Metal and photocatalyst-free alkylboration of [1.1.1]propellane enabled by red-light-induced electron transfer

Yuying Wang, Jianyang Dong,* Yulin Xiao, Zhilin Wang, Weilin Wu, and Dong Xue*

Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, China

*E-mail: jydong@snnu.edu.cn

xuedong_welcome@snnu.edu.cn

Supporting Information

Contents

1. General Information

All reactions were performed under argon atmosphere with glass storage tube unless otherwise stated. Reagents were purchased from commercial sources and were used as received. Solvents were purified by VG-P7 solvent drying system or commercial dry solvent. Thin layer chromatography (TLC) was performed to monitor reactions by UV light (254 nm) or phosphomolybdate chromogenic agent. Silica gel column chromatography was performed using 200-300 Mesh silica gel.

The reaction tube used in the experiment was a 10 mL liquid storage sealed tube with a polytetrafluoroethylene thread plug (Figure S1). The general reactions were carried with the assembled photoreactor. Each of lamp include: 30 W red LED (620-630 nm, 10 LED lamp beads in series), aluminium radiator with fan, electric driver (XC-8W600-OS). The LED beads were purchased from Zhuhai UV Optoelectronics Co., Ltd. (TH-UV395T3WL-3535 60).

^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 400 MHz, 100 MHz on a Bruker Avance 400 spectrometer. All chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual $CDCl_3$ (7.26 ppm), CD_3OD (3.31 ppm), acetone-d_6 (2.05 ppm) or DMSO-d_6 (2.50 ppm) as internal standards. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), the number of protons (n) for a given resonance was indicated by *n*H. Coupling constants were reported as a *J* value in Hz. ^{19}F NMR chemical shifts were reported in ppm. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm), CD_3OD (49.00 ppm), acetone-d_6 (29.84 ppm and 206.26 ppm) or DMSO-d_6 (39.52 ppm) as internal standards. HRMS data were obtained by ESI-TOF or APCI-TOF method with Bruker mass spectrometer (MAXIS).

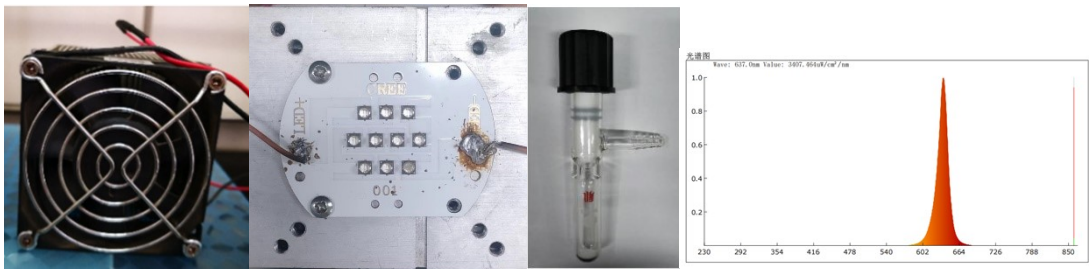


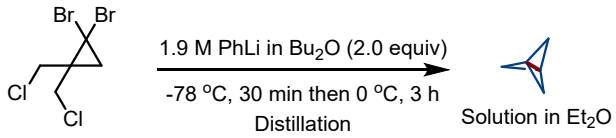
Figure S1. Pictures of photoreactors

(Note: The reaction tube is 3 cm away from the lamp bead, the temperature of the

reaction mixture is room temperature, the kettle has no external heating device and is equipped with a fan for cooling.)

2. Preparation of [1.1.1]Propellane (Solution in Et_2O) and Katritzky Salts.

2.1 Preparation of [1.1.1]Propellane (Solution in Et_2O).



1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (10.0 g, 34.1 mmol) was added to 15 mL of Et_2O. The solvent was cooled to -78 °C under Argon atmosphere. Then 42 mL PhLi (42.0 mL, 80.0 mmol, 2.35 equiv, 1.9 M solvent in *n*-Bu_2O) was added slowly dropwise. The mixture was stirred at -78 °C for 30 min, then warmed to 0 °C and stirred for another 3 h. The reaction flask was fitted with a diaphragm vacuum pump refluxed alcohol at -20 °C. A pump was used to evacuate the system down slowly from 200 mbar to 30 mbar, and the solvent was held at this pressure for 5 min. This resulted in the distillation of the Et_2O/[1.1.1]propellane solvent. The concentration was checked by ^1H NMR by taking a 100 µL aliquot of the stock solvent and determining the ratio of [1.1.1]propellane to an added standard, such as 1,3,5-Trimethylbenzene (50%-60% yield, typically concentrations are 0.9-1.1M with this protocol). This solvent should be kept in a -24 °C freezer with argon atmosphere.

Determination of [1.1.1]propellane concentration (Figure S2): 0.1 mmol of 1,3,5-trimethoxybenzene (16.8 mg) and 50 µL of [1.1.1]propane solution was added to a NMR tube containing an appropriate amount of $CDCl_3$. The concentration of [1.1.1]propellane was calculated based on the ratio of 1,3,5-trimethoxybenzene to [1.1.1]propellane.

$$c([1.1.1]\text{propellane}) = Int([1.1.1]\text{propellane}) \times 1.0\text{M} = 1.20 \times 1.0\ \text{M} = 1.2\ \text{M}$$

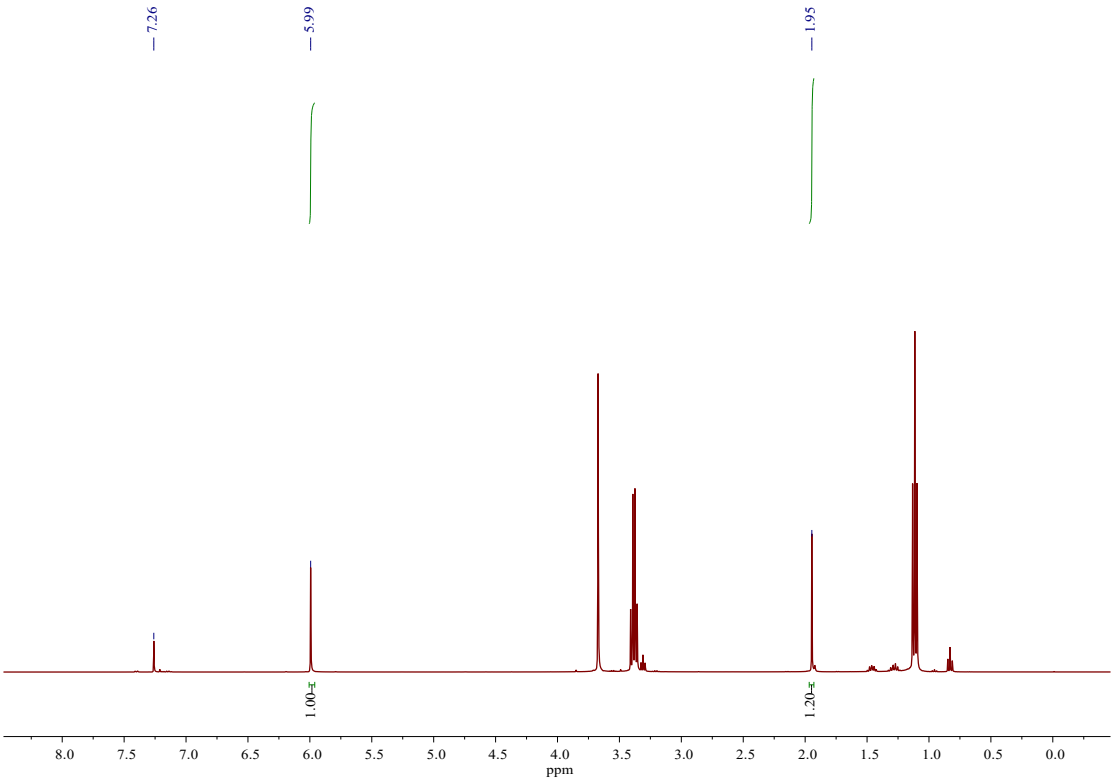
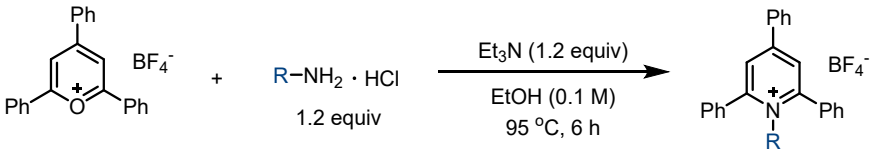
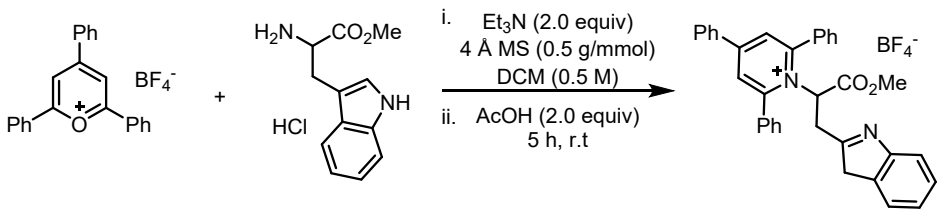


Figure S2. ^{1}H NMR spectrum for the [1.1.1]propellane solution with 1,3,5-trimethoxybenzene in $CDCl_3$

2.2 Preparation of Katritzky Salts.[1-4]



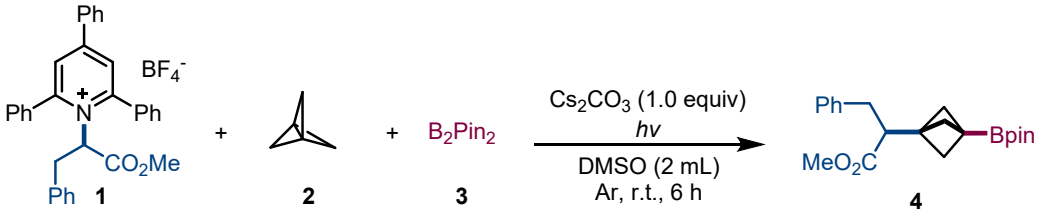
All pyridinium salts used in this study were prepared following a procedure by Hong *et al*.[1-3] A Schlenk tube equipped with a magnetic stirrer bar was charged with amine hydrochloride (1.2 equiv). Ethanol (1.0M) and triethyl amine (1.2 equiv) was added to the reaction vessel and the tube sealed. The resulting suspension was stirred for 30 min at room temperature. Triphenylpyrylium tetrafluoroborate (1.0 equiv) was added, the tube sealed and stirred for overnight at 95 °C. The mixture was then allowed to cool to room temperature. If product precipitation occurred during reflux, the solid was filtered, washed with EtOH and then Et_2O, and dried under high vacuum. If product precipitation did not occur during reflux, the solution was diluted with Et_2O, and vigorously stirred for 1 h to induce trituration. The resulting solid pyridinium salt was filtered and washed with Et_2O. If the solid did not precipitate, it was purified by flash column chromatography with DCM : acetone = 10:1.



Amino acid methyl ester (1.0 equiv), 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv), and crushed 4 Å MS (0.5 g per a mmol) were added to a round-bottomed flask. The flask was fitted with a septum and para-filmed. A vent needle was added, and CH_2Cl_2 (0.5M) and then Et_3N (2.0 equiv) were added. The vent needle was removed, and the mixture was stirred for 20 min at room temperature. The vent needle was replaced, and AcOH (2.0 equiv) was added. The vent needle was removed, and the mixture was stirred for 5 h at room temperature. The mixture was filtered through a short pad of celite. The flask and celite were then rinsed with CH_2Cl_2 (25 mL). The filtrate was then washed with HCl (1 M, 4 × 60 mL), sat. $NaHCO_3$ (4 × 60 mL), and sat. NaCl (1× 60 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The resulting solid was dried under high vacuum. If diketone byproduct was present in more than 10%, the product was purified by silica gel chromatography.

3. Optimization of Reaction Conditions

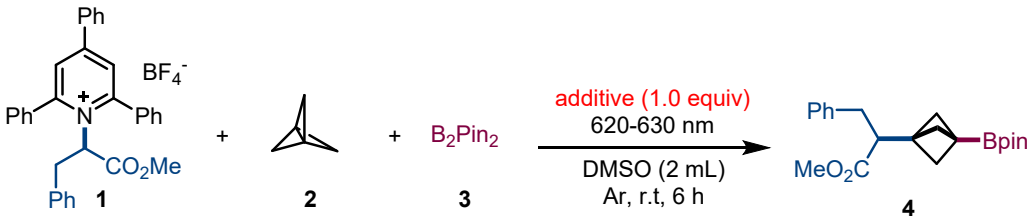
Table S1. Screening of light sources.



Entry	light sources	Yield (%)
1	360-365 nm	60
2	390-395 nm	72
3	460-465 nm	70
4	530-535 nm	68
5	620-630 nm	70
6	6000K	70

Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), B_2Pin_2 (0.3 mmol), Cs_2CO_3 (0.1 mmol), DMSO (2 mL), Ar, 6 h. Yields were determined by ^1H NMR analysis using 1,3,5-Trimethoxybenzene as internal standard.

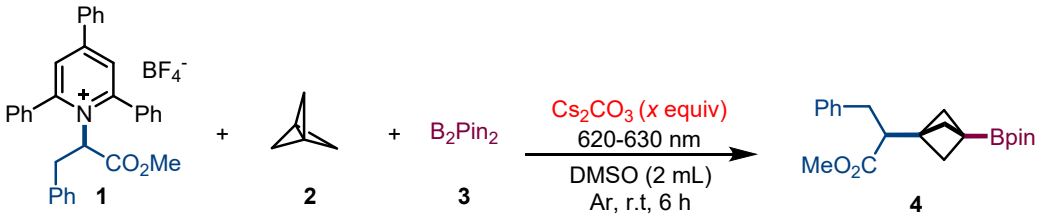
Table S2. Screening of additive.



Entry	additive	Yield (%)
1	K_2HPO_4	60
2	K_2CO_3	64
3	**Cs_2CO_3**	**70**
4	K_3PO_4	56
5	Na_2CO_3	62
6	DABCO	NR

Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), B_2Pin_2 (0.3 mmol), additive (0.1 mmol), DMSO (2 mL), 620-630 nm, Ar, r.t, 6 h. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as internal standard. NR, no reaction.

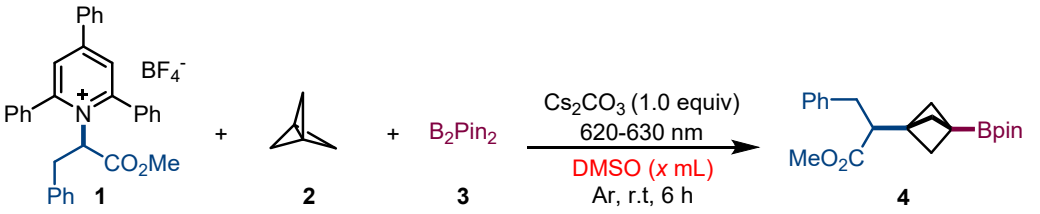
Table S3. Screening of the amount of Cs_2CO_3.



Entry	Cs_2CO_3 (*x* equiv)	Yield (%)
1	0.75	60
2	**1.0**	**70**
3	1.5	43
4	2.0	44

Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), B_2Pin_2 (0.3 mmol), Cs_2CO_3 (*x* equiv), DMSO (2 mL), 620-630 nm, Ar, r.t, 6 h. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as internal standard.

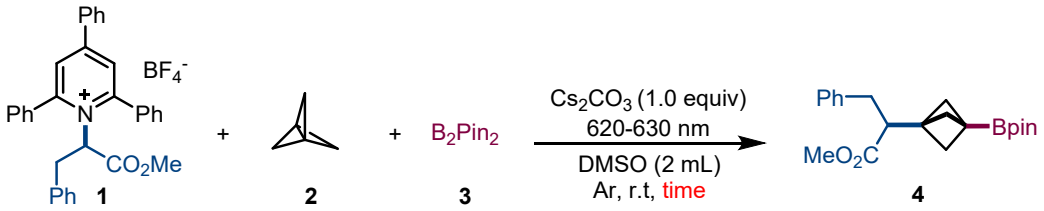
Table S4. Screening of the amount of solvent.



Entry	DMSO (x mL)	Yield (%)
1	6.0	65
2	5.0	65
3	**4.0**	**67**
4	3.0	60

Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), B_2Pin_2 (0.3 mmol), Cs_2CO_3 (0.1 mmol), 620-630 nm, Ar, r.t, 6 h. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as internal standard.

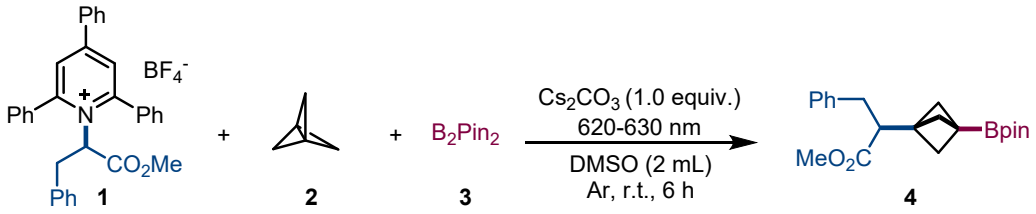
Table S5. Screening of reaction time.



Entry	time	Yield (%)
1	2 h	50
2	4 h	60
3	**6 h**	**70**
4	8 h	70
5	10 h	67
6	12 h	70

Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), B_2Pin_2 (0.3 mmol), Cs_2CO_3 (0.1 mmol), DMSO (2 mL), 620-630 nm, Ar, r.t. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as internal standard.

Table S6. Control experiments.



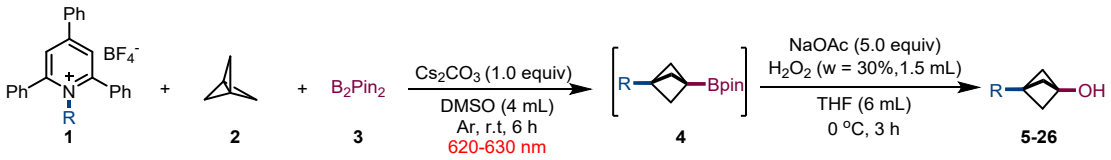
Entry	Deviation from the standard conditions	Yield (%)
1	standard conditions	70
2	no light	18
3	no light and heat to 80 ^oC	18
4	no Cs_2CO_3	NR
5	air	51

Reaction conditions: **1** (0.2 mmol), **2** (0.1 mmol), B_2Pin_2 (0.3 mmol), Cs_2CO_3 (0.1 mmol), DMSO (2 mL), 620-625 nm, Ar, r.t, 6 h. Yields were determined by ^1H NMR analysis

using 1,3,5-trimethoxylbenzene as internal standard. NR, no reaction.

4. General Procedure for Bicyclo[1.1.1]pentane Alcohols Synthesis.

4.1 Standard Procedure for Bicyclo[1.1.1]pentane Alcohols Synthesis.



To an oven-dried 10 mL glass storage tube with a stir bar were added Cs_2CO_3 (0.3 mmol, 1.0 equiv), B_2Pin_2 (0.9 mmol, 3.0 equiv), Katritzky salt (0.6 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.3 mmol), DMSO (4.0 mL) were added via a syringe, respectively. The reaction mixture was placed in a photo-parallel reactor. The mixture was then stirred rapidly and irradiated for 6 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Then transfer the mixture to a 25 ml round bottom flask. NaOAc (1.5 mmol, 5.0 equiv) and THF (6 ml) were added to the mixture and cooled to 0 °C, followed by slow dropwise addition of H_2O_2 (W = 30%, 2.25 ml). The reaction was carried out at 0 °C for 3 hours. At the end of the reaction, the reaction was quenched using $Na_2S_2O_3$ and diluted with Et_2O, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

pre-reaction: **post-reaction:**

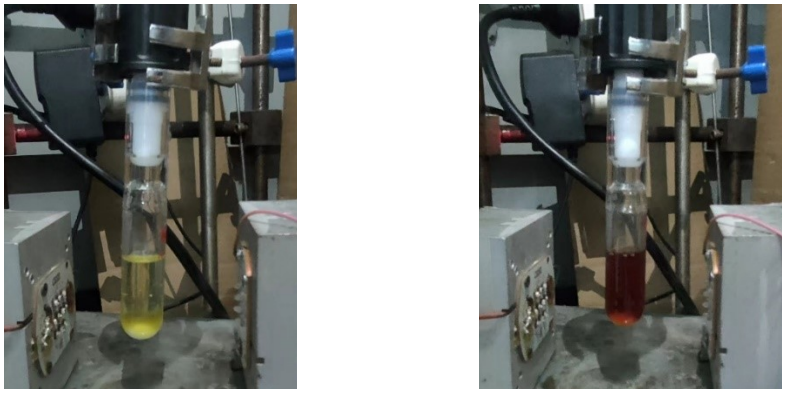
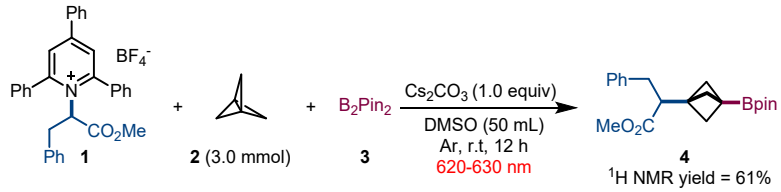
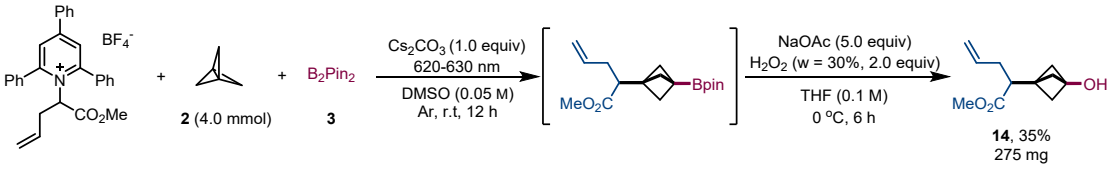


Figure S3. Picture of the reaction

4.2 Standard Procedure for Gram-Scale Synthesis of BCP Alcohols.



To an oven-dried 100 mL glass storage tube with a stir bar were added Cs_2CO_3 (3.0 mmol, 1.0 equiv), B_2Pin_2 (9.0 mmol, 3.0 equiv), Katritzky salt **1** (6.0 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (3.0 mmol), DMSO (50 mL) were added via a syringe, respectively. The reaction mixture was placed in a photo-parallel reactor. The mixture was then stirred rapidly and irradiated for 12 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The product methyl 3-phenyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propanoate **4** has a yield of 61%. The Yield was determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as internal standard.



To an oven-dried 100 mL glass storage tube with a stir bar were added Cs_2CO_3 (4.0 mmol, 1.0 equiv), B_2Pin_2 (12.0 mmol, 3.0 equiv), Katritzky salt (8.0 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (4.0 mmol), DMSO (70 mL) were added via a syringe, respectively. The reaction mixture was placed in a photo-parallel reactor. The mixture was then stirred rapidly and irradiated for 12 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Then transfer the mixture to a 100 ml round bottom flask. NaOAc (20.0 mmol, 5.0 equiv) and THF (40 mL) were

added to the mixture and cooled to 0 °C, followed by slow dropwise addition of H_2O_2 (W = 30%, 20 ml). The reaction was carried out at 0 °C for 6 hours. At the end of the reaction, the reaction was quenched using $Na_2S_2O_3$ and diluted with Et_2O, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel. The methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)pent-4-enoate **14** was obtained by silica gel column chromatography (Petroleum ether/EtOAc = 8:1) as a yellow oil (275 mg, 35% yield).

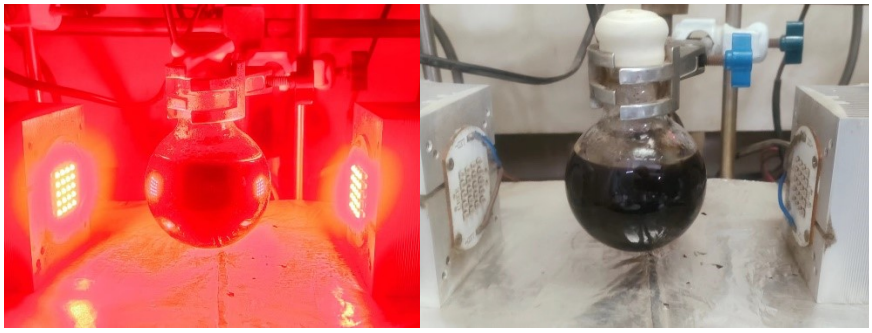
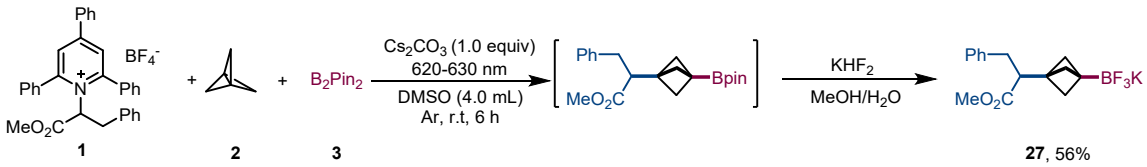


Figure S4. Picture of the reaction

4.3 Post-Functionalizations



To an oven-dried 10 mL glass storage tube with a stir bar were added Cs_2CO_3 (0.3 mmol, 1.0 equiv), B_2Pin_2 (0.9 mmol, 3.0 equiv), Katritzky salt **1** (0.4 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.3 mmol), DMSO (4.0 mL) were added via a syringe, respectively. The reaction mixture was placed in a photo-parallel reactor. The mixture was then stirred rapidly and irradiated for 6 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3×30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure, and then passed through a plug of silica (Petroleum ether/EtOAc = 5:1) and concentrated under reduced pressure. The crude, pale-yellow solid material was dissolved in MeOH (1.5 mL) and KHF_2 (0.3 mL, 4.5 equiv, 4.5 M aq solution) was added dropwise at ambient

temperature. The reaction mixture was stirred vigorously at rt for 4 h. After 4 h, the solvents were evaporated to dryness under reduced pressure. The resulting crude material was extracted with hot acetone (3×10 mL), followed by filtration. The combined filtrates were concentrated and then triturated with approximately 30 mL of Et_2O. The resultant precipitate was collected by vacuum filtration and dried under vacuum to afford BCP BF_3K **27** as a white solid (56.4 mg, 56%).

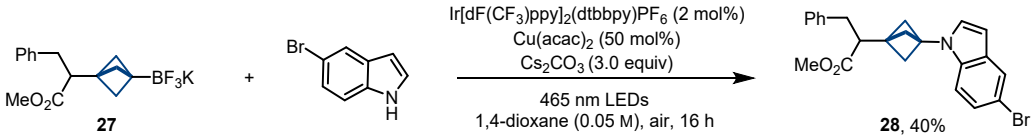
^{1}H NMR (400 MHz, Acetone) δ 7.27 – 7.09 (m, 5H), 3.50 (s, 3H), 2.84 – 2.79 (m, 1H), 2.72 – 2.58 (m, 2H), 1.47 – 1.37 (m, 6H).

^{13}C NMR (100 MHz, Acetone) δ173.96, 141.65, 129.45, 128.96, 126.61, 52.23, 50.91, 49.40, 43.23, 35.36, 25.49.

^{19}F NMR (376 MHz, Acetone) δ -146.41.

^{11}B NMR (128 MHz, Acetone) δ 3.78.

HRMS(ESI-TOF) m/z $[M-K]^+$ calcd. for $C_{15}H_{17}BF_3O_2K$ 297.1279, found 297.1283.

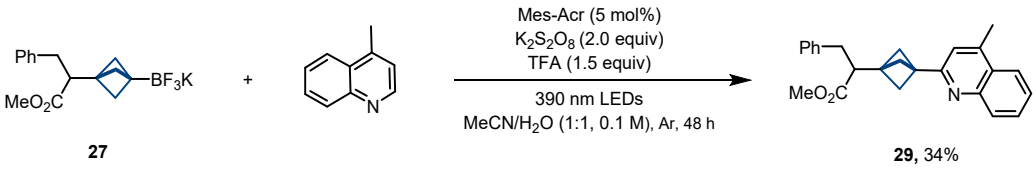


To an oven-dried 10 mL glass storage tube with a stir bar were added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.0 mg, 0.001 mmol, 2 mol%), BCP BF_3K **27** (33.6 mg, 0.1 mmol, 1 equiv), 5- bromo-1*H*-indole (9.8 mg, 0.05 mmol, 1 equiv), $Cu(acac)_2$ (6.5 mg, 0.025 mmol, 50 mol%) and Cs_2CO_3 (48.9 mg, 0.15 mmol, 3 equiv). Then 1,4-dioxane (1 mL, 0.05 M) were added via a syringe. The mixture was irradiated with a 10 W blue LED for 16 h. Solvent was removed in vacuo, and the crude material was purified by column chromatography (Petroleum ether/EtOAc = 25:1). The product **28** was obtained as a yellow oil. (8.5 mg, 40%).[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.9 Hz, 1H), 7.29 – 7.11 (m, 7H), 6.94 (d, *J* = 3.3 Hz, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 3.57 (s, 3H), 3.08 – 2.93 (m, 2H), 2.81 – 2.72 (m, 1H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 138.9, 134.6, 131.1, 128.8, 128.7, 127.4, 126.7, 124.7, 123.6, 113.2, 112.3, 101.3, 52.8, 51.8, 49.6, 47.4, 37.4, 35.7.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}BrNO_2$ 446.0726, found 446.0733.

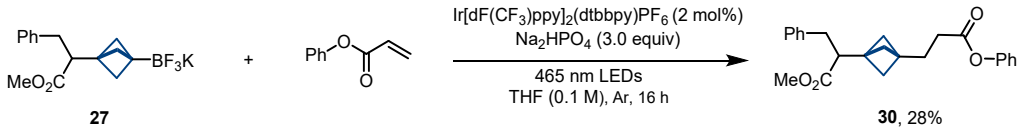


To an oven-dried 10 mL glass storage tube with a stir bar were added Mes-Acr$^+$ ClO_4^- (2.1 mg, 0.005 mmol, 5 mol%), BCP BF_3K **27** (33.6 mg, 0.1 mmol, 1.0 equiv) and $K_2S_2O_8$ (54.0 mg, 0.2 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then 4-methylquinoline (20 µL, 0.1 mmol, 1.0 equiv), TFA (12 µL, 0.1 mmol, 1.0 equiv) and MeCN/H_2O (0.5 mL/0.5 mL, 0.1 M) were added via a syringe. The mixture was irradiated with a 10 W purple LED for 48 h. The reaction mixture was diluted with DCM, and the organic layer was washed with $NaHCO_3$ and H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure, and the crude material was purified by column chromatography (Petroleum ether/EtOAc = 10:1). The product **29** was obtained as a colorless oil. (12.6 mg, 34%).[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 7.17 (s, 1H), 3.64 (s, 3H), 3.09 – 2.99 (m, 2H), 2.90 – 2.79 (m, 1H), 2.68 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 139.6, 129.3, 128.9, 128.6, 127.2, 126.4, 126.0, 123.7, 119.8, 51.6, 51.6, 49.1, 42.5, 39.8, 35.2, 29.9, 18.9.

HRMS(APCI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}NO_2$ 372.1958, found 372.1967.



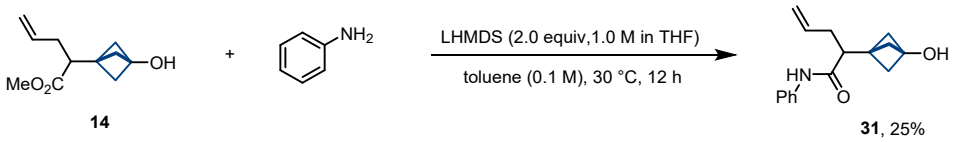
To an oven-dried 10 mL glass storage tube with a stir bar were added $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 2 mol%), BCP BF_3K **27** (33.6 mg, 0.1 mmol, 1 equiv) and Na_2HPO_4 (42.6 mg, 0.3 mmol, 3 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then 2-propenoicacid (21 µL, 0.15 mmol, 1.5 equiv) and THF (1 mL) were added via a syringe, respectively. The mixture was irradiated with a 10 W blue LED for 16 h. Solvent was removed in vacuo, and the crude material was purified by column chromatography (Petroleum ether/EtOAc = 10:1). The product **30** was obtained as a white solid. (10.6 mg, 28%).[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.19 (t, *J* = 6.8 Hz, 3H), 7.09 (d, *J* = 7.3 Hz, 3H), 7.03 – 6.94 (m, 2H), 3.52 (d, *J* = 2.1 Hz, 3H), 2.91 – 2.77 (m, 2H), 2.69 – 2.61

(m, 1H), 2.45 (t, *J* = 7.6, 2.1 Hz, 2H), 1.86 (t, *J* = 7.5, 2.1 Hz, 2H), 1.55 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.1, 150.9, 139.7, 129.6, 128.8, 128.5, 126.4, 125.9, 121.6, 51.4, 49.7, 49.1, 40.0, 38.6, 35.2, 31.8, 26.9.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{26}O_4$ 401.1723, found 401.1729.

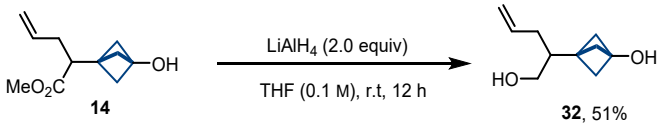


To a 10 mL seal tube fitted with a magnetic stir bar was added **14** (0.2 mmol, 1.0 equiv) in toluene (2 mL). The tube was sealed, evacuated and backfilled with argon three times. $PhNH_2$ (22 µL, 0.24 mmol, 1.2 equiv), and LHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol, 2.0 equiv) were then added to the reaction mixture with vigorous stirring at room temperature. The reaction mixture was left stirring at 30 °C for 12 h. Afterwards, the reaction mixture was quenched with NH_4Cl (aq, 1.0 M, 1 mL), diluted with EtOAc (10 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the crude material was purified by column chromatography (Petroleum ether/EtOAc = 2:1). The product **31** was obtained as a yellow oil. (12.8 mg, 25%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.17 – 7.05 (m, 2H), 5.80 (s, 1H), 5.07 (dd, *J* = 36.9, 13.8 Hz, 2H), 2.71 (s, 1H), 2.59 – 2.44 (m, 2H), 2.24 – 2.16 (m, 1H), 2.07 – 1.73 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 137.7, 135.7, 129.2, 124.6, 120.2, 117.2, 62.64, 53.4, 47.6 34.2, 32.3.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{19}NO_2$ 280.1308, found 280.1316.



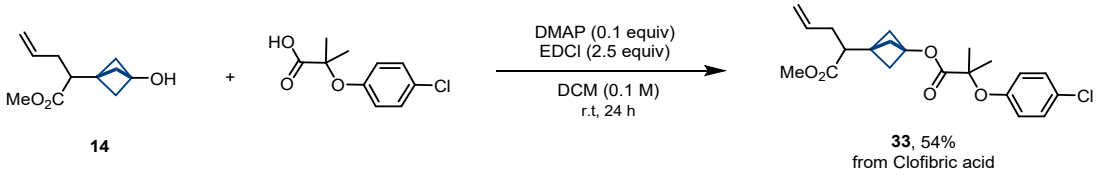
To a cooled (0 °C), stirred suspension of the compound **14** (0.2 mmol, 1.0 equiv) in THF (2.0 mL) was added $LiAlH_4$ (0.4 mmol, 2.0 equiv). The reaction was stirred for 12 h at room temperature. The reaction was quenched with (aq) NH_4Cl (10 mL), then the aqueous phase was extracted with (2 × 10 mL) EtOAc. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by column chromatography (Petroleum ether/EtOAc = 2:1). The product **32** was

obtained as a yellow oil. (17.2 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.73 (m, 1H), 5.14 – 4.93 (m, 2H), 3.64 – 3.48 (m, 2H), 2.81 (s, 1H), 2.15 – 2.02 (m, 2H), 1.82 (s, 7H), 0.96 – 0.75 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 116.4, 64.7, 62.7, 53.2, 39.3, 34.3, 32.6.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{16}O_2$ 191.1043, found 191.1049.



14 **33**, 54% from Clofibric acid

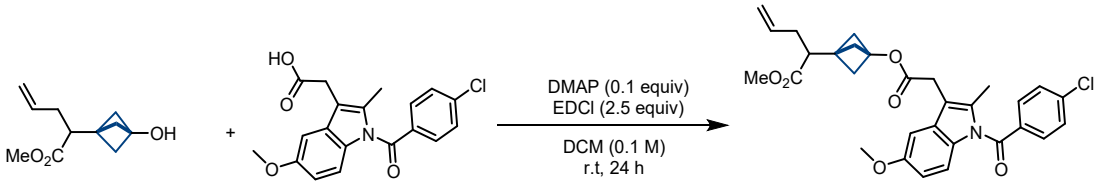
To a round bottom flask charged with **14** (0.2 mmol, 1.0 equiv.), DMAP (0.02 mmol, 0.1 equiv), EDCl (0.5 mmol, 2.5 equiv), and DCM (2 mL) was added clofibric acid (0.22 mmol, 1.1 equiv). The mixture was stirred at room temperature for 24 h, and then quenched by water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed in vacuo. The crude material was purified by column chromatography (Petroleum ether/EtOAc = 50:1). The product **33** was obtained as a colorless oil. (41.4 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.81 – 5.62 (m, 1H), 5.11 – 4.96 (m, 2H), 3.66 (s, 3H), 2.80 – 2.69 (m, 1H), 2.47 – 2.33 (m, 1H), 2.25 – 2.16 (m, 1H), 2.08 (q, *J* = 9.3 Hz, 6H), 1.54 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 173.3, 154.1, 135.3, 129.2, 127.5, 120.7, 117.0, 79.6, 63.9, 53.0, 51.7, 44.5, 34.8, 33.9, 25.2, 25.2.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}ClO_5$ 415.1283, found 415.1289.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{26}H_{27}FO_4$ 445.1786, found 445.1795.



14 **34**, 90% from Indomethacin

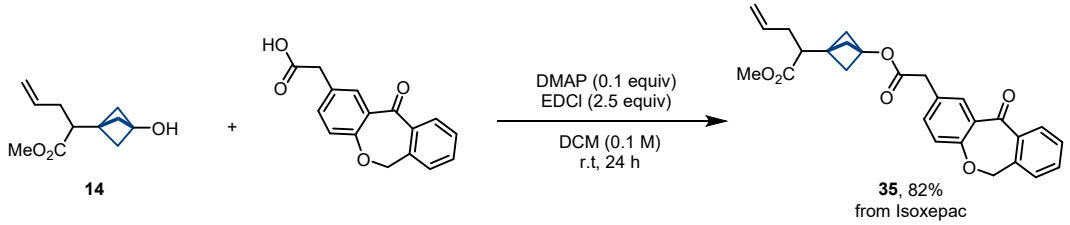
To a round bottom flask charged with **14** (0.2 mmol, 1.0 equiv.), DMAP (0.02 mmol, 0.1 equiv), EDCl (0.5 mmol, 2.5 equiv), and DCM (2 mL) was added indomethacin (0.22 mmol, 1.1 equiv). The mixture was stirred at room temperature for 24 h, and then quenched by water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed in vacuo. The crude

material was purified by column chromatography (Petroleum ether/EtOAc = 10:1). The product **34** was obtained as a yellow oil. (96.3 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.69 – 6.59 (m, 1H), 5.80 – 5.64 (m, 1H), 5.11 – 4.96 (m, 2H), 3.82 (s, 3H), 3.65 (s, 3H), 3.61 (s, 2H), 2.78 – 2.70 (m, 1H), 2.36 (s, 4H), 2.23 – 2.14 (m, 1H), 2.09 (q, *J* = 9.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 170.2, 168.3, 156.1, 139.3, 136.0, 135.3, 134.0, 131.3, 130.9, 130.7, 129.2, 116.9, 115.0, 112.4, 111.7, 101.3, 63.5, 55.8, 53.1, 51.6, 44.5, 34.7, 33.9, 30.6, 13.4.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{30}H_{30}ClNO_6$ 558.1654, found 558.1662.



To a round bottom flask charged with **14** (0.2 mmol, 1.0 equiv.), DMAP (0.02 mmol, 0.1 equiv), EDCI (0.5 mmol, 2.5 equiv), and DCM (2 mL) was added isoxepac (0.22 mmol, 1.1 equiv). The mixture was stirred at room temperature for 24 h, and then quenched by water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4. The solvent was removed in vacuo. The crude material was purified by column chromatography (Petroleum ether/EtOAc = 10:1). The product **35** was obtained as a yellow oil. (72.7 mg, 82%).

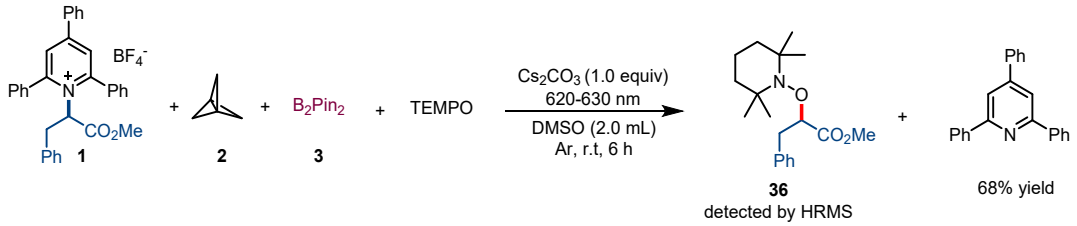
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.78 – 5.64 (m, 1H), 5.16 (s, 2H), 5.09 – 4.95 (m, 2H), 3.64 (s, 3H), 3.59 (s, 2H), 2.79 – 2.65 (m, 1H), 2.44 – 2.31 (m, 1H), 2.23 – 2.13 (m, 1H), 2.13 – 2.02 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 173.3, 170.8, 160.6, 140.50, 136., 135.6, 135.3, 132.8, 132.6, 129.6, 129.3, 127.9, 127.6, 125.2, 121.1, 116.9, 73.7, 63.4, 53.1, 51.6, 44.5, 40.3, 34.7, 33.9.

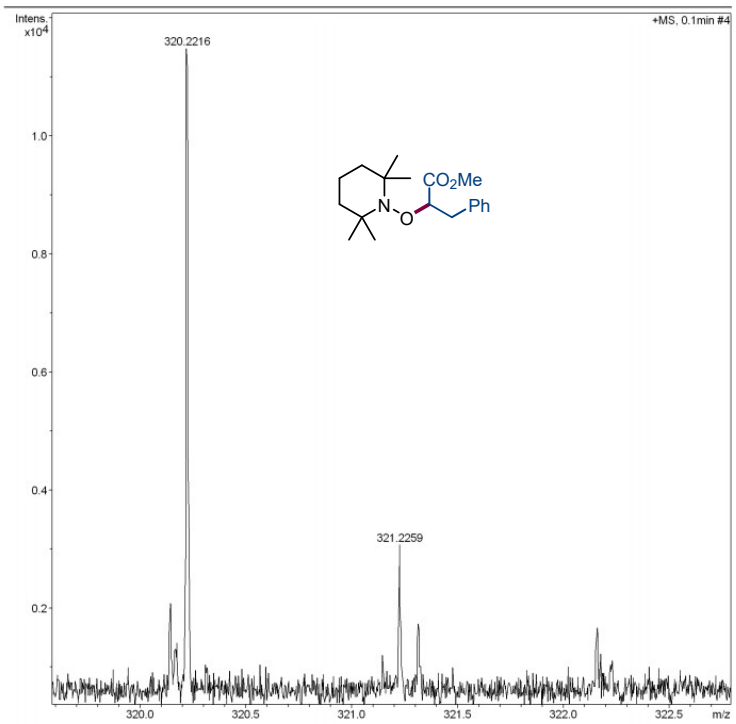
HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{26}O_6$ 469.1622, found 469.1628.

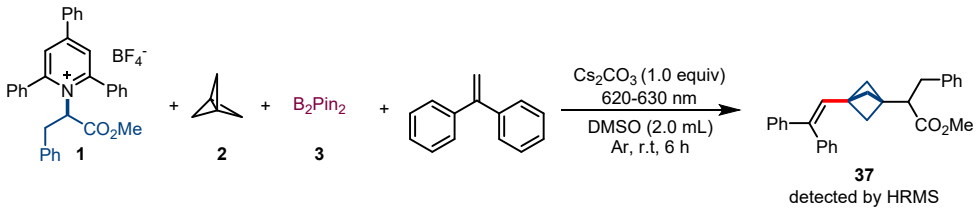
5. Mechanistic Investigations.

5.1 Radical-Trapping Experiments

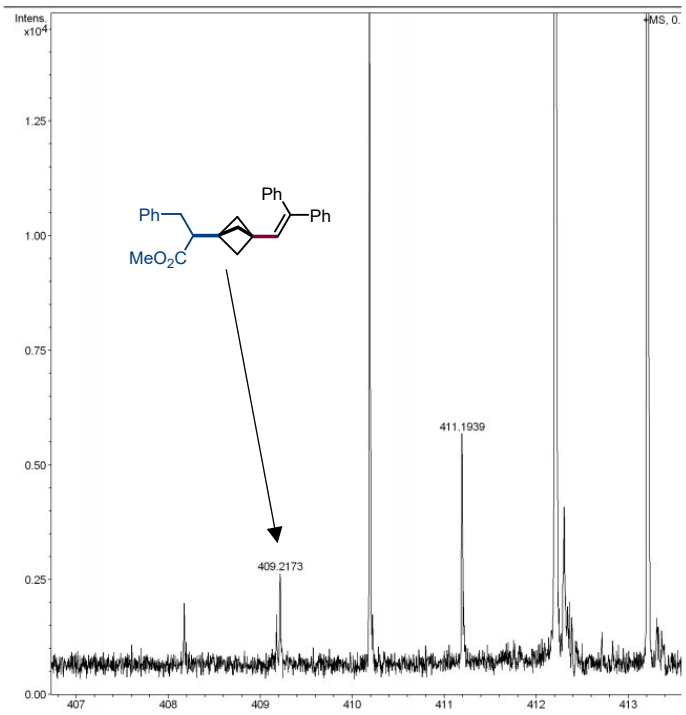


To an oven-dried 10 mL glass storage tube with a stir bar were added Cs_2CO_3 (0.1 mmol, 1.0 equiv), B_2Pin_2 (0.3 mmol, 3.0 equiv), Katritzky salt **1** (0.2 mmol, 2.0 equiv) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (0.25 mmol, 2.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.1 mmol) and DMSO (2.0 mL) were added via a syringe. The reaction mixture was placed in a photo-parallel reactor. The mixture was stirred and irradiated for 6 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography. The 2,4,6-triphenylpyridine was obtained by silica gel column chromatography (Petroleum ether/EtOAc = 100:1) as a white solid (20.8 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.6 Hz, 4H), 7.91 (s, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.58-7.43 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.3, 139.7, 139.2, 129.2, 129.1, 129.0, 128.8, 127.3, 127.2, 117.2. And the *α*-ester radical-trapping product **36** was detected by high-resolution mass spectrometry. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{29}NO_3$ 320.2220, found 320.2216.

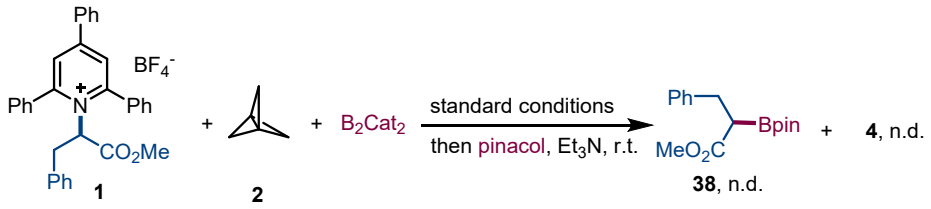




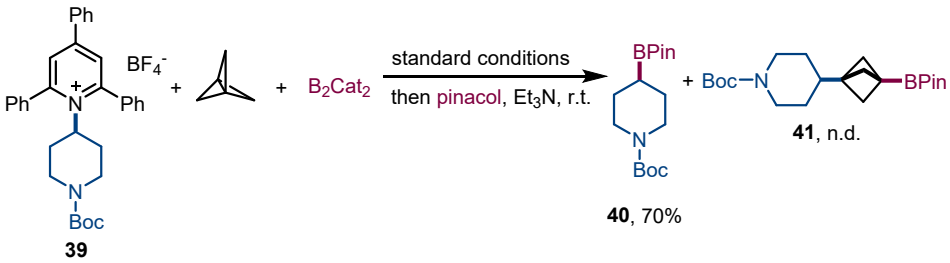
To an oven-dried 10 mL glass storage tube with a stir bar were added Cs_2CO_3 (0.1 mmol, 1.0 equiv), B_2Pin_2 (0.3 mmol, 3.0 equiv), Katritzky salt **1** (0.2 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.1 mmol), 1,1-diphenylethylene (0.25 mmol, 2.5 equiv) and DMSO (2.0 mL) were added via a syringe. The reaction mixture was placed in a photo-parallel reactor. The mixture was stirred and irradiated for 6 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The BCP radical-trapping product **37** was detected by high-resolution mass spectrometry. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{28}O_2$ 409.2162, found 409.2137.



5.2 Reaction with B_2Cat_2



To an oven-dried 10 mL glass storage tube with a stir bar were added Katritzky salt **1** (0.1 mmol, 1.0 equiv), Cs_2CO_3 (0.1 mmol, 1.0 equiv), B_2Cat_2 (0.15 mmol, 1.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.1 mmol) and DMAc (1.0 mL) were added via a syringe. The reaction mixture was placed in a photo-parallel reactor. The mixture was stirred and irradiated for 16 hours. The average temperature of reaction mixture was room temperature without extra heating. Then pinacol (106.2 mg, 0.9 mmol, 9.0 equiv) in Et_3N (133 µL) was added and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Compound **4** and **38** were not detected.

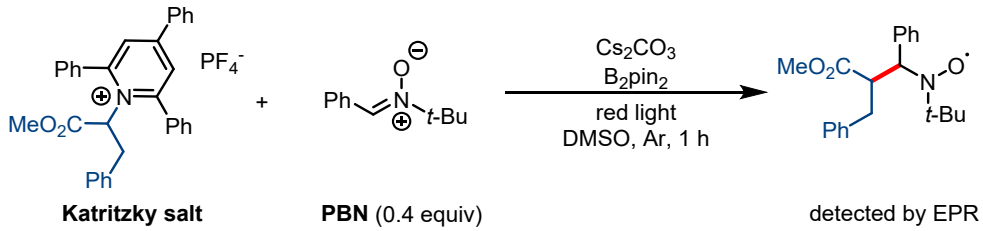


To an oven-dried 10 mL glass storage tube with a stir bar were added Katritzky salt **39** (0.1 mmol, 1.0 equiv), Cs_2CO_3 (0.1 mmol, 1.0 equiv), B_2Cat_2 (0.15 mmol, 1.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.1 mmol) and DMAc (1.0 mL) were added via a syringe. The reaction mixture was placed in a photo-parallel reactor. The mixture was stirred and irradiated for 16 hours. The average temperature of reaction mixture was room temperature without extra heating. Then pinacol (106.2 mg, 0.9 mmol, 9.0 equiv) in Et_3N (133 µL) was added and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Compound **41** were not detected. The product **40** was purified by column chromatography (Petroleum ether/EtOAc = 12:1). The product **40** was obtained as a colorless oil. (13.0 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 2H), 2.90 (t, J = 10.8 Hz, 2H), 1.69 – 1.54 (m, 2H), 1.51 – 1.38 (m, 11H), 1.21 (s, 12H), 1.11 – 1.05 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 83.2, 79.1, 44.6, 28.6, 27.1, 24.9, 19.9.

5.3 Photoinduced EPR studies



In a nitrogen-filled glove box, Katritzky salt (0.1 mmol, 55.7 mg), Cs_2CO_3 (0.1 mmol, 1.0 equiv), B_2pin_2 (0.1 mmol), PBN (0.04 mmol, 7.1 mg) were added in an oven-dried 10 mL storage tube with a magnetic stir bar, anhydrous DMSO (2.0 mL) was added subsequently. The tube was sealed with the Teflon screw valve and removed from the glovebox. After the mixture was irradiated with 50 W red LEDs (620-630 nm) for 1

hour, the tube was moved back to glove box. The reaction solution (approximately 100 μL) was transferred to an oven-dried EPR tube and sealed with a rubber cap, then removed from the glove box. The EPR spectrum was recorded at room temperature.

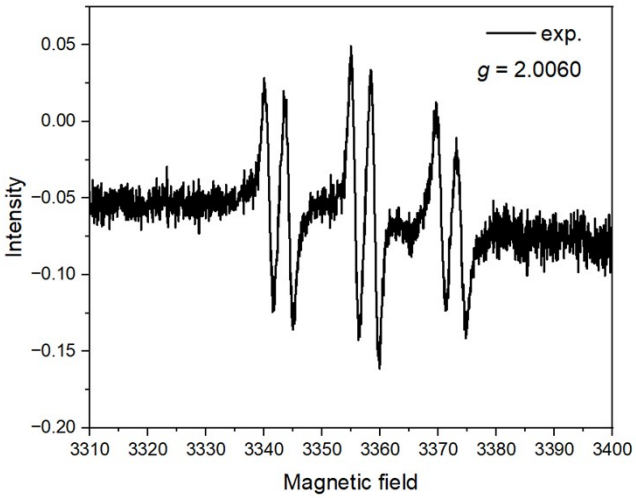


Figure S5. EPR spectrum of carbon radical trapped by PBN

5.4 UV-vis Spectroscopic Analysis

UV/vis absorption spectra of 0.1 M in 5 mL DMSO solutions of the following freshly prepared sample were recorded in 1.0 cm path quartz cuvettes: Katritzky salt **1**-B_2Pin_2-Cs_2CO_3-[1.1.1]propellane(2:3:1:1). As Cs_2CO_3 could not completely dissolve, the corresponding sample solutions were filtered prior to the measurement

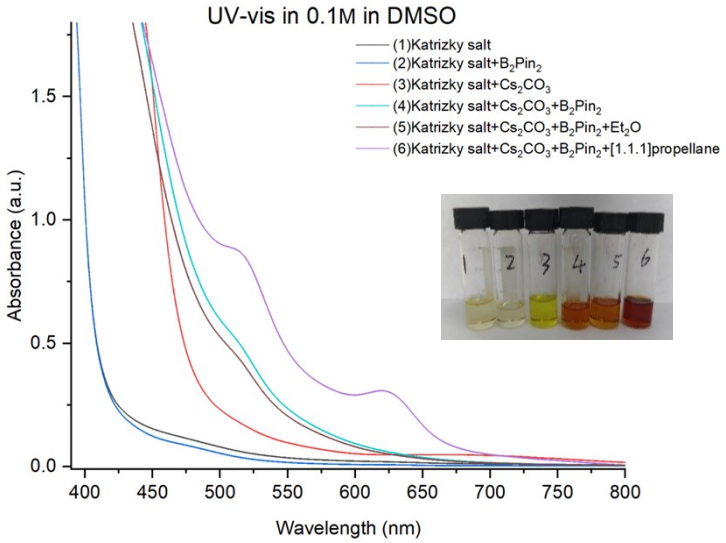


Figure S6. UV−vis absorption spectra of each species and their mixtures

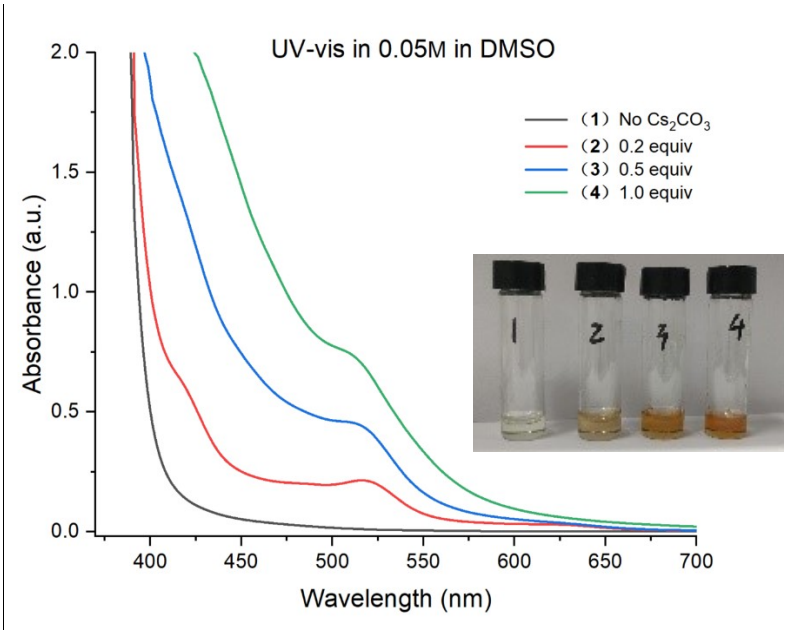


Figure S7. UV−vis absorption spectra of each species and their mixtures

5.5 On-OFF Experiment

Standard reactions were set up parallel on a 0.2 mmol scale according to the standard condition. After being irradiated for 1 h. The reaction mixture was added with 1,3,5-trimethoxylbenzene (0.1 mmol) and diluted with EtOAc, then the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The Yield was determined by ^1H NMR analysis using 1,3,5-trimethoxylbenzene as internal standard. Then the reaction mixture was stirred for 1 h with light-off. All of the following yields were analyzed in the identical way after 1 hour light on or off.

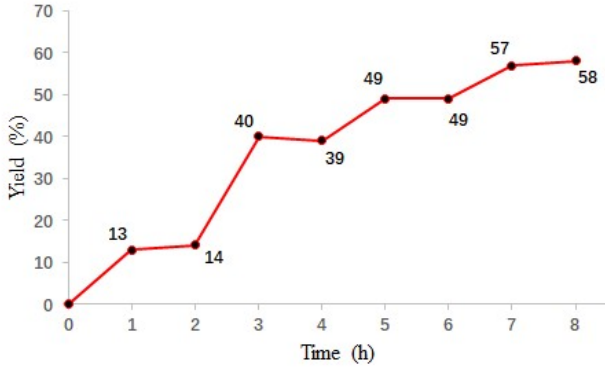


Figure S8. Time profile of the transformation with the light ON/OFF over time.

5.6 ^{11}B NMR spectra.

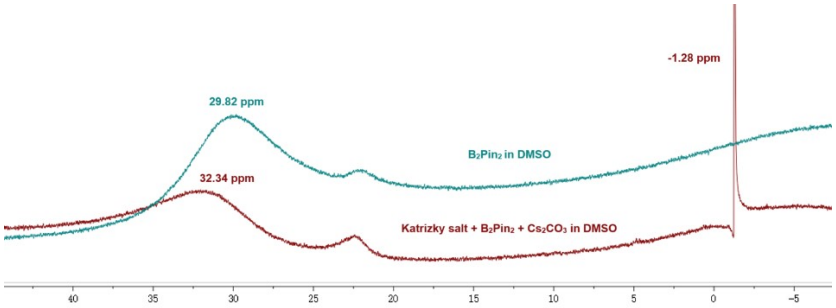


Figure S9. ^{11}B NMR spectra.

6. References.

(1) F. J. R. Klauck, M. J. James, F. Glorius. *Angew. Chem. Int. Ed.* 2017, **56**, 12336−12339.

(2) I. Kim, H. Im, H. Lee, S. Hong. *Chem. Sci.* 2020, **11**, 3192−3197.

(3) S. Z. Sun, Y. M. Cai, D. L. Zhang, J. B. Wang, H. Q. Yao, X. Y. Rui, R. Martin, M. Shang. *J. Am. Chem. Soc.* 2022, **144**, 1130−1137.

(4) M. E. Hoerrner, K. M. Baker, C. H. Basch, E. M. Bampo, M. P. Watson. *Org. Lett.* 2019, **21**, 7356−7360.

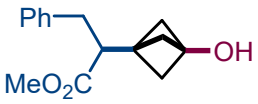
(5) I. F. Yu, J. L. Manske, A. Diéguez-Vázquez, A. Misale, A. E. Pashenko, P. K. Mykhailiuk, S. V. Ryabukhin, D. M. Volochnyuk, J. F. Hartwig. *Nat. Chem.* 2023, **15**, 685−693.

(6) W. Z. Dong, E. Yen-Pon, L. B. Li, A. Bhattacharjee, A. Jolit, G. A. Molander. *Nat. Chem.* 2022, **14**, 1068−1077.

(7) J. K. Matsui, D. N. Primer, G. A. Molander. *Chem. Sci.* 2017, **8**, 3512−3522.

(8) J. Yi, S. O. Badir, R. Alam, G. A. Molander. *Org. Lett.* 2019, **21**, 4853−4858.

7. Spectra of Synthesized Compounds.

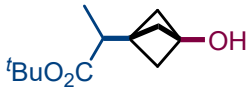


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (5): The product **5** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (47.2 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.15 – 7.04 (m, 3H), 3.51 (s, 3H), 2.96 – 2.80 (m, 2H), 2.72 – 2.58 (m, 1H), 1.78 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 139.3, 128.8, 128.5, 126.5, 62.5, 53.4, 51.6, 46.8, 35.9, 32.0.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{18}O_3$ 269.1148, found 269.1150.

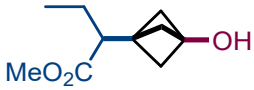


***Tert*-butyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)propanoate (6):** The product **6** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (14.0 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (q, *J* = 7.0 Hz, 1H), 1.82 (s, 6H), 1.44 (s, 9H), 1.05 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 80.4, 62.6, 52.9, 39.7, 32.5, 28.3, 14.3.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{20}O_3$ 235.1305, found 235.1309.

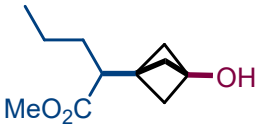


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)butanoate (7): The product **7** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 5:1) as a colorless oil (29.2 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.93 (br, 1H), 2.49 (dd, *J* = 10.2, 4.5 Hz, 1H), 1.88 – 1.72 (m, 6H), 1.67 – 1.54 (m, 1H), 1.50 – 1.36 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 62.4, 53.3, 51.5, 46.7, 31.9, 23.1, 12.4.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{16}O_3$ 207.0992, found 207.0998.

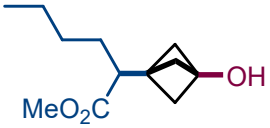


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)pentanoate (8): The product **8** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (34.4 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (d, *J* = 1.5 Hz, 3H), 2.69 (br, 1H), 2.62 – 2.55 (m, 1H), 1.80 (q, *J* = 9.4 Hz, 6H), 1.64 – 1.54 (m, 1H), 1.38 – 1.21 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 62.5, 53.3, 51.5, 44.8, 32.0, 31.9, 21.1, 14.1.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{18}O_3$ 221.1148, found 221.1155.

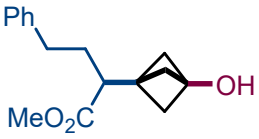


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)hexanoate (9): The product **9** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 5:1) as a yellow oil (21.0 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.61 – 2.54 (m, 1H), 1.88 – 1.77 (m, 6H), 1.66 – 1.57 (m, 1H), 1.39 – 1.13 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 53.3, 51.5, 45.0, 31.9, 30., 29.61, 22.7, 14.1.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{20}O_3$ 235.1305, found 235.1314.

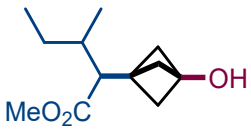


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-4-phenylbutanoate (10): The product **10** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 5:1) as a yellow oil (30.5 mg, 39% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.14 (m, 3H), 3.69 (s, 3H), 2.69 – 2.58 (m, 3H), 2.56 – 2.48 (m, 1H), 2.00 – 1.93 (m, 1H), 1.88 – 1.75 (m, 6H), 1.70 – 1.65 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 141.6, 128.5, 126.1, 62.5, 53.3, 51.6, 44.5, 34.1, 31.9, 31.7.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{20}O_3$ 283.1305, found 283.1313.



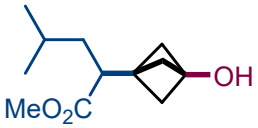
Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-3-methylpentanoate (11): The product **11** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (21.7 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (d, *J* = 1.8 Hz, 3H), 2.72 (br, 1H), 2.49 (dd, *J* = 28.8, 7.5 Hz, 1H), 1.95 – 1.82 (m, 6H), 1.77 – 1.44 (m, 2H), 1.43 – 1.27 (m, 1H), 1.19 – 1.00 (m, 1H), 0.98 – 0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 174.0, 62.8, 62.7, 54.5, 54.3, 51.3, 51.2, 50.6, 49.2,

36.2, 36.0, 31.2, 31.1, 27.6, 17.2, 16.9, 11.3, 11.1.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{20}O_3$ 235.1305, found 235.1304.

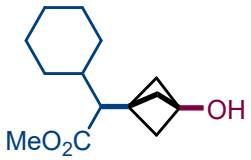


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-4-methylpentanoate (12): The product **12** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (31.2 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.68 (dd, *J* = 10.8, 4.0 Hz, 1H), 1.80 (q, *J* = 9.4 Hz, 6H), 1.66 – 1.57 (m, 1H), 1.55 – 1.42 (m, 1H), 1.19 – 1.08 (m, 1H), 0.87 (t, *J* = 5.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 62.6, 53.2, 51.5, 42.9, 38.8, 32.1, 26.5, 23.4, 21.9.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{20}O_3$ 235.1305, found 235.1307.

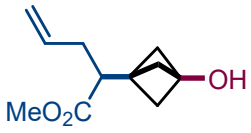


Methyl 2-cyclohexyl-2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)acetate (13): The product **13** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (38.5 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (s, 3H), 2.40 (d, *J* = 8.1 Hz, 1H), 1.95 – 1.79 (m, 7H), 1.78 – 1.48 (m, 6H), 1.21 – 1.10 (m, 2H), 1.02 – 0.89 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 62.8, 54.5, 51.2, 51.1, 39.3, 31.7, 31.2, 31.0, 26.3, 26.2.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{22}O_3$ 261.1461, found 261.1469.



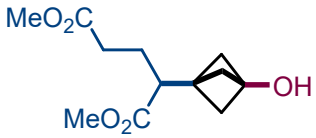
Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)pent-4-enoate (14): The product **14** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 5:1) as a yellow oil (18.8 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.63 (m, 1H), 5.10 – 4.93 (m, 2H), 3.66 (s, 3H), 2.76 – 2.67 (m, 1H), 2.56 (br, 1H), 2.41 – 2.30 (m, 1H), 2.22 – 2.11 (m, 1H), 1.83 (q, *J* = 9.4

Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 135.6, 116.8, 62.6, 53.4, 51.6, 44.7, 34.1, 31.8.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{16}O_3$ 219.0992, found 219.1001.

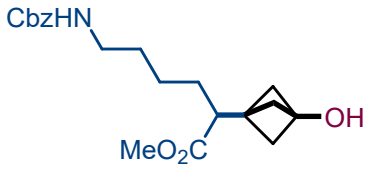


Dimethyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)pentanedioate (15): The product **15** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 2:1) as a yellow oil (24.7 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.66 (s, 3H), 2.69 – 2.61 (m, 1H), 2.39 – 2.21 (m, 2H), 1.94 – 1.74 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.5, 62.5, 53.3, 51.8, 51.7, 44.1, 32.1, 31.9, 24.9.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{18}O_5$ 265.1046, found 265.1051.

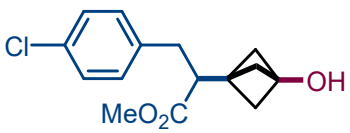


Methyl 6-(((benzyloxy)carbonyl)amino)-2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)hexanoate (16): The product **16** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 5:1) as a yellow solid (49.8 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 5.08 (s, 2H), 4.77 (s, 1H), 3.66 (s, 3H), 3.25 – 3.09 (m, 2H), 2.73 – 2.49 (m, 2H), 1.91 – 1.73 (m, 6H), 1.70 – 1.55 (m, 2H), 1.54 – 1.43 (m, 2H), 1.42 – 1.16 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 156.5, 136.7, 128.7, 128.2, 66.8, 62.5, 53.3, 51.6, 44.9, 40.9, 31.9, 29.9, 29.4, 25.0.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{27}NO_5$ 384.1781, found 384.1788.

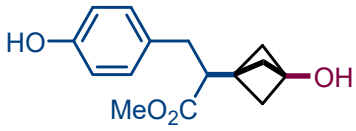


Methyl 3-(4-chlorophenyl)-2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)propanoate (17): The product **17** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a yellow oil (31.9 mg, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 3.58 (s, 3H), 2.96 – 2.85 (m, 2H), 2.73 – 2.64 (m, 1H), 1.90 – 1.79 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 137.8, 132.3, 130.2, 128.7, 62.5, 53.4, 51.6, 46.8, 35.3, 32.0.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{17}ClO_3$ 303.0758, found 303.0763.

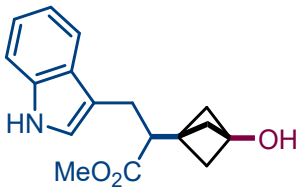


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-3-(4-hydroxyphenyl)propanoate (18): The product **18** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1) as a yellow solid (31.5 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.14 (br, 1H), 3.58 (s, 3H), 2.94 – 2.80 (m, 2H), 2.68 – 2.61 (m, 1H), 2.51 (br, 1H), 1.83 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 154.3, 131.3, 129.9, 115.4, 62.5, 53.4, 51.6, 47.2, 35.1, 31.9.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{18}O_4$ 285.1097, found 285.1098.

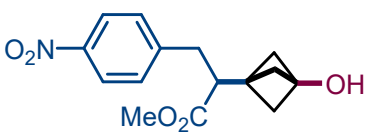


Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-3-(1*H*-indol-3-yl)propanoate (19): The product **19** was purified by silica gel column chromatography (DCM/Acetone = 20:1) as a yellow oil (55.6 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 3.58 (s, 3H), 3.15 – 3.05 (m, 2H), 2.93 – 2.83 (m, 1H), 1.95 – 1.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 136.3, 127.4, 122.1, 122.1, 119.4, 118.7, 113.5, 111.3, 62.4, 53.3, 51.6, 45.9, 32.1, 25.5.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{19}NO_3$ 308.1257, found 308.1265.



Methyl 2-(3-hydroxybicyclo[1.1.1]pentan-1-yl)-3-(4-nitrophenyl)propanoate (20): The product **20** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 3:1) as a yellow oil (20.1 mg, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.58 (s, 3H), 3.09 – 2.96 (m, 2H), 2.84 – 2.77 (m, 1H), 1.93 – 1.79 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 147.1, 146.9, 129.7, 123.8, 62.4, 53.4, 51.8, 46.5, 35.7, 32.1, 25.0.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{17}NO_5$ 314.0999, found 314.0991.

3-Isopropylbicyclo[1.1.1]pentan-1-ol (21): The product **21** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 10:1) as a yellow oil (13.3 mg, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 1H), 1.85 – 1.76 (m, 1H), 1.69 (s, 6H), 0.84 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.6, 51.4, 35.7, 29.8, 26.8, 19.7.

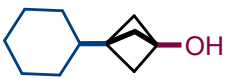
HRMS(EI-TOF) m/z: $[M]^{+\cdot}$ calcd for $C_8H_{14}O$ 126.1045, found 126.1042.

3-(*sec*-Butyl)bicyclo[1.1.1]pentan-1-ol (22): The product **22** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 10:1) as a yellow oil (16.8 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 1H), 1.71 (s, 6H), 1.56 – 1.48 (m, 1H), 1.44 – 1.35 (m, 1H), 1.04 – 0.95 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.7, 51.9, 35.3, 33.5, 27.1, 16.4, 12.3.

HRMS(EI-TOF) m/z: $[M]^{+\cdot}$ calcd for $C_9H_{16}O$ 140.1201, found 140.1195.

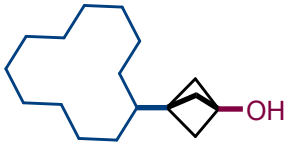


3-cyclohexylbicyclo[1.1.1]pentan-1-ol (23): The product **23** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 10:1) as a yellow oil (16.9 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 1H), 1.76 – 1.65 (m, 7H), 1.66 – 1.55 (m, 3H), 1.46 – 1.37 (m, 1H), 1.24 – 1.04 (m, 3H), 0.92 – 0.76 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.6, 51.6, 36.2, 34.6, 30.2, 26.3, 26.2.

HRMS(EI-TOF) m/z: $[M]^{+\cdot}$ calcd for $C_{11}H_{18}O$, 166.1358, found 166.1352.



3-Cyclododecylbicyclo[1.1.1]pentan-1-ol (24): The product **24** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 10:1) as a white solid (37.5 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 1H), 1.66 (s, 6H), 1.60 – 1.54 (m, 1H), 1.33 – 1.12 (m, 22H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 62.8, 52.5, 34.8, 31.9, 27.8, 24.4, 24.0, 24.0, 23.5, 23.2.

HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{30}O$ 273.2189, found 273.2297.

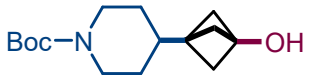
3-(3,3-difluorocyclobutyl)bicyclo[1.1.1]pentan-1-ol (25): The product **25** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 10:1) as a white soild (23.0 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 – 2.51 (m, 2H), 2.47 (s, 1H), 2.37 (q, J = 7.1, 5.8 Hz, 1H), 2.29 – 2.13 (m, 2H), 1.78 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 119.73 (dd, J = 284.3, 273.5 Hz), 38.39 (dd, J = 23.3, 21.6 Hz), 22.04 (dd, J = 12.6, 6.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -83.01 (d, J = 192.5 Hz), -95.32 (d, J = 191.9 Hz).

HRMS(EI-TOF) m/z: $[M]^{+\cdot}$ calcd for $C_9H_{12}F_2O$, 174.0856, found 174.0848.

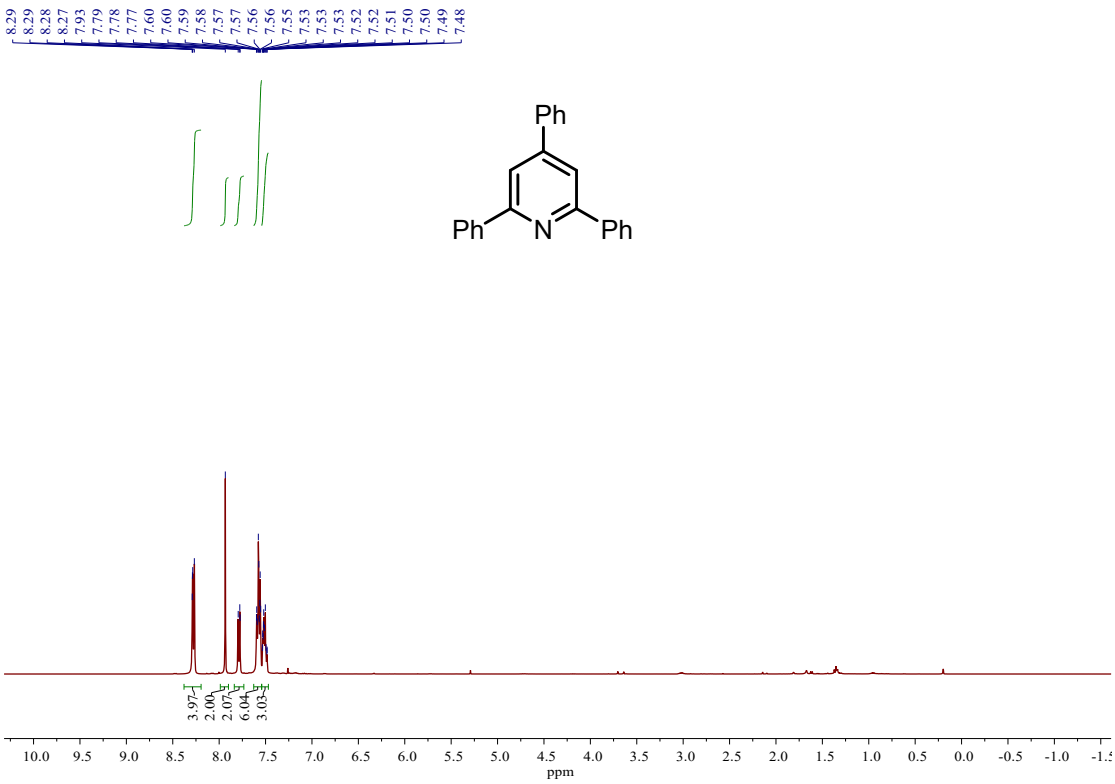


***Tert*-butyl 4-(3-hydroxybicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (26):** The product **26** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 5:1) as a colorless oil (33.6 mg, 42% yield).

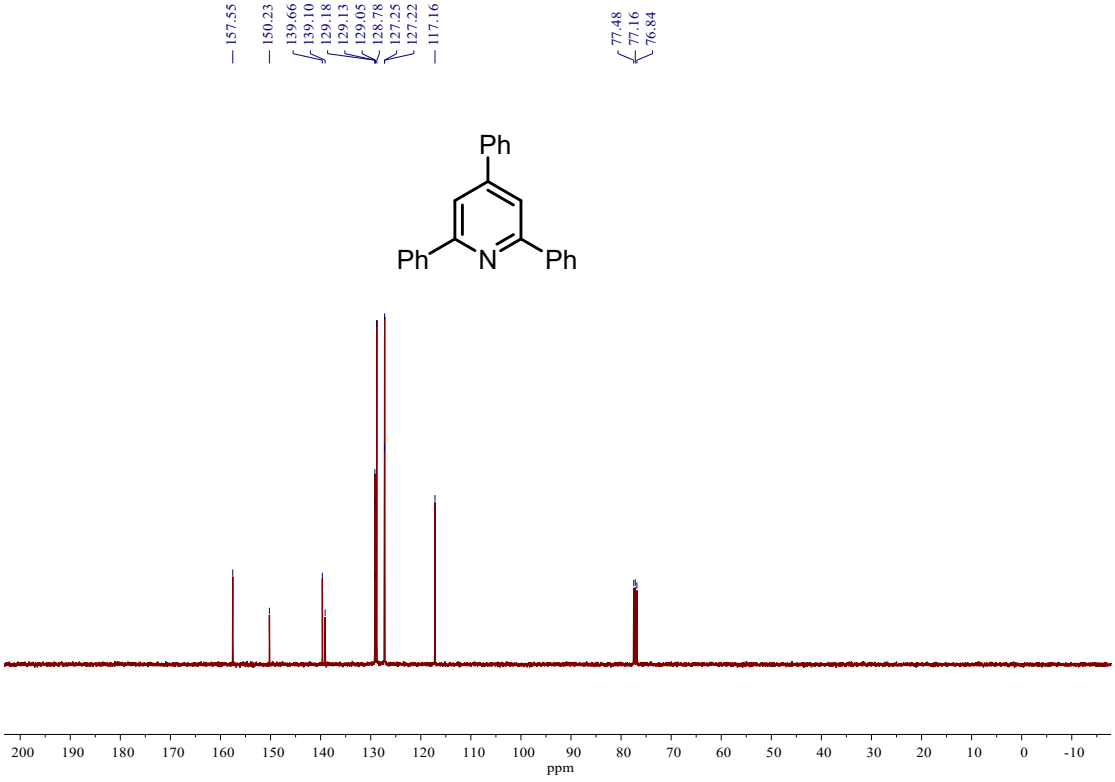
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 – 4.02 (m, 2H), 2.63 (t, *J* = 11.7 Hz, 2H), 1.71 (s, 6H), 1.61 – 1.52 (m, 3H), 1.44 (s, 9H), 1.11 – 0.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 79.5, 62.6, 51.7, 34.7, 34.1, 29.3, 28.6.

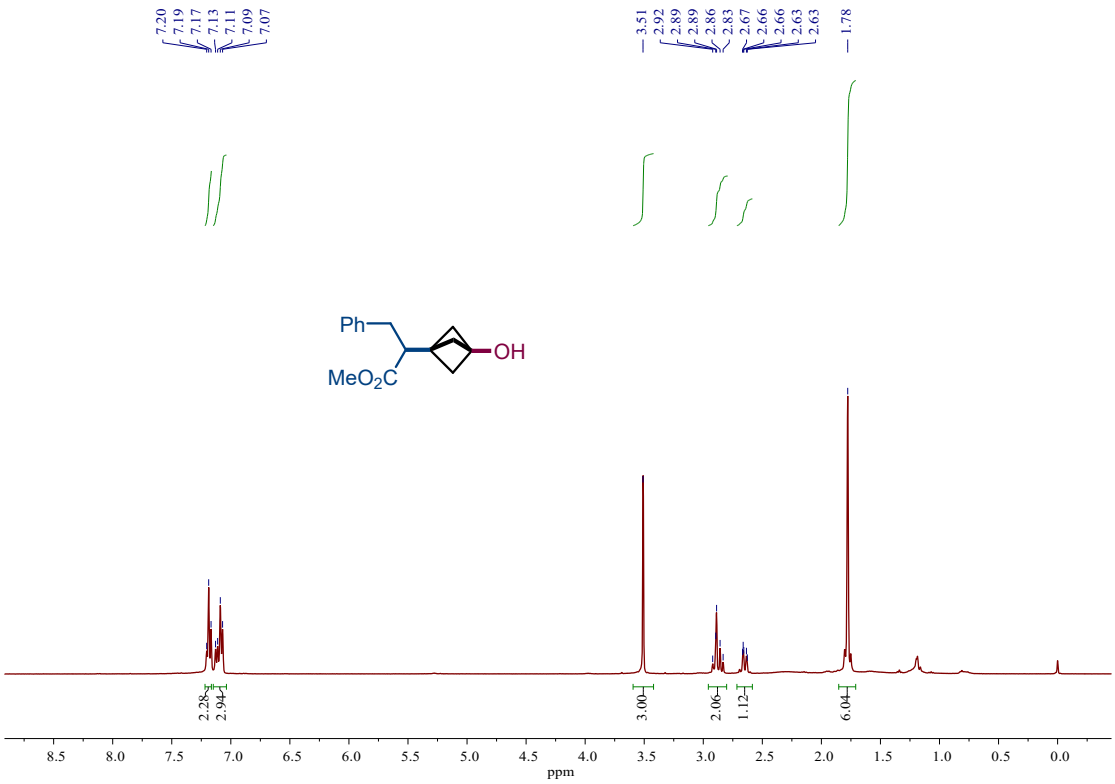
HRMS(APCI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{25}NO_3$ 290.1727, found 290.1733.



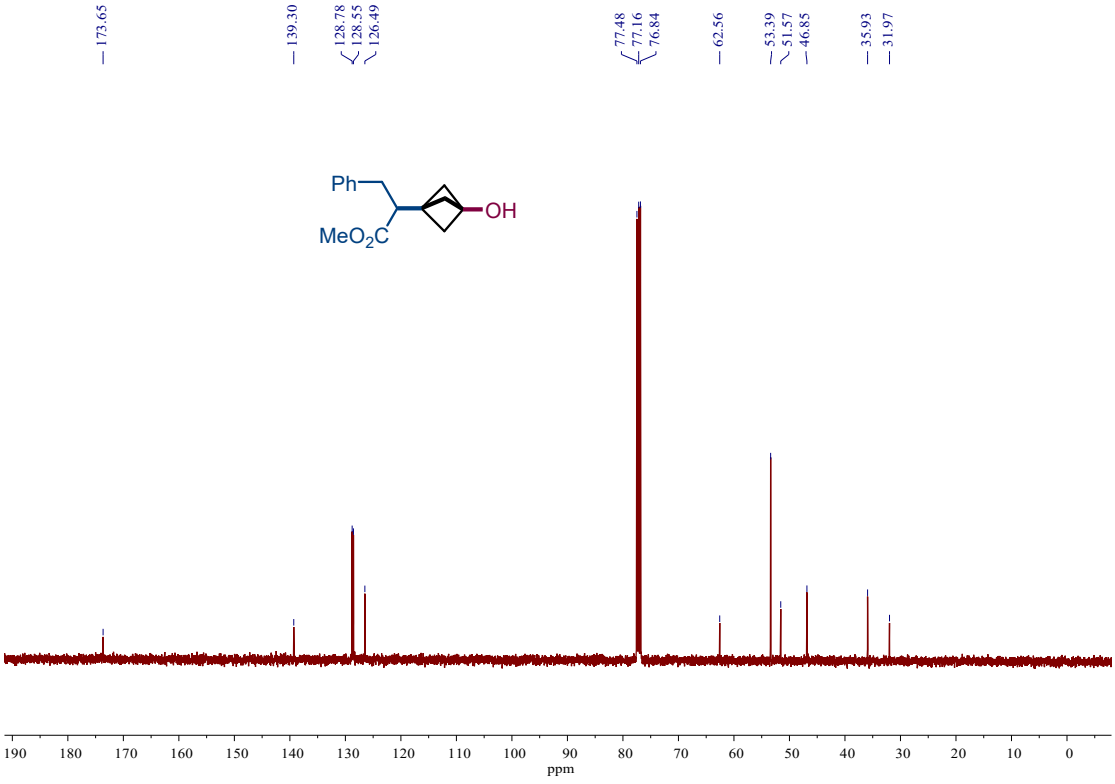
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2,4,6-triphenylpyridine



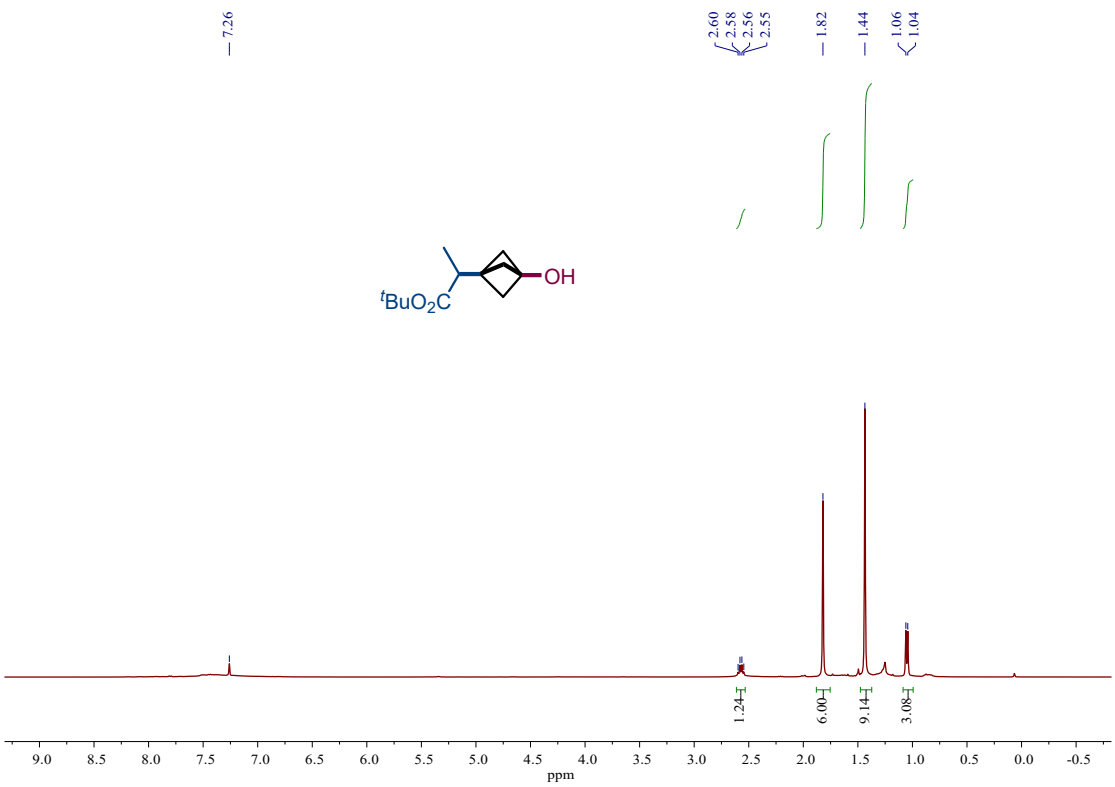
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2,4,6-triphenylpyridine



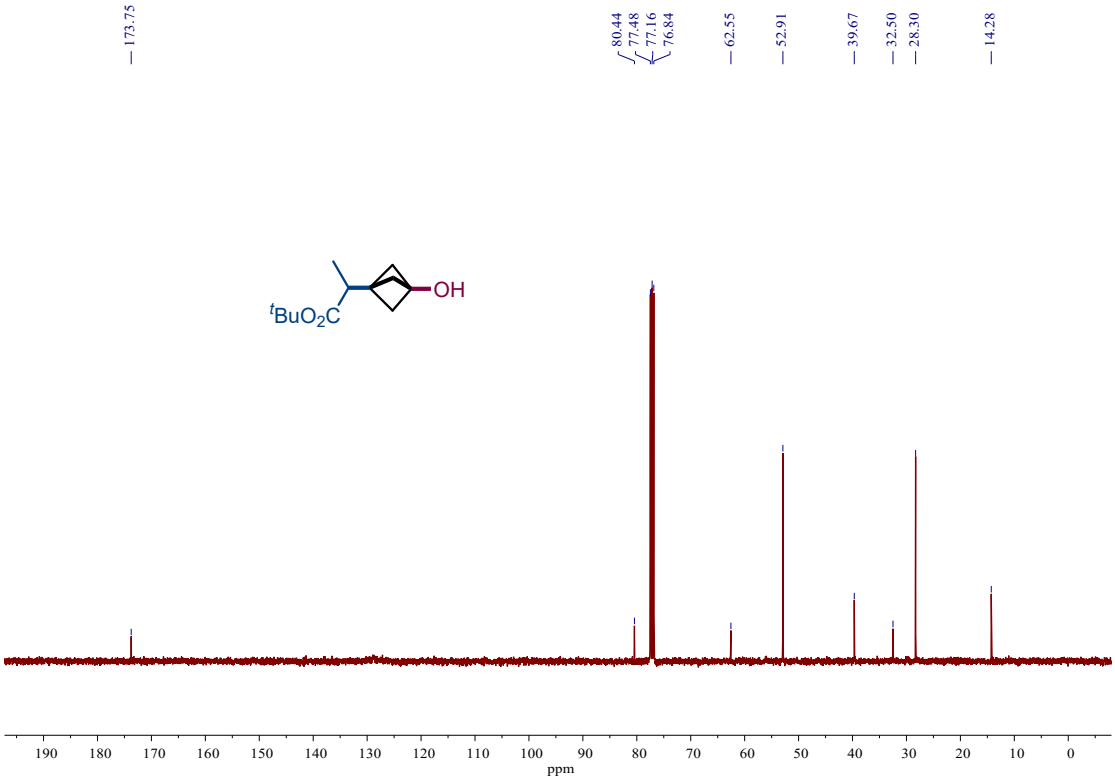
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5



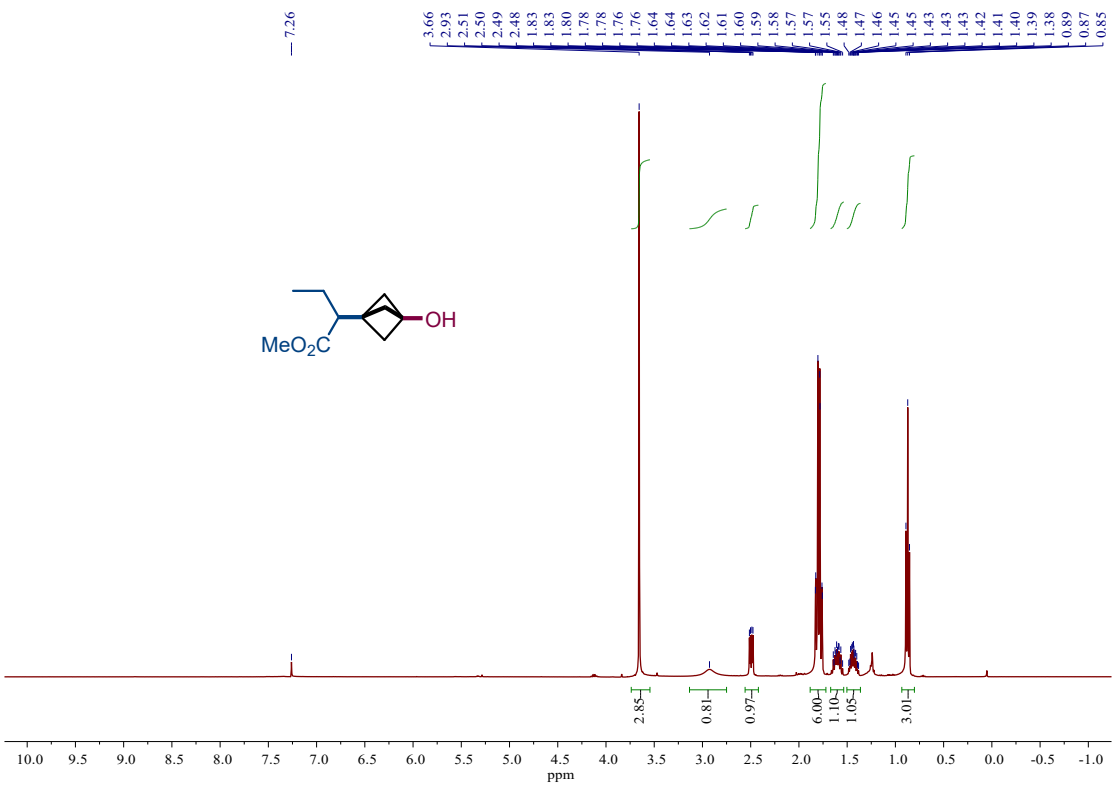
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5



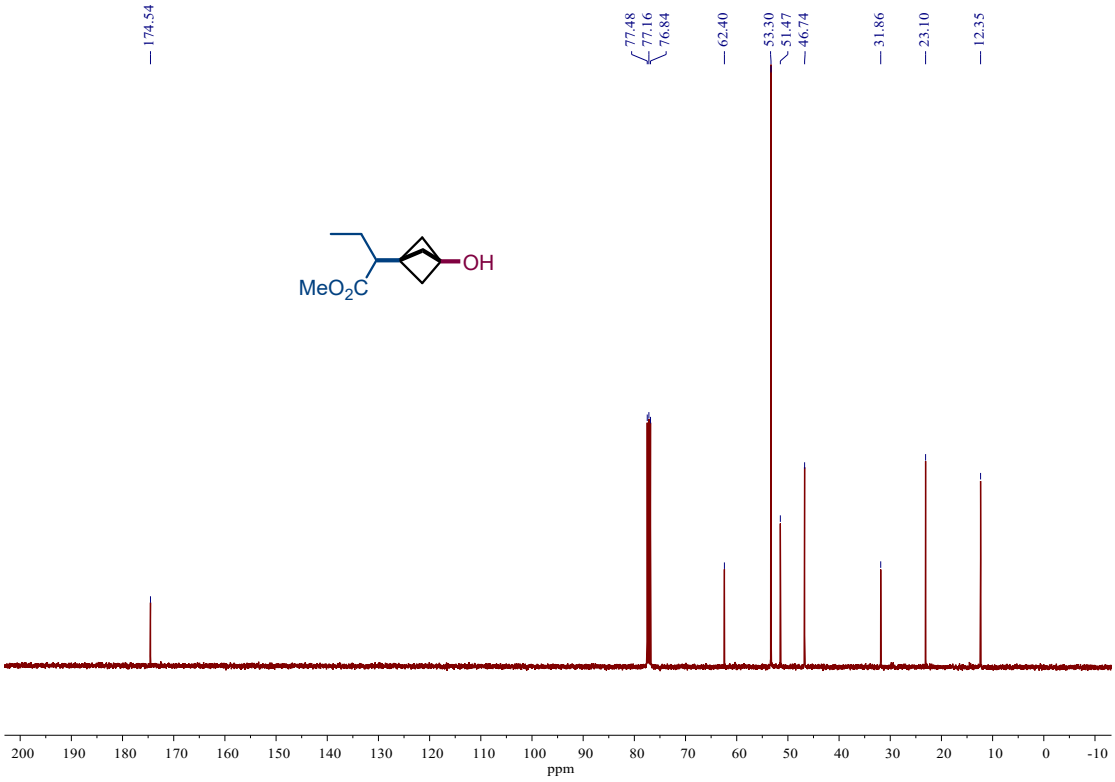
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6



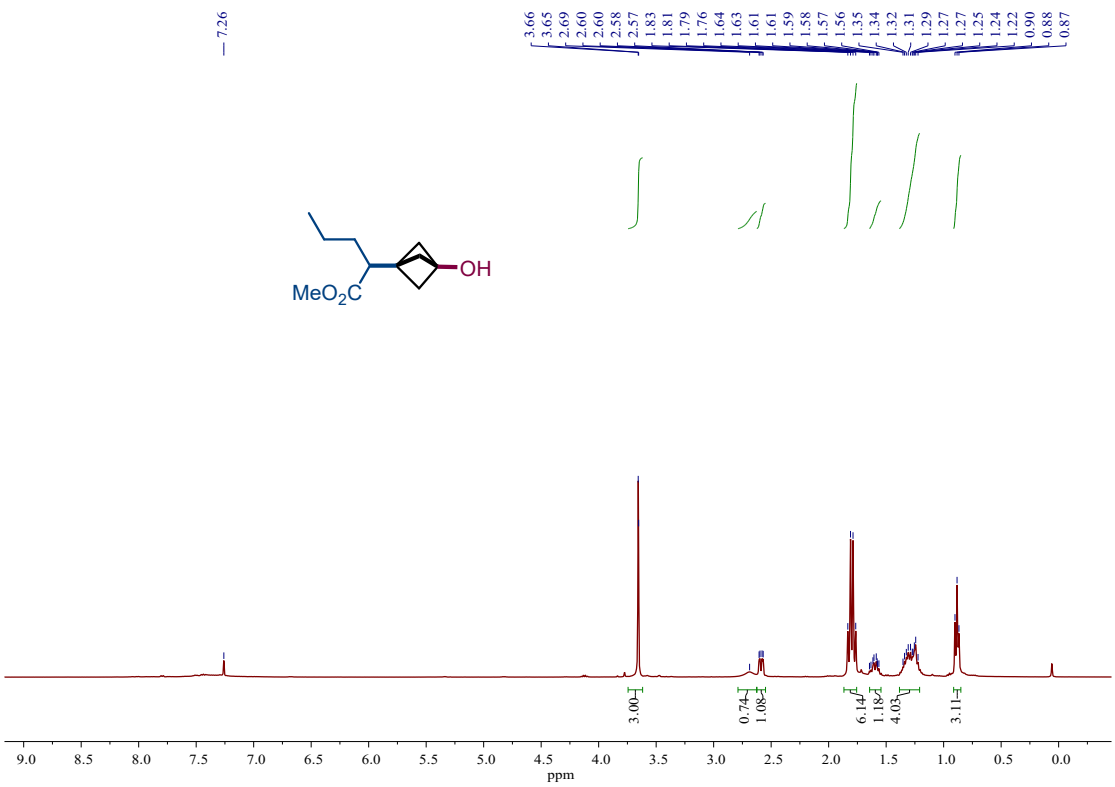
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 6



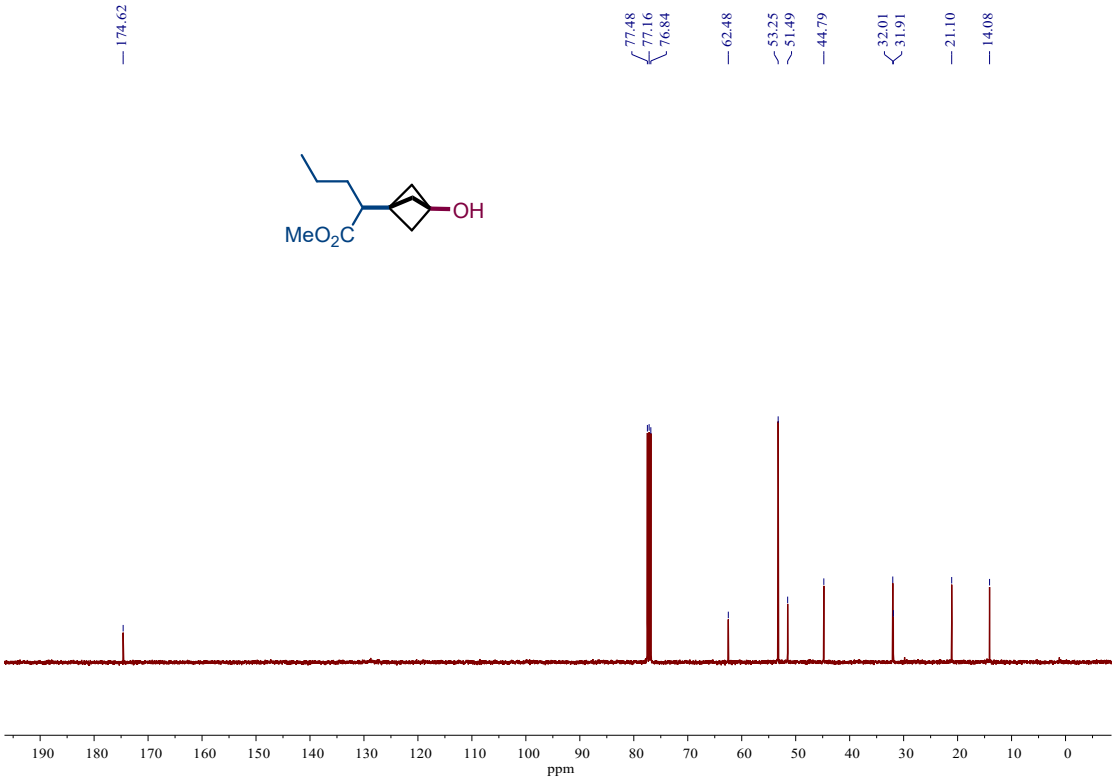
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 7



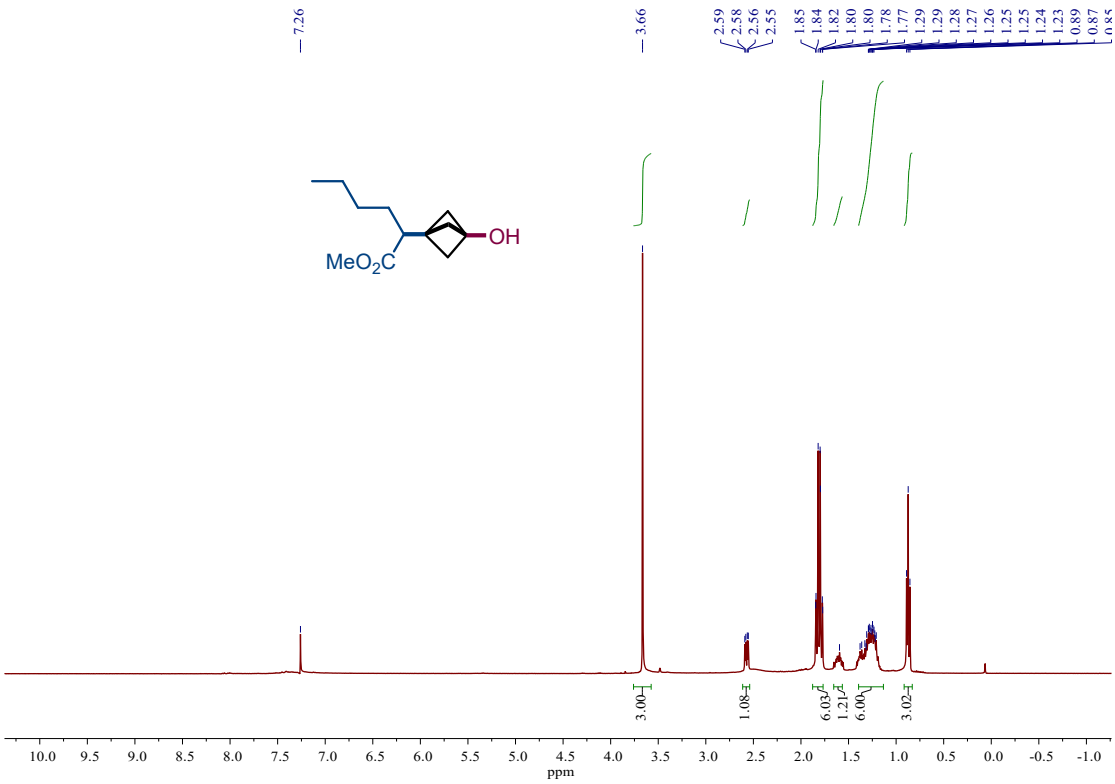
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 7



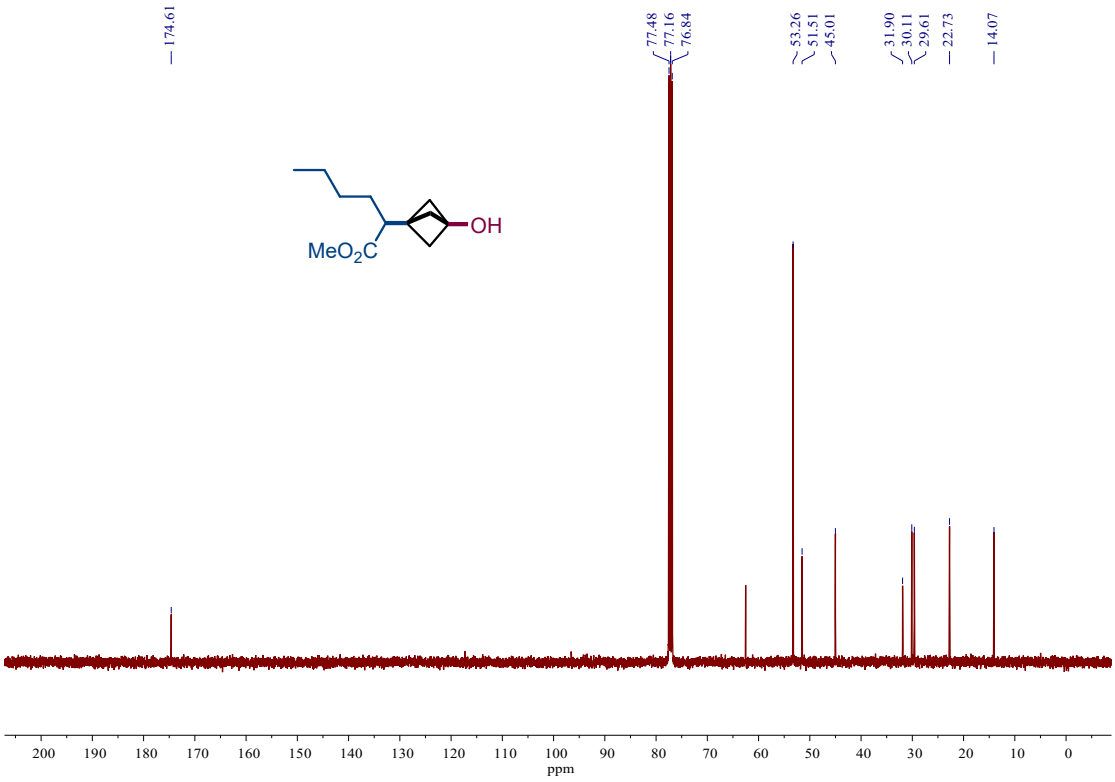
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 8



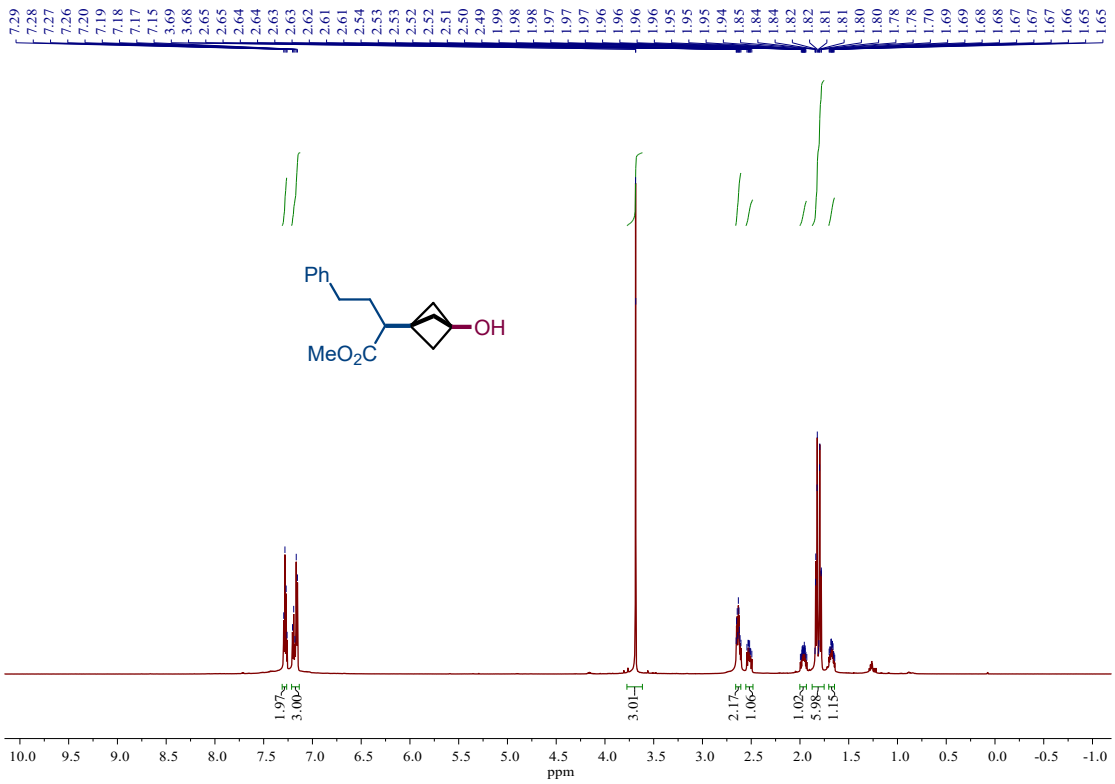
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 8



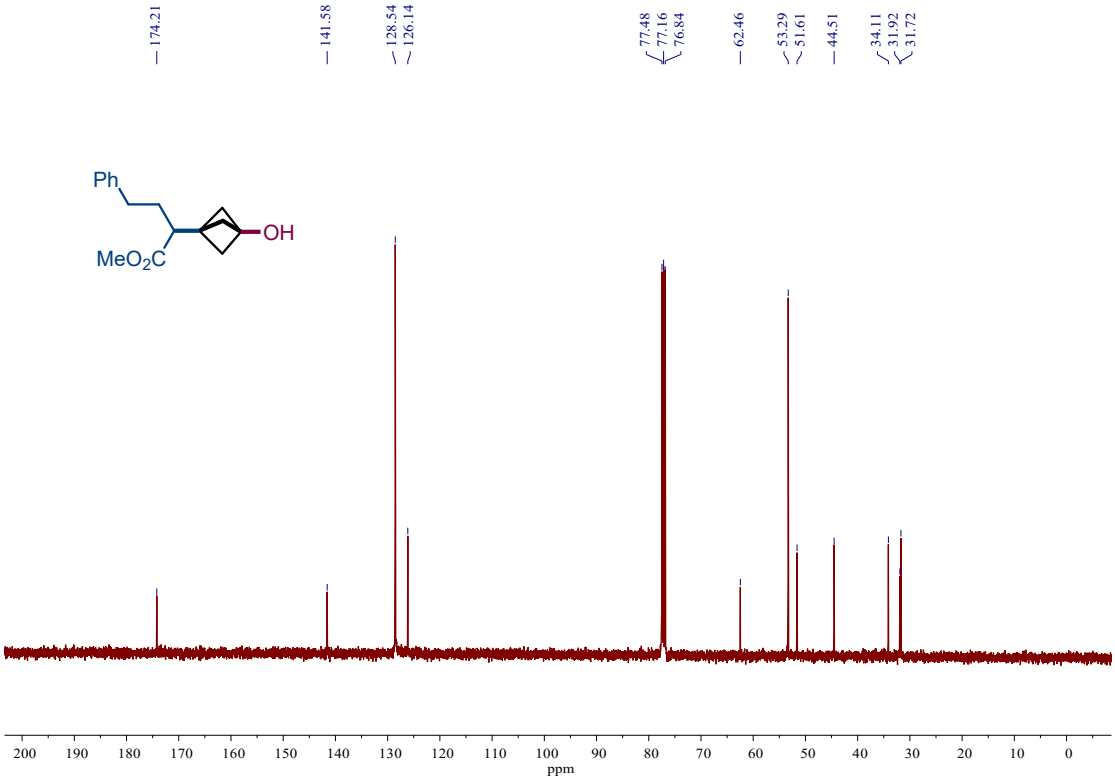
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 9



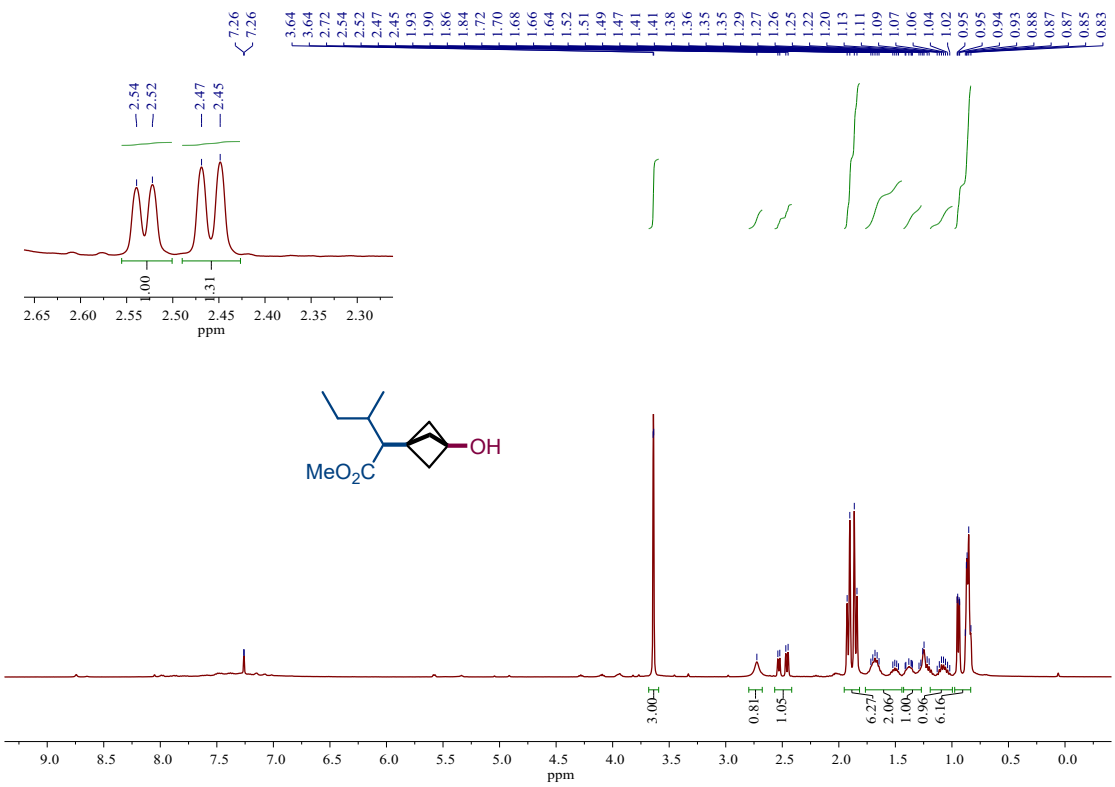
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 9



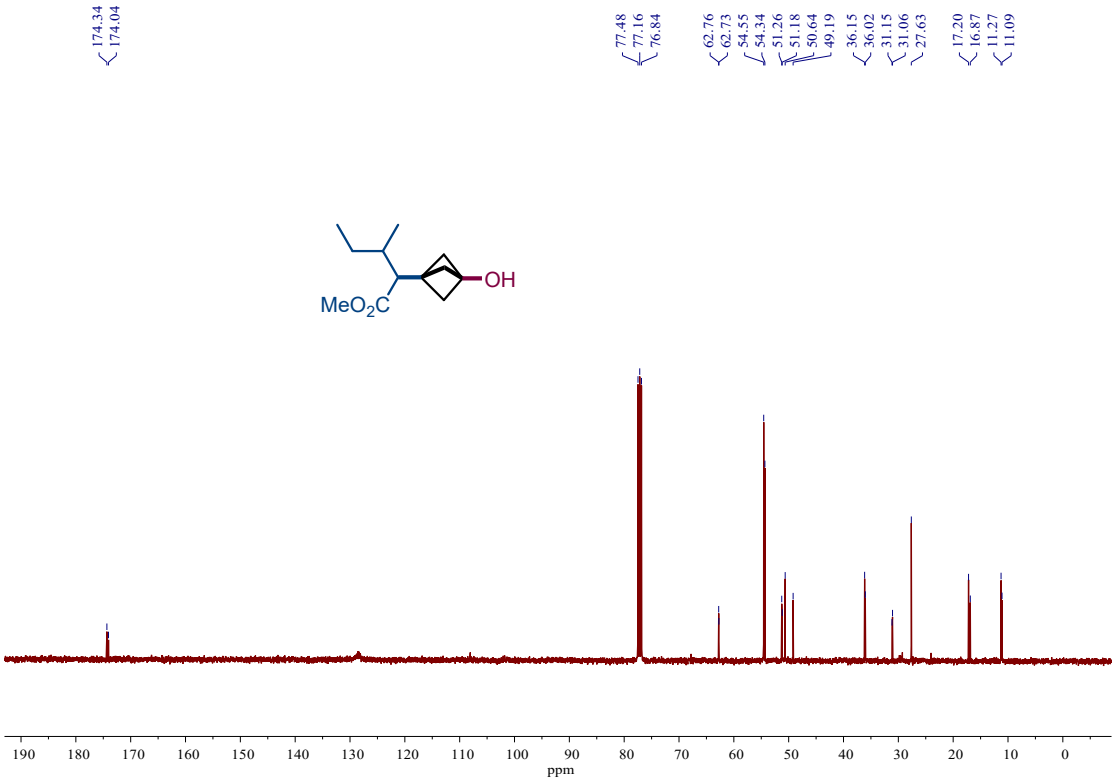
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 10



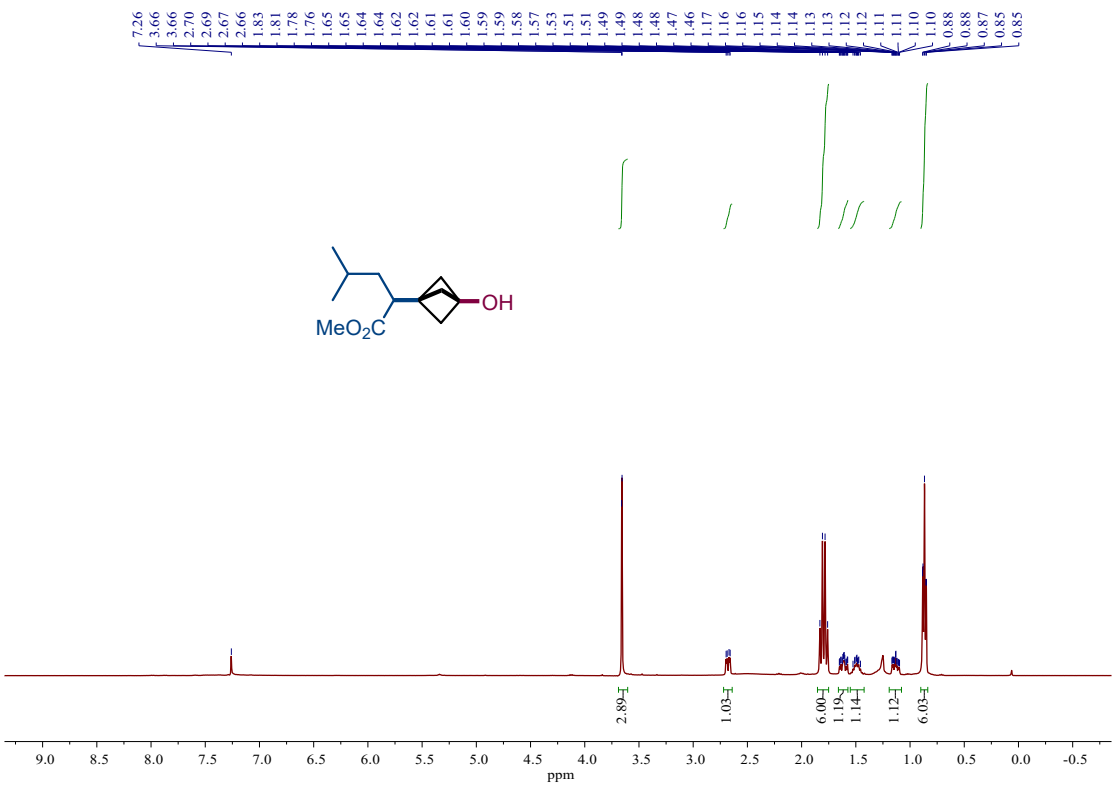
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 10



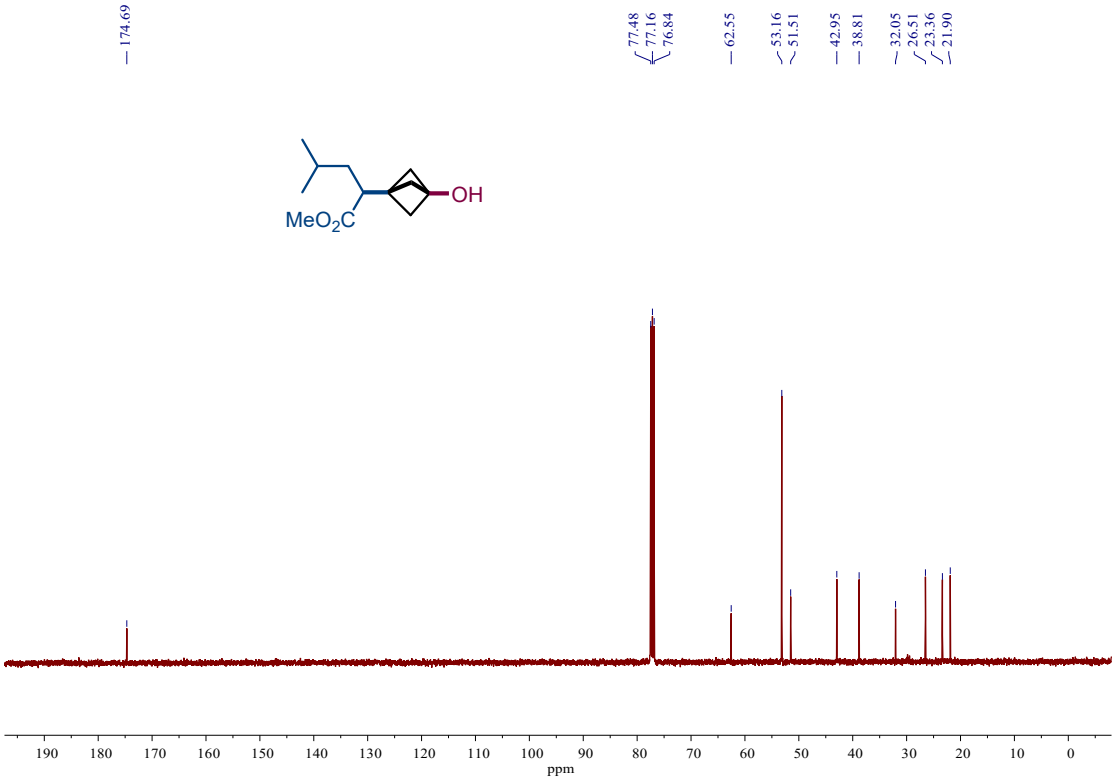
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 11



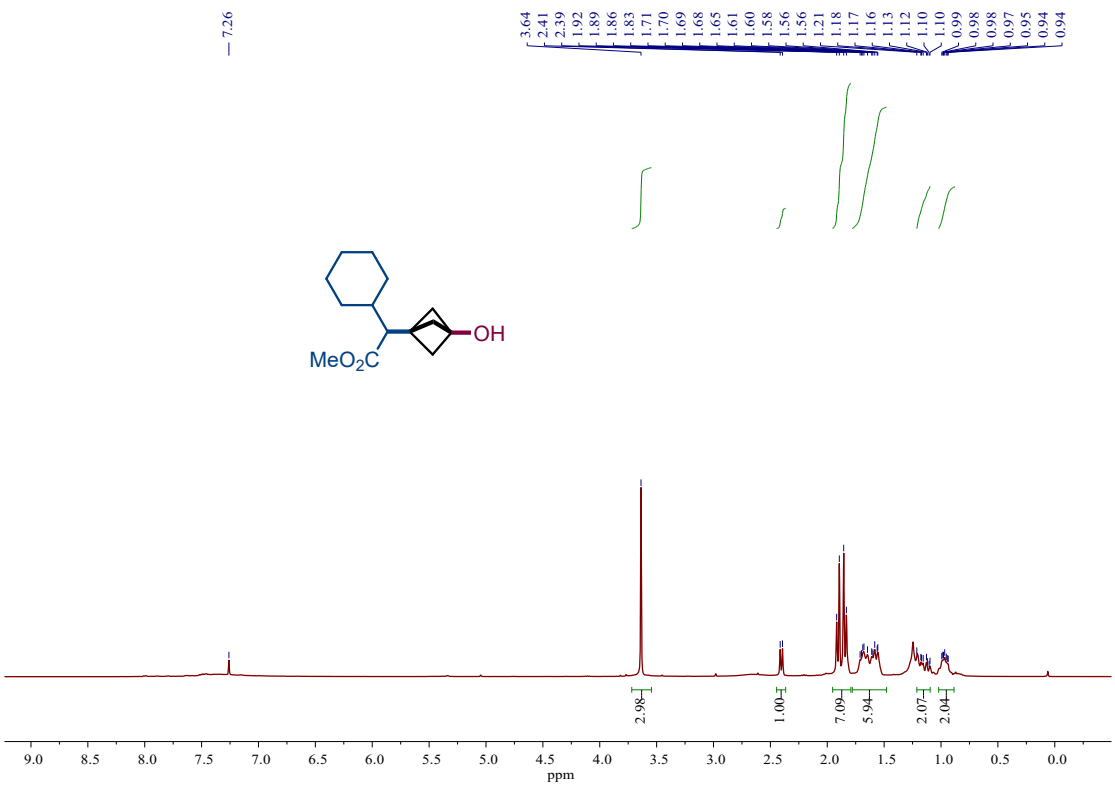
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 11



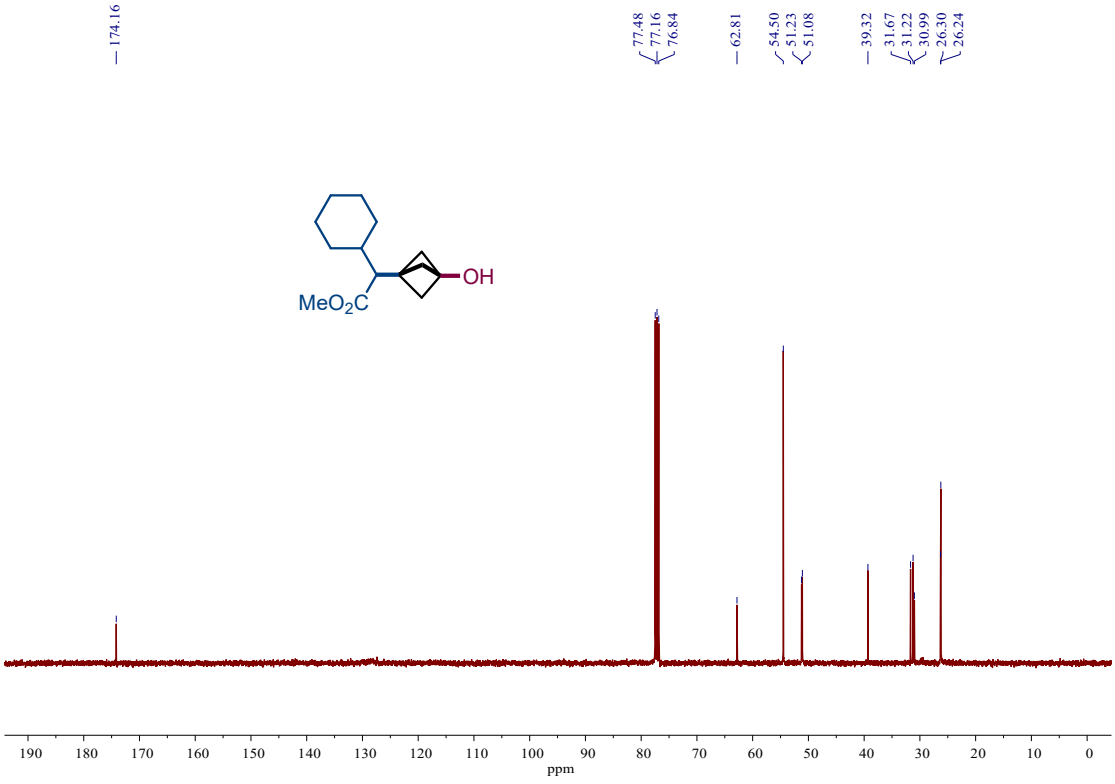
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 12



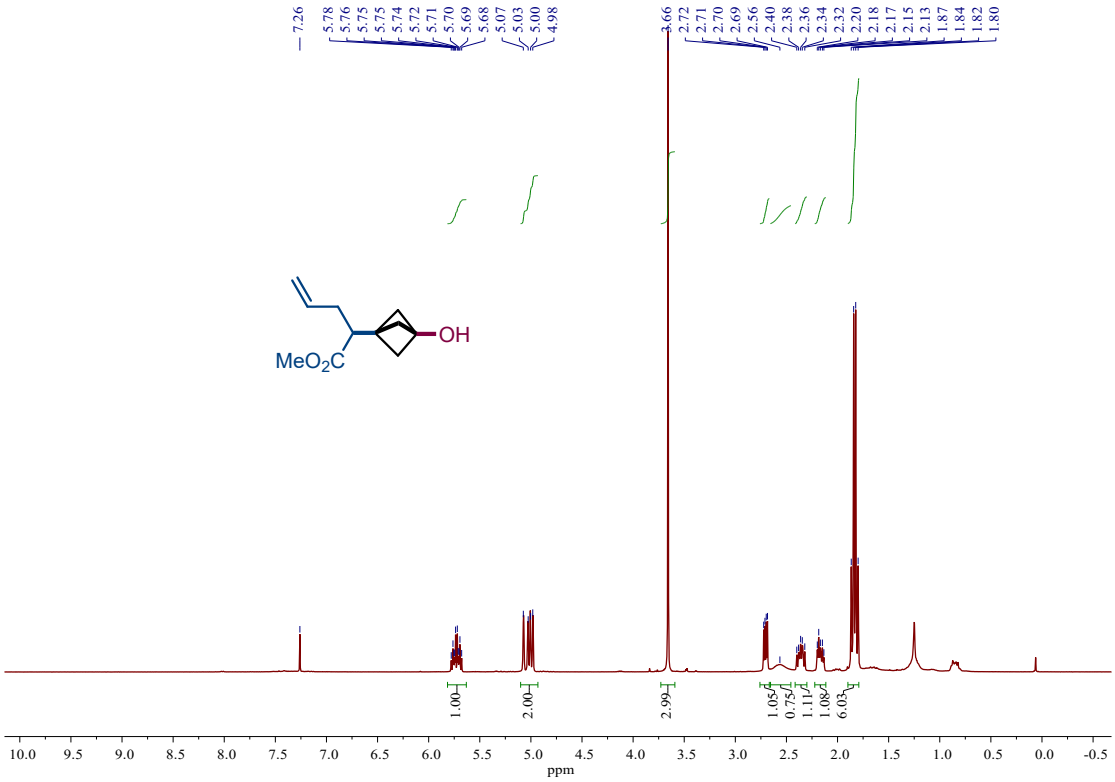
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 12



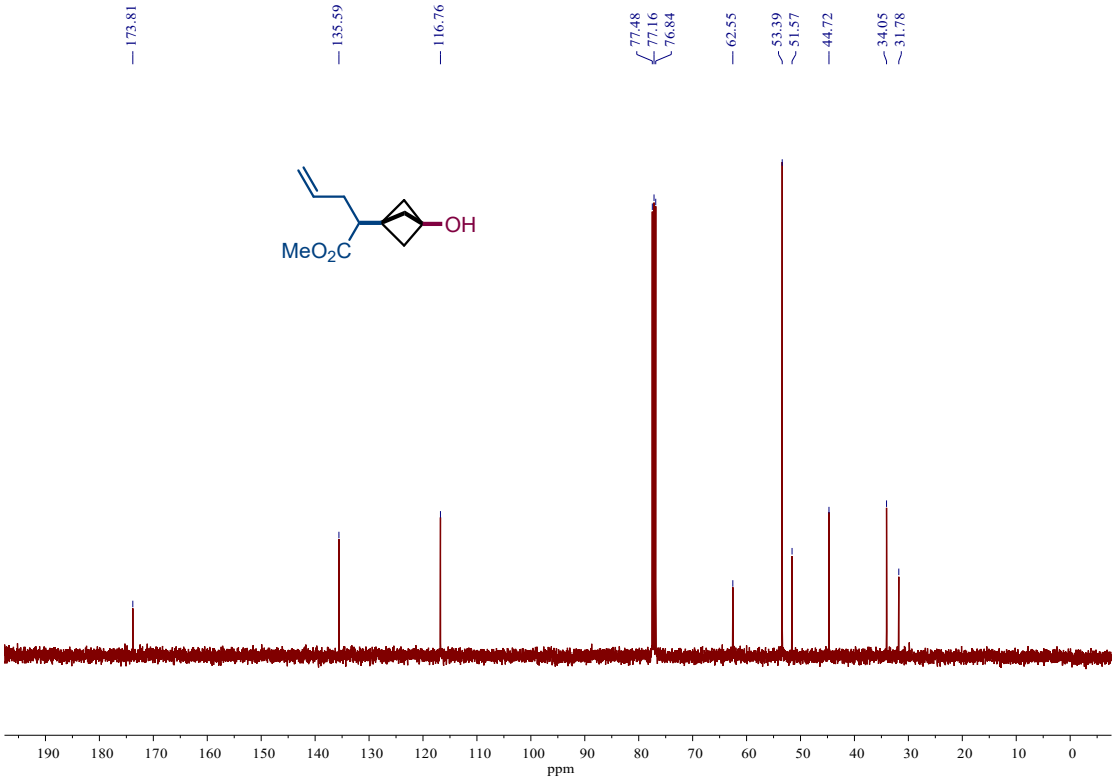
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 13



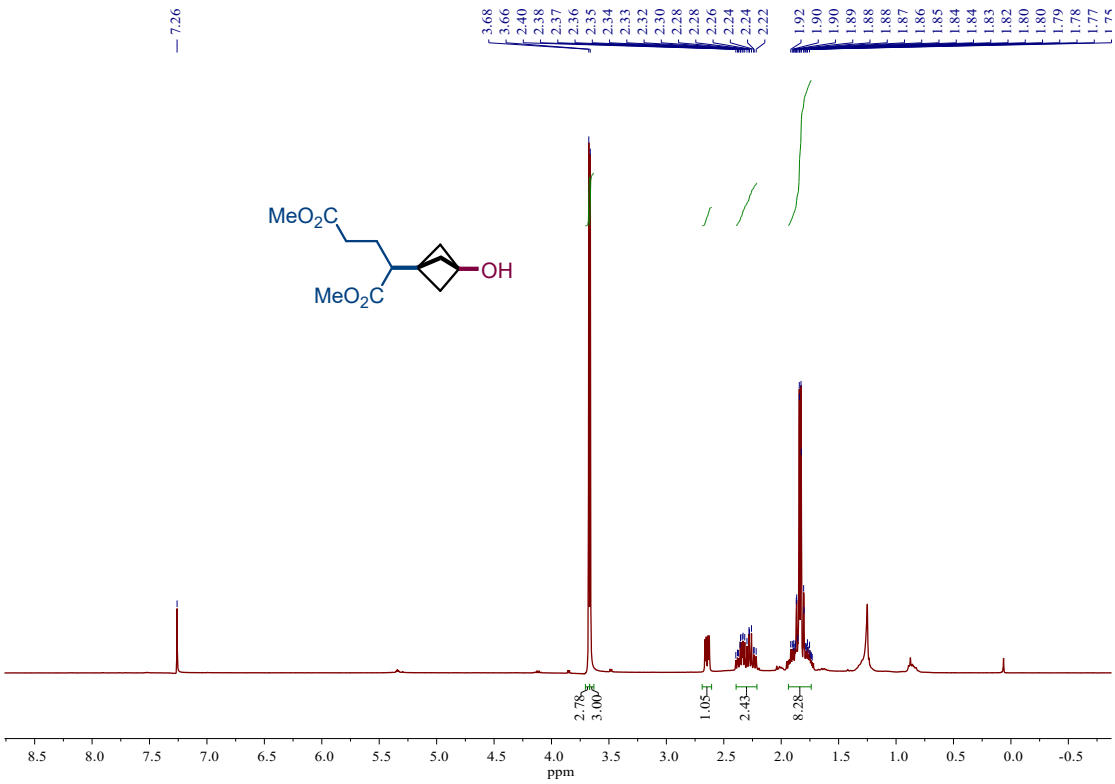
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 13



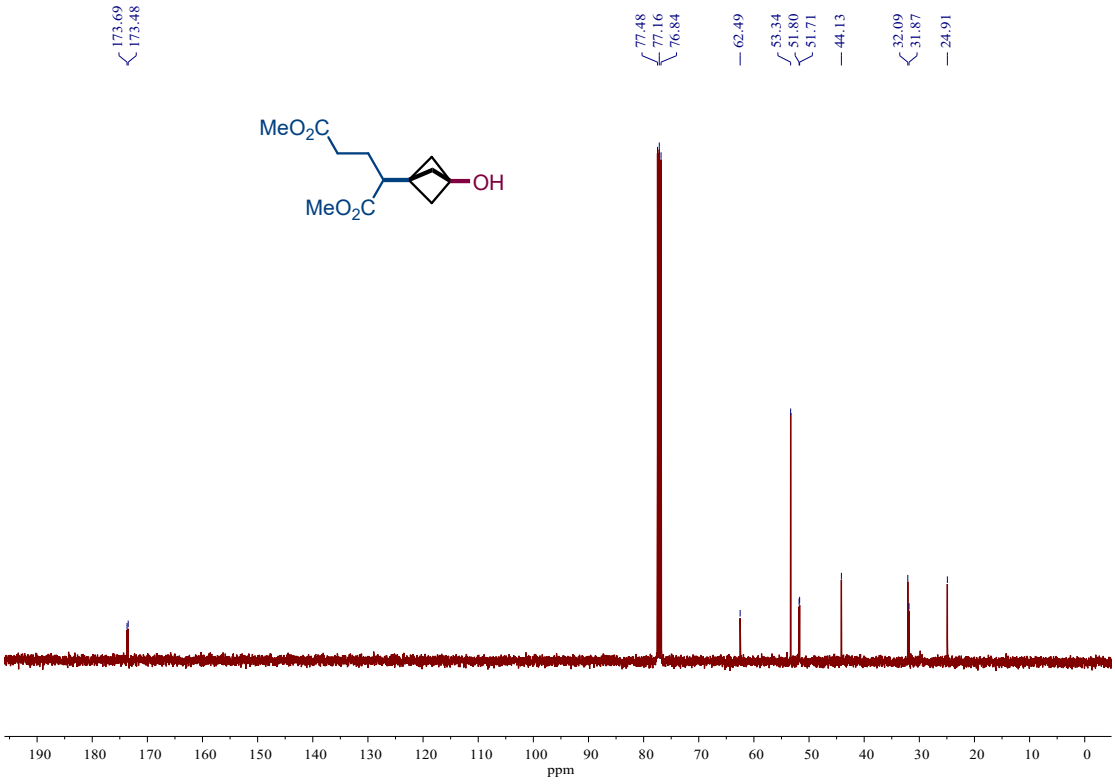
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 14



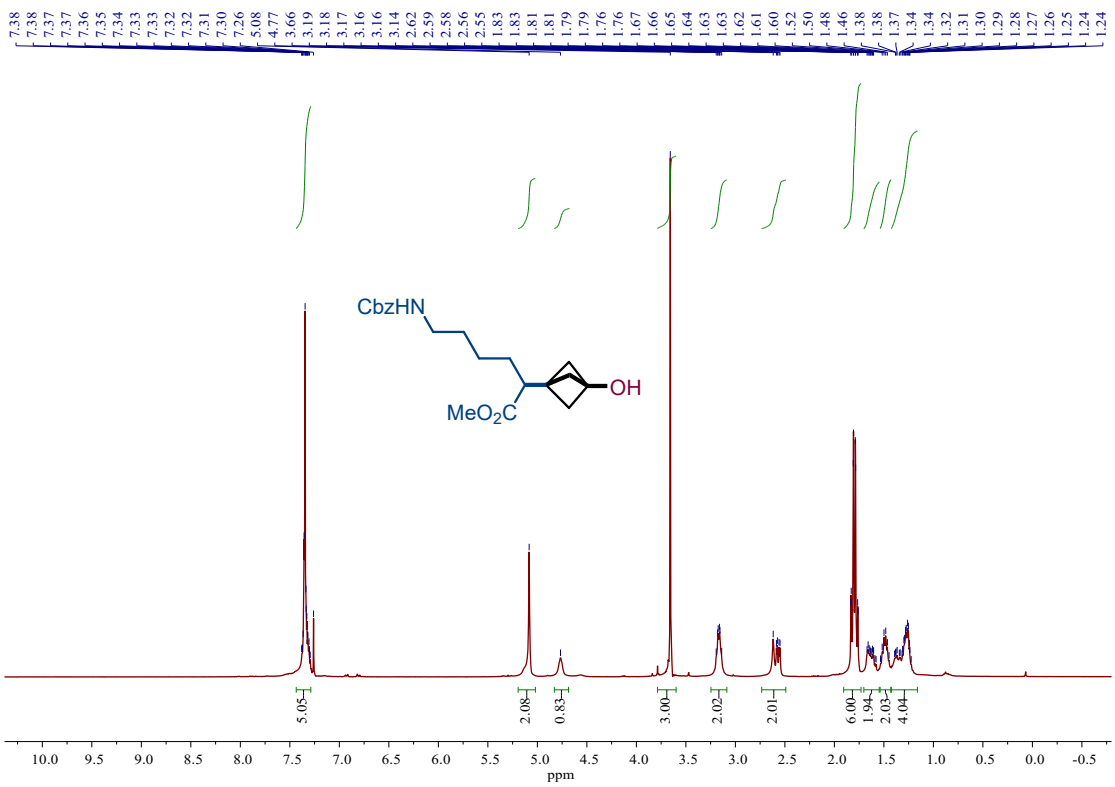
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 14



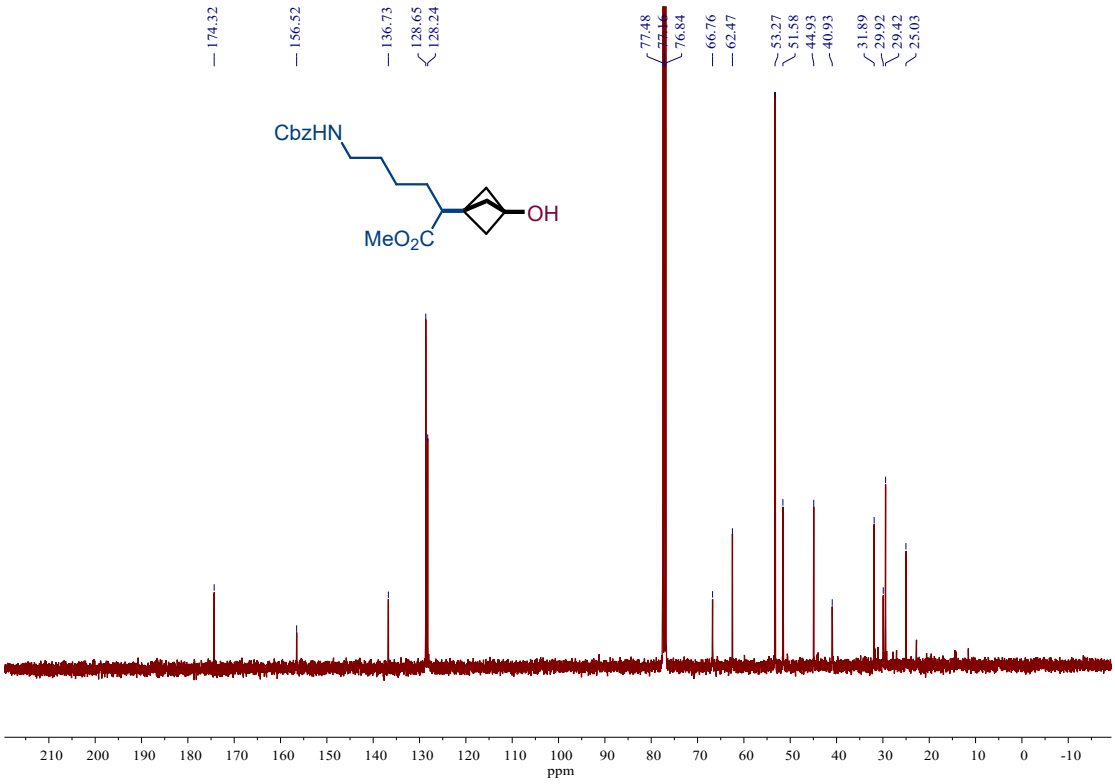
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 15



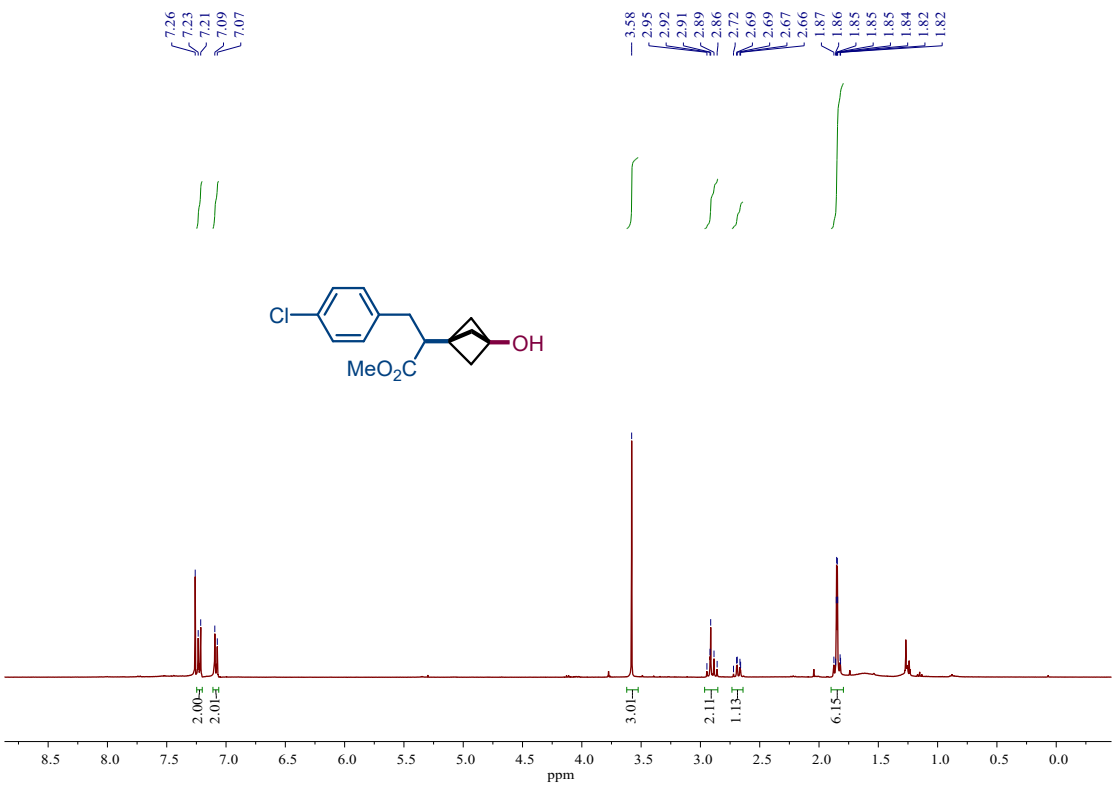
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 15



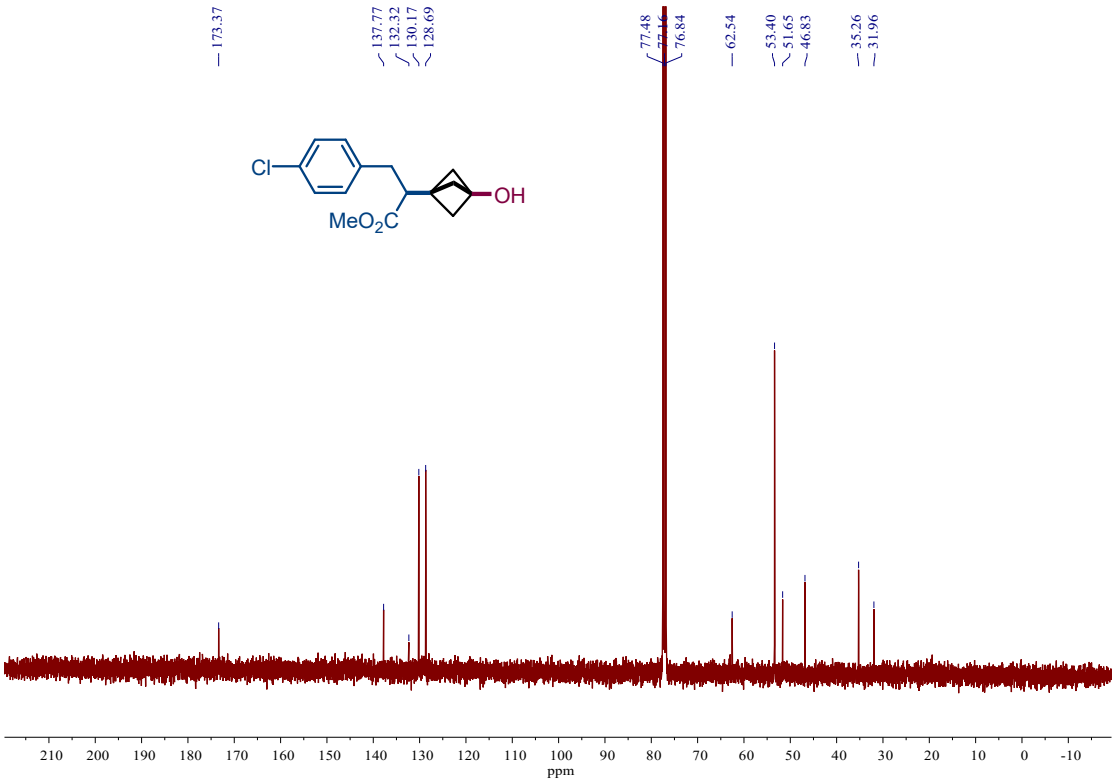
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 16



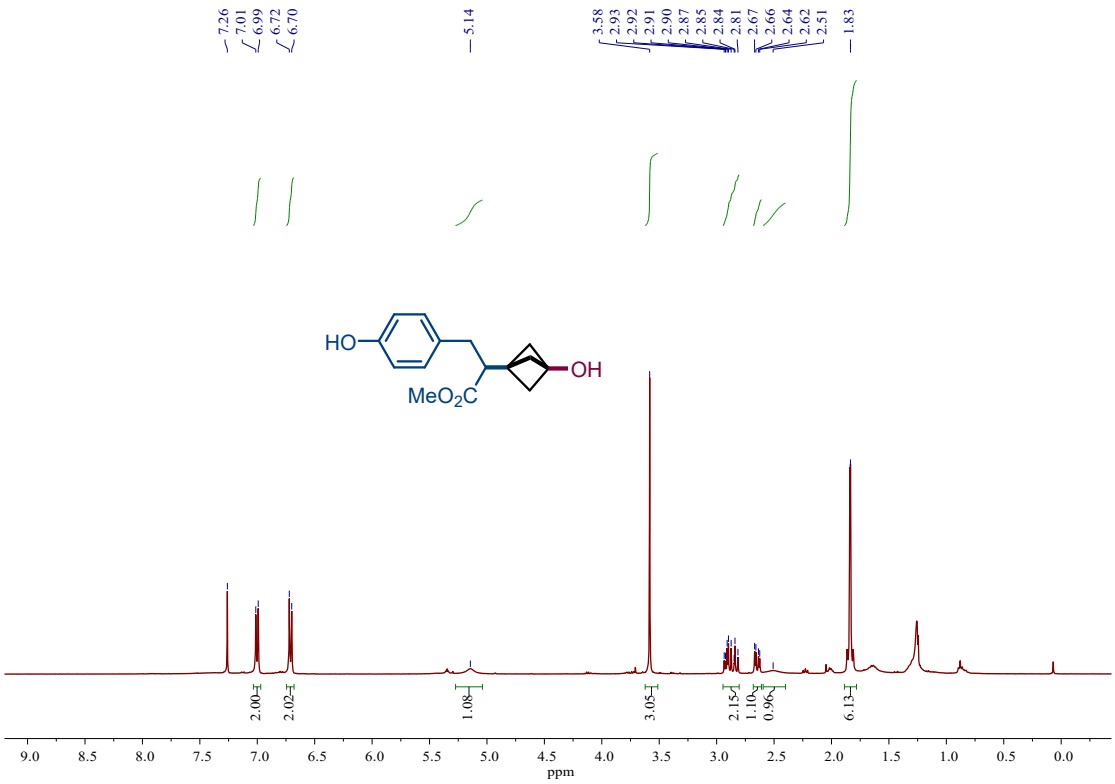
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 16



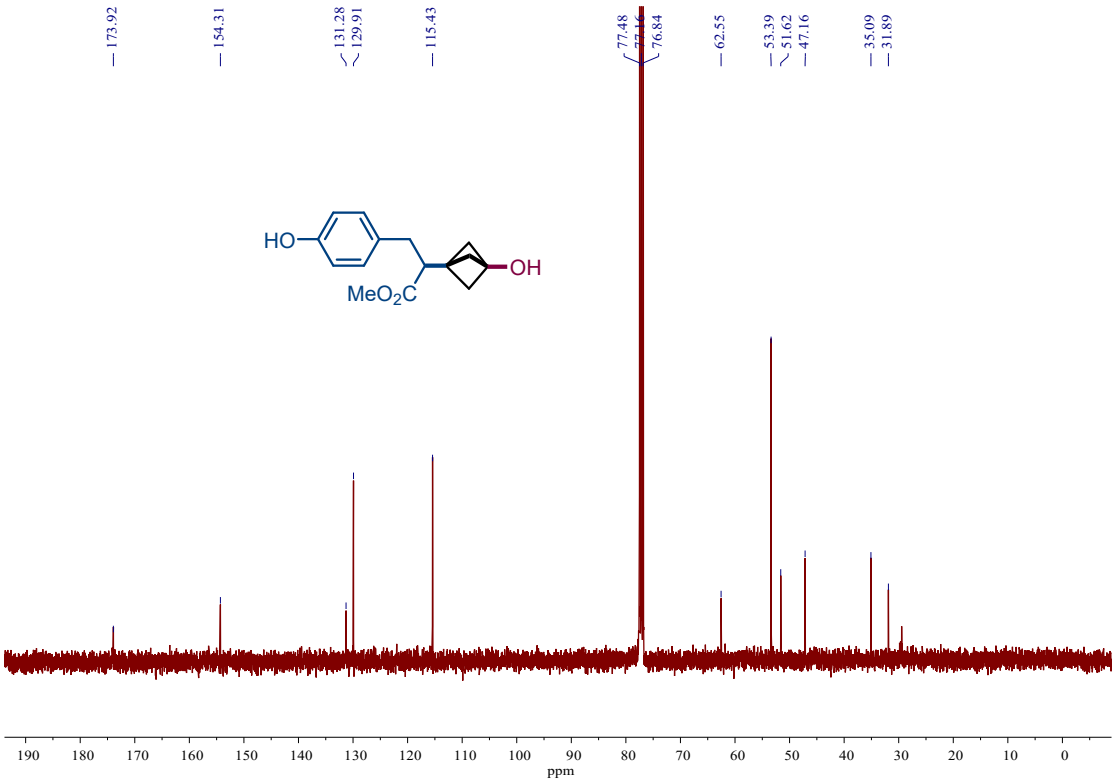
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 17



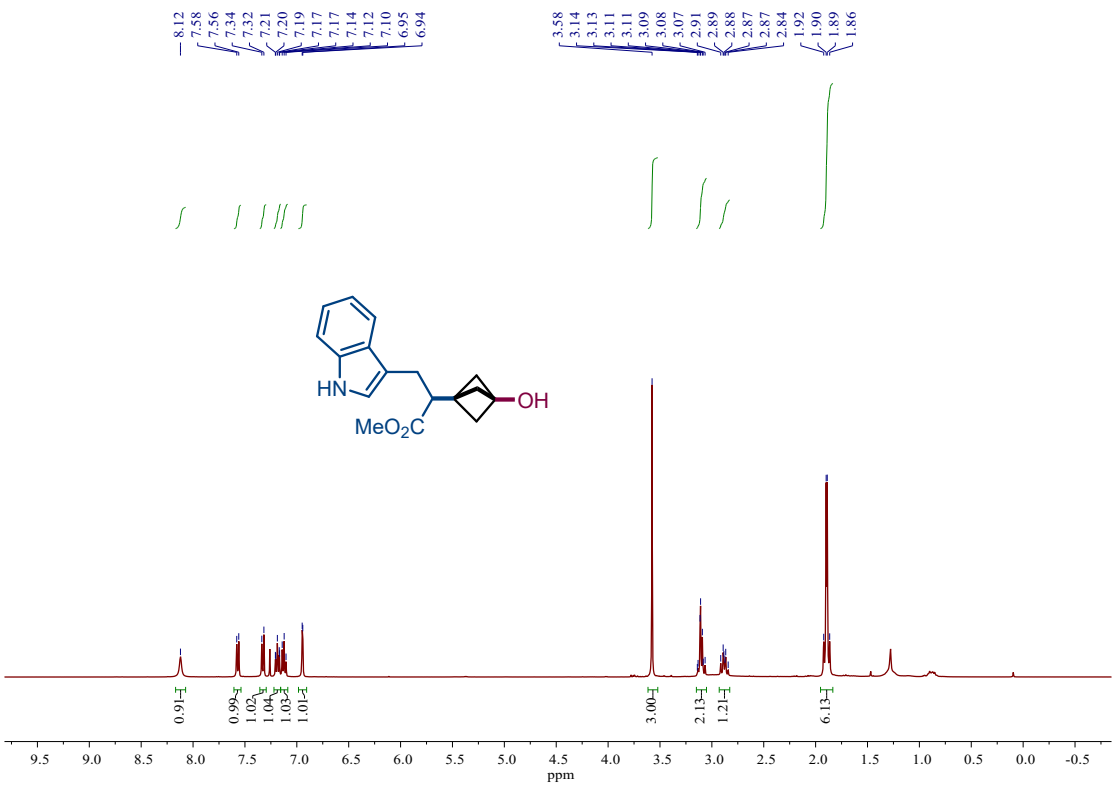
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 17



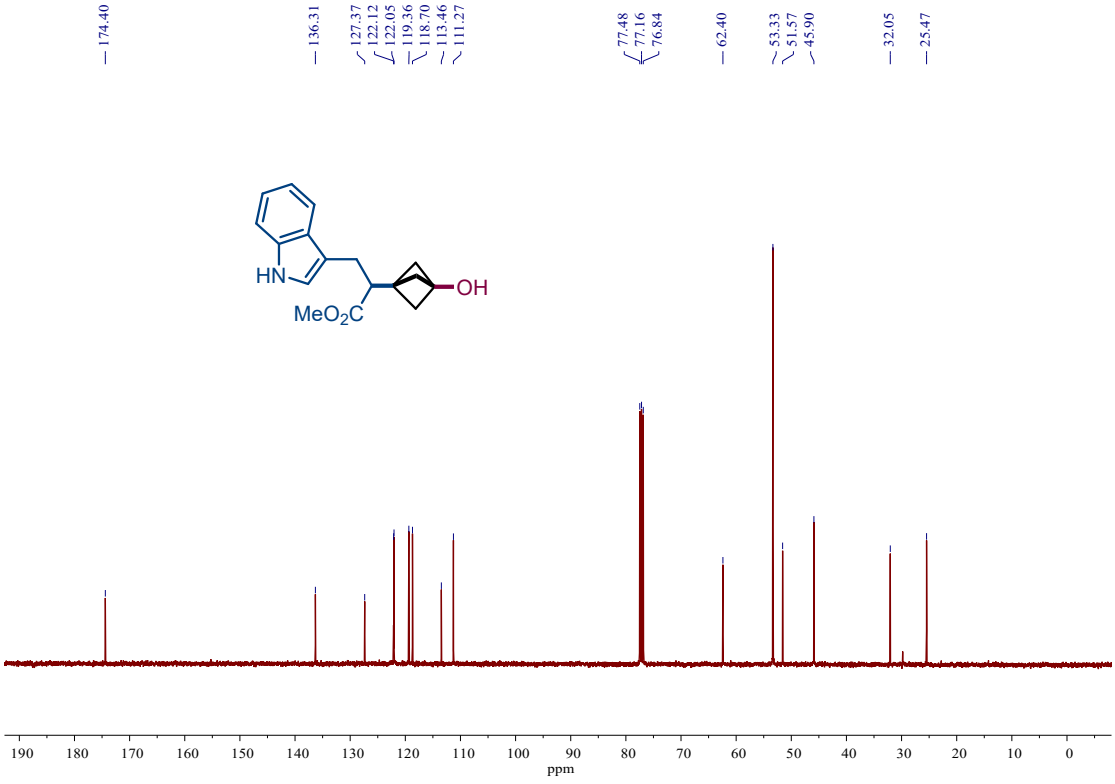
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 18



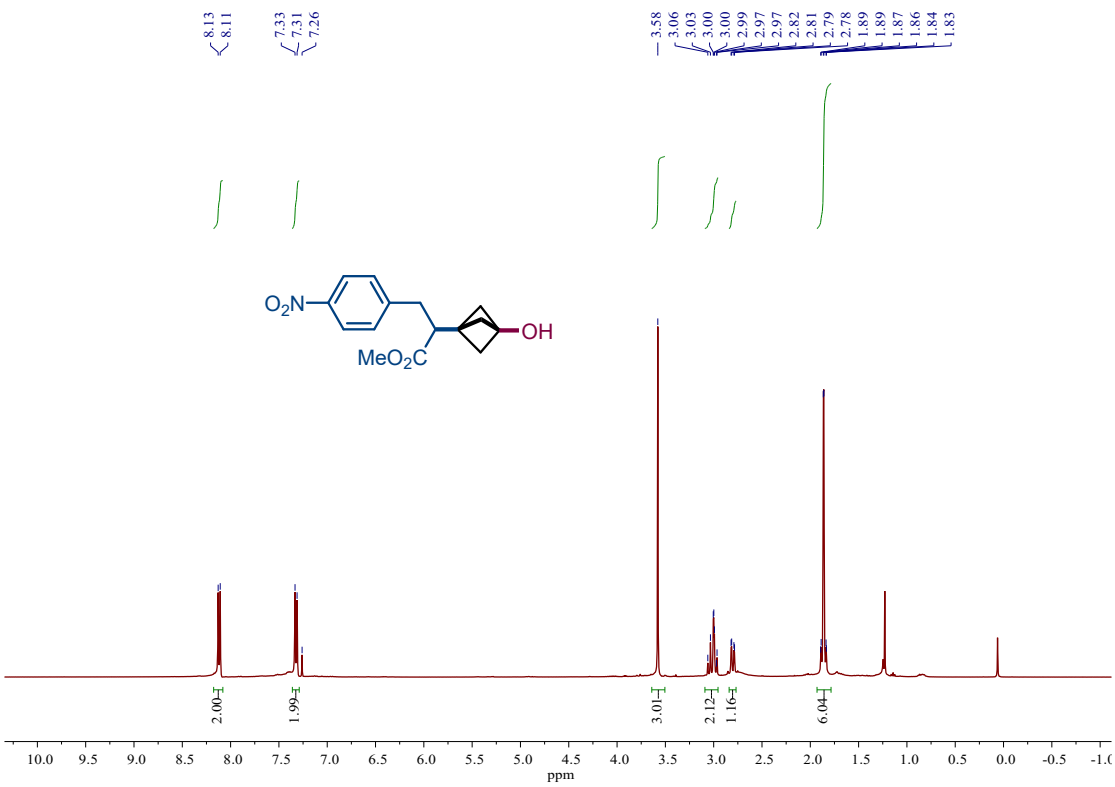
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 18



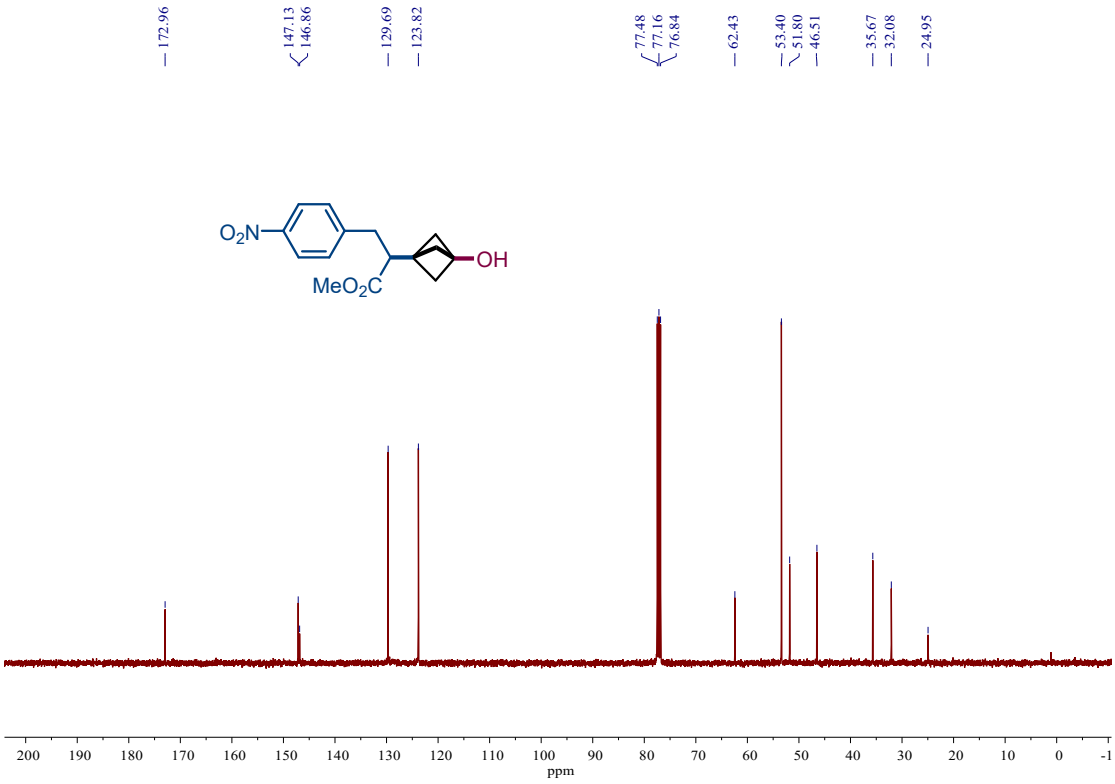
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 19



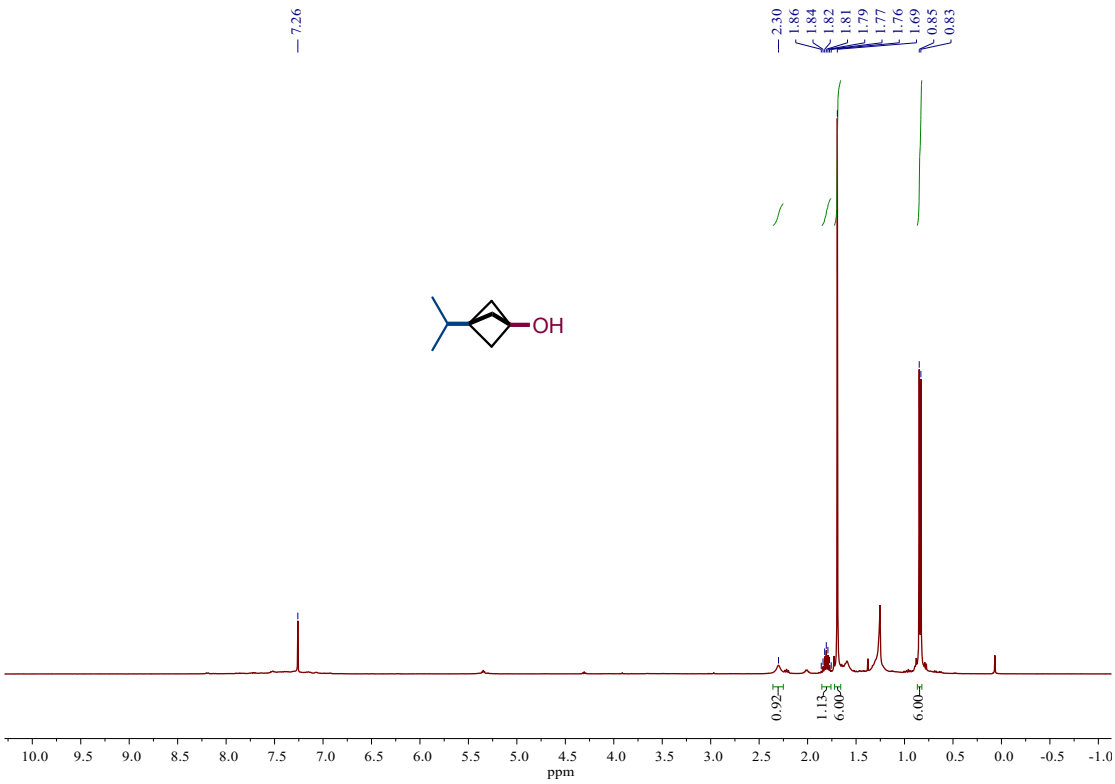
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 19



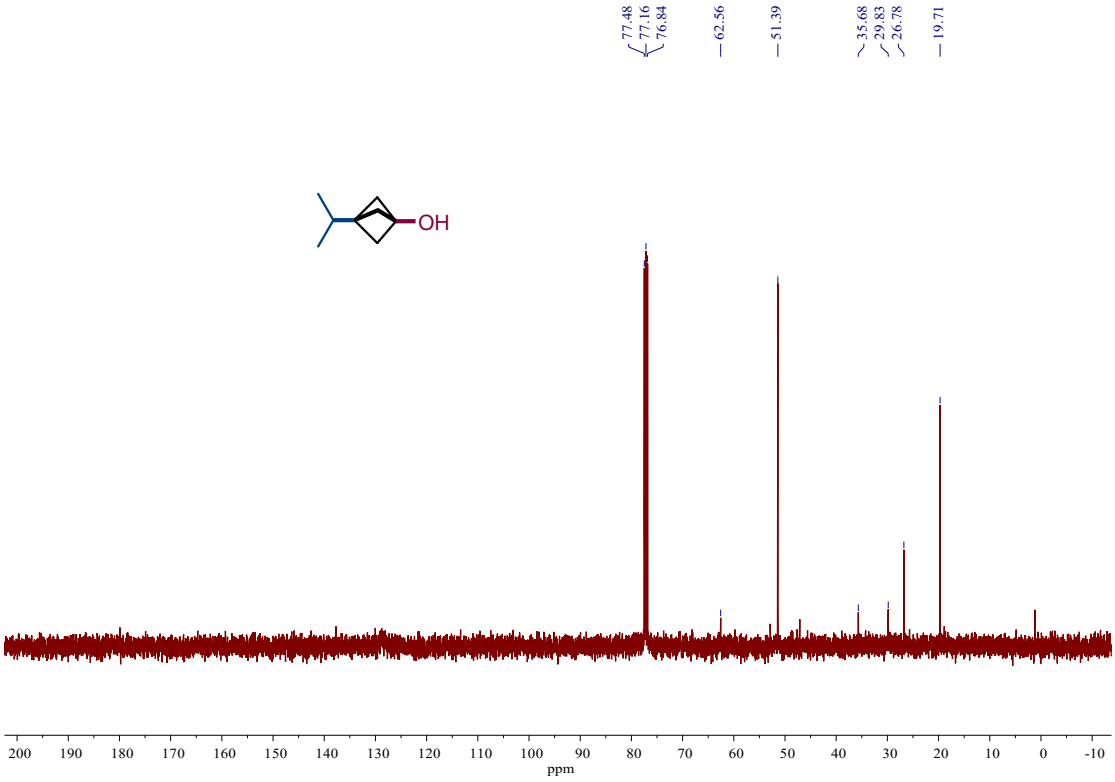
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 20



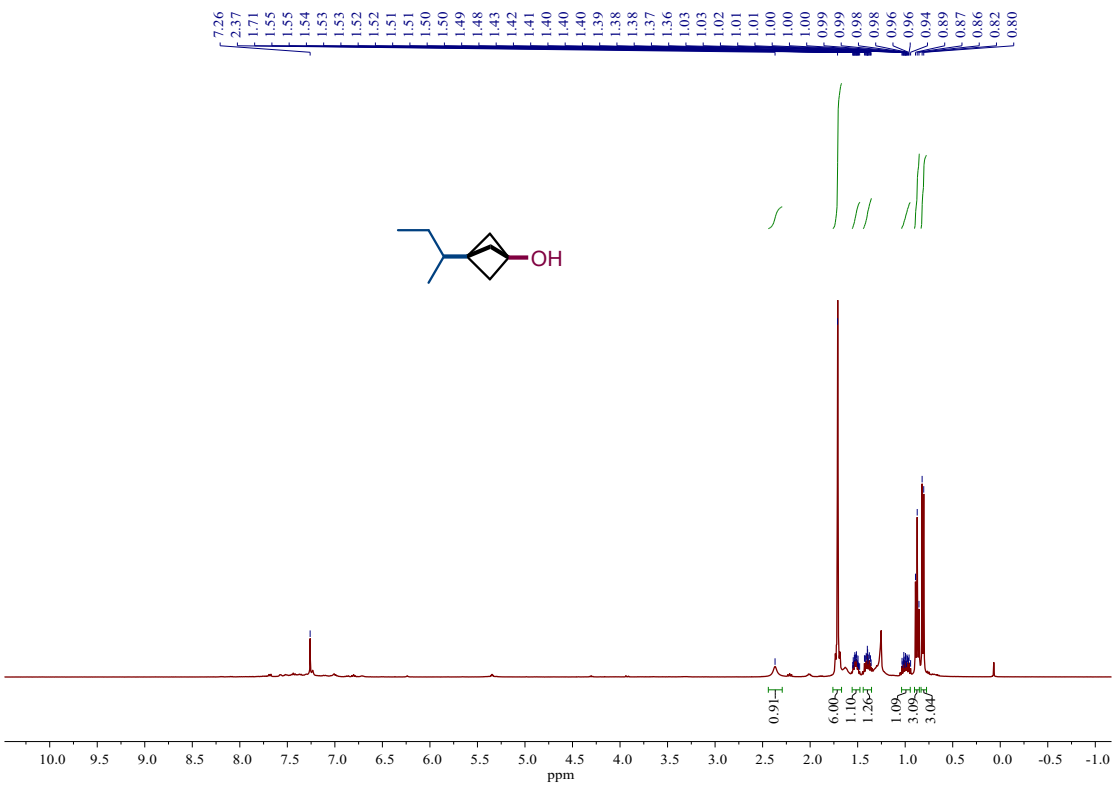
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 20



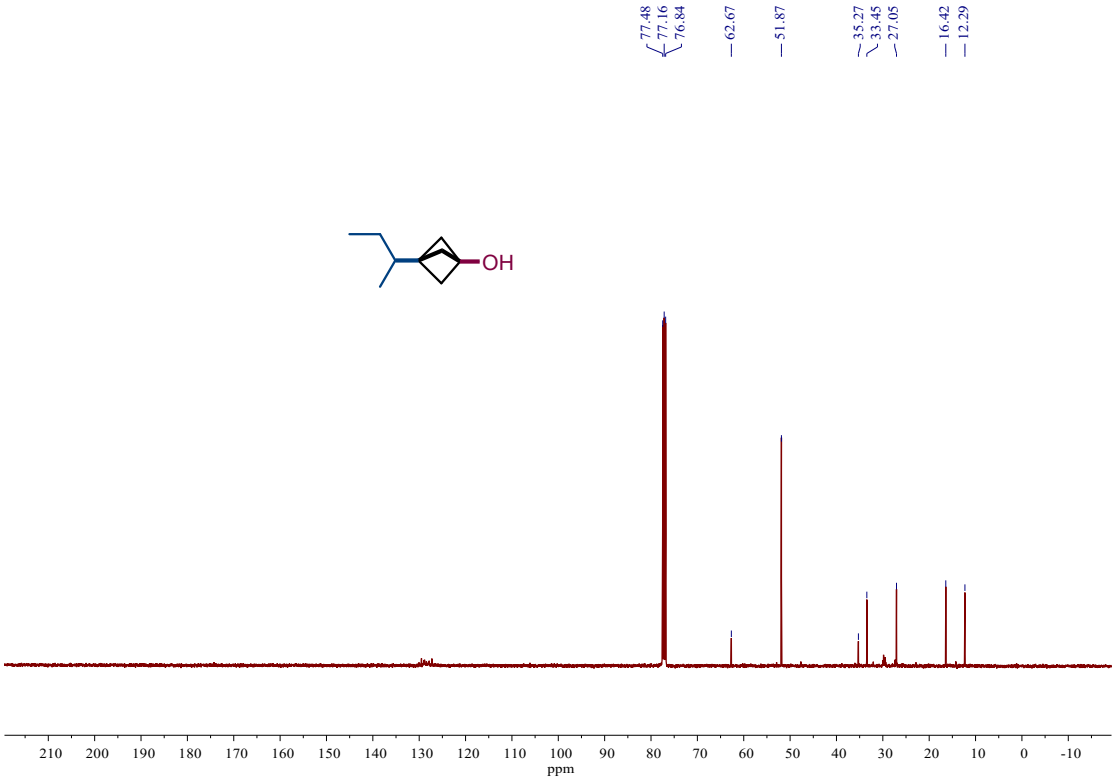
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 21



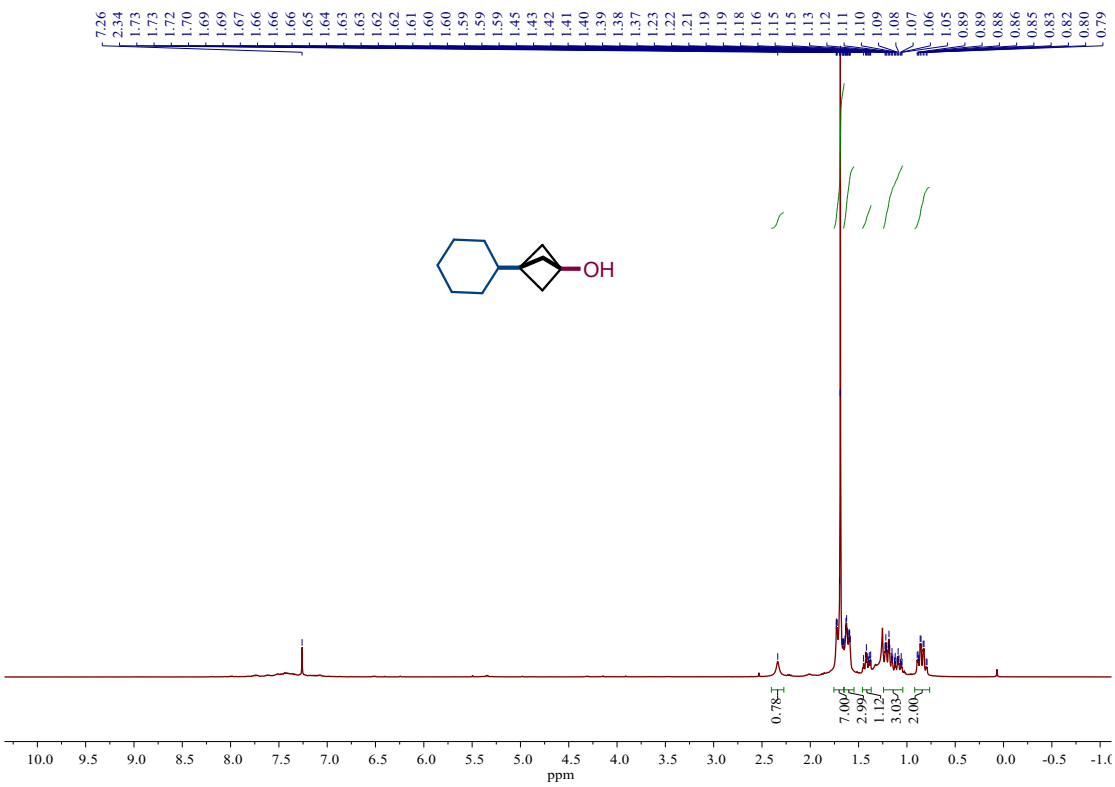
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 21



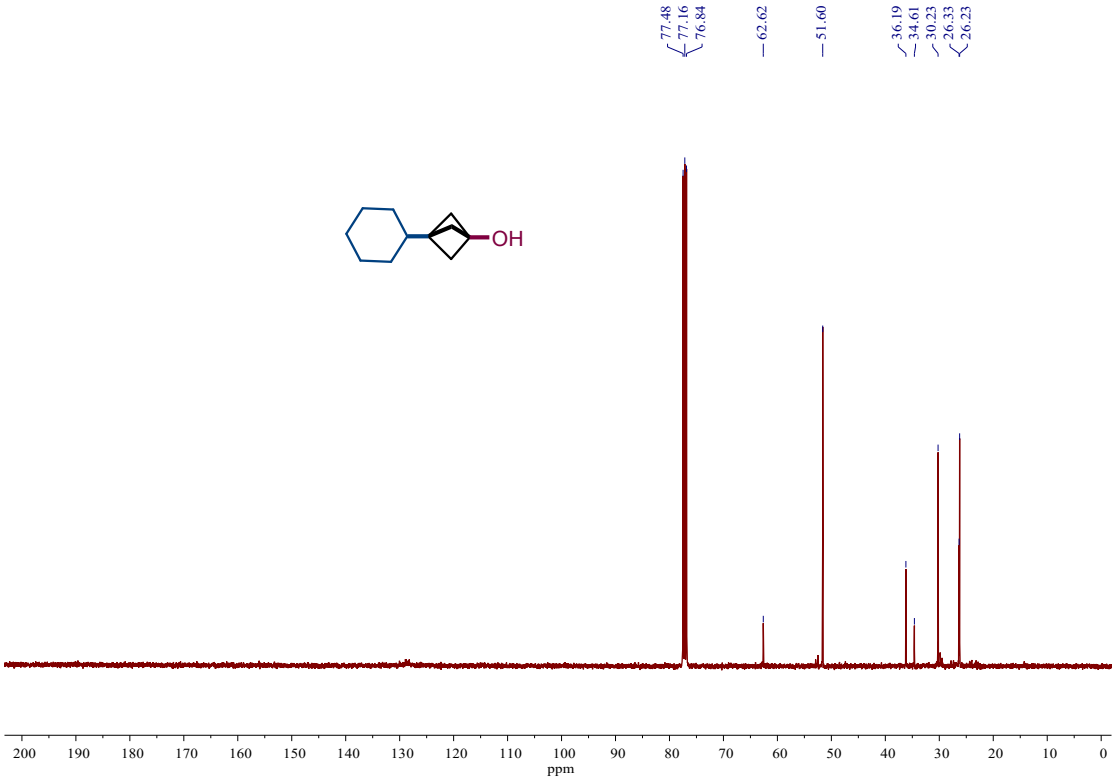
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 22



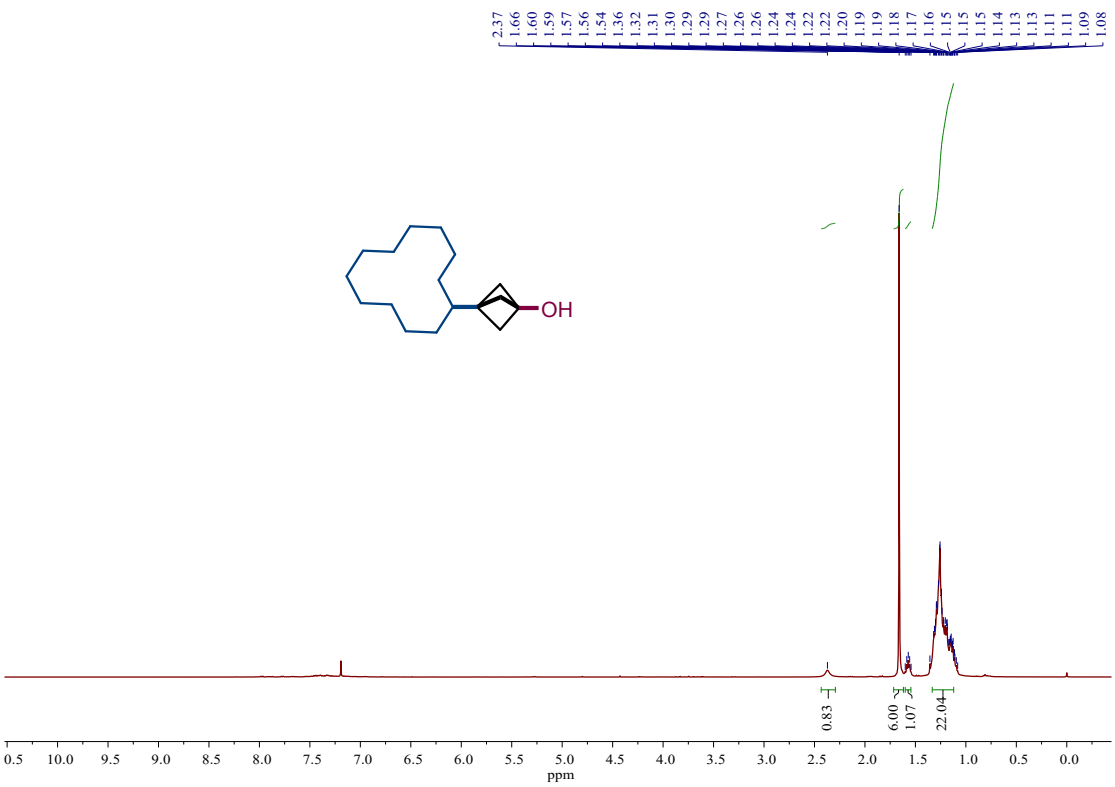
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 22



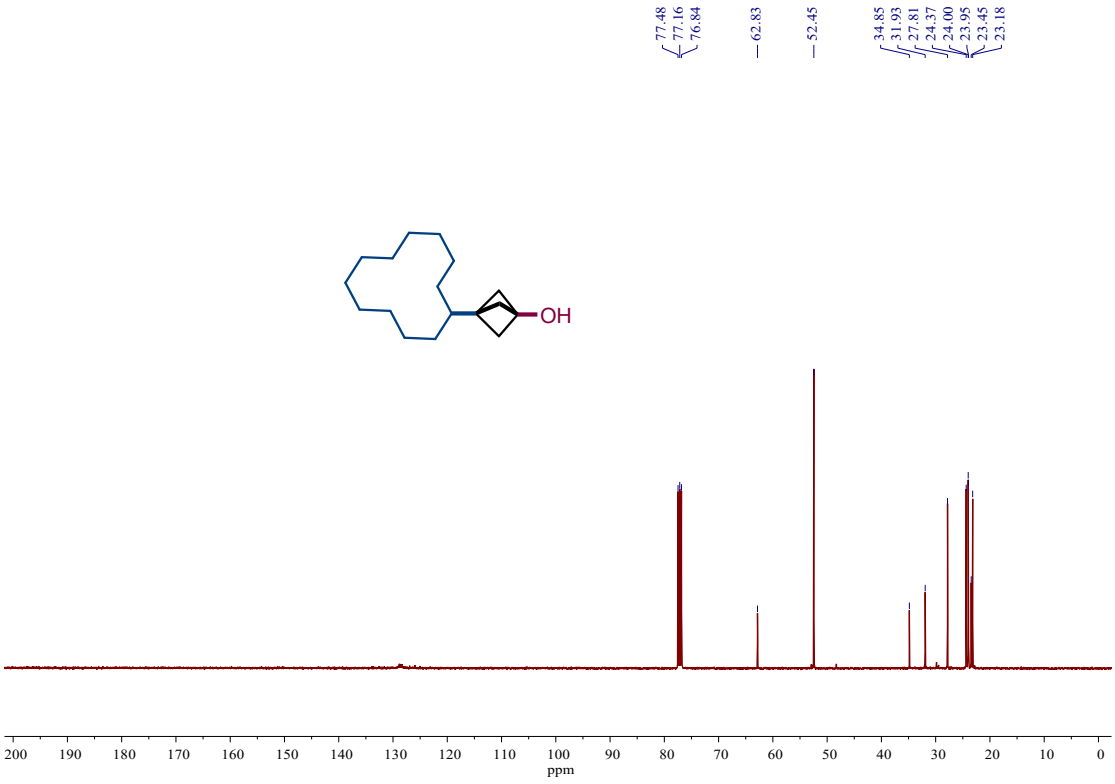
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 23



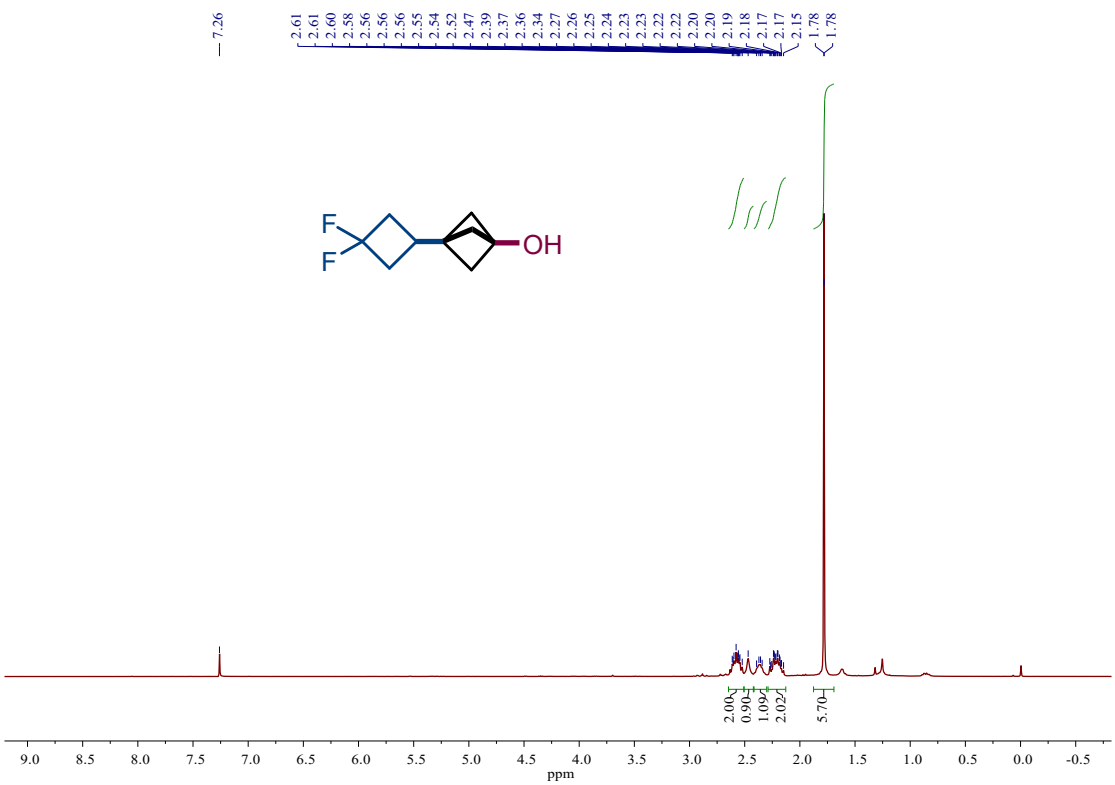
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 23



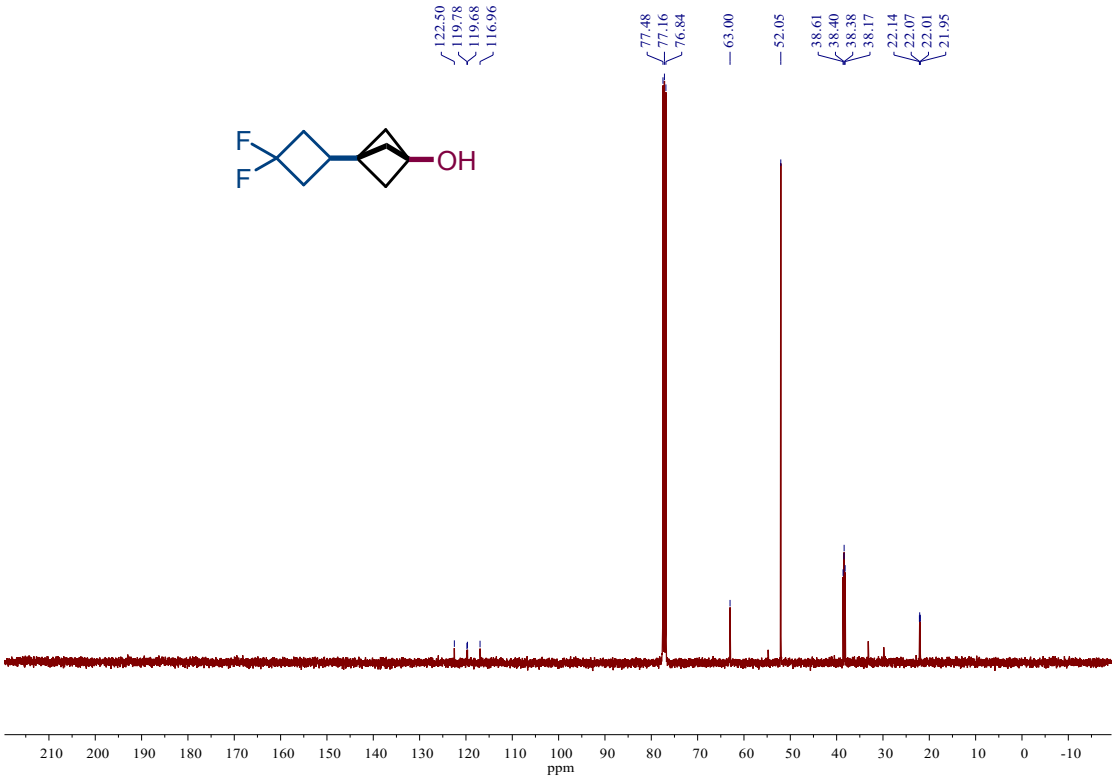
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 24



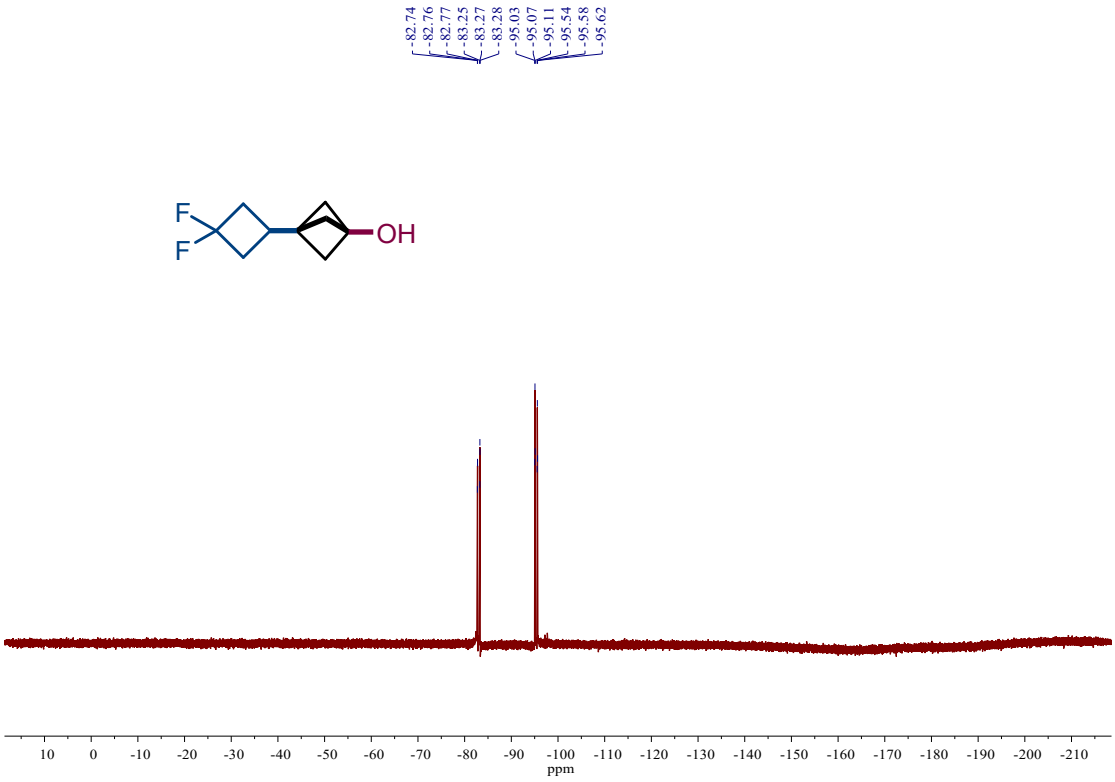
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 24



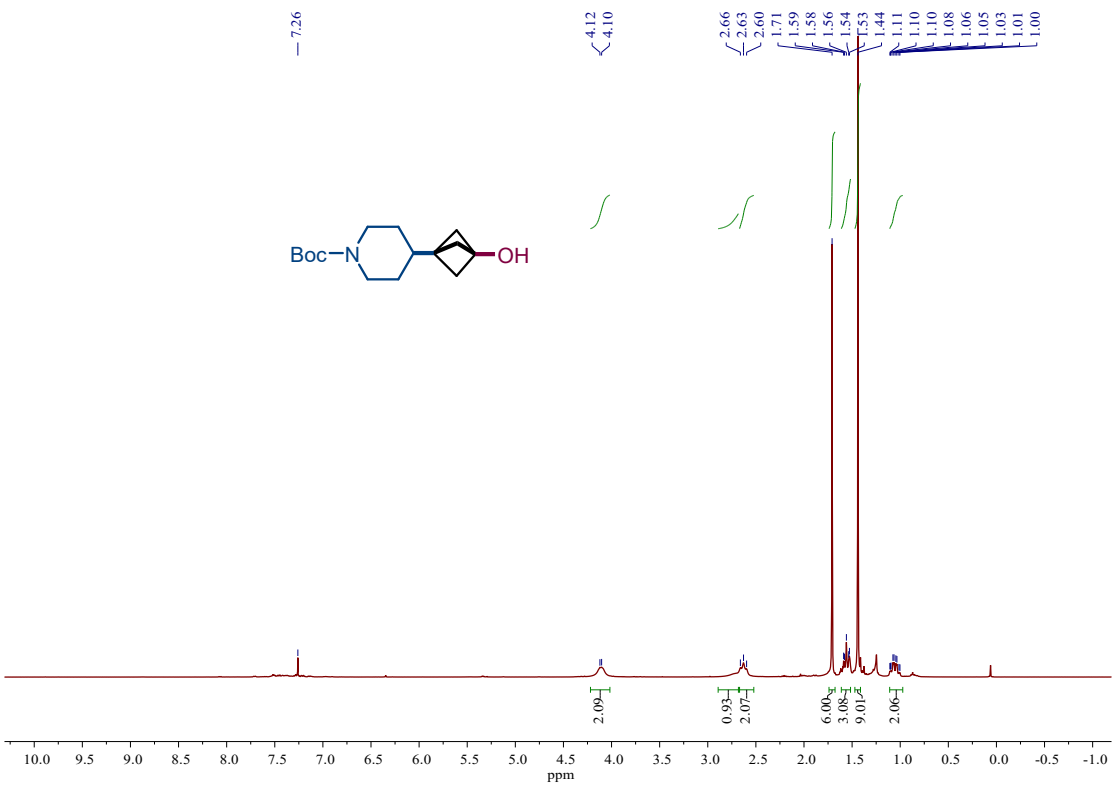
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 25



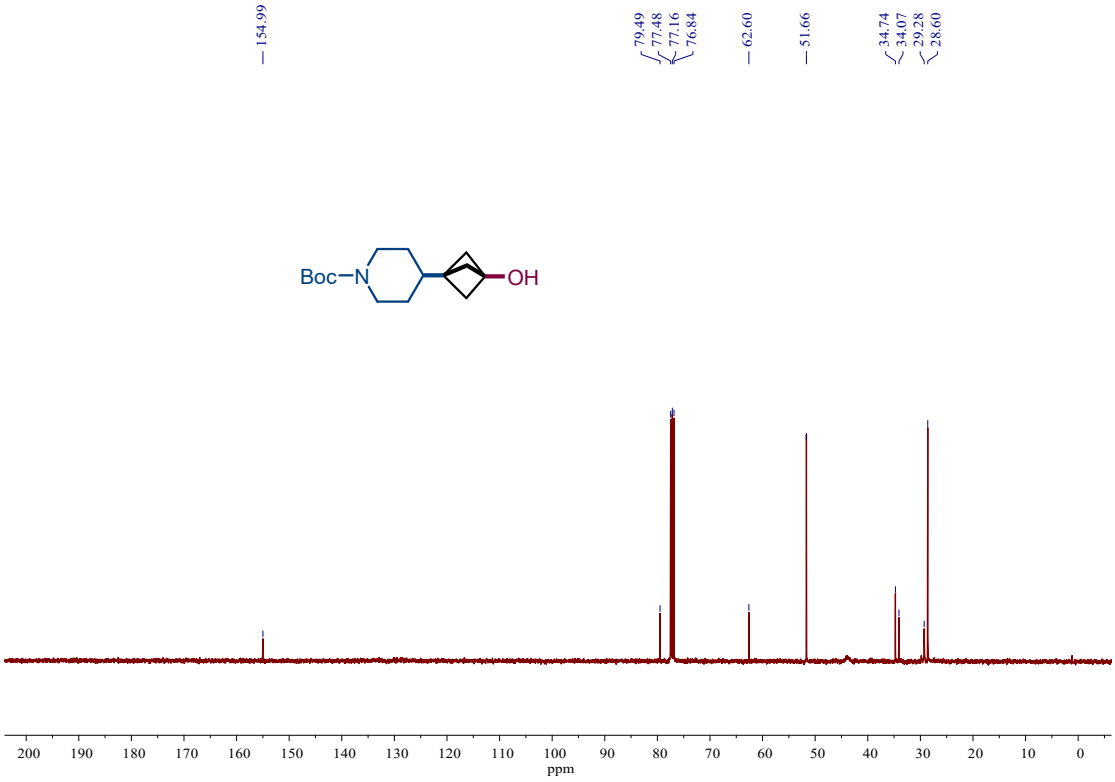
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 25



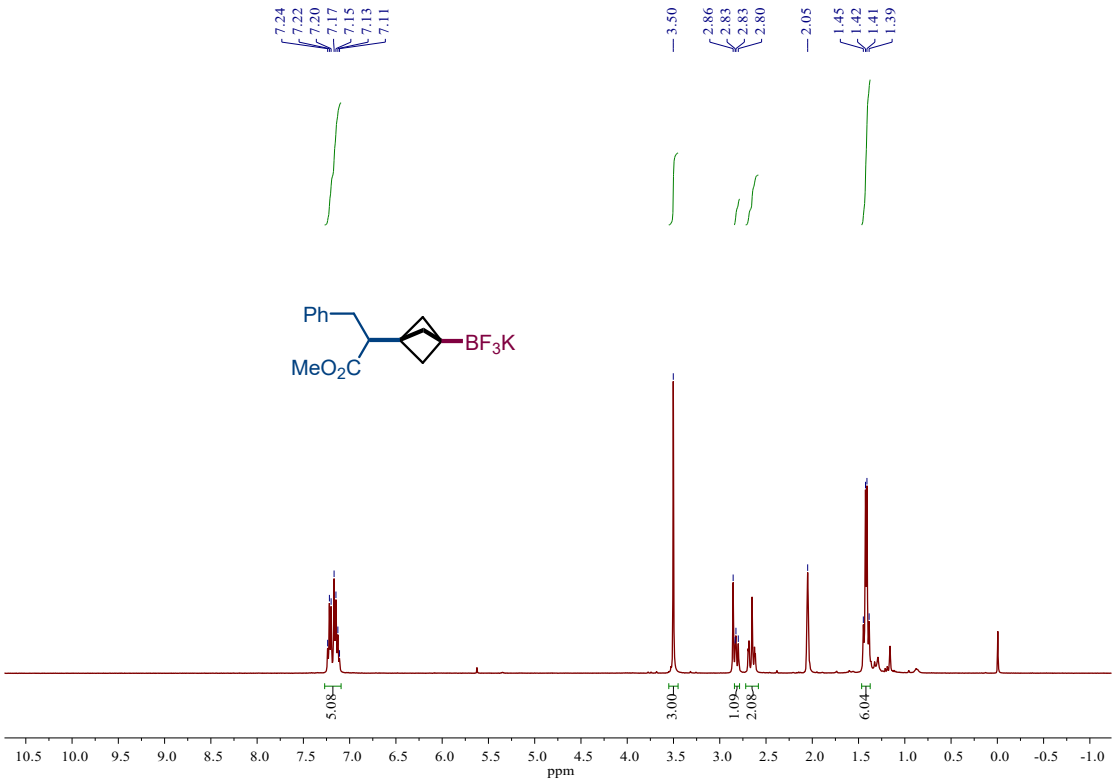
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 25



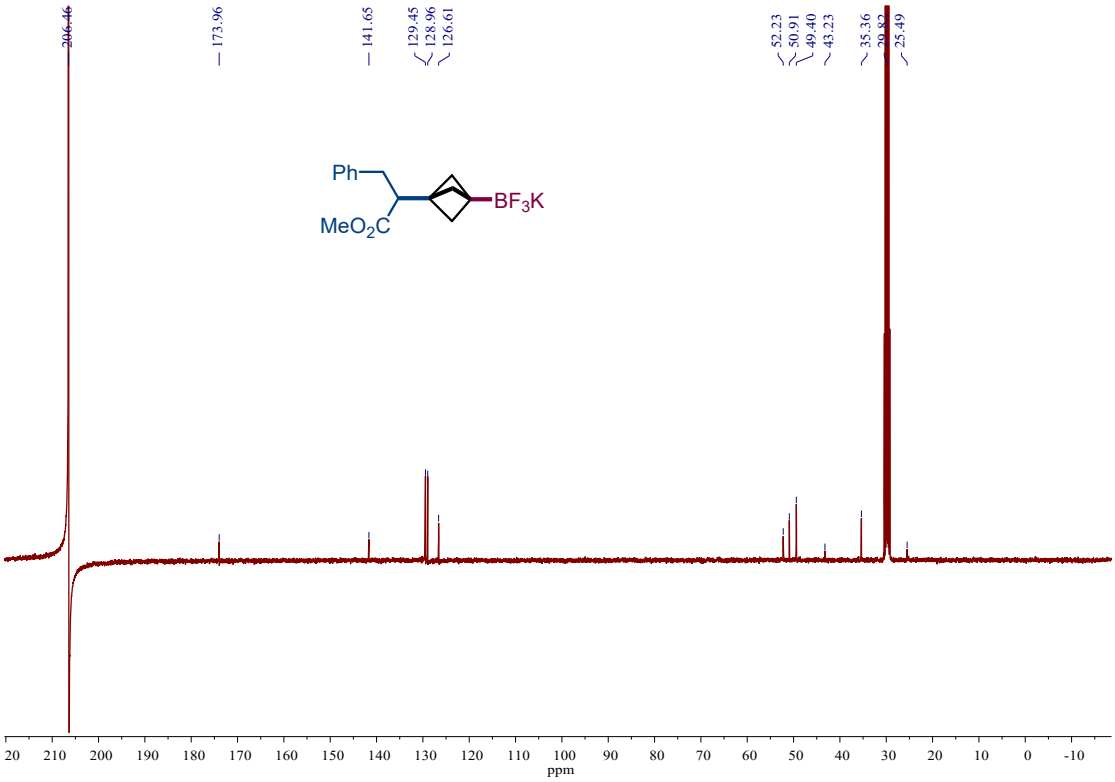
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 26



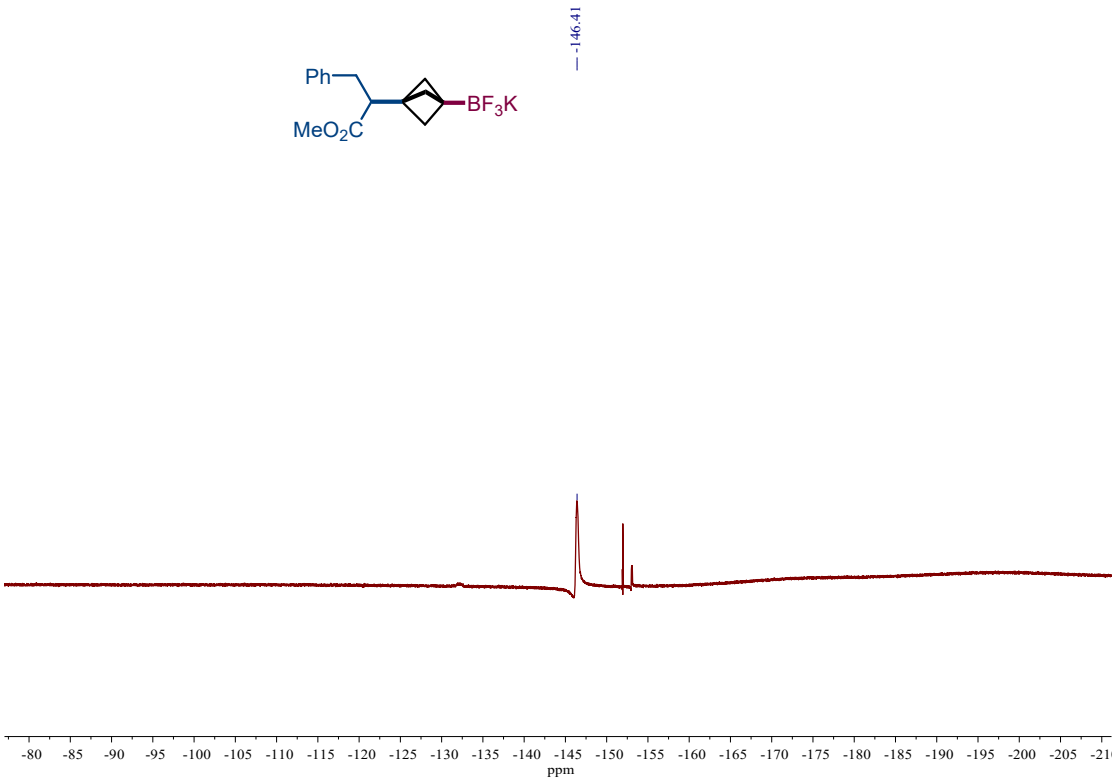
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 26



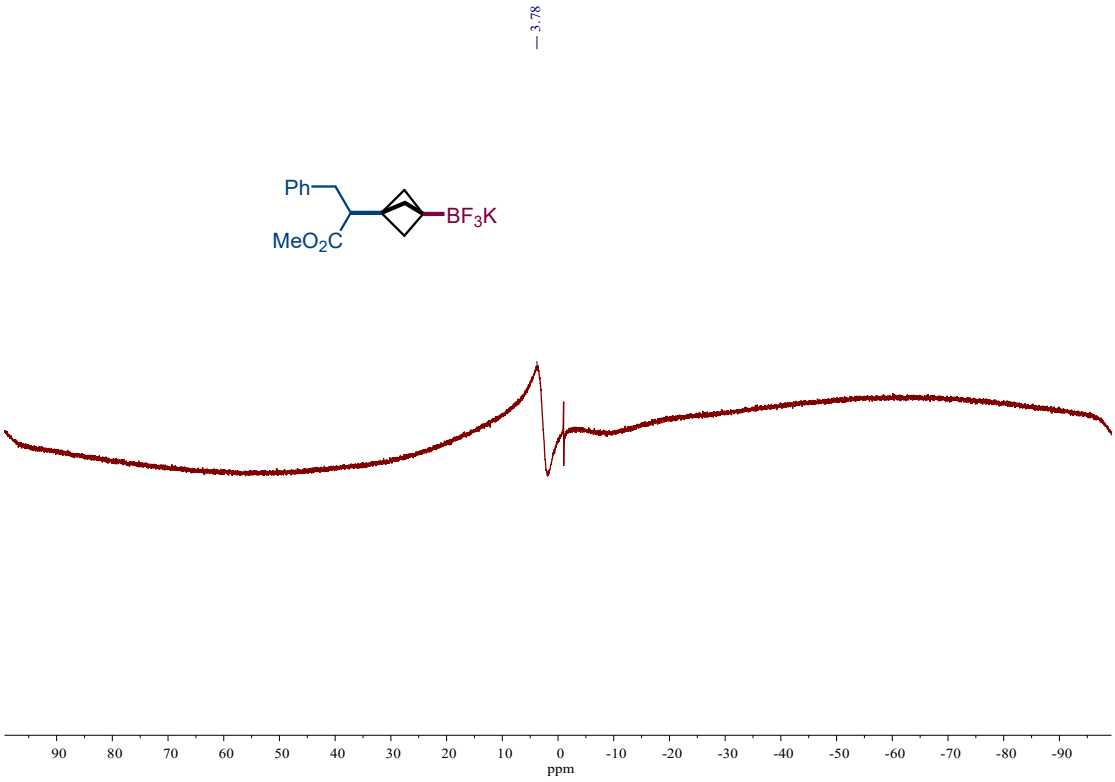
^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound 27



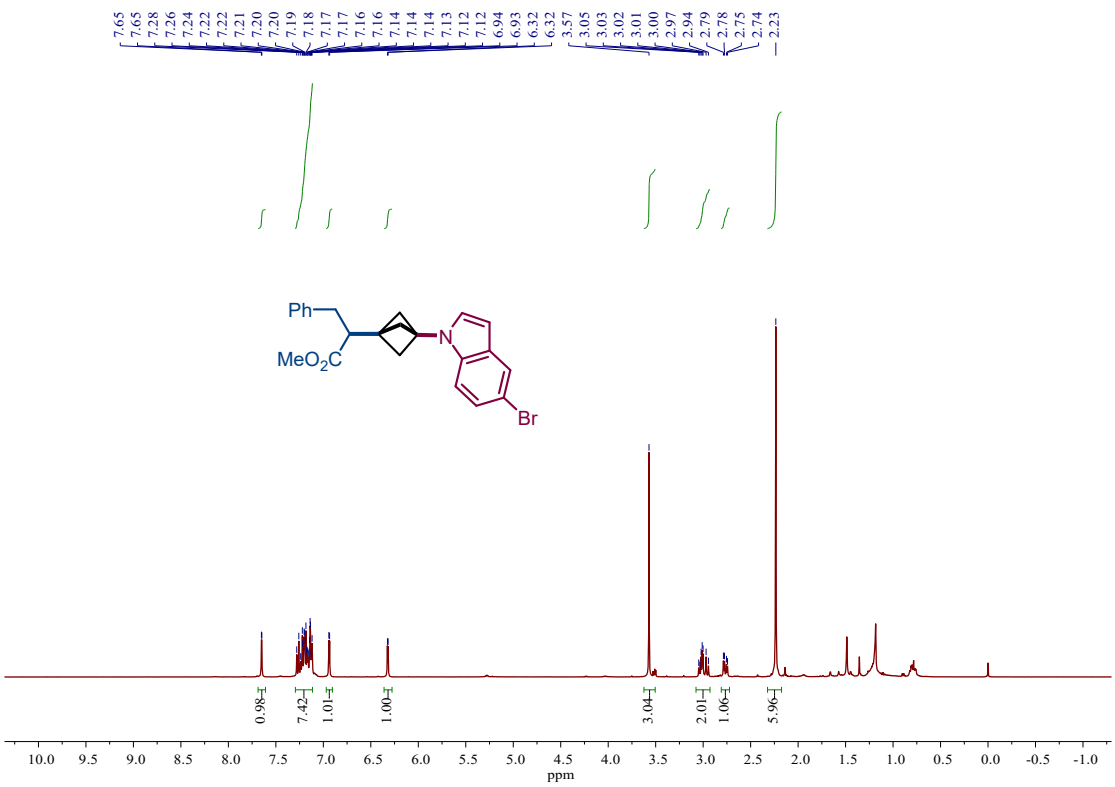
^{13}C NMR (100 MHz, Acetone-d_6) spectrum of compound 27



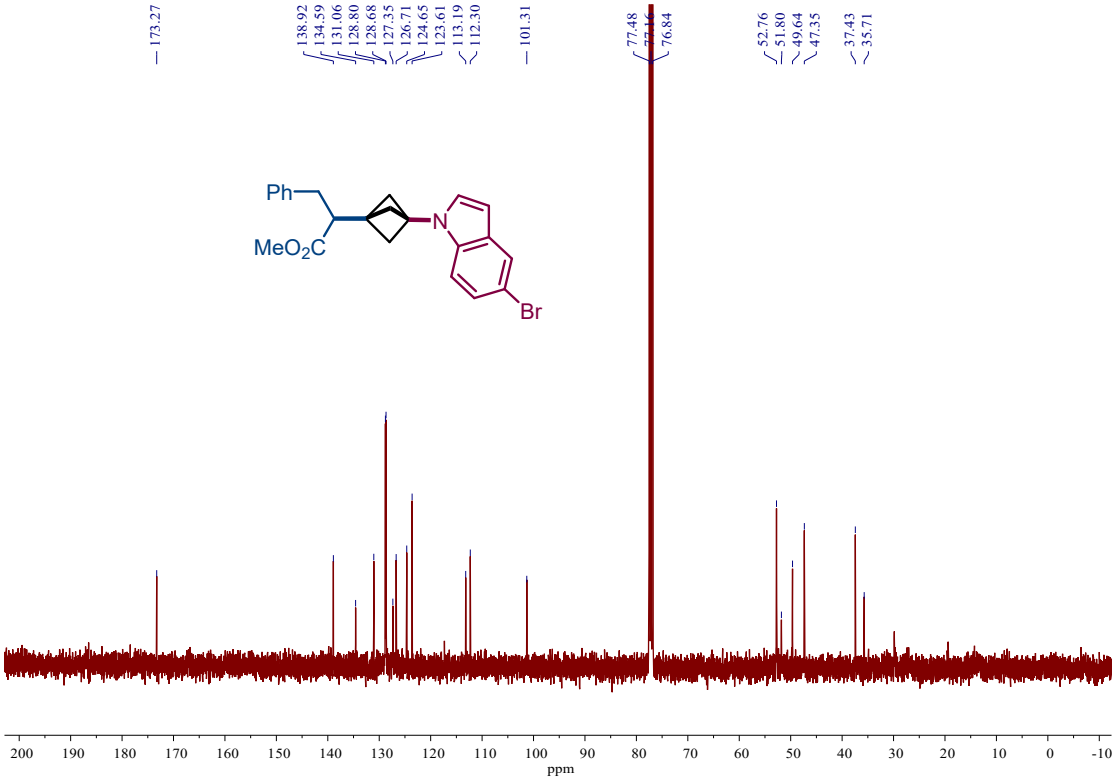
^{19}F NMR (376 MHz, Acetone-d_6) spectrum of compound 27



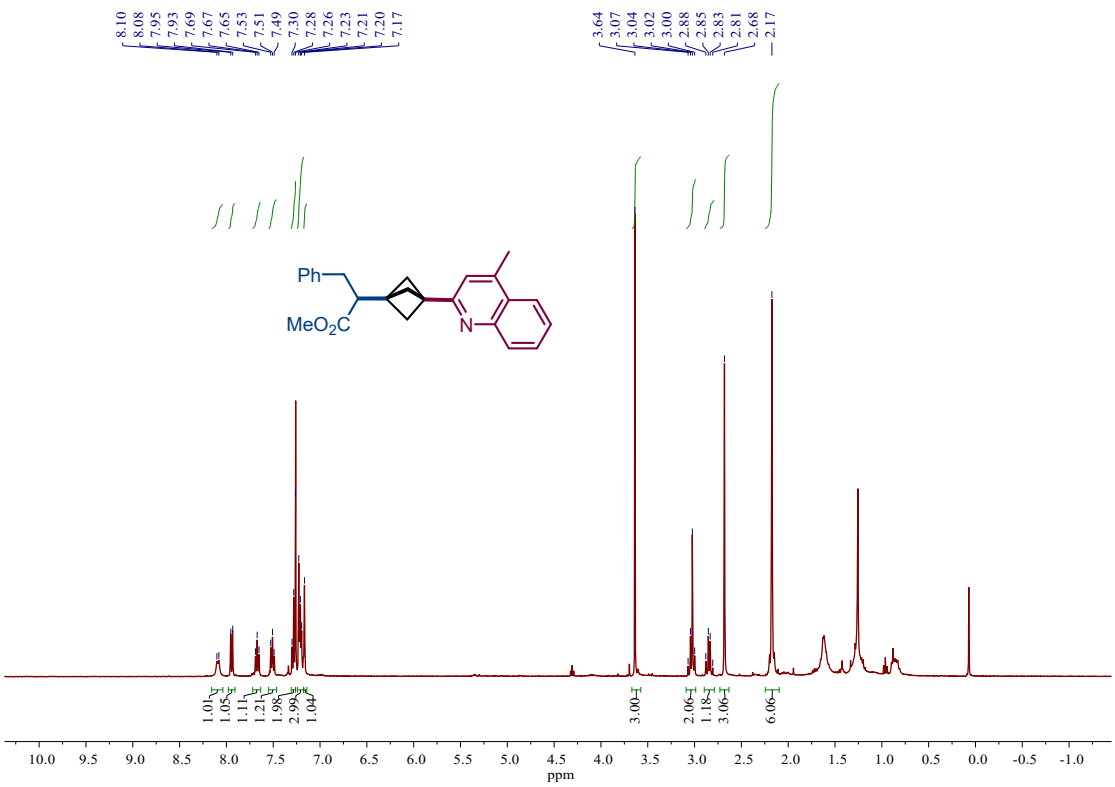
^{11}B NMR (128 MHz, Acetone-d_6) spectrum of compound 27



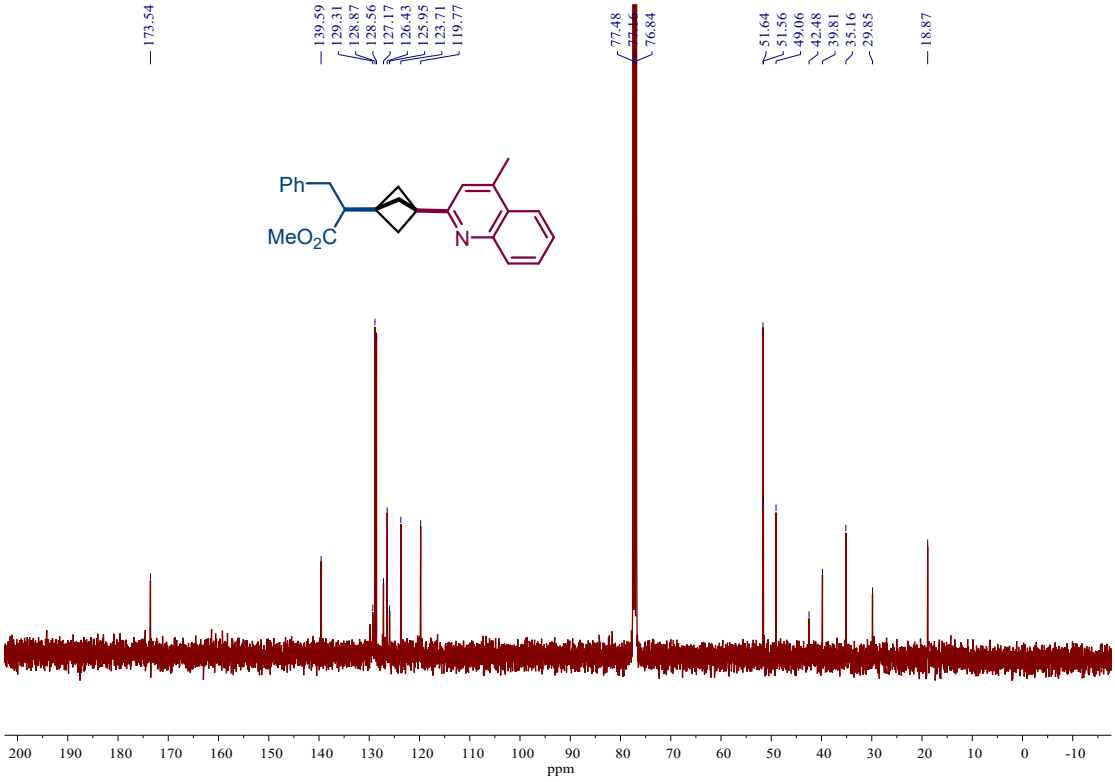
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 28



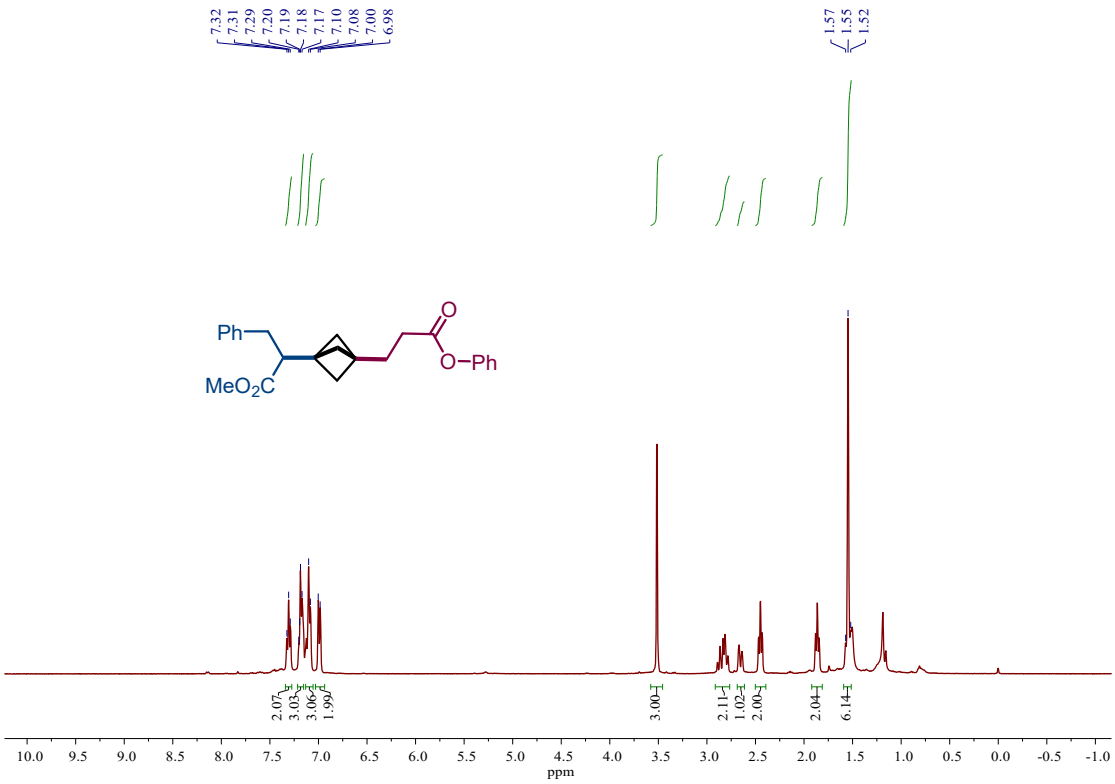
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 28



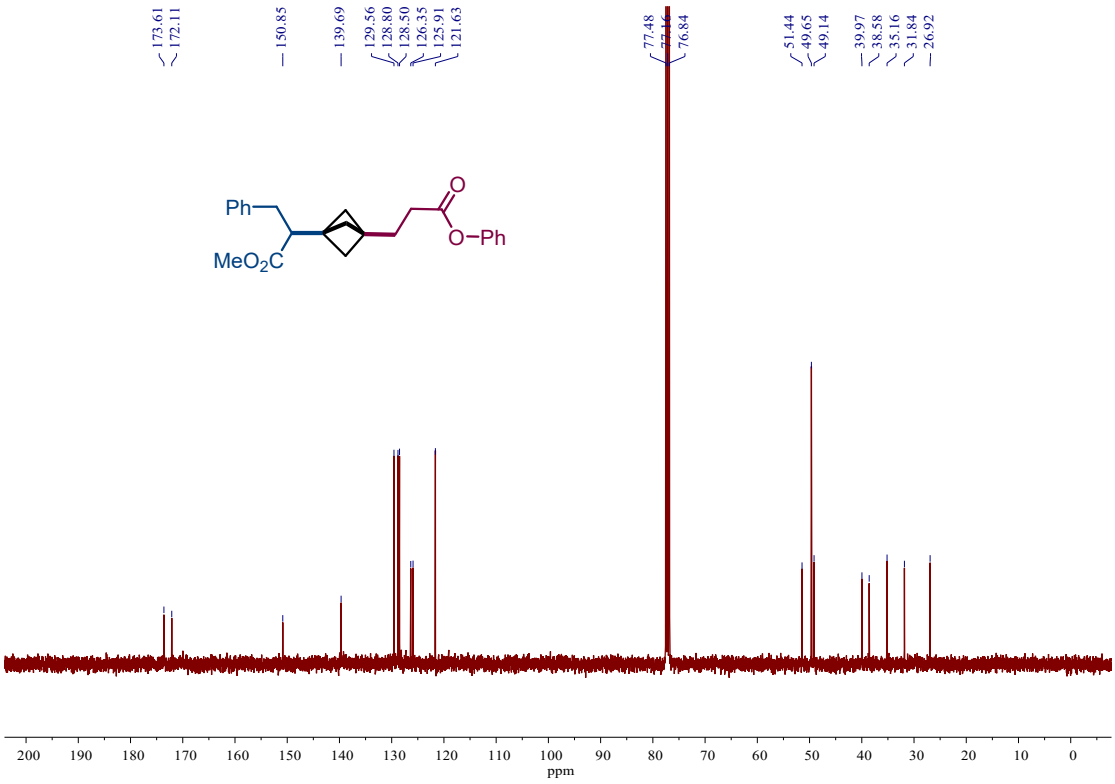
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 29



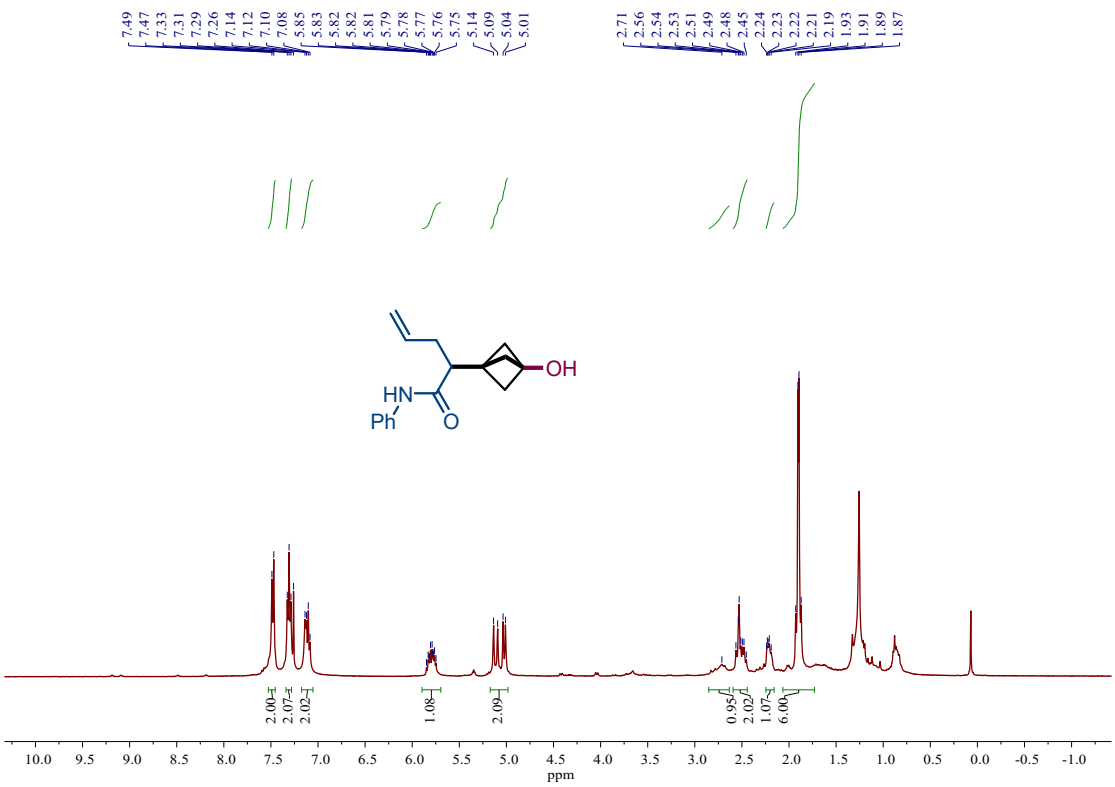
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 29



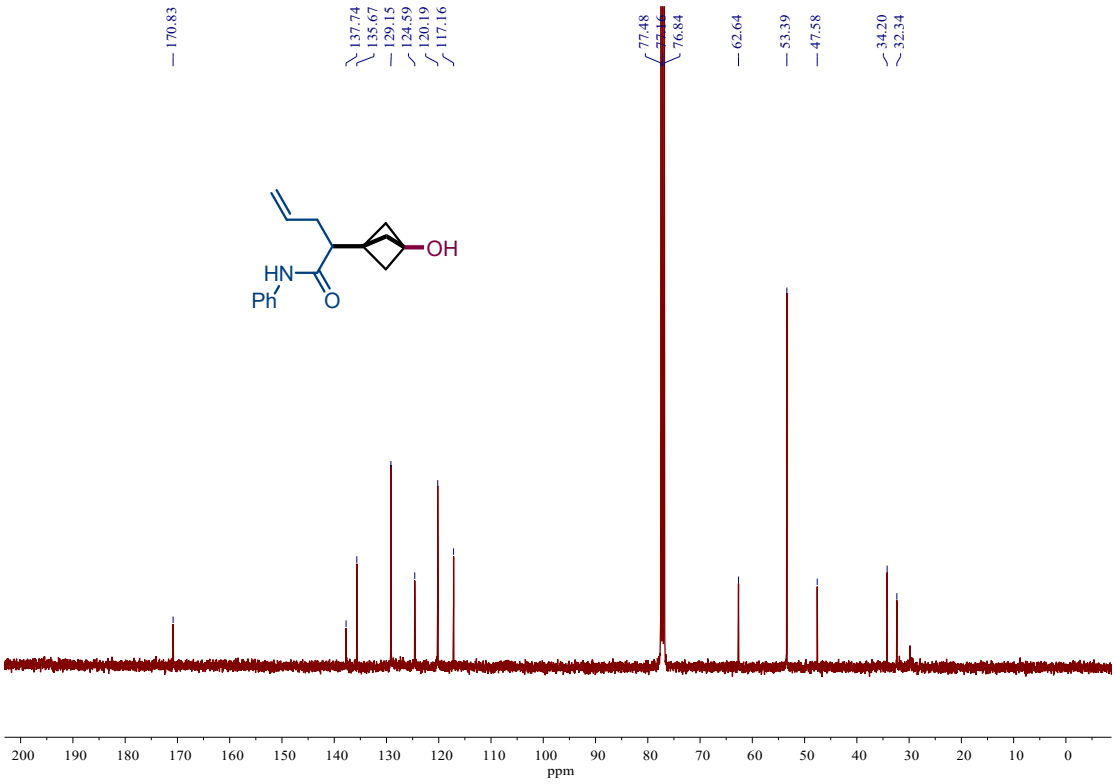
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 30



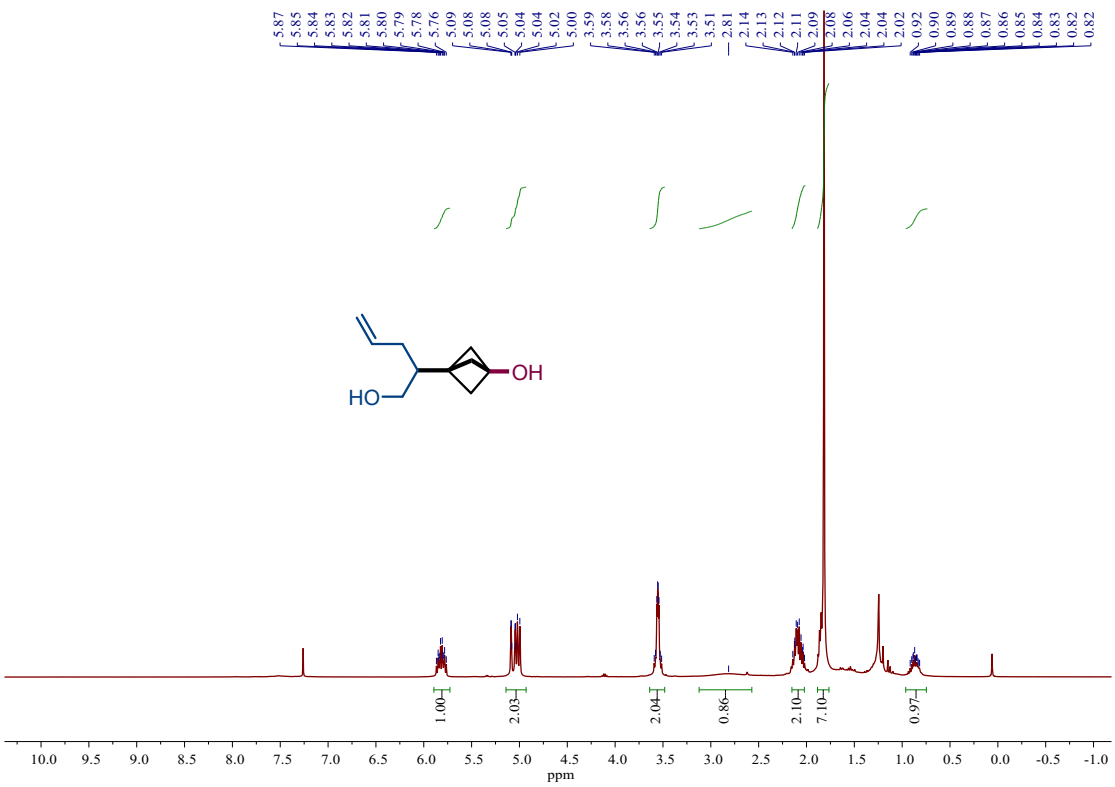
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 30



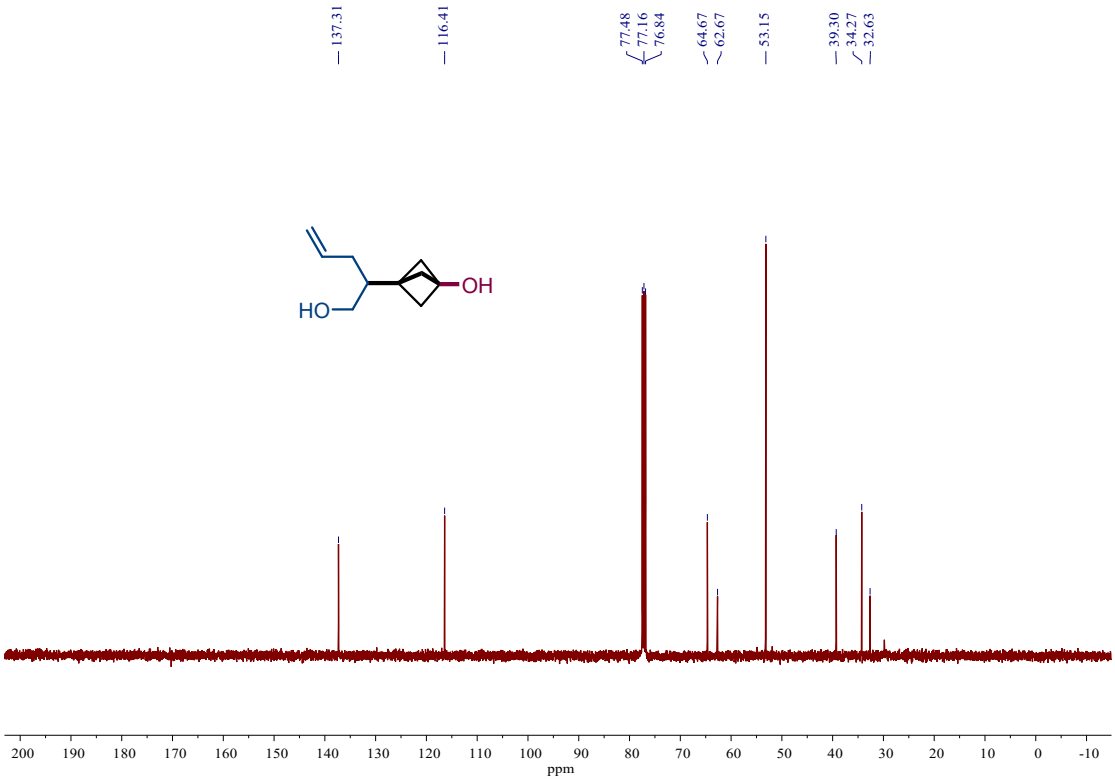
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 31



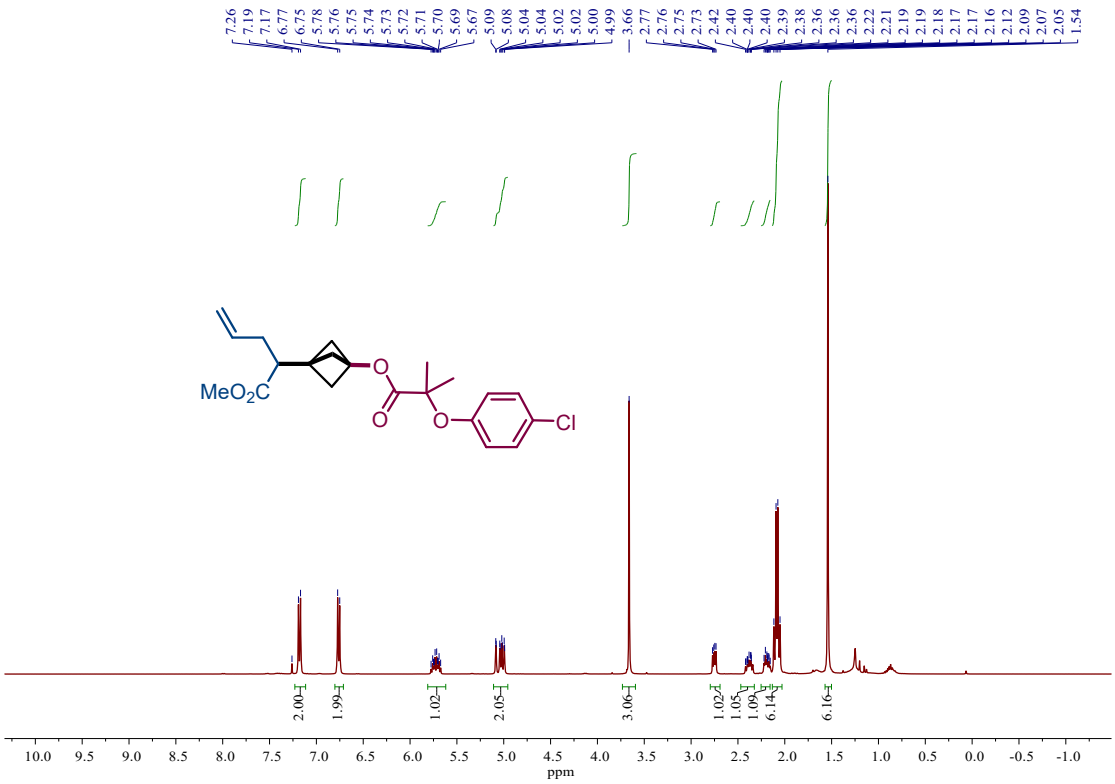
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 31



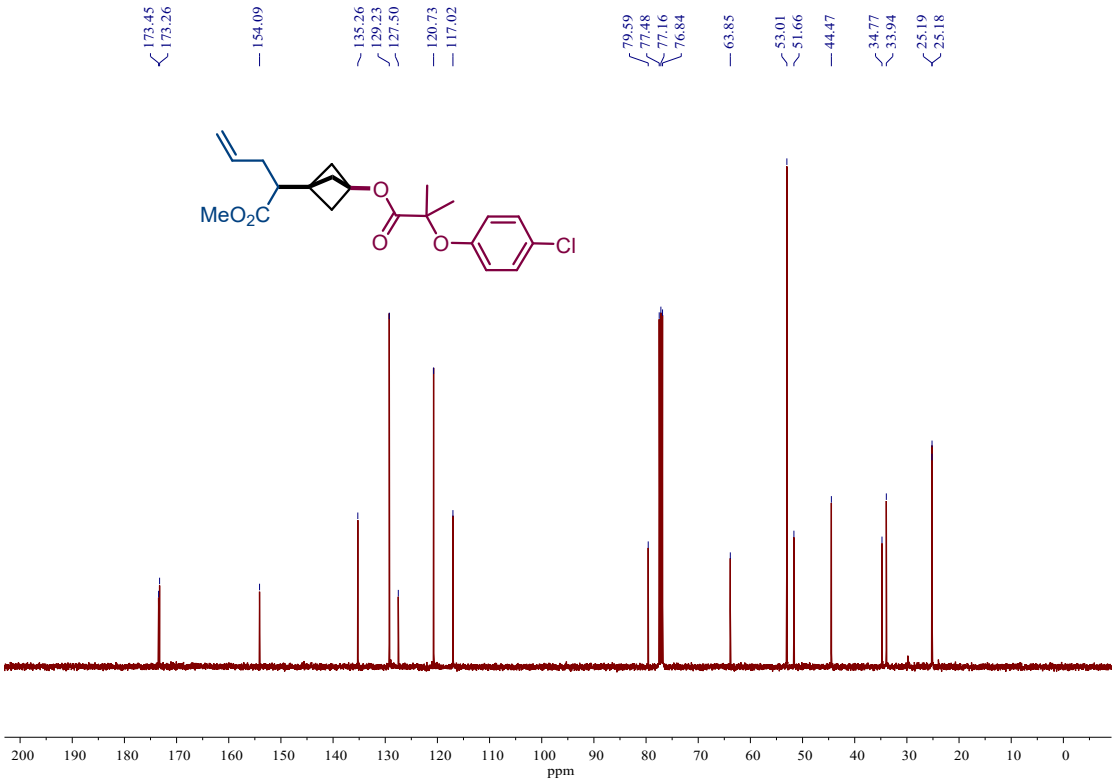
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 32



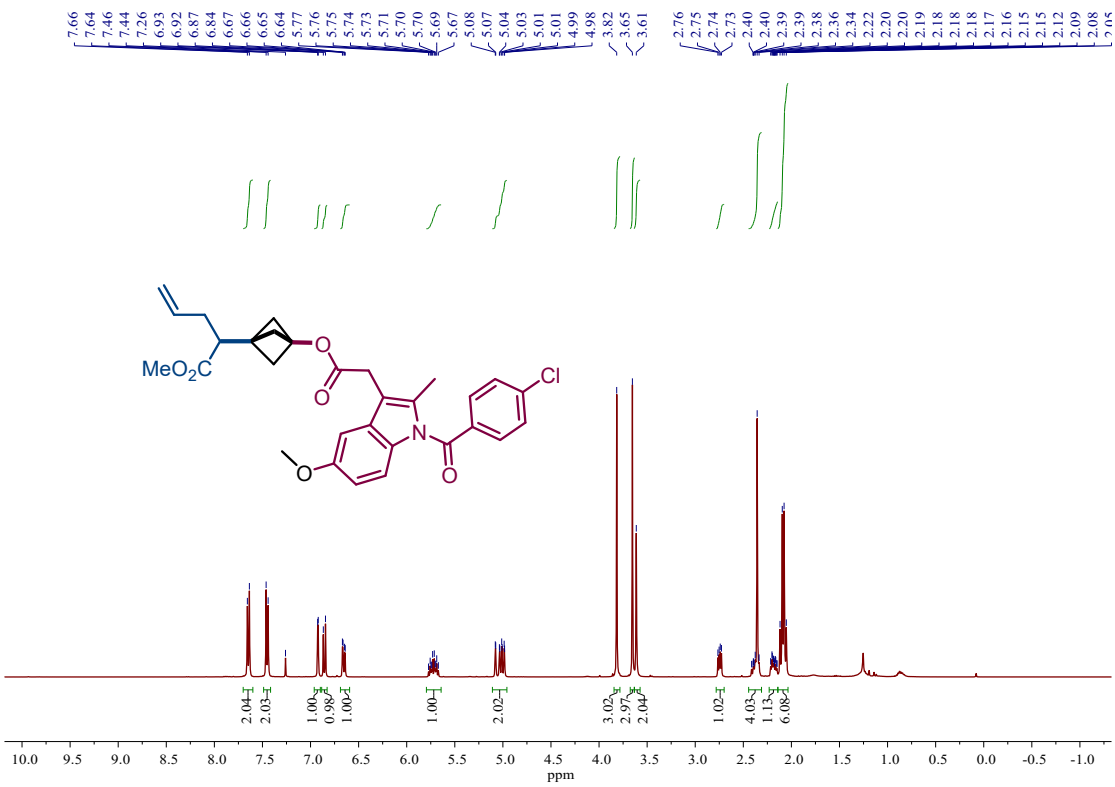
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 32



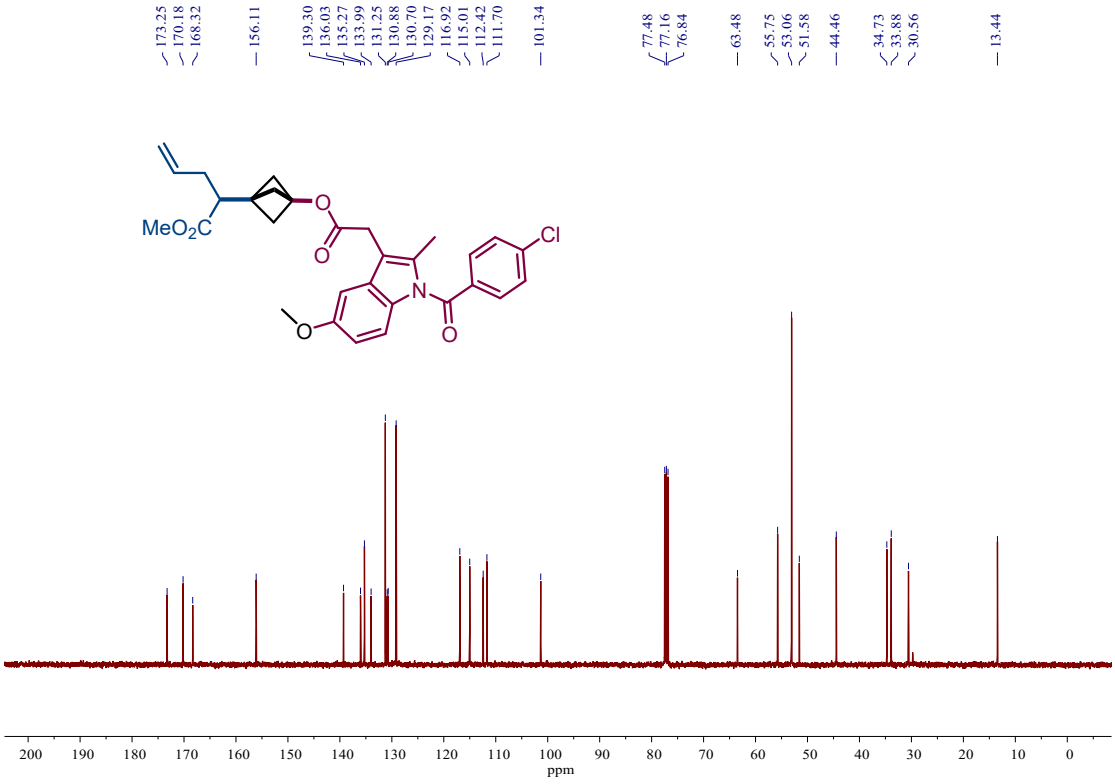
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 33



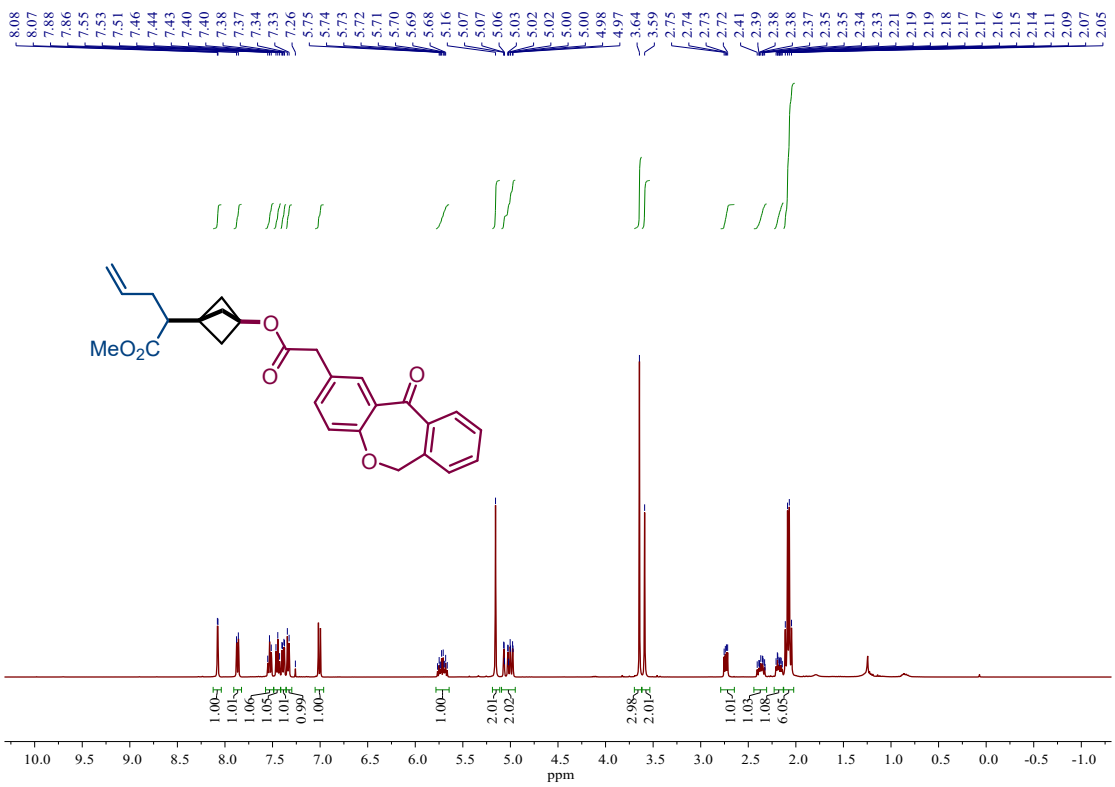
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 33



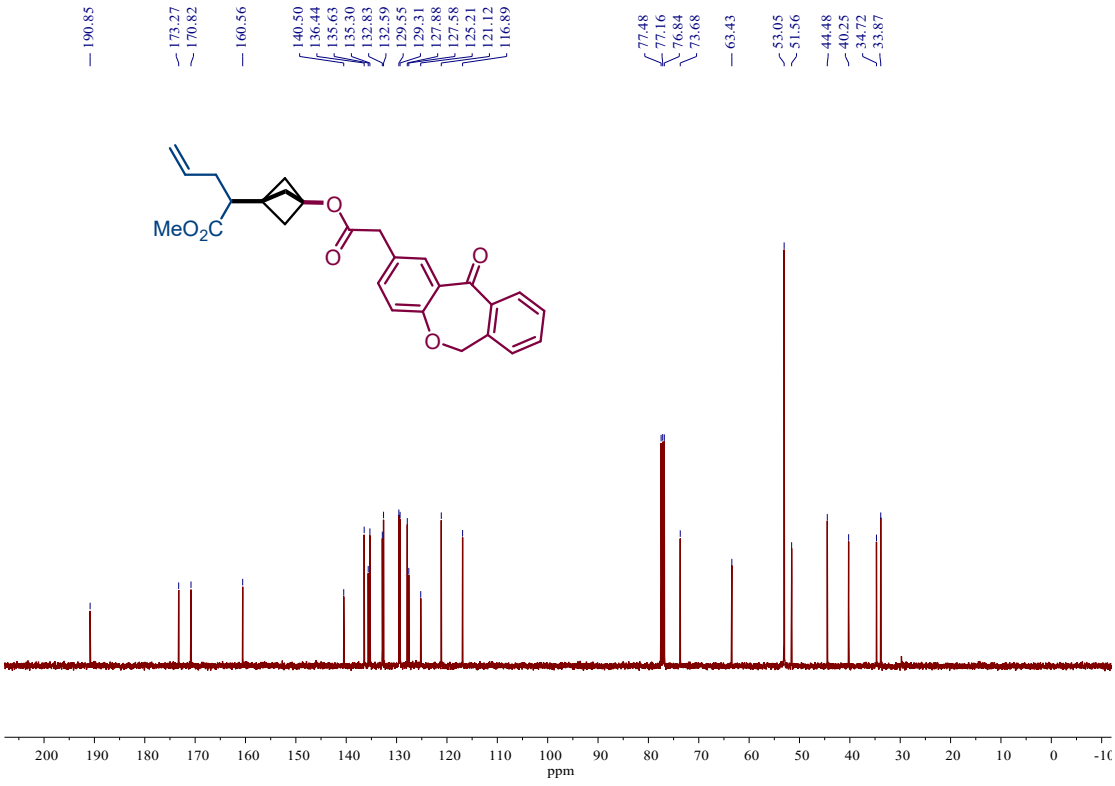
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 34



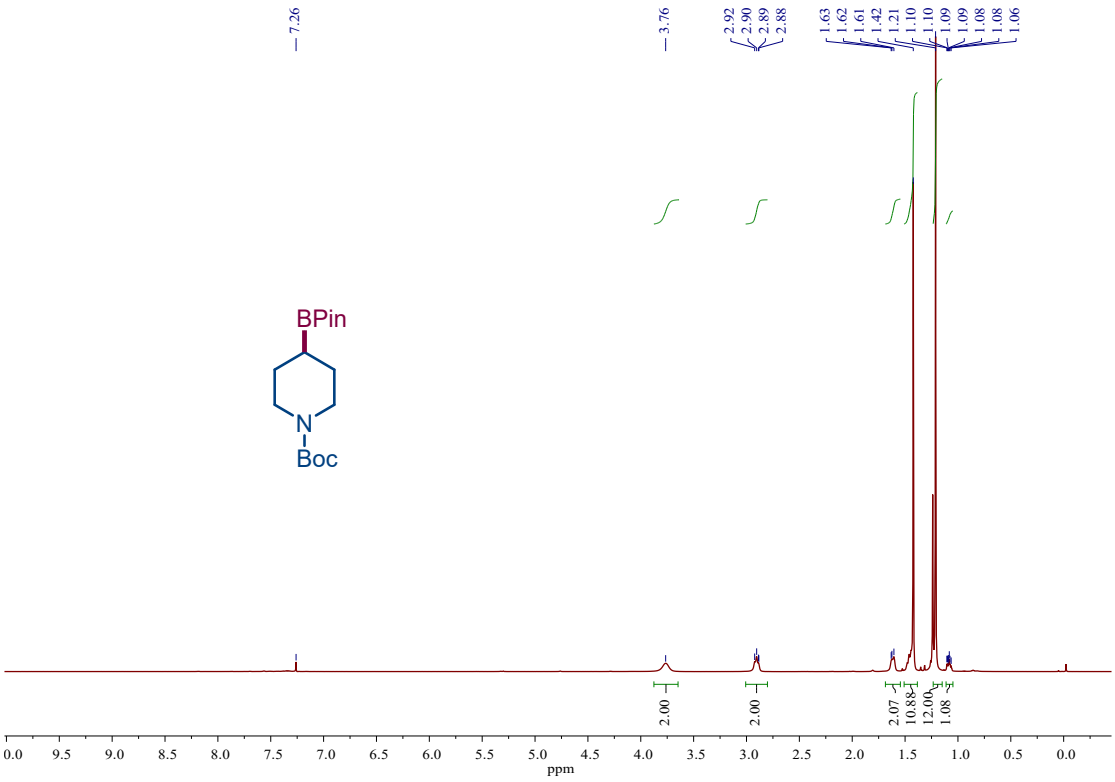
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 34



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 35



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 35



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 40