Supporting Information

A Metal- and Solvent-Free Bromination of Electron-Deficient Allyl and Benzyl C-H Bonds

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Content

1. Reagents

All commercial materials were used as received unless otherwise noted. Superdry solvents and deuterated solvents were purchased from Energy Chemical. Starting materials for this study were purchased from Leyan or were synthesized according to reported procedures.

TLC were performed on silica gel Leyan HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λmax = 254 nm). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Shanghai Haohong Scientific Co., Ltd.

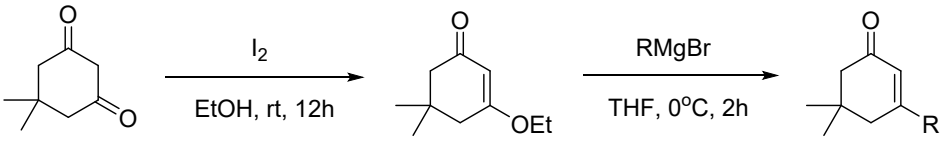
2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectrometry (HRMS) data were obtained on an LC-MS instrument (ESI-HRMS, Agilent 6520 Q-TOF LC/MS).

All reactions were carried out in a 15 mL glass tube.

3. Synthesis of substrates

3.1 General Procedures for the synthesis of 2a-6a.



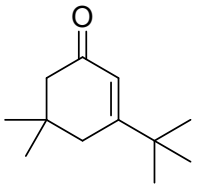
S1 **S2** **2a-6a**

S2 was synthesized according to reported procedure.[1]

S2 (0.35 g, 2.5 mmol) in 10 mL THF was added to RMgBr (2 M in THF, 5 mmol) at 0 ℃ over 1 min. After addition was completed, the resulting mixture was allowed to stir 1 h at this temperature. It was allowed to warm to room temperature and stirred for an additional 2 h. 2 M HCl (10 mL) was added to the reaction with stirring for 5 min. An additional 2 M HCl (20 mL) were added. The resulting mixture was extracted with ethyl

acetate (2 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The volatiles were removed in vacuo. The residue was subjected to flash column chromatography on silica gel to afford ketone **2a-6a**.

3-(*tert*-butyl)-5,5-dimethylcyclohex-2-en-1-one

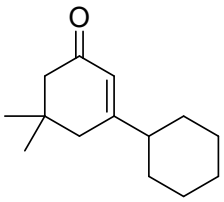


2a

R_f = 0.7, 2% acetone in hexane, yellowish liquid (558 mg, 62% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (s, 1H), 2.24 – 2.22 (m, 4H), 1.13 (s, 9H), 1.04 (s, 6H). [2]

5,5-dimethyl-[1,1'-bi(cyclohexan)]-1-en-3-one

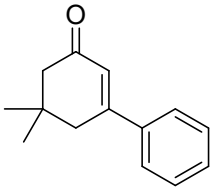


3a

R_f = 0.7, 2% acetone in hexane, yellowish solid (607 mg, 59% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (d, *J* = 0.7 Hz, 1H), 2.23 (s, 2H), 2.20 (d, *J* = 0.7 Hz, 2H), 2.05 – 2.00 (m, 1H), 1.84 – 1.74 (m, 5H), 1.33 – 1.21 (m, 5H), 1.04 (s, 6H).[3]

5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one

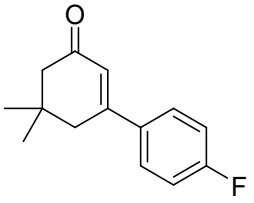


4a

R_f = 0.6, 1% acetone in hexane, yellowish solid (608 mg, 61% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.45 – 7.42 (m, 3H), 6.44 (t, *J* = 1.3 Hz, 1H), 2.68 (d, *J* = 1.2 Hz, 2H), 2.37 (s, 2H), 2.07 (s, 1H), 1.16 (s, 6H). Spectra data are consistent with those reported in the literature.[4]

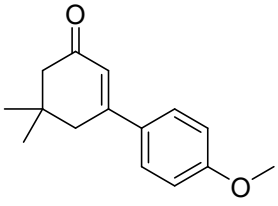
4'-fluoro-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one



5a

R_f = 0.6, 1% acetone in hexane, yellowish solid (583 mg, 57% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.39 (s, 1H), 2.64 (d, *J* = 1.4 Hz, 2H), 2.36 (s, 2H), 1.15 (s, 6H).[4]

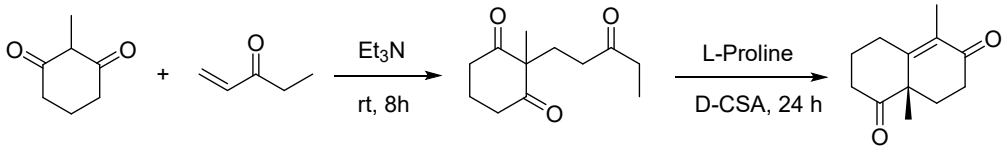
4'-methoxy-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one



6a

R_f = 0.6, 1% acetone in hexane, yellowish solid (634 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.41 (s, 1H), 3.87 (s, 3H), 2.65 (d, *J* = 0.7 Hz, 2H), 2.35 (s, 2H), 1.15 (s, 6H). Spectra data are consistent with those reported in the literature.[5]

3.2 Synthesis of 17a.

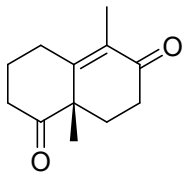


S3 **S4** **S5** **7a**

2-methyl-1,3-cyclohexanedione **S3** (1.35 g, 11 mmol) was added, and 1-penten-3-one **S4** (1.2 mL, 12 mmol) and triethylamine (135 μL, 1.1 mmol) were added sequentially, and the reaction was carried out at room temperature for 8 h. Water (50 mL) was added to the reaction solution to quench the reaction, extracted with ethyl acetate (3x50 mL), washed with saturated salt water after combining organic phases, dried with anhydrous sodium sulfate, and the crude product was separated and purified by column chromatography after concentration (petroleum ether/ethyl acetate = 4:1) to obtain compound **S5** liquid (2.3 g, yield 92%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.77 – 2.69 (m, 2H), 2.62 (ddd, *J* = 16.1, 7.4, 5.2 Hz, 2H), 2.38 (q, *J* = 7.3 Hz, 2H), 2.33 – 2.28 (m, 2H), 2.09 – 2.00 (m, 3H), 1.90 (tt, *J* = 14.1, 4.6 Hz, 1H), 1.23 (s, 3H), 1.01 (t, *J* = 7.3 Hz, 3H).[6]

Compound **S5** (2.0 g, 9.5 mmol) was dissolved in anhydrous *N, N*-dimethylformamide (10 mL), L-phenylalanine (1.1 g, 9.5 mmol), (+)-10-camphorsulfonic acid (1.1 g, 4.7 mmo1) were added sequentially, and after 18h of reaction at room temperature under the protection of N_2, the temperature was raised to 30 °C, and the temperature was increased to 10 °C every 24 hours to 70 °C. After removing most of the solvent *N, N*-dimethylformamide under reduced pressure, the reaction was quenched with saturated sodium bicarbonate solution (50 mL), extracted with ethyl acetate (3 x 50 mL), washed with saturated salt water after merging organic phases, dried with anhydrous sodium sulfate, and the crude product was separated and purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to obtain compound **17a** with 52% yield.

(*S*)-5,8a-dimethyl-3,4,8,8a-tetrahydronaphthalene-1,6(2*H*,7*H*)-dione



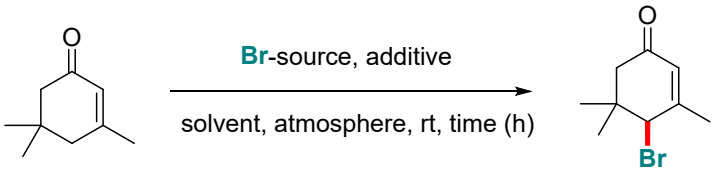
7a

R_f = 0.7, 2% acetone in hexane, yellowish liquid (634 mg, 63% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.87 (dtd, *J* = 15.9, 5.0, 0.9 Hz, 1H), 2.77 – 2.60 (m, 2H), 2.51 (dddd, *J* = 20.1, 10.5, 5.7, 2.9 Hz, 3H), 2.44 – 2.38 (m, 1H), 2.14 (dt, *J* = 13.6, 5.6 Hz, 1H), 2.09 – 2.05 (m, 2H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.42 (s, 3H).[6]

4. Reaction optimization for bromination of Isophorone

All screening reactions were carried out at a 0.5 mmol scale in a 15 mL glass tube. Isophorone **1a** (69.1 mg, 0.5 mmol, 1.0 equiv), other specified reagents were added to a 15 mL glass tube. The reaction carried out at room temperature without magnetic stir bar. After the reaction completed as monitored with TLC, the solvent of the reaction mixture was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (53 μL) as an external standard for ^{1}H-NMR analysis. The composition of reaction mixture was based on the methyl peaks at 5.89 ppm (s, 1H) for compound **1a**, 5.85 ppm (s, 1H) for compound **1b**.



1a **1b**

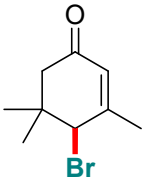
entry	NHPI (equiv)/DBDMH (equiv)/ /solvent/atmosphere/time (h)	Rsm[a] (%)	yield of **1b** (%)[b]
1	NHPI (0.2 equiv), DBDMH (1.0 equiv) DCM (1.5 mL), air, 10 min	<10%	80%
2	NHPI (0.2 equiv), DBDMH (1.0 equiv) DCM (1.5 mL), air, 30 min	<10%	73%
3	NHPI (0.2 equiv), DBDMH (1.0 equiv) DCM (1.5 mL), air, 1 h	<10%	69%
4	NHPI (0.2 equiv), DBDMH (1.0 equiv) CH_3CN (1.5 mL), air, 10 min	<10%	47%
5	NHPI (0.2 equiv), DBDMH (1.0 equiv) EA (1.5 mL), air, 10 min	<10%	53%
6	NHPI (0.2 equiv), DBDMH (1.0 equiv) HFIP (1.5 mL), air, 10 min	<10%	64%
7	NHPI (0.2 equiv), DBDMH (2.0 equiv) DCM (1.5 mL), air, 10 min	<10%	79%
8	NHPI (0.2 equiv), DBDMH (0.6 equiv) DCM (1.5 mL), air, 10 min	<10%	82%
9	NHPI (0.1 equiv), DBDMH (0.6 equiv) DCM (1.5 mL), air, 10 min	<10%	81%
10	NHPI (0.05 equiv), DBDMH (0.6 equiv) DCM (1.5 mL), air, 10 min	<10%	84%
11	NHPI (0 equiv), DBDMH (0.6 equiv) DCM (1.5 mL), air, 10 min	>90%	ND[c]
12	NHPI (0.1 equiv), DBDMH (0.6 equiv) DCM (5.0 equiv), air, 10 min	<10%	87%[d]
13	NHPI (0.1 equiv), NBS (1.0 equiv) DCM (5.0 equiv), air, 10 min	21%	65%
14	NHPI (0.05 equiv), DBDMH (0.6 equiv) S.F.[e], air, 10 min	56%	34%
15	NHPI (0.05 equiv), DBDMH (0.6 equiv) S.F., air, 30 min	<10%	85%
16	NHPI (0.05 equiv), DBDMH (0.6 equiv) S.F., N_2, 10 min	<10%	84%

[a] RSM is the short for of recovery starting material. [b] Yields are based on ^{1}H-NMR analysis on a 0.5 mmol scale. [c] ND = not detected. [d] Isolated yield. [e] SF = solvent free.

5. General procedure and substrate scope

General conditions A: Substrates (0.5 mmol, 1.0 equiv), DBDMH (0.6 mmol) and NHPI (0.05 equiv), were add to the glass tube. The mixture without solvent at room temperature under air irradiation for 3 h (If it is a solid substrate, a solvent DCM (5.0 equiv) needs to be added.). The mixture was directly purified by silica gel flash chromatography to give the desired products.

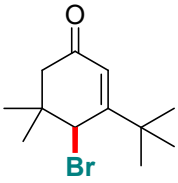
4-bromo-3,5,5-trimethylcyclohex-2-en-1-one



1b R_f = 0.6, 2% acetone in hexane, white solid (92 mg, 85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (s, 1H), 4.31 (d, J = 1.3 Hz, 1H), 2.61 (dd, J = 16.7, 0.6 Hz, 1H), 2.17 (dd, J = 16.6, 1.0 Hz, 1H), 2.13 (d, J = 1.3 Hz, 3H), 1.27 (s, 3H), 1.16 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.13, 157.15, 126.08, 61.74, 46.31, 37.60, 29.96, 24.99, 22.67. Spectra data are consistent with those reported in the literature.[7]

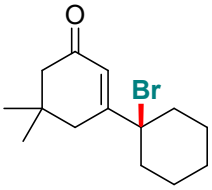
4-bromo-3-(*tert*-butyl)-5,5-dimethylcyclohex-2-en-1-one



2b R_f = 0.6, 2% acetone in hexane, white solid (113 mg, 88% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (d, J = 2.8 Hz, 1H), 4.52 (s, 1H), 2.74 (dd, J = 17.5, 2.4 Hz, 1H), 2.19 (dd, J = 17.5, 0.8 Hz, 1H), 1.33 (s, 3H), 1.27 (s, 9H), 1.13 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.25, 168.52, 124.18, 57.13, 46.68, 38.16, 36.38, 29.77, 29.39, 24.66. Spectra data are consistent with those reported in the literature.[8]

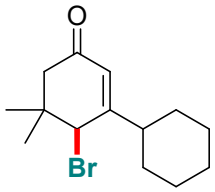
1'-bromo-5,5-dimethyl-[1,1'-bi(cyclohexan)]-1-en-3-one



3b R_f = 0.5, 2% acetone in hexane, yellowish solid (79 mg, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (s, 1H), 2.48 (s, 2H), 2.31 – 2.26 (m, 4H), 1.84 (dd, J = 13.5, 5.8 Hz, 4H), 1.66 (dd, J = 12.2, 6.9 Hz, 3H), 1.37 – 1.30 (m, 1H), 1.10 (s, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 200.78, 162.45, 122.14, 72.34, 51.27, 40.48, 38.21, 33.72, 27.86, 25.03, 23.34. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{22}BrO^+$ 285.0849; Found: 285.0847.

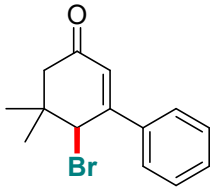
6-bromo-5,5-dimethyl-[1,1'-bi(cyclohexan)]-1-en-3-one



3b'

R_f = 0.6, 2% acetone in hexane, yellowish solid (52 mg, 37% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.82 (s, 1H), 4.41 (d, J = 1.4 Hz, 1H), 2.66 (d, J = 17.1 Hz, 1H), 2.26 – 2.20 (m, 1H), 2.17 (d, J = 16.8 Hz, 1H), 1.93 – 1.72 (m, 6H), 1.41 – 1.32 (m, 3H), 1.28 (s, 3H), 1.12 (s, 3H), 1.08 (dd, J = 12.1, 3.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.87, 162.49, 122.14, 72.36, 51.28, 40.49, 38.21, 33.75, 27.88, 25.04, 23.35. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{22}BrO^+$ 285.0849; Found: 285.0852.

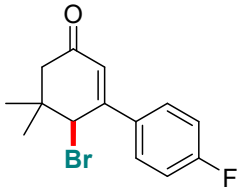
6-bromo-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one



4b

R_f = 0.7, 2% acetone in hexane, yellowish solid (103 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.50 – 7.47 (m, 3H), 6.34 (s, 1H), 4.92 (d, J = 1.3 Hz, 1H), 2.80 (d, J = 17.0 Hz, 1H), 2.32 (d, J = 17.0 Hz, 1H), 1.40 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.38, 156.51, 136.40, 130.51, 129.03, 126.59, 124.23, 58.29, 46.57, 37.76, 30.10, 24.77. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{16}BrO^+$ 280.1845; Found: 280.1849.

6-bromo-4'-fluoro-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one

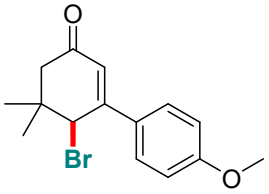


5b

R_f = 0.7, 2% acetone in hexane, yellowish solid (118 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.16 (t, J = 8.6 Hz, 2H), 6.29 (s, 1H), 4.85 (d, J = 1.2 Hz, 1H), 2.77 (d, J = 17.0 Hz, 1H), 2.31 (d, J = 17.0 Hz,

1H), 1.39 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.15, 165.04, 163.04, 155.28, 132.49, 132.47, 128.68, 128.61, 124.08, 124.07, 116.26, 116.08, 58.22, 46.45, 37.76, 30.07, 24.75. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.59, -109.60. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{15}BrFO^+$ 297.0285; Found: 297.0289.

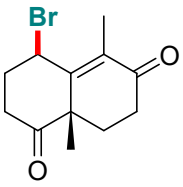
6-bromo-4'-methoxy-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one



6b

R_f = 0.7, 2% acetone in hexane, yellowish solid (103 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.9 Hz, 2H), 7.01 – 6.97 (m, 2H), 6.33 (s, 1H), 4.91 (d, J = 1.2 Hz, 1H), 3.89 (s, 3H), 2.77 (d, J = 17.0 Hz, 1H), 2.30 (d, J = 17.0 Hz, 1H), 1.39 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.34, 161.64, 155.75, 128.24, 128.18, 122.34, 114.48, 58.13, 55.44, 46.53, 37.70, 30.14, 24.76. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{18}BrO^+$ 310.2105; Found: 310.2111.

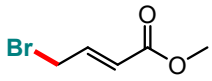
(8a*S*)-4-bromo-5,8a-dimethyl-3,4,8,8a-tetrahydronaphthalene-1,6(2*H*,7*H*)-dione



7b

R_f = 0.5, 2% acetone in hexane, yellowish solid (103 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.41 (t, J = 4.1 Hz, 1H), 3.21 (ddd, J = 14.8, 12.2, 4.8 Hz, 1H), 2.56 (ddt, J = 20.0, 9.4, 5.1 Hz, 3H), 2.45 – 2.32 (m, 2H), 2.23 – 2.17 (m, 1H), 2.00 – 1.93 (m, 1H), 1.92 (d, J = 5.6 Hz, 3H), 1.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.11, 197.57, 155.53, 134.42, 49.41, 45.85, 33.97, 33.26, 32.01, 30.64, 26.77, 11.40. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{18}BrO^+$ 272.1615; Found: 272.1617.

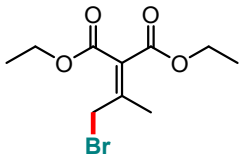
methyl (*E*)-4-bromobut-2-enoate



8b R_f = 0.5, 2% acetone in hexane, light yellow oil (132 mg,89% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (dt, J_1 = 15.0, J_2 =7.4 Hz, 1H), 6.04 (d, J = 15.4 Hz, 1H), 4.02 (d, J = 7.4 Hz, 2H), 3.77 (s, 3H).[9]

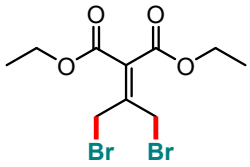
diethyl 2-(1-bromopropan-2-ylidene)malonate



9b R_f = 0.4, 2% acetone in hexane, colorless oil (223 mg, 84% yield)

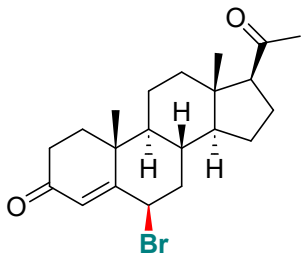
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 (s, 2H), 4.24 – 4.18 (m, 4H), 2.09 (s, 3H), 1.25 (td, J_1 = 7.1, J_2 = 2.2 Hz, 6H). [9]

diethyl 2-(1,3-dibromopropan-2-ylidene)malonate



10b R_f = 0.5, 3% acetone in hexane, light yellow oil (143 mg, 63% yield). **^{1}H NMR** (500 MHz, CDCl3) δ 4.43 (s, 4H), 4.31 (q, J = 7.1 Hz, 4H), 1.33 (t, J = 7.1 Hz, 6H).[9]

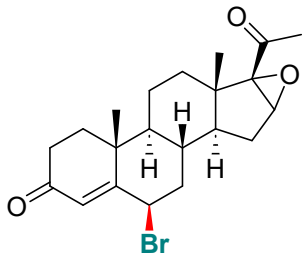
(6*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-6-bromo-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[a]phenanthren-3-one



11b R_f = 0.5, 10% acetone in hexane, white solid (157 mg, 80%

yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 4.99 (dd, J = 3.8, 2.0 Hz, 1H), 2.56 (td, J = 7.1, 3.9 Hz, 2H), 2.43 (dd, J = 14.4, 3.0 Hz, 1H), 2.26 (ddd, J = 16.2, 9.2, 5.8 Hz, 2H), 2.17 – 2.12 (m, 4H), 2.09 (ddd, J = 10.2, 5.6, 2.8 Hz, 2H), 1.74 – 1.64 (m, 6H), 1.56 (s, 4H), 1.50 – 1.44 (m, 1H), 1.39 – 1.19 (m, 3H), 0.99 (td, J = 11.5, 4.3 Hz, 1H), 0.75 (s, 3H). **^{13}C NMR** (126 MHz, CDCl3) δ 208.98, 199.46, 165.28, 127.02, 63.43, 55.32, 52.82, 51.90, 43.93, 40.76, 38.51, 38.36, 37.84, 34.10, 31.43, 30.70, 24.29, 22.85, 22.18, 20.97, 13.34.

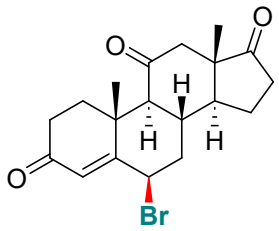
(2*R*,6a*R*,6b*S*,8a*S*,8b*S*,10a*S*,10b*R*)-8b-acetyl-2-bromo-6a,8a-dimethyl-1,2,5,6,6a,6b,7,8,8a,8b,9a,10,10a,10b-tetradecahydro-4*H*-naphtho[2',1':4,5]indeno[1,2-b]oxiren-4-one



12b

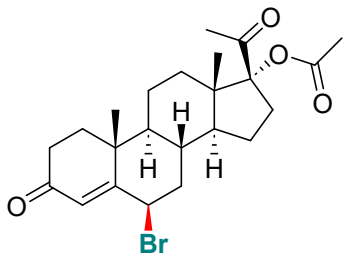
R_f = 0.5, 10% acetone in hexane, white solid (156 mg, 77% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.90 (s, 1H), 4.99 (dd, J = 4.0, 1.8 Hz, 1H), 3.74 (s, 1H), 2.55 (ddd, J = 17.5, 15.1, 4.9 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.23 – 2.10 (m, 3H), 2.07 – 2.03 (m, 4H), 1.97 (dd, J = 13.3, 6.2 Hz, 1H), 1.71 – 1.62 (m, 3H), 1.60 – 1.52 (m, 4H), 1.42 (ddd, J = 13.0, 4.7, 2.4 Hz, 2H), 1.27 – 1.20 (m, 1H), 1.15 (s, 3H), 0.95 (td, J = 12.0, 4.7 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.54, 199.45, 165.03, 127.16, 70.67, 60.30, 53.11, 51.86, 44.33, 41.64, 40.54, 38.46, 37.71, 34.08, 31.12, 28.54, 27.32, 25.90, 22.02, 20.37, 15.30. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{21}H_{28}BrO_3^+$ 408.3555; Found: 408.3552.

(6*R*,8*S*,9*S*,10*R*,13*S*,14*S*)-6-bromo-10,13-dimethyl-6,7,8,9,10,12,13,14,15,16-decahydro-1H-cyclopenta[a]phenanthrene-3,11,17(2*H*)-trione



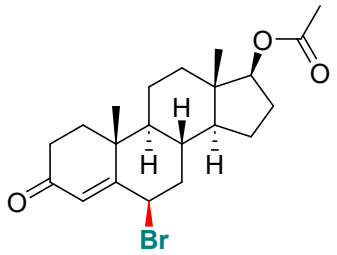
13b R_f = 0.5, 20% acetone in hexane, white solid (155 mg, 82% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.03 (dd, J = 3.6, 2.0 Hz, 1H), 2.85 (ddd, J = 13.3, 4.7, 2.6 Hz, 1H), 2.65 – 2.58 (m, 3H), 2.55 – 2.47 (m, 2H), 2.40 – 2.30 (m, 3H), 2.18 – 2.13 (m, 1H), 1.99 – 1.86 (m, 3H), 1.80 – 1.75 (m, 4H), 1.64 – 1.57 (m, 1H), 0.96 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 216.46, 206.39, 199.33, 163.45, 127.95, 62.39, 50.34, 50.29, 50.14, 48.89, 40.10, 38.47, 36.64, 35.85, 33.92, 31.62, 21.81, 21.58, 14.85. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{24}BrO_3^+$ 380.3015; Found: 408.3552.

(6*R*,8*R*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-acetyl-6-bromo-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl acetate



14b R_f = 0.5, 20% acetone in hexane, white solid (198 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 5.00 (d, J = 1.7 Hz, 1H), 3.01 – 2.95 (m, 1H), 2.58 (ddd, J = 17.6, 15.3, 4.9 Hz, 1H), 2.46 – 2.41 (m, 1H), 2.27 (d, J = 15.0 Hz, 1H), 2.13 (dd, J = 19.6, 6.1 Hz, 5H), 2.07 (t, J = 3.7 Hz, 4H), 2.02 – 1.97 (m, 1H), 1.79 – 1.69 (m, 6H), 1.62 (dd, J = 9.5, 3.3 Hz, 1H), 1.57 – 1.52 (m, 4H), 1.07 – 1.02 (m, 1H), 0.75 (s, 3H). **^{13}C NMR** (126 MHz, CDCl3) δ 203.78, 199.39, 170.57, 165.12, 127.02, 96.56, 52.23, 51.75, 50.36, 46.79, 40.75, 38.30, 37.79, 34.08, 30.86, 30.78, 30.24, 26.42, 23.77, 22.20, 21.20, 20.58, 14.40. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{23}H_{32}BrO_4^+$ 451.1478; Found: 451.1475.

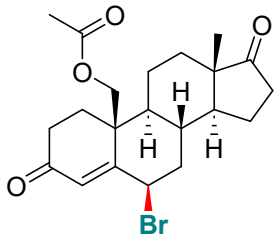
(6*R*,8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-6-bromo-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl acetate



15b

R_f = 0.5, 20% acetone in hexane, white solid (169 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (s, 1H), 4.99 (dd, *J* = 3.8, 2.0 Hz, 1H), 4.66 – 4.59 (m, 1H), 2.56 (ddd, *J* = 17.5, 15.2, 4.9 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.22 (ddt, *J* = 12.7, 9.1, 2.8 Hz, 2H), 2.14 – 2.04 (m, 5H), 1.83 (dt, *J* = 12.8, 3.3 Hz, 1H), 1.70 – 1.41 (m, 10H), 1.26 – 1.11 (m, 2H), 0.98 – 0.90 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.48, 171.10, 165.29, 127.06, 82.29, 52.89, 51.96, 49.64, 42.56, 40.42, 38.40, 37.82, 36.51, 34.09, 30.57, 27.39, 23.38, 22.21, 21.13, 20.51, 12.07. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{21}H_{30}BrO_3^+$ 409.1373; Found: 409.1369.

((6*R*,8*R*,9*S*,10*S*,13*S*,14*S*)-6-bromo-13-methyl-3,17-dioxo-1,2,3,6,7,8,9,11,12,13,14,15,16,17-tetradecahydro-10*H*-cyclopenta[a]phenanthren-10-yl)methyl acetate

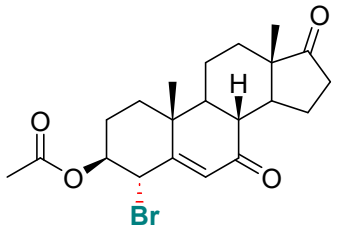


16b

R_f = 0.5, 20% acetone in hexane, white solid (160 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (s, 1H), 5.03 (d, *J* = 2.2 Hz, 1H), 4.73 (d, *J* = 11.3 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 2.71 (ddd, *J* = 17.8, 15.2, 5.6 Hz, 1H), 2.47 – 2.37 (m, 3H), 2.29 (qd, *J* = 11.1, 2.9 Hz, 1H), 2.05 – 1.98 (m, 4H), 1.97 – 1.88 (m, 2H), 1.83 (ddd, *J* = 20.0, 12.2, 4.1 Hz, 2H), 1.75 (dd, *J* = 11.4, 3.9 Hz, 1H), 1.68 – 1.61 (m, 1H), 1.55 (dt, *J* = 13.2, 9.4 Hz, 1H), 1.37 – 1.31 (m, 1H), 1.29 – 1.25 (m, 1H), 1.12

(t, J = 9.8 Hz, 1H), 0.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 219.23, 199.25, 170.35, 158.25, 129.96, 68.18, 53.30, 51.36, 50.50, 47.47, 41.10, 39.54, 35.52, 34.59, 31.52, 30.90, 21.57, 21.09, 20.55, 13.90. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{21}H_{28}BrO_4^+$ 423.1165; Found: 423.1166.

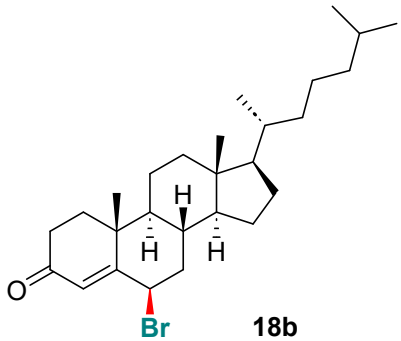
(3*S*,4*S*,8*R*,10*R*,13*S*)-4-bromo-10,13-dimethyl-7,17-dioxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl acetate



17b

R_f = 0.5, 10% acetone in hexane, white solid (165 mg, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.96 (s, 1H), 5.13 – 5.08 (m, 1H), 4.57 (dt, J = 12.0, 4.0 Hz, 1H), 2.80 – 2.74 (m, 1H), 2.55 – 2.46 (m, 2H), 2.29 – 2.06 (m, 6H), 2.02 – 1.97 (m, 1H), 1.90 – 1.81 (m, 3H), 1.68 – 1.55 (m, 7H), 1.36 (td, J = 13.8, 3.4 Hz, 1H), 1.27 (dd, J = 7.6, 4.4 Hz, 1H), 0.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 220.08, 200.71, 170.11, 162.68, 129.76, 71.64, 53.88, 51.53, 47.88, 45.97, 44.98, 38.40, 35.83, 35.59, 30.57, 24.14, 22.90, 21.05, 21.01, 19.82, 13.72. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{21}H_{28}BrO_4^+$ 423.1165; Found: 423.1161.

(6*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-6-bromo-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[a]phenanthren-3-one (18b)

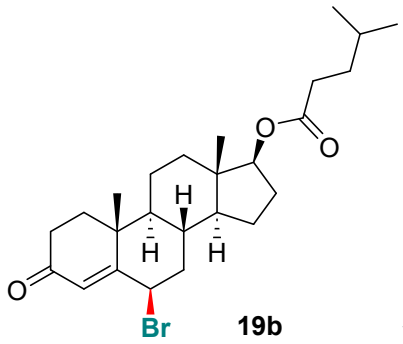


18b

R_f = 0.5, 10% acetone in hexane, white solid (204 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.91 (s, 1H), 4.99 (s, 1H), 2.61 – 2.51 (m,

1H), 2.41 (d, *J* = 17.3 Hz, 1H), 2.25 (d, *J* = 15.0 Hz, 1H), 2.14 – 2.03 (m, 3H), 1.87 (dt, *J* = 19.0, 7.5 Hz, 1H), 1.75 – 1.44 (m, 10H), 1.42 – 1.29 (m, 4H), 1.12 (dddd, *J* = 26.0, 21.8, 13.1, 7.6 Hz, 8H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 6H), 0.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.73, 165.84, 126.88, 56.13, 55.21, 52.97, 52.42, 42.50, 40.91, 39.49(2C), 38.38, 37.82, 36.12, 35.73, 34.16, 30.69, 28.12, 28.01, 24.12, 23.81, 22.82, 22.57, 22.18, 20.98, 18.66, 12.01. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{27}H_{44}BrO^+$ 463.2570; Found: 463.2571.

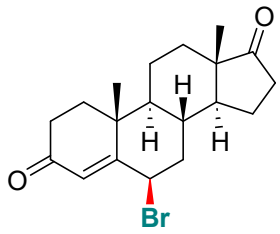
(6*S*,8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-6-bromo-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl 4-methylpentanoate (19b)



19b

R_f = 0.6, 20% acetone in hexane, white solid (206 mg, 86% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (s, 1H), 4.98 (s, 1H), 4.62 (t, *J* = 8.5 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.40 (d, *J* = 17.3 Hz, 1H), 2.33 – 2.28 (m, 2H), 2.24 (d, *J* = 15.2 Hz, 1H), 2.20 – 2.13 (m, 1H), 2.13 – 2.01 (m, 2H), 1.84 – 1.79 (m, 1H), 1.72 – 1.36 (m, 14H), 1.23 – 1.09 (m, 2H), 0.96 – 0.88 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.46, 174.01, 165.27, 127.05, 81.99, 52.86, 52.00, 49.62, 42.59, 40.40, 38.38, 37.80, 36.52, 34.09, 33.90, 32.59, 30.55, 27.65, 27.40, 23.40, 22.25, 22.24, 22.21, 20.50, 12.10. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{38}BrO_3^+$ 465.1999; Found: 465.1999.

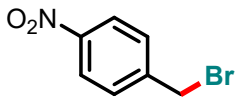
(6*R*,8*R*,9*S*,10*R*,13*S*,14*S*)-6-bromo-10,13-dimethyl-1,6,7,8,9,10,11,12,13,14,15,16-dodecahydro-3H-cyclopenta[a]phenanthrene-3,17(2*H*)-dione



20b

R_f = 0.5, 20% acetone in hexane, white solid (170 mg, 98% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.03 (dd, *J* = 4.0, 2.1 Hz, 1H), 2.61 – 2.49 (m, 2H), 2.41 (dddd, *J* = 17.4, 14.8, 4.2, 2.1 Hz, 2H), 2.26 (qd, *J* = 11.1, 3.0 Hz, 1H), 2.16 – 2.06 (m, 2H), 2.00 – 1.88 (m, 2H), 1.70 (dddd, *J* = 17.5, 12.6, 6.8, 2.9 Hz, 4H), 1.60 – 1.51 (m, 4H), 1.40 – 1.27 (m, 2H), 1.03 – 0.96 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 219.80, 199.34, 164.81, 127.23, 53.02, 51.63, 50.25, 47.55, 39.71, 38.43, 37.81, 35.66, 34.08, 31.20, 30.41, 22.24, 21.68, 20.29, 13.77. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{26}BrO_2^+$ 365.1111; Found: 365.1114.

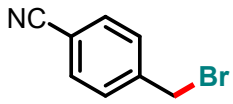
1-(bromomethyl)-4-nitrobenzene



21b

R_f = 0.4, 5% acetone in hexane, colorless solid (75 mg, 73% yield) ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.20 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 4.54 (s, 2H).[9]

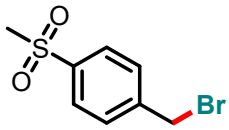
4-(bromomethyl)benzonitrile



22b

R_f = 0.4, 5% acetone in hexane, colorless solid (69 mg, 71% yield) ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.64 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 4.49 (s, 2H).[9]

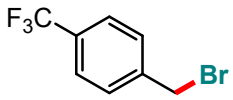
1-(bromomethyl)-4-(methylsulfonyl)benzene



23b R_f = 0.4, 5% acetone in hexane, colorless solid (69 mg, 77% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 4.53 (s, 2H), 3.08 (s, 3H).[9]

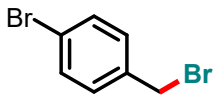
1-(bromomethyl)-4-(trifluoromethyl)benzene



24b R_f = 0.4, 5% acetone in hexane, colorless solid (71 mg, 76% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 4.52 (s, 2H). **^{19}F NMR** (471 MHz, CDCl3) δ -60.00, -60.04. [9]

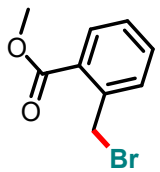
1-bromo-4-(bromomethyl)benzene



25b R_f = 0.4, 4% acetone in hexane, colorless solid (87 mg, 71% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 4.46 (s, 2H). [9]

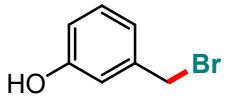
methyl 2-(bromomethyl)benzoate



26b R_f = 0.4, 5% acetone in hexane, colorless oil (100 mg, 88% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.42 – 7.36 (m, 1H), 4.98 (s, 2H), 3.96 (s, 3H).[9]

3-(bromomethyl)phenol

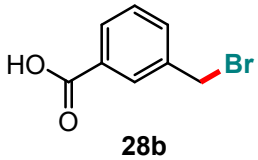


27b

R_f = 0.6, 10% acetone in hexane, colorless oil (55 mg, 59% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.24 (t, J = 7.9 Hz, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.91 – 6.89 (m, 1H), 6.79 (dd, J = 8.1, 2.2 Hz, 1H), 4.46 (s, 2H). [9]

3-(bromomethyl)benzoic acid

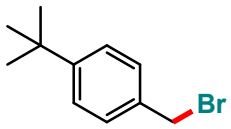


28b

R_f = 0.5, 15% acetone in hexane, colorless oil (73 mg, 68% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 4.57 (s, 2H). [9]

1-(bromomethyl)-4-(tert-butyl)benzene

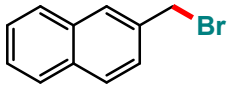


29b

R_f = 0.4, 5% acetone in hexane, colorless oil (95 mg, 84% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 4.57 (s, 2H), 1.40 (s, 9H). [9]

2-(bromomethyl)naphthalene

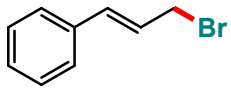


30b

R_f = 0.6, 5% acetone in hexane, yellow oil (97mg, 88% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, J_1 = 12.1, J_2 = 6.9 Hz, 4H), 7.53 (dd, J_1 = 8.7, J_2 = 6.3 Hz, 3H), 4.70 (s, 2H). [9]

(3-bromoprop-1-en-1-yl)benzene



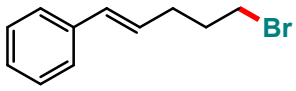
31b

R_f = 0.4, 5% acetone in hexane, yellow oil (70 mg, 71% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 6.68 (d, J = 15.6 Hz, 1H), 6.44 (dd,

J_1 = 15.6, J_2 = 7.8 Hz, 1H), 4.20 (d, J = 7.8 Hz, 2H).[10]

(5-bromopent-1-en-1-yl)benzene

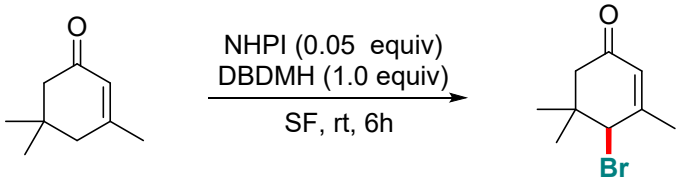


1c

R_f = 0.4, 5% acetone in hexane, yellow oil (23 mg, 52% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.7 Hz, 2H), 7.34 (dd, J = 8.0, 4.2 Hz, 2H), 7.28 – 7.24 (m, 1H), 6.52 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.8, 6.9 Hz, 1H), 3.50 (t, J = 7.0 Hz, 2H), 2.81 (qd, J = 7.0, 1.3 Hz, 2H). [11]

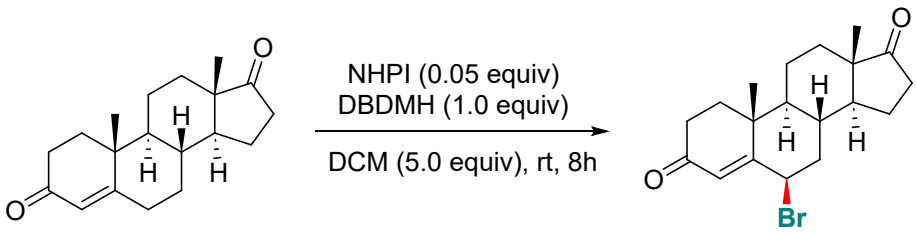
6. Gram-scale experiment



10.0 g, 72.5 moml

isolated yield of **1b**: **84%**

Substrates **1a** (72.5 mmol, 1.0 equiv.) and DBDMH (1.0 equiv.) were add to the glass tube. The mixture without solvent at room temperature irradiation for 6 h. The mixture was directly purified by silica gel flash chromatography to give the desired product **1b** (13.1 g, 84%) as white solid.



10.0 g, 35.0 mmol

isolated yield of **20b**: **91%**

Substrates **20a** (35.0 mmol, 1.0 equiv.) and DBDMH (1.0 equiv.) were add to the glass tube, a solvent DCM (5.0 equiv.) needs to be added the mixture and then at room temperature irradiation for 8 h The mixture was directly purified by silica gel flash chromatography to give the desired product **20b** (11.6 g, 91%) as white solid.

7. X-ray crystallographic data for compound 20b

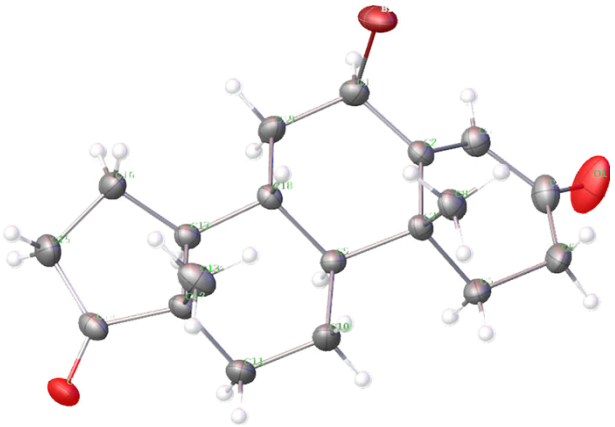
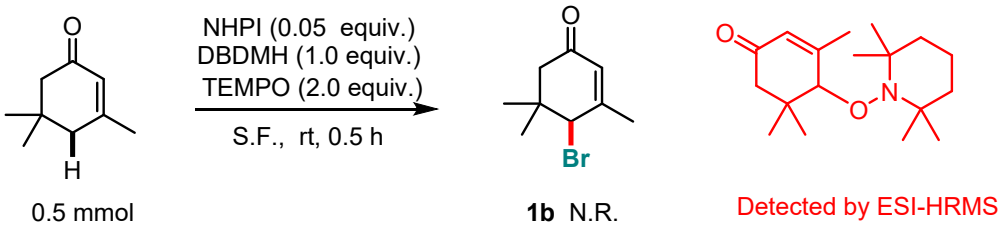


Figure S1. X-ray structure of compound **20b**

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **20b** in a mixture of CH_2Cl_2 and hexane at room temperature. The X-ray data of compound **20b** is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2361001.

8. Mechanistic studies

Spin trapping experiment with TEMPO



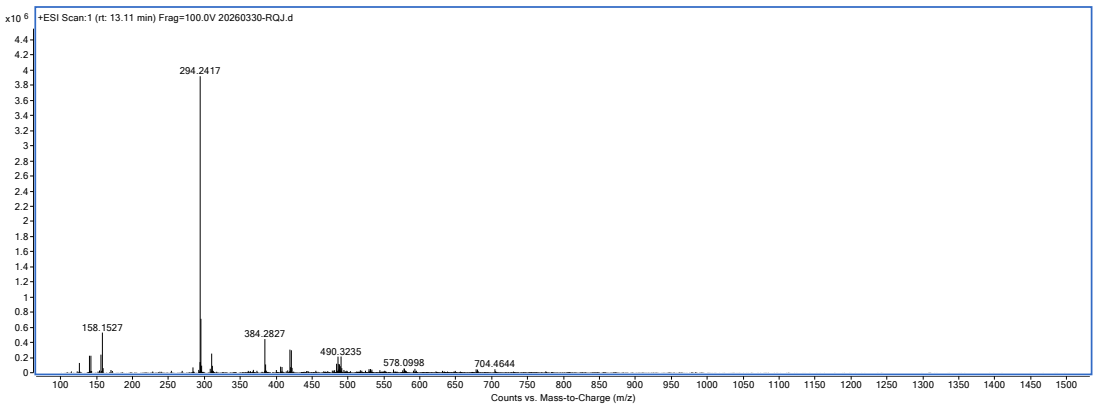


Figure S2. ESI-HRMS mass spectra

Cyclic voltammograms were measured using a CHI 730E bipotentiostat equipped with electrochemical analysis software. A reaction was set up using General Procedure

with three electrodes: Sn as working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter as electrode, the electrodes were polished with 0.05 μm aluminum oxide, ultrasonically rinsed with ethanol and ultrapure water before measurements. The solvent deoxygenated by nitrogen bubbling for 0.5 h. The CV plotting convention was IUPAC. The starting point was 0.0 V.

cyclic voltammetry experiment of blank sample using glassy carbon working electrode at 100 mV/S. A solution of Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

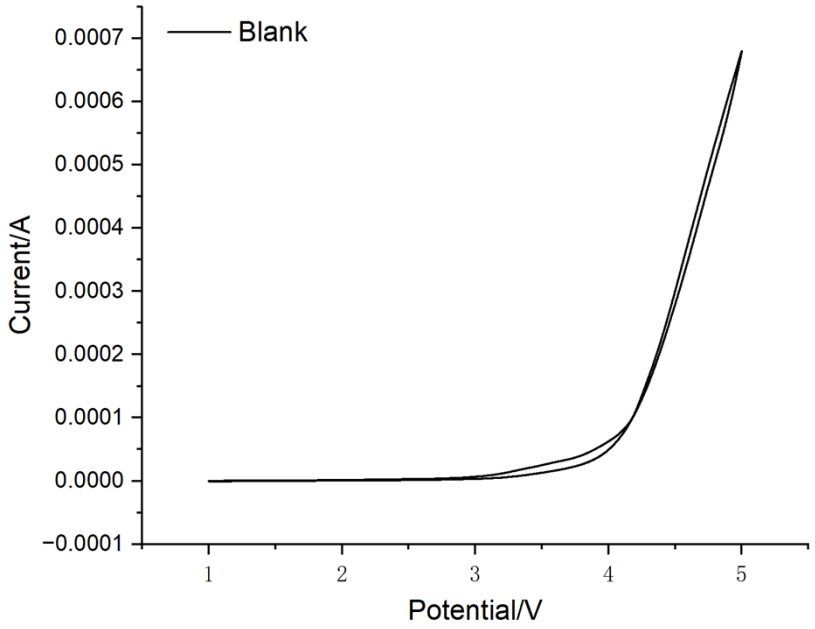


Figure S3. CV curve of blank

A solution of DBDMH (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

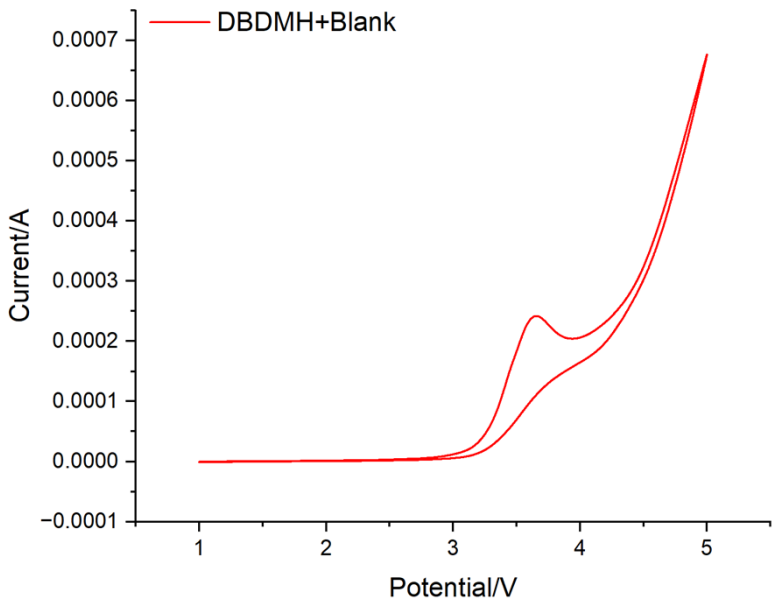


Figure S4. CV curve of DBDMH

A solution of NHPI (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

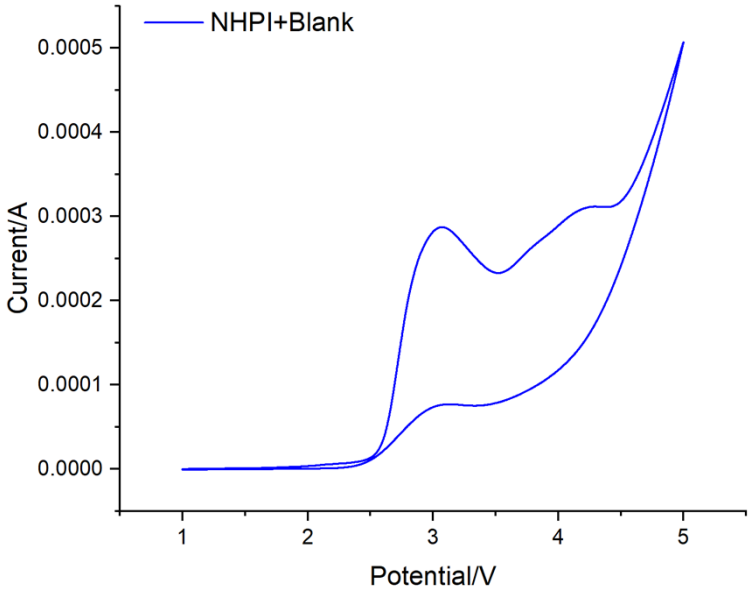


Figure S5. CV curve of NHPI

A solution of DBDMH (0.05 mmol) and NHPI (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

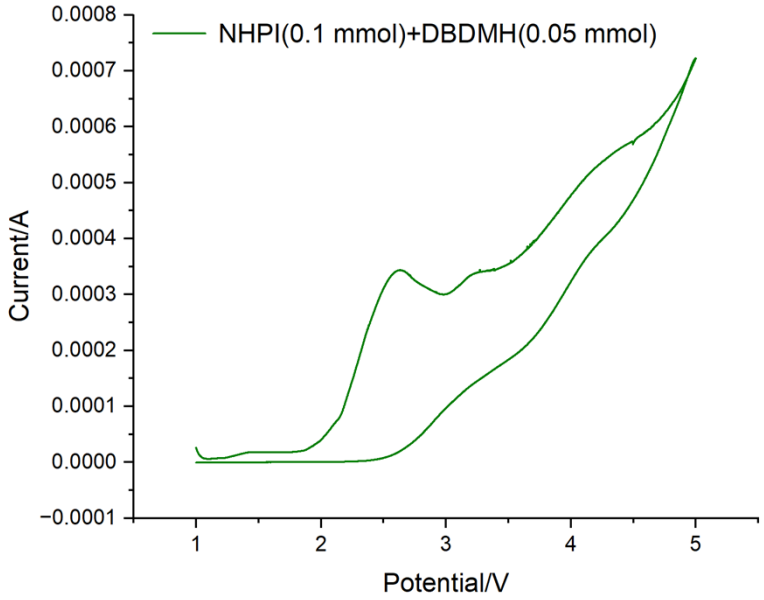


Figure S6. CV curve of DBDMH (0.05 mmol) and NHPI (0.1 mmol)

A solution of DBDMH (0.1 mmol) and NHPI (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

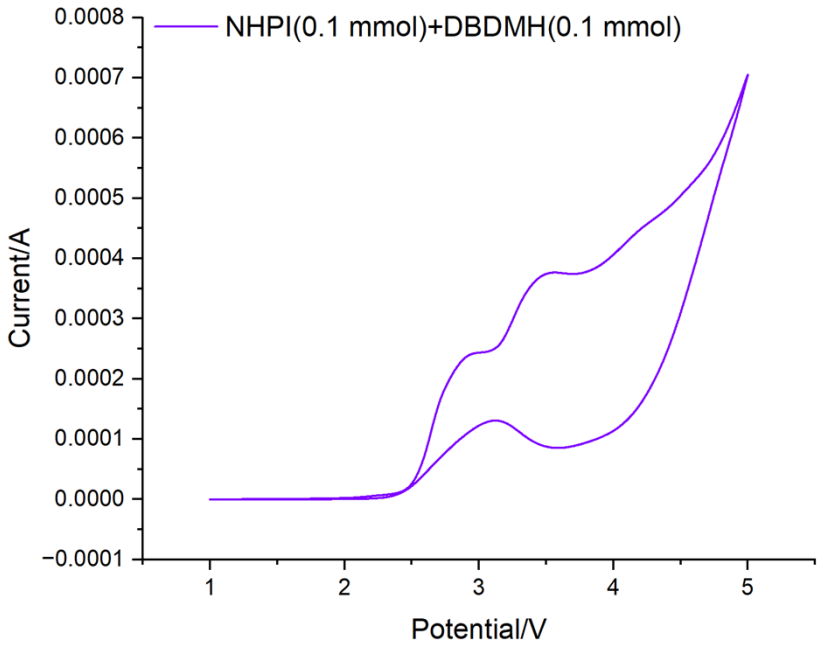


Figure S7. CV curve of DBDMH (0.1 mmol) and NHPI (0.1 mmol)

A solution of DBDMH (0.2 mmol) and NHPI (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel

electrode (SCE). Potential sweep rate was 100 mV/s.

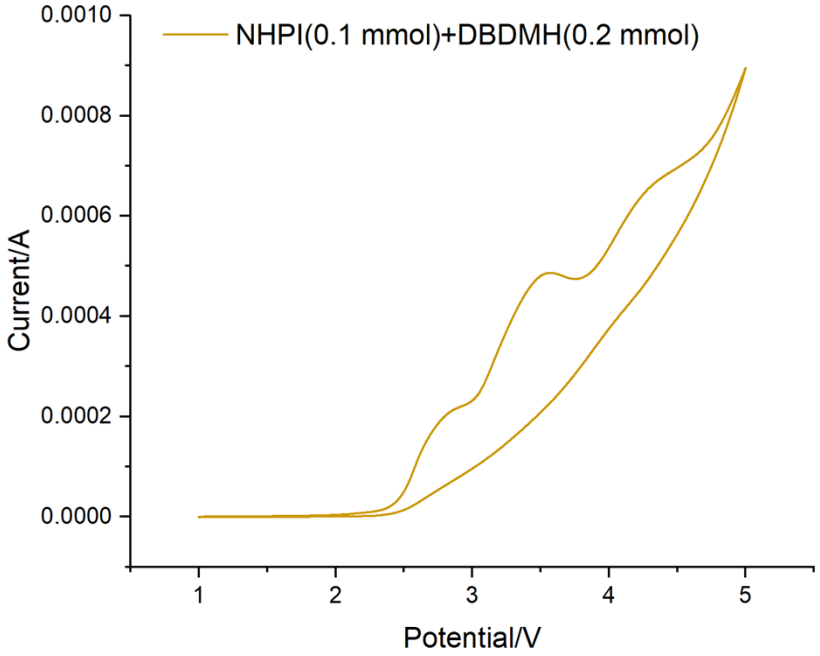


Figure S8. CV curve of DBDMH (0.2 mmol) and NHPI (0.1 mmol)

A solution of DBDMH (0.5 mmol) and NHPI (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous DCM was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

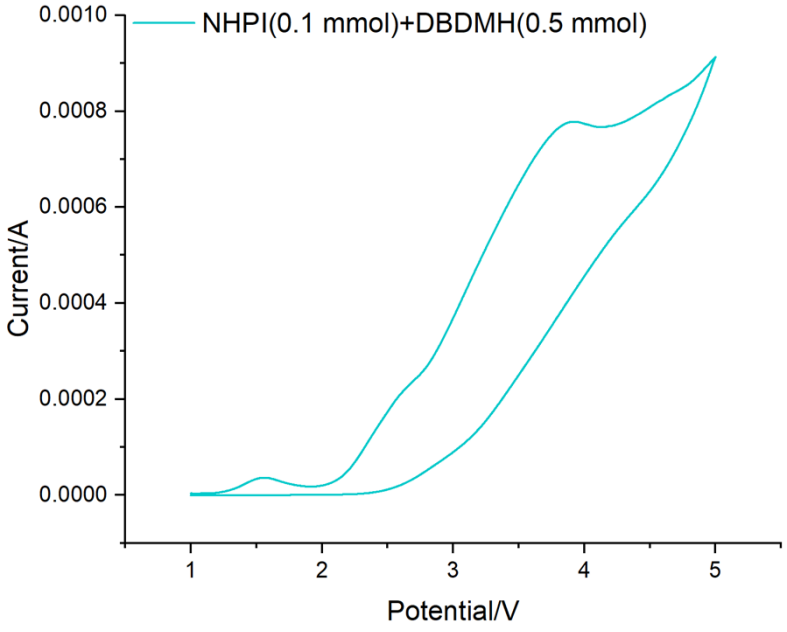


Figure S9. CV curve of DBDMH (0.5 mmol) and NHPI (0.1 mmol)

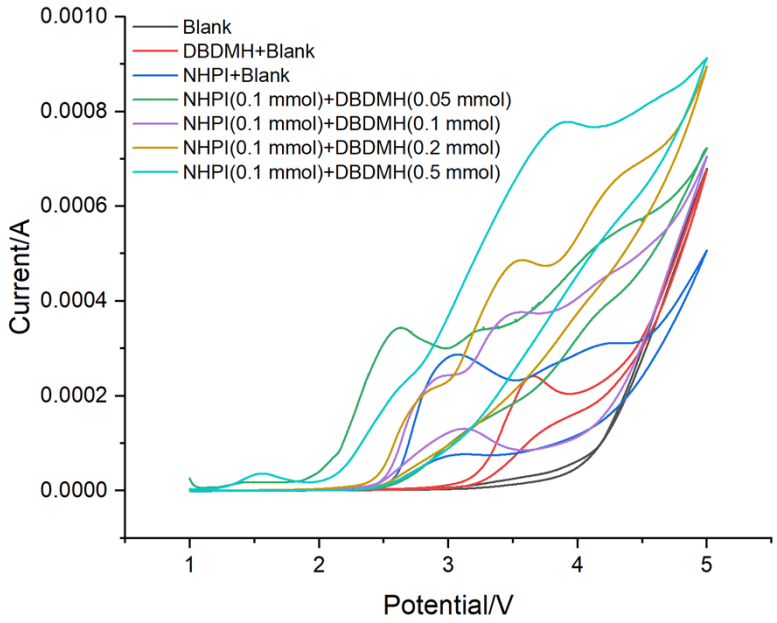


Figure S10. CV curve

Result:

In DCM (vs. SCE), the oxidation peak of DBDMH was observed at 3.50 V.

In DCM (vs. SCE), the oxidation peak of NHPI appeared at 2.73 V.

In the mixed system, a gradual decrease in the oxidation peak current of NHPI as the concentration of DBDMH is increased.

Based on the monitoring of reaction products, the determination of the oxidation potentials of DBDMH and NHPI, and the measurement of the redox potential of their mixture, we propose the following mechanism. In this reaction system, DBDMH acts both as an oxidant driving the conversion of NHPI to PINO and as a bromine source.

9. References

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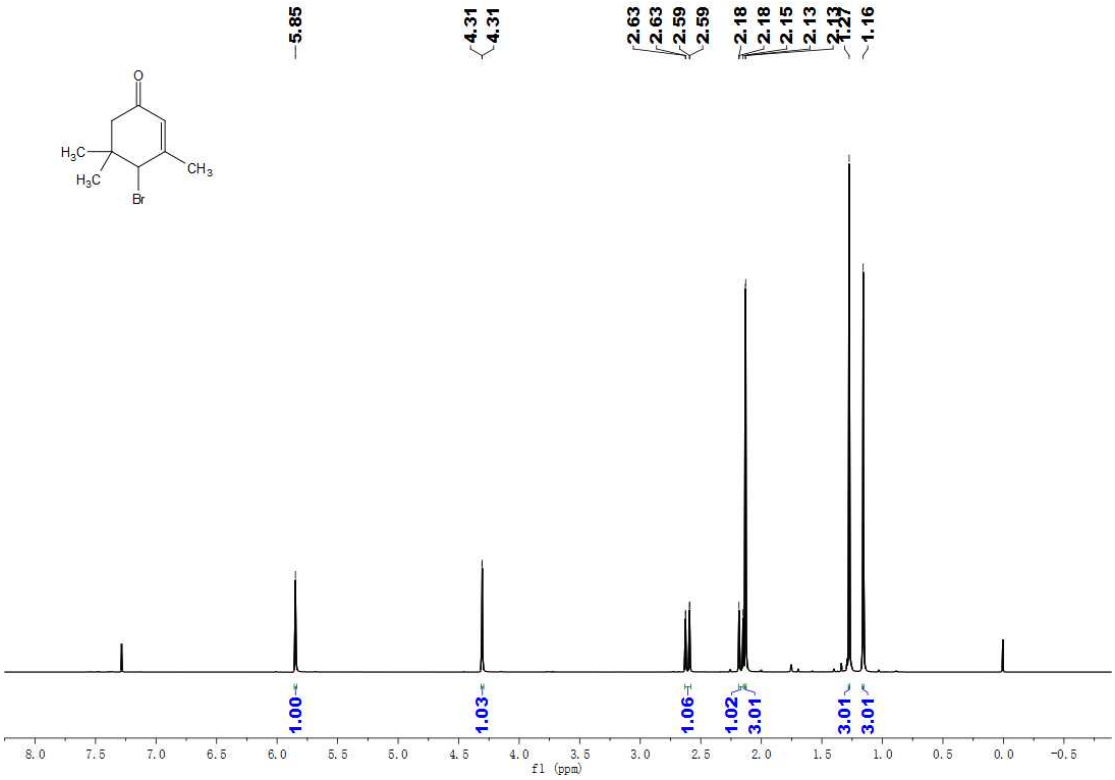
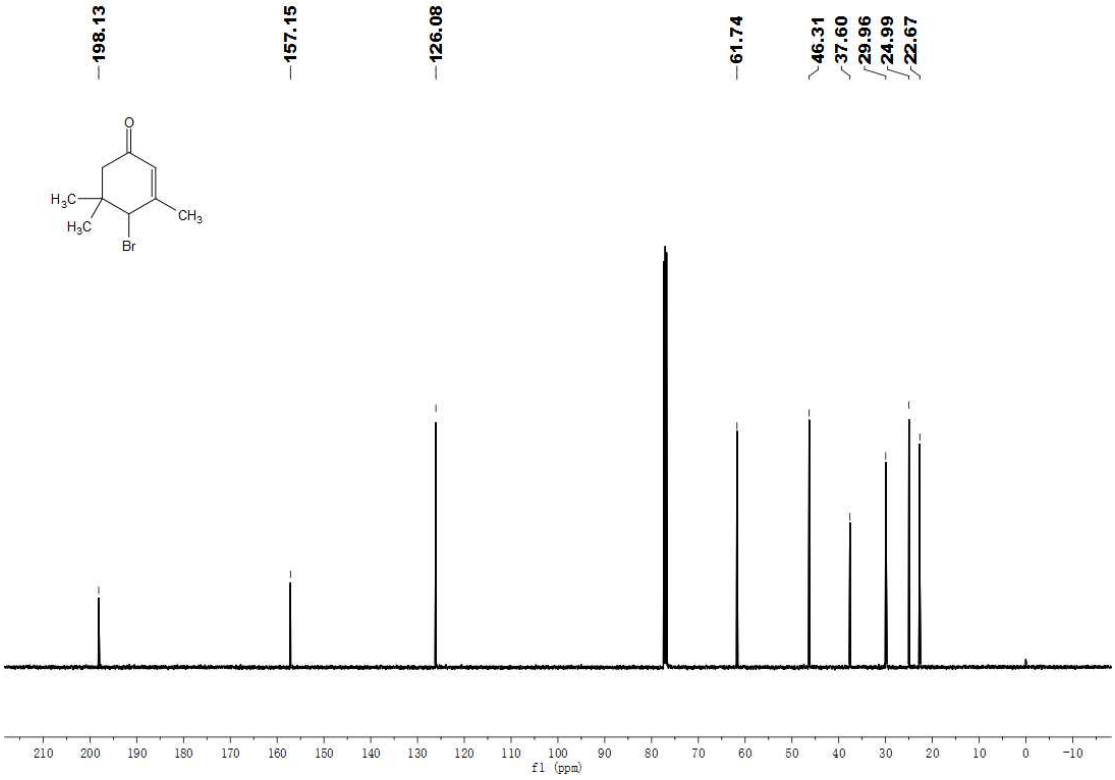
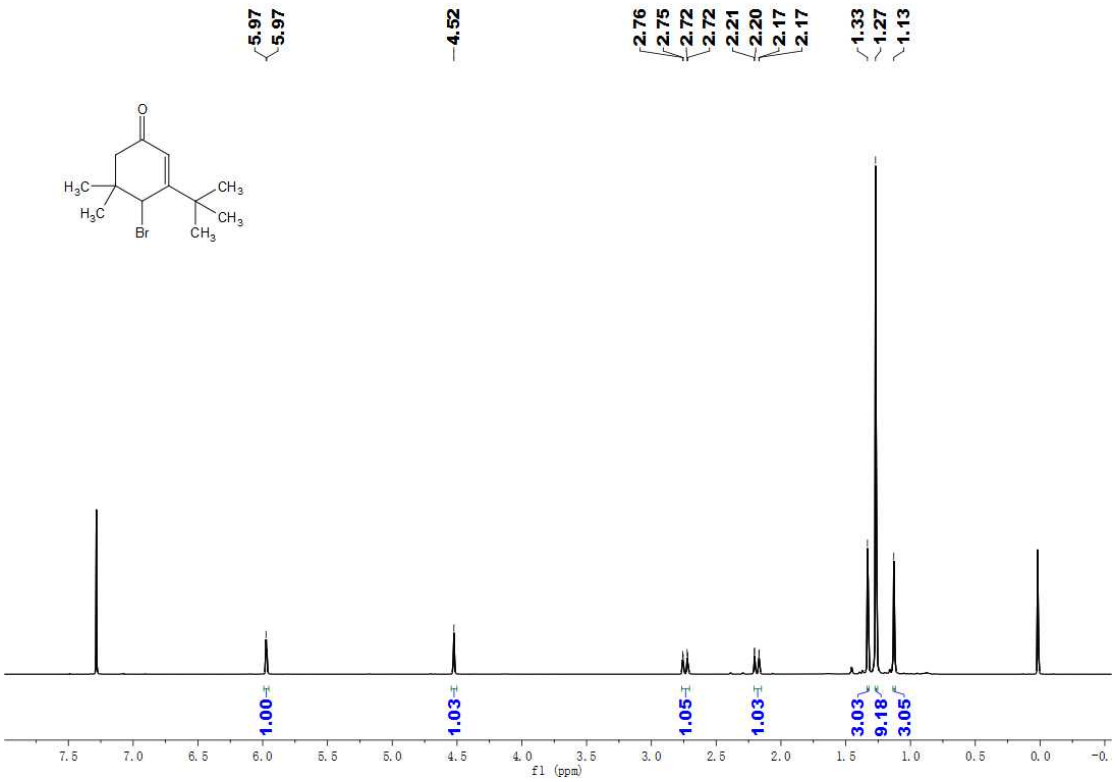
10. ^{1}H-NMR and ^{13}C-NMR spectra



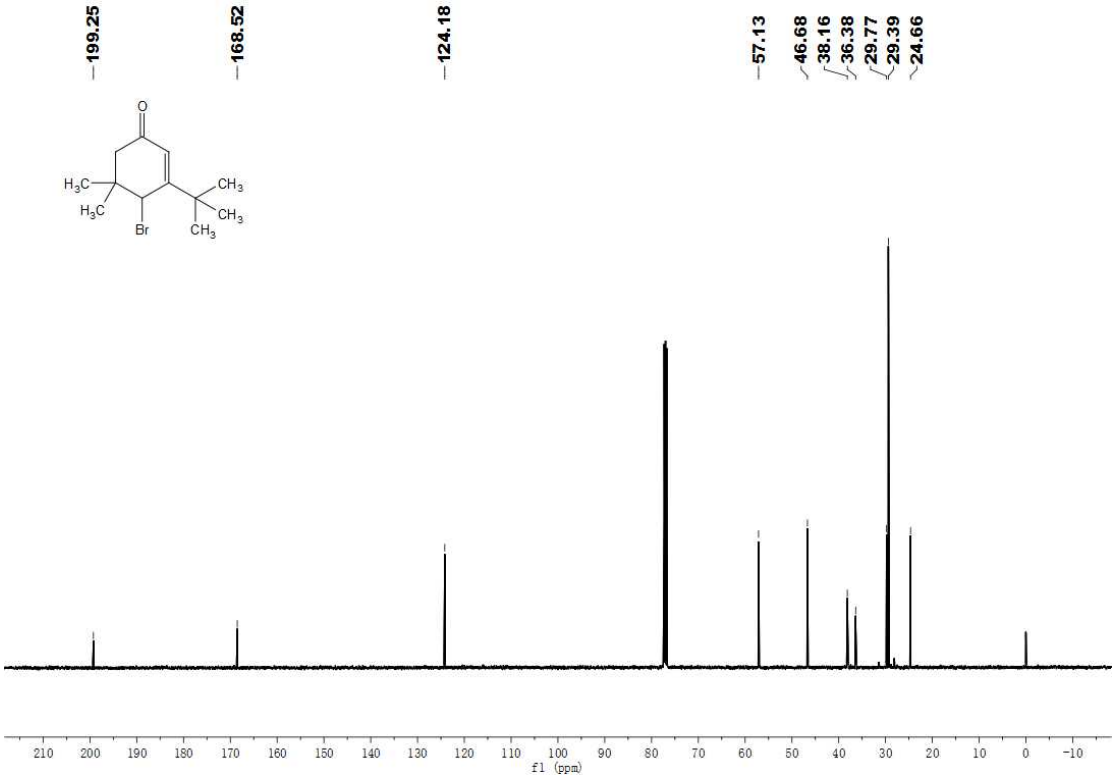
^{1}H-NMR of compound **1b** (500 MHz, $CDCl_3$)



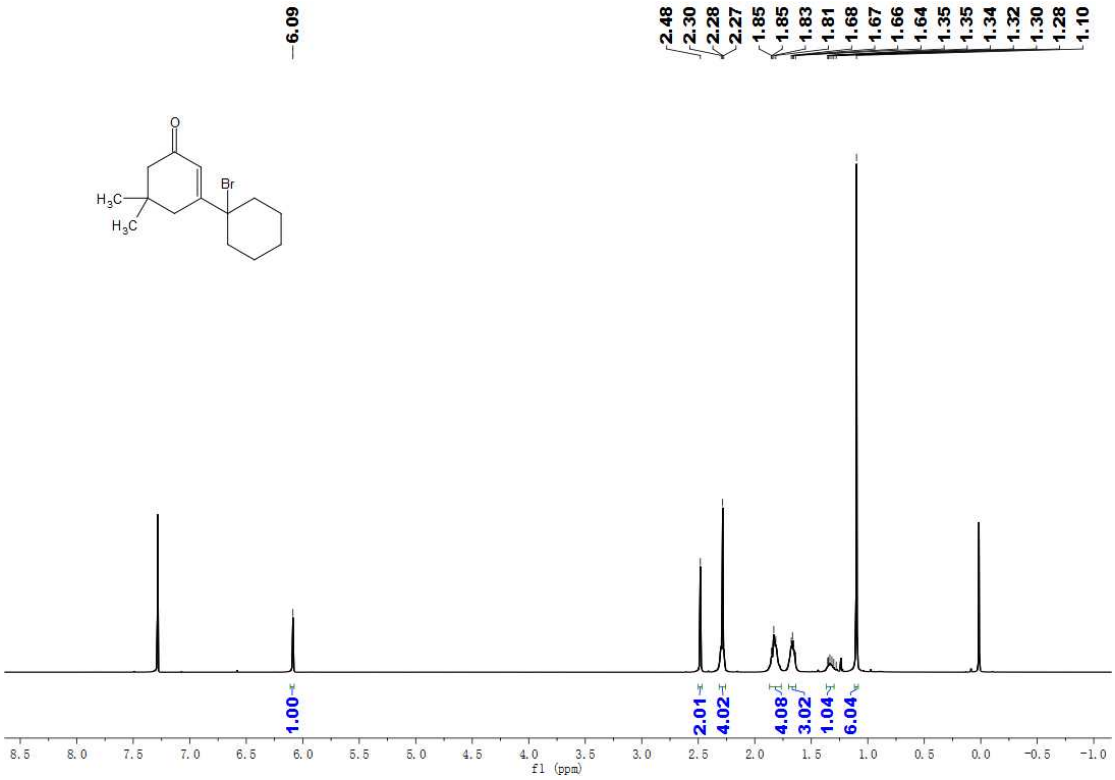
^{13}C-NMR of compound **1b** (126 MHz, $CDCl_3$)



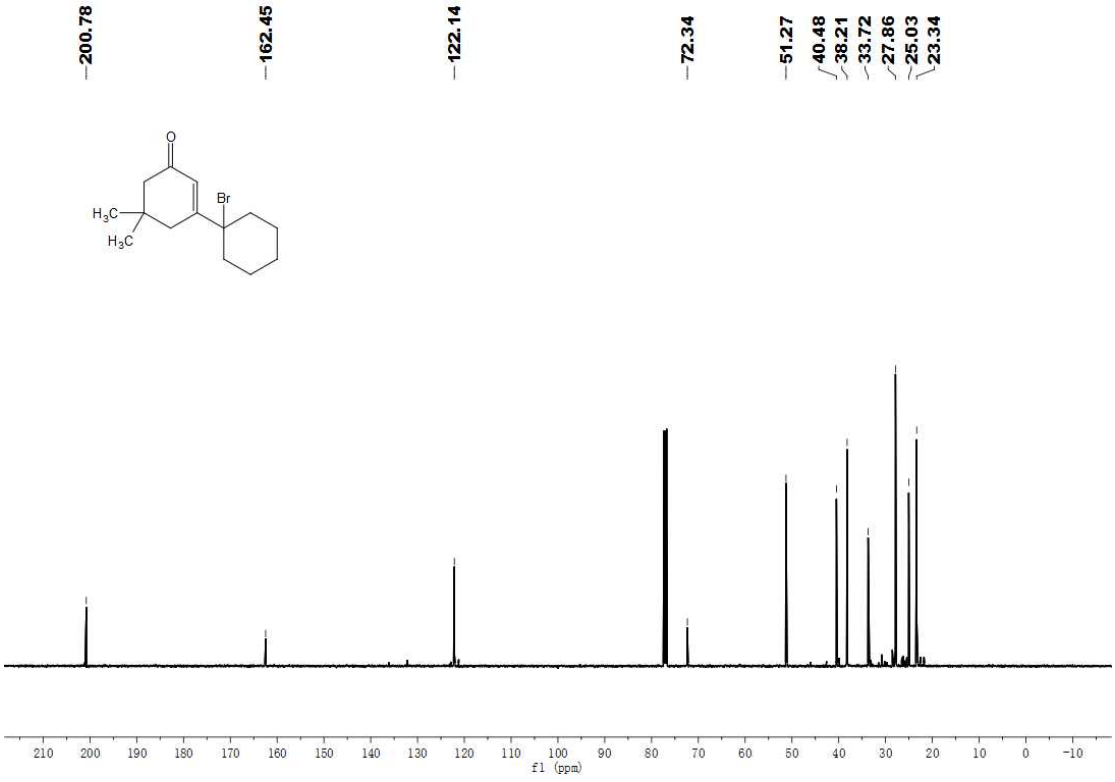
^{1}H-NMR of compound **2b** (500 MHz, $CDCl_3$)



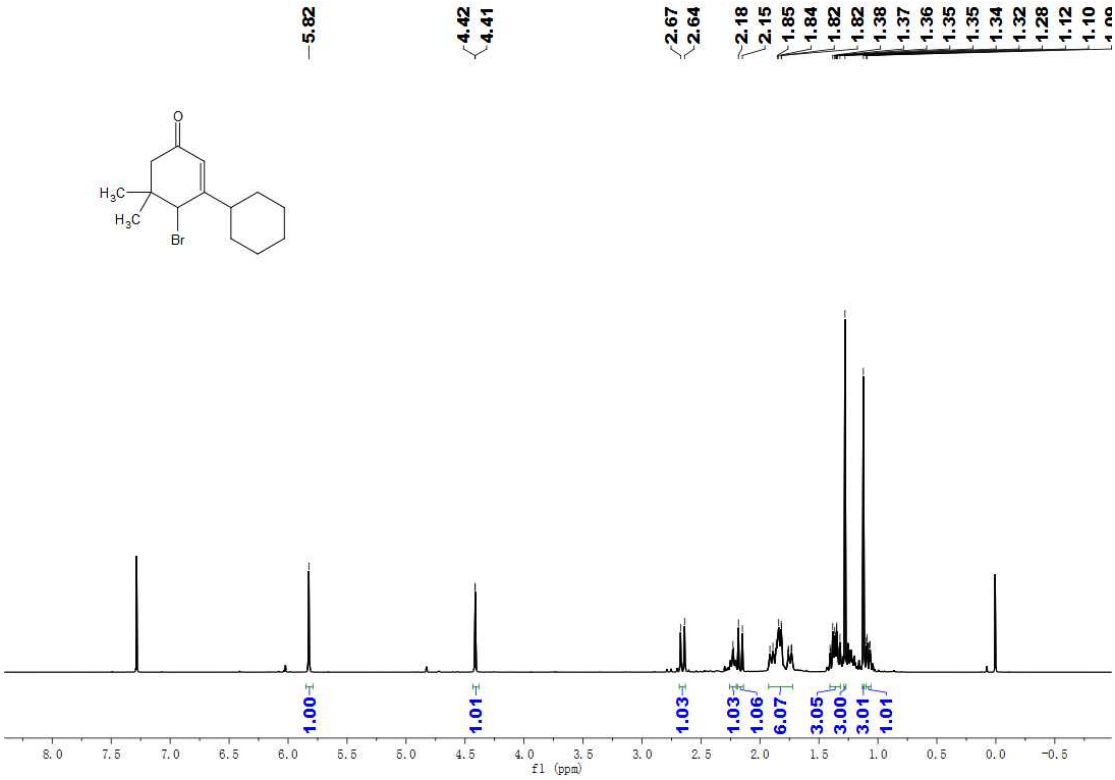
^{13}C-NMR of compound **2b** (126 MHz, $CDCl_3$)



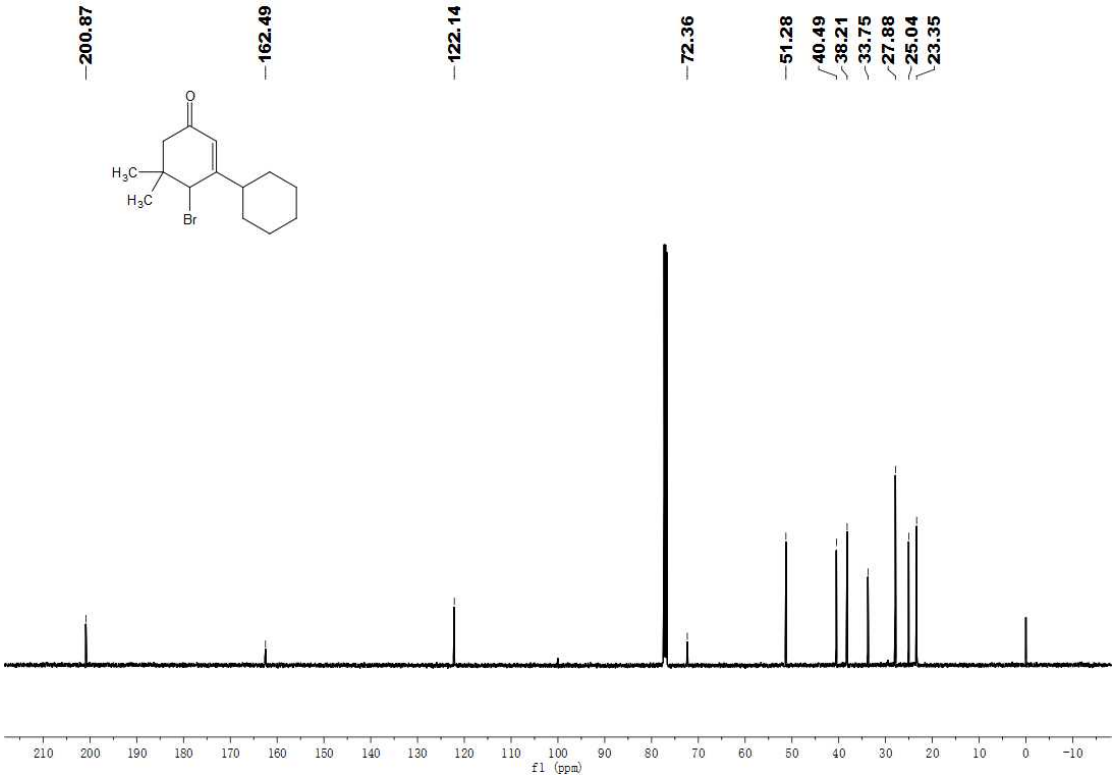
^{1}H-NMR of compound **3b** (500 MHz, $CDCl_3$)



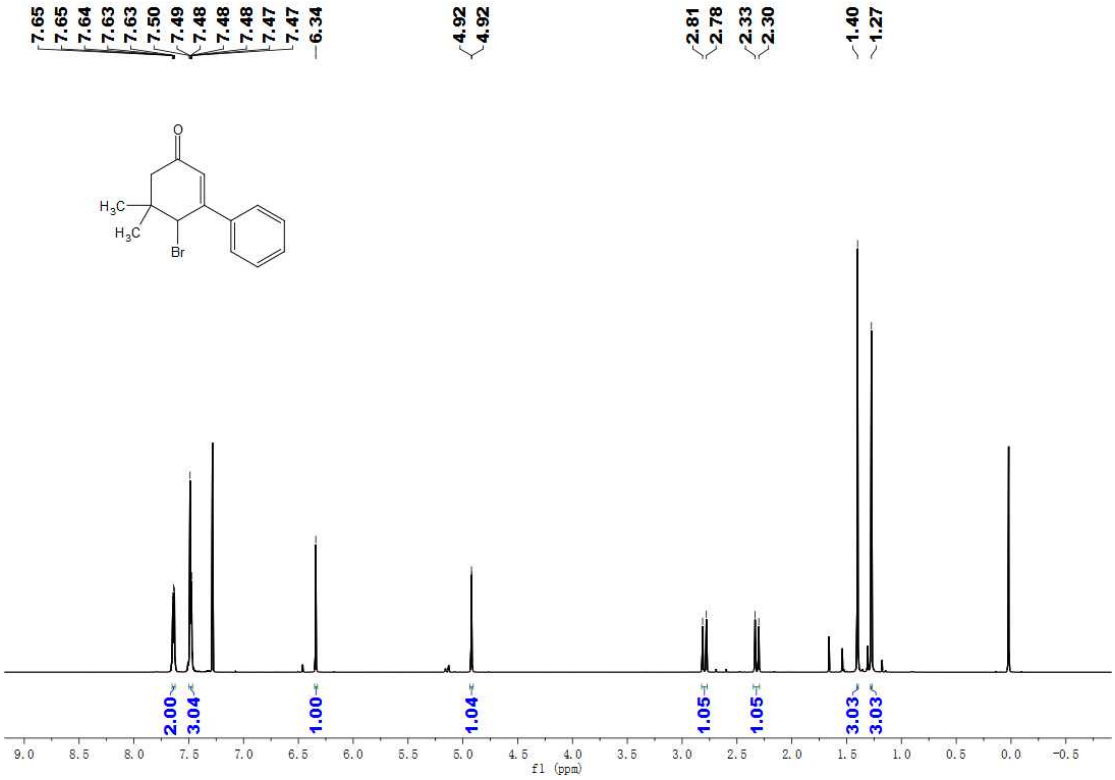
^{13}C-NMR of compound **3b** (126 MHz, $CDCl_3$)



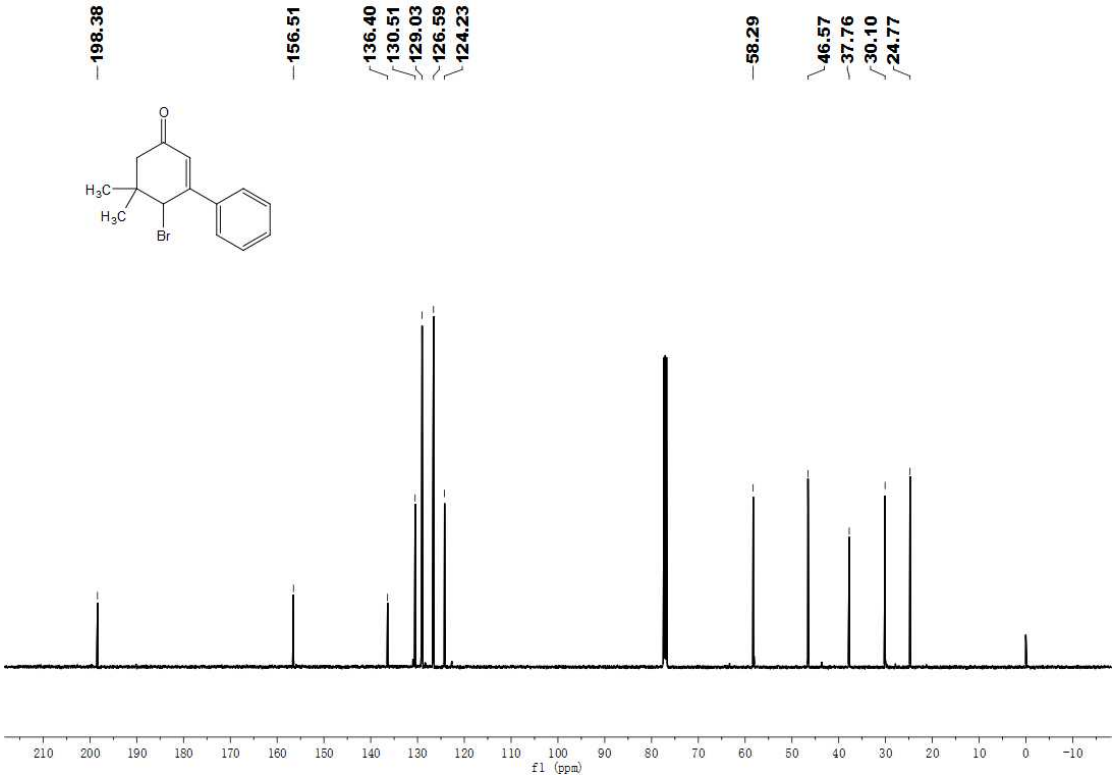
^{1}H-NMR of compound **3b'** (500 MHz, $CDCl_3$)



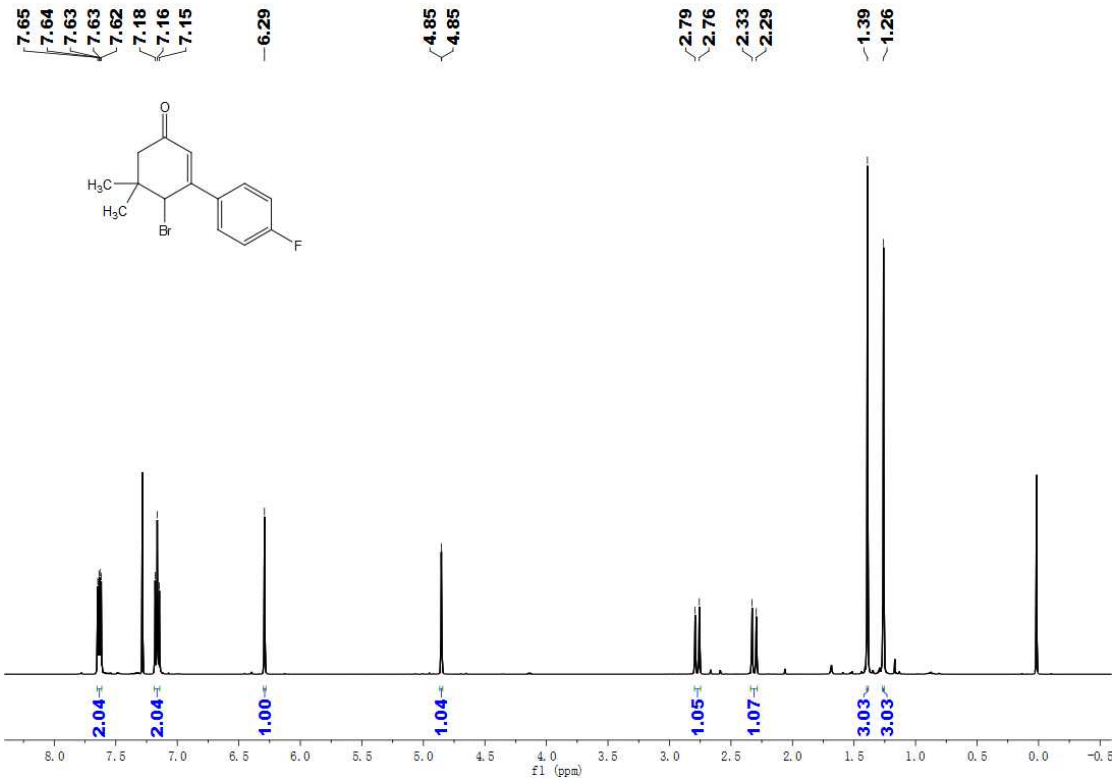
^{13}C-NMR of compound **3b'** (126 MHz, $CDCl_3$)



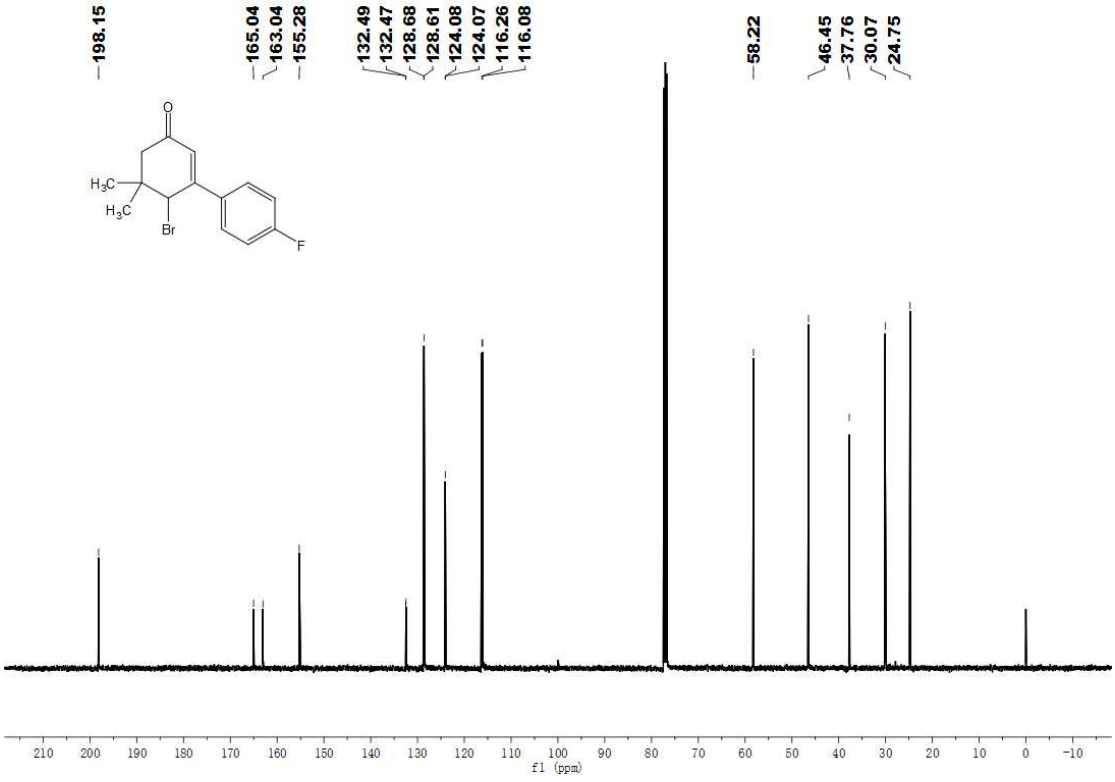
^{1}H-NMR of compound **4b** (500 MHz, $CDCl_3$)



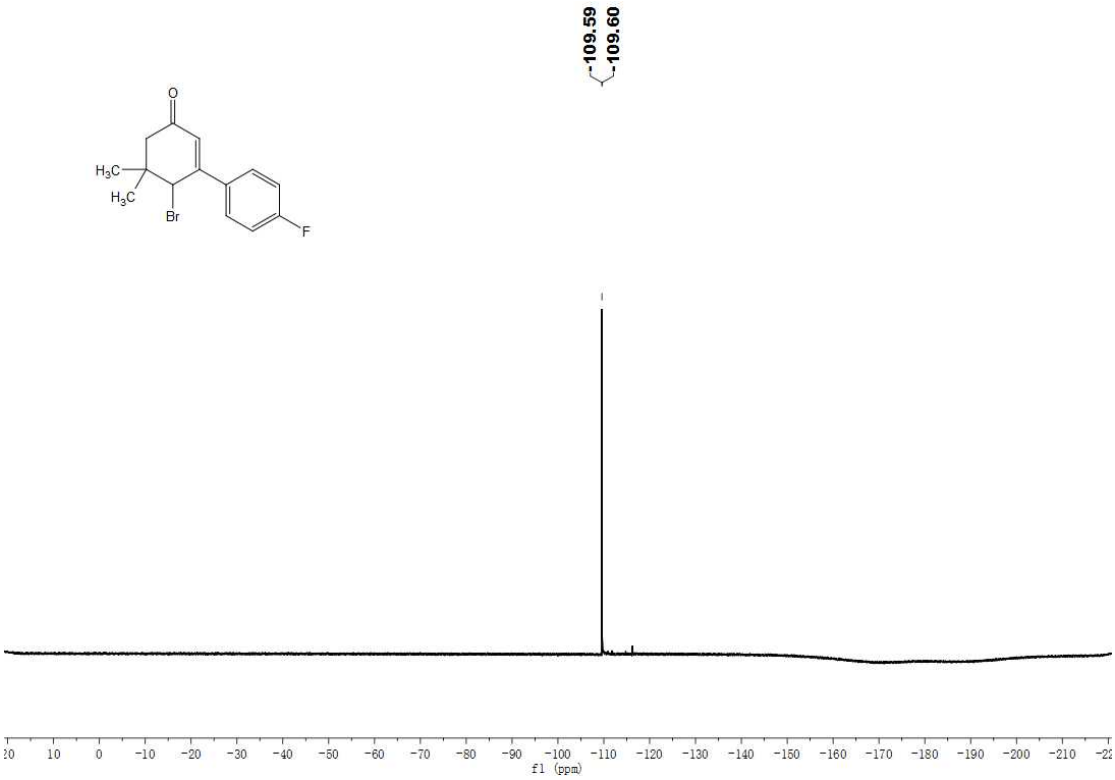
^{13}C-NMR of compound **4b** (126 MHz, $CDCl_3$)



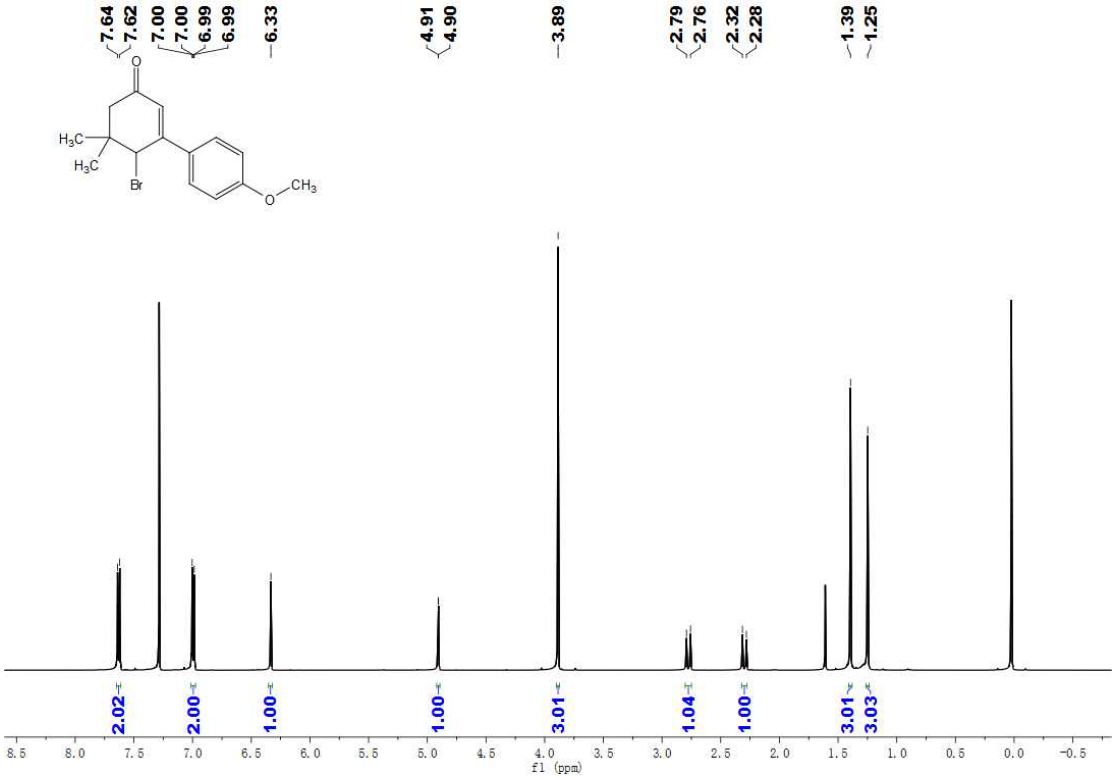
^{1}H-NMR of compound **5b** (500 MHz, $CDCl_3$)



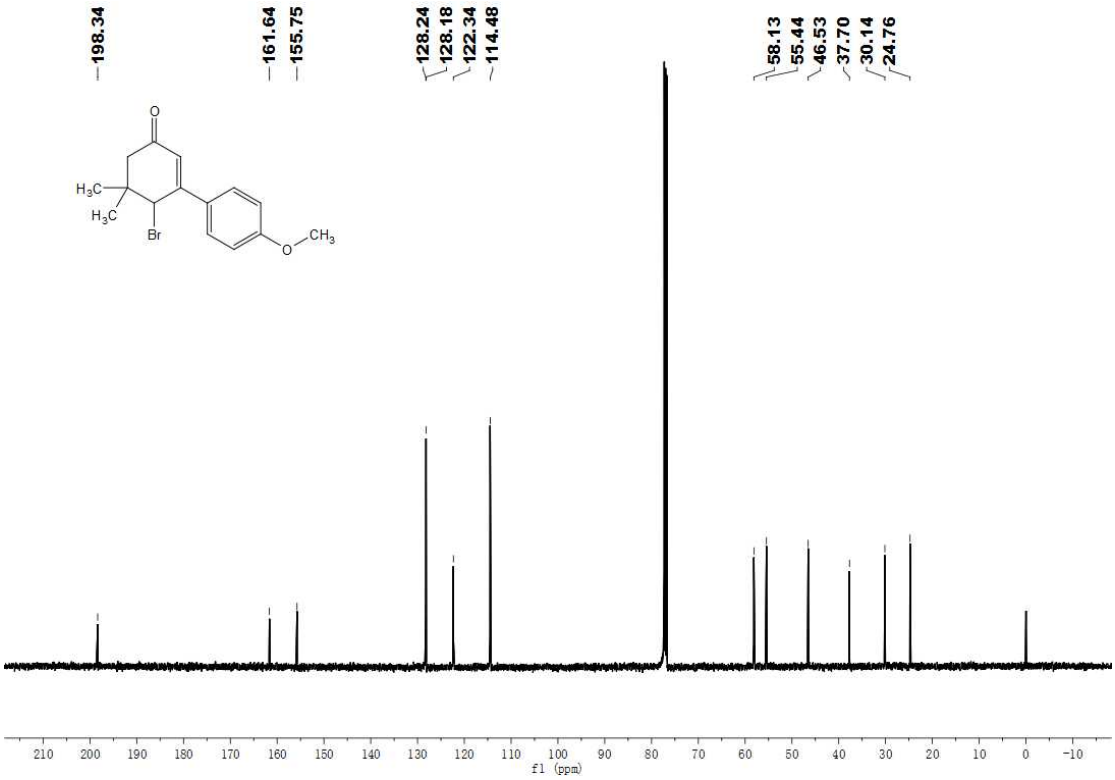
^{13}C-NMR of compound **5b** (126 MHz, $CDCl_3$)



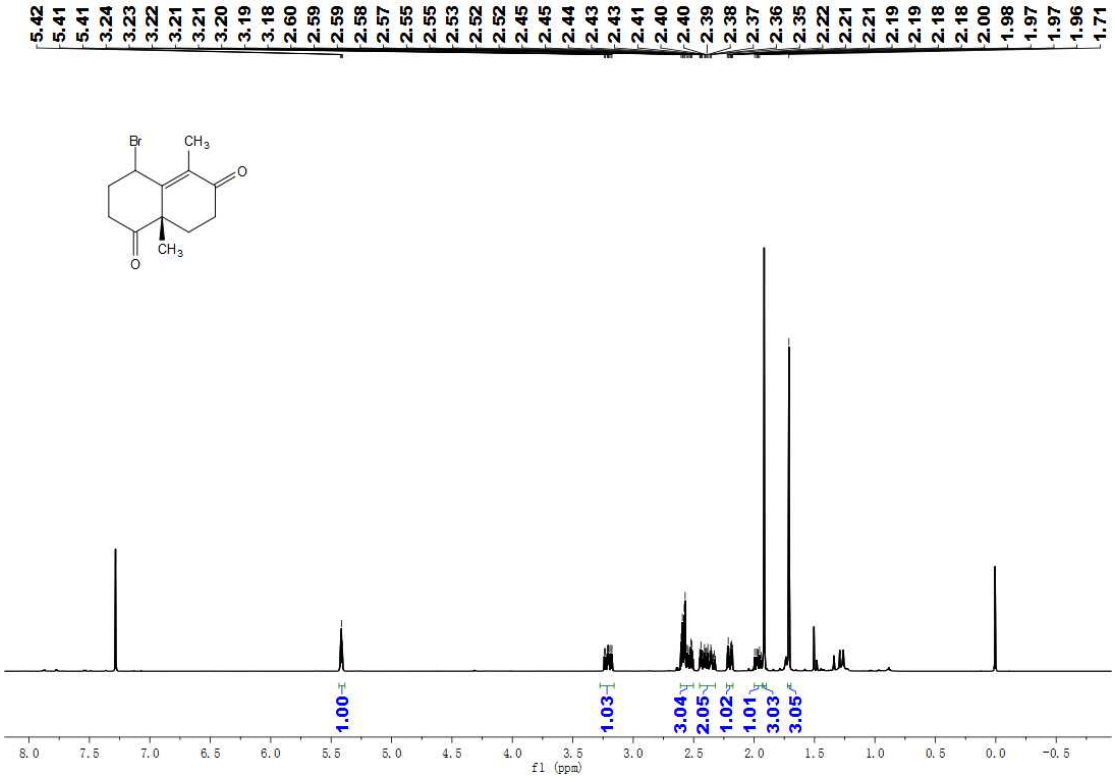
^{19}F NMR of compound **5b** (471 MHz, $CDCl_3$)



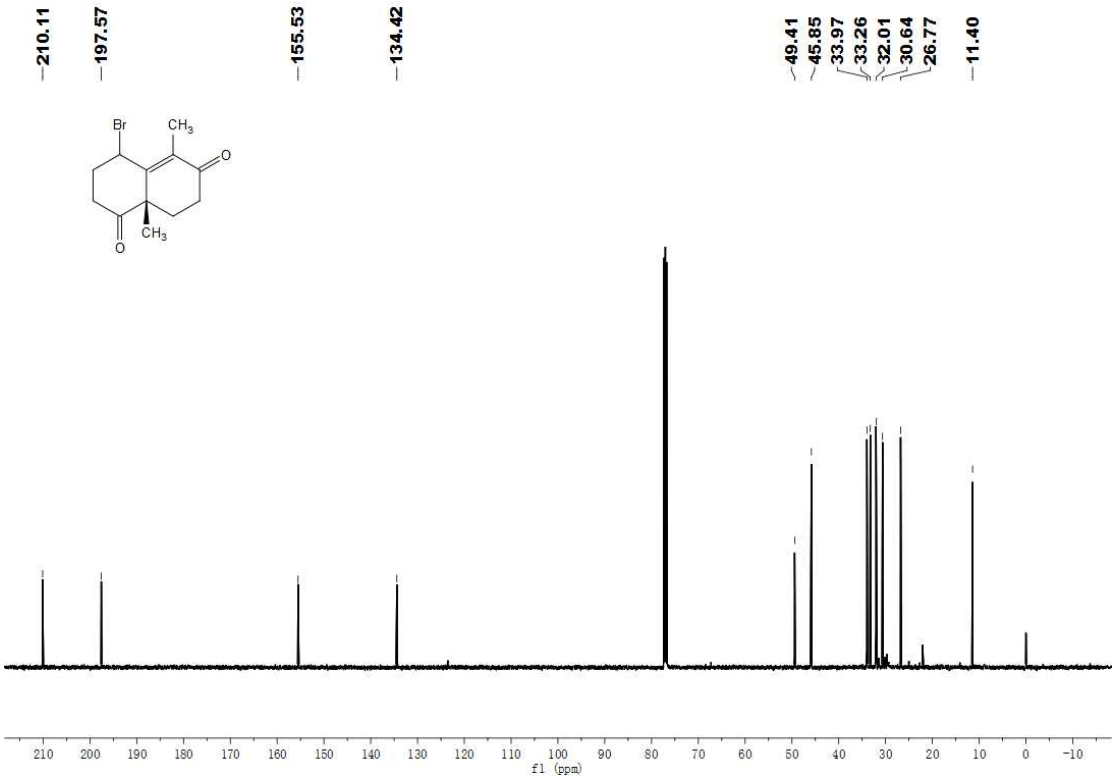
^{1}H-NMR of compound **6b** (500 MHz, $CDCl_3$)



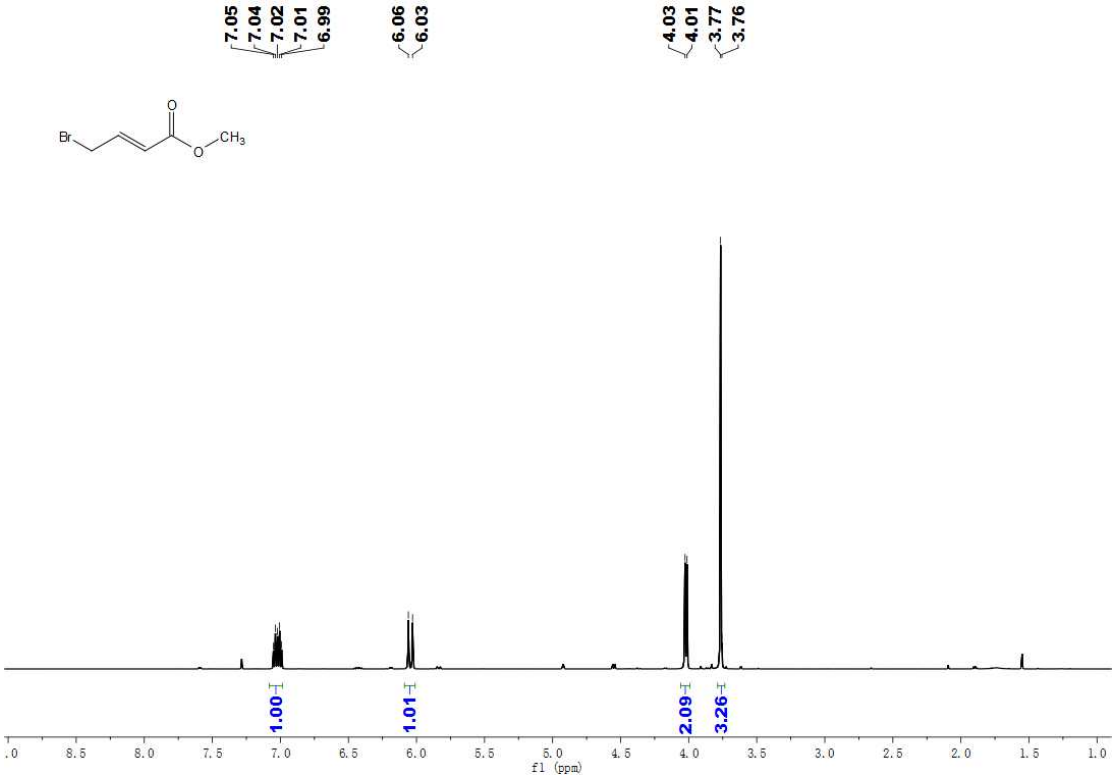
^{13}C-NMR of compound **6b** (126 MHz, $CDCl_3$)



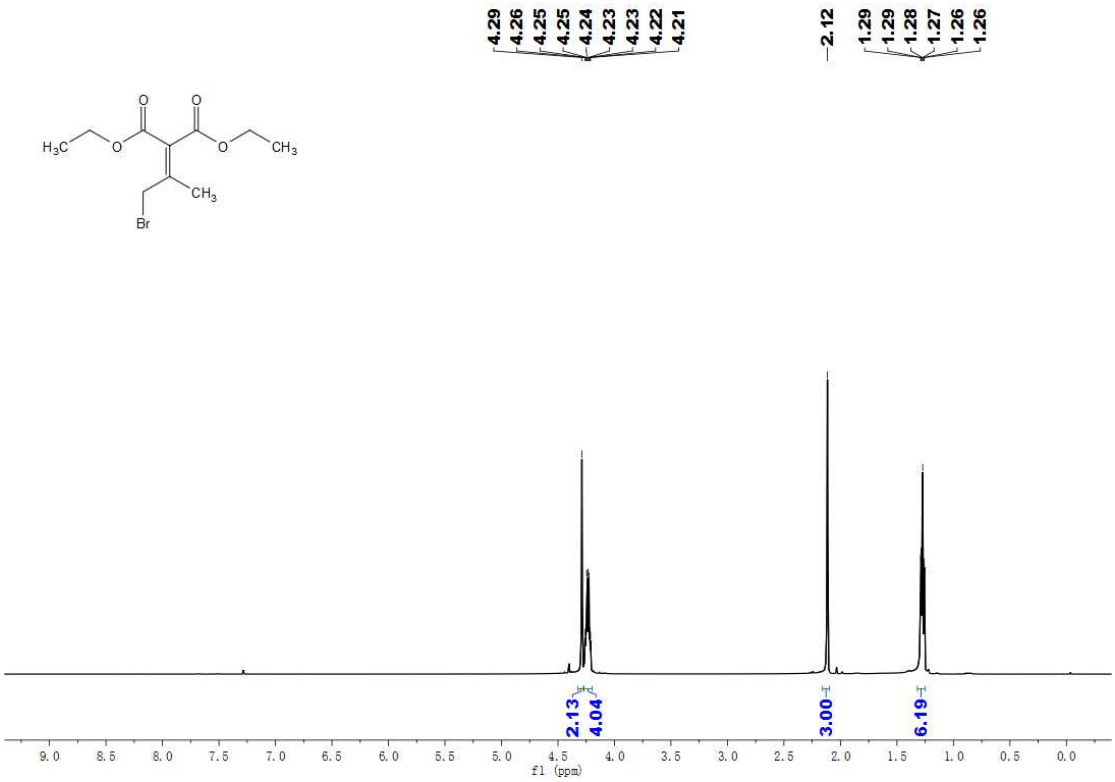
^{1}H-NMR of compound **7b** (500 MHz, $CDCl_3$)



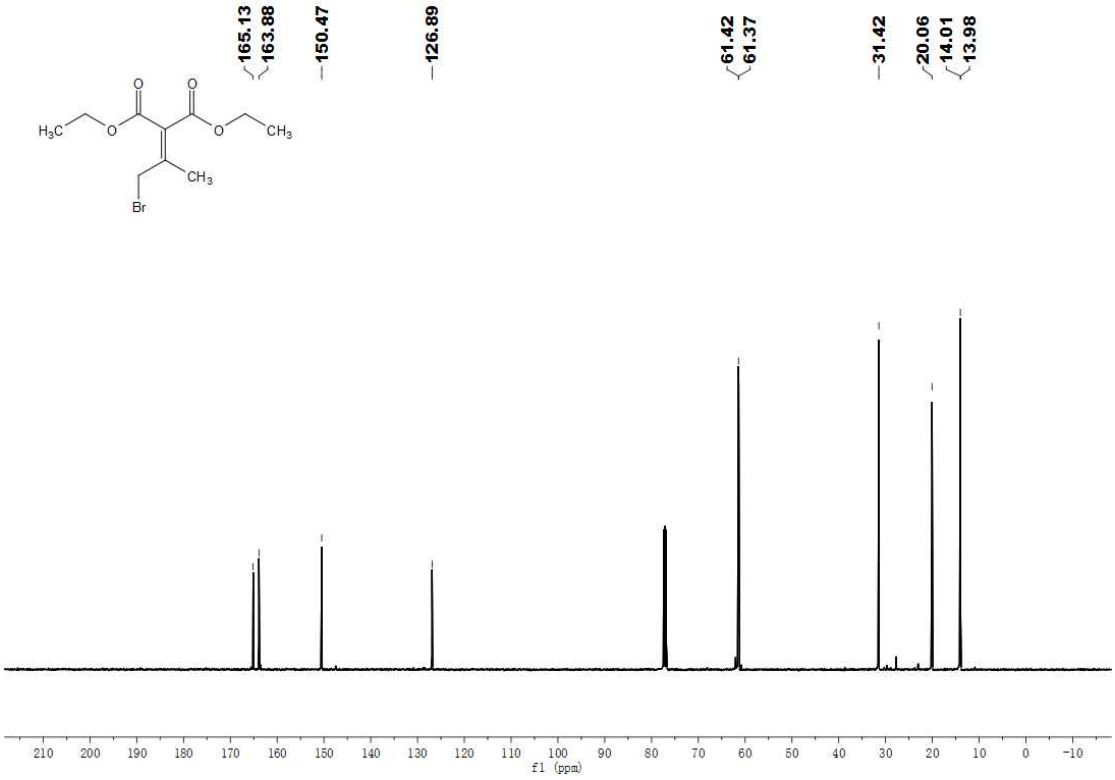
^{13}C-NMR of compound **7b** (126 MHz, $CDCl_3$)



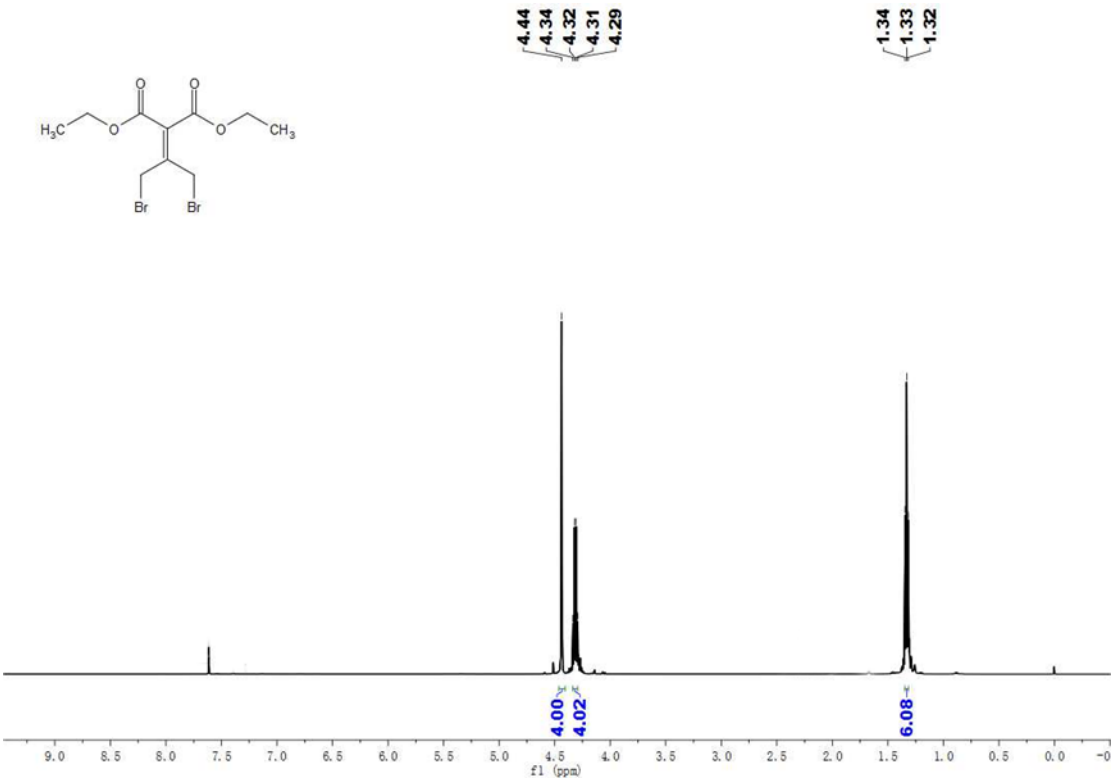
^{1}H-NMR of compound **8b** (500 MHz, $CDCl_3$)



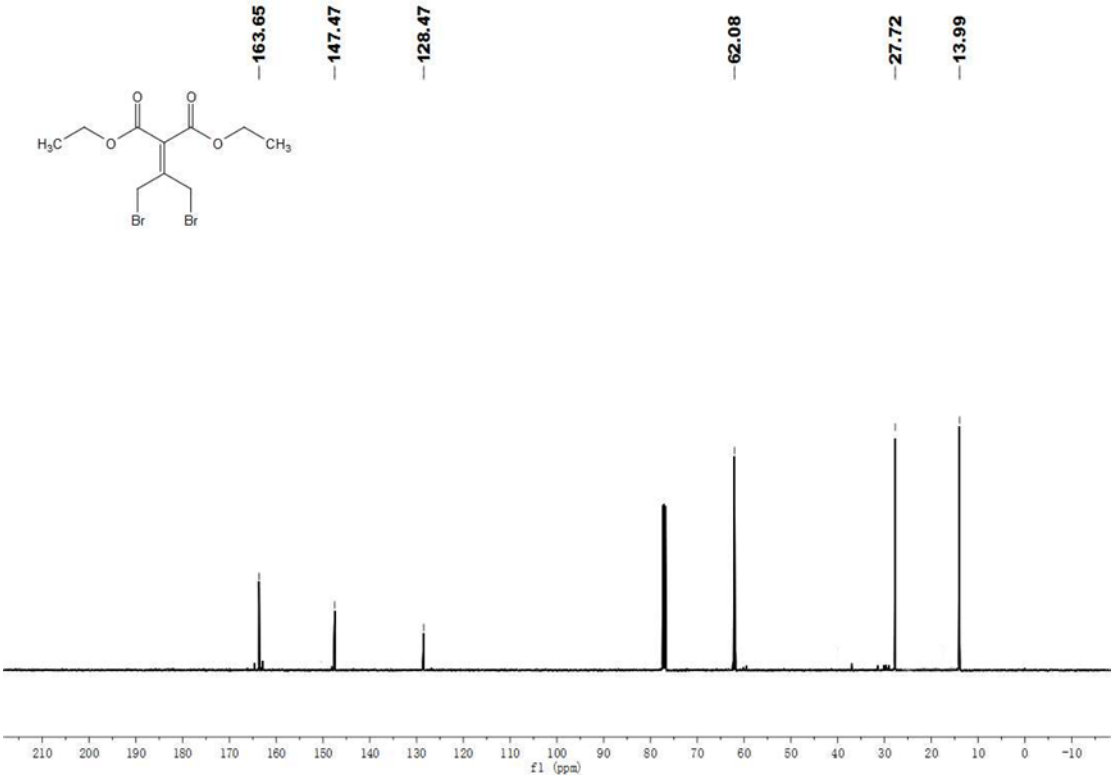
^{1}H-NMR of compound **9b** (500 MHz, $CDCl_3$)



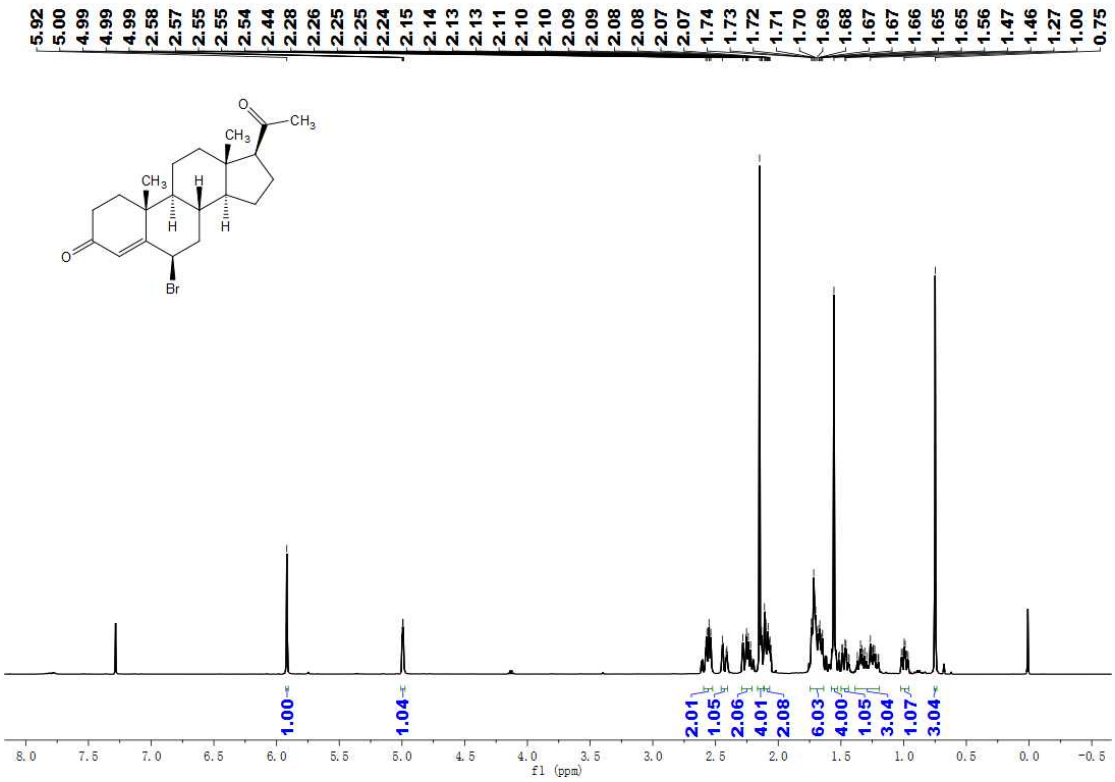
^{13}C-NMR of compound **9b** (126 MHz, $CDCl_3$)



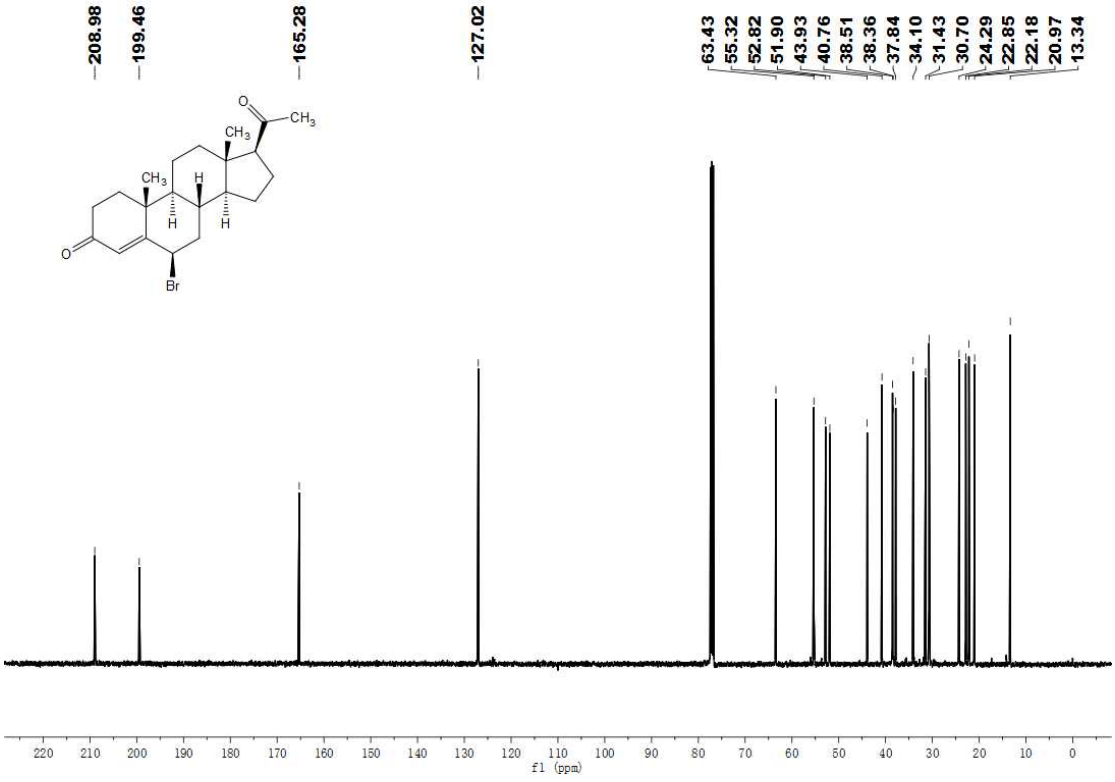
^{1}H-NMR of compound **10b** (500 MHz, $CDCl_3$)



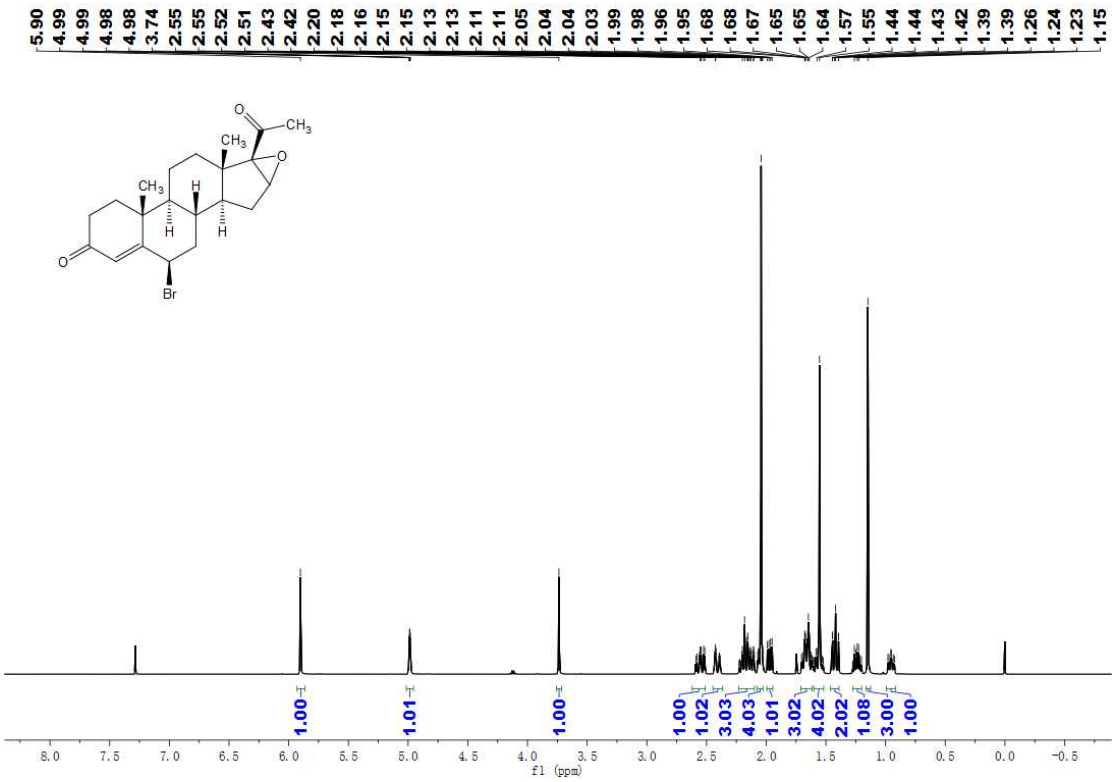
^{13}C-NMR of compound **10b** (126 MHz, $CDCl_3$)



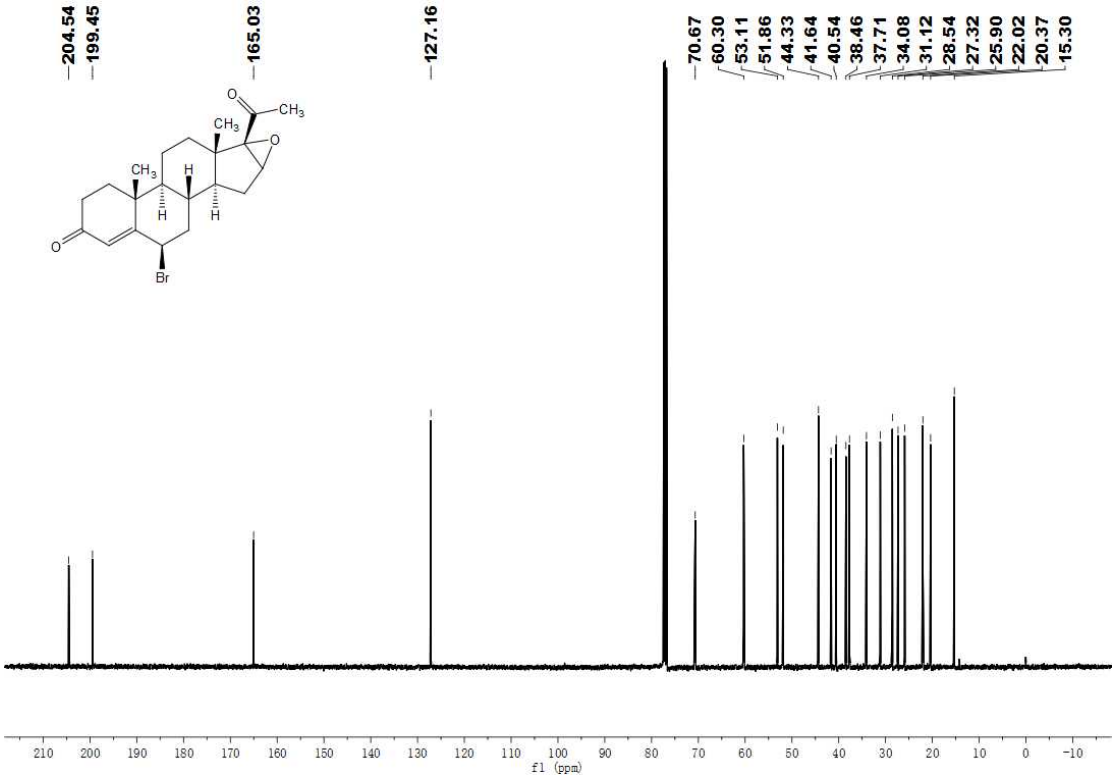
^{1}H-NMR of compound **11b** (500 MHz, $CDCl_3$)



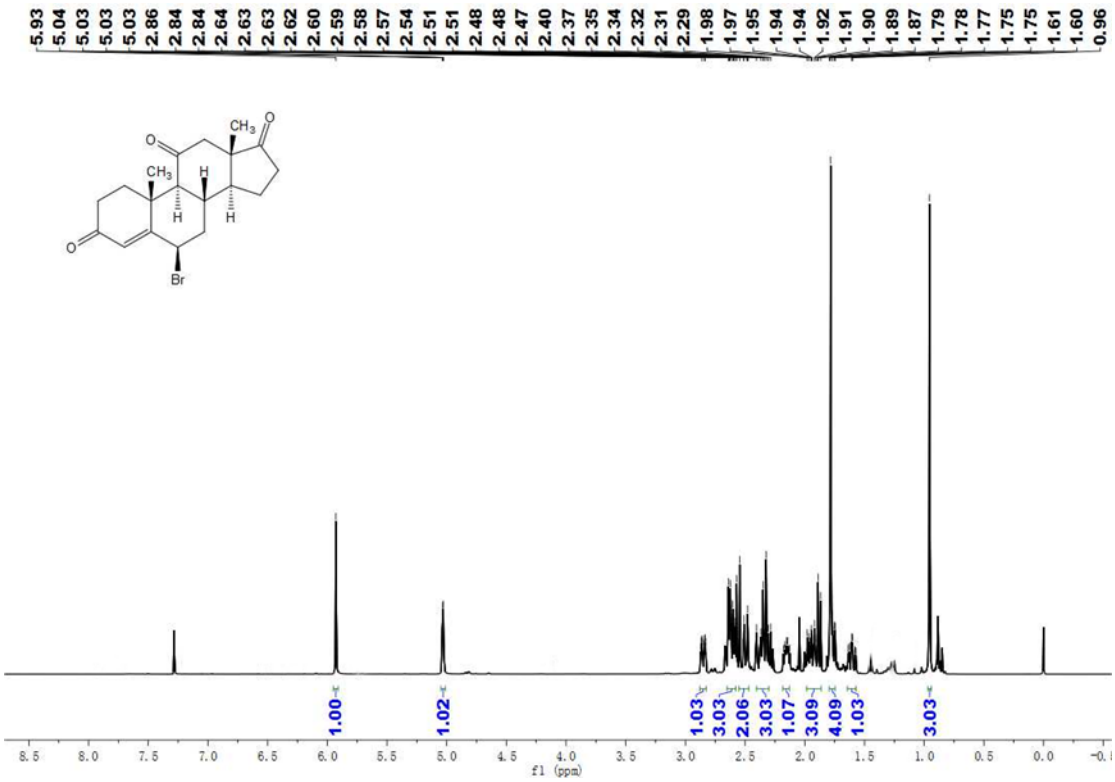
^{13}C-NMR of compound **11b** (126 MHz, $CDCl_3$)



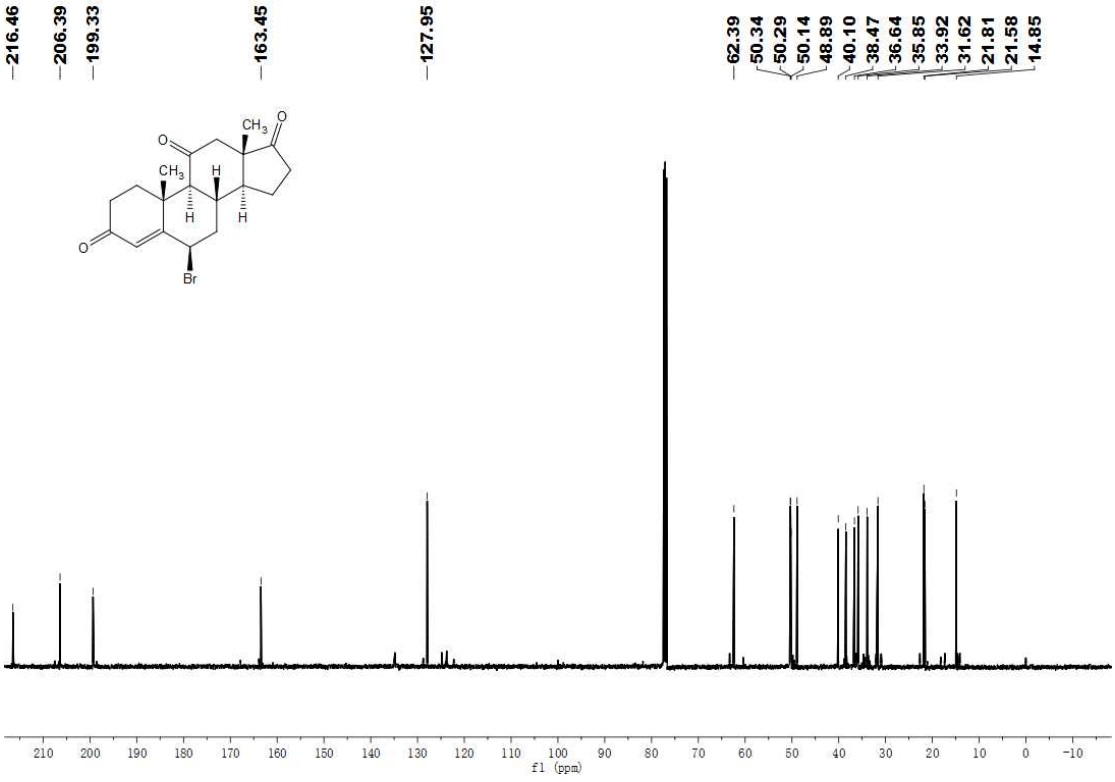
^{1}H-NMR of compound **12b** (500 MHz, $CDCl_3$)



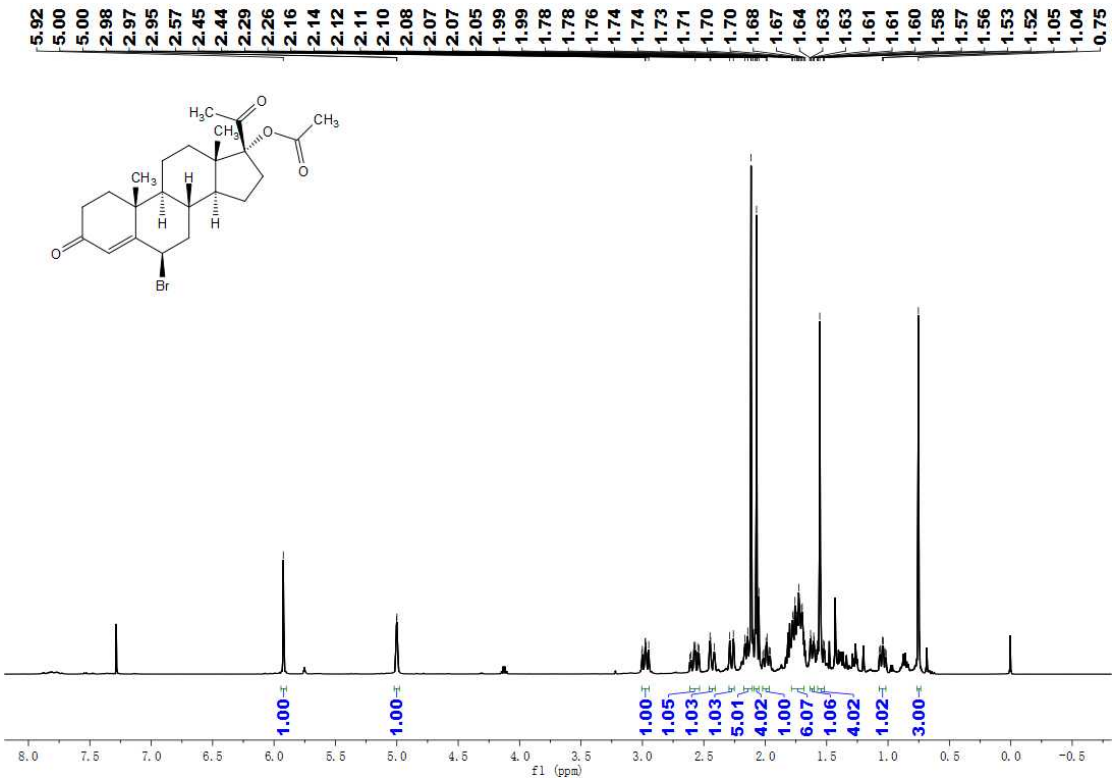
^{13}C-NMR of compound **12b** (126 MHz, $CDCl_3$)



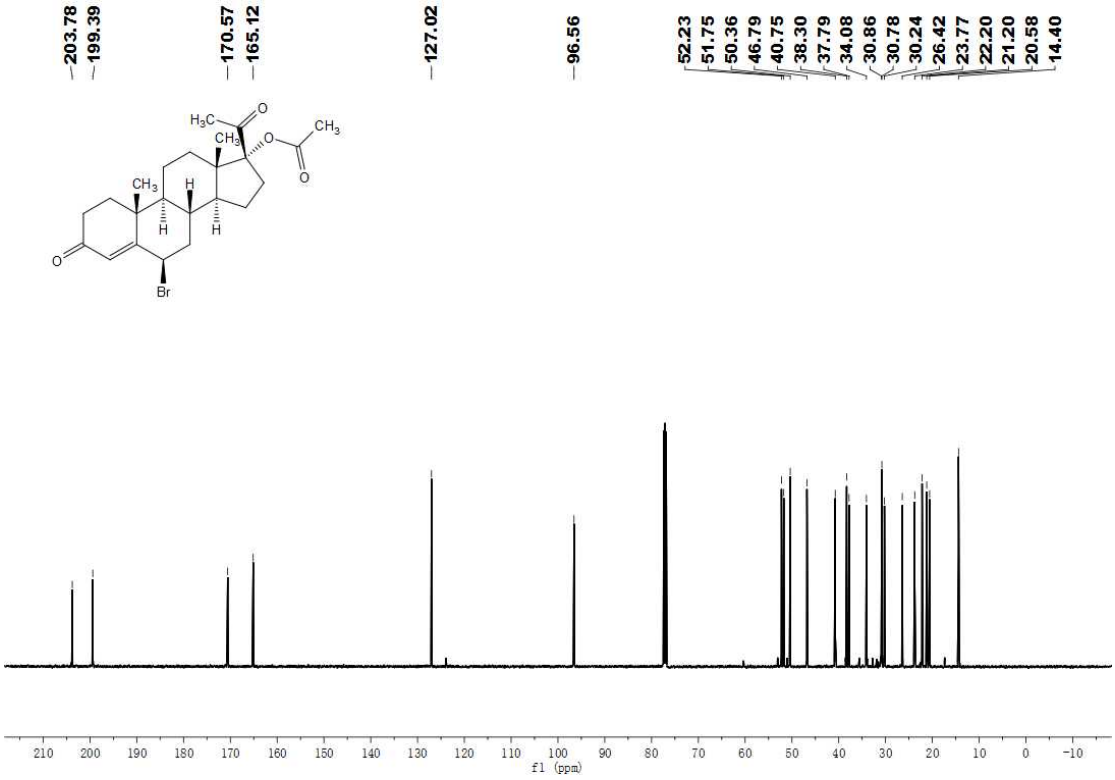
^{1}H-NMR of compound **13b** (500 MHz, $CDCl_3$)



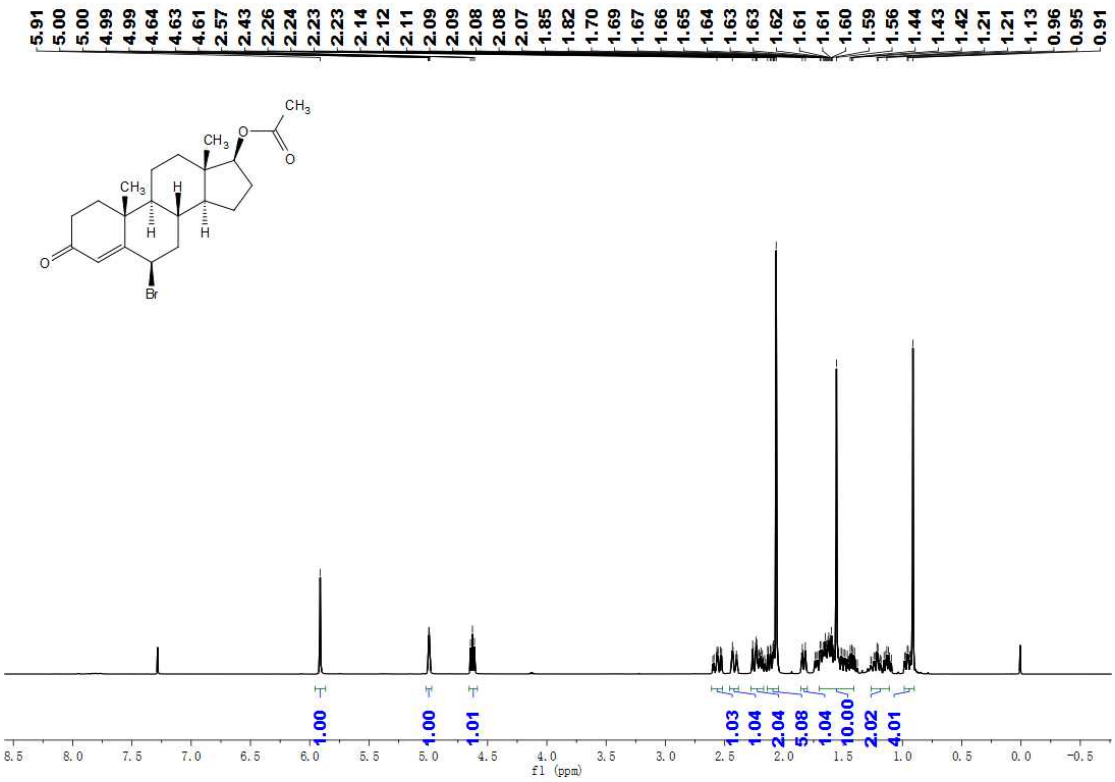
^{13}C-NMR of compound **13b** (126 MHz, $CDCl_3$)



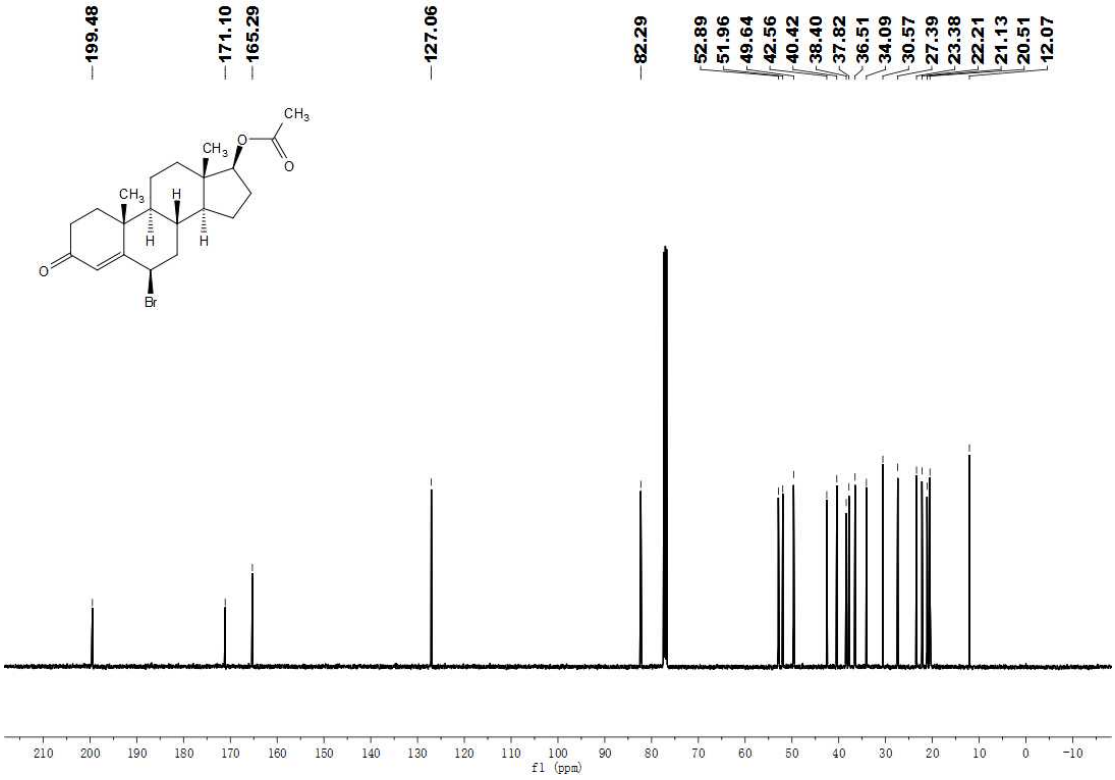
^{1}H-NMR of compound **14b** (500 MHz, $CDCl_3$)



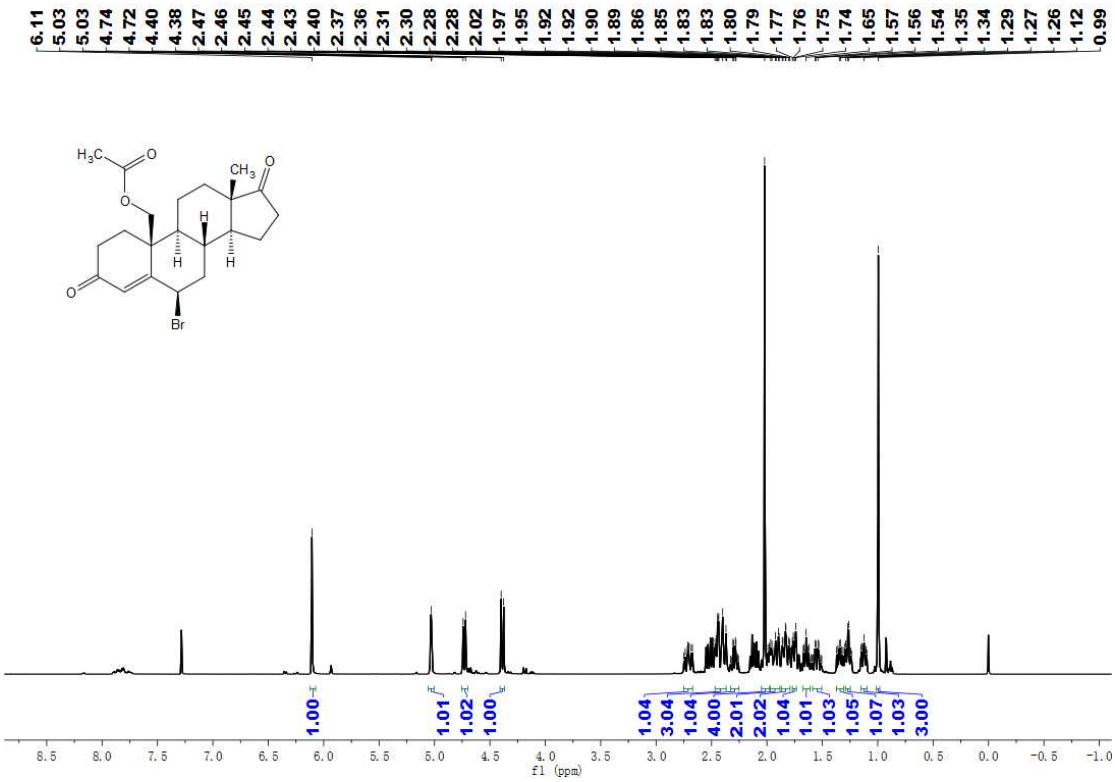
^{13}C-NMR of compound **14b** (126 MHz, $CDCl_3$)



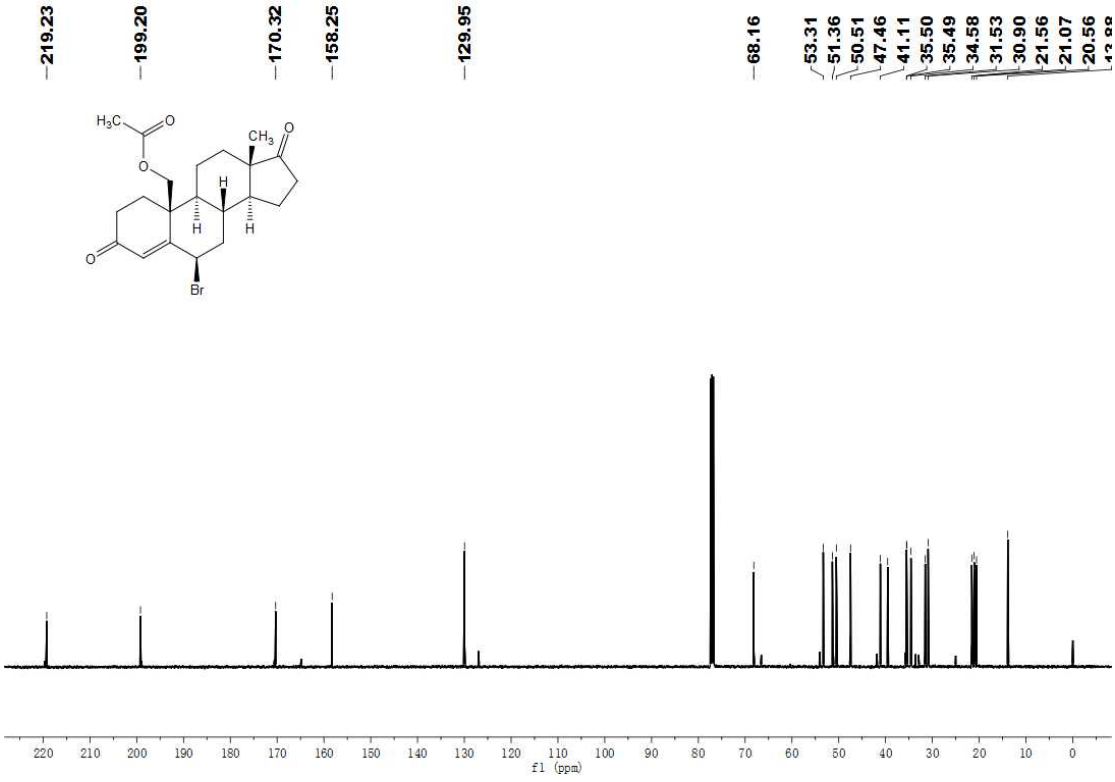
^{1}H-NMR of compound **15b** (500 MHz, $CDCl_3$)



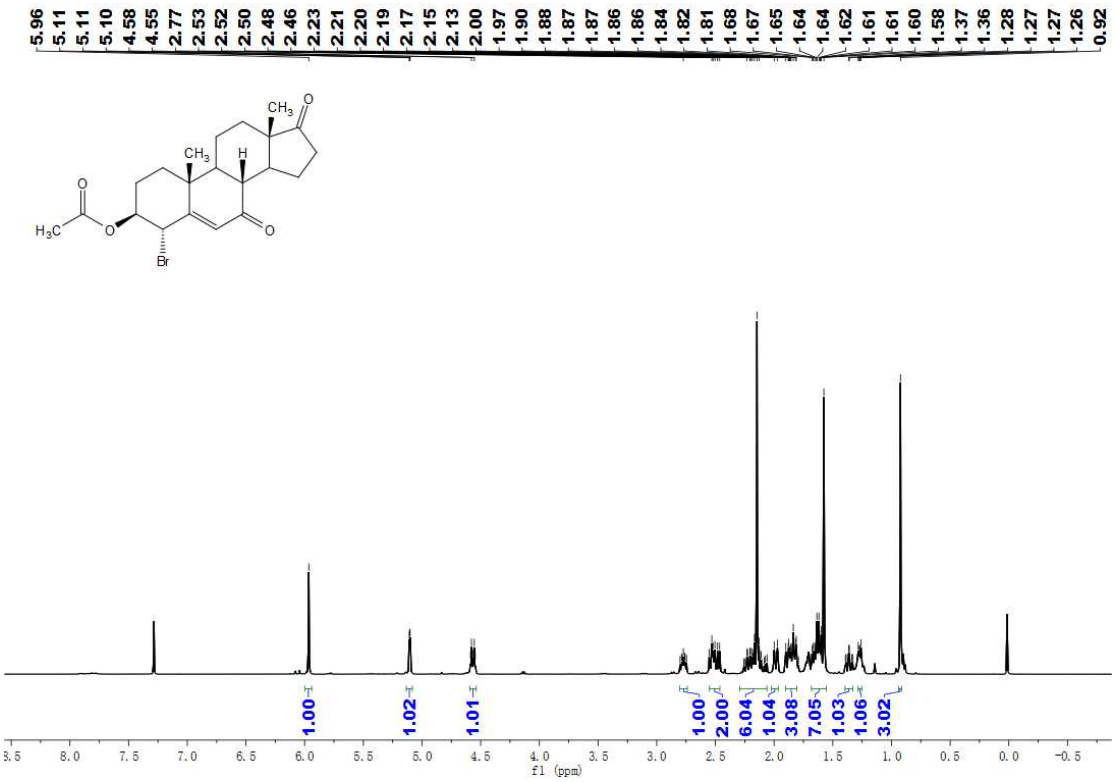
^{13}C-NMR of compound **15b** (126 MHz, $CDCl_3$)



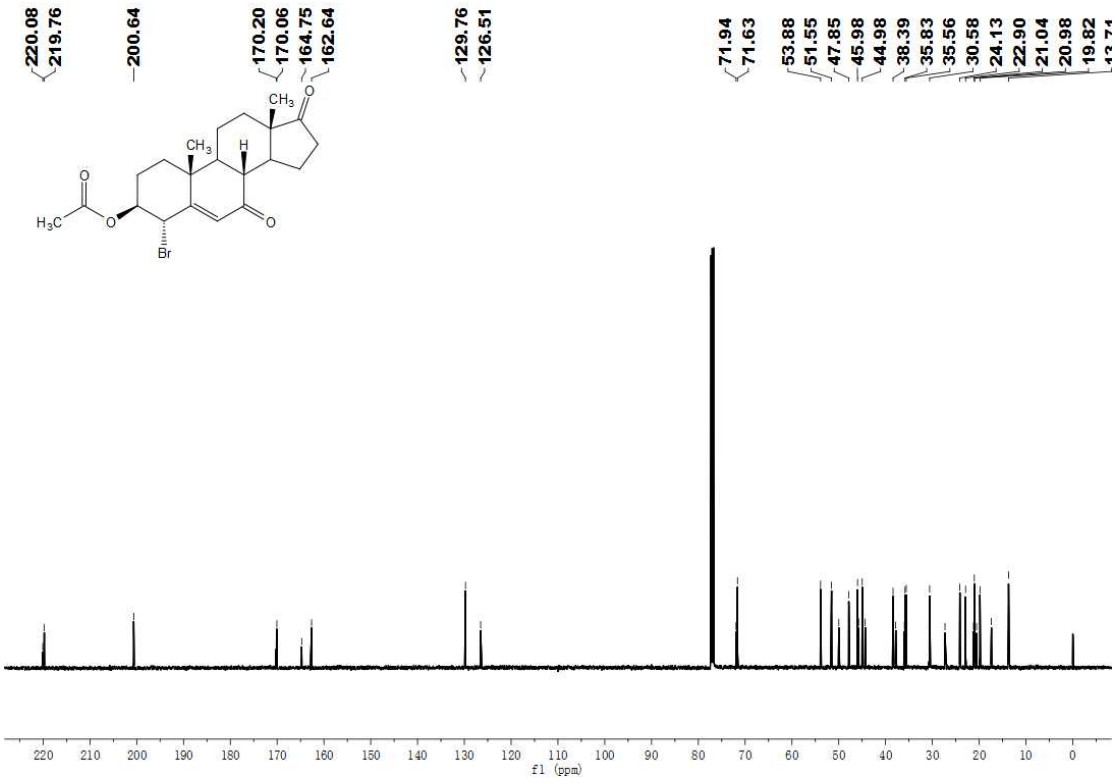
^{1}H-NMR of compound **16b** (500 MHz, $CDCl_3$)



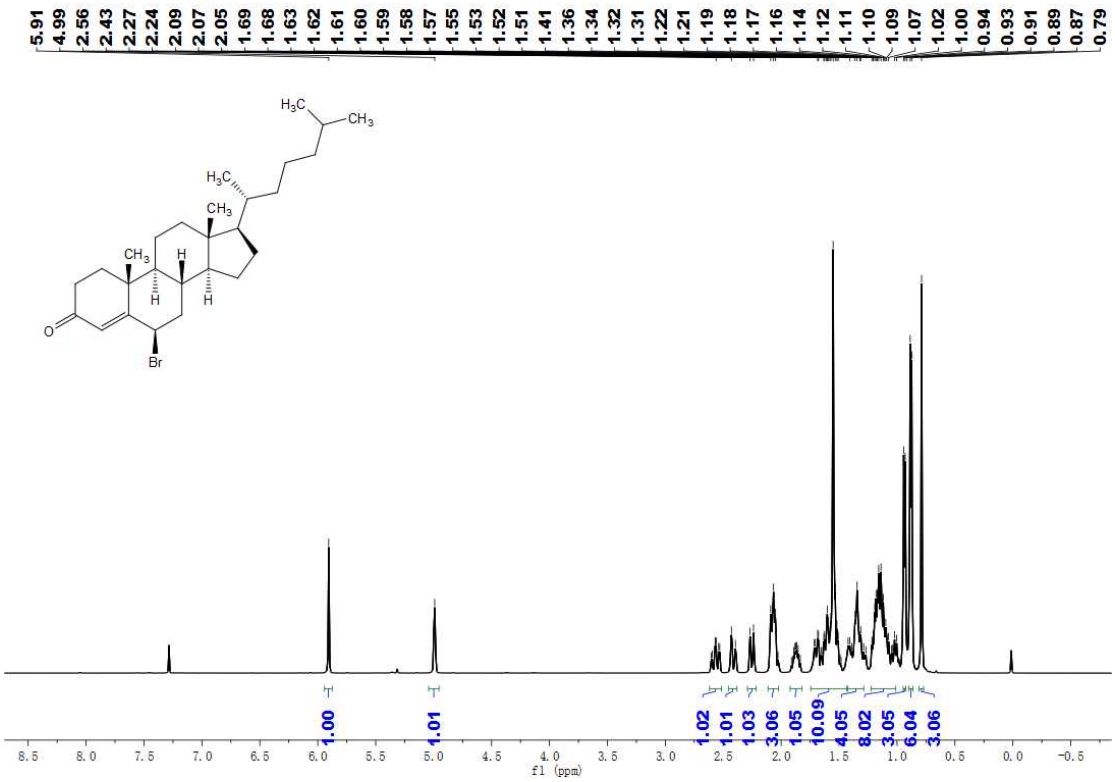
^{13}C-NMR of compound **16b** (126 MHz, $CDCl_3$)



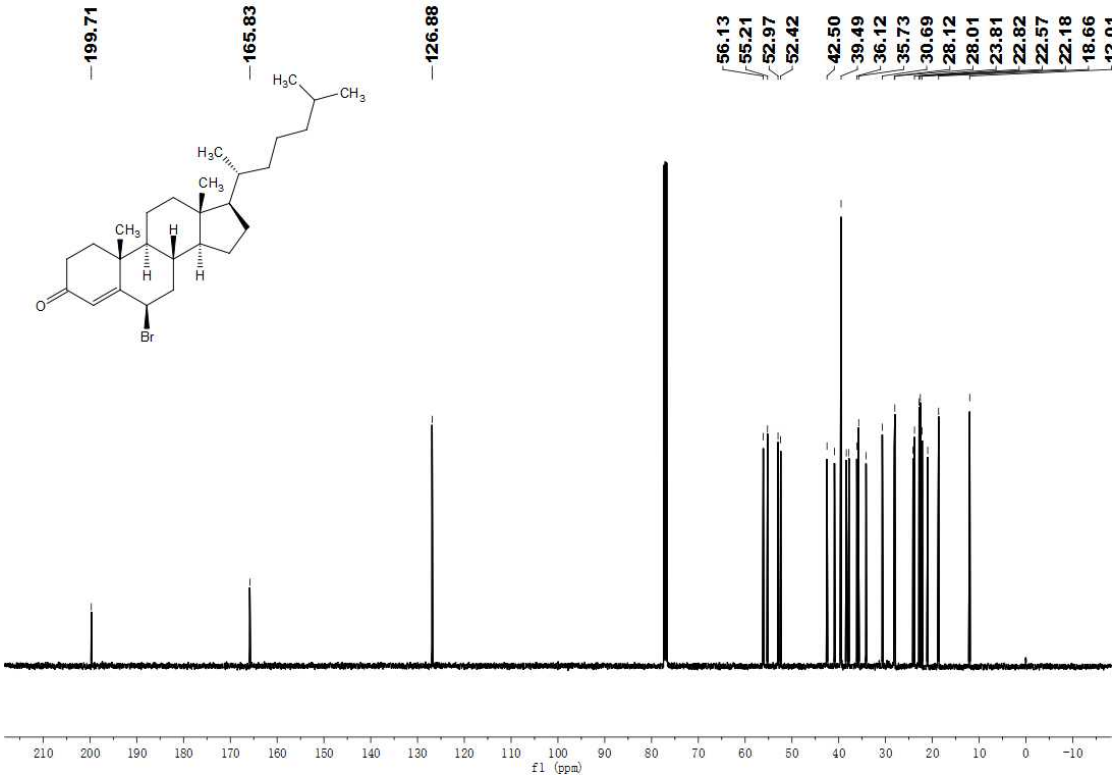
^{1}H-NMR of compound **17b** (500 MHz, $CDCl_3$)



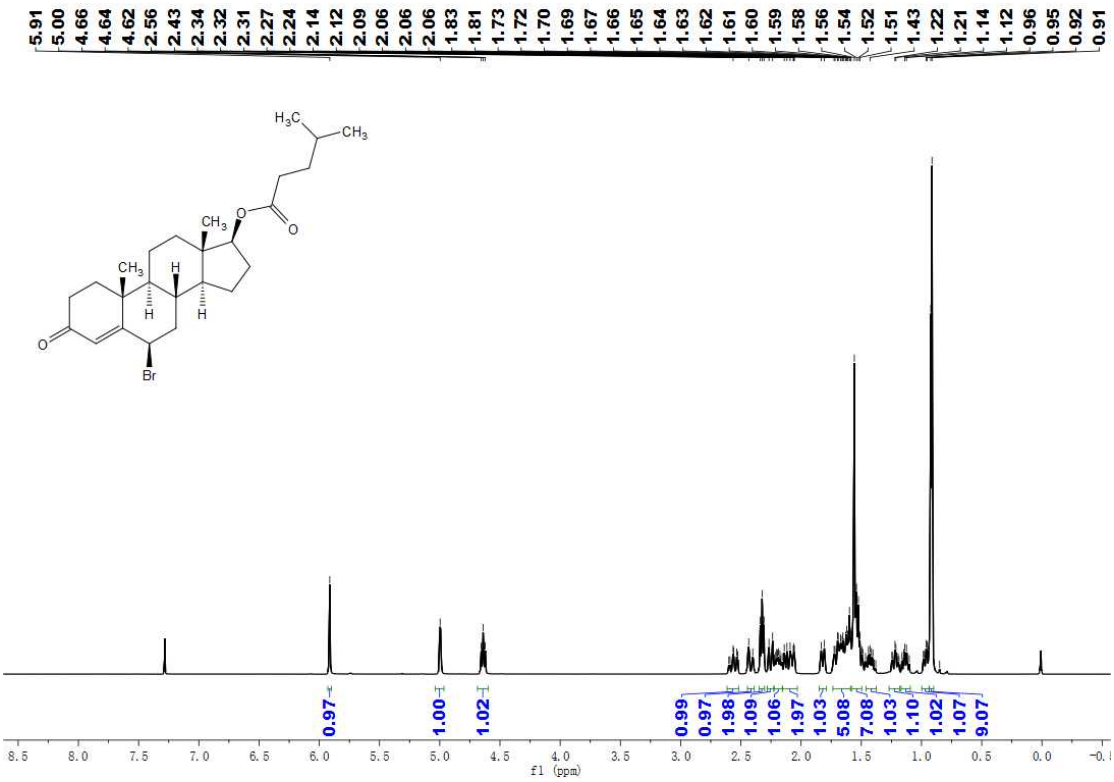
^{13}C-NMR of compound **17b** (126 MHz, $CDCl_3$)



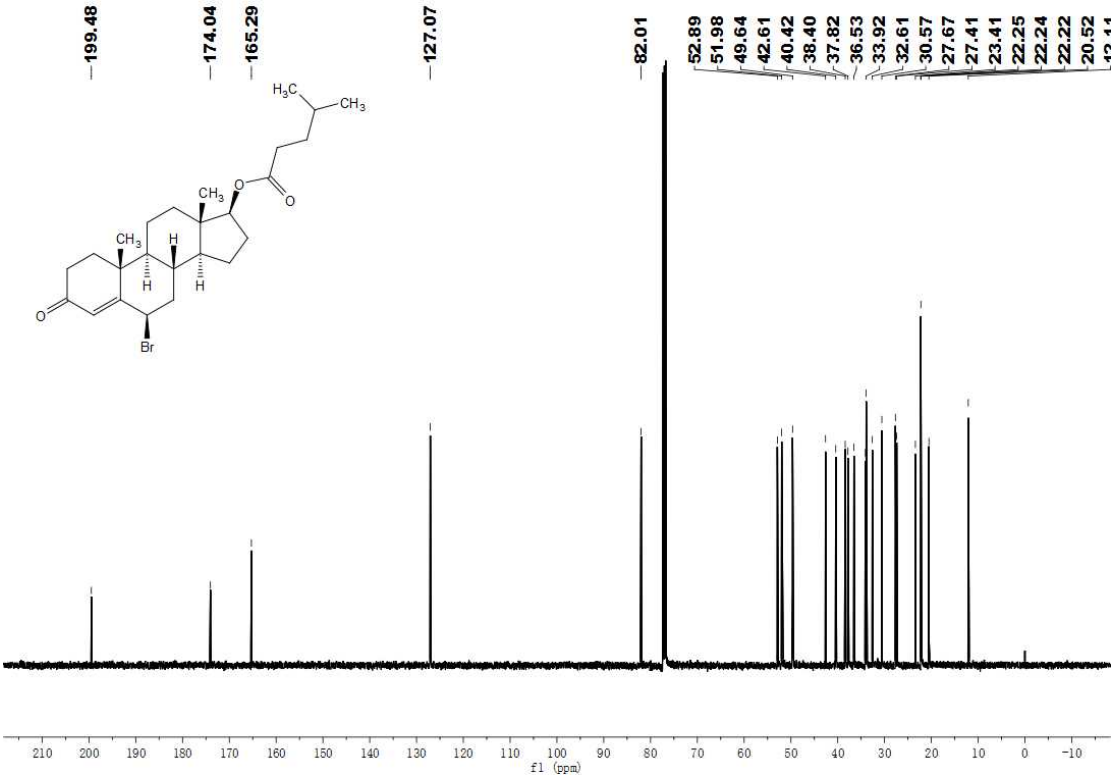
^{1}H-NMR of compound **18b** (500 MHz, $CDCl_3$)



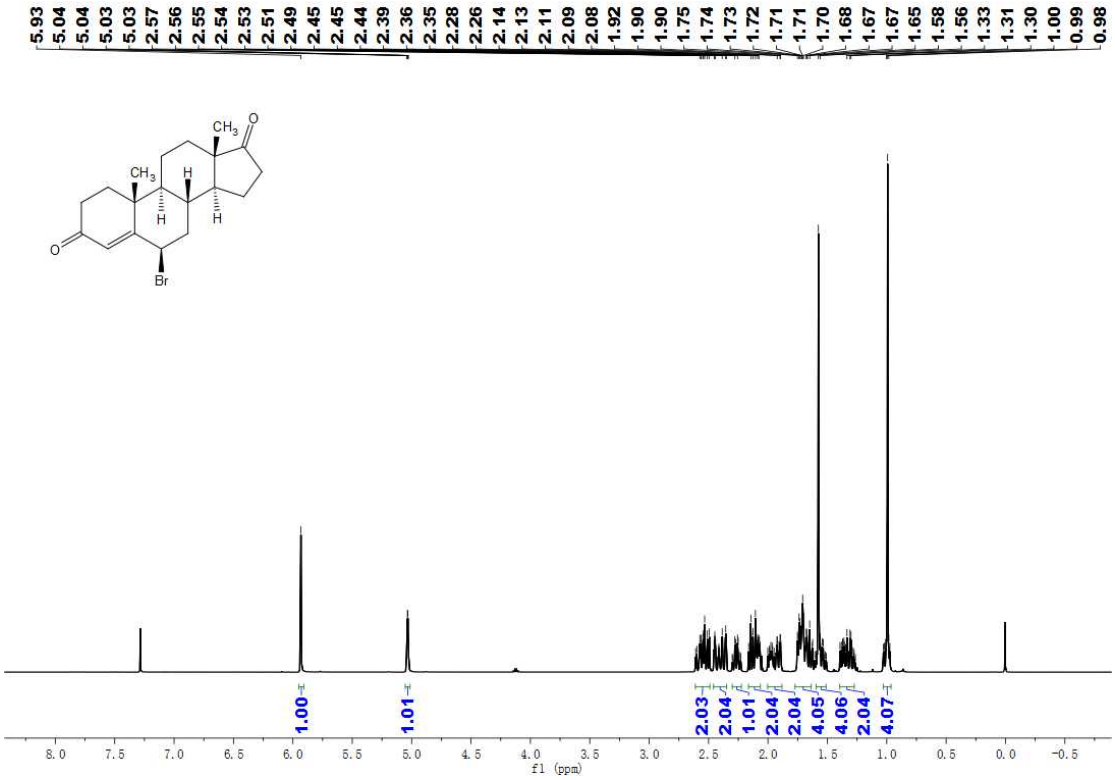
^{13}C-NMR of compound **18b** (126 MHz, $CDCl_3$)



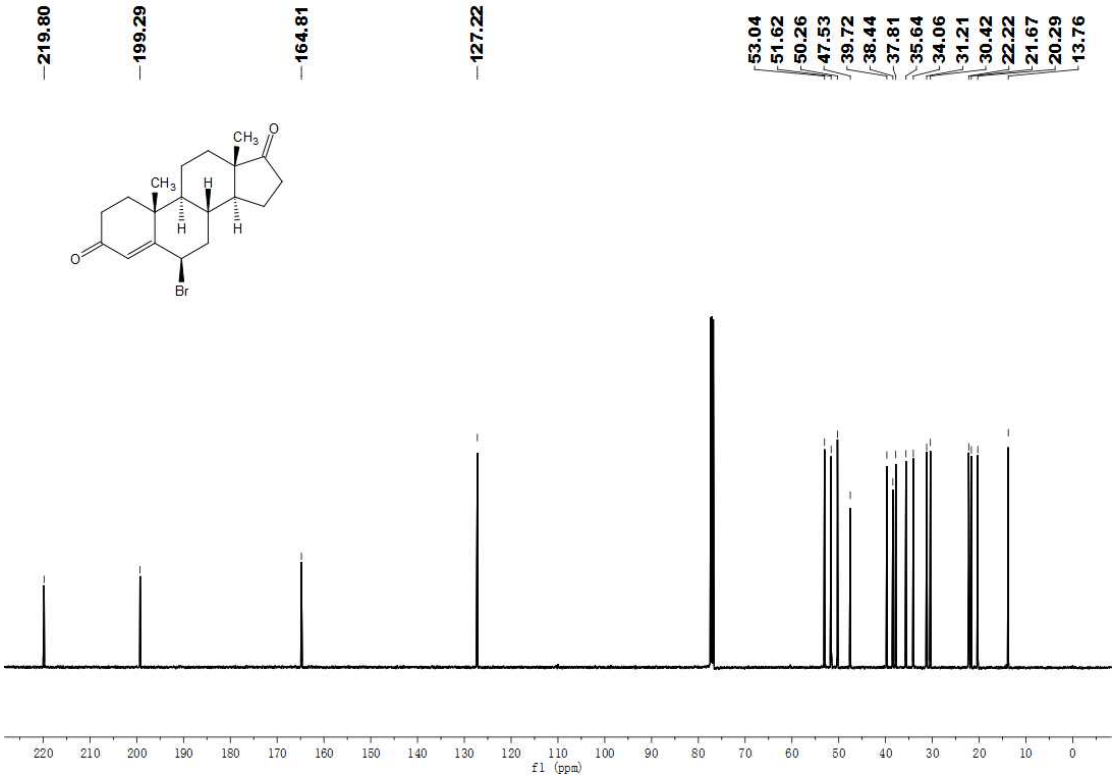
^{1}H-NMR of compound **19b** (500 MHz, $CDCl_3$)



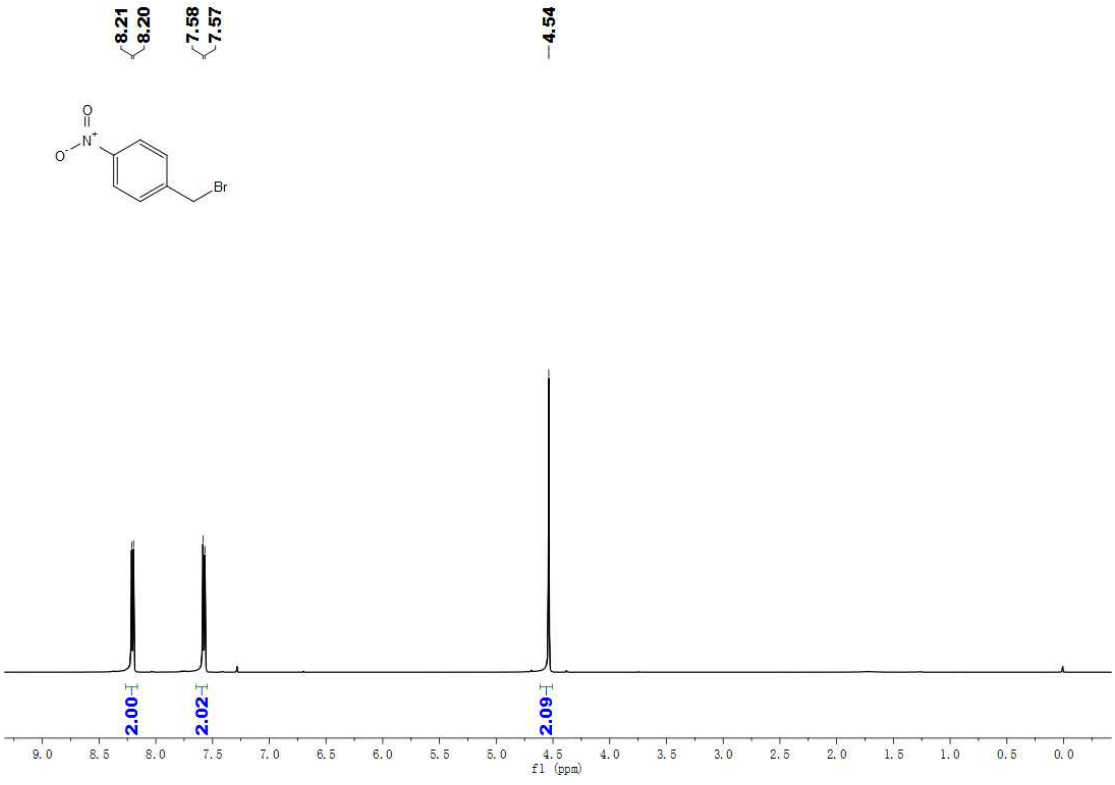
^{13}C-NMR of compound **19b** (126 MHz, $CDCl_3$)



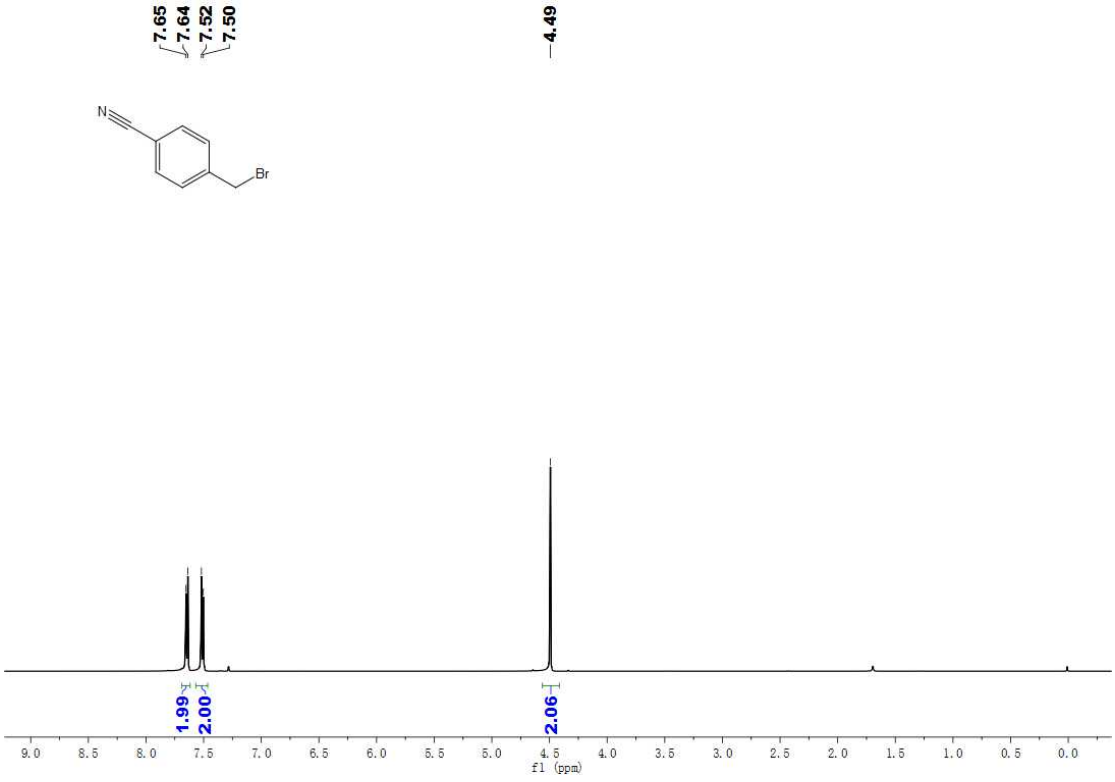
^{1}H-NMR of compound **20b** (500 MHz, $CDCl_3$)



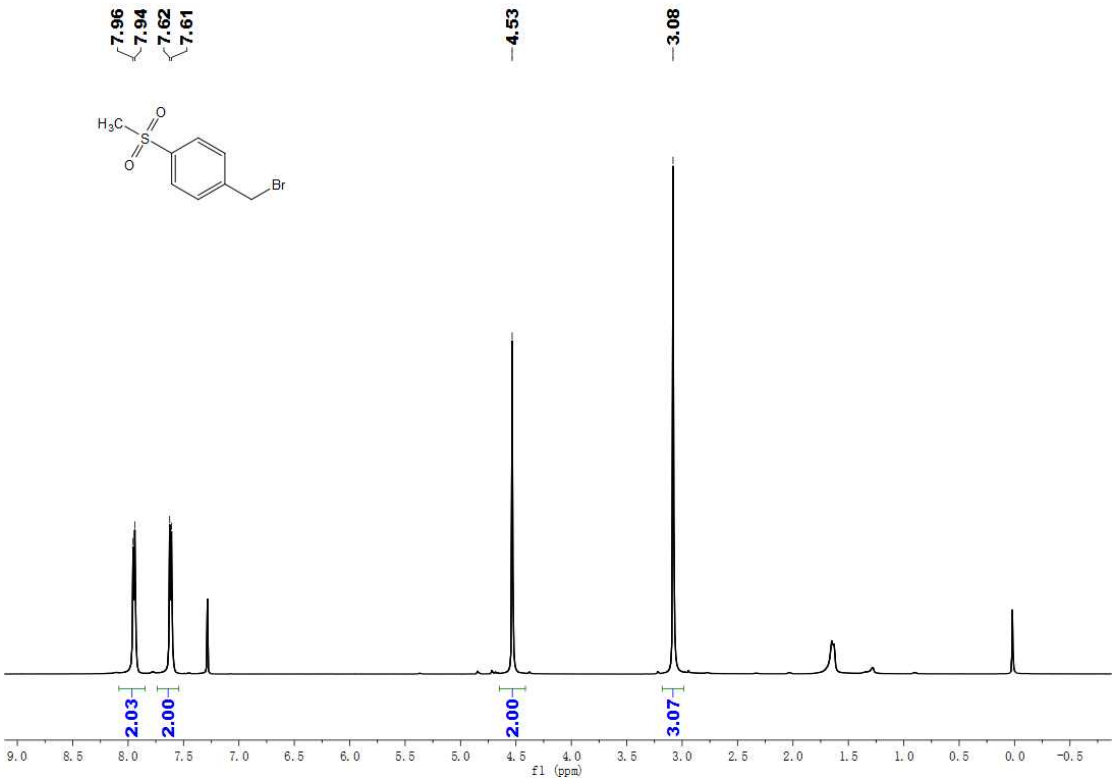
^{13}C-NMR of compound **20b** (126 MHz, $CDCl_3$)



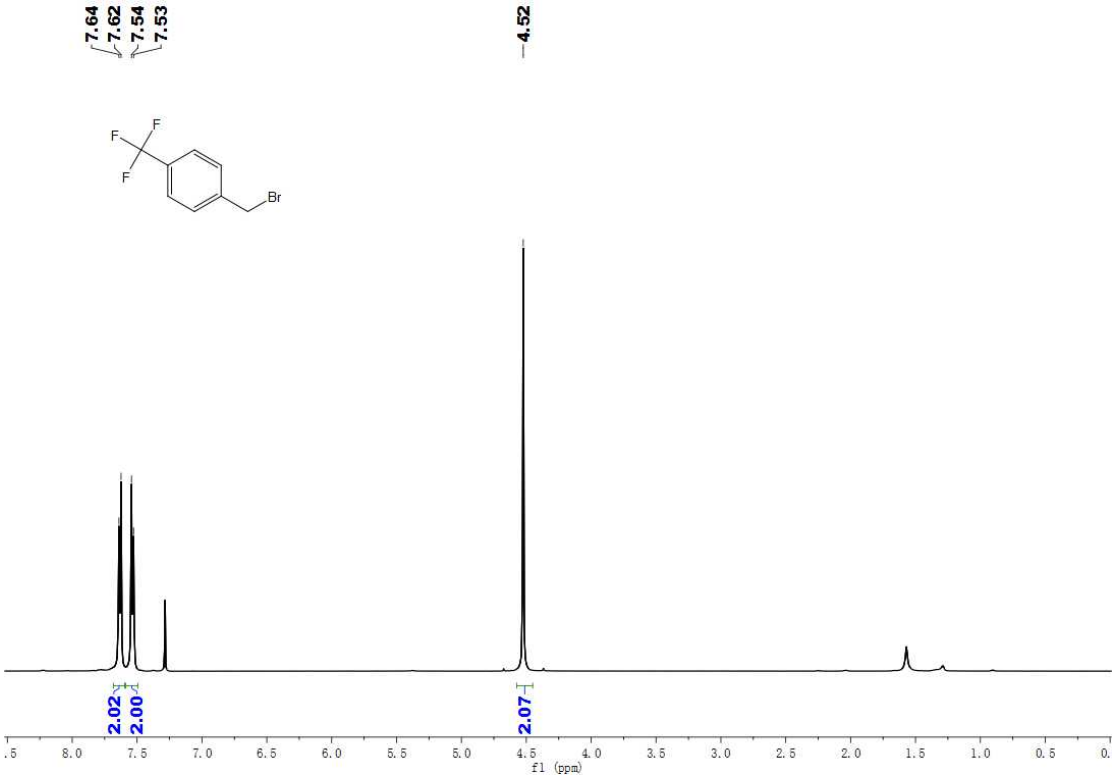
^{1}H-NMR of compound **21b** (500 MHz, $CDCl_3$)



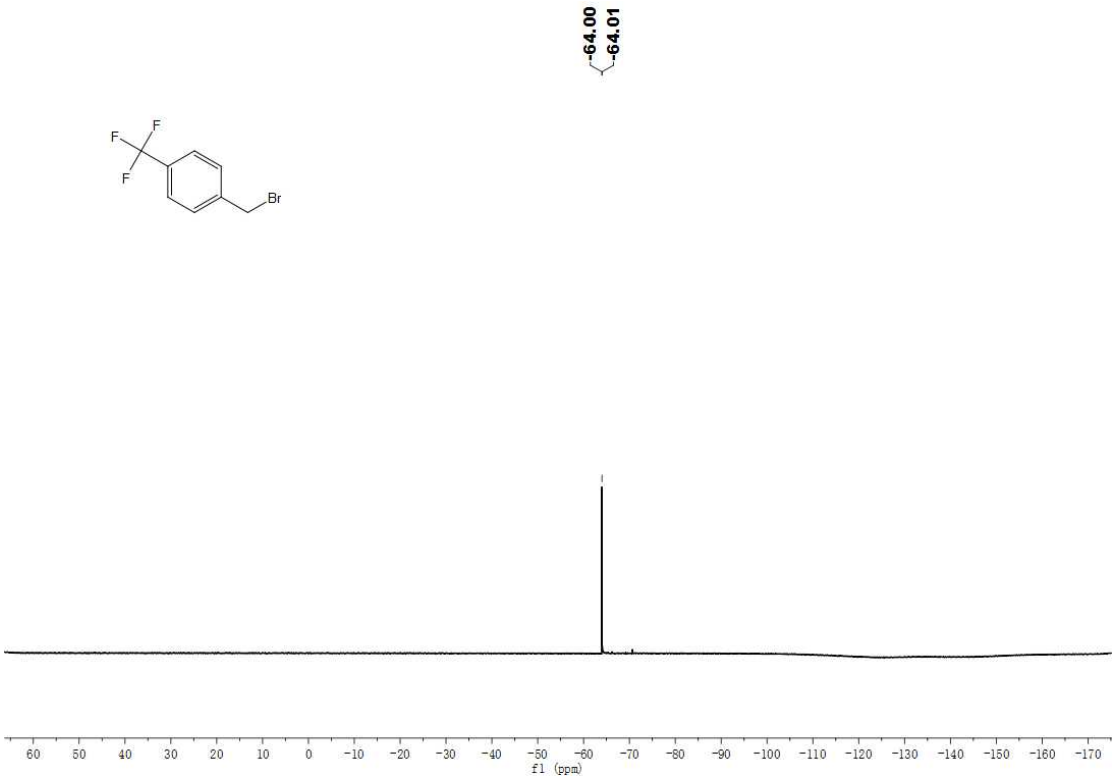
^{1}H-NMR of compound **22b** (500 MHz, $CDCl_3$)



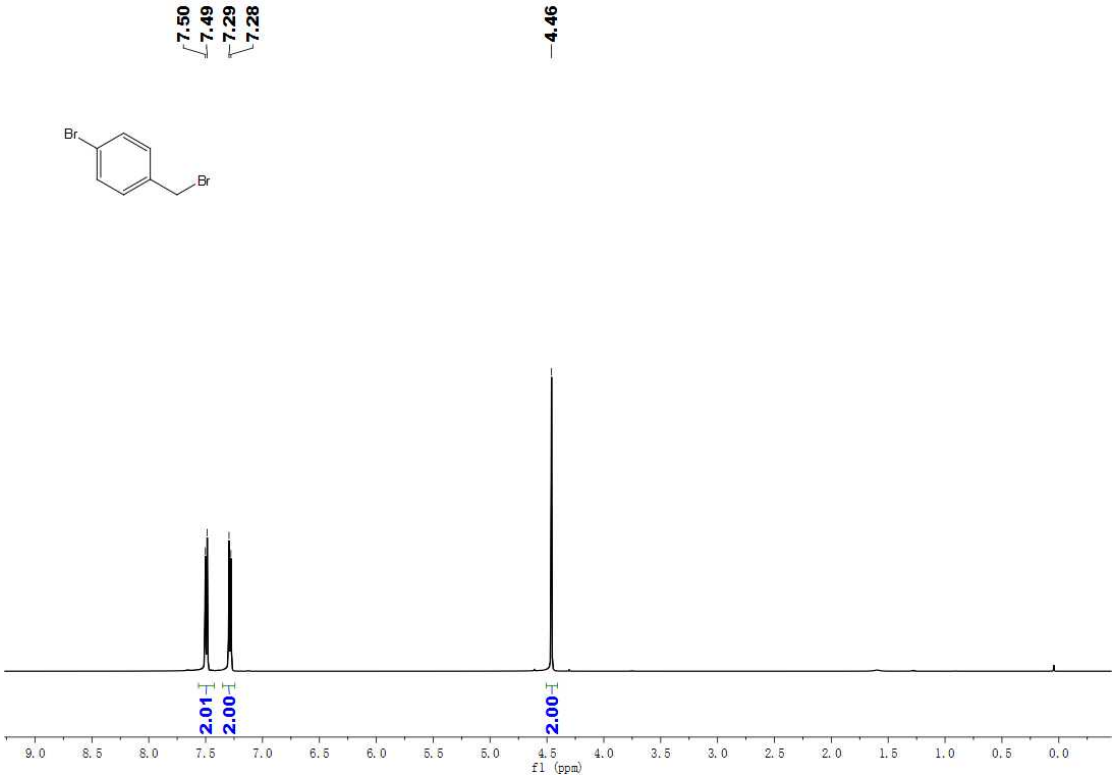
^{1}H-NMR of compound **23b** (500 MHz, $CDCl_3$)



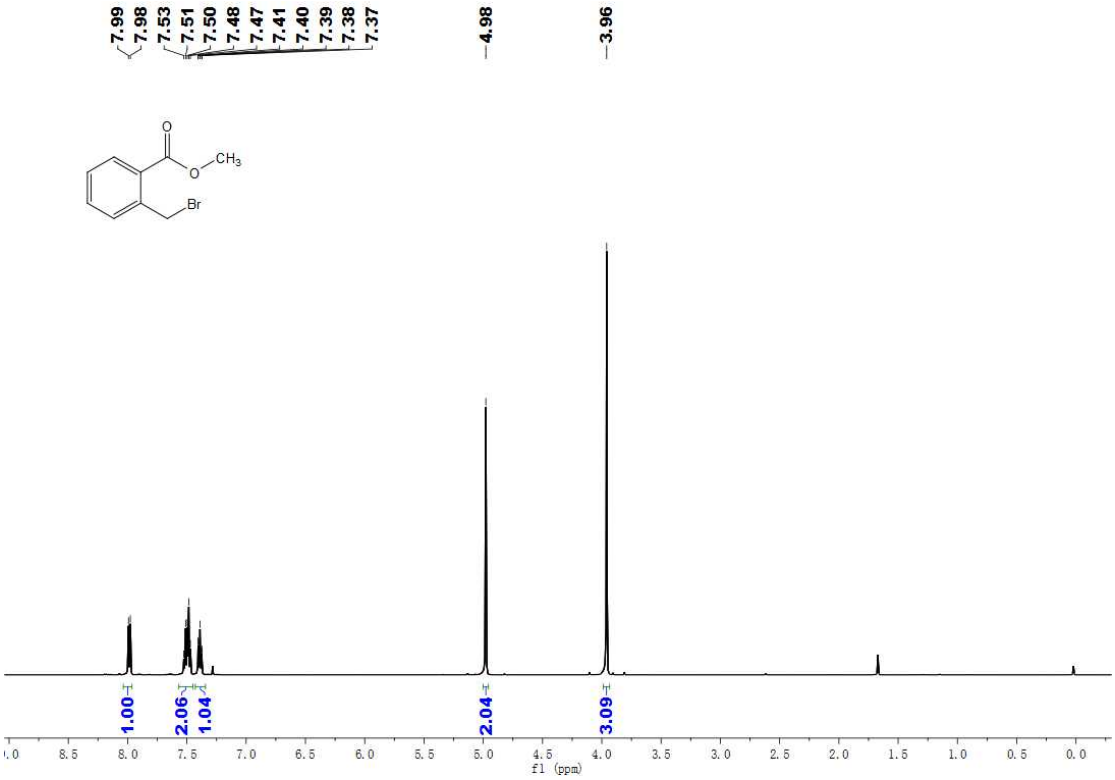
^{1}H-NMR of compound **24b** (500 MHz, $CDCl_3$)



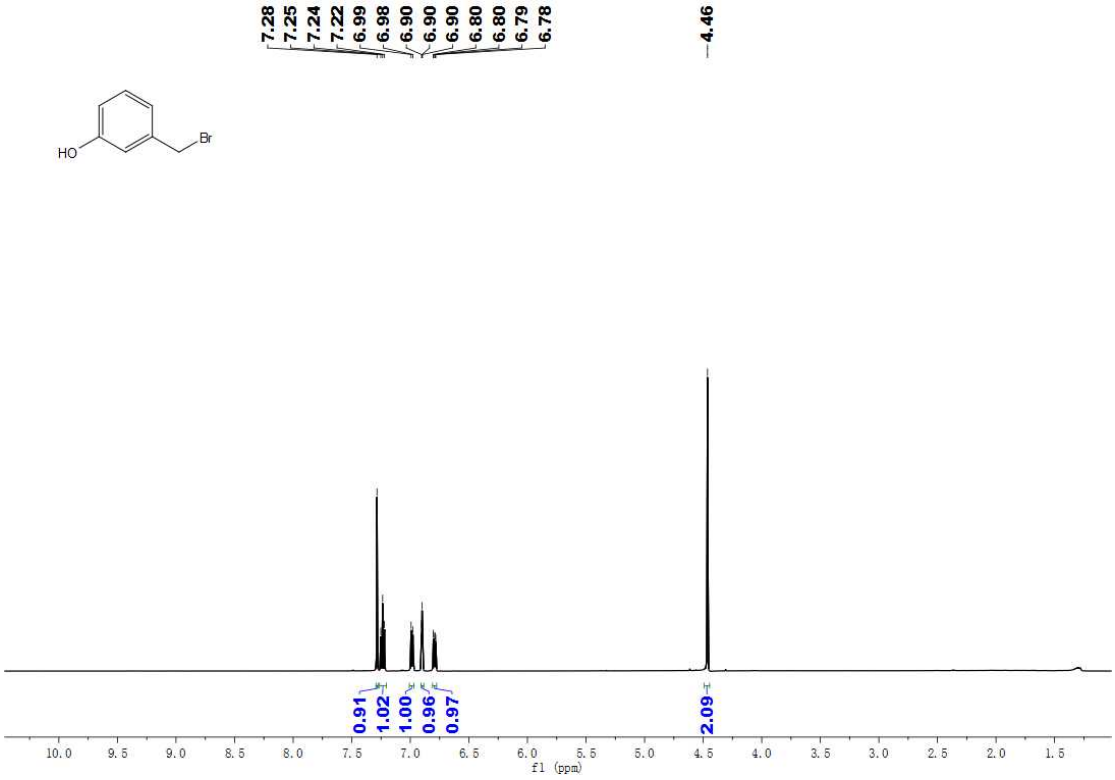
^{19}F NMR of compound **24b** (471 MHz, $CDCl_3$)



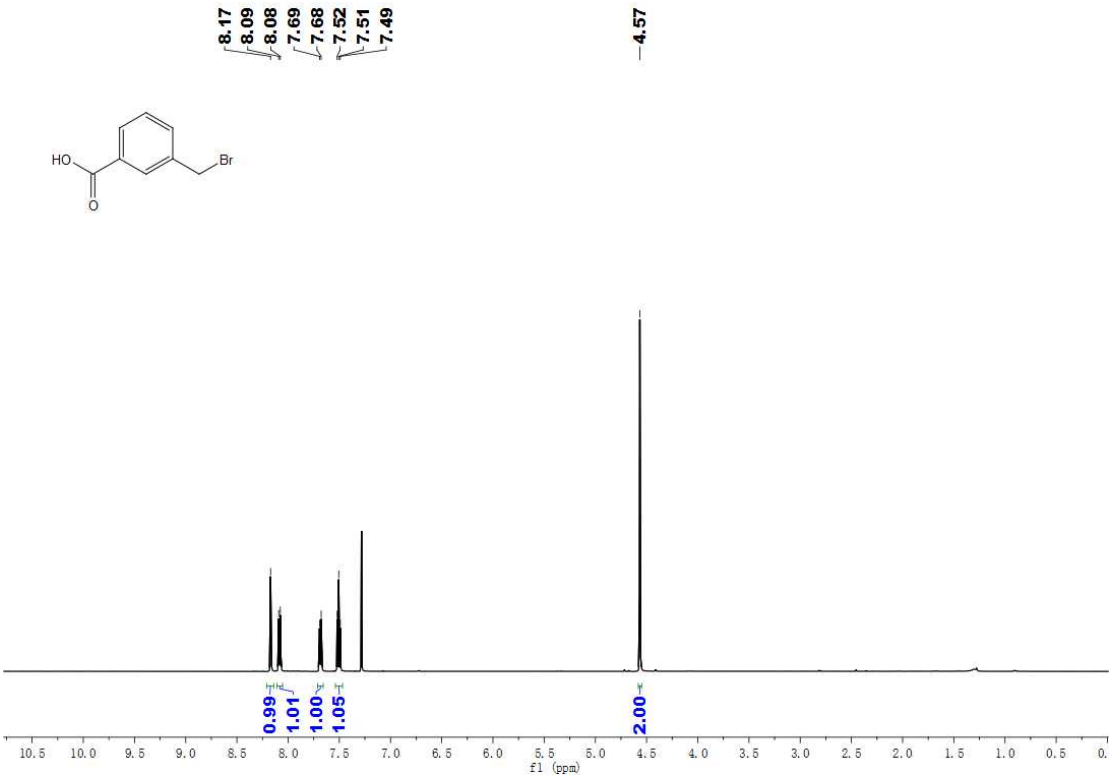
^{1}H-NMR of compound **25b** (500 MHz, $CDCl_3$)



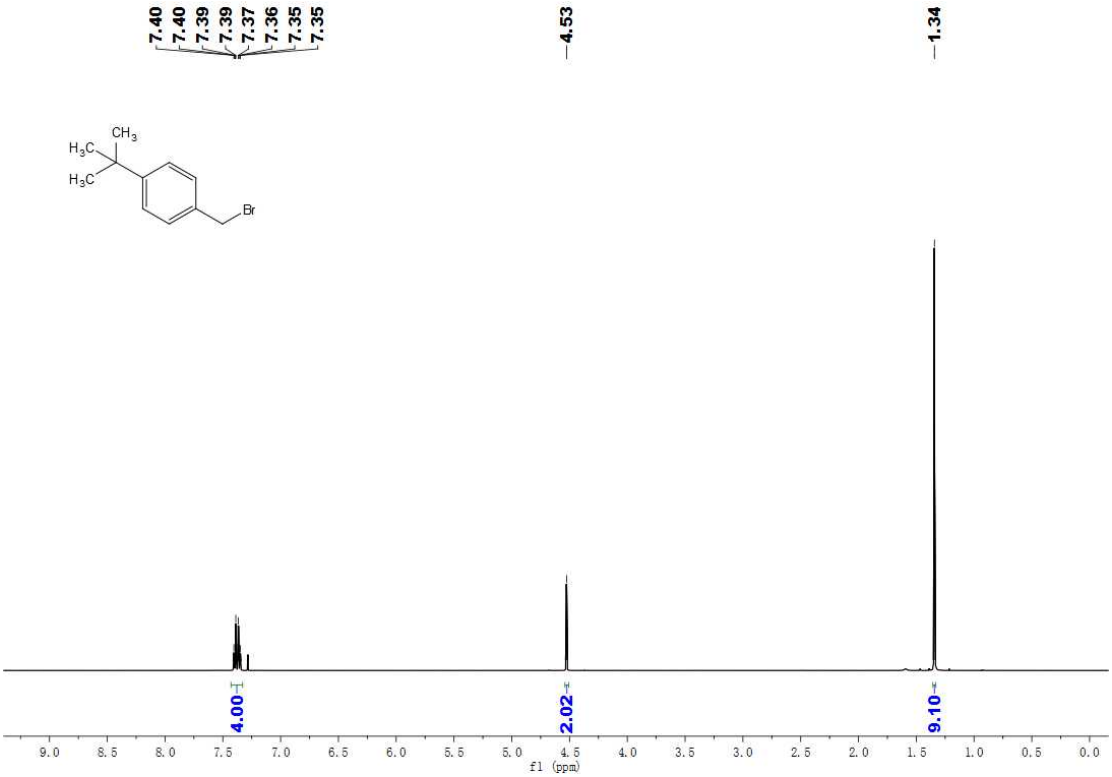
^{1}H-NMR of compound **26b** (500 MHz, $CDCl_3$)



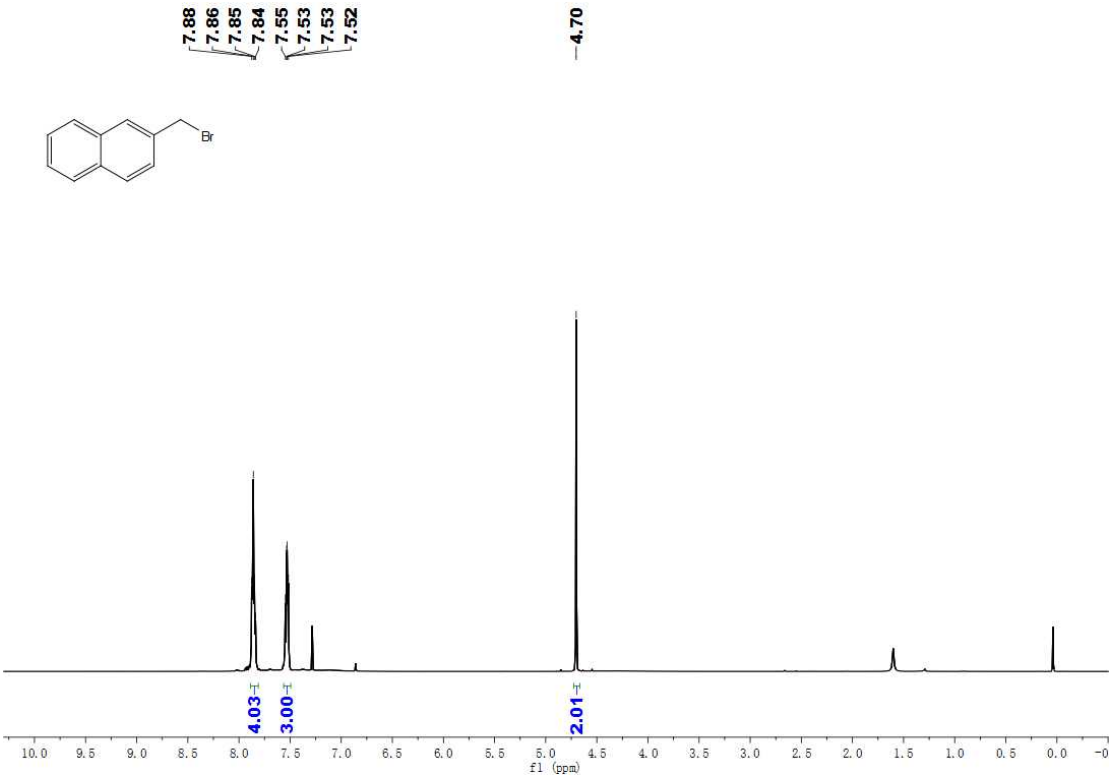
^{1}H-NMR of compound **27b** (500 MHz, $CDCl_3$)



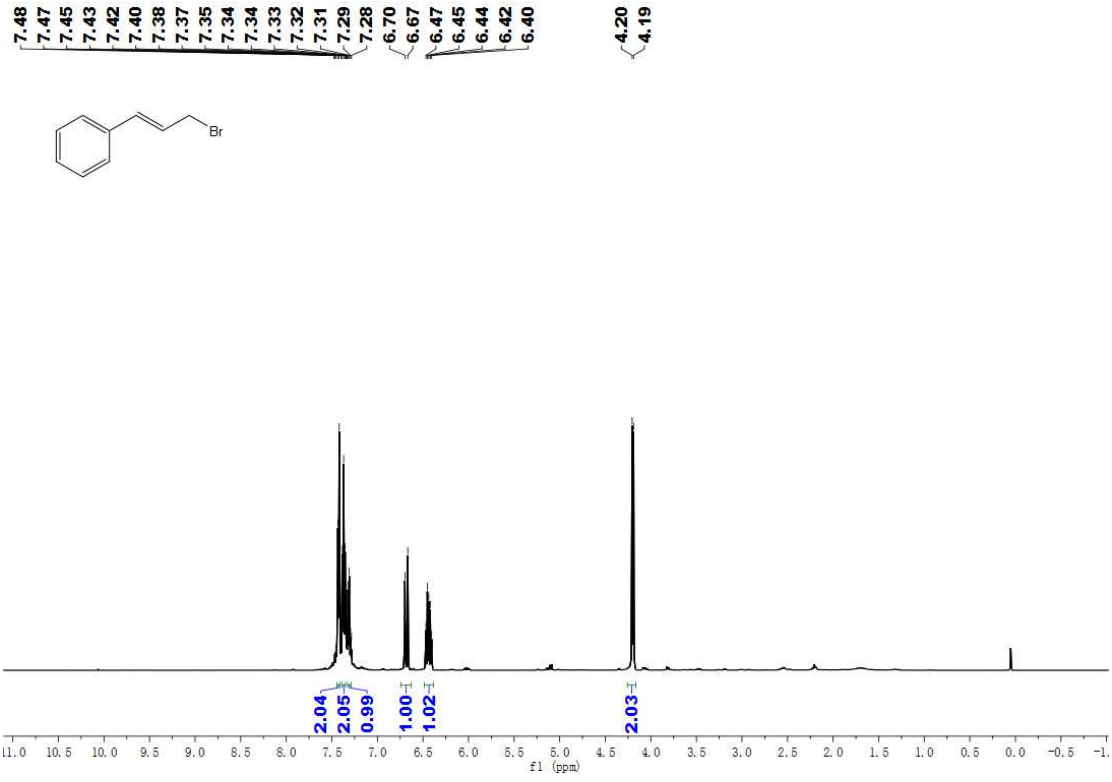
^{1}H-NMR of compound **28b** (500 MHz, $CDCl_3$)



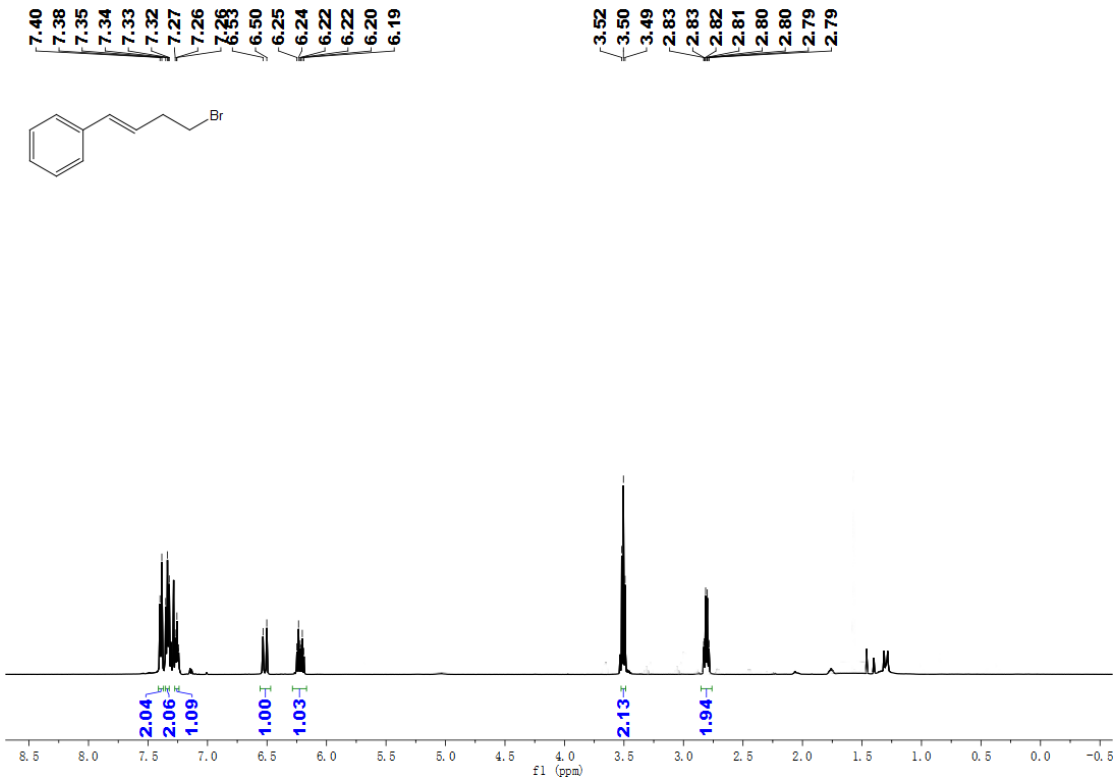
^{1}H-NMR of compound **29b** (500 MHz, $CDCl_3$)



^{1}H-NMR of compound **30b** (500 MHz, $CDCl_3$)



^{1}H-NMR of compound **31b** (500 MHz, $CDCl_3$)



^{1}H-NMR of compound **1c** (500 MHz, $CDCl_3$)