Photochemical α-selective radical ring-opening reactions of 1,3-disubstituted acyl bicyclobutanes with alkyl halides: modular access to the functionalized cyclobutenes

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Supporting Information

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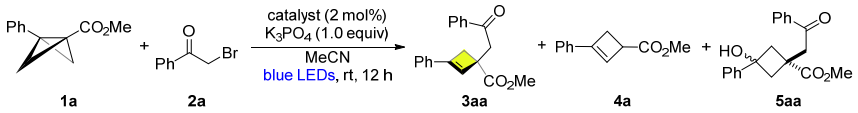
1 General Information

All reactions were performed in flame-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes. Bicyclo[1.1.0]butanes (BCBs)[1] were prepared according to reported procedures. Other commercially available reagents were purchased from *Sigma-Adrich*, *Leyan* and *Bide* Chemical Company. *N,N*-Dimethylacetamide (DMA), N,N-Dimethylformamide (DMF), Chlorobenzene (PhCl) and Acetonitrile (MeCN) were purchased from *Energy Chemical* (99%, Extra Dry) and used as received. All other solvents (THF, dioxane and 1,2-dichloroethane *etc*.) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (Petroleum ether, CH_2Cl_2, and ethyl acetate) were distilled prior to use. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ^1H, ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.0 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplett, q = quartet, m = multiplet), coupling constants (Hz), and integration. The full-scan mass spectra were taken on a hybrid quadrupole-orbitrap mass spectrometer equipped with a heated electrospray ionization source (ThermoFischer Scientific, Bremen, Germany). X-ray data were taken on a Bruker SMART APEX II X-Ray diffractometer equipped with a large area CCD detector. Acknowledgement: the ^1H, ^{13}C NMR spectra and HRMS (ESI) were performed at Analytical Instrumentation Center of Hunan University.

2 Optimization of Reaction Conditions (Table S1-S3)

Table S1. Catalyst Optimization[a,b]



entry	catalyst	conv. (%)[b]	yield of **3aa** (%)[b]	yield of **4a** (%)[b]	yield of **5aa** (%)[b]
1	*fac*-Ir(ppy)$_3$	83	30	5	12
2	[Ir{dF(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$	25	0	5	0
3	Ru(bpy)$_3$Cl$_2$·6H$_2$O	20	6	<5	<5
4	Ru(bpy)$_3$(PF$_6$)$_2$	43	7	<5	<5
5	Eosin Y	10	<5	<5	0
6	4-CzIPN	50	7	<5	0
7	[Acr$^+$-Mes]ClO$_4$	0	0	0	0
8	10H-phenothiazine	8	0	0	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2.0 mol%) and K_3PO_3 (1.0 equiv) in MeCN (2.0 mL) stirred at rt in blue LEDs for 12 h. [b]The yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

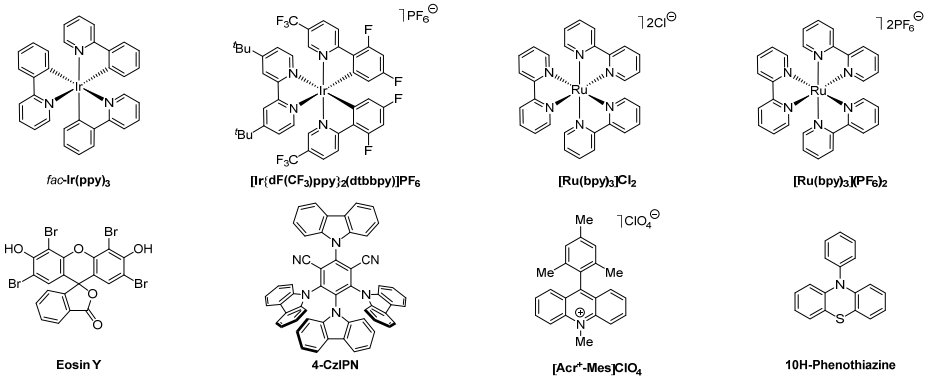
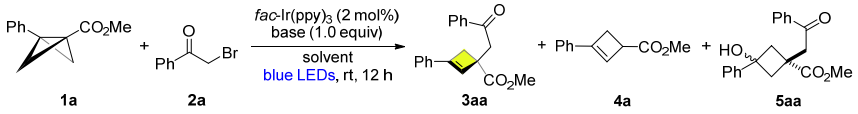


Table S2. Solvent and Base Optimization[a,b]

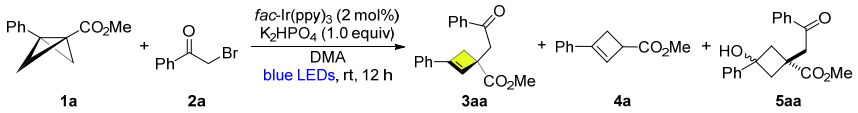


entry	solvent	base	conv. (%)[b]	yield of **3aa** (%)[b]	yield of **4a** (%)[b]	yield of **5aa** (%)[b]
1	MeCN	K_3PO_4	83	30	5	12
2	THF	K_3PO_4	100	43	9	6
3	dioxane	K_3PO_4	12	<5	<5	0
4	DCE	K_3PO_4	100	0	36	<5
5	acetone	K_3PO_4	100	23	10	8
6	PhCl	K_3PO_4	100	0	64	0
7	DMF	K_3PO_4	100	58	<5	6
8	DMF	K_2HPO_4	100	62	<5	11
9	DMF	KH_2PO_4	96	30	0	5

10	DMF	K_2CO_3	100	38	<5	<5
11	DMF	Na_2CO_3	100	35	<5	<5
12	DMF	NaOAc	100	25	<5	<5
13	DMF	Et_3N	100	11	5	0
14	DMF	DBU	100	20	25	0
15	DMA	K_2HPO_4	100	71	<5	5
16	NMP	K_2HPO_4	100	70	0	0
17	DMSO	K_2HPO_4	100	35	0	6

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (2.0 mol%) and base (1.0 equiv) in solvent (2.0 mL) stirred at rt in blue LEDs for 12 h. [b]The yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

Table S3. Other Optimizations[a,b]



1a 2a 3aa 4a 5aa

entry	Variation from standard conditions	conv. (%)[b]	yield of **3aa** (%)[b]	yield of **4a** (%)[b]	yield of **5aa** (%)[b]
1	K_2HPO_4 (1.5 equiv) was used	100	68	<5	<5
2	K_2HPO_4 (2.0 equiv) was used	100	67	<5	<5
3	H_2O (0.5 equiv) as additive	100	71	<5	7
4	H_2O (2.0 equiv) as additive	100	64	<5	11
5	Without *fac*-Ir(ppy)$_3$	5	0	5	0
6	In dark	36	0	<5	0
7	Raction time: 6 h	100	70	<5	9
8	Raction time: 3 h	100	71	<5	6

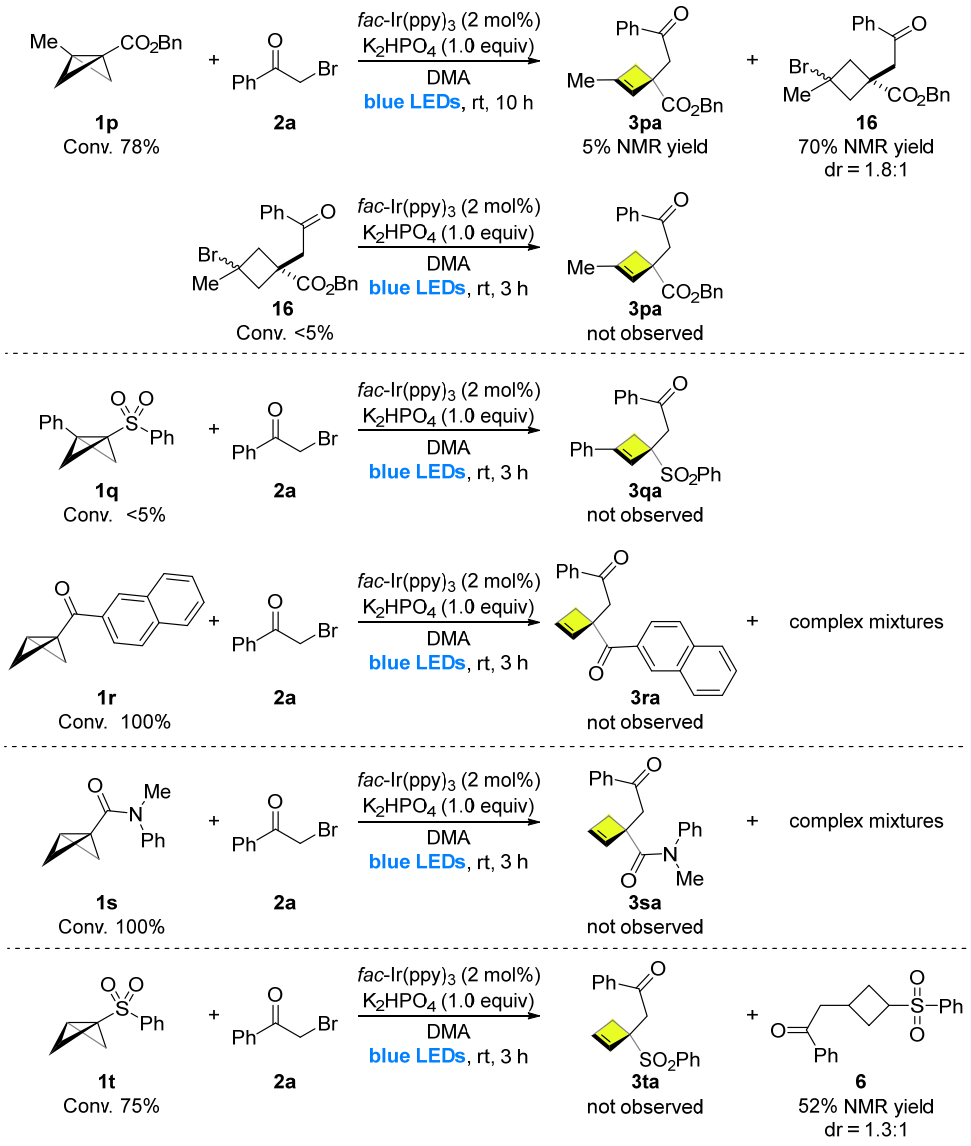
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), *fac*-Ir(ppy)$_3$ (2.0 mol%) and K_2HPO_4 (1.0 equiv) in DMA (2.0 mL) stirred at rt in blue LEDs for 12 h. [b]The yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard.

3 Unsuccessful Substrates

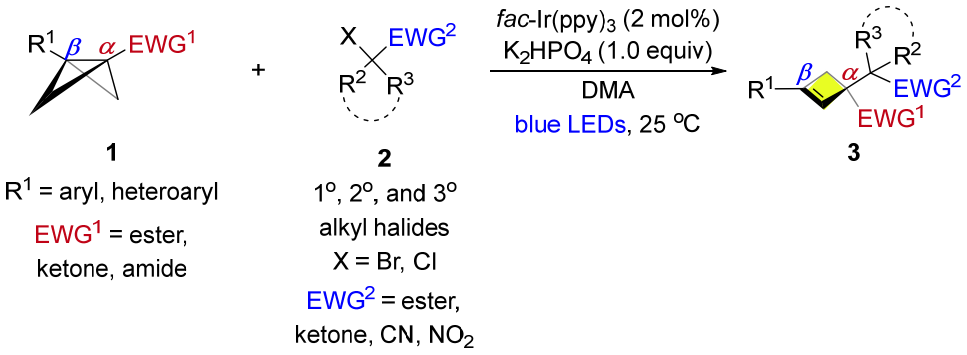
The following Scheme S1 list the BCB substrates that were unsuccessfully tested. The reactions were carried out according to conditions A and were analyzed by crude ^{1}H NMR with CH_2Br_2 as an internal standard. The reaction is not limited to aryl-substituted BCBs. Alkyl-substituted BCB **1p** was also found to be compatible, albeit with a low yield under conditions A. However, the reaction with 1,3-disubstituted BCB sulfone **1q** did not afford the desired product. Additionally, we investigated the influence of the substituent at the β-position of BCB in this site-selective reaction. The reaction between monosubstituted BCB ketone **1r** and monosubstituted BCB amide **1s** resulted in a complex mixture. However, the ring-opening reaction of

monosubstituted BCB sulfone **1t** with **2a** produced the desired cyclobutane product **6** through regular addition reaction, with a 52% NMR yield and a 1.3:1 diastereomeric ratio.

Scheme S1 Unsuccessful BCBs

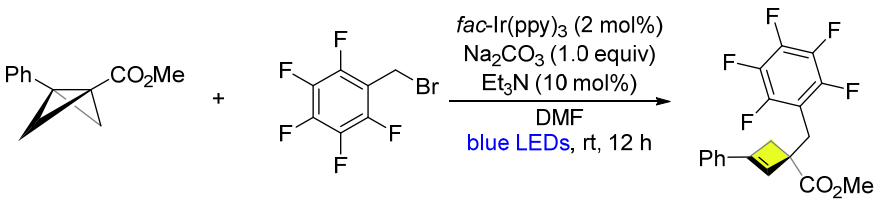


4 General Procedure for the Radical Ring-Opening Reactions of BCBs with Alkyl Halides (Condition A)



In glove box, to a flame-dried Schlenk tube was charged with the BCB **1** (0.20 mmol), alkyl halide **2** (0.30 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (4 μmol, 2 mol%), and K_2HPO_4 (0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of the dimethylacetamide (DMA) (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. Then the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3**.

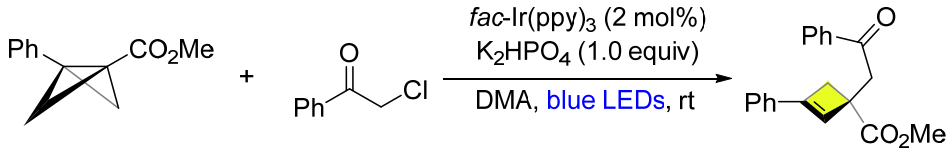
5 Procedure for the Radical Ring-Opening Reactions of BCB 1a with Benzyl Bromide 2w (Condition B)



In glove box, to a flame-dried Schlenk tube was charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (37.6 mg, 0.20 mmol), *fac*-Ir(ppy)$_3$ (2.6 mg, 4 μmol, 2 mol%) and Na_2CO_3 (21.2 mg, 0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times). Then, 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene **2w** (78.3 mg, 0.30 mmol, 1.5 equiv) and Et_3N (2.0 mg, 0.02 mmol, 10 mol%) were added, followed by the addition of the DMF (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 12 h.

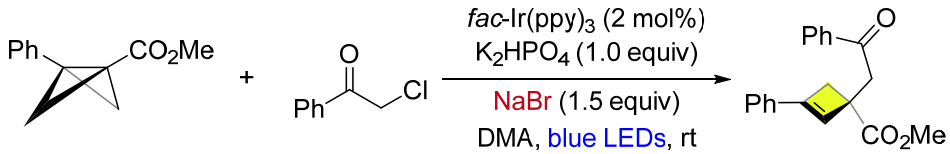
Then the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (50/1) afforded **3aw** as a colorless oil (66.3 mg, 90% yield).

6 Procedure for the Radical Ring-Opening Reactions of BCB 1a with *α*-Chloroacetophenone



1a **2a'** **3aa**, 55% NMR yield

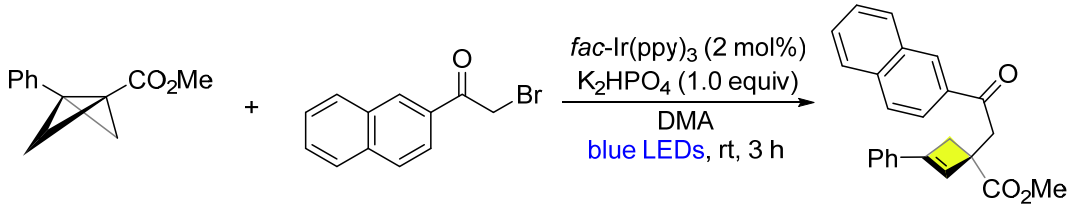
In glove box, to a flame-dried Schlenk tube was charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (37.6 mg, 0.2 mmol), 2-chloro-1-phenylethan-1-one **2a′** (46.4 mg, 0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2.6 mg, 4 μmol, 2 mol%), and K_2HPO_4 (34.8 mg, 0.2 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of the DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. Then the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers was washed with brine (2 × 10 mL) and dried over anhydrous $MgSO_4$.The filtrate was concentrated in *vacuo* and analyzed by ^{1}H NMR spectroscopy to obtain the NMR yield of **3aa** (55% NMR yield) with CH_2Br_2 as an internal standard. ***Note:*** *Further improvement of the yield was achieved when NaBr was used as additive.*



1a **2a'** **3aa**, 70% NMR yield

In glove box, to a flame-dried Schlenk tube was charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (37.6 mg, 0.2 mmol), 2-chloro-1-phenylethan-1-one **2a′** (46.4 mg, 0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2.6 mg, 4 μmol, 2 mol%), K_2HPO_4 (34.8 mg, 0.2 mmol, 1.0 equiv), and NaBr (30.9 mg, 0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of the DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. Then the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers was washed with brine (2 × 10 mL) and dried over anhydrous $MgSO_4$.The filtrate was concentrated in *vacuo* and analyzed by ^{1}H NMR spectroscopy to obtain the NMR yield of **3aa** (70% NMR yield) with CH_2Br_2 as an internal standard.

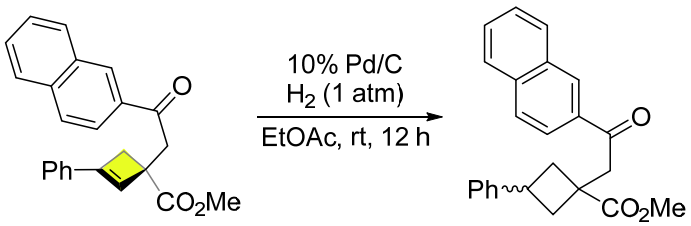
7 Scale-Up Experiment



1a (1.0 mmol) **2j** **3aj**, 90%

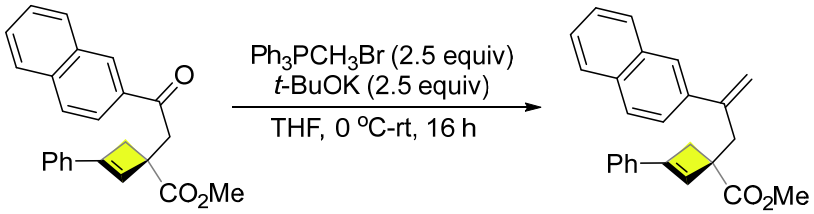
In glove box, to a flame-dried Schlenk tube is charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (188.2 mg, 1.0 mmol), 2-bromo-1-(naphthalen-2-yl)ethan-1-one **2j** (373.7 mg, 1.5 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (13.1 mg, 20 μmol, 2 mol%), and K_2HPO_4 (174.2 mg, 1.0 mmol, 1.0 equiv). The tube is evacuated and backfilled with N_2 (3 times) followed by the addition of the DMA (10 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. Then the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 20 mL). The combined organic phase was washed with brine (2 × 20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel using petroleum ether/EtOAc(20/1) afforded **3aj** as a white solid (320.8 mg, 90% yield).

8 Synthetic Transformations



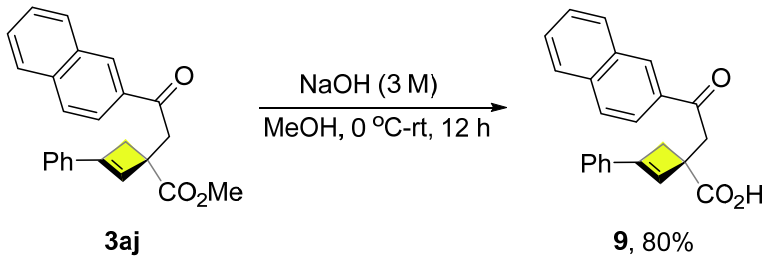
3aj **7**, 90%
d.r. = 6.4:1

Synthesis of (7): To a solution of cyclobutene **3aj** (35.6 mg, 0.1 mmol) in EtOAc (5 mL) was added 10% Pd/C (10 mg). A balloon filled with hydrogen gas was attached to the flask containing the suspension, which was then briefly evacuated and backfilled with hydrogen gas three times. The mixture was stirred overnight at room temperature and filtered through Celite. After the solvent was evaporated in vacuo, the crude material was purified by flash chromatography on silica gel using petroleum ether/EtOAc(20/1) afforded **7** as a colorless oil (32.2 mg, 90% yield, d.r. = 6.4:1).



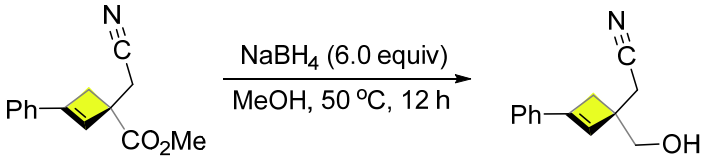
3aj **8**, 83%

Synthesis of (8): To methyl triphenylphosphonium bromide (89.3 mg, 0.25 mmol, 2.5 equiv) charged in a 25 mL oven dried flask was added anhydrous *t*-BuOK/THF (1 M, 2.5 eq). The resulting yellow suspension was stirred at 0 °C for 45 min and a solution of **3aj** (35.6 mg, 0.1 mmol) in THF (1 mL) added dropwise. The resulting mixture was warmed gradually to room temperature and stirred until **3aj** disappeared (monitored by TLC). The reaction mixture was quenched with water, extracted with EtOAc, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purification by flash chromatography on silica gel using petroleum ether/ EtOAc (10/1) afforded **8** as a colorless oil (30.5 mg, 83% yield).



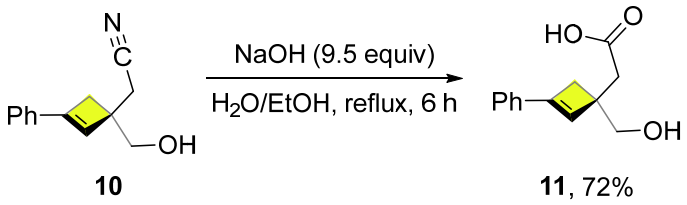
3aj **9**, 80%

Synthesis of (9): A reaction tube was charged with **3aj** (35.6 mg, 0.1 mmol) and MeOH (1 mL) under N_2 atmosphere. 3 M NaOH (0.1 mL, 0.3 mmol, 3.0 equiv) was added to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature until complete conversion of the starting material as observed from TLC analysis. 3 M HCl was added to acidify the reaction mixture and the resulting solution was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over Na_2SO_4. Then, filtered and concentrated under reduced pressure the crude material was purified by flash chromatography on silica gel using petroleum ether/EtOAc (1/2) afforded **9** as a white solid (27.4 mg, 80% yield).



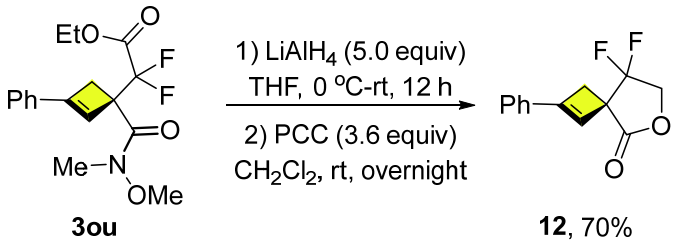
3am **10**, 86%

Synthesis of (10): 3am (22.7 mg, 0.1 mmol) was dissolved in MeOH (1.0 mL) at room temperature, and then $NaBH_4$ (22.7 mg, 0.6 mmol, 6 equiv) was added at the same temperature. The resulting mixture was allowed to warm to 50 °C. After completion, H_2O was added, and the mixture was extracted with diethyl ether. The combined organic phases were washed with saturated brine and dried over Na_2SO_4. Then, filtered and concentrated under reduced pressure, the residue was purification by flash chromatography on silica gel using petroleum ether/ EtOAc (2/1) afforded **10** as a colorless oil (17.3 mg, 86% yield).



10 **11**, 72%

Synthesis of (11): 10 (19.9 mg, 0.1 mmol) was dissolved in H_2O/EtOH (1:1, 2.0 mL) at room temperature, and then NaOH (38.0 mg, 0.95 mmol, 9.5 equiv) was added at the same temperature. The resulting mixture was allowed to warm to reflux. After completion, the reaction was cooled to room temperature. 3 M HCl was added to acidify the reaction mixture and the resulting solution was extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4. Then, filtered and concentrated under reduced pressure, the residue was purification by flash chromatography on silica gel using petroleum ether/ EtOAc (1/3) afforded **11** as a white solid (15.7 mg, 72% yield).

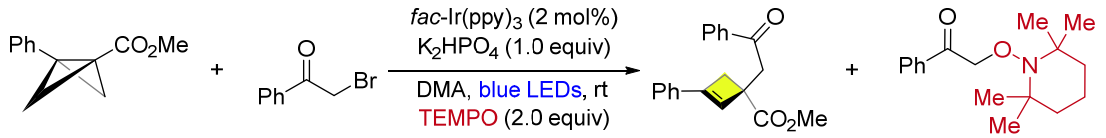


3ou **12**, 70%

Synthesis of (12): A solution of **3ou** (33.9 mg, 0.10 mmol, 1.0 equiv) in THF (1.0 mL) was added dropwise to a suspension of $LiAlH_4$ (19.0 mg, 0.5 mmol, 5.0 equiv) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 12 h (monitored by TLC). The reaction was quenched by addition of aq. NaOH (1 M, 0.3 mL) and water (1.5 mL). The mixture was stirred at room temperature for 30 min and extracted with EtOAc (3 x 10 mL). The organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. Then, the crude product mixture in CH_2Cl_2 (1 mL) was added to a mixture of PCC (77.6 mg, 0.36 mmol, 3.6 equiv) and SiO_2 (77.6 mg) in CH_2Cl_2 (2 mL). The orange mixture was stirred overnight then diluted with Et_2O (6 mL) and filtered through a celite pad and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether/ EtOAc (20/1) afforded **12** as a colorless oil (16.5 mg, 70% yield).

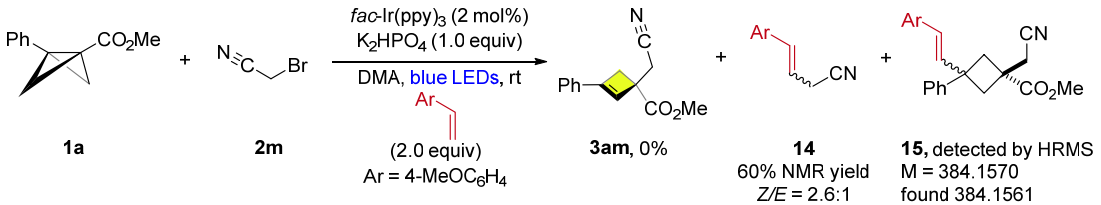
9 Mechanism Studies

9.1 Radical Trapping Experiments



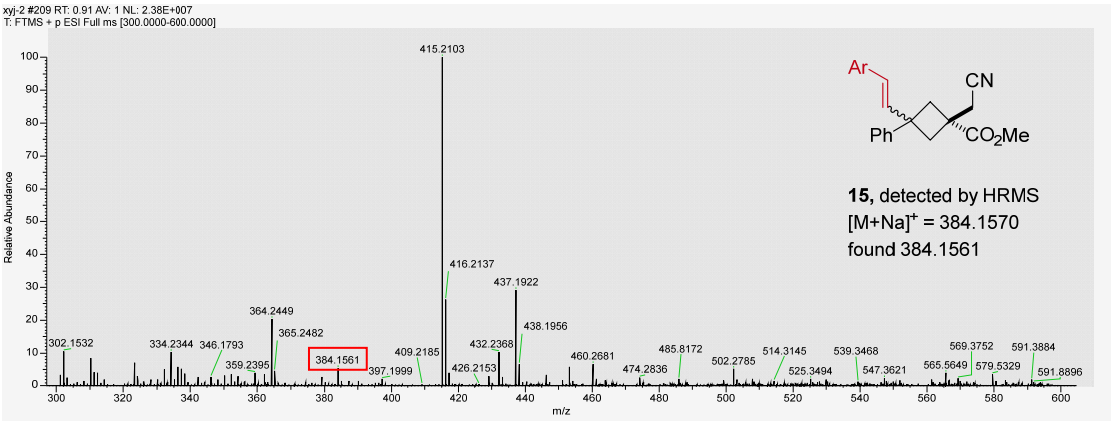
1a **2a** **3aa**, 0% **13**, 82% NMR yield

In glove box, to a flame-dried Schlenk tube was charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (37.6 mg, 0.20 mmol), 2-bromo-1-phenylethan-1-one **2a** (59.7 mg, 0.30 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2.6 mg, 4 μmol, 2 mol%), K_2HPO_4 (34.8 mg, 0.20 mmol, 1.0 equiv), and TEMPO (62.5 mg, 0.4 mmol, 2.0 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of the DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. The reaction was inhibited and the radical trapping product **13** was obtained in 82% NMR yield, which revealed that the transformation was likely to proceed through a radical pathway.

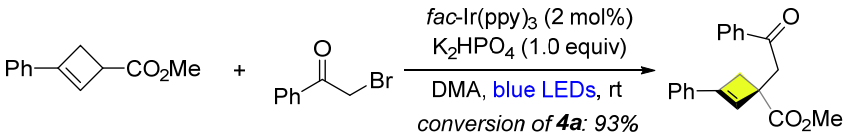


1a **2m** **3am**, 0% **14** 60% NMR yield *Z*/*E* = 2.6:1 **15**, detected by HRMS M = 384.1570 found 384.1561

In glove box, to a flame-dried Schlenk tube was charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (37.6 mg, 0.20 mmol), *fac*-Ir(ppy)$_3$ (2.6 mg, 4 μmol, 2 mol%), K_2HPO_4 (34.8 mg, 0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of a solution of 2-bromoacetonitrile **2m** (36.0 mg, 0.30 mmol, 1.5 equiv) and 4-methoxystyrene (53 μL 53.7 mg, 0.40 mmol, 2.0 equiv) in DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. The aimed cyclobutene **3am** together with **14** and **15** was detected by ^{1}H NMR and HRMS, indicating that the reaction proceeds via a radical pathway with *α*-selectivity.

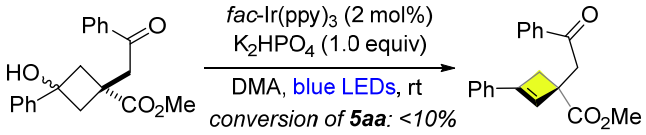


9.2 Control Experiments



4a **2a** **3aa**, 0%

In glove box, to a flame-dried Schlenk tube was charged with the cyclobutene **4a** (18.8 mg, 0.10 mmol), 2-bromo-1-phenylethan-1-one **2a** (29.9 mg, 0.15 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (1.3 mg, 2 μmol, 2 mol%), and K_2HPO_4 (17.4 mg, 0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of the DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. The aimed product **3aa** was not detected, which demonstrated that the reaction was not proceeding via the cyclobutene intermediate **4a**.

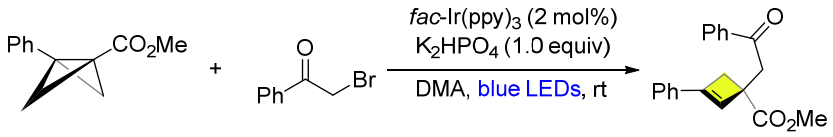


5aa **3aa**, 0%

In glove box, to a flame-dried Schlenk tube was charged with the cyclobutane **5aa** (38.7 mg, 0.10 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 2 μmol, 2 mol%), and K_2HPO_4 (17.4 mg, 0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times)

followed by the addition of the DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature for 3 h. No desired product was observed.

9.3 Light On/Off Experiment



1a **2a** **3aa**

In glove box, to a flame-dried Schlenk tube was charged with the methyl-3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** (37.6 mg, 0.20 mmol), 2-bromo-1-phenylethan-1-one **2a** (59.7 mg, 0.30 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (2.6 mg, 4 μmol, 2 mol%), and K_2HPO_4 (34.8 mg, 0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with N_2 (3 times) followed by the addition of the DMA (2 mL). The reaction mixture was irradiating with 12 W blue LEDs at room temperature. The light was turned off at intervals of 20 minutes, and the reaction was allowed to stir in the dark for 30 minutes before the LED was turned back on. Five parallel experiments were carried out to fit each point. After the reaction was completed, the reaction mixture was poured into water and then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed with brine (2 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The yield was calculated by NMR with CH_2Br_2 as an internal standard.

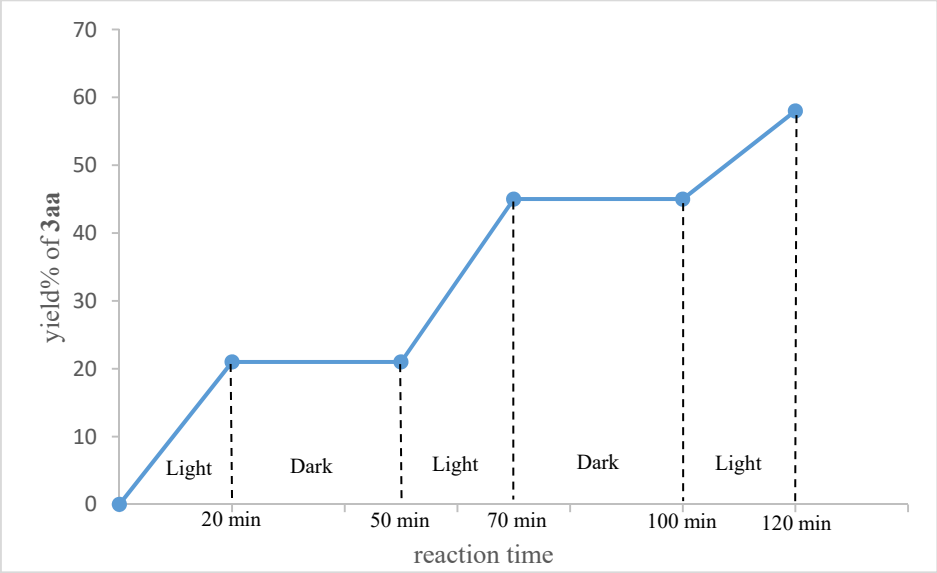


Figure S1. Light on/off experiment

9.4 Stern-Volmer Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM *fac*-Ir(ppy)$_3$ in degassed dry CH_3CN added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 395 nm and fluorescence was measured from 450 nm to 650 nm. Control experiments showed that the excited state *fac*-Ir(ppy)$_3$ was mainly quenched by 2-bromo-1-phenylethan-1-one **2a**

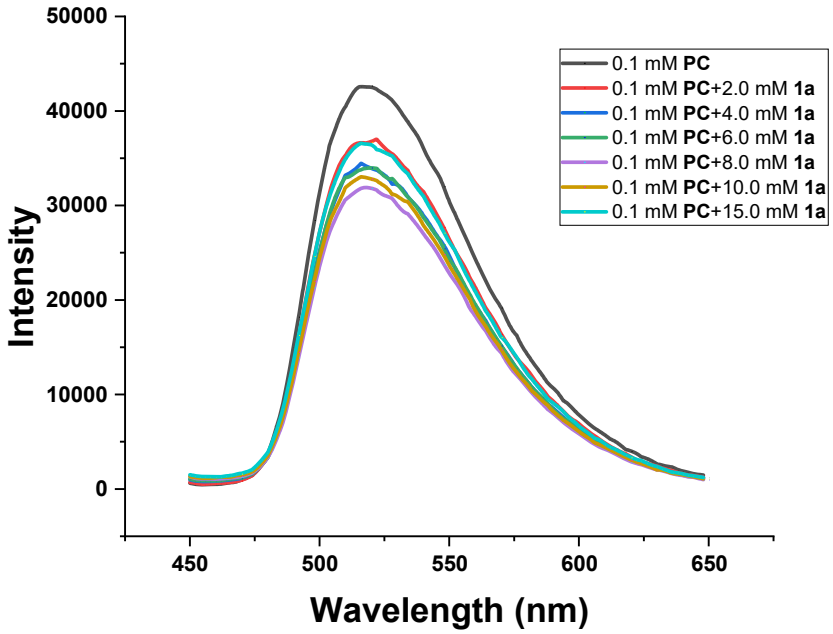


Figure S2. Fluorescence quenching experiments date with $Ir(ppy)_3$ and variable **1a**

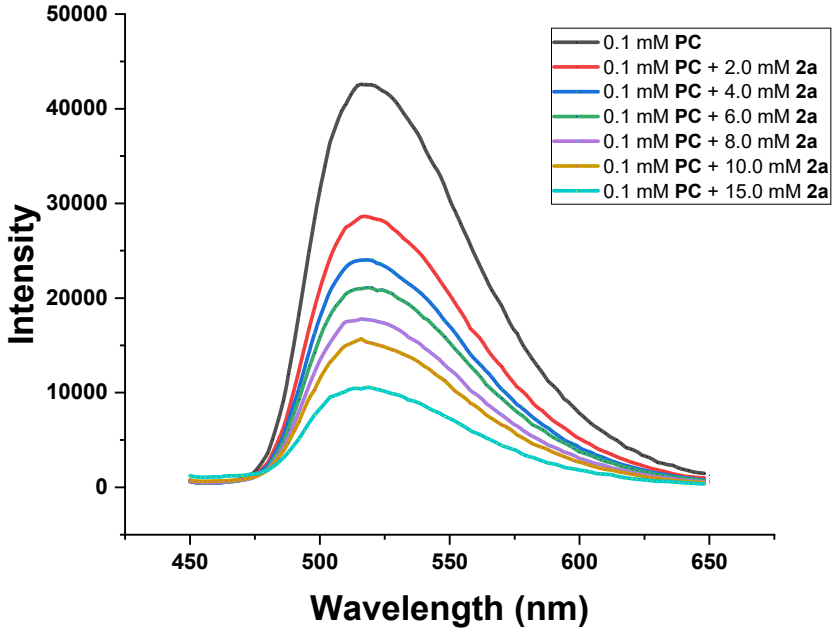


Figure S3. Fluorescence quenching experiments date with $Ir(ppy)_3$ and variable **2a**

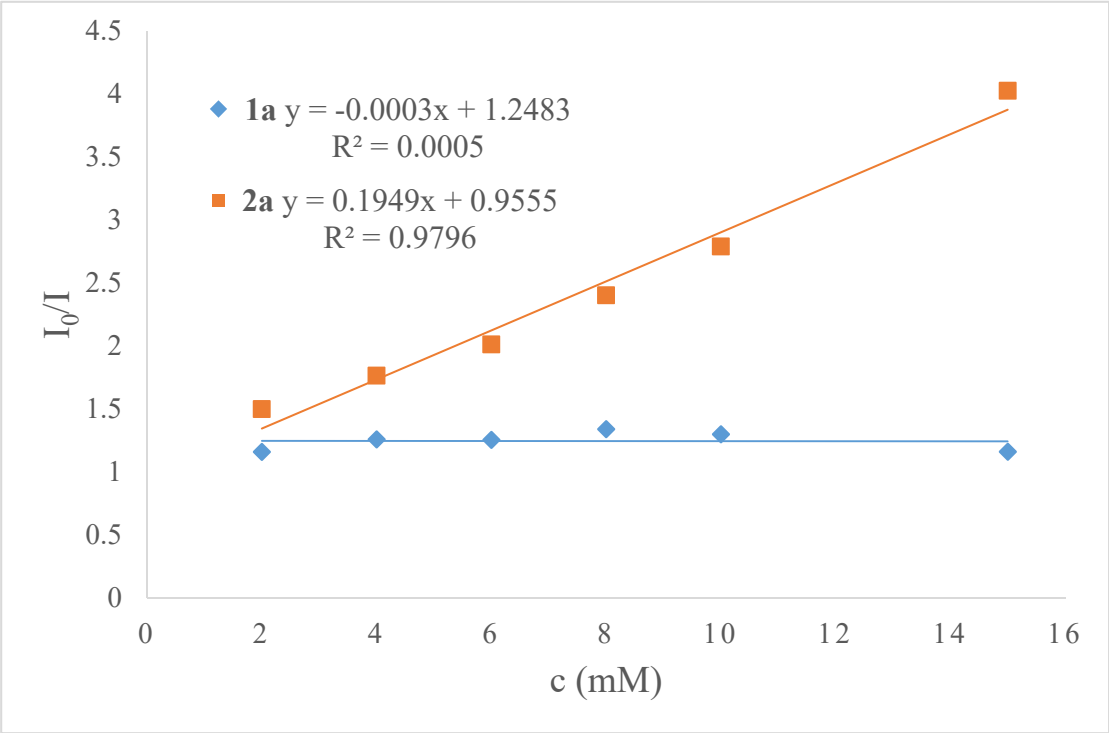
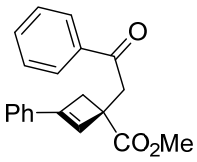


Figure S4. Stern-Volmer plots of $Ir(ppy)_3$ with different quenchers

10 Characterization Data of the Products

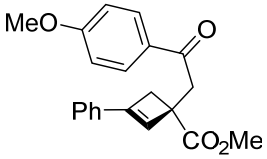


3aa
$C_{20}H_{18}O_3$
M = 306.36 g/mol

Methyl-1-(2-oxo-2-phenylethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3aa**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-phenylethan-1-one (**2a**, 59.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3aa** as a colorless oil (41.1 mg, 67% yield).

3aa: $\mathbf{R_f}$ = 0.45 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47-7.44 (m, 2H), 7.38-7.26 (m, 5H), 6.51 (s, 1H), 3.73 (d, *J* = 17.2 Hz, 1H), 3.71 (s, 3H), 3.58 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* =

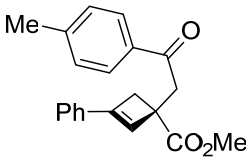
13.2 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.1, 175.0, 146.8, 136.5, 133.5, 133.2, 128.8, 128.5, 128.4, 128.3, 128.0, 124.8, 52.2, 47.4, 45.1, 38.6 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{18}O_3Na$: 329.1148; Found: 329.1145.



3ab
$C_{21}H_{20}O_4$
M = 336.39 g/mol

Methyl-1-(2-(4-methoxyphenyl)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ab**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(4-methoxyphenyl)ethan-1-one (**2b**, 68.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ab** as a colorless oil (40.4 mg, 60% yield).

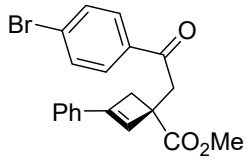
3ab: **R_f** = 0.4 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.38-7.26 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.50 (s, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 3.68 (d, *J* = 17.6 Hz, 1H), 3.53 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.73 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.6, 175.1, 163.6, 146.7, 133.6, 130.3, 129.7, 129.0, 128.42, 128.36, 124.8, 113.7, 55.4, 52.2, 47.5, 44.8, 38.6 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{21}H_{20}O_4Na$: 359.1254; Found: 359.1258.



3ac
$C_{21}H_{20}O_3$
M = 320.39 g/mol

Methyl-1-(2-oxo-2-(*p*-tolyl)ethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ac**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(p-tolyl)ethan-1-one (**2c**, 63.9 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ac** as a white solid (48.7 mg, 76% yield).

3ac: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.38-7.24 (m, 7H), 6.50 (s, 1H), 3.71 (s, 3H), 3.70 (d, *J* = 17.6 Hz, 1H), 3.56 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.73 (d, *J* = 13.2 Hz, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.7, 175.0, 146.7, 144.0, 134.1, 133.6, 129.2, 128.9, 128.4, 128.3, 128.1, 124.8, 52.2, 47.4, 45.0, 38.6, 21.6 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{21}H_{20}O_3Na$: 343.1305; Found: 343.1306.

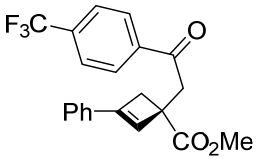


3ad
$C_{20}H_{17}BrO_3$
M = 385.26 g/mol

Methyl-1-(2-(4-bromophenyl)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ad**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(4-bromophenyl)ethan-1-one (**2d**, 83.4 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ad** as a colorless oil (43.9 mg, 57% yield).

3ad: $\mathbf{R_f}$ = 0.50 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.38-7.28 (m, 5H), 6.49 (s, 1H), 3.71 (s, 3H), 3.69 (d, *J* = 18.8 Hz, 1H), 3.53 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.1, 174.9, 146.9, 135.2,

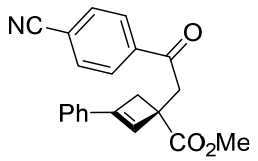
133.5, 131.9, 129.5, 128.7, 128.5, 128.41, 128.39, 124.8, 52.3, 47.3, 45.0, 38.6 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{17}BrO_3Na$: 407.0253; Found: 407.0252.



3ae
$C_{21}H_{17}F_3O_3$
M = 374.36 g/mol

Methyl-1-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ae**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2e**, 80.1 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ae** as a colorless oil (41.2 mg, 55% yield).

3ae: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.39-7.29 (m, 5H), 6.51 (s, 1H), 3.74 (d, *J* = 18.4 Hz, 1H), 3.72 (s, 3H), 3.58 (d, *J* = 18.0 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 2.76 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.3, 174.8, 147.1, 139.2, 134.5 (q, *J* = 32.5 Hz), 133.4, 128.6, 128.5, 128.42, 128.37, 125.7 (q, *J* = 3.6 Hz), 124.8, 123.5 (q, *J* = 271.0 Hz), 52.3, 47.4, 45.3, 38.7 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.12 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{21}H_{17}F_3O_3Na$: 309.1022; Found: 309.1021.

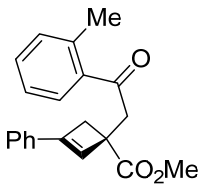


3af
$C_{21}H_{17}NO_3$
M = 331.37 g/mol

Methyl-1-(2-(4-cyanophenyl)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3af**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg,

0.2 mmol) and 4-(2-bromoacetyl)benzonitrile (**2f**, 67.2 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3af** as a colorless oil (36.5 mg, 55% yield).

3af: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.39-7.31 (m, 5H), 6.50 (s, 1H), 3.73 (d, *J* = 15.2 Hz, 1H), 3.71 (s, 3H), 3.56 (d, *J* = 18.0 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.76 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.9, 174. 8, 147.1, 139.4, 133.3, 132.5, 128.6, 128.42, 128.41, 128.3, 124.8, 117.9, 116.4, 52.3, 47.3, 45.2, 38.6 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{21}H_{17}NO_3Na$: 354.1101; Found: 354.1103.

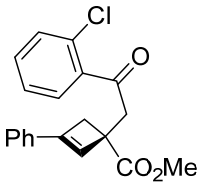


3ag
$C_{21}H_{20}O_3$
M = 320.39 g/mol

Methyl-1-(2-oxo-2-(o-tolyl)ethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ag**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(o-tolyl)ethan-1-one (**2g**, 63.9 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ag** as a colorless oil (40.4 mg, 63% yield).

3ag: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.39-7.23 (m, 8H), 6.50 (s, 1H), 3.71 (s, 3H), 3.64 (d, *J* = 17.6 Hz, 1H), 3.50 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H), 2.51 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 202.1, 175.0, 146.8, 138.3, 137.3, 133.6, 131.9, 131.4, 128.9, 128.6, 128.5, 128.4, 125.6, 124.8, 52.2, 47.8, 47.7, 38.7,

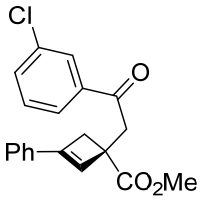
21.3 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{21}H_{20}O_3Na$: 343.1305; Found: 343.1303.



3ah
$C_{20}H_{17}ClO_3$
M = 340.80 g/mol

Methyl-1-(2-(2-chlorophenyl)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ah**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(2-chlorophenyl)ethan-1-one (**2h**, 70.0 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ah** as a colorless oil (42.3 mg, 62% yield).

3ah: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 1H), 7.41-7.31 (m, 8H), 6.50 (s, 1H), 3.72 (s, 3H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.55 (d, *J* = 18.0 Hz, 1H), 3.36 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 201.0, 174.8, 147.0, 138.7, 133.5, 131.9, 131.1, 130.6, 129.3, 128.6, 128.5, 128.4, 126.9, 124.9, 52.3, 49.1, 47.8, 38.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{17}ClO_3Na$: 363.0758; Found: 363.0760.

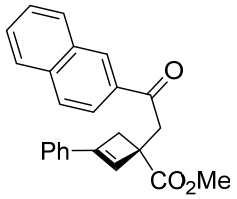


3ai
$C_{20}H_{17}ClO_3$
M = 340.80 g/mol

Methyl-1-(2-(2-chlorophenyl)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ai**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(2-chlorophenyl)ethan-1-one (**2i**, 70.0 mg, 0.3 mmol) at rt

for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1 to 10/1) afforded **3ai** as a colorless oil (47.8 mg, 70% yield).

3ai: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.42-7.29 (m, 6H), 6.49 (s, 1H), 3.71 (s, 3H), 3.68 (d, *J* = 16.8 Hz, 1H), 3.53 (d, *J* = 18.0 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.9, 174.8, 147.0, 138.1, 134.9, 133.5, 133.1, 129.9, 128.6, 128.5, 128.4, 128.2, 126.1, 124.8, 52.2, 47.4, 45.1, 38.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{17}ClO_3Na$: 363.0758; Found: 363.0753.

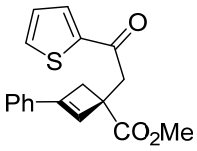


3aj
$C_{24}H_{20}O_3$
M = 356.42 g/mol

Methyl-1-(2-(naphthalen-2-yl)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3aj**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3aj** as a white solid (64.9 mg, 91% yield).

3aj: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.4 Hz, 2H), 7.60-7.52 (m, 2H), 7.39-7.24 (m, 5H), 6.55 (s, 1H), 3.86 (d, *J* = 17.6 Hz, 1H), 3.72 (s, 3H), 3.71 (d, *J* = 17.6 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 2.79 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 175.1, 146.8, 135.6, 133.9, 133.6, 132.4, 129.8, 129.5, 128.9, 128.5, 128.43, 128.38, 127.8, 126.8, 124.8, 123.7, 52.2, 47.6, 45.2,

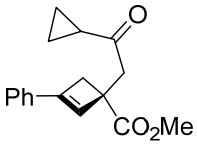
38.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{24}H_{20}O_3Na$: 379.1305; Found: 379.1305.



3ak
$C_{18}H_{16}O_3S$
M = 312.38 g/mol

Methyl-1-(2-oxo-2-(thiophen-2-yl)ethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ak**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-(thiophen-2-yl)ethan-1-one (**2k**, 61.5 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ak** as a colorless oil (35.6 mg, 57% yield).

3ak: $\mathbf{R_f}$ = 0.45 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 3.6 Hz, 1H), 7.63 (d, *J* = 4.8 Hz, 1H), 7.38-7.26 (m, 5H), 7.13 (t, *J* = 4.4 Hz, 1H), 6.50 (s, 1H), 3.70 (s, 3H), 3.66 (d, *J* = 17.2 Hz, 1H), 3.50 (d, *J* = 17.2 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.9, 174.8, 146.8, 143.8, 133.63, 133.55, 132.0, 128.8, 128.5, 128.4, 128.1, 124.8, 52.2, 47.5, 45.6, 38.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{18}H_{16}O_3SNa$: 355.0712; Found: 355.0712.

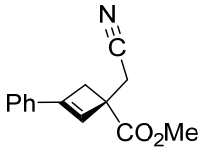


3al
$C_{17}H_{18}O_3$
M = 270.33 g/mol

Methyl-1-(2-cyclopropyl-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3al**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-1-cyclopropylethan-1-one (**2l**, 48.9 mg, 0.3 mmol) at rt for 3 h

according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3al** as a colorless oil (23.8 mg, 44% yield).

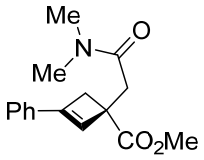
3al: $\mathbf{R_f}$ = 0.5 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 4H), 7.30-7.26 (m, 1H), 6.42 (s, 1H), 3.69 (s, 3H), 3.31 (d, *J* = 18.0 Hz, 1H), 3.27 (d, *J* = 13.2 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.65 (d, *J* = 13.2 Hz, 1H), 1.97-1.91 (m, 1H), 1.07-1.03 (m, 2H), 0.91- 0.86 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 208.7, 174.9, 146.6, 133.6, 128.8, 128.4, 128.3, 124.8, 52.1, 49.3, 47.3, 38.6, 20.6, 10.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{18}O_3Na$: 293.1148; Found: 293.1148.



3am
$C_{14}H_{13}NO_2$
M = 227.26 g/mol

Methyl-1-(cyanomethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3am**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromoacetonitrile (**2m**, 36.0 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3am** as a white solid (27.7 mg, 61% yield).

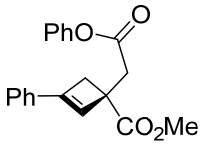
3am: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 5H), 6.34 (s, 1H), 3.76 (s, 3H), 3.31 (d, *J* = 13.2 Hz, 1H), 2.99 (d, *J* = 16.4 Hz, 1H), 2.93 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.8, 148.7, 132.6, 129.1, 128.5, 126.0, 125.0, 117.3, 52.7, 47.1, 38.1, 24.2 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{14}H_{13}O_2Na$: 250.0838; Found: 250.0838.



3an
$C_{16}H_{19}NO_3$
M = 273.33 g/mol

Methyl-1-(2-(dimethylamino)-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3an**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 2-bromo-*N*,*N*-dimethylacetamide (**2n**, 49.8 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded **3an** as a colorless oil (24.6 mg, 45% yield).

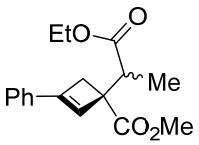
3an: $\mathbf{R_f}$ = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.32 (m, 4H), 7.30-7.26 (m, 1H), 6.50 (s, 1H), 3.72 (s, 3H), 3.29 (d, *J* = 13.2 Hz, 1H), 3.07 (d, *J* = 16.4 Hz, 1H), 3.00 (s, 3H), 2.95 (s, 3H), 2.88 (d, *J* = 16.0 Hz, 1H), 2.69 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.4, 170.7, 146.4, 133.7, 129.4, 128.3, 124.7, 52.2, 47.9, 40.2, 38.4, 37.0, 35.1 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{16}H_{19}NO_3Na$: 296.1257; Found: 296.1255.



3ao
$C_{20}H_{18}O_4$
M = 322.36 g/mol

Methyl-1-(2-oxo-2-phenoxyethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ao**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and phenyl 2-bromoacetate (**2o**, 64.5 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ao** as a colorless oil (40.0 mg, 62% yield).

3ao: **R_f** = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.30 (m, 7H), 7.24-7.19 (m, 1H), 7.11-7.08 (m, 2H), 6.50 (s, 1H), 3.73 (s, 3H), 3.34 (d, *J* = 13.2 Hz, 1H), 3.24 (d, *J* = 16.8 Hz, 1H), 3.10 (d, *J* = 16.4 Hz, 1H), 2.84 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.4, 170.1, 150.5, 147.3, 133.3, 129.3, 128.7, 128.4, 128.2, 125.8, 124.9, 121.5, 52.3, 47.5, 40.7, 38.5 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{18}O_4Na$: 345.1097; Found: 345.1095.

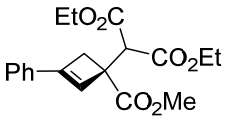


3ap
$C_{17}H_{20}O_4$
M = 288.34 g/mol

Methyl-1-(1-ethoxy-1-oxopropan-2-yl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ap**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and ethyl 2-bromopropanoate (**2p**, 54.3 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ap** as a colorless oil (31.1 mg, 54% yield, d.r. = 1.7:1). The diastereomer of **3ap** cannot be separated by chromatography. Additionally, the diastereomer of **3ap** exhibits slight chemical shifts, making it difficult to determine the major diastereomer. Treatment of **3ap** (dr = 1.7:1) with either conditions A or K_2HPO_4 did not result in any changes to the diastereomeric ratio of **3ap**. The low diastereomeric ratio of **3ap** may be attributed to inadequate selectivity in the elimination reaction facilitated by the base.

3ap: **R_f** = 0.35 (petroleum ether/EtOAc = 10/1). For major diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 5H), 6.38 (s, 1H), 4.20-4.09 (m, 2H), 3.70 (s, 3H), 3.14-3.07 (m, 2H), 2.94 (d, *J* = 13.2 Hz, 1H), 1.27-1.21 (m, 6H) ppm. For minor diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 5H), 6.33 (s, 1H), 4.20-4.09 (m, 2H), 3.70 (s, 3H), 3.27 (d, *J* = 13.2 Hz, 1H), 3.14-3.07 (m, 1H), 2.82 (d, *J* = 13.2 Hz, 1H), 1.27-1.21 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.5, 174.3, 174.21, 174.17, 147.8, 147.2, 133.3, 128.50, 128.45, 128.3, 127.8, 127.1, 124.83,

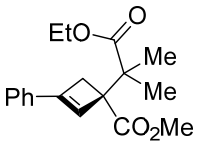
124.80, 60.5, 60.4, 52.8, 52.3, 52.0, 43.6, 43.3, 36.5, 34.9, 14.2, 12.6, 12.3 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{20}O_4Na$: 311.1254; Found: 311.1252.



3aq
$C_{19}H_{22}O_6$
M = 346.38 g/mol

Diethyl-2-(1-(methoxycarbonyl)-3-phenylcyclobut-2-en-1-yl)malonate (**3aq**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and diethyl 2-bromomalonate (**2q**, 71.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3aq** as a colorless oil (43.6 mg, 63% yield).

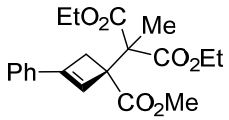
3aq: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 4H), 7.32-7.29 (m, 1H), 6.37 (s, 1H), 4.21-4.18 (m, 4H), 4.10 (s, 1H), 3.72 (s, 3H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 1.25-1.20 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.6, 167.9, 167.8, 148.1, 133.1, 128.7, 128.3, 126.7, 124.9, 61.43, 61.39, 55.9, 52.4, 49.8, 36.6, 14.00, 13.99 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{19}H_{22}O_6Na$: 369.1309; Found: 369.1302.



3ar
$C_{18}H_{22}O_4$
M = 302.37 g/mol

Methyl-1-(1-ethoxy-2-methyl-1-oxopropan-2-yl)-3-phenylcyclobut-2-ene-1-carboxylate (**3ar**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and ethyl 2-bromo-2-methylpropanoate (**2r**, 58.5 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ar** as a colorless oil (29.6 mg, 49% yield).

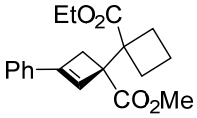
3ar: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.34 (m, 5H), 7.32-7.29 (m, 1H), 6.39 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.66 (s, 3H), 3.05 (s, 2H), 1.28 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.7, 174.3, 147.6, 133.4, 128.42, 128.37, 127.7, 124.8, 60.5, 56.6, 51.9, 45.0, 34.9, 21.9, 21.5, 14.2 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{18}H_{22}O_4Na$: 325.1410; Found: 325.1406.



3as
$C_{20}H_{24}O_6$
M = 360.41 g/mol

Diethyl-2-(1-(methoxycarbonyl)-3-phenylcyclobut-2-en-1-yl)-2-methylmalonate (**3as**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and diethyl 2-bromo-2-methylmalonate (**2s**, 75.9 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3as** as a colorless oil (68.5 mg, 95% yield).

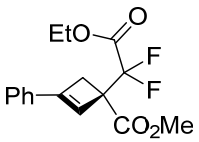
3as: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 5H), 6.38 (s, 1H), 4.25-4.16 (m, 4H), 3.69 (s, 3H), 3.14 (d, *J* = 13.6 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H), 1.64 (s, 3H), 1.28-1.22 (m, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.8, 171.2, 171.1, 147.9, 133.1, 128.5, 128.3, 127.5, 124.8, 61.35, 61.31, 57.4, 54.1, 52.1, 35.4, 17.8, 13.91, 13.88 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{24}O_6Na$: 383.1465; Found: 383.1462.



3at
$C_{19}H_{22}O_4$
M = 314.38 g/mol

1'-ethyl-1-methyl-3-phenyl-[1,1'-bi(cyclobutan)]-2-ene-1,1'-dicarboxylate (**3at**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and ethyl-1-bromocyclobutane-1-carboxylate (**2t**, 62.1 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3at** as a colorless oil (56.6 mg, 90% yield).

3at: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.32-7.29 (m, 1H), 6.42 (s, 1H), 4.19 (q, *J* = 4.8 Hz, 2H), 3.64 (s, 3H), 3.17 (d, *J* = 13.6 Hz, 1H), 2.82 (d, *J* = 13.2 Hz, 1H), 2.54-2.48 (m, 1H), 2.39-2.32 (m, 1H), 2.26-2.19 (m, 2H), 2.14-2.02 (m, 1H), 1.83-1.72 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.3, 174.3, 149.2, 133.3, 128.5, 128.4, 126.0, 124.9, 60.5, 54.6, 51.8, 50.1, 35.1, 27.1, 26.6, 15.9, 14.1 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{19}H_{22}O_4Na$: 337.1410; Found: 337.1407.

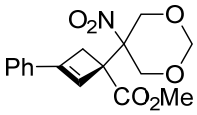


3au
$C_{16}H_{16}F_2O_4$
M = 310.30 g/mol

Methyl-1-(2-ethoxy-1,1-difluoro-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3au**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2u**, 60.9 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3au** as a colorless oil (38.5 mg, 62% yield).

3au: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.34 (m, 5H), 6.31 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 3.29 (d, *J* = 13.2 Hz, 1H), 3.20 (d, *J* = 13.6 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3 (t, *J* = 4.5 Hz), 163.5 (t, *J* = 32.3 Hz), 150.9, 132.5, 129.2, 128.5,

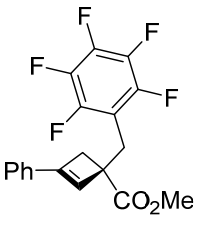
125.1, 122.1 (t, *J* = 3.6 Hz), 113.8 (t, *J* = 252.2 Hz), 62.8, 54.4 (t, *J* = 26.2 Hz), 52.6, 34.2 (t, *J* = 4.3 Hz), 13.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.90 (d, *J* = 267.7 Hz), -113.12 (d, *J* = 267.7 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{16}H_{16}F_2O_4Na$: 333.0909; Found: 333,0908.



3av
$C_{16}H_{17}NO_6$
M = 319.31 g/mol

Methyl-1-(5-nitro-1,3-dioxan-5-yl)-3-phenylcyclobut-2-ene-1-carboxylate (**3av**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 5-bromo-5-nitro-1,3-dioxane (**2v**, 63.6 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3av** as a colorless oil (43.4 mg, 68% yield).

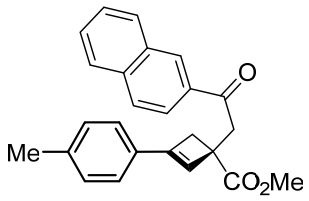
3av: **R_f** = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 5H), 6.25 (s, 1H), 5.02-4.96 (m, 2H), 4.89 (dd, *J* = 12.8 and 2.0 Hz, 1H), 4.66 (d, *J* = 6.0 Hz, 1H), 4.10 (d, *J* = 13.2 Hz, 1H), 4.06 (d, *J* = 13.2 Hz, 1H), 3.72 (s, 3H), 3.27 (d, *J* = 14.0 Hz, 1H), 3.21 (d, *J* = 14.0 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3, 149.0, 131.9, 129.6, 128.6, 125.1, 123.5, 93.4, 87.9, 68.0, 67.9, 53.5, 52.9, 35.8 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{16}H_{17}NO_6Na$: 342.0948; Found: 342.0948.



3aw
$C_{19}H_{13}F_5O_2$
M = 368.30 g/mol

Methyl-1-((perfluorophenyl)methyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3aw**): Prepared from methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1a**, 37.6 mg, 0.2 mmol) and 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (**2w**, 78.3 mg, 0.3 mmol) at rt for 3 h according to the **Condition B**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (50/1) afforded **3aw** as a colorless oil (66.3 mg, 90% yield).

3aw: $\mathbf{R_f}$ = 0.60 (petroleum ether/EtOAc = 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.24 (m, 5H), 6.30 (s, 1H), 3.72 (s, 3H), 3.37-3.26 (m, 2H), 3.21 (d, *J* = 13.2 Hz, 1H), 2.73 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.1, 147.0, 146.7 (m), 144.3 (m), 138.7 (m), 133.1, 128.7, 128.4, 127.1, 124.9, 111.1(m), 52.3, 50.6, 37.5, 28.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -142.07 (dd, *J* = 22.5, 7.8 Hz), -155.97 (t, *J* = 20.9 Hz), -162.46 (td, *J* = 22.6, 8.2 Hz). **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{19}H_{13}F_5O_2Na$: 391.0728; Found: 391.0726.

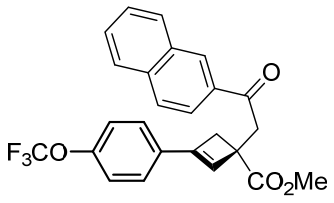


3bj
$C_{25}H_{22}O_3$
M = 370.45 g/mol

Methyl-1-(2-(naphthalen-2-yl)-2-oxoethyl)-3-(*p*-tolyl)cyclobut-2-ene-1-carboxylate (**3bj**): Prepared from methyl methyl 3-(*p*-tolyl)bicyclo[1.1.0]butane-1-carboxylate (**1b**, 40.4 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3bj** as a white solid (54.1 mg, 73% yield).

3bj: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.04-8.02 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89-7.85 (m, 2H), 7.61-7.52 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 3.72 (d, *J* = 18.0 Hz, 1H), 3.72 (s, 3H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H), 2.34 (s, 3H)

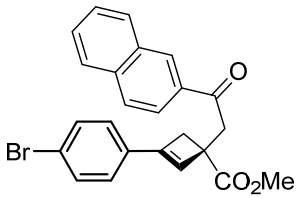
ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.1, 175.2, 146.8, 138.4, 135.6, 133.9, 132.4, 130.9, 129.8, 129.5, 129.0, 128.44, 128.40, 127.7, 126.7, 124.8, 123.7, 52.2, 47.5, 45.3, 38.7, 21.4 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{23}O_3Na$: 393.1461; Found: 393.1459.



3cj
$C_{25}H_{19}F_3O_4$
M = 440.42 g/mol

Methyl-1-(2-(naphthalen-2-yl)-2-oxoethyl)-3-(4-(trifluoromethoxy)phenyl)cyclobut-2-ene-1-carboxylate (**3cj**): Prepared from methyl 3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.0]butane-1-carboxylate (**1c**, 54.4 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3cj** as a white solid (49.3 mg, 56% yield).

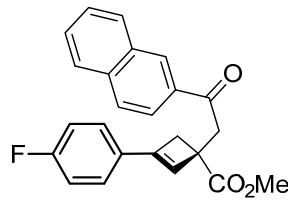
3cj: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 8.8 Hz, 2H), 7.62-7.53 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.56 (s, 1H), 3.87 (d, *J* = 17.6 Hz, 1H), 3.73-3.69 (s, 4H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.79 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9, 174.7, 149.1 (q, *J* = 1.7 Hz), 135.7, 133.9, 132.5, 132.4, 130.0, 129.8, 129.5, 128.53, 128.48, 127.8, 126.8, 126.4, 123.7, 120.9, 120.4 (q, *J* = 255.8 Hz), 52.3, 47.6, 45.0, 38.7 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.82 (s) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{19}F_3O_4Na$: 463.1128; Found: 463.1119.



3dj
$C_{24}H_{19}BrO_3$
M = 435.32 g/mol

Methyl-3-(4-bromophenyl)-1-(2-(naphthalen-2-yl)-2-oxoethyl)cyclobut-2-ene-1-carboxylate (**3dj**): Prepared from methyl 3-(4-bromophenyl)bicyclo[1.1.0]butane-1-carboxylate (**1d**, 53.4 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3dj** as a white solid (69.7 mg, 80% yield).

3dj: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.04-8.01 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.89-7.85 (m, 2H), 7.61-7.52 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.56 (s, 1H), 3.87 (d, *J* = 17.6 Hz, 1H), 3.72 (s, 3H), 3.70 (d, *J* = 16.4 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9, 174.7, 145.7, 135.6, 133.7, 132.4, 132.4, 131.5, 129.8, 129.5, 128.5, 128.4, 127.7, 126.8, 126.4, 123.6, 122.4, 52.3, 47.6, 45.0, 38.6 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{24}H_{19}BrO_3Na$: 457.0410; Found: 457.0407.

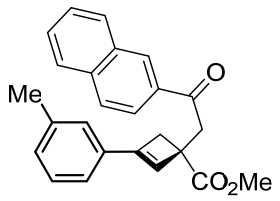


3ej
$C_{24}H_{19}FO_3$
M = 374.41 g/mol

Methyl-3-(4-fluorophenyl)-1-(2-(naphthalen-2-yl)-2-oxoethyl)cyclobut-2-ene-1-carboxylate (**3ej**): Prepared from methyl 3-(4-fluorophenyl)bicyclo[1.1.0]butane-1-carboxylate (**1e**, 41.2 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**,

74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ej** as a white solid (52.4 mg, 70% yield).

3ej: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.03 (dd, *J* = 8.8 and 1.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 8.8 Hz, 2H), 7.62-7.53 (m, 2H), 7.35 (dd, *J* = 8.8 and 5.2 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.49 (s, 1H), 3.87 (d, *J* = 17.6 Hz, 1H), 3.73 (s, 3H), 3.72 (d, *J* = 17.6 Hz, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 175.0, 162.8 (d, *J* = 246.8 Hz), 145.8, 135.6, 133.8, 132.4, 130.0 (d, *J* = 3.3 Hz), 129.8, 129.5, 128.51, 128.45, 128.4 (d, *J* = 2.4 Hz), 127.8, 126.8 (d, *J* = 4.7 Hz), 126.7, 123.6, 115.4 (d, *J* = 21.7 Hz), 52.3, 47.4, 45.1, 38.7 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.27 (s) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{24}H_{19}FO_3Na$: 397.1210; Found: 397.1205.

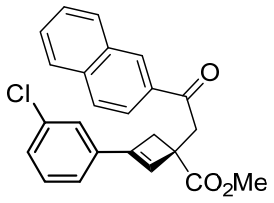


3fj
$C_{25}H_{22}O_3$
M = 370.45 g/mol

Methyl-1-(2-(naphthalen-2-yl)-2-oxoethyl)-3-(*m*-tolyl)cyclobut-2-ene-1-carboxylate (**3fj**): Prepared from methyl 3-(*m*-tolyl)bicyclo[1.1.0]butane-1-carboxylate (**1f**, 40.4 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3fj** as a white solid (51.9 mg, 70% yield).

3fj: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.4 Hz, 2H), 7.60-7.51 (m, 2H), 7.25-7.17 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 1H), 6.52 (s, 1H), 3.85 (d, *J* = 17.6 Hz, 1H), 3.72 (s, 3H), 3.70 (d, *J* = 17.6 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.78 (d, *J* = 13.2 Hz, 1H), 2.34 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 175.1,

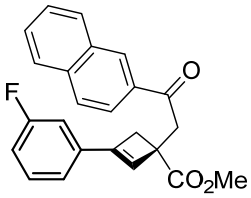
147.0, 138.0, 135.6, 133.9, 133.6, 132.5, 129.8, 129.5, 129.3, 128.7, 128.44, 128.41, 128.3, 127.7, 126.7, 125.5, 123.7, 122.0, 52.2, 47.6, 45.2, 38.7, 21.3 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{22}O_3Na$: 393.1461; Found: 393.1458.



3gj
$C_{24}H_{19}ClO_3$
M = 390.86 g/mol

Methyl-3-(3-chlorophenyl)-1-(2-(naphthalen-2-yl)-2-oxoethyl)cyclobut-2-ene-1-carboxylate (**3gj**): Prepared from methyl 3-(3-chlorophenyl)bicyclo[1.1.0]butane-1-carboxylate (**1g**, 44.6 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3gj** as a white solid (46.9 mg, 60% yield).

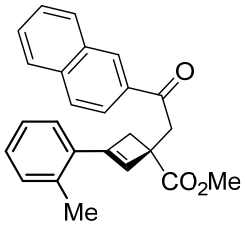
3gj: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.02 (dd, *J* = 8.4 and 1.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.4 Hz, 2H), 7.61-7.52 (m, 2H), 7.34 (s, 1H), 7.26-7.24 (m, 3H), 6.59 (s, 1H), 3.88 (d, *J* = 17.6 Hz, 1H), 3.73 (s, 3H), 3.70 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.8, 174.7, 145.5, 135.6, 135.4, 134.5, 133.8, 132.4, 130.7, 129.8, 129.7, 129.5, 128.5, 128.5, 128.4, 127.7, 126.8, 125.0, 123.6, 123.0, 52.3, 47.7, 45.0, 38.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{24}H_{19}ClO_3Na$: 413.0915; Found: 413.0909.



3hj
$C_{24}H_{19}FO_3$
M = 374.41 g/mol

Methyl-3-(3-fluorophenyl)-1-(2-(naphthalen-2-yl)-2-oxoethyl)cyclobut-2-ene-1-carboxylate (**3hj**): Prepared from methyl 3-(3-fluorophenyl)bicyclo[1.1.0]butane-1-carboxylate (**1h**, 41.2 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3hj** as a white solid (52.4 mg, 70% yield).

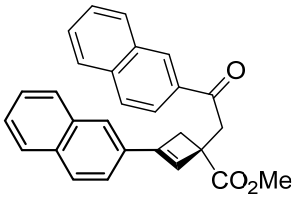
3hj: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.8 Hz, 2H), 7.61-7.52 (m, 2H), 7.33-7.28 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 9.6 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 3.88 (d, *J* = 17.6 Hz, 1H), 3.73 (s, 3H), 3.71 (d, *J* = 17.2 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.78 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9, 174.7, 162.9 (d, *J* = 244.7 Hz), 145.7 (d, *J* = 2.5 Hz), 135.8 (d, *J* = 7.7 Hz), 135.6, 133.8, 132.4, 130.5, 130.0 (d, *J* = 8.2 Hz), 129.8, 129.5, 128.5, 128.4, 127.7, 123.6, 120.6 (d, *J* = 2.7 Hz), 120.6, 115.3 (d, *J* = 21.2 Hz), 111.6 (d, *J* = 21.5 Hz), 52.3, 47.6, 45.0, 38.7 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.12 (s) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{24}H_{19}FO_3Na$: 397.1210; Found: 397.1205.



3ij
$C_{25}H_{22}O_3$
M = 370.45 g/mol

Methyl-1-(2-(naphthalen-2-yl)-2-oxoethyl)-3-(*o*-tolyl)cyclobut-2-ene-1-carboxylate (**3ij**): Prepared from methyl 3-(*o*-tolyl)bicyclo[1.1.0]butane-1-carboxylate (**1b**, 40.4 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ij** as a colorless oil (37.0 mg, 50% yield).

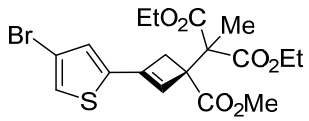
3ij: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 9.2 Hz, 2H), 7.61-7.52 (m, 2H), 7.25-7.17 (m, 4H), 6.44 (s, 1H), 3.89 (d, *J* = 17.6 Hz, 1H), 3.74 (d, *J* = 17.6 Hz, 1H), 3.73 (s, 3H), 3.50 (d, *J* = 13.2 Hz, 1H), 2.87 (d, *J* = 13.2 Hz, 1H), 2.43 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.1, 175.1, 146.7, 137.3, 135.6, 134.0, 132.5, 132.5, 132.3, 130.7, 129.8, 129.5, 128.5, 128.4, 128.3, 127.8, 126.8, 126.7, 125.8, 123.7, 52.2, 47.9, 45.4, 40.2, 21.7 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{22}O_3Na$: 393.1461; Found: 393.1459.



3jj
$C_{28}H_{22}O_3$
M = 406.48 g/mol

Methyl-3-(naphthalen-2-yl)-1-(2-(naphthalen-2-yl)-2-oxoethyl)cyclobut-2-ene-1-carboxylate (**3jj**): Prepared from methyl 3-(naphthalen-2-yl)bicyclo[1.1.0]butane-1-carboxylate (**1j**, 47.6 mg, 0.2 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1-one (**2j**, 74.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3jj** as a white solid (66.7 mg, 82% yield).

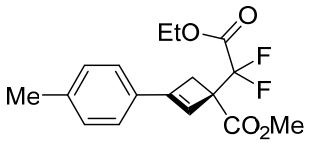
3jj: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.88-7.77 (m, 6H), 7.70 (s, 1H), 7.59-7.51 (m, 3H), 7.48-7.44 (m, 2H), 6.65 (s, 1H), 3.90 (d, *J* = 17.6 Hz, 1H), 3.74 (d, *J* = 17.2 Hz, 1H), 3.74 (s, 3H), 3.52 (d, *J* = 12.8 Hz, 1H), 2.89 (d, *J* = 12.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 175.0, 146.9, 135.6, 133.9, 133.3, 133.2, 132.5, 131.1, 129.8, 129.6, 129.5, 128.44, 128.42, 128.2, 128.1, 127.7, 126.7, 126.4, 126.3, 124.1, 123.7, 122.6, 52.2, 47.7, 45.2, 38.8 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{28}H_{22}O_3Na$: 429.1461; Found: 429.1460.



3ks
$C_{18}H_{21}BrO_6S$
M = 445.32 g/mol

Diethyl 2-(3-(4-bromothiophen-2-yl)-1-(methoxycarbonyl)cyclobut-2-en-1-yl)-2-methylmalonate (**3ks**): Prepared from methyl-3-(4-bromothiophen-2-yl)bicyclo[1.1.0]butane-1-carboxylate (**1k**, 54.6 mg, 0.2 mmol) and diethyl 2-bromo-2-methylmalonate (**2s**, 75.9 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3ks** as a yellow oil (63.3 mg, 71% yield).

3ks: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.17 (s, 1H), 6.92 (s, 1H), 6.19 (s, 1H), 4.24-4.16 (m, 4H), 3.70 (s, 3H), 3.10 (d, *J* = 13.2 Hz, 1H), 3.03 (d, *J* = 17.6 Hz, 1H), 1.62 (s, 3H), 1.25 (q, *J* = 7.6 Hz, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.2, 171.0, 170.9, 140.4, 138.1, 127.8, 127.5, 123.2, 110.2, 61.51, 61.46, 57.4, 55.2, 52.3, 36.6, 17.9, 14.0, 13.9 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{18}H_{21}BrO_6SNa$: 467.0134; Found: 467.0126.

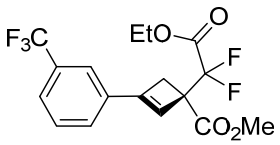


3bu
$C_{17}H_{18}F_2O_4$
M = 324.32 g/mol

Methyl-1-(2-ethoxy-1,1-difluoro-2-oxoethyl)-3-(*p*-tolyl)cyclobut-2-ene-1-carboxylate (**3bu**): Prepared from methyl 3-(*p*-tolyl)bicyclo[1.1.0]butane-1-carboxylate(**1b**, 40.4 mg, 0.2 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2u**, 60.8 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3bu** as a yellow oil (33.7 mg, 52% yield).

3bu: $\mathbf{R_f}$ = 0.35 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.23 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.73

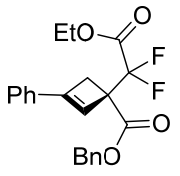
(s, 3H), 3.26 (d, *J* = 13.2 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 2.36 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4 (t, *J* = 4.5 Hz), 163.5 (t, *J* = 32.4 Hz), 150.9, 139.4, 129.9, 129.1, 125.1, 121.0 (t, *J* = 3.6 Hz), 113.9 (t, *J* = 252.0 Hz), 62.8, 54.4 (t, *J* = 26.1 Hz), 52.6, 34.2 (t, *J* = 4.1 Hz), 21.4, 13.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.95 (d, *J* = 267.7 Hz), -113.15 (d, *J* = 267.7 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{18}F_2O_4Na$: 347.1065; Found: 347.1063.



3lu
$C_{17}H_{15}F_5O_4$
M = 378.30 g/mol

Methyl-1-(2-ethoxy-1,1-difluoro-2-oxoethyl)-3-(3-(trifluoromethyl)phenyl)cyclobut-2-ene-1-carboxylate (**3lu**): Prepared from methyl 3-(3-(trifluoromethyl)phenyl)bicyclo[1.1.0]butane-1-carboxylate (**1l**, 51.2 mg, 0.2 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2u**, 60.8 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3lu** as a yellow oil (41.6 mg, 55% yield).

3lu: **R_f** = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.61-7.57 (m, 2H), 7.53-7.49 (m, 1H), 6.43 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.32 (d, *J* = 13.2 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.9 (t, *J* = 4.4 Hz), 163.3 (t, *J* = 32.1 Hz), 149.5, 133.2, 131.1 (q, *J* = 32.3 Hz), 129.1, 128.3, 125.7 (q, *J* = 3.7 Hz), 124.4 (t, *J* = 3.4 Hz), 123.9 (q, *J* = 271.0 Hz), 122.0 (q, *J* = 3.6 Hz), 113.7 (t, *J* = 252.8 Hz), 63.0, 54.6 (t, *J* = 26.3 Hz), 52.7, 34.2 (t, *J* = 4.2 Hz), 13.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.90 (s), -111.90 (d, *J* = 268.8 Hz), -113.17 (d, *J* = 268.8 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{15}F_5O_4Na$: 401.0783; Found: 401.0777.



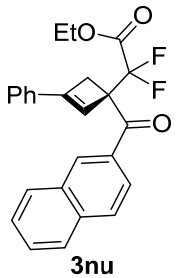
3mu

$C_{22}H_{20}F_2O_4$

M = 386.39 g/mol

Benzyl-1-(2-ethoxy-1,1-difluoro-2-oxoethyl)-3-phenylcyclobut-2-ene-1-carboxylate (**3mu**): Prepared from benzyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate (**1m**, 52.9 mg, 0.2 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2u**, 60.8 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3mu** as a yellow oil (31.7 mg, 41% yield).

3mu: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 10H), 6.32 (s, 1H), 5.18 (dd, *J* = 15.6 and 12.4 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.29 (d, *J* = 13.2 Hz, 2H), 3.21 (d, *J* = 13.6 Hz, 2H), 1.25 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.5 (t, *J* = 4.5 Hz), 163.4 (t, *J* = 32.5 Hz), 151.0, 135.1, 132.6, 129.2, 128.6, 128.5, 128.4, 128.2, 125.2, 122.18 (t, *J* = 4.5 Hz), 113.8 (t, *J* = 269.0 Hz), 67.35, 62.80, 54.6 (t, *J* = 26.0 Hz), 34.2 (t, *J* = 4.1 Hz), 13.8 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.43 (d, *J* = 268.1 Hz), -112.68 (d, *J* = 268.1 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{20}F_2O_4Na$: 409.1222; Found: 409.1220.



3nu

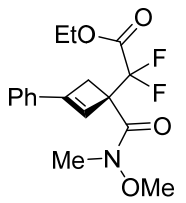
$C_{25}H_{20}F_2O_3$

M = 406.43 g/mol

Ethyl-2-(1-(2-naphthoyl)-3-phenylcyclobut-2-en-1-yl)-2,2-difluoroacetate (**3nu**): Prepared from naphthalen-2-yl(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (**1n**, 56.9

mg, 0.2 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2u**, 60.8 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3nu** as a yellow oil (28.4 mg, 51% yield).

3nu: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.90-7.83 (m, 3H), 7.60-7.50 (m, 2H), 7.42-7.34 (m, 5H), 6.64 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 13.8 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.6 (t, *J* = 1.8 Hz), 163.4 (t, *J* = 31.9 Hz), 150.7, 135.3, 133.7, 132.5, 132.2, 130.8, 129.7, 129.4, 128.7, 128.6, 128.2, 127.7, 126.8, 125.2, 124.6, 124.1 (t, *J* = 3.8 Hz), 114.8 (t, *J* = 253.6 Hz), 63.0, 60.2 (t, *J* = 24.5 Hz), 36.1 (t, *J* = 4.3 Hz), 13.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.34 (d, *J* = 256.4 Hz), -110.57 (d, *J* = 256.4 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{20}F_2O_3Na$: 429.1273; Found: 429.1267.

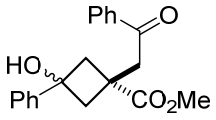


3ou
$C_{17}H_{19}F_2NO_4$
M = 339.34 g/mol

Ethyl-2,2-difluoro-2-(1-(methoxy(methyl)carbamoyl)-3-phenylcyclobut-2-en-1-yl)acetate (**3ou**): Prepared from *N*-methoxy-*N*-methyl-3-phenylbicyclo[1.1.0]butane-1-carboxamide(**1o**, 43.4 mg, 0.2 mmol) and ethyl 2-bromo-2,2-difluoroacetate (**2u**, 60.8 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded **3ou** as a yellow oil (46.2 mg, 68% yield).

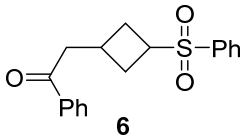
3ou: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 5H), 6.37 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 3.42 (d, *J* = 13.6 Hz, 1H), 3.24 (d, *J* = 13.2 Hz, 1H), 3.22 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.8 (t, *J* = 2.5 Hz), 163.5 (t, *J* = 32.2 Hz), 149.4, 132.7, 129.0, 128.5, 125.0, 122.3 (t, *J* = 3.7 Hz), 114.6 (t, *J* = 253.6 Hz), 62.8, 61.6, 55.3 (t, *J* =

25.2 Hz), 35.6 (t, *J* = 5.0 Hz), 33.2, 13.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.59 (d, *J* = 251.5 Hz), -112.65 (d, *J* = 251.5 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{19}F_2NO_4Na$: 362.1174; Found: 362.1172.



5aa
$C_{20}H_{20}O_4$
M = 324.38 g/mol

Methyl 3-hydroxy-1-(2-oxo-2-phenylethyl)-3-phenylcyclobutane-1-carboxylate (**5aa**): yellow oil. **R_f** = 0.25 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51-7.46 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 4.01 (s, 2H), 3.67 (s, 3H), 3.25 (d, *J* = 14.2 Hz, 2H), 2.41 (d, *J* = 14.2 Hz, 2H), 2.12 (broad s, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.1, 176.3, 146.2, 136.7, 133.2, 128.6, 128.5, 128.1, 127.4, 124.7, 73.9, 52.2, 46.6, 44.4, 37.9 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{20}H_{20}O_4Na$: 347.1249; Found: 347.1254.



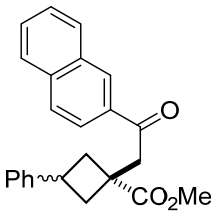
6
$C_{18}H_{18}O_3S$
M = 314.40 g/mol

1-phenyl-2-(3-(phenylsulfonyl)cyclobutyl)ethan-1-one (**6**): Prepared from 1-(phenylsulfonyl)bicyclo[1.1.0]butane (**1t**, 38.9 mg, 0.2 mmol) and 2-bromo-1-phenylethan-1-one (**2a**, 59.7 mg, 0.3 mmol) at rt for 3 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **6** as a yellow oil (26.4 mg, 42% combined isolated yield).

For the major diastereomer: **R_f** = 0.45 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.59-7.53 (m, 3H), 7.47 (t, *J* = 7.2 Hz, 2H), 3.80-3.72 (m, 1H), 3.22 (d, *J* = 6.8 Hz, 2H), 2.88-2.80 (m, 1H), 2.52-2.45 (m, 2H), 2.34-2.27 (m, 2H) ppm. **^{13}C NMR** (150

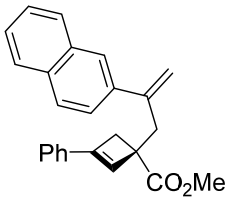
MHz, $CDCl_3$): δ 198.5, 138.0, 136.5, 133.6, 133.3, 129.2, 128.6, 128.1, 127.9, 54.1, 44.6, 28.8, 25.5 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{19}O_3S$: 315.1049; Found: 315.1035.

For the minor diastereomer: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 4H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.59-7.52 (m, 3H), 7.45 (t, *J* = 7.2 Hz, 2H), 3.88-3.80 (m, 1H), 3.15 (d, *J* = 7.2 Hz, 2H), 3.07-2.96 (m, 1H), 2.86-2.79 (m, 2H), 2.10-2.03 (m, 2H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 198.3, 137.8, 136.5, 133.6, 133.3, 129.2, 128.7, 128.3, 127.9, 54.8, 44.1, 28.0, 26.8 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{18}H_{19}O_3S$: 315.1049; Found: 315.1032.



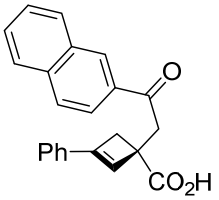
7
$C_{24}H_{22}O_3$
M = 358.44 g/mol

Methyl 1-(2-(naphthalen-2-yl)-2-oxoethyl)-3-phenylcyclobutane-1-carboxylate (**7**): yellow oil. $\mathbf{R_f}$ = 0.45 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.92-7.87 (m, 2H), 7.63-7.55 (m, 2H), 7.34-7.28 (m, 4H), 7.22-7.19 (m, 1H), 3.89 (s, 2H), 3.71 (s, 3H), 3.64-3.59 (m, 1H), 2.87 (dd, *J* = 11.6 and 10.4 Hz, 2H), 2.48 (dd, *J* = 10.8 and 10.0 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.7, 176.0, 144.5, 135.7, 134.1, 132.5, 129.7, 129.5, 128.52, 128.48, 128.4, 127.8, 126.8, 126.6, 126.3, 123.7, 52.1, 44.9, 40.3, 37.3, 33.8 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{24}H_{22}O_3Na$: 381.1461; Found: 381.1463.



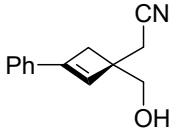
8
$C_{25}H_{22}O_2$
M = 354.45 g/mol

Methyl-1-(2-(naphthalen-2-yl)allyl)-3-phenylcyclobut-2-ene-1-carboxylate (**8**): colorless oil. $\mathbf{R_f}$ = 0.45 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81-7.76 (m, 4H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.46-7.44 (m, 2H), 7.31-7.24 (m, 5H), 6.16 (s, 1H), 5.42 (s, 1H), 5.21 (s, 1H), 3.47 (s, 3H), 3.30 (d, *J* = 14.4 Hz, 1H), 3.18 (d, *J* = 12.8 Hz, 1H), 3.16 (d, *J* = 14.4 Hz, 1H), 2.77 (d, *J* = 12.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.9, 145.80, 145.76, 139.0, 133.7, 133.2, 132.8, 129.1, 128.29, 128.26, 128.1, 127.7, 127.5, 126.1, 125.8, 125.1, 125.0, 124.8, 115.5, 51.7, 50.8, 42.2, 38.5 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{25}H_{22}O_2Na$: 377.1512; Found: 377.1511.



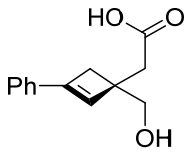
9
$C_{23}H_{18}O_3$
M = 342.39 g/mol

1-(2-oxopropyl)-3-phenylcyclobut-2-ene-1-carboxylic acid (**9**): white solid. $\mathbf{R_f}$ = 0.3 (petroleum ether/EtOAc = 1/2). **^{1}H NMR** (400 MHz, CD_3COCD_3): δ 8.71 (s, 1H), 8.12-8.06 (m, 2H), 8.01-7.97 (m, 2H), 7.67-7.59 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 6.64 (s, 1H), 3.90 (d, *J* = 17.6 Hz, 1H), 3.81 (d, *J* = 18.0 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.84 (d, *J* = 13.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, CD_3COCD_3): δ 197.8, 175.0, 146.8, 135.7, 134.4, 134.2, 132.8, 129.9, 129.8, 129.6, 128.5, 128.4, 128.3, 127.7, 126.8, 124.8, 123.6, 47.5, 44.7, 38.5 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{23}H_{18}O_3Na$: 365.1148; Found: 365.1145.



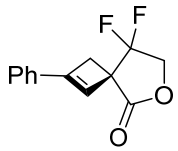
10
$C_{13}H_{13}NO$
M = 199.25 g/mol

2-(1-(hydroxymethyl)-3-phenylcyclobut-2-en-1-yl)acetonitrile (**10**): colorless oil. $\mathbf{R_f}$ = 0.3 (petroleum ether/EtOAc = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.29 (m, 5H), 6.38 (s, 1H), 3.80 (dd, *J* = 13.6 and10.8 Hz, 2H), 2.76-2.64 (m, 4H), 1.85 (broad s, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.8, 133.4, 128.7, 128.4, 128.1, 124.8, 118.2, 67.2, 44.9, 36.7, 23.2 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{13}H_{13}NONa$: 222.0889; Found:222.0888.



11
$C_{13}H_{14}O_3$
M = 218.25 g/mol

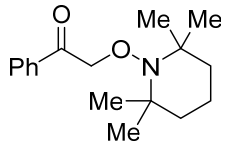
2-(1-(hydroxymethyl)-3-phenylcyclobut-2-en-1-yl)acetic acid (**11**): white solid. $\mathbf{R_f}$ = 0.3 (petroleum ether/EtOAc = 1/3). **^{1}H NMR** (400 MHz, CD_3COCD_3): δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 6.54 (s, 1H), 3.73 (s, 2H), 2.93 (broad s, 2 H), 2.76 (d, *J* = 15.2 Hz, 1H), 2.66 (d, *J* = 3.6 Hz, 2H), 2.63 (d, *J* = 15.2 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, CD_3COCD_3): δ 172.8, 144.9, 134.8, 131.8, 128.4, 127.9, 124.6, 67.2, 45.4, 38.5, 37.1 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{13}H_{14}O_3Na$: 241.0835; Found: 241.0831.



12
$C_{13}H_{10}F_2O_2$
M = 236.22 g/mol

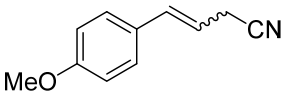
8,8-difluoro-2-phenyl-6-oxaspiro[3.4]oct-1-en-5-one (**12**): colorless oil. $\mathbf{R_f}$ = 0.5 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.36 (m, 5H), 6.20 (s, 1H), 4.57-4.43 (m, 2H), 3.26 (d, *J* = 12.8 Hz, 1H), 3.06 (d, *J* = 12.8 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.1 (dd, *J* = 13.3 and 4.8 Hz), 151.6, 132.1, 129.6, 128.6, 125.2, 123.0 (dd, *J* = 252.2 and 247.1 Hz), 119.1 (dd, *J* = 7.1 and 1.6 Hz), 70.5 (t, *J* = 32.4 Hz), 50.2 (t, *J* = 25.8 Hz), 33.7 (dd, *J* = 6.7 and 3.0 Hz) ppm. **^{19}F**

NMR (376 MHz, $CDCl_3$) δ -107.69 (d, *J* = 238.8 Hz), -111.71 (d, *J* = 238.8 Hz) ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{13}H_{10}F_2O_2Na$: 259.0541; Found: 259.0540.



13
$C_{17}H_{25}NO_2$
M = 275.39 g/mol

1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (**13**): colorless oil. $\mathbf{R_f}$ = 0.6 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.92 (d, *J* = 7.6 Hz, 2H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.43 (t, *J* = 7.6 Hz, 2H), 4.09 (s, 2H), 0.58-0.53 (m, 1H), 0.47-0.43 (m, 4H), 0.33-0.30 (m, 1H), 0.16 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.7, 135.4, 133.2, 128.5, 127.9, 81.3, 60.1, 39.7, 32.8, 20.2, 17.0 ppm. **HRMS** (ESI) *m/z*: $[M+Na]^+$ calcd. for $C_{17}H_{25}NO_2Na$: 298.1778; Found: 298.1772.



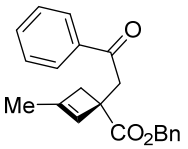
14
$C_{11}H_{11}NO$
M = 173.22 g/mol

4-(4-methoxyphenyl)but-3-enenitrile (**14**): colorless oil.

(*Z*)-**14**: $\mathbf{R_f}$ = 0.60 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 11.2 Hz, 1H), 5.63-5.57 (m, 1H), 3.82 (s, 3H), 3.29 (d, *J* = 7.2 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.1, 134.1, 129.8, 127.6, 118.2, 117.3, 114.0, 55.3, 17.1 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{11}H_{12}NO$: 174.0913; Found: 174.0911.

(*E*)-**14**: $\mathbf{R_f}$ = 0.55 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 5.94-5.87 (m, 1H), 3.81 (s, 3H), 3.26 (d, *J* = 5.6 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.6,

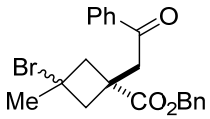
134.0, 128.4, 127.7, 117.5, 114.3, 114.1, 55.3, 20.7 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{11}H_{12}NO$: 174.0913; Found: 174.0910.



3pa
$C_{21}H_{20}O_3$
M = 320.39 g/mol

Benzyl-3-methyl-1-(2-oxo-2-phenylethyl)cyclobut-2-ene-1-carboxylate (**3pa**): Prepared from benzyl-3-methylbicyclo[1.1.0]butane-1-carboxylate (**1p**, 40.5 mg, 0.2 mmol) and 2-bromo-1-phenylethan-1-one (**2a**, 59.7 mg, 0.3 mmol) at rt for 10 h according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (20/1) afforded **3pa** as a colorless oil (1.9 mg, 3% yield). The desired **3pa** containing unknown by-products that cannot be separated using flash chromatography on silica gel.

3pa: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.60-7.55 (m, 1H), 7.51-7.44 (m, 2H), 7.37-7.27 (m, 5H), 5.96 (s, 1H), 5.13 (d, *J* = 6.0 Hz, 2H), 3.62 (d, *J* = 18.0 Hz, 1H), 3.51 (d, *J* = 17.4 Hz, 1H), 3.01 (d, *J* = 13.2 Hz, 1H), 2.35 (d, *J* = 13.2 Hz, 1H), 1.77 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 198.3, 174.8, 147.9, 136.6, 136.3, 133.1, 131.0, 128.5, 128.4, 128.0, 127.8, 127.7, 66.3, 48.0, 45.0, 42.4, 16.8 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{21}O_3$: 321.1485; Found: 321.1483.



16
$C_{21}H_{21}BrO_3$
M = 401.30 g/mol

Benzyl 3-bromo-3-methyl-1-(2-oxo-2-phenylethyl)cyclobutane-1-carboxylate (**16**): Prepared from benzyl 3-methylbicyclo[1.1.0]butane-1-carboxylate (**1p**, 40.5 mg, 0.2 mmol) and 2-bromo-1-phenylethan-1-one (**2a**, 59.7 mg, 0.3 mmol) at rt for 10 h

according to the **Condition A**. Purification by flash chromatography on silica gel using petroleum ether/EtOAc (10/1) afforded **16** as a colorless oil (48.2 mg, 60% combined isolated yield).

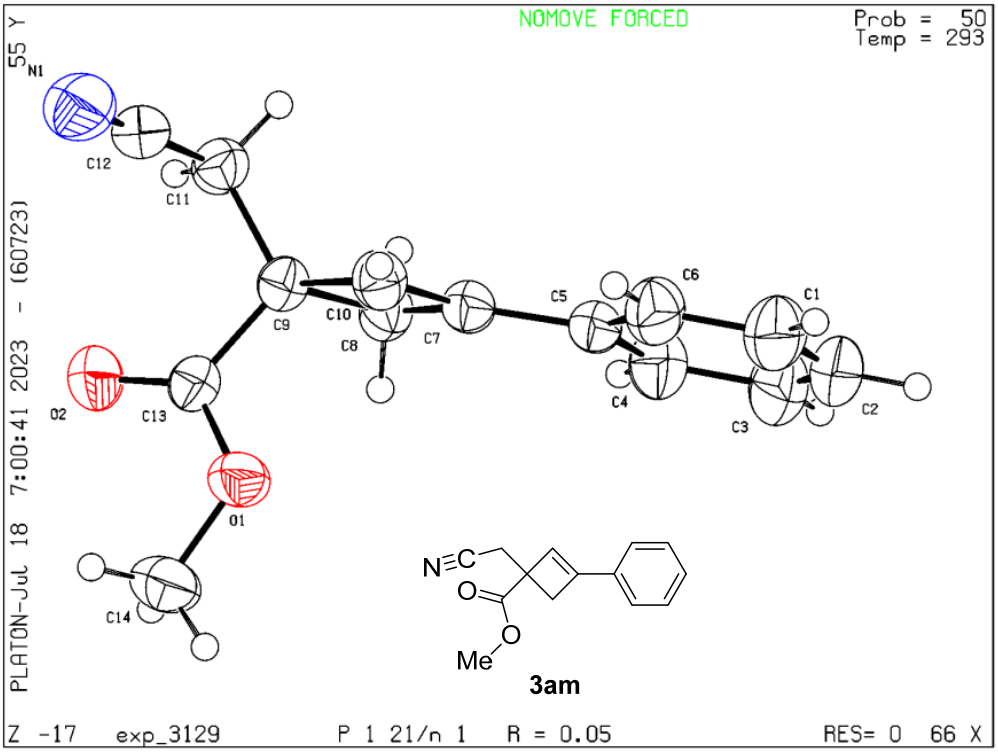
For the major diastereomer: $\mathbf{R_f}$ = 0.40 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 5H), 5.12 (s, 2H), 3.93 (s, 2H), 3.15 (d, *J* = 14.4 Hz, 2H), 2.82 (d, *J* = 14.4 Hz, 2H), 1.96 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 197.4, 175.0, 136.3, 135.7, 133.4, 128.6, 128.5, 128.1, 128.02, 127.99, 66.9, 56.7, 49.2, 47.5, 38.8, 34.5 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{22}BrO_3$: 401.0747; Found: 401.0729.

For the minor diastereomer: $\mathbf{R_f}$ = 0.30 (petroleum ether/EtOAc = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.37-7.29 (m, 5H), 5.18 (s, 2H), 3.55 (s, 2H), 3.54 (d, *J* = 14.4 Hz, 2H), 2.55 (d, *J* = 14.4 Hz, 2H), 1.99 (s, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$): δ 196.9, 174.6, 136.2, 135.8, 133.5, 128.6, 128.4, 128.03, 127.96, 127.9, 67.0, 54.3, 49.2, 46.6, 39.0, 35.9 ppm. **HRMS** (ESI) *m/z*: $[M+H]^+$ calcd. for $C_{21}H_{22}BrO_3$: 401.0747; Found: 401.0727.

11 Crystal Structure of 3am

Note: The thermal ellipsoids are 50% probability level. The crystals are grown by slow solvent (CH_2Cl_2/*n*-Hexane) evaporation at room temperature. CCDC number of **3am** is 2287475.

Datablock exp_3129 - ellipsoid plot



Datablock: exp_3129

Bond precision: C-C = 0.0028 A Wavelength=1.54184

Cell: a=10.84837(19) b=8.49086(12) c=14.3960(3)
alpha=90 beta=111.998(2) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1229.50(4)	1229.50(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C14 H13 N O2	C14 H13 N O2
Sum formula	C14 H13 N O2	C14 H13 N O2
Mr	227.25	227.25
Dx,g cm-3	1.228	1.228
Z	4	4
Mu (mm-1)	0.666	0.666
F000	480.0	480.0
F000'	481.46	
h,k,lmax	12,10,17	12,10,17
Nref	2160	2160
Tmin,Tmax	0.852,0.936	0.640,1.000
Tmin'	0.819	

Correction method= # Reported T Limits: Tmin=0.640 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 66.595

R(reflections)= 0.0481(2012) wR2(reflections)= 0.1439(2160)

S = 1.079 Npar= 155

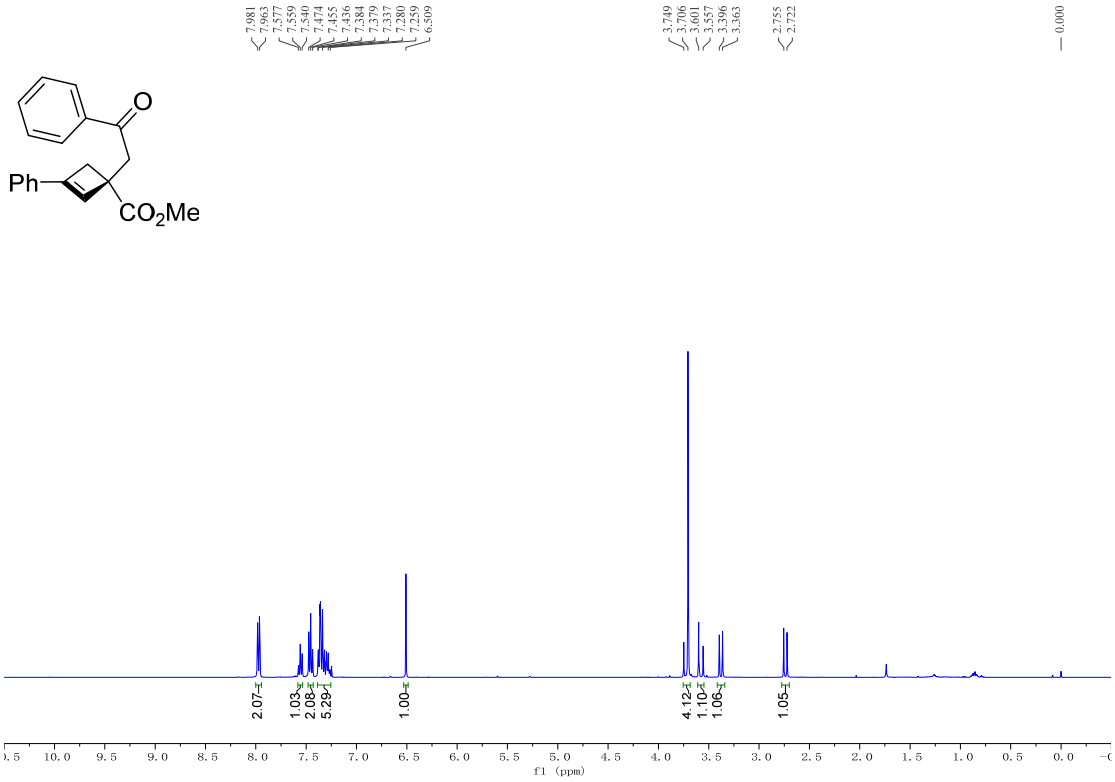
12 References

[1] (a) Dhake, K.; Woelk, K. J.; Becica, J.; Un, A.; Jenny, S. E.; Leitch, D. C.; *Angew. Chem. Int. Ed.* **2022**, *61*, e202204719. (b) Livingstone, K.; Siebold, K.; Meyer, S.; Heras, V. M.; Daniliuc, C. G.; Gilmour, R. *ACS Catal*. **2022**, *12*, 14507. (c) Guo, R.; Chang, Y.-C.; Herter, L.; Salome, C.; Braley, S. E.; Fessard, T. C.; Brown, M. K. *J. Am. Chem. Soc.* **2022***, 144,* 7988; d) Sharland, J. C.; Davies, H. M. L. *Org. Lett.* **2023**, *25*, 5214.

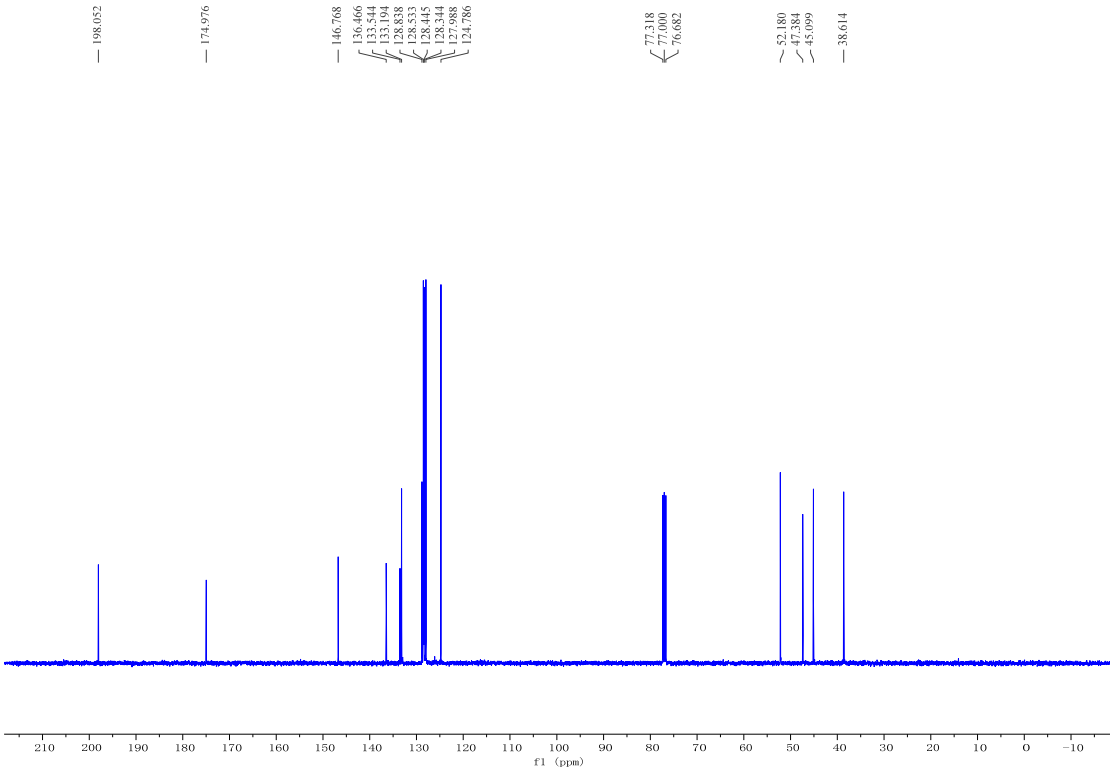
13 NMR Spectra

^{1}H and ^{13}C NMR Spectra for Compound 3aa:

^{1}H NMR (400 MHz, $CDCl_3$)

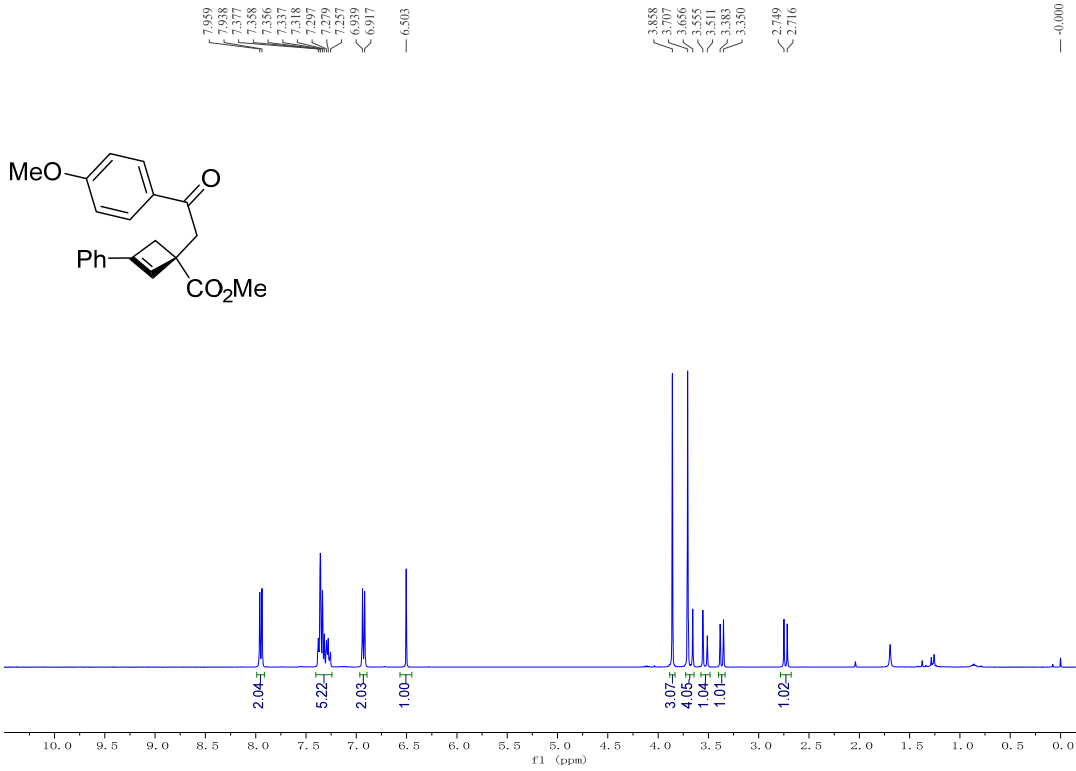


^{13}C NMR (100 MHz, $CDCl_3$)

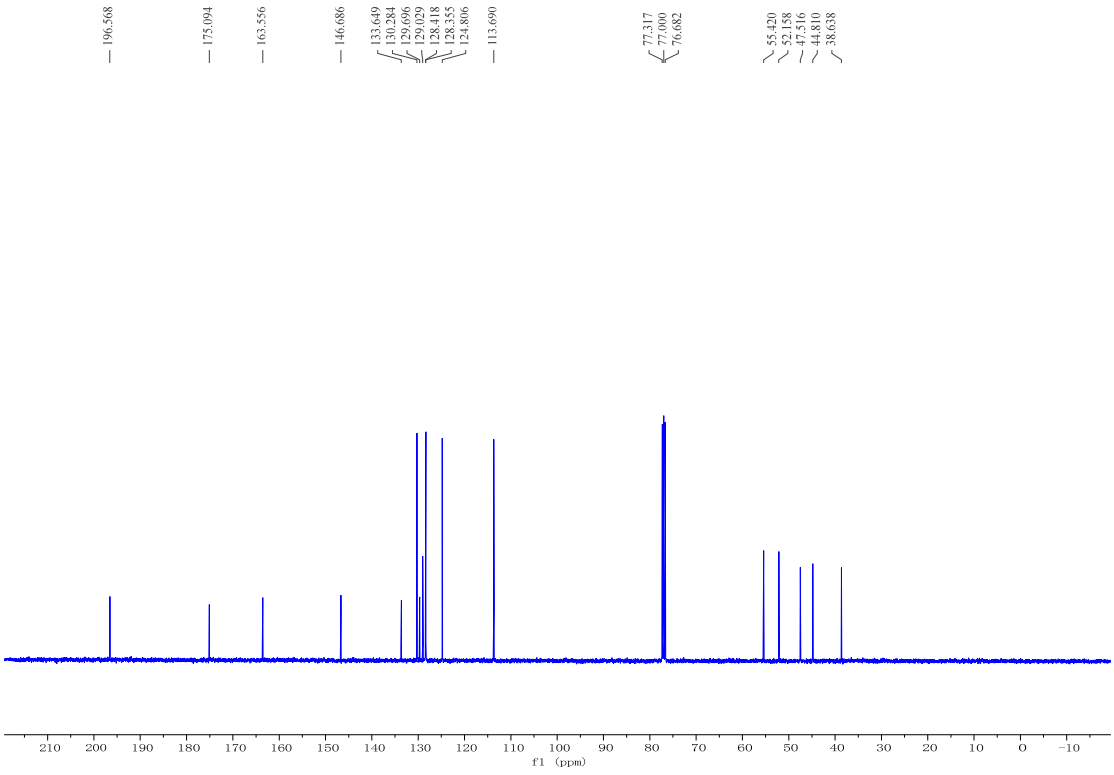


^{1}H and ^{13}C NMR Spectra for Compound 3ab:

^{1}H NMR (400 MHz, $CDCl_3$)

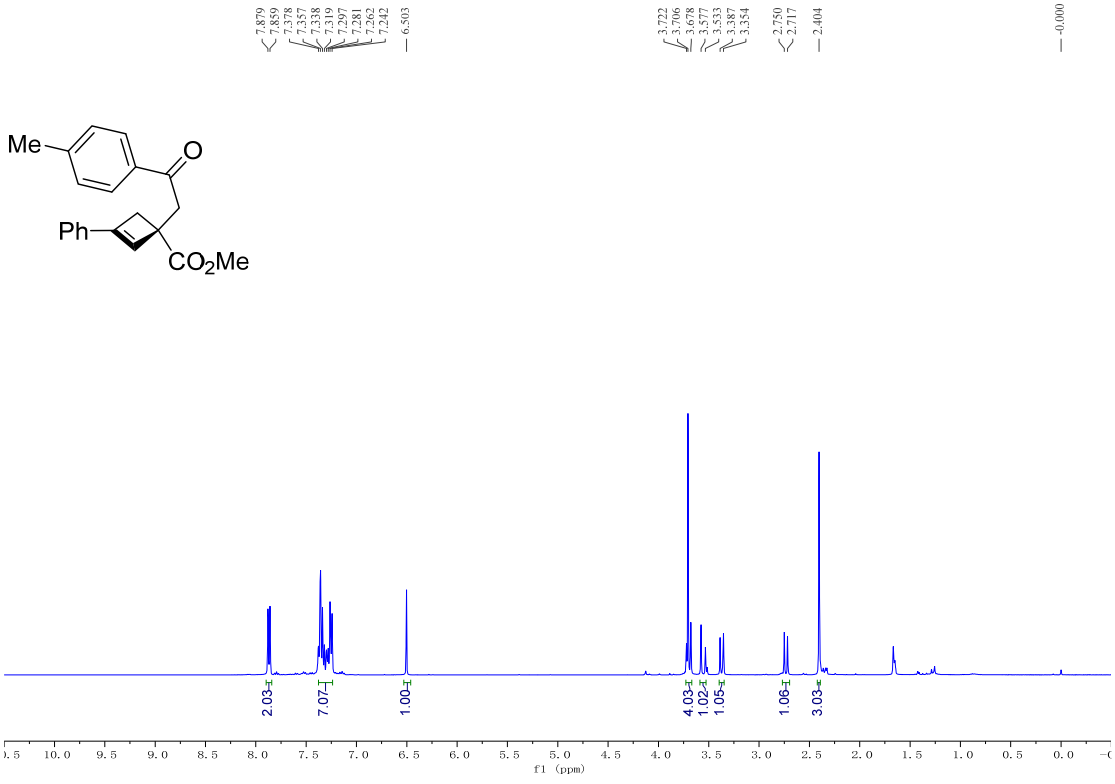


^{13}C NMR (100 MHz, $CDCl_3$)

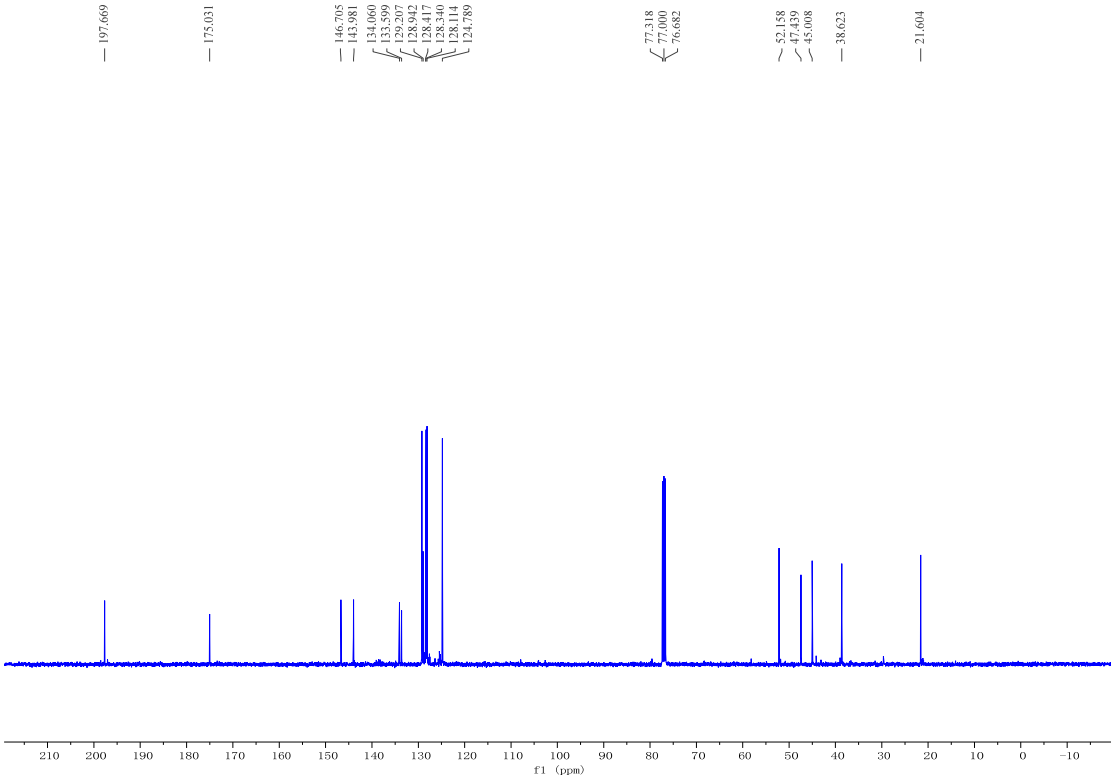


^{1}H and ^{13}C NMR Spectra for Compound 3ac:

^{1}H NMR (400 MHz, $CDCl_3$)

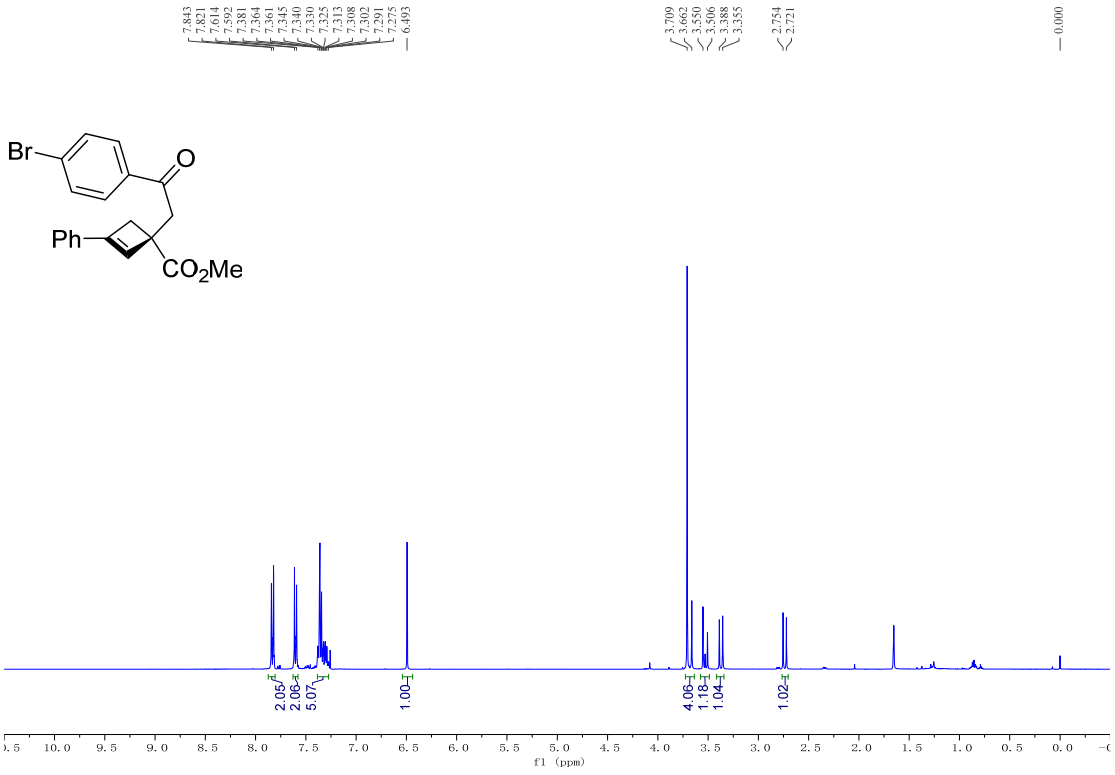


^{13}C NMR (100 MHz, $CDCl_3$)

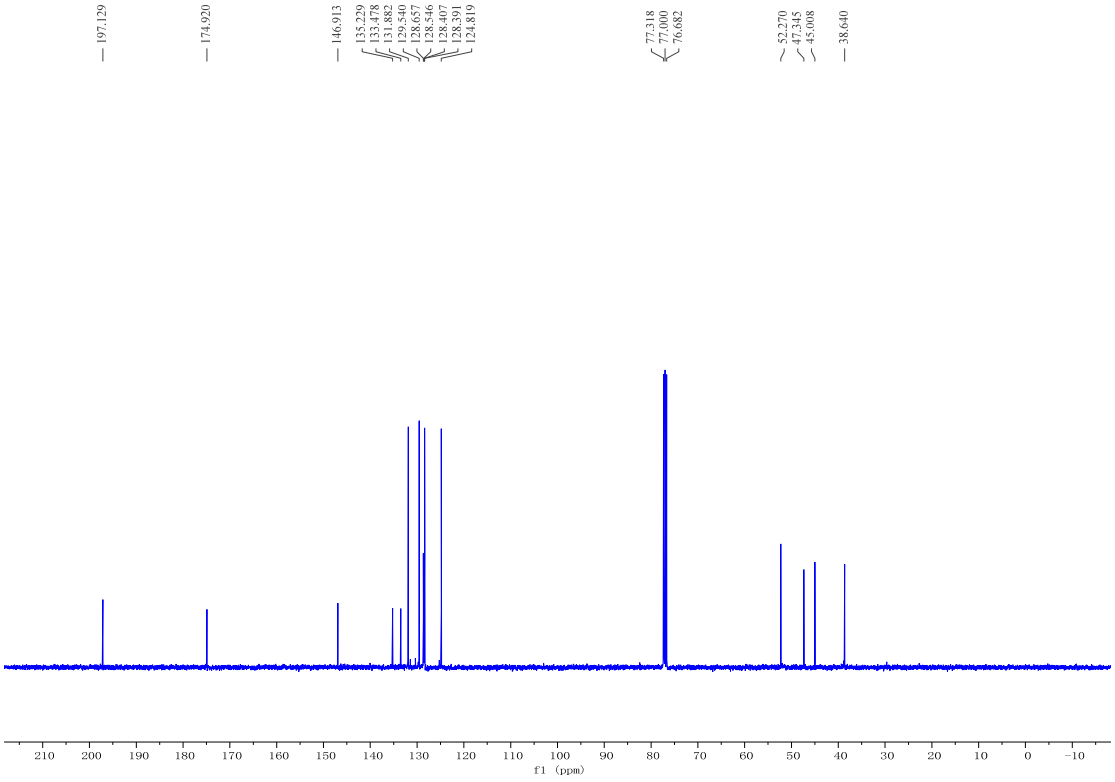


^{1}H and ^{13}C NMR Spectra for Compound 3ad:

^{1}H NMR (400 MHz, $CDCl_3$)

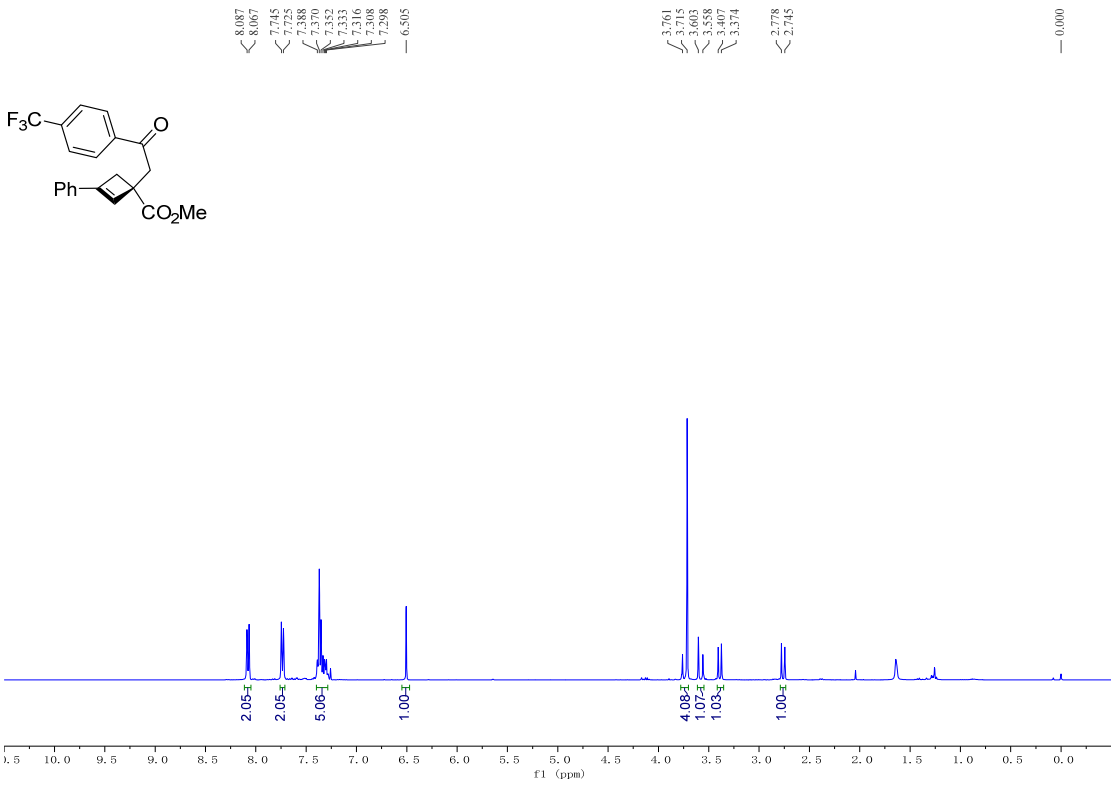


^{13}C NMR (100 MHz, $CDCl_3$)

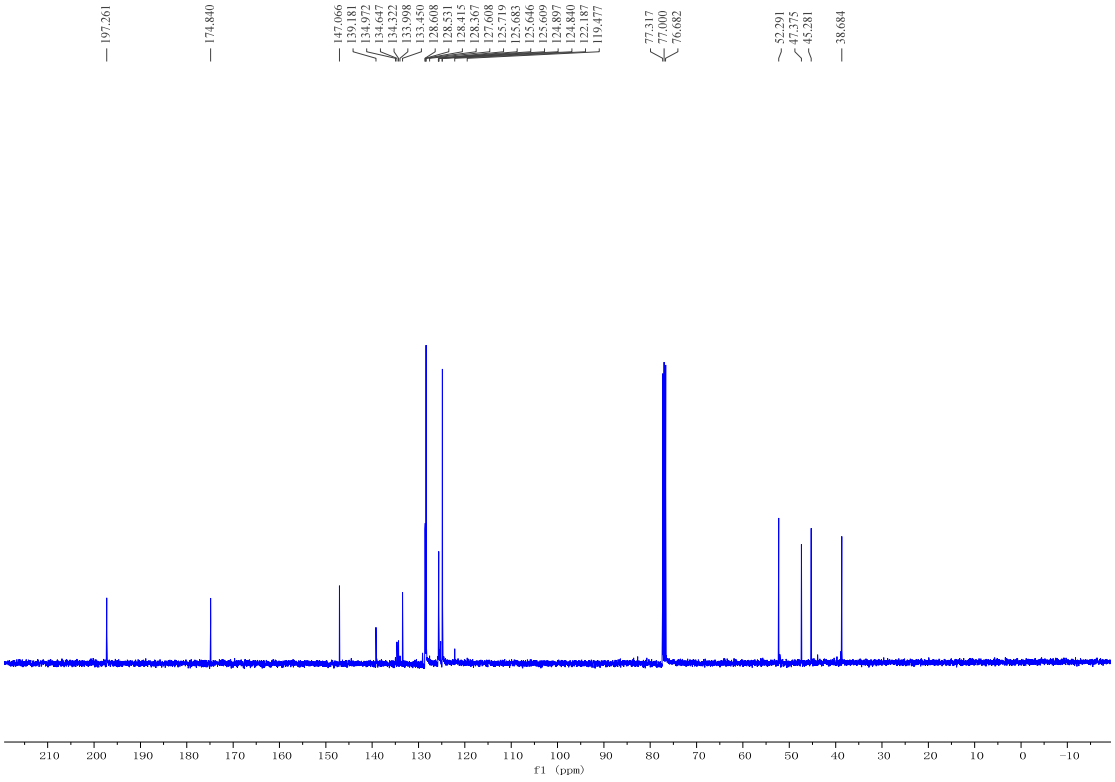


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3ae:

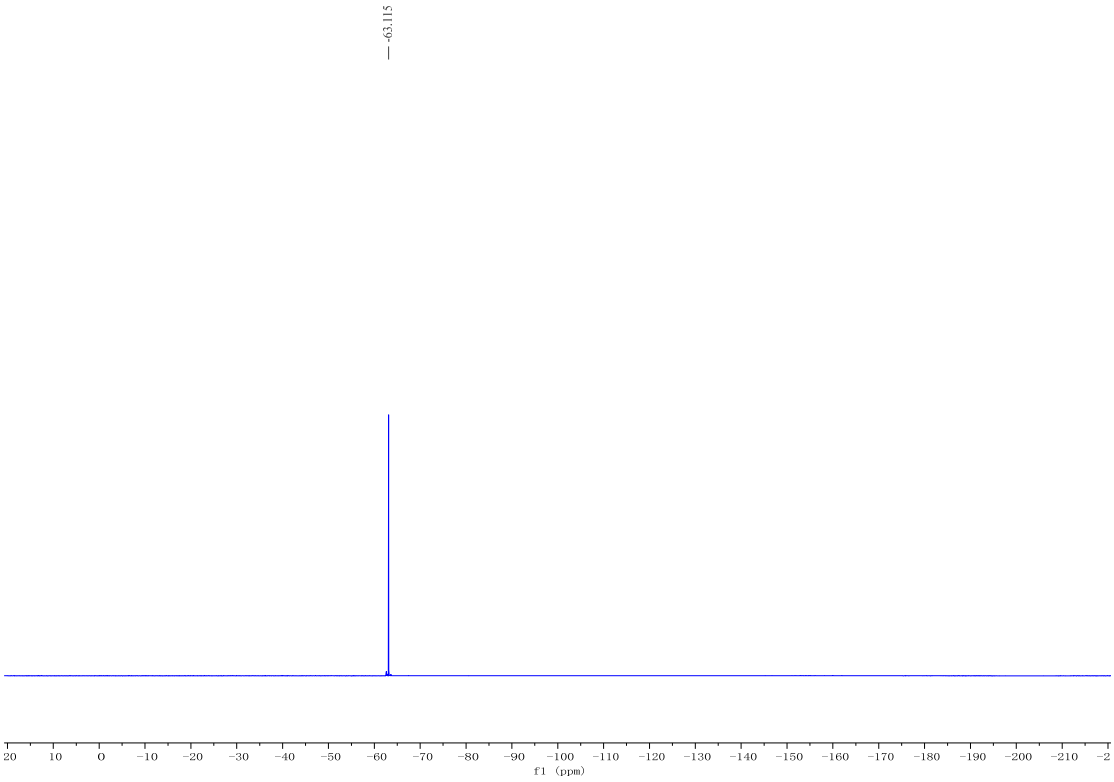
^{1}H NMR (400 MHz, $CDCl_3$)



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

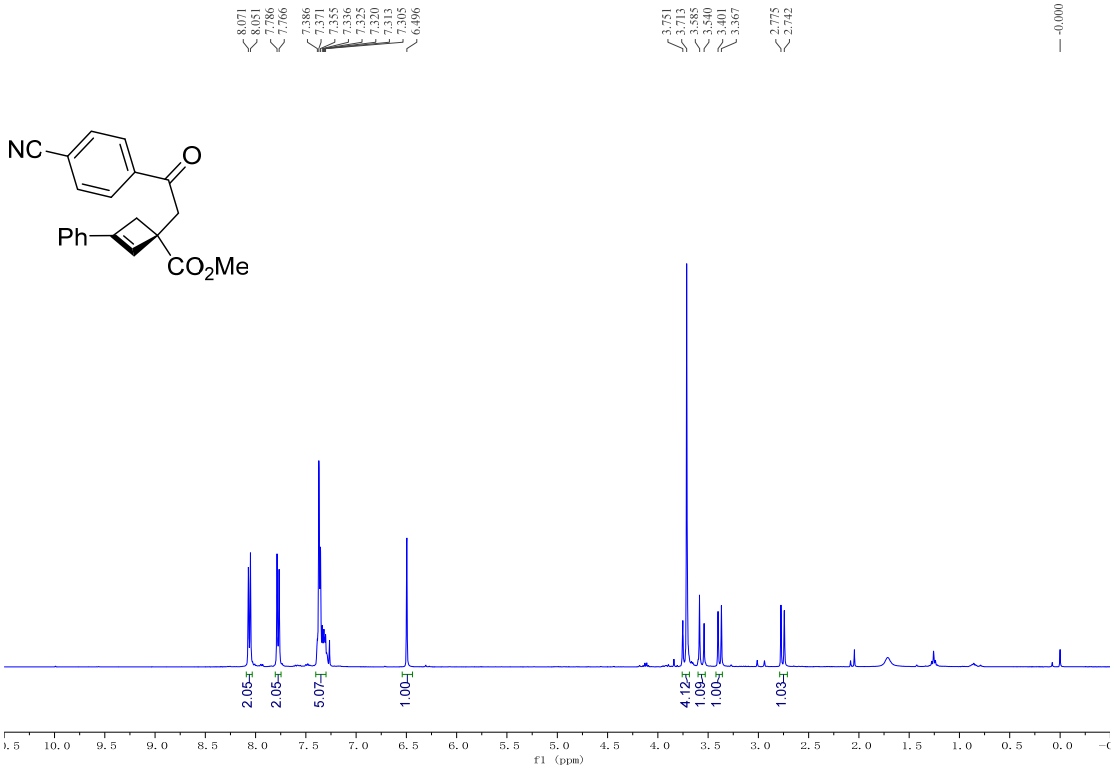


^{19}F NMR (376 MHz, $CDCl_3$)

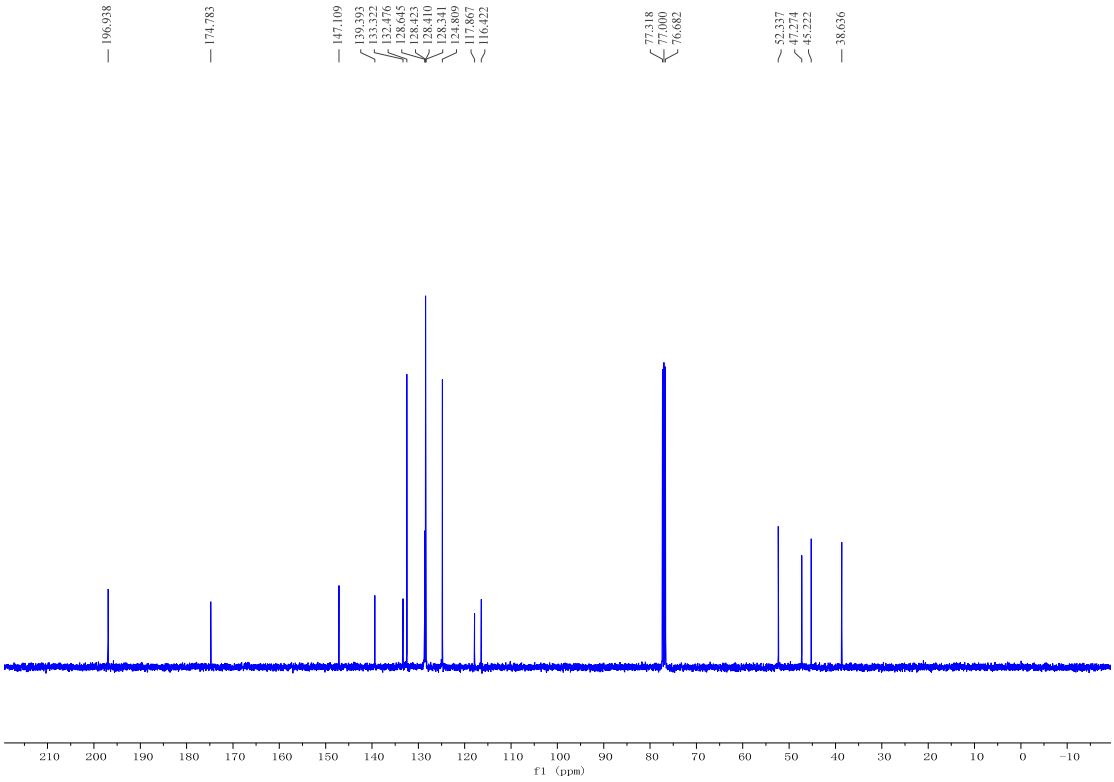


^{1}H and ^{13}C NMR Spectra for Compound 3af:

^{1}H NMR (400 MHz, $CDCl_3$)

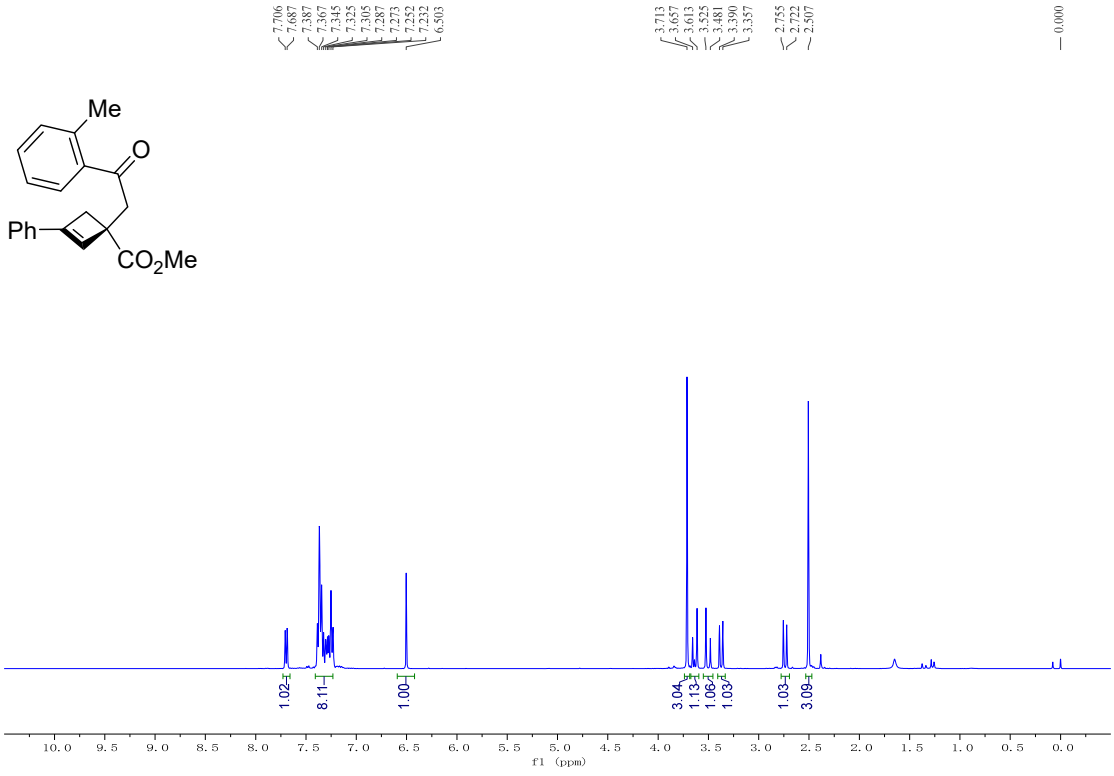


^{13}C NMR (100 MHz, $CDCl_3$)

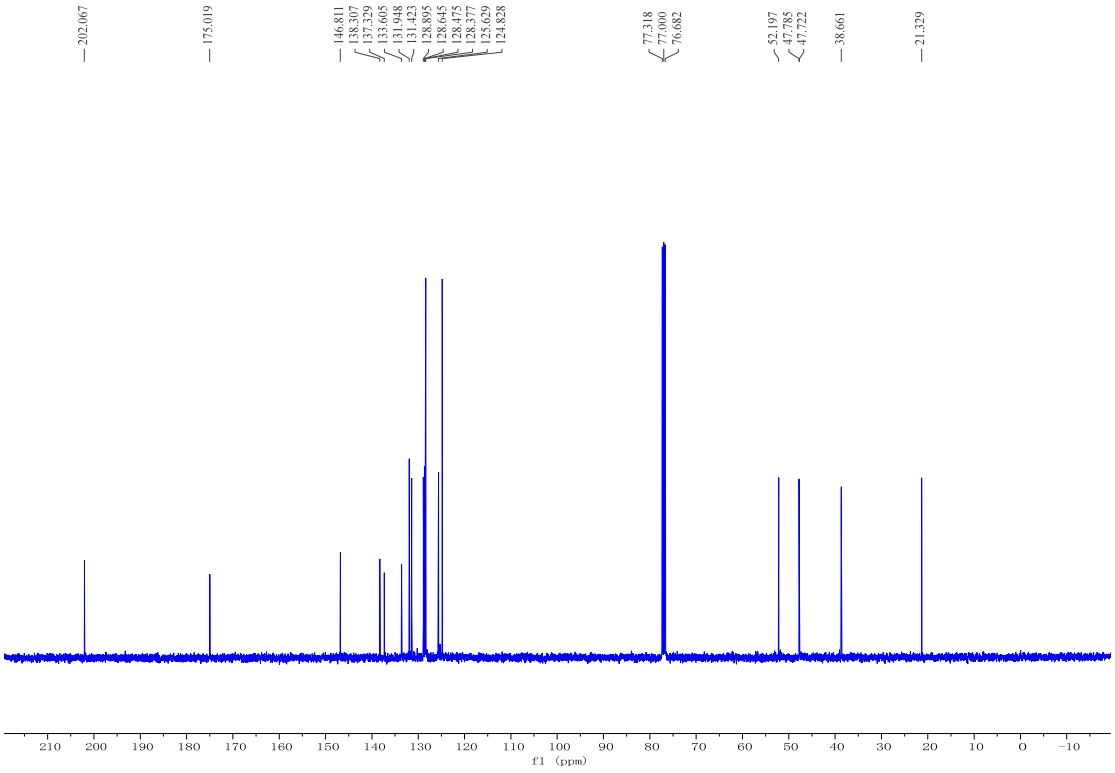


^{1}H and ^{13}C NMR Spectra for Compound 3ag:

^{1}H NMR (400 MHz, $CDCl_3$)

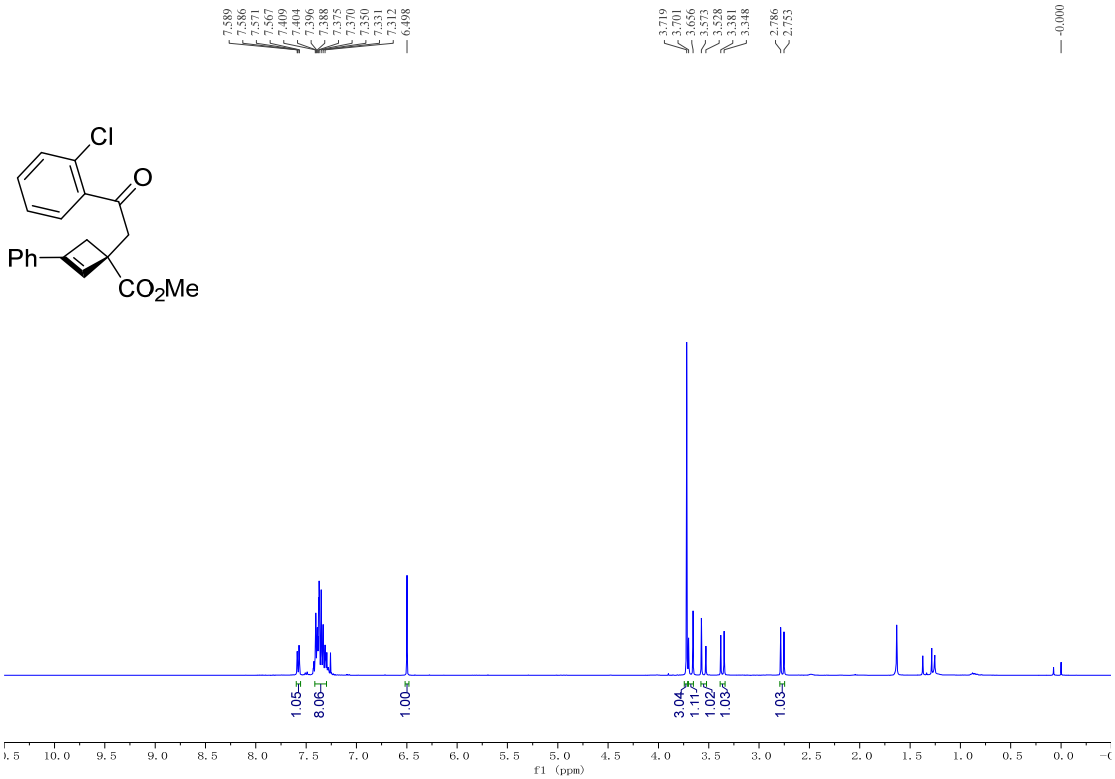


^{13}C NMR (100 MHz, $CDCl_3$)

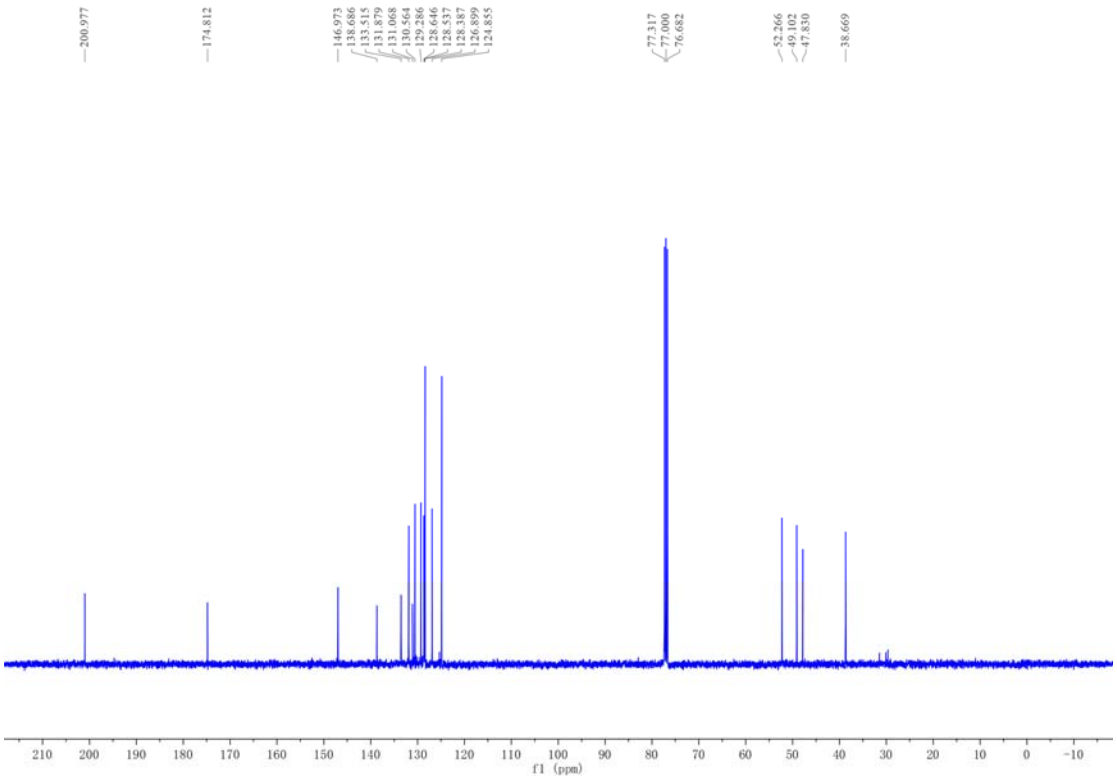


^{1}H and ^{13}C NMR Spectra for Compound 3ah:

^{1}H NMR (400 MHz, $CDCl_3$)

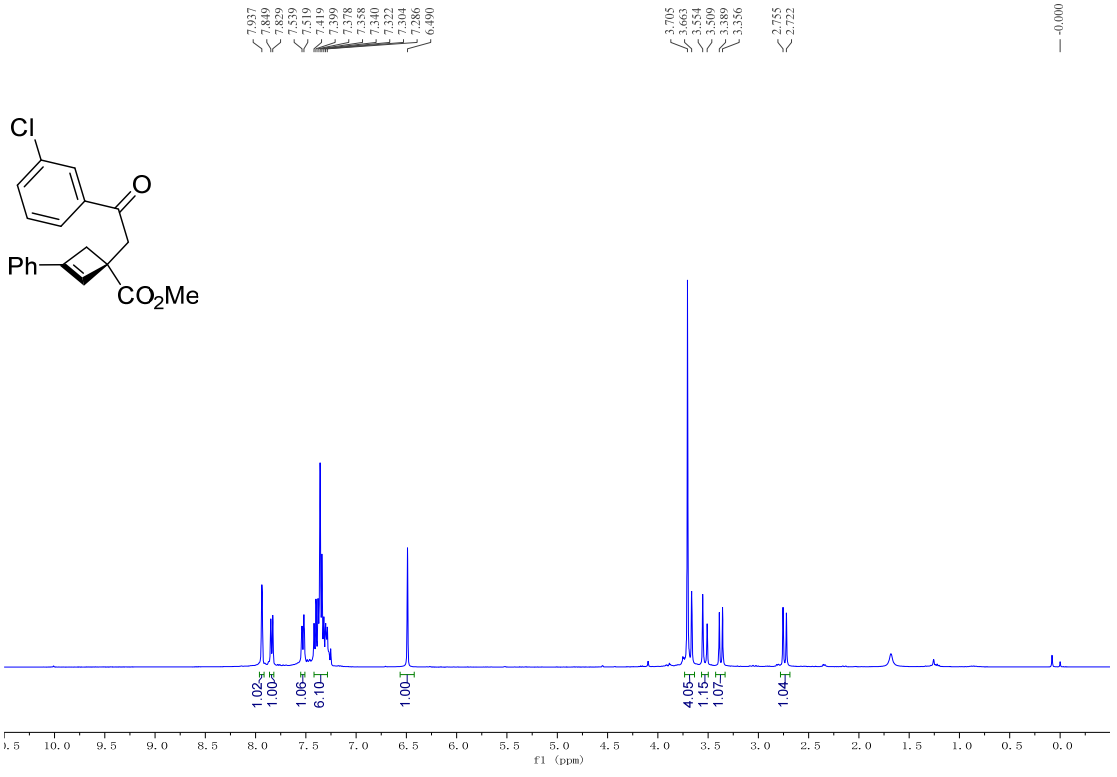


^{13}C NMR (100 MHz, $CDCl_3$)

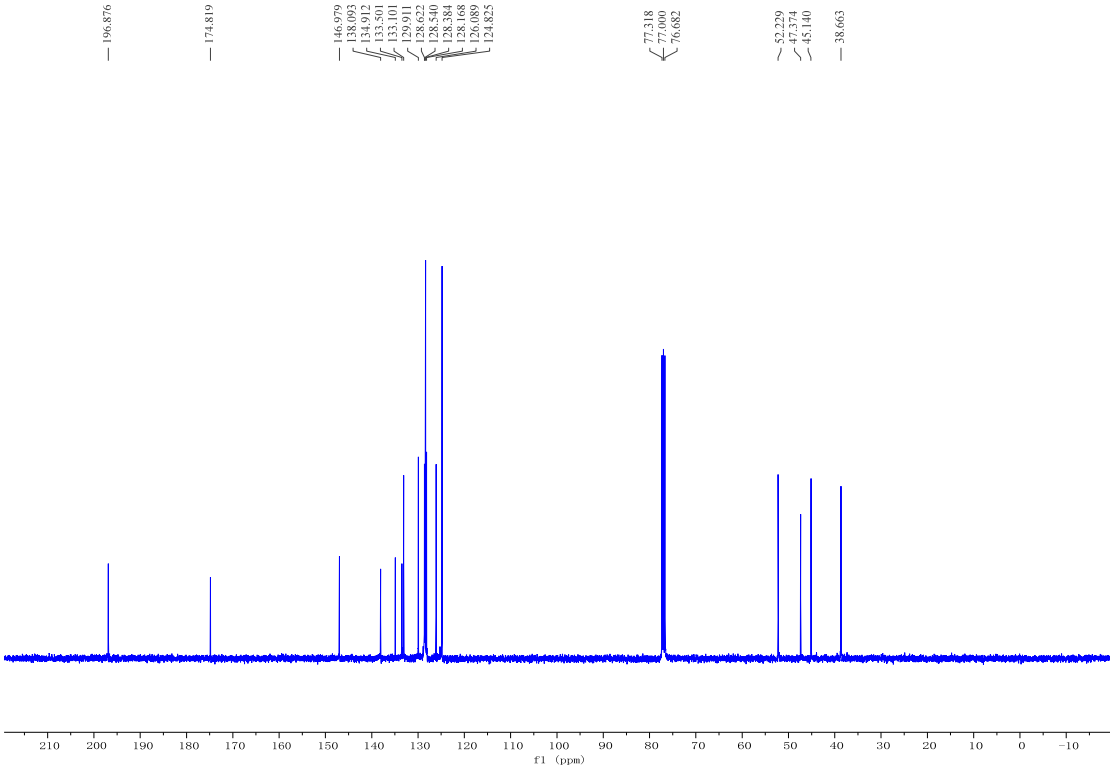


^{1}H and ^{13}C NMR Spectra for Compound 3ai:

^{1}H NMR (400 MHz, $CDCl_3$)

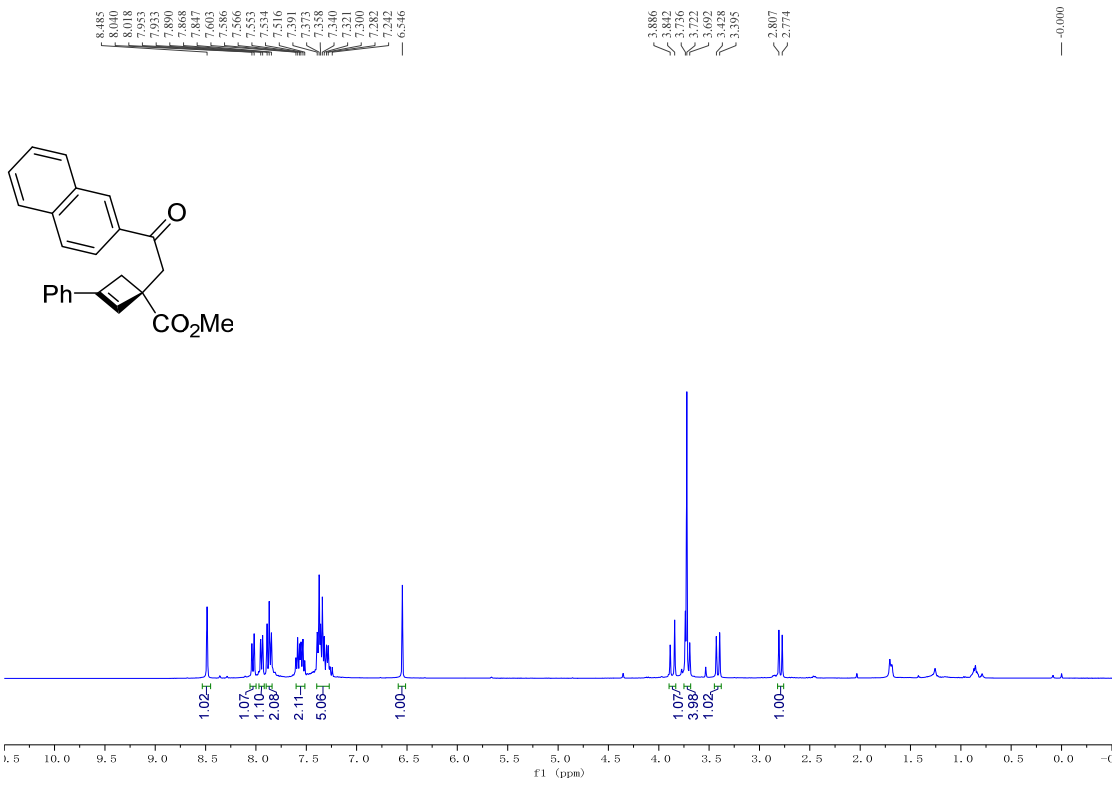


^{13}C NMR (100 MHz, $CDCl_3$)

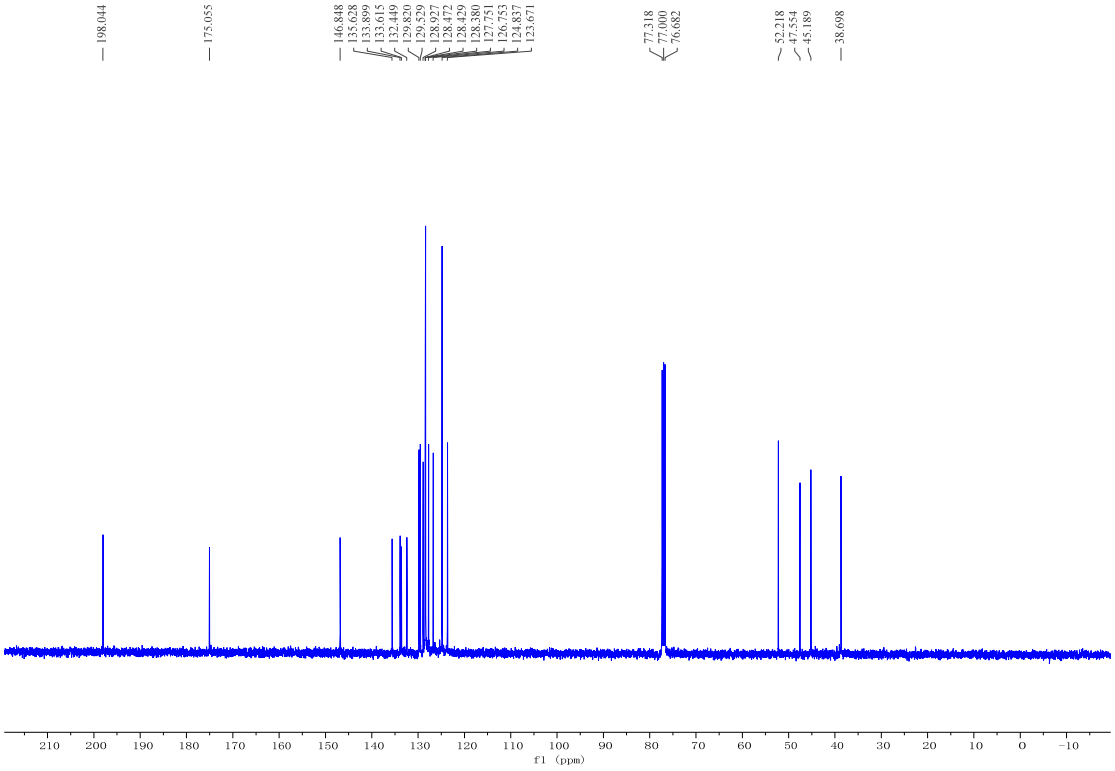


^{1}H and ^{13}C NMR Spectra for Compound 3aj:

^{1}H NMR (400 MHz, $CDCl_3$)

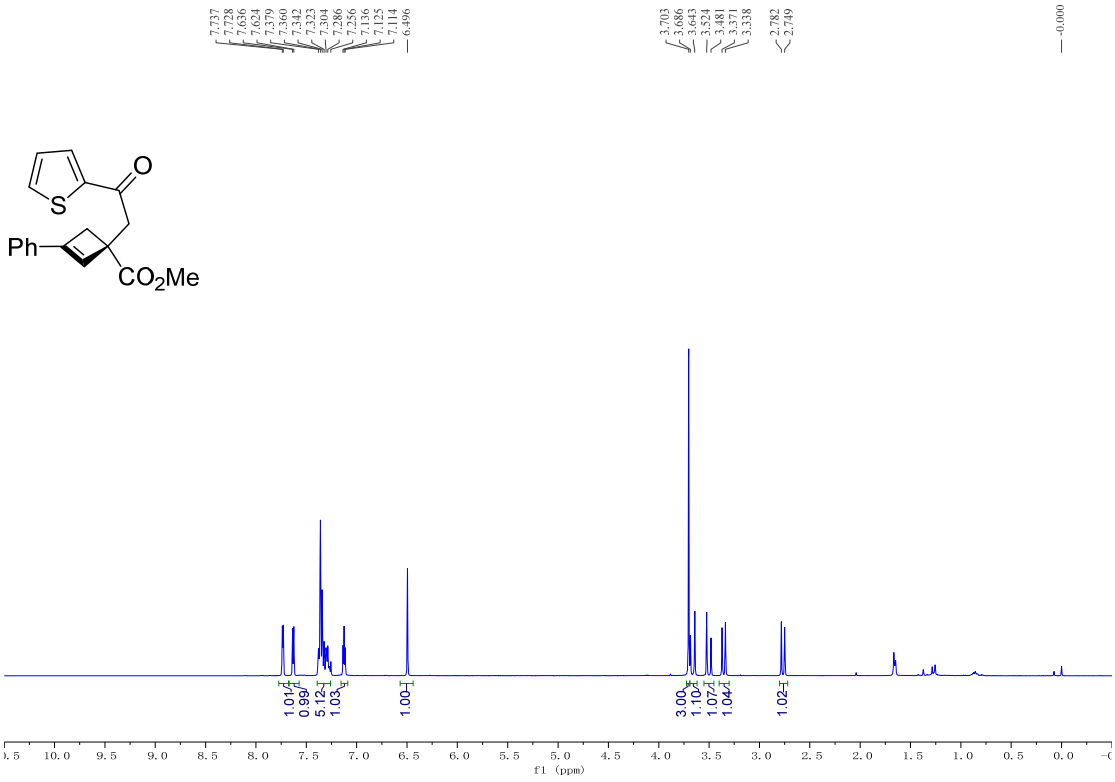


^{13}C NMR (100 MHz, $CDCl_3$)

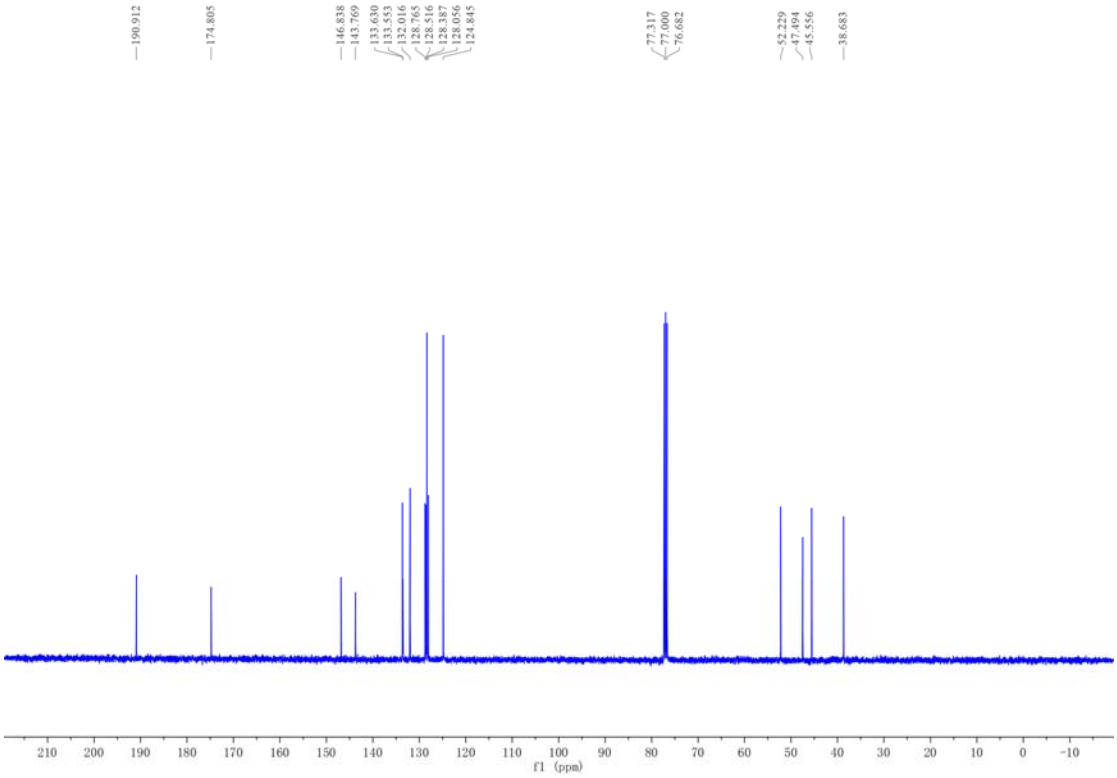


^{1}H and ^{13}C NMR Spectra for Compound 3ak:

^{1}H NMR (400 MHz, $CDCl_3$)

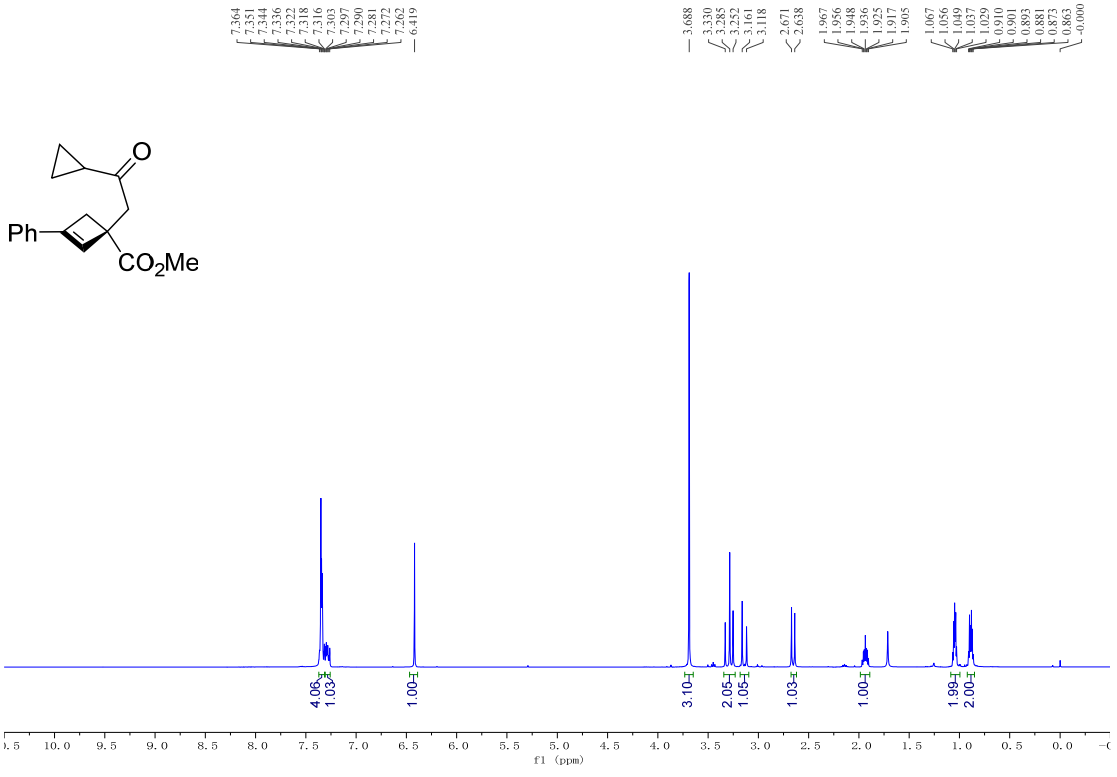


^{13}C NMR (100 MHz, $CDCl_3$)

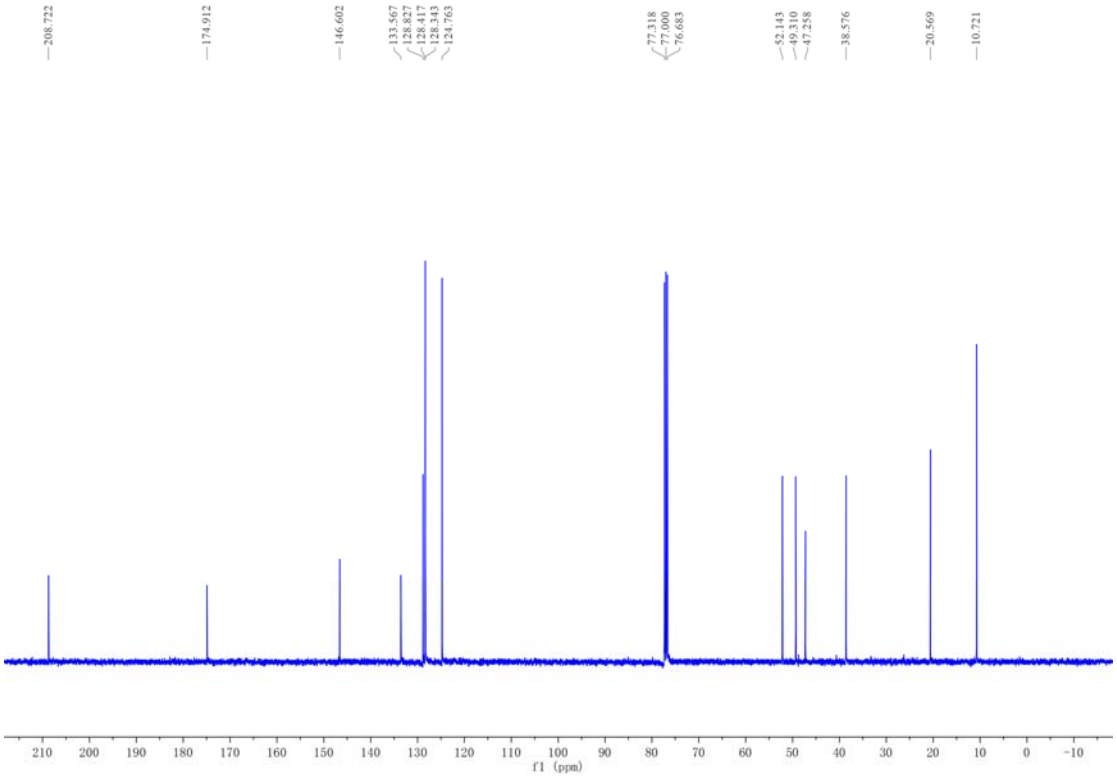


^{1}H and ^{13}C NMR Spectra for Compound 3al:

^{1}H NMR (400 MHz, $CDCl_3$)

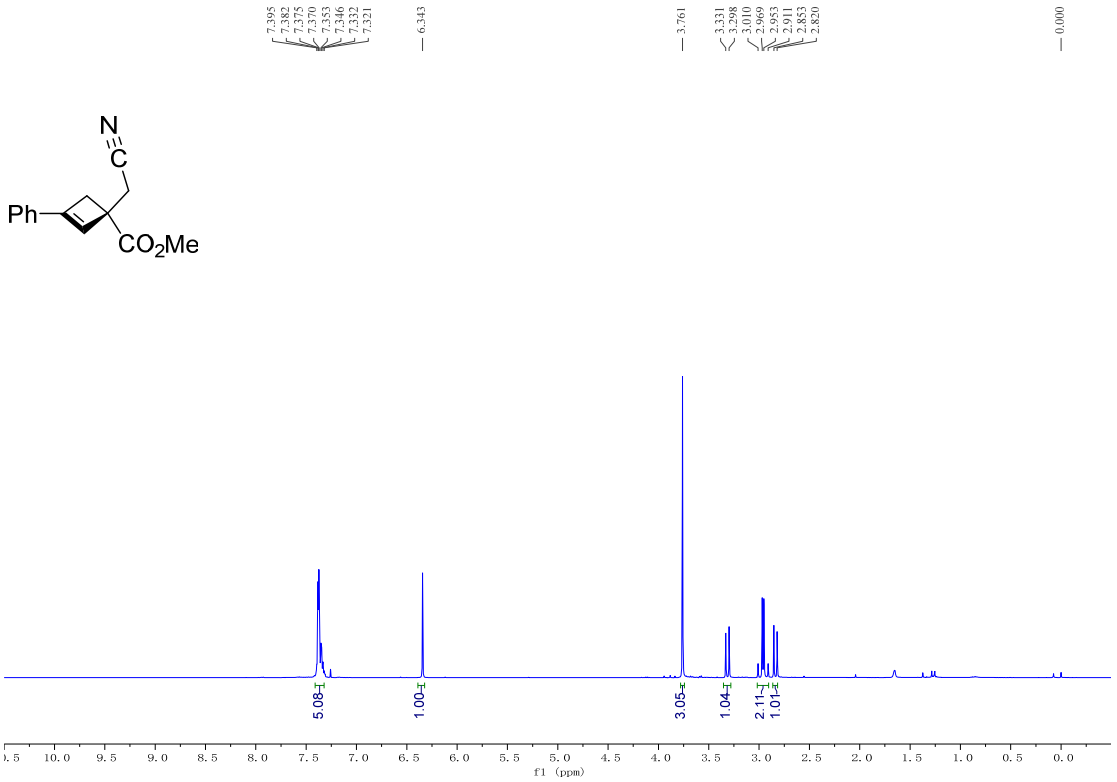


^{13}C NMR (100 MHz, $CDCl_3$)

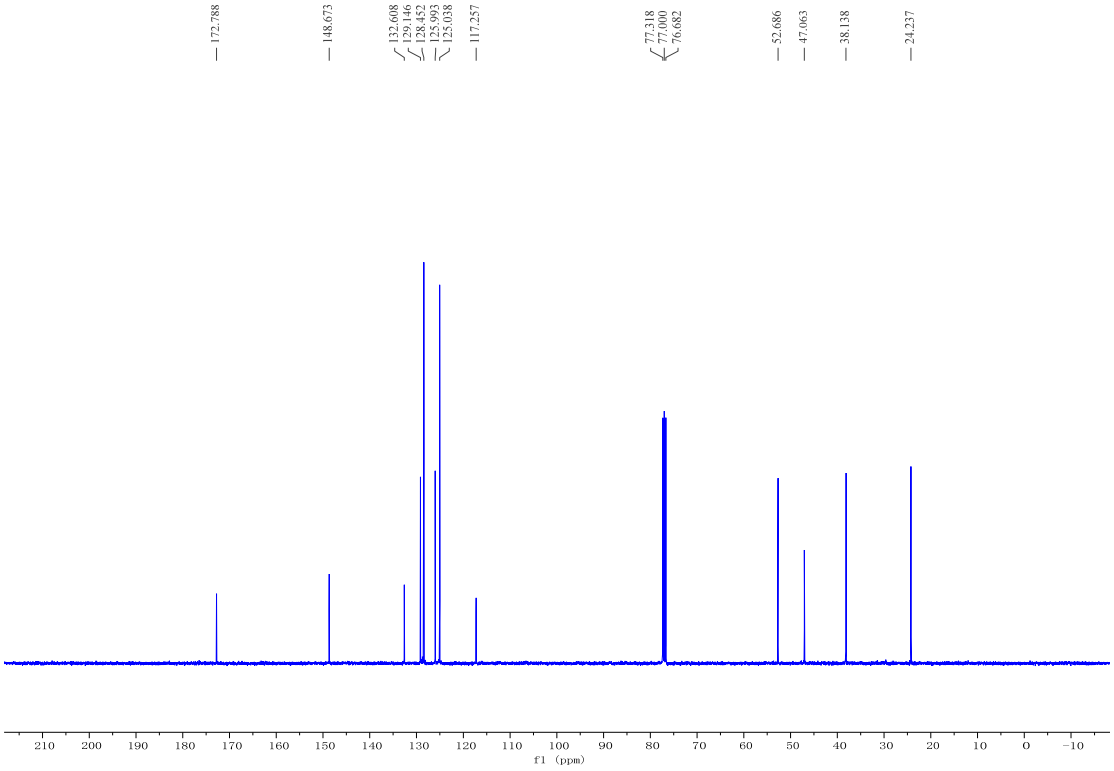


^{1}H and ^{13}C NMR Spectra for Compound 3am:

^{1}H NMR (400 MHz, $CDCl_3$)

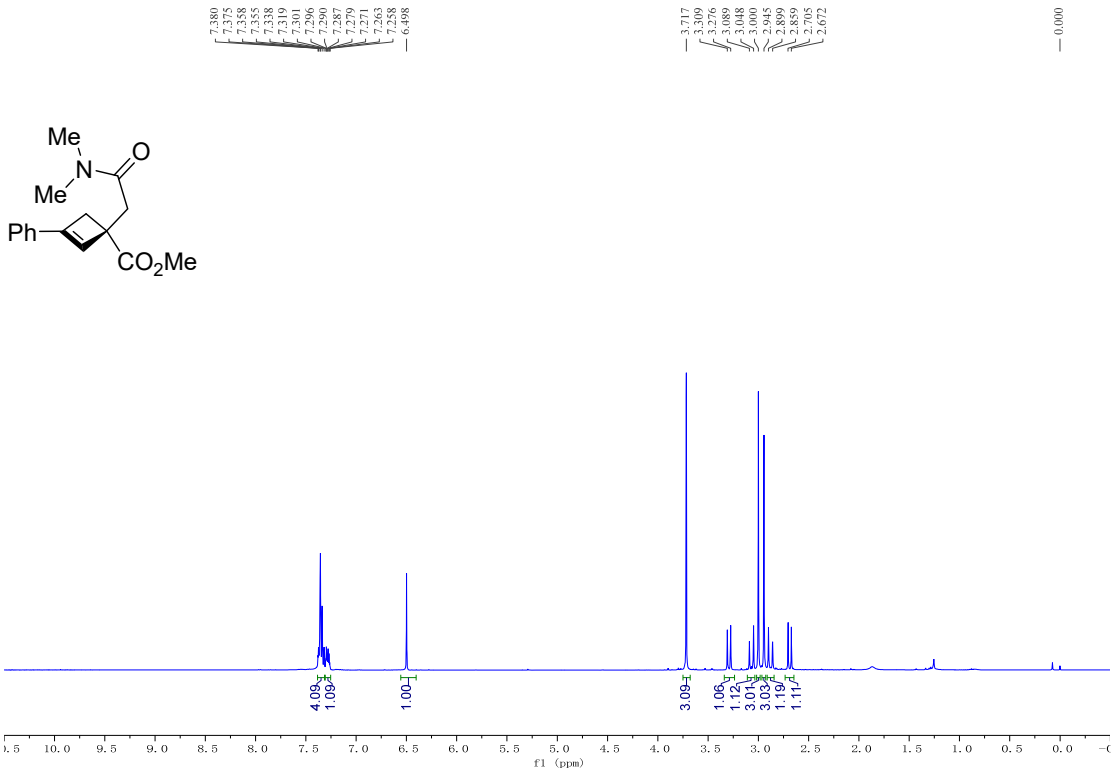


^{13}C NMR (100 MHz, $CDCl_3$)

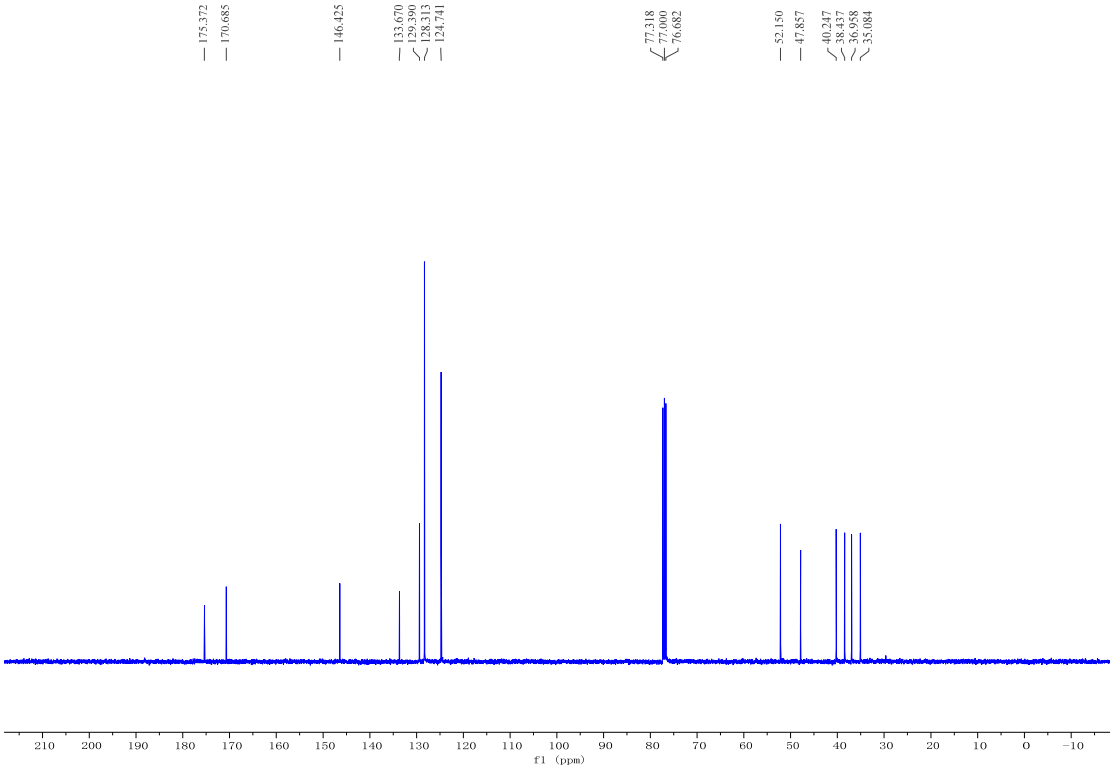


^{1}H and ^{13}C NMR Spectra for Compound 3an:

^{1}H NMR (400 MHz, $CDCl_3$)

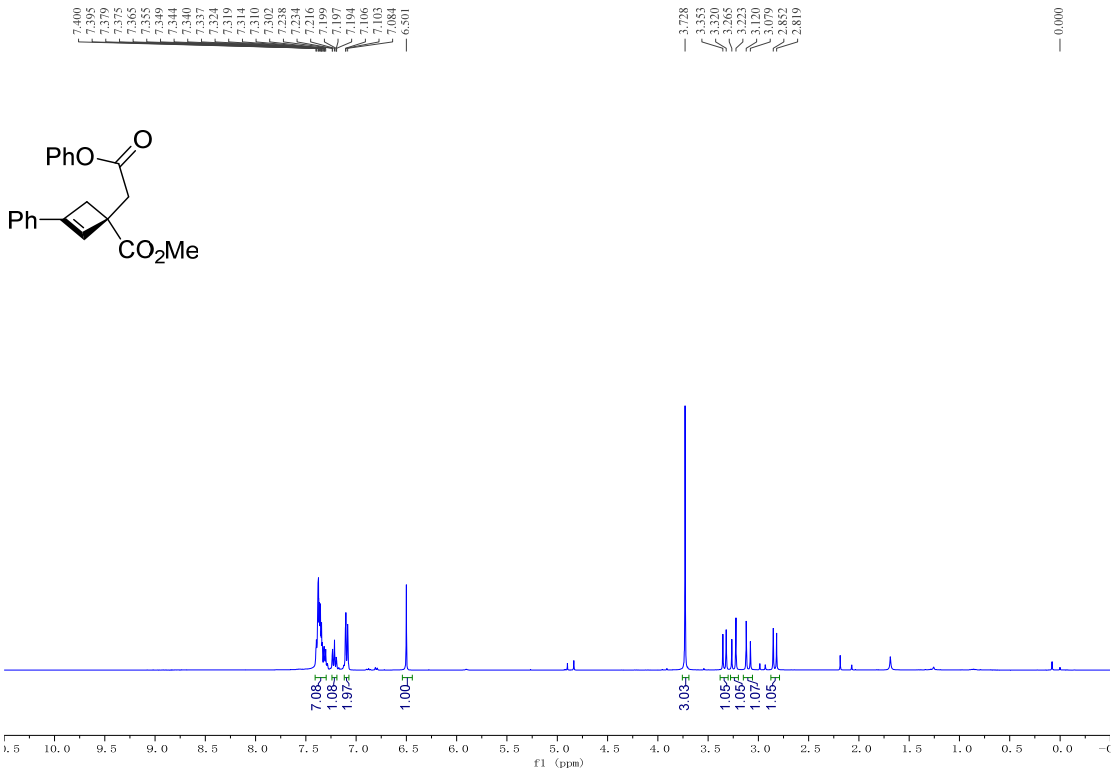


^{13}C NMR (100 MHz, $CDCl_3$)

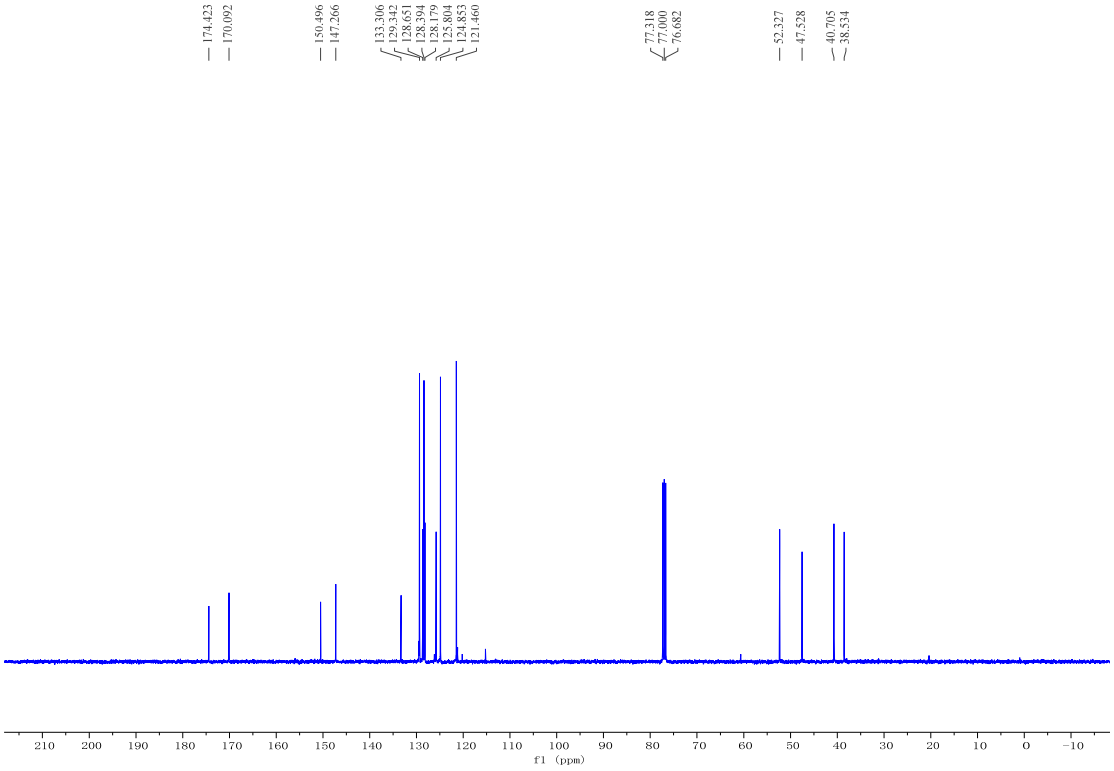


^{1}H and ^{13}C NMR Spectra for Compound 3ao:

^{1}H NMR (400 MHz, $CDCl_3$)

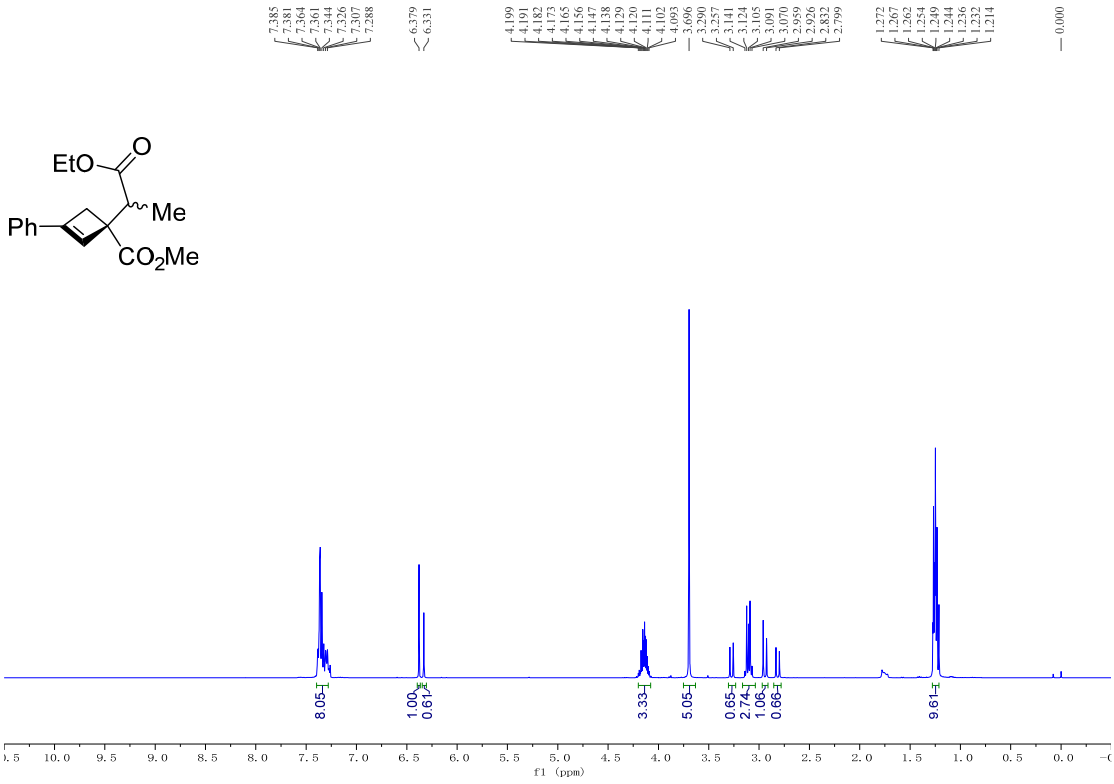


^{13}C NMR (100 MHz, $CDCl_3$)

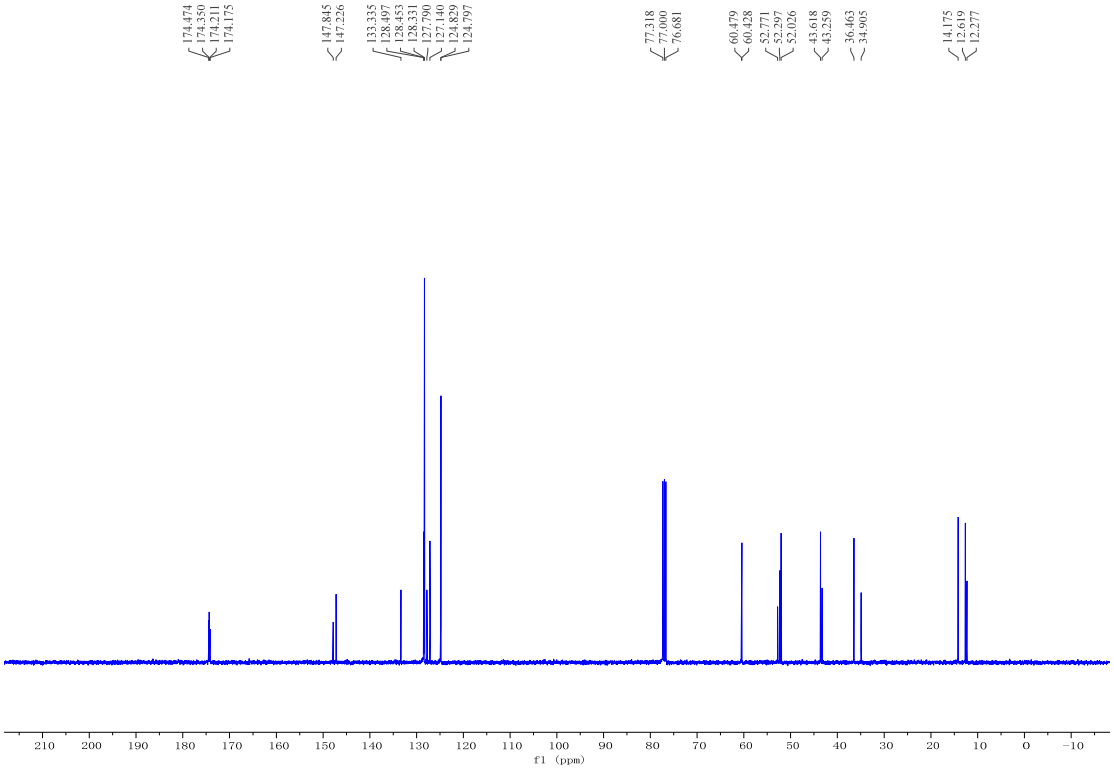


^{1}H and ^{13}C NMR Spectra for Compound 3ap:

^{1}H NMR (400 MHz, $CDCl_3$)

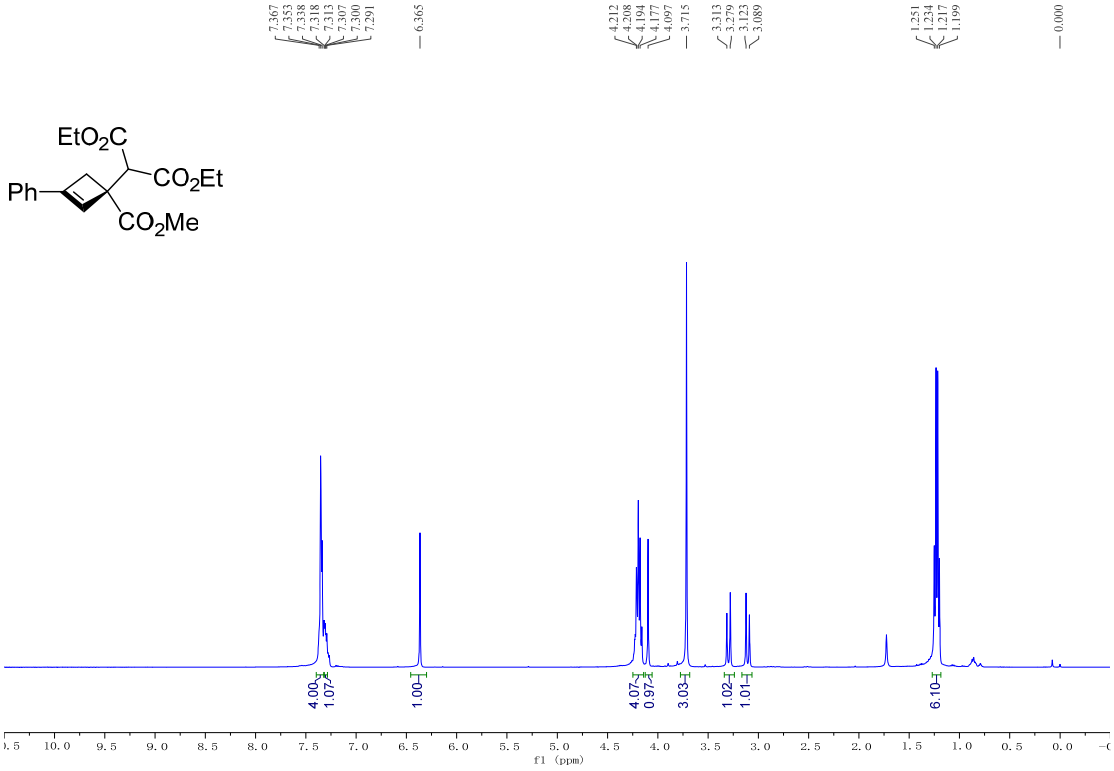


^{13}C NMR (100 MHz, $CDCl_3$)

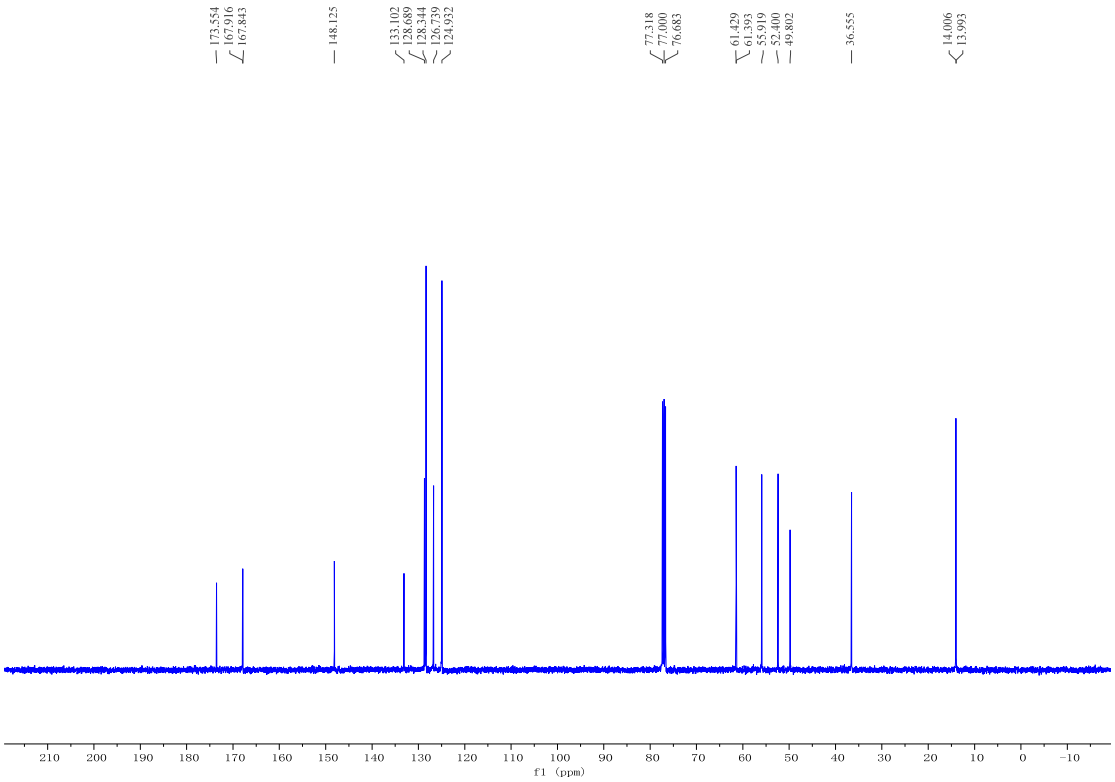


^{1}H and ^{13}C NMR Spectra for Compound 3aq:

^{1}H NMR (400 MHz, $CDCl_3$)

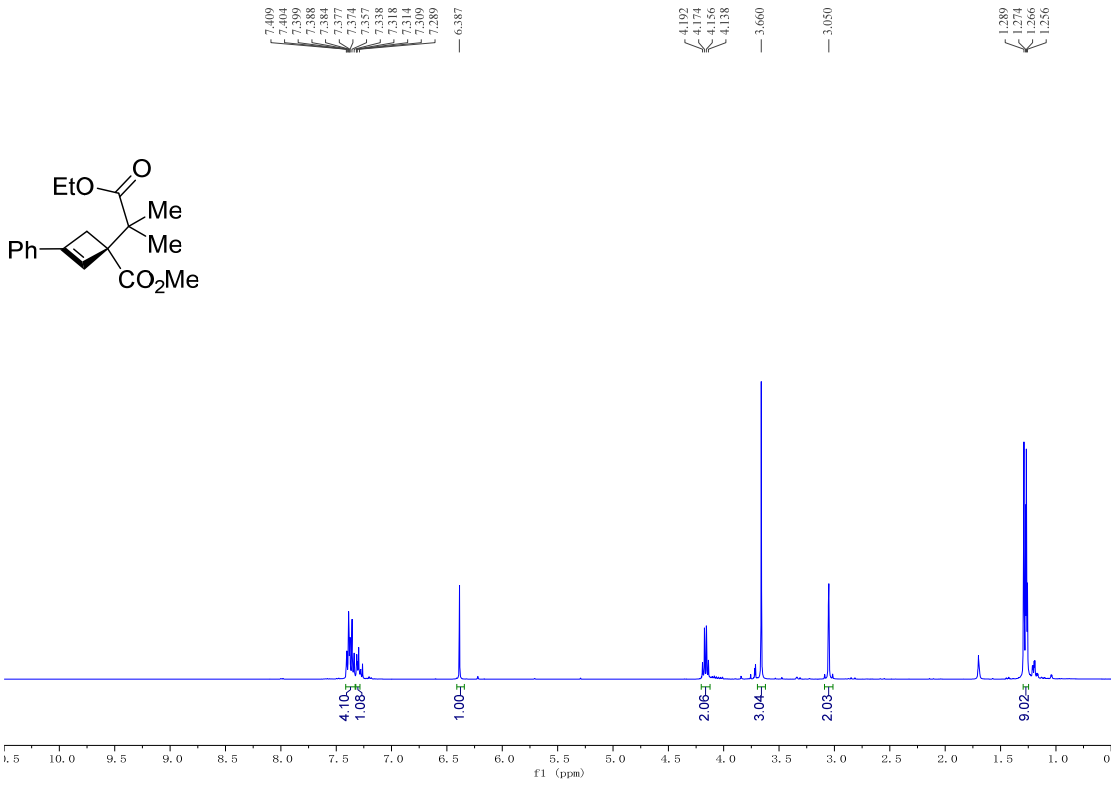


^{13}C NMR (100 MHz, $CDCl_3$)

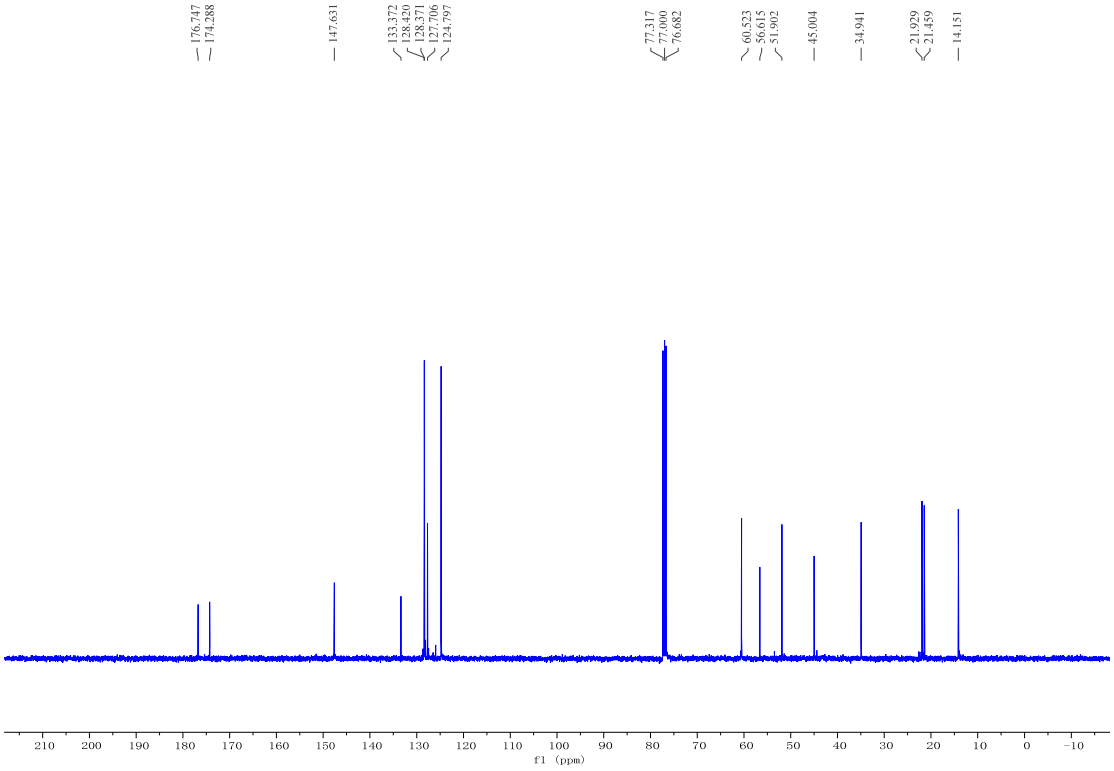


^{1}H and ^{13}C NMR Spectra for Compound 3ar:

^{1}H NMR (400 MHz, $CDCl_3$)

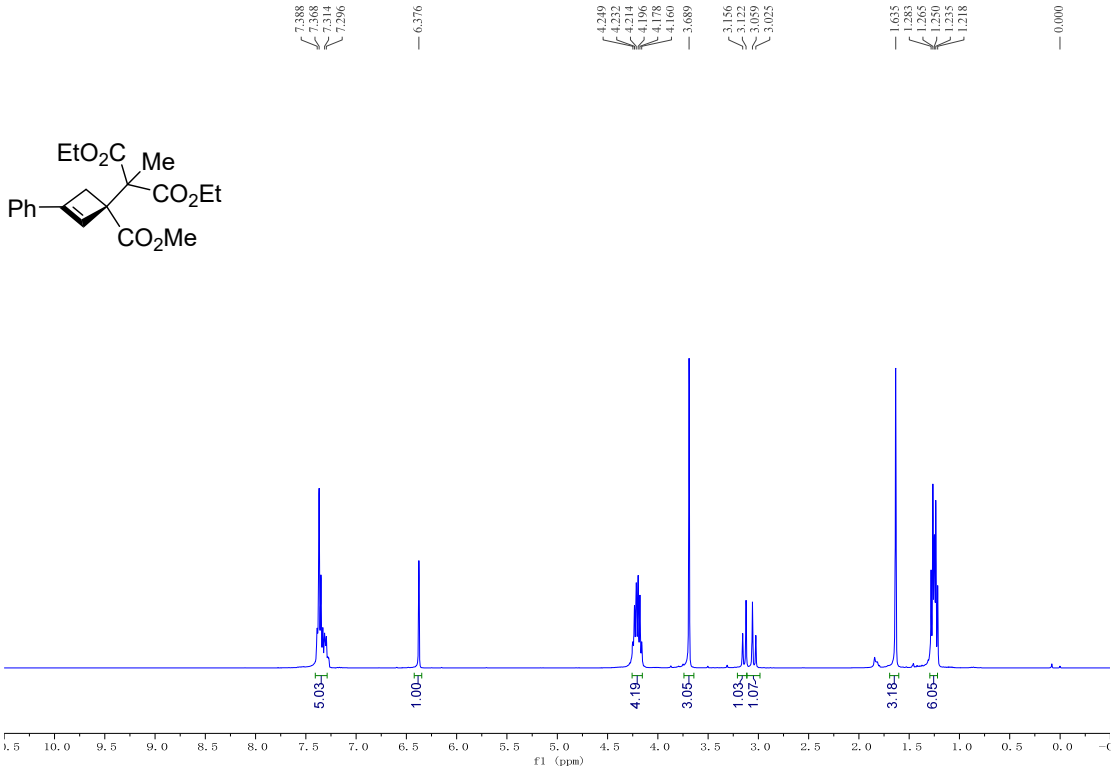


^{13}C NMR (100 MHz, $CDCl_3$)

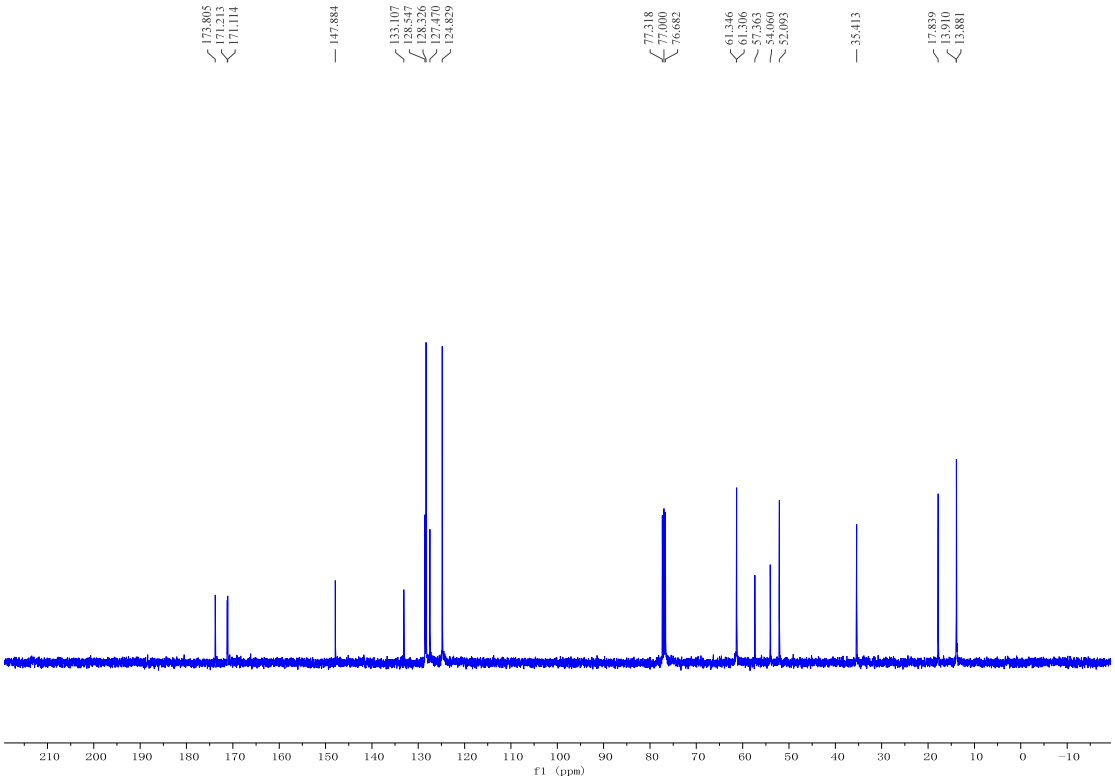


^{1}H and ^{13}C NMR Spectra for Compound 3as:

^{1}H NMR (400 MHz, $CDCl_3$)

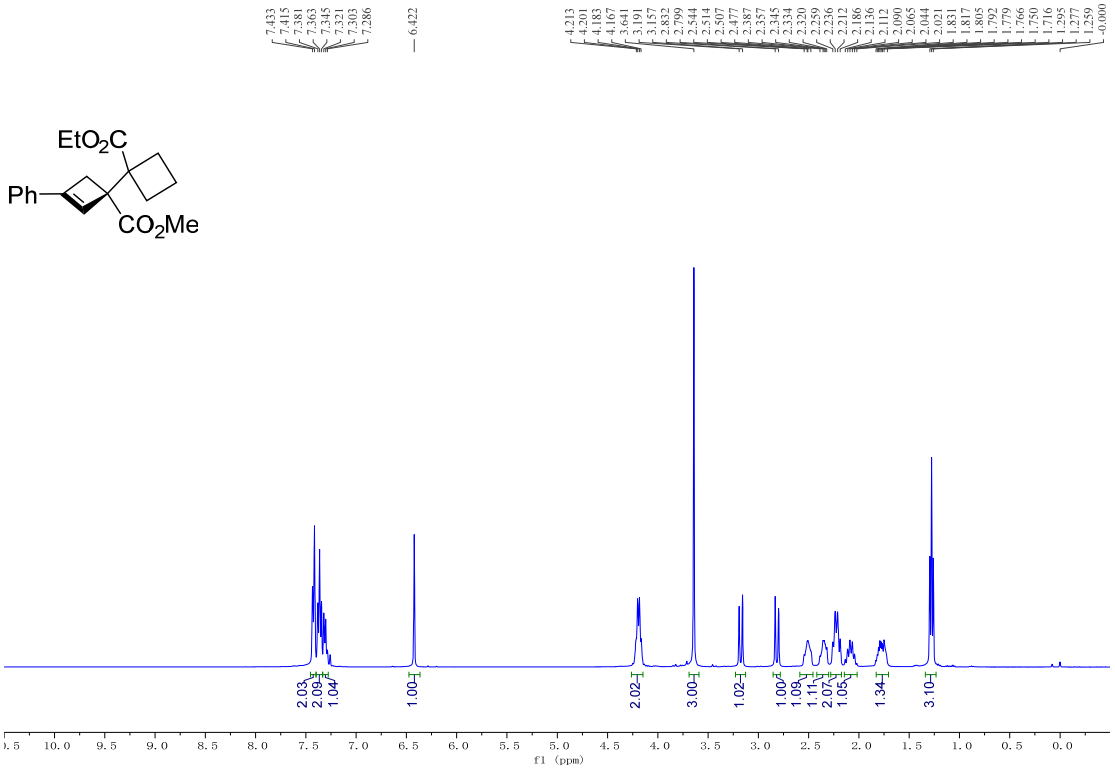


^{13}C NMR (100 MHz, $CDCl_3$)

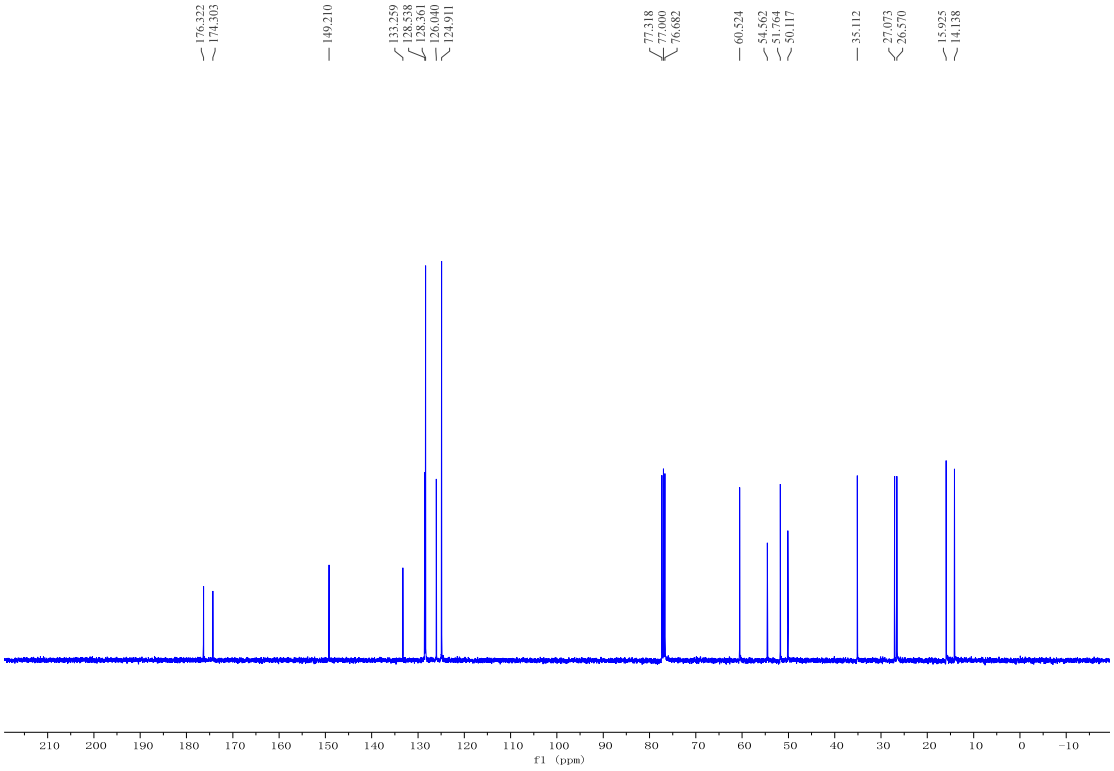


^{1}H and ^{13}C NMR Spectra for Compound 3at:

^{1}H NMR (400 MHz, $CDCl_3$)

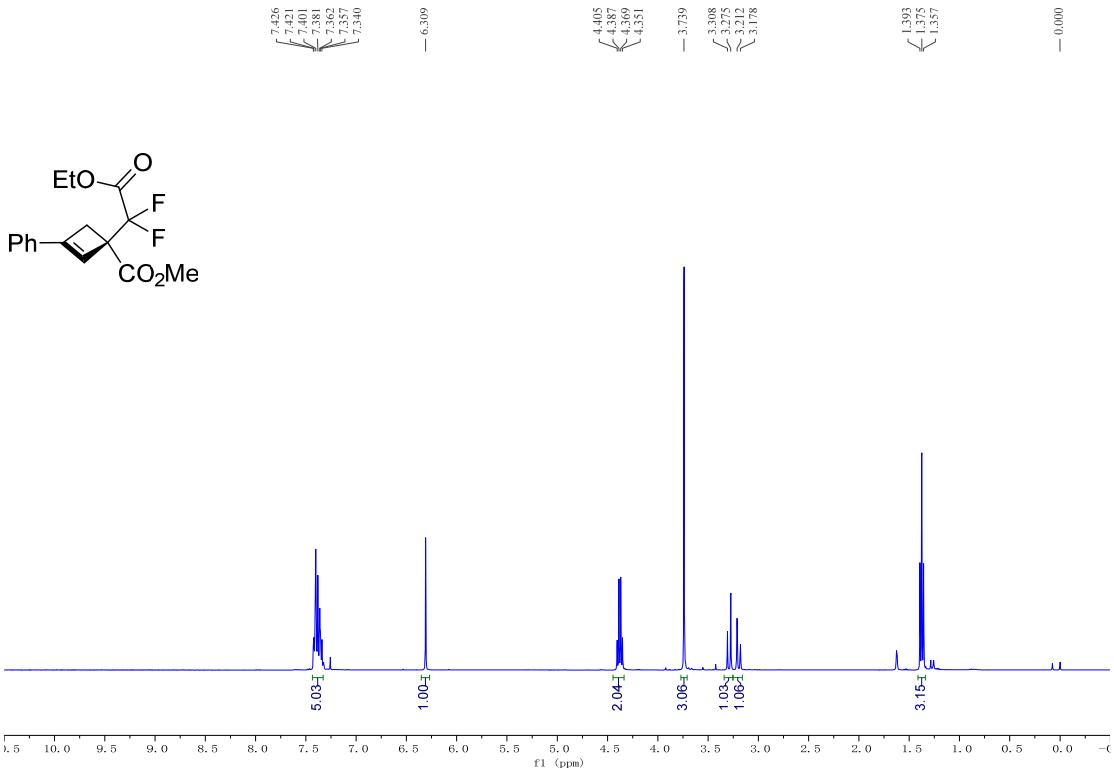


^{13}C NMR (100 MHz, $CDCl_3$)

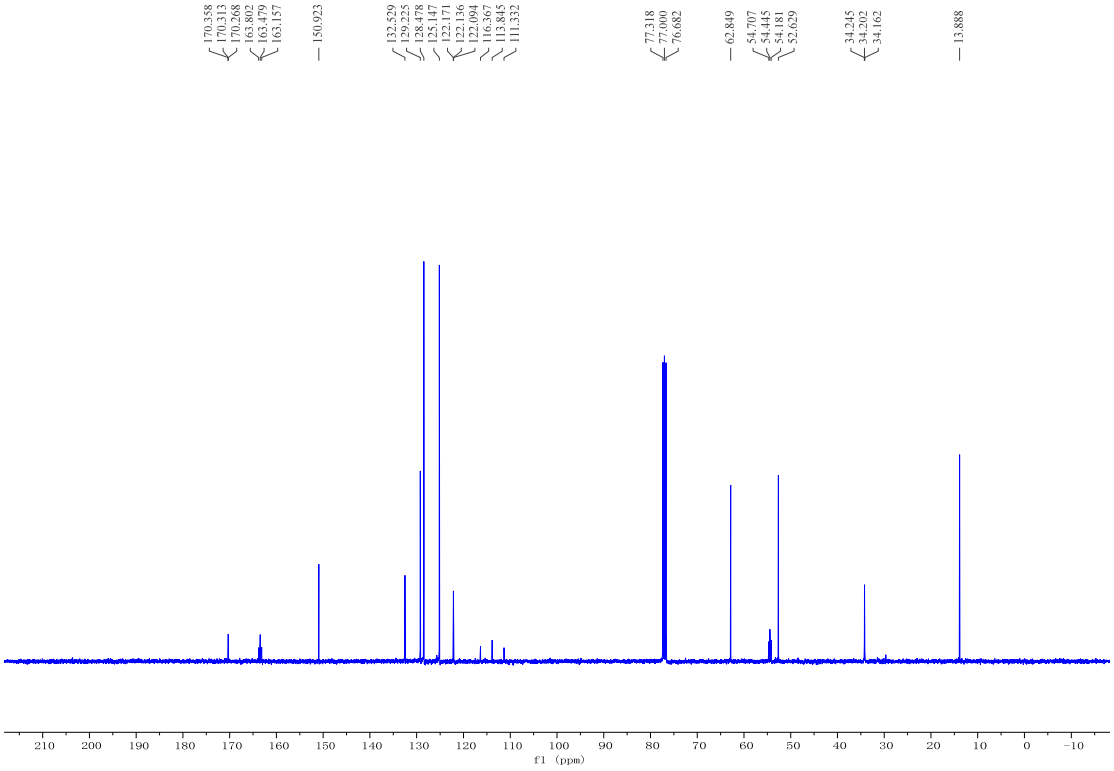


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3au:

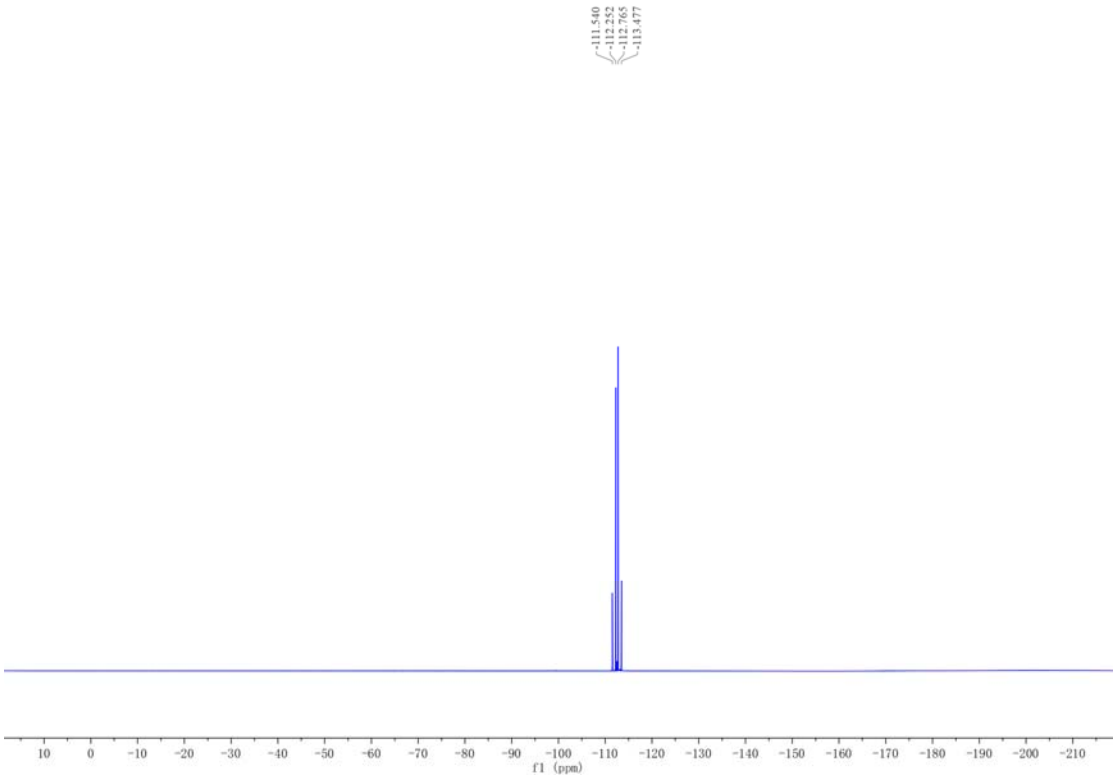
^{1}H NMR (400 MHz, $CDCl_3$)



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

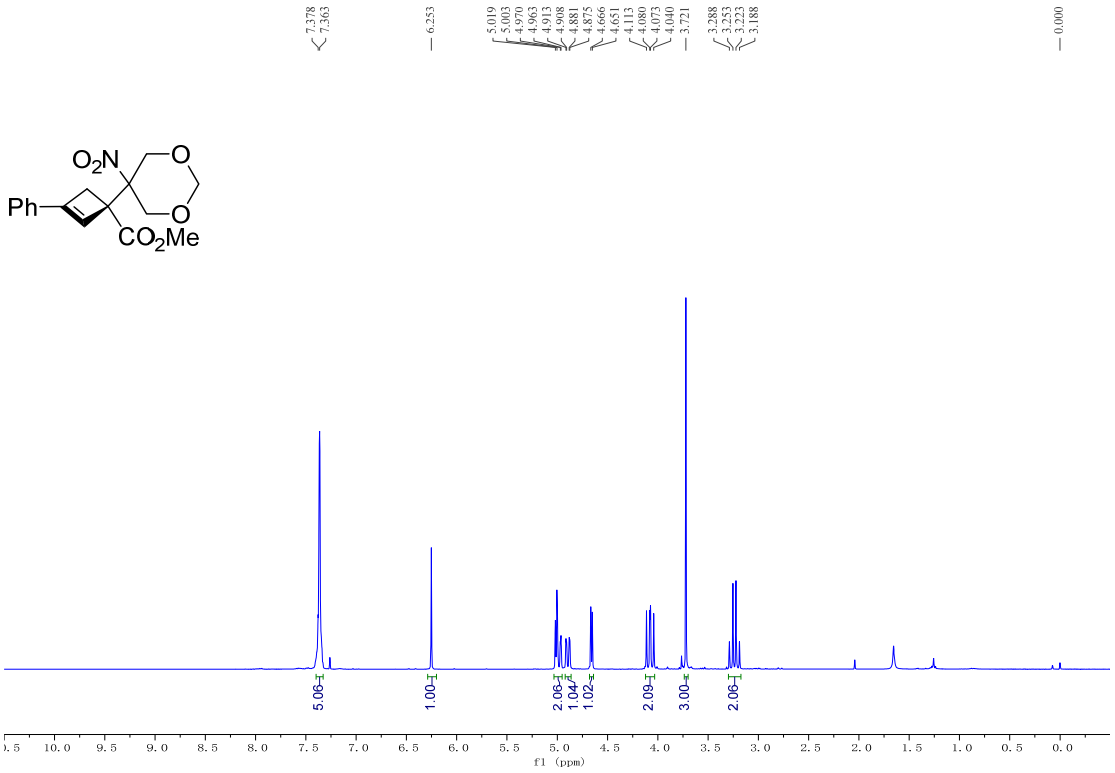


^{19}F NMR (376 MHz, $CDCl_3$)

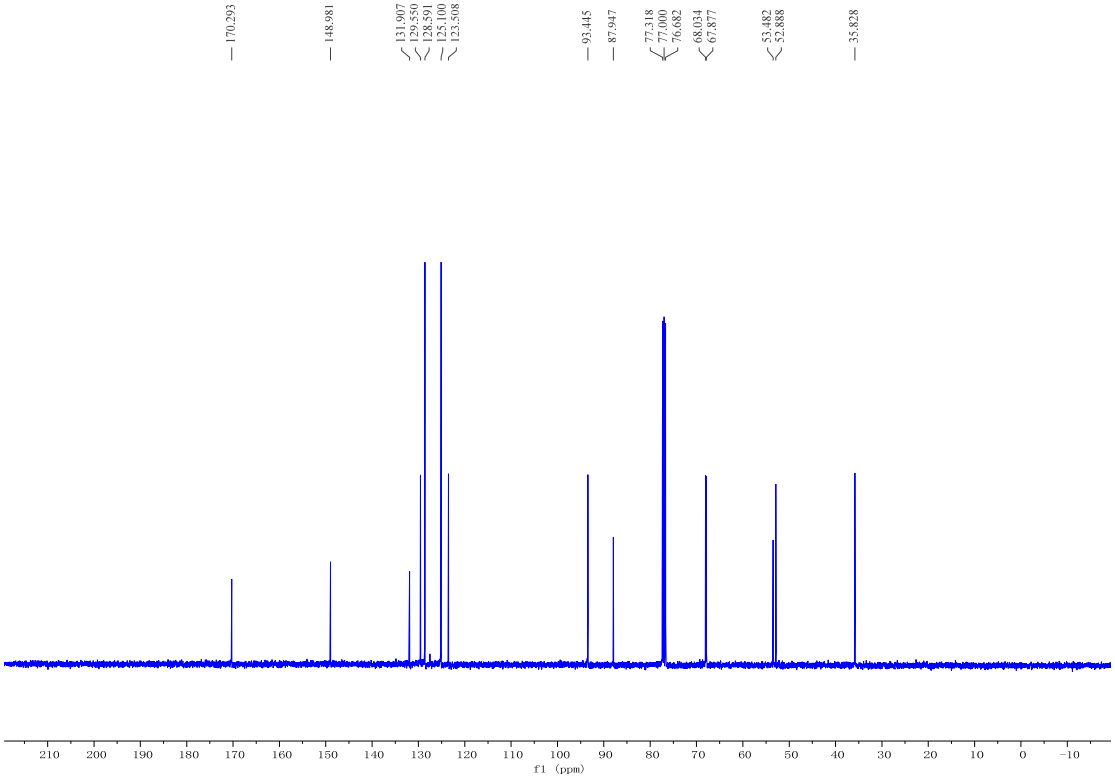


^{1}H and ^{13}C NMR Spectra for Compound 3av:

^{1}H NMR (400 MHz, $CDCl_3$)

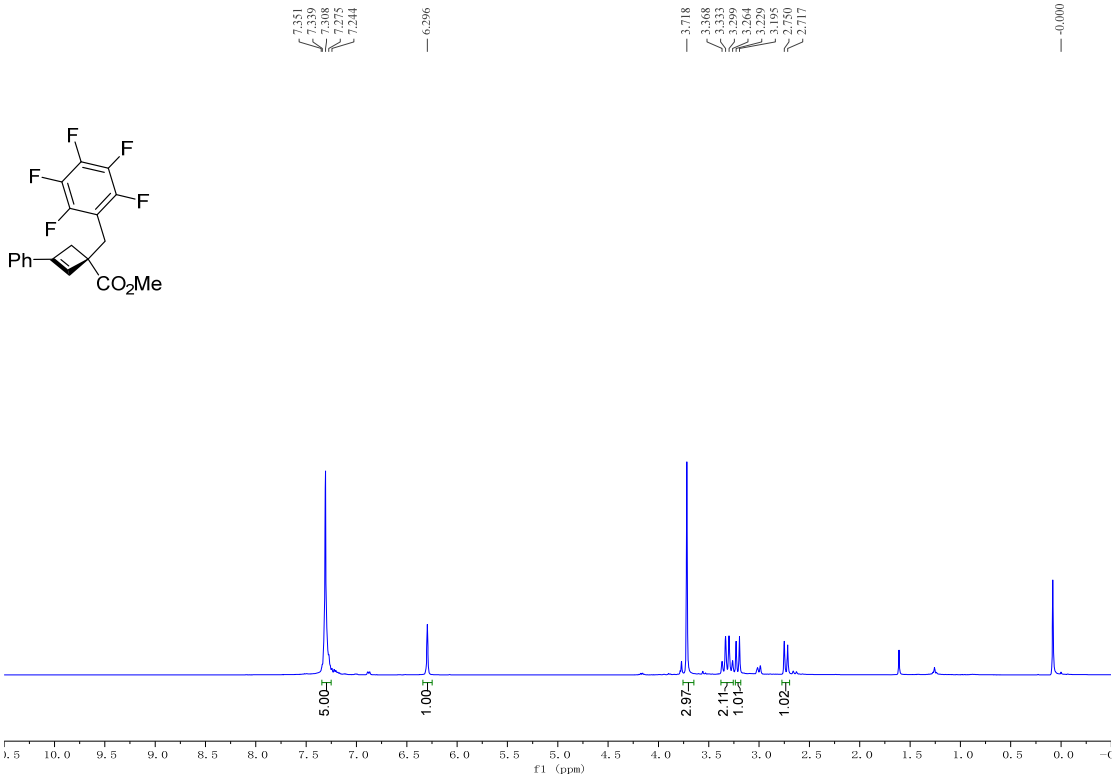


^{13}C NMR (100 MHz, $CDCl_3$)

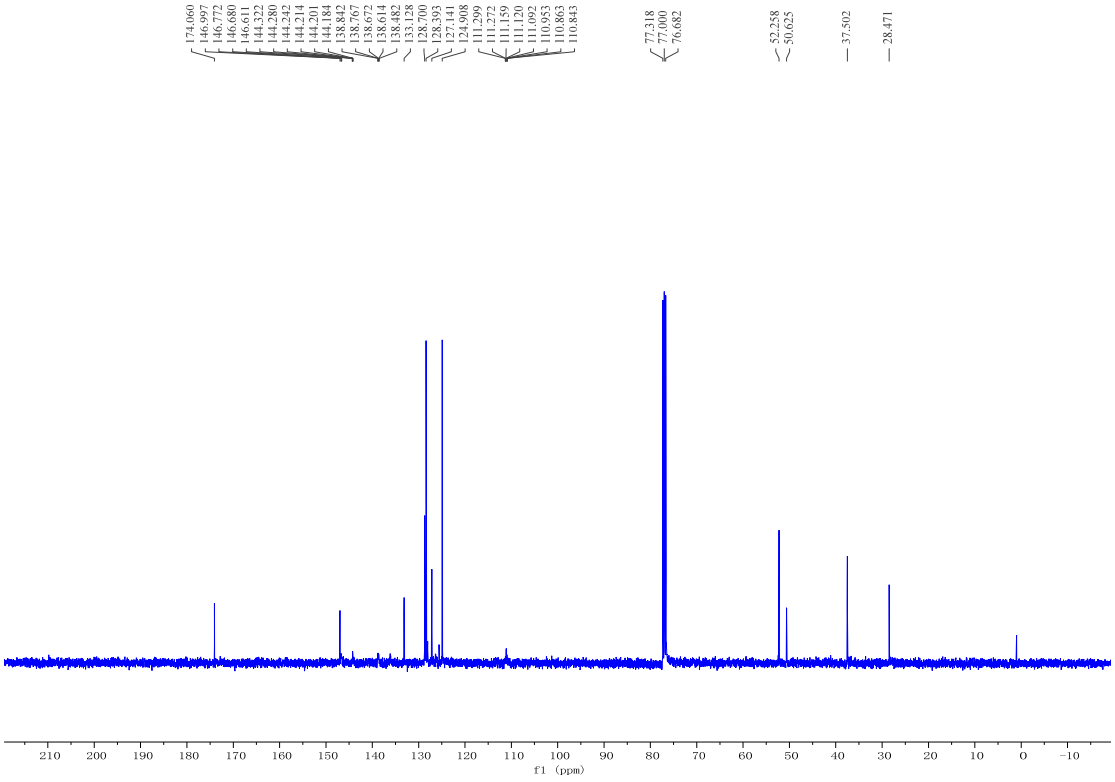


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3aw:

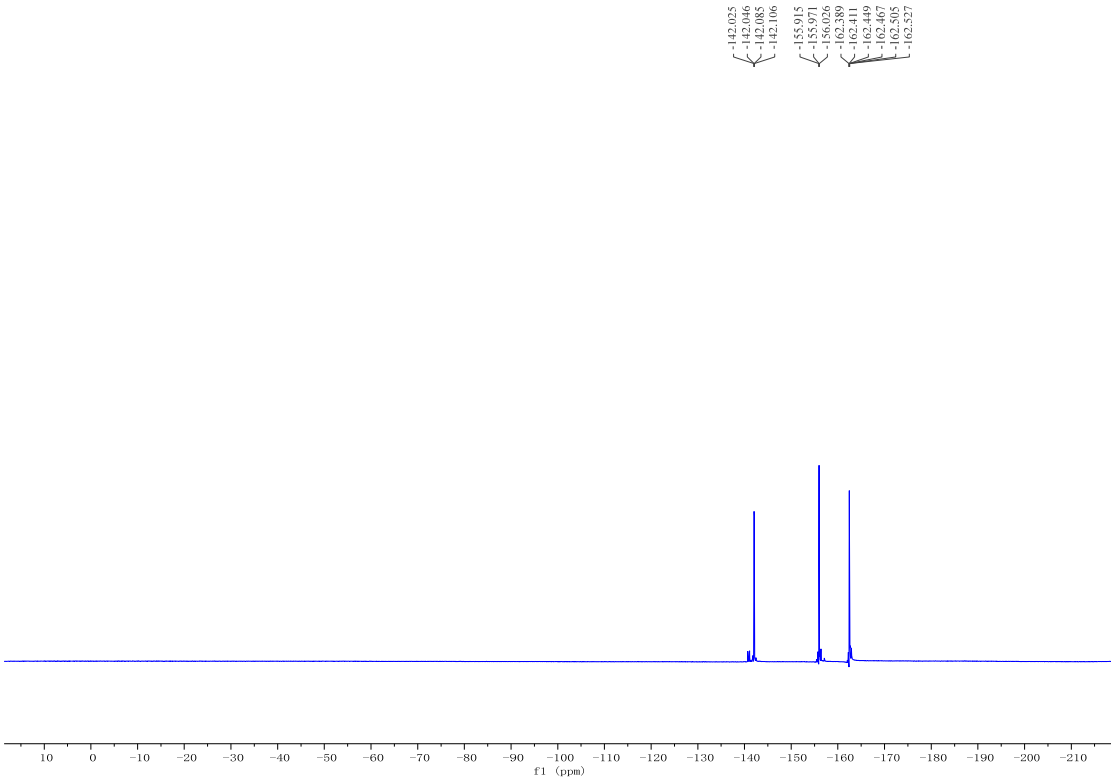
^{1}H NMR (400 MHz, $CDCl_3$)



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

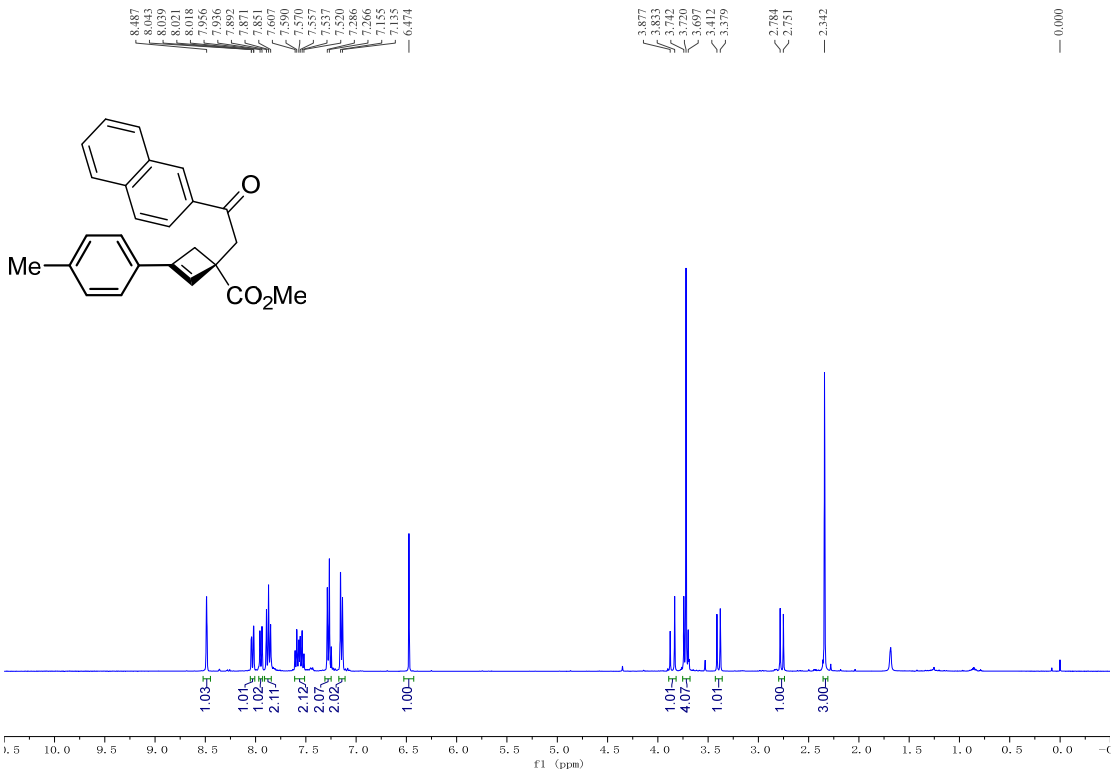


^{19}F NMR (376 MHz, $CDCl_3$)

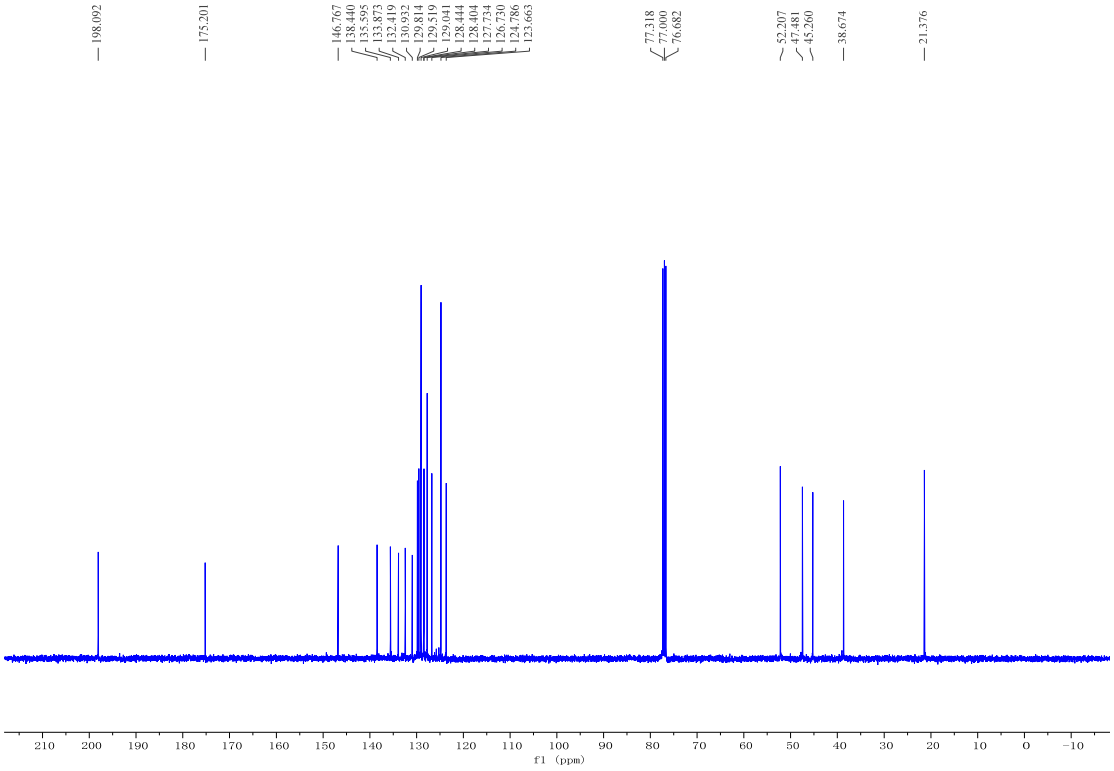


^{1}H and ^{13}C NMR Spectra for Compound 3bj:

^{1}H NMR (400 MHz, $CDCl_3$)

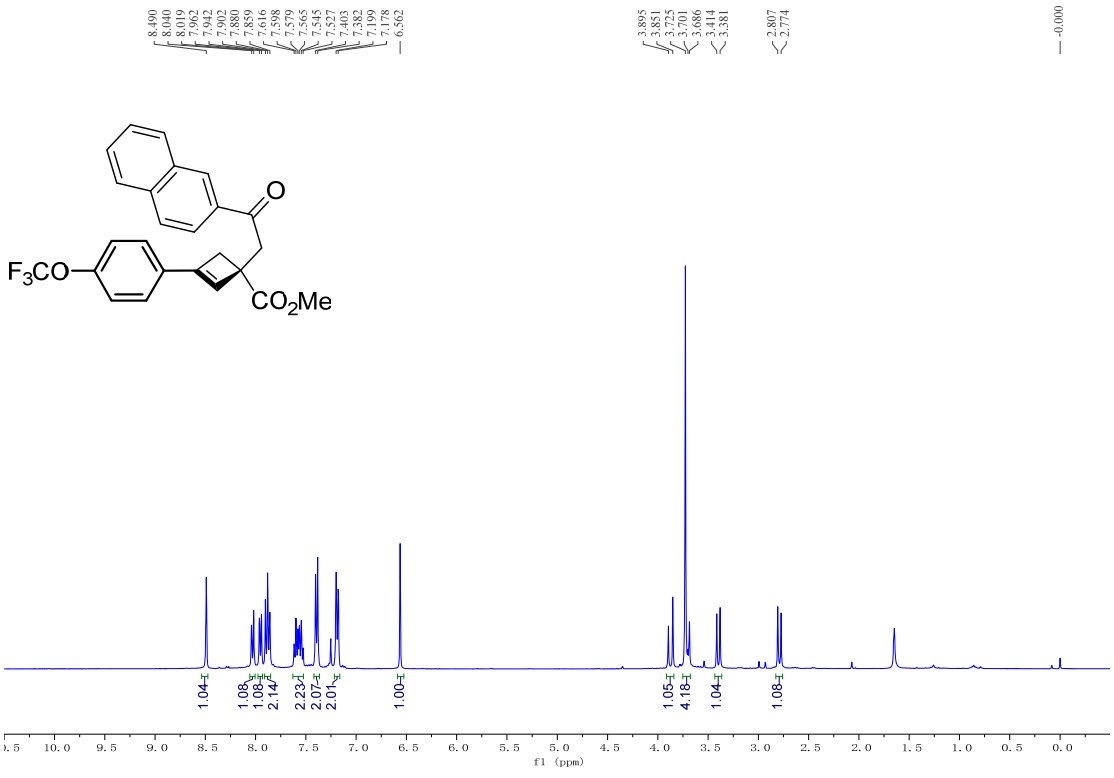


^{13}C NMR (100 MHz, $CDCl_3$)

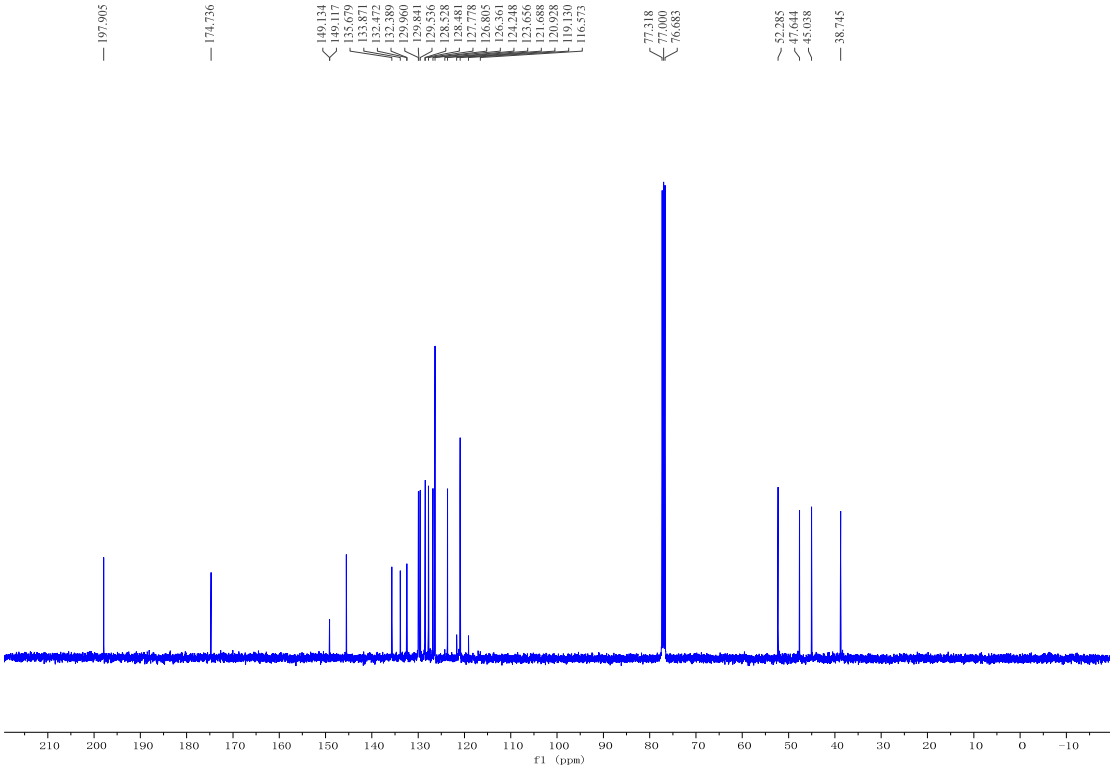


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3cj:

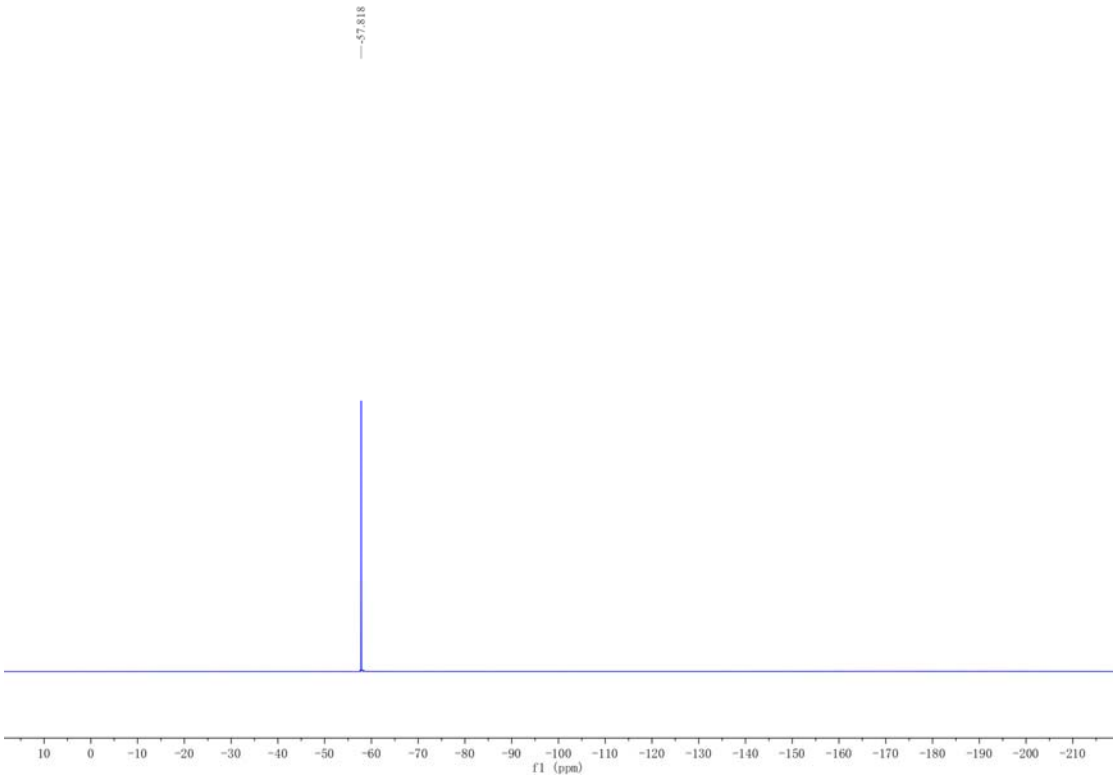
^{1}H NMR (400 MHz, $CDCl_3$)



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

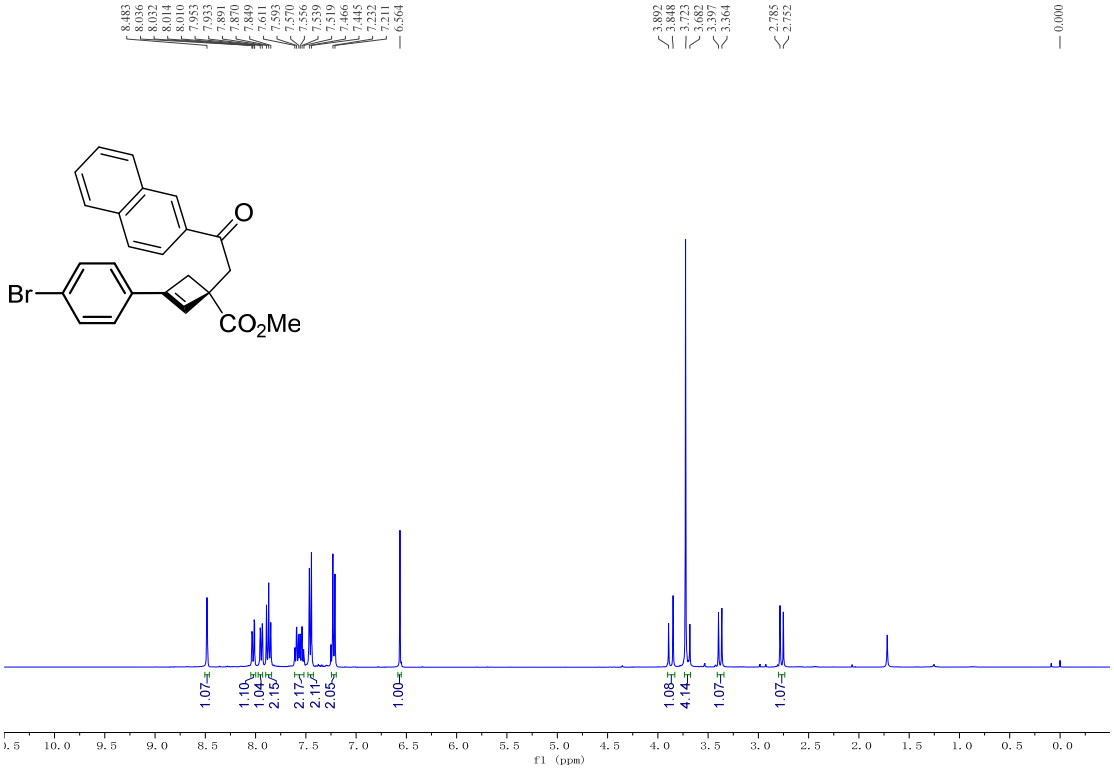


^{19} FNMR (376 MHz, $CDCl_3$)

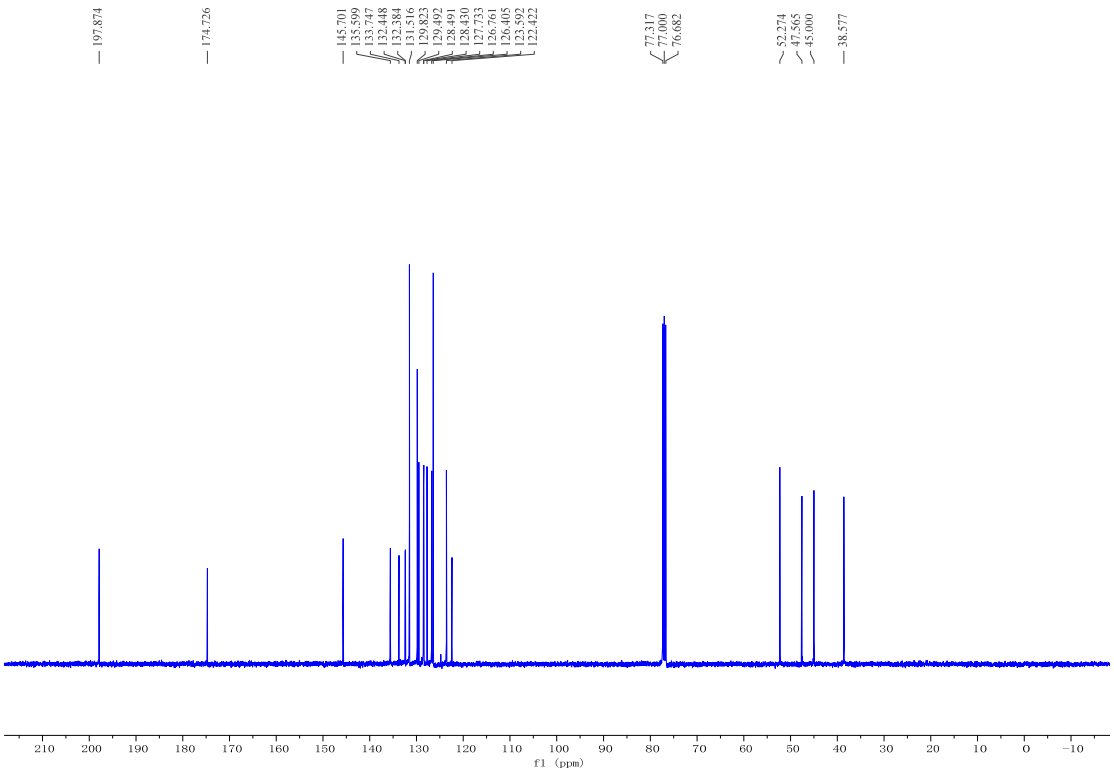


^{1}H and ^{13}C NMR Spectra for Compound 3dj:

^{1}H NMR (400 MHz, $CDCl_3$)

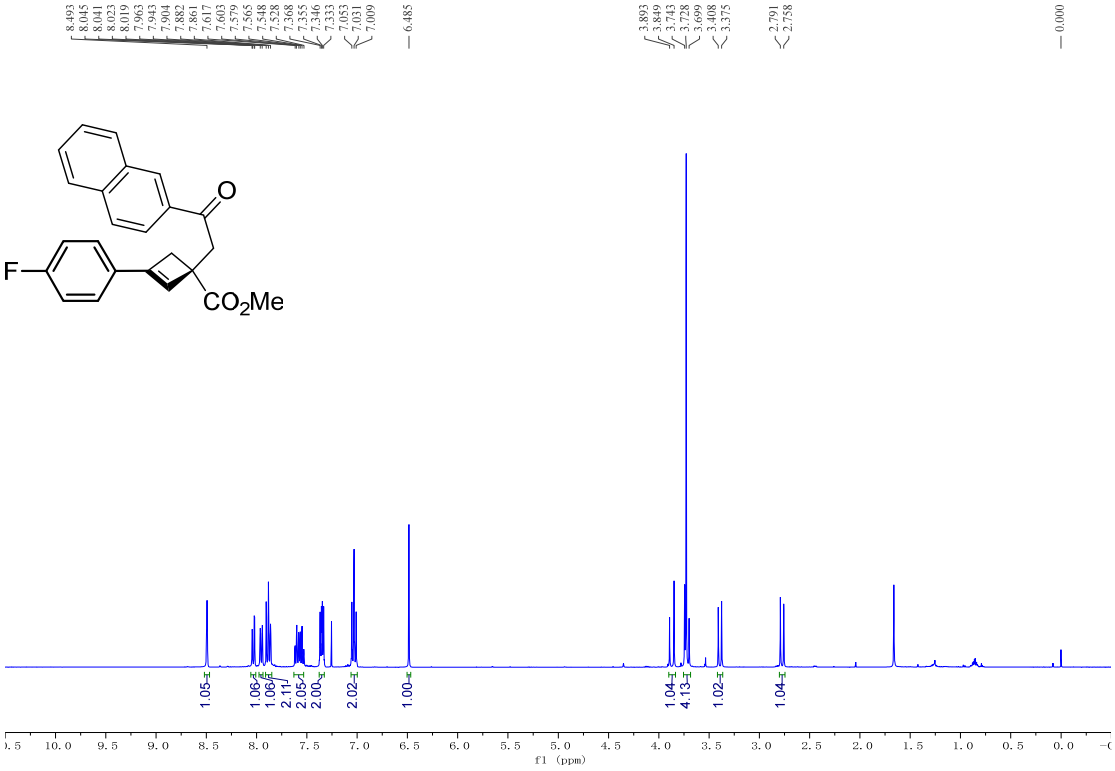


^{13}C NMR (100 MHz, $CDCl_3$)

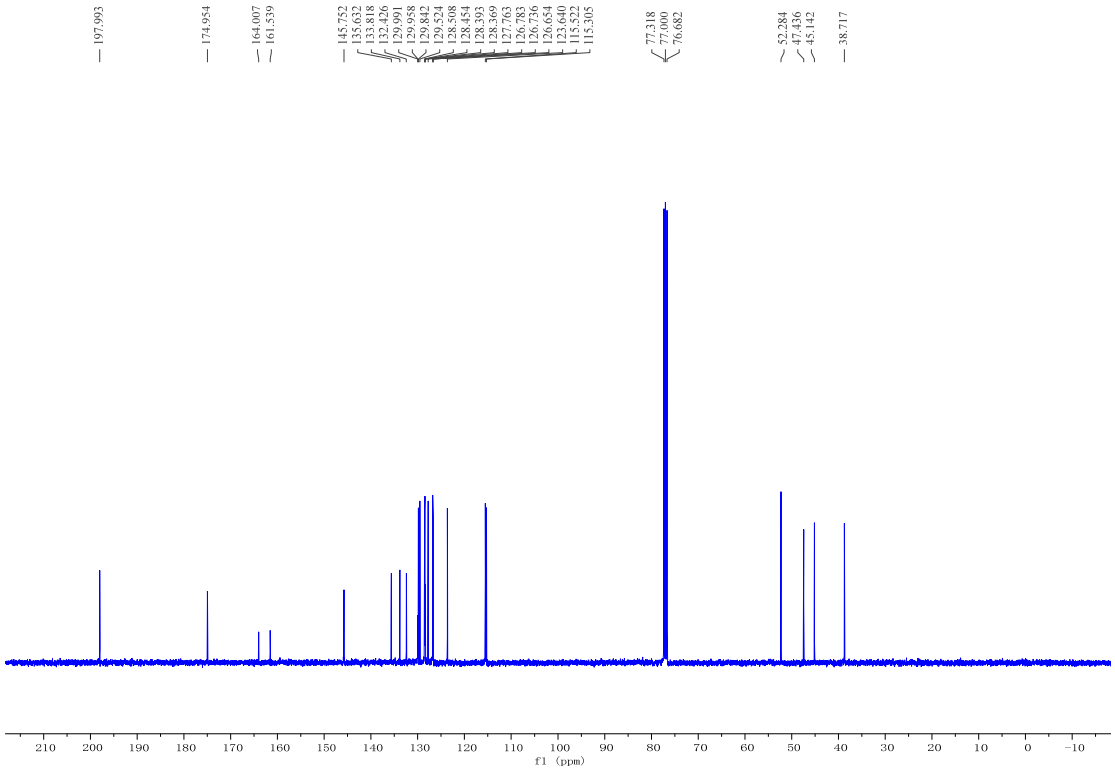


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3ej:

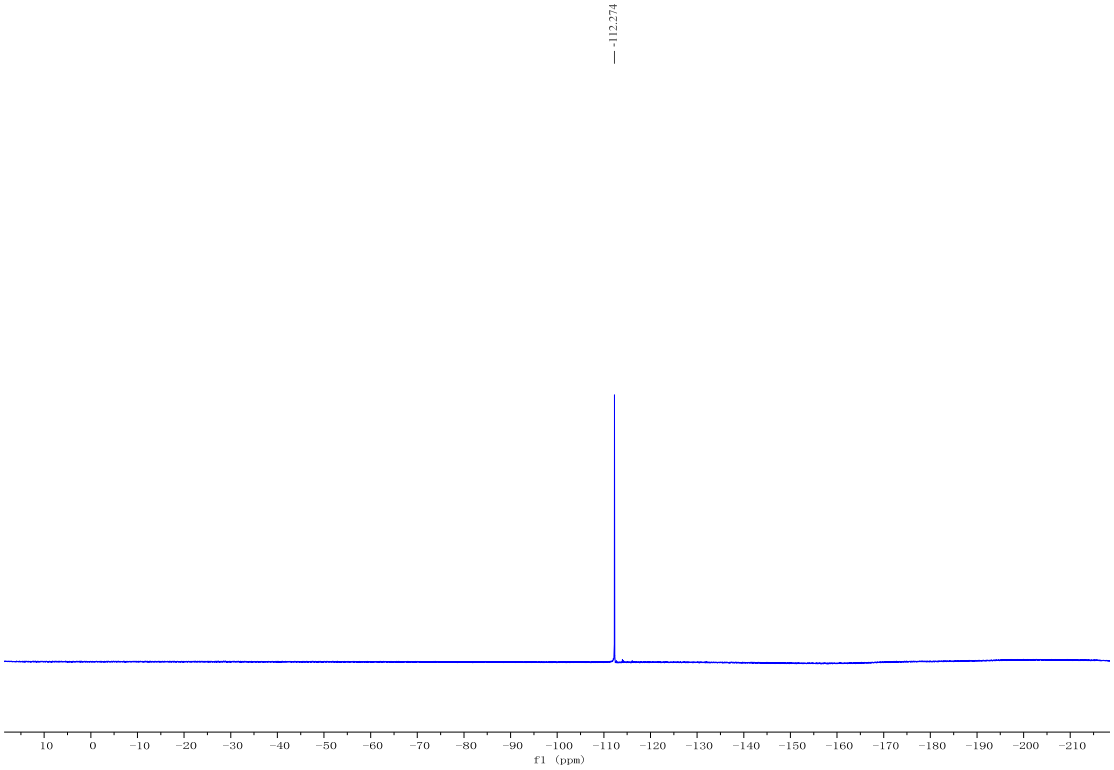
^{1}H NMR (400 MHz, $CDCl_3$)



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

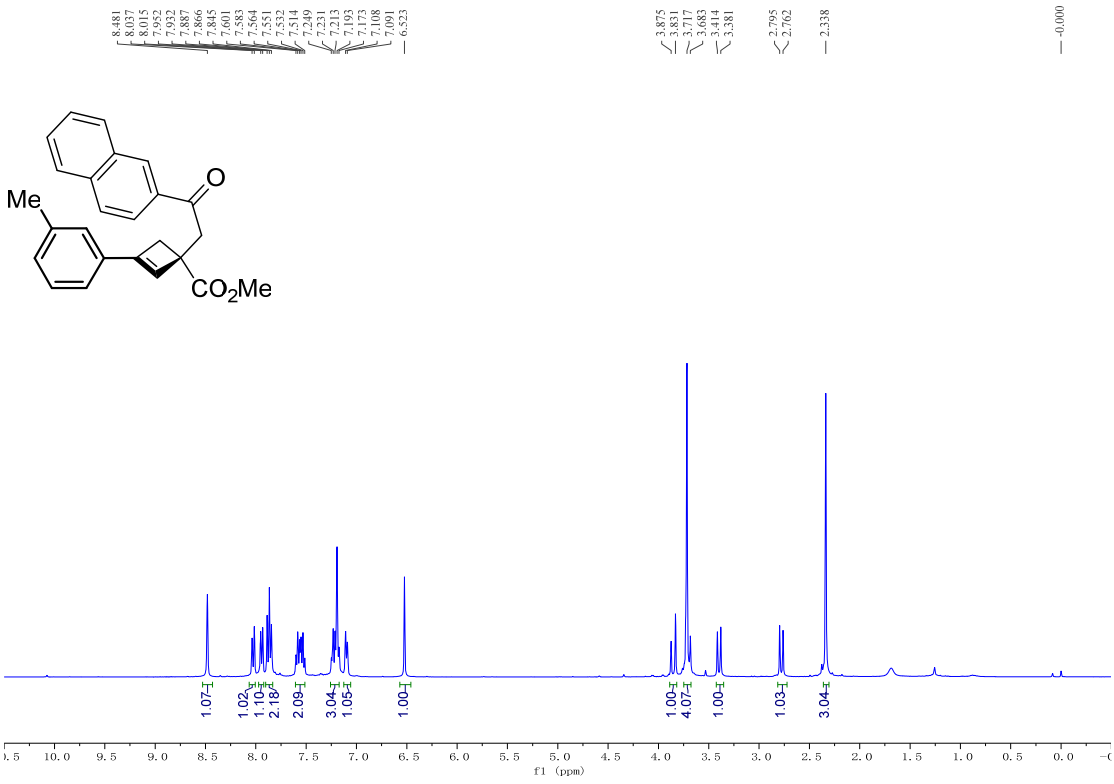


^{19} FNMR (376 MHz, $CDCl_3$)

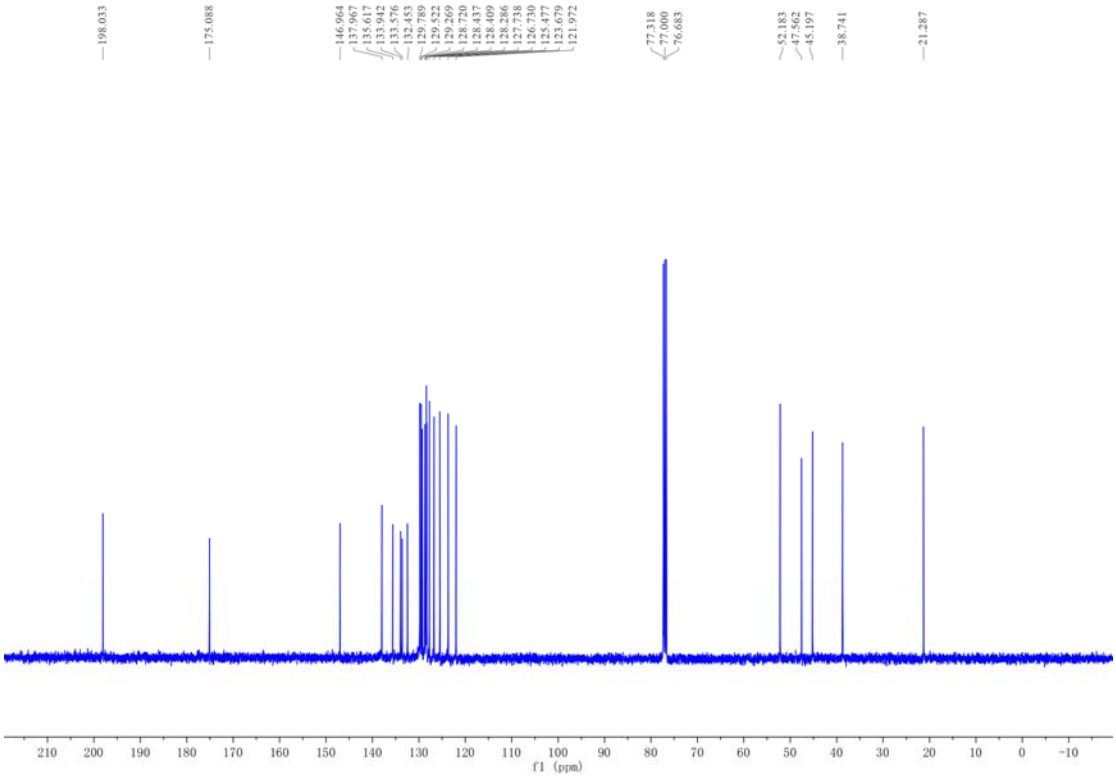


^{1}H and ^{13}C NMR Spectra for Compound 3fj:

^{1}H NMR (400 MHz, $CDCl_3$)

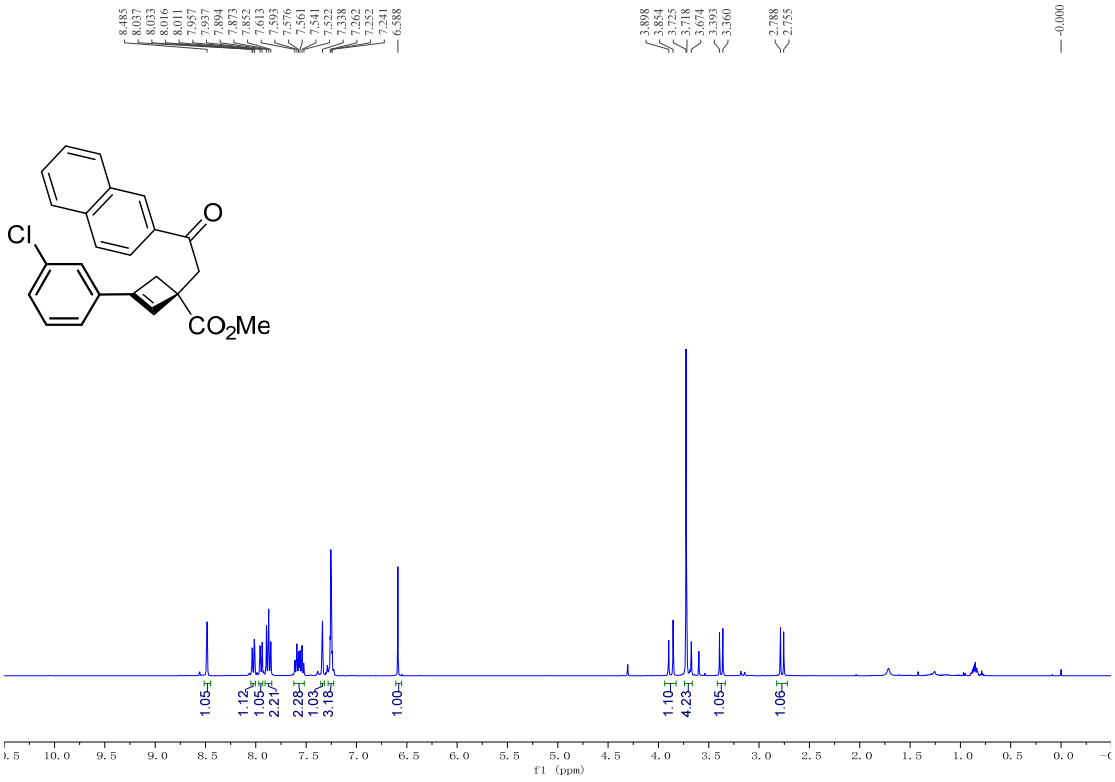


^{13}C NMR (100 MHz, $CDCl_3$)

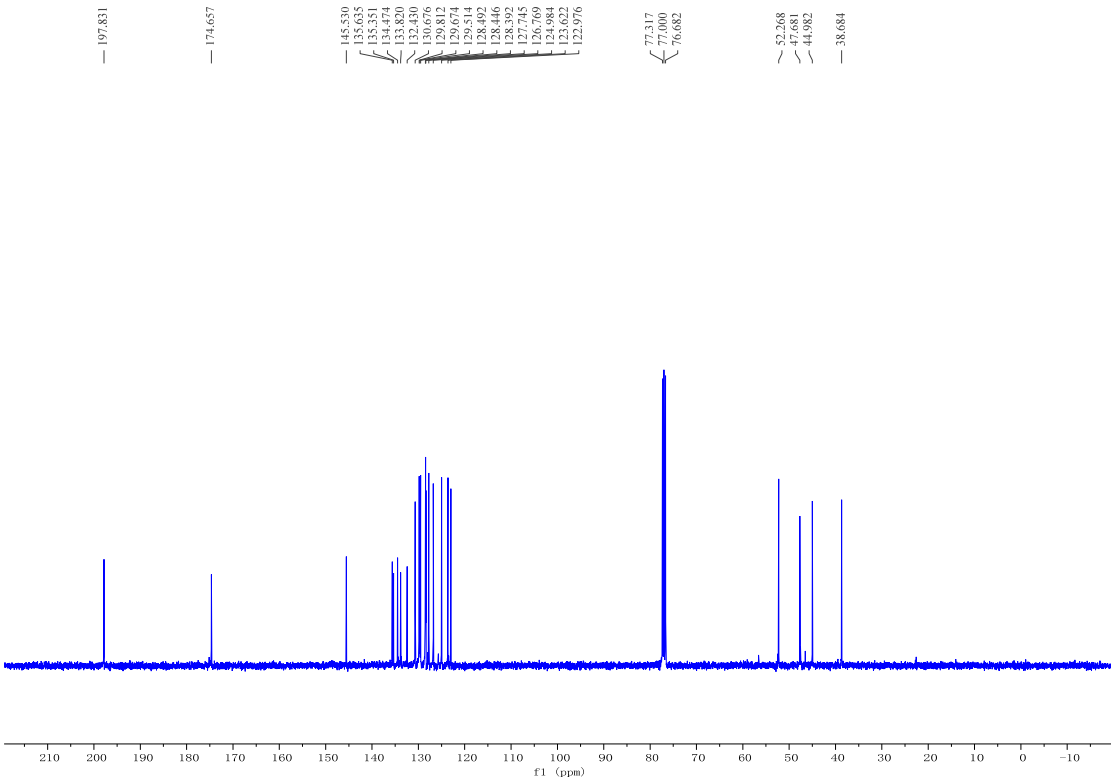


^{1}H and ^{13}C NMR Spectra for Compound 3gj:

^{1}H NMR (400 MHz, $CDCl_3$)

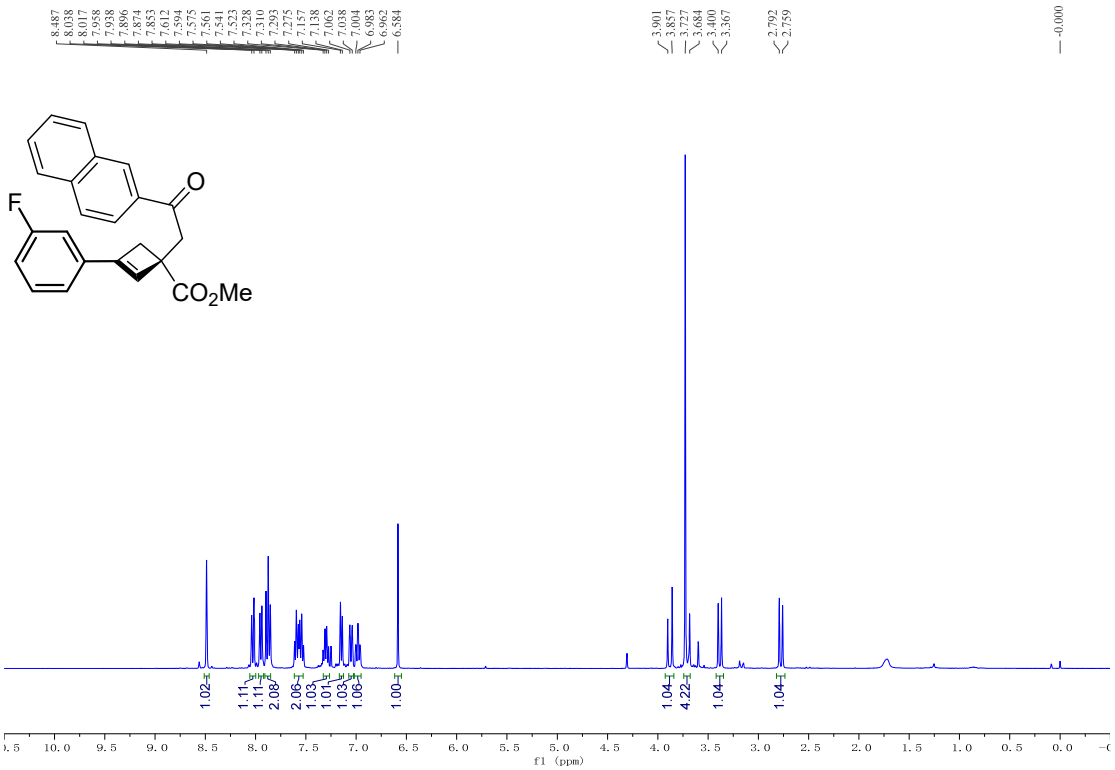


^{13}C NMR (100 MHz, $CDCl_3$)

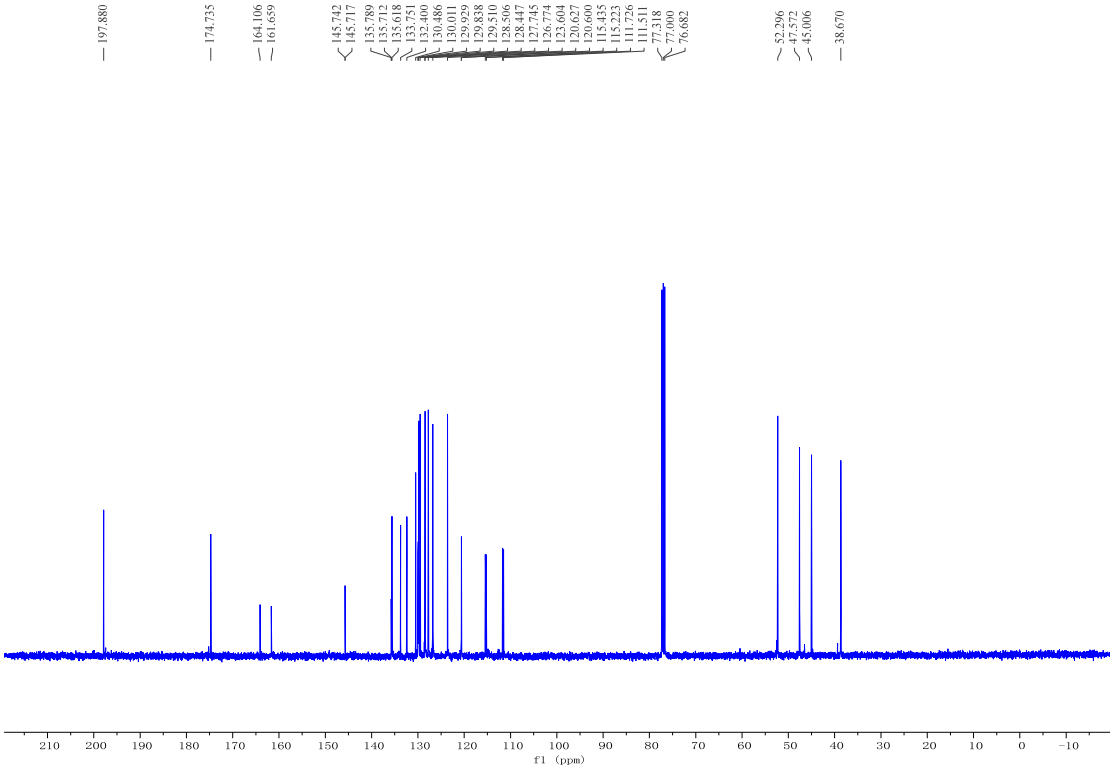


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3hj:

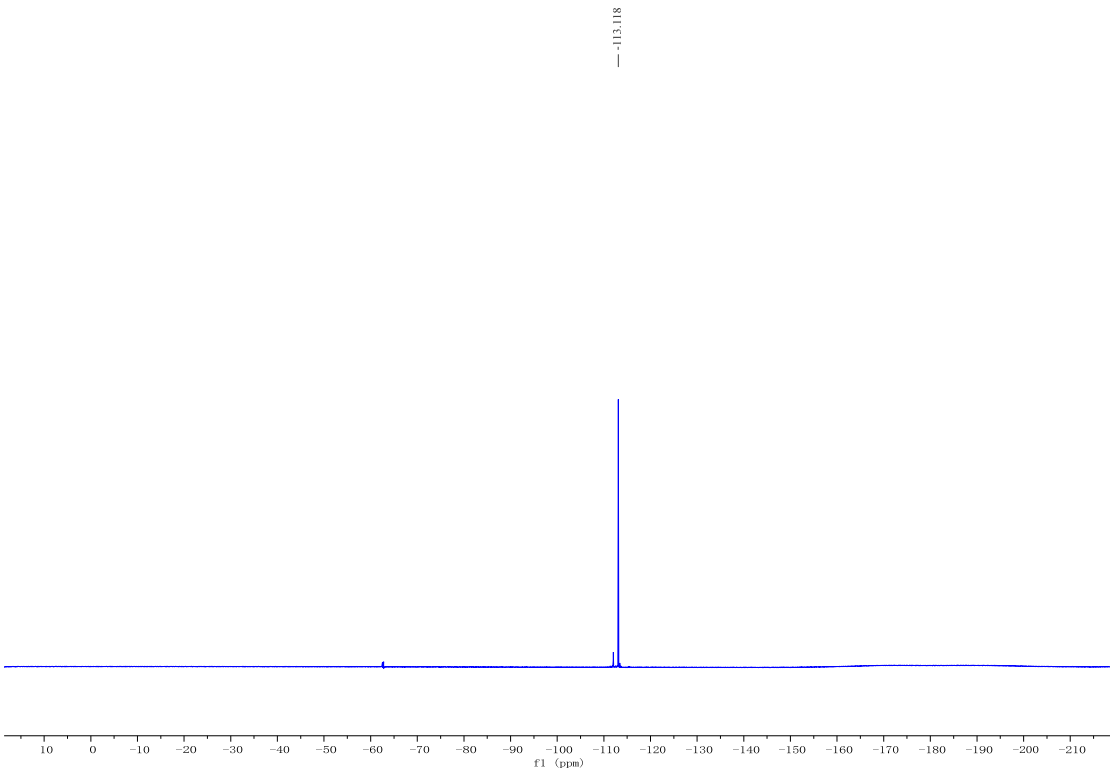
^{1}H NMR (400 MHz, $CDCl_3$)



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

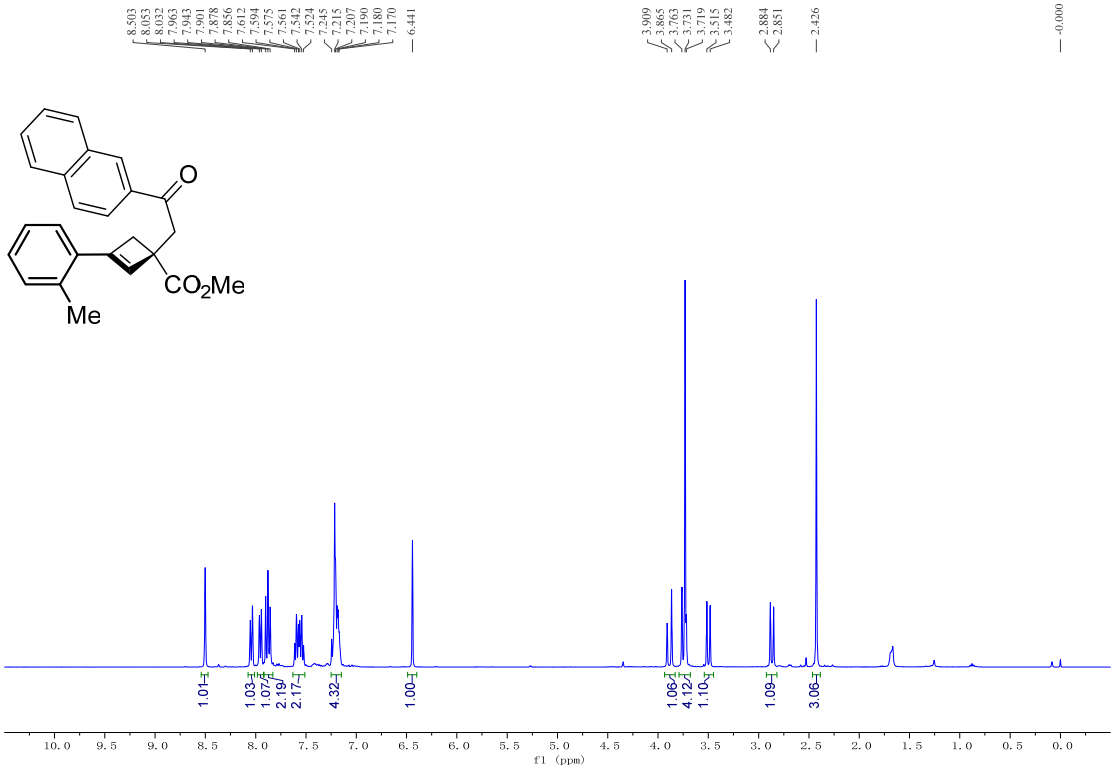


^{19}FNMR (376 MHz, $CDCl_3$)

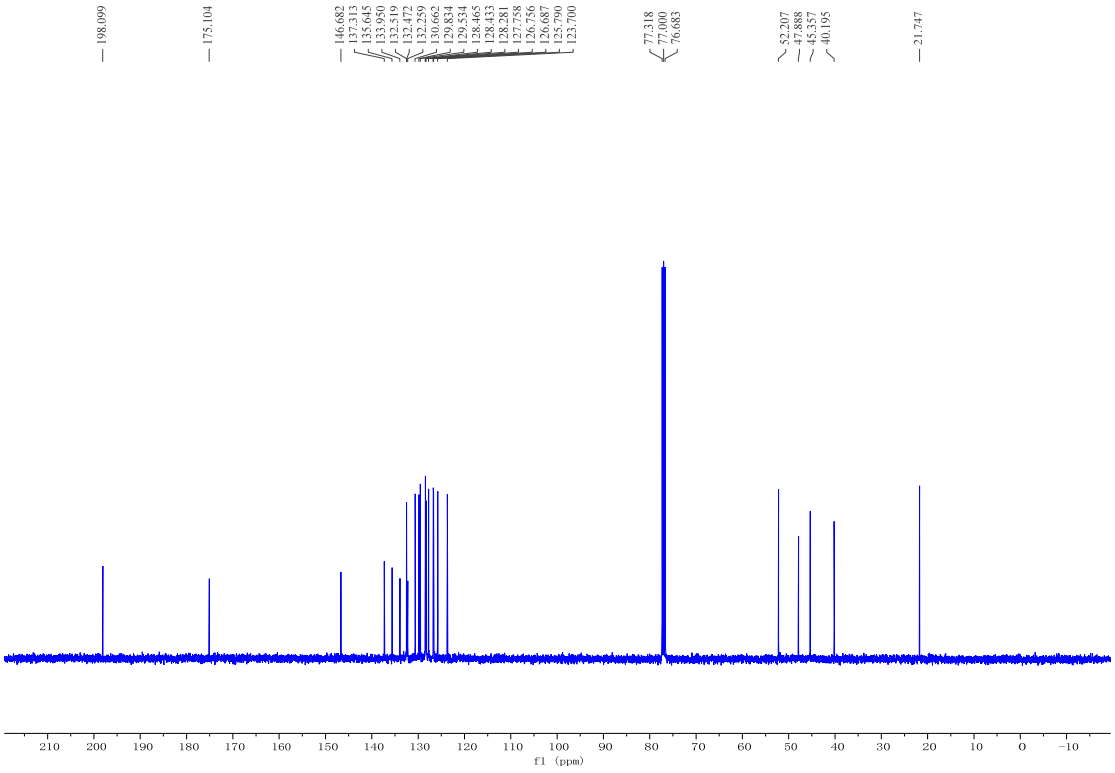


^{1}H and ^{13}C NMR Spectra for Compound 3ij:

^{1}H NMR (400 MHz, $CDCl_3$)

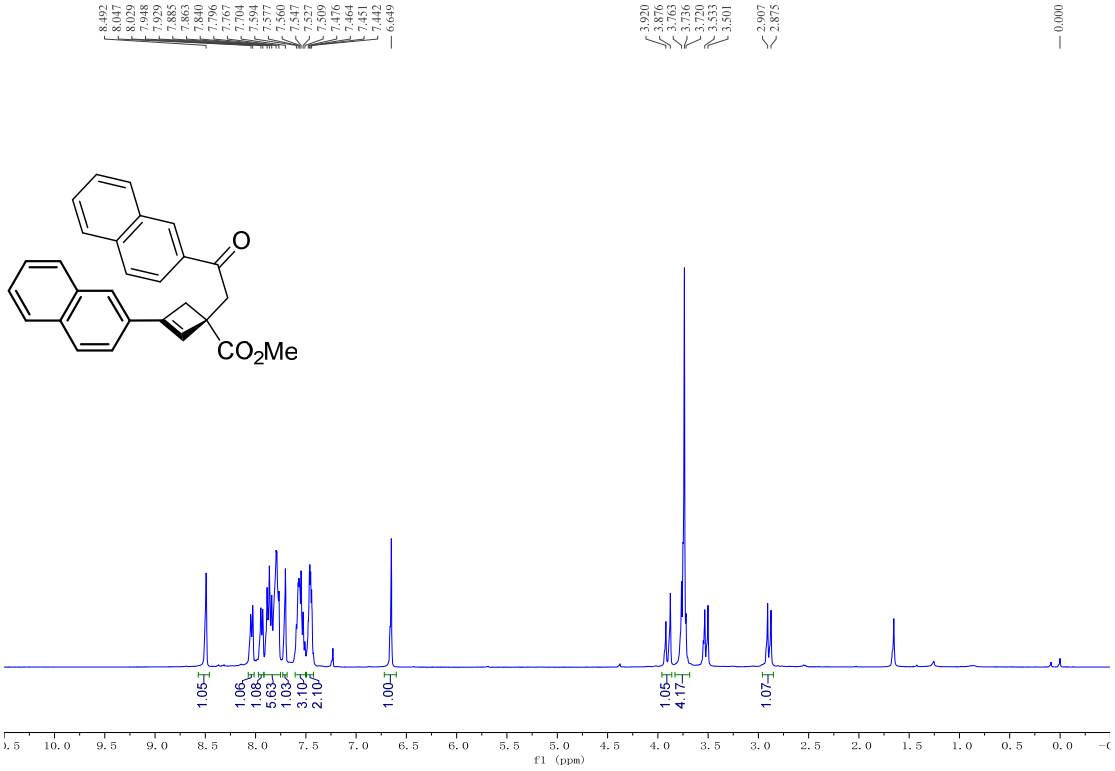


^{13}C NMR (100 MHz, $CDCl_3$)

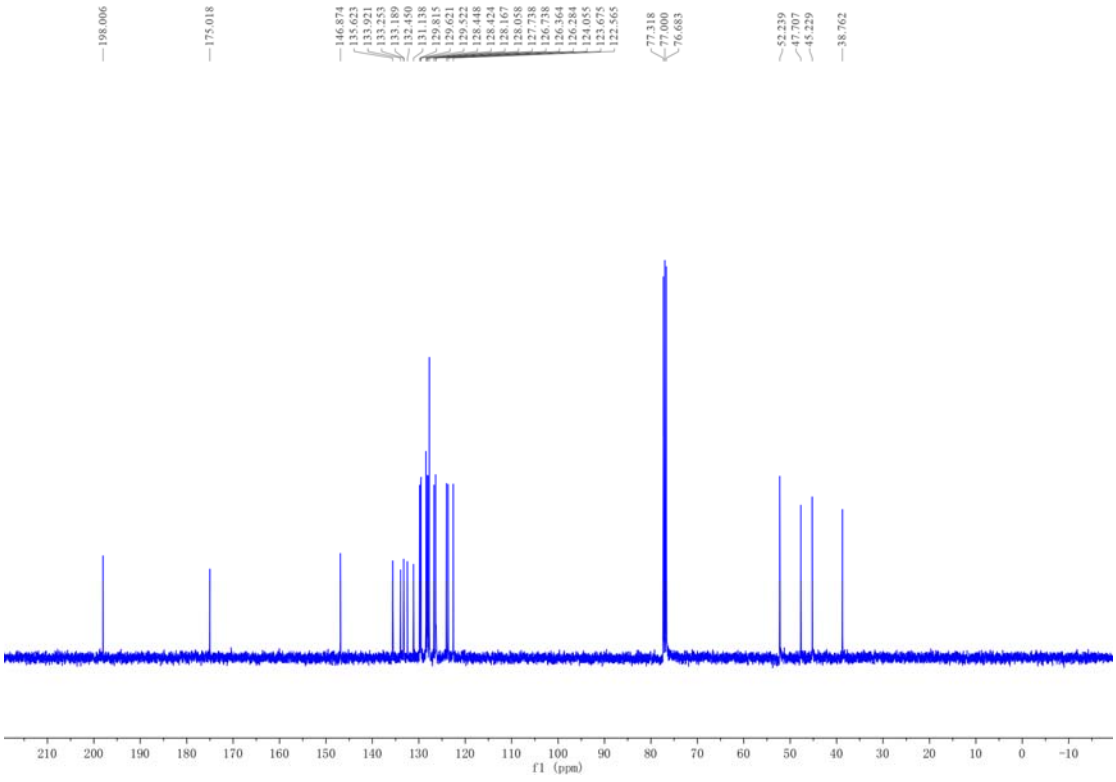


^{1}H and ^{13}C NMR Spectra for Compound 3jj:

^{1}H NMR (400 MHz, $CDCl_3$)

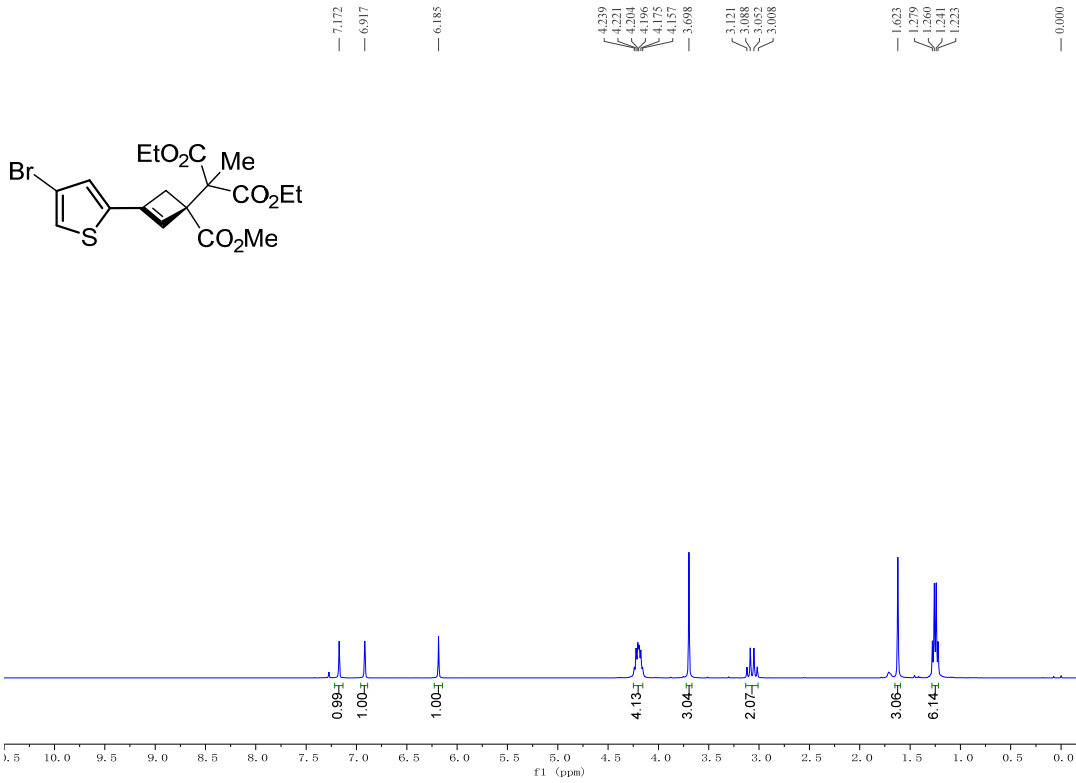


^{13}C NMR (100 MHz, $CDCl_3$)

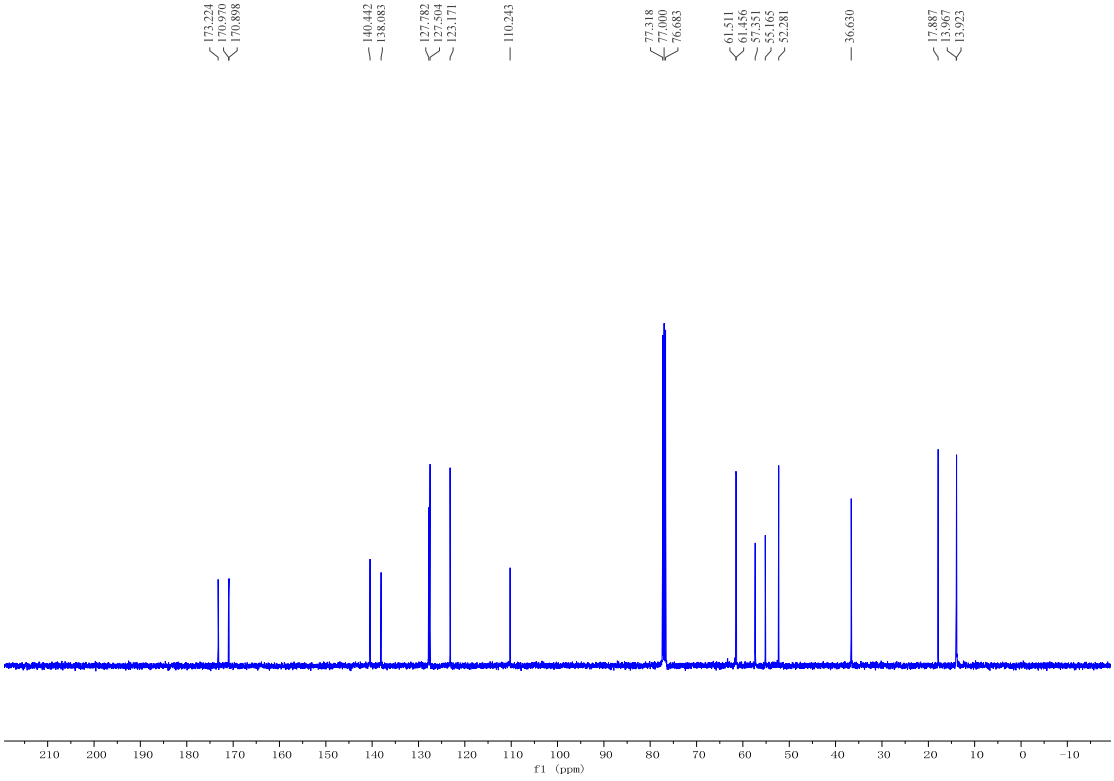


^{1}H and ^{13}C NMR Spectra for Compound 3ks:

^{1}H NMR (400 MHz, $CDCl_3$)

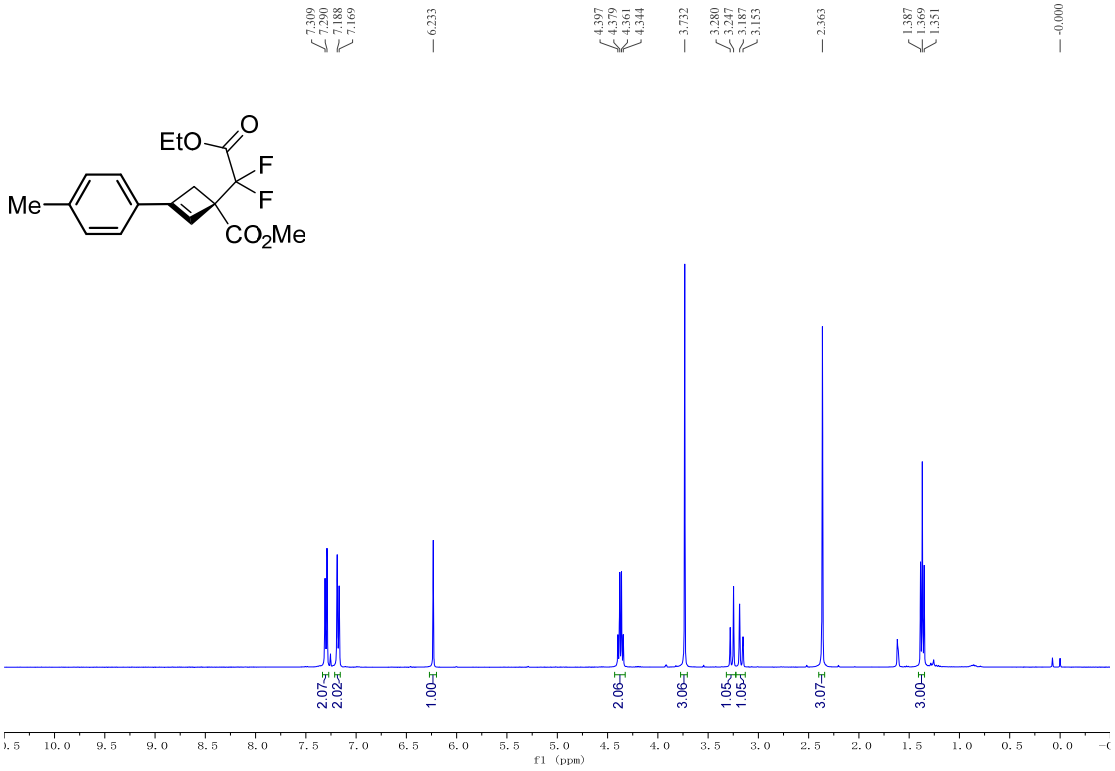


^{13}C NMR (100 MHz, $CDCl_3$)

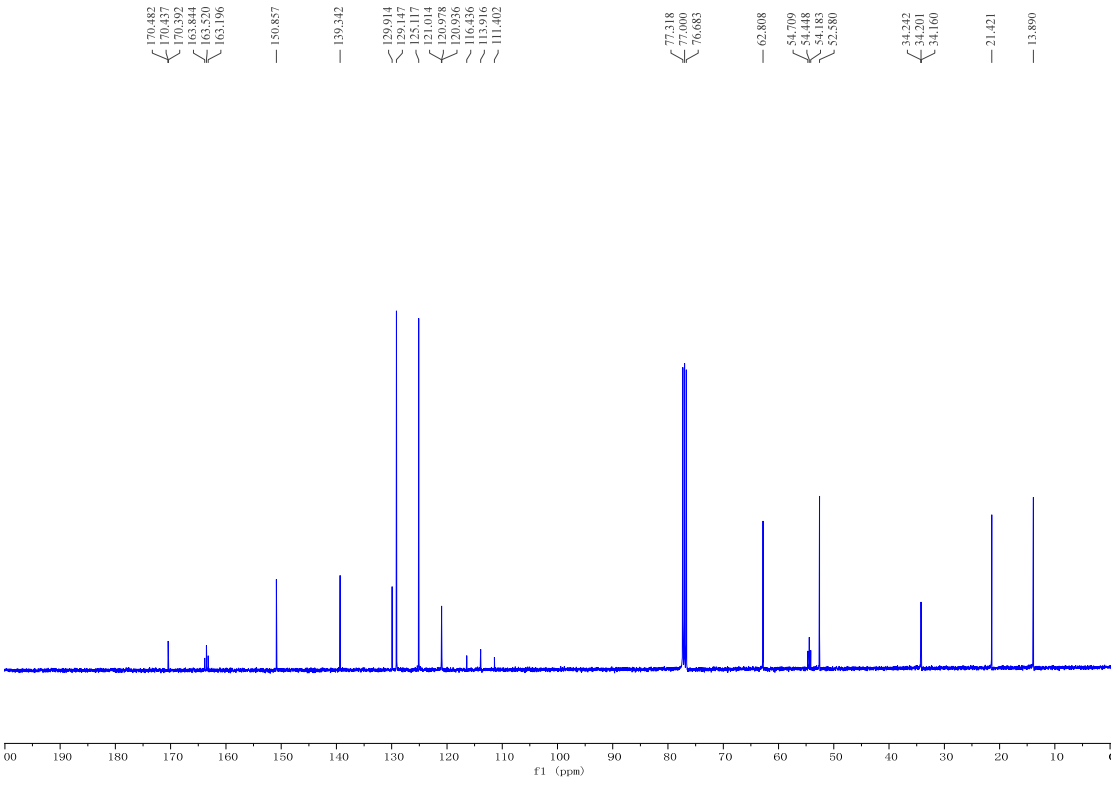


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3bu:

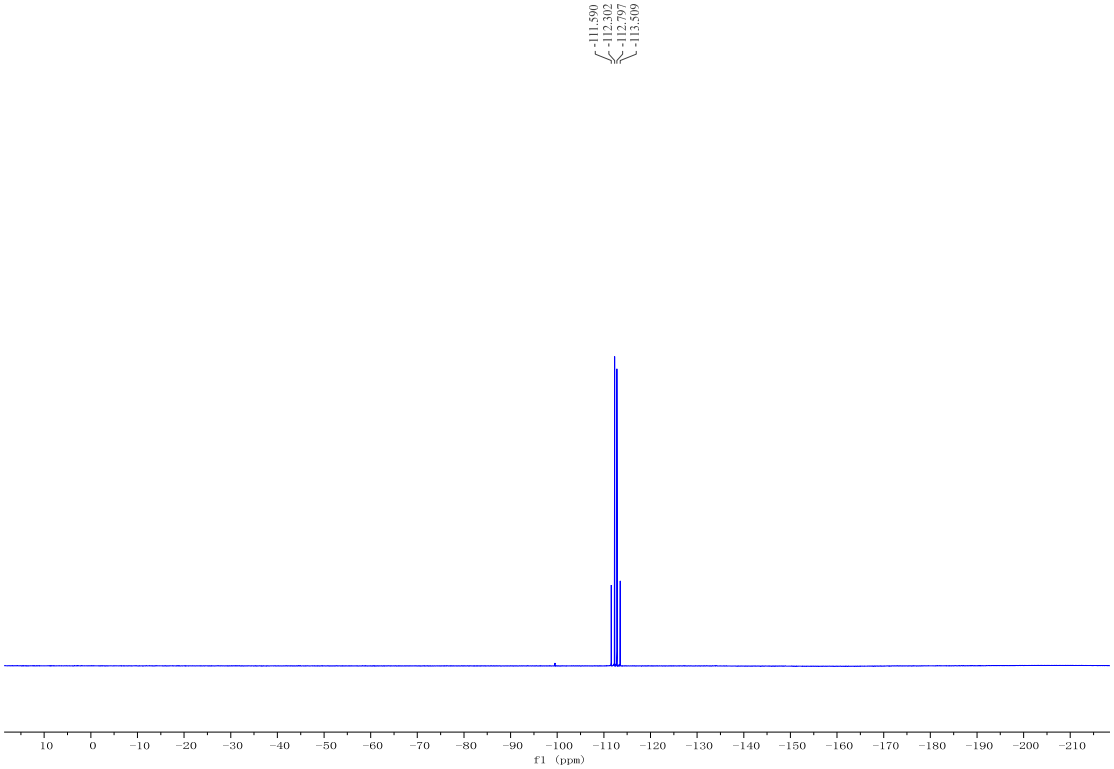
^{1}H NMR (400 MHz, $CDCl_3$)



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

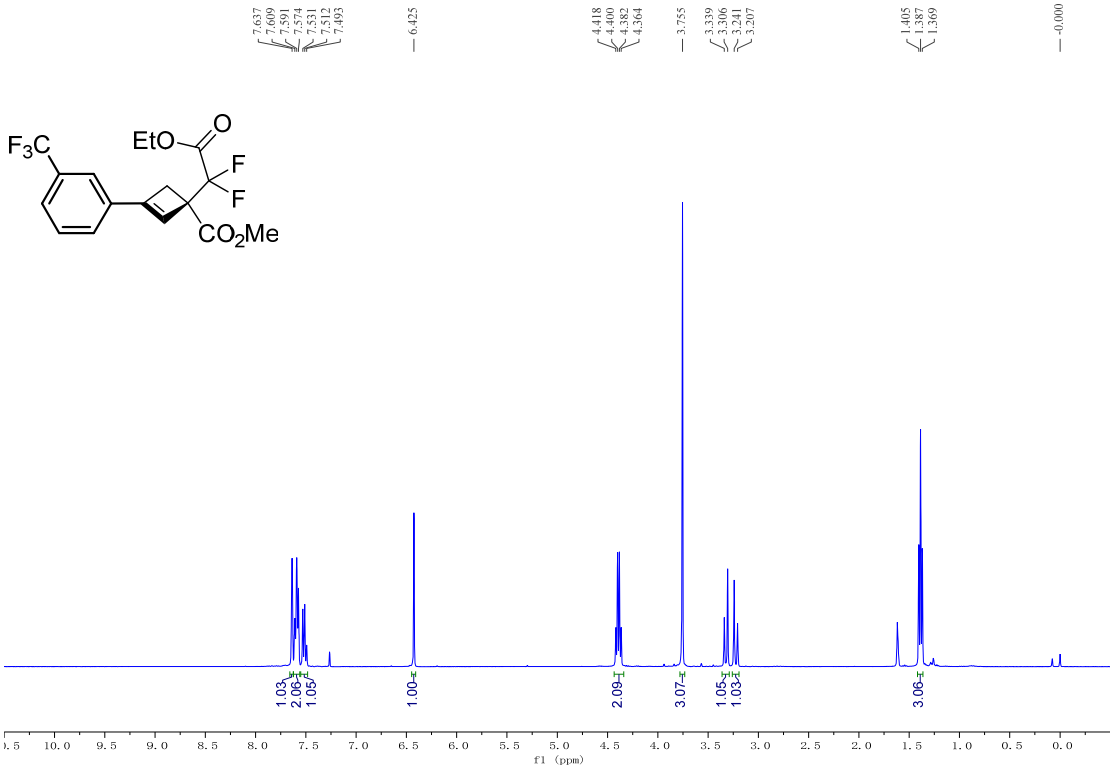


^{19} FNMR (376 MHz, $CDCl_3$)

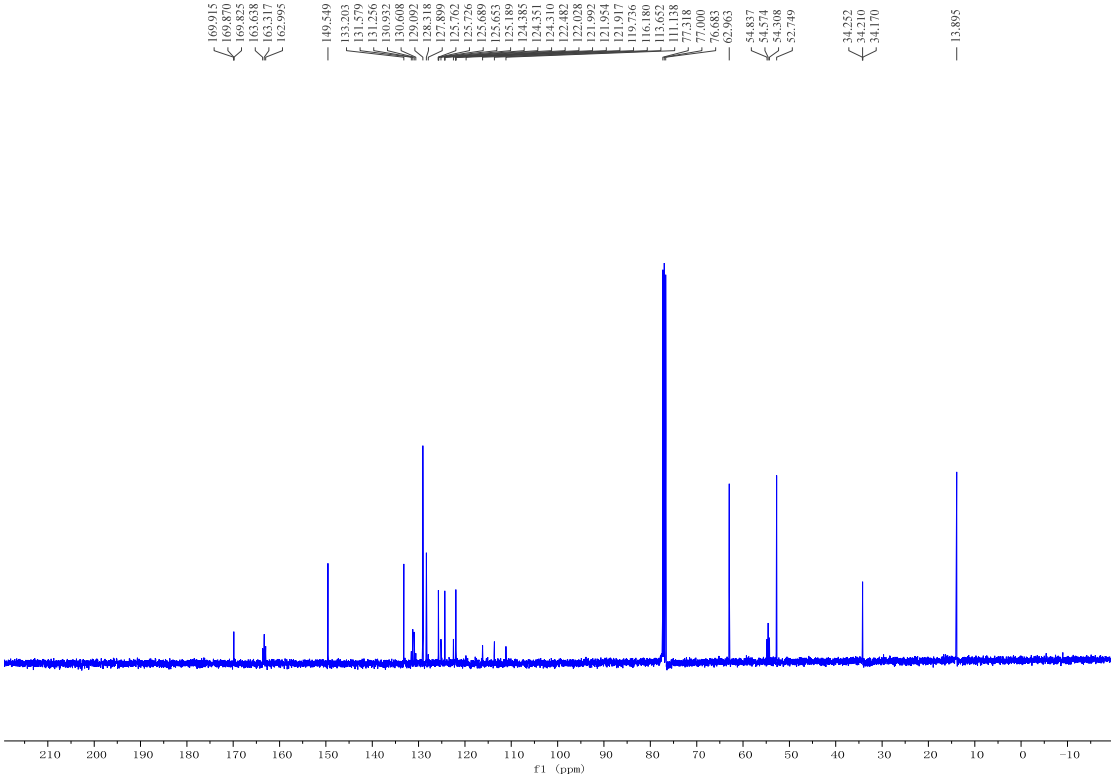


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3lu:

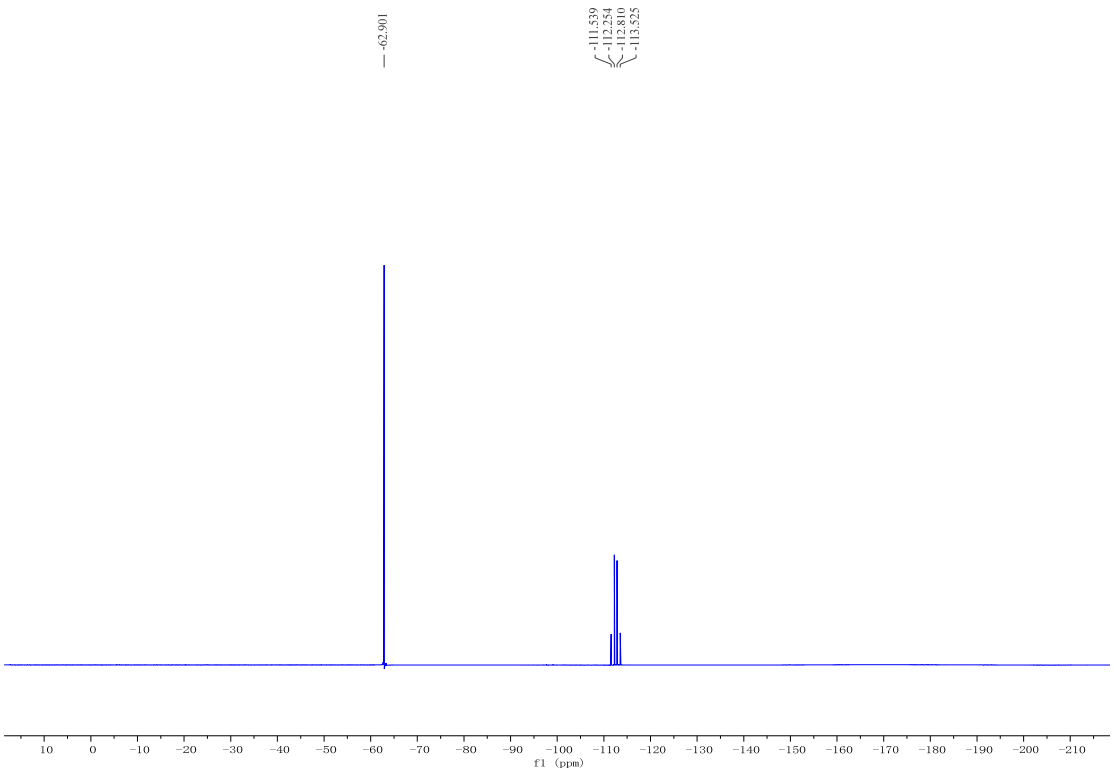
^{1}H NMR (400 MHz, $CDCl_3$)



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

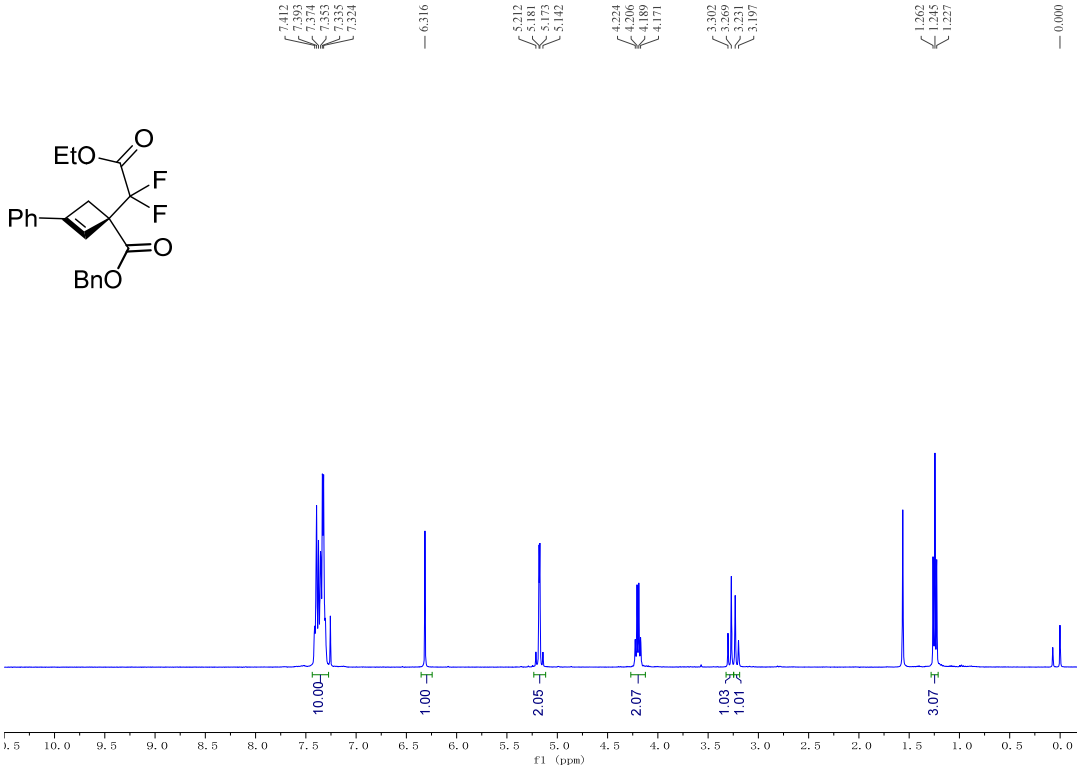


^{19}FNMR (376 MHz, $CDCl_3$)

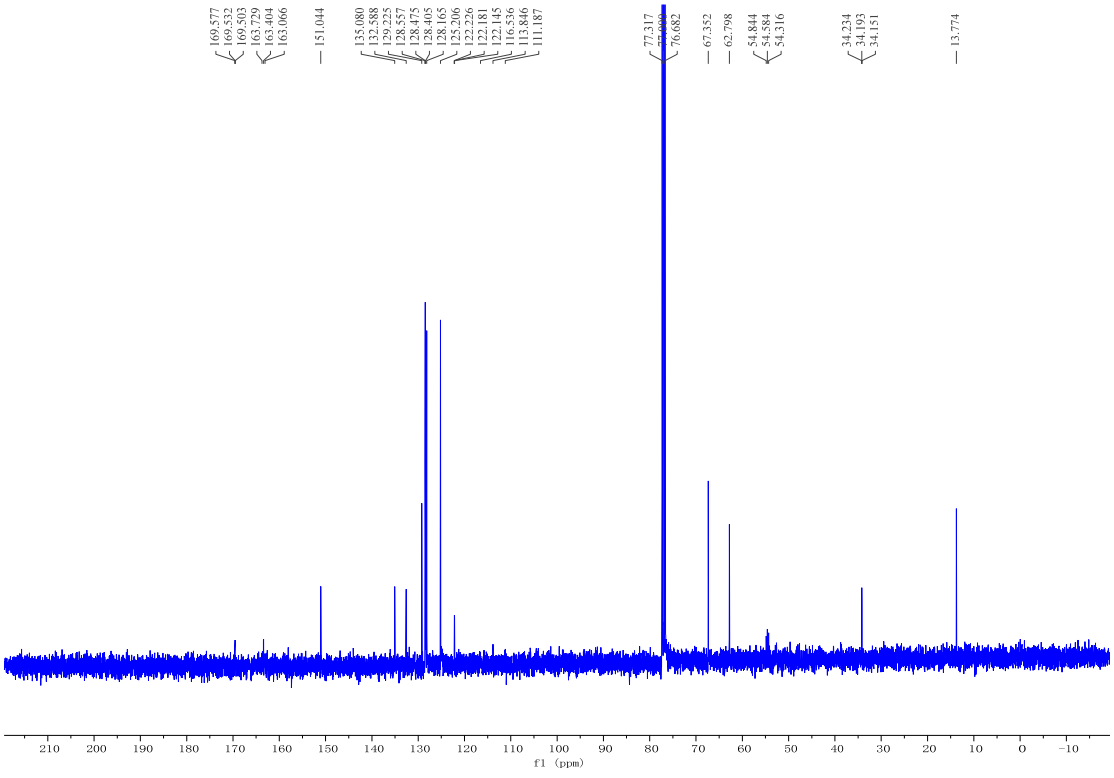


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3mu:

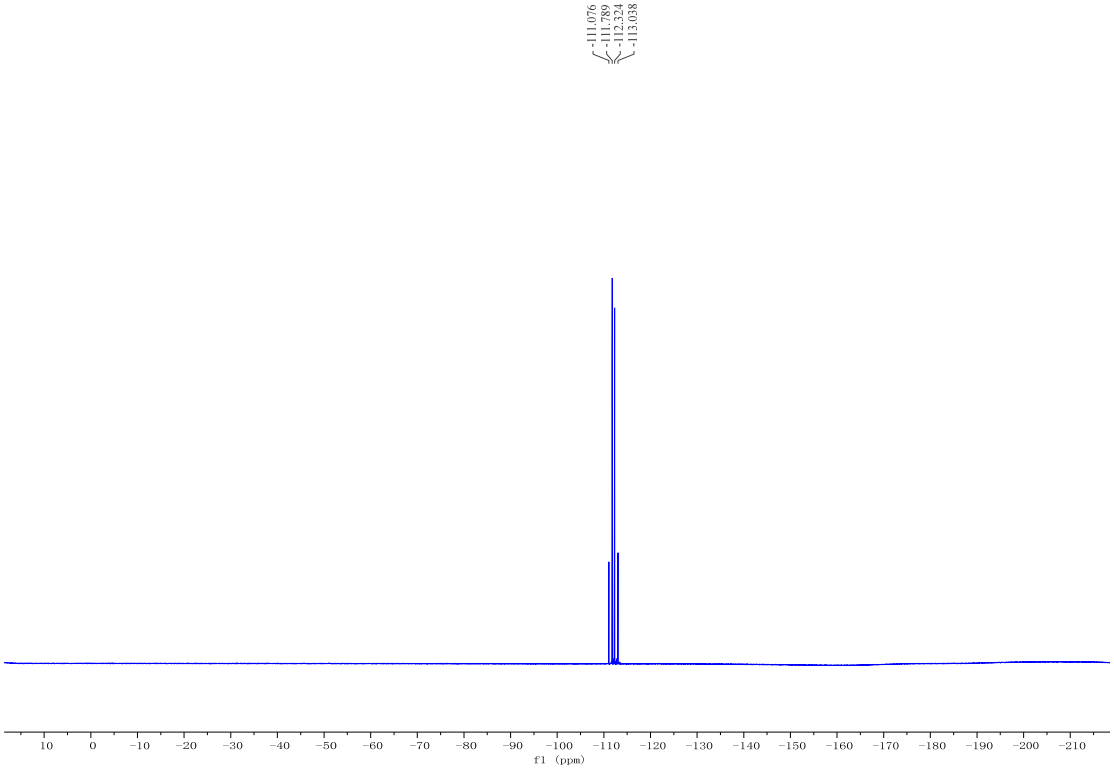
^{1}H NMR (400 MHz, $CDCl_3$)



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

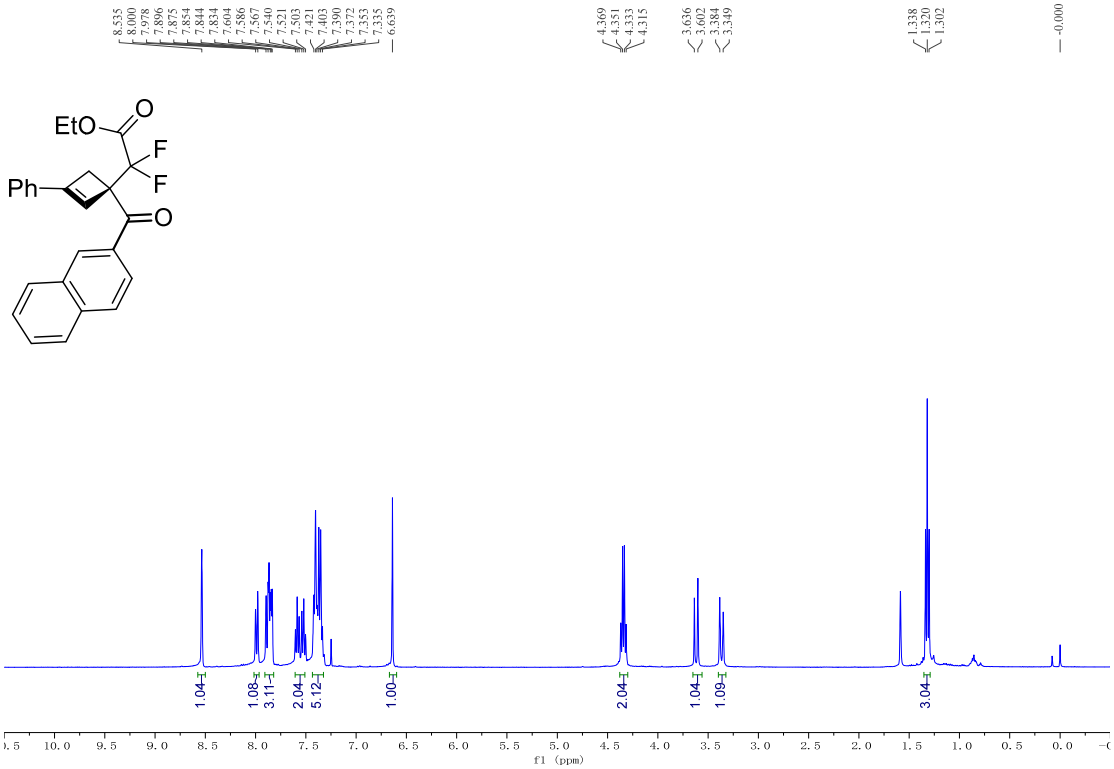


^{19}FNMR (376 MHz, $CDCl_3$)

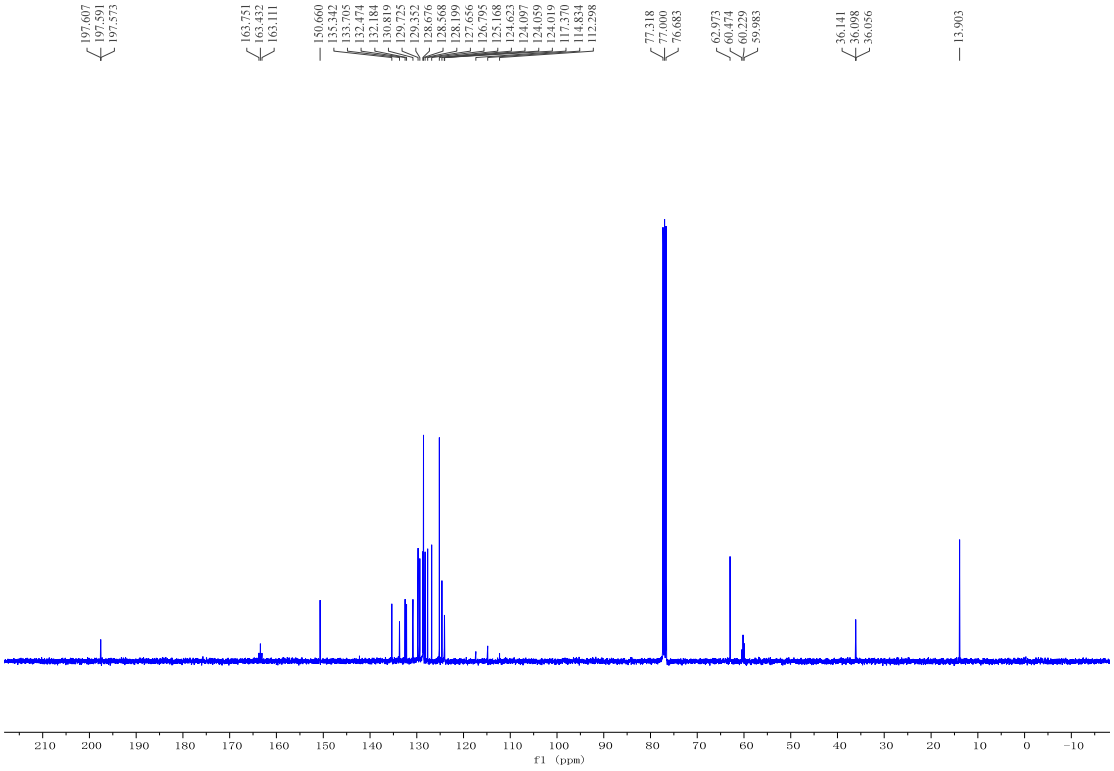


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3nu:

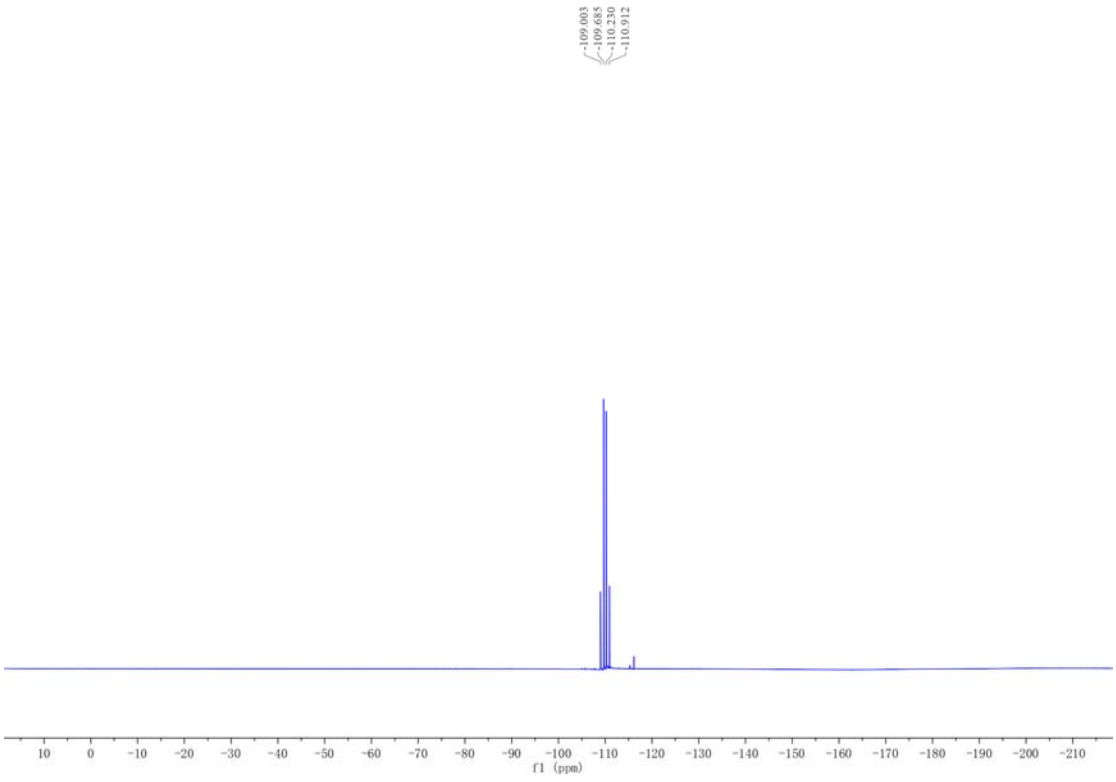
^{1}H NMR (400 MHz, $CDCl_3$)



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

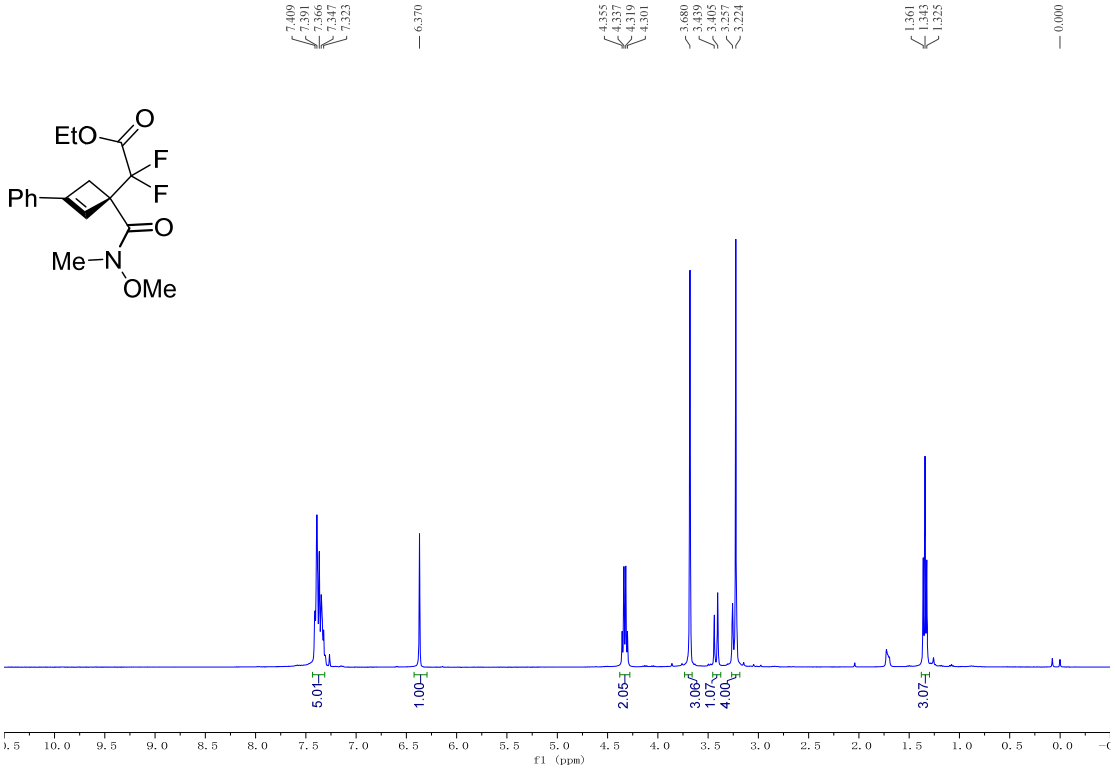


^{19}FNMR (376 MHz, $CDCl_3$)

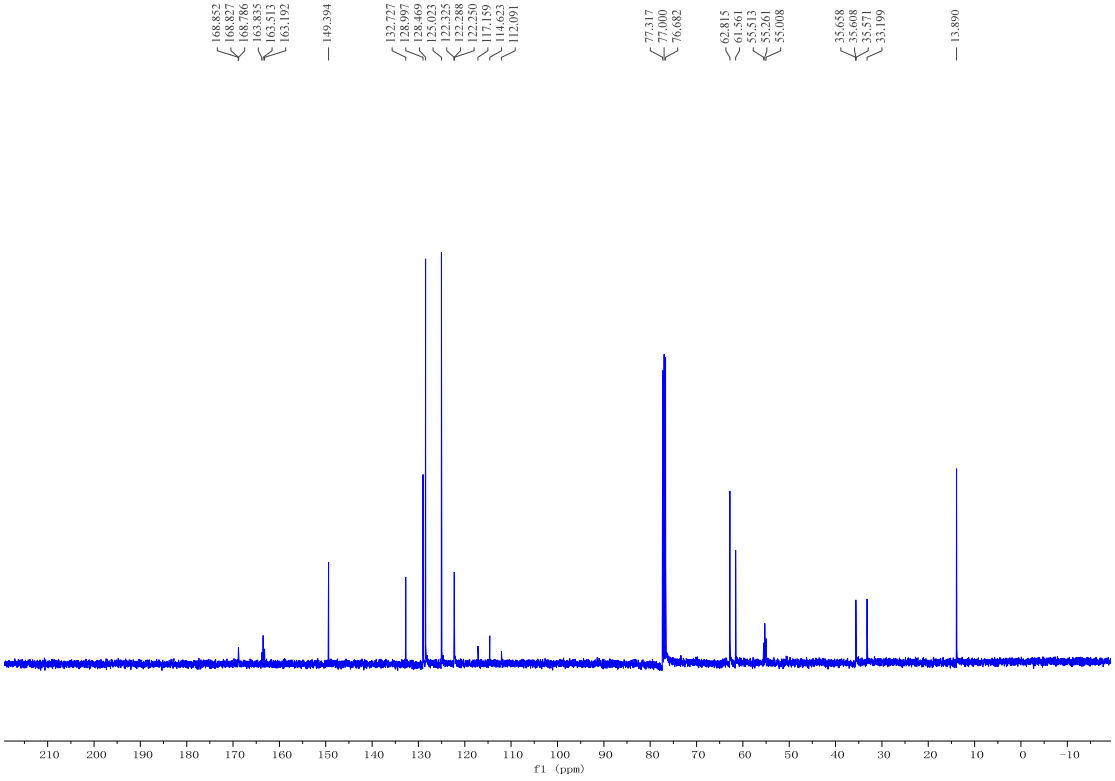


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 3ou:

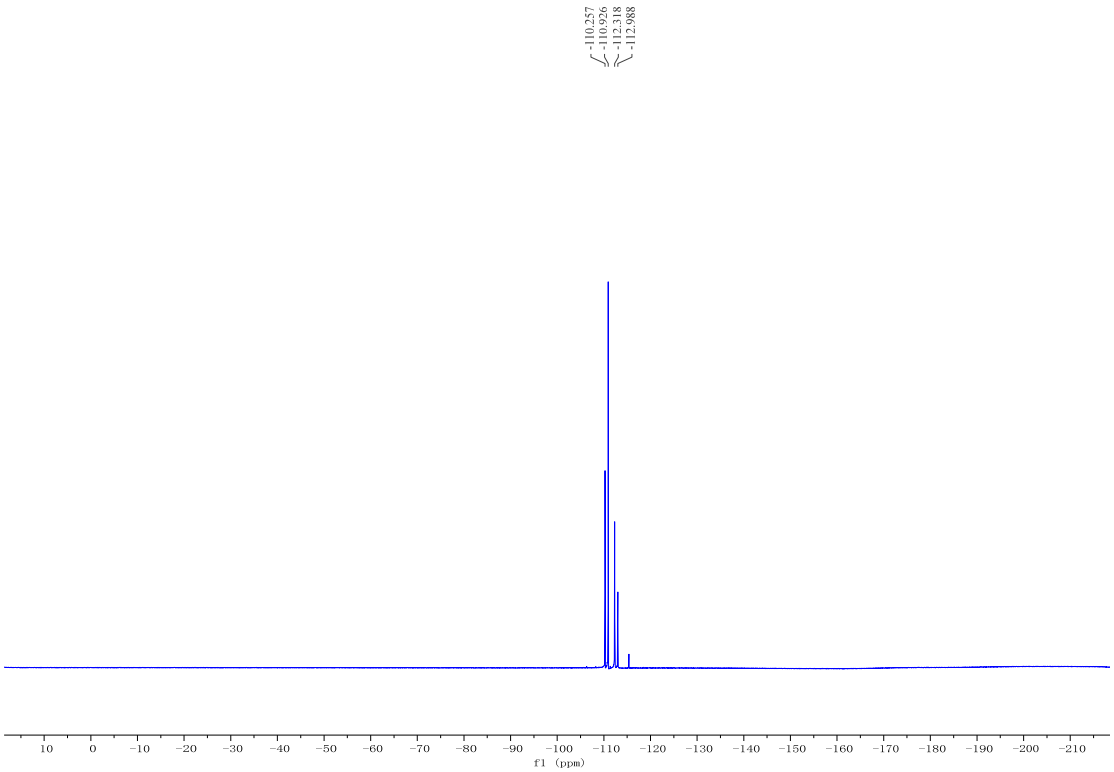
^{1}H NMR (400 MHz, $CDCl_3$)



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

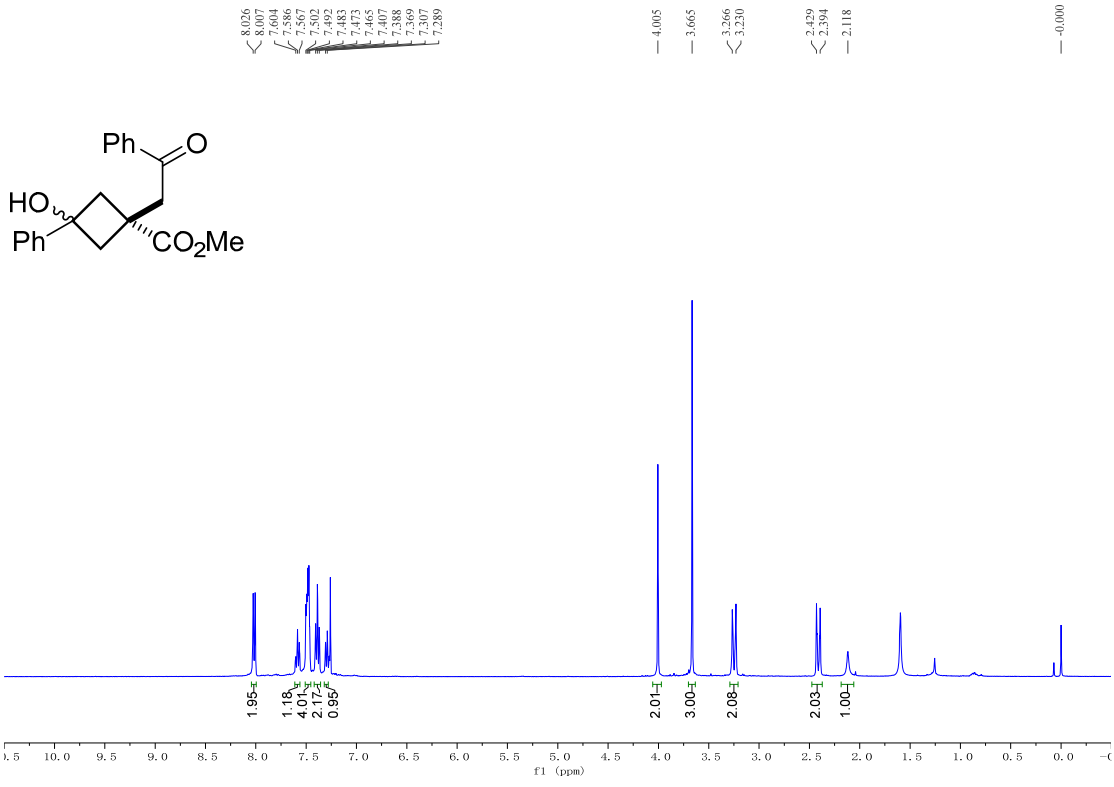


^{19} FNMR (376 MHz, $CDCl_3$)

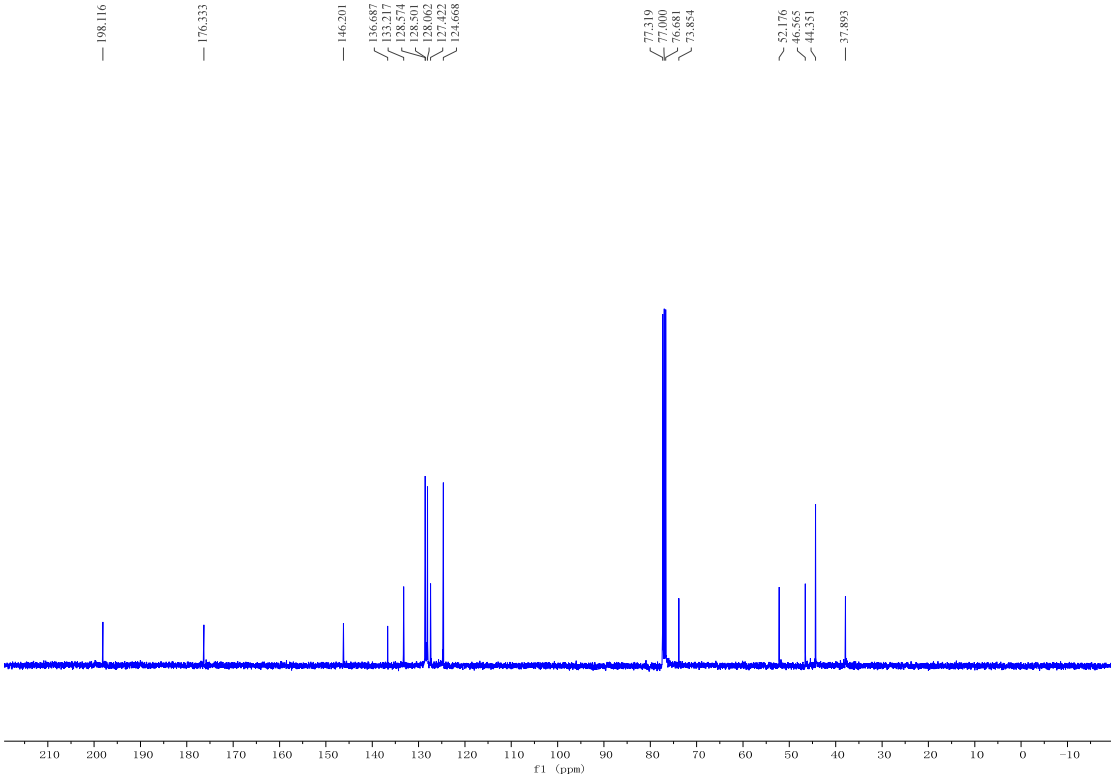


^{1}H and ^{13}C NMR Spectra for Compound 5aa:

^{1}H NMR (400 MHz, $CDCl_3$)

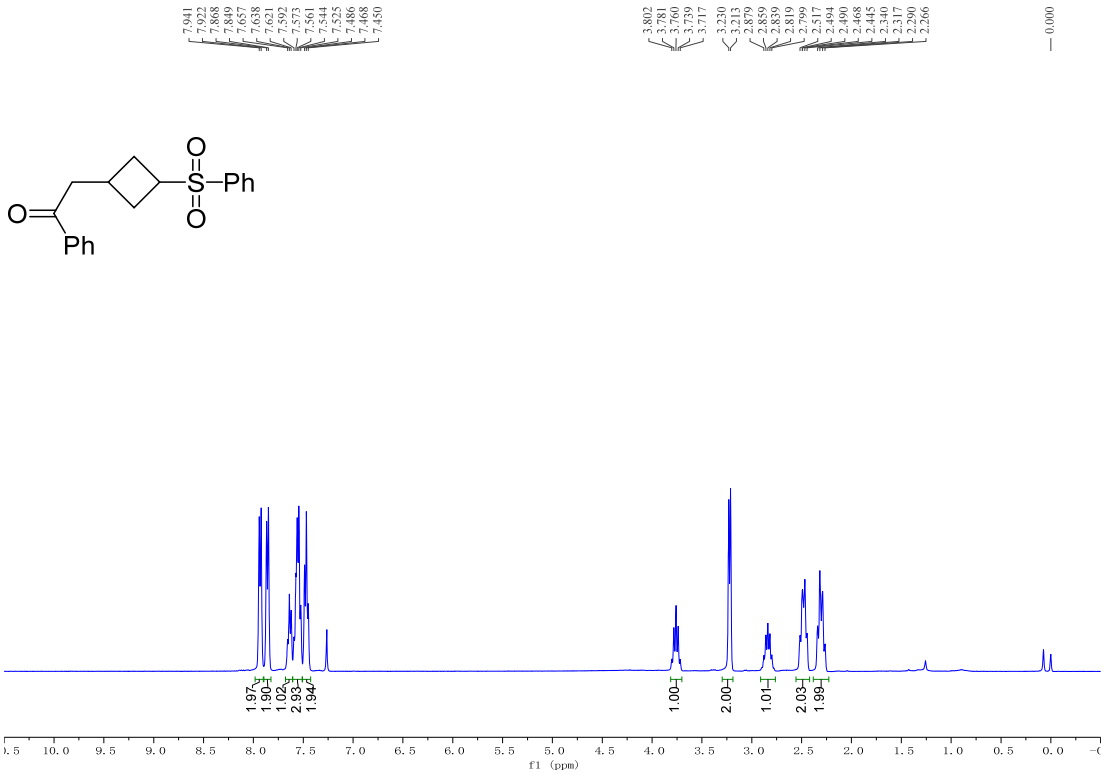


^{13}C NMR (400 MHz, $CDCl_3$)

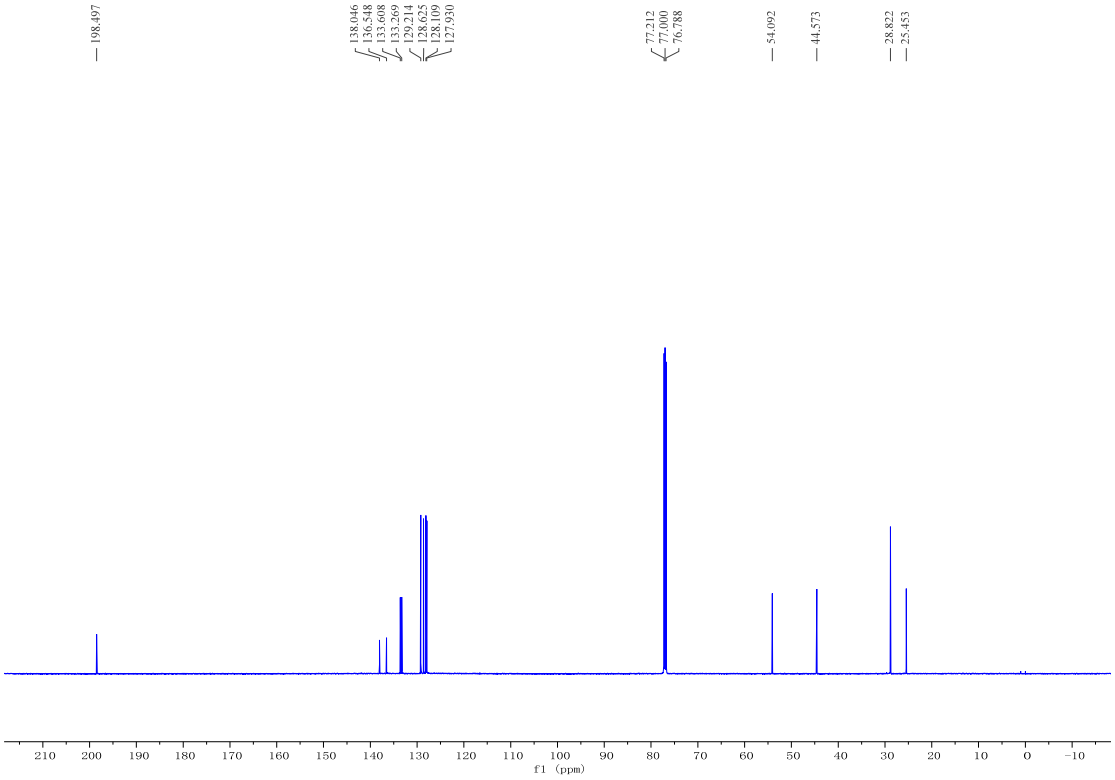


^{1}H and ^{13}C NMR Spectra for Compound 6:

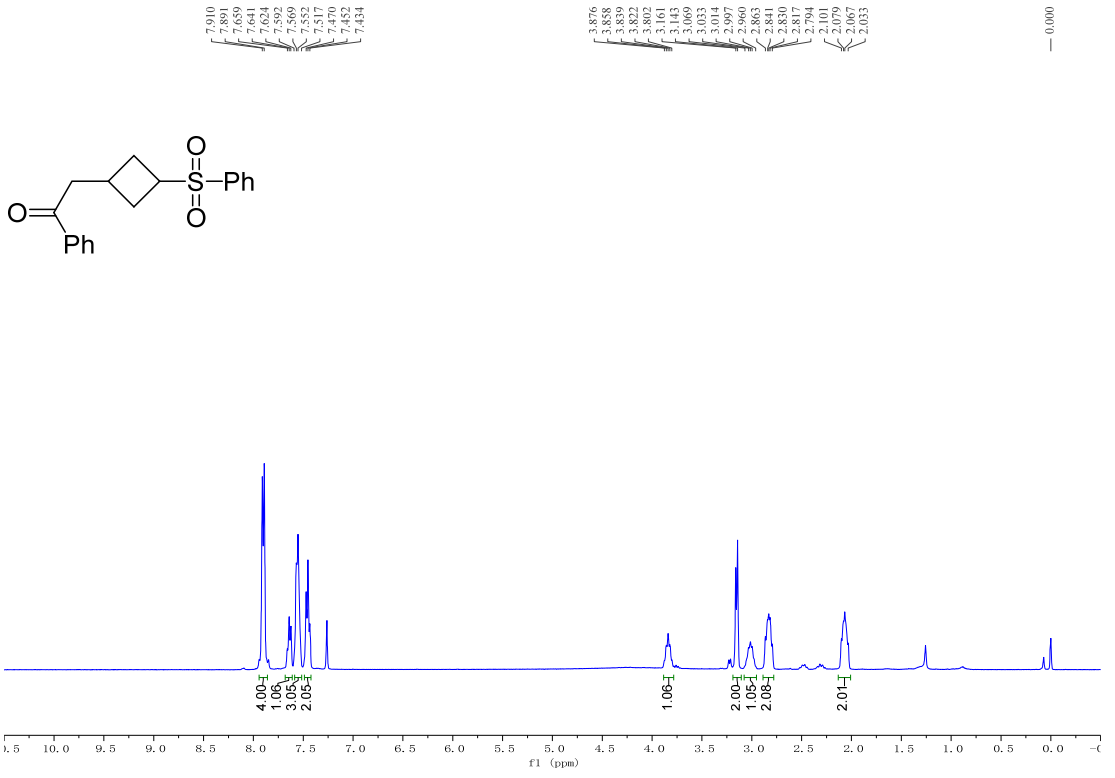
^{1}H NMR (400 MHz, $CDCl_3$) for the major diastereomer



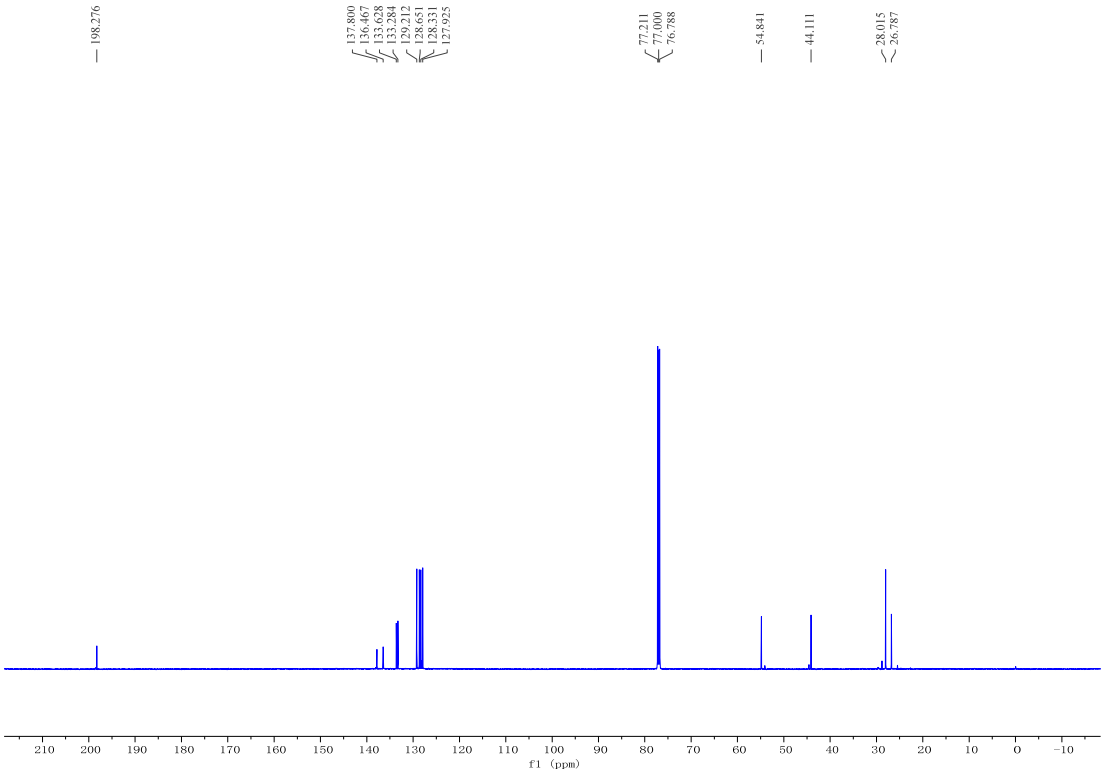
^{13}C NMR (150 MHz, $CDCl_3$) for the major diastereomer



^{1}H NMR (400 MHz, $CDCl_3$) for the minor diastereomer

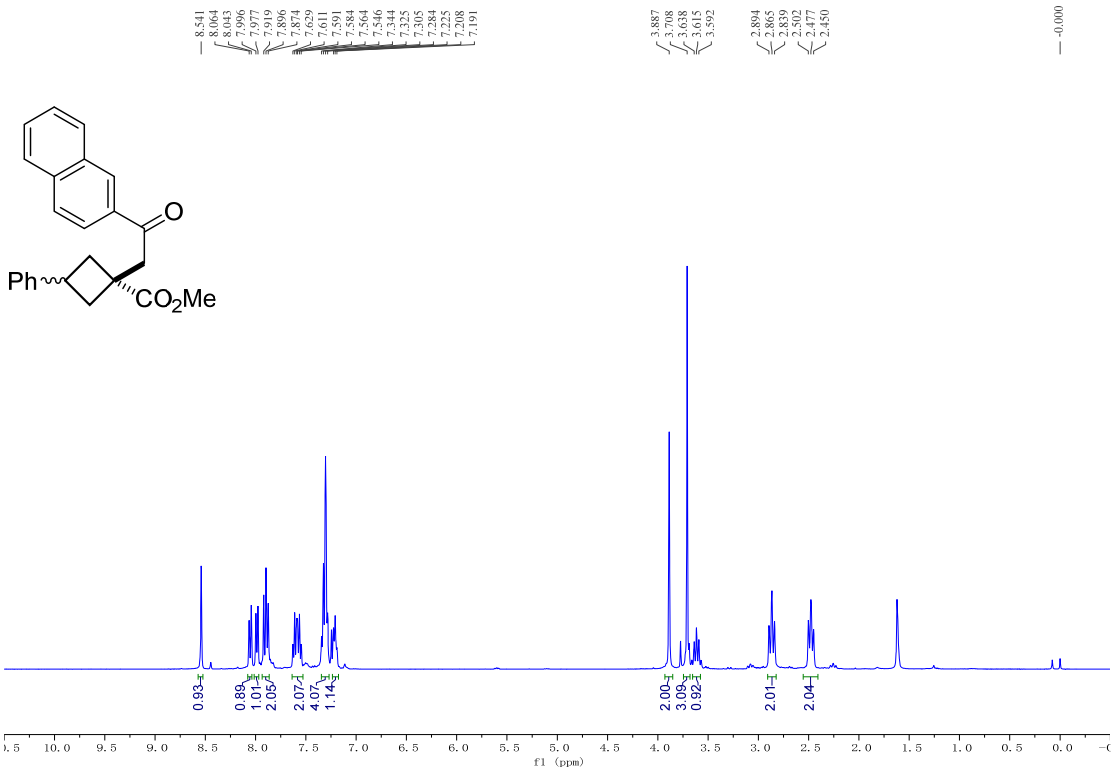


^{13}C NMR (150 MHz, $CDCl_3$) for the minor diastereomer

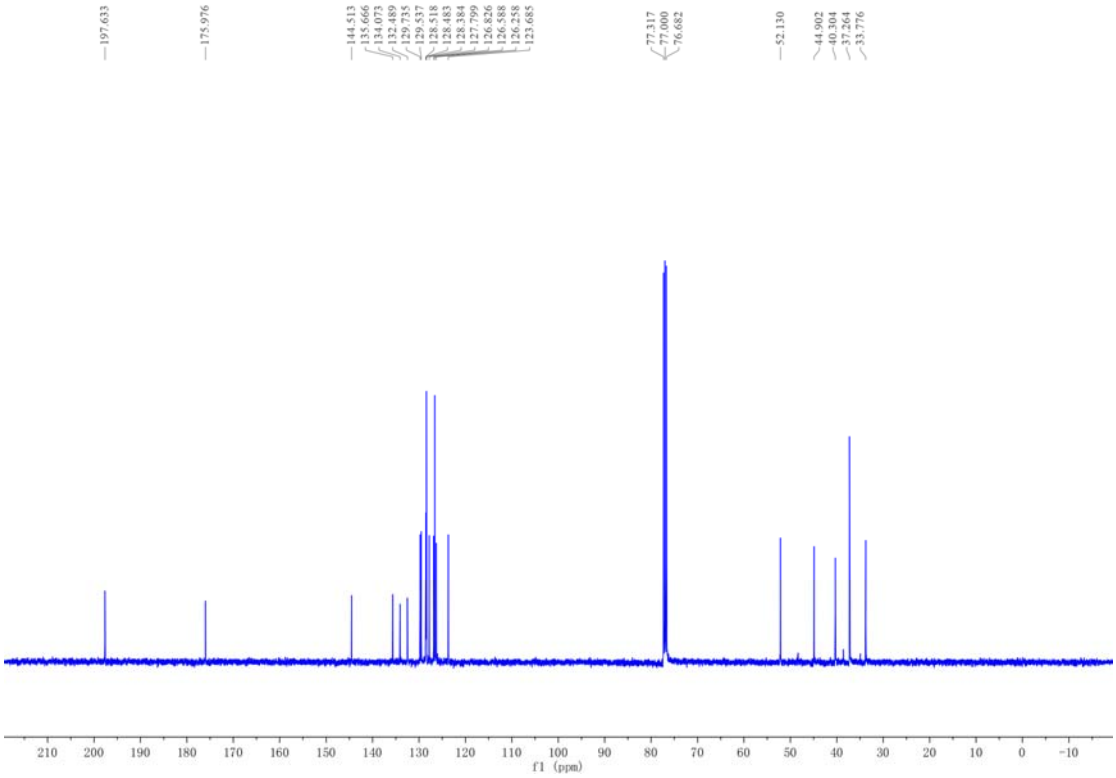


^{1}H and ^{13}C NMR Spectra for Compound 7:

^{1}H NMR (400 MHz, $CDCl_3$)

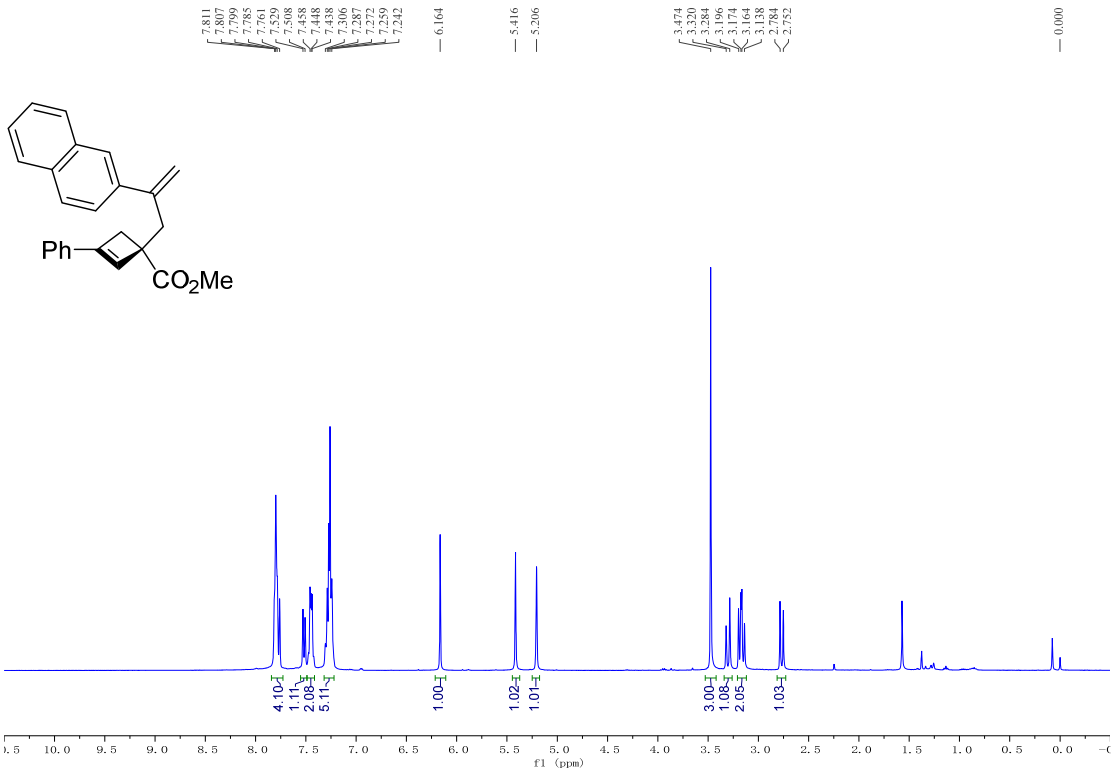


^{13}C NMR (100 MHz, $CDCl_3$)

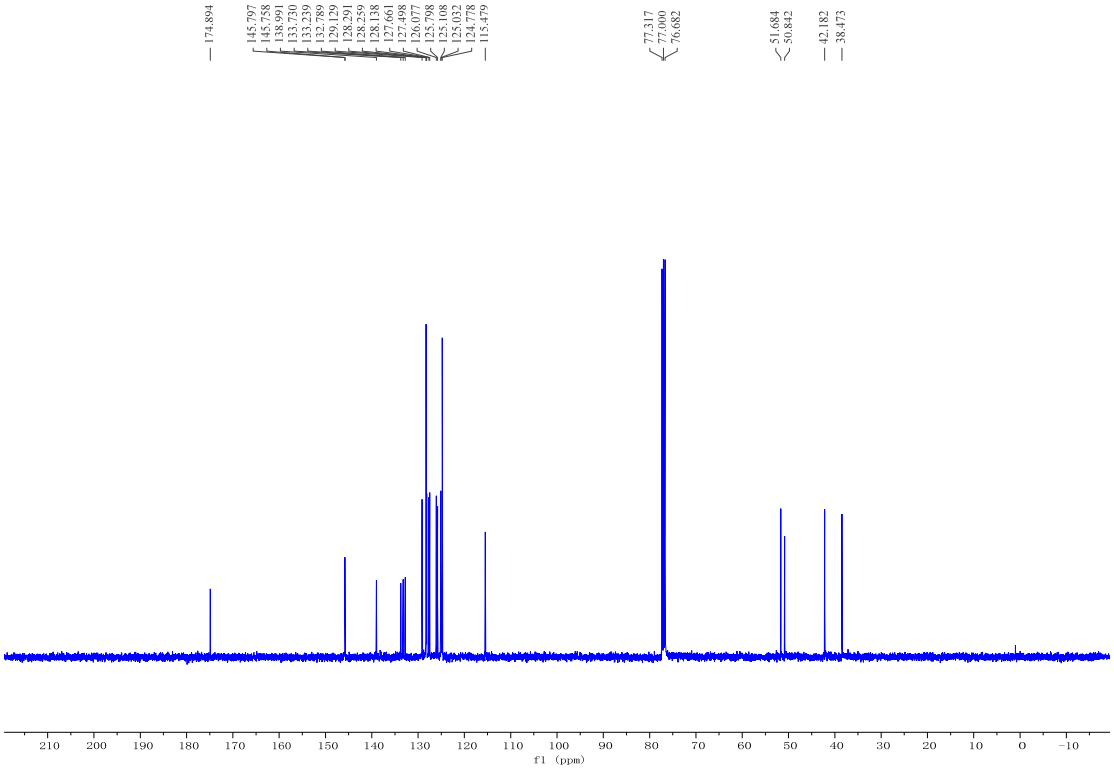


^{1}H and ^{13}C NMR Spectra for Compound 8

^{1}H NMR (400 MHz, $CDCl_3$)

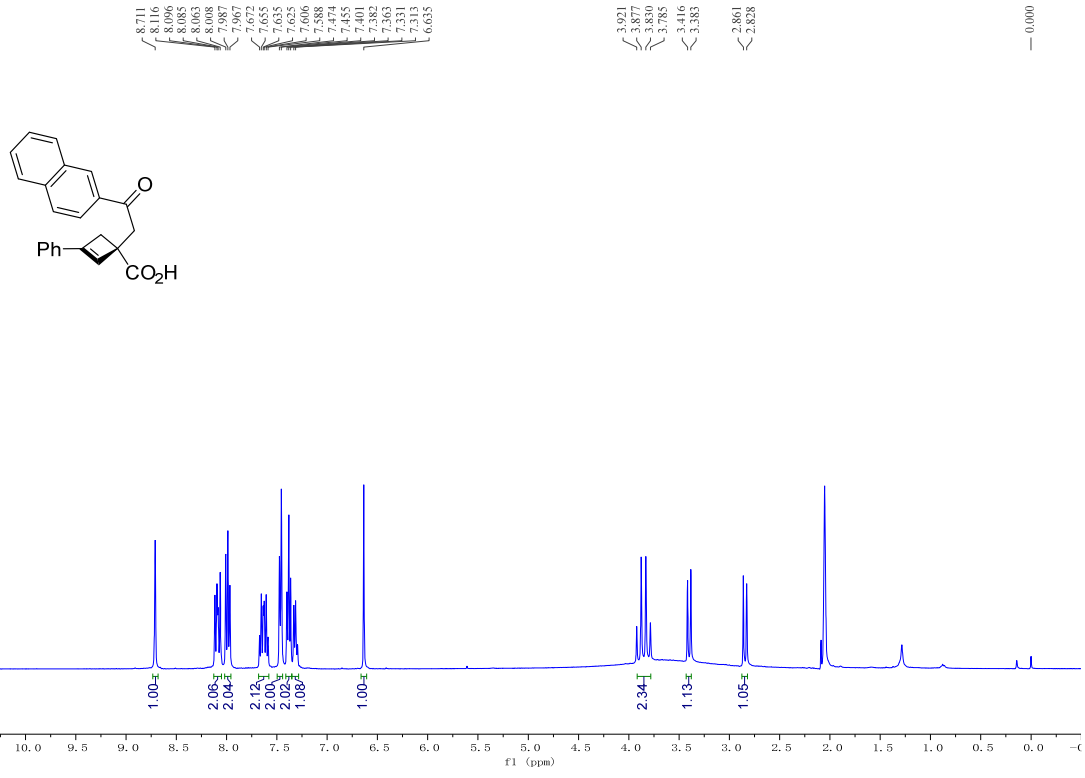


^{13}C NMR (100 MHz, $CDCl_3$)

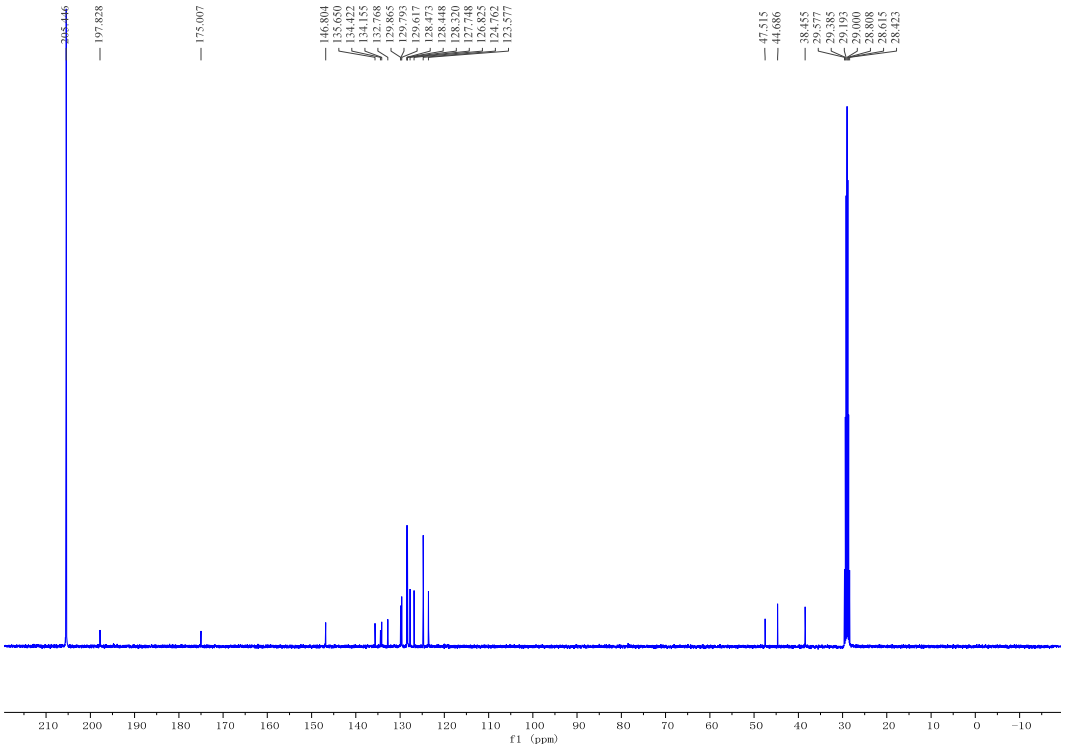


^{1}H and ^{13}C NMR Spectra for Compound 9:

^{1}H NMR (400 MHz, CD_3COCD_3)

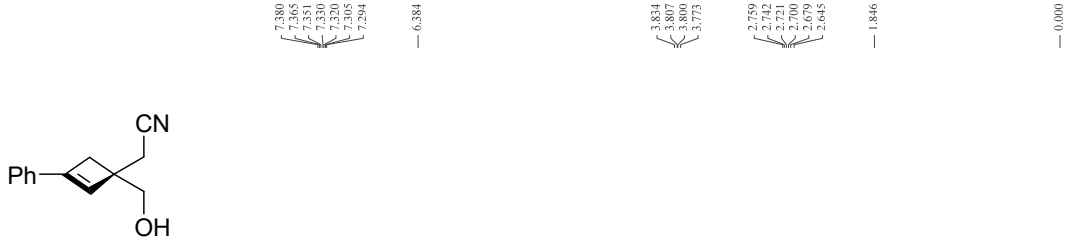


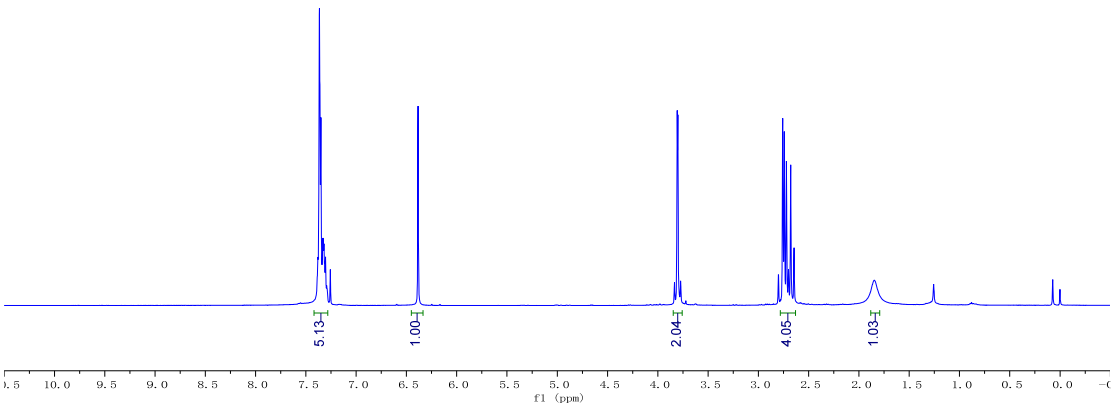
^{13}C NMR (100 MHz, CD_3COCD_3)



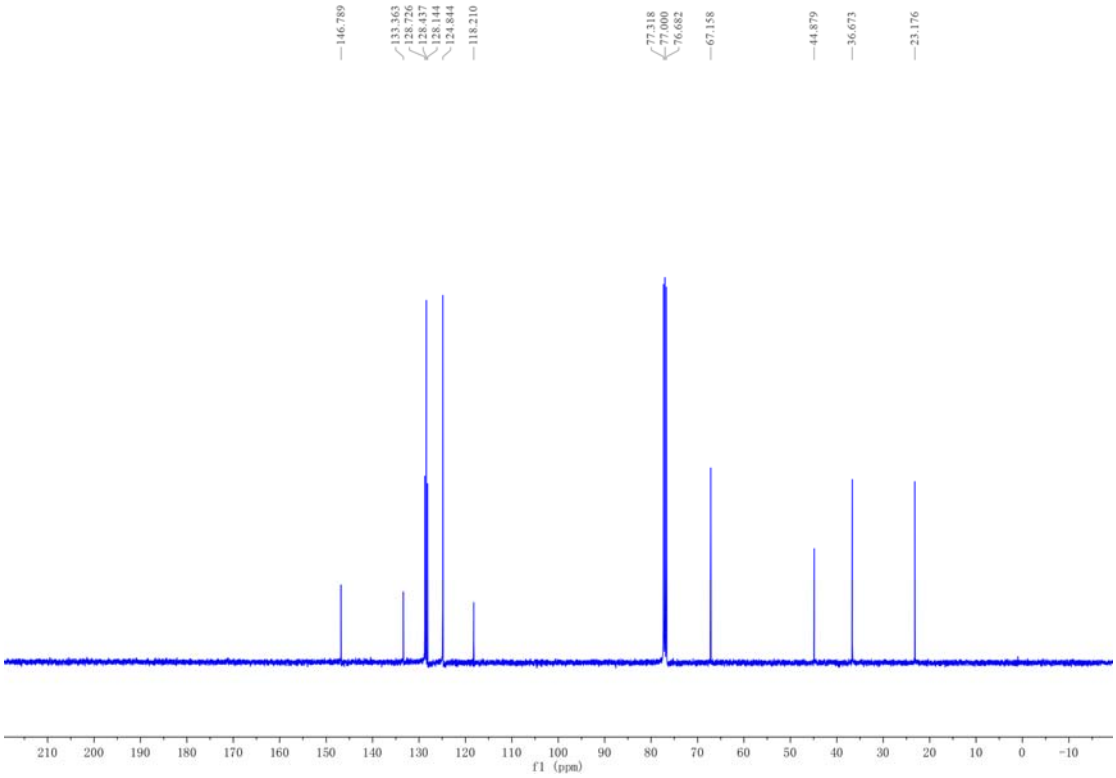
^{1}H and ^{13}C NMR Spectra for Compound 10:

^{1}H NMR (400 MHz, $CDCl_3$)



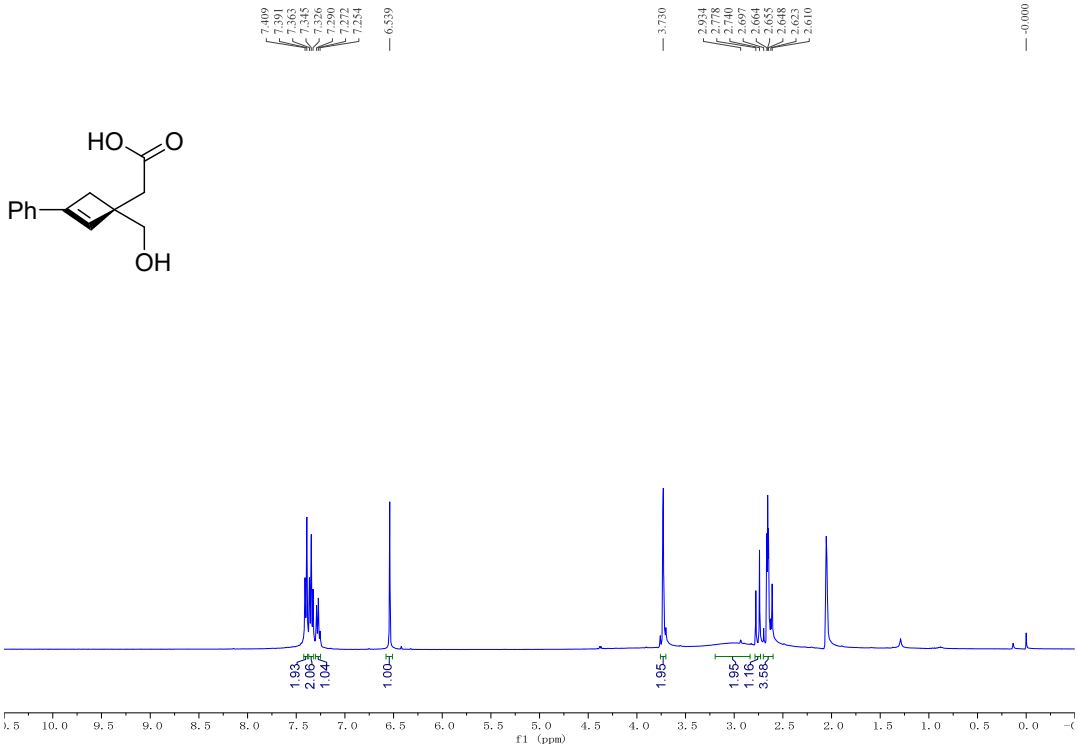


^{13}C NMR (100 MHz, $CDCl_3$)

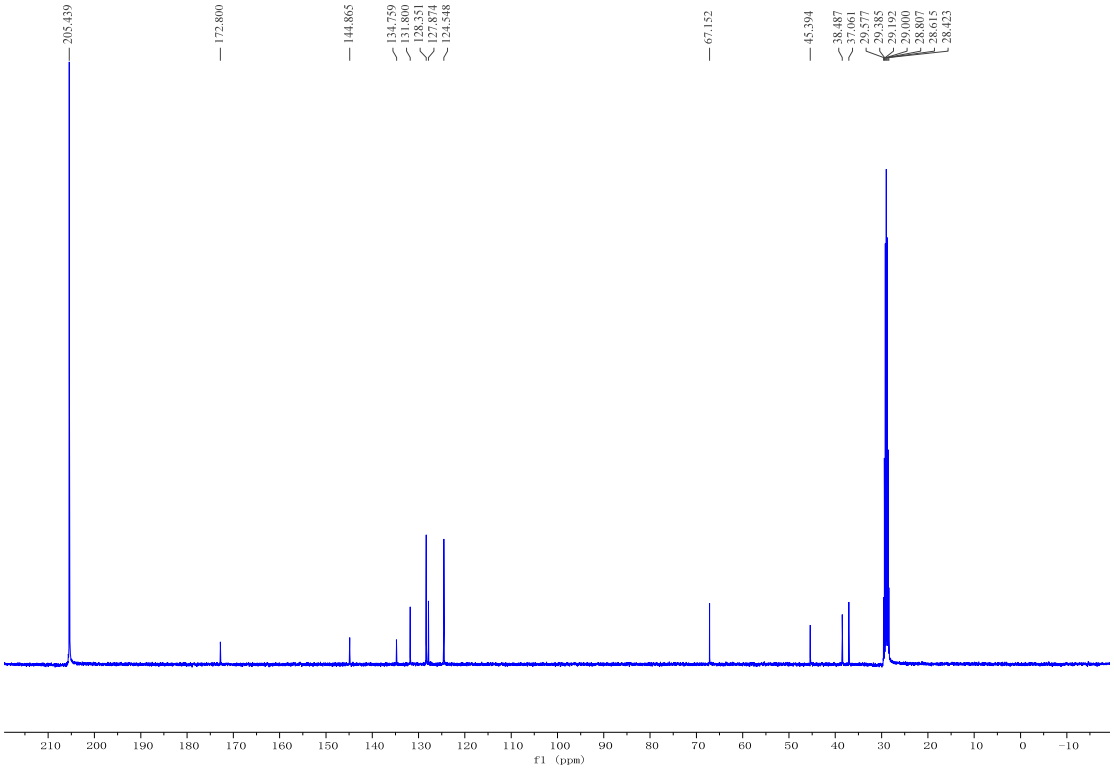


^{1}H and ^{13}C NMR Spectra for Compound 11:

^{1}H NMR (400 MHz, CD_3COCD_3)

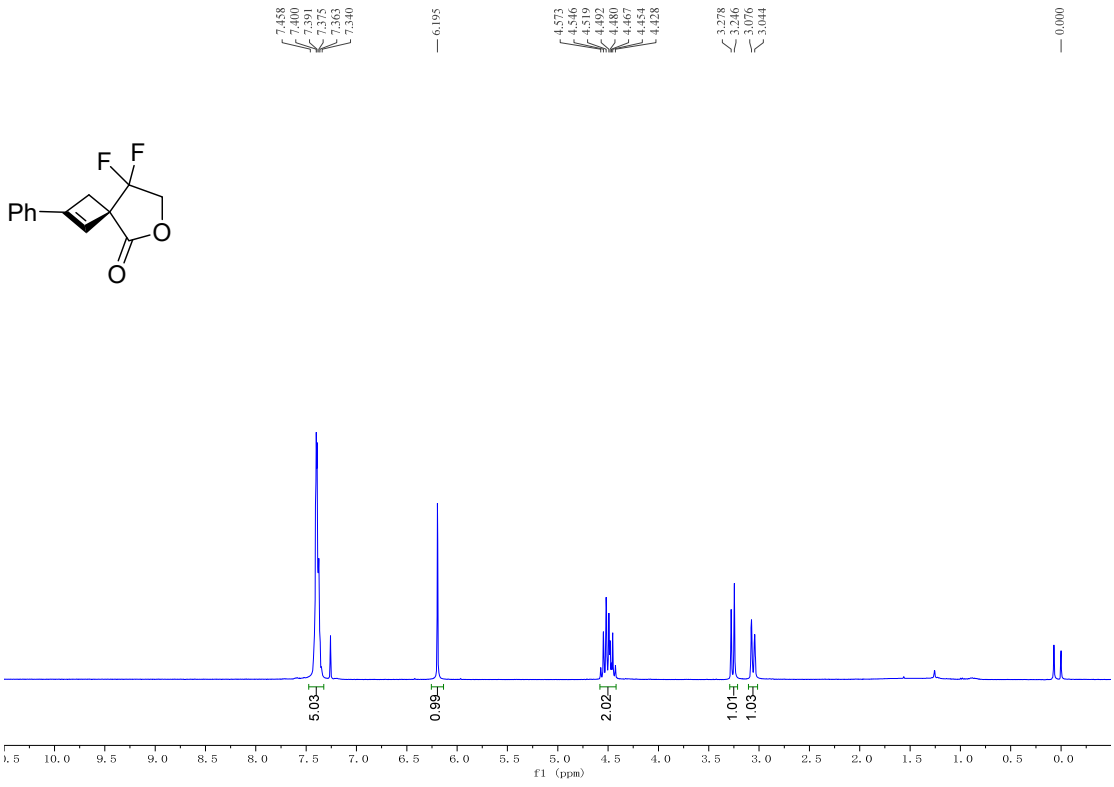


^{13}C NMR (100 MHz, CD_3COCD_3)

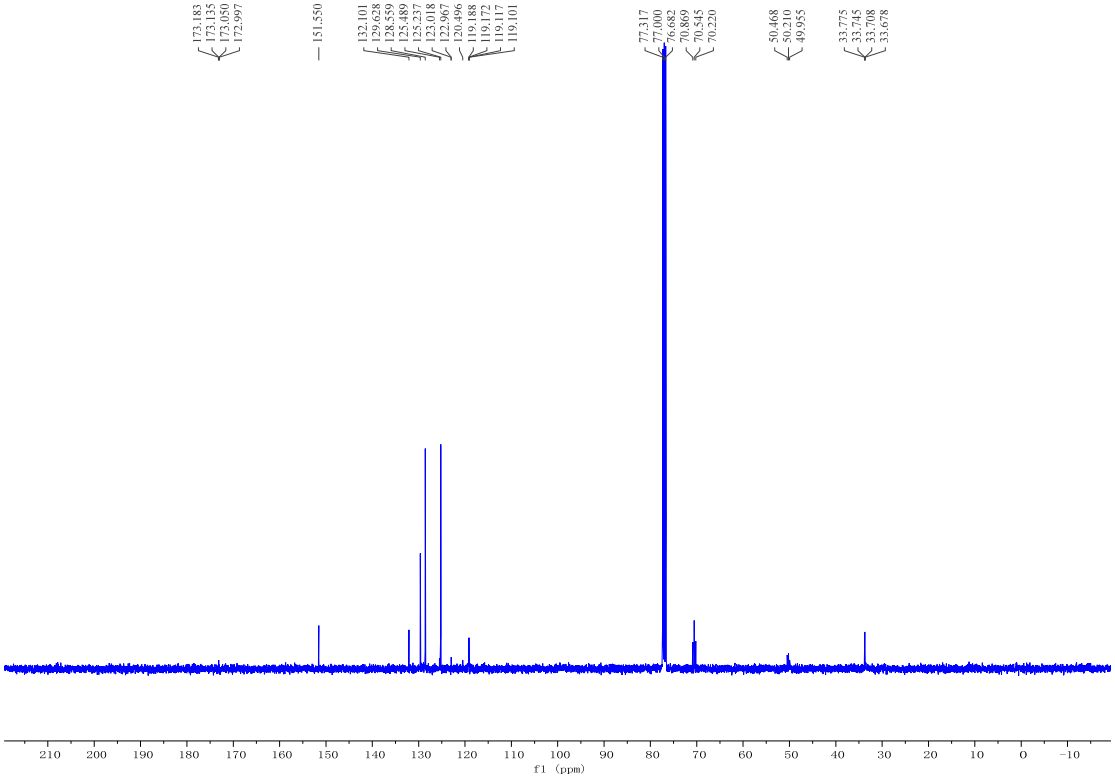


^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for Compound 12:

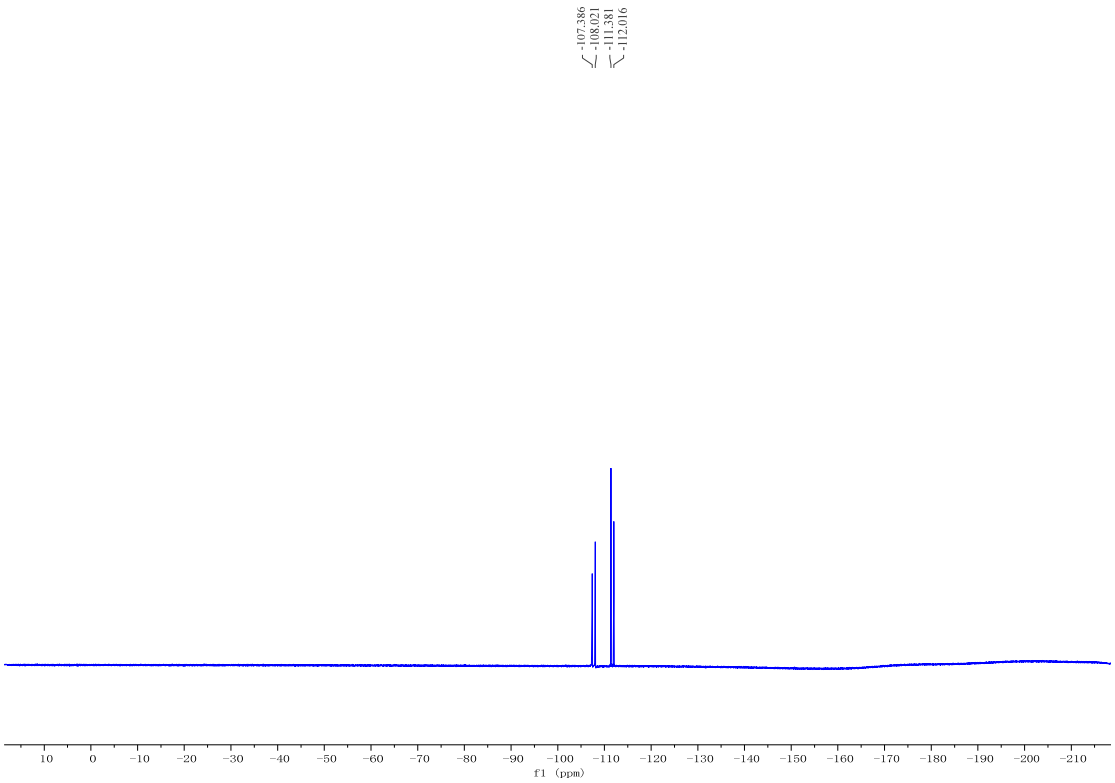
^{1}H NMR (400 MHz, $CDCl_3$)



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

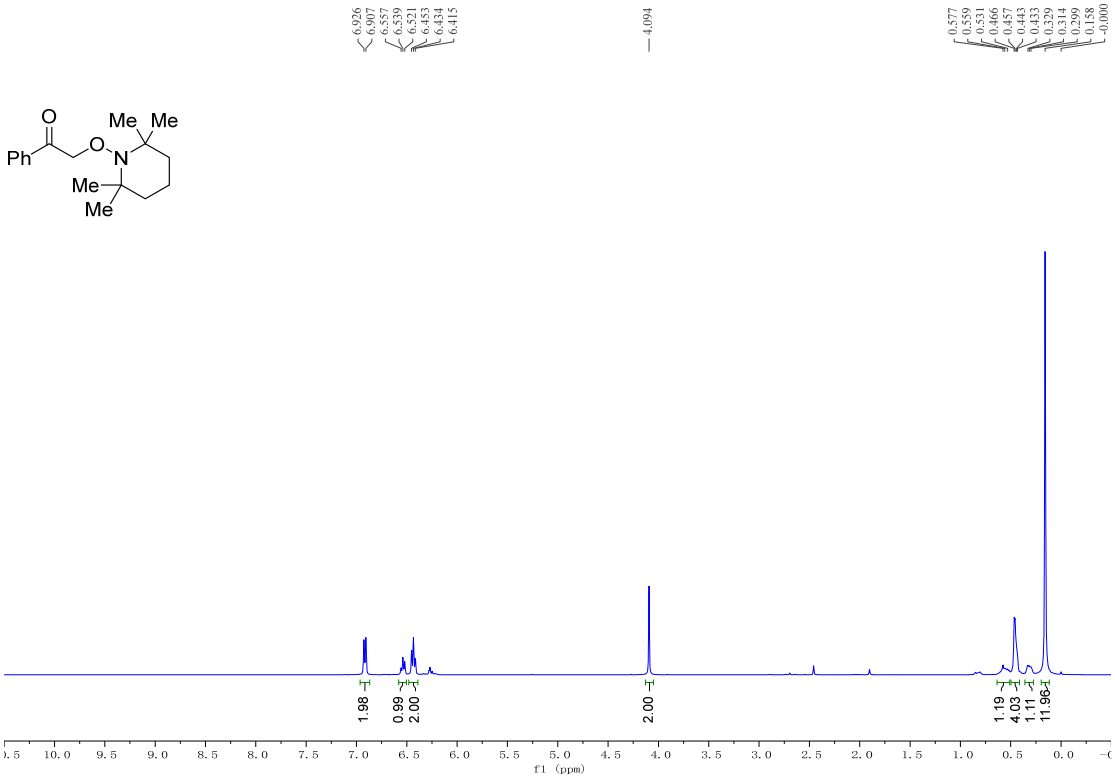


^{19}F NMR (376 MHz, $CDCl_3$)

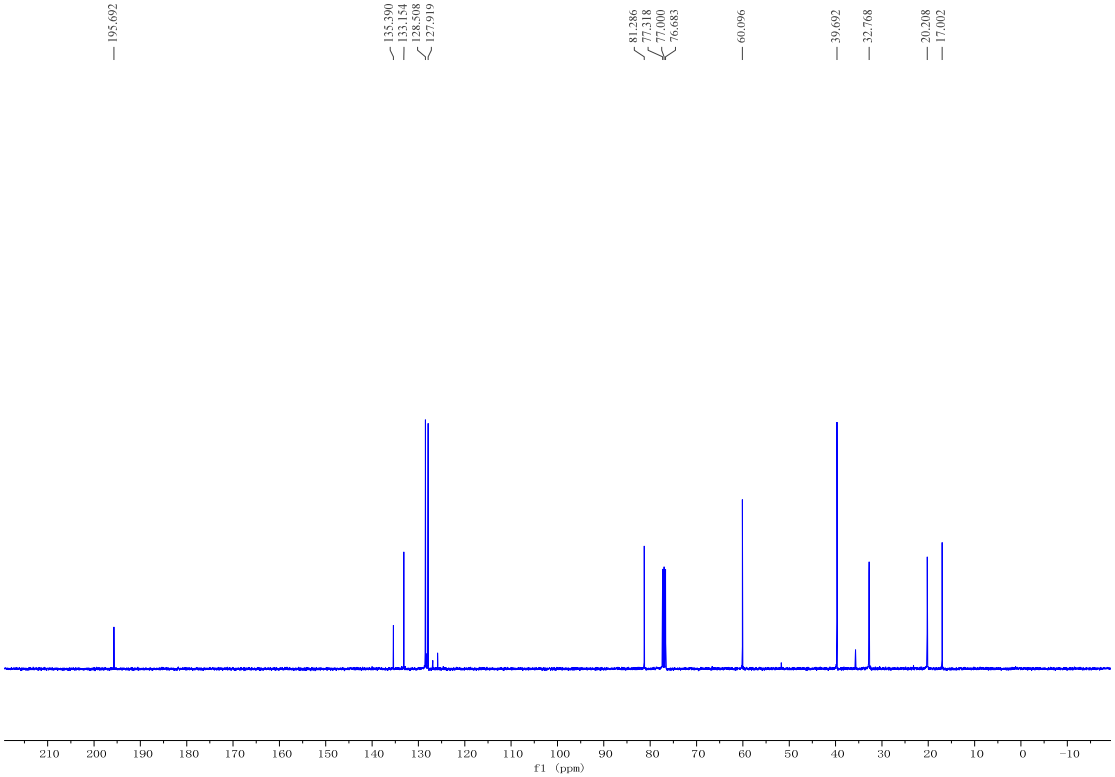


^{1}H and ^{13}C NMR Spectra for Compound 13:

^{1}H NMR (400 MHz, $CDCl_3$)

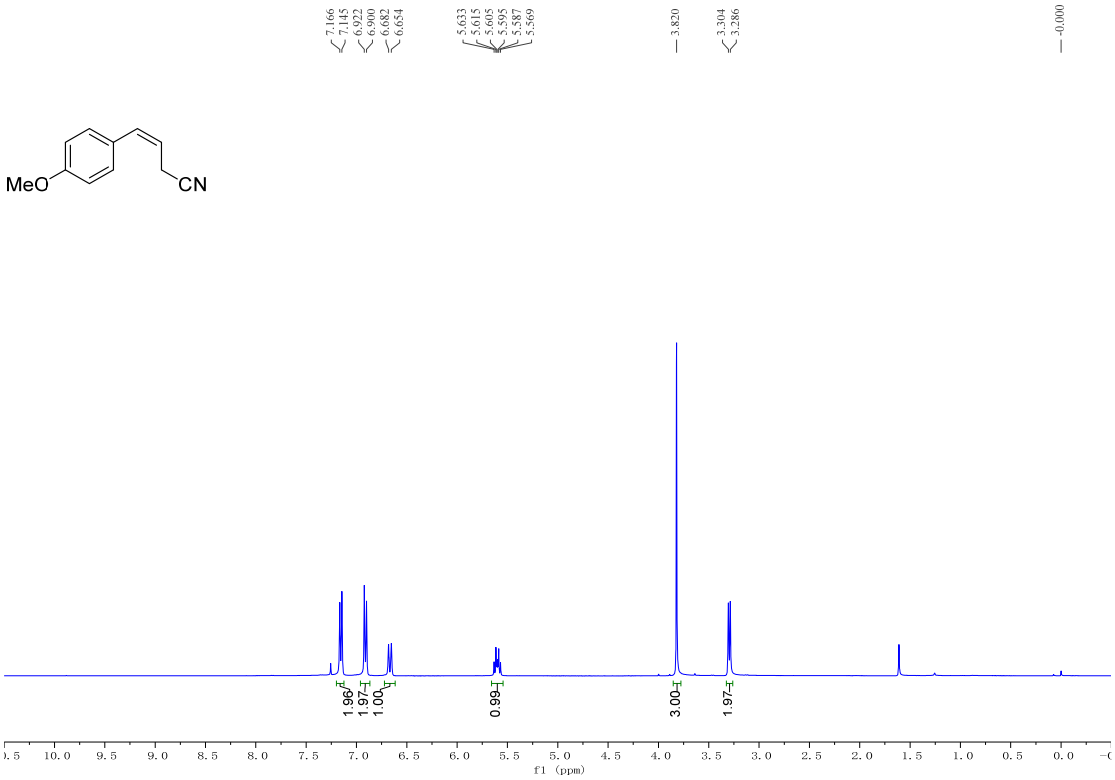


^{13}C NMR (100 MHz, $CDCl_3$)

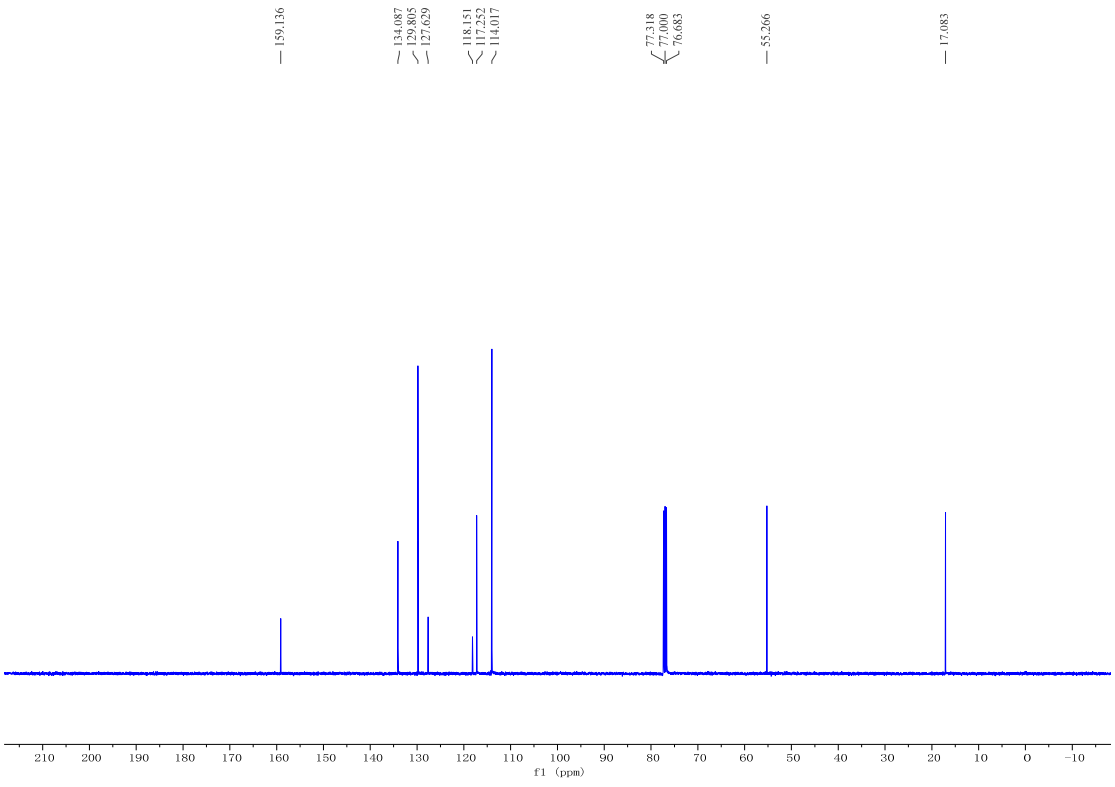


^{1}H and ^{13}C NMR Spectra for Compound (*Z*)-14:

^{1}H NMR (400 MHz, $CDCl_3$)

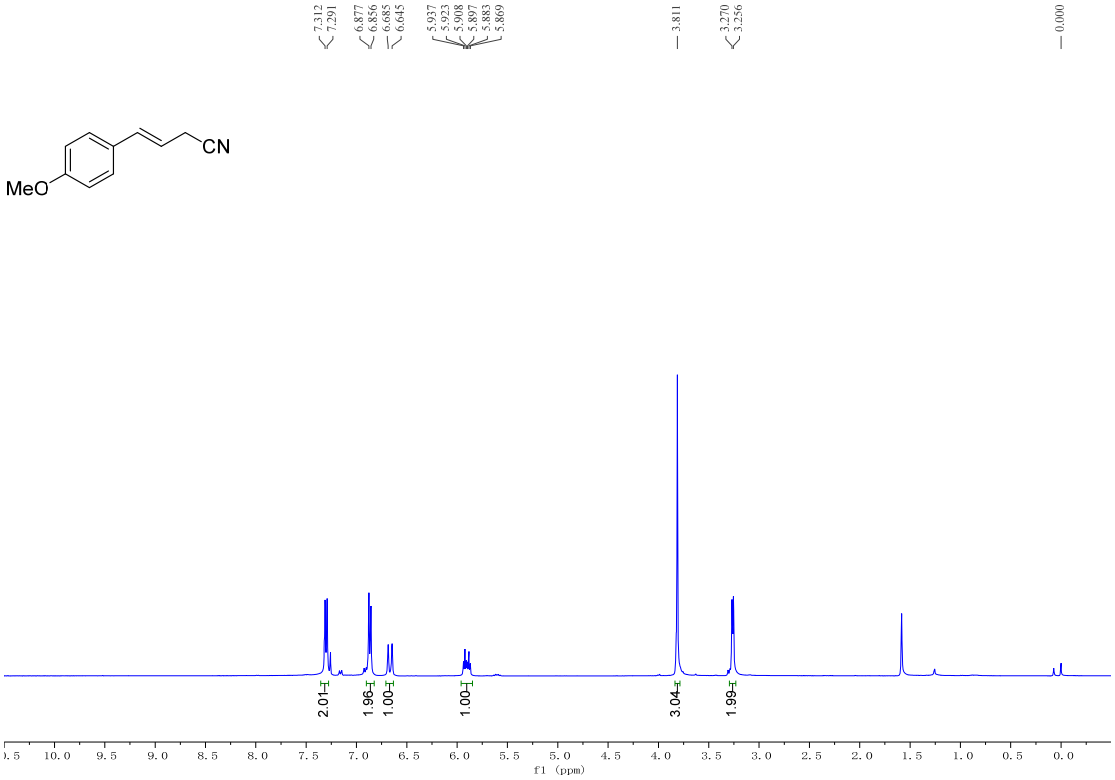


^{13}C NMR (100 MHz, $CDCl_3$)

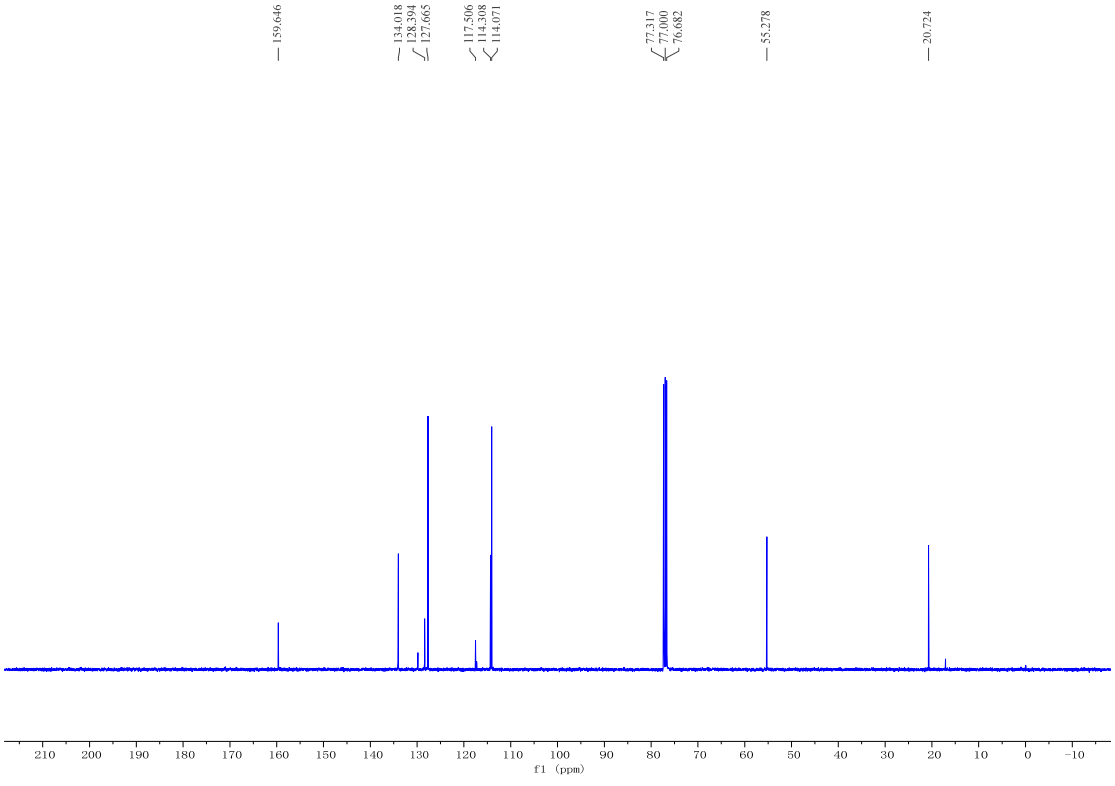


^{1}H and ^{13}C NMR Spectra for Compound (*E*)-14:

^{1}H NMR (400 MHz, $CDCl_3$)

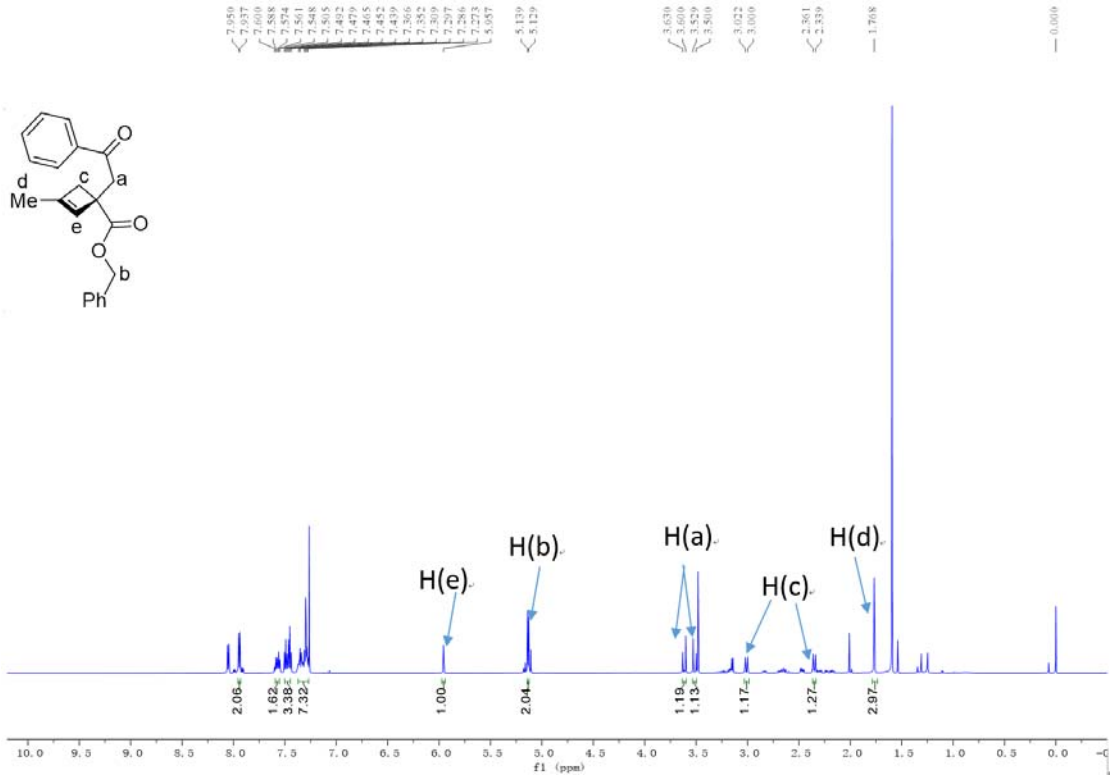


^{13}C NMR (100 MHz, $CDCl_3$)

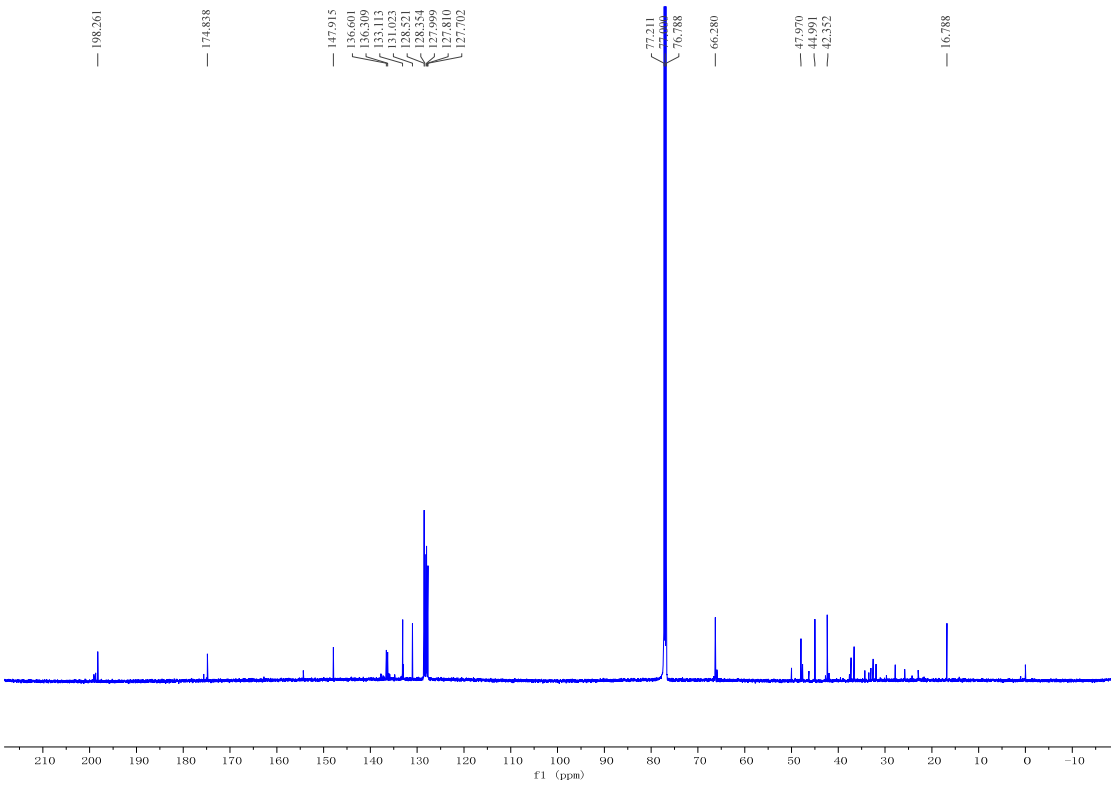


^{1}H and ^{13}C NMR Spectra for Compound 3pa:

^{1}H NMR (600 MHz, $CDCl_3$): the desired **3pa** containing unknown by-products that cannot be separated using flash chromatography on silica gel.

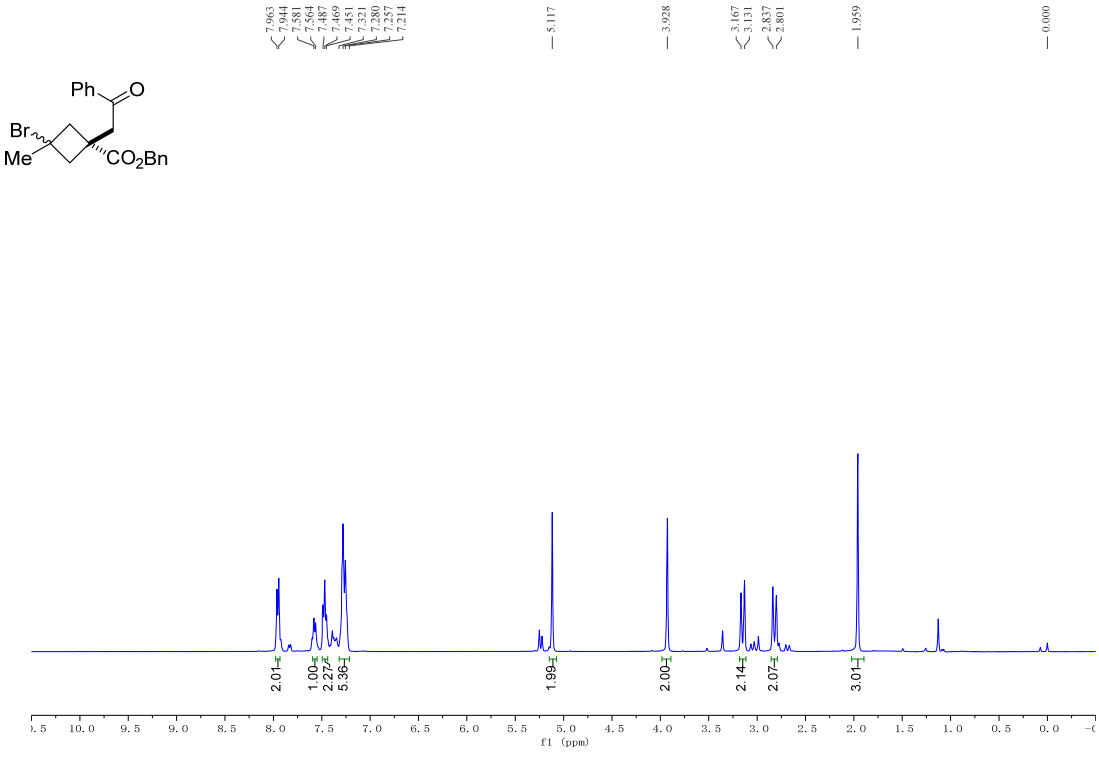


^{13}C NMR (150 MHz, $CDCl_3$)

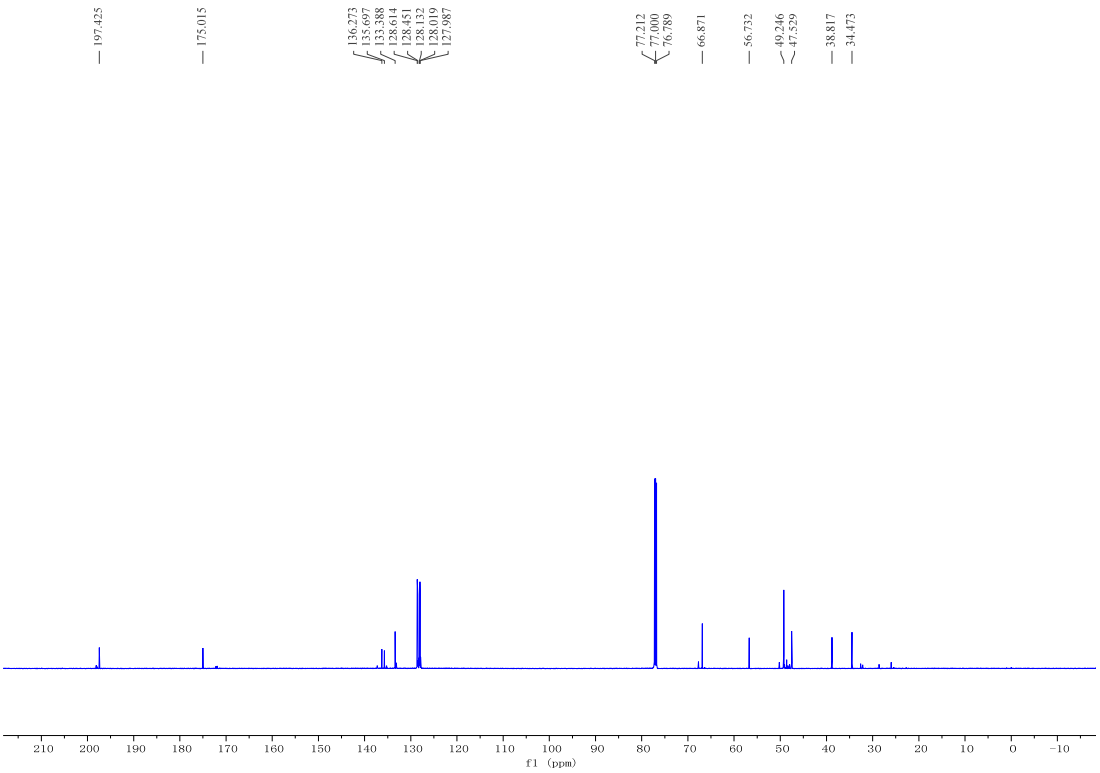


^{1}H and ^{13}C NMR Spectra for Compound 16:

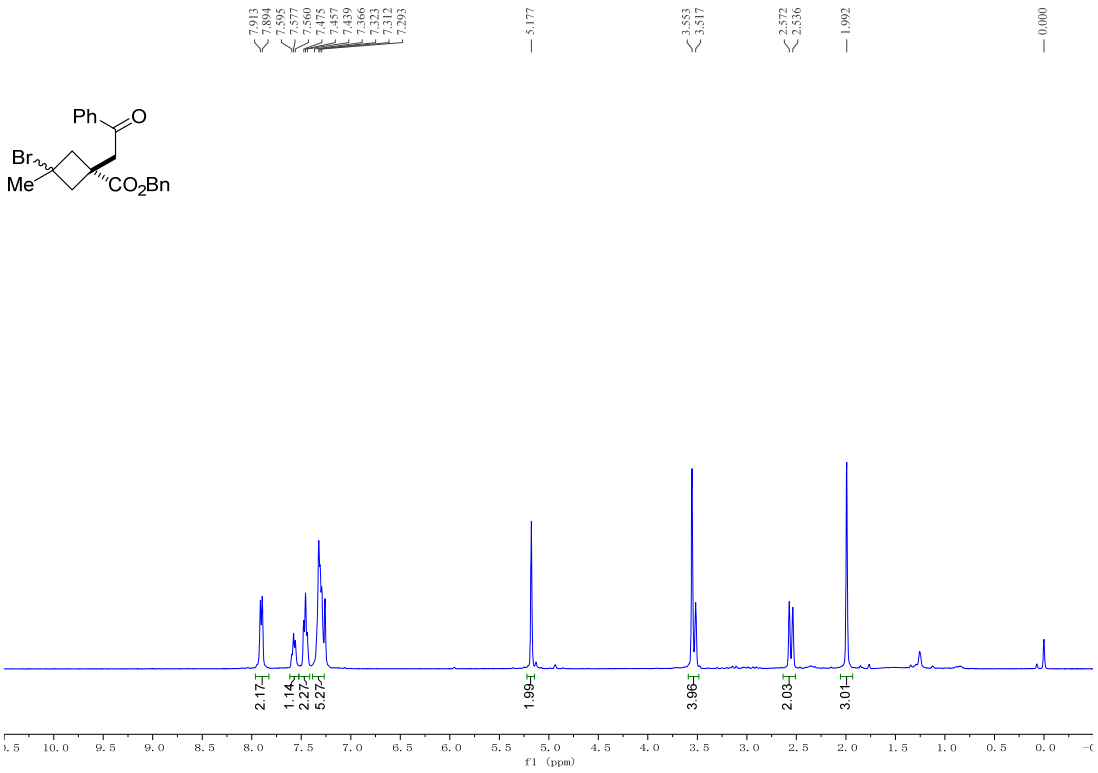
^{1}H NMR (400 MHz, $CDCl_3$) for the major diastereomer (containing unknown by-products that cannot be separated using flash chromatography on silica gel.)



^{13}C NMR (150 MHz, $CDCl_3$) for the major diastereomer



^{1}H NMR (400 MHz, $CDCl_3$) for the minor diastereomer



^{13}C NMR (150 MHz, $CDCl_3$) for the minor diastereomer