Electronic Supplementary Material (ESI) for Chemical Communications


**Supporting Information**

# HOTf Mediated Cascade Reactions of 1-Arenoylcyclopropanecarboxylic Acids with Arenes

*Gen-Qiang Chen, Xiang-Ying Tang and Min Shi**

State Key Laboratory of Organometallic Chemistry,

Shanghai Institute of Organic Chemistry,

Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai, 200032, China.

***Mshi@mail.sioc.ac.cn***. *Fax* 86-21-64166128

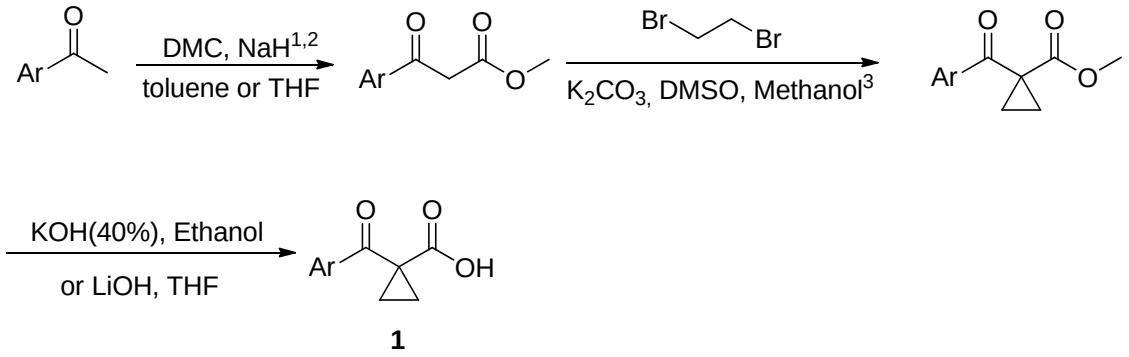
## CONTENTS

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. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

2. **General Reaction Procedure**

**Representative procedures for the preparation of substrates**:

The substrates **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l** and **1m** were synthesized according to the following Scheme. The substrate **1a** was synthesized starting from ethyl benzoylacetate and the substrate **8** was prepared from 1,1-dibenzoylmethane (see belows). The substrate **7** was synthesized from spiro[cyclopropane-1,2'-indene]-1',3'-dione (see belows).




**1**

1,3-Dicarbonyl compounds were synthesized according to the procedures reported in the previous literature.[1,2]

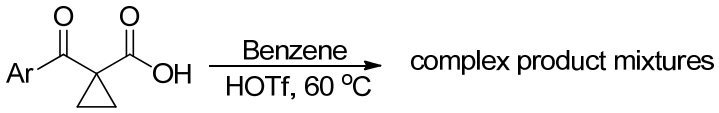
The esters were synthesized according to slightly modified procedure reported in the previous literature:[3] To a 100 mL mono-neck flask were added 1,3-dicarbonyl compound (2.910 g, 13.62 mmol), potassium carbonate (3.76 g, 27.24 mmol), 2.20 mL methanol (54.48 mmol) and 30 mL DMSO. The resulting mixture was allowed to stir at room temperature for 30 min, and then 5.45 mL 1, 2-dibromoethane (54.48 mmol) was added in one portion. The flask was moved to a 25-60 $^{o}$C oil bath, and continued to stir for two days. The reaction wad quenched by addition of 250 mL water, then extracted with DCM (30 mL x 3). The combined organic layer was back washed with saturated NaCl solution (250 mL x 3), dried over anhydrous sodium sulfate and then evaporated. The residue was then purified by column chromatography on silica gel (PE/EA = 40/1) and 2.189 g of colorless liquid or white solid was obtained as product. All of the products were obtained in 60%-80% yields. The hydrolysis was performed with KOH as base; however, for *p*-F substituted substrate **1e**, LiOH was used to avoid the substitution of fluoro group. The substrate was further purified by recrystallization from DCM or methanol.

**General procedure for the HOTf mediated cascade reactions of substrates 1a-g**:

To a 25 mL flame and vacuum dried Schlenk tube, 0.3 mmol substrate **1**, 0.2 mL benzene or *p*-xylene and 0.8 mL HOTf were added. The resulting mixture was allowed to stir at 60 $^{o}$C in an oil bath (for benzene) or at room temperature (for *p*-xylene). The reaction was quenched by addition of 25 mL water, and then extracted with DCM (25 mL x 3). The combined organic layer was dried over anhydrous sodium sulfate, and the residue was purified by column chromatography (PE/EA = 40/1).

3. Some unsuccessful examples are summarized in **Table SI-1** and **Table SI-2**

**Table SI-1**. HOTf Mediated Cascade Reactions of **1h**-**1m** and Benzene

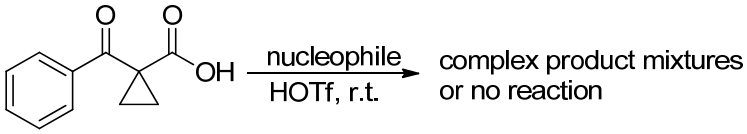



**1**

| entry[a] | Ar | t (h) |
|---|---|---|
| 1 | *p*-methoxyphenyl, **1h** | 0.5 |
| 2 | 1-naphthyl, **1i** | 1.0 |
| 3 | *o*-chlorophenyl, **1j** | 0.5 |
| 4 | 2-furanyl, **1k** | 0.5 |
| 5 | 2-thiophene, **1l** | 0.5 |
| 6 | 2-pyridyl, **1m** | 0.5 |

[a] Reaction conditions: 0.3 mmol of **1**, 0.2 mL of benzene and 0.8 mL of HOTf.

**Table SI-2**. Reactions of **1a** with Other Nucleophiles

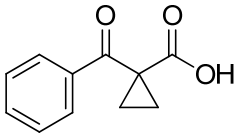



**1**

| entry[a] | Nu | quantity | t (h) |
|---|---|---|---|
| 1 | toluene | 6.3 equiv | 0.5 |
| 2 | 1,4-dimethoxybenzene | 3.3 equiv | 0.5 |
| 3 | 1,4-dibromobenzene | 5.0 equiv | 5.5 |
| 4 | 4-bromotoluene | 5.4 equiv | 5.5 |
| 5 | o-xylene[b] | 5.5 equivl | 0.5 |
| 6 | indole | 1.0 equiv | 12 |

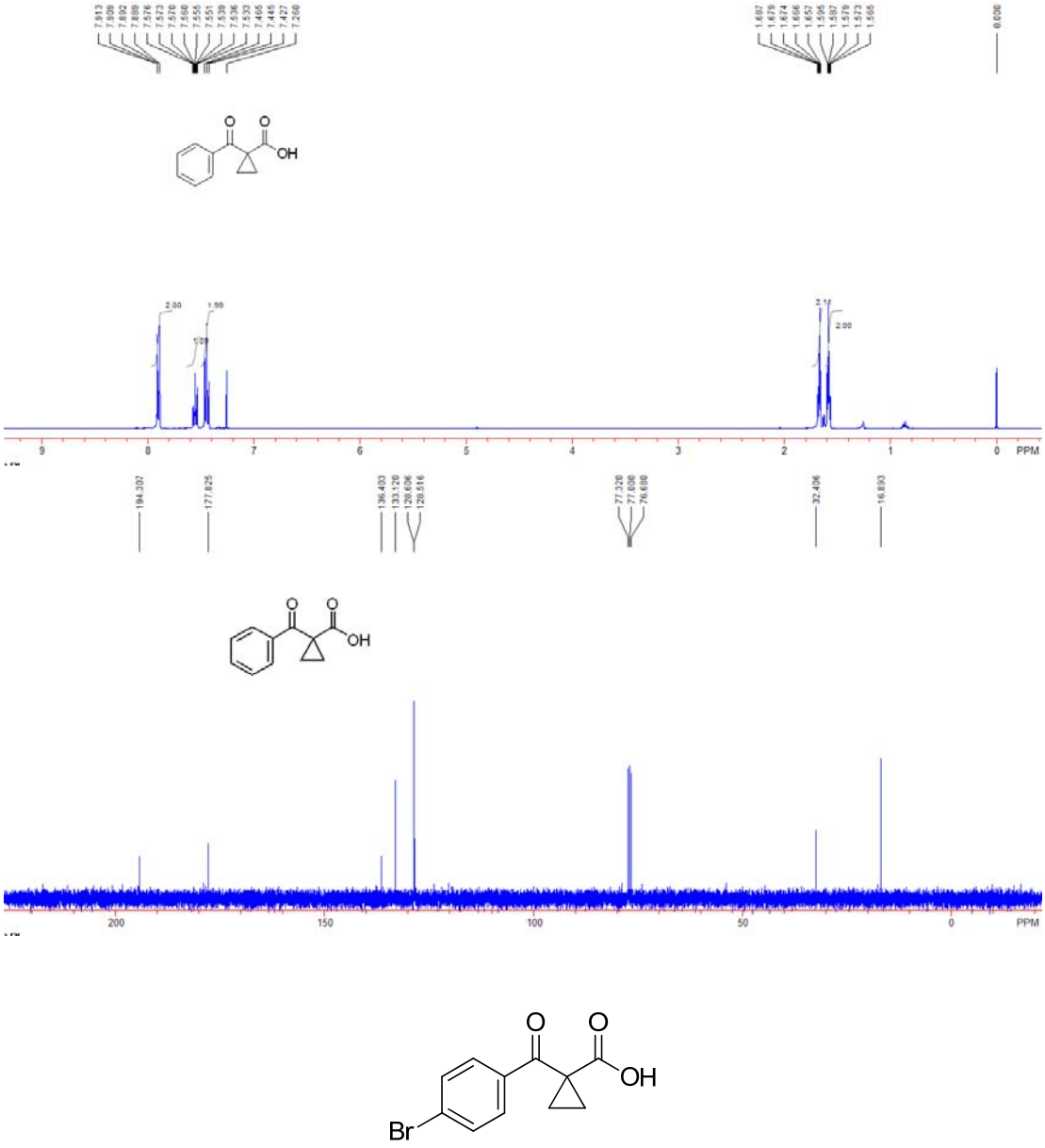
[a] Reaction conditions: 0.3 mmol of **1**, 0.8 mL of HOTf. [b] $^{1}H$ and $^{13}C$ NMR indicate that the product was mixture of isomers of the expected product (see: S38).

3. **Spectroscopic Data**




**1-Benzoylcyclopropanecarboxylic acid 1a**:

This is a known compound.[4] A white solid, $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.57-1.60 (m, 2H, $CH_2$), 1.66-1.69 (m, 2H, $CH_2$), 7.45 (dd, $J_1$ = 8.0 Hz, $J_2$ = 7.6 Hz, 2H, Ar), 7.56 (ddt, $J_1$ = 7.6 Hz, $J_2$ = 7.6 Hz, $J_3$ = 1.2 Hz, 1H, Ar), 7.90 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 16.8, 32.3, 128.4, 128.5, 133.0, 136.3, 177.7, 194.2.

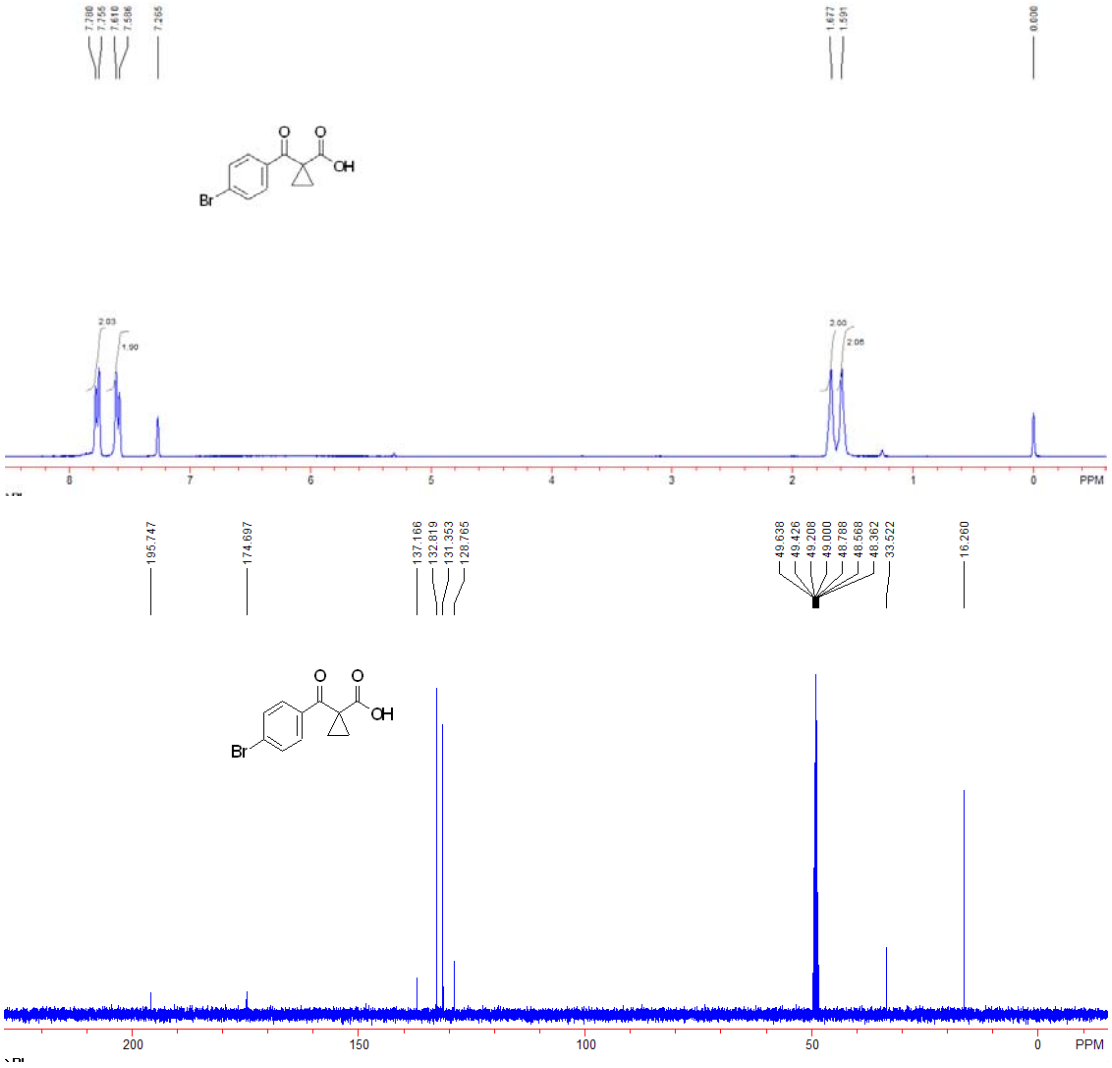


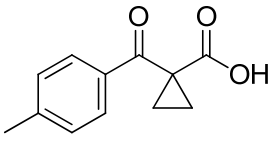




**1-(4-Bromobenzoyl)cyclopropanecarboxylic acid 1b**:

A white solid, Mp: 176-178 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.59 (s, 2H, $CH_2$), 1.68 (s, 2H, $CH_2$), 7.60 (d, *J* = 7.5 Hz, 2H, Ar), 7.77 (d, *J* = 7.5 Hz, 2H, Ar). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 16.3, 33.5, 128.8, 131.4, 132.8, 137.2, 174.7, 195.7. IR (Neat) ν 3090, 3010, 2878, 1673, 1583, 1558, 1456, 1443, 1397, 1329, 1171, 1068, 1001, 935, 839 cm$^{-1}$. MS (ESI) m/e 267.0 ($M^{+}$-1). HRMS (ESI) calcd. for $C_{11}H_8O_3Br$: 266.96623, Found: 266.96657.

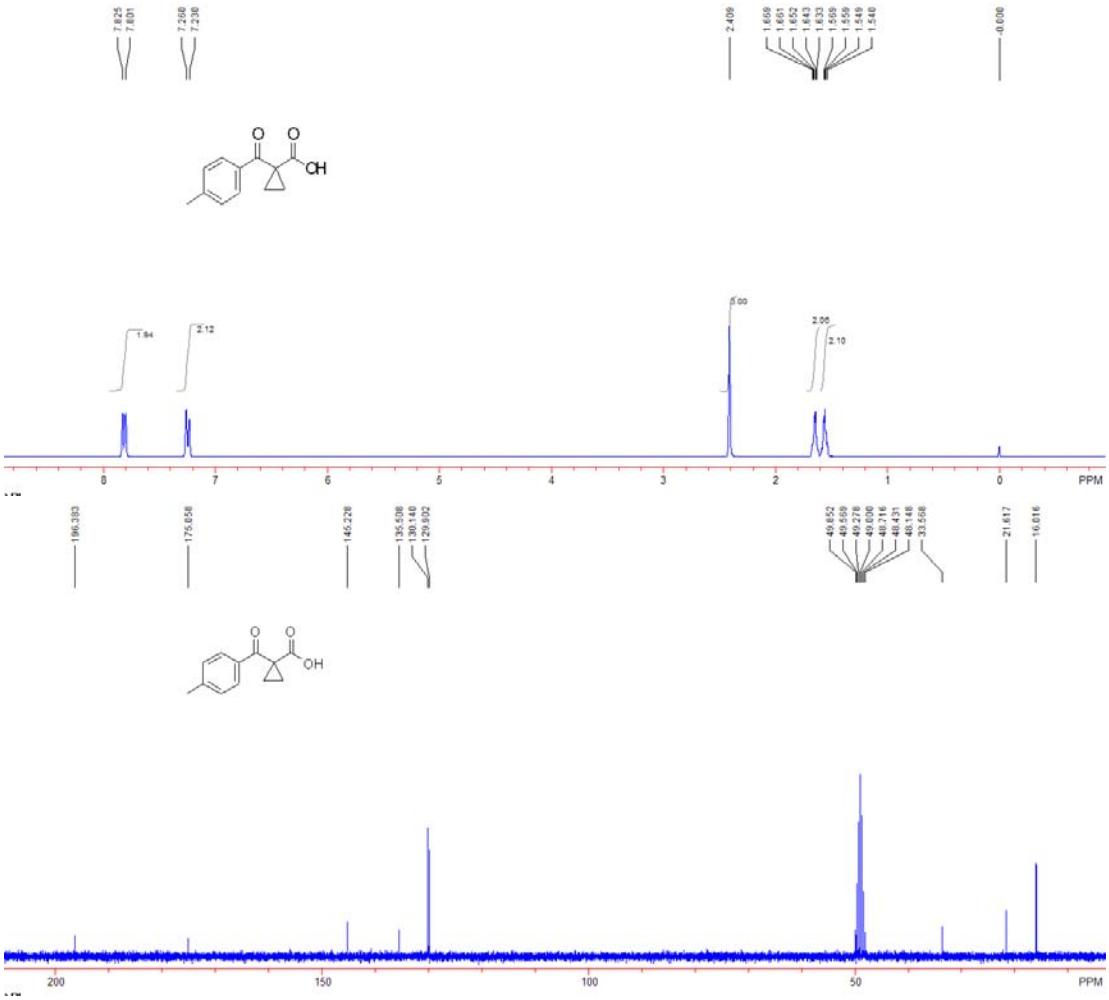


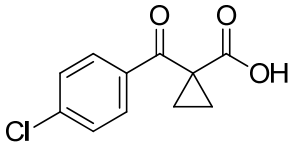




**1-(4-Methylbenzoyl)cyclopropanecarboxylic acid 1c**:

A white solid, Mp: 142-144 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.54-1.57 (m, 2H, $CH_2$), 1.63-1.67 (m, 2H, $CH_2$), 2.41 (s, 3H, $CH_3$), 7.25 (d, *J* = 7.2 Hz, 2H, Ar), 7.81 (d, *J* = 7.2 Hz, 2H, Ar). $^{13}$C NMR (75 MHz, $CD_3OD$, TMS): δ 16.0, 21.6, 33.6, 129.9, 130.1, 135.5, 145.2, 175.1, 196.4. IR

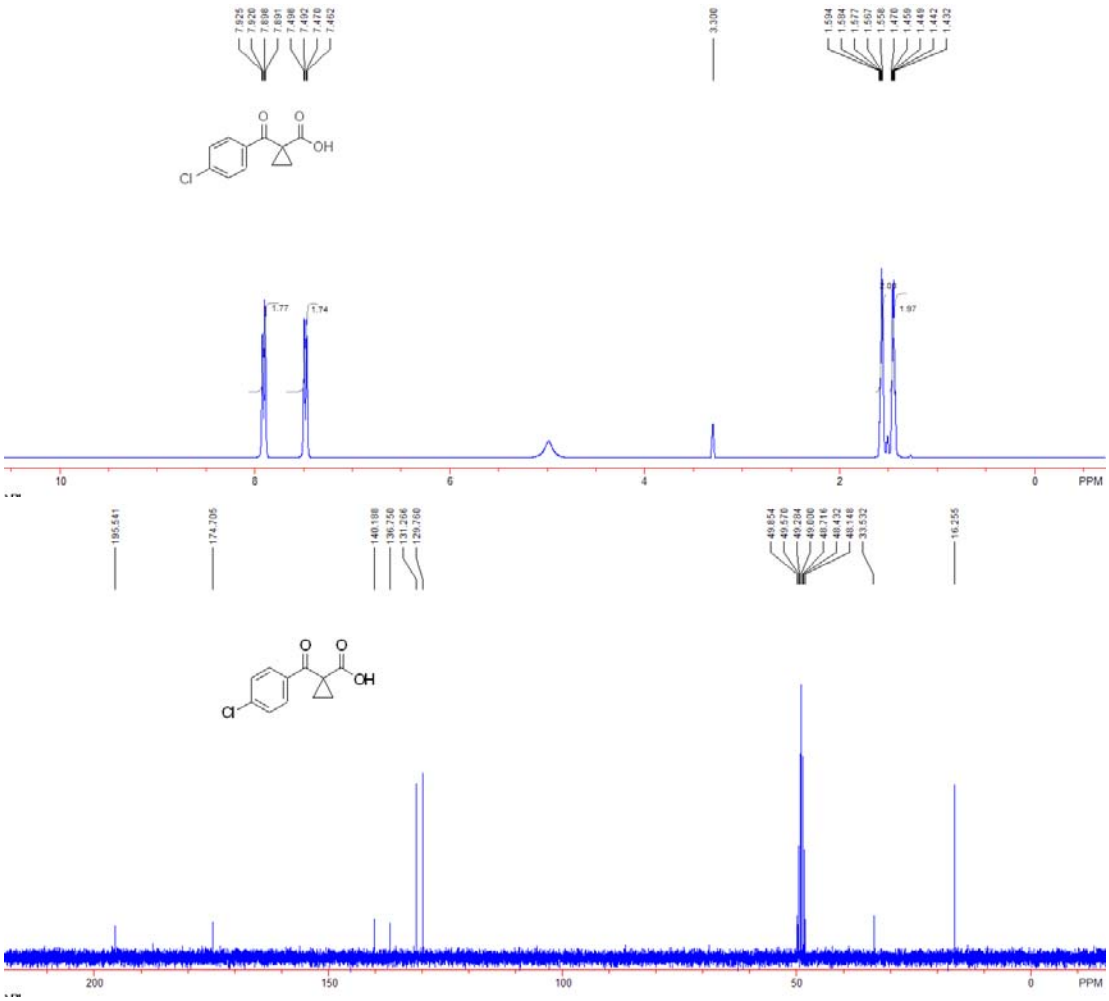
(Neat) ν 3023, 2922, 2581, 1670, 1604, 1421, 1323, 1223, 1171, 1034, 1005, 934, 835 $cm^{-1}$. Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57%; H, 5.92%. Found: C, 70.28%; H, 6.11%.

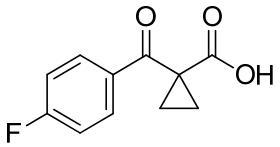



**1-(4-Chlorobenzoyl)cyclopropanecarboxylic acid 1d**:

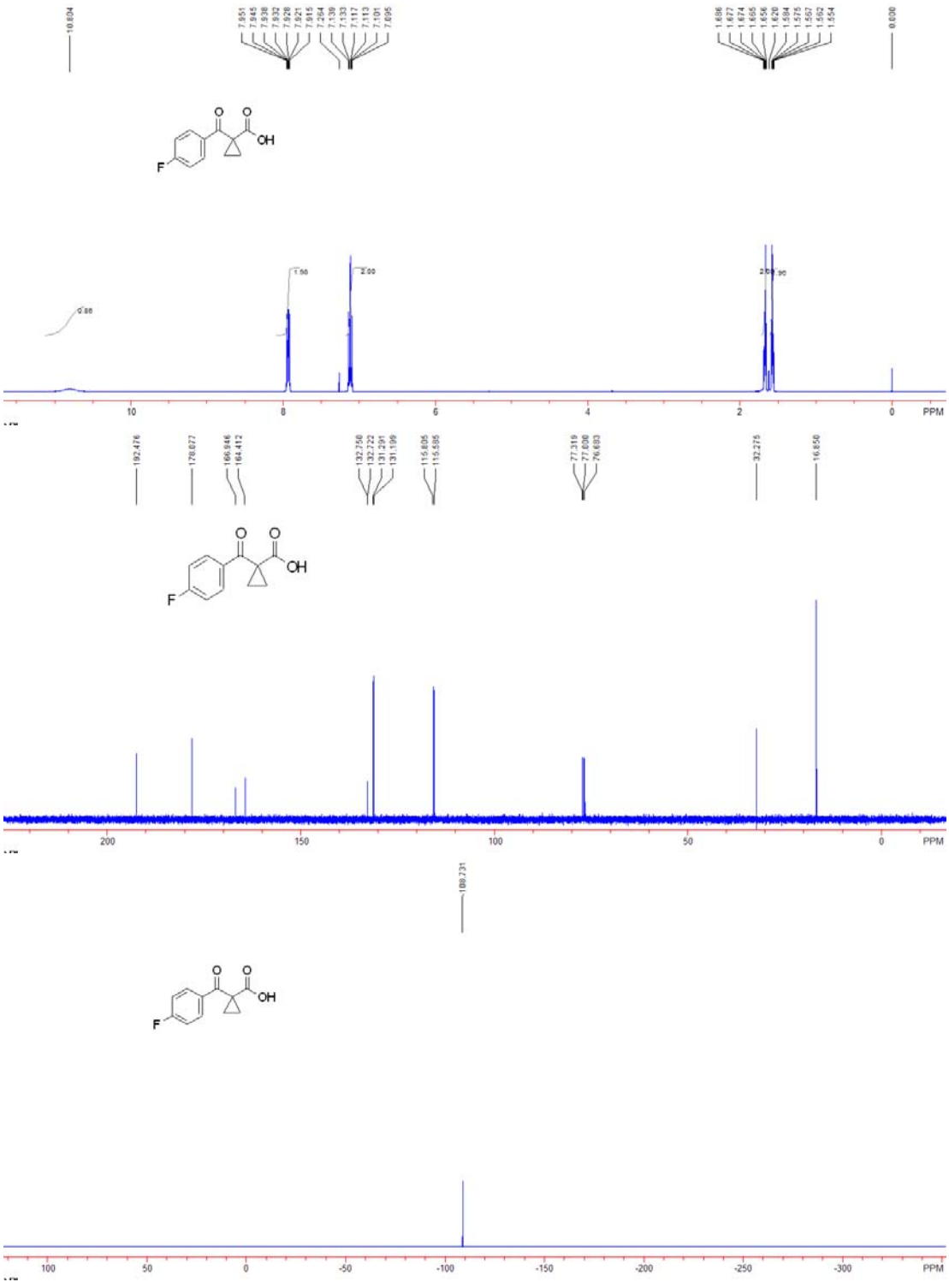
This is a known compound.[5] A white solid, $^1$H NMR (300 MHz, $CD_3OD$, TMS): δ 1.44-1.47 (m, 2H, $CH_2$), 1.56-1.59 (m, 2H, $CH_2$), 7.48 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.8 Hz, 2H, Ar), 7.91 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.8 Hz, 2H, Ar). $^{13}$C NMR (75 MHz, $CD_3OD$, TMS): δ 16.3, 33.5, 129.8, 131.3, 136.8, 140.2, 174.7, 195.5.

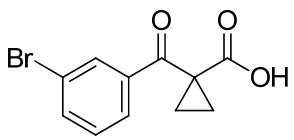



**1-(4-Fluorobenzoyl)cyclopropanecarboxylic acid 1e**:

This is a known compound.[6] A white solid, $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.55-1.58 (m, 2H, $CH_2$), 1.66-1.69 (m, 2H, $CH_2$), 7.10-7.14 (m, 2H, Ar), 7.92-7.95 (m, 2H, Ar), 10.80 (br, 1H, OH). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 16.9, 32.3, 115.7 (d, $J_{CF}$ = 22.0 Hz), 131.2 (d, $J_{CF}$ = 9.2 Hz), 132.7 (d, $J_{CF}$ = 2.8 Hz), 165.7 (d, $J_{CF}$ = 253.4 Hz), 178.1, 192.5. $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -108.7.

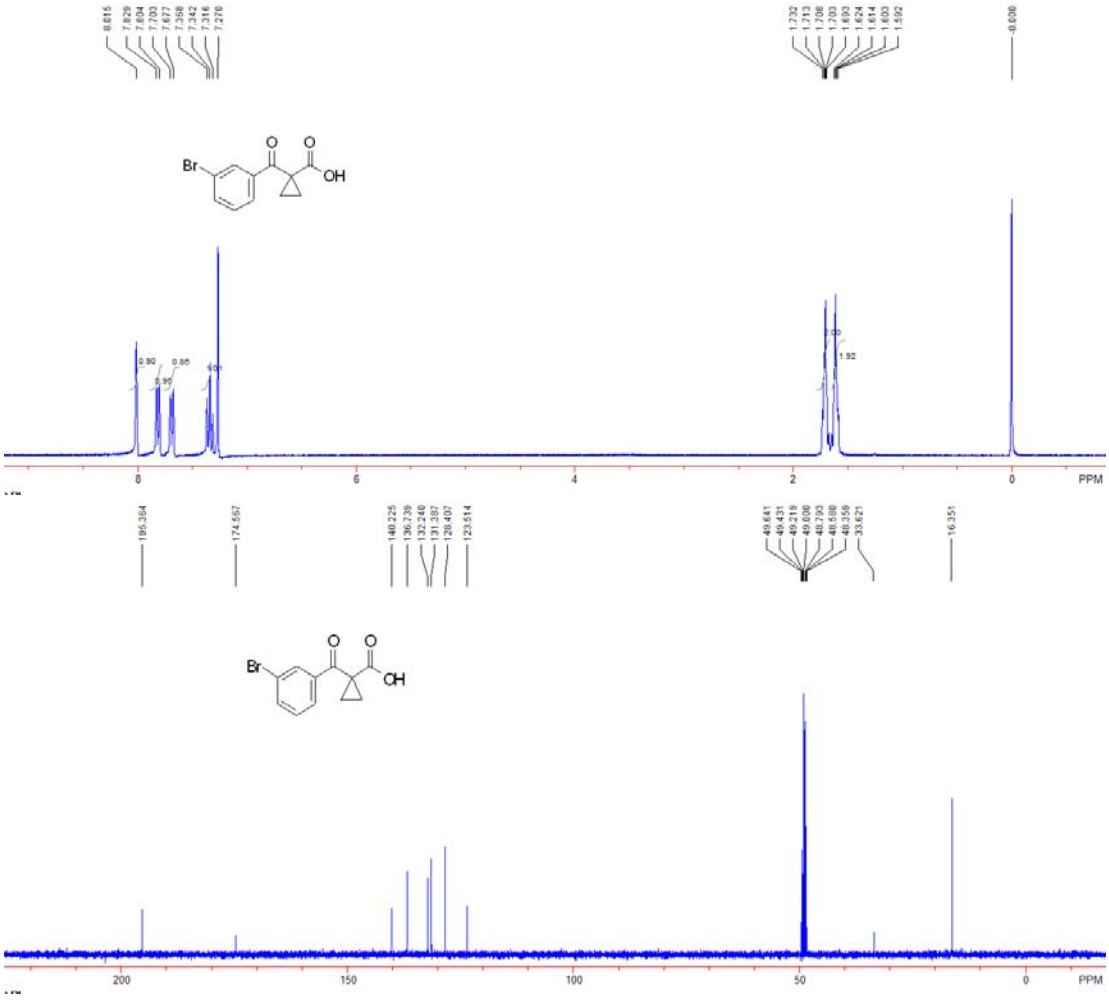


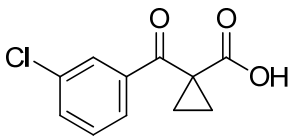




**1-(3-Bromobenzoyl)cyclopropanecarboxylic acid 1f**:

A white solid, Mp: 179-181 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.59-1.62 (m, 2H, $CH_2$), 1.69-1.73 (m, 2H, $CH_2$), 7.34 (dd, $J_1$ = 7.8 Hz, $J_2$ = 7.8 Hz, 1H, Ar), 7.69 (d, $J$ = 7.8 Hz, 1H, Ar),

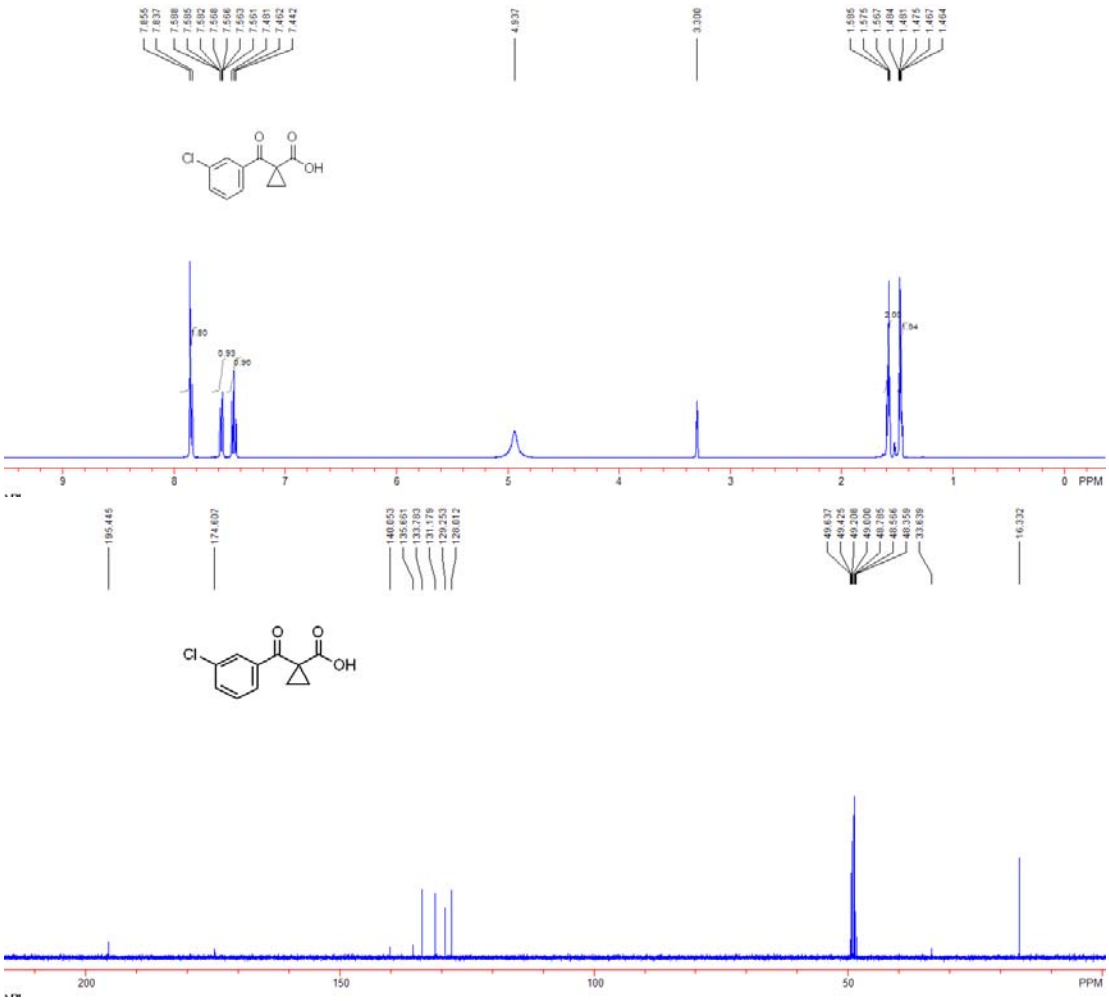
7.82 (d, *J* = 7.5 Hz, 1H, Ar), 8.02 (s, 1H, Ar). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 16.4, 33.6, 123.5, 128.4, 131.4, 132.2, 136.8, 140.2, 174.6, 195.4. IR (Neat) ν 3087, 3068, 2926, 2894, 2839, 1675, 1565, 1423, 1320, 1313, 1213, 1190, 1172, 922, 687 cm$^{-1}$. MS (ESI) m/e 293.0 ($M^+$+Na). HRMS (ESI) calcd. for $C_{11}H_8O_3Br$: 266.96623, Found: 266.96620.

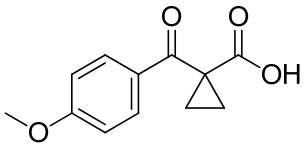



**1-(3-Chlorobenzoyl)cyclopropanecarboxylic acid 1g**:

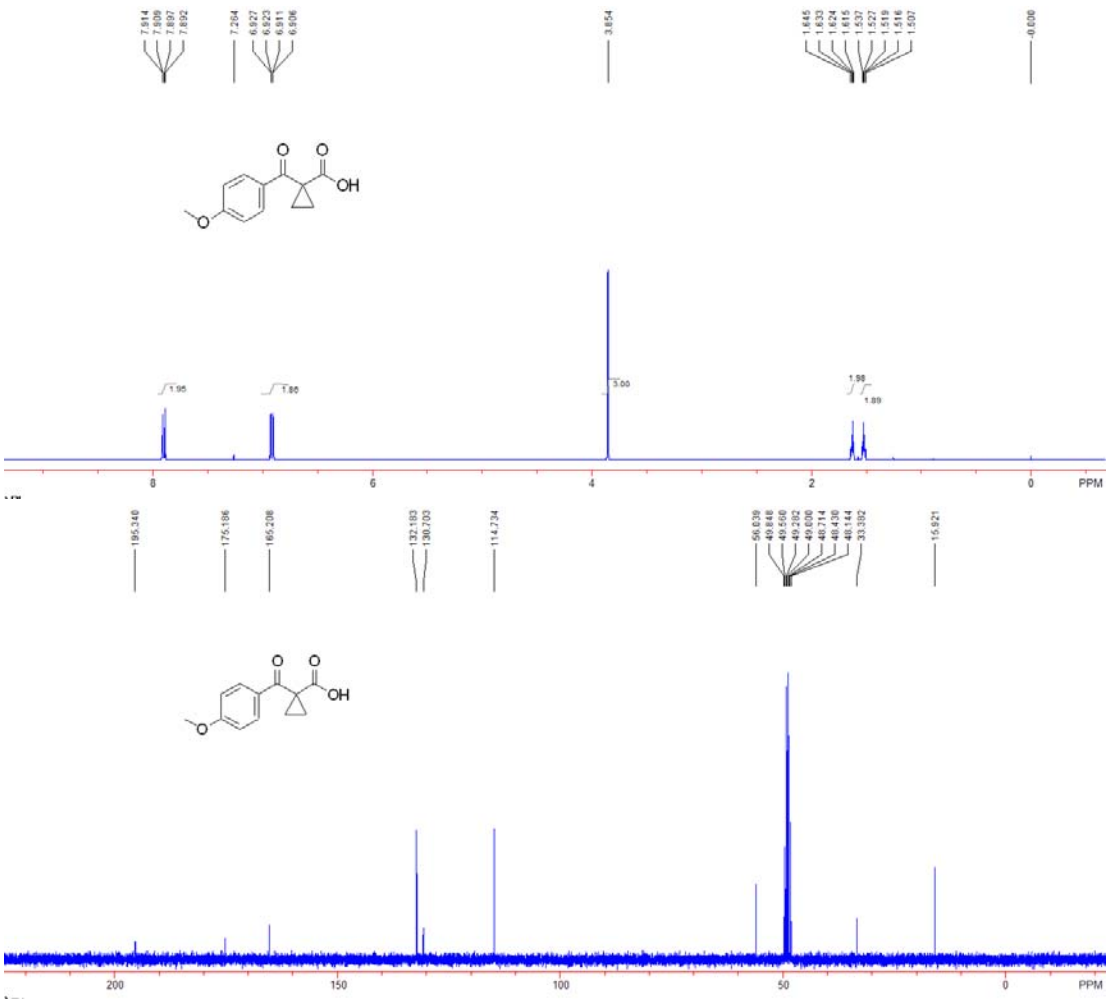
A white solid, Mp: 129-131 $^{o}$C. $^{1}$H NMR (400 MHz, $CD_3OD$, TMS): δ 1.46-1.48 (m, 2H, $CH_2$), 1.57-1.59 (m, 2H, $CH_2$), 4.94 (br, 1H, OH), 7.46 (dd, $J_1$ = 8.0 Hz, $J_2$ = 7.6 Hz, 1H, Ar), 7.56-7.59 (m, 1H, Ar), 7.84-7.86 (m, 2H, Ar). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 16.3, 33.6, 128.0, 129.3, 131.2, 133.8, 135.7, 140.1, 174.6, 195.4. IR (Neat) ν 3070, 2919, 2850, 2590, 1675, 1570, 1464, 1426, 1322, 1215, 1175, 1076, 1026, 921, 700 cm$^{-1}$. Anal. Calcd. for $C_{11}H_9ClO_3$: C, 58.81%; H, 4.04%. Found: C, 58.60%; H, 4.06%.

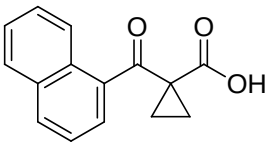




**1-(4-Methoxybenzoyl)cyclopropanecarboxylic acid 1h**:

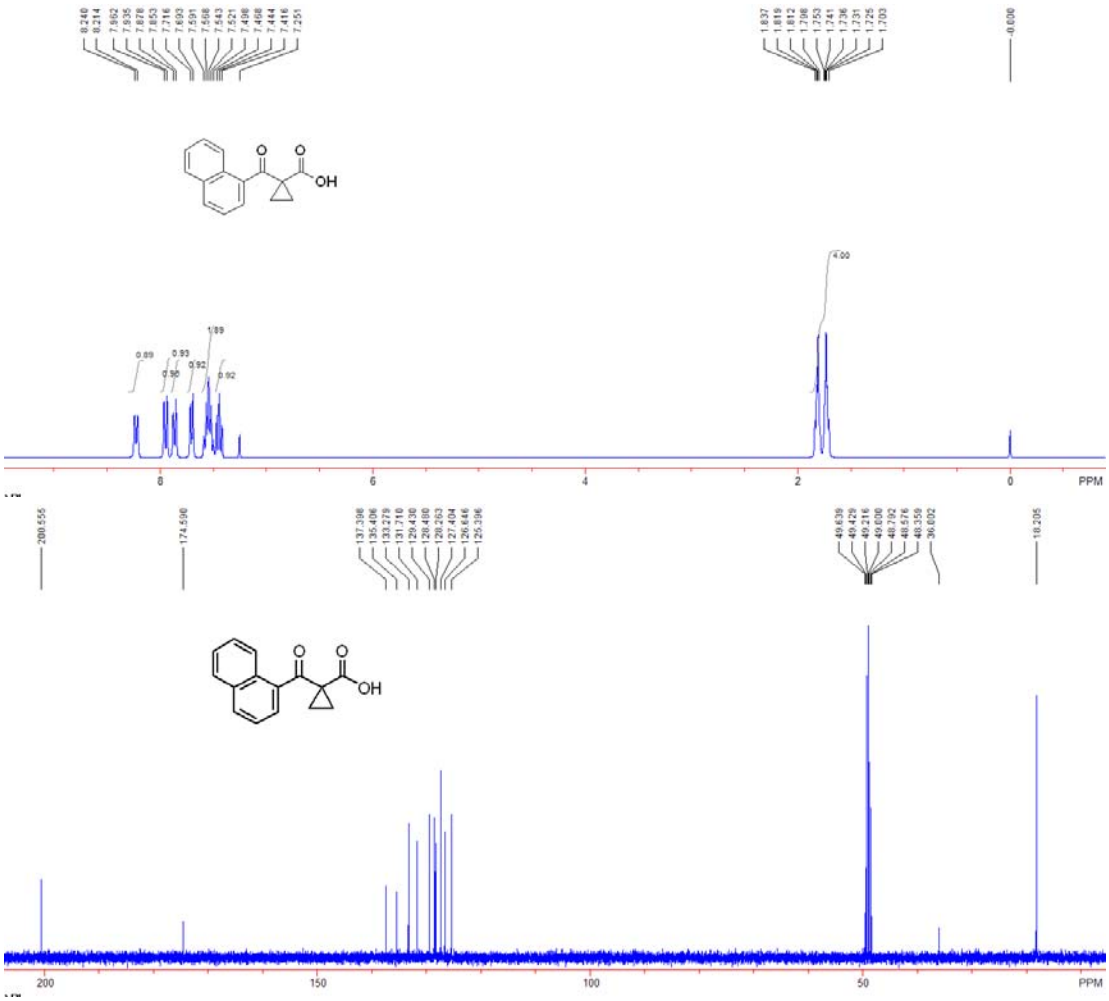
A white solid, Mp: 141-142 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.51-1.54 (m, 2H, $CH_2$), 1.62-1.65 (m, 2H, $CH_2$), 3.85 (s, 3H, $CH_3$), 6.91 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 2H, Ar), 7.90 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 2H, Ar). $^{13}$C NMR (75 MHz, $CD_3OD$, TMS): δ 15.9, 33.4, 56.0, 114.7, 130.7, 132.2, 165.2, 175.2, 195.3. IR (Neat) ν 2962, 2928, 2855, 1730, 1672, 1600, 1328, 1262, 1164, 1015, 842, 611 cm$^{-1}$. Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45%; H, 5.49%. Found: C, 65.54%; H, 5.52%.

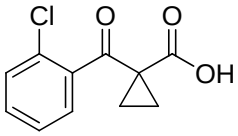



**1-(1-Naphthoyl)cyclopropanecarboxylic acid 1i**:

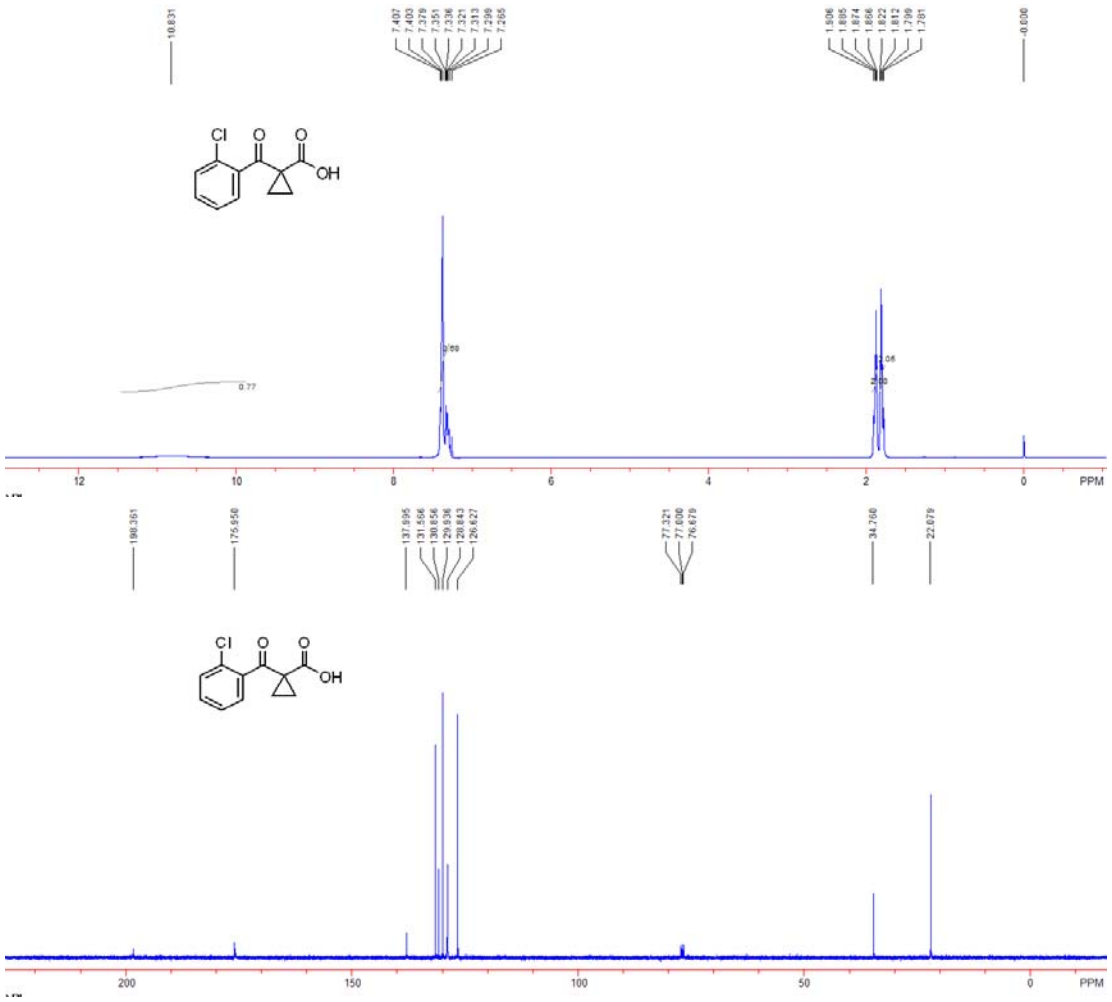
A white solid, Mp: 155-157 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.70-1.75 (m, 2H, $CH_2$), 1.80-1.84 (m, 2H, $CH_2$), 7.44 (dd, $J_1$ = 8.4 Hz, $J_2$ = 7.2 Hz, 1H, Ar), 7.50-7.59 (m, 2H, Ar), 7.70 (d, $J_1$ = 6.9 Hz, 1H, Ar), 7.87 (d, $J$ = 7.2 Hz, 1H, Ar), 7.95 (d, $J$ = 8.4 Hz, 1H, Ar), 8.23 (d, $J$ = 8.4 Hz, 1H, Ar). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 18.2, 36.0, 125.4, 126.6, 127.4, 128.3, 128.5, 129.4, 131.7, 133.3, 135.4, 137.4, 174.6, 200.6. IR (Neat) ν 3048, 2606, 1698, 1507, 1428, 1308, 1263, 1225, 1202, 866, 772 cm$^{-1}$. MS (ESI) m/e 239.1 ($M^{+}$-1). HRMS (ESI) calcd. for $C_{15}H_{11}O_3$: 239.07137, Found: 239.07112.

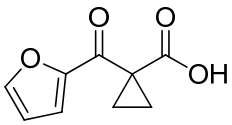



**1-(2-Chlorobenzoyl)cyclopropanecarboxylic acid 1j**:

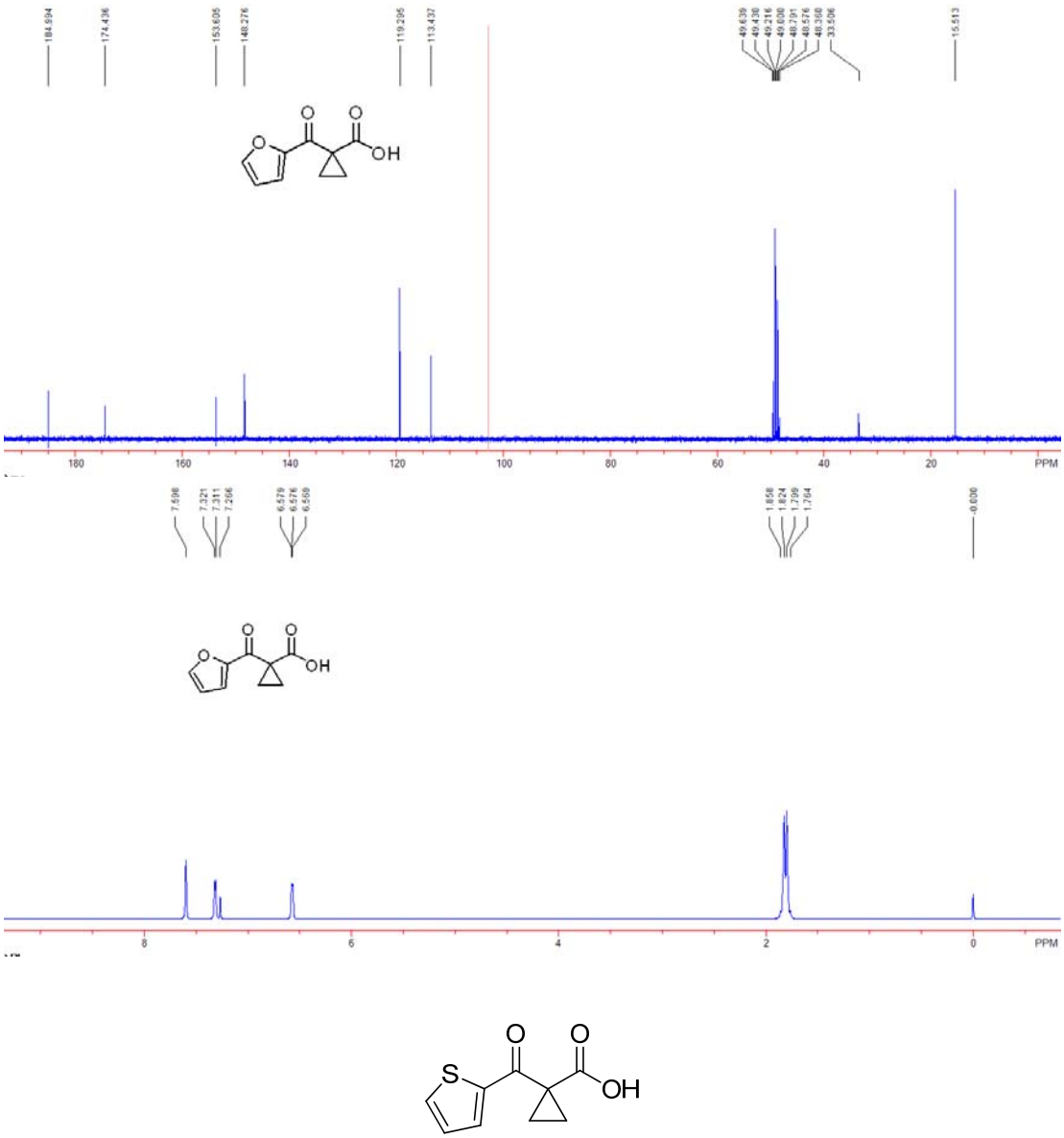
A white solid, Mp: 121-123 $^{o}$C $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.78-1.82 (m, 2H, $CH_2$), 1.87-1.91 (m, 2H, $CH_2$), 7.27-7.41 (m, 4H, Ar), 10.83 (br, 1H, OH). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 22.1, 34.8, 126.6, 128.8, 129.9, 130.9, 131.6, 138.0, 176.0, 198.4. IR (Neat) ν 3325, 3076, 3027, 2904, 2707, 1694, 1590, 1469, 1434, 1314, 1210, 1190, 1065, 1001, 772 cm$^{-1}$. Anal. Calcd. for $C_{11}H_9ClO_3$: C, 58.81%; H, 4.04%. Found: C, 58.57%; H, 4.26%.




**1-(Furan-2-carbonyl)cyclopropanecarboxylic acid 1k**:

A white solid, Mp: 103-105 $^{o}$C $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.76-1.80 (m, 2H, $CH_2$), 1.82-1.86 (m, 2H, $CH_2$), 6.57-6.58 (m, 1H, Ar), 7.32 (d, *J* = 3.0 Hz, 1H, Ar), 7.60 (s, 1H, Ar). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 15.5, 33.5, 113.4, 119.3, 148.3, 153.6, 174.4, 185.0. IR (Neat) ν 3130, 3021, 2903, 1667, 1583, 1562, 1308, 1201, 1039, 1010, 600 cm$^{-1}$. MS (ESI) m/e 179.0 ($M^{+}$-1). HRMS (ESI) calcd. for $C_9H_8O_4Na$: 203.03148, Found: 203.03086.

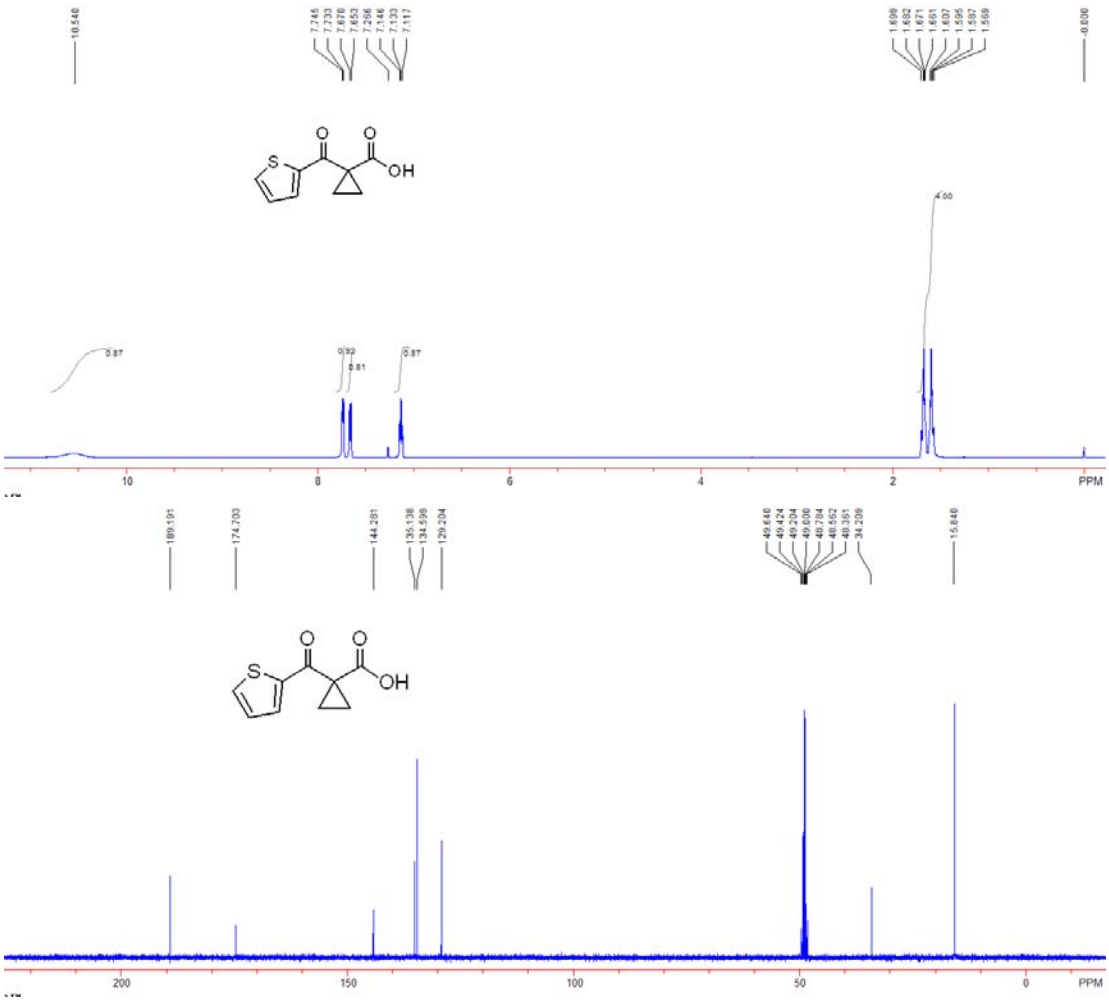


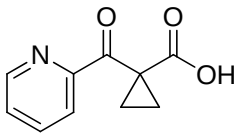




**1-(Thiophene-2-carbonyl)cyclopropanecarboxylic acid 1l**:

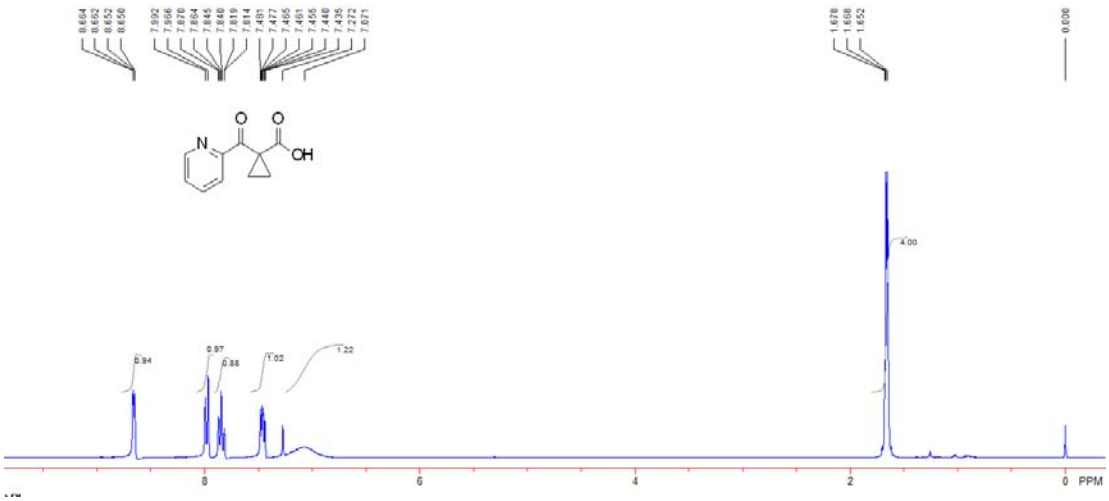
A white solid, Mp: 135-137 $^{o}$C $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.57-1.61 (m, 2H, $CH_2$), 1.66-1.70 (m, 2H, $CH_2$), 7.13 (dd, $J_1$ = 4.8 Hz, $J_2$ = 3.6 Hz, 1H, Ar), 7.66 (d, $J$ = 5.1 Hz, 1H, Ar), 7.74 (d, $J$ = 3.6 Hz, 1H, Ar), 10.54 (br, 1H, OH). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ 15.8, 34.2, 129.2, 134.6, 135.1, 144.3, 174.7, 189.2. IR (Neat) ν 3105, 1674, 1651, 11411, 1352, 1311, 1234, 1057, 738 $cm^{-1}$. MS (ESI) m/e 195.0 ($M^{+}$-1). HRMS (ESI) calcd. for $C_9H_7O_3S$: 195.01214, Found: 195.01175.

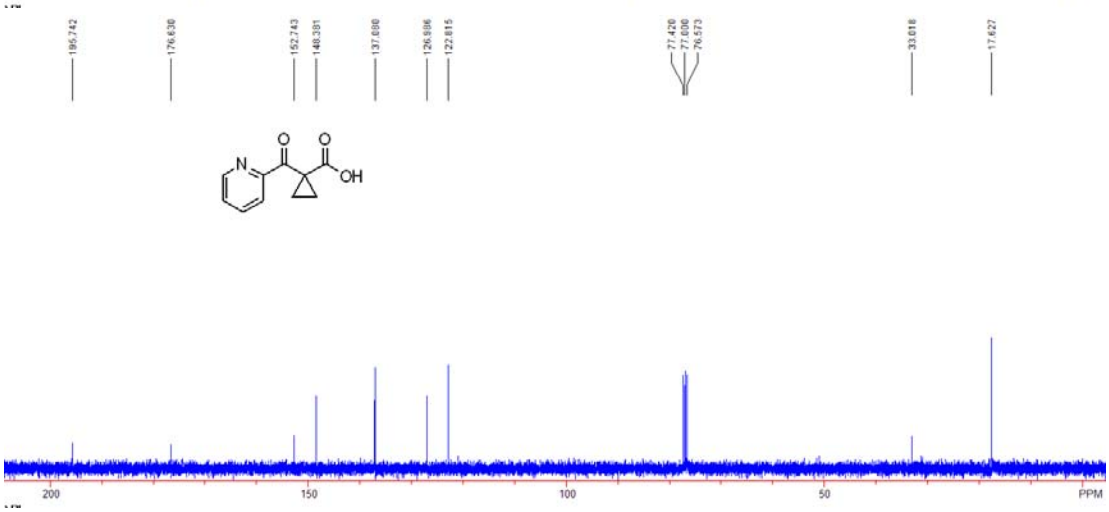


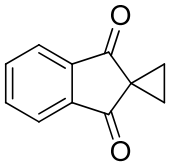




**1-Picolinoylcyclopropanecarboxylic acid 1m**:

A grey solid, Mp: 104-106 $^{o}$C $^{1}$H NMR (300 MHz, $CDCl_3$, TMS): δ 1.65-1.68 (m, 4H, $CH_2$), 7.07 (br, 1H, OH), 7.44-7.48 (m, 1H, Ar), 7.84 (ddd, $J_1$ = 6.0 Hz, $J_2$ = 4.8 Hz, $J_3$ = 1.5 Hz, 1H, Ar), 7.98 (d, $J$ = 7.8 Hz, 1H, Ar), 8.66 (dd, $J_1$ = 3.6 Hz, $J_2$ = 0.6 Hz, 1H, Ar). $^{13}$C NMR (75 MHz, $CDCl_3$, TMS): δ 17.6, 33.0, 122.8, 127.0, 137.1, 148.4, 152.7, 176.6, 195.7. IR (Neat) ν 3058, 3015, 2925, 1690, 1585, 1570, 1420, 1438, 1331, 1222, 1177, 1015, 809, 749 cm$^{-1}$. MS (%) m/e 146 ($M^{+}$-45, 19.92), 132 (4.38), 119 (23.43), 118 (100.00), 106 (6.91), 93 (9.67), 78 (51.19), 69 (15.72), 51 (20.19) 41 (19.53). HRMS (EI) calcd. for $C_{10}H_9NO_3$: 191.0582, Found: 191.0584.

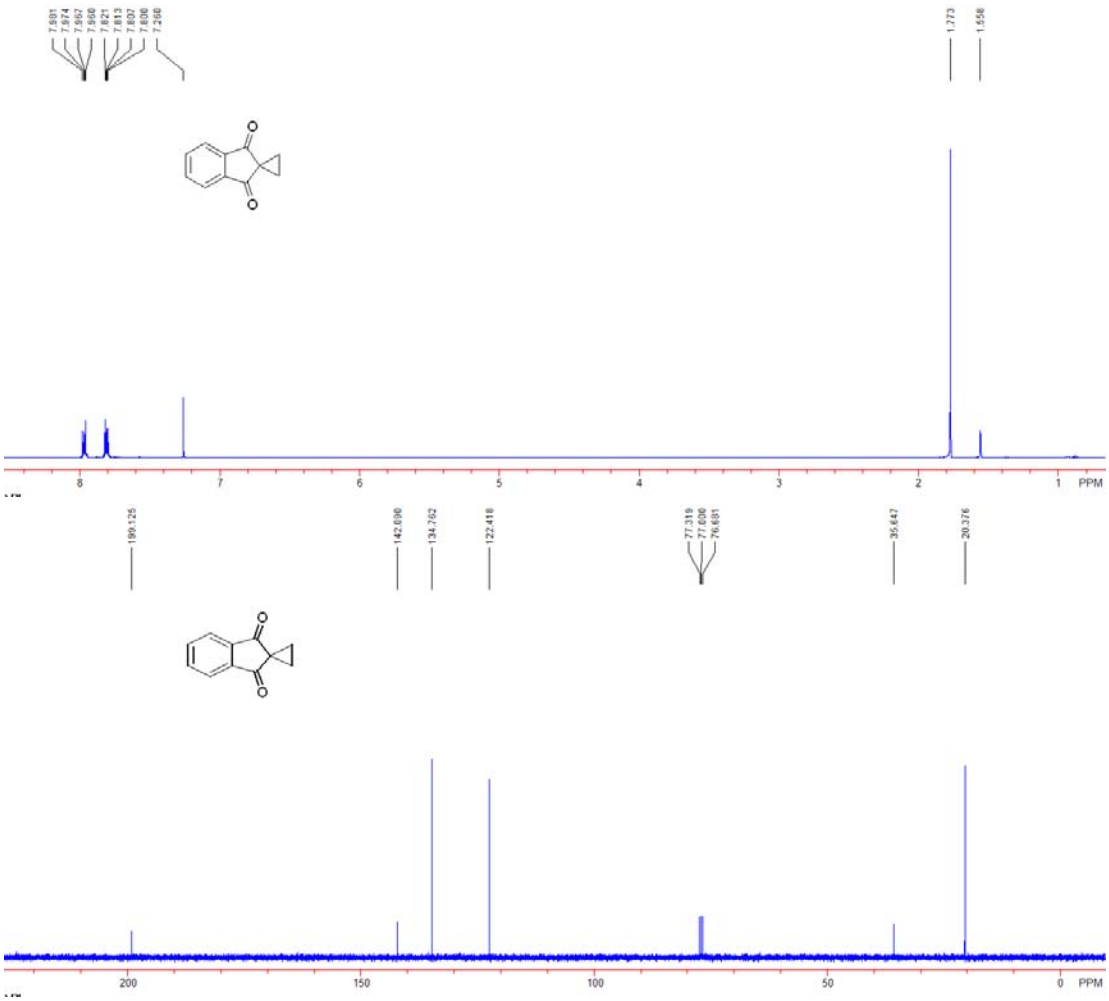


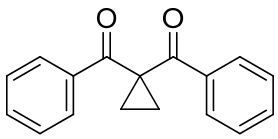




**Spiro[cyclopropane-1,2'-indene]-1',3'-dione 7**:

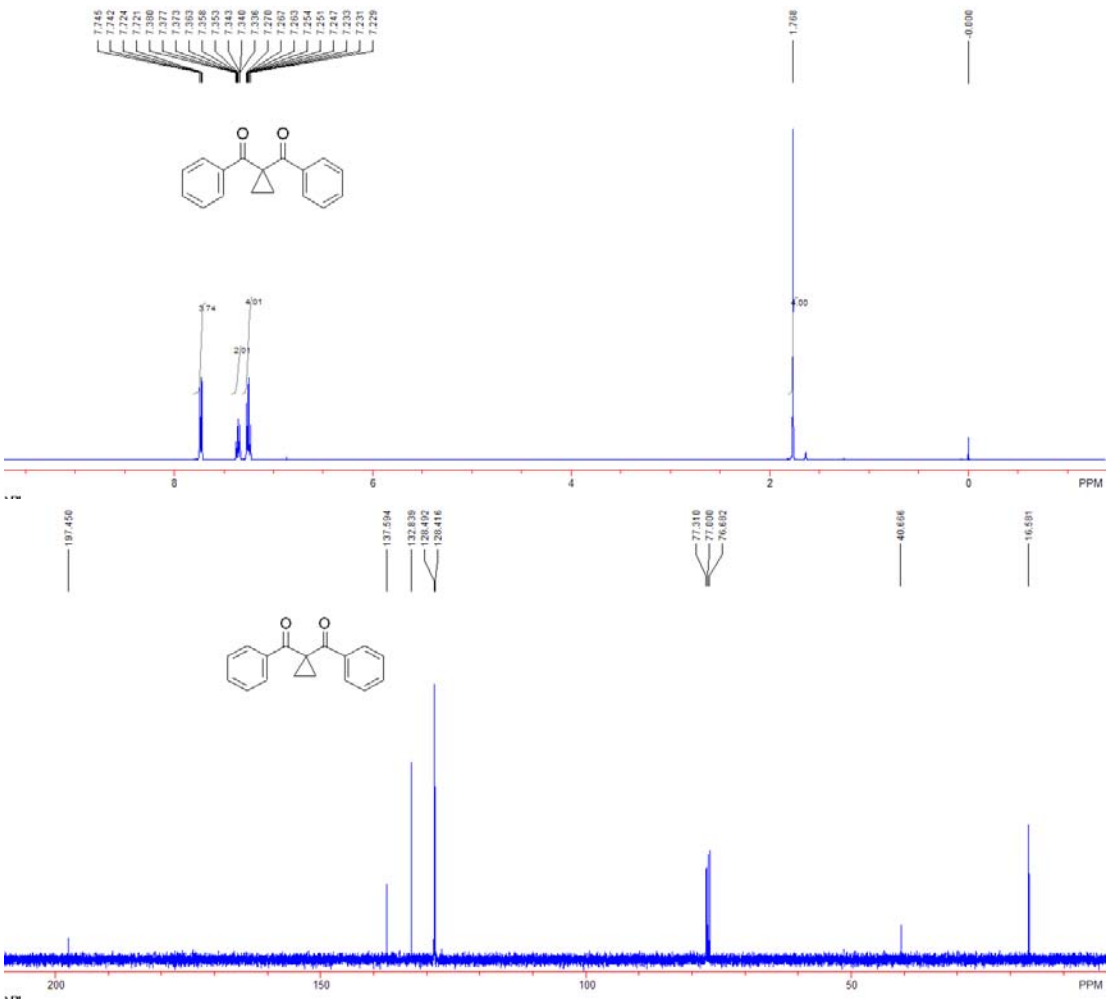
This is a known compound.[8] A white solid, $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.77 (s, 4H, $CH_2$), 7.81 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.8 Hz, 2H, Ar), 7.97 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.8 Hz, 2H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 20.4, 35.6, 122.4, 134.8, 142.1, 199.1.

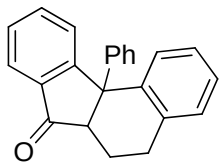




**Cyclopropane-1,1-diylbis(phenylmethanone) 8**:

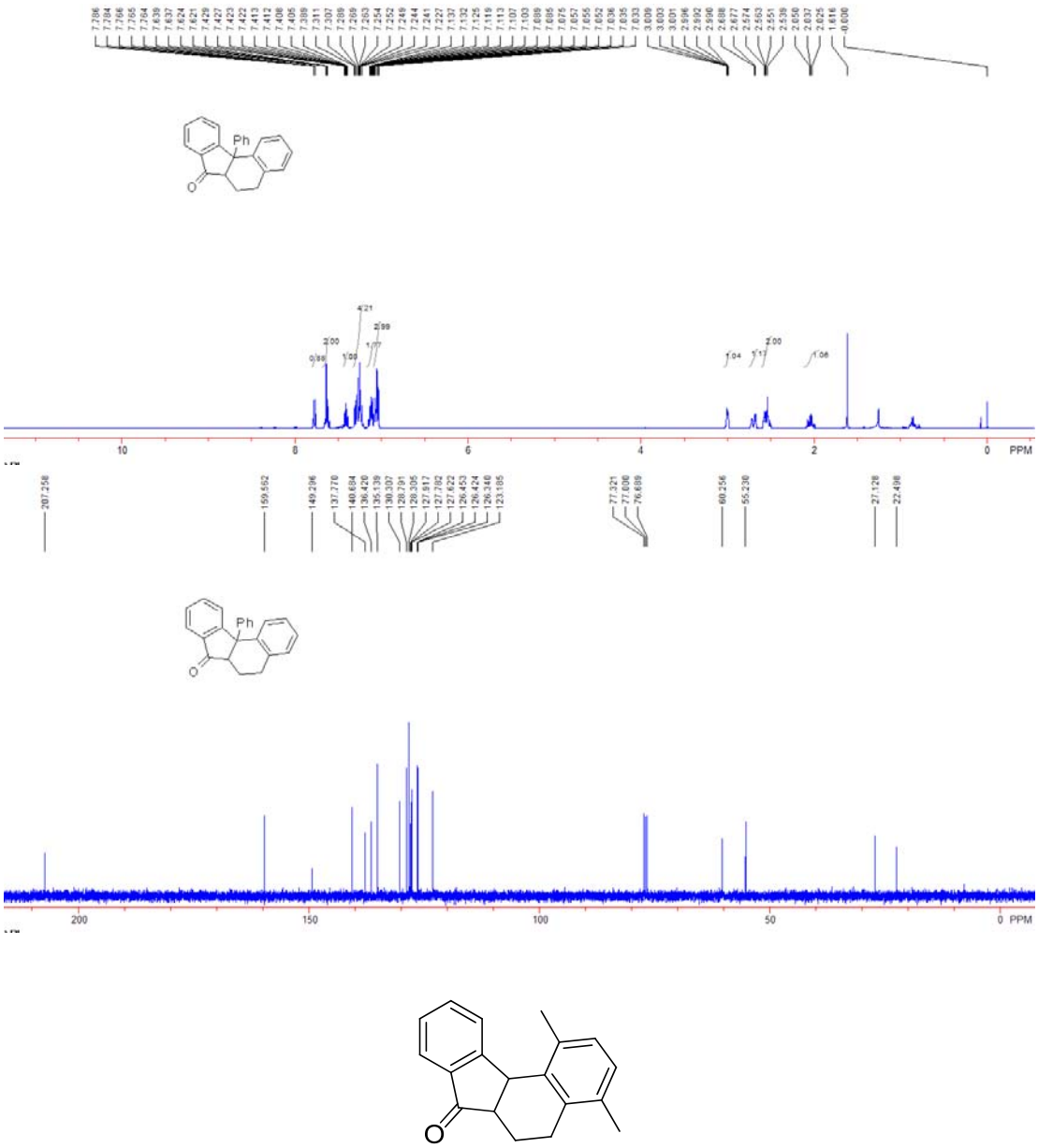
This is a known compound.[7] A white solid, $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.77 (s, 4H, $CH_2$), 7.25 (ddt, $J_1$ = 8.0 Hz, $J_2$ = 7.2 Hz, $J_3$ = 1.2 Hz , 4H, Ar), 7.34-7.38 (ddt, $J_1$ = 7.2 Hz, $J_2$ = 7.2 Hz, $J_3$ = 1.2 Hz, 2H, Ar), 7.74 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 4H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 16.6, 40.7, 128.42, 128.49, 132.8, 137.6, 197.5.






**1*b*-Phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 2a**:

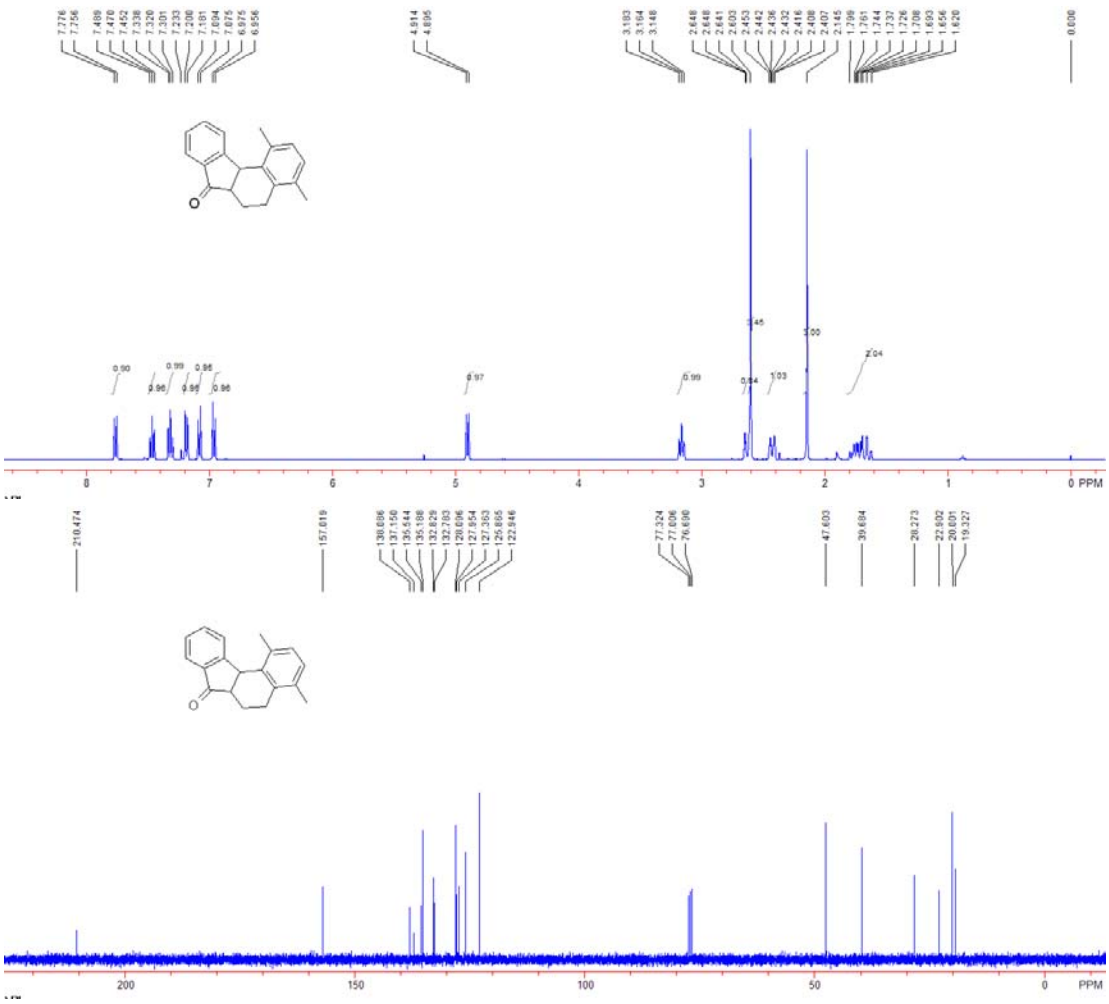
78 mg, yield: 84%; A white solid, Mp: 140-143 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 2.03-2.05 (m, 1H, $CH_2$), 2.54-2.57 (m, 2H, $CH_2$), 2.68-2.69 (m, 1H, $CH_2$), 2.99-3.01 (m, 1H, CH), 7.03-7.14 (m, 5H, Ar), 7.23-7.31 (m, 4H, Ar), 7.39-7.43 (m, 1H, Ar), 7.62-7.77 (m, 2H, Ar), 7.78 (d, *J* = 8.0 Hz, 1H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 22.5, 27.1, 55.2, 60.3, 123.2, 126.3, 126.4, 126.5, 127.6, 127.7, 127.9, 128.3, 128.7, 130.3, 135.1, 136.4, 137.8, 140.7, 149.3, 159.5, 207.3. IR (Neat) ν 2934, 2861, 1701, 1599, 1583, 1482, 1458, 1379, 1280, 1264, 1253, 1237, 972, 830, 769 $cm^{-1}$. MS (%) m/e 310 ($M^+$, 100.00), 295 (14.87), 292 (16.67), 291 (10.87), 233 (8.22), 215 (11.28), 165 (4.38), 126 (5.70), 101 (5.78). HRMS (EI) calcd. for $C_{23}H_{18}O$: 310.1358, Found: 310.1362.

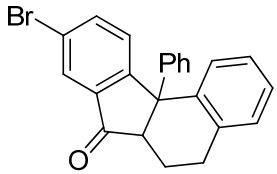





**1,4-Dimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 4a**:

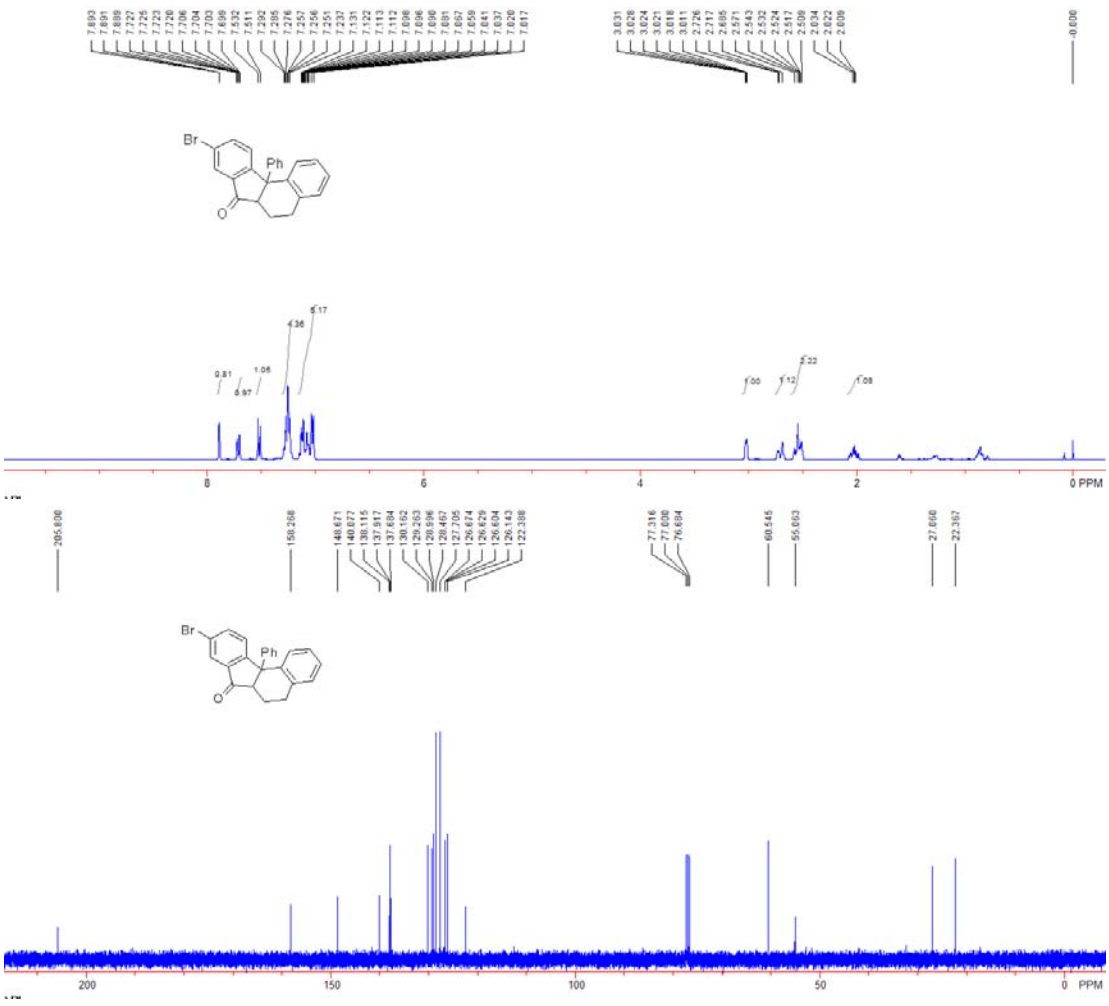
63 mg yield: 80%; A white solid, Mp: 153-155 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS): δ 1.62-1.80 (m, 2H, $CH_2$), 2.15 (s, 3H, $CH_3$), 2.41-2.45 (m, 1H, $CH_2$), 2.60 (s, 3H, $CH_3$), 2.64-2.65 (m, 1H, $CH_2$), 3.15-3.18 (m, 1H, CH), 4.91 (d, *J* = 7.6 Hz, 1H, CH), 6.97 (d, *J* = 7.6 Hz, 1H, Ar), 7.08 (d, *J* = 7.6 Hz, 1H, Ar), 7.19 (d, *J* = 7.6 Hz, 1H, Ar), 7.32 (dd, $J_1$ = 7.6 Hz, $J_2$ = 7.2 Hz, 1H, Ar), 7.47 (dd, $J_1$ = 7.6 Hz, $J_2$ = 7.2 Hz, 1H, Ar), 7.77 (d, *J* = 7.6 Hz, 1H, Ar); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 19.3, 20.0, 22.9, 28.3, 39.7, 47.6, 122.9, 125.9, 127.4, 128.0, 128.1, 132.78, 132.83, 135.2, 135.5, 137.2, 138.1, 157.0, 210.5. IR (Neat) ν 3059, 3023, 2925, 2851, 1713, 1652, 1599, 1490, 1462, 1268, 981, 749, 702, 681, 639 cm$^{-1}$. MS (%) m/e 262 ($M^+$, 100.00), 248 (17.13), 247 (83.25), 245 (13.02), 229 (38.28), 219 (14.71), 128 (12.99), 43 (42.75), 42 (43.75). HRMS (EI) calcd. for $C_{19}H_{18}O$: 262.1358, Found: 262.1356.

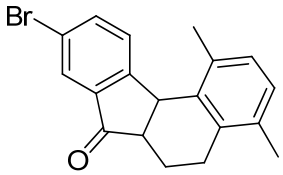





**9-bromo-11*b*-phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 2b**:

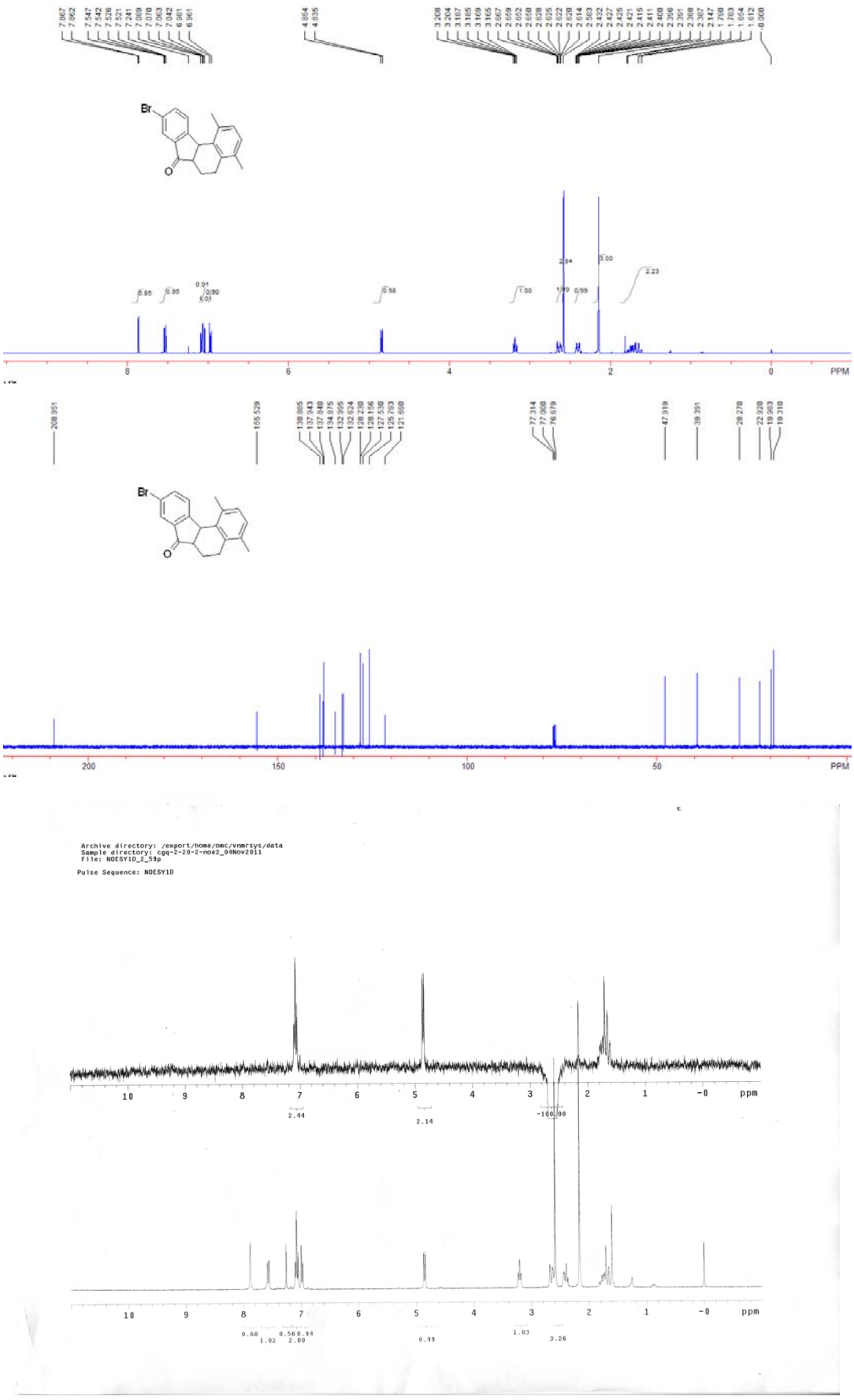
97 mg, yield: 83%; A white solid, Mp: 150-153 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 2.01-2.03 (m, 1H, $CH_2$), 2.51-2.57 (m, 2H, $CH_2$), 2.69-2.73 (m, 1H, $CH_2$), 3.01-3.03 (m, 1H, CH), 7.02-7.13 (m, 5H, Ar), 7.26-7.29 (m, 4H, Ar), 7.52 (d, *J* = 8.4 Hz, 1H, Ar), 7.72-7.73 (m, 1H, Ar), 7.89 (s, 1H, Ar); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 22.4, 27.1, 55.1, 60.5, 122.4, 126.1, 126.60, 126.63, 126.7, 127.7, 128.5, 129.0, 129.3, 130.2, 137.7, 137.9, 138.1, 140.1, 148.7, 158.3, 205.8. IR (Neat) ν 3059, 3023, 2932, 2359, 1716, 1684, 1506, 1459, 1445, 1216, 770 $cm^{-1}$. MS (%) m/e 388 ($M^+$, 100.00), 390 ($M^+$, 97.98), 373 (12.09), 311 (13.24), 297 (12.48), 292 (10.30), 291 (24.42), 232 (34.14), 218 (9.98), 202 (37.95). HRMS (EI) calcd. for $C_{23}H_{17}OBr$: 388.0463, Found: 388.0464.



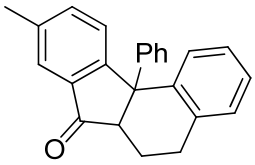




**9-Fluoro-1,4-dimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 4b**:

70 mg yield: 68%; A white solid, Mp: 155-158 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.61-1.79 (m, 2H, $CH_2$), 2.15 (s, 3H, $CH_3$), 2.40-2.44 (m, 1H, $CH_2$), 2.62 (s, 3H, $CH_3$), 2.63-2.67 (m, 1H, $CH_2$), 3.18-3.22 (m, 1H, CH), 4.87 (d, *J* = 7.6 Hz, 1H, CH), 6.97 (d, *J* = 7.6 Hz, 1H, Ar), 7.07 (d, *J* = 7.6 Hz, 1H, Ar), 7.12 (d, *J* = 8.4 Hz, 1H, Ar), 7.53 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H, Ar), 7.86 (d, *J* = 2.0 Hz, 1H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 19.3, 20.0, 22.9, 28.3, 39.4, 47.9, 121.7, 125.8, 127.5, 128.16, 128.23, 132.6, 133.0, 134.9, 137.8, 137.9, 138.9, 155.5, 209.0. IR (Neat) ν 2925, 2854, 1713, 1462, 1413, 1232, 1203, 1111, 819 cm$^{-1}$. MS (%) m/e 340 ($M^+$, 100.00), 342 ($M^+$, 97.98), 327 (72.20), 325 (74.34), 307 (16.72), 246 (26.85), 215 (11.80), 143 (20.25), 115 (29.75), 101 (32.62). HRMS (EI) calcd. for $C_{19}H_{17}OBr$: 340.0463, Found: 340.0460.

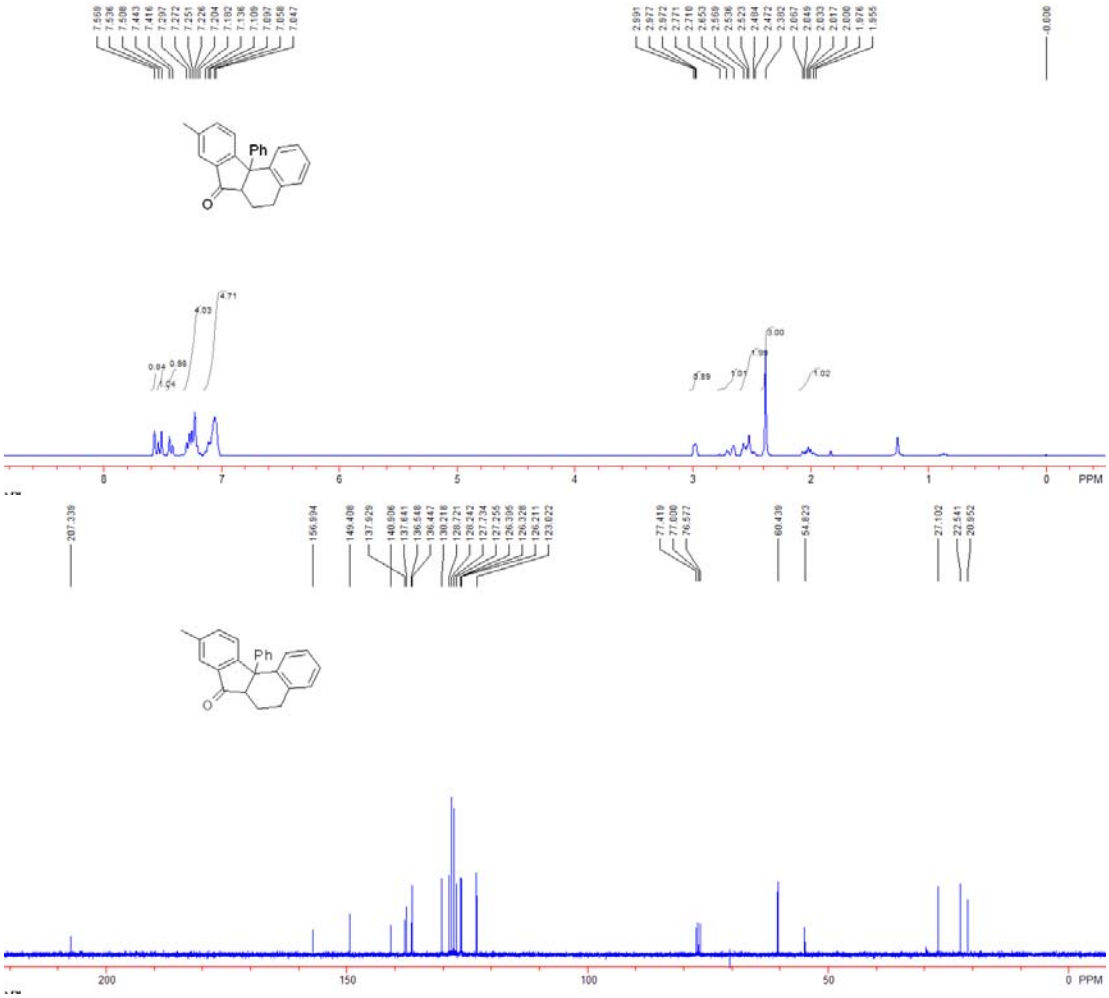


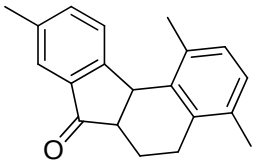

NOE spectroscopy of **4b**




**9-Methyl-11*b*-phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 2c**:

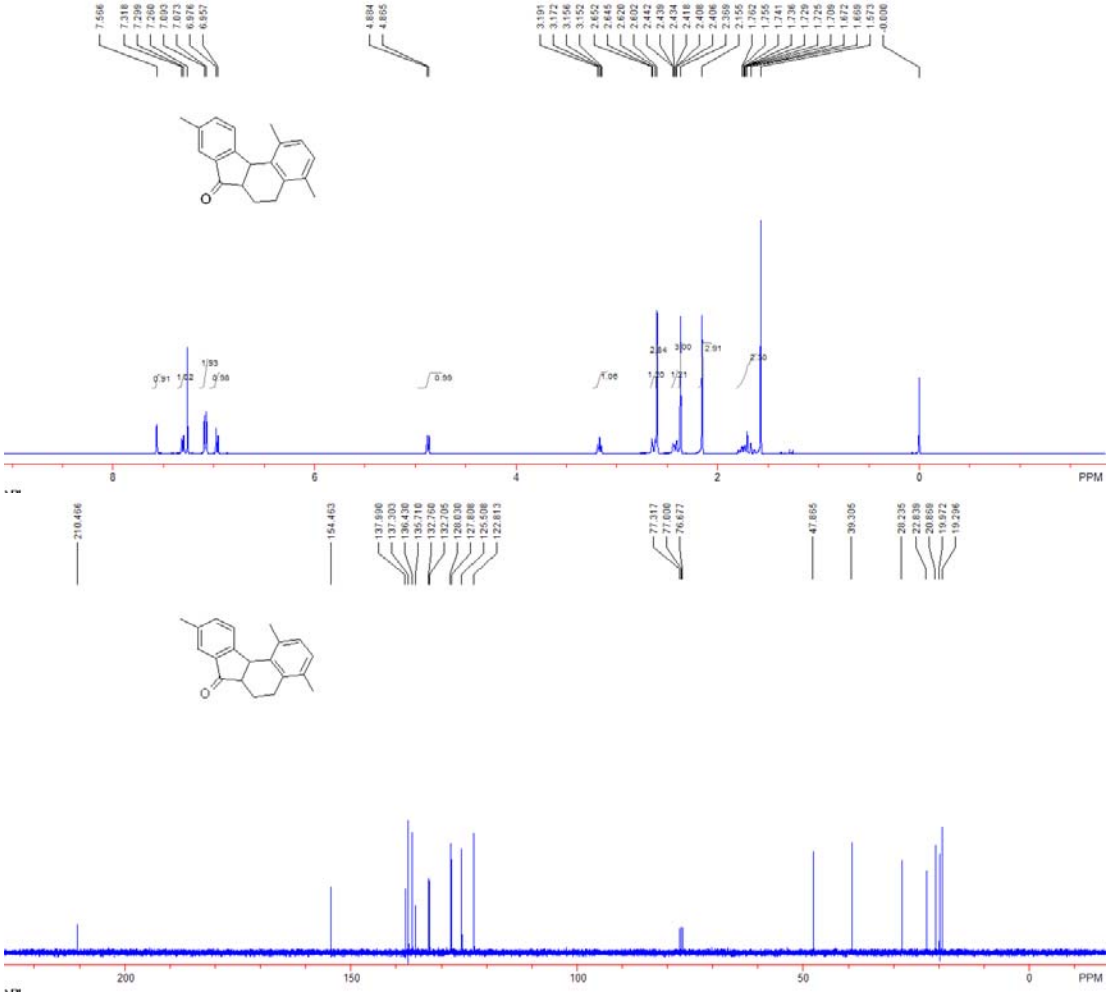
70 mg, yield: 72%; A white solid, Mp: 151-153 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS) δ 1.96-2.07 (m, 1H, $CH_2$), 2.38 (s, 3H, $CH_3$), 2.47-2.57 (m, 2H, $CH_2$), 2.65-2.77 (m, 1H, $CH_2$), 2.97-2.99 (m, 1H, CH), 7.05-7.14 (m, 5H, Ar), 7.18-7.30 (m, 4H, Ar), 7.43 (d, *J* = 8.1 Hz, 1H, Ar), 7.52 (d, *J* = 8.1 Hz, 1H, Ar), 7.57 (s, 1H, Ar); $^{13}$C NMR (75 MHz, $CDCl_3$, TMS) δ 21.0, 22.5, 27.1, 54.8, 60.4, 123.0, 126.2, 126.3, 126.4, 127.3, 127.7, 128.2, 128.7, 130.2, 136.4, 136.5, 137.6, 137.9, 140.9, 149.4, 157.0, 207.3. IR (Neat) ν 3058, 3023, 2851, 1713, 1615, 1488, 1444, 1285, 1269, 1237, 1154, 1117, 759, 738, 700 cm$^{-1}$. MS (%) m/e 324 ($M^+$, 100.00), 309 (16.24), 306 (11.26), 291 (8.43), 247 (10.61), 233 (11.10), 132 (4.32), 126 (4.77), 115 (4.21). HRMS (EI) calcd. for $C_{24}H_{20}O$: 324.1514, Found: 324.1510.

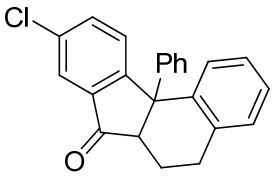




**1,4,9-Trimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 4c**:

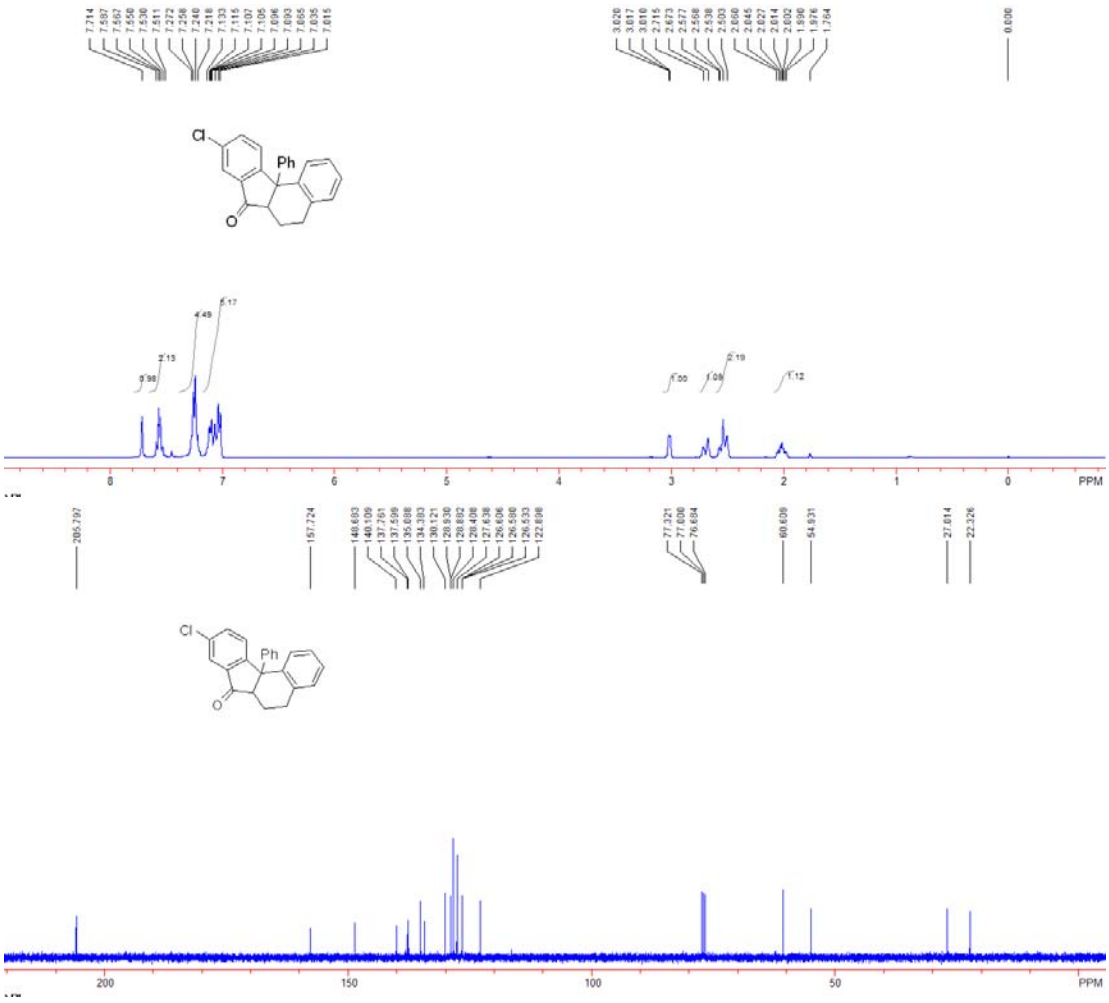
78 mg, yield: 94%; A white solid, Mp: 148-150 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.67-1.76 (m, 2H, $CH_2$), 2.16 (s, 3H, $CH_3$), 2.37 (s, 3H, $CH_3$), 2.41-2.44 (m, 1H, CH), 2.62 (s, 3H, $CH_3$), 2.645-2.65 (m, 1H, CH), 3.15-3.19 (m, 1H, CH), 4.87 (d, *J* = 7.6 Hz, 1H, CH), 6.97 (d, *J* = 7.6 Hz, 1H, Ar), 7.08 (d, *J* = 7.6 Hz, 2H, Ar), 7.31 (d, *J* = 7.6 Hz, 1H, Ar), 7.57 (s, 1H, Ar); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 19.3, 19.9, 20.9, 22.8, 28.2, 39.3, 47.9, 122.8, 125.5, 127.8, 128.0, 132.7, 132.8, 135.7, 136.4, 137.3, 138.0, 154.5, 210.5. IR (Neat) ν 3000, 2925, 2861, 1708, 1613, 1487, 1456, 1436, 1280, 1245, 1182, 1153, 1110, 1032, 826 cm$^{-1}$. MS (%) m/e 276 ($M^+$, 100.00), 262 (15.42), 261 (75.22), 259 (11.64), 258 (12.35), 233 (10.32), 128 (14.14), 115 (20.76), 108 (12.25). HRMS (EI) calcd. for $C_{20}H_{20}O$: 276.1514, Found: 276.1512.

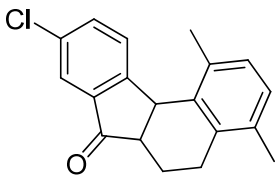





**9-Chloro-11*b*-phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 2d**:

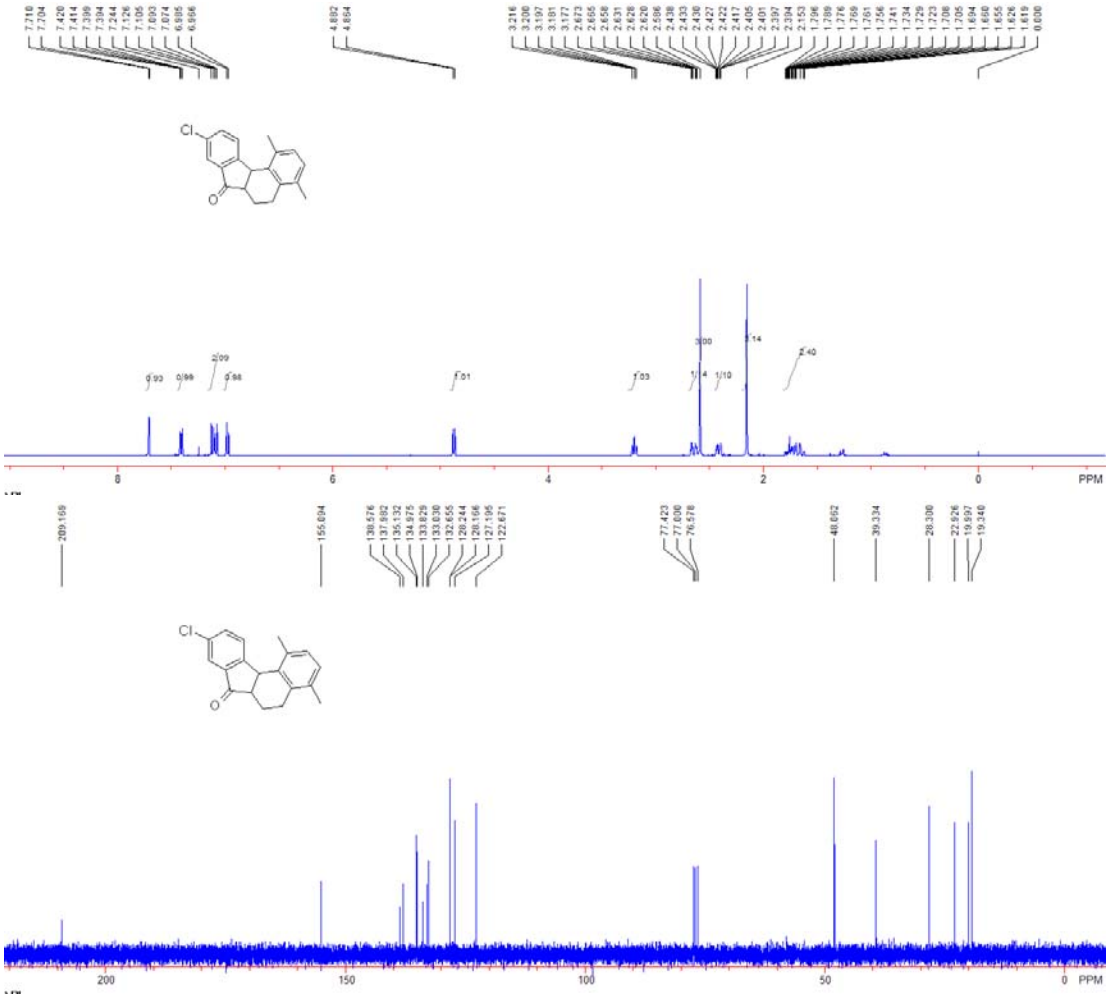
95 mg, yield: 92%; A white solid, Mp: 137-139 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.98-2.06 (m, 1H, $CH_2$), 2.50-2.58 (m, 2H, $CH_2$), 2.67-2.72 (m, 1H, $CH_2$), 3.01-3.02 (m, 1H, CH), 7.02-7.13 (m, 5H, Ar), 7.22-7.27 (m, 4H, Ar), 7.51-7.59 (m, 2H, Ar), 7.71 (s, 1H, Ar); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 22.3, 27.0, 54.9, 60.6, 122.9, 126.5, 126.58, 126.61, 127.6, 128.4, 128.88, 128.93, 130.1, 134.4, 135.1, 137.6, 137.8, 140.1, 148.7, 157.7, 205.8. IR (Neat) ν 2924, 2851, 1713, 1686, 1676, 1460, 1297, 1167, 1026, 748, 702 cm$^{-1}$. MS (%) m/e 344 ($M^+$, 100.00), 345 ($M^+$, 26.76), 329 (13.76), 309 (7.02), 291 (19.88), 267 (13.61), 253 (14.77), 202 (12.52), 126 (8.09), 101 (10.32). HRMS (EI) calcd. for $C_{23}H_{17}OCl$: 344.0968, Found: 344.0973.

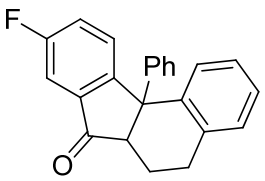





**9-Chloro-1,4-dimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 4d**:

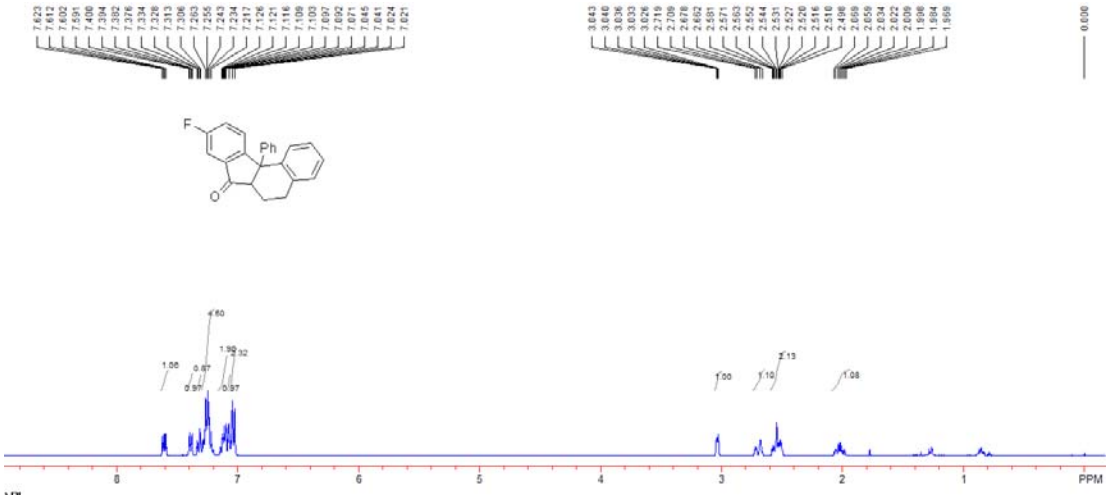
61 mg yield: 69%; A white solid, Mp: 149-151 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.62-1.80 (m, 2H, $CH_2$), 2.15 (s, 3H, $CH_3$), 2.40-2.44 (m, 1H, $CH_2$), 2.59 (s, 3H, $CH_3$), 2.62-2.67 (m, 1H, $CH_2$), 3.18-3.22 (m, 1H, CH), 4.87 (d, *J* = 7.6 Hz, 1H, CH), 6.98 (d, *J* = 7.6 Hz, 1H, Ar), 7.08 (d, *J* = 7.6 Hz, 1H, Ar), 7.11 (d, *J* = 8.4 Hz, 1H, Ar), 7.41 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.4 Hz, 1H, Ar), 7.71 (d, *J* = 2.4 Hz, 1H, Ar); $^{13}$C NMR (75 MHz, $CDCl_3$, TMS) δ 19.3, 20.0, 22.9, 28.3, 39.3, 48.1, 122.7, 127.2, 128.17, 128.24, 132.7, 133.0, 133.8, 135.0, 135.1, 138.0, 138.6, 155.1, 209.2. IR (Neat) ν 2928, 2866, 1713, 1596, 1483, 1464, 1422, 1266, 1252, 1233, 826 cm$^{-1}$. MS (%) m/e 296 ($M^+$, 100.00), 297 ($M^+$, 24.81), 283 (28.23), 279 (8.67), 263 (18.62), 243 (13.31), 128 (16.15), 119 (10.67), 126 (8.09), 101 (21.32). HRMS (EI) calcd. for $C_{19}H_{17}OCl$: 296.0968, Found: 296.0967.

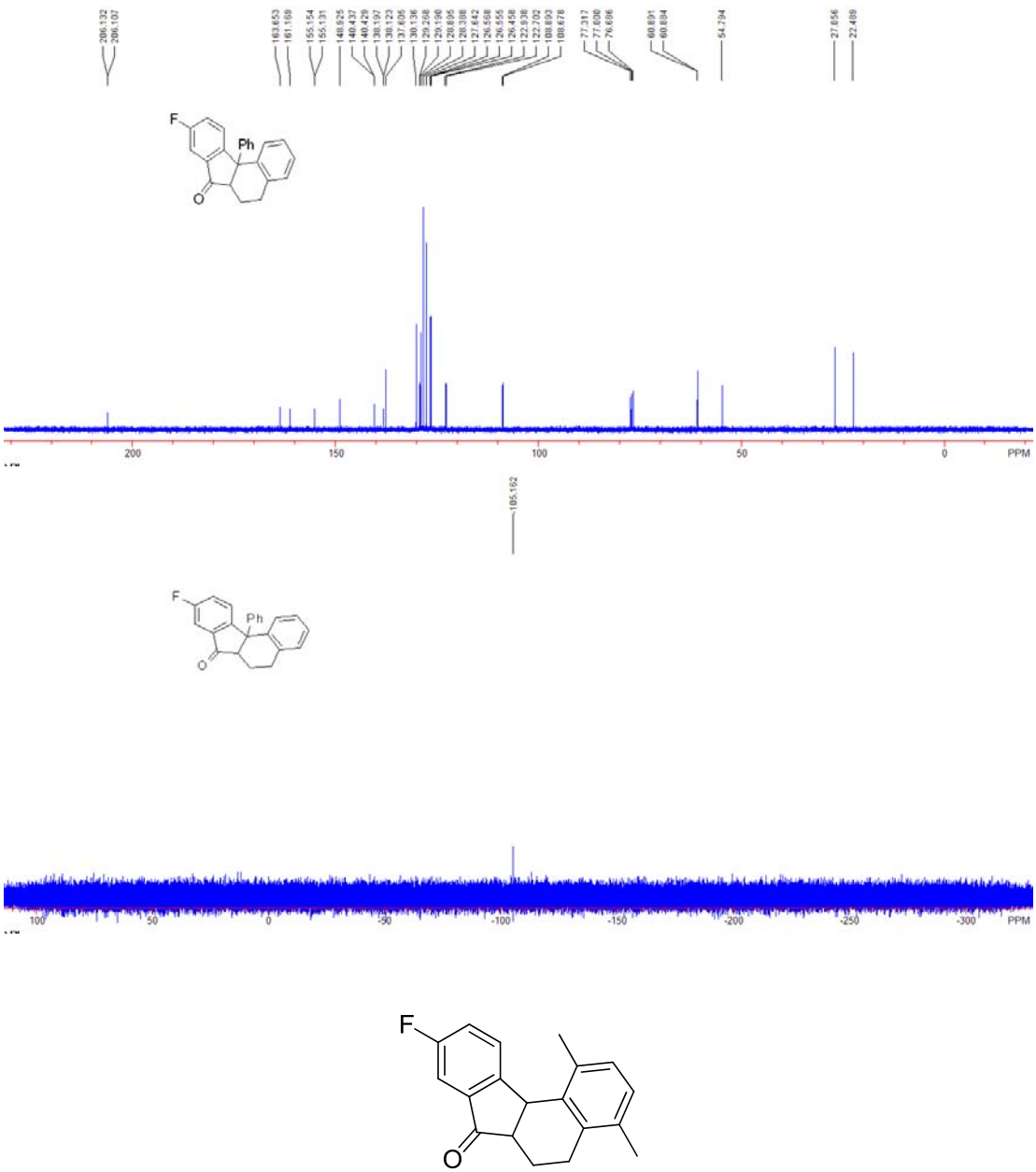





**9-Fluoro-11*b*-phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 2e**:

87 mg yield: 88%; A white solid, Mp: 120-123 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.97-2.07 (m, 1H, $CH_2$), 2.50-2.58 (m, 2H, $CH_2$), 2.66-2.72 (m, 1H, $CH_2$), 3.03-3.04 (m, 1H, CH), 7.02-7.13 (m, 5H, Ar), 7.22-7.26 (m, 4H, Ar), 7.31-7.33 (m, 1H, Ar), 7.38-7.40 (m, 1H, Ar), 7.61 (dd, $J_{HF}$ = 8.4 Hz, $J_{HH}$ = 4.4 Hz, 1H, Ar); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 22.5, 27.1, 54.8, 60.9 (d, $J_{CF}$ = 0.7 Hz), 108.8 (d, $J_{CF}$ = 21.5 Hz), 122.8 (d, $J_{CF}$ = 23.6 Hz), 126.5 (d, $J_{CF}$ = 7.8 Hz), 126.6, 127.6, 128.4, 128.9, 129.2 (d, $J_{CF}$ = 7.8 Hz), 130.1, 137.6, 138.2 (d, $J_{CF}$ = 7.4 Hz), 140.4 (d, $J_{CF}$ = 0.8 Hz), 148.9, 155.1 (d, $J_{CF}$ = 2.3 Hz), 162.4 (d, $J_{CF}$ = 248.4 Hz), 206.1 (d, $J_{CF}$ = 2.5 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -105.2. IR (Neat) ν 3061, 3023, 2853, 1719, 1609, 1479, 1438, 1273, 785 cm$^{-1}$. MS (%) m/e 340 ($M^+$, 100.00), 313 (15.69), 310 (16.55), 270 (7.02), 251 (18.15), 249 (12.46), 237 (19.88), 233 (26.38), 220 (11.50). HRMS (EI) calcd. for $C_{23}H_{17}OF$: 328.1263, Found: 328.1267.





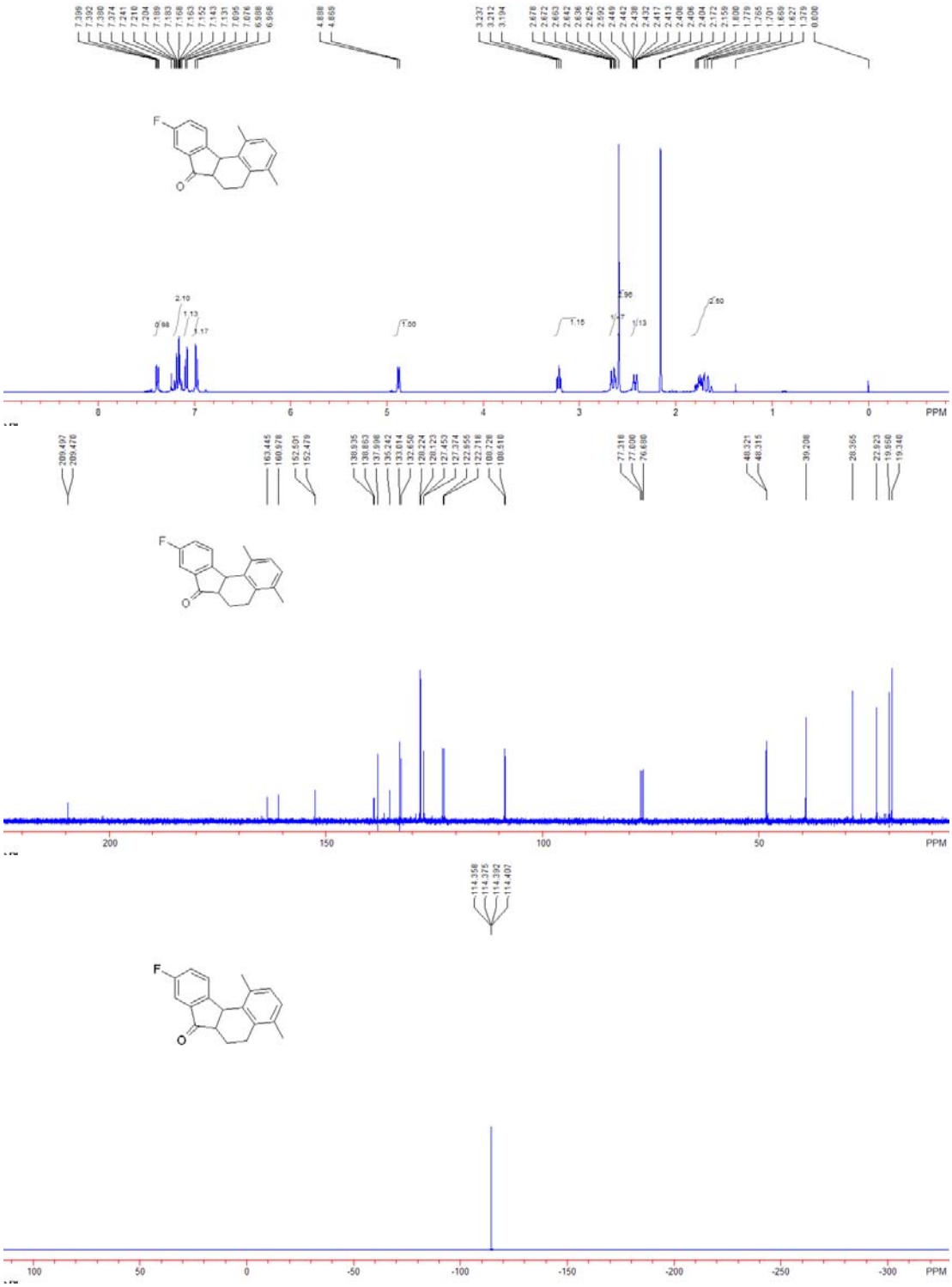


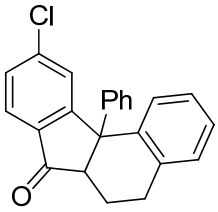


**9-Fluoro-1, 4-dimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 4e:**

62 mg, yield: 74%; A white solid, Mp: 132-135 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.62-1.80 (m, 2H, $CH_2$), 2.16 (s, 3H, $CH_3$), 2.40-2.45 (m, 1H, $CH_2$), 2.59 (s, 3H, $CH_3$), 2.63-2.68 (m, 1H, $CH_2$), 3.19-3.24 (m, 1H, CH), 4.88 (d, $J$ = 7.6 Hz, 1H, CH), 6.98 (d, $J$ = 8.0 Hz, 1H, Ar), 7.09 (d, $J$ = 8.0 Hz, 1H, Ar), 7.13-7.21 (m, 2H, Ar), 7.40 (dd, $J_{HF}$ = 7.6 Hz, $J_{HH}$ = 2.4 Hz, 1H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 19.3, 20.0, 22.9, 28.4, 39.2, 48.3 (d, $J_{CF}$ = 0.6 Hz), 108.6 (d, $J_{CF}$ = 21.8 Hz), 122.8 (d, $J_{CF}$ = 23.7 Hz), 127.4 (d, $J_{CF}$ = 7.9 Hz), 128.1, 128.2, 132.7, 133.0, 135.2, 138.0, 138.9 (d, $J_{CF}$ = 7.2 Hz), 152.5 (d, $J_{CF}$ = 2.2 Hz), 162.2 (d, $J_{CF}$ = 246.7 Hz), 209.5 (d, $J_{CF}$ = 2.7 Hz).$^{19}$F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -114.4. IR (Neat) ν 3069, 3011, 2928, 2867, 1716, 1610, 1482, 1269, 784 cm$^{-1}$. MS (%) m/e 280 ($M^+$, 100.00), 266 (19.97), 265 (98.22), 263 (12.15), 247

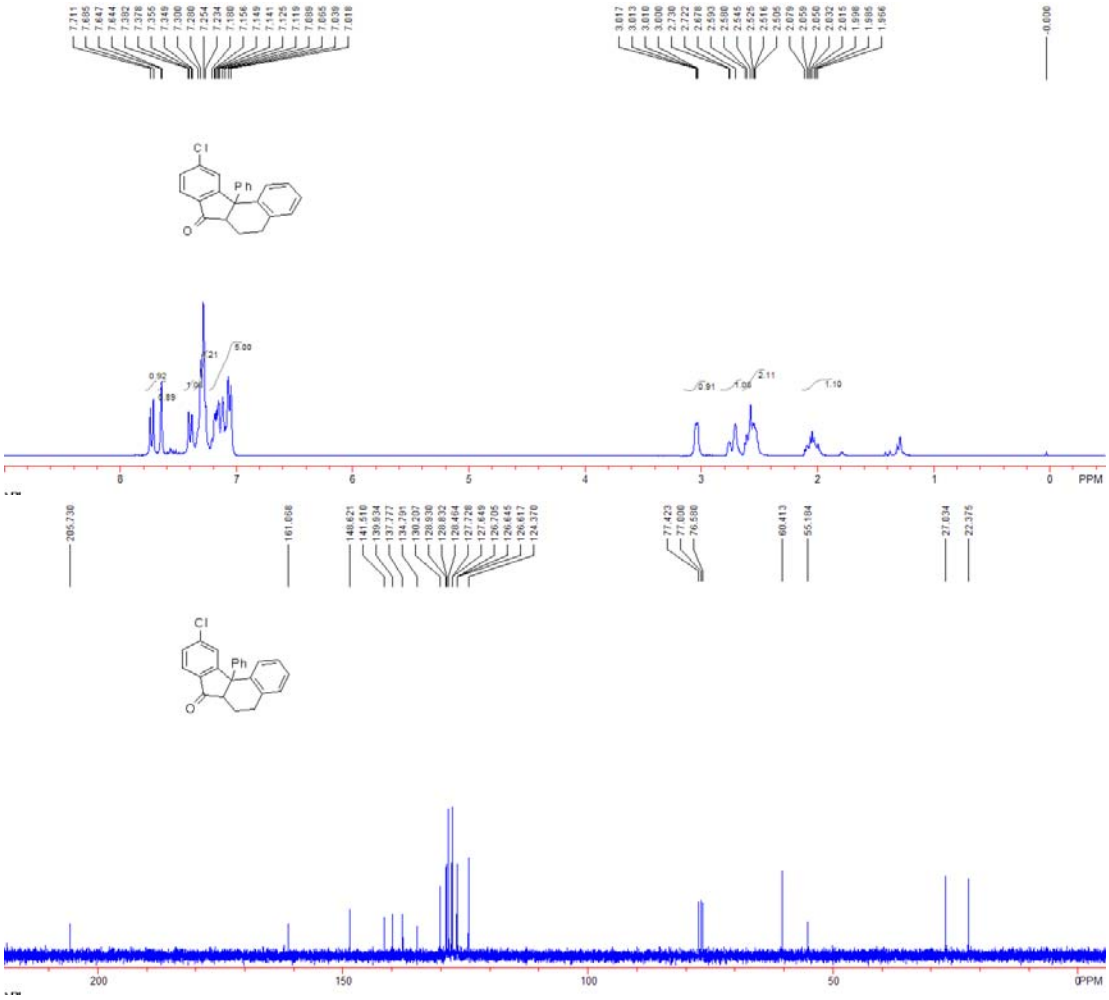
(35.08), 237 (13.01), 220 (13.22), 143 (8.45), 128 (8.13). HRMS (EI) calcd. for $C_{19}H_{17}OF$: 280.1263, Found: 280.1265.

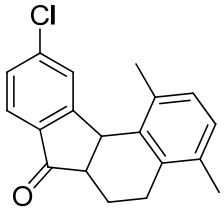





**10-Chloro-11*b*-phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 3f**:

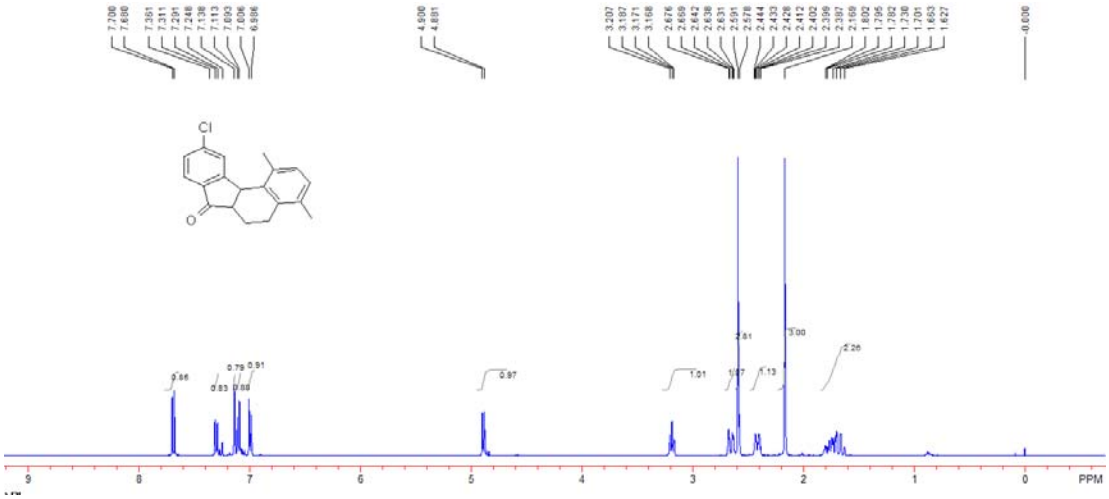
69 mg yield: 67%; A white solid, Mp: 130-133 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS) δ 1.97-2.08 (m, 1H, $CH_2$), 2.51-2.59 (m, 2H, $CH_2$), 2.68-2.73 (m, 1H, $CH_2$), 3.00-3.02 (m, 1H, CH), 7.02-7.18 (m, 5H, Ar), 7.23-7.30 (m, 4H, Ar), 7.37 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz, 1H, Ar), 7.65 (d, $J$ = 0.9 Hz, 1H, Ar), 7.70 (d, $J$ = 7.8 Hz, 1H, Ar). $^{13}$C NMR (75 MHz, $CDCl_3$, TMS): δ 22.4, 27.0, 55.2, 60.4, 124.4, 126.62, 126.65, 126.71, 127.6, 127.7, 128.5, 128.8, 128.9, 130.2, 134.8, 137.8, 139.9, 141.5, 148.6, 161.1, 205.7. IR (Neat) ν 3059, 3024, 2927, 2852, 1716, 1595, 1572, 1225, 702 cm$^{-1}$. MS (%) m/e 340 ($M^+$, 100.00), 344 ($M^+$, 100.00), 346 ($M^+$, 98.00), 329 (14.60), 309 (8.88), 291 (22.37), 267 (15.17), 249 (13.01), 231 (19.92) 202 (22.90), 203 (14.56). HRMS (EI) calcd. for $C_{23}H_{17}OCl$: 344.0968, Found: 344.0965.

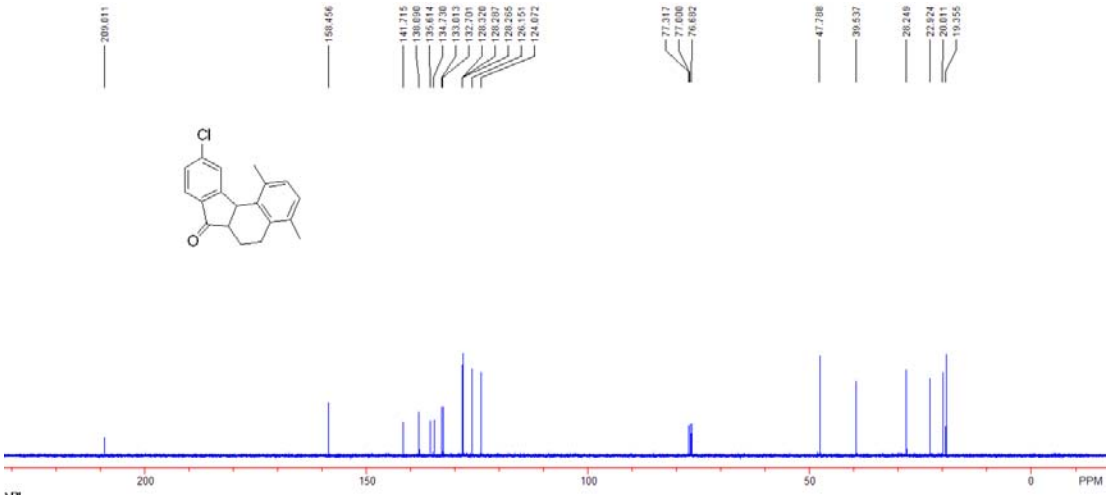


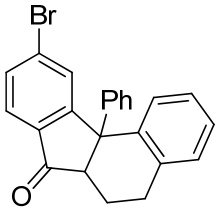



**10-Chloro-1,4-dimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 5f**:

60 mg yield: 67%; A white solid, Mp: 125-127 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.63-1.80 (m, 2H, $CH_2$), 2.17 (s, 3H, $CH_3$), 2.39-2.44 (m, 1H, $CH_2$), 2.59 (s, 3H, $CH_3$), 2.63-2.68 (m, 1H, $CH_2$), 3.17-3.21 (m, 1H, CH), 4.89 (d, 1H, *J* = 7.6 Hz, CH), 6.99 (d, *J* = 8.0 Hz, 1H, Ar), 7.11 (d, *J* = 8.0 Hz, 1H, Ar), 7.14 (s, 1H, Ar), 7.30 (d, *J* = 8.0 Hz, 1H, Ar), 7.69 (d, *J* = 8.0 Hz, 1H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 19.4, 20.0, 22.9, 28.2, 39.5, 47.8, 124.1, 126.2, 128.27, 128.29, 128.3, 132.7, 133.0, 134.7, 135.6, 138.1, 141.7, 158.5, 209.0. IR (Neat) ν 3064, 3011, 2928, 2867, 1712, 1596, 1575, 1267, 835 cm$^{-1}$. MS (%) m/e 296 ($M^+$, 100.00), 298 ($M^+$, 34.04), 283 (30.62), 281 (94.94), 279 (10.09), 263 (23.61), 243 (22.20), 202 (17.10), 143 (13.22) 128 (14.39). HRMS (EI) calcd. for $C_{19}H_{17}OCl$: 296.0968, Found: 296.0967.

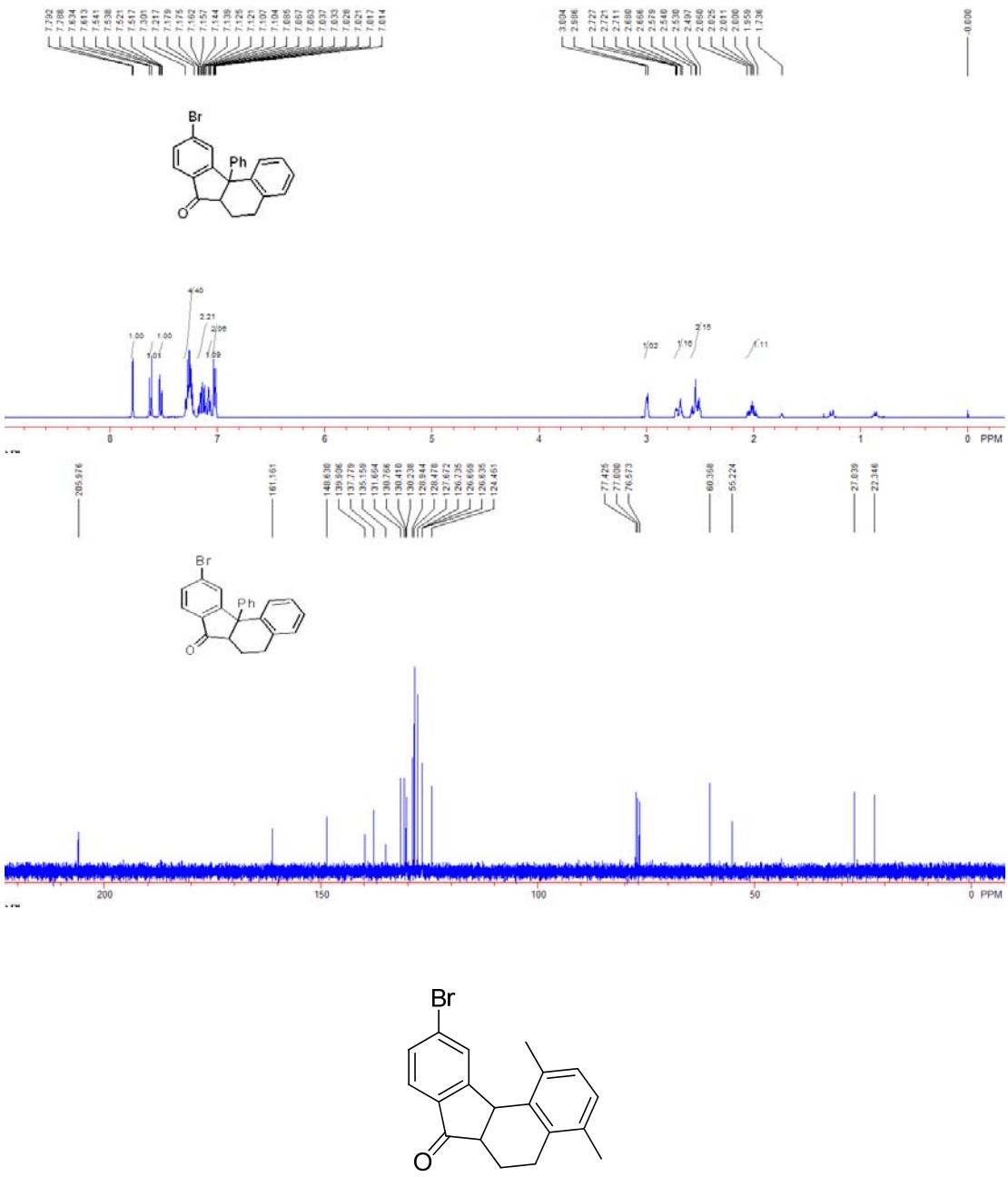





**10-Bromo-11*b*-phenyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 3g**:

85 mg, yield: 73%; A white solid, Mp: 130-133 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$, TMS) δ 1.96-2.06 (m, 1H, $CH_2$), 2.50-2.58 (m, 2H, $CH_2$), 2.67-2.73 (m, 1H, $CH_2$), 2.99-3.00 (m, 1H, CH), 7.01-7.18 (m, 5H, Ar), 7.22-7.30 (m, 4H, Ar), 7.53 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz, 1H, Ar) 7.62 (d, $J$ = 8.4 Hz, 1H, Ar), 7.79 (d, $J$ = 1.6 Hz, 1H, Ar). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS): δ 22.3, 27.0, 55.2, 60.4, 124.5, 126.6, 126.67, 126.74, 127.7, 128.5, 128.9, 130.2, 130.4, 130.8, 131.7, 135.2, 137.8, 139.9, 148.6, 161.2, 206.0. IR (Neat) ν 3058, 3024, 2929, 2853, 1716, 1591, 1573, 1224, 717 cm$^{-1}$. MS (%) m/e 340 ($M^+$, 100.00), 388 ($M^+$, 100.00), 390 ($M^+$, 98.00), 375 (10.82), 373 (13.17), 311 (12.49), 299 (13.61), 291 (27.22), 231 (32.40) 202 (36.87). HRMS (EI) calcd. for $C_{23}H_{17}OBr$: 388.0463, Found: 388.0459.



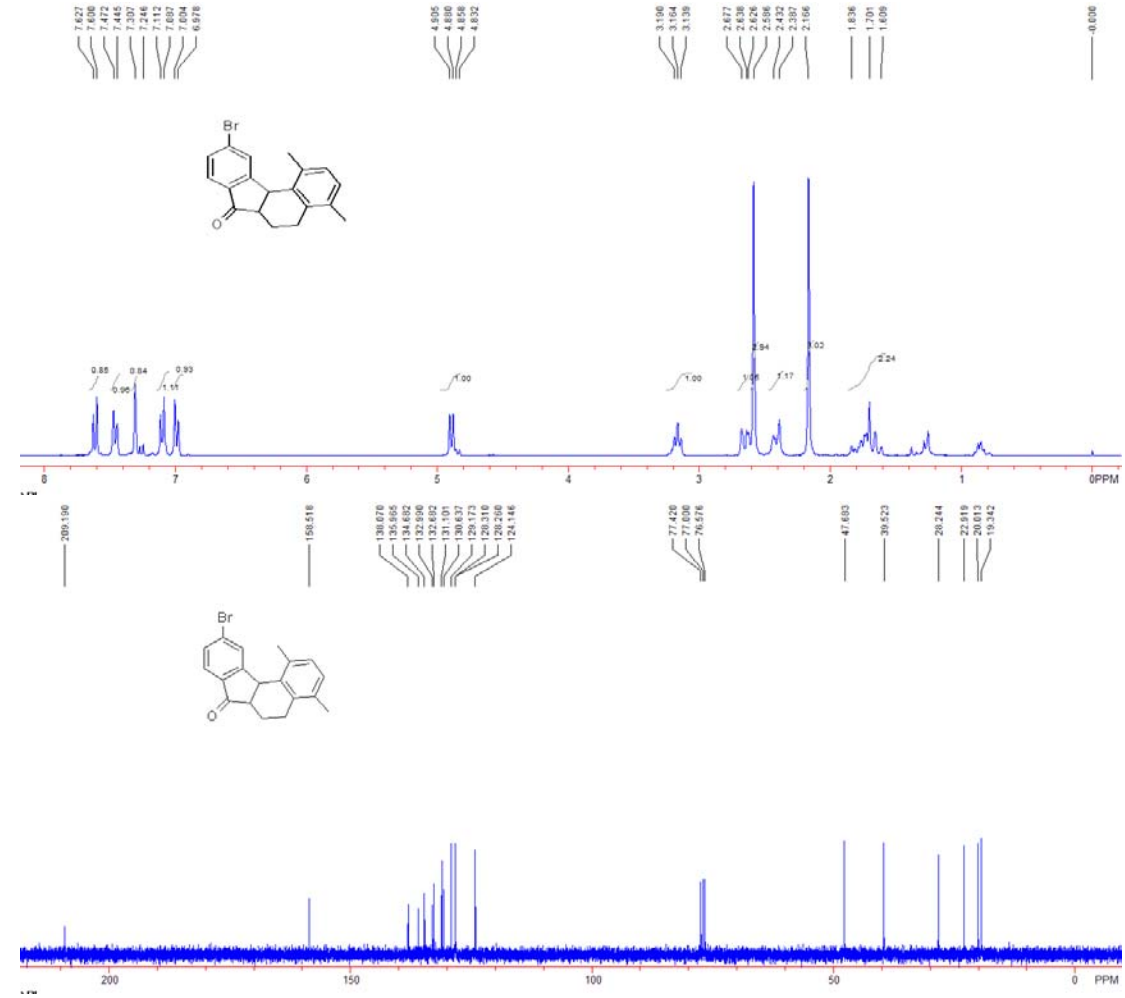


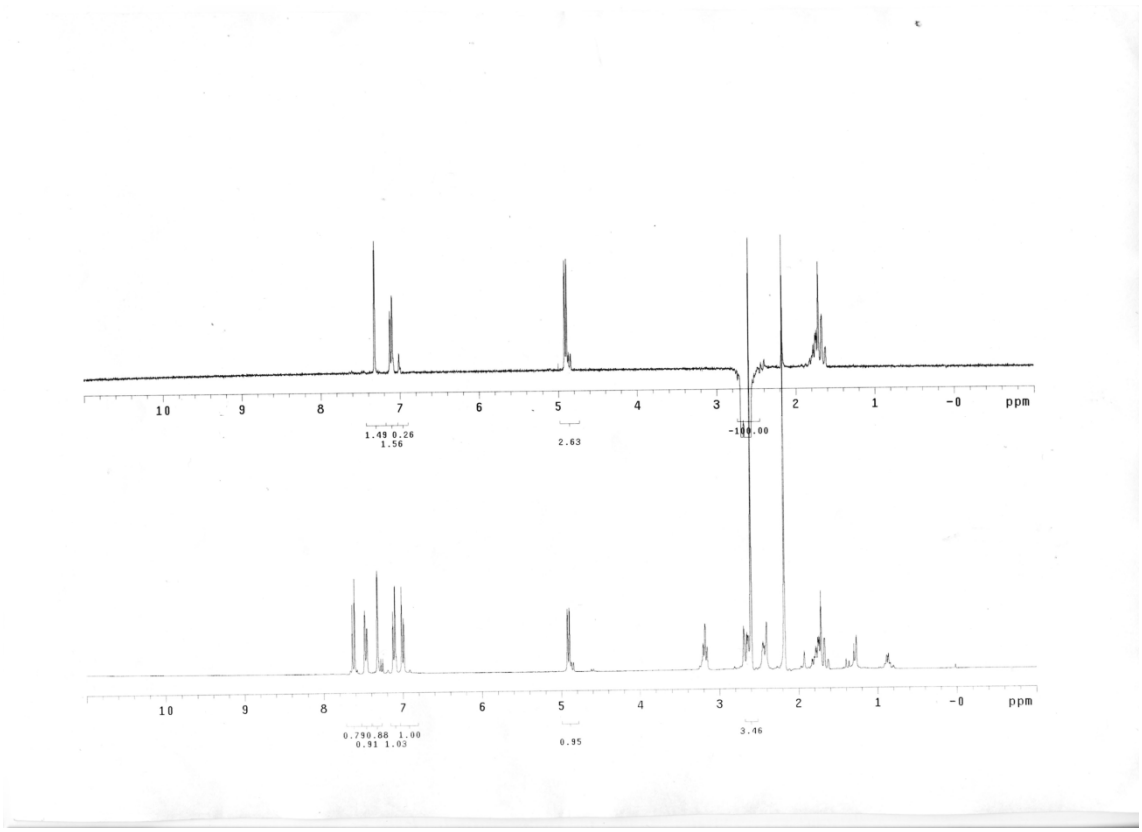


**10-Bromo-1,4-dimethyl-6,6*a*-dihydro-5*H*-benzo[*c*]fluoren-7(11*bH*)-one 5g**:

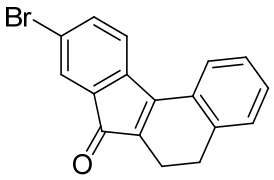
88 mg, yield: 86%; A white solid, Mp: 130-133 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS) δ 1.61-1.84 (m, 2H, $CH_2$), 2.17 (s, 3H, $CH_3$), 2.39-2.43 (m, 1H, $CH_2$), 2.59 (s, 3H, $CH_3$), 2.63-2.68 (m, 1H, $CH_2$), 3.14-3.19 (m, 1H, CH), 4.89 (d, *J* = 7.5 Hz, 1H, CH), 6.99 (d, *J* = 7.8 Hz, 1H, Ar), 7.10 (d, *J* = 7.8 Hz, 1H, Ar), 7.31 (s, 1H, Ar), 7.46 (d, *J* = 8.1 Hz, 1H, Ar), 7.61 (d, *J* = 8.1 Hz, 1H, Ar). $^{13}$C NMR (75 MHz, $CDCl_3$, TMS) δ 19.3, 20.0, 22.9, 28.2, 39.5, 47.7, 124.1, 128.26, 128.31, 129.2, 130.6, 131.1, 132.6, 133.0, 134.7, 136.0, 138.1, 158.5, 209.2. IR (Neat) ν 3059, 3016, 2926, 2854, 1713, 1591, 1571, 832, 765 cm$^{-1}$. MS (%) m/e 340 ($M^+$, 100.00), 342 ($M^+$, 100.00), 327 ($M^+$, 74.86), 246 (30.31), 243 (26.40), 203 (20.39), 202 (29.77), 115 (24.15), 101 (20.08) 75 (11.91). HRMS (EI)

calcd. for $C_{19}H_{17}OBr$: 340.0463, Found: 340.0465.



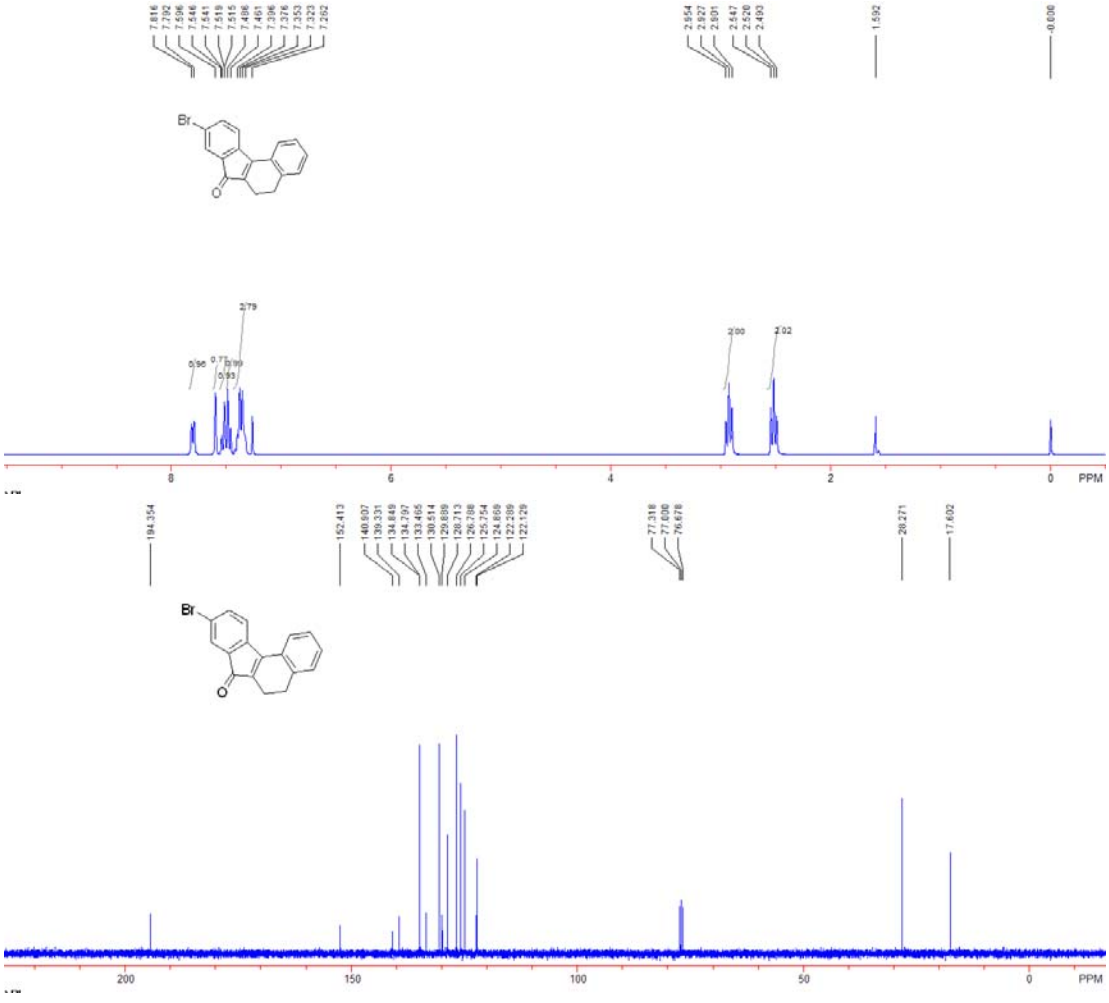



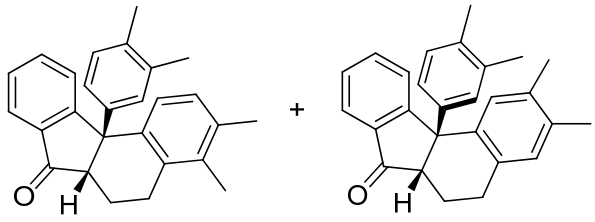
NOE spectroscopy of **5g**



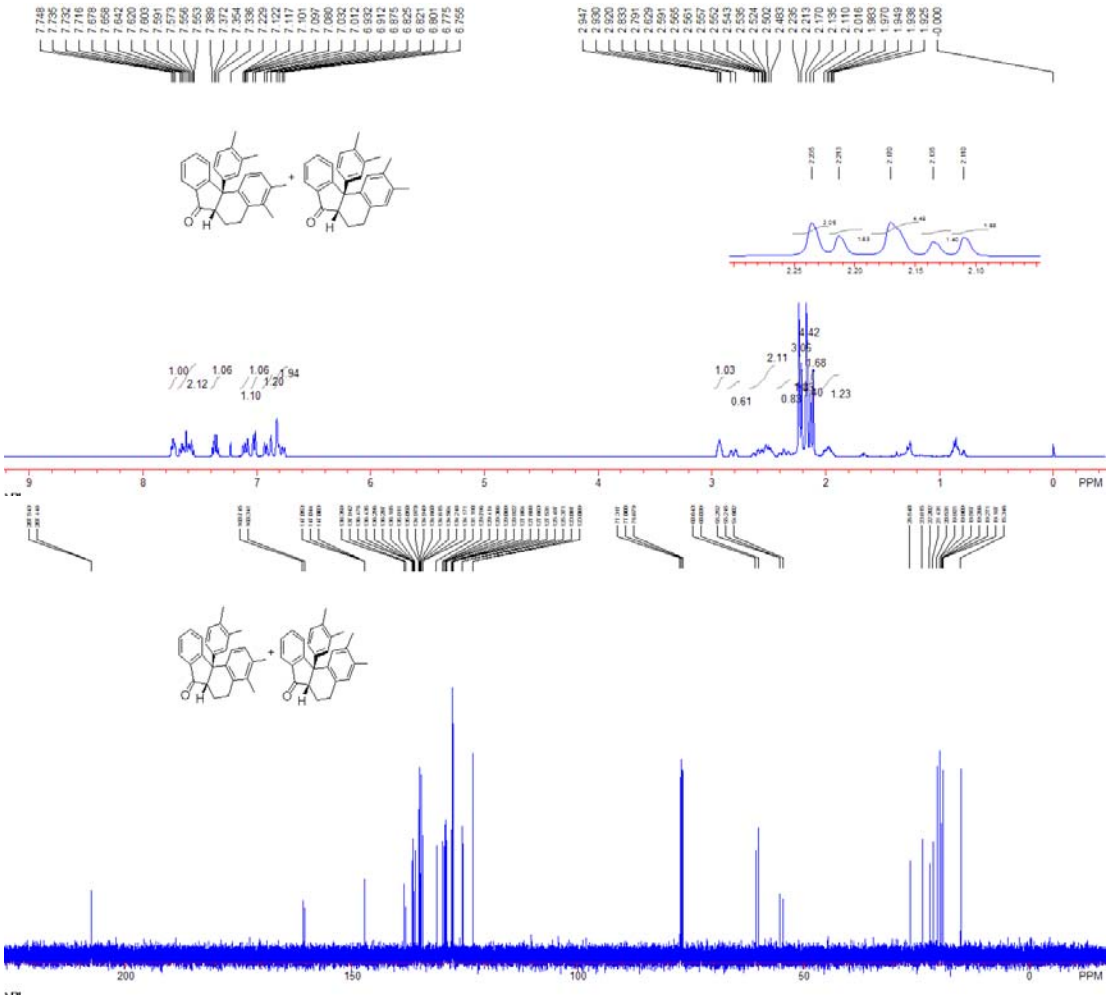

**9-Bromo-5*H*-benzo[*c*]fluoren-7(6*H*)-one 9**:

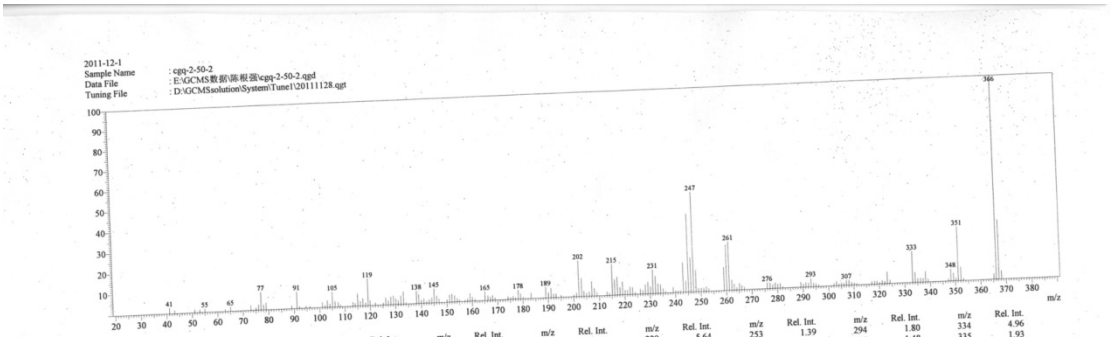
60 mg, yield: 67%; A red solid, Mp: 135-137 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$, TMS) δ 2.52 (t, *J* = 8.1 Hz, 2H, $CH_2$), 2.93 (t, *J* = 8.1 Hz, 2H, $CH_2$), 7.32-7.40 (m, 3H, Ar), 7.47 (d, *J* = 7.5 Hz, 1H, Ar), 7.53 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.5 Hz, 1H, Ar), 7.60 (s, 1H, Ar), 7.80 (d, *J* = 7.2 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) δ 17.6, 28.3, 122.1, 122.3, 124.9, 125.8, 126.8, 128.7, 129.9, 130.5, 133.5, 134.80, 134.85, 139.3, 140.9, 152.4, 194.4. IR (Neat) ν 3069, 3027, 2933, 2846, 1699, 1598, 1413, 1181, 725 cm$^{-1}$. MS (%) m/e 309 ($M^+$, 42.14), 311 ($M^+$, 52.75), 293 (10.77), 231 (59.88), 230 (30.94), 202 (100.00), 200 (33.35), 116 (16.69), 101 (69.96) 88 (22.74). HRMS (EI) calcd. for $C_{17}H_{11}OBr$: 309.9993, Found: 309.9991.



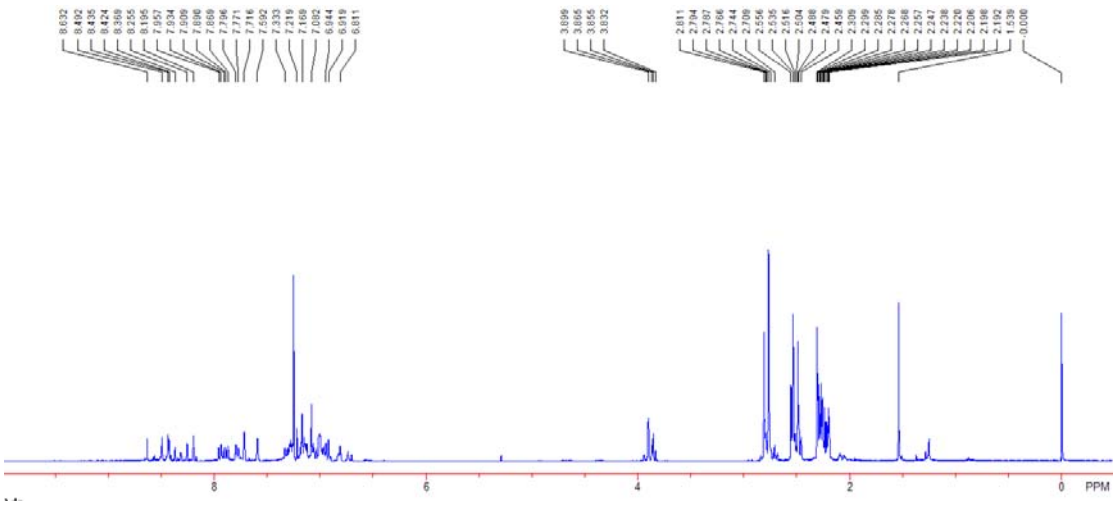


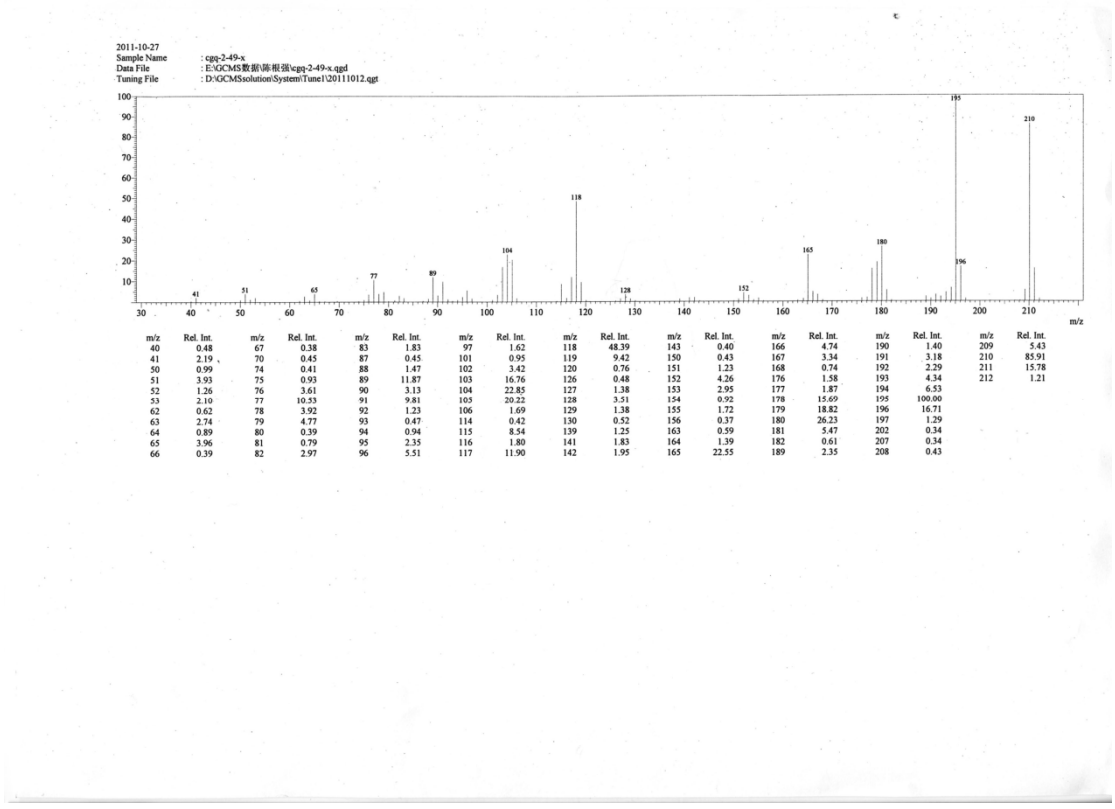
**6**






| m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 41 | 2.80 | 105 | 7.31 | 134 | 0.81 | 165 | 4.26 | 203 | 8.88 | 229 | 5.64 | 253 | 1.39 | 294 | 1.80 | 334 | 4.96 | | |
| 43 | 1.56 | 106 | 2.78 | 138 | 6.09 | 166 | 2.36 | 204 | 2.53 | 230 | 3.43 | 259 | 11.25 | 295 | 1.48 | 335 | 1.93 | | |
| 51 | 1.63 | 107 | 2.39 | 139 | 4.44 | 167 | 1.65 | 205 | 1.73 | 231 | 11.52 | 260 | 22.05 | 296 | 0.93 | 336 | 1.94 | | |
| 53 | 1.37 | 108 | 1.11 | 140 | 1.70 | 168 | 2.42 | 206 | 2.25 | 232 | 8.36 | 261 | 23.49 | 302 | 0.96 | 337 | 1.86 | | |
| 55 | 1.74 | 113 | 1.93 | 141 | 2.22 | 169 | 1.22 | 207 | 6.97 | 233 | 4.59 | 262 | 5.01 | 303 | 2.15 | 338 | 5.14 | | |
| 63 | 1.08 | 114 | 1.47 | 142 | 1.03 | 174 | 1.46 | 208 | 3.73 | 234 | 4.25 | 263 | 2.94 | 304 | 0.93 | 339 | 1.47 | | |
| 65 | 2.08 | 115 | 6.05 | 143 | 1.61 | 175 | 0.91 | 209 | 1.64 | 235 | 2.24 | 264 | 1.21 | 305 | 1.26 | 347 | 1.15 | | |
| 73 | 2.40 | 116 | 2.23 | 144 | 2.47 | 176 | 1.46 | 213 | 1.88 | 236 | 0.95 | 265 | 3.15 | 306 | 1.20 | 348 | 5.74 | | |
| 75 | 1.30 | 117 | 3.62 | 145 | 6.76 | 177 | 0.86 | 214 | 1.09 | 239 | 2.70 | 266 | 2.10 | 307 | 2.42 | 349 | 3.86 | | |
| 76 | 2.55 | 118 | 1.44 | 146 | 3.32 | 178 | 4.32 | 215 | 14.89 | 240 | 0.94 | 267 | 1.32 | 308 | 2.49 | 350 | 1.39 | | |
| 77 | 8.65 | 119 | 12.88 | 147 | 1.75 | 179 | 2.60 | 216 | 7.59 | 241 | 1.00 | 276 | 2.87 | 309 | 1.44 | 351 | 26.02 | | |
| 78 | 2.46 | 120 | 2.49 | 150 | 1.33 | 180 | 0.89 | 217 | 8.73 | 242 | 0.93 | 277 | 2.68 | 310 | 1.02 | 352 | 6.57 | | |
| 79 | 3.45 | 122 | 1.21 | 151 | 3.43 | 183 | 2.69 | 218 | 3.65 | 243 | 14.31 | 278 | 1.86 | 311 | 0.83 | 353 | 1.20 | | |
| 89 | 1.53 | 125 | 1.01 | 152 | 3.92 | 189 | 5.15 | 219 | 6.40 | 244 | 5.51 | 279 | 2.69 | 317 | 1.40 | 365 | 2.69 | | |
| 91 | 8.09 | 126 | 3.45 | 153 | 3.11 | 190 | 2.55 | 220 | 2.17 | 245 | 37.89 | 280 | 1.99 | 318 | 1.41 | 366 | 100.00 | | |
| 92 | 1.00 | 127 | 2.11 | 154 | 1.80 | 191 | 4.55 | 221 | 2.18 | 246 | 16.67 | 281 | 2.30 | 319 | 1.55 | 367 | 28.65 | | |
| 95 | 0.95 | 128 | 3.80 | 155 | 0.96 | 192 | 1.84 | 222 | 3.70 | 247 | 48.39 | 282 | 0.80 | 320 | 0.80 | 368 | 4.15 | | |
| 96 | 0.86 | 129 | 4.22 | 157 | 0.74 | 193 | 1.82 | 223 | 3.51 | 248 | 10.26 | 289 | 2.37 | 321 | 1.63 | | | | |
| 101 | 2.57 | 130 | 2.81 | 158 | 1.31 | 195 | 1.00 | 224 | 1.00 | 249 | 1.63 | 290 | 1.53 | 322 | 1.23 | | | | |
| 102 | 1.19 | 131 | 1.98 | 159 | 3.76 | 200 | 0.84 | 226 | 2.46 | 250 | 1.63 | 291 | 2.18 | 323 | 5.70 | | | | |
| 103 | 3.35 | 132 | 4.09 | 160 | 1.94 | 201 | 1.96 | 227 | 1.82 | 251 | 1.75 | 292 | 1.95 | 324 | 1.67 | | | | |
| 104 | 1.57 | 133 | 6.03 | 161 | 1.08 | 202 | 17.34 | 228 | 4.41 | 252 | 2.27 | 293 | 4.12 | 333 | 15.08 | | | | |

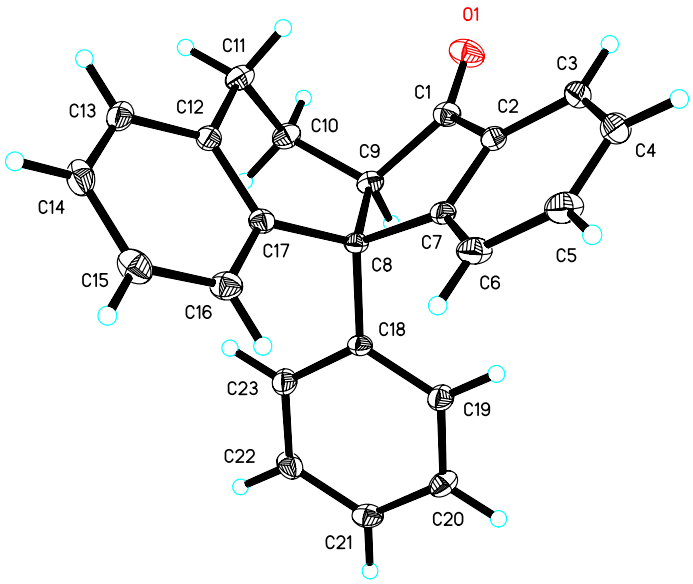


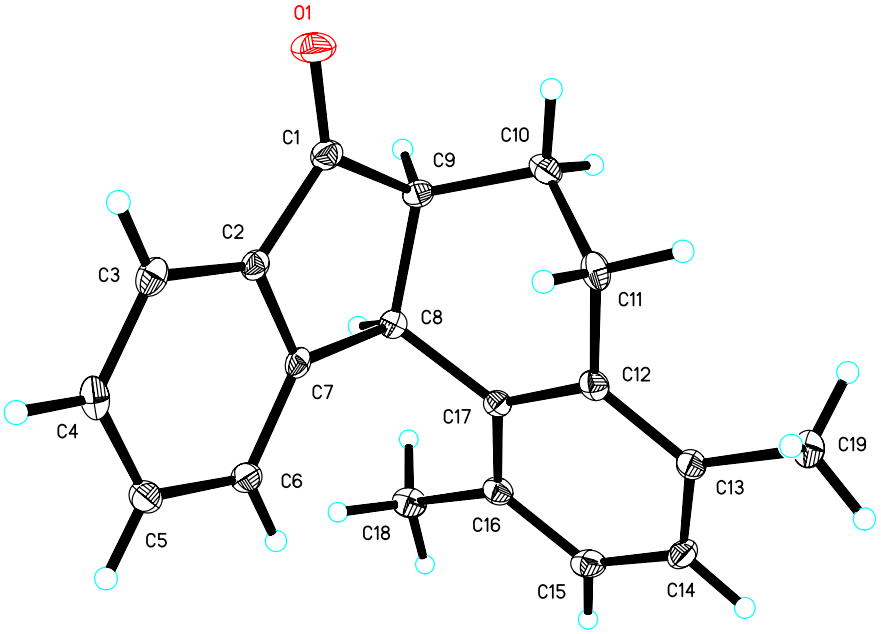

| m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. | m/z | Rel. Int. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | 0.48 | 67 | 0.38 | 83 | 1.83 | 97 | 1.62 | 118 | 48.39 | 143 | 0.40 | 166 | 4.74 | 190 | 1.40 | 209 | 5.43 |
| 41 | 2.19 | 70 | 0.45 | 87 | 0.45 | 101 | 0.95 | 119 | 9.42 | 150 | 0.43 | 167 | 3.34 | 191 | 3.18 | 210 | 85.91 |
| 50 | 0.99 | 74 | 0.41 | 88 | 1.47 | 102 | 3.42 | 120 | 0.76 | 151 | 1.23 | 168 | 0.74 | 192 | 2.29 | 211 | 15.78 |
| 51 | 3.93 | 75 | 0.93 | 89 | 11.87 | 103 | 16.76 | 126 | 0.48 | 152 | 4.26 | 176 | 1.58 | 193 | 4.34 | 212 | 1.21 |
| 52 | 1.26 | 76 | 3.61 | 90 | 3.13 | 104 | 22.85 | 127 | 1.38 | 153 | 2.95 | 177 | 1.87 | 194 | 6.53 | | |
| 53 | 2.10 | 77 | 10.33 | 91 | 9.81 | 105 | 20.22 | 128 | 3.51 | 154 | 0.92 | 178 | 15.69 | 195 | 100.00 | | |
| 62 | 0.62 | 78 | 3.92 | 92 | 1.23 | 106 | 1.69 | 129 | 1.38 | 155 | 1.72 | 179 | 18.82 | 196 | 16.71 | | |
| 63 | 2.74 | 79 | 4.77 | 93 | 0.47 | 114 | 0.42 | 130 | 0.52 | 156 | 0.37 | 180 | 26.23 | 197 | 1.29 | | |
| 64 | 0.89 | 80 | 0.39 | 94 | 0.94 | 115 | 8.54 | 139 | 1.25 | 163 | 0.59 | 181 | 5.47 | 202 | 0.34 | | |
| 65 | 3.96 | 81 | 0.79 | 95 | 2.35 | 116 | 1.80 | 141 | 1.83 | 164 | 1.39 | 182 | 0.61 | 207 | 0.34 | | |
| 66 | 0.39 | 82 | 2.97 | 96 | 5.51 | 117 | 11.90 | 142 | 1.95 | 165 | 22.55 | 189 | 2.35 | 208 | 0.43 | | |

MS spectroscopy of the byproduct **G** (Scheme 5)

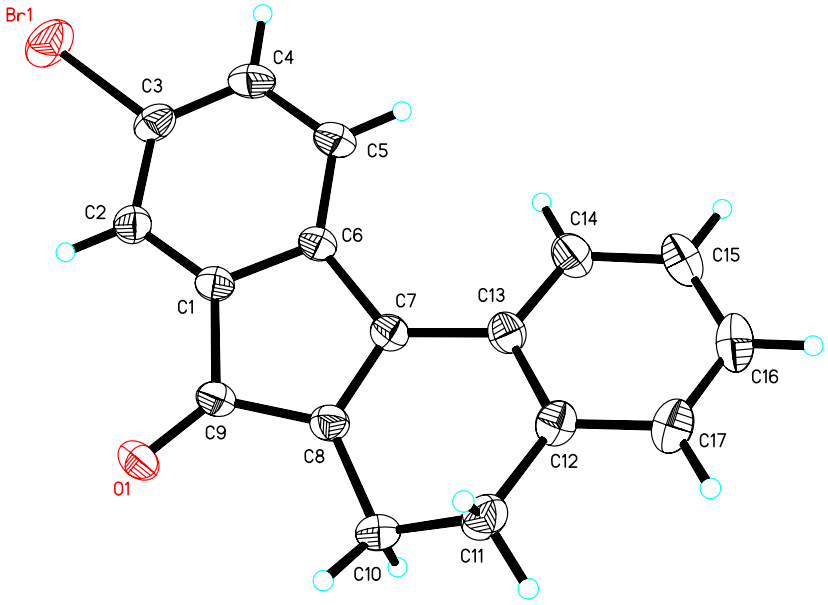
## 4. **Crystallographic Information**



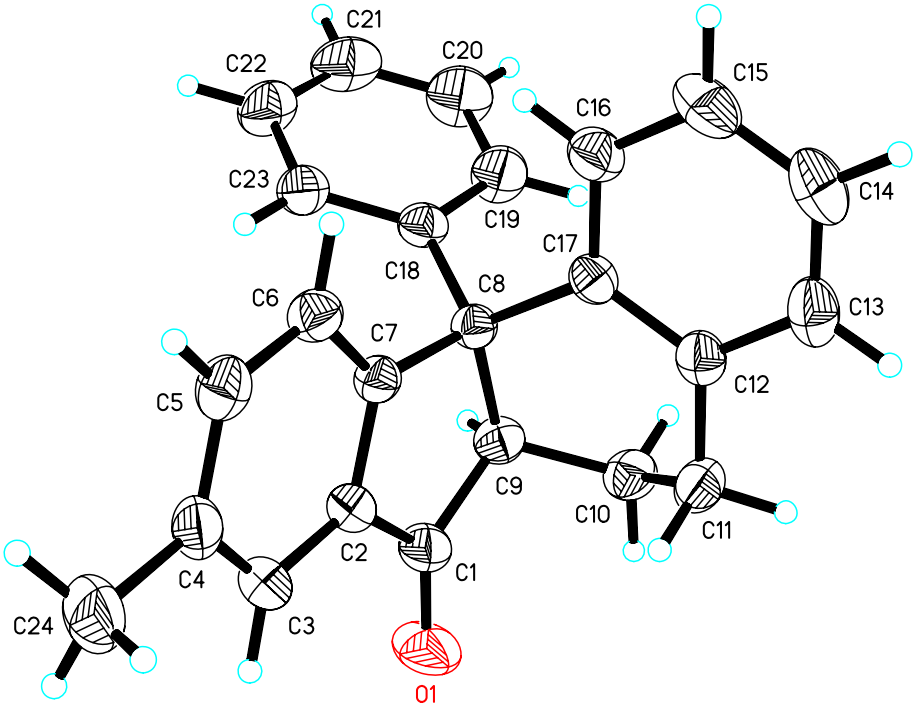

The crystal data of **2a** have been deposited in CCDC with number 834559. Empirical Formula: $C_{23}H_{18}O$; Formula Weight: 310.37; Crystal Color, Habit: colorless; Crystal Dimensions: 0.30 x 0.25 x 0.20 mm; Crystal System: Monoclinic; Lattice Parameters: a = 13.066(3)Å, b = 11.863(3)Å, c = 10.534(2)Å, $\alpha = 90^{o}$, $\beta = 98.516(3)^{o}$, $\gamma = 90^{o}$, V = 1614.7(6)$Å^3$; Space group: Cc; Z = 4; $D_{calc}$= 1.277 g/$cm^3$; $F_{000}$ = 656; Final R indices [I>2sigma(I)] R1 = 0.0461, wR2 = 0.1104.



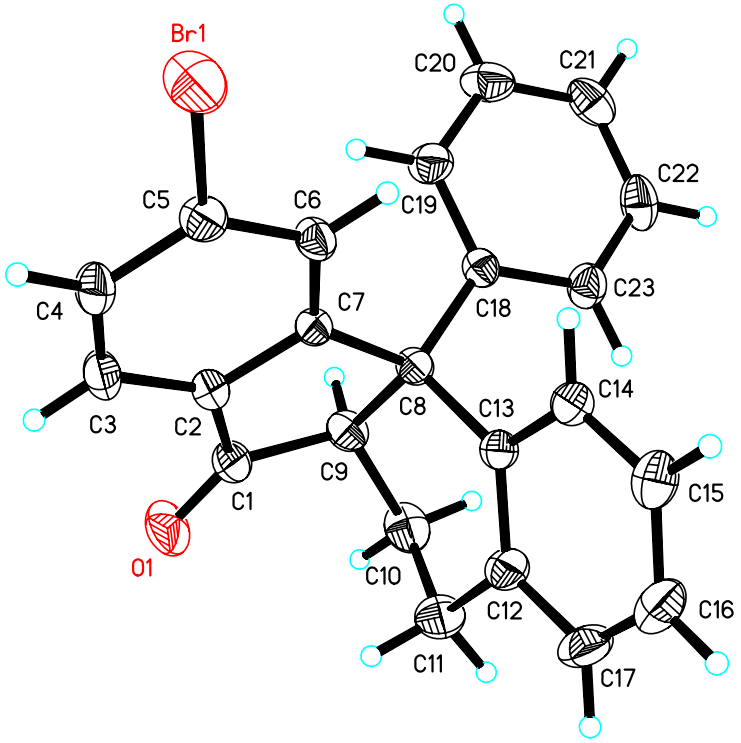

The crystal data of **4a** have been deposited in CCDC with number 837266. Empirical Formula: $C_{19}H_{18}O$; Formula Weight: 262.33; Crystal Color, Habit: colorless; Crystal Dimensions: 0.20 x 0.10 x 0.05 mm; Crystal System: Orthorhombic; Lattice Parameters: a = 14.653(3)Å, b = 7.9432(18)Å, c = 23.492(5)Å, $\alpha = 90^{o}$, $\beta = 90^{o}$, $\gamma = 90^{o}$, V = 2734.4(11)Å$^3$; Space group: Pbca; Z = 8; $D_{calc}$= 1.274 g/cm$^3$; $F_{000}$ = 1120; Final R indices [I>2sigma(I)] R1 = 0.0590, wR2 = 0.1234.




The crystal data of **9** have been deposited in CCDC with number 844935. Empirical Formula: $C_{17}H_{11}BrO$; Formula Weight: 311.17; Crystal Color, Habit: colorless; Crystal Dimensions: 0.315 x 0.203 x 0.186 mm; Crystal System: Monoclinic; Lattice Parameters: a = 8.4862(9)Å, b = 21.575(2)Å, c = 6.9770(7)Å, $\alpha = 90^{o}$, $\beta = 91.788(2)^{o}$, $\gamma = 90^{o}$, V = 1276.8(2)Å$^3$; Space group: P2(1)/c; Z = 4; $D_{calc}$= 1.619 g/cm$^3$; $F_{000}$ = 624; Final R indices [I>2sigma(I)] R1 = 0.0341, wR2 = 0.0838.




The crystal data of **2c** have been deposited in CCDC with number 848746. Empirical Formula: $C_{24}H_{20}O$; Formula Weight: 324.40; Crystal Color, Habit: colorless; Crystal Dimensions: 0.269 x 0.213 x 0.157 mm; Crystal System: Monoclinic; Lattice Parameters: a = 9.997(2)Å, b = 8.7960(19)Å, c = 20.266(5)Å, $\alpha$ = 90°, $\beta$ = 99.471(4)°, $\gamma$ = 90°, V = 1757.8(7)Å$^3$; Space group: P2(1)/c; Z = 4; $D_{calc}$= 1.226 g/cm$^3$; $F_{000}$ = 688; Final R indices [I>2sigma(I)] R1 = 0.0426, wR2 = 0.01094.




The crystal data of **3g** have been deposited in CCDC with number 855051. Empirical Formula: $C_{23}H_{17}BrO$; Formula Weight: 389.28; Crystal Color, Habit: colorless; Crystal Dimensions: 0.321 x 0.225 x 0.165 mm; Crystal System: Triclinic; Lattice Parameters: a = 7.6582(8)Å, b = 9.1199(10)Å, c = 14.2106(19)Å, $\alpha$ = 71.294(2)$^o$, $\beta$ = 81.511(3)$^o$, $\gamma$ = 68.506(2)$^o$, V = 874.18(18)Å$^3$; Space group: P-1; Z = 2; $D_{calc}$= 1.479 g/cm$^3$; $F_{000}$ = 396; Final R indices [I>2sigma(I)] R1 = 0.0413, wR2 = 0.1062.

4. **Reference**

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