Supporting Information

Visible-Light Mediated Cobaloxime-Catalyzed Isomerization and Hydroalkenylation of Bicyclo[1.1.0]butanes

Ben Mao,[a] Sheng-Hao Jiang,[a] Zheng Xiong,[a] Yin Wei*[b] and Min Shi*[a,b]

[a]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China. mshi@mail.sioc.ac.cn.

[b]State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, University of Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

CONTENTS

1. General Remarks

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR), 600 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 151 MHz (^{13}C NMR) and 565 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shifts were reported in ppm, and are referenced to internal TMS or the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.00 ppm for ^{13}C NMR). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, EI, DART and HRMS was measured on a HP-5989 instrument. Commercially available reagents were used without further purification. Organic solvents used were dried by standard methods when necessary. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl and petroleum at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

The photoreaction setup is reassembled as following picture with a purple LED, a fan and a magnetic stirrer. The reaction tube was about 5.0 cm far from the light source. The 30 W purple LED (Wavelength: 390 – 400 nm) was directly purchased online from Taobao.com.

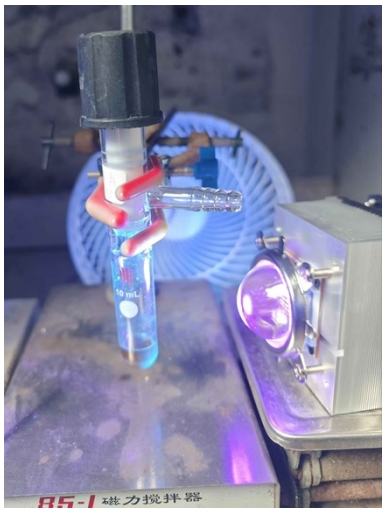
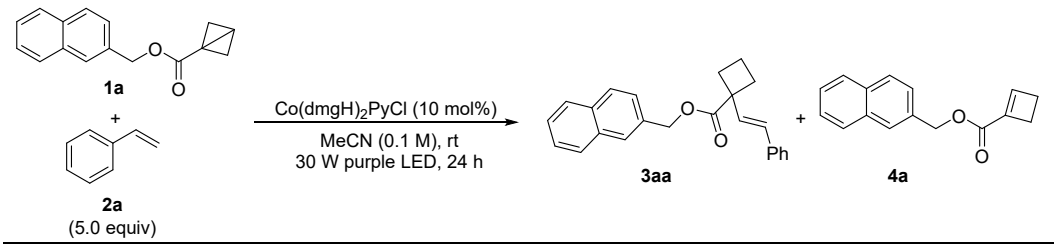


Figure S1. The photoreaction setup

2. Optimization of Reaction Conditions

In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.1 mmol), styrene **2a**, catalyst and other additives were added. The tube was degassed by alternating vacuum evacuation (5 min) and argon backfill for three times. Then the degassed solvent was injected into the tube. The mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, 1,3,5-trimethoxybenzene (1.0 equiv) used as an internal standard was added after removal of the tube from the light source. The solvent was removed under reduced pressure and the resulting crude was analyzed by ^{1}H NMR.

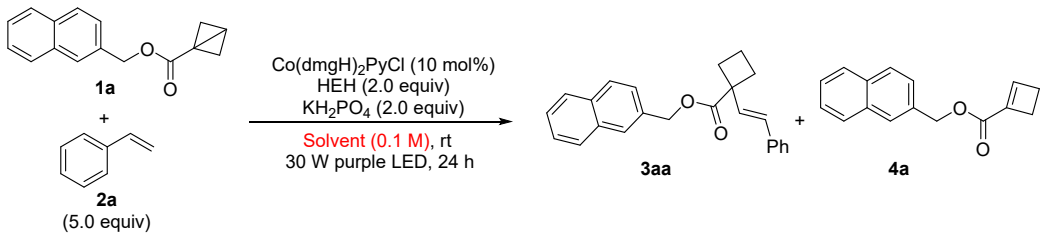
2.1 Table S1. Screening of Catalytic System



Entry	Additive	**3aa**, Yield (%)[a]	**4a**, Yield (%)[a]
1	Zn (2.0 equiv), NH_4Cl (2.0 equiv)	11	16
2	Mn (2.0 equiv), NH_4Cl (2.0 equiv)	15	44
3	HEH (2.0 equiv), KH_2PO_4 (2.0 equiv)	22	32

[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

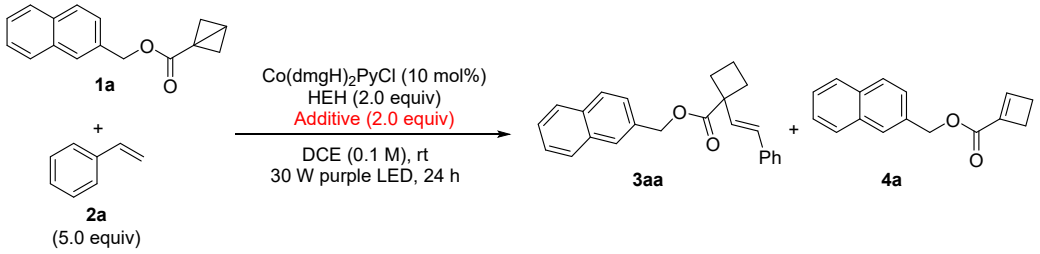
2.2 Table S2. Solvent Optimization



Entry	Solvent	**3aa**, Yield (%)[a]	**4a**, Yield (%)[a]
1	MeCN	22	32
2	DMAc	5	20
3	NMP	6	15
4	acetone	12	15
5	THF	20	23
6	DME	22	30
7	$PhCF_3$	36	31
8	DCE	40	38

[a]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

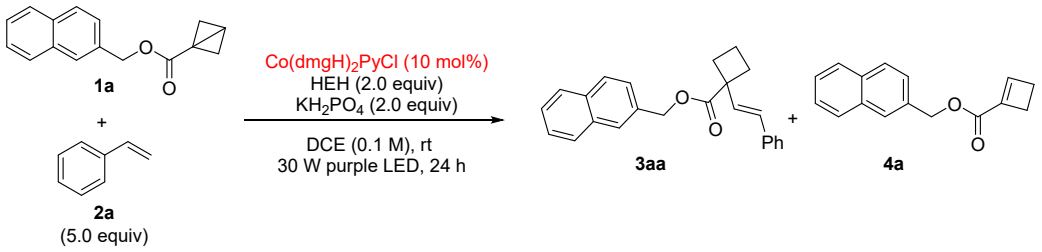
2.3 Table S3. Additive Optimization



Entry	Base	**3aa**, Yield (%)[a]	**4a**, Yield (%)[a]
1	KH_2PO_4	40	38
2	Li_2CO_3	25	24
3	Na_2CO_3	21	31
4	K_2CO_3	17	13
5	$KHCO_3$	16	20
6	Et_3N	n.d.	n.d.
7	$^iPr_2NEt$	n.d.	n.d.
8	Na-Gly	35	25
9	w/o	12	15

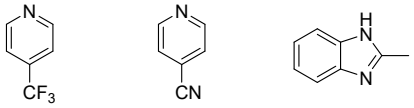
[a]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

2.4 Table S4. [Co] Catalyst Optimization



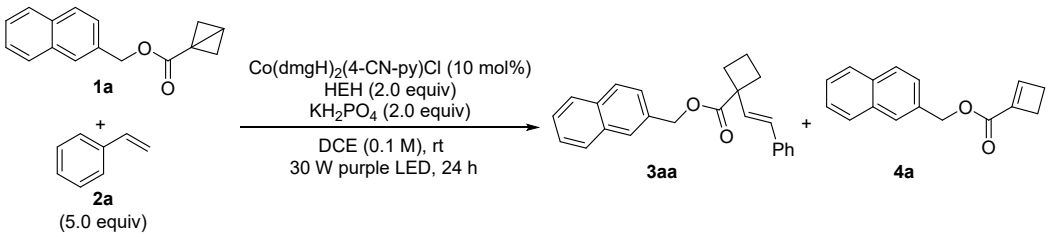
Entry	Deviation	**3aa**, Yield (%)[a]	**4a**, Yield (%)[a]
1	none	40	38
2	$Co(dmgH)_2$(4-OMe-py)Cl	28	34
3	$Co(dmgH)_2$(DMAP)Cl	18	35
4	$Co(dmgH)_2$(4-CF_3-py)Cl	46	39
5	$Co(dmgH)_2$(4-CN-py)Cl	48	38
6	$Co(dmgH)(dmgH_2)Cl_2$	35	31
7	$Co(dmgH)(dmgH_2)Cl_2$ + **L1** (15 mol%)	48	36
8	$Co(dmgH)(dmgH_2)Cl_2$ + **L2** (15 mol%)	50	33
9	$Co(dmgH)(dmgH_2)Cl_2$ + **L3** (15 mol%)	20	15
10	$CoBr_2$(10 mol%), DPEphos (15 mol%)	n.d.	n.d.
11	$Co(acac)_2$ (10 mol%), DPEphos (15 mol%)	n.d.	n.d.
12	$Co(Salen^{tBu, tBu})$ (5 mol%)	n.d.	n.d.

[a]Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.



L1 **L2** **L3**

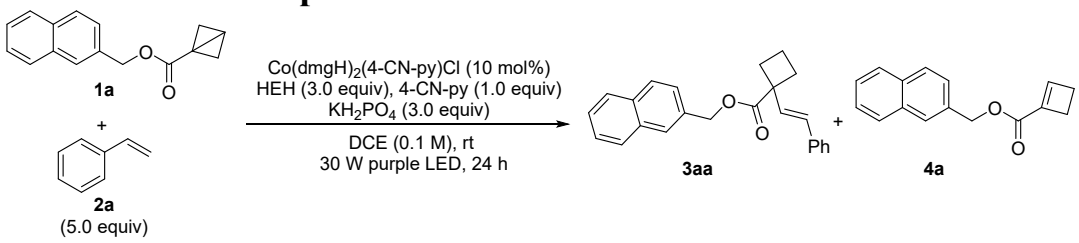
2.5 Table S5. Further Optimization of Product 3aa



Entry	Deviation	**3aa**, Yield (%)[a]	**4a**, Yield (%)[a]
1	none	48	38
2	[Co] (2 mol%)	10	20
3	**2a** (10.0 equiv)	10	9
4	DCE (0.05 M)	43	33
5	4-CN-py (2.0 equiv) added	35	39
6	4-CN-py (0.5 equiv) added	62	29
7	HEH (3.0 equiv), KH_2PO_4 (3.0 equiv) 4-CN-py (1.0 equiv)	72 (70)[b]	23

[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield on 0.2 mmol scale.

2.6 Table S6. Control Experiments



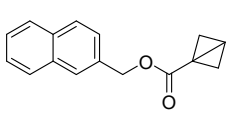
Entry	Deviation	**3aa**, Yield (%)	**4a**, Yield (%)
1	none	72	23
2	w/o [Co]	n.d.	n.d.
3	w/o HEH	n.d.	n.d.
4	w/o light	n.d.	n.d.
5	w/o **2a**	n.d.	87
6	w/o **2a**, 4-CN-py	n.d.	91 (86)[b]

[a]Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield on 0.2 mmol scale.

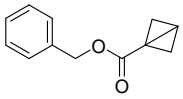
3. Preparation of Substrates and Catalysts

The bicyclo[1.1.0]butanes (BCBs, substrates **1**) were synthesized according to the previous report. The procedures for the synthesis of substrates **1a** – **1l** were slightly modified based on the previous reports.[1, 2] The procedures for the synthesis of substrates **1m**, **1o**, and **1p** were in consistent with the reported literature.[3-5] The substrates of alkenes **2a** – **2p**, and **2r** – **2z** were all commercially available. The cobalt catalysts used were commercially available except $Co(dmgH)_2$(4-CN-py)Cl and $Co(dmgH)_2$(4-CF_3-py)Cl.

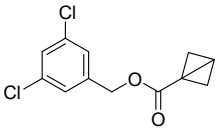
Substrates of BCBs



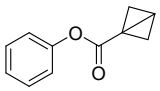
1a



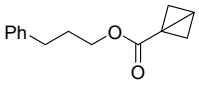
1b



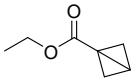
1c



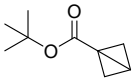
1d



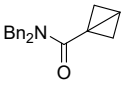
1e



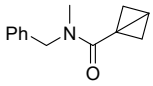
1f



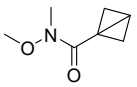
1g



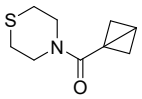
1h



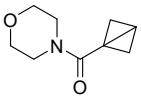
1i



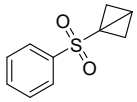
1j



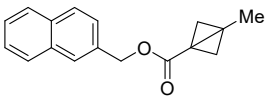
1k



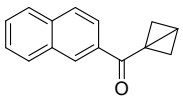
1l



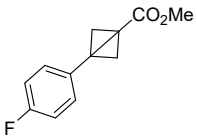
1m



1n

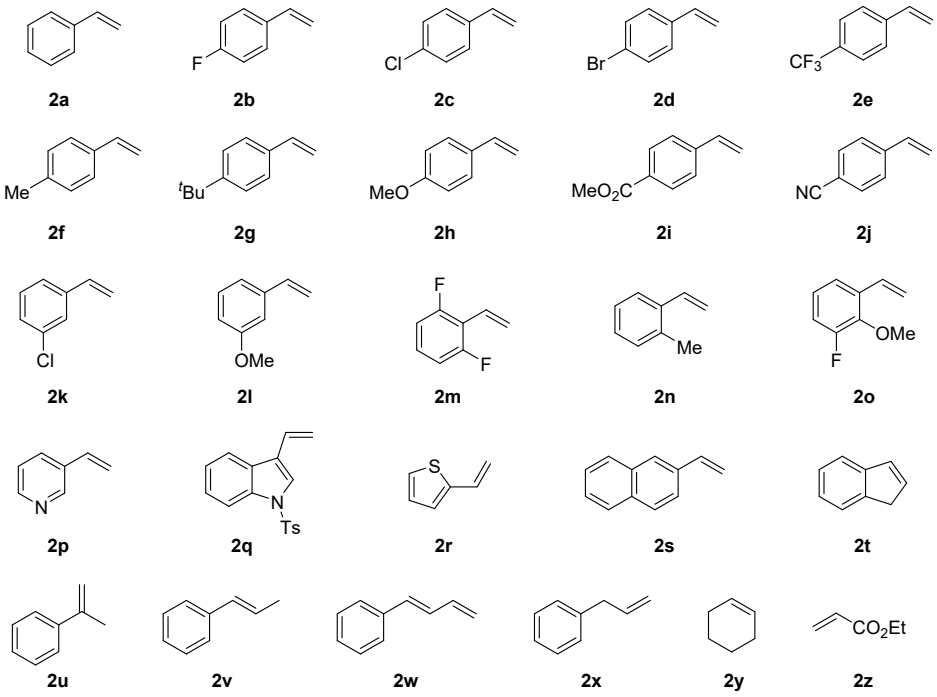


1o

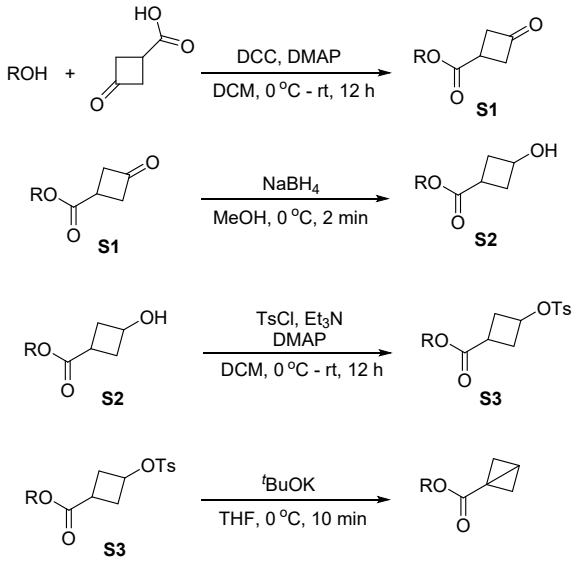


1p

Substrates of Alkenes



General Procedure A for the Synthesis of Substrates 1a – 1g



Step 1: A solution of the corresponding alcohol (10 mmol, 1.0 equiv), 3-oxocyclobutane-1-carboxylic acid (1.14 g, 10 mmol, 1.0 equiv) and 4-dimethylaminopyridine (122.2 mg, 1.0 mmol, 0.1 equiv) in DCM (40 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (2.27 g, 11 mmol, 1.1 equiv) in DCM (10.0 mL) was added dropwise for 15 min. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced

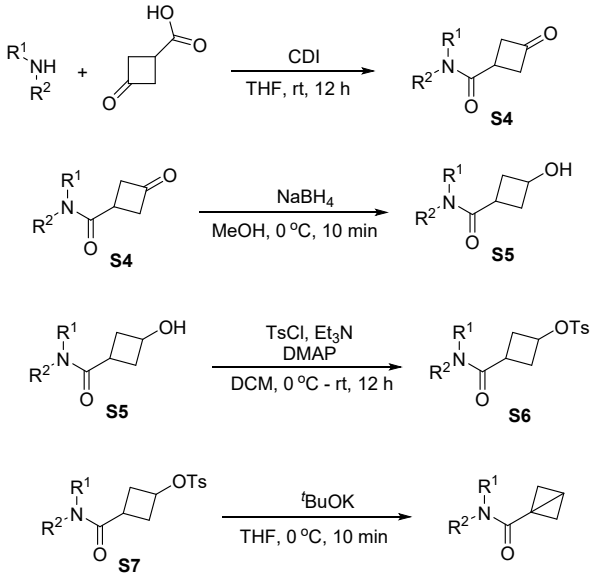
pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 4/1) to afford the compounds **S1** in good yields.

Step 2: A round bottom flask equipped with a magnetic stir bar was added compound **S1** and methanol (0.33 M). The solution was stirred at 0 °C in an ice bath for 10 min. Then $NaBH_4$ (0.5 equiv) was added slowly and the resulting mixture was allowed to stirred for 2.0 min. Afterwards, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford compound **S2**, which was directly used without further purification.

Step 3: A solution of compound **S2** and 4-dimethylaminopyridine (0.1 equiv) in DCM (1.0 M) was stirred at 0 °C in an ice bath. Then Et_3N (1.2 equiv) and 4-toluenesulfonyl chloride (1.2 equiv) was added to the solution. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, water (15 mL) was added to the solution and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 4/1) to afford the compound **S3** in good yields (ranging from 70% to 90%).

Step 4: A solution of compound **S3** (5.0 mmol, 1.0 equiv) in THF (0.2 M) was stirred at 0 °C in an ice bath for 10 min. Afterwards, ^{t}BuOK (1.1equiv, 1.0 M in THF) was added dropwise for 15 min. The resulting mixture was allowed to stir for another 10 min. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 30/1) to afford the substrate BCBs in moderate yields.

General Procedure B for the Synthesis of Substrates 1h – 1l



Step 1: A solution of 3-oxocyclobutane-1-carboxylic acid (1.14 g, 10 mmol, 1.0 equiv) and 1,1'-carbonyldiimidazole (1.62 g, 10 mmol, 1.0 equiv) in THF (30 mL) was stirred at room temperature for 2.0 h. Then, the corresponding amine (10 mmol, 1.0 equiv) was added to the solution and the resulting mixture was allowed to stir for another 10 h. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 1/1) to afford the compounds **S4** in good yields (ranging from 80% - 90%).

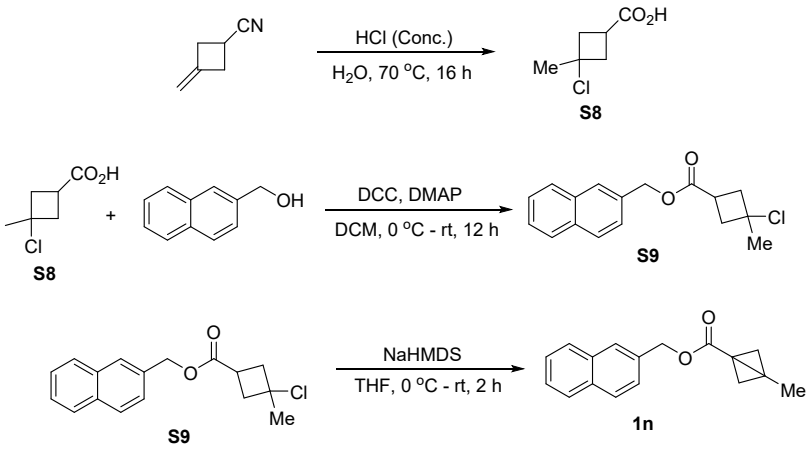
Step 2: A round bottom flask equipped with a magnetic stir bar was added compound **S4** and methanol (0.33 M). The solution was stirred at 0 °C in an ice bath for 10 min. Then $NaBH_4$ (0.5 equiv) was added slowly and the resulting mixture was allowed to stirred for 10 min. Afterwards, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford compound **S5**, which was directly used without further purification.

Step 3: A solution of compound **S5** and 4-dimethylaminopyridine (0.1 equiv) in DCM (1.0 M) was stirred at 0 °C in an ice bath. Then Et_3N (1.2 equiv) and 4-toluenesulfonyl chloride (1.2 equiv) was

added to the solution. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, water (15 mL) was added to the solution and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 1/1) to afford the compounds **S6** in good yields (ranging from 70% to 90%).

Step 4: A solution of compound **S6** (5.0 mmol, 1.0 equiv) in THF (0.2 M) was stirred at 0 °C in an ice bath for 10 min. Afterwards, ^{t}BuOK (1.1 equiv, 1.0 M in THF) was added dropwise for 15 min. The resulting mixture was allowed to stir for another 10 min. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 4/1) to afford the substrate BCBs in moderate yields.

Synthesis of Substrate 1n[6]



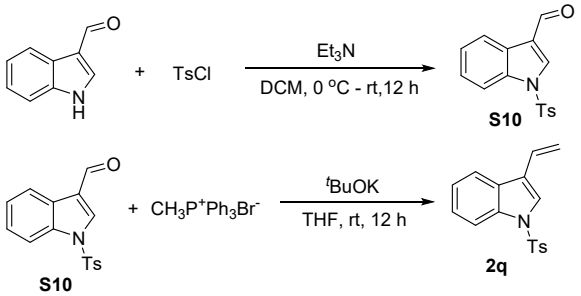
Step 1: A round bottom flask equipped with a magnetic stir bar was added 3-methylenecyclobutane-1-carbonitrile (0.93 g, 10.0 mmol, 1.0 equiv) and concentrated HCl solution (10 mL). The flask was heated to 70 °C in an oil bath and stirred vigorously for 16 h. Upon completion, the solution was cooled to room temperature and the diluted with water (25 mL). The resulting mixture was extracted with Et_2O for 3 times (3 × 25 mL). The combined organic layer was

washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford **S8**, which was directly used without further purification.

Step 2: A solution of the compound **S8** (assuming 10 mmol, 1.0 equiv), naphthalen-2-ylmethanol (1.58 g, 10 mmol, 1.0 equiv) and 4-dimethylaminopyridine (122.2 mg, 1.0 mmol, 0.1 equiv) in DCM (40 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (2.27 g, 11 mmol, 1.1 equiv) in DCM (10.0 mL) was added dropwise for 15 min. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 4/1) to afford the compound **S9** (2.39 g, 83% yield) as a pale green oil.

Step 3: A solution of compound **S9** (2.30 g, 8.0 mmol) in THF (20 mL, 0.4 M) was stirred at 0 °C under Ar in an ice bath for 10 min. Afterwards, NaHMDS (4.8 mL, 1.2 equiv, 2.0 M in THF) was added dropwise for 15 min. The resulting mixture was warmed to room temperature and stirred for 2.0 h. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc for 3 times (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 20/1) to afford the substrate **1n** (1.25 g, 62% yield) as a colorless oil.

Synthesis of Substrate 2q[7]

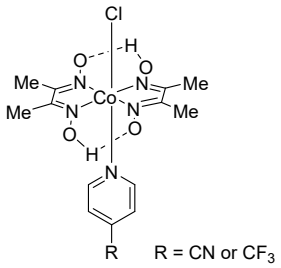


Step 1: A solution of 1*H*-indole-3-carbaldehyde (0.73 g, 5.0 mmol, 1.0 equiv) and 4-methylbenzenesulfonyl chloride (1.14 g, 6.0 mmol, 1.2 equiv) in DCM (10 mL, 0.5 M) was stirred at 0 °C in an ice bath for 5.0 minutes, then Et_3N (0.84 mL, 6.0 mmol, 1.2 equiv) was injected in one portion. The resulting mixture was warmed to room temperature and stirred for 12 h. Upon

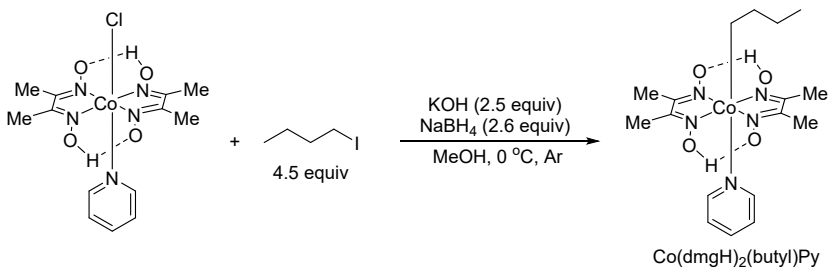
completion, the reaction was quenched with a sat. NH_4Cl solution and extracted with $CHCl_2$ for 3 times (3 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 4/1) to afford the compound **S10** (1.36 g, 91% yield) as a yellow solid.

Step 2: A solution of methyltriphenylphosphonium bromide (2.14 g, 6.0 mmol, 1.5 equiv) and ^{t}BuOK (0.67 g, 6.0 mmol, 1.5 equiv) in THF (20.0 mL) was stirred at room temperature for 1.0 h. Afterwards the compound **S10** (1.20 g, 4.0 mmol, 1.0 equiv) in THF (5.0 mL) was added and the solution was stirred for another 11 h. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 6/1) to afford the substrate **2q** (0.65 g, 55% yield) as a white solid.

Synthesis of Cobalt Catalyst[8]



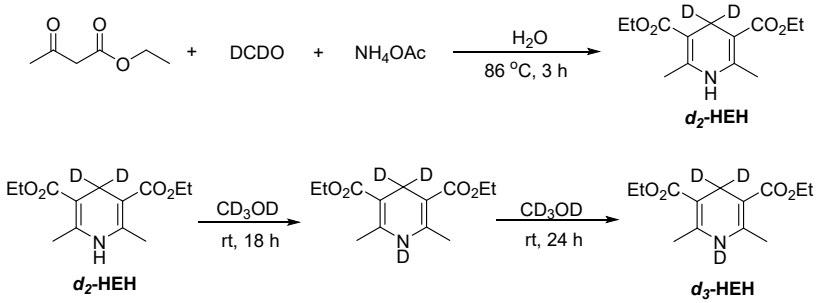
A solution of $Co(dmgH)(dmgH_2)Cl_2$ (1.0 equiv) and the corresponding pyridine derivative (1.0 equiv) in MeOH (0.03 M) was stirred at room temperature for 3.0 h. Afterwards, a brown precipitate was formed. The flask was cooled to -10 ^{o}C and the resulting mixture was filtered and washed with water, ethanol, and Et_2O to afford the cobalt catalyst. The catalyst was directly used without further purification after drying.[8a]



In a two-neck round-bottom flask (100 mL), KOH (84.2 mg, 1.5 mmol, 2.5 equiv) and $Co(dmgH)_2pyCl$ (242.2 mg, 0.6 mmol, 1.00 equiv) were dissolved in 20 mL of methanol. The flask was cooled to 0 °C and the solution was degassed by a forced flow of argon via a needle adaptor for 20 min. Then $NaBH_4$ (59.0 mg, 2.6 equiv) was added into the reaction mixture under argon. The resulting mixture was allowed to stirred for 5 min. Subsequently, ^{n}BuI (0.31 mL, 2.7 mmol, 4.50 equiv.) was added to the reaction mixture. The reaction mixture was stirred at 0 °C for another 30 minutes. Upon completion, acetone (4 mL) and water (60 mL) were added. The resulting precipitate was collected by filtration over a Büchner funnel, rinsed with water (30 mL) and dried at room temperature under vacuum to afford $Co(dmgH)_2$(butyl)py (81.7 mg, 32% yield) as an orange solid.[8b, 8c]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 4.8 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.35 – 7.28 (m, 2H), 2.13 (s, 12H), 1.68 – 1.59 (m, 2H), 1.26 – 1.15 (m, 2H), 0.94 – 0.85 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.0, 149.0, 137.3, 125.1, 33.0, 23.7, 14.0, 12.0 (The signal from the carbon bound to cobalt was absent).

Synthesis of Deuterated Hantzsch Esters[9]

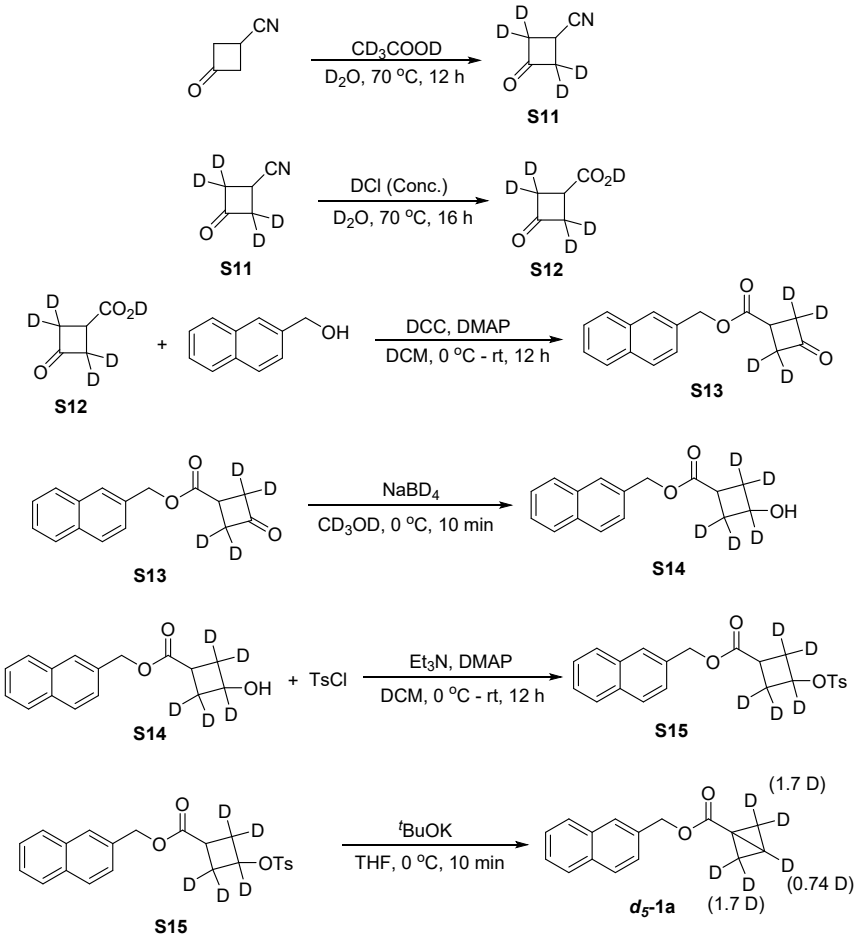


In an oven-dried round bottom flask equipped with a magnetic stir bar, ethyl acetoacetate (1.5 mL, 12.0 mmol, 4.0 equiv), d_2-paraformaldehyde (96.1 mg, 3.0 mmol, 1.0 equiv), ammonium acetate (0.46 g, 6.0 mmol, 2.0 equiv) and water (6.0 mL) was added. The mixture was stirred vigorously at 86 °C in an oil bath for 3.0 hours. After cooling down to room temperature, the mixture was filtered and the obtained precipitate was dried to afford compound ***d_2*-HEH** (525.0 mg, 69% yield) as a yellow solid.

A solution of compound ***d_2*-HEH** (0.51 g, 2.0 mmol) in CD_3OD (4.0 mL) was stirred under Ar at

room temperature for 18 h. The solvent was evaporated and another CD_3OD (2.0 mL) was added. The resulting mixture was allowed to stir for another 24 h. The deuterated Hantzsch Esters was obtained after removing the solvent as a pale green solid (492.0 mg, 96% yield). The spectral data of deuterated Hantzsch Esters is consisted with the previous reports.[9] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.17 (q, J = 7.1 Hz, 4H), 2.19 (s, 6H), 1.29 (t, J = 7.1 Hz, 6H).

Synthesis of Deuterated Substrate *d_5*-1a[10]



Step 1: A solution of the 3-oxocyclobutane-1-carbonitrile (1.43 g, 15 mmol, 1.0 equiv), acetic acid-d_4 in D_2O (6.0 mL) was stirred at 70 °C in an oil bath for 12 h. Upon completion, anhydrous Na_2SO_4 was added and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 15 mL). Then the solvent was removed under reduced pressure to afford compound **S11** (1.48 g, 99% yield) as a pale yellow solid, which was directly used without further purification.

Step 2: A solution of the compound **S11** (1.48 g, 15 mmol, 1.0 equiv) in deuterium chloride (15 mL) was stirred at 70 °C in an oil bath for 16 h. Upon completion, the solution was cooling down to room temperature, and diluted with D_2O (25 mL). The resulting mixture was extracted with Et_2O for 3 times (3 × 20 mL). Then the solvent was removed under reduced pressure to afford compound **S12** (1.37 g, 77% yield) as a white solid, which was directly used without further purification.

Step 3: A solution of naphthalen-2-ylmethanol (10 mmol, 1.0 equiv), compound **S12** (1.19 g, 10 mmol, 1.0 equiv) and 4-dimethylaminopyridine (122.2 mg, 1.0 mmol, 0.1 equiv) in DCM (40 mL) was stirred at 0 °C in an ice bath for 10 min. Afterwards, the solution of dicyclohexylcarbodiimide (2.27 g, 11 mmol, 1.1 equiv) in DCM (10.0 mL) was added dropwise for 15 min. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 4/1) to afford the compound **S13** as a white solid (2.2 g, 85% yield).

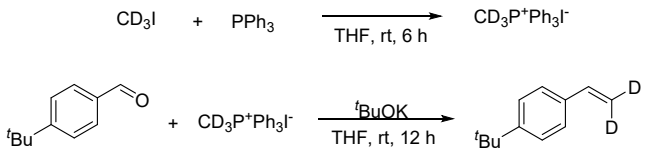
Step 4: A round bottom flask equipped with a magnetic stir bar was added compound **S13** (8.5 mmol, 2.2 g) and methanol-d_4 (25 mL). The solution was stirred at 0 °C in an ice bath for 10 min. Then $NaBD_4$ (4.25 mmol, 177.9 mg, 0.5 equiv) was added slowly and the resulting mixture was allowed to being stirred for 2.0 min. Afterwards, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford compound **S14**, which was directly used without further purification.

Step 5: A solution of compound **S14** (2.09 g, 8.0 mmol) and 4-dimethylaminopyridine (97.8 mg, 0.8 mmol, 0.1 equiv) in DCM (8.0 mL) was stirred at 0 °C in an ice bath. Then Et_3N (1.3 mL, 1.2 equiv) and 4-toluenesulfonyl chloride (1.83 g, 1.2 equiv) was added to the solution. The reaction system was warmed to room temperature and stirred for 12 h. Upon completion, water (15 mL) was added to the solution and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 4/1) to afford the compound **S15** as a yellow solid (2.36 g, 71% yield).

Step 6: A solution of compound **S15** (2.08 g, 5.0 mmol, 1.0 equiv) in THF (0.2 M) was stirred at 0 °C in an ice bath for 10 min. Afterwards, ^{t}BuOK (5.5 mL, 1.1 equiv, 1.0 M in THF) was added dropwise for 15 min. The resulting mixture was allowed to stir for another 10 min. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 30/1) to afford the substrate *d*$_5$-**1a** as a colorless oil (0.91 g, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.50 – 7.43 (m, 3H), 5.31 (s, 2H), 2.40 – 2.39 (m, 0.3H), 2.14 – 2.13 (m, 0.26H), 1.18 – 1.17 (m, 0.3H); **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{16}H_9D_5O_2$ 243.1302; found 243.1305.

Synthesis of Deuterated Substrate *d*$_2$-2g[11]



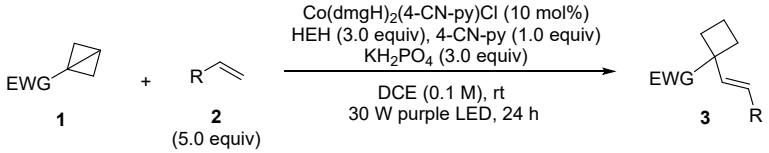
Step 1: In an oven-dried round bottom flask equipped with a magnetic stir bar, triphenylphosphine (1.31 g, 5.0 mmol, 1 equiv) and THF (25 mL) was added. The mixture was stirred at room temperature for 10 min. Then CD_3I (0.37 mL, 6.0 mmol, 1.2 equiv) was added dropwise. Upon completion, the mixture was filtered and washed by anhydrous THF (20 mL). The (methyl-*d*$_3$)triphenylphosphonium iodide was obtained as a white solid (1.34 g, 66% yield).

Step 2: A solution of (methyl-*d*$_3$)triphenylphosphonium iodide (1.22 g, 3.0 mmol, 1.5 equiv) and ^{t}BuOK (336.6 mg, 3.0 mmol, 1.5 equiv) in THF (10 mL) was stirred at room temperature for 1.0 h. Afterwards 4-(*tert*-butyl)benzaldehyde (0.34 mL, 2.0 mmol, 1.0 equiv) in THF (3.0 mL) was added and the resulting solution was stirred for another 11 h. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE) to afford the substrate ***d*$_2$-2g** (246.0 mg, 76% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 6.74 – 6.63 (m, 1H), 5.69 (d, *J* = 17.6 Hz, 0.17H), 5.17 (d, *J* = 10.8 Hz, 0.17H), 1.32 (s, 9H).

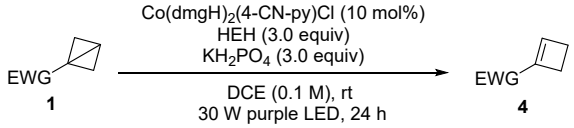
4. General Procedure for the Synthesis of Products

General Procedure C for the Synthesis of Product 3



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1** (0.2 mmol, 1.0 equiv), alkene **2** (1.0 mmol, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product **3**.

General Procedure D for the Synthesis of Product 4



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1** (0.2 mmol, 1.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product **4**.

For most of these cobalt-catalyzed reactions, the color of reaction solutions would change from yellow to brown after light irradiation. Here, we take the model reaction (**1a** and **2a**) as an example.

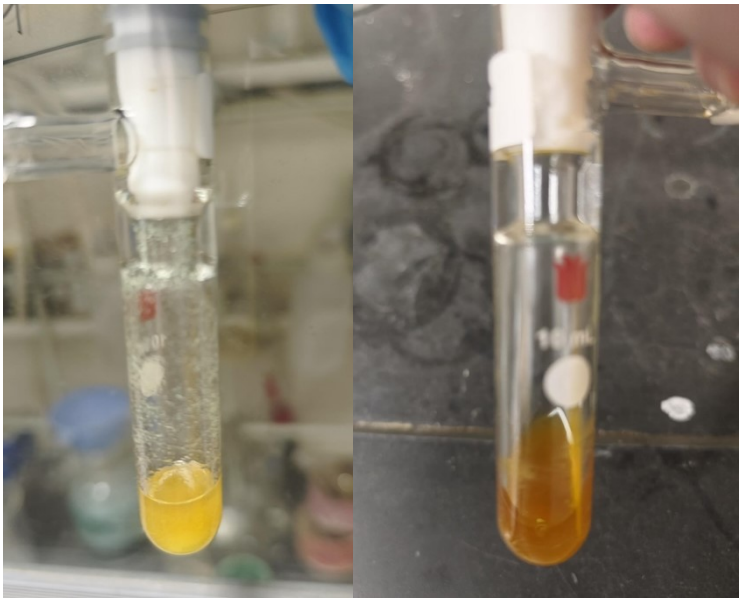
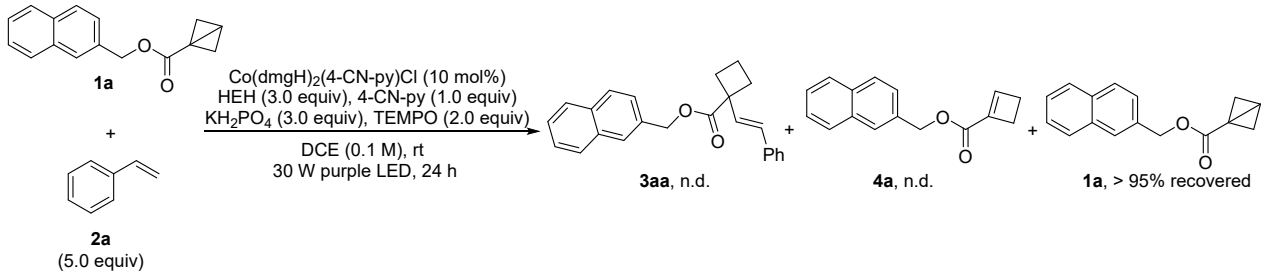


Figure S2. Color changes of the model reaction (left: before irradiation; right: after irradiation)

5. Mechanistic Studies

5.1 Radical Trapping Experiments



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (47.7 mg, 0.2 mmol, 1.0 equiv), styrene **2a** (0.11 mL, 1.0 mmol, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv), TEMPO (62.5 mg, 2.0 equiv) and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure. Products **3aa** and **4a** were not detected, and substrate **1a** was almost kept unchanged. Also, we did not obtain any TEMPO-adduct.

5.2 UV/vis Absorption Studies

All the UV-Vis absorption spectra were recorded on the SHIMADZU UV-2600 UV-visible spectrophotometer.

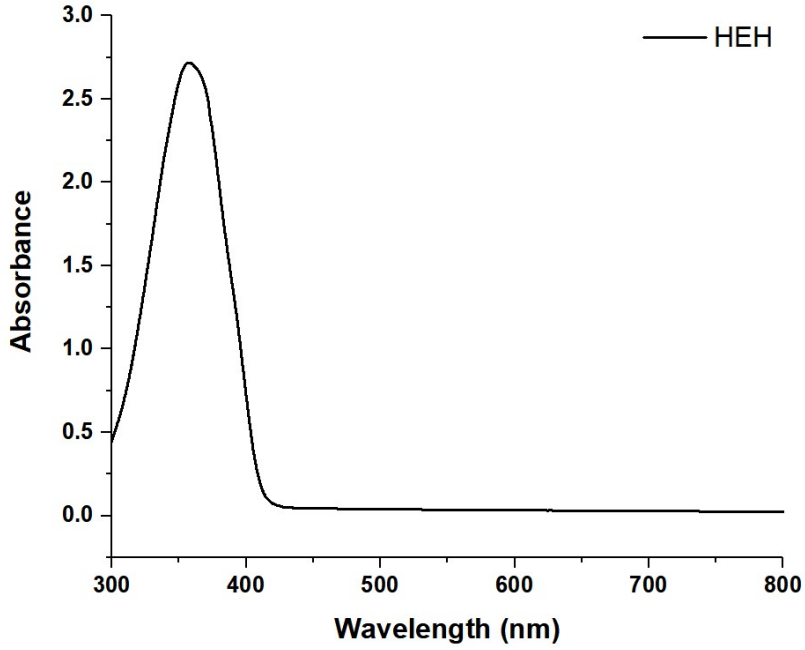


Figure S3. UV-Vis absorption spectra of **HEH** (0.1 mM) in DCE

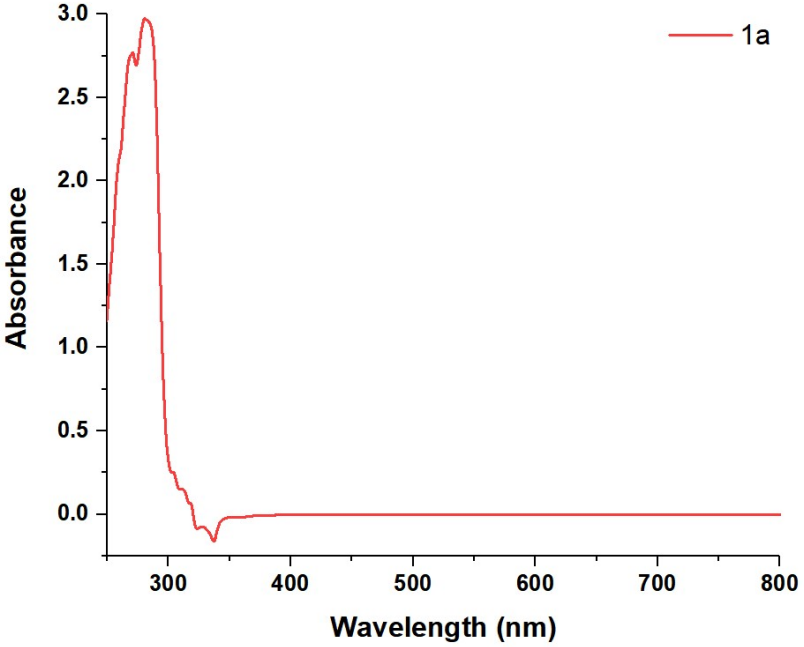


Figure S4. UV-Vis absorption spectra of **1a** (0.1 mM) in DCE

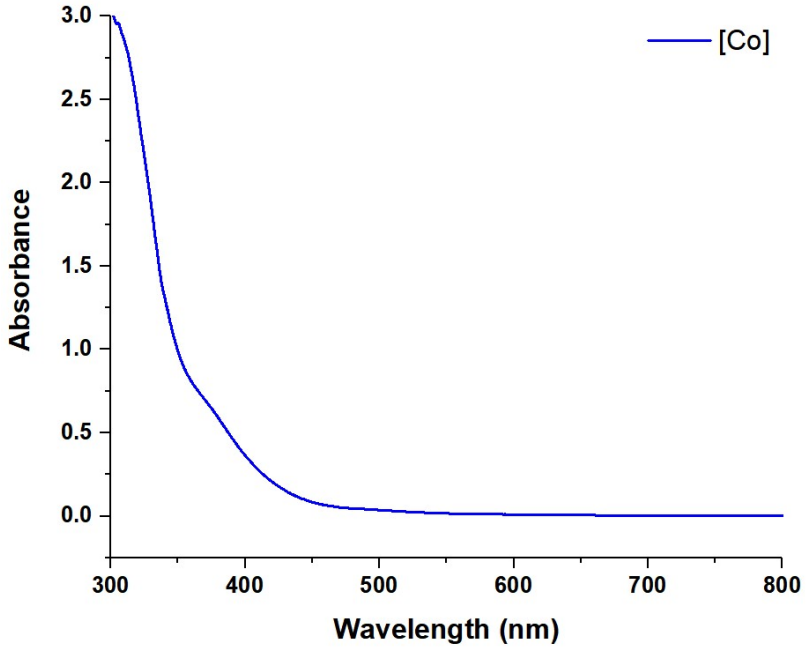


Figure S5. UV-Vis absorption spectra of $Co(dmgH)_2(4\text{-CN-py})Cl$ (0.1 mM) in DCE

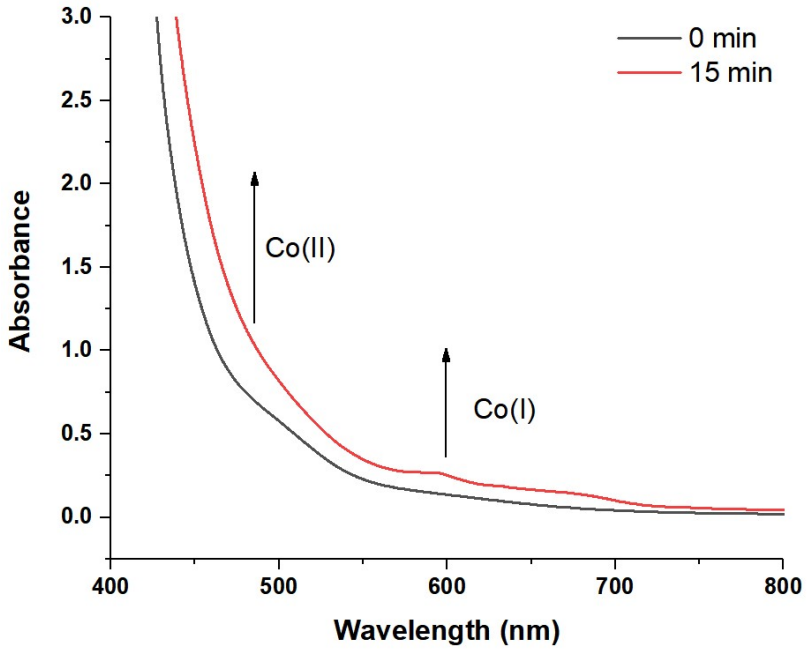


Figure S6. UV-Vis absorption spectra of the standard reaction mixtures (black line, using the model substrate BCB **1a** and styrene **2a**) and after 15 min (red line) of irradiation with 30 W purple LED under Ar. Two absorption bands at 450-500 nm and 550-700 nm appeared after 15 min irradiation and agreed with the formation of Co^{II} and Co^{I} intermediates, respectively.[12]

5.3 Emission Quenching Studies[13]

All the emission intensities were recorded by Hitachi F-4600 FL spectrometer. Solutions of HEH (1×10^{-2} M) in dry DCE were excited at 405 nm and the emission intensity was collected at the maximum wavelength 445 nm. Solutions of different concentration of $Co(dmgH)_2(4\text{-CN-py})Cl$, **1a** and **2a** were prepared respectively and introduced to a 1.0 cm path length quartz cuvette equipped with a Teflon® septum.

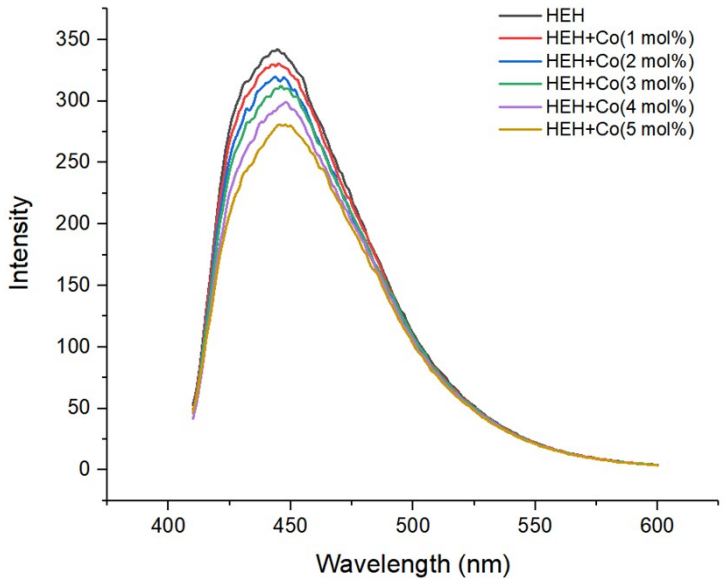


Figure S7. Stern-Volmer Quenching of HEH with [Co]

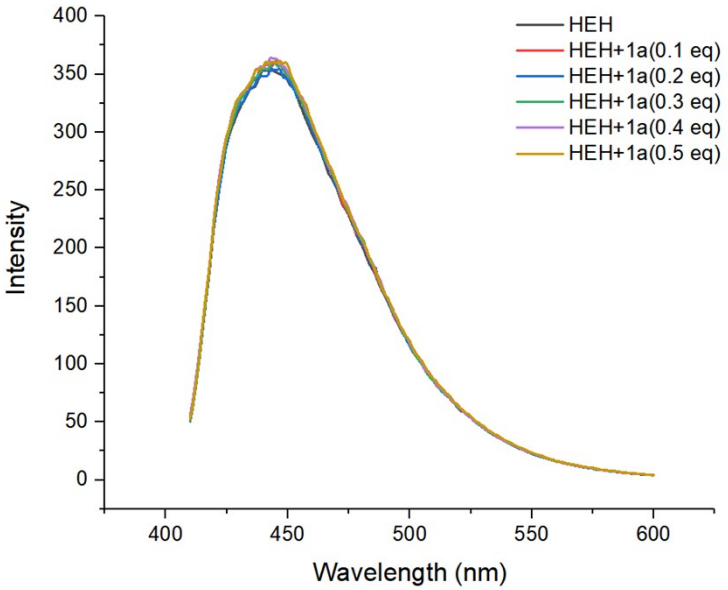


Figure S8. Stern-Volmer Quenching of HEH with Substrate **1a**

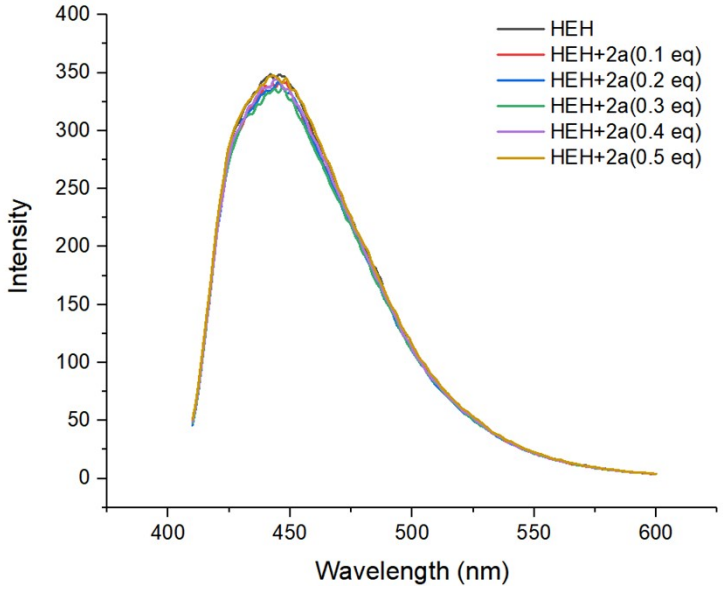


Figure S9. Stern-Volmer Quenching of HEH with **2a**

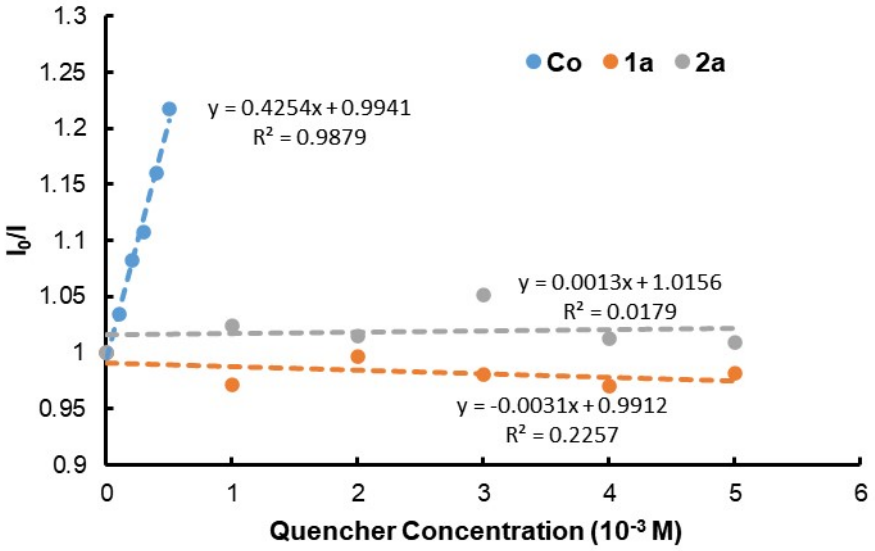
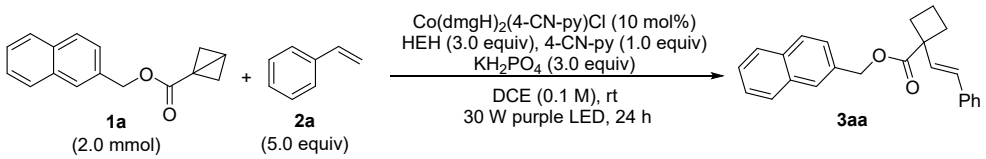


Figure S10. Stern-Volmer Quenching of HEH with [Co], **1a**, and **2a**

5.4 Dark-light Experiment



In a flame dried Schlenk tube (50 mL) equipped with a magnetic stir bar, substrate **1a** (0.48 g, 2.0 mmol, 1.0 equiv), styrene **2a** (1.1 mL, 10 mmol, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (85.6 mg, 10

mol%), HEH (1.52g, 3.0 equiv), isonicotinonitrile (208.2 mg, 1.0 equiv), and KH_2PO_4 (0.82 g, 3.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (20 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. The lights were turned on and off per two hours, and samples taken from the solution (0.3 mL per time) were analyzed by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.

Time (h)	**0**	**2**	**4**	**6**	**8**	**10**	**12**
Yield (%)	0	11	11	23	23	35	35

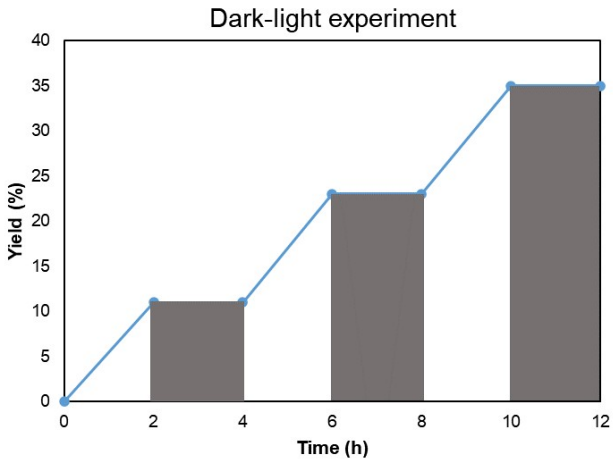
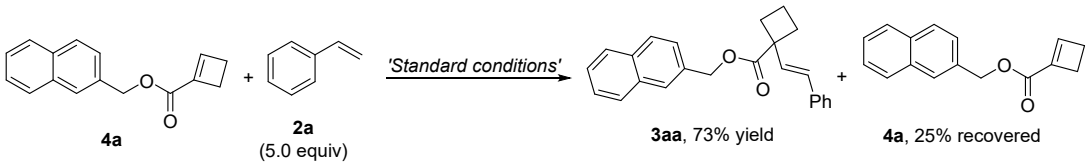


Figure S11. Light/dark cycle experiments

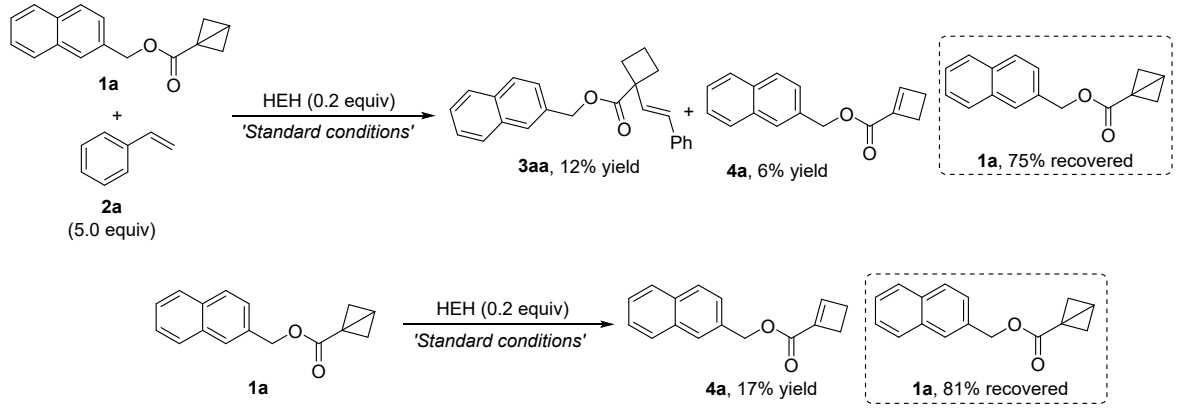
5.5 Investigation of the Transformations of 4a



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **4a** (0.2 mmol, 1.0 equiv), alkene **2a** (1.0 mmol, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill

for three times. Then, the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by a silica gel flash chromatography to afford the product **3aa** in 73% yield. In addition, the substrate **4a** was recovered in 25% yield.

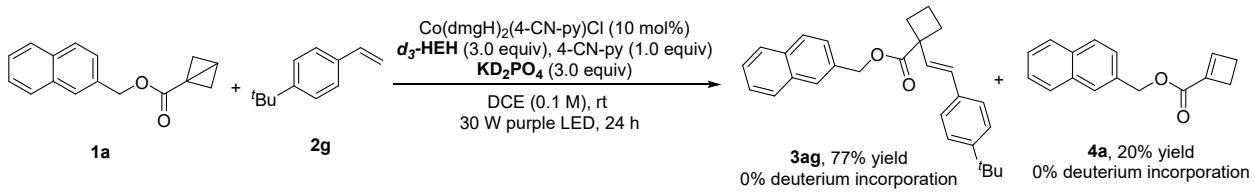
5.6 Investigation of Catalytic Amount of HEH



Based on general procedures C and D, a catalytic amount of HEH (0.2 equiv) was added to the two above reactions, respectively. We found that most of substrate **1a** was recovered in these Co-catalyzed reactions.

5.7 Deuterium Studies

Deuterated Hantzsch Esters and KD_2PO_4 Used Instead



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.2 mmol, 47.7 mg, 1.0 equiv), alkene **2g** (1.0 mmol, 160.3 mg, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), d_3-HEH (153.8 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) and KD_2PO_4 (82.9 mg, 3.0 equiv, 98% D, which is commercially available) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred

for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the products **3ag** and **4a** with 0% deuterium incorporation.

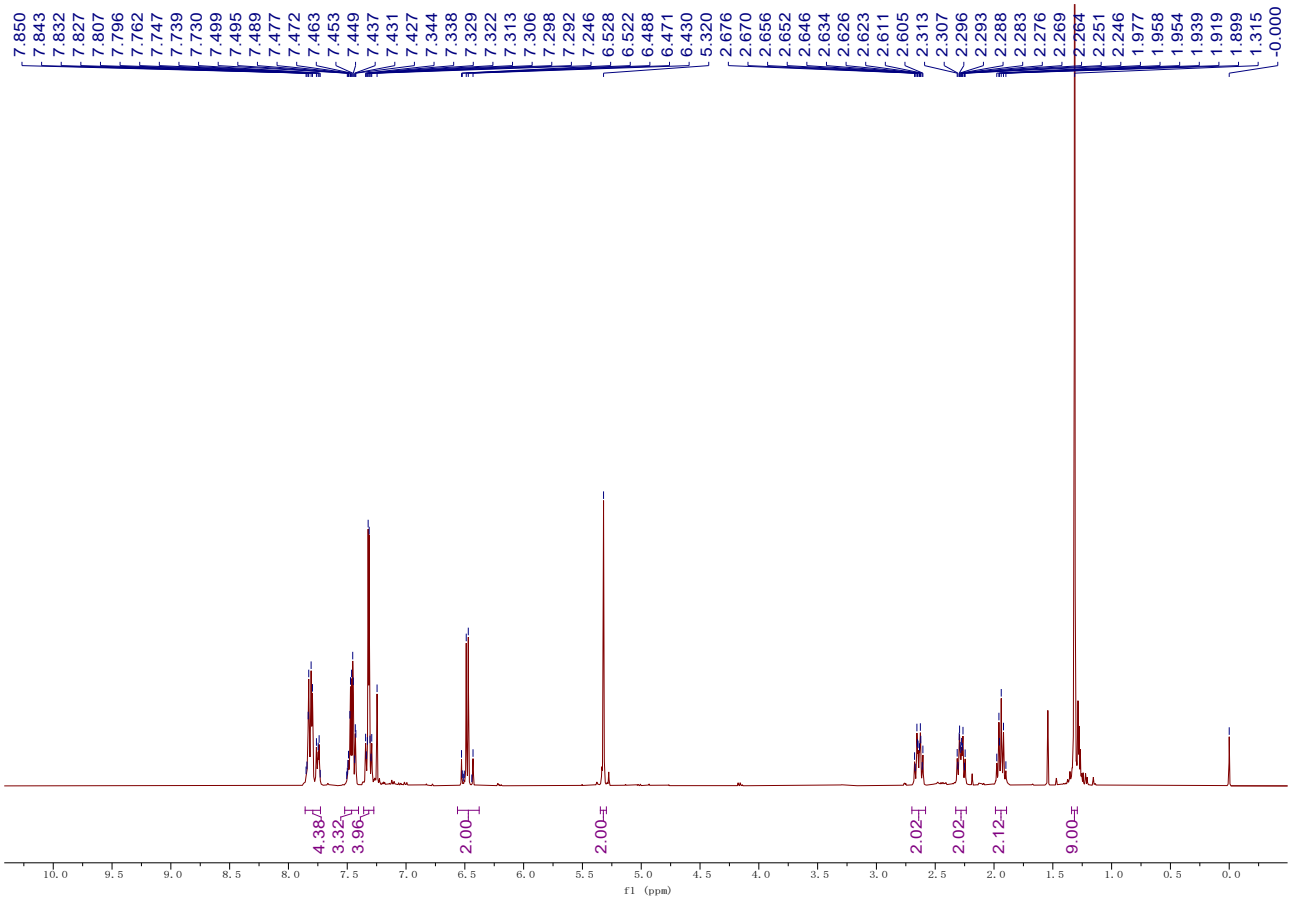


Figure S12. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **3ag**) of deuterium studies with ***d_3*-HEH** and **KD_2PO_4**

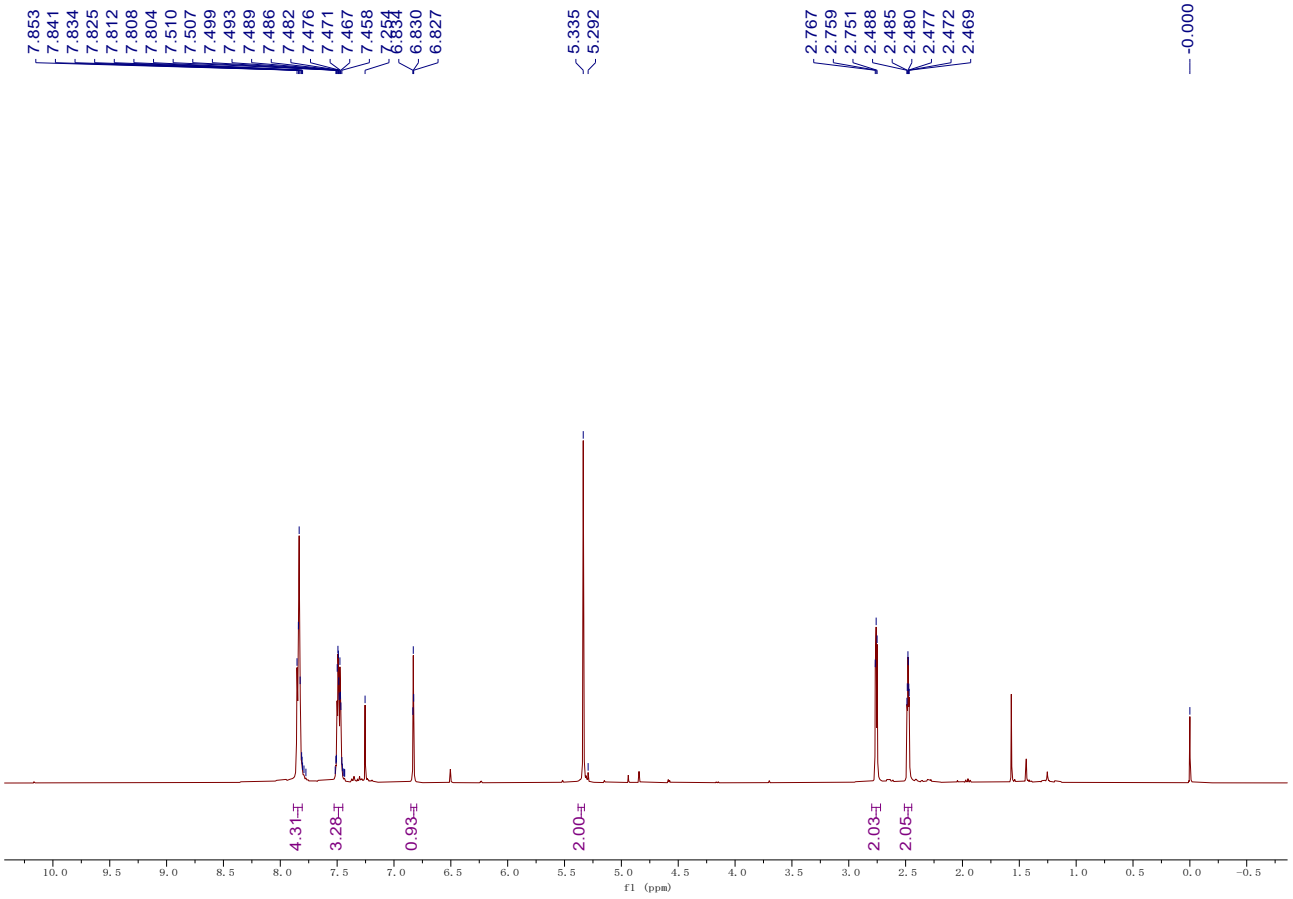
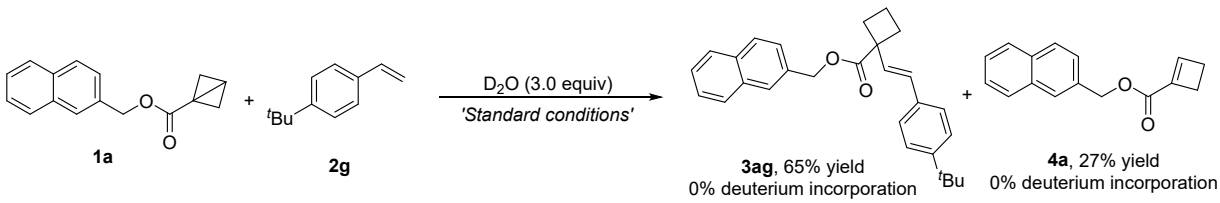


Figure S13. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **4a**) of deuterium studies with ***d_3*-HEH** and **KD_2PO_4**

D_2O was Added under the Standard Conditions



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.2 mmol, 47.7 mg, 1.0 equiv), alkene **2g** (1.0 mmol, 160.3 mg, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) KH_2PO_4 (81.6 mg, 3.0 equiv), and D_2O (11 μL, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain

temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified products **3ag** and **4a** with 0% deuterium incorporation.

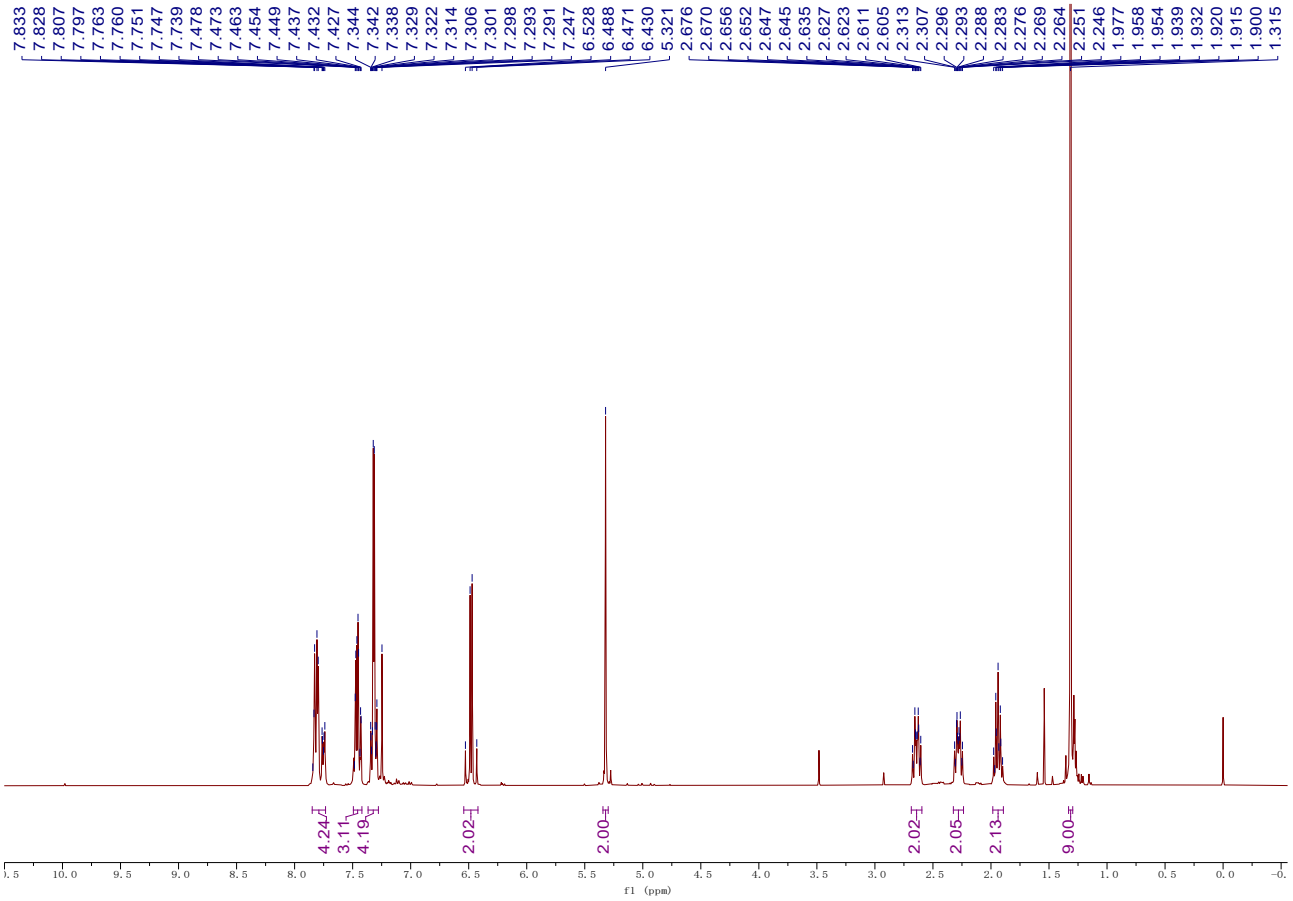


Figure S14. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **3ag**) of deuterium studies with **D_2O**

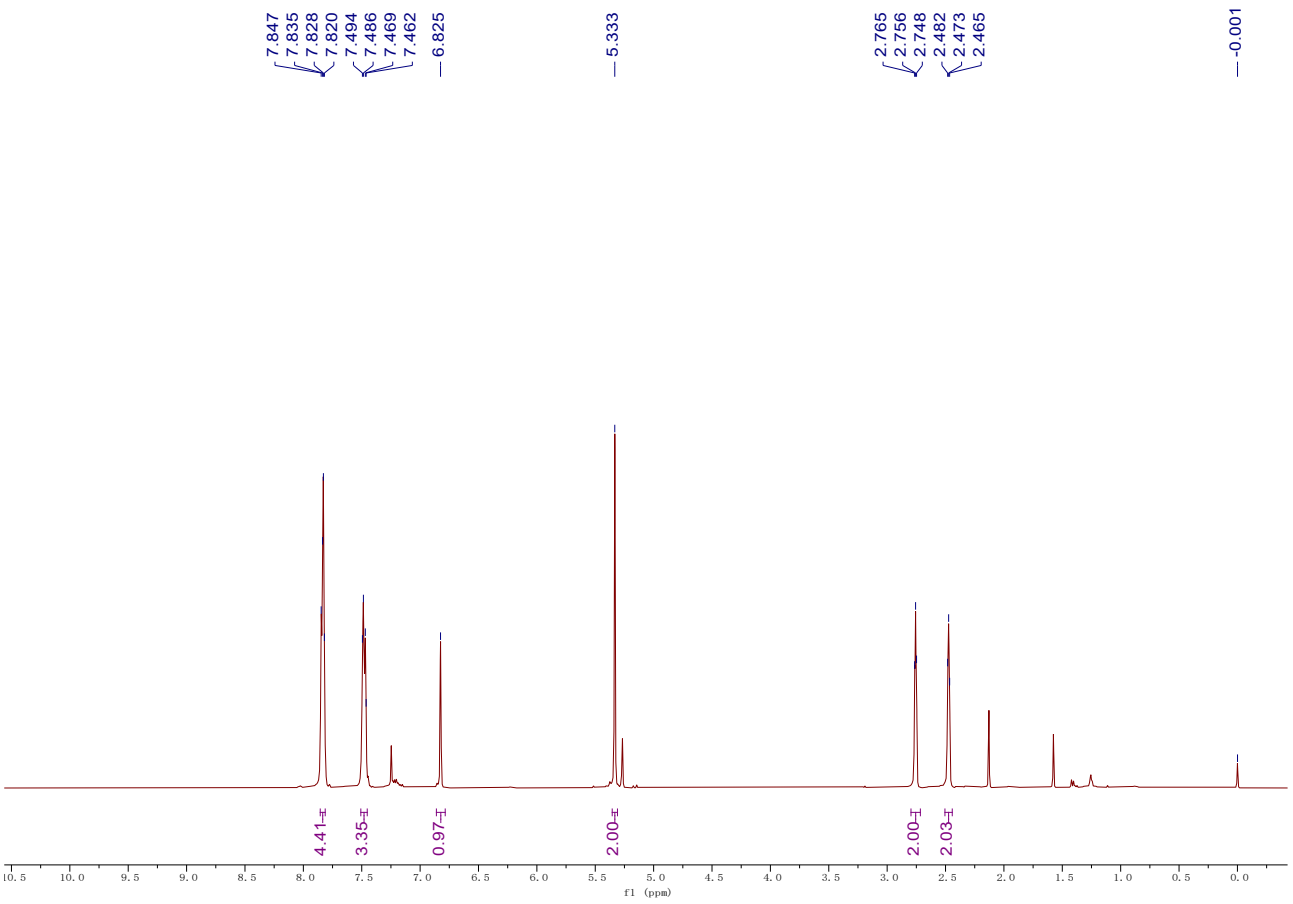
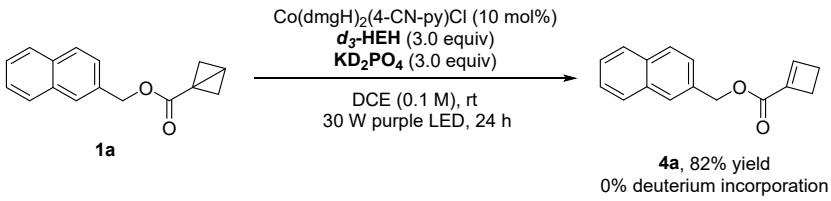


Figure S15. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **4a**) of deuterium studies with **D_2O**

Deuterated Hantzsch Esters and KD_2PO_4 Used Instead in Absence of Alkene



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.2 mmol, 47.7 mg, 1.0 equiv), $Co(dmgH)_2$(4-CN-py)Cl (8.6 mg, 10 mol%), d_3-HEH (153.8 mg, 3.0 equiv), and KD_2PO_4 (82.9 mg, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the product **4a** in 82% yield with 0%

deuterium incorporation.

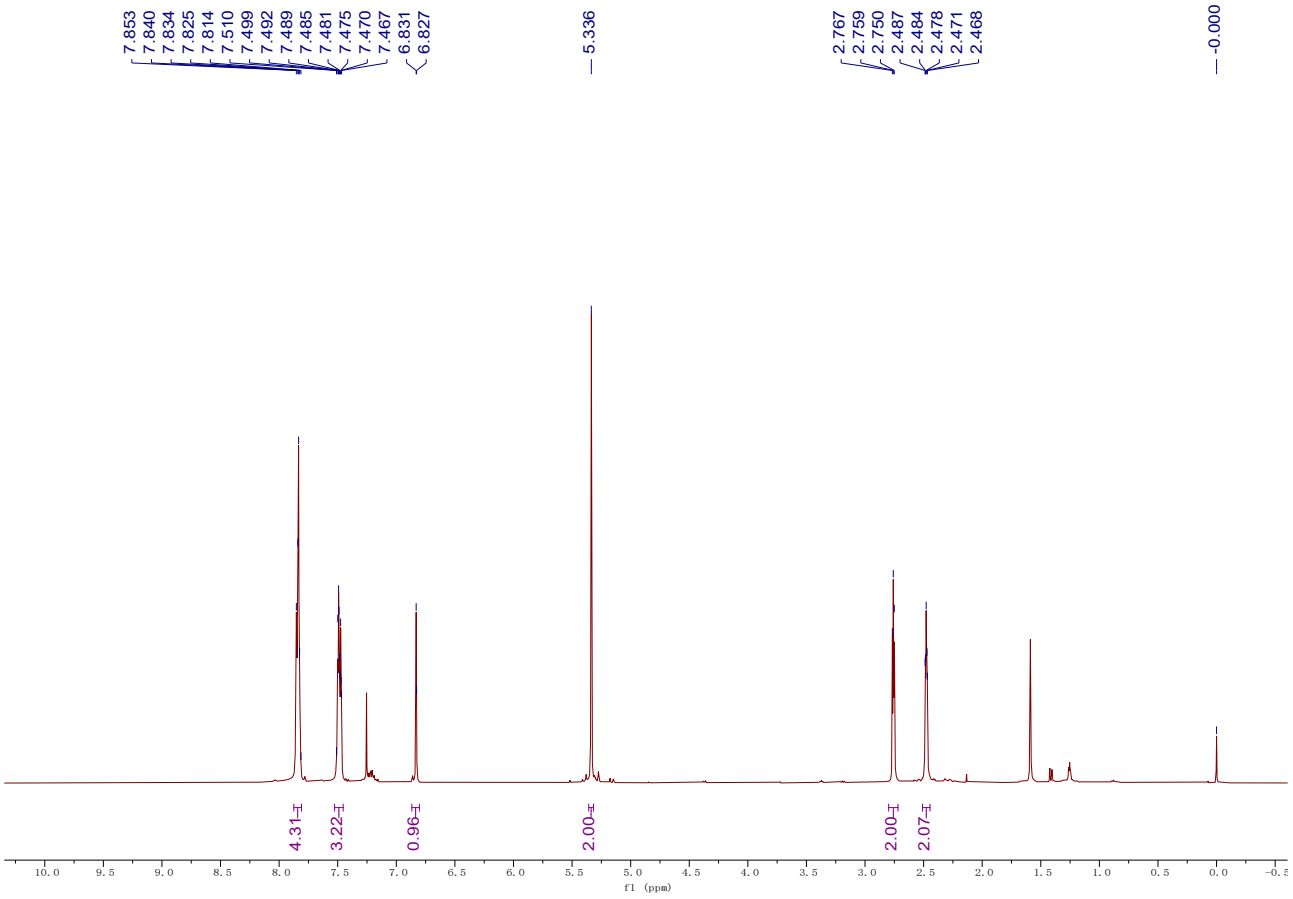
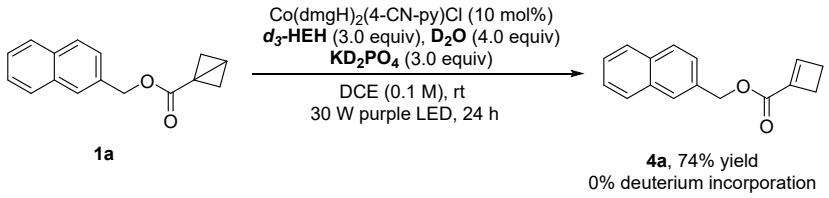


Figure S16. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **4a**) of deuterium studies with ***d_3*-HEH** and **KD_2PO_4**

Deuterated Hantzsch Esters, KD_2PO_4 and D_2O Used Instead in Absence of Alkene



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.2 mmol, 47.7 mg, 1.0 equiv), $Co(dmgH)_2$(4-CN-py)Cl (8.6 mg, 10 mol%), *d_3*-HEH (153.8 mg, 3.0 equiv), D2O (15 μL, 4.0 equiv), and KD_2PO_4 (82.9 mg, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a

fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the product **4a** in 74% yield with 0% deuterium incorporation.

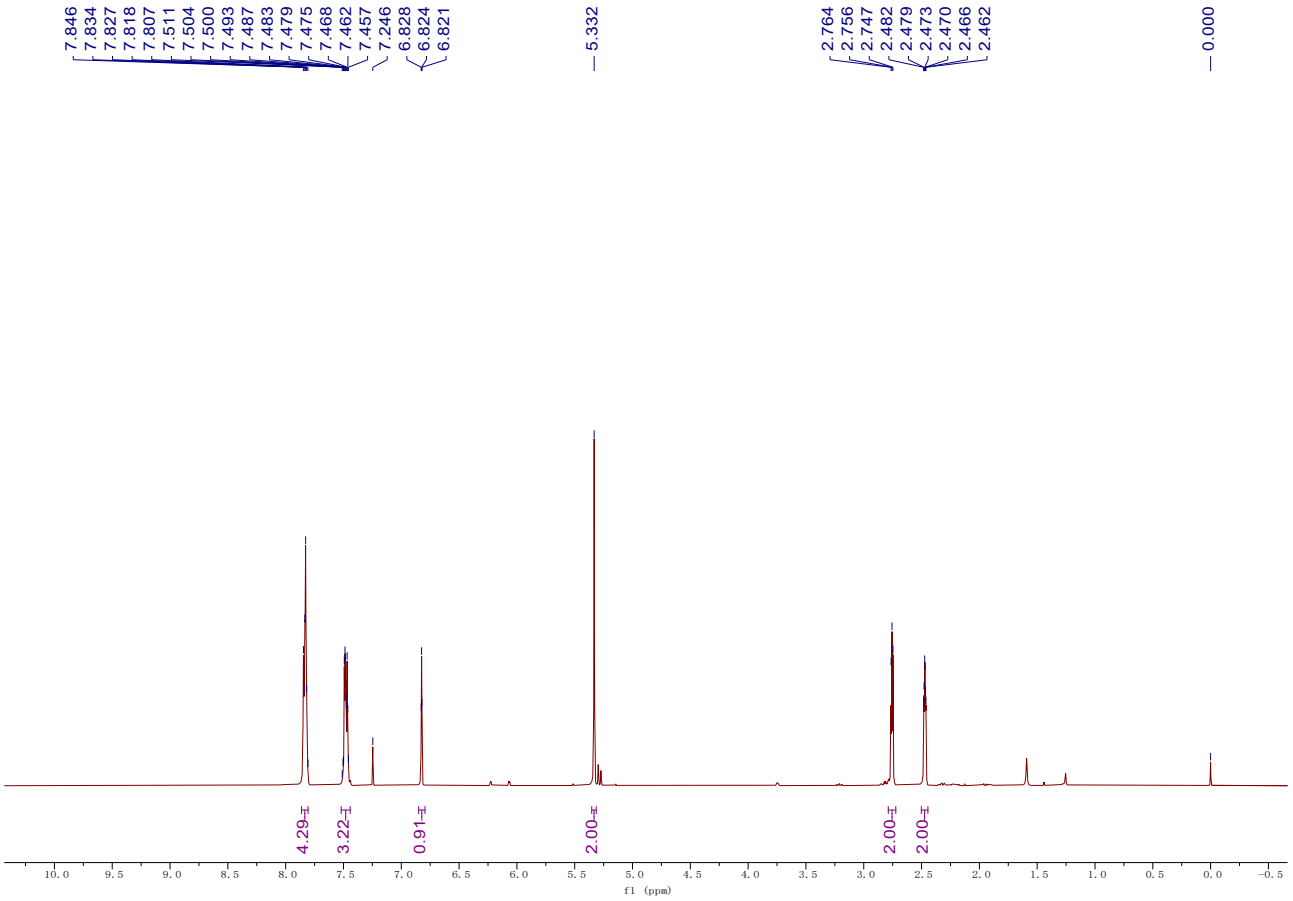
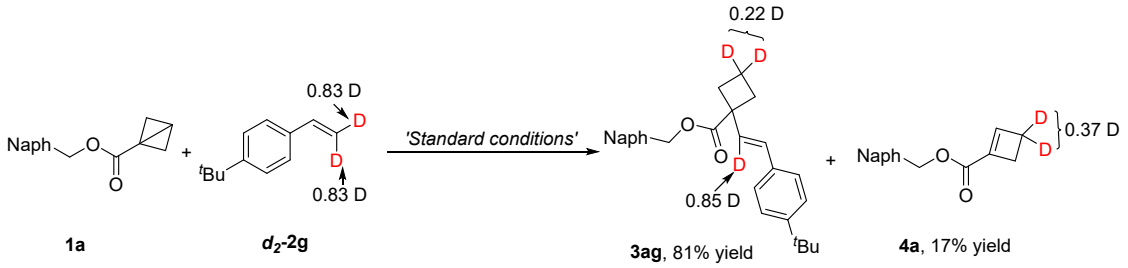


Figure S17. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **4a**) of deuterium studies with ***d_3*-HEH**, **KD_2PO_4** and **D_2O**

The Substrate *d_2*-2g Was Used Instead



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.2 mmol, 47.7 mg, 1.0 equiv), alkene ***d_2*-2g** (1.0 mmol, 162.3 mg, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) and KH_2PO_4

(81.6 mg, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified products.

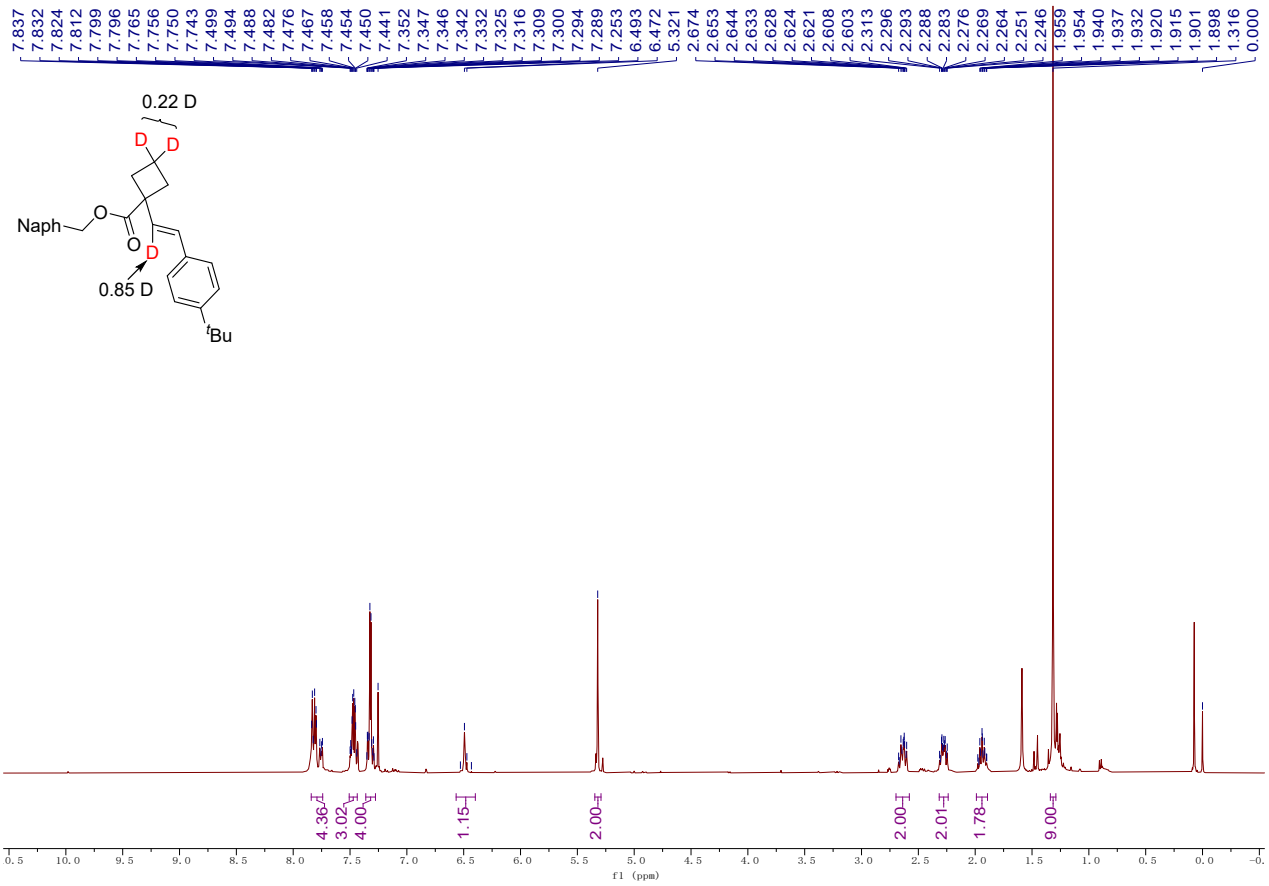


Figure S18. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **3ag**) of deuterium studies with ***d_2*-2g**

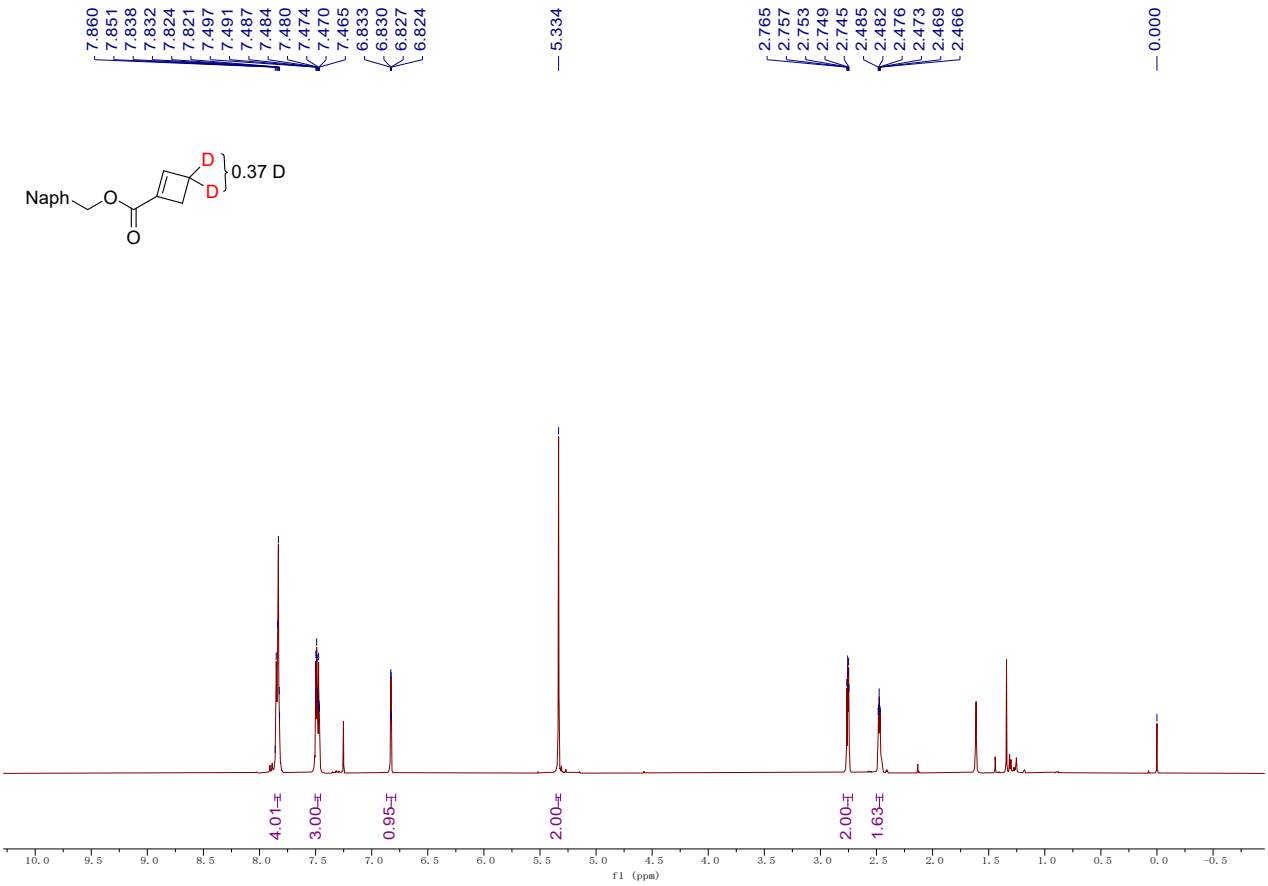
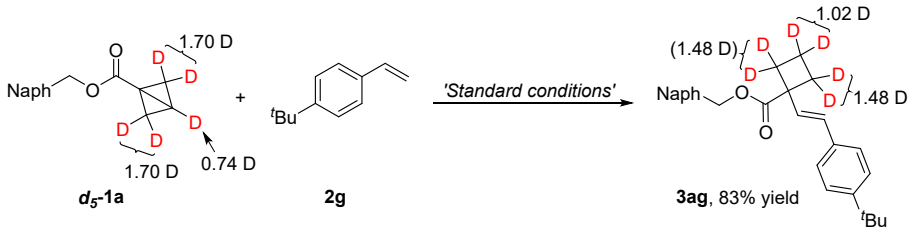


Figure S19. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **4a**) of deuterium studies with ***d_2*-2g**

The Substrate *d_5*-1a Was Used Instead



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate ***d_5*-1a** (0.2 mmol, 48.7 mg, 1.0 equiv), alkene **2g** (1.0 mmol, 160.3 mg, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a

silica gel flash chromatography to afford the purified product.

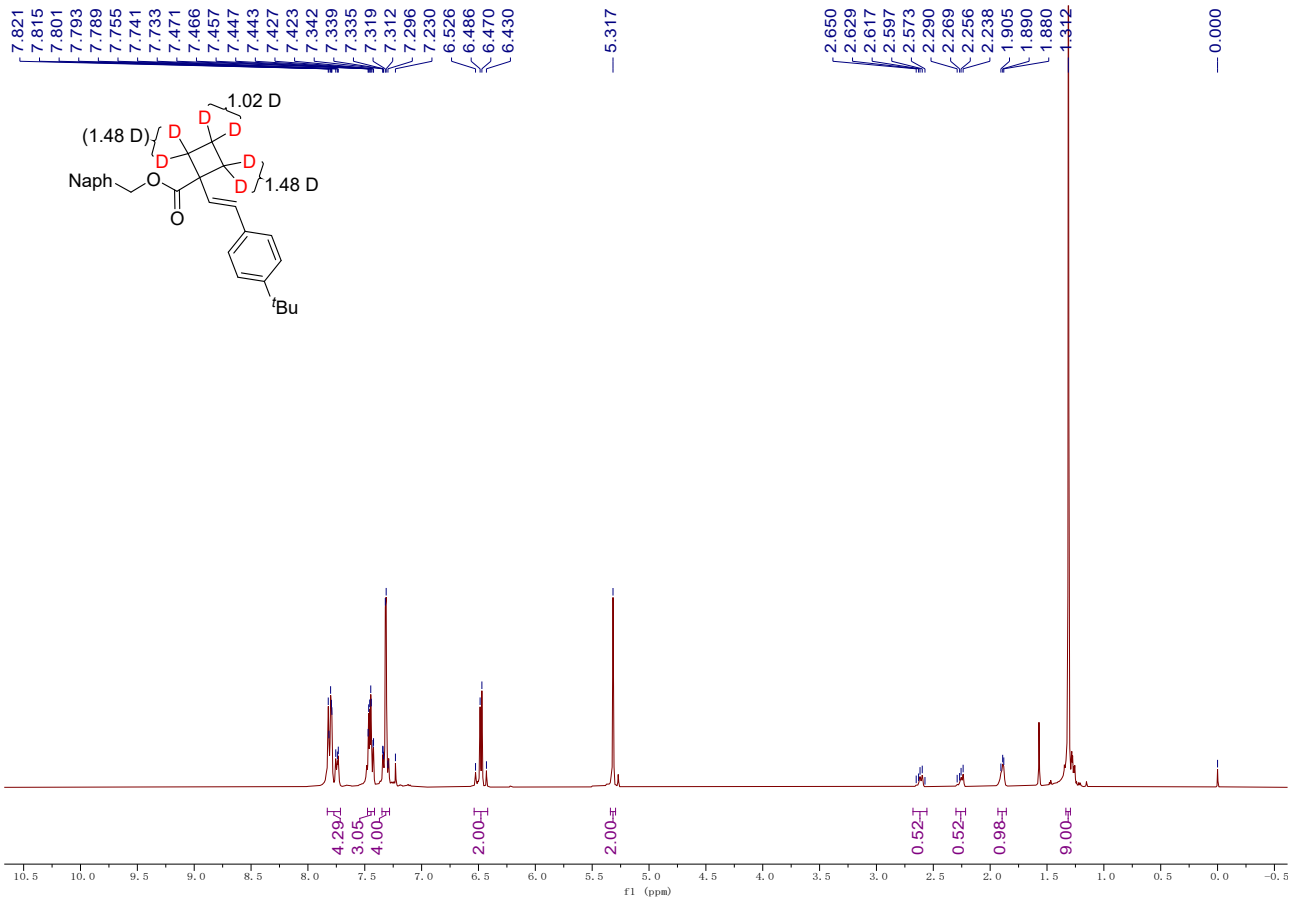
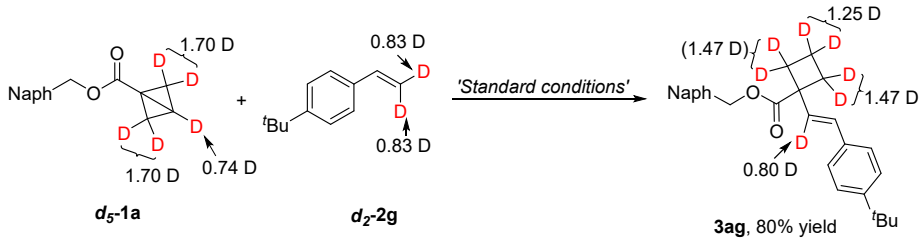


Figure S20. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **3ag**) of deuterium studies with ***d_5*-1a**

The Substrate *d_5*-1a and *d_2*-2g Was Used Instead



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate ***d_5*-1a** (0.2 mmol, 48.7 mg, 1.0 equiv), alkene ***d_2*-2g** (1.0 mmol, 160.3 mg, 5.0 equiv), $Co(dmgH)_2$(4-CN-py)Cl (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), isonicotinonitrile (20.8 mg, 1.0 equiv) and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (2.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away

from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product.

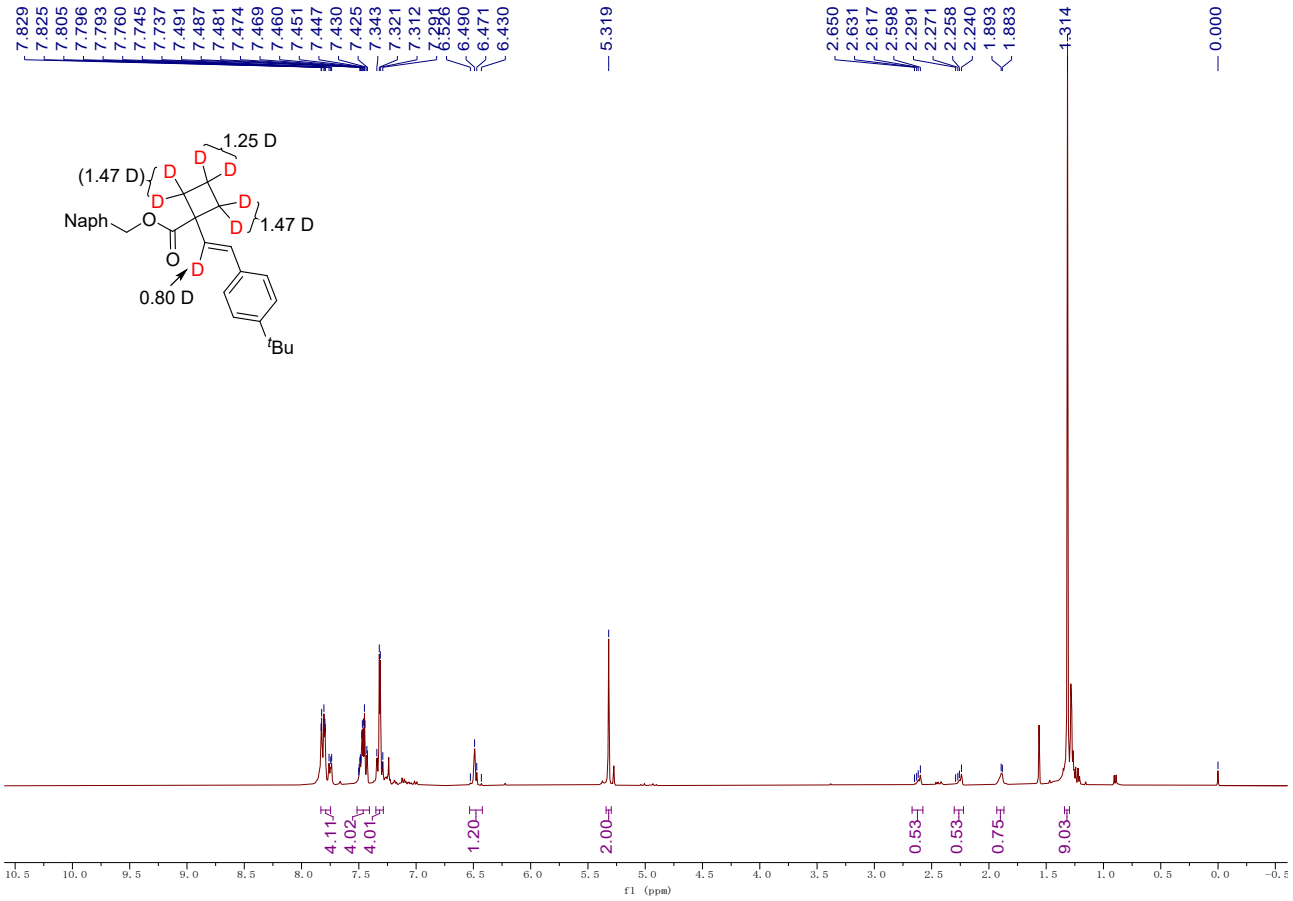
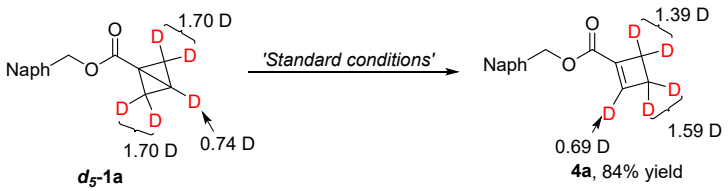


Figure S21. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **3ag**) of deuterium studies with ***d_5*-1a and *d_2*-2g**

The Substrate *d_5*-1a Was Used Instead in the Absence of Alkene



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate ***d_5*-1a** (0.2 mmol, 48.7 mg, 1.0 equiv), $Co(dmgH)_2$(4-CN-py)Cl (8.6 mg, 10 mol%), HEH (152.0 mg, 3.0 equiv), and KH_2PO_4 (81.6 mg, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (2.0 mL, 0.1

M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product.

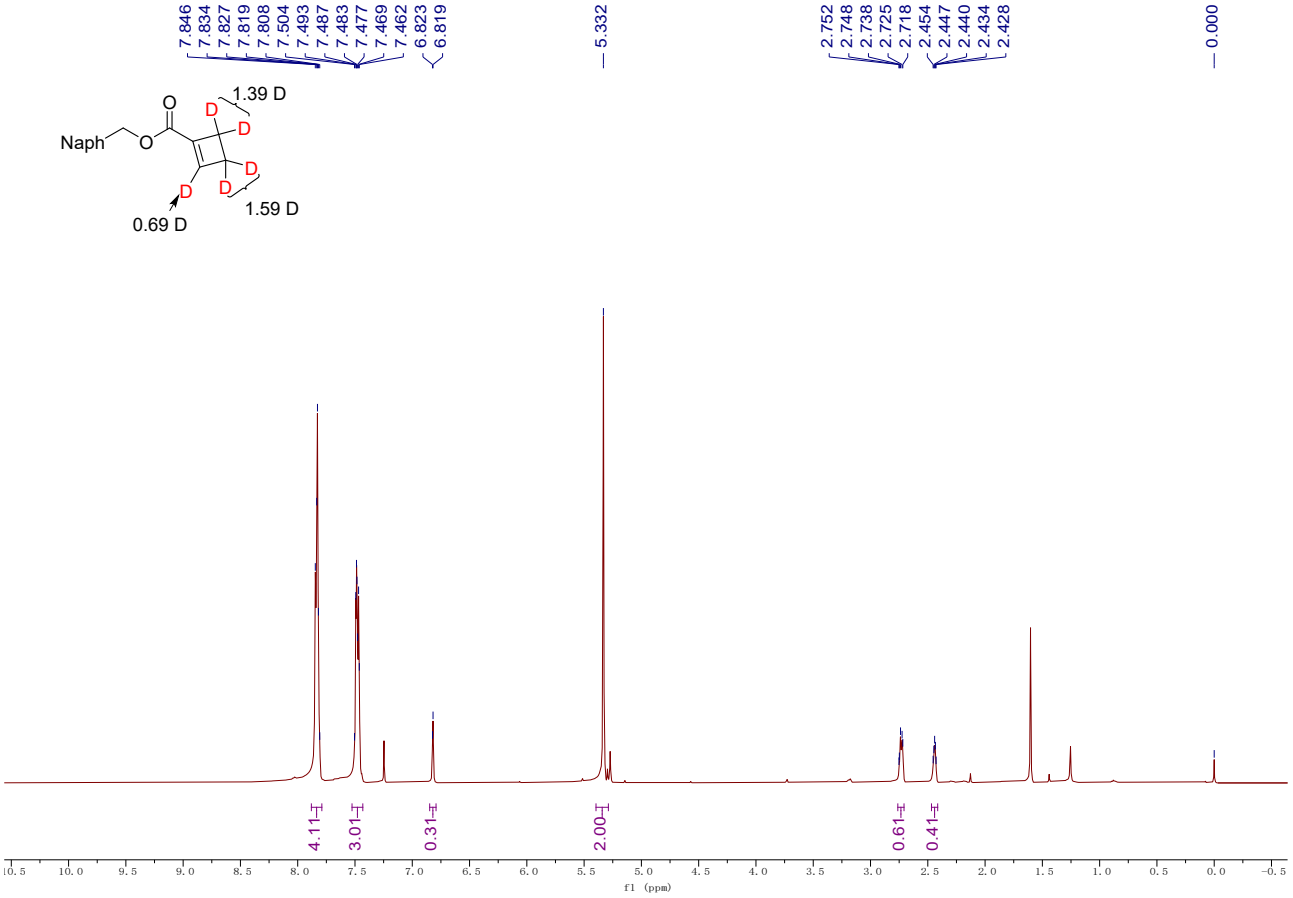
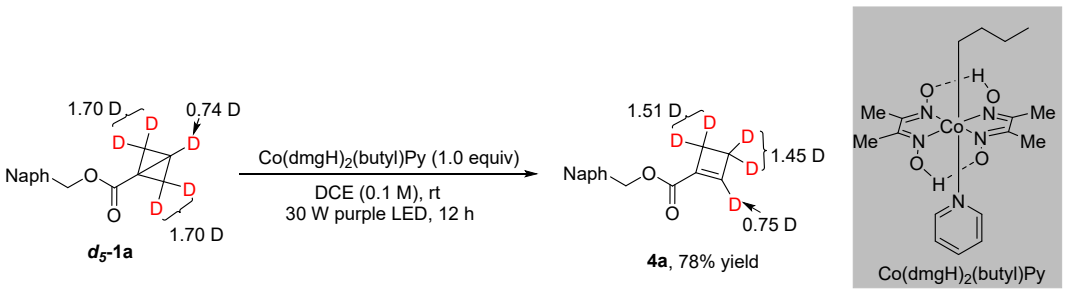


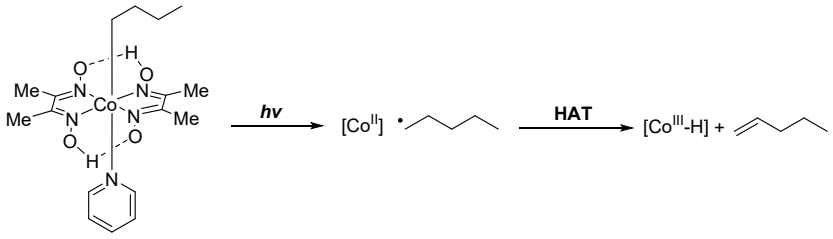
Figure S22. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **3ag**) of deuterium studies with ***d_5*-1a** in the absence of alkene

Stoichiometric Co(dmgH)$_2$(butyl)py Was Used Instead in the Absence of Alkene



In a flame dried Schlenk tube (10 mL) equipped with a magnetic stir bar, substrate **1a** (0.1 mmol, 24.3 mg, 1.0 equiv) and Co(dmgH)$_2$(butyl)py (42.5 mg, 1.0 equiv) were added. The reaction tube

was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (1.0 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 12 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the product **4a** in 78% yield.



To further determine whether Co-H adds to BCB directly, stoichiometric $Co(dmgH)_2$(butyl)py was used. Under irradiation, such Co-complex would generate Co-H.[8c] If this Co-H adds to the BCB, the C3 position should have less than 1 D incorporation. This is inconsistent with the experimental results.

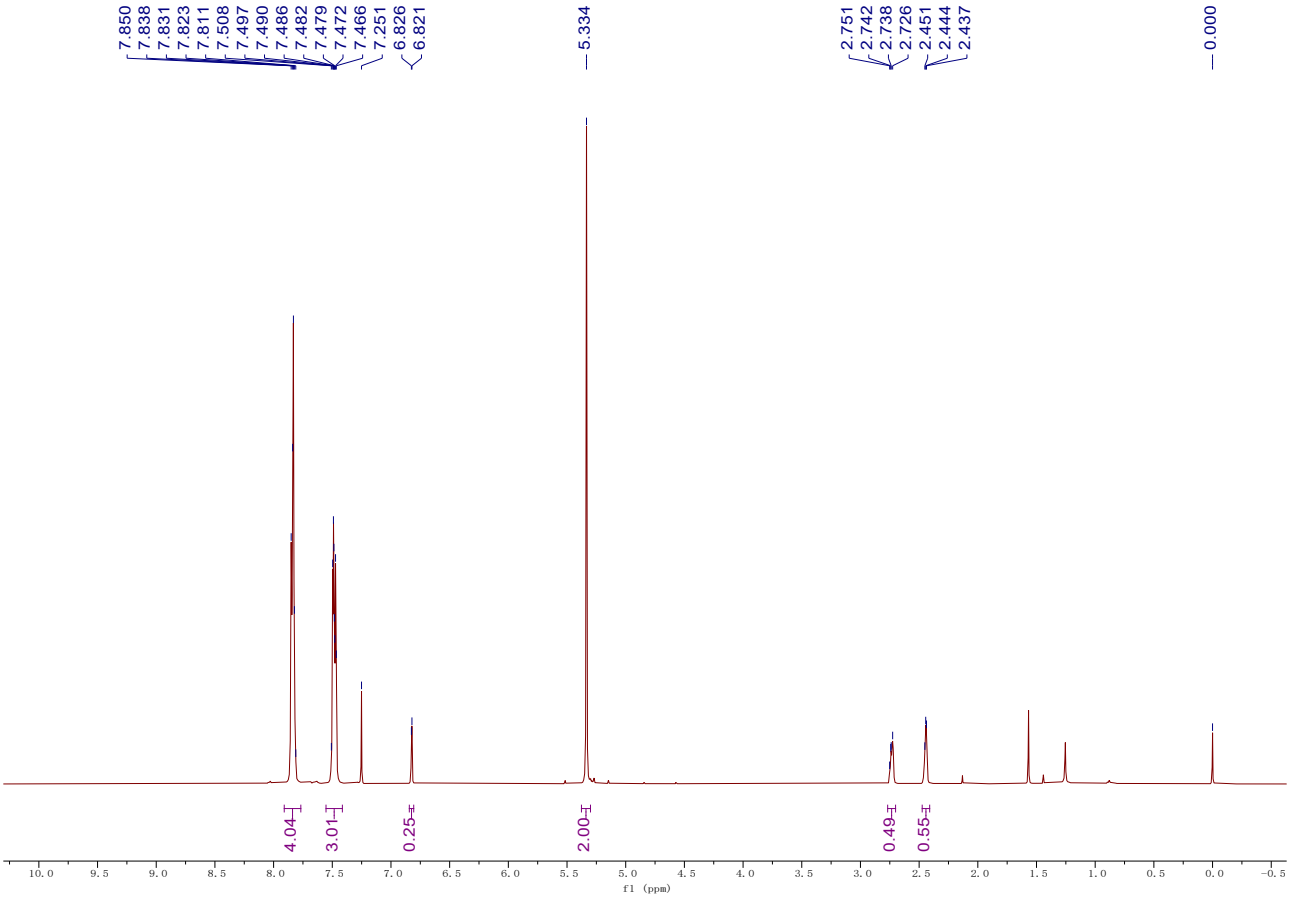


Figure S23. **^{1}H NMR** (400 MHz, $CDCl_3$) spectrum (compound **4a**) of deuterium studies with

Stoichiometric $Co(dmgH)_2$(butyl)py in the absence of alkene.

5.8 Detection of Generated Hydrogen Gas

Qualitative detection of hydrogen was achieved by GC-2060 on TDX-01 packed column. In a flame dried Schlenk tube (50 mL) equipped with a magnetic stir bar, substrate **1a** (0.24 g, 1.0 mmol, 1.0 equiv), styrene **2a** (0.57 mL, 5.0 mmol, 5.0 equiv), $Co(dmgH)_2$(4-CN-py)Cl (42.8 mg, 10 mol%), HEH (0.76g, 3.0 equiv), isonicotinonitrile (104.1 mg, 1.0 equiv), and KH_2PO_4 (0.41 g, 3.0 equiv) were added. The tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then, the degassed solvent DCE (10 mL, 0.1 M) was injected into the tube under argon. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the sealed tube was cooled in liquid nitrogen. Nitrogen (3 mL) was injected into the reaction tube as an internal standard. Then gas in the tube was injected into gas chromatography with syringe. By comparing the retention time with the standard mixed gas (10% H_2 in N_2), it is determined that the generated gas is hydrogen gas.

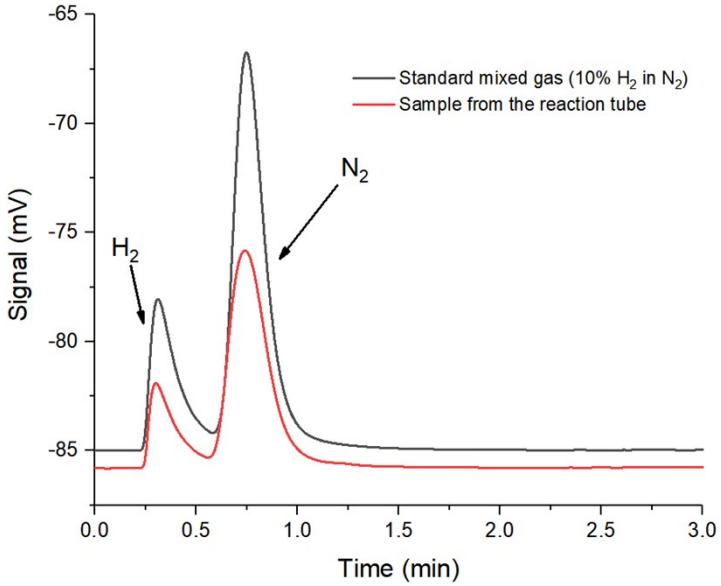
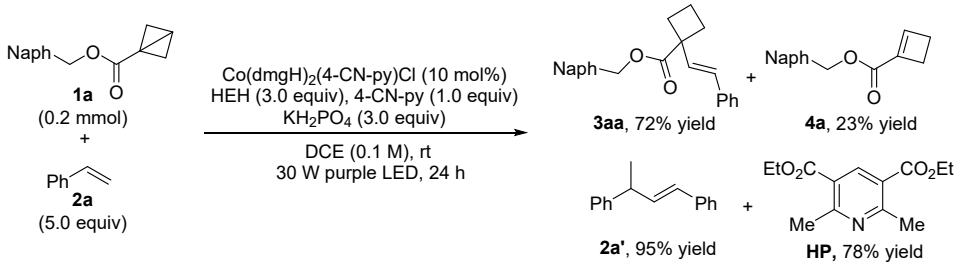


Figure S24. Detection of generated hydrogen gas with GC

6. Analysis of Internal Mixtures and Some Unsuccessful Examples

6.1 Analysis of Internal Mixtures

According to the general procedure C, the internal reaction mixture includes the hydroalkenylation product **3**, isomerization product **4**, as well as a dimer from alkene.



Herein, we take the model substrate **1a** (0.2 mmol) as an example. The side-product **2a'** generated probably through cobalt hydride catalyzed dimerization of styrene **2a** was obtained as a colorless oil (39.6 mg, 95% yield, calculated based on 0.2 mmol).

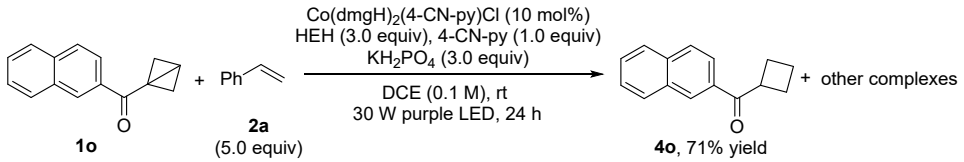
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 8H), 7.23 – 7.17 (m, 2H), 6.46 – 6.34 (m, 2H), 3.64 (qd, *J* = 7.0, 4.8 Hz, 1H), 1.47 (d, *J* = 7.0 Hz, 3H). The spectroscopic data were consistent with those of previously reported.[12]

The corresponding pyridine compound (HP) transformed from HEH was also isolated (78% conversion calculated based on 0.6 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 4H), 2.85 (s, 6H), 1.42 (t, *J* = 7.1 Hz, 6H).

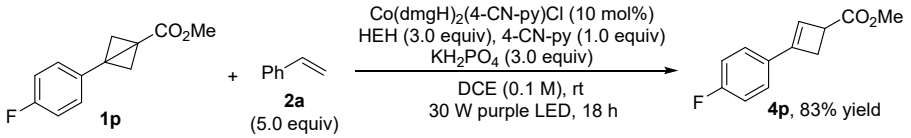
6.2 Analysis of Some Unsuccessful Examples

In the investigation on the substrate scope, some examples were tested but failed to afford the desired products. Herein we provide the detailed transformations of corresponding reactions.

For the unsuccessful BCBs

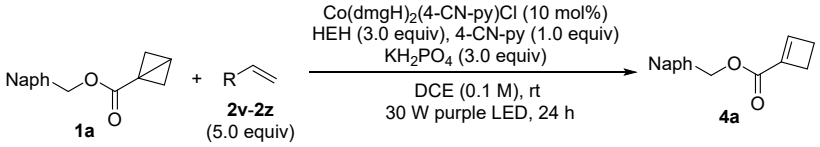


The substrate **1o** could not afford the desired hydroalkenylation product under the standard conditions. Apart from other complexes, we isolated the cyclobutane product **4o** in 71% yield in this protocol.



The substrate **1p** was almost converted into the product **4p** under the standard conditions.

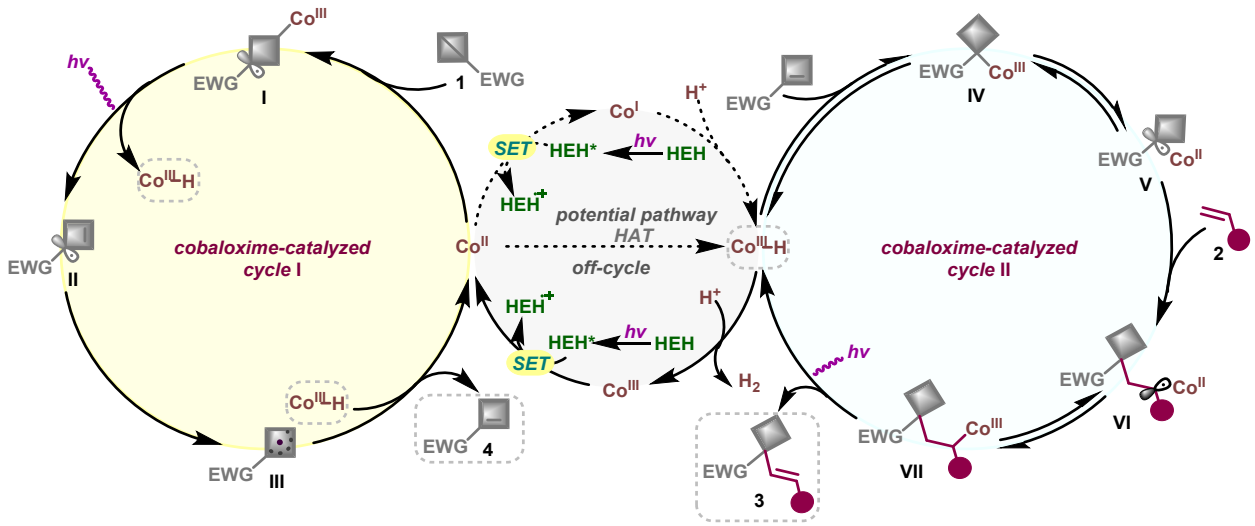
For the unsuccessful alkenes



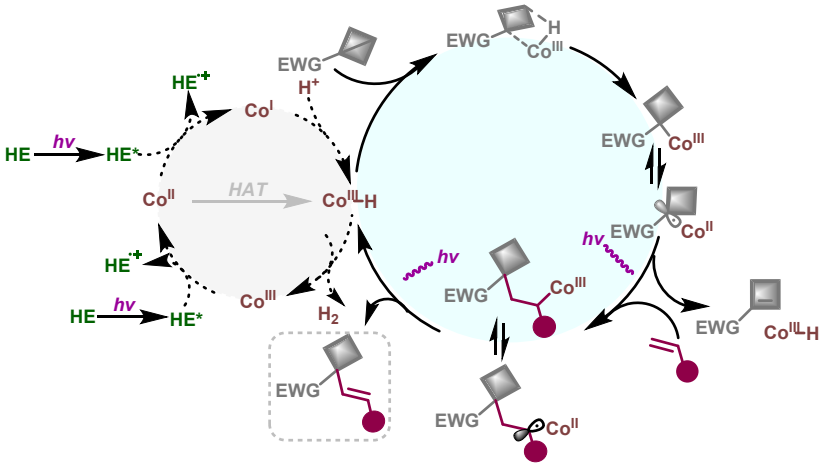
When the alkenes **2v**-**2z** were used as substrates, no coupling products **3** were obtained under the standard conditions. the isomerization product **4a** was obtained as a single product.

7. Proposed Reaction Mechanism

Scheme S1. Proposed Mechanism



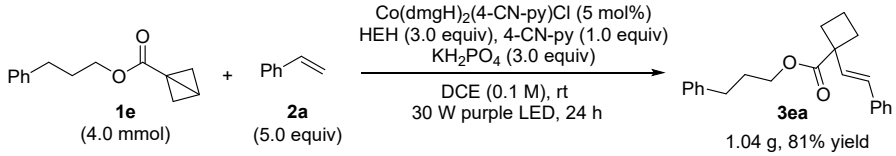
Scheme S2. Infeasible Mechanism involving Direct CoH Addition



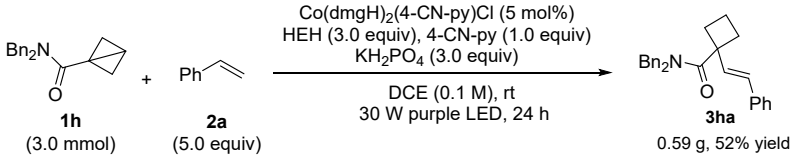
Based on the PdH-enabled hydroalkenylation of BCBs protocol, we also consider the possibility of a direct CoH addition promoted mechanism. However, deuterium labeling studies revealed that the H source from the additives did not participate in the BCBs transformations process, which was different from the situation in the PdH-catalyzed method. As a result, we could not explain the origination of CoH species and how this reaction was initiated. Even so, this CoH addition mechanism could not be excluded considering the π-like property of BCB. Herein, we supplement this CoH enabled direct CoH addition as a potential mechanism for reference.

8. Synthetic Applications

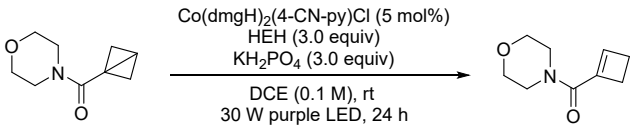
8.1 Scale-up Experiments.



In a flame dried Schlenk tube (100 mL) equipped with a magnetic stir bar, substrate **1e** (0.87 g, 4.0 mmol, 1.0 equiv), alkene **2a** (20.0 mmol, 2.3 mL, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (85.6 mg, 5 mol%), HEH (3.04 g, 3.0 equiv), isonicotinonitrile (416.4 mg, 1.0 equiv) and KH_2PO_4 (1.63 g, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (40 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product **3ea** (1.04 g, 81% yield).



In a flame dried Schlenk tube (100 mL) equipped with a magnetic stir bar, substrate **1h** (3.0 mmol, 0.83 g, 1.0 equiv), alkene **2a** (15.0 mmol, 1.7 mL, 5.0 equiv), $Co(dmgH)_2(4\text{-CN-py})Cl$ (64.2 mg, 5 mol%), HEH (2.28 g, 3.0 equiv), isonicotinonitrile (312.3 mg, 1.0 equiv) and KH_2PO_4 (1.22 g, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (30 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product **3ha** (0.59 g, 52% yield).



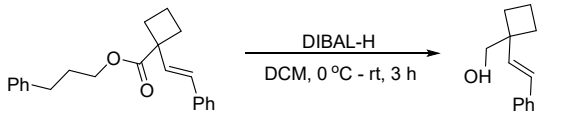
1l
(5.0 mmol)

4l
0.75 g, 73% yield

In a flame dried Schlenk tube (100 mL) equipped with a magnetic stir bar, substrate **1l** (5.0 mmol, 0.84 g, 1.0 equiv), $Co(dmgH)_2$(4-CN-py)Cl (107.0 mg, 5 mol%), HEH (3.80 g, 3.0 equiv), and KH_2PO_4 (2.04 g, 3.0 equiv) were added. The reaction tube was degassed by alternating vacuum evacuation (10 min) and argon backfill for three times. Then the degassed solvent DCE (50 mL, 0.1 M) was injected into the tube. The resulting mixture was stirred for 10 min before being placed 5.0 cm away from the purple LED (30 W) and stirred for 24 h with a fan to maintain temperature. Upon completion, the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography to afford the purified product **4l**.

8.2 Product Transformations

Synthesis of Compound 5



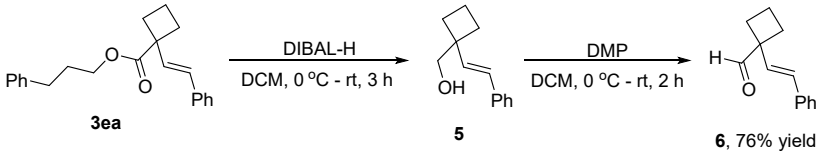
3ea

5, 96% yield

A solution of compound **3ea** (96.0 mg, 0.3 mmol) in DCM (0.6 mL) was stirred at 0 °C in an ice bath for 5.0 min, then DIBAL-H (1.2 mL, 1.0 M) was injected into the tube slowly. The reaction system was warmed to room temperature and stirred for 3.0 h. Upon completion, a solution of NaOH (1.0 M) was added into the reaction tube and the resulting mixture was filtered with a pad of celite. The filtrate was concentrated to dryness and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **5** (54.2 mg, 96% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 1H), 6.42 (d, *J* = 16.1 Hz, 1H), 6.26 (d, *J* = 16.1 Hz, 1H), 3.65 (s, 2H), 2.15 – 2.06 (m, 2H), 2.03 – 1.87 (m, 4H), 1.55 (br, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.1, 135.0, 129.0, 128.5, 127.2, 126.1, 68.7, 46.1, 28.5, 15.5; **IR (neat)**: ν 3364, 3025, 2976, 2931, 1646, 1599, 1493, 1448, 1027, 966, 747 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{13}H_{16}O$ 188.1196; found 188.1204.

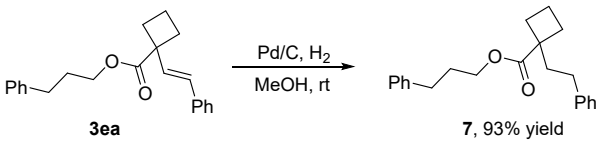
Synthesis of Compound 6



A solution of compound **3ea** (96.0 mg, 0.3 mmol) in DCM (0.6 mL) was stirred at 0 °C in an ice bath for 5.0 min, then DIBAL-H (1.2 mL, 1.0 M) was injected into the tube slowly. The reaction system was warmed to room temperature and stirred for 3.0 h. Upon completion, a solution of NaOH (1.0 M) was added into the tube and the resulting mixture was filtered with a pad of celite. The filtrate was concentrated to dryness and the residue was dissolved with DCM (6.0 mL). In an ice bath, a solution of Dess-Martin periodinane (190.8 mg, 0.45 mmol) in DCM (3.0 mL) was injected into the mixture. The reaction system was warmed to room temperature and stirred for another 2.0 h. Upon completion, aqueous saturated sodium bicarbonate was added and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 5.0 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **6** (42.4 mg, 76% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.22 (m, 1H), 6.46 (d, *J* = 16.3 Hz, 1H), 6.32 (d, *J* = 16.3 Hz, 1H), 2.58 – 2.48 (m, 2H), 2.26 – 2.15 (m, 2H), 2.04 – 1.89 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.9, 136.6, 131.2, 128.9, 128.6, 127.8, 126.3, 55.3, 27.8, 15.6; **IR (neat)**: ν 3028, 2940, 1719, 1606, 1493, 1450, 1275, 1176, 1072, 750 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{13}H_{14}O$ 186.1039; found 186.1043.

Synthesis of Compound 7

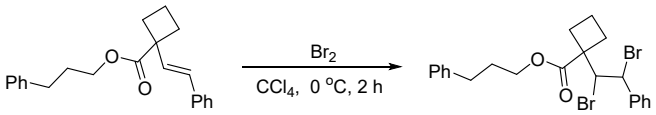


To a flask was added compound **3ea** (64.0 mg, 0.2 mmol), Pd/C (21.3 mg, 0.1 equiv, 10% Pd) and menthol (8.0 mL). The mixture was stirred vigorously at room temperature for 8.0 hours under 1.0 atm H_2. Upon completion, the resulting mixture was filtered with a pad of celite. The filtrate was

concentrated to dryness and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **7** (60.0 mg, 93% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 4H), 7.15 – 7.07 (m, 6H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.49 – 2.33 (m, 4H), 2.08 – 1.96 (m, 2H), 1.96 – 1.79 (m, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.9, 141.9, 141.1, 128.41, 128.35, 128.32, 128.28, 126.0, 125.8, 63.6, 47.7, 39.9, 32.2, 31.4, 30.3, 30.1, 15.7; **IR (neat)**: ν 3026, 2937, 2857, 1721, 1602, 1495, 1452, 1323, 1162, 1101, 1029, 910, 743, 696 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_2$ 322.1927; found 322.1930.

Synthesis of Compound 8



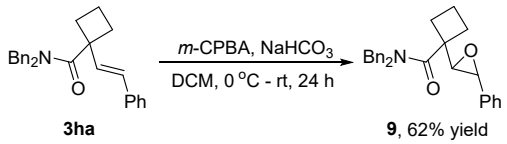
3ea **8**, 95% yield (d.r. = 5 : 3)

An oven-dried Schlenk tube (10 mL) equipped with a magnetic stir bar was added compound **3** (64.0 mg, 0.2 mmol) and CCl_4 (4.0 mL). Then bromine (16 μL, 1.5 equiv) was added into the tube. The mixture was allowed to stir at 0 °C for 2.0 h. Upon completion, 10% aqueous sodium thiosulfate and aqueous saturated sodium bicarbonate were added and the resulting mixture was extracted with CH_2Cl_2 for 3 times (3 × 5.0 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **8** (90.7 mg, 95% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.43 – 7.28 (m, 9H), 7.26 – 7.17 (m, 5H), 5.68 – 5.53 (m, 1.6H), 4.85 (d, *J* = 10.5 Hz, 0.6H), 4.67 (d, *J* = 8.2 Hz, 1H), 4.32 – 4.27 (m, 1.2H), 4.24 – 4.12 (m, 2H), 2.84 – 2.79 (m, 1.2H), 2.76 – 2.71 (m, 2H), 2.68 – 2.58 (m, 1H), 2.56 – 2.48 (m, 1.6H), 2.34 – 1.97 (m, 6H), 1.93 – 1.83 (m, 2.6H), 1.70 – 1.62 (m, 1H), 1.54 – 1.51 (m, 0.6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.6 (*minor isomer*), 173.5, 141.0 (*minor isomer*), 140.9, 140.8 (*minor isomer*), 139.1, 128.8, 128.7 (*minor isomer*), 128.62, 128.57, 128.5, 128.43, 128.37, 128.3, 127.8 *(mixtures of major and minor isomer between* 128.62 – 127.8*)*, 126.10, 126.07 (*minor isomer*), 66.6, 64.5 (*minor isomer*), 64.4, 63.5 (*minor isomer*), 57.4, 53.4 (*minor isomer*), 53.1 (*minor isomer*),

52.9, 35.4, 32.33 (*minor isomer*), 32.29, 32.2, 32.0 (*minor isomer*), 30.3 (*minor isomer*), 30.2, 15.9 (*minor isomer*), 15.8; **IR (neat)**: ν 3026, 2950, 1726, 1495, 1453, 1201, 1157, 1029, 745 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{24}O_2Br_2Na$ 501.0035; found 501.0031.

Synthesis of Compound 9

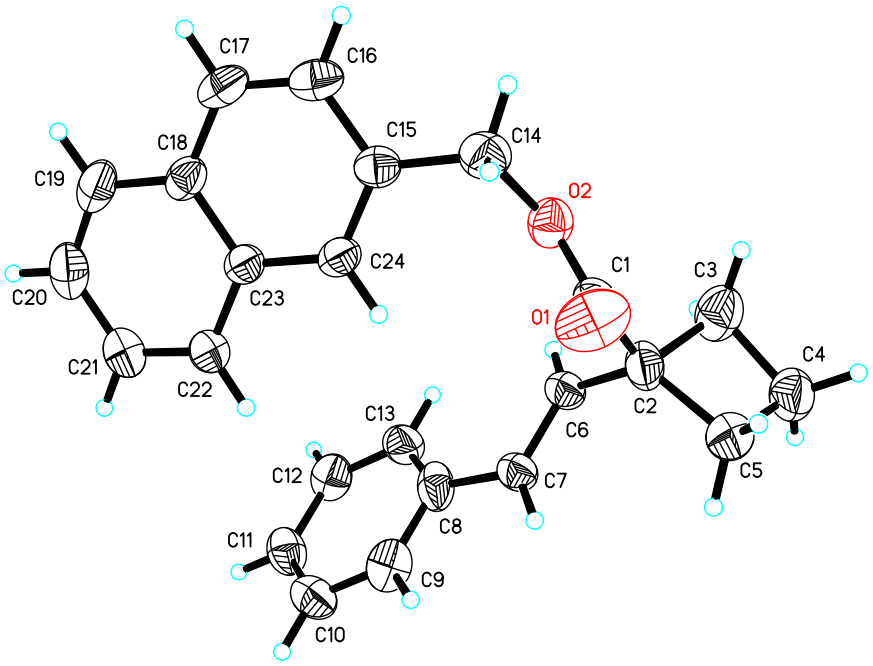


3ha **9**, 62% yield

A solution of compound **3ha** (76.2 mg, 0.2 mmol), 3-chloroperoxybenzoic acid (61.6 mg, 2.0 equiv, 85%) and sodium bicarbonate (20.2 mg, 1.2 equiv) in DCM (10 mL) was stirred at room temperature for 24 h. Upon completion, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated to dryness and the residue was purified by a flash column chromatography on silica gel (PE/EA = 4/1) to afford the product **9** (49.4 mg, 62% yield) as a yellow oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 6H), 7.24 – 7.19 (m, 5H), 7.16 – 7.09 (m, 4H), 4.52 (s, 2H), 4.42 (s, 2H), 3.85 (d, *J* = 2.2 Hz, 1H), 3.36 (d, *J* = 2.1 Hz, 1H), 2.73 – 2.59 (m, 2H), 2.28 – 2.15 (m, 2H), 2.03 – 1.90 (m, 1H), 1.87 – 1.77 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.7, 137.0, 136.7, 136.3, 128.8, 128.5, 128.3, 128.0, 127.5, 127.2, 126.8, 125.6, 65.5, 55.7, 49.7, 48.6, 47.6, 29.1, 28.3, 15.7; **IR (neat)**: ν 2947, 1634, 1495, 1452, 1417, 1362, 1223, 1076, 891, 749 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{27}H_{27}O_2N$ 397.2036; found 397.2045.

9. X-ray Data.



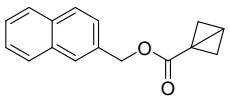
Single crystals of **3aa** were grown in EtOAc and hexanes. EtOAc (1.0 mL) was added to **3** (30 mg in a 4.0 mL vial) followed by hexanes (0.5 mL). The 4.0 mL vial was capped with a needle and placed at room temperature in the experimental cabinet for 48 h, whereupon the crystals were formed.

The crystal data of **3aa** have been deposited in CCDC with number 2327264. Empirical Formula: $C_{24}H_{22}O_2$; Formula Weight: 342.41; Crystal Color, Habit: colorless, Crystal Dimensions: 0.190 x 0.150 x 0.050 mm; Crystal System: Triclinic; Lattice Parameters: a = 5.9017(13)Å, b = 7.7429(18)Å, c = 20.619(5)Å, α = 81.177(7)°, β = 85.875(7)°, γ = 86.043(7)°, V = 927.0(4)Å^3; Space group: P -1; Z = 2; D_{calc}= 1.227 g/cm^3; F_{000} = 364; Final R induces [I>2sigma(I)]: R1 = 0.0663; wR2 = 0.1310.

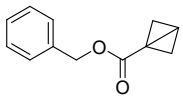
Table S7. Crystal data and structure refinement for 3aa.

Empirical formula	C24 H22 O2	
Formula weight	342.41	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.9017(13) Å	α= 81.177(7)°.
	b = 7.7429(18) Å	β= 85.875(7)°.
	c = 20.619(5) Å	γ = 86.043(7)°.
Volume	927.0(4) $Å^3$	
Z	2	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	364	
Crystal size	0.190 x 0.150 x 0.050 mm^3	
Theta range for data collection	2.667 to 25.999°.	
Index ranges	-7<=h<=7, -9<=k<=9, -25<=l<=25	
Reflections collected	16436	
Independent reflections	3633 [R(int) = 0.0621]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6142	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3633 / 36 / 254	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1310	
R indices (all data)	R1 = 0.1337, wR2 = 0.1628	
Extinction coefficient	0.023(4)	
Largest diff. peak and hole	0.223 and -0.162 $e.Å^{-3}$	

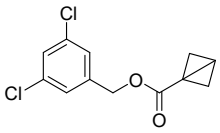
10. Characterization Data of Substrates



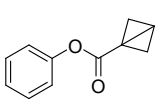
naphthalen-2-ylmethyl bicyclo[1.1.0]butane-1-carboxylate (1a): A colorless oil, 667.1 mg, 56% yield. Eluent: PE/EA = 30/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.53 – 7.41 (m, 3H), 5.31 (s, 2H), 2.41 (d, *J* = 3.6 Hz, 2H), 2.15 – 2.09 (m, 1H), 1.20 – 1.15 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.0, 133.6, 133.1, 133.0, 128.3, 127.9, 127.7, 127.1, 126.24, 126.18, 125.7, 66.5, 35.7, 16.9, 9.1; **IR (neat)**: ν 3057, 2943, 1709, 1509, 1407, 1367, 1192, 1142, 1019, 816, 749 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{14}O_2Na$ 261.0886; found 261.0887.



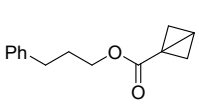
benzyl bicyclo[1.1.0]butane-1-carboxylate (1b): A colorless oil, 602.2 mg, 64% yield. Eluent: PE/EA = 30/1. The spectroscopic data were consistent with those of previously reported.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 5.15 (s, 2H), 2.39 (d, *J* = 3.5 Hz, 2H), 2.14 – 2.06 (m, 1H), 1.16 (d, *J* = 2.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.9, 136.2, 128.5, 128.0, 127.9, 66.2, 35.6, 16.7, 9.1.



3,5-dichlorobenzyl bicyclo[1.1.0]butane-1-carboxylate (1c): A colorless oil, 694.0 mg, 54% yield. Eluent: PE/EA = 30/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.22 (s, 2H), 5.08 (s, 2H), 2.40 (d, *J* = 3.5 Hz, 2H), 2.20 – 2.13 (m, 1H), 1.21 (d, *J* = 2.9 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.6, 139.6, 135.1, 128.2, 126.1, 64.6, 35.8, 17.4, 9.0; **IR (neat)**: ν 2967, 1710, 1592, 1570, 1433, 1403, 1352, 1190, 1132, 1102, 888, 849, 797, 752 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{12}O_2Cl_2$ 257.0131; found 257.0125.

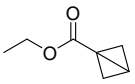


phenyl bicyclo[1.1.0]butane-1-carboxylate (1d): A colorless oil, 453.0 mg, 34% yield. Eluent: PE/EA = 30/1. The spectroscopic data were consistent with those of previously reported.[14] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.52 (d, *J* = 3.5 Hz, 2H), 2.37 – 2.31 (m, 1H), 1.31 (d, *J* = 2.9 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.7, 150.8, 129.3, 125.6, 121.5, 36.2, 18.1, 9.3.

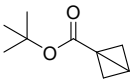


3-phenylpropyl bicyclo[1.1.0]butane-1-carboxylate (1e): A colorless oil, 703.0

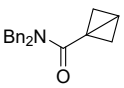
mg, 65% yield. Eluent: PE/EA = 30/1. The spectroscopic data were consistent with those of previously reported.[15] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 4.12 (t, *J* = 6.5 Hz, 2H), 2.72 – 2.64 (m, 2H), 2.34 (d, *J* = 3.5 Hz, 2H), 2.08 – 2.02 (m, 1H), 2.00 – 1.91 (m, 2H), 1.14 (d, *J* = 2.8 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.0, 141.2, 128.4, 128.3, 125.9, 63.9, 35.5, 32.1, 30.2, 16.4, 9.0.



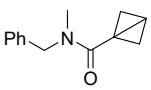
ethyl bicyclo[1.1.0]butane-1-carboxylate (1f): A colorless oil, 327.9 mg, 52% yield. Eluent: PE/EA = 30/1. The spectroscopic data were consistent with those of previously reported.[16] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 2.36 (d, *J* = 3.1 Hz, 2H), 2.10 – 2.02 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 – 1.11 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.0, 60.5, 35.4, 28.0, 16.2, 14.2.



***tert*-butyl bicyclo[1.1.0]butane-1-carboxylate (1g)**: A colorless oil, 447.0 mg, 58% yield. Eluent: PE/EA = 30/1. The spectroscopic data were consistent with those of previously reported.[16] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.29 (d, *J* = 4.6 Hz, 2H), 2.02 – 1.95 (m, 1H), 1.45 (s, 9H), 1.08 (d, *J* = 1.9 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.3, 80.2, 35.3, 28.0, 15.7, 10.0.

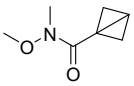


***N*,*N*-dibenzylbicyclo[1.1.0]butane-1-carboxamide (1h)**: A yellow solid, 693.0 mg, 50% yield. Eluent: PE/EA = 4/1. The spectroscopic data were consistent with those of previously reported.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.03 (m, 10H), 4.82 (s, 2H), 4.58 (s, 2H), 2.27 (d, *J* = 3.4 Hz, 2H), 2.10 (t, *J* = 3.1 Hz, 1H), 1.10 (d, *J* = 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 137.1, 128.9, 128.5, 128.3, 127.4, 126.6, 50.5, 47.7, 36.9, 13.4, 8.2.

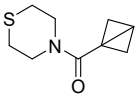


***N*-benzyl-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (1i)**: A pale yellow solid, 523.1 mg, 52% yield. Eluent: PE/EA = 4/1. The spectroscopic data were consistent with those of previously reported.[2] *Note*: this compound is a mixture of rotamers in a 1:1 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.15 (m, 10H, mixture of rotamers), 4.91 (s, 2H), 4.61 (s, 2H), 3.15 (s, 3H), 2.92 (s, 3H), 2.33 – 2.26 (m, 2H), 2.25 – 2.20 (m, 2H), 2.09 – 1.95 (m, 2H, mixture of

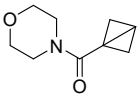
rotamers), 1.23 – 1.15 (m, 2H), 1.13 – 1.04 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 171.6, 137.3, 128.8, 128.6, 128.1, 127.4, 127.3, 126.5, 54.2, 51.0, 37.3, 36.7, 36.0, 33.6, 13.9, 13.0, 8.1.



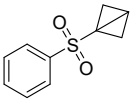
***N*-methoxy-*N*-methylbicyclo[1.1.0]butane-1-carboxamide (1j)**: A colorless liquid, 310.0 mg, 44% yield. Eluent: PE/EA = 4/1. The spectroscopic data were consistent with those of previously reported.[17] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.25 (s, 3H), 2.41 – 2.36 (m, 2H), 2.17 – 2.09 (m, 1H), 1.16 – 1.11 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.8, 61.0, 36.1, 33.4, 15.0, 8.4.



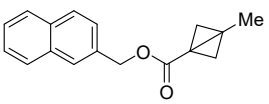
bicyclo[1.1.0]butan-1-yl(thiomorpholino)methanone (1k): A white solid, 522.3 mg, 57% yield. Eluent: PE/EA = 4/1. The spectroscopic data were consistent with those of previously reported.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.47 – 3.71 (m, 4H), 2.89 – 2.43 (m, 4H), 2.21 (d, *J* = 3.4 Hz, 2H), 2.03 – 1.94 (m, 1H), 1.17 (d, *J* = 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.6, 49.2, 44.7, 37.1, 28.2, 27.1, 13.8, 7.8.



bicyclo[1.1.0]butan-1-yl(morpholino)methanone (1l): A pale yellow oil, 426.1 mg, 51% yield. Eluent: PE/EA = 4/1. The spectroscopic data were consistent with those of previously reported.[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.95 – 3.53 (m, 8H), 2.23 (d, *J* = 3.4 Hz, 2H), 2.03 – 1.95 (m, 1H), 1.18 (d, *J* = 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.5, 66.8, 47.2, 42.6, 37.1, 13.9, 7.6.

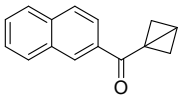


1-(phenylsulfonyl)bicyclo[1.1.0]butane (1m): A white solid, 516.2 mg, 54% yield. Eluent: PE/EA = 4/1. The spectroscopic data were consistent with those of previously reported.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.67 – 7.52 (m, 3H), 2.61 – 2.55 (m, 1H), 2.52 (d, *J* = 3.7 Hz, 2H), 1.39 (d, *J* = 2.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.9, 133.0, 129.1, 127.1, 38.2, 23.0, 12.6.

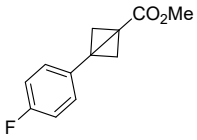


naphthalen-2-ylmethyl 3-methylbicyclo[1.1.0]butane-1-carboxylate (1n): A colorless oil, 1.25 g, 62% yield. Eluent: PE/EA = 20/1. **^{1}H NMR** (400

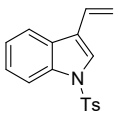
MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.53 – 7.41 (m, 3H), 5.31 (s, 2H), 2.28 – 2.20 (m, 2H), 1.49 (s, 3H), 1.29 – 1.22 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.0, 134.0, 133.1, 133.0, 128.2, 127.9, 127.6, 127.1, 126.2, 126.1, 125.8, 66.2, 38.8, 28.0, 13.1, 12.7; **IR (neat)**: ν 2963, 1695, 1454, 1377, 1319, 1209, 1138, 955, 862, 748 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{24}H_{22}O_2$ 252.1145; found 252.1152.



bicyclo[1.1.0]butan-1-yl(naphthalen-2-yl)methanone (1o): A white solid, 562.3 mg, 54% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.05 – 7.80 (m, 4H), 7.63 – 7.51 (m, 2H), 2.70 (d, *J* = 3.6 Hz, 2H), 2.36 – 2.12 (m, 1H), 1.55 (d, *J* = 3.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 199.7, 135.1, 135.1, 132.2, 130.3, 129.3, 128.0, 128.0, 127.8, 126.7, 124.8, 38.0, 21.4, 17.1.

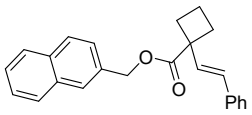


methyl 3-(4-fluorophenyl)bicyclo[1.1.0]butane-1-carboxylate (1p): A white solid, 494.9 mg, 48% yield. Eluent: PE/EA = 30/1. The spectroscopic data were consistent with those of previously reported.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 2H), 7.07 – 6.94 (m, 2H), 3.50 (s, 3H), 2.93 – 2.84 (m, 2H), 1.64 – 1.57 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.9, 162.1 (d, *J* = 246.1 Hz), 129.4 (d, *J* = 3.5 Hz), 127.5 (d, *J* = 8.4 Hz), 115.5 (d, *J* = 21.8 Hz), 51.8, 35.9, 32.3, 22.8.

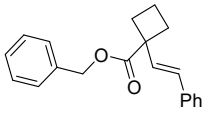


1-tosyl-3-vinyl-1H-indole (2q): A white solid, 650.0 mg, 55% yield. Eluent: PE/EA = 6/1. The spectroscopic data were consistent with those of previously reported.[7] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 1H), 7.79 – 7.70 (m, 3H), 7.60 (s, 1H), 7.36 – 7.29 (m, 1H), 7.26 (s, 1H), 7.20 (d, *J* = 4.9 Hz, 2H), 6.80 – 6.72 (m, 1H), 5.78 (dd, *J* = 17.8, 3.6 Hz, 1H), 5.34 (dd, *J* = 11.5, 3.6 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.0, 135.5, 135.1, 129.9, 129.0, 127.5, 126.8, 124.9, 124.0, 123.5, 120.9, 120.4, 115.3, 113.7, 21.5;

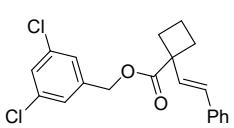
11. Characterization Data of Products



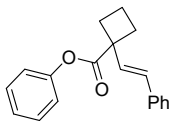
naphthalen-2-ylmethyl (*E*)-1-styrylcyclobutane-1-carboxylate (3aa): A colorless oil, 47.8 mg, 70% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.71 (m, 4H), 7.48 – 7.41 (m, 3H), 7.35 (dt, *J* = 8.0, 1.8 Hz, 2H), 7.29 (td, *J* = 7.6, 2.0 Hz, 2H), 7.25 – 7.19 (m, 1H), 6.57 – 6.42 (m, 2H), 5.32 (s, 2H), 2.71 – 2.58 (m, 2H), 2.33 – 2.24 (m, 2H), 2.00 – 1.90 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.3, 136.9, 133.6, 133.2, 133.0, 131.2, 129.2, 128.6, 128.3, 128.0, 127.7, 127.5, 127.0, 126.3, 126.24, 126.17, 125.6, 66.6, 50.0, 30.9, 16.0; **IR (neat)**: ν 3055, 3025, 2943, 2853, 1727, 1447, 1219, 1197, 1100, 964, 815, 743 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{24}H_{22}O_2$ 342.1614; found 342.1603.



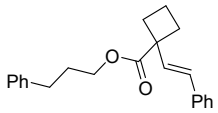
benzyl (*E*)-1-styrylcyclobutane-1-carboxylate (3ba): A colorless oil, 42.0 mg, 72% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 9H), 7.25 – 7.20 (m, 1H), 6.51 (d, *J* = 16.8 Hz, 1H), 6.46 (d, *J* = 16.4 Hz, 1H), 5.17 (s, 2H), 2.63 (dt, *J* = 11.5, 8.2 Hz, 2H), 2.28 (dt, *J* = 11.2, 7.6 Hz, 2H), 2.00 – 1.89 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.3, 136.9, 136.2, 131.2, 129.1, 128.53, 128.50, 128.1, 127.8, 127.4, 126.3, 66.4, 50.0, 30.9, 16.0; **IR (neat)**: ν 3028, 2945, 1724, 1496, 1455, 1284, 1217, 1196, 1097, 963, 741, 692 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}O_2$ 293.1536; found 293.1530.



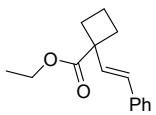
3,5-dichlorobenzyl (*E*)-1-styrylcyclobutane-1-carboxylate (3ca): A colorless oil, 61.2 mg, 85% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.18 (m, 6H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.09 (s, 2H), 2.63 (dt, *J* = 11.7, 8.2 Hz, 2H), 2.35 – 2.25 (m, 2H), 2.01 – 1.91 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.9, 139.5, 136.7, 135.1, 130.7, 129.6, 128.5, 128.2, 127.6, 126.3, 125.9, 64.7, 49.8, 30.9, 16.0; **IR (neat)**: ν 3074, 2945, 1728, 1592, 1569, 1432, 1363, 1216, 1196, 1102, 936, 852, 797, 742 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{19}O_2Cl_2$ 361.0757; found 361.0749.



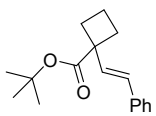
phenyl (*E*)-1-styrylcyclobutane-1-carboxylate (3da): A colorless oil, 45.5 mg, 82% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.30 (m, 4H), 7.26 – 7.18 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.59 (d, *J* = 16.1 Hz, 1H), 2.78 (dt, *J* = 11.7, 8.2 Hz, 2H), 2.39 (dt, *J* = 11.9, 7.8 Hz, 2H), 2.11 – 1.98 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.0, 151.0, 136.8, 130.6, 129.7, 129.4, 128.6, 127.6, 126.4, 125.7, 121.4, 50.1, 31.0, 16.0; **IR (neat)**: ν 2944, 1744, 1592, 1491, 1447, 1186, 1161, 1082, 1068, 964, 740, 688 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{19}O_2$ 279.1380; found 279.1374.



3-phenylpropyl (*E*)-1-styrylcyclobutane-1-carboxylate (3ea): A colorless oil, 53.0 mg, 83% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.28 – 7.11 (m, 6H), 6.53 (d, *J* = 16.1 Hz, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.66 – 2.56 (m, 2H), 2.33 – 2.22 (m, 2H), 2.03 – 1.89 (m, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.5, 141.1, 136.9, 131.4, 129.0, 128.5, 128.39, 128.37, 127.4, 126.3, 126.0, 64.0, 50.0, 32.1, 30.9, 30.2, 16.0; **IR (neat)**: ν 2945, 2858, 1723, 1491, 1453, 1283, 1239, 1218, 1197, 1103, 964, 814, 742, 693 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{25}O_2$ 321.1849; found 321.1843.

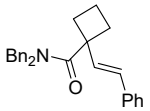


ethyl (*E*)-1-styrylcyclobutane-1-carboxylate (3fa): A colorless oil, 35.0 mg, 76% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.52 (d, *J* = 16.1 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.61 (dt, *J* = 12.3, 8.6 Hz, 2H), 2.26 (dt, *J* = 11.3, 7.8 Hz, 2H), 1.99 – 1.89 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.5, 137.0, 131.4, 128.8, 128.5, 127.4, 126.3, 60.8, 49.9, 30.9, 15.9, 14.2; **IR (neat)**: ν 2981, 1723, 1447, 1365, 1239, 1199, 1099, 1026, 963, 742 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{19}O_2$ 231.1380; found 231.1376.

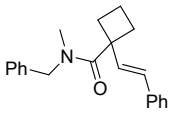


tert-butyl (*E*)-1-styrylcyclobutane-1-carboxylate (3ga): A colorless oil, 41.7 mg,

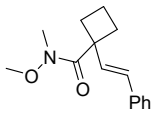
81% yield. Eluent: PE/EA = 15/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.50 (d, *J* = 16.1 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 2.56 (dt, *J* = 12.2, 8.2 Hz, 2H), 2.27 – 2.16 (m, 2H), 1.96 – 1.86 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.8, 137.2, 132.0, 128.51, 128.45, 127.3, 126.3, 80.4, 50.7, 30.9, 28.0, 15.8; **IR (neat)**: ν 2976, 1718, 1494, 1448, 1391, 1366, 1289, 1250, 1161, 1106, 963, 848, 742 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{23}O_2$ 259.1693; found 259.1686.



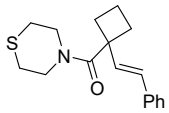
(*E*)-*N*,*N*-dibenzyl-1-styrylcyclobutane-1-carboxamidee (3ha): A yellow oil, 43.4 mg, 57% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 13H), 7.13 (d, *J* = 6.8 Hz, 2H), 6.55 (d, *J* = 16.2 Hz, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 4.53 (s, 2H), 4.27 (s, 2H), 2.87 – 2.74 (m, 2H), 2.25 – 2.14 (m, 2H), 2.10 – 1.94 (m, 1H), 1.90 – 1.76 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.7, 137.3, 136.7, 136.3, 132.1, 128.8, 128.6, 128.5, 127.5, 127.43, 127.36, 127.0, 126.2, 50.5, 49.7, 47.3, 32.2, 15.2; **IR (neat)**: ν 2940, 2863, 1632, 1494, 1450, 1413, 1361, 1216, 1075, 1028, 965, 744, 694 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{28}ON$ 382.2165; found 382.2159.



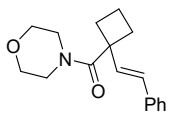
(*E*)-*N*-benzyl-*N*-methyl-1-styrylcyclobutane-1-carboxamide (3ia): A yellow oil, 39.8 mg, 65% yield. Eluent: PE/EA = 4/1. *Note*: this compound is a mixture of rotamers in a 2.5:1 ratio. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 11H), 7.25 – 7.20 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 15.2 Hz, 1.8H), 6.41 (d, *J* = 16.2 Hz, 1H), 4.61 (s, 2H), 4.36 (s, 0.8H), 2.85 (s, 1.2H), 2.80 – 2.73 (m, 2.8H), 2.73 (s, 3H), 2.28 – 2.17 (m, 2.8H), 2.08 – 1.98 (m, 1.4H), 1.89 – 1.78 (m, 1.4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.7 (*minor isomer*), 175.1, 137.5, 136.9, 136.8 (*minor isomer*), 136.5 (*minor isomer*), 132.2 (*minor isomer*), 131.8, 128.7 (*minor isomer*), 128.6, 128.1, 128.0 (*minor isomer*), 127.49 (*minor isomer*), 127.45, 127.4 (*minor isomer*), 127.3, 126.23 (*minor isomer*), 126.16, 52.9 (*minor isomer*), 51.5, 50.6 (*minor isomer*), 50.4, 34.8, 33.6 (*minor isomer*), 32.02 (*minor isomer*), 31.98, 15.2 (*minor isomer*), 15.1; **IR (neat)**: ν 2935, 1629, 1494, 1448, 1396, 1265, 1069, 1028, 965, 744 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{24}ON$ 306.1852; found 306.1847.



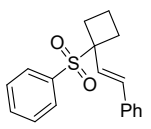
(*E*)-*N*-methoxy-N-methyl-1-styrylcyclobutane-1-carboxamide (3ja): A yellow oil, 27.0 mg, 55% yield. Eluent: PE/EA = 4/1. Containing a trace amount of impurity that failed to be separated. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.9 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.49 (d, *J* = 16.4 Hz, 1H), 3.60 (s, 3H), 3.17 (s, 3H), 2.64 (td, *J* = 9.5, 2.7 Hz, 2H), 2.26 – 2.17 (m, 2H), 2.02 – 1.93 (m, 1H), 1.85 – 1.73 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.4, 137.1, 131.8, 128.7, 128.6, 127.4, 126.2, 60.8, 50.4, 31.3, 30.4, 15.7; **IR (neat)**: ν 3055, 2039, 2872, 1652, 1494, 1447, 1370, 1181, 998, 966, 747 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{20}O_2N$ 246.1489; found 246.1489.



(*E*)-(1-styrylcyclobutyl)(thiomorpholino)methanone (3ka): A colorless oil, 35.0 mg, 61% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.22 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 16.4 Hz, 1H), 3.90 (t, *J* = 5.0 Hz, 2H), 3.49 (t, *J* = 5.0 Hz, 2H), 2.74 – 2.66 (m, 2H), 2.63 (t, *J* = 5.0 Hz, 2H), 2.48 (t, *J* = 5.0 Hz, 2H), 2.27 – 2.16 (m, 2H), 2.10 – 1.95 (m, 1H), 1.83 (dtt, *J* = 11.4, 9.5, 3.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.9, 136.7, 132.0, 128.7, 128.2, 127.6, 126.2, 50.3, 48.1, 44.6, 31.9, 27.5, 27.4, 15.1; **IR (acetone)**: ν 2915, 1711, 1628, 1448, 1418, 1288, 1252, 1197, 1025, 961, 745, 693 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{22}ONS$ 288.1417; found 288.1411.

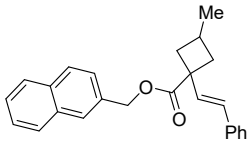


(*E*)-morpholino(1-styrylcyclobutyl)methanone (3la): A colorless oil, 34.1 mg, 63% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 6.50 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 3.75 – 3.60 (m, 4H), 3.53 (t, *J* = 4.8 Hz, 2H), 3.25 (t, *J* = 4.8 Hz, 2H), 2.76 – 2.64 (m, 2H), 2.27 – 2.15 (m, 2H), 2.08 – 1.97 (m, 1H), 1.90 – 1.81 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.8, 136.7, 132.1, 128.7, 128.1, 127.6, 126.2, 67.0, 66.4, 50.1, 46.3, 42.5, 31.9, 15.2; **IR (acetone)**: ν 2956, 2852, 1629, 1448, 1423, 1271, 1229, 1112, 1055, 965, 845, 746, 693 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{22}O_2N$ 272.1645; found 272.1640.

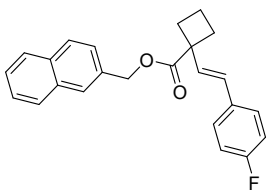


(*E*)-(2-(1-(phenylsulfonyl)cyclobutyl)vinyl)benzene (3ma): A white solid, 37.1 mg,

62% yield. Eluent: PE/EA = 4/1. M.p.: 75 – 77 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.0 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 5H), 6.23 (s, 2H), 3.07 – 2.97 (m, 2H), 2.27 – 2.19 (m, 2H), 2.17 – 2.09 (m, 1H), 2.04 – 1.95 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.8, 135.7, 134.5, 133.5, 129.8, 128.7, 128.5, 128.3, 126.5, 125.7, 67.2, 27.8, 15.2; **IR (acetone)**: ν 2958, 2852, 1445, 1139, 1108, 1024, 819, 764, 719 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{18}H_{18}O_2S$ 298.1022; found 298.1030.

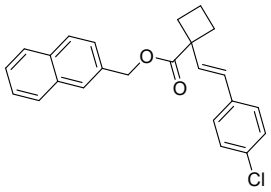


naphthalen-2-ylmethyl (*E*)-3-methyl-1-styrylcyclobutane-1-carboxylate (3na): A colorless oil, 30.6 mg, 43% yield. Eluent: PE/EA = 10/1, *d.r.* = 5:3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 6.4H), 7.49 – 7.43 (m, 4.8H), 7.38 – 7.28 (m, 6.4H), 7.24 – 7.20 (m, 1.6H), 6.56 (d, *J* = 16.1 Hz, 1H), 6.53 – 6.45 (m, 1.6H), 6.39 (d, *J* = 16.0 Hz, 0.6H), 5.34 (s, 1.2H), 5.31 (s, 2H), 2.86 – 2.73 (m, 1.6H), 2.51 – 2.32 (m, 4.4H), 2.28 – 2.20 (m, 2H), 2.00 – 1.85 (m, 1.6H), 1.10 – 1.06 (m, 4.8H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.6 (*minor isomer*), 175.3, 136.9, 133.65 (*minor isomer*), 133.61, 133.2 (*minor isomer*), 133.0, 132.4 (*minor isomer*), 131.0, 129.3, 129.2 (*minor isomer*), 128.54, 128.52 (*minor isomer*), 128.32 (*minor isomer*), 128.30, 128.0 (*minor isomer*), 127.7, 127.5, 127.4 (*minor isomer*), 126.9, 126.34, 126.27 (*minor isomer*), 126.22, 126.15 (*minor isomer*), 125.59, 125.58 (*minor isomer*), 66.6 (*minor isomer*), 66.5, 47.2 (*minor isomer*), 45.8, 39.2 (*minor isomer*), 38.2, 25.2 (*minor isomer*), 24.2, 22.0 (*minor isomer*), 21.5; **IR (acetone)**: ν 2950, 2864, 1724, 1600, 1450, 1220, 1199, 1120, 963, 855, 814, 743 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{25}H_{24}O_2$ 356.1771; found 356.1774.

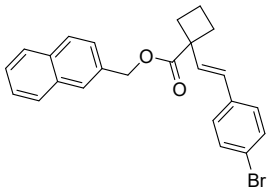


naphthalen-2-ylmethyl (*E*)-1-(4-fluorostyryl)cyclobutane-1-carboxylate (3ab): A colorless oil, 46.8 mg, 65% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 4H), 7.52 – 7.40 (m, 3H), 7.29 (dd, *J* = 8.8, 5.4 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 5.33 (s, 2H), 2.71 – 2.58 (m, 2H), 2.27 (dt, *J* = 12.5, 7.9 Hz, 2H), 2.01 – 1.88 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.2, 162.23 (d, *J* = 246.7 Hz), 133.6, 133.1, 133.04, 133.01, 131.0 (d, *J* = 2.8 Hz), 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.0, 126.2 (d, *J* = 8.3 Hz), 125.6, 115.4 (d, *J* = 21.9 Hz), 66.6, 50.0, 30.9, 16.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.7; **IR (acetone)**:

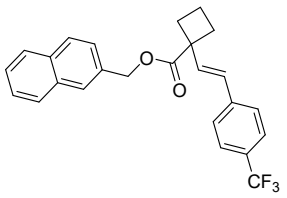
ν 2945, 1724, 1601, 1507, 1225, 1194, 1157, 1091, 964, 854, 812, 745 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{22}O_2F$ 361.1598; found 361.1629.



naphthalen-2-ylmethyl (*E*)-1-(4-chlorostyryl)cyclobutane-1-carboxylate (3ac): A colorless oil, 50.4 mg, 67% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 4H), 7.52 – 7.41 (m, 3H), 7.25 (s, 4H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.42 (d, *J* = 16.4 Hz, 1H), 5.33 (s, 2H), 2.65 (dt, *J* = 11.0, 8.4 Hz, 2H), 2.33 – 2.22 (m, 2H), 1.99 – 1.89 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.1, 135.4, 133.5, 133.1, 133.0, 131.9, 128.7, 128.3, 128.0, 127.9, 127.7, 127.5, 127.1, 126.3, 126.2, 125.6, 66.6, 50.0, 30.9, 16.0; **IR (acetone)**: ν 3066, 2934, 2872, 1723, 1489, 1218, 1089, 1012, 965, 855, 811, 764 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{24}H_{21}O_2Cl$ 376.1225; found 376.1216.

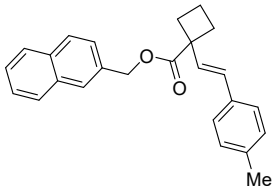


naphthalen-2-ylmethyl (*E*)-1-(4-bromostyryl)cyclobutane-1-carboxylate (3ad): A colorless oil, 57.1 mg, 68% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.50 – 7.42 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 16.1 Hz, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 5.33 (s, 2H), 2.71 – 2.59 (m, 2H), 2.33 – 2.21 (m, 2H), 2.00 – 1.90 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.0, 135.8, 133.5, 133.1, 133.0, 132.0, 131.6, 128.3, 128.0, 127.9, 127.8, 127.7, 127.1, 126.3, 126.2, 125.6, 121.2, 66.6, 50.0, 30.9, 16.0; **IR (acetone)**: ν 3055, 2944, 1725, 1487, 1274, 1218, 1195, 1097, 1072, 1008, 965, 855, 813, 747 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{24}H_{22}O_2Br$ 421.0798; found 421.0806.

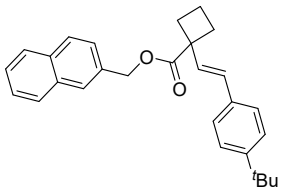


naphthalen-2-ylmethyl (*E*)-1-(4-(trifluoromethyl)styryl)cyclobutane -1-carboxylate (3ae): A white solid, 50.8 mg, 62% yield. Eluent: PE/EA = 10/1. M.p.: 88 – 90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.73 (m, 4H), 7.56 – 7.40 (m, 7H), 6.59 (d, *J* = 16.1 Hz, 1H), 6.50 (d, *J* = 16.1 Hz, 1H), 5.34 (s, 2H), 2.67 (dt, *J* = 12.5, 8.3 Hz, 2H), 2.35 – 2.24 (m, 2H), 2.02 – 1.92 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.9, 140.4, 134.0, 133.5, 133.14, 133.07, 129.3 (q, *J* = 32.6 Hz), 128.4,

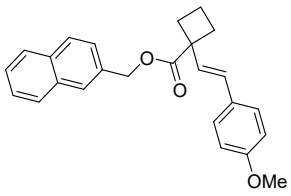
128.0, 127.9, 127.7, 127.2, 126.5, 126.31, 126.28, 125.7, 125.47 (q, J = 4.0 Hz), 124.2 (q, J = 272.0 Hz), 66.7, 50.1, 30.9, 16.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.4; **IR (acetone)**: ν 2946, 1726, 1615, 1508, 1321, 1161, 1116, 1066, 1015, 966, 855, 814, 746 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{22}O_2F_3$ 411.1566; found 411.1548.



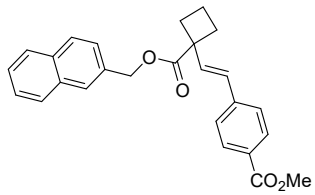
naphthalen-2-ylmethyl (*E*)-1-(4-methylstyryl)cyclobutane-1-carboxylate (3af): A colorless oil, 53.4 mg, 75% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 4H), 7.49 – 7.41 (m, 3H), 7.25 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.46 (d, J = 16.1 Hz, 1H), 6.43 (d, J = 16.1 Hz, 1H), 5.32 (s, 2H), 2.70 – 2.57 (m, 2H), 2.32 (s, 3H), 2.31 – 2.23 (m, 2H), 1.99 – 1.89 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.4, 137.2, 134.1, 133.6, 133.1, 133.0, 130.1, 129.2, 129.0, 128.3, 127.9, 127.6, 126.9, 126.21, 126.17, 126.1, 125.6, 66.5, 50.0, 30.9, 21.1, 16.0; **IR (acetone)**: ν 2944, 1724, 1511, 1437, 1511, 1437, 1219, 1195, 1095, 965, 855, 812, 745 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{25}O_2$ 357.1849; found 357.1864.



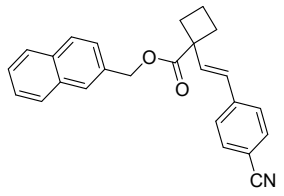
naphthalen-2-ylmethyl (*E*)-1-(4-(tert-butyl)styryl)cyclobutane -1-carboxylate (3ag): A white solid, 66.1 mg, 83% yield. Eluent: PE/EA = 10/1. M.p.: 81 – 83 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.70 (m, 4H), 7.51 – 7.40 (m, 3H), 7.39 – 7.24 (m, 4H), 6.51 (d, J = 16.1 Hz, 1H), 6.45 (d, J = 16.1 Hz, 1H), 5.32 (s, 2H), 2.64 (dt, J = 12.1, 8.1 Hz, 2H), 2.34 – 2.22 (m, 2H), 2.01 – 1.87 (m, 2H), 1.31 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.4, 150.6, 134.1, 133.6, 133.2, 133.0, 130.4, 129.0, 128.3, 128.0, 127.6, 126.9, 126.2, 126.1, 126.0, 125.6, 125.5, 66.5, 50.0, 34.5, 31.3, 30.9, 16.0; **IR (acetone)**: ν 2951, 2915, 1724, 1558, 1456, 1266, 1221, 1098, 967, 856, 817, 741 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{31}O_2$ 399.2319; found 399.2315.



naphthalen-2-ylmethyl (*E*)-1-(4-methoxystyryl)cyclobutane-1-carboxylate (3ah): A colorless oil, 64.7 mg, 87% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.50 – 7.41 (m, 3H), 7.32 – 7.25 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.45 (d, *J* = 16.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 5.32 (s, 2H), 3.79 (s, 3H), 2.70 – 2.57 (m, 2H), 2.34 – 2.21 (m, 2H), 2.01 – 1.86 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.4, 159.1, 133.7, 133.1, 133.0, 129.6, 129.0, 128.6, 128.3, 127.9, 127.6, 127.5, 126.9, 126.2, 126.1, 125.6, 113.9, 66.5, 55.2, 50.0, 31.0, 16.0; **IR (acetone)**: ν 2960, 2852, 1730, 1652, 1456, 1260, 1088, 1019, 797 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}O_3Na$ 395.1618; found 395.1624.

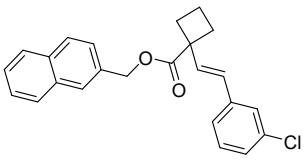


methyl (*E*)-4-(2-(1-((naphthalen-2-ylmethoxy)carbonyl)cyclobutyl)vinyl)benzoate (3ai): A white solid, 49.6 mg, 62% yield. Eluent: PE/EA = 10/1. M.p.: 98 – 100 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.84 – 7.74 (m, 4H), 7.51 – 7.42 (m, 3H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 6.51 (d, *J* = 16.1 Hz, 1H), 5.34 (s, 2H), 3.90 (s, 3H), 2.72 – 2.60 (m, 2H), 2.35 – 2.24 (m, 2H), 2.01 – 1.92 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.9, 166.8, 141.4, 133.9, 133.4, 133.1, 133.0, 129.9, 128.9, 128.34, 128.32, 127.9, 127.7, 127.1, 126.3, 126.23, 126.18, 125.6, 66.7, 52.0, 50.1, 30.9, 16.0; **IR (acetone)**: ν 2990, 2937, 2870, 1713, 1603, 1455, 1437, 1268, 1182, 972, 816, 748 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{31}O_2$ 401.1747; found 401.1740.

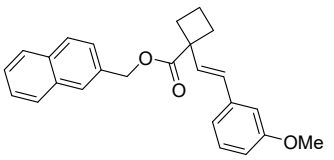


naphthalen-2-ylmethyl (*E*)-1-(4-cyanostyryl)cyclobutane-1-carboxylate (3aj): A colorless oil, 41.8 mg, 57% yield. Eluent: PE/EA = 6/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 4H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 6.46 (d, *J* = 16.1 Hz, 1H), 5.34 (s, 2H), 2.67 (dt, *J* = 12.3, 8.6 Hz, 2H), 2.35 – 2.23 (m, 2H), 2.03 – 1.93 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.7, 141.4, 135.3, 133.4, 133.11, 133.07, 132.3, 128.4, 127.9, 127.7, 127.2, 126.8, 126.34, 126.32, 125.7, 118.9, 110.6, 66.8, 50.1, 30.9, 16.0; **IR (acetone)**: ν 2985, 2945, 2224, 1724, 1603, 1282, 1219, 1197, 1099, 967, 857, 815, 748 cm^{-1}; **HRMS** (DART)

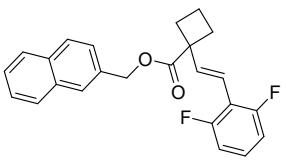
m/z: $[M+H]^+$ Calcd. for $C_{25}H_{22}O_2N$ 368.1645; found 368.1652.



naphthalen-2-ylmethyl (*E*)-1-(3-chlorostyryl)cyclobutane-1-carboxylate (3ak): A colorless oil, 49.5 mg, 66% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 4H), 7.52 – 7.40 (m, 3H), 7.34 (s, 1H), 7.22 – 7.15 (m, 3H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 5.33 (s, 2H), 2.65 (dt, *J* = 12.1, 8.4 Hz, 2H), 2.33 – 2.21 (m, 2H), 2.01 – 1.89 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.0, 138.8, 134.5, 133.5, 133.1, 133.0, 132.8, 129.7, 128.4, 127.94, 127.92, 127.7, 127.4, 127.1, 126.3, 126.2, 125.6, 124.6, 66.6, 50.0, 30.9, 16.0; **IR (acetone)**: ν 3057, 2945, 2867, 1725, 1593, 1565, 1473, 1272, 1196, 1101, 962, 889, 855, 815, 775, 747 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{22}O_2Cl$ 377.1303; found 377.1292.

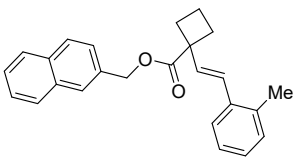


naphthalen-2-ylmethyl (*E*)-1-(3-methoxystyryl)cyclobutane-1-carboxylate (3al): A light-yellow oil, 47.4 mg, 64% yield. Eluent: PE/EA = 8/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 4H), 7.50 – 7.42 (m, 3H), 7.26 – 7.16 (m, 1H), 6.96 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.89 (t, *J* = 2.1 Hz, 1H), 6.79 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.55 – 6.42 (m, 2H), 5.33 (s, 2H), 3.78 (s, 3H), 2.71 – 2.59 (m, 2H), 2.34 – 2.23 (m, 2H), 2.02 – 1.89 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.3, 159.8, 138.3, 133.6, 133.1, 133.0, 131.5, 129.5, 129.1, 128.3, 128.0, 127.6, 127.0, 126.22, 126.16, 125.6, 119.0, 113.3, 111.5, 66.5, 55.2, 50.0, 30.9, 16.0; **IR (acetone)**: ν 3046, 2943, 1724, 1597, 1578, 1453, 1433, 1261, 1192, 1155, 1099, 1045, 964, 814, 746 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{25}O_3$ 373.1798; found 373.1840.

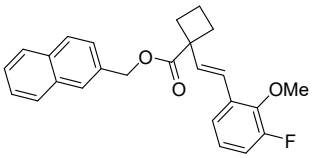


naphthalen-2-ylmethyl (*E*)-1-(2,6-difluorostyryl)cyclobutane -1-carboxylate (3am): A colorless oil, 46.2 mg, 61% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 4H), 7.52 – 7.42 (m, 3H), 7.18 – 7.07 (m, 1H), 6.93 – 6.79 (m, 3H), 6.56 (d, *J* = 16.5 Hz, 1H), 5.34 (s, 2H), 2.72 – 2.59 (m, 2H), 2.32 (dt, *J* = 12.4, 7.9 Hz, 2H), 2.02 – 1.91 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.0, 160.84 (d, *J* = 251.4 Hz), 160.80 (d, *J* = 251.4 Hz), 138 (t, *J* = 8.1 Hz), 133.6, 133.1 (d, *J* = 20.7 Hz),

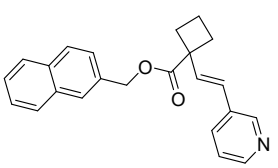
128.3, 127.99, 127.96, 127.9, 127.8, 127.7, 126.9, 126.2, 126.1, 125.5, 115.9, 114.2 (t, J = 16.4 Hz), 111.5 (d, J = 5.6 Hz), 111.4 (d, J = 5.6 Hz), 66.6, 50.9, 30.8, 16.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.2; **IR (acetone)**: ν 2947, 1727, 1583, 1463, 1264, 1231, 1198, 1103, 997, 972, 815, 778, 746 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{21}O_2F_2$ 379.1504; found 379.1530.



naphthalen-2-ylmethyl (*E*)-1-(2-methylstyryl)cyclobutane-1-carboxylate (3an): A colorless oil, 52.7 mg, 74% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.71 (m, 4H), 7.50 – 7.37 (m, 4H), 7.17 – 7.06 (m, 3H), 6.72 (d, J = 16.0 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 5.32 (s, 2H), 2.72 – 2.60 (m, 2H), 2.35 – 2.22 (m, 5H), 2.03 – 1.88 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.3, 136.0, 135.3, 133.6, 133.1, 133.0, 132.6, 130.2, 128.3, 127.9, 127.6, 127.3, 127.1, 127.0, 126.2, 126.1, 126.0, 125.63, 125.59, 66.5, 50.2, 31.0, 19.7, 16.0; **IR (acetone)**: ν 2944, 1724, 1601, 1508, 1272, 1189, 1094, 964, 854, 814, 744 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{25}O_2$ 357.1849; found 357.1840.

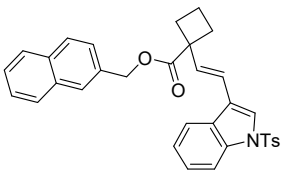


naphthalen-2-ylmethyl (*E*)-1-(3-fluoro-2-methoxystyryl)cyclobutane-1-carboxylate (3ao): A yellow oil, 56.3 mg, 72% yield. Eluent: PE/EA = 8/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 4H), 7.50 – 7.43 (m, 3H), 7.23 – 7.18 (m, 1H), 7.01 – 6.91 (m, 2H), 6.81 (d, J = 16.2 Hz, 1H), 6.54 (d, J = 16.2 Hz, 1H), 5.33 (s, 2H), 3.82 (s, 3H), 2.72 – 2.60 (m, 2H), 2.37 – 2.25 (m, 2H), 2.02 – 1.90 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.2, 155.87 (d, J = 246.2 Hz), 144.98 (d, J = 11.3 Hz), 133.5, 133.3, 133.1, 133.0, 132.04 (d, J = 2.9 Hz), 128.3, 127.9, 127.6, 127.0, 126.25, 126.19, 125.6, 123.6 (d, J = 8.7 Hz), 122.9 (d, J = 4.1 Hz), 121.6 (d, J = 3.6 Hz), 115.5 (d, J = 19.6 Hz), 66.6, 61.4 (d, J = 5.6 Hz), 50.3, 30.9, 16.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -131.2. **IR (acetone)**: ν 3055, 2937, 1724, 1474, 1430, 1275, 1250, 1208, 1100, 1069, 1004, 972, 855, 813, 775, 744 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{24}O_3F$ 391.1704; found 391.1739.

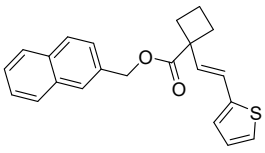


naphthalen-2-ylmethyl (*E*)-1-(2-(pyridin-3-yl)vinyl)cyclobutane-1-

carboxylate (3ap): A yellow oil, 41.9 mg, 61% yield. Eluent: PE/EA = 6/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.46 (d, *J* = 5.1 Hz, 1H), 7.87 – 7.74 (m, 4H), 7.65 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.22 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.57 (d, *J* = 16.3 Hz, 1H), 6.47 (d, *J* = 16.1 Hz, 1H), 5.34 (s, 2H), 2.73 – 2.61 (m, 2H), 2.35 – 2.24 (m, 2H), 2.03 – 1.92 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 174.9, 148.5, 148.3, 133.6, 133.4, 133.13, 133.07, 132.7, 128.4, 127.9, 127.7, 127.2, 126.32, 126.27, 125.70, 125.65, 66.8, 50.1, 30.9, 16.0; **IR (acetone)**: ν 3027, 2944, 2850, 1723, 1568, 1413, 1272, 1243, 1191, 1098, 965, 855, 815, 748, 707 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{22}O_2N$ 344.1645; found 344.1674.

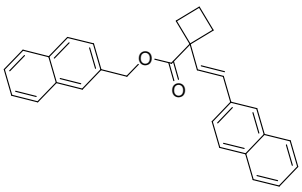


naphthalen-2-ylmethyl (*E*)-1-(2-(1-tosyl-1*H*-indol-3-yl)vinyl) cyclobutane-1-carboxylate (3aq): A yellow oil, 60.0 mg, 52% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.79 (m, 3H), 7.78 – 7.70 (m, 3H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.52 – 7.40 (m, 3H), 7.35 – 7.26 (m, 1H), 7.23 – 7.11 (m, 3H), 6.6 (d, *J* = 16.4 Hz, 1H), 6.5 (d, *J* = 16.4 Hz, 1H), 5.35 (s, 2H), 2.67 (dt, *J* = 12.3, 8.2 Hz, 2H), 2.40 – 2.21 (m, 5H), 2.03 – 1.91 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.2, 145.0, 135.5, 135.1, 133.5, 133.14, 133.05, 132.6, 129.9, 128.9, 128.4, 127.9, 127.7, 127.2, 126.8, 126.3, 126.2, 125.7, 124.9, 123.7, 123.4, 120.4, 120.1, 119.8, 113.7, 66.7, 50.3, 30.9, 21.5, 16.0; **IR (acetone)**: ν 3057, 2937, 1725, 1445, 1372, 1271, 1187, 1173, 1122, 1041, 974, 813, 745 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{30}O_4NS$ 536.1890; found 536.1890.

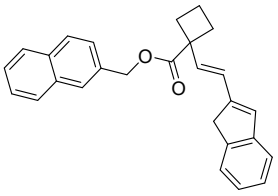


naphthalen-2-ylmethyl (*E*)-1-(2-(thiophen-2-yl)vinyl)cyclobutane- 1-carboxylate (3ar): A yellow oil, 38.4 mg, 55% yield. Eluent: PE/EA = 12/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 4H), 7.52 – 7.41 (m, 3H), 7.15 (d, *J* = 5.1 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.91 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.33 (s, 2H), 2.69 – 2.57 (m, 2H), 2.32 – 2.19 (m, 2H), 2.00 – 1.88 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.1, 142.1, 133.6, 133.2, 133.0, 130.8, 128.3, 128.0, 127.7, 127.3, 126.9, 126.2, 126.2, 125.6, 125.5, 124.1, 122.7, 66.6, 49.9, 30.9, 16.0; **IR (acetone)**: ν 3060, 2944, 1726, 1496, 1271, 1196, 1098, 953, 854, 814, 747 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$

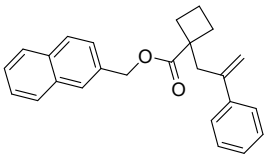
Calcd. for $C_{22}H_{21}O_2S$ 349.1257; found 349.1259.



naphthalen-2-ylmethyl (*E*)-1-(2-(naphthalen-2-yl)vinyl)cyclobutane-1-carboxylate (3as): A colorless oil, 53.2 mg, 68% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 7H), 7.66 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.38 (m, 5H), 6.7 (d, *J* = 16.0 Hz, 1H), 6.6 (d, *J* = 16.0 Hz, 1H), 5.36 (s, 2H), 2.69 (dt, *J* = 12.3, 8.3 Hz, 2H), 2.34 (dt, *J* = 12.0, 7.7 Hz, 2H), 2.04 – 1.92 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.3, 134.3, 133.62, 133.58, 133.2, 133.0, 132.9, 131.6, 129.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.1, 126.3, 126.24, 126.21, 126.18, 125.8, 125.7, 123.5, 66.6, 50.2, 31.0, 16.1; **IR (EtOH)**: ν 3054, 2944, 1723, 1598, 1507, 1360, 1271, 1217, 1096, 961, 893, 856, 811, 742 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{28}H_{24}O_2$ 392.1771; found 392.1759.

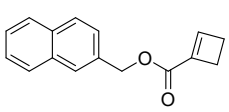


naphthalen-2-ylmethyl (*E*)-1-(2-(1H-inden-2-yl)vinyl)cyclobutane-1-carboxylate (3at): A colorless oil, 39.0 mg, 55% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.71 (s, 1H), 7.67 (d, *J* = 6.8 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.30 (m, 3H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.76 (s, 1H), 5.31 (s, 2H), 3.37 (s, 2H), 2.81 – 2.69 (m, 2H), 2.48 – 2.35 (m, 2H), 2.03 – 1.90 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.1, 149.9, 144.5, 143.3, 133.5, 133.1, 133.0, 128.3, 128.0, 127.6, 127.5, 126.9, 126.4, 126.2, 126.2, 125.5, 124.4, 123.6, 120.7, 66.6, 50.2, 38.4, 31.6, 16.4; **IR (acetone)**: ν 3055, 2946, 1726, 1603, 1459, 1272, 1226, 1195, 1106, 1093, 855, 814, 751 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{23}O_2$ 355.1693; found 355.1728.

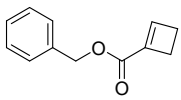


naphthalen-2-ylmethyl 1-(2-phenylallyl)cyclobutane-1-carboxylate (3au): A colorless oil, 54.1 mg, 76% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.72 (s, 1H), 7.49 – 7.44 (m, 2H), 7.38 – 7.31 (m, 3H), 7.29 – 7.22 (m, 3H), 5.19 (d, *J* = 1.1 Hz, 1H), 5.02 (s, 2H), 4.94 (d, *J* = 1.5 Hz, 1H), 3.04 (s, 2H), 2.50 – 2.40 (m, 2H), 2.04 – 1.95 (m, 2H), 1.94 – 1.85 (m, 2H); **^{13}C NMR** (151 MHz,

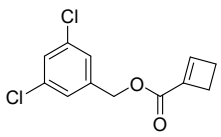
$CDCl_3$) δ 176.4, 145.5, 141.9, 133.6, 133.1, 133.0, 128.15, 128.08, 127.9, 127.6, 127.3, 127.0, 126.4, 126.2, 126.1, 125.7, 114.4, 66.2, 47.4, 42.9, 30.3, 15.8; **IR (acetone)**: ν 3055, 2943, 1725, 1319, 1246, 1191, 1115, 898, 855, 815, 777, 746 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{25}O_2$ 357.1849; found 357.1847.



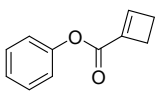
naphthalen-2-ylmethyl cyclobut-1-ene-1-carboxylate (4a): A colorless oil, 41.0 mg, 86% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 4H), 7.51 – 7.44 (m, 3H), 6.86 – 6.78 (m, 1H), 5.33 (s, 2H), 2.79 – 2.70 (m, 2H), 2.46 (td, *J* = 3.4, 1.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.0, 147.1, 138.4, 133.5, 133.2, 133.1, 128.3, 128.0, 127.7, 127.3, 126.25, 126.20, 125.9, 65.9, 29.1, 27.2; **IR (acetone)**: ν 3055, 2928, 1713, 1603, 1313, 1277, 1237, 1108, 907, 855, 814, 748 cm^{-1}; **HRMS** (DART) m/z: $[M]^+$ Calcd. for $C_{12}H_{13}O_2$ 238.0988; found 238.0985.



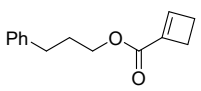
benzyl cyclobut-1-ene-1-carboxylate (4b): A colorless oil, 34.3 mg, 91% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[19] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 6.83 – 6.79 (m, 1H), 5.18 (s, 2H), 2.75 (t, *J* = 3.2 Hz, 2H), 2.50 – 2.44 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.0, 147.0, 138.4, 136.1, 128.5, 128.1, 65.7, 29.1, 27.2;



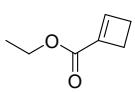
3,5-dichlorobenzyl cyclobut-1-ene-1-carboxylate (4c): A yellow oil, 47.7 mg, 93% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 6.94 – 6.81 (m, 1H), 5.11 (s, 2H), 2.76 (t, *J* = 3.3 Hz, 2H), 2.54 – 2.47 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.5, 147.9, 139.4, 137.9, 135.1, 128.2, 126.3, 64.0, 29.1, 27.3; **IR (neat)**: ν 2973, 2920, 1719, 1570, 1432, 1367, 1312, 1237, 1186, 1112, 851, 798 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{11}O_2Cl_2$ 257.0131; found 257.0126.



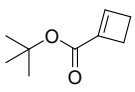
phenyl cyclobut-1-ene-1-carboxylate (4d): A colorless oil, 31.3 mg, 90% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.96 (m, 1H), 2.84 (t, *J* = 3.2 Hz 2H), 2.55 (t, *J* = 3.4 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.2, 150.5, 148.9, 138.0, 129.3, 125.7, 121.5, 29.2, 27.4;



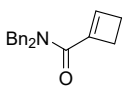
3-phenylpropyl cyclobut-1-ene-1-carboxylate (4e): A colorless oil, 41.0 mg, 95% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.78 – 6.74 (m, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 2.75 – 2.67 (m, 4H), 2.46 (t, *J* = 3.4 Hz, 2H), 2.05 – 1.93 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.2, 146.3, 141.1, 138.7, 128.33, 128.31, 125.9, 63.3, 32.1, 30.1, 29.0, 27.0; **IR (neat)**: ν 2928, 1715, 1603, 1496, 1315, 1238, 1186, 1116, 908, 744 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_2$ 217.1223; found 217.1220.



ethyl cyclobut-1-ene-1-carboxylate (4f): A colorless liquid, 23.8 mg, 94% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[19] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 – 6.71 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.73 (t, *J* = 3.3 Hz, 2H), 2.46 (t, *J* = 3.4 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4, 146.2, 138.9, 60.1, 29.1, 27.0, 14.3.

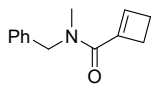


***tert*-butyl cyclobut-1-ene-1-carboxylate (4g)**: A colorless liquid, 26.5 mg, 86% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[19] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 – 6.64 (m, 1H), 2.68 (t, *J* = 3.2 Hz, 2H), 2.44 – 2.38 (m, 2H), 1.48 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.9, 144.9, 140.4, 80.2, 29.1, 28.1, 26.4.

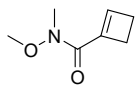


***N*,*N*-dibenzylcyclobut-1-ene-1-carboxamide (4h)**: A yellow oil, 40.0 mg, 72% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 6H), 7.26 – 7.22 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.44 – 6.34 (m, 1H), 4.61 (s, 2H), 4.58 (s, 2H), 2.87 – 2.81 (m, 2H), 2.46 – 2.39 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.3, 141.6, 140.6, 136.9, 136.7, 128.8,

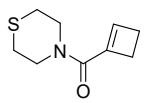
128.5, 128.4, 127.5, 127.3, 126.5, 49.9, 47.9, 31.6, 27.0; **IR (neat)**: ν 2925, 1711, 1624, 1581, 1452, 1421, 1360, 1247, 1077, 954, 737 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{20}ON$ 278.1539; found 278.1535.



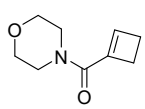
***N*-benzyl-*N*-methylcyclobut-1-ene-1-carboxamide (4i)**: A yellow oil, 29.8 mg, 74% yield. Eluent: PE/EA = 4/1. *Note*: this compound is a mixture of rotamers in a 1:1 ratio. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 8H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.55 – 6.43 (m, 1H), 6.40 – 6.26 (m, 1H), 4.71 (s, 2H), 4.63 (s, 2H), 3.06 (s, 3H), 2.94 (s, 3H), 2.88 (t, *J* = 3.3 Hz, 2H), 2.82 (t, *J* = 3.3 Hz, 2H), 2.48 (t, *J* = 3.6 Hz, 2H), 2.42 (t, *J* = 3.4 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.6, 163.6, 141.8, 140.8, 137.1, 136.9, 128.8, 128.6, 128.1, 127.5, 127.3, 126.4, 53.6, 51.1, 35.1, 33.6, 31.6, 27.1, 27.0; **IR (neat)**: ν 2928, 2841, 1709, 1623, 1581, 1401, 1359, 1220, 1074, 738 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{16}ON$ 202.1226; found 202.1224.



***N*-methoxy-*N*-methylcyclobut-1-ene-1-carboxamide (4j)**: A colorless liquid, 24.8 mg, 88% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 – 6.64 (m, 1H), 3.70 (s, 3H), 3.24 (s, 3H), 2.84 – 2.79 (m, 2H), 2.52 – 2.45 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8, 144.7, 139.3, 61.4, 32.5, 30.5, 27.5; **IR (neat)**: ν 2933, 1634, 1585, 1417, 1381, 1261, 1185, 989, 950, 915, 851 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_7H_{12}O_2N$ 142.0863; found 142.0880.

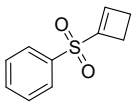


cyclobut-1-en-1-yl(thiomorpholino)methanone (4k): A yellow oil, 31.1 mg, 85% yield. Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.44 – 6.38 (m, 1H), 3.96 – 3.88 (m, 4H), 2.86 – 2.81 (m, 2H), 2.67 – 2.62 (m, 4H), 2.50 (t, *J* = 3.4 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8, 140.6, 48.4, 44.3, 31.7, 27.3; **IR (neat)**: ν 2948, 2919, 1616, 1581, 1457, 1427, 1253, 1118, 1126, 959, 839 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_9H_{14}ONS$ 184.0791; found 184.0804.

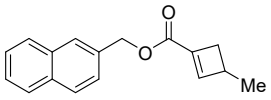


cyclobut-1-en-1-yl(morpholino)methanone (4l): A yellow oil, 26.0 mg, 78% yield.

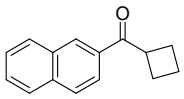
Eluent: PE/EA = 4/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.46 – 6.39 (m, 1H), 3.72 – 3.66 (m, 8H), 2.87 – 2.81 (m, 2H), 2.52 – 2.47 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 141.0, 140.5, 66.8, 46.2, 41.9, 31.6, 27.4; **IR (neat)**: ν 2953, 2920, 2849, 1615, 1583, 1429, 1279, 1249, 1111, 1026, 913, 832 cm^{-1}; **HRMS** (DART) m/z: $[M+H]^+$ Calcd. for $C_9H_{14}O_2N$ 168.1019; found 168.1017.



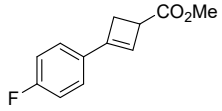
(cyclobut-1-en-1-ylsulfonyl)benzene (4m): A colorless oil, 31.9 mg, 82% yield. Eluent: PE/EA = 3/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.68 – 7.62 (m, 1H), 7.60 – 7.53 (m, 2H), 6.78 – 6.57 (m, 1H), 2.81 – 2.74 (m, 2H), 2.56 – 2.51 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 143.6, 138.8, 133.5, 129.2, 127.9, 29.9, 26.9; **IR (neat)**: ν 2933, 1622, 1477, 1302, 1149, 1120, 1078, 866, 757 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{10}H_{10}O_2S$ 194.0396; found 194.0404.



naphthalen-2-ylmethyl 3-methylcyclobut-1-ene-1-carboxylate (4n): A colorless oil, 27.8 mg, 55% yield. Eluent: PE/EA = 10/1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 4H), 7.50 – 7.46 (m, 3H), 6.86 (d, *J* = 1.2 Hz, 1H), 5.33 (s, 2H), 2.90 (dd, *J* = 13.2, 4.3 Hz, 1H), 2.86 – 2.79 (m, 1H), 2.23 (dd, *J* = 13.2, 1.5 Hz, 1H), 1.18 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.5, 152.0, 136.3, 133.4, 133.14, 133.06, 128.3, 127.9, 127.7, 127.3, 126.22, 126.18, 125.9, 65.9, 36.4, 34.9, 18.1; **IR (neat)**: ν 2956, 1716, 1604, 1452, 1372, 1274, 1235, 1145, 893, 855, 747 cm^{-1}; **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{17}H_{16}O_2$ 252.1145; found 252.1148.



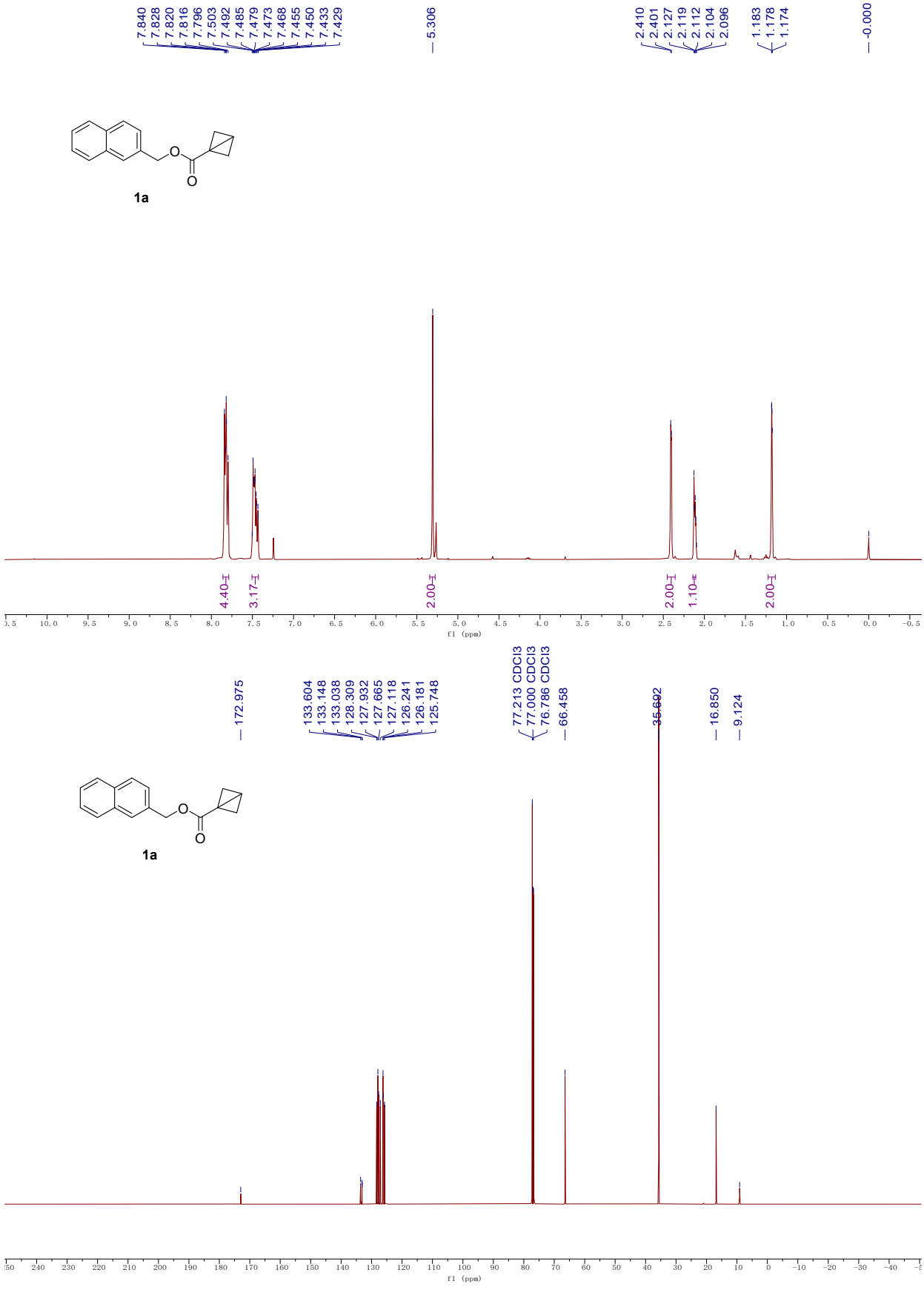
cyclobutyl(naphthalen-2-yl)methanone (4o): A colorless oil, 32.0 mg, 76% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.97 (dd, *J* = 18.7, 8.3 Hz, 2H), 7.91 – 7.83 (m, 2H), 7.63 – 7.50 (m, 2H), 4.23 – 4.10 (m, 1H), 2.56 – 2.43 (m, 2H), 2.42 – 2.32 (m, 2H), 2.20 – 2.06 (m, 1H), 2.01 – 1.90 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.0, 135.5, 133.0, 132.6, 129.8, 129.5, 128.4, 128.3, 127.7, 126.6, 124.2, 42.3, 25.2, 18.2;

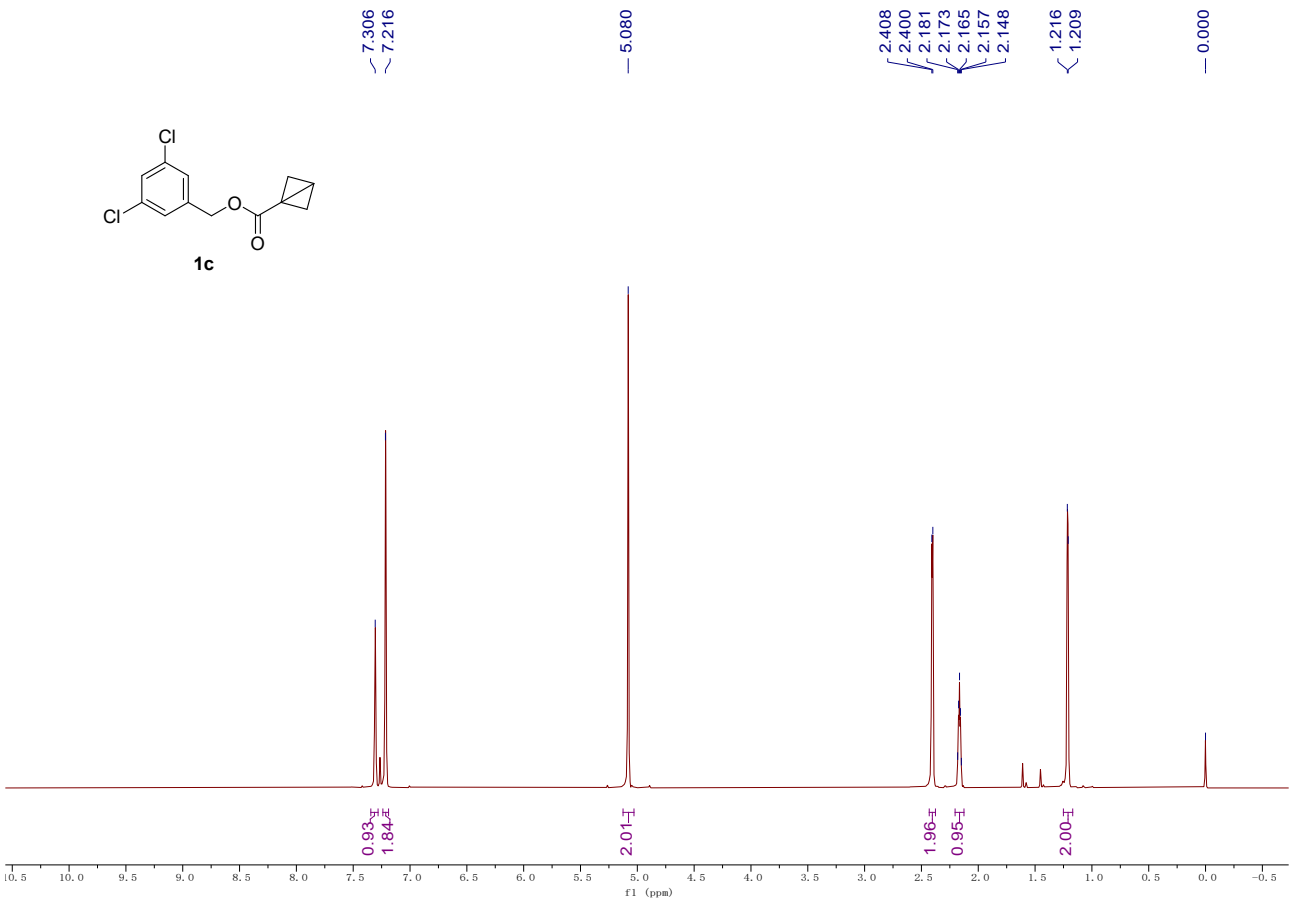


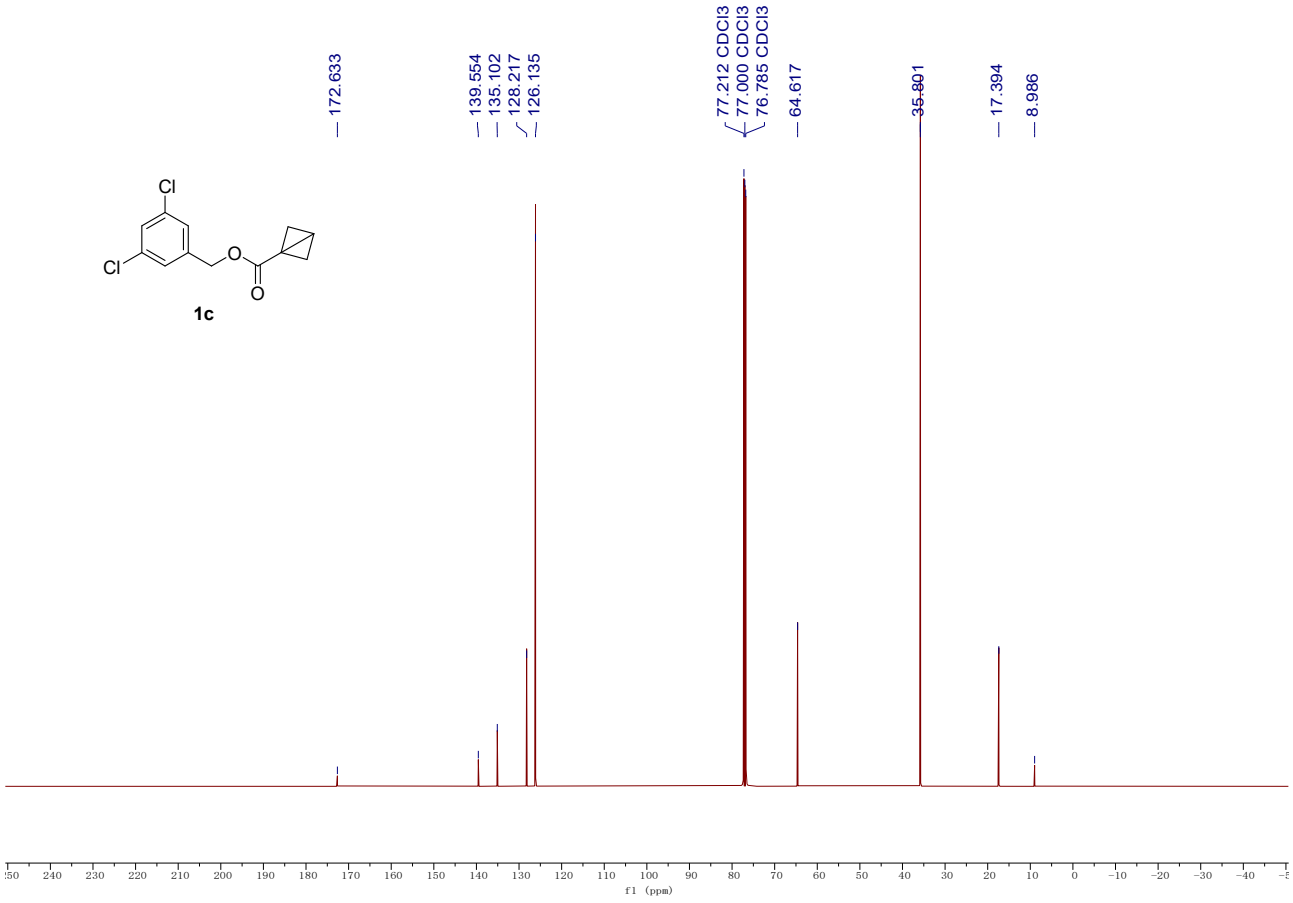
methyl 3-(4-fluorophenyl)cyclobut-2-ene-1-carboxylate (4p): A colorless oil,

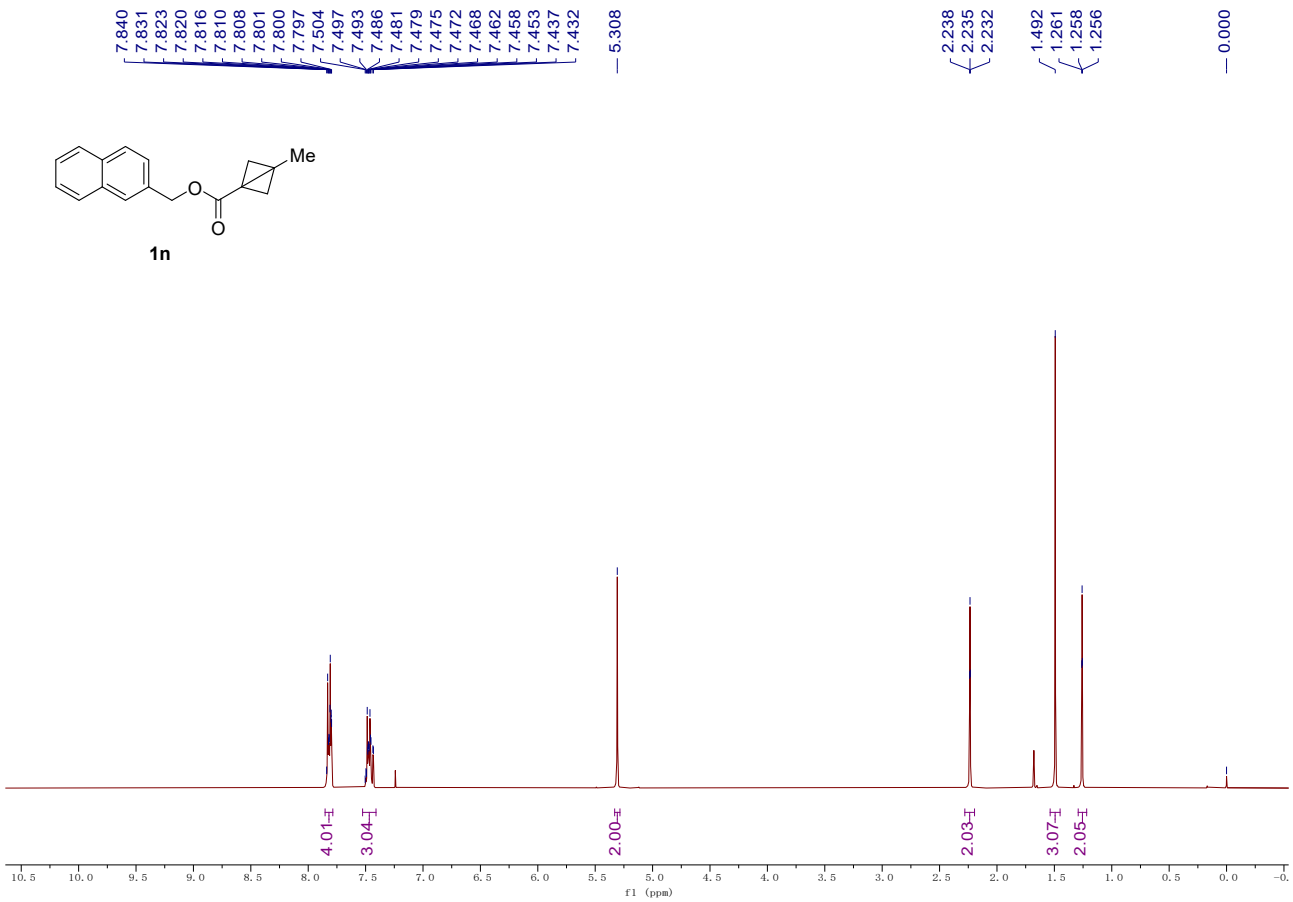
36.3 mg, 88% yield. Eluent: PE/EA = 10/1. The spectroscopic data were consistent with those of previously reported.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.05 – 6.99 (m, 2H), 6.21 (d, *J* = 1.6 Hz, 1H), 3.72 (s, 3H), 3.66 – 3.63 (m, 1H), 3.05 (dd, *J* = 13.0, 4.7 Hz, 1H), 2.98 (dd, *J* = 13.0, 2.2 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.8, 162.7 (d, *J* = 248.3 Hz), 147.1, 130.1 (d, *J* = 3.5 Hz), 126.5 (d, *J* = 8.7 Hz), 123.9 (d, *J* = 3.4 Hz), 115.3 (d, *J* = 22.1 Hz), 51.8, 41.1, 32.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.6.

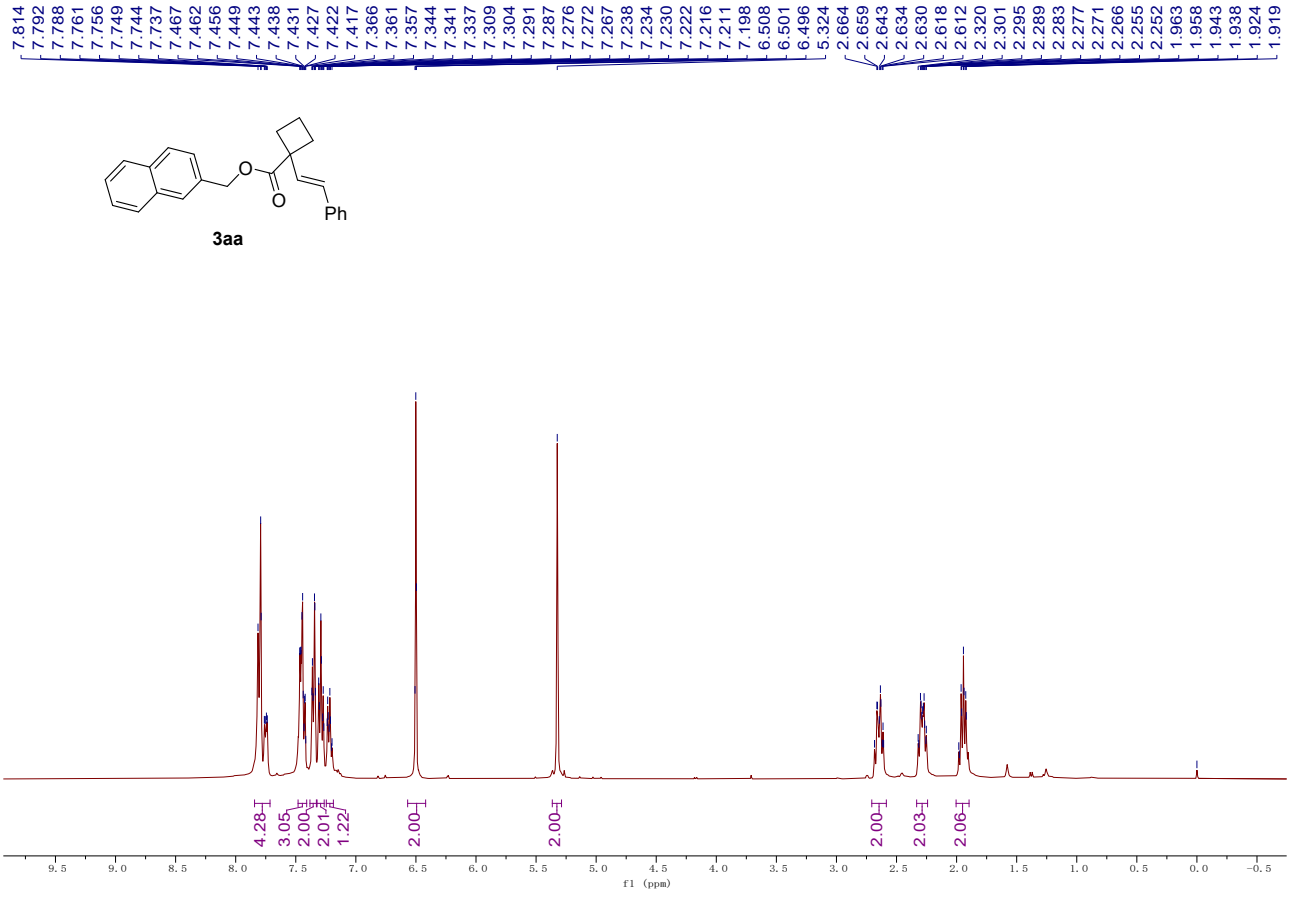
12. NMR Spectra

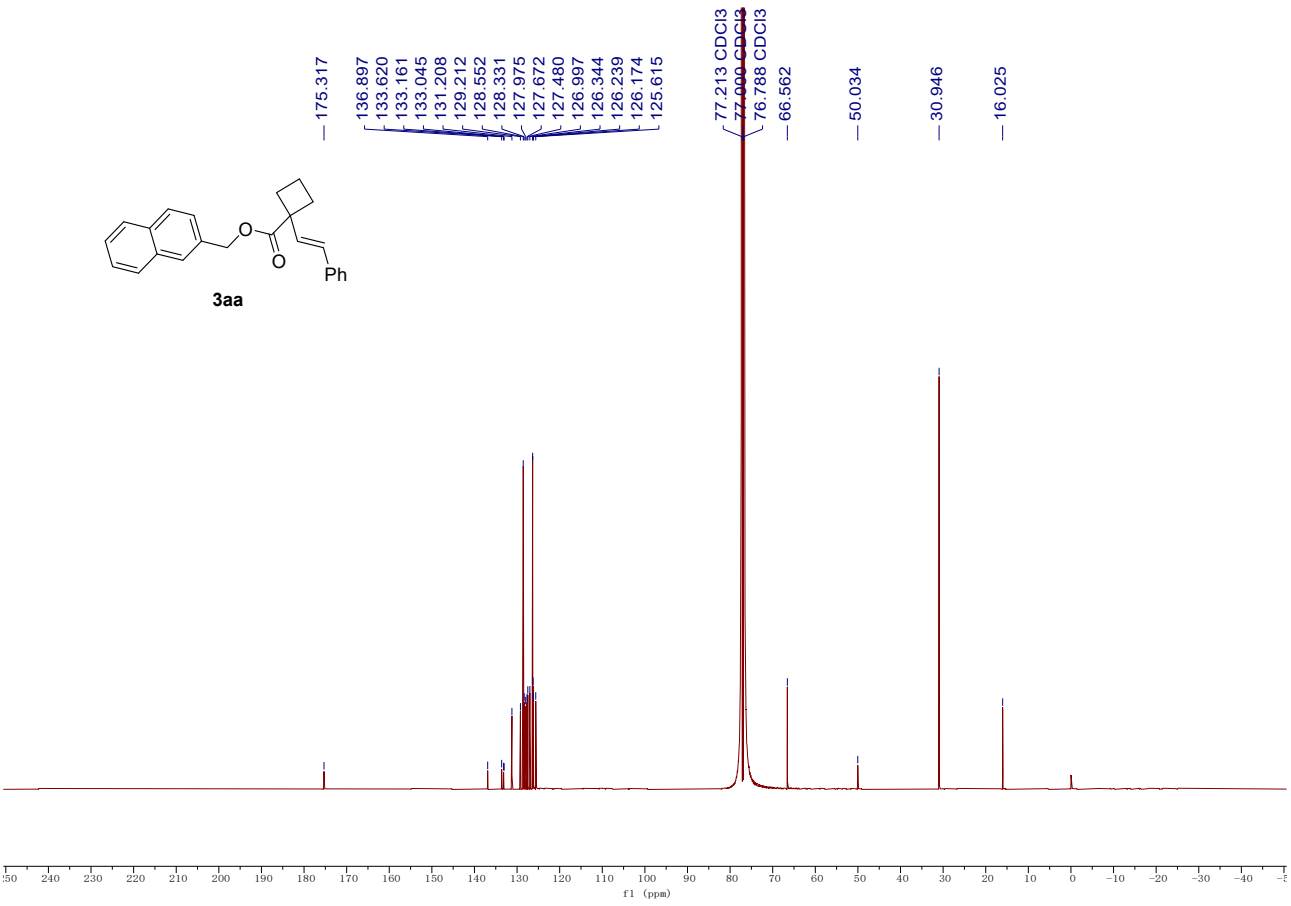


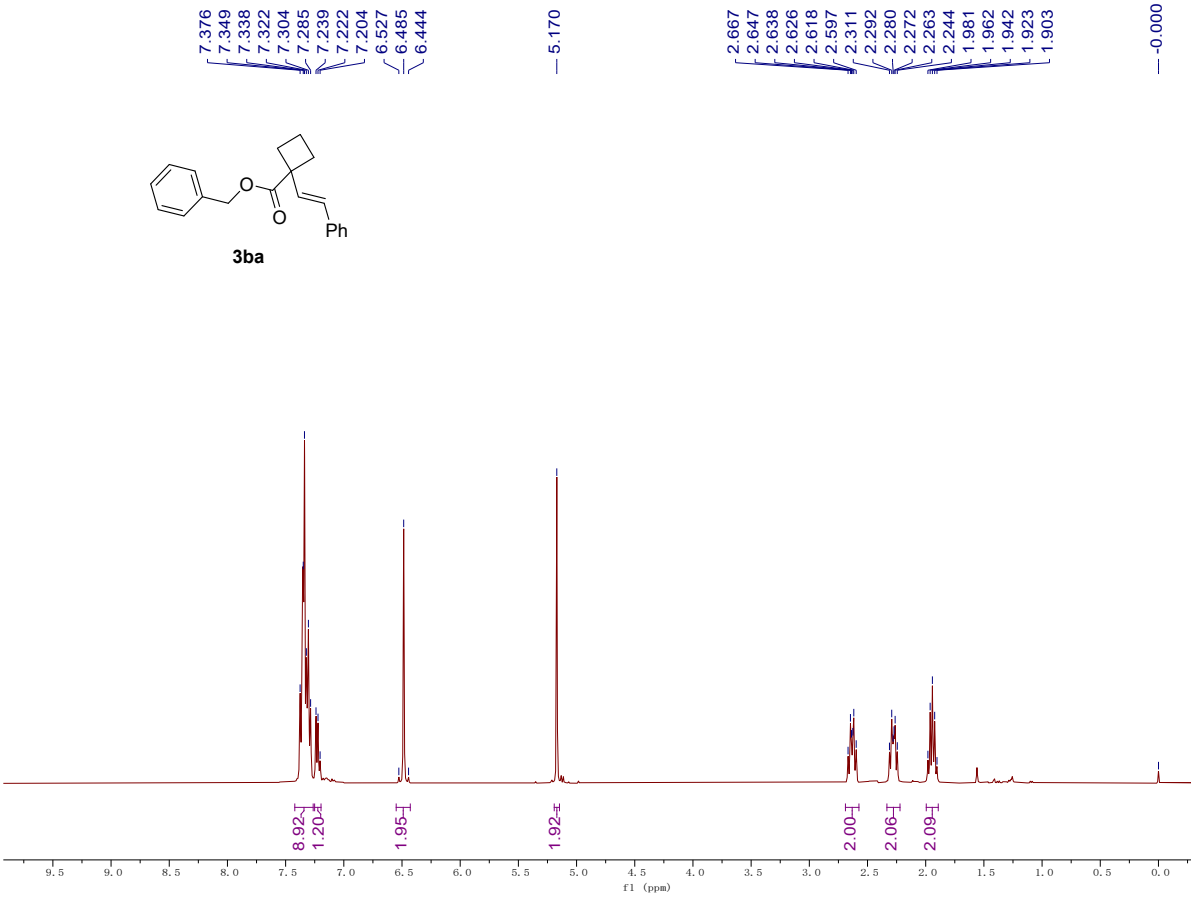

7.306
7.216
5.080
2.408
2.400
2.181
2.173
2.165
2.157
2.148
1.216
1.209
0.000
Cl
Cl
O
O
1c
0.93
1.84
2.01
1.96
0.95
2.00
f1 (ppm)

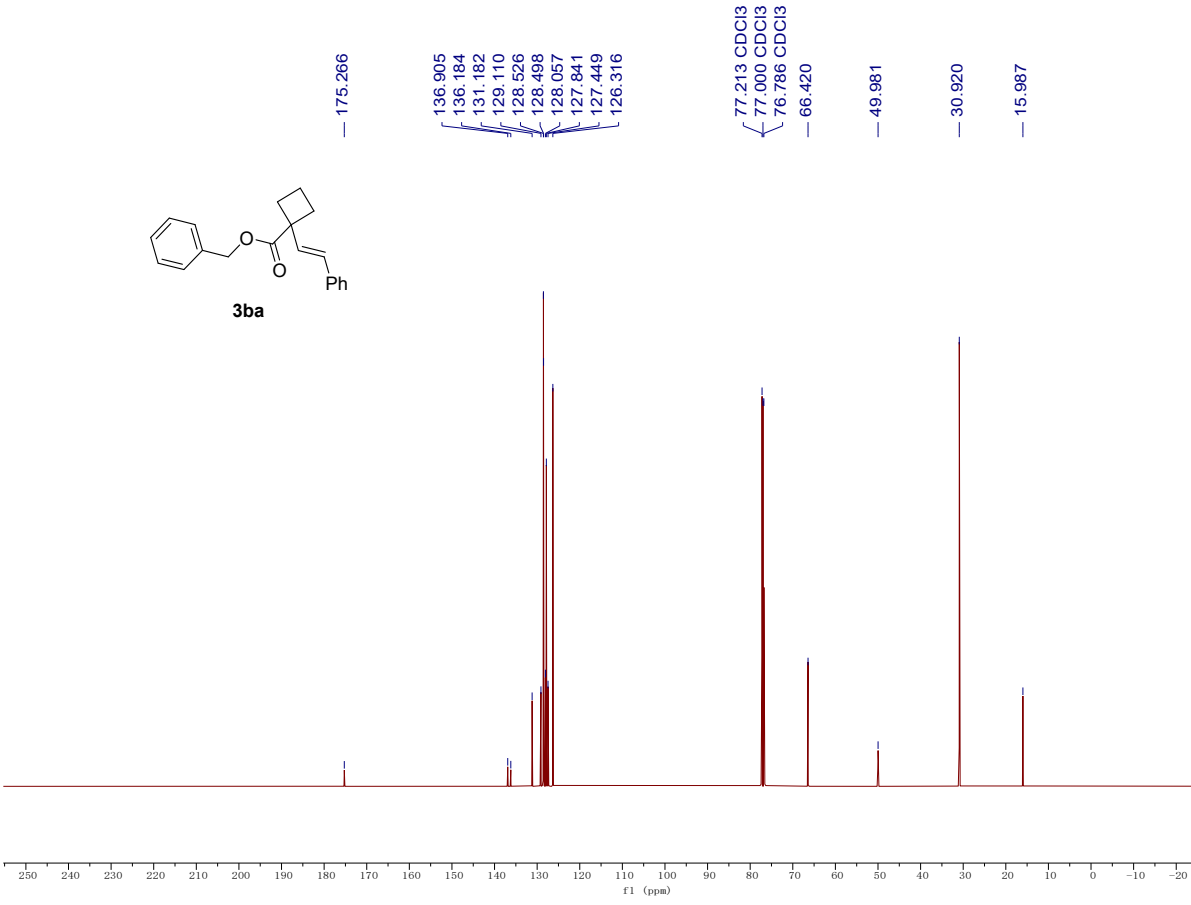

172.633
139.554
135.102
128.217
126.135
77.212 CDCl3
77.000 CDCl3
76.785 CDCl3
64.617
35.801
17.394
8.986
Cl
Cl
O
O
1c
f1 (ppm)

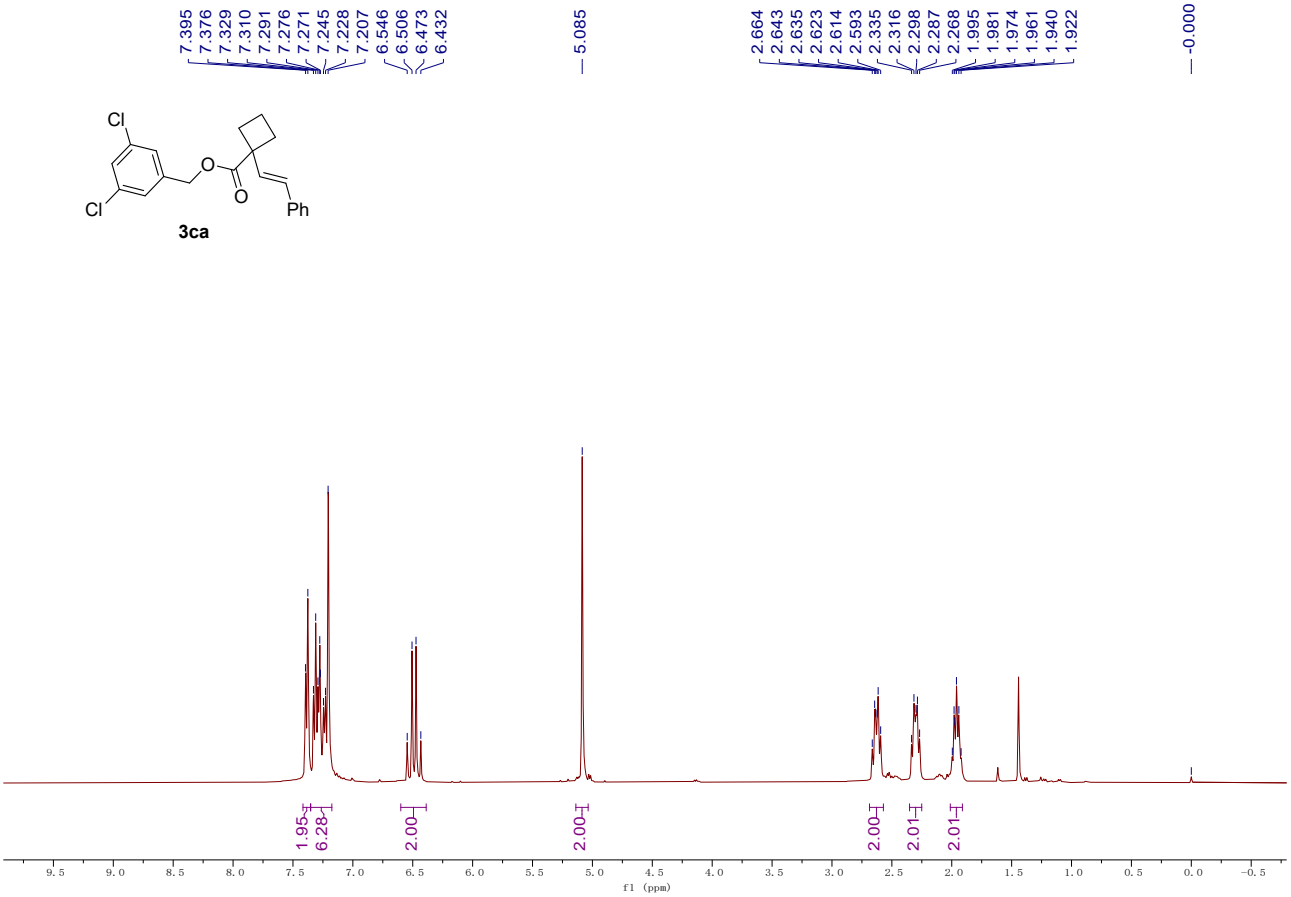

7.840
7.831
7.823
7.820
7.816
7.810
7.808
7.801
7.800
7.797
7.504
7.497
7.493
7.486
7.481
7.479
7.475
7.472
7.468
7.462
7.458
7.453
7.437
7.432
5.308
2.238
2.235
2.232
1.492
1.261
1.258
1.256
0.000
Me
O
O
1n
4.01
3.04
2.00
2.03
3.07
2.05
f1 (ppm)
171.994
134.002
133.128
132.999
128.233
127.904
127.644
127.121
126.198
126.126
125.805
77.215 CDCl3
77.000 CDCl3
76.788 CDCl3
66.230
38.820
27.967
13.061
12.685
Me
O
O
1n
f1 (ppm)

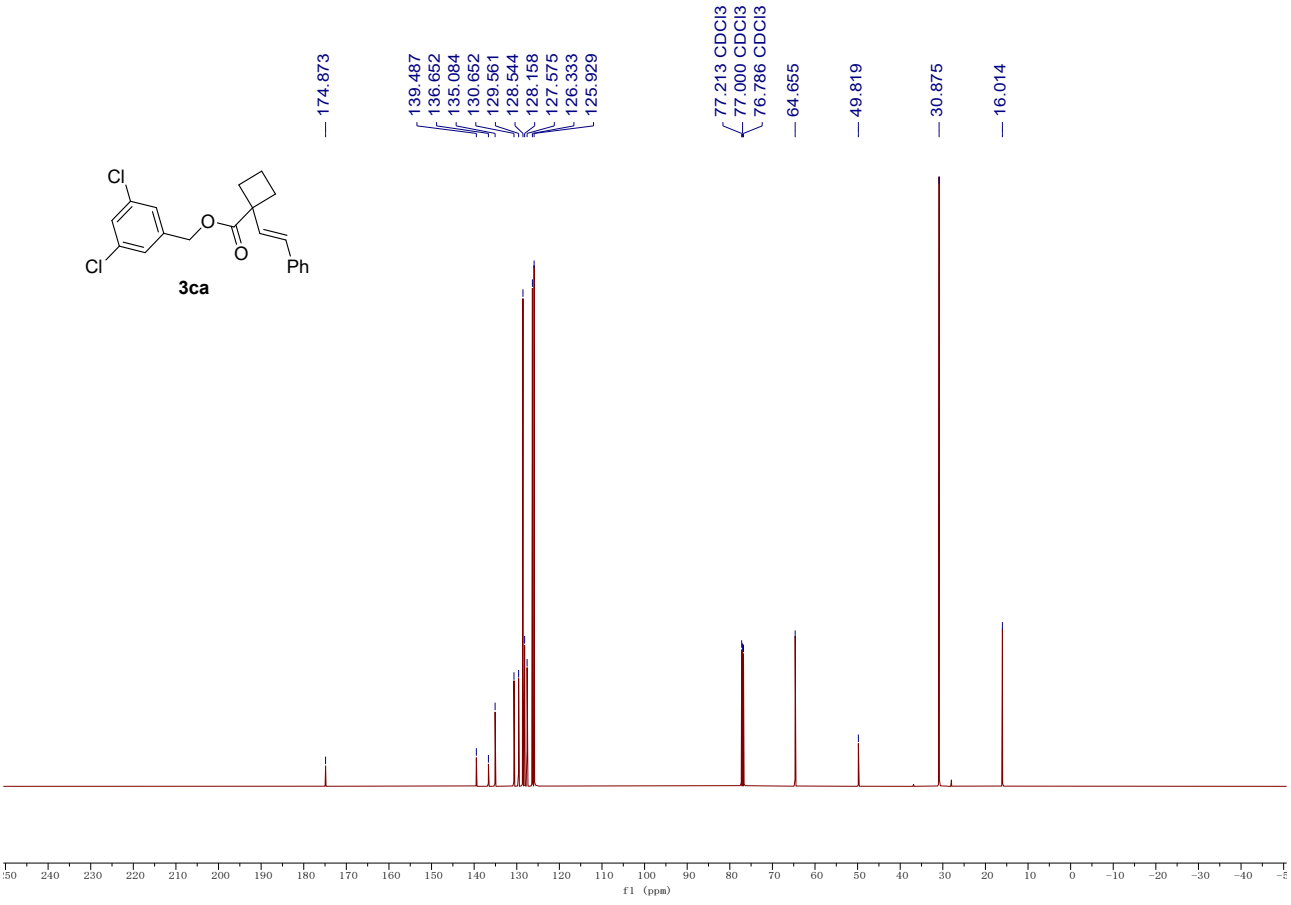

7.814
7.792
7.788
7.761
7.756
7.749
7.744
7.737
7.467
7.462
7.456
7.449
7.443
7.438
7.431
7.427
7.422
7.417
7.366
7.361
7.357
7.344
7.341
7.337
7.309
7.304
7.291
7.287
7.276
7.272
7.267
7.238
7.234
7.230
7.222
7.216
7.211
7.198
6.508
6.501
6.496
5.324
2.664
2.659
2.643
2.634
2.630
2.618
2.612
2.320
2.301
2.295
2.289
2.283
2.277
2.271
2.266
2.255
2.252
1.963
1.958
1.943
1.938
1.924
1.919
O
O
Ph
3aa
4.28
3.05
2.00
2.01
1.22
2.00
2.00
2.00
2.03
2.06
f1 (ppm)

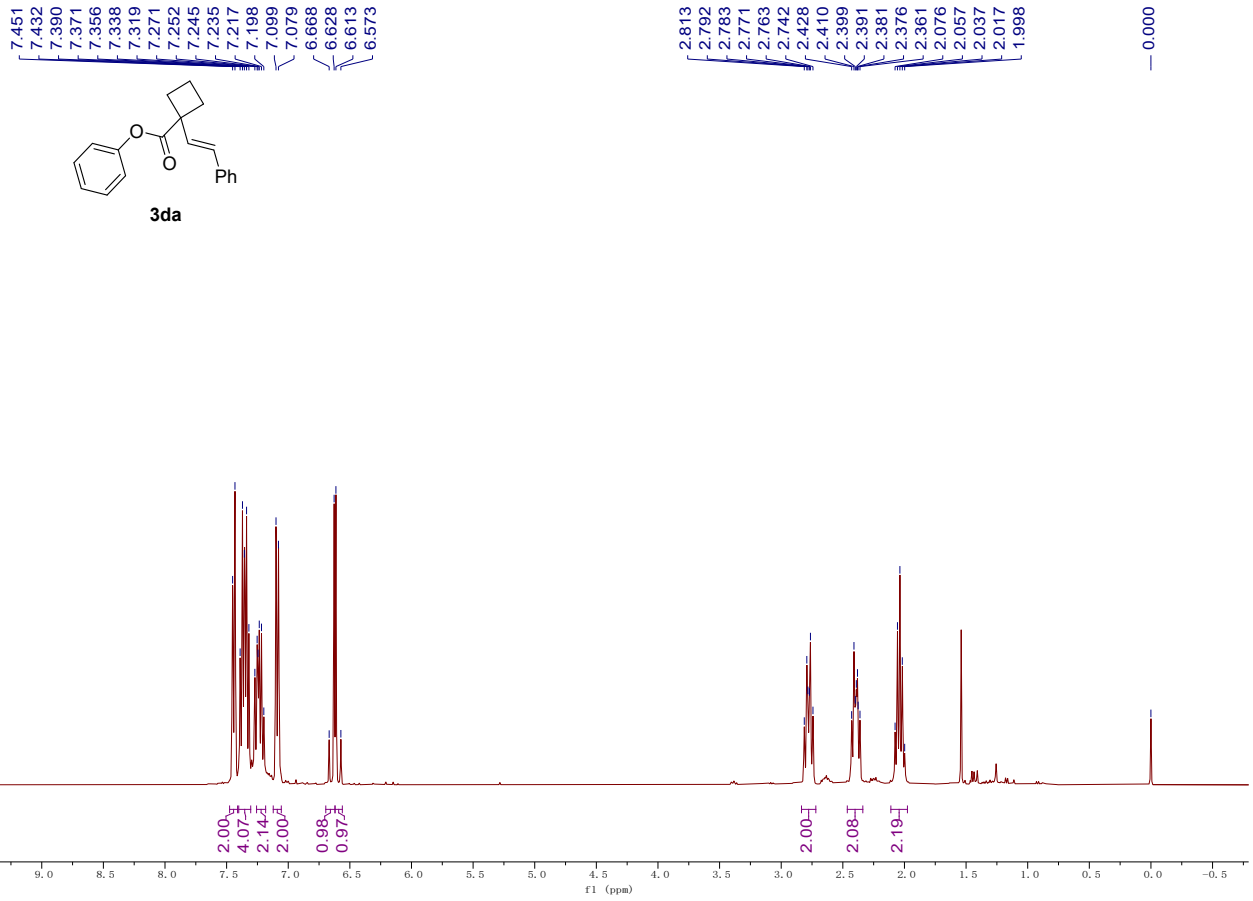

175.317
136.897
133.620
133.161
133.045
131.208
129.212
128.552
128.331
127.975
127.672
127.480
126.997
126.344
126.239
126.174
125.615
77.213 CDCl3
77.000 CDCl3
76.788 CDCl3
66.562
50.034
30.946
16.025
O
O
Ph
3aa
f1 (ppm)

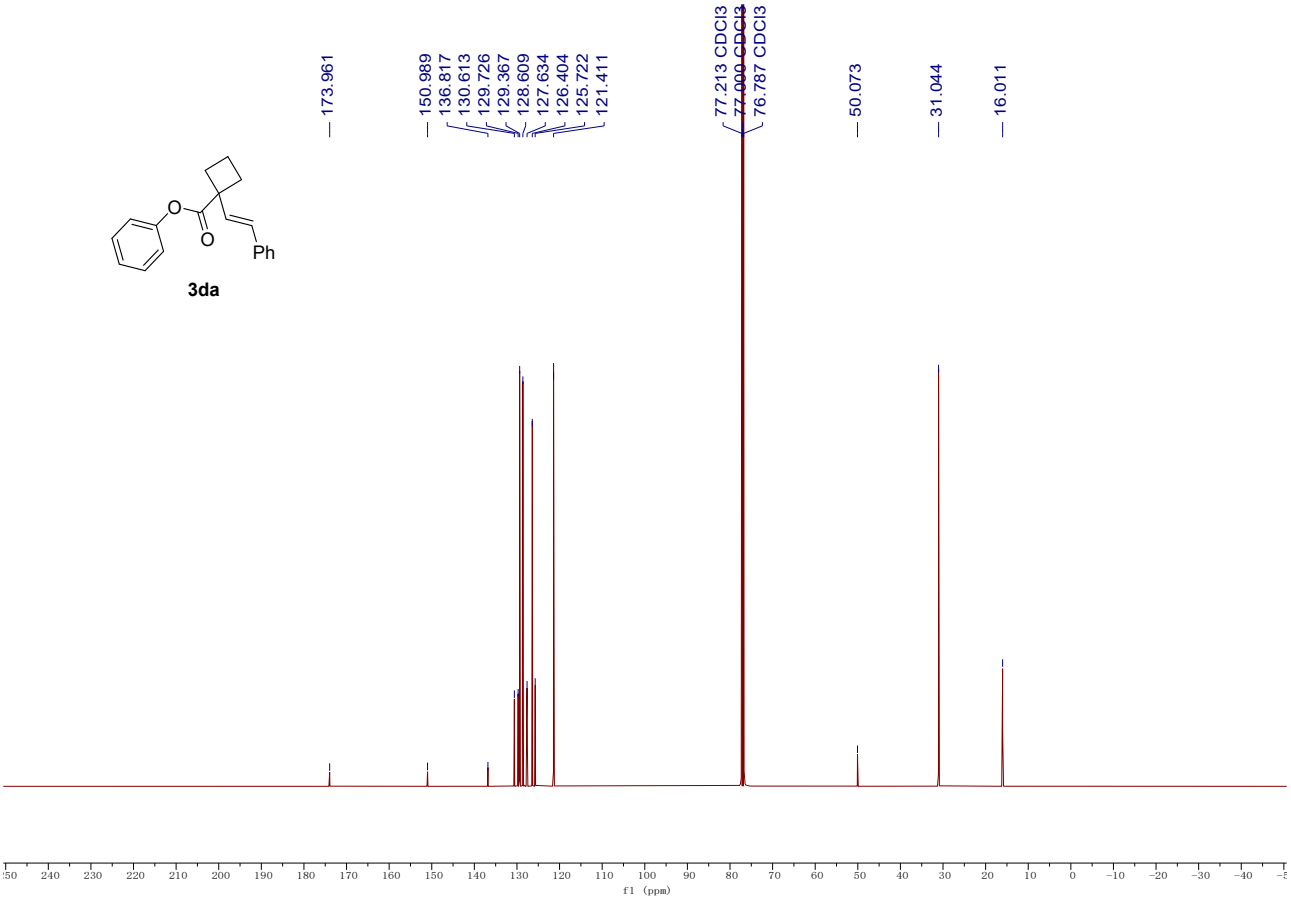

7.376
7.349
7.338
7.322
7.304
7.285
7.239
7.222
7.204
6.527
6.485
6.444
5.170
2.667
2.647
2.638
2.626
2.618
2.597
2.311
2.292
2.280
2.272
2.263
2.244
1.981
1.962
1.942
1.923
1.903
-0.000
O
O
Ph
3ba
8.92
1.20
1.95
1.92
2.00
2.06
2.09
f1 (ppm)


175.266
136.905
136.184
131.182
129.110
128.526
128.498
128.057
127.841
127.449
126.316
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
66.420
49.981
30.920
15.987
O
O
Ph
3ba
f1 (ppm)


7.395
7.376
7.329
7.310
7.291
7.276
7.271
7.245
7.228
7.207
6.546
6.506
6.473
6.432
5.085
2.664
2.643
2.635
2.623
2.614
2.593
2.335
2.316
2.298
2.287
2.268
1.995
1.981
1.974
1.961
1.940
1.922
-0.000
Cl
Cl
O
O
Ph
3ca
1.95
6.28
2.00
2.00
2.00
2.01
2.01
f1 (ppm)

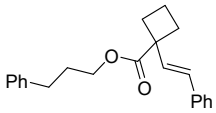

174.873
139.487
136.652
135.084
130.652
129.561
128.544
128.158
127.575
126.333
125.929
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
64.655
49.819
30.875
16.014
Cl
Cl
O
O
Ph
3ca
f1 (ppm)


7.451
7.432
7.390
7.371
7.356
7.338
7.319
7.271
7.252
7.245
7.235
7.217
7.198
7.099
7.079
6.668
6.628
6.613
6.573
2.813
2.792
2.783
2.771
2.763
2.742
2.428
2.410
2.399
2.391
2.381
2.376
2.361
2.076
2.057
2.037
2.017
1.998
0.000
O
O
Ph
3da
2.00
4.07
2.14
2.00
0.98
0.97
2.00
2.08
2.19
f1 (ppm)

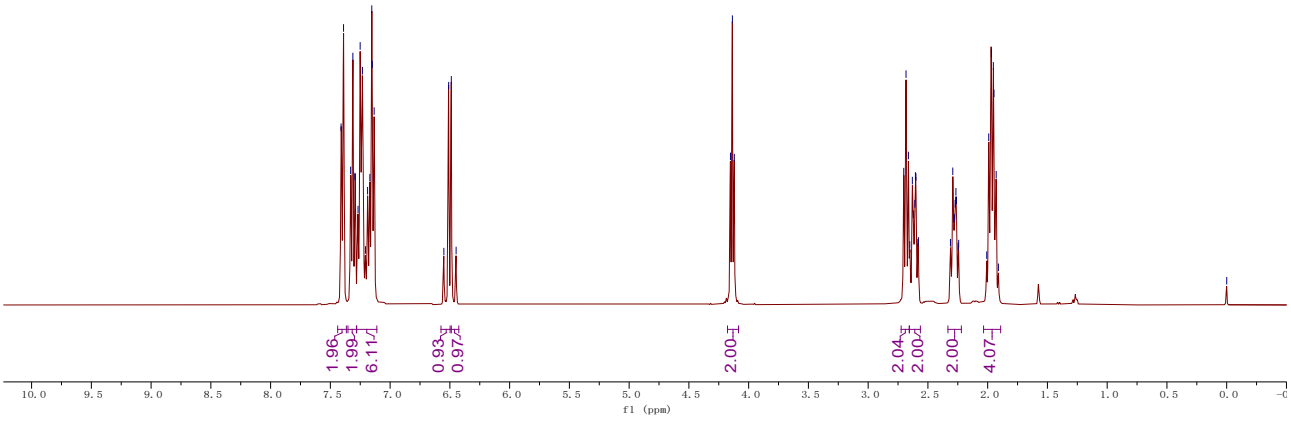

173.961
150.989
136.817
130.613
129.726
129.367
128.609
127.634
126.404
125.722
121.411
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
50.073
31.044
16.011
O
O
Ph
3da
f1 (ppm)

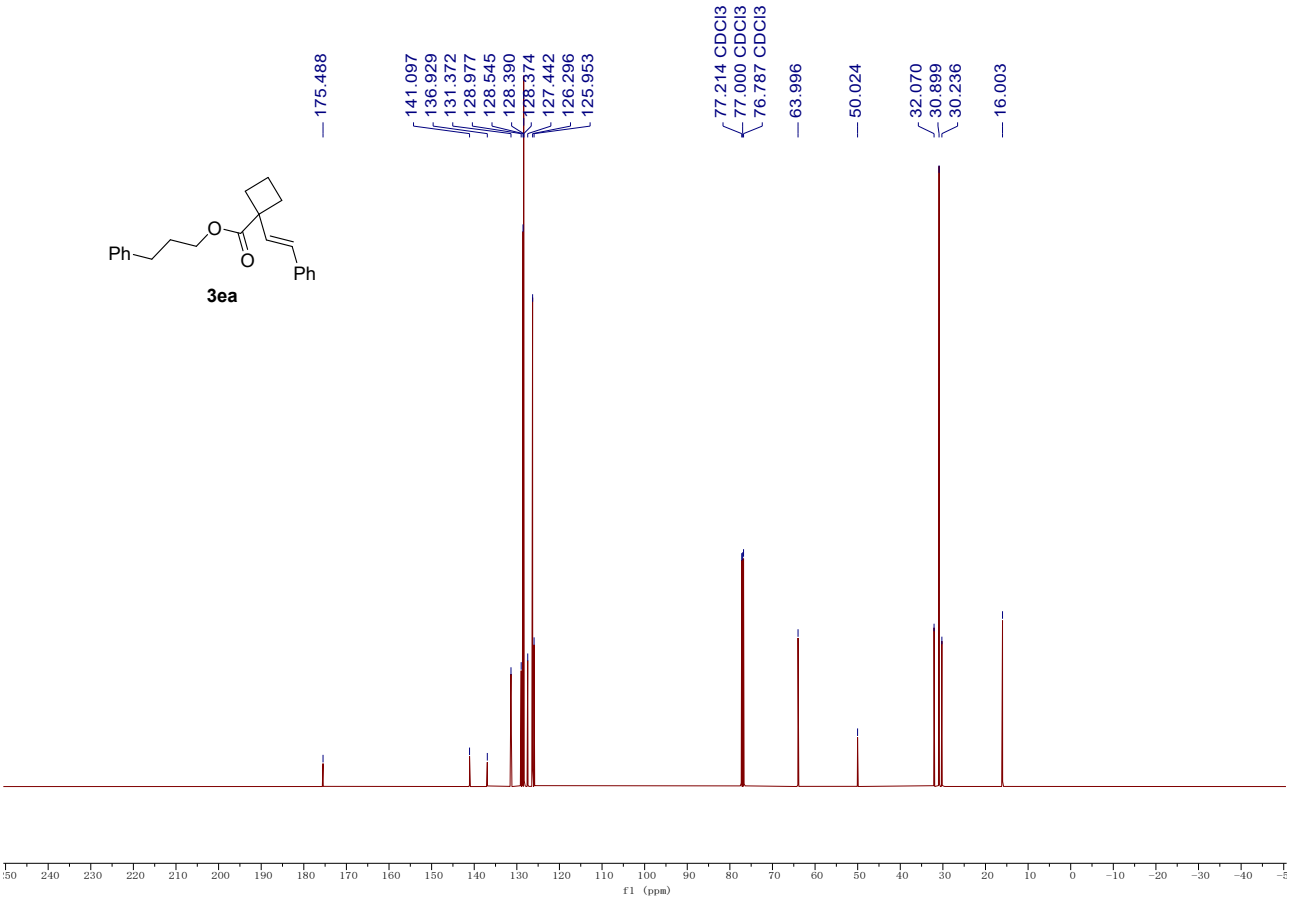

7.410
7.390
7.330
7.312
7.295
7.269
7.251
7.232
7.206
7.189
7.169
7.154
7.149
7.134
6.550
6.510
6.488
6.448


4.152
4.136
4.120
2.702
2.683
2.663
2.652
2.630
2.622
2.609
2.604
2.600
2.584
2.579
2.311
2.292
2.284
2.279
2.272
2.266
2.261
2.247
2.243
2.008
1.991
1.969
1.953
1.947
1.929
1.910
-0.000


Ph
O
O
Ph

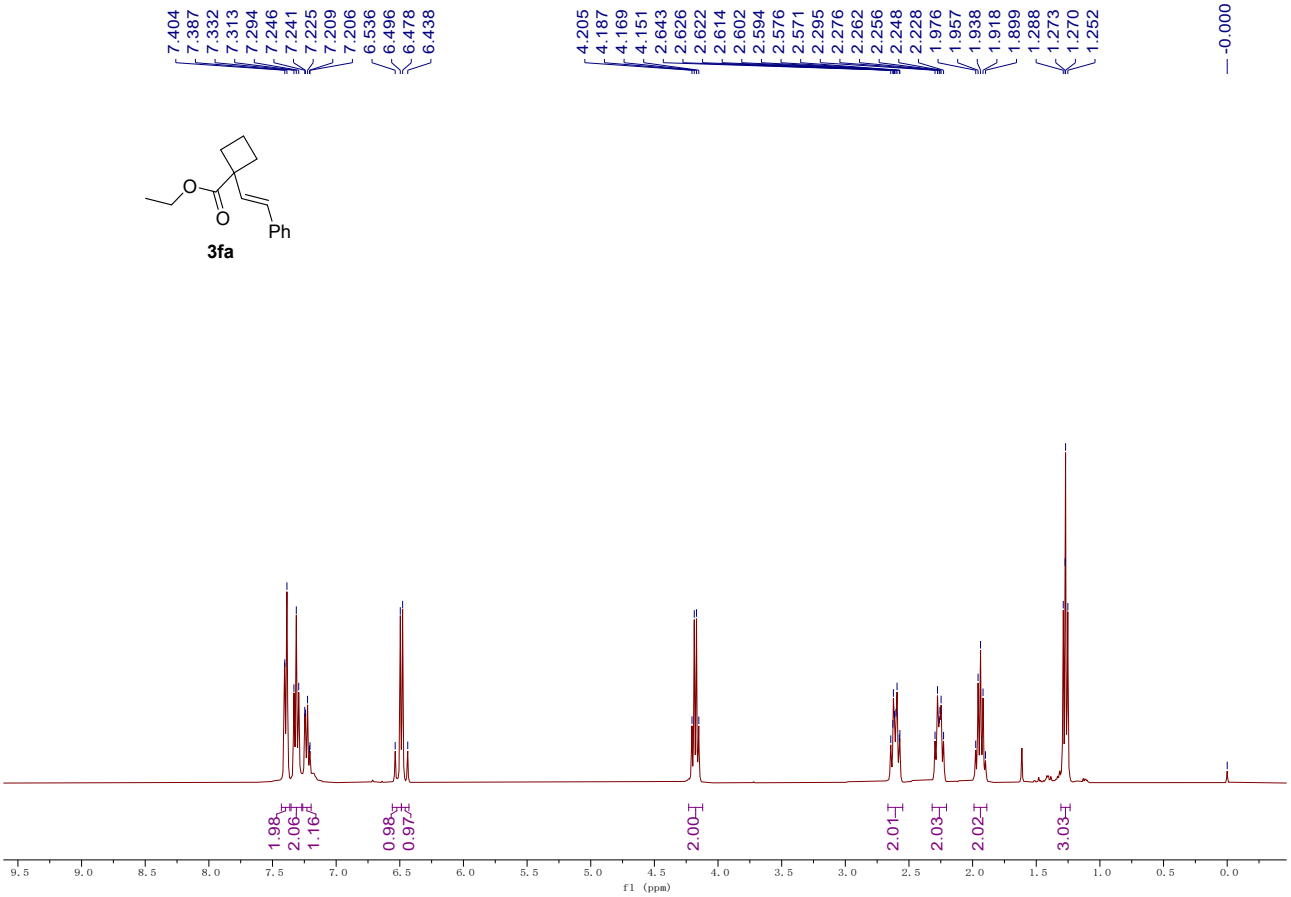
3ea

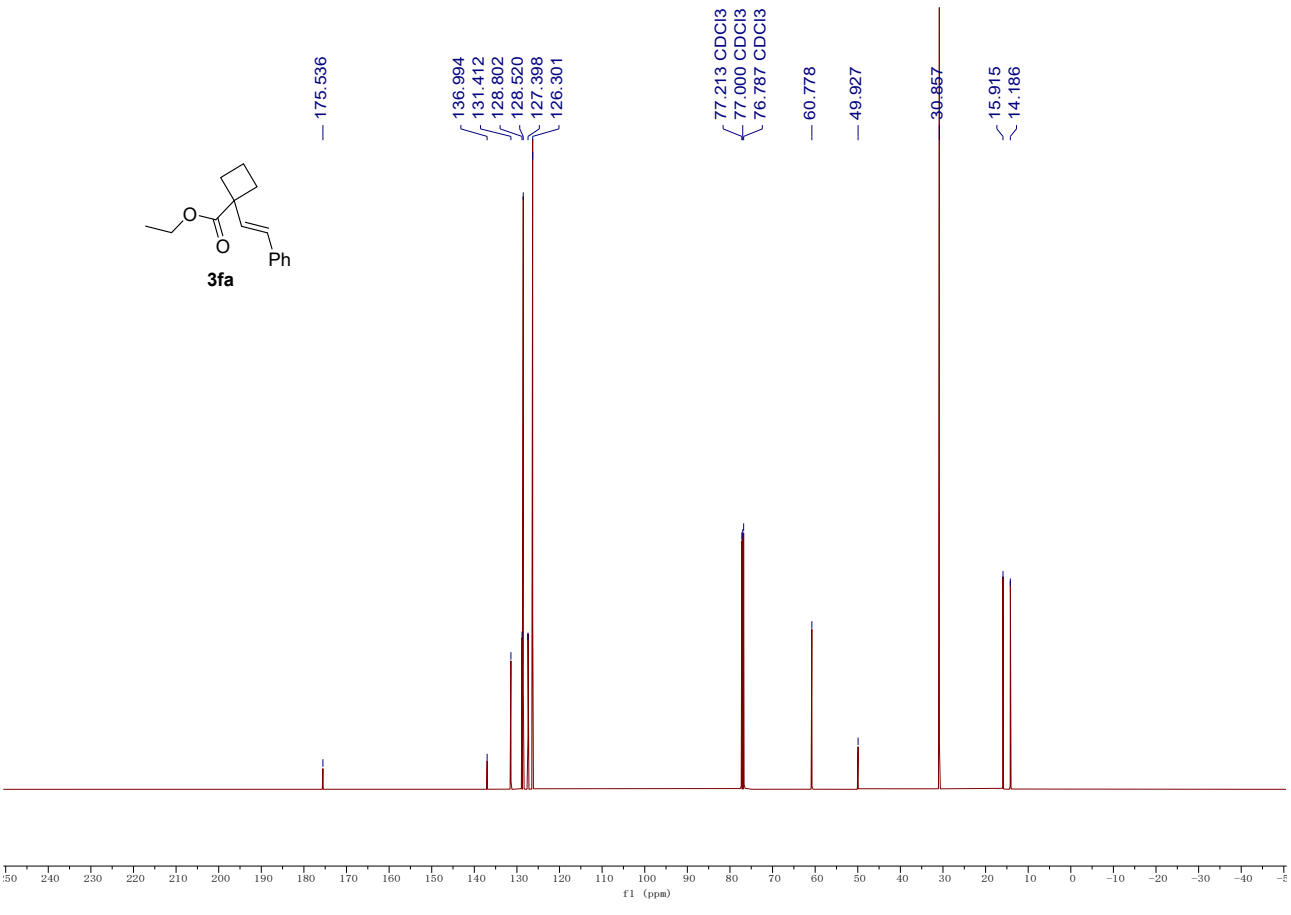

1.96
1.99
6.11
0.93
0.97
2.00
2.04
2.00
2.00
4.07
f1 (ppm)

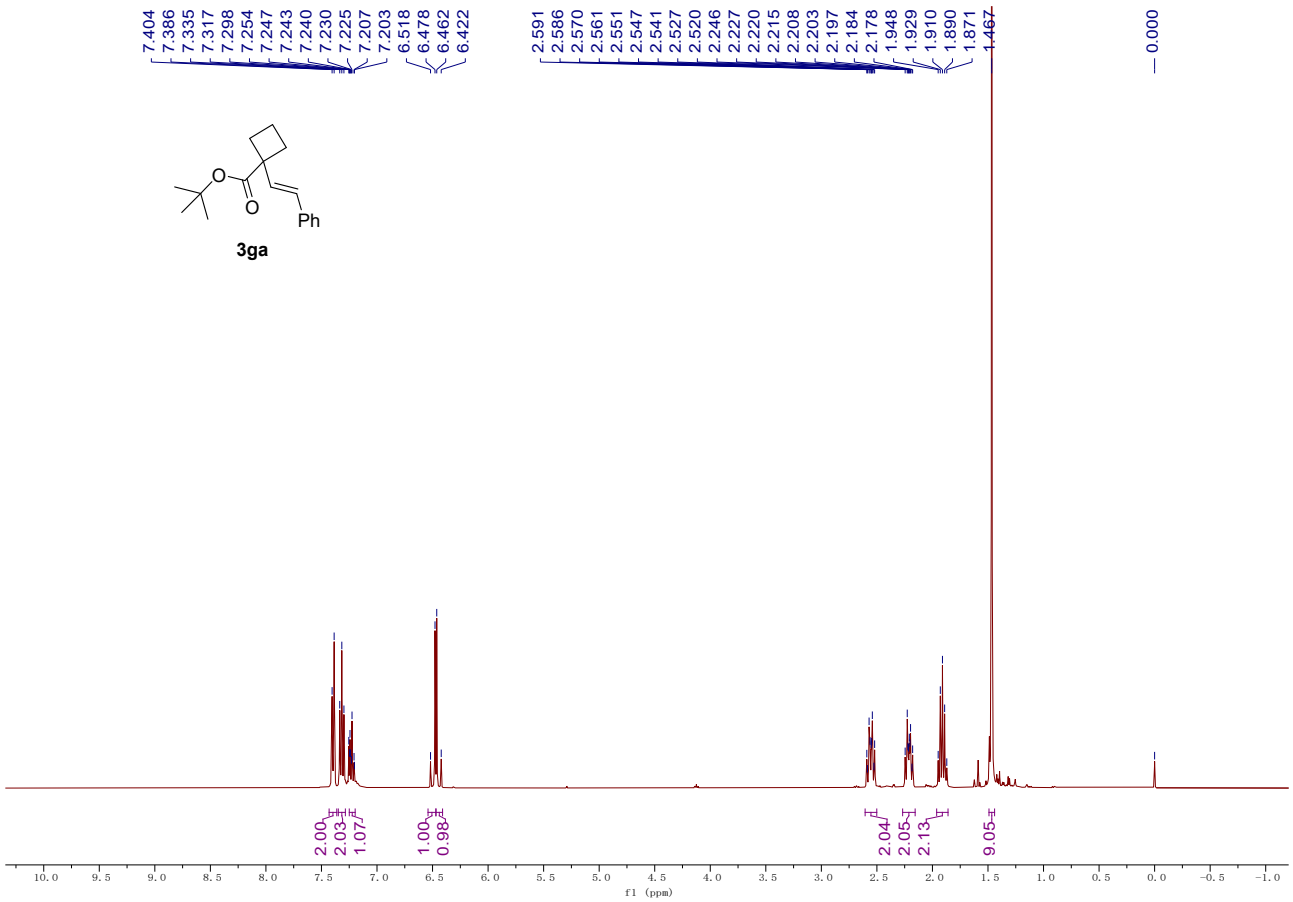

175.488
141.097
136.929
131.372
128.977
128.545
128.390
128.374
127.442
126.296
125.953
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
63.996
50.024
32.070
30.899
30.236
16.003
f1 (ppm)

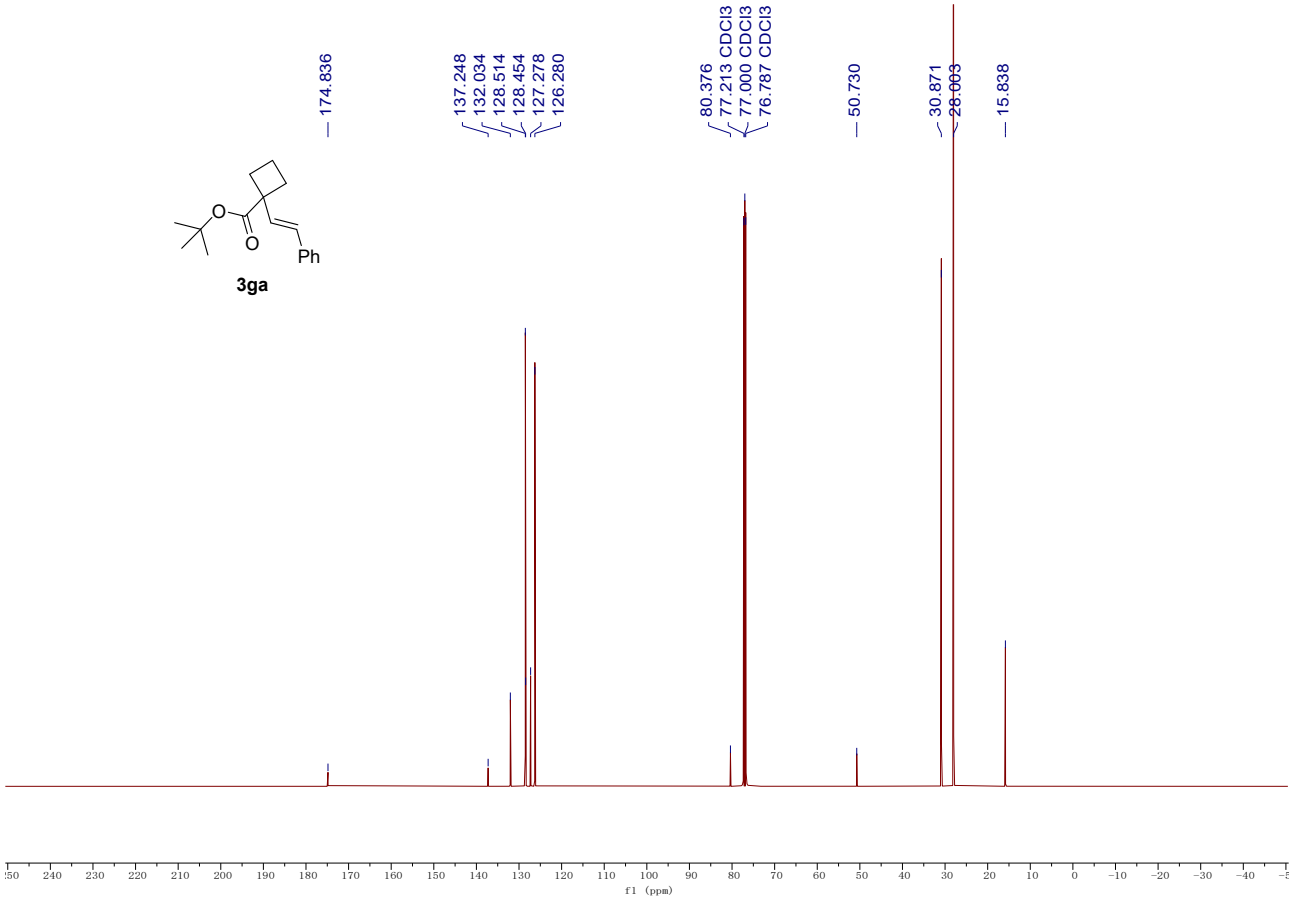
Ph
O
O
Ph

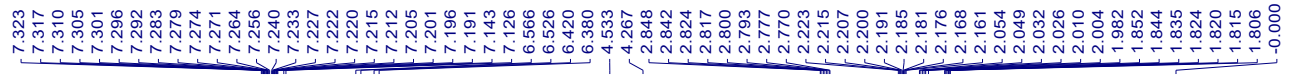
3ea

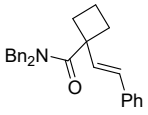

7.404
7.387
7.332
7.313
7.294
7.246
7.241
7.225
7.209
7.206
6.536
6.496
6.478
6.438
4.205
4.187
4.169
4.151
2.643
2.626
2.622
2.614
2.602
2.594
2.576
2.571
2.295
2.276
2.262
2.256
2.248
2.228
1.976
1.957
1.938
1.918
1.899
1.288
1.273
1.270
1.252
-0.000
O
O
Ph
3fa
1.98
2.06
1.16
0.98
0.97
2.00
2.01
2.03
2.02
3.03
f1 (ppm)


175.536
136.994
131.412
128.802
128.520
127.398
126.301
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
60.778
49.927
30.857
15.915
14.186
O
O
Ph
3fa
f1 (ppm)

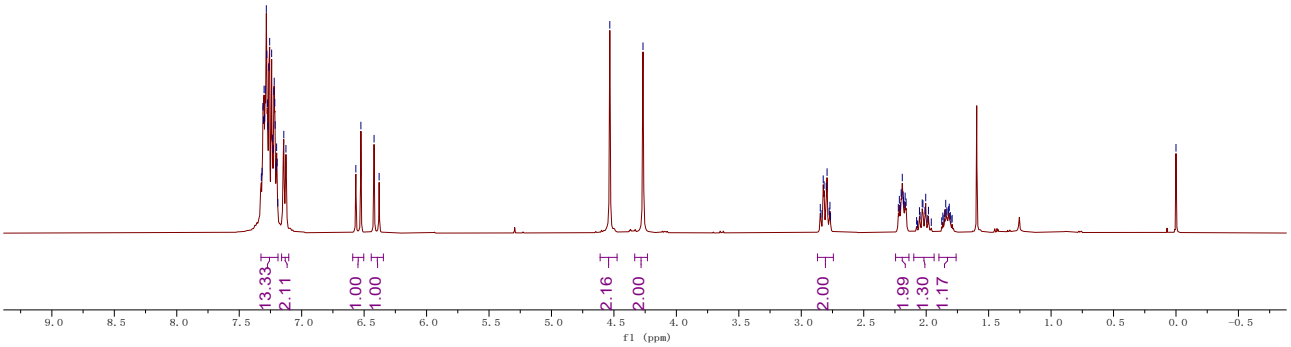

7.404
7.386
7.335
7.317
7.298
7.254
7.247
7.243
7.240
7.230
7.225
7.207
7.203
6.518
6.478
6.462
6.422
2.591
2.586
2.570
2.561
2.551
2.547
2.541
2.527
2.520
2.246
2.227
2.220
2.215
2.208
2.203
2.197
2.184
2.178
1.948
1.929
1.910
1.890
1.871
1.467
0.000
O
O
Ph
3ga
2.00
2.03
1.07
1.00
0.98
2.04
2.05
2.13
9.05
f1 (ppm)

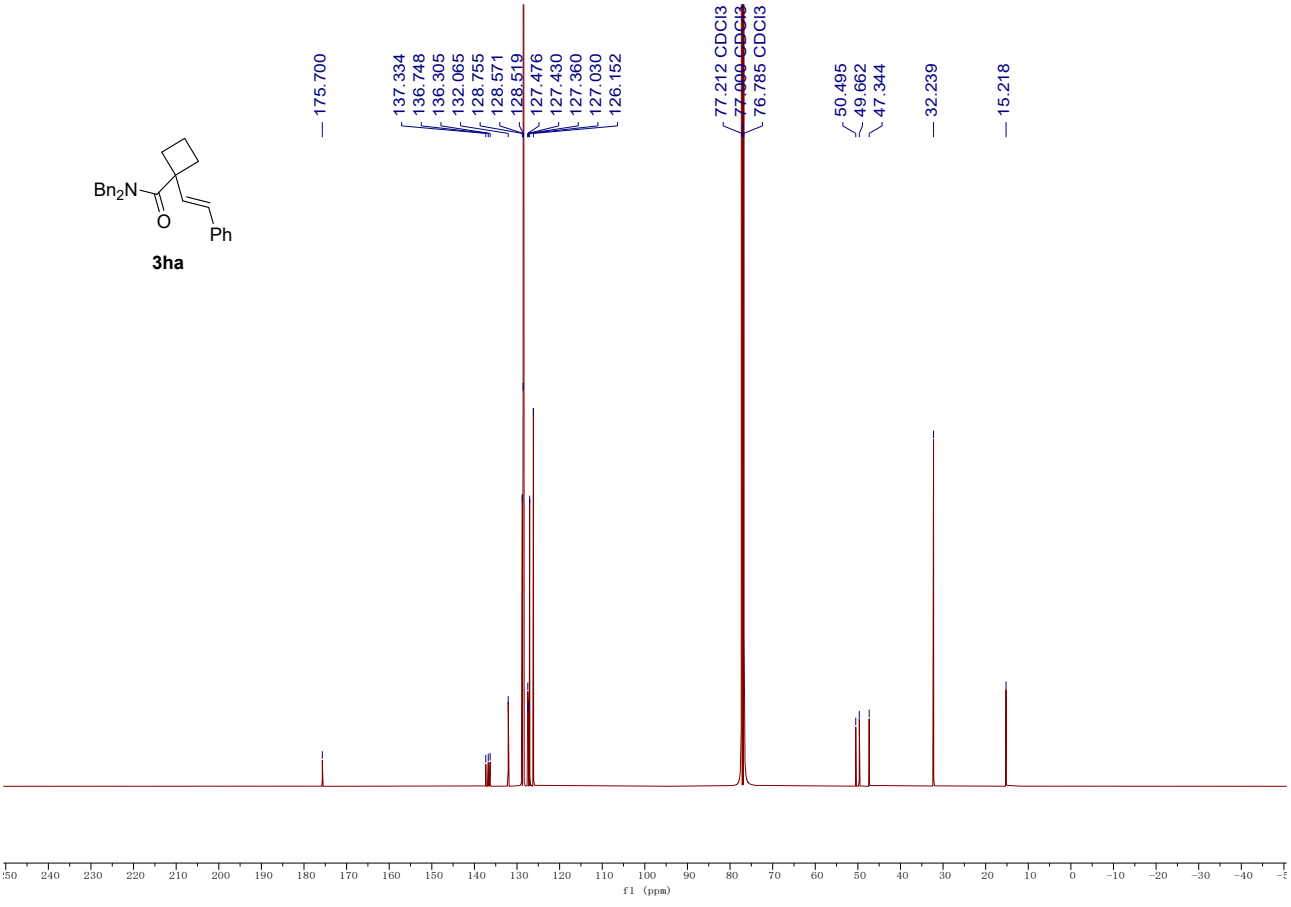

174.836
137.248
132.034
128.514
128.454
127.278
126.280
80.376
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
50.730
30.871
28.093
15.838
O
O
Ph
3ga
f1 (ppm)


7.323
7.317
7.310
7.305
7.301
7.296
7.292
7.283
7.279
7.274
7.271
7.264
7.256
7.240
7.233
7.227
7.222
7.220
7.215
7.212
7.205
7.201
7.196
7.191
7.143
7.126
6.566
6.526
6.420
6.380
4.533
4.267
2.848
2.842
2.824
2.817
2.800
2.793
2.777
2.770
2.223
2.215
2.207
2.200
2.191
2.185
2.181
2.176
2.168
2.161
2.054
2.049
2.032
2.026
2.010
2.004
1.982
1.852
1.844
1.835
1.824
1.820
1.815
1.806
-0.000


Bn2N
O
Ph

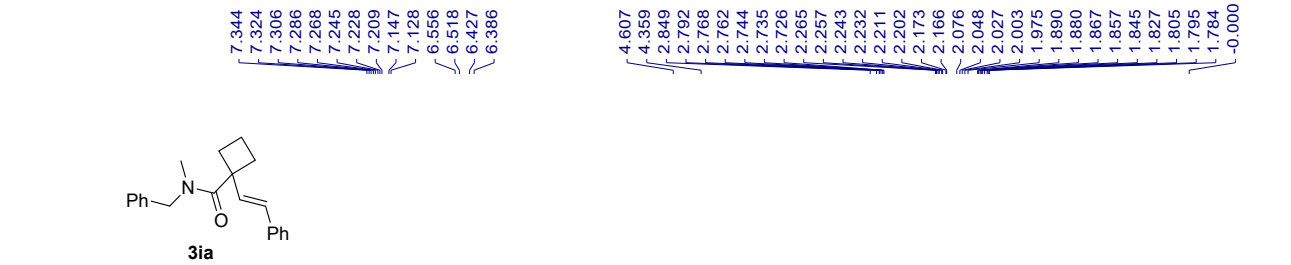
3ha


13.33
2.11
1.00
1.00
2.16
2.00
2.00
1.99
1.30
1.17
f1 (ppm)


175.700
137.334
136.748
136.305
132.065
128.755
128.571
128.519
127.476
127.430
127.360
127.030
126.152
77.212 CDCl3
77.000 CDCl3
76.785 CDCl3
50.495
49.662
47.344
32.239
15.218
f1 (ppm)

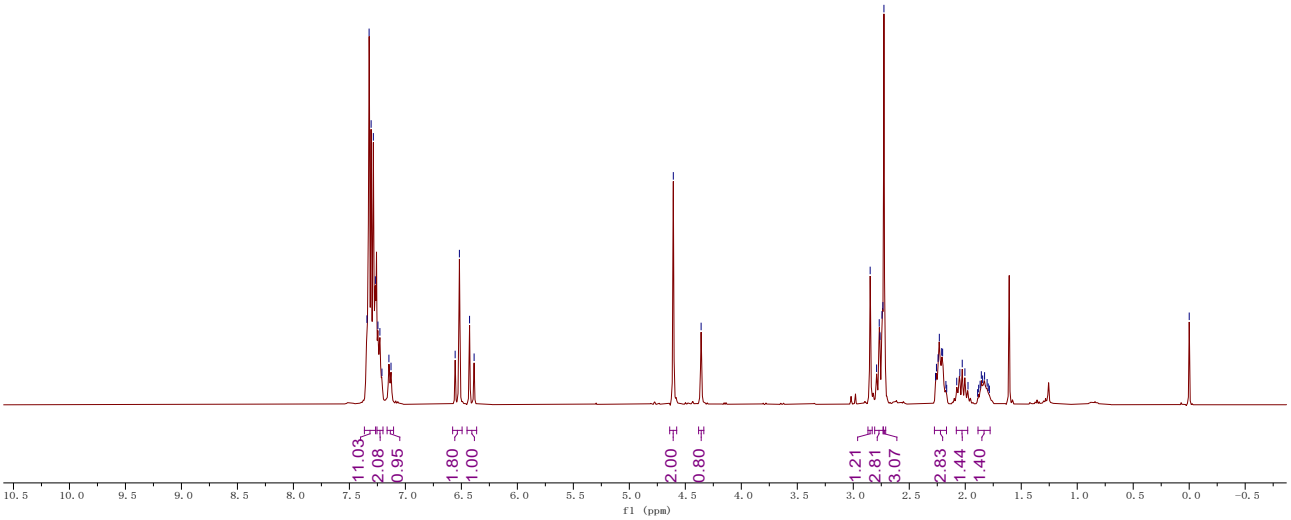
Bn2N
O
Ph

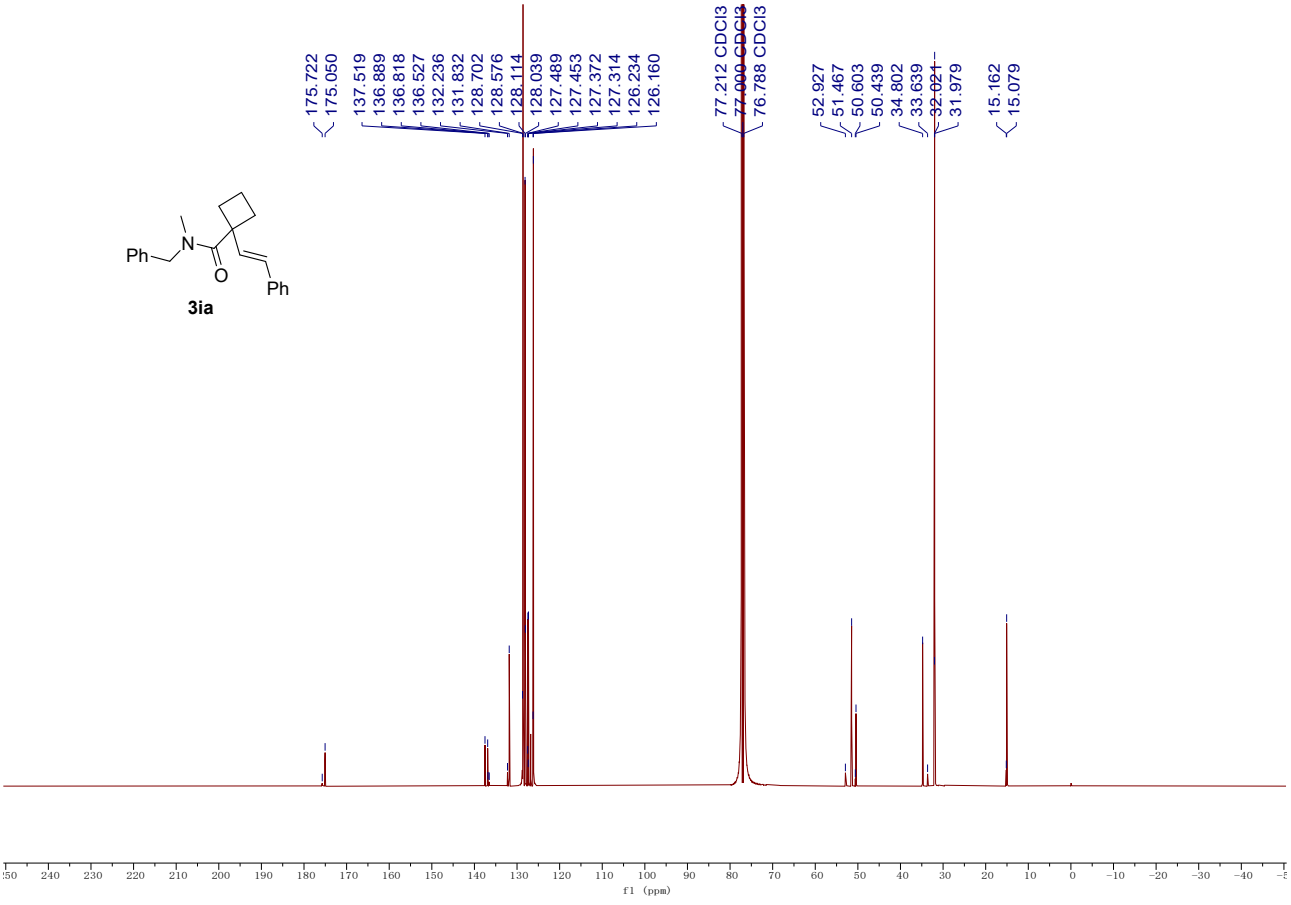
3ha


7.344
7.324
7.306
7.286
7.268
7.245
7.228
7.209
7.147
7.128
6.556
6.518
6.427
6.386
4.607
4.359
2.849
2.792
2.768
2.762
2.744
2.735
2.726
2.265
2.257
2.243
2.232
2.211
2.202
2.173
2.166
2.076
2.048
2.027
2.003
1.975
1.890
1.880
1.867
1.857
1.845
1.827
1.805
1.795
1.784
-0.000

Ph
N
O
Ph

3ia

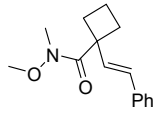

11.03
2.08
0.95
1.80
1.00
2.00
0.80
1.21
2.81
3.07
2.83
1.44
1.40
f1 (ppm)


175.722
175.050
137.519
136.889
136.818
136.527
132.236
131.832
128.702
128.576
128.114
128.039
127.489
127.453
127.372
127.314
126.234
126.160
77.212 CDCl3
77.000 CDCl3
76.788 CDCl3
52.927
51.467
50.603
50.439
34.802
33.639
32.021
31.979
15.162
15.079
f1 (ppm)

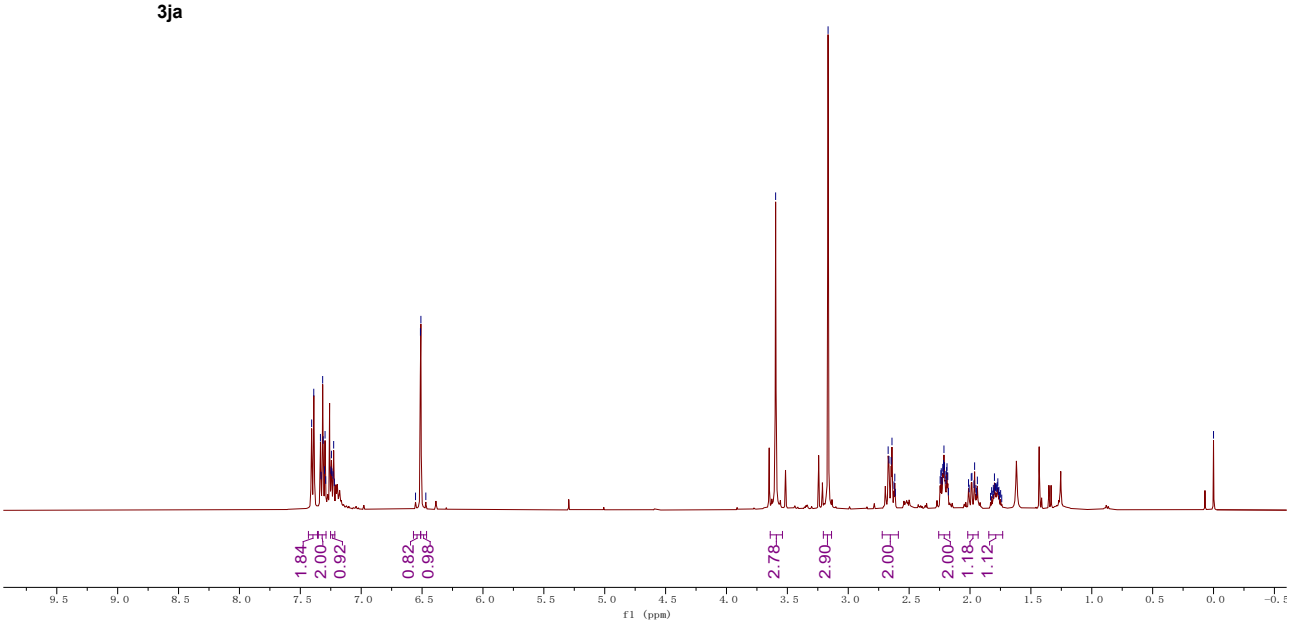
Ph
N
O
Ph

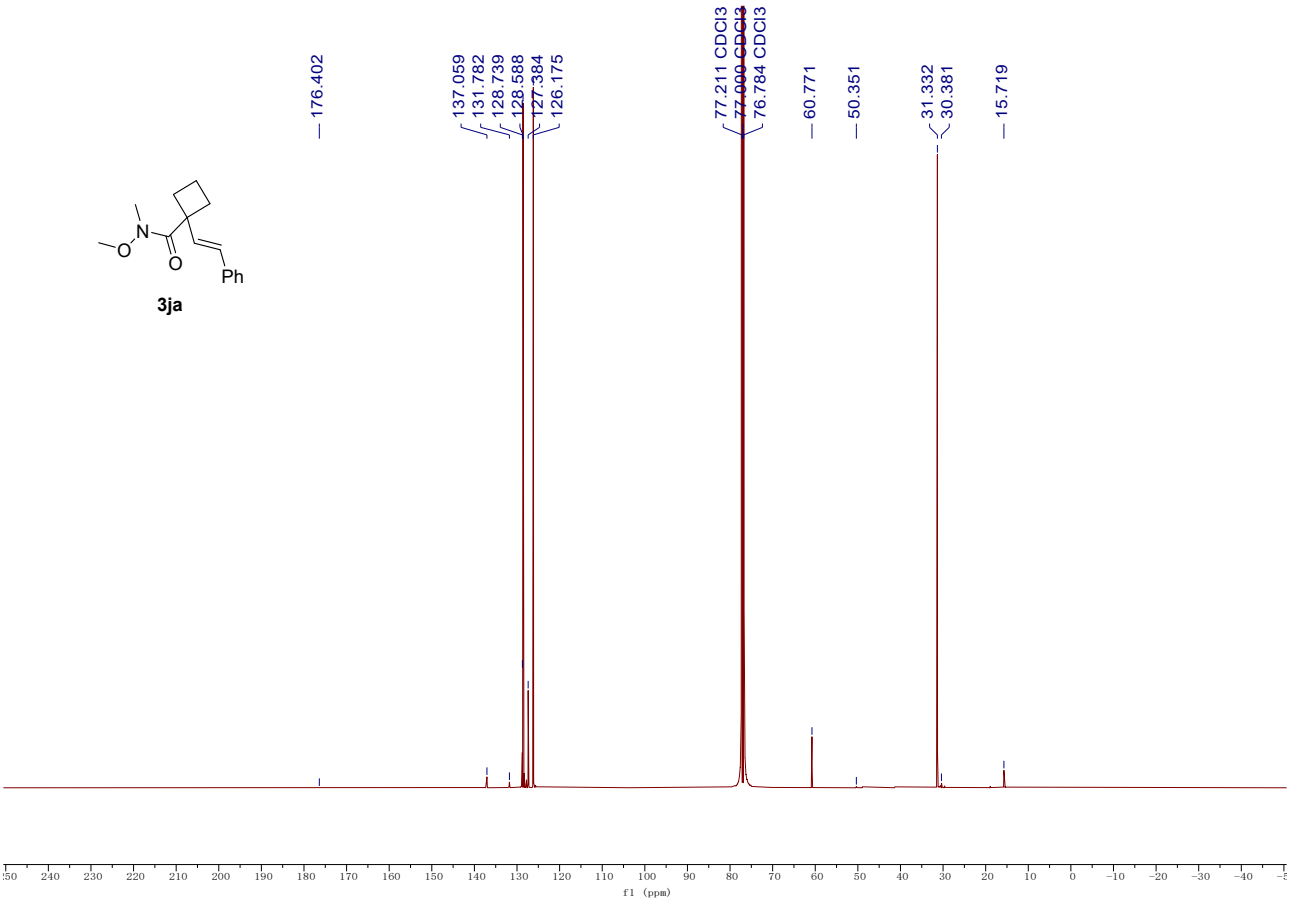
3ia

Containing a trace amount of impurity that failed to be separated.

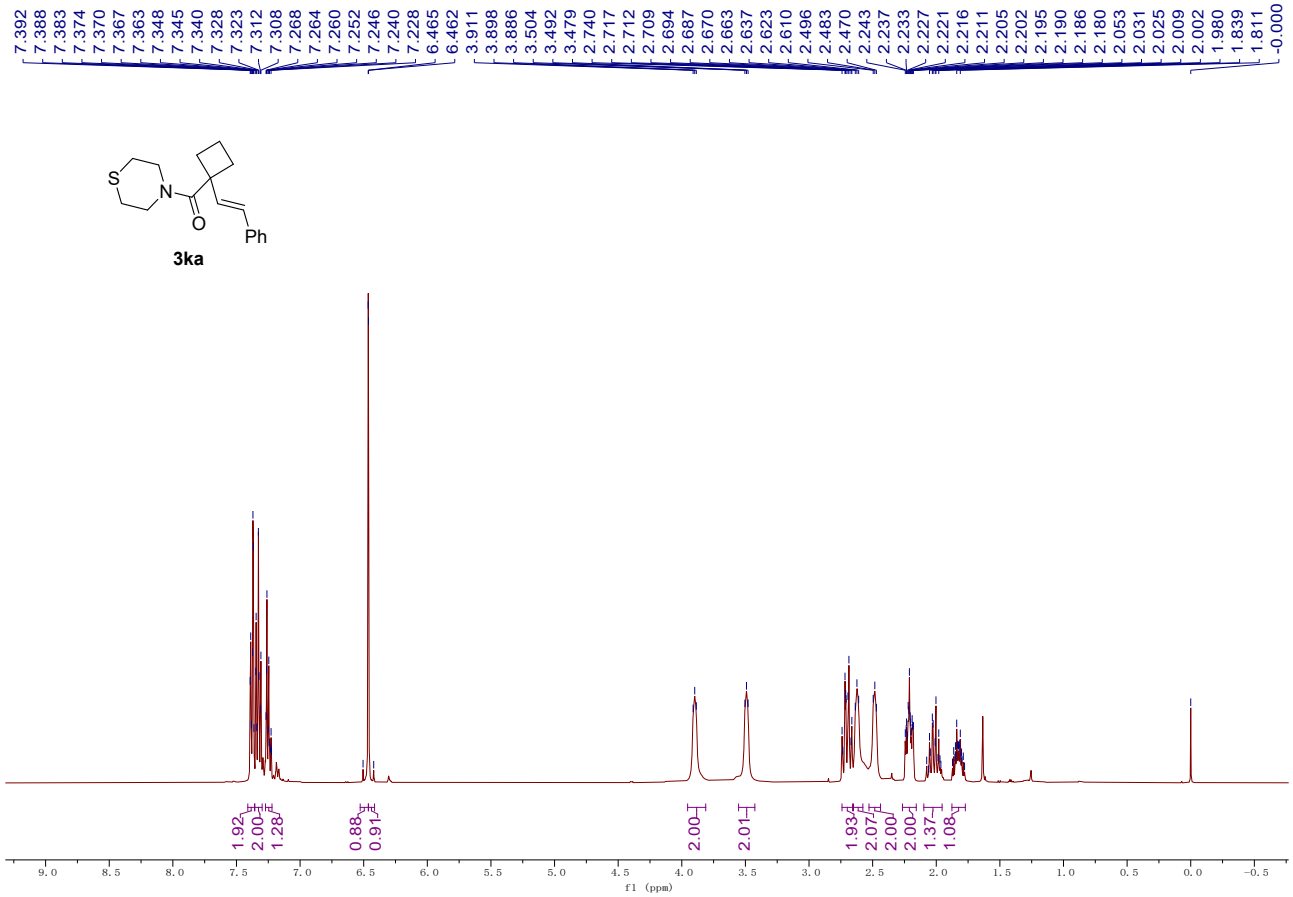


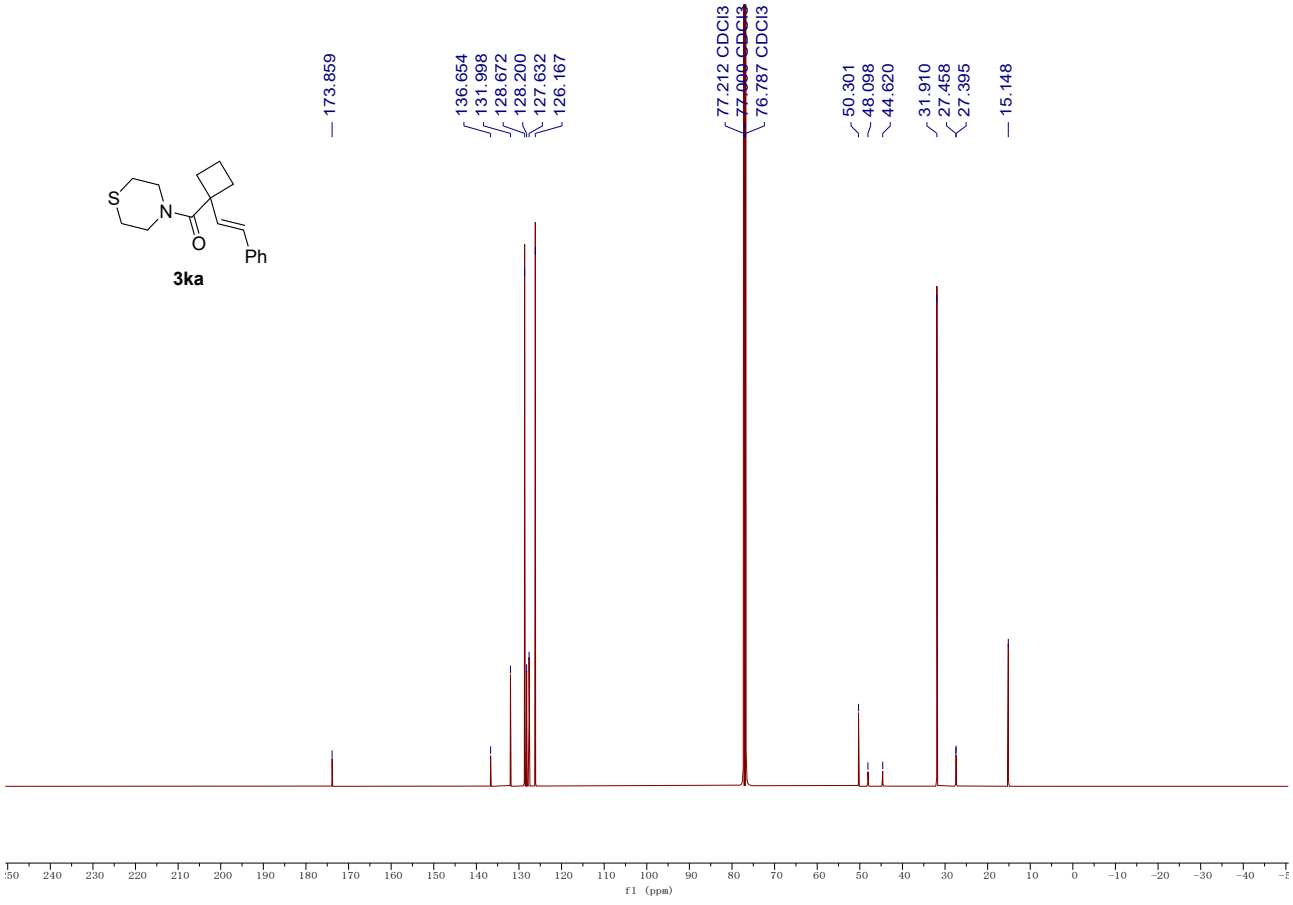
3ja



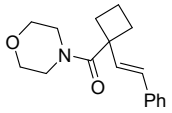


3ja

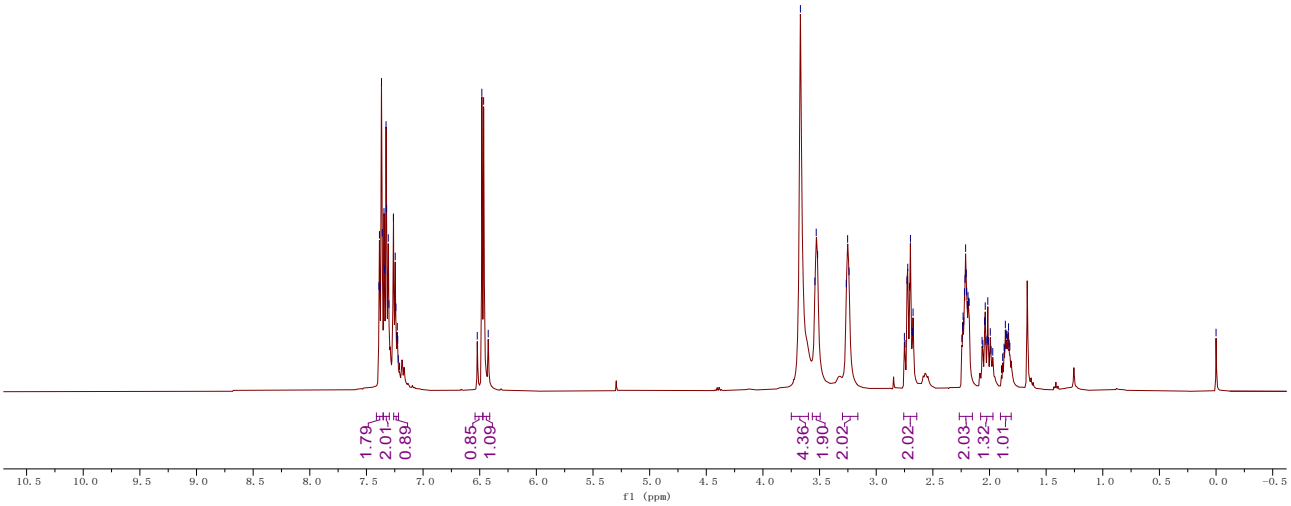

7.392
7.388
7.383
7.374
7.370
7.367
7.363
7.348
7.345
7.340
7.328
7.323
7.312
7.308
7.268
7.264
7.260
7.252
7.246
7.240
7.228
6.465
6.462
3.911
3.898
3.886
3.504
3.492
3.479
2.740
2.717
2.712
2.709
2.694
2.687
2.670
2.663
2.637
2.623
2.610
2.496
2.483
2.470
2.243
2.237
2.233
2.227
2.221
2.216
2.211
2.205
2.202
2.195
2.190
2.186
2.180
2.053
2.031
2.025
2.009
2.002
1.980
1.839
1.811
-0.000
S
N
O
Ph
3ka
1.92
2.00
1.28
0.88
0.91
2.00
2.01
1.93
2.07
2.00
2.00
1.37
1.08
f1 (ppm)

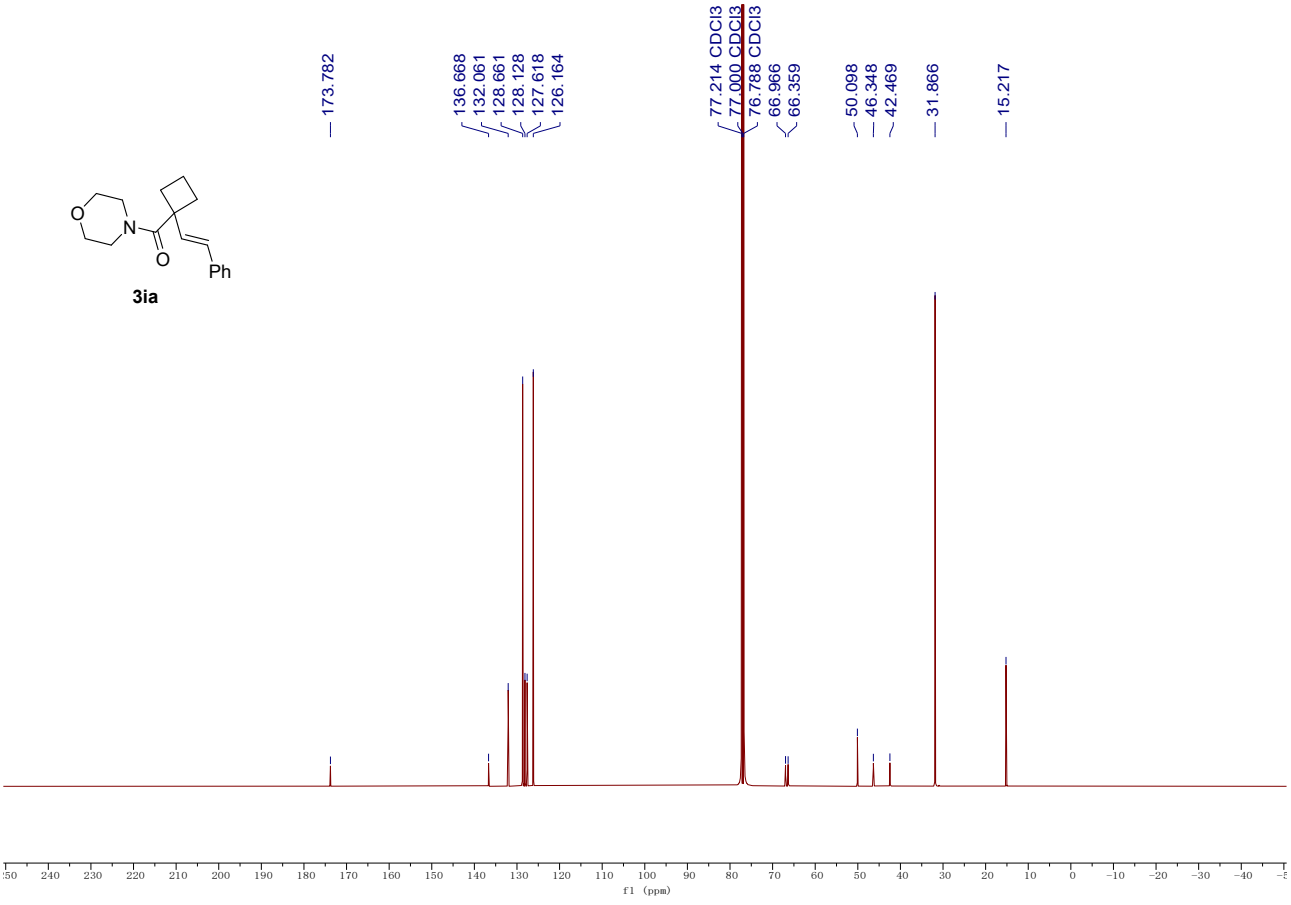

173.859
136.654
131.998
128.672
128.200
127.632
126.167
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
50.301
48.098
44.620
31.910
27.458
27.395
15.148
S
N
O
Ph
3ka
f1 (ppm)


7.390
7.385
7.380
7.367
7.360
7.345
7.339
7.327
7.322
7.307
7.302
7.262
7.246
7.240
7.232
7.228
7.224
6.522
6.481
6.466
6.425
3.669
3.541
3.530
3.517
3.264
3.252
3.240
2.751
2.746
2.728
2.722
2.706
2.698
2.681
2.675
2.244
2.238
2.233
2.227
2.221
2.216
2.211
2.205
2.201
2.196
2.190
2.185
2.179
2.066
2.043
2.038
2.032
2.021
2.015
2.009
1.993
1.860
1.855
1.849
1.843
1.837
1.832
1.826
0.000


O
N
O
Ph

3ia

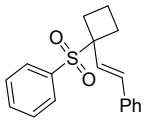

1.79
2.01
0.89
0.85
1.09
4.36
1.90
2.02
2.02
2.03
1.32
1.01
f1 (ppm)


173.782
136.668
132.061
128.661
128.128
127.618
126.164
77.214 CDCl3
77.000 CDCl3
76.788 CDCl3
66.966
66.359
50.098
46.348
42.469
31.866
15.217
f1 (ppm)

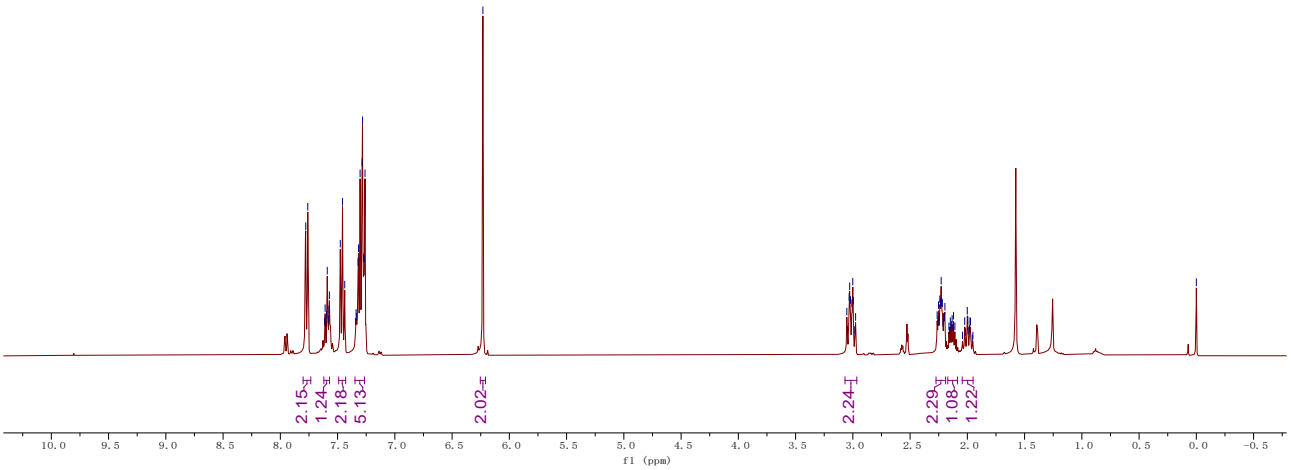
O
N
O
Ph

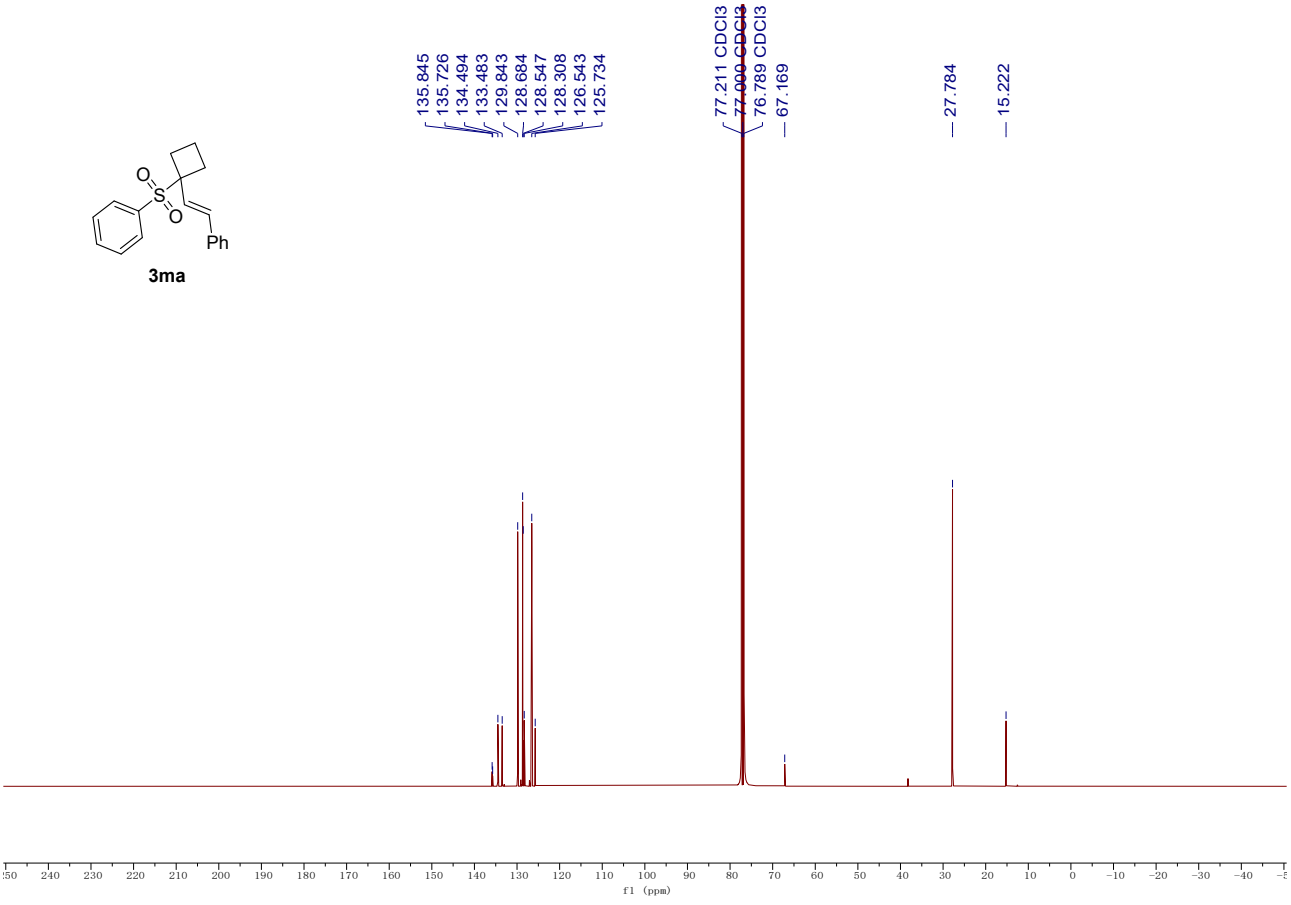
3ia


7.778
7.761
7.612
7.609
7.605
7.595
7.590
7.582
7.575
7.572
7.477
7.457
7.438
7.343
7.339
7.334
7.321
7.317
7.303
7.286
7.282
7.272
7.269
7.261
6.231
3.052
3.047
3.032
3.028
3.021
3.008
3.000
2.995
2.982
2.976
2.264
2.257
2.252
2.246
2.240
2.234
2.229
2.223
2.219
2.213
2.207
2.201
2.196
2.161
2.157
2.149
2.145
2.137
2.133
2.124
2.121
2.109
2.023
2.001
1.996
1.993
1.981
1.977
1.972
0.000


O
S
O
Ph

3ma

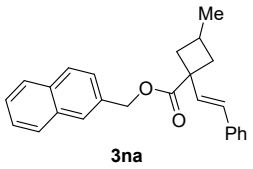

2.15
1.24
2.18
5.13
2.02
2.24
2.29
1.08
1.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


135.845
135.726
134.494
133.483
129.843
128.684
128.547
128.308
126.543
125.734
77.211 CDCl3
77.000 CDCl3
76.789 CDCl3
67.169
27.784
15.222
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

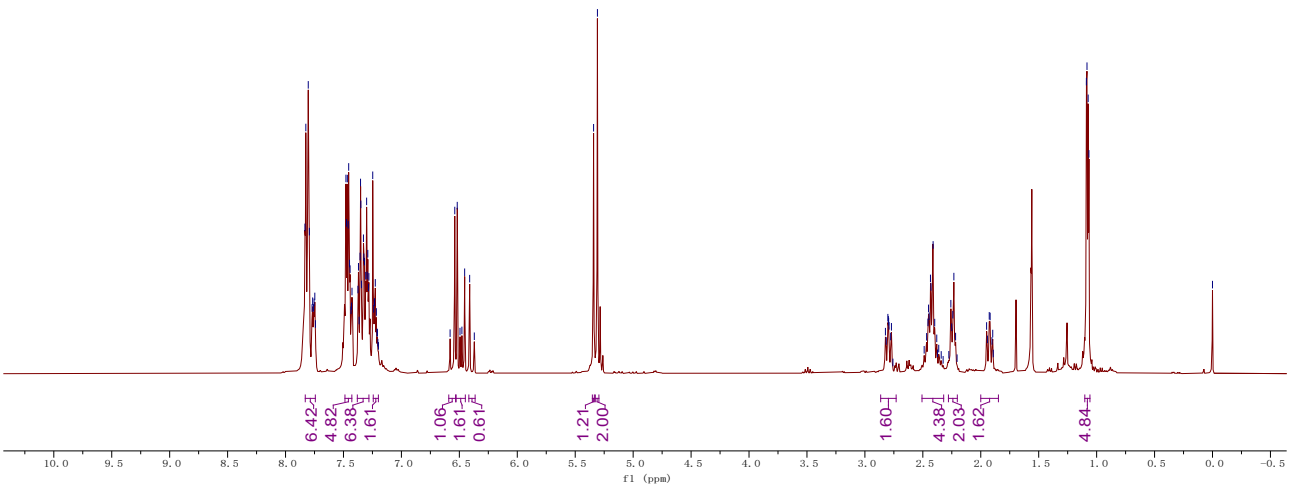
O
S
O
Ph

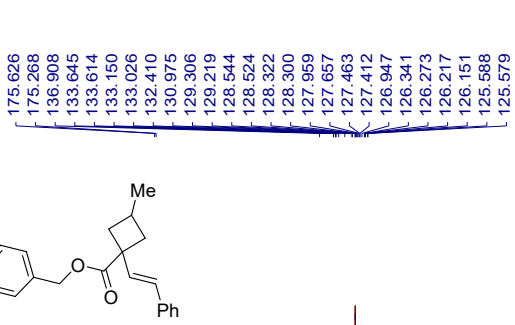
3ma


7.833
7.825
7.804
7.794
7.771
7.766
7.758
7.754
7.747
7.479
7.474
7.467
7.459
7.455
7.448
7.443
7.435
7.430
7.427
7.375
7.371
7.365
7.357
7.353
7.350
7.345
7.328
7.324
7.318
7.308
7.300
7.295
7.290
7.285
7.281
7.248
7.239
7.233
7.230
7.225
7.216
6.540
6.518
6.454
6.411
5.342
5.308
2.802
2.798
2.795
2.451
2.446
2.434
2.430
2.411
2.258
2.241
2.232
1.927
1.919
1.088
1.083
1.073
1.066
0.000


Me
O
O
Ph

3na

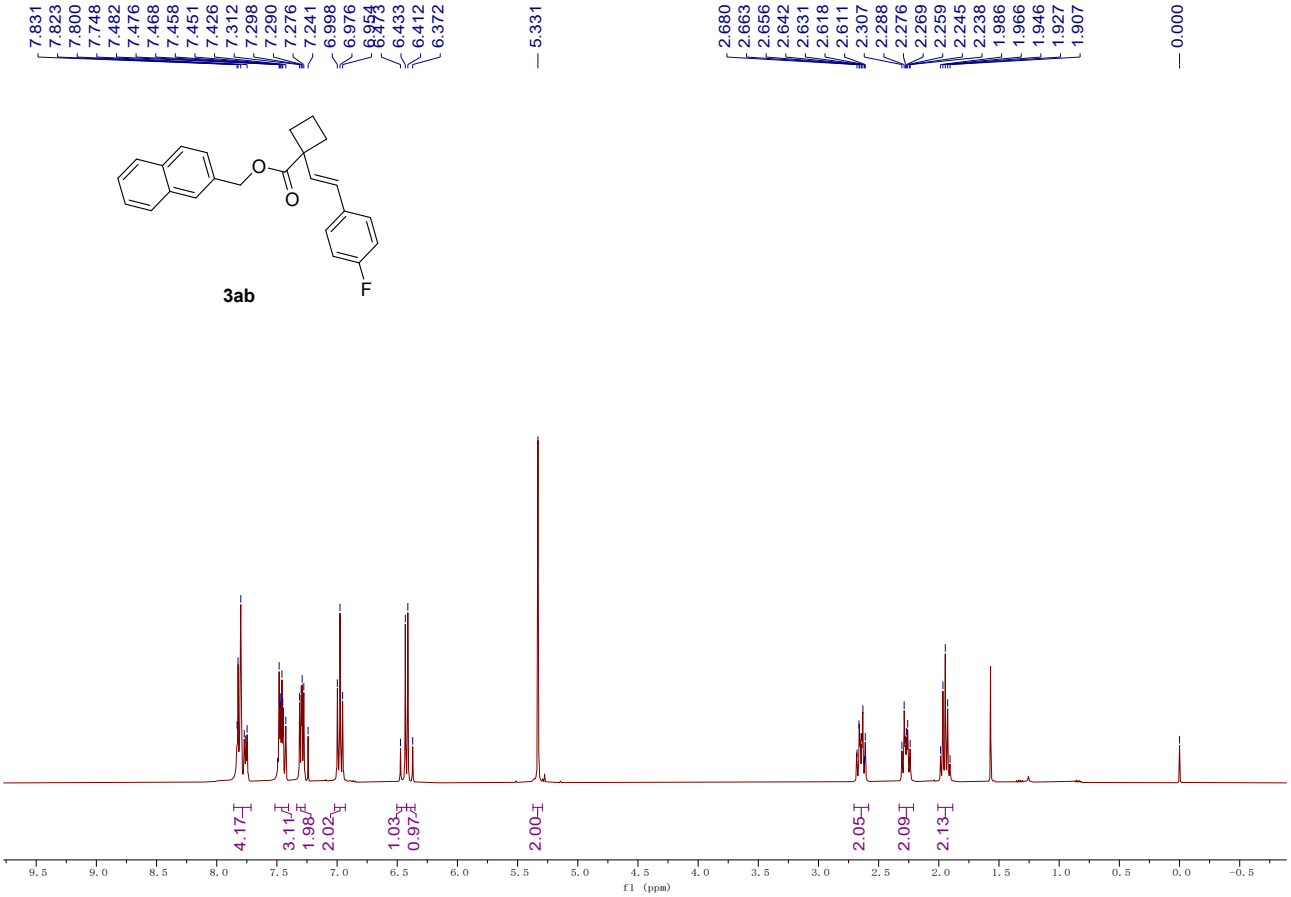

6.42
4.82
6.38
1.61
1.06
1.61
0.61
1.21
2.00
1.60
4.38
2.03
1.62
4.84
f1 (ppm)

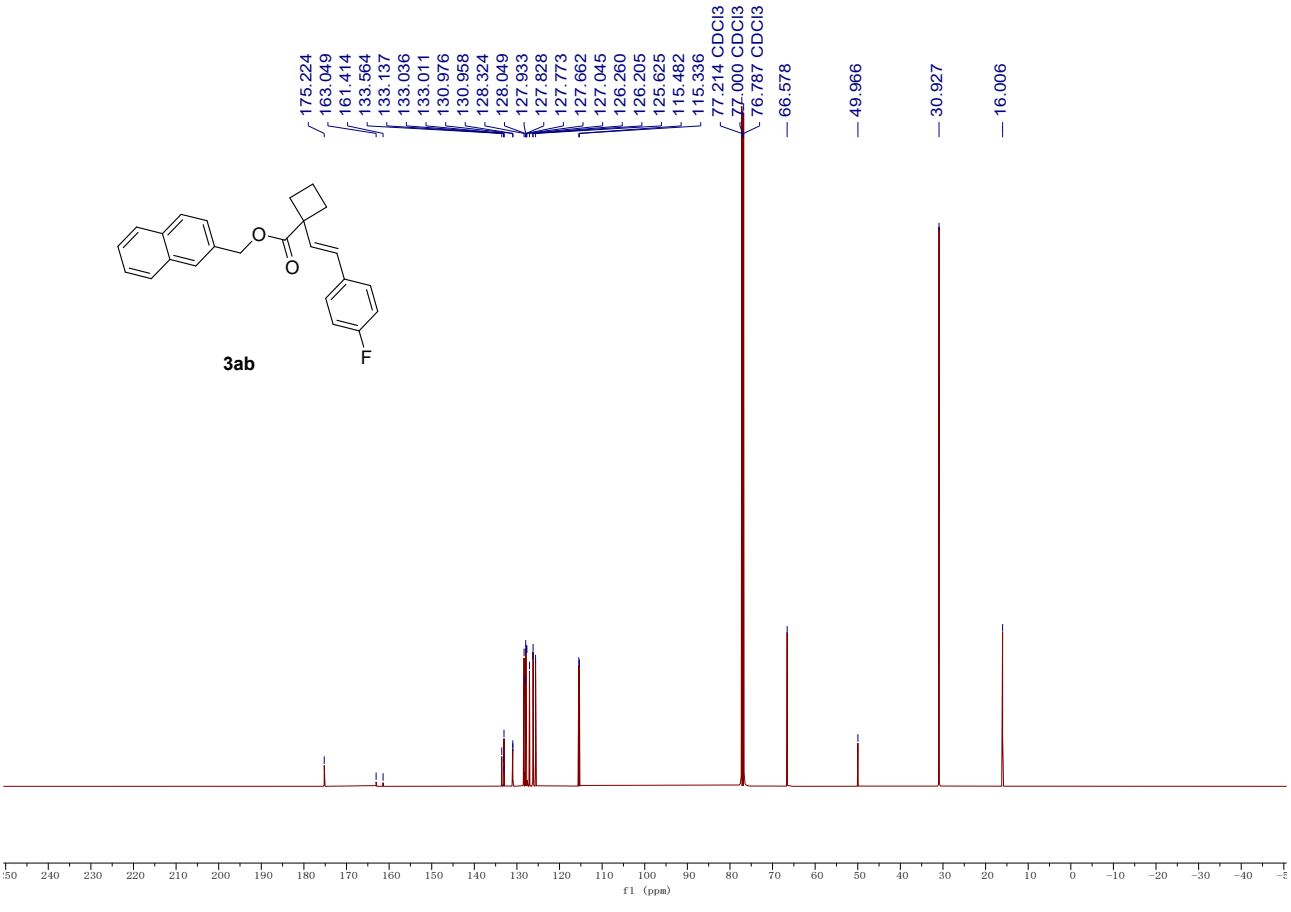

175.626
175.268
136.908
133.645
133.614
133.150
133.026
132.410
130.975
129.306
129.219
128.544
128.524
128.322
128.300
127.959
127.657
127.463
127.412
126.947
126.341
126.273
126.217
126.151
125.588
125.579
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
66.646
66.471
47.208
45.780
39.212
38.241
25.174
24.172
22.040
21.520

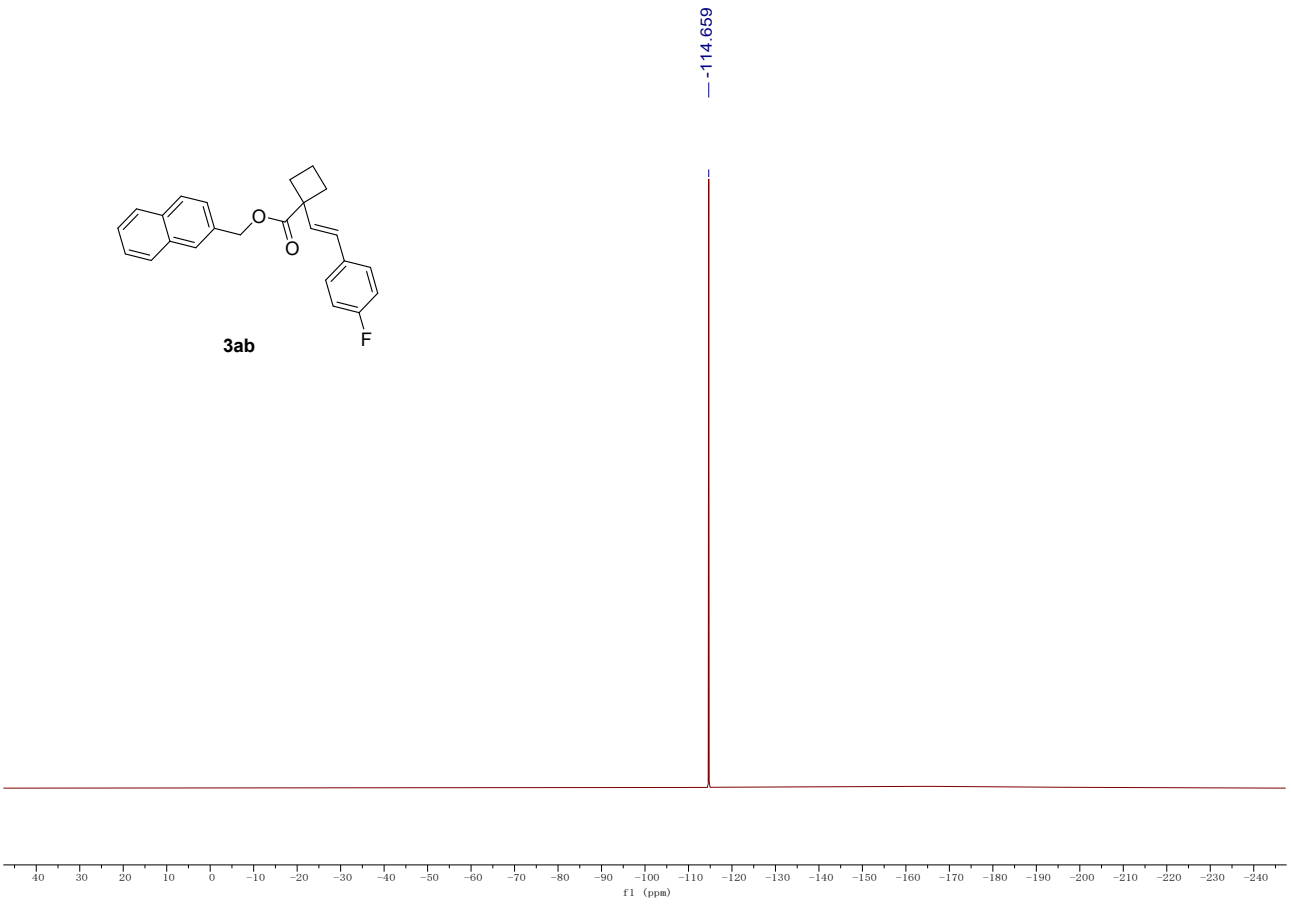
Me
O
O
Ph

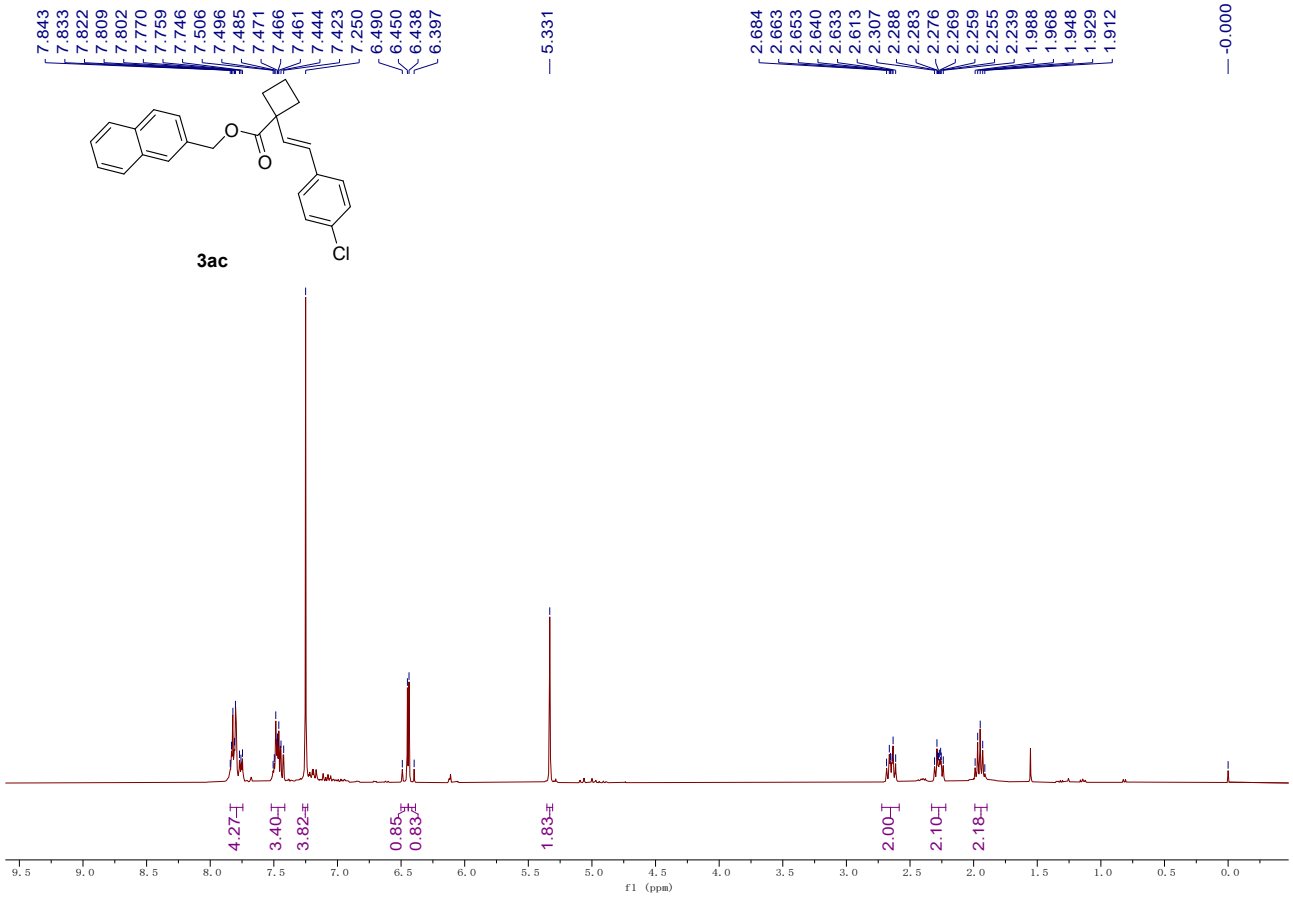
3na

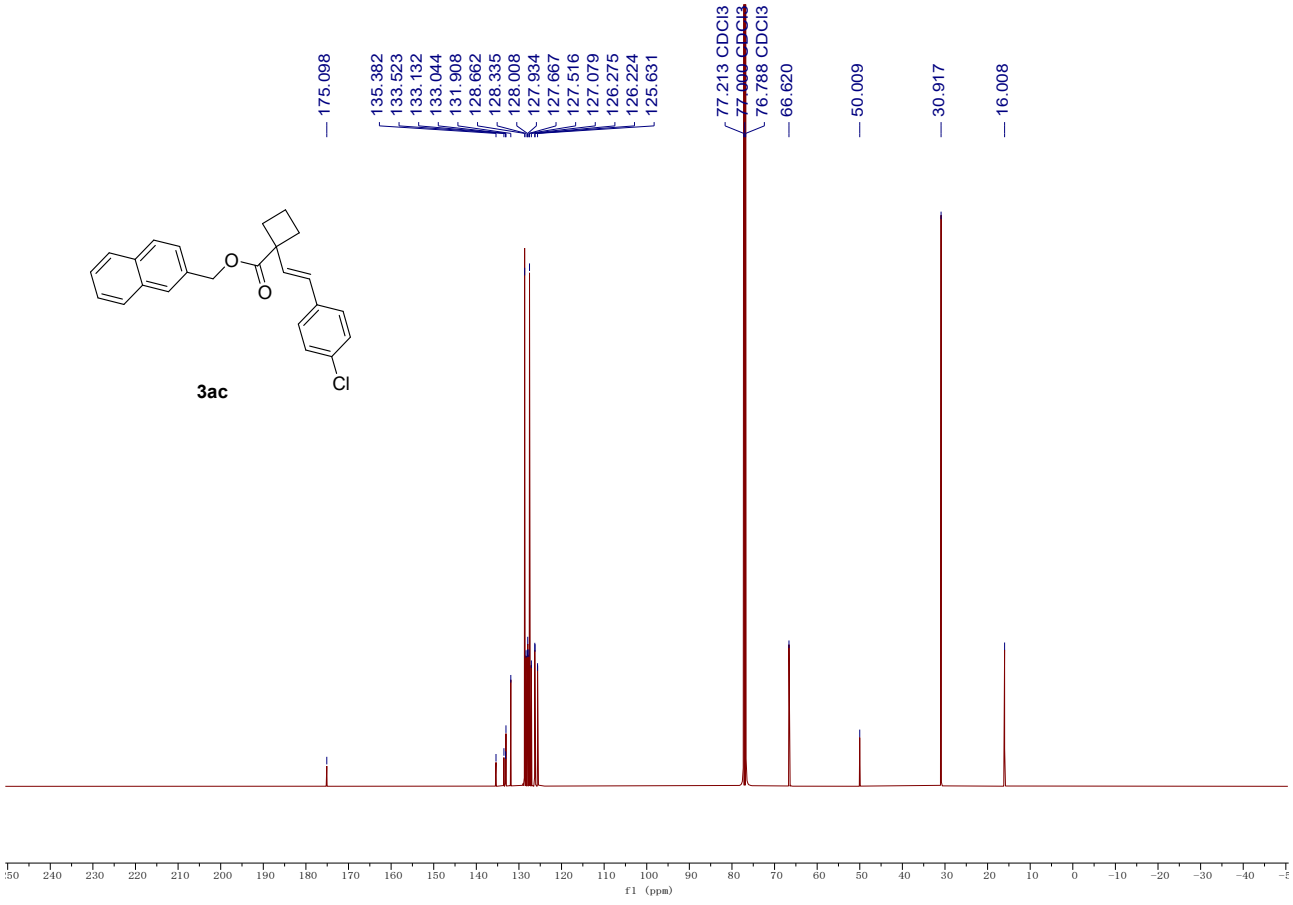
f1 (ppm)

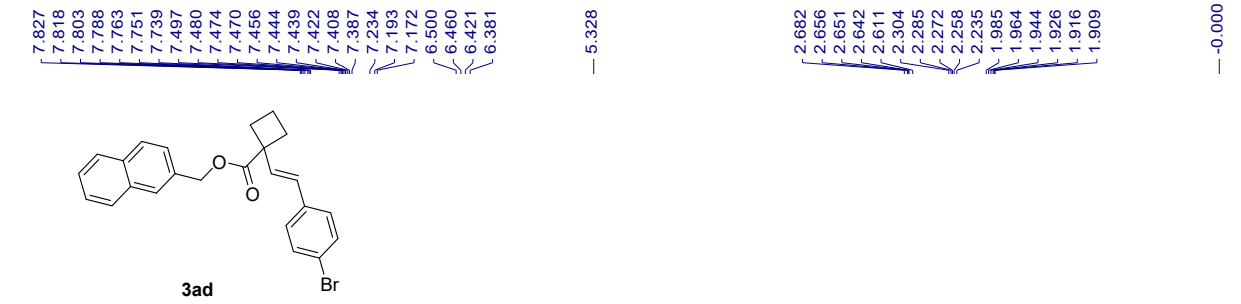

7.831
7.823
7.800
7.748
7.482
7.476
7.468
7.458
7.451
7.426
7.312
7.298
7.290
7.276
7.241
6.998
6.976
6.954
6.433
6.412
6.372
5.331
2.680
2.663
2.656
2.642
2.631
2.618
2.611
2.307
2.288
2.276
2.269
2.259
2.245
2.238
1.986
1.966
1.946
1.927
1.907
0.000
O
O
F
3ab
4.17
3.11
1.98
2.02
1.03
0.97
2.00
2.05
2.09
2.13
f1 (ppm)


175.224
163.049
161.414
133.564
133.137
133.036
133.011
130.976
130.958
128.324
128.049
127.933
127.828
127.773
127.662
127.045
126.260
126.205
125.625
115.482
115.336
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
66.578
49.966
30.927
16.006
O
O
F
3ab
f1 (ppm)

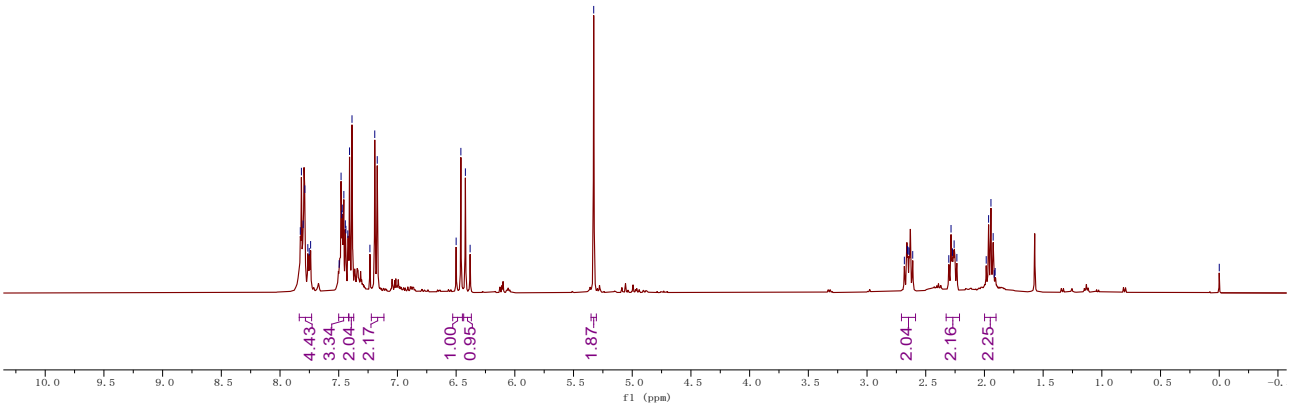

-114.659
O
O
F
3ab
40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)

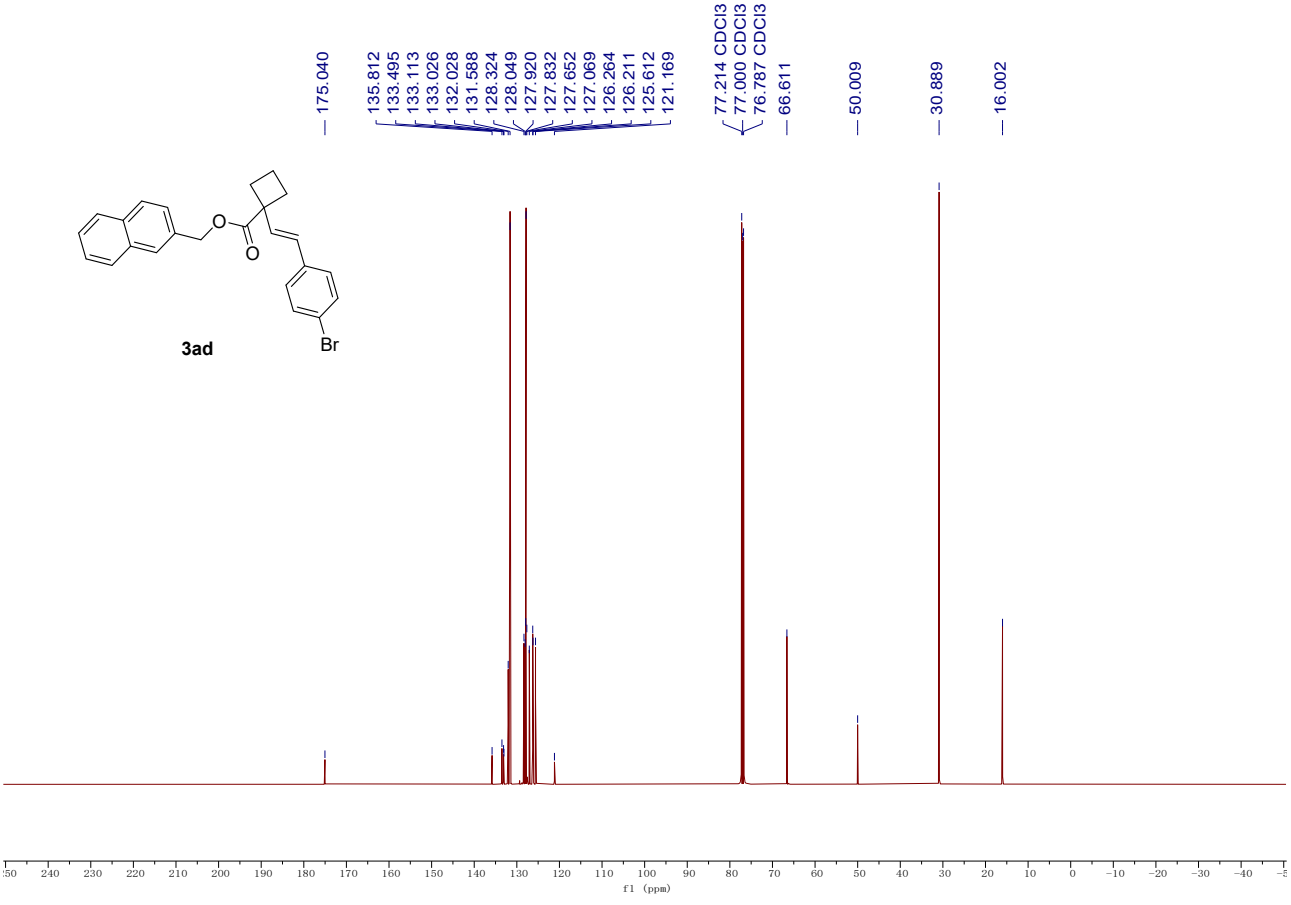

7.843
7.833
7.822
7.809
7.802
7.770
7.759
7.746
7.506
7.496
7.485
7.471
7.466
7.461
7.444
7.423
7.250
6.490
6.450
6.438
6.397
5.331
2.684
2.663
2.653
2.640
2.633
2.613
2.307
2.288
2.283
2.276
2.269
2.259
2.255
2.239
1.988
1.968
1.948
1.929
1.912
-0.000
O
O
Cl
3ac
4.27
3.40
3.82
0.85
0.83
1.83
2.00
2.10
2.18
f1 (ppm)


175.098
135.382
133.523
133.132
133.044
131.908
128.662
128.335
128.008
127.934
127.667
127.516
127.079
126.275
126.224
125.631
77.213 CDCl3
77.000 CDCl3
76.788 CDCl3
66.620
50.009
30.917
16.008
O
O
Cl
3ac
f1 (ppm)


7.827
7.818
7.803
7.788
7.763
7.751
7.739
7.497
7.480
7.474
7.470
7.456
7.444
7.439
7.422
7.408
7.387
7.234
7.193
7.172
6.500
6.460
6.421
6.381
5.328
2.682
2.656
2.651
2.642
2.611
2.304
2.285
2.272
2.258
2.235
1.985
1.964
1.944
1.926
1.916
1.909
-0.000
O
O
Br

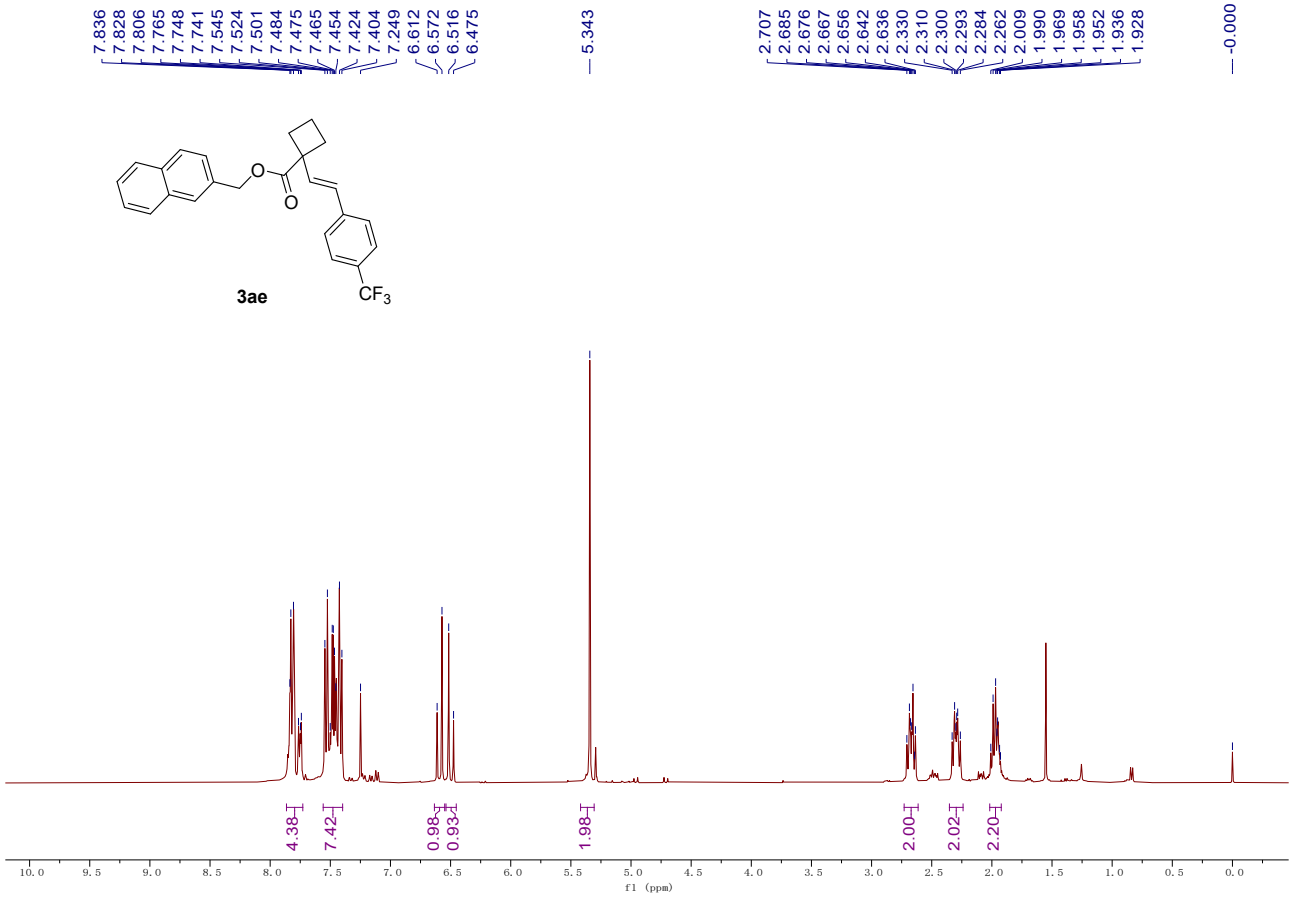
3ad

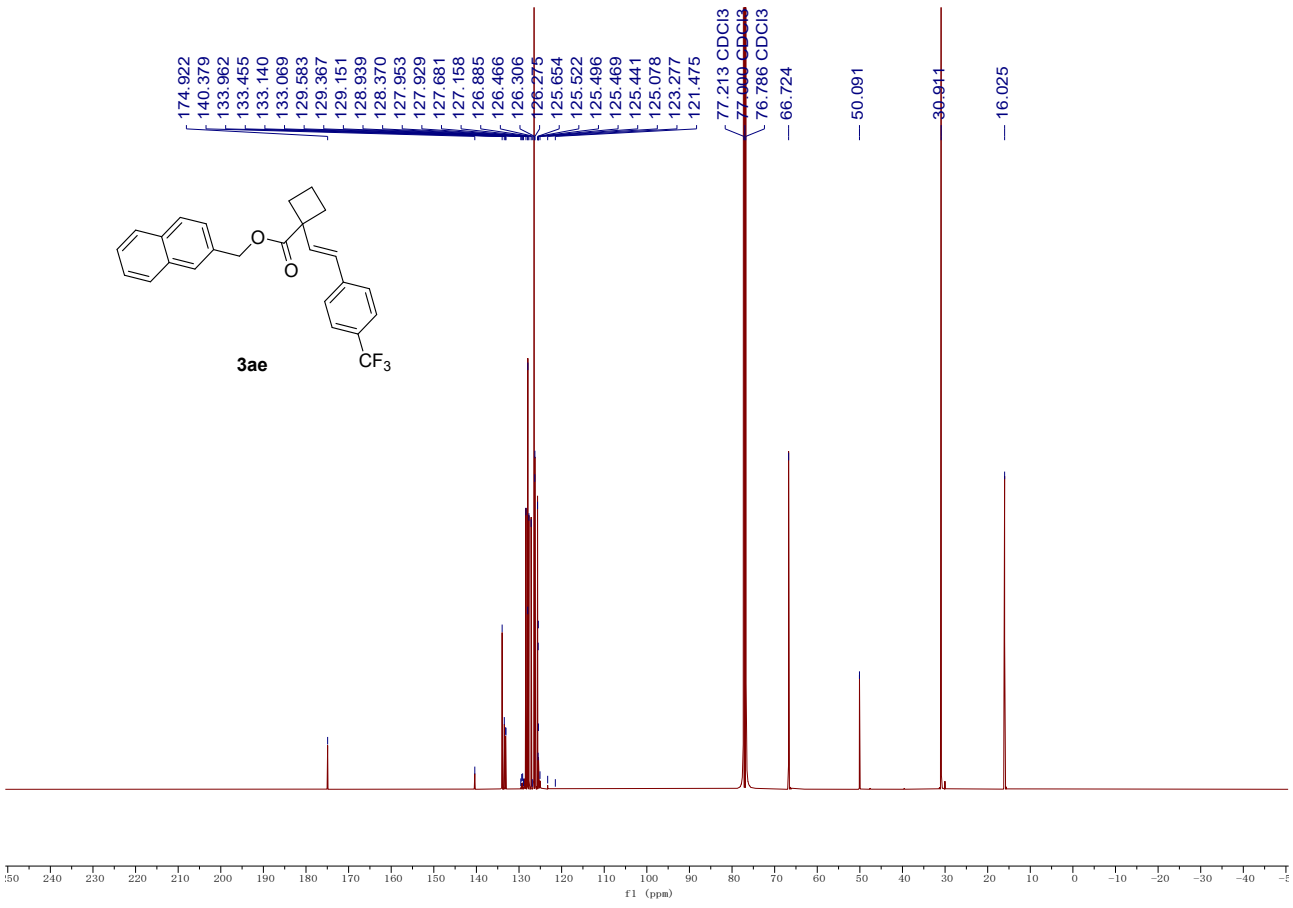

4.43
3.34
2.04
2.17
1.00
0.95
1.87
2.04
2.16
2.25
f1 (ppm)

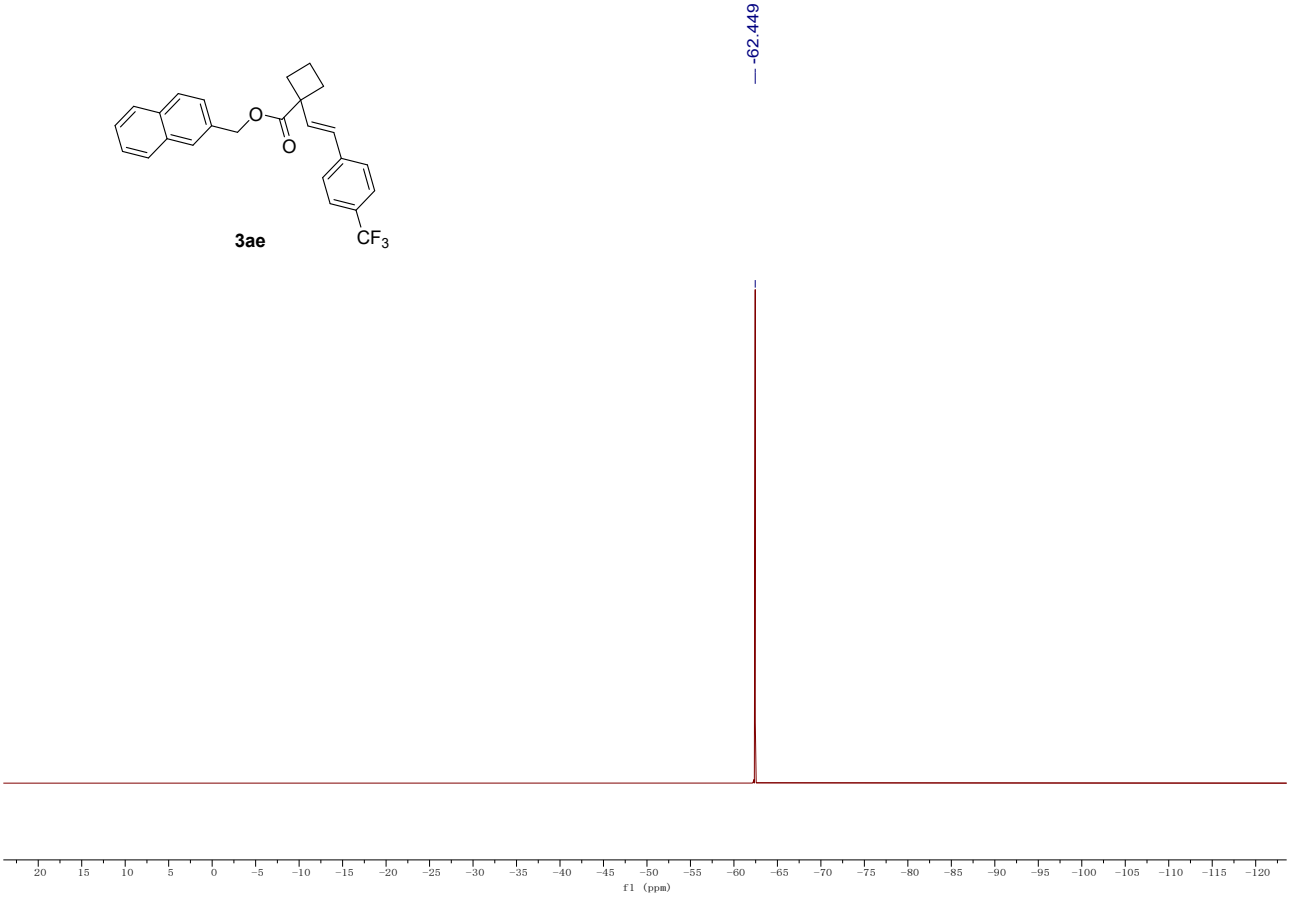

175.040
135.812
133.495
133.113
133.026
132.028
131.588
128.324
128.049
127.920
127.832
127.652
127.069
126.264
126.211
125.612
121.169
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
66.611
50.009
30.889
16.002
f1 (ppm)

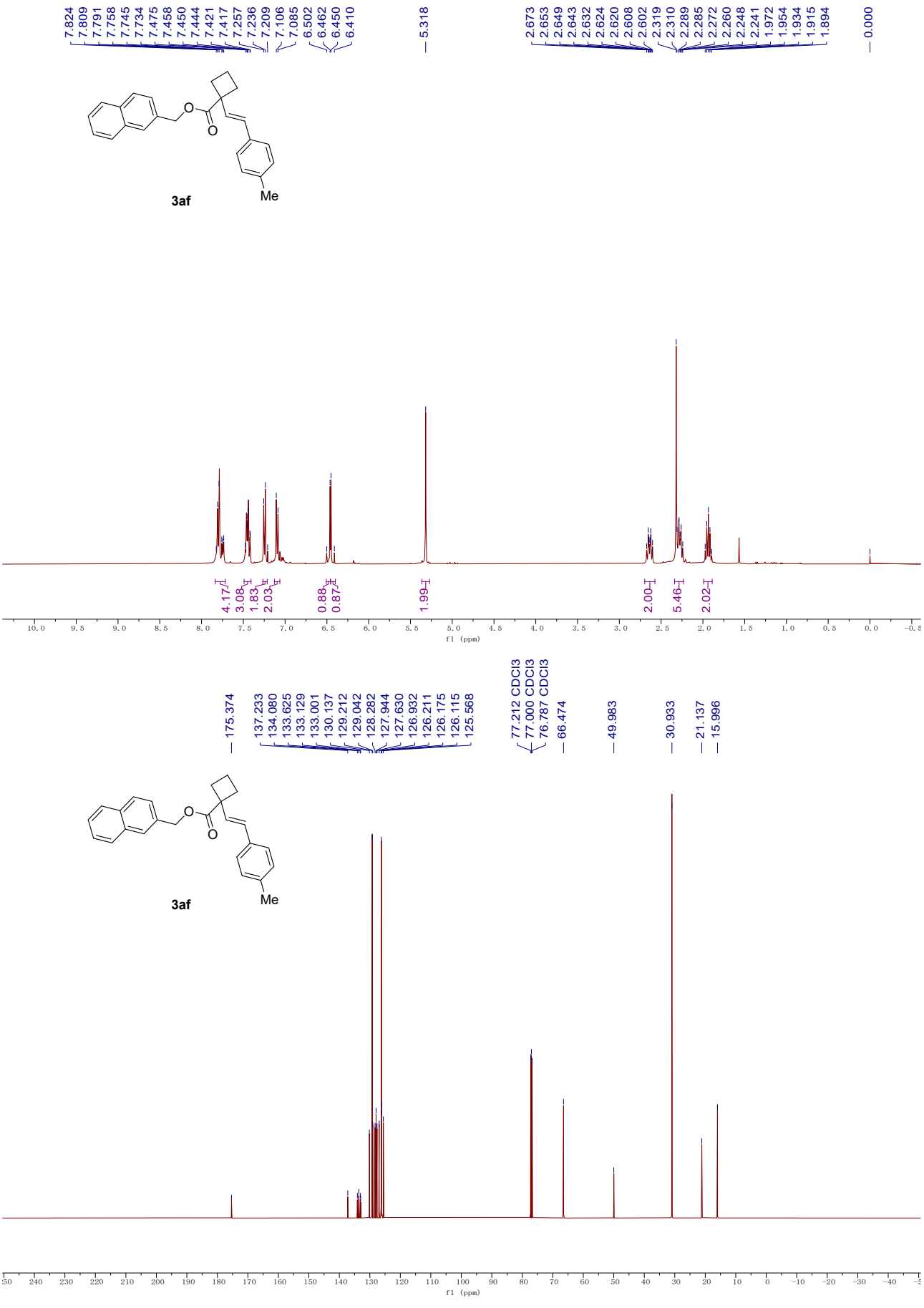
O
O
Br

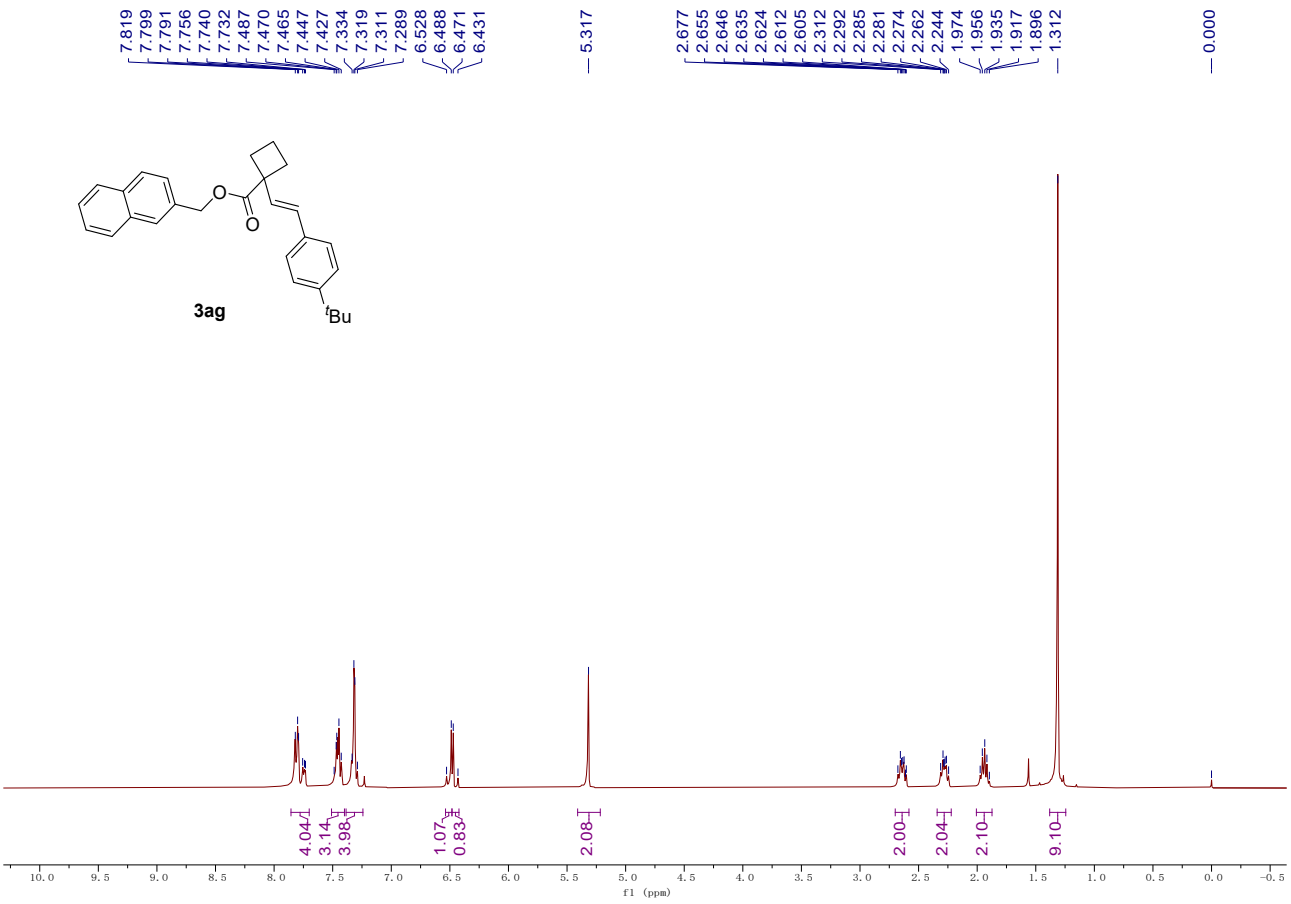
3ad

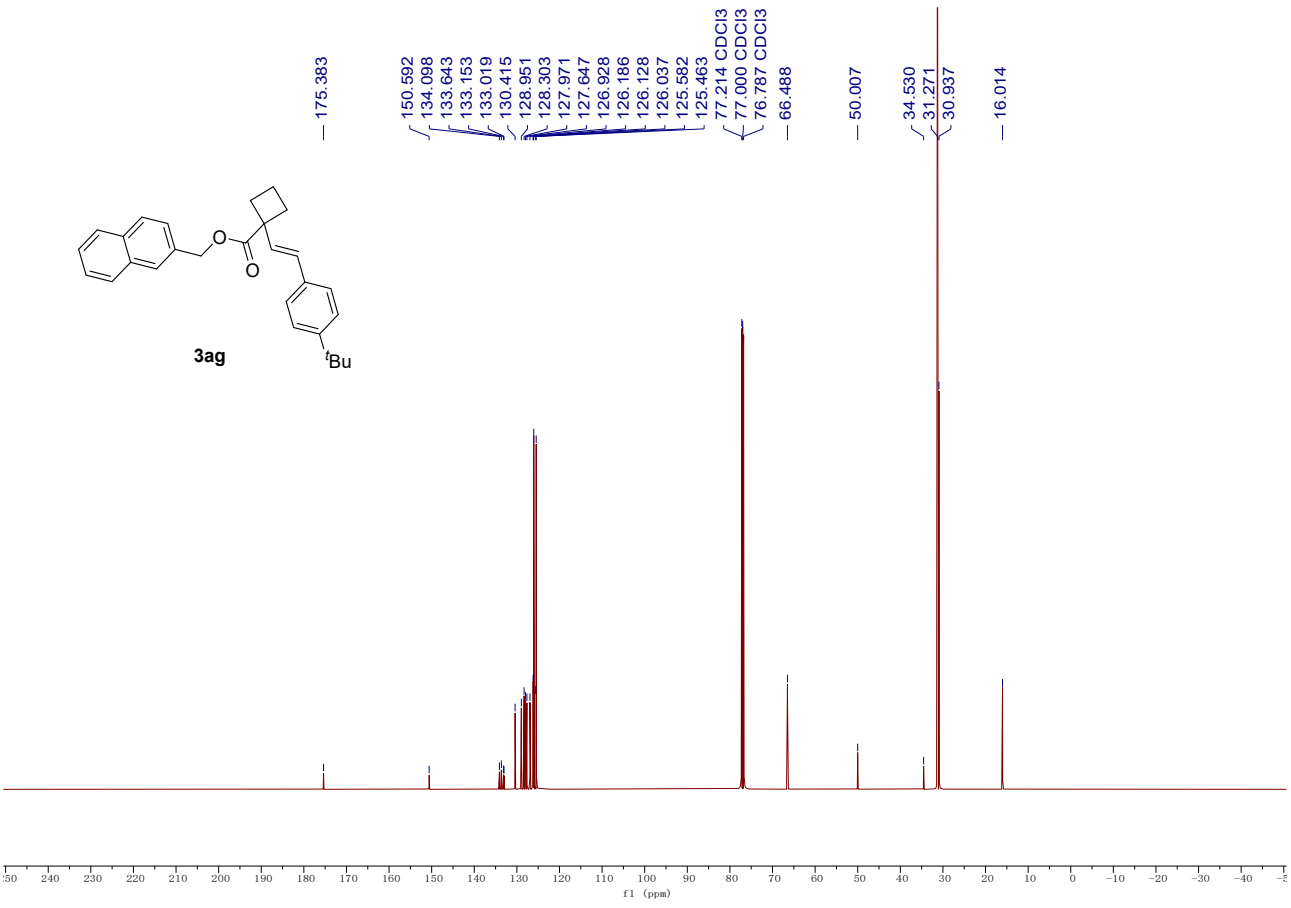

7.836
7.828
7.806
7.765
7.748
7.741
7.545
7.524
7.501
7.484
7.475
7.465
7.454
7.424
7.404
7.249
6.612
6.572
6.516
6.475
5.343
2.707
2.685
2.676
2.667
2.656
2.642
2.636
2.330
2.310
2.300
2.293
2.284
2.262
2.009
1.990
1.969
1.958
1.952
1.936
1.928
-0.000
O
O
3ae
CF3
4.38
7.42
0.98
0.93
1.98
2.00
2.02
2.20
f1 (ppm)

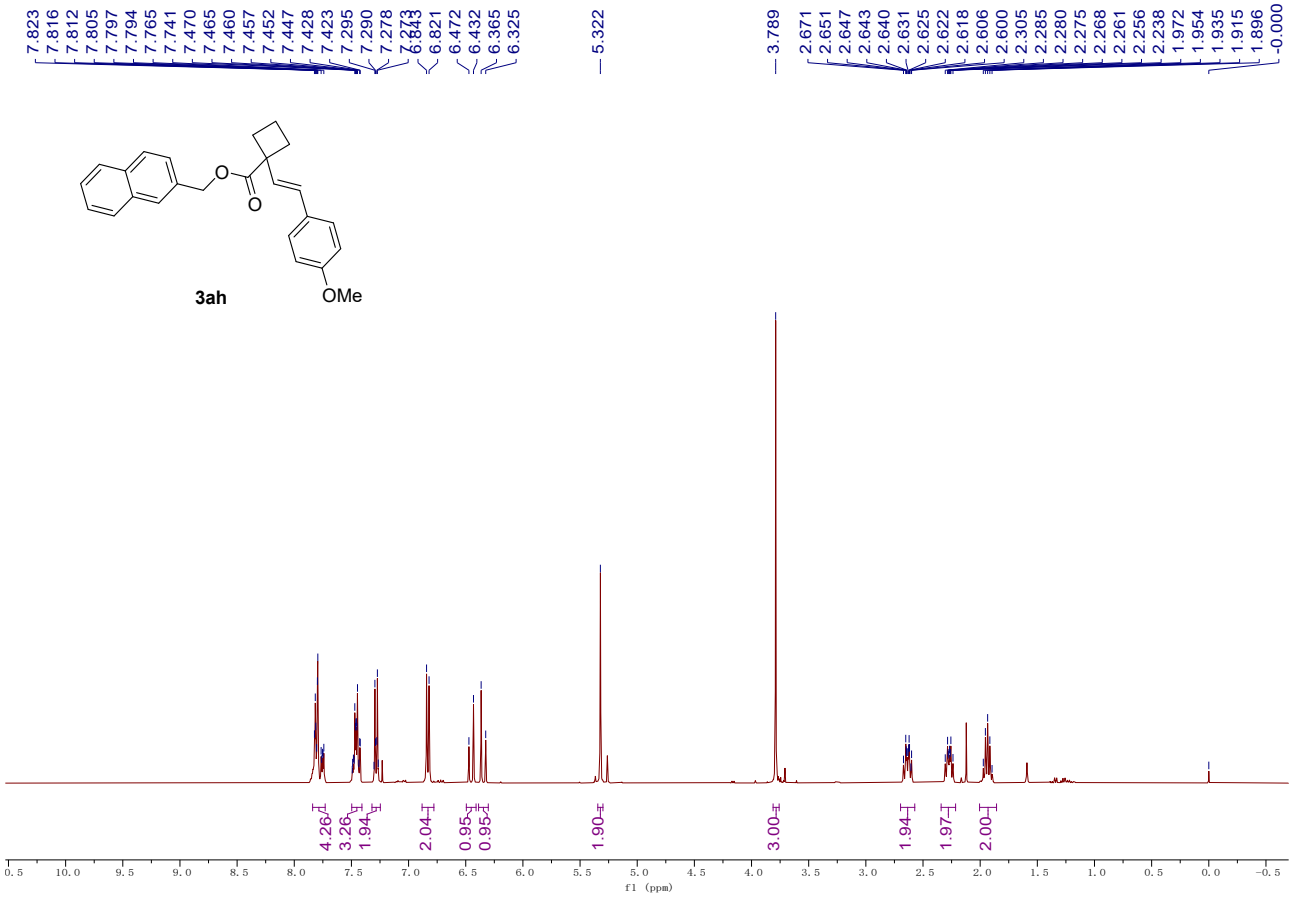

174.922
140.379
133.962
133.455
133.140
133.069
129.583
129.367
129.151
128.939
128.370
127.953
127.929
127.681
127.158
126.885
126.466
126.306
126.275
125.654
125.522
125.496
125.469
125.441
125.078
123.277
121.475
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
66.724
50.091
30.911
16.025
O
O
3ae
CF3
f1 (ppm)

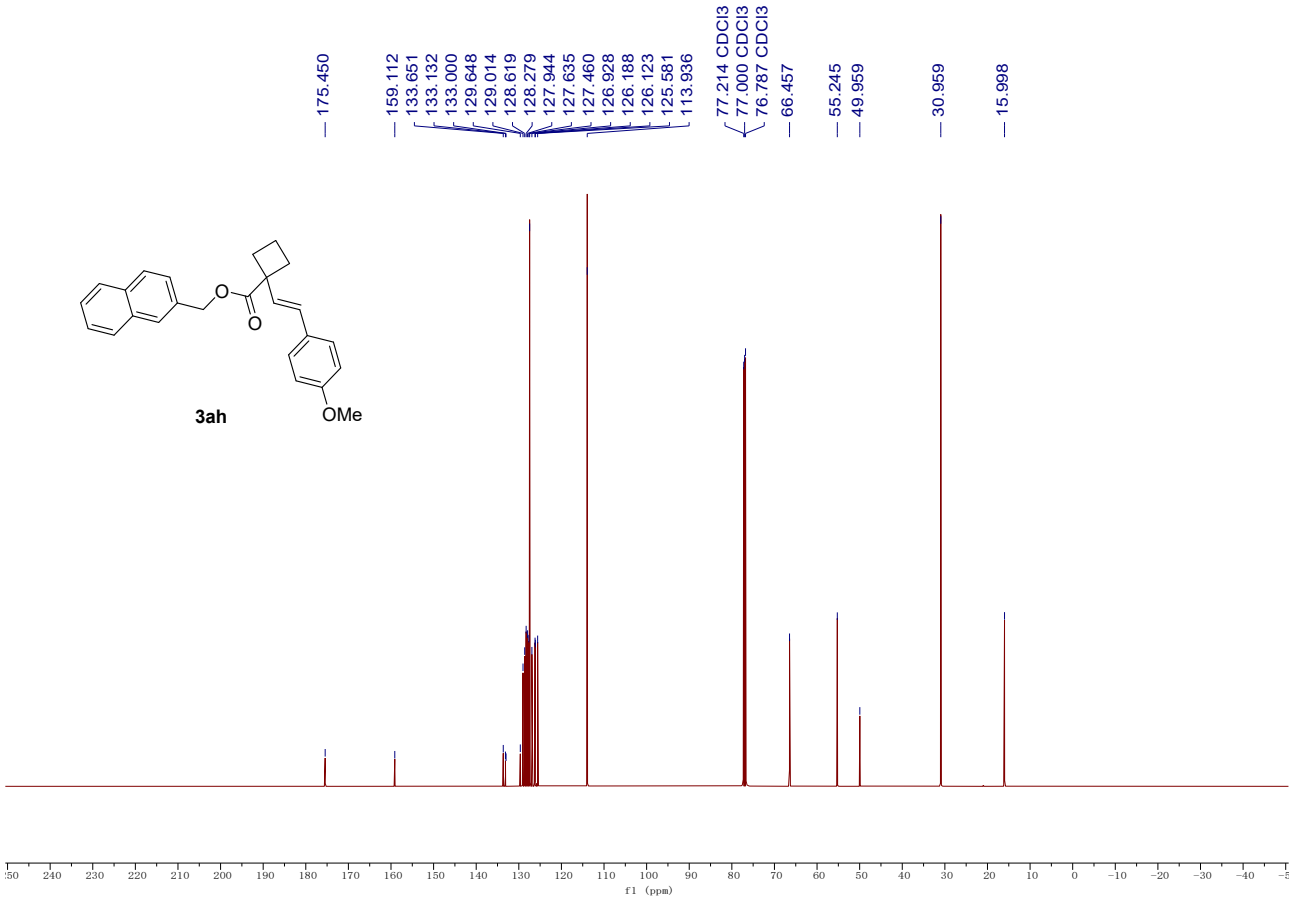

-62.449
O
O
CF3
3ae
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120
f1 (ppm)

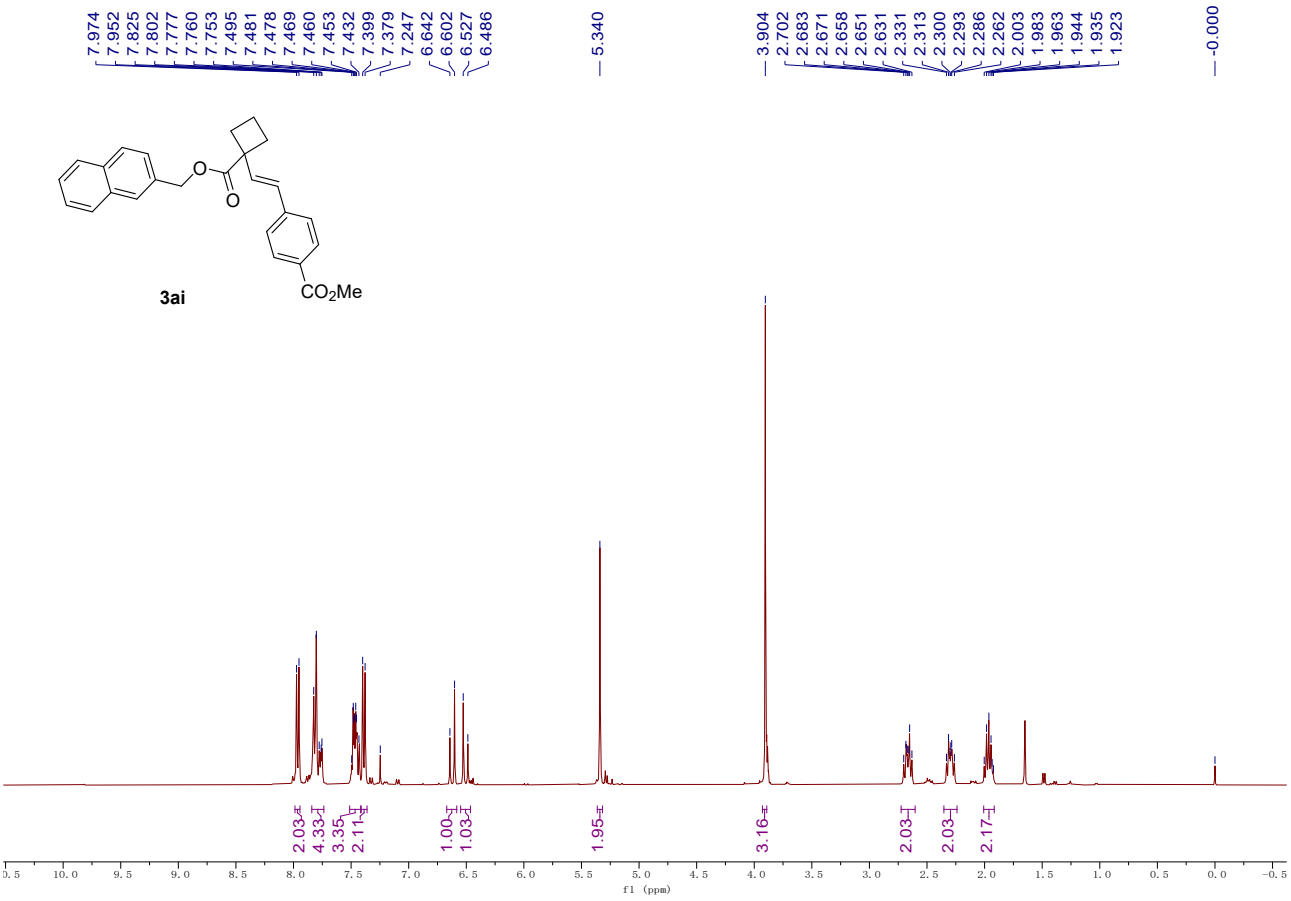

7.824
7.809
7.791
7.758
7.745
7.734
7.475
7.458
7.450
7.444
7.421
7.417
7.257
7.236
7.209
7.106
7.085
6.502
6.462
6.450
6.410
5.318
2.673
2.653
2.649
2.643
2.632
2.624
2.620
2.608
2.602
2.319
2.310
2.289
2.285
2.272
2.260
2.248
2.241
1.972
1.954
1.934
1.915
1.894
0.000
O
O
Me
3af
4.17
3.08
1.83
2.03
0.88
0.87
1.99
2.00
5.46
2.02
f1 (ppm)
175.374
137.233
134.080
133.625
133.129
133.001
130.137
129.212
129.042
128.282
127.944
127.630
126.932
126.211
126.175
126.115
125.568
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
66.474
49.983
30.933
21.137
15.996
O
O
Me
3af
f1 (ppm)

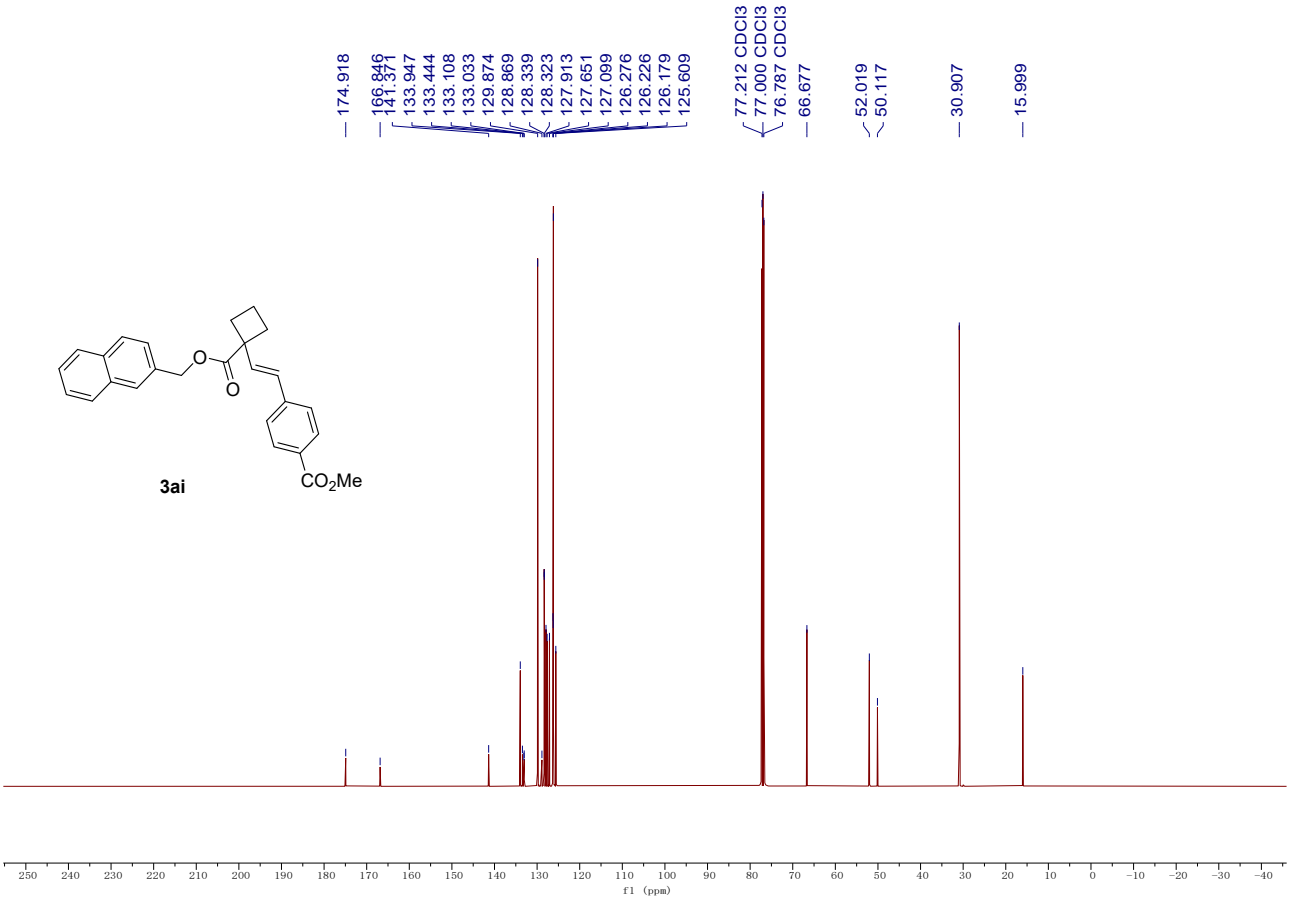

7.819
7.799
7.791
7.756
7.740
7.732
7.487
7.470
7.465
7.447
7.427
7.334
7.319
7.311
7.289
6.528
6.488
6.471
6.431
5.317
2.677
2.655
2.646
2.635
2.624
2.612
2.605
2.312
2.292
2.285
2.281
2.274
2.262
2.244
1.974
1.956
1.935
1.917
1.896
1.312
0.000
3ag
tBu
4.04
3.14
3.98
1.07
0.83
2.08
2.00
2.04
2.10
9.10
f1 (ppm)

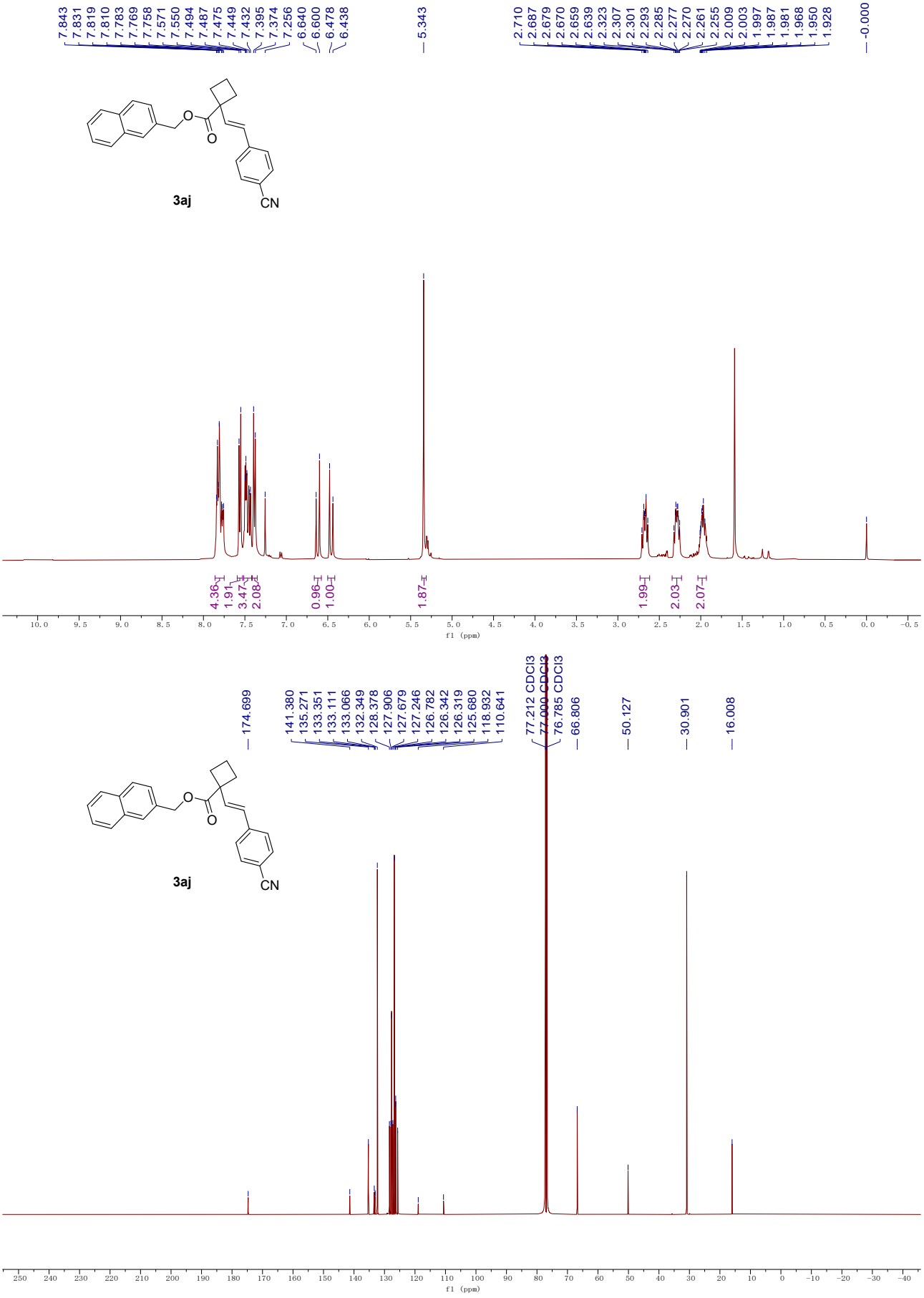

175.383
150.592
134.098
133.643
133.153
133.019
130.415
128.951
128.303
127.971
127.647
126.928
126.186
126.128
126.037
125.582
125.463
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
66.488
50.007
34.530
31.271
30.937
16.014
3ag
tBu
f1 (ppm)

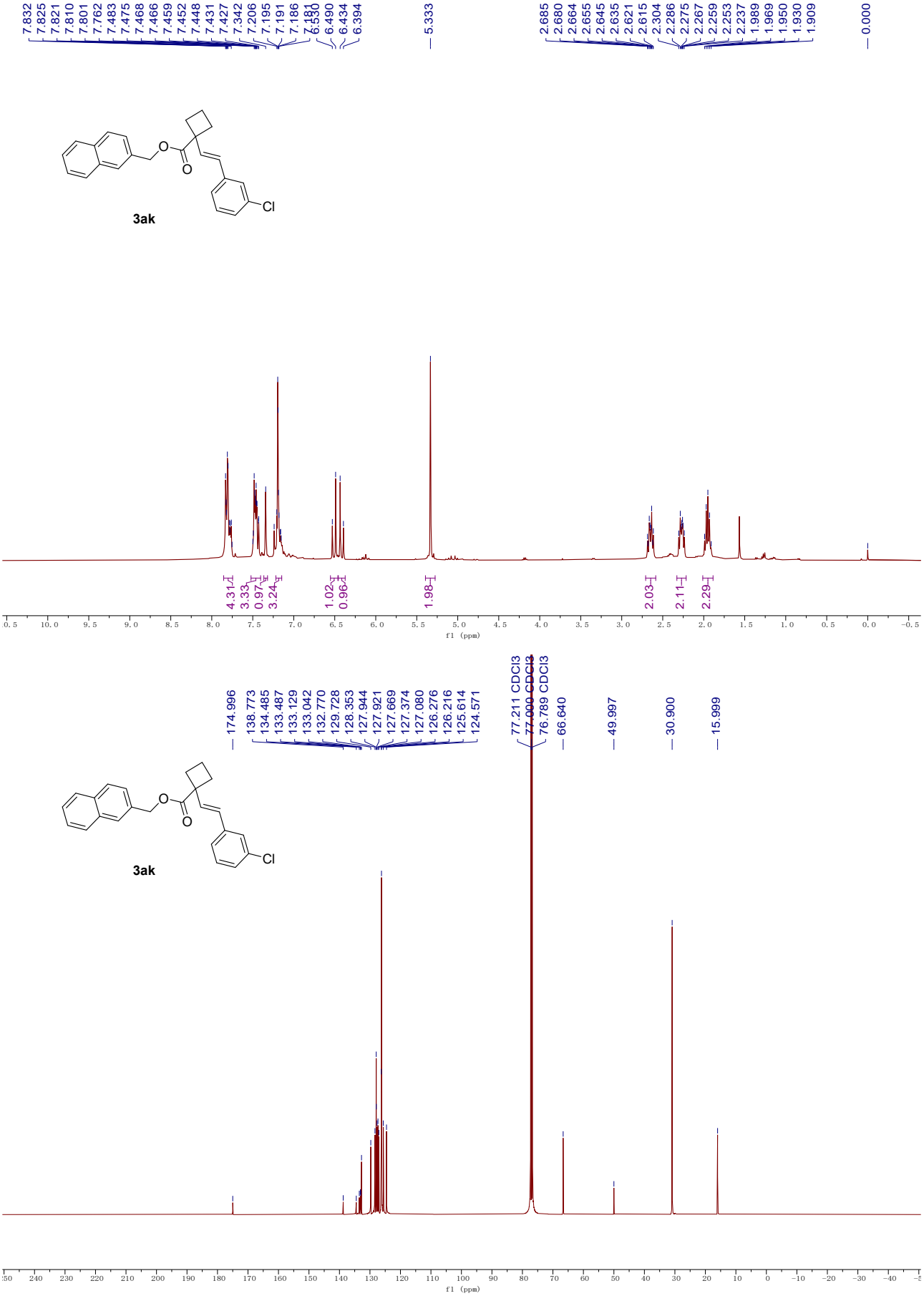

7.823
7.816
7.812
7.805
7.797
7.794
7.765
7.741
7.470
7.465
7.460
7.457
7.452
7.447
7.428
7.423
7.295
7.290
7.278
6.843
6.821
6.472
6.432
6.365
6.325
5.322
3.789
2.671
2.651
2.647
2.643
2.640
2.631
2.625
2.622
2.618
2.606
2.600
2.305
2.285
2.280
2.275
2.268
2.261
2.256
2.238
1.972
1.954
1.935
1.915
1.896
-0.000
O
O
3ah
OMe
4.26
3.26
1.94
2.04
0.95
0.95
1.90
3.00
1.94
1.97
2.00
f1 (ppm)


175.450
159.112
133.651
133.132
133.000
129.648
129.014
128.619
128.279
127.944
127.635
127.460
126.928
126.188
126.123
125.581
113.936
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
66.457
55.245
49.959
30.959
15.998
O
O
3ah
OMe
f1 (ppm)

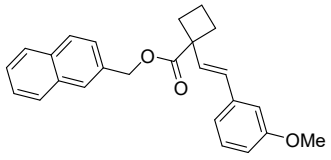

7.974
7.952
7.825
7.802
7.777
7.760
7.753
7.495
7.481
7.478
7.469
7.460
7.453
7.432
7.399
7.379
7.247
6.642
6.602
6.527
6.486
5.340
3.904
2.702
2.683
2.671
2.658
2.651
2.631
2.331
2.313
2.300
2.293
2.286
2.262
2.003
1.983
1.963
1.944
1.935
1.923
-0.000
O
O
CO2Me
3ai
2.03
4.33
3.35
2.11
1.00
1.03
1.95
3.16
2.03
2.03
2.17
f1 (ppm)


174.918
166.846
141.371
133.947
133.444
133.108
133.033
129.874
128.869
128.339
128.323
127.913
127.651
127.099
126.276
126.226
126.179
125.609
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
66.677
52.019
50.117
30.907
15.999
O
O
CO2Me
3ai
f1 (ppm)


7.843
7.831
7.819
7.810
7.783
7.769
7.758
7.571
7.550
7.494
7.487
7.475
7.449
7.432
7.395
7.374
7.256
6.640
6.600
6.478
6.438
5.343
2.710
2.687
2.679
2.670
2.659
2.639
2.323
2.307
2.301
2.293
2.285
2.277
2.270
2.261
2.255
2.009
2.003
1.997
1.987
1.981
1.968
1.950
1.928
-0.000
O
O
CN
3aj
4.36
1.91
3.47
2.08
0.96
1.00
1.87
1.99
2.03
2.07
f1 (ppm)
174.699
141.380
135.271
133.351
133.111
133.066
132.349
128.378
127.906
127.679
127.246
126.782
126.342
126.319
125.680
118.932
110.641
77.212 CDCl3
77.000 CDCl3
76.785 CDCl3
66.806
50.127
30.901
16.008
O
O
CN
3aj
f1 (ppm)

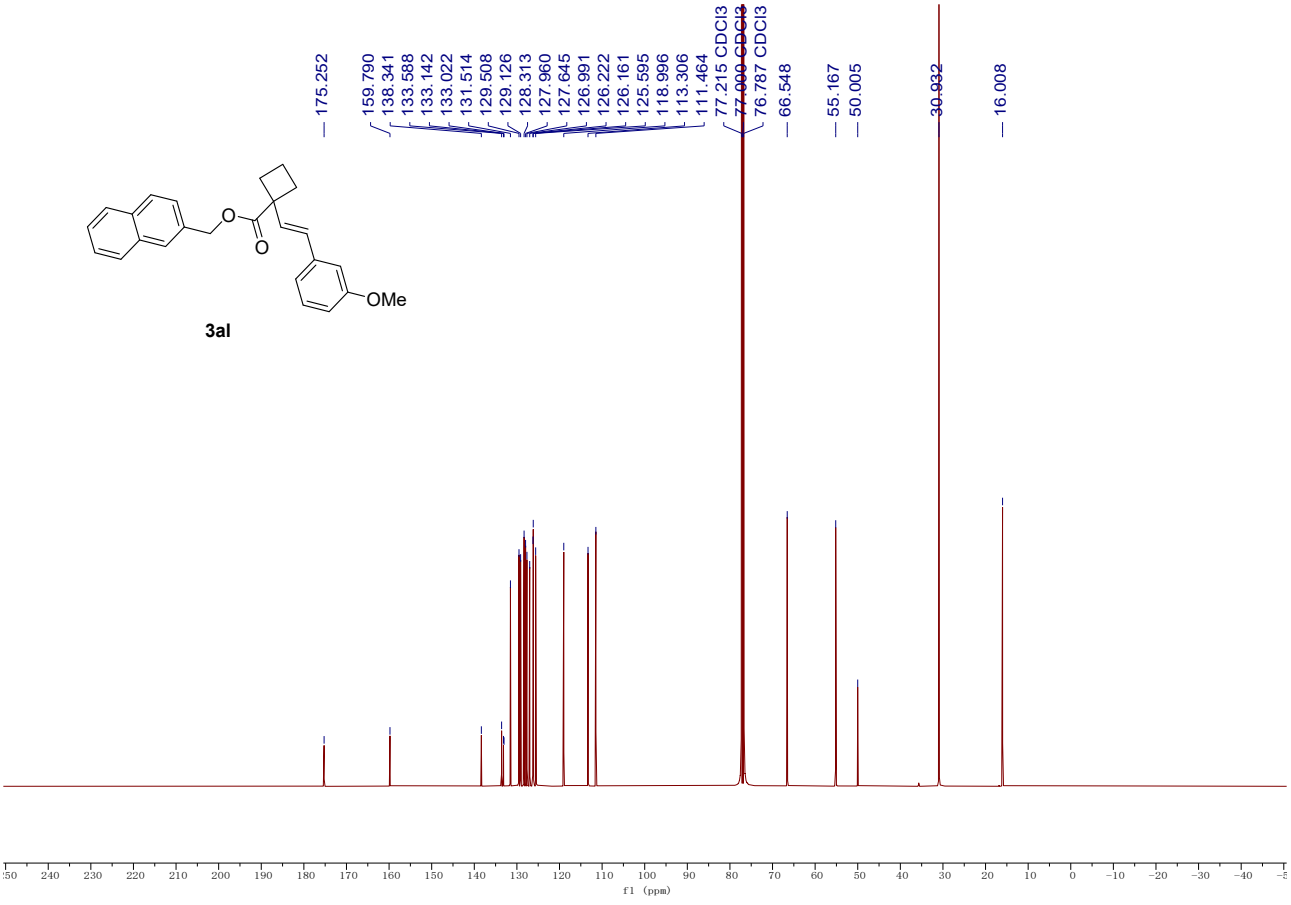

7.832
7.825
7.821
7.810
7.801
7.762
7.483
7.475
7.468
7.466
7.459
7.452
7.448
7.431
7.427
7.342
7.206
7.195
7.191
7.186
6.490
6.434
6.394
5.333
2.685
2.680
2.664
2.655
2.645
2.635
2.621
2.615
2.304
2.286
2.275
2.267
2.259
2.253
2.237
1.989
1.969
1.950
1.930
1.909
0.000
O
O
Cl
3ak
4.31
3.33
0.97
3.24
1.02
0.96
1.98
2.03
2.11
2.29
f1 (ppm)
174.996
138.773
134.485
133.487
133.129
133.042
132.770
129.728
128.353
127.944
127.921
127.669
127.374
127.080
126.276
126.216
125.614
124.571
77.211 CDCl3
77.000 CDCl3
76.789 CDCl3
66.640
49.997
30.900
15.999
O
O
Cl
3ak
f1 (ppm)


7.838
7.823
7.815
7.801
7.774
7.769
7.762
7.758
7.751
7.492
7.486
7.482
7.475
7.469
7.465
7.462
7.450
7.439
7.433
7.428
7.239
7.232
7.213
7.193
6.969
6.965
6.962
6.949
6.946
6.943
6.898
6.892
6.887
6.800
6.798
6.794
6.791
6.780
6.777
6.773
6.771
6.486
5.330
3.777
2.684
2.664
2.654
2.644
2.640
2.635
2.632
2.613
2.322
2.302
2.296
2.291
2.284
2.278
2.272
2.254
1.987
1.968
1.949
1.929
-0.000


O
O
OMe

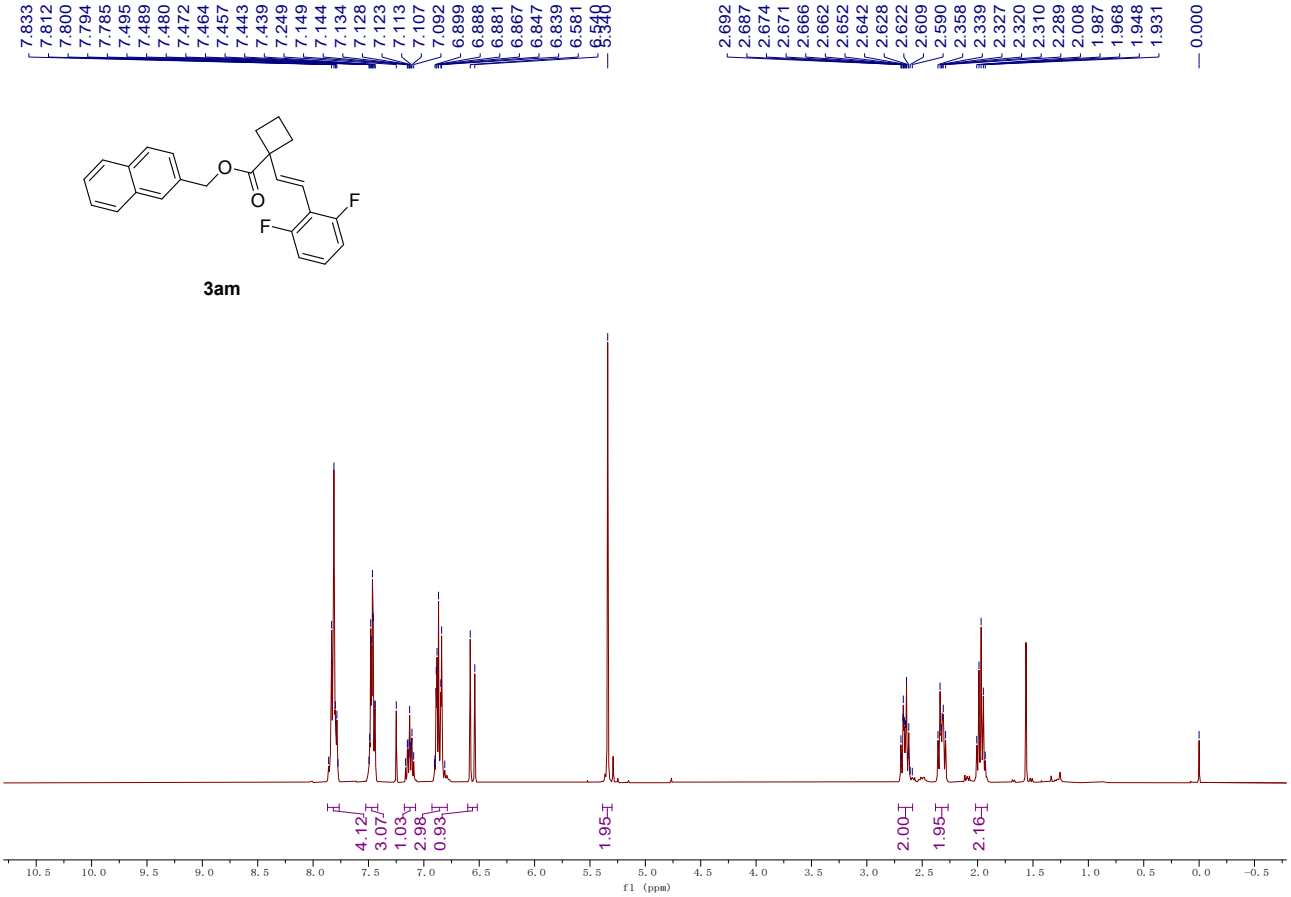
3al

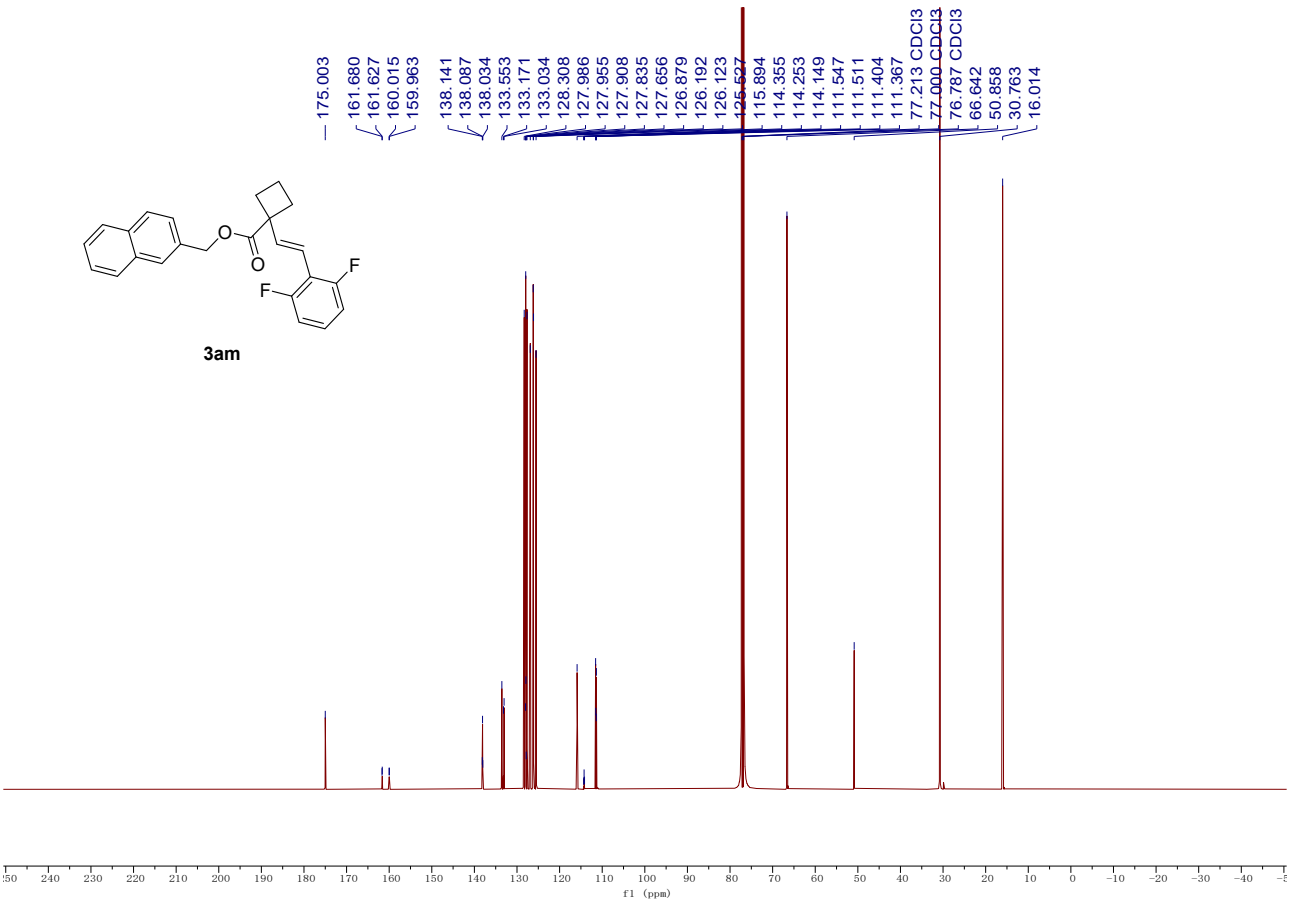
4.36
3.15
1.24
1.06
0.97
1.01
1.99
1.87
2.98
2.00
2.02
2.11
f1 (ppm)

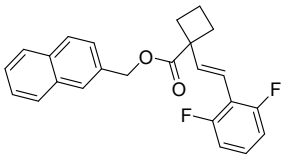

175.252
159.790
138.341
133.588
133.142
133.022
131.514
129.508
129.126
128.313
127.960
127.645
126.991
126.222
126.161
125.595
118.996
113.306
111.464
77.215 CDCl3
77.000 CDCl3
76.787 CDCl3
66.548
55.167
50.005
30.932
16.008
f1 (ppm)

O
O
OMe

3al

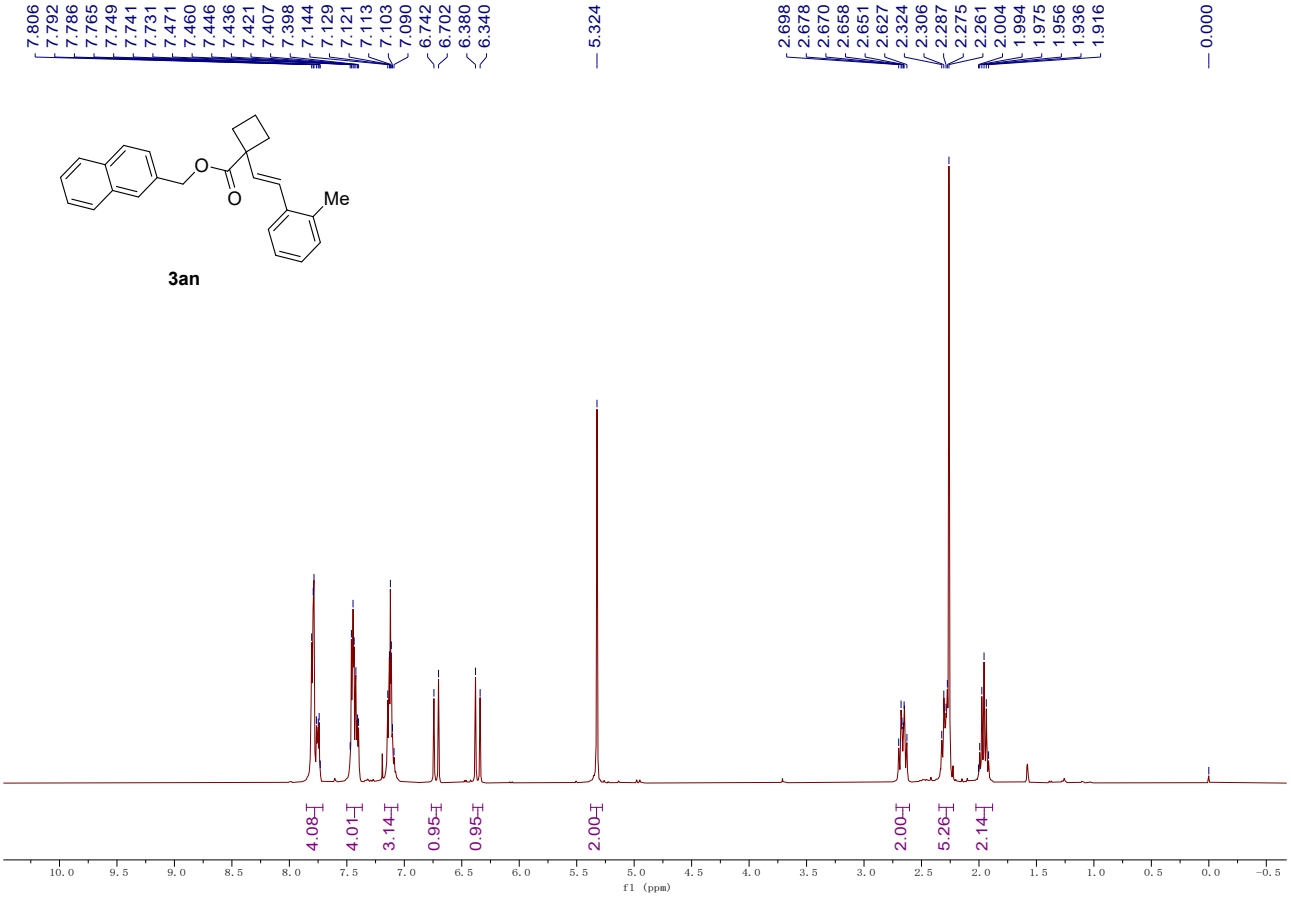

7.833
7.812
7.800
7.794
7.785
7.495
7.489
7.480
7.472
7.464
7.457
7.443
7.439
7.249
7.149
7.144
7.134
7.128
7.123
7.113
7.107
7.092
6.899
6.888
6.881
6.867
6.847
6.839
6.581
6.540
5.340
2.692
2.687
2.674
2.671
2.666
2.662
2.652
2.642
2.628
2.622
2.609
2.590
2.358
2.339
2.327
2.320
2.310
2.289
2.008
1.987
1.968
1.948
1.931
0.000
O
O
F
F
3am
4.12
3.07
1.03
2.98
0.93
1.95
2.00
1.95
2.16
f1 (ppm)

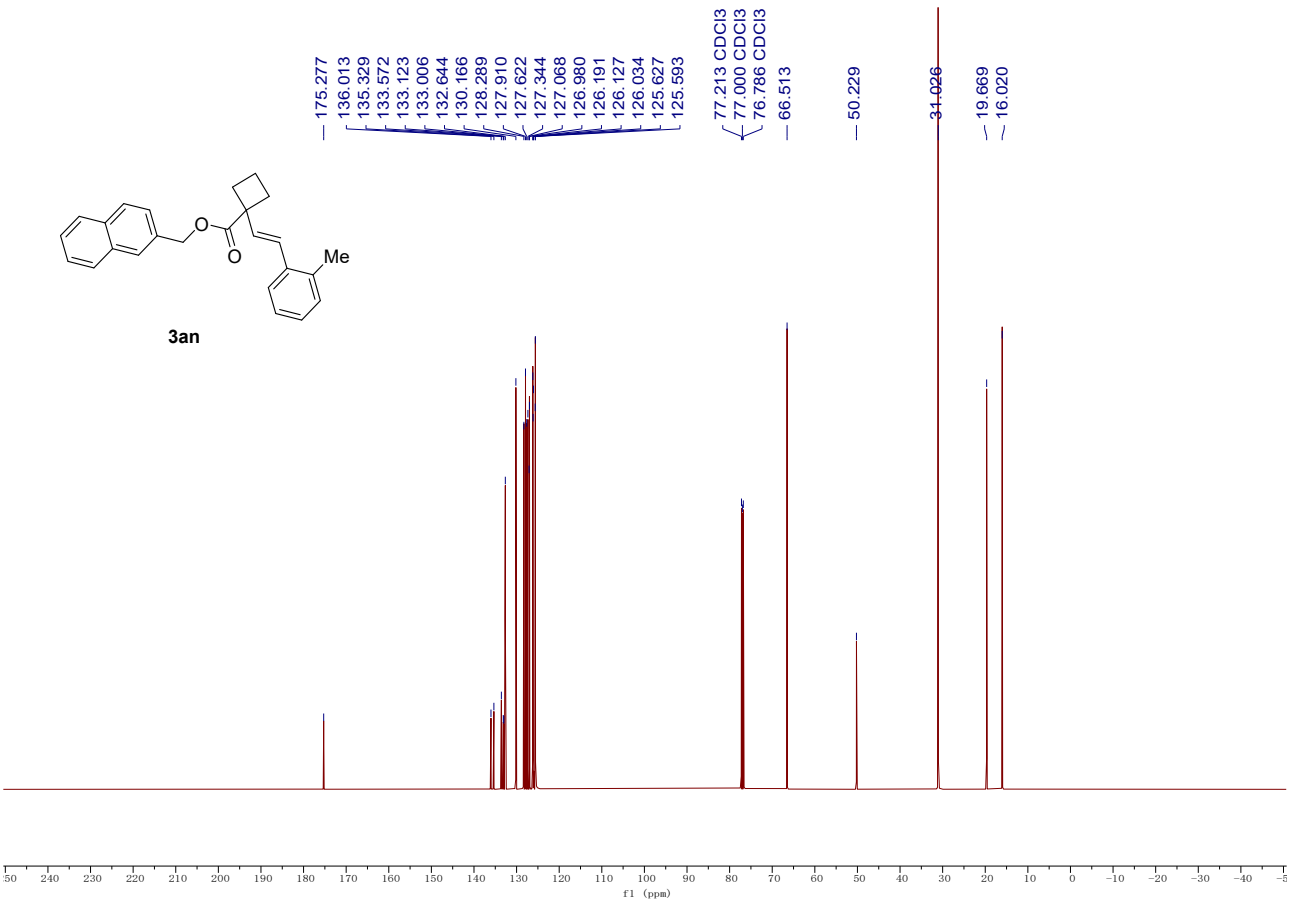

175.003
161.680
161.627
160.015
159.963
138.141
138.087
138.034
133.553
133.171
133.034
128.308
127.986
127.955
127.908
127.835
127.656
126.879
126.192
126.123
125.527
115.894
114.355
114.253
114.149
111.547
111.511
111.404
111.367
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
66.642
50.858
30.763
16.014
O
O
F
F
3am
f1 (ppm)

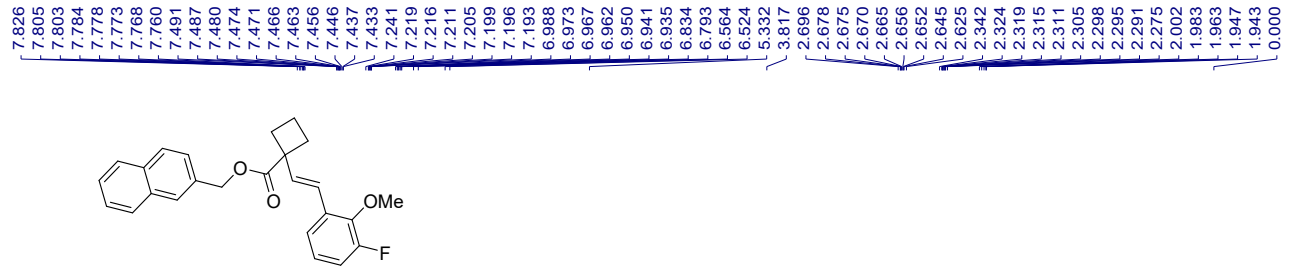

O
O
F
F

3am

-113.206
40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)

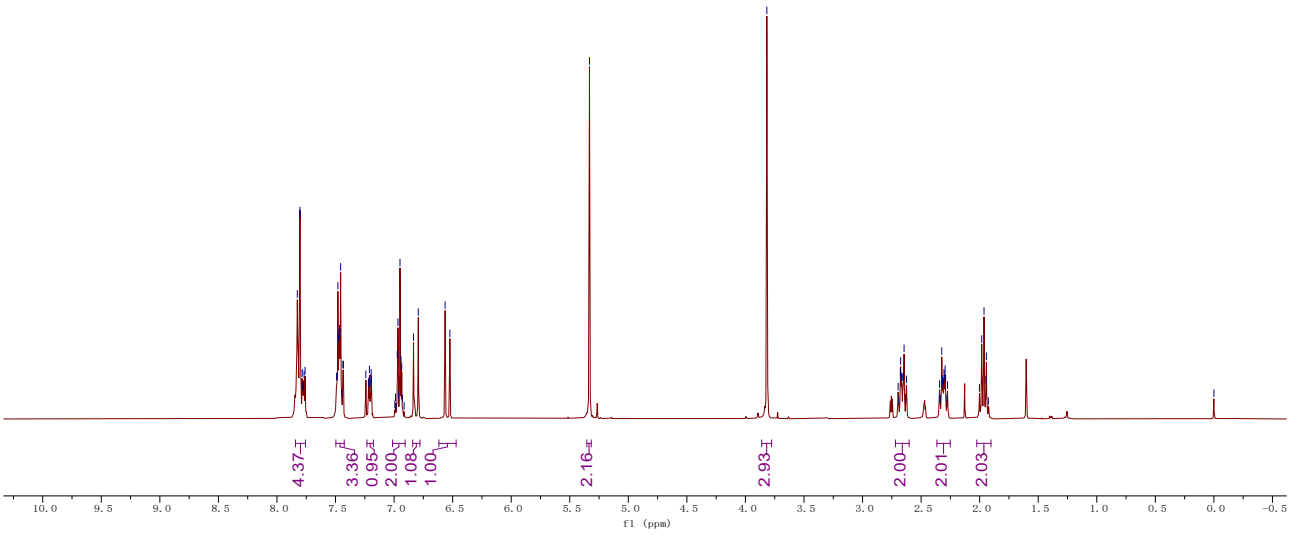

7.806
7.792
7.786
7.765
7.749
7.741
7.731
7.471
7.460
7.446
7.436
7.421
7.407
7.398
7.144
7.129
7.121
7.113
7.103
7.090
6.742
6.702
6.380
6.340
5.324
2.698
2.678
2.670
2.658
2.651
2.627
2.324
2.306
2.287
2.275
2.261
2.004
1.994
1.975
1.956
1.936
1.916
0.000
O
O
Me
3an
4.08
4.01
3.14
0.95
0.95
2.00
2.00
5.26
2.14
f1 (ppm)

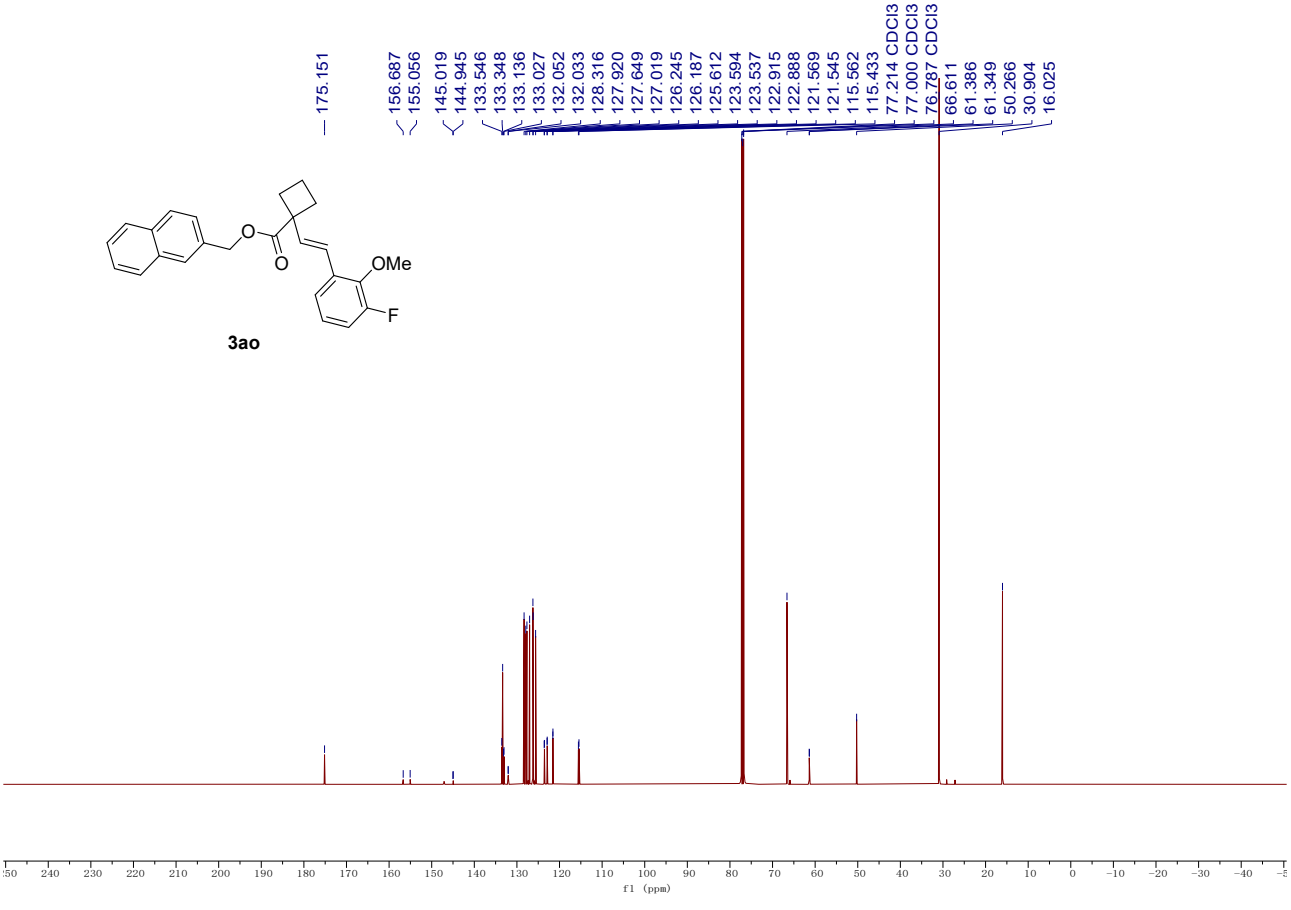

175.277
136.013
135.329
133.572
133.123
133.006
132.644
130.166
128.289
127.910
127.622
127.344
127.068
126.980
126.191
126.127
126.034
125.627
125.593
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
66.513
50.229
31.026
19.669
16.020
O
O
Me
3an
f1 (ppm)


7.826
7.805
7.803
7.784
7.778
7.773
7.768
7.760
7.491
7.487
7.480
7.474
7.471
7.466
7.463
7.456
7.446
7.437
7.433
7.241
7.219
7.216
7.211
7.205
7.199
7.196
7.193
6.988
6.973
6.967
6.962
6.950
6.941
6.935
6.834
6.793
6.564
6.524
5.332
3.817
2.696
2.678
2.675
2.670
2.665
2.656
2.652
2.645
2.625
2.342
2.324
2.319
2.315
2.311
2.305
2.298
2.295
2.291
2.275
2.002
1.983
1.963
1.947
1.943
0.000

O
O
OMe
F

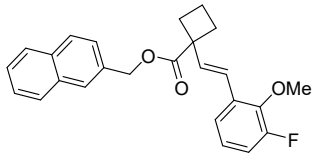
3ao


4.37
3.36
0.95
2.00
1.08
1.00
2.16
2.93
2.00
2.01
2.03
f1 (ppm)


175.151
156.687
155.056
145.019
144.945
133.546
133.348
133.136
133.027
132.052
132.033
128.316
127.920
127.649
127.019
126.245
126.187
125.612
123.594
123.537
122.915
122.888
121.569
121.545
115.562
115.433
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
66.611
61.386
61.349
50.266
30.904
16.025
f1 (ppm)

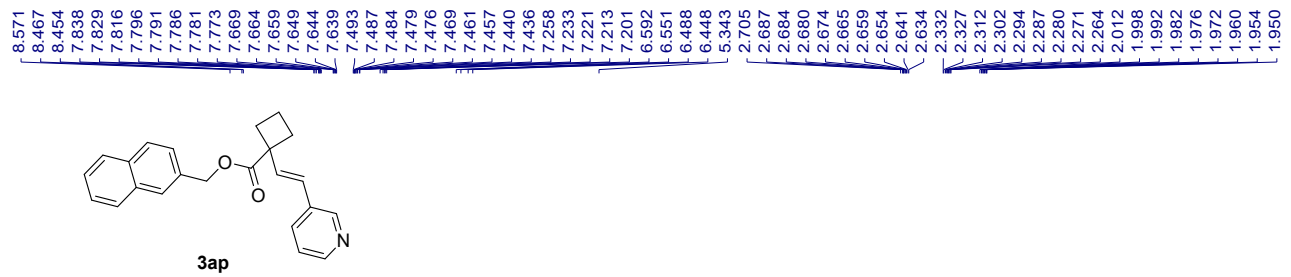
O
O
OMe
F

3ao

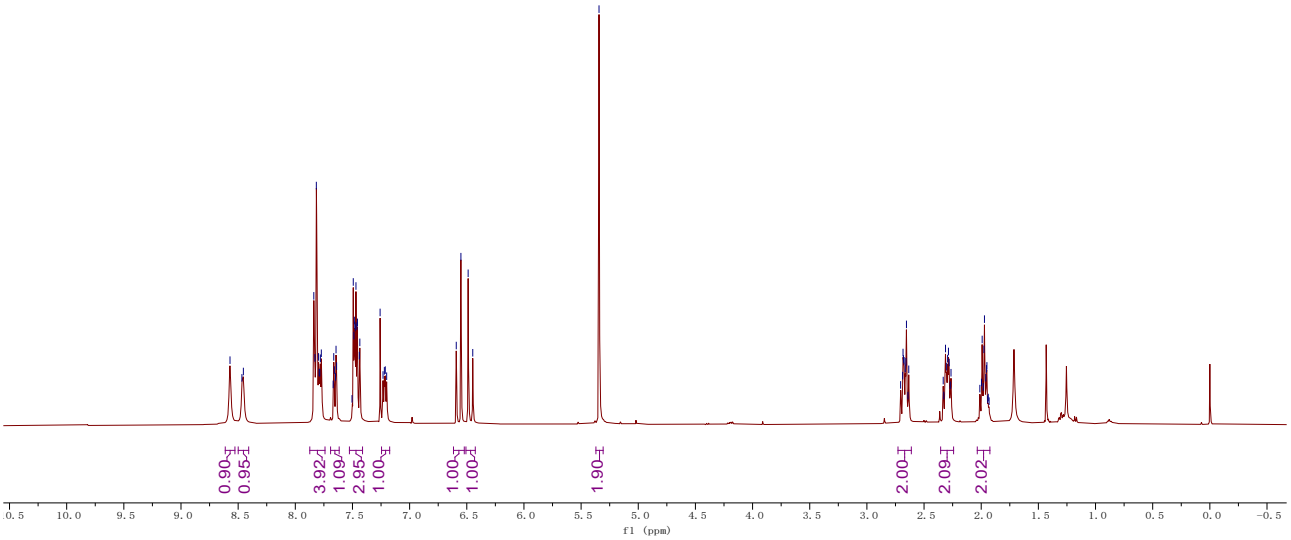

O
O
OMe
F

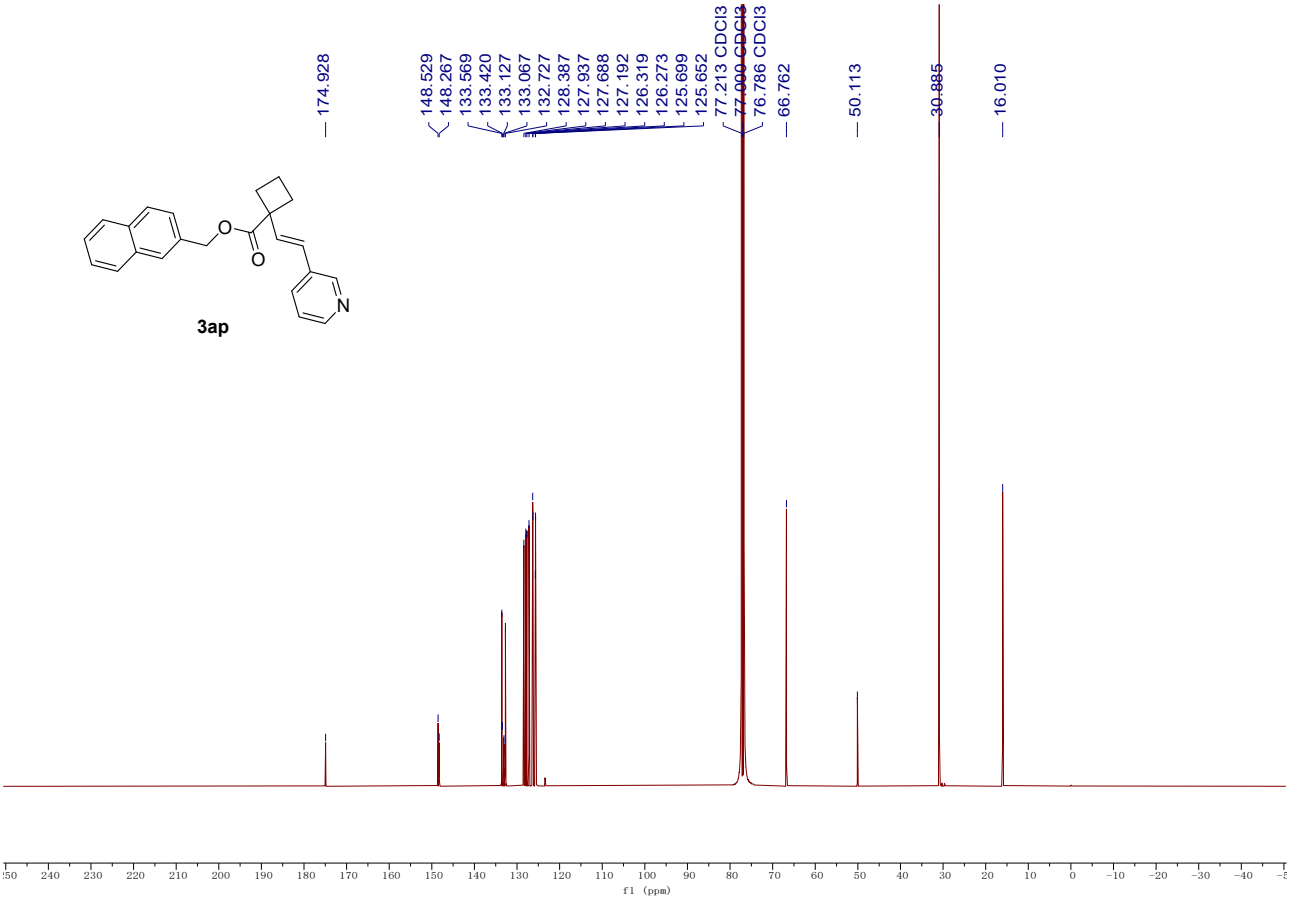
3ao

-131.212
40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)

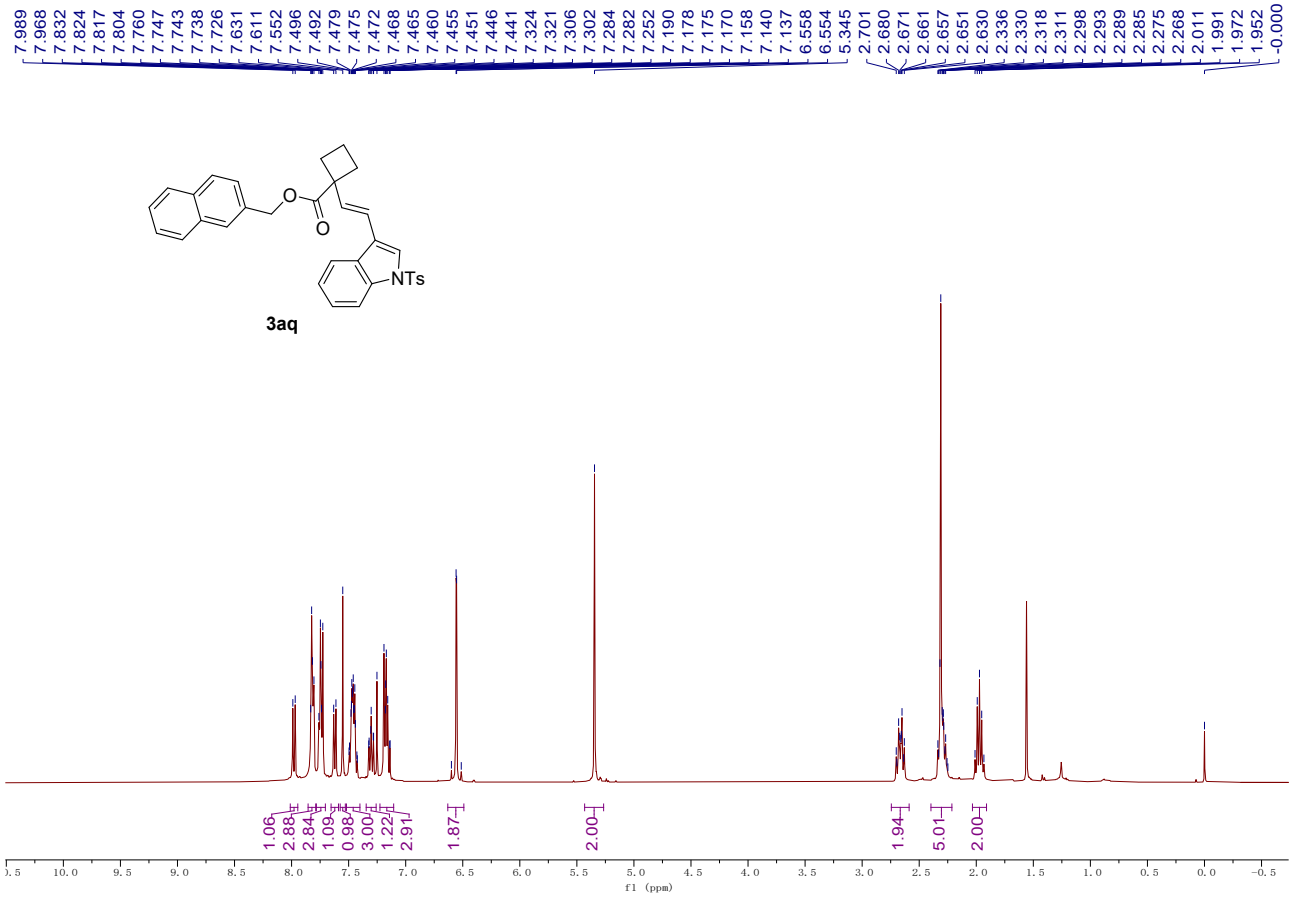

8.571
8.467
8.454
8.838
7.829
7.816
7.796
7.791
7.786
7.781
7.773
7.669
7.664
7.659
7.649
7.644
7.639
7.493
7.487
7.484
7.479
7.476
7.469
7.461
7.457
7.440
7.436
7.258
7.233
7.221
7.213
7.201
6.592
6.551
6.488
6.448
5.343
2.705
2.687
2.684
2.680
2.674
2.665
2.659
2.654
2.641
2.634
2.332
2.327
2.312
2.302
2.294
2.287
2.280
2.271
2.264
2.012
1.998
1.992
1.982
1.976
1.972
1.960
1.954
1.950

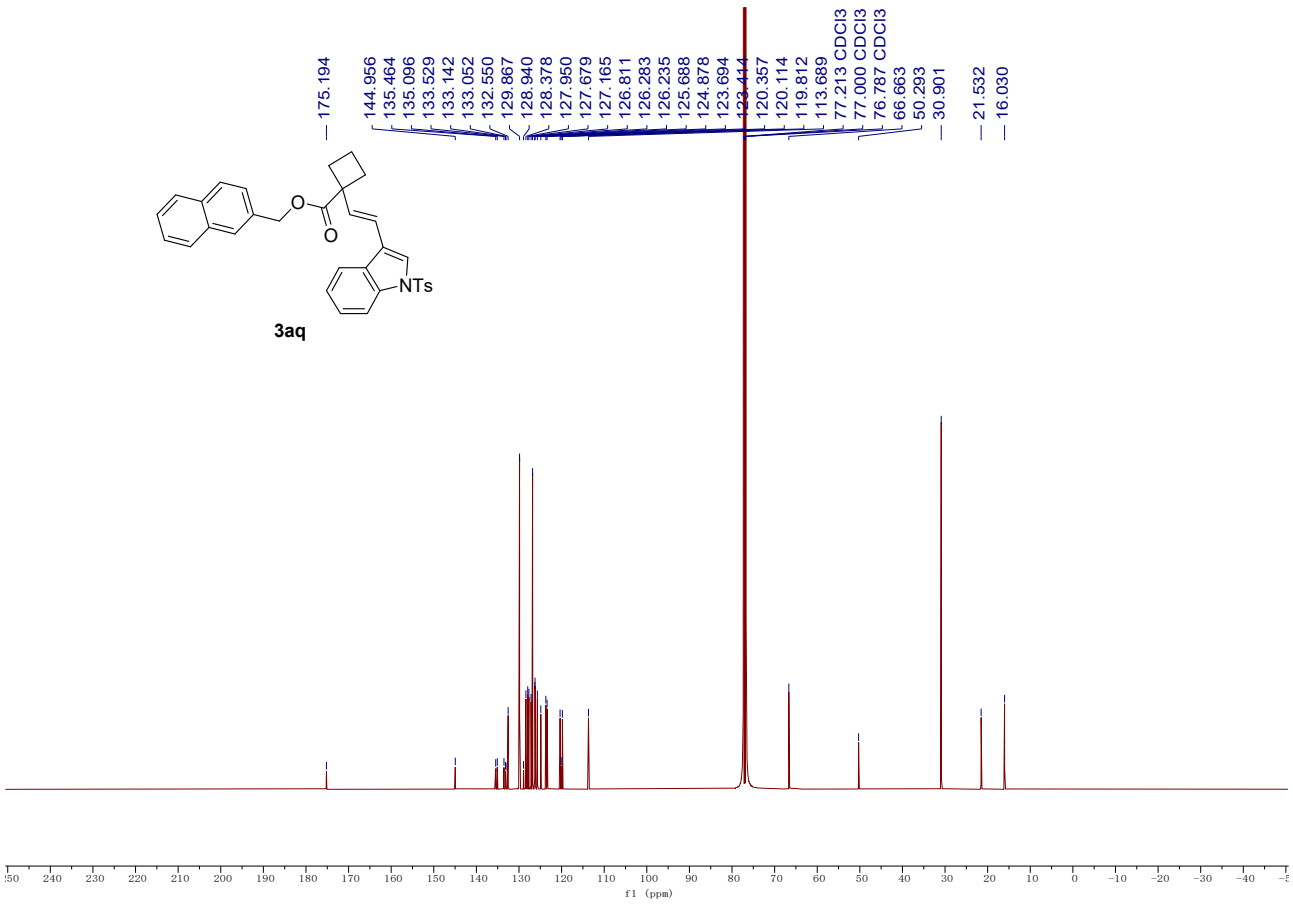
3ap

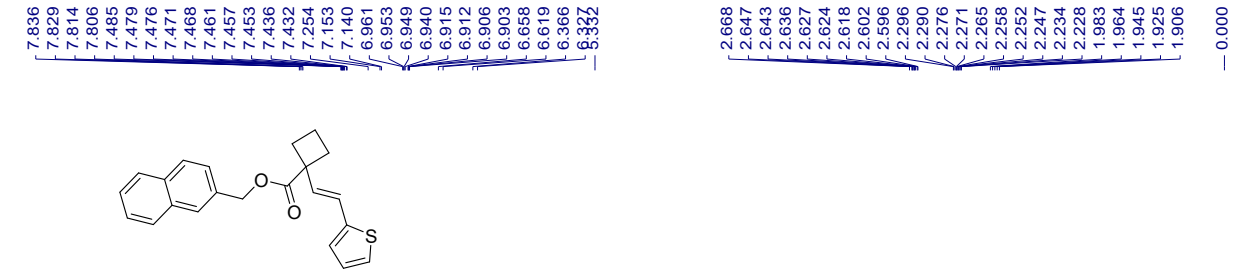

0.90
0.95
3.92
1.09
2.95
1.00
1.00
1.00
1.90
2.00
2.09
2.02
f1 (ppm)


174.928
148.529
148.267
133.569
133.420
133.127
133.067
132.727
128.387
127.937
127.688
127.192
126.319
126.273
125.699
125.652
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
66.762
50.113
30.885
16.010
f1 (ppm)

3ap

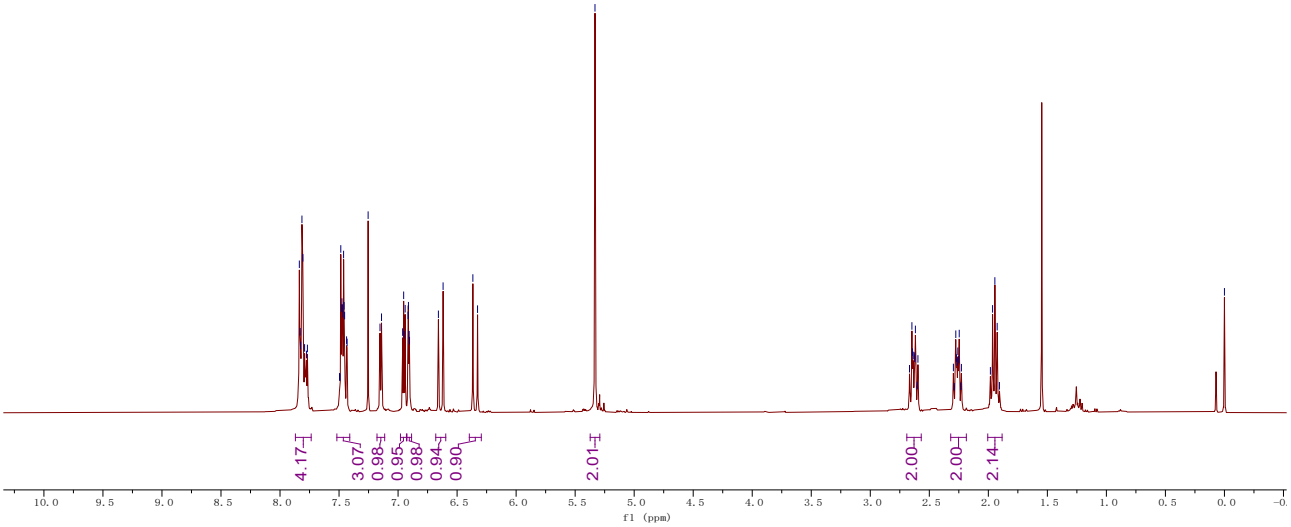

7.989
7.968
7.832
7.824
7.817
7.804
7.760
7.747
7.743
7.738
7.726
7.631
7.611
7.552
7.496
7.492
7.479
7.475
7.472
7.468
7.465
7.460
7.455
7.451
7.446
7.441
7.324
7.321
7.306
7.302
7.284
7.282
7.252
7.190
7.178
7.175
7.170
7.158
7.140
7.137
6.558
6.554
5.345
2.701
2.680
2.671
2.661
2.657
2.651
2.630
2.336
2.330
2.318
2.311
2.298
2.293
2.289
2.285
2.275
2.268
2.011
1.991
1.972
1.952
-0.000
O
O
NTs
3aq
1.06
2.88
2.84
1.09
0.98
3.00
1.22
2.91
1.87
2.00
1.94
5.01
2.00
f1 (ppm)

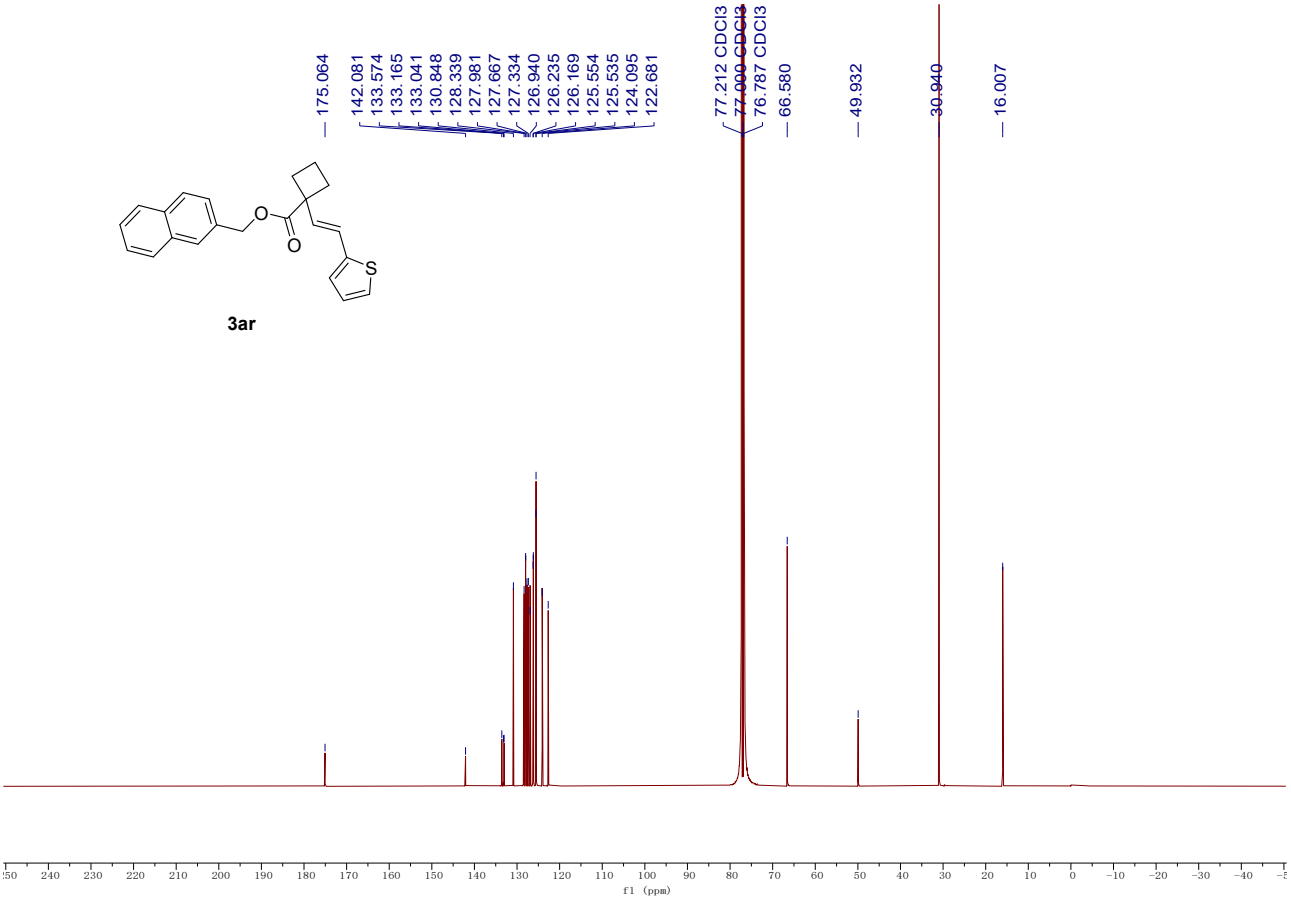

175.194
144.956
135.464
135.096
133.529
133.142
133.052
132.550
129.867
128.940
128.378
127.950
127.679
127.165
126.811
126.283
126.235
125.688
124.878
123.694
123.414
120.357
120.114
119.812
113.689
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
66.663
50.293
30.901
21.532
16.030
O
O
NTs
3aq
f1 (ppm)


7.836
7.829
7.814
7.806
7.485
7.479
7.476
7.471
7.468
7.461
7.457
7.453
7.436
7.432
7.254
7.153
7.140
6.961
6.953
6.949
6.940
6.915
6.912
6.906
6.903
6.658
6.619
6.366
5.332
2.668
2.647
2.643
2.636
2.627
2.624
2.618
2.602
2.596
2.296
2.290
2.276
2.271
2.265
2.258
2.252
2.247
2.234
2.228
1.983
1.964
1.945
1.925
1.906
0.000

O
O
S

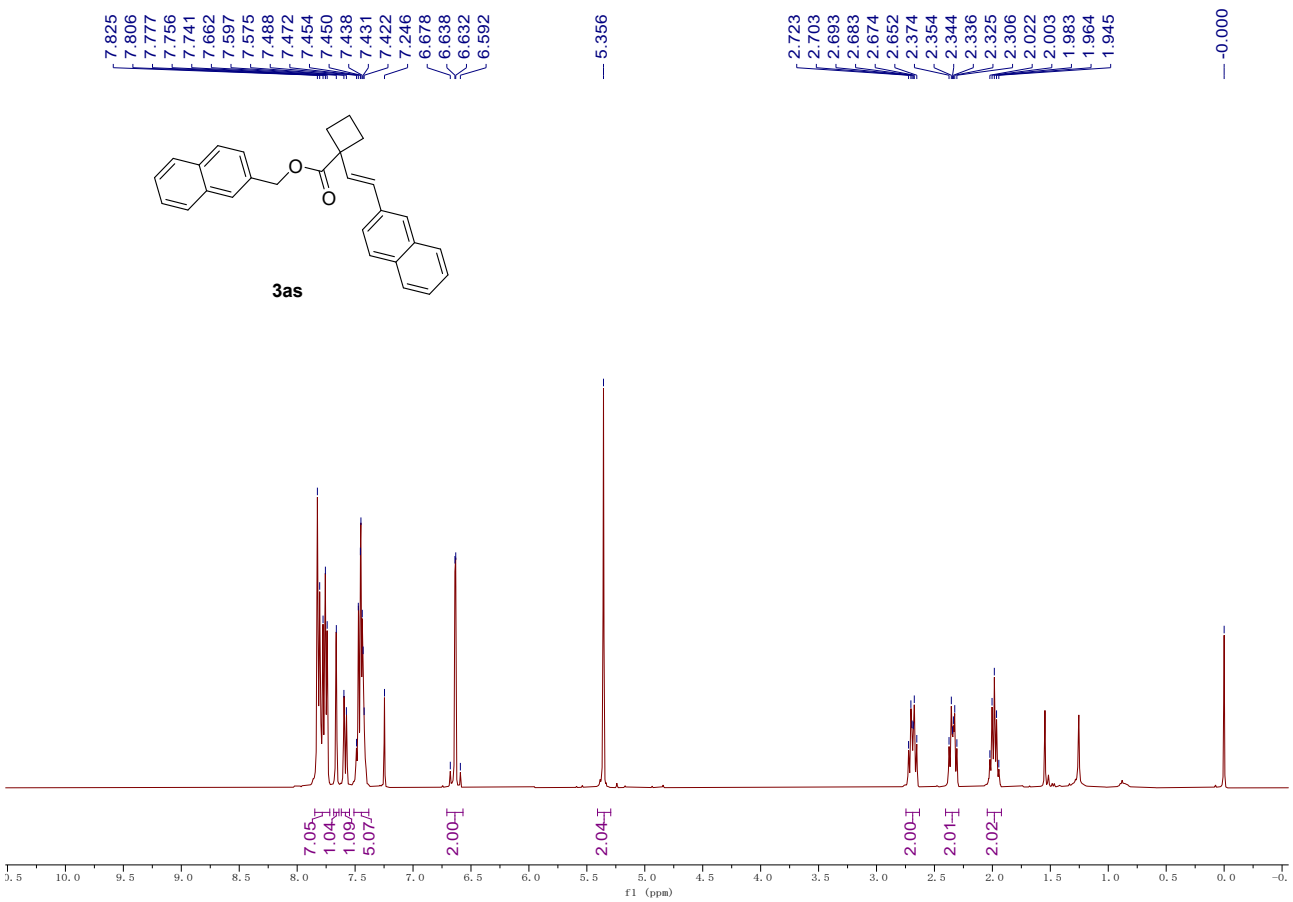
3ar

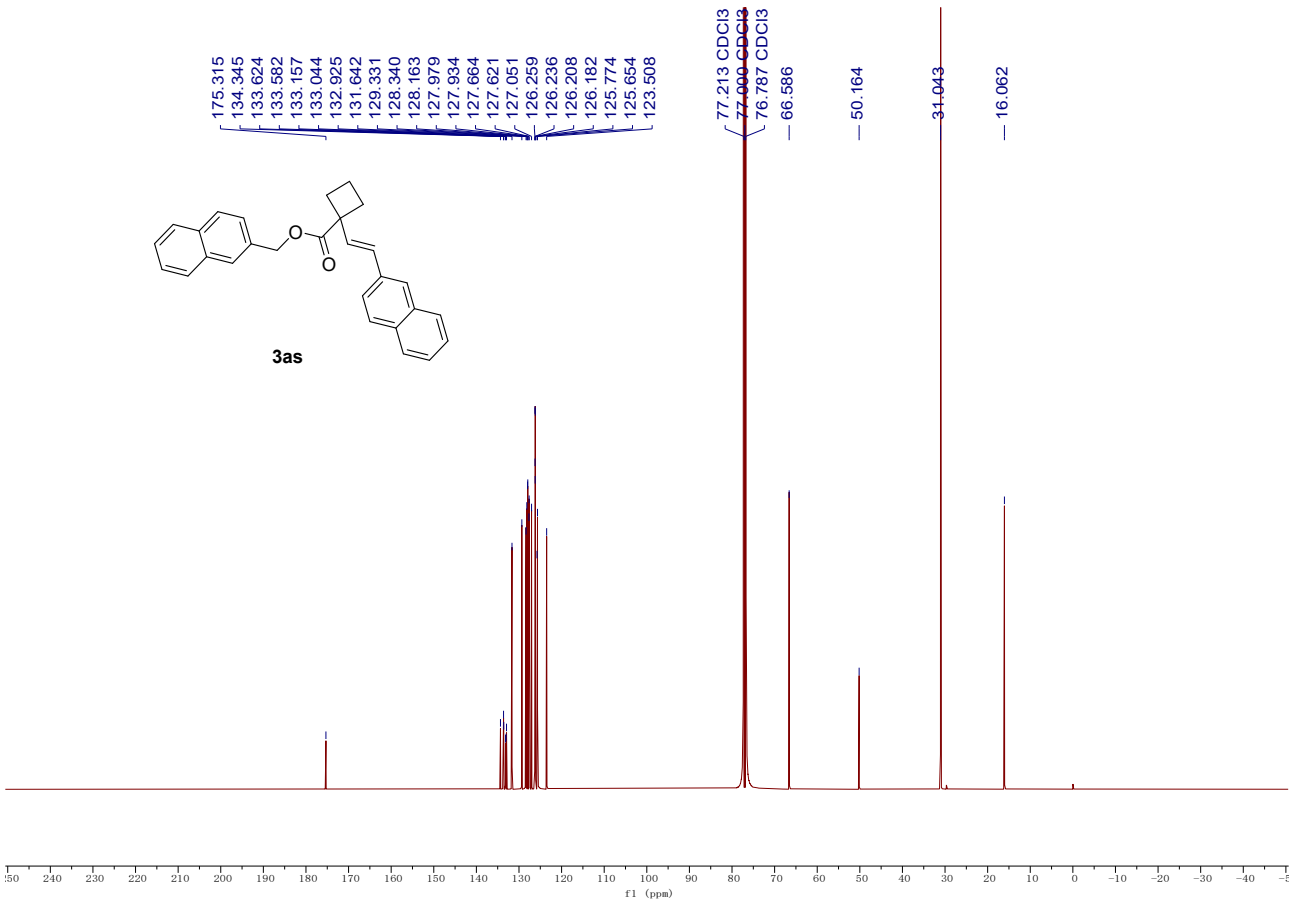

4.17
3.07
0.98
0.95
0.98
0.94
0.90
2.01
2.00
2.00
2.14
f1 (ppm)

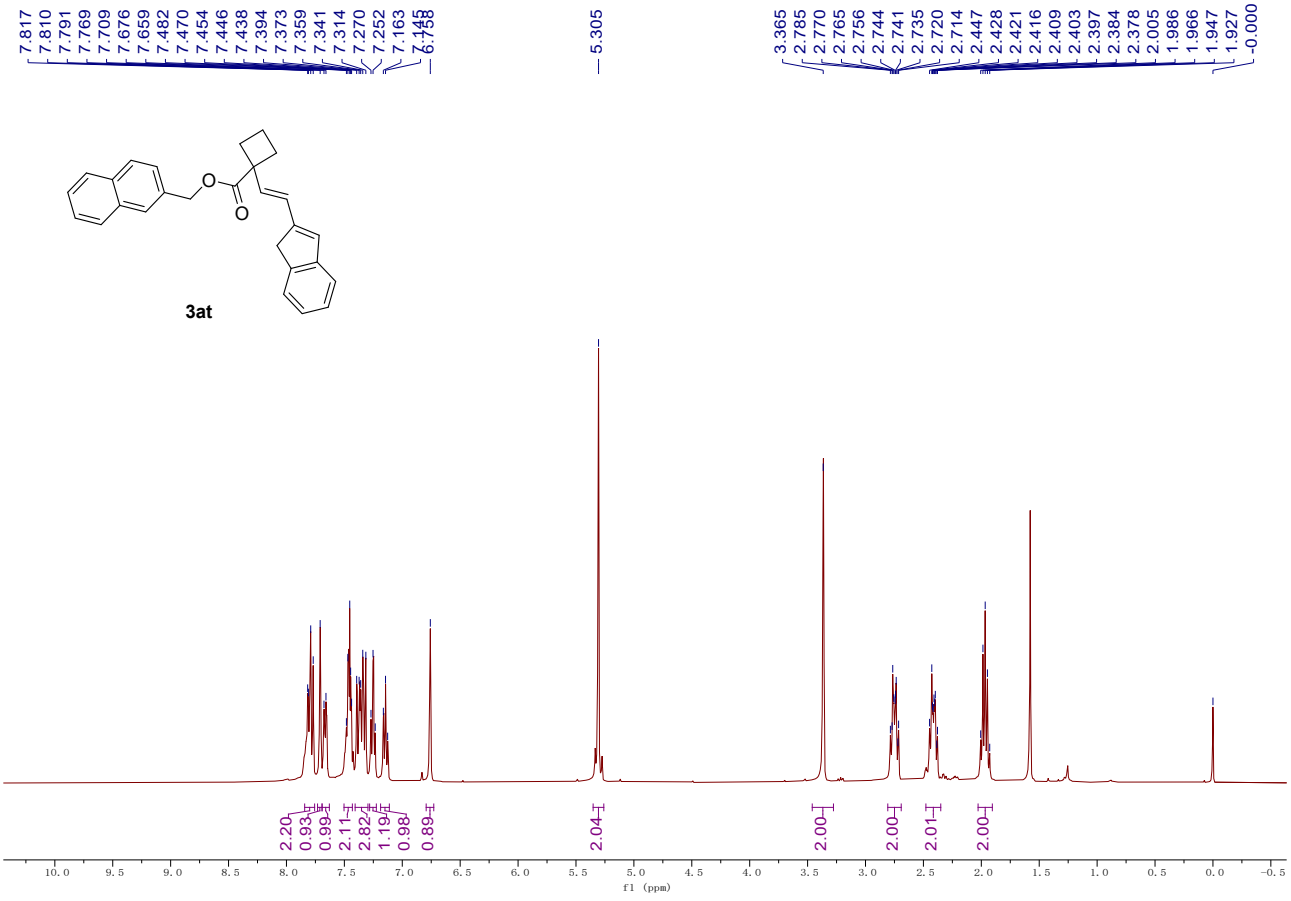

175.064
142.081
133.574
133.165
133.041
130.848
128.339
127.981
127.667
127.334
126.940
126.235
126.169
125.554
125.535
124.095
122.681
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
66.580
49.932
30.940
16.007
f1 (ppm)

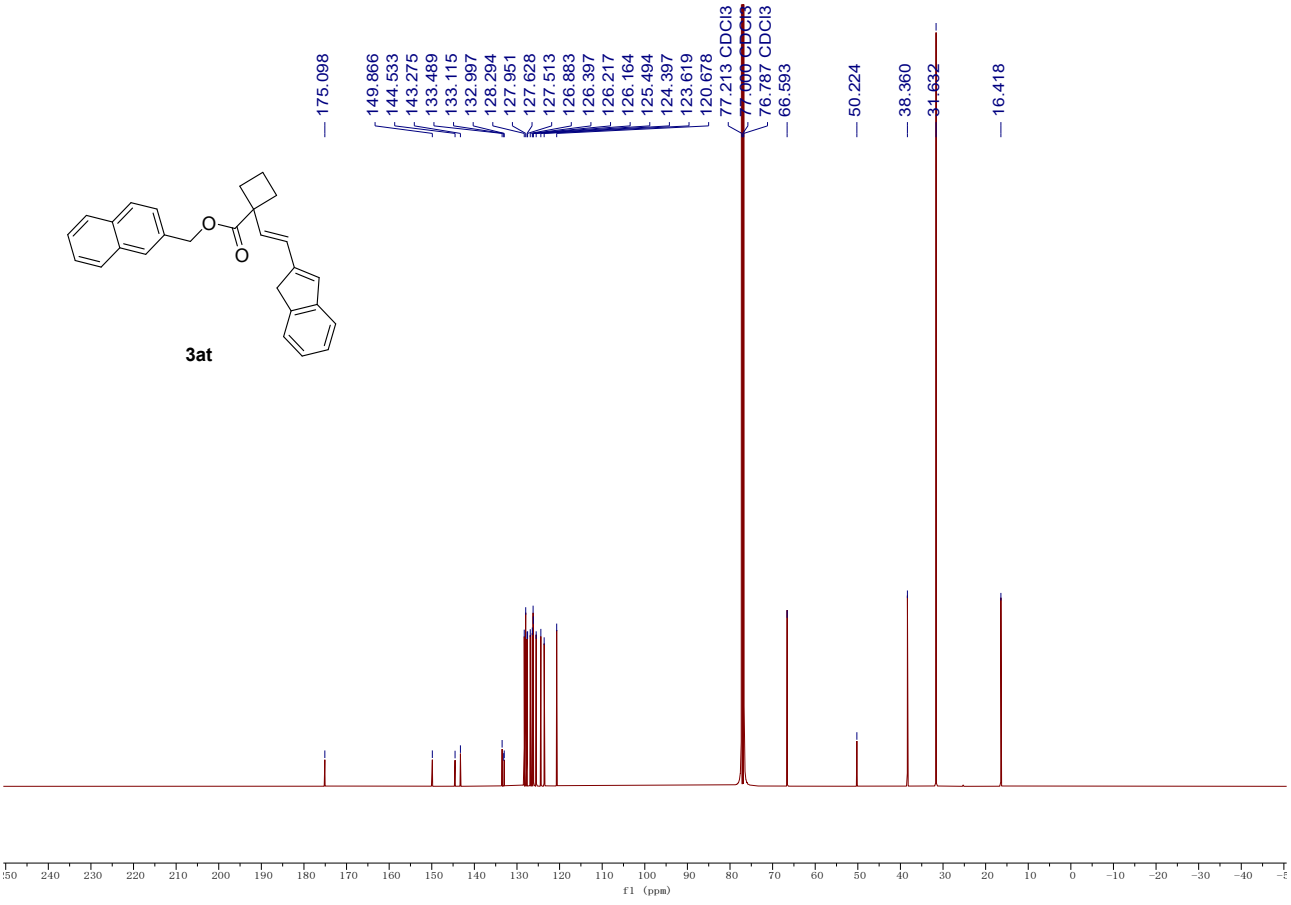
O
O
S

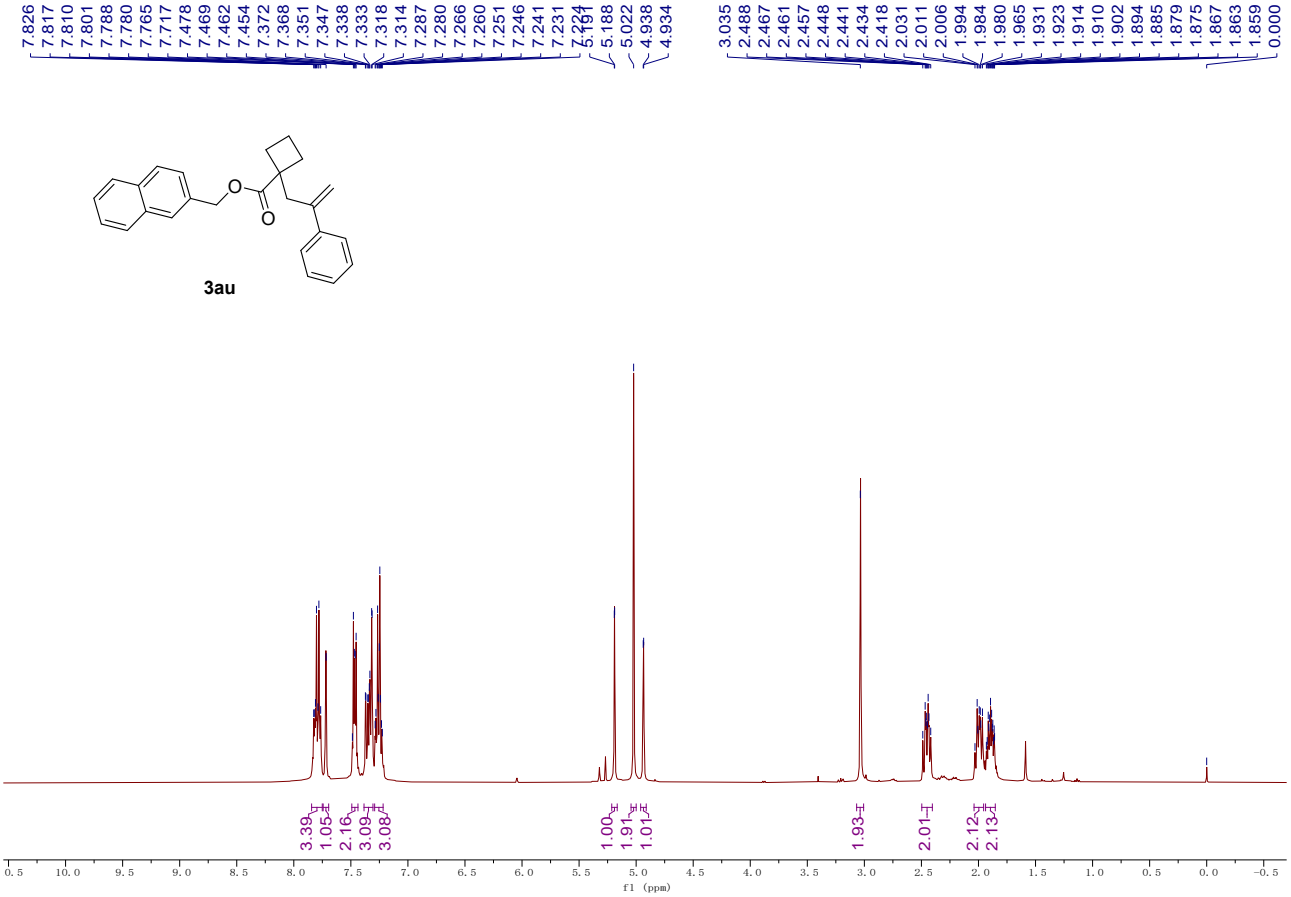
3ar

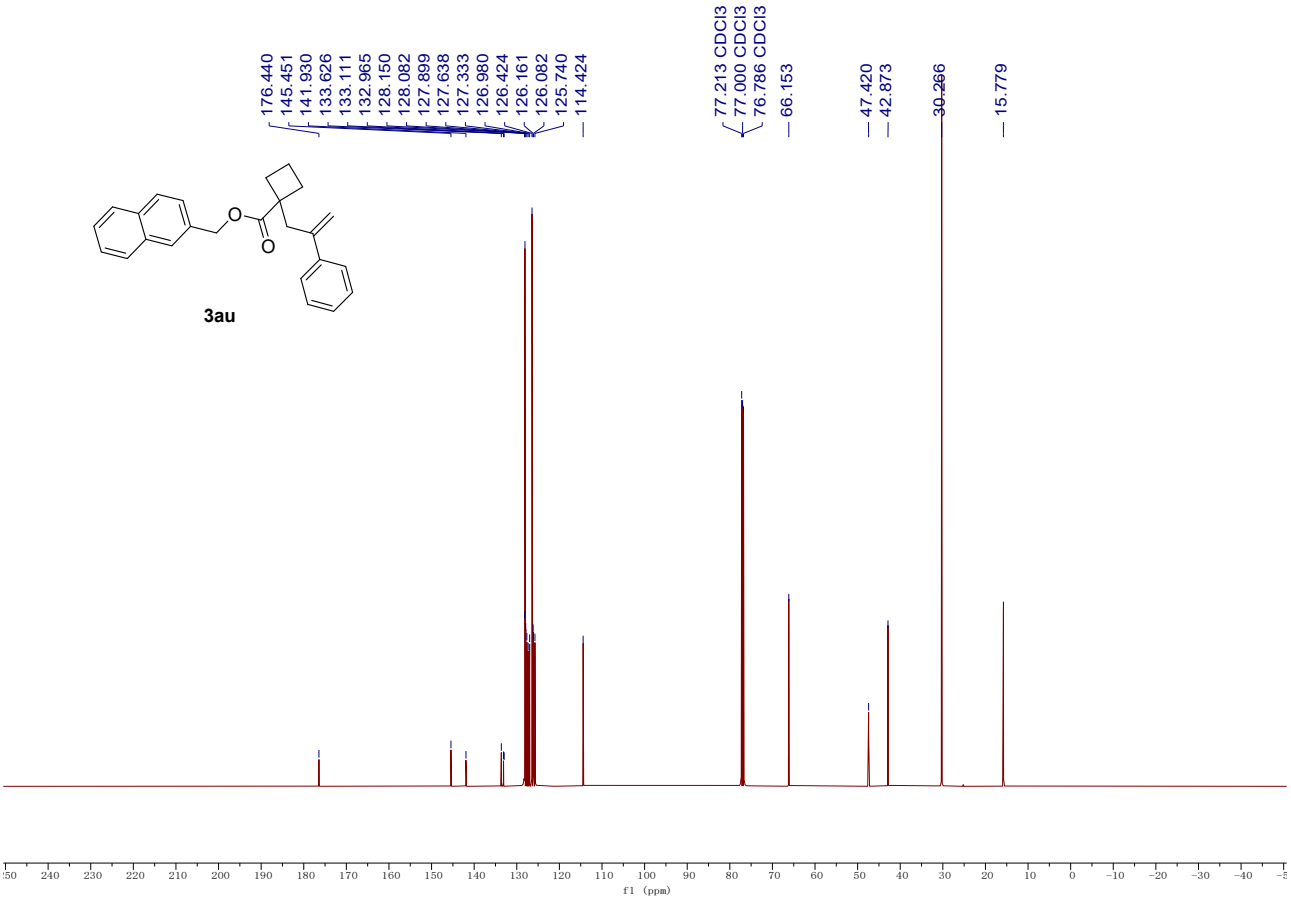

7.825
7.806
7.777
7.756
7.741
7.662
7.597
7.575
7.488
7.472
7.454
7.450
7.438
7.431
7.422
7.246
6.678
6.638
6.632
6.592
5.356
2.723
2.703
2.693
2.683
2.674
2.652
2.374
2.354
2.344
2.336
2.325
2.306
2.022
2.003
1.983
1.964
1.945
-0.000
3as
7.05
1.04
1.09
5.07
2.00
2.04
2.00
2.01
2.02
f1 (ppm)

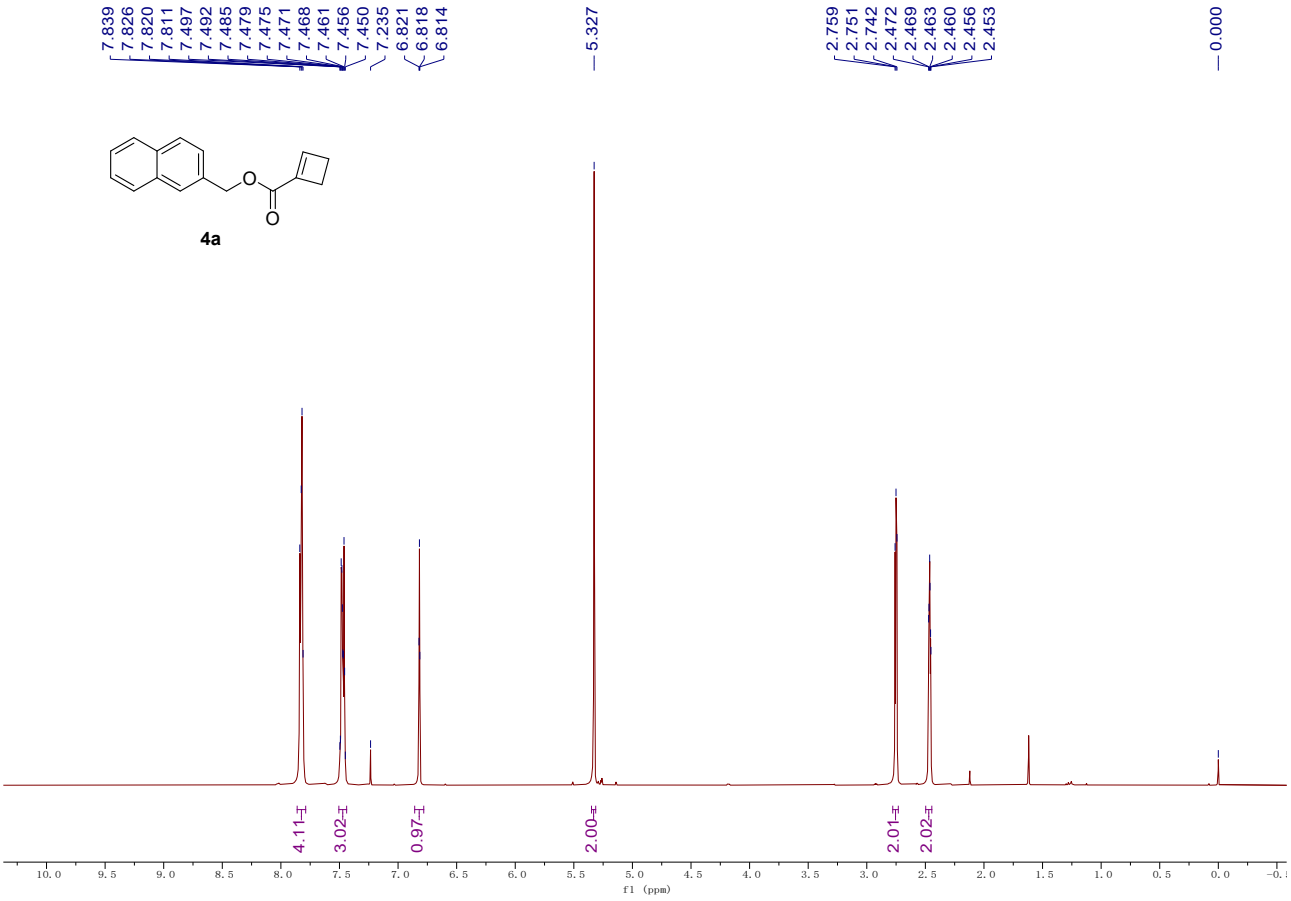

175.315
134.345
133.624
133.582
133.157
133.044
132.925
131.642
129.331
128.340
128.163
127.979
127.934
127.664
127.621
127.051
126.259
126.236
126.208
126.182
125.774
125.654
123.508
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
66.586
50.164
31.043
16.062
3as
f1 (ppm)

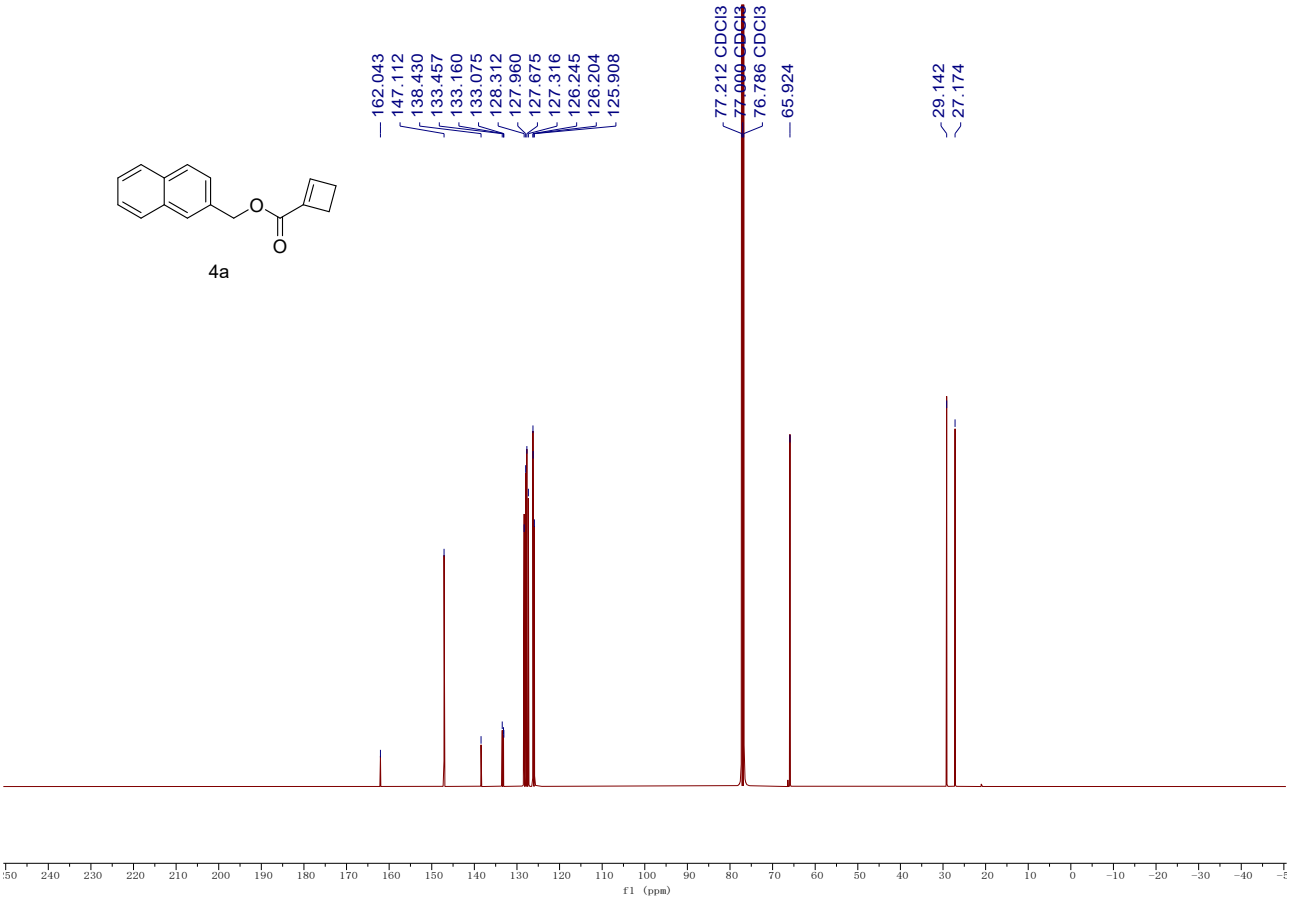

7.817
7.810
7.791
7.769
7.709
7.676
7.659
7.482
7.470
7.454
7.446
7.438
7.394
7.373
7.359
7.341
7.314
7.270
7.252
7.163
7.145
6.758
5.305
3.365
2.785
2.770
2.765
2.756
2.744
2.741
2.735
2.720
2.714
2.447
2.428
2.421
2.416
2.409
2.403
2.397
2.384
2.378
2.005
1.986
1.966
1.947
1.927
-0.000
O
O
3at
2.20
0.93
0.99
2.11
2.82
1.19
0.98
0.89
2.04
2.00
2.00
2.01
2.00
f1 (ppm)

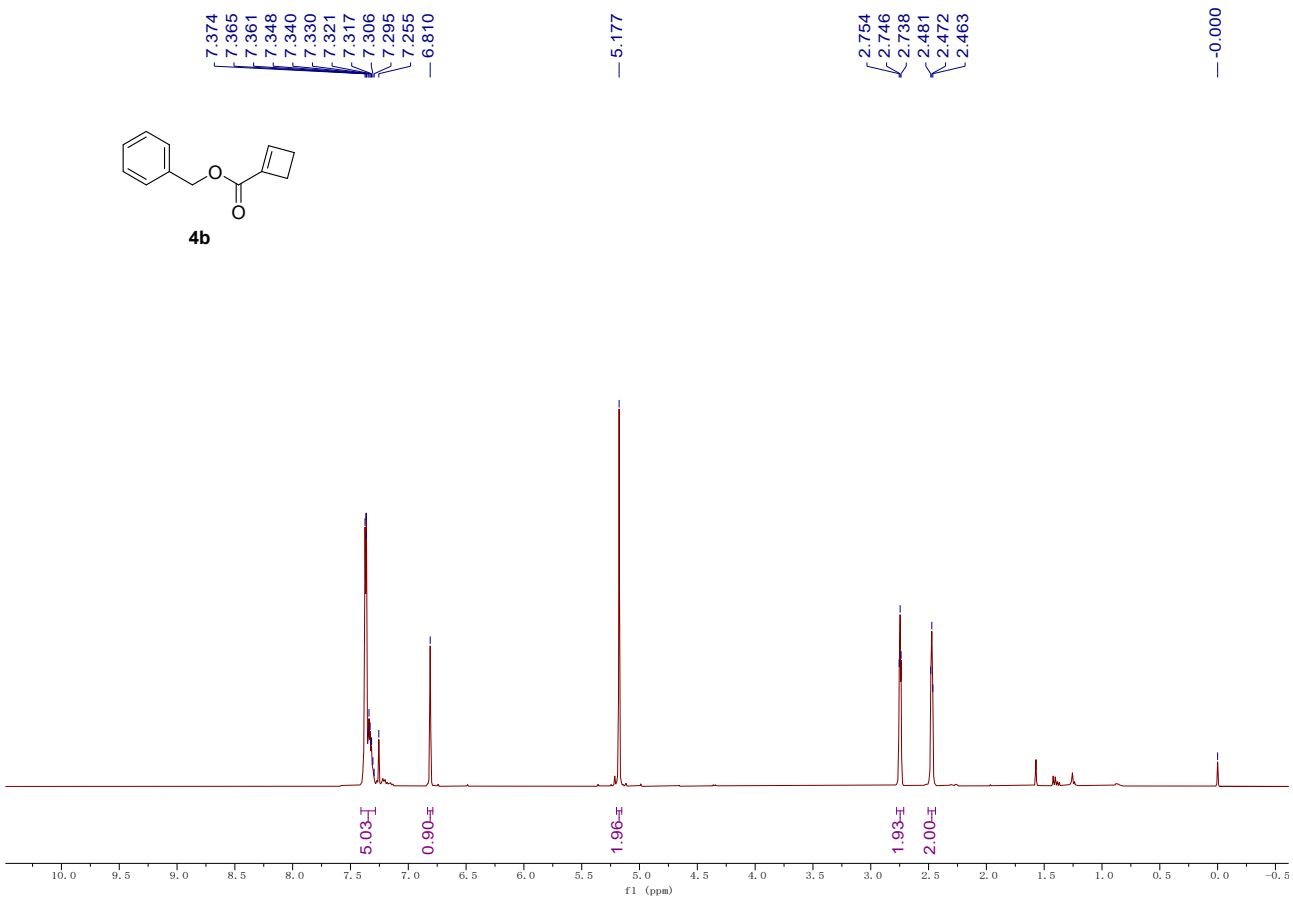

175.098
149.866
144.533
143.275
133.489
133.115
132.997
128.294
127.951
127.628
127.513
126.883
126.397
126.217
126.164
125.494
124.397
123.619
120.678
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
66.593
50.224
38.360
31.632
16.418
O
O
3at
f1 (ppm)

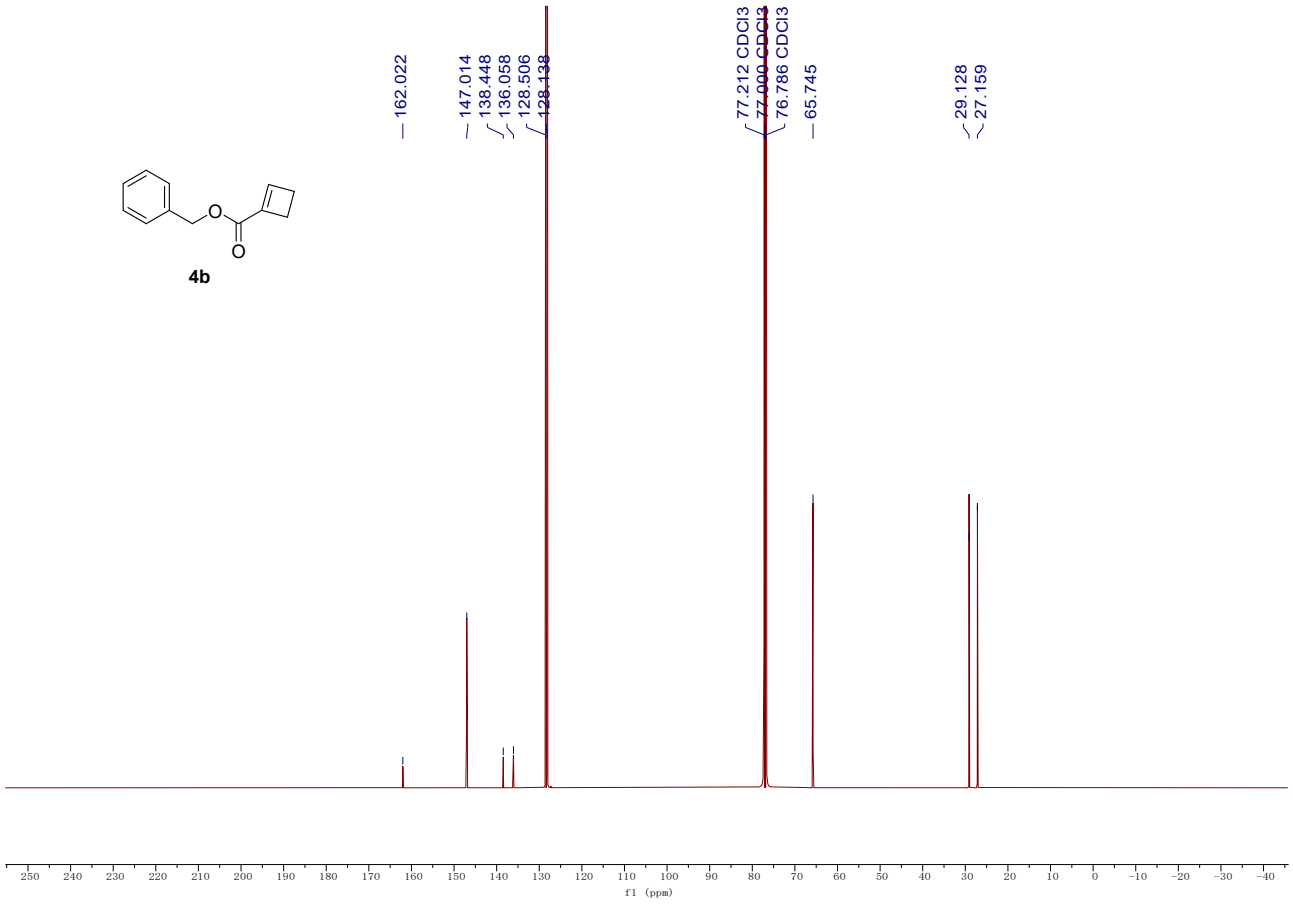

7.826
7.817
7.810
7.801
7.788
7.780
7.765
7.717
7.478
7.469
7.462
7.454
7.372
7.368
7.351
7.347
7.338
7.333
7.318
7.314
7.287
7.280
7.266
7.260
7.251
7.246
7.241
7.231
7.224
5.191
5.188
5.022
4.938
4.934
3.035
2.488
2.467
2.461
2.457
2.448
2.441
2.434
2.418
2.031
2.011
2.006
1.994
1.984
1.980
1.965
1.931
1.923
1.914
1.910
1.902
1.894
1.885
1.879
1.875
1.867
1.863
1.859
0.000
O
O
3au
3.39
1.05
2.16
3.09
3.08
1.00
1.91
1.01
1.93
2.01
2.12
2.13
f1 (ppm)

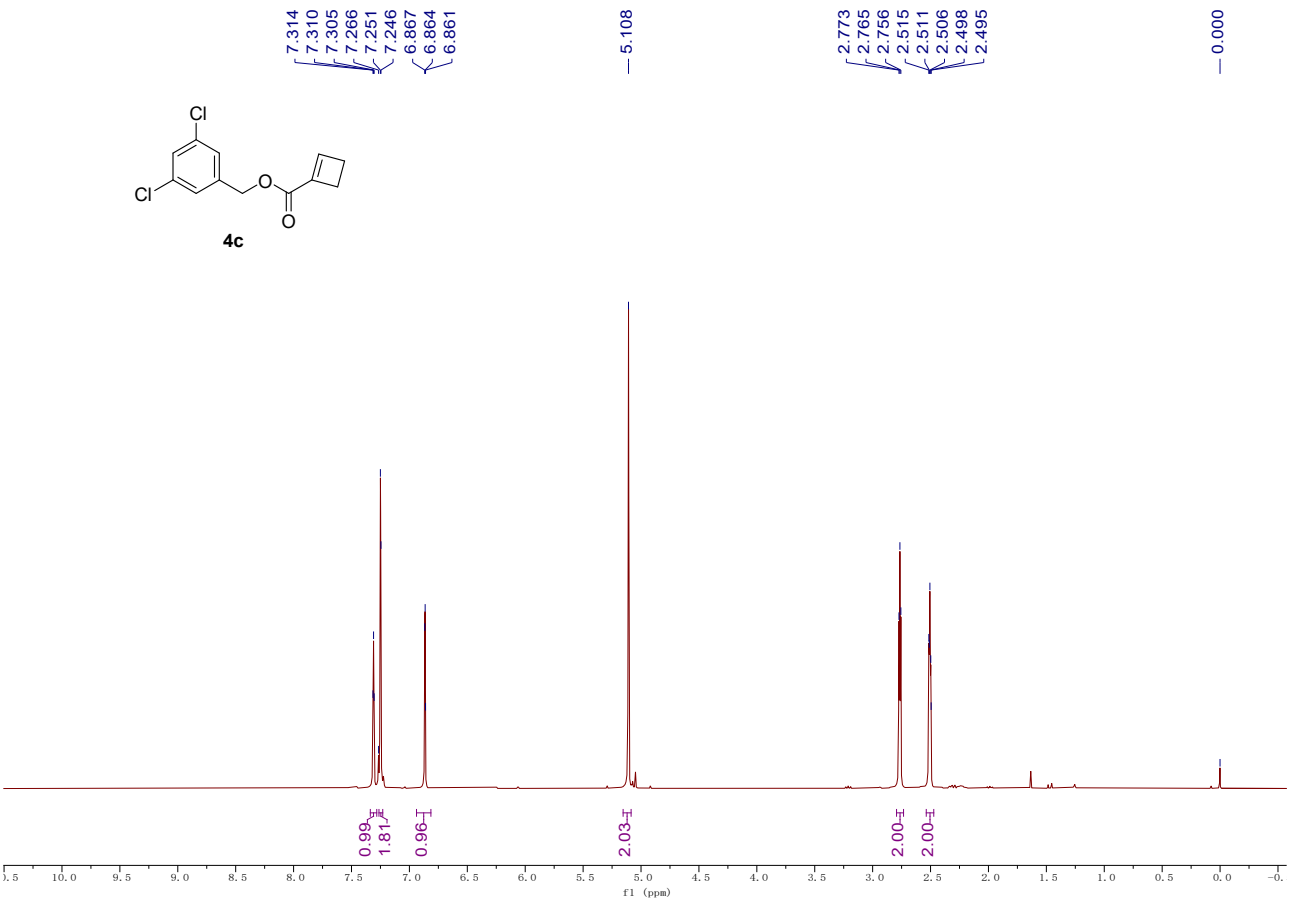

176.440
145.451
141.930
133.626
133.111
132.965
128.150
128.082
127.899
127.638
127.333
126.980
126.424
126.161
126.082
125.740
114.424
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
66.153
47.420
42.873
30.266
15.779
O
O
3au
f1 (ppm)

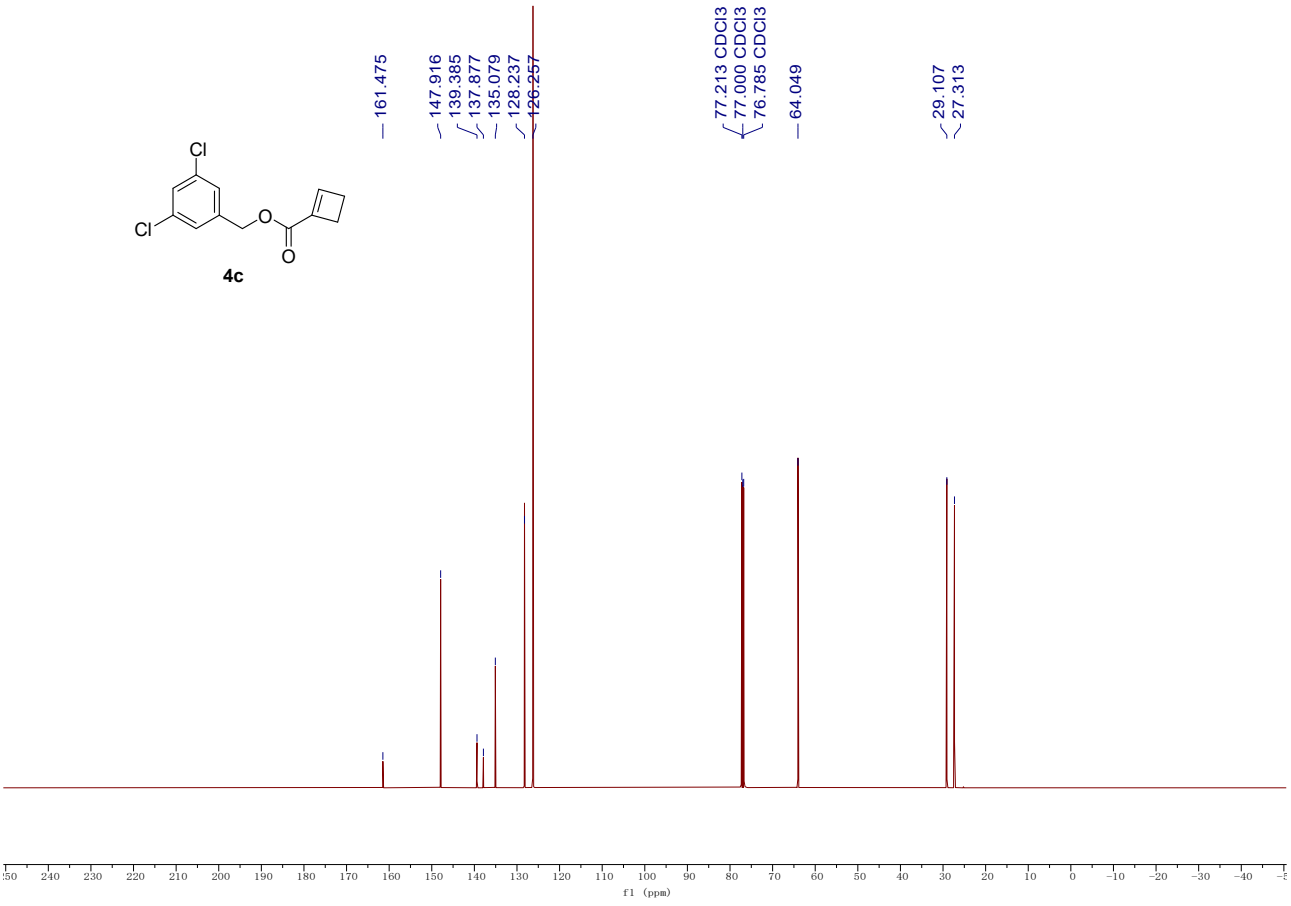

7.839
7.826
7.820
7.811
7.497
7.492
7.485
7.479
7.475
7.471
7.468
7.461
7.456
7.450
7.235
6.821
6.818
6.814
5.327
2.759
2.751
2.742
2.472
2.469
2.463
2.460
2.456
2.453
0.000
4a
4.11
3.02
0.97
2.00
2.01
2.02
f1 (ppm)

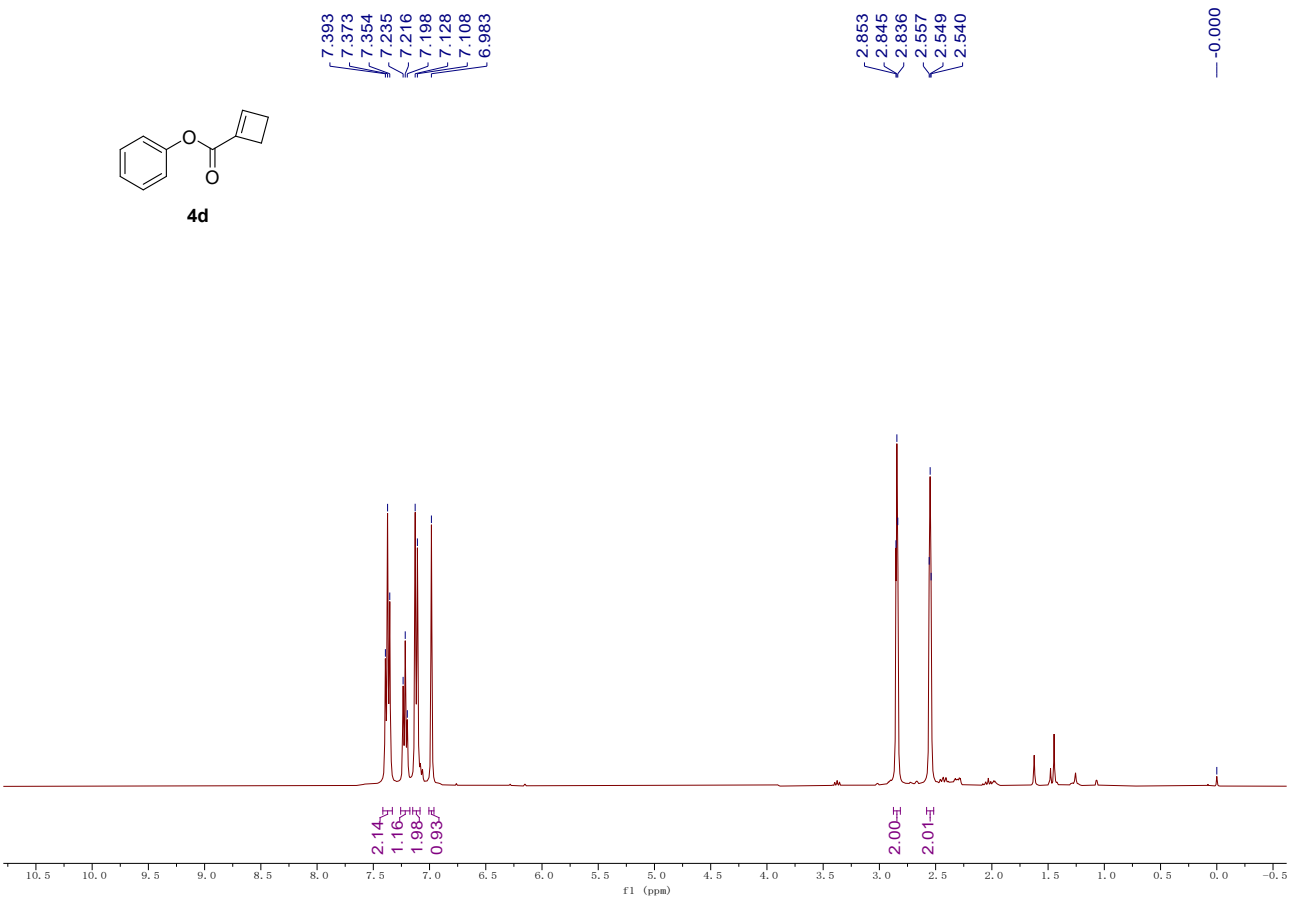

162.043
147.112
138.430
133.457
133.160
133.075
128.312
127.960
127.675
127.316
126.245
126.204
125.908
77.212 CDCl3
77.000 CDCl3
76.786 CDCl3
65.924
29.142
27.174
4a
f1 (ppm)

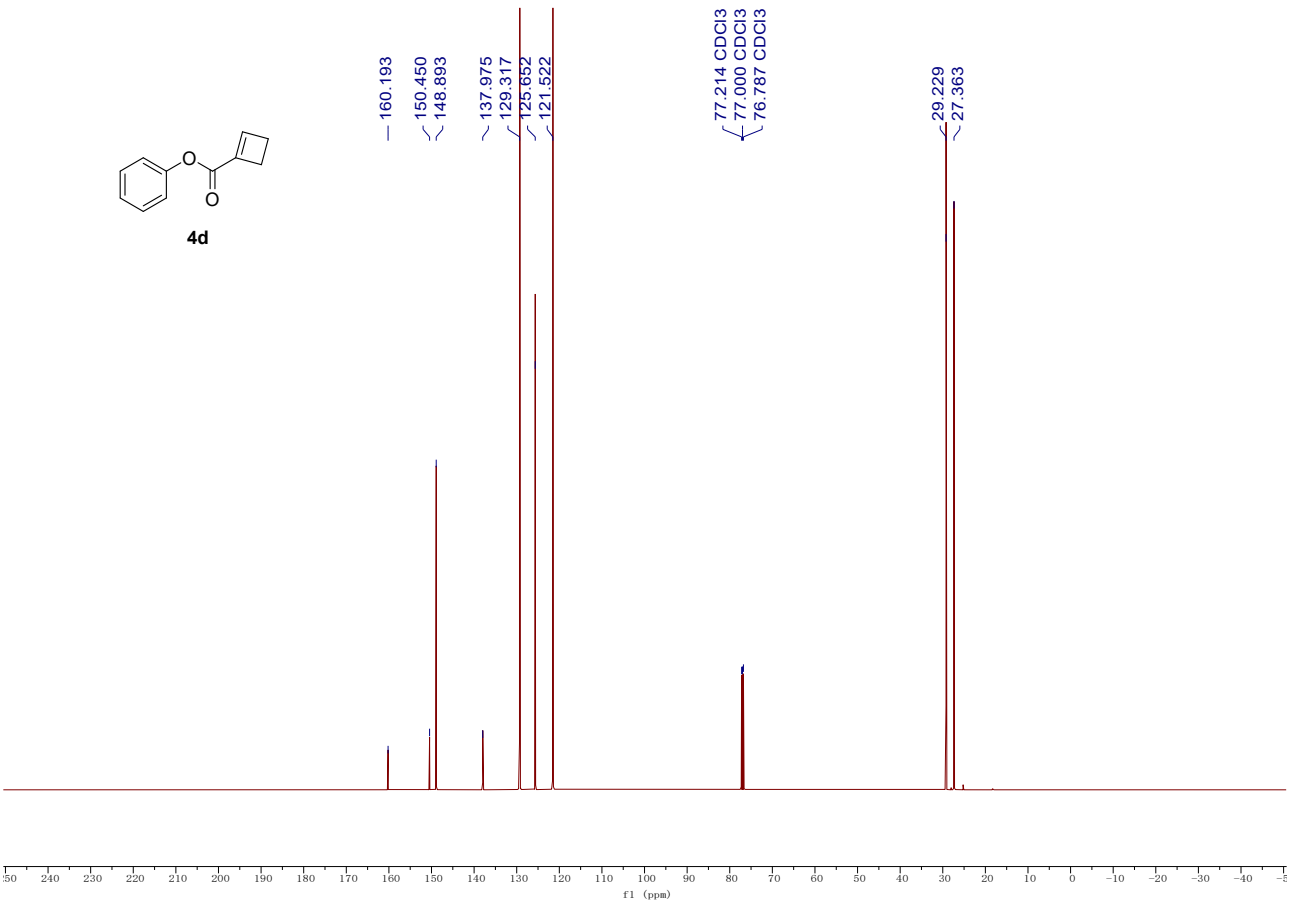

7.374
7.365
7.361
7.348
7.340
7.330
7.321
7.317
7.306
7.295
7.255
6.810
5.177
2.754
2.746
2.738
2.481
2.472
2.463
-0.000
O
O
4b
5.03
0.90
1.96
1.93
2.00
f1 (ppm)

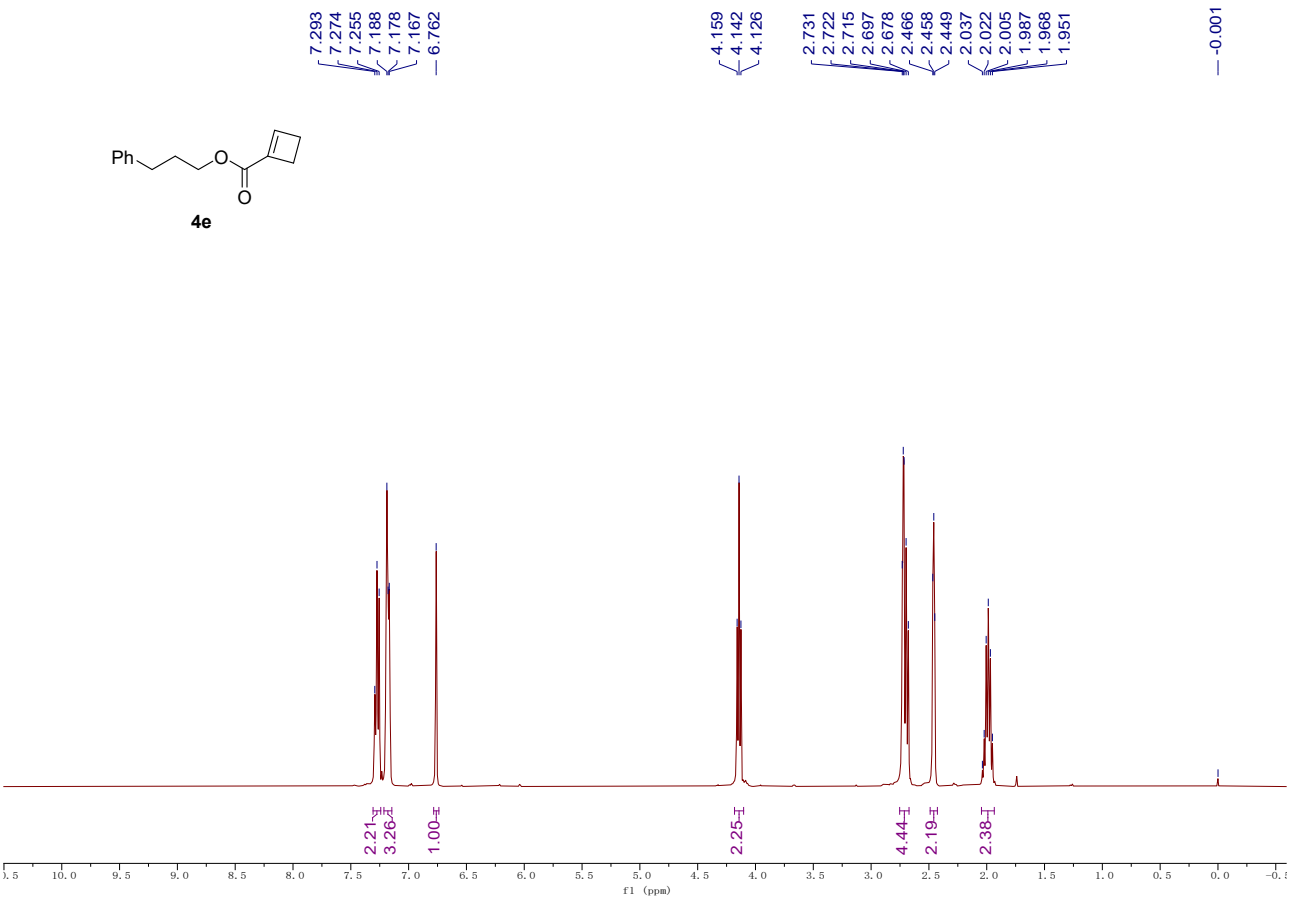

162.022
147.014
138.448
136.058
128.506
128.138
77.212 CDCl3
77.000 CDCl3
76.786 CDCl3
65.745
29.128
27.159
O
O
4b
f1 (ppm)

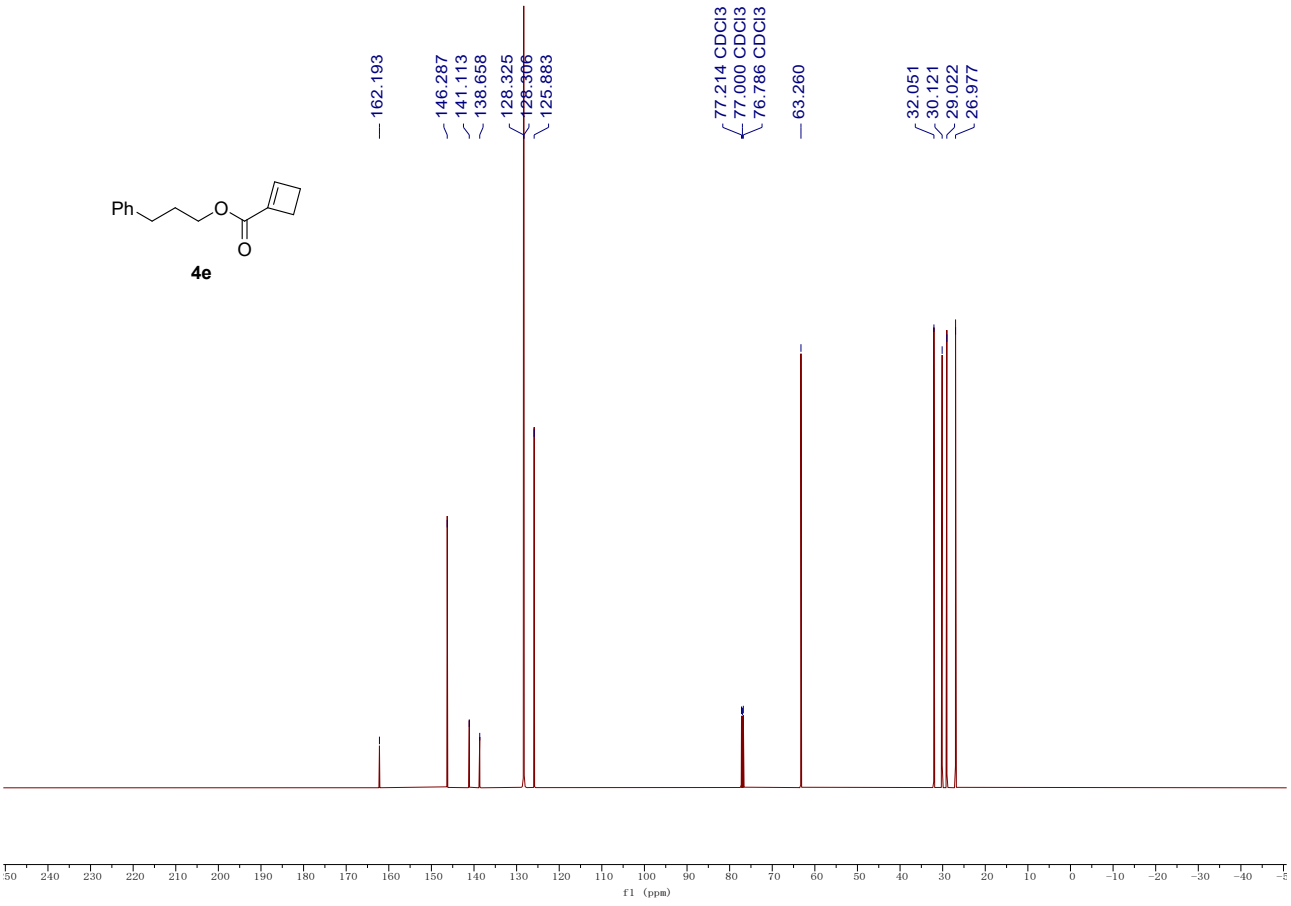

7.314
7.310
7.305
7.266
7.251
7.246
6.867
6.864
6.861
5.108
2.773
2.765
2.756
2.515
2.511
2.506
2.498
2.495
0.000
Cl
Cl
O
O
4c
0.99
1.81
0.96
2.03
2.00
2.00
f1 (ppm)

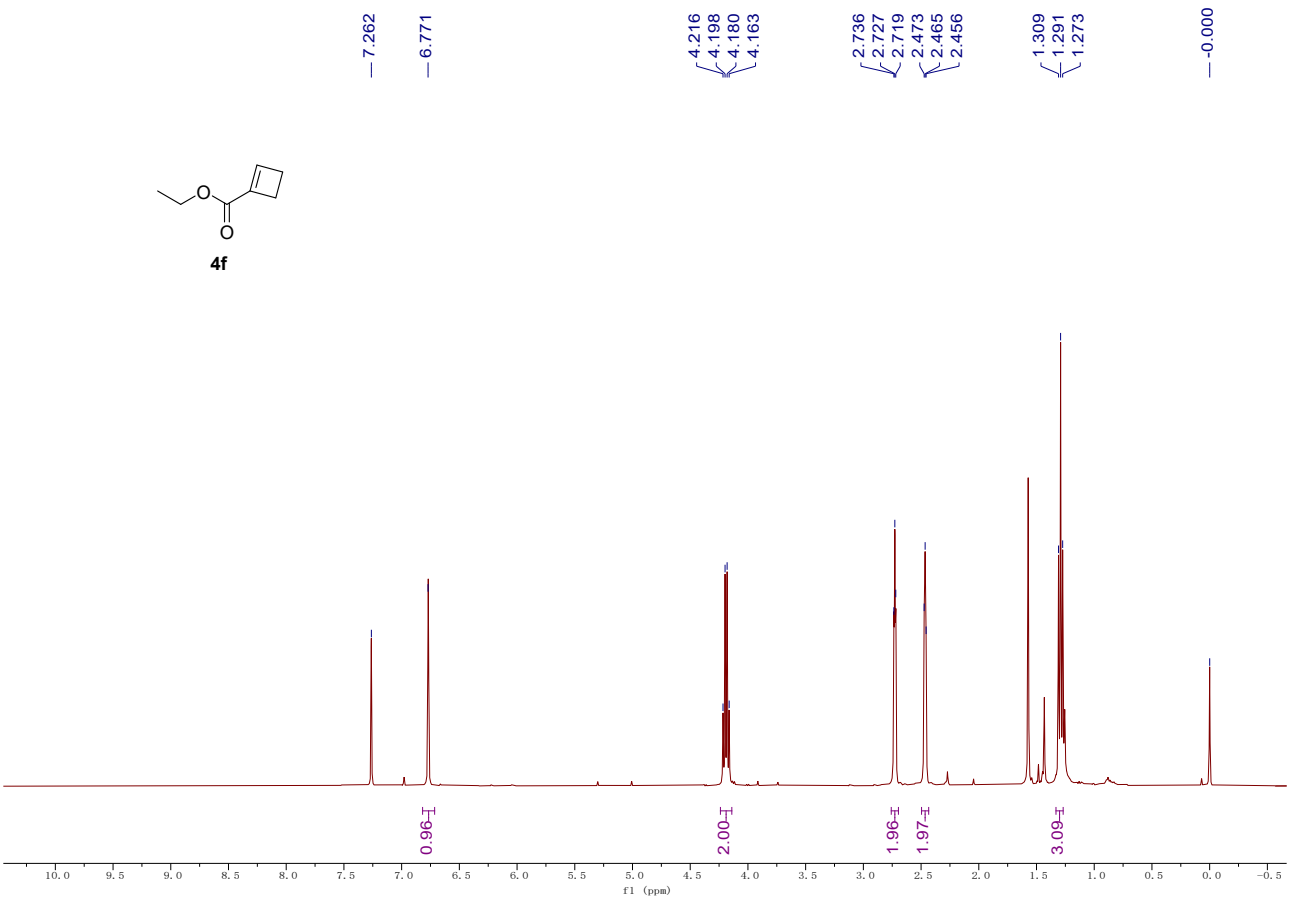

161.475
147.916
139.385
137.877
135.079
128.237
126.257
77.213 CDCl3
77.000 CDCl3
76.785 CDCl3
64.049
29.107
27.313
Cl
Cl
O
O
4c
f1 (ppm)

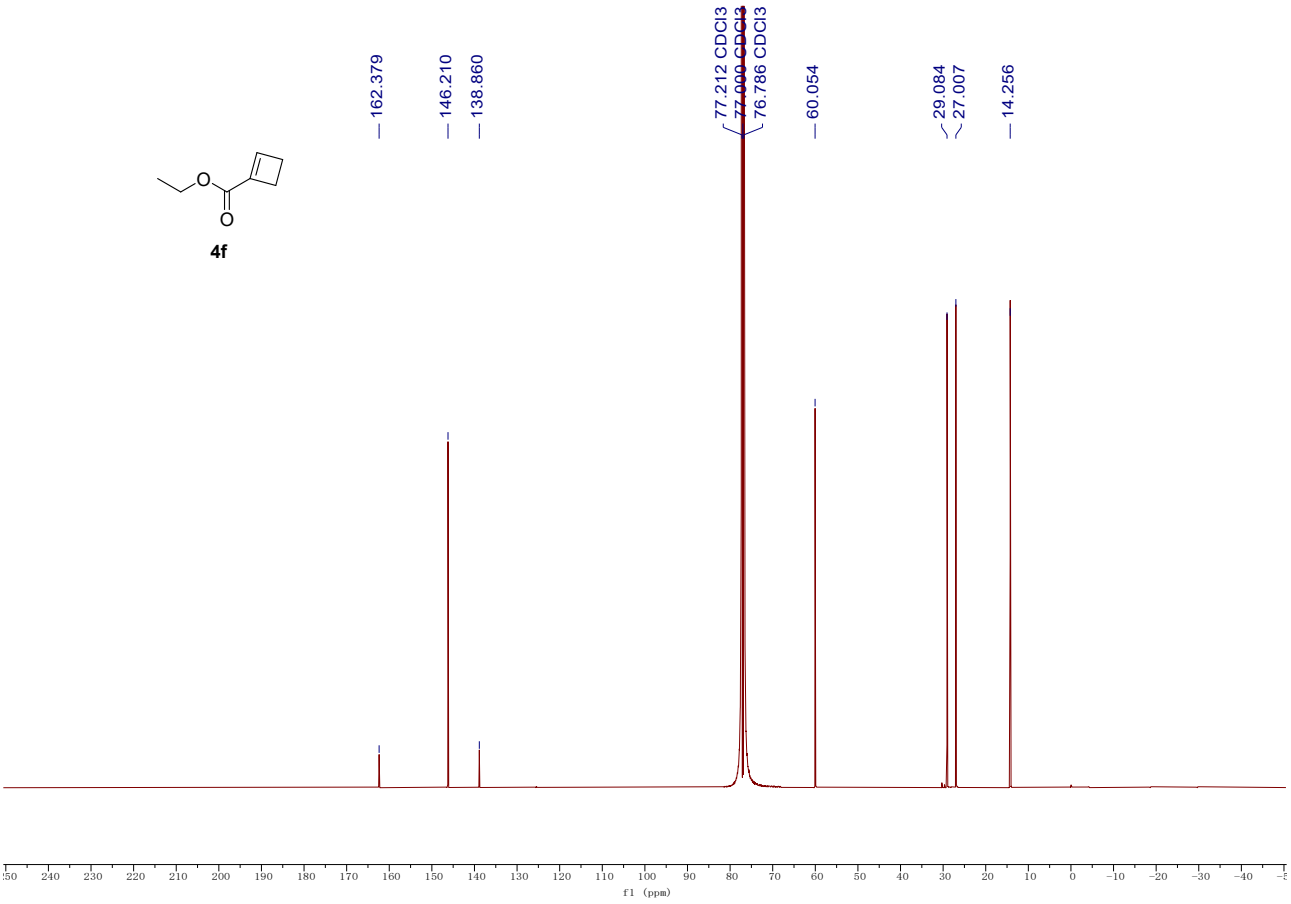

7.393
7.373
7.354
7.235
7.216
7.198
7.128
7.108
6.983
2.853
2.845
2.836
2.557
2.549
2.540
-0.000
O
O
4d
2.14
1.16
1.98
0.93
2.00
2.01
f1 (ppm)

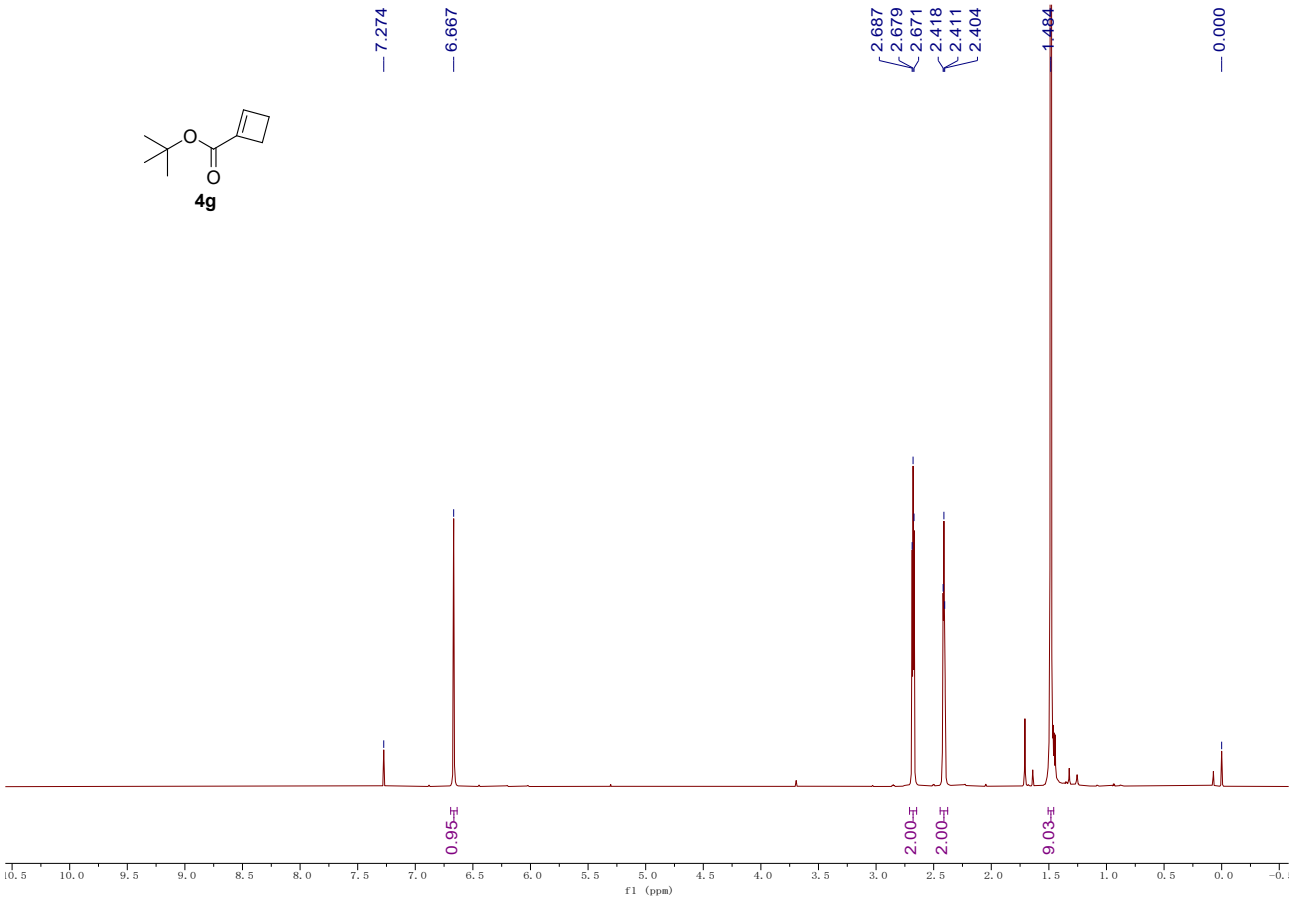

160.193
150.450
148.893
137.975
129.317
125.652
121.522
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
29.229
27.363
O
O
4d
f1 (ppm)

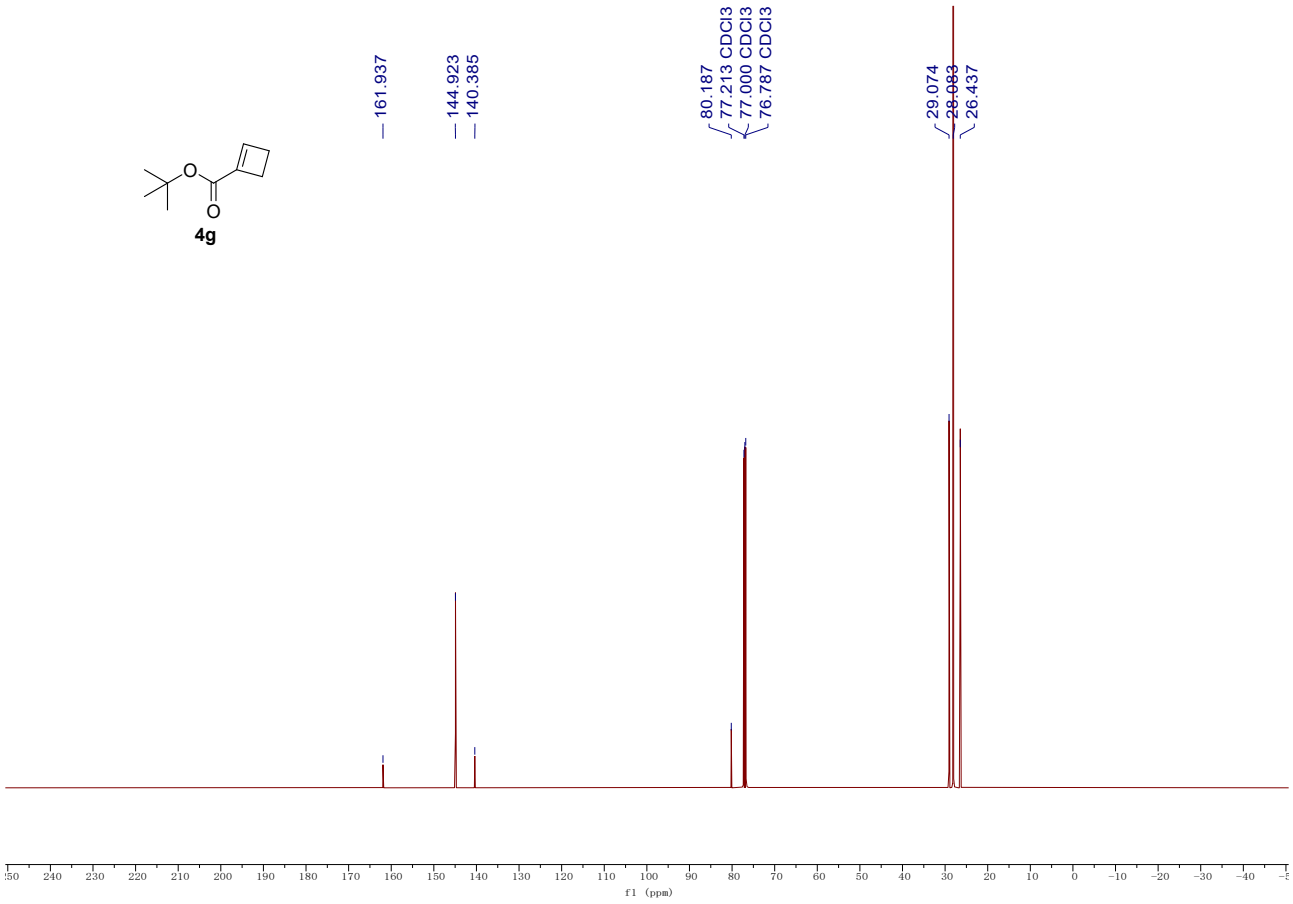

7.293
7.274
7.255
7.188
7.178
7.167
6.762
4.159
4.142
4.126
2.731
2.722
2.715
2.697
2.678
2.466
2.458
2.449
2.037
2.022
2.005
1.987
1.968
1.951
-0.001
Ph
O
O
4e
2.21
3.26
1.00
2.25
4.44
2.19
2.38
f1 (ppm)

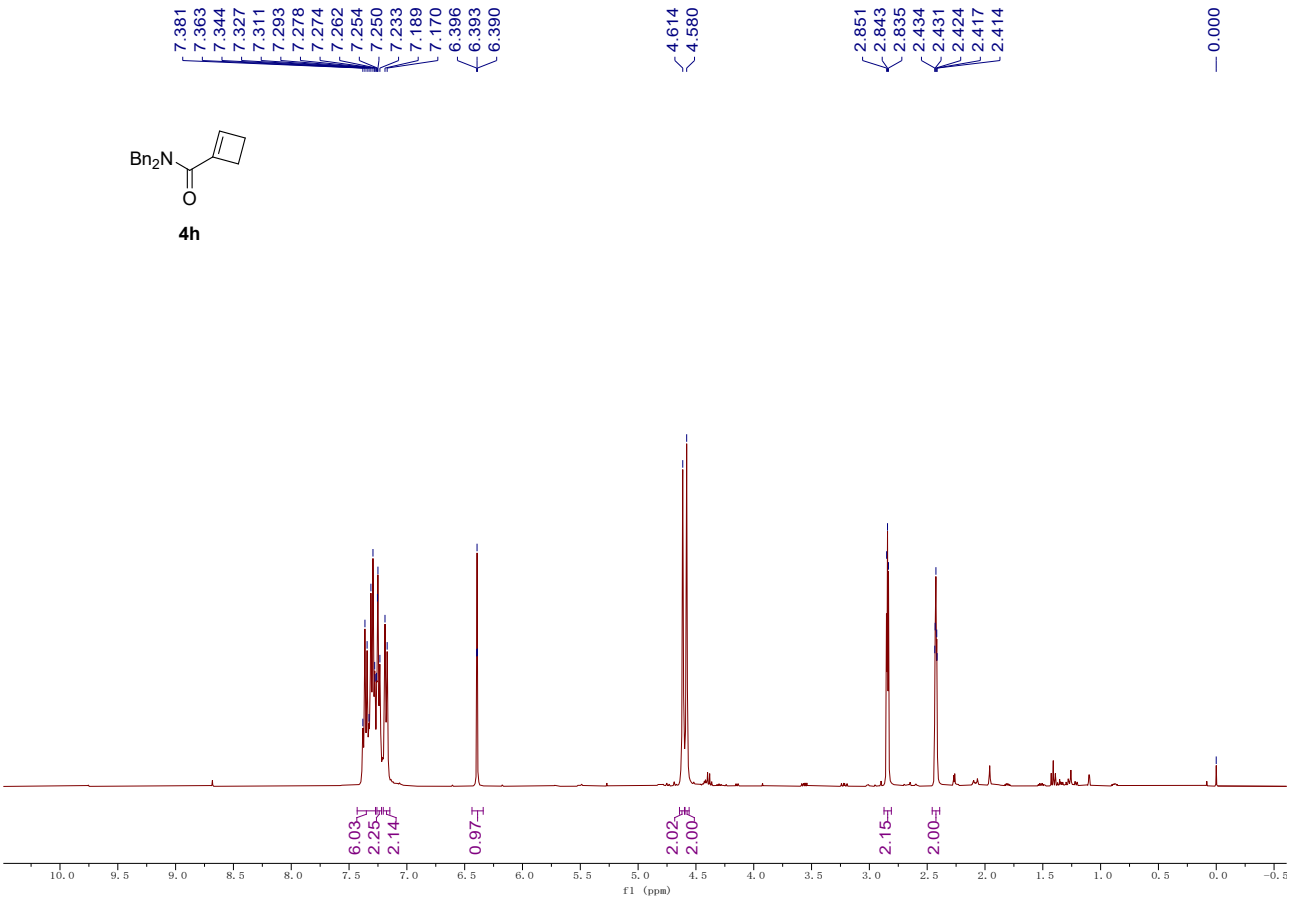

162.193
146.287
141.113
138.658
128.325
128.306
125.883
77.214 CDCl3
77.000 CDCl3
76.786 CDCl3
63.260
32.051
30.121
29.022
26.977
Ph
O
O
4e
f1 (ppm)

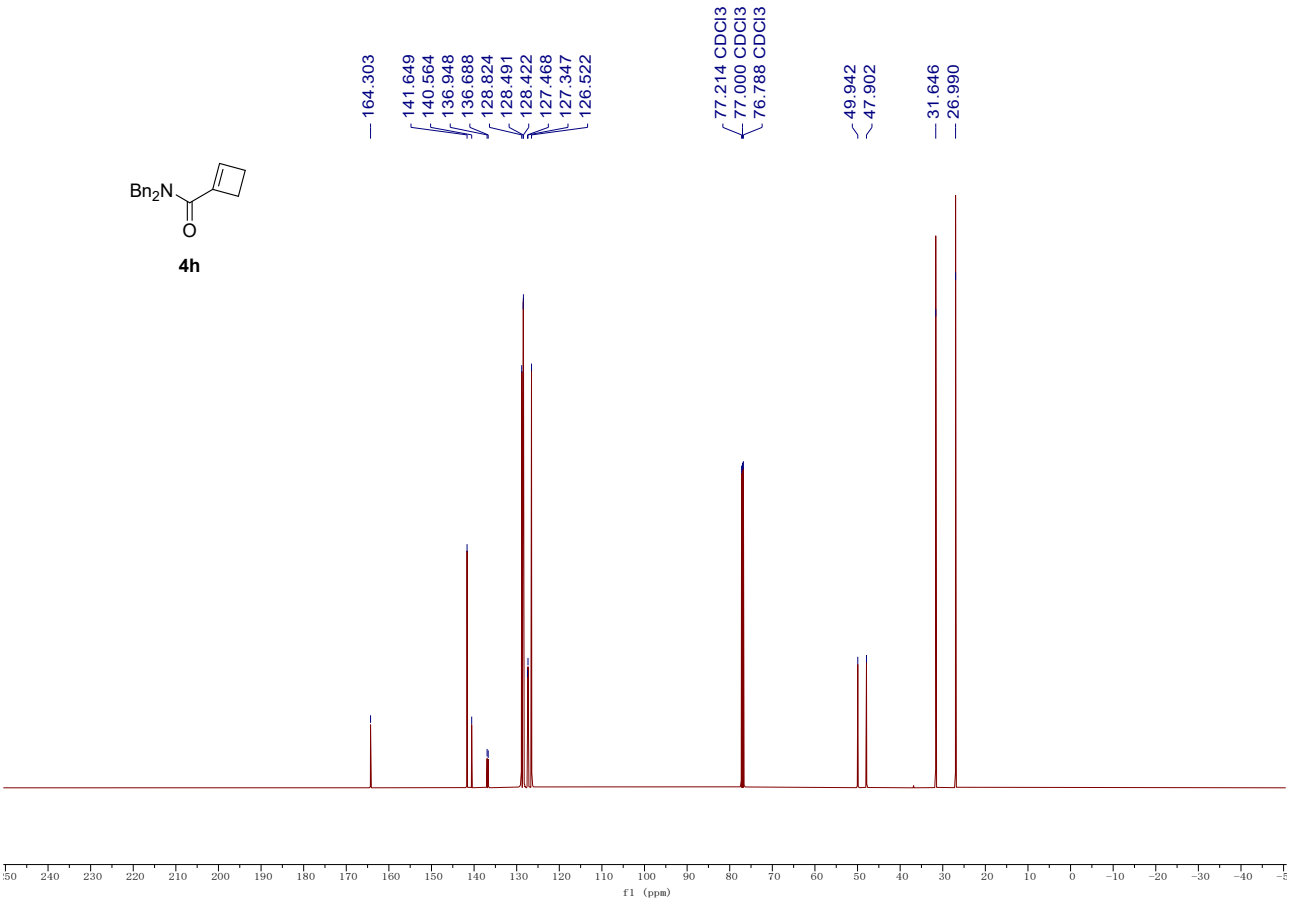

7.262
6.771
4.216
4.198
4.180
4.163
2.736
2.727
2.719
2.473
2.465
2.456
1.309
1.291
1.273
0.000
O
O
4f
0.96
2.00
1.96
1.97
3.09
f1 (ppm)

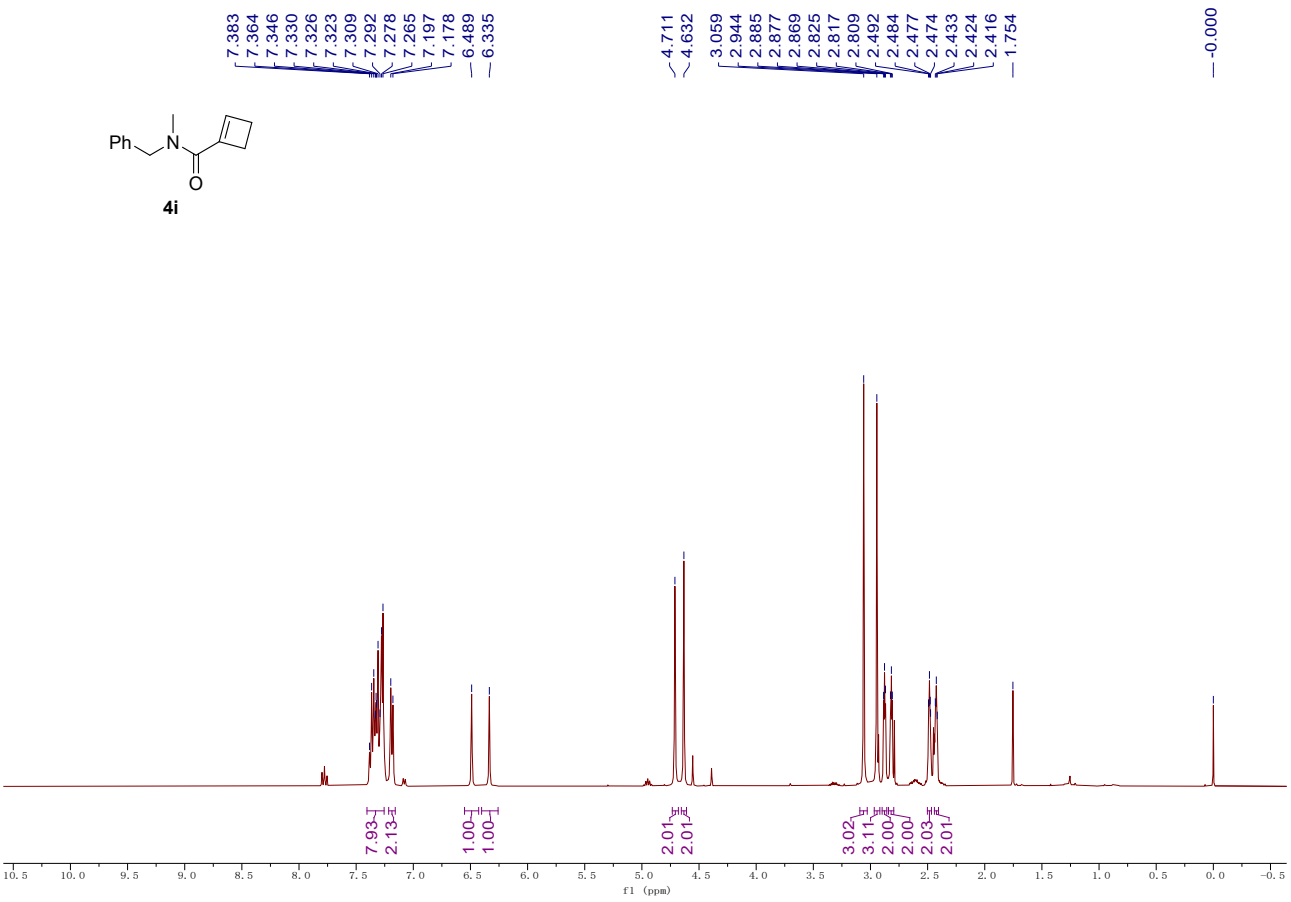

162.379
146.210
138.860
77.212 CDCl3
77.000 CDCl3
76.786 CDCl3
60.054
29.084
27.007
14.256
O
O
4f
f1 (ppm)

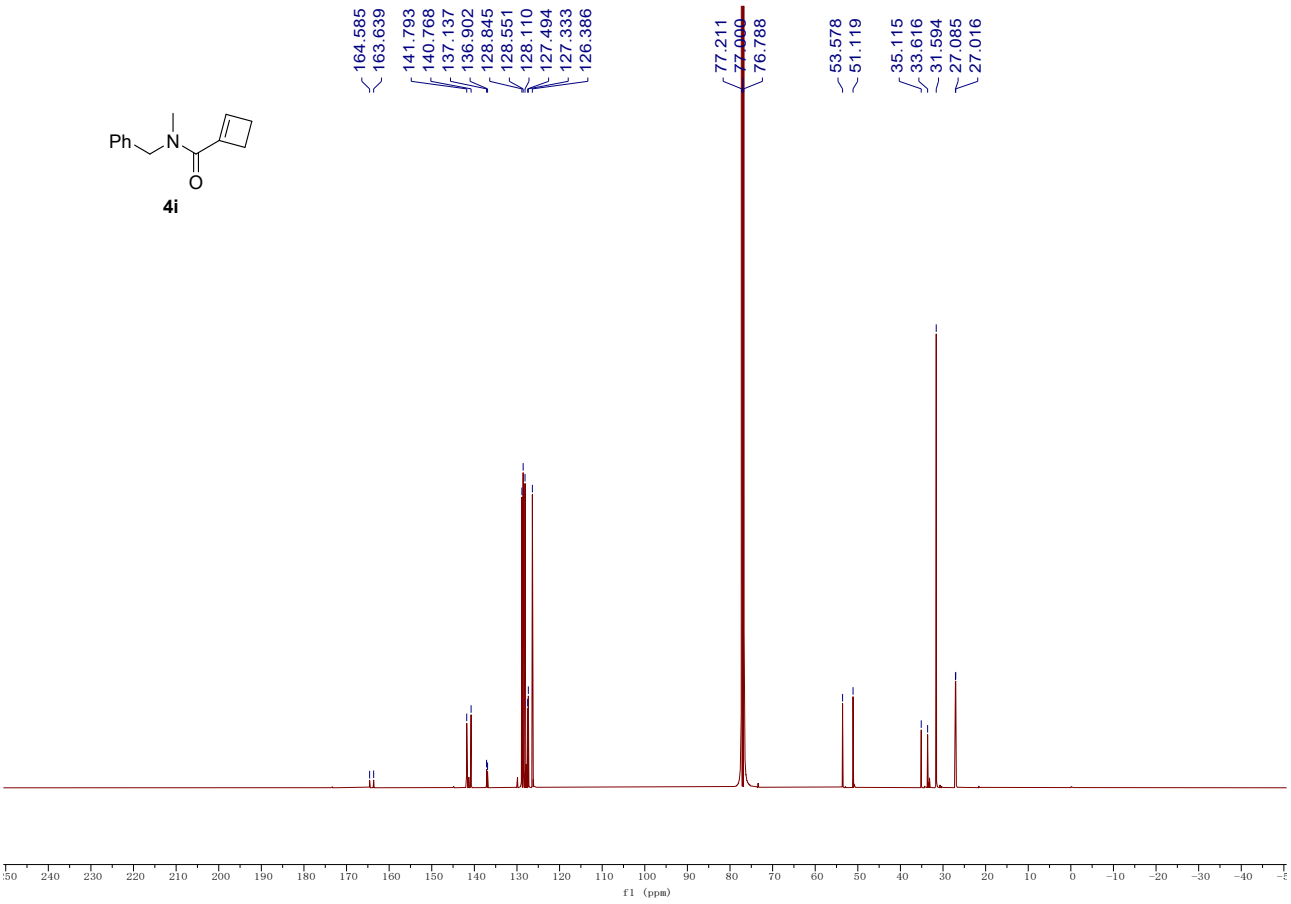

7.274
6.667
2.687
2.679
2.671
2.418
2.411
2.404
1.484
0.000
0.95
2.00
2.00
9.03
f1 (ppm)
4g

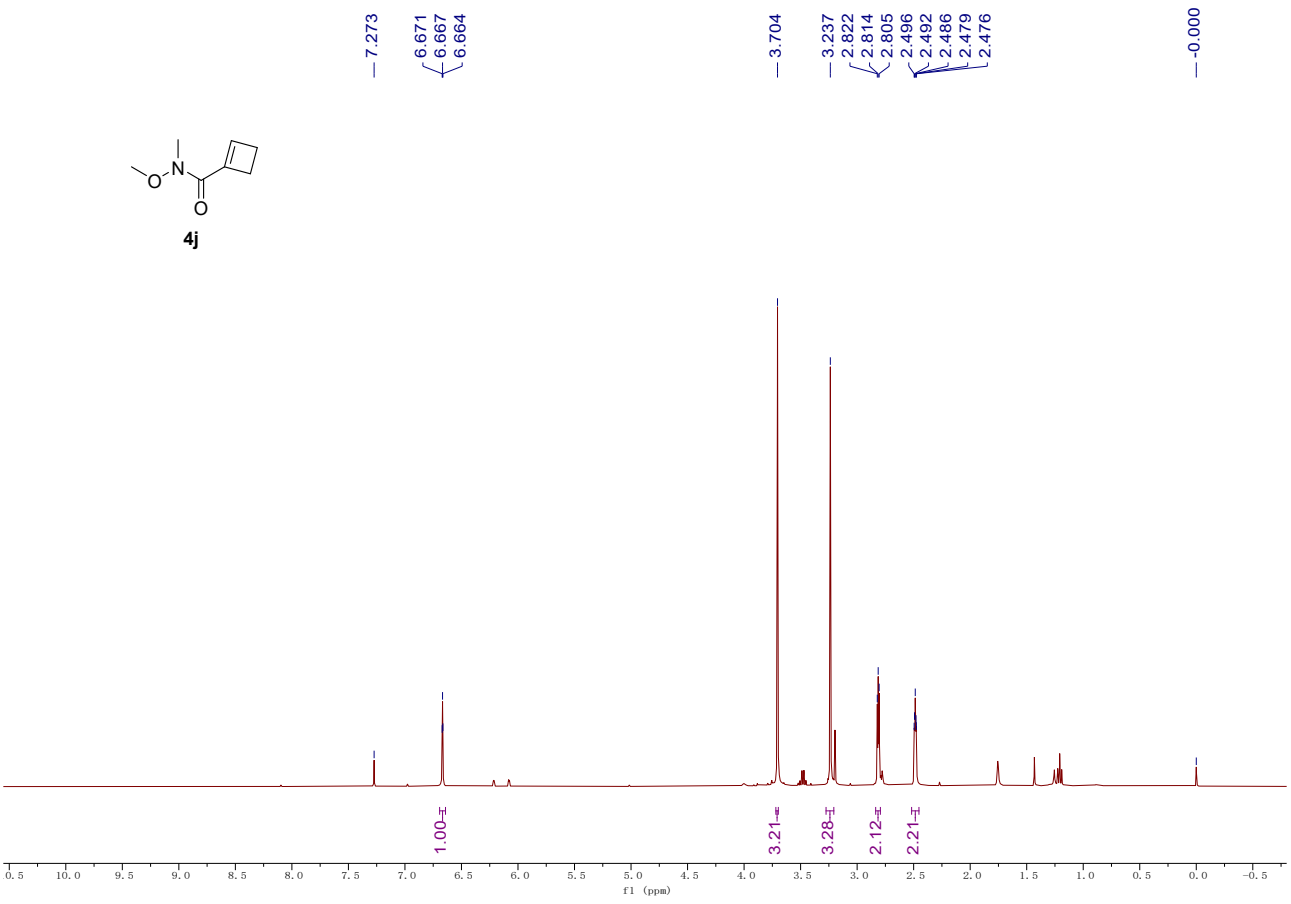

161.937
144.923
140.385
80.187
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
29.074
28.083
26.437
f1 (ppm)
4g


7.381
7.363
7.344
7.327
7.311
7.293
7.278
7.274
7.262
7.254
7.250
7.233
7.189
7.170
6.396
6.393
6.390
4.614
4.580
2.851
2.843
2.835
2.434
2.431
2.424
2.417
2.414
0.000
Bn2N
O
4h
6.03
2.25
2.14
0.97
2.02
2.00
2.15
2.00
f1 (ppm)

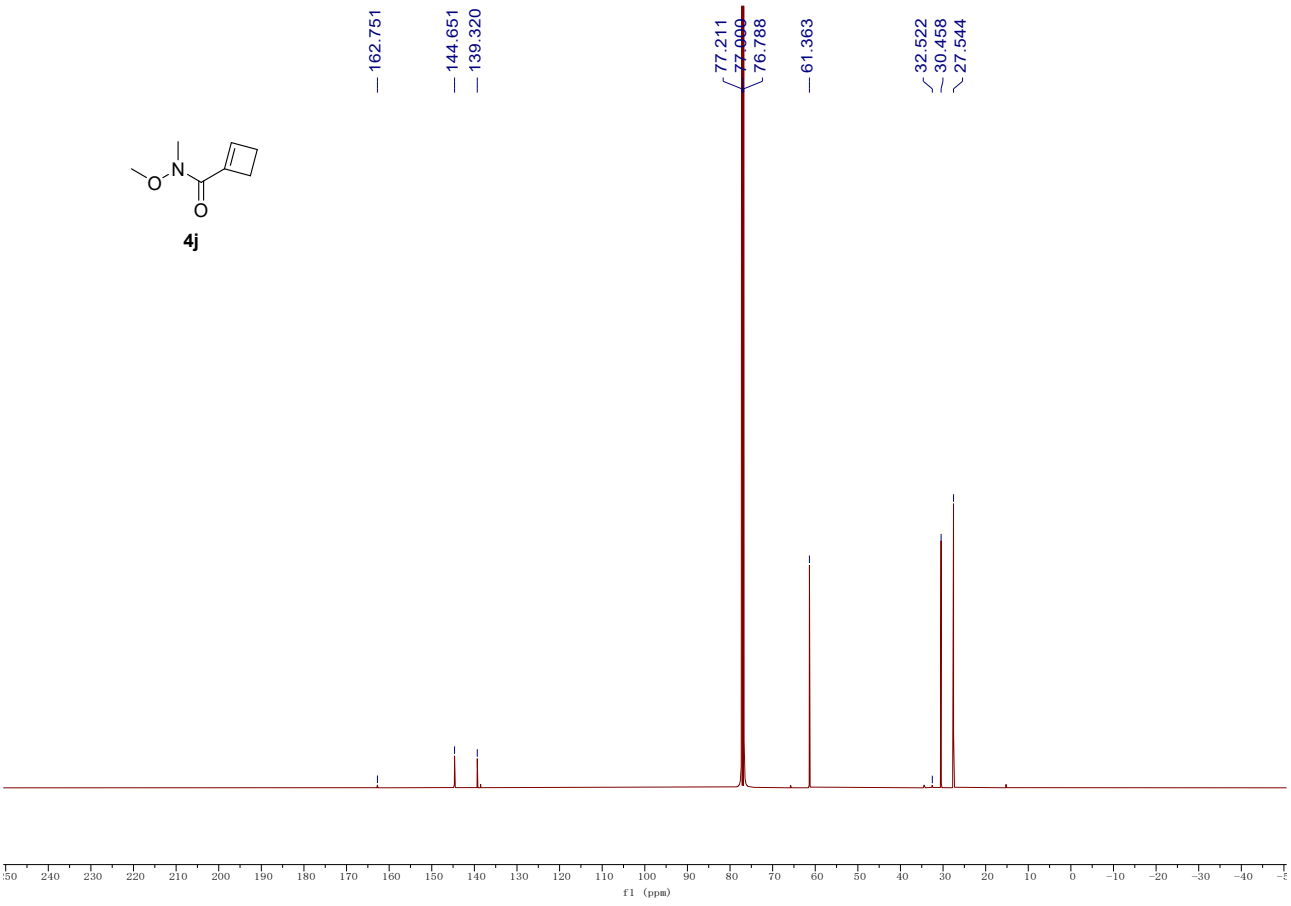

164.303
141.649
140.564
136.948
136.688
128.824
128.491
128.422
127.468
127.347
126.522
77.214 CDCl3
77.000 CDCl3
76.788 CDCl3
49.942
47.902
31.646
26.990
Bn2N
O
4h
f1 (ppm)


7.383
7.364
7.346
7.330
7.326
7.323
7.309
7.292
7.278
7.265
7.197
7.178
6.489
6.335
4.711
4.632
3.059
2.944
2.885
2.877
2.869
2.825
2.817
2.809
2.492
2.484
2.477
2.474
2.433
2.424
2.416
1.754
-0.000
Ph
N
O
4i
7.93
2.13
1.00
1.00
2.01
2.01
3.02
3.11
2.00
2.00
2.03
2.01
f1 (ppm)

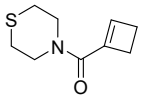

164.585
163.639
141.793
140.768
137.137
136.902
128.845
128.551
128.110
127.494
127.333
126.386
77.211
77.000
76.788
53.578
51.119
35.115
33.616
31.594
27.085
27.016
Ph
N
O
4i
f1 (ppm)


7.273
6.671
6.667
6.664
3.704
3.237
2.822
2.814
2.805
2.496
2.492
2.486
2.479
2.476
-0.000
1.00
3.21
3.28
2.12
2.21
f1 (ppm)

4j

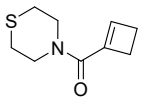

162.751
144.651
139.320
77.211
77.000
76.788
61.363
32.522
30.458
27.544
f1 (ppm)

4j



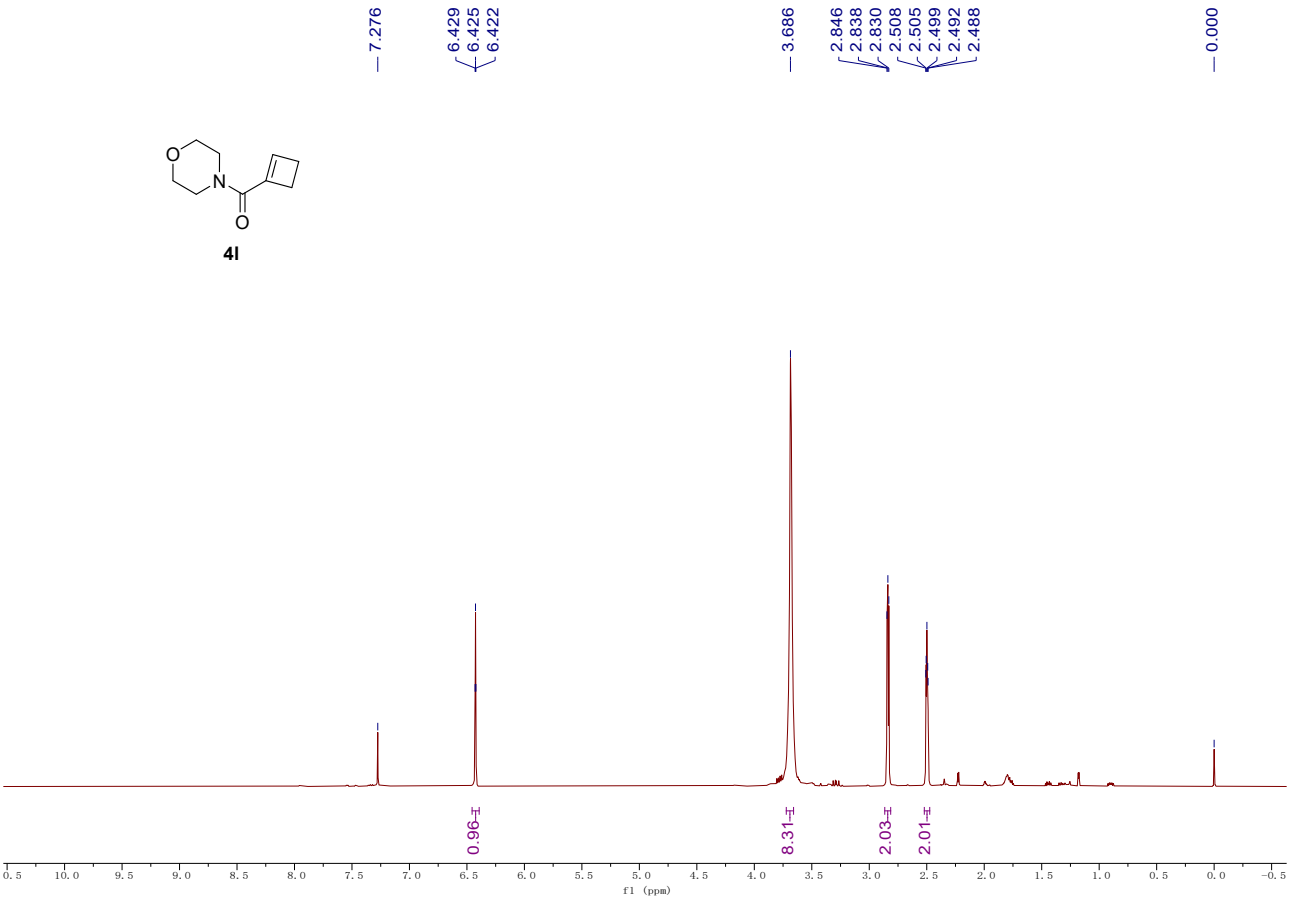
4k

7.294
6.417
6.408
6.408
6.402
3.920
2.842
2.834
2.825
2.656
2.642
2.630
2.506
2.498
2.489
0.000
1.01
4.31
2.20
4.30
2.14
f1 (ppm)

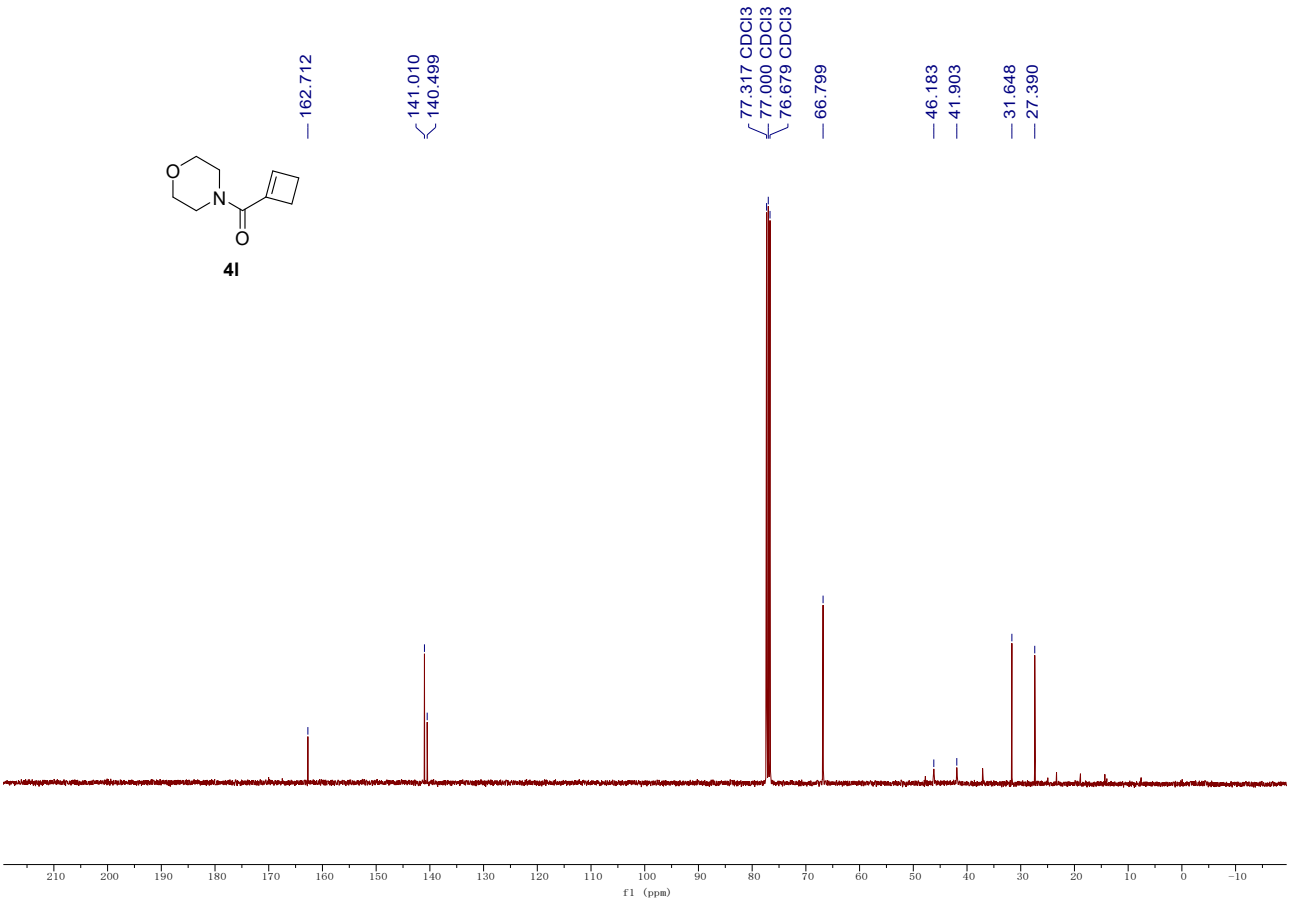


4k

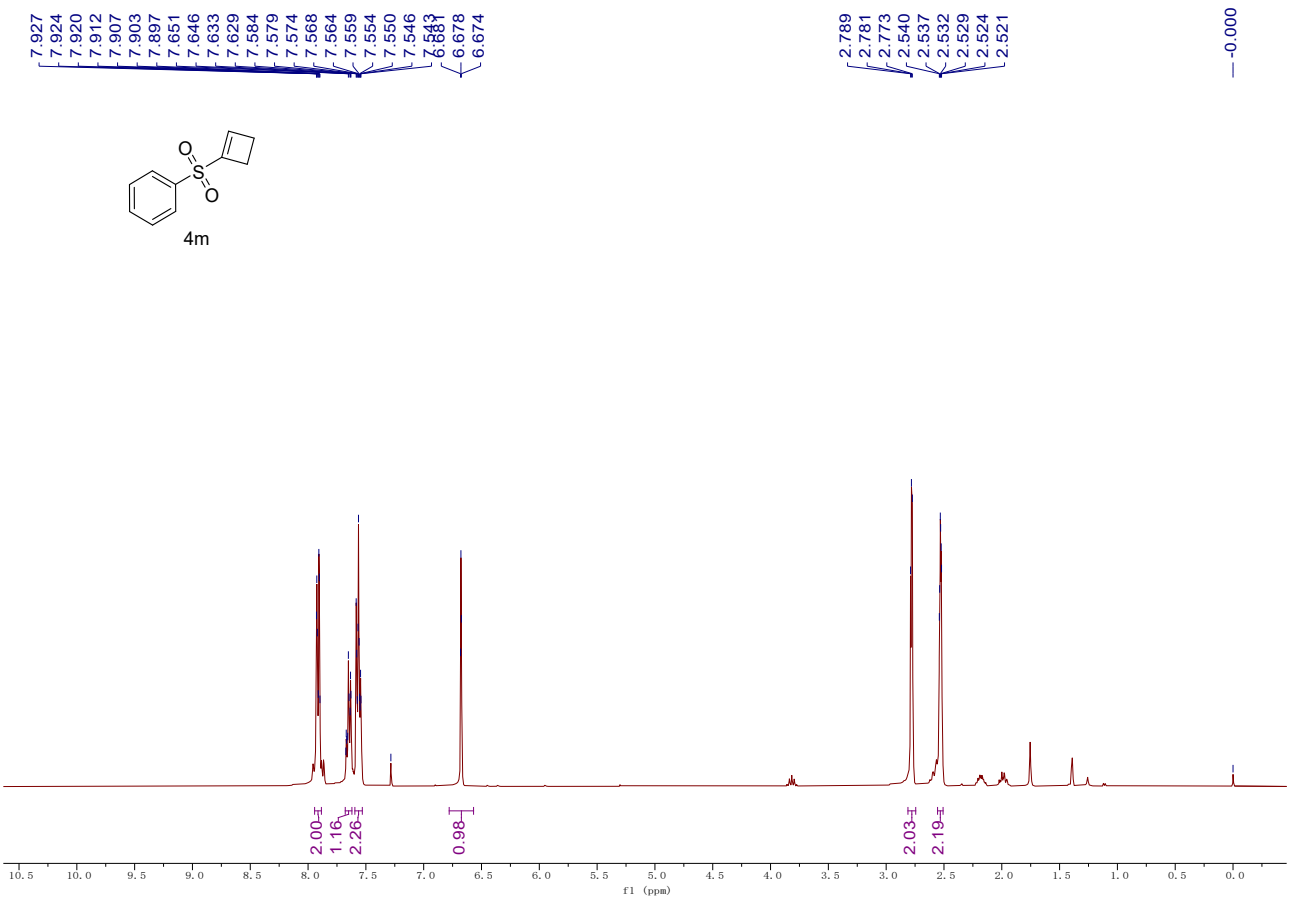
162.779
140.552
77.216
77.000
76.789
48.421
44.257
31.654
27.278
f1 (ppm)

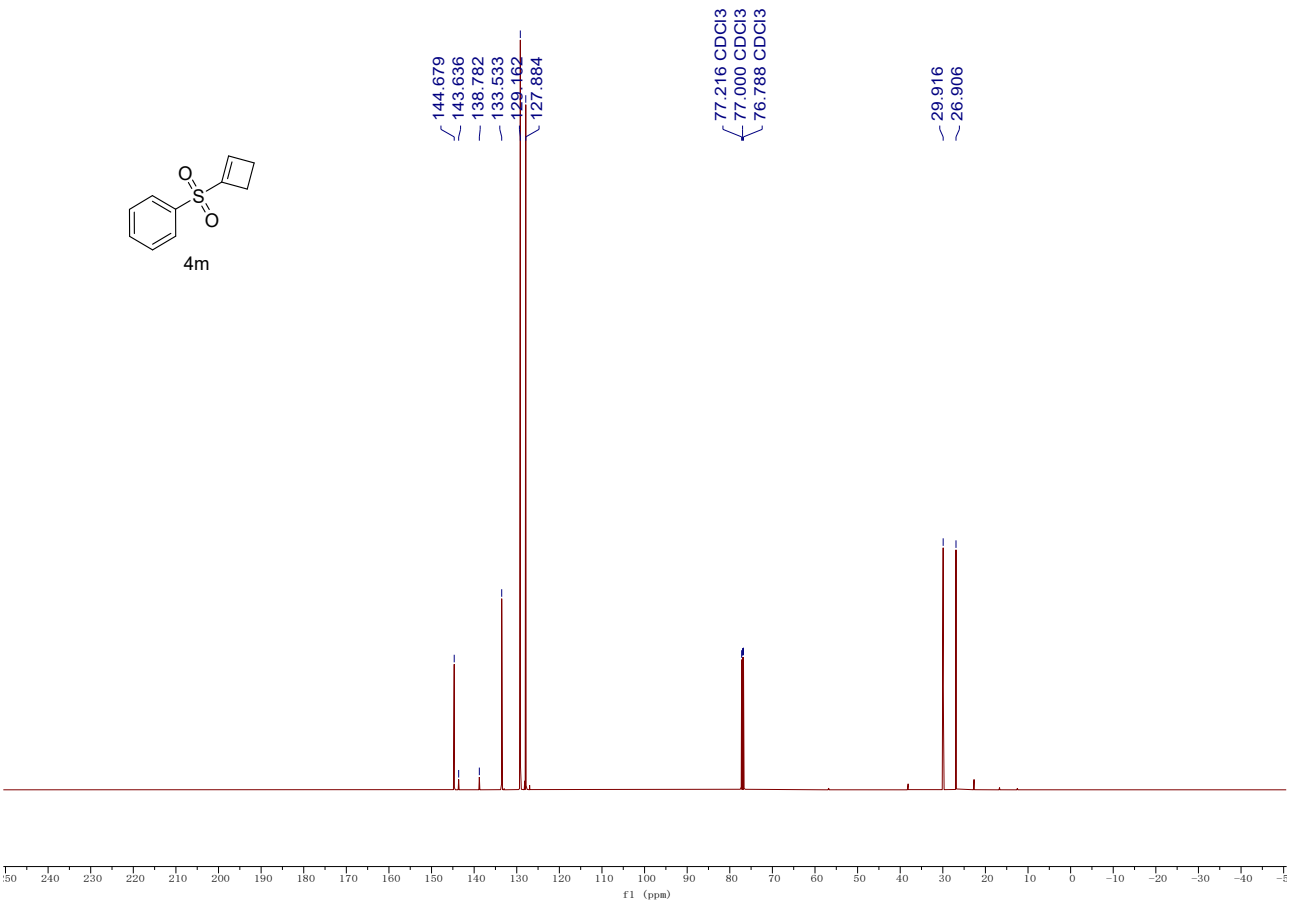

7.276
6.429
6.425
6.422
3.686
2.846
2.838
2.830
2.508
2.505
2.499
2.492
2.488
0.000
0.96
8.31
2.03
2.01
f1 (ppm)

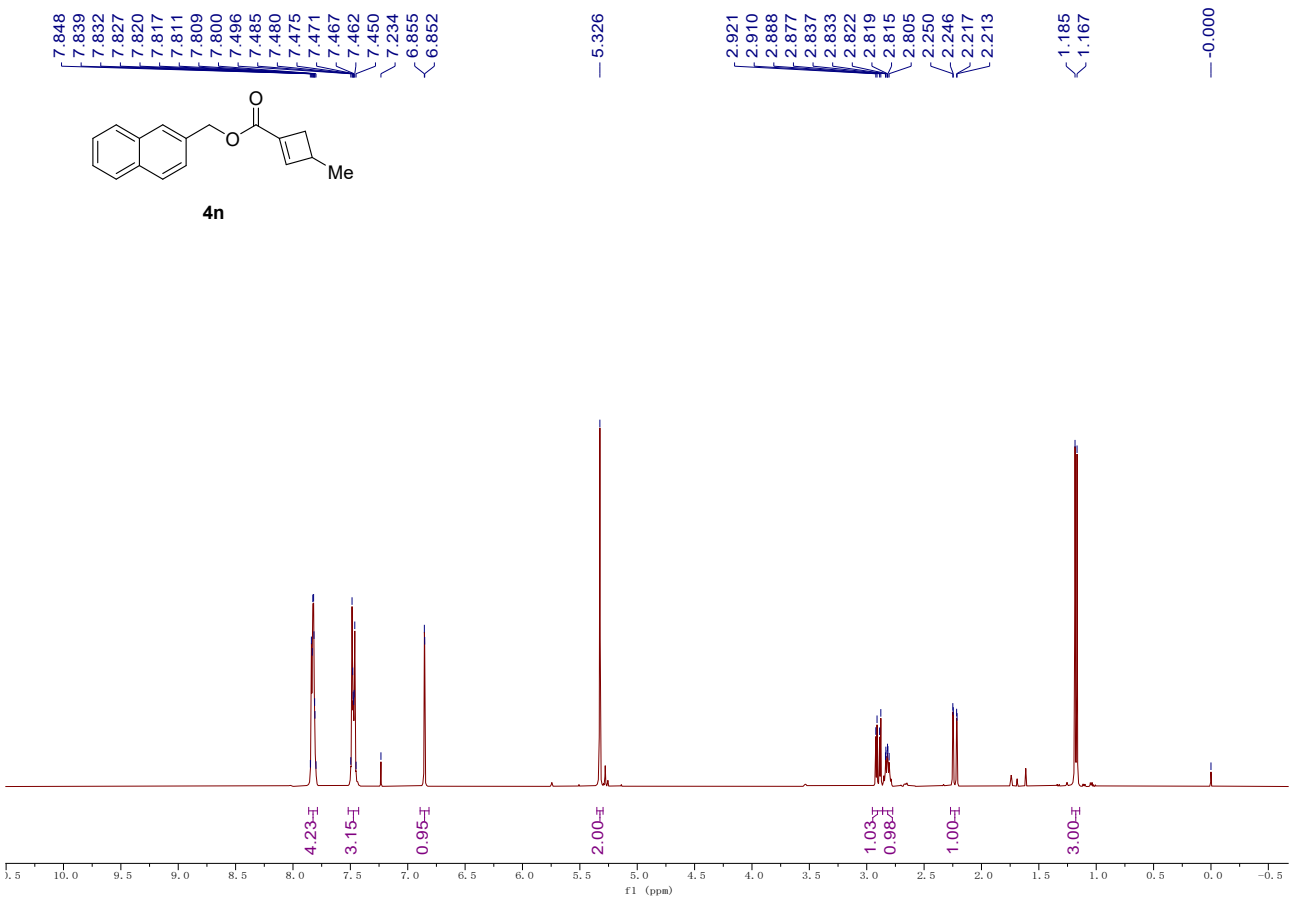
4l

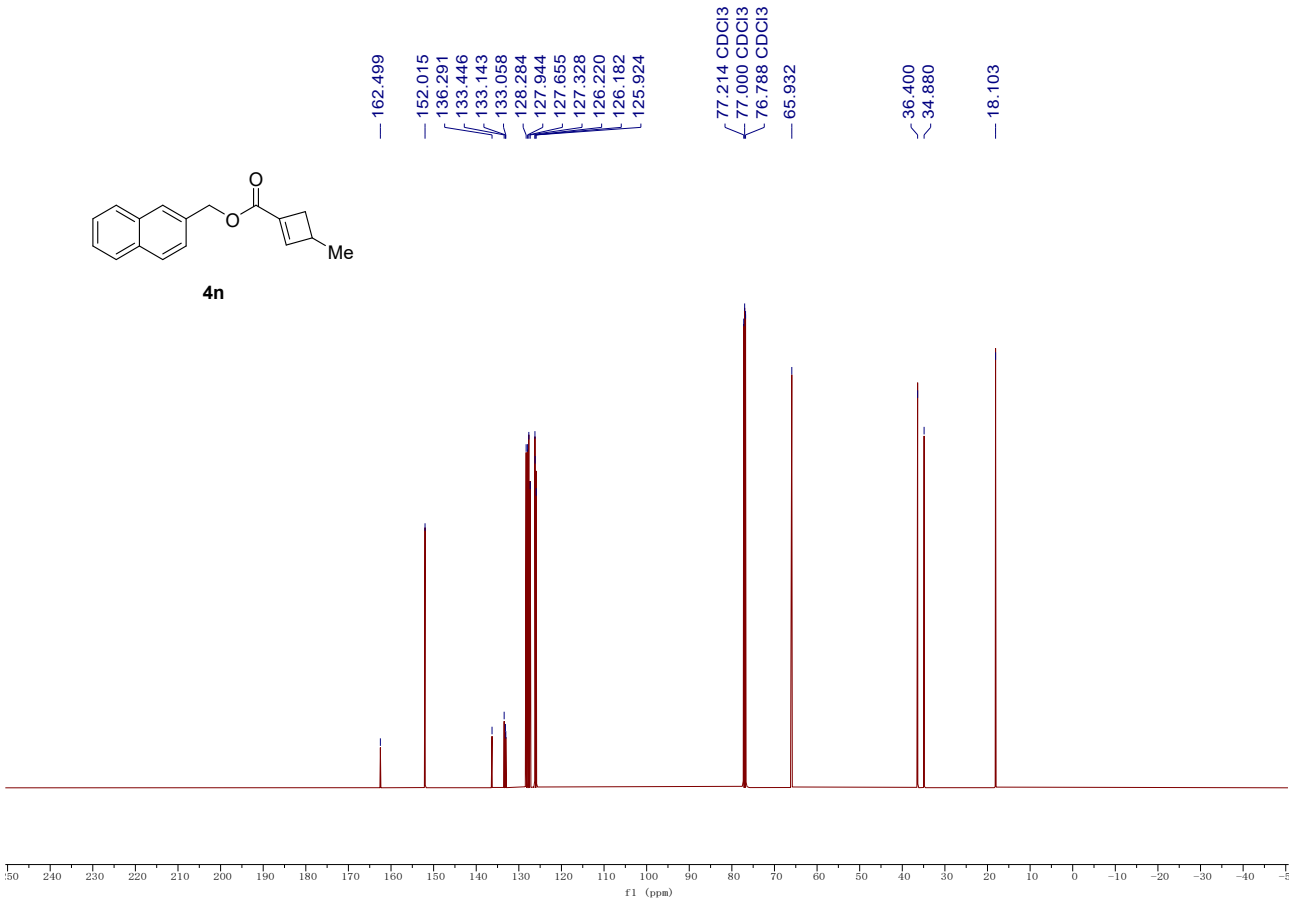

162.712
141.010
140.499
77.317 CDCl3
77.000 CDCl3
76.679 CDCl3
66.799
46.183
41.903
31.648
27.390
f1 (ppm)

4l

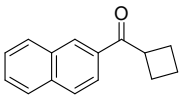

7.927
7.924
7.920
7.912
7.907
7.903
7.897
7.651
7.646
7.633
7.629
7.584
7.579
7.574
7.568
7.564
7.559
7.554
7.550
7.546
6.681
6.678
6.674
2.789
2.781
2.773
2.540
2.537
2.532
2.529
2.524
2.521
-0.000
4m
2.00
1.16
2.26
0.98
2.03
2.19
f1 (ppm)


144.679
143.636
138.782
133.533
129.162
127.884
77.216 CDCl3
77.000 CDCl3
76.788 CDCl3
29.916
26.906
4m
f1 (ppm)

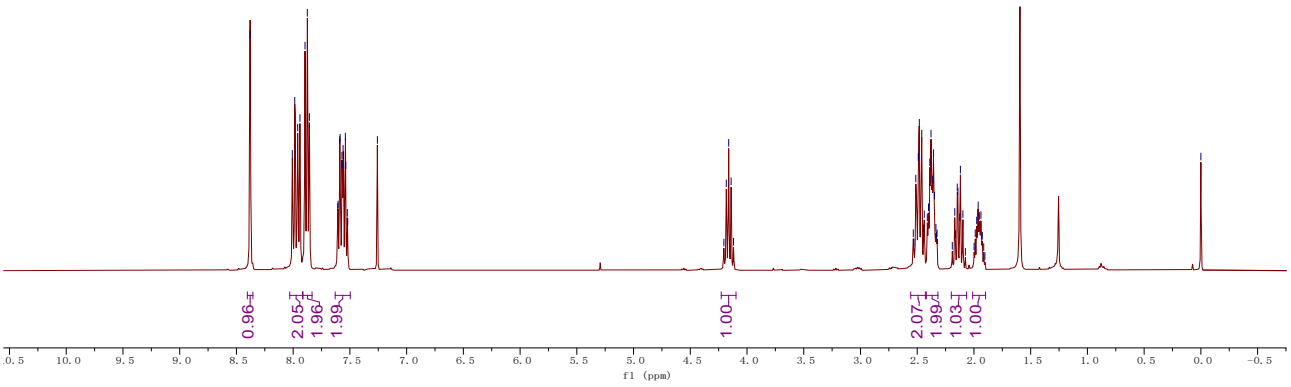

7.848
7.839
7.832
7.827
7.820
7.817
7.811
7.809
7.800
7.496
7.485
7.480
7.475
7.471
7.467
7.462
7.450
7.234
6.855
6.852
5.326
2.921
2.910
2.888
2.877
2.837
2.833
2.822
2.819
2.815
2.805
2.250
2.246
2.217
2.213
1.185
1.167
-0.000
O
O
Me
4n
4.23
3.15
0.95
2.00
1.03
0.98
1.00
3.00
f1 (ppm)

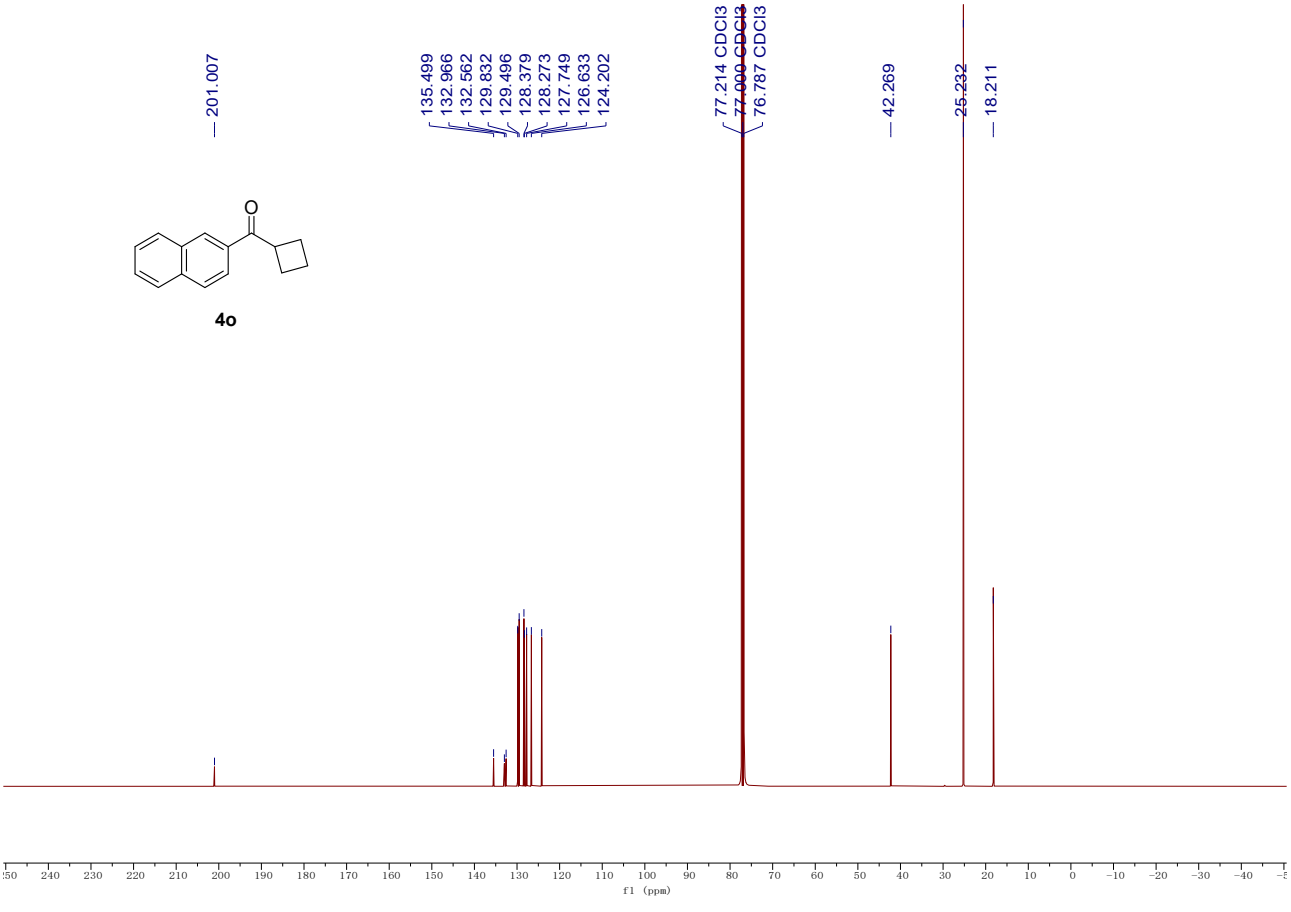

162.499
152.015
136.291
133.446
133.143
133.058
128.284
127.944
127.655
127.328
126.220
126.182
125.924
77.214 CDCl3
77.000 CDCl3
76.788 CDCl3
65.932
36.400
34.880
18.103
O
O
Me
4n
f1 (ppm)


8.381
8.008
7.986
7.960
7.940
7.896
7.875
7.857
7.607
7.604
7.590
7.586
7.570
7.566
7.560
7.556
7.540
7.536
7.523
7.519
7.258
4.204
4.183
4.162
4.140
4.119
2.534
2.529
2.512
2.491
2.482
2.460
2.444
2.438
2.411
2.400
2.389
2.378
2.367
2.356
2.347
2.335
2.331
2.325
2.191
2.169
2.163
2.147
2.141
2.125
2.119
2.098
2.075
1.999
1.988
1.976
1.963
1.952
1.938
1.926
1.914
1.904
-0.000

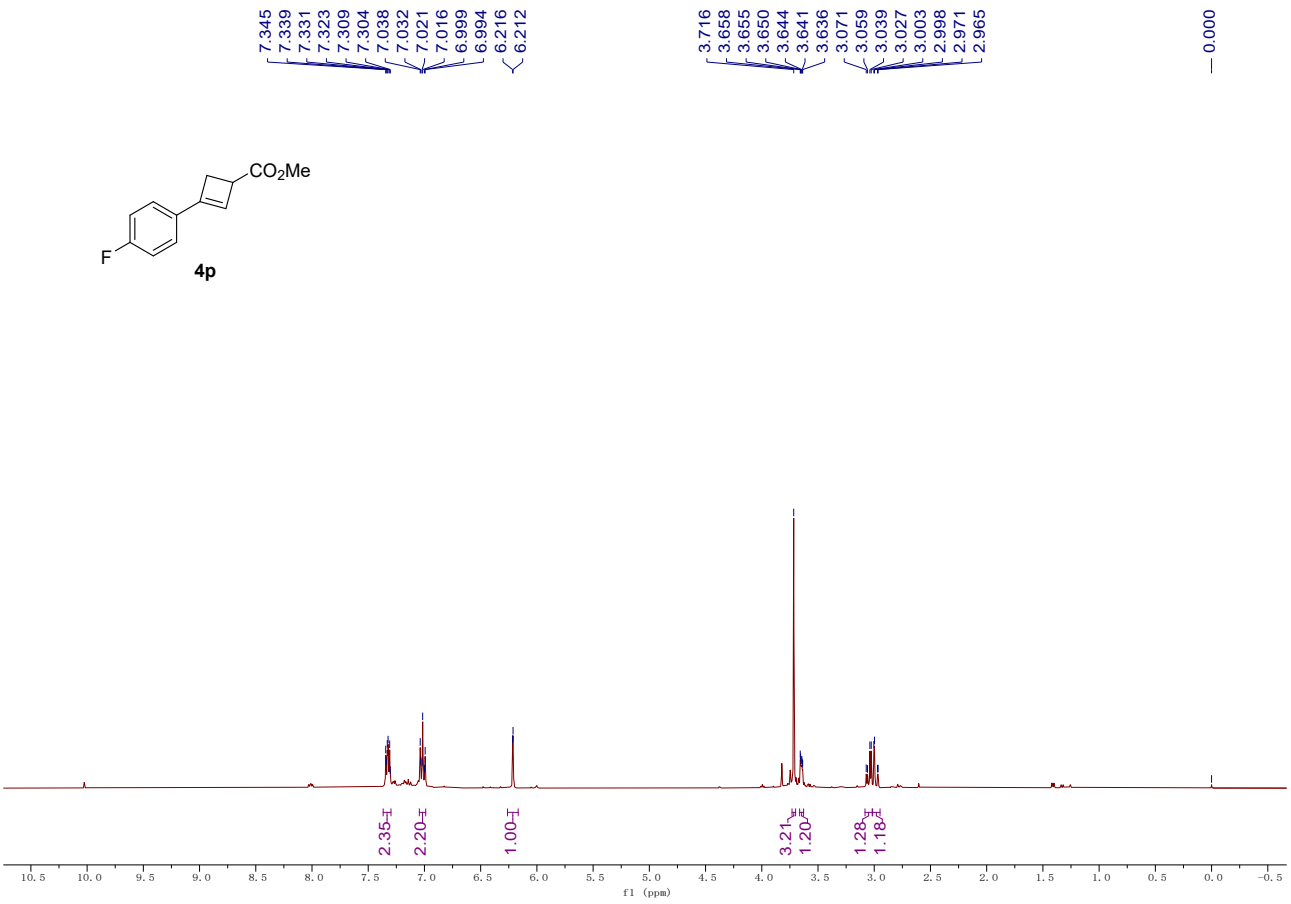


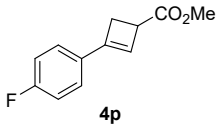
4o


0.96
2.05
1.96
1.99
1.00
2.07
1.99
1.03
1.00
f1 (ppm)


201.007
135.499
132.966
132.562
129.832
129.496
128.379
128.273
127.749
126.633
124.202
77.214 CDCl3
77.000 CDCl3
76.787 CDCl3
42.269
25.232
18.211
f1 (ppm)

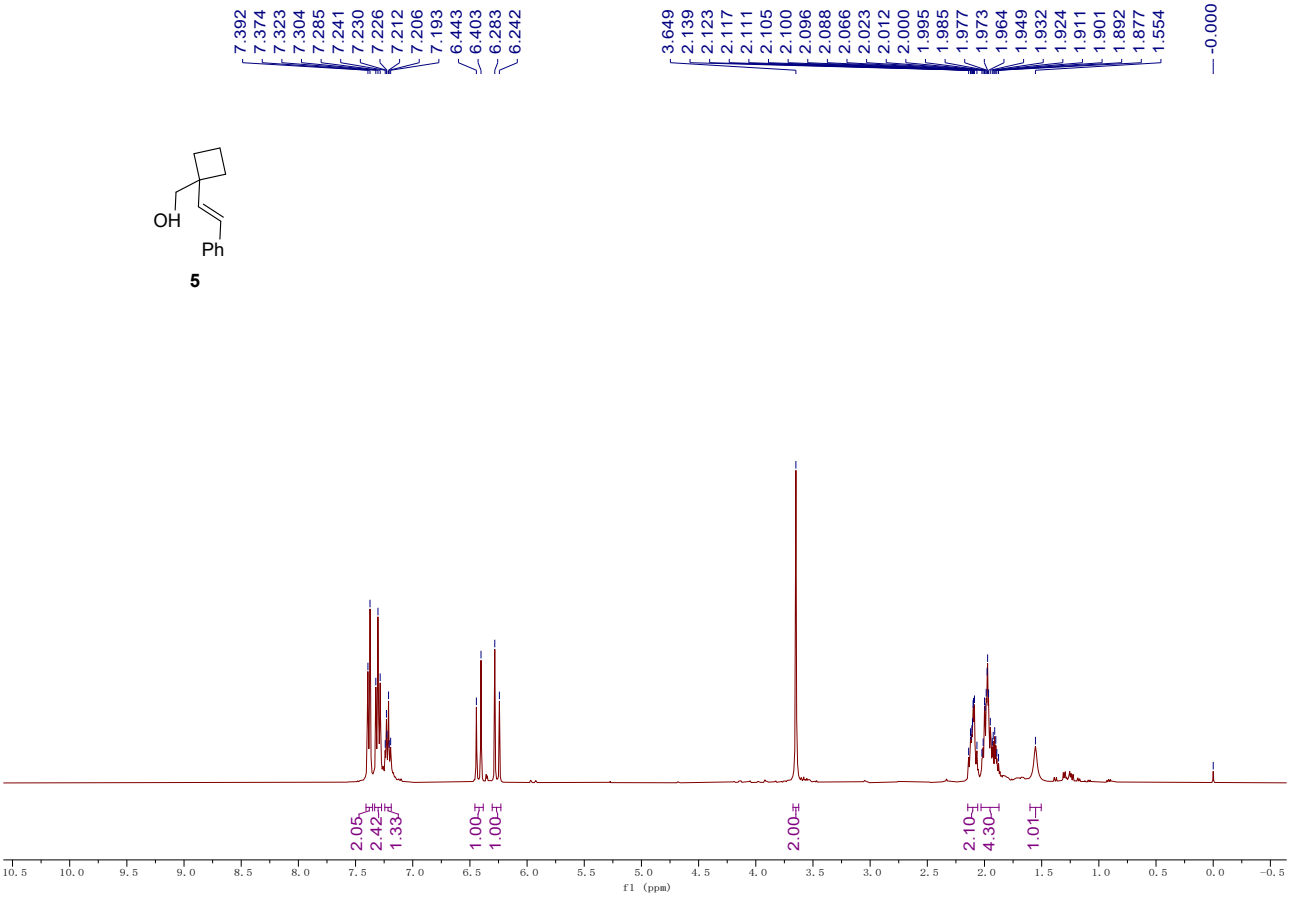
4o

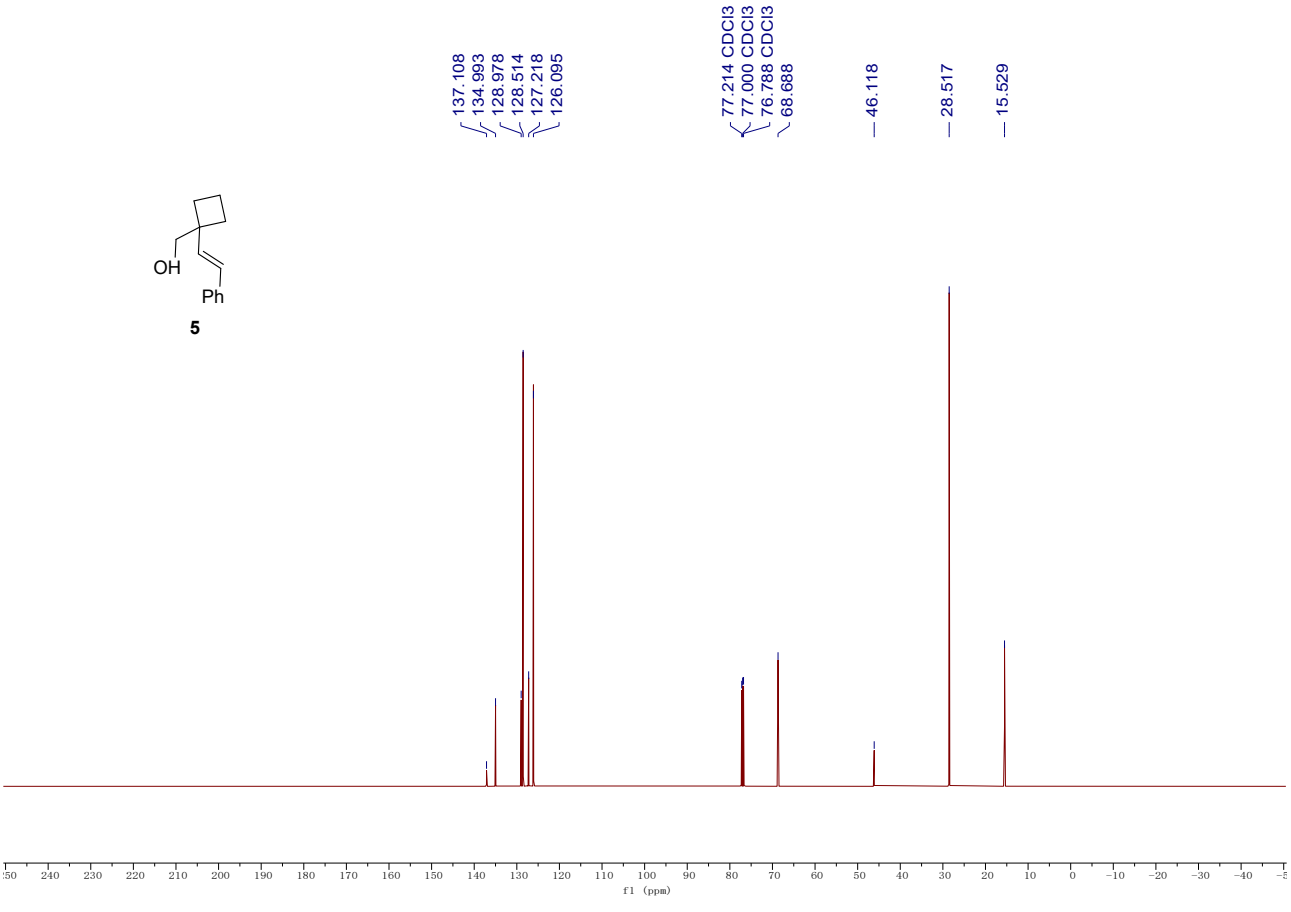

7.345
7.339
7.331
7.323
7.309
7.304
7.038
7.032
7.021
7.016
6.999
6.994
6.216
6.212
3.716
3.658
3.655
3.650
3.644
3.641
3.636
3.071
3.059
3.039
3.027
3.003
2.998
2.971
2.965
0.000
CO2Me
F
4p
2.35
2.20
1.00
3.21
1.20
1.28
1.18
f1 (ppm)
173.805
163.496
161.851
147.129
130.064
130.040
126.522
126.465
123.876
123.854
115.405
115.259
77.211
77.000
76.788
51.803
41.076
32.564
CO2Me
F
4p
f1 (ppm)

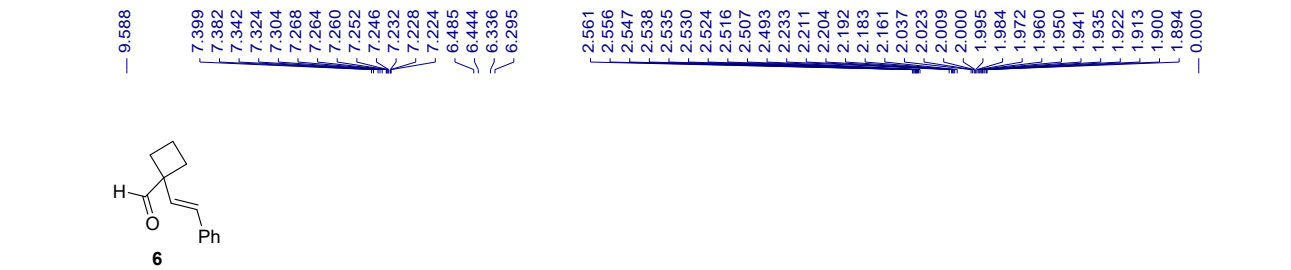

CO2Me
F

4p

-112.576
40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)

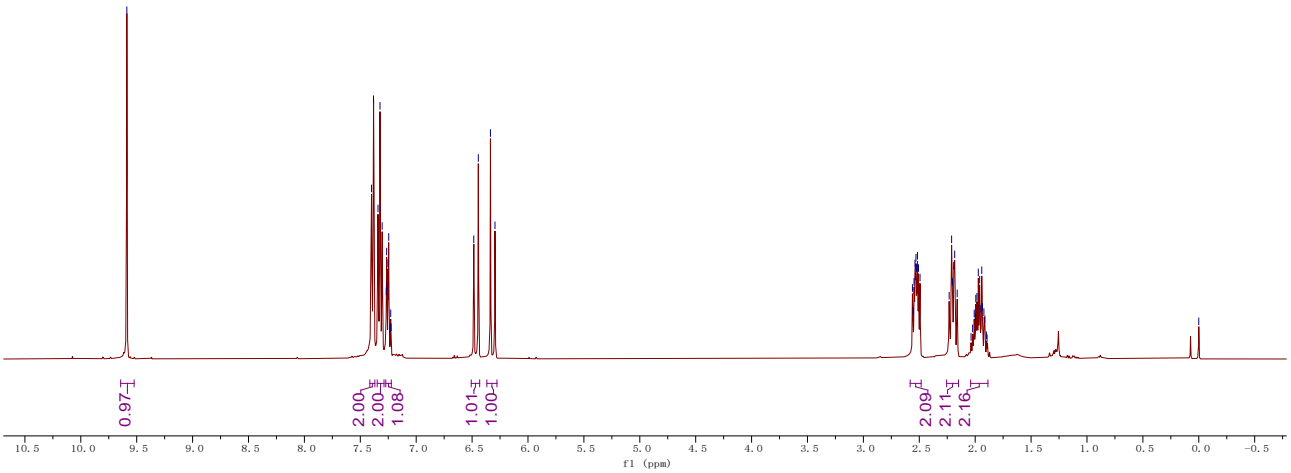

7.392
7.374
7.323
7.304
7.285
7.241
7.230
7.226
7.212
7.206
7.193
6.443
6.403
6.283
6.242
3.649
2.139
2.123
2.117
2.111
2.105
2.100
2.096
2.088
2.066
2.023
2.012
2.000
1.995
1.985
1.977
1.973
1.964
1.949
1.932
1.924
1.911
1.901
1.892
1.877
1.554
-0.000
OH
Ph
5
2.05
2.42
1.33
1.00
1.00
2.00
2.10
4.30
1.01
f1 (ppm)

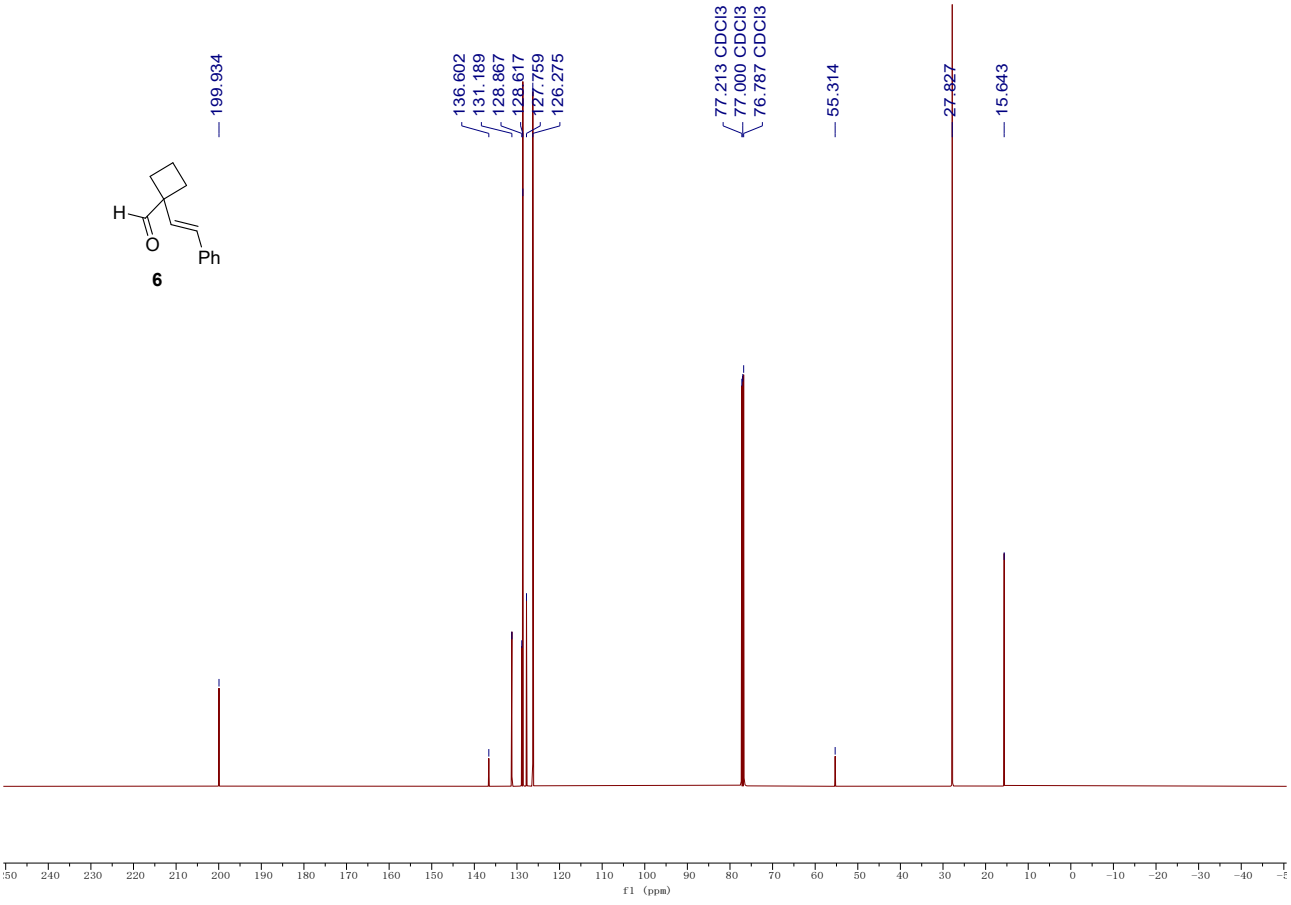

137.108
134.993
128.978
128.514
127.218
126.095
77.214 CDCl3
77.000 CDCl3
76.788 CDCl3
68.688
46.118
28.517
15.529
OH
Ph
5
f1 (ppm)


9.588
7.399
7.382
7.342
7.324
7.304
7.268
7.264
7.260
7.252
7.246
7.232
7.228
7.224
6.485
6.444
6.336
6.295
2.561
2.556
2.547
2.538
2.535
2.530
2.524
2.516
2.507
2.493
2.233
2.211
2.204
2.192
2.183
2.161
2.037
2.023
2.009
2.000
1.995
1.984
1.972
1.960
1.950
1.941
1.935
1.922
1.913
1.900
1.894
0.000

H
O
Ph

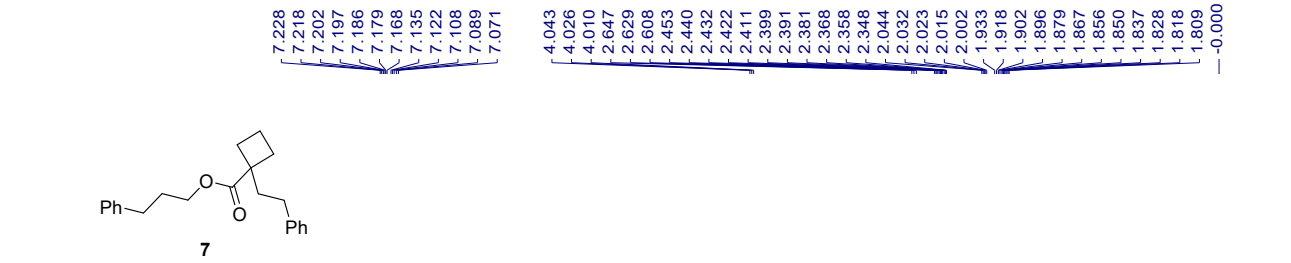
6


0.97
2.00
2.00
1.08
1.01
1.00
2.09
2.11
2.16
f1 (ppm)


199.934
136.602
131.189
128.867
128.617
127.759
126.275
77.213 CDCl3
77.000 CDCl3
76.787 CDCl3
55.314
27.827
15.643
f1 (ppm)

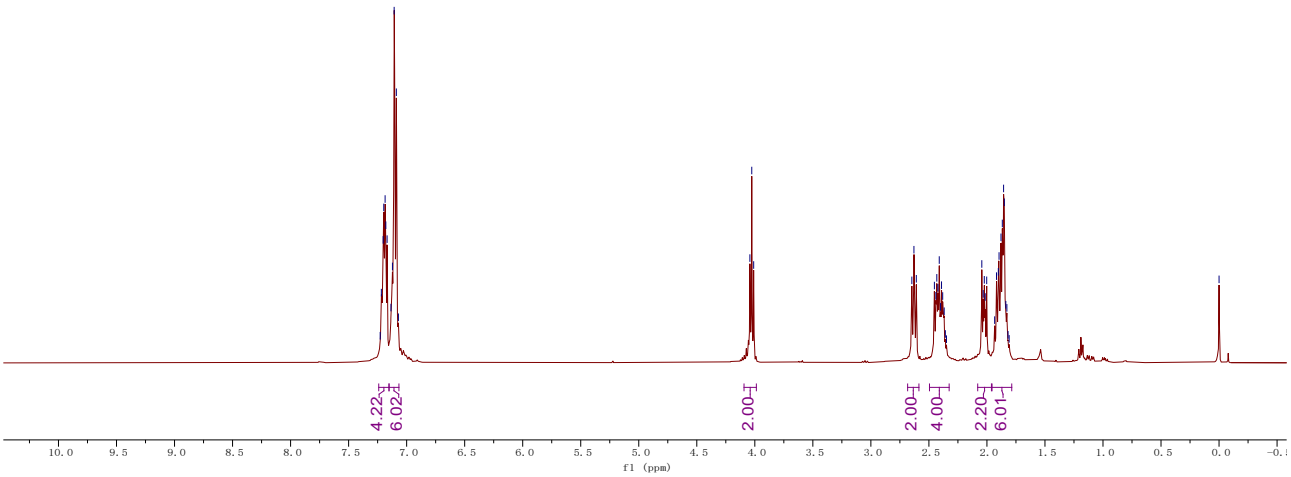
H
O
Ph

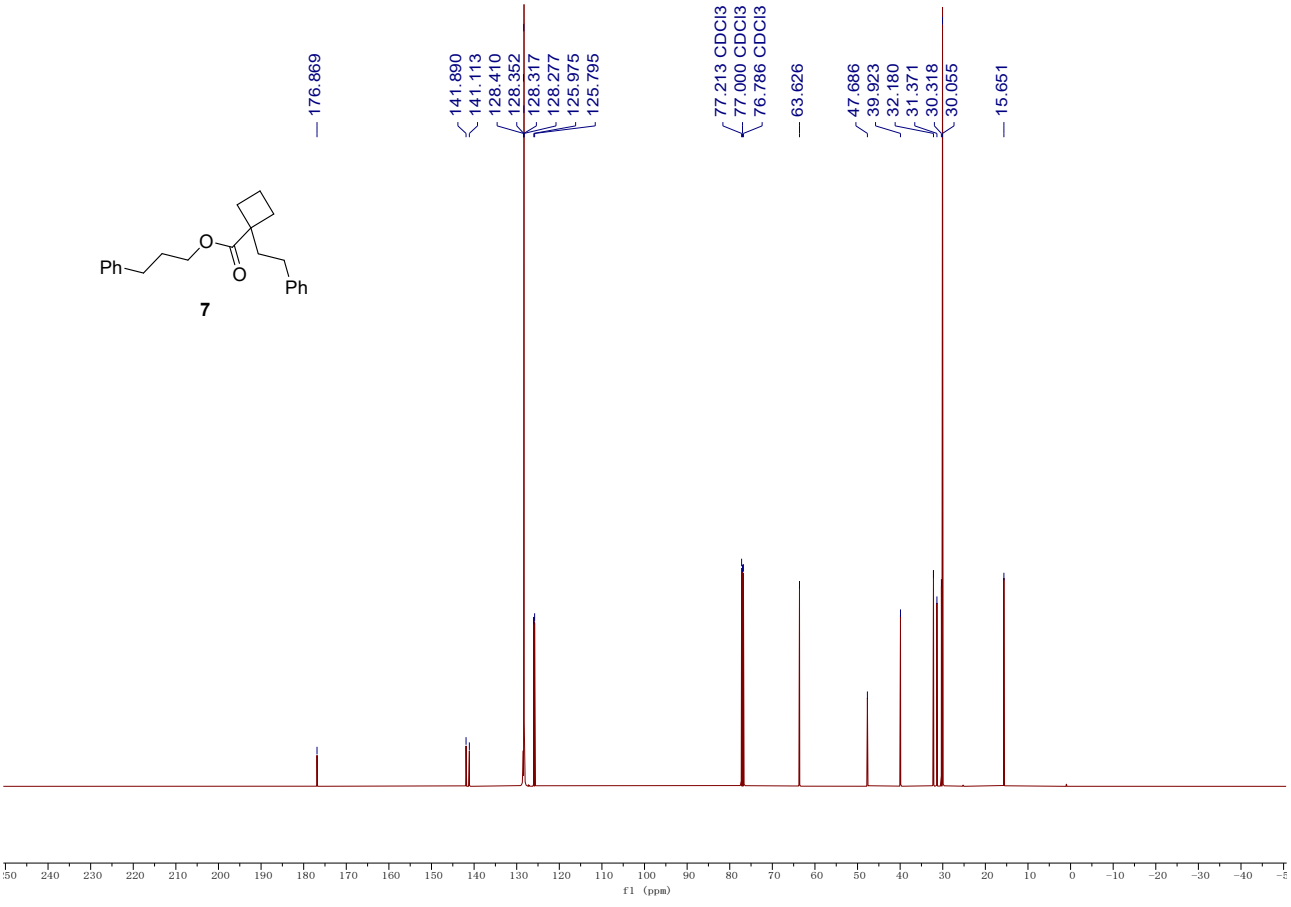
6


7.228
7.218
7.202
7.197
7.186
7.179
7.168
7.135
7.122
7.108
7.089
7.071
4.043
4.026
4.010
2.647
2.629
2.608
2.453
2.440
2.432
2.422
2.411
2.399
2.391
2.381
2.368
2.358
2.348
2.044
2.032
2.023
2.015
2.002
1.933
1.918
1.902
1.896
1.879
1.867
1.856
1.850
1.837
1.828
1.818
1.809
-0.000

Ph
O
O
Ph

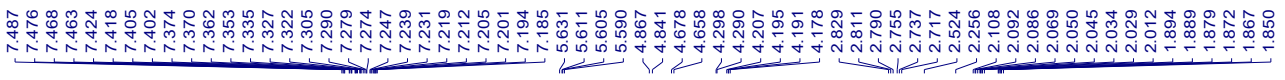
7

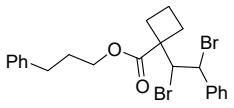

4.22
6.02
2.00
2.00
4.00
2.20
6.01
f1 (ppm)


176.869
141.890
141.113
128.410
128.352
128.317
128.277
125.975
125.795
77.213 CDCl3
77.000 CDCl3
76.786 CDCl3
63.626
47.686
39.923
32.180
31.371
30.318
30.055
15.651
f1 (ppm)

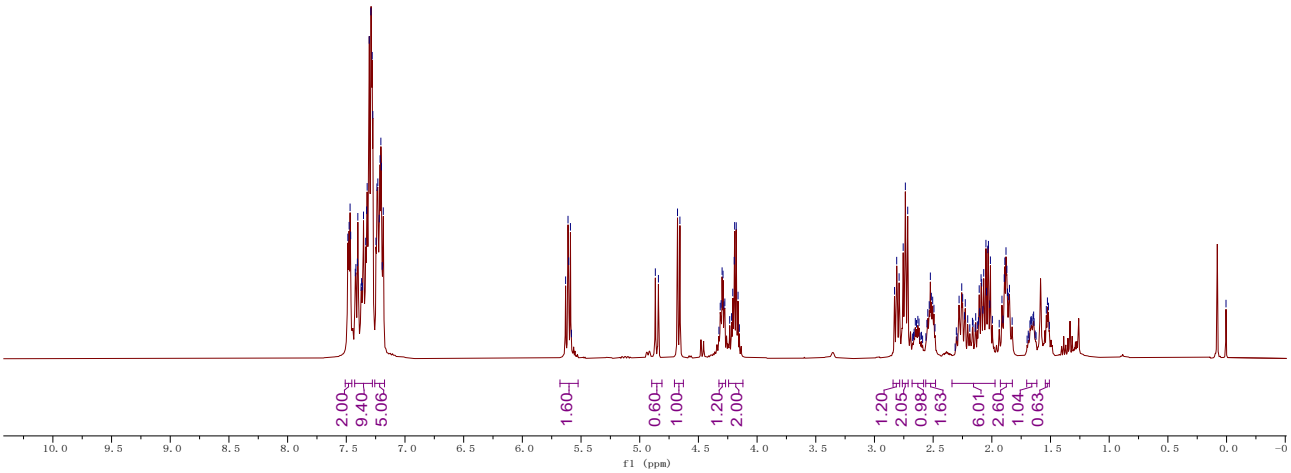
Ph
O
O
Ph

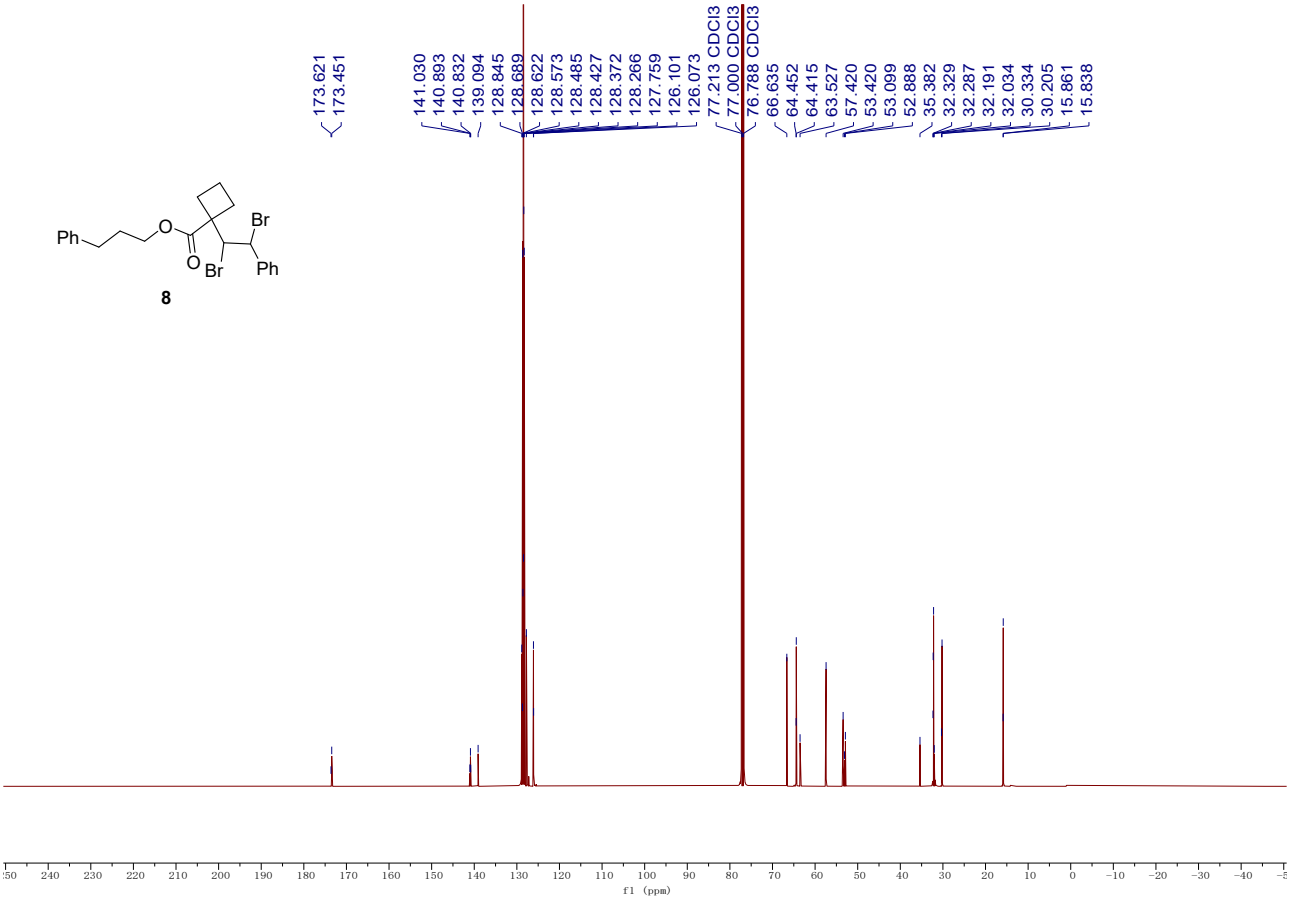
7


7.487
7.476
7.468
7.463
7.424
7.418
7.405
7.402
7.374
7.370
7.362
7.353
7.335
7.327
7.322
7.305
7.290
7.279
7.274
7.247
7.239
7.231
7.219
7.212
7.205
7.201
7.194
7.185
5.631
5.611
5.605
5.590
4.867
4.841
4.678
4.658
4.298
4.290
4.207
4.195
4.191
4.178
2.829
2.811
2.790
2.755
2.737
2.717
2.524
2.256
2.108
2.092
2.086
2.069
2.050
2.045
2.034
2.029
2.012
1.894
1.889
1.879
1.872
1.867
1.850


Ph
O
O
Br
Br
Ph

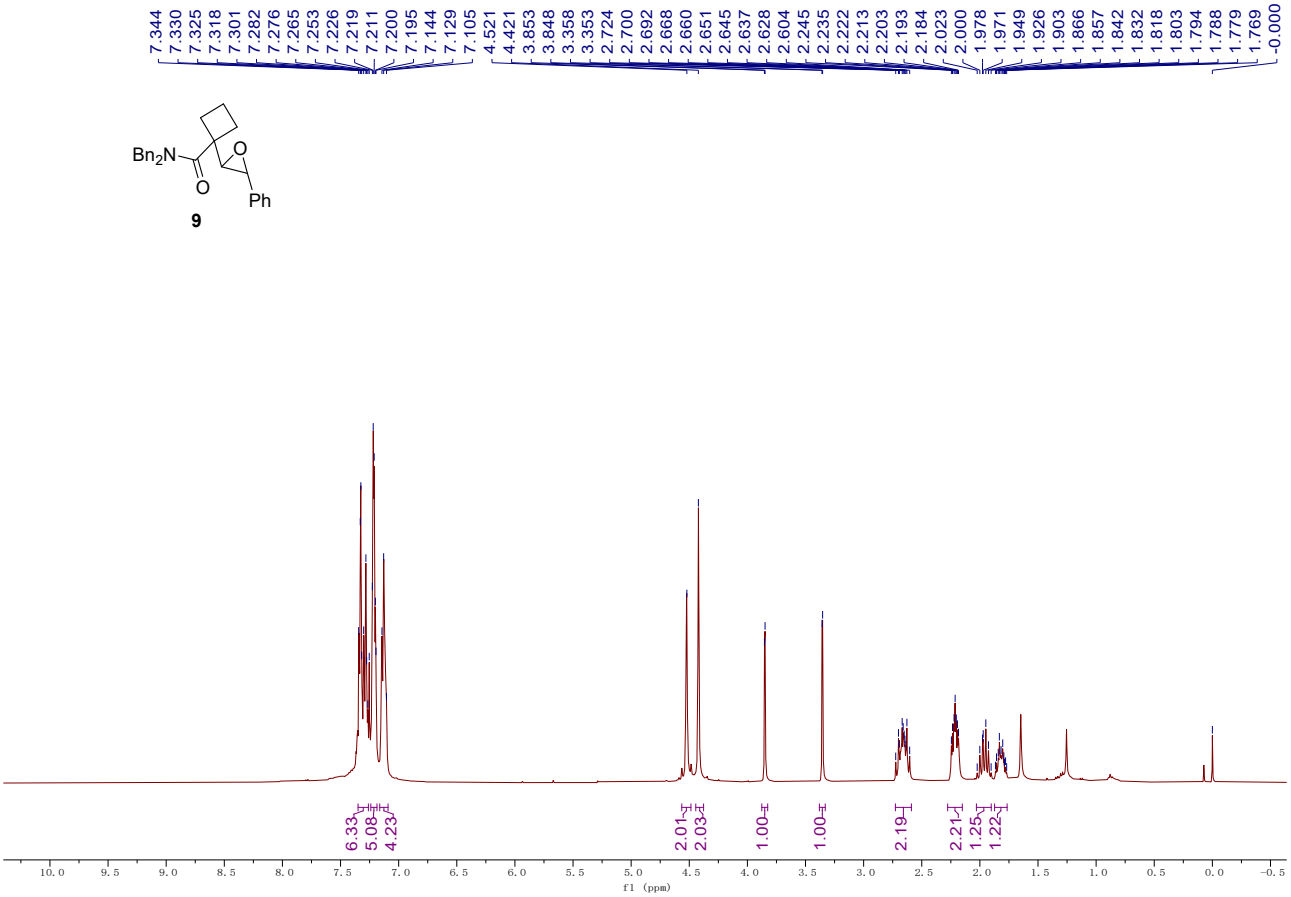
8

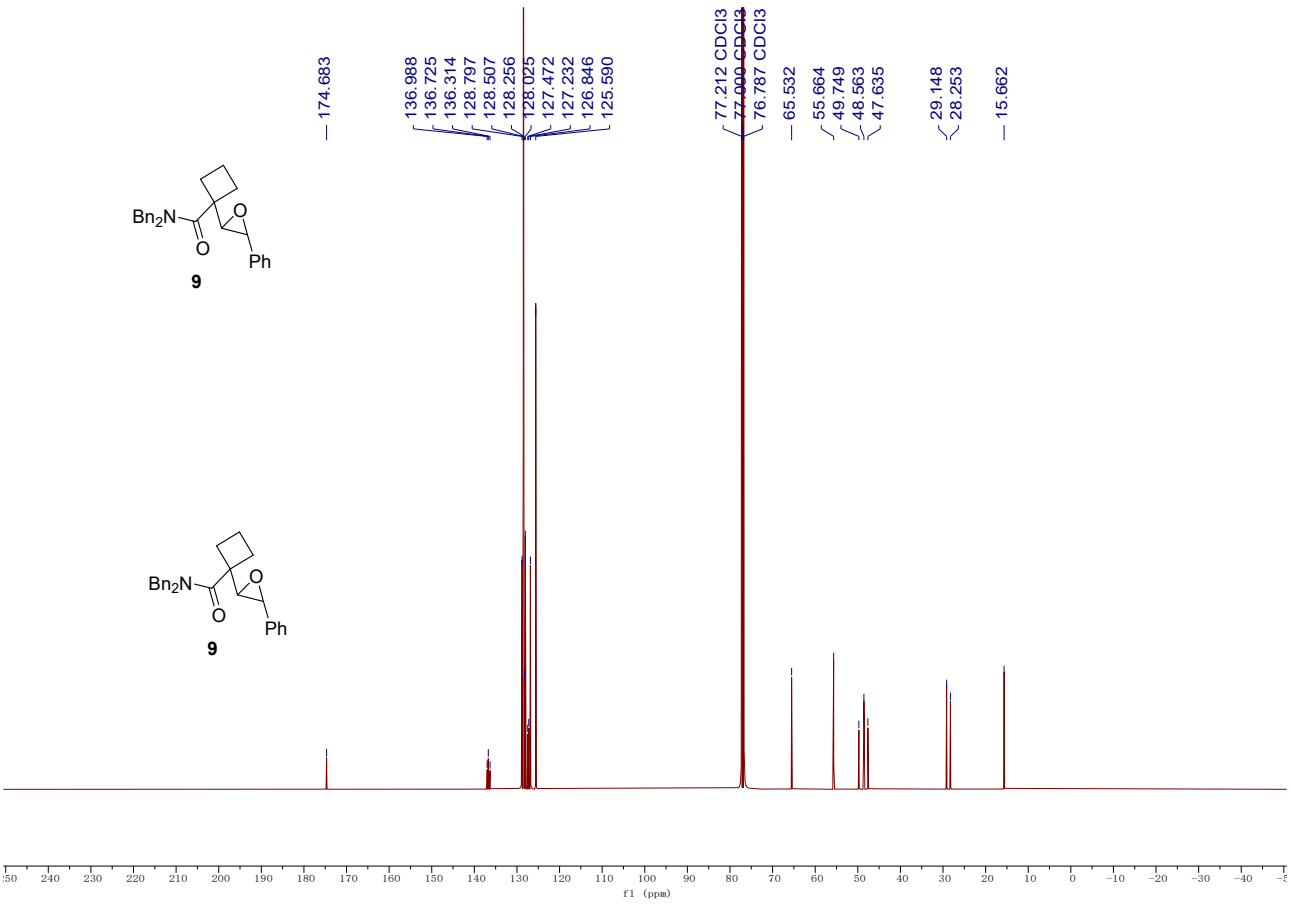

2.00
9.40
5.06
1.60
0.60
1.00
1.20
2.00
1.20
2.05
0.98
1.63
6.01
2.60
1.04
0.63
f1 (ppm)

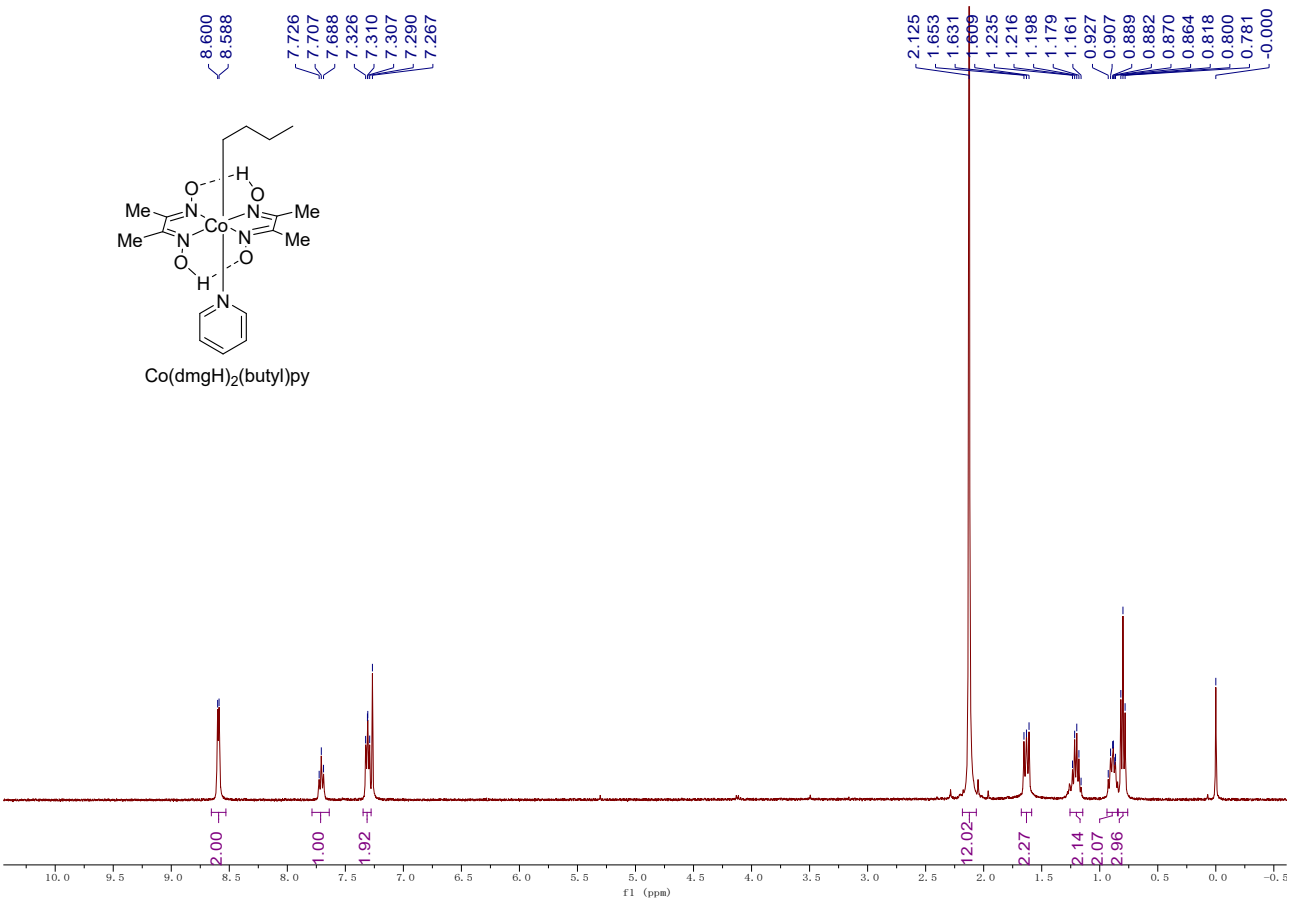

173.621
173.451
141.030
140.893
140.832
139.094
128.845
128.689
128.622
128.573
128.485
128.427
128.372
128.266
127.759
126.101
126.073
77.213 CDCl3
77.000 CDCl3
76.788 CDCl3
66.635
64.452
64.415
63.527
57.420
53.420
53.099
52.888
35.382
32.329
32.287
32.191
32.034
30.334
30.205
15.861
15.838
f1 (ppm)

Ph
O
O
Br
Br
Ph

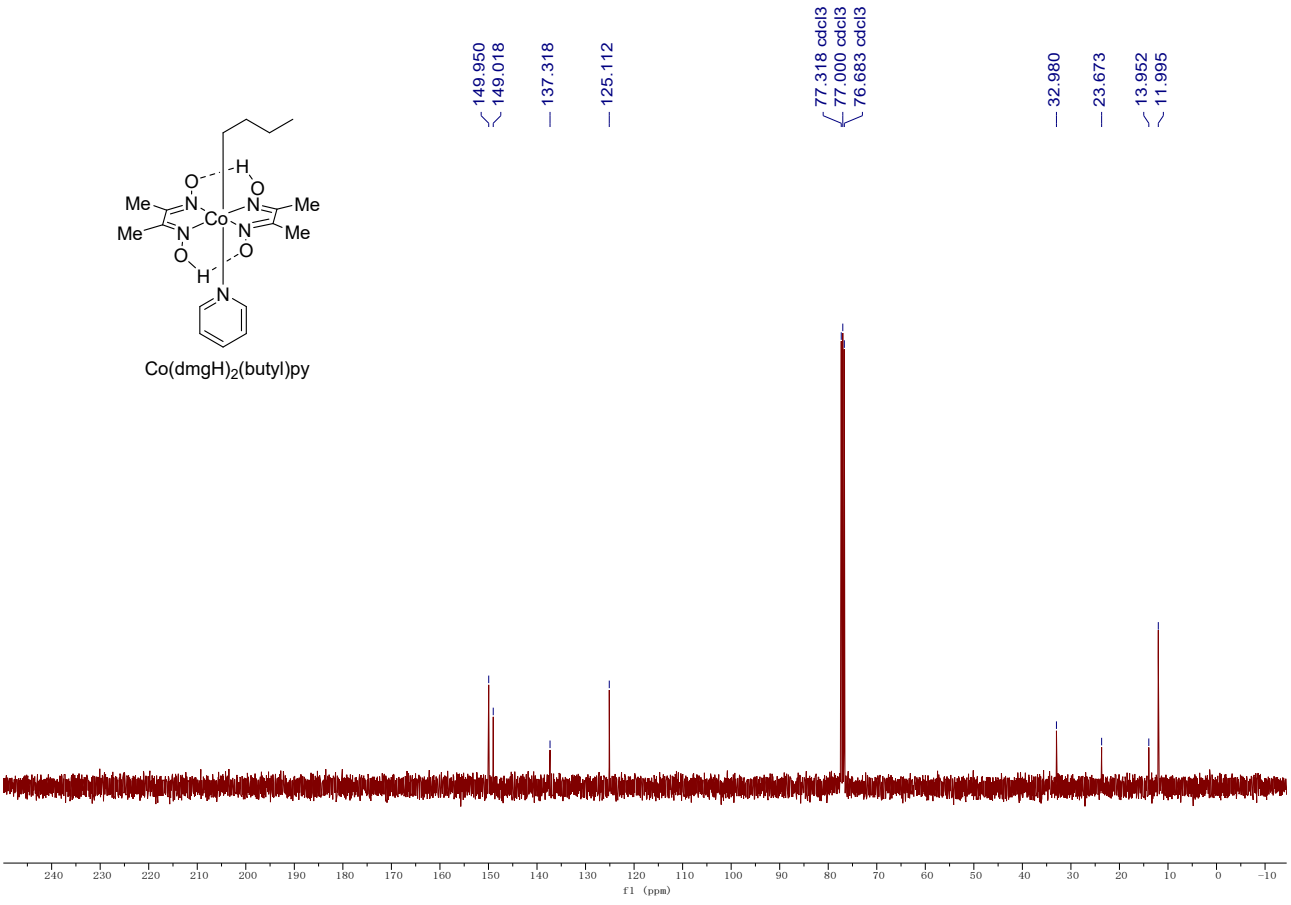
8


7.344
7.330
7.325
7.318
7.301
7.282
7.276
7.265
7.253
7.226
7.219
7.211
7.200
7.195
7.144
7.129
7.105
4.521
4.421
3.853
3.848
3.358
3.353
2.724
2.700
2.692
2.668
2.660
2.651
2.645
2.637
2.628
2.604
2.245
2.235
2.222
2.213
2.203
2.193
2.184
2.023
2.000
1.978
1.971
1.949
1.926
1.903
1.866
1.857
1.842
1.832
1.818
1.803
1.794
1.788
1.779
1.769
-0.000
Bn2N
O
O
Ph
9
6.33
5.08
4.23
2.01
2.03
1.00
1.00
2.19
2.21
1.25
1.22
f1 (ppm)

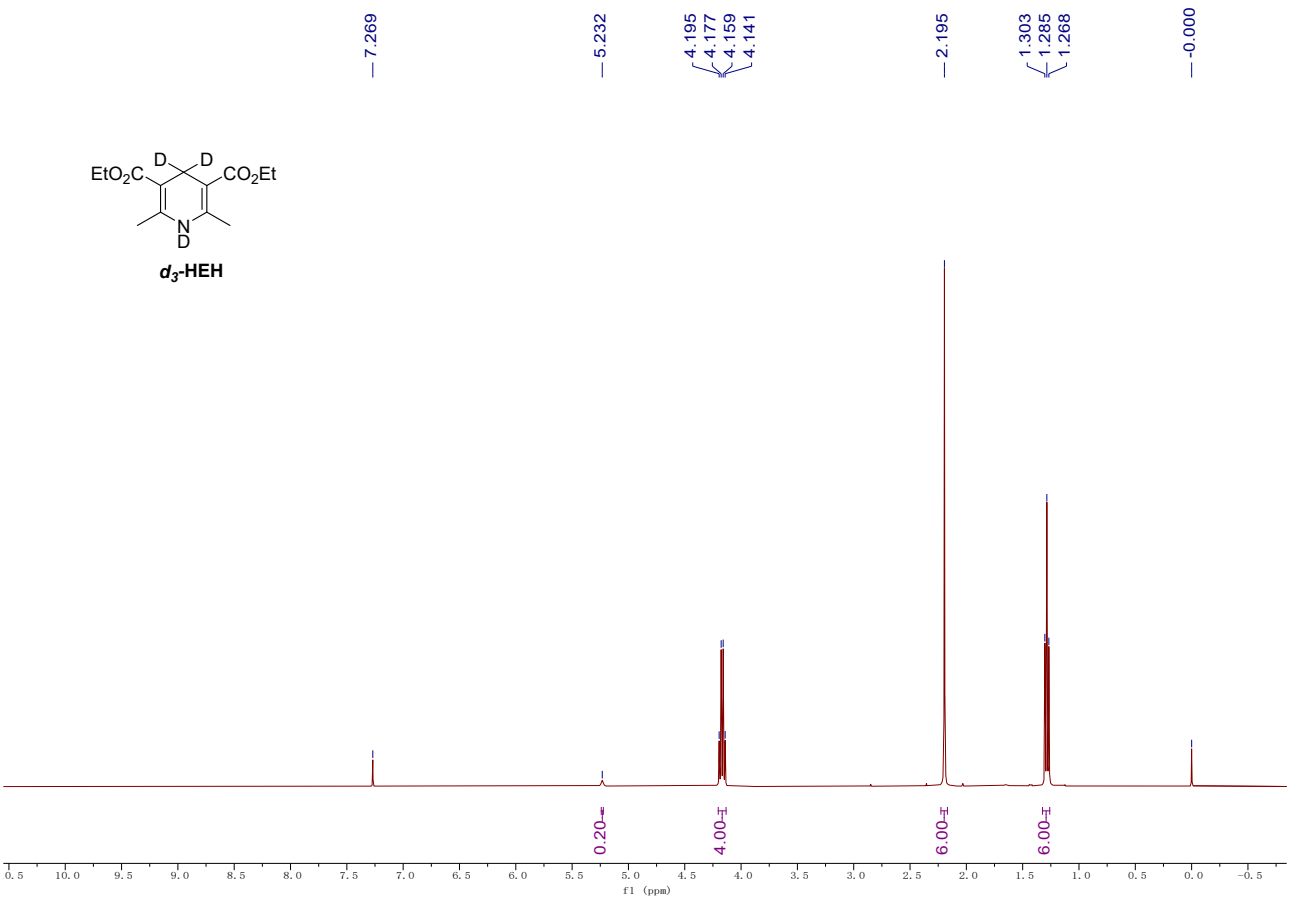

174.683
136.988
136.725
136.314
128.797
128.507
128.256
128.025
127.472
127.232
126.846
125.590
77.212 CDCl3
77.000 CDCl3
76.787 CDCl3
65.532
55.664
49.749
48.563
47.635
29.148
28.253
15.662
Bn2N
O
O
Ph
9
f1 (ppm)

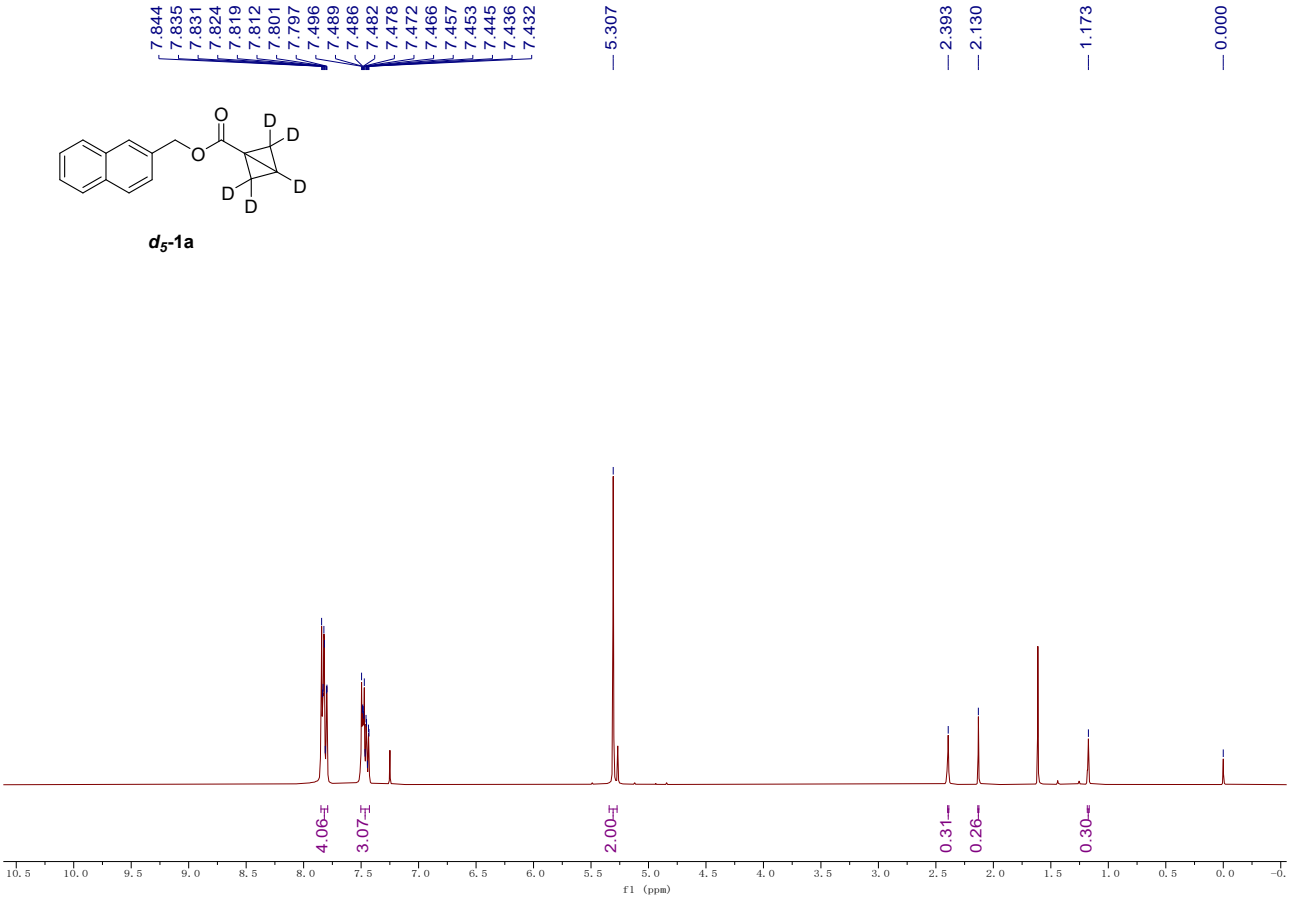


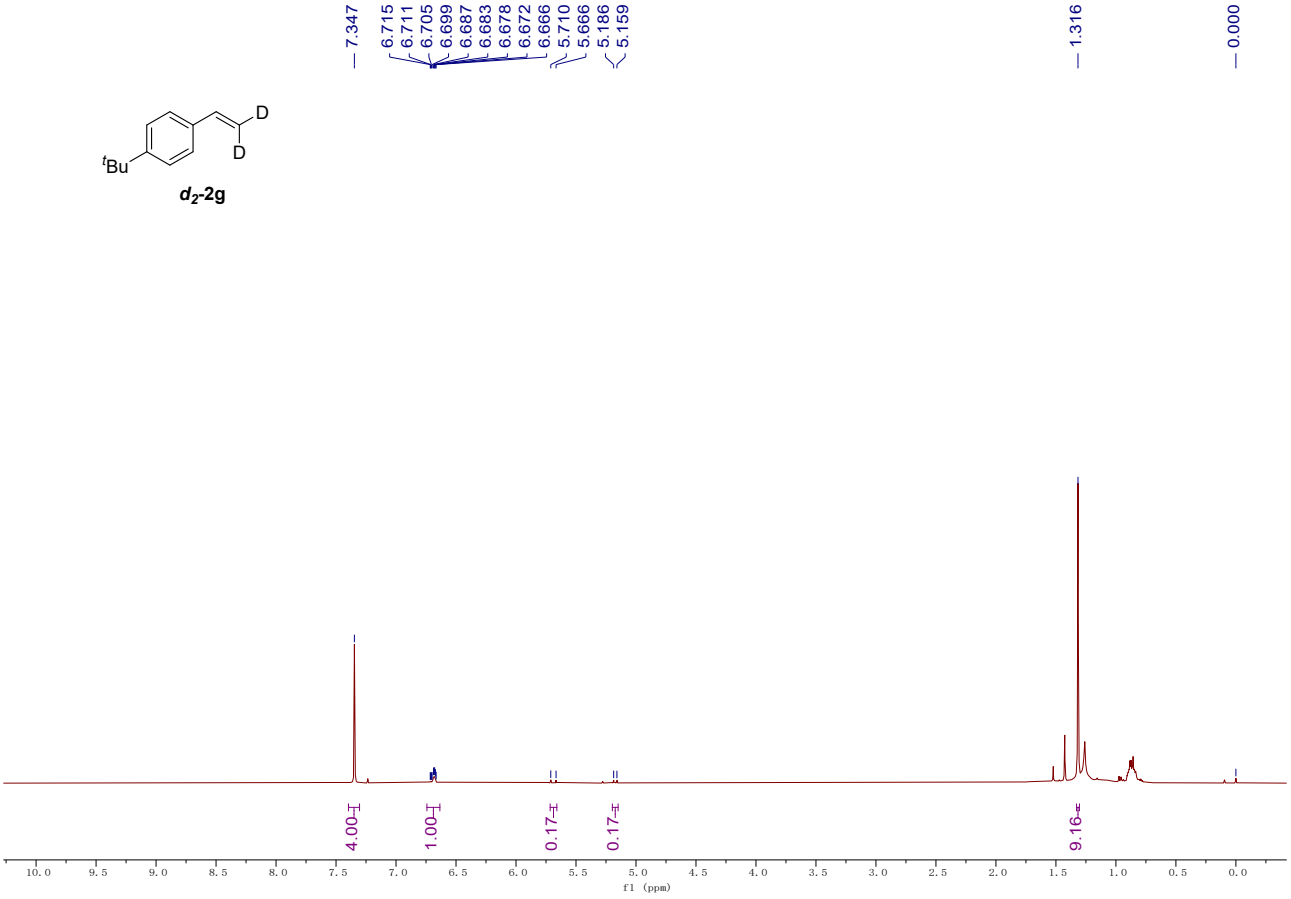
$Co(dmgH)_2(butyl)py$

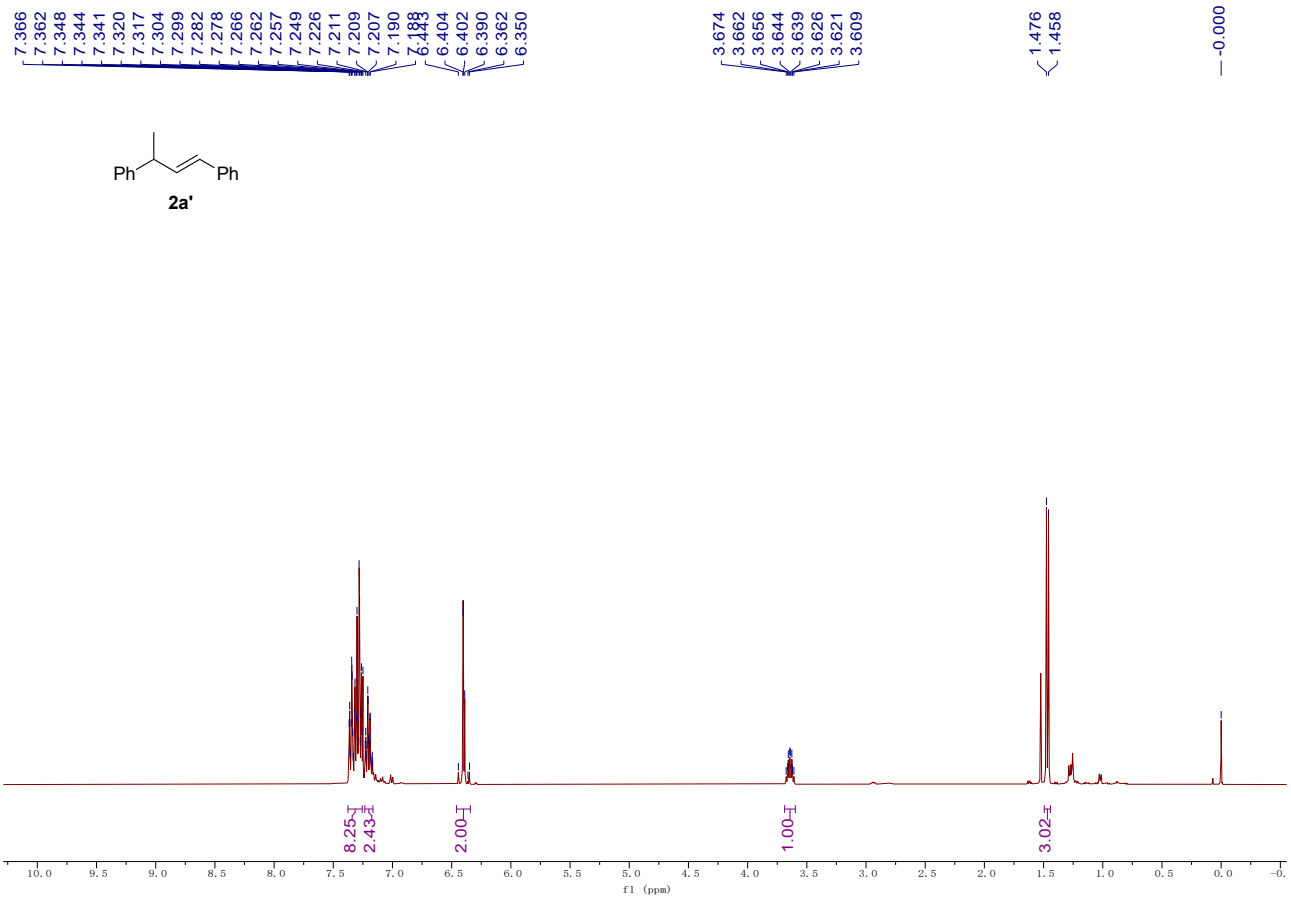


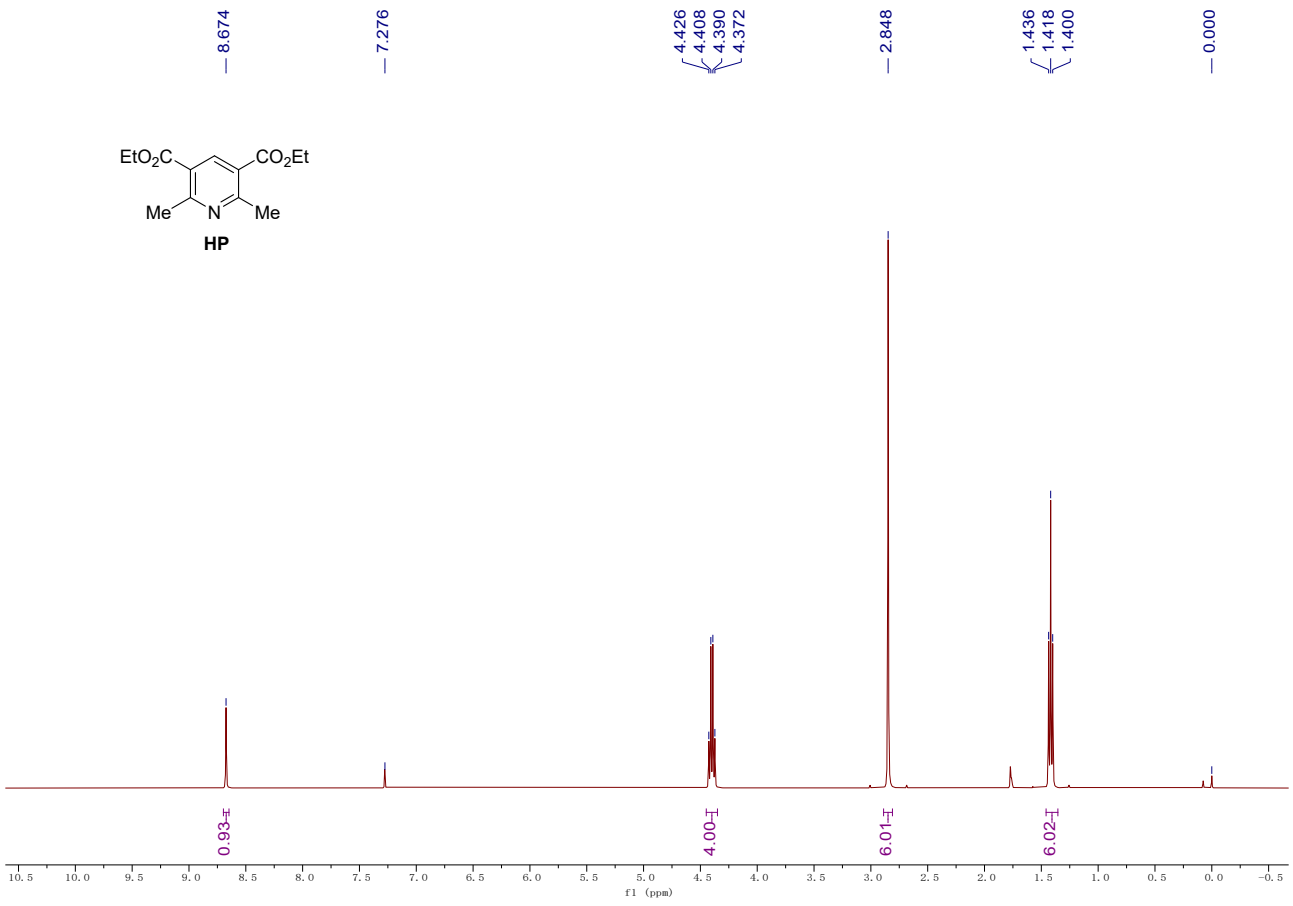
$Co(dmgH)_2(butyl)py$


7.269
5.232
4.195
4.177
4.159
4.141
2.195
1.303
1.285
1.268
-0.000
EtO2C
CO2Et
D
D
N
D
d3-HEH
0.20
4.00
6.00
6.00
f1 (ppm)


7.844
7.835
7.831
7.824
7.819
7.812
7.801
7.797
7.496
7.489
7.486
7.482
7.478
7.472
7.466
7.457
7.453
7.445
7.436
7.432
5.307
2.393
2.130
1.173
0.000
O
O
D
D
D
D
D
d5-1a
4.06
3.07
2.00
0.31
0.26
0.30
f1 (ppm)


7.347
6.715
6.711
6.705
6.699
6.687
6.683
6.678
6.672
6.666
5.710
5.666
5.186
5.159
1.316
0.000
D
D
tBu
d2-2g
4.00
1.00
0.17
0.17
9.16
f1 (ppm)


7.366
7.362
7.348
7.344
7.341
7.320
7.317
7.304
7.299
7.282
7.278
7.266
7.262
7.257
7.249
7.226
7.211
7.209
7.207
7.190
6.404
6.402
6.390
6.362
6.350
3.674
3.662
3.656
3.644
3.639
3.626
3.621
3.609
1.476
1.458
-0.000
Ph
Ph
2a'
8.25
2.43
2.00
1.00
3.02
f1 (ppm)


8.674
7.276
4.426
4.408
4.390
4.372
2.848
1.436
1.418
1.400
0.000
EtO2C
CO2Et
Me
N
Me
HP
0.93
4.00
6.01
6.02
f1 (ppm)

13. Reference

1) B. D. Schwartz, A. P. Smyth, P. E. Nashar, M. G. Gardiner and L. R. Malins, Investigating Bicyclobutane–Triazolinedione Cycloadditions as a Tool for Peptide Modification, *Org. Lett.*, 2022, **24**, 1268-1273.

2) H. Wang, H. Shao, A. Das, S. Dutta, H. T. Chan, C. Daniliuc, K. N. Houk and F. Glorius, Dearomative ring expansion of thiophenes by bicyclobutane insertion, *Science*, 2023, **381**, 75-81.

3) H. Gao, L. Guo, C. Shi, Y. Zhu, C. Yang and W. Xia, Transition Metal-Free Radical α-Oxy C-H Cyclobutylation via Photoinduced Hydrogen Atom Transfer, *Adv. Synth. Catal.*, 2022, **364**, 2140-2145.

4) D. Ni, S. Hu, X. Tan, Y. Yu, Z. Li and L. Deng, Intermolecular Formal Cycloaddition of Indoles with Bicyclo[1.1.0]butanes by Lewis Acid Catalysis, *Angew. Chem. Int. Ed.*, 2023, **62**, e202308606-e202308606.

5) S.-L. Lin, Y.-H. Chen, H.-H. Liu, S.-H. Xiang and B. Tan, Enantioselective Synthesis of Chiral Cyclobutenes Enabled by Bronsted Acid-Catalyzed Isomerization of BCBs, *J. Am. Chem. Soc.*, 2023, **145**, 21152-21158.

6) R. Guo, Y.-C. Chang, L. Herter, C. Salome, S. E. Braley, T. C. Fessard and M. K. Brown, Strain-Release [2π + 2σ] Cycloadditions for the Synthesis of Bicyclo[2.1.1]hexanes Initiated by Energy Transfer, *J. Am. Chem. Soc.*, 2022, **144**, 7988-7994.

7) S. Yu, A. Noble, R. B. Bedford and V. K. Aggarwal, Methylenespiro[2.3]hexanes via Nickel-Catalyzed Cyclopropanations with [1.1.1]Propellane, *J. Am. Chem. Soc.*, 2019, **141**, 20325-20334.

8) (a) J.-L. Tu, W. Tang, S.-H. He, M. Su and F. Liu, Acceptorless dehydrogenative amination of alkenes for the synthesis of *N*-heterocycles, *Sci. China Chem.*, 2022, **65**, 1330-1337; (b) X. Sun, J. Chen and T. Ritter, Catalytic dehydrogenative decarboxyolefination of carboxylic acids, *Nat. Chem.*, 2018, **10**, 1229-1233; (c) K. C. Cartwright, E. Joseph, C. G. Comadoll and J. A. Tunge, Photoredox/Cobalt Dual-Catalyzed Decarboxylative Elimination of Carboxylic Acids: Development and Mechanistic Insight, *Chem. Eur. J.*, 2020, **26**, 12454-12471.

9) X.-Y. Zhang, C. Ning, B. Mao, Y. Wei and M. Shi, A visible-light mediated ring opening

reaction of alkylidenecyclopropanes for the generation of homopropargyl radicals, *Chem. Sci.*, 2021, **12**, 9088-9095.

10) S. Miki, S.-i. Matsumura, T. Ohno and Z.-i. Yoshida, Co(II)porphyrin catalyzed isomerization of bicyclobutanecarbonitrile, *Tetrahedron Lett.*, 1986, **27**, 3669-3672.

11) Y.-H. Yao, H.-Y. Yang, M. Chen, F. Wu, X.-X. Xu and Z.-H. Guan, Asymmetric Markovnikov Hydroaminocarbonylation of Alkenes Enabled by Palladium-Monodentate Phosphoramidite Catalysis, *J. Am. Chem. Soc.*, 2021, **143**, 85-91.

12) H. Cao, Y. Kuang, X. Shi, K. L. Wong, B. B. Tan, J. M. C. Kwan, X. Liu and J. Wu, Photoinduced site-selective alkenylation of alkanes and aldehydes with aryl alkenes, *Nat. Commun.*, 2020, **11**, 1956.

13) E. Bergamaschi, V. J. Mayerhofer and C. J. Teskey, Light-Driven Cobalt Hydride Catalyzed Hydroarylation of Styrenes, *ACS Catal.*, 2022, **12**, 14806-14811.

14) X. Wu, W. Hao, K.-Y. Ye, B. Jiang, G. Pombar, Z. Song and S. Lin, Ti-Catalyzed Radical Alkylation of Secondary and Tertiary Alkyl Chlorides Using Michael Acceptors, *J. Am. Chem. Soc.*, 2018, **140**, 14836-14843.

15) M. Ociepa, A. J. Wierzba, J. Turkowska and D. Gryko, Polarity-Reversal Strategy for the Functionalization of Electrophilic Strained Molecules via Light-Driven Cobalt Catalysis, *J. Am. Chem. Soc.*, 2020, **142**, 5355-5361.

16) T. Pinkert, M. Das, M. L. Schrader and F. Glorius, Use of Strain-Release for the Diastereoselective Construction of Quaternary Carbon Centers, *J. Am. Chem. Soc.*, 2021, **143**, 7648-7654.

17) P.-F. Chen, D.-S. Li, W.-T. Ou, F. Xue and H.-P. Deng, 2-Isopropylthioxanthone-Catalyzed Divergent Functionalization of Bicyclo[1.1.0]butanes under Visible-Light Irradiation, *Org. Lett.*, 2023, **25**, 6184-6188.

18) K. J. Woelk, K. Dhake, N. D. Schley and D. C. Leitch, Enolate addition to bicyclobutanes enables expedient access to 2-oxo-bicyclohexane scaffolds, *Chem. Commun.*, 2023, **59**, 13847-13850.

19) Y.-J. Chen, T.-J. Hu, C.-G. Feng and G.-Q. Lin, Synthesis of chiral cyclobutanes via rhodium/diene-catalyzed asymmetric 1,4-addition: a dramatic ligand effect on the

diastereoselectivity, *Chem. Commun.*, 2015, **51**, 8773-8776.

20) Y.-J. Wu, C. Ma, J.-F. Qiao, X.-Y. Cheng and Y.-F. Liang, Nickel-catalysed highly regioselective synthesis of β-acyl naphthalenes under reductive conditions, *Chem. Commun.*, 2024, **60**, 5723-5726.