

Supporting Information

Palladium-Catalyzed Arene C-H Activation/Ketone C-H Functionalization Reaction: Route to Spirodihydroindenones

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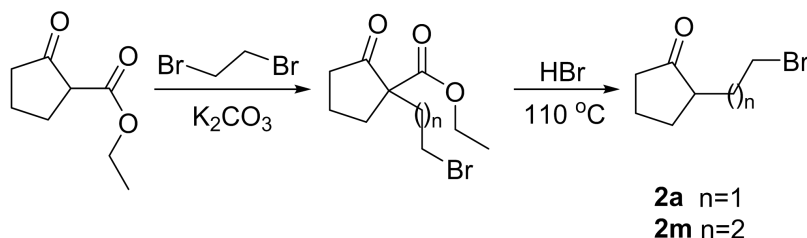
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1.General Methods.

The starting materials were purchased and used without further purification. Unless otherwise noted, reactions were carried out under an argon atmosphere. For Column chromatography, 200-300 mesh silica gel was employed and preparative TLC (PTLC). Analytical TLC was performed with silica gel GF254 plates. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in CDCl_3 using TMS as internal standard. All products and were further characterized by high resolution mass spectra (HRMS, FTMS, ESI full ms [100-2000]); copies of their ^1H NMR and ^{13}C NMR spectra are provided.

2. Synthesis of compound 2a, 2m, 2n, 2o, 2p

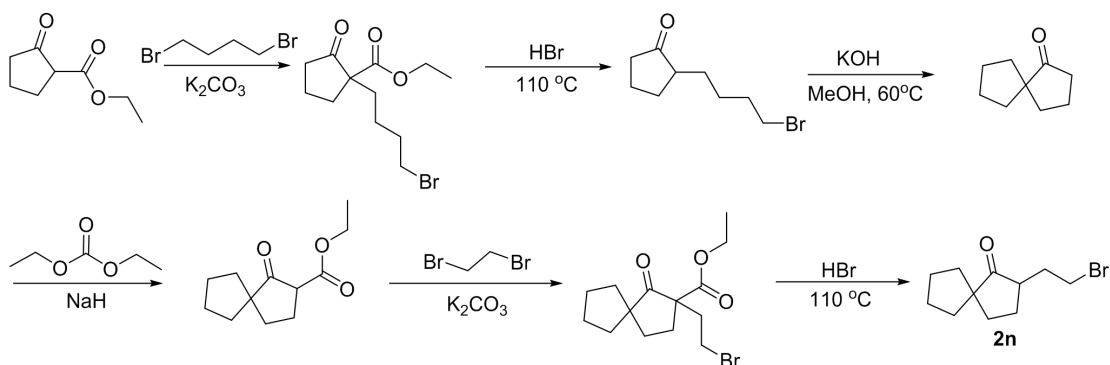
2-(2-bromoethyl)cyclopentan-1-one (2a) and 2-(3-bromopropyl)cyclopentan-1-one (2m)



2a, 2m was synthesized according to the previous literatures, the residue was distilled under vacuum distillation to give product **2a, 2m**.

The NMR spectroscopy and GC-MS data were in full accordance with the data in the reported literatures.¹

2-(2-bromoethyl)spiro[4.4]nonan-1-one (2n)



A mixture of ethyl 2-oxocyclopentanecarboxylate (50 mmol), potassium carbonate (100 mmol) and 1,4-dibromobutane (200 mmol) was dissolved in acetone (100 mL) and heated at 65 °C for 20 h, The suspension was filtered, the filtrate was concentrated and the residue was purified with chromatography column on silica gel to afford the ethyl 1-(4-bromobutyl)-2-oxocyclopentane-1-carboxylate.¹

Ethyl 1-(4-bromobutyl)-2-oxocyclopentane-1-carboxylate (40 mmol) was dissolved in hydrobromic acid (48%, 80 mL) and the solution was heated at 110 °C for 18 h until the evolution of carbon dioxide ceased. The solution was cooled to room temperature, diluted with water (70 mL) and extracted with EtOAc (120 mL). The aqueous phase was neutralised with solid sodium hydrogen carbonate and again extracted with diethyl ether. The combined organic phases were washed with a saturated solution of sodium hydrogen carbonate (100 mL), dried (Na_2SO_4), filtered and concentrated. The residue was purified with chromatography column on silica gel to afford the 2-(4-bromobutyl)cyclopentan-1-one.

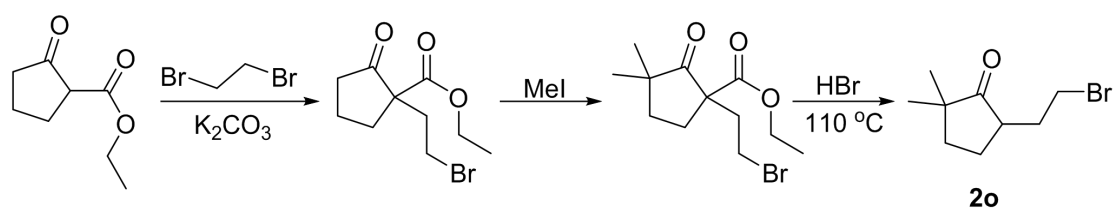
A mixture of 2-(4-bromobutyl)cyclopentan-1-one (30 mmol), KOH (60 mmol) was dissolved in MeOH (60 mL) and heated at 65 °C overnight. After removing the solvent by reduced pressure distillation, diluted with water. The mixture was extracted with ethyl ether and the combined organic layers were washed with saturated brine, dried over Na_2SO_4 . The solvent was removed under vacuo, and the residue was purified with chromatography column on silica gel to afford the spiro[4.4]nonan-1-one.

NaH (60 mmol) was added slowly in diethyl carbonate (60 mL). The mixture was heated at 130 °C for 30 min, and then cooled to 90 °C. A solution of the spiro[4.4]nonan-1-one (20 mmol) in diethyl carbonate (10 mL) was added dropwise from the needle over 2 h. After the addition,

the mixture was stirred at 90 °C overnight. When the reaction was cooled to room temperature, glacial acetic acid (10 mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The organic layer was separated, and the water layer was extracted with EtOAc (3 × 50 mL). The combined organic solution was washed with water (100 mL) and brine (100 mL), then dried over Na₂SO₄. The mixture was distilled under reduced pressure or subjected chromatography to give ethyl 1-oxospiro[4.4]nonane -2-carboxylate.

2m was synthesized via two step from ethyl 1-oxospiro[4.4]nonane -2-carboxylate according to the method of synthesizing **2a**. The residue was purified with chromatography column (Petroleum ether/EtOAc =20:1).

5-(2-bromoethyl)-2,2-dimethylcyclopentanone (**2o**)



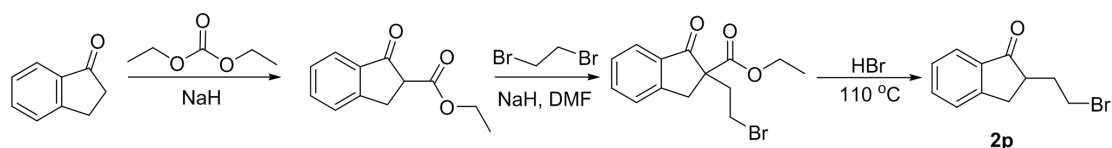
A mixture of ethyl 2-oxocyclopentanecarboxylate (50 mmol), potassium carbonate (100 mmol) and 1,2-dibromoethane (200 mmol) was dissolved in acetone (100 mL) and heated at 65 °C for 20 h, The suspension was filtered, the filtrate was concentrated and the residue

was purified with chromatography column on silica gel to afford the ethyl 1-(2-bromoethyl)-2-oxocyclopentane-1-carboxylate.¹

Ethyl 1-(2-bromoethyl)-2-oxocyclopentane-1-carboxylate (40 mmol) was dissolved in THF. NaH (100 mmol) was added slowly, and MeI (100 mmol) was dropped in succession. The mixture was stirred overnight. The ice-water was added, and extracted with ethyl acetate (120 mL). The combined organic phases were washed with a saturated solution of sodium hydrogen carbonate (100 mL), dried (Na₂SO₄), filtered and concentrated. The residue was purified with chromatography column on silica gel to afford the ethyl-1-(2-bromoethyl)-3,3-dimethyl-2-oxocyclopentane-1-carboxylate.

Ethyl-1-(2-bromoethyl)-3,3-dimethyl-2-oxocyclopentane-1-carboxylate (30 mmol) was dissolved in hydrobromic acid (48%, 60mL) and the solution was heated at 110 °C for 18 h until the evolution of carbon dioxide ceased. The solution was cooled to room temperature, diluted with water (70 mL) and extracted with diethyl ether (120 mL). The aqueous phase was neutralised with solid sodium hydrogen carbonate and again extracted with diethyl ether. The combined organic phases were washed with a saturated solution of sodium hydrogen carbonate (100 mL), dried (Na₂SO₄), filtered and concentrated. The residue was purified with chromatography column on silica gel to afford compound **2o** (Petroleum ether/EtOAc =20:1).

2-(2-bromoethyl)-2,3-dihydro-1H-inden-1-one (2p)



To a dried three-necked flask equipped with a dropping funnel, a condenser and a magnetic stirrer was added NaH (80 mmol), diethyl carbonate (50 mmol), and toluene (25 mL). The mixture was heated to reflux. A solution of 1-indanone (30 mmol) in toluene (15 mL) was added dropwise from the dropping funnel over 2 h. After the addition, the mixture was heated to reflux overnight. When the reaction was cooled to room temperature, glacial acetic acid (10 mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The toluene layer was separated, and the water layer was extracted with EtOAc (3×50 mL). The combined organic solution was washed with water (100 mL) and brine (100 mL), then dried over Na₂SO₄. The mixture was distilled under reduced pressure or subjected chromatography to give the desired product ethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate.²

To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added ethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (15 mmol) and DMF (60 mL), and NaH (20 mmol) was added slowly at room temperature. After the evolution of hydrogen ceased, 1,2-Dibromoethane was added slowly.

The mixture was stirred overnight. When the reaction was considered complete, the mixture was extracted with ethyl ether and the combined organic layers were washed with saturated brine, dried over Na₂SO₄. The solvent was removed under vacuo, and the residue was purified with chromatography column on silica gel to afford the ethyl 2-(2-bromoethyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate.

Ethyl-2-(2-bromoethyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (10 mmol) was dissolved in hydrobromic acid (48%, 40 mL) and the solution was heated at 110 °C for 30 min until the evolution of carbon dioxide ceased. The solution was cooled to room temperature, diluted with water (50 mL) and extracted with EtOAc (100 mL). The aqueous phase was neutralised with solid sodium hydrogen carbonate and again extracted with EtOAc. The combined organic phases were washed with a saturated solution of sodium hydrogen carbonate (100 mL), dried (Na₂SO₄), filtered and concentrated. The residue was purified with chromatography column on silica gel to afford the **2p**.¹ The residue was purified with chromatography column (Petroleum ether/EtOAc =20:1).

Reference

- 1 J. Heimann, H. J. Schäfer, R. Fröhlich, B. Wibbeling, *Eur. J. Org. Chem.*, 2003, 2919.
- 2 Y. Jiang, X. Chen, Y. Zheng, Z. Xue, C. Shu, W. Yuan, X. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 7304.

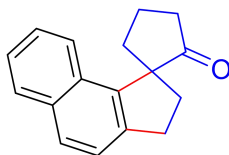
3. General Procedure for the Synthesis of spirodihydroindenes.

In a 5 mL tube, aryl iodide (0.2 mmol, 1.0 equiv), Pd(OAc)₂ (10 mol %), P(*m*-Cl-C₆H₄)₃ (20 mol %), 2-(2-Bromo-ethyl)-cyclopentanone (3.5 equiv), Cs₂CO₃ (4.0 equiv.) was added and charged with argon more than three times. Norbornene (2.0 equiv.) in THF (2 mL) was added injected into the tube. Afterwards, the mixture was allowed to stir at room temperature for 20 min, and the reaction tube was then immersed in an oil bath, which was preheated at 60 °C for 18 h. When the reaction was considered complete, the residue was purified with chromatography column on silica gel or preparative TLC (PTLC) (Petroleum ether/EtOAc = 40:1 - 100:1).

4. Characterization Data

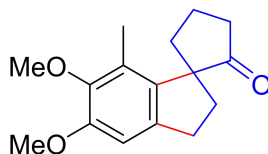
2,3-dihydrospiro[cyclopenta[α]naphthalene-1,1'-cyclopentan]-2'-one

(3a)



White solid (63%, 29.8 mg): m.p. 87-89 °C, ^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.80 (m, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.47 – 7.30 (m, 4H), 3.24 – 3.06 (m, 2H), 2.83 – 2.55 (m, 2H), 2.45 – 2.33 (m, 1H), 2.33 – 2.17 (m, 4H), 2.12 – 1.98 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 222.9, 142.7, 139.7, 133.7, 129.3, 128.7, 128.7, 126.1, 124.6, 123.7, 122.9, 63.1, 38.3, 37.7, 35.3, 31.7, 20.6. HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{16}\text{O}$ $[\text{M}+\text{H}]^+$ 237.1274, found 237.1278; IR (cm^{-1}): 3052, 2656, 2849, 1731, 1591, 1624, 1465, 1448, 810, 780, 742.

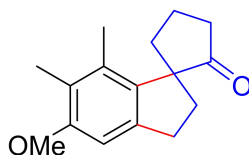
5',6'-dimethoxy-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3b)



White solid (74%, 38.7 mg): m.p. 82-84 °C, ^1H NMR (400 MHz, CDCl_3) δ 6.66 (s, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.03 – 2.82 (m, 2H), 2.51 – 2.42 (m, 2H), 2.20 – 2.06 (m, 5H), 2.02 (s, 3H), 1.98 – 1.83 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 223.0, 152.4, 146.5, 134.0, 136.2, 127.2, 105.8, 62.5, 60.2, 55.7, 38.1, 38.0, 34.7, 31.1, 20.4, 12.8. HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$

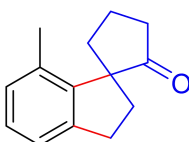
$[M+H]^+$ 261.1485, found 261.1489; IR (cm^{-1}): 2952, 1734, 1599, 1478, 1466, 1455, 1335, 1226, 1104, 997, 834.

5'-methoxy-6',7'-dimethyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3c)



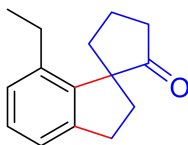
Colorless oil (70%, 34.2 mg): ^1H NMR (400 MHz, CDCl_3) δ 6.62 (s, 1H), 3.78 (s, 3H), 3.08 – 2.77 (m, 2H), 2.56 – 2.41 (m, 2H), 2.25 – 1.88 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 223.5, 157.5, 142.7, 135.8, 132.6, 123.9, 104.3, 62.5, 55.6, 38.0, 37.8, 34.9, 31.3, 20.4, 17.3, 11.7. HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$ $[M+H]^+$ 245.1536, found 245.1540; IR (cm^{-1}): 2949, 2869, 1734, 1596, 1465, 1118, 1052, 1004, 834.

7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3d)



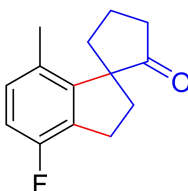
White solid (52%, 20.6 mg): m.p. 63-65 $^{\circ}\text{C}$, ^1H NMR (400 MHz, CDCl_3) δ 7.13 – 7.02 (m, 2H), 6.95 (d, J = 7.2 Hz, 1H), 3.05 – 2.89 (m, 2H), 2.53 – 2.44 (m, 2H), 2.23 – 2.05 (m, 8H), 2.01 – 1.89 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 222.7, 144.9, 143.6, 133.3, 128.8, 127.7, 122.0, 62.5, 38.2, 37.5, 34.5, 30.9, 20.6, 19.5. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$ $[M+H]^+$ 201.1274, found 201.1277; IR (cm^{-1}): 2955, 2870, 1733, 1593, 1465, 1450, 1165, 1124, 773.

7'-ethyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3e)



Colorless oil (60%, 25.8 mg): ^1H NMR (400 MHz, CDCl_3) δ 7.16 (t, $J = 7.5$ Hz, 1H), 7.05 (d, $J = 7.5$ Hz, 2H), 3.05 – 2.89 (m, 2H), 2.55 – 2.45 (m, 2H), 2.37 (q, $J = 7.5$ Hz, 2H), 2.23 – 2.12 (m, 2H), 2.12 – 2.02 (m, 3H), 2.01 – 1.87 (m, 1H), 1.19 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 222.8, 144.8, 143.2, 139.3, 127.8, 126.5, 121.8, 62.5, 38.1, 37.6, 35.4, 31.0, 25.8, 20.5, 14.3. HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ $[\text{M}+\text{K}]^+$ 253.0989, found 253.0992; IR (cm^{-1}): 2961, 2874, 1734, 1590, 1471, 1449, 1164, 1122, 801, 787, 750, 566.

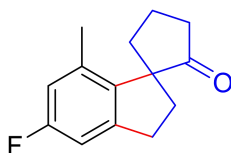
4'-fluoro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3f)



Colorless oil (52%, 22.4 mg): ^1H NMR (400 MHz, CDCl_3) δ 6.91 (dd, $J = 8.1$, 5.2 Hz, 1H), 6.79 (t, $J = 8.5$ Hz, 1H), 3.16 – 2.82 (m, 2H), 2.57 – 2.36 (m, 2H), 2.23 – 2.03 (m, 8H), 2.00 – 1.87 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 221.9, 157.6 (d, $J = 243.8$ Hz), 146.5 (d, $J = 5.3$ Hz), 130.7 (d, $J = 18.6$ Hz), 130.4 (d, $J = 6.9$ Hz), 128.7 (d, $J = 3.6$ Hz), 114.0 (d, $J = 20.3$ Hz), 62.9 (d, $J = 1.5$ Hz), 38.2, 37.6, 34.5, 26.7, 20.5, 18.8; ^{19}F NMR (376 MHz, CDCl_3) δ -122.63. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{15}\text{FO}$ $[\text{M}+\text{H}]^+$ 219.1180, found

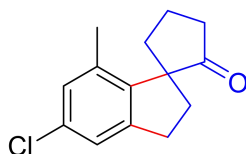
219.1182; IR (cm⁻¹): 2959, 2870, 1736, 1491, 1451, 1373, 1234, 1133, 1047, 889, 810, 733.

5'-fluoro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one
(3g)



Colorless oil (61%, 26.5 mg): ¹H NMR (400 MHz, CDCl₃) δ 6.74 (d, *J* = 8.5 Hz, 1H), 6.66 (dd, *J* = 10.0, 1.8 Hz, 1H), 3.10 – 2.76 (m, 2H), 2.53 – 2.36 (m, 2H), 2.24 – 1.98 (m, 8H), 1.98 – 1.86 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 222.4, 162.6 (d, *J* = 244.2 Hz), 147.0 (d, *J* = 8.7 Hz), 139.1 (d, *J* = 2.4 Hz), 135.0 (d, *J* = 8.7 Hz), 115.5 (d, *J* = 22.3 Hz), 108.9 (d, *J* = 21.8 Hz), 61.7, 38.1, 37.9, 34.5, 31.0 (d, *J* = 2.3 Hz), 20.4, 19.6 (d, *J* = 1.4 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -116.78. HRMS (ESI) Calcd for C₁₄H₁₅FO [M+H]⁺ 219.1180, found 219.1181; IR (cm⁻¹): 2961, 2925, 2855, 1725, 1605, 1596, 1470, 1447, 1165, 1110, 884, 845.

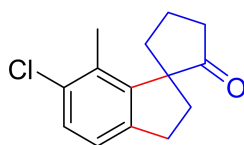
5'-chloro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one
(3h)



Colorless oil (51%, 23.7 mg): ¹H NMR (400 MHz, CDCl₃) δ 7.04 (s, 1H), 6.96 (s, 1H), 3.04 – 2.86 (m, 2H), 2.55 – 2.39 (m, 2H), 2.27 – 1.84 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 222.1, 146.8, 142.2, 134.8, 133.1, 128.8,

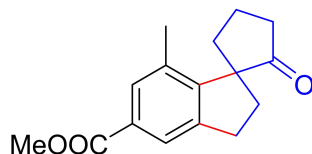
122.2, 62.0, 38.1, 37.6, 34.5, 30.8, 20.5, 19.4. HRMS (ESI) Calcd for $C_{14}H_{15}ClO$ $[M+H]^+$ 235.0884, found 235.0885; IR (cm^{-1}): 2957, 2867, 1730, 1589, 1461, 1447, 1309, 1164, 889, 856, 842.

6'-chloro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3i)



Colorless oil (47%, 22.2 mg): 1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.9 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 3.04 – 2.83 (m, 2H), 2.54 – 2.46 (m, 2H), 2.26 – 2.08 (m, 7H), 2.07 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 222.1, 145.6, 143.5, 133.2, 131.3, 128.5, 122.7, 63.1, 38.0, 37.8, 34.6, 30.6, 20.4, 17.3. HRMS (ESI) Calcd for $C_{14}H_{15}ClO$ $[M+H]^+$ 235.0884, found 235.0885; IR (cm^{-1}): 2955, 2869, 1735, 1589, 1450, 1269, 1165, 1136, 1120, 1075, 811.

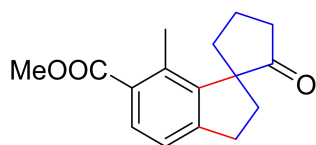
Methyl-7'-methyl-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-5'-carboxylate (3j)



Yellow oil (47%, 24.1 mg): 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.67 (s, 1H), 3.88 (s, 3H), 3.12 – 2.86 (m, 2H), 2.56 – 2.41 (m, 2H), 2.26 – 2.03 (m, 8H), 2.01 – 1.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.8, 167.2, 149.0, 145.3, 133.4, 130.4, 129.6, 123.1, 62.5, 51.9, 38.2, 37.5, 34.4, 30.6,

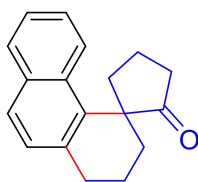
20.6, 19.5. HRMS (ESI) Calcd for $C_{16}H_{18}O_3$ $[M+H]^+$ 259.1329, found 259.1331; IR (cm^{-1}): 2953, 2870, 1731, 1719, 1607, 1586, 1450, 1436, 1338, 1297, 1231, 1210, 1164, 1100, 1005, 772.

Methyl-7'-methyl-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-6'-carboxylate (3k)



colorless oil (61%, 31.4 mg): 1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.9 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 3.85 (s, 3H), 3.08 – 2.91 (m, 2H), 2.58 – 2.46 (m, 2H), 2.30 (s, 3H), 2.26 – 2.05 (m, 5H), 2.03 – 1.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.2, 168.3, 149.2, 145.4, 135.3, 130.3, 129.3, 121.62, 62.6, 51.7, 37.8, 37.4, 34.4, 31.1, 20.4, 18.4. HRMS (ESI) Calcd for $C_{16}H_{18}O_3$ $[M+H]^+$ 259.1329, found 259.1326.

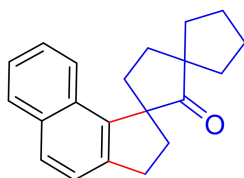
2',3'-dihydro-1'H-spiro[cyclopentane-1,4'-phenanthren]-2-one (3m)



White solid (23%, 11.4 mg): m.p. 138-140 $^{\circ}C$, 1H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.27 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 3.11 – 2.99 (m, 1H), 2.99 – 2.83 (m, 2H), 2.79 – 2.58 (m, 2H), 2.37 – 2.13 (m, 3H), 2.10 – 1.95 (m, 2H), 1.93 – 1.80 (m, 1H), 1.78 – 1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 223.0, 137.1, 133.6, 132.9, 130.3, 129.5, 128.2, 127.6, 125.3, 124.8, 124.3, 54.3,

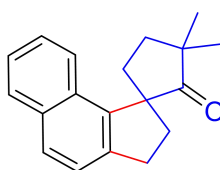
36.7, 36.4, 32.7, 31.3, 18.8, 18.4. HRMS (ESI) Calcd for $C_{18}H_{18}O$ $[M+H]^+$ 251.1430, found 251.1430; IR (cm^{-1}): 3048, 2934, 2733, 1510, 1456, 1162, 1134, 806, 780, 741.

2'',3''-dihydrodispiro[cyclopentane-1,1'-cyclopentane-3',1''-cyclopenta[*a*]naphthalen]-2'-one (3n)



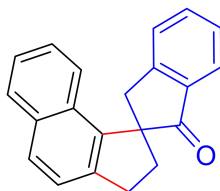
Yellow oil (40%, 23.3 mg): 1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.43 – 7.31 (m, J = 5.1, 3.6 Hz, 4H), 3.24 – 3.03 (m, 2H), 2.42 – 2.30 (m, 1H), 2.30 – 2.20 (m, 2H), 2.19 – 2.04 (m, 4H), 2.03 – 1.90 (m, 3H), 1.89 – 1.73 (m, 3H), 1.65 – 1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 226.7, 142.7, 139.9, 133.6, 129.2, 128.9, 128.6, 125.9, 124.5, 124.0, 122.9, 63.8, 56.7, 39.6, 39.4, 37.8, 35.9, 32.5, 31.7, 25.7, 25.6. HRMS (ESI) Calcd for $C_{21}H_{22}O$ $[M+H]^+$ 291.1743, found 291.1745; IR (cm^{-1}): 3051, 2948, 2067, 1727, 1593, 1516, 1447, 1380, 1319, 1142, 1030, 873, 810, 784, 740.

3,3-dimethyl-2',3'-dihydrospiro[cyclopentane-1,1'-cyclopenta[*a*]naphthalen]-2-one (3o)



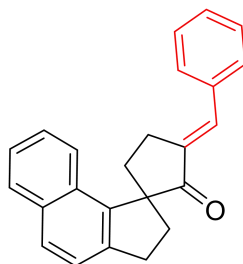
colorless oil (32%, 17.0 mg): ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.81 (m, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.47 – 7.29 (m, 4H), 3.24 – 3.01 (m, 2H), 2.44 – 2.16 (m, 3H), 2.14 – 1.95 (m, 3H), 1.46 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 225.9, 142.6, 139.5, 133.6, 129.2, 128.9, 128.7, 125.9, 124.5, 123.7, 122.9, 63.9, 45.1, 38.1, 36.1, 31.6, 31.5, 26.9, 26.4. HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ $[\text{M}+\text{H}]^+$ 265.1587, found 265.1584.

2,3-dihydrospiro[cyclopenta[α]naphthalene-1,2'-inden]-1'(3'H)-one (3p)



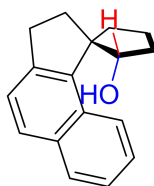
White solid (22%, 12.6 mg): m.p. 168-170 $^{\circ}\text{C}$, ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.58 – 7.48 (m, 2H), 7.43 (d, J = 8.3 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 3.50 (q, J = 17.5 Hz, 2H), 3.34 – 3.19 (m, 2H), 2.74 – 2.60 (m, 1H), 2.26 – 2.15 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.0, 152.6, 143.2, 140.1, 136.5, 135.3, 133.5, 129.1, 129.0, 128.8, 127.9, 126.8, 126.5, 124.8, 124.7, 123.3, 123.1, 62.7, 41.3, 41.0, 32.3. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{16}\text{O}$ $[\text{M}+\text{H}]^+$ 285.1274, found 285.1277; IR (cm^{-1}): 2956, 2923, 2850, 1738, 1711, 1607, 1463, 1374, 1241, 1094, 1047, 808, 734.

(E)-3'-benzylidene-2,3-dihydrospiro[cyclopenta[α]naphthalene-1,1'-cyclopentan]-2'-one (5)



White solid (63%, 40.9 mg): m.p. 162-164 °C ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.82 (m, 1H), 7.75 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 7.1 Hz, 3H), 7.48 (t, J = 7.4 Hz, 2H), 7.45 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 3.35 – 3.00 (m, 4H), 2.43 – 2.30 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.6, 142.7, 140.4, 135.9, 135.6, 134.3, 133.7, 130.8, 129.6, 129.1, 128.8, 128.7, 126.2, 124.6, 124.3, 122.9, 62.7, 38.0, 32.5, 31.9, 27.2. HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{20}\text{O}$ $[\text{M}+\text{H}]^+$ 325.1587, found 325.1587; IR (cm^{-1}): 3054, 2934, 2870, 2848, 1709, 1624, 1573, 1448, 1185, 1168, 1150, 899, 812, 780, 742, 692.

2,3-dihydrospiro[cyclopenta[*a*]naphthalene-1,1'-cyclopentan]-2'-ol (6)

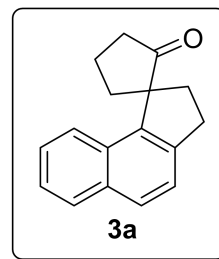
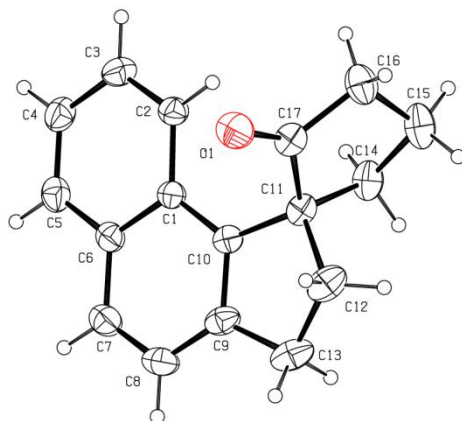


In a 5 mL tube, compound **3a** (0.2 mmol, 47.2 mg) was dissolved in MeOH (2 mL), and NaBH_4 (0.4 mmol, 15 mg) was added, the mixture was stirred overnight. The ice-water was added, extracted with ethyl acetate, dried (Na_2SO_4) and concentrated. The residue was purified with chromatography column on silica gel. White solid (86%, 41.1 mg): m.p. 90-92 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, J = 8.5 Hz, 1H), 7.82 (d, J =

7.9 Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 7.49 – 7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 4.14 (d, $J = 3.5$ Hz, 1H), 3.11 – 3.00 (m, 2H), 2.98 – 2.87 (m, 1H), 2.37 – 2.22 (m, 1H), 2.20 – 2.11 (m, 1H), 2.11 – 1.97 (m, 3H), 1.94 – 1.84 (m, 1H), 1.78 – 1.69 (m, 1H), 1.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 139.5, 133.6, 132.0, 128.9, 128.4, 125.8, 125.3, 124.5, 123.4, 79.4, 62.9, 42.8, 37.6, 34.1, 31.4, 23.8. HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ $[\text{M}+\text{K}]^+$ 277.0989, found 277.0989; IR (cm^{-1}): 3537, 3435, 3048, 2946, 2874, 1620, 1592, 1451, 1439, 1374, 1102, 1089, 1028, 813, 780, 743.

5. The crystal structure of product 3a

Crystallographic data for compound **3a** (CCDC - 1530948) has been deposited with Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk)



The ellipsoid contour percent probability level is 30% in the caption of the thermal ellipsoid plot.

Bond precision: C-C = 0.0042 Å Wavelength=0.71073

Cell: a=7.7380(5) b=11.6560(8) c=14.0895(8)
alpha=90 beta=90 gamma=90

Temperature: 299 K

	Calculated	Reported
Volume	1270.79(14)	1270.79(14)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C17 H16 O	C17 H16 O
Sum formula	C17 H16 O	C17 H16 O
Mr	236.30	236.30
Dx, g cm ⁻³	1.235	1.235
Z	4	4
Mu (mm ⁻¹)	0.075	0.075
F000	504.0	504.0
F000'	504.21	
h,k,lmax	9, 14, 17	9, 14, 17
Nref	2517[1466]	2423
Tmin,Tmax	0.981,0.989	0.186,1.000
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.186 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.65/0.96

Theta(max)= 26.010

R(reflections)= 0.0553(1723)

wR2(reflections)= 0.1329(2423)

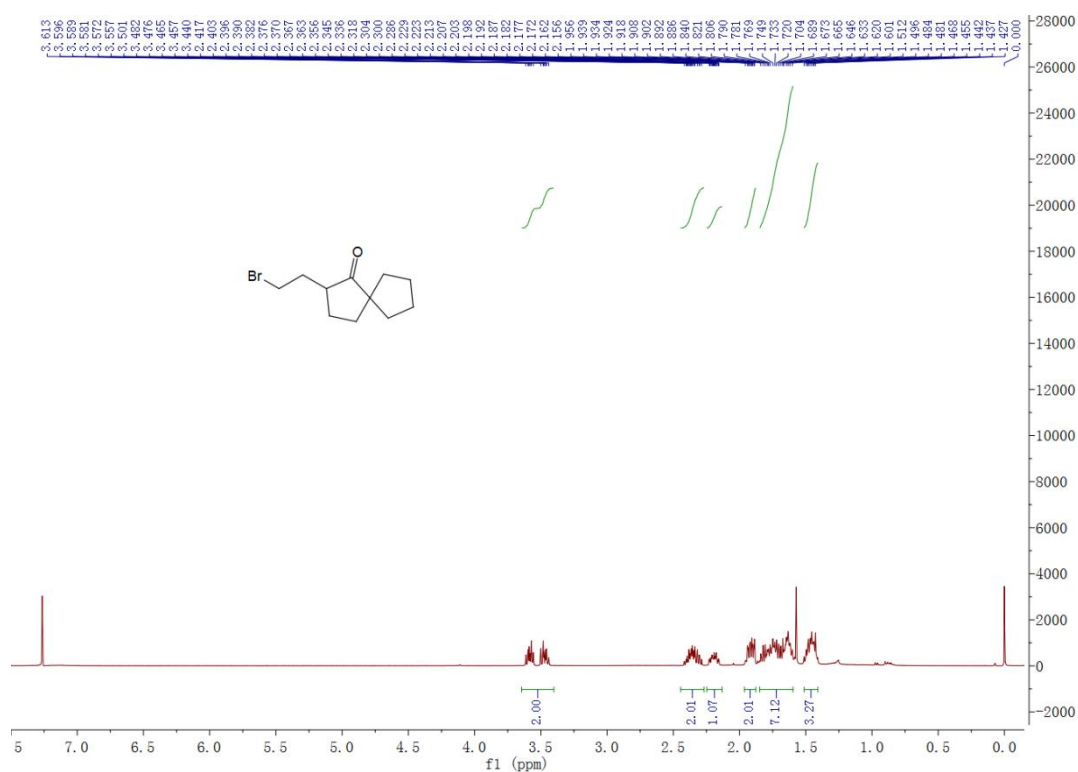
S = 1.109

Npar= 163

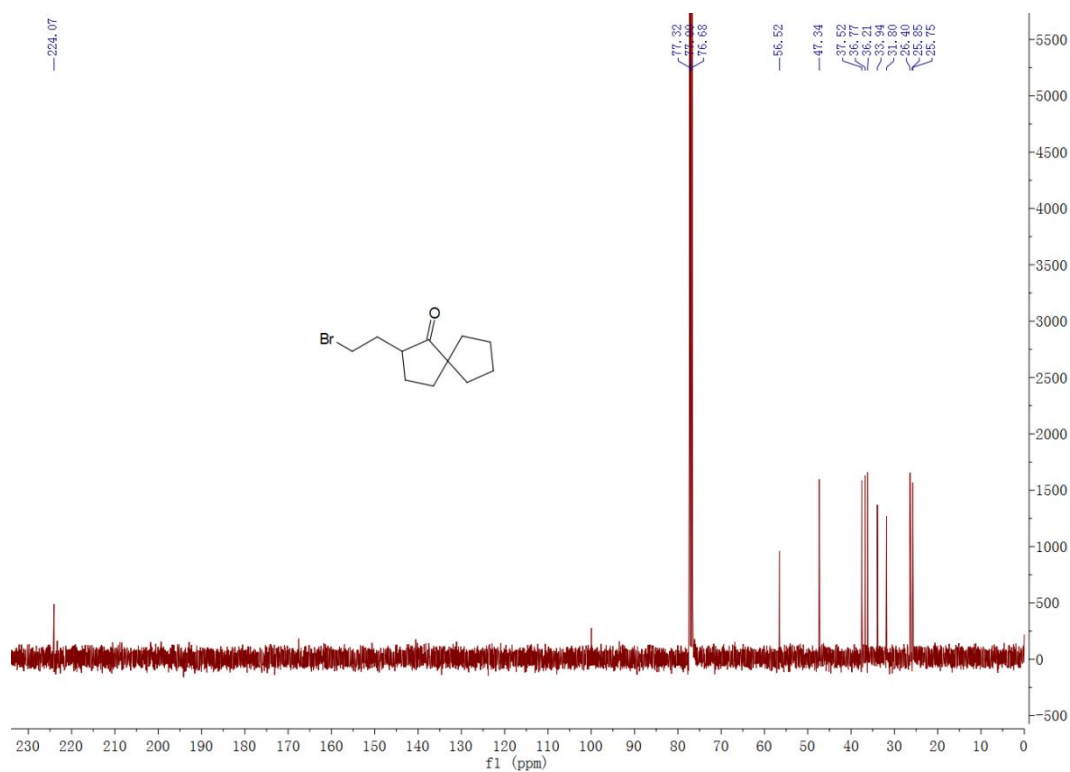
6.NMR Spectroscopic Data

2-(2-bromoethyl)spiro[4.4]nonan-1-one (2n)

^1H NMR (400 MHz, CDCl_3)

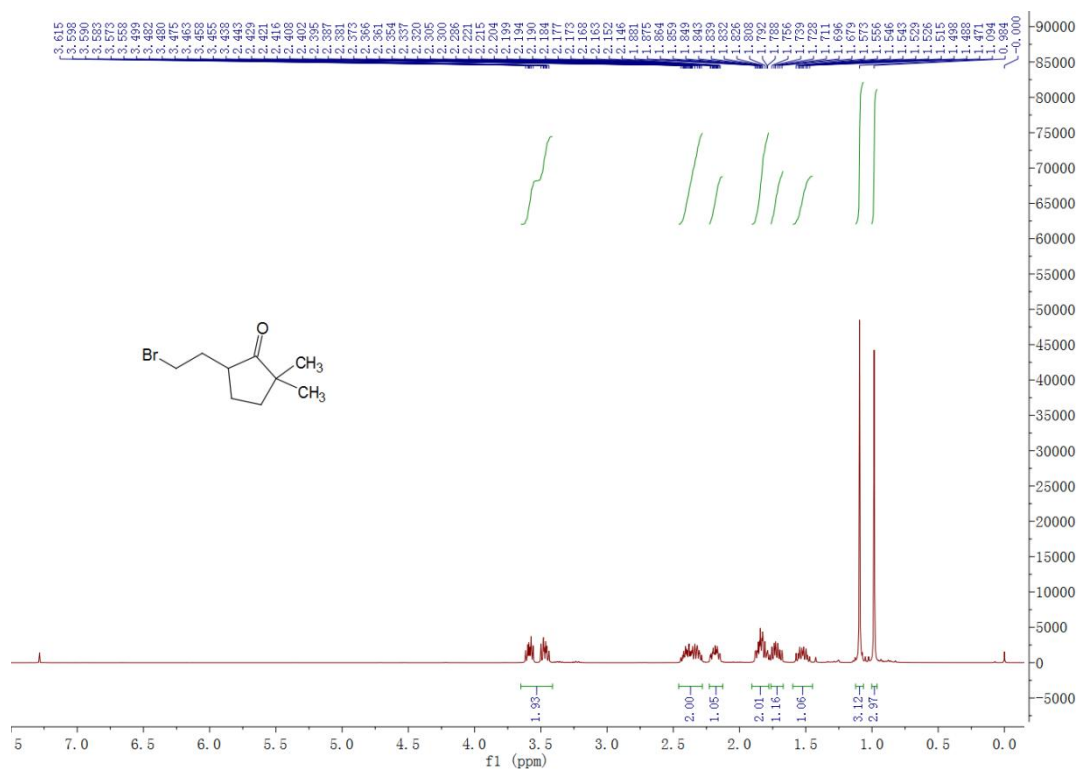


^{13}C NMR (100 MHz, CDCl_3)

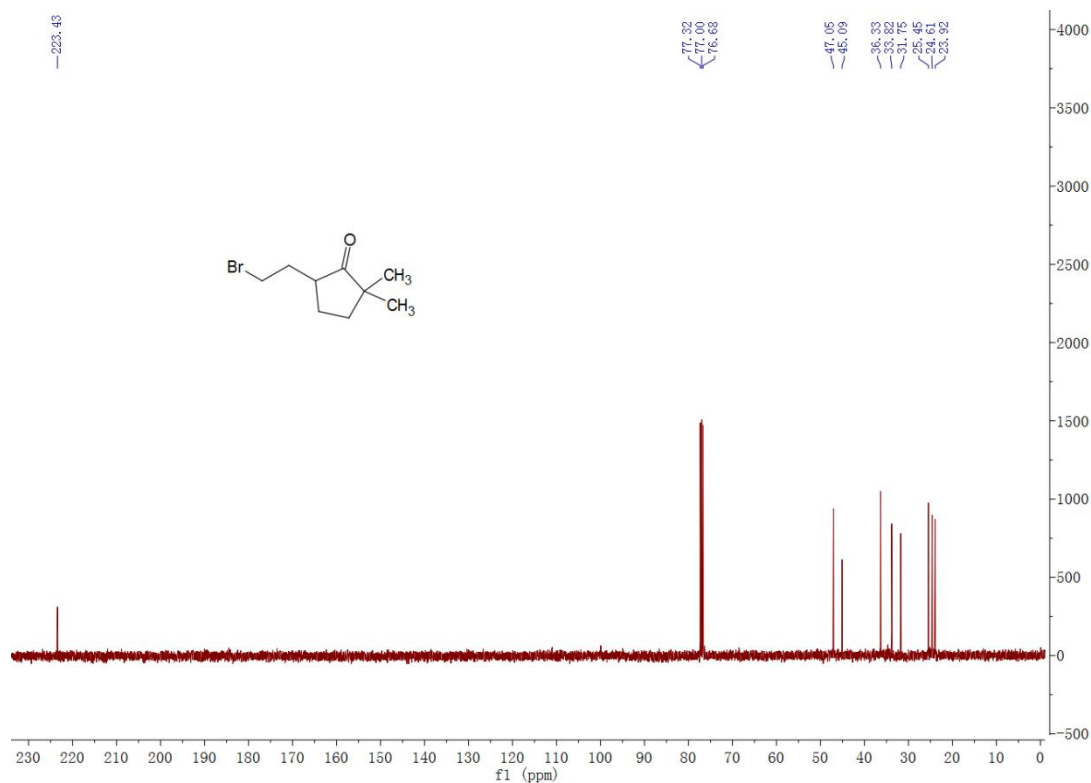


5-(2-bromoethyl)-2,2-dimethylcyclopentanone (2o)

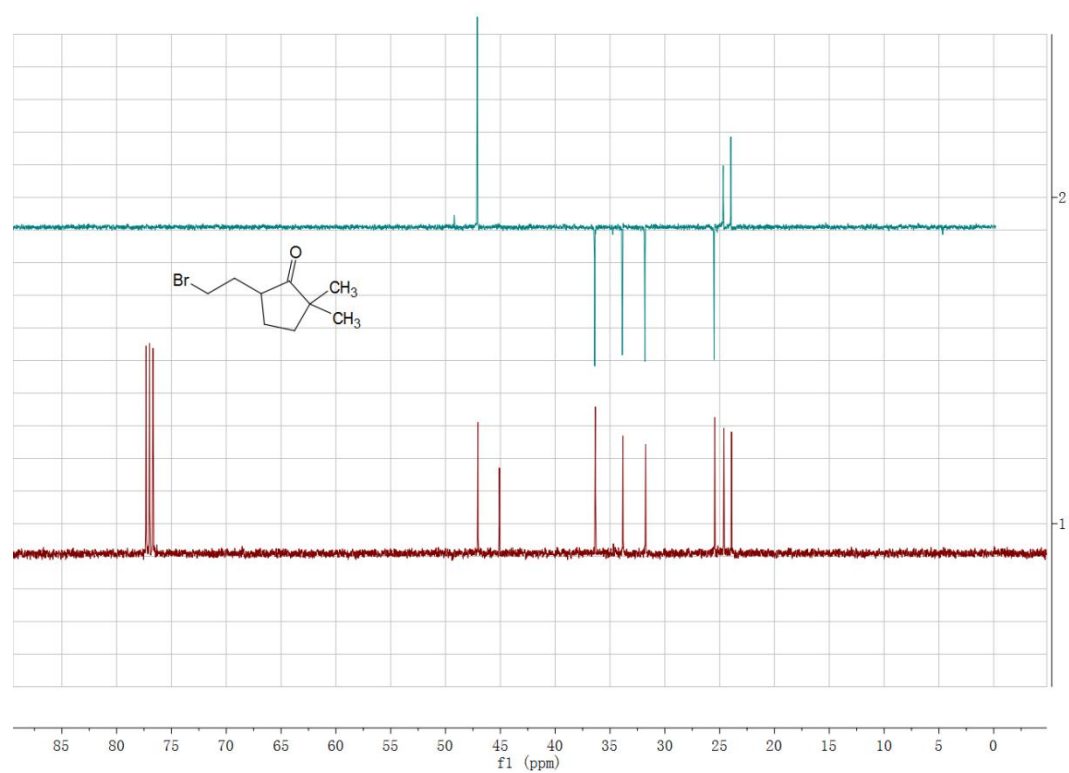
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

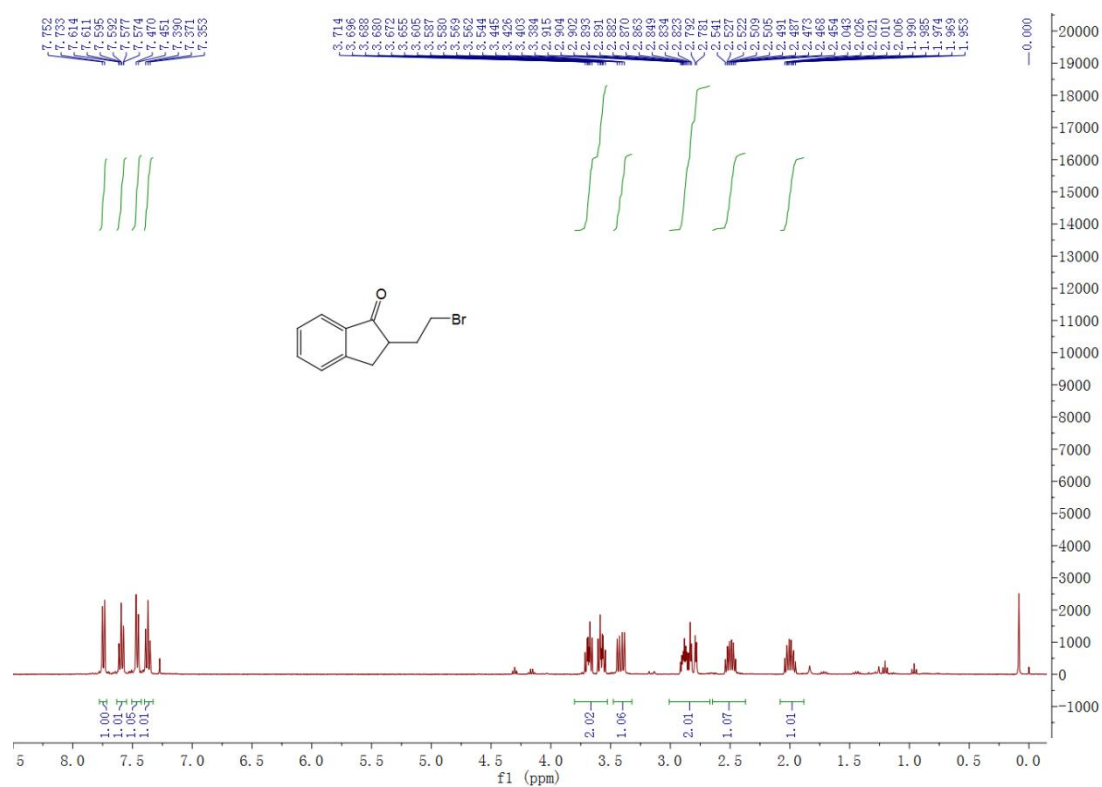


Dept-135



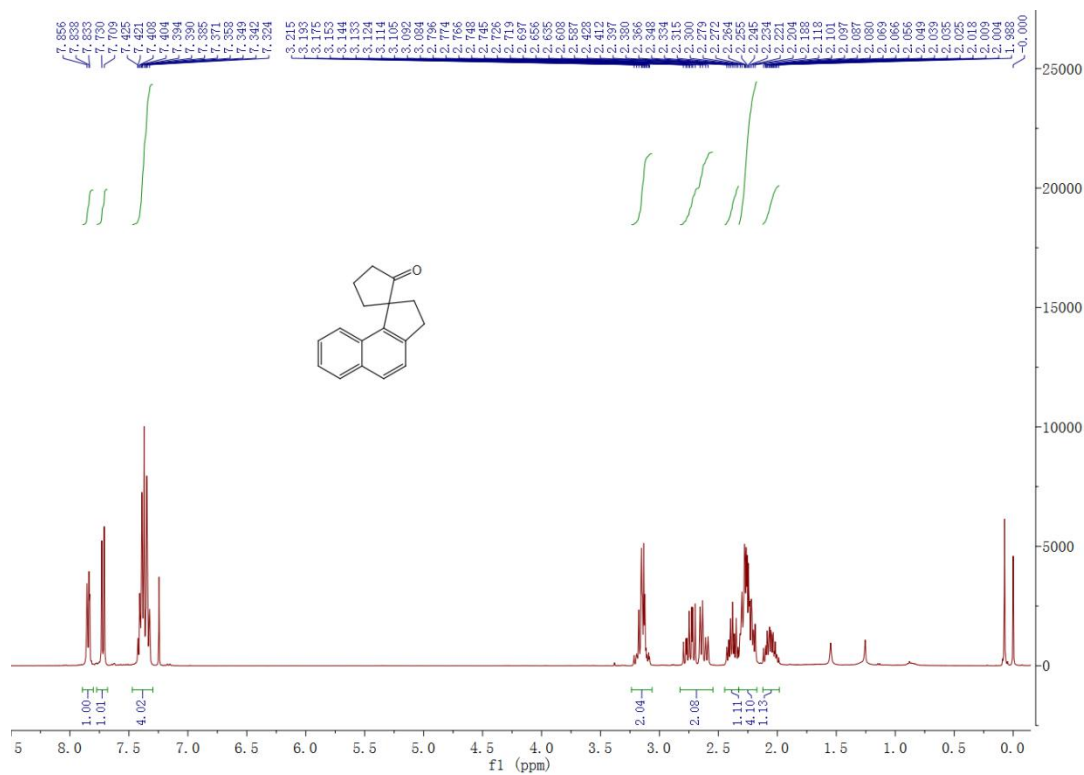
2-(2-bromoethyl)-2,3-dihydro-1H-inden-1-one (2p)

¹H NMR (400 MHz, CDCl₃)

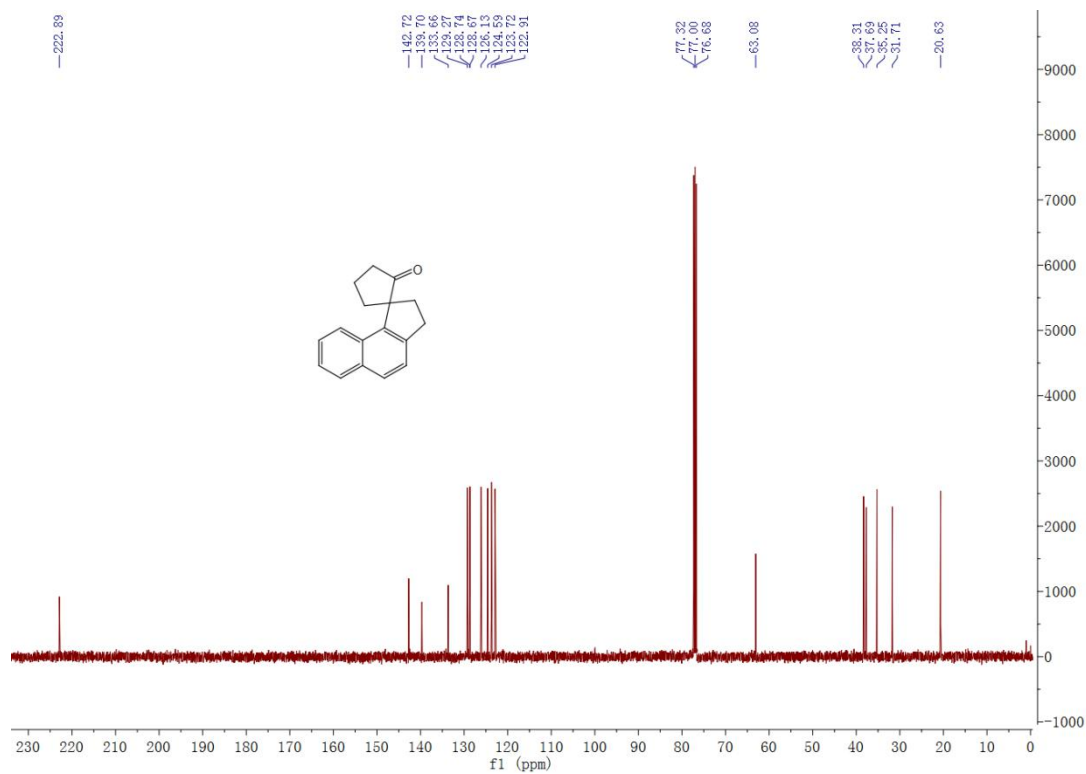


2,3-dihydrospiro[cyclopenta[*a*]naphthalene-1,1'-cyclopentan]-2'-one (3a)

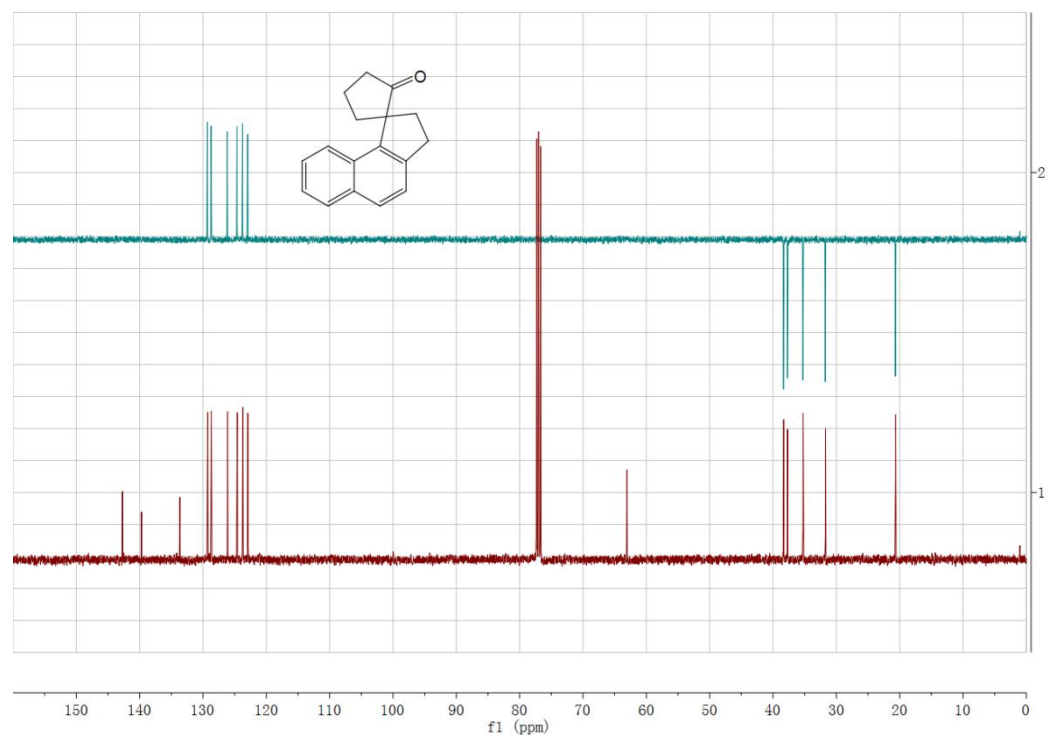
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

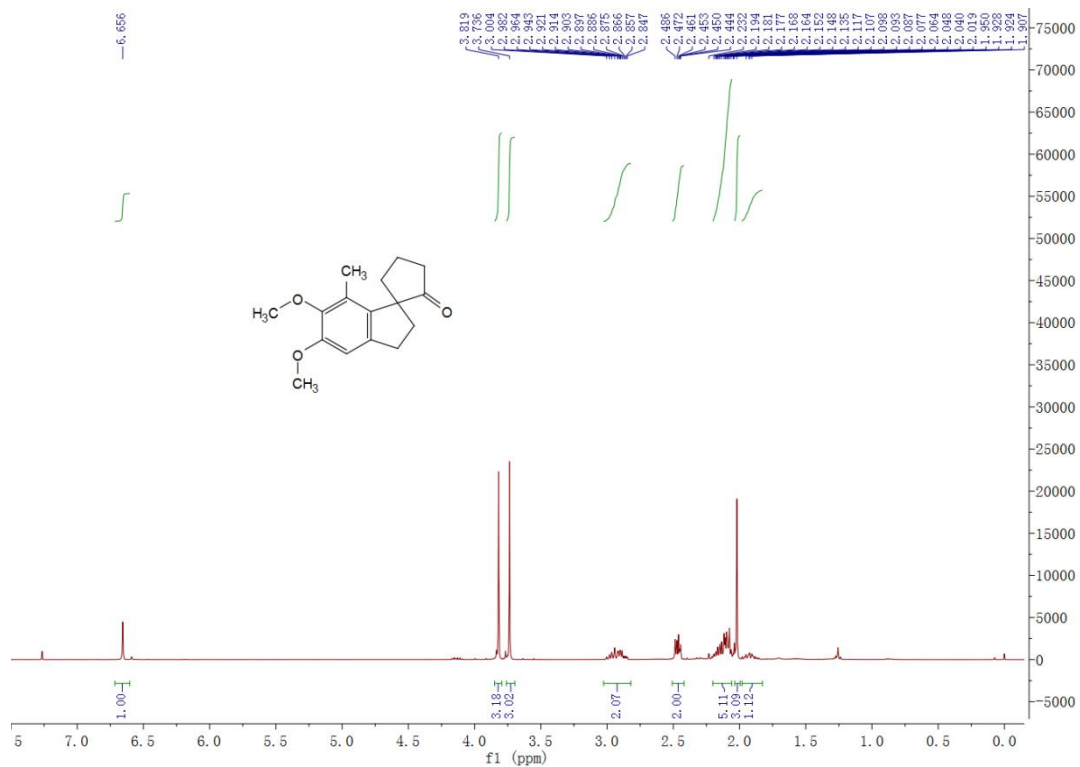


Dept-135

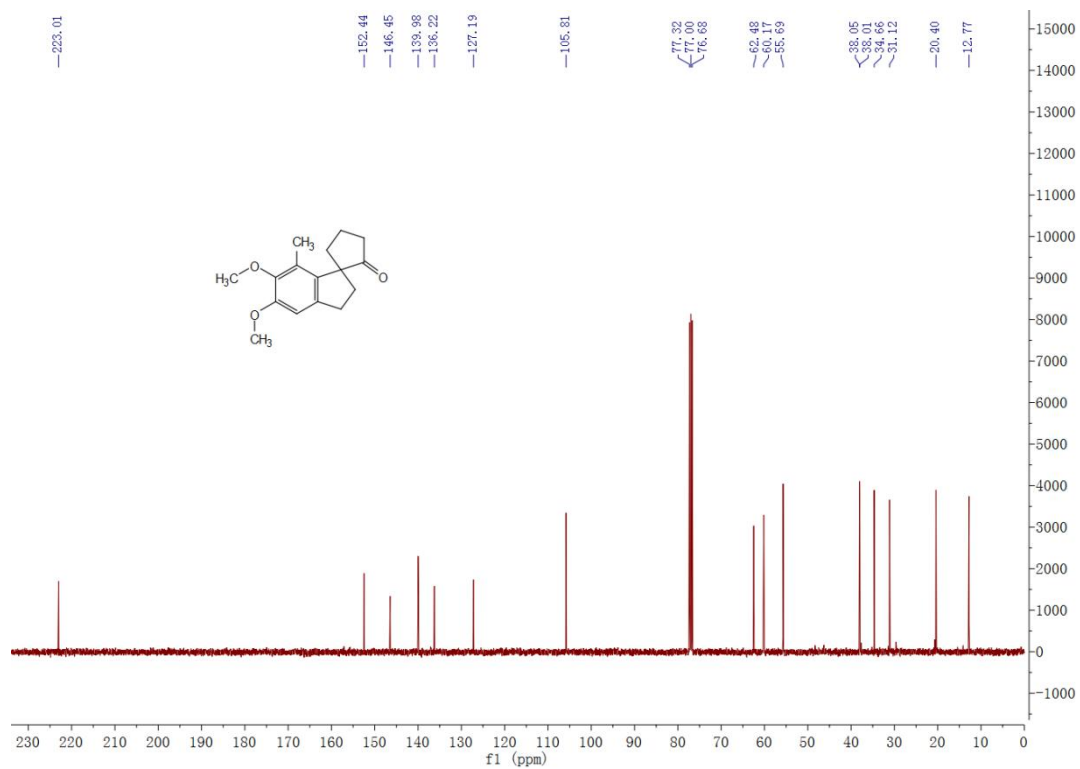


5',6'-dimethoxy-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3b)

^1H NMR (400 MHz, CDCl_3)

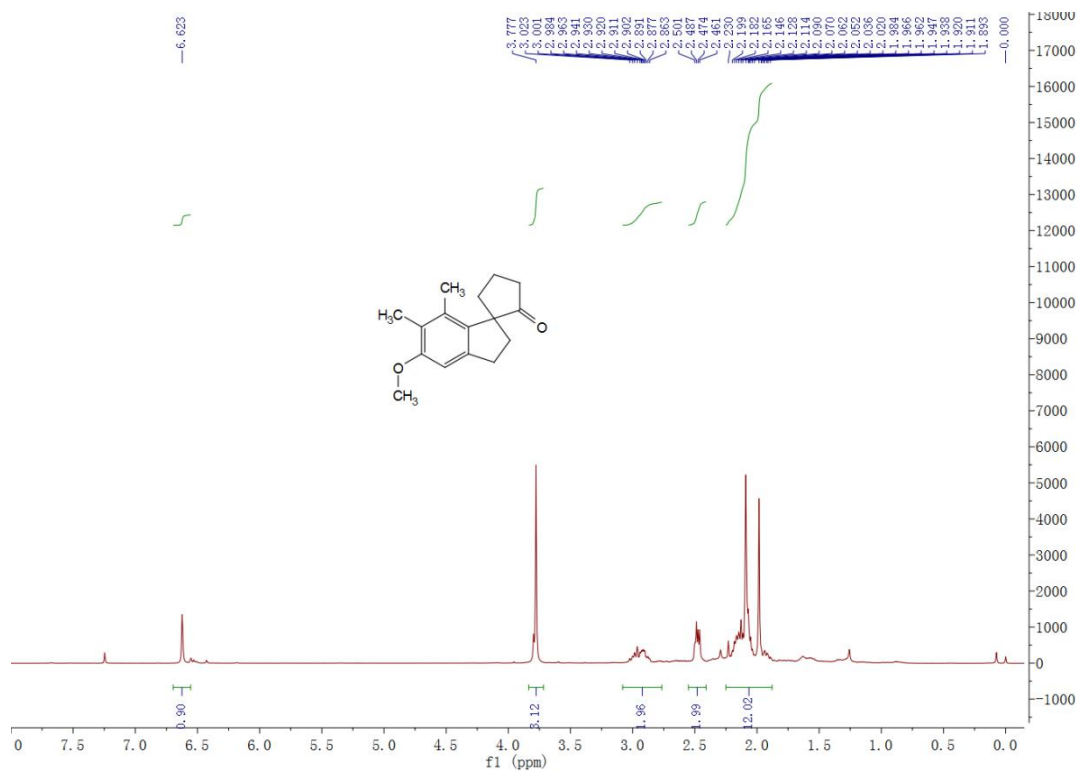


^{13}C NMR (100 MHz, CDCl_3)

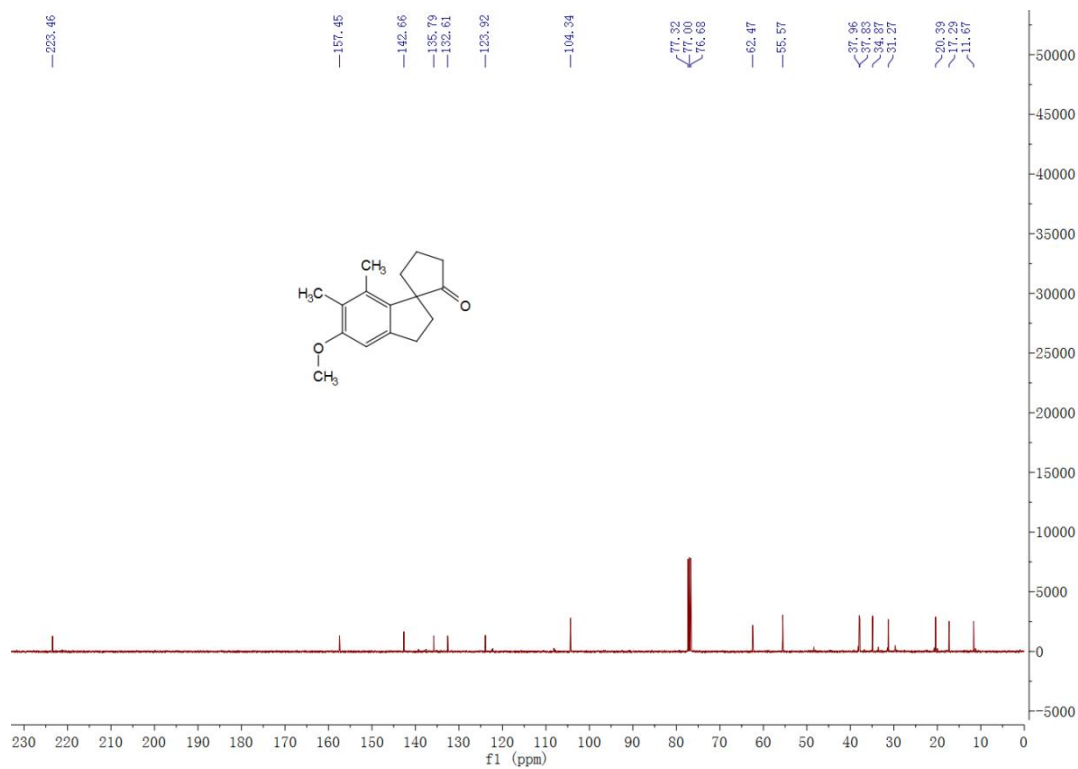


5'-methoxy-6',7'-dimethyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3c)

^1H NMR (400 MHz, CDCl_3)

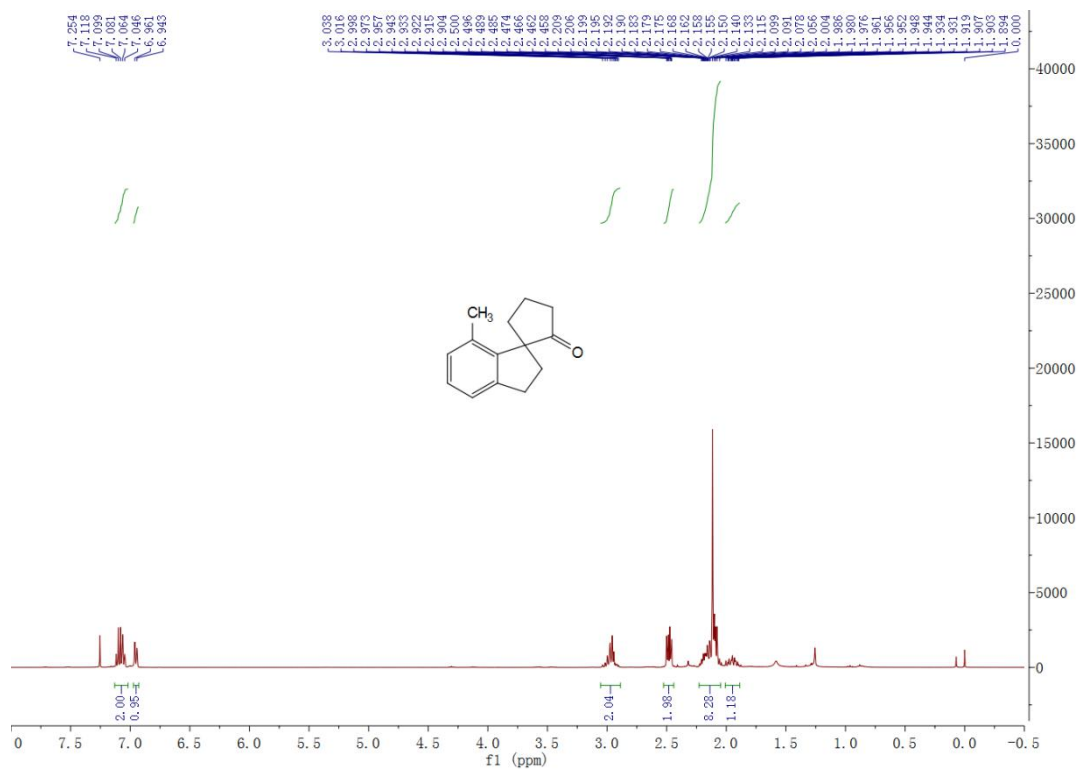


^{13}C NMR (100 MHz, CDCl_3)

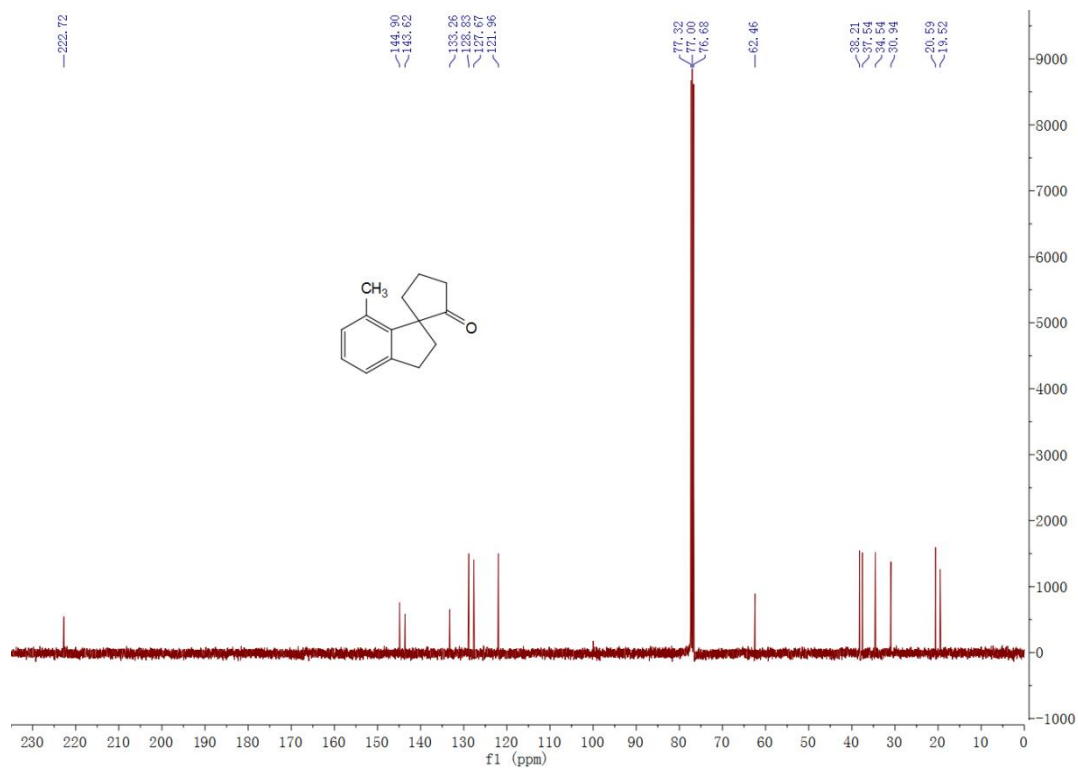


7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3d)

^1H NMR (400 MHz, CDCl_3)

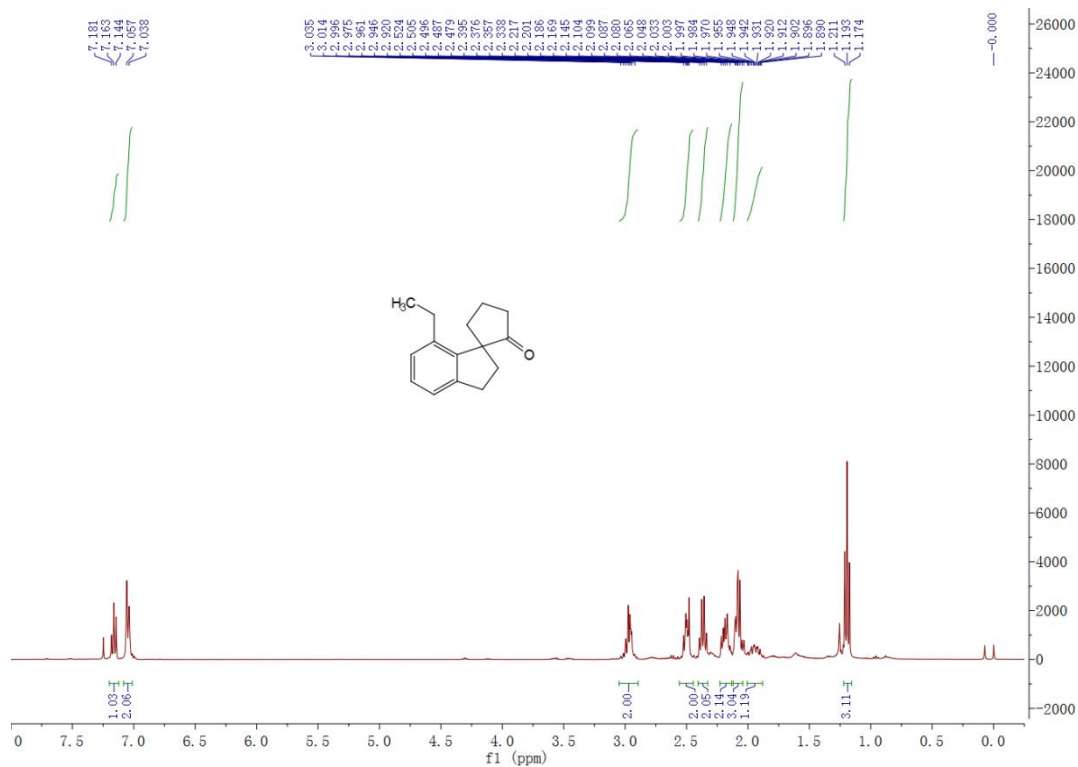


^{13}C NMR (100 MHz, CDCl_3)

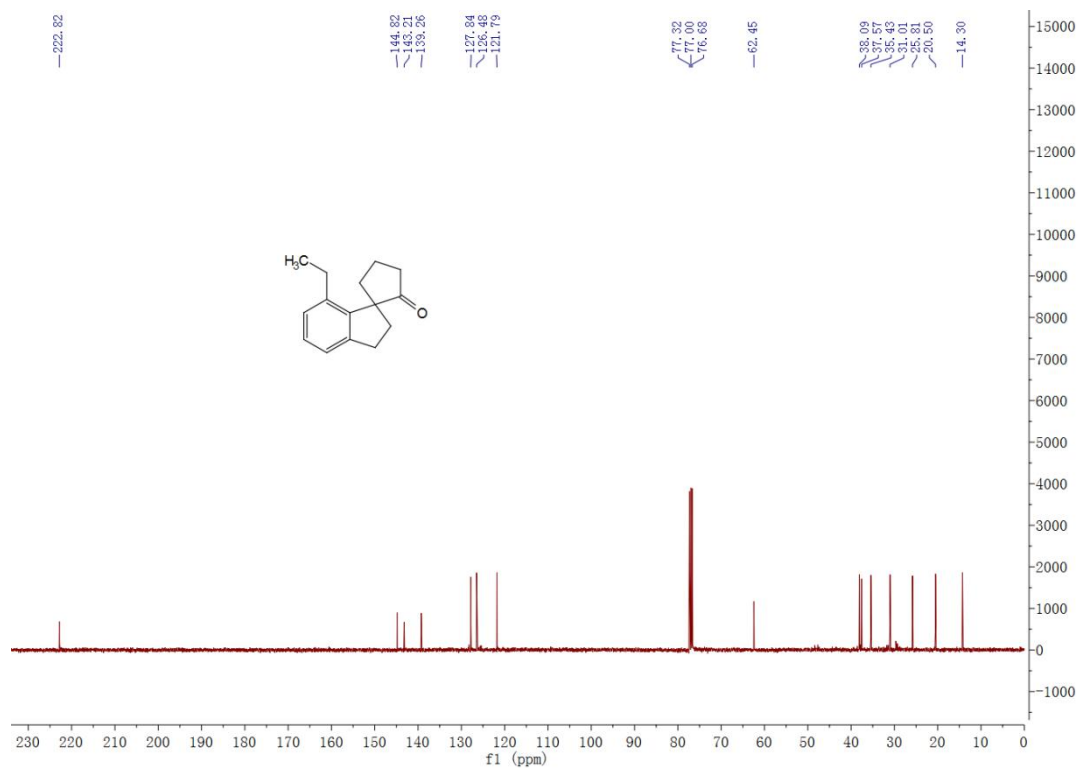


7'-ethyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3e)

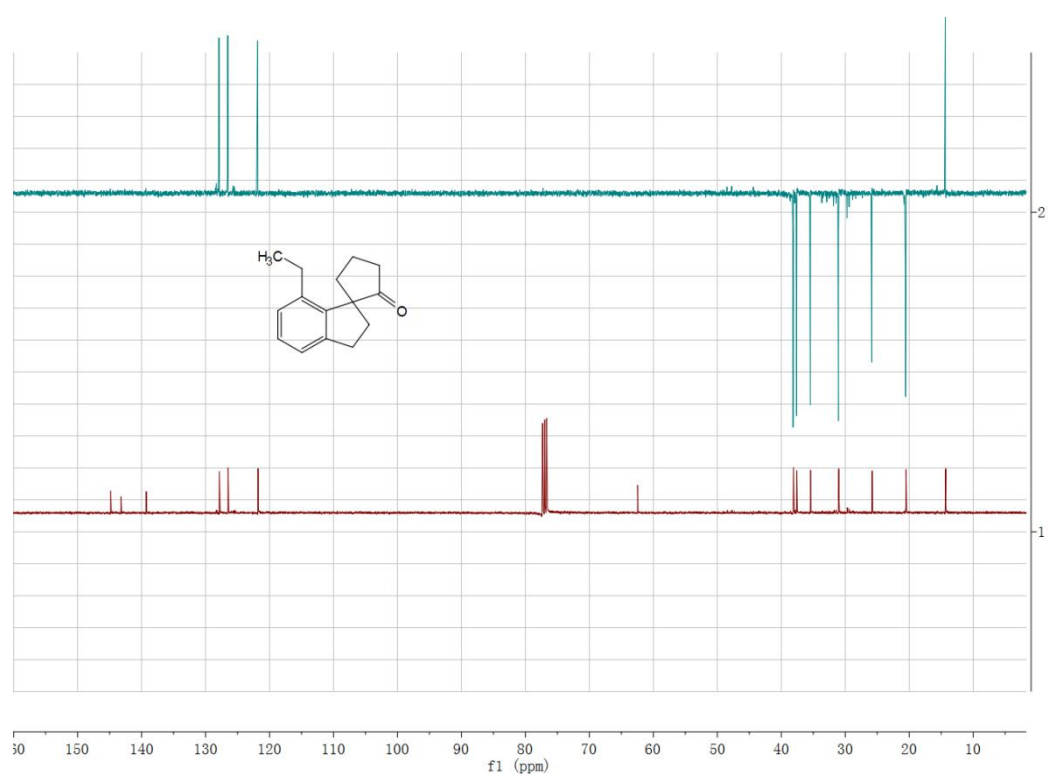
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

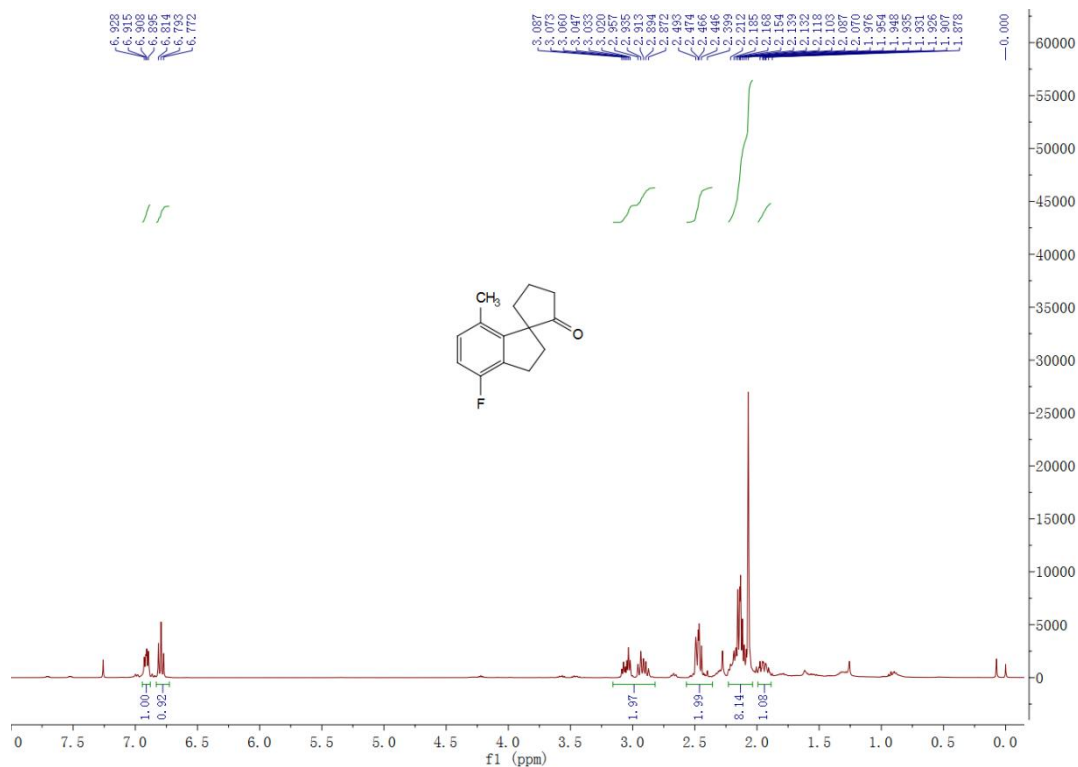


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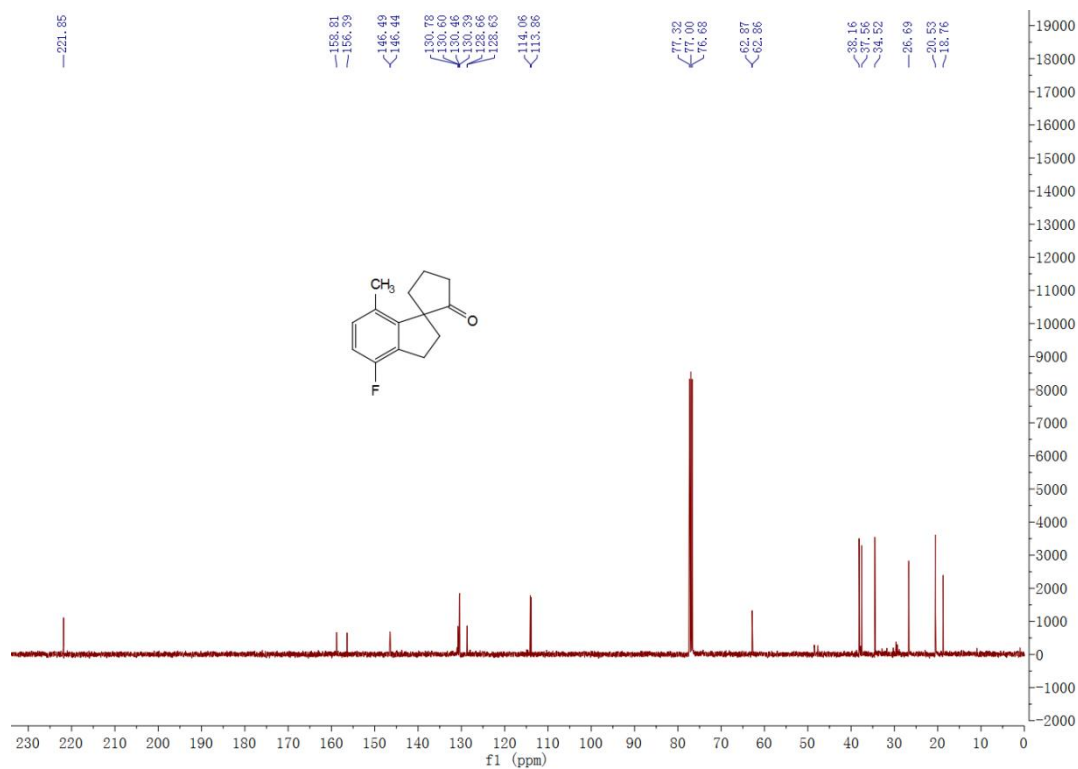


4'-fluoro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3f)

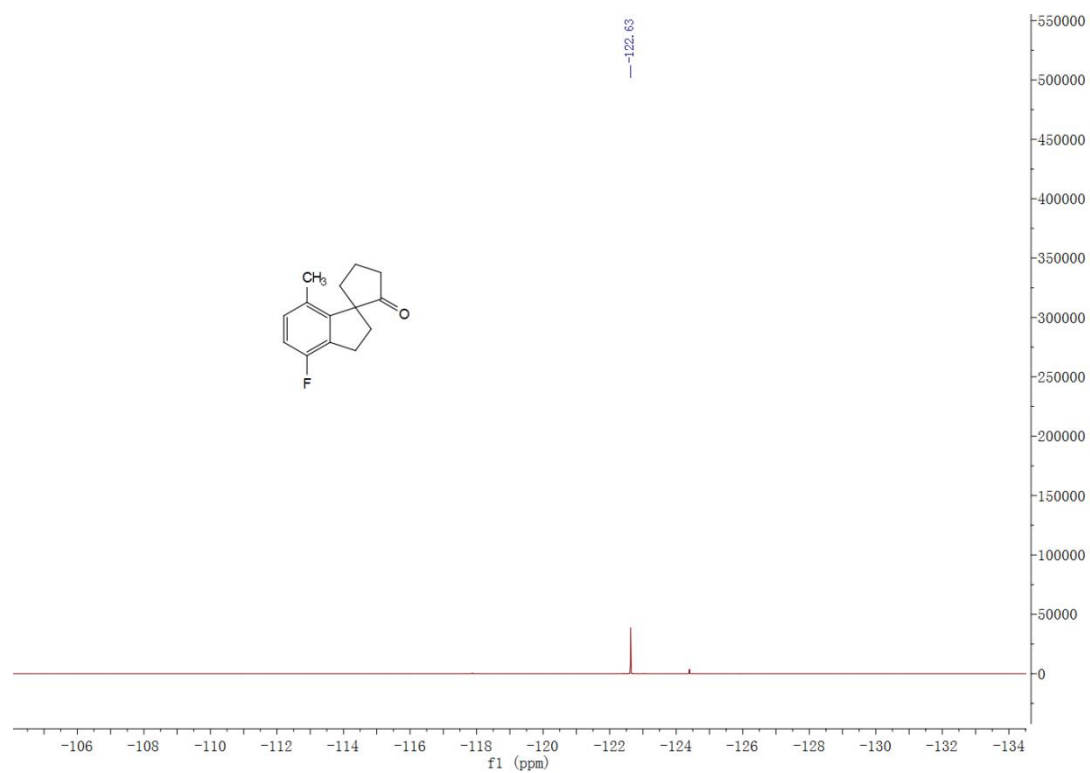
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (100 MHz, CDCl_3)

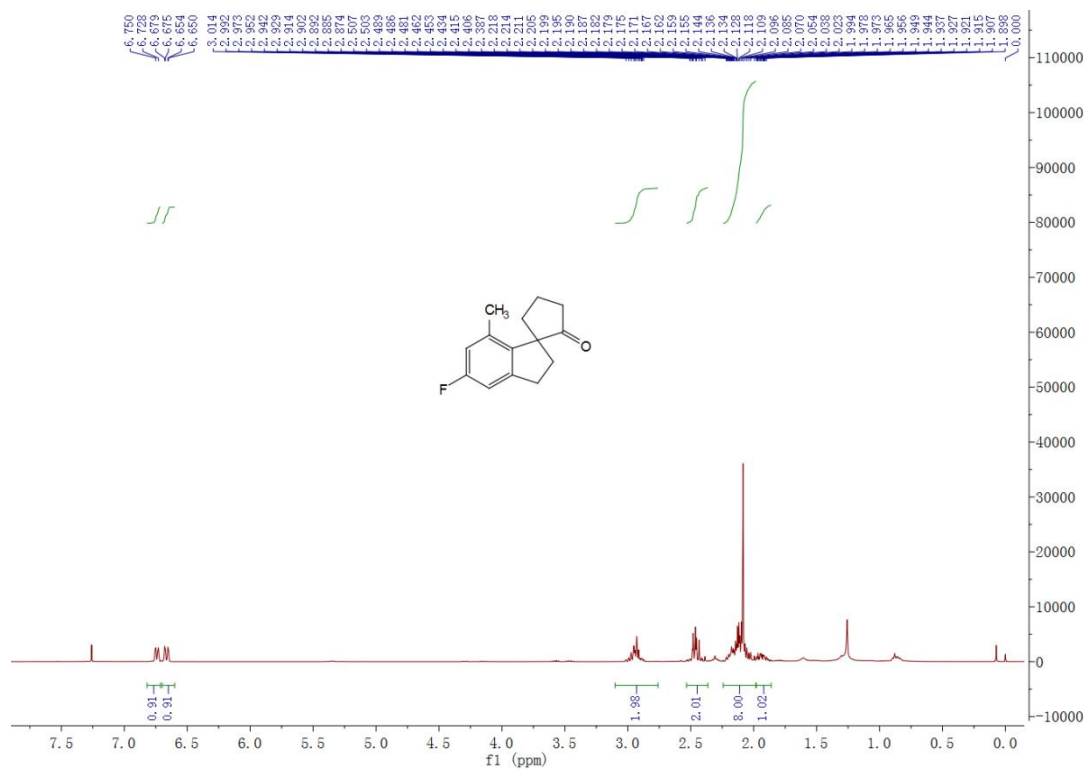


^{19}F NMR (376 MHz, CDCl_3)

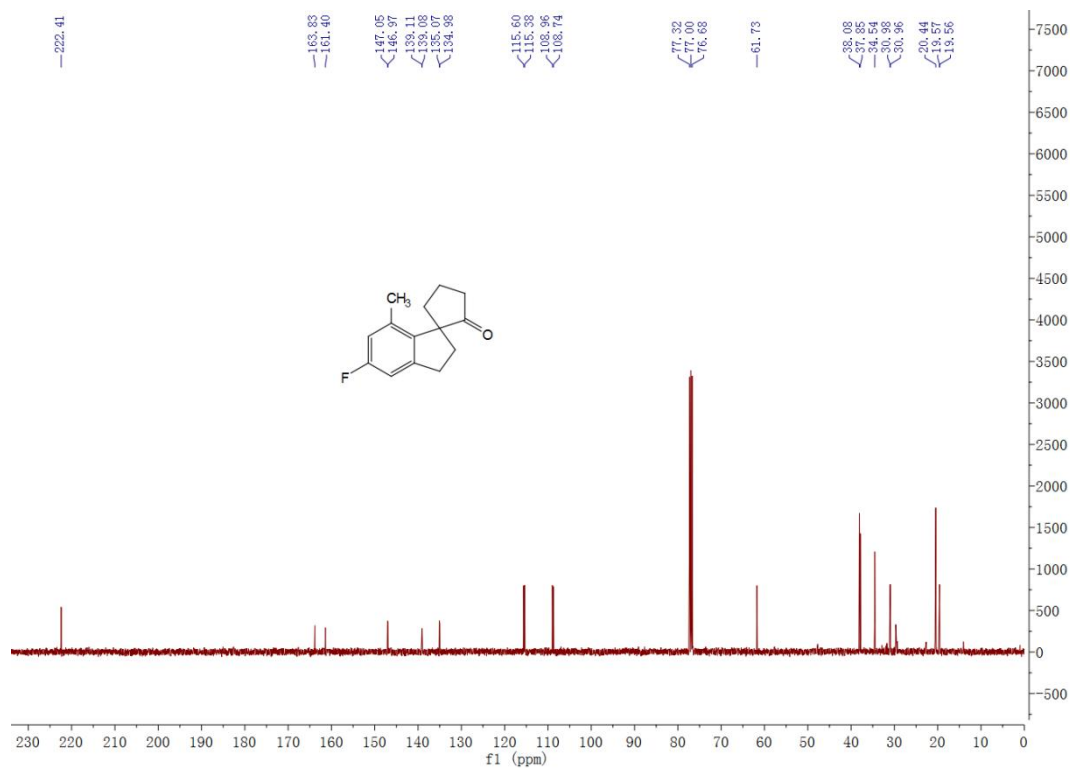


5'-fluoro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3g)

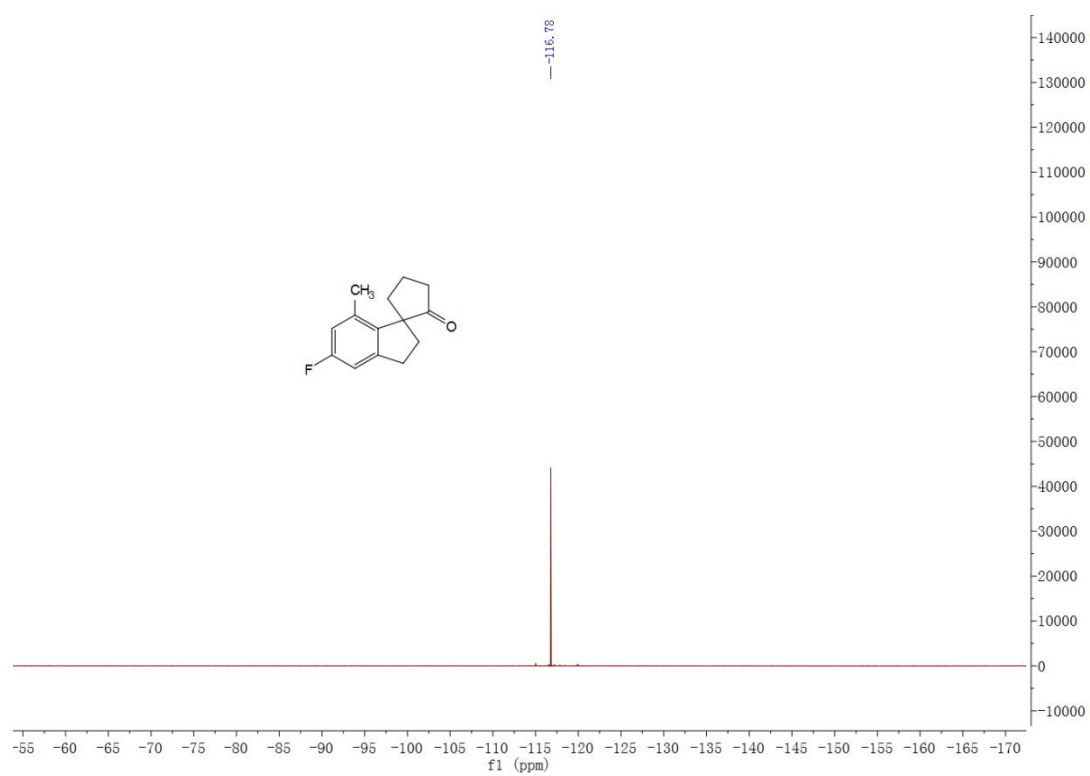
^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (100 MHz, CDCl_3)

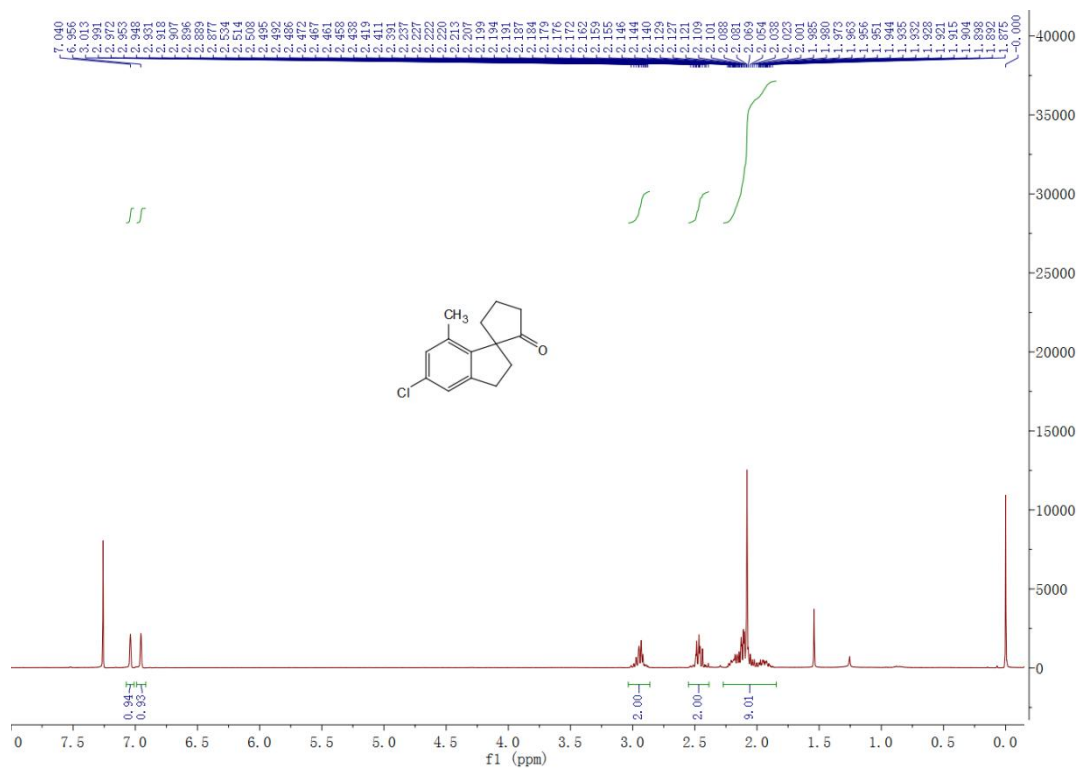


^{19}F NMR (376 MHz, CDCl_3)

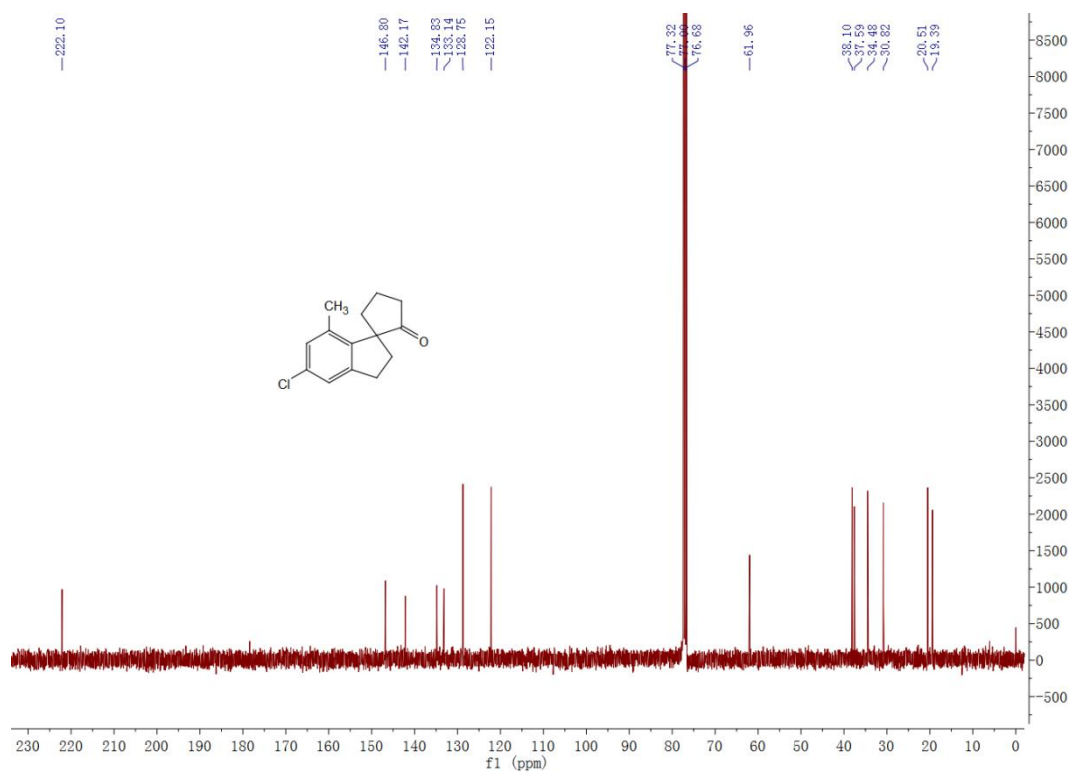


5'-chloro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3h)

^1H NMR (400 MHz, CDCl_3)

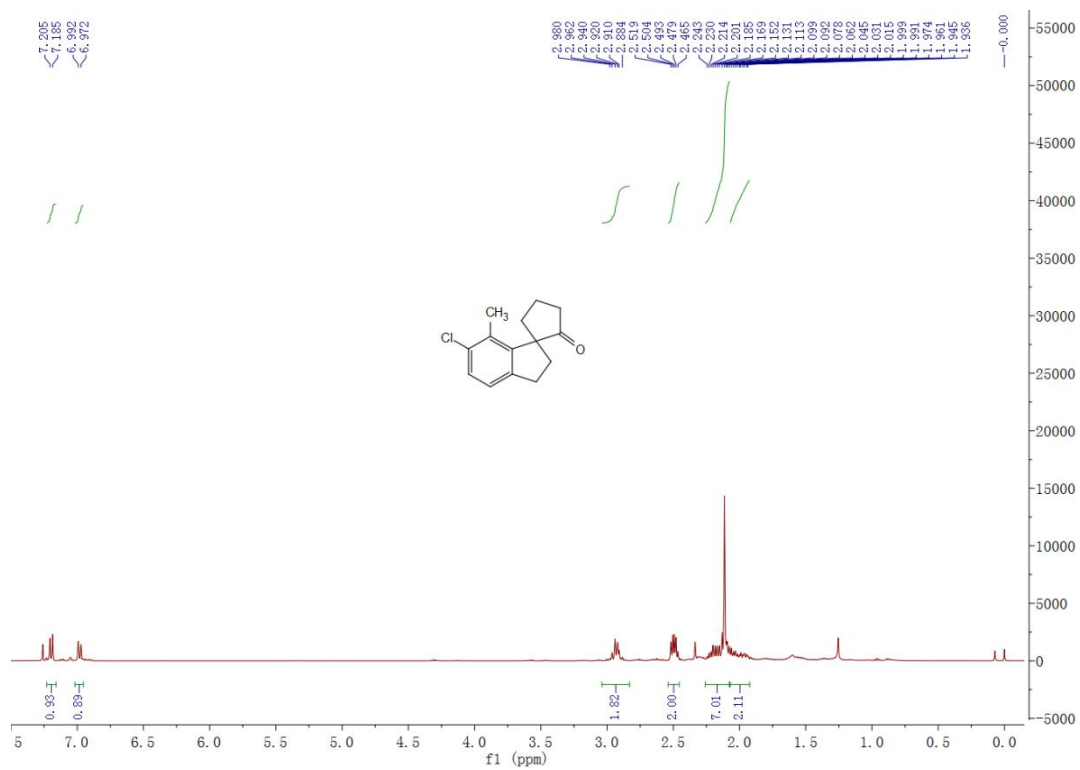


^{13}C NMR (100 MHz, CDCl_3)

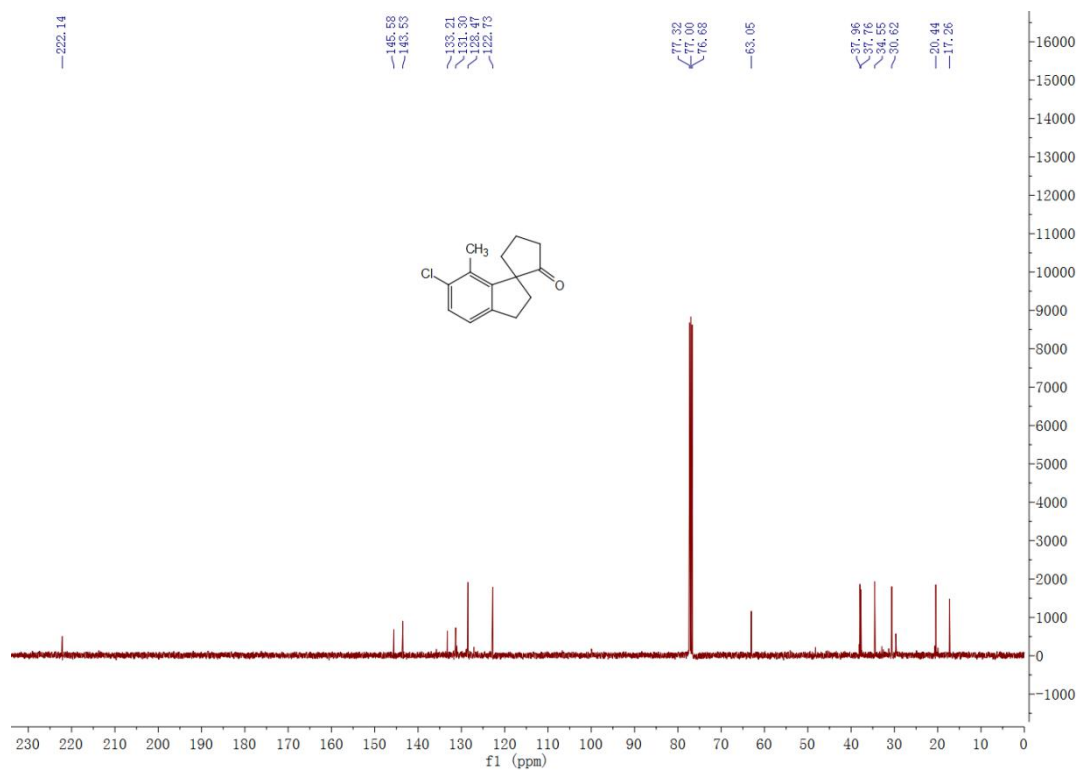


6'-chloro-7'-methyl-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3i)

^1H NMR (400 MHz, CDCl_3)

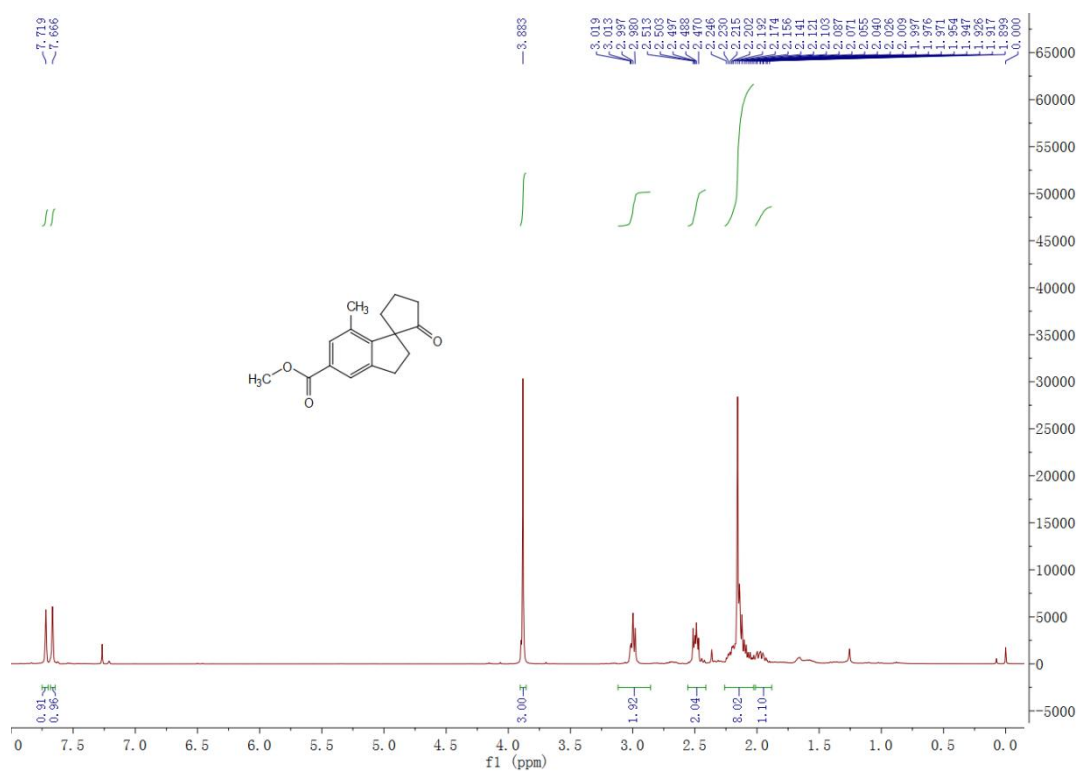


^{13}C NMR (100 MHz, CDCl_3)

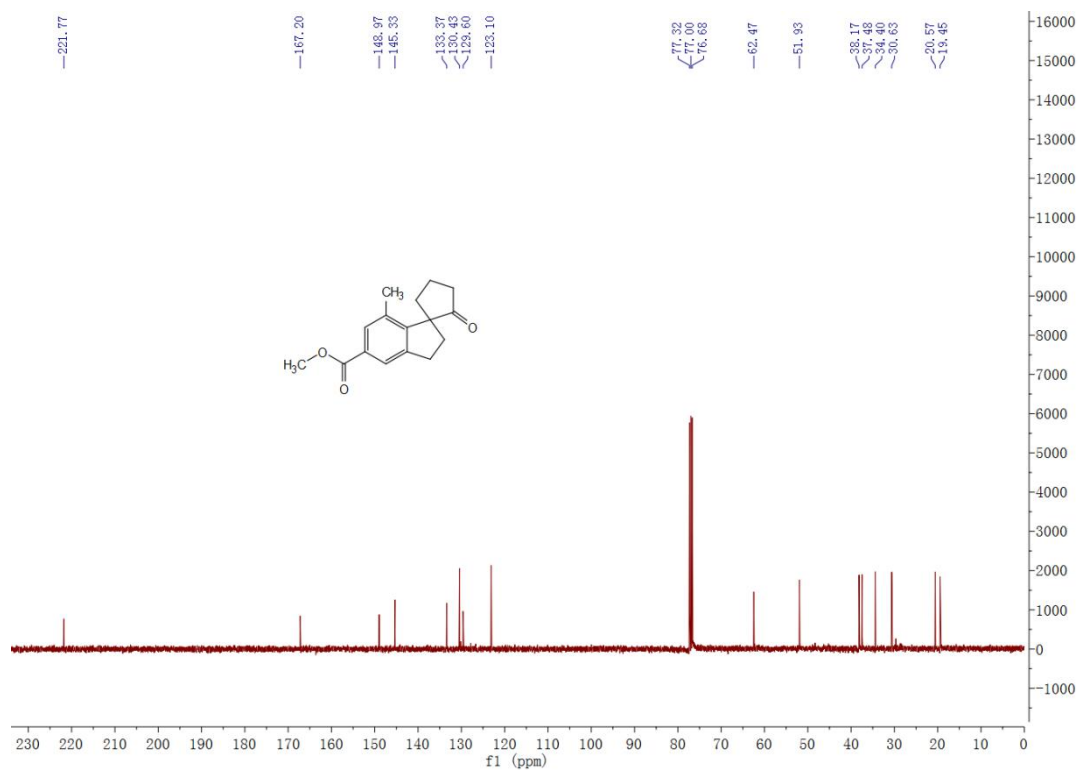


methyl 7'-methyl-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-5'-carboxylate (3j)

^1H NMR (400 MHz, CDCl_3)

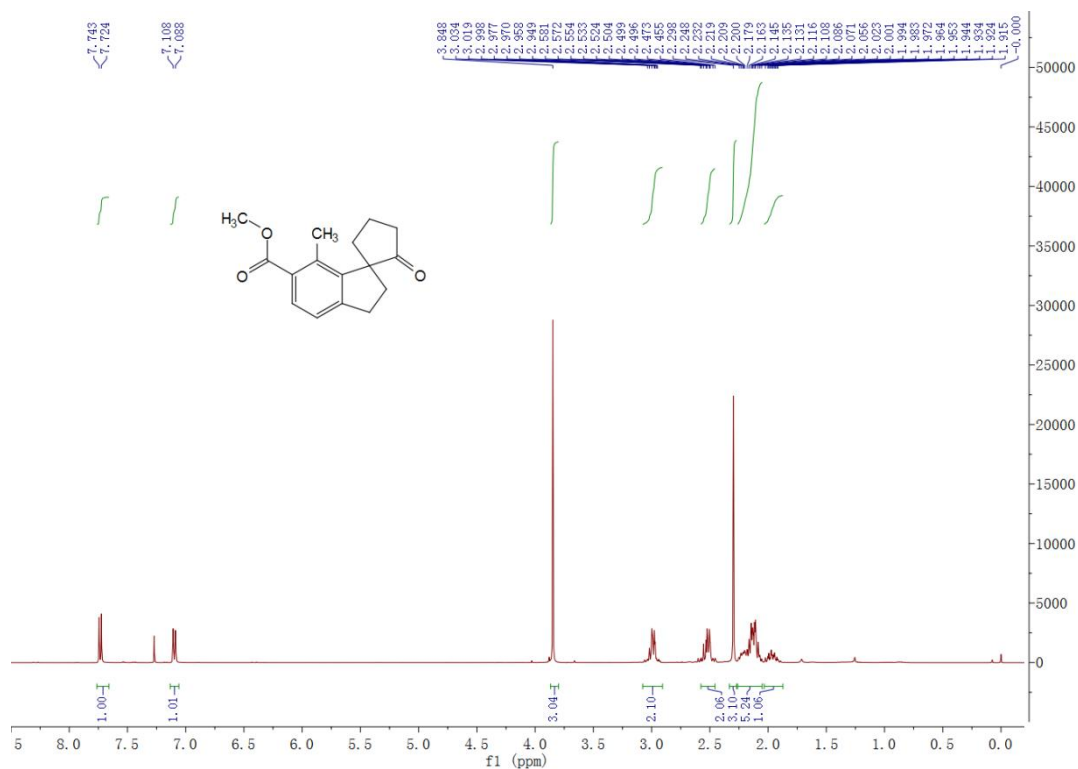


^{13}C NMR (100 MHz, CDCl_3)

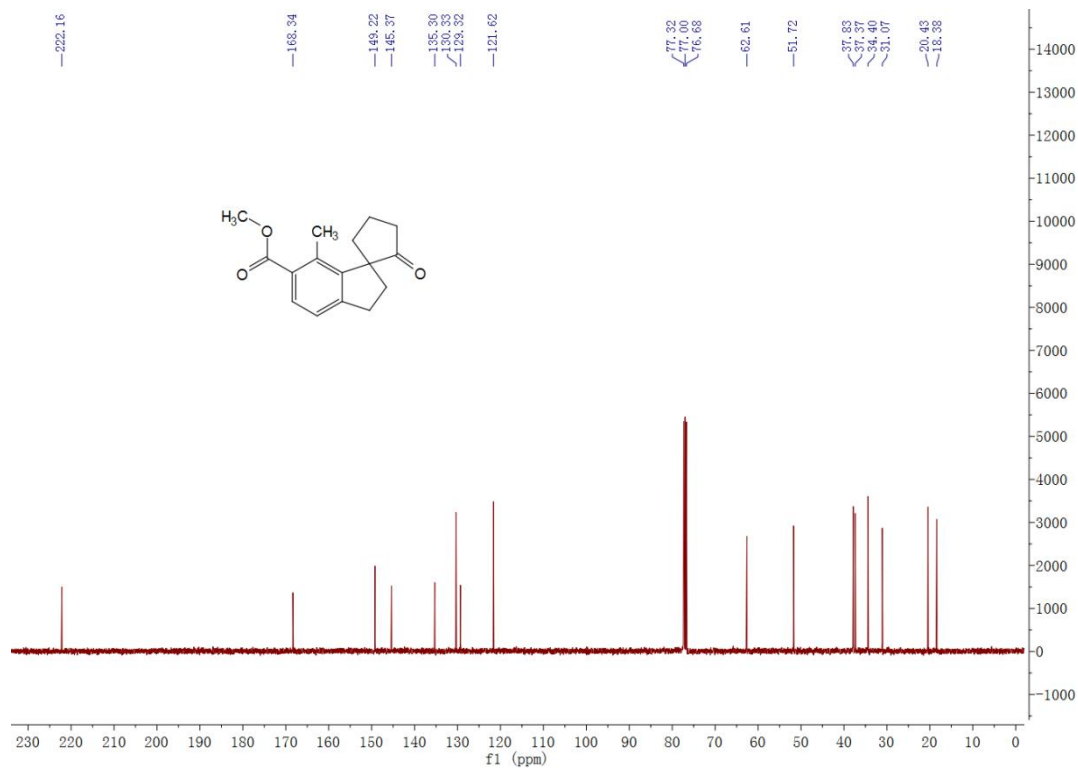


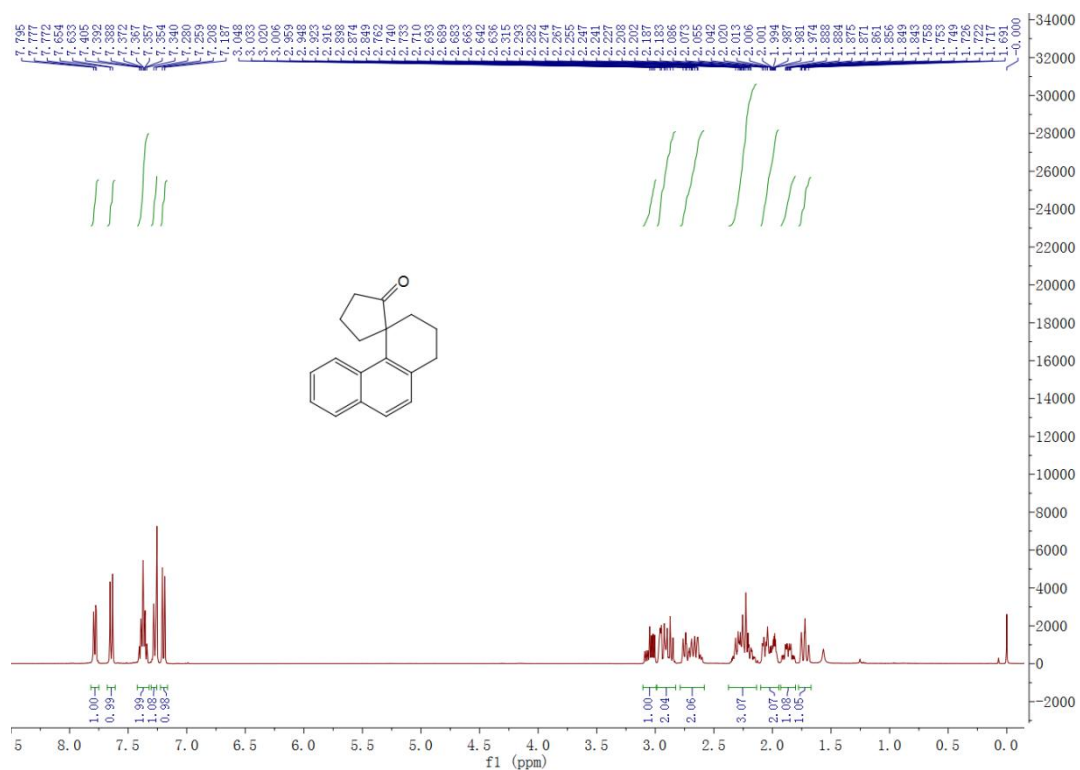
methyl 7'-methyl-2-oxo-2',3'-dihydrospiro[cyclopentane-1,1'-indene]-6'-carboxylate (3k)

^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (100 MHz, CDCl_3)



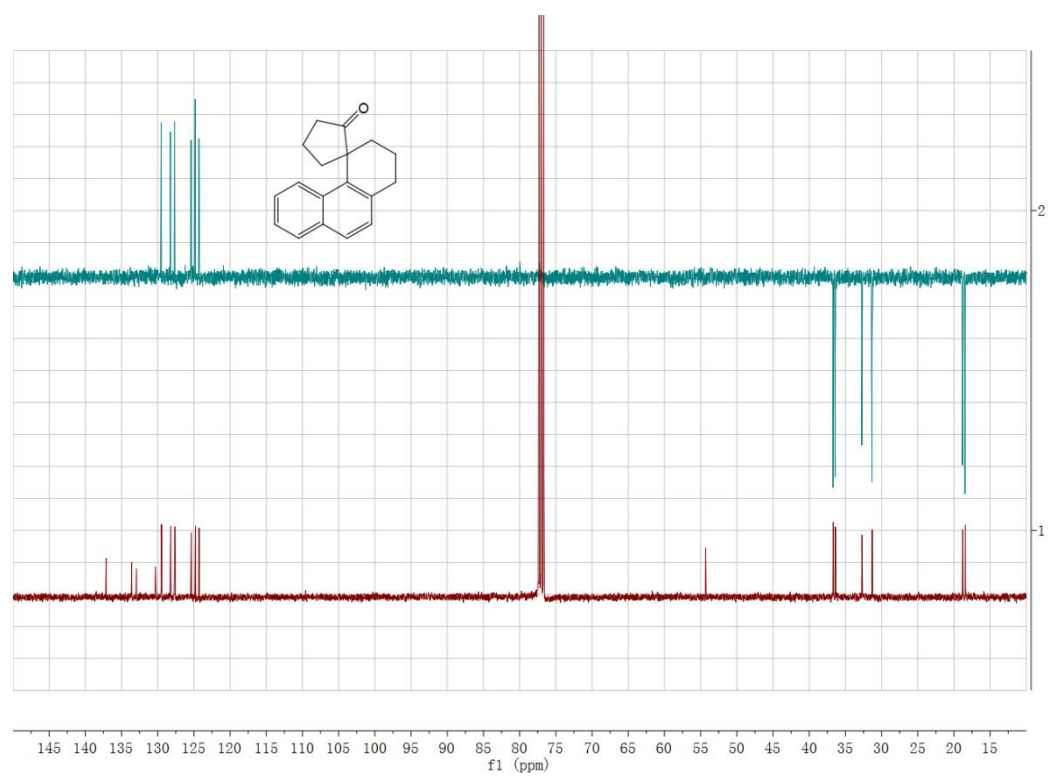
¹H NMR (400 MHz, CDCl₃)

Chemical structure of 1,2,3,4-tetrahydronaphthalen-1(1H)-one is shown above the spectrum.

Chemical shifts (ppm) labeled on the spectrum:

- 222.96
- 137.13
- 133.60
- 132.94
- 132.82
- 129.48
- 128.21
- 127.63
- 125.34
- 124.28
- 77.32
- 77.00
- 76.68
- 54.30
- 36.67
- 36.38
- 32.70
- 31.30
- 18.79
- 18.44

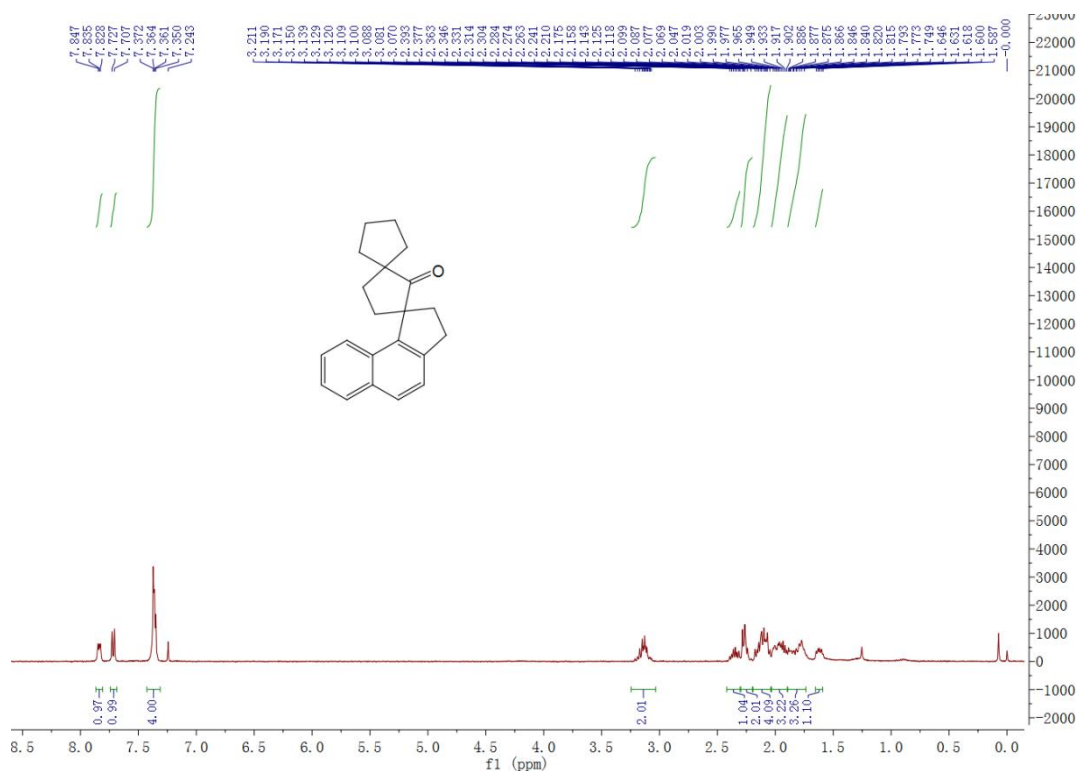
Dept-135



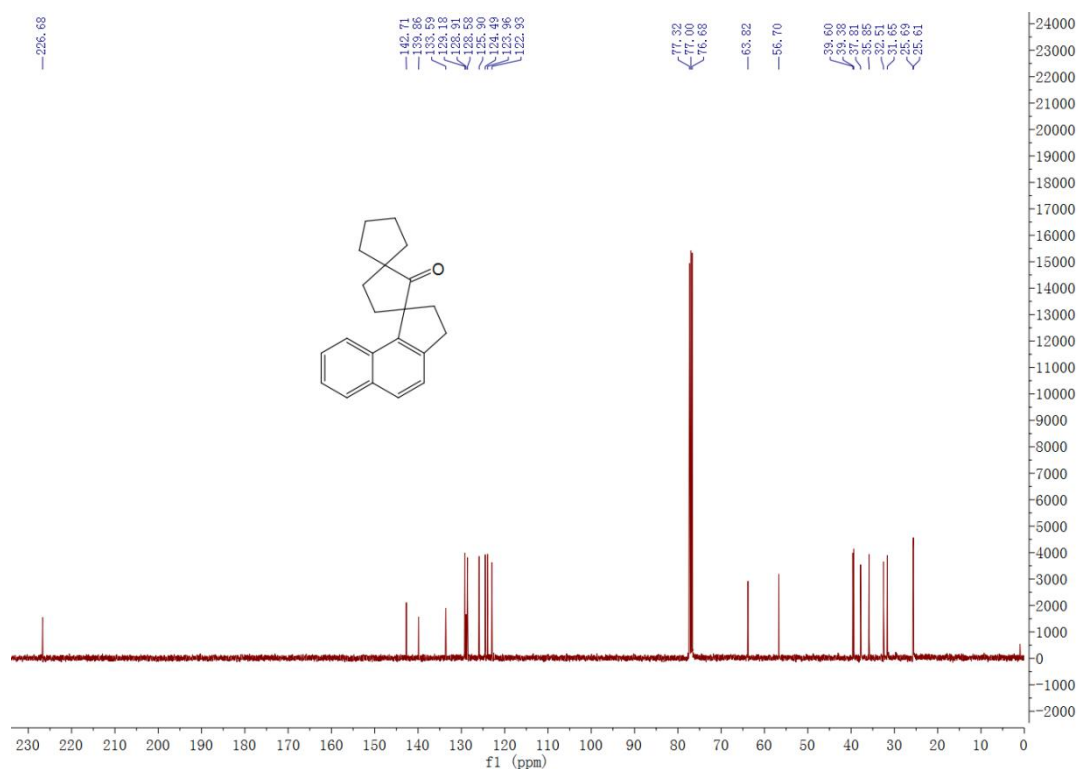
2'',3''-dihydrodispiro[cyclopentane-1,1'-cyclopentane-3',1''-cyclopenta[*a*]naphthalen]-2'-one

(3n)

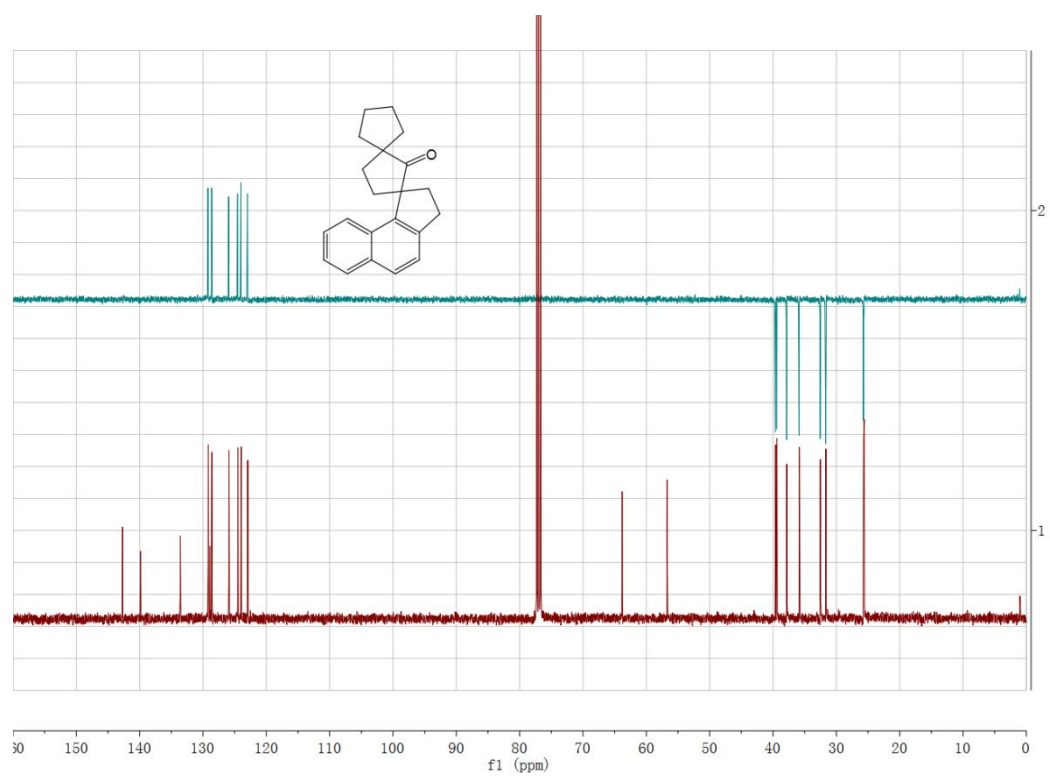
¹H NMR (400 MHz, CDCl₃)

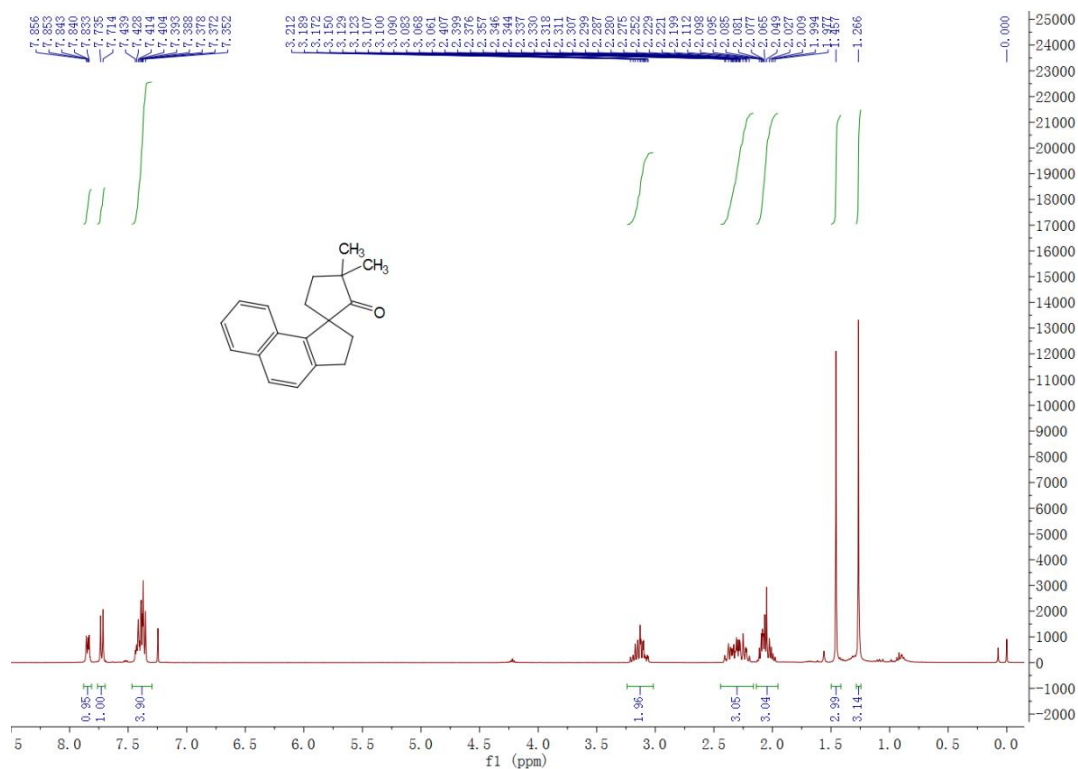


¹³C NMR (100 MHz, CDCl₃)



Dept-135



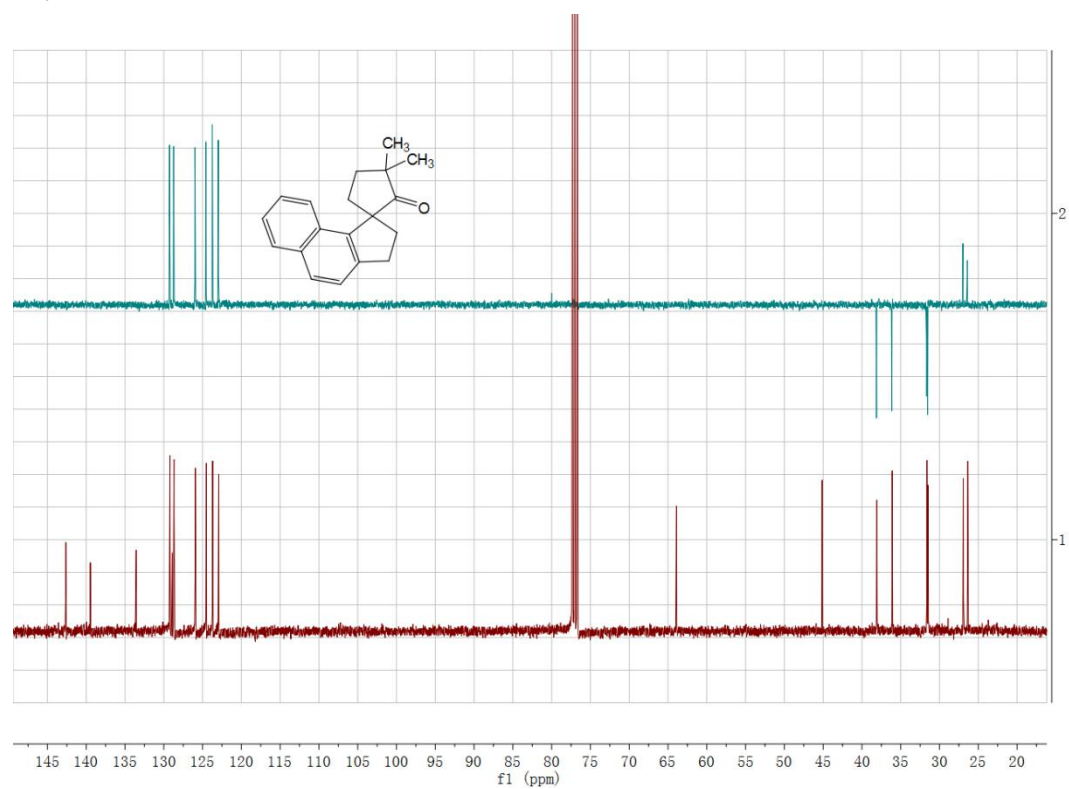
¹H NMR (400 MHz, CDCl₃)

Chemical structure: 1,2,3,4-tetrahydronaphthalen-1(1H)-one-2,3-dimethyl

¹³C NMR spectrum (ppm):

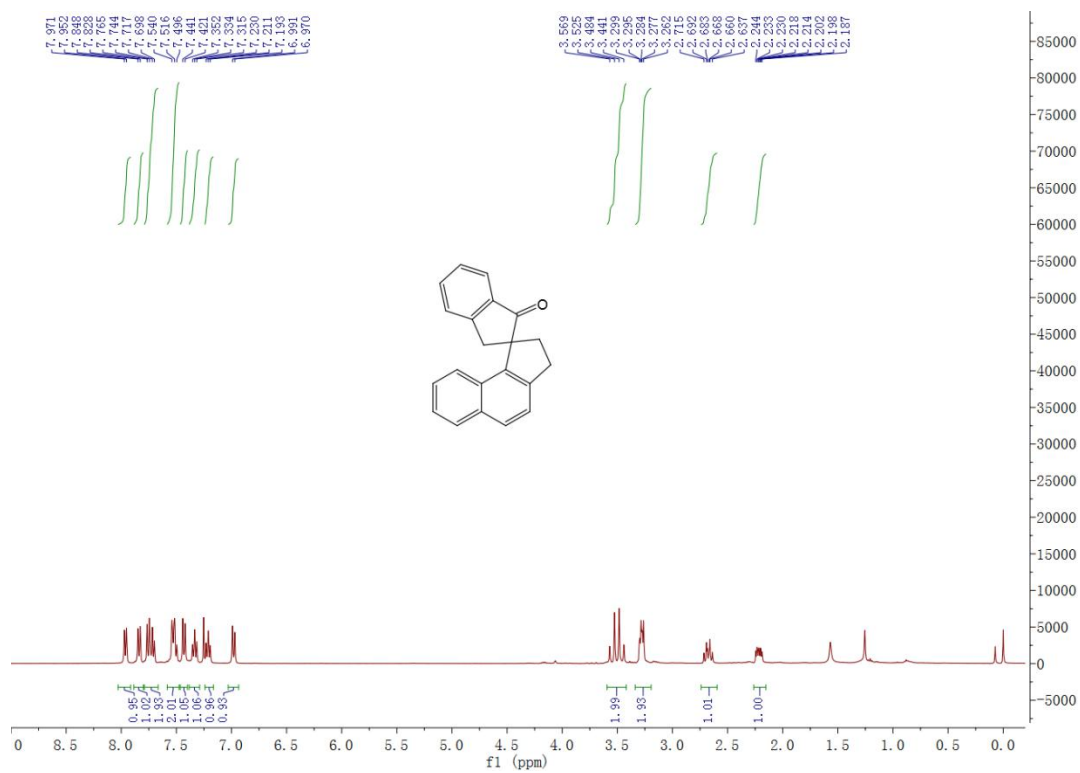
- 235.88
- 142.64
- 139.47
- 133.57
- 129.21
- 128.91
- 128.69
- 125.99
- 124.52
- 123.71
- 122.92
- 77.32
- 77.00
- 76.68
- 63.91
- 45.14
- 38.08
- 36.10
- 31.62
- 28.88
- 26.32
- 26.37

Dept-135

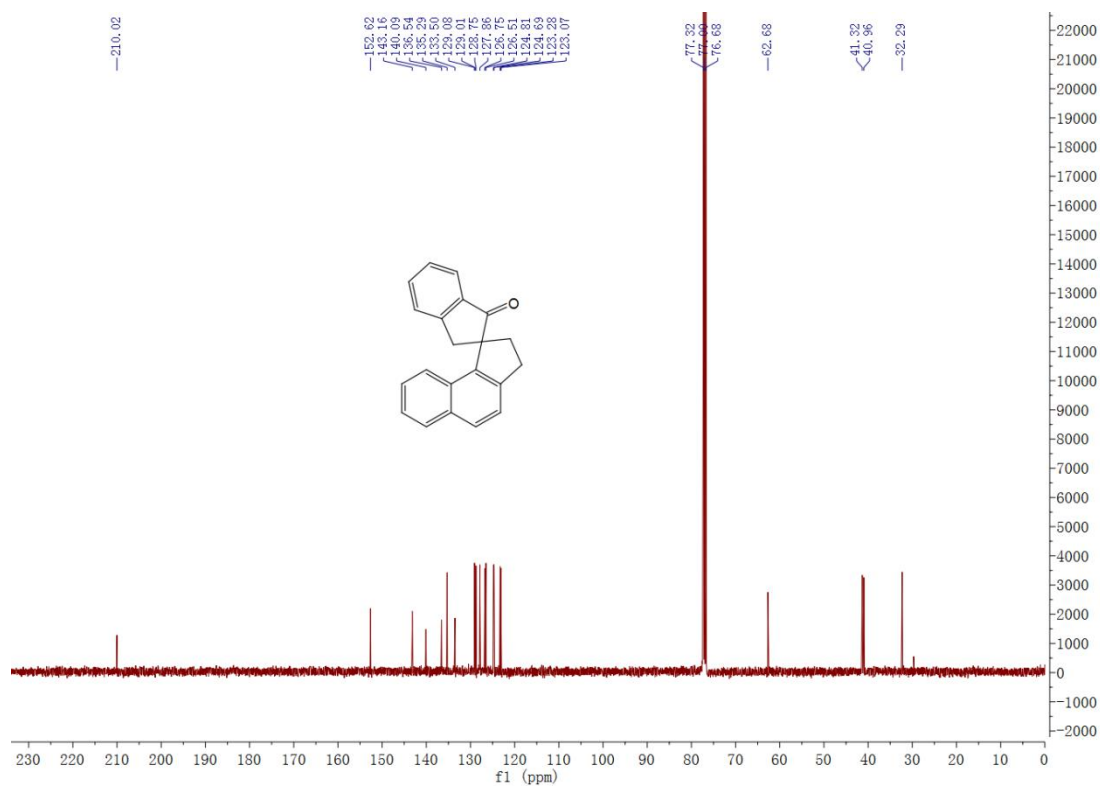


2,3-dihydrospiro[cyclopenta[*a*]naphthalene-1,2'-inden]-1'(3'*H*)-one (3p)

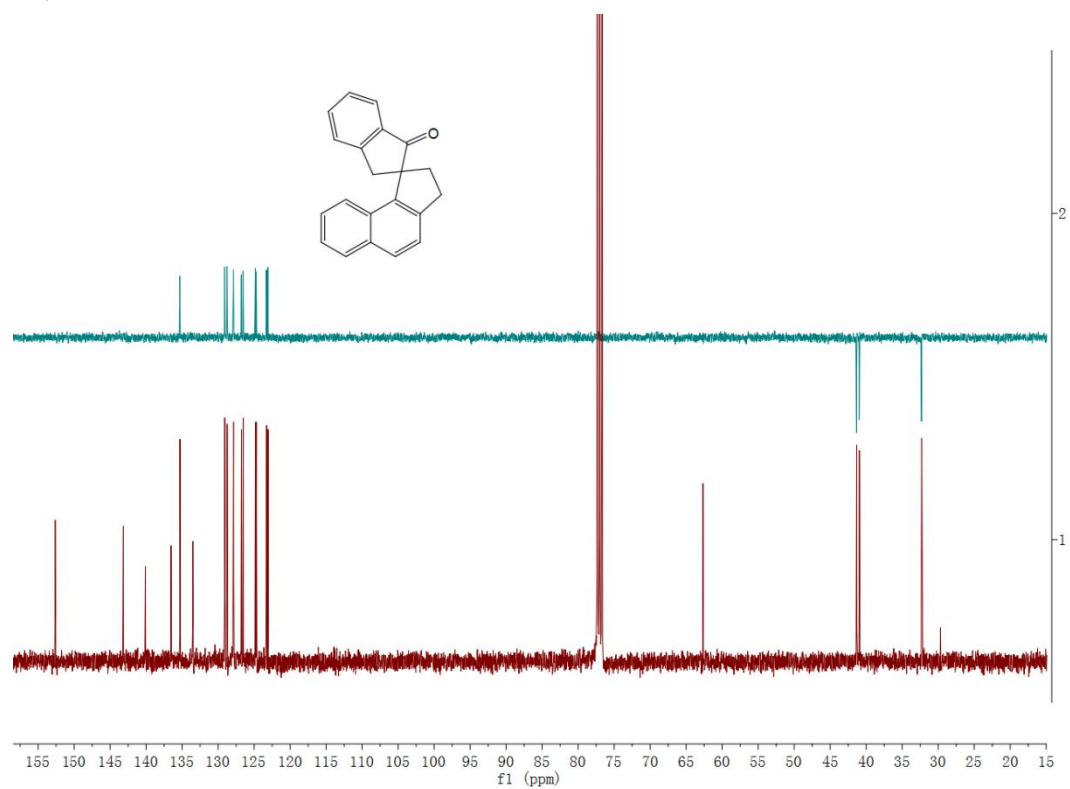
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

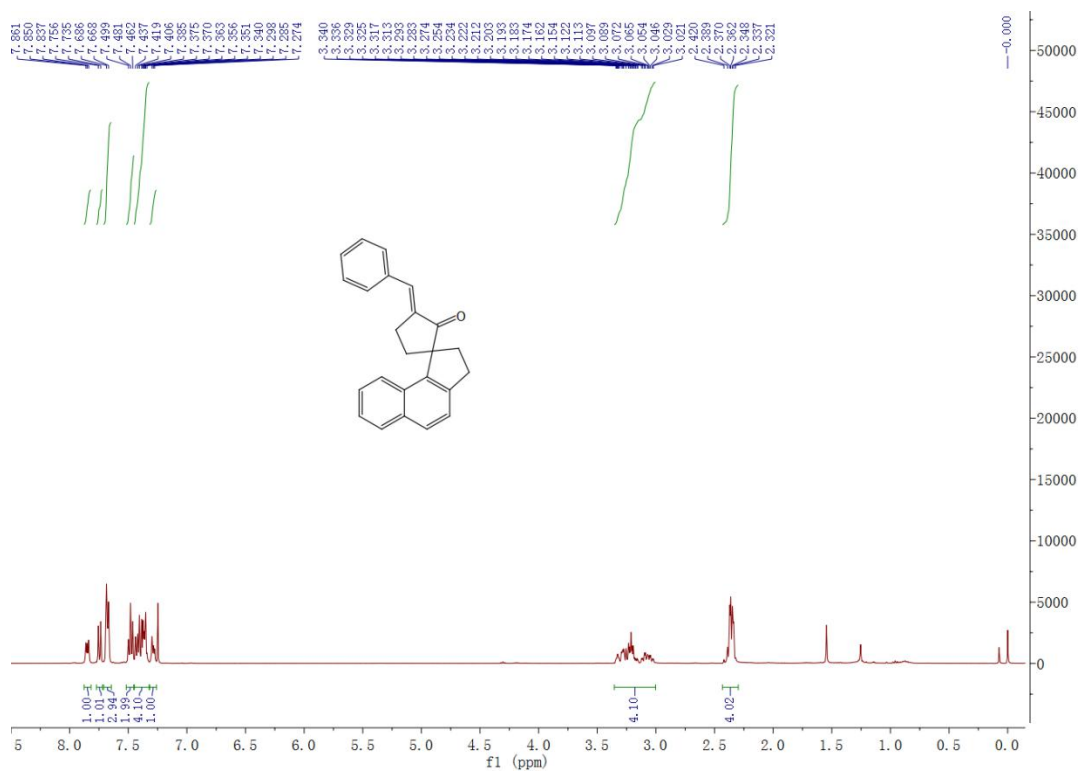


Dept-135

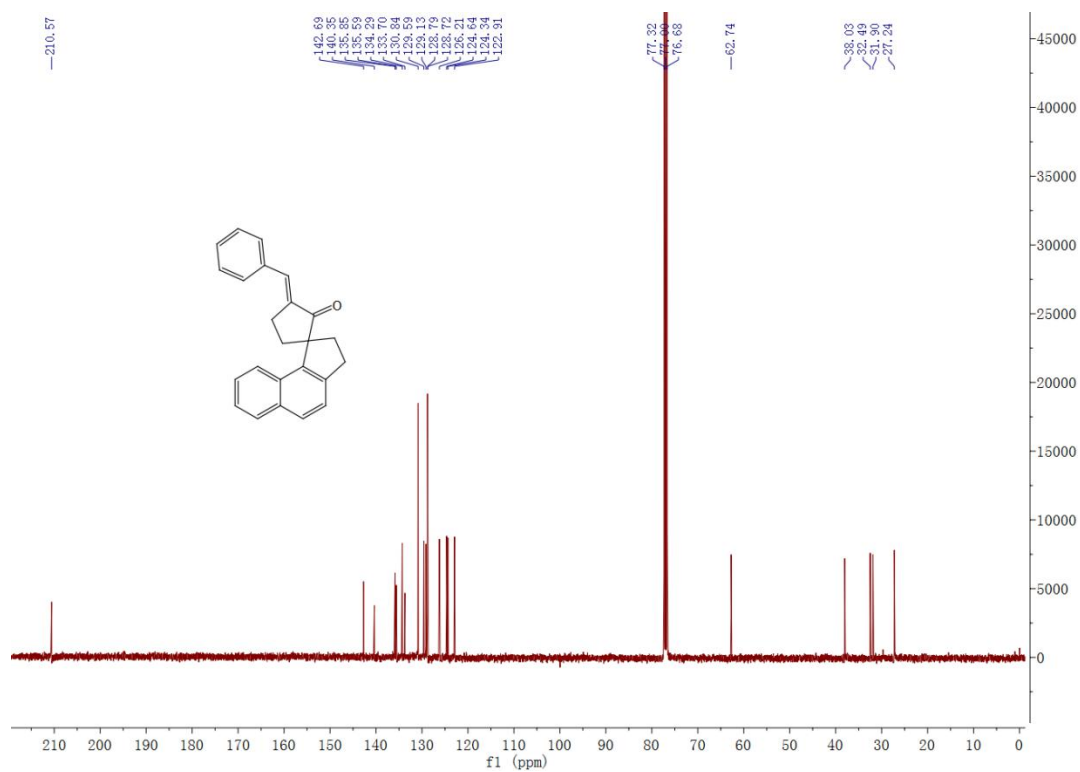


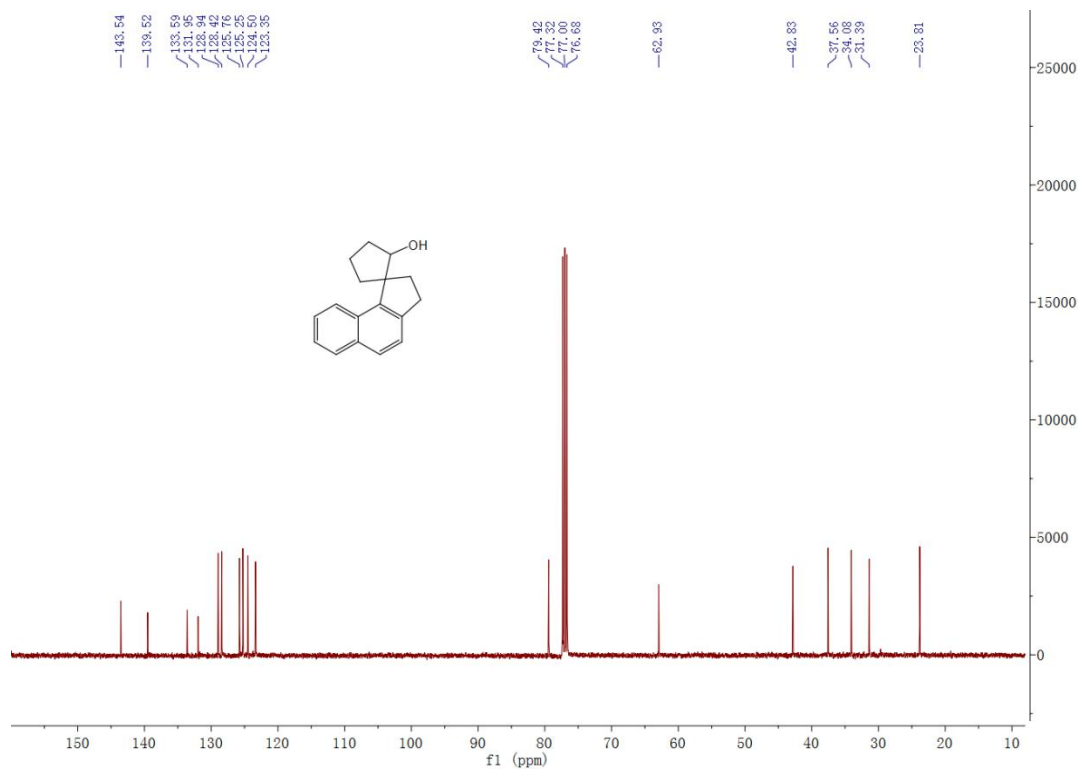
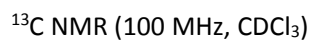
(E)-3'-benzylidene-2,3-dihydrospiro[cyclopenta[*a*]naphthalene-1,1'-cyclopentan]-2'-one (5)

¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)

6. The NOE of compound 6: NOE (600 MHz, CDCl₃)

