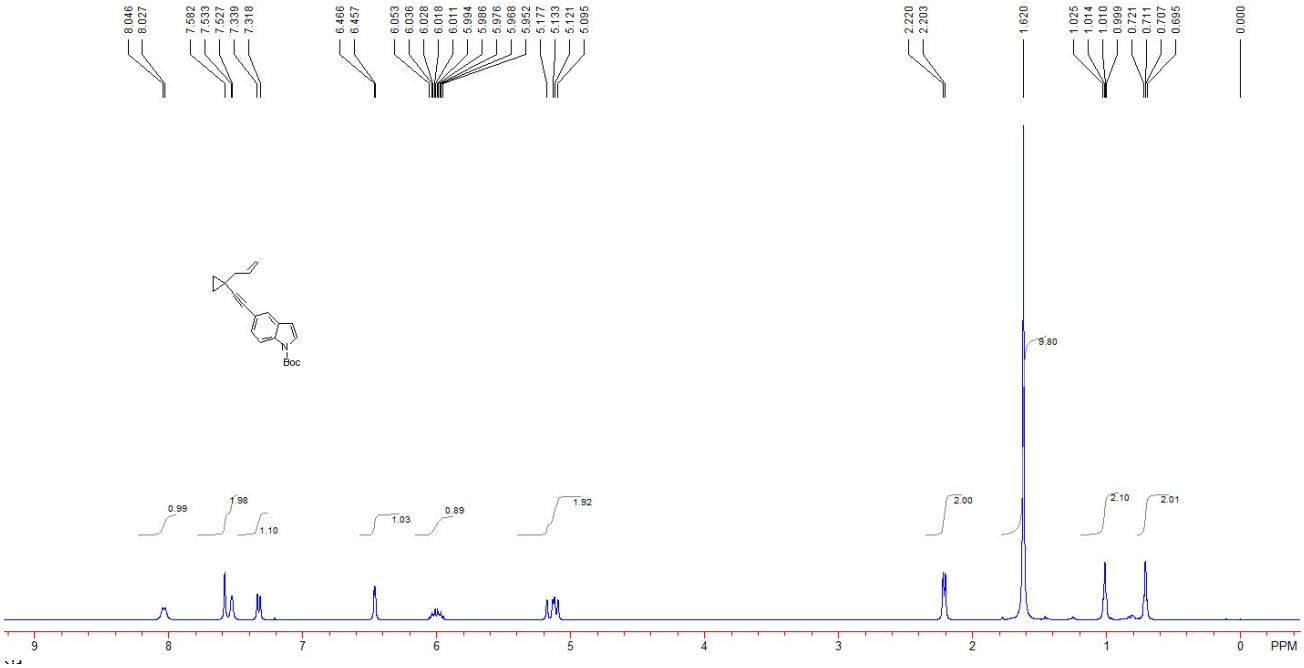
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.00 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.22 (d, J = 6.4 Hz, 2H, CH_2), 5.08-5.18 (m, 2H, =CH_2), 5.96-6.07 (m, 1H, =CH), 6.43-6.44 (m, 1H, Ar), 7.04-7.07 (m, 1H, Ar), 7.14-7.21 (m, 2H, Ar), 7.70 (s, 1H, Ar), 7.98 (br, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 14.9, 42.2, 78.2, 92.0, 102.4, 110.9, 114.8, 116.4, 124.3, 124.9, 125.6, 127.6, 134.9, 135.7.

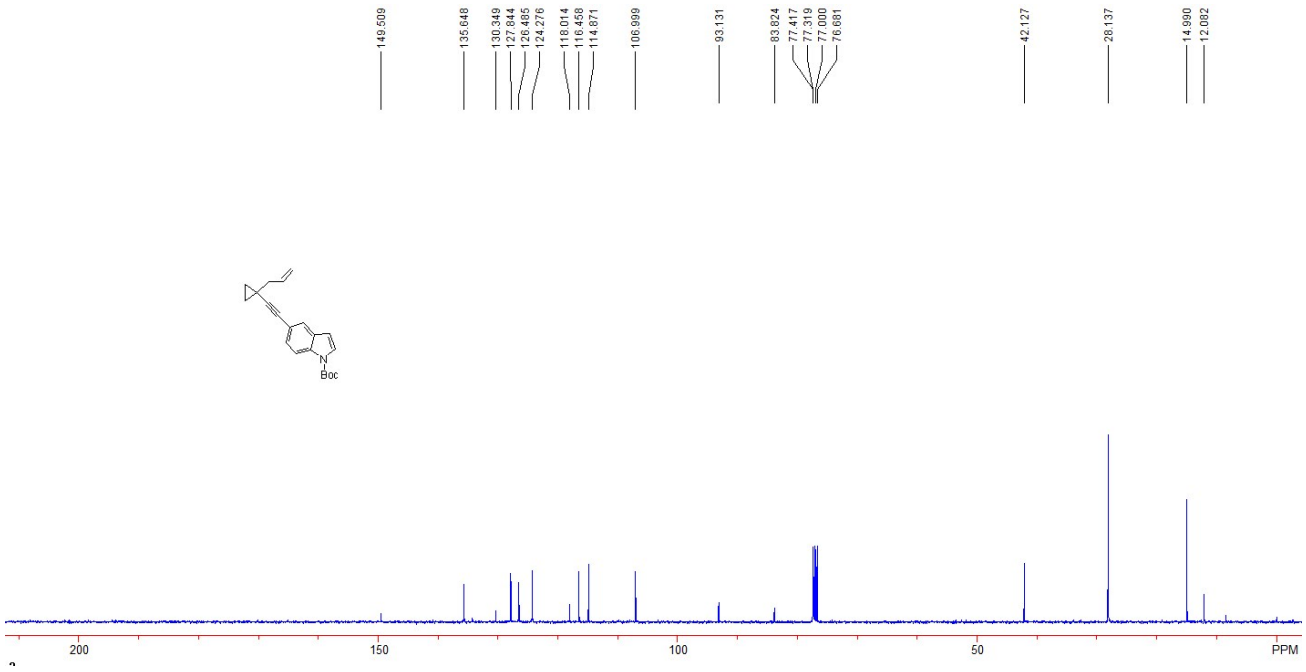


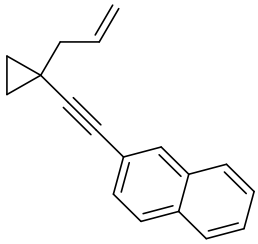


***tert*-Butyl 5-((1-allylcyclopropyl)ethynyl)-1*H*-indole-1-carboxylate 1o**:

This is a known compound.[5] A white solid. Mp: 57-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (dd, J_1 = 6.0 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.01 (dd, J_1 = 6.0 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.62 (s, 9H, CH_3), 2.21 (d, J = 6.8 Hz, 2H, CH_2), 5.11 (d, J = 10.4 Hz, 1H, =CH_2), 5.17 (d, J = 17.6 Hz, 1H, =CH_2), 5.95-6.05 (m, 1H, =CH), 7.33 (d, J = 8.4 Hz, 1H, Ar), 7.53 (d, J = 2.0 Hz, 1H, Ar), 7.58 (s, 1H, Ar), 8.04 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 15.0, 28.1, 42.1, 83.8, 93.1, 107.0, 114.9, 116.5, 118.0, 124.3, 126.5, 127.8, 130.3, 135.6, 149.5.

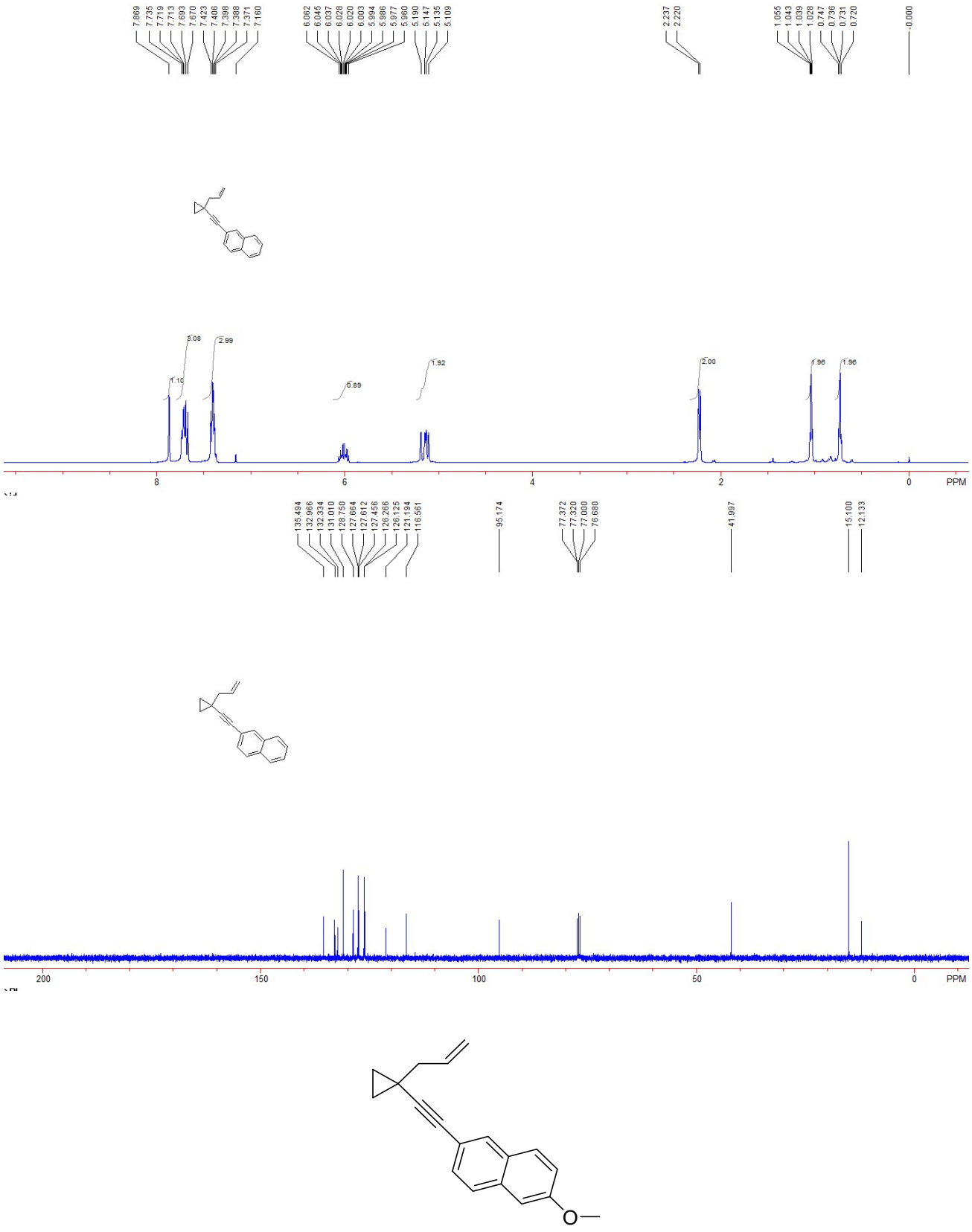






2-((1-Allylcyclopropyl)ethynyl)naphthalene 1p:

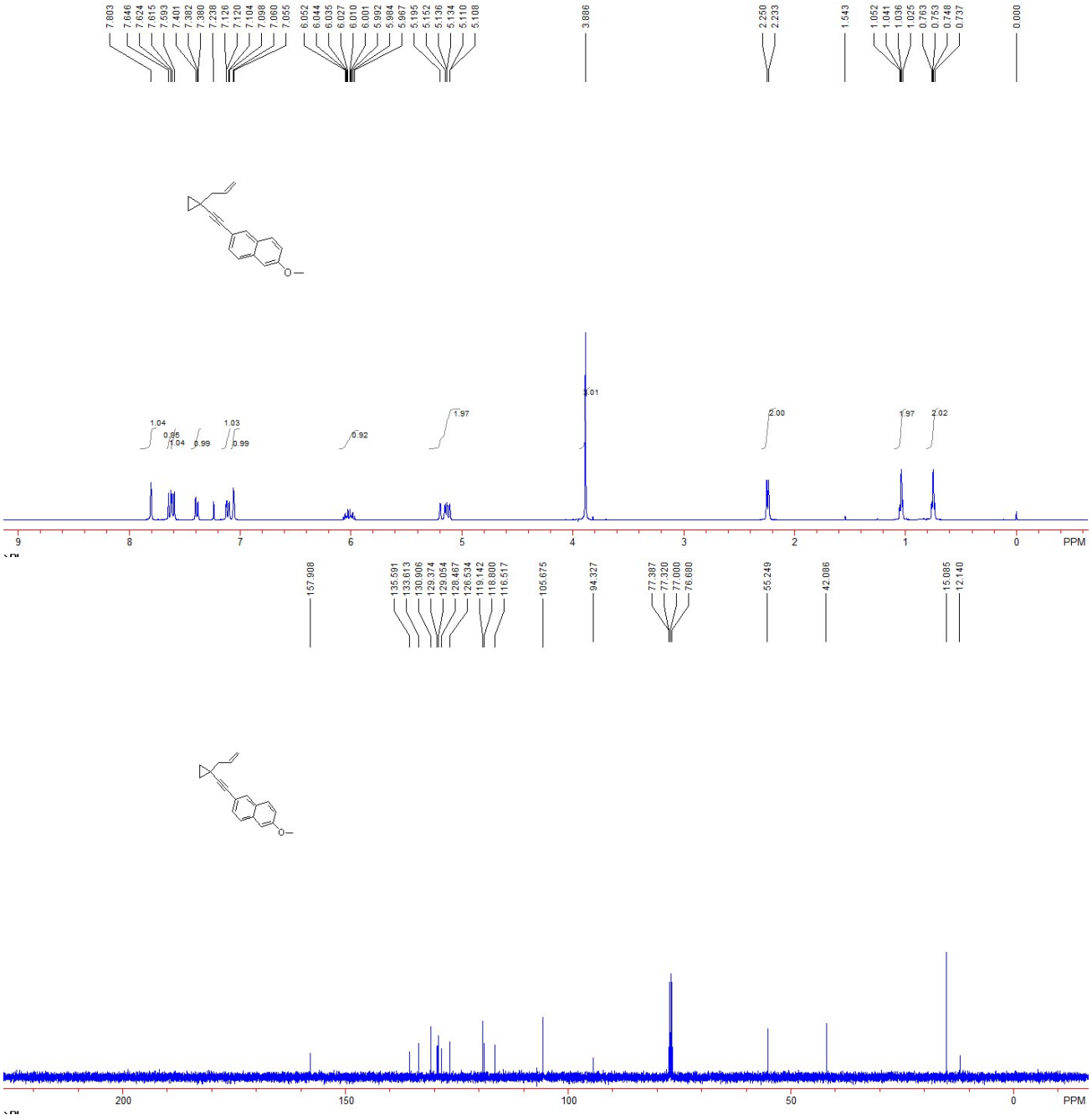
This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.74 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.04 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.29 (d, J = 6.8 Hz, 2H, CH_2), 5.12 (d, J = 10.4 Hz, 1H, =CH_2), 5.17 (d, J = 17.2 Hz, 1H, =CH_2), 5.96-6.06 (m, 1H, =CH), 7.37-7.42 (m, 3H, Ar), 7.67-7.74 (m, 3H, Ar), 7.87 (s, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 15.1, 42.0, 77.4, 95.2, 116.6, 121.2, 126.1, 126.3, 127.5, 127.6, 127.7, 128.8, 131.0, 132.3, 133.0, 135.5.

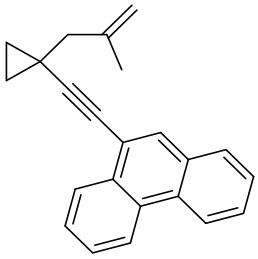


2-((1-Allylcyclopropyl)ethynyl)-6-methoxynaphthalene 1q:

This is a known compound.[5] A white solid. Mp: 90-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.75 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.04 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.24 (d, *J*

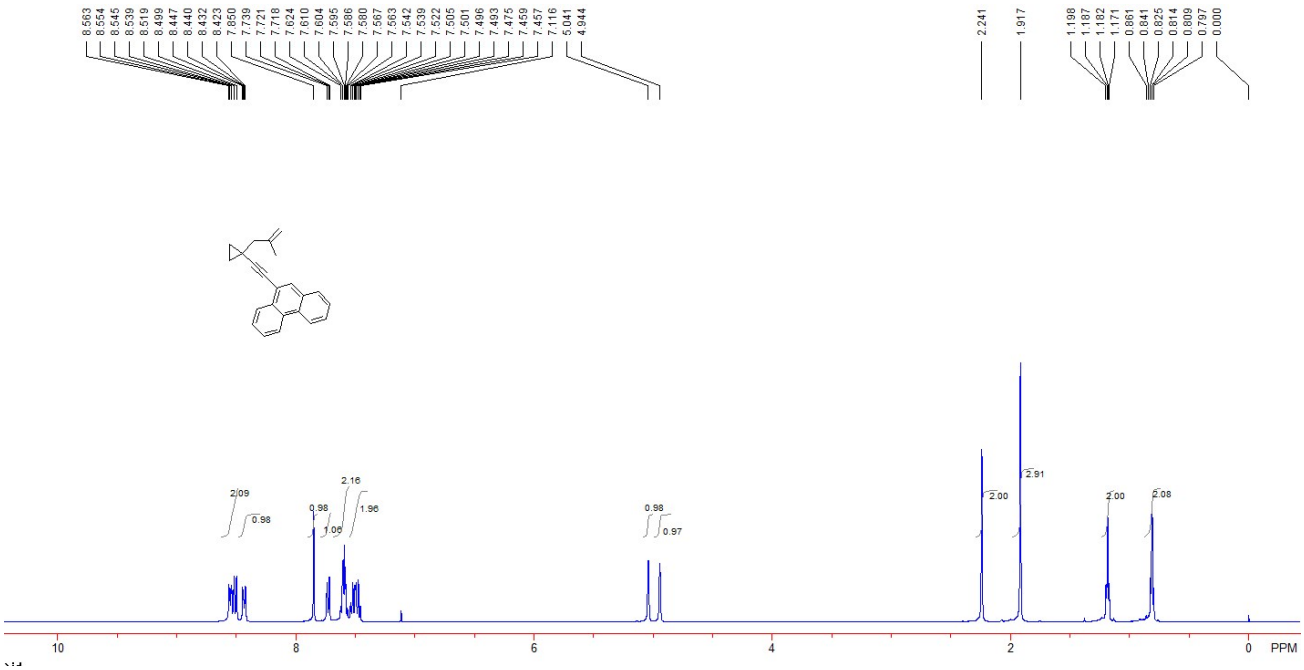
= 6.8 Hz, 2H, CH_2), 3.89 (s, 3H, CH_3), 5.12 (dd, J_1 = 10.4 Hz, J_2 =0.8 Hz, 1H, =CH_2), 5.17 (d, J = 17.2 Hz, 1H, =CH_2), 5.97-6.05 (m, 1H, =CH), 7.06 (d, J = 2.0 Hz, 1H, Ar), 7.11 (dd, J_1 = 8.8 Hz, J_2 =2.4 Hz, 1H, Ar), 7.38-7.40 (m, 1H, Ar), 7.60 (d, J = 8.8 Hz, 1H, Ar), 7.64 (d, J = 8.8 Hz, 1H, Ar), 7.80 (s, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 12.1, 15.1, 42.1, 55.2, 77.4, 94.3, 105.7, 116.5, 118.8, 119.1, 126.5, 128.5, 129.1, 130.9, 133.6, 135.6, 157.9.

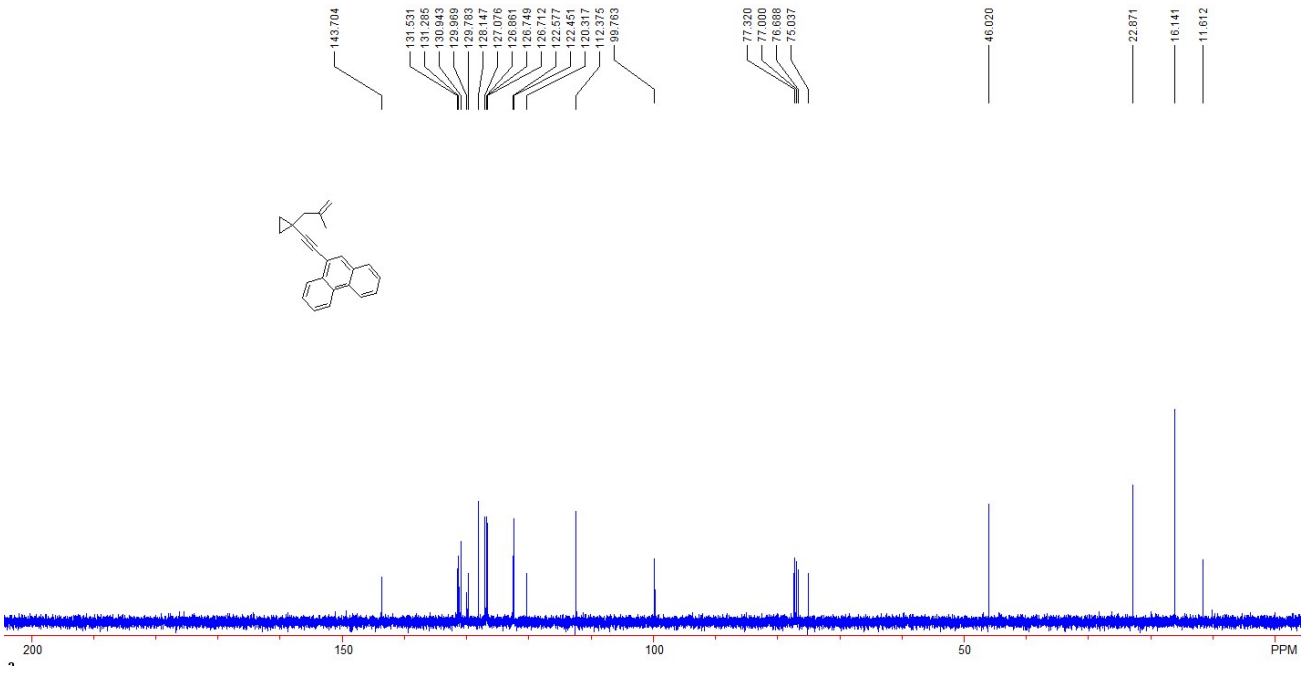


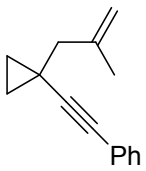


9-((1-(2-Methylallyl)cyclopropyl)ethynyl)phenanthrene 1r:

This is a known compound.[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.80-0.86 (m, 2H, CH_2), 1.18 (dd, J_1 = 6.4 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.92 (s, 3H, CH_3), 2.24 (s, 2H, CH_2), 4.94 (s, 1H, =CH_2), 5.04 (s, 1H, =CH_2), 7.46-7.57 (m, 2H, Ar), 7.58-7.62 (m, 2H, Ar), 7.72-7.74 (m, 1H, Ar), 7.85 (s, 1H, Ar), 8.44 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 1H, Ar), 8.50-8.56 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.6, 16.1, 22.9, 46.0, 75.0, 99.8, 112.4, 120.3, 122.5, 122.6, 126.71, 126.75, 126.9, 127.1, 128.1, 129.8, 130.0, 130.9, 131.3, 131.5, 143.7.

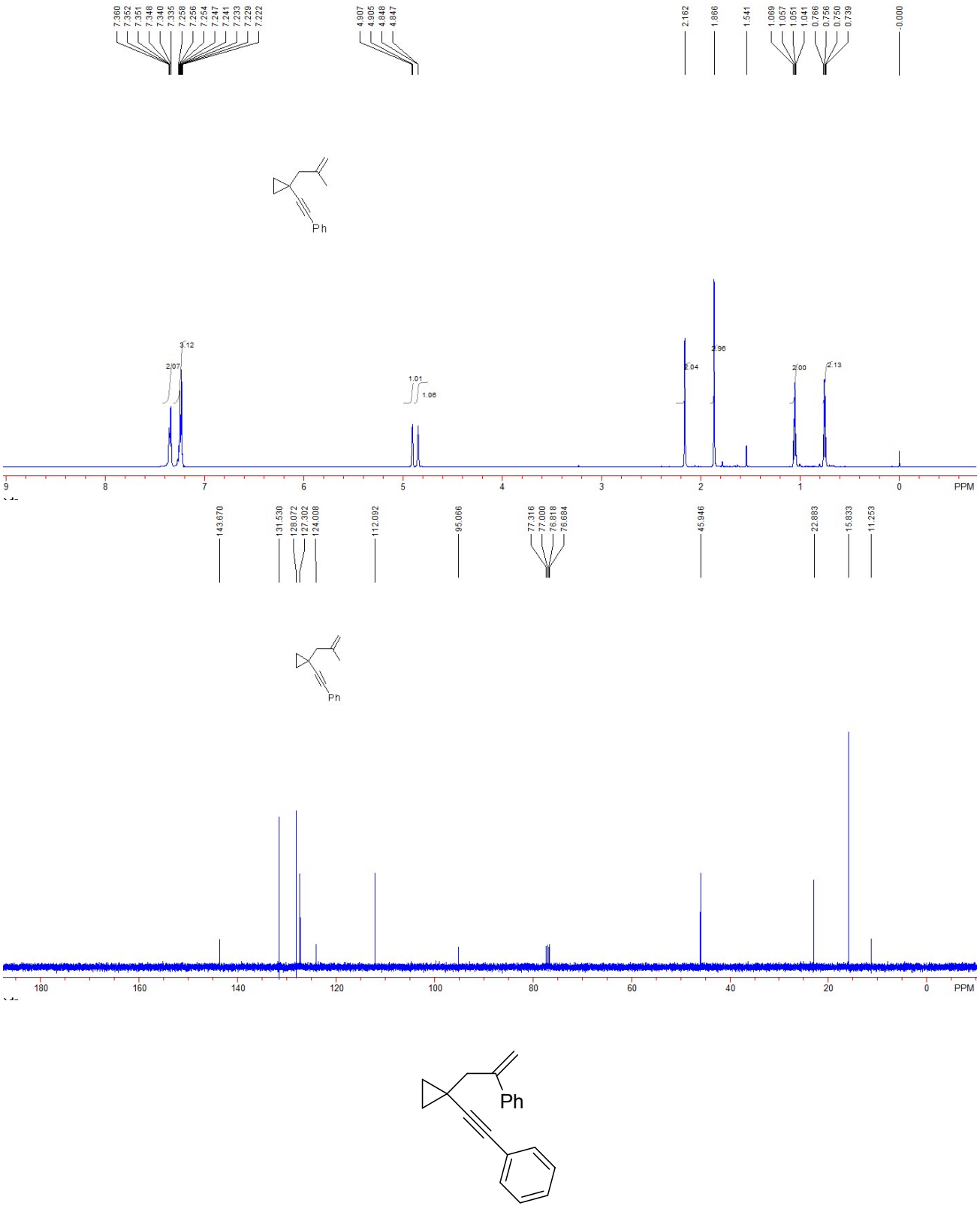






((1-(2-methylallyl)cyclopropyl)ethynyl)benzene 1s:

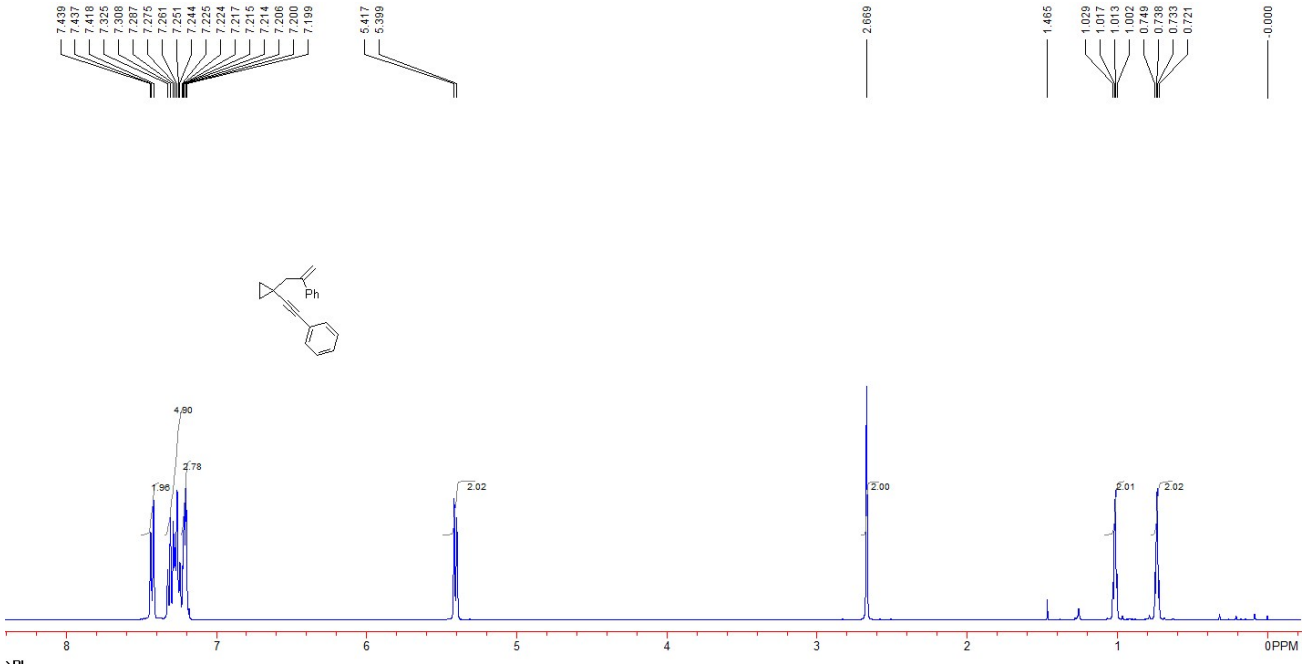
0.749 g, yield = 83%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.75 (dd, J_1 = 6.4 Hz, J_2 = 4.0 Hz, 2H, CH_2), 1.05 (dd, J_1 = 6.4 Hz, J_2 = 4.0 Hz, 2H, CH_2), 1.87 (s, 3H, CH_3), 2.16 (s, 2H, CH_2), 4.85 (d, J = 0.8 Hz, 1H, =CH), 4.91 (d, J = 0.8 Hz, 1H, =CH), 7.22-7.26 (m, 3H, Ar), 7.34-7.36 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.3, 15.8, 22.9, 45.9, 76.8, 95.1, 112.1, 124.0, 127.3, 128.1, 131.5, 143.7. IR (CH_2Cl_2) ν 3079, 2927, 2226, 1598, 1492, 1026, 890, 754, 691 cm^{-1}. MS (%) m/e 196 (M^+, 9.10), 181 (100.00), 165 (63.64), 141 (52.45), 115 (94.28), 91 (29.40), 77 (29.25), 63 (17.85), 51 (12.74). HRMS (EI) calcd. for $C_{15}H_{16}$: 196.1252, found: 196.1256.

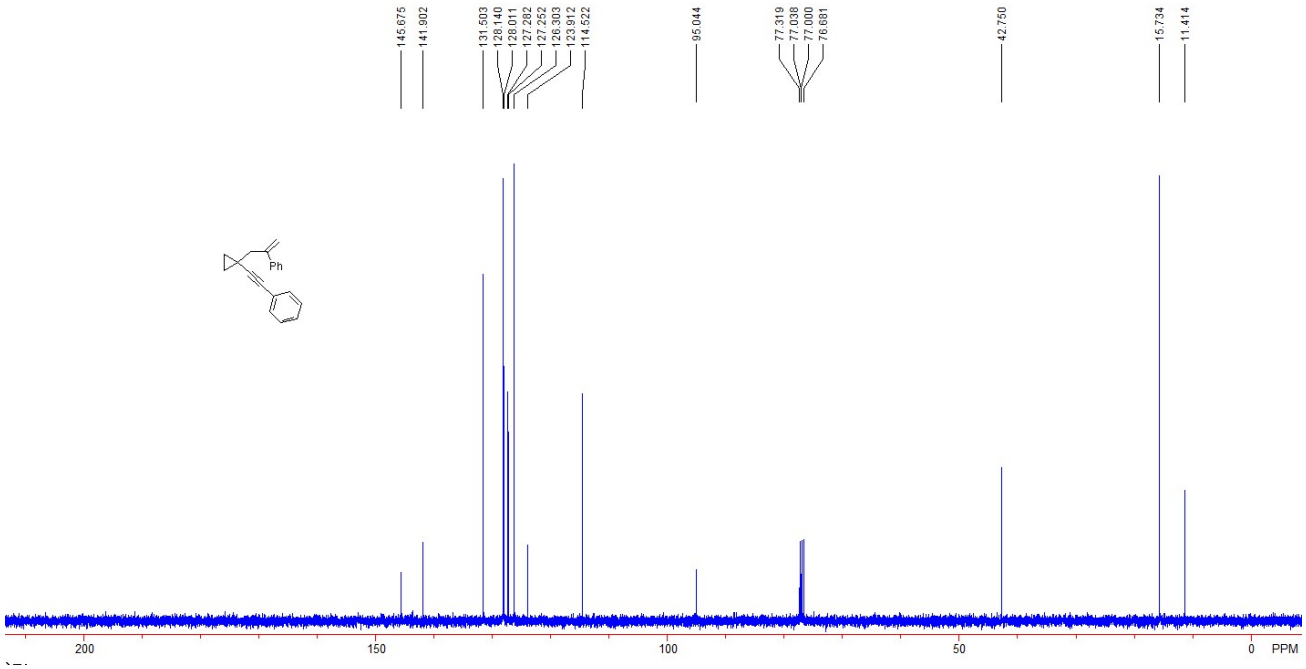


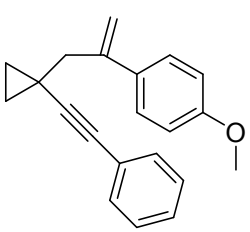
((1-(2-Phenylallyl)cyclopropyl)ethynyl)benzene 1t:

0.539 g, yield = 69%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.74 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.02 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.67 (s, 2H, CH_2), 5.40 (s, 1H, =CH_2), 5.42 (s, 1H, =CH_2), 7.20-7.23 (m, 3H, Ar), 7.24-7.33 (m, 5H, Ar), 7.42-7.44 (m, 2H, Ar). ^{13}C

NMR (100 MHz, $CDCl_3$, TMS): δ 11.4, 15.7, 42.8, 77.3, 95.0, 114.5, 123.9, 126.3, 127.25, 127.28, 128.0, 128.1, 131.5, 141.9, 145.7. IR (CH_2Cl_2) ν 3080, 3007, 2923, 1597, 1493, 898, 754, 690 cm^{-1}. MS (%) m/e 258 (M^+, 32.55), 243 (36.29), 228 (39.09), 215 (23.18), 154 (38.19), 141 (46.11), 115 (100.00), 91 (61.78), 77 (54.03). HRMS (EI) calcd. for $C_{20}H_{18}$: 258.1409, found: 258.1406.

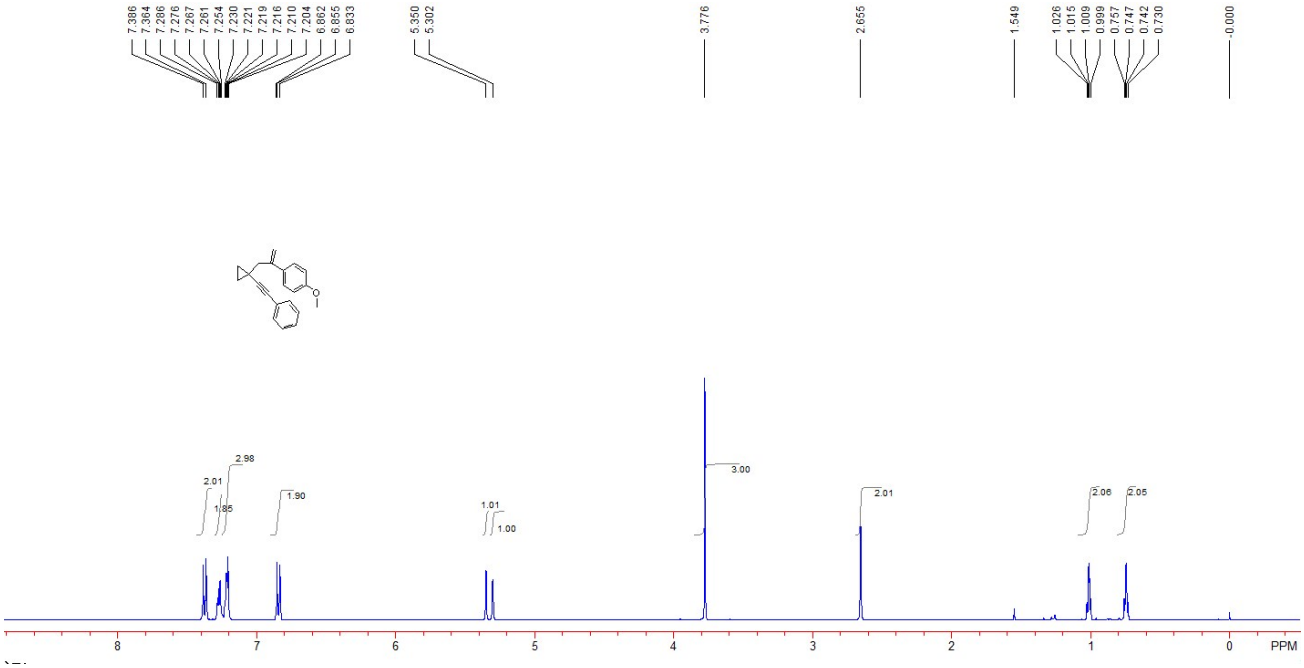


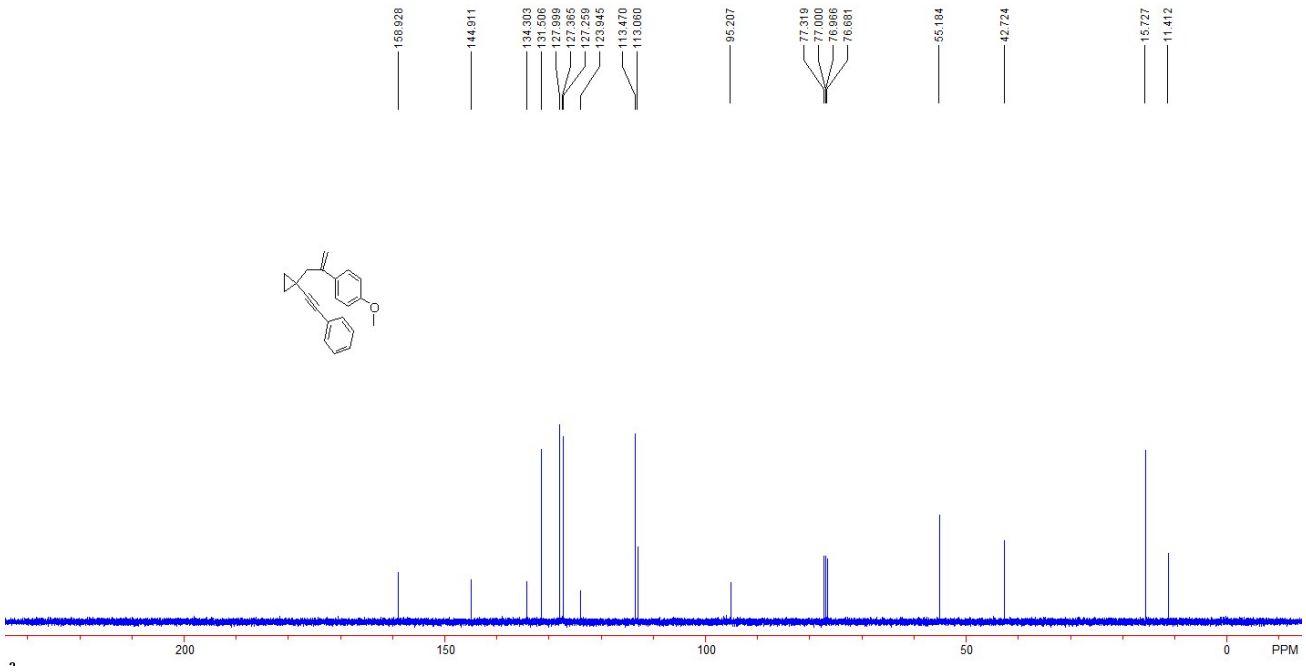


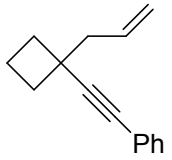


1-Methoxy-4-(3-(1-(phenylethynyl)cyclopropyl)prop-1-en-2-yl)benzene 1u:

0.769 g, yield = 70%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.74 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 1.01 (dd, J_1 = 6.8 Hz, J_2 = 4.4 Hz, 2H, CH_2), 2.66 (s, 2H, CH_2), 3.78 (s, 3H, CH_3), 5.30 (s, 1H, =CH_2), 5.35 (s, 1H, =CH_2), 6.84 (d, J = 8.8 Hz, 2H, Ar), 7.20-7.23 (m, 3H, Ar), 7.25-7.29 (m, 2H, Ar), 7.38 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.4, 15.7, 42.7, 55.2, 77.0, 95.2, 113.1, 113.5, 123.9, 127.3, 127.4, 128.0, 131.5, 134.3, 144.9, 158.9. IR (CH_2Cl_2) ν 3077, 2931, 2835, 1606, 1511, 1245, 1179, 1031, 833, 755 cm^{-1}. MS (%) m/e 288 (M^+, 75.58), 273 (32.47), 257 (37.45), 215 (31.69), 184 (30.84), 165 (30.14), 141 (43.55), 115 (100.00), 91 (51.58). HRMS (EI) calcd. for $C_{21}H_{20}O$: 288.1514, found: 288.1511.

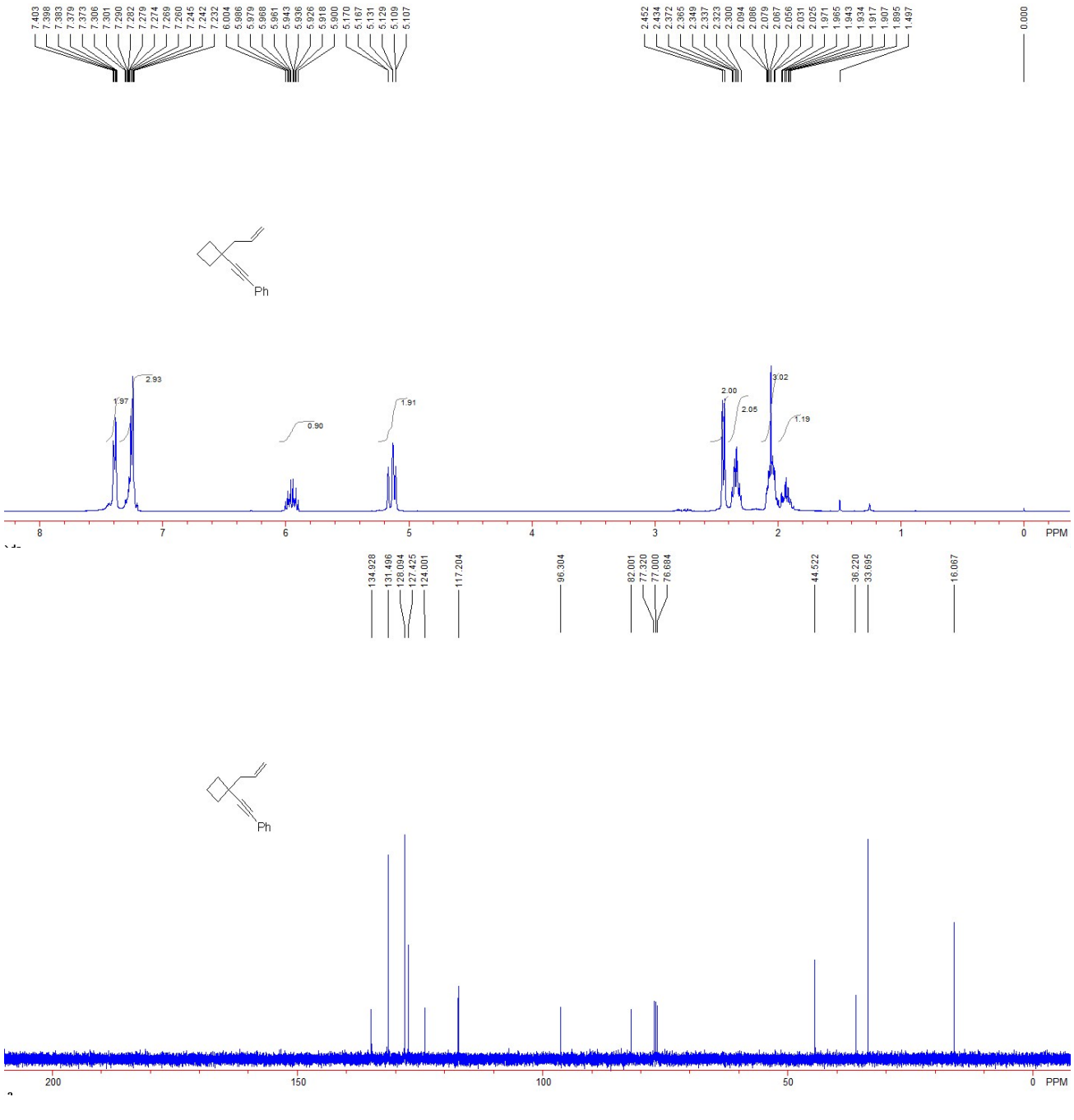






((1-Allylcyclobutyl)ethynyl)benzene 2a:

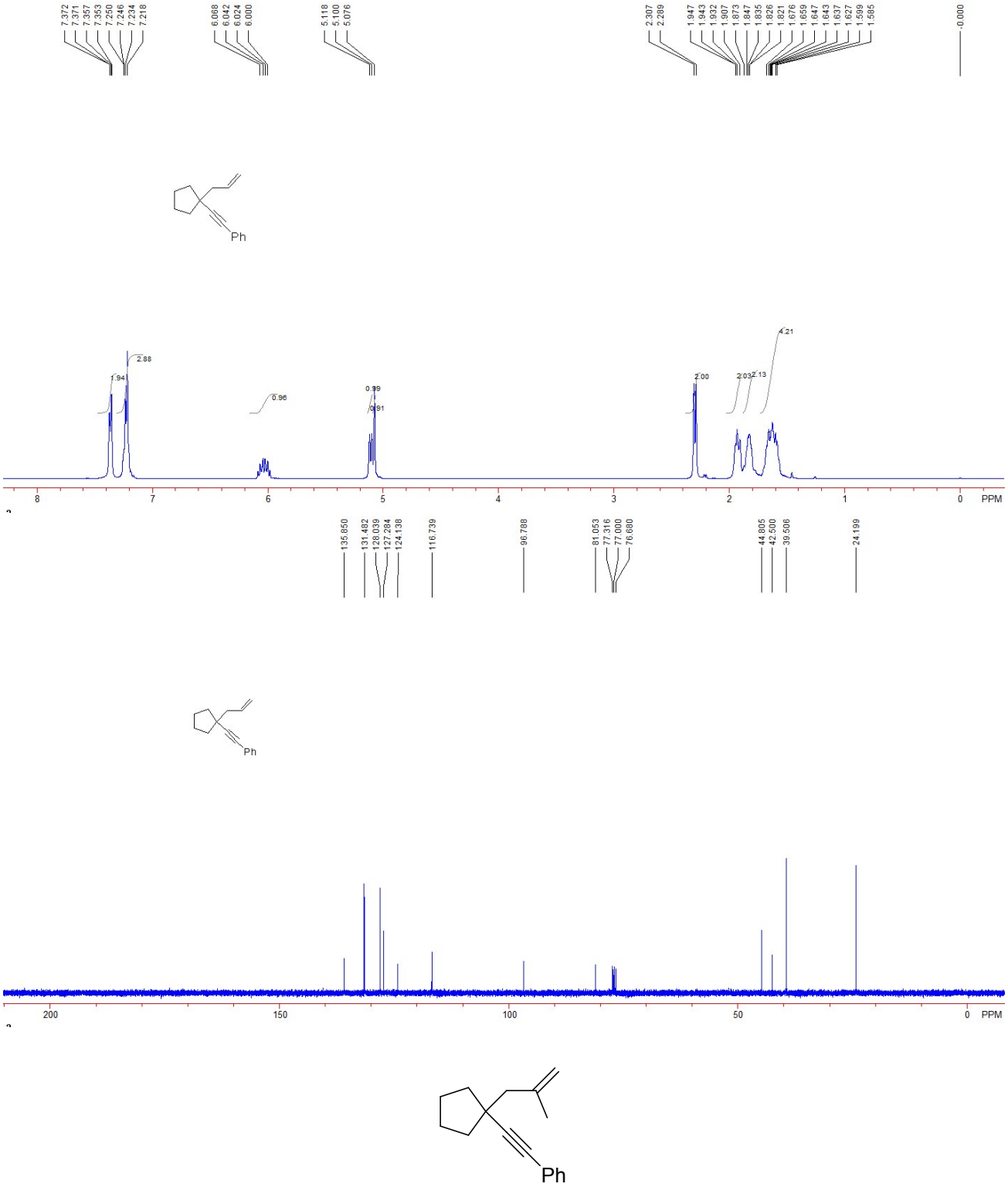
0.498 g, yield = 25%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.90-1.97 (m, 1H, CH_2), 2.03-2.10 (m, 3H, CH_2), 2.03-2.10 (m, 3H, CH_2), 2.30-2.37 (m, 2H, CH_2), 2.44 (d, J = 7.2 Hz, 2H, CH_2), 5.12 (dd, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H, =CH_2), 5.15 (dd, J_1 = 15.6 Hz, J_2 = 0.8 Hz, 1H, =CH_2), 5.90-6.00 (m, 1H, =CH), 7.23-7.31 (m, 3H, Ar), 7.37-7.40 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.1, 33.7, 36.2, 44.5, 82.0, 96.3, 117.2, 124.0, 127.4, 128.1, 131.5, 134.9. IR (CH_2Cl_2) ν 3078, 2981, 2850, 1492, 991, 912, 754, 689 cm^{-1}. MS (%) m/e 196 (M^+, 4.66), 167 (100.00), 153 (43.15), 127 (69.71), 115 (21.51), 77 (35.82), 63 (7.30), 51 (8.19), 41 (5.06). HRMS (EI) calcd. for $C_{15}H_{16}$: 196.1252, found: 196.1247.



((1-Allylcyclopentyl)ethynyl)benzene 2b:

0.497 g, yield = 28%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.59-1.67 (m, 4H, CH_2), 1.82-1.97 (m, 2H, CH_2), 1.91-1.95 (m, 2H, CH_2), 2.30 (d, J = 7.2 Hz, 2H, CH_2), 5.09 (d, J = 9.6 Hz, 1H, =CH_2), 5.10 (d, J = 16.8 Hz, 1H, =CH_2), 6.00-6.07 (m, 1H, =CH), 7.22-7.25 (m, 3H, Ar), 7.35-7.37 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.2, 39.5, 42.5, 44.8, 81.1, 96.8, 116.7,

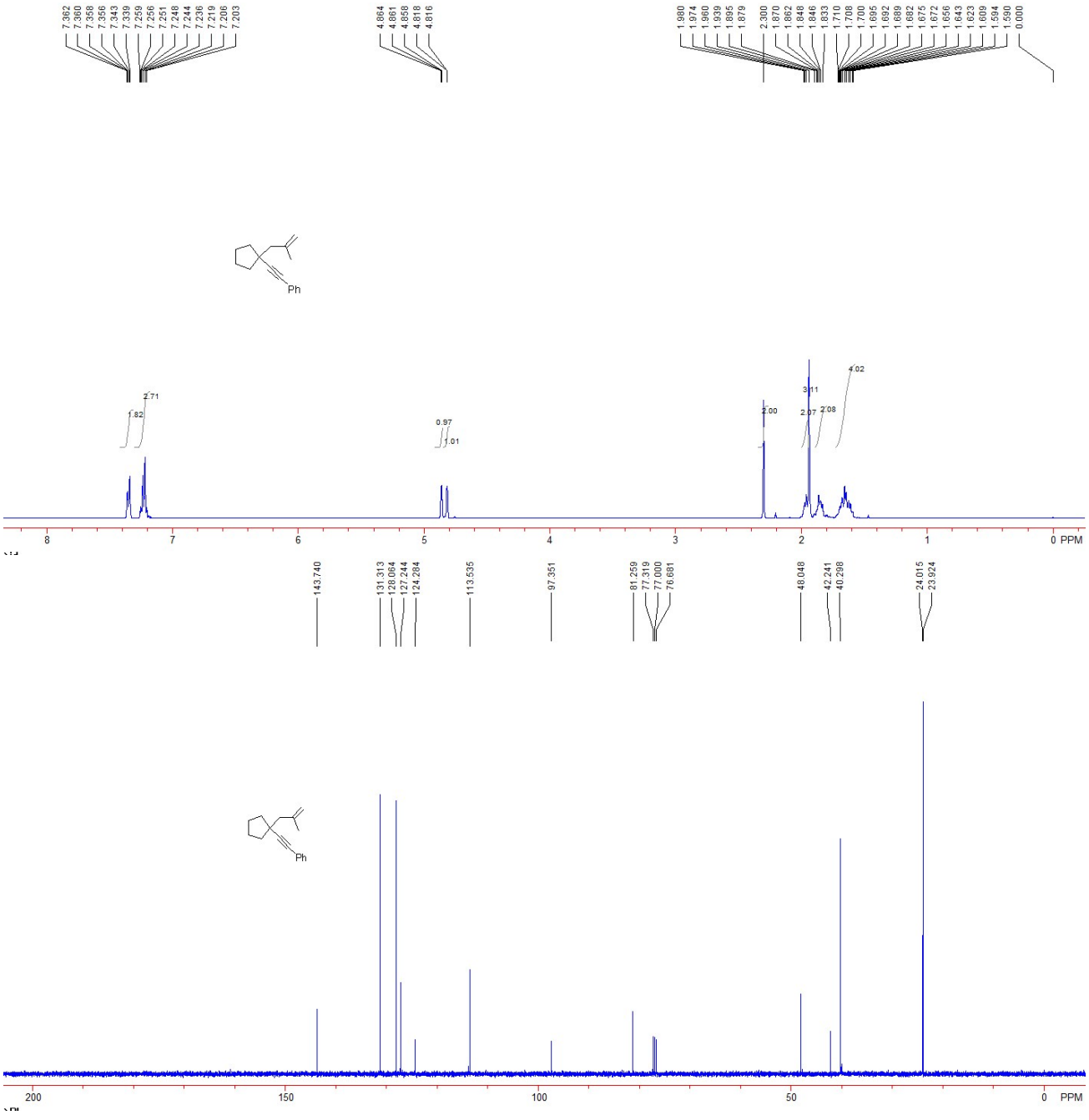
124.1, 127.3, 128.0, 131.5, 135.9. IR (CH_2Cl_2) ν 3077, 2958, 2870, 1491, 1442, 995, 911 cm^{-1}. MS (%) m/e 210 (M^+, 2.10), 169 (100.00), 154 (19.91), 141 (65.07), 128 (26.14), 115 (54.80), 91 (88.75), 77 (19.57). HRMS (EI) calcd. for $C_{16}H_{18}$: 210.1409, found: 210.1404.

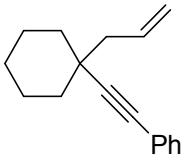


((1-(2-Methylallyl)cyclopentyl)ethynyl)benzene 2c:

0.794 g, yield = 35%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.59-1.71 (m, 4H, CH_2),

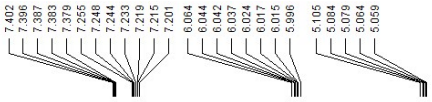
1.83-1.90 (m, 2H, CH_2), 1.94 (s, 3H, CH_3), 1.96-1.98 (m, 2H, CH_2), 2.30 (s, 2H, CH_2), 4.82 (d, J = 0.8 Hz, 1H, =CH_2), 4.81-4.82 (m, 1H, =CH_2), 4.85-4.86 (m, 1H, =CH_2), 7.20-7.26 (m, 3H, Ar), 7.34-7.36 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 23.9, 24.0, 40.3, 42.2, 48.0, 81.3, 97.4, 113.5, 124.3, 127.2, 128.1, 131.3, 143.7. IR (CH_2Cl_2) ν 3074, 2959, 2871, 1643, 1491, 1442, 889, 753, 690 cm^{-1}. MS (%) m/e 224 (M^+, 2.92), 196 (30.09), 169 (48.60), 154 (25.73), 141 (86.34), 115 (81.88), 106 (19.98), 91 (100.00), 77 (17.85). HRMS (EI) calcd. for $C_{17}H_{20}$: 224.1565, found: 224.1559.

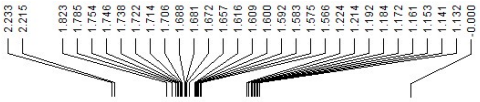


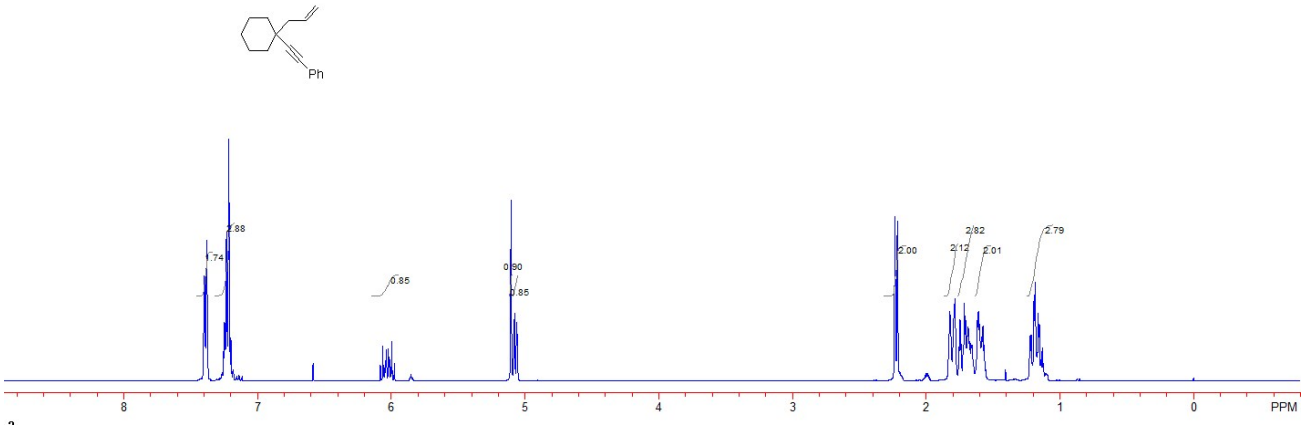


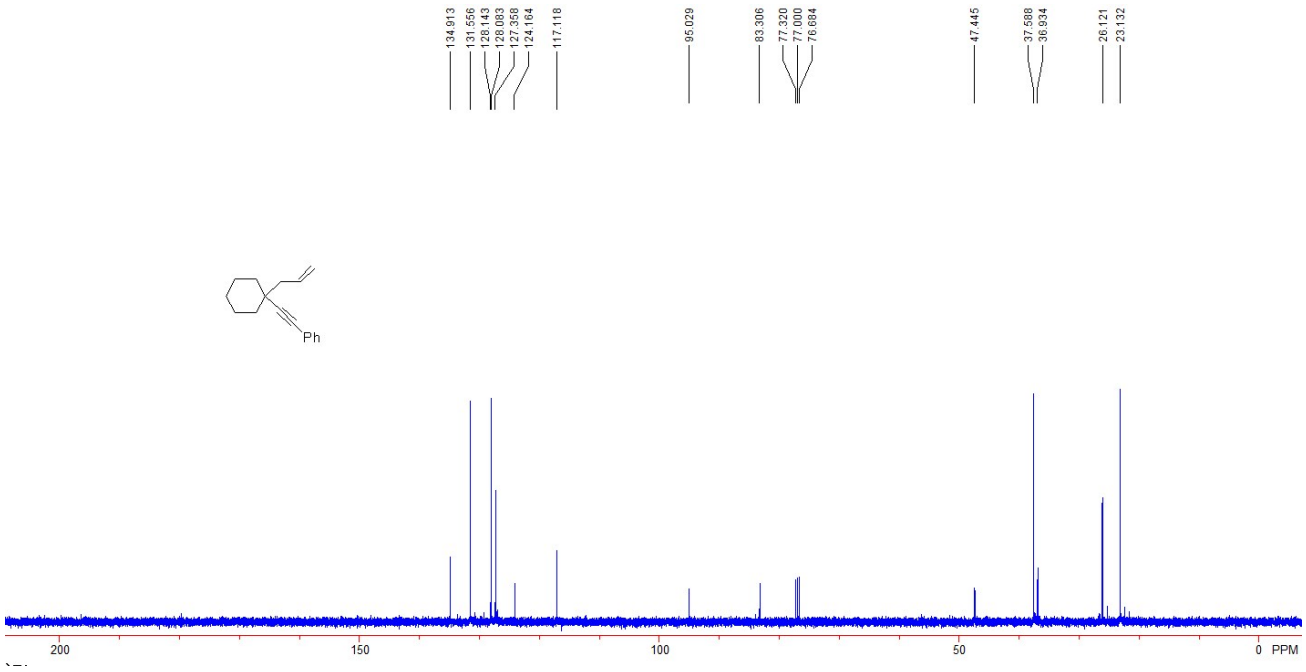
((1-Allylcyclohexyl)ethynyl)benzene 2d:

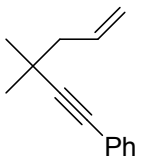
This is a known compound.[6] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13-1.22 (m, 3H, CH_2), 1.57-1.66 (m, 2H, CH_2), 1.67-1.69 (m, 3H, CH_2), 1.71-1.74 (m, 2H, CH_2), 2.22 (d, J = 7.2 Hz, 2H, CH_2), 5.08 (d, J = 18.4 Hz, 1H, =CH_2), 5.09 (d, J = 10.4 Hz, 1H, =CH_2), 6.00-6.06 (m, 1H, =CH), 7.20-7.25 (m, 3H, Ar), 7.26-7.40 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 23.1, 26.1, 36.9, 47.4, 83.3, 95.0, 117.1, 124.2, 127.4, 128.1, 131.6, 134.9.





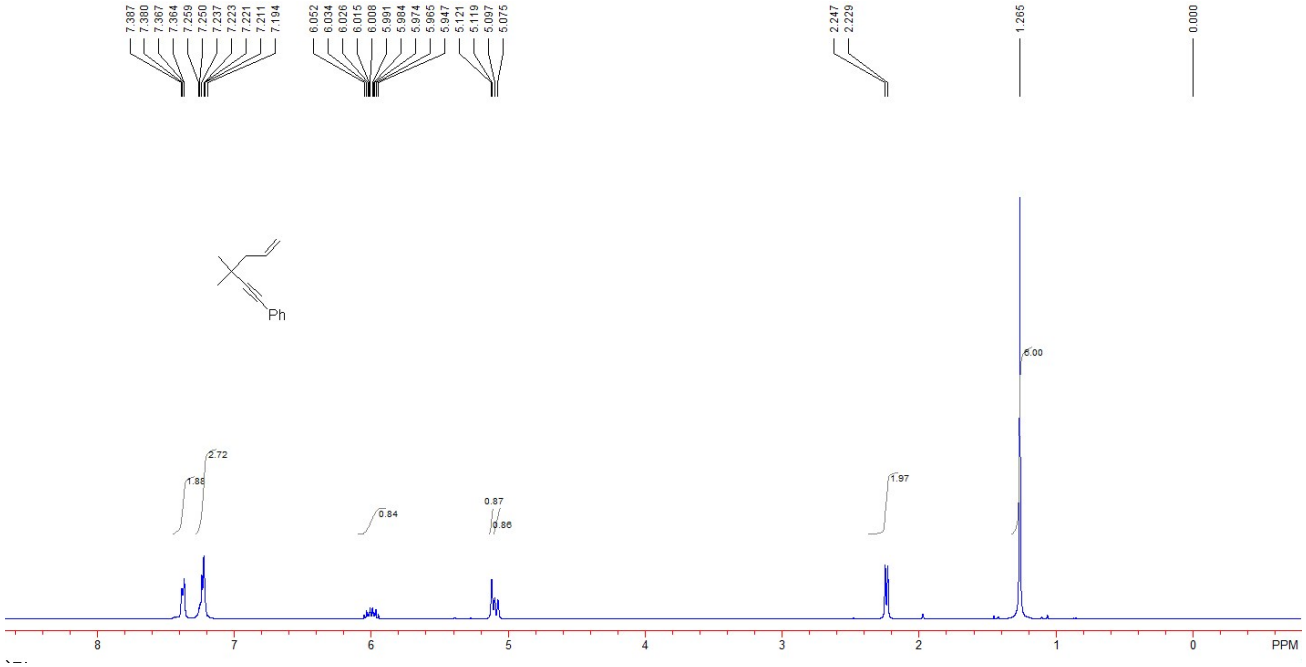


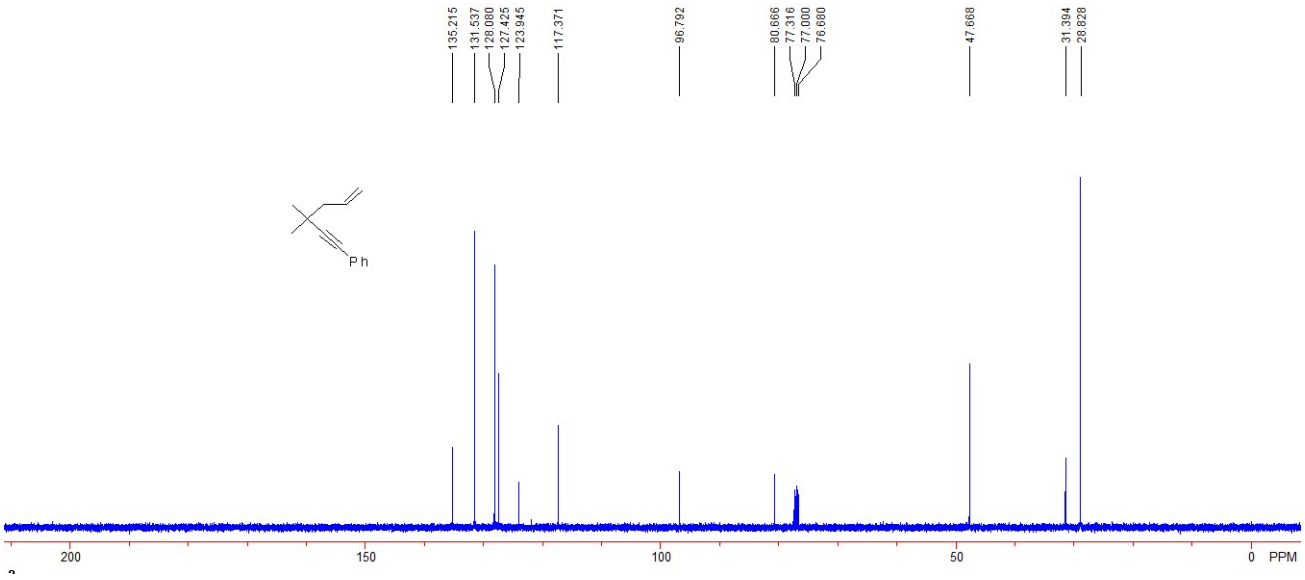


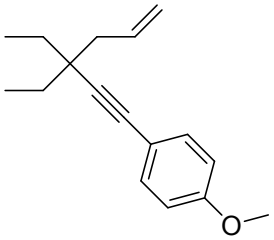


(3,3-Dimethylhex-5-en-1-yn-1-yl)benzene 2e:

This is a known compound.[7] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (m, 6H, CH_3), 2.24 (d, J = 7.2 Hz, 2H, CH_2), 5.10 (d, J = 18.4 Hz, 1H, =CH_2), 5.11 (d, 9.2 Hz, 1H, =CH_2), 5.95-6.05 (m, 1H, =CH), 7.19-7.26 (m, 3H, Ar), 7.36-7.39 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 28.8, 31.4, 47.7, 80.7, 96.8, 117.4, 123.9, 127.4, 128.1, 131.5, 135.2.

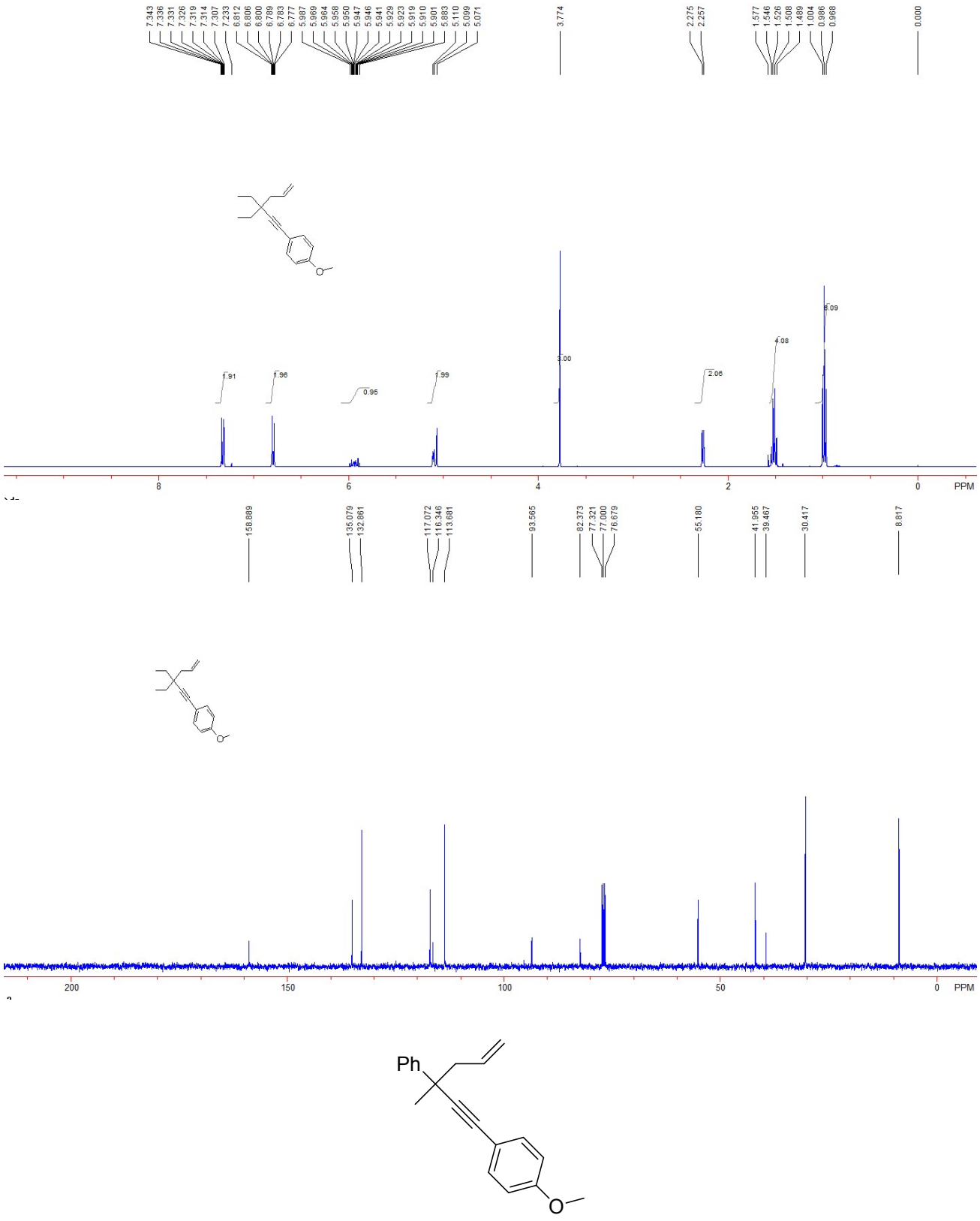






1-(3,3-Diethylhex-5-en-1-yn-1-yl)-4-methoxybenzene 2f:

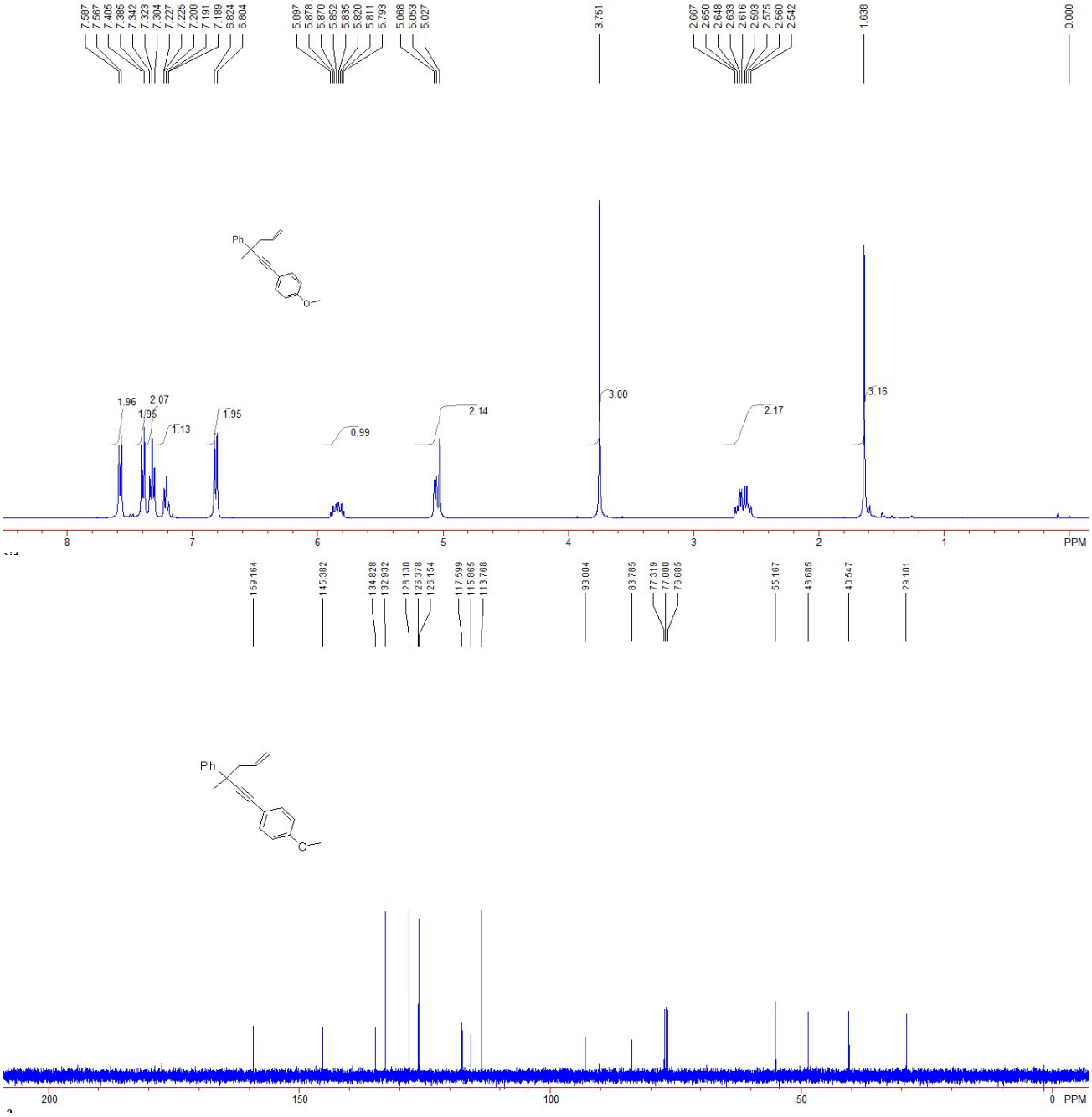
0.402 g, yield = 52%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.99 (t, *J* = 7.2 Hz, 6H, CH_3), 1.52 (q, *J* = 7.2 Hz, 4H, CH_2), 2.27 (d, *J* = 7.2 Hz, 2H, CH_2), 3.77 (s, 3H, CH_3), 5.085 (d, *J* = 11.2 Hz, 1H, =CH_2), 5.091 (d, *J* = 15.6 Hz, 1H, =CH_2), 5.88-5.99 (m, 1H, =CH), 6.78-6.81 (m, 2H, Ar), 7.31-7.34 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 8.8, 39.5, 42.0, 55.2, 82.4, 93.6, 113.7, 116.3, 117.1, 132.9, 135.1, 158.9. IR (CH_2Cl_2) ν 3074, 2966, 2836, 1606, 1508, 1244, 1034, 912, 829 cm^{-1}. MS (%) m/e 242 (M^+, 11.09), 201 (100.00), 186 (6.40), 172 (12.79), 159 (14.04), 145 (31.97), 128 (17.43), 115 (12.03), 91 (7.50). HRMS (EI) calcd. for $C_{17}H_{22}O$: 242.1671, found: 242.1667.

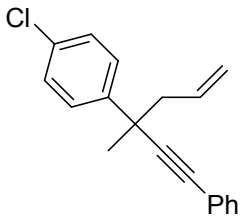


1-Methoxy-4-(3-methyl-3-phenylhex-5-en-1-yn-1-yl)benzene 2g:

1.038 g, yield = 80%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64 (s, 3H, CH_3), 2.54-2.67 (m, 2H, CH_2), 3.75 (s, 3H, CH_3), 5.04 (d, J = 10.4 Hz, 1H, =CH_2), 5.05 (d, J = 16.4 Hz, 1H, =CH_2), 5.79-5.90 (m, 1H, =CH), 6.81 (d, J = 8.0 Hz, 2H, Ar), 7.19-7.23 (m, 1H, Ar), 7.32 (dd, J_1 =

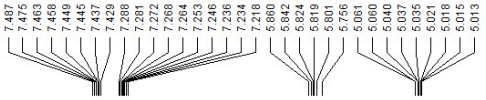
7.6 Hz, J_2 = 7.6 Hz, 2H, Ar), 7.40 (d, J = 8.0 Hz, 2H, Ar), 7.58 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.2, 36.3, 46.1, 47.4, 55.2, 82.9, 93.6, 113.7, 116.1, 117.6, 126.3, 127.6, 130.7, 132.7, 135.1, 138.0, 159.0. IR (CH_2Cl_2) ν 3077, 2976, 2929, 1598, 1490, 1444, 913, 754, 690 cm^{-1}. MS (%) m/e 276 (M^+, 1.98), 235 (100.00), 220 (2.42), 202 (4.10), 191 (5.48), 165 (3.48), 89 (1.79), 77 (2.71). HRMS (EI) calcd. for $C_{20}H_{20}O$: 276.1514, found: 276.1517.

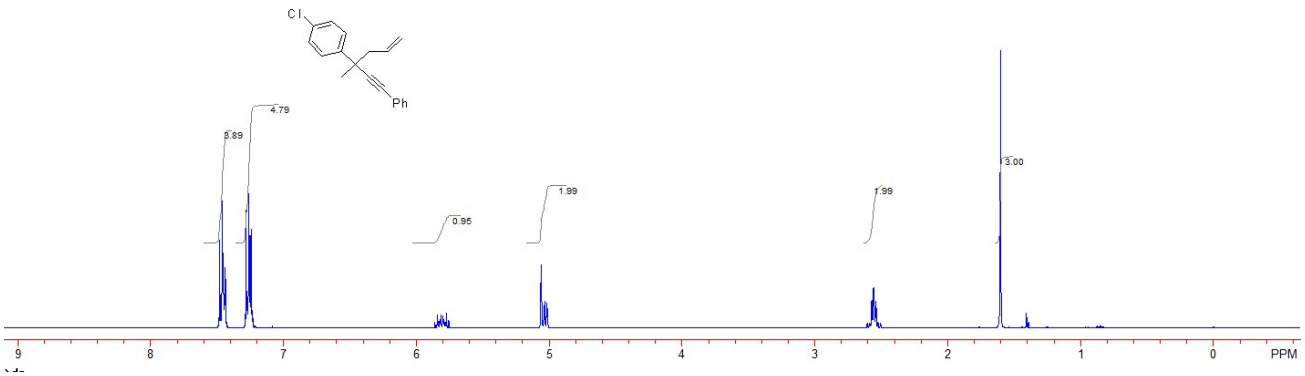


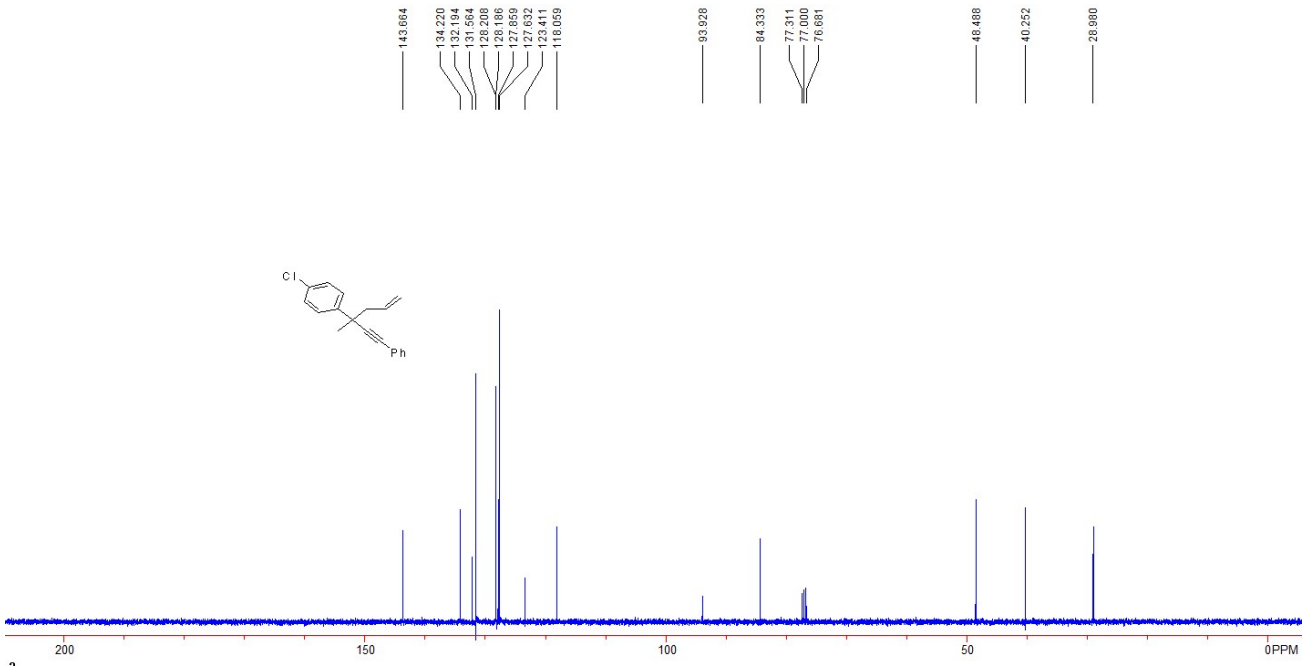


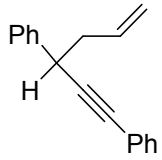
1-Chloro-4-(3-methyl-1-phenylhex-5-en-1-yn-3-yl)benzene 2h:

1.051 g, yield = 94%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.60 (s, 3H, CH_3), 2.51-2.60 (m, 2H, CH_2), 5.01-5.06 (m, 2H, $=CH_2$), 5.76-5.86 (m, 1H, =CH), 7.22-7.29 (m, 5H, Ar), 7.43-7.49 (m, 4H, Ar),. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.0, 40.3, 48.5, 84.3, 93.9, 118.1, 123.4, 127.6, 127.9, 128.2, 131.6, 132.2, 134.2, 143.7. IR (CH_2Cl_2) ν 3078, 2977, 2929, 1489, 1095, 1013, 915, 826, 690 cm^{-1}. MS (%) m/e 280 (M^+, 0.57), 265 (0.18), 239 (100.00), 202 (15.05), 189 (3.54), 127 (15.55), 115 (2.04), 101 (9.45), 77 (5.76). HRMS (EI) calcd. For $C_{19}H_{17}Cl$: 280.1019, found: 280.1013.



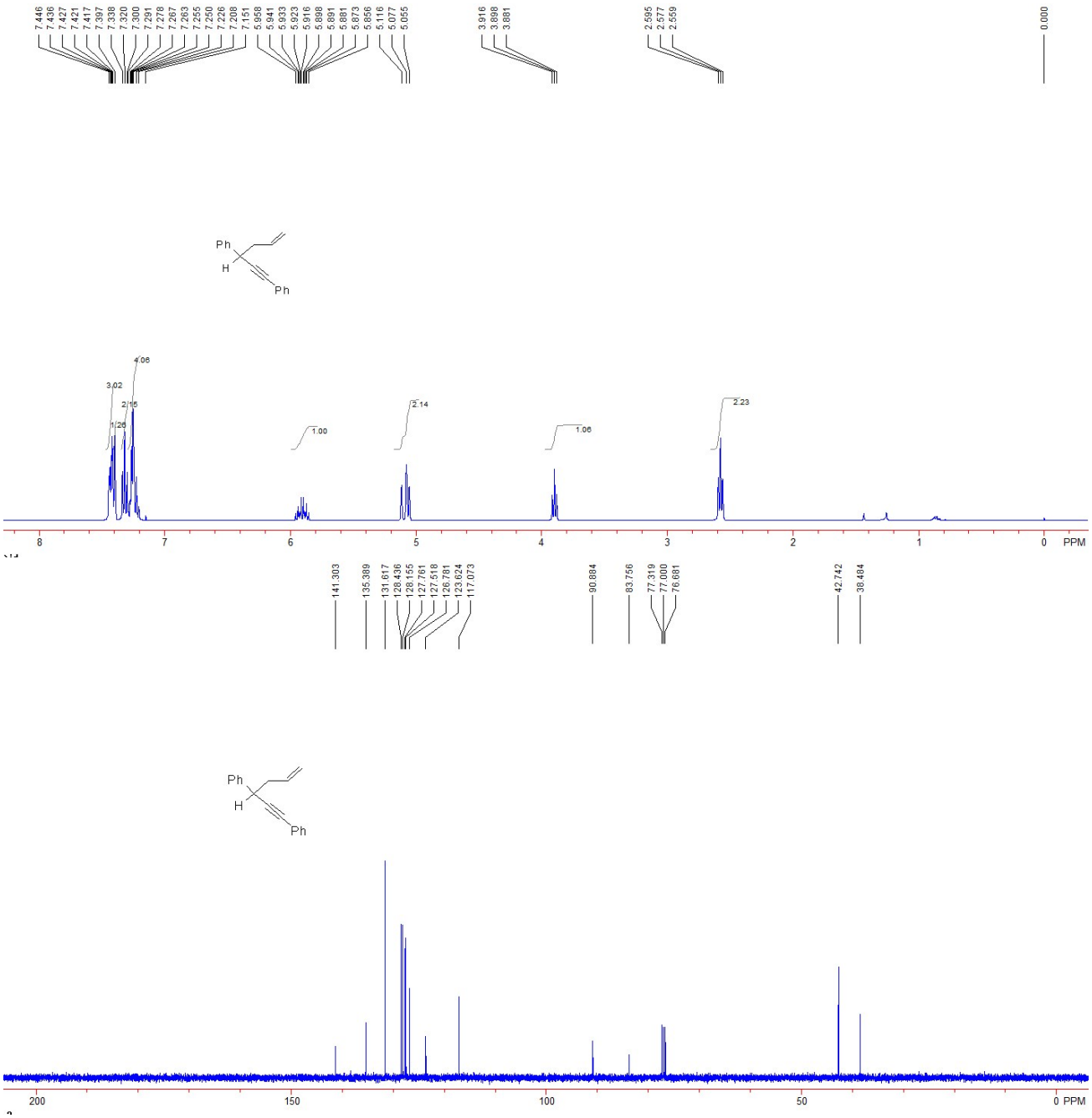


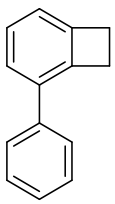




Hex-5-en-1-yne-1,3-diyldibenzene 2i:

This is a known compound.[8] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.58 (t, J = 16.0 Hz, 2H, CH_2), 3.90 (dd, J_1 = 7.2 Hz, J_2 = 6.8 Hz, 1H, CH), 5.07 (d, J = 8.8 Hz, 1H, =CH_2), 5.10 (d, J = 15.6 Hz, 1H, =CH_2), 5.86-5.96 (m, 1H, =CH), 7.15-7.29 (m, 4H, Ar), 7.30-7.34 (m, 2H, Ar), 7.40 (s, 1H, Ar), 7.42-7.44 (m, 3H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 38.5, 42.7, 83.8, 90.9, 117.1, 123.6, 126.8, 127.5, 127.8, 128.2, 128.4, 131.6, 135.4, 141.3.

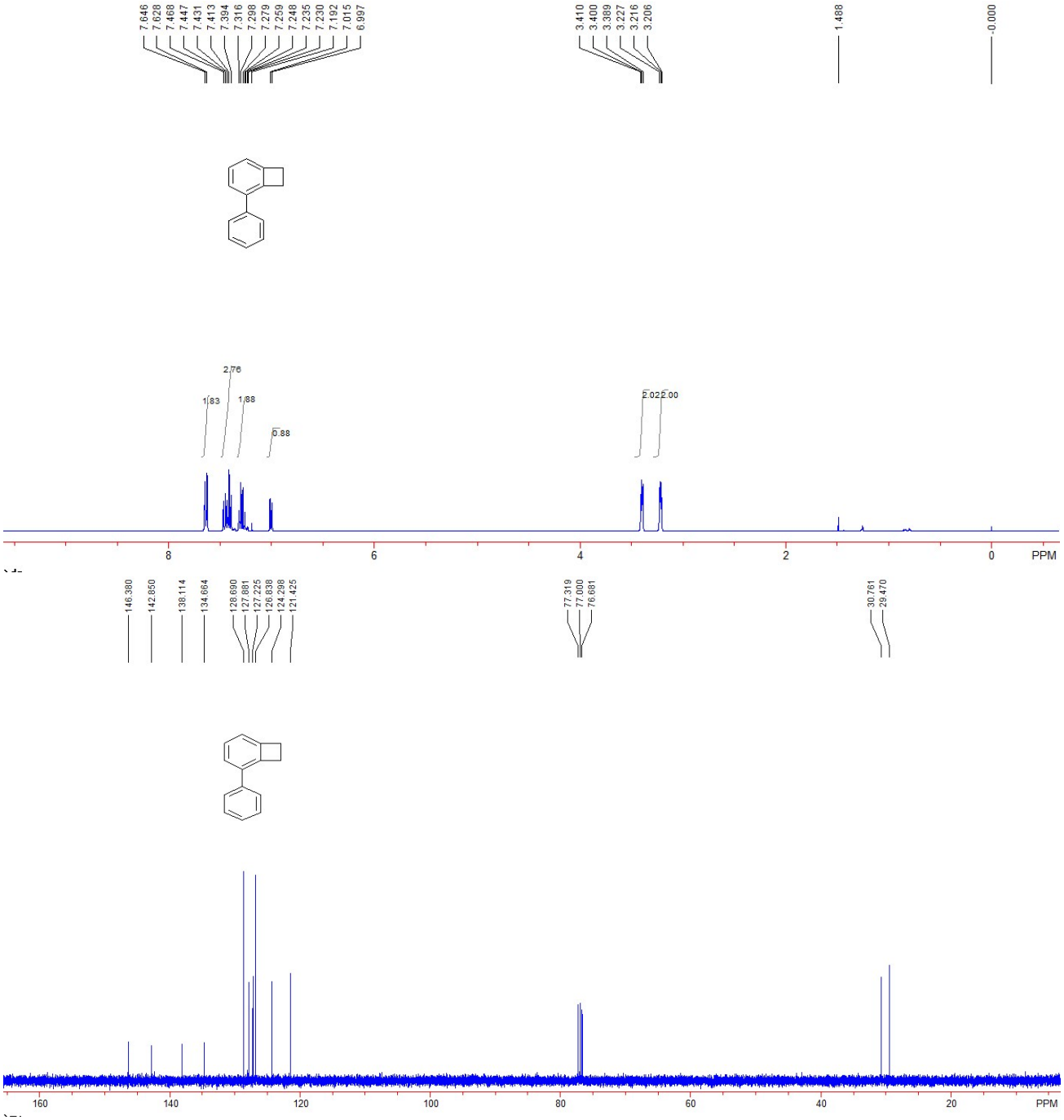


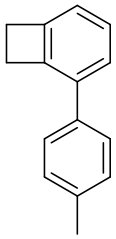


2-Phenylbicyclo[4.2.0]octa-1,3,5-triene 3a:

This is a known compound.[9] 33 mg, yield: 89%. A white solid. Mp: 59-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.22 (d, J = 4.0 Hz, 2H, CH_2), 3.40 (d, J = 4.0 Hz, 2H, CH_2), 7.01 (d, J = 7.2 Hz, 1H, Ar), 7.19-7.32 (m, 2H, Ar), 7.39-7.47 (m, 3H, Ar), 7.64 (d, J = 7.2 Hz, 1H, Ar). ^{13}C NMR (100

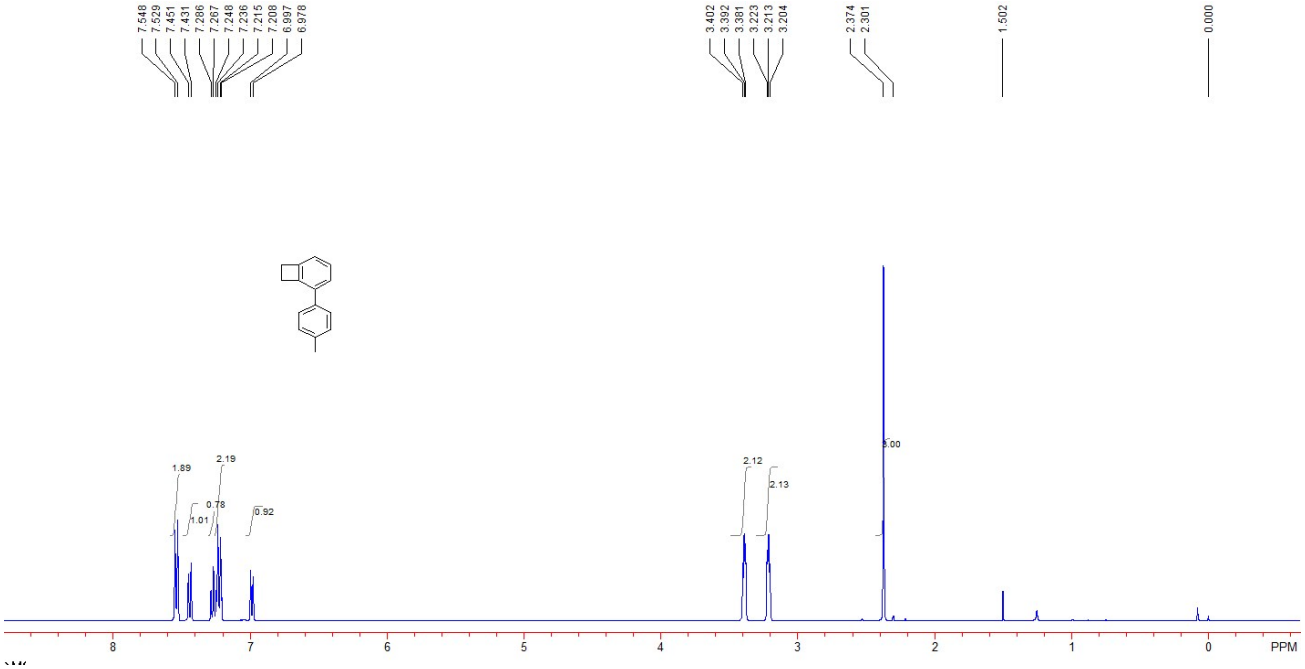
MHz, $CDCl_3$, TMS): δ 29.5, 30.8, 121.4, 124.3, 126.8, 127.2, 127.9, 128.7, 134.7, 138.1, 142.9, 146.4. IR (CH_2Cl_2) ν 3060, 2961, 2921, 1567, 1465, 1410, 793, 775, 740, 685 cm^{-1}. MS (%) m/e 180 (M^+, 63.66), 165 (100.00), 139 (4.29), 115 (6.93), 102 (3.99), 89 (30.91), 76 (31.65), 63 (15.02), 51 (12.99). HRMS (EI) calcd. for $C_{14}H_{12}$: 180.0939, found: 180.0936.

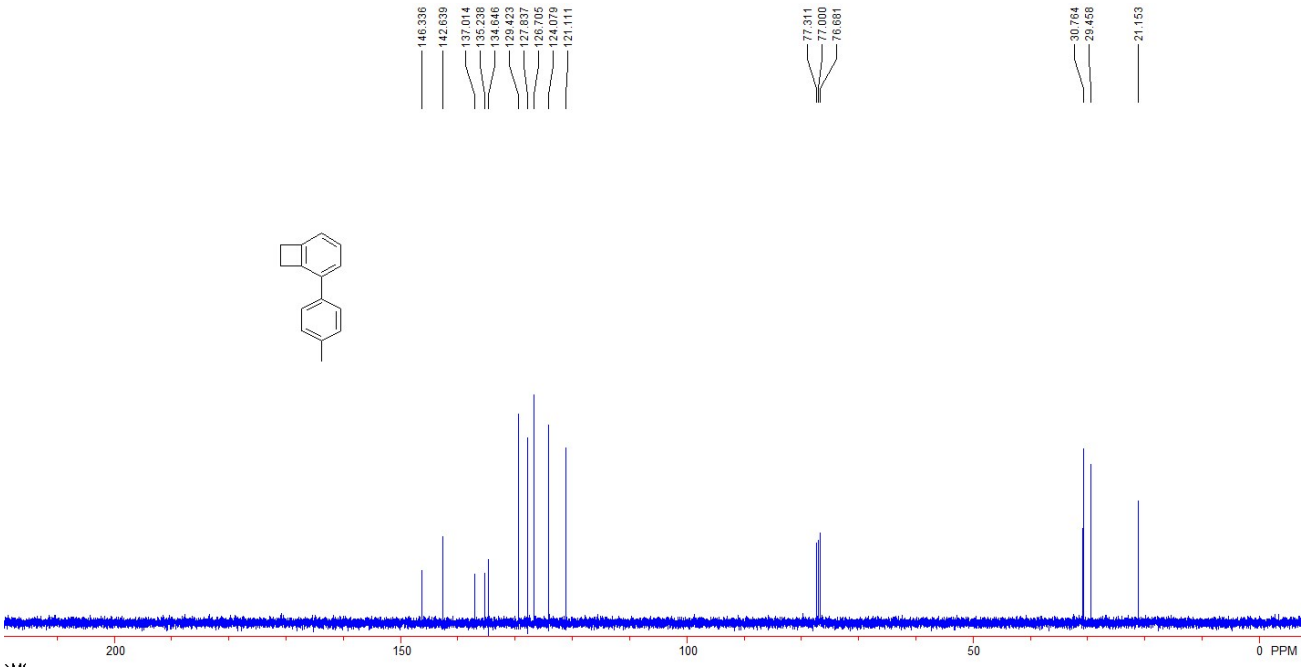




2-(*p*-Tolyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3b:

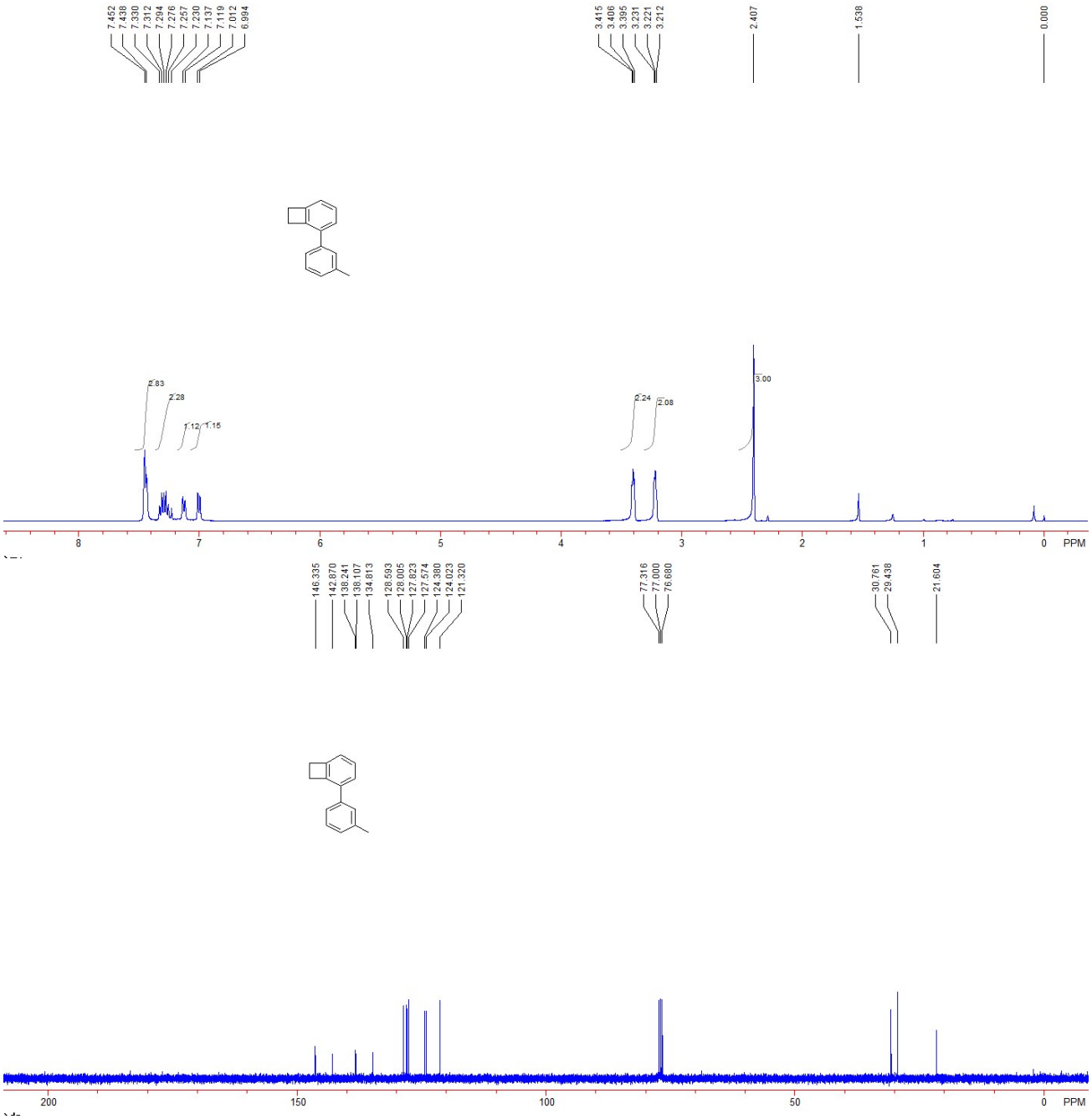
35 mg, yield: 90%. A white solid. Mp: 63-65 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.37 (s, 3H, CH_3), 3.21 (t, J = 4.0 Hz, 2H, CH_2), 3.39 (t, J = 4.0 Hz, 2H, CH_2), 7.00 (d, J = 7.6 Hz), 7.21-7.24 (m, 2H, Ar), 7.27 (dd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.44 (d, J = 8.0 Hz, 1H, Ar), 7.54 (d, J = 7.6 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.2, 29.5, 30.8, 121.1, 124.1, 126.7, 127.8, 129.4, 134.6, 135.2, 137.0, 142.6, 146.3. IR (CH_2Cl_2) ν 3023, 2920, 2861, 1519, 1468, 822, 782, 757 cm^{-1}. MS (%) m/e 194 (M^+, 63.29), 179 (100.00), 165 (6.61), 152 (8.82), 115 (4.00), 89 (16.41), 76 (10.09), 51 (3.58). HRMS (EI) calcd. for $C_{15}H_{14}$: 194.1096, found: 194.1092.

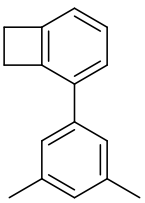




2-(M-tolyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3c:

34 mg, yield: 87%. A white solid. Mp: 63-65 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.41 (s, 3H, CH_3), 3.22 (t, J = 4.0 Hz, 2H, CH_2), 3.41 (t, J = 4.0 Hz, 2H, CH_2), 7.01 (d, J = 7.2 Hz, 1H, Ar), 7.13 (d, J = 7.2 Hz, 1H, Ar), 7.23-7.33 (m, 2H, Ar), 7.44-7.45 (m, 3H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.6, 29.4, 30.8, 121.3, 124.0, 124.4, 127.6, 127.8, 128.0, 128.6, 134.8, 138.1, 138.2, 142.9, 146.3. IR (CH_2Cl_2) ν 3053, 2920, 2853, 1605, 1466, 1899, 780, 753, 697 cm^{-1}. MS (%) m/e 194 (M^+, 58.81), 179 (100.00), 165 (7.29), 152 (12.13), 139 (3.80), 115 (5.50), 89 (21.28), 76 (10.72), 63 (5.24). HRMS (EI) calcd. for $C_{15}H_{14}$: 194.1096, found: 194.1104.

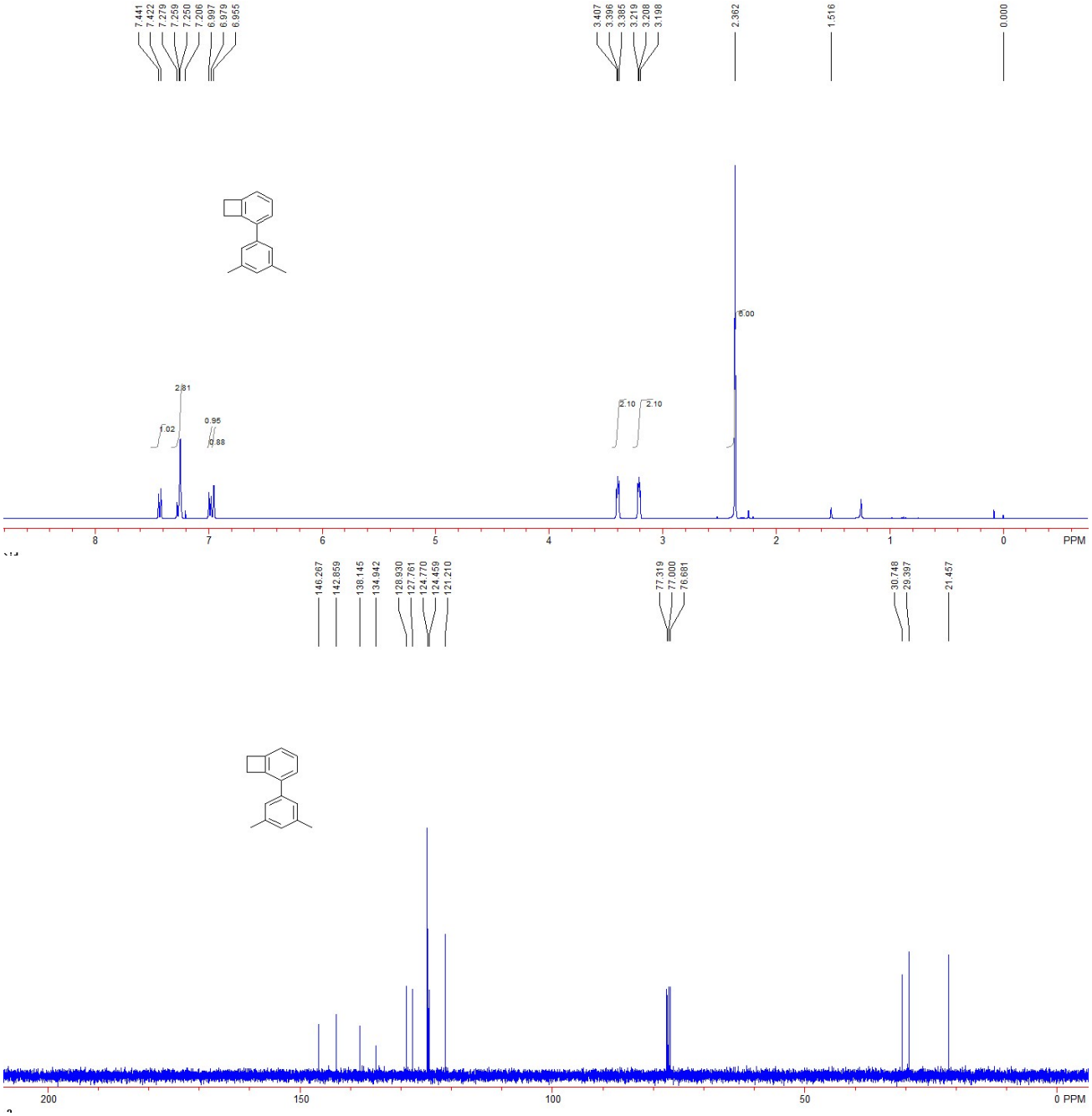


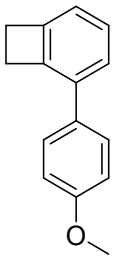


2-(3,5-Dimethylphenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3d:

38 mg, yield: 93%. A white solid. Mp: 62-65 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.36 (s, 6H, CH_3), 3.21 (t, J = 4.0 Hz, 2H, CH_2), 3.40 (t, J = 4.0 Hz, 2H, CH_2), 6.96 (s, 1H, Ar), 6.99 (d, J = 7.2 Hz, 1H, Ar), 7.25-7.28 (m, 3H, Ar), 7.43 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$,

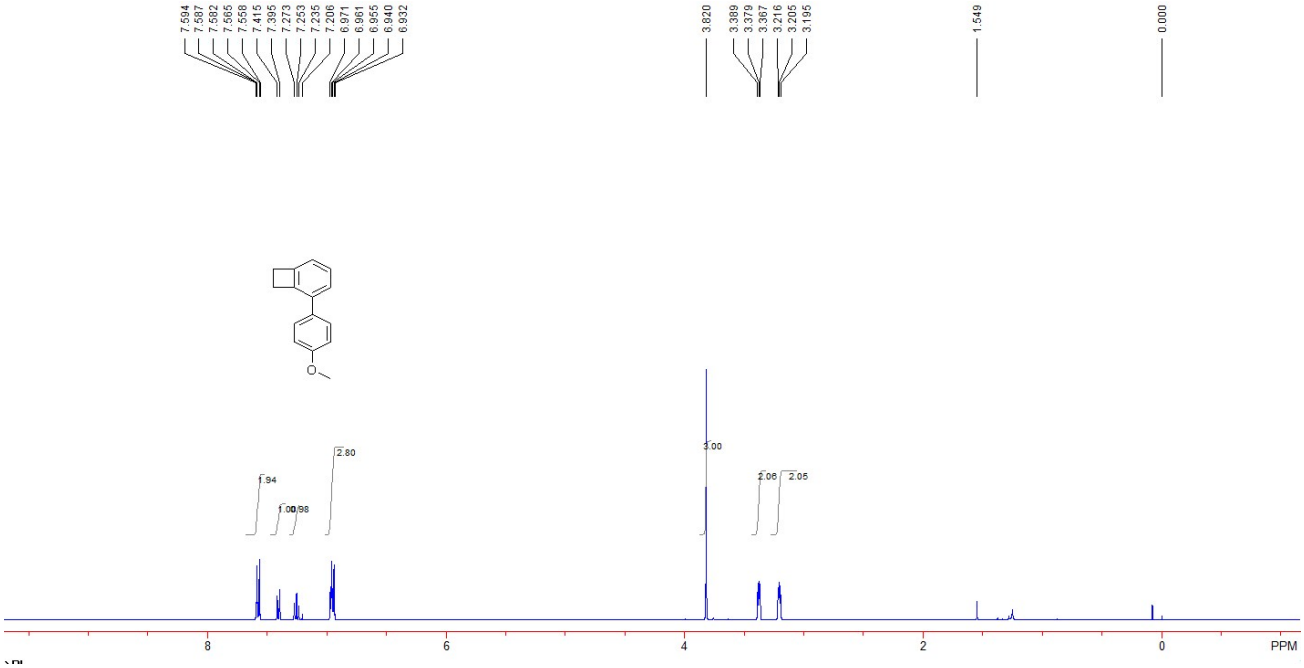
TMS): δ 21.5, 29.4, 30.8, 121.2, 124.5, 124.8, 127.8, 128.9, 134.9, 138.1, 142.9, 146.3. IR (CH_2Cl_2) ν 3019, 2921, 2854, 1603, 1462, 848, 785, 695 cm^{-1}. MS (%) m/e 208 (M^+, 61.48), 193 (100.00), 165 (8.95), 152 (5.96), 115 (3.33), 103 (7.13), 89 (12.51), 82 (6.57). HRMS (EI) calcd. for $C_{16}H_{16}$: 208.1252, found: 208.1256.

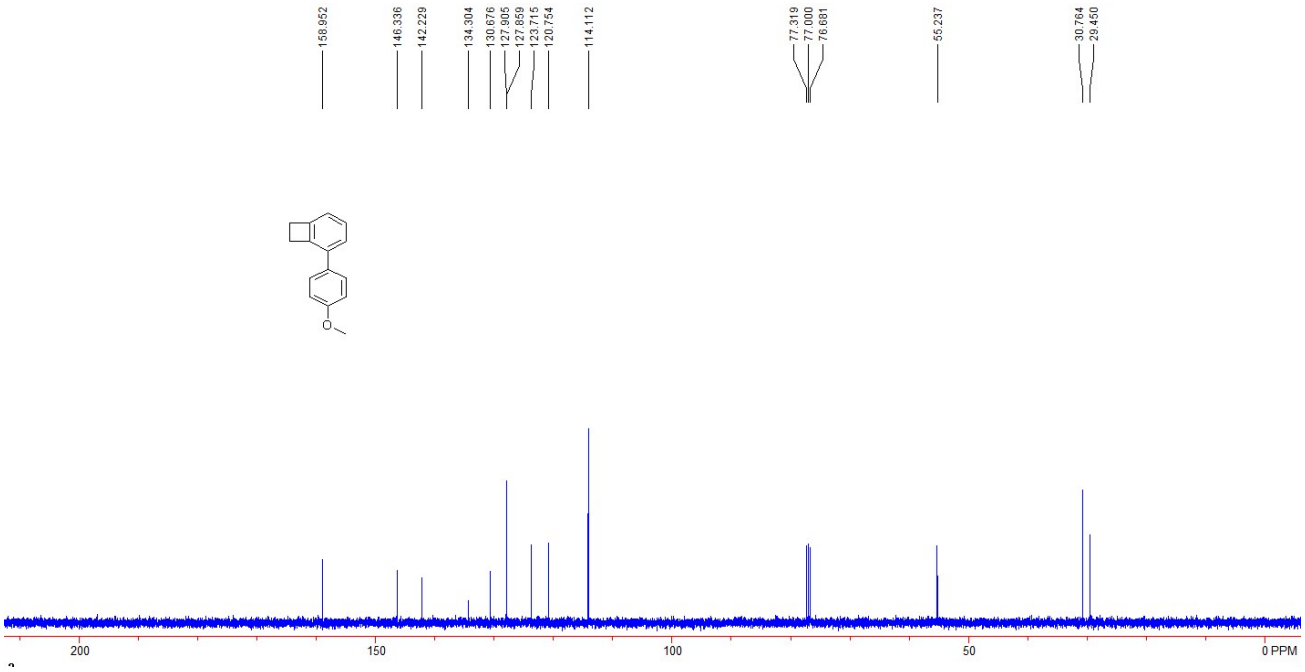


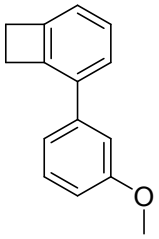


2-(4-Methoxyphenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3e:

39 mg, yield: 93%. A white solid. Mp: 99-102 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.21 (t, J = 4.0 Hz, 2H, CH_2), 3.38 (t, J = 4.0 Hz, 2H, CH_2), 3.82 (s, 3H, CH_3), 6.94-6.97 (m, 3H, Ar), 7.25 (dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 1H, Ar), 7.41 (d, J = 8.0 Hz, 1H, Ar), 7.56-7.59 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.8, 55.2, 114.1, 120.8, 123.7, 127.86, 127.91, 130.7, 134.3, 142.2, 146.3, 159.0. IR (CH_2Cl_2) ν 3051, 2922, 2836, 1606, 1518, 1458, 1027, 829, 786 cm^{-1}. MS (%) m/e 210 (M^+, 100.00), 195 (89.43), 178 (19.72), 165 (33.97), 152 (26.28), 115 (7.68), 89 (10.52). HRMS (EI) calcd. for $C_{15}H_{14}O$: 210.1045, found: 210.1048.

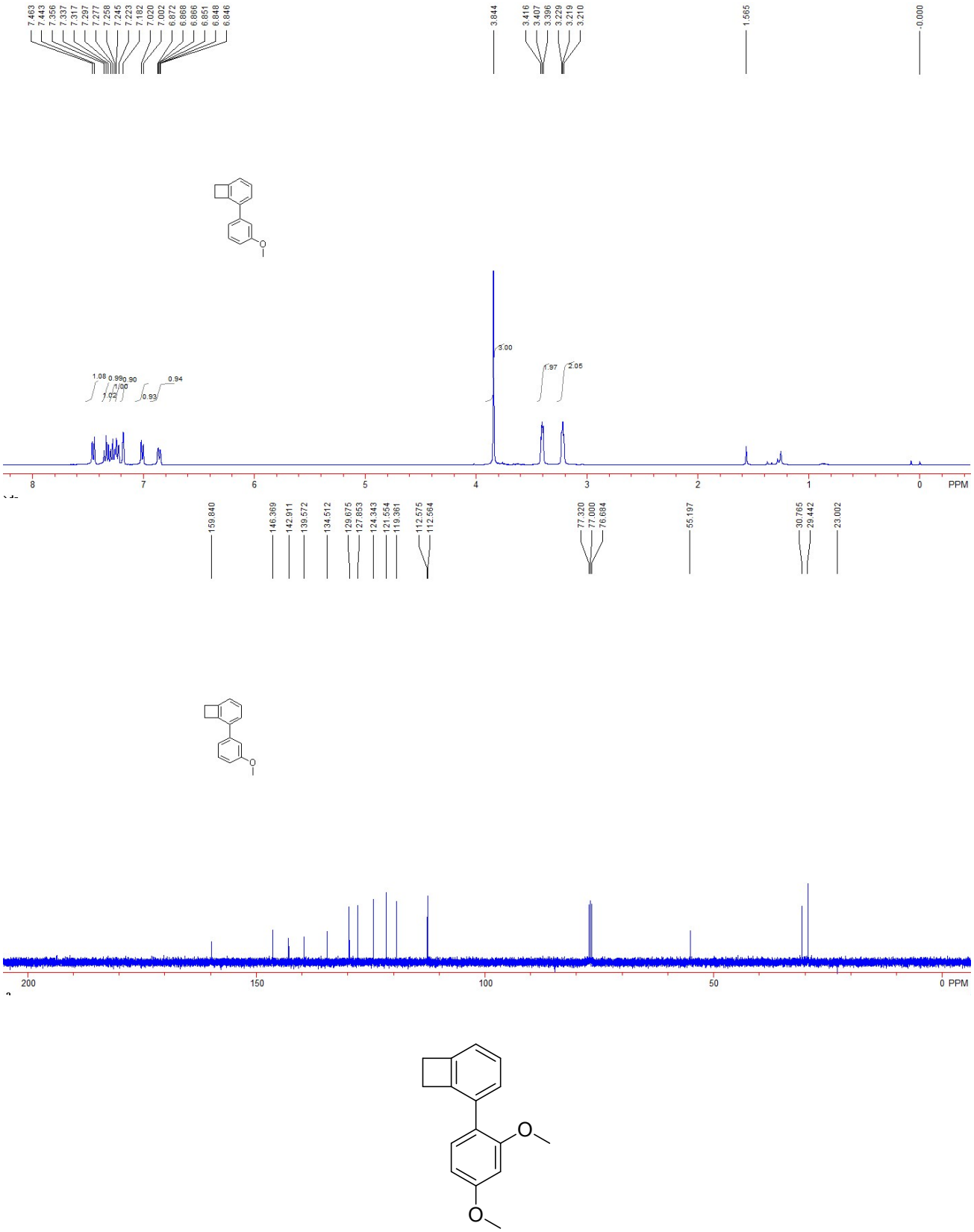






2-(3-Methoxyphenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3f:

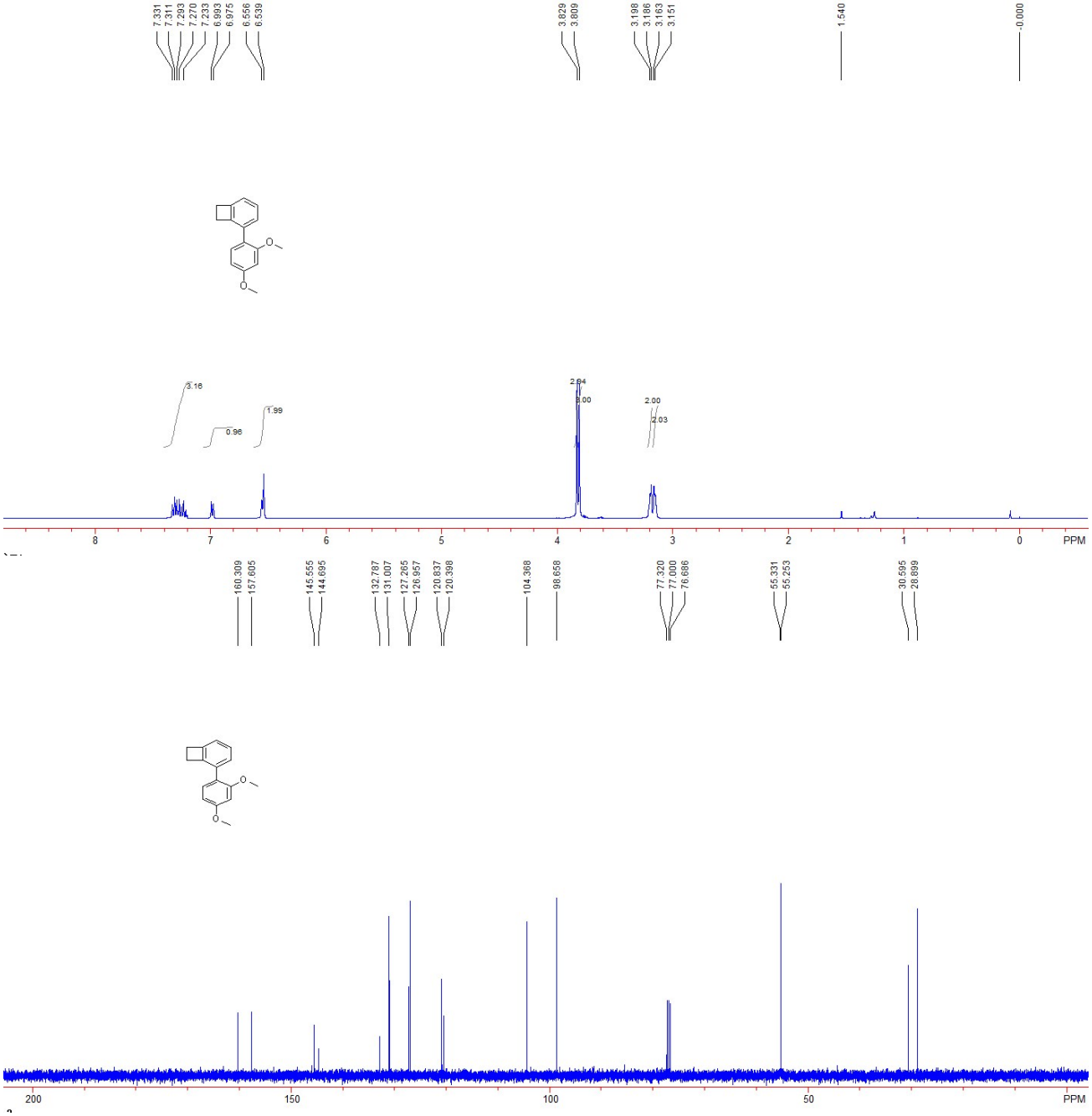
38 mg, yield: 90%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.22 (t, J = 4.0 Hz, 2H, CH_2), 3.41 (t, J = 4.0 Hz, 2H, CH_2), 3.84 (s, 3H, CH_3), 6.85-6.87 (m, 1H, Ar), 7.01 (d, J = 7.2 Hz, 1H, Ar), 7.18 (s, 1H, Ar), 7.23 (d, J = 7.2 Hz, 1H, Ar), 7.28 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.34 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.45 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 23.0, 29.4, 30.8, 55.2, 112.56, 112.58, 119.4, 121.6, 124.3, 127.9, 129.7, 134.5, 139.6, 142.9, 146.4, 159.8. IR (CH_2Cl_2) ν 3055, 2921, 2832, 1600, 1217, 1040, 778, 693 cm^{-1}. MS (%) m/e 210 (M^+, 100.00), 195 (72.61), 179 (30.40), 165 (48.36), 152 (32.59), 139 (11.14), 115 (10.45), 89 (12.96), 76 (11.38). HRMS (EI) calcd. for $C_{15}H_{14}O$: 210.1045, found: 210.1038.

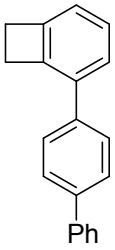


2-(2,4-Dimethoxyphenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3g:

31 mg, yield: 63%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.15-3.20 (m, 4H, CH_2), 3.81 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.54-6.56 (m, 2H, Ar), 6.98 (d, J = 7.2 Hz, 1H, Ar), 7.23-7.33

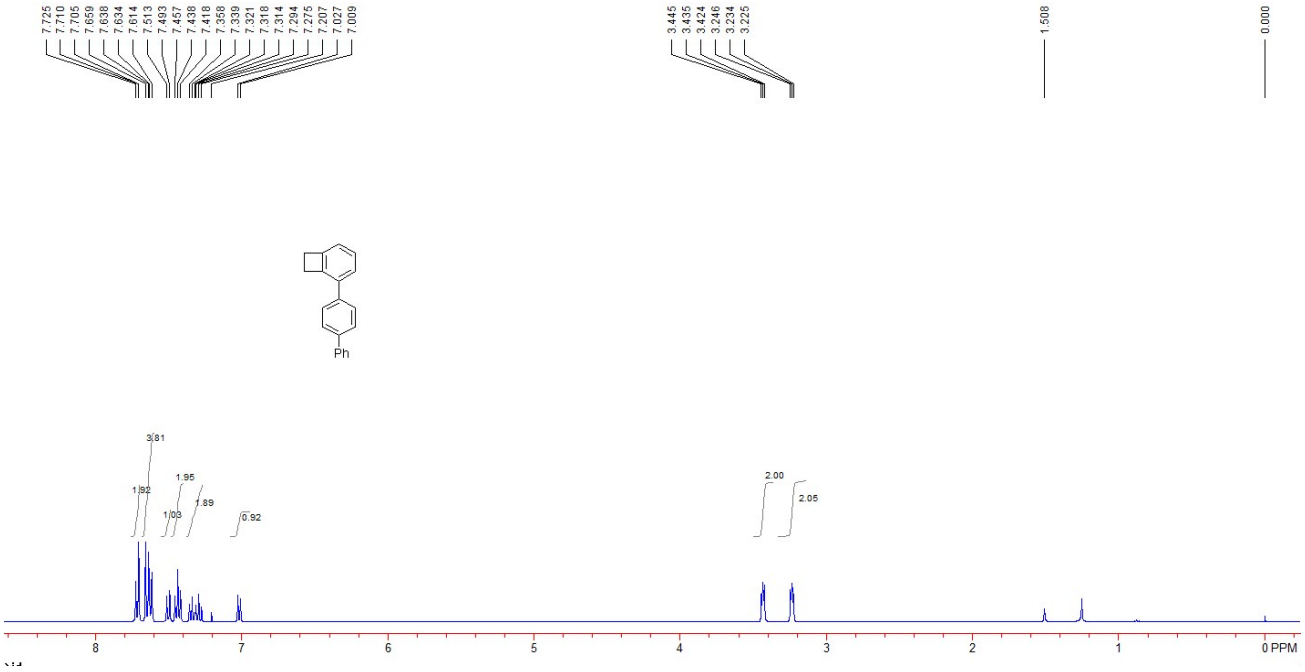
(m, 3H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 28.9, 30.6, 55.25, 55.33, 98.7, 104.4, 130.4, 120.8, 127.0, 127.3, 131.0, 132.8, 144.7, 145.6, 157.6, 160.3. IR (CH_2Cl_2) ν 3000, 2922, 2833, 1609, 1509, 1303, 1207, 1032, 784 cm^{-1}. MS (%) m/e 240 (M^+, 100.00), 225 (53.89), 209 (24.98), 194 (11.40), 165 (28.28), 152 (18.51), 139 (8.82), 115 (8.39), 89 (5.48). HRMS (EI) calcd. for $C_{16}H_{16}O_2$: 240.1150, found: 240.1158.

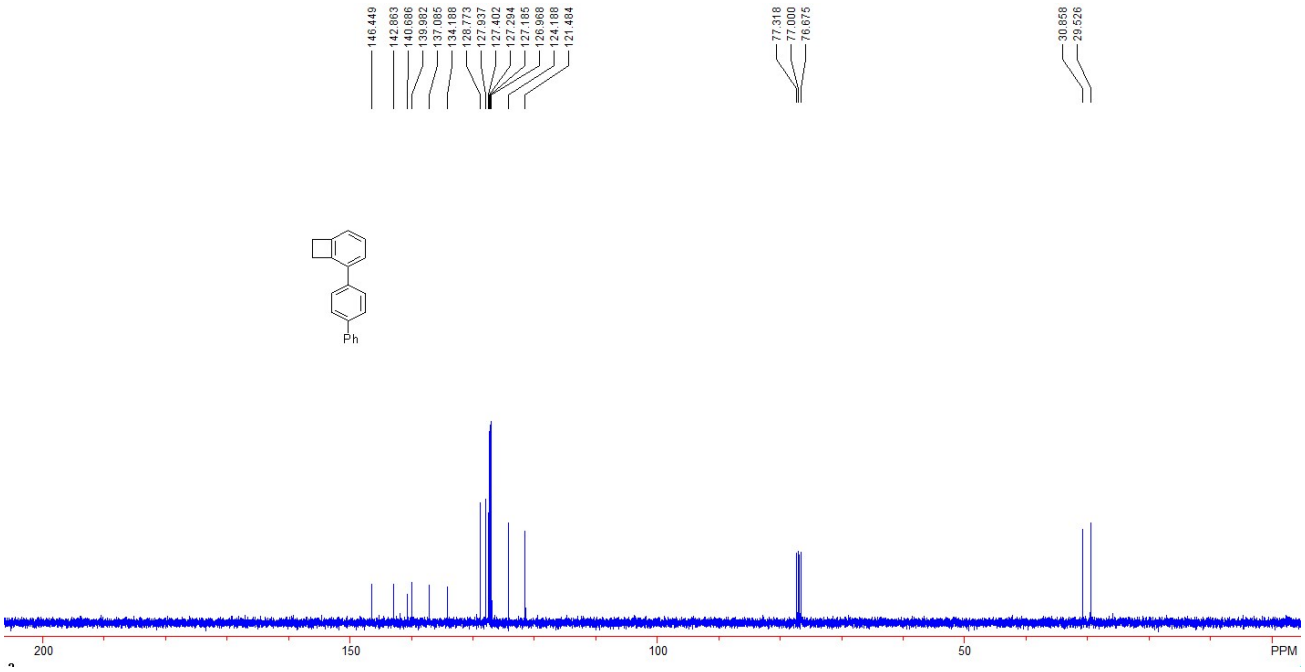


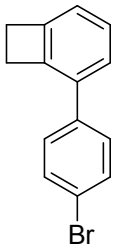


2-([1,1'-Biphenyl]-4-yl)bicyclo[4.2.0]octa-1(6),2,4-triene 3h:

47 mg, yield: 92%. A white solid. Mp: 90-93 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.23 (t, J = 4.0 Hz, 2H, CH_2), 3.44 (t, J = 4.0 Hz, 2H, CH_2), 7.02 (d, J = 7.2 Hz, 1H, Ar), 7.28-7.36 (m, 2H, Ar), 7.44 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 2H, Ar), 7.50 (d, J = 8.0 Hz, 1H, Ar), 7.61-7.66 (m, 4H, Ar), 7.71-7.73 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.9, 121.5, 124.2, 127.0, 127.2, 127.3, 127.4, 127.9, 128.8, 134.2, 137.1, 140.0, 140.7, 142.9, 146.4. IR (CH_2Cl_2) ν 3030, 2925, 1466, 1391, 840, 771, 751, 692 cm^{-1}. MS (%) m/e 256 (100.00), 241 (85.30), 226 (7.57), 178 (13.19), 165 (3.50), 152 (4.80), 126 (7.70), 120 (9.26), 77 (5.18). HRMS (EI) calcd. for $C_{20}H_{16}$: 256.1252, found: 256.1251.

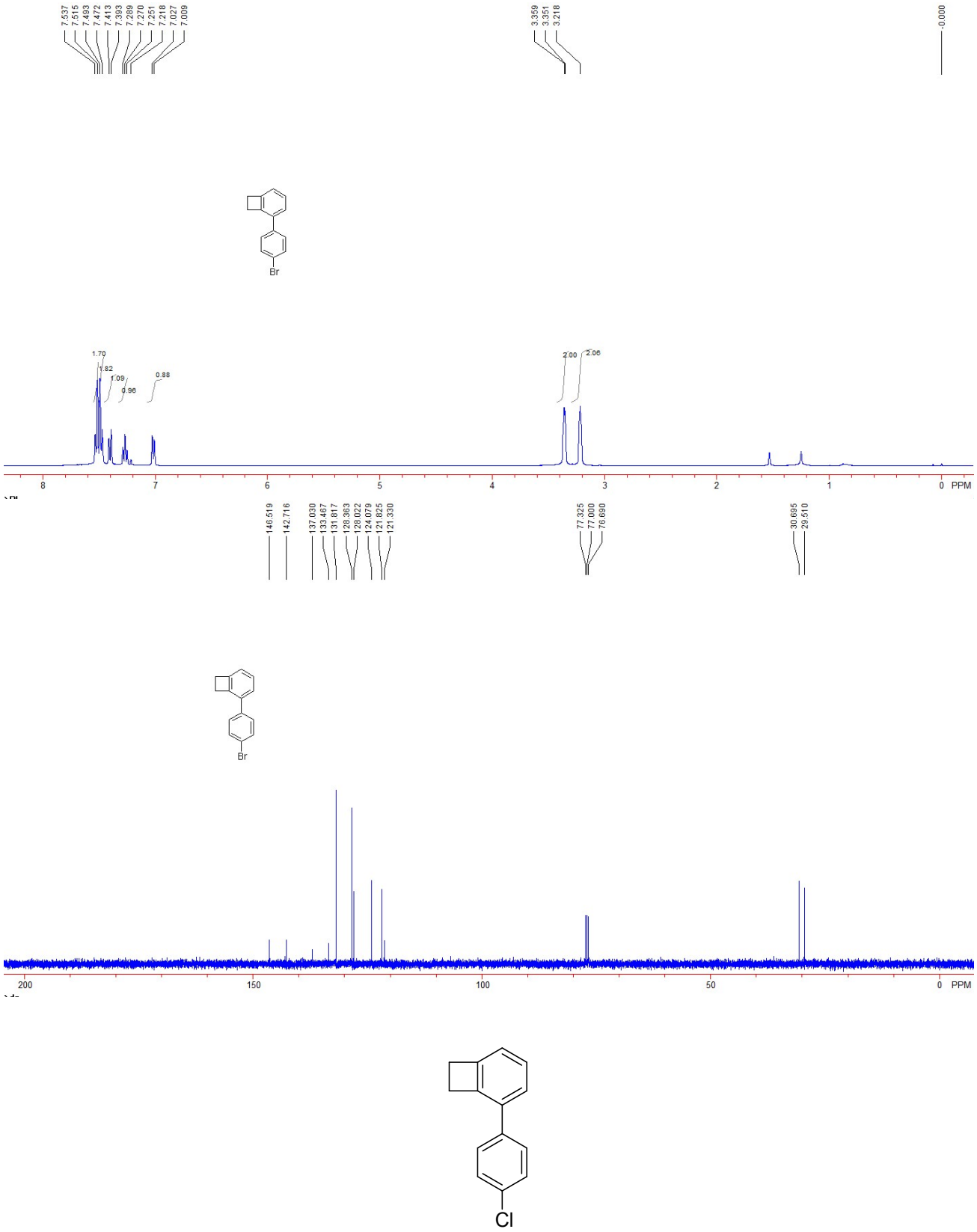






2-(4-Bromophenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3i:

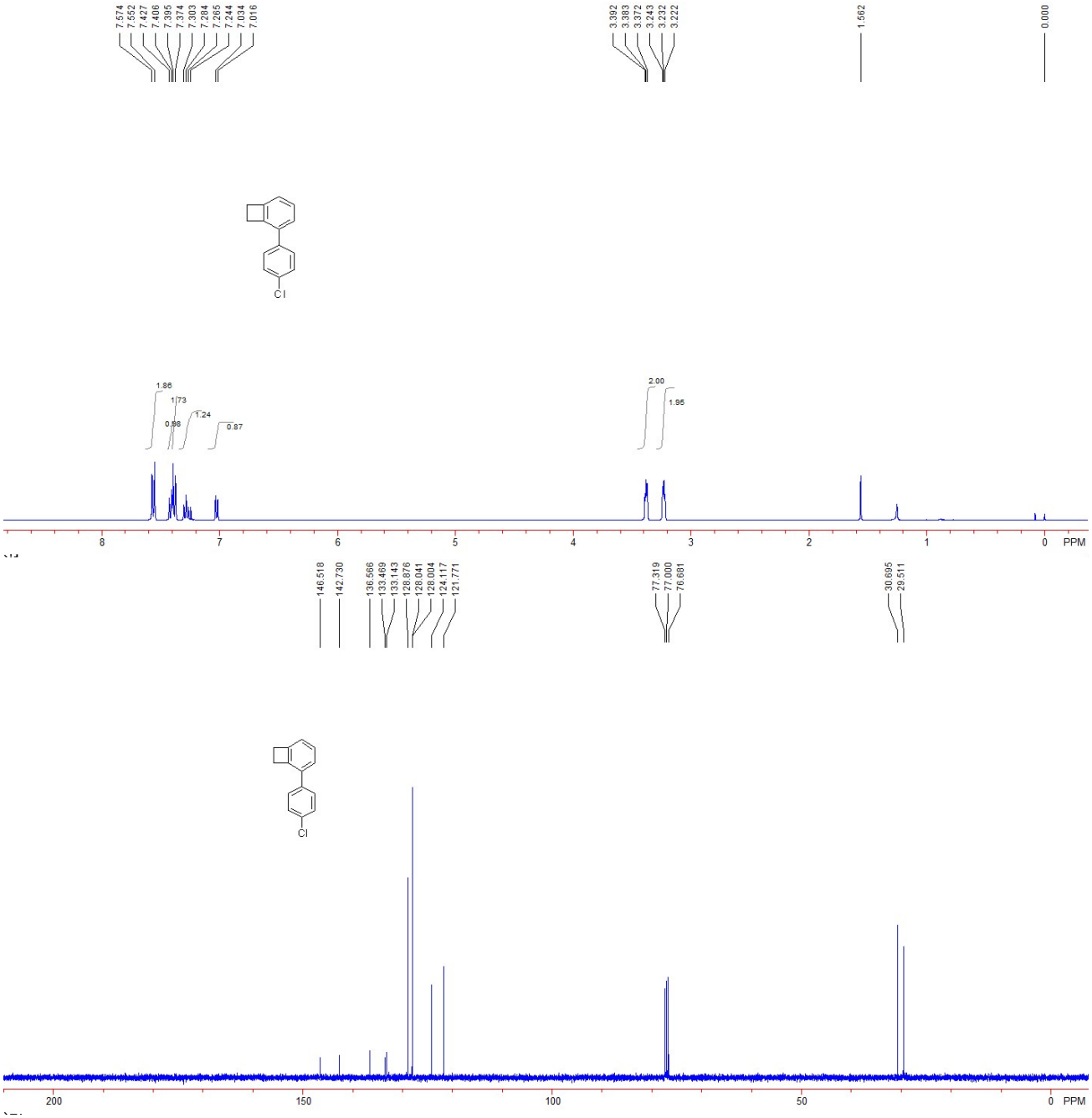
47 mg, yield: 92%. A white solid. Mp: 87-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.22 (br, 2H, CH_2), 3.36 (d, J = 3.2 Hz, 2H, CH_2), 7.02 (d, J = 7.2 Hz, 1H, Ar), 7.27-7.31 (m, 2H, Ar), 7.40 (d, J = 8.0 Hz, 1H, Ar), 7.48 (d, J = 8.4 Hz, 1H, Ar), 7.53 (d, J = 8.4 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.7, 121.3, 121.8, 124.1, 128.0, 128.4, 131.8, 133.5, 137.0, 142.7, 146.5. IR (CH_2Cl_2) ν 3056, 2961, 2922, 2853, 1465, 1078, 1008, 833, 784, 758 cm^{-1}. MS (%) m/e 258 (M^+, 25.84), 179 (100.00), 178 (78.89), 152 (11.68), 89 (25.39), 76 (31.21), 63 (8.72), 51 (5.22). HRMS (EI) calcd. for $C_{14}H_{11}Br$: 258.0044, found: 258.0047.

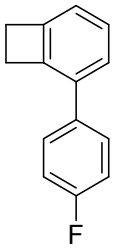


2-(4-Chlorophenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3j:

39 mg, yield: 90%. A white solid. Mp: 83-85 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.23 (t, J = 4.0 Hz, 2H, CH_2), 3.38 (t, J = 4.0 Hz, 2H, CH_2), 7.03 (d, J = 7.2 Hz, 1H, Ar), 7.24-7.30 (m, 2H, Ar),

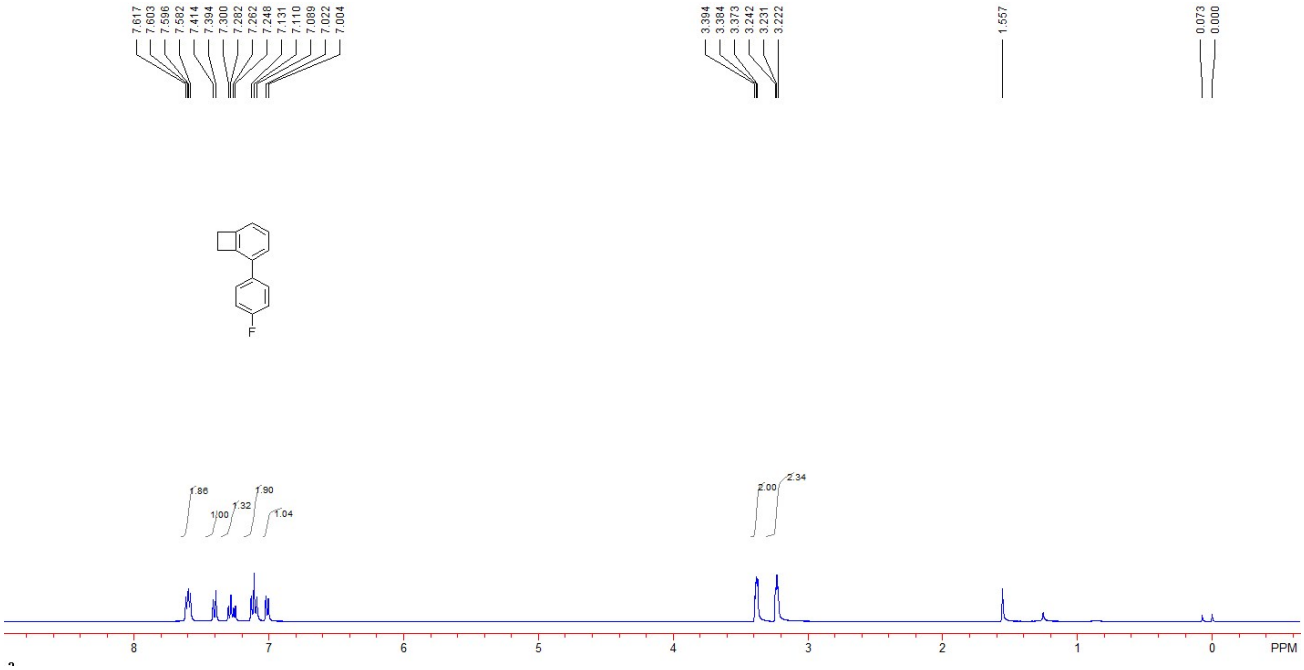
7.38 (d, *J* = 8.4 Hz, 2H, Ar), 7.42 (d, *J* = 8.4 Hz, 1H, Ar), 7.56 (d, *J* = 8.4 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.7, 121.8, 124.1, 128.00, 128.04, 128.9, 133.1, 133.5, 136.6, 142.7, 146.5. IR (CH_2Cl_2) ν 3058, 2920, 2853, 1463, 1093, 1010, 837, 784, 758 cm^{-1}. MS (%) m/e 214 (M^+, 43.56), 179 (100.00), 152 (12.66), 126 (3.20), 99 (2.71), 89 (30.43), 76 (32.32), 63 (7.91), 51 (5.00). HRMS (EI) calcd. for $C_{14}H_{11}Cl$: 214.0549, found: 214.0557.

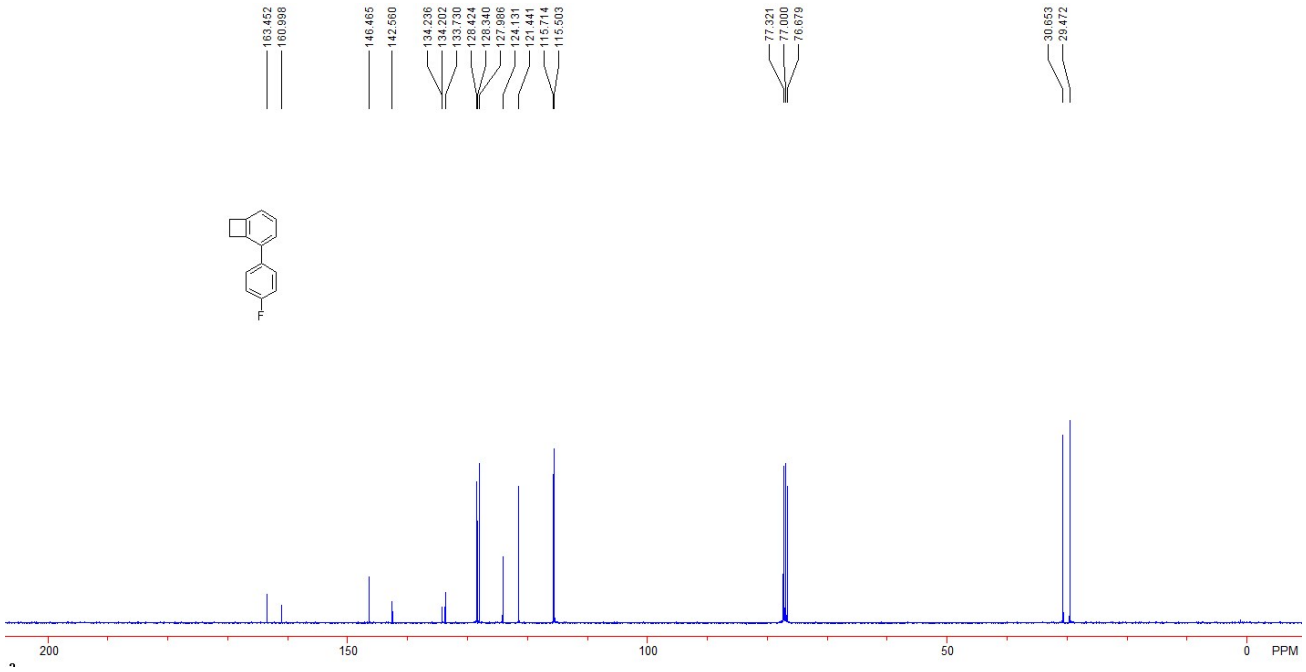


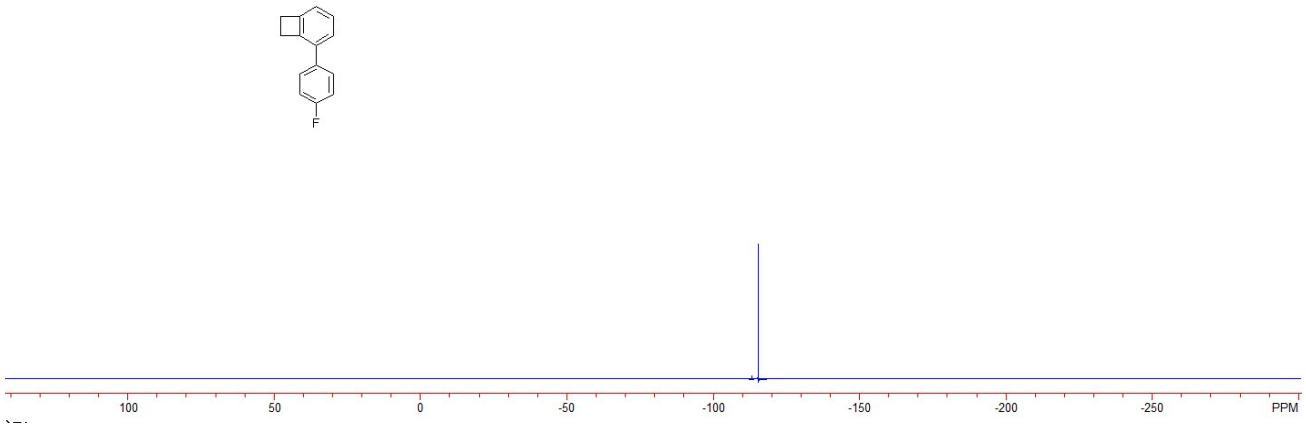


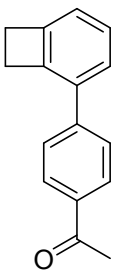
2-(4-Fluorophenyl)bicyclo[4.2.0]octa-1(6),2,4-triene 3k:

36 mg, yield: 91%. A white solid. Mp: 75-77 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.23 (t, J = 4.0 Hz, 2H, CH_2), 3.38 (t, J = 4.0 Hz, 2H, CH_2), 7.01 (d, J = 7.2 Hz, 1H,. Ar), 7.09-7.13 (m, 2H, Ar), 7.25-7.30 (m, 1H, Ar), 7.40 (d, J = 8.0 Hz, 1H, Ar), 7.58-7.62 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.7, 115.6 (d, J = 21.1 Hz), 121.4, 124.1, 128.0, 128.4 (d, J = 8.4 Hz), 133.7, 134.2 (d, J = 3.4 Hz), 142.6, 146.5, 162.2 (d, J = 245.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -115.2. IR (CH_2Cl_2) ν 3059, 2923, 2850, 1514, 1469, 1232, 837, 784, 760 cm^{-1}. MS (%) m/e 198 (M^+, 80.31), 183 (100.00), 177 (11.17), 157 (2.81), 133 (6.11), 98 (22.00), 85 (16.56), 75 (8.54), 63 (6.39). HRMS (EI) calcd. for $C_{14}H_{11}F$: 198.0845, found: 198.0846.





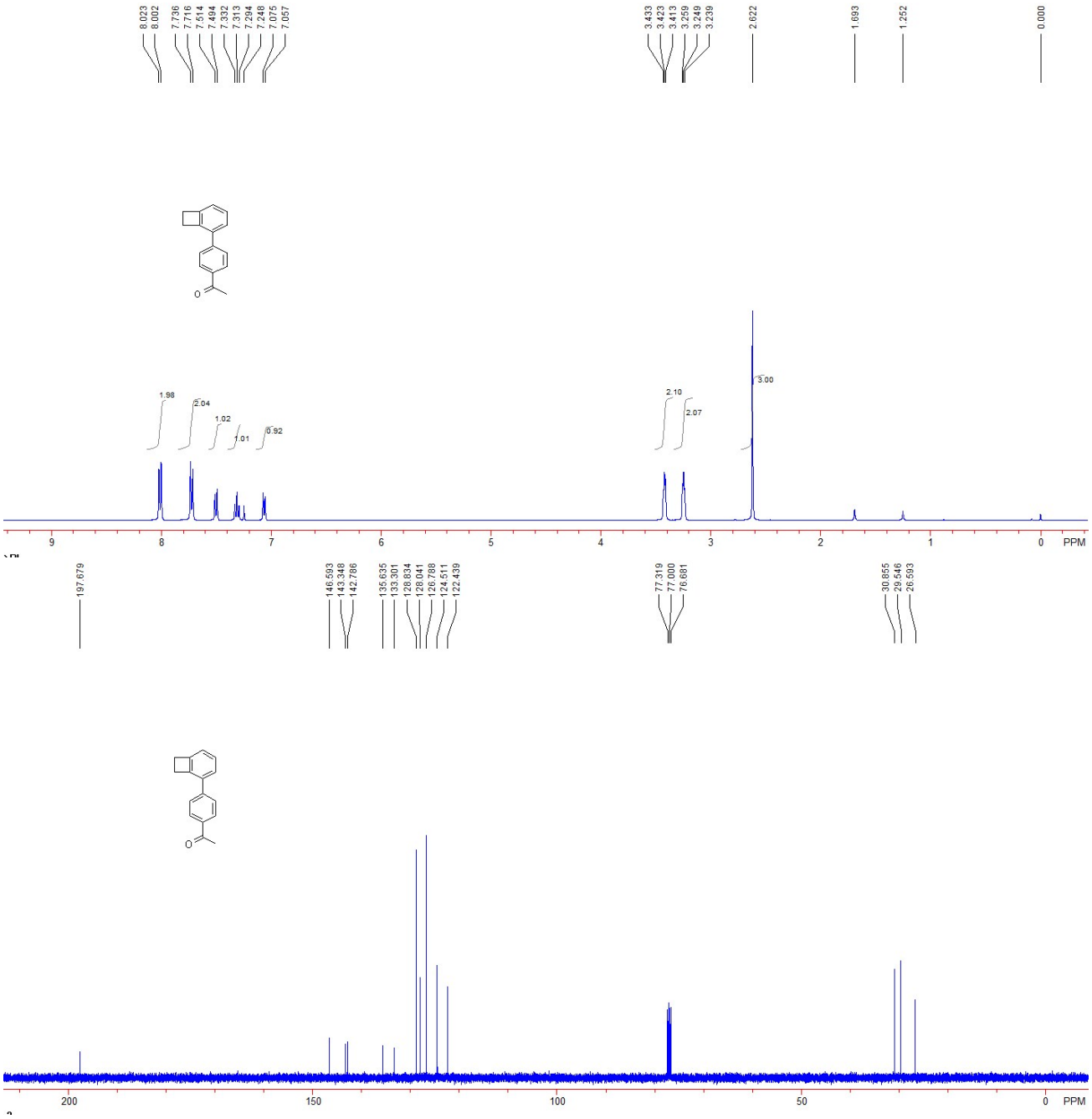


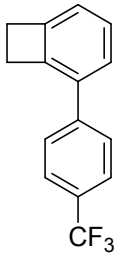


1-(4-(Bicyclo[4.2.0]octa-1(6),2,4-trien-2-yl)phenyl)ethan-1-one 3l:

38 mg, yield = 84%. A white solid. Mp: 117-119 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.62 (s, 3H, CH_3), 3.25 (t, J = 4.0 Hz, 2H, CH_2), 3.42 (t, J = 4.0 Hz, 2H, CH_2), 7.07 (d, J = 7.2 Hz, 1H, Ar),

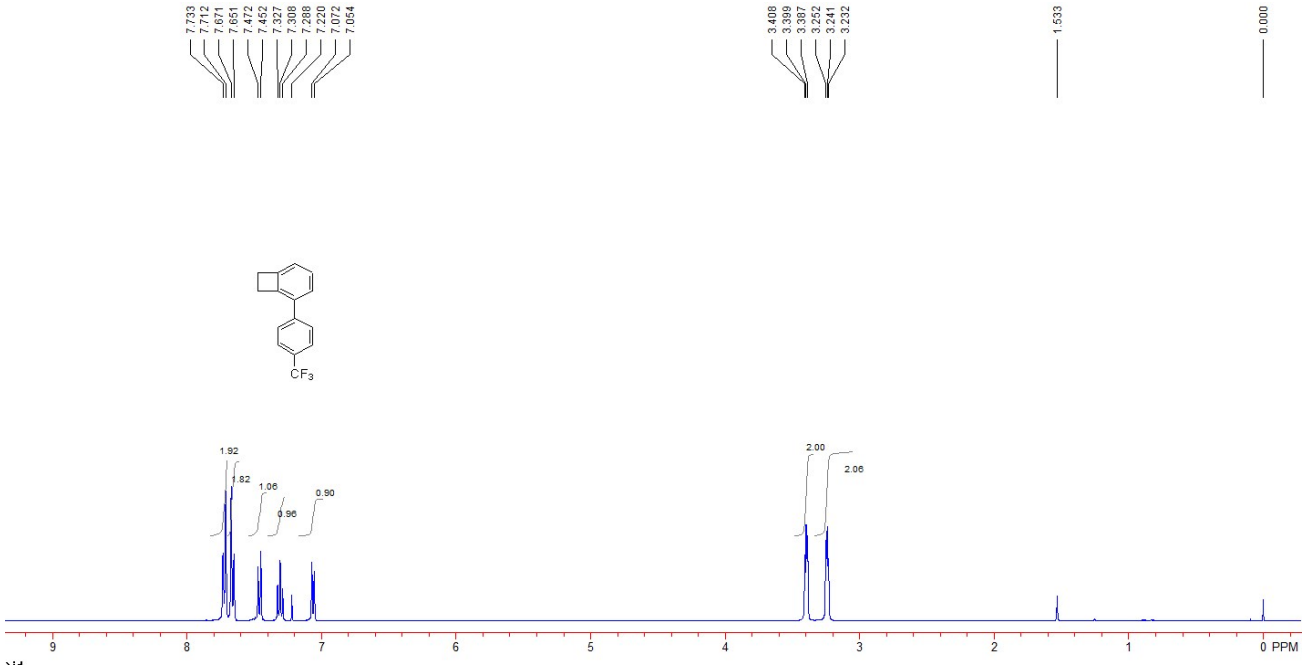
7.31 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.50 (d, J = 8.0 Hz, 1H, Ar), 7.73 (d, J = 8.0 Hz, 2H, Ar), 8.01 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 26.6, 29.5, 30.9, 122.4, 124.5, 126.8, 128.0, 128.8, 133.3, 135.6, 142.8, 143.3, 146.6, 197.7. IR (CH_2Cl_2) ν 3053, 2962, 2925, 1678, 1602, 1393, 1353, 1269, 958, 793 cm^{-1}. MS (%) m/e 222 (M^+, 83.84), 207 (29.28), 179 (82.60), 165 (13.15), 152 (20.19), 103 (15.35), 89 (19.73), 76 (19.14), 43 (100.00). HRMS (EI) calcd. for $C_{16}H_{14}O$: 222.1045, found: 222.1048.

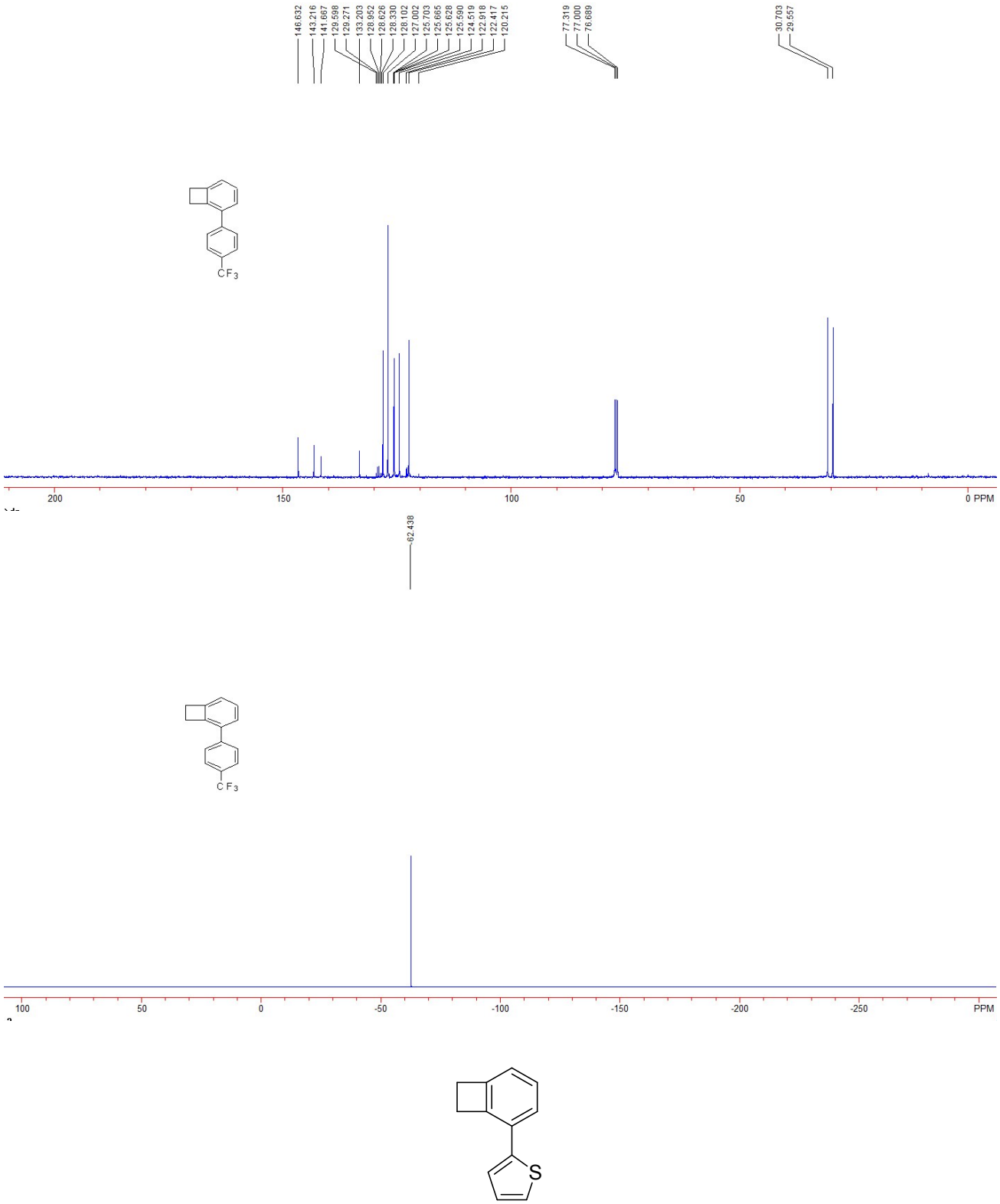




2-(4-(Trifluoromethyl)phenyl)bicyclo[4.2.0]octa-1,3,5-triene 3m:

42 mg, yield: 84%. A white solid. Mp: 99-101 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.24 (t, J = 4.0 Hz, 2H, CH_2), 3.40 (t, J = 4.0 Hz, 2H, CH_2), 7.06 (d, J = 7.2 Hz, 1H, Ar), 7.31 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.46 (d, J = 8.0 Hz, 1H, Ar), 7.66 (d, J = 8.0 Hz, 2H, Ar), 7.72 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.6, 30.7, 122.4, 124.2 (q, J = 267.2 Hz), 124.5, 125.6 (q, J = 3.7 Hz), 127.0, 128.1, 129.1 (q, J = 31.9 Hz), 133.2, 141.7, 143.2, 146.6. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.4. IR (CH_2Cl_2) ν 2967, 2918, 2828, 1619, 1323, 1110, 844, 787, 735 cm^{-1}. MS (%) m/e 248 (M^+, 100.00), 233 (89.86), 227 (11.24), 207 (5.60), 179 (96.58), 152 (15.38), 114 (5.54), 89 (10.72), 51 (7.19). HRMS (EI) calcd. for $C_{15}H_{11}F_3$: 248.0813, found: 248.0805.

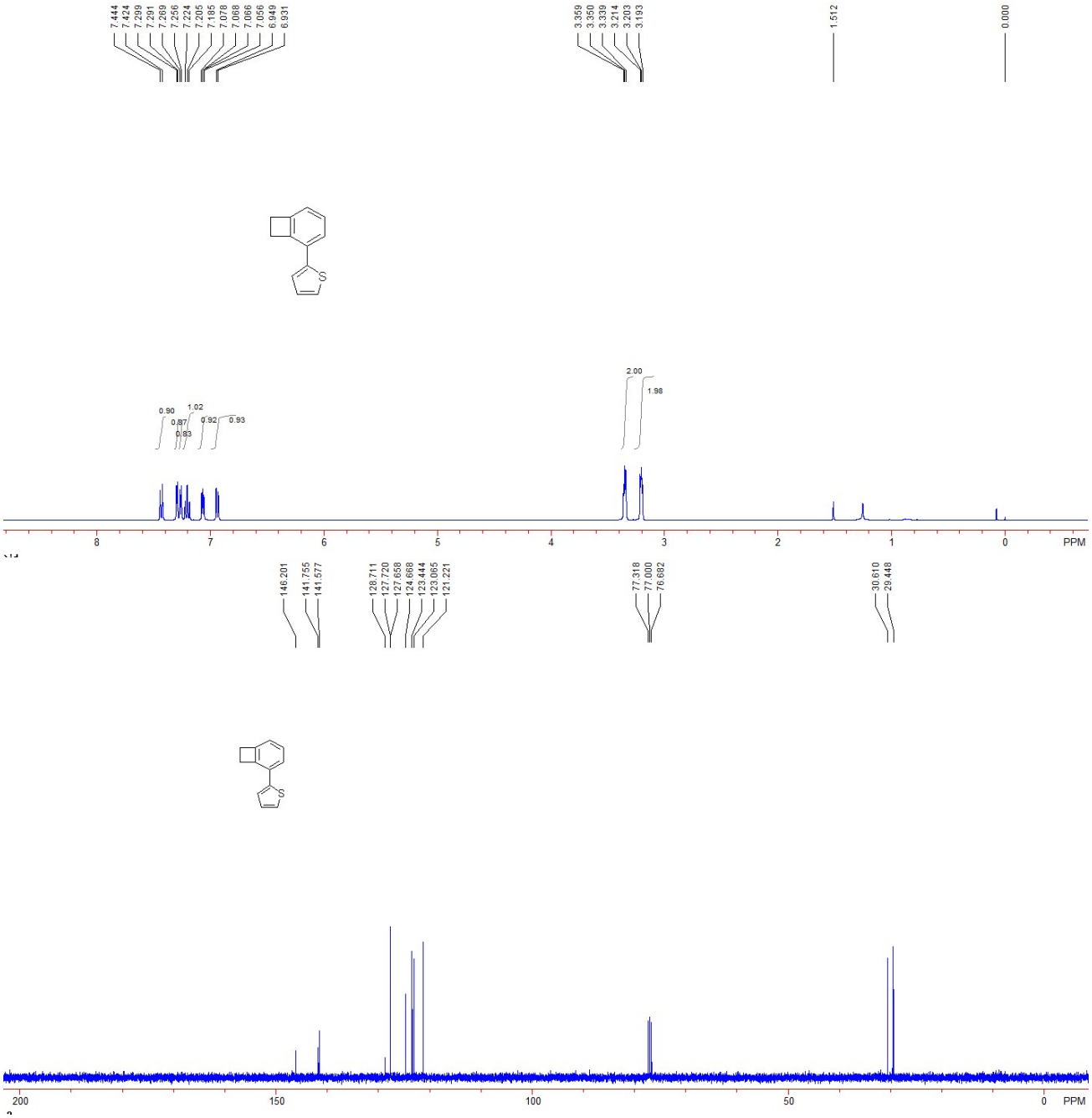


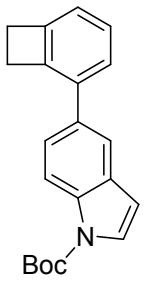


2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-2-yl)thiophene 3n:

33 mg, yield: 89%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.20 (d, J = 3.2 Hz, 2H, CH_2), 3.36 (d, J = 3.2 Hz, 2H, CH_2), 6.94 (d, J = 7.2 Hz, 1H, Ar), 7.07 (dd, J = 4.8 Hz, J = 4.0 Hz, 1H, Ar), 7.21 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.26 (d, J = 4.8 Hz, 1H, Ar), 7.30 (d, J = 4.0 Hz,

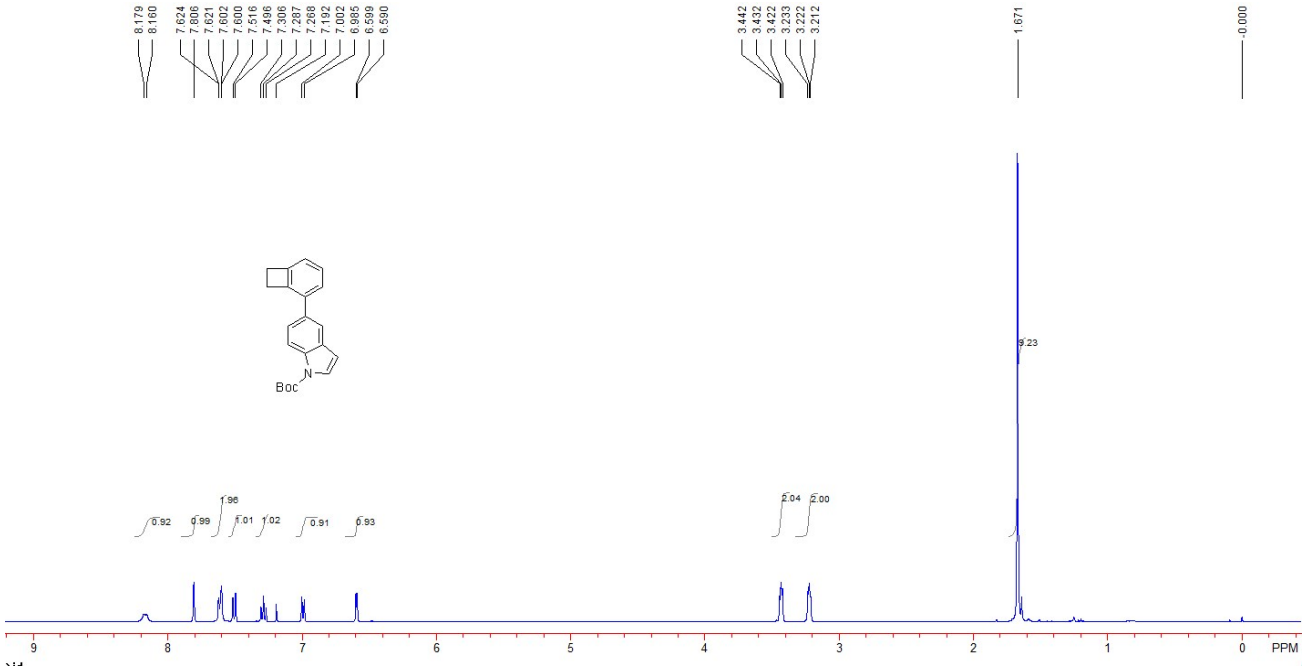
1H, Ar), 7.43 (d, J = 8.0 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.7, 121.3, 123.1, 123.4, 124.7, 127.7, 128.7, 141.6, 141.8, 146.2. IR (CH_2Cl_2) ν 3057, 2920, 2850, 1602, 1420, 848, 781, 755, 690 cm^{-1}. MS (%) m/e 186 (M^+, 100.00), 171 (53.54), 152 (19.96), 139 (9.88), 115 (23.09), 92 (13.90), 79 (9.54), 63 (12.07), 51 (7.47). HRMS (EI) calcd. for $C_{12}H_{10}S$: 186.0503, found: 186.0504.

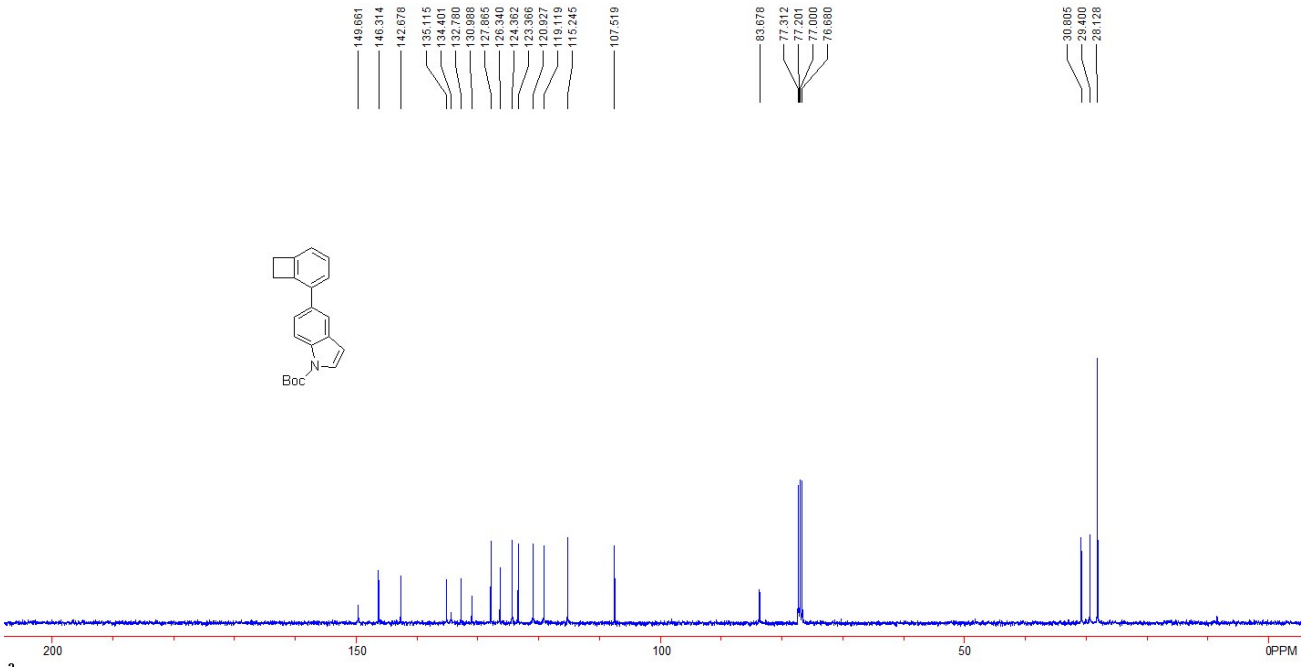


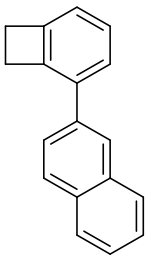


***tert*-Butyl 5-(bicyclo[4.2.0]octa-1(6),2,4-trien-2-yl)-1H-indole-1-carboxylate 3o**:

61 mg, yield = 98%. A white solid. Mp: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.67 (s, 9H, CH_3), 3.22 (t, J = 4.0 Hz, 2H, CH_2), 3.43 (t, J = 4.0 Hz, 2H, CH_2), 6.59 (d, J = 3.6 Hz, 1H, Ar), 6.99 (d, J = 7.2 Hz, 1H, Ar), 7.29 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.51 (d, J = 8.0 Hz, 1H, Ar), 7.61 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 2H, Ar), 7.81 (s, 1H, Ar), 8.17 (d, J = 7.6 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 28.1, 29.4, 30.8, 83.7, 107.5, 115.2, 119.1, 120.9, 123.4, 124.4, 126.3, 127.9, 131.0, 132.8, 134.1, 135.1, 142.7, 146.3, 149.7. IR (CH_2Cl_2) ν 3059, 2976, 2922, 1731, 1393, 1364, 1239, 1131, 1021, 725 cm^{-1}. MS (ESI) *m/z*: 320.2 (M^++H); HRMS (ESI) Calcd. for $C_{21}H_{22}NO_2$ (M^++H) requires 320.1639, found: 320.1645.

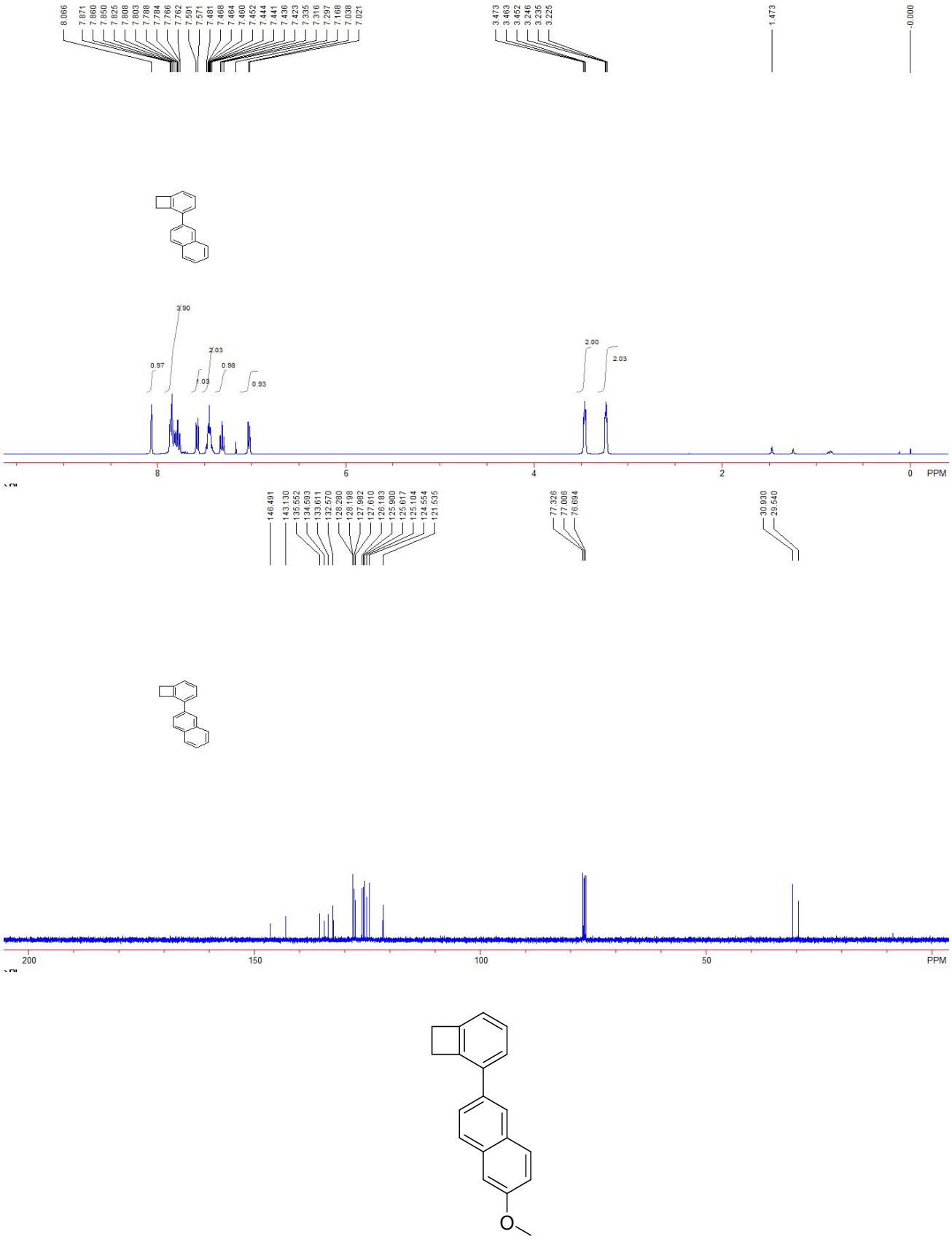






2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-2-yl)naphthalene 3p:

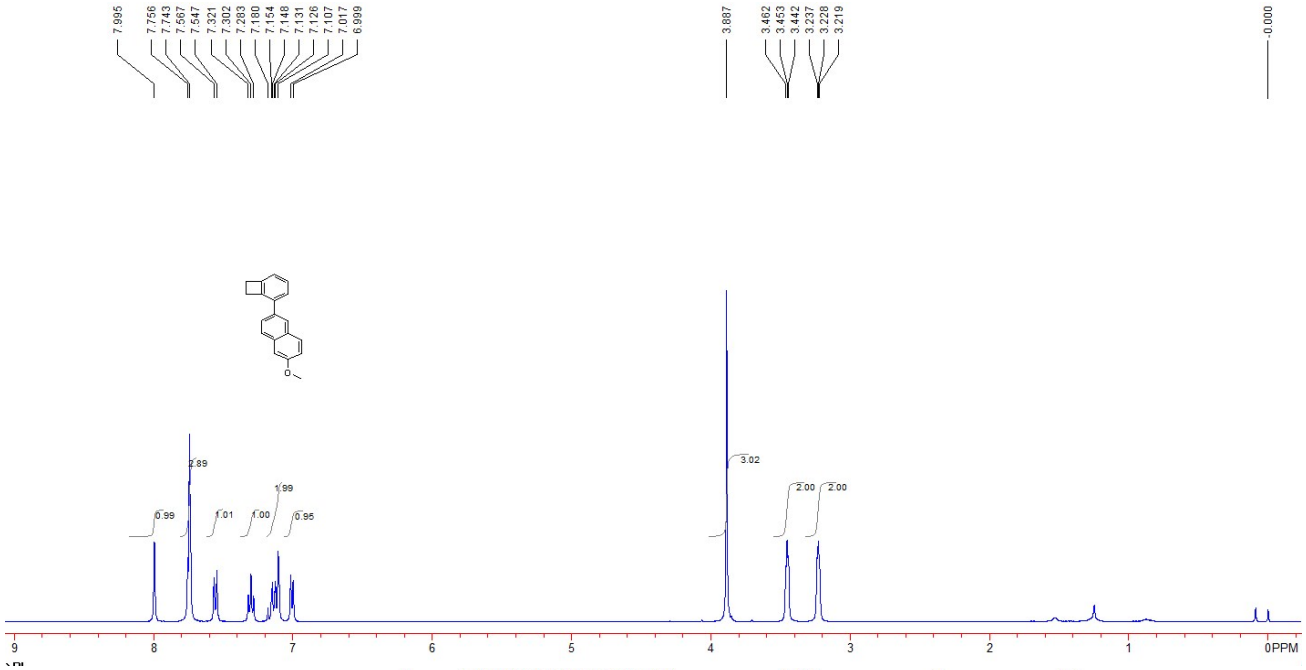
42 mg, yield: 91%. A white solid. Mp: 100-101 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.24 (t, J = 4.0 Hz, 2H, CH_2), 3.46 (t, J = 4.0 Hz, 2H, CH_2), 7.03 (d, J = 7.6 Hz, 1H, Ar), 7.32 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.42-7.48 (m, 2H, Ar), 7.58 (d, J = 8.0 Hz, 1H, Ar), 7.76-7.87 (m, 4H, Ar), 8.07 (s, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.9, 121.5, 124.6, 125.1, 125.6, 125.9, 126.2, 127.6, 128.0, 128.2, 128.3, 132.6, 133.6, 134.6, 135.6, 143.1, 146.5. IR (CH_2Cl_2) ν 3053, 2964, 2922, 1596, 1446, 1275, 858, 787, 749 cm^{-1}. MS (%) m/e 230 (M^+, 100.00), 215 (91.84), 202 (13.99), 189 (5.17), 176 (2.79), 126 (2.10), 114 (19.31), 101 (12.41), 51 (3.46). HRMS (EI) calcd. for $C_{18}H_{14}$: 230.1096, found: 230.1095.

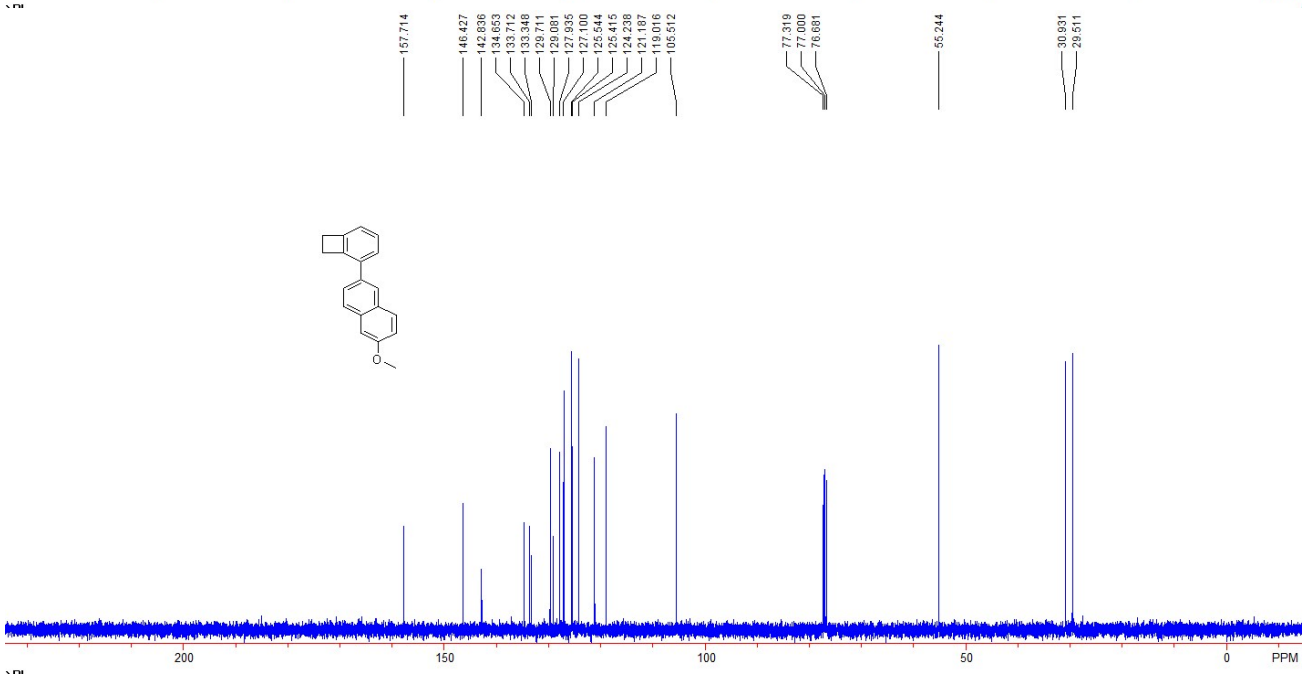


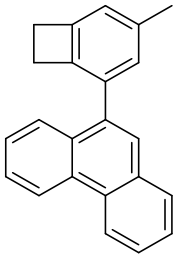
2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-2-yl)-6-methoxynaphthalene 3q:

47 mg, yield = 90%. A white solid. Mp: 131-133 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.23 (t, *J*

= 3.6 Hz, 2H, CH_2), 3.45 (t, J = 3.6 Hz, 2H, CH_2), 3.89 (s, 3H, CH_3), 7.01 (d, J = 7.2 Hz, 1H, Ar), 7.11-7.18 (m, 2H, Ar), 7.30 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H, Ar), 7.56 (d, J = 8.0 Hz, 1H, Ar), 7.74-7.76 (m, 3H, Ar), 8.00 (s, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.9, 55.2, 105.5, 119.0, 121.2, 124.2, 125.4, 125.5, 127.1, 127.9, 129.1, 129.7, 133.3, 133.7, 134.7, 142.8, 146.4, 157.7. IR (CH_2Cl_2) ν 2958, 2920, 2850, 1604, 1208, 1028, 857, 792, 784 cm^{-1}. MS (%) m/e 260 (M^+, 100.00), 245 (41.42), 229 (20.20), 215 (30.76), 202 (20.74), 189 (7.34), 130 (7.74), 122 (12.93), 108 (12.83), 94 (2.37). HRMS (EI) calcd. for $C_{19}H_{16}O$: 260.1201, found: 260.1199.

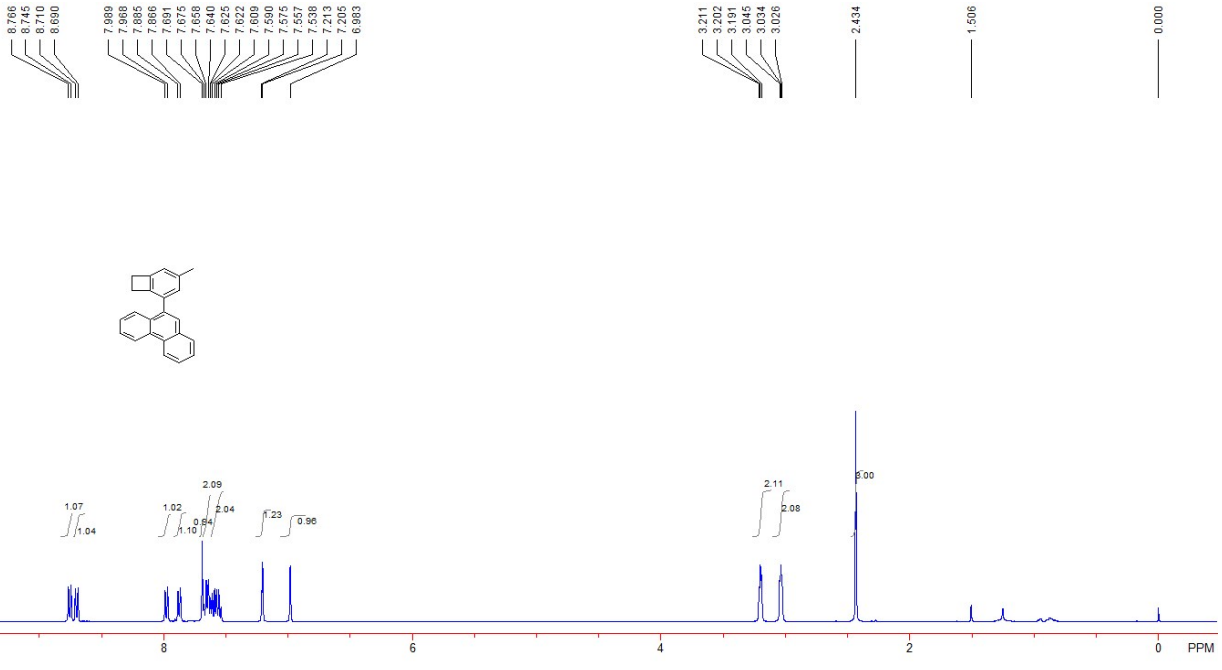


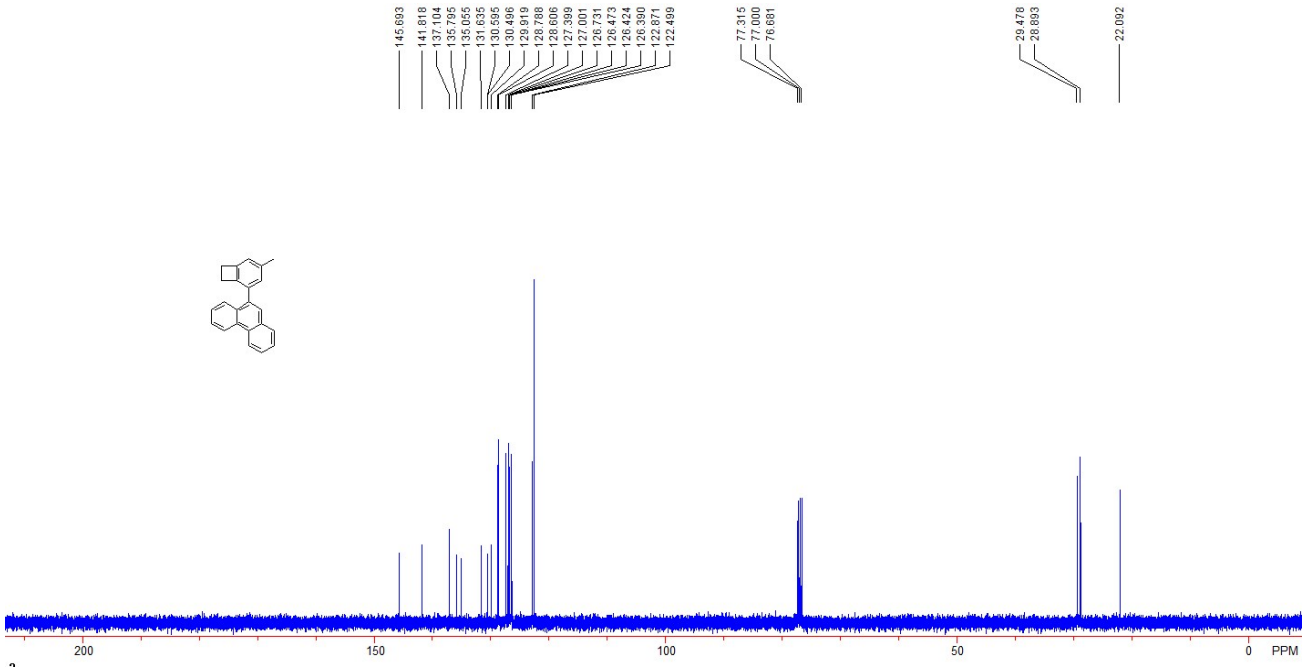




1-(4-(Bicyclo[4.2.0]octa-1(6),2,4-trien-2-yl)phenyl)ethan-1-one 3r:

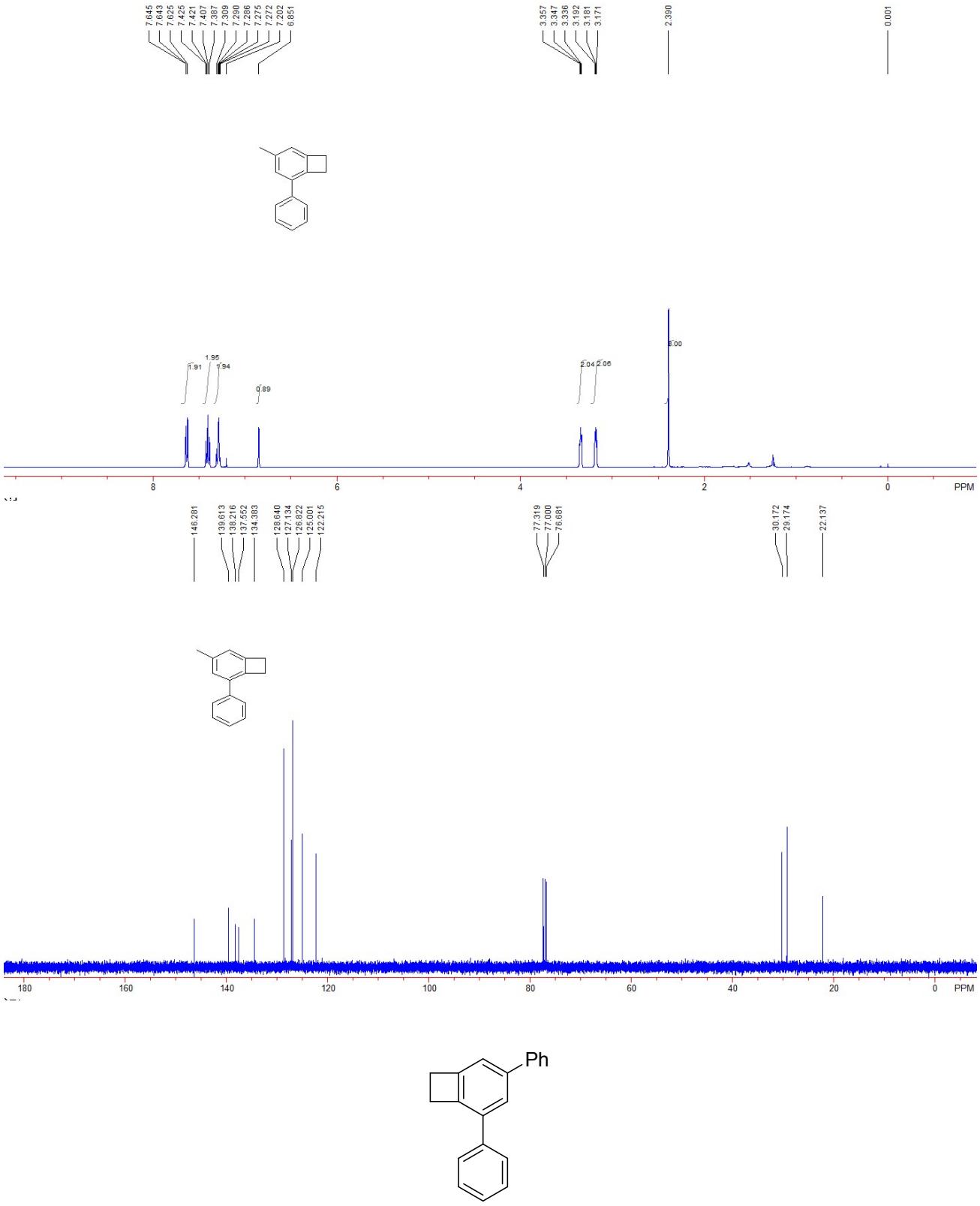
43 mg, yield = 73%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.43 (s, 3H, CH_3), 3.03 (t, *J* = 4.0 Hz, 2H, CH_2), 3.20 (t, *J* = 4.0 Hz, 2H, CH_2), 6.98 (s, 1H, Ar), 7.21 (s, 1H, Ar), 7.54-7.63 (m, 2H, Ar), 7.64-7.69 (m, 2H, Ar), 7.88 (d, *J* = 7.6 Hz, 1H, Ar), 7.98 (d, *J* = 8.4 Hz, 1H, Ar), 8.70 (d, *J* = 8.0 Hz, 1H, Ar), 8.76 (d, *J* = 8.4 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 22.1, 28.9, 29.5, 122.5, 122.9, 126.4, 126.5, 126.7, 127.0, 127.4, 128.6, 128.8, 129.9, 130.5, 130.6, 131.6, 135.1, 135.8, 137.1, 141.8, 145.7. IR (CH_2Cl_2) ν 3050, 2921, 2857, 1596, 1450, 907, 856, 748, 726 cm^{-1}. MS (%) m/e 294 (M^+, 100.00), 289 (6.73), 279 (91.74), 265 (12.30), 252 (11.86), 239 (5.25), 147 (6.08), 138 (18.22), 126 (9.44). HRMS (EI) calcd. for $C_{23}H_{18}$: 294.1409, found: 294.1400.





4-Methyl-2-phenylbicyclo[4.2.0]octa-1,3,5-triene 3s:

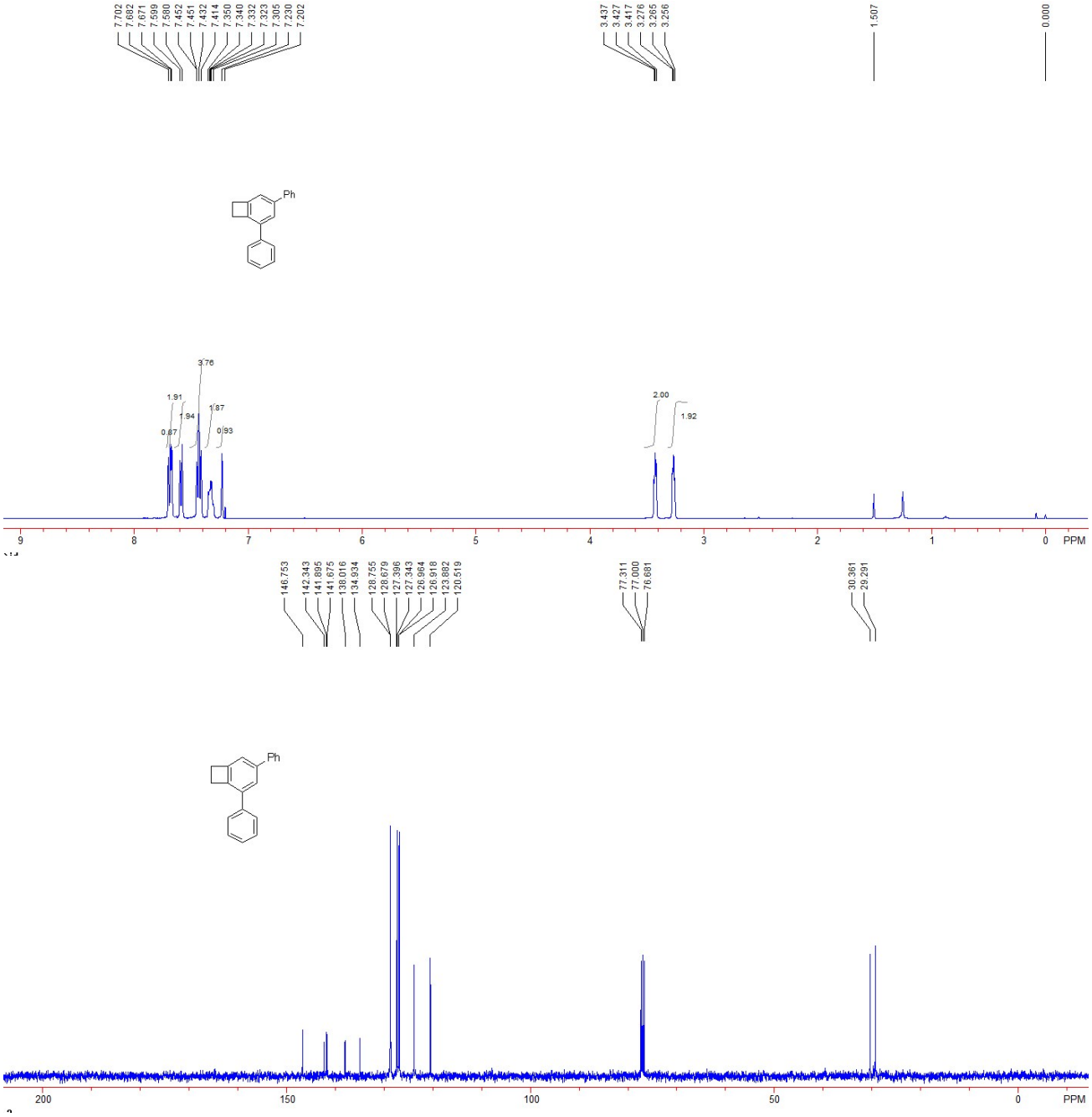
27 mg, yield = 70%. A white solid. Mp: 62-65 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.39 (s, 3H, CH_3), 3.18 (d, J = 4.0 Hz, 2H, CH_2), 3.35 (d, J = 4.0 Hz, 2H, CH_2), 6.85 (s, 1H, Ar), 7.27-7.31 (m, 2H, Ar), 7.39-7.43 (m, 2H, Ar), 7.63-7.65 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 22.1, 29.2, 30.2, 122.2, 125.0, 126.8, 127.1, 128.6, 134.4, 137.6, 138.2, 139.6, 146.3. IR (CH_2Cl_2) ν 3026, 2918, 2856, 1500, 1449, 1206, 1075, 855, 776, 758, 694 cm^{-1}. MS (%) m/e 194 (M^+, 44.20), 179 (100.00), 165 (12.84), 152 (11.35), 115 (8.01), 89 (21.75), 76 (11.30), 63 (9.58), 52 (2.08). HRMS (EI) calcd. for $C_{15}H_{14}$: 194.1096, found: 194.1098.

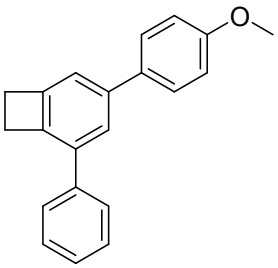


2,4-Diphenylbicyclo[4.2.0]octa-1(6),2,4-triene 3t:

26 mg, yield: 51%. A white solid. Mp: 103-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.27 (t, J = 4.0 Hz, 2H, CH_2), 3.43 (t, J = 4.0 Hz, 2H, CH_2), 7.23 (s, 1H, Ar), 7.31-7.35 (m, 2H, Ar), 7.41-7.45 (m, 4H, Ar), 7.59 (d, J = 7.6 Hz, 2H, Ar), 7.68 (d, J = 4.4 Hz, 2H, Ar), 7.70 (s, 1H, Ar). ^{13}C NMR

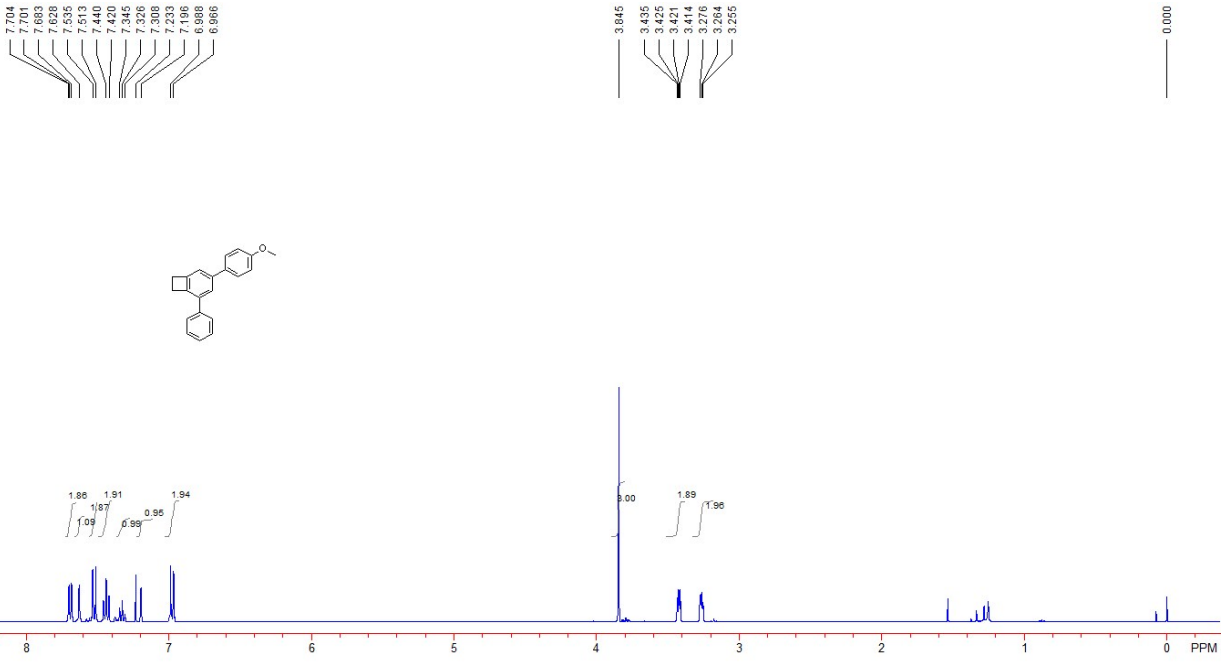
(100 MHz, $CDCl_3$, TMS): δ 29.3, 30.4, 120.5, 123.9, 126.9, 127.3, 128.7, 128.8, 134.9, 138.0, 141.7, 141.9, 142.3, 146.8. IR (CH_2Cl_2) ν 3030, 2918, 2823, 1580, 1459, 875, 773, 697 cm^{-1}. MS (%) m/e 256 (M^+, 100.00), 241 (69.25), 226 (7.11), 178 (11.10), 165 (10.83), 126 (11.40), 120 (2.73), 101 (5.24), 77 (4.96). HRMS (EI) calcd. for $C_{20}H_{16}$: 256.1252, found: 256.1248.

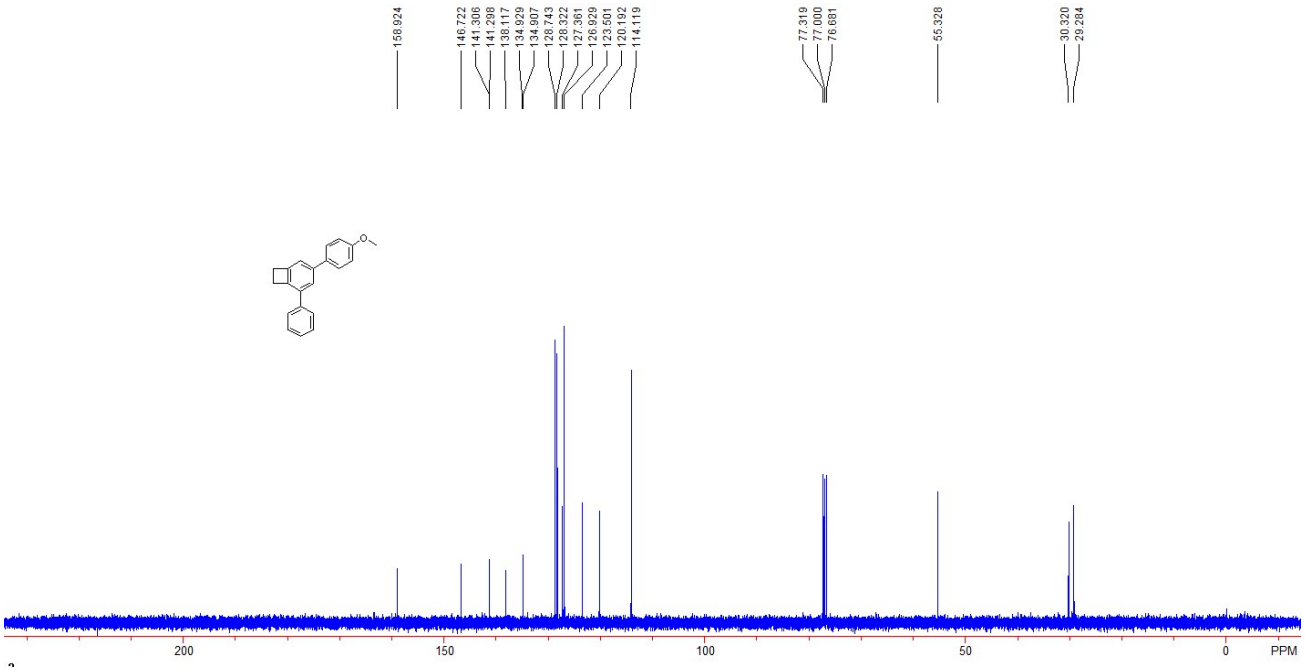


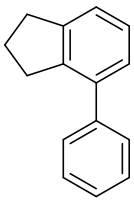


4-(4-Methoxyphenyl)-2-phenylbicyclo[4.2.0]octa-1(6),2,4-triene 3u:

30 mg, yield = 54%. A white solid. Mp: 128-130 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.26-3.28 (m, 2H, CH_2), 3.41-3.44 (m, 2H, CH_2), 3.85 (s, 3H, CH_3), 6.98 (d, J = 8.8 Hz, 2H, Ar), 7.20 (s, 1H, Ar), 7.31-7.35 (m, 1H, Ar), 7.42-7.44 (m, 2H, Ar), 7.52 (d, J = 8.8 Hz, 2H, Ar), 7.63 (s, 1H, Ar), 7.68-7.70 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.3, 30.3, 55.3, 114.1, 120.2, 123.5, 126.9, 127.4, 128.3, 128.7, 134.91, 134.93, 138.1, 141.30, 141.31, 146.7, 158.9. IR (CH_2Cl_2) ν 3033, 2920, 2833, 1607, 1515, 1244, 1178, 1030, 828, 695 cm^{-1}. MS (%) m/e 286 (M^+, 100.00), 271 (46.71), 255 (40.27), 239 (16.93), 228 (13.31), 178 (9.02), 121 (13.31), 101 (6.18), 77 (2.81). HRMS (EI) calcd. for $C_{21}H_{18}O$: 286.1358, found: 286.1367.

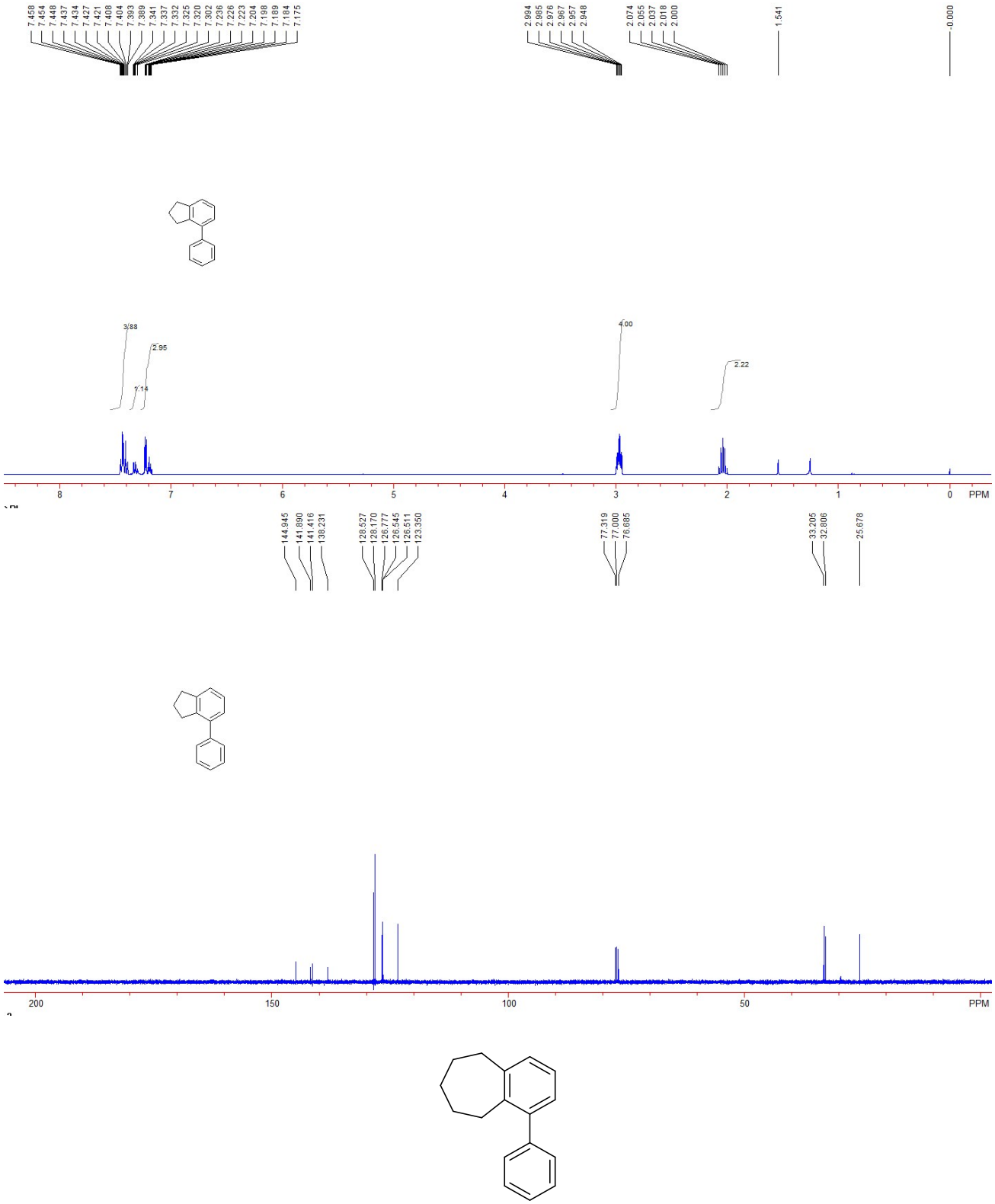






4-Phenyl-2,3-dihydro-1*H*-indene 4a:

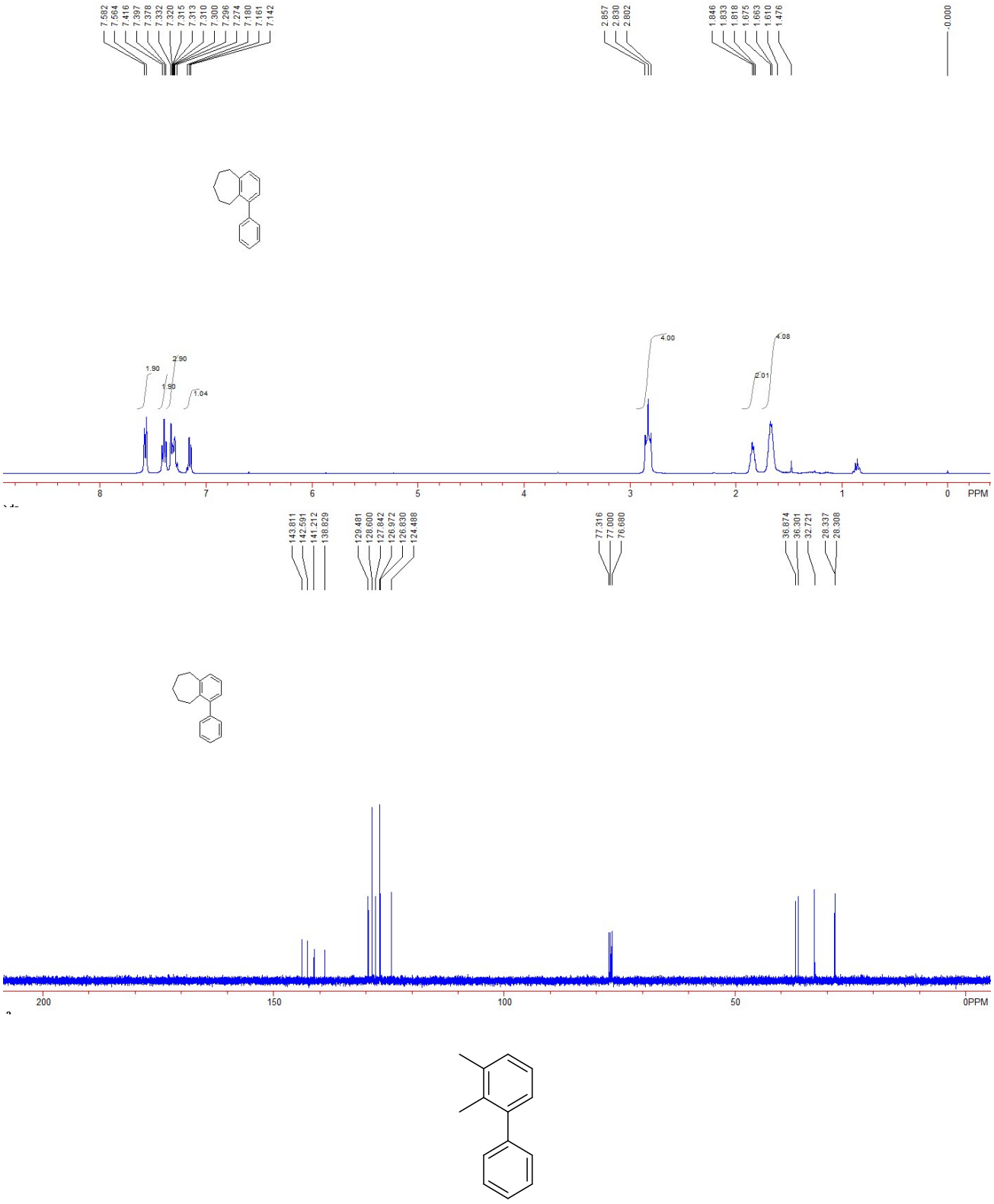
29 mg, yield = 75%. This is a known compound.[10] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.00-2.07 (m, 2H, CH_2), 2.95-2.99 (m, 4H, CH_2), 7.18-7.24 (m, 3H, Ar), 7.30-7.34 (m, 1H, Ar), 7.39-7.46 (m, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.7, 32.8, 33.2, 123.4, 126.51, 126.55, 126.8, 128.2, 128.5, 138.2, 141.4, 141.9, 144.9.



1-Phenyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene 4d:

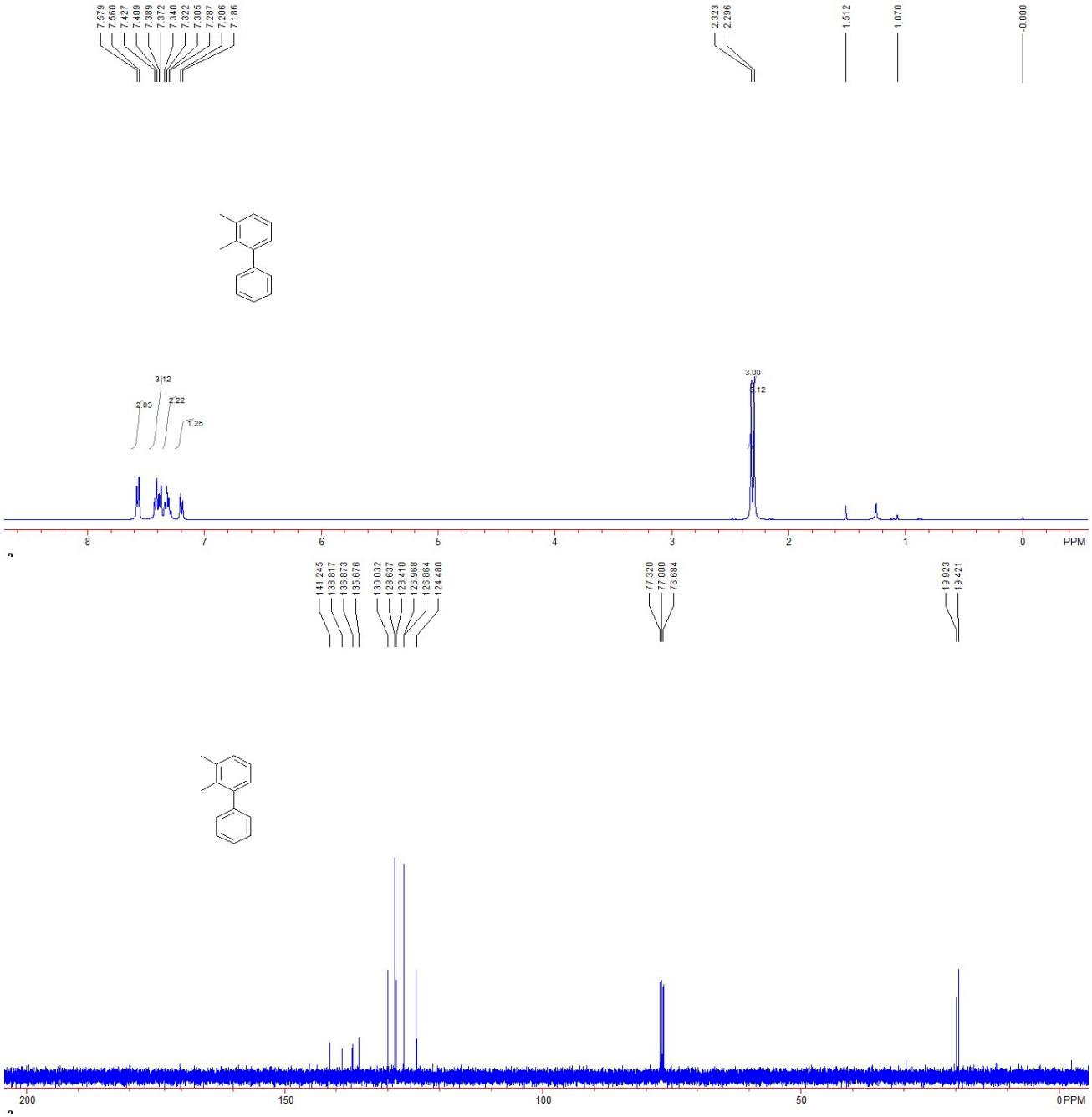
38 mg, yield = 84%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.61-1.68 (m, 4H, CH_2), 1.82-1.85 (m, 2H, CH_2), 2.83 (t, J = 10.8 Hz, 4H, CH_2), 7.14-7.18 (m, 1H, Ar), 7.27-7.33 (m, 3H, Ar), 7.40 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 2H, Ar), 7.57 (d, J = 7.2 Hz, 2H, Ar). ^{13}C NMR (100 MHz,

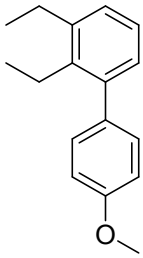
$CDCl_3$, TMS): δ 28.31, 28.33, 32.7, 36.3, 36.9, 124.5, 126.8, 127.8, 128.6, 129.5, 138.8, 141.2, 142.6, 143.8. IR (CH_2Cl_2) ν 3024, 2918, 1600, 1484, 1447, 820, 760, 695 cm^{-1}. MS (%) m/e 222 (M^+, 100.00), 207 (9.55), 193 (15.80), 178 (21.98), 165 (26.62), 152 (8.44), 115 (10.55), 89 (6.96). HRMS (EI) calcd. for $C_{17}H_{18}$: 222.1409, found: 222.1405.



2,3-Dimethyl-1,1'-biphenyl 4f:

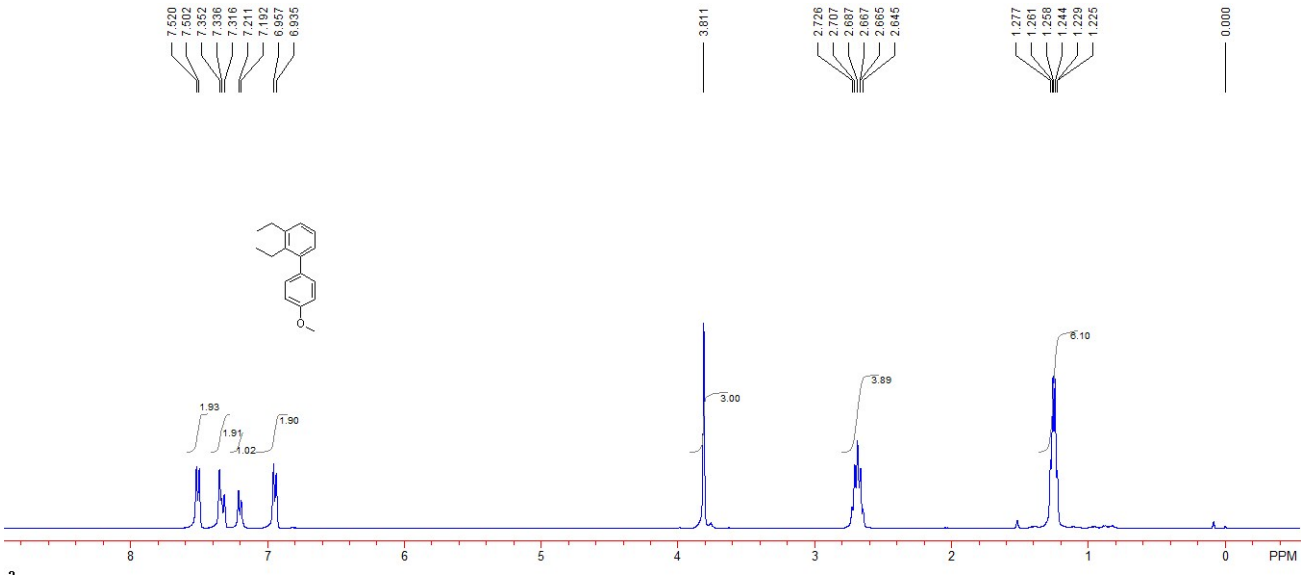
28 mg, yield = 75%. This is a known compound.[11] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.30 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 7.20 (d, J = 8.0 Hz, 1H, Ar), 7.29-7.34 (m, 2H, Ar), 7.37-7.43 (m, 3H, Ar), 7.56-7.58 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.4, 19.9, 124.5, 126.9, 127.0, 128.4, 128.6, 130.0, 135.7, 136.9, 138.8, 141.2.

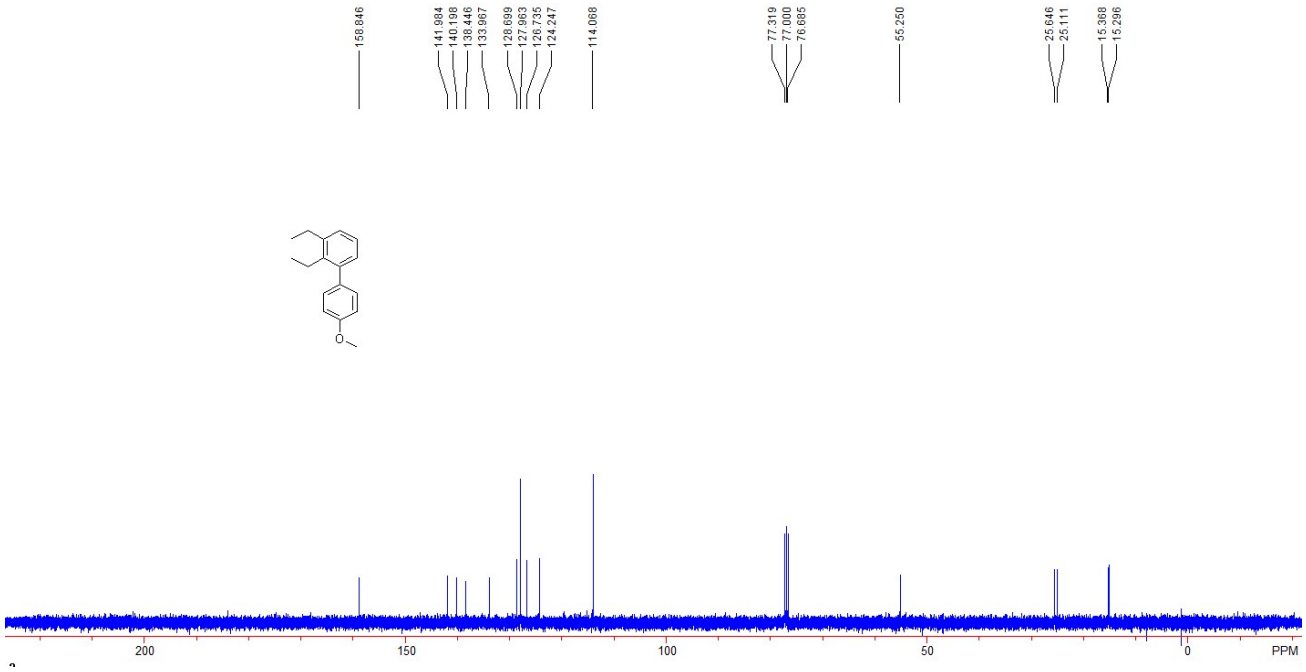


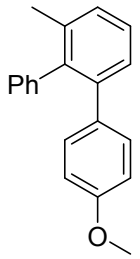


2,3-Diethyl-4'-methoxy-1,1'-biphenyl 4g:

40 mg, yield = 83%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.23-1.28 (m, 6H, CH_3), 2.65-2.73 (m, 4H, CH_2), 3.81 (s, 3H, CH_3), 6.95 (d, *J* = 8.0 Hz, 2H, Ar), 7.18-7.21 (m, 1H, Ar), 7.32-7.35 (m, 2H, Ar). 7.51 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 15.3, 15.4, 25.1, 25.6, 55.3, 114.1, 124.2, 126.7, 128.0, 128.7, 134.0, 138.4, 140.2, 142.0, 158.8. IR (CH_2Cl_2) ν 2963, 2872, 2834, 1609, 1491, 1245, 1179, 1038, 820 cm^{-1}. MS (%) m/e 240 (M^+, 100.00), 225 (69.69), 210 (15.98), 195 (10.91), 165 (12.63), 152 (9.83), 115 (6.93), 89 (4.40), 77 (3.12). HRMS (EI) calcd. for $C_{17}H_{20}O$: 240.1514, found: 240.1519.

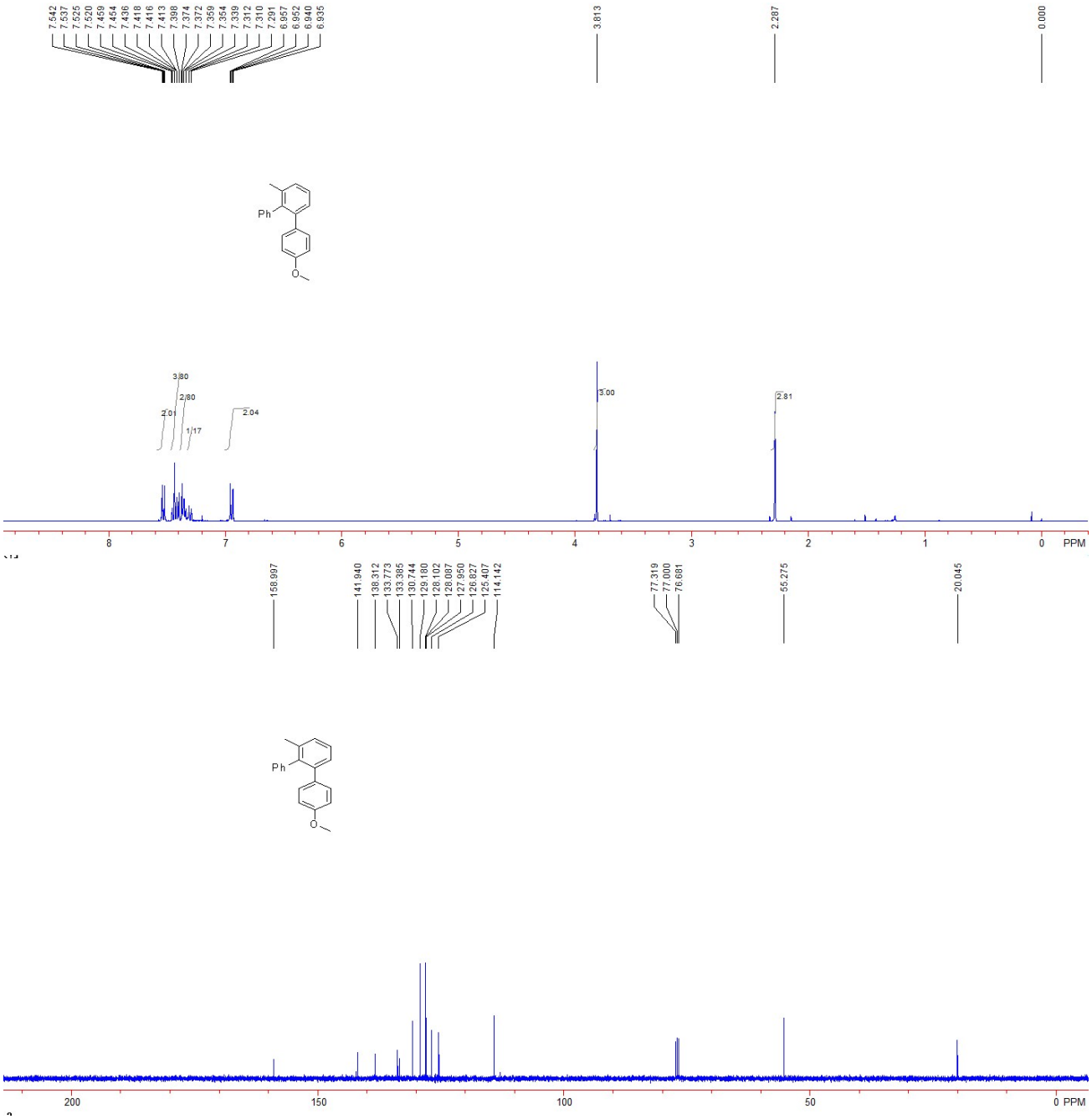






4-Methoxy-3'-methyl-1,1':2',1''-terphenyl 4h:

34 mg, yield = 62%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.29 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 6.95 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H, Ar), 7.29-7.31 (m, 1H, Ar), 7.34-7.37 (m, 3H, Ar), 7.40-7.46 (m, 4H, Ar), 7.53 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 20.0, 55.3, 114.1, 125.4, 126.8, 128.0, 128.1, 129.2, 130.7, 133.4, 133.8, 138.3, 141.9, 159.0. IR (CH_2Cl_2) ν 3047, 2931, 2835, 1609, 1484, 1246, 1177, 838, 701 cm^{-1}. MS (%) m/e 274 (M^+, 100.00), 259 (28.88), 231 (9.87), 215 (11.63), 165 (5.93), 152 (2.37), 137 (3.77), 115 (3.25), 101 (5.77). HRMS (EI) calcd. for $C_{20}H_{18}O$: 274.1358, found: 274.1361.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6.940
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Ph
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2.80
2.01
1.17
2.04
3.00
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7
6
5
4
3
2
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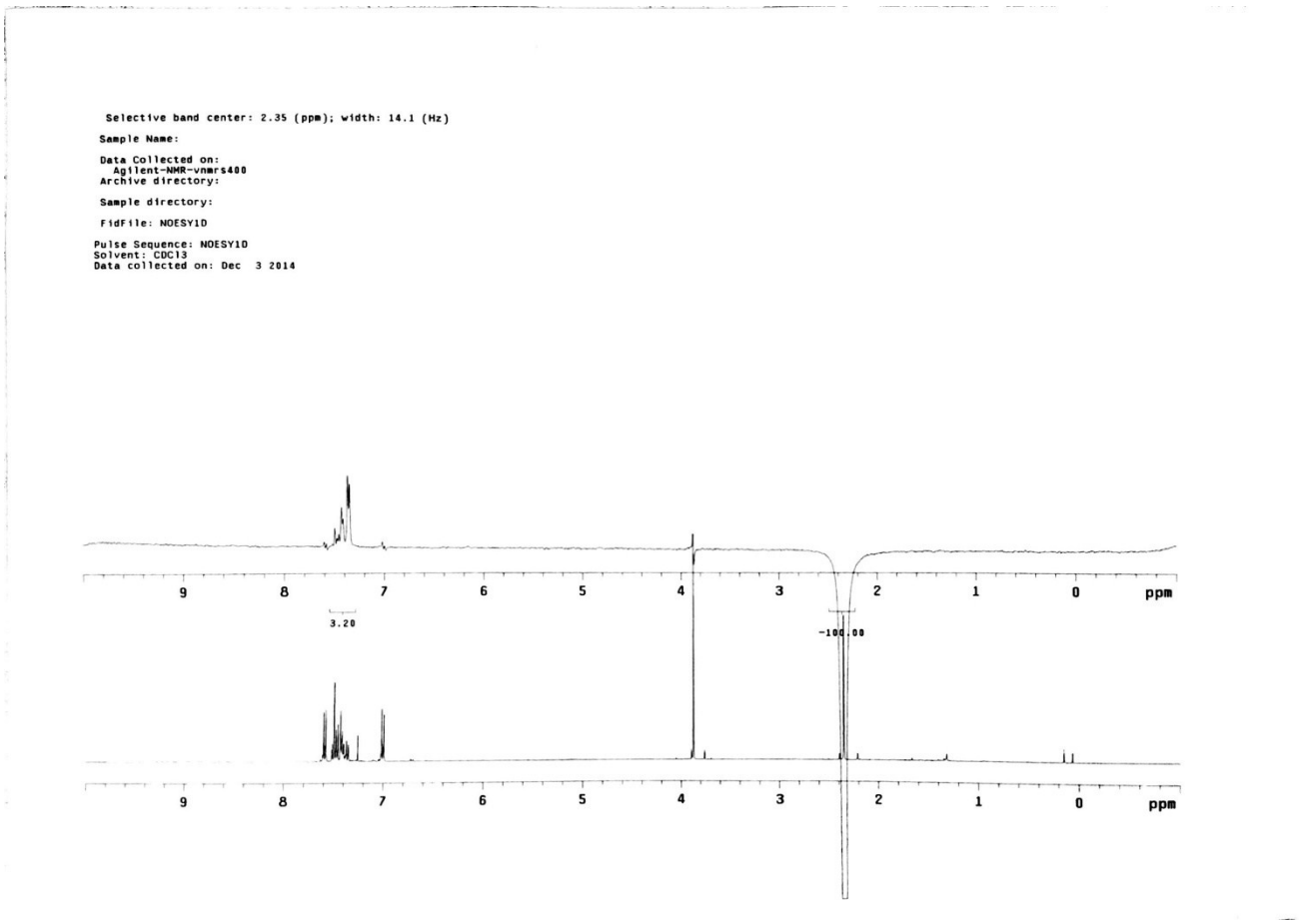
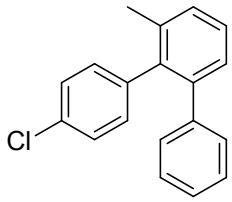
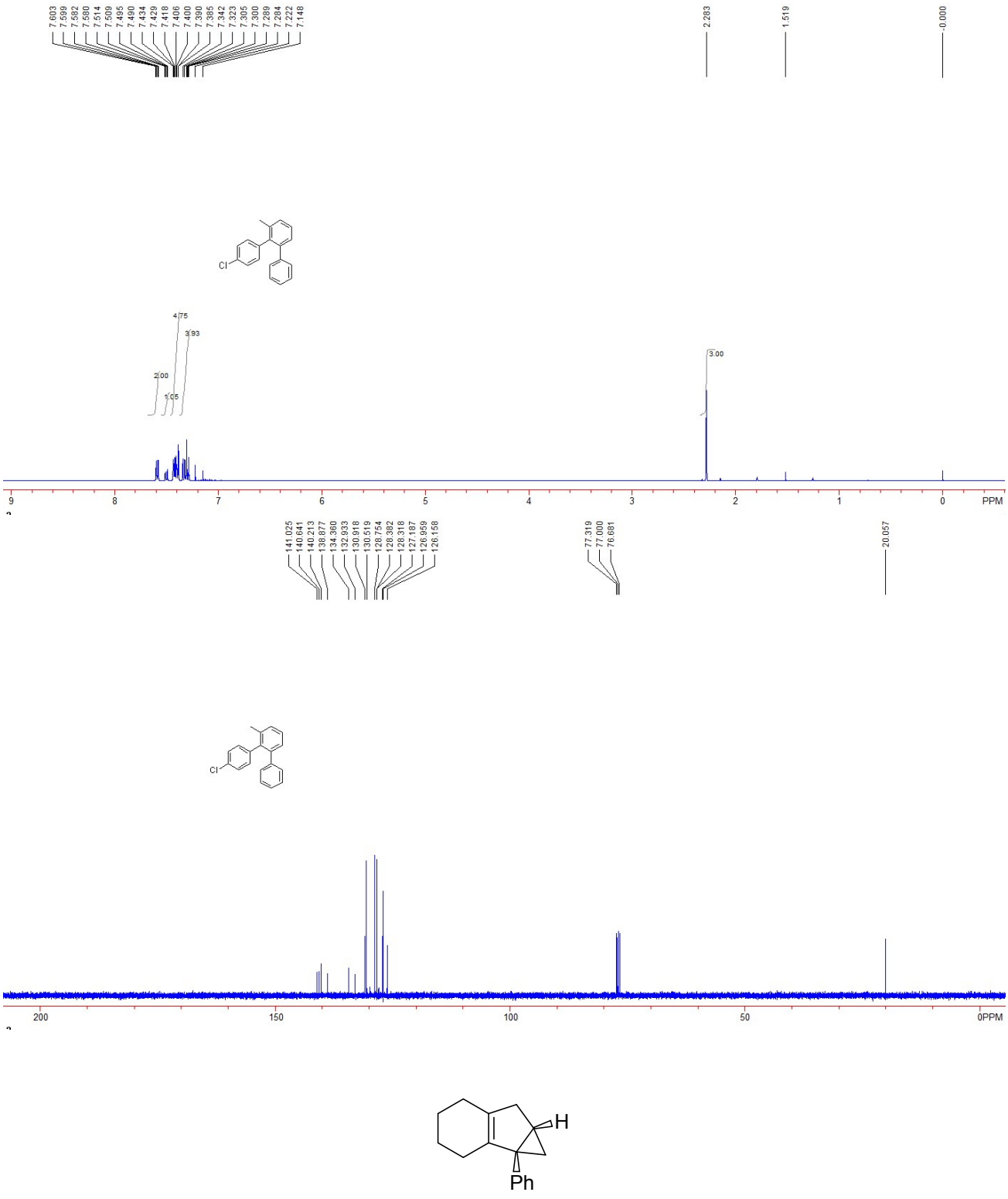




4''-chloro-3'-methyl-1,1':2',1''-terphenyl 4i:

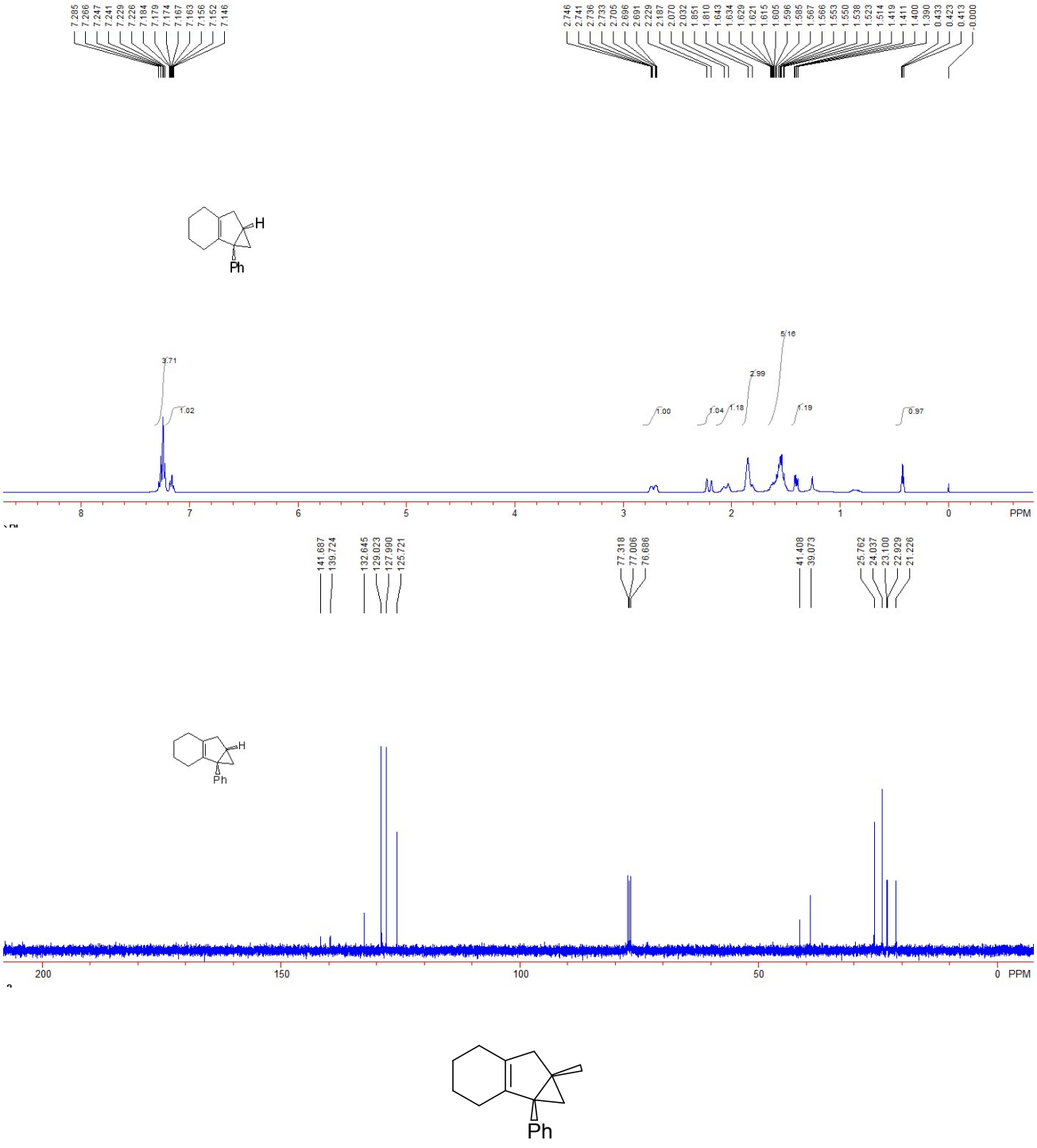
32 mg, yield = 57%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.28 (s, 3H, CH_3), 7.28-7.34 (m, 4H, Ar), 7.39-7.43 (m, 5H, Ar), 7.50 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H, Ar), 7.58-7.60 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 20.1, 126.2, 127.0, 128.3, 128.4, 128.8, 130.5, 130.9, 132.9, 134.4, 138.9, 140.2, 140.6, 141.0. IR (CH_2Cl_2) ν 3027, 2921, 1477, 1385, 1090, 1017, 828, 748, 696 cm^{-1}. MS (%) m/e 278 (M^+, 100.00), 243 (20.56), 228 (13.70), 215 (6.63), 165 (20.28), 120 (11.45), 107 (4.09), 91 (9.17), 77 (3.90). HRMS (EI) calcd. for $C_{19}H_{15}Cl$: 278.0862, found: 278.0867.



1a-Phenyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*a*]indene 5b:

38 mg, yield = 90%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.41-0.43 (m, 1H, CH_2), 0.39-0.42 (m, 1H, CH_2), 1.51-1.64 (m, 5H), 1.81-1.85 (m, 3H), 2.05 (d, *J* = 15.2 Hz, 1H), 2.21 (d, *J* = 16.8 Hz, 1H), 2.69-2.75 (m, 1H), 7.15-7.18 (m, 1H, Ar), 7.23-7.29 (m, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.2, 22.9, 23.1, 24.0, 25.8, 39.1, 41.4, 125.7, 128.0, 129.0, 132.6, 139.7,

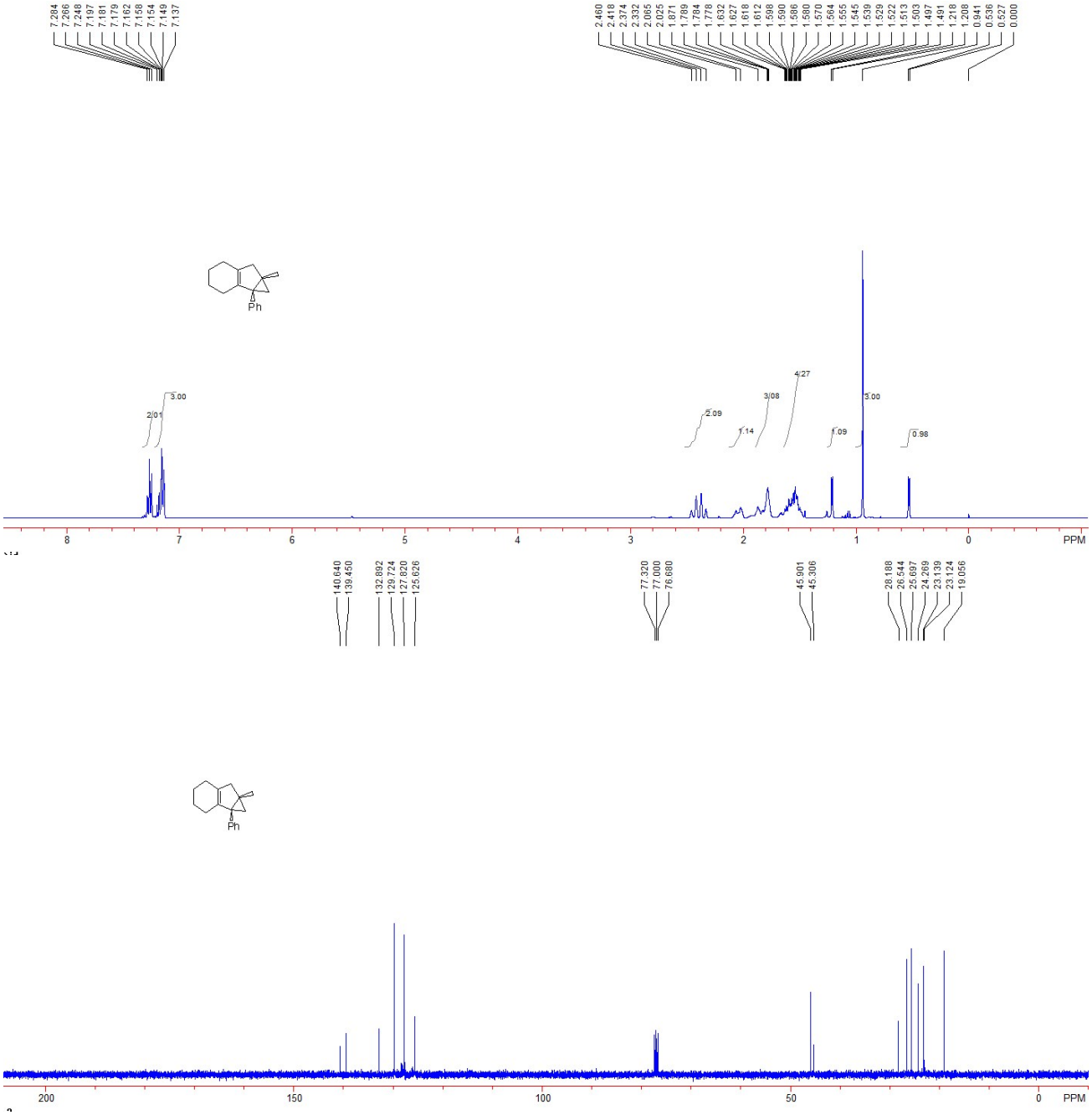
141.7. IR (CH_2Cl_2) ν 3346, 3057, 2927, 1658, 1445, 1265, 1021, 735, 699 cm^{-1}. MS (%) m/e 210 (M^+, 100.00), 195 (33.96), 181 (28.75), 167 (59.96), 152 (17.18), 128 (15.59), 115 (24.68), 91 (44.87), 77 (19.15). HRMS (EI) calcd. for $C_{16}H_{18}$: 210.1408, found: 210.1409.

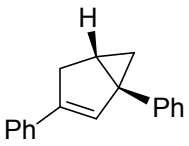


6a-Methyl-1a-phenyl-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*a*]indene 5c:

44 mg, yield = 97%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.53 (d, J = 4.0 Hz, 1H, CH_2), 0.94 (s, 3H, CH_3), 1.21 (d, J = 4.0 Hz, 1H, CH_2), 1.49-1.63 (m, 4H, CH_2), 1.78-1.87 (m, 3H,

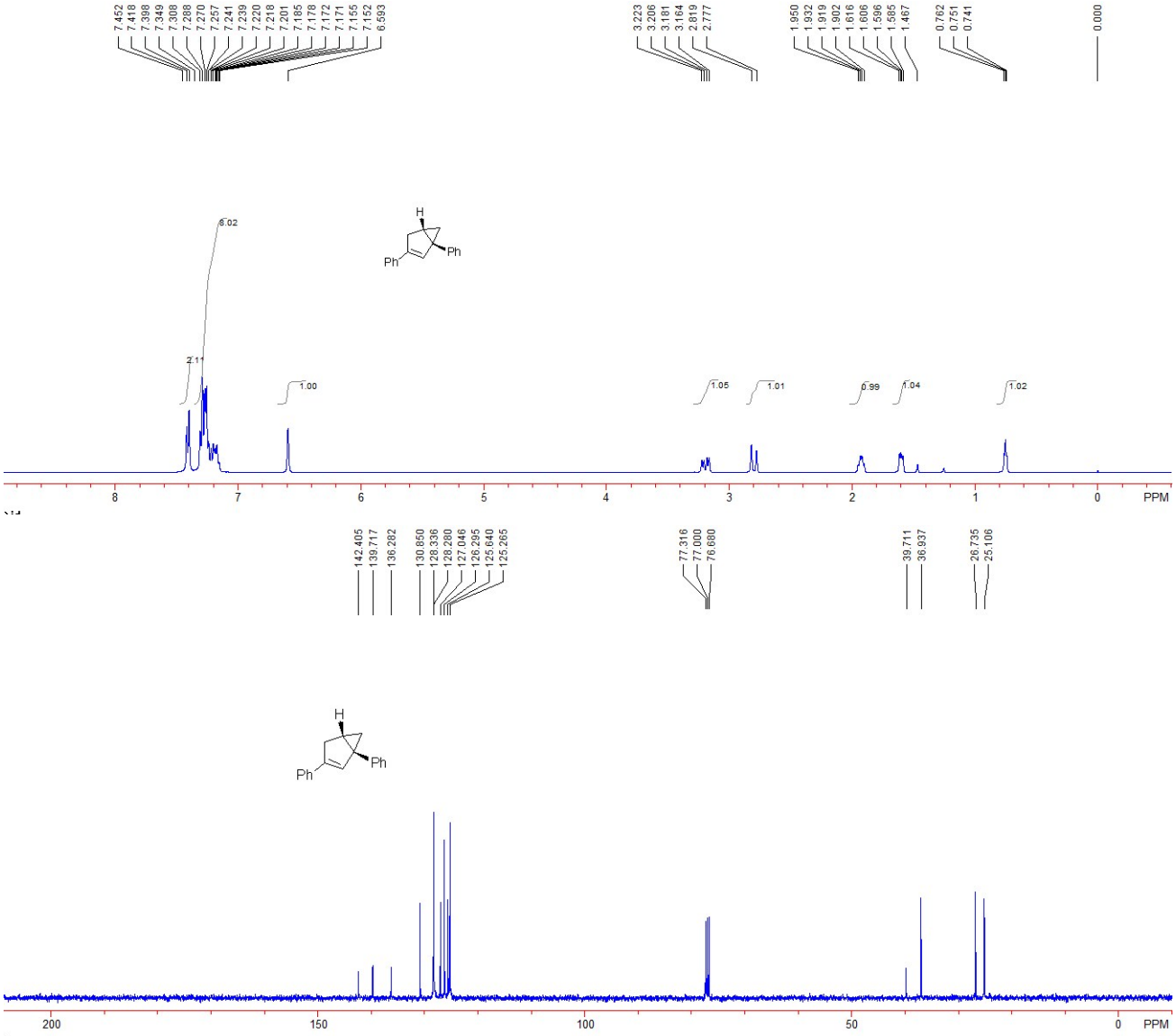
CH_2), 2.03-2.07 (m, 1H, CH_2), 2.35 (d, J = 16.8 Hz, 1H, CH_2), 2.44 (d, J = 16.8 Hz, 1H, CH_2), 7.14-7.20 (m, 3H, Ar), 7.25-7.28 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 23.12, 23.14, 24.3, 25.7, 26.5, 28.2, 45.3, 45.9, 125.6, 127.8, 129.7, 132.9, 139.5, 140.6. IR (CH_2Cl_2) ν 3056, 2925, 2832, 1686, 1444, 1265, 1023, 735 cm^{-1}. MS (%) m/e 224 (M^+, 99.93), 209 (70.55), 181 (30.88), 167 (100.00), 152 (15.73), 128 (14.37), 115 (22.38), 91 (36.40), 77 (19.84). HRMS (EI) calcd. for $C_{17}H_{20}$: 224.1565, found: 224.1464.

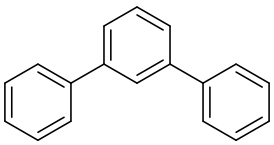




1,3-diphenylbicyclo[3.1.0]hex-2-ene 5i:

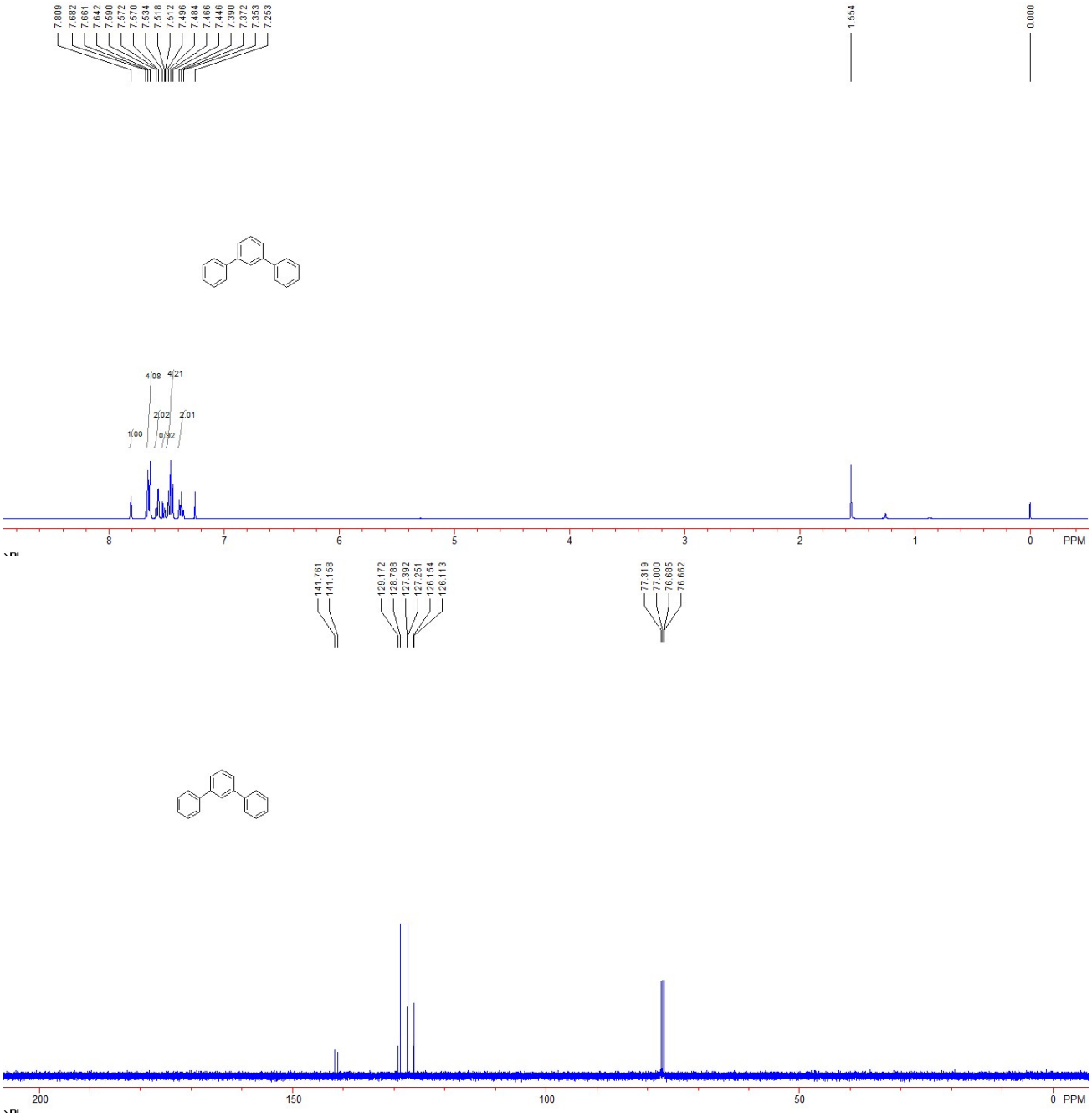
This is a known compound.[8] yield: 91%; A white solid. Mp: 59-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.22 (d, *J* = 4.0 Hz, 2H, CH_2), 3.40 (d, *J* = 4.0 Hz, 2H, CH_2), 7.01 (d, *J* = 7.2 Hz, 1H, Ar), 7.19-7.32 (m, 2H, Ar), 7.39-7.47 (m, 3H, Ar), 7.64 (d, *J* = 7.2 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.5, 30.8, 121.4, 124.3, 126.8, 127.2, 127.9, 128.7, 134.7, 138.1, 142.9, 146.4.



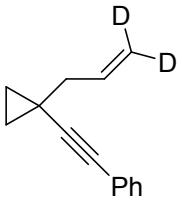


1,1':3',1''-Terphenyl 6i:

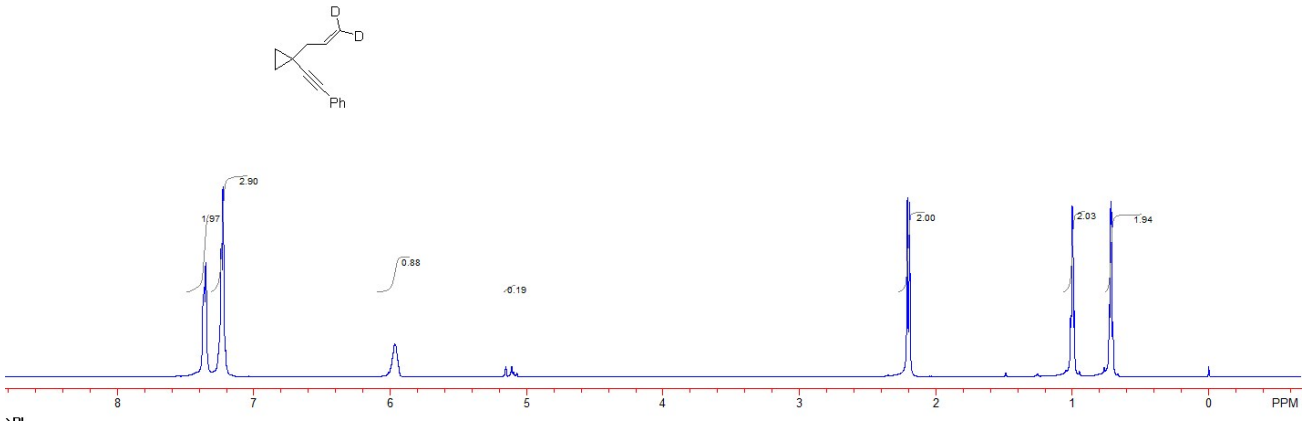
3 mg, yield = 7%. This is a known compound.[12] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.35-7.39 (m, 2H, Ar), 7.45-7.50 (m, 4H, Ar), 7.51-7.53 (m, 1H, Ar), 7.57-7.59 (m, 4H, Ar), 7.81 (s, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 126.1, 126.2, 127.3, 127.4, 128.8, 129.2, 141.2, 141.8.

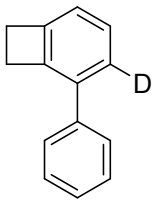


4. ^{1}H NMR Spectra of the Deuterated Compounds.

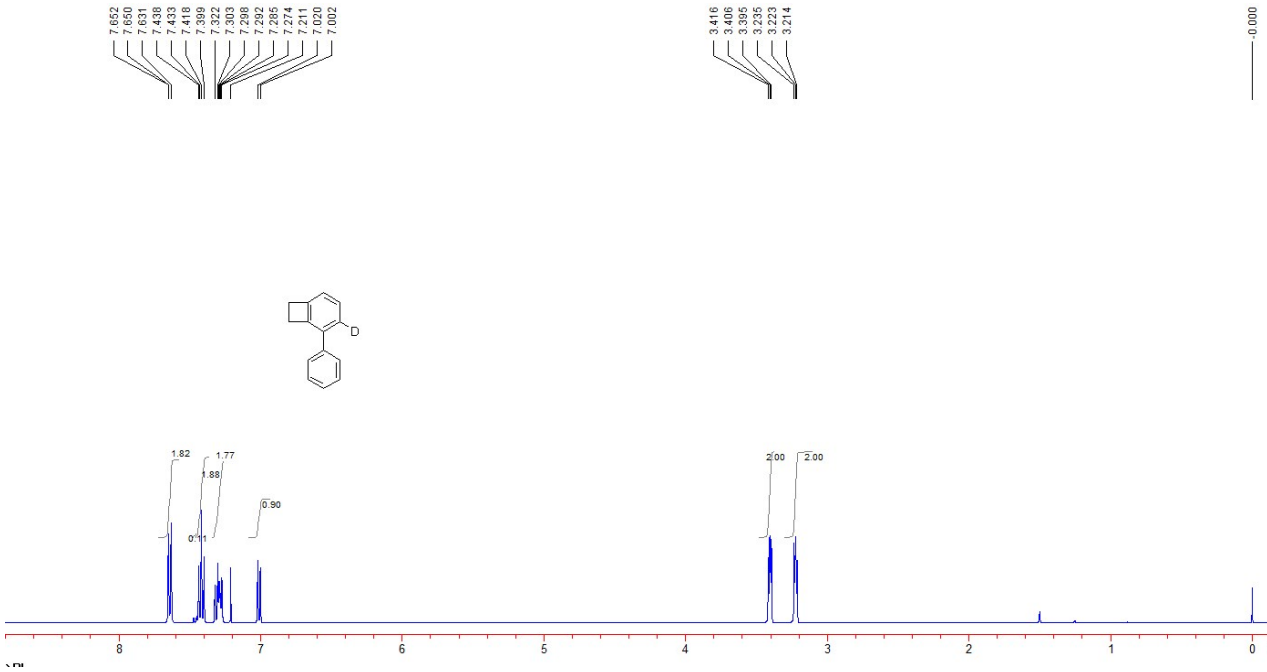


[D_2-1a]





[D_1-3a]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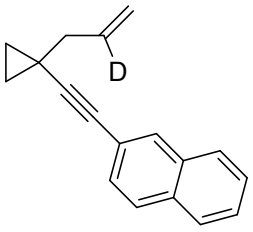
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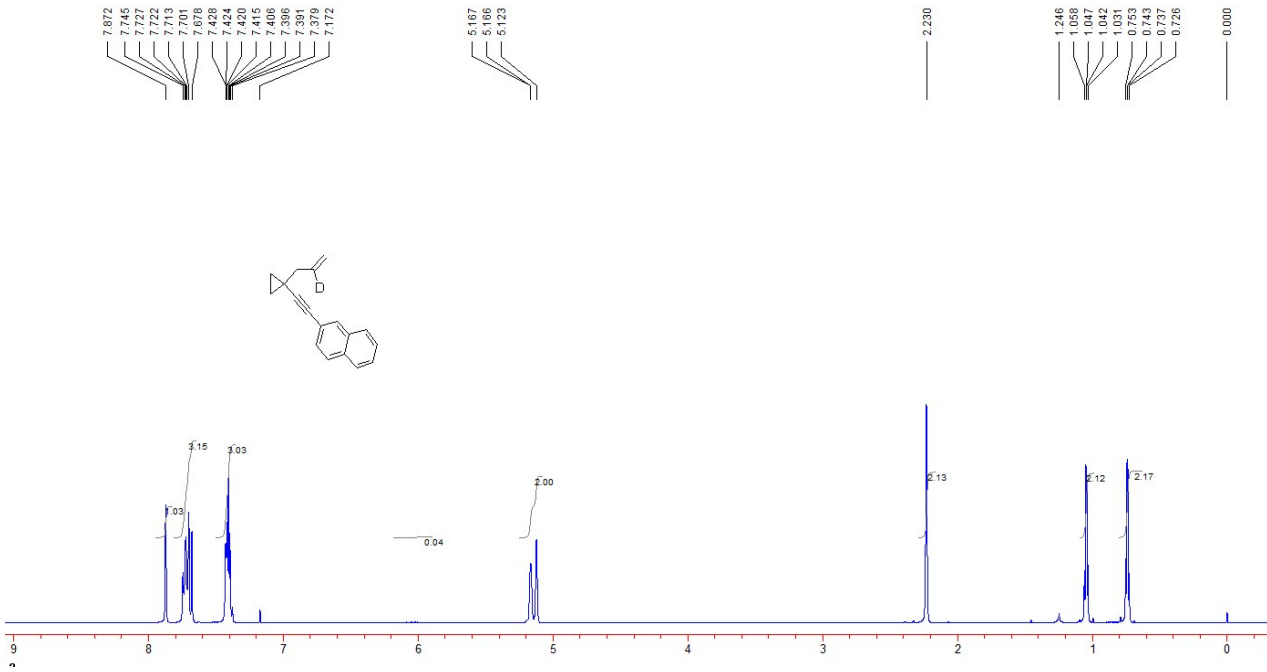
[D_1-1p]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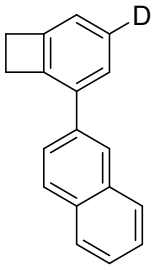
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[D_1-3p]


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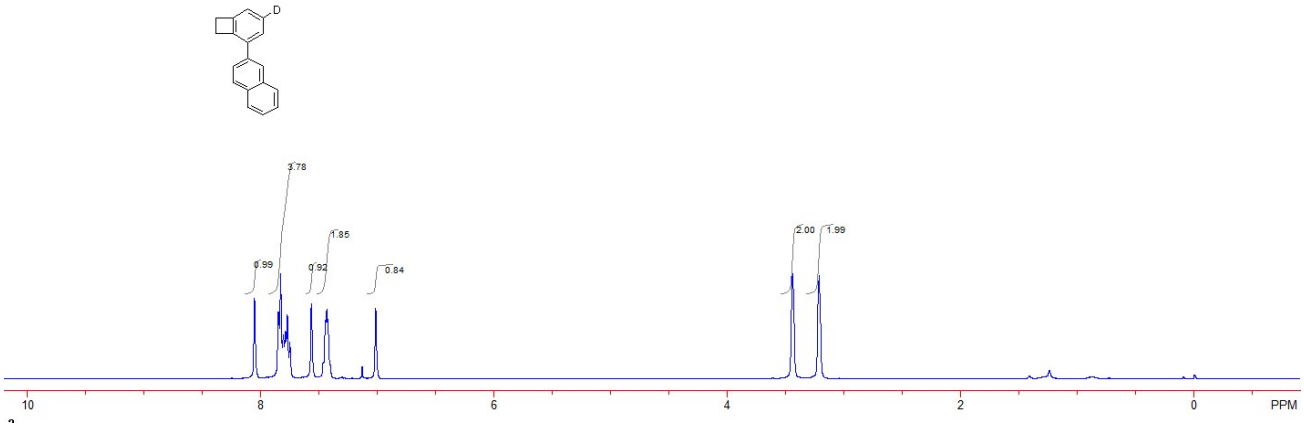
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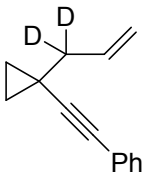
D
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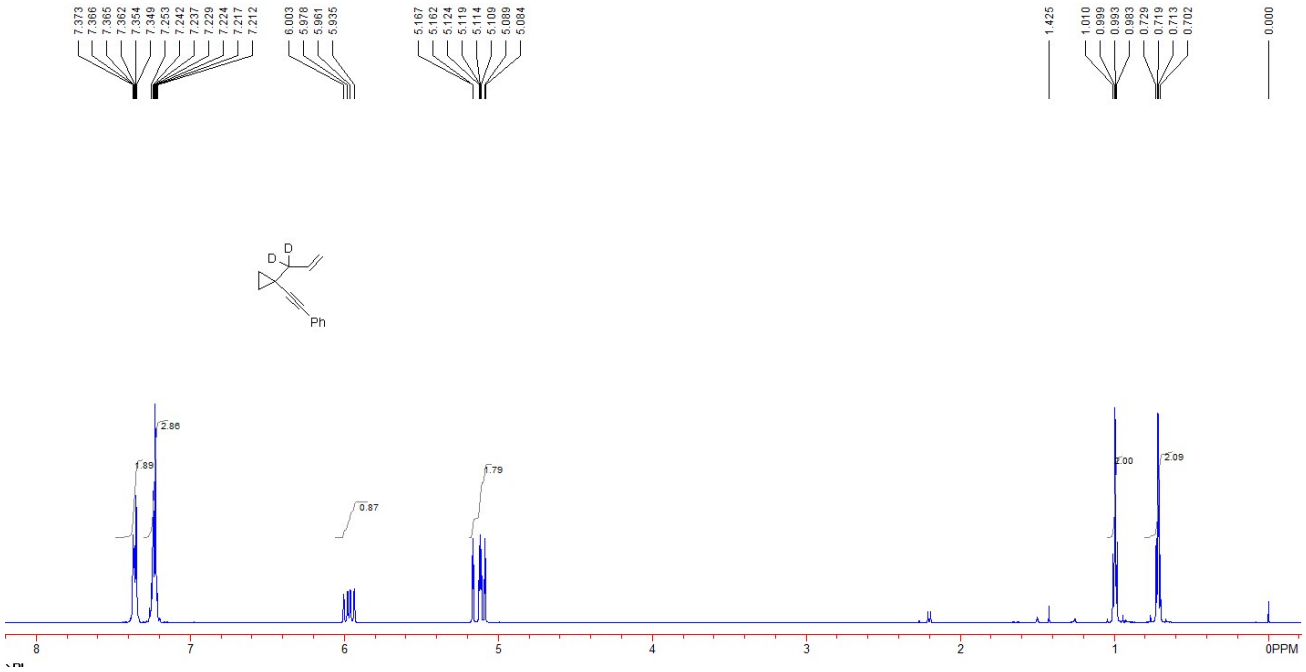
[D_1-1a']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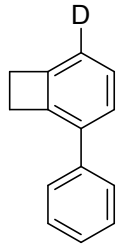
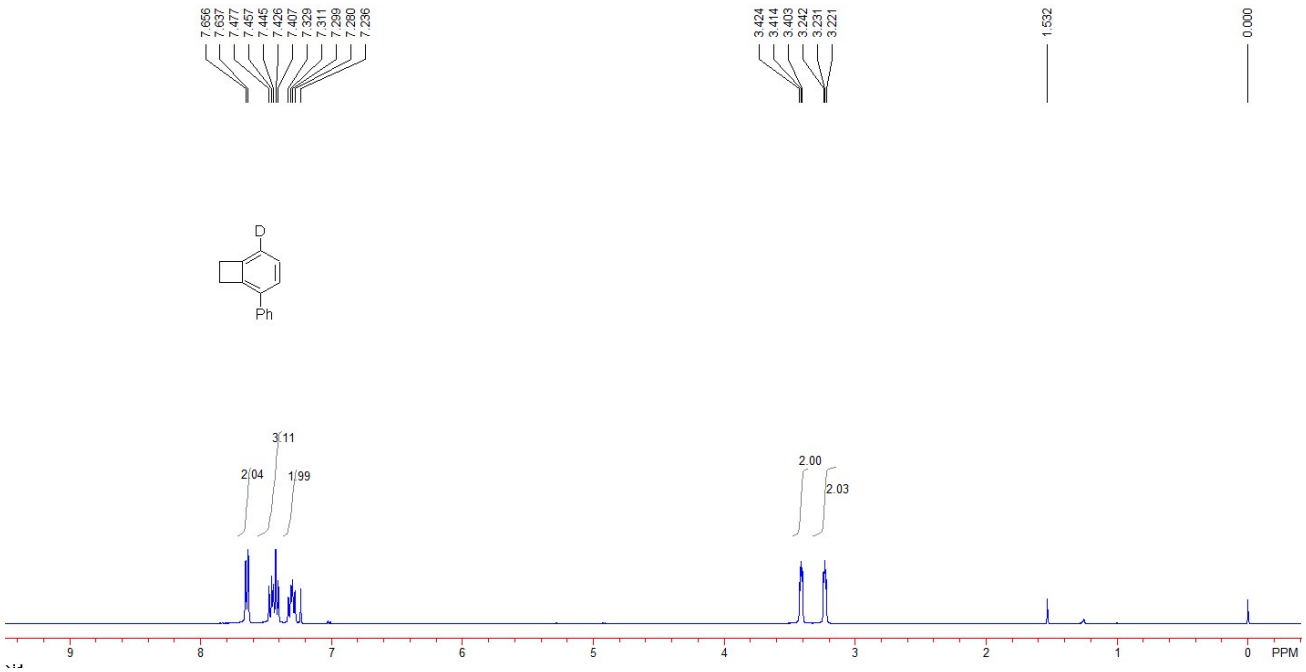

D

[D_2-3a']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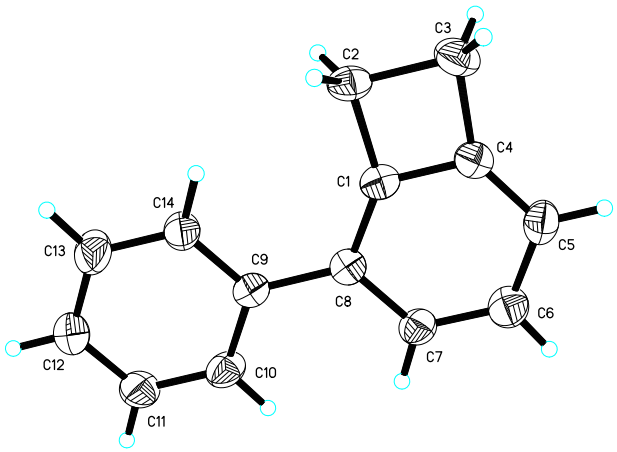
PPM

5. Crystallographic Information.



The crystal data of **3a** have been deposited in CCDC with number 873625. Empirical Formula: $C_{14}H_{12}$; Formula Weight: 180.24; Crystal Color, Habit: colorless; Crystal Dimensions: 0.231 x 0.203 x 0.157 mm; Crystal System: Monoclinic; Lattice Parameters: a = 18.222(9)Å, b = 5.648(3)Å, c = 20.014(9)Å, α = 90°, β = 97.925(11)°, γ = 90°, V = 2040.1(17)Å^3; Space group: P2(1)/c; Z = 8; D_{calc}= 1.174 g/cm^3; F_{000} = 768; Final R indices [I>2sigma(I)] R1 = 0.1149, wR2 = 0.2699.

6. Reference

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