

Supporting Information

Rhodium-catalyzed Tandem Pauson-Khand Type Reactions of 1,4 Enynes Tethered by a Cyclopropyl Group

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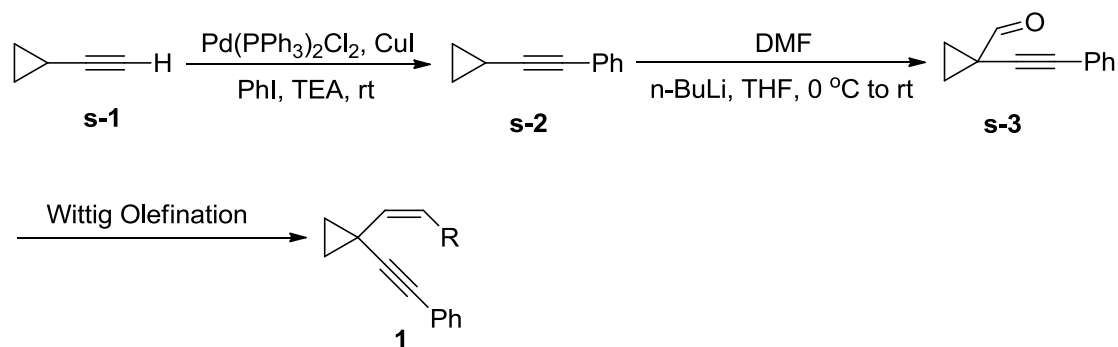
1. **General Remarks.** ^1H and ^{13}C NMR spectra were recorded at the 300 and 75 MHz or the 400 and 100 MHz, respectively. Mass and HRMS spectra were recorded by EI or ESI method. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. 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 Reaction Procedure

Representative procedures for the preparation of substrates:

The substrates **1a**, **1a'**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k** and **1l** were synthesized according to Scheme S1. The compound **s-3** was synthesized according to reported procedure.^[1]

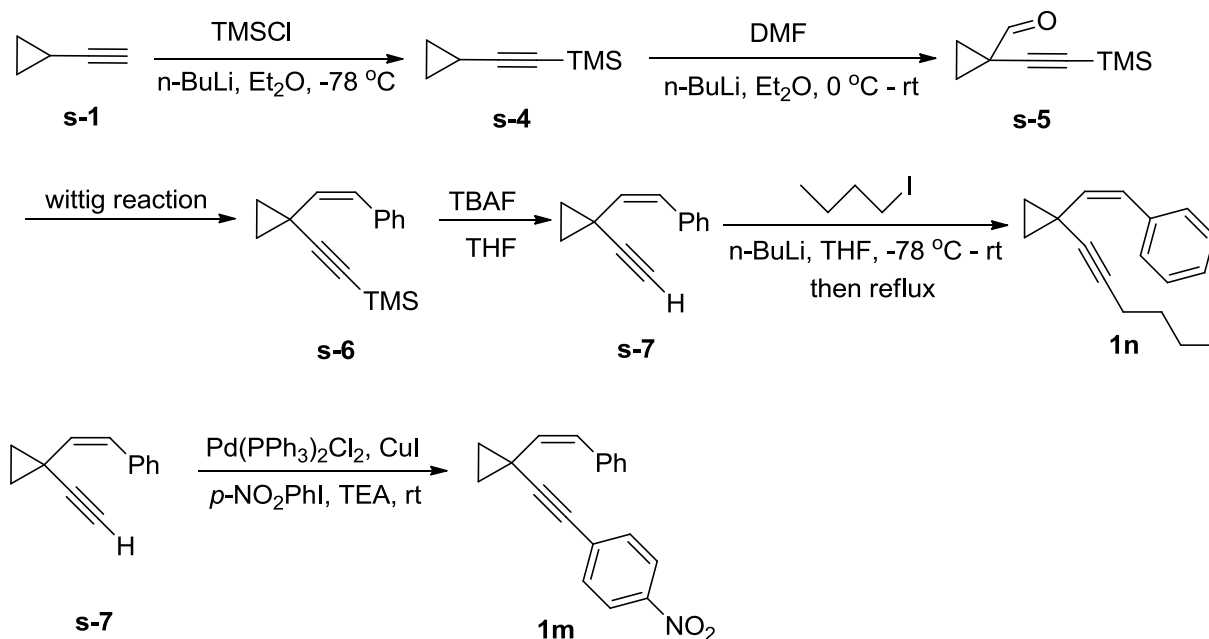
Synthesis of substrate **1a-1l**: to a 50 mL flame and vacuum dried flask was added 4.33 mmol the corresponding Wittig salt, and 30 mL anhydrous THF, then 1.6 mL *n*-BuLi (2.5M in hexane) was added dropwise at 0 °C. After 10 minutes, 615 mg of **s-3** was added to the mixture dropwise. The reaction was allowed to stir overnight. The product was purified by column chromatography using PE as eluent. The *cis* product was obtained as major product in about 60-80% yields.



Scheme S1

The substrates **1m** and **1n** were synthesized according to Scheme S2. The compound **s-7** was synthesized according to reported procedure.^[2,3,1] (a) Synthesis of substrate **1m**: To a 100 mL flame and vacuum dried three-neck flask was added 336 mg **s-7**, 500 mg *p*-nitroiodobenzene and 25 mL TEA, then the mixture was solidified by liquid nitrogen, evacuated and filled with argon for 5 times. 71 mg of (PPh₃)₂PdCl₂, 38 mg of CuI was added afterwards. The flask was evacuated and filled with argon for 5 times again. The flask was allowed to warm to rt and stir for 12 hours. The product was purified by column chromatography (PE/EA = 20/1), 505 mg of product was afforded as product (yield = 87%). (b) The substrate **1n** was synthesized according to literature procedure.^[4] To a 100 mL flame and vacuum dried three-neck flask was added 969 mg of **s-7** and 25 mL dry THF, 2.5 mL *n*-BuLi (2.5M in hexane) was added dropwise at -78 °C, the mixture was allowed to warm to rt overnight. 1.32 mL *n*-butyl iodide

was added dropwise, the mixture was allowed to stir at reflux for 12 hours. The reaction was not complete. ¹H-NMR indicates that the conversion is about 60% (The product cannot be isolated by column chromatography). The product was obtained by vacuum distillation or by gel permeation chromatography.



Scheme S2

General procedure for the rhodium catalyzed cascade reactions of substrates 1a-o:

To a 25 mL flame and vacuum dried Schlenk tube was added the substrate **1** (0.2 mmol) and the catalyst. The tube was evacuated and filled with CO for 5 times, then the solvent was added, and the tube was allowed to stir in an oil bath. The product was purified by column chromatography or preparative silica gel plates using PE and EA as eluent (PE/EA = 4/1).

3. Optimization of the reaction conditions.

We initiated our investigations by seeking the optimal conditions for the tandem Pauson-Khand type reaction of 1,4 enyne **1a** in the presence of rhodium catalyst and the results are indicated in Table 1. With $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (5 mol %) as the catalyst, the product **2a** was afforded in 35% yield (100 °C, 8 h). The yield of **2a** could be improved to 55% or 60% when the reaction was carried out at 120 °C or when the reaction time was extended to 18 h at 140 °C (Table SI-1, entries 1-3). The rhodium catalyst was also screened in xylene. $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$, $[\text{Rh}(\text{COD})\text{Cl}]_2$ and Wilkinson catalyst were found to be ineffective in this transformation and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was identified as the best catalyst (Table SI-1, entries 5-7). Upon further screening of various solvents such as TCE (1,1,2,2-tetrachloroethane), diglyme, nonane, toluene, acetonitrile and mixed solvent (n-decane/p-xylene = 3/1), no improvement in yield was observed (Table SI-1, entries 8-13). It has been reported that adding NMO (4-methylmorpholine N-oxide) could promote Pauson-Khand reaction because it can lead to dissociation of CO from the metal center. However, this additive did not improve the outcome of our reaction (Table SI-1, entry 14). Other additives such as AgSbF_6 and $(\text{C}_6\text{F}_5)_3\text{P}$ were also ineffective to improve the yield of **2a** (Table SI-1, entries 15 and 16). Increasing or decreasing the pressure of CO or increasing the employed amount of Rh(I) catalyst did not give better results either (Table SI-1, entries 17-19).

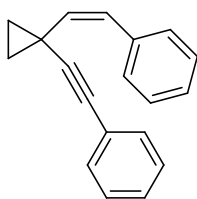
Table SI-1. Optimization of the Reaction Conditions

1a $\xrightarrow[\text{solvent (2 mL)}]{\text{catalyst (5 mol\%), CO, additive}}$ **2a**

entry ^a	catalyst	additive	time (h)	solvent	P (atm)	T (°C)	yield (%) ^b
1	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	8	<i>p</i> -xylene	1	100	35
2 ^c	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	8	<i>p</i> -xylene	1	120	55
3	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	<i>p</i> -xylene	1	140	60
4	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	<i>p</i> -xylene (4 mL)	1	140	53
5	$\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$	-	24	<i>p</i> -xylene	1	140	complex
6	$\text{Rh}(\text{PPh}_3)_3\text{Cl}$	-	12	<i>p</i> -xylene	1	140	complex
7	$[\text{Rh}(\text{COD})\text{Cl}]_2$	-	21	<i>p</i> -xylene	1	140	complex
8	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	TCE	1	120	25
9	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	diglyme	1	140	no reaction
10	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	24	Nonane	1	140	33
11	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	decane/ <i>p</i> -xylene (3/1)	1	140	55
12	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	12	toluene	1	100	52
13	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	CH_3CN	1	100	no reaction
14	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	NMO	12	<i>p</i> -xylene	1	140	no reaction
15	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	AgSbF_6	12	<i>p</i> -xylene	1	100	complex
16	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	$(\text{C}_6\text{F}_5)_3\text{P}$	12	<i>p</i> -xylene	1	100	complex
17	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	<i>p</i> -xylene	30	140	complex
18	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	-	18	<i>p</i> -xylene	< 1 ^d	140	50
19	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (10 mol%)	-	18	<i>p</i> -xylene	1	140	54

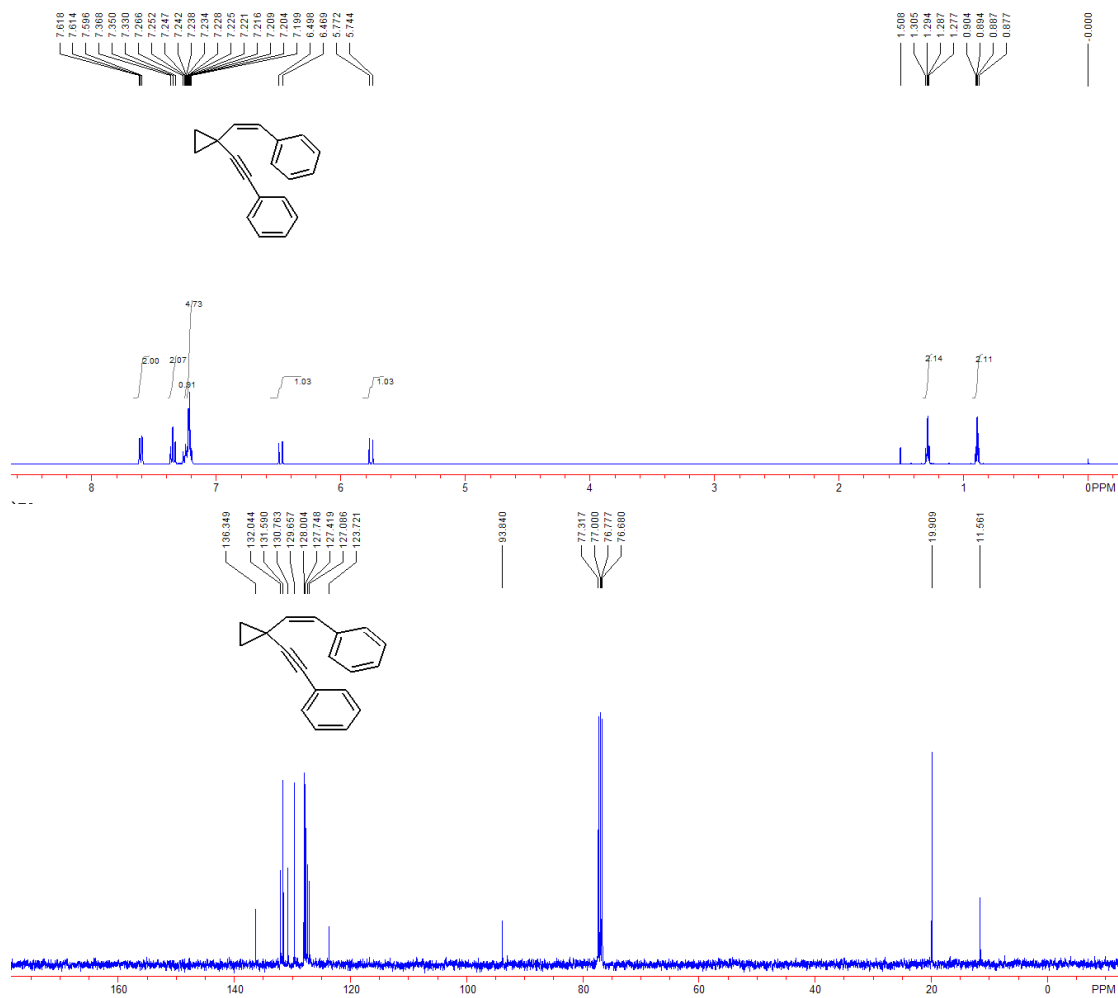
^a The reaction was performed in a 25 mL flame and vacuum dried Schlenk tube. **1** (0.2 mmol) and the catalyst (4 mg, 5 mol%) was added and the tube was evacuated and filled with CO for 5 times, then the solvent was added and the tube was allowed to stir in an oil bath. ^b Isolated yields. ^c The unreacted starting material was recovered in 23% yield as E/Z isomeric mixtures (E/Z = 1/4). ^d CO and Ar mixed atmosphere.

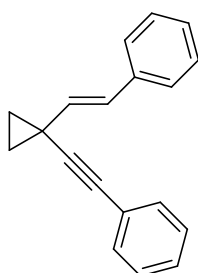
4. Spectroscopic Data.



(Z)-(2-(1-(Phenylethynyl)cyclopropyl)vinyl)benzene 1a:

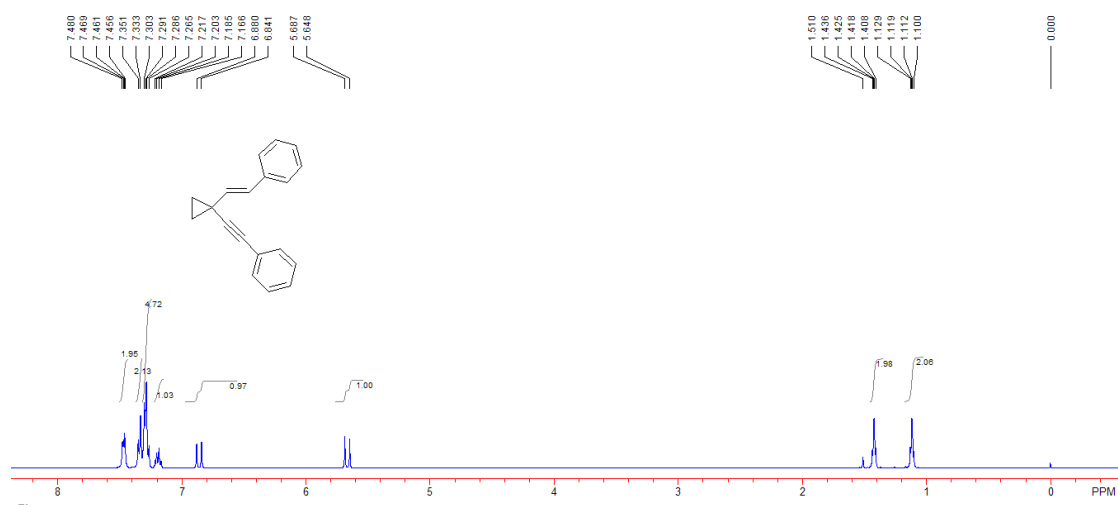
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.89 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.29 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 5.76 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.48 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 7.20-7.23 (m, 5H, Ar), 7.24-7.33 (m, 1H, Ar), 7.35 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.2$ Hz, Ar), 7.62 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 11.6, 19.9, 76.7, 93.8, 123.7, 127.1, 127.4, 127.7, 128.0, 129.7, 130.8, 131.6, 132.0, 136.3. IR (Neat) ν 3077, 3008, 1596, 1490, 1445, 1028, 773, 730, 689 cm^{-1} . MS (%) m/e 244 (M^+ , 56.42), 229 (85.65), 215 (62.81), 202 (18.39), 165 (58.98), 115 (100.00), 107 (37.52), 91 (41.85), 77 (13.78). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{16}$: 244.1252, Found: 244.1246.

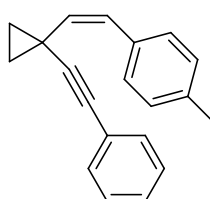
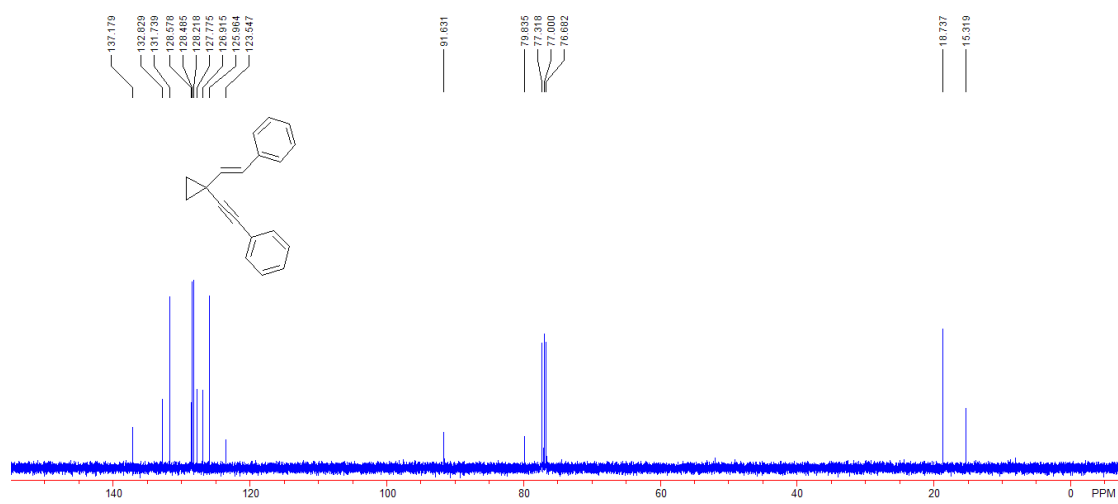




(E)-2-(1-(Phenylethynyl)cyclopropyl)vinylbenzene 1a':

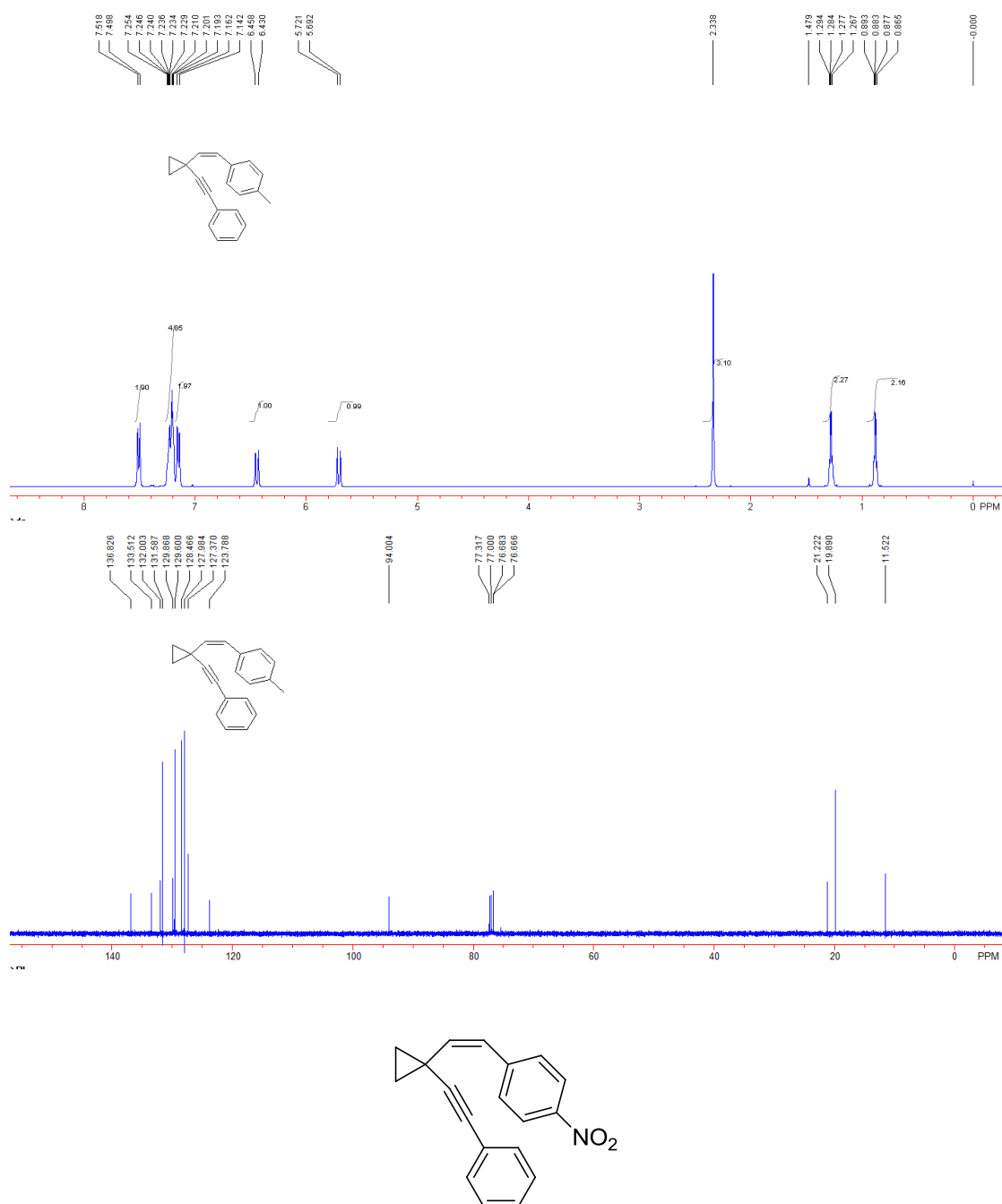
A white solid. Mp: 65-67 °C. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.12 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.4$ Hz, 2H, CH_2), 1.42 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.4$ Hz, 2H, CH_2), 5.68 (d, $J = 15.6$ Hz, 1H, $=\text{CH}$), 6.86 (d, $J = 15.6$ Hz, 1H, $=\text{CH}$), 7.17-7.22 (m, 1H, Ar), 7.29-7.30 (m, 5H, Ar), 7.34 (d, $J = 7.2$ Hz, 2H, Ar), 7.46-7.48 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 15.3, 18.7, 79.8, 91.6, 123.5, 126.0, 126.9, 127.8, 128.2, 128.5, 128.6, 131.7, 132.8, 137.2. IR (Neat) ν 3080, 3024, 3004, 1652, 1698, 1490, 1275, 960, 749, 689 cm^{-1} . MS (%) m/e 244 (M^+ , 86.33), 243 (68.01), 229 (100.00), 228 (84.12), 215 (60.63), 165 (73.92), 128 (25.02), 115 (88.49), 91 (35.15). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{16}$: 244.1252, Found: 244.1250.





(Z)-1-Methyl-4-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1b:

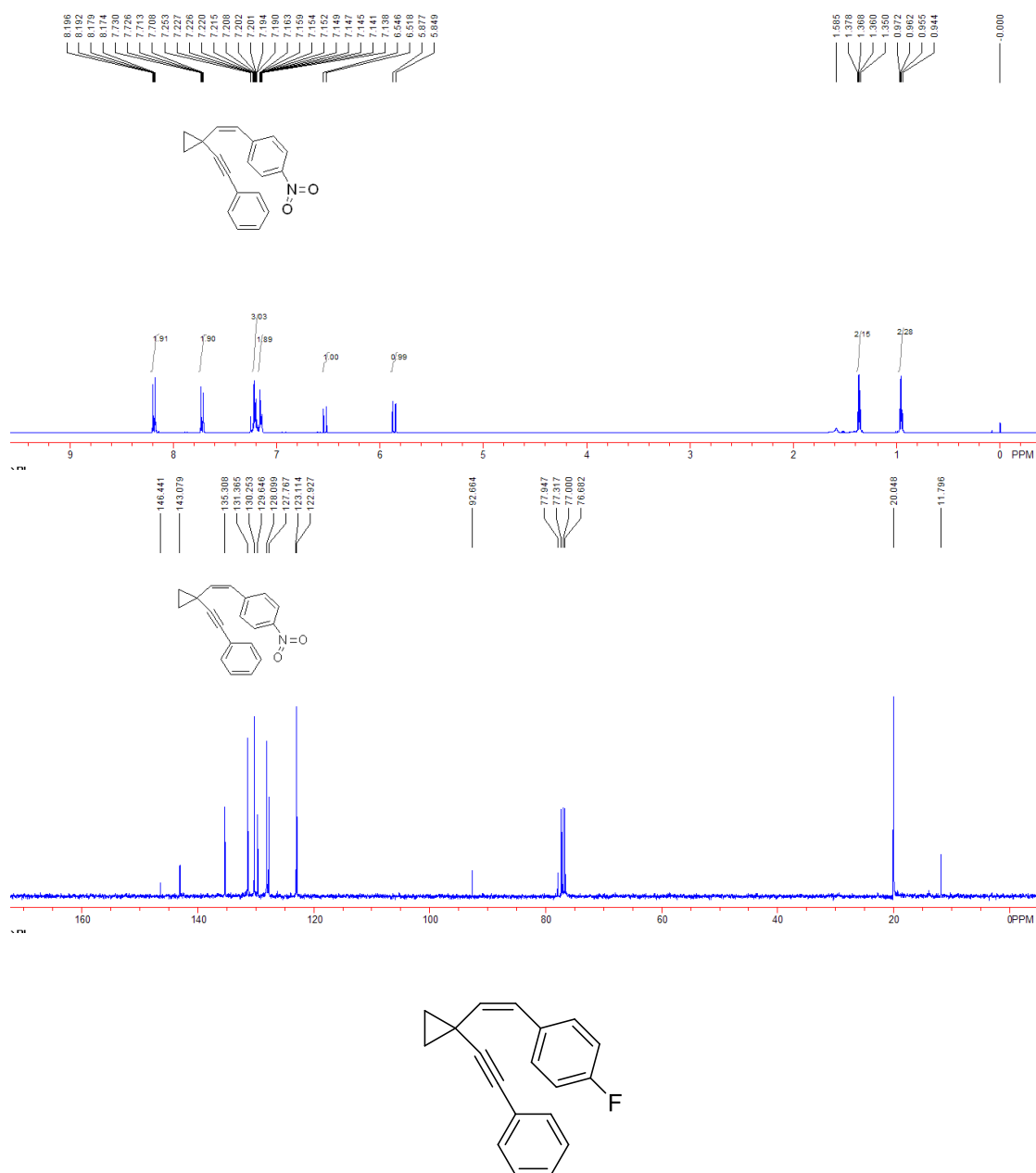
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.88 (dd, $J_1 = 6.4$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.28 (dd, $J_1 = 6.4$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 2.34 (s, 3H, CH_3), 5.71 (d, $J = 11.6$ Hz, 1H, $=\text{CH}$), 6.44 (d, $J = 11.6$ Hz, 1H, $=\text{CH}$), 7.15 (d, $J = 8.0$ Hz, 2H, Ar), 7.19-7.25 (m, 5H, Ar), 7.51 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 11.5, 19.9, 21.2, 76.7, 94.0, 123.8, 127.4, 128.0, 128.5, 129.6, 129.9, 131.6, 132.0, 133.5, 136.8. IR (Neat) ν 3081, 2919, 2857, 1595, 1509, 907, 753, 730, 689 cm^{-1} . MS (%) m/e 258 (M^+ , 53.09), 243 (75.80), 228 (67.85), 215 (34.93), 165 (51.73), 128 (41.24), 115 (100.00), 101 (32.26), 91 (55.24). HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{18}$: 258.1409, Found: 258.1413.



(Z)-1-Nitro-4-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1c:

Yellowish oil. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.96 (dd, *J*₁ = 6.8 Hz, *J*₂ = 4.4 Hz, 2H, CH₂), 1.36 (dd, *J*₁ = 6.8 Hz, *J*₂ = 4.4 Hz, 2H, CH₂), 5.86 (d, *J* = 11.2 Hz, 1H, =CH), 6.53 (d, *J* = 11.6 Hz, 1H, =CH), 7.14-7.16 (m, 2H, Ar), 7.19-7.23 (m, 3H, Ar), 7.72 (dd, *J*₁ = 6.8 Hz, *J*₂ = 1.6 Hz, 2H, Ar), 8.19 (dd, *J*₁ = 6.8 Hz, *J*₂ = 1.6 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 11.8, 20.0, 77.9, 92.7, 123.0, 123.1, 127.8, 128.1, 129.6, 130.3, 131.4, 135.3, 143.1, 146.4. IR (Neat) ν 3077, 3016, 2955, 2449, 1595, 1512, 855, 754, 687 cm⁻¹. MS (%) *m/e* 289 (M⁺, 66.42), 272 (33.83), 242 (67.95), 228 (57.39), 213 (42.69), 165 (47.91), 115 (100.00),

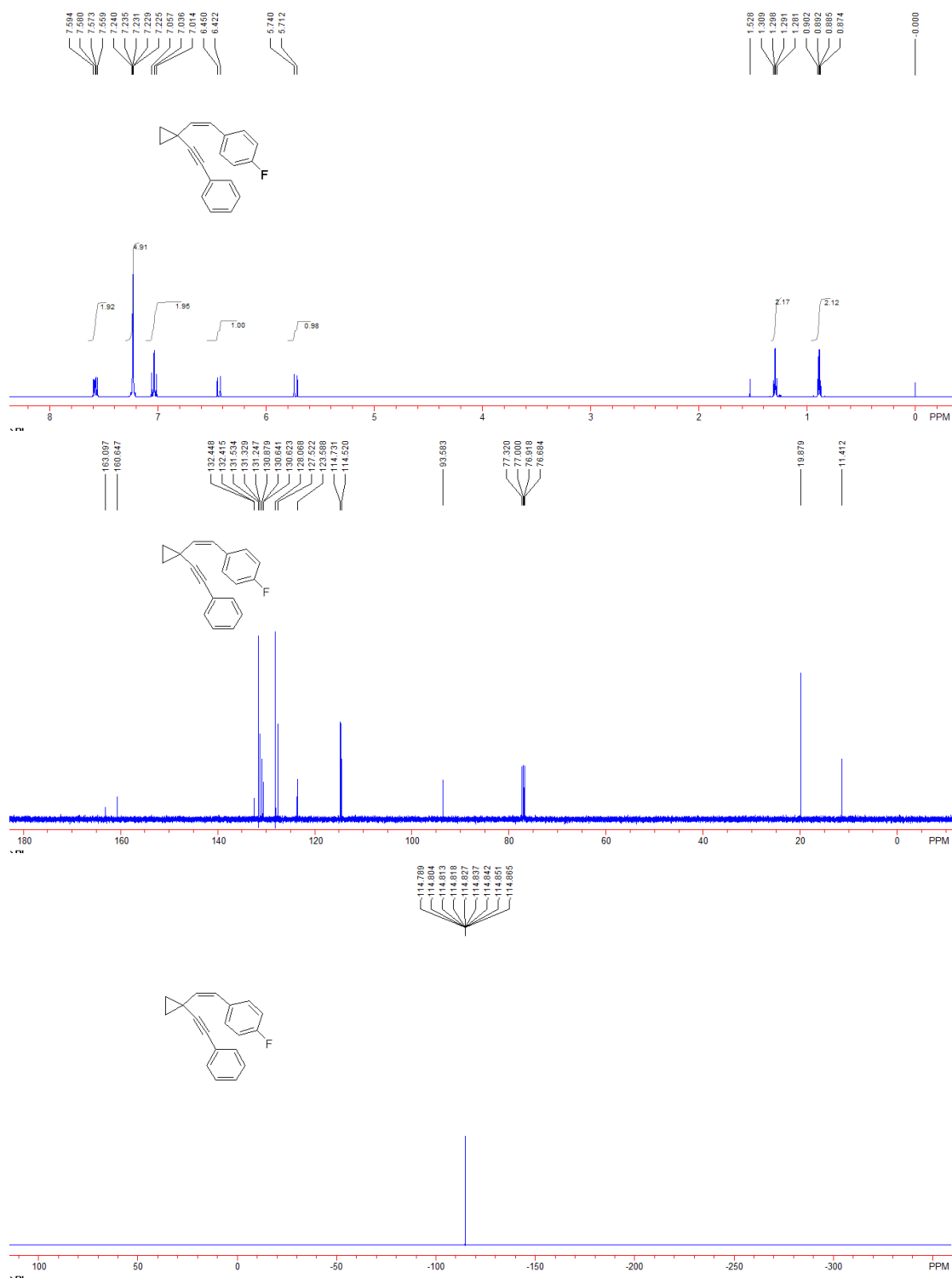
105 (6.84), 107 (30.24). HRMS (EI) calcd. for C₁₉H₁₅NO₂: 289.1103, Found: 289.1101.

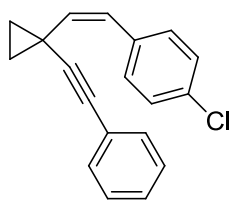


(Z)-1-Fluoro-4-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1d:

Colorless oil. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.90 (dd, *J*₁ = 6.8 Hz, *J*₂ = 4.4 Hz, 2H, CH₂), 1.30 (dd, *J*₁ = 6.8 Hz, *J*₂ = 4.4 Hz, 2H, CH₂), 5.73 (d, *J* = 11.2 Hz, 1H, =CH), 6.44 (d, *J* = 11.2 Hz, 1H, =CH), 7.04 (dd, *J*₁ = 8.8 Hz, *J*₂ = 8.4 Hz, 2H, Ar), 7.23-7.24 (m, 5H, Ar), 7.58 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 11.4, 19.9, 76.9, 93.6, 114.6 (d, *J* = 21.1 Hz), 123.6, 127.5, 128.1, 130.6 (d, *J* = 1.8 Hz), 130.9, 131.3 (d, *J* = 8.3 Hz), 131.5, 132.4 (d, *J* = 3.3 Hz), 161.9 (d, *J* = 245.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -114.8 (tt, *J*₁ = 8.7 Hz, *J*₂ = 5.6 Hz). IR (Neat) ν 3081, 3012, 2853, 1597, 1506,

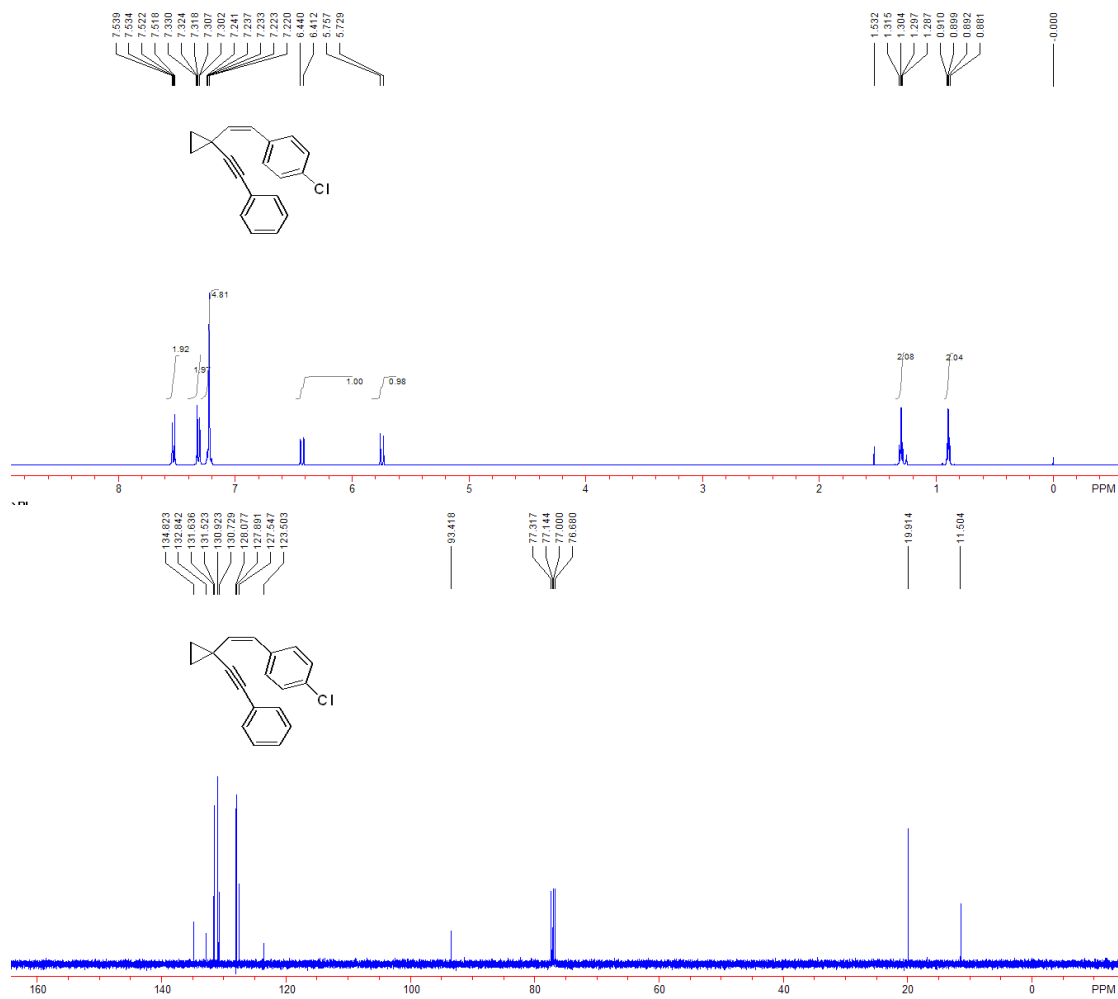
1228, 838, 753, 689 cm^{-1} . MS (%) m/e 262 (M^+ , 87.36), 247 (93.88), 233 (83.38), 183 (44.99), 165 (39.84), 133 (40.15), 115 (100.00), 109 (46.35), 91 (33.11). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{15}\text{F}$: 262.1158, Found: 262.1156.

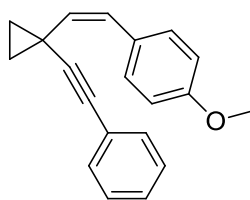




(Z)-1-Chloro-4-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1e:

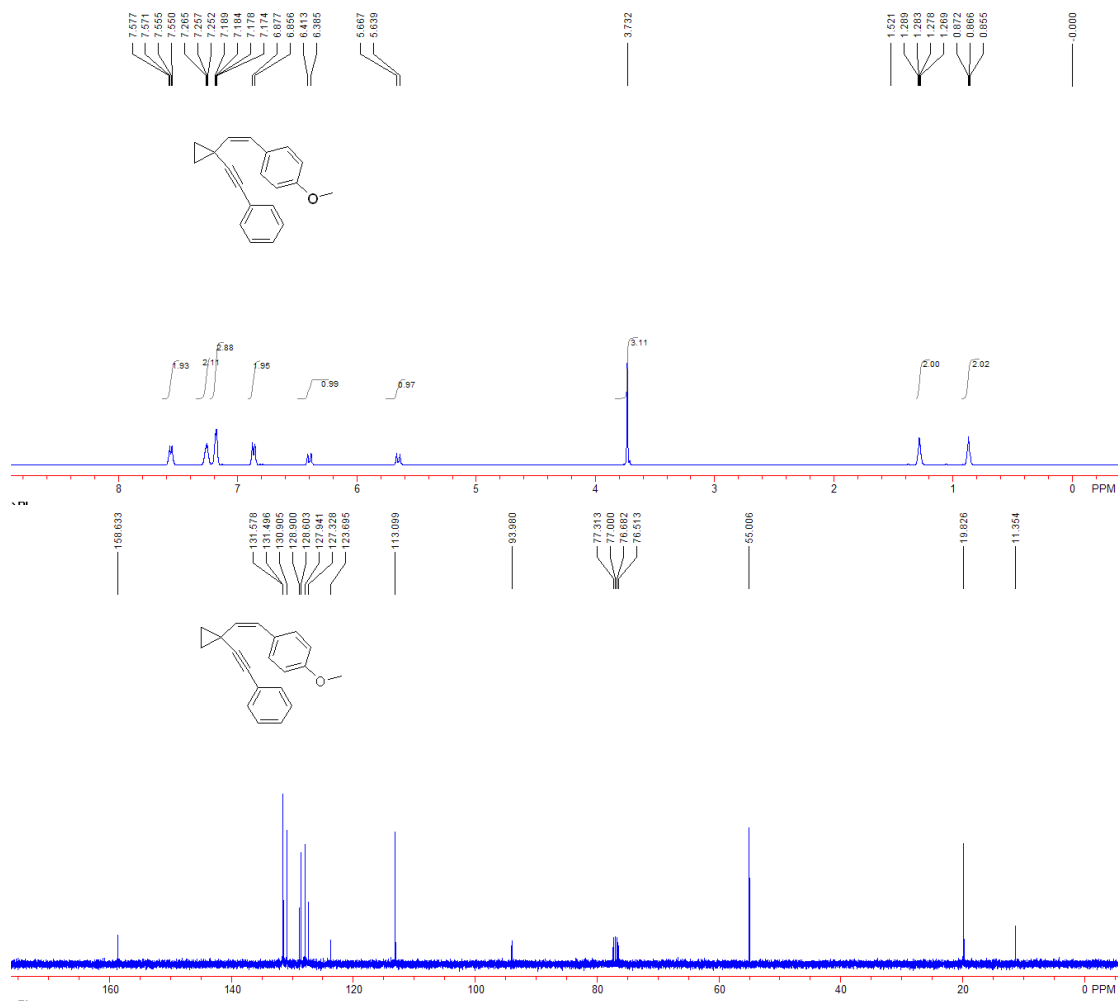
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.90 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.4$ Hz, 2H, CH_2), 1.30 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.4$ Hz, 2H, CH_2), 5.74 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.43 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 7.22-7.24 (m, 5H, Ar), 7.31 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz, 2H, 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 11.5, 19.9, 77.3, 93.4, 123.5, 127.5, 127.9, 128.1, 130.7, 130.9, 131.5, 131.6, 132.8, 134.8. IR (Neat) ν 3077, 3012, 2923, 1594, 1489, 1090, 842, 753, 689 cm^{-1} . MS (%) m/e 280 (M^+ , 7.89), 278 (M^+ , 23.47), 243 (81.19), 228 (68.66), 215 (42.41), 165 (55.63), 139 (21.28), 115 (100.00), 107 (52.12), 91 (40.35). HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{15}\text{Cl}$: 278.0862, Found: 278.0866.

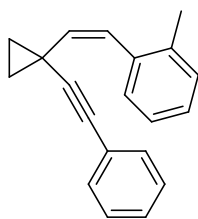




(Z)-1-Methoxy-4-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1f:

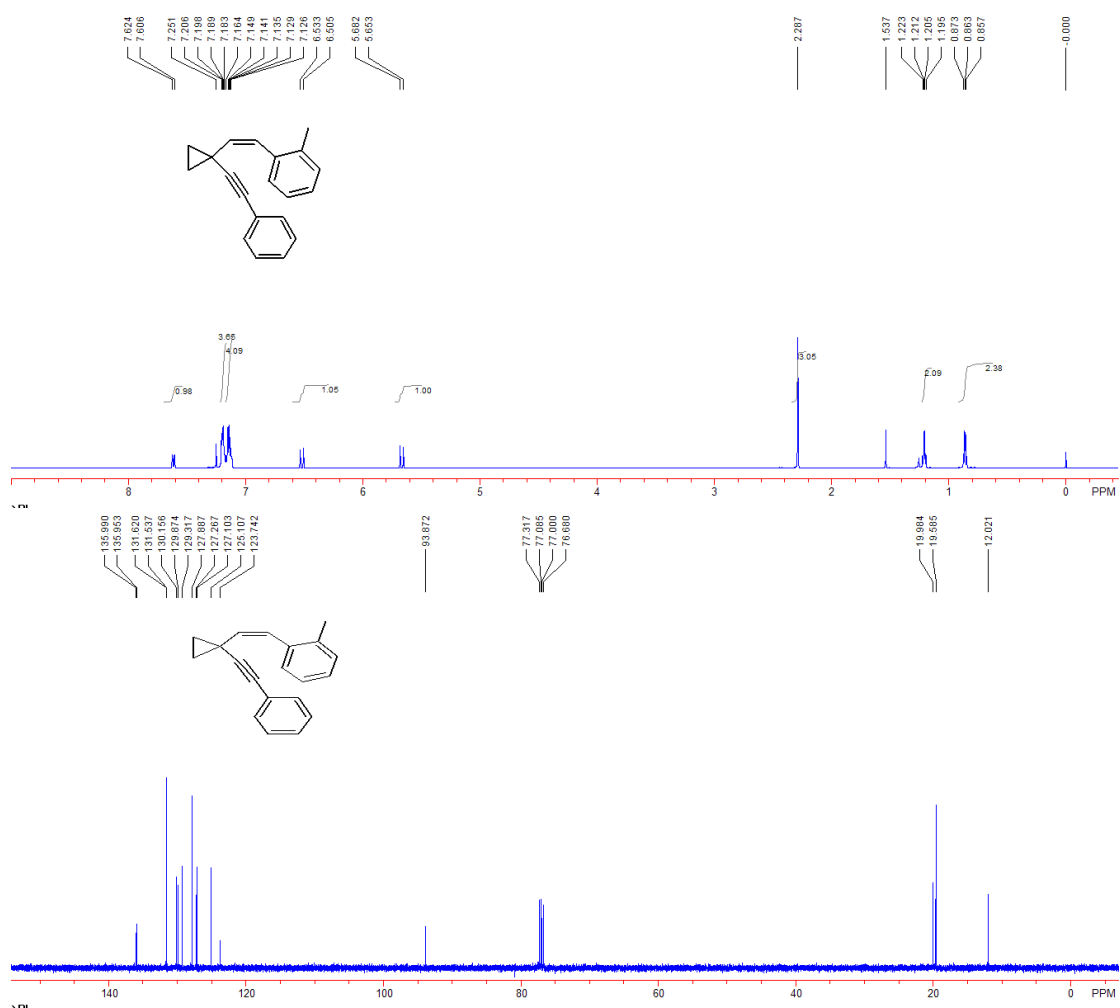
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.86-0.87 (m, 2H, CH_2), 1.27-1.29 (m, 2H, CH_2), 3.73 (s, 3H, CH_3), 5.65 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.40 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.87 (d, $J = 8.4$ Hz, 2H, Ar), 7.17-7.19 (m, 3H, Ar), 7.25-7.27 (m, 2H, Ar), 7.56 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 11.4, 19.8, 55.0, 76.5, 94.0, 113.1, 123.7, 127.3, 127.9, 128.6, 128.9, 130.9, 131.5, 131.6, 158.6. IR (Neat) ν 3008, 2954, 2834, 1607, 1508, 1250, 907, 754, 729 cm^{-1} . MS (%) m/e 274 (M^+ , 100.00), 259 (43.41), 228 (34.49), 243 (63.55), 228 (34.49), 215 (53.15), 202 (87.35), 115 (78.44), 91 (31.15). HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{18}\text{O}$: 274.1358, Found: 274.1360.

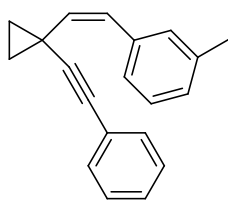




(Z)-1-Methyl-2-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1g:

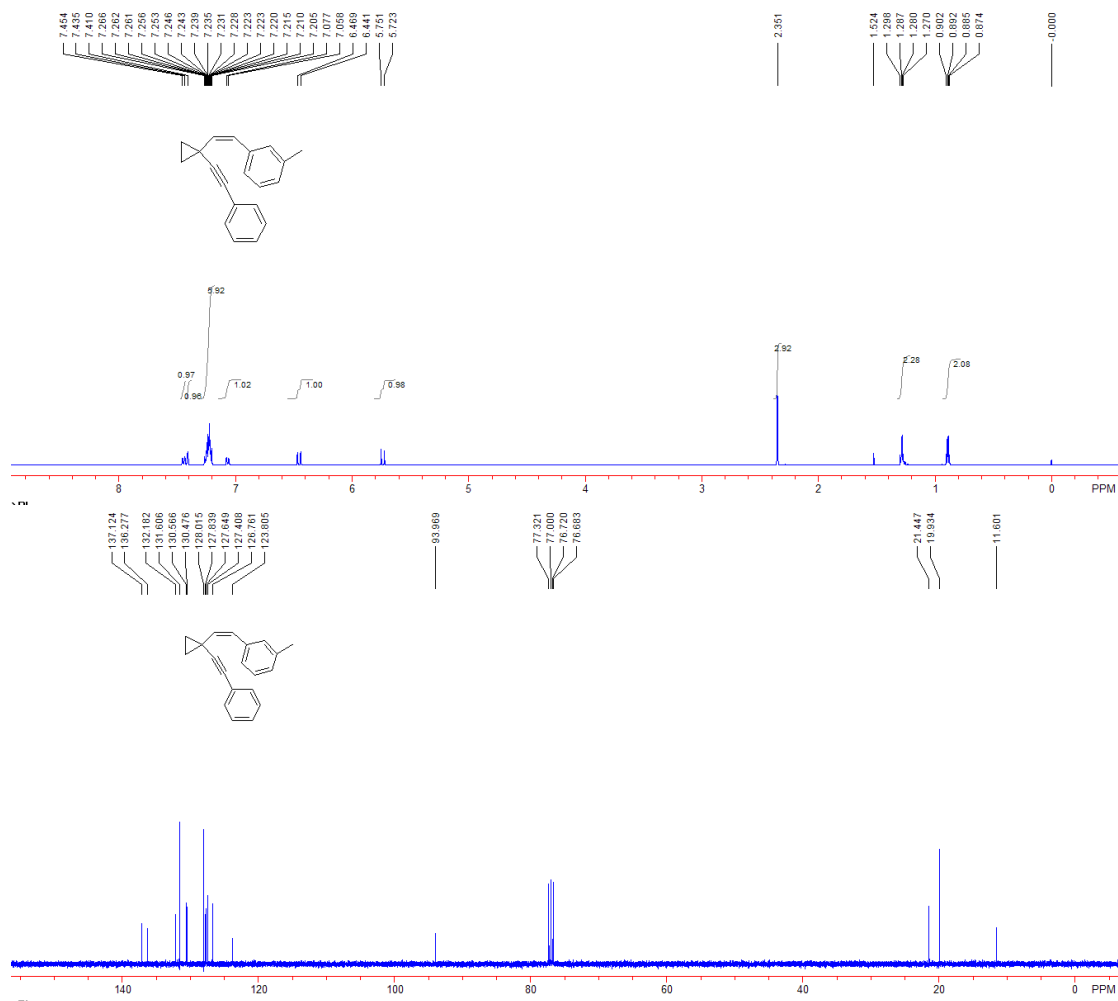
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.86 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.21 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 5.67 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.52 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 7.13-7.16 (m, 4H, Ar), 7.18-7.25 (m, 4H, Ar), 7.62 (d, $J = 7.2$ Hz, 1H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 12.0, 19.6, 20.0, 77.1, 93.9, 123.7, 125.1, 127.1, 127.3, 127.9, 129.3, 129.9, 130.2, 131.5, 131.6, 135.95, 135.99. IR (Neat) ν 3053, 3012, 2920, 1596, 1491, 923, 753, 735, 689 cm^{-1} . MS (%) m/e 258 (M^+ , 37.37), 243 (70.32), 228 (68.03), 215 (33.36), 165 (50.12), 128 (41.48), 115 (100.00), 91 (38.07), 77 (9.79). HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{18}$: 258.1409, Found: 258.1411.

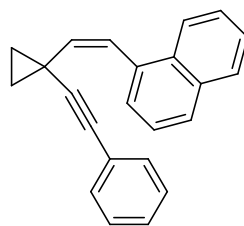




(Z)-1-Methyl-3-(2-(1-(phenylethynyl)cyclopropyl)vinyl)benzene 1h:

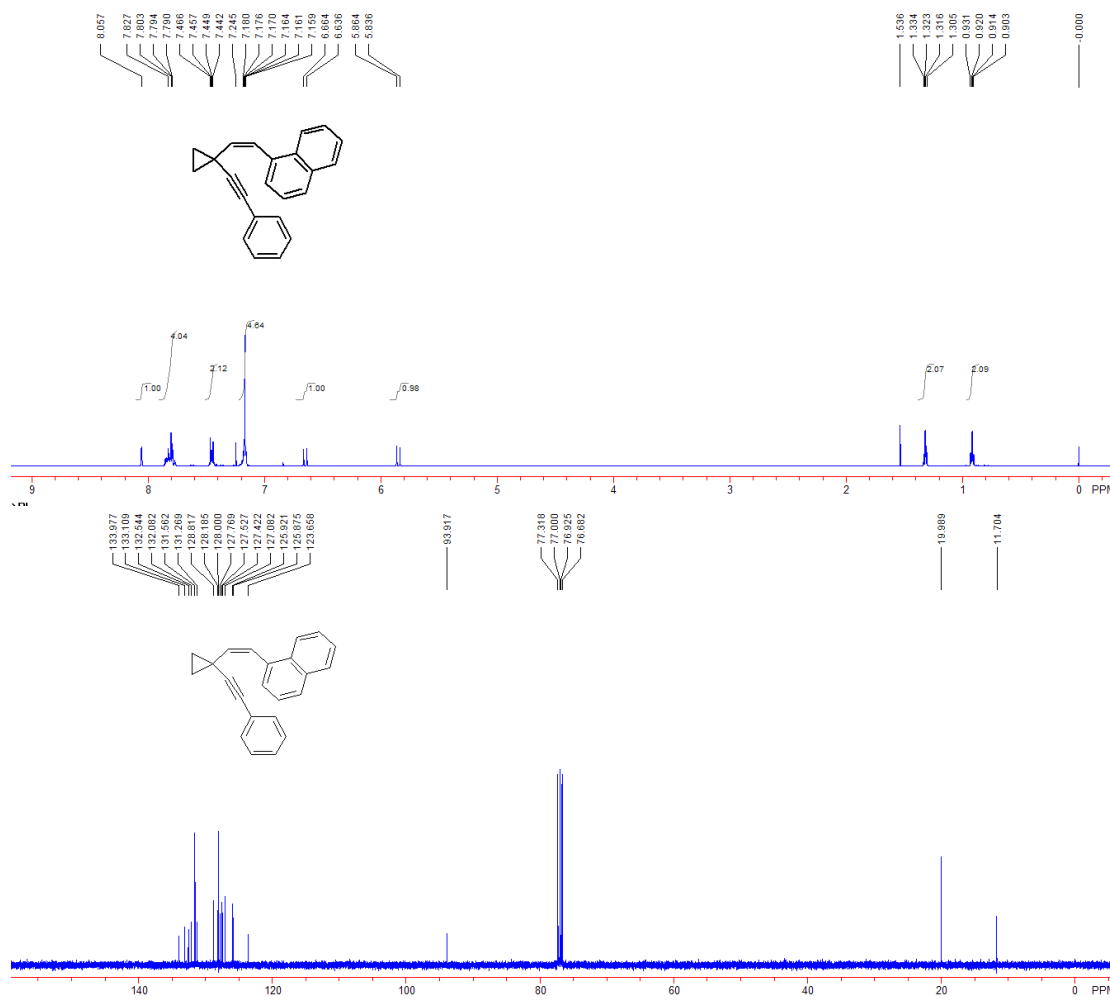
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.89 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.28 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 2.35 (s, 3H, CH_3), 5.74 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.45 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 7.07 (d, $J = 7.6$ Hz, 1H, Ar), 7.21-7.26 (m, 6H, Ar), 7.41 (s, 1H, Ar), 7.44 (d, $J = 7.6$ Hz, 1H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 11.6, 19.9, 21.4, 76.7, 94.0, 123.8, 126.8, 127.4, 127.6, 127.8, 128.0, 130.5, 130.6, 131.6, 132.2, 136.3, 137.1. IR (Neat) ν 3020, 2920, 2855, 1597, 1490, 911, 777, 753, 688 cm^{-1} . MS (%) m/e 258 (M^+ , 37.37), 243 (70.32), 228 (68.03), 215 (33.36), 165 (50.12), 128 (41.48), 115 (100.00), 91 (38.07), 77 (9.79). HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{18}$: 258.1409, Found: 258.1408.

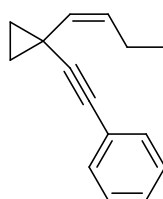




(Z)-1-(2-(1-(Phenylethynyl)cyclopropyl)vinyl)naphthalene 1i:

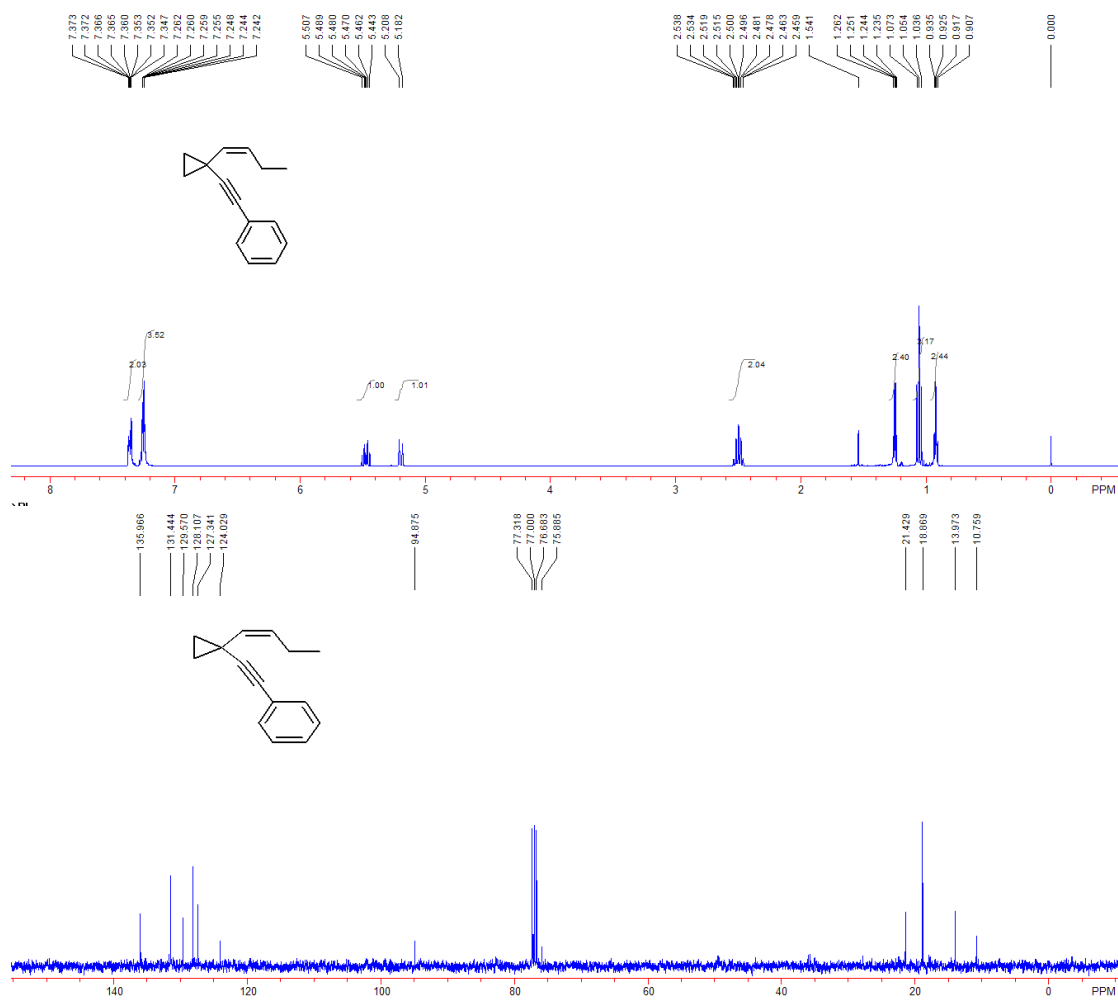
A white solid. Mp: 74-76 °C. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.92 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.4$ Hz, 2H, CH_2), 1.32 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.4$ Hz, 2H, CH_2), 5.85 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.65 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 7.16-7.18 (m, 5H, Ar), 7.44-7.46 (m, 2H, Ar), 7.79-7.83 (m, 4H, Ar), 8.06 (s, 1H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 11.7, 20.0, 76.7, 93.9, 123.7, 125.88, 125.92, 127.1, 127.4, 127.5, 127.8, 128.0, 128.2, 128.8, 131.3, 131.6, 132.1, 132.5, 133.1, 134.0. IR (Neat) ν 3081, 3009, 2919, 2850, 1596, 1491, 859, 752, 689 cm^{-1} . MS (%) m/e 294 (M^+ , 100.00), 279 (75.78), 265 (66.19), 239 (13.00), 215 (36.84), 202 (33.54), 165 (47.87), 152 (23.66), 132 (65.45), 115 (55.30), 91 (19.44). HRMS (EI) calcd. for $\text{C}_{23}\text{H}_{18}$: 294.1409, Found: 294.1410.

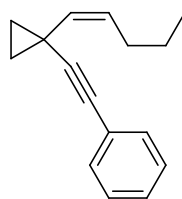




(Z)-((1-(But-1-en-1-yl)cyclopropyl)ethynyl)benzene 1j:

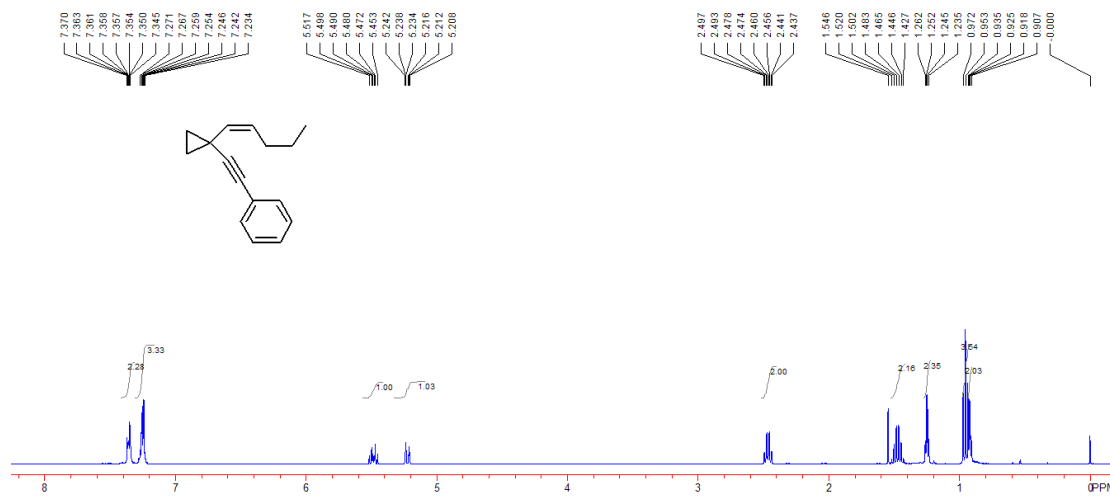
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.92 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.05 (t, $J = 7.2$ Hz, 3H, CH_3), 1.25 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 2.46-2.54 (m, 2H, CH_2), 5.20 (d, $J = 10.4$ Hz, 1H, $=\text{CH}$), 5.48 (dt, $J_1 = 10.4$ Hz, $J_2 = 7.2$ Hz, 1H, $=\text{CH}$), 7.24-7.26 (m, 3H, Ar), 7.35-7.37 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 10.8, 14.0, 18.9, 21.4, 75.9, 94.9, 124.0, 127.3, 128.1, 129.6, 131.4, 136.0. IR (Neat) ν 3008, 2964, 2927, 1596, 1491, 959, 754, 724, 690 cm^{-1} . MS (%) m/e 196 (M^+ , 9.38), 181 (58.63), 165 (100.00), 152 (51.03), 126 (55.33), 115 (88.45), 103 (19.12), 92 (88.09), 77 (18.20). HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{16}$: 196.1252, Found: 196.1251.

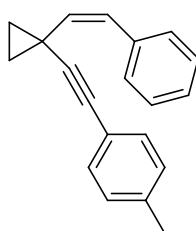
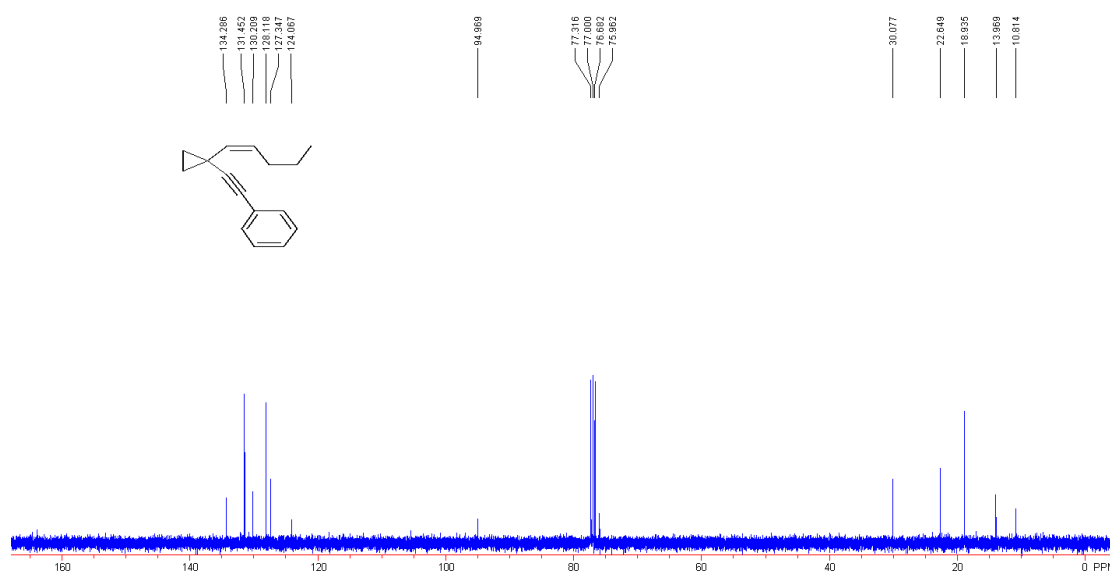




(Z)-((1-(Pent-1-en-1-yl)cyclopropyl)ethynyl)benzene 1k:

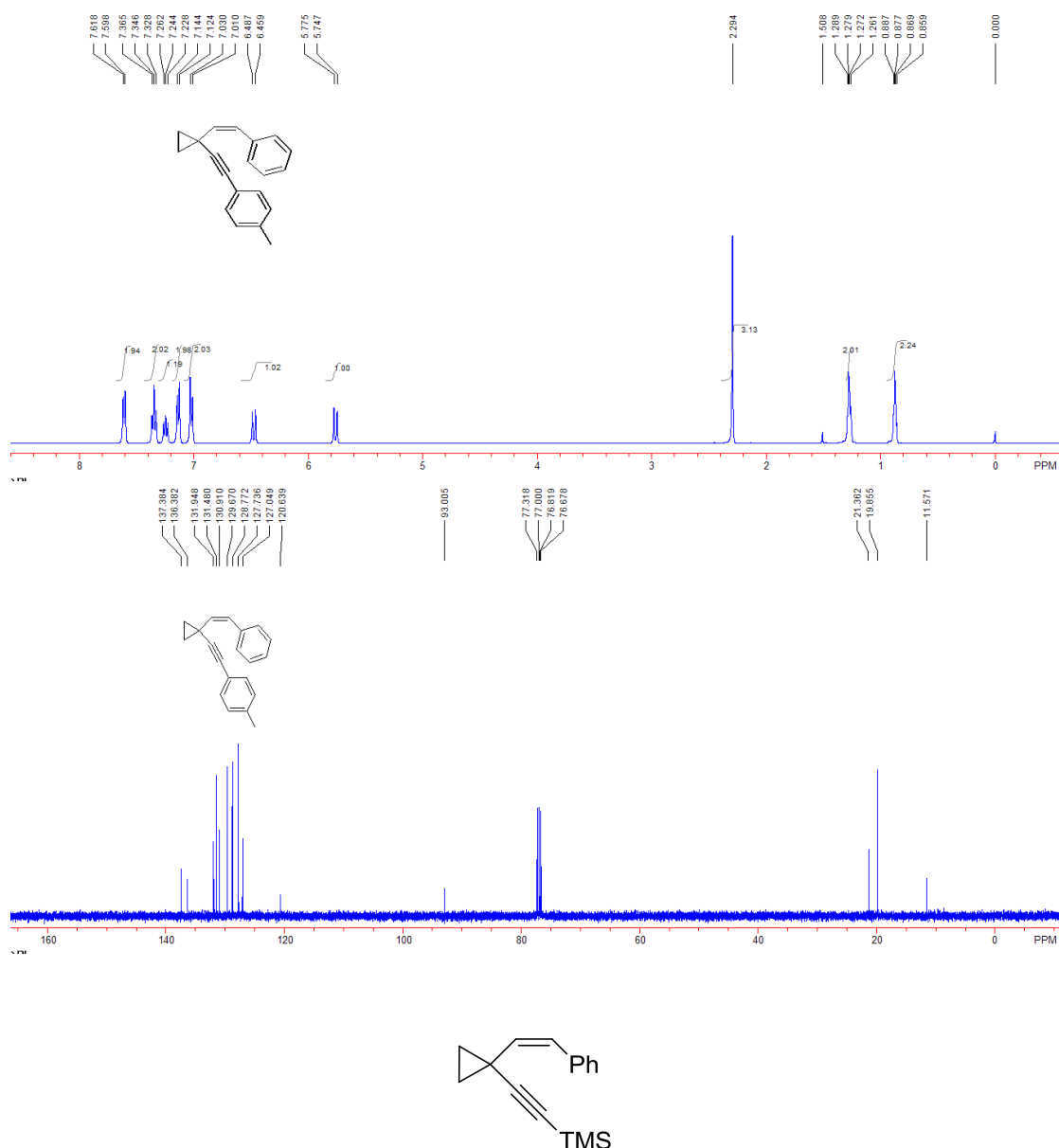
Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.92 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), 1.25 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.43-1.52 (m, 2H, CH_2), 2.44-2.50 (m, 2H, CH_2), 5.25 (dt, $J_1 = 10.4$ Hz, $J_2 = 1.6$ Hz, 1H, $=\text{CH}$), 5.49 (dt, $J_1 = 10.4$ Hz, $J_2 = 7.2$ Hz, 1H, $=\text{CH}$), 7.23-7.27 (m, 3H, Ar), 7.35-7.37 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 10.8, 14.0, 18.9, 22.6, 30.1, 76.0, 95.0, 124.1, 127.3, 128.1, 130.2, 131.5, 134.3. IR (Neat) ν 3010, 2959, 2927, 2870, 1491, 1027, 958, 754, 690 cm^{-1} . MS (%) m/e 210 (M^+ , 6.27), 195 (15.65), 181 (50.04), 165 (100.00), 152 (47.36), 126 (42.64), 115 (81.20), 106 (79.68), 77 (18.23). HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{18}$: 210.1409, Found: 210.1406.





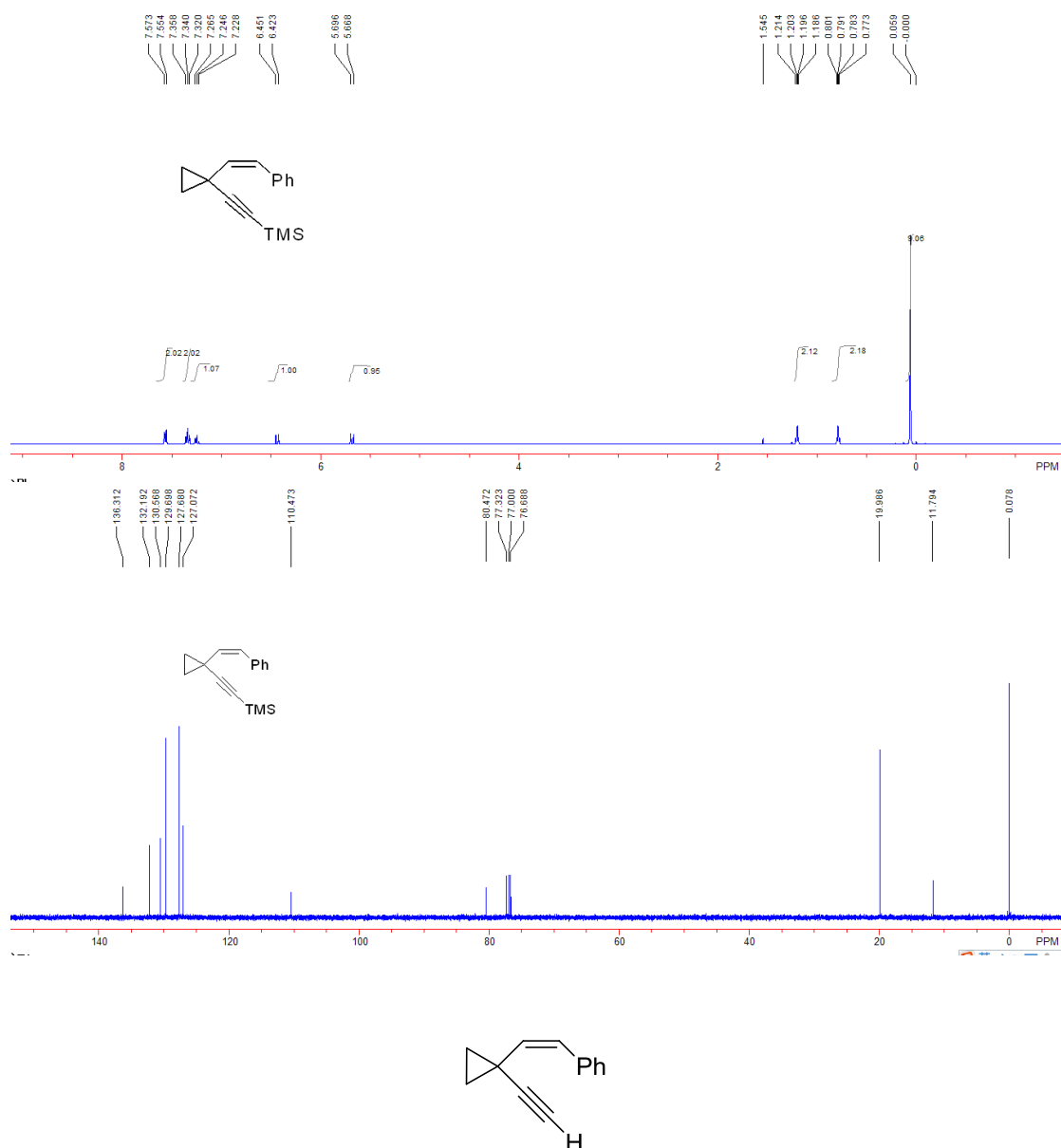
(Z)-1-Methyl-4-((1-styrylcyclopropyl)ethynyl)benzene 1l:

Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.87 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 1.28 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 5.76 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 6.47 (d, $J = 11.2$ Hz, 1H, $=\text{CH}$), 7.02 (d, $J = 8.0$ Hz, 2H, Ar), 7.13 (d, $J = 8.0$ Hz, 2H, Ar), 7.24 (dd, $J_1 = 7.2$ Hz, $J_2 = 6.4$ Hz, 1H, Ar), 7.35 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.2$ Hz, 2H, Ar), 7.61 (d, $J = 8.0$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 11.6, 19.9, 21.4, 76.8, 93.0, 120.6, 127.1, 127.7, 128.8, 129.7, 130.9, 131.5, 132.0, 136.4, 137.4. IR (Neat) ν 3010, 2920, 2853, 1509, 1493, 1029, 815, 697, 688 cm^{-1} . MS (%) m/e 258 (M^+ , 66.47), 243 (79.21), 228 (82.23), 215 (49.56), 165 (77.97), 141 (32.20), 115 (100.00), 101 (42.82), 91 (49.27). HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{18}$: 258.1409, Found: 258.1406.



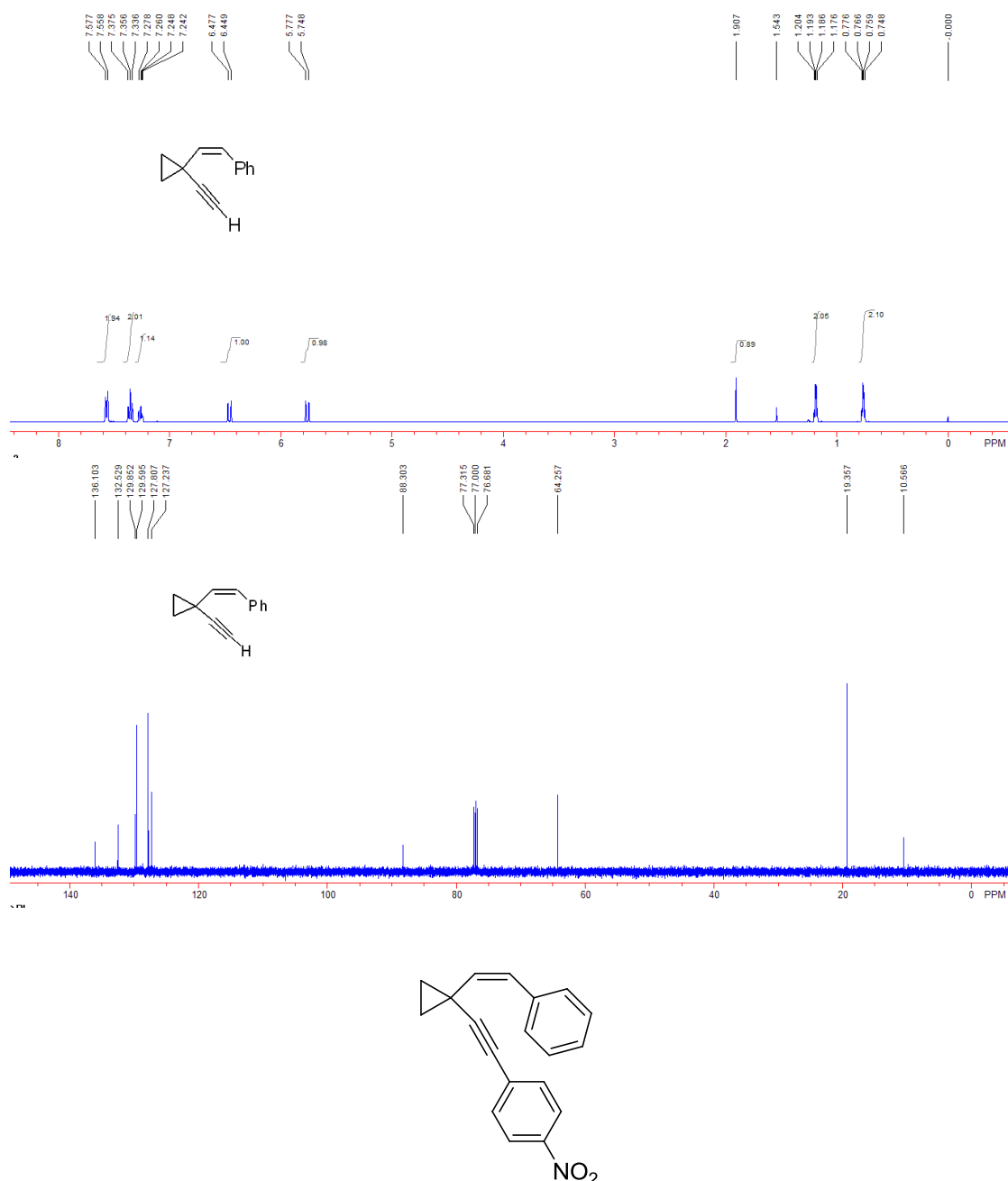
(Z)-Trimethyl((1-styrylcyclopropyl)ethynyl)silane s-6:

Colorless oil. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.06 (s, 9H, CH₃), 0.78 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 1.20 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 5.68 (d, $J = 11.2$ Hz, 1H, =CH), 6.44 (d, $J = 11.2$ Hz, 1H, =CH), 7.23-7.27 (m, 1H, Ar), 7.34 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.2$ Hz, 2H, Ar), 7.56 (d, $J = 7.2$ Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 0.1, 11.8, 20.0, 80.5, 110.5, 127.1, 127.7, 129.7, 130.6, 132.2, 136.3. IR (Neat) ν 3053, 3013, 2958, 2154, 1248, 837, 758, 695, 679 cm⁻¹. MS (%) m/e 240 (M⁺, 15.18), 225 (45.81), 166 (22.19), 129 (19.40), 115 (16.51), 105 (25.17), 73 (100.00), 59 (20.39). HRMS (EI) calcd. for C₁₆H₂₀Si: 240.1334, Found: 240.1333.



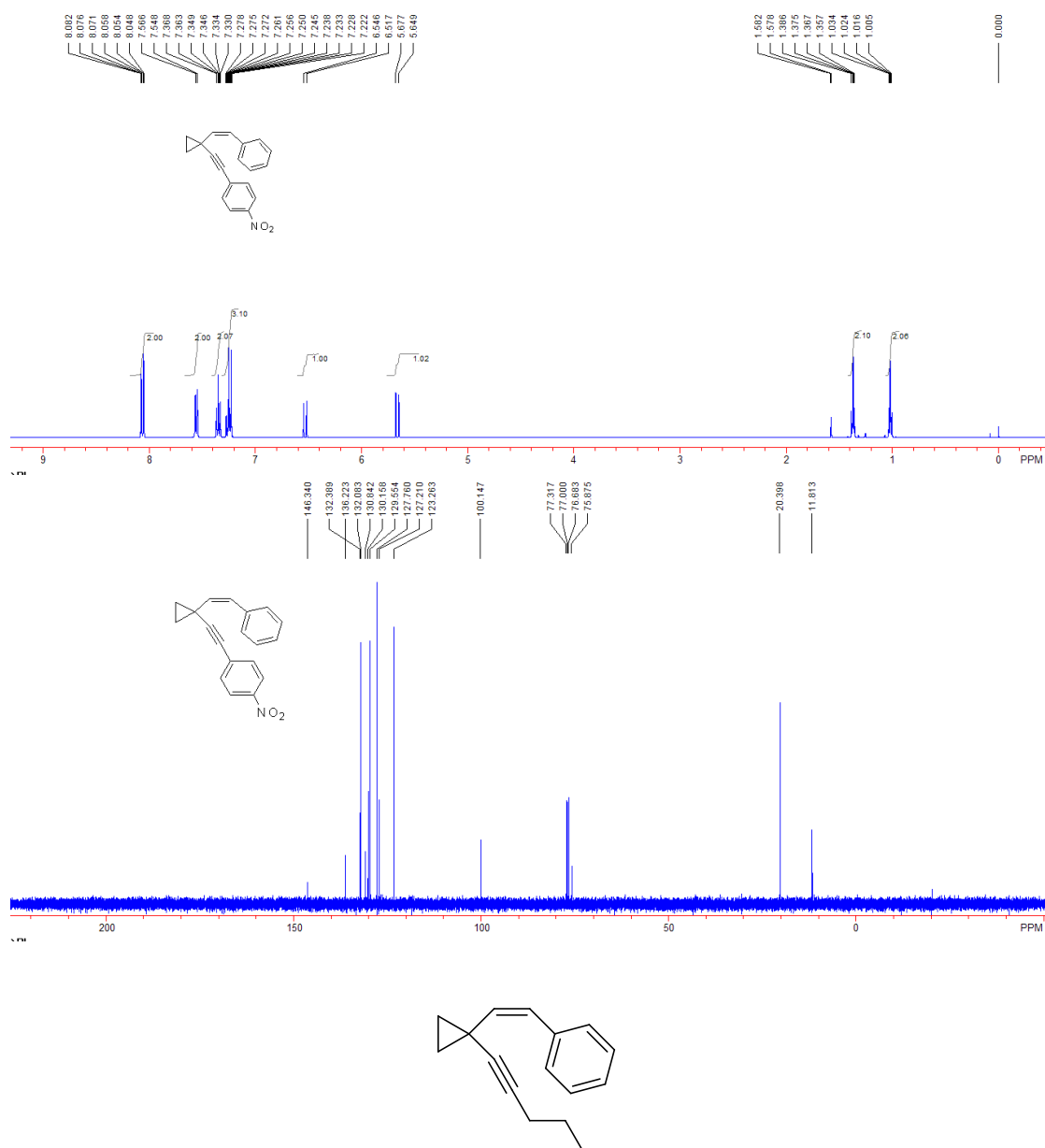
(Z)-2-(1-Ethynylcyclopropyl)vinylbenzene s-7:

Colorless oil. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.76 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 1.19 (dd, $J_1 = 6.8$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 1.91 (s, 1H, CH), 5.76 (d, $J = 11.2$ Hz, 1H, =CH), 6.46 (d, $J = 11.2$ Hz, 1H, =CH), 7.24-7.28 (m, 1H, Ar), 7.36 (dd, $J_1 = 8.0$ Hz, $J_2 = 7.6$ Hz, 2H, Ar), 7.57 (d, $J = 7.6$ Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 10.6, 19.4, 64.3, 88.3, 127.2, 127.8, 129.6, 129.9, 132.5, 136.1. IR (Neat) ν 3291, 3012, 2107, 1494, 1447, 1030, 914, 771, 693 cm⁻¹. MS (%) m/e 168 (M⁺, 28.79), 167 (69.95), 152 (100.00), 139 (58.31), 129 (32.99), 115 (41.27), 89 (16.56), 63 (15.83). HRMS (EI) calcd. for C₁₃H₁₁: 167.0861, Found: 167.0860.



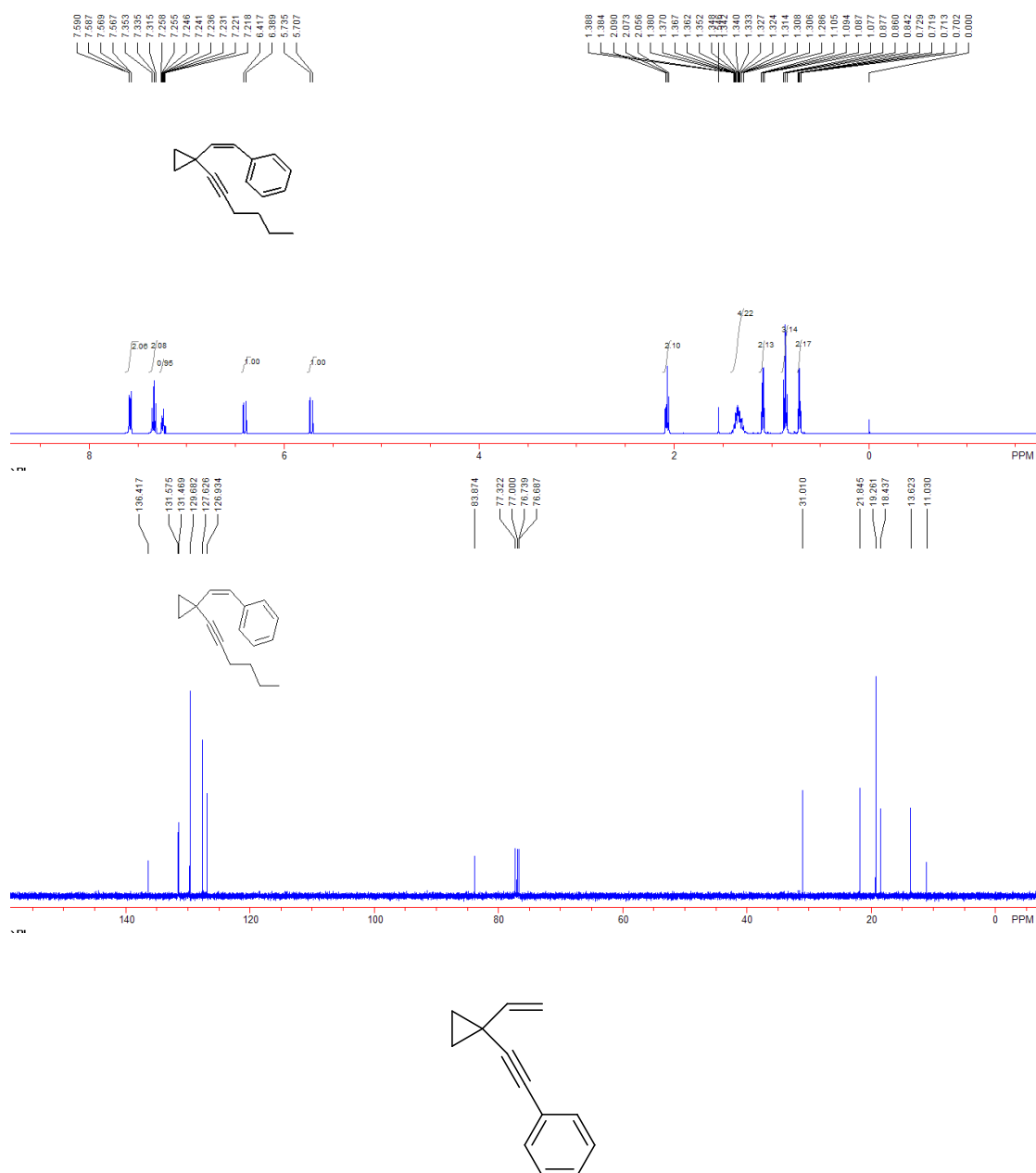
(Z)-1-Nitro-4-((1-styrylcyclopropyl)ethynyl)benzene 1m:

Yellowish oil. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.02 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 1.37 (dd, $J_1 = 7.2$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 5.66 (d, $J = 11.2$ Hz, 1H, =CH), 6.53 (d, $J = 11.2$ Hz, 1H, =CH), 7.22-7.28 (m, 3H, Ar), 7.33-7.37 (m, 2H, Ar), 7.56 (d, $J = 7.2$ Hz, 2H, Ar), 8.05-8.08 (m, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 11.8, 20.4, 75.9, 100.1, 123.3, 127.2, 127.8, 129.6, 130.2, 130.8, 132.1, 132.4, 136.2, 146.3. IR (Neat) ν 3079, 3012, 2929, 2214, 1592, 1513, 1106, 851, 688 cm⁻¹. MS (%) m/e 289 (M⁺, 53.62), 242 (56.56), 241 (57.37), 228 (100), 215 (67.85), 213 (72.4), 165 (55.72), 105 (6.84), 107 (30.24). HRMS (EI) calcd. for C₁₉H₁₅NO₂: 289.1103, Found: 289.1104.



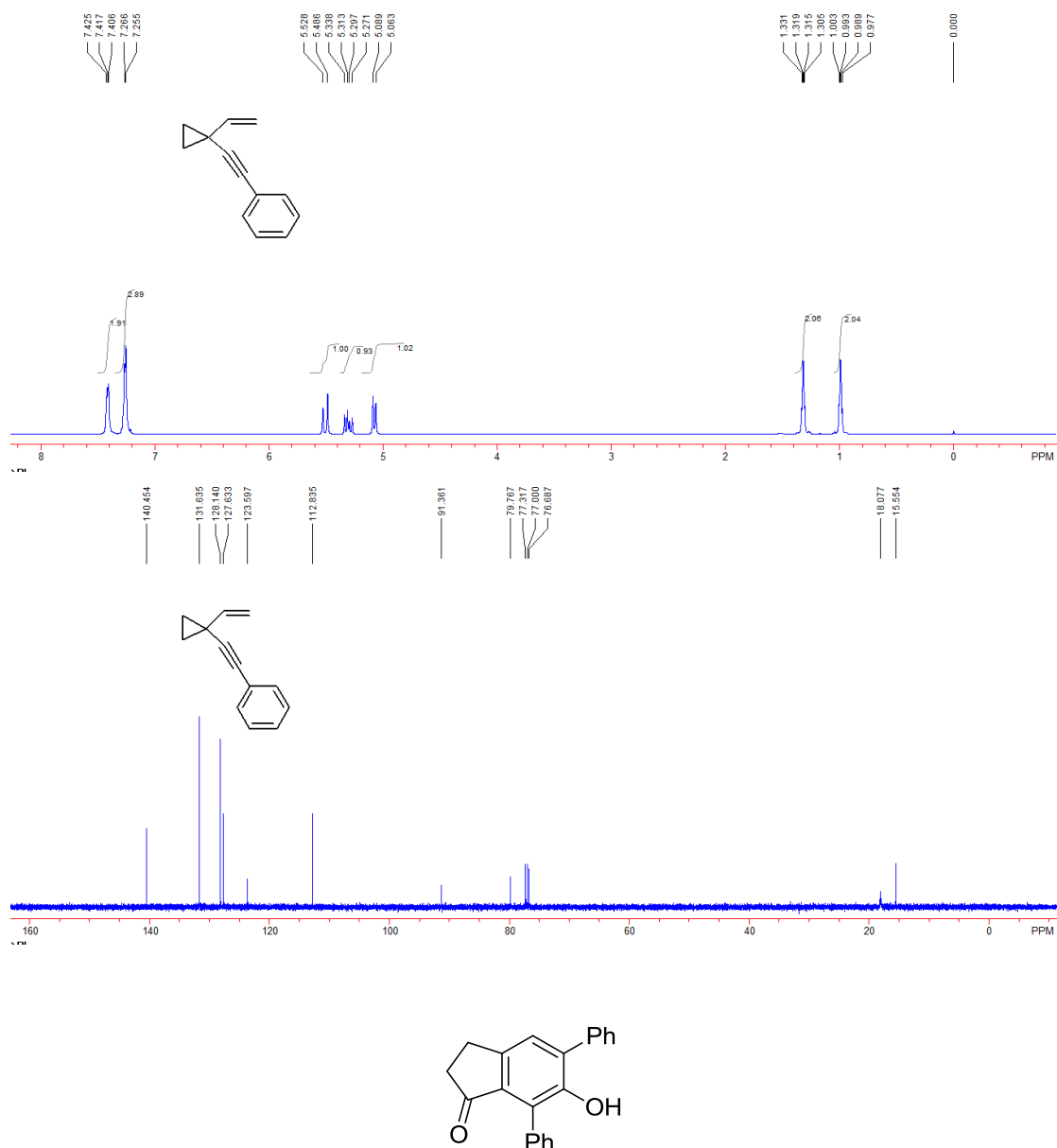
(Z)-2-(1-(Hex-1-yn-1-yl)cyclopropyl)vinyl)benzene 1n:

Colorless oil. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.72 (dd, *J*₁ = 6.8 Hz, *J*₂ = 4.0 Hz, 2H, CH₂), 0.86 (t, *J* = 7.2 Hz, 3H, CH₃), 1.09 (dd, *J*₁ = 6.8 Hz, *J*₂ = 4.0 Hz, 2H, CH₂), 1.29-1.39 (m, 4H, CH₂), 2.07 (t, *J* = 7.2 Hz, 2H, CH₂), 5.72 (d, *J* = 11.2 Hz, 1H, =CH), 6.40 (d, *J* = 11.2 Hz, 1H, =CH), 7.22-7.26 (m, 1H, Ar), 7.34 (dd, *J*₁ = 8.0 Hz, *J*₂ = 7.2 Hz, 2H, Ar), 7.58 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 11.0, 13.6, 18.4, 19.3, 21.8, 31.0, 76.7, 83.9, 126.9, 127.6, 129.7, 131.5, 131.6, 136.4. IR (Neat) ν 3011, 2956, 2930, 1494, 1447, 1028, 918, 776, 692 cm⁻¹. MS (%) *m/e* 224 (M⁺, 23.73), 209 (13.95), 181 (42.53), 167 (100.00), 152 (59.10), 128 (50.76), 115 (55.03), 91 (32.45), 77 (17.91). HRMS (EI) calcd. for C₁₇H₂₀: 224.1565, Found: 224.1567.



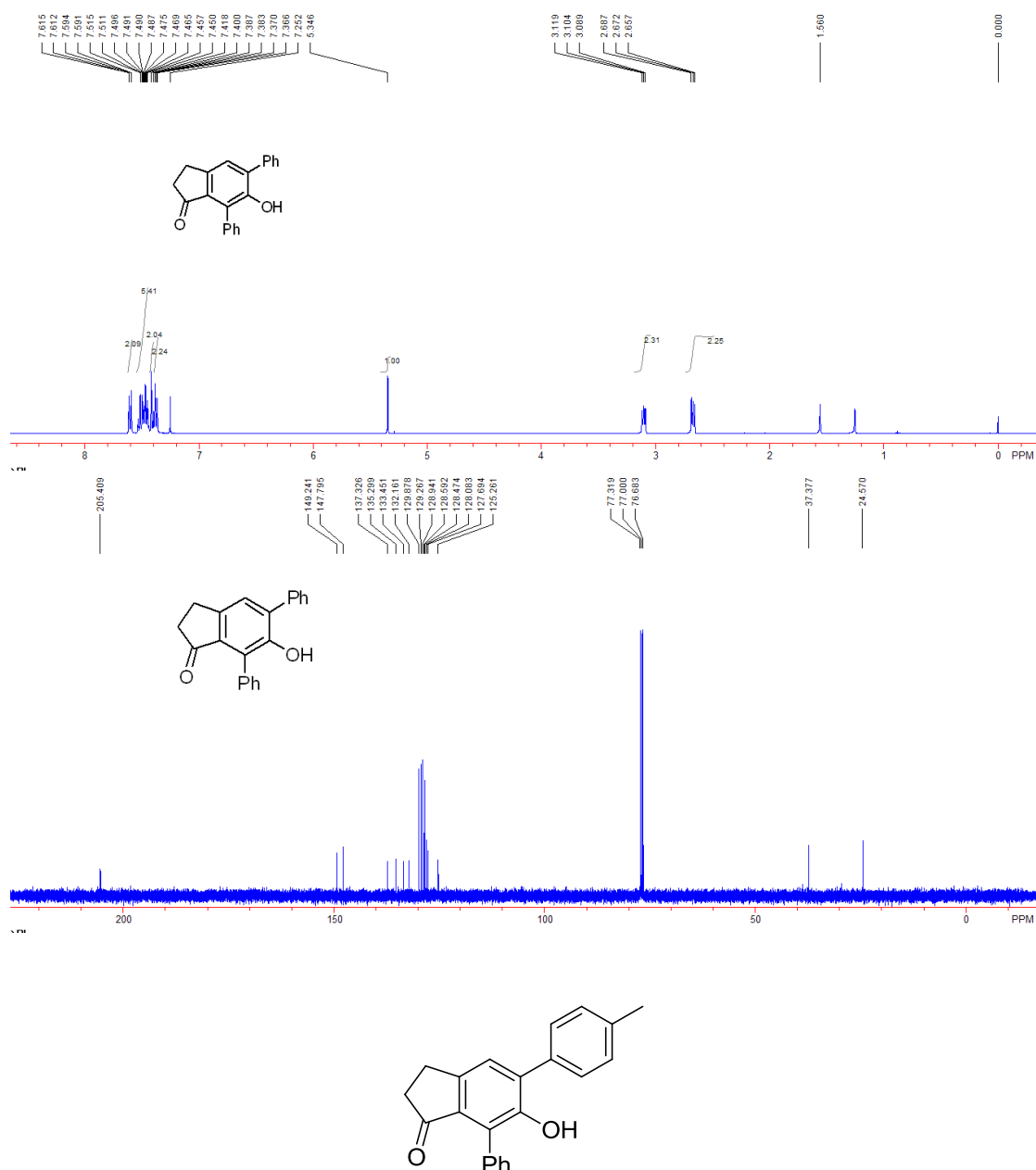
((1-Vinylcyclopropyl)ethynyl)benzene 1o:

Colorless oil. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.99 (dd, $J_1 = 5.6$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 1.32 (dd, $J_1 = 5.6$ Hz, $J_2 = 4.0$ Hz, 2H, CH₂), 5.08 (d, $J = 10.8$ Hz, 1H, =CH), 5.31 (dd, $J_1 = 16.8$ Hz, $J_2 = 10.8$ Hz, 1H, =CH), 5.51 (d, $J = 16.8$ Hz, 1H, =CH), 7.26-7.27 (m, 3H, Ar), 7.41-7.43 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 15.6, 18.1, 79.8, 91.4, 112.8, 123.6, 127.6, 128.1, 131.6, 140.5. IR (Neat) ν 3087, 3008, 2859, 1633, 1490, 961, 903, 753, 689 cm⁻¹. MS (%) m/e 168 (M^+ , 74.24), 167 (100.00), 152 (74.85), 139 (80.31), 152 (47.36), 126 (33.58), 115 (59.02), 102 (9.32), 89 (19.40). HRMS (EI) calcd. for $\text{C}_{13}\text{H}_{12}$: 168.0939, Found: 168.0942.



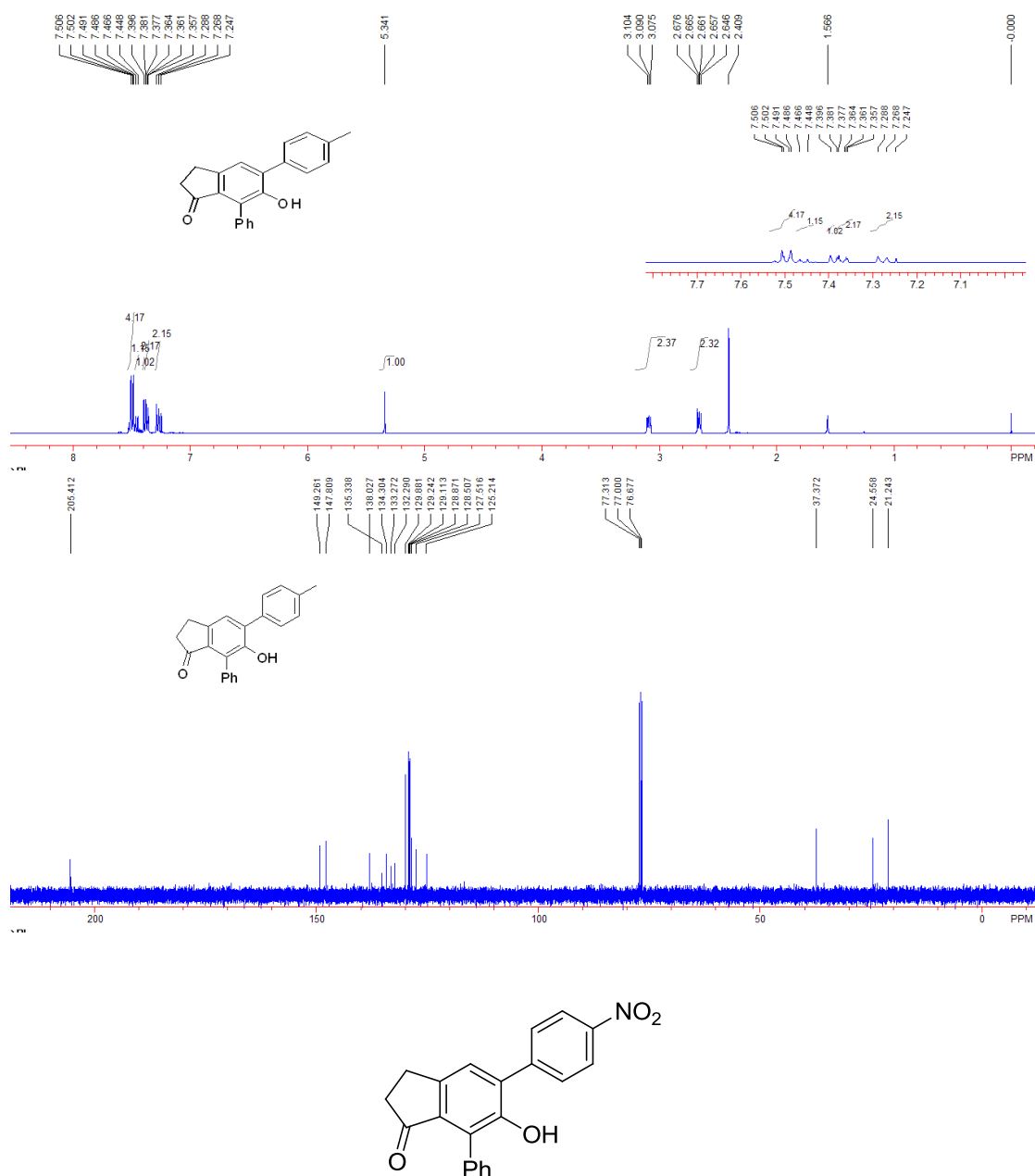
6-Hydroxy-5,7-diphenyl-2,3-dihydro-1H-inden-1-one 2a:

36 mg, yield: 60%; A white solid. Mp: 193-194 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.67 (t, *J* = 6.0 Hz, 2H, CH₂), 3.10 (t, *J* = 6.0 Hz, 2H, CH₂), 5.35 (s, 1H, OH), 7.37-7.39 (m, 2H, Ar), 7.40-7.42 (m, 2H, Ar), 7.45-7.59 (m, 5H, Ar), 7.61 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.2 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 24.6, 37.4, 125.3, 127.7, 128.1, 128.5, 128.6, 128.9, 129.3, 129.9, 132.2, 133.5, 135.3, 137.3, 147.8, 149.2, 205.4. IR (Neat) ν 3515, 3056, 2923, 1699, 1594, 1414, 1250, 732, 696 cm⁻¹. MS (%) *m/e* 300 (M⁺, 82.41), 299 (100.00), 283 (2.74), 257 (12.70), 239 (2.77), 228 (3.83), 189 (1.24), 150 (2.15), 126 (3.89), 115(6.53). HRMS (EI) calcd. for C₂₁H₁₆O₂: 300.1150, Found: 300.1149.



6-Hydroxy-7-phenyl-5-(p-tolyl)-2,3-dihydro-1H-inden-1-one 2b:

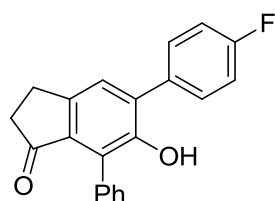
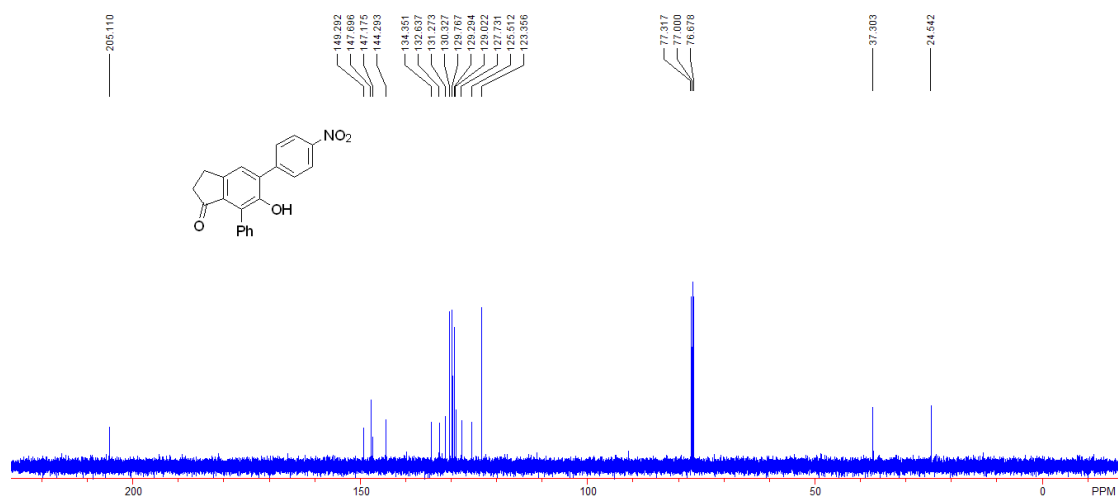
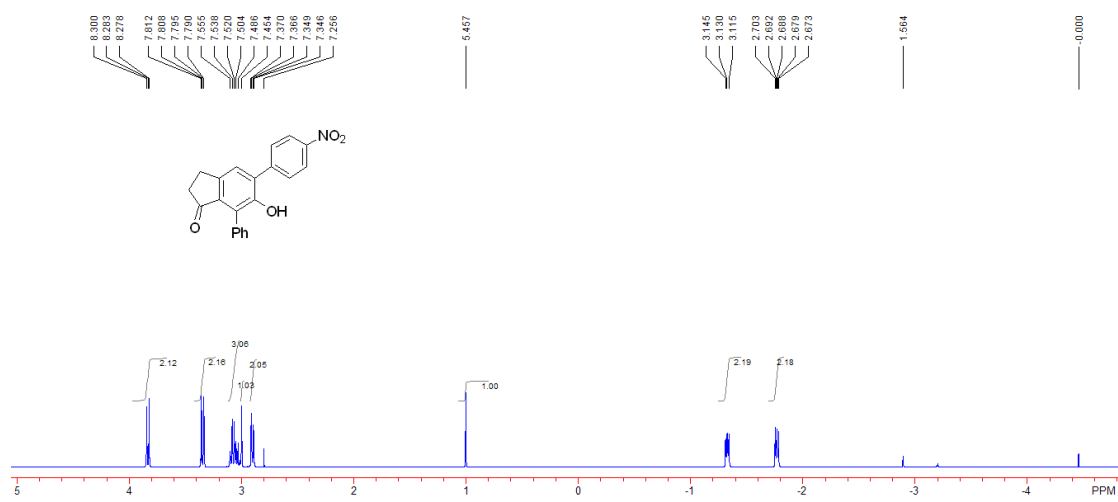
32 mg, yield: 51%; A white solid. Mp: 194-195 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.41 (s, 3H, CH₃), 2.65-2.68 (m, 2H, CH₂), 3.09 (t, *J* = 6.0 Hz, 2H, CH₂), 5.34 (s, 1H, OH), 7.28 (d, *J* = 8.0 Hz, 2H, Ar), 7.36-7.38 (m, 2H, Ar), 7.40 (s, 1H, Ar), 7.45-7.47 (m, 1H, Ar), 7.49-7.51 (m, 4H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 21.2, 24.6, 37.4, 125.2, 127.5, 128.5, 128.9, 129.1, 129.2, 129.9, 132.3, 133.3, 134.3, 135.3, 138.0, 147.8, 149.3, 205.4. IR (Neat) ν 3505, 3400, 2922, 1700, 1596, 1428, 1263, 822, 731 cm⁻¹. MS (%) *m/e* 314 (M⁺, 100.00), 313 (75.93), 299 (53.61), 271 (16.22), 156 (11.28), 126 (9.12), 115 (13.85), 101 (6.14), 91 (3.79), 77(2.62). HRMS (EI) calcd. for C₂₂H₁₈O₂: 314.1307, Found: 314.1308.



6-Hydroxy-5-(4-nitrophenyl)-7-phenyl-2,3-dihydro-1H-inden-1-one 2c:

29 mg, yield: 45%; A brown solid. Mp: 213-215 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.67-2.70 (m, 2H, CH₂), 3.13 (t, *J* = 6.0 Hz, 2H, CH₂), 5.46 (s, 1H, OH), 7.36 (dd, *J*₁ = 6.8 Hz, *J*₂ = 1.6 Hz, 2H, Ar), 7.45 (s, 1H, Ar), 7.49-7.56 (m, 3H, Ar), 7.80 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.0 Hz, 2H, Ar), 8.29 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.0 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 24.5, 37.3, 123.4, 125.5, 127.7, 129.0, 129.3, 129.8, 130.3, 131.3, 132.6, 134.4, 144.3, 147.2, 147.7, 149.3, 205.1. IR (Neat) ν 3508, 2924, 2853, 1704, 1592, 1515, 1344, 855, 699 cm⁻¹. MS (%) *m/e* 345 (M⁺, 100.00), 344 (84.96), 328 (10.97), 315 (4.69), 298 (15.04), 256 (5.34), 149 (10.74), 126 (5.85), 113 (10.23), 94(3.25). HRMS (EI) calcd. for C₂₁H₁₅NO₄: 345.1001,

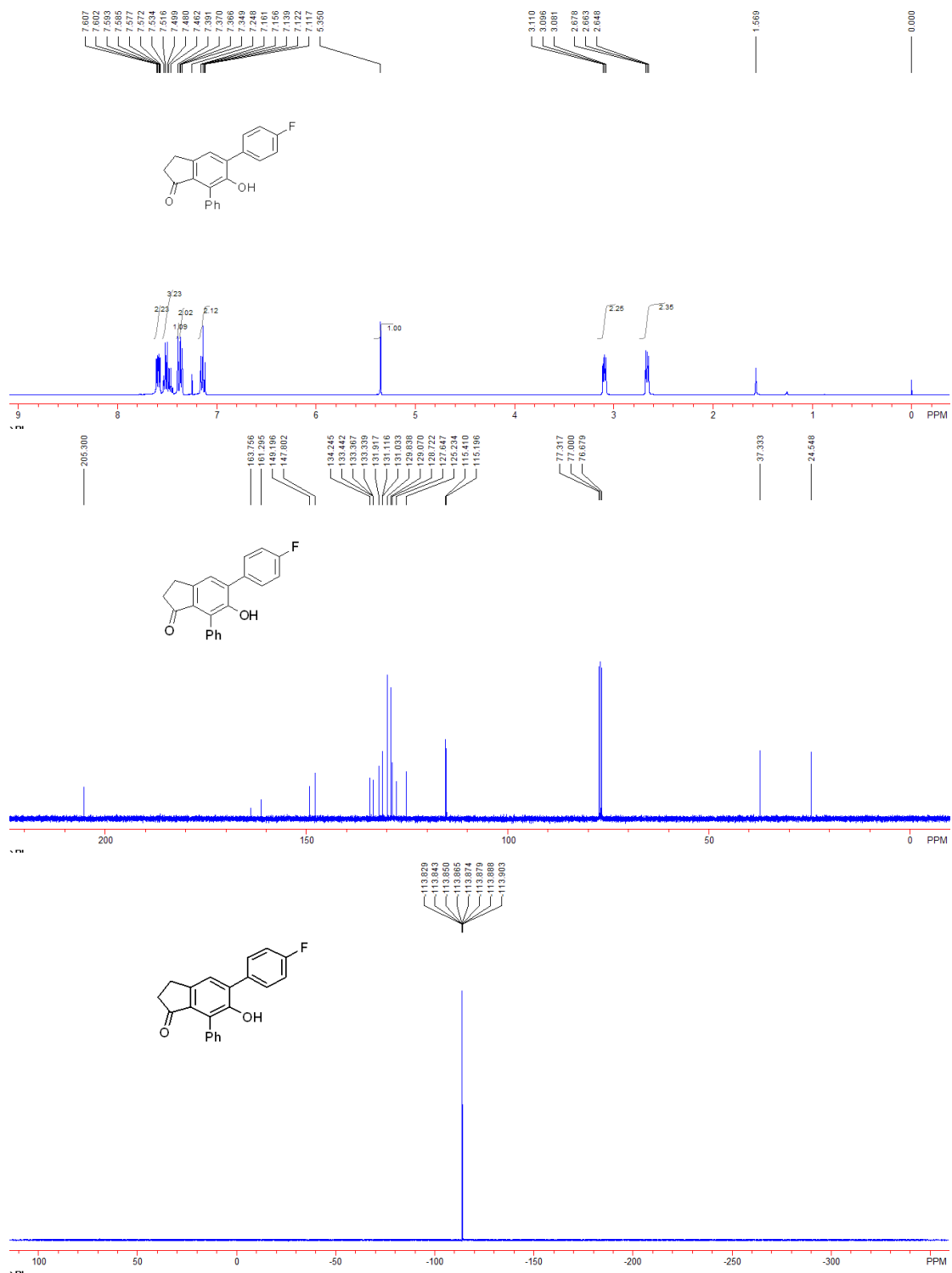
Found: 345.1006.

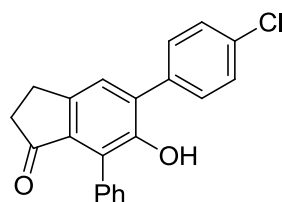


5-(4-Fluorophenyl)-6-hydroxy-7-phenyl-2,3-dihydro-1H-inden-1-one 2d:

30 mg, yield: 47%; A white solid. Mp: 198-200 °C ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.66 (t, *J* = 6.0 Hz, 2H, CH₂), 3.10 (t, *J* = 6.0 Hz, 2H, CH₂), 5.35 (s, 1H, OH), 7.12-7.16 (m, 2H, Ar), 7.35-7.37 (m, 2H, Ar), 7.39 (s, 1H, Ar), 7.46-7.53 (m, 2H, Ar), 7.57-7.61 (m, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 24.5, 37.3, 115.3 (d, *J* = 20.4 Hz), 125.2, 127.6, 128.7, 129.1, 129.8, 131.1 (d, *J* = 8.3 Hz), 131.9, 133.35 (d, *J* = 2.8 Hz), 133.4, 134.2, 147.8, 149.2, 162.5 (d, *J* = 246.1 Hz), 205.3. ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -113.9 (m). IR (Neat) ν 3519, 3051, 2919, 1700, 1603, 1510, 1224, 837, 732 cm⁻¹. MS (%) *m/e* 318 (M⁺, 98.98), 317

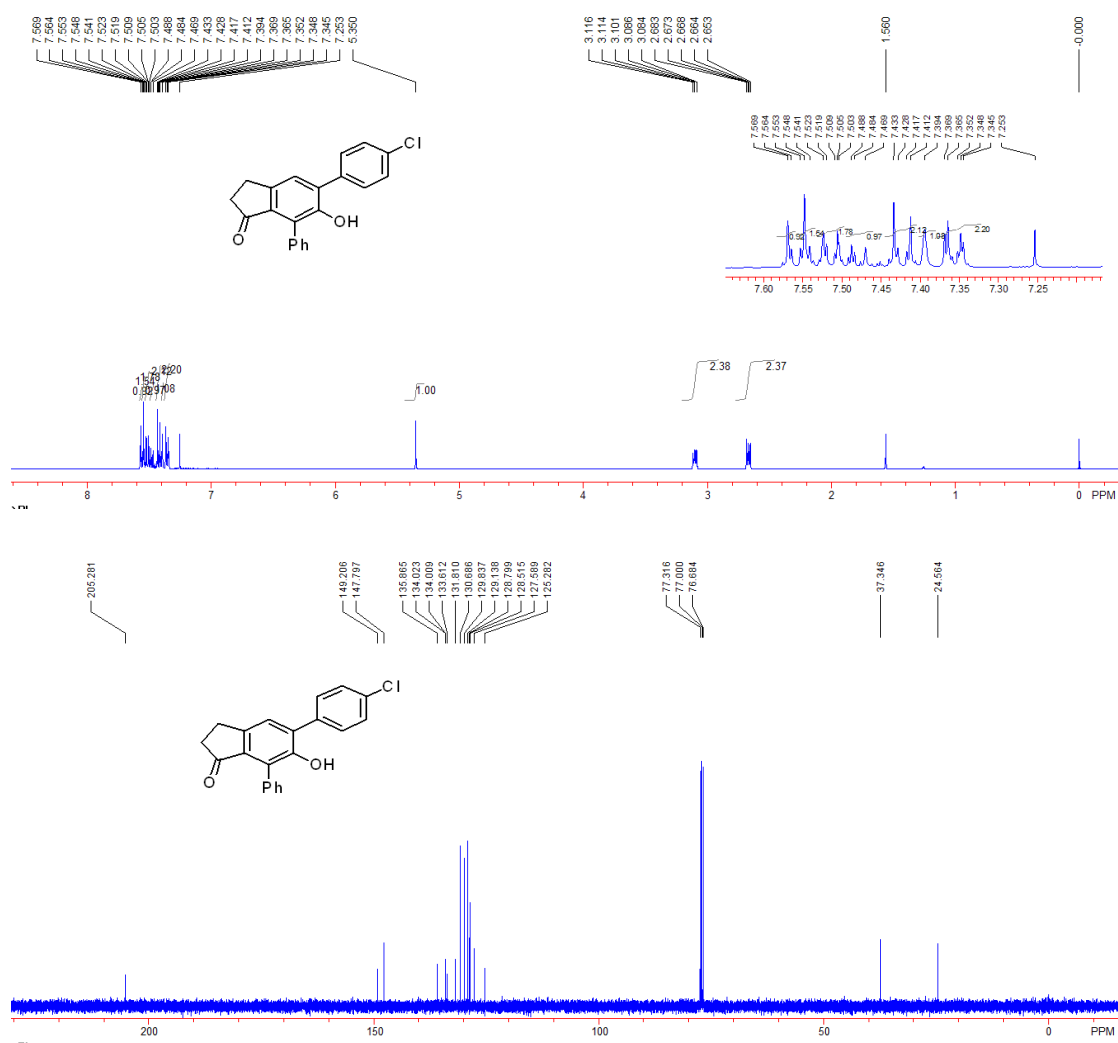
(100.00), 301 (5.60), 275 (18.49), 149 (9.14), 115 (7.27), 110 (4.28), 77 (1.61), 63 (1.01), 50 (0.38). HRMS (EI) calcd. for C₂₁H₁₅FO₂: 318.1056, Found: 318.1052.

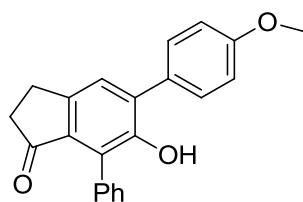




6-Hydroxy-5-(4-chlorophenyl)-7-phenyl-2,3-dihydro-1H-inden-1-one 2e:

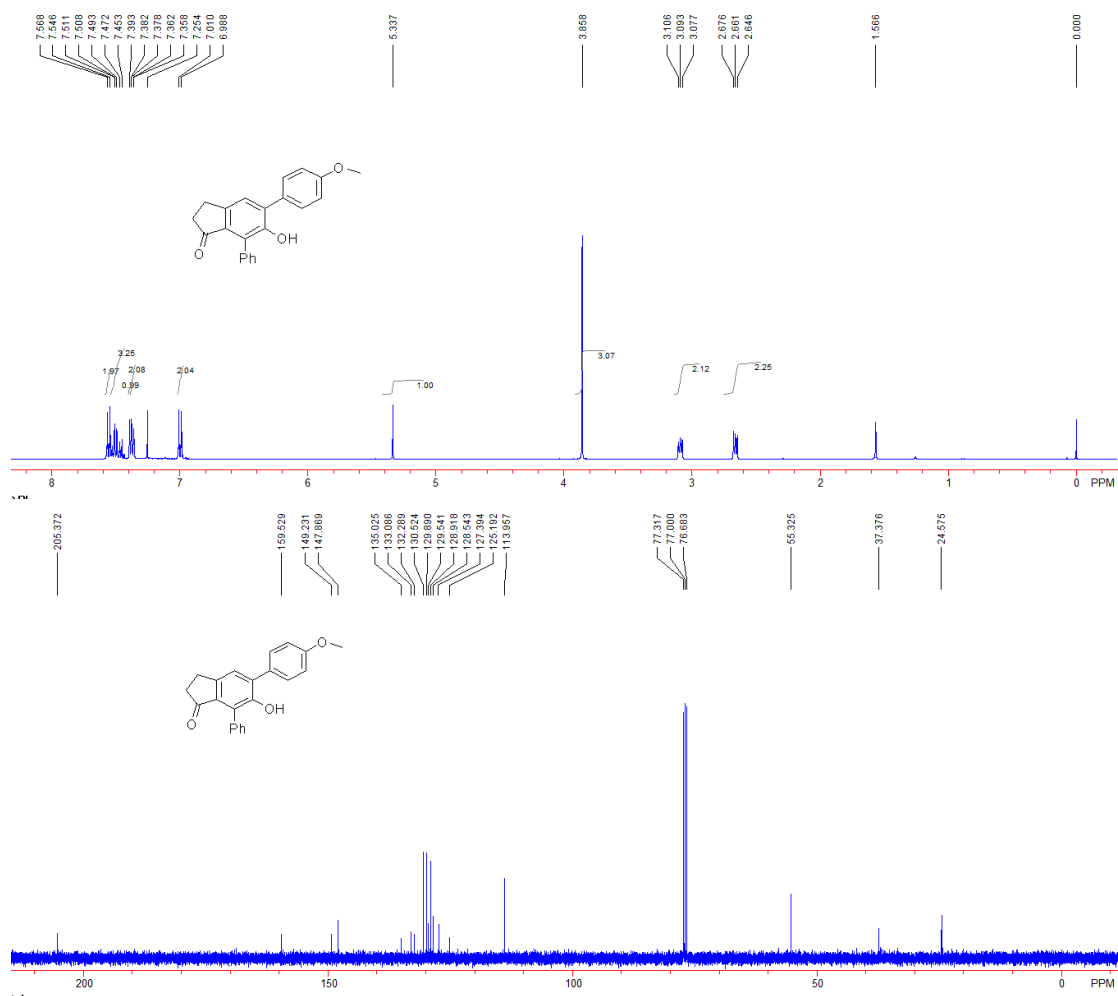
28 mg, yield: 42%; A white solid. Mp: 207-209 °C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.65-2.68 (m, 2H, CH_2), 3.08-3.12 (m, 2H, CH_2), 5.35 (s, 1H, OH), 7.35-7.37 (m, 2H, Ar), 7.39 (s, 1H, Ar), 7.41-7.43 (m, 2H, Ar), 7.47-7.57 (m, 5H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 24.6, 37.3, 125.3, 127.6, 128.5, 128.8, 129.1, 129.8, 130.7, 131.8, 133.6, 134.01, 134.02, 135.9, 147.8, 149.2, 205.3. IR (Neat) ν 3412, 2920, 1704, 1595, 1493, 1433, 1014, 831, 751 cm^{-1} . MS (%) m/e 336 (M^+ , 34.97), 335 (54.50), 334 (M^+ , 97.52), 333 (100.00), 291 (14.98), 149 (19.76), 113 (19.15), 107 (10.77). HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{15}\text{ClO}_2$: 334.0761, Found: 334.0762.

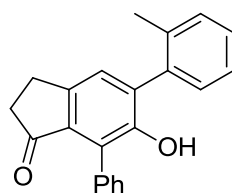




6-Hydroxy-5-(4-methoxyphenyl)-7-phenyl-2,3-dihydro-1H-inden-1-one 2f:

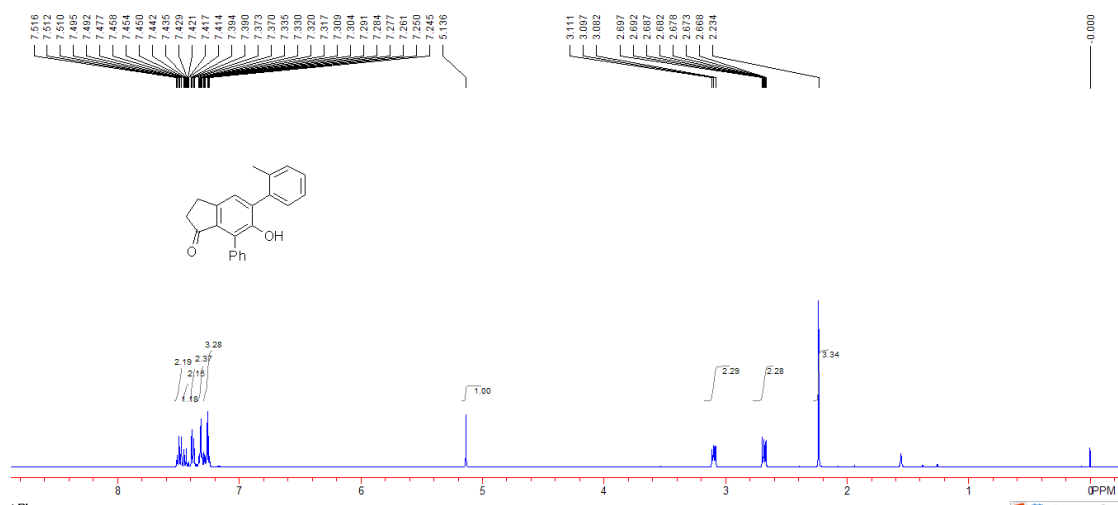
29 mg, yield: 44%; A white solid. Mp: 208-211 °C. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.66 (t, J = 6.0 Hz, 2H, CH_2), 3.09 (t, J = 6.0 Hz, 2H, CH_2), 3.86 (s, 3H, CH_3), 5.34 (s, 1H, OH), 7.00 (d, J = 8.8 Hz, 2H, Ar), 7.37 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H, Ar), 7.39 (s, 1H, Ar), 7.45-7.51 (m, 3H, Ar), 7.56 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 24.6, 37.4, 55.3, 114.0, 125.2, 127.4, 128.5, 128.9, 129.5, 129.9, 130.5, 132.3, 133.1, 135.0, 147.9, 149.2, 159.5, 205.4. IR (Neat) ν 2954, 2923, 2852, 1702, 1685, 1511, 1245, 1026, 732 cm^{-1} . MS (%) m/e 330 (M^+ , 100.00), 329 (68.40), 315 (6.13), 299 (10.10), 287 (10.42), 215 (5.16), 202 (5.78), 165 (8.57), 159 (3.47), 115 (5.99). HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_3$: 330.1256, Found: 330.1253.

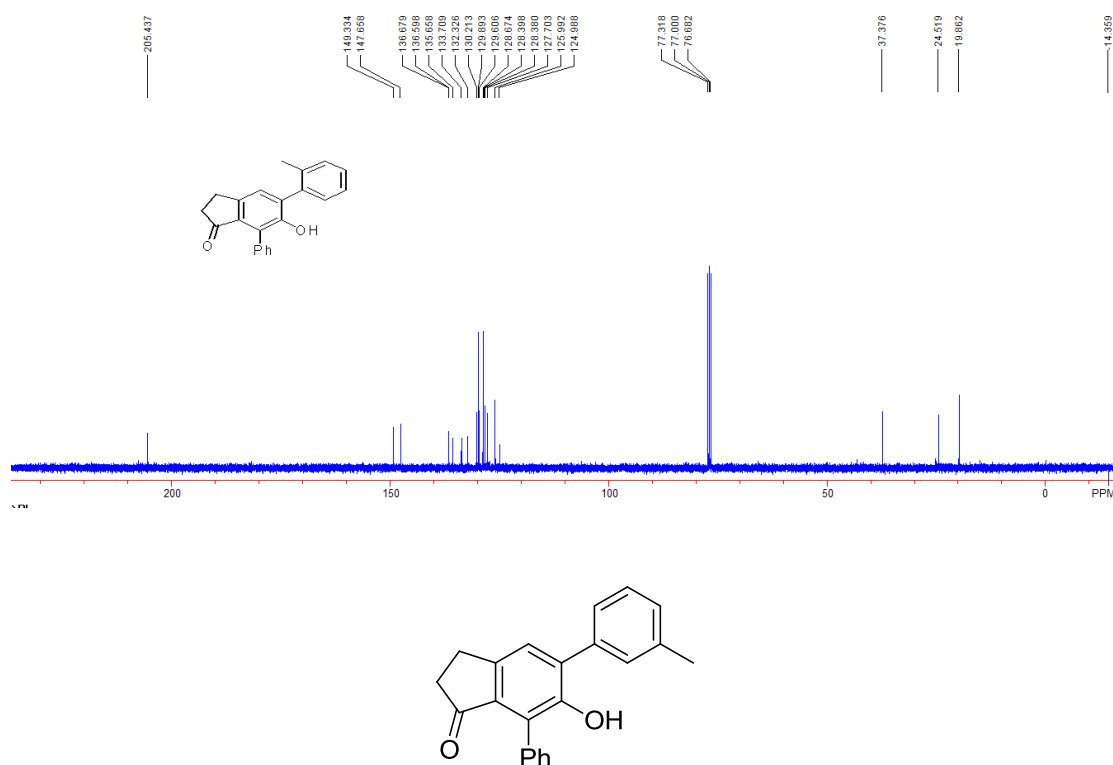




6-Hydroxy-7-phenyl-5-(*o*-tolyl)-2,3-dihydro-1*H*-inden-1-one 2g:

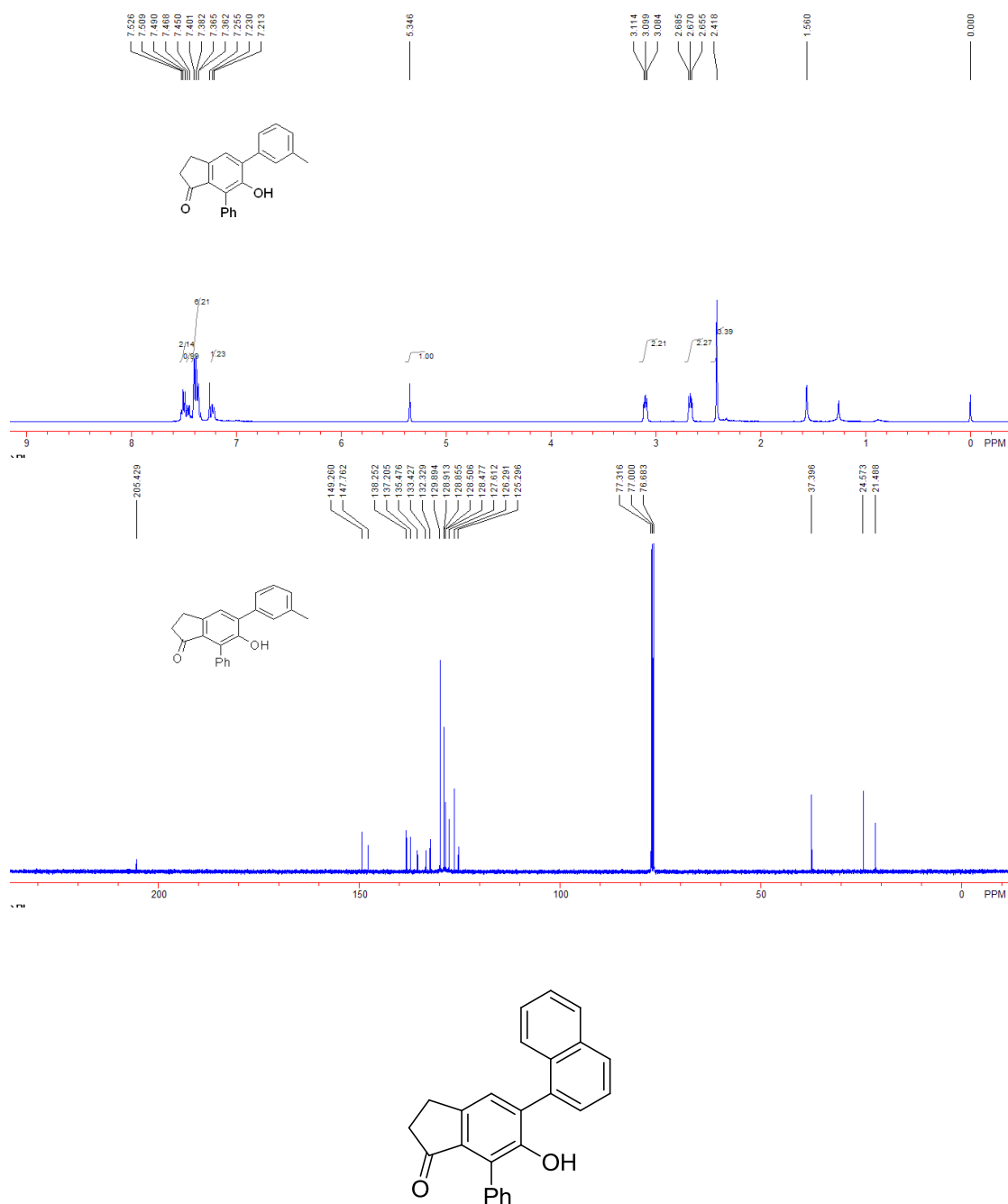
29 mg, yield: 46%; A white solid. Mp: 194-195 °C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.23 (s, 3H, CH_3), 2.67-2.70 (m, 2H, CH_2), 3.10 (t, $J = 6.0$ Hz, 2H, CH_2), 5.14 (s, 1H, OH), 7.25-7.29 (m, 3H, Ar), 7.30-7.34 (m, 2H, Ar), 7.37-7.39 (m, 2H, Ar), 7.41-7.46 (m, 1H, Ar), 7.48-7.52 (m, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 19.9, 24.5, 37.4, 125.0, 126.0, 127.7, 128.38, 128.40, 128.7, 129.6, 129.9, 130.2, 132.3, 133.7, 135.7, 136.6, 136.7, 147.7, 149.3, 205.4. IR (Neat) ν 3526, 3057, 2924, 1701, 1596, 1421, 907, 729, 697 cm^{-1} . MS (%) m/e 314 (M^+ , 100.00), 313 (48.13), 299 (93.33), 297 (42.50), 271 (12.81), 257 (8.71), 239 (6.51), 156 (13.00), 126 (10.99), 115 (18.76). HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_2$: 314.1307, Found: 314.1306.





6-Hydroxy-7-phenyl-5-(*m*-tolyl)-2,3-dihydro-1*H*-inden-1-one 2h:

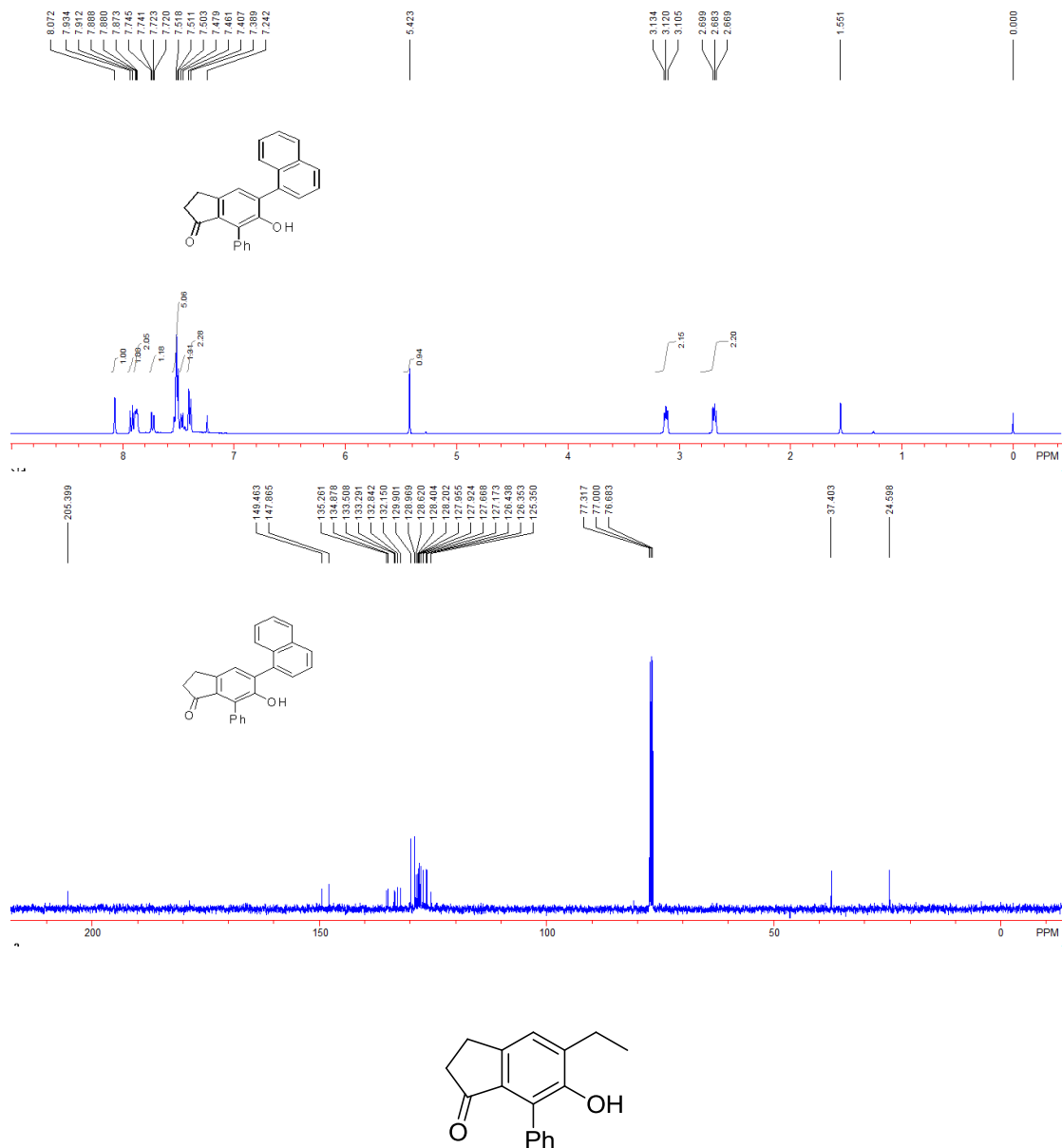
33 mg, yield: 52%; A white solid. Mp: 197-198 °C ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.42 (s, 3H, CH_3), 2.67 (t, $J = 6.0$ Hz, 2H, CH_2), 3.10 (t, $J = 6.0$ Hz, 2H, CH_2), 5.35 (s, 1H, OH), 7.22 (d, $J = 6.8$ Hz, 1H, Ar), 7.36-7.40 (m, 6H, Ar), 7.46 (d, $J = 7.2$ Hz, 2H, Ar), 7.51 (dd, $J_1 = 7.6$ Hz, $J_2 = 6.8$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 21.5, 24.6, 37.4, 125.3, 126.3, 127.6, 128.48, 128.51, 128.86, 128.91, 129.9, 132.3, 133.4, 135.5, 137.2, 138.3, 147.8, 149.3, 205.4. IR (Neat) ν 3521, 2923, 2854, 1705, 1597, 1279, 1205, 748, 697 cm^{-1} . MS (%) m/e 314 (M^+ , 100.00), 313 (83.53), 299 (65.06), 271 (16.60), 257 (5.37), 239 (5.90), 156 (11.77), 126 (9.40), 115 (14.45), 77 (2.63). HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_2$: 314.1307, Found: 314.1304.



6-Hydroxy-5-(naphthalen-1-yl)-7-phenyl-2,3-dihydro-1*H*-inden-1-one 2i:

30 mg, yield: 43%; A white solid. Mp: 195-198 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.68 (t, 2H, *J* = 6.0 Hz, CH₂), 3.12 (t, *J* = 6.0 Hz, 2H, CH₂), 5.42 (s, 1H, OH), 7.40 (d, *J* = 7.2 Hz, 2H, Ar), 7.49 (d, *J* = 9.6 Hz, 1H, Ar), 7.50-7.52 (m, 5H, Ar), 7.73 (dd, *J*₁ = 8.8 Hz, *J*₂ = 1.6 Hz, 1H, Ar), 7.87-7.89 (m, 2H, Ar), 7.92 (d, *J* = 8.8 Hz, 1H, Ar), 8.07 (s, 1H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 24.6, 37.4, 125.4, 126.35, 126.44, 127.2, 127.7, 127.9, 128.0, 128.2, 128.4, 128.6, 129.0, 129.9, 132.2, 132.8, 133.3, 133.5, 134.9, 135.3, 147.9, 149.5, 205.4. IR (Neat) ν 3516, 3054, 2922, 1699, 1594, 1417, 1263, 858, 732 cm⁻¹. MS (%) m/e 350 (M⁺,

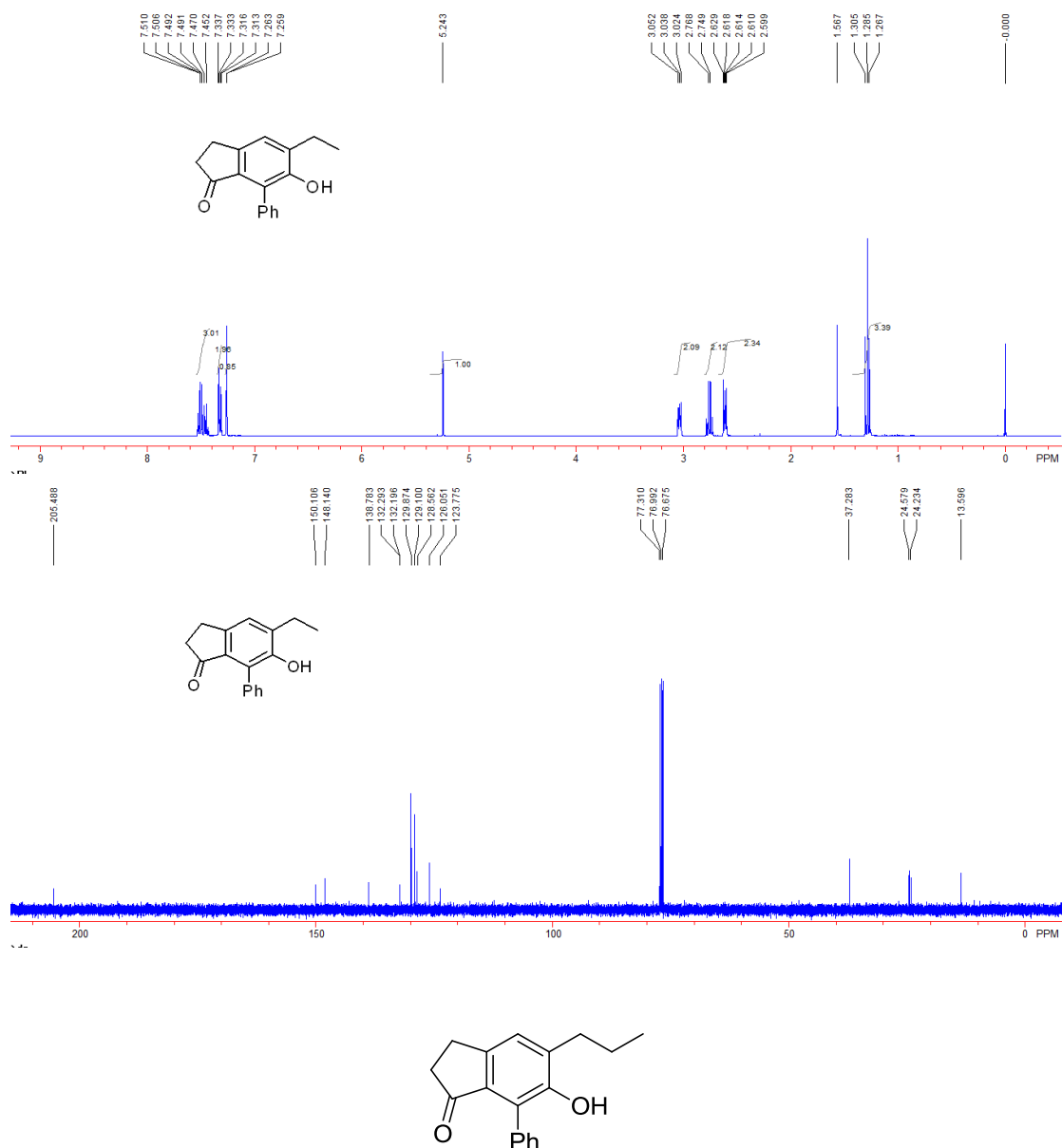
100.00), 349 (95.58), 307 (13.68), 289 (3.96), 276 (4.25), 175 (8.41), 165 (6.08), 152 (6.72), 138 (8.58), 115(5.16). HRMS (EI) calcd. for C₂₅H₁₈O₂: 350.1307, Found: 350.1302.



5-Ethyl-6-hydroxy-7-phenyl-2,3-dihydro-1H-inden-1-one 2j:

24 mg, yield: 44%; A white solid. Mp: 188-189 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.29 (t, *J* = 7.2 Hz, 3H, CH₃), 2.60-2.63 (m, 2H, CH₂), 2.76 (q, *J* = 7.2 Hz, 2H, CH₂), 3.04 (t, *J* = 5.6 Hz, 2H, CH₂), 5.24 (s, 1H, OH), 7.26 (s, 1H, Ar), 7.32 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz, 2H, Ar), 7.49-7.51 (m, 3H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 13.6, 24.2, 24.6, 37.3, 123.8, 126.1, 128.6, 129.1, 129.9, 132.2, 132.3, 138.8, 148.1, 150.1, 205.5. IR (Neat) ν 3527, 2964, 2928, 1698, 1597, 1444, 1210, 870, 698 cm⁻¹. MS (%) m/e 252 (M⁺, 100.00), 251 (83.01), 237 (100.00), 237 (5.73), 209 (23.36), 165 (25.27), 152 (16.86), 128 (10.49), 118 (8.01).

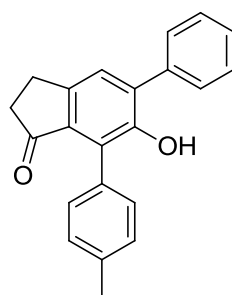
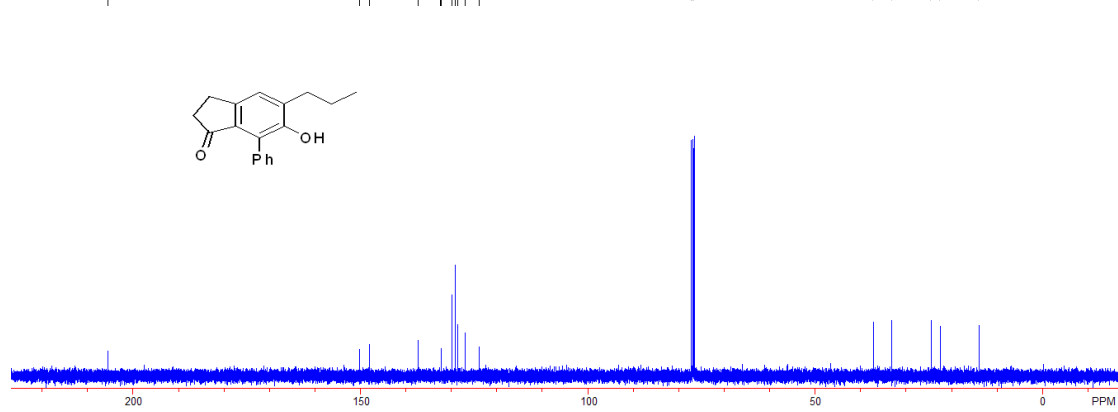
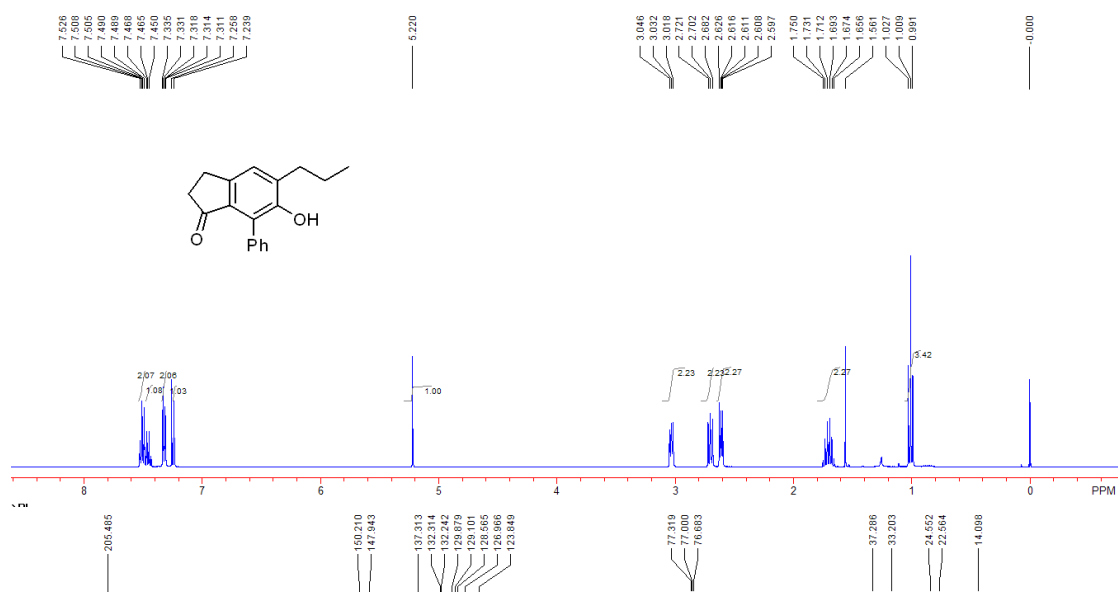
(19.26), 103(8.56). HRMS (EI) calcd. for $C_{17}H_{16}O_2$: 252.1150, Found: 252.1152.



6-Hydroxy-7-phenyl-5-propyl-2,3-dihydro-1H-inden-1-one 2k:

22 mg, yield: 41%; A white solid. Mp: 189-191 °C. 1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.01 (t, $J = 7.2$ Hz, 3H, CH_3), 1.66-1.75 (m, 2H, CH_2), 2.60-2.63 (m, 2H, CH_2), 2.70 (t, $J = 7.2$ Hz, 2H, CH_2), 3.03 (t, $J = 5.6$ Hz, 2H, CH_2), 5.22 (s, 1H, OH), 7.24 (d, $J = 7.6$ Hz, 1H, Ar), 7.32 (dd, $J_1 = 6.8$ Hz, $J_2 = 1.6$ Hz, 2H, Ar), 7.45-7.47 (m, 1H, Ar), 7.49-7.53 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 22.6, 24.6, 33.2, 37.3, 123.8, 127.0, 128.6, 129.1, 129.9, 132.2, 132.3, 137.3, 147.9, 150.2, 205.5. IR (Neat) ν 3529, 2925, 2869, 1699, 1595, 1598, 1267, 1110, 733 cm^{-1} . MS (%) m/e 266 (M^+ , 81.85), 265 (18.76), 251 (100.00), 237 (30.70), 223 (12.16), 195 (20.72), 178 (14.24), 165 (36.92), 152 (22.81), 115(17.14). HRMS (EI) calcd.

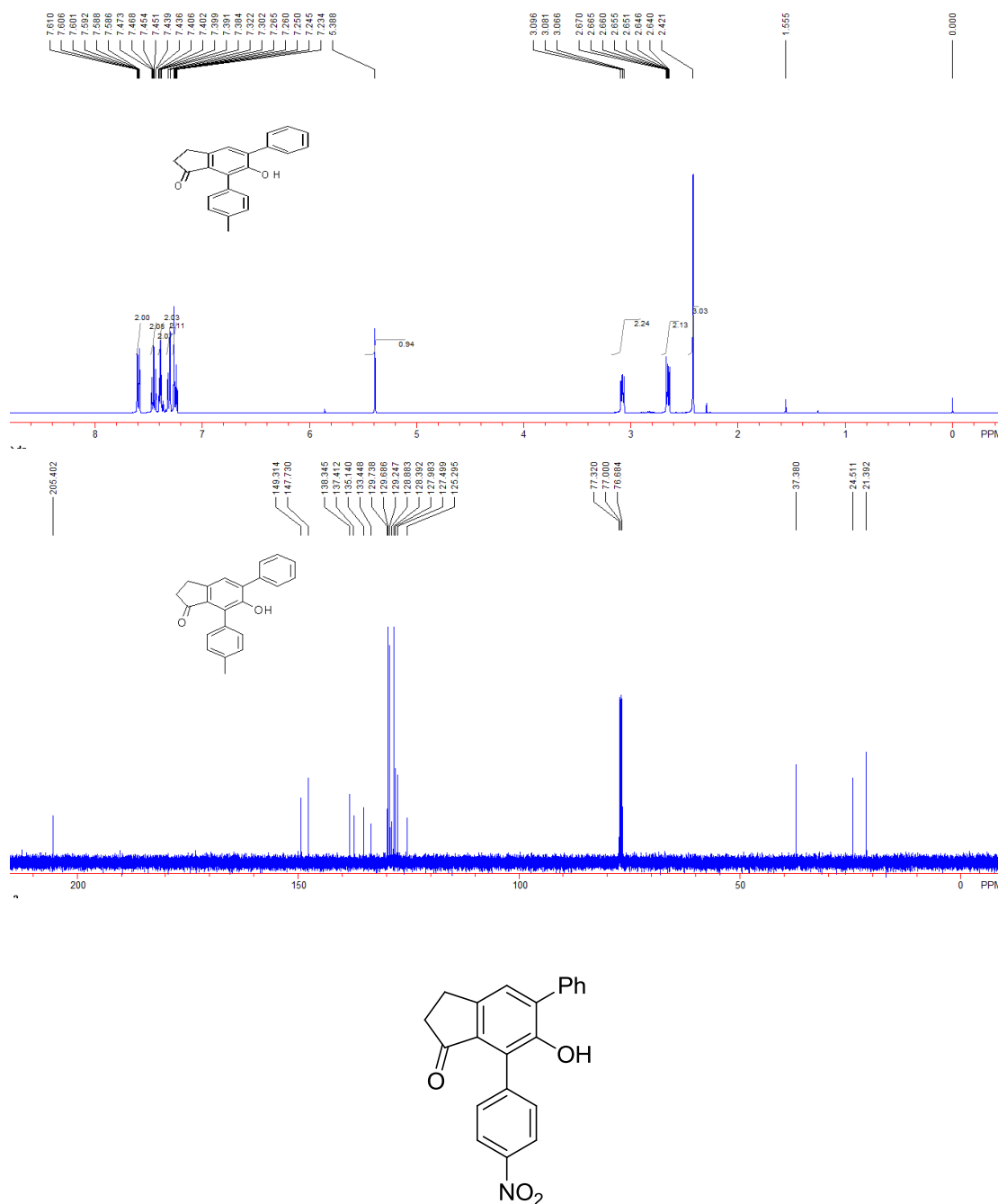
for C₁₈H₁₈O₂: 266.1307, Found: 266.1310.



6-Hydroxy-5-phenyl-7-(p-tolyl)-2,3-dihydro-1H-inden-1-one 2l:

35 mg, yield: 55%; A white solid. Mp: 195-197 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.42 (s, 3H, CH₃), 2.64-2.67 (m, 2H, CH₂), 3.08 (t, *J* = 6.0 Hz, 2H, CH₂), 5.39 (s, 1H, OH), 7.23-7.27 (m, 2H, Ar), 7.31 (d, *J* = 8.0 Hz, 2H, Ar), 7.38-7.41 (m, 2H, Ar), 7.45 (dt, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 2H, Ar), 7.60 (dt, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 21.4, 24.5, 37.4, 125.3, 127.5, 128.0, 128.4, 128.9, 129.3, 129.7, 133.4, 135.1,

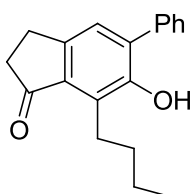
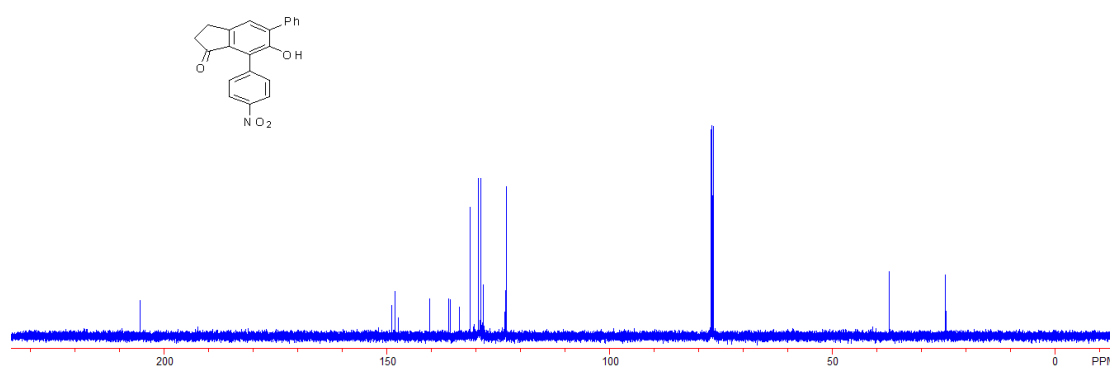
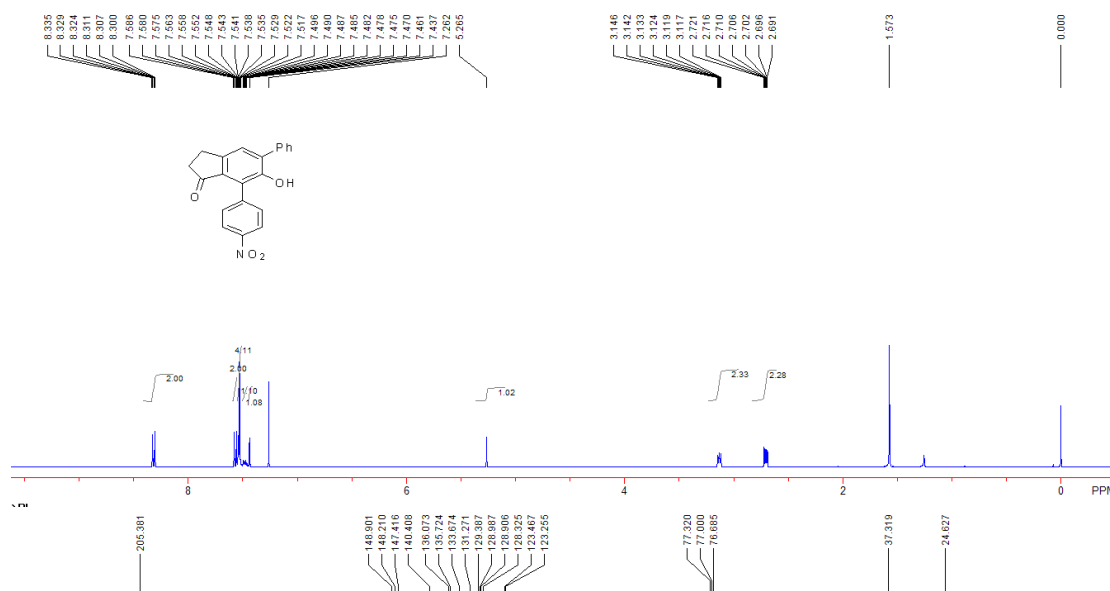
137.4, 138.3, 147.7, 149.3, 205.4. IR (Neat) ν 3509, 2921, 2857, 1699, 1593, 1417, 1256, 732, 697 cm^{-1} . MS (%) m/e 314 (M^+ , 100.00), 313 (88.27), 299 (27.73), 271 (14.58), 257 (7.74), 239 (4.34), 215 (3.70), 165 (5.04), 129 (2.28), 115 (9.14). HRMS (EI) calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_2$: 314.1307, Found: 314.1309.



6-Hydroxy-7-(4-nitrophenyl)-5-phenyl-2,3-dihydro-1H-inden-1-one 2m:

26 mg, yield: 40%; A white solid. Mp: 214-216 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.69-2.72 (m, 2H, CH_2), 3.12-3.15 (m, 2H, CH_2), 5.27 (s, 1H, OH), 7.44 (s, 1H, Ar), 7.46-7.50 (m, 1H, Ar), 7.52-7.55 (m, 4H, Ar), 7.57 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz, 2H, Ar), 8.32 (dd, $J_1 =$

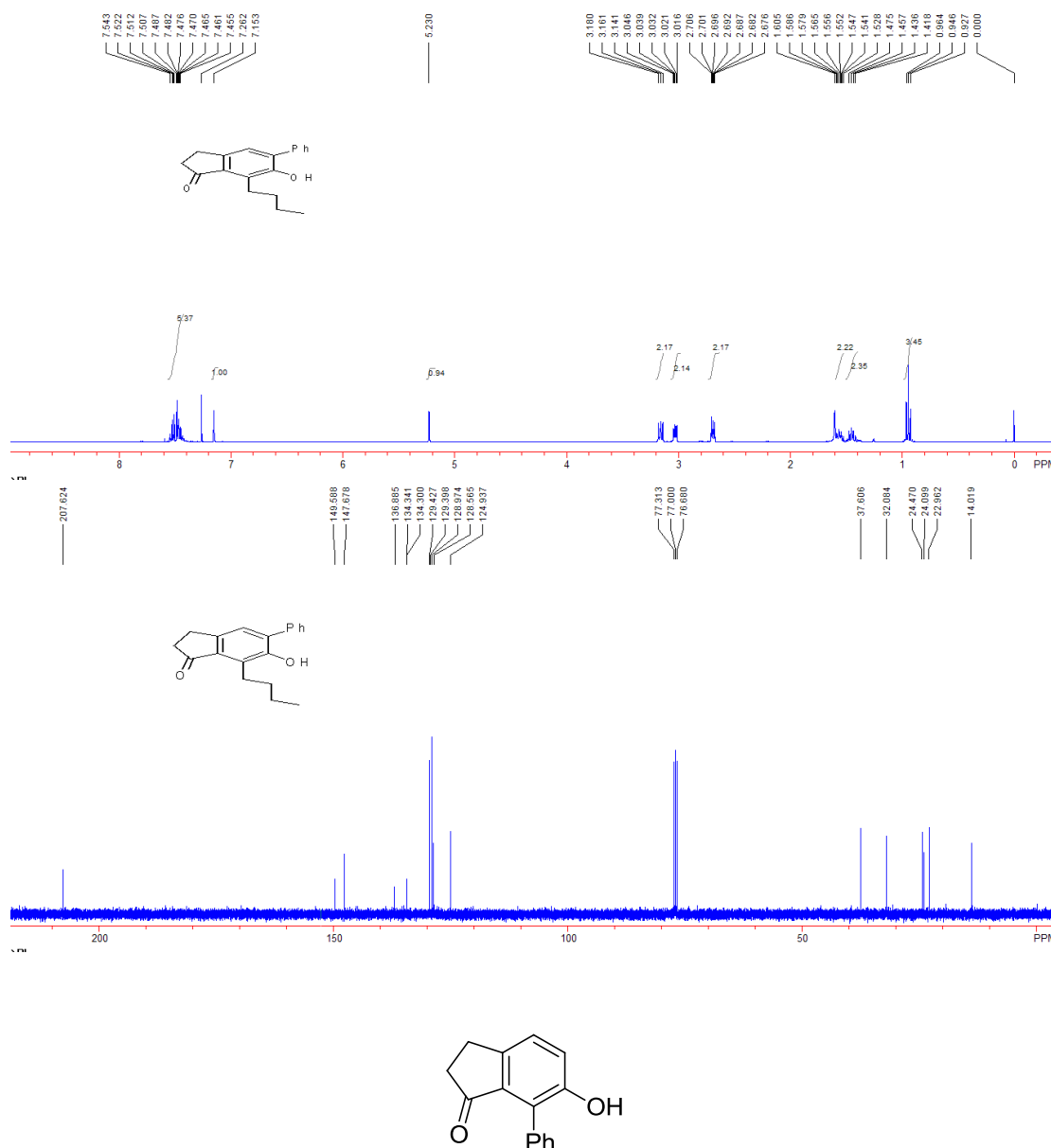
6.8 Hz, $J_2 = 2.0$ Hz, 2H, Ar). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 24.6, 37.3, 123.3, 123.5, 128.3, 128.9, 129.0, 129.4, 131.3, 133.7, 135.7, 136.1, 140.4, 147.4, 148.2, 148.9, 205.4. IR (Neat) ν 3538, 3392, 2927, 2053, 1700, 1515, 1345, 908, 731 cm^{-1} . MS (%) m/e 345 (M^+ , 17.24), 167 (30.88), 149 (100.00), 71 (18.72), 57 (30.19), 55 (15.40), 43 (19.77), 41 (18.42). HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{15}\text{NO}_4$: 345.1001, Found: 345.1003.



7-Butyl-6-hydroxy-5-phenyl-2,3-dihydro-1H-inden-1-one 2n:

28 mg, yield: 49%; A white solid. Mp: 190-192 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 0.95 (t, $J = 7.6$ Hz, 3H, CH_3), 1.46 (q, $J = 7.6$ Hz, 2H, CH_2), 1.51-1.58 (m, 2H, CH_2), 2.68-2.71 (m, 2H, CH_2), 3.02-3.05 (m, 2H, CH_2), 3.16 (t, $J = 7.6$ Hz, 2H, CH_2), 5.23 (s, 1H, OH), 7.15 (s,

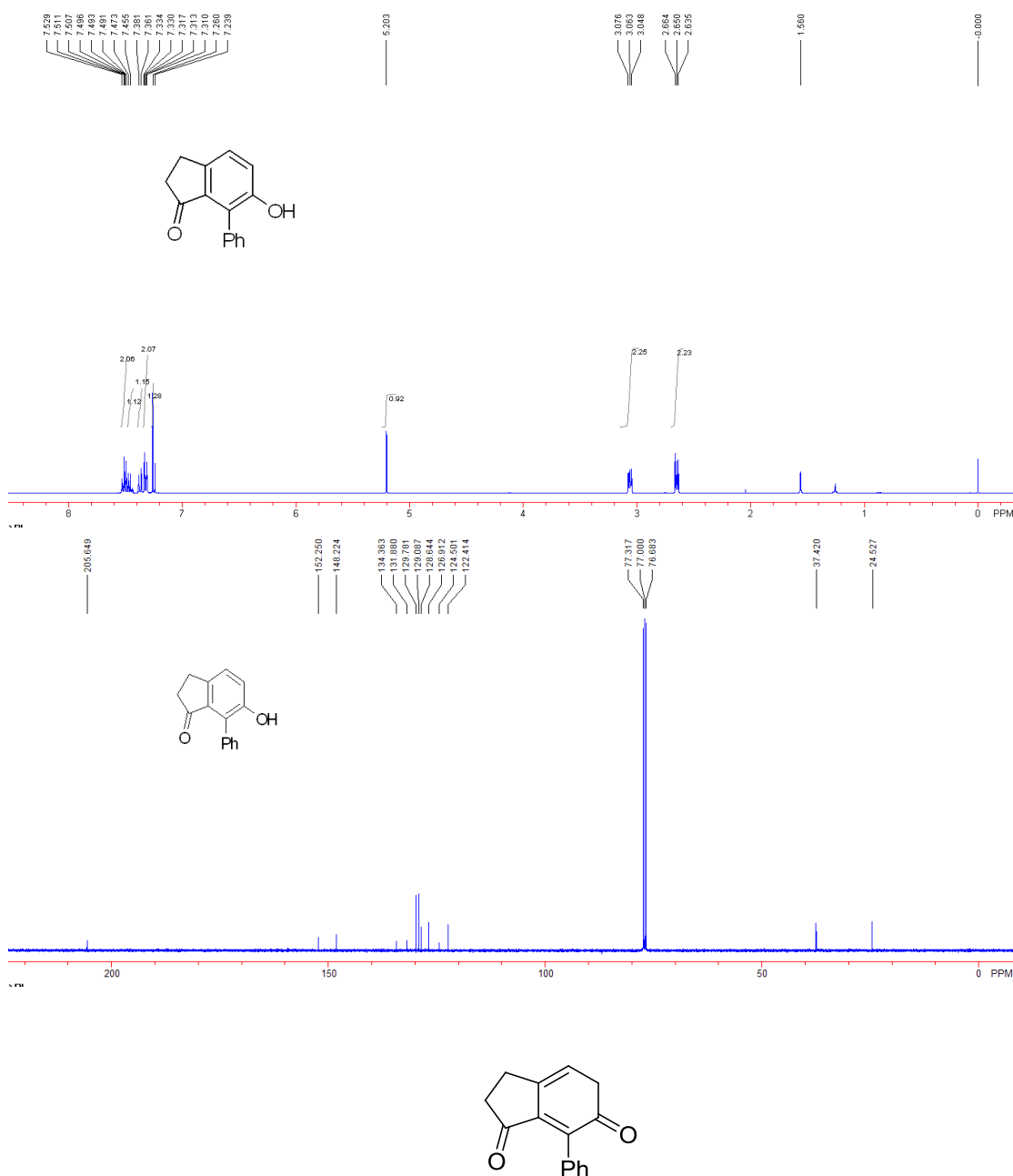
1H, Ar), 7.46-7.54 (m, 5H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 14.0, 23.0, 24.1, 24.5, 32.1, 37.6, 124.9, 128.6, 129.0, 129.40, 129.43, 134.30, 134.34, 136.9, 147.7, 149.6, 207.6. IR (Neat) ν 3547, 3391, 2928, 1682, 1599, 1456, 1235, 905, 701 cm⁻¹. MS (%) m/e 280 (M⁺, 38.29), 251 (59.35), 238(73.44), 237 (44.76), 195(31.78), 167 (41.56), 165 (30.74), 149 (100.00). HRMS (EI) calcd. for C₁₉H₂₀O₂: 280.1463, Found: 280.1462.



6-Hydroxy-7-phenyl-2,3-dihydro-1H-inden-1-one 2o:

10 mg, yield: 21%; This is a known compound. [⁵] ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.65 (t, *J* = 6.0 Hz, 2H, CH₂), 3.06 (t, *J* = 6.0 Hz, 2H, CH₂), 5.20 (s, 1H, OH), 7.25 (d, *J* = 8.0 Hz, 2H, Ar), 7.31-7.33 (m, 2H, Ar), 7.37 (d, *J* = 8.0 Hz, 1H, Ar), 7.46-7.47 (m, 1H, Ar), 7.49-7.53 (m, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 24.5, 37.4, 122.4, 124.5, 126.9, 128.6, 129.1,

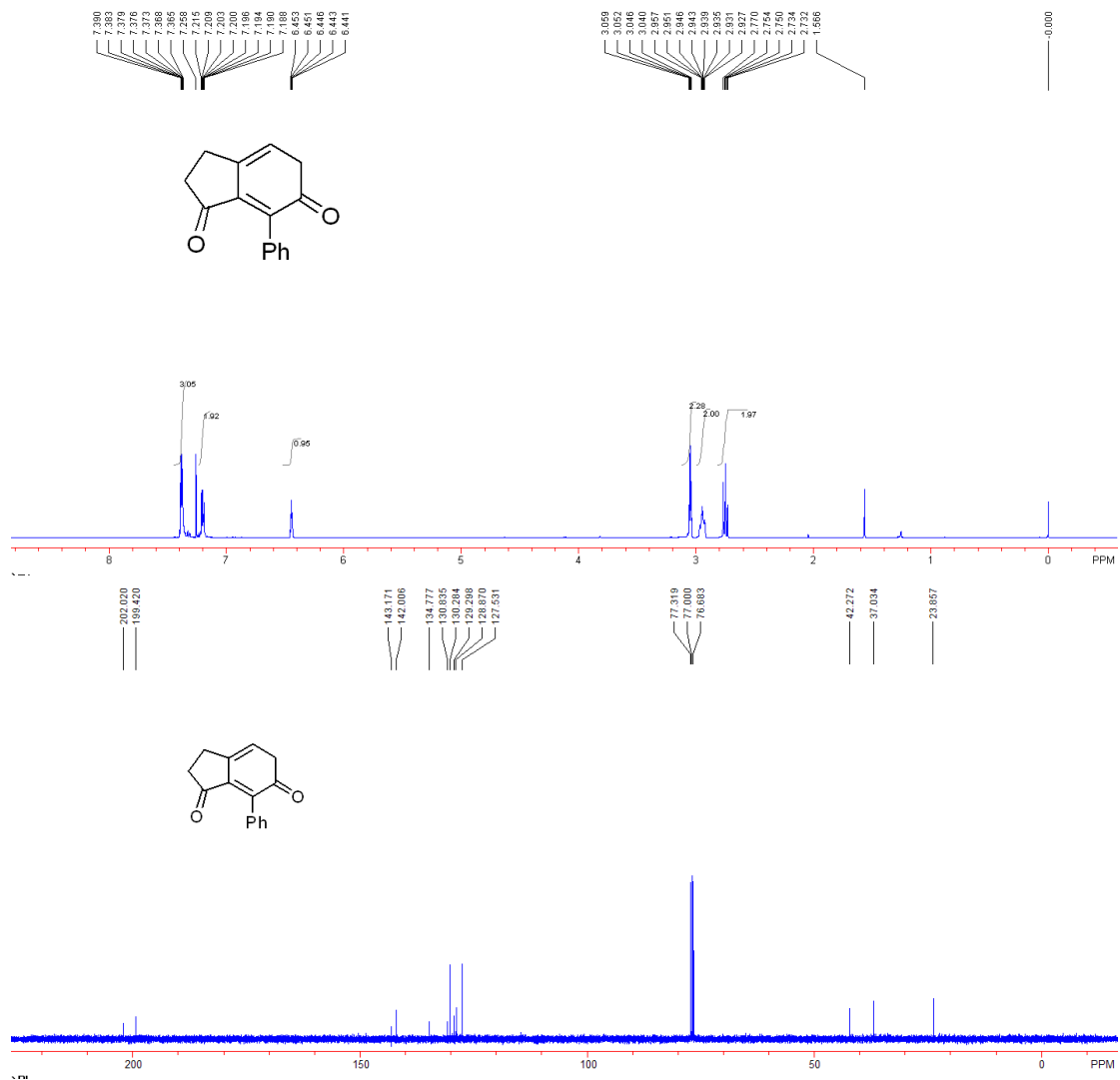
129.8, 131.9, 134.4, 148.2, 152.3, 205.6. MS (%) m/e 224 (M^+ , 96.20), 223 (100.00), 207 (10.22), 195 (11.46), 181 (26.44), 165 (15.23), 126 (4.78), 115 (16.30), 89 (15.06). HRMS (EI) calcd. for $C_{15}H_{12}O_2$: 224.0837, Found: 224.0834.



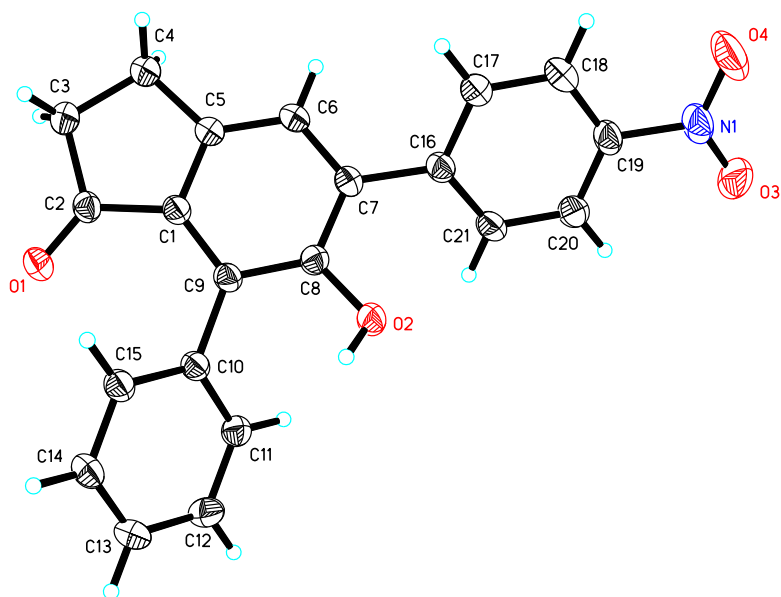
7-Phenyl-2,3-dihydro-1H-indene-1,6(5H)-dione 2o':

10 mg, yield: 21%; A white solid. Mp: 155-157 °C. 1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.73-2.77 (m, 2H, CH₂), 2.93-2.96 (m, 2H, CH₂), 3.04-3.06 (m, 2H, CH₂), 6.44-6.45 (m, 1H, =CH), 7.19-7.22 (m, 2H, Ar), 7.37-7.39 (m, 3H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 23.9, 37.0, 42.3, 127.5, 128.9, 129.3, 130.3, 130.8, 134.8, 142.0, 143.17, 199.4, 202.0. IR (Neat) ν 3062, 2923, 2851, 1728, 1708, 1667, 1155, 891, 695 cm^{-1} . MS (%) m/e 224 (M^+ ,

12.55), 220 (2.85), 159 (24.59), 99 (38.25), 81 (32.87), 72 (29.28), 59 (22.15), 57 (15.73), 43 (100.00), 41 (25.73). HRMS (EI) calcd. for C₁₅H₁₂O₂: 224.0837, Found: 224.0835.



5. Crystallographic Information



The crystal data of **2c** have been deposited in CCDC with number 889520. Empirical Formula: $C_{21}H_{15}NO_4$; Formula Weight: 345.34; Crystal Color, Habit: colorless; Crystal Dimensions: 0.313 x 0.212 x 0.075 mm; Crystal System: Monoclinic; Lattice Parameters: $a = 14.5884(15)\text{\AA}$, $b = 7.8609(8)\text{\AA}$, $c = 14.6943(15)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 102.614(2)^\circ$, $\gamma = 90^\circ$, $V = 1644.4(3)\text{\AA}^3$; Space group: $P2(1)/c$; $Z = 4$; $D_{calc} = 1.395\text{ g/cm}^3$; $F_{000} = 720$; Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0415$, $wR2 = 0.1111$.

6. Reference

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