Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photocatalyzed radical multicomponent alkylacylation of [1.1.1]propellane to synthesize 1,3-disubstituted BCP ketones

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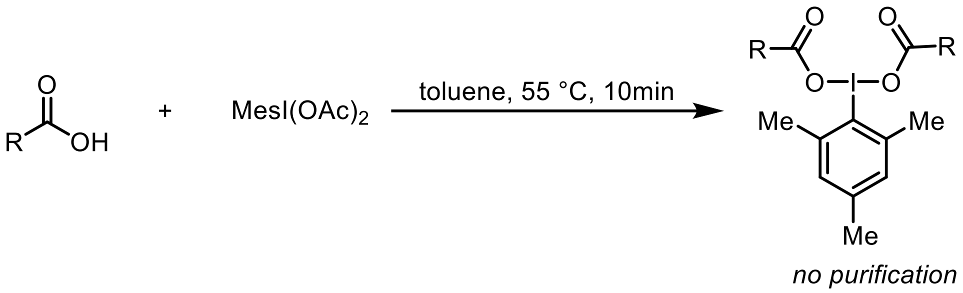
1. **General Information**

Unless otherwise noted, all reactions were performed in a 10 mL reaction vial at room temperature under N_2. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured in $CDCl_3$ and recorded on Varian 400 or Brucker ARX 600 spectrometer. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, t, d, s, dd referred to multiplet, triplet, doublet, singlet, doublet of doublet. Gas chromatography-mass spectrometry (GC-MS) was performed on an Thermo Fisher Trace ISQ 7000. Gas chromatography (GC) was performed on a Shimadzu GC 2010-pro system equipped with a split-mode capillary injection system and flame ionization detectors. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer from Sichuan University. All reagents and solvents were commercially available and directly used without any further purification.

Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial suppliers (Adamas-beta®, Macklin, Energy and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh). Visible light irradiation was performed with 30 W Led lamp at $\lambda_{ir} = 450 \pm 10$ nm for phtotcatalytic reactions. The Led lamps used in this research were brought from Sichuan Zhiyan Technology Co., Ltd. (Figure S1)

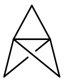
2. Preparation of Substrates

Preparation of the hypervalent iodine(III) carboxylates:[1]



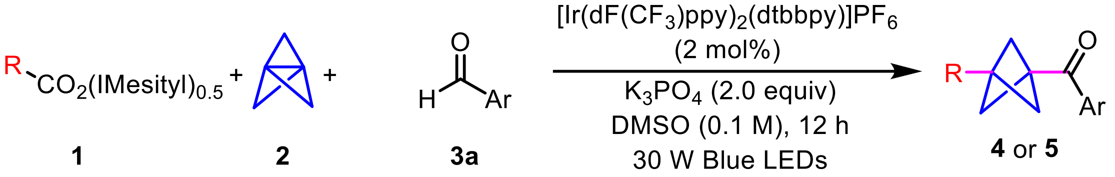
A 250 mL round-bottom flask was charged with iodomesitylene diacetate (10 mmol), carboxylic acid (20.5 mmol, 2.05 equiv), and 100 mL toluene. The flask was attached to a rotary evaporator with the water bath heated to 50 ºC and the solvent (and the generated acetic acid) was removed over a time period of ~10 min. A second 50 mL aliquot of toluene was added to the flask and the evaporation step was repeated. Repeat the evaporation step for two more times with 50 mL toluene each time. The products are typically generated in >99% yield. After further removal of residual toluene under high vacuum, these iodomesitylene dicarboxylates can be directly used in the reaction without further purification.

Preparation of a [1.1.1]propellane stock solution:



The synthesis procedure and determination of stock solution concentration was determined based on the literature procedure.[2,3] To a flame-dried round-bottom flask equipped with a stirrer bar was added 1,1-dibromo-2,2- bis(chloromethyl)cyclopropane (5.0 g, 16.9 mmol, 1.0 equiv). The reaction vessel was evacuated and back-filled with nitrogen three times, and then anhydrous Et_2O (10 mL) was added. The reaction vessel was cooled to −45 °C (dry ice / isopropanol bath). Phenyllithium (17.8 mL, 1.9 M in Bu_2O, 33.7 mmol, 2.0 equiv) was added dropwise over 15 min at –45 °C, and the resulting mixture was stirred for 15 min at −45 °C. The cooling bath was replaced with an ice bath, and the reaction mixture was warmed to 0 °C, and then stirred at this temperature for 2 h. The mixture was then distilled at room temperature (10 mbar) using a rotary evaporator, the receiving flask of which was immersed in a dry ice / acetone bath. The TCP-containing distillate (15 mL, TCP concentration 0.60 M in Et_2O, 51%) was transferred to a flame-dried septum-sealed bottle under an inert atmosphere, and stored at −20 °C. The yield was determined by ^1H NMR spectroscopy with 1,2-dichloroethane as an internal standard.

3. Standard Reaction Conditions

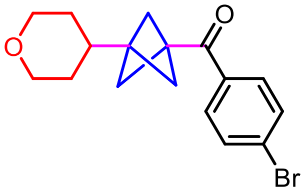


To a 10 mL reaction vial equipped with a stir bar was added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), aldehyde (0.2 mmol, 1.0 equiv), and hypervalent iodine(III) carboxylate (0.20 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Once judged to be complete, the solution was transferred to a separatory funnel and diluted with deionized H_2O (20 mL) and Et_2O (20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 X 10 mL). The combined organic layers were washed with deionized H_2O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired BCP ketones.

Figure S1. Blue LED reactors

4. Characterization Data of Products

(4-Bromophenyl)(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (4a)



4a

4a was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4a** as a colorless solid (50.7 mg, 76% yield).

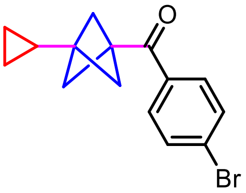
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 4.00 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.37 (td, *J* = 12.1, 2.0 Hz, 2H), 2.09 (s, 6H), 1.66 (tt, *J* = 12.0, 3.9 Hz, 1H), 1.53 (ddd, *J* = 12.7, 3.3, 1.3 Hz, 2H), 1.32 (ddd, *J* = 25.5, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.0, 135.3, 131.8, 130.4, 128.0, 67.7, 51.1, 43.7, 43.4, 35.2, 28.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{17}H_{20}O_2Br$ 335.0641; found 335.0640.

(4-Bromophenyl)(3-cyclopropylbicyclo[1.1.1]pentan-1-yl)methanone (4b)



4b

4b was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl dicyclopropanecarboxylate **1b** (83.2 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4b** as a colorless solid (27.8 mg, 48% yield).

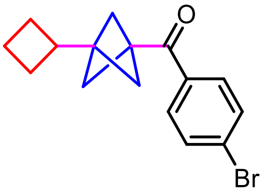
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.04 (s, 6H), 0.92 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.52 – 0.34 (m, 2H), 0.24 – 0.11 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.7, 133.0, 129.4, 128.1, 125.6, 50.3, 41.0, 39.7, 8.7, 0.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}OBr$ 291.0379; found 291.0379.

(4-Bromophenyl)(3-cyclobutylbicyclo[1.1.1]pentan-1-yl)methanone (4c)



4c

4c was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 μmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl dicyclobutanecarboxylate **1c** (88.8 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4c** as a colorless solid (32.2 mg, 53% yield).

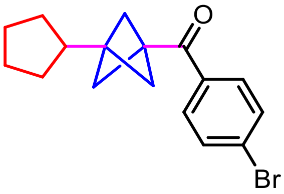
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.53 – 2.36 (m, 1H), 2.09 (s, 6H), 2.03 – 1.93 (m, 2H), 1.93 – 1.83 (m, 1H), 1.81 – 1.72 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 135.4, 131.7, 130.4, 127.9, 51.4, 43.7, 43.3, 35.8, 24.2, 18.1.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}OBr$ 305.0536; found 305.0536.

(4-Bromophenyl)(3-cyclopentylbicyclo[1.1.1]pentan-1-yl)methanone (4d)



4d

4d was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl dicyclopentanecarboxylate **1d** (94.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4d** as a colorless solid (44.5 mg, 70% yield).

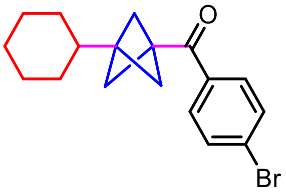
TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.06 (s, 6H), 1.99 (p, *J* = 7.9 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.60 – 1.48 (m, 4H), 1.27 (dddd, *J* = 14.2, 12.6, 6.3, 2.8 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.2, 135.4, 131.7, 130.4, 127.9, 51.9, 44.0, 43.5, 40.0, 28.9, 25.7.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for C$_{17}$H$_{20}$OBr 319.0692; found 319.0692.

(4-Bromophenyl)(3-cyclohexylbicyclo[1.1.1]pentan-1-yl)methanone (4e)



4e

4e was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl dicyclohexanecarboxylate **1e** (100.0 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4e** as a colorless solid (48.4 mg, 73% yield).

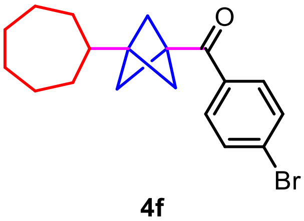
TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.06 (s, 6H), 1.78 – 1.71 (m, 2H), 1.68 – 1.62 (m, 3H), 1.37 (tt, *J* = 11.8, 3.4 Hz, 1H), 1.29 – 1.17 (m, 2H), 1.17 – 1.05 (m, 1H), 0.89 (qd, *J* = 12.6, 3.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 135.5, 131.7, 130.4, 127.9, 51.3, 44.6, 43.3, 37.8, 29.1, 26.2, 26.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}OBr$ 333.0849; found 333.0846.

(4-Bromophenyl)(3-cycloheptylbicyclo[1.1.1]pentan-1-yl)methanone (4f)



4f

4f was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl dicycloheptanecarboxylate **1f** (105.6 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4f** as a colorless solid (45.0 mg, 65% yield).

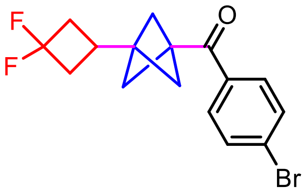
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.07 (s, 6H), 1.80 – 1.62 (m, 4H), 1.62 – 1.54 (m, 3H), 1.52 – 1.44 (m, 2H), 1.44 – 1.37 (m, 2H), 1.17 (ddd, *J* = 17.4, 10.4, 5.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 135.5, 131.7, 130.4, 127.9, 51.4, 45.3, 43.5, 39.6, 30.6, 28.5, 26.4.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{24}OBr$ 347.1005; found 347.0997.

(4-Bromophenyl)(3-(3,3-difluorocyclobutyl)bicyclo[1.1.1]pentan-1-yl)methanone (4g)



4g

4g was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(3,3-difluorocyclobutane-1-carboxylate) **1g** (103.2 mg, 0.20 mmol, 1.0

equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4g** as a colorless solid (42.2 mg, 62% yield).

TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

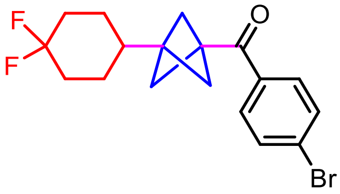
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 2.66 – 2.46 (m, 2H), 2.43 – 2.20 (m, 3H), 2.15 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 135.2, 131.8, 130.4, 128.2, 119.5 (dd, *J* = 283.4, 274.7 Hz), 61.8, 51.4, 43.6, 42.3 (d, *J* = 3.3 Hz), 37.3 (t, *J* = 22.6 Hz), 23.3 (dd, *J* = 11.6, 6.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -83.25 – -83.91 (m), -93.92 – -94.67 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}OF_2Br$ 341.0347; found 341.0346.

(4-Bromophenyl)(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (4h)



4h

4h was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(4,4-difluorocyclohexane-1-carboxylate) **1h** (114.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4h** as a colorless solid (55.2 mg, 75% yield).

TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

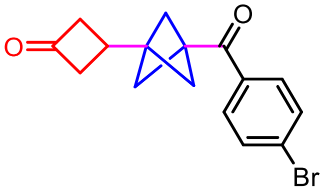
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 2.18 – 2.13 (m, 2H), 2.11 (s, 6H), 1.79 – 1.62 (m, 4H), 1.51 (t, *J* = 11.6 Hz, 1H), 1.33 – 1.17 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 135.3, 131.8, 130.4, 128.1, 125.4 – 121.5 (m), 51.5, 43.4 (d, *J* = 2.8 Hz), 43.1, 36.0, 33.2 (dd, *J* = 25.5, 22.6 Hz), 25.4 (d, *J* = 9.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -91.54 (d, *J* = 235.9 Hz), -101.75 – -103.20 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{20}OF_2Br$ 369.0660; found 369.0659.

3-(3-(4-Bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)cyclobutan-1-one (4i)



4i

4i was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(3-oxocyclobutane-1-carboxylate) **1i** (94.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4i** as a colorless solid (36.2 mg, 57% yield).

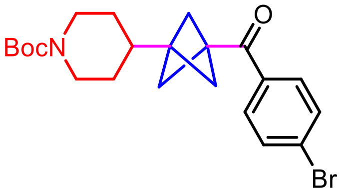
TLC R$_f$ = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 3.24 – 2.98 (m, 2H), 2.94 – 2.72 (m, 2H), 2.63 (tt, *J* = 9.0, 6.2 Hz, 1H), 2.19 (s, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 206.5, 196.3, 135.1, 131.9, 130.4, 128.2, 51.4, 49.6, 43.6, 42.8, 24.1.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{16}H_{16}O_2Br$ 319.0328; found 319.0324.

Tert-butyl 4-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4j)



4j

4j was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), 1,1'-di-tert-butyl O'^{4},O^4-(mesityl-λ^3-iodanediyl) bis(piperidine-1,4-dicarboxylate) **1j** (140.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4j** as a colorless solid (61.4 mg, 71% yield).

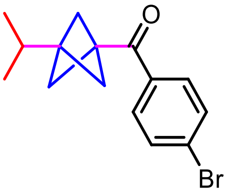
TLC R$_f$ = 0.40 (Hexane/EtOAc = 5:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 4.15 (s, 2H), 2.65 (s, 2H), 2.08 (s, 6H), 1.71 – 1.50 (m, 3H), 1.45 (s, 9H), 1.16 – 1.05 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 154.8, 135.3, 131.8, 130.4, 128.0, 79.4, 51.2, 43.7, 43.4, 36.3, 28.5, 28.2.

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{28}O_3NBrNa$ 456.1145; found 456.1137.

(4-Bromophenyl)(3-isopropylbicyclo[1.1.1]pentan-1-yl)methanone (4k)



4k

4k was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 μmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2-methylpropanoate) **1k** (84.0 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4k** as a colorless solid (39.1 mg, 67% yield).

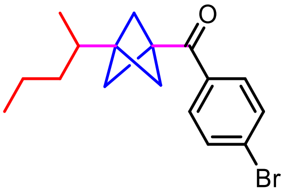
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.06 (s, 6H), 1.74 (dt, *J* = 13.6, 6.8 Hz, 1H), 0.87 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 135.4, 131.7, 130.4, 127.9, 51.0, 45.5, 43.0, 28.3, 18.6.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{18}OBr$ 293.0536; found 293.0536.

(4-Bromophenyl)(3-(pentan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone (4l)



4l

4l was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 μmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2-methylpentanoate) **1l** (95.2 mg, 0.20 mmol, 1.0 equiv), 4-

bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4l** as a colorless solid (49.9 mg, 78% yield).

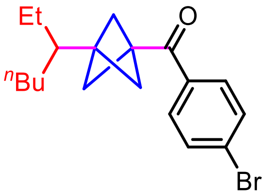
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.07 (s, 6H), 1.56 (ddd, *J* = 9.0, 6.8, 4.5 Hz, 1H), 1.46 – 1.31 (m, 2H), 1.31 – 1.21 (m, 1H), 1.06 – 0.95 (m, 1H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 135.4, 131.7, 130.4, 127.9, 51.4, 45.2, 43.3, 35.5, 32.9, 20.7, 15.8, 14.3.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{22}OBr$ 321.0849; found 321.0846.

(4-Bromophenyl)(3-(heptan-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone (4m)



4m

4m was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 μmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2-ethylhexanoate) **1m** (106.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4m** as a colorless solid (48.7 mg, 70% yield).

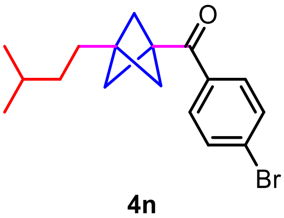
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.13 (s, 6H), 1.41 – 1.10 (m, 9H), 1.02 – 0.82 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 135.5, 131.7, 130.4, 127.9, 52.5, 44.8, 43.8, 39.8, 30.3, 29.9, 23.8, 23.1, 14.1, 12.1.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{26}OBr$ 349.1162; found 349.1156.

(4-Bromophenyl)(3-isopentylbicyclo[1.1.1]pentan-1-yl)methanone (4n)



4n

4n was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(4-methylpentanoate) **1n** (95.2 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4n** as a colorless solid (43.5 mg, 68% yield).

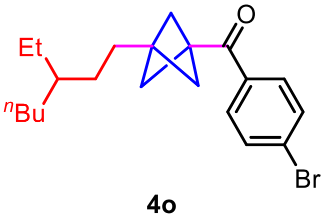
TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 2.10 (s, 6H), 1.58 – 1.40 (m, 3H), 1.23 – 0.98 (m, 2H), 0.88 (d, J = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.1, 135.4, 131.7, 130.4, 127.9, 53.3, 44.1, 41.0, 35.4, 29.2, 28.1, 22.6.

HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{17}$H$_{22}$OBr 321.0849; found 321.0849.

(4-Bromophenyl)(3-(3-ethylheptyl)bicyclo[1.1.1]pentan-1-yl)methanone (4o)



4o

4o was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(4-ethyloctanoate) **1o** (117.6 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4o** as a colorless solid (45.8 mg, 61% yield).

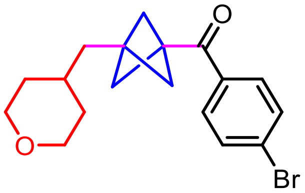
TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.11 (s, 6H), 1.47 (t, *J* = 7.8 Hz, 2H), 1.42 – 1.13 (m, 11H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.1, 135.4, 131.7, 130.5, 127.9, 53.3, 44.1, 41.1, 38.7, 32.8, 29.5, 29.0, 28.3, 25.8, 23.2, 14.2, 10.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{21}H_{30}OBr$ 377.1475; found 377.1474.

(4-Bromophenyl)(3-((tetrahydro-2H-pyran-4-yl)methyl)bicyclo[1.1.1]pentan-1-yl)methanone (4p)



4p

4p was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2-(tetrahydro-*2H*-pyran-4-yl)acetate) **1p** (106.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4p** as a colorless solid (44.5 mg, 64% yield).

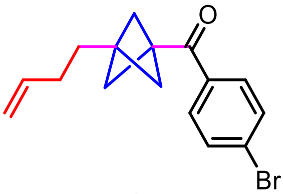
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 3.94 (dd, *J* = 11.2, 4.1 Hz, 2H), 3.40 (td, *J* = 11.9, 1.9 Hz, 2H), 2.18 (s, 6H), 1.66 – 1.52 (m, 3H), 1.49 (d, *J* = 6.2 Hz, 2H), 1.32 (ddd, *J* = 15.4, 12.9, 4.4 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 196.6, 135.3, 131.8, 130.4, 128.0, 68.0, 54.5, 39.9, 38.7, 33.6, 33.3, 29.6.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{22}O_2Br$ 349.0798; found 349.0797.

(4-Bromophenyl)(3-(but-3-en-1-yl)bicyclo[1.1.1]pentan-1-yl)methanone (4q)



4q

4q was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(pent-4-enoate) **1q** (88.8 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4q** as a colorless solid (28.6 mg, 47% yield).

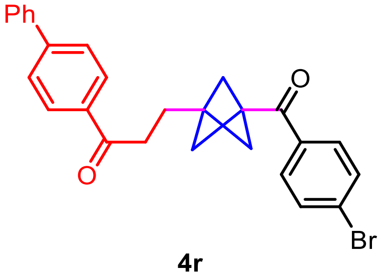
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 5.83 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.04 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.96 (dd, *J* = 10.2, 1.1 Hz, 1H), 2.13 (s, 6H), 2.12 – 2.02 (m, 2H), 1.68 – 1.60 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 196.9, 138.4, 135.4, 131.7, 130.4, 127.9, 114.6, 53.5 44.2 40.7, 30.6 30.6

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for C$_{16}$H$_{18}$OBr 305.0536; found 305.0535.

1-([1,1'-Biphenyl]-4-yl)-3-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)propan-1-one (4r)



4r

4r was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate) **1r** (150.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4r** as a colorless solid (40.3 mg, 44% yield).

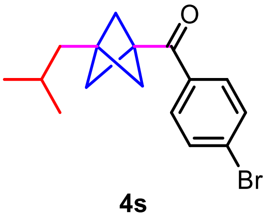
TLC R$_f$ = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.38 (m, 1H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.17 (s, 6H), 2.04 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.1, 196.6, 145.8,139.9 135.6 135.3 131.8 130.4, 129.0, 128.6, 128.3 128.0, 127.3, 127.3 55.2 53.4 44.0, 40.3, 35.2 25.8

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{24}O_2Br$ 459.0954; found 459.0943.

(4-Bromophenyl)(3-isobutylbicyclo[1.1.1]pentan-1-yl)methanone (4s)



4s

4s was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(3-methylbutanoate) **1s** (89.6 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4s** as a colorless solid (43.4 mg, 71% yield).

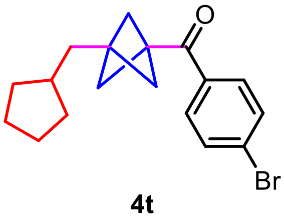
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 2.17 (s, 6H), 1.66 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.43 (d, *J* = 6.6 Hz, 2H), 0.92 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 135.4, 131.7, 130.4, 127.9 54.4 44.5, 40.6 40.5, 26.5, 23.4.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{20}OBr$ 307.0692; found 307.0692.

(4-Bromophenyl)(3-(cyclopentylmethyl)bicyclo[1.1.1]pentan-1-yl)methanone (4t)



4t

4t was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2-cyclopentylacetate) **1t** (100.0 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4t** as a colorless solid (48.4 mg, 73% yield).

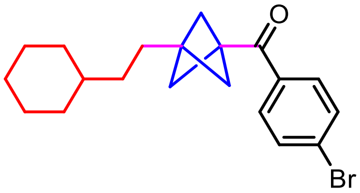
TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.14 (s, 6H), 1.92 – 1.75 (m, 3H), 1.64 – 1.57 (m, 4H), 1.55 (d, *J* = 6.3 Hz, 2H), 1.53 – 1.43 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.0, 135.4, 131.7, 130.4, 127.9, 54.2, 44.5, 40.9, 38.1, 37.8, 33.3, 25.3.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{22}OBr$ 333.0849; found 333.0849.

(4-Bromophenyl)(3-(2-cyclohexylethyl)bicyclo[1.1.1]pentan-1-yl)methanone (4u)



4u

4u was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(3-cyclohexylpropanoate) **1u** (111.2 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4u** as a colorless solid (59.0 mg, 82% yield).

TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

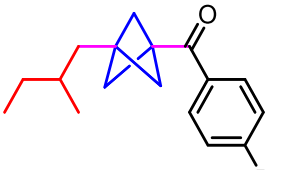
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.10 (s, 6H), 1.69 (d, *J* = 10.6 Hz, 4H), 1.66 – 1.56 (m, 1H), 1.50 (dd, *J* = 9.4, 6.7 Hz, 2H), 1.35 – 1.02 (m, 6H), 0.87 (dd, *J* = 22.0, 10.6 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.1, 135.4, 131.7, 130.4, 127.9, 53.3, 44.1, 41.1, 37.7, 33.9, 33.4, 28.6, 26.7, 26.4.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{20}H_{26}OBr$ 361.1162; found 361.1161.

(4-Bromophenyl)(3-(2-methylbutyl)bicyclo[1.1.1]pentan-1-yl)methanone (4v)

H^+



4v

4v was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(3-methylpentanoate) **1v** (95.2 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4v** as a colorless solid (46.7 mg, 73% yield).

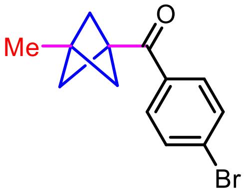
TLC R$_f$ = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 2.16 (s, 6H), 1.54 (dd, *J* = 14.1, 4.8 Hz, 1H), 1.42 (td, *J* = 12.4, 6.2 Hz, 1H), 1.38 – 1.30 (m, 2H), 1.22 – 1.08 (m, 1H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 196.9, 135.4, 131.7, 130.4, 127.9, 54.4, 44.5, 40.5, 38.3, 32.8, 30.1, 19.9, 11.3.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for C$_{17}$H$_{22}$OBr 321.0849; found 321.0846.

(4-Bromophenyl)(3-methylbicyclo[1.1.1]pentan-1-yl)methanone (4w)



4w

4w was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl diacetate **1w** (72.8 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4w** as a colorless solid (34.3 mg, 65% yield).

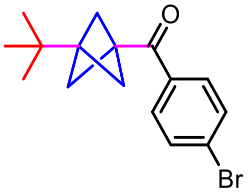
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 2.15 (s, 6H), 1.24 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 135.4, 131.7, 130.4, 127.9, 55.1, 44.1, 37.4, 18.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{14}OBr$ 265.0223; found 265.0223.

(4-Bromophenyl)(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)methanone (4x)



4x

4x was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2,2-dimethylpropanoate) **1x** (89.6 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4x** as a colorless solid (34.9 mg, 57% yield).

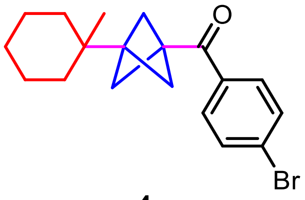
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 2.06 (s, 6H), 0.89 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 135.5, 131.7, 130.4, 127.9, 49.9, 48.8, 41.6, 29.5, 25.8.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{20}OBr$ 307.0692; found 307.0691.

(4-Bromophenyl)(3-(1-methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (4y)



4y

4y was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(1-methylcyclohexane-1-carboxylate) **1y** (105.6 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4y** as a colorless solid (57.4 mg, 83% yield).

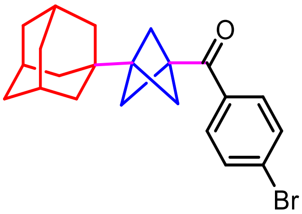
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 2.06 (s, 6H), 1.61 – 1.58 (m, 1H), 1.57 – 1.48 (m, 2H), 1.48 – 1.33 (m, 2H), 1.28 – 1.17 (m, 4H), 1.16 – 1.04 (m, 1H), 0.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 135.5, 131.7, 130.4, 127.9, 49.7, 49.4, 42.0, 33.4, 31.5, 26.3, 21.9, 19.4.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{24}OBr$ 347.1005; found 347.1003.

(3-(Adamantan-1-yl)bicyclo[1.1.1]pentan-1-yl)(4-bromophenyl)methanone (4z)



4z

4z was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(adamantane-1-carboxylate) **1z** (120.8 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4z** as a colorless solid (47.6 mg, 62% yield).

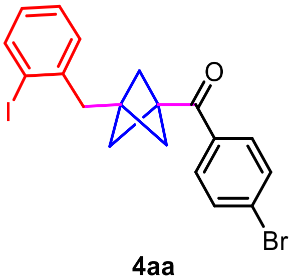
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 2.03 (s, 6H), 1.99 (s, 3H), 1.71 (d, J = 12.2 Hz, 3H), 1.61 (d, J = 11.4 Hz, 3H), 1.45 (d, J = 2.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 135.5, 131.7, 130.4, 127.9, 49.1, 48.3, 42.0, 38.2, 36.9, 30.8, 28.1.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{26}OBr$ 385.1162; found 385.1154.

(4-Bromophenyl)(3-(2-iodobenzyl)bicyclo[1.1.1]pentan-1-yl)methanone (4aa)



4aa

4aa was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(2-(2-iodophenyl)acetate) **1aa** (153.4 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4aa** as a colorless solid (48.4 mg, 52% yield).

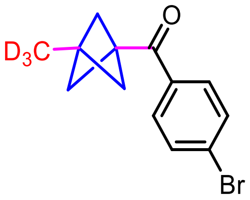
TLC R_f = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 7.14 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.91 (td, *J* = 7.7, 1.7 Hz, 1H), 3.07 (s, 2H), 2.15 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 141.8, 139.7, 135.3, 131.7, 130.4, 129.9, 128.4, 128.1, 128.0, 100.6, 53.7, 45.1, 42.6, 40.6.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{17}OBrI$ 466.9502; found 466.9495.

(4-Bromophenyl)(3-(methyl-d3)bicyclo[1.1.1]pentan-1-yl)methanone (4ab)



4ab

4ab was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(acetate-*d*$_6$) **1ab** (74.0 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **4ab** as a colorless solid (35.7 mg, 67% yield).

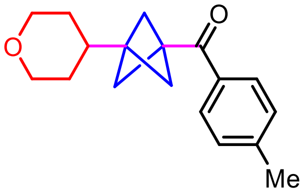
TLC R_f = 0.60 (Hexane/EtOAc = 15:1, v/v).

1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 2.14 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 135.4, 131.7, 130.4, 127.9, 55.1, 44.2, 37.2, 28.47 – 13.25 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{11}D_3OBr$ 268.0411; found 268.0414.

(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(*p*-tolyl)methanone (5a)



5a

5a was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), *p*-tolualdehyde **3b** (23.6 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5a** as a colorless oil (43.2 mg, 80% yield).

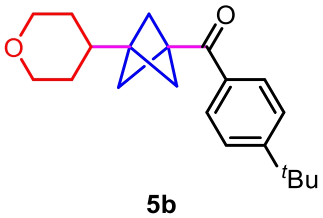
TLC R_f = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.00 (dd, *J* = 11.3, 4.4 Hz, 2H), 3.38 (td, *J* = 12.1, 1.9 Hz, 2H), 2.40 (s, 3H), 2.09 (s, 6H), 1.73 – 1.59 (m, 1H), 1.53 (dd, *J* = 13.0, 2.0 Hz, 2H), 1.32 (ddd, *J* = 25.4, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 143.6, 134.1, 129.1, 129.1, 67.7, 51.1, 43.6, 43.5, 35.3, 28.9, 21.7.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{23}O_2$ 271.1693; found 271.1693.

(4-(*Tert*-butyl)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5b)



5b

5b was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-*tert*-butylbenzaldehyde **3c** (33.4 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5b** as a colorless oil (50.5 mg, 81% yield).

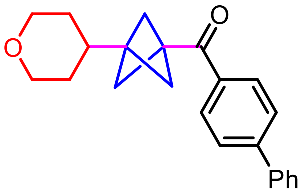
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 4.00 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.38 (td, *J* = 12.2, 2.0 Hz, 2H), 2.10 (s, 6H), 1.65 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.56 – 1.50 (m, 2H), 1.34 (s, 9H), 1.32 – 1.31 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 197.6, 156.6, 134.0, 128.9, 125.4, 67.8, 51.1, 43.6, 43.5, 35.3, 31.1, 28.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{21}H_{29}O_2$ 313.2162; found 313.2163.

[1,1'-Biphenyl]-4-yl(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5c)



5c

5c was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-biphenylcarboxaldehyde **3d** (36.4 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5c** as a colorless solid (48.5 mg, 73% yield).

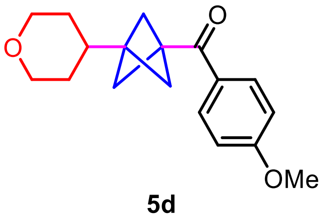
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.62 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 4.01 (dd, *J* = 11.3, 4.4 Hz, 2H), 3.39 (td, *J* = 12.1, 2.0 Hz, 2H), 2.14 (s, 6H), 1.67 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.55 (ddd, *J* = 12.6, 3.3, 1.3 Hz, 2H), 1.34 (ddd, *J* = 25.4, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 145.5, 140.0, 135.3, 129.5, 129.0, 128.2, 127.3, 127.1, 67.8, 51.1, 43.7, 43.6, 35.3, 28.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{25}O_2$ 333.1847; found 333.1847.

(4-Methoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5d)



5d

5d was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), *p*-anisaldehyde **3e** (24.3 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5d** as a colorless oil (34.9 mg, 61% yield).

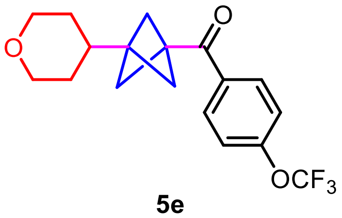
TLC R_f = 0.50 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.00 (dd, *J* = 11.2, 4.2 Hz, 2H), 3.87 (s, 3H), 3.51 – 2.93 (m, 2H), 2.09 (s, 6H), 1.65 (tt, *J* = 12.0, 3.8 Hz, 1H), 1.53 (d, *J* = 13.0 Hz, 2H), 1.32 (qd, *J* = 12.5, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 163.3, 131.3, 129.7, 113.6, 67.8, 55.5, 51.1, 43.5, 43.4, 35.3, 28.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{23}O_3$ 287.1642; found 287.1642.

(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanone (5e)



5e

5e was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-(trifluoromethoxy)benzaldehyde **3f** (28.5 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5e** as a colorless oil (34.0 mg, 50% yield).

TLC R$_f$ = 0.50 (Hexane/EtOAc = 8:1, v/v).

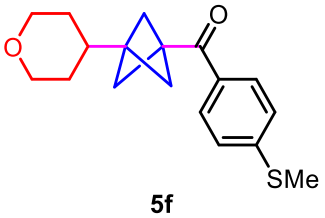
^{1}H NMR (600 MHz, CDCl$_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.99 (dd, *J* = 11.3, 4.2 Hz, 2H), 3.36 (t, *J* = 11.5 Hz, 2H), 2.09 (s, 6H), 1.65 (tt, *J* = 11.9, 3.6 Hz, 1H), 1.52 (d, *J* = 12.9 Hz, 2H), 1.30 (qd, *J* = 12.5, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 196.4, 152.4, 134.8, 130.9, 121.7 – 119.1 (m), 67.7, 51.1, 43.8, 43.4, 35.2, 28.9.

^{19}F NMR (565 MHz, CDCl$_3$) δ -57.60 (s).

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{20}O_3F_3$ 341.1357; found 341.1358.

(4-(Methylthio)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5f)



5f

5f was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-(methylthio)benzaldehyde **3g** (26.6 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5f** as a colorless solid (38.1 mg, 63% yield).

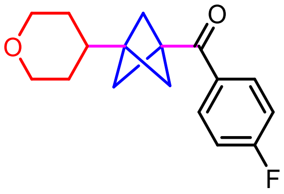
TLC R_f = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 4.00 (dd, *J* = 11.1, 4.1 Hz, 2H), 3.37 (td, *J* = 12.1, 2.0 Hz, 2H), 2.51 (s, 3H), 2.09 (s, 6H), 1.74 – 1.60 (m, 1H), 1.53 (ddd, *J* = 12.6, 3.3, 1.3 Hz, 2H), 1.32 (ddd, *J* = 25.5, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.9, 145.6, 132.9, 129.4, 124.9, 67.7, 51.1, 43.6, 43.4, 35.3, 28.9, 14.8.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{23}O_2S$ 303.1413; found 303.1413.

(4-Fluorophenyl)(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5g)



5g

5g was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-fluorobenzaldehyde **3h** (21.4 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5g** as a colorless oil (38.9 mg, 71% yield).

TLC R_f = 0.60 (Hexane/EtOAc = 10:1, v/v).

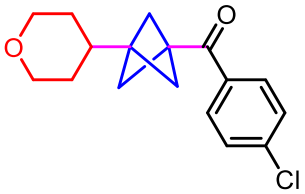
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.9, 5.5 Hz, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 4.00 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.38 (td, *J* = 12.1, 2.0 Hz, 2H), 2.10 (s, 6H), 1.80 – 1.59 (m, 1H), 1.53 (ddd, *J* = 12.7, 3.2, 1.3 Hz, 2H), 1.32 (ddd, *J* = 25.5, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.3, 165.5 (d, *J* = 254.7 Hz), 133.0 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 9.6 Hz), 115.6 (d, *J* = 21.8 Hz), 67.7, 51.1, 43.7, 43.4, 35.2, 28.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -105.24 (dt, *J* = 15.2, 7.5 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{20}O_2F$ 275.1442; found 275.1443.

(4-Chlorophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5h)



5h

5h was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-chlorobenzaldehyde **3i** (28.0 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5h** as a colorless solid (39.4 mg, 68% yield).

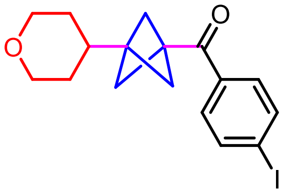
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 4.00 (dd, *J* = 11.3, 4.4 Hz, 2H), 3.37 (td, *J* = 12.1, 1.9 Hz, 2H), 2.09 (s, 6H), 1.71 – 1.58 (m, 1H), 1.53 (dd, *J* = 13.0, 1.9 Hz, 2H), 1.32 (ddd, *J* = 25.4, 12.4, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 196.8, 139.3, 134.9, 130.3, 128.8, 67.7, 51.1, 43.7, 43.43, 35.2, 28.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{17}H_{20}O_2Cl$ 291.1146; found 291.1146.

(4-Iodophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5i)



5i

5i was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-iodobenzaldehyde **3j** (46.4 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5i** as a colorless solid (28.3 mg, 37% yield).

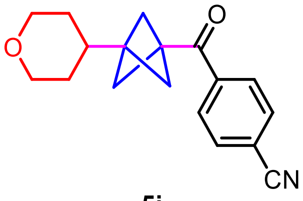
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 4.00 (dd, *J* = 11.3, 4.2 Hz, 2H), 3.37 (td, *J* = 12.1, 1.9 Hz, 2H), 2.09 (s, 6H), 1.65 (tt, *J* = 11.9, 3.7 Hz, 1H), 1.53 (dd, *J* = 12.9, 2.0 Hz, 2H), 1.31 (ddd, *J* = 25.4, 12.3, 4.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 137.8, 135.8, 130.3, 100.8, 67.7, 51.1, 43.7, 43.4, 35.2, 28.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{20}O_2I$ 383.0502; found 383.0502.

4-(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (5j)



5j

5j was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-cyanobenzaldehyde **3k** (26.2 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5j** as a colorless solid (31.5 mg, 56% yield).

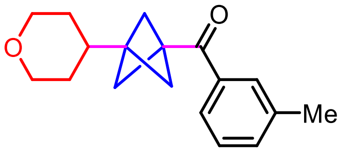
TLC R_f = 0.50 (Hexane/EtOAc = 5:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 4.00 (dd, *J* = 11.3, 4.3 Hz, 2H), 3.37 (td, *J* = 12.1, 1.8 Hz, 2H), 2.11 (s, 6H), 1.67 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.53 (dd, *J* = 13.0, 1.9 Hz, 2H), 1.32 (ddd, *J* = 25.3, 12.5, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 139.7, 132.4, 129.2, 118.0, 116.1, 67.7, 51.1, 44.0, 43.5, 35.2, 28.8.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_2$ 282.1489; found 282.1484.

(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(*m*-tolyl)methanone (5k)



5k

5k was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), *m*-tolualdehyde **3l** (23.6 µL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5k** as a colorless oil (44.3 mg, 82% yield).

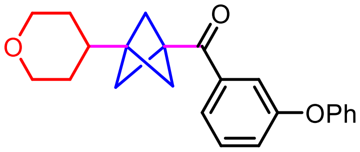
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.77 (s, 1H), 7.37 – 7.33 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.00 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.38 (td, *J* = 12.1, 2.0 Hz, 2H), 2.40 (s, 3H), 2.10 (s, 6H), 1.73 – 1.59 (m, 1H), 1.53 (ddd, *J* = 12.7, 3.3, 1.3 Hz, 2H), 1.32 (ddd, *J* = 25.5, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 198.3, 138.3, 136.7, 133.6, 129.3, 128.3, 126.2, 67.7, 51.1, 43.6, 43.6, 35.3, 28.9, 21.5.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{18}H_{23}O_2$ 271.1693; found 271.1694.

(3-Phenoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5l)



5l

5l was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 3-phenoxybenzaldehyde **3m** (39.6 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5l** as a colorless solid (58.4 mg, 84% yield).

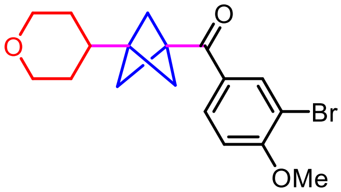
TLC R$_f$ = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.73 – 7.69 (m, 1H), 7.57 (dd, *J* = 2.3, 1.7 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.18 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.03 (dd, *J* = 8.6, 1.0 Hz, 2H), 3.99 (dd, *J* = 11.4, 4.4 Hz, 2H), 3.36 (td, *J* = 12.1, 2.0 Hz, 2H), 2.05 (s, 6H), 1.75 – 1.58 (m, 1H), 1.50 (ddd, *J* = 12.7, 3.3, 1.3 Hz, 2H), 1.29 (ddd, *J* = 25.5, 12.3, 4.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 157.7, 156.4, 138.2, 130.0, 129.8, 124.0, 123.4, 122.8, 119.4, 118.5, 67.7, 51.0, 43.6, 43.5, 35.2, 28.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{25}O_3$ 349.1798; found 349.1798.

(3-Bromo-4-methoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5m)



5m

5m was prepared according to the general procedure outlined above using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 3-bromo-4-methoxybenzaldehyde **3n** (42.8 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5m** as a colorless solid (48.8 mg, 67% yield).

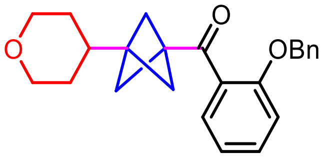
TLC R_f = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.1 Hz, 1H), 7.98 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 4.00 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.96 (s, 3H), 3.37 (td, *J* = 12.1, 2.0 Hz, 2H), 2.09 (s, 6H), 1.66 (ddd, *J* = 15.5, 9.6, 3.6 Hz, 1H), 1.56 – 1.49 (m, 2H), 1.32 (ddd, *J* = 12.3, 10.5, 6.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.3, 159.4, 134.4, 130.6, 130.2, 111.7, 111.0, 67.7, 56.5, 51.2, 43.7, 43.3, 35.2, 28.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}O_3Br$ 365.0747; found 365.0748.

(2-(Benzyloxy)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5n)



5n

5n was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 2-(benzyloxy)benzaldehyde **3o** (42.4 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5n** as a colorless solid (41.3 mg, 57% yield).

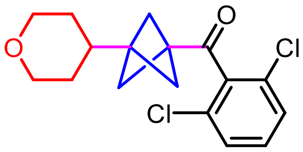
TLC R$_f$ = 0.50 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.46 – 7.30 (m, 7H), 7.12 – 6.86 (m, 2H), 5.10 (s, 2H), 3.94 (dd, *J* = 11.3, 4.3 Hz, 2H), 3.32 (td, *J* = 12.2, 1.9 Hz, 2H), 1.83 (s, 6H), 1.52 (tt, *J* = 11.8, 3.8 Hz, 1H), 1.39 (dd, *J* = 13.0, 1.9 Hz, 2H), 1.17 (ddd, *J* = 25.3, 12.2, 4.4 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 203.1, 156.1, 136.3, 131.9, 129.8, 128.9, 128.6, 128.2, 127.8, 120.7, 112.6, 70.6, 67.7, 49.6, 44.3, 42.8, 35.2, 28.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{24}H_{27}O_3$ 363.1955; found 363.1955.

(2,6-Dichlorophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5o)



5o

5o was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 2,6-dichlorobenzaldehyde **3p** (34.8 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5o** as a colorless solid (45.2 mg, 72% yield).

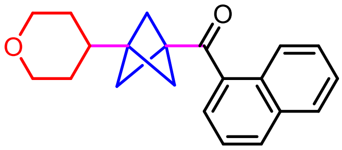
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34 – 7.30 (m, 2H), 7.28 (dd, *J* = 7.2, 1.9 Hz, 1H), 3.99 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.36 (td, *J* = 12.1, 2.0 Hz, 2H), 1.97 (s, 6H), 1.65 – 1.57 (m, 1H), 1.54 – 1.43 (m, 2H), 1.27 (ddd, *J* = 25.5, 12.3, 4.6 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 200.2, 138.5, 130.7, 130.4, 127.9, 67.7, 49.7, 44.1, 43.0, 35.2, 28.8.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{17}H_{19}O_2Cl_2$ 325.0757; found 325.0755.

Naphthalen-1-yl(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5p)



5p

5p was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 1-naphthaldehyde **3q** (31.2 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5p** as a colorless solid (31.2 mg, 51% yield).

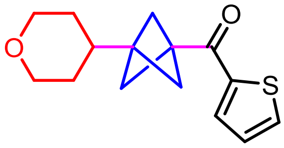
TLC R$_f$ = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.78 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.54 (dddd, *J* = 19.3, 8.0, 6.8, 1.4 Hz, 2H), 7.48 (dd, *J* = 8.2, 7.2 Hz, 1H), 3.99 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.36 (td, *J* = 12.1, 2.1 Hz, 2H), 2.05 (s, 6H), 1.64 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.50 (ddd, *J* = 12.7, 3.3, 1.4 Hz, 2H), 1.29 (ddd, *J* = 25.6, 12.3, 4.6 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 202.6, 135.5, 133.9, 131.7, 130.2, 128.4, 127.6, 126.8, 126.4, 125.7, 124.2, 67.7, 50.4, 44.7, 43.2, 35.2, 28.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for $C_{21}H_{23}O_2$ 307.1693; found 307.1694.

(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (5q)



5q

5q was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 2-thenaldehyde **3r** (18.7 μL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5q** as a colorless solid (39.3 mg, 75% yield).

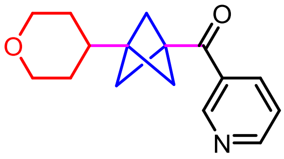
TLC R$_f$ = 0.50 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.82 (dd, *J* = 3.8, 0.8 Hz, 1H), 7.63 (dd, *J* = 4.9, 0.8 Hz, 1H), 7.13 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.00 (dd, *J* = 11.3, 4.3 Hz, 2H), 3.37 (td, *J* = 12.2, 1.9 Hz, 2H), 2.08 (s, 6H), 1.67 (ddd, *J* = 12.0, 7.9, 4.0 Hz, 1H), 1.53 (dd, *J* = 12.9, 2.0 Hz, 2H), 1.32 (ddd, *J* = 25.4, 12.4, 4.6 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 190.5, 142.8, 133.5, 132.9, 128.0, 67.7, 52.2, 50.7, 43.1, 35.2, 28.9.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for C$_{15}$H$_{19}$O$_2$S 263.1100; found 263.1102.

Pyridin-3-yl(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5r)



5r

5r was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 3-pyridinecarboxaldehyde **3s** (18.8 μL, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5r** as a colorless oil (35.0 mg, 68% yield).

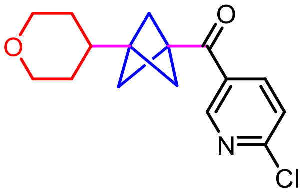
TLC R_f = 0.50 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (d, *J* = 2.0 Hz, 1H), 8.75 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.24 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.41 (dd, *J* = 7.9, 4.8 Hz, 1H), 4.00 (dd, *J* = 11.3, 4.3 Hz, 2H), 3.37 (td, *J* = 12.1, 1.9 Hz, 2H), 2.12 (s, 6H), 1.67 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.53 (dd, *J* = 13.0, 2.0 Hz, 2H), 1.32 (ddd, *J* = 25.4, 12.4, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 153.1, 150.2, 136.1, 132.1, 123.7, 67.7, 50.9, 43.9, 43.4, 35.2, 28.8.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{20}NO_2$ 258.1489; found 258.1489.

(6-Chloropyridin-3-yl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (5s)



5s

5s was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 μmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 2-chloropyridine-5-carbaldehyde **3t** (28.3 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5s** as a colorless solid (40.7 mg, 70% yield).

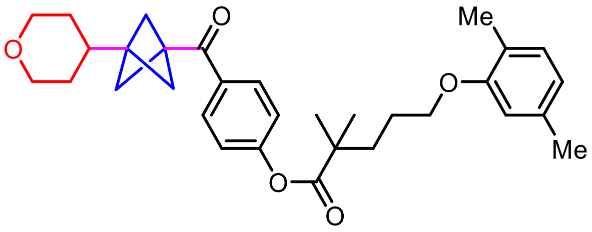
TLC R_f = 0.50 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.4 Hz, 1H), 8.19 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 4.00 (dd, *J* = 11.3, 4.3 Hz, 2H), 3.37 (td, *J* = 12.1, 1.9 Hz, 2H), 2.11 (s, 6H), 1.67 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.52 (dd, *J* = 12.9, 2.0 Hz, 2H), 1.31 (ddd, *J* = 25.4, 12.4, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.6, 155.4, 150.5, 138.7, 130.9, 124.6, 67.6, 51.0, 44.0, 43.4, 35.1, 28.8.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{19}O_2NCl$ 292.1099; found 292.1099.

4-(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (5t)



5t, 76%

5t was prepared according to the general procedure outlined above using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 μmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 4-formylphenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **3u** (70.8 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et$_2$O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5t** as a colorless solid (63.5 mg, 63% yield).

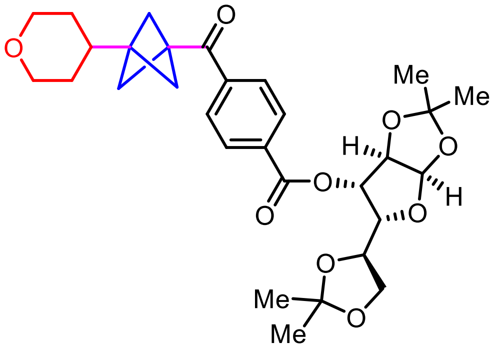
TLC R$_f$ = 0.40 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.63 (s, 1H), 4.12 – 3.91 (m, 4H), 3.38 (td, *J* = 12.1, 1.9 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 2.10 (s, 6H), 1.97 – 1.83 (m, 4H), 1.66 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.54 (dd, *J* = 13.0, 2.0 Hz, 2H), 1.38 (s, 6H), 1.33 (ddd, *J* = 25.4, 12.4, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 196.7, 175.9, 156.8, 154.5, 136.5, 134.1, 130.5, 130.4, 123.6, 121.6, 120.8, 111.9, 67.7, 67.7, 51.1, 43.7, 43.5, 42.6, 37.1, 35.2, 28.9, 25.3, 25.1, 21.4, 15.8.

HRMS (ESI) *m/z*: [M+H]$^+$ Calcd for C$_{32}$H$_{41}$O$_5$ 505.2949; found 505.2949.

(*3aR*,*5R*,*6S*,*6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzoate (5u)



5u

5u was prepared according to the general procedure outlined above using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.20 mmol, 1.0 equiv), 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-formylbenzoate **3v** (78.4 mg, 0.2 mmol, 1.0 equiv), propellane **2** (0.6 M in Et_2O, 0.67 mL, 0.40 mmol, 2.0 equiv), and DMSO (2.0 mL). Purification by column chromatography to provide the desired product **5u** as a colorless solid (61.7 mg, 57% yield).

TLC R_f = 0.30 (Hexane/EtOAc = 5:1, v/v).

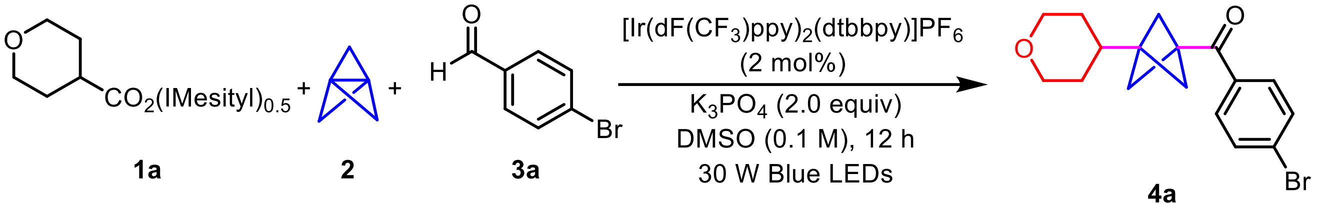
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 5.95 (d, *J* = 3.6 Hz, 1H), 5.51 (d, *J* = 2.7 Hz, 1H), 4.63 (d, *J* = 3.6 Hz, 1H), 4.40 – 4.23 (m, 2H), 4.12 (dd, *J* = 8.6, 5.6 Hz, 1H), 4.08 (dd, *J* = 8.7, 4.6 Hz, 1H), 4.01 (dd, *J* = 11.1, 4.1 Hz, 2H), 3.52 – 3.29 (m, 2H), 2.11 (s, 6H), 1.66 (ddd, *J* = 12.0, 7.8, 3.7 Hz, 1H), 1.56 (s, 3H), 1.55 – 1.47 (m, 2H), 1.41 (s, 3H), 1.37 – 1.33 (m, 2H), 1.32 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.5, 164.4, 140.4, 132.9, 129.8, 128.8, 112.5, 109.5, 108.1, 105.1, 83.3, 79.9, 72.6, 67.7, 51.1, 43.6, 35.2, 28.9, 26.9, 26.7, 26.2, 26.2, 25.2.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{30}H_{39}O_9$ 543.2589; found 543.2503.

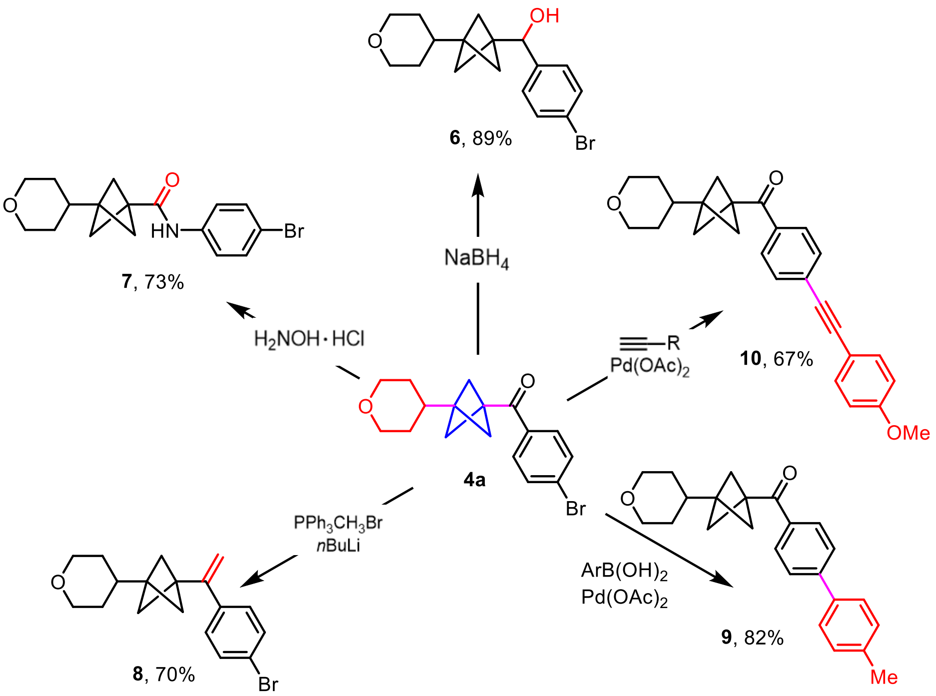
5. Further Functionalization

(a) Large-scale (2.0 mmol) experiment:



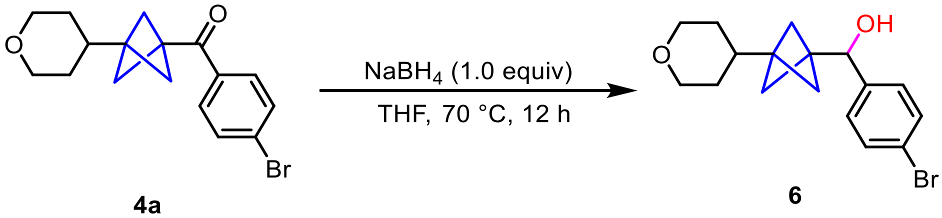
To a 50 mL reaction vial equipped with a stir bar was added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (45.0 mg, 40 µmol, 2 mol%), K_3PO_4 (848.0 mg, 4.0 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** (370 mg, 2.0 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (1008 mg, 2.0 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (20 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 6.67 mL, 4.0 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Once judged to be complete, the solution was transferred to a separatory funnel and diluted with deionized H_2O (50 mL) and Et_2O (50 mL). The layers were separated, and the aq layer was extracted with Et_2O (4 X 40 mL). The combined organic layers were washed with deionized H_2O (2 X 40 mL) followed by brine (40 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the **4a** as a colorless soild (1.30 mmol, 434.2 mg, 65% yield).

(b) Product diversification:



Scheme S1. Product diversification

(4-Bromophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanol (6)



To a 10 mL reaction vial equipped with a stir bar was added **4a** (33.4 mg, 0.10 mmol, 1.0 equiv) in dry THF (1.0 mL). Then NaBH$_4$ (3.8 mg, 0.10 mmol, 1.0 equiv) was added and the reaction was allowed to run for 12 hours at 70 °C in an oil bath. After this time, the reaction was quenched with water, and extracted with Et$_2$O (3 X 10 mL). The combined organic layers were dried (Na$_2$SO$_4$), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO$_2$ column chromatography (gradient Hexane/EtOAc) to give the desired product **6** as a colorless oil (29.9 mg, 89% yield).

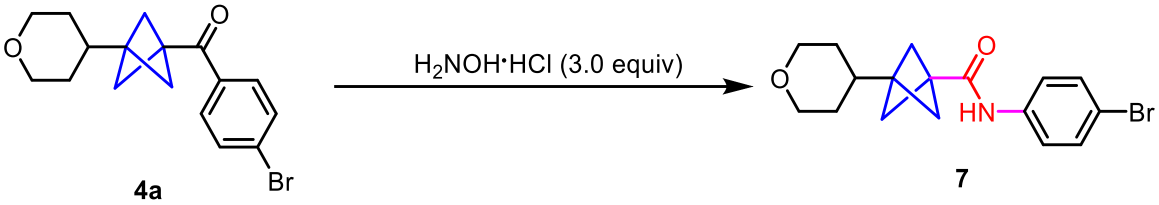
TLC R$_f$ = 0.40 (Hexane/EtOAc = 5:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.67 (s, 1H), 3.93 (dd, *J* = 11.1, 4.1 Hz, 2H), 3.31 (td, *J* = 12.2, 2.0 Hz, 2H), 1.83 (s, 1H), 1.53 (tt, *J* = 11.8, 3.8 Hz, 1H), 1.44 – 1.29 (m, 8H), 1.19 (qd, *J* = 12.4, 4.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.7, 131.2, 127.7, 121.1, 73.3, 67.8, 45.4, 43.2, 42.1, 35.5, 29.0.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{22}O_2Br$ 337.0798; found 337.0392.

N-(4-Bromophenyl)-3-(tetrahydro-*2H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carboxamide (7)



To a 10 mL reaction vial equipped with a stir bar was added **4a** (33.4 mg, 0.10 mmol, 1.0 equiv), hydroxylammonium chloride (21.0 mg, 0.3 mmol, 3.0 equiv), and TFA (0.4 mL). The reaction mixture was allowed to stir at 70 °C in an oil bath for 24 h. After this time, the reaction was quenched with sat. aq. $NaHCO_3$, and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired product **7** as a white solid (25.5 mg, 73% yield).

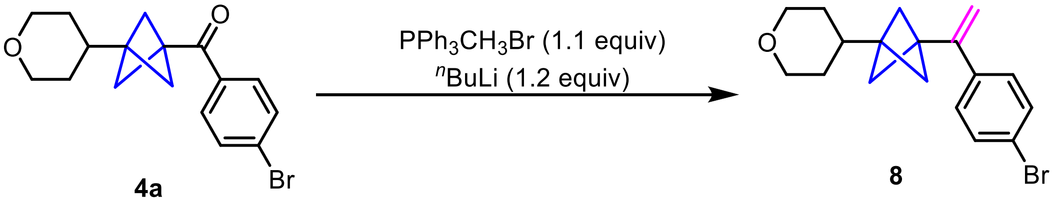
TLC R_f = 0.40 (Hexane/EtOAc = 3:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 4H), 7.15 (s, 1H), 4.00 (dd, *J* = 11.3, 4.4 Hz, 2H), 3.37 (td, *J* = 12.1, 2.0 Hz, 2H), 1.93 (s, 6H), 1.70 – 1.54 (m, 1H), 1.51 (dd, *J* = 13.0, 2.0 Hz, 2H), 1.36 – 1.26 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 136.7, 132.0, 121.3, 116.9, 67.7, 48.9, 42.1, 39.6, 35.0, 28.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{21}O_2NBr$ 350.0750; found 350.0749.

4-(3-(1-(4-Bromophenyl)vinyl)bicyclo[1.1.1]pentan-1-yl)tetrahydro-*2H*-pyran (8)



To a 10 mL reaction vial equipped with a stir bar was added methylphosphonium bromide (40.0 mg, 0.11 mmol, 1.1 equiv), and dry THF (1 mL). The solution was subjected to an ice bath, and then ^{n}BuLi

(0.1 mL, 1.2 M in hexanes, 1.2 equiv) was added dropwise. The reaction mixture was allowed to stir for 1 h at 0 °C. Lastly, **4a** (33.4 mg, 0.10 mmol, 1.0 equiv) dissolved in 0.5 mL of THF was added. The reaction mixture was allowed to warm to rt, and then heated to 70 °C in an oil bath for 12 h. After this time, the reaction was quenched with water, and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired product **8** as a colorless solid (23.2 mg, 70% yield).

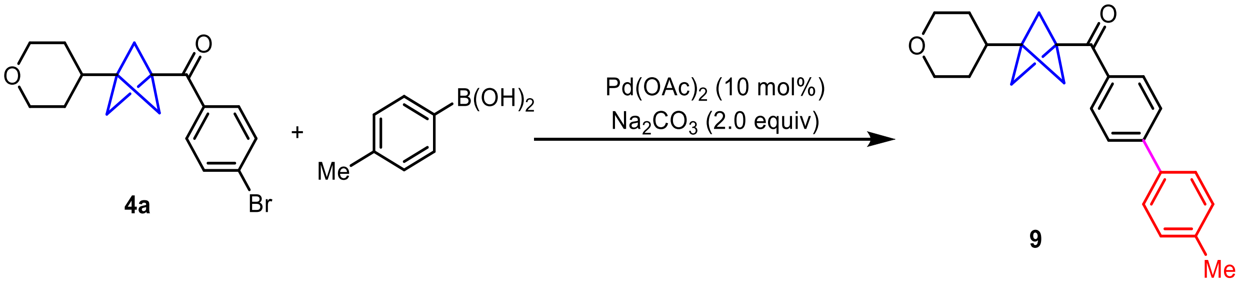
TLC R_f = 0.70 (Hexane/EtOAc = 15:1, v/v).

^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.15 (d, *J* = 1.7 Hz, 1H), 5.08 (d, *J* = 1.7 Hz, 1H), 3.98 (dd, *J* = 11.4, 4.5 Hz, 2H), 3.36 (td, *J* = 12.2, 2.0 Hz, 2H), 1.76 (s, 6H), 1.59 (dt, *J* = 11.8, 3.8 Hz, 1H), 1.49 (ddd, *J* = 12.7, 3.3, 1.3 Hz, 2H), 1.39 – 1.20 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 139.6, 131.1, 128.8, 121.2, 113.9, 67.8, 49.6, 42.4, 42.0, 35.3, 29.1.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}OBr$ 333.0849; found 333.0848.

(4'-Methyl-[1,1'-biphenyl]-4-yl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (9)



To a 10 mL reaction vial equipped with a stir bar was added **4a** (33.4 mg, 0.10 mmol, 1.0 equiv), 4-tolylboronic acid (27.2 mg, 0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), Na_2CO_3 (21.2 mg, 0.2 mmol, 2.0 equiv), and EtOH/H_2O (1 mL, 1:1). The reaction mixture was allowed to stir at 80 °C in an oil bath for 24 h. After this time, the reaction was quenched with sat. aq. $NaHCO_3$, and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired product **9** as a colorless solid (28.4 mg, 82% yield).

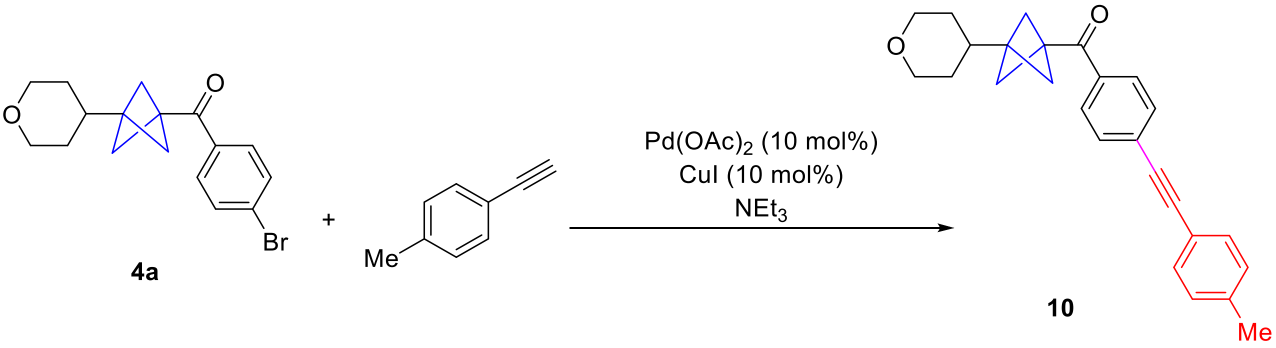
TLC R_f = 0.60 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 4.01 (dd, *J* = 11.3, 4.4 Hz, 2H), 3.39 (td, *J* = 12.1, 2.0 Hz, 2H), 2.41 (s, 3H), 2.13 (s, 6H), 1.67 (tt, *J* = 11.8, 3.8 Hz, 1H), 1.55 (ddd, *J* = 12.7, 3.3, 1.3 Hz, 2H), 1.34 (ddd, *J* = 25.4, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.5, 145.5, 138.2, 137.0, 135.1, 129.7, 129.5, 127.1, 126.8, 67.8, 51.1, 43.6, 43.6, 35.3, 28.9, 21.2.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{27}O_2$ 347.2006; found 347.2005.

(3-(Tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(*p*-tolylethynyl)phenyl)methanone (10)



To a 10 mL reaction vial equipped with a stir bar was added **4a** (33.4 mg, 0.10 mmol, 1.0 equiv), 4-ethynyltoluene (25.3 µL, 0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), CuI (1.0 mg, 0.01 mmol, 10 mol%), and NEt_3 (0.5 mL). The reaction mixture was allowed to stir at 50 °C in an oil bath for 24 h. After this time, the reaction was quenched with sat. aq. $NaHCO_3$, and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired product **10** as a colorless solid (24.8 mg, 67% yield).

TLC R_f = 0.60 (Hexane/EtOAc = 10:1, v/v).

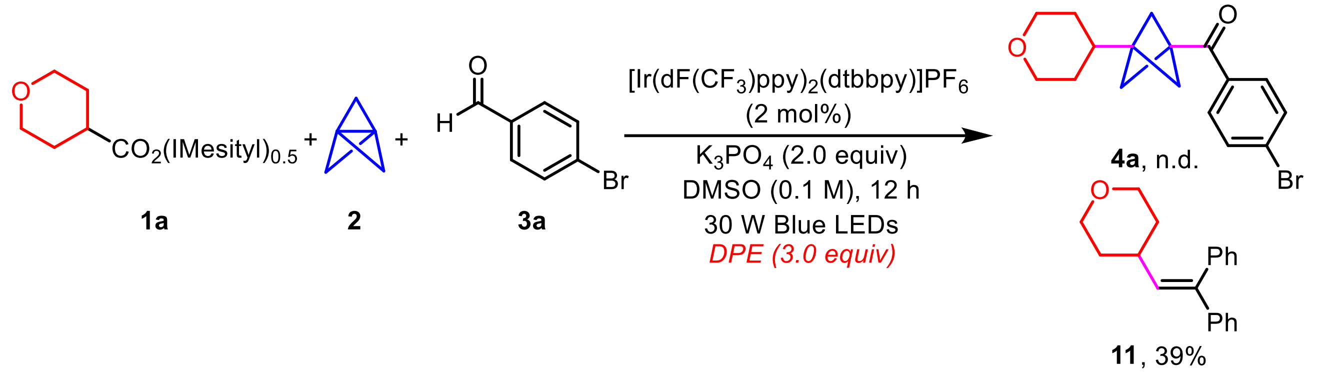
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.01 (dd, *J* = 11.2, 4.3 Hz, 2H), 3.38 (td, *J* = 12.1, 1.9 Hz, 2H), 2.38 (s, 3H), 2.11 (s, 6H), 1.66 (tt, *J* = 11.9, 3.8 Hz, 1H), 1.54 (dd, *J* = 13.0, 2.0 Hz, 2H), 1.33 (ddd, *J* = 25.4, 12.3, 4.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 139.1, 135.6, 131.7, 131.5, 129.2, 128.8, 128.2, 119.6, 93.0, 88.1, 67.7, 51.1, 43.7, 43.5, 35.3, 28.9, 21.6.

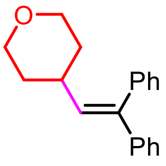
HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{27}O_2$ 371.2006; found 370.2004.

6. Mechanistic Studies

(A) Radical trapping experiment:



To a 10 mL reaction vial equipped with a stir bar was added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), 1,1-diphenylethylene (DPE, 108.0 mg, 0.60 mmol, 3.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Then, the reaction aliquot was taken out by a syringe and quenched with water, organic part taken in EtOAc and GC-MS chromatography was carried out. No results found that no BCP ketone product **4a** was formed and the DPE trapped alkyl radical product was observed. The solution was transferred to a separatory funnel and diluted with deionized H_2O (20 mL) and Et_2O (20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 X 10 mL). The combined organic layers were washed with deionized H_2O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the DPE trapped alkyl radical product **11** as a colorless solid (20.6 mg, 39% yield).



11

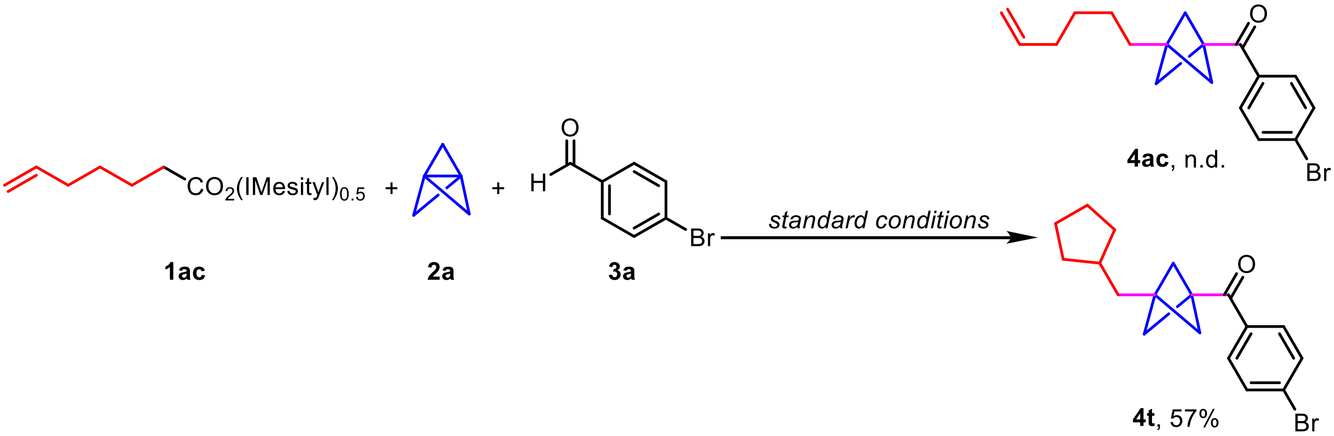
TLC R_f = 0.70 (Hexane/EtOAc = 15:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.17 (m, 3H), 7.15 (dd, *J* = 10.5, 4.6 Hz, 3H), 7.10 (d, *J* = 7.0 Hz, 2H), 5.82 (d, *J* = 9.8 Hz, 1H), 3.90 – 3.75 (m, 2H), 3.23 (td, *J* = 11.3, 3.3 Hz, 2H), 2.41 – 2.21 (m, 1H), 1.65 – 1.41 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 141.0, 140.2, 133.7, 129.6, 128.3, 128.1, 127.2, 127.1, 127.1, 67.4, 35.6, 32.9.

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}O$ 265.1587; found 265.1588.

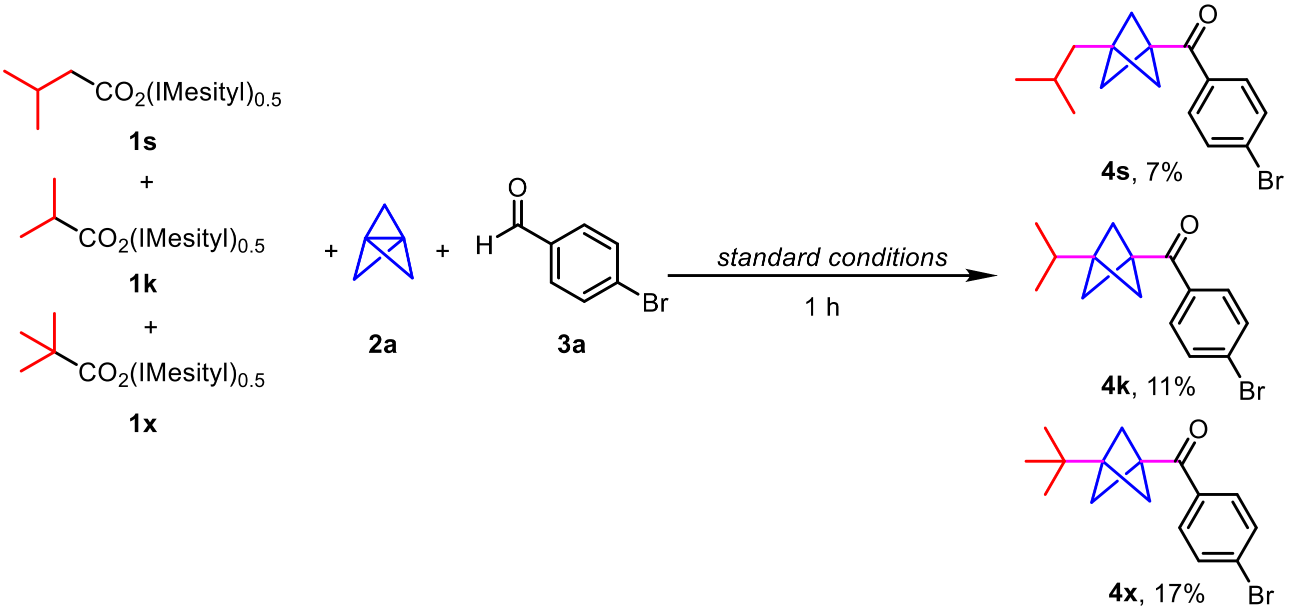
(B) Radical clock experiment:



To a 10 mL reaction vial equipped with a stir bar was added [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(hept-6-enoate) **1ac** (100.0 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Then, the reaction aliquot was taken out by a syringe and quenched with water, organic part taken in EtOAc and GC-MS chromatography was carried out.

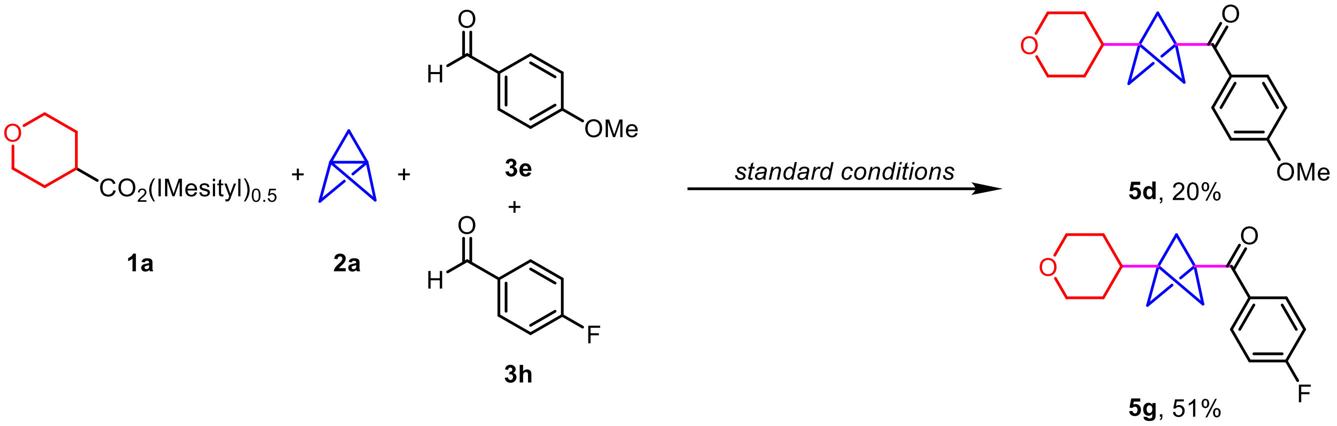
No results found that no BCP ketone product **4ac** was formed and the cyclized BCP ketone **4t** product was observed. The solution was transferred to a separatory funnel and diluted with deionized H_2O (20 mL) and Et_2O (20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 X 10 mL). The combined organic layers were washed with deionized H_2O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give **4t** as a colorless solid (37.8 mg, 57% yield).

(C) Primary vs secondary vs tertiary radical competition experiment:



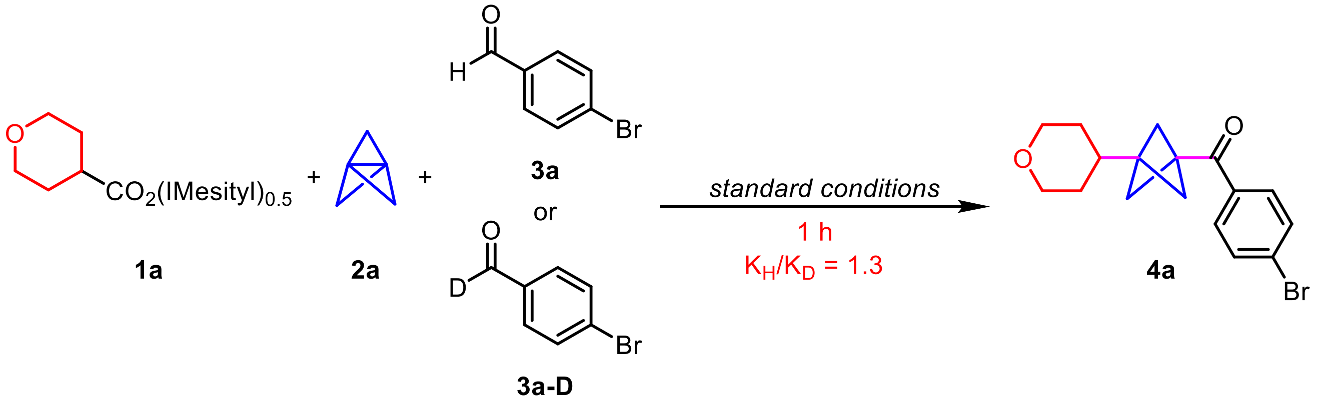
To a 10 mL reaction vial equipped with a stir bar was added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), mesityl-λ^3-iodanediyl bis(2-methylpropanoate) **1s** (89.6 mg, 0.2 mmol, 1.0 equiv), mesityl-λ^3-iodanediyl bis(3-methylbutanoate) **1k** (84.0 mg, 0.2 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(2,2-dimethylpropanoate) **1x** (89.6 mg, 0.2 mmol, 1.0 equiv)were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 1 hour. Then, the reaction aliquot was taken out by a syringe and quenched with water, organic part taken in EtOAc and GC-MS chromatography was carried out. The yields were determined using dodecane as standard.

(D) Electron-donating vs -withdrawing aldehydes competition experiment:



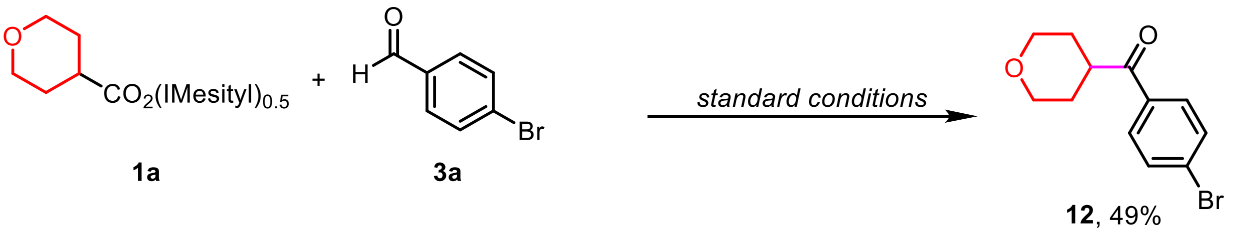
To a 10 mL reaction vial equipped with a stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), *p*-anisaldehyde **3e** (24.3 µL, 0.2 mmol, 1.0 equiv), 4-fluorobenzaldehyde **3h** (21.4 µL, 0.2 mmol, 1.0 equiv) and mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N$_2$ atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Then, the solution was transferred to a separatory funnel and diluted with deionized H$_2$O (20 mL) and Et$_2$O (20 mL). The layers were separated, and the aq layer was extracted with Et$_2$O (3 X 10 mL). The combined organic layers were washed with deionized H$_2$O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na$_2$SO$_4$), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO$_2$ column chromatography (gradient Hexane/EtOAc) to give **5d** (11.4 mg, 20% yield) and **5g** (27.9 mg, 51% yield).

(E) Intermolecular KIE experiment:



To two separate 10 mL reaction vials equipped with a stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** or **3a-D** (37.0 mg, 0.2 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N$_2$ atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture *via* a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 1 hour. Then, the solution was transferred to a separatory funnel and diluted with deionized H$_2$O (20 mL) and Et$_2$O (20 mL). The layers were separated, and the aq layer was extracted with Et$_2$O (3 X 10 mL). The combined organic layers were washed with deionized H$_2$O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na$_2$SO$_4$), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO$_2$ column chromatography (gradient Hexane/EtOAc) to give **4a** as a colorless solid (28.6 mg and 22.0 mg, 42% and 33% yields, respectively).

(F) Two-component coupling experiment:



To a 10 mL reaction vial equipped with a stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N$_2$ atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Then, the solution was transferred to a separatory funnel and diluted with deionized H$_2$O (20 mL) and Et$_2$O (20 mL). The layers were separated, and the aq layer was extracted with Et$_2$O (3 X 10 mL). The combined organic layers were washed with deionized H$_2$O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na$_2$SO$_4$), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO$_2$ column chromatography (gradient Hexane/EtOAc) to give **12** as a colorless solid (26.3 mg, 49% yield).

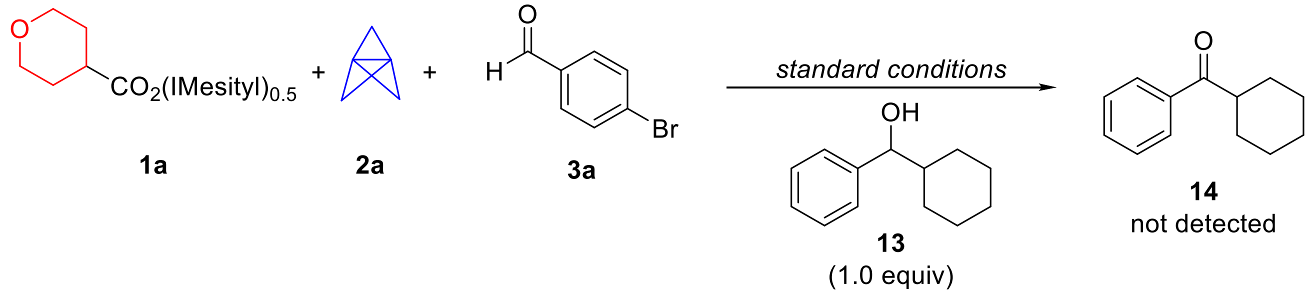
TLC R$_f$ = 0.50 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 4.05 (ddd, *J* = 11.5, 3.9, 2.5 Hz, 2H), 3.55 (td, *J* = 11.6, 2.3 Hz, 2H), 3.44 (tt, *J* = 11.2, 3.8 Hz, 1H), 1.87 (dtd, *J* = 13.9, 11.5, 4.3 Hz, 2H), 1.81 – 1.67 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 200.8, 134.5, 132.1, 129.8, 128.3, 67.2, 42.6, 29.0.

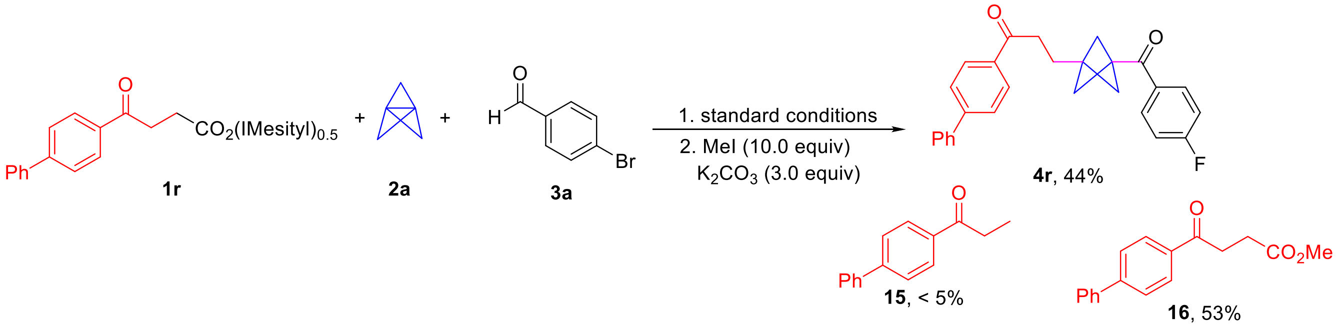
This matched literature characterization.[5]

(G) Oxidation of alcohol:



To a 10 mL reaction vial equipped with a stir bar was added [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (4.5 mg, 4 µmol, 2 mol%), K$_3$PO$_4$ (84.8 mg, 0.40 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), cyclohexyl(phenyl)methanol **13** (19.0 mg, 0.10 mmol, 1.0 equiv) and mesityl-λ^3-iodanediyl bis(tetrahydro-2*H*-pyran-4-carboxylate) **1a** (100.8 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture via a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Then, the reaction aliquot was taken out by a syringe and quenched with water, organic part taken in EtOAc and GC-MS chromatography was carried out. And ketone product **14** was not observed.

(H) Isolation of byproducts:



To a 10 mL reaction vial equipped with a stir bar was added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (4.5 mg, 4 µmol, 2 mol%), K_3PO_4 (84.8 mg, 0.40 mmol, 2.0 equiv), 4-bromobenzaldehyde **3a** (37.0 mg, 0.2 mmol, 1.0 equiv), and mesityl-λ^3-iodanediyl bis(4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate) **1r** (150.4 mg, 0.2 mmol, 1.0 equiv) were added. The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. The flask was then charged with DMSO (2 mL, 0.1 M) via a syringe. Next, a solution of [1.1.1]propellane in diethyl ether solution (0.6 M, 0.67 mL, 0.40 mmol, 2.0 equiv) was quickly added to the reaction mixture via a syringe. The reaction was stirred and irradiated using 30 W blue LED lamps for 12 hours. Then, the solution was added K_2CO_3 (41.4 mg, 0.30 mmol, 3.0 equiv) and MeI (62.3 µL, 1.0 mmol, 10.0 equiv) and stirred at room temperature for another 3 hours. After the reaction time, the solution was transferred to a separatory funnel and diluted with deionized H_2O (20 mL) and Et_2O (20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 X 10 mL). The combined organic layers were washed with deionized H_2O (2 X 10 mL) followed by brine (10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation.

Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give **16** as a colorless solid (14.2 mg, 53% yield).

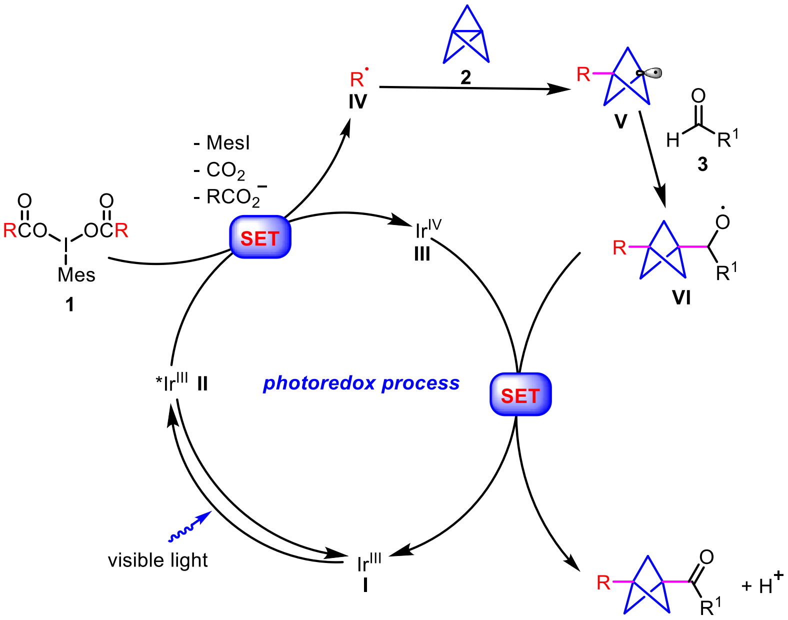
TLC R_f = 0.50 (Hexane/EtOAc = 8:1, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 3.72 (s, 3H), 3.36 (t, *J* = 6.6 Hz, 2H), 2.80 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 173.4, 145.9, 139.9, 135.2, 129.0, 128.7, 128.3, 127.3 51.9, 33.4, 28.1

This matched literature characterization.[6]

7. Proposed Mechanism

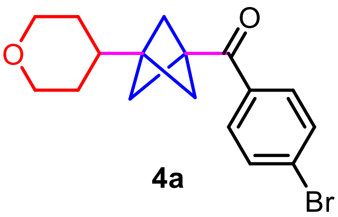


Scheme S2. Proposed mechanism

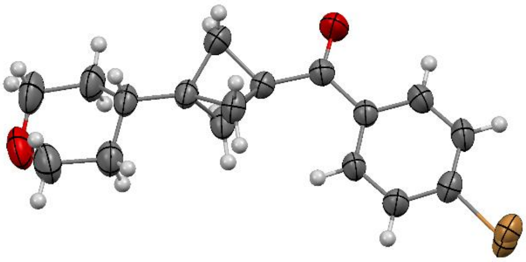
Based on the present results and previous reports,[7] a plausible reaction mechanism for the photoredox-mediated radical multicomponent alkylacylation of propellane is depicted in Scheme S2 but further mechanistic studies are need to elucidate the viability of mechanism in this transformation. Initially, under light irradiation, the photocatalyst **I** is excited, leading to the formation of the *Ir(III) complex **II**. The hypervalent iodide(III) carboxylate **1** reductively quenches the excited photocatalyst *Ir(III) **II**, resulting in the generation of an alkyl radical intermediate and Ir(IV) **III**. For the alkyl radical **IV**, it exhibits slower reactivity towards radical addition to aldehydes compared to its reaction with [1.1.1]propellane. Consequently, the alkyl radical **IV** preferentially undergoes radical addition to [1.1.1]propellane, leading to the formation of BCP radical **V**. The BCP radical **V** can then reacted with aldehyde, resulting in the formation of the alkoxyl radical **VI**. Finally, the alkoxyl radical **VI** is oxidized by the photocatalyst **III** ($E_{1/2}$(Ir^{IV}/Ir^{III}) = + 1.69 V versus SCE in acetonitrile), leading to the formation of BCP ketones and completing the photocatalytic cycle.

8. X-ray Single Crystal Data for Compound 4a

Single crystals of $C_{17}H_{19}O_2Br$ **[4a]**. A suitable crystal was selected and **[4a]** on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 298.50(13) K during data collection.



4a



2227374 (4a)

Table 1 Crystal data and structure refinement for 4a

Identification code	**4a**
Empirical formula	$C_{17}H_{19}BrO_2$
Formula weight	335.23
Temperature/K	298.50(13)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.24710(10)
b/Å	6.54100(10)
c/Å	20.9312(3)
α /°	90
β /°	96.2190(10)
γ /°	90
Volume/Å^3	1530.79(3)
Z	4
ρ calcg/cm^3	1.455
μ /mm^{-1}	3.645
F(000)	688.0
Crystal size/mm^3	0.18 × 0.16 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.908 to 153.992
Index ranges	$-14 \leqslant h \leqslant 14, -8 \leqslant k \leqslant 3, -25 \leqslant l \leqslant 26$
Reflections collected	10079
Independent reflections	3042 [R_{int} = 0.0218, R_{sigma} = 0.0200]

Data/restraints/parameters	3042/12/192
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2 σ (I)]	R1 = 0.0256, wR_2 = 0.0702
Final R indexes [all data]	R1 = 0.0283, wR_2 = 0.0720
Largest diff. peak/hole / e Å^{-3}	0.20/-0.17

9. References

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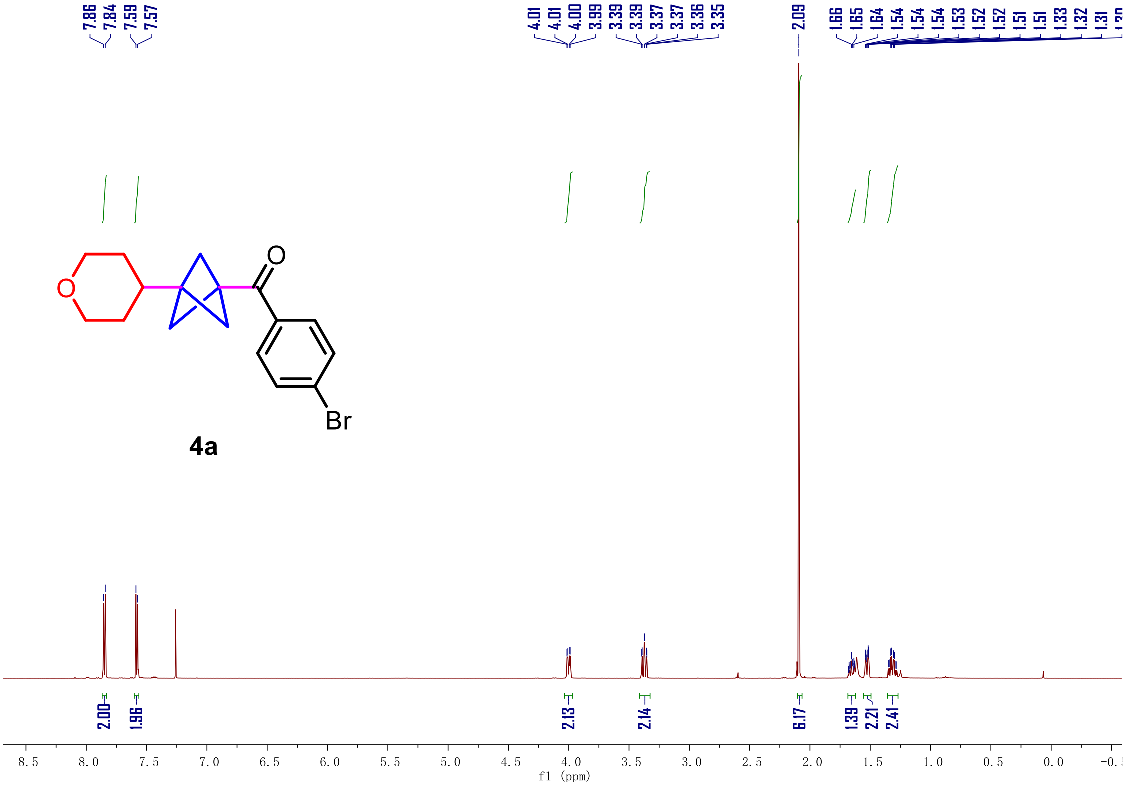
10. NMR Spectra

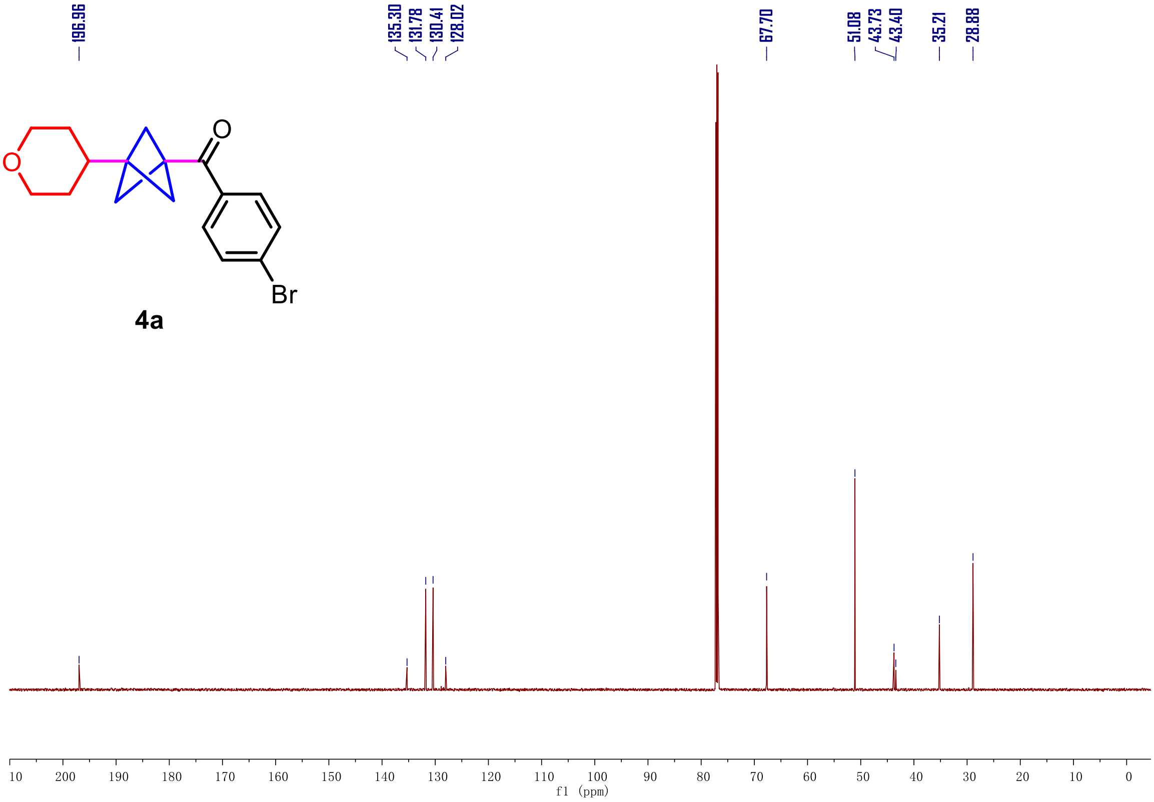
^{1}H NMR spectrum of (4-bromophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4a**)

600 MHz, $CDCl_3$, 23 ℃



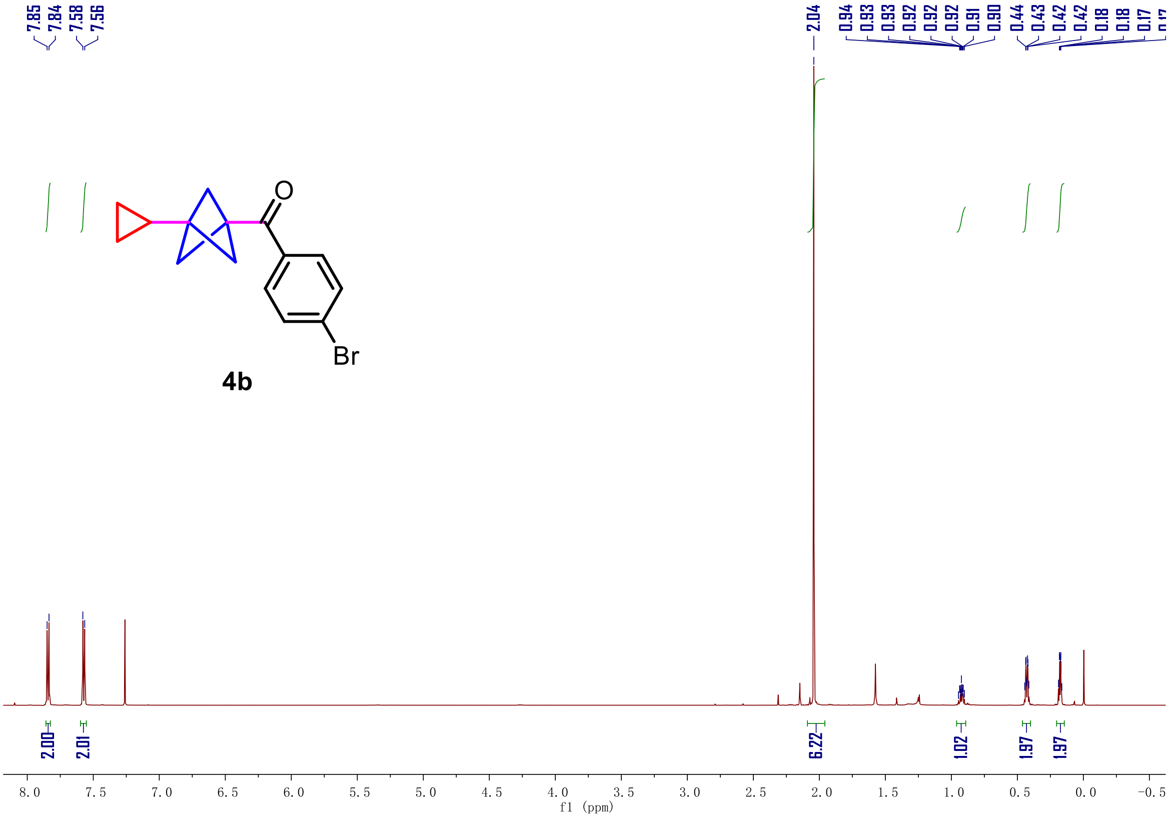
^{13}C NMR spectrum of (4-bromophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4a**)

151 MHz, $CDCl_3$, 23 ℃



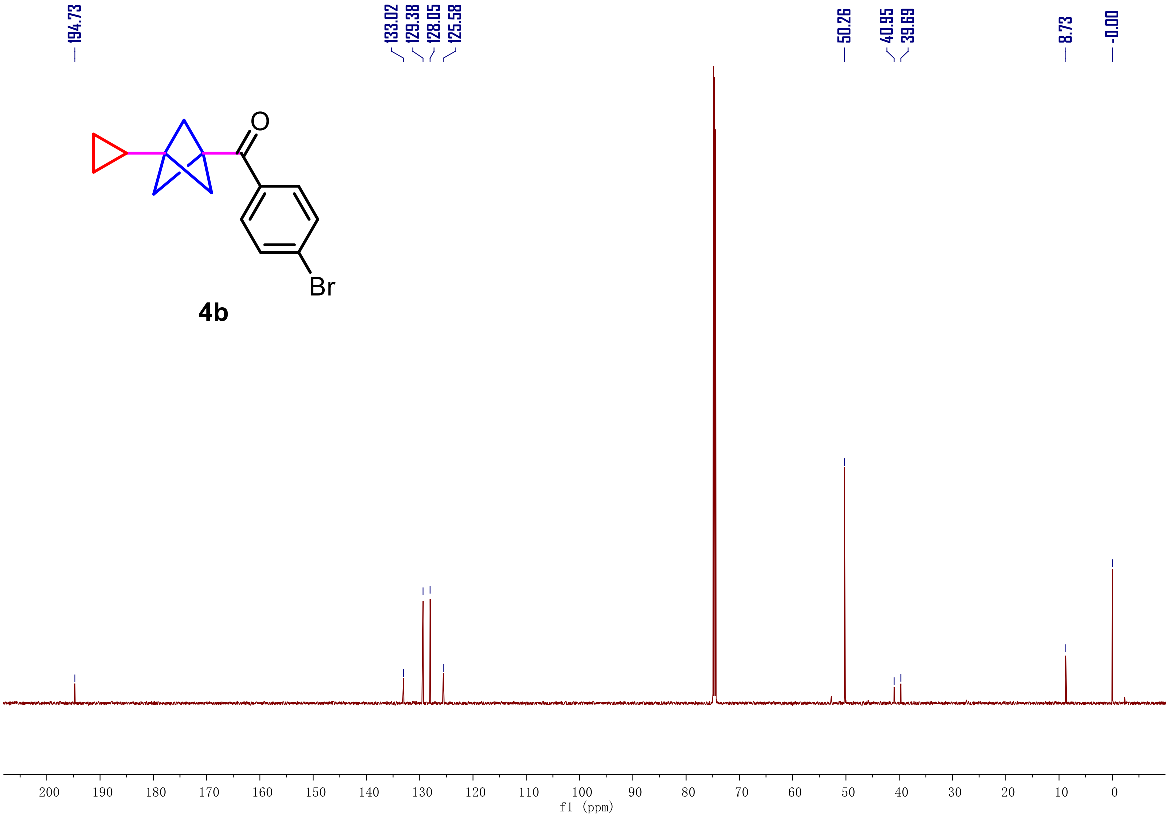
^{1}H NMR spectrum of (4-bromophenyl)(3-cyclopropylbicyclo[1.1.1]pentan-1-yl)methanone (**4b**)

600 MHz, $CDCl_3$, 23 ℃



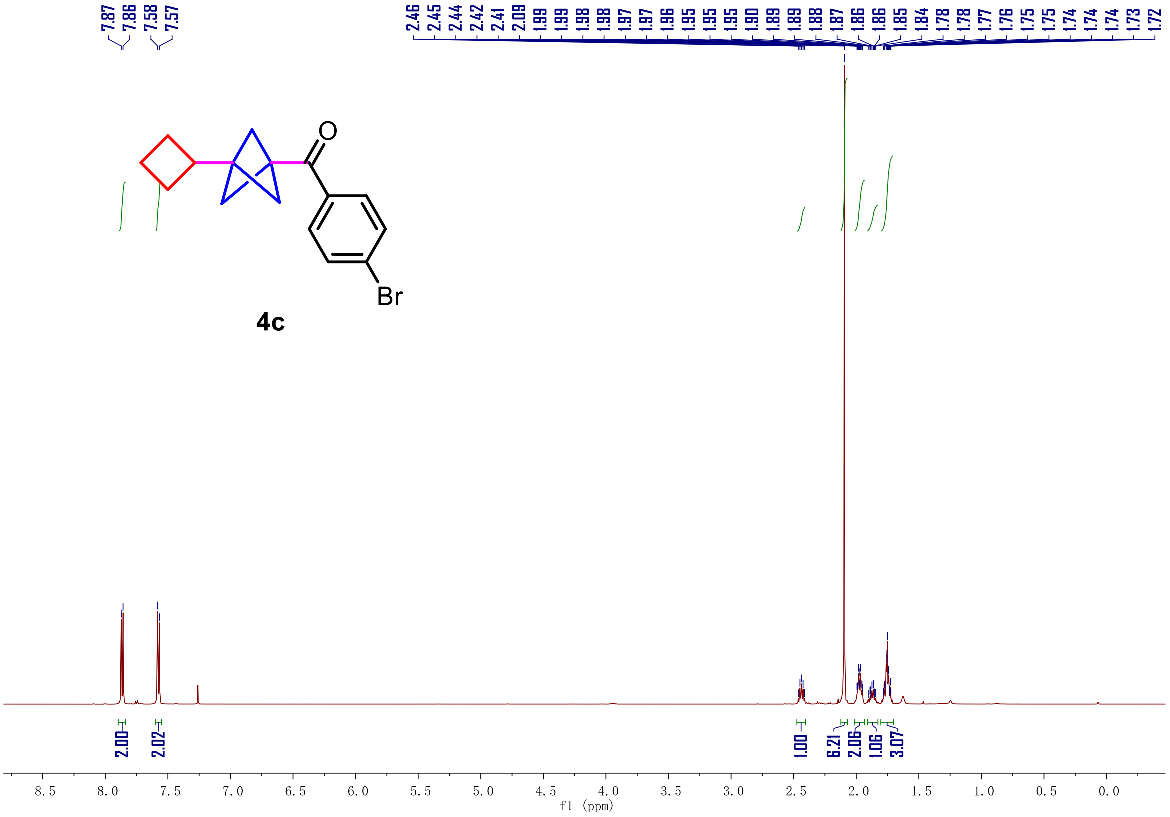
^{13}C NMR spectrum of (4-bromophenyl)(3-cyclopropylbicyclo[1.1.1]pentan-1-yl)methanone (**4b**)

151 MHz, $CDCl_3$, 23 ℃



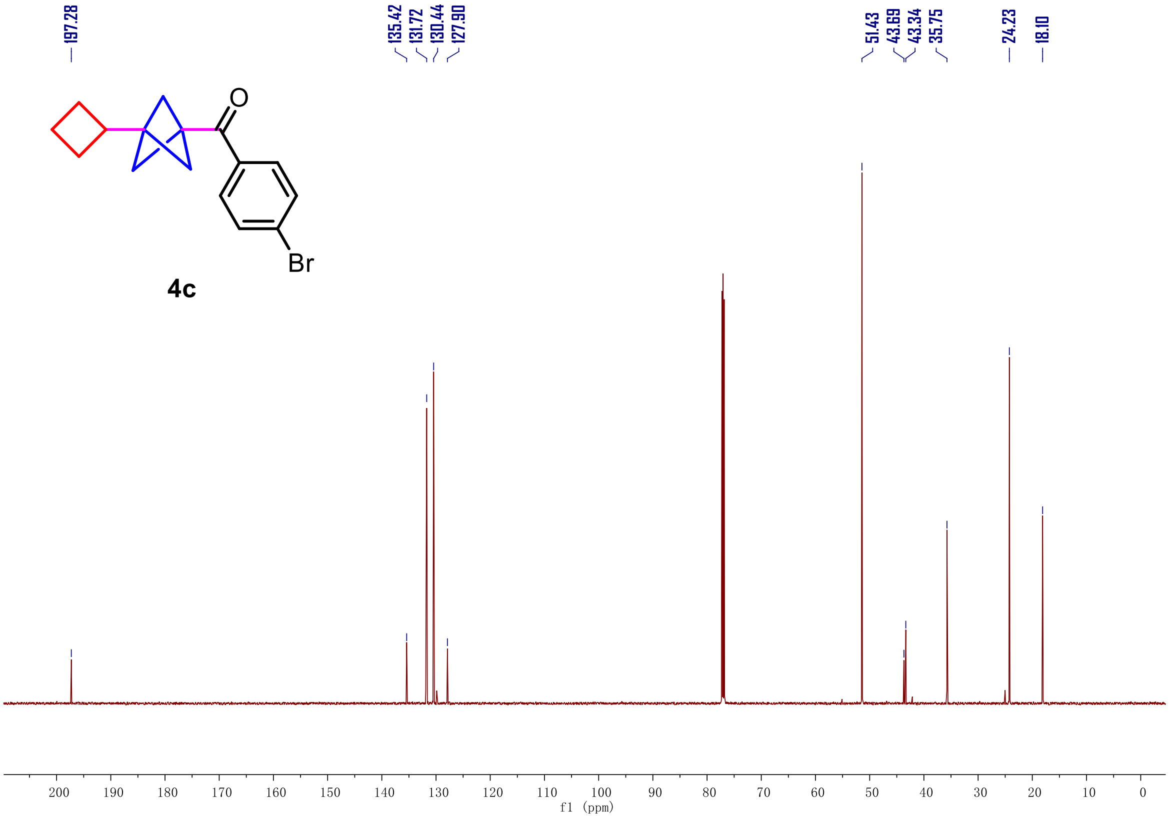
^{1}H NMR spectrum of (4-bromophenyl)(3-cyclobutylbicyclo[1.1.1]pentan-1-yl)methanone (**4c**)

600 MHz, CDCl$_3$, 23 ℃



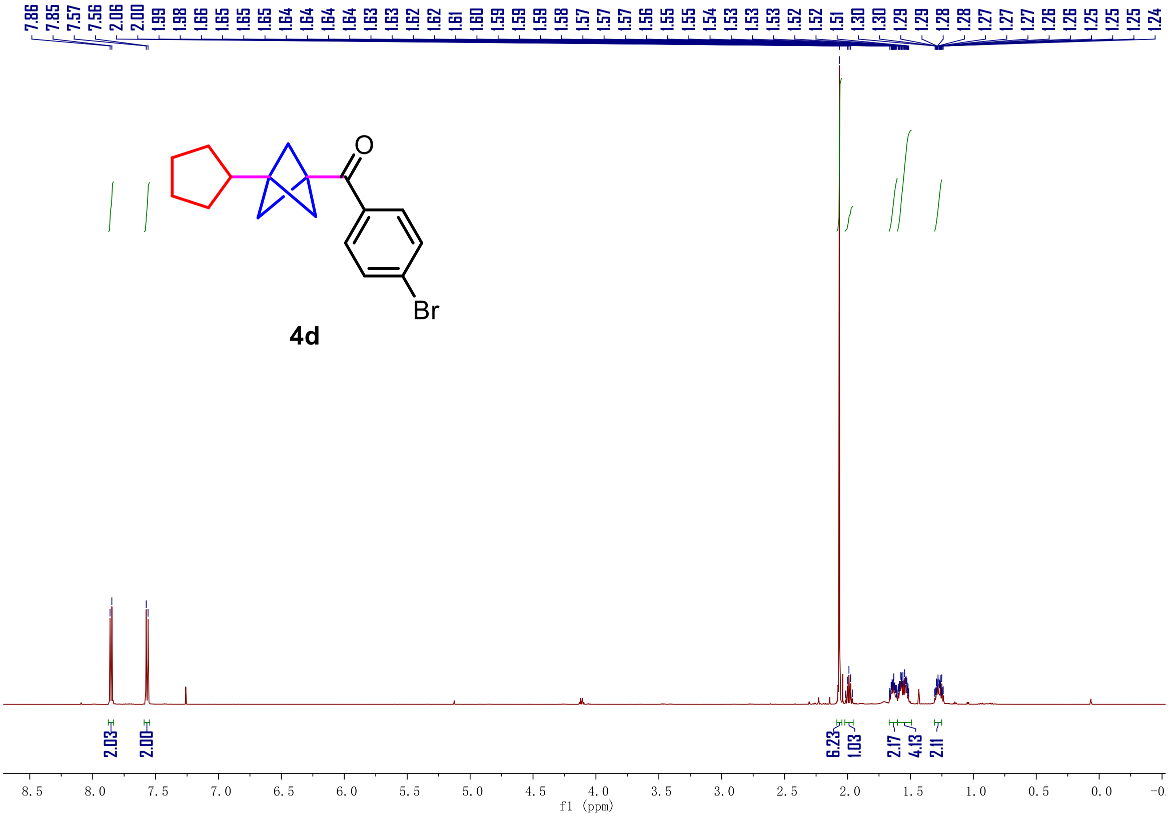
^{13}C NMR spectrum of (4-bromophenyl)(3-cyclobutylbicyclo[1.1.1]pentan-1-yl)methanone (**4c**)

151 MHz, CDCl$_3$, 23 ℃



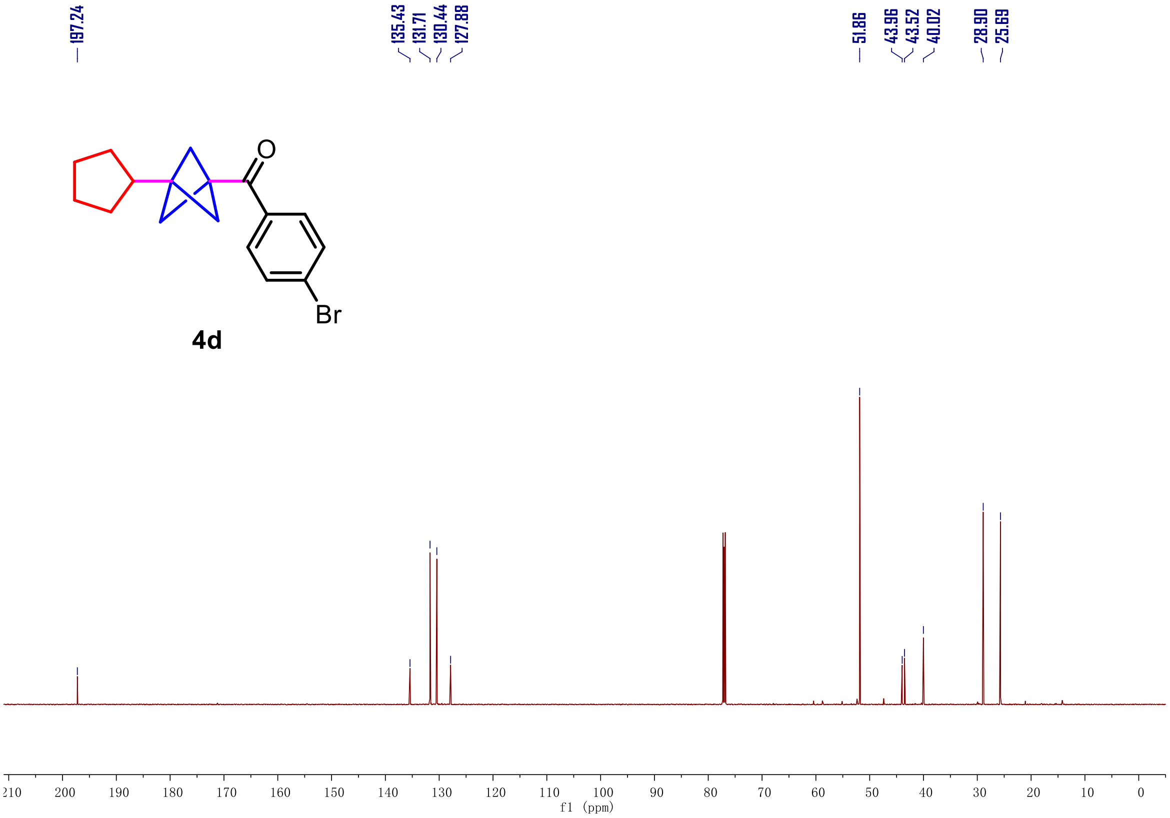
^{1}H NMR spectrum of (4-bromophenyl)(3-cyclopentylbicyclo[1.1.1]pentan-1-yl)methanone (**4d**)

600 MHz, $CDCl_3$, 23 ℃



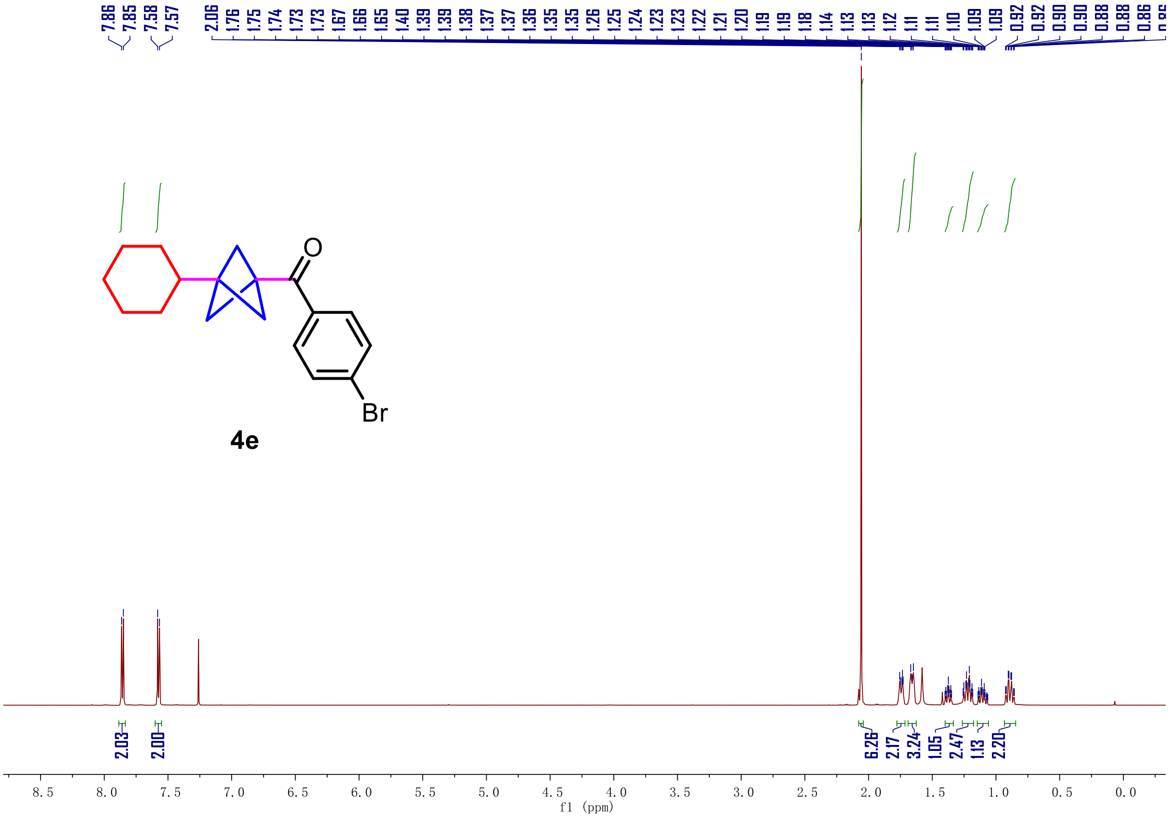
^{13}C NMR spectrum of (4-bromophenyl)(3-cyclopentylbicyclo[1.1.1]pentan-1-yl)methanone (**4d**)

151 MHz, $CDCl_3$, 23 ℃



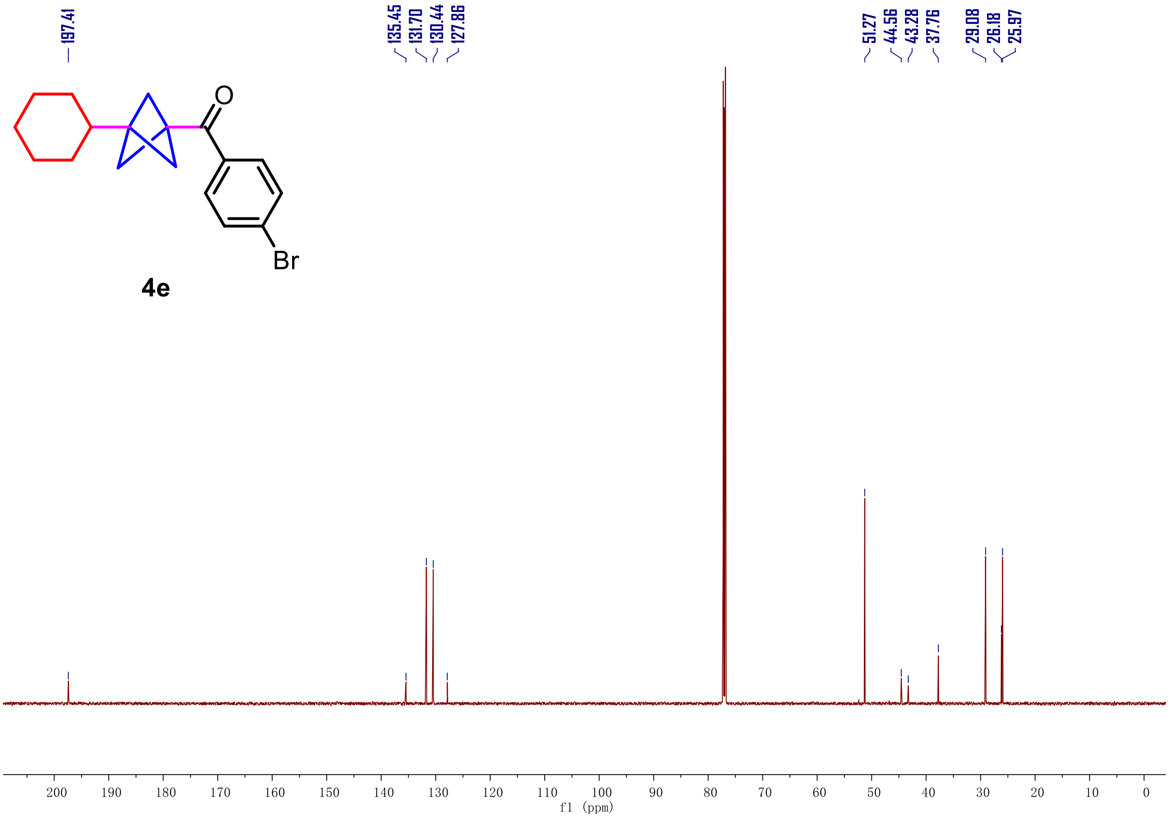
^{1}H NMR spectrum of (4-bromophenyl)(3-cyclohexylbicyclo[1.1.1]pentan-1-yl)methanone (**4e**)

600 MHz, $CDCl_3$, 23 ℃



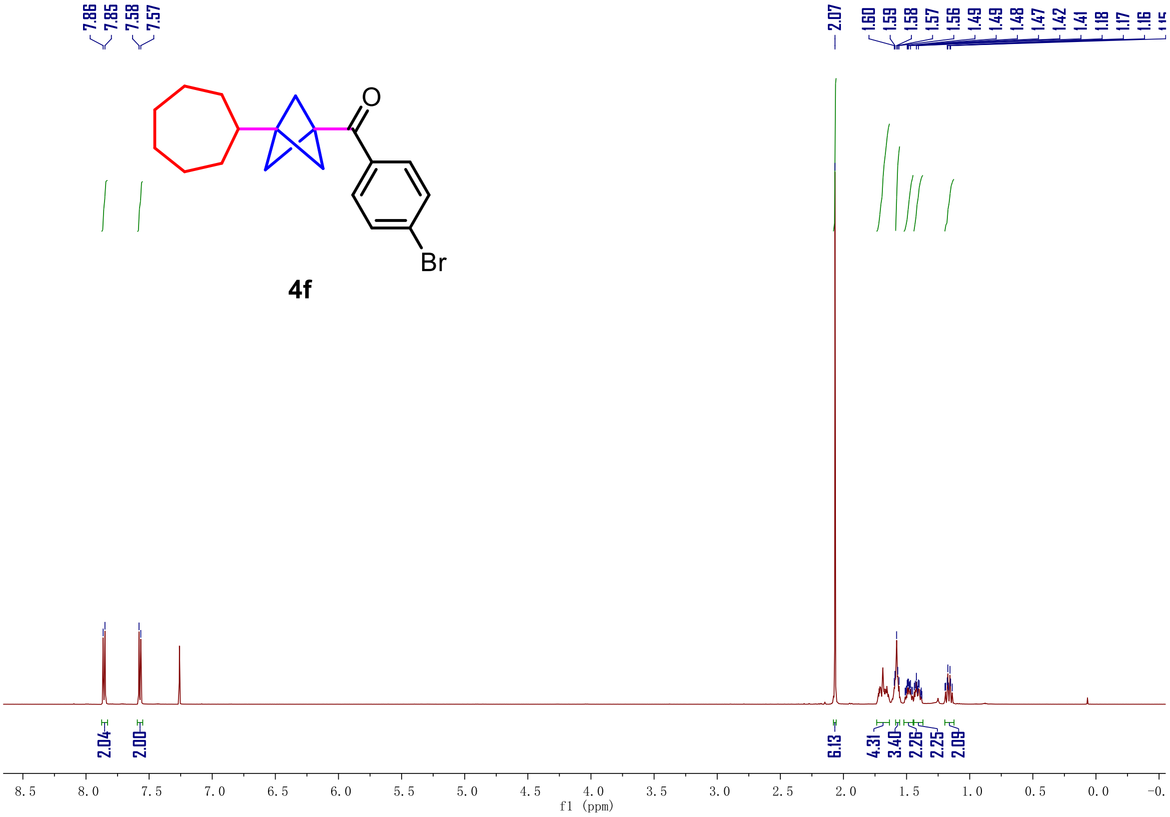
^{13}C NMR spectrum of (4-bromophenyl)(3-cyclohexylbicyclo[1.1.1]pentan-1-yl)methanone (**4e**)

151 MHz, $CDCl_3$, 23 ℃



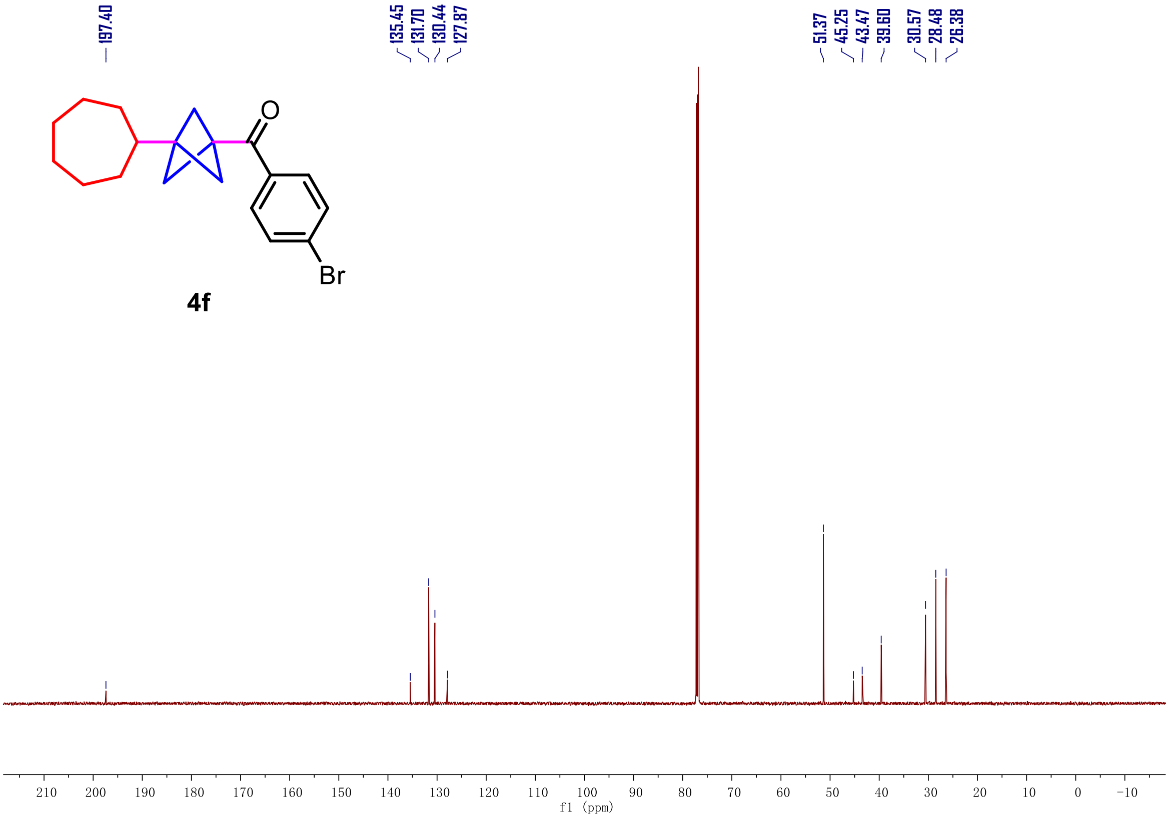
^{1}H NMR spectrum of (4-bromophenyl)(3-cycloheptylbicyclo[1.1.1]pentan-1-yl)methanone (**4f**)

600 MHz, CDCl$_3$, 23 ℃



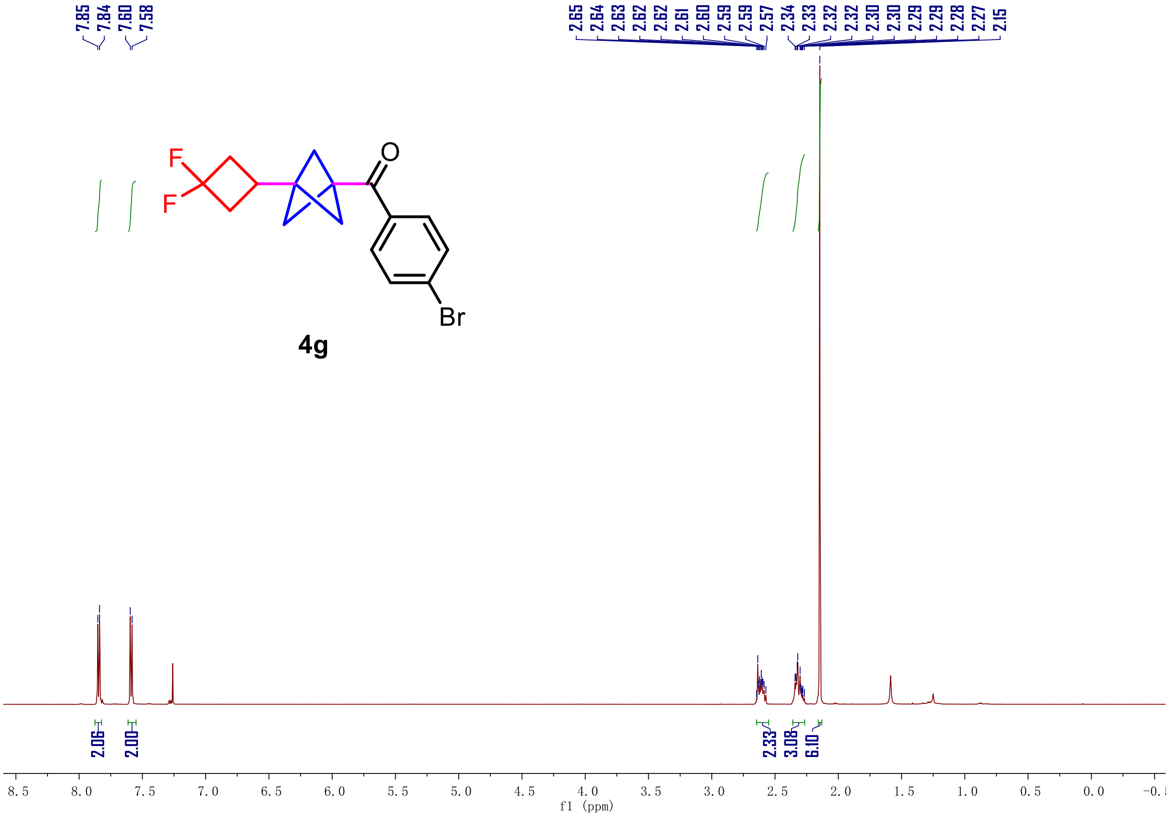
^{13}C NMR spectrum of (4-bromophenyl)(3-cycloheptylbicyclo[1.1.1]pentan-1-yl)methanone (**4f**)

151 MHz, CDCl$_3$, 23 ℃



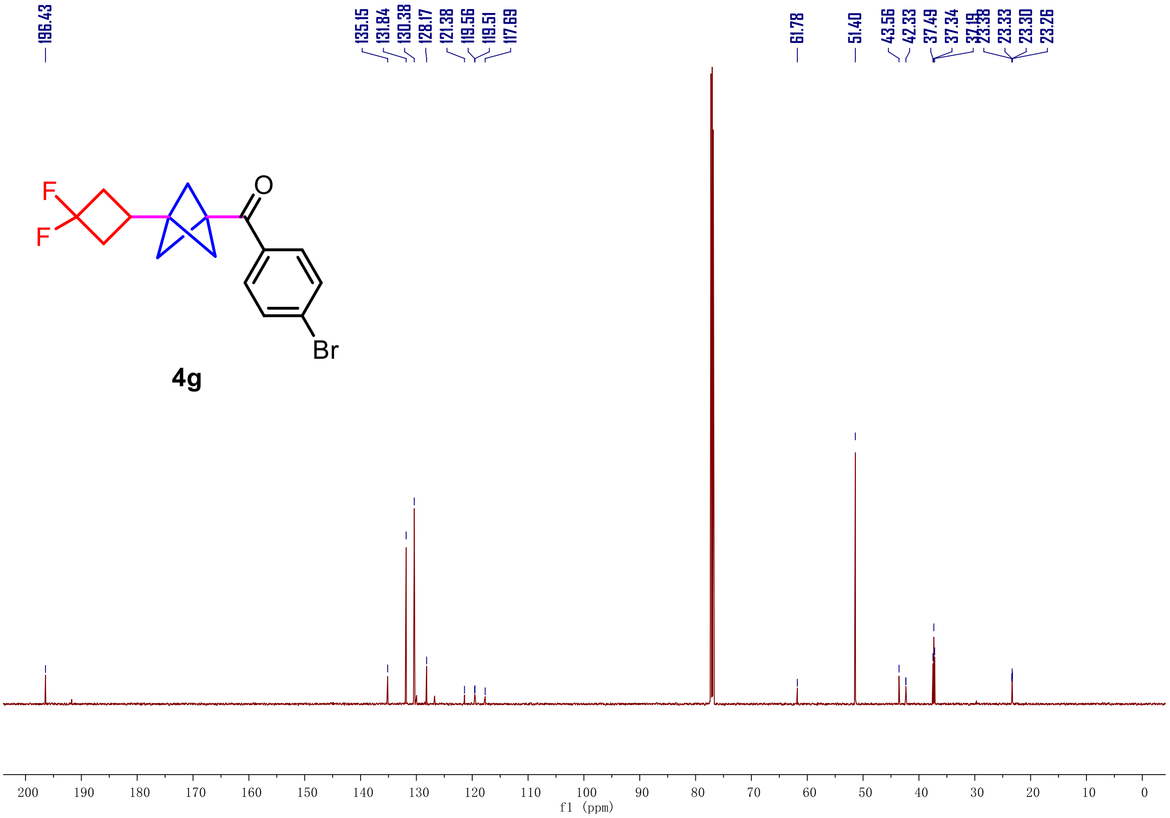
^{1}H NMR spectrum of (4-bromophenyl)(3-(3,3-difluorocyclobutyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4g**)

600 MHz, $CDCl_3$, 23 ℃



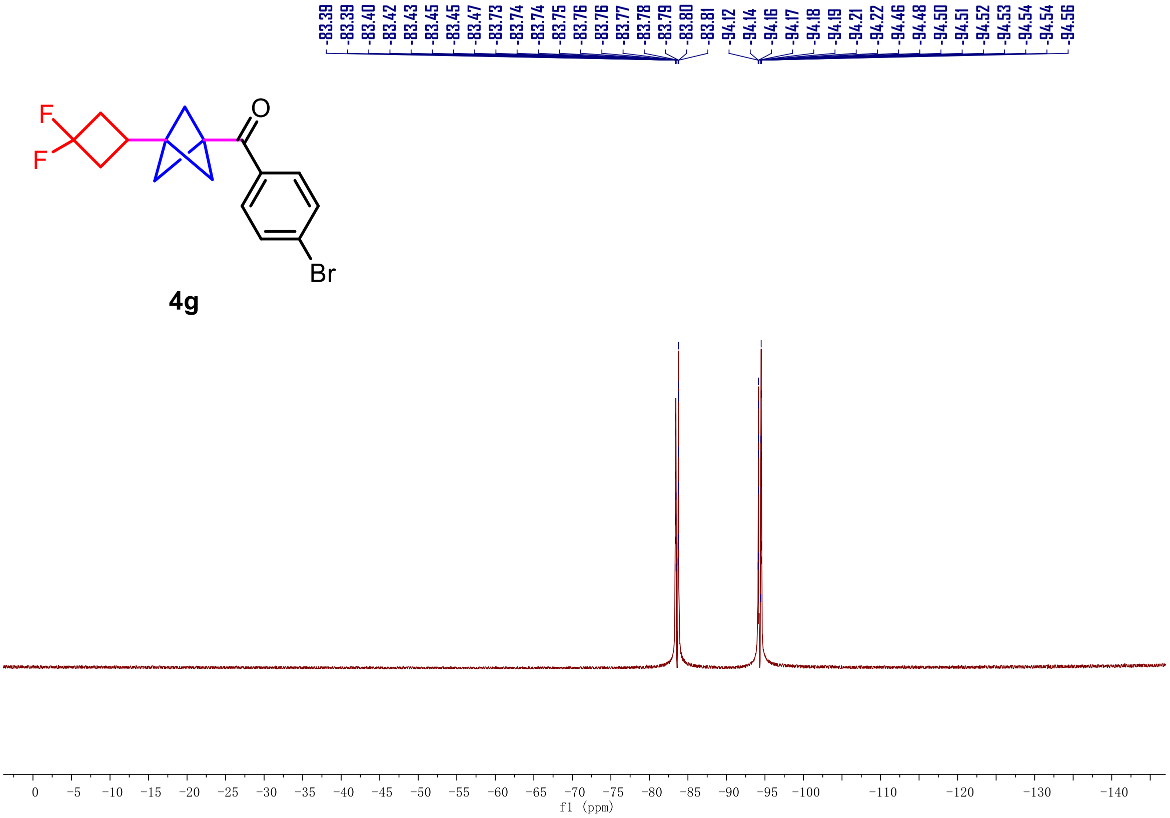
^{13}C NMR spectrum of (4-bromophenyl)(3-(3,3-difluorocyclobutyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4g**)

151 MHz, $CDCl_3$, 23 ℃



^{19}F NMR spectrum of (4-bromophenyl)(3-(3,3-difluorocyclobutyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4g**)

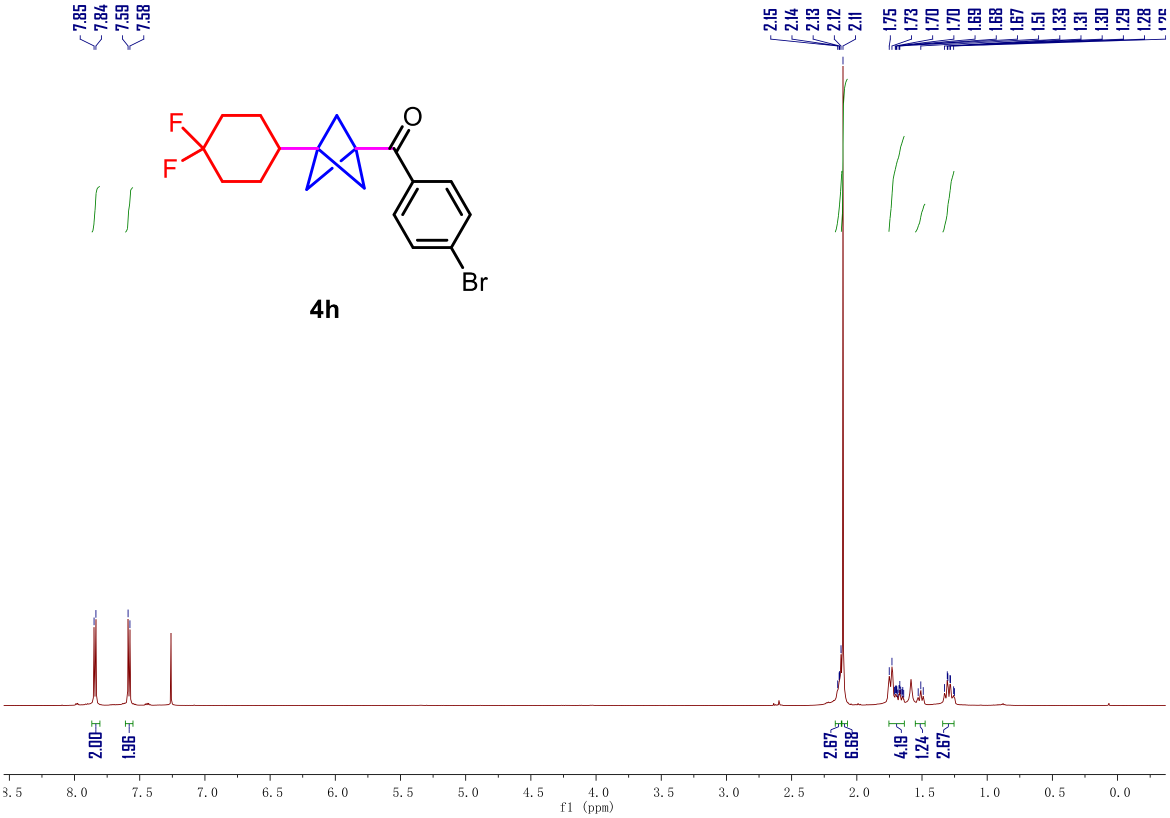
565 MHz, $CDCl_3$, 23 ℃



4g

^{1}H NMR spectrum of (4-bromophenyl)(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4h**)

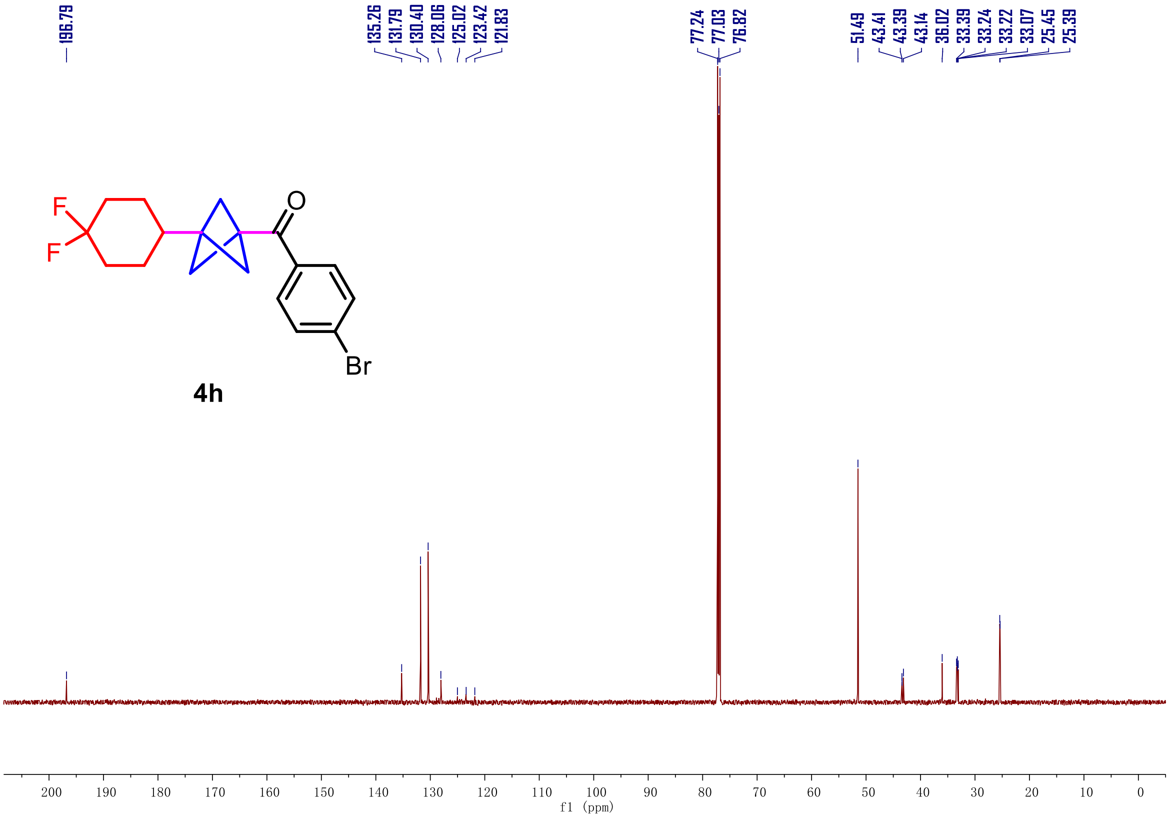
600 MHz, $CDCl_3$, 23 ℃



4h

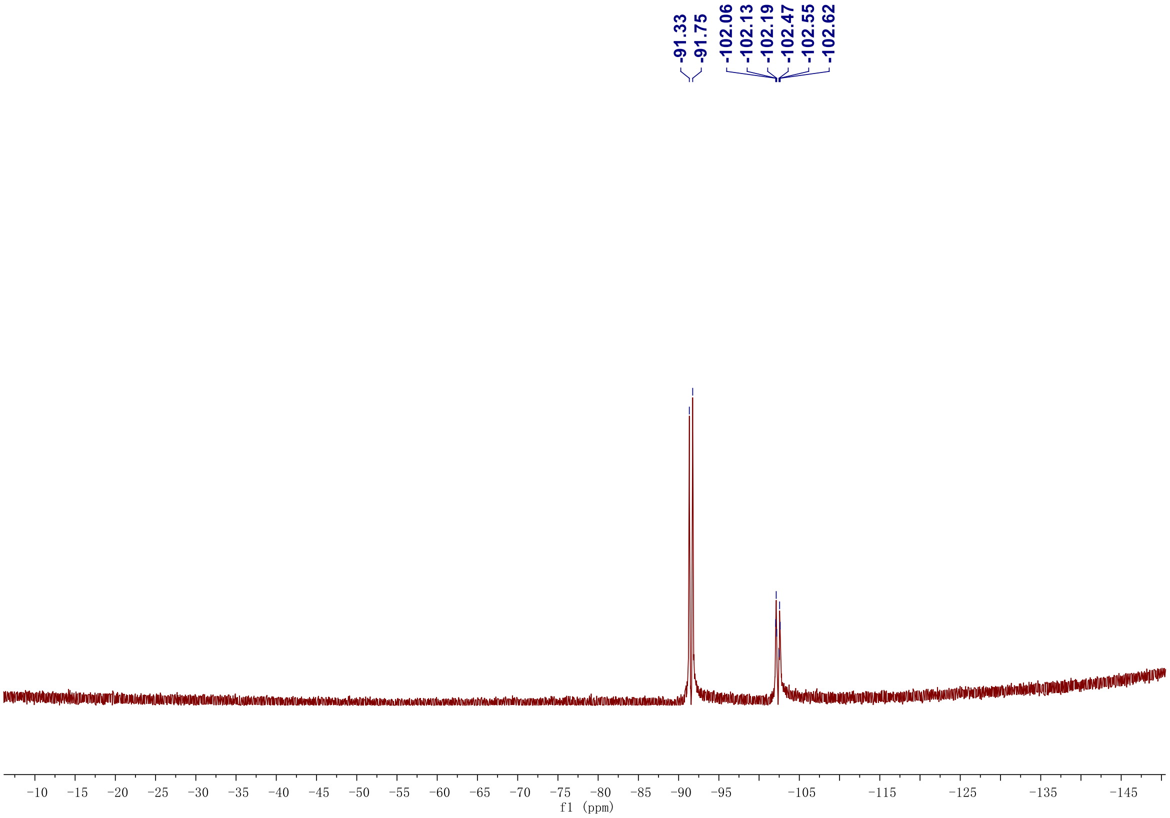
^{13}C NMR spectrum of (4-bromophenyl)(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4h**)

151 MHz, $CDCl_3$, 23 ℃



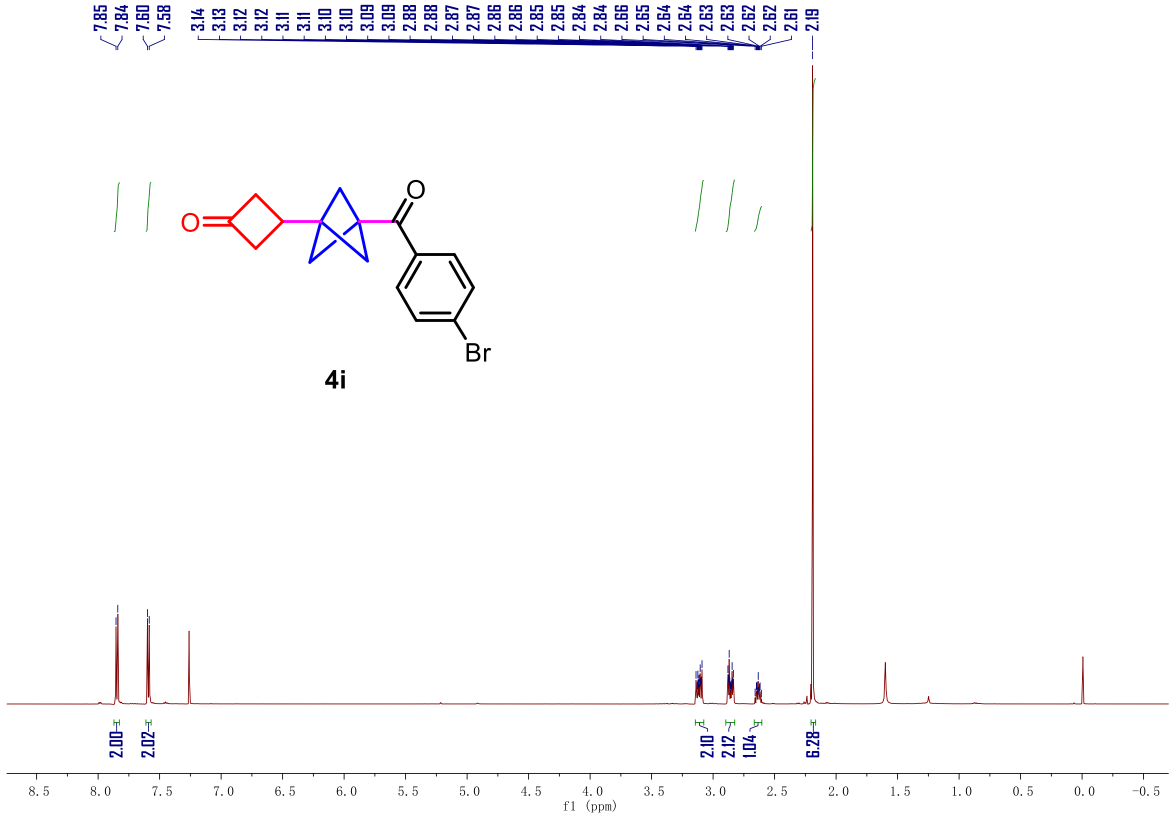
^{19}F NMR spectrum of (4-bromophenyl)(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4h**)

565 MHz, $CDCl_3$, 23 ℃



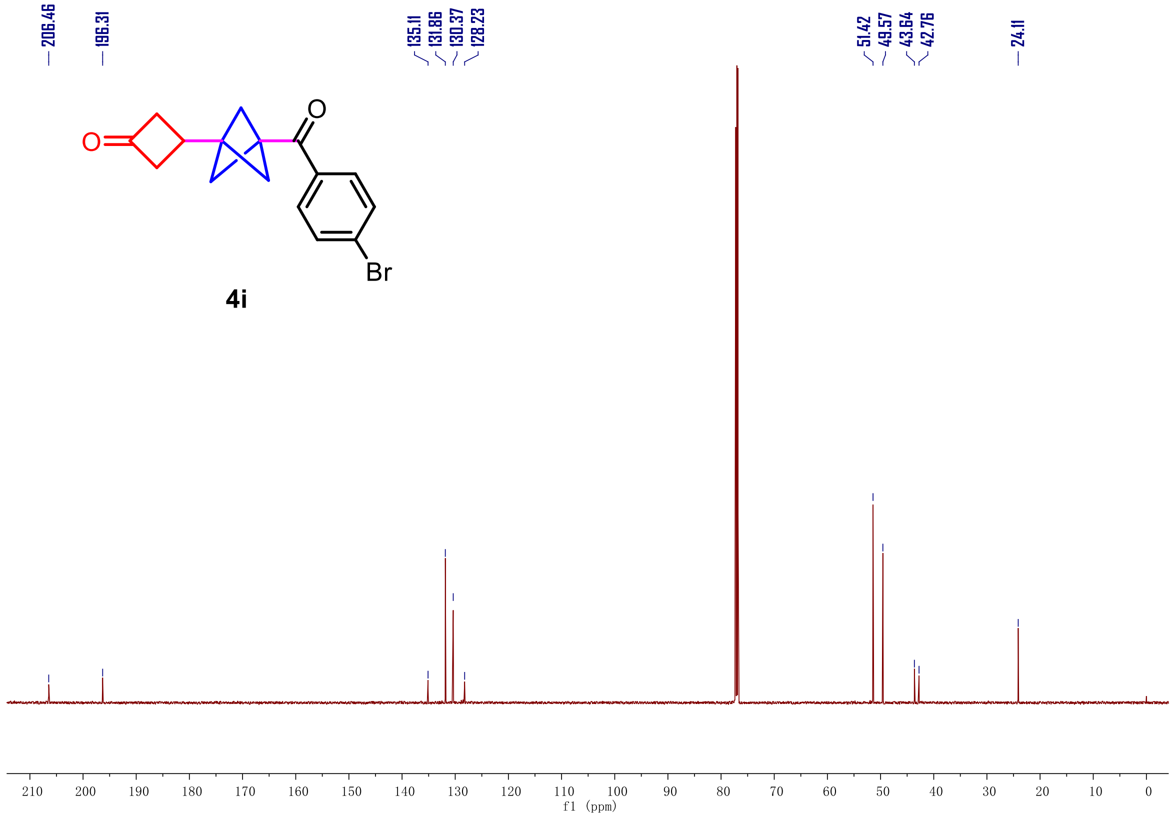
^{1}H NMR spectrum of 3-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)cyclobutan-1-one (**4i**)

600 MHz, $CDCl_3$, 23 ℃



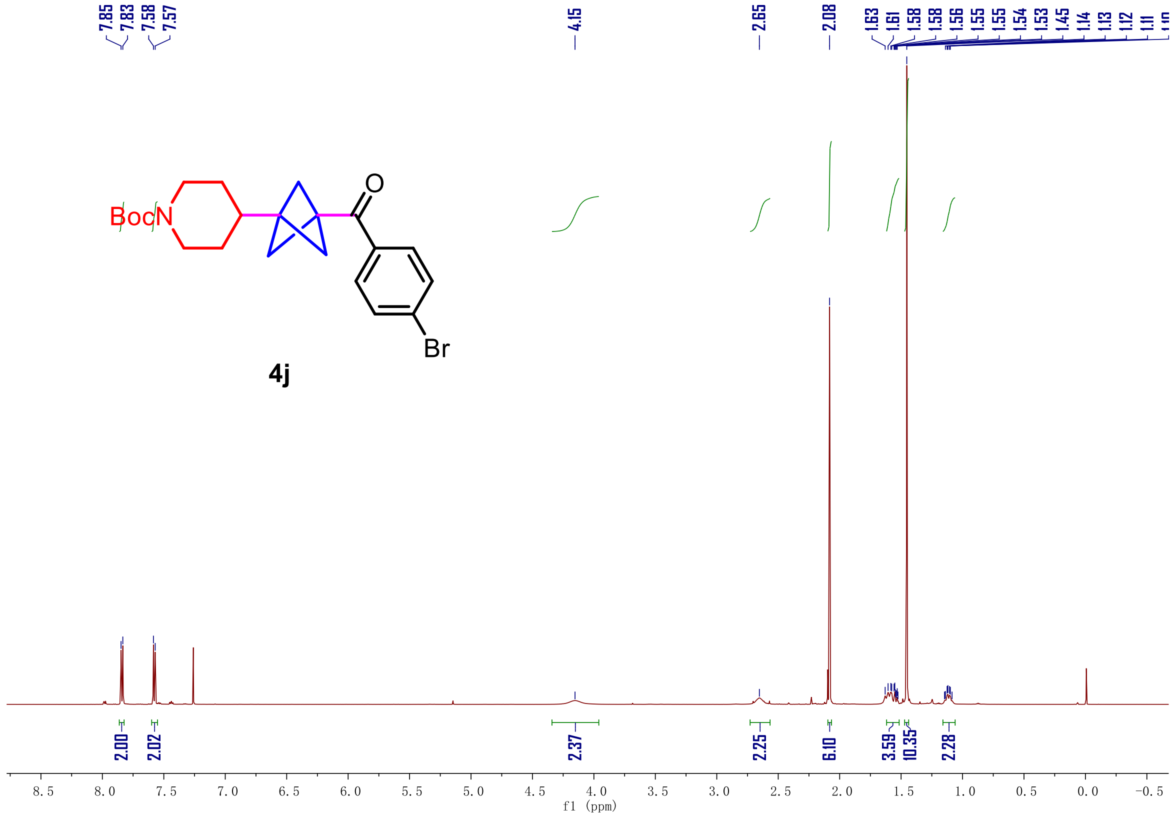
^{13}C NMR spectrum of 3-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)cyclobutan-1-one (**4i**)

151 MHz, $CDCl_3$, 23 ℃



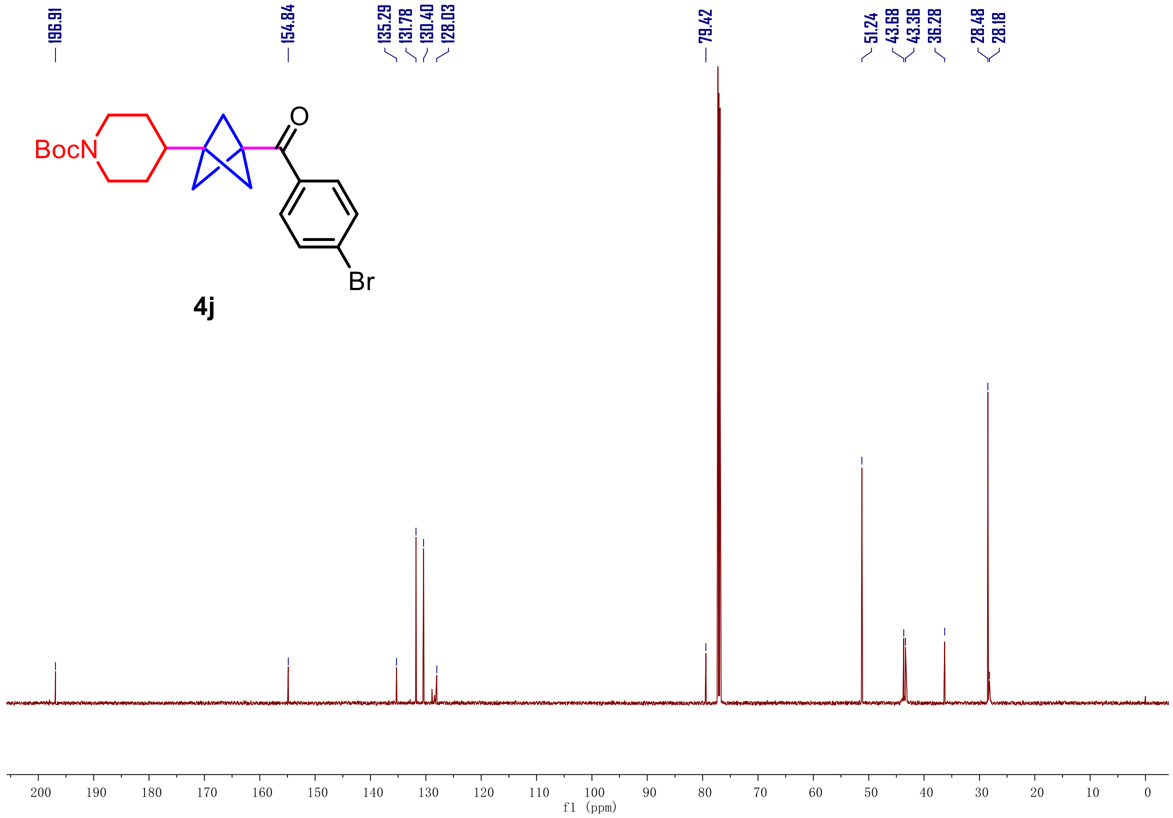
^{1}H NMR spectrum of *tert*-butyl 4-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (**4j**)

600 MHz, $CDCl_3$, 23 ℃



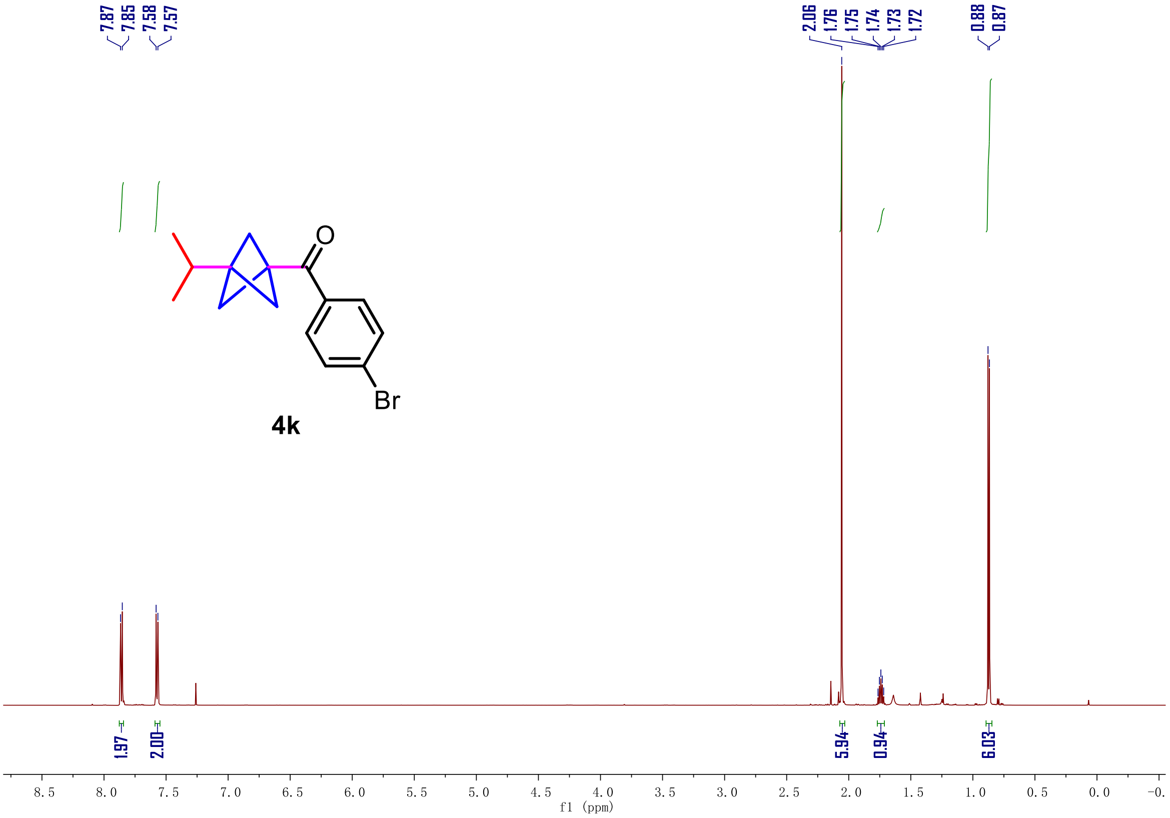
^{13}C NMR spectrum of *tert*-butyl 4-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (**4j**)

151 MHz, $CDCl_3$, 23 ℃



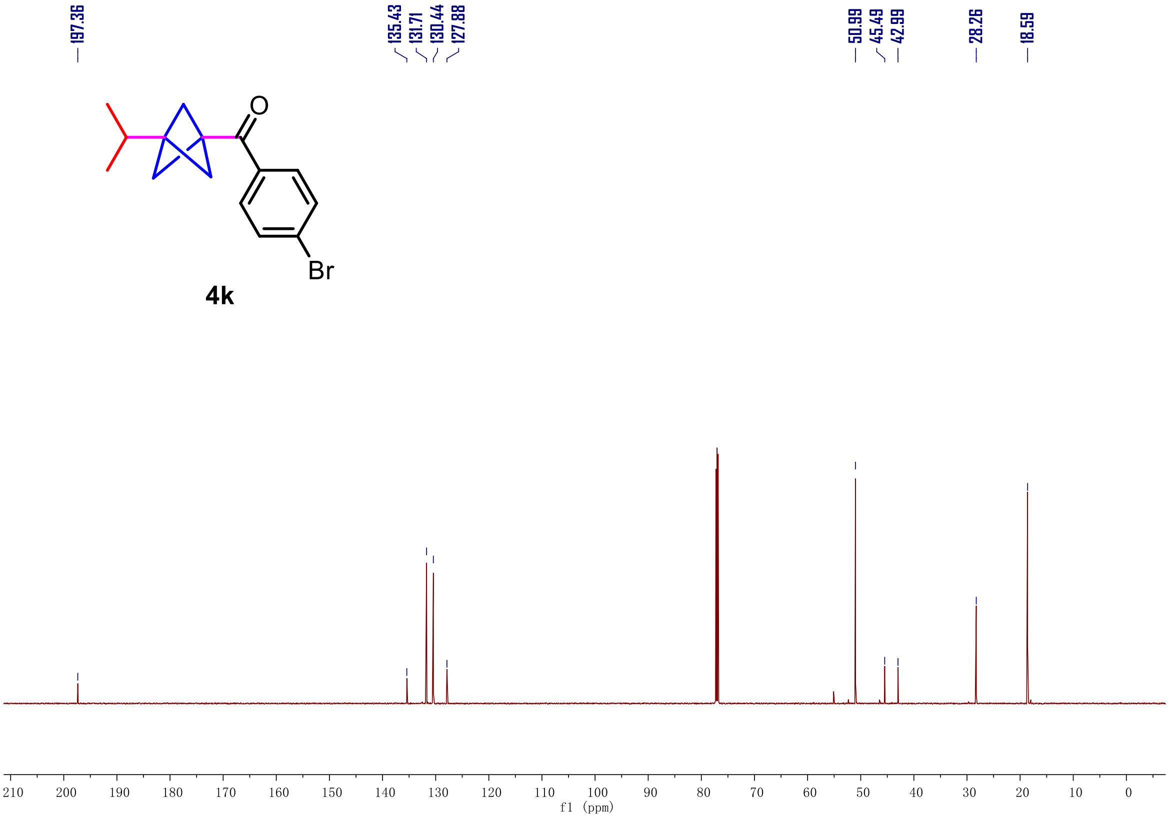
^{1}H NMR spectrum of (4-bromophenyl)(3-*iso*propylbicyclo[1.1.1]pentan-1-yl)methanone (**4k**)

600 MHz, $CDCl_3$, 23 ℃



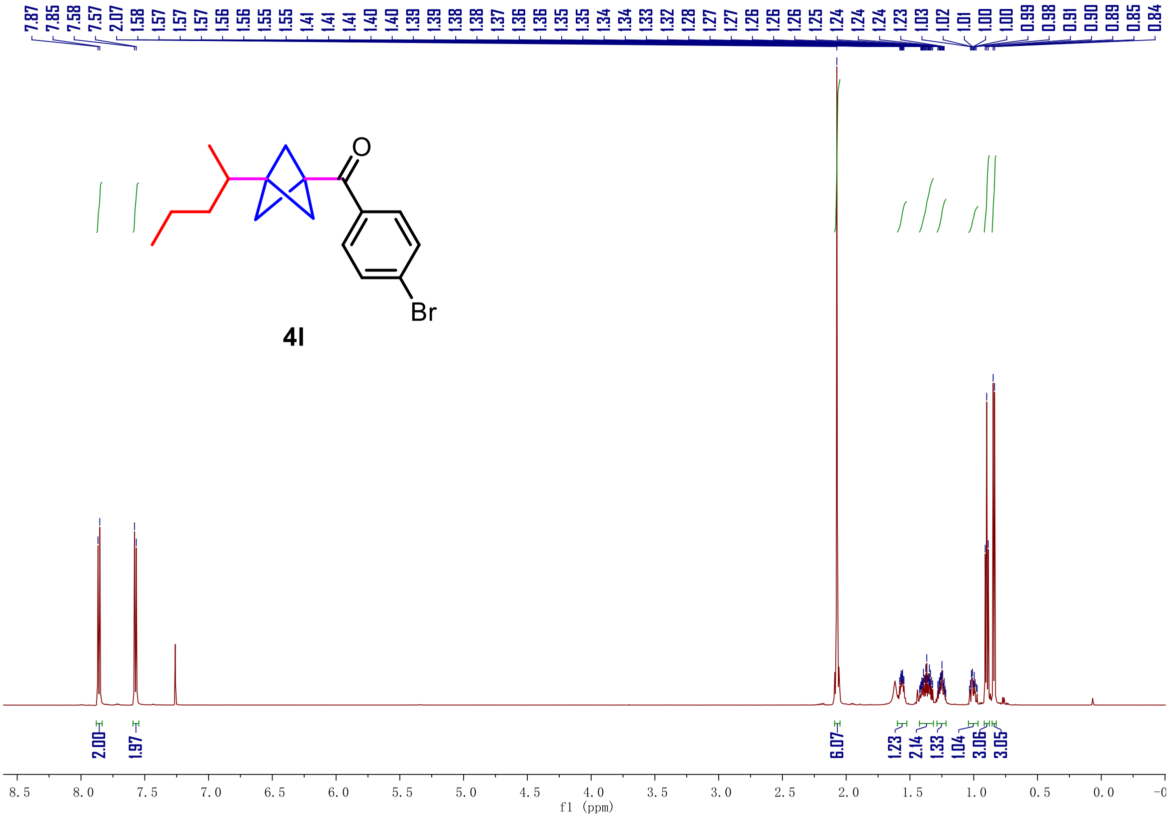
^{13}C NMR spectrum of (4-bromophenyl)(3-*iso*propylbicyclo[1.1.1]pentan-1-yl)methanone (**4k**)

151 MHz, $CDCl_3$, 23 ℃



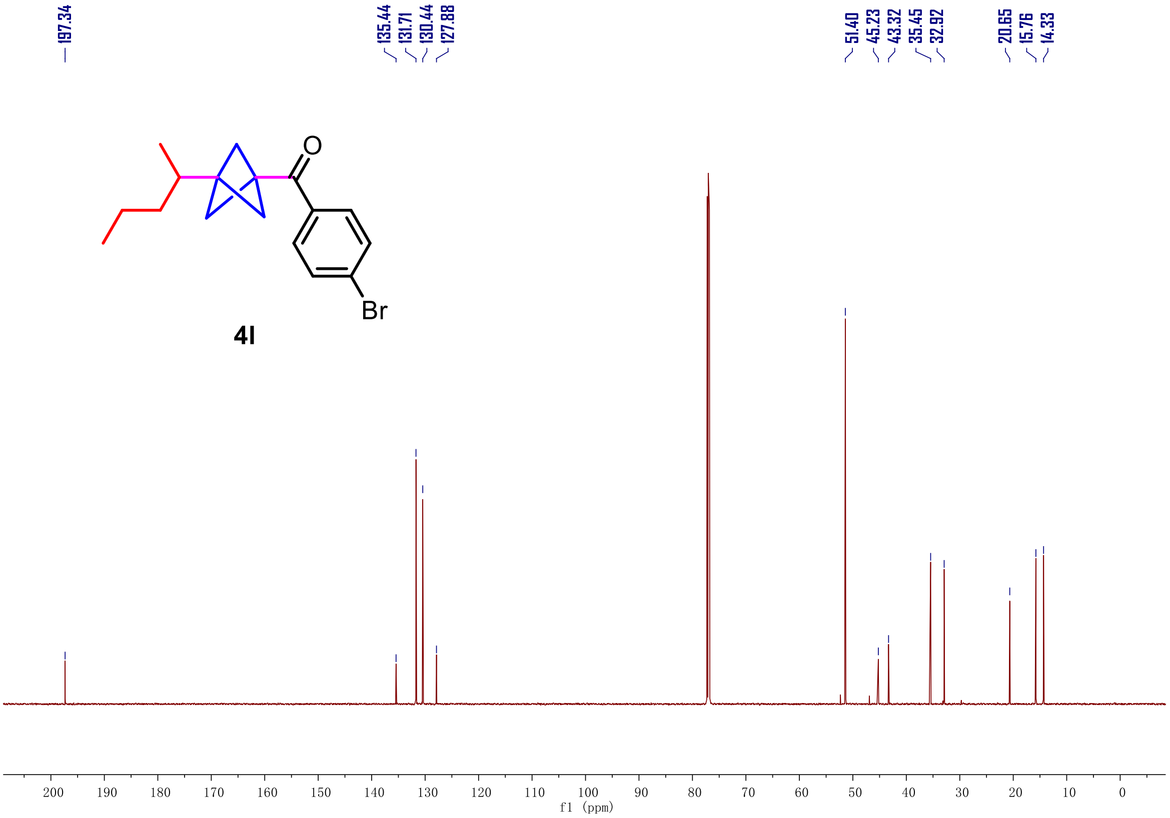
^{1}H NMR spectrum of (4-bromophenyl)(3-(pentan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4l**)

600 MHz, CDCl$_3$, 23 ℃



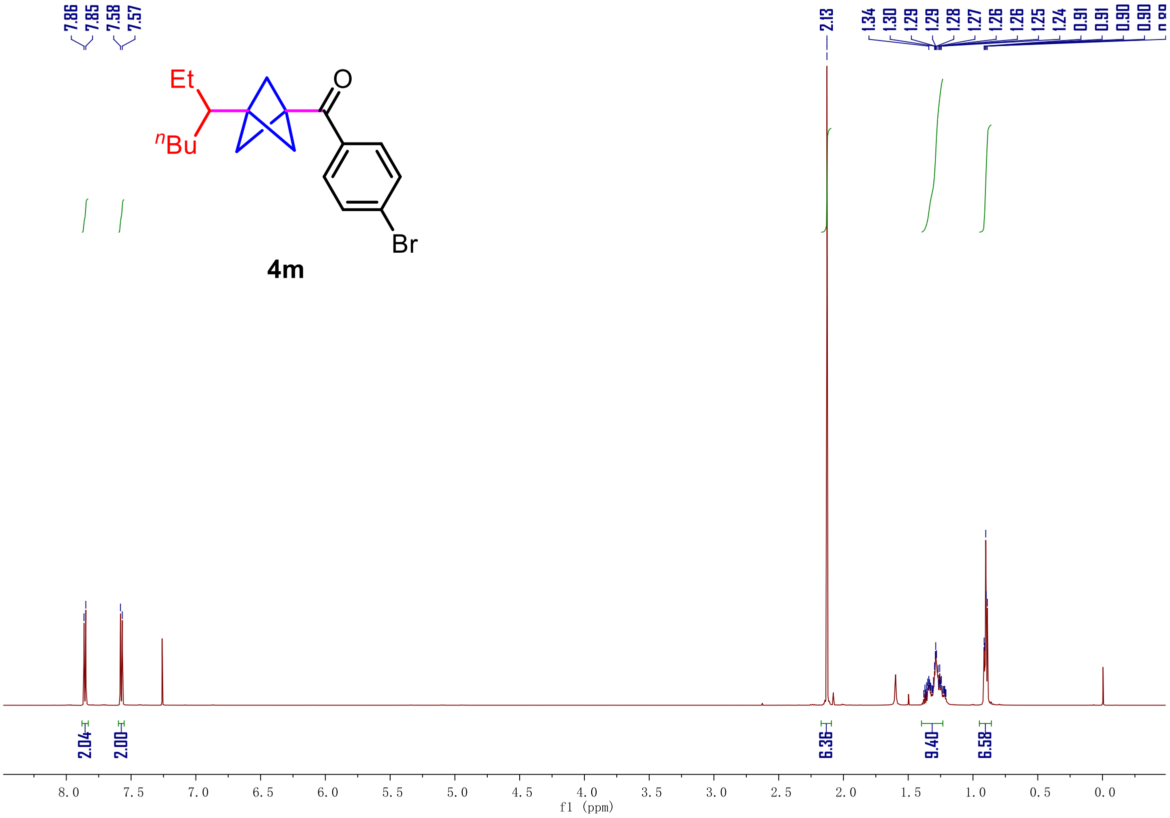
^{13}C NMR spectrum of (4-bromophenyl)(3-(pentan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4l**)

151 MHz, CDCl$_3$, 23 ℃



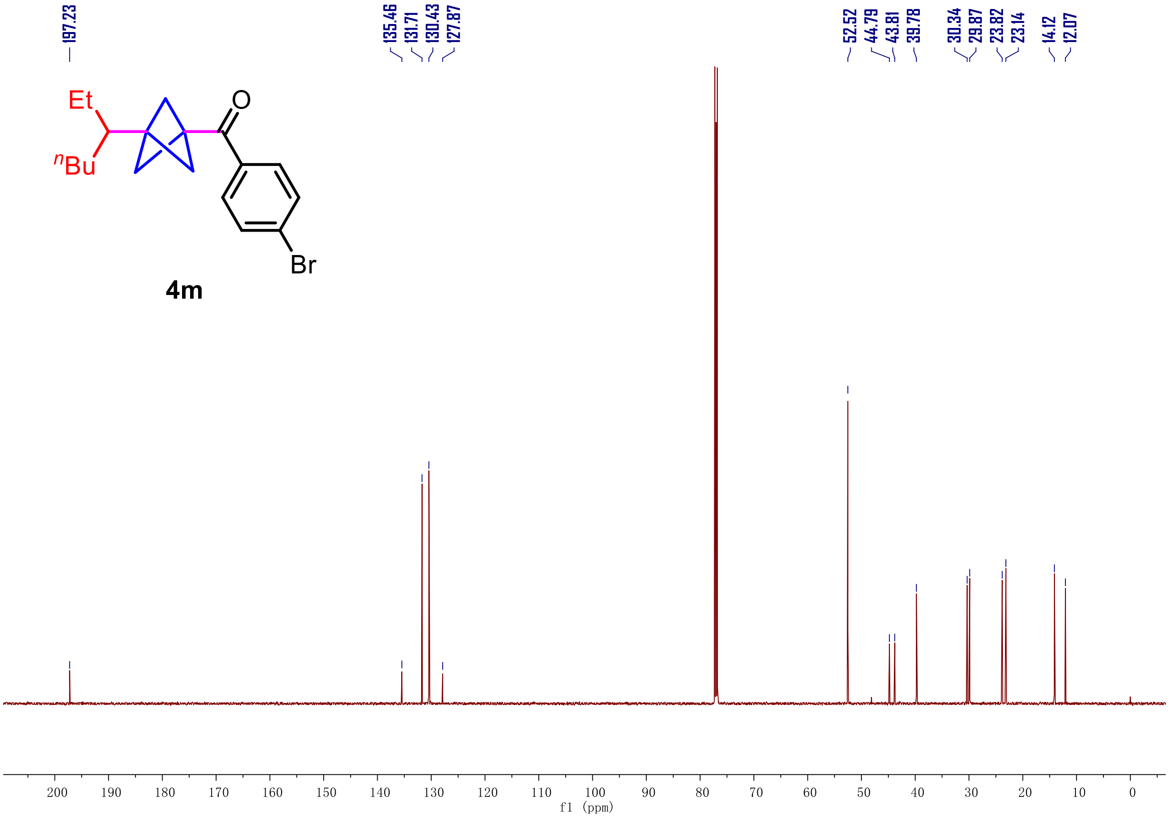
^{1}H NMR spectrum of (4-bromophenyl)(3-(heptan-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4m**)

600 MHz, $CDCl_3$, 23 ℃



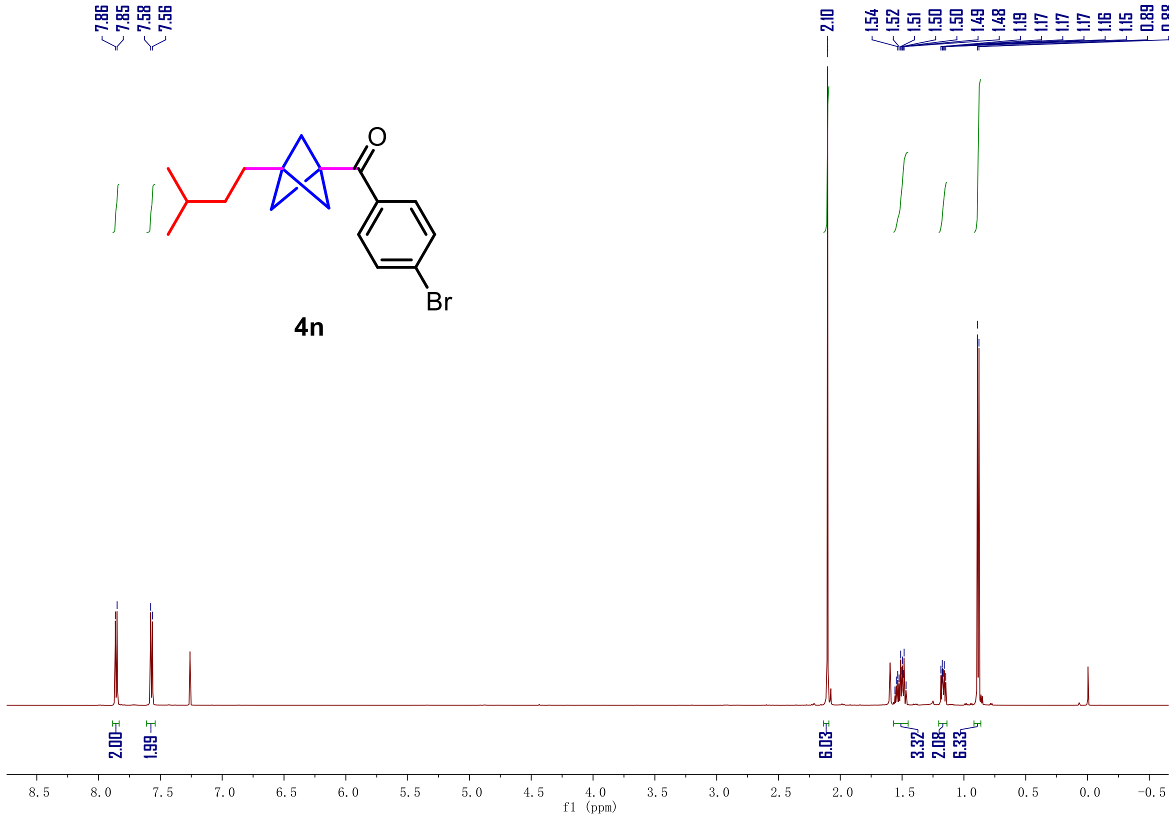
^{13}C NMR spectrum of (4-bromophenyl)(3-(heptan-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4m**)

151 MHz, $CDCl_3$, 23 ℃



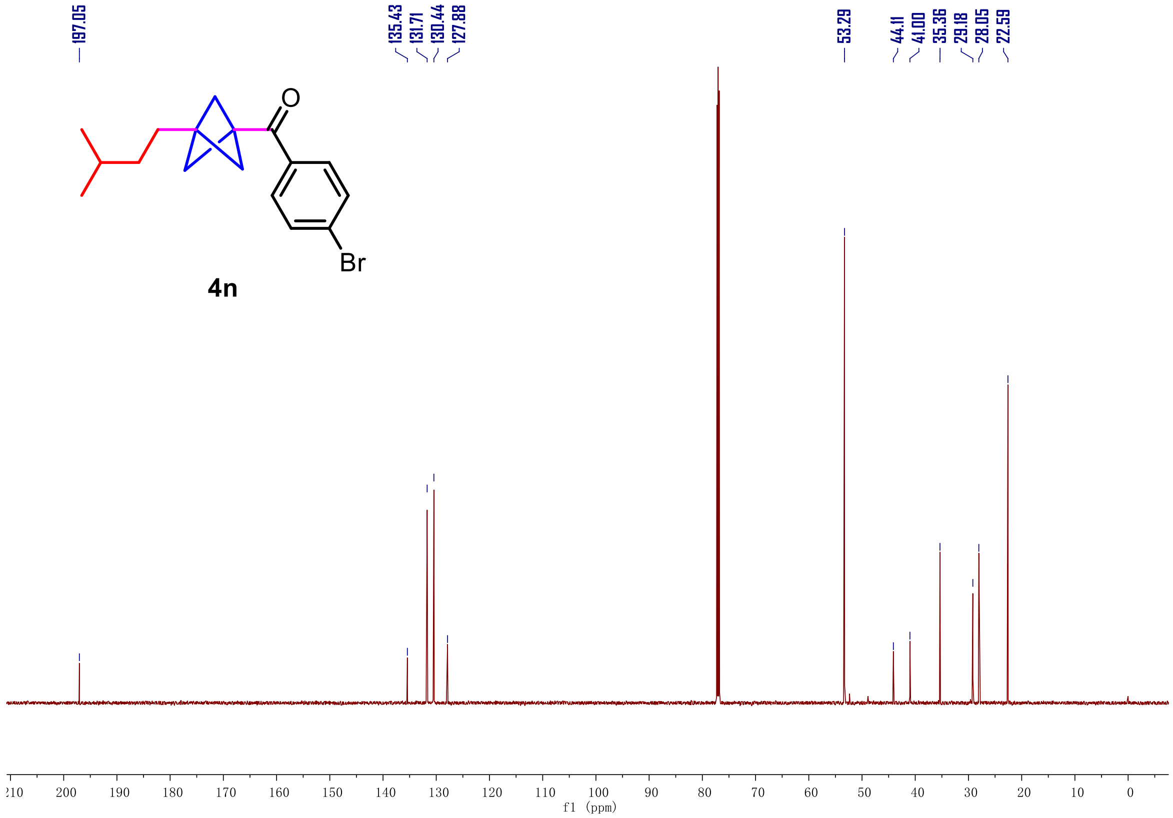
^{1}H NMR spectrum of (4-bromophenyl)(3-*iso*pentylbicyclo[1.1.1]pentan-1-yl)methanone (**4n**)

600 MHz, $CDCl_3$, 23 ℃



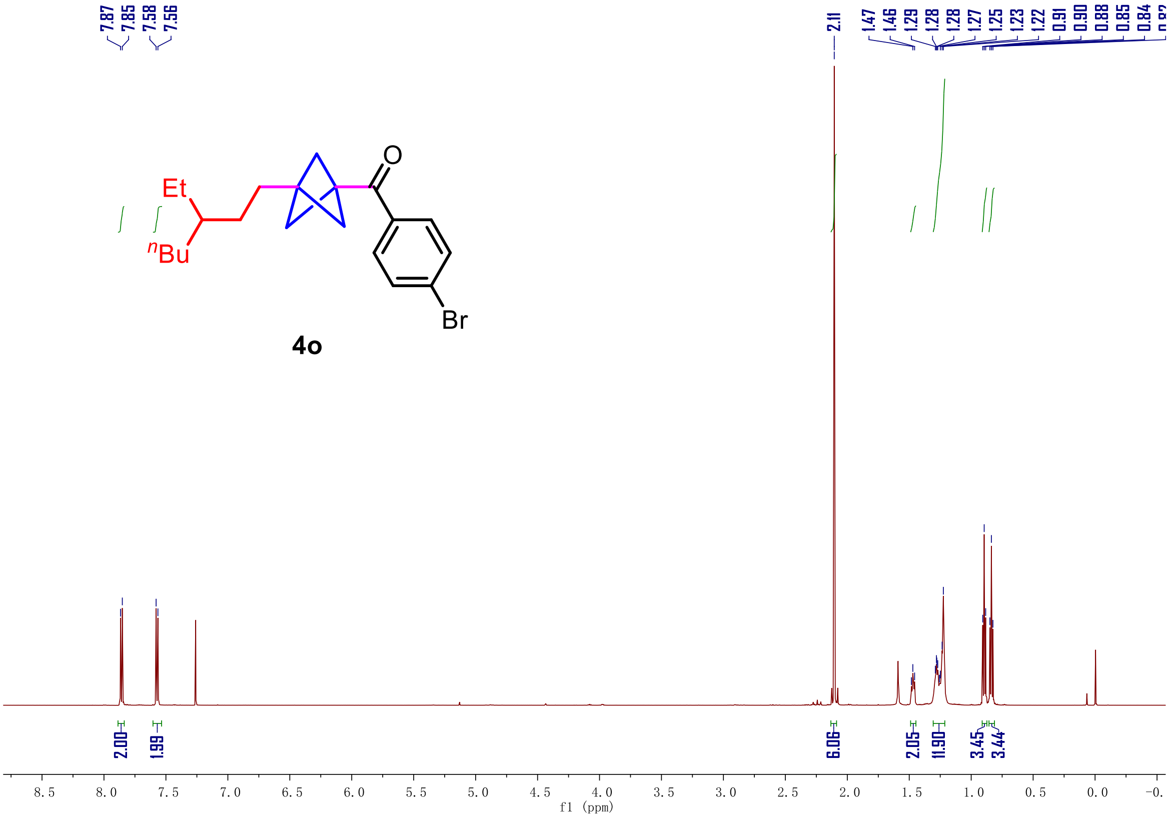
^{13}C NMR spectrum of (4-bromophenyl)(3-*iso*pentylbicyclo[1.1.1]pentan-1-yl)methanone (**4n**)

151 MHz, $CDCl_3$, 23 ℃



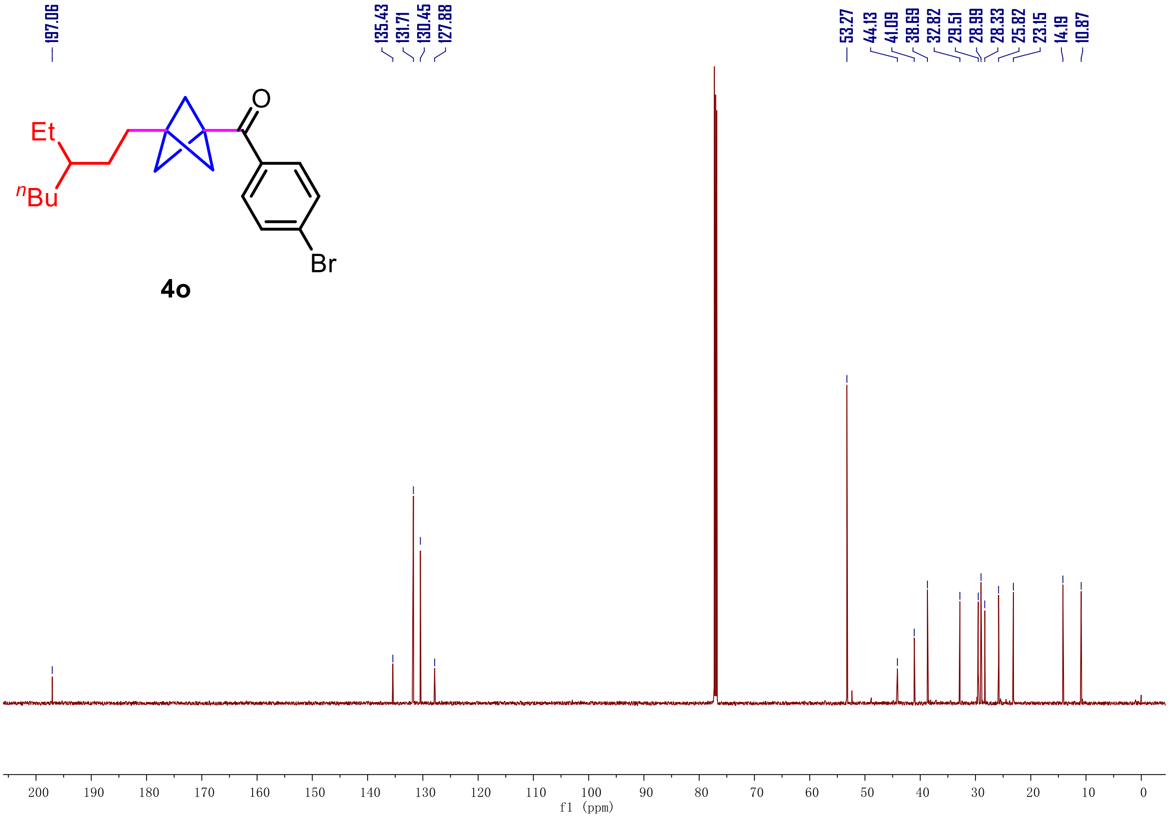
^{1}H NMR spectrum of (4-bromophenyl)(3-(3-ethylheptyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4o**)

600 MHz, $CDCl_3$, 23 ℃



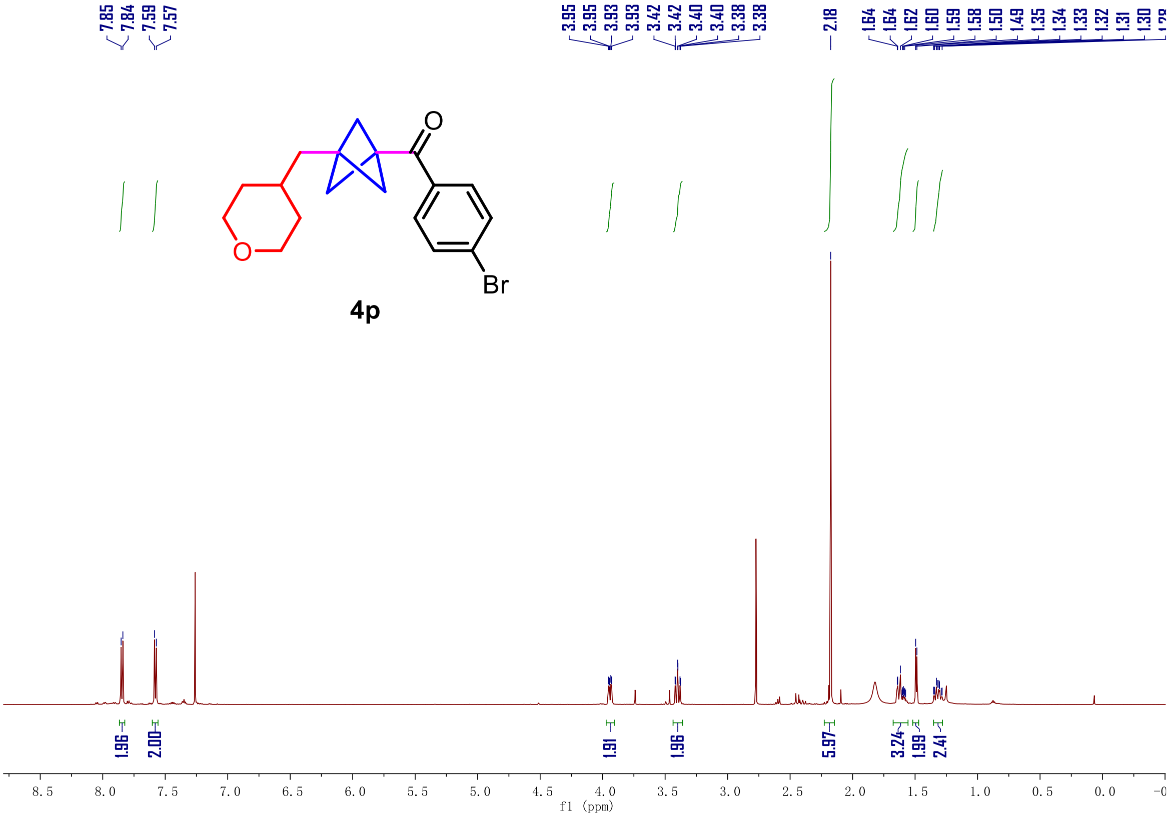
^{13}C NMR spectrum of (4-bromophenyl)(3-(3-ethylheptyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4o**)

151 MHz, $CDCl_3$, 23 ℃



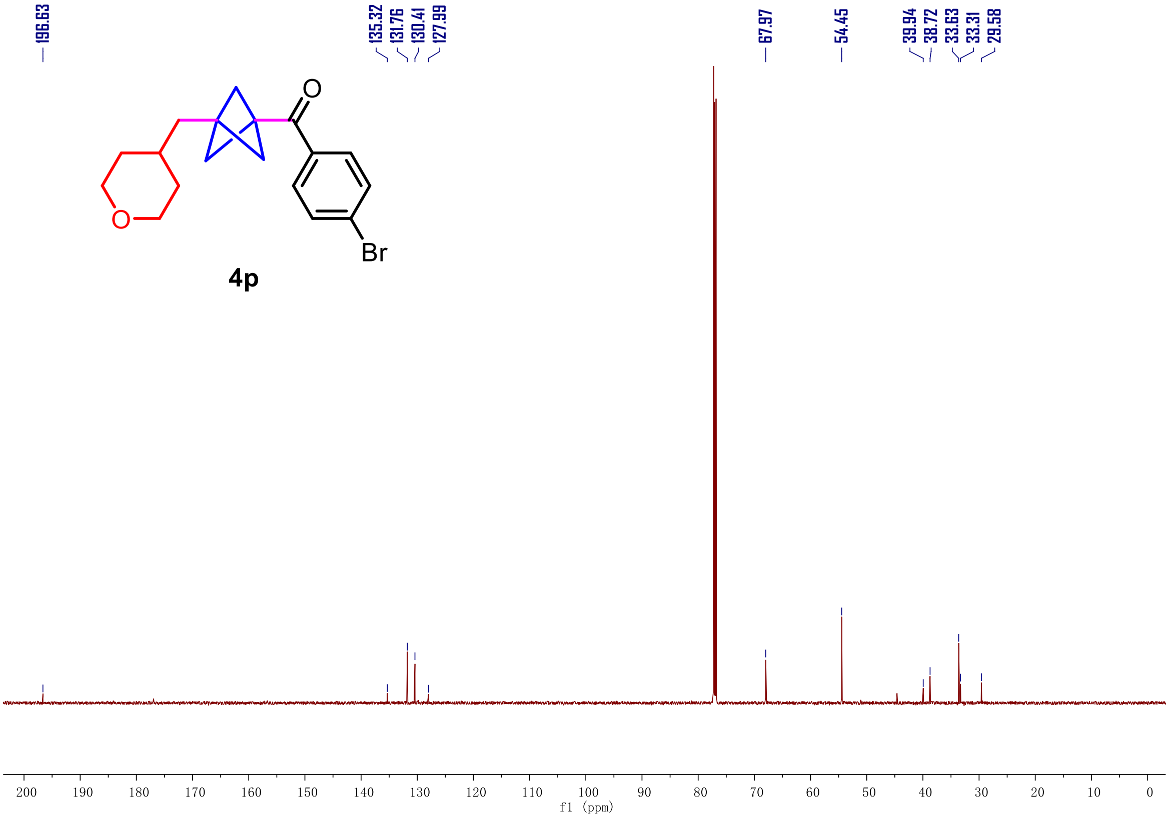
^{1}H NMR spectrum of (4-bromophenyl)(3-((tetrahydro-2H-pyran-4-yl)methyl)bicyclo[1.1.1]pentan-1-yl)methanone

(**4p**) 600 MHz, $CDCl_3$, 23 ℃



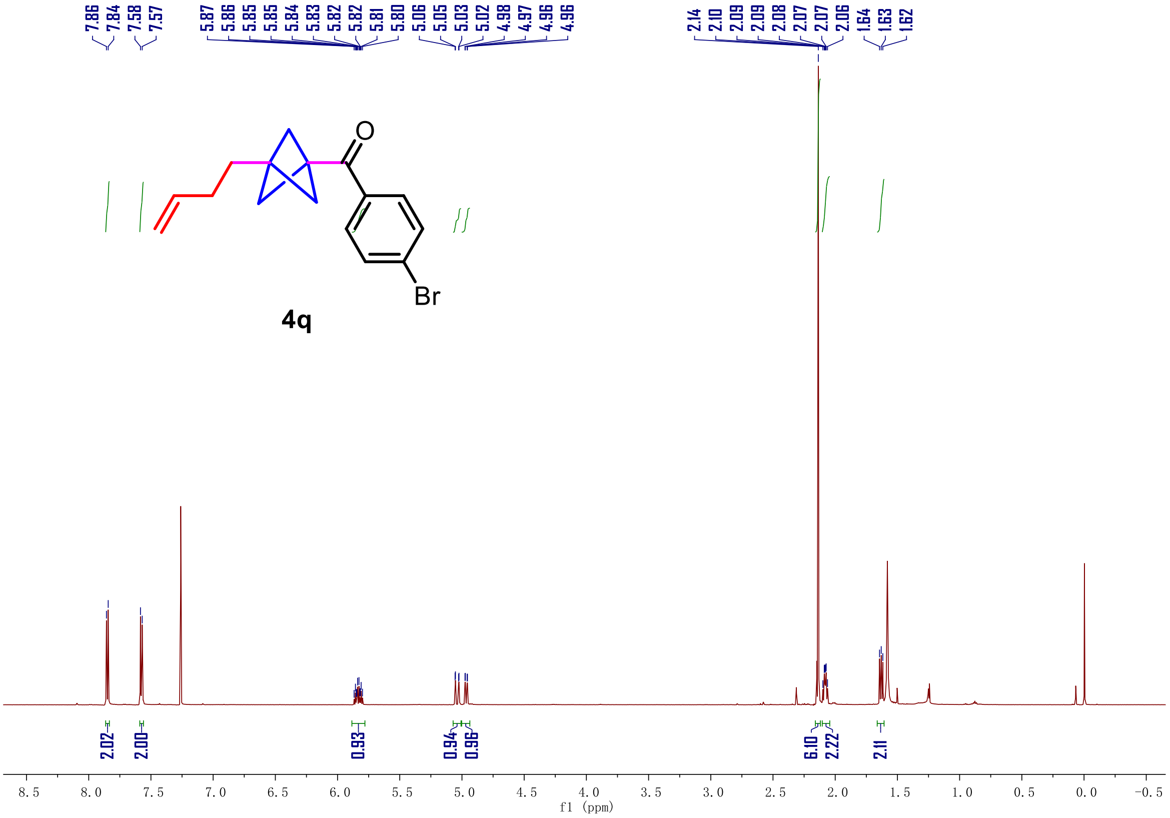
^{13}C NMR spectrum of (4-bromophenyl)(3-((tetrahydro-2H-pyran-4-yl)methyl)bicyclo[1.1.1]pentan-1-yl)methanone

(**4p**) 151 MHz, $CDCl_3$, 23 ℃



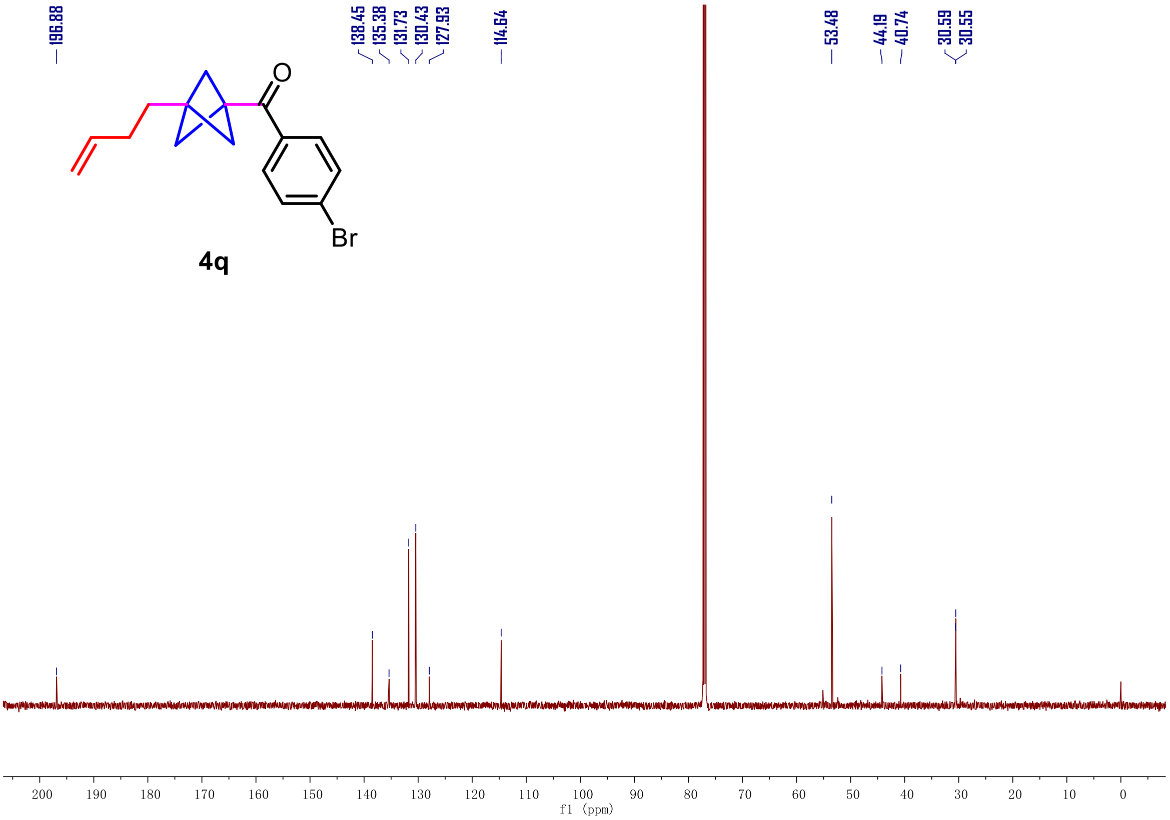
^{1}H NMR spectrum of (4-bromophenyl)(3-(but-3-en-1-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4q**)

600 MHz, $CDCl_3$, 23 ℃



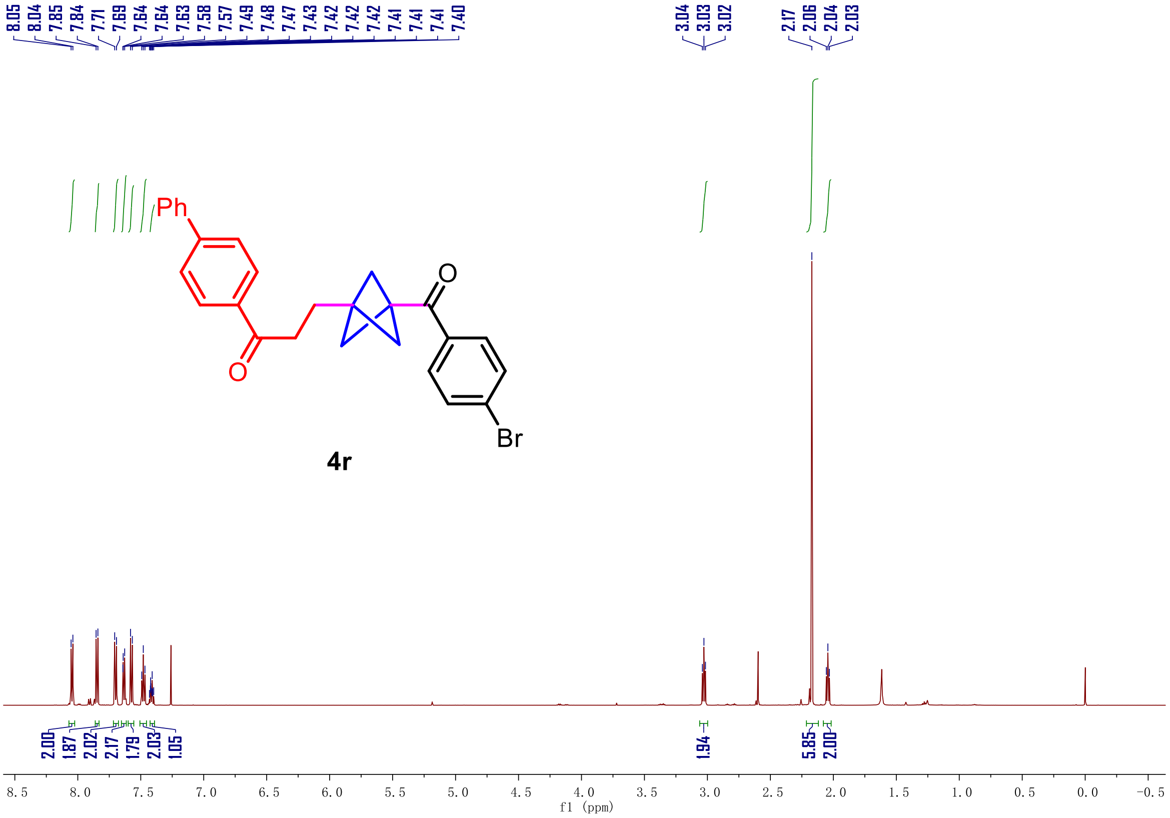
^{13}C NMR spectrum of (4-bromophenyl)(3-(but-3-en-1-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**4q**)

151 MHz, $CDCl_3$, 23 ℃



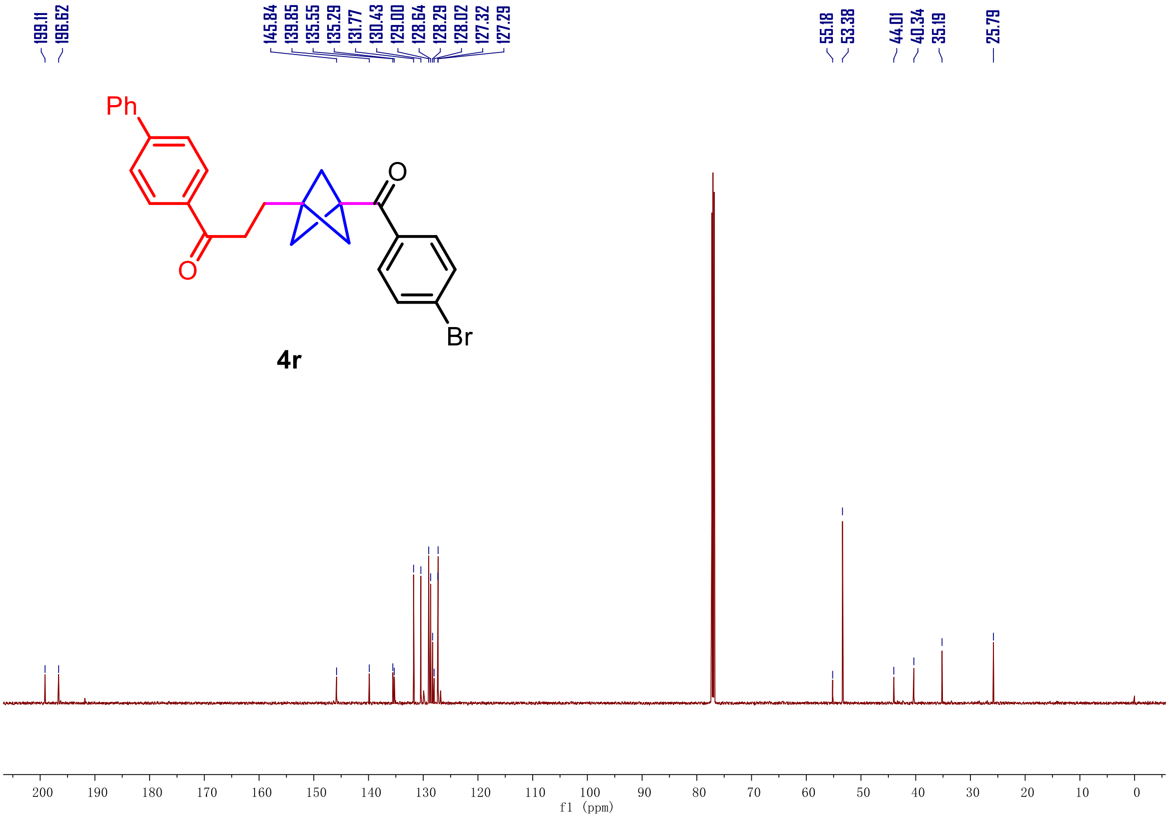
^{1}H NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-3-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)propan-1-one (**4r**)

600 MHz, CDCl$_3$, 23 ℃



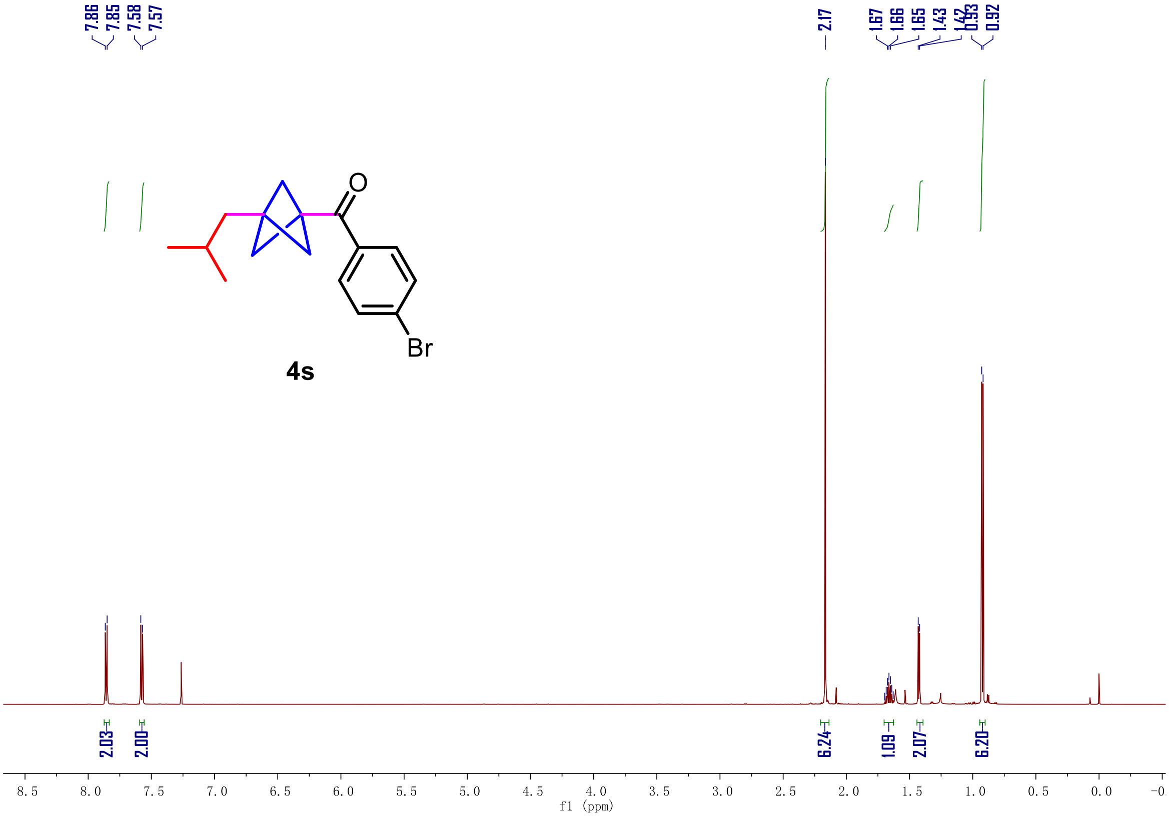
^{13}C NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-3-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)propan-1-one (**4r**)

151 MHz, CDCl$_3$, 23 ℃



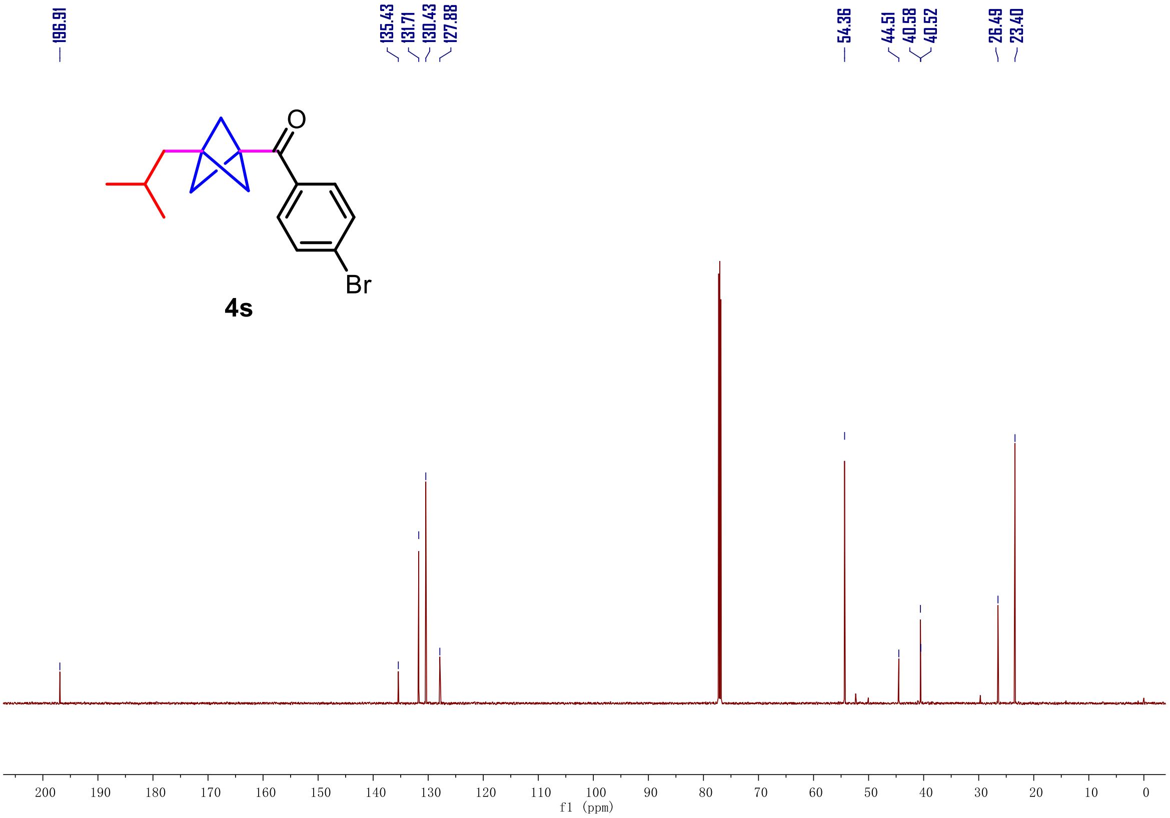
^{1}H NMR spectrum of (4-bromophenyl)(3-isobutylbicyclo[1.1.1]pentan-1-yl)methanone (**4s**)

600 MHz, $CDCl_3$, 23 ℃



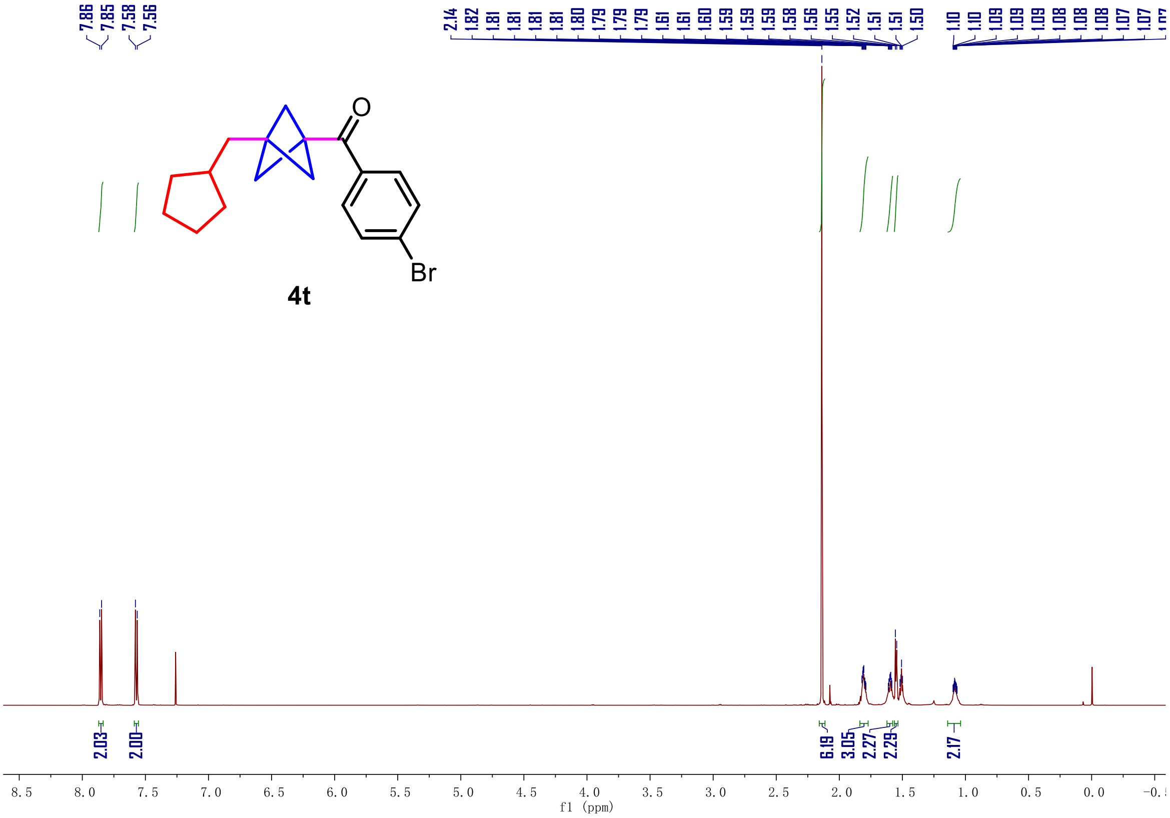
^{13}C NMR spectrum of (4-bromophenyl)(3-isobutylbicyclo[1.1.1]pentan-1-yl)methanone (**4s**)

151 MHz, $CDCl_3$, 23 ℃



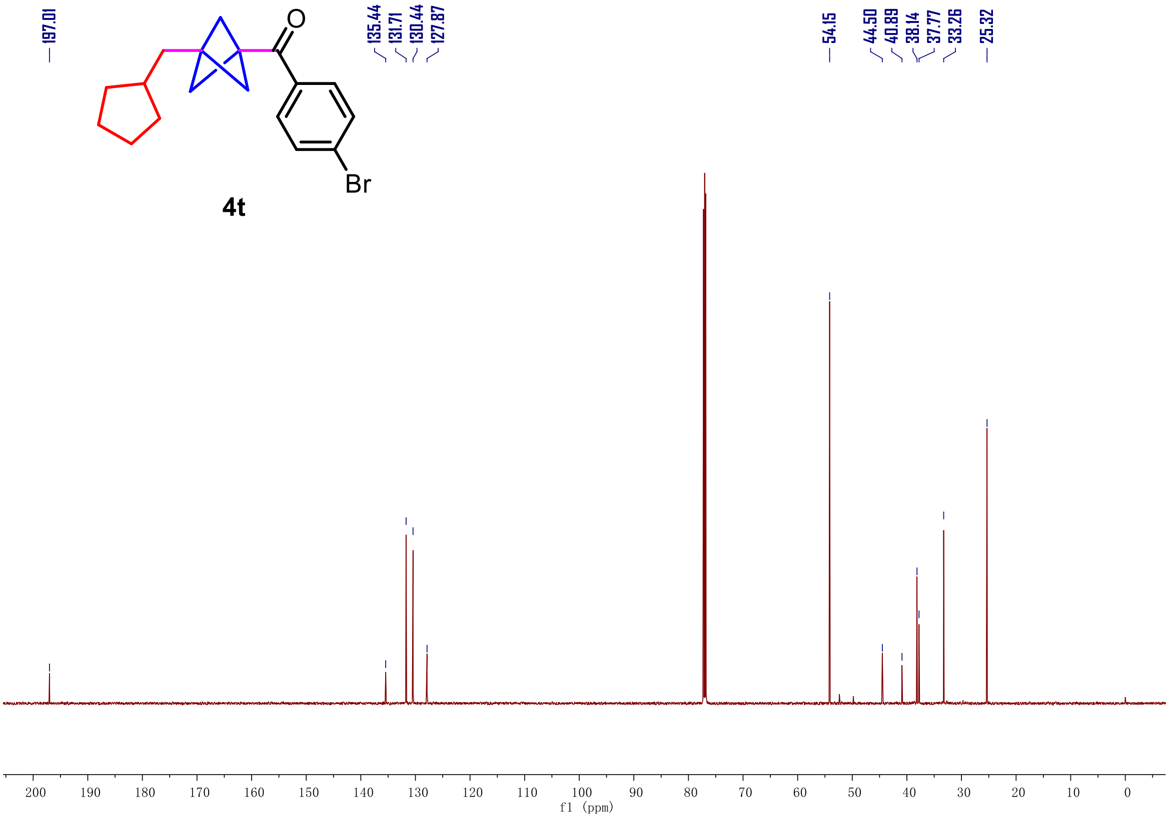
^{1}H NMR spectrum of (4-bromophenyl)(3-(cyclopentylmethyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4t**)

600 MHz, CDCl$_3$, 23 ℃



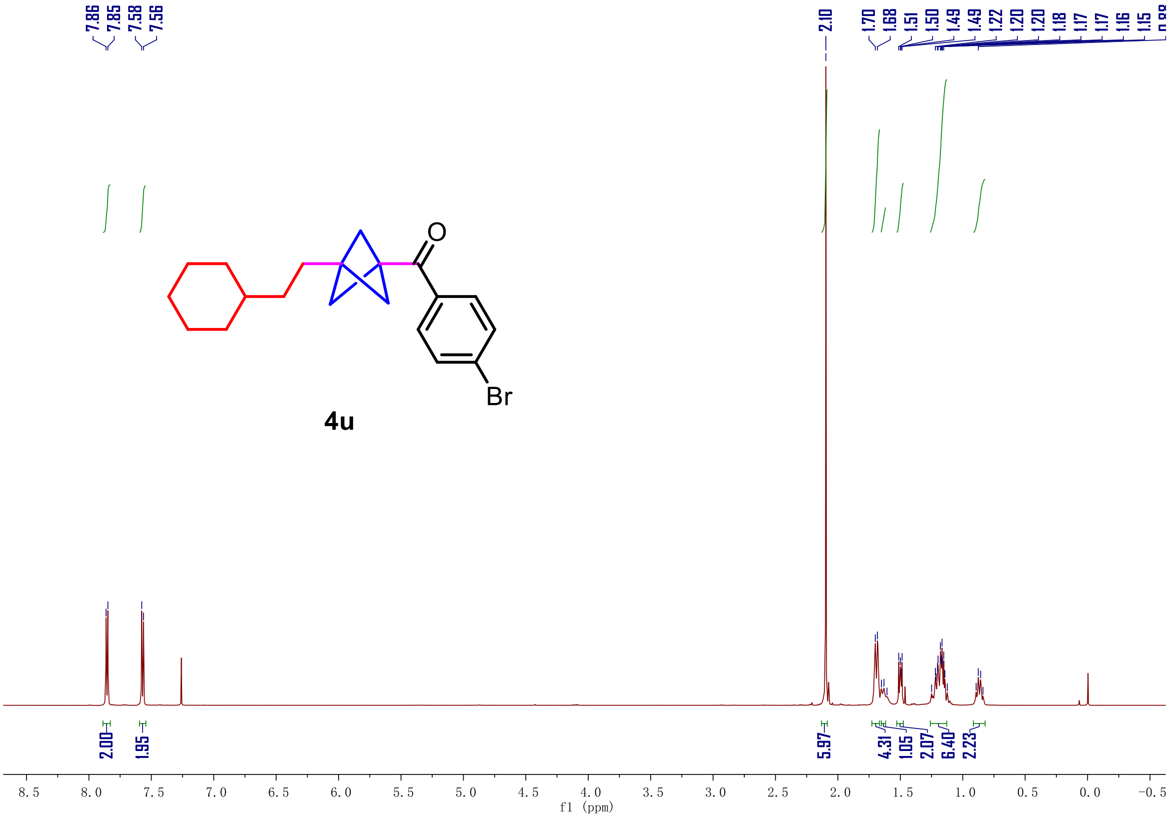
^{13}C NMR spectrum of (4-bromophenyl)(3-(cyclopentylmethyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4t**)

151 MHz, CDCl$_3$, 23 ℃



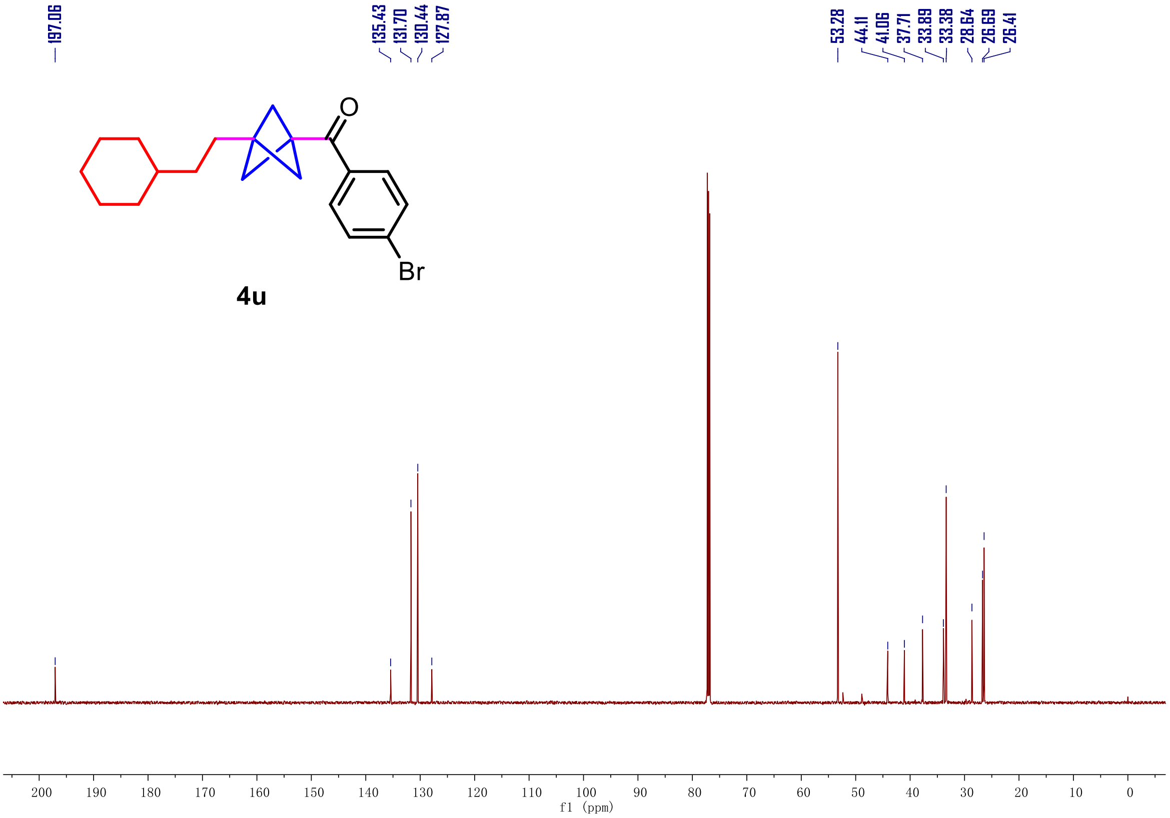
^{1}H NMR spectrum of (4-bromophenyl)(3-(2-cyclohexylethyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4u**)

600 MHz, $CDCl_3$, 23 ℃



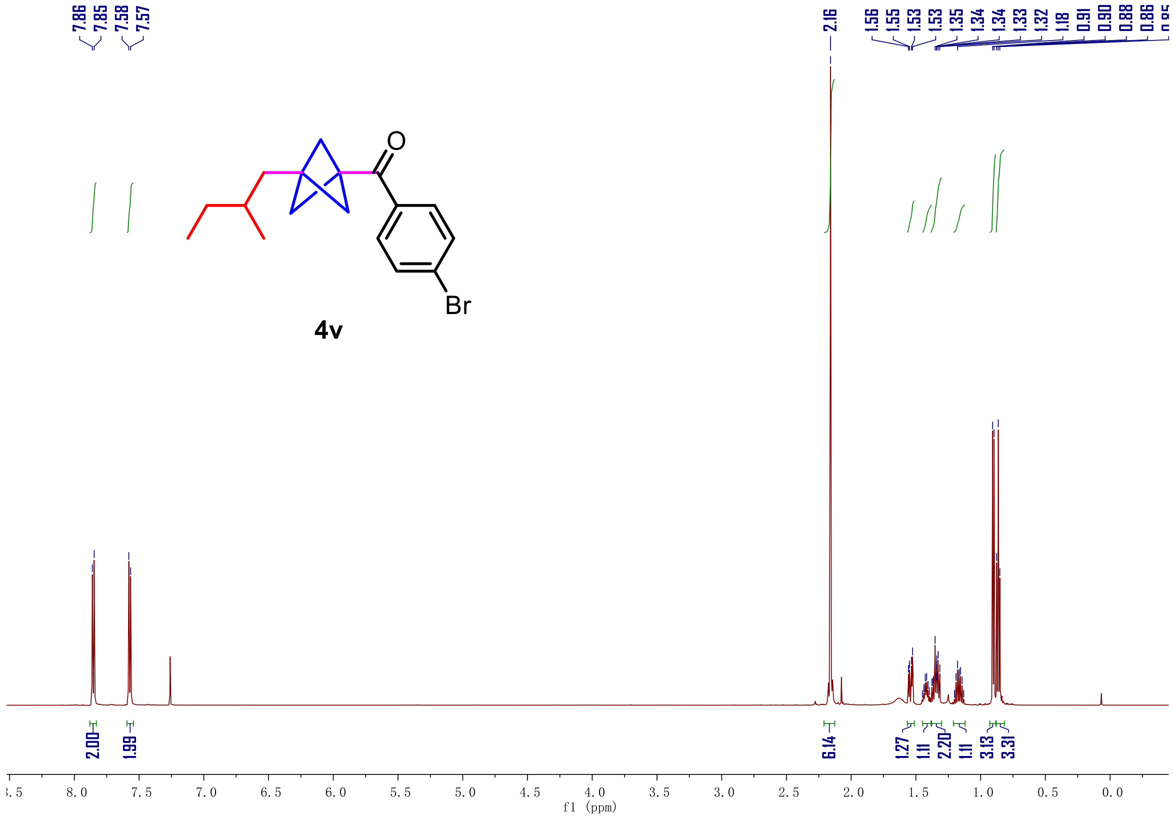
^{13}C NMR spectrum of (4-bromophenyl)(3-(2-cyclohexylethyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4u**)

151 MHz, $CDCl_3$, 23 ℃



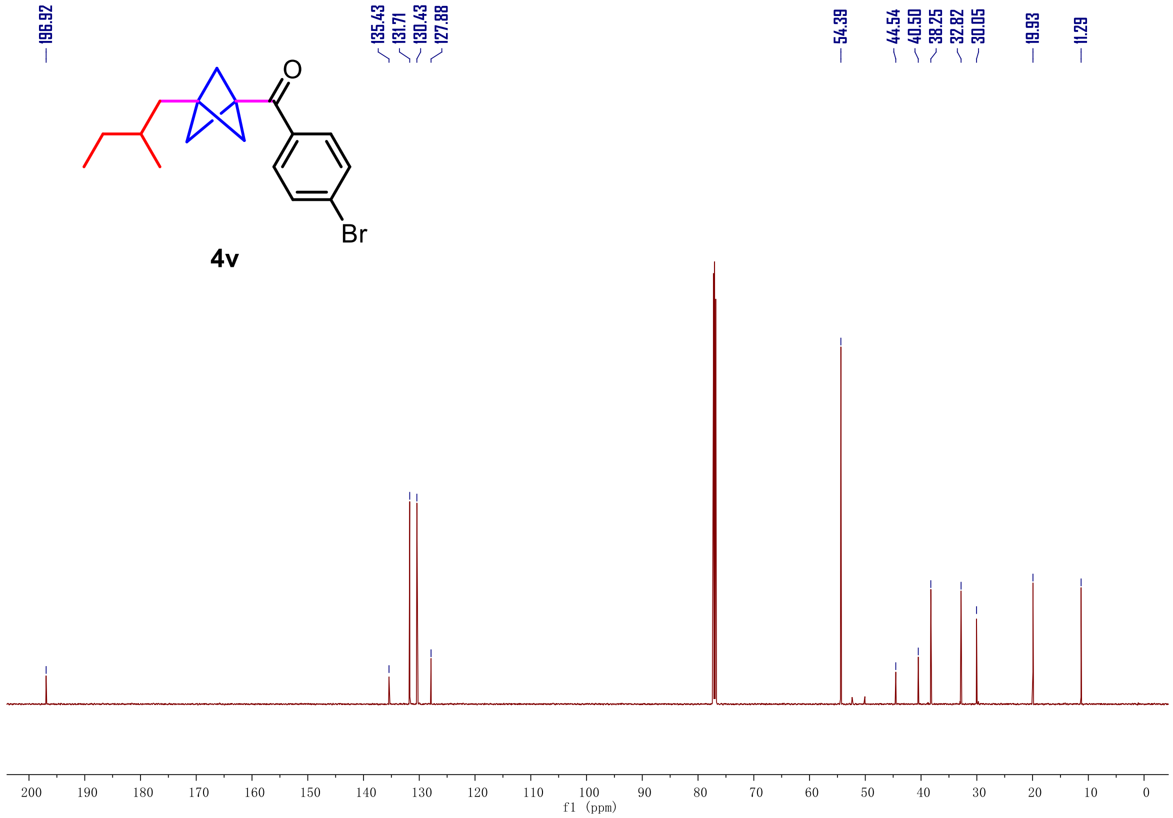
^{1}H NMR spectrum of (4-bromophenyl)(3-(2-methylbutyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4v**)

600 MHz, $CDCl_3$, 23 ℃



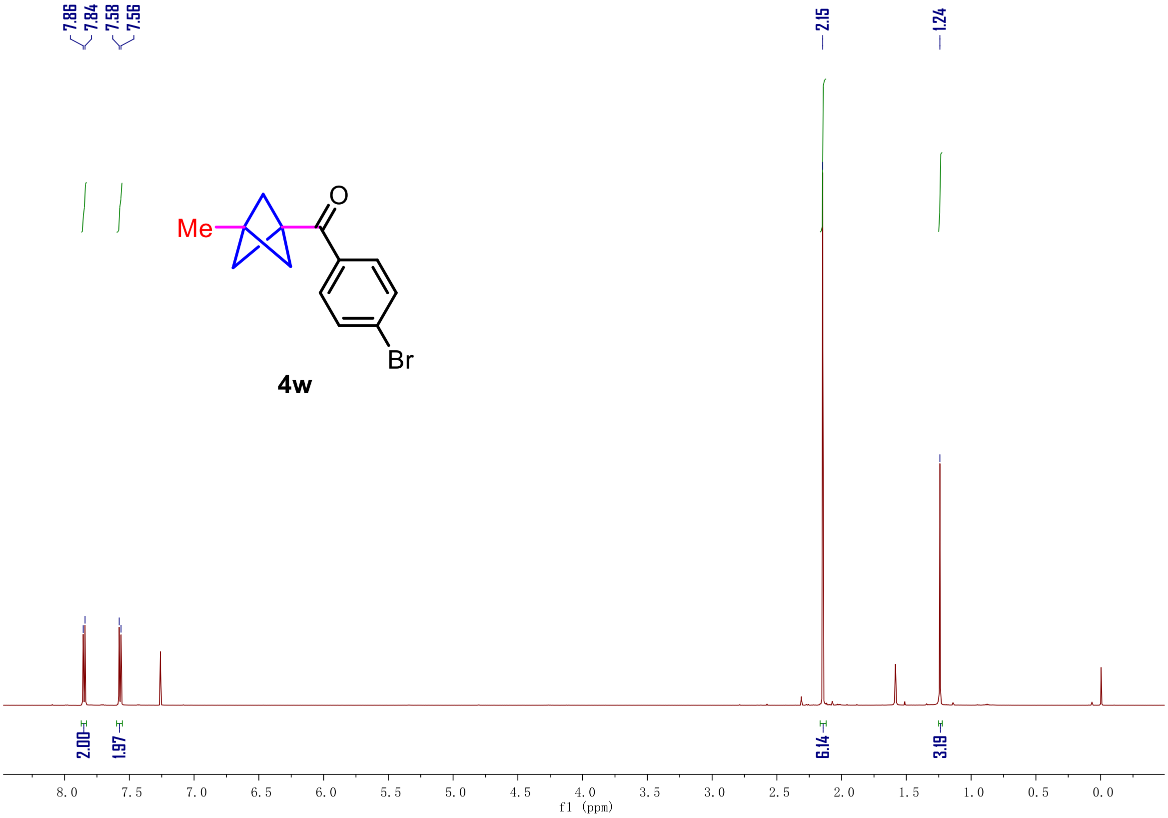
^{13}C NMR spectrum of (4-bromophenyl)(3-(2-methylbutyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4v**)

151 MHz, $CDCl_3$, 23 ℃



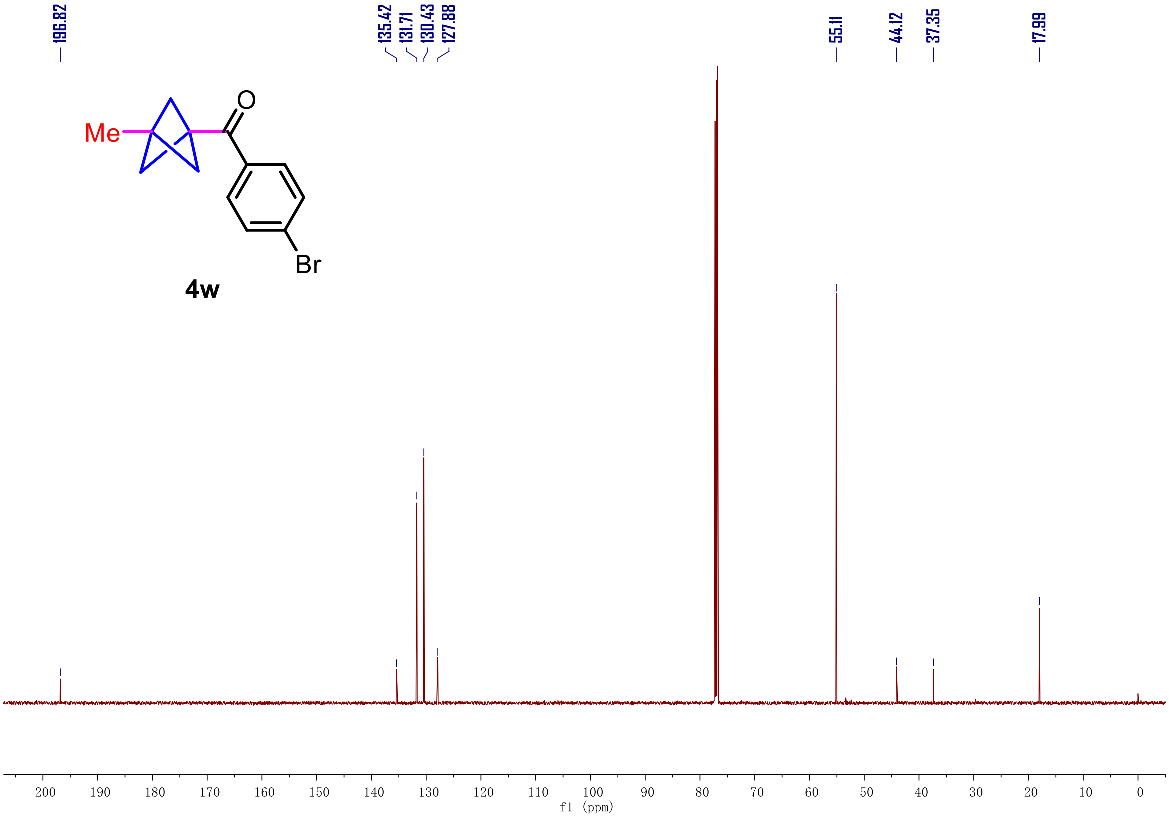
^{1}H NMR spectrum of (4-bromophenyl)(3-methylbicyclo[1.1.1]pentan-1-yl)methanone (**4w**)

600 MHz, $CDCl_3$, 23 ℃



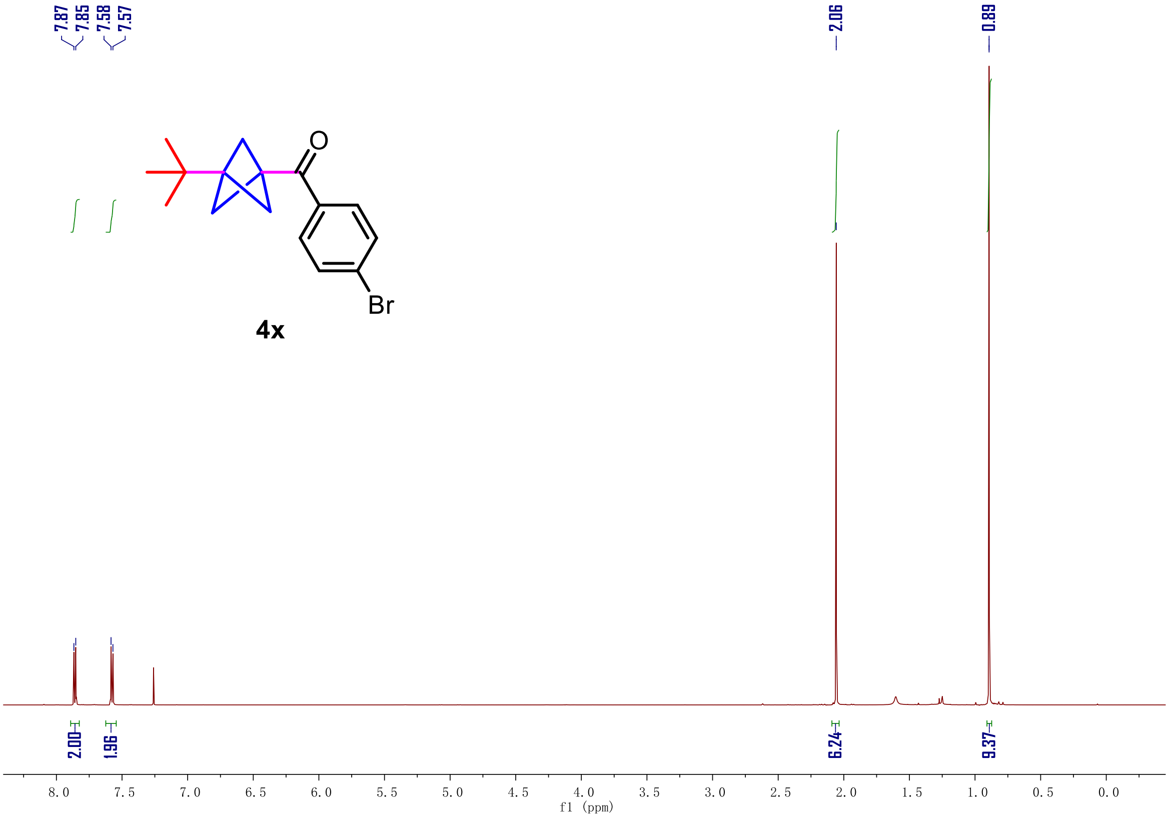
^{13}C NMR spectrum of (4-bromophenyl)(3-methylbicyclo[1.1.1]pentan-1-yl)methanone (**4w**)

151 MHz, $CDCl_3$, 23 ℃



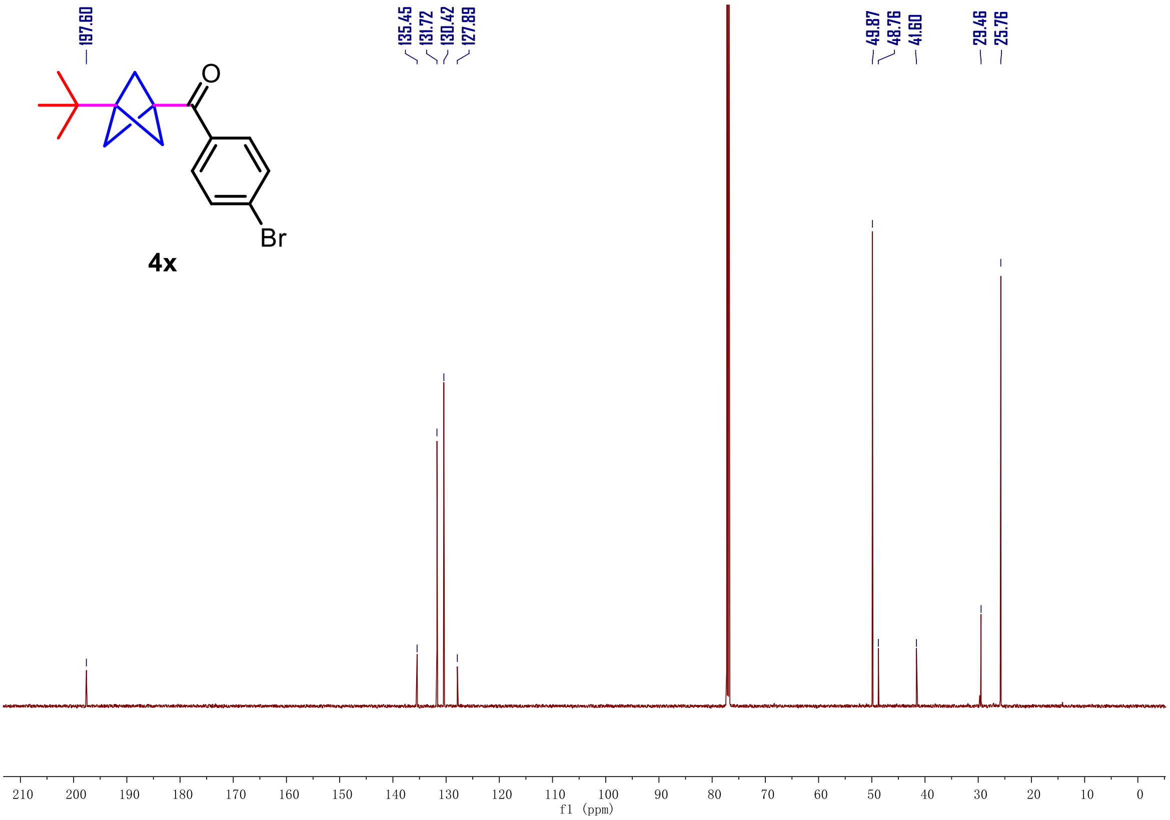
^{1}H NMR spectrum of (4-bromophenyl)(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4x**)

600 MHz, $CDCl_3$, 23 ℃



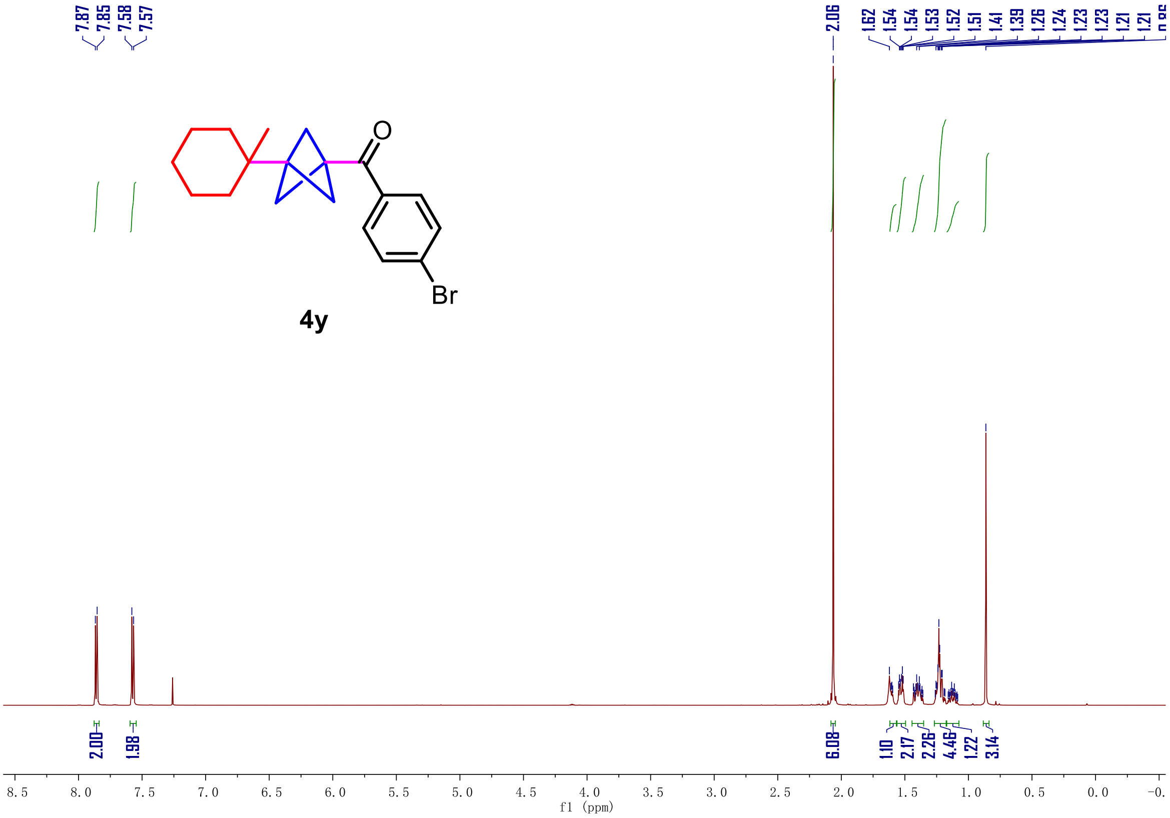
^{13}C NMR spectrum of (4-bromophenyl)(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4x**)

151 MHz, $CDCl_3$, 23 ℃



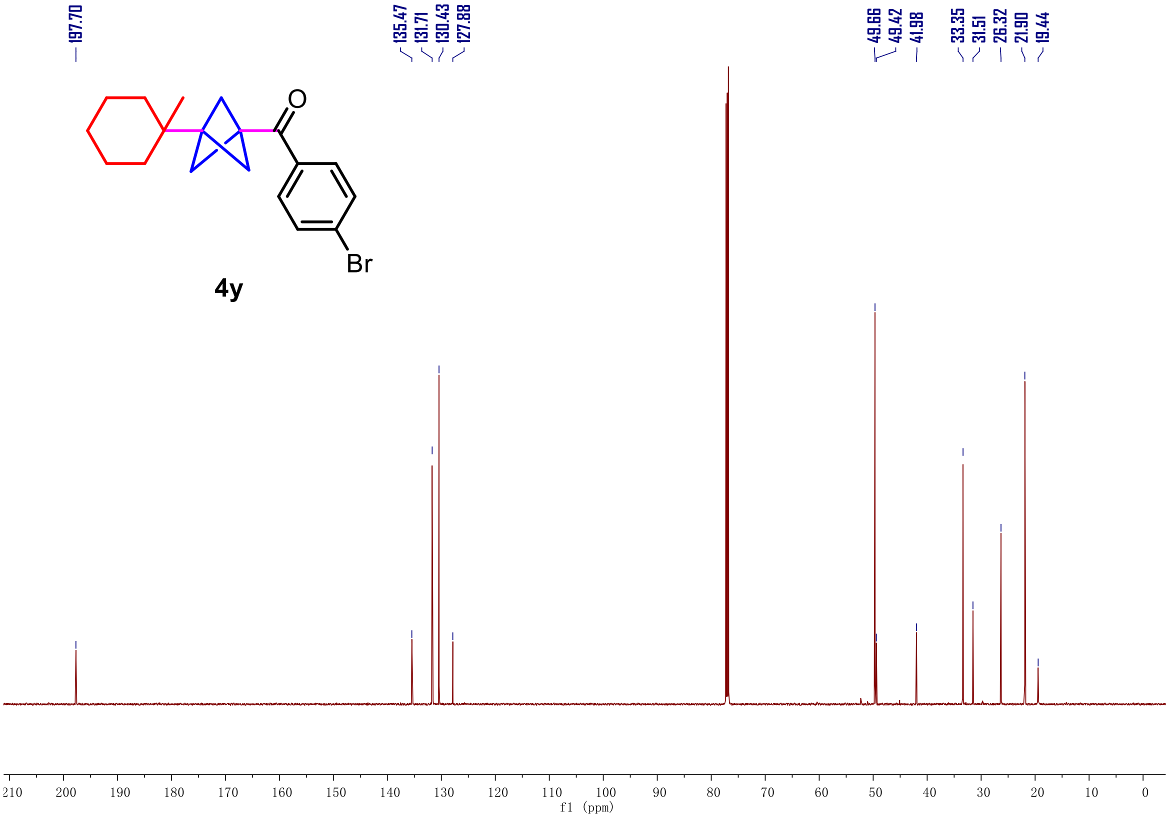
^{1}H NMR spectrum of (4-bromophenyl)(3-(1-methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4y**)

600 MHz, $CDCl_3$, 23 ℃



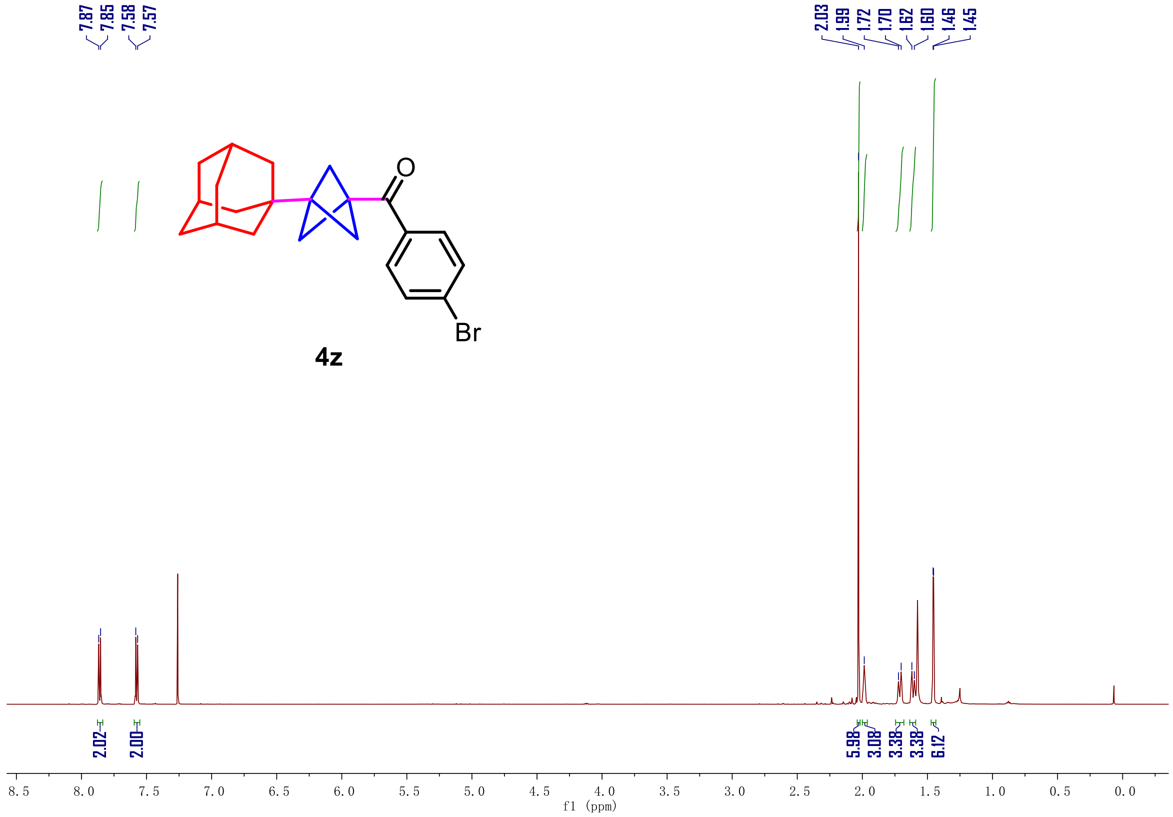
^{13}C NMR spectrum of (4-bromophenyl)(3-(1-methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4y**)

151 MHz, $CDCl_3$, 23 ℃



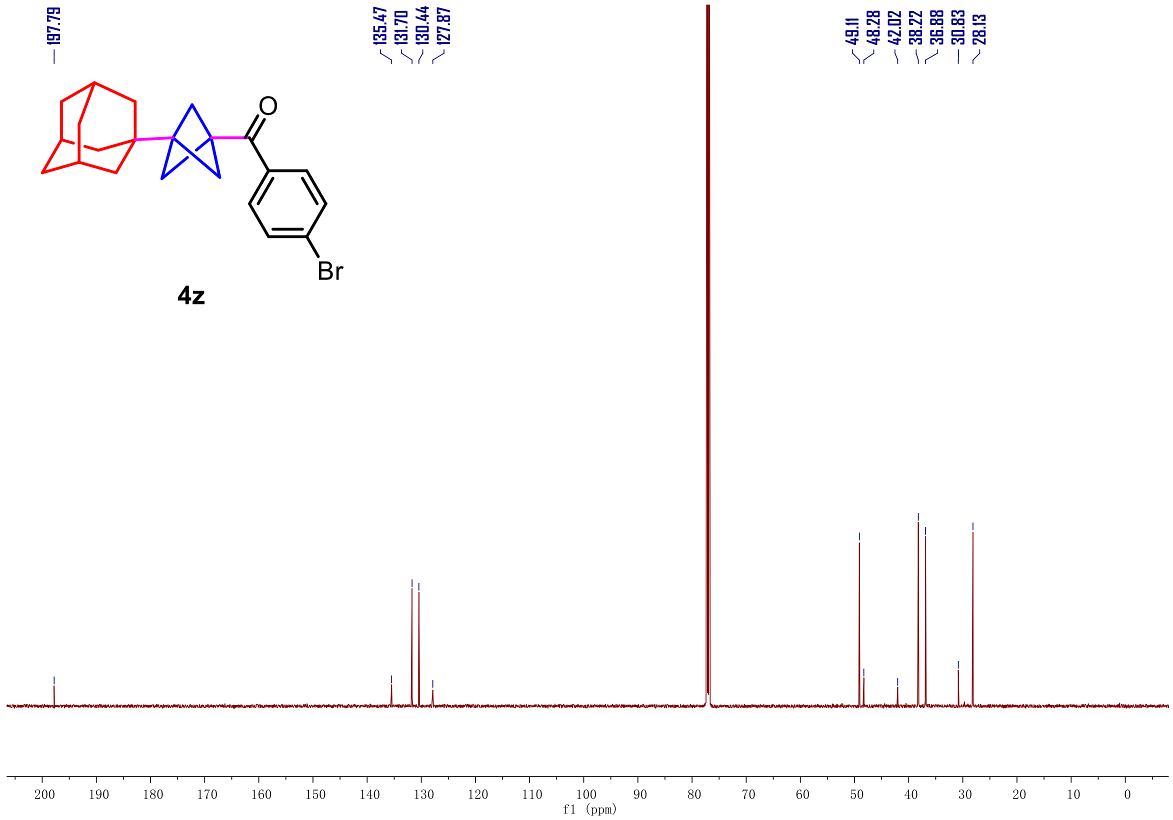
^{1}H NMR spectrum of (3-(adamantan-1-yl)bicyclo[1.1.1]pentan-1-yl)(4-bromophenyl)methanone (**4z**)

600 MHz, $CDCl_3$, 23 ℃



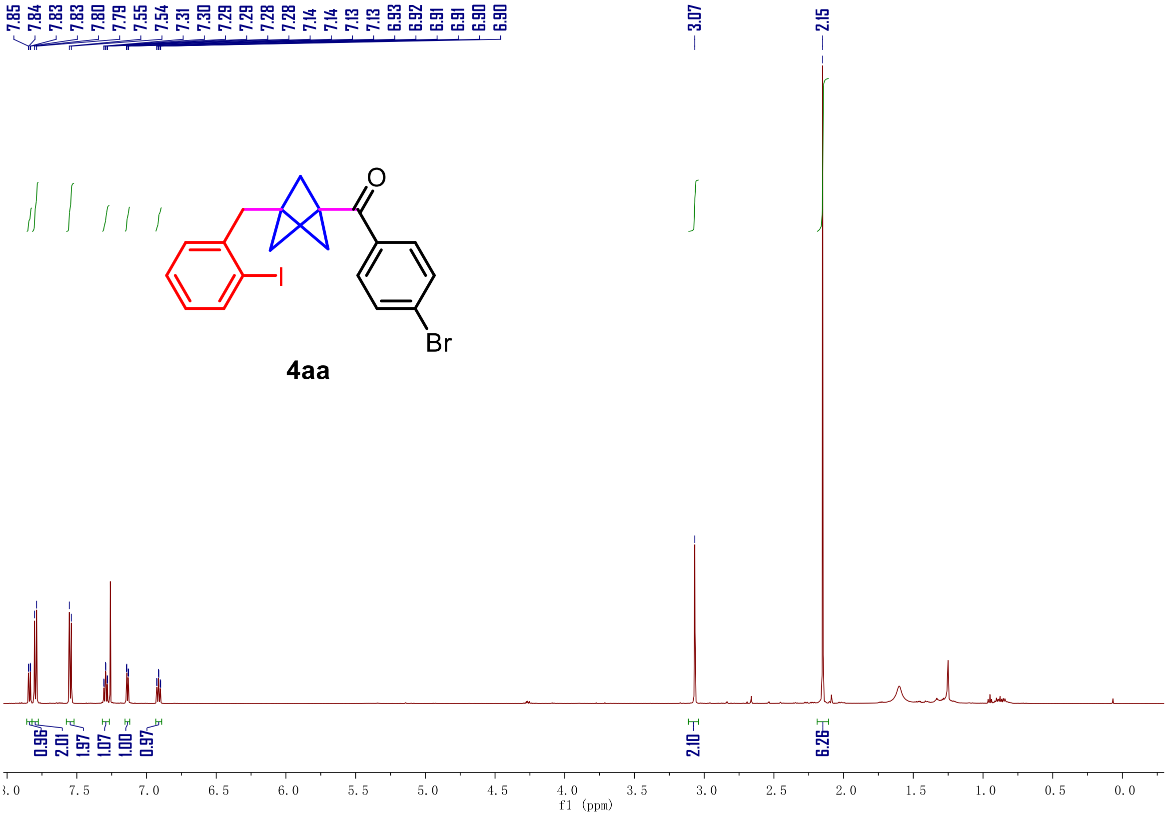
^{13}C NMR spectrum of (3-(adamantan-1-yl)bicyclo[1.1.1]pentan-1-yl)(4-bromophenyl)methanone (**4z**)

151 MHz, $CDCl_3$, 23 ℃



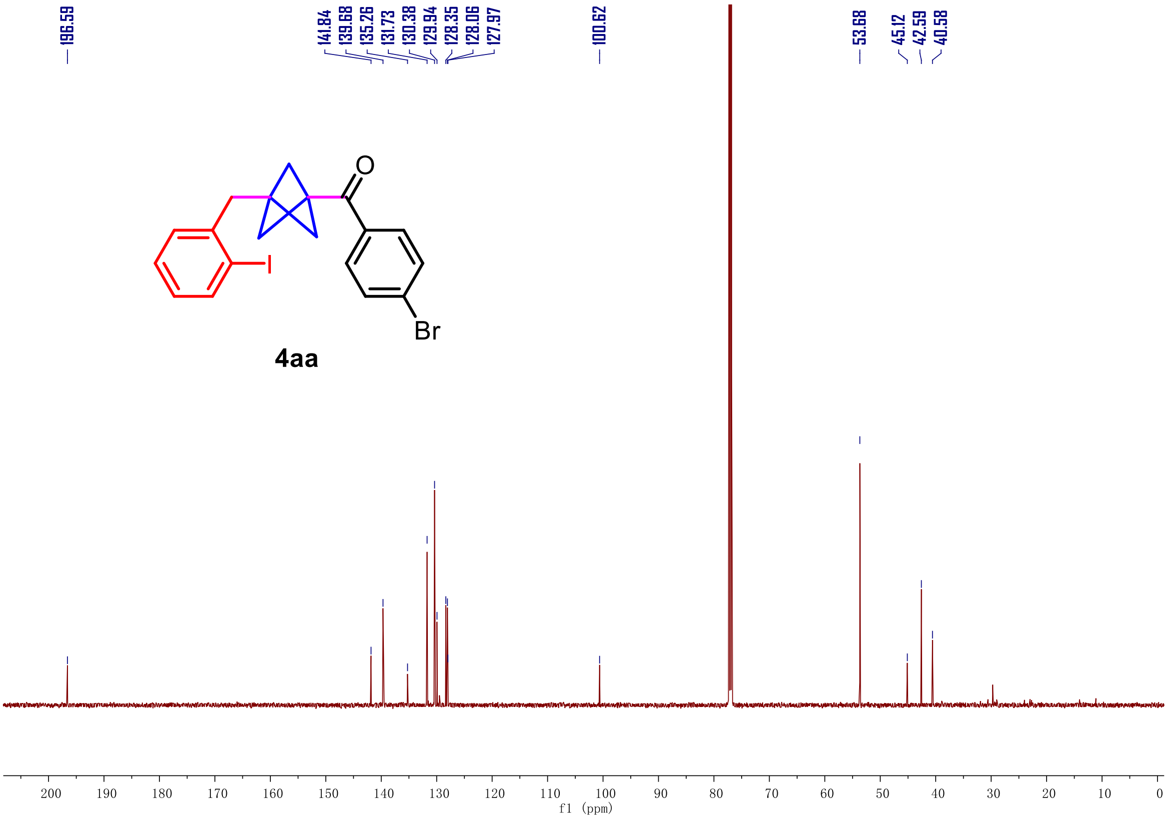
^{1}H NMR spectrum of (4-bromophenyl)(3-(2-iodobenzyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4aa**)

600 MHz, $CDCl_3$, 23 ℃



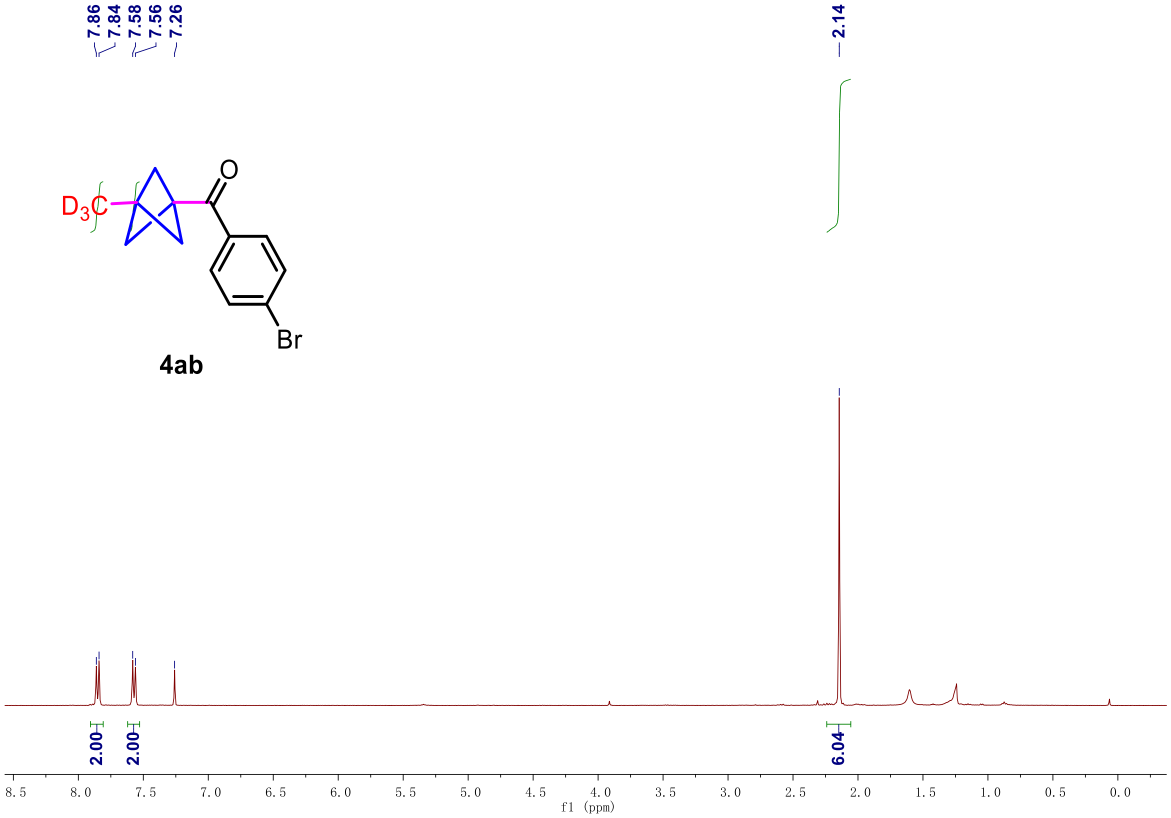
^{13}C NMR spectrum of (4-bromophenyl)(3-(2-iodobenzyl)bicyclo[1.1.1]pentan-1-yl)methanone (**4aa**)

151 MHz, $CDCl_3$, 23 ℃



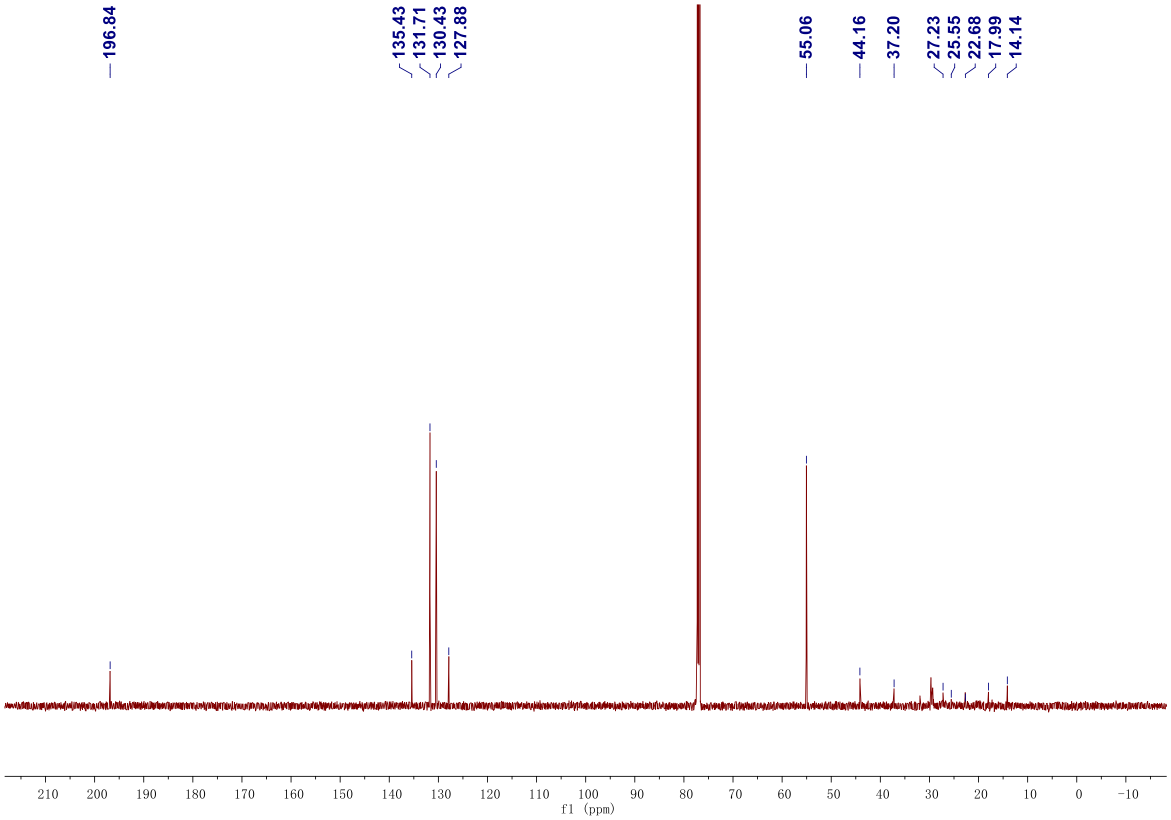
^{1}H NMR spectrum of (4-bromophenyl)(3-(methyl-d_3)bicyclo[1.1.1]pentan-1-yl)methanone (**4ab**)

600 MHz, $CDCl_3$, 23 ℃



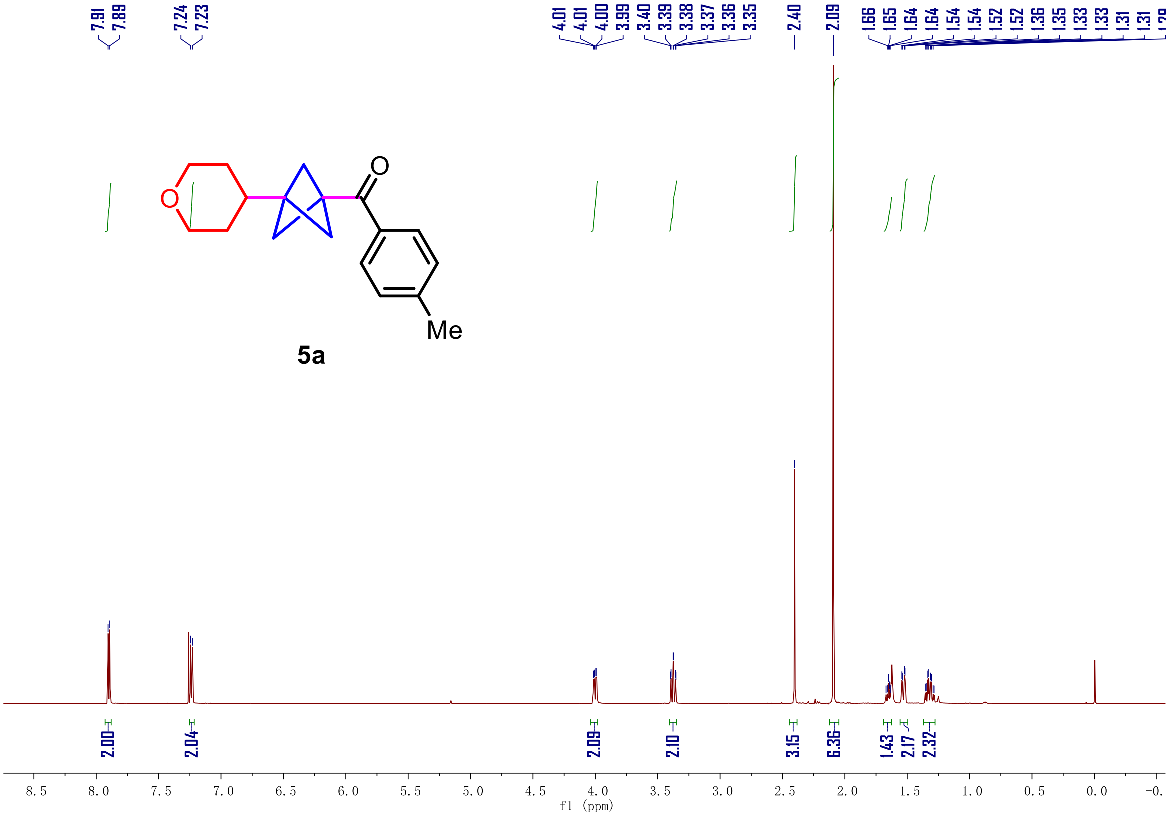
^{13}C NMR spectrum of (4-bromophenyl)(3-(methyl-d_3)bicyclo[1.1.1]pentan-1-yl)methanone (**4ab**)

151 MHz, $CDCl_3$, 23 ℃



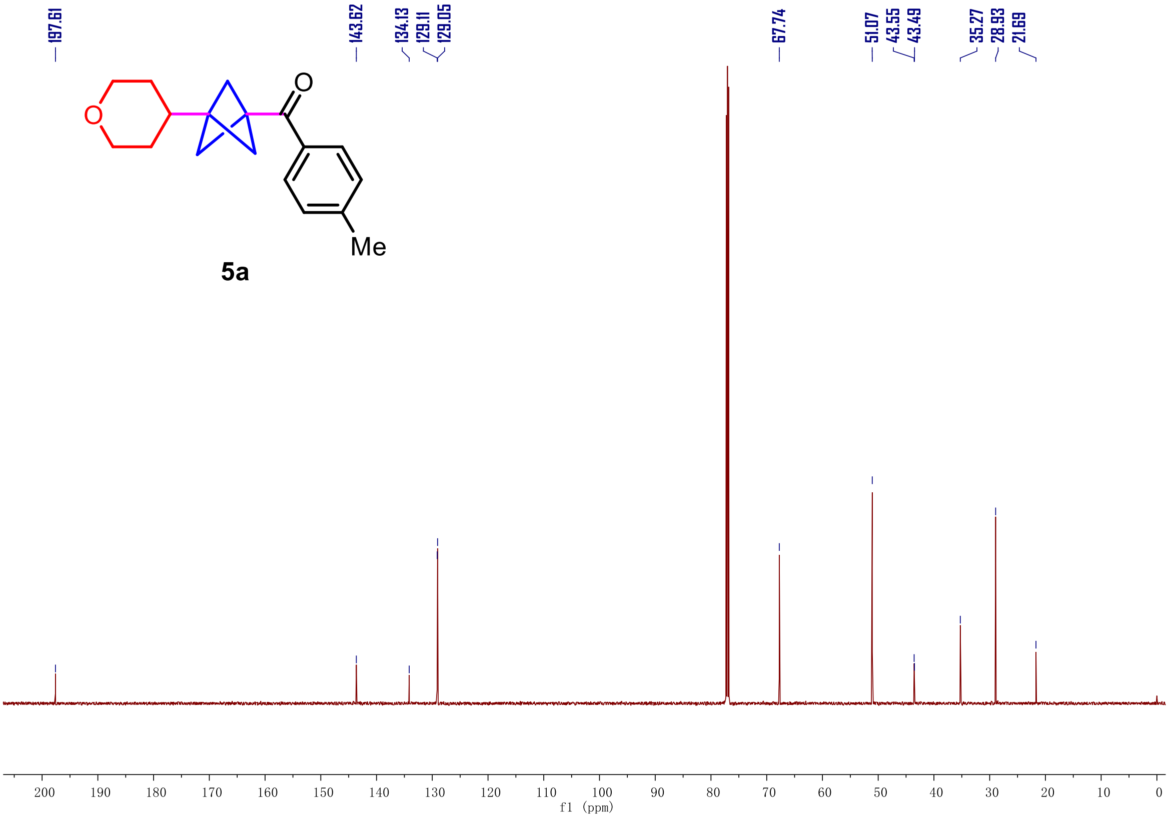
^{1}H NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(p-tolyl)methanone (**5a**)

600 MHz, $CDCl_3$, 23 ℃



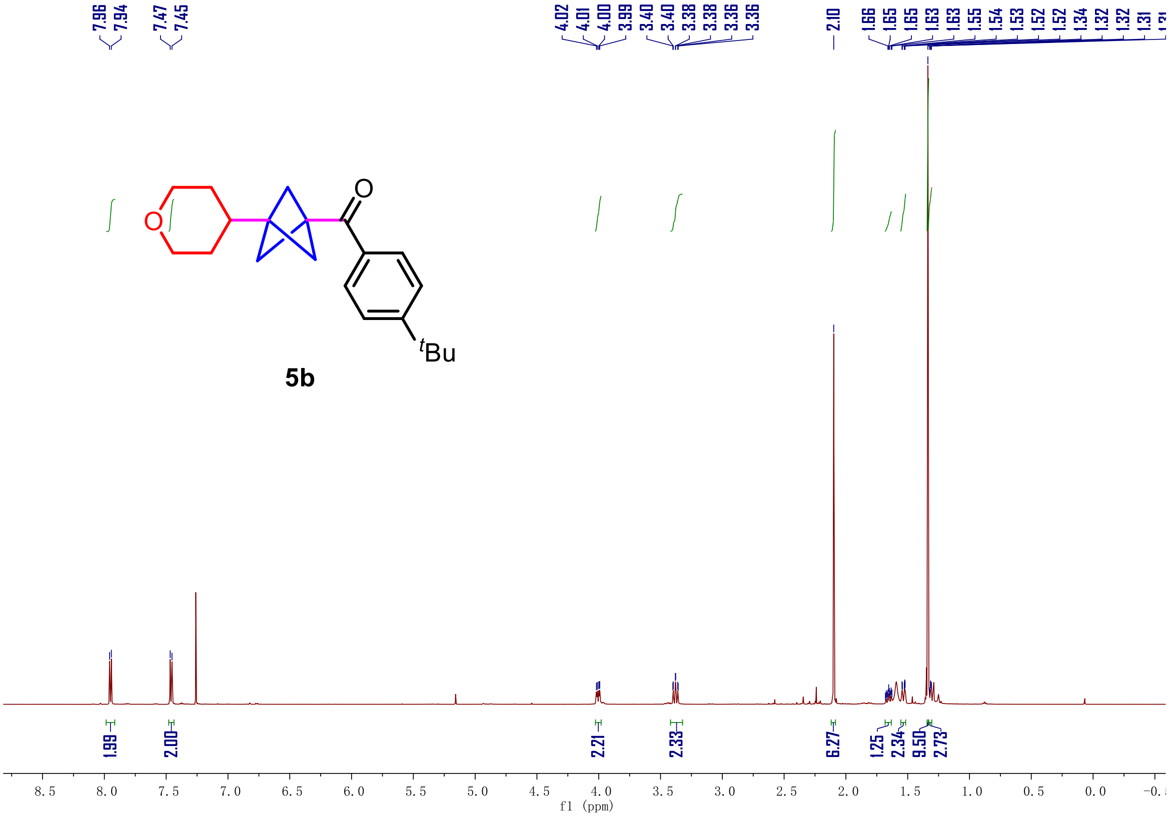
^{13}C NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(p-tolyl)methanone (**5a**)

151 MHz, $CDCl_3$, 23 ℃



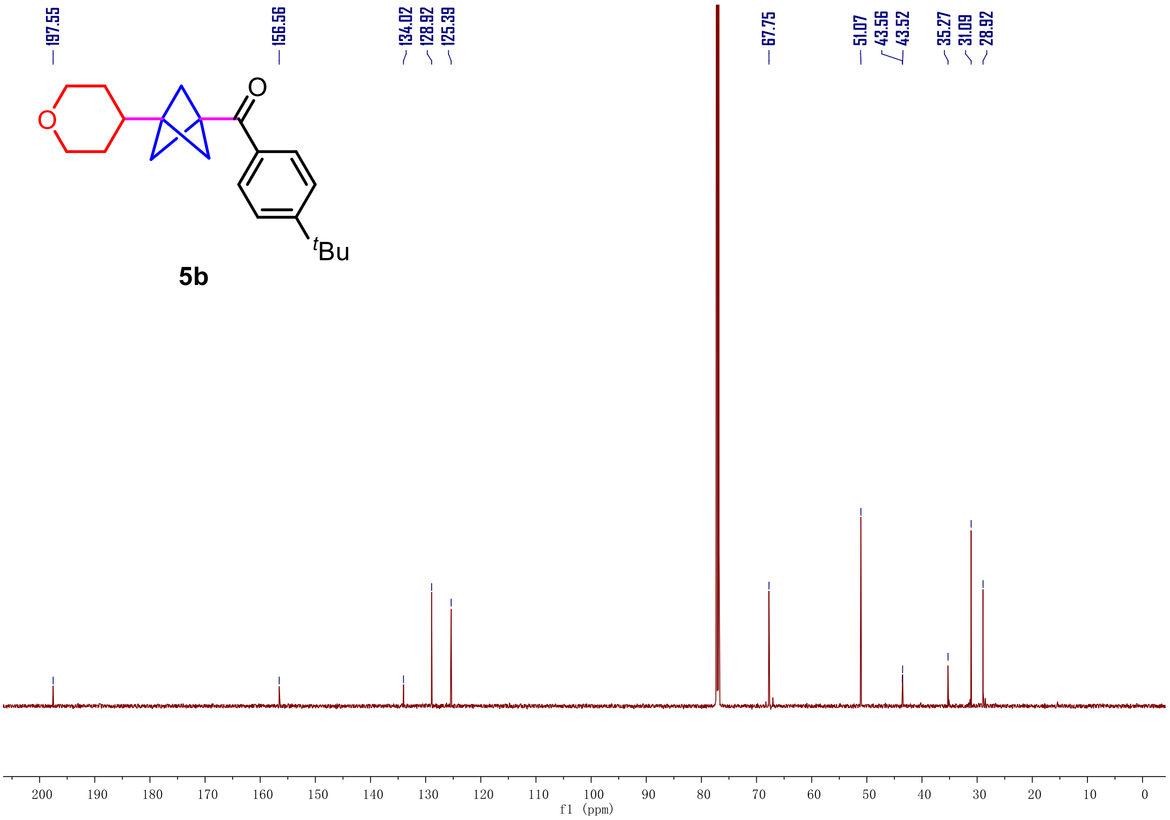
^{1}H NMR spectrum of (4-(*tert*-butyl)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5b**)

600 MHz, $CDCl_3$, 23 ℃



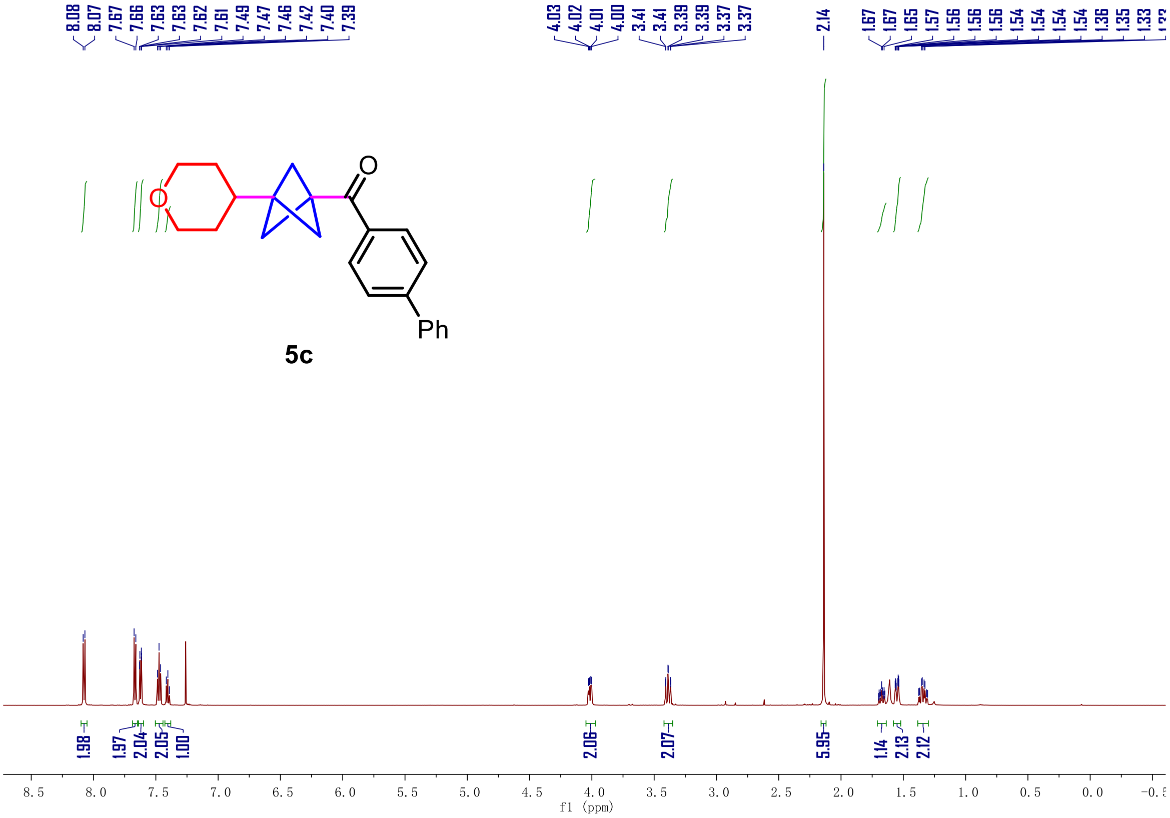
^{13}C NMR spectrum of (4-(*tert*-butyl)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5b**)

151 MHz, $CDCl_3$, 23 ℃



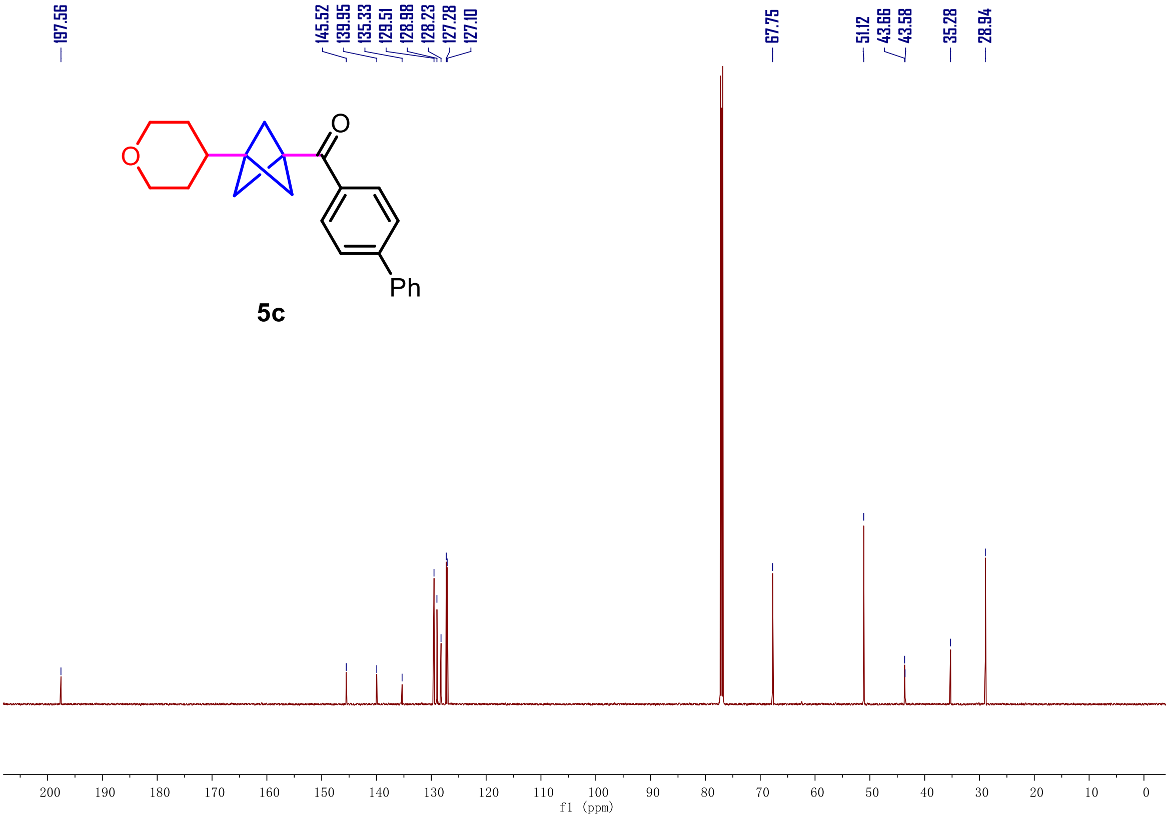
^{1}H NMR spectrum of [1,1'-biphenyl]-4-yl(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5c**)

600 MHz, $CDCl_3$, 23 ℃



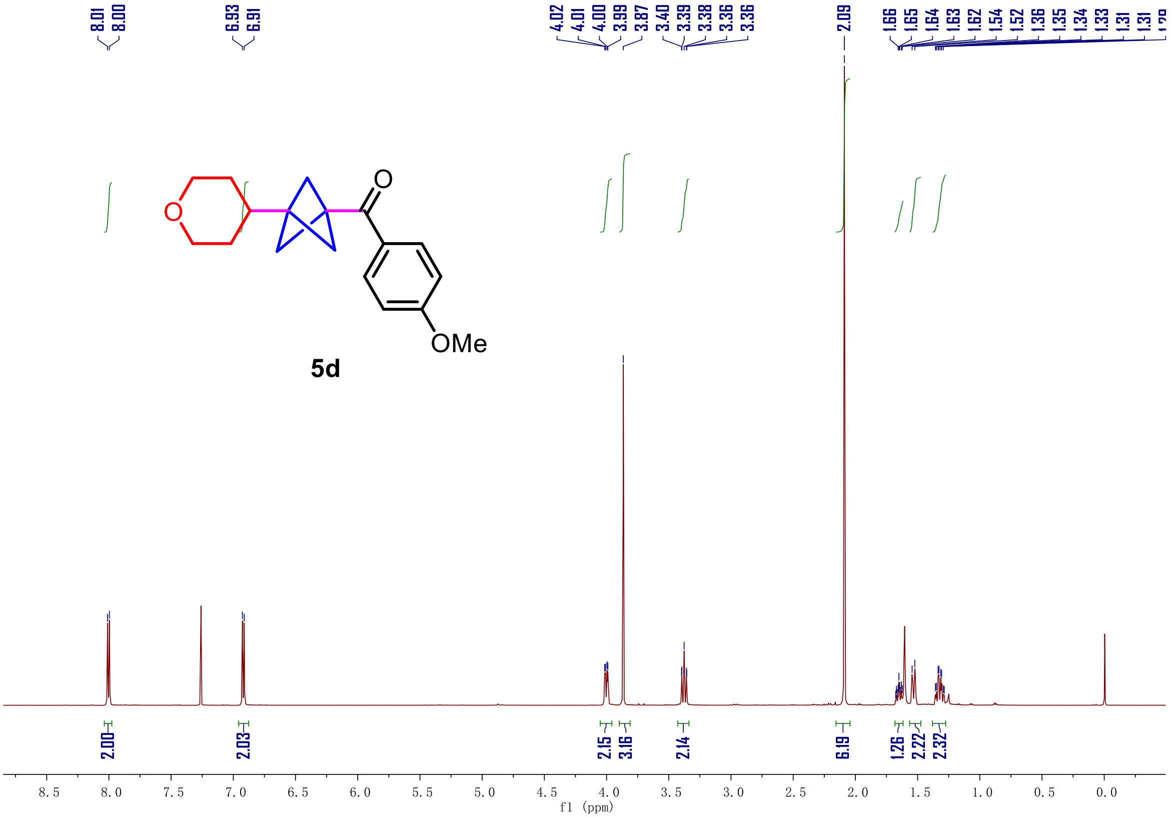
^{13}C NMR spectrum of [1,1'-biphenyl]-4-yl(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5c**)

151 MHz, $CDCl_3$, 23 ℃



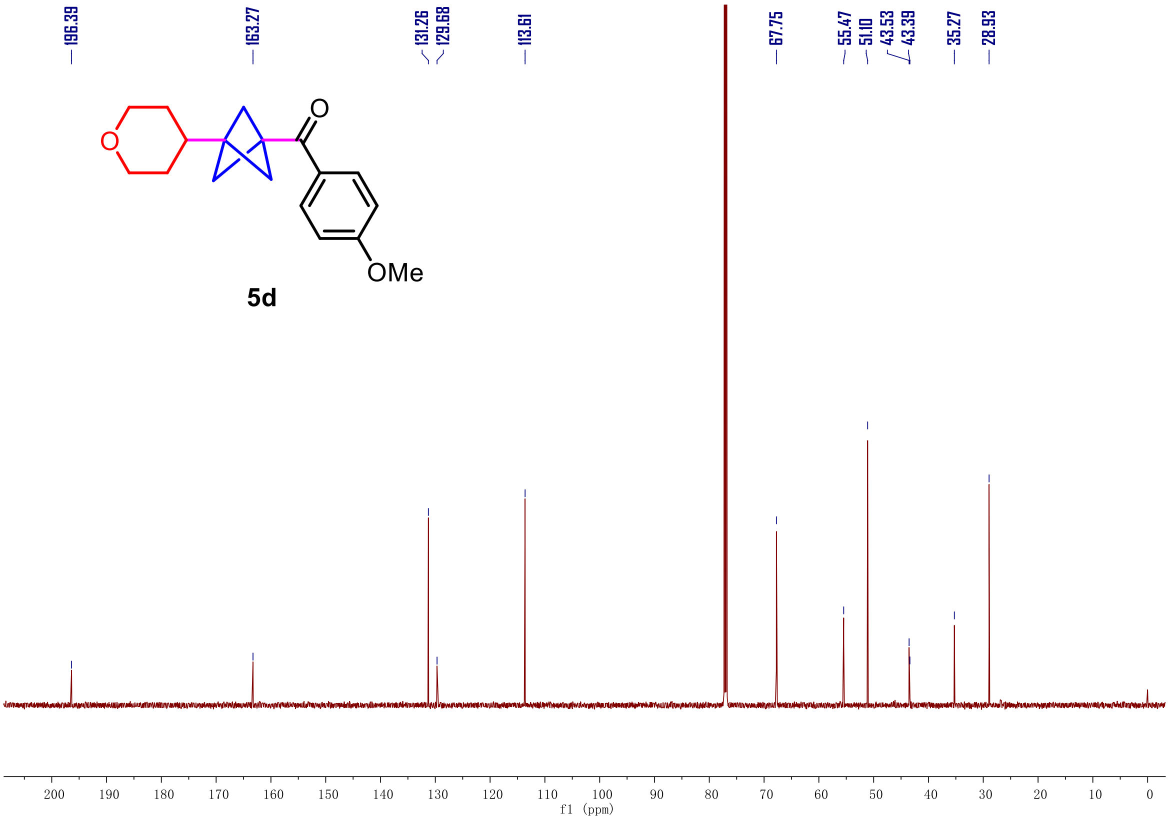
^{1}H NMR spectrum of (4-methoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5d**)

600 MHz, $CDCl_3$, 23 ℃

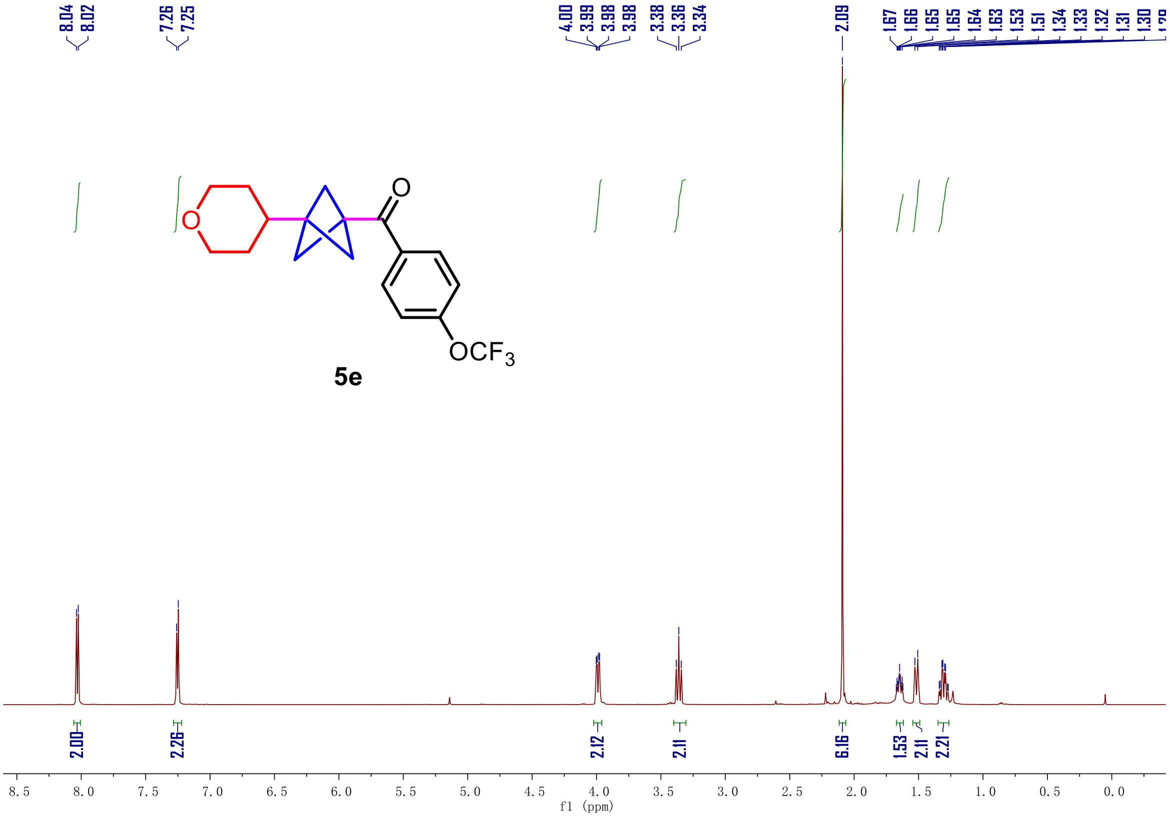


^{13}C NMR spectrum of (4-methoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5d**)

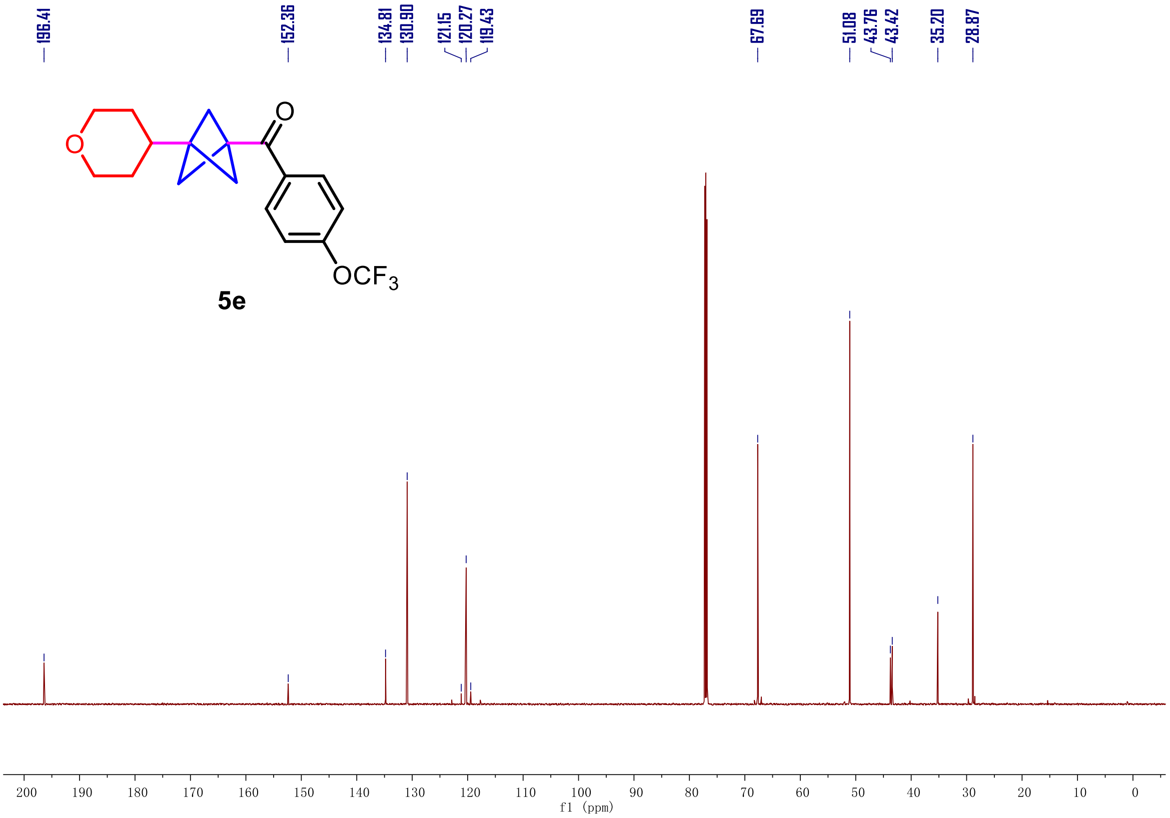
151 MHz, $CDCl_3$, 23 ℃



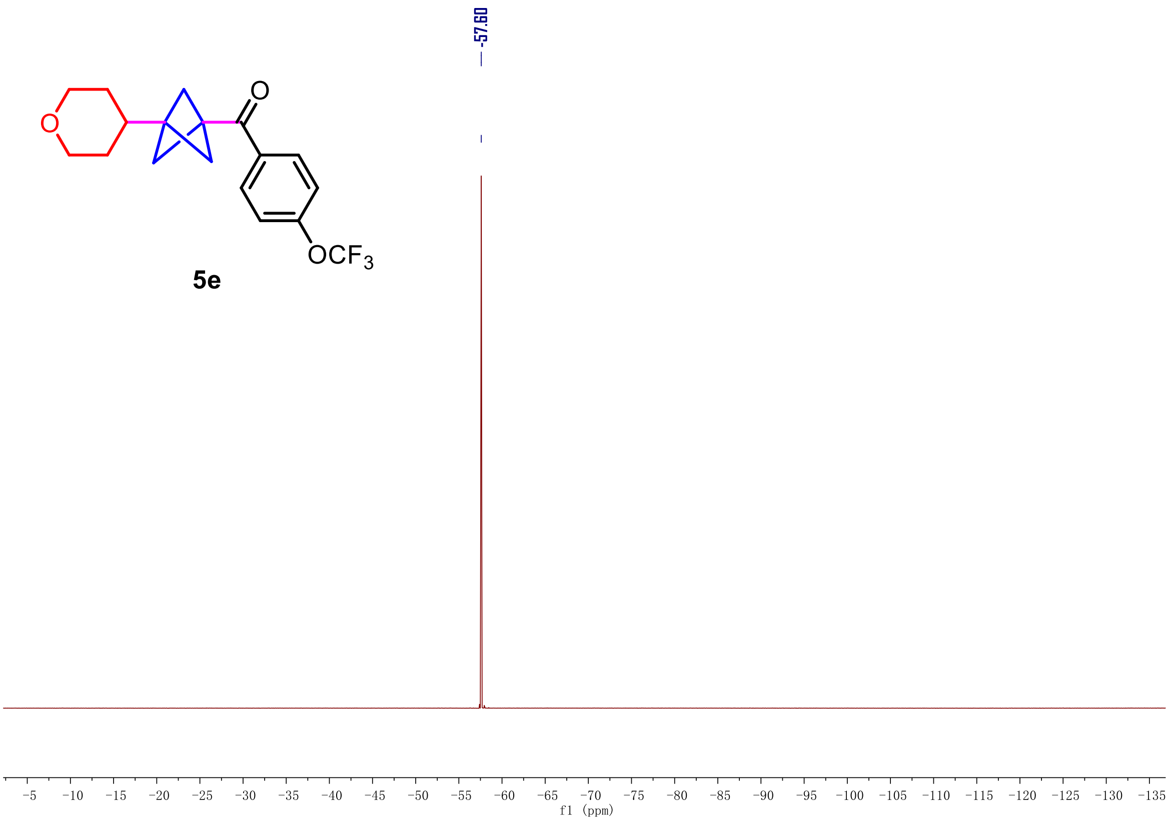
^{1}H NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanone (**5e**) 600 MHz, CDCl$_3$, 23 ℃



^{13}C NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanone (**5e**) 151 MHz, CDCl$_3$, 23 ℃

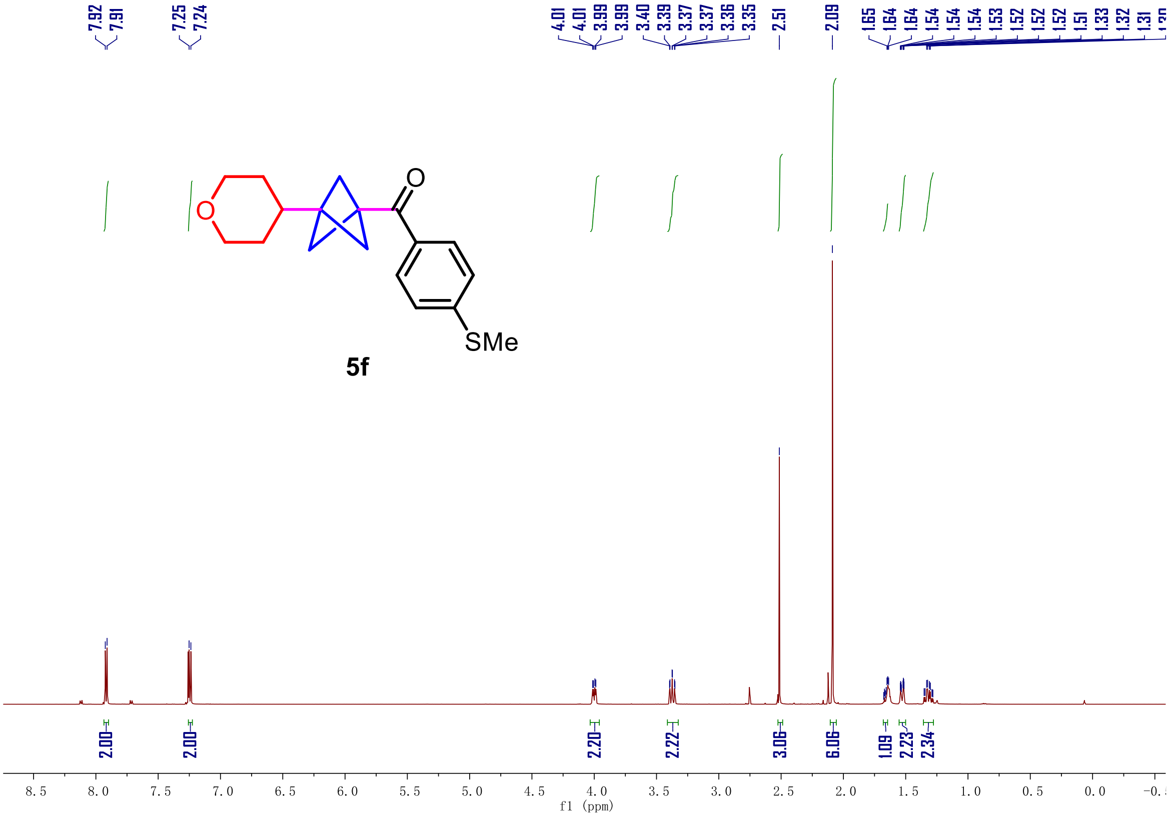


^{19}F NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanone (**5e**) 565 MHz, $CDCl_3$, 23 ℃



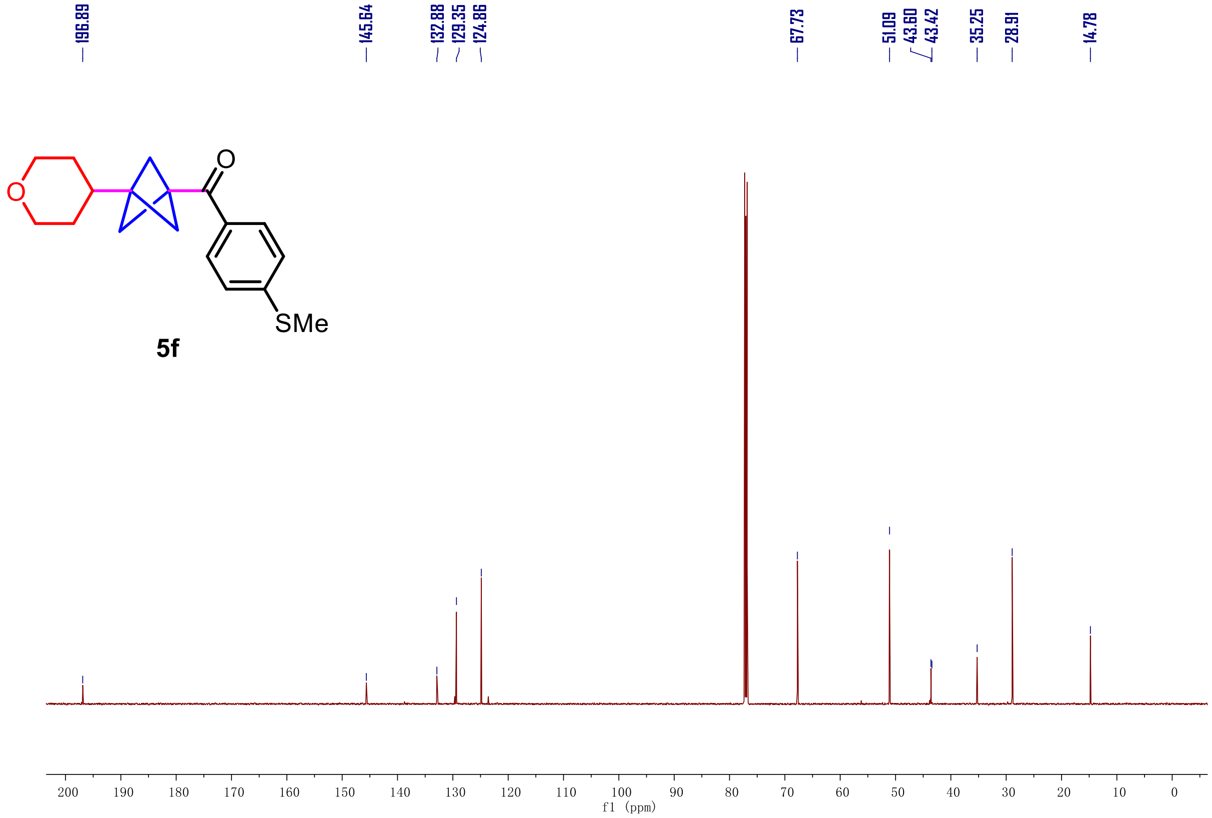
^{1}H NMR spectrum of (4-(methylthio)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5f**)

600 MHz, $CDCl_3$, 23 ℃



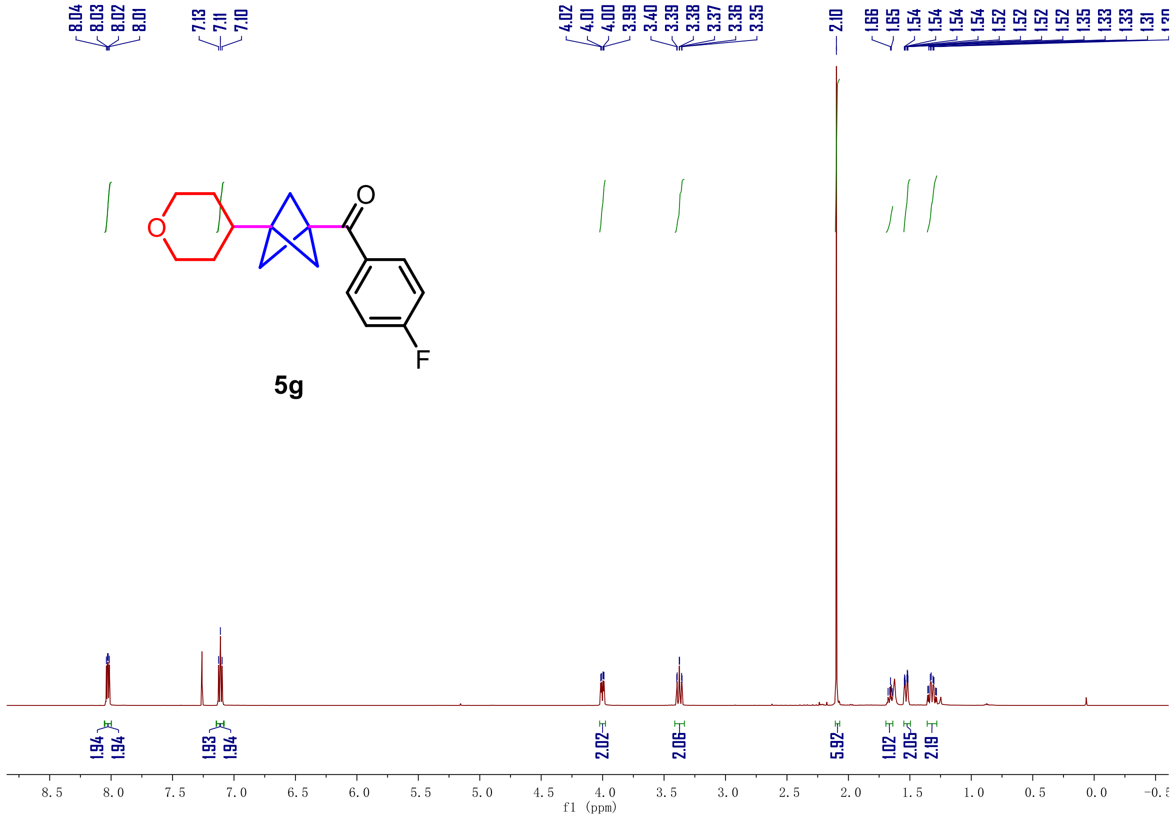
^{13}C NMR spectrum of (4-(methylthio)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone(**5f**)

600 MHz, CDCl$_3$, 23 ℃



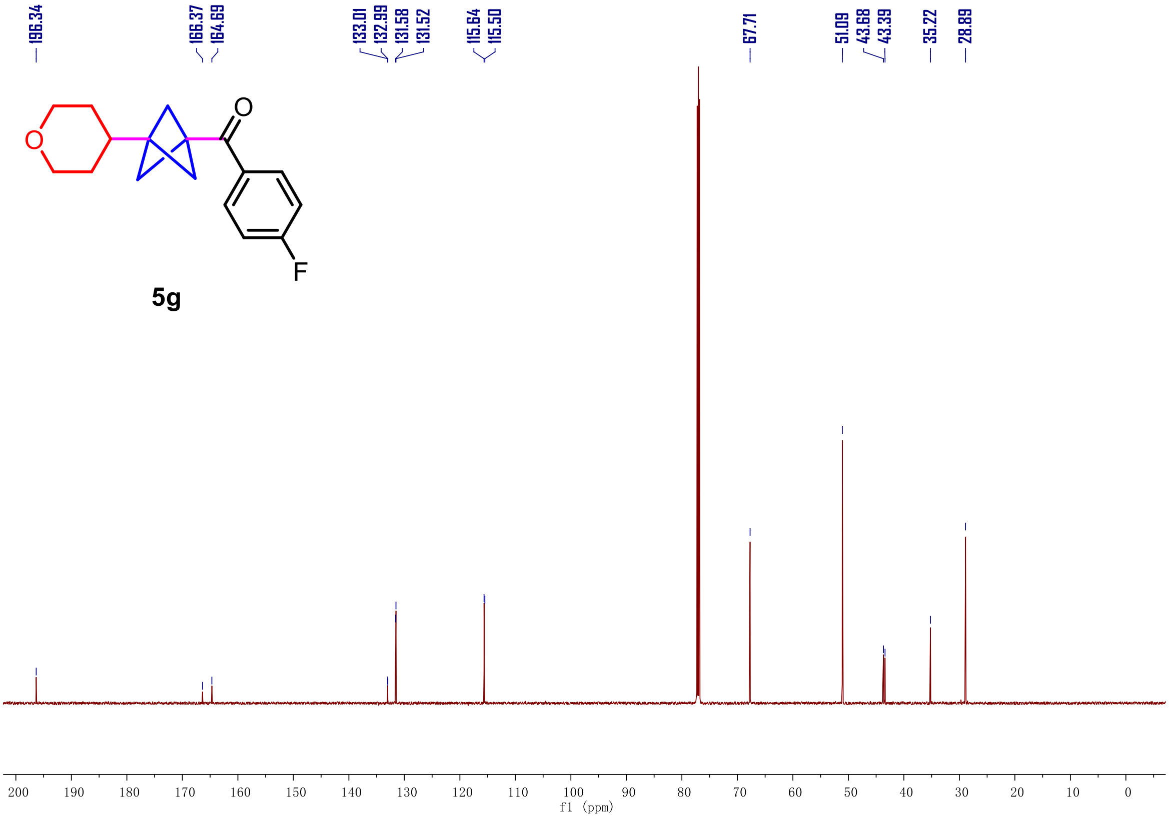
^{1}H NMR spectrum of (4-fluorophenyl)(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5g**)

600 MHz, CDCl$_3$, 23 ℃



^{13}C NMR spectrum of (4-fluorophenyl)(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5g**)

151 MHz, CDCl$_3$, 23 ℃

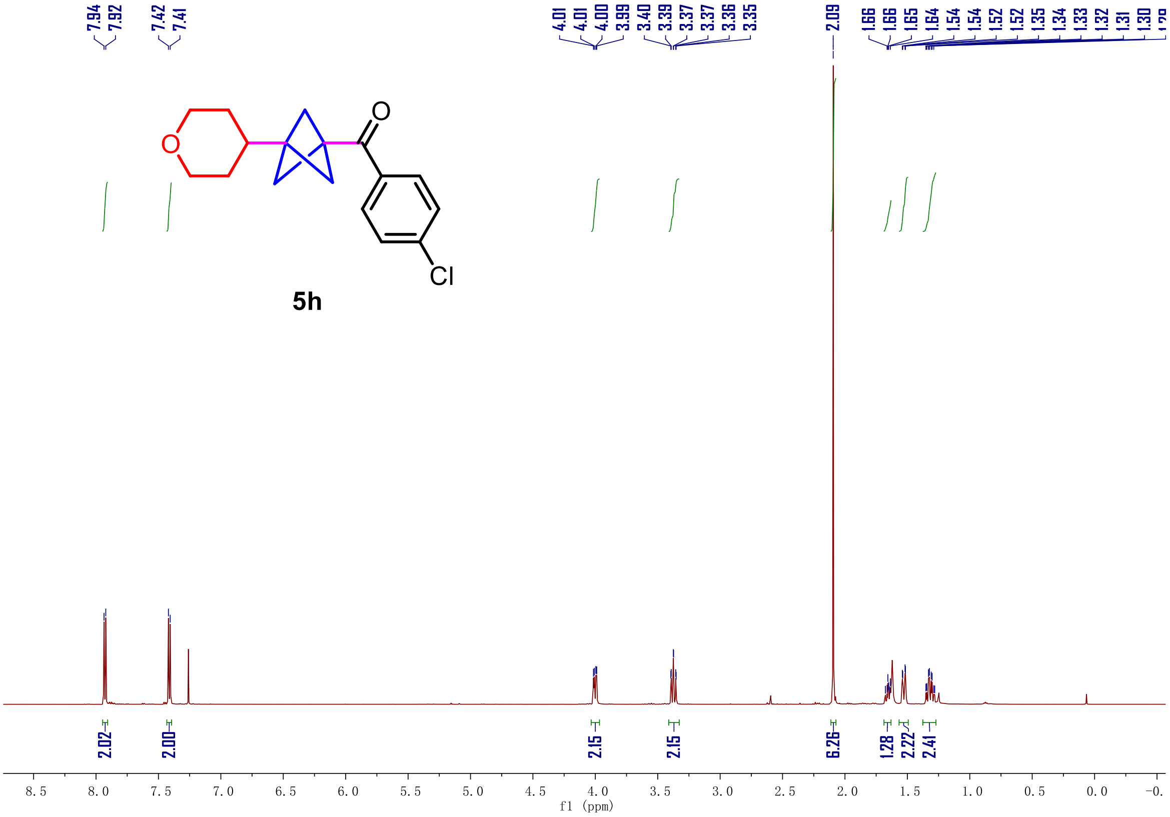


^{19}F NMR spectrum of (4-fluorophenyl)(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5g**)

600 MHz, CDCl$_3$, 23 ℃

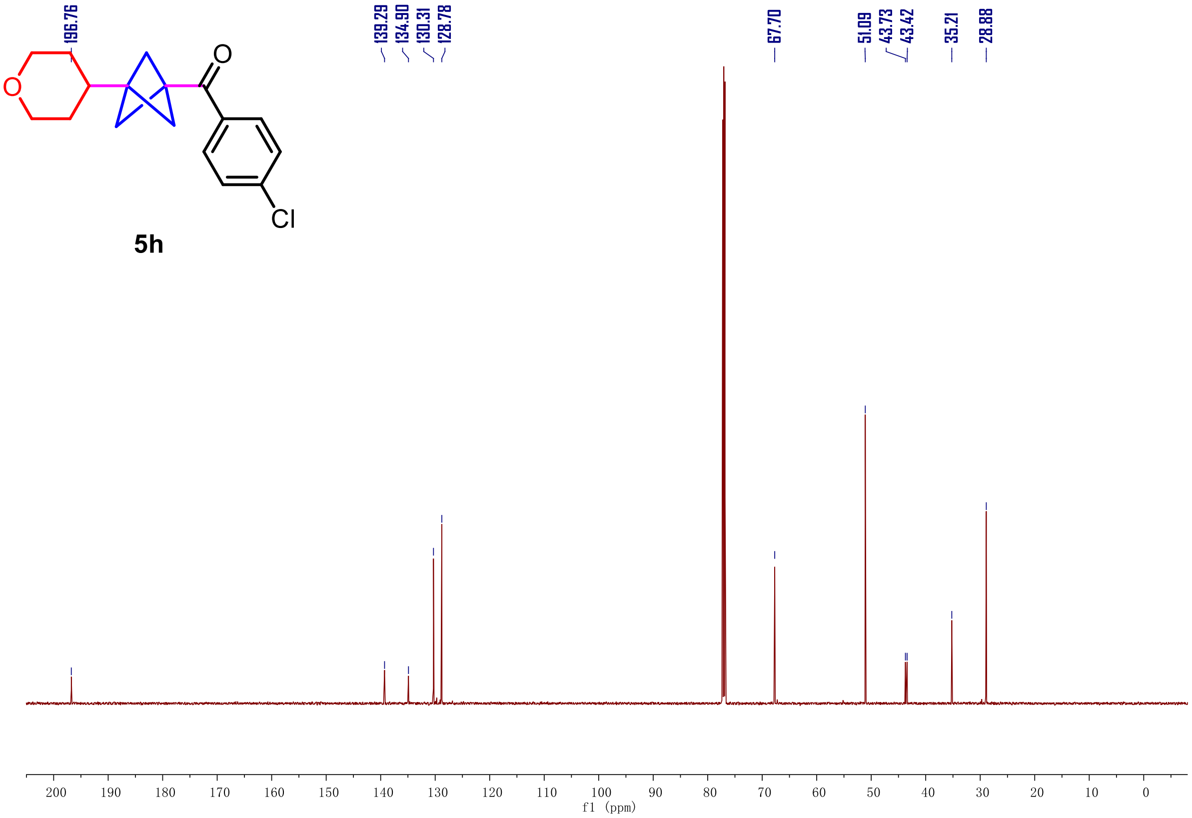
^{1}H NMR spectrum of (4-chlorophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5h**)

600 MHz, $CDCl_3$, 23 ℃



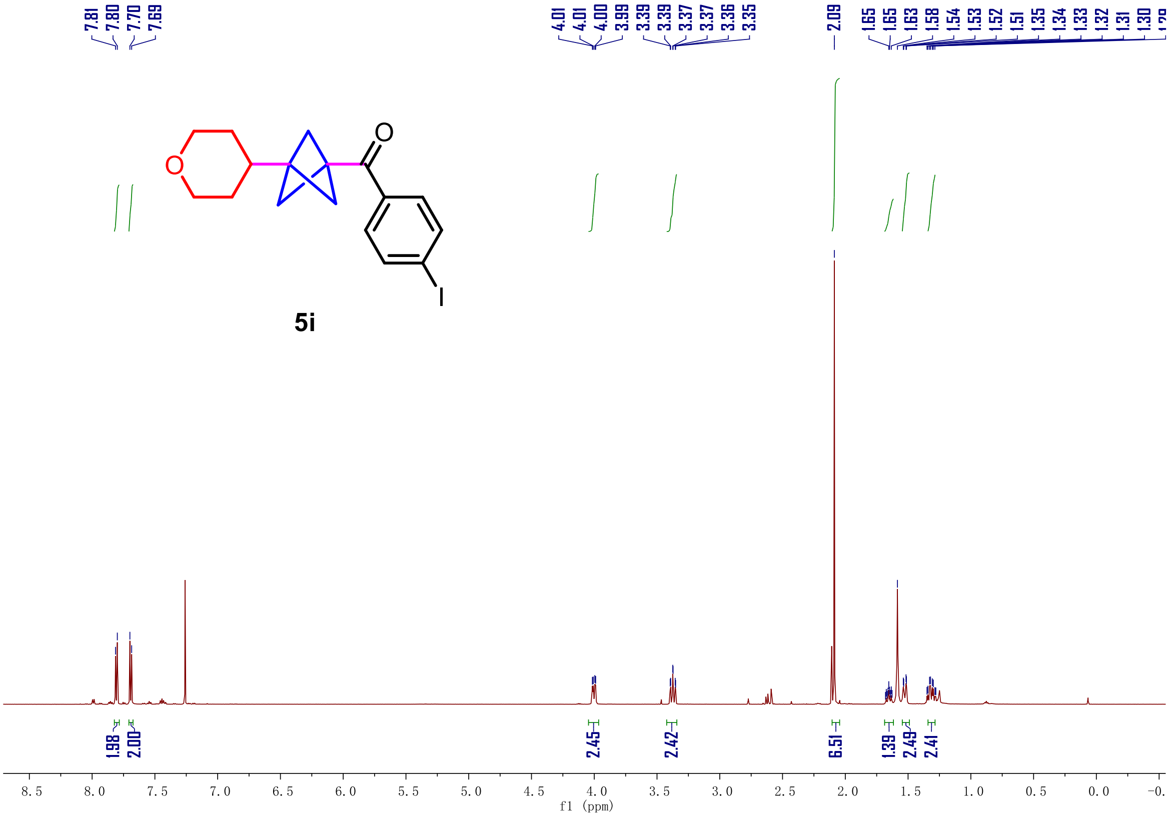
^{13}C NMR spectrum of (4-chlorophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5h**)

151 MHz, $CDCl_3$, 23 ℃



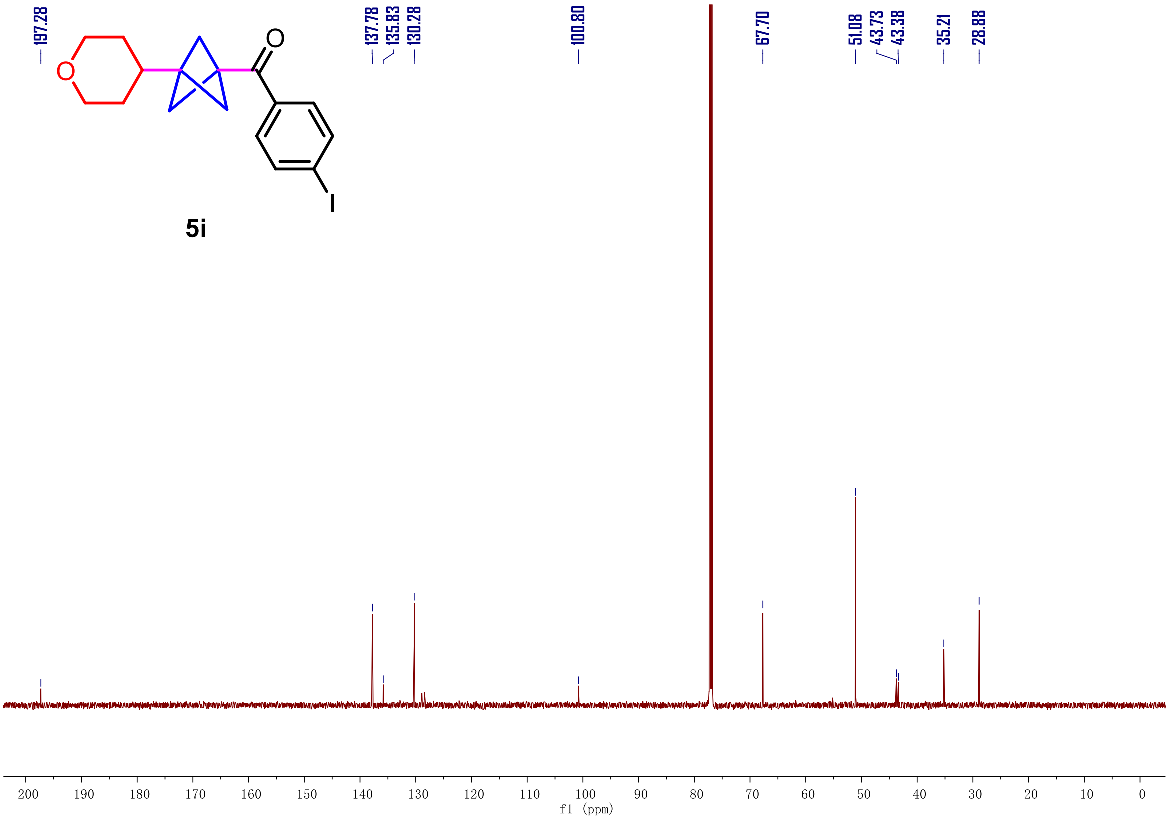
^{1}H NMR spectrum of (4-iodophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5i**)

600 MHz, $CDCl_3$, 23 ℃



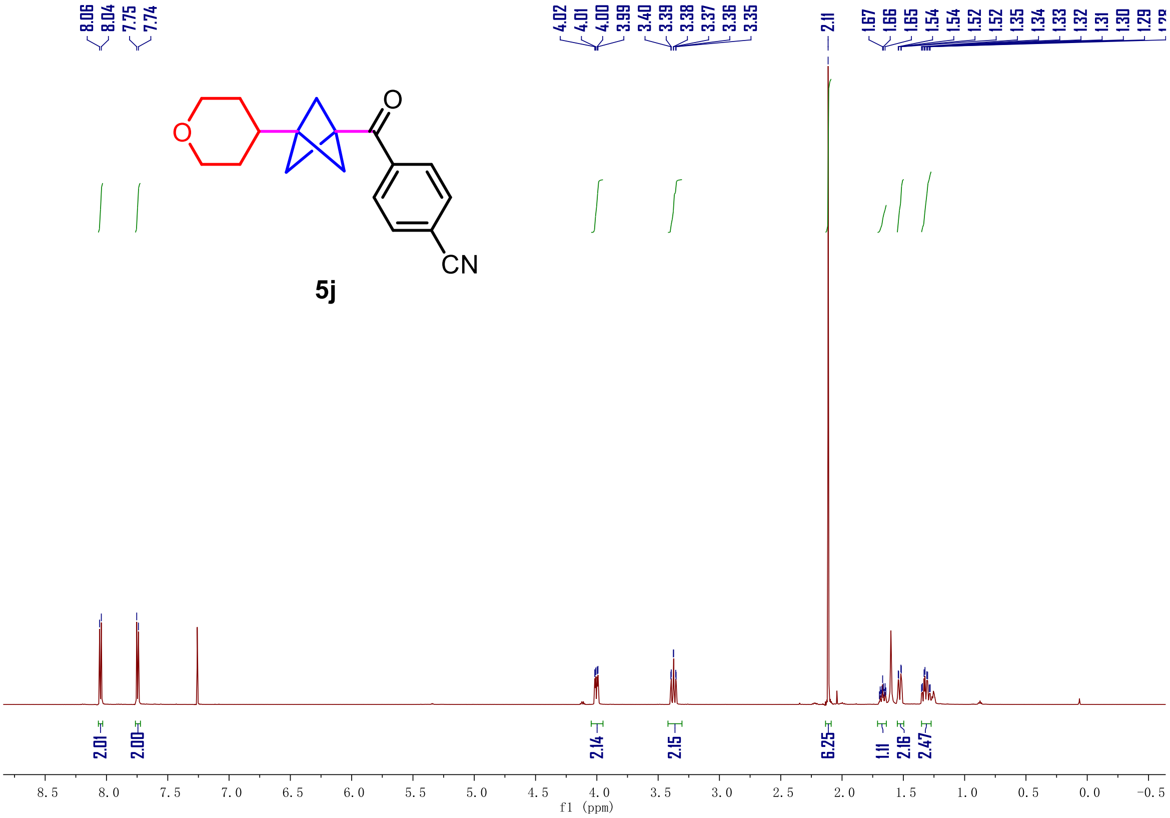
^{13}C NMR spectrum of (4-iodophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5i**)

151 MHz, $CDCl_3$, 23 ℃



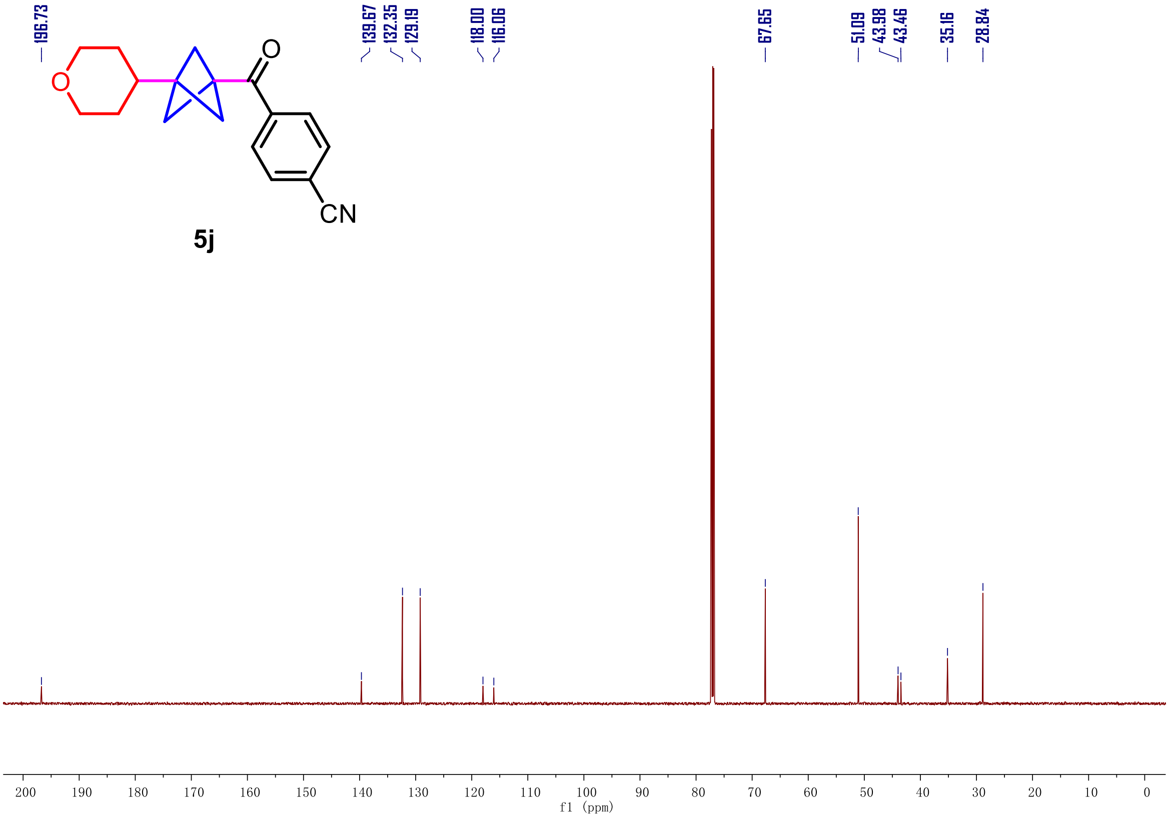
^{1}H NMR spectrum of 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (**5j**)

600 MHz, $CDCl_3$, 23 ℃



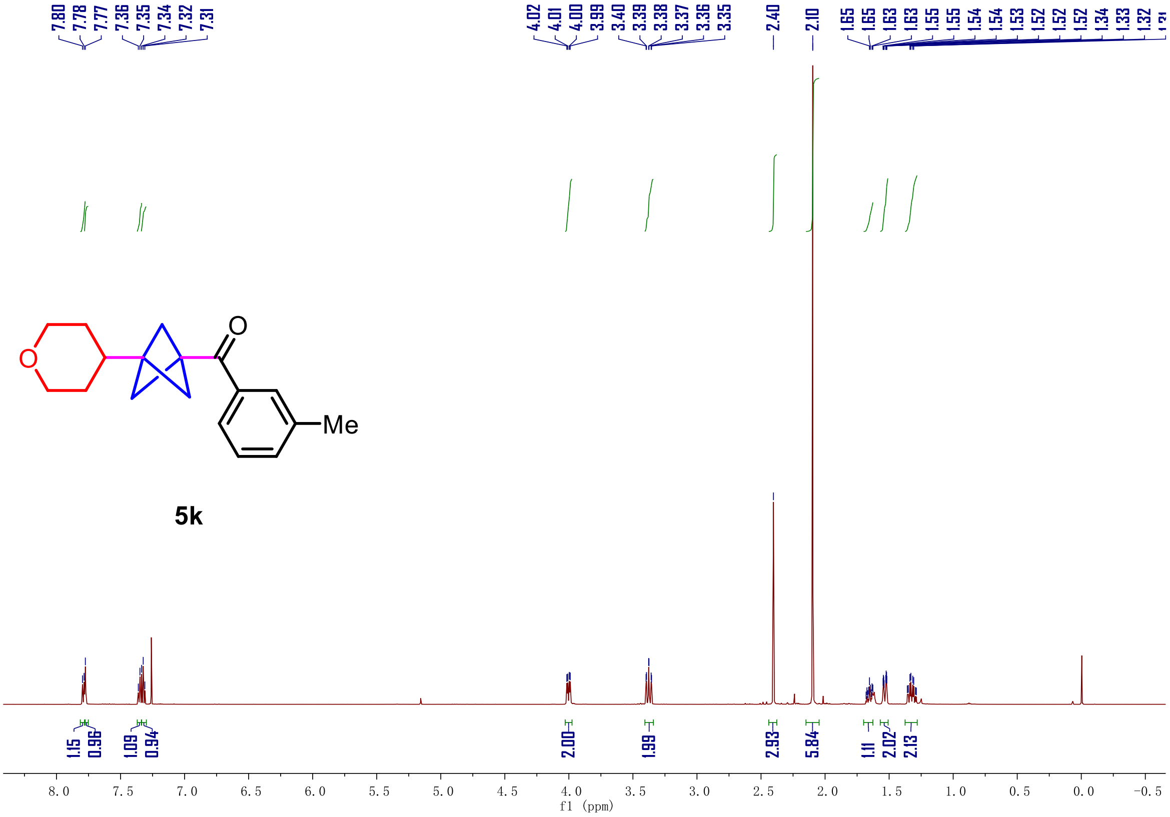
^{13}C NMR spectrum of 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (**5j**)

151 MHz, $CDCl_3$, 23 ℃



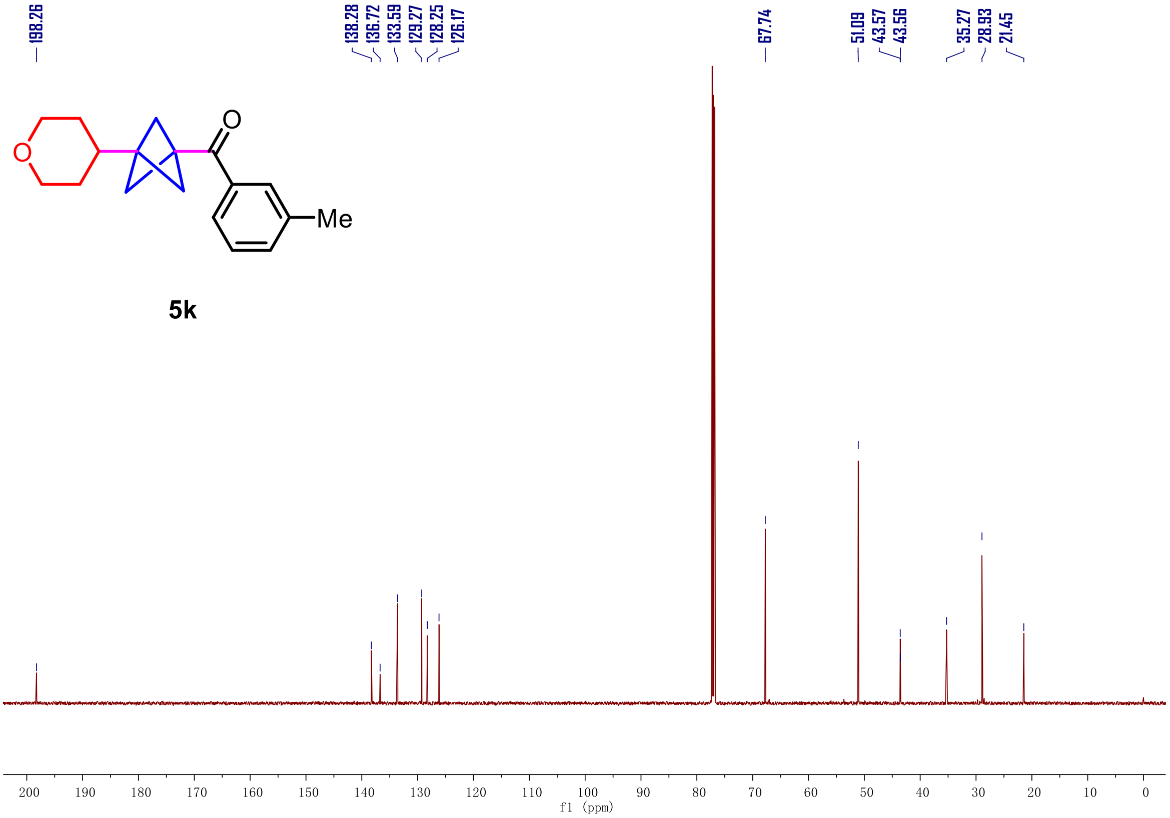
^{1}H NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(*m*-tolyl)methanone (**5k**)

600 MHz, $CDCl_3$, 23 ℃



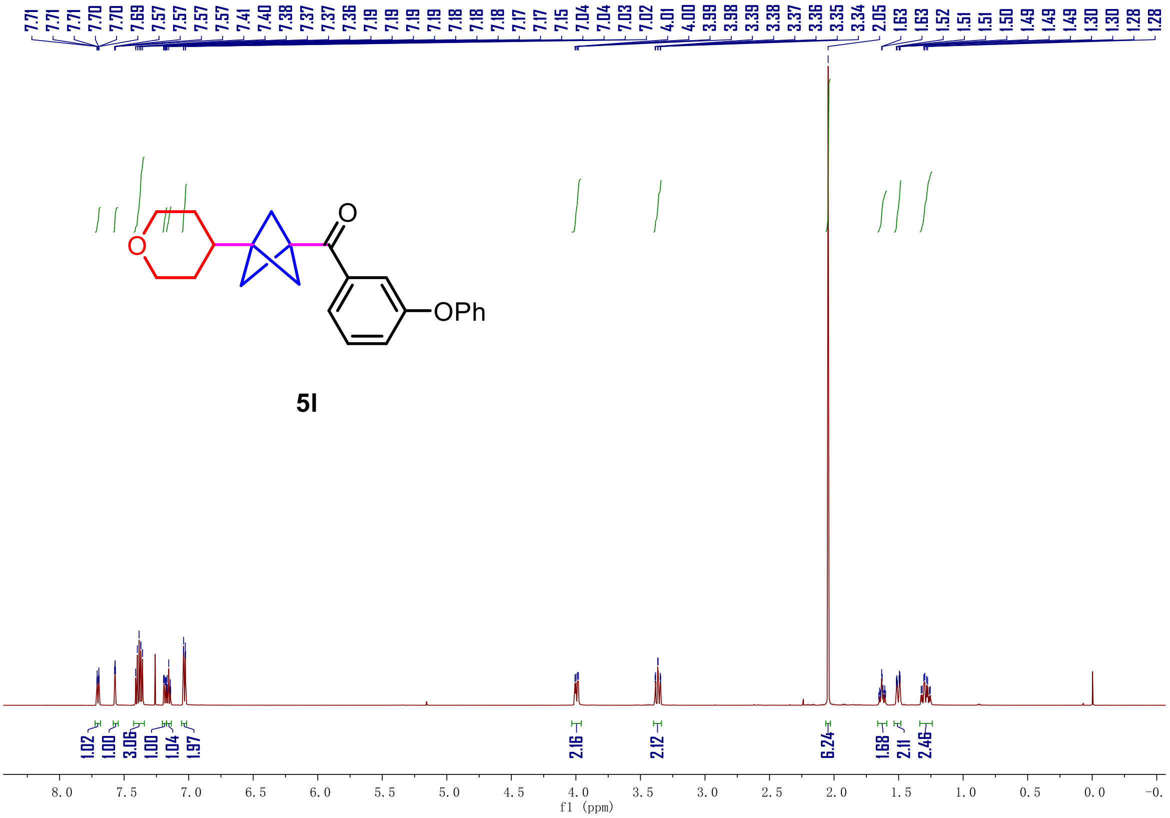
^{13}C NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(*m*-tolyl)methanone (**5k**)

151 MHz, $CDCl_3$, 23 ℃



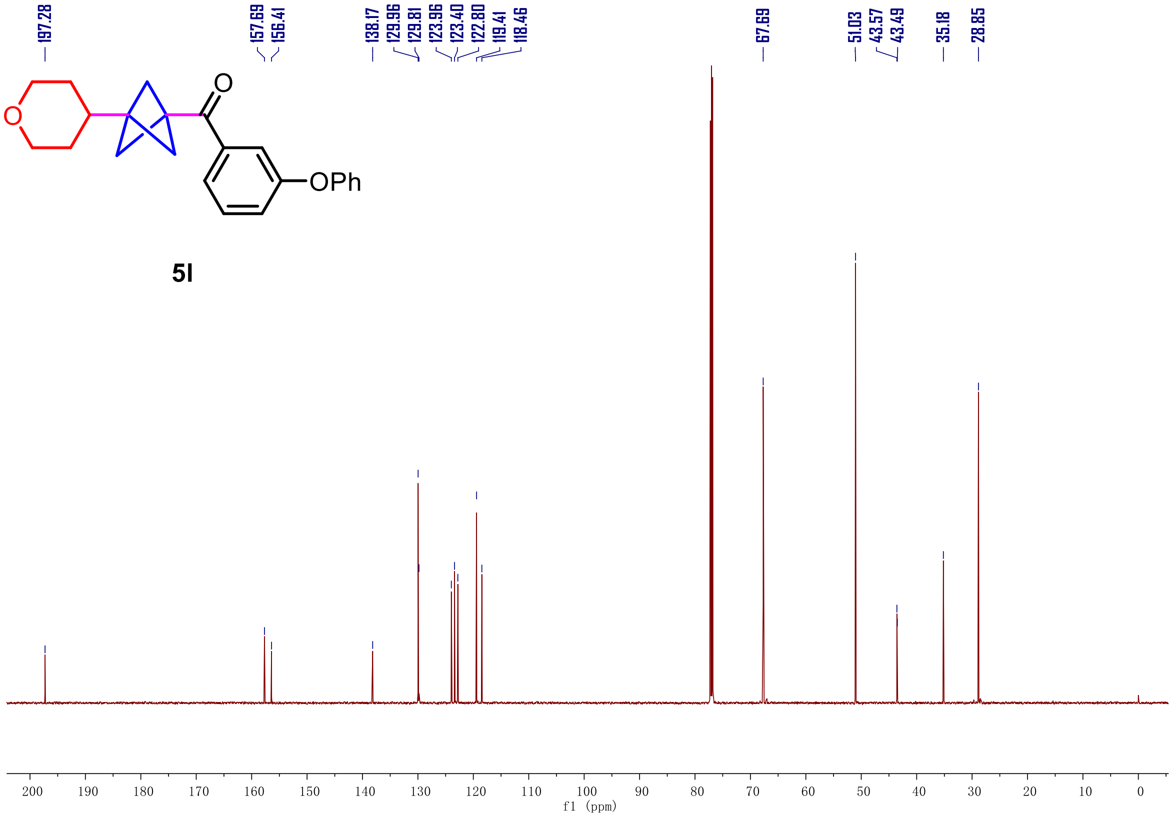
^{1}H NMR spectrum of (3-phenoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5l**)

600 MHz, $CDCl_3$, 23 ℃

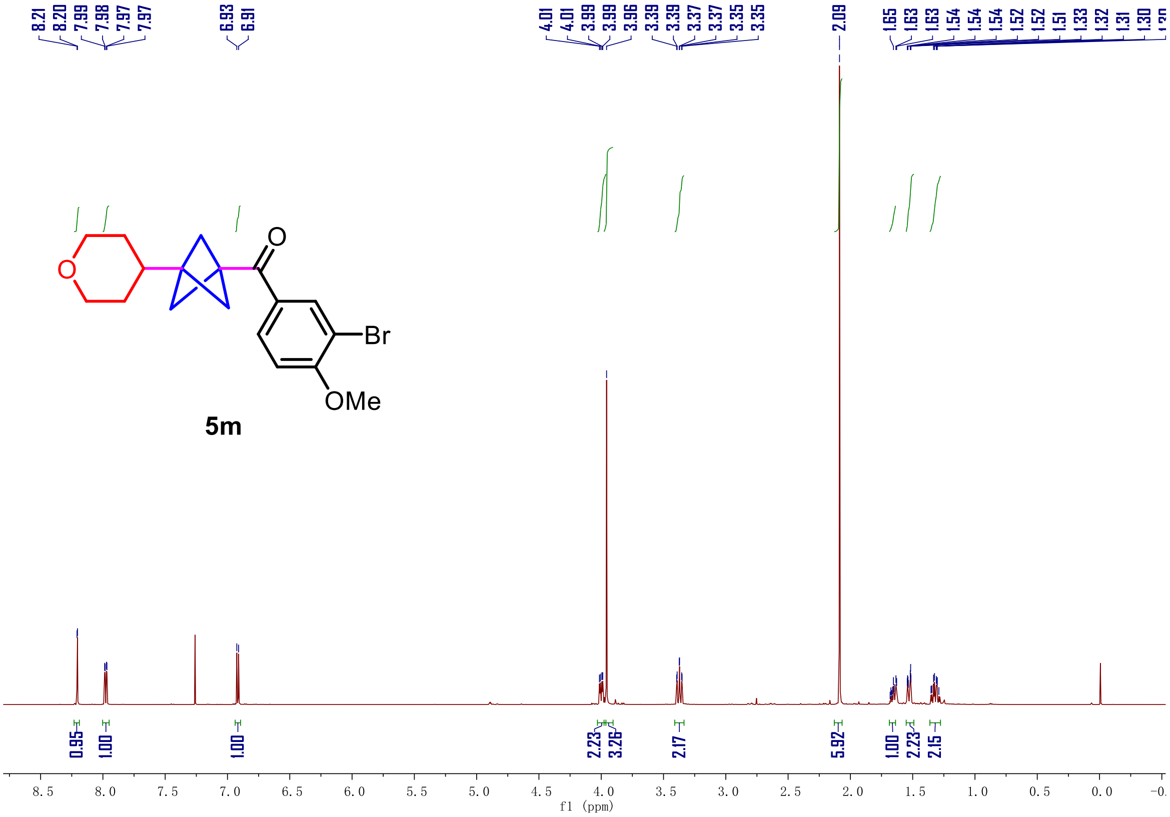


^{13}C NMR spectrum of (3-phenoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5l**)

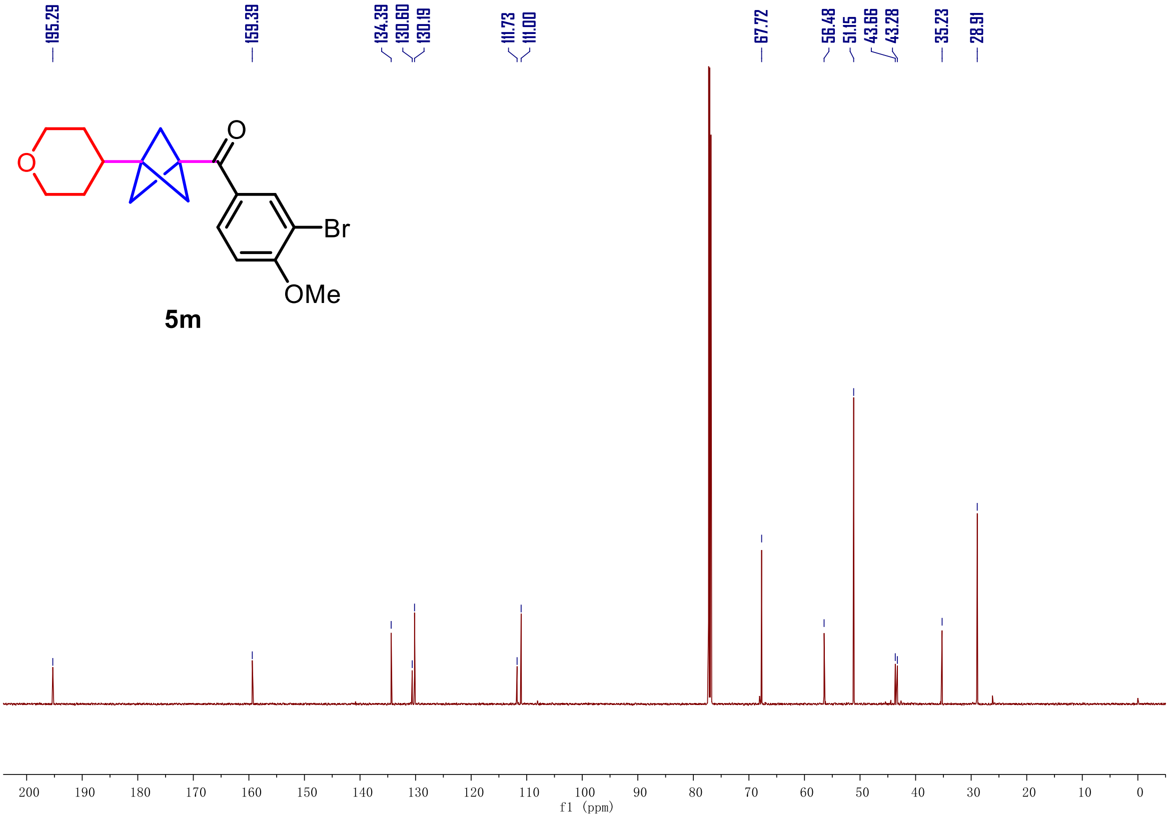
151 MHz, $CDCl_3$, 23 ℃



^{1}H NMR spectrum of (3-bromo-4-methoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5m**) 600 MHz, $CDCl_3$, 23 ℃

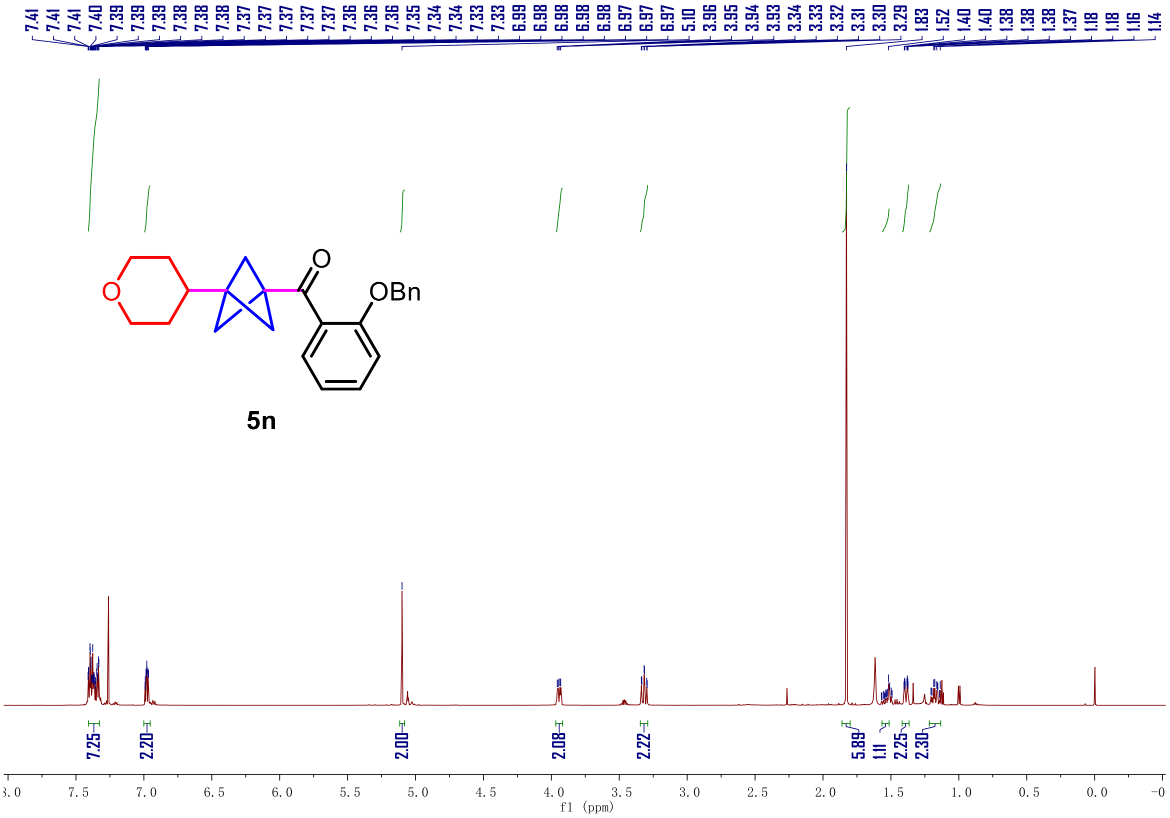


^{13}C NMR spectrum of (3-bromo-4-methoxyphenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5m**) 151 MHz, $CDCl_3$, 23 ℃

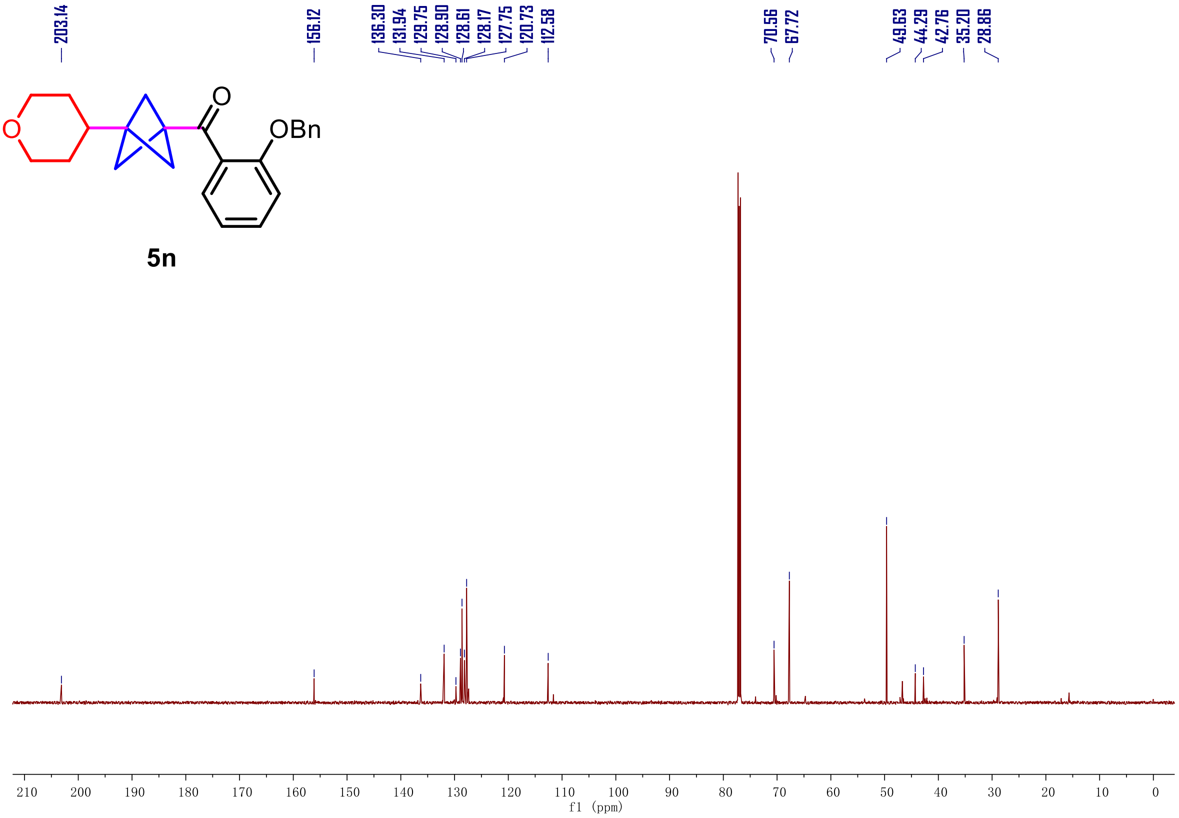


^{1}H NMR spectrum of (2-(benzyloxy)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5n**)

600 MHz, $CDCl_3$, 23 ℃

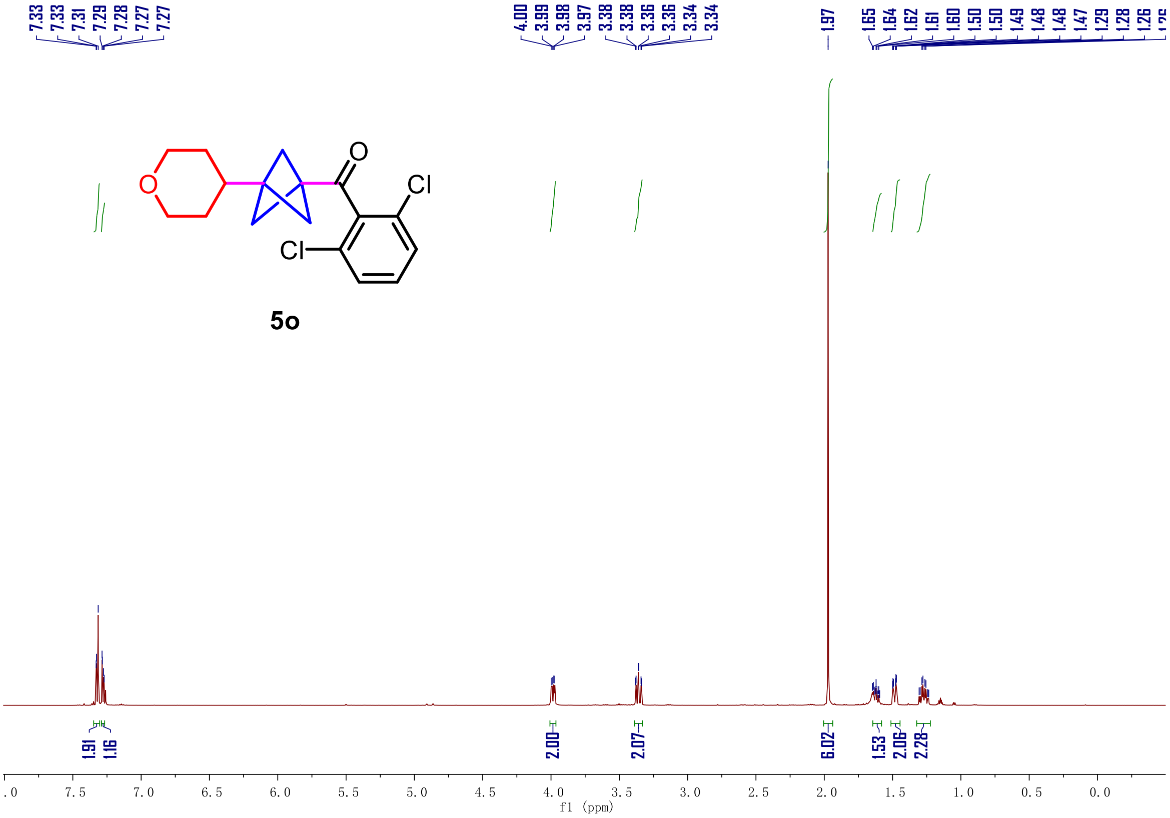


^{13}C NMR spectrum of (2-(benzyloxy)phenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5n**) 151 MHz, $CDCl_3$, 23 ℃



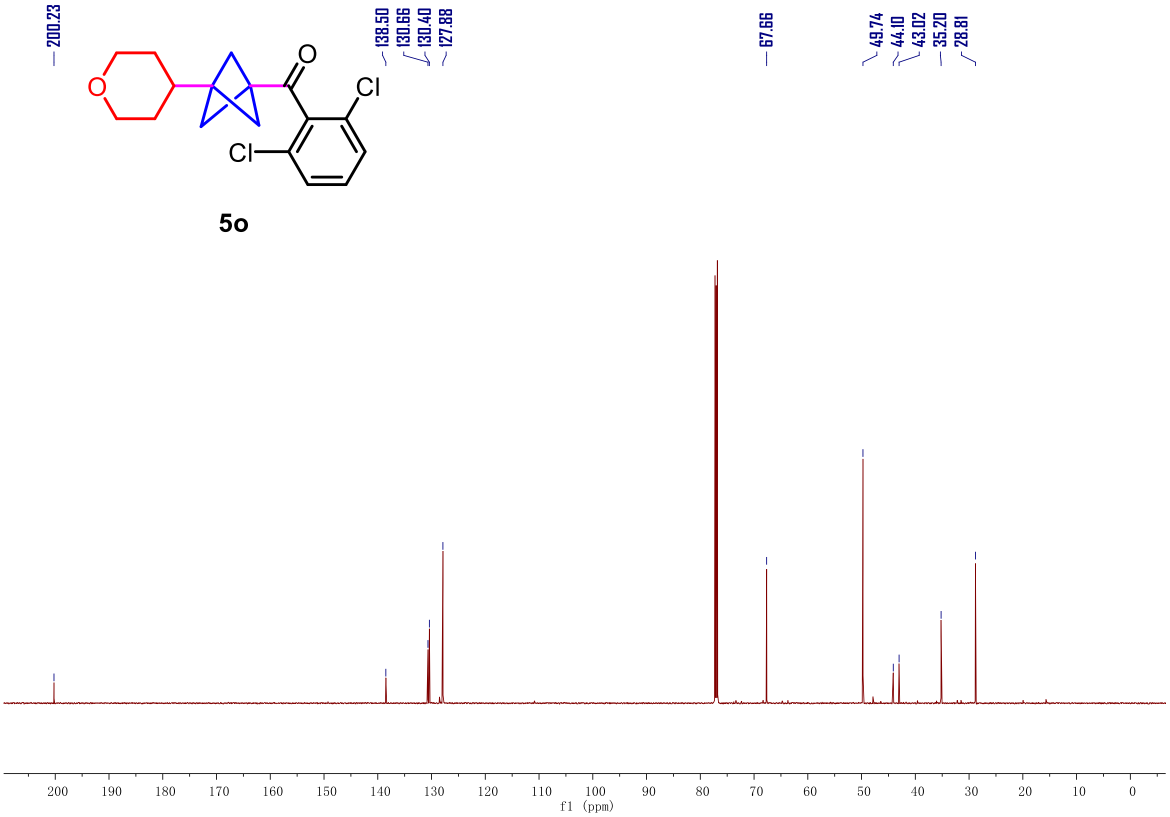
^{1}H NMR spectrum of (2,6-dichlorophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5o**)

600 MHz, $CDCl_3$, 23 ℃



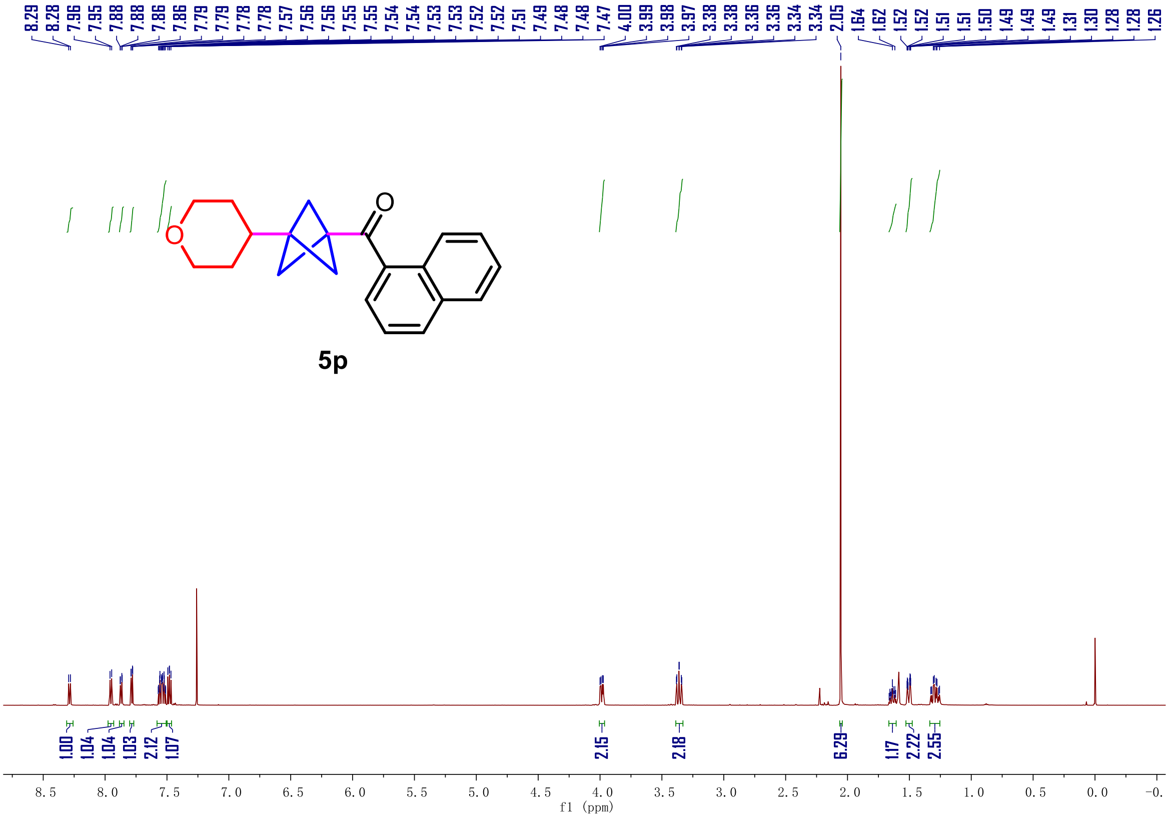
^{13}C NMR spectrum of (2,6-dichlorophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5o**)

151 MHz, $CDCl_3$, 23 ℃



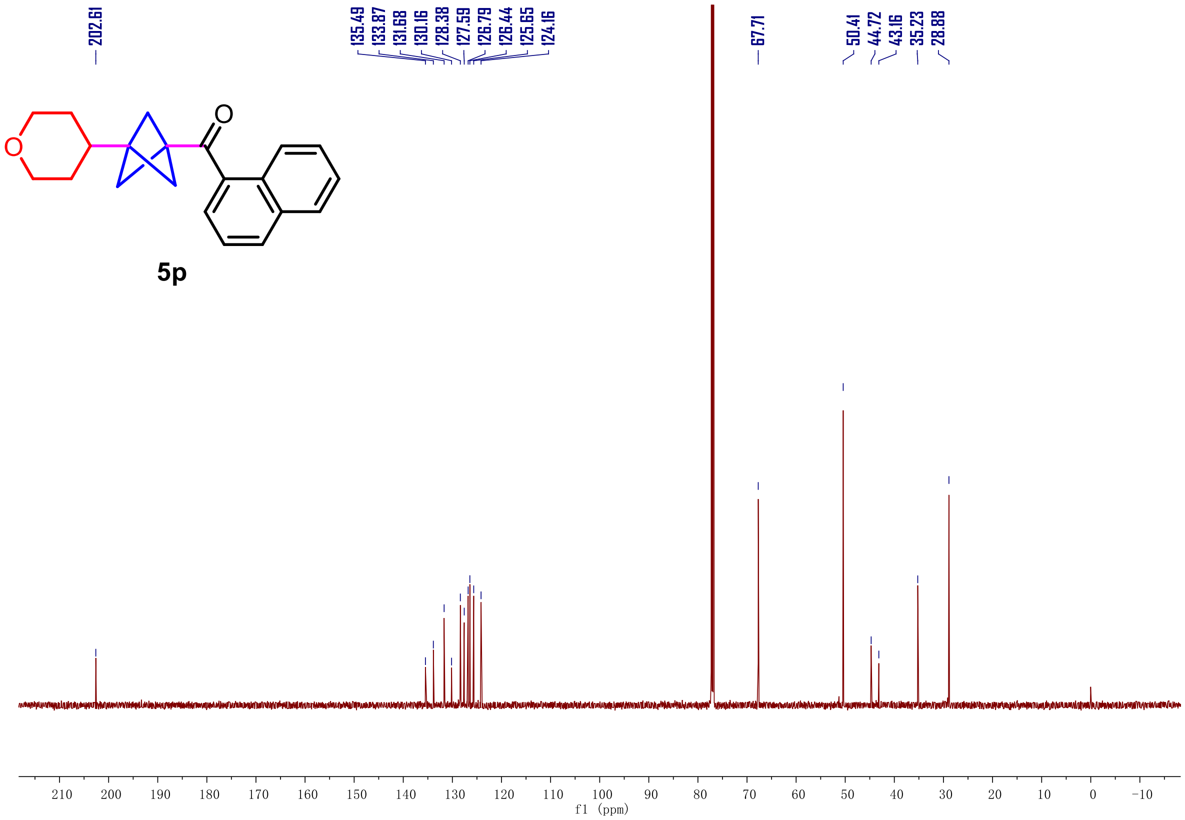
^{1}H NMR spectrum of naphthalen-1-yl(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5p**)

600 MHz, $CDCl_3$, 23 ℃



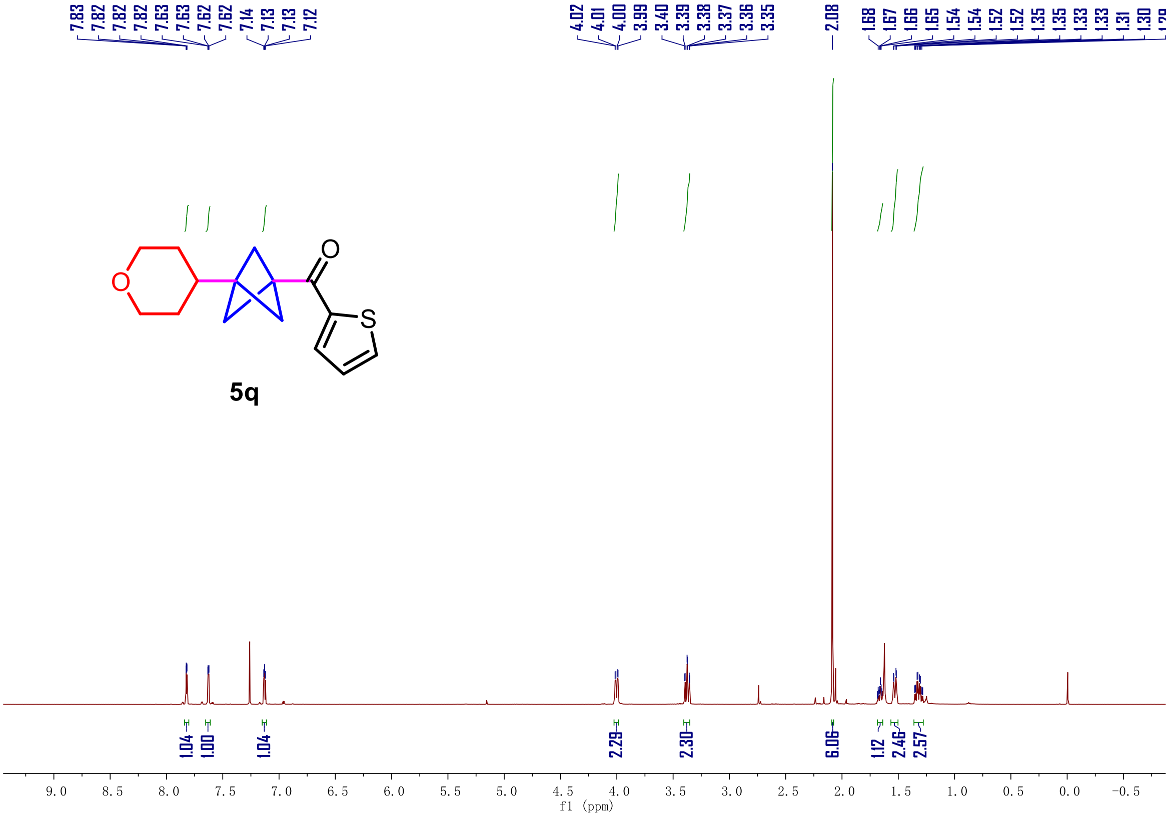
^{13}C NMR spectrum of naphthalen-1-yl(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5p**)

151 MHz, $CDCl_3$, 23 ℃



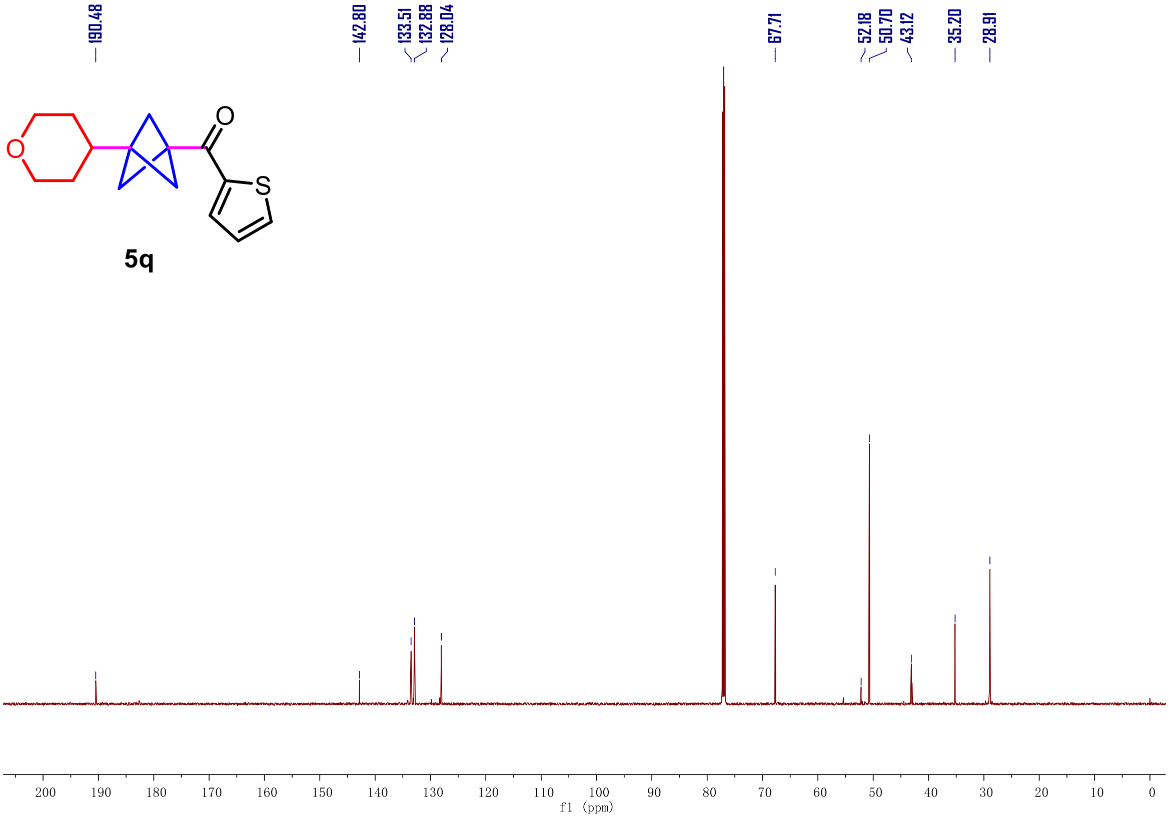
^{1}H NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (**5q**)

600 MHz, CDCl$_3$, 23 ℃



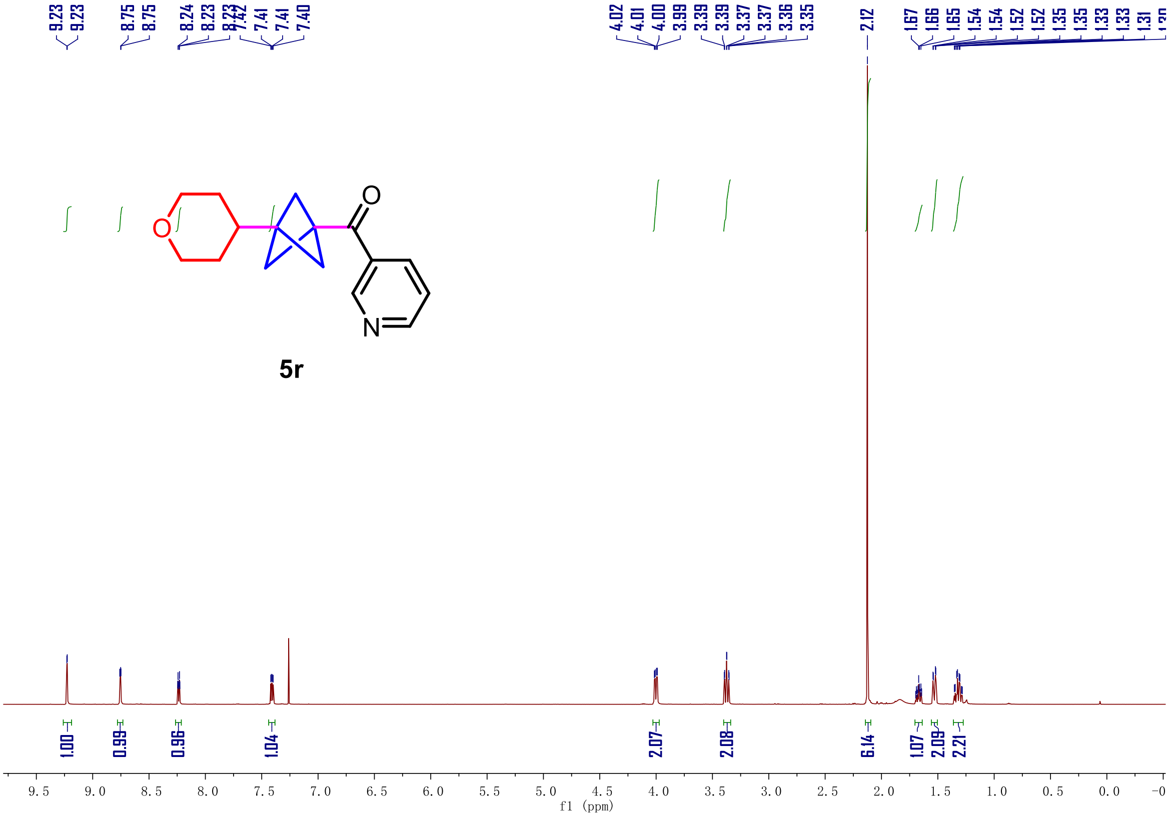
^{13}C NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (**5q**)

151 MHz, CDCl$_3$, 23 ℃



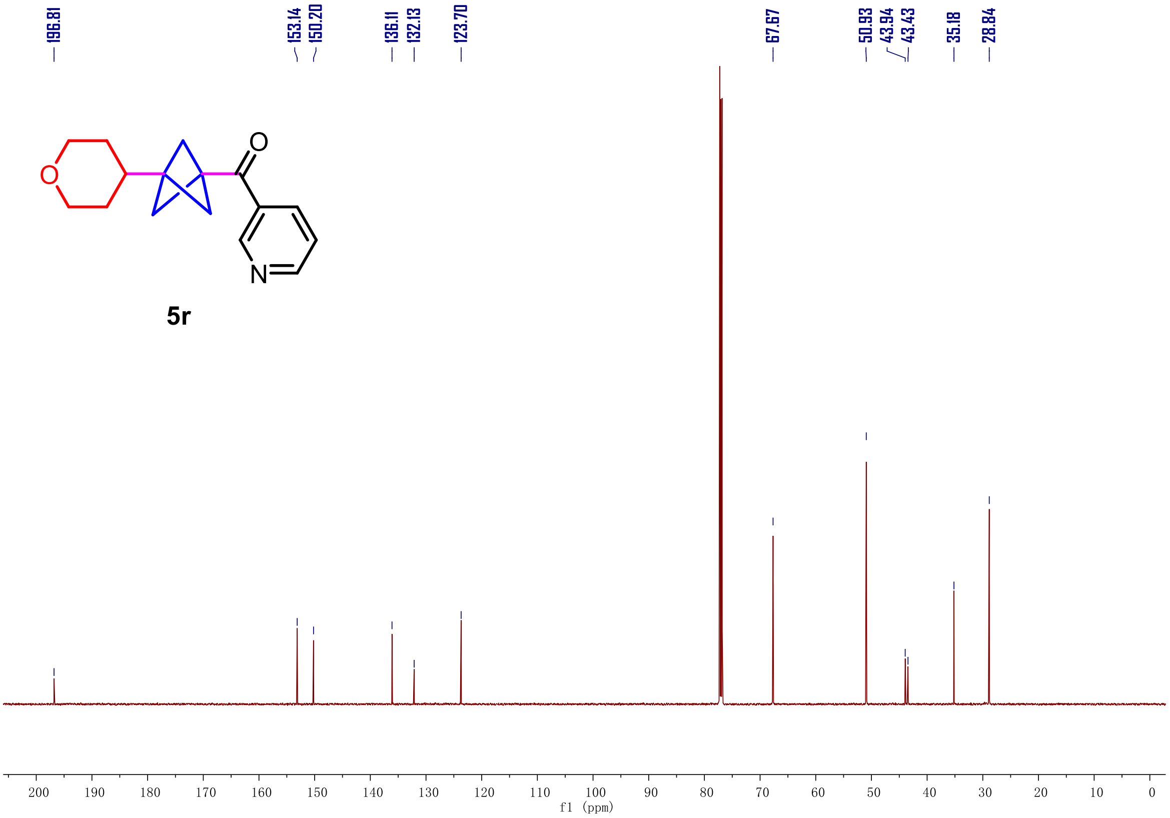
^{1}H NMR spectrum of pyridin-3-yl(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5r**)

600 MHz, $CDCl_3$, 23 ℃



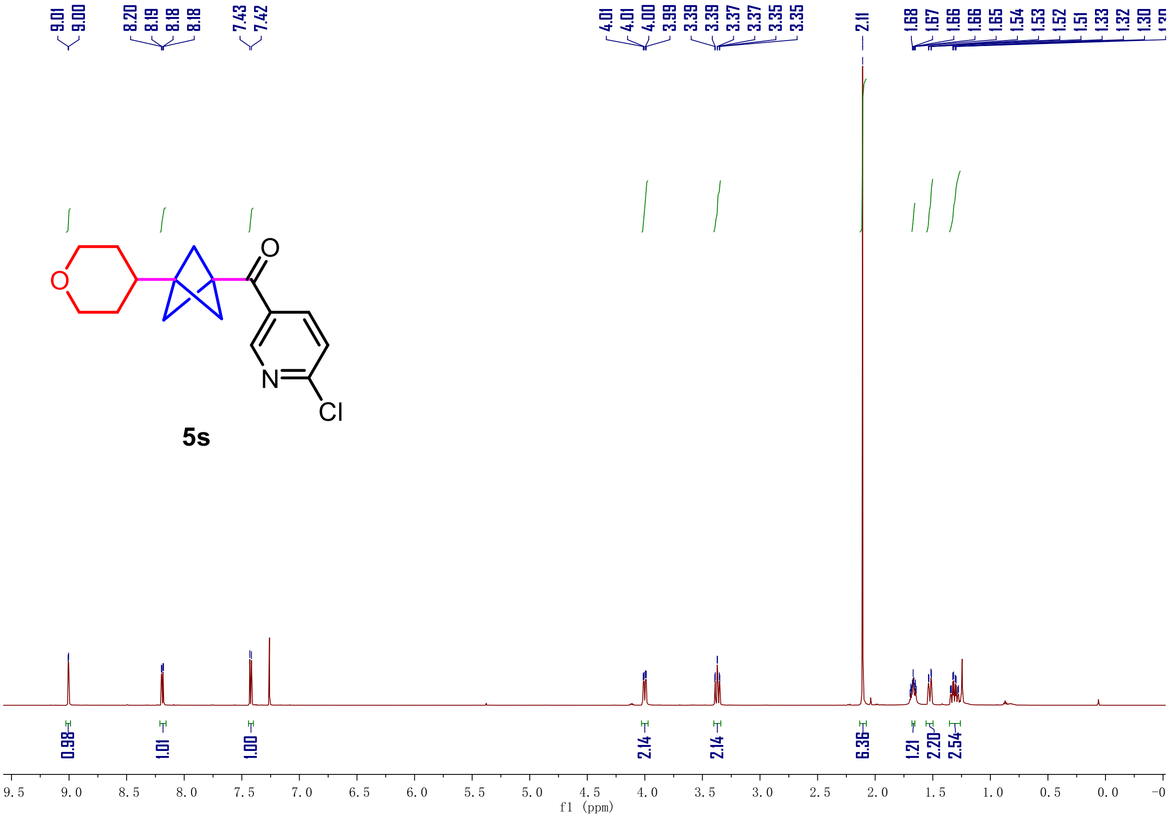
^{13}C NMR spectrum of pyridin-3-yl(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5r**)

151 MHz, $CDCl_3$, 23 ℃



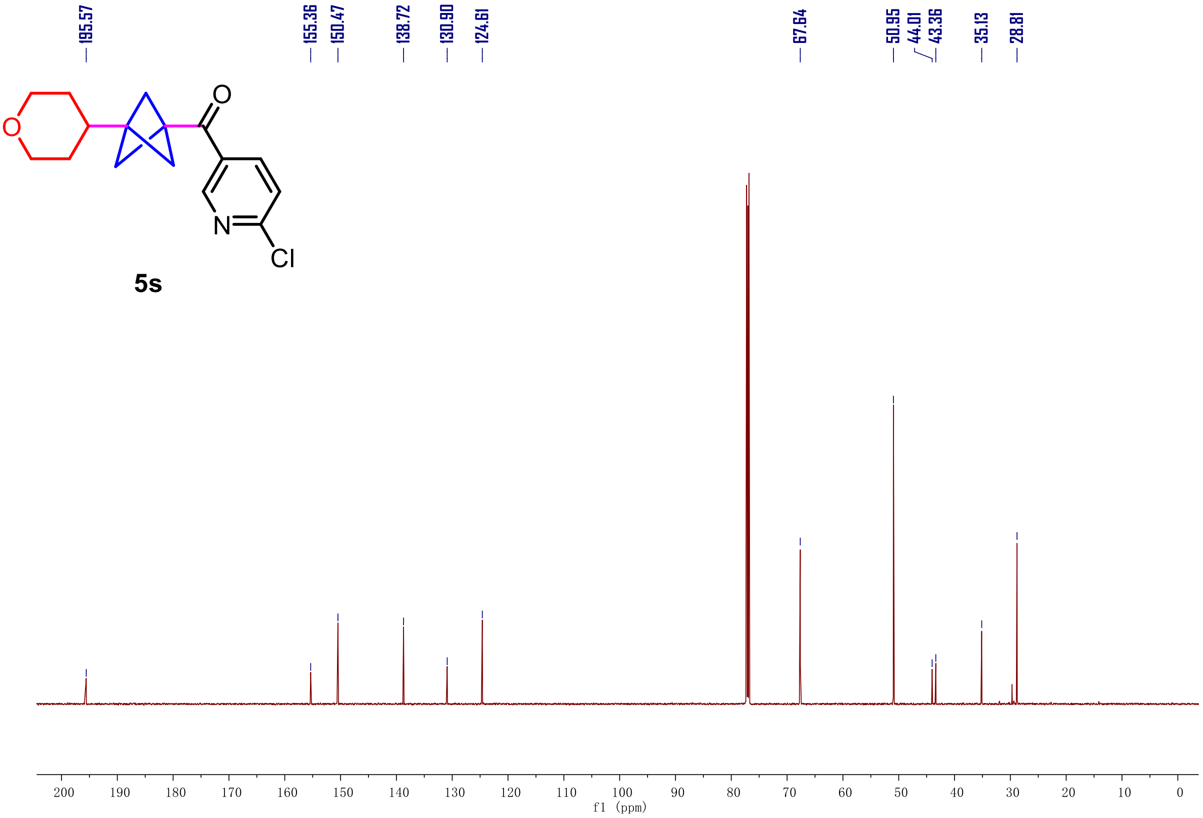
^{1}H NMR spectrum of (6-chloropyridin-3-yl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5s**)

600 MHz, $CDCl_3$, 23 ℃

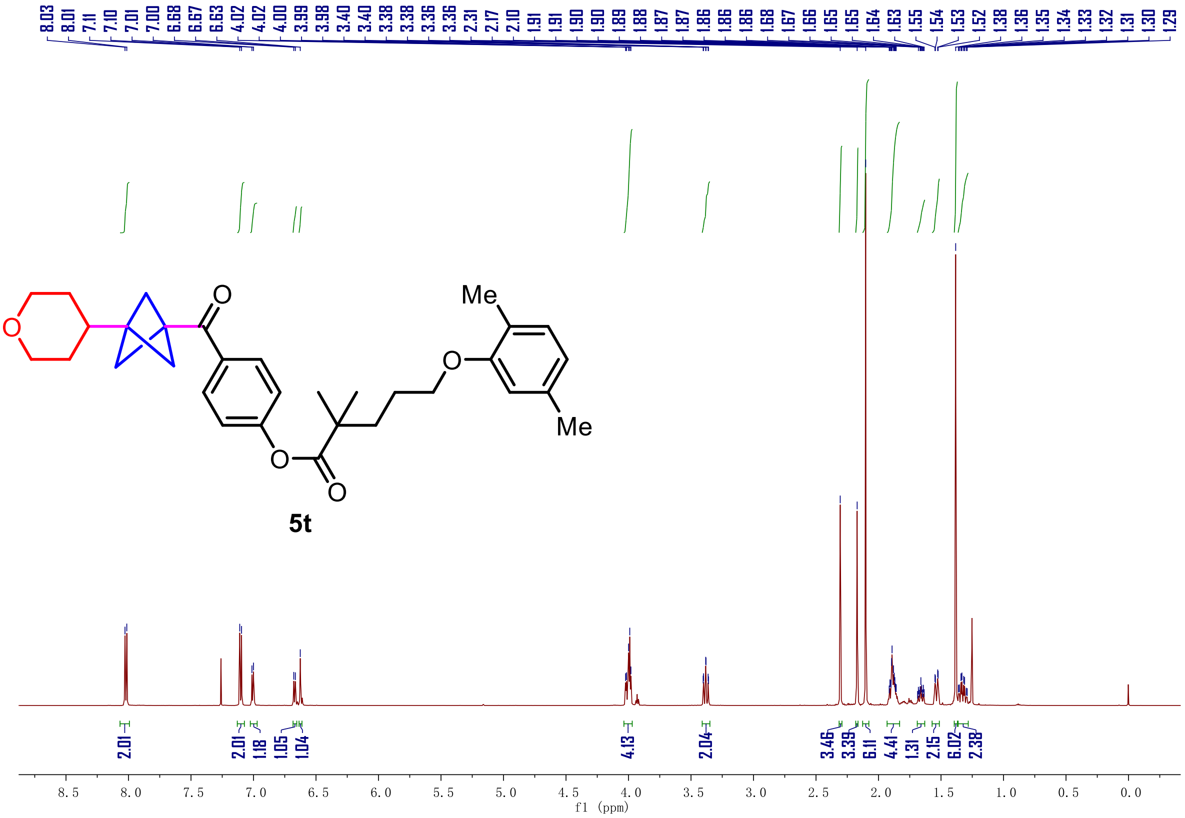


^{13}C NMR spectrum of (6-chloropyridin-3-yl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**5s**)

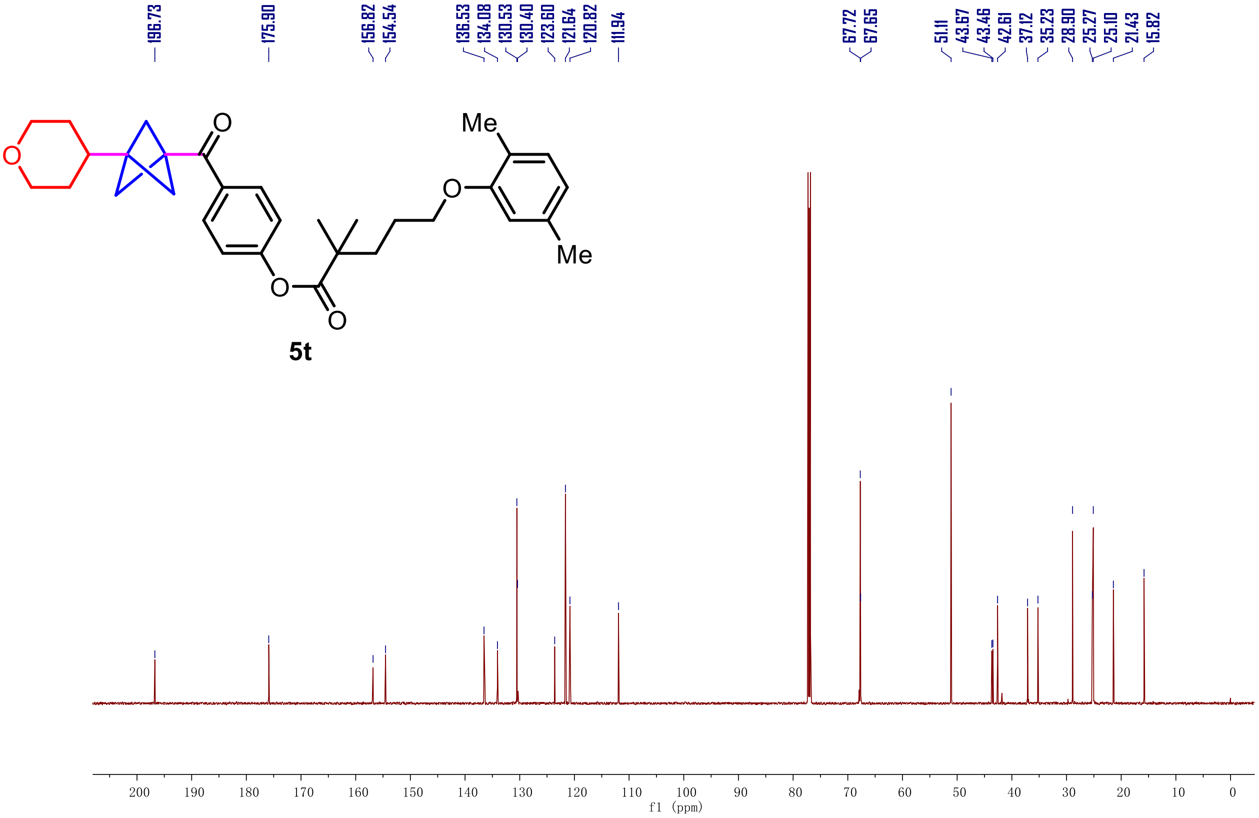
600 MHz, $CDCl_3$, 23 ℃



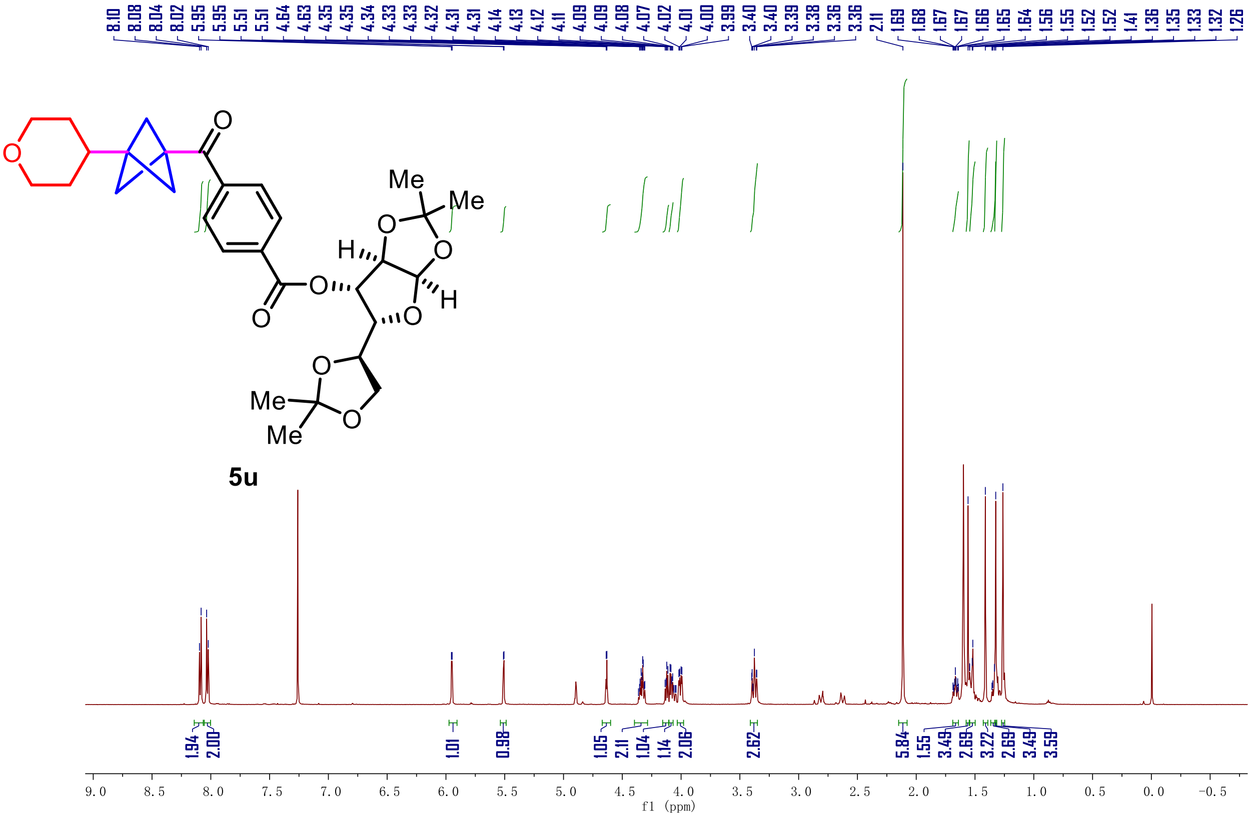
^{1}H NMR spectrum of 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**5t**) 600 MHz, $CDCl_3$, 23 ℃



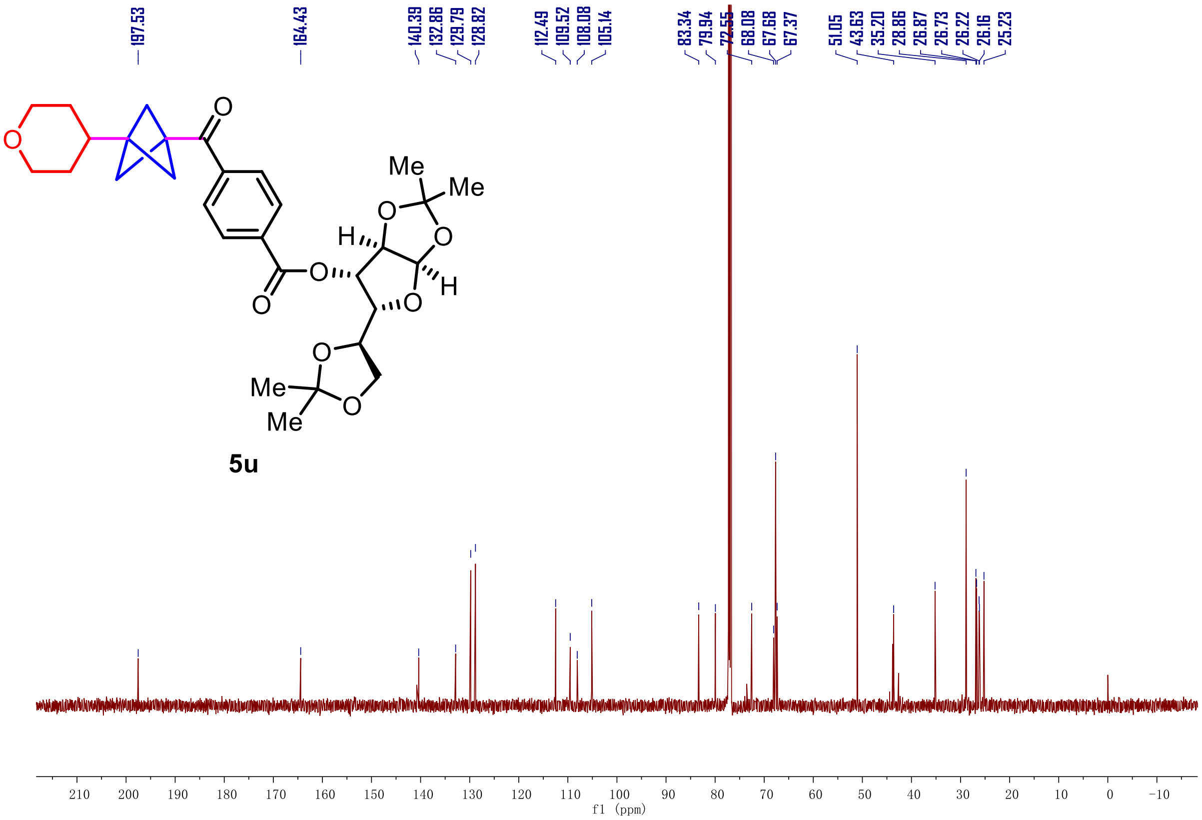
^{13}C NMR spectrum of 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**5t**) 151 MHz, $CDCl_3$, 23 ℃



^{1}H NMR spectrum of (*3aR*,*5R*,*6S*,*6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzoate (**5u**) 600 MHz, $CDCl_3$, 23 ℃

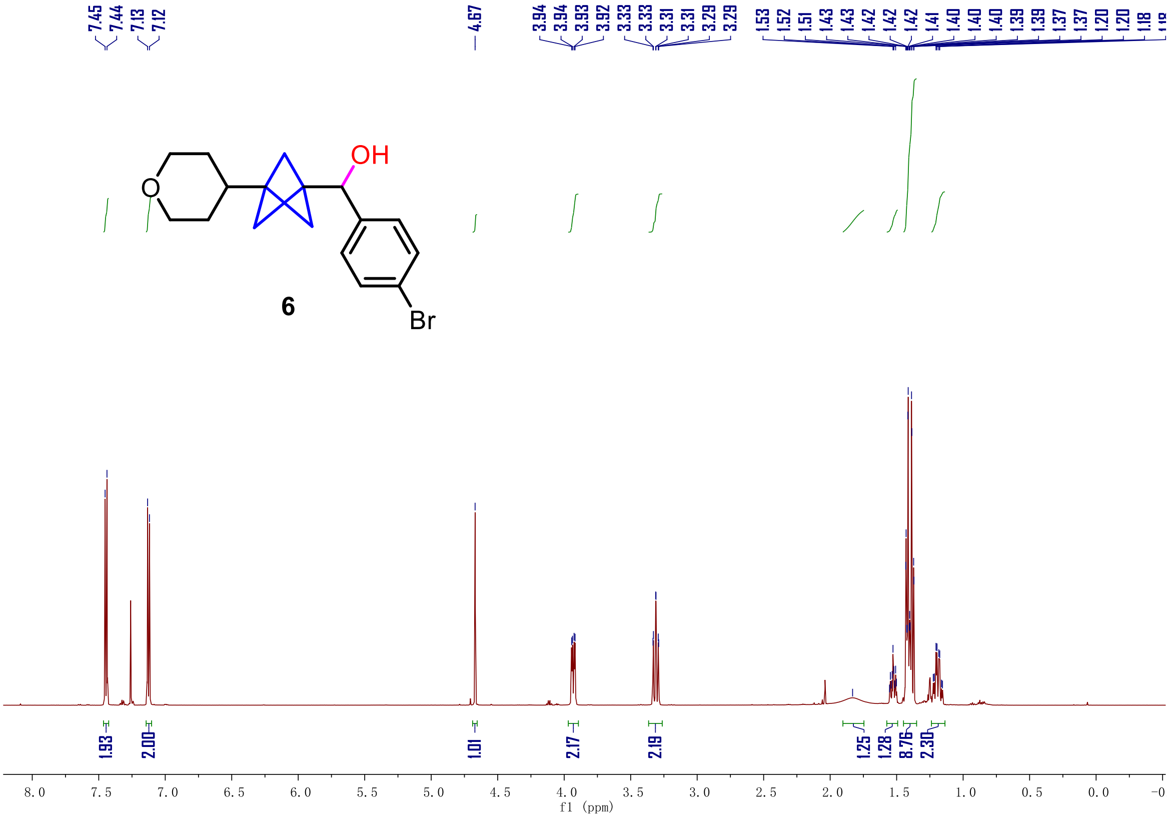


^{13}H NMR spectrum of (*3aR*,*5R*,*6S*,*6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzoate (**5u**) 151 MHz, $CDCl_3$, 23 ℃



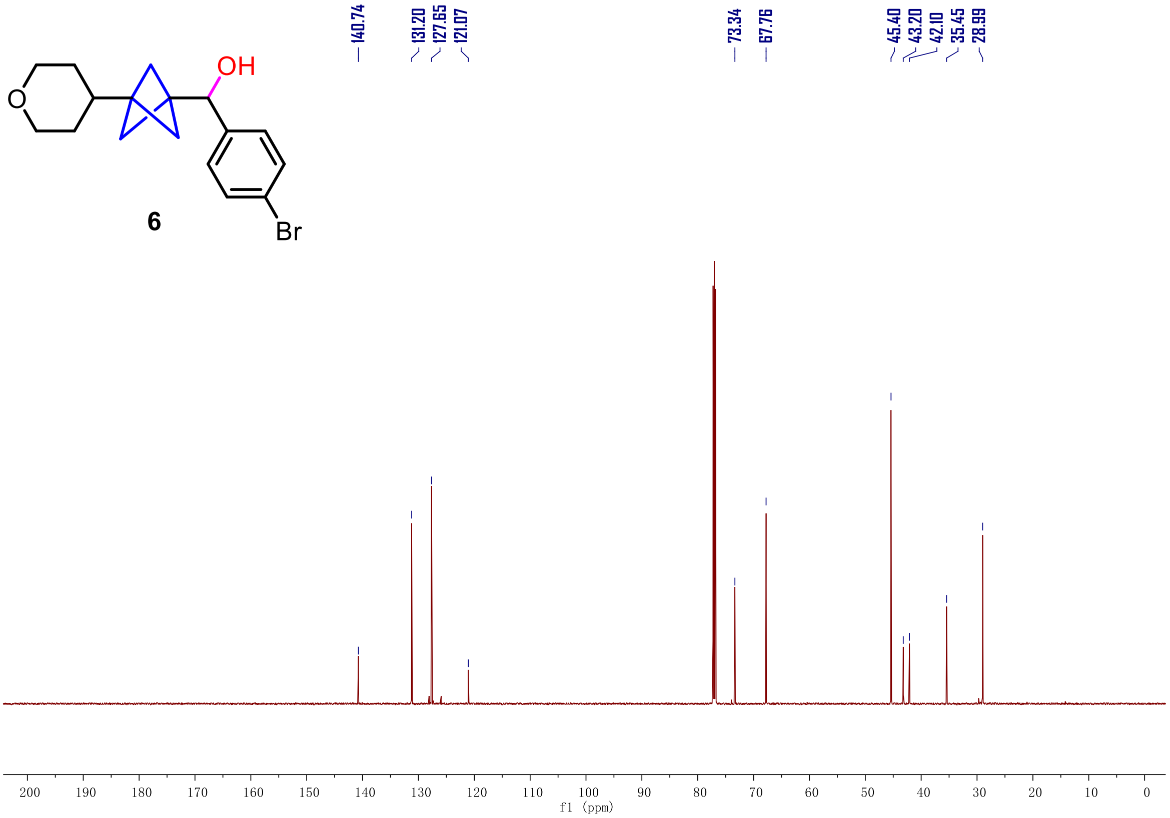
^{1}H NMR spectrum of (4-bromophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanol (**6**)

600 MHz, $CDCl_3$, 23 ℃



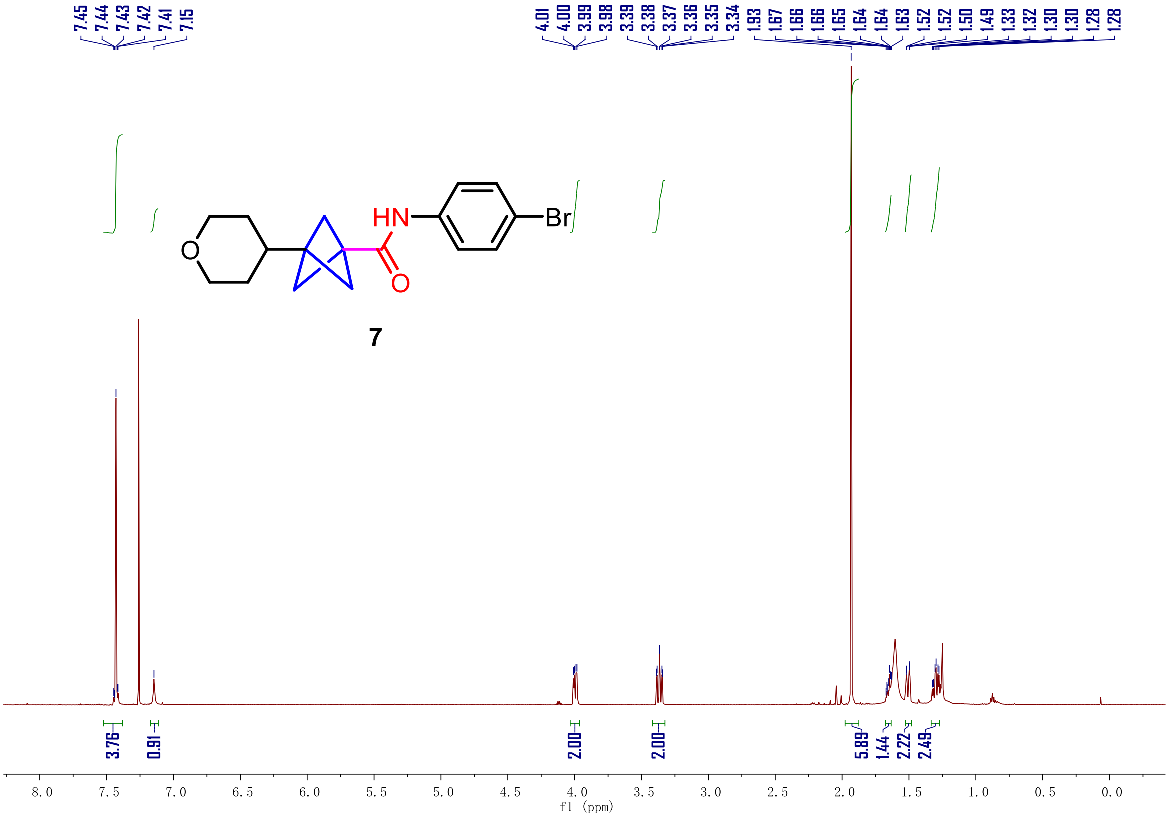
^{13}C NMR spectrum of (4-bromophenyl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanol (**6**)

151 MHz, $CDCl_3$, 23 ℃



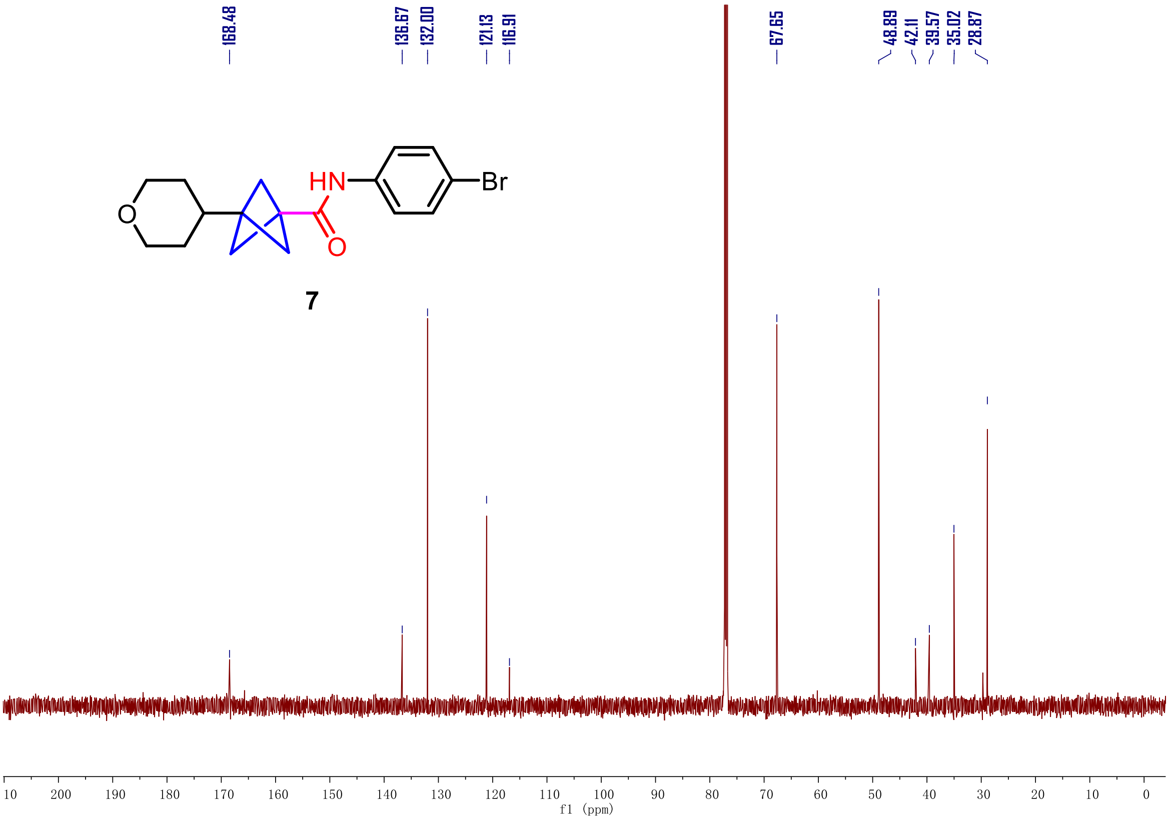
^{1}H NMR spectrum of *N*-(4-bromophenyl)-3-(tetrahydro-*2H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carboxamide (**7**)

600 MHz, $CDCl_3$, 23 ℃



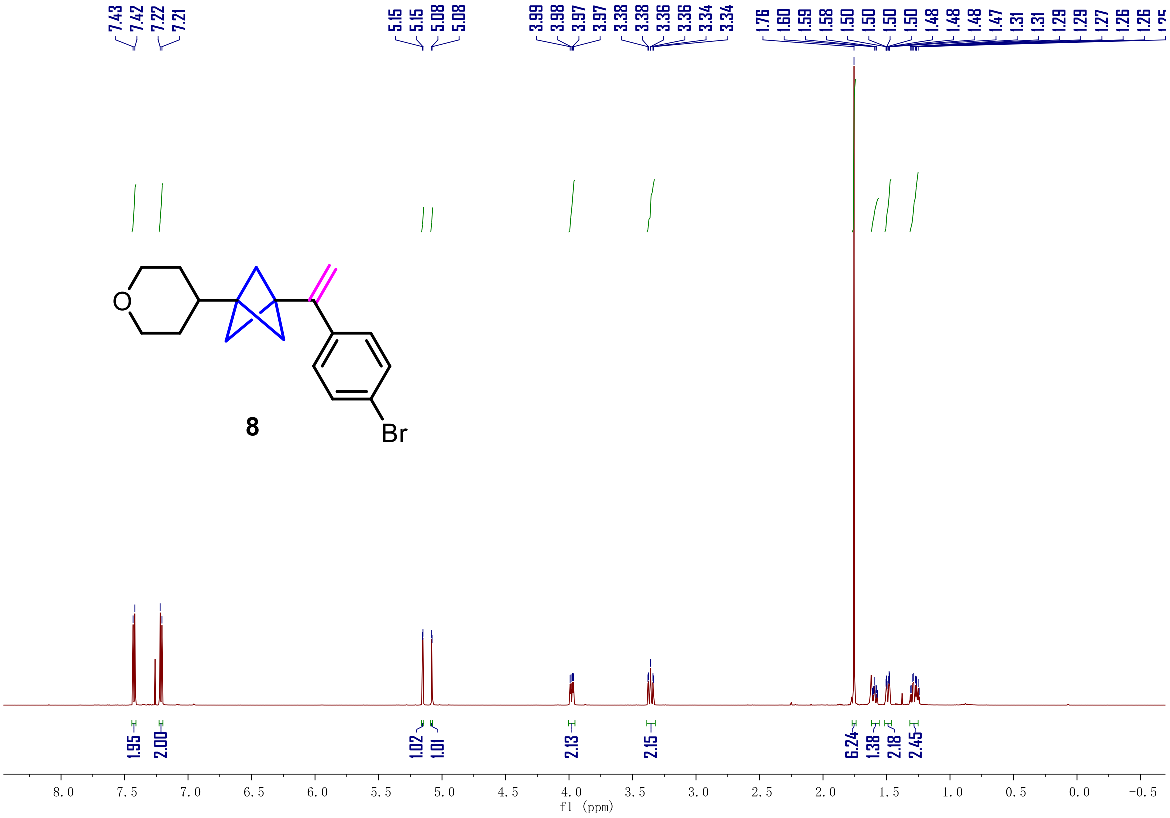
^{13}C NMR spectrum of *N*-(4-bromophenyl)-3-(tetrahydro-*2H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carboxamide (**7**)

151 MHz, $CDCl_3$, 23 ℃



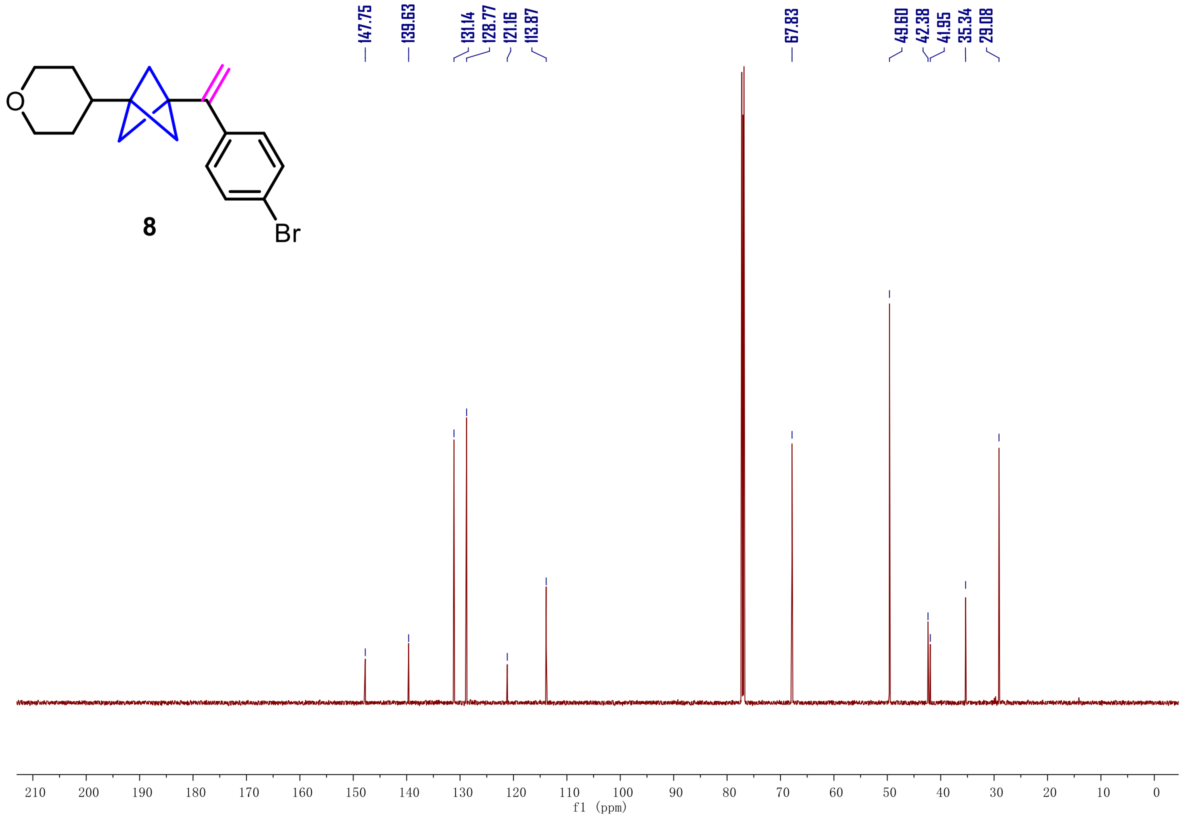
^{1}H NMR spectrum of 4-(3-(1-(4-bromophenyl)vinyl)bicyclo[1.1.1]pentan-1-yl)tetrahydro-2H-pyran (**8**)

600 MHz, $CDCl_3$, 23 ℃

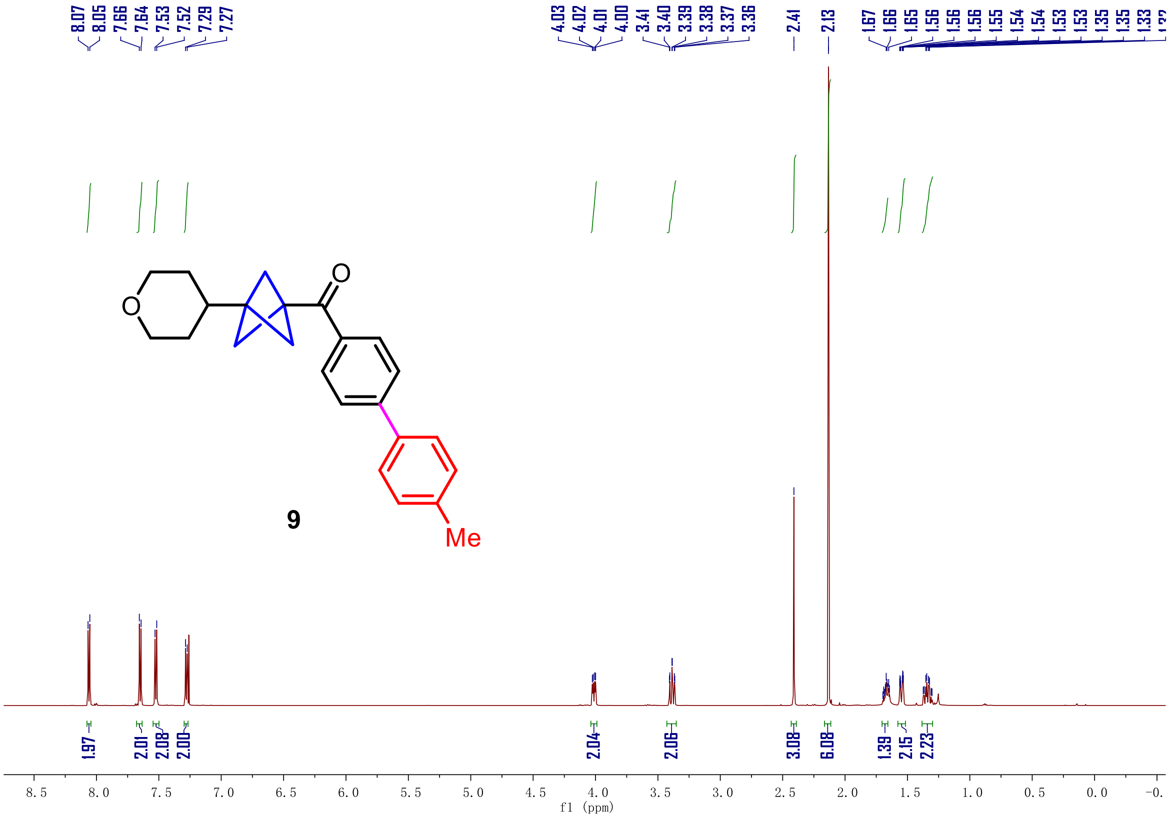


^{13}C NMR spectrum of 4-(3-(1-(4-bromophenyl)vinyl)bicyclo[1.1.1]pentan-1-yl)tetrahydro-2H-pyran (**8**)

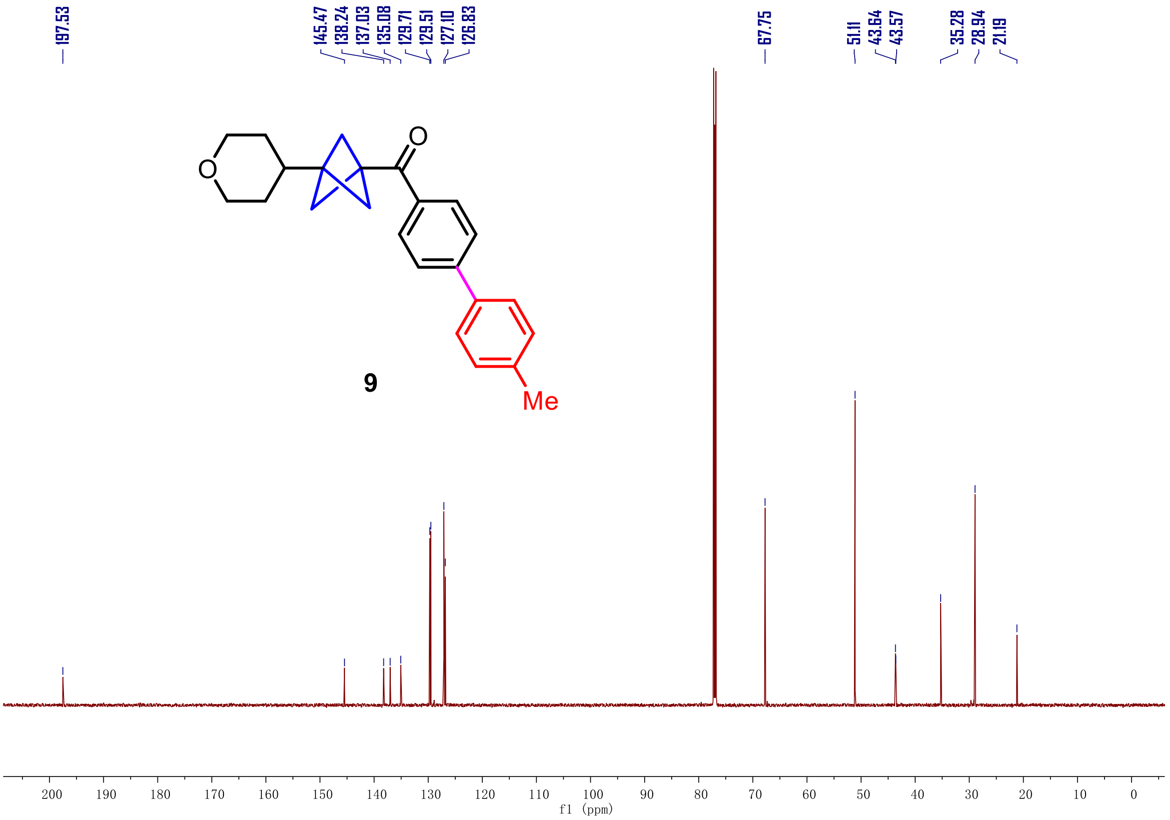
151 MHz, $CDCl_3$, 23 ℃



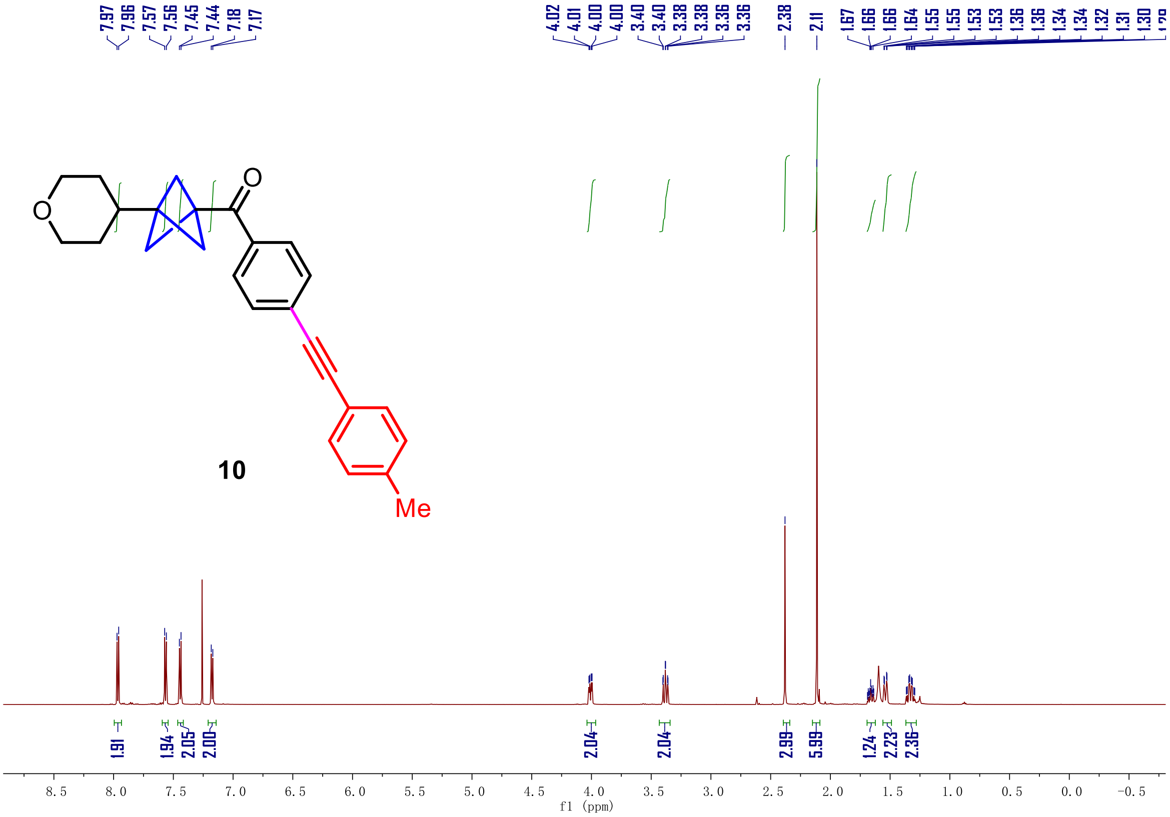
^{1}H NMR spectrum of (4'-methyl-[1,1'-biphenyl]-4-yl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**9**) 600 MHz, CDCl$_3$, 23 ℃



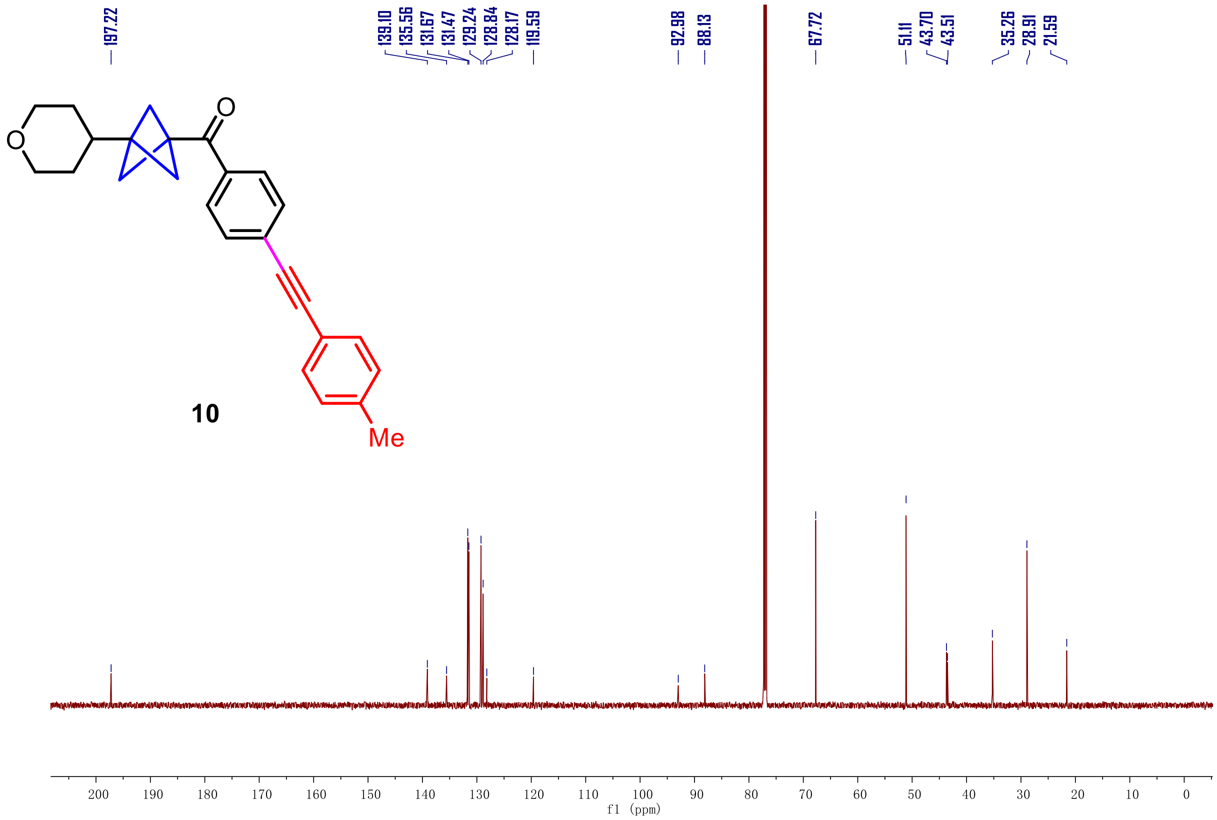
^{13}C NMR spectrum of (4'-methyl-[1,1'-biphenyl]-4-yl)(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanone (**9**) 151 MHz, CDCl$_3$, 23 ℃



^{1}H NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(*p*-tolylethynyl)phenyl)methanone (**10**) 600 MHz, CDCl$_3$, 23 ℃

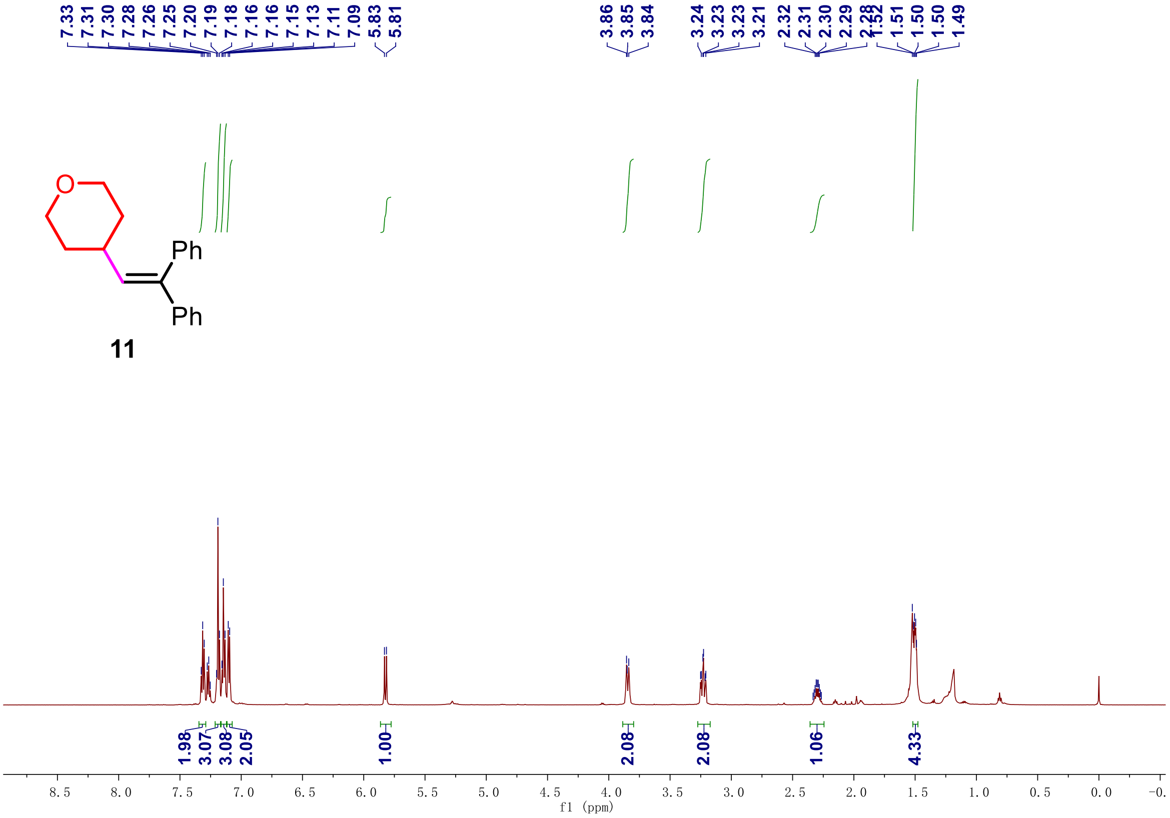


^{13}C NMR spectrum of (3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(*p*-tolylethynyl)phenyl)methanone (**10**) 151 MHz, CDCl$_3$, 23 ℃



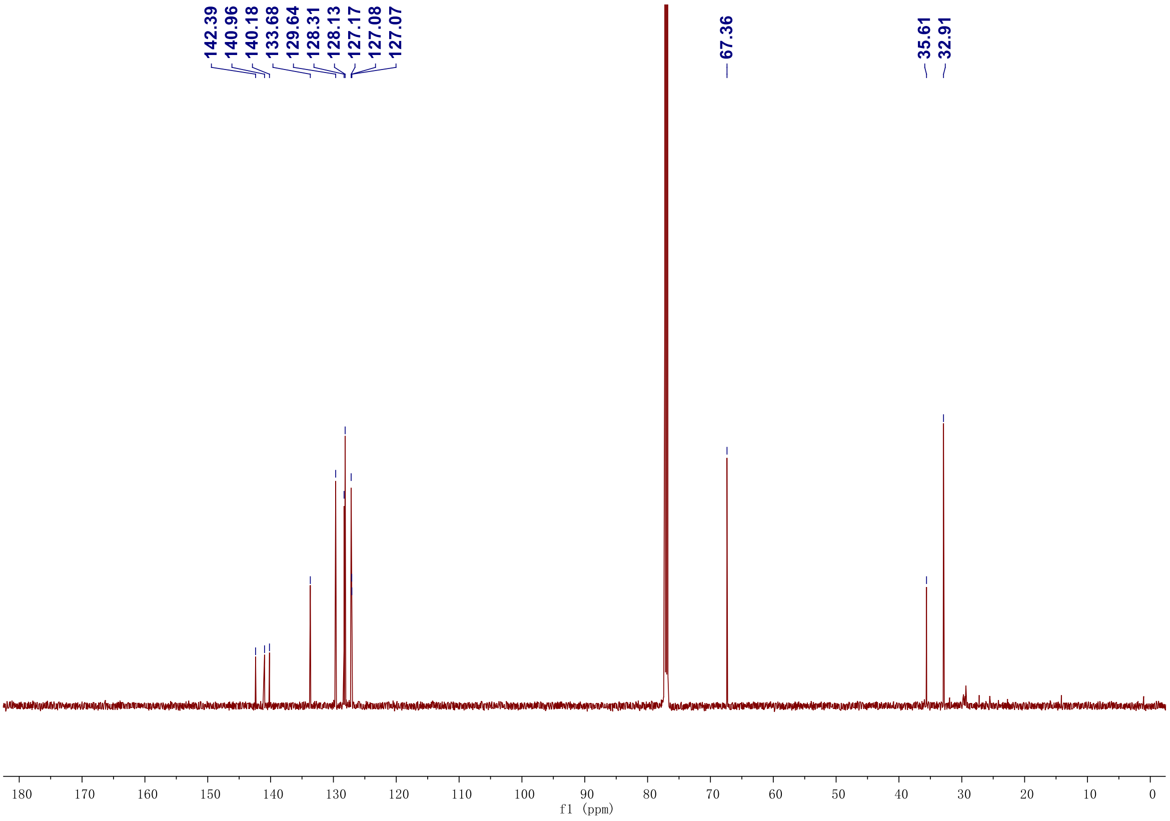
^{1}H NMR spectrum of 4-(2,2-diphenylvinyl)tetrahydro-2H-pyran (**11**)

600 MHz, $CDCl_3$, 23 ℃



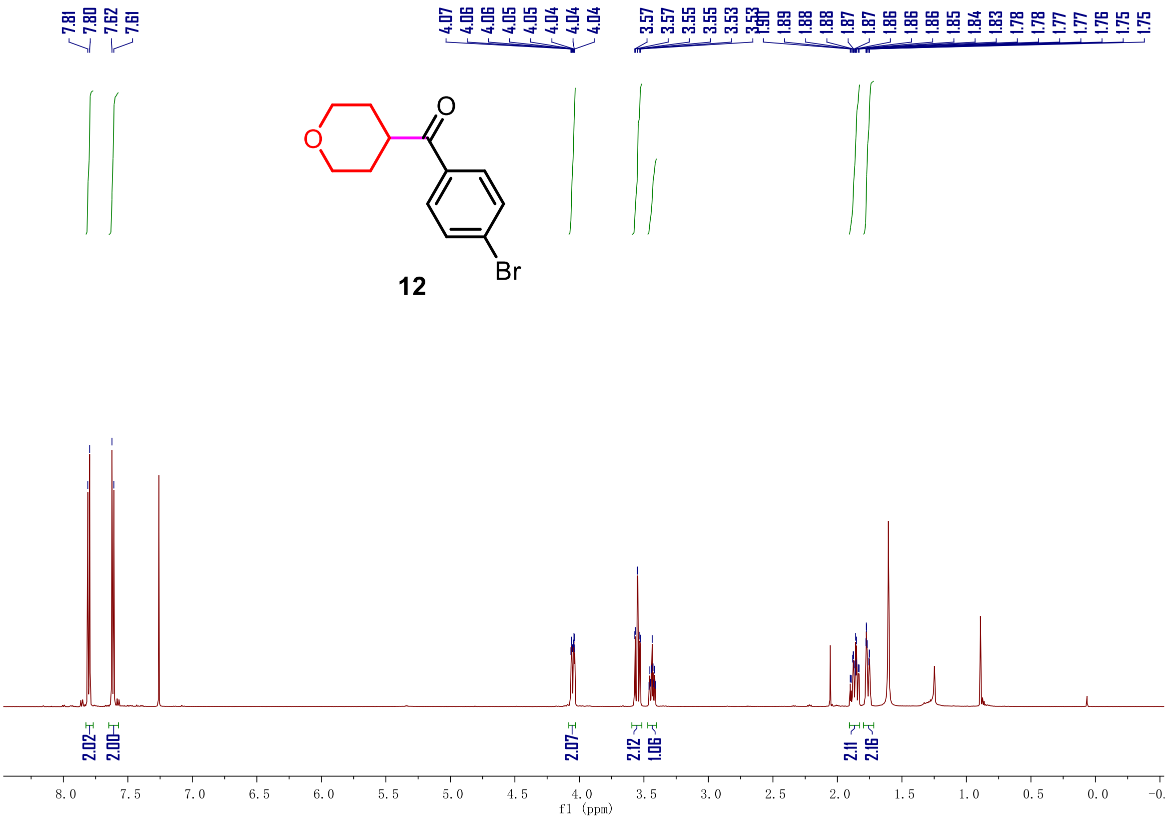
^{13}C NMR spectrum of 4-(2,2-diphenylvinyl)tetrahydro-2H-pyran (**11**)

151 MHz, $CDCl_3$, 23 ℃



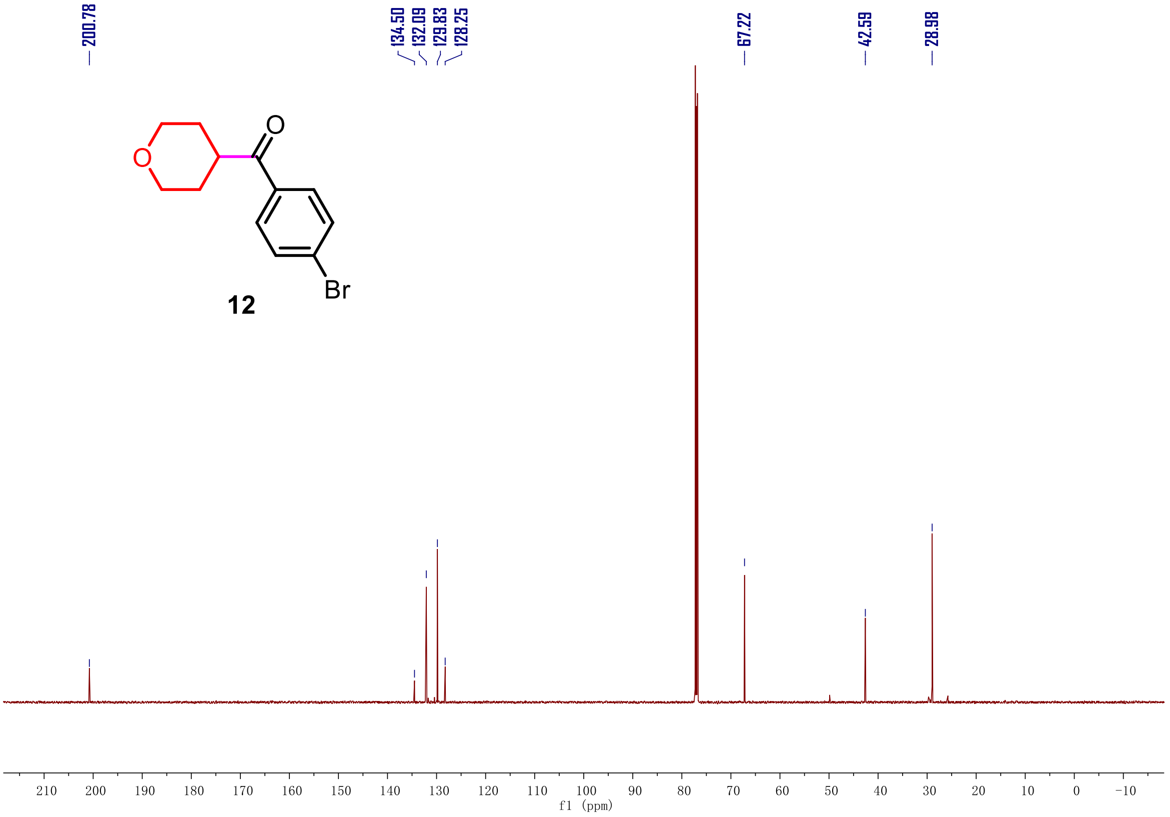
^{1}H NMR spectrum of (4-bromophenyl)(tetrahydro-*2H*-pyran-4-yl)methanone (**12**)

600 MHz, CDCl$_3$, 23 ℃



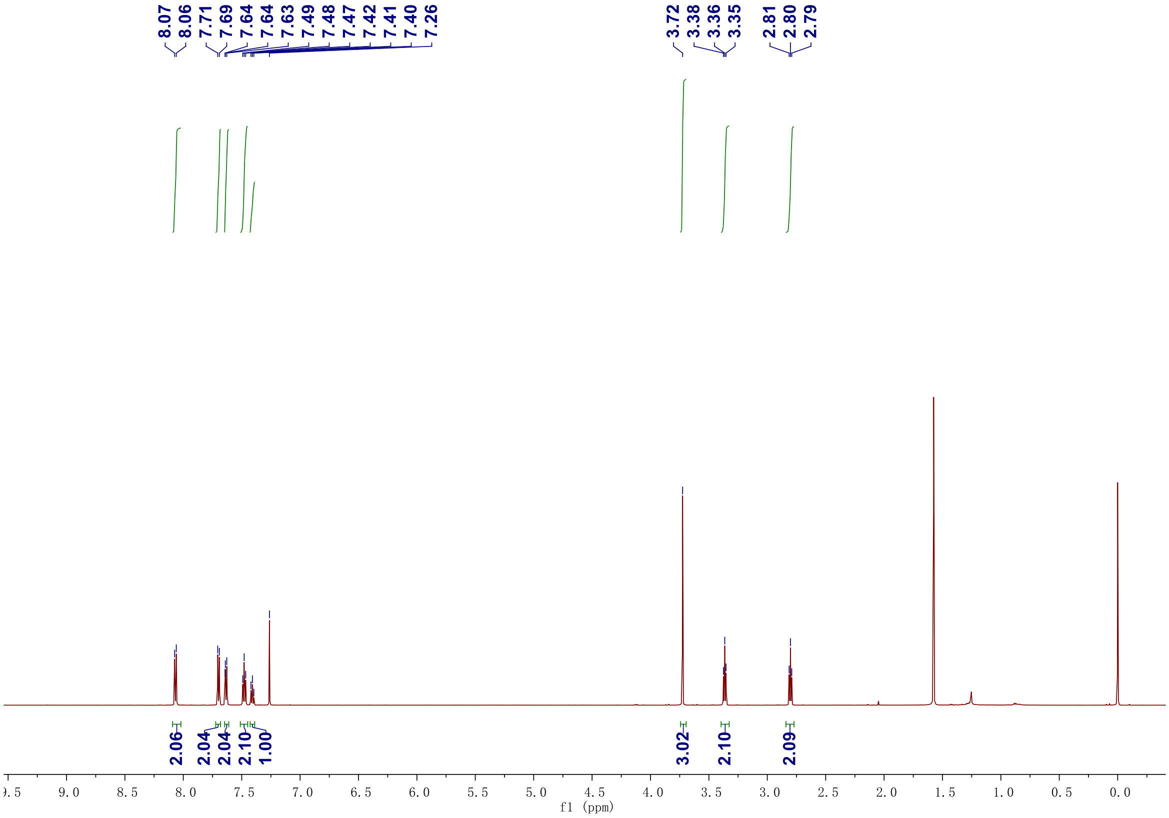
^{13}C NMR spectrum of (4-bromophenyl)(tetrahydro-*2H*-pyran-4-yl)methanone (**12**)

151 MHz, CDCl$_3$, 23 ℃



^{1}H NMR spectrum of methyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (**16**)

600 MHz, $CDCl_3$, 23 ℃



^{13}C NMR spectrum of methyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (**16**)

151 MHz, $CDCl_3$, 23 ℃