One Step Synthesis of Unsymmetrical 1,3-Disubstituted BCP Ketones via Nickel/Photoredox-Catalyzed [1.1.1]Propellane Multicomponent Dicarbofunctionalization

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General Considerations **S2**

Additional Optimization Details **S3**

Preparation of Propellane (solution in Et_2O) **S6**

Synthesis of Organotrifluoroborates **S7**

General Procedure for Three-Component Coupling **S12**

Reaction Limitations **S33**

Further Transformations **S34**

Mechanistic Studies **S37**

References **S40**

Spectra of Synthesized Compounds **S41**

1. General Considerations

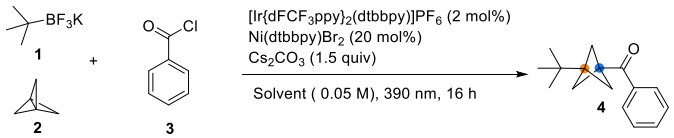
1.1 General: For purple light irradiation, a Kessil PR160L-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) was placed 1.5 inches away from the reaction vials. NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K using 400, 500 and 600 MHz spectrometers. Flash chromatography was carried out using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of leucine enkephalin for ESI-LC/MS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Melting points (°C) are uncorrected. UV/vis studies were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific.

1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Dry DME, dioxane, DMA, DMF and were obtained from Acros Organics and used as received. THF and Et_2O were purchased and dried via a solvent delivery system. Acyl chlorides were purchased from commercial suppliers and used as received. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration.

2. Additional Optimization Details

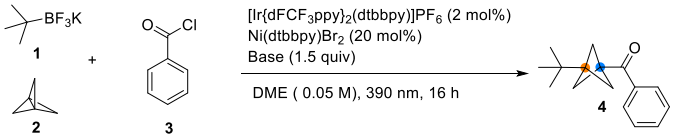
General Optimization Procedure: To a 4 mL reaction vial equipped with a stirrer bar was added *t*-BuBF$_3$K **1** (24.6 mg, 0.15 mmol, 1.5 equiv), benzoyl chloride **2** (14.2 mg, 0.1 mmol, 1 equiv), Cs_2CO_3 (49.6 mg, 0.15 mmol, 1.5 equiv), the [Ir{dFCF$_3$ppy}$_2$(dtbbpy)]PF$_6$ (2.2 mg, 0.02 mmol, 2 mol %), and Ni(dtbbpy)Br$_2$ (0.02 mmol, 9.72 mg, 0.2 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with 2.0 mL of dry DME via syringe, Then the vial was charged with the [1.1.1]propellane (0.37 mL, 0.3 mmol, 3.0 equiv, 0.8 M soln in Et_2O). The cap was sealed with Parafilm®, and the reaction was irradiated for 16 h. Irradiation was performed with a Kessil® PR160 390 nm lamp according to the procedure outlined in the Photochemical Reactor Design and Setup section. The temperature of the reaction was maintained at approximately 27 ºC via a fan. After 16 h, an aliquot of a solution of 1,3,5-trimethoxybenzene (16.8 mg in 0.1 mL DME) was added to each vial. The reaction mixture concentrated via rotary evaporation, then re-dissolved in 250 µL of $CDCl_3$. The resulting soln was passed through a hydrophobic PTFE 0.2 µm syringe-driven filter unit and dispensed into an NMR tube. NMR yields were calculated based on relative integrations of the aromatic peak of 1,3,5-trimethoxybenzene and the BCP proton in the BCP ketone products.

Table 1. Solvent Screen



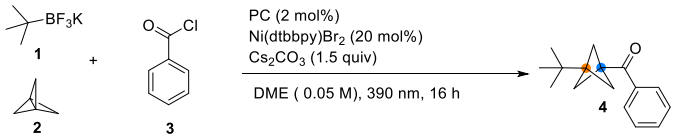
Entry	Solvent	NMR yield(%)
1	**DME**	**63**
2	THF	35
3	dioxane	41
4	MTBE	15
5	TFT	18
6	triglyme	32
7	DMA	0
8	CH_3CN	0
9	DME(0.1 M)	57
10	DME(0.05 M)	54

Table 2. Base Screen



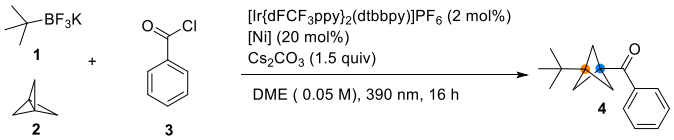
Entry	Base	NMR yield(%)
1	**Cs_2CO_3**	**63**
2	K_2HPO_4	31
3	K_3PO_4	24
4	K_2CO_3	26
5	KF	48
6	DBU	0
7	Cs_2CO_3 (1.0 equiv)	51
8	Cs_2CO_3 (2.0 equiv)	54

Table 3. Photocatalyst Screen



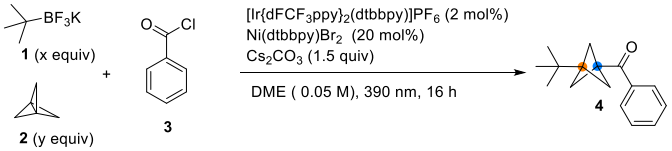
Entry	PC	NMR yield(%)
1	**$[Ir\{dFCF_3ppy\}_2(dtbbpy)]PF_6$**	**63**
2	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	38
3	$[Ir(dtbpy)(bpy)_2]PF_6$	0
4	$Ru(bpy)_3$	0
5	4CzIPN	0

Table 4. Nickel/Ligand Screen



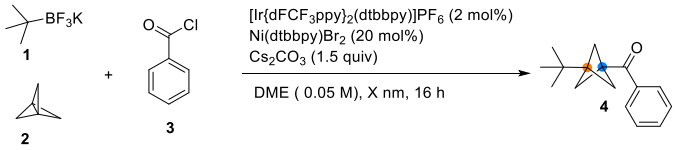
Entry	[Ni]	NMR yield(%)
1	**$Ni(dtbbpy)Br_2$**	**63**
2	$Ni(dOMebpy)Br_2$	37
3	$Ni(bpy)Br_2$	28
4	$Ni(Phen)Br_2$	24
5	$Ni(dtbbpy)Br_2$ (10 mol%)	56
6	$Ni(dtbbpy)Br_2$ (15 mol%)	60

Table 5 Stoichiometry Variation Screen



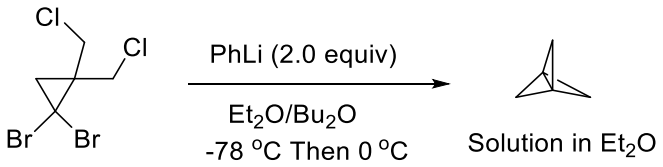
Entry	X	Y	NMR yield(%)
1	1.2	3	57
2	**1.5**	**3**	**63**
3	2.0	3	61
4	1.5	2	53
5	1.5	4	61

Table 6 LED Light Screen



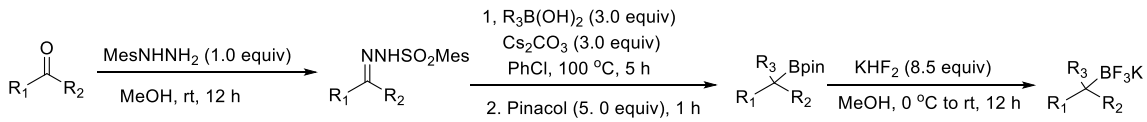
Entry	X	NMR yield(%)
1	456	23
2	440	27
3	427	41
4	**390**	**63**
5	blue LED	18

3. Preparation of Propellane (solution in Et_2O)[1]

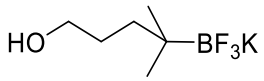


A flame-dried flask equipped with a stir bar was charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane.(5.0 g, 16.8 mmol). To this was added 10 mL of Et_2O. The solution was cooled to –78 ºC (a white suspension formed). 20 mL of PhLi (20 mL, 38 mmol, 2.3 equiv, 1.9 M soln in *n*-Bu_2O) was added slowly dropwise. The mixture was stirred at –78 ºC for 15 min, then warmed to 0 ºC and stirred for another 2 h. The reaction flask was fitted with a flask-to-flask vacuum distillation piece attached to a receiving flask cooled to –78 ºC. A pump was used to evacuate the system down slowly to ~10 Torr, and the solution was held at this pressure for 10 min. This resulted in the distillation of the Et_2O/ propellane soluyion. The concentration was checked by NMR by taking a 100 μL aliquot of the stock solution and determining the ratio of propellane to an added standard, such as mesitylene (35%-45% yield - typically concentrations are 0.6-0.9 M with this protocol). This solution should be kept at a –20 º C freezer, and the propellane is stable for at least several months under these conditions.

4. Synthesis of Organotrifluoroborates[2]



To a solution of ketone (1.0 equiv) in MeOH (1.0 M) at rt, 2- mesitylenesulfonyl hydrazide (1.0 equiv) was added. The solution was stirred at rt for 1-12 h, over which time a white solid precipitates. TLC showed the complete consumption of both starting materials. The solid was filtered and washed with cold Et_2O, providing the desired 2-mesitylenesulfonyl hydrazone. A screw-capped culture tube was charged with Cs_2CO_3 (4.9 g, 15 mmol, 3.0 equiv), boronic acid (15 mmol, 3.0 equiv) and 2-mesitylenesulfonyl hydrazone (5 mmol, 1.0 equiv). Then the tube was evacuated and backfilled 3 times with argon, followed by addition of chlorobenzene (1.0 mL) via a syringe. After stirring for at 100 °C for 5 h, the reaction mixture was cooled to rt. Next, pinacol (2.95 g, 25 mmol, 5.0 equiv) was added, and the reaction was stirred at 100 °C for another 1 h. The suspended solution was then filtered over Celite and washed with Et_2O. The solvent was removed under high vacuum, and the resultant crude Bpin was taken up in MeOH (0.1 M) and cooled to 0 ° C in an ice-water bath. After 5 min, aq KHF_2 (8.5 equiv, 4.5 M) was added dropwise via an addition funnel. After complete addition, the ice bath was removed, and the reaction was allowed to stir overnight. After this time, the crude reaction mixture was concentrated via rotary evaporation. The crude solid was taken up in portions of boiling acetone and filtered through a coarse fritted glass funnel to remove inorganic byproducts. The filtrate was concentrated via rotary evaporation, and the crude solid was washed with a 1:1 mixture of pentane/CH_2Cl_2 then CH_2Cl_2 to afford pure organotrifluoroborate

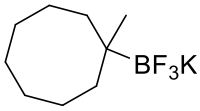


4-Methyl-4-(trifluoro-l4-boraneyl)pentan-1-ol, Potassium Salt (197 mg, 19% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point: 216-217 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ 3.40 (t, J = 7.1 Hz, 2H), 3.21(s, 1H), 1.57 – 1.47 (m, 2H), 1.13 – 1.05 (m, 2H), 0.65 (s, 6H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 63.7, 36.7, 25.7, 24.5; ^{19}F NMR (376 MHz, acetone-d_6) δ -150.52; ^{11}B NMR (128 MHz, acetone-d_6) δ 5.4.

IR (ATR): ν = 3518, 3004, 1709, 1420, 1220, 1092, 902, 529 cm^{-1}

MS (ESI) calcd for $C_6H_{13}BF_3O$ [M-K]$^+$: 169.10; Found: 169.26.

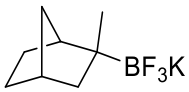
HRMS (ESI) not found.



Trifluoro(1-methylcyclooctyl)-l4-borane, Potassium Salt (301 mg, 26% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point > 250 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ 1.72 – 1.37 (m, 12H), 1.29 – 1.15 (m, 2H), 0.67 (s, 3H); ^{13}C NMR (151 MHz, acetone-d_6) δ 32.48, 29.57, 25.77, 24.26, 23.92; ^{19}F NMR (565 MHz, acetone-d_6) δ -150.5. ^{11}B NMR (128 MHz, acetone-d_6) δ 5.4.

IR (ATR): ν = 2919, 2958, 1476, 1183, 960, 919 cm^{-1}

HRMS (ESI) calcd for $C_9H_{17}BF_3$ [M-K]$^+$: 193.1375; Found: 193.1370.



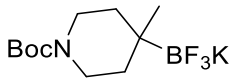
Trifluoro(2-methylbicyclo[2.2.1]heptan-2-yl)-l4-borane, Potassium Salt (388 mg, 36% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point > 250 °C. (dr = 5:4) ^{1}H NMR (600 MHz, acetone-d_6) δ 1.98 (t, J = 7.1 Hz, 1H), 1.75 – 1.67 (m, 3H), 1.38 (d, J = 13.1 Hz, 1H), 1.28 – 1.23 (m, 1H), 1.10 – 1.02 (m, 2H), 0.89 (d, J = 8.9 Hz, 1H), 0.76 (s, 3H), 0.42 (dd, J = 11.3, 2.5 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6) δ 46.15, 42.89, 42.24, 42.20, 39.00, 38.23,

38.08, 36.87, 29.54, 28.42, 27.18, 26.52, 25.06, 22.00.^{19}F NMR (376 MHz, acetone-d_6) δ -145.25. ^{11}B NMR (128 MHz, acetone-d_6) δ 4.8.

IR (ATR): ν = 2944, 2866, 1711, 1483, 1257, 1024, 916 829 cm^{-1}

MS (ESI) calcd for $C_8H_{13}BF_3$ [M-K]$^+$: 177.10 ; Found: 177.28.

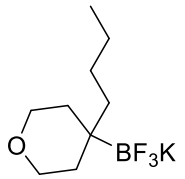
HRMS (ESI) not found.



***tert*-Butyl 4-Methyl-4-(trifluoro-l4-boraneyl)piperidine-1-carboxylate, Potassium Salt** (472 mg, 31% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point > 250 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ 3.42 (t, J = 10.8 Hz, 2H), 3.37 – 3.27 (m, 2H), 1.67 – 1.55 (m, 2H), 0.95 (t, J = 11.1 Hz, 2H),1.42(s, 9H), 0.75 (s, 3H); ^{13}C NMR (151 MHz, acetone-d_6) δ 154.5, 77.1, 40.9, 34.6, 27.8, 22.7; ^{19}F NMR (565 MHz, acetone-d_6) δ -150.22; ^{11}B NMR (128 MHz, acetone-d_6) δ 4.8.

IR (ATR): ν = 2922, 1667, 1432, 1366, 1252, 1170, 901 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{20}BF_3NO_2$ [M-K]$^+$: 266.1535; Found: 266.1539.

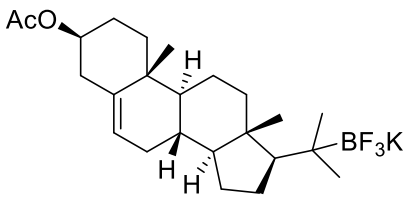


(4-Butyltetrahydro-2H-pyran-4-yl)trifluoro-l4-borane, Potassium Salt (533 mg, 46% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point : 226 -227°C ^{1}H NMR (600 MHz, acetone-d_6) δ 3.58 – 3.44 (m, 2H), 3.38 (ddd, J = 10.6, 6.5, 3.8 Hz, 2H), 1.52 (ddd, J = 13.5, 6.7, 3.5 Hz, 2H), 1.19 (td, J = 9.0, 4.7 Hz, 2H), 1.08 (td, J = 15.0, 12.5, 5.5 Hz, 4H), 0.93 (ddd, J = 12.8, 8.0, 3.8 Hz, 2H), 0.73 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, acetone-d_6) δ 64.4, 38.5, 34.0, 27.1, 24.3, 13.8. ^{19}F NMR (565 MHz, acetone-d_6) δ -145.35. ^{11}B NMR (128 MHz, acetone-d_6) δ 5.0.

IR (ATR): ν =2929, 2863, 1232, 1025, 953, 544 cm^{-1}

MS (ESI) calcd for $C_9H_{17}BF_3O$ [M-K]$^+$: 209.13 ; Found: 209.36.

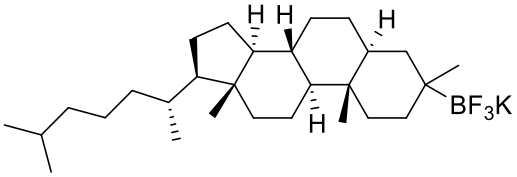
HRMS (ESI) not found.



(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(2-(trifluoro-l4-boraneyl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl Acetate, Potassium Salt (858 mg, 37% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point > 250 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ 5.24 (dq, *J* = 5.2, 1.6 Hz, 1H), 4.38 (ddt, *J* = 16.4, 8.4, 4.5 Hz, 1H), 2.18 – 2.14 (m, 2H), 1.83 (s, 3H), 1.82 – 1.80 (m, 1H), 1.77 (dt, *J* = 13.4, 3.6 Hz, 1H), 1.69 (dq, *J* = 12.4, 3.6 Hz, 1H), 1.57 (td, *J* = 9.5, 7.1 Hz, 2H), 1.50 – 1.23 (m, 8H), 1.04 – 0.97 (m, 2H), 0.90 (s, 3H), 0.87 – 0.76 (m, 3H), 0.74 (s, 3H), 0.66 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (151 MHz, acetone-d_6) δ 169.4, 139.8, 122.5, 73.4, 57.2, 57.1, 50.5, 44.1, 40.2, 38.0, 37.0, 36.5, 31.9, 31.6, 29.5, 27.6, 24.3, 24.2, 23.7, 22.8, 20.9, 20.3, 18.7, 13.7; ^{19}F NMR (376 MHz, acetone-d_6) δ -148.86; ^{11}B NMR (128 MHz, acetone-d_6) δ 5.3.

IR (ATR): ν = 2939, 1732, 1248, 1036, 962, 946 cm^{-1}

HRMS (ESI) calcd for $C_{24}H_{37}BF_3O_2$ [M-K]$^+$: 425.2839; Found: 425. 2832



Trifluoro((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-l4-borane, Potassium Salt (688 mg, 285 yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point : 207-208 °C dr = 5:1 ^{1}H NMR (400 MHz, acetone-d_6) δ 1.96-2.04 (m, 1H), 1.91 – 1.79 (m, 1H), 1.75 – 1.50 (m, 6H), 1.49 – 1.29 (m, 8H), 1.24 (s, 3H), 1.24 (s, 3H), 1.21 – 0.99 (m, 12H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.76-0.79 (m, 1H), 0.76-0.79 (m, 1H), 0.70 (s, 3H), 0.66-0.68 (m, 1H); ^{13}C NMR (151 MHz, acetone-d_6) δ 56.8, 56.6, 56.3, 55.1, 54.8, 46.0, 42.5, 42.4, 42.3, 40.6, 40.3, 40.0, 39.3, 38.1, 36.8, 36.0,

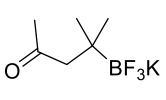
35.7, 35.7, 35.5, 35.4, 33.0, 32.4, 32.3, 32.1, 28.0, 27.8, 25.6, 24.1, 24.0, 23.9, 23.6, 22.1, 21.9, 20.8, 18.2, 11.7, 11.6, 11.5, 11.5.

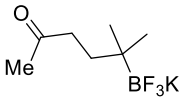
^{19}F NMR (376 MHz, acetone-d_6) δ -145.56, -155.60. ^{11}B NMR (128 MHz, acetone-d_6) δ 5.2.

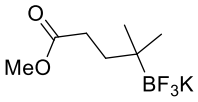
IR (ATR): ν = 2929, 2851, 1379, 1145, 1026, 853, 693 cm^{-1}

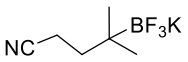
HRMS (ESI) calcd for $C_{28}H_{49}BF_3$ $[M\text{-}K]^+$: 453.3879; Found: 453.3863.

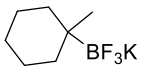
Trifluoroborates below were synthesized according to known literature procedures[3-8]

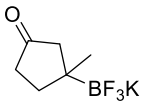


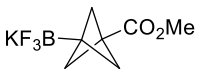


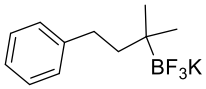


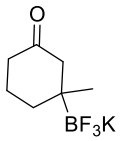


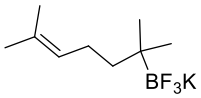


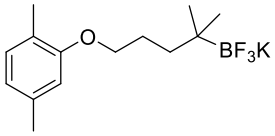


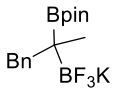


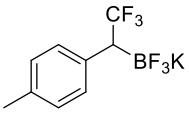


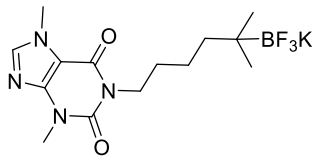




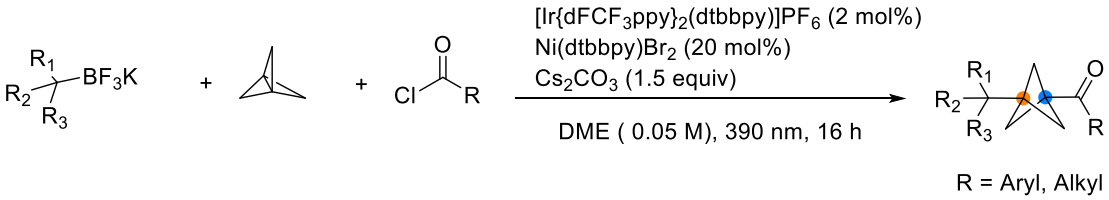






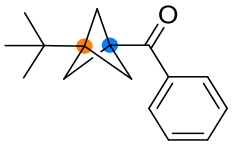


5. General Procedure



R = Aryl, Alkyl

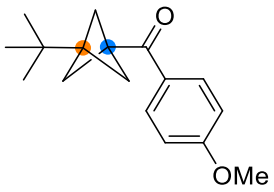
To an 8.0 mL clear borosilicate glass vial with a screw top equipped with a magnetic stir bar was added [Ir{dFCF$_3$ppy}$_2$(dtbbpy)]PF$_6$ (6.73 mg, 0.06 mmol, 2 mol %), NiBr$_2$(dtbbpy) (29.21 mg, 0.06 mmol, 20 mol %), Cs$_2$CO$_3$ (146 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate (0.45 mmol, 1.5 equiv), the acyl chloride (if solid, 0.30 mmol, 1.0 equiv), The vial was then sealed with a screw-cap containing a PTFE-lined silicone septum. An inlet needle was inserted, and the atmosphere was exchanged for N$_2$ via three evacuation-backfill cycles. The vial was then charged with 6.0 mL of dry DME via syringe, and the acyl chloride (if liquid, 0.50 mmol, 1.0 equiv) was added via syringe. Finally, the via was charged with [1.1.1]propellane (1.13 mL, 0.9 mmol, 3.0 equiv, 0.8 M soln in Et$_2$O). The reaction was then sparged for ~2 min with N$_2$ or Ar, the cap was sealed with Parafilm®, and the reaction mixture was irradiated with a Kessil® PR160 390 nm lamp for 16 h. Upon reaction completion, The resulting soln was passed through a pad of Celite®, eluting with either CH$_2$Cl$_2$ or EtO$_2$ followed by SiO$_2$ column chromatography (hexanes/EtOAc).



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 4 (43.7 mg, 64% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.00 (d, J = 7.1 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.3 Hz 2H), 2.08 (s, 6H), 0.90 (s, 9H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 198.6, 136.8, 132.7, 128.8, 128.3, 49.8, 48.6, 41.7, 29.4, 25.7.

IR (ATR): ν = 2959, 2908, 2872, 1666, 1340, 1209, 872 696 cm^{-1}

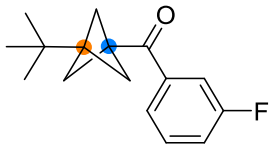
HRMS (EI) calcd for C$_{16}$H$_{20}$O [M]$^+$: 228.1514; Found: 228.1526.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-methoxyphenyl)methanone 5 (39.4 mg, 51% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 2.06 (s, 6H), 0.90 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 163.1, 131.2, 129.8, 113.5, 55.4, 49.8, 48.5, 41.5, 29.4, 25.7.

IR (ATR): ν = 2960, 1655, 1601, 1509, 1259, 1211, 1167, 1028, 809 cm^{-1}.

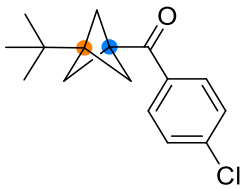
HRMS (EI) calcd for $C_{17}H_{22}O_2$ $[M]^+$: 258.1620; Found: 258.1627.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(3-fluorophenyl)methanone 6 (33.9 mg, 46% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.66 (ddd, *J* = 9.5, 2.7, 1.5 Hz, 1H), 7.42 (td, *J* = 8.0, 5.6 Hz, 1H), 7.23 (tdd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 2.07 (s, 6H), 0.90 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8; ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 (d, *J* = 2.0 Hz), 162.6 (d, *J* = 247.7 Hz), 138.7 (d, *J* = 6.0 Hz), 130.0 (d, *J* = 7.6 Hz), 124.6 (d, *J* = 3.1 Hz), 119.7 (d, *J* = 21.5 Hz), 115.5 (d, *J* = 22.1 Hz), 49.8, 48.7, 41.6, 29.4, 25.7.

IR (ATR): ν = 2959, 2910, 1671, 1587, 1482, 1296, 1203, 876, 791 cm^{-1}

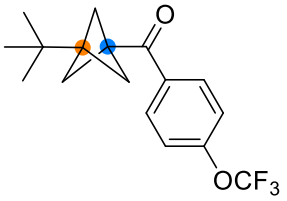
HRMS (EI) calcd for $C_{16}H_{19}FO$ $[M]^+$: 246.1420; Found: 246.1439.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanone 7 (28.2 mg, 36% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 2.06 (s, 6H), 0.90 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 139.1, 135.0, 130.3, 128.7, 49.8, 48.7, 41.6, 29.4, 25.7.

IR (ATR): ν = 2955, 1664, 1586, 1208, 1091, 872 cm^{-1}

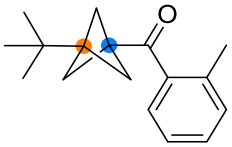
HRMS (EI) calcd for $C_{16}H_{19}ClO$ $[M]^+$: 262.1124; Found: 262.1116.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanone 8 (42.1 mg, 45% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 2H), 7.27 (dd, J = 8.8 ,1.6 Hz, 2H), 2.07 (s, 6H), 0.90 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.62; ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 152.3, 135.0, 130.8, 120.3 (q, J = 271.7 Hz) 120.2, 49.8, 48.7, 41.6, 29.4, 25.7.

IR (ATR): ν = 2960, 2873, 1668, 1602, 1505, 1363, 1258, 1210, 874 cm^{-1}

HRMS (EI) calcd for $C_{17}H_{19}F_3O_2$ $[M]^+$: 312.1337; Found: 312.1346.

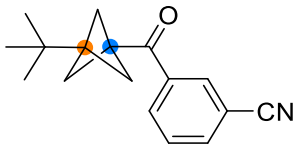


(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(o-tolyl)methanone 9 (30.4 mg, 42% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.6, 1.5 Hz, 1H), 7.32 (td, J = 7.5, 1.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 2.38 (s, 3H), 1.95 (s, 6H), 0.86 (s, 9H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 203.6, 137.9, 136.9, 131.4, 130.3, 127.7, 125.0, 48.9, 48.3, 42.5, 29.4, 25.7, 20.37.

IR (ATR): ν = 2958, 2871, 1672, 1459, 1300, 1282, 1209, 759 cm^{-1}

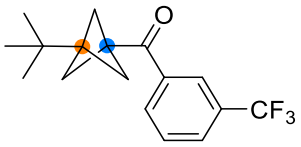
HRMS (EI) calcd for $C_{17}H_{22}O$ $[M]^+$: 242.1671; Found: 242.1703.



3-(3-(*tert*-Butyl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile 10 (22.7 mg, 30% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 2.09 (s, 6H), 0.91 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.5, 137.5, 135.6, 132.7, 132.5, 129.5, 118.0, 112.9, 49.9, 49.0, 41.5, 29.4, 25.7.

IR (ATR): ν = 2959, 2250, 1683, 1673, 1260, 1203, 1093, 798 cm^{-1}

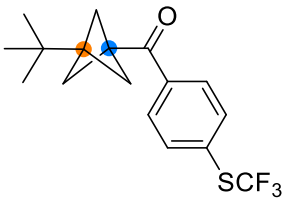
HRMS (EI) calcd for $C_{17}H_{19}NO$ $[M]^+$: 253.1467; Found: 253.1468.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(3-(trifluoromethyl)phenyl)methanone 11 (40.8 mg, 46% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 2.09 (s, 6H), 0.91 (d, *J* = 1.6 Hz, 9H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.85; ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.2, 137.2, 131.9, 131.0 (q, *J* = 32.9 Hz), 129.1 (q, *J* = 3.9 Hz), 129.0, 125.6 (q, *J* = 3.9 Hz), 123.7 (q, *J* = 271.7 Hz) 49.9, 48.8, 41.6, 29.4, 25.7.

IR (ATR): ν = 2961, 1673, 1330, 1207, 1169, 1131 1075 cm^{-1}

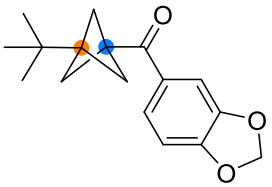
HRMS (EI) calcd for $C_{17}H_{19}F_3O$ $[M]^+$: 296.1388; Found: 242.1379.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-((trifluoromethyl)thio)phenyl)methanone 12 (31.4 mg, 32% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 5.8 Hz, 2H), 2.08 (s, 6H), 0.90 (s, 9H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -41.77. ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 138.2, 135.5, 130.4 (q, *J* = 10.0Hz), 129.6, 128.9 (q, *J* = 308 Hz) 49.8, 48.8, 41.7, 29.4, 25.7.

IR (ATR): ν = 2960, 2908, 1656, 1489, 1259, 1118, 1087, 938 cm^{-1}

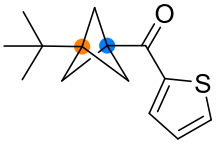
HRMS (EI) calcd for $C_{17}H_{19}F_3OS$ $[M]^+$: 328.1109; Found: 328.1109.



Benzo[d][1,3]dioxol-5-yl(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)methanone 13 (38.3 mg, 47% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 10.5 Hz, 1H), 7.47 (s, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.03 (s, 2H), 2.05 (s, 6H), 0.89 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 151.4, 147.9, 131.5, 125.3, 108.6, 107.7, 101.7, 49.9, 48.5, 41.5, 29.4, 25.7.

IR (ATR): ν = 2958, 2908, 1656, 1487, 1360, 1261, 1243, 1038, 934 cm^{-1}

HRMS (EI) calcd for $C_{17}H_{20}O_3$ $[M]^+$: 272.1412; Found: 272.1406.

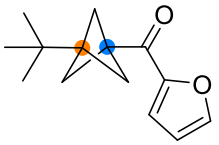


(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone 14 (19.6 mg, 28% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 3.8 Hz, 1H), 7.62 (d, *J* = 4.9

Hz, 1H), 7.13 (t, J = 4.4 Hz, 1H), 2.05 (s, 6H), 0.90 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.1, 143.0, 133.3, 132.8, 128.0, 49.5, 48.1, 41.2, 29.4, 25.8.

IR (ATR): ν = 2959, 2907, 1644, 1413, 1362, 1209, 720 cm^{-1}

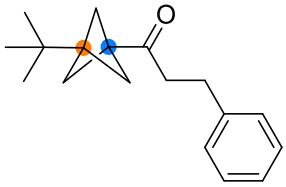
HRMS (EI) calcd for $C_{14}H_{18}SO$ $[M]^+$: 239.1078; Found: 239.1068.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(furan-2-yl)methanone 15 (20.9 mg, 32% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 2.6 Hz, 1H), 7.22 (s, 1H), 6.52 (dt, J = 3.6, 1.8 Hz, 1H), 2.02 (s, 6H), 0.89 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.1, 152.3, 146.3, 118.1, 111.9, 48.9, 48.3, 40.3, 29.4, 25.7.

IR (ATR): ν = 2958, 2872, 1661, 1464, 1362, 1202, 1054 cm^{-1}

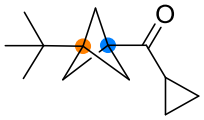
HRMS (EI) calcd for $C_{14}H_{18}O_2$ $[M]^+$: 218.1307; Found: 218.1301.



1-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 16 (46.8 mg, 61 yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.7 Hz, 2H), 7.22 – 7.15 (m, 3H), 2.87 (t, J = 7.7 Hz, 2H), 2.76 (t, J = 7.7 Hz, 2H), 1.77 (s, 6H), 0.83 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.4, 141.2, 128.4, 128.3, 126.0, 47.6, 47.6, 41.5, 40.4, 29.4, 29.3, 25.6.

IR (ATR): ν = 2958, 2870, 1702, 1362, 1200, 1094, 951, 698 cm^{-1}.

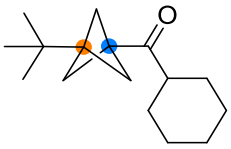
HRMS (EI) calcd for $C_{18}H_{24}O$ $[M]^+$: 256.1827; Found: 256.1829.



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(cyclopropyl)methanone 17 (31.1 mg, 54% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.08 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.85 (s, 6H), 1.06 – 0.98 (m, 2H), 0.84-0.88 (m, 11H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.3, 47.7, 47.6, 42.0, 29.4, 25.7, 17.0, 11.1.

IR (ATR): ν = 2965, 2870, 1683, 1391, 1202, 1085, 964 cm^{-1}

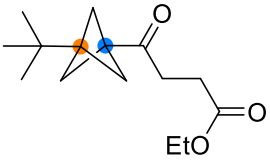
HRMS (EI) calcd for $C_{12}H_{17}O$ $[M\text{-}CH_3]^+$: 177.1279; Found: 177.1267;



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(cyclohexyl)methanone 18 (29.4 mg, 42% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.60 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.82 (s, 6H), 1.77 – 1.73 (m, 4H), 1.38 – 1.10 (m, 6H), 0.85 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 212.2, 48.0, 47.9, 47.3, 41.2, 29.3, 28.4, 25.8, 25.7, 25.7.

IR (ATR): ν = 2931, 2856, 1695, 1449, 1362, 954, 761 cm^{-1}

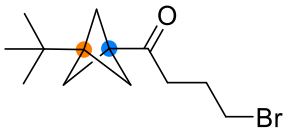
HRMS (EI) calcd for $C_{16}H_{26}O$ $[M]^+$: 234.1984; Found: 234.2000.



Ethyl 4-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-4-oxobutanoate 19 (35.5 mg, 47% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 1.83 (s, 6H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.85 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.2, 172.8, 60.6, 47.6, 47.6, 41.3, 33.3, 29.3, 27.6, 25.7, 14.2.

IR (ATR): ν = 2960, 1737, 1705, 1364, 1202, 1097 cm^{-1}

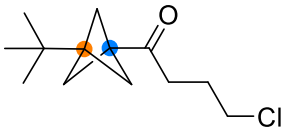
HRMS (EI) calcd for $C_{15}H_{24}O_3$ $[M]^+$: 252.1725; Found: 252.1731.



4-Bromo-1-(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)butan-1-one 20 (33.4 mg, 41% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.44 (t, *J* = 6.4 Hz, 2H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.14 – 2.07 (m, 2H), 1.82 (s, 6H), 0.85 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.0, 47.6, 47.5, 41.5, 36.5, 33.4, 29.3, 26.1, 25.7.

IR (ATR): ν = 2959, 2909, 2871, 1701, 1509, 1362, 1201, 1089, 803 cm^{-1}

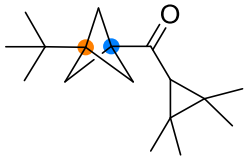
HRMS (EI) calcd for $C_{13}H_{21}BrO$ $[M]^+$: 272.0776; Found: 272.0784.



1-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-4-chlorobutan-1-one 21 (28.1 mg, 47% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.57 (t, *J* = 6.3 Hz, 2H), 2.63 (t, *J* = 7.0 Hz, 2H), 2.02 (tt, *J* = 7.0, 6.3 Hz, 2H), 1.82 (s, 6H), 0.85 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 47.6, 47.5, 44.5, 41.5, 35.3, 29.3, 26.0, 25.6.

IR (ATR): ν = 2960, 2871, 1702, 1363, 1260, 1202, 1095, 803 cm^{-1}

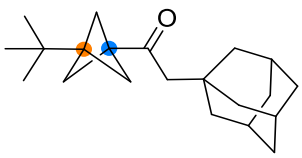
HRMS (EI) calcd for $C_{12}H_{18}ClO$ $[M\text{-}CH_3]^+$: 213.1046; Found: 213.1047



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(2,2,3,3-tetramethylcyclopropyl)methanone 22 (26.7 mg, 36% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76 (s, 6H), 1.20 (d, *J* = 1.3 Hz, 13H), 0.85 (s, 9H;; ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.1, 47.2, 47.0, 43.3, 40.3, 34.2, 29.3, 25.7, 23.8, 16.3.

IR (ATR): ν = 2955, 1680, 1409, 1260, 1200, 1100, 807 cm^{-1}

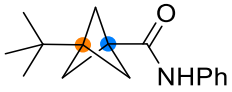
HRMS (EI) calcd for $C_{17}H_{28}O$ $[M]^+$: 248.2140; Found: 248.2138.



2-(Adamantan-1-yl)-1-(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)ethan-1-one 23 (46.8 mg, 52% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.17 (s, 2H), 1.94 (s, 3H), 1.77 (s, 6H), 1.68 (d, *J* = 12.3 Hz, 3H), 1.65 – 1.60 (m, 9H), 0.84 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.5, 51.1, 47.5, 47.3, 43.0, 42.5, 36.8, 33.6, 29.3, 28.6, 25.7.

IR (ATR): ν = 2956, 2901, 1702, 1451, 1393, 1360, 1199, 1082, 872, 803 cm^{-1}

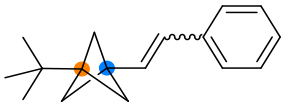
HRMS (EI) calcd for $C_{21}H_{32}O$ $[M]^+$: 300.2453; Found: 300.2453.



3-(*tert*-Butyl)-*N*-phenylbicyclo[1.1.1]pentane-1-carboxamide 24 (11.6 mg, 16% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.2 Hz, 2H), 7.31 (td, *J* = 7.7, 2.1 Hz, 1H), 7.15 (br, 1H), 7.09 (dt, *J* = 7.7, 4.0 Hz, 2H), 1.90 (s, 6H), 0.88 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 137.7, 129.0, 124.2, 119.5, 47.6, 47.1, 37.8, 29.3, 25.8.

IR (ATR): ν = 2957, 1659, 1599, 1440, 1206, 753, 692 cm^{-1}

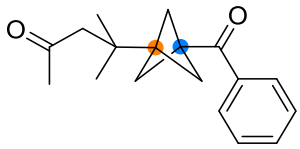
HRMS (ESI) calcd for $C_{16}H_{22}NO$ $[M+H]^+$: 244.1701; Found: 244.1406.



1-(*tert*-Butyl)-3-styrylbicyclo[1.1.1]pentane 25 (18.9 mg, 28% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.25 – 7.21 (m, 3H), 6.48 (d, *J* = 12.0 Hz, 1H), 5.70 (d, *J* = 12.0 Hz, 1H), 1.56 (s, 6H), 0.77 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 131.9, 130.2, 129.1, 127.5, 126.5, 49.8, 49.2, 35.9, 29.4, 25.8.

IR (ATR): ν = 2958, 2902, 2705, 1670, 1027, 1095, 1045, 830 cm^{-1}

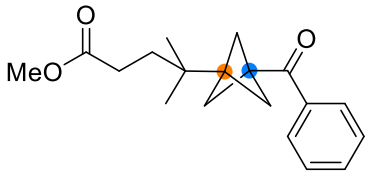
HRMS (EI) calcd for $C_{27}H_{22}$ $[M]^+$: 226.1722; Found: 226.1718.



4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentan-2-one 26 (41.1 mg, 51% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.47 (t, *J* =7.5 Hz 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 2H), 2.16 (s, 3H), 2.09 (s, 6H), 1.03 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 198.1, 136.6, 132.8, 128.8, 128.4, 50.6, 49.8, 48.5, 41.7, 32.5, 32.4, 22.9;

IR (ATR): ν = 2966, 2913, 2875, 1713, 1664, 1448, 1361, 1330, 1177 cm^{-1}

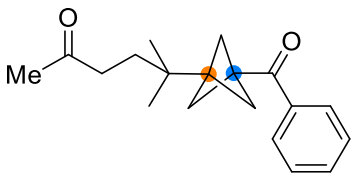
HRMS (EI) calcd for $C_{18}H_{22}O_2$ $[M]^+$: 270.1620; Found: 270.1631.



Methyl 4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentanoate 27 (37.8 mg, 42% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 3.68 (s, 3H), 2.35 – 2.26 (m, 2H), 2.11 (s, 6H), 1.66 – 1.52 (m, 2H), 0.85 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 174.6, 136.7, 132.7, 128.8, 128.4, 51.6, 50.0, 48.5, 41.9, 33.4, 31.6, 29.6, 22.4.

IR (ATR): ν = 2964, 1737, 1665, 1297, 1207, 872, 766, 697 cm^{-1}

HRMS (EI) calcd for $C_{19}H_{24}O_3$ $[M]^+$: 300.1725; Found: 300.1737.

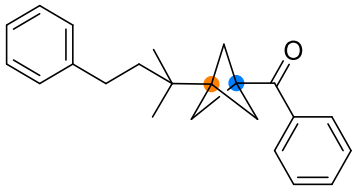


5-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-5-methylhexan-2-one 28 (31.5 mg, 37% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 2.47 – 2.39 (m, 2H), 2.17 (s, 3H), 2.11 (s, 6H), 1.55

– 1.49 (m, 2H), 0.84 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.1, 198.2, 136.6, 132.8, 128.8, 128.4, 50.0, 48.6, 42.0, 39.1, 31.9, 31.4, 30.0, 22.6.

IR (ATR): ν = 2928, 2868, 1667, 1448, 1209, 800, 696 cm^{-1}

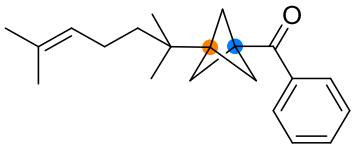
HRMS (EI) calcd for $C_{19}H_{24}O_2$ $[M]^+$: 284.1776; Found: 284.1783.



(3-(2-Methyl-4-phenylbutan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 29 (43.8 mg, 46% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.4 Hz, 2H), 7.54 (t, *J* = 6.6 Hz, 1H), 7.44 (t, *J* = 6.7 Hz 2H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.24 – 7.16 (m, 3H), 2.64 – 2.54 (m, 2H), 2.13 (s, 6H), 1.56 – 1.51 (m, 2H), 0.95 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 143.2, 136.7, 132.7, 128.8, 128.4, 128.3, 128.3, 125.7, 50.1, 48.8, 42.0, 41.1, 32.1, 31.0, 22.7.

IR (ATR): ν = 2963, 1715, 1665, 1448, 1207, 872, 767, 697cm^{-1}

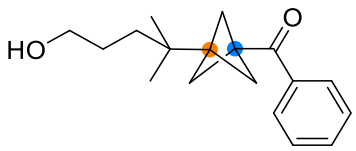
HRMS (EI) calcd for $C_{23}H_{26}O$ $[M]^+$: 318.1984; Found: 300.1978.



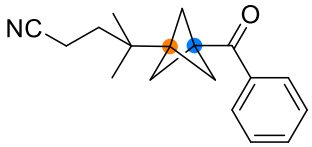
(3-(2,6-Dimethylhept-5-en-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 30 (45.2 mg, 51% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 5.14 (ddq, *J* = 8.5, 5.7, 1.4 Hz, 1H), 2.12 (s, 6H), 2.03 – 1.92 (m, 2H), 1.72 (s, 3H), 1.64 (s, 3H), 1.29 – 1.23 (m, 2H), 0.89 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 136.8, 132.7, 131.1, 128.8, 128.3, 125.0, 50.1, 48.9, 42.0, 38.6, 31.8, 25.7, 23.1, 17.6.

IR (ATR): ν = 2964, 2912, 2872, 1666, 1598, 1580, 1448, 1362, 1177, 696 cm^{-1}

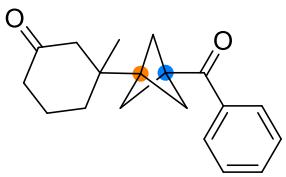
HRMS (EI) calcd for $C_{21}H_{28}O$ $[M]^+$: 296.2140; Found: 296.2130.



(3-(5-Hydroxy-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 31 (25.2 mg, 31% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.03 (s, 6H), 1.57 – 1.42 (m, 3H), 1.24 – 1.17 (m, 2H), 0.79 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 136.7, 132.7, 128.8, 128.4, 63.8, 50.1, 48.8, 42.0, 34.5, 31.6, 27.8, 22.7.
IR (ATR): ν = 3518, 3004, 1709, 1359, 1220, 902, 529 cm^{-1}
HRMS (ESI) calcd for $C_{18}H_{25}O_2$ $[M+H]^+$: 273.1855; Found: 273.1847.



4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentanenitrile 32 (43.2 mg, 54% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.5 Hz, 2H), 7.55 (t, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 2.32 (dd, *J* = 8.9, 7.4 Hz, 2H), 2.12 (s, 6H), 1.67 (dd, *J* = 8.9, 7.4 Hz, 2H), 0.90 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.8, 136.5, 132.9, 128.8, 128.4, 120.3, 49.9, 48.1, 41.9, 34.3, 32.0, 22.2, 12.7.
IR (ATR): ν = 2966, 2874, 2245, 1663, 1448, 1208, 767, 698 cm^{-1}
HRMS (EI) calcd for $C_{18}H_{21}ON$ $[M]^+$: 267.1623; Found: 267.1612.

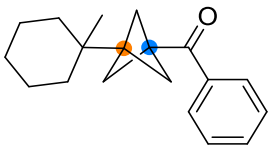


3-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-3-methylcyclohexan-1-one 33 (32.1 mg, 38% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 2.34 (d, *J* = 14.6 Hz, 1H), 2.27 (t, *J* = 10.4 Hz, 2H), 2.13 (s, 6H), 2.04 – 1.99 (m, 2H), 1.85 (dtt, *J* = 19.6, 12.8, 3.8 Hz, 1H), 1.72 – 1.64 (m,

1H), 1.53 (d, J = 13.8 Hz, 1H), 0.90 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.8, 197.8, 136.5, 132.9, 128.8, 128.4, 49.8, 49.5, 47.9, 41.9, 40.8, 37.8, 32.4, 22.3, 20.7.

IR (ATR): ν = 2963, 1710, 1664, 1260, 1207, 1023, 798, 697 cm^{-1}

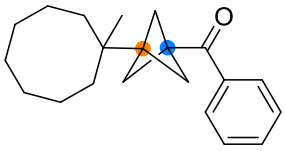
HRMS (EI) calcd for $C_{19}H_{22}O_2$ $[M]^+$: 282.1620; Found: 282.1629.



(3-(1-Methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 34 (45 mg, 56% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.1 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 2.09 (s, 6H), 1.62 (dt, J = 12.5, 3.8 Hz, 1H), 1.52 (t, J = 4.2 Hz, 1H), 1.46 – 1.33 (m, 2H), 1.27 – 1.20 (m, 5H), 1.13 (dt, J = 12.1, 3.8 Hz, 1H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 136.8, 132.6, 128.9, 128.3, 49.6, 49.3, 42.0, 33.3, 31.5, 26.3, 21.9, 19.4.

IR (ATR): ν = 2960, 2925, 1666, 1445, 1260, 1205, 805, 798, 696 cm^{-1}

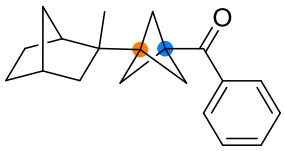
HRMS (EI) calcd for $C_{19}H_{24}O$ $[M]^+$: 268.1827; Found: 268.1812.



(3-(1-Methylcyclooctyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 35 (37.2 mg, 42% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 6.5 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 2.11 (s, 6H), 1.67 – 1.51 (m, 7H), 1.52 – 1.39 (m, 5H), 1.43 – 1.20 (m, 2H), 0.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 136.8, 132.6, 128.8, 128.3, 50.5, 49.4, 42.3, 34.3, 32.1, 28.6, 25.6, 23.5, 23.2.

IR (ATR): ν = 2958, 2915, 1665, 1447, 1205, 805, 756, 696 cm^{-1}

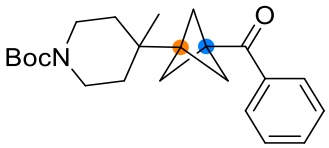
HRMS (EI) calcd for $C_{21}H_{28}O$ $[M]^+$: 296.2140; Found: 296.2127.



(3-(2-Methylbicyclo[2.2.1]heptan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 36 (39.8 mg, 47% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. dr =4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 2.21 – 2.16 (m, 1H), 2.10 (s, 6H), 2.00 (d, *J* = 3.8 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.50 (ddd *J* = 9.5, 4.3, 2.3 Hz , 2H), 1.36 – 1.29 (m, 1H), 1.14 (ddq, *J* = 8.9, 2.7, 1.3 Hz, 2H), 0.93 (s, 3H), 0.77 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 136.8, 132.6, 128.8, 128.3, 50.7, 48.1, 46.3, 43.2, 43.0, 41.2, 38.6, 37.7, 28.0, 25.0, 21.7.

IR (ATR): ν = 2964, 2871, 1665, 1598, 1580, 1319, 1205 695 cm^{-1}

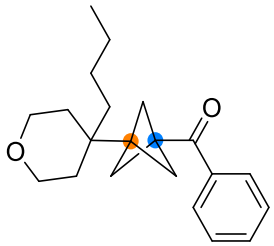
HRMS (EI) calcd for $C_{20}H_{24}O$ $[M]^+$: 280.1827; Found: 280.1824.



***tert*-Butyl 4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpiperidine-1-carboxylate 37** (45.3 mg, 41% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point 103-104 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (td, *J* = 7.8, 1.6 Hz, 2H), 3.88 (bs, 2H), 2.93 (t, *J* = 12.7 Hz, 2H), 2.10 (s, 6H), 1.41-1.15 (m, 11H), 1.34 – 1.14 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 154.9, 136.6, 132.8, 128.8, 128.4, 79.3, 49.6, 48.4, 42.2, 40.0, 32.5, 30.4, 28.4, 18.4.

IR (ATR): ν = 2970, 2918, 2870, 1691, 1666, 1207, 1150, 697 cm^{-1}

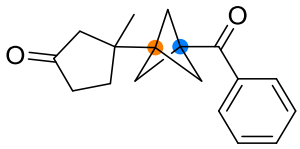
HRMS (ESI) calcd for $C_{23}H_{31}O_3Na$ $[M+Na]^+$: 392.2202; Found: 392.2190.



(3-(4-Butyltetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl) methanone 38 (54.2 mg, 58% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point 76-77 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H) , 7.44 (t, *J* = 7.7 Hz, 2H), 3.77 (dt, *J* = 11.7, 4.1 Hz, 2H), 3.58 (td, *J* = 11.2, 2.5 Hz, 2H), 2.17 (s, 6H), 1.54 (ddd, *J* = 13.8, 10.9, 4.5 Hz, 2H), 1.51 – 1.44 (m, 2H), 1.35 – 1.29 (m, 4H), 1.30 – 1.21 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.1, 136.7, 132.8, 128.8, 128.4, 63.8, 51.0, 48.4, 42.6, 32.5, 31.8, 31.6, 26.4, 23.7, 14.1.

IR (ATR): ν = 2955, 2850, 1665, 1450, 1356, 1205, 549 cm^{-1}

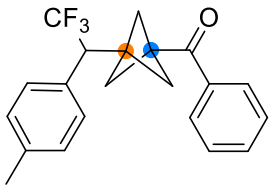
HRMS (EI) calcd for $C_{21}H_{28}O_2$ $[M]^+$: 312.2089; Found: 312.2100.



3-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-3-methylcyclopentan-1-one 39 (28.1 mg, 35% yield) was prepared following the General Procedure. This product was obtained as a white solid, Melting point 63-65 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 2.37 – 2.27 (m, 2H), 2.24 (d, *J* = 17.9 Hz, 1H), 2.14 (qd, *J* = 9.8, 2.0 Hz, 6H), 2.02 – 1.96 (m, 2H), 1.72 (dd, *J* = 13.0, 9.1 Hz , 1H), 1.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 219.0, 197.6, 136.5, 132.9, 128.8, 128.5, 50.2, 48.5, 46.7, 42.3, 38.8, 37.3, 31.7, 22.8.

IR (ATR): ν = 2962, 2874, 1740, 1663, 1597, 1448, 1319, 1212, 1176, 872 cm^{-1}

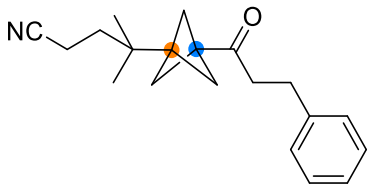
HRMS (EI) calcd for $C_{18}H_{20}O_2$ $[M]^+$: 368.1463; Found: 368.1469.



Phenyl(3-(2,2,2-trifluoro-1-(*p*-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl)methanone 40 (33.1 mg, 32% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.15 (d, *J* = 6.8 Hz, 2H), 3.47 (q, *J* = 10.0 Hz, 1H), 2.36 (s, 3H), 2.28 (q, *J* = 9.6 Hz, 6H); ^{19}F NMR (565 MHz, $CDCl_3$) δ -65.78 (d, *J* = 10.0 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 137.9, 136.4, 132.9, 129.9, 129.4, 128.8, 128.7, 128.5, 126.5 (q, *J* = 281.3 Hz), 53.5, 50.9 (q, *J* = 26.4 Hz), 44.6, 38.9, 21.1.

IR (ATR): ν = 2983, 1666, 1336, 1260,1172, 1131, 1101, 1025 695 cm^{-1}

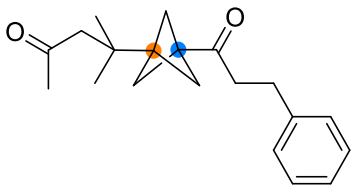
HRMS (EI) calcd for $C_{21}H_{19}F_3O$ $[M]^+$: 344.1388; Found: 344.1384.



4-Methyl-4-(3-(3-phenylpropanoyl)bicyclo[1.1.1]pentan-1-yl)pentanenitrile 41 (31.8 mg, 36% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.16 (m, 3H), 2.87 (td, *J* = 7.7, 2.3 Hz, 2H), 2.75 (t, *J* = 8.1 Hz, 2H), 2.27 (t, *J* = 7.1 Hz, 2H), 1.81 (s, 6H), 1.59 (t, *J* = 8.1 Hz, 2H), 0.83 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.6, 141.1, 128.5, 128.3, 126.1, 120.2, 47.7, 47.1, 41.7, 40.4, 34.2, 31.8, 29.4, 22.1, 12.6.

IR (ATR): ν = 2956, 2852, 2250, 1260, 1098, 1048, 798 cm^{-1}

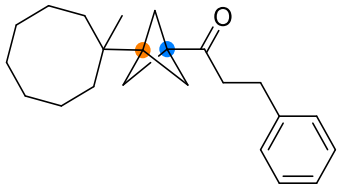
HRMS (EI) calcd for $C_{20}H_{25}NO$ $[M]^+$: 295.1936; Found: 295.1929.



4-Methyl-4-(3-(3-phenylpropanoyl)bicyclo[1.1.1]pentan-1-yl)pentan-2-one 42 (42.9 mg, 48% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ7.27 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.16 (m, 3H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 8.1 Hz, 2H), 2.27 (s, 2H), 2.13 (s, 3H), 1.79 (s, 6H), 0.96 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.4, 207.9, 141.1, 128.5, 128.3, 126.1, 50.5, 47.6, 47.5, 42.9, 41.5, 40.4, 32.4, 29.4, 22.8.

IR (ATR): ν = 2964, 2912, 2873, 1701, 1604, 1496, 1453, 1192, 1154, 699 cm^{-1}

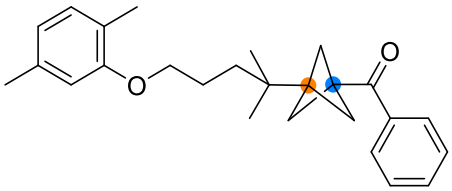
HRMS (EI) calcd for $C_{20}H_{26}O_2$ $[M]^+$: 298.1933; Found: 298.1942.



1-(3-(1-Methylcyclooctyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 43 (56.3 mg, 58% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.16 (m, 3H),7.00 (d, *J* = 7.4 Hz, 1H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.75 (dd, *J* = 8.3, 7.1 Hz, 2H), 1.80 (s, 6H), 1.61 – 1.43 (m, 6H), 1.50 – 1.34 (m, 5H), 1.29 – 1.04 (m, 2H), 0.75 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.4, 141.2, 128.4, 128.3, 126.0, 48.3, 48.3, 42.2, 40.4, 34.2, 32.0, 29.4, 28.6, 25.6, 23.4, 23.1.

IR (ATR): ν = 2959, 2914, 2870, 1702, 1448, 1376, 692 cm^{-1}

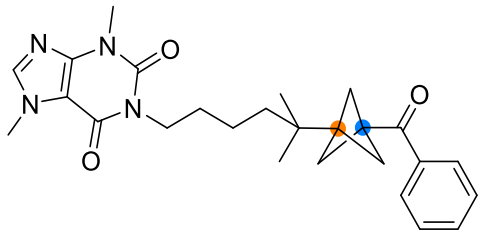
HRMS (EI) calcd for $C_{23}H_{32}O$ $[M]^+$: 324.2453; Found: 324.2460.



(3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 44 (43.9 mg, 39% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 2.19 (s, 3H), 2.12 (s, 6H), 1.85 – 1.71 (m, 2H), 1.44 – 1.37 (m, 2H), 0.90 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 157.0, 136.7, 136.5, 132.7, 130.3, 128.9, 128.4, 123.5, 120.6, 112.0, 68.5, 50.1, 48.8, 42.0, 35.0, 31.7, 24.6, 21.4, 15.8.

IR (ATR): ν = 2960, 2872, 1666, 1581, 1448, 1264, 1207, 1026, 766 cm^{-1}

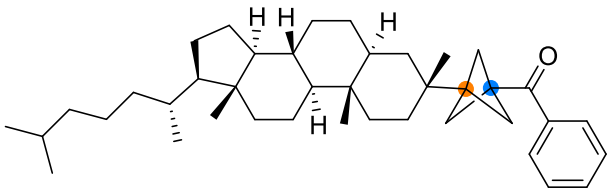
HRMS (EI) calcd for $C_{26}H_{32}O_2$ $[M]^+$: 376.2402; Found: 376.2393.



1-(5-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-5-methylhexyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione 45 (47.1 mg, 35% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.49 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 4.07 – 3.96 (m, 5H), 3.57 (s, 3H), 2.08 (s, 6H), 1.69 – 1.58 (m, 2H), 1.42 – 1.33 (m, 2H), 1.31 – 1.24 (m, 2H), 0.84 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 155.3, 151.4, 148.7, 141.3, 136.8, 132.6, 128.8, 128.3, 107.7, 50.0, 48.8, 41.4, 38.2, 33.5, 31.8, 29.6, 28.9, 24.6, 22.8, 21.9.

IR (ATR): ν = 2934, 2859, 1698, 1672, 1605, 1415, 1234, 1021 cm^{-1}.

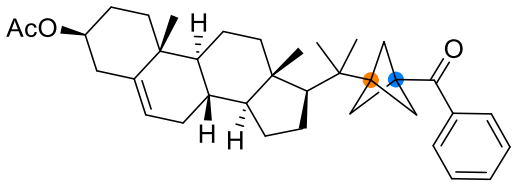
HRMS (EI) calcd for $C_{26}H_{33}N_4O_3$ $[M+H]^+$: 449.2553; Found: 449.2562.



Phenyl(3-((3*R*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone 46 (56.7 mg, 34% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. dr = 10:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.54 (td, *J* = 7.4, 1.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 2.19 (s, 6H), 1.96 (dt, *J* = 12.5, 3.6 Hz, 1H), 1.86 – 1.76 (m, 1H), 1.70 – 1.61 (m, 1H), 1.55 – 1.43 (m, 5H), 1.31-1.38(m, 5H), 1.27 – 1.20 (m, 6H), 1.17 – 1.06 (m, 8H), 1.04 – 0.95 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 2.7 Hz, 3H), 0.86 (d, *J* = 2.8 Hz, 3H), 0.80 (s, 3H), 0.75 (s, 3H), 0.64 (s, 3H) 0.60-0.64 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 136.8, 132.7, 128.8, 128.3, 56.6, 56.3, 54.7, 52.3, 47.7, 42.6, 42.6, 42.1, 40.0, 39.5, 38.4, 36.1, 35.9, 35.8, 35.6, 35.5, 32.2, 31.6, 31.1, 29.0, 28.7, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 20.9, 18.6, 12.1, 11.4.

IR (ATR): ν = 2963, 1715, 1665, 1448, 1364, 1207, 1177, 697 cm^{-1}

HRMS (EI) calcd for $C_{40}H_{60}O[M]^{+}$:556.4644; Found:556.4653.

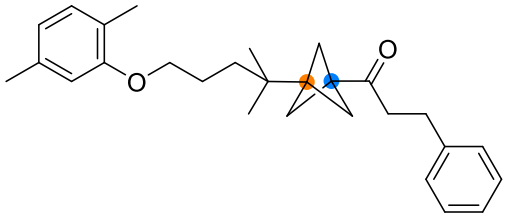


(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-(2-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)propan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl Acetate 47 (80.7 mg, 51% yield) was prepared following the General Procedure. This product was obtained as white solid, Melting point 163-165 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.0 Hz, 2H), 5.51 – 5.32 (m, 1H), 4.60 (dt, *J* = 11.5, 6.1 Hz, 1H), 2.31-2.35(m, 2H), 2.09 (q, *J* = 9.6 Hz, 6H), 2.03(s, 3H), 1.97 (d, *J* = 15.8 Hz, 1H), 1.86 (d, *J* = 11.9 Hz, 2H), 1.73 – 1.36 (m, 10H), 1.18-1.26 (m, 2H), 1.17 – 1.05 (m, 3H), 1.02 (s, 3H), 1.00 (s, 3H), 0.93 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ

198.7, 170.5, 139.6, 136.8, 132.7, 128.8, 128.3, 122.6, 73.9, 56.2, 55.8, 50.7, 50.7, 49.9, 44.1, 41.7, 40.3, 38.1, 37.0, 36.5, 35.5, 31.8, 31.3, 27.7, 25.2, 24.5, 24.4, 21.4, 21.0, 19.5, 19.3, 13.9.

IR (ATR): ν = 2963, 1731, 1663, 1447, 1363, 1331, 1248, 1036, 696 cm^{-1}

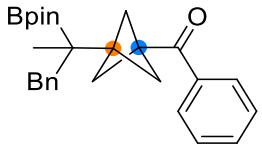
HRMS (EI) calcd for $C_{36}H_{48}O_3$ $[M]^+$: 528.3603; Found: 528.3592.



1-(3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 48 (49.6 mg, 41% yield) was prepared following the General Procedure. This product was obtained as white solid, Melting point 59-60 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.91 (t, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 1.82 (s, 6H), 1.78 – 1.70 (m, 2H), 1.37 – 1.30 (m, 2H), 0.83 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.2, 157.0, 141.2, 136.4, 130.3, 128.4, 128.3, 126.0, 123.5, 120.6, 112.0, 68.4, 47.9, 47.7, 41.9, 40.4, 34.9, 31.6, 29.4, 24.6, 22.7, 21.4, 15.8.

IR (ATR): ν = 2960, 1702, 1508, 1453, 1364, 1265, 1157, 803, 699 cm^{-1}

HRMS (EI) calcd for $C_{28}H_{36}O_2$ $[M]^+$: 404.2715; Found: 404.2707.



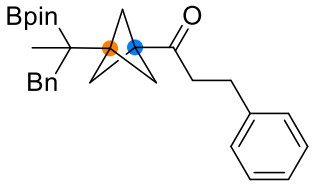
Phenyl(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone 49 (69.8 mg, 56% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6. 9 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.15 (t, *J* = 7.1 Hz, 1H), 3.01 (d, *J* = 12.8 Hz, 1H), 2.25 (d, *J* = 12.9 Hz, 1H), 2.20 (q, *J* = 9.6 Hz, 6H), 1.24 (s, 6H), 1.16 (s, 6H), 0.88

(s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.3, 140.3, 136.8, 132.7, 130.2, 128.9, 128.4, 127.7, 125.8, 83.5, 51.1, 46.6, 43.3, 41.4, 25.4, 24.9, 17.8; ^{11}B NMR (128 MHz, $CDCl_3$): 34.2.

IR (ATR): ν =2976, 2923, 1665, 1449, 1327, 1205, 1139, 872 cm^{-1}

HRMS (EI) calcd for $C_{27}H_{33}BO_3$ $[M]^+$: 416.2523; Found: 416.2544.



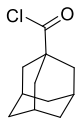
3-Phenyl-1-(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)propan-1-one 50 (59.1 mg, 45% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.13 (m, 8H), 2.93 (d, *J* = 12.9 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.18 (d, *J* = 12.9 Hz, 1H), 1.89 (q, *J* = 9.6 Hz, 6H), 1.23 (s, 6H), 1.14 (s, 6H), 0.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.1, 141.2, 140.2, 130.2, 128.5, 128.3, 127.7, 126.0, 125.8, 83.5, 48.9, 45.6, 43.2, 41.3, 40.5, 29.5, 25.4, 24.9, 17.7; ^{11}B NMR (128 MHz, $CDCl_3$): 34.0.

IR (ATR): ν = 3027, 2976, 2925, 1701,1603, 1453, 1377, 1314, 1140, 859 cm^{-1}

HRMS (ESI) calcd for $C_{29}H_{38}BO_3$ $[M+H]^+$: 445.2919; Found: 445.2921.

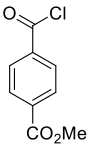
6. Reaction Limitations

Failed examples

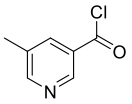


< 10%

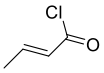
< 10%



< 10%



NO



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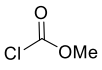
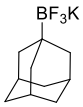
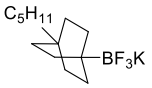
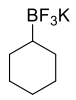


NO

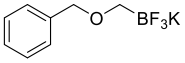




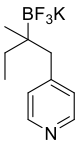
(a mxiture of two - component product and three component product, it is difficult to isolate)



two - component product

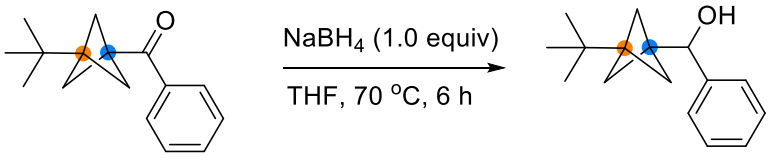


NO



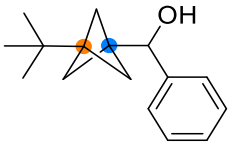
NO

7. Further transformations



4 **51**, 86%

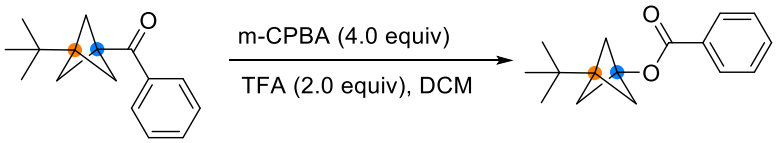
To a 4 mL reaction vial equipped with a stir bar was added **4** (22.8 mg, 0.10 mmol, 1.0 equiv) in dry THF (1.0 mL). Then $NaBH_4$ (3.8 mg, 0.10 mmol, 1.0 equiv) was added, and the reaction was allowed to stir for 12 h at 70 °C in an oil bath. After this time, the reaction was quenched with H_2O and 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 **51** as a colorless oil (19.7 mg, 86% yield).



(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanol 51 ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 4.64 (d, *J* = 2.9 Hz, 1H), 1.75 (d, *J* = 3.4 Hz, 1H), 1.36 – 1.28 (m, 6H), 0.72 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.9, 128.0, 127.2, 125.9, 74.1, 45.2, 40.3, 29.5, 25.8.

IR (ATR): ν = 3397, 2958, 2905, 2867, 1361, 1195, 1016, 704 cm^{-1}

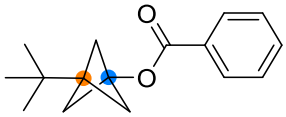
HRMS (ESI) calcd for $C_{16}H_{21}$ [M-OH]$^+$: 213.1638; Found: 213.1659.



4 **52**, 76%

To a 4 mL reaction vial equipped with a stir bar was added **4** (22.8 mg, 0.10 mmol, 1.0 equiv), *m*-CPBA (70.0 mg, 0.4 mmol, 4.0 equiv), TFA (15.4 µL, 0.2 mmol, 2.0 equiv), and dry CH_2Cl_2 (1 mL). The reaction mixture was allowed to stir at rt for 48 h. After this time, the reaction was quenched with sat aq $NaHCO_3$ (2 mL), and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent

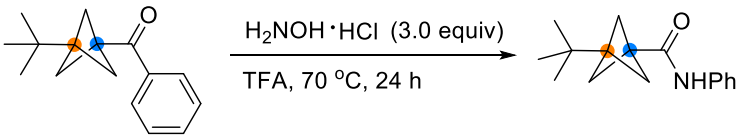
was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient hexane/EtOAc) to give the desired product **52** as a colorless oil (18.5 mg, 76% yield)



3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl Benzoate 52 ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.55 (ddt, *J* = 8.7, 7.2, 1.3 Hz, 1H), 7.43 (dd, *J* = 8.2, 7.4 Hz, 2H), 2.07 (s, 6H), 0.93 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 132.8, 130.6, 129.6, 128.3, 63.8, 50.1, 42.6, 28.8, 26.6.

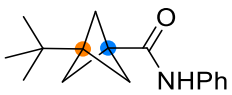
IR (ATR): ν = 2959, 2878, 1725, 1451, 1280, 1095, 708 cm^{-1}

HRMS (EI) calcd for $C_{15}H_{17}O_2$ $[M\text{-}CH_3]^+$: 229.1229; Found: 229.1237.



4 **24**, 81%

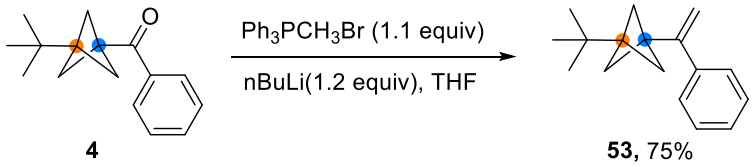
To a 4 mL reaction vial equipped with a stir bar was added **4** (22.8 mg, 0.10 mmol, 1.0 equiv), hydroxylammonium chloride (21.0 mg, 0.3 mmol, 3.0 equiv), and TFA (0.4 mL). The reaction mixture was allowed to stir at 70 °C in an oil bath for 24 h. After this time, the reaction was quenched with sat aq $NaHCO_3$ (1 mL) 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 **24** as a white solid (19.6 mg, 81% yield).



3-(*tert*-Butyl)-*N*-phenylbicyclo[1.1.1]pentane-1-carboxamide 24 Melting point 54-55 °C ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.2 Hz, 2H), 7.31 (td, *J* = 7.7, 2.1 Hz, 1H), 7.15 (br, 1H), 7.09 (dt, *J* = 7.7, 4.0 Hz, 2H), 1.90 (s, 6H), 0.88 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 137.7, 129.0, 124.2, 119.5, 47.6, 47.1, 37.8, 29.3, 25.8.

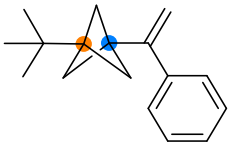
IR (ATR): ν = 2957, 1659, 1599, 1440, 1206, 753, 692 cm^{-1}

HRMS (ESI) calcd for $C_{16}H_{22}NO$ $[M+H]^+$: 244.1701; Found: 244.1706.



4 **53**, 75%

To a 10 mL reaction vial equipped with a stir bar was added Ph_3PCH_3Br (40.0 mg, 0.11 mmol, 1.1 equiv) and dry THF (1 mL). The reaction vial was immersed in 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. Subsequently, **4** (25.0 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 H_2O 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 **53** as a colorless oil (16.9 mg, 75% yield).



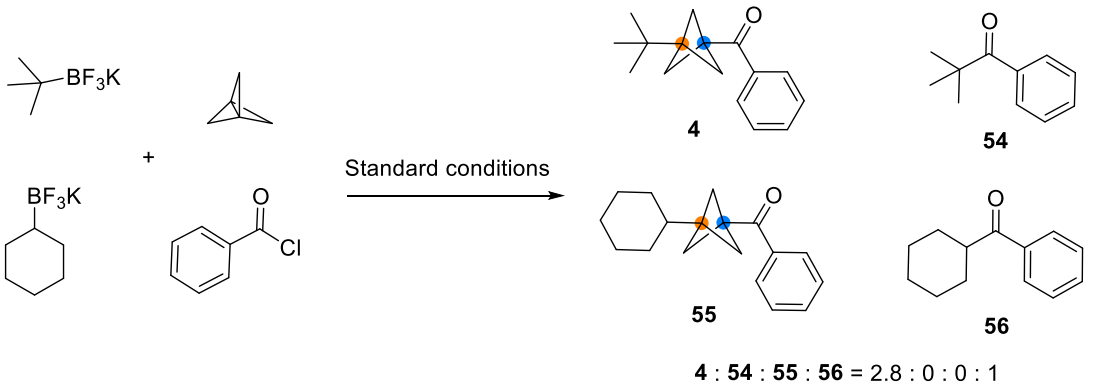
1-(*tert*-Butyl)-3-(1-phenylvinyl)bicyclo[1.1.1]pentane 53 ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 6.9 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 5.16 (d, *J* = 1.9 Hz, 1H), 5.07 (d, *J* = 1.9 Hz, 1H), 1.75 (s, 6H), 0.86 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2, 140.9, 127.9, 127.1, 127.0, 113.0, 48.4, 47.3, 40.1, 29.4, 25.9.

IR (ATR): ν = 2958, 2878, 1635, 1456, 1208, 915 656 cm^{-1}

HRMS (EI) calcd for $C_{17}H_{22}$ $[M]^+$: 226.1722; Found: 226.1739.

8. Mechanistic Studies

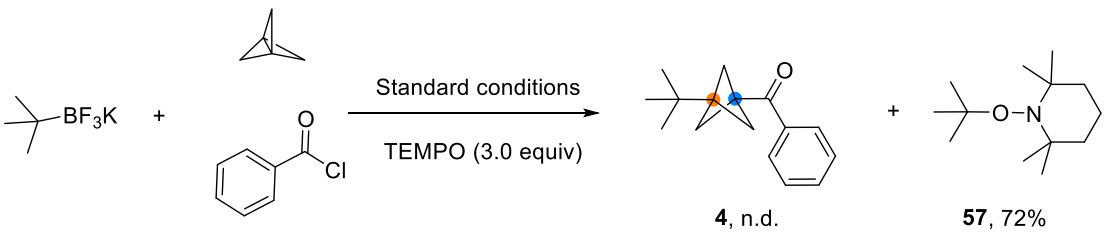
8. 1 Competition Experiment



4 : **54** : **55** : **56** = 2.8 : 0 : 0 : 1

To a 4 mL reaction vial equipped with a stirrer bar was added *t*-$BuBF_3K$ (24.6 mg, 0.15 mmol, 1.5 equiv), $CyBF_3K$ (28.5 mg, 0.15 mmol, 1.5 equiv), benzoyl chloride (14.2 mg, 0.1 mmol, 1 equiv), Cs_2CO_3 (65.6 mg, 0.2 mmol, 2 equiv), $[Ir\{dFCF_3ppy\}_2(dtbbpy)]PF_6$ (2.2 mg, 0.02 mmol, 2 mol %), and $Ni(dtbbpy)Br_2$ (0.02 mmol, 9.72 mg, 0.2 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with 2.0 mL of dry DME via syringe, then the vial was charged with the [1.1.1]propellane (0.37 mL, 0.3 mmol, 3.0 equiv, 0.8 M soln in Et_2O). The cap was sealed with Parafilm®, and the reaction was irradiated for 16 h. Irradiation was performed with a Kessil® PR160 390 nm lamp according to the procedure outlined in the Photochemical Reactor Design and Setup section. The temperature of the reaction was maintained at approximately 27 ºC via a fan. After 16 h, the reaction mixture was subjected to GC-MS for analysis. The observed ratio of of **4**:**56** was 2.8 :1, and **54** and **55** were not observed.

8.2 Radical-trapping experiment

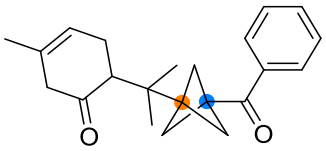


To a 4 mL reaction vial equipped with a stirrer bar was added *t*-$BuBF_3K$ (24.6 mg, 0.15 mmol, 1.5 equiv), TEMPO (46.8 mg, 0.3 mmol, 3.0 equiv), benzoyl chloride (14.2 mg, 0.1 mmol, 1 equiv), Cs_2CO_3 (65.6 mg, 0.2 mmol, 2 equiv), the $[Ir\{dFCF_3ppy\}_2(dtbbpy)]PF_6$ (2.2 mg, 0.02 mmol, 2 mol %), and $Ni(dtbbpy)Br_2$ (0.02 mmol, 9.72 mg, 0.2 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with 2.0 mL of dry DME via syringe, Then the vial was charged with the [1.1.1]propellane (0.37 mL, 0.3 mmol, 3.0 equiv, 0.8 M soln in Et_2O). The cap was sealed with Parafilm®, and the reaction was irradiated for 16 h. Irradiation was performed with a Kessil® PR160 390 nm lamp according to the procedure outlined in the Photochemical Reactor Design and Setup section. The temperature of the reaction was maintained at approximately 27 °C via a fan. After 16 h, an aliquot of a solution of 1,3,5-trimethoxybenzene (16.8 mg in 0.1 mL DME) was added, and the reaction mixture was subjected to GC-MS for analysis. Desired product **4** was not detected, but the TEMPO adduct was observed, the yield of which was determined by GC.

8.3 Radical ring-opening reaction

To an 8.0 mL clear borosilicate glass vial with a screw top equipped with a magnetic stir bar was added $Ir\{dF(CF_3)_2ppy\}_2(dtbbpy)]PF_6$ (6.73 mg, 0.06 mmol, 2 mol%), $NiBr_2(dtbbpy)$ (29.21 mg, 0.06 mmol, 20 mol %), Cs_2CO_3 (146 mg, 0.45 mmol, 1.5 equiv), organotrifluoroborate (0.45 mmol, 1.5 equiv), and the benzoyl chloride (if solid, 0.30 mmol, 1.0 equiv). The vial was then sealed with a screw-cap containing a PTFE-lined silicone septum. An inlet needle was inserted, and the atmosphere was exchanged for N_2 via three evacuation-backfill cycles. The vial was then charged with 6.0 mL of dry DME via syringe, and the acyl chlorides (if liquid, 0.50 mmol, 1.0 equiv) were added via syringe. Finally, the via was charged with [1.1.1]propellane (1.13 mL, 0.9 mmol, 3.0 equiv, 0.8 M soln in Et_2O). The reaction was then sparged for ~2 min with N_2 or Ar, the cap was sealed with Parafilm®, and the reaction mixture was irradiated with a Kessil® PR160 390 nm lamp for 16 h. Upon reaction completion, the resulting

soln was passed through a pad of Celite®, eluting with either CH_2Cl_2 or EtO_2 followed by SiO_2 column chromatography (hexanes/EtOAc).



6-(2-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)propan-2-yl)-3-methylcyclohex-3-en-1-one 58 (40.1 mg, 42% yield) was prepared following the General Procedure. This product was obtained as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.0 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 5.44 (tt, *J* = 2.8, 1.5 Hz, 1H), 2.86 (d, *J* = 19.5 Hz, 1H), 2.58 (d, *J* = 21.1 Hz, 1H), 2.51 – 2.43 (m, 2H), 2.30 – 2.21 (m, 1H), 2.07 (s, 6H), 1.62 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.5, 198.2, 136.7, 132.7, 132.4, 128.8, 128.4, 121.0, 53.2, 51.4, 48.2, 47.3, 42.1, 33.7, 28.9, 22.4, 22.3, 21.4.

IR (ATR): ν = 2967, 1717, 1664, 1447, 1334, 1209, 873, 697 cm^{-1}

HRMS (ESI) calcd for $C_{22}H_{26}O_2$ $[M]^+$: 322.1933; Found: 322.1937.

9. References

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2. Yang, Y.; Tsien, J.; Ben David, A.; Hughes, J. M. E.; Merchant, R. R.; Qin, T. Practical and Modular Construction of C(sp3)-Rich Alkyl Boron Compounds. *J. Am. Chem. Soc*. **2021**, *143*, 471−480.

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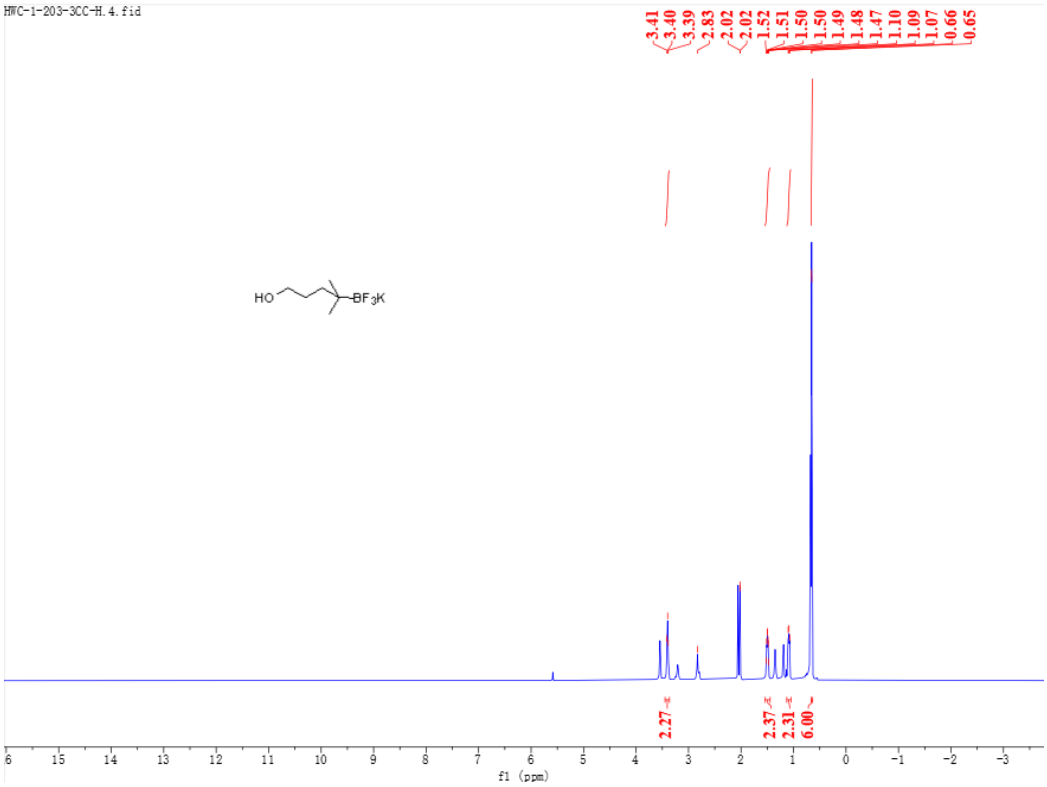
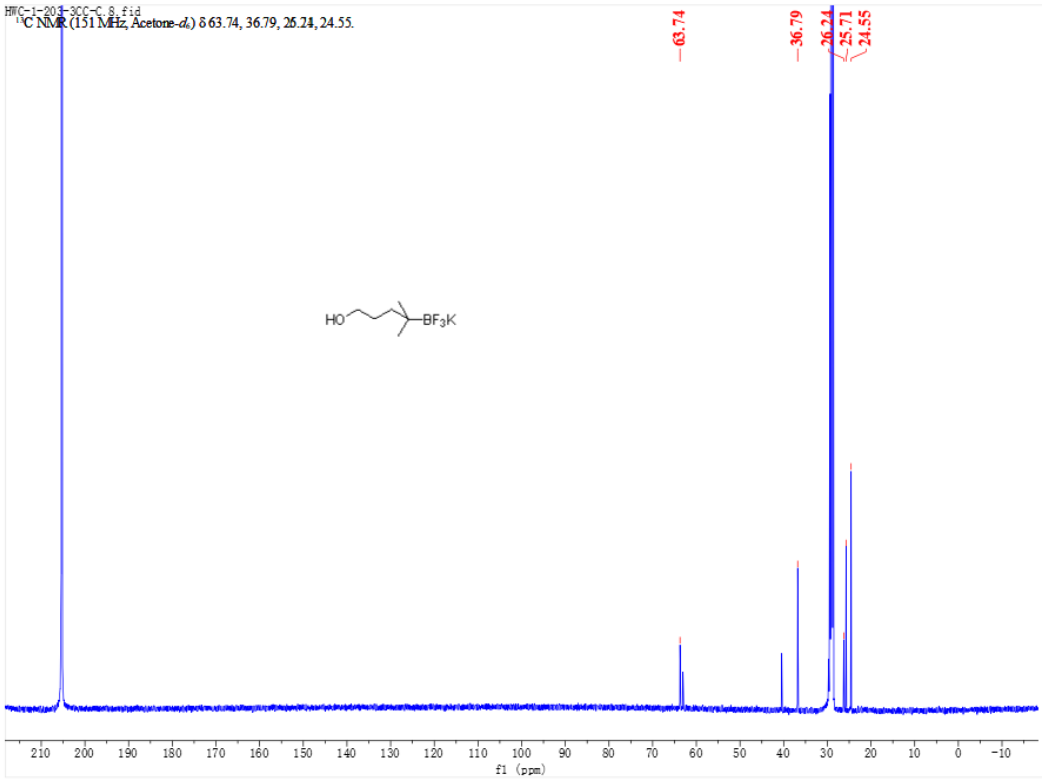
10. Spectra of Synthesized Compounds

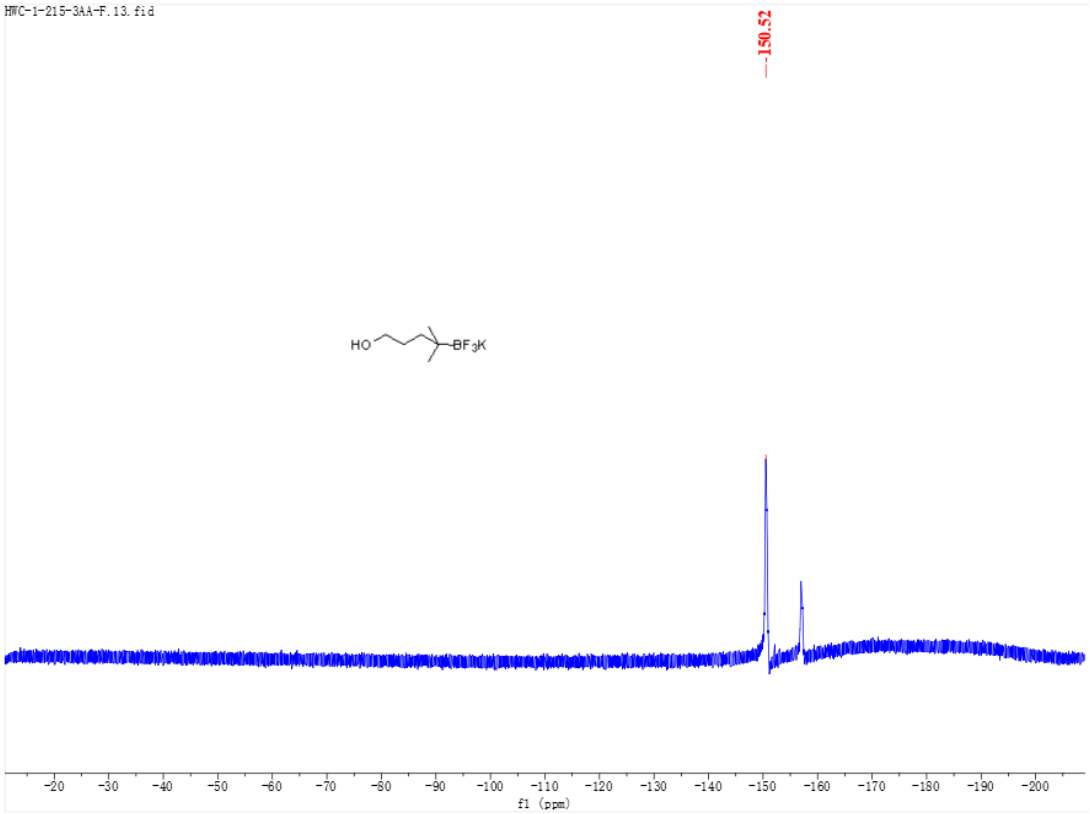
^{1}H NMR (600 MHz, acetone-d_6) spectrum of 4-Methyl-4-(trifluoro-l4-boraneyl)pentan-1-ol, Potassium Salt



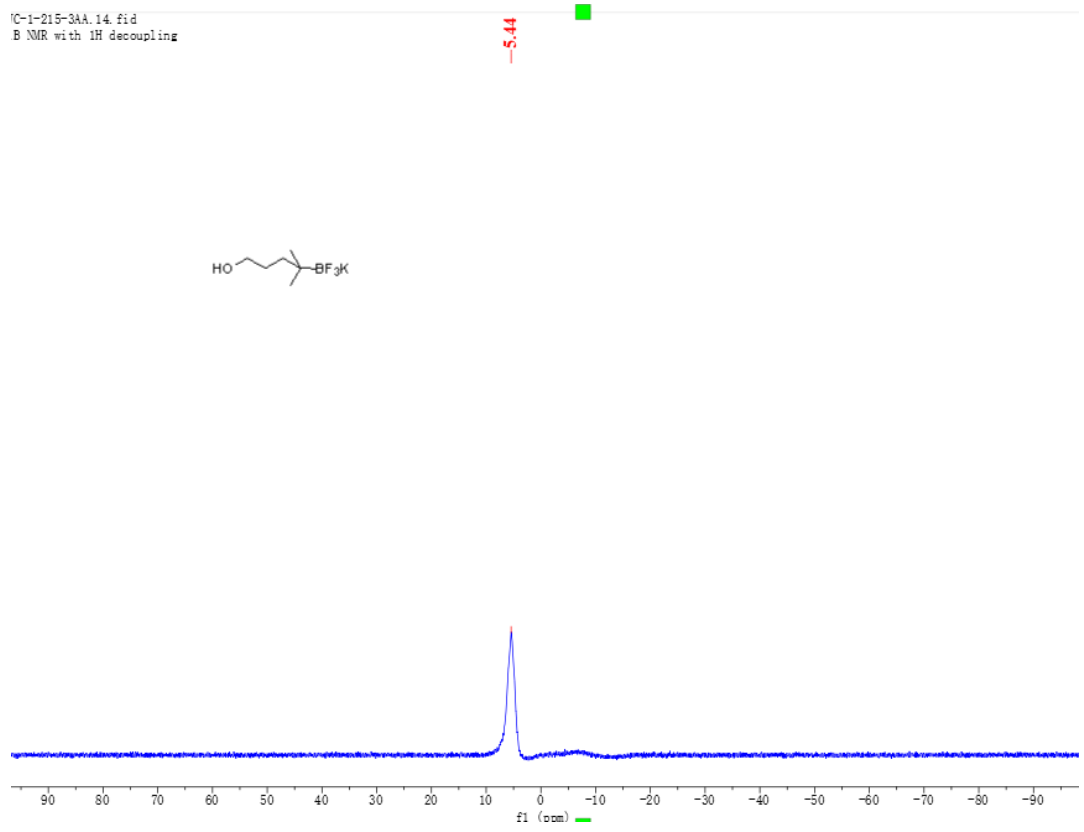
^{13}C NMR (151 MHz, acetone-d_6) spectrum of 4-Methyl-4-(trifluoro-l4-boraneyl)pentan-1-ol, Potassium Salt



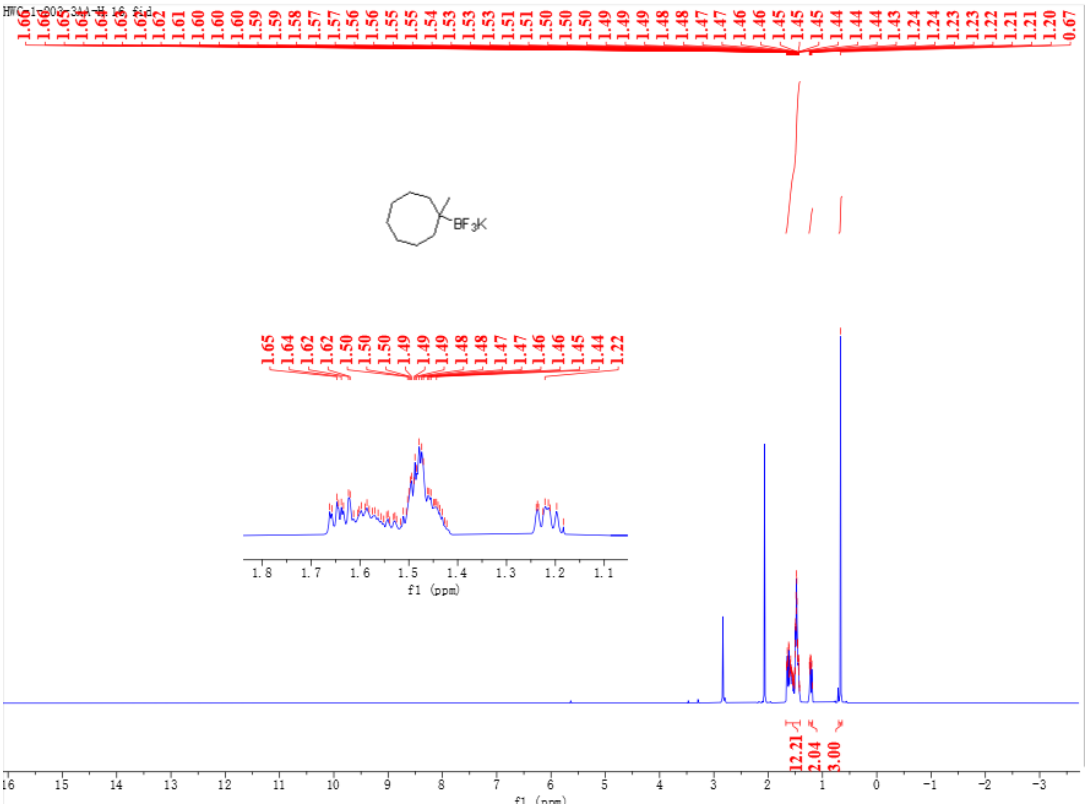
^{19}F NMR (565 MHz, acetone-d_6) spectrum of 4-Methyl-4-(trifluoro-l4-boraneyl)pentan-1-ol, Potassium Salt



^{11}B NMR (128 MHz, acetone-d_6) spectrum of 4-Methyl-4-(trifluoro-l4-boraneyl)pentan-1-ol, Potassium Salt



^{1}H NMR (600 MHz, acetone-d_6) spectrum of Trifluoro(1-methylcyclooctyl)-l4-borane, Potassium Salt



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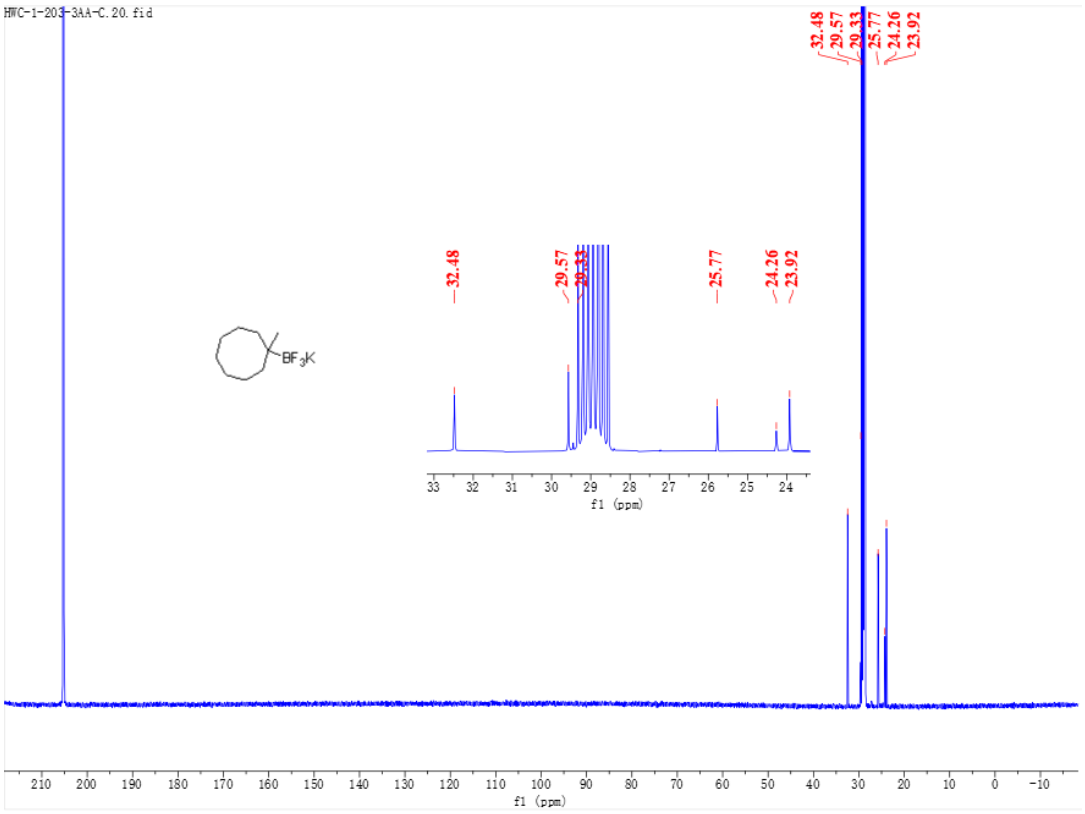

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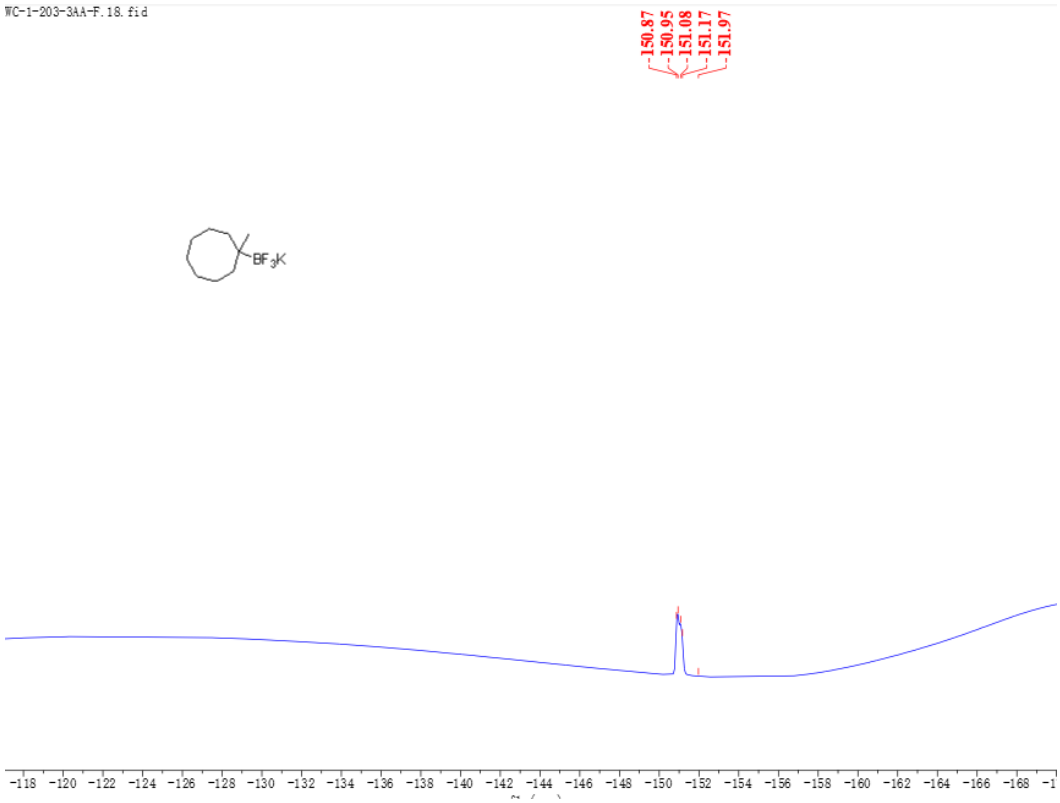

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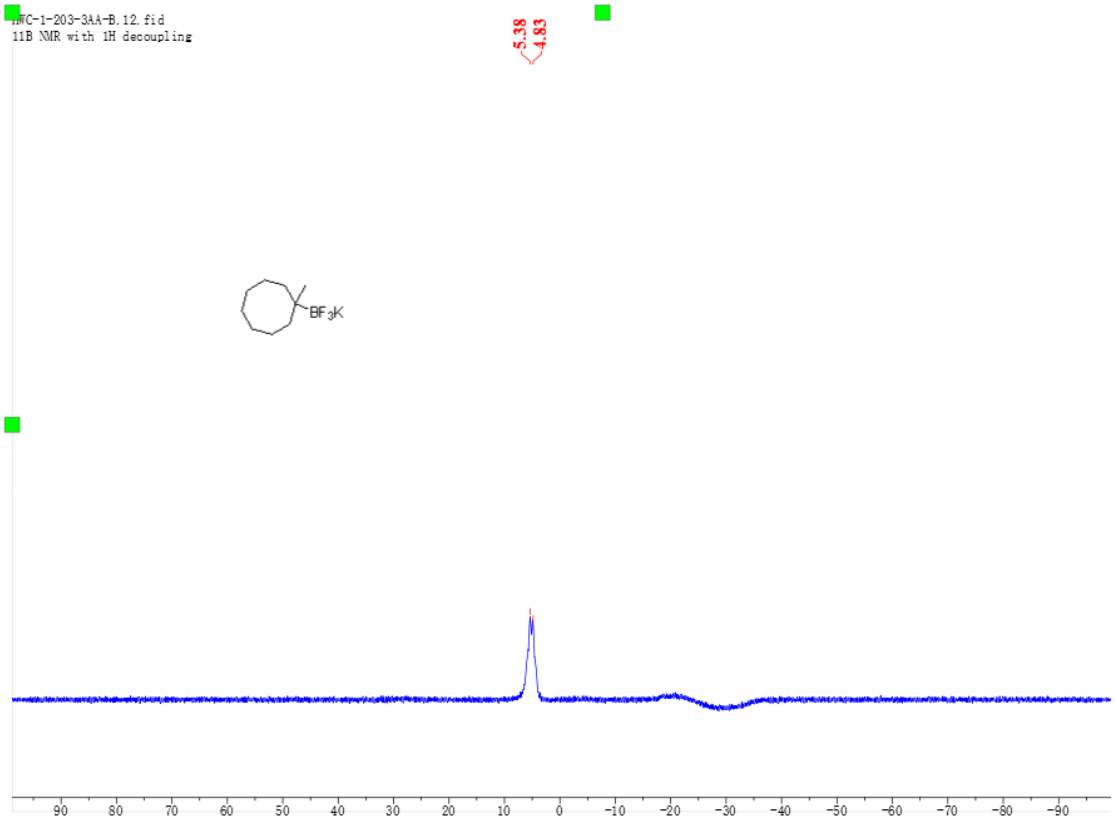
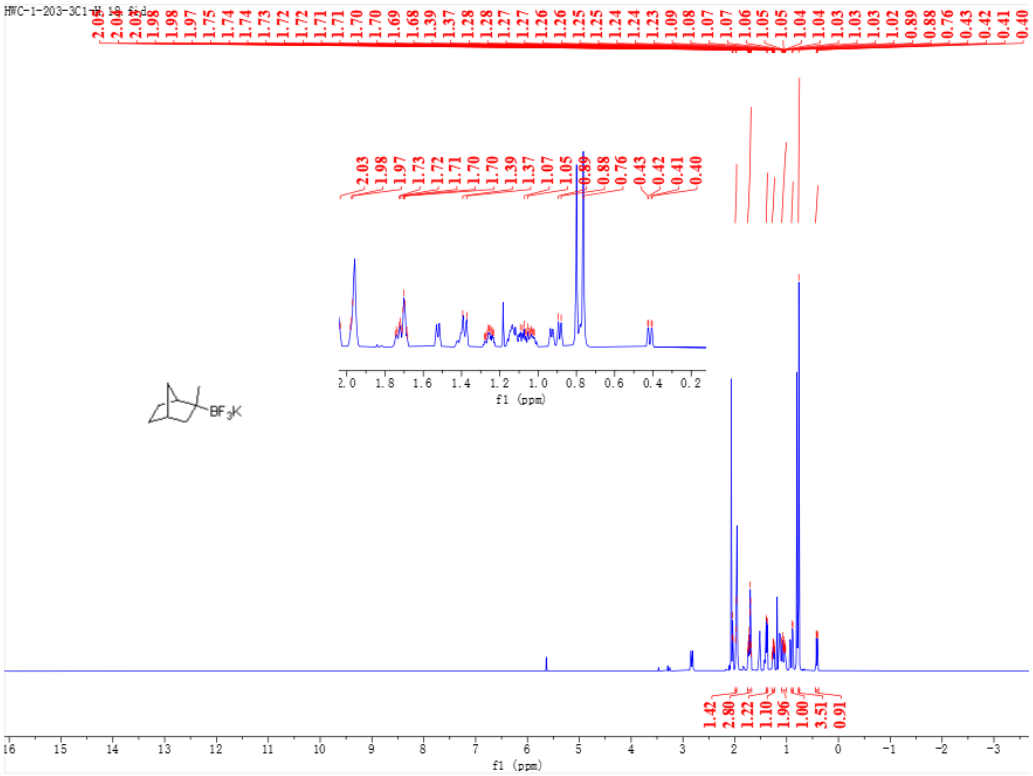
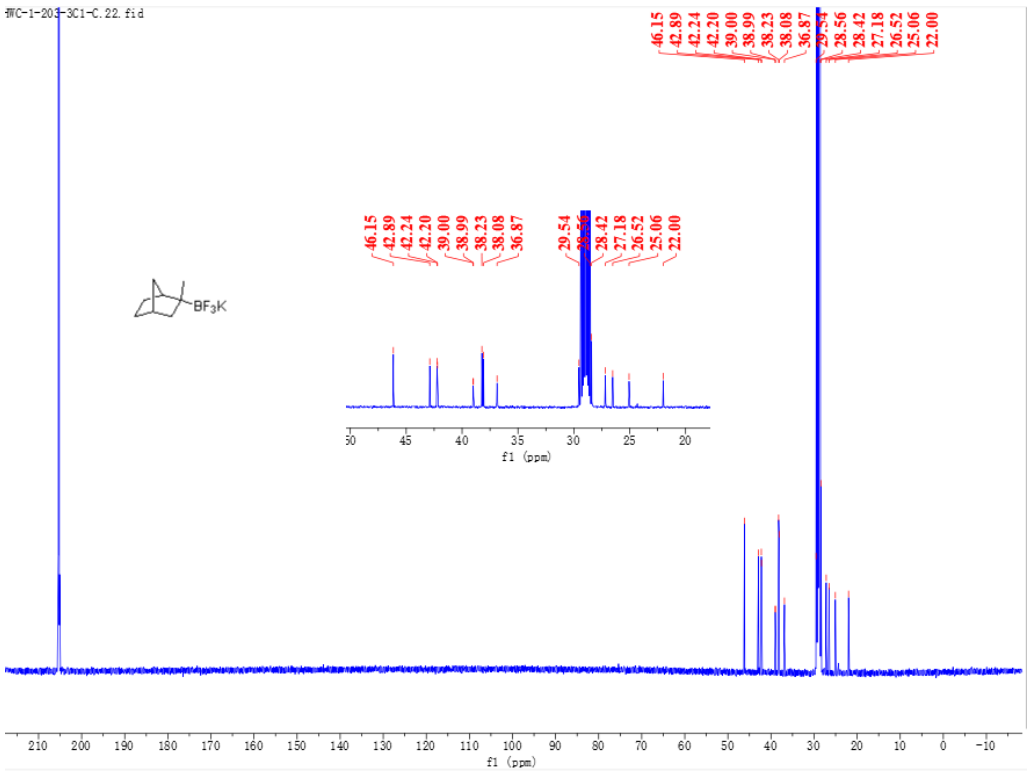


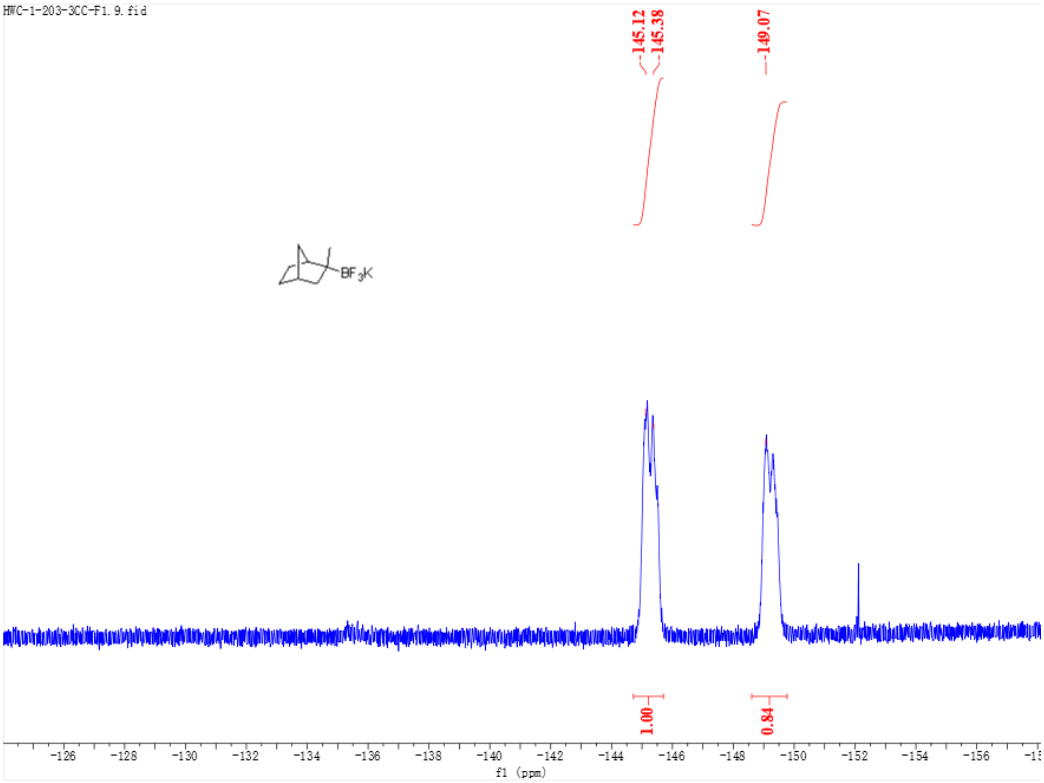
^{1}H NMR (600 MHz, acetone-d_6) spectrum of Trifluoro-2-methylbicyclo[2.2.1]heptan-2-yl)-l4-borane, Potassium Salt



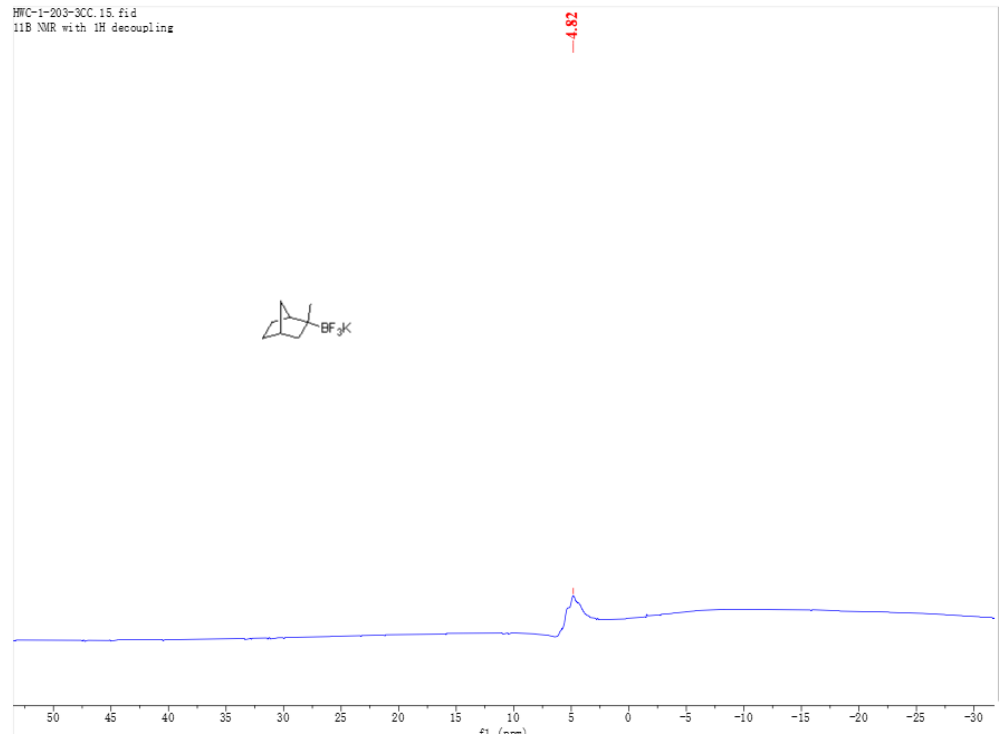
^{13}C NMR (151 MHz, acetone-d_6) spectrum of Trifluoro-2-methylbicyclo[2.2.1]heptan-2-yl)-l4-borane, Potassium Salt



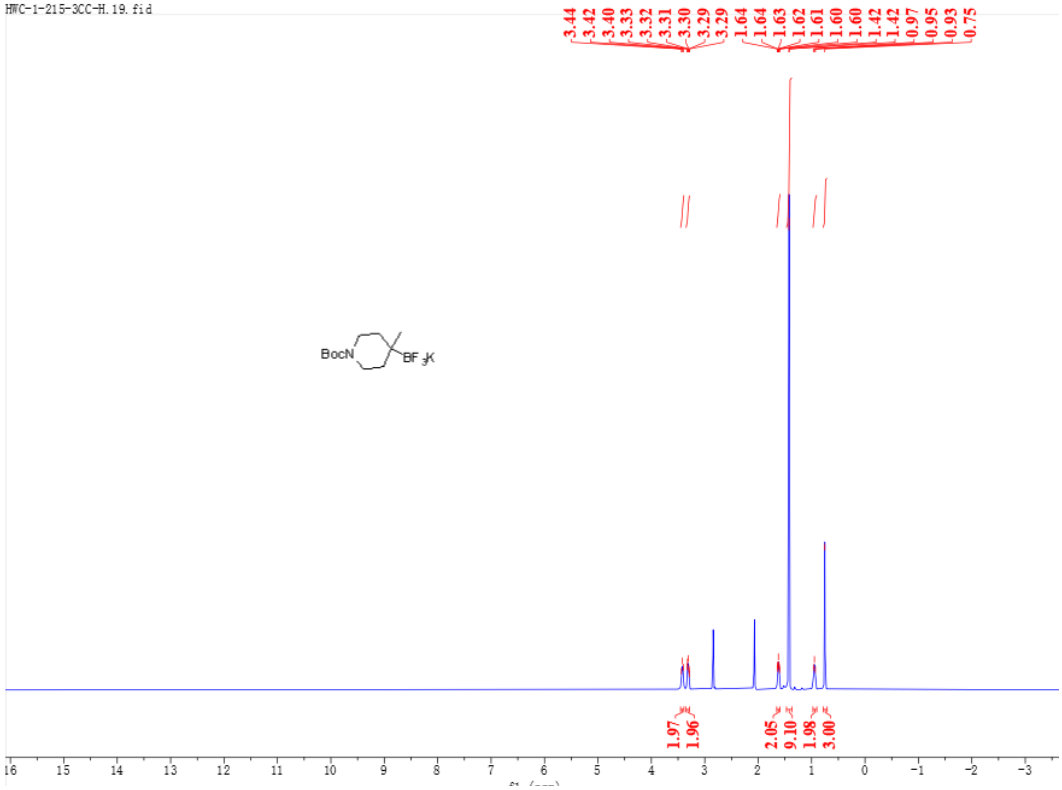
^{19}F NMR (565 MHz, acetone-d_6) spectrum of Trifluoro-2-methylbicyclo[2.2.1]heptan-2-yl)-l4-borane, Potassium Salt



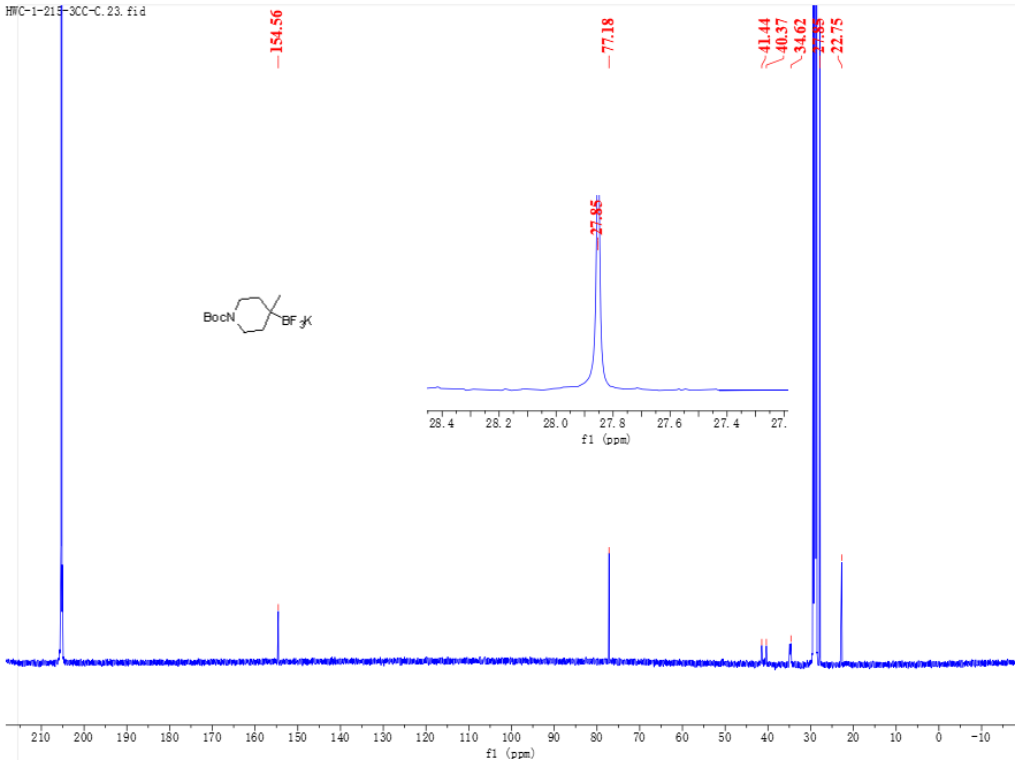
^{11}B NMR (128 MHz, acetone-d_6) spectrum of Trifluoro-2-methylbicyclo[2.2.1]heptan-2-yl)-l4-borane, Potassium Salt



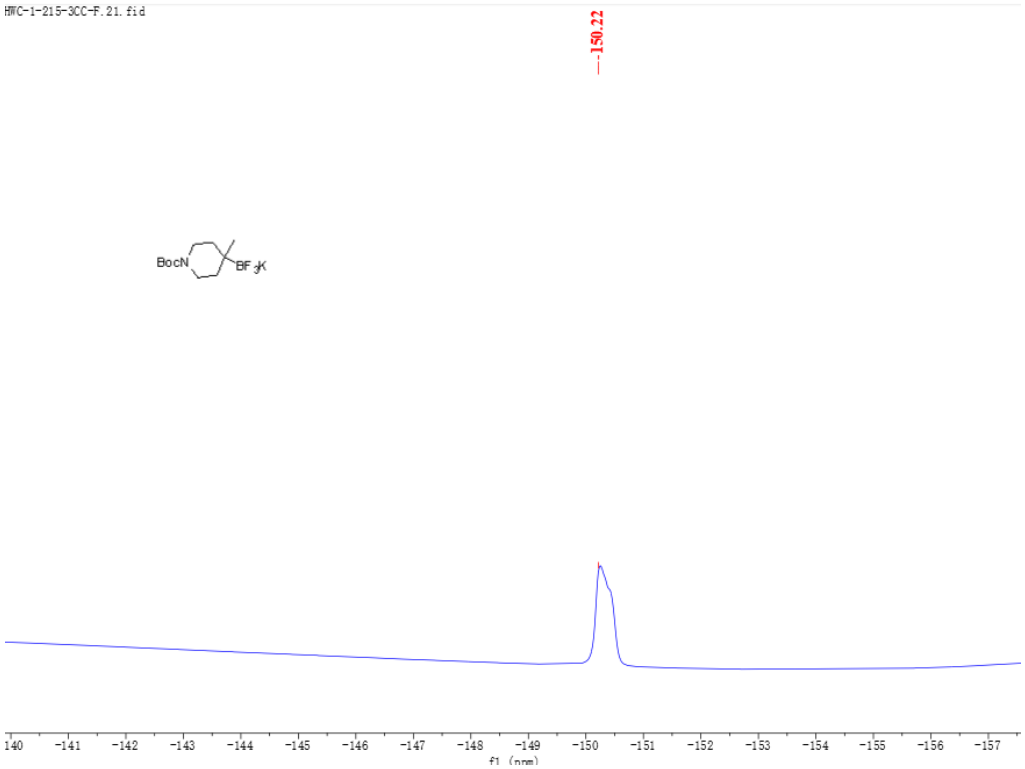
^{1}H NMR (600 MHz, acetone-d_6) spectrum of *tert*-Butyl 4-Methyl-4-(trifluoro-l4-boraneyl)piperidine-1-carboxylate, Potassium Salt



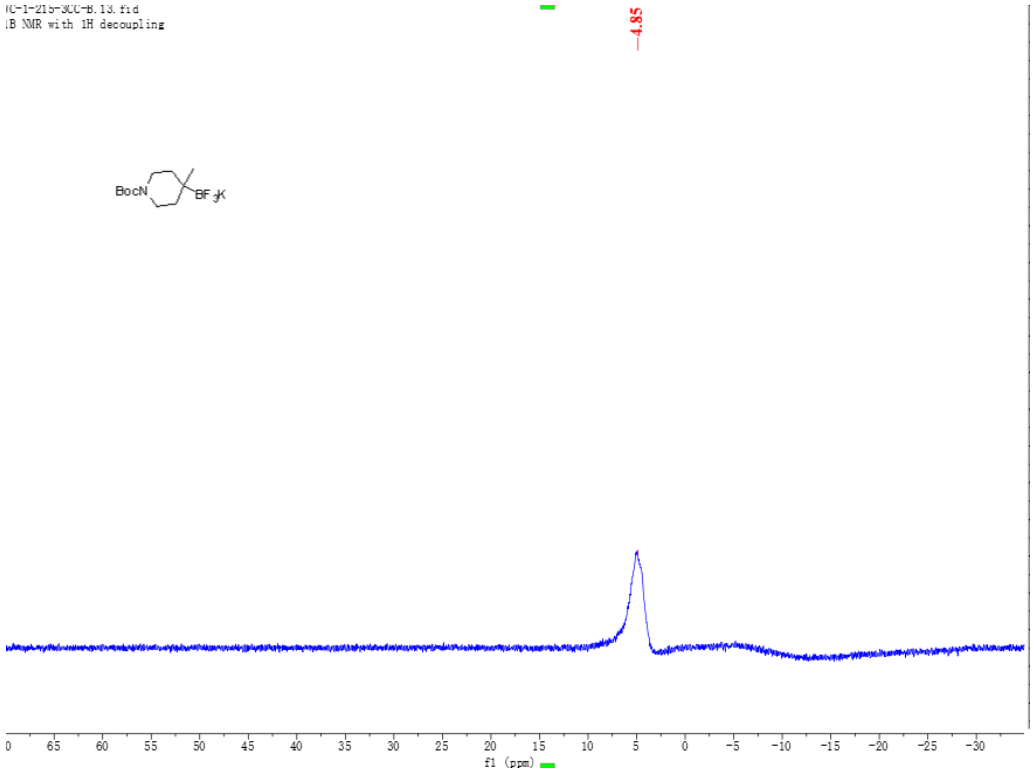
^{13}C NMR (151 MHz, acetone-d_6) spectrum of *tert*-Butyl 4-Methyl-4-(trifluoro-l4-boraneyl)piperidine-1-carboxylate, Potassium Salt



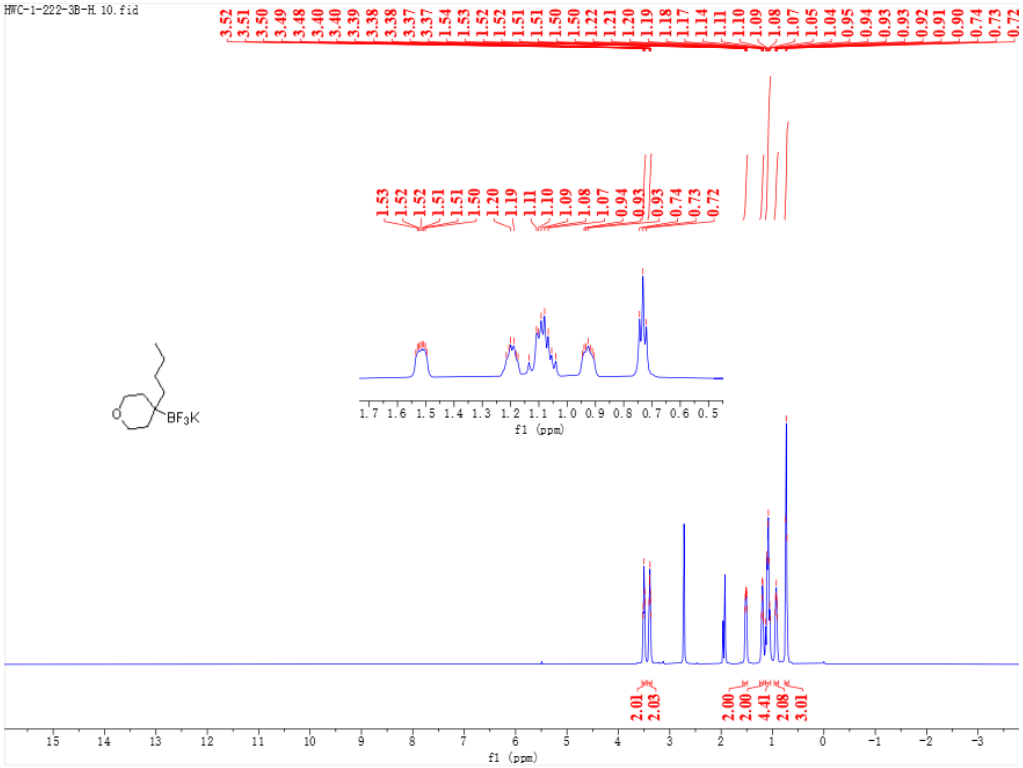
^{19}F NMR (565 MHz, acetone-d_6) spectrum of *tert*-Butyl 4-Methyl-4-(trifluoro-l4-boraneyl)piperidine-1-carboxylate, Potassium Salt



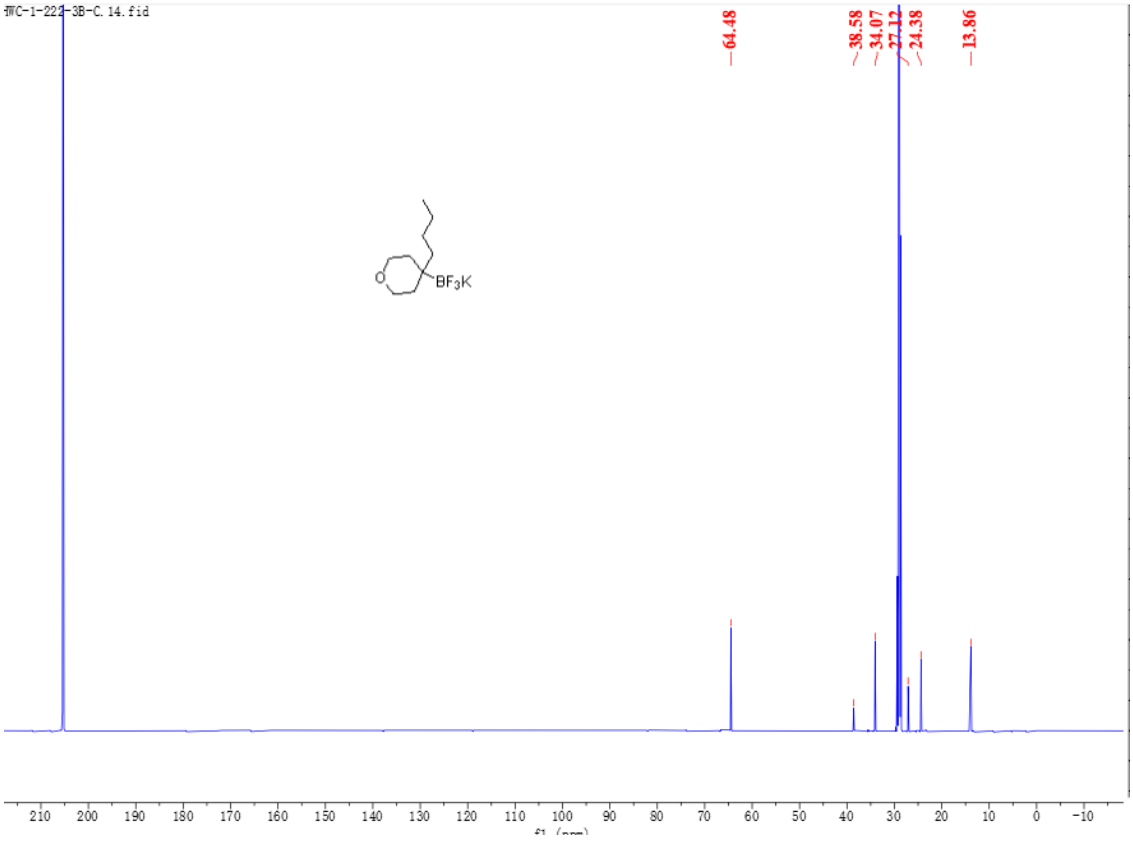
^{11}B NMR (128 MHz, acetone-d_6) spectrum of tert-Butyl 4-Methyl-4-(trifluoro-l4-boraneyl)piperidine-1-carboxylate, Potassium Salt



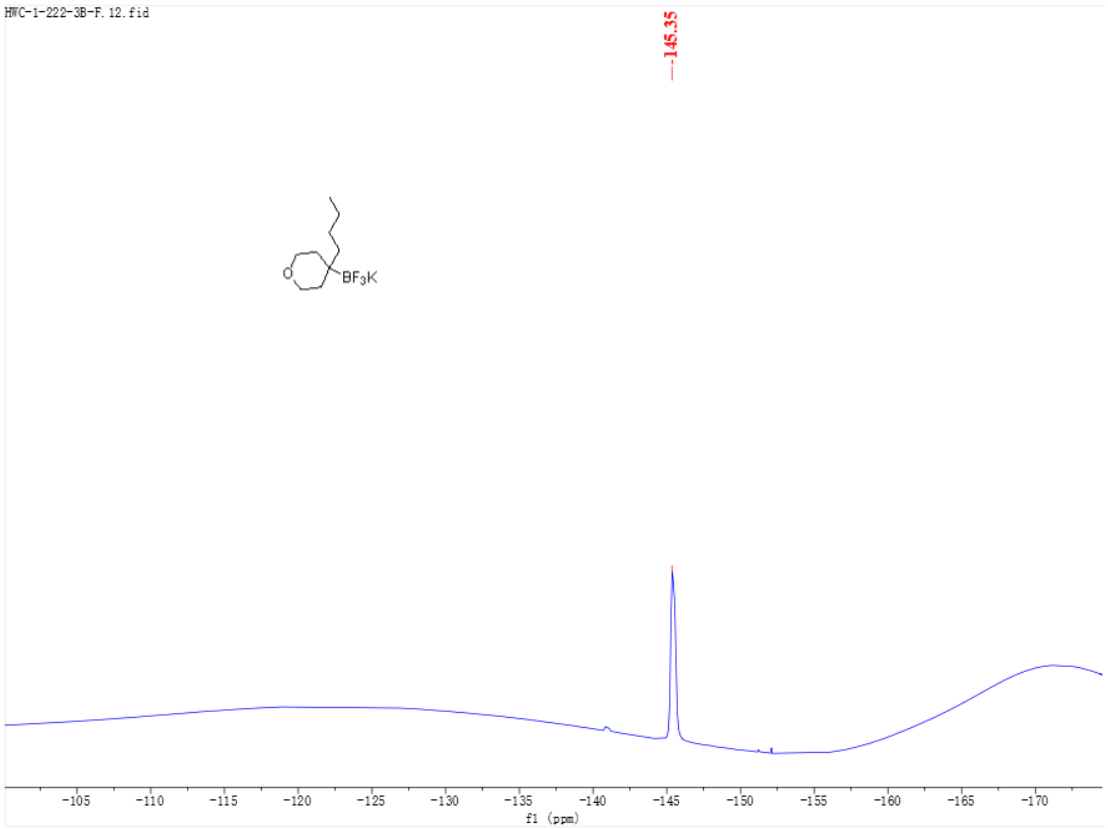
^{1}H NMR (600 MHz, acetone-d_6) spectrum of (4-Butyltetrahydro-2H-pyran-4-yl)trifluoro-l4-borane, Potassium Salt



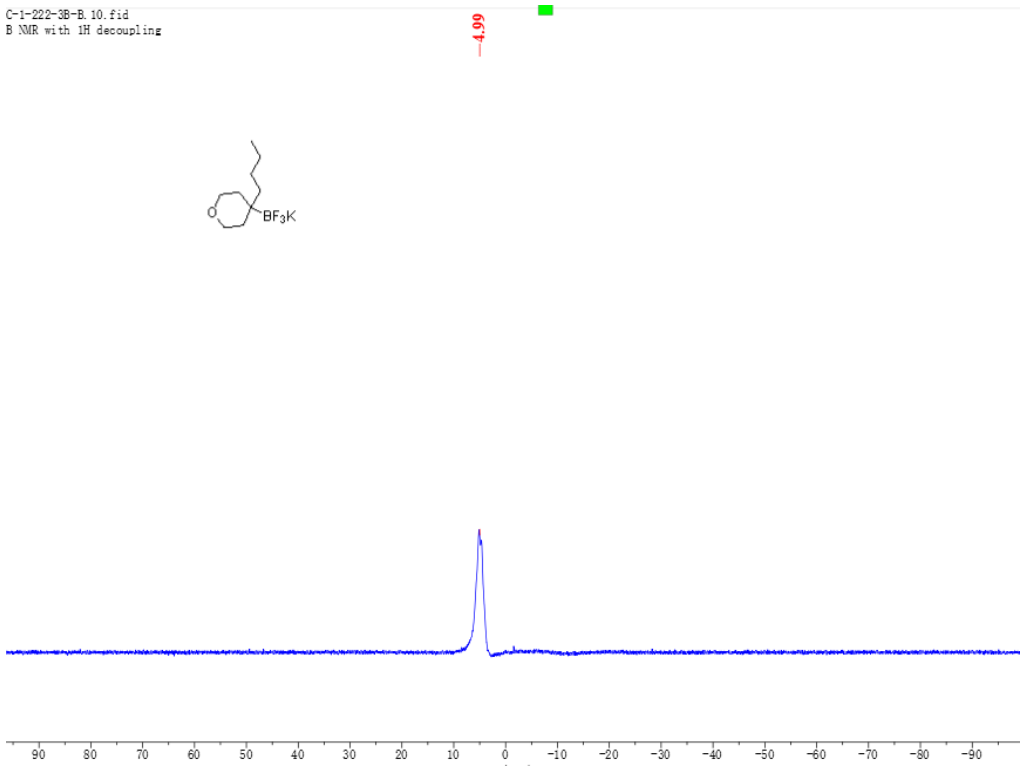
^{13}C NMR (151 MHz, acetone-d_6) spectrum of (4-Butyltetrahydro-2H-pyran-4-yl)trifluoro-l4-borane, Potassium Salt



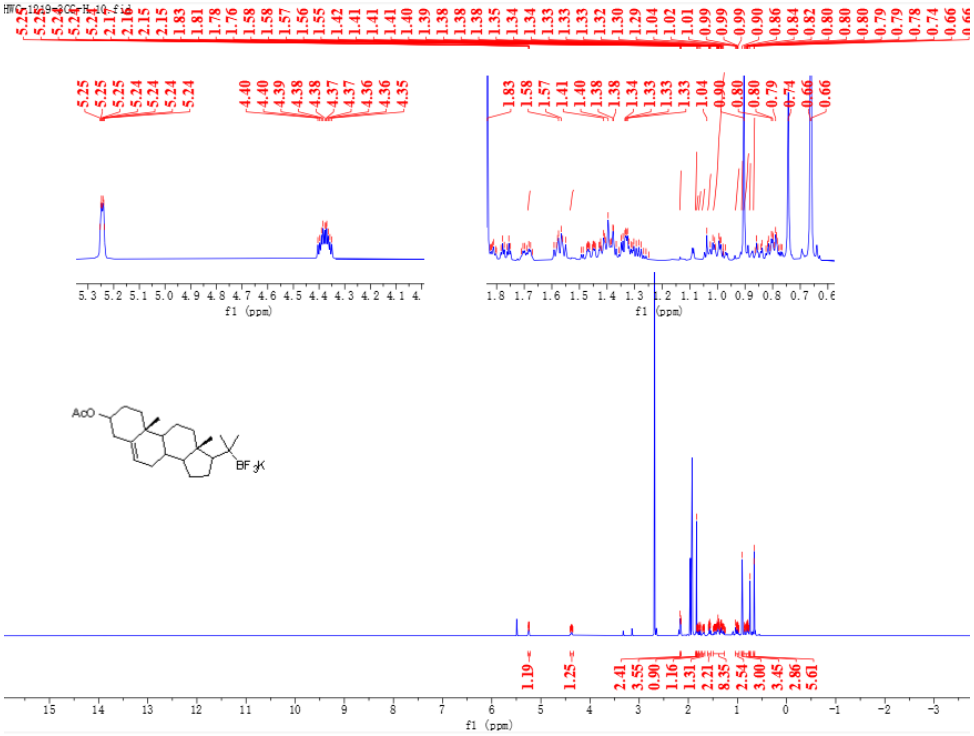
^{19}F NMR (565 MHz, acetone-d_6) spectrum of (4-Butyltetrahydro-2H-pyran-4-yl)trifluoro-l4-borane, Potassium Salt



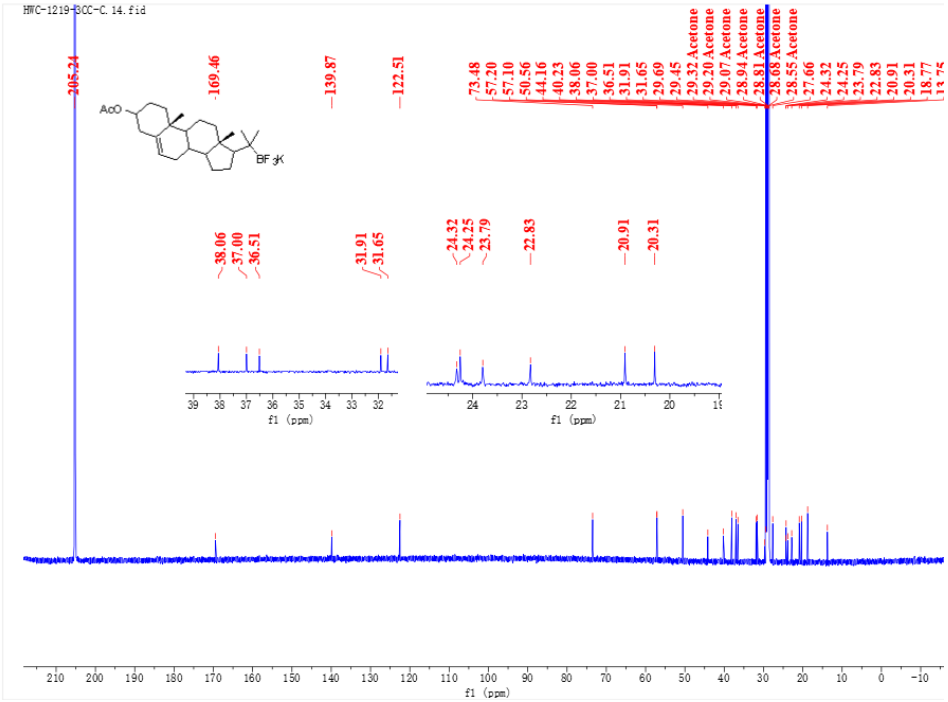
^{11}B NMR (128 MHz, acetone-d_6) spectrum of (4-Butyltetrahydro-2H-pyran-4-yl)trifluoro-l4-borane, Potassium Salt



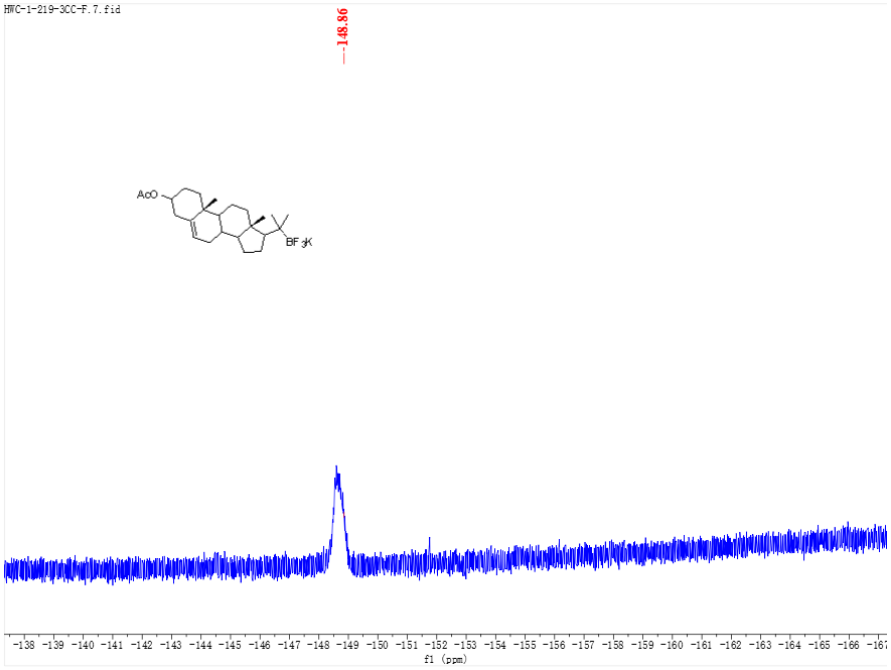
^{1}H NMR (600 MHz, acetone-d_6) spectrum of (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(2-(trifluoro-l4-boraneyl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl Acetate, Potassium Salt



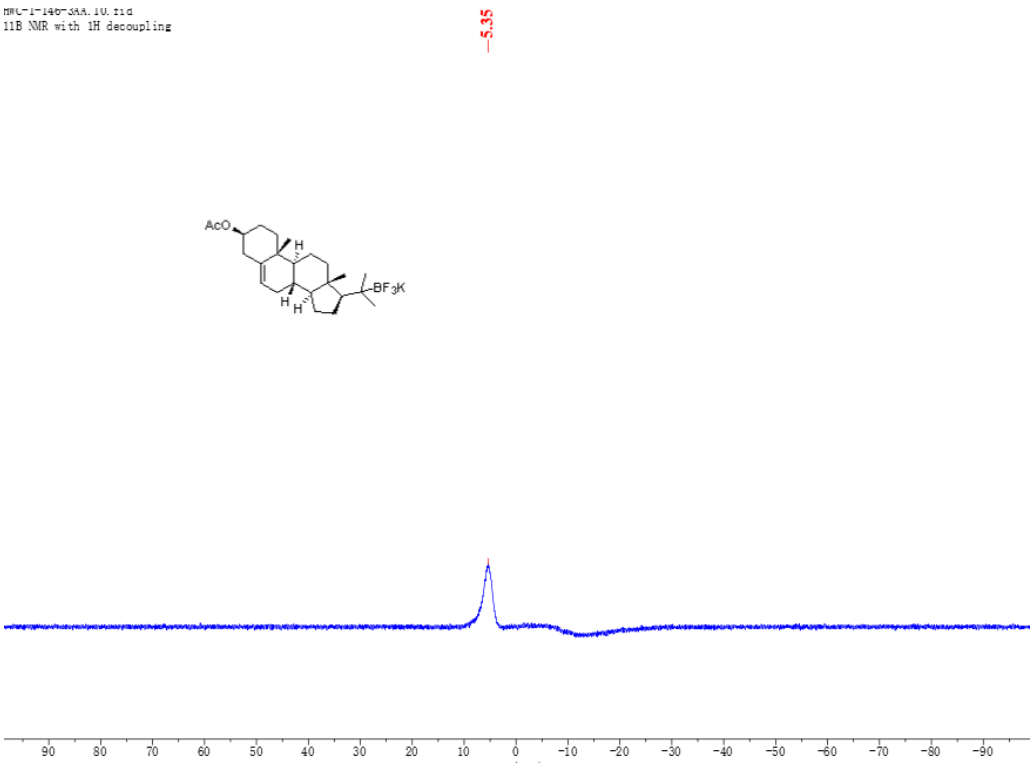
^{13}C NMR (151 MHz, acetone-d_6) spectrum of (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(2-(trifluoro-l4-boraneyl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl Acetate, Potassium Salt



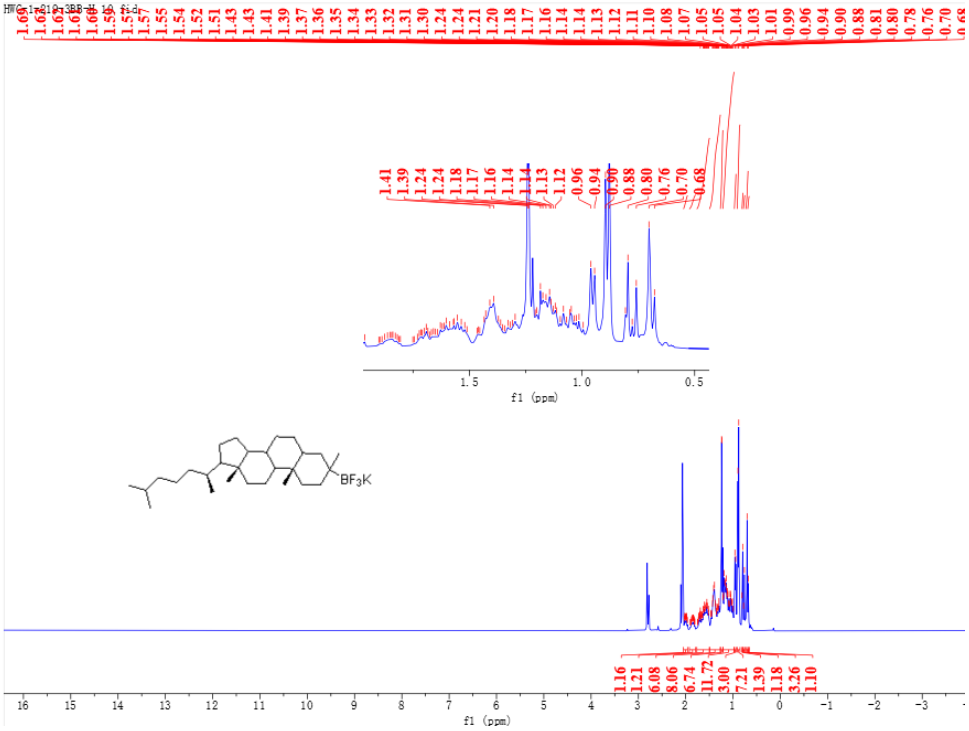
^{19}F NMR (565 MHz, acetone-d_6) spectrum of (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(2-(trifluoro-l4-boraneyl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl Acetate, Potassium Salt



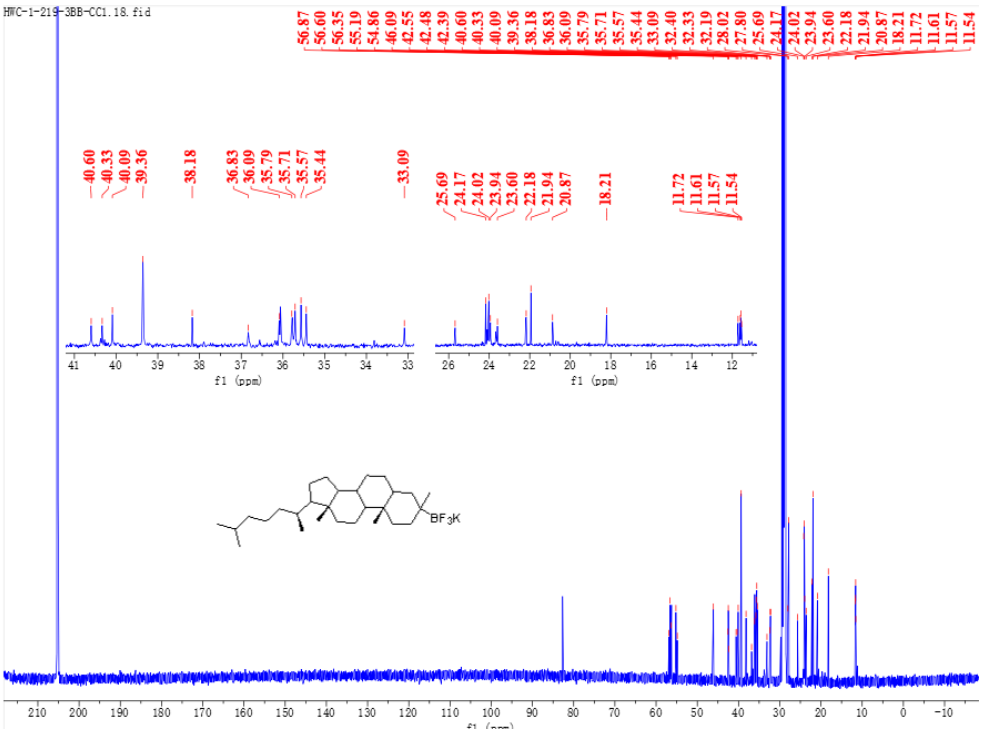
^{11}B NMR (128 MHz, acetone-d_6) spectrum of (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-10,13-Dimethyl-17-(2-(trifluoro-l4-boraneyl)propan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl Acetate, Potassium Salt



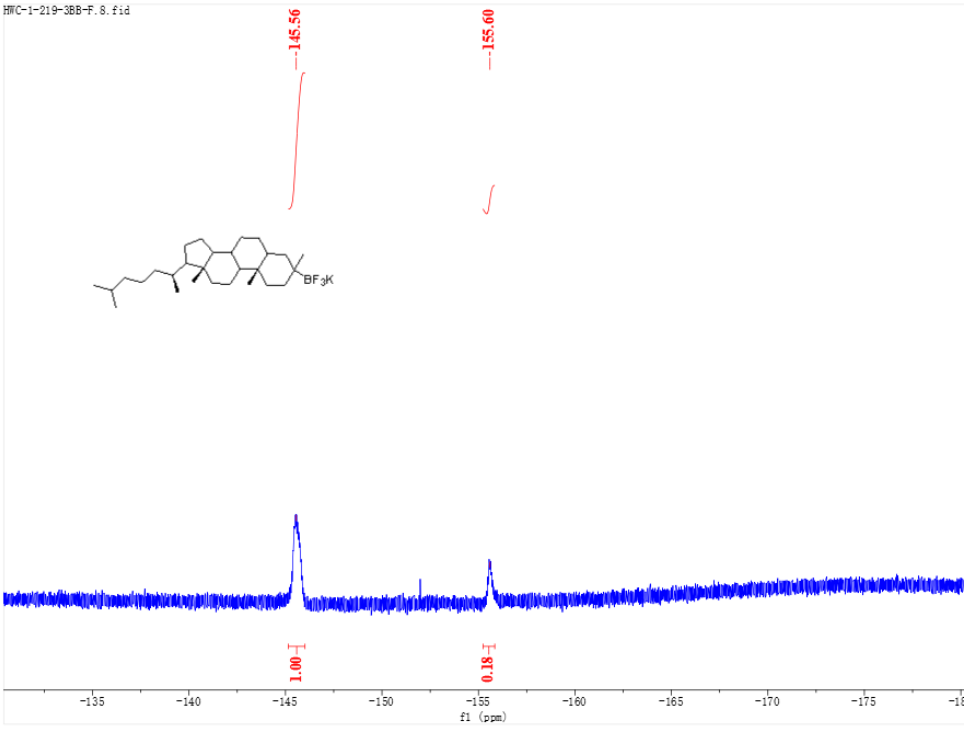
^{1}H NMR (600 MHz, acetone-d_6) spectrum of Trifluoro((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-Trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-l4-borane, Potassium Salt



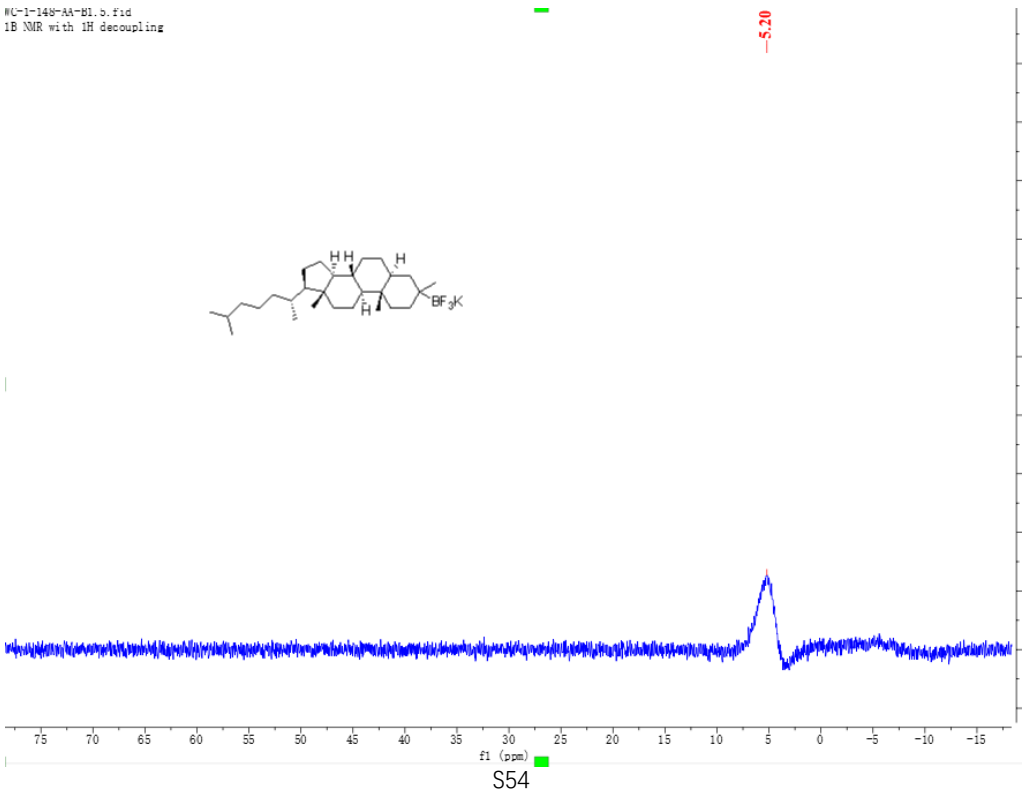
^{13}C NMR (151 MHz, acetone-d_6) spectrum of Trifluoro((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-l4-borane, Potassium Salt



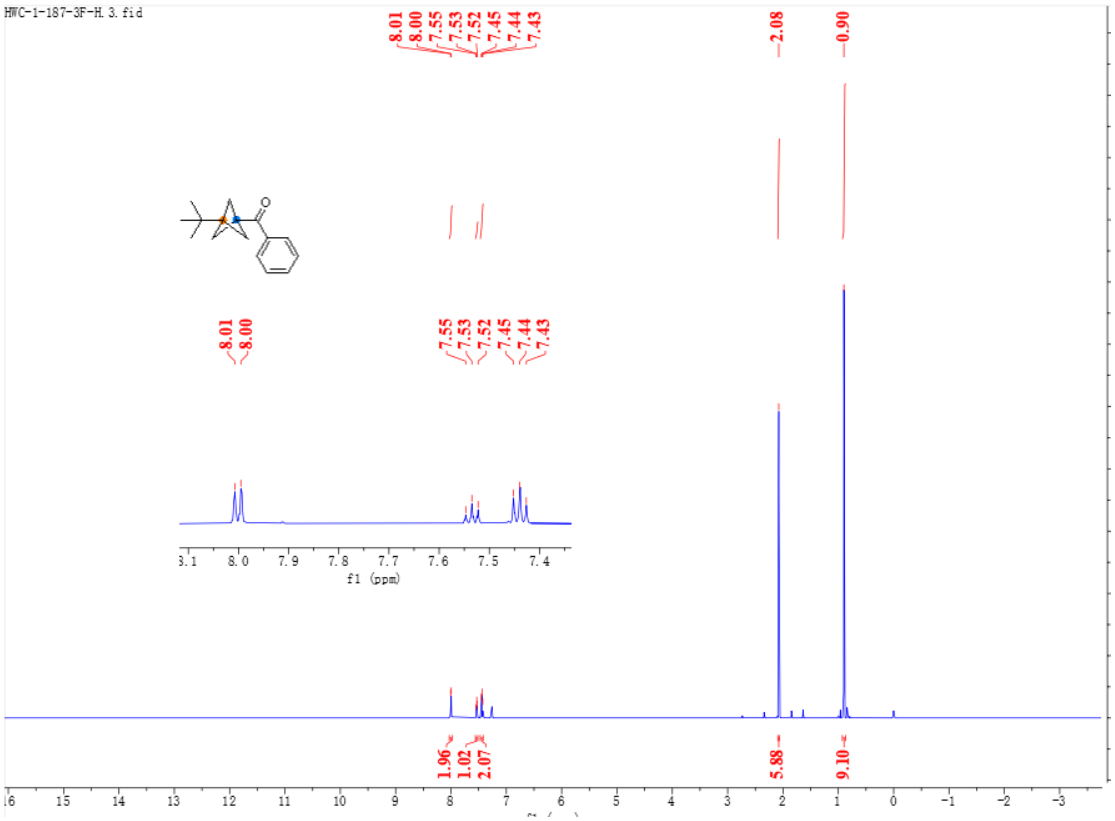
^{19}F NMR (565 MHz, acetone-d_6) spectrum of Trifluoro((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-l4-borane, Potassium Salt



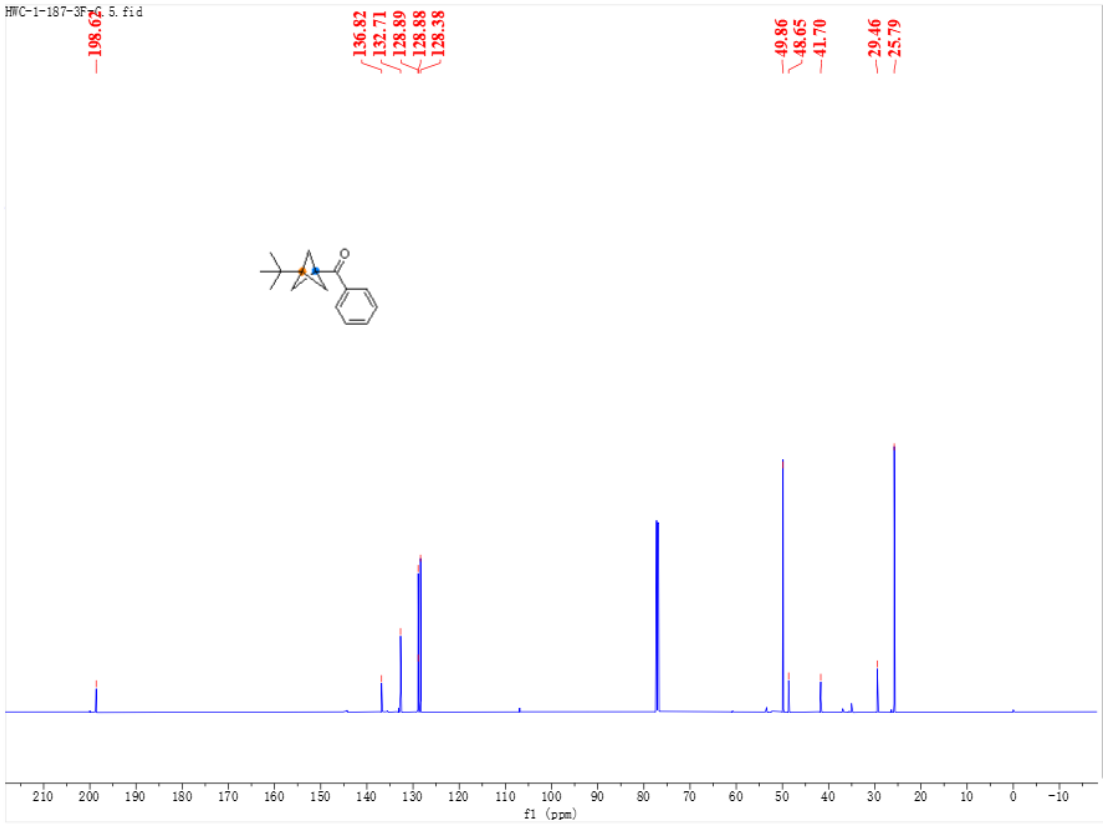
^{11}B NMR (128 MHz, acetone-d_6) spectrum of Trifluoro((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,*17R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-l4-borane, Potassium Salt



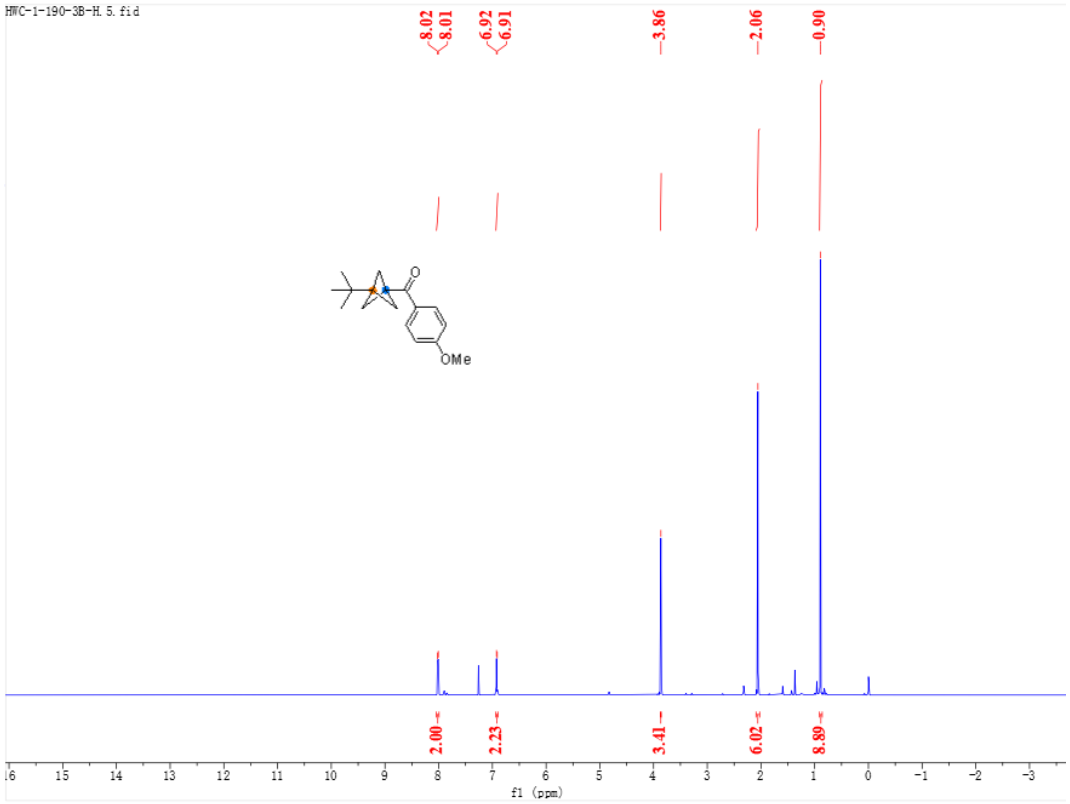
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 4



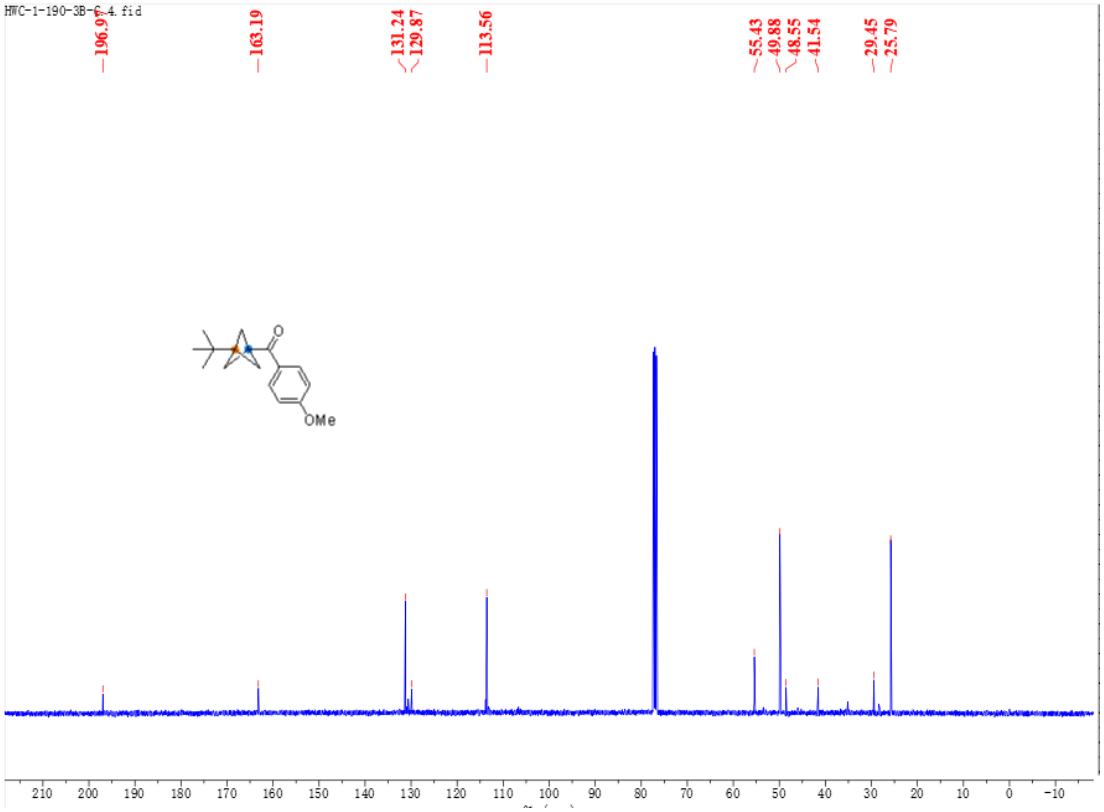
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 4



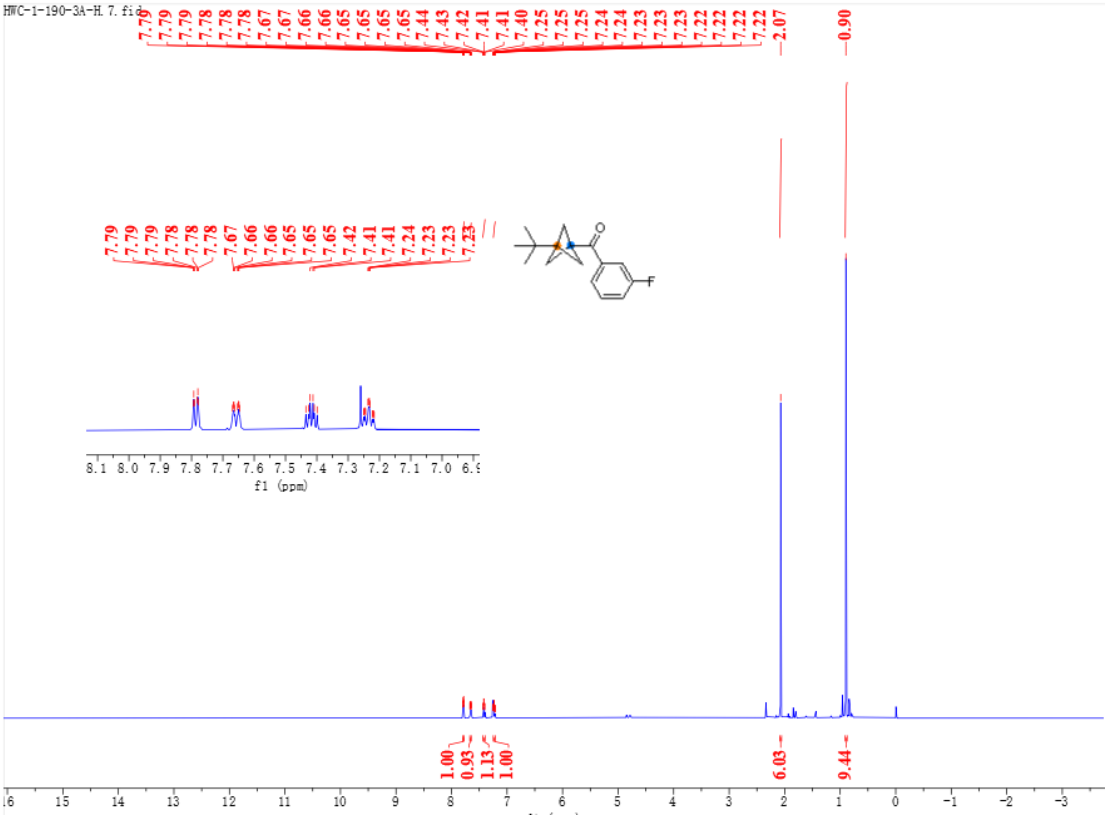
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-methoxyphenyl)methanone 5



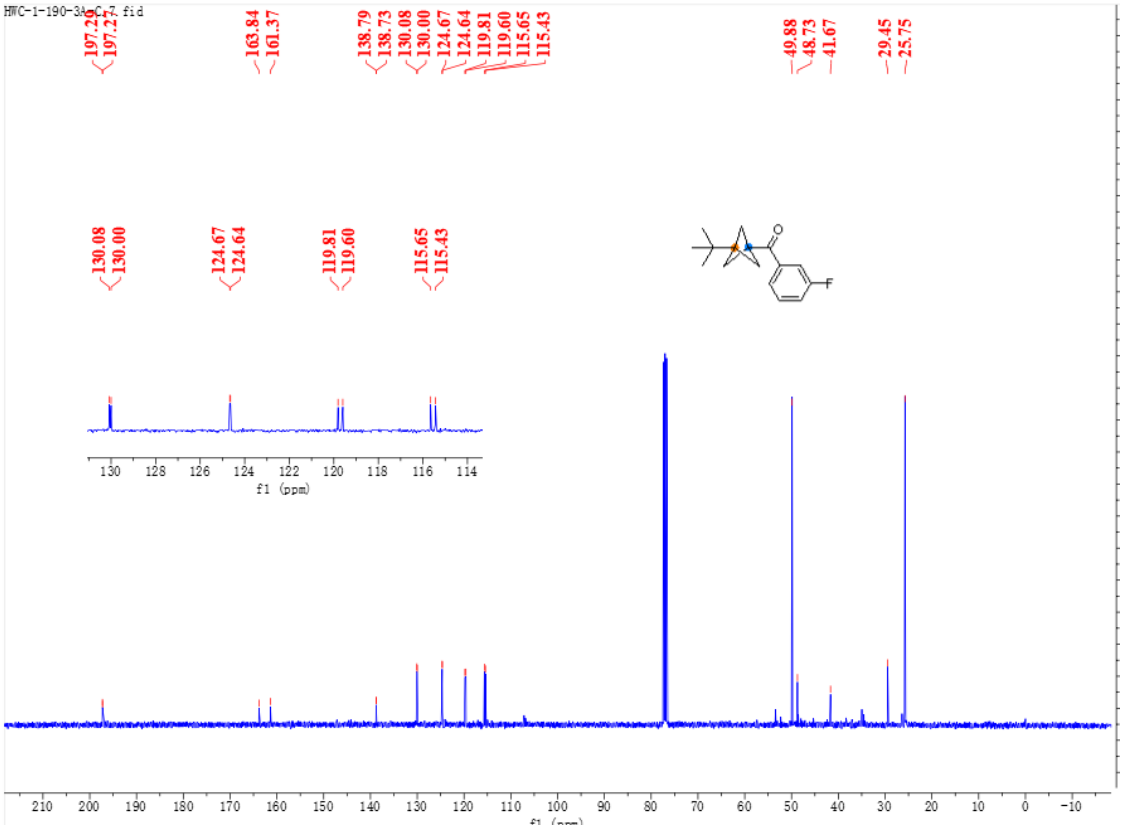
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(tert-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-methoxyphenyl)methanone 5



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(3-fluorophenyl)methanone 6



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(3-fluorophenyl)methanone 6



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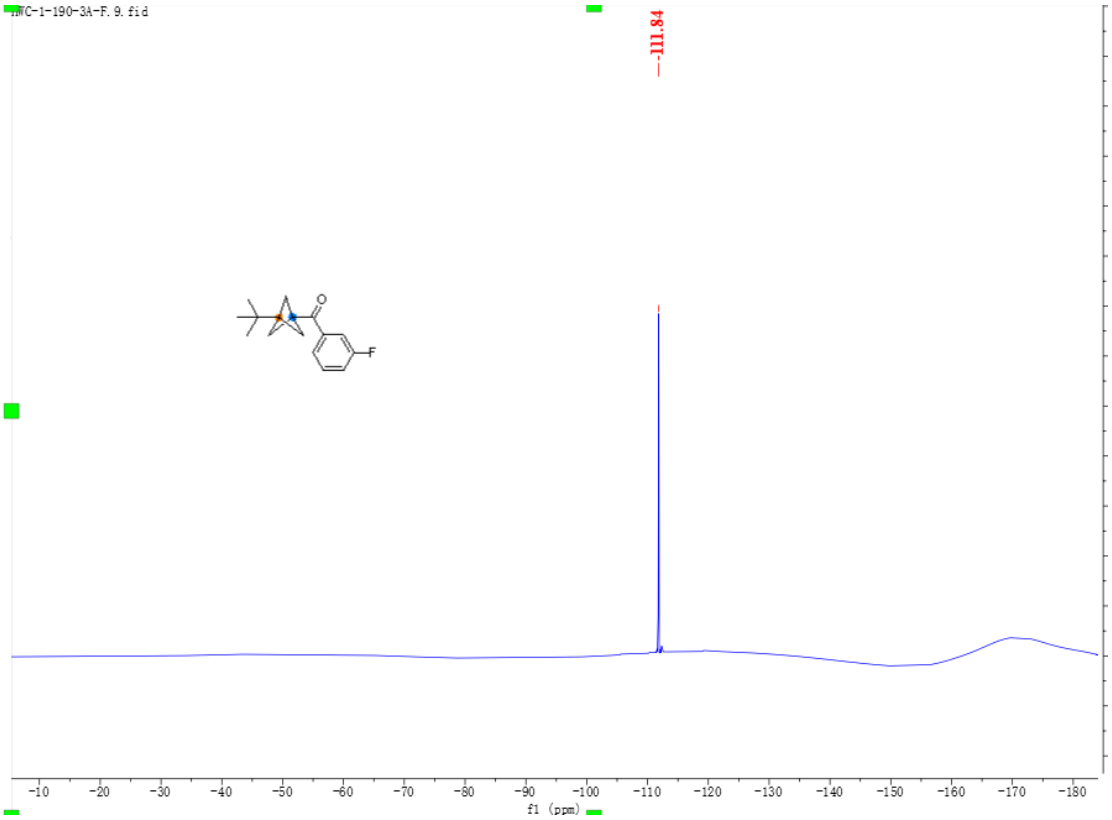

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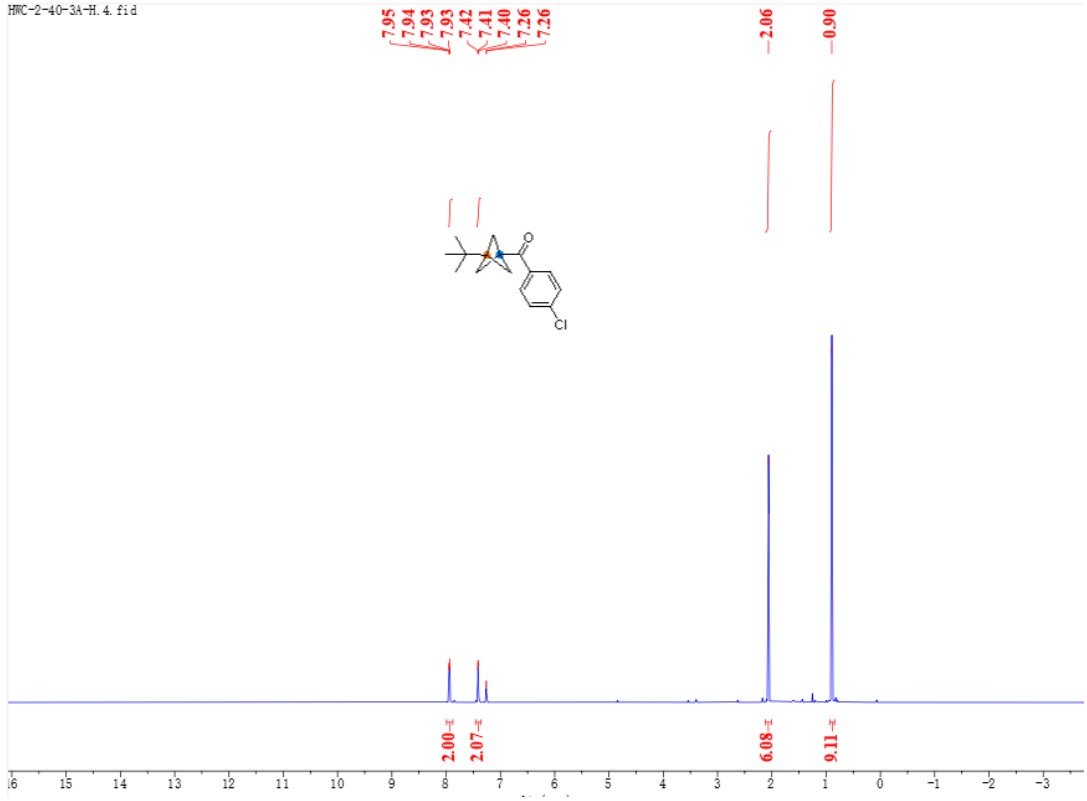
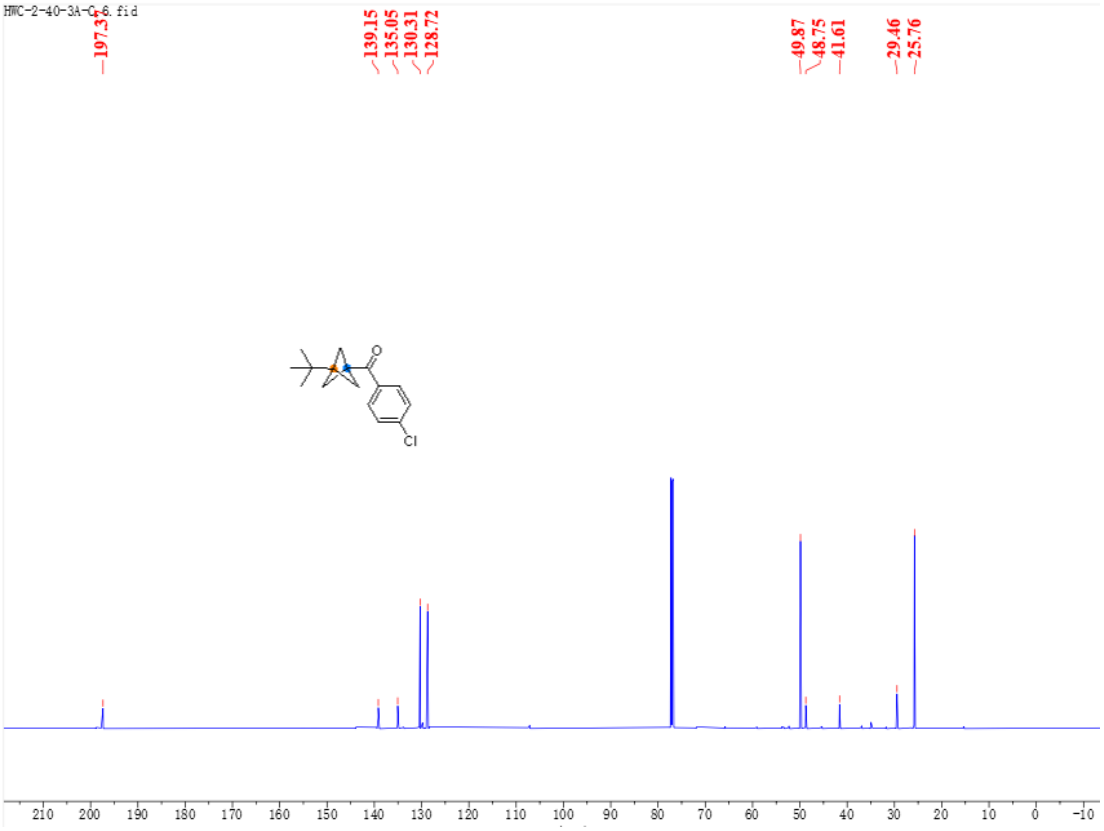
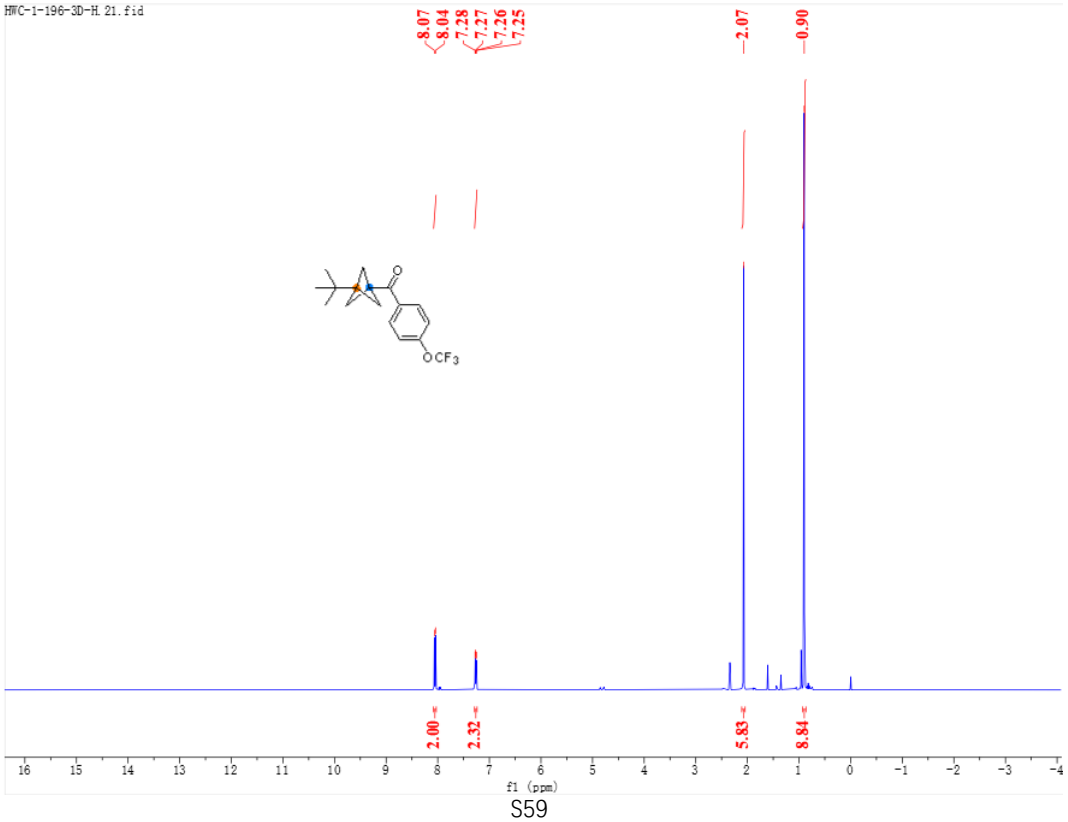


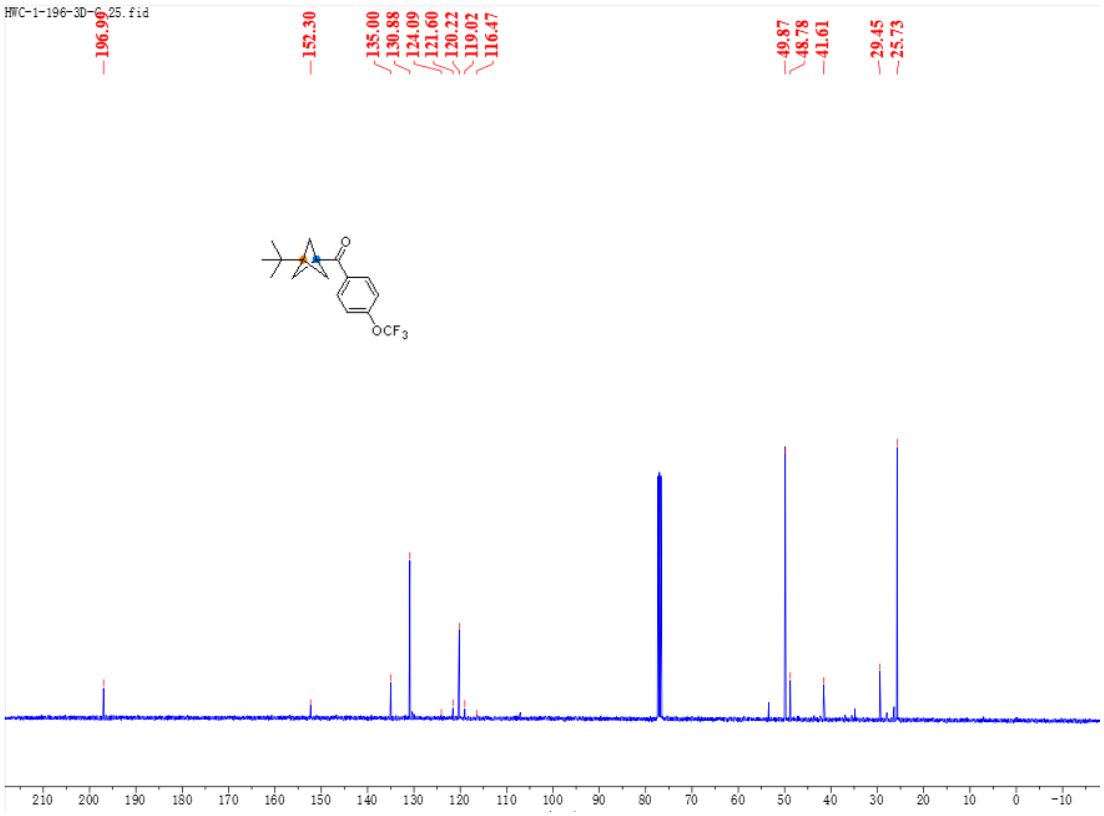
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-chlorophenyl)methanone 7



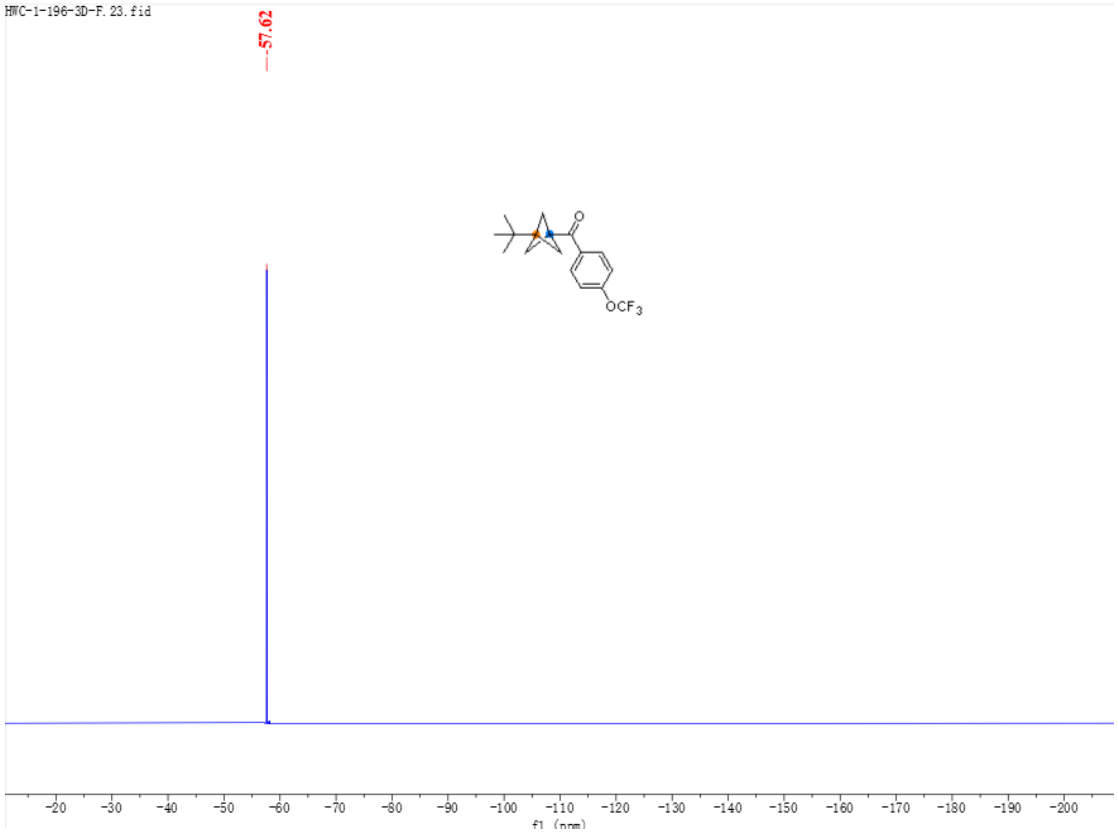
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-yl)(4-(trifluoromethoxy)phenyl)methanone 8



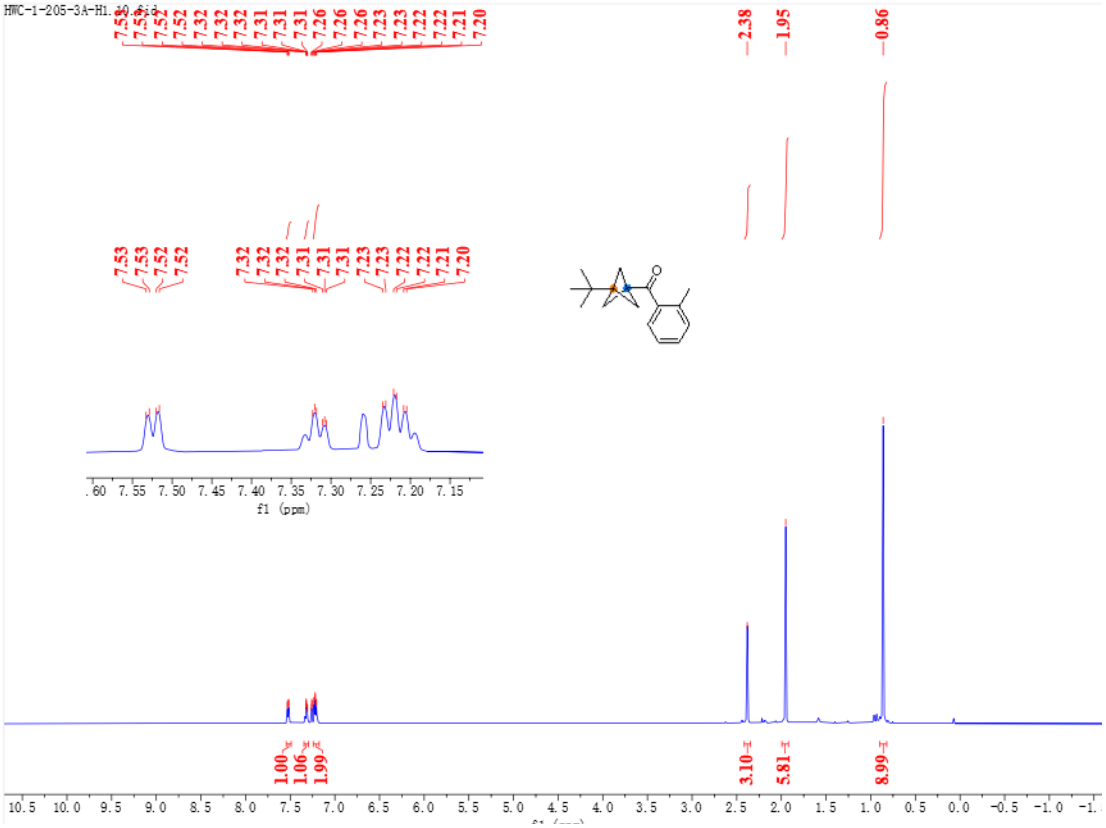
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-yl)(4-(trifluoromethoxy)phenyl)methanone 8



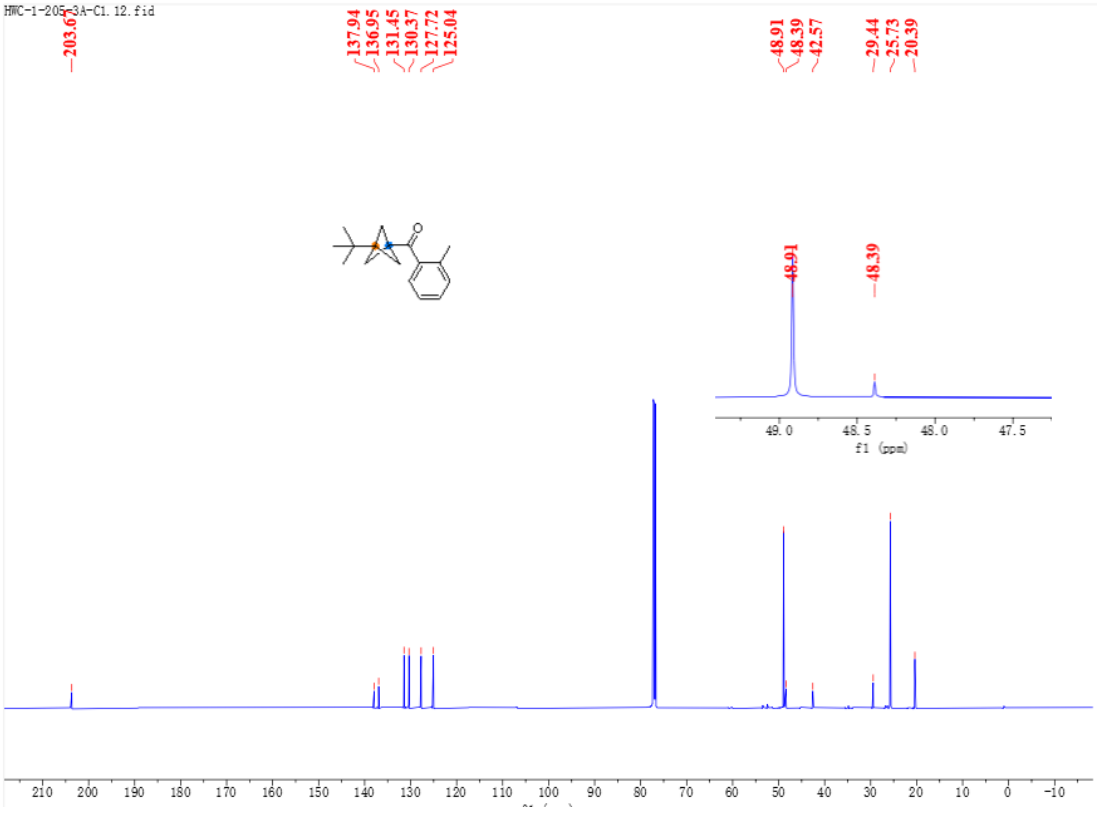
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-yl)(4-(trifluoromethoxy)phenyl)methanone 8



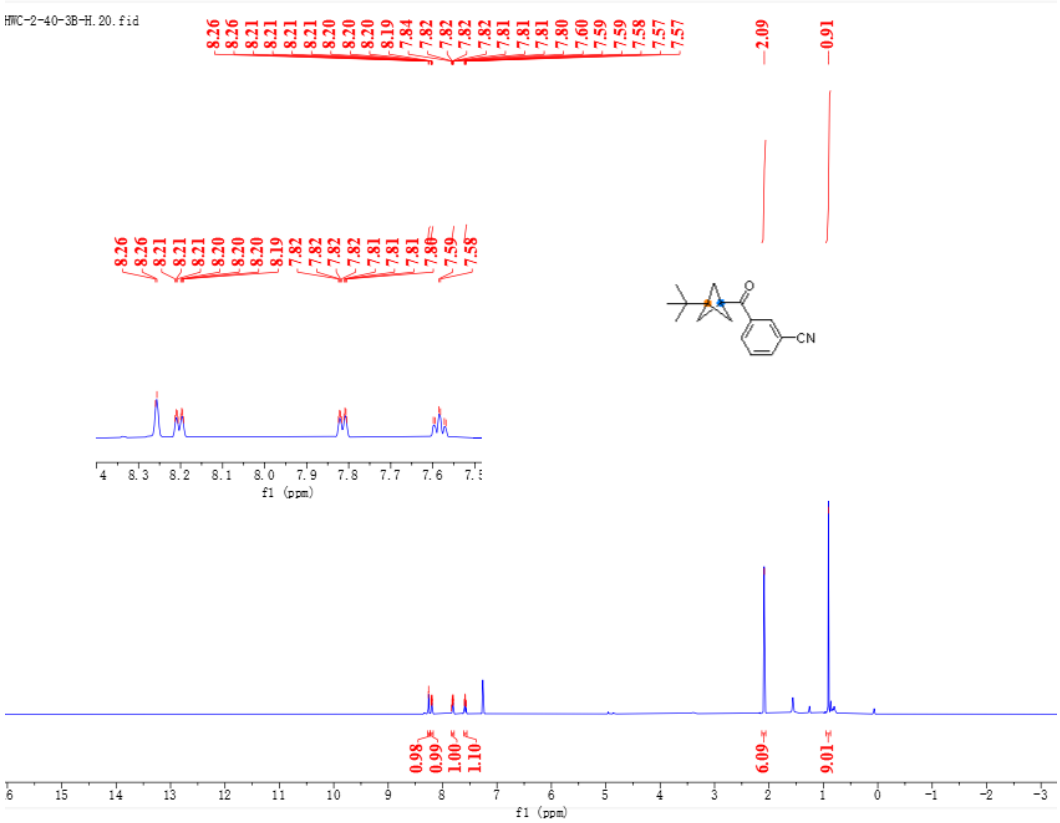
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(o-tolyl)methanone 9



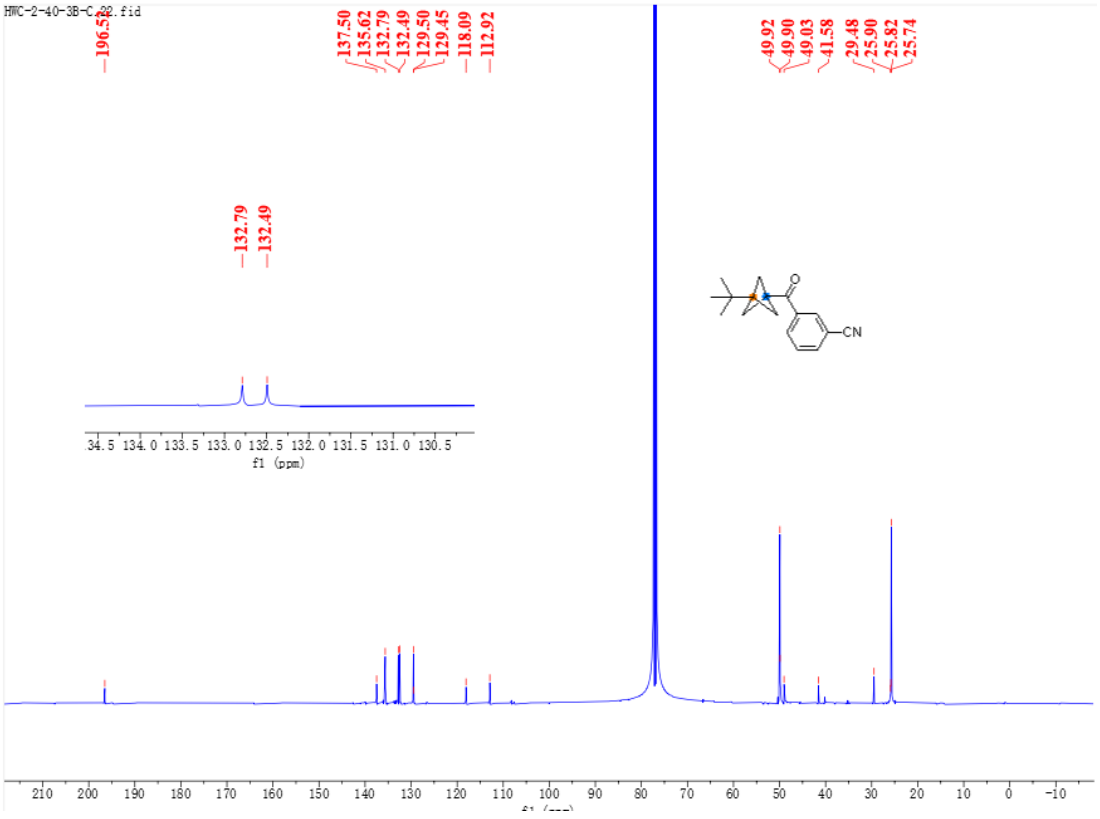
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(o-tolyl)methanone 9



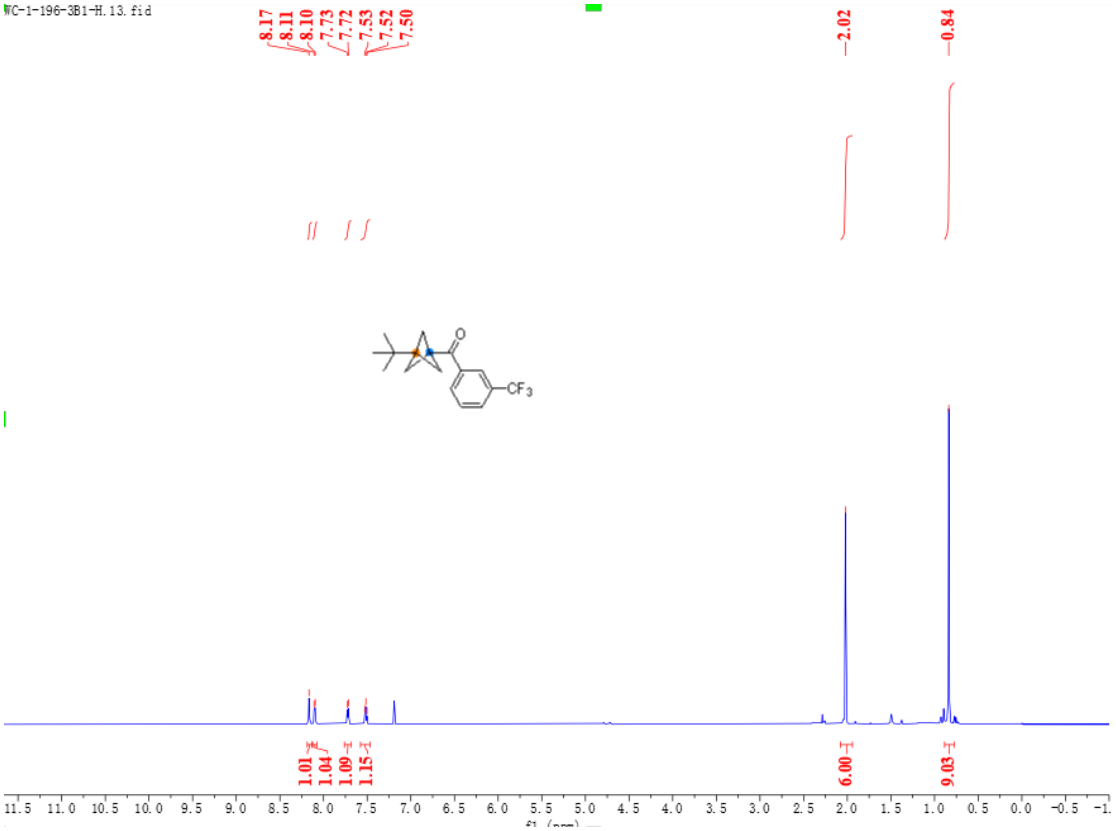
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
3-(3-(*tert*-Butyl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile 10



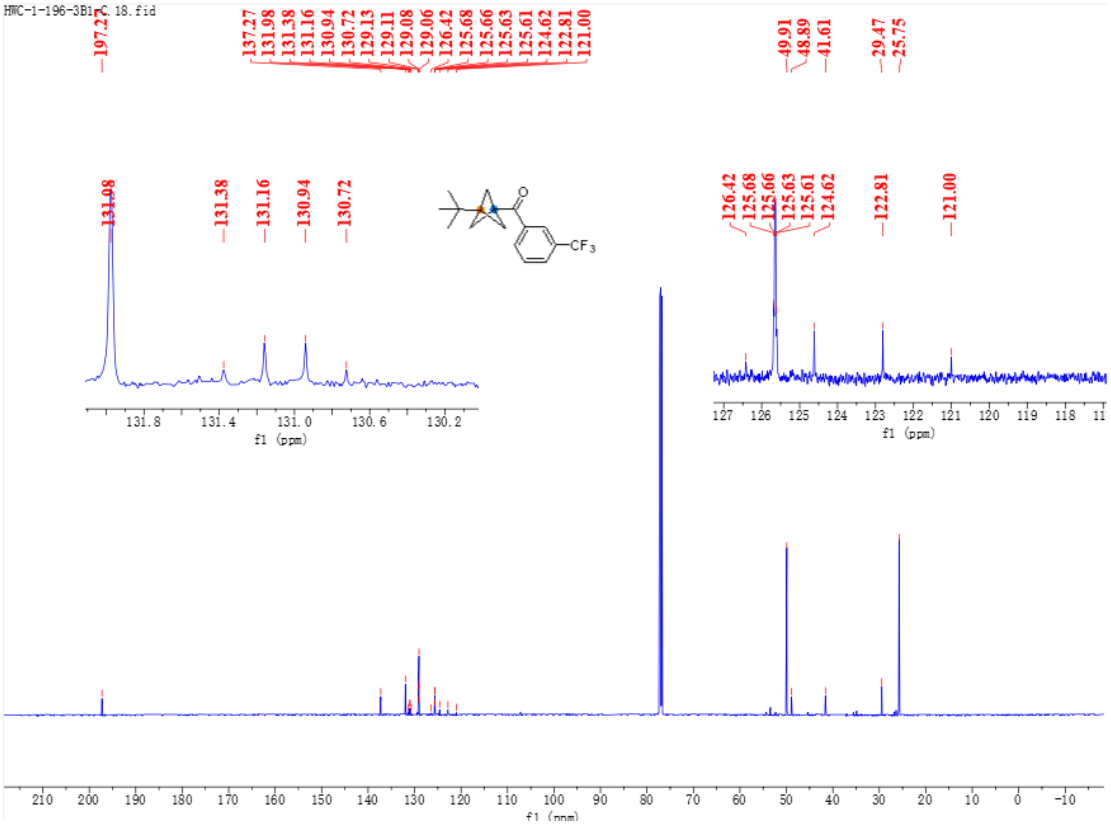
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
3-(3-(*tert*-Butyl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile 10



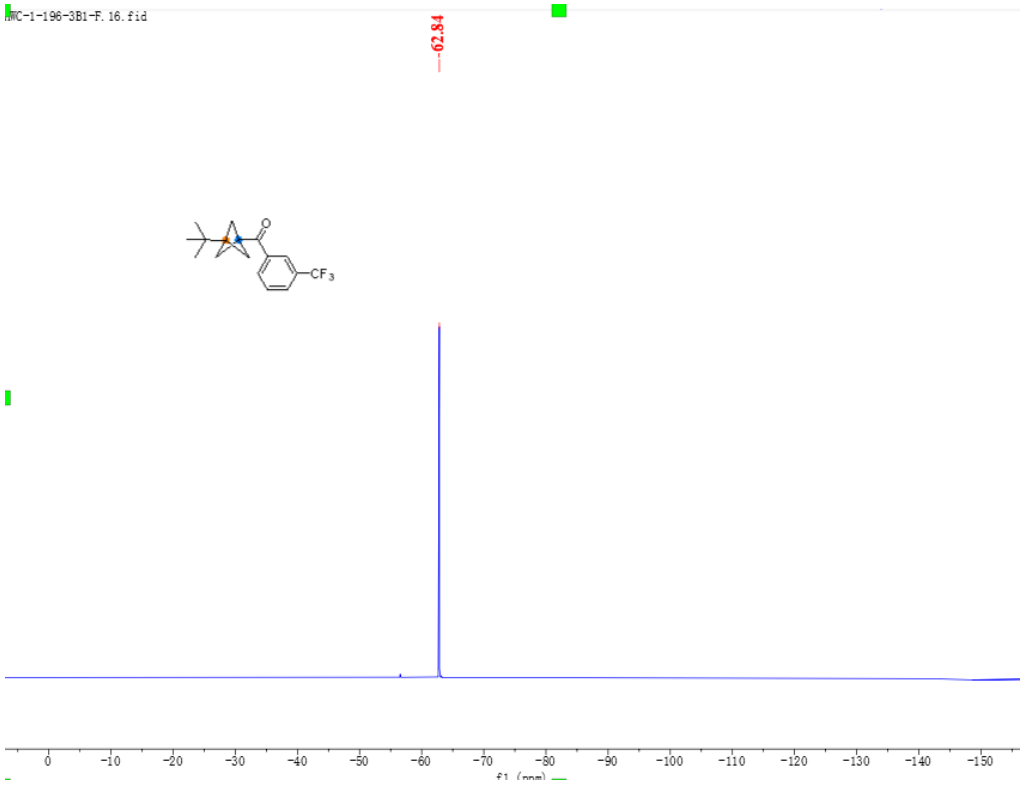
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-yl)(3-(trifluoromethyl)phenyl)methanone 11



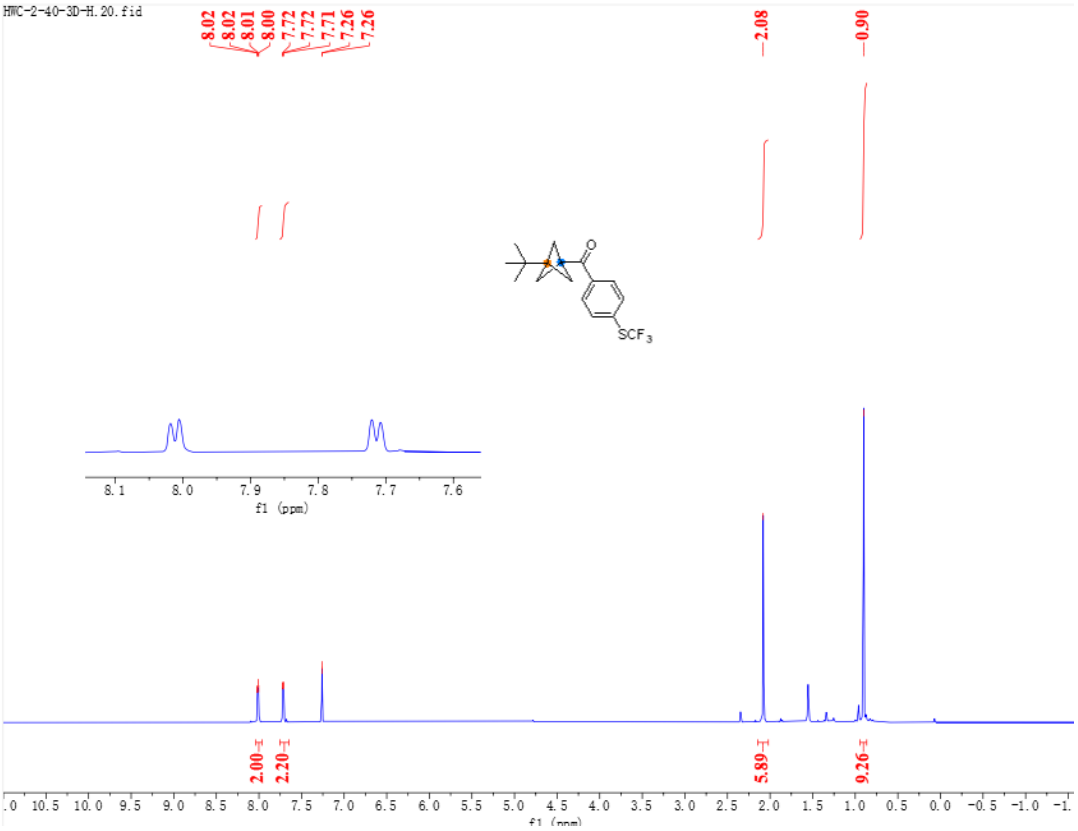
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-yl)(3-(trifluoromethyl)phenyl)methanone 11



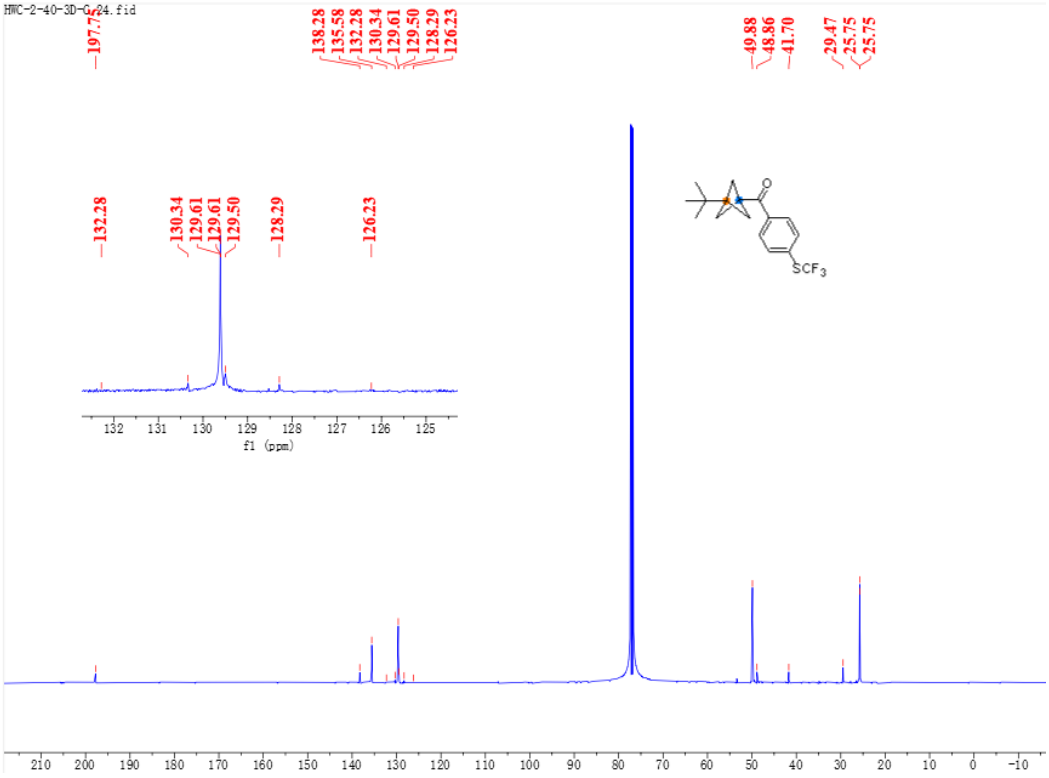
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of (3-(tert-Butyl)bicyclo[1.1.1]pentan-yl)(3-(trifluoromethyl)phenyl)methanone 11



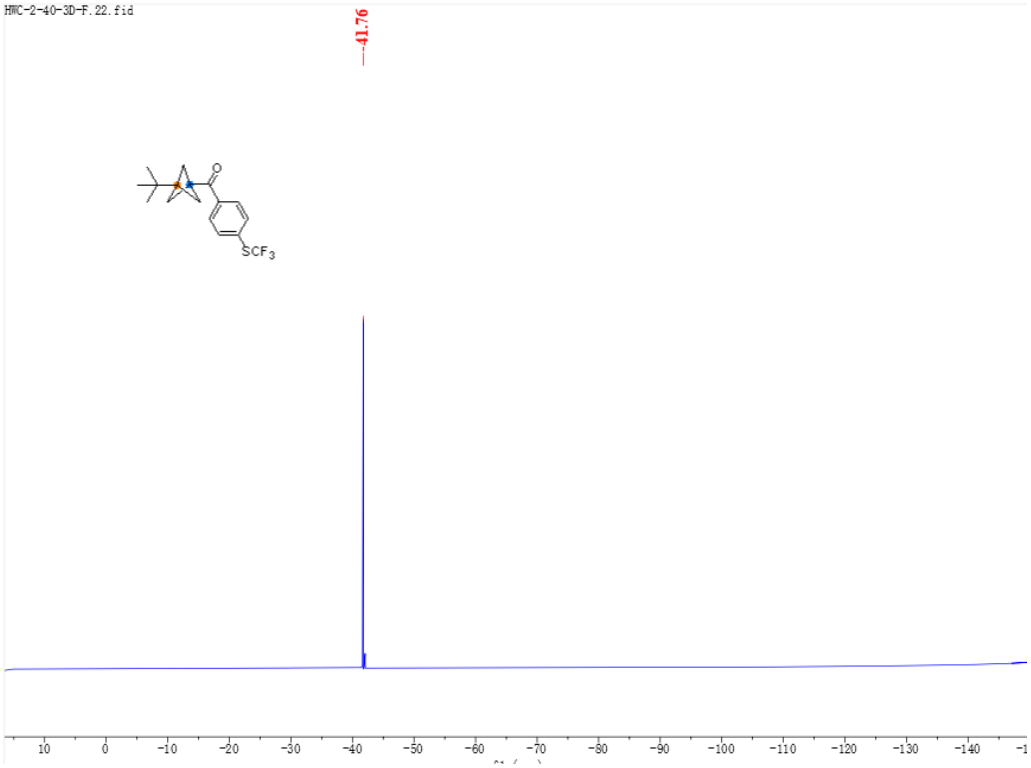
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-((trifluoromethyl)thio)phenyl)methanone 12



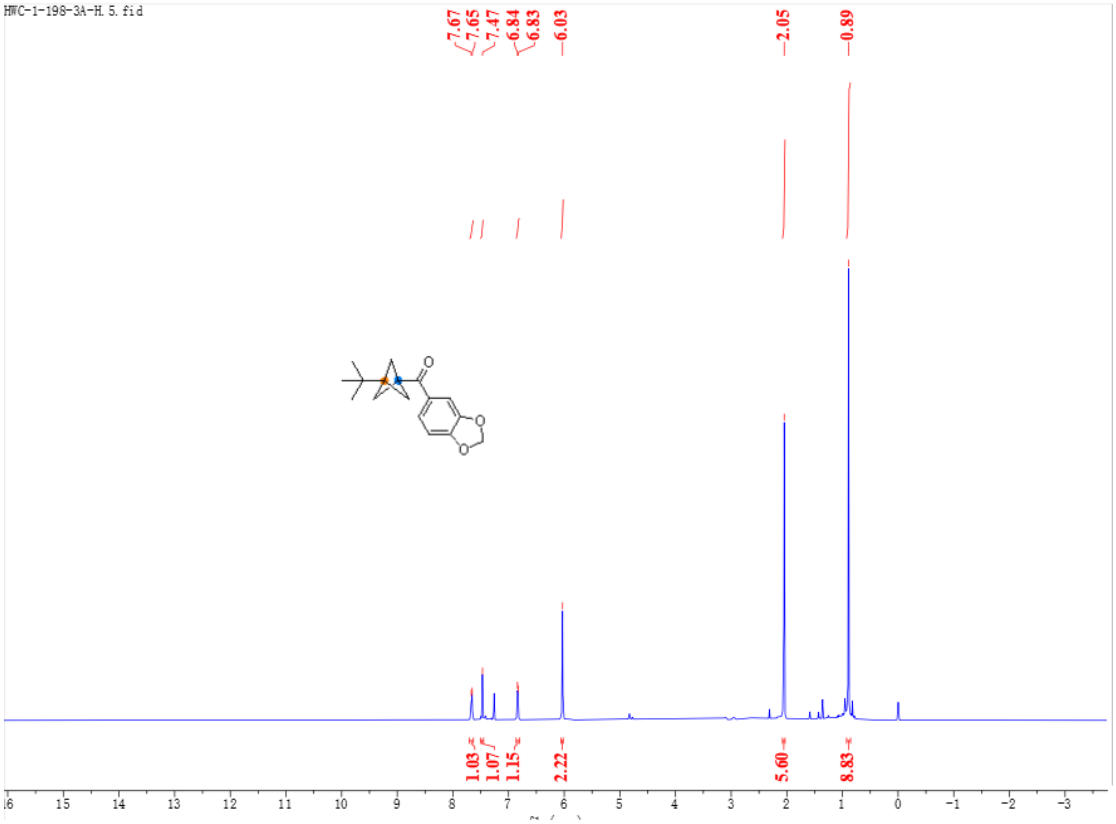
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-((trifluoromethyl)thio)phenyl)methanone 12



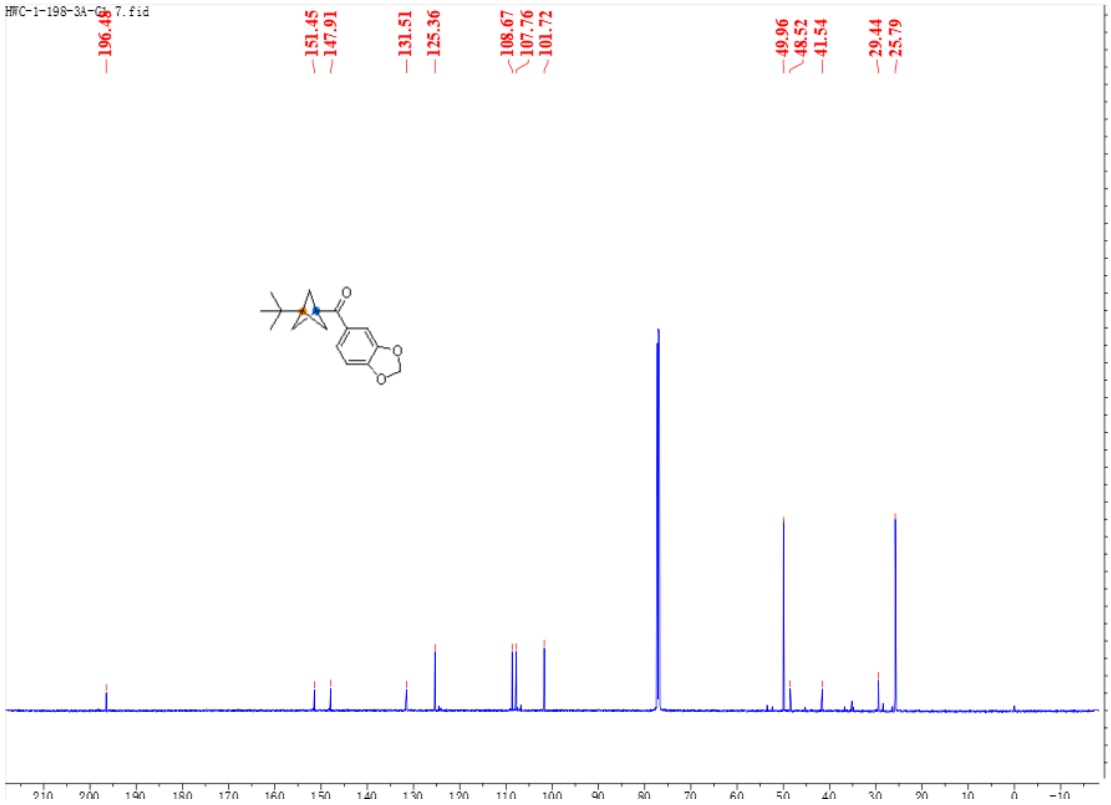
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(4-((trifluoromethyl)thio)phenyl)methanone 12



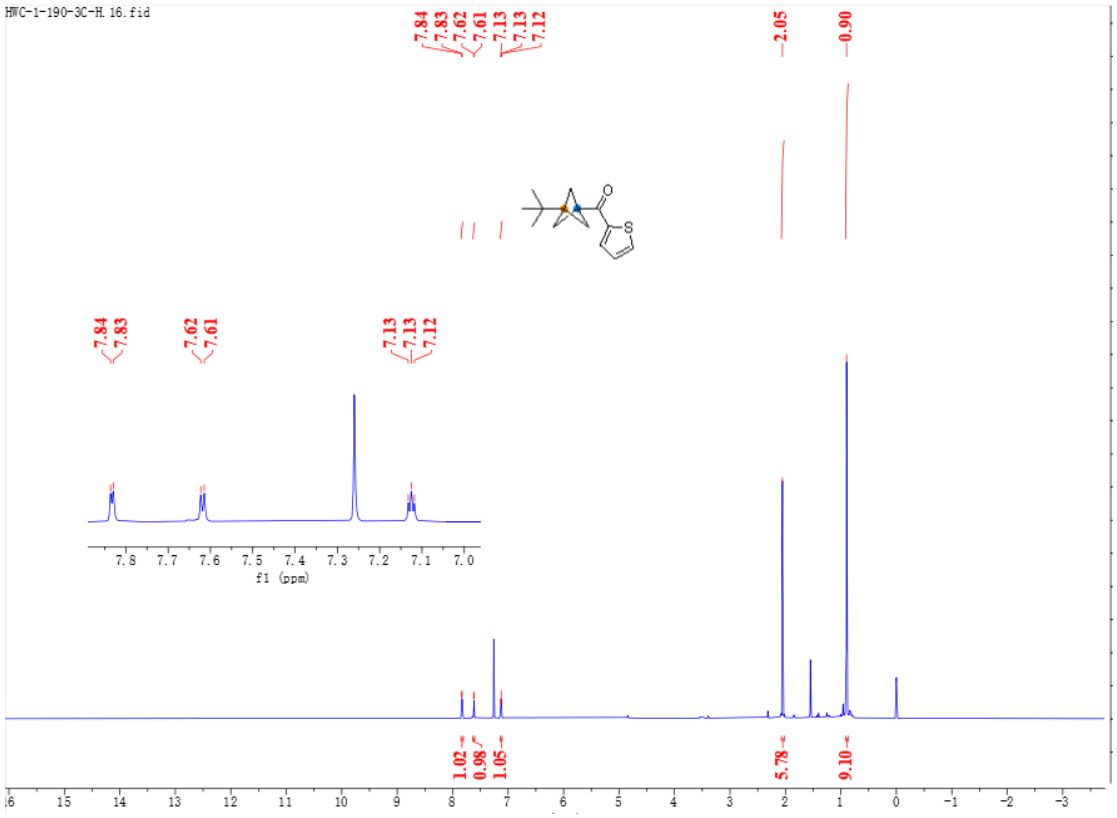
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Benzo[d][1,3]dioxol-5-yl(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)methanone 13



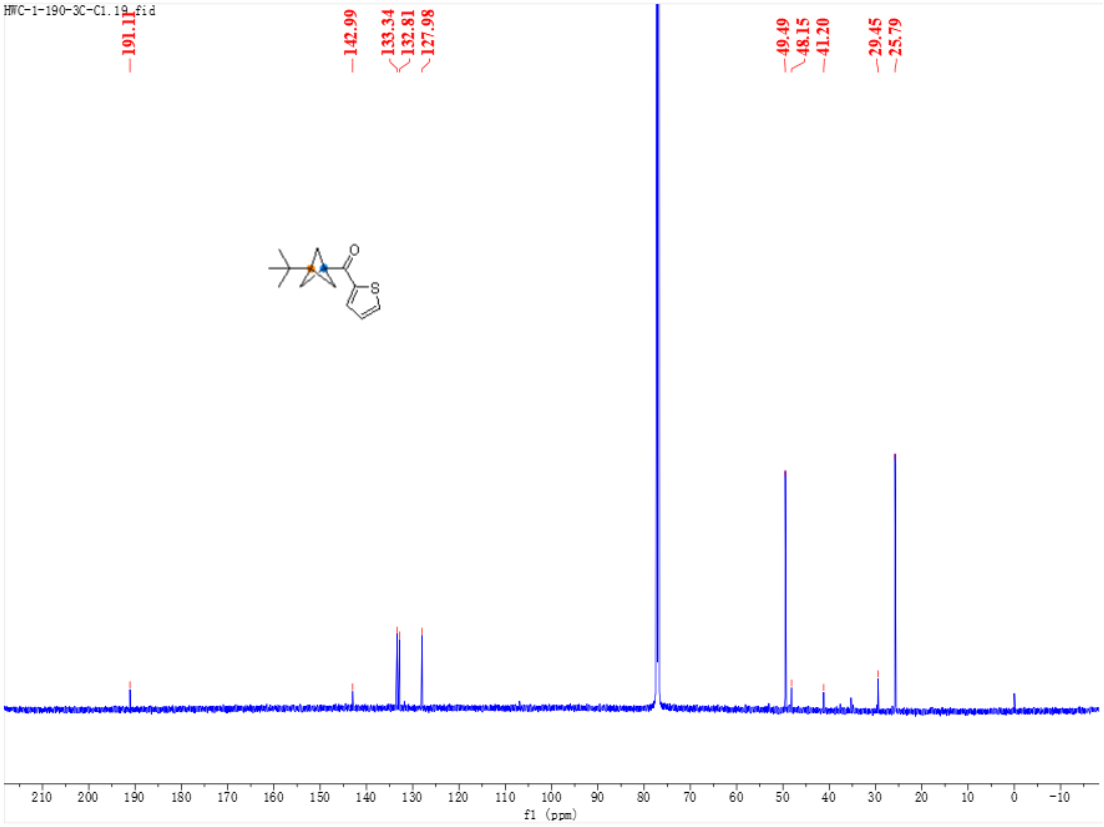
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of Benzo[d][1,3]dioxol-5-yl(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)methanone 13



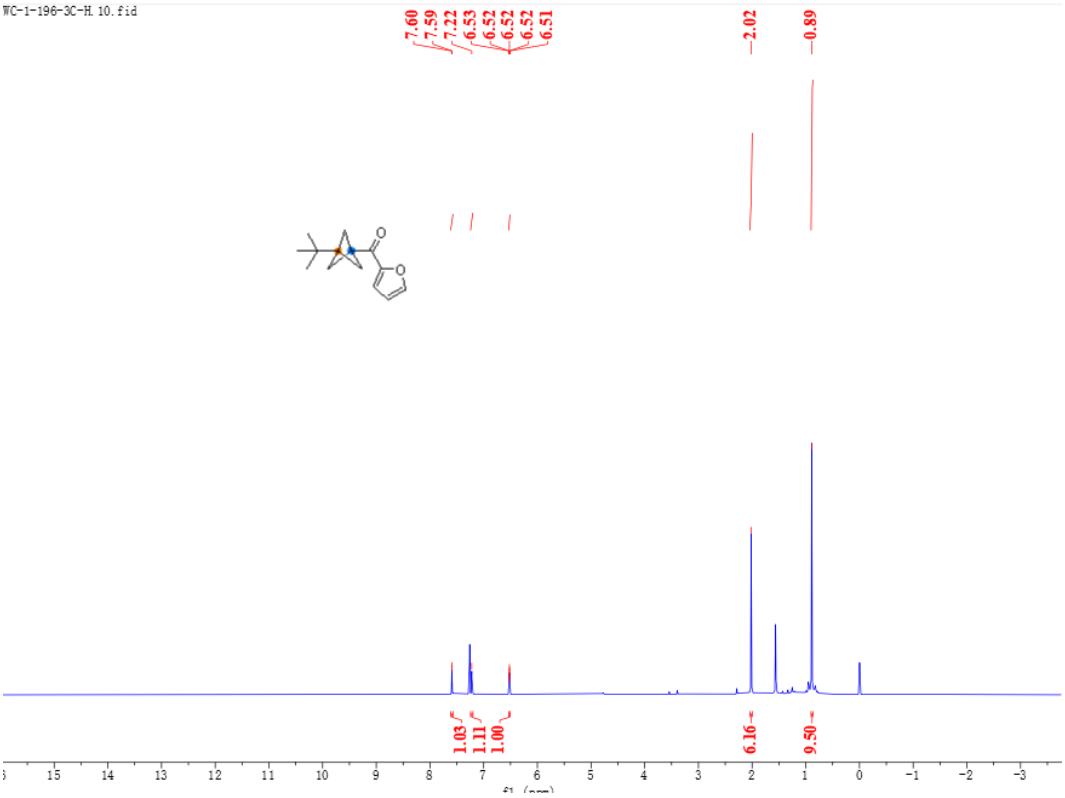
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(furan-2-yl)methanone 14



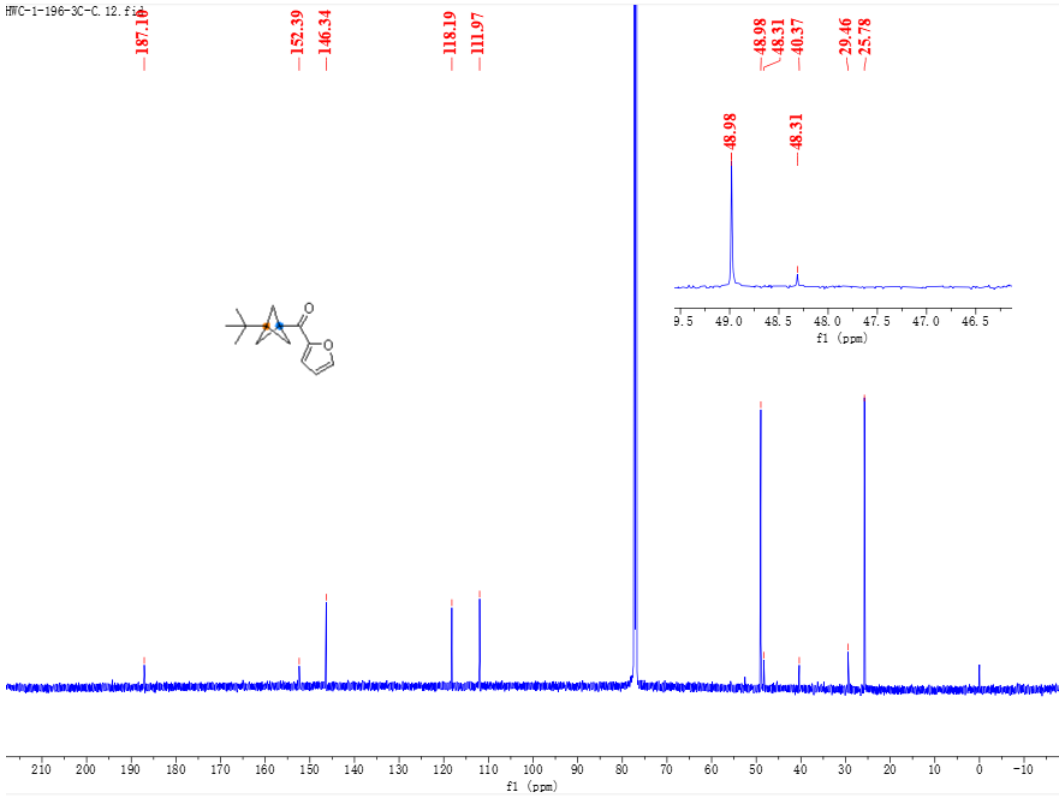
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(furan-2-yl)methanone 14



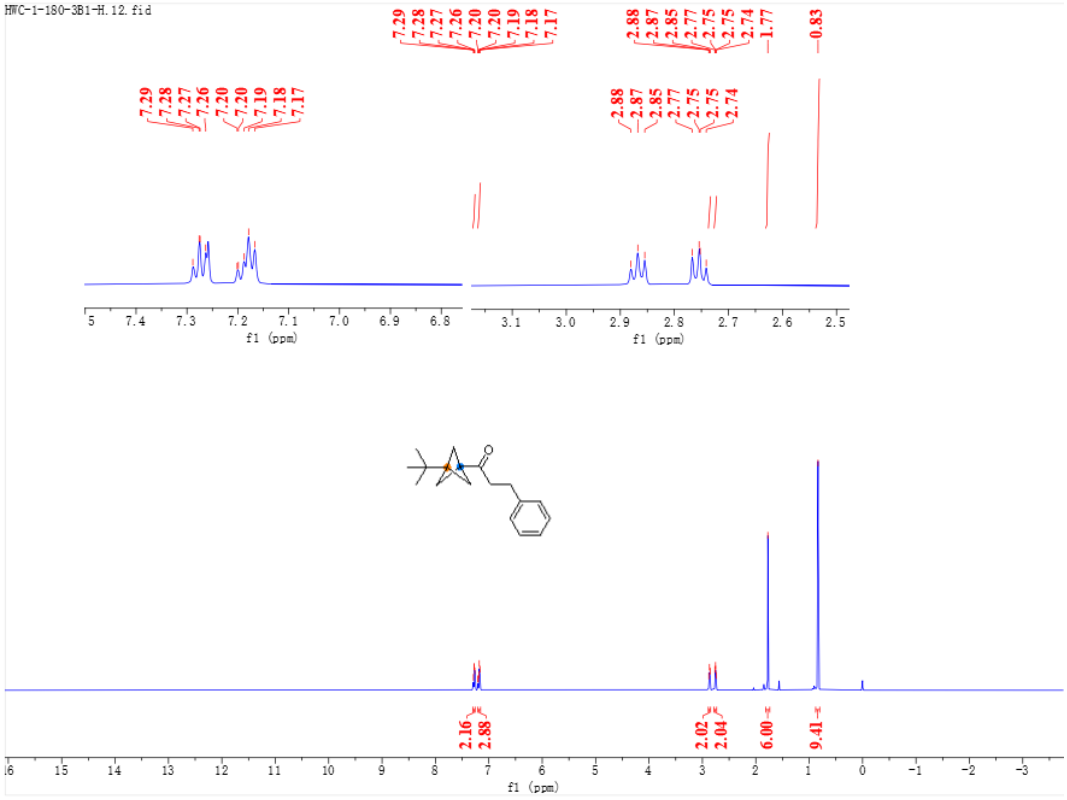
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone 15



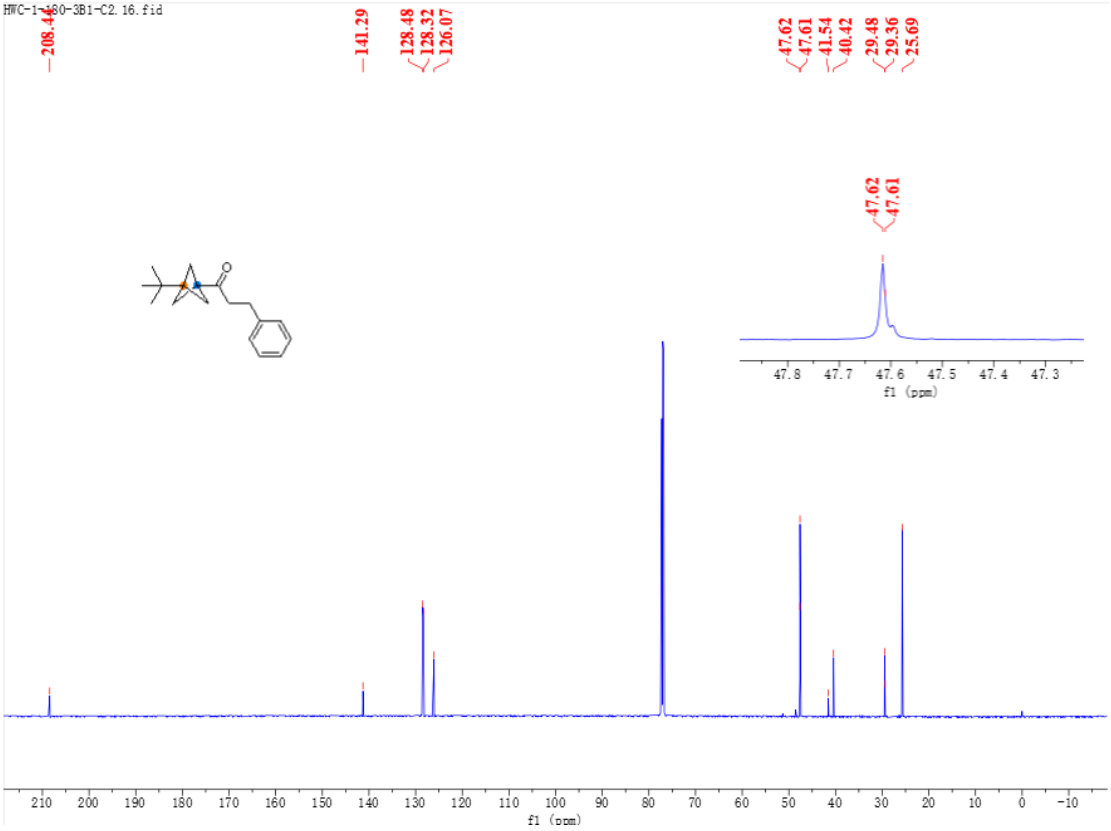
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone 15



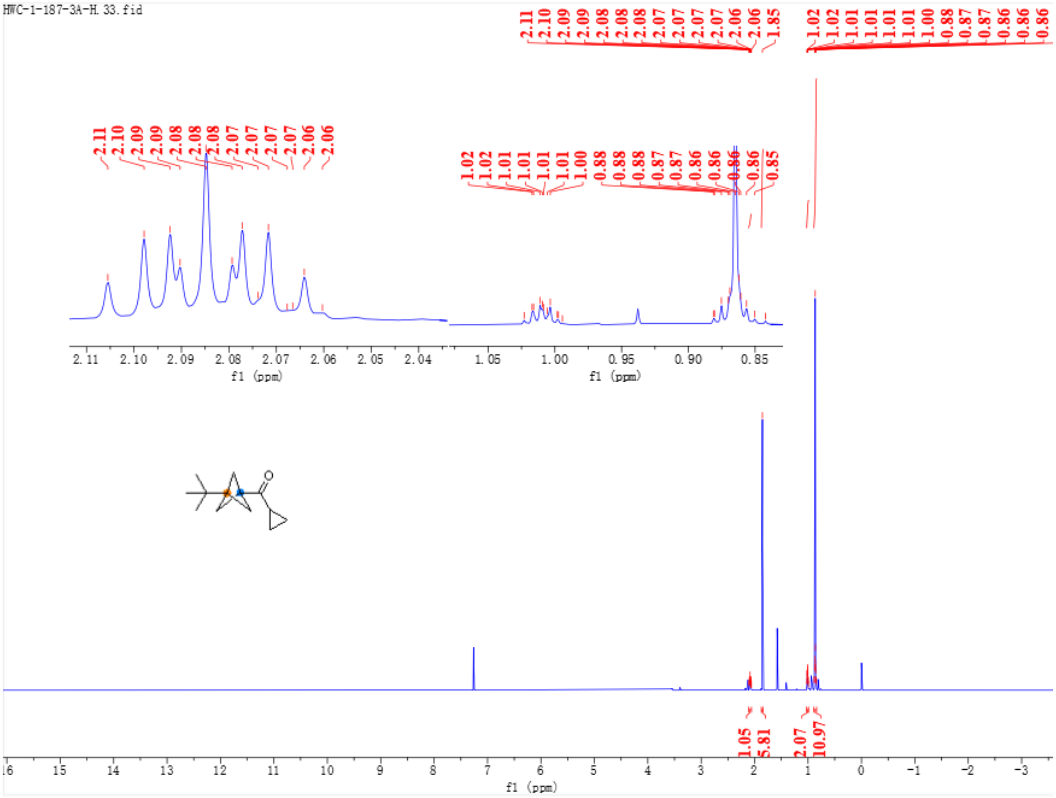
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 16



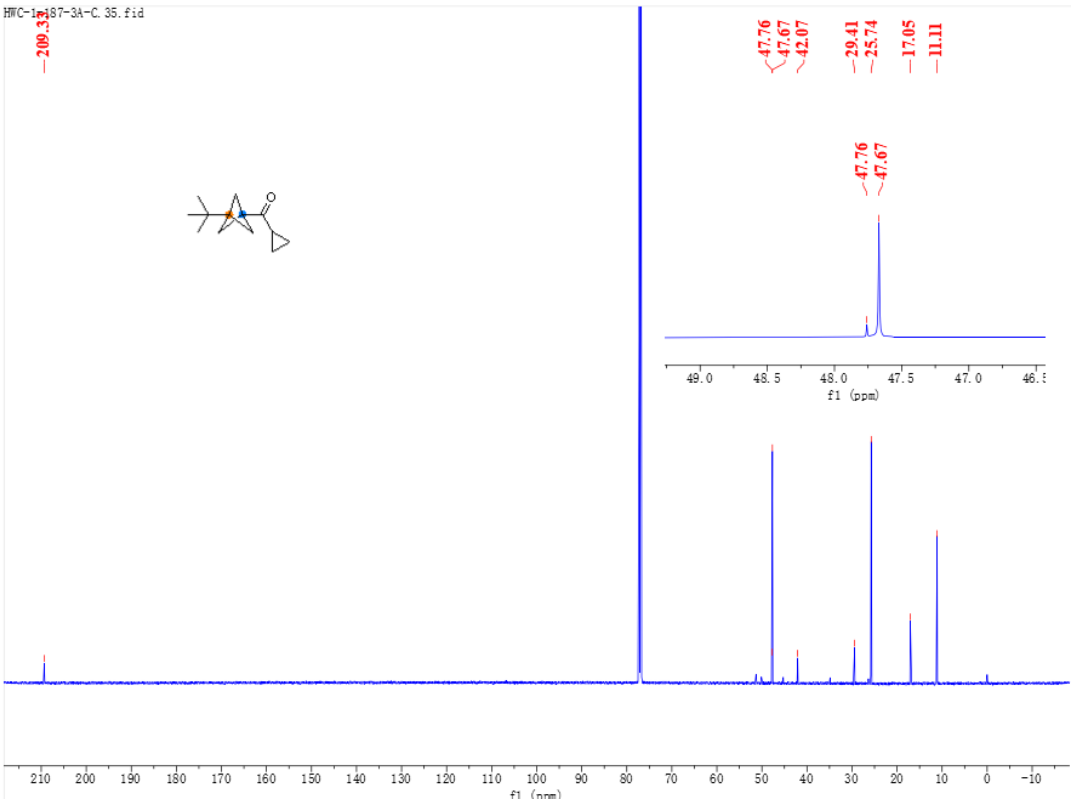
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 1-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 16



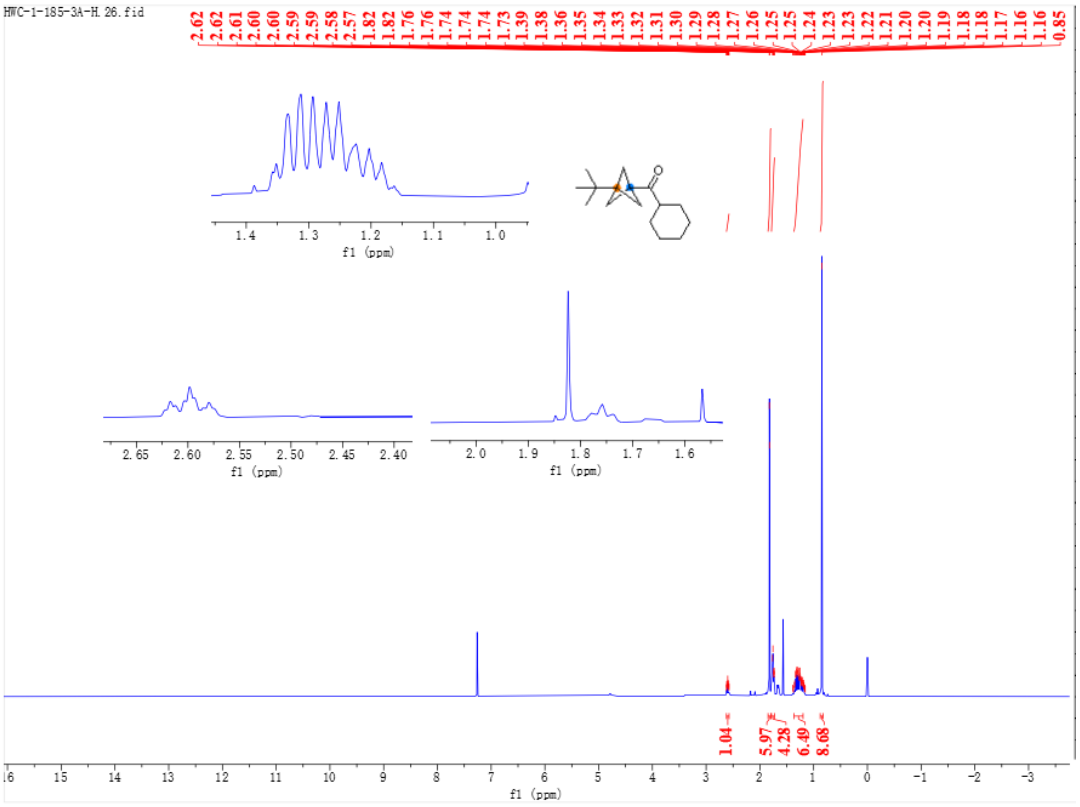
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(cyclopropyl)methanone 17



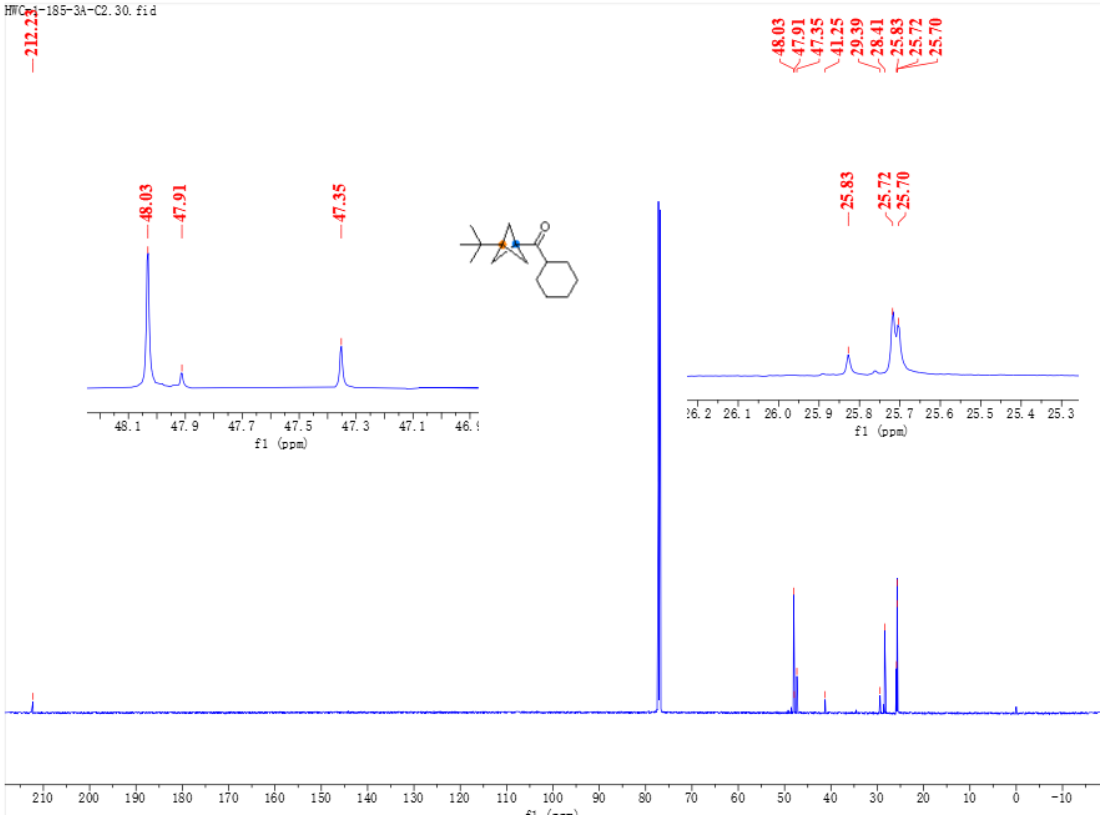
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(cyclopropyl)methanone 17



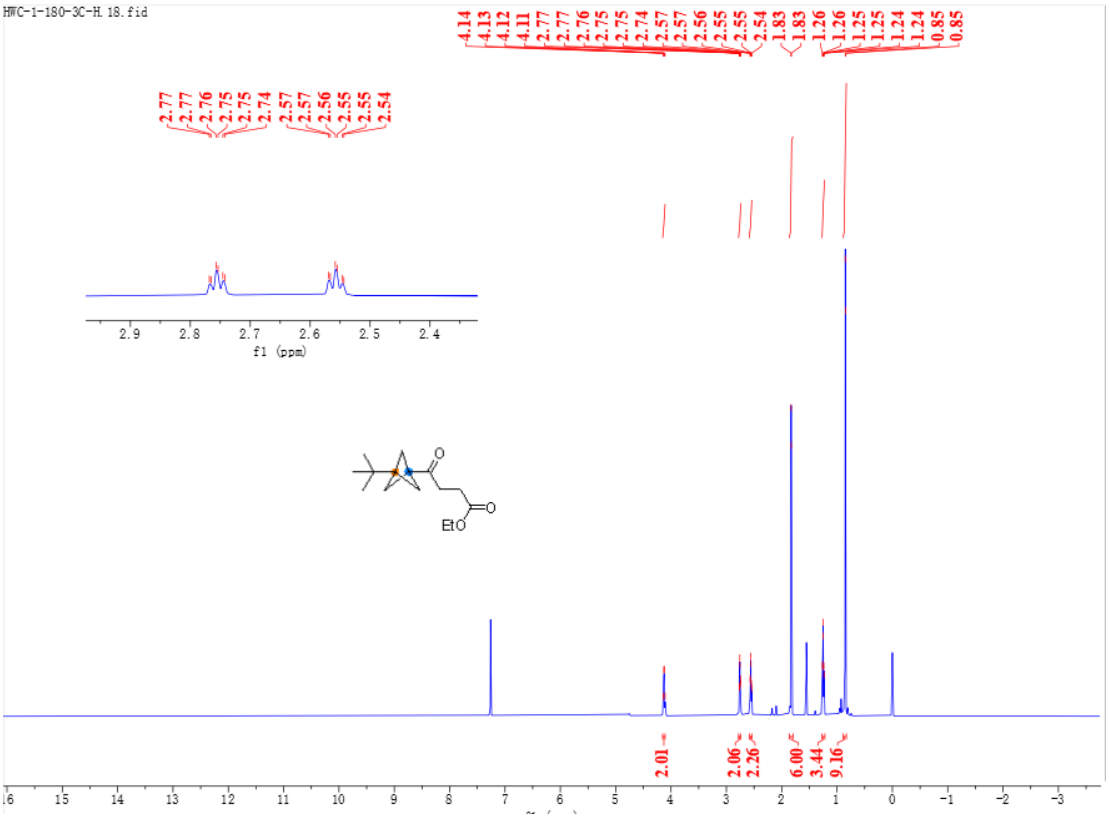
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(cyclohexyl)methanone 18



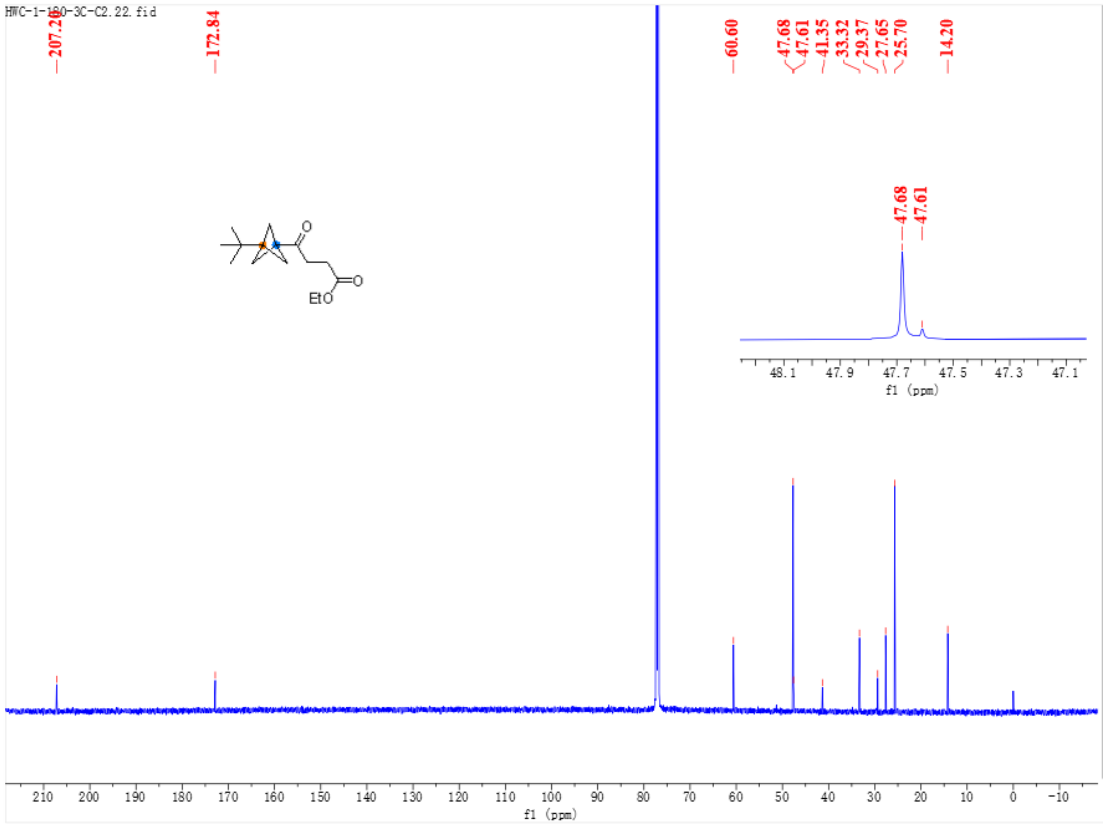
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(cyclohexyl)methanone 18



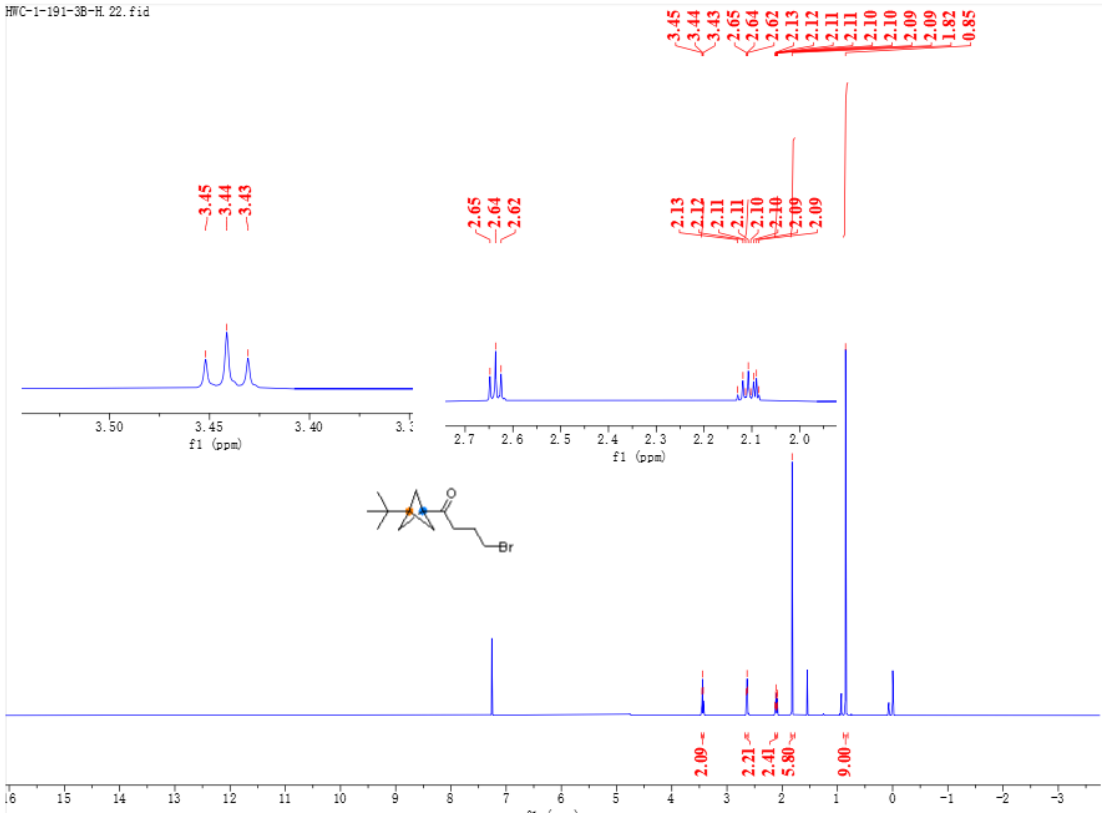
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
Ethyl 4-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-4-oxobutanoate 19



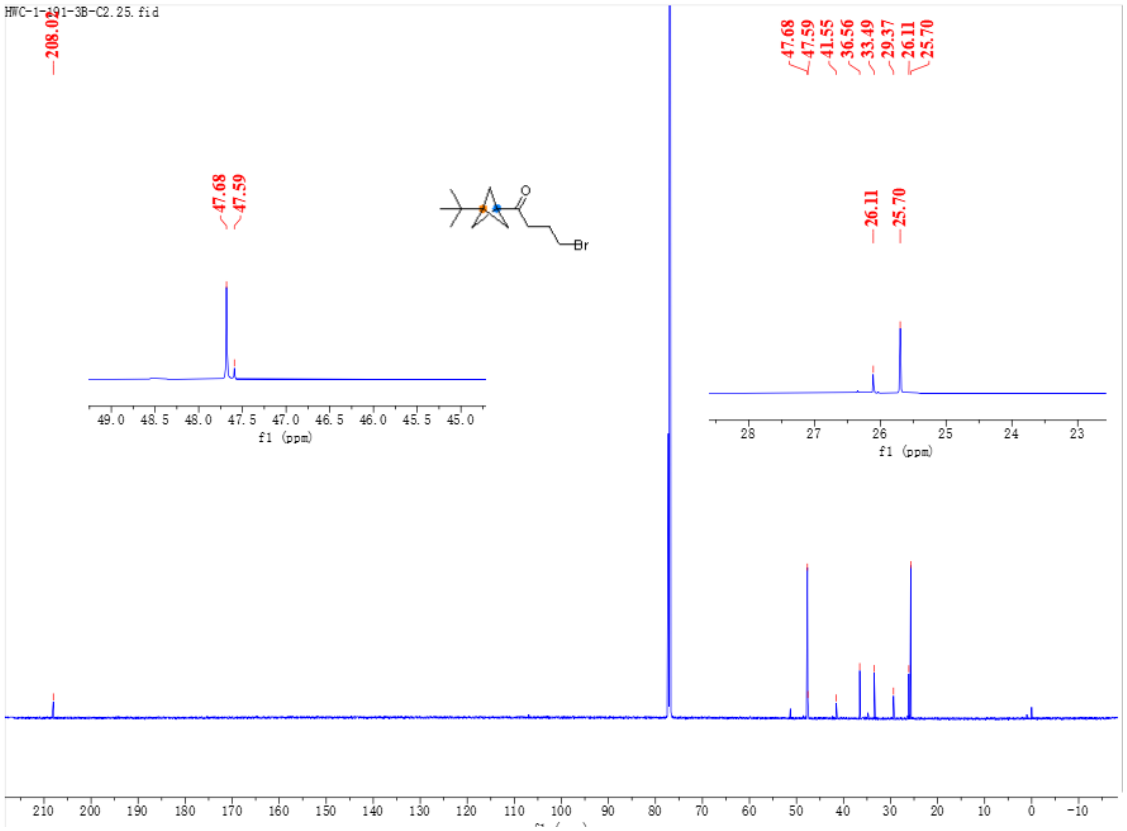
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
Ethyl 4-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-4-oxobutanoate 19



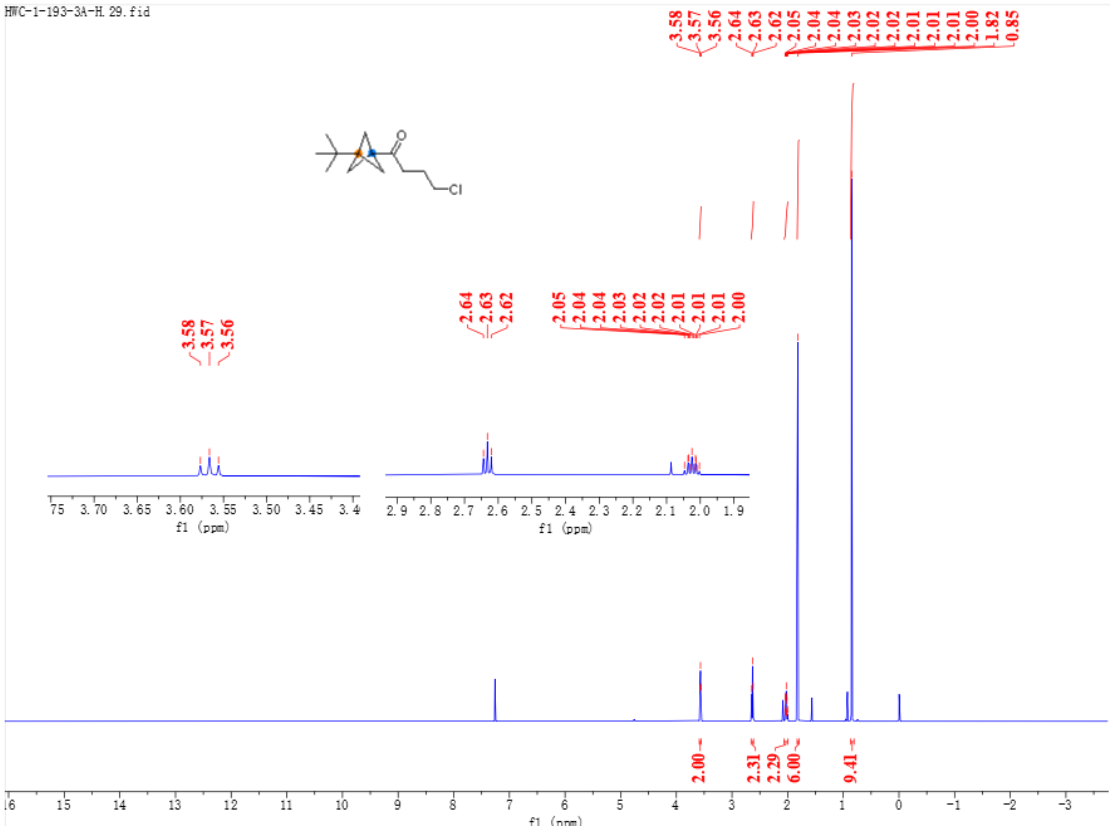
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
4-Bromo-1-(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)butan-1-one 20



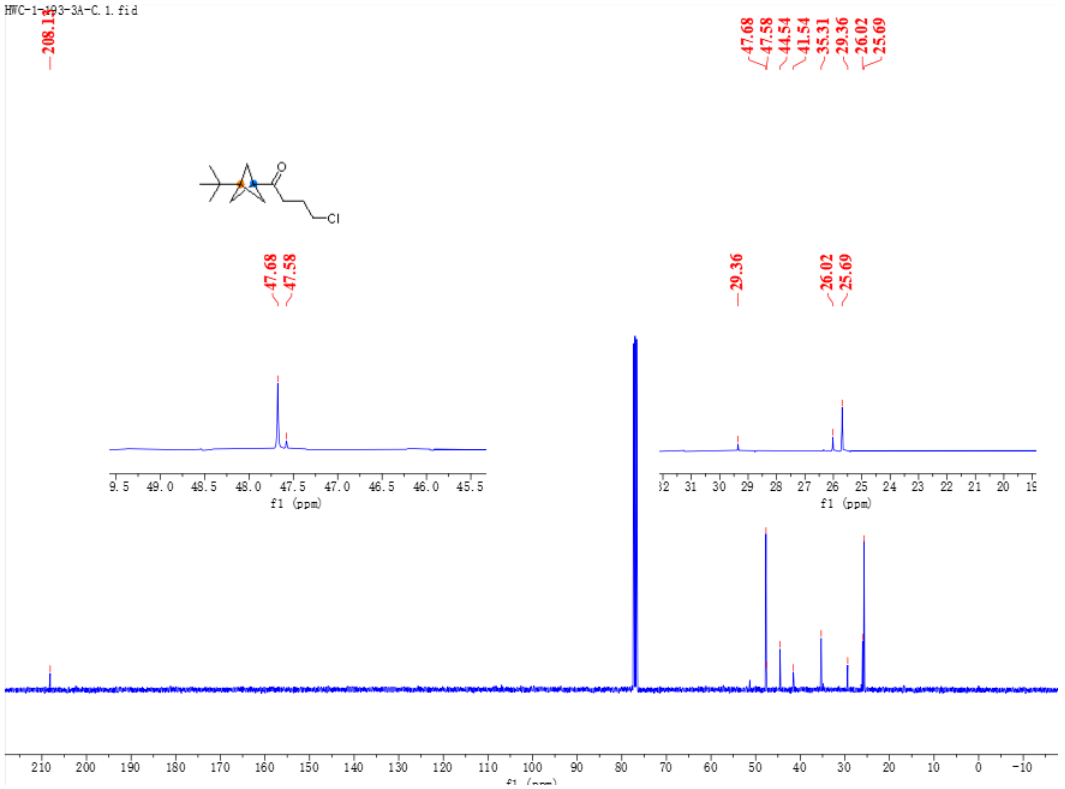
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
4-Bromo-1-(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)butan-1-one 20



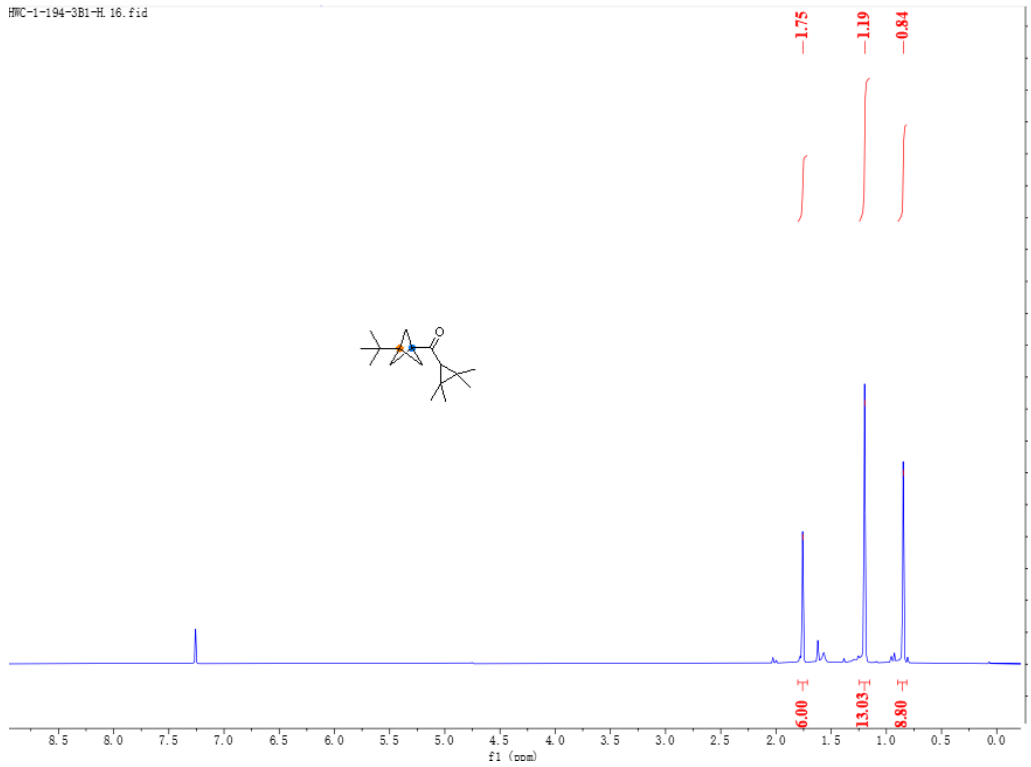
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-4-chlorobutan-1-one 21



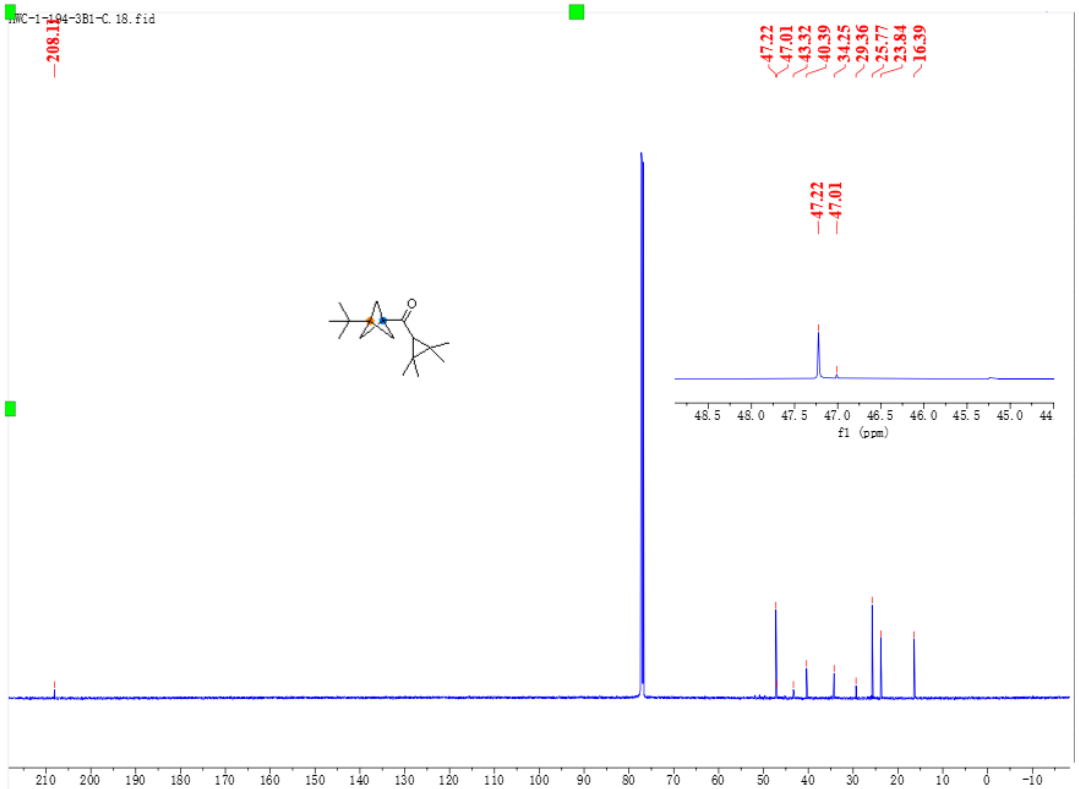
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 1-(3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)-4-chlorobutan-1-one 21



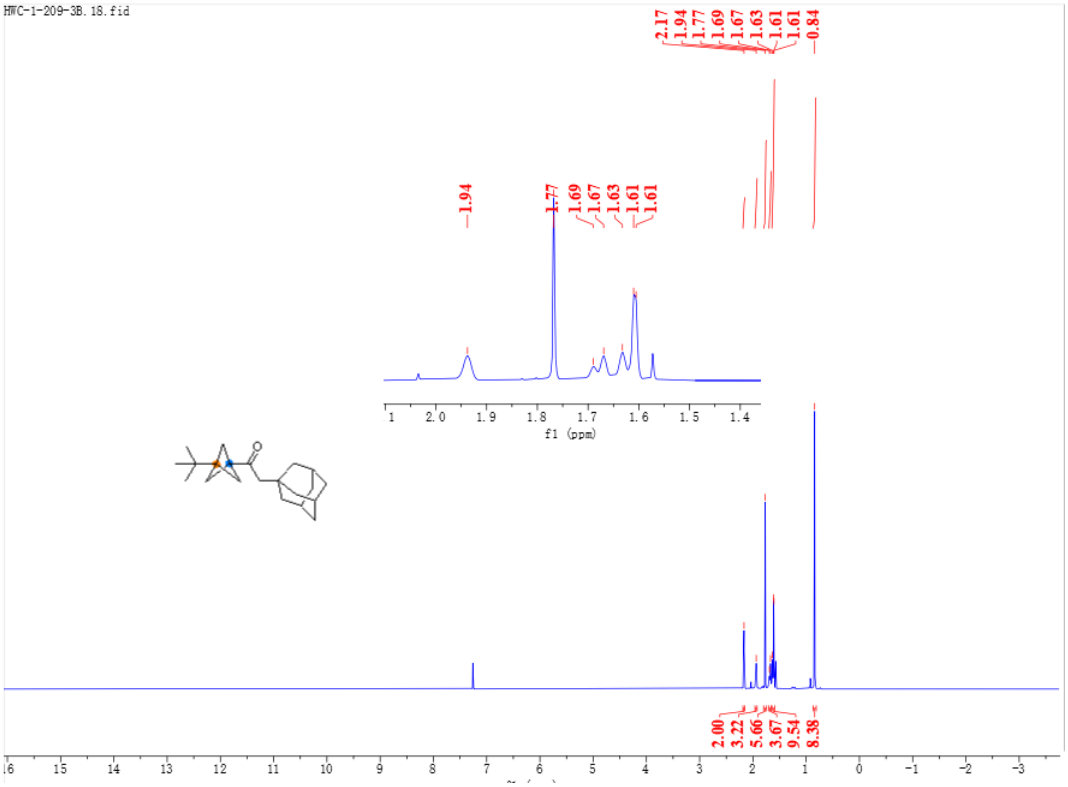
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(2,2,3,3-tetramethylcyclopropyl)methanone 22



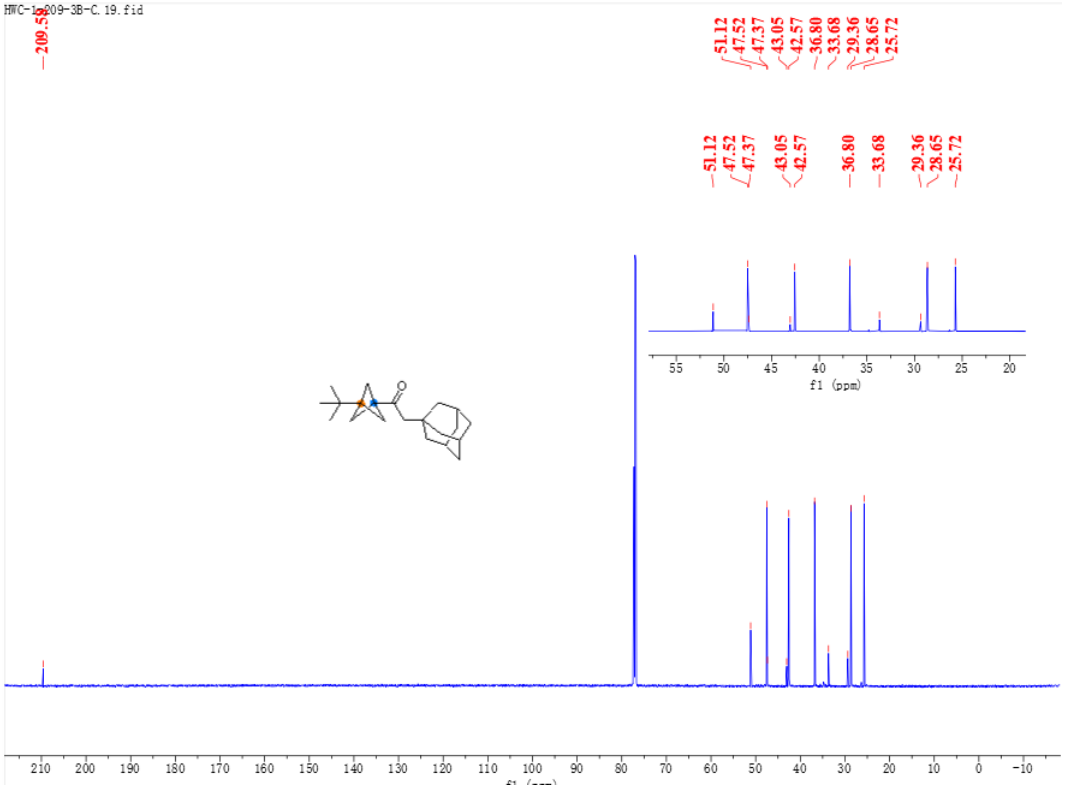
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(2,2,3,3-tetramethylcyclopropyl)methanone 22



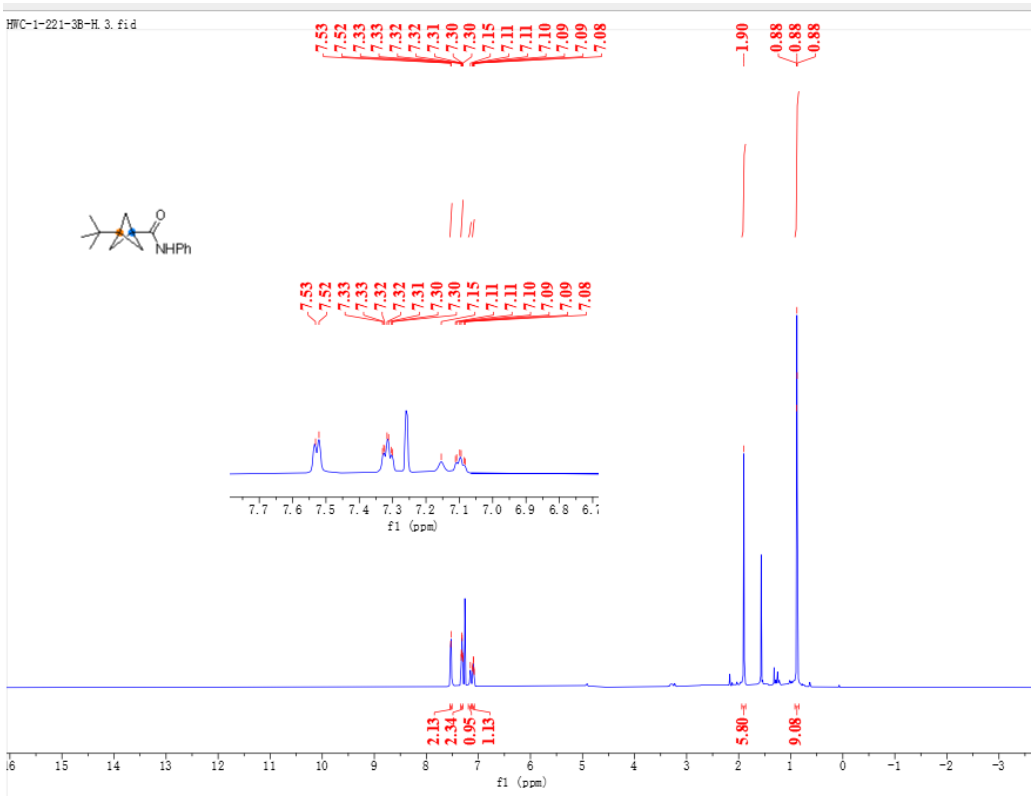
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 2-Adamantan-1-yl)-1-(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)ethan-1-one 23



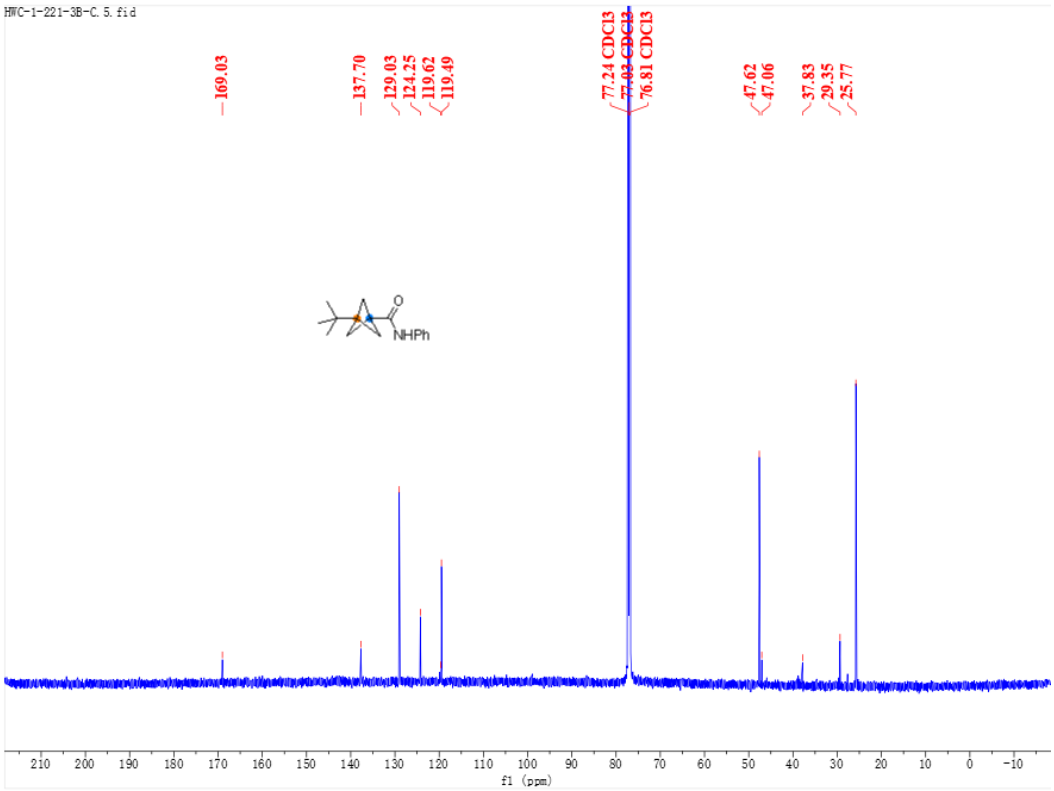
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 2-Adamantan-1-yl)-1-(3-(*tert*-butyl)bicyclo[1.1.1]pentan-1-yl)ethan-1-one 23



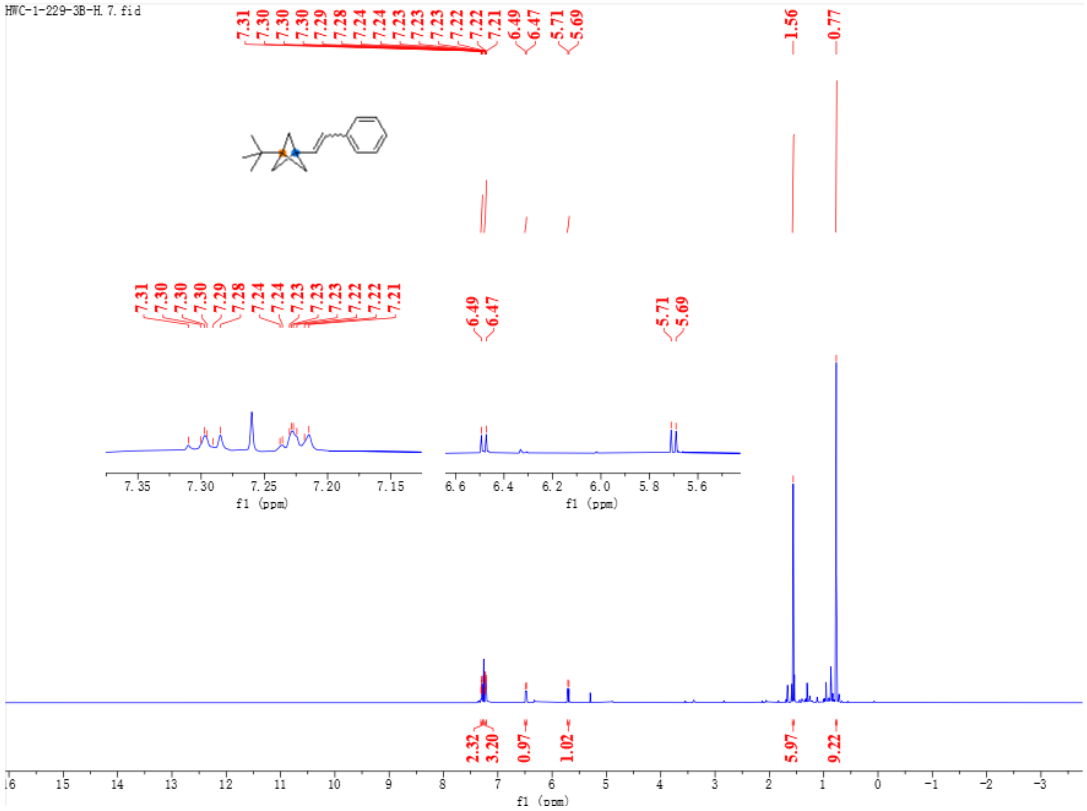
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3-(*tert*-Butyl)-*N*-phenylbicyclo[1.1.1]pentane-1-carboxamide 24



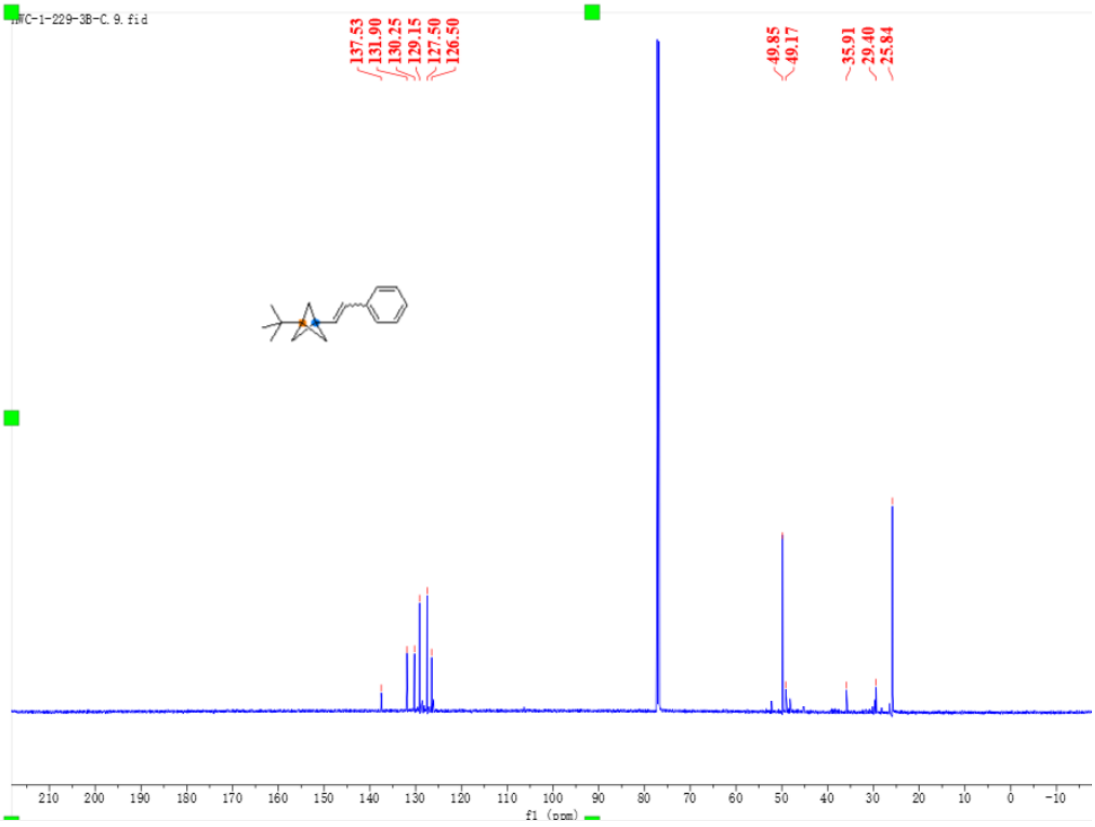
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3-(*tert*-Butyl)-*N*-phenylbicyclo[1.1.1]pentane-1-carboxamide 24



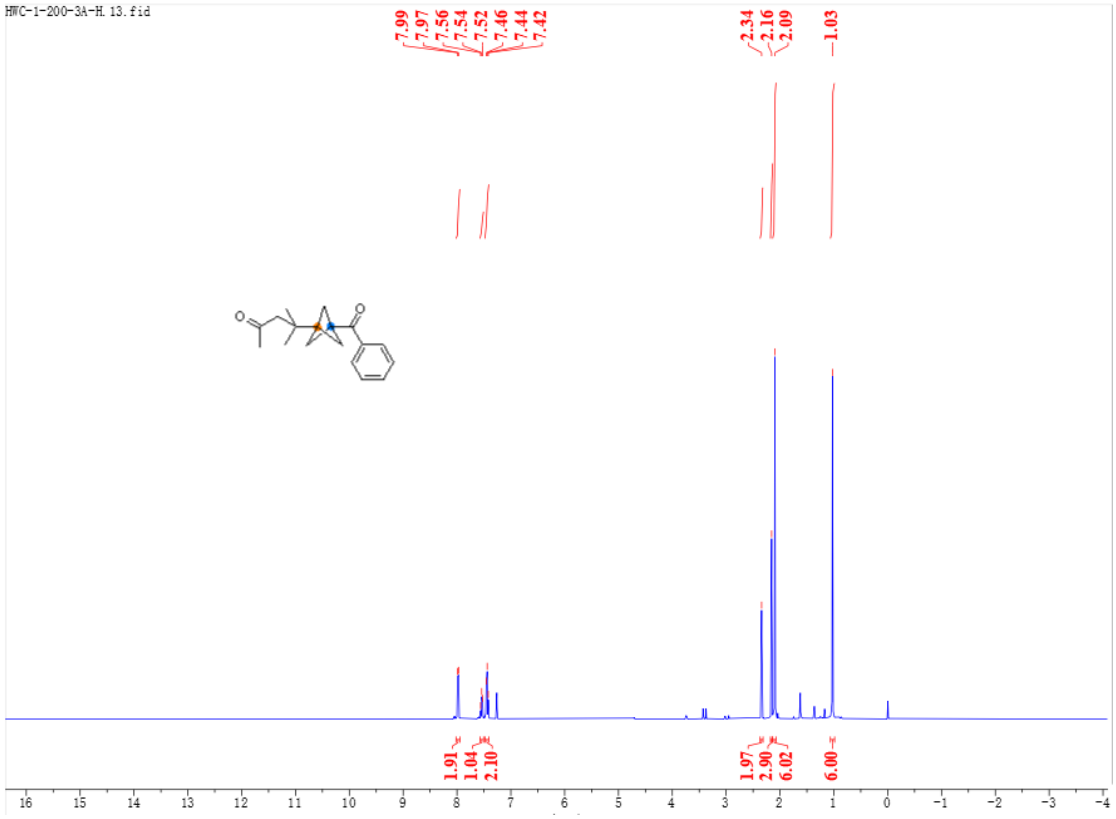
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
1-(*tert*-Butyl)-3-styrylbicyclo[1.1.1]pentane 25



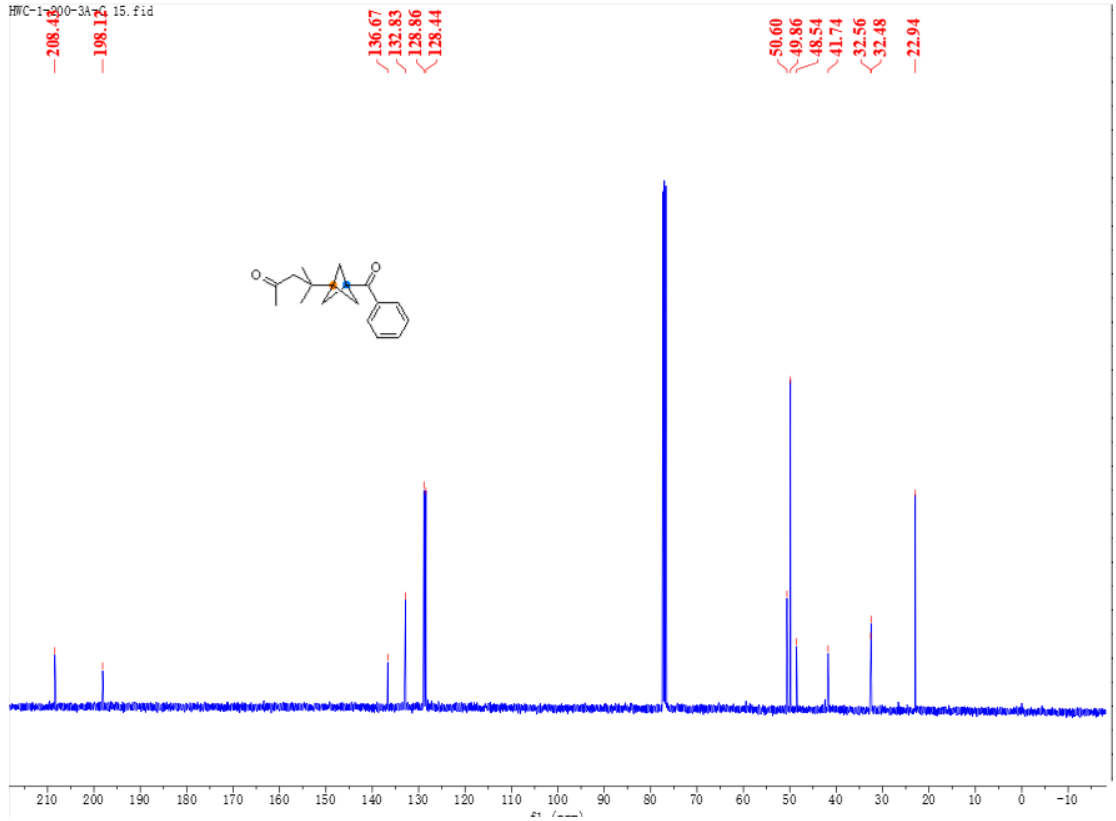
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
1-(*tert*-butyl)-3-styrylbicyclo[1.1.1]pentane 25



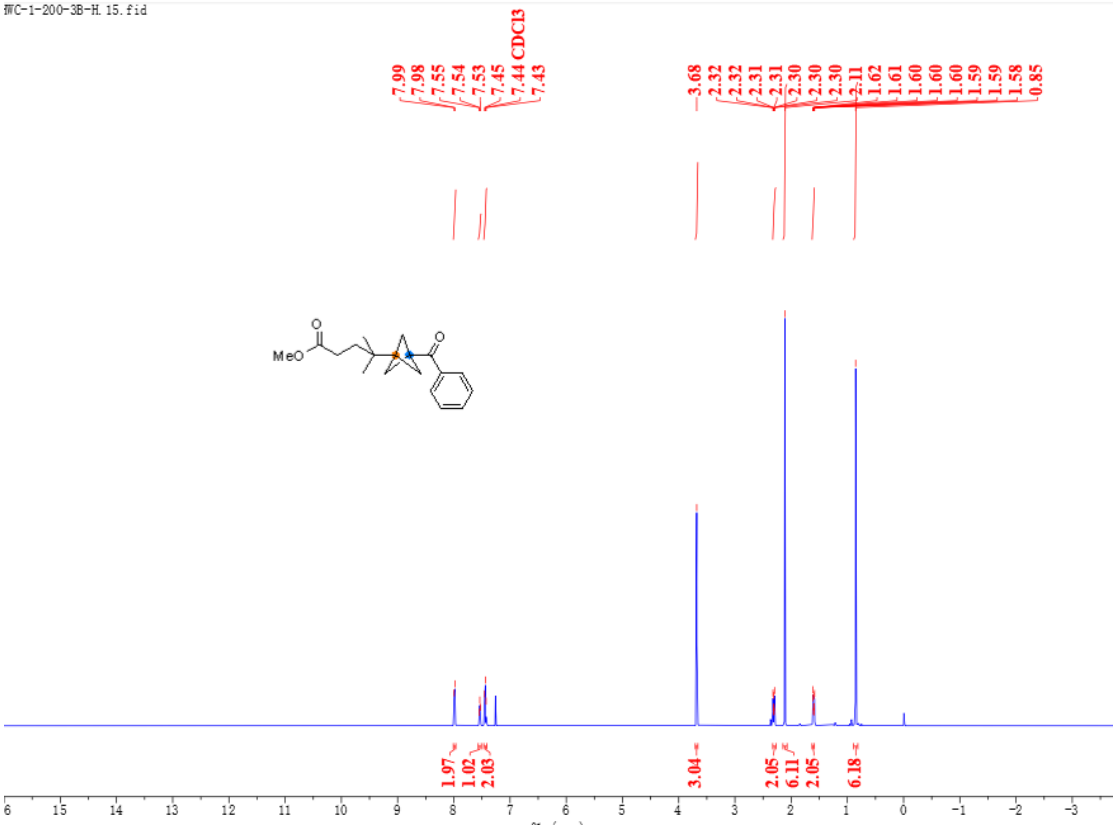
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentan-2-one 26



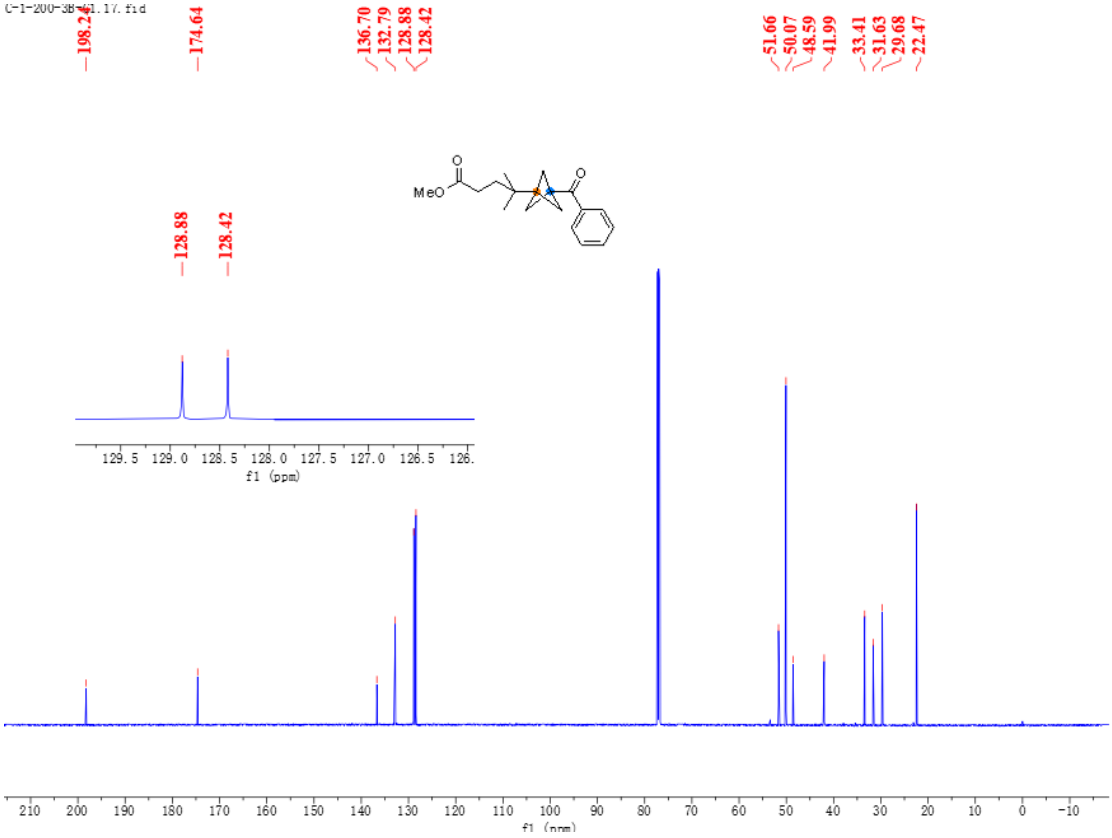
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentan-2-one 26



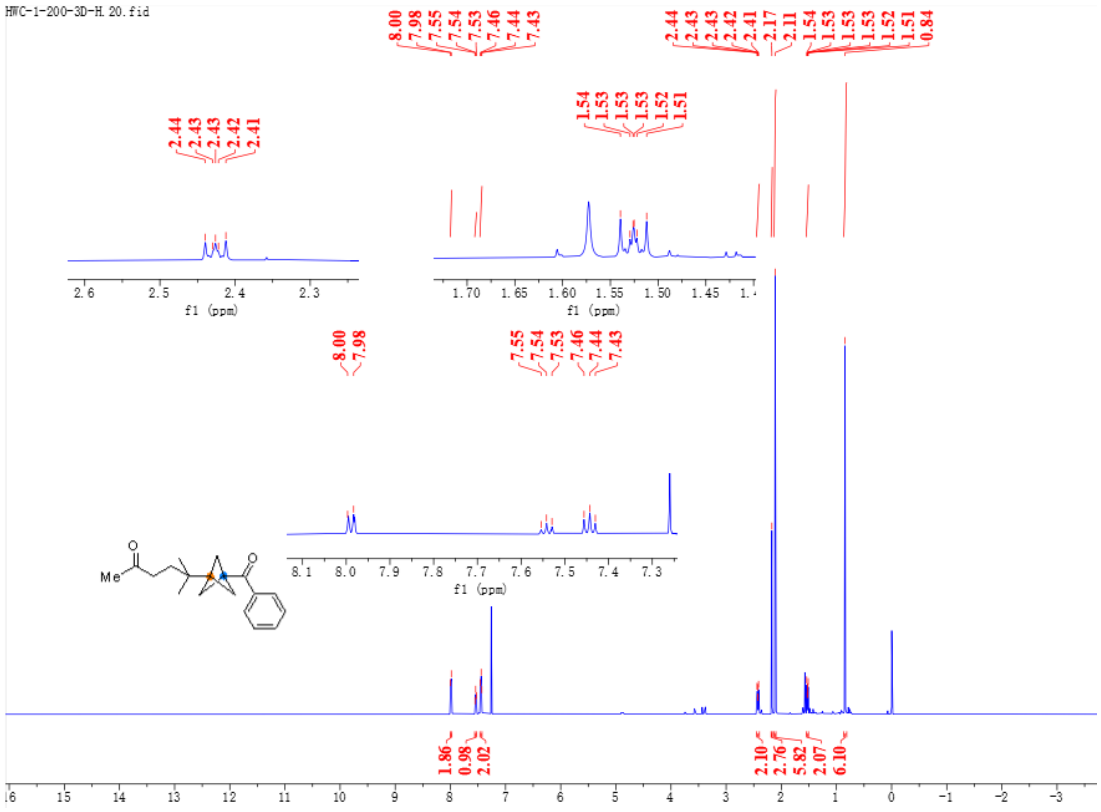
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
Methyl 4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentanoate 27



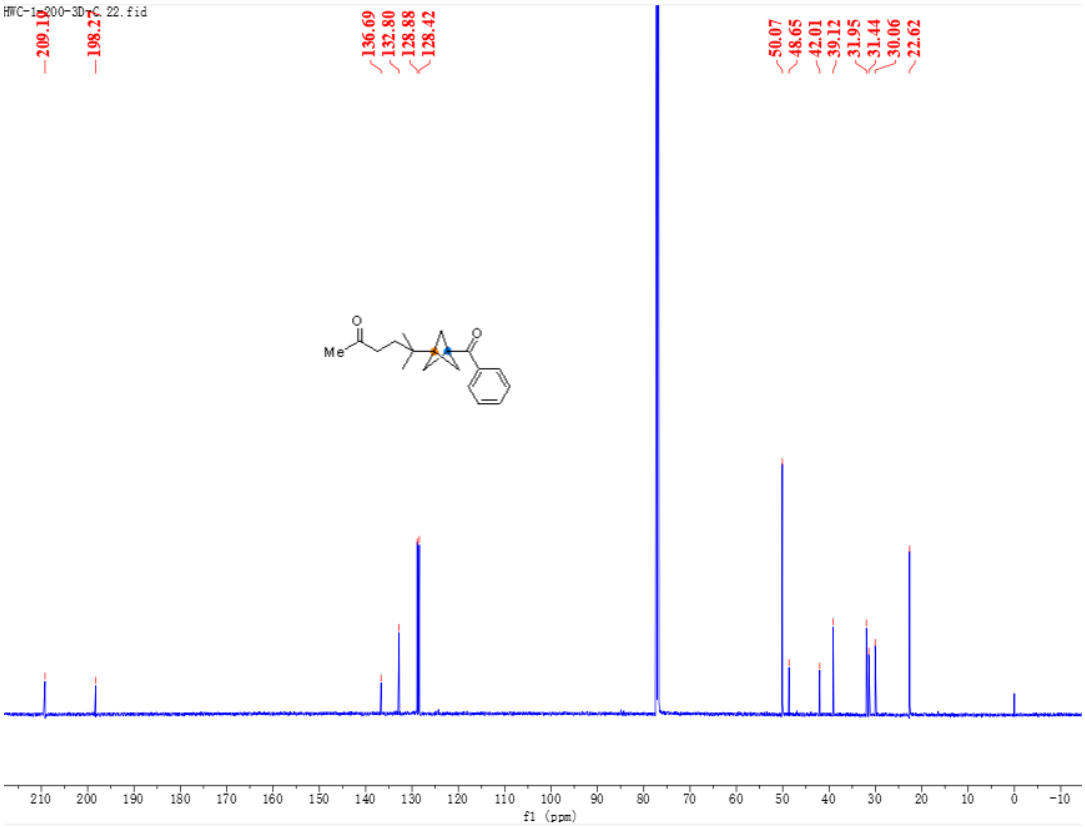
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
Methyl 4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentanoate 27



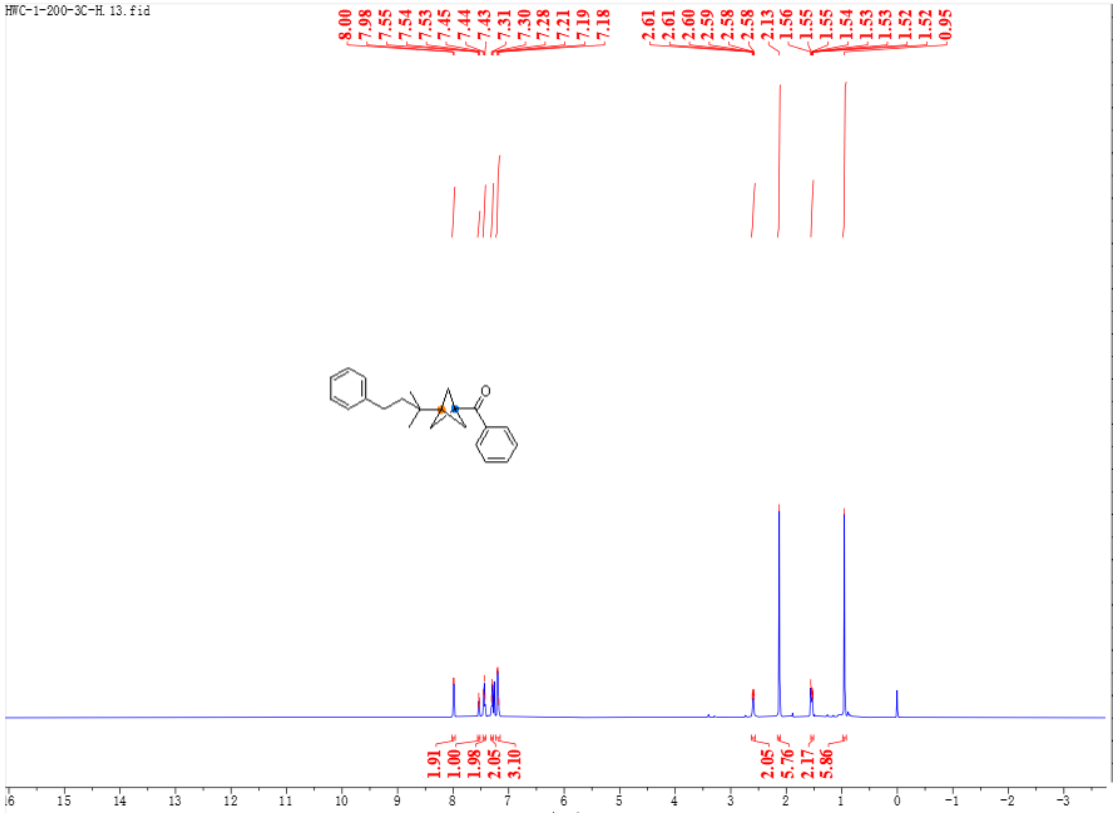
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
5-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-5-methylhexan-2-one 28



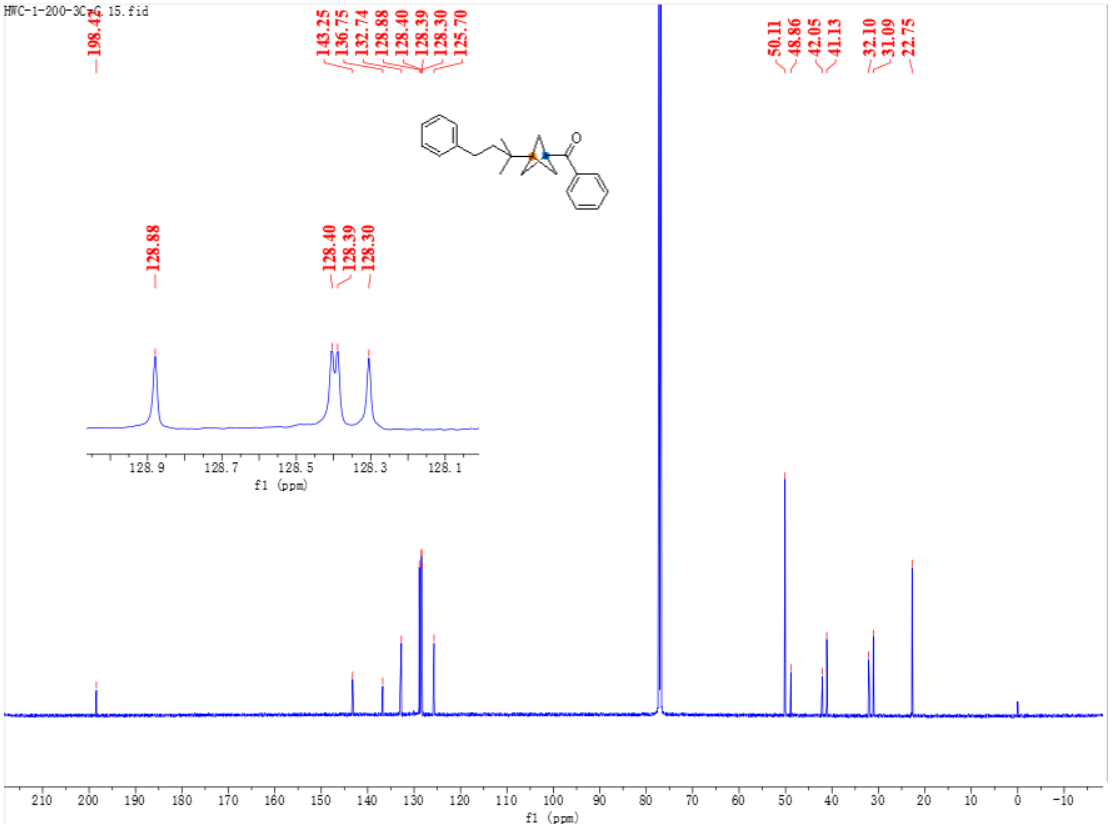
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
5-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-5-methylhexan-2-one 28



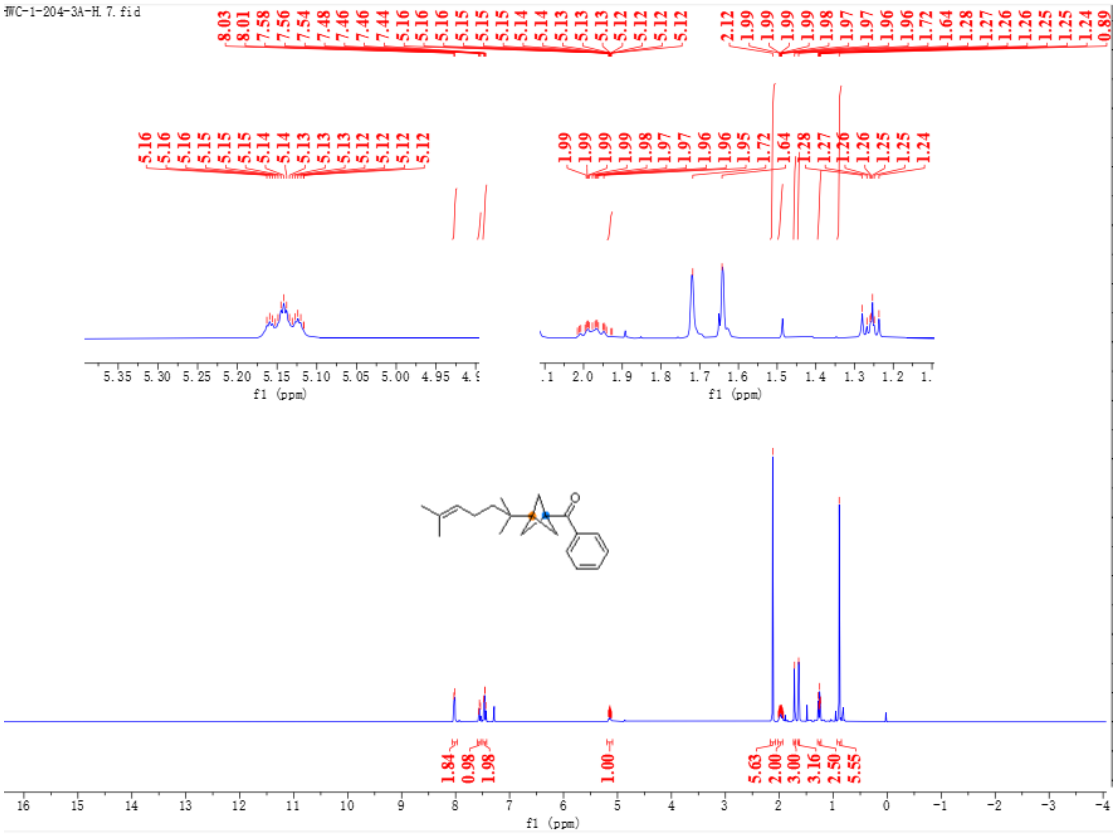
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(2-Methyl-4-phenylbutan-2-yl)bicyclo[1.1.1]pentan-yl)(phenyl)methanone 29



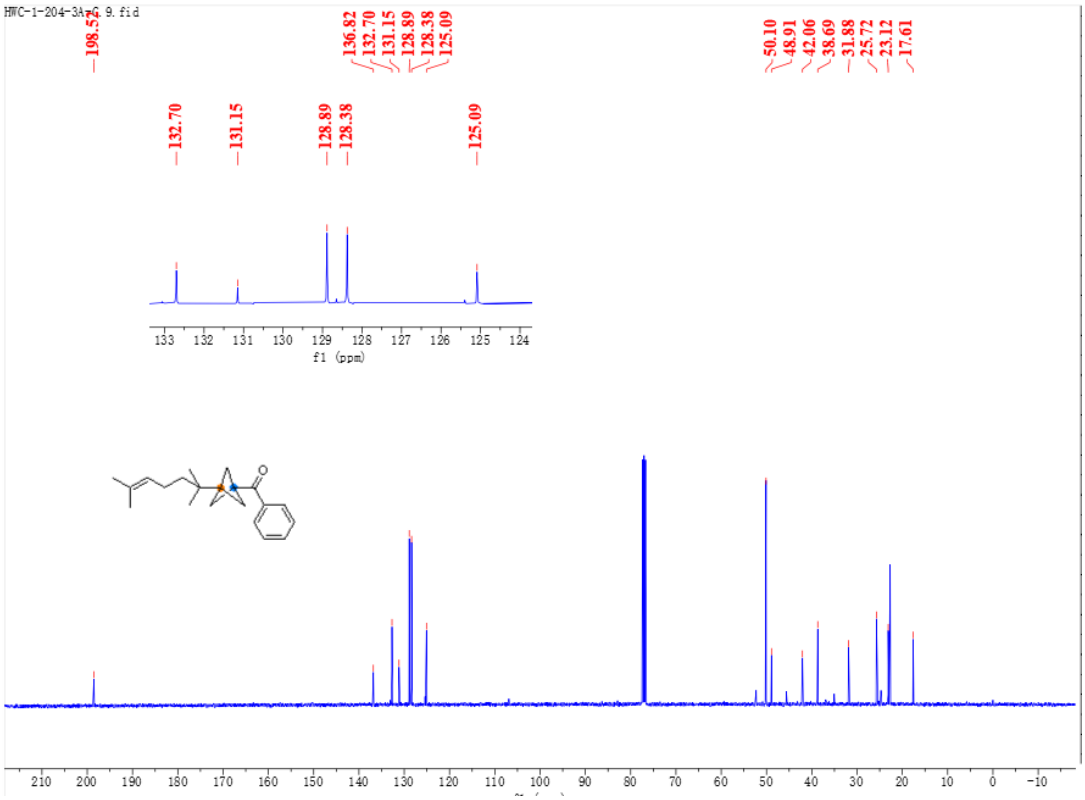
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(2-Methyl-4-phenylbutan-2-yl)bicyclo[1.1.1]pentan-yl)(phenyl)methanone 29



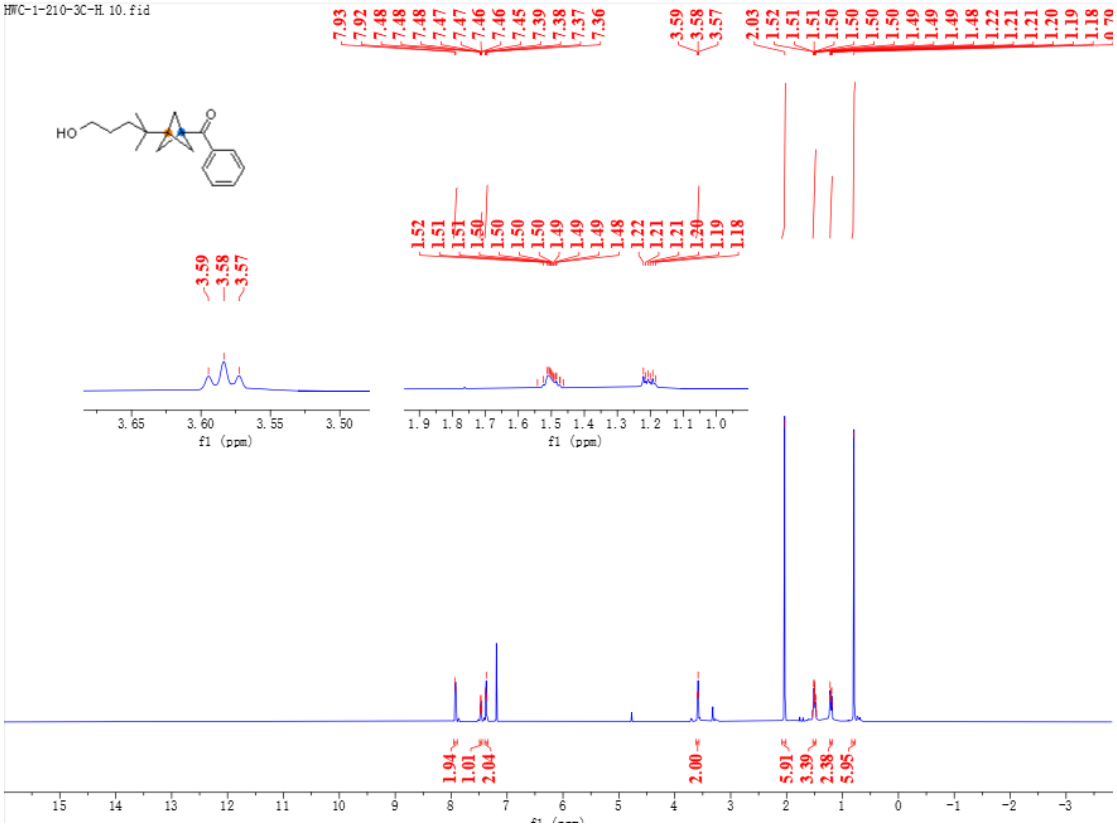
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(2,6-Dimethylhept-5-en-2-yl)bicyclo[1.1.1]pentan-yl)(phenyl)methanone 30



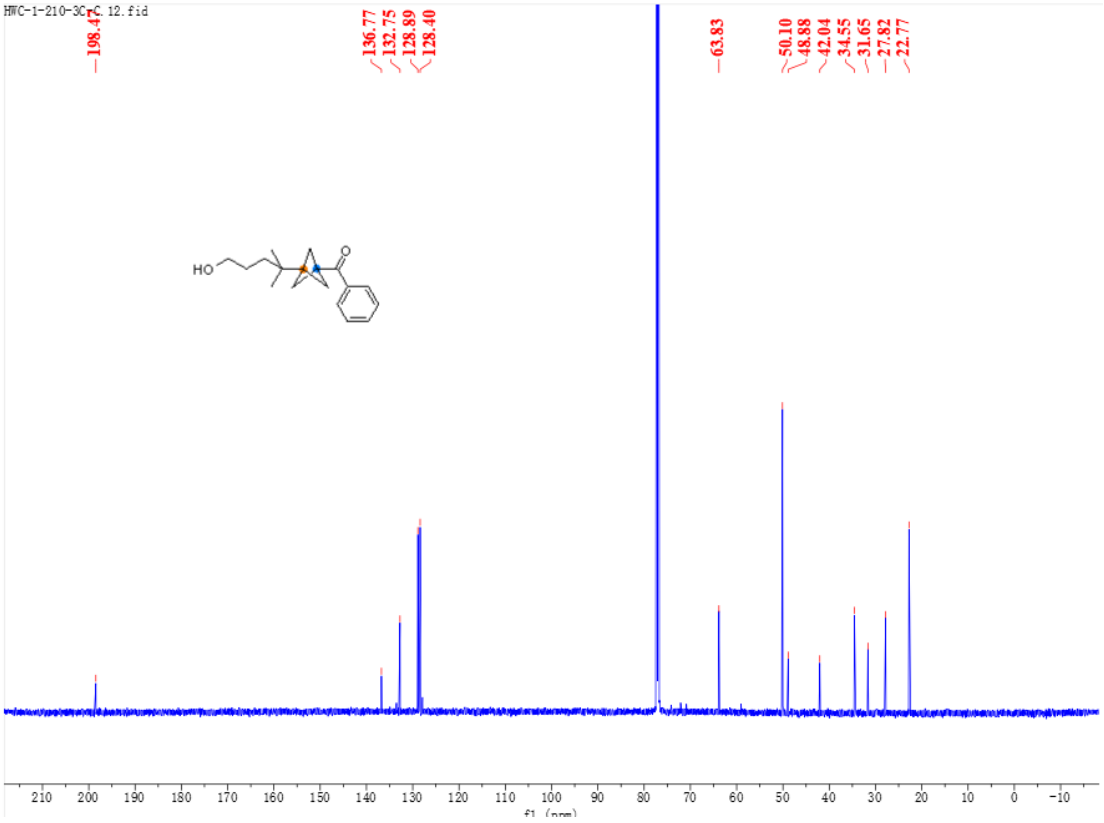
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(2,6-Dimethylhept-5-en-2-yl)bicyclo[1.1.1]pentan-yl)(phenyl)methanone 30



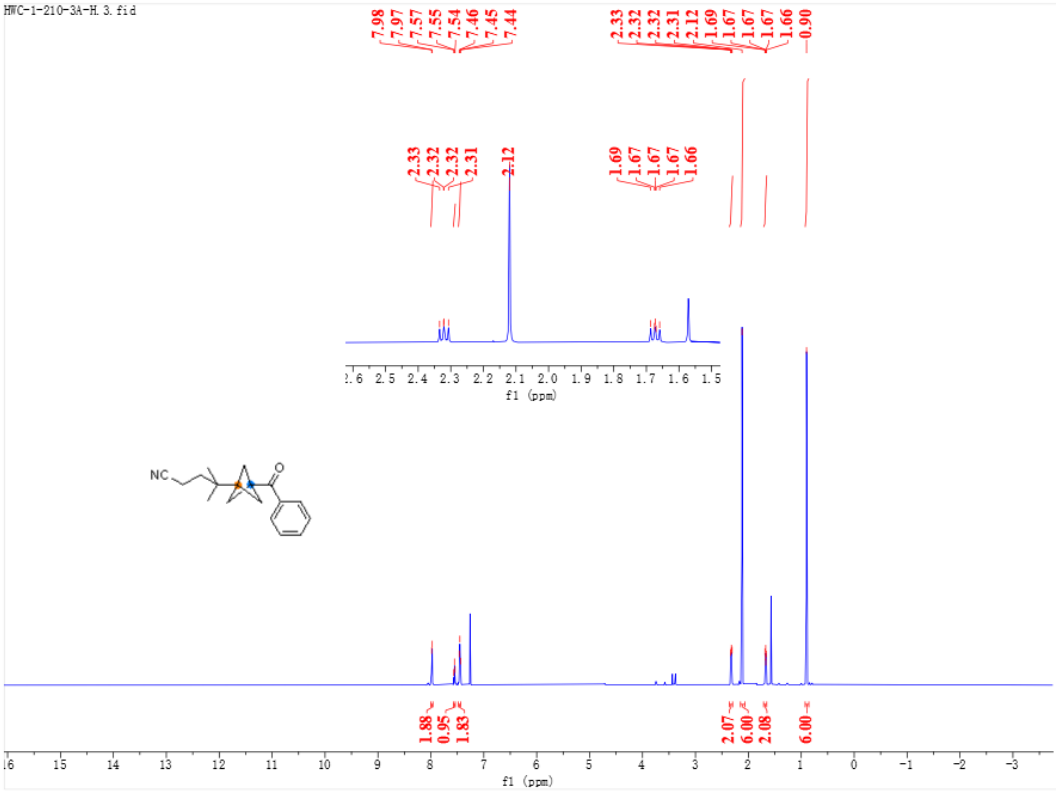
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(5-Hydroxy-2-methylpentan-yl)bicyclo[1.1.1]pentan-yl)(phenyl)methanone 31



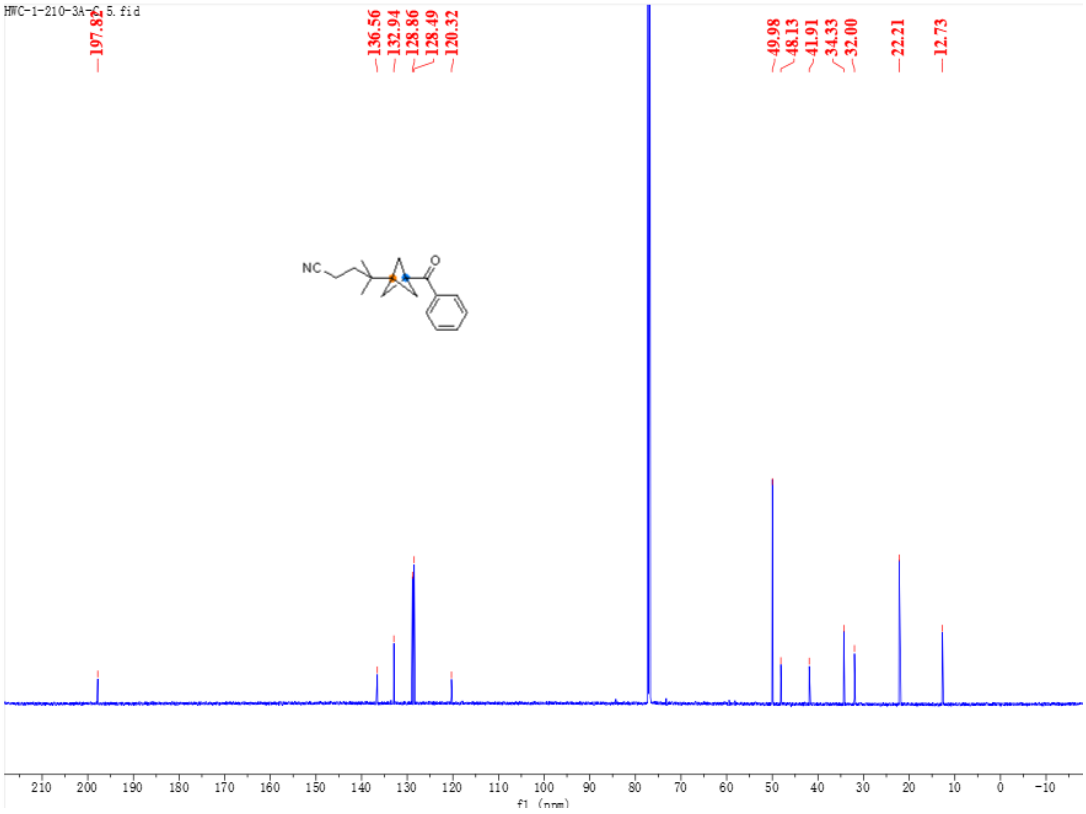
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(5-Hydroxy-2-methylpentan-yl)bicyclo[1.1.1]pentan-yl)(phenyl)methanone 31



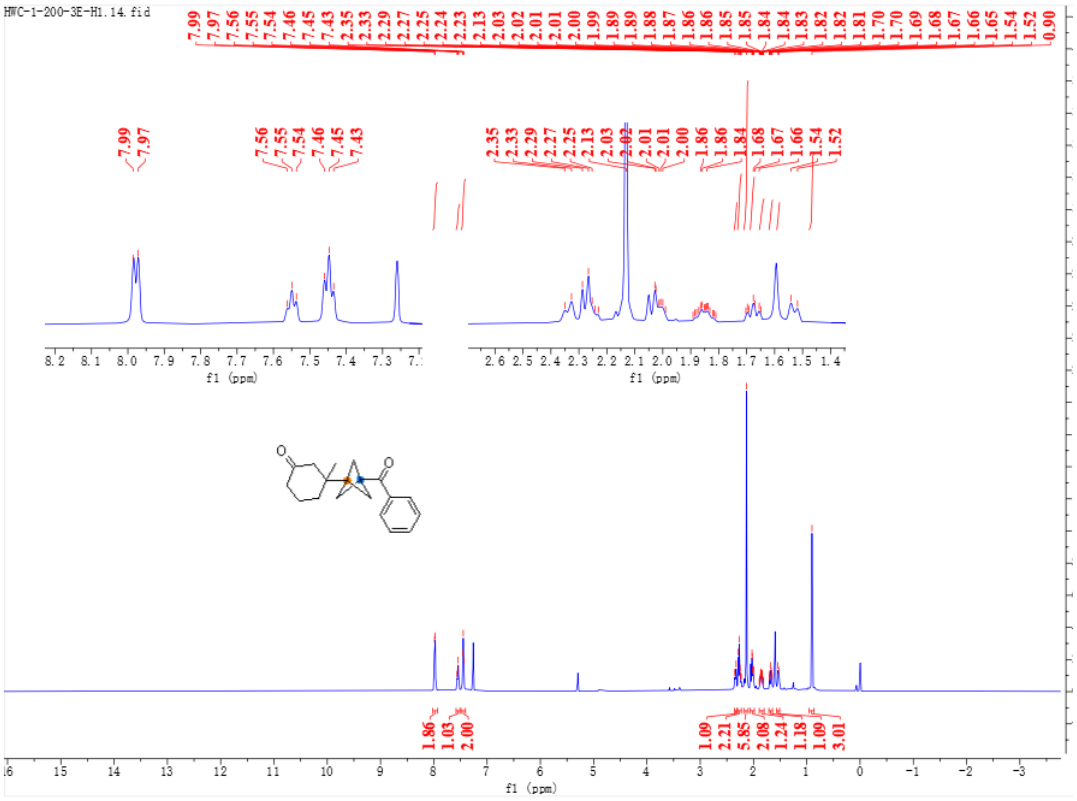
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentanenitrile 32



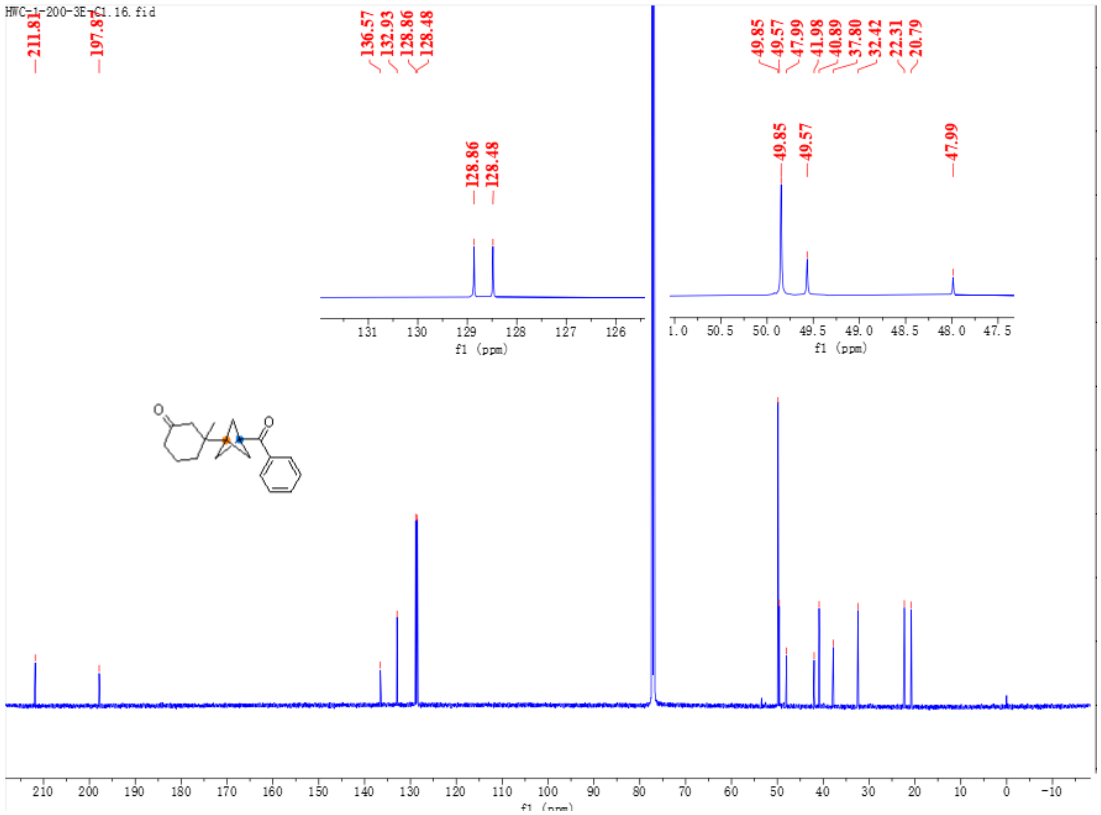
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpentanenitrile 32



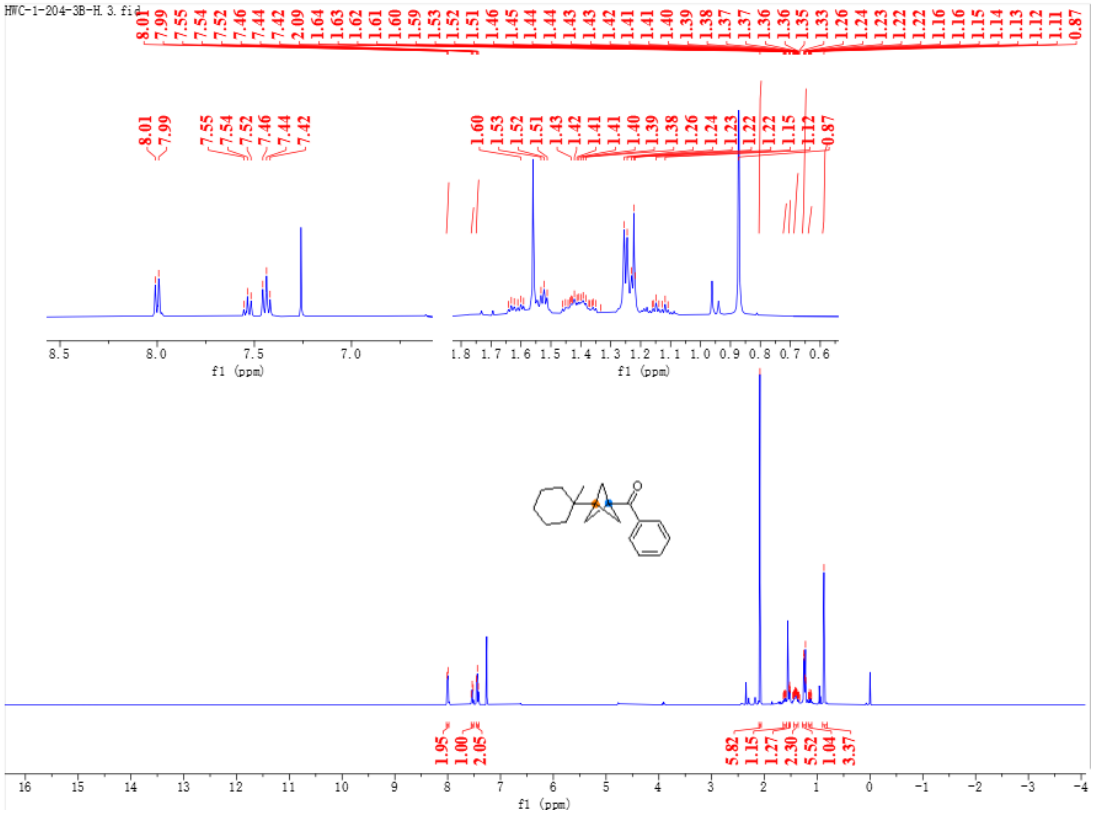
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
3-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-3-methylcyclohexan-1-one 33



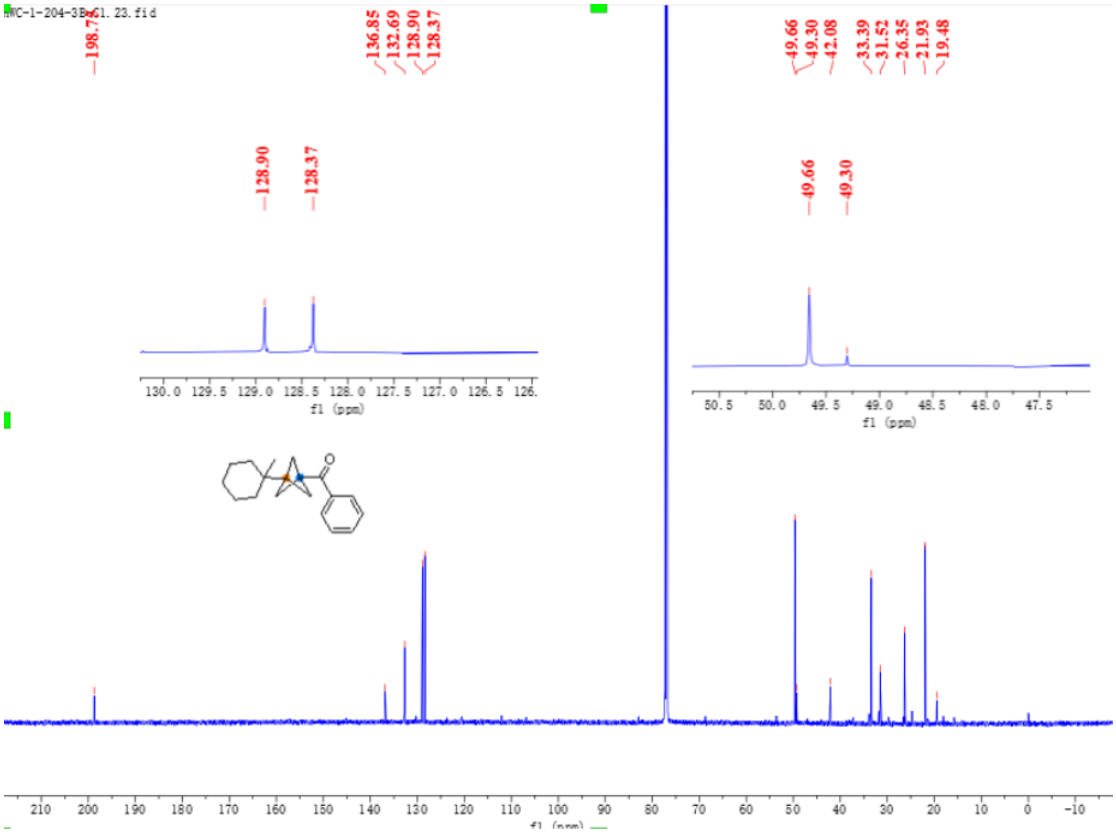
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
3-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-3-methylcyclohexan-1-one 33



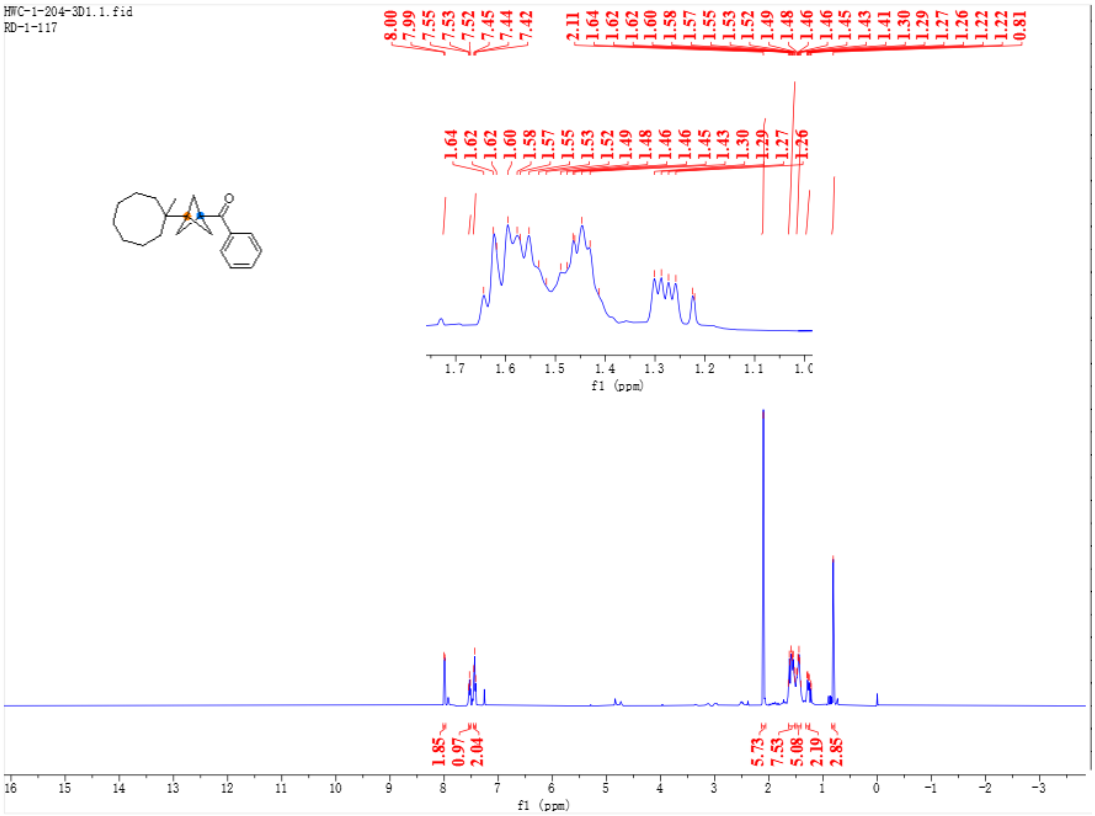
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(1-Methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 34



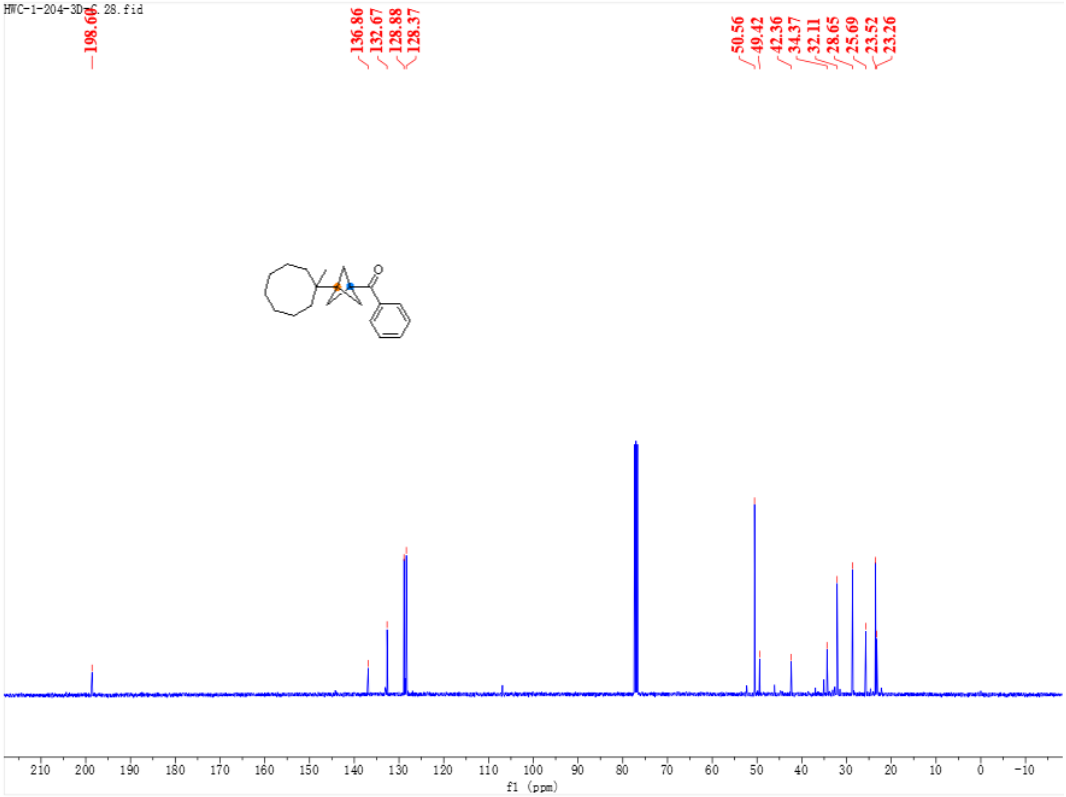
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(1-Methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 34



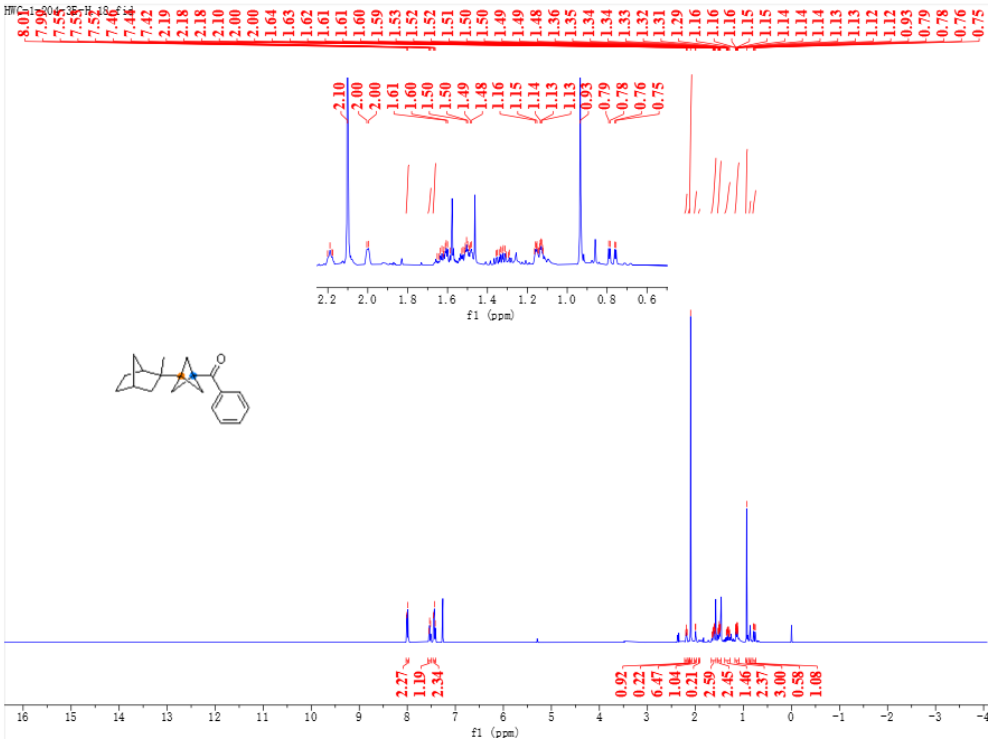
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(1-Methylcyclooctyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 35



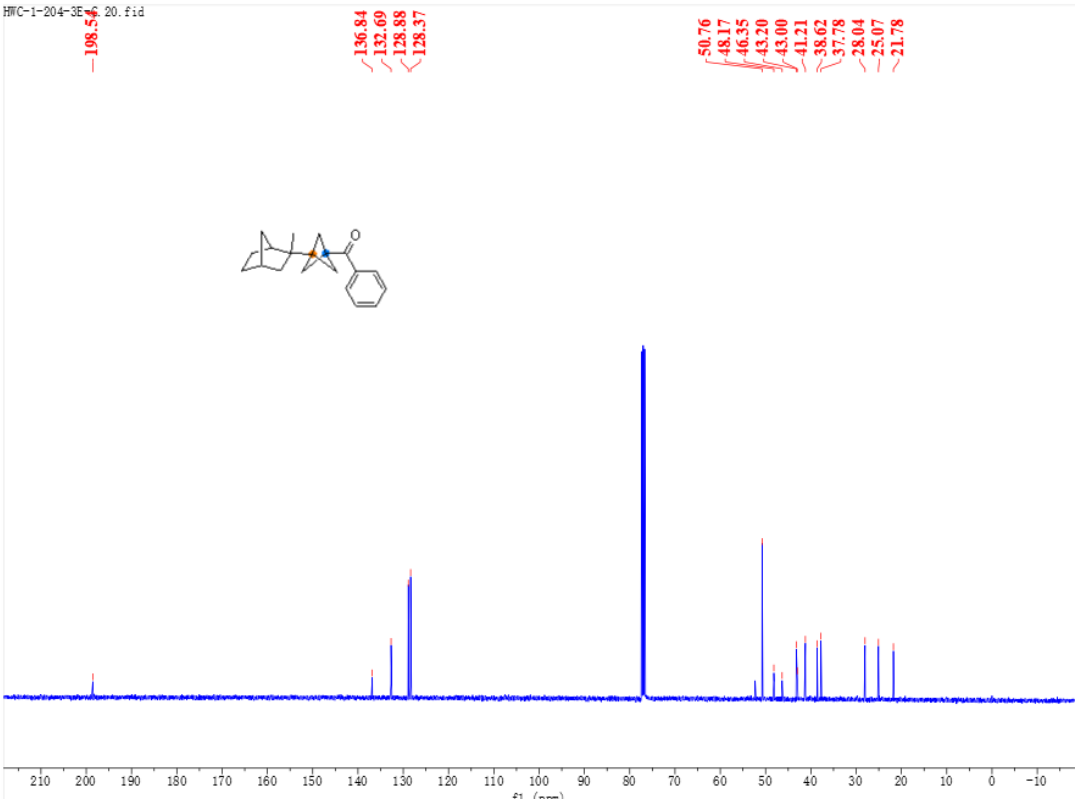
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(1-Methylcyclooctyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 35



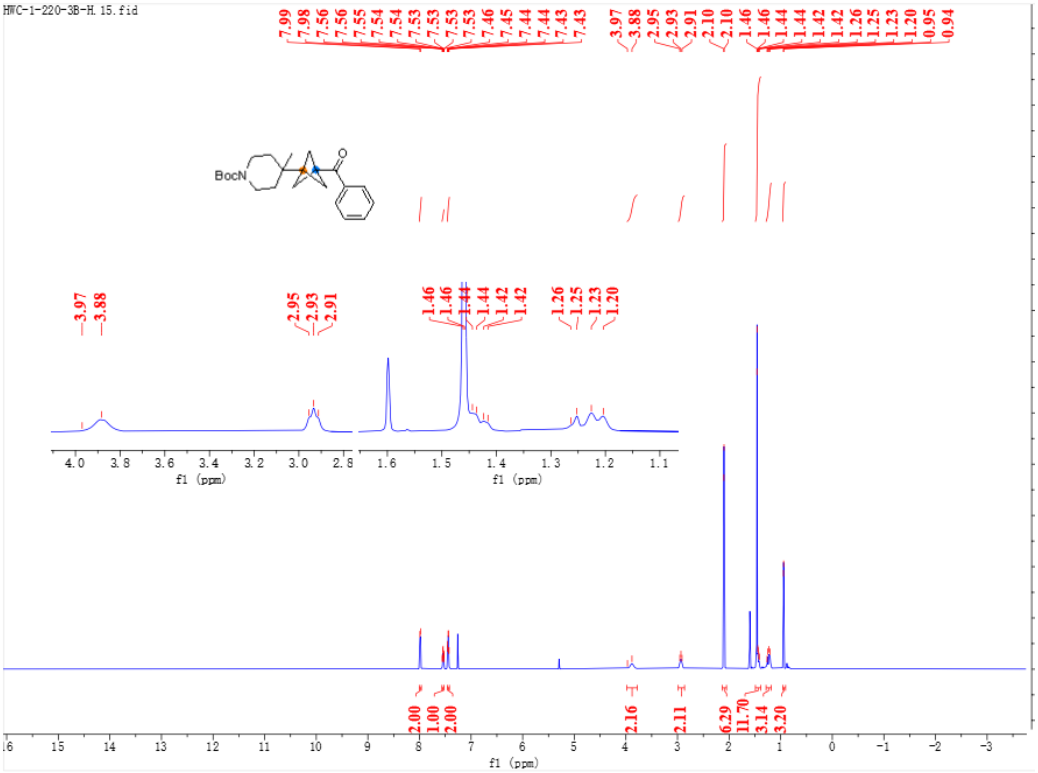
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 2-Methylbicyclo[2.2.1]heptan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 36



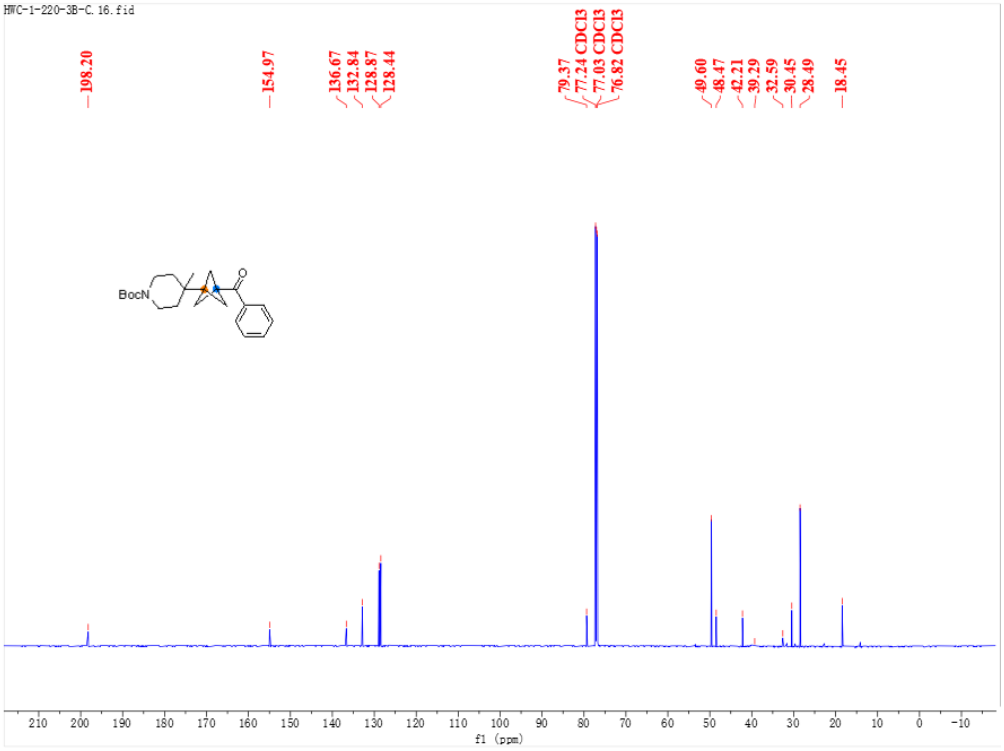
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 2-Methylbicyclo[2.2.1]heptan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 36



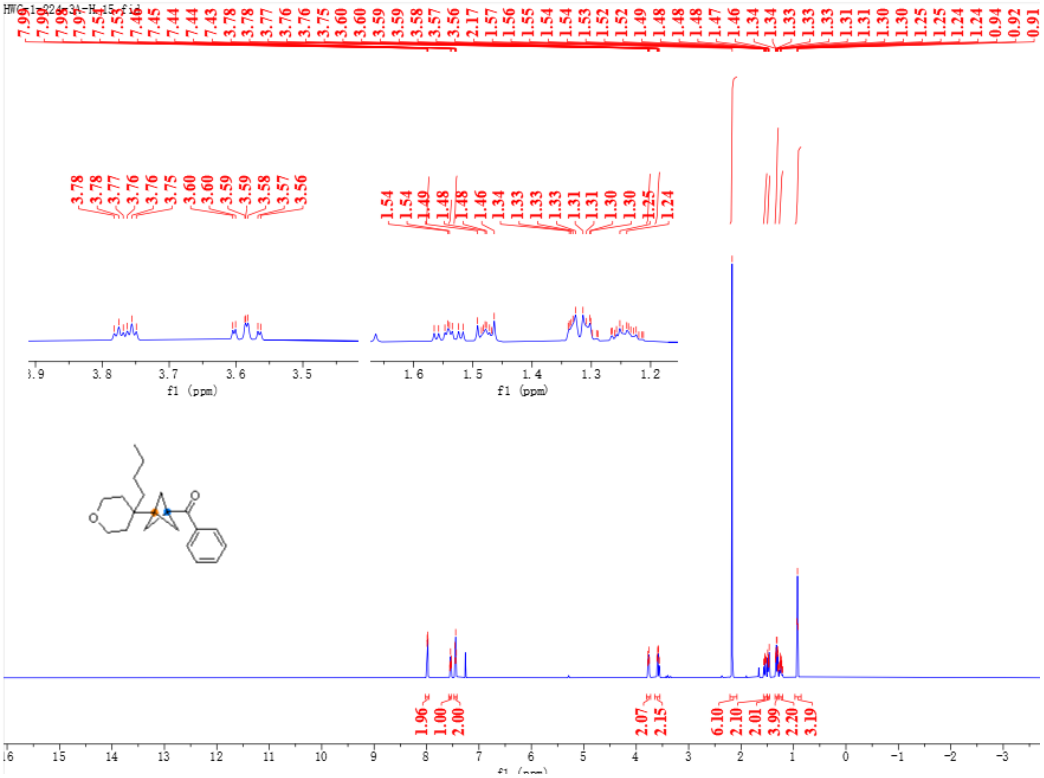
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *tert*-Butyl 4-(3-benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpiperidine-1-carboxylate 37



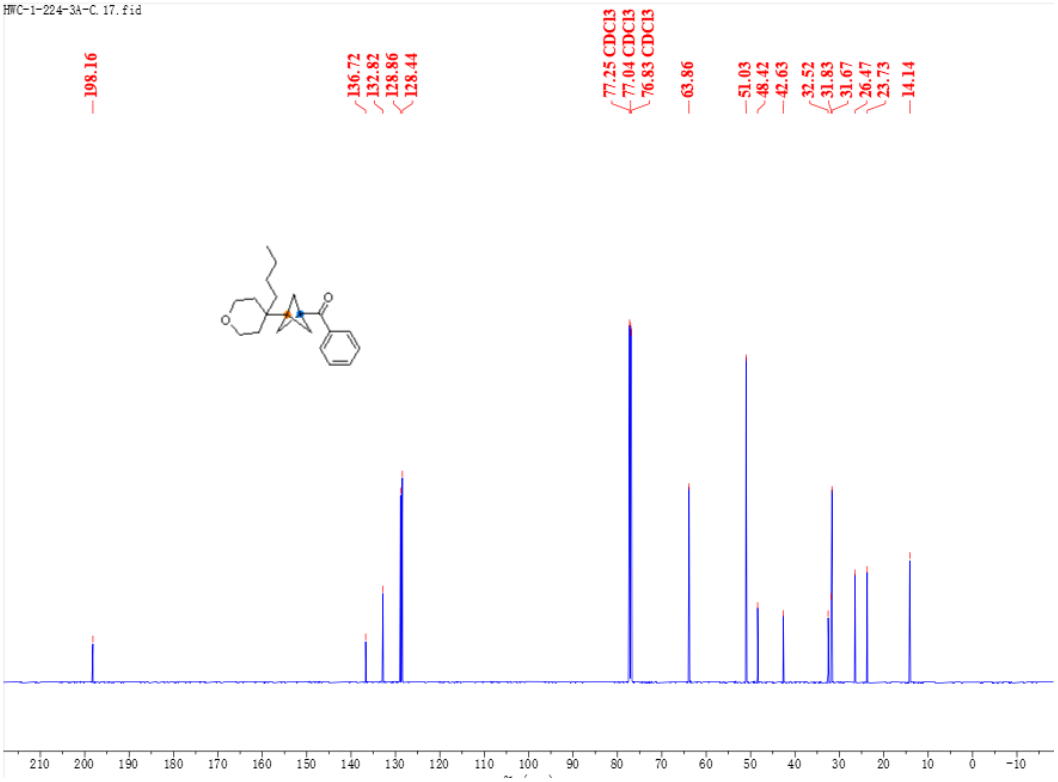
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of *tert*-Butyl 4-(3-benzoylbicyclo[1.1.1]pentan-1-yl)-4-methylpiperidine-1-carboxylate 37



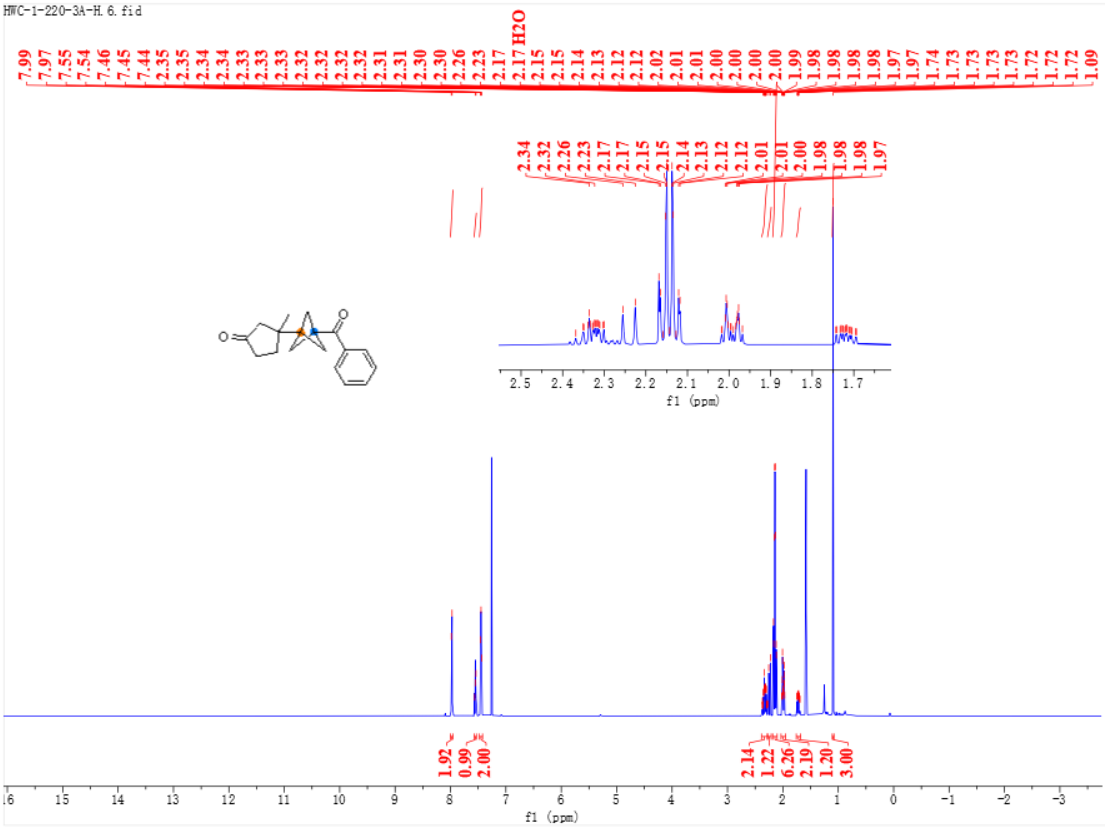
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(4-Butyltetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl) methanone 38



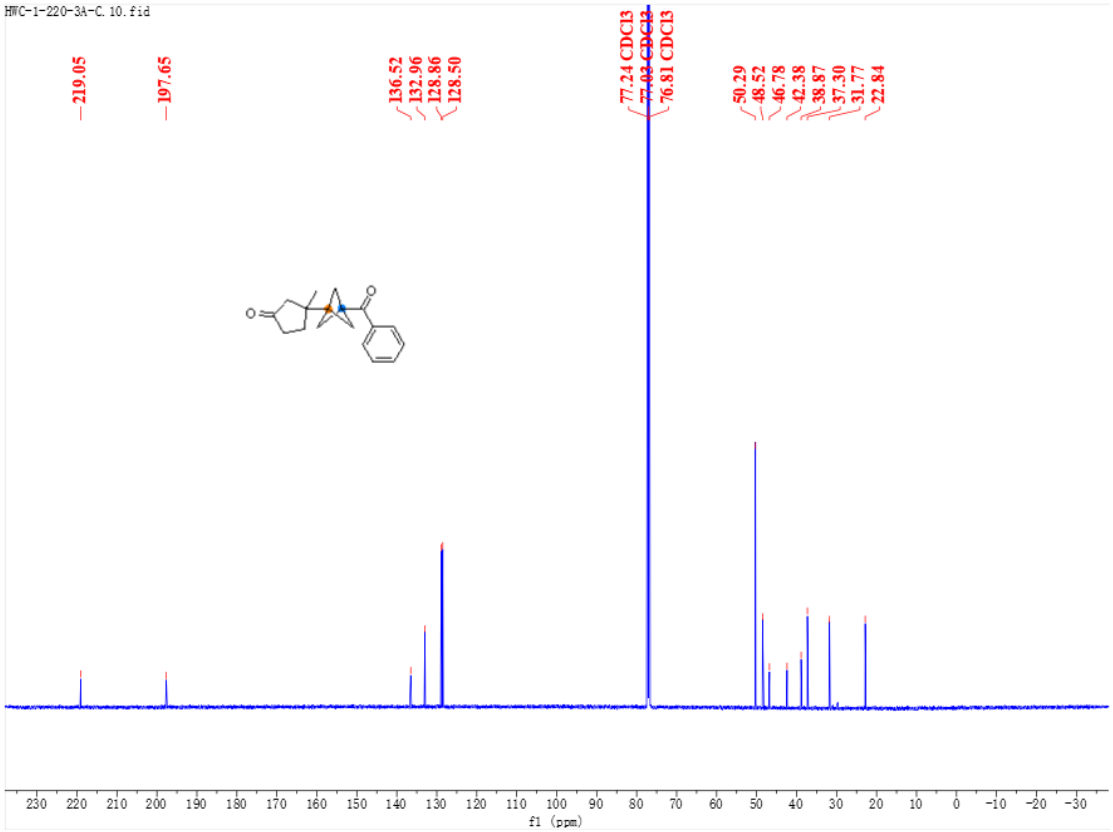
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(4-Butyltetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl) methanone 38



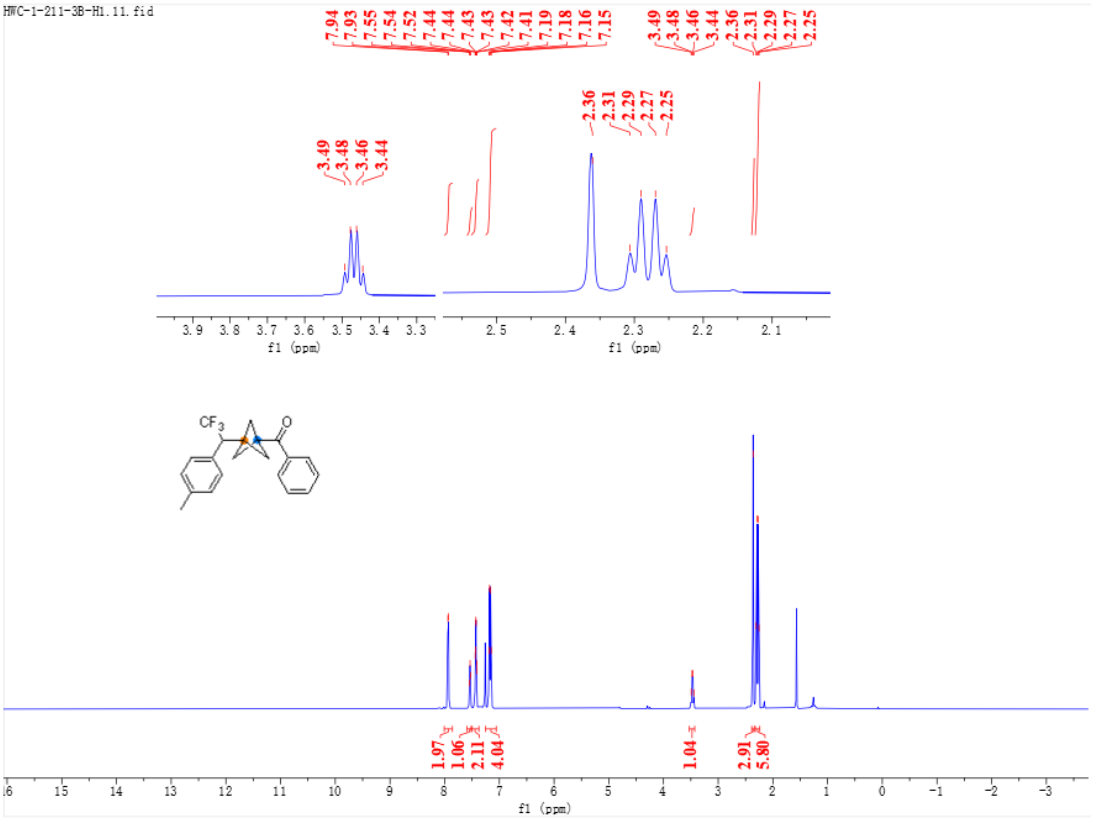
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-3-methylcyclopentan-1-one 39



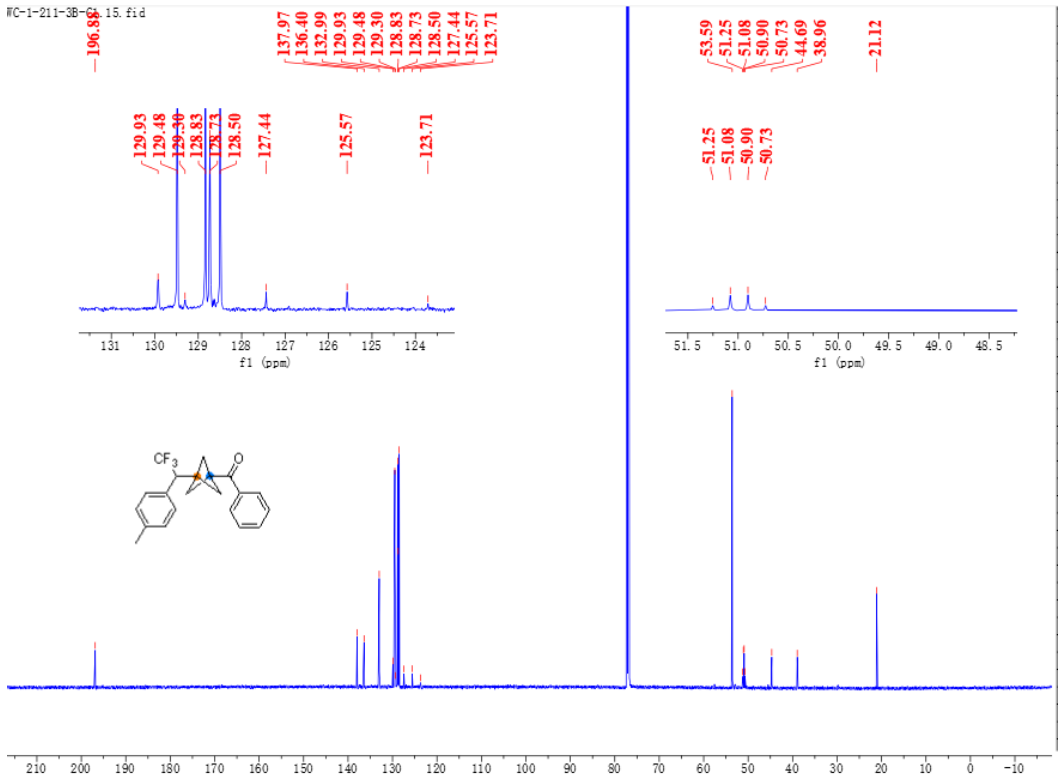
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-3-methylcyclopentan-1-one 39



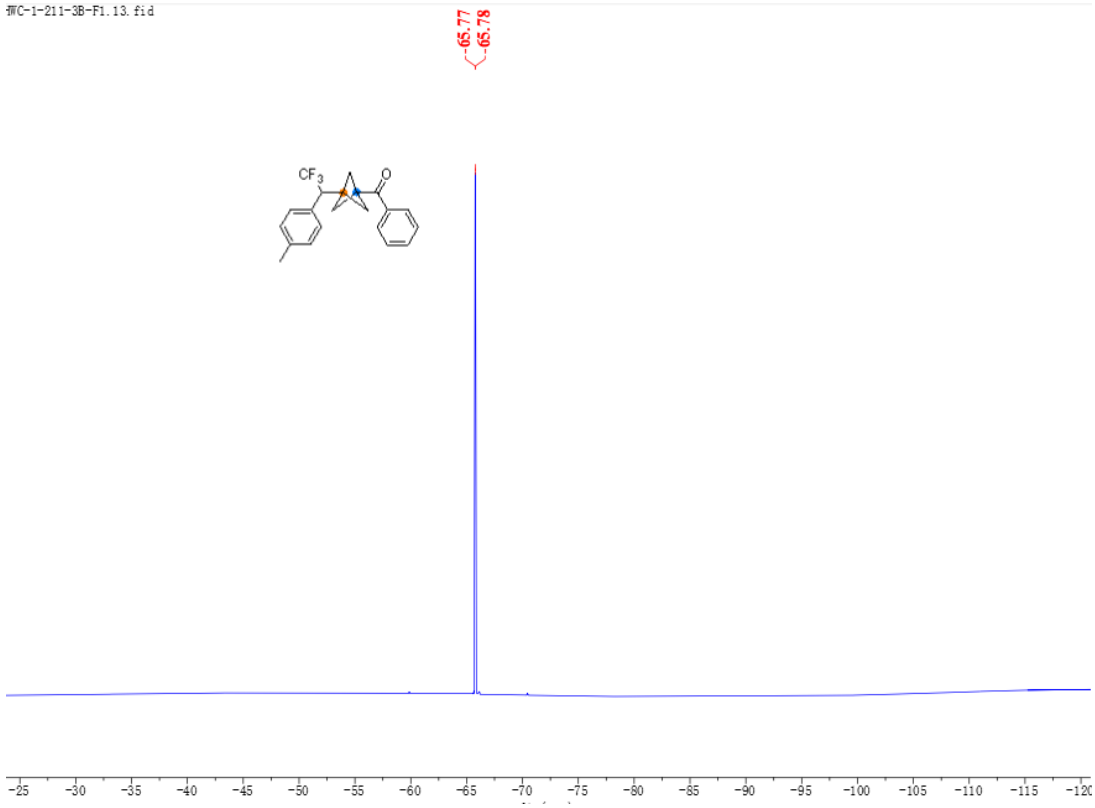
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Phenyl(3-(2,2,2-trifluoro-1-(*p*-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl)methanone 40



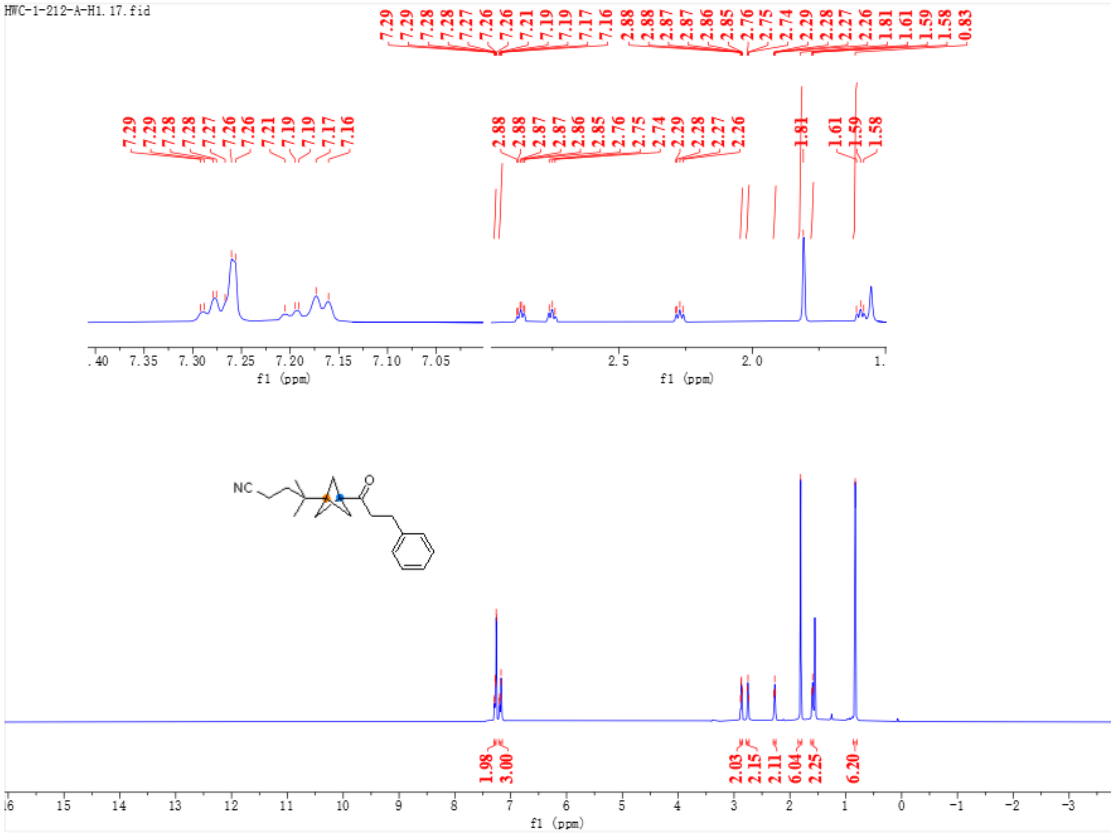
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of Phenyl(3-(2,2,2-trifluoro-1-(*p*-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl)methanone 40



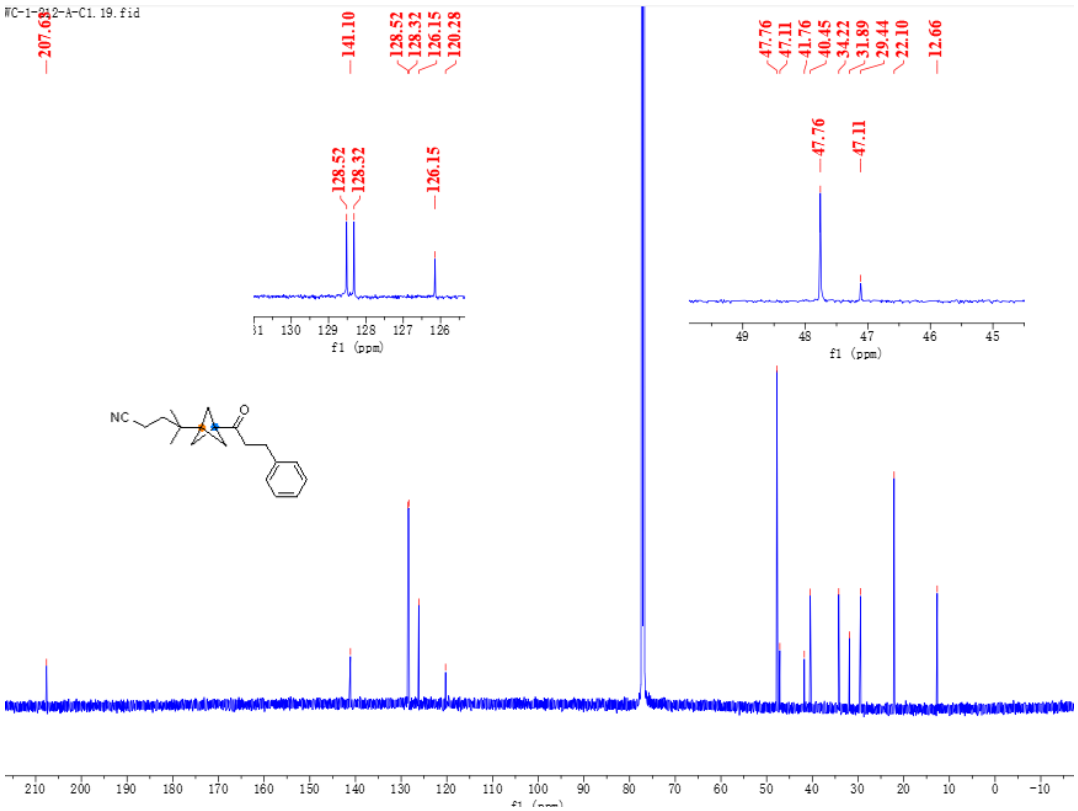
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of Phenyl(3-(2,2,2-trifluoro-1-(*p*-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl)methanone 40



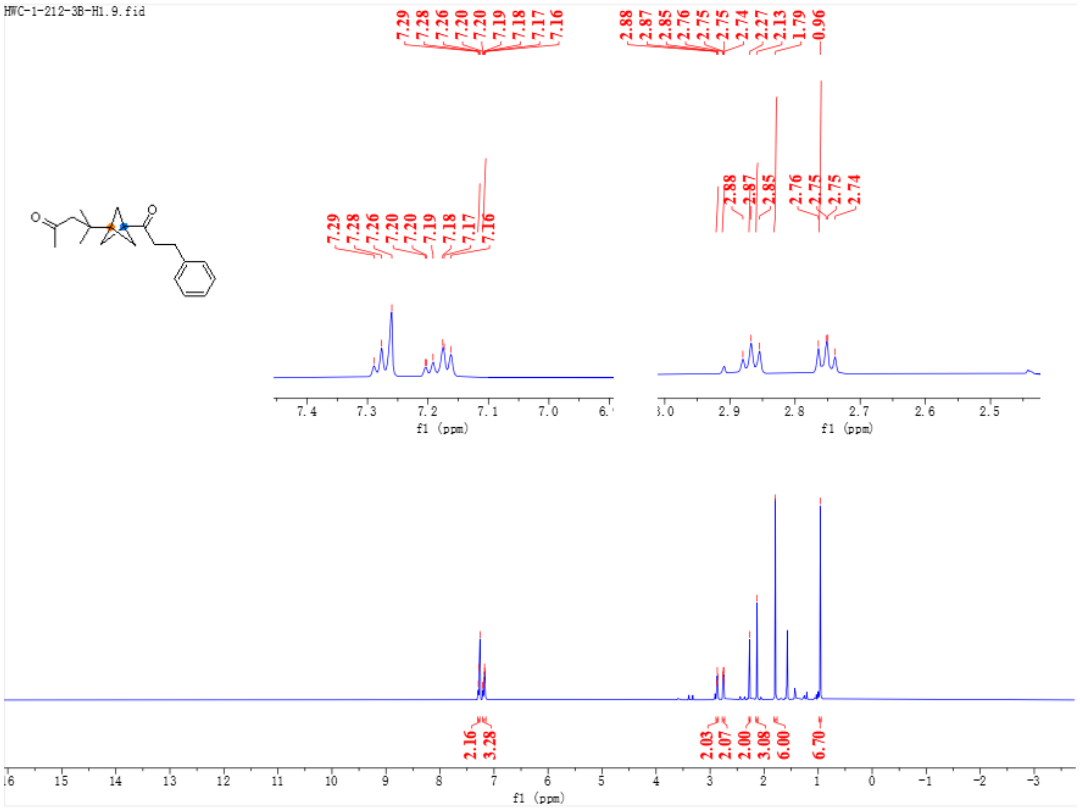
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-Methyl-4-(3-(3-phenylpropanoyl)bicyclo[1.1.1]pentan-1-yl)pentanenitrile 41



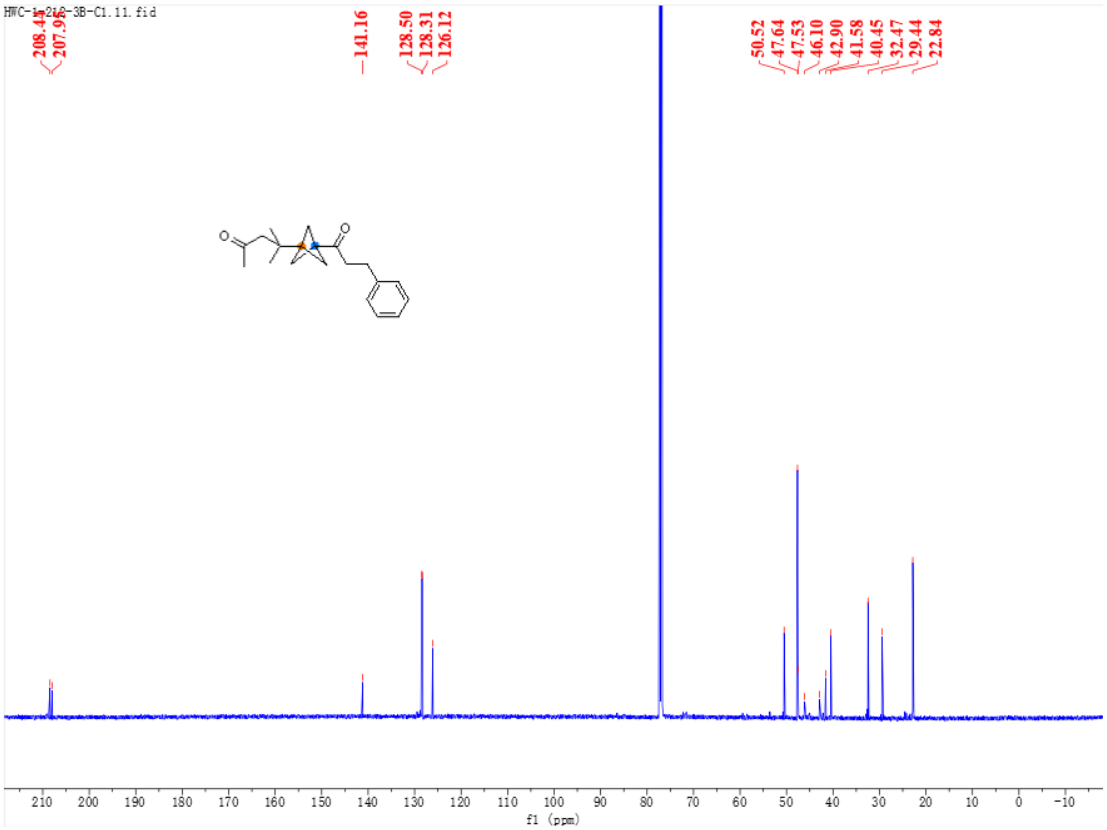
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-Methyl-4-(3-(3-phenylpropanoyl)bicyclo[1.1.1]pentan-1-yl)pentanenitrile 41



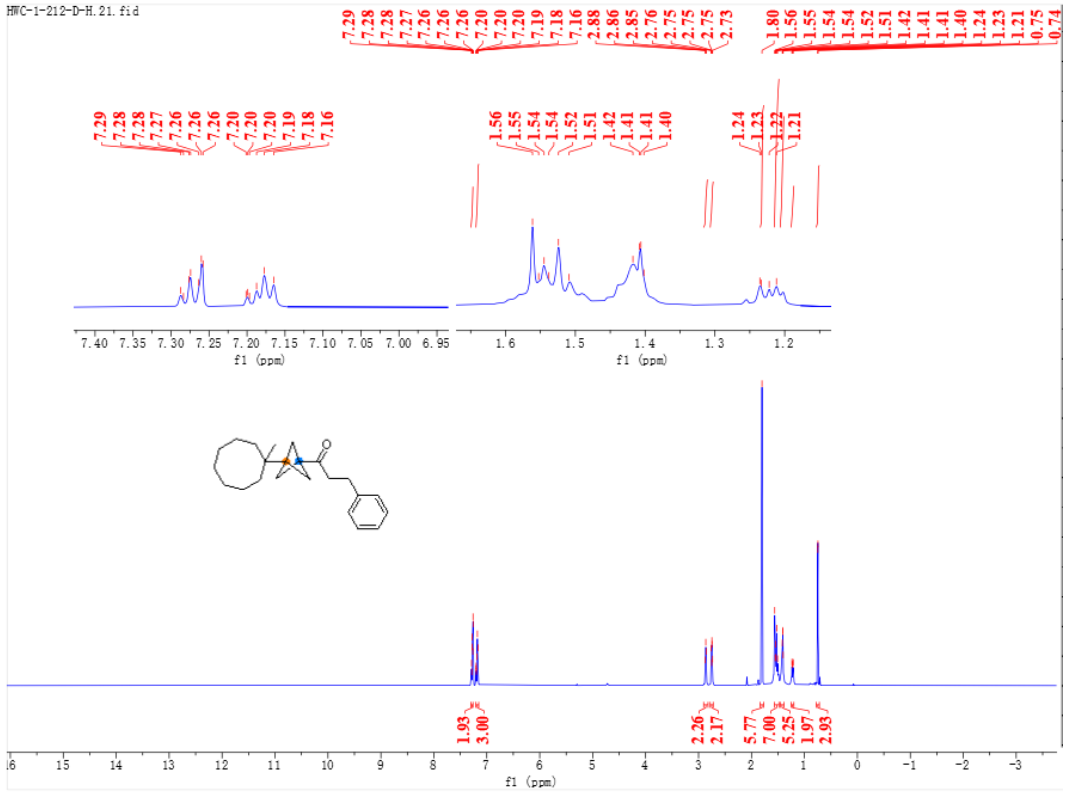
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-Methyl-4-(3-(3-phenylpropanoyl)bicyclo[1.1.1]pentan-1-yl)pentan-2-one 42



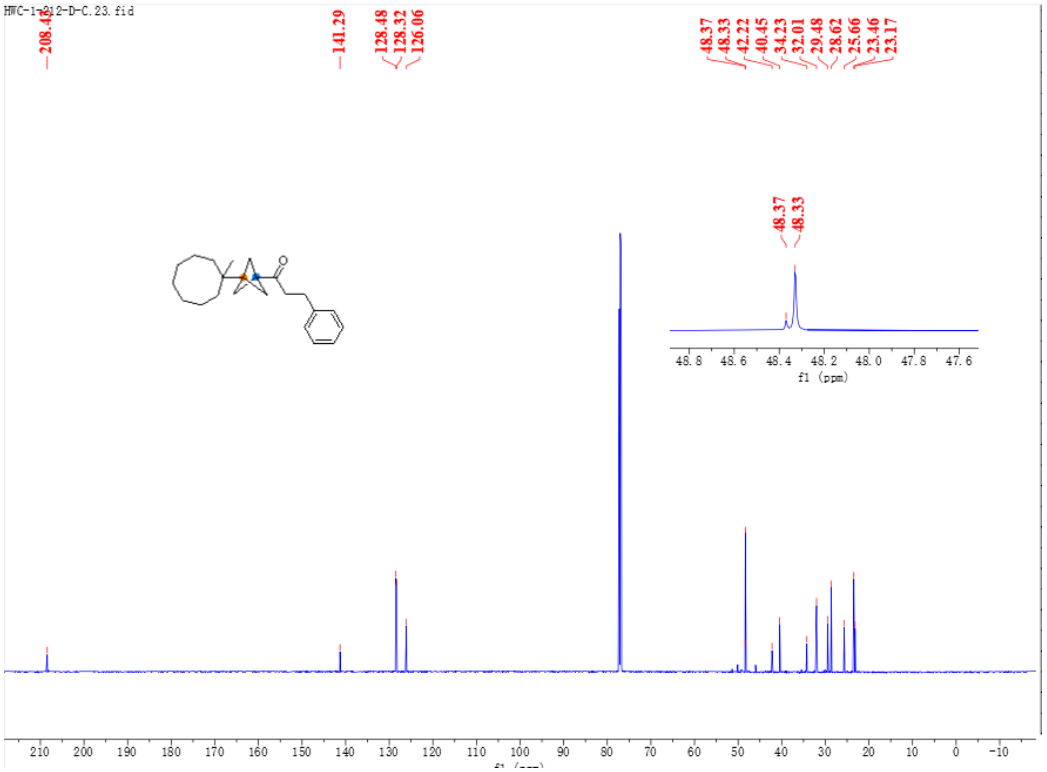
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-Methyl-4-(3-(3-phenylpropanoyl)bicyclo[1.1.1]pentan-1-yl)pentan-2-one 42



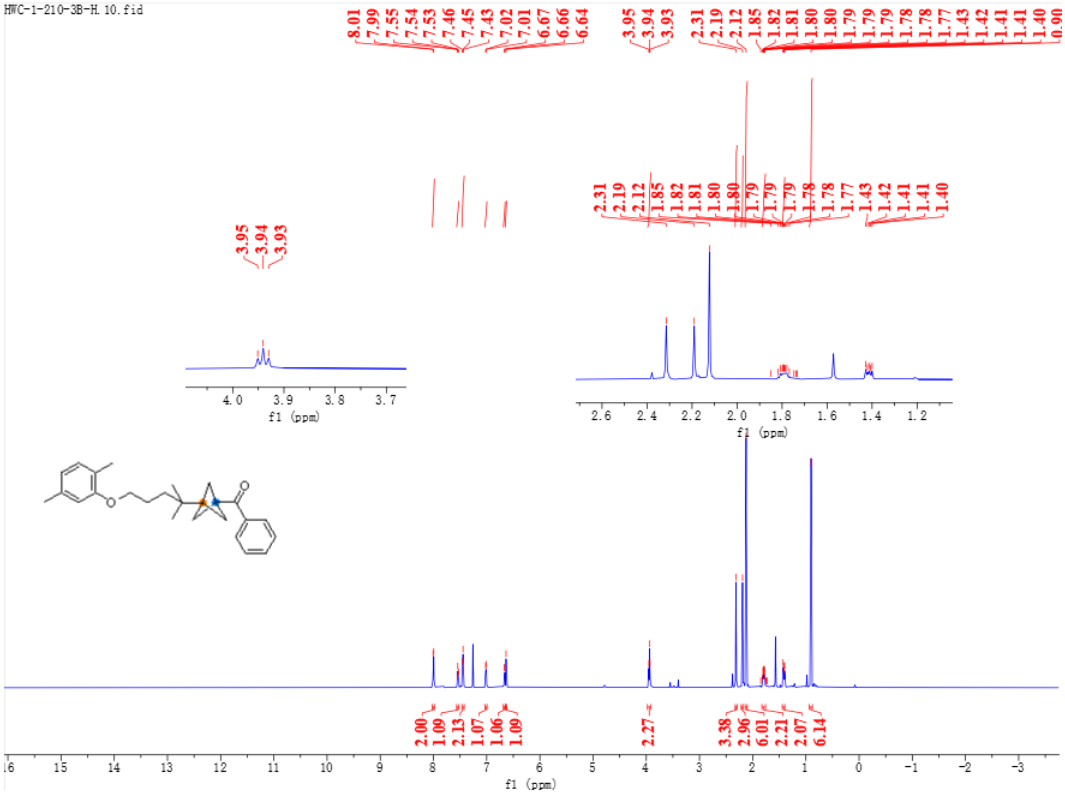
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1-(3-(1-Methylcyclooctyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 43



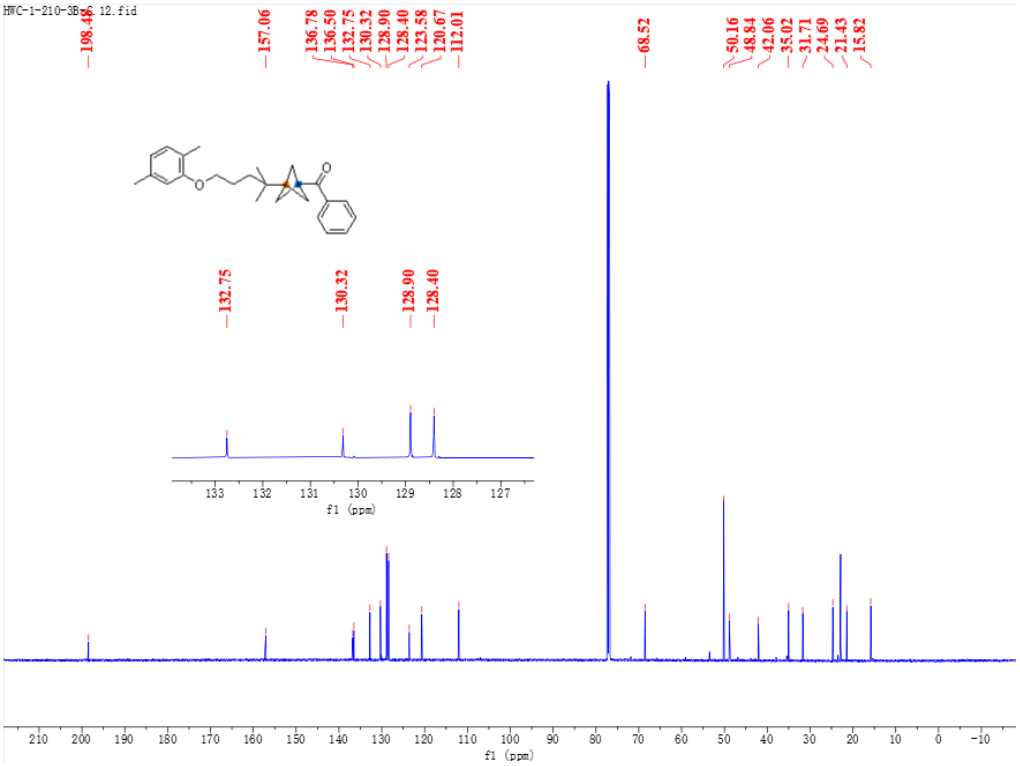
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 1-(3-(1-Methylcyclooctyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 43



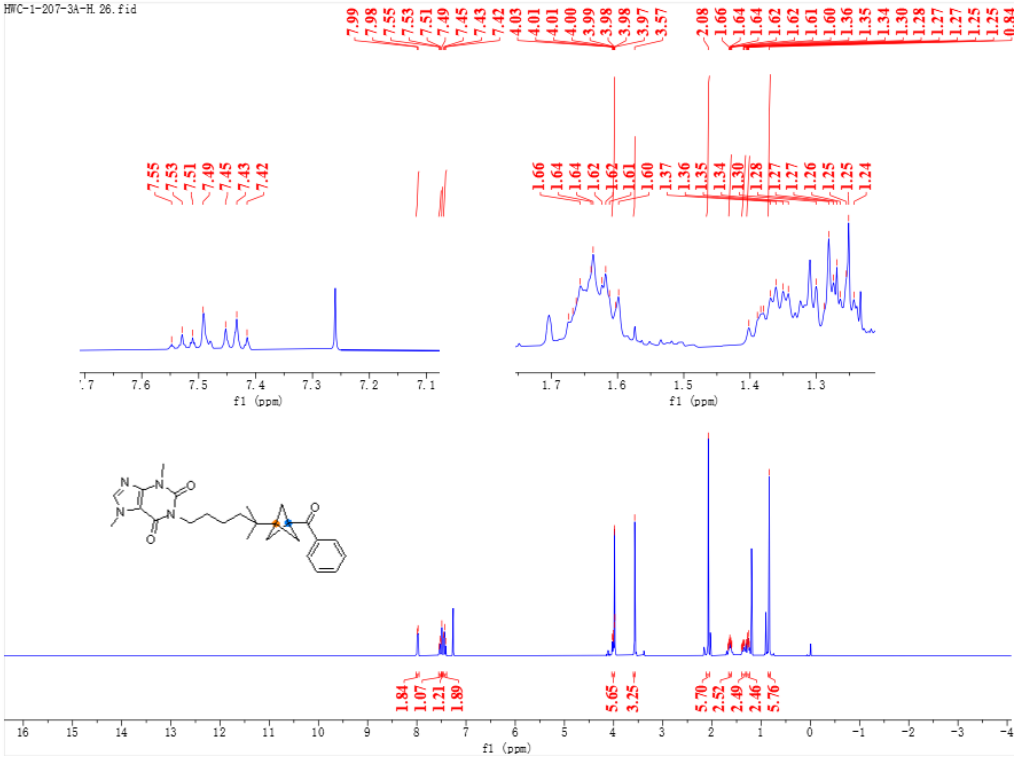
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 44



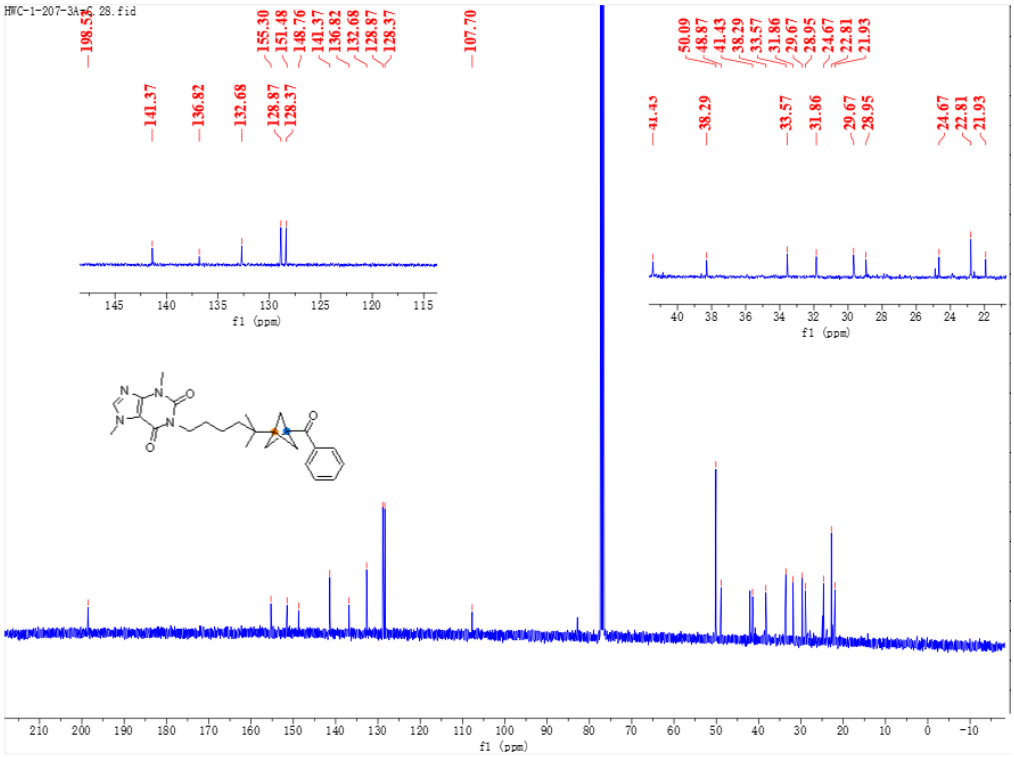
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanone 44



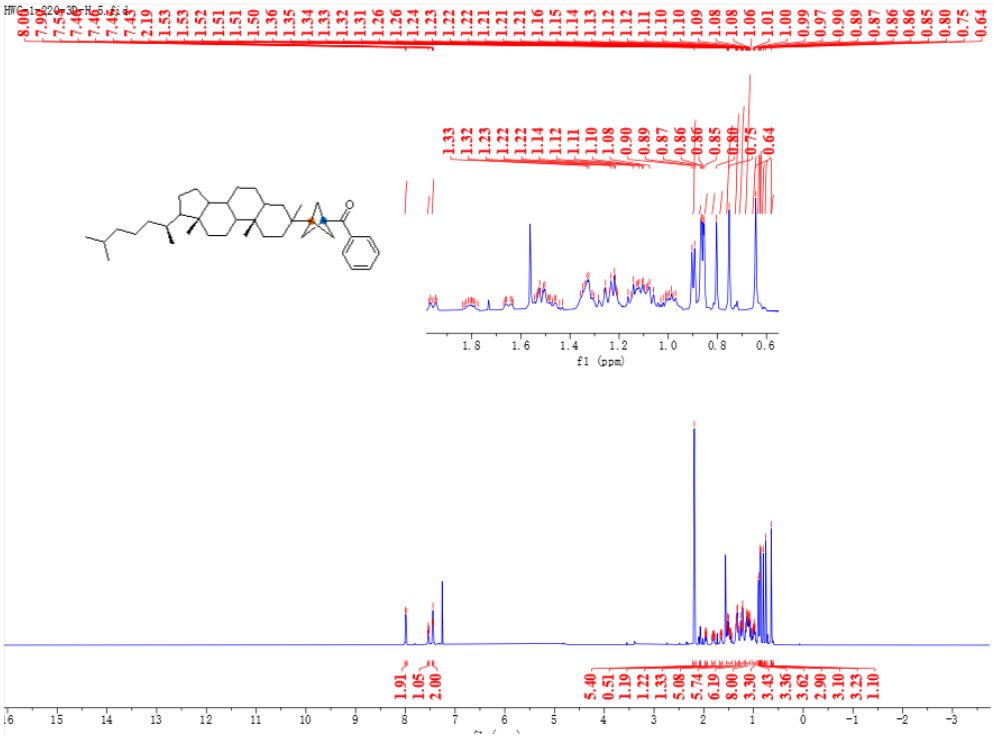
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1-(5-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-5-methylhexyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione 45



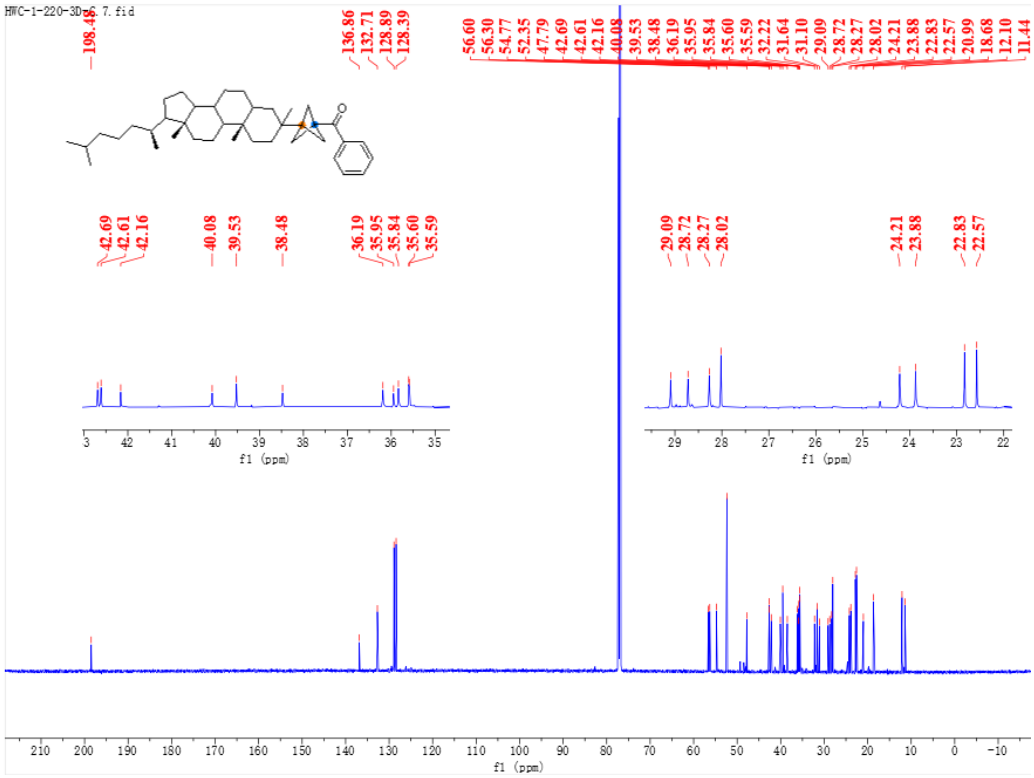
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 1-(5-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)-5-methylhexyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione 45



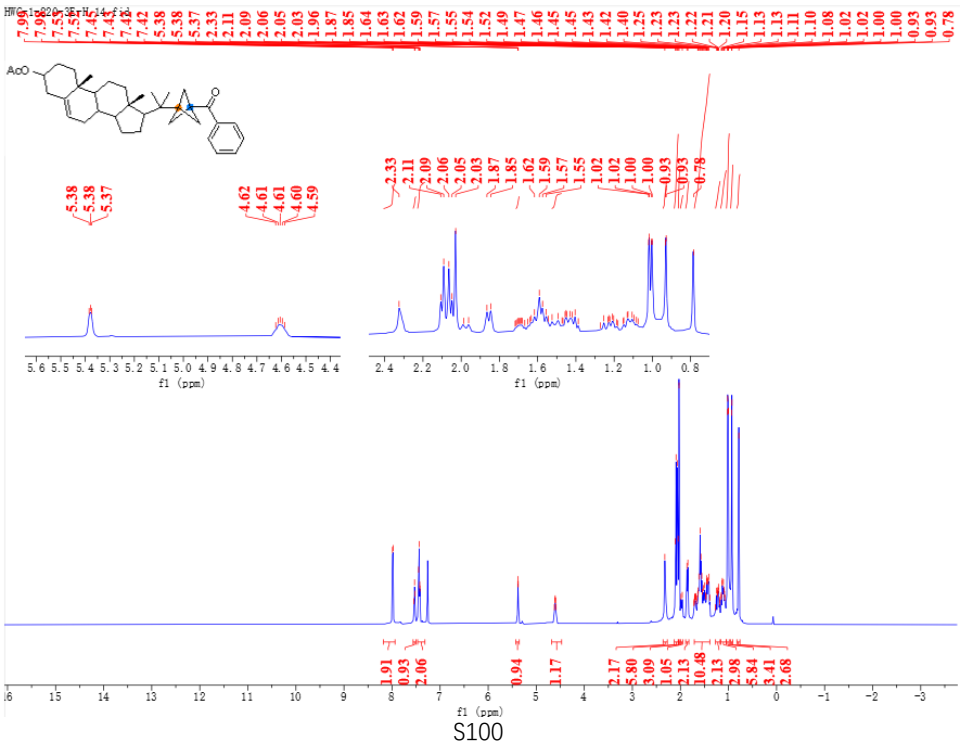
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Phenyl(3-((3*R*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone 46



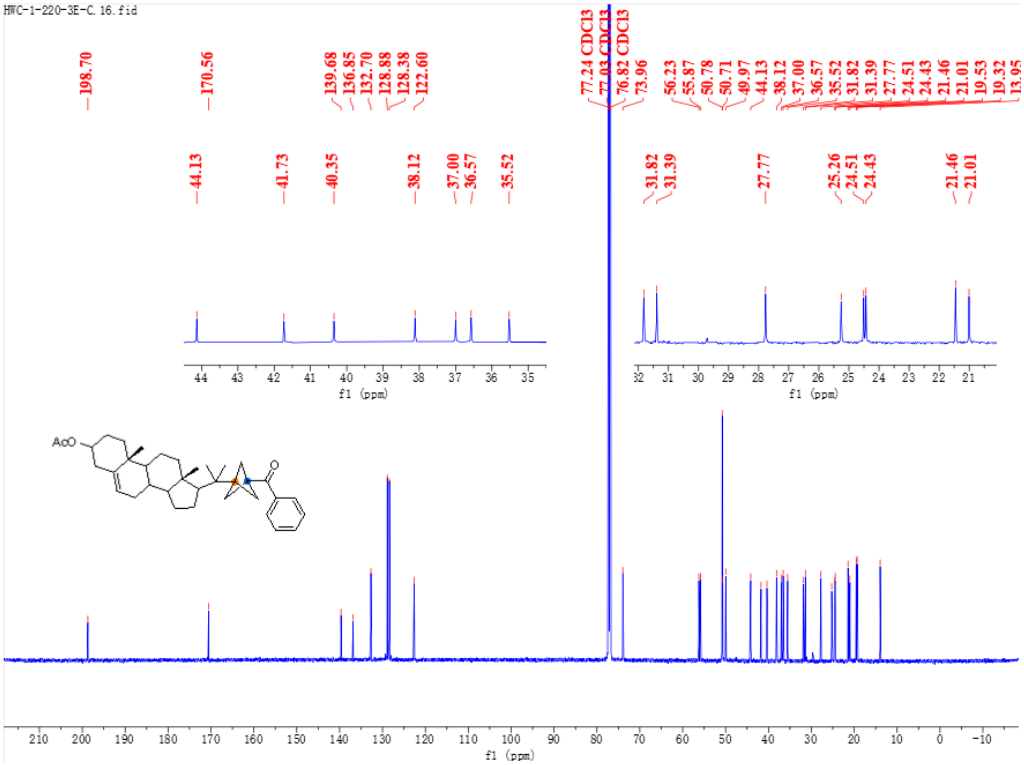
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of Phenyl(3-((3*R*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,10,13-trimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone 46



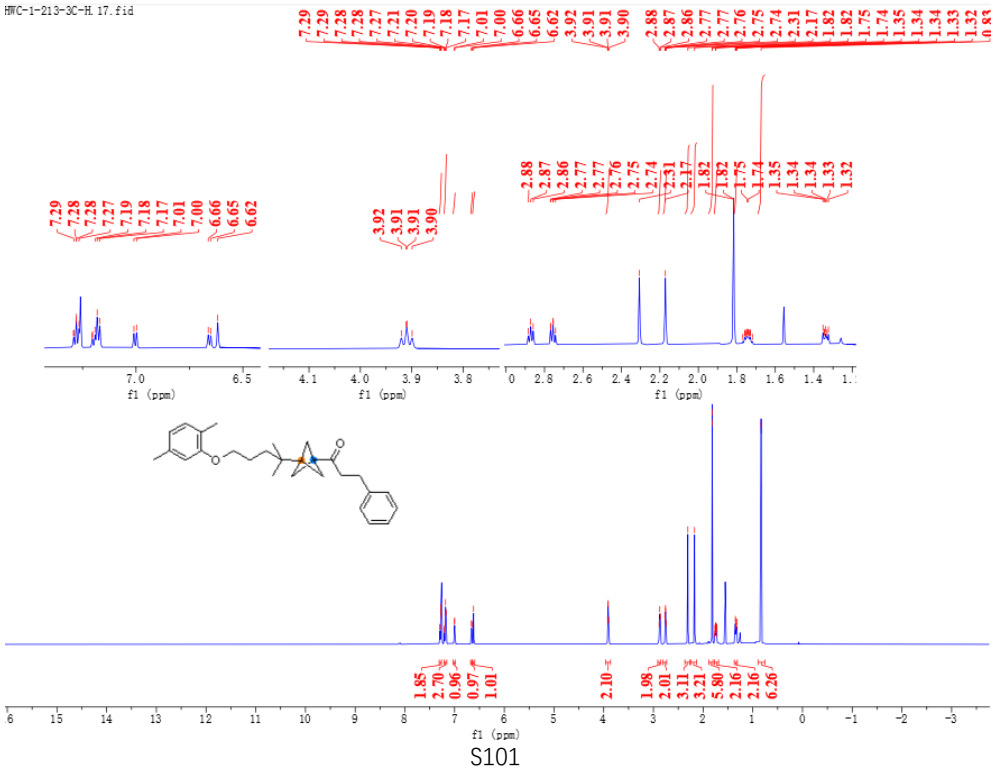
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-(2-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)propan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl Acetate 47



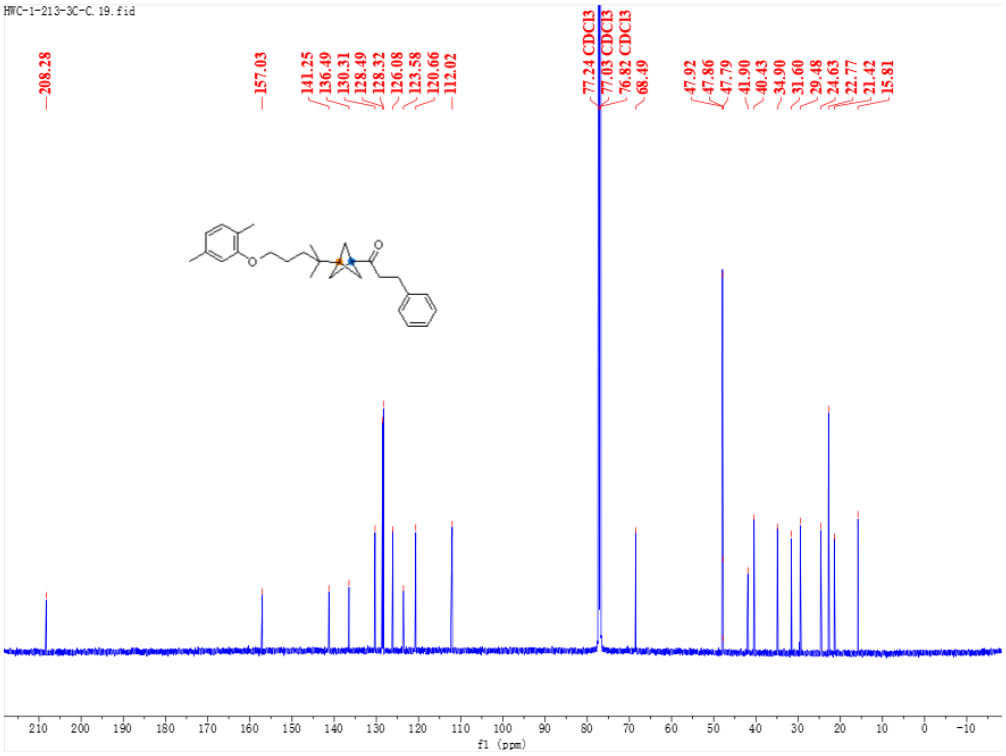
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-(2-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)propan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl Acetate 47



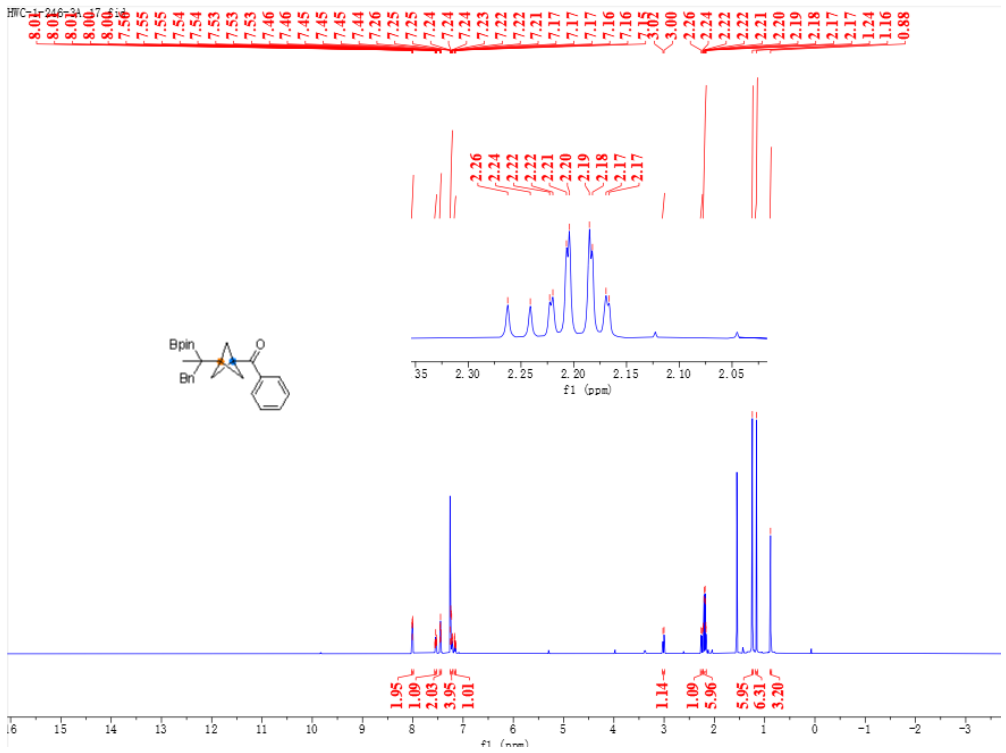
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1-(3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 48



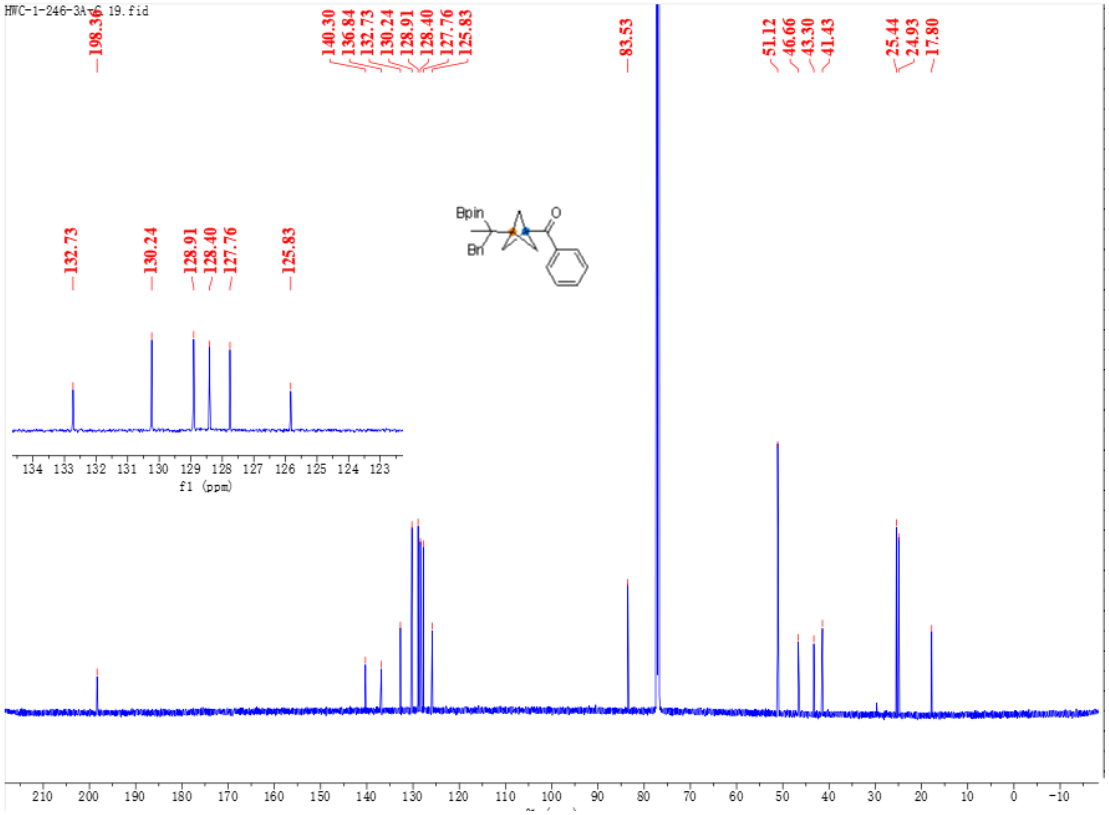
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 1-(3-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropan-1-one 48



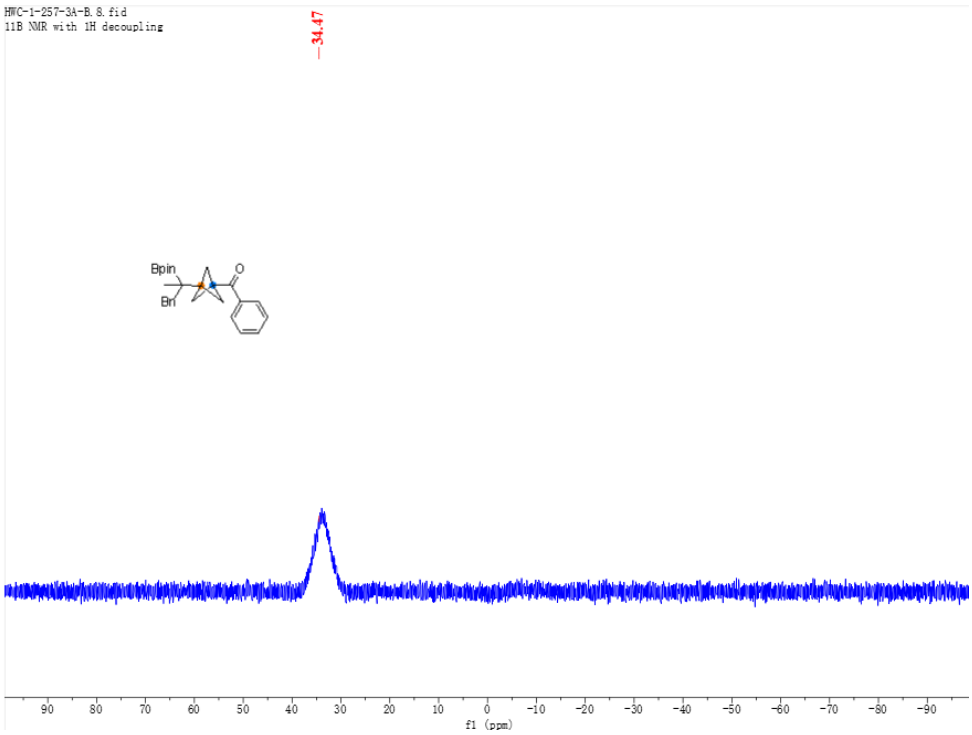
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Phenyl(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone 49



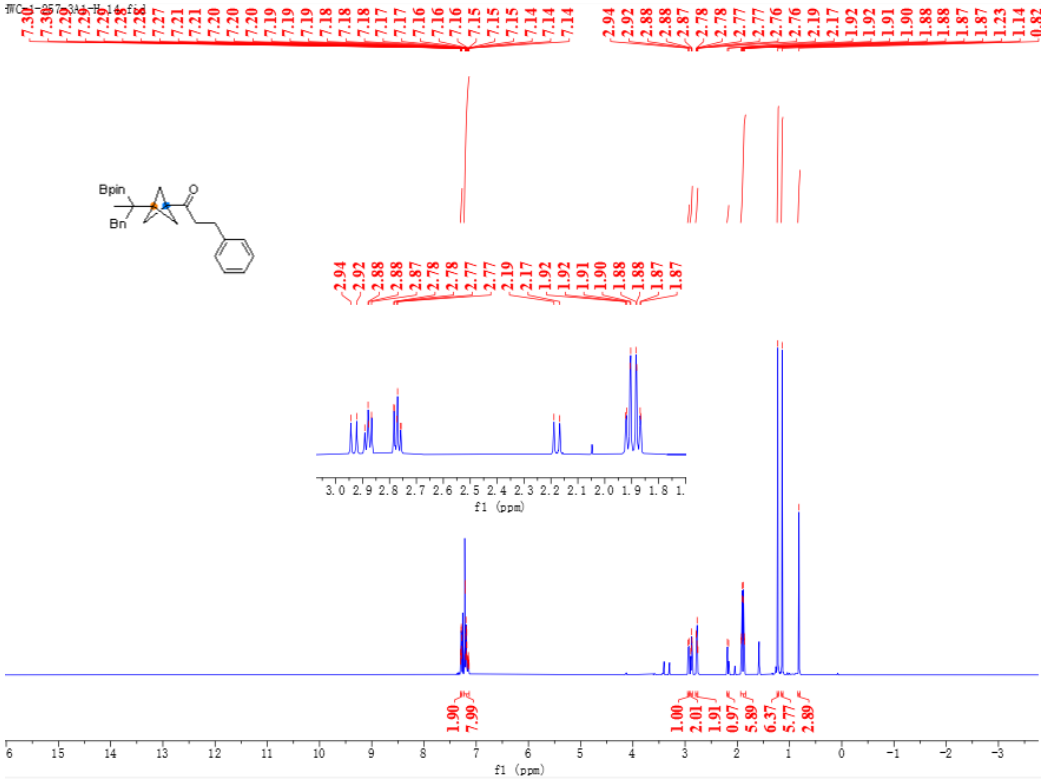
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of Phenyl(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone 49



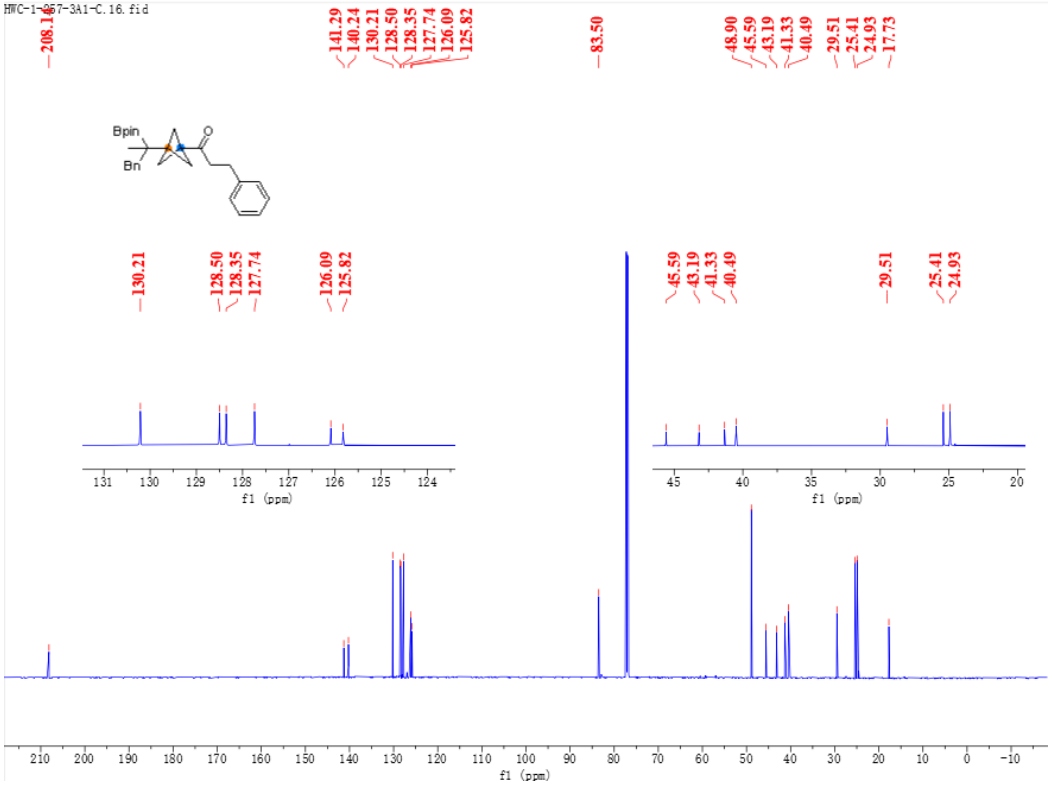
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of Phenyl(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone 49



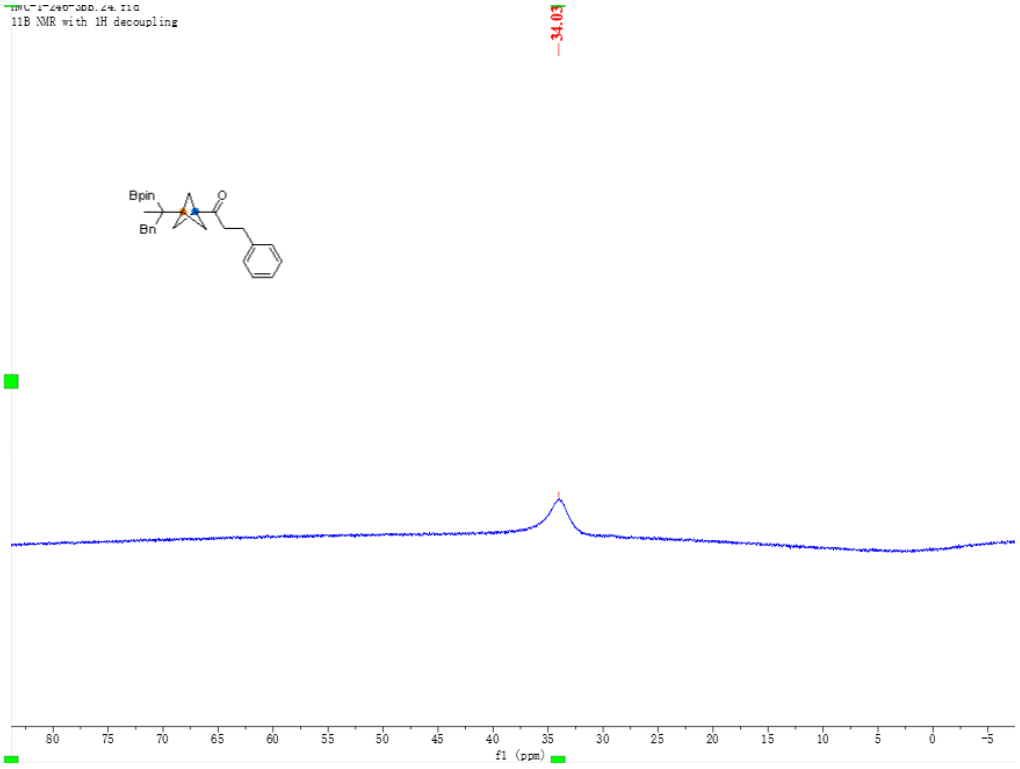
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3-Phenyl-1-(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)propan-1-one 50



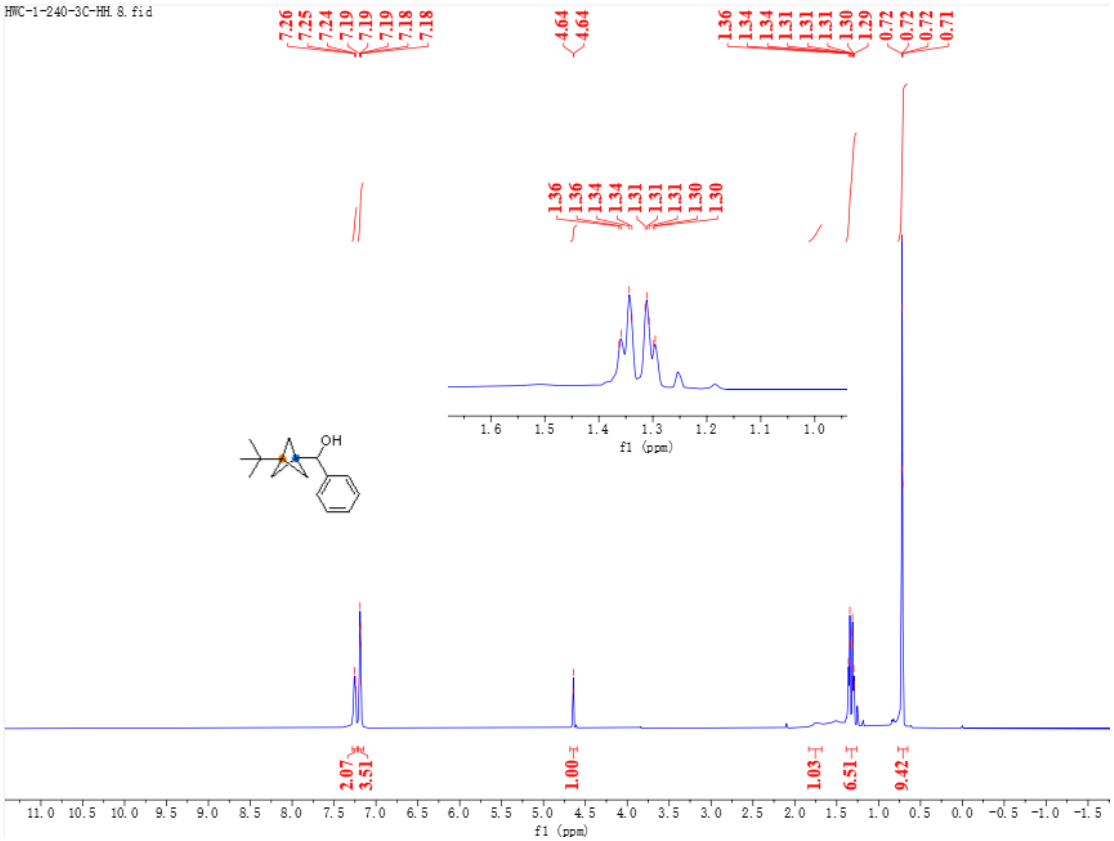
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3-Phenyl-1-(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)propan-1-one 50



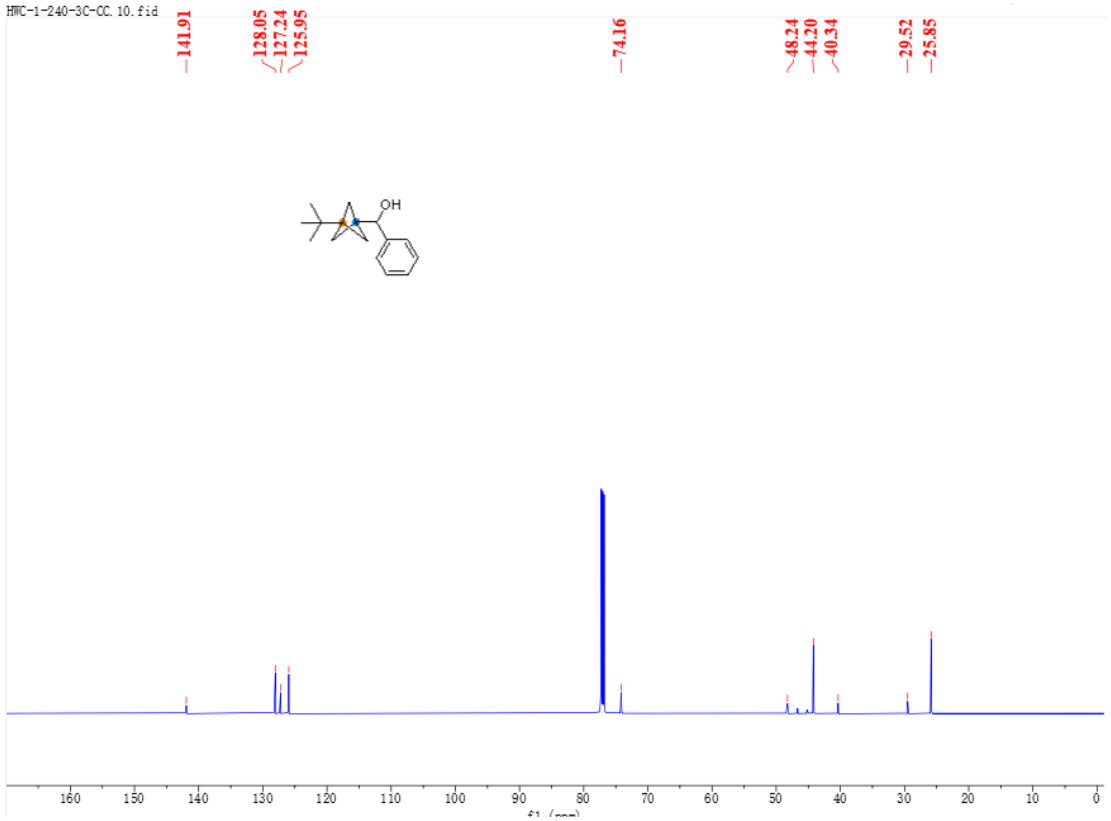
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of 3-Phenyl-1-(3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)propan-1-one 50



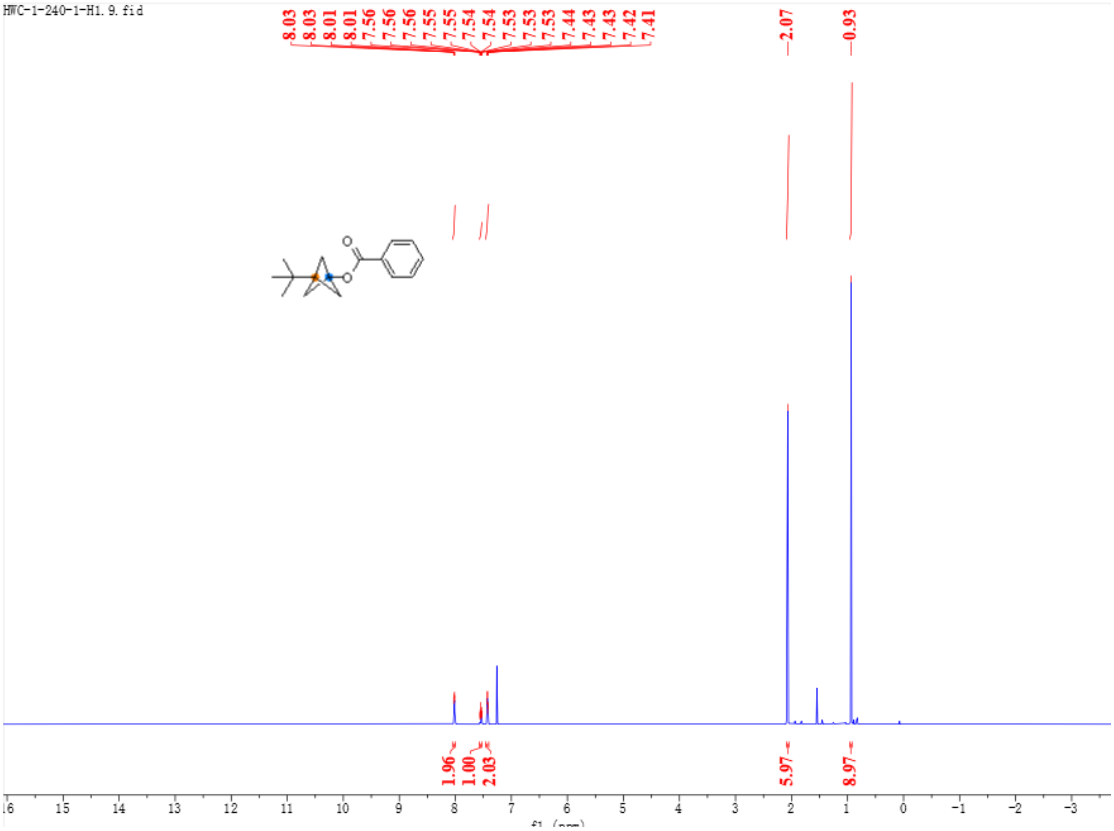
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanol 51



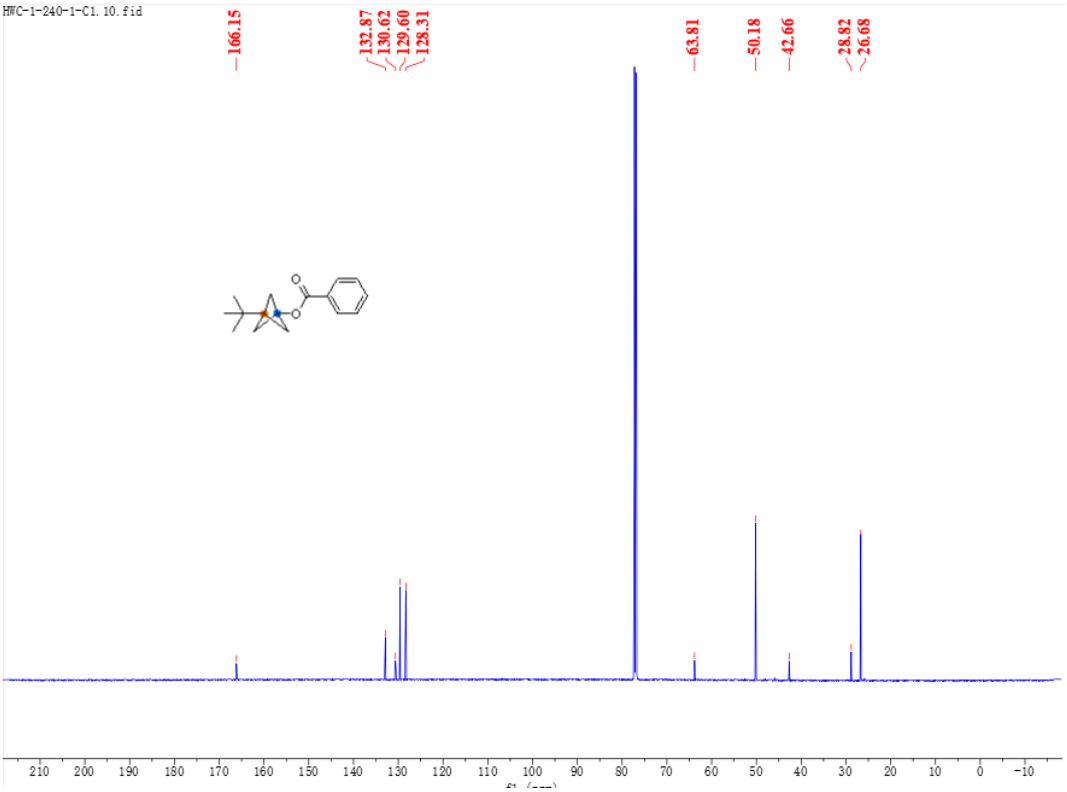
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl)(phenyl)methanol 51



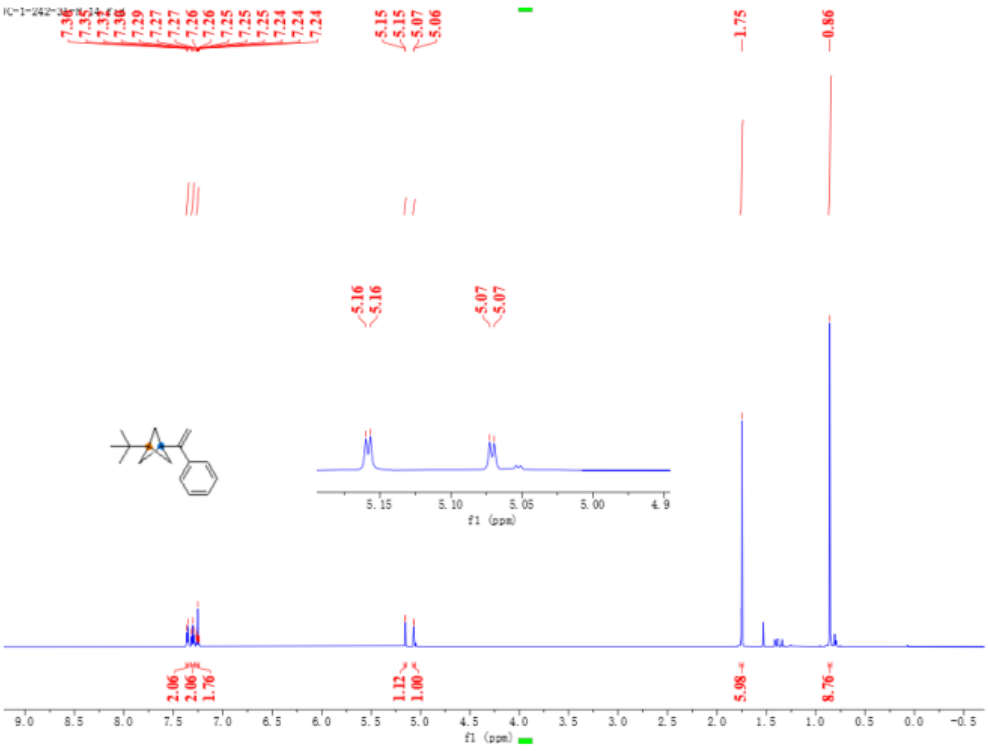
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl Benzoate 52



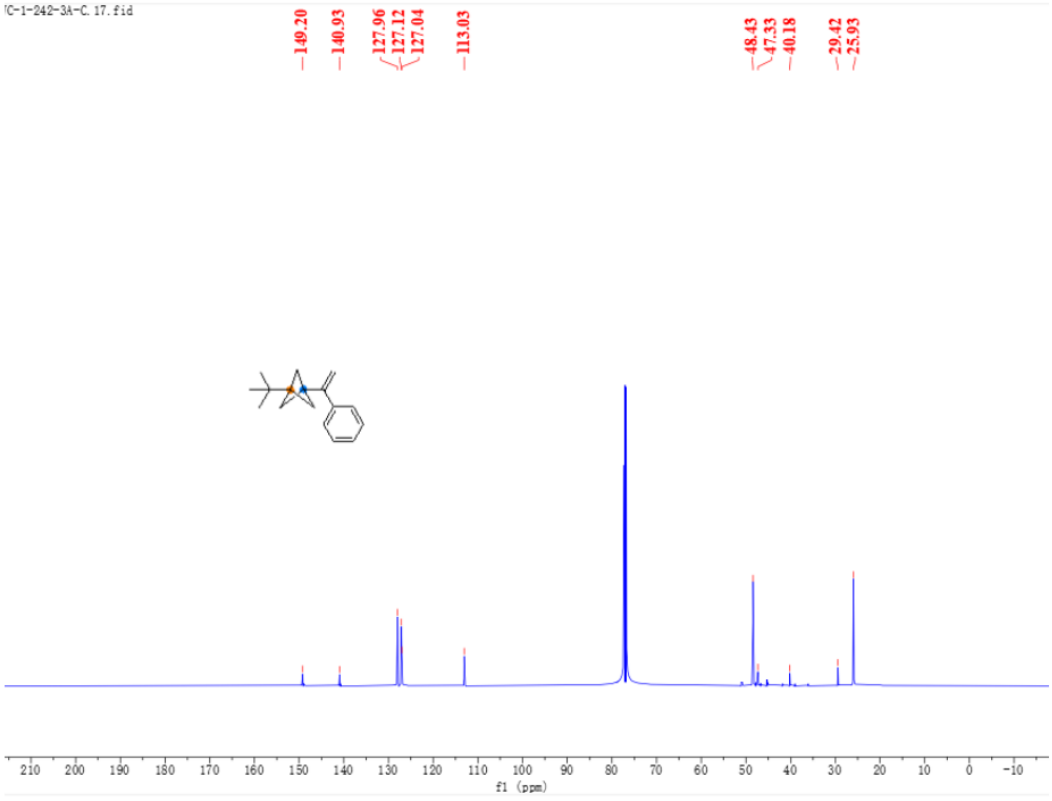
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of
3-(*tert*-Butyl)bicyclo[1.1.1]pentan-1-yl Benzoate 52



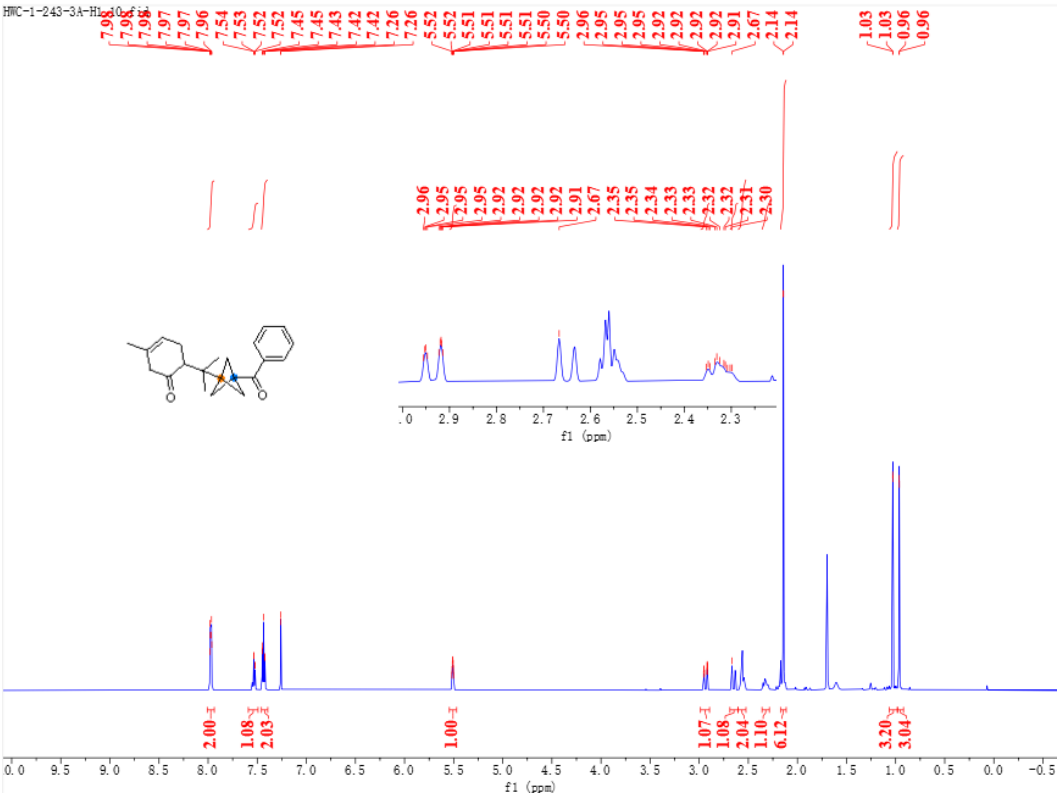
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of
1-(*tert*-Butyl)-3-(1-phenylvinyl)bicyclo[1.1.1]pentane 53



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 1-(*tert*-Butyl)-3-(1-phenylvinyl)bicyclo[1.1.1]pentane 53



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6-(2-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)propan-2-yl)-3-methylcyclohex-3-en-1-one 58



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 6-(2-(3-Benzoylbicyclo[1.1.1]pentan-1-yl)propan-2-yl)-3-methylcyclohex-3-en-1-one 58