Supplemental information

Synthesis of Constrained Bicycloalkanes through Bibase-Promoted Brook rearrangement/Radical-Polar Crossover Cyclization

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1. General Information

1.1. Solvents, Reagents and Starting Materials

All reagents were used as received unless otherwise stated from Sigma-Aldrich, Energy Chemical, Adamas-beta®, and Bidepharm. Water is de-ionised and brine refers to a saturated aqueous solution of NaCl. MeCN was anhydrous, purchased from Energy Chemical and Adamas-beta® and used as received. Dichloromethane (CH_2Cl_2) was anhydrous (purification using a column composed of activated alumina). 4CzIPN was prepared following the method of papers.[1]

1.2. Chromatography and Instrumentation

Flash column chromatography was carried out using silica gel (Aldrich, silica gel 60, 40-63 μm). Analytical thin-layer chromatography (TLC) was performed using aluminium-backed silica plates (0.25 mm, Merck, silica gel 60 F254). Compounds were visualised under UV light or by staining with aqueous basic potassium permanganate, an ethanolic solution of phosphomolybdic acid (PMA), or an ethanolic solution of ninhydrin.

^{1}H, ^{13}C and ^{11}B NMR spectra were acquired at various field strengths, as indicated, using Bruker 400 MHz, Varian VNMR 400 MHz, Varian VNMR 500 MHz, and Bruker Cryo 500 MHz spectrometers. All NMR spectra were recorder at 25 °C unless otherwise stated. Chemical shifts (δ) are given in parts per million (ppm) and referenced to $CDCl_3$ (^{1}H: 7.26 ppm) or DMSO-d_6 (^{1}H: 2.50 ppm). Coupling constants (*J*) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, h = heptet, m = multiplet, dd = doublet of doublets, etc.). The ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons).

Gas chromatography (GC) was performed on an Agilent Technologies 6890N Network GC System using an Agilent HP-5 column (15 m × 0.25 mm × 0.25 μm).

High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF instrument using electrospray ionisation (ESI). Low-resolution mass spectra (LRMS) were recorded on an Agilent 7820A

GC-MS equipped with a HP-5MS UI column (30 m x 0.25 mm x 0.25 μm) using electron ionisation (EI).

Infra-red (IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer as a thin film. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}).

Melting points were recorded in degrees Celsius (℃), using a Kofler hot-stage microscope apparatus and are reported uncorrected.

For quantum yield experiments, commercially available potassium ferrioxalate trihydrate (Alfa Aesar) was used for actinometry, and all the absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis Spectrophotometer.

1.3. Photochemical Equipment and Setup

The blue LED lamps were either 30 W 425 nm blue LED with a fan or 40 W Kessil PR160-427 nm LED Photoredox Lights (used with the intensity dial set to 100) from Anhui Chem-n Instrument CO., Ltd.

During the course of the photoredox reactions, heat generated from the LED lamps resulted in warming of the reaction mixtures to approximately 40 °C. For reactions performed in MeCN, fan cooling was used to maintain a temperature of 25–30 °C.

Reaction set-up:

The reaction vials were positioned 5 cm from a single 30 W blue LED lamp (Figure S1).

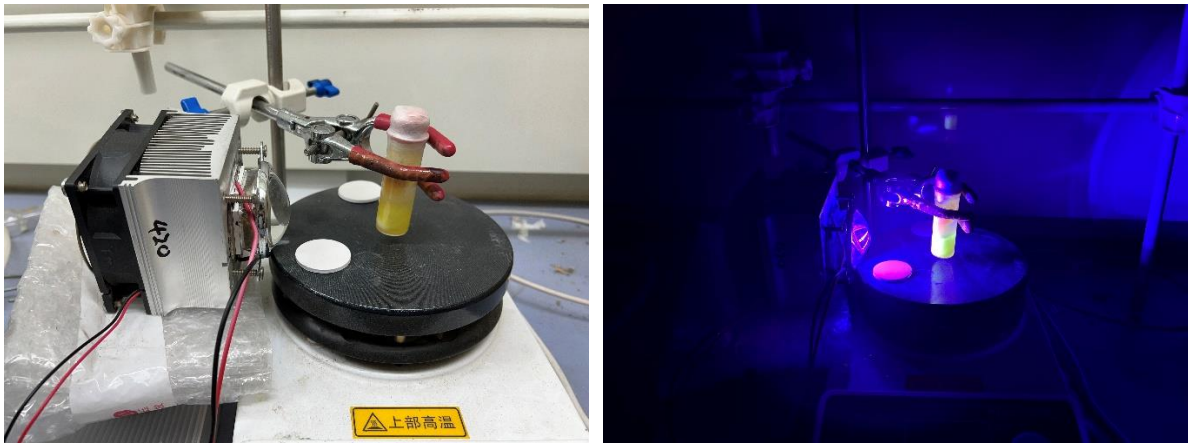
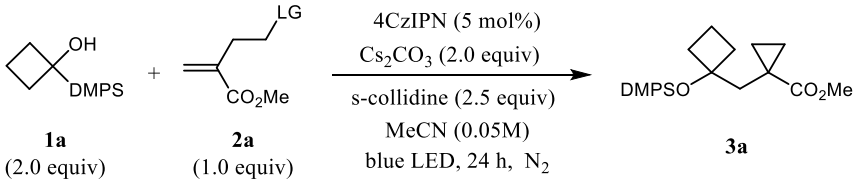


Figure S1. Photoredox reaction setup.

2. Optimization studies

Table 1. Optimization of the reaction conditions.[a]

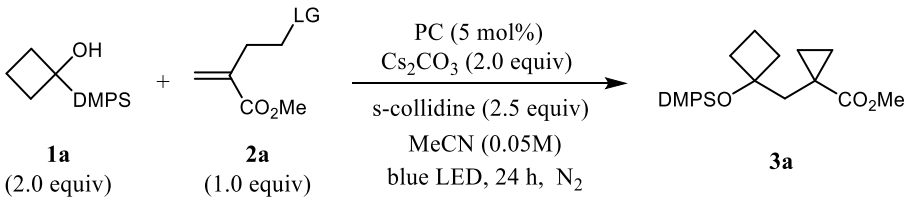


1a (2.0 equiv) **2a** (1.0 equiv) **3a**

Entry	Variation from standard conditions	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	none	90	100
2	1 mol% 4CzIPN	70	100
3	Without Cs_2CO_3	60	100
4	Without s-collidine	65	100
5	Et_3N instead of s-collidine	0	100
6	1.5 equiv of **1a**	50	70
7	Eosin Y (5 mol%) instead of 4CzIPN	44	100
8[c]	Ir-dF (1 mol%) instead of 4CzIPN	85	100
9[d]	$Ru(bpy)_3Cl_2$ (1 mol%) instead of 4CzIPN	0	0
10	DCE instead of MeCN	65	100
11	Without light	0	0
12	Without 4CzIPN	0	0
13	Under air	75	100

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), 4CzIPN (5 mol%), Cs_2CO_3 (2.0 mmol), s-collidine (2.5 mml), solvent (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$, LG = - OTs. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Ir-dF = $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$. [d] bpy = 2,2-bipyridine.

Scheme S1. Optimization the reaction by changing the photo-catalyst (related to Table 1)[a]

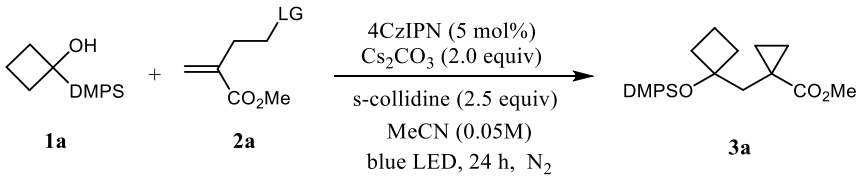


1a (2.0 equiv) **2a** (1.0 equiv) **3a**

Entry	photocatalyst	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	4CzIPN (5 mol%)	90	100
2	4CzIPN (3 mol%)	74	100
3	4CzIPN (1 mol%)	70	100
4	Eosin Y (5 mol%)	44	100
5[c]	Ir-dF (1 mol%)	85	100
6[d]	$Ru(bpy)_3Cl_2·6H_2O$ (1mol%)	0	0
7	Ir(ppy)3 (1mol%)	0	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), PC, Cs_2CO_3 (2.0 mmol), s-collidine (2.5 mmol), MeCN (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$, LG = - OTs. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Ir-dF = $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$. [d] bpy = 2,2-bipyridine. [e] ppy = 2-phenylpyridine.

Scheme S2. Optimization of ratio of two reactants (related to Table 1)[a]

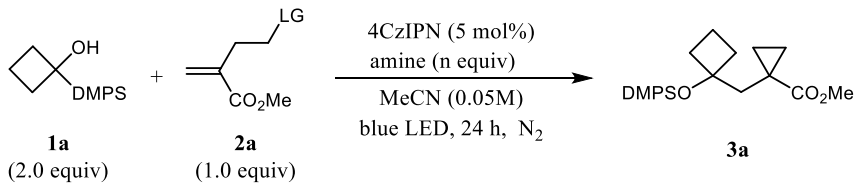


1a **2a** **3a**

Entry	**1a**/**2a**	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	1/1	45	60
2	1.5/1	50	70
3	2/0	90	100

[a] Reaction conditions: **1a**, **2a**, 4CzIPN (5 mol%), Cs_2CO_3 (2.0 mmol), s-collidine (2.5 mmol), MeCN (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$, LG = - OTs. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Scheme S3. Optimization the reaction by changing the amine (related to Table 1)[a]



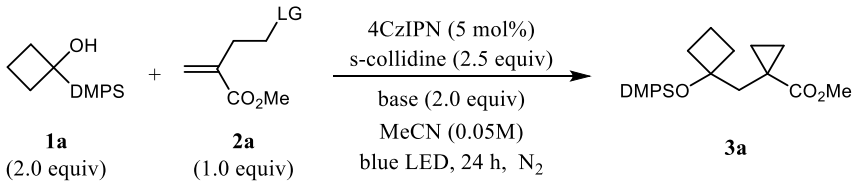
1a (2.0 equiv) **2a** (1.0 equiv) **3a**

Entry	Amine (n equiv)	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	Et_3N (2.5 equiv)	0	100
2	Pyridine (2.5 equiv)	30	100
3	4-aminopyridine (2.5 equiv)	5	100

4	2,3-lutidine (2.5 equiv)	38	100
5	2-chloroprydine (2.5 equiv)	0	97
6	4-dimethylaminopridine (2.5 equiv)	0	100
7	s-collidine (4.5 equiv)	75	100
8	s-collidine (2.5 equiv)	60	100
9	s-collidine (2.0 equiv)	30	100
10	s-collidine (1.0 equiv)	25	100

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), 4CzIPN (5 mol%), amine (2.5 mmol), MeCN (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$, LG = - OTs. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Scheme S4. Optimization the reaction by changing the base (related to Table 1)[a]

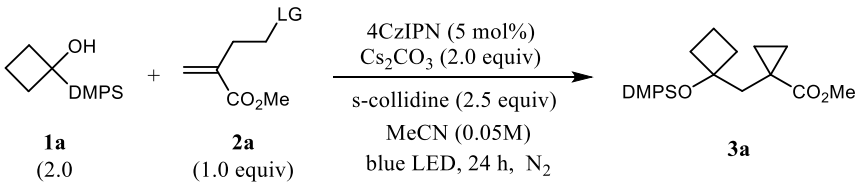


1a (2.0 equiv) **2a** (1.0 equiv) **3a**

Entry	base	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	Cs_2CO_3 (without s-collidine)	65	100
2	Cs_2CO_3	90	100
3	Na_2CO_3	75	100

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), 4CzIPN (5 mol%), base (2.0 mmol), s-collidine (2.5 mmol), MeCN (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$, LG = - OTs. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Scheme S5. Optimization the reaction by changing the solvent (related to Table 1)[a]



1a (2.0 equiv) **2a** (1.0 equiv) **3a**

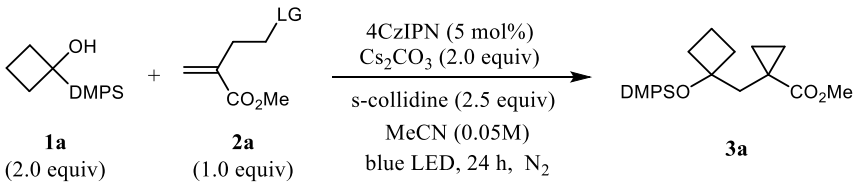
55

Entry	solvent	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	1,4-dioxane	42	100
2	DMF	20	100
3	DMSO	0	100
4	MeCN	90	100

5	DCE	65	100
6	THF	50	100

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), 4CzIPN (5 mol%), Cs_2CO_3 (2.0 mmol), s-collidine (2.5 mmol), solvent (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$, LG = - OTs. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Scheme S6. Optimization the reaction by changing the leaving group (related to Table 1)[a]

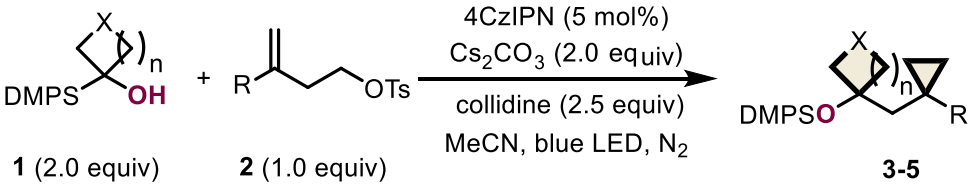


1a (2.0 equiv) **2a** (1.0 equiv) **3a**

Entry	LG	Yield of **3a** (%)[b]	Conversion of **2a** (%)[b]
1	Cl	50	100
2	Br	65	100
3	I	0	100
4	OMs	75	100
5	OTs	90	100

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), 4CzIPN (5 mol%), Cs_2CO_3 (2.0 mmol), s-collidine (2.5 mmol), MeCN (2.0 mL), 25 ºC, 24 h, N_2, 30 W blue LED, in vials; DMPS = - $SiMe_2Ph$. [b] Yields and conversions were determined after aqueous workup by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

3.General Procedure A for Photo Reaction



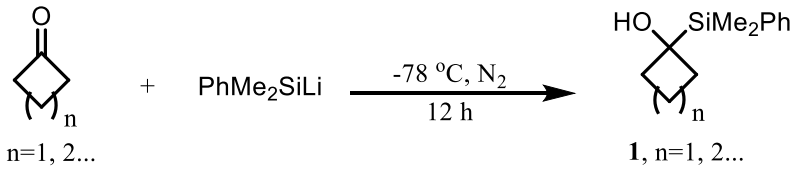
1 (2.0 equiv) **2** (1.0 equiv) **3-5**

To a dry 7 mL vial equipped with a magnetic stir bar was added the olefin precursor (1.0 equiv), 4CzIPN (5 mol%), Cs_2CO_3 (2.0 equiv), s-collidine (2.5 equiv) and α-silyl cyclic alcohol (2.0 equiv). Then anhydrous MeCN (0.05M) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The reaction inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for typically 24 h with TLC monitoring. After the reaction completion,

the solvent was removed in *vacuo* by rotary evaporation and crude product was then purified by flash SiO_2 column chromatography gave the corresponding product.

4. Synthesis of Substrates

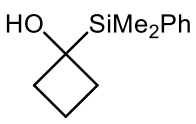
General Procedure B:



In a glovebox, to an oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar was added lithium (620.1 mg, 78.0 mmol, 7.8 equiv.), dry THF (20 mL) and chlorodimethylphenylsilane (2219.2 mg, 13.0 mmol, 1.3 equiv.) sequentially. Under N_2 atmosphere, the resulting mixture was stirred at 0 ºC for 8 h. The resulting $PhMe_2SiLi$ solution was used directly in the next step without further purification. Under N_2 atmosphere, to a solution of cyclic ketones in toluene (20 mL), $PhMe_2SiLi$ (1.3−1.5 equiv.) were added at −78 ℃ in 60 minutes. The resulting mixture was stirred at −78 ℃ for 12 h. The reaction was quenched by addition of saturated NH_4Cl aqueous solution (40 mL). Then the resulting mixture was extracted with EA (3×40 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified with column chromatography on silica gel (200~300 mesh) with PE/EA = 10/1 (v/v) as eluent to afford the desired product **1**.

All recorded spectroscopic data of **1a-1a′** matched those previously reported in the literature.[2]

1-(Dimethyl(phenyl)silyl)cyclobutan-1-ol (1a)

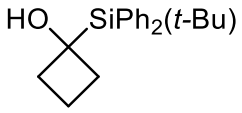


Prepared following the General Procedure B using cyclobutanone. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **1a** (1.40 g, 6.78 mmol, 68%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.70 – 7.59 (m, 2H), 7.47 – 7.35 (m, 3H), 2.41 – 2.30 (m, 2H), 2.09 – 1.93 (m, 2H), 1.79 – 1.67 (m, 1H), 1.58 (s, 1H), 1.33 – 1.18 (m, 1H), 0.42 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.3, 134.2, 129.4, 127.9, 67.9, 35.3, 12.9, -6.3 ppm.

1-(tert-butyldiphenylsilyl)cyclobutan-1-ol (1aa)

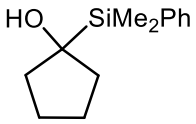


Prepared following the General Procedure B using cyclobutanone. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **1aa** (268 mg, 0.91 mmol, 18%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 – 7.78 (m, 4H), 7.48 – 7.39 (m, 6H), 2.69 – 2.57 (m, 2H), 2.15 – 2.03 (m, 2H), 1.67 (s, 1H), 1.58 – 1.48 (m, 1H), 1.23 (s, 9H), 0.58 – 0.43 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.4, 133.9, 129.1, 127.5, 70.5, 38.5, 28.9, 19.2, 13.1 ppm.

1-(Dimethyl(phenyl)silyl)cyclopentan-1-ol (1b)

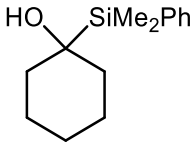


Prepared following the General Procedure B using cyclopentanone. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **1b** (1.33 g, 6.04 mmol, 60%) as a pale orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.57 (m, 2H), 7.43 – 7.34 (m, 3H), 1.90 – 1.77 (m, 2H), 1.71 – 1.62 (m, 4H), 1.60 – 1.51 (m, 2H), 1.00 (s, 1H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.8, 134.3, 129.2, 127.8, 74.9, 37.6, 23.7, -5.7 ppm.

1-(Dimethyl(phenyl)silyl)cyclohexan-1-ol (1c)

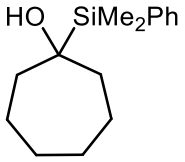


Prepared following the General Procedure B using cyclohexanone. Purification by flash column chromatography (7% EtOAc/Petroleum ether) gave the title compound **1c** (1.14 g, 4.86 mmol, 72%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.53 (m, 2H), 7.40 – 7.34 (m, 3H), 1.71 – 1.57 (m, 5H), 1.53 – 1.37 (m, 4H), 1.23 – 1.13 (m, 1H), 1.12 (s, 1H), 0.35 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.3, 134.5, 129.2, 127.7, 65.4, 33.0, 25.9, 19.9, -6.4 ppm.

1-(Dimethyl(phenyl)silyl)cycloheptan-1-ol (1d)

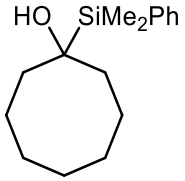


Prepared following the General Procedure B using cycloheptanone. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **1d** (1.76 g, 7.08 mmol, 71%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.52 (m, 2H), 7.42 – 7.34 (m, 3H), 1.82 – 1.58 (m, 8H), 1.51 – 1.44 (m, 2H), 1.36 – 1.26 (m, 2H), 0.90 (s, 1H), 0.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.7, 134.6, 129.2, 127.7, 68.4, 37.6, 29.8, 21.8, -5.9 ppm.

1-(Dimethyl(phenyl)silyl)cyclooctan-1-ol (1e)

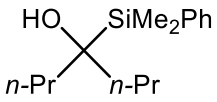


Prepared following the General Procedure B using cyclooctanone. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **1e** (1.83 g, 6.96 mmol, 70%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.56 (m, 2H), 7.40 – 7.34 (m, 3H), 1.84 – 1.66 (m, 5H), 1.66 – 1.54 (m, 5H), 1.48 – 1.41 (m, 2H), 1.40 – 1.34 (m, 2H), 0.77 (s, 1H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 136.9, 134.6, 129.1, 127.7, 68.7, 33.2, 28.2, 24.6, 21.2, -5.2 ppm.

4-(dimethyl(phenyl)silyl)heptan-4-ol (1f)

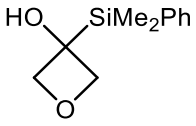


Prepared following the General Procedure B using heptan-4-one. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **1f** (1.79 g, 7.16 mmol, 72%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 – 7.56 (m, 2H), 7.40 – 7.33 (m, 3H), 1.56 (s, 1H), 1.54 – 1.47 (m, 4H), 1.26 (tt, J = 9.8, 4.1 Hz, 4H), 0.86 (t, J = 7.2 Hz, 6H), 0.84 (s, 1H), 0.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 137.2, 134.5, 129.1, 127.7, 69.1, 39.6, 16.6, 14.8, -4.5 ppm.

3-(dimethyl(phenyl)silyl)oxetan-3-ol (1g)

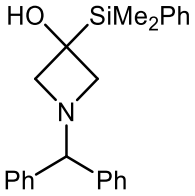


Prepared following the General Procedure B using oxetan-3-one. Purification by flash column chromatography (67% EtOAc/Petroleum ether) gave the title compound **1g** (0.70 g, 3.35 mmol, 50%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.60 – 7.53 (m, 2H), 7.39 – 7.34 (m, 3H), 4.78 (d, J = 7.8 Hz, 2H), 4.63 (d, J = 7.7 Hz, 2H), 0.47 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 134.6, 134.0, 129.9, 128.2, 83.1, 67.8, -6.4 ppm.

1-benzhydryl-3-(dimethyl(phenyl)silyl)azetidin-3-ol (1h)

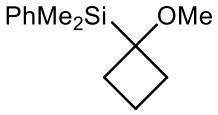


Prepared following the General Procedure B using 1-benzhydrylazetidin-3-one. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **1h** (1.69 g, 4.49 mmol, 67%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.59 (m, 2H), 7.46 – 7.38 (m, 3H), 7.36 – 7.31 (m, 4H), 7.29 – 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 4.30 (s, 1H), 3.57 – 3.46 (m, 2H), 2.95 – 2.85 (m, 2H), 0.51 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 142.4, 135.8, 134.2, 129.6, 128.4, 127.9, 127.2, 127.0, 78.0, 65.1, 63.0, -6.1 ppm.

(1-methoxycyclobutyl)dimethyl(phenyl)silane（1a′）

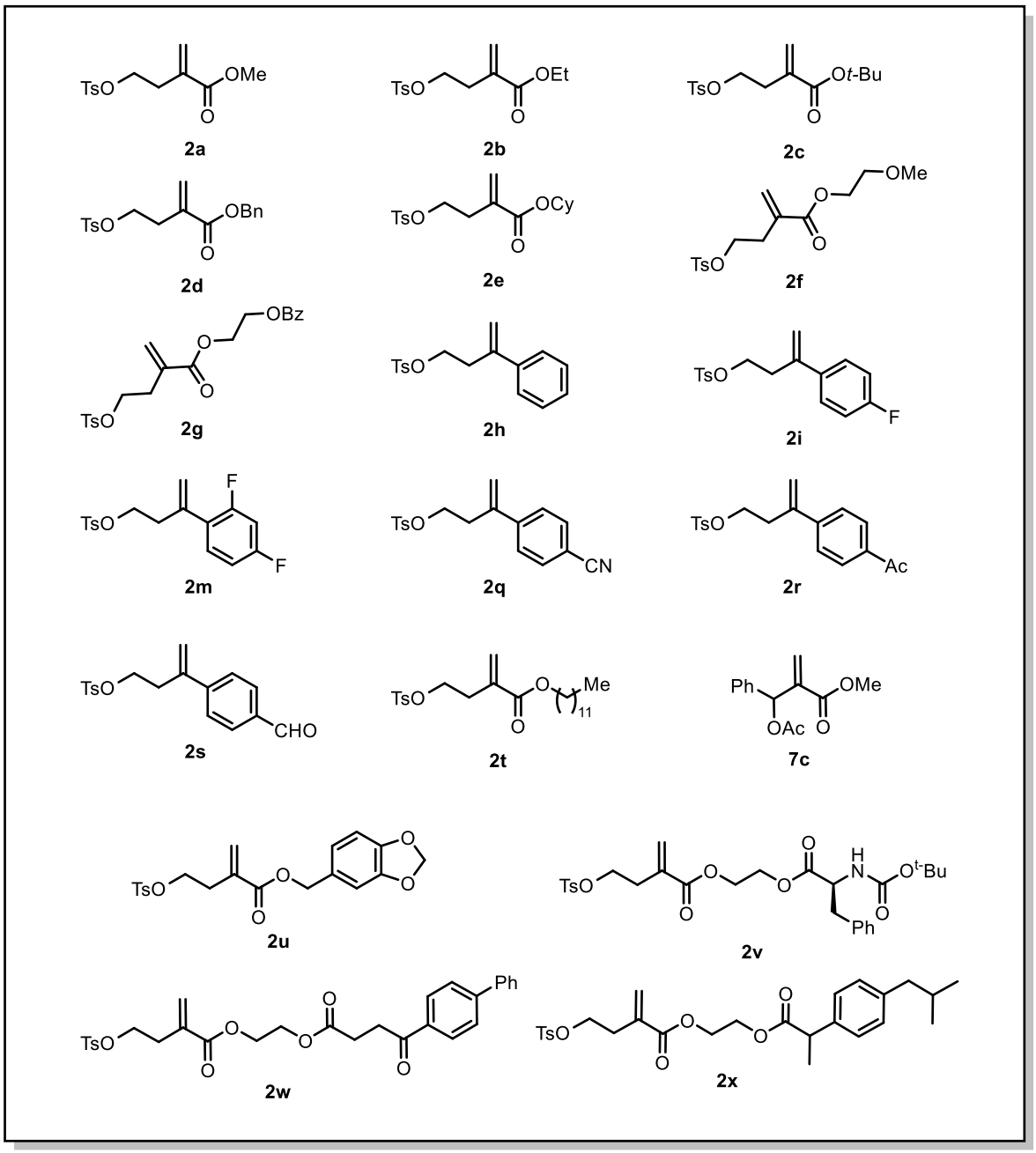


Under N_2 atmosphere, NaH (36 mg, 1.5 mmol, 1.5 equiv) was added to a 25 mL oven-dry flask, THF (2 mL, dry), 1a (206 mg, 1 mmol, 1.0 equiv) was added sequentially. For stirred at room temperature for 0.5 h, Then MeI (426 mg, 3.0 mmol, 3.0 equiv) was added to reaction. stirred at 80 ºC for overnight. The reaction was quenched by addition of H_2O (5 mL). and the resulting mixture was extracted three times with Ethyl acetate (3×10 mL) and the combined organic layer was dried over Na_2SO_4. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **1a′** (75 mg, 0.34 mmol, 34%) as a yellow oil.

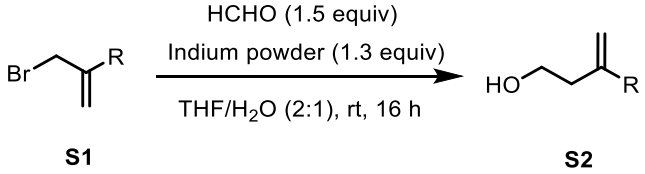
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.66 – 7.61 (m, 2H), 7.40 – 7.35 (m, 3H), 3.21 (s, 3H), 2.38 – 2.25 (m, 2H), 2.14 – 2.05 (m, 2H), 1.73 – 1.61 (m, 1H), 1.25 – 1.12 (m, 1H), 0.41 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 137.5, 134.2, 129.1, 127.7, 73.4, 51.1, 28.8, 13.1, -5.2 ppm.

The following olefin precursor have been previously reported by our group.[3]



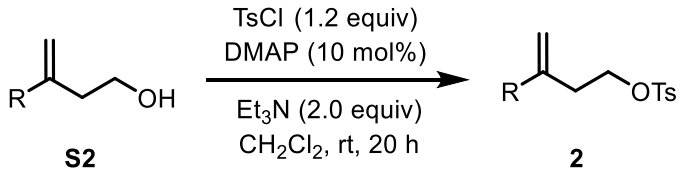
General Procedure C: [3]



S1 **S2**

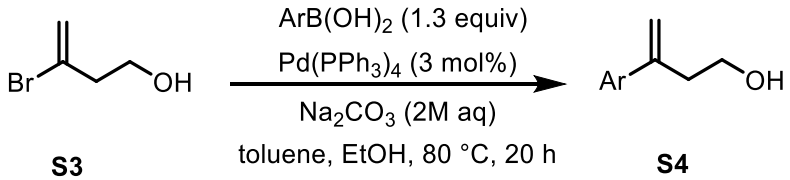
S2 was prepared following a modified literature procedure: [3] To a flask equipped with a magnetic stir bar was added **S1** (1.00 equiv), THF and H_2O (2:1, 0.3 M) were then added with vigorous stirring, followed by formaldehyde (1.50 equiv) and indium powder (1.30 equiv). The reaction mixture was stirred vigorously for 16 h, then partitioned between EtOAc (30 mL) and H_2O (50 mL). The phases were separated and the aqueous phase was extracted into EtOAc (2 × 30 mL). The combined organic phases were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography gave **S2**.

General Procedure D: [3]



To alcohol **S2** (1.00 equiv) in CH_2Cl_2 (0.5 M) at rt was added triethylamine (2.00 equiv), DMAP (0.100 equiv) and *p*-toluenesulfonyl chloride (1.20 equiv). After 20 h, aqueous 1 M HCl (20 mL) was added and the phases were separated. The aqueous phase was extracted into DCM (3 × 20 mL) and the combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography gave the substrate **2**.

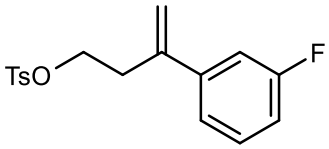
General Procedure E: [3]



S3 was prepared following a modified literature procedure:[i] Under an N_2 atmosphere 3-bromobut-3-en-1-ol **S5** (1.0 equiv), $Pd(PPh_3)_4$ (3.0 mol%) and $ArB(OH)_2$ (1.30 equiv) were placed in a thick-walled glass vessel. Na_2CO_3 (2.5 equiv), EtOH and toluene (1/2, 0.5 M) were added and the solution was stirred

at 80 ℃ for 40 h. The reaction was cooled to rt and H_2O_2 (30%, 1.5 mL) was added and the mixture was stirred for 30 min. Then partitioned between EtOAc (20 mL) and H_2O (30 mL). The phases were separated and the aqueous phase was extracted into EtOAc (2 ×30 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography gave **S4**.

3-(3-fluorophenyl)but-3-en-1-yl 4-methylbenzenesulfonate (2j)



Prepared following the General Procedure E and D using (3-fluorophenyl)boronic acid. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **2j** (660 mg, 2.06 mmol, 46% over 2 steps) as a pale yellow oil.

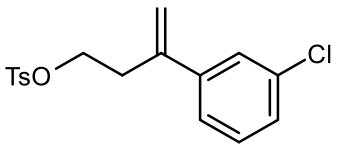
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.75 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 7.28 – 7.21 (m, 1H), 7.06 – 7.01 (m, 1H), 6.98 – 6.87 (m, 2H), 5.35 (s, 1H), 5.13 (s, 1H), 4.09 (t, J = 6.9 Hz, 2H), 2.82 (t, J = 6.9, 1.2 Hz, 2H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.8 (d, J = 246.7 Hz), 144.8, 141.9 (d, J = 7.6 Hz), 141.7, 132.8, 129.9 (d, J = 8.5 Hz), 129.8, 127.8, 121.5 (d, J = 2.8 Hz), 116.4, 114.5 (d, J = 21.3 Hz), 112.9 (d, J = 23.0 Hz), 68.3, 34.6, 21.6 ppm.

^{19}F NMR (397 MHz, $CDCl_3$): δ_F -113.0 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{17}FNaOS_3$ $[M+Na]^+$ 343.0775, found 343.0774.

3-(3-chlorophenyl)but-3-en-1-yl 4-methylbenzenesulfonate (2k)



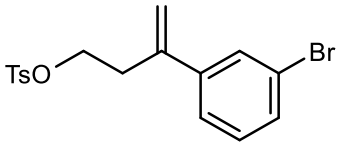
Prepared following the General Procedure E and D using (3-chlorophenyl)boronic acid. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **2k** (721 mg, 2.05 mmol, 68% over 2 steps) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 3.2 Hz, 3H), 7.13 (d, J = 6.9 Hz, 1H), 5.34 (s, 1H), 5.13 (s, 1H), 4.09 (t, J = 7.0 Hz, 2H), 2.82 (t, J = 7.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 144.8, 141.7, 141.6, 134.4, 132.9, 129.8, 129.7, 127.8, 127.8, 126.2, 124.1, 116.6, 68.2, 34.6, 21.6 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{17}ClNaOS_3$ $[M+Na]^+$ 359.0479, found 359.0479.

3-(3-bromophenyl)but-3-en-1-yl 4-methylbenzenesulfonate (2l)



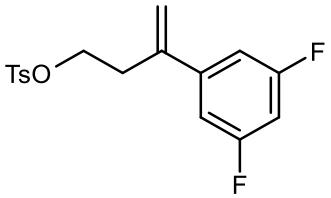
Prepared following the General Procedure E and D using (3-beomophenyl)boronic acid. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **2l** (412 mg, 1.1 mmol, 36% over 2 steps) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.70 (d, J = 8.3 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.24 (m, 3H), 7.20 – 7.10 (m, 2H), 5.33 (s, 1H), 5.12 (s, 1H), 4.08 (t, J = 6.9 Hz, 2H), 2.81 (t, J = 6.8 Hz, 2H), 2.43 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 144.8, 141.6, 132.8, 130.7, 129.9, 129.8, 129.1, 127.8, 125.9, 124.5, 122.6, 116.6, 68.2, 34.5, 21.6 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{17}BrNaO_3S$ $[M+Na]^+$ 402.9974, found 402.9975.

3-(3,5-difluorophenyl)but-3-en-1-yl 4-methylbenzenesulfonate (2n)



Prepared following the General Procedure E and D using (3,5-difluorophenyl)boronic acid. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **2l** (257 mg, 0.78 mmol, 39% over 2 steps) as a pale yellow oil.

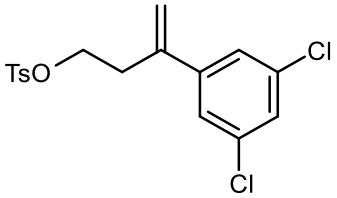
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.77 – 6.65 (m, 3H), 5.36 (s, 1H), 5.17 (s, 1H), 4.08 (t, J = 6.7 Hz, 2H), 2.78 (t, J = 6.8, 1.1 Hz, 2H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.9 (dd, J = 236.1, 13.0 Hz), 144.9, 143.1, 141.0, 129.8, 127.8, 117.4, 108.9 (dd, J = 18.8, 7.2 Hz), 103.0 (t, J = 25.5 Hz), 67.9, 34.4, 21.6 ppm.

^{19}F NMR (397 MHz, $CDCl_3$): δ_F -109.6 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{16}F_2NaO_3S$ $[M+Na]^+$ 361.0680, found 361.0681.

3-(3,5-dichlorophenyl)but-3-en-1-yl 4-methylbenzenesulfonate (2o)



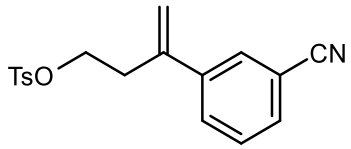
Prepared following the General Procedure E and D using (3,5-dichlorophenyl)boronic acid. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **2o** (934 mg, 2.52 mmol, 51% over 2 steps) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.24 (t, J = 1.9 Hz, 1H), 7.09 (d, J = 1.8 Hz, 2H), 5.35 (s, 1H), 5.18 (s, 1H), 4.08 (t, J = 6.7 Hz, 2H), 2.79 (t, J = 6.6 Hz, 2H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 144.9, 140.8, 135.0, 132.7, 129.8, 127.8, 127.6, 124.6, 117.8, 67.8, 34.4, 21.7 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{16}Cl_2NaO_3S$ $[M+Na]^+$ 393.0089, found 393.0089.

3-(3-cyanophenyl)but-3-en-1-yl 4-methylbenzenesulfonate (2p)



Prepared following the General Procedure E and D using (3,5-dichlorophenyl)boronic acid. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **2p** (687 mg, 2.3 mmol, 30% over 2 steps) as a colorless oil.

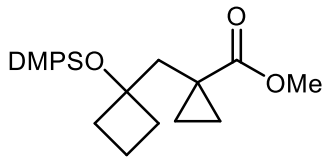
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.70 (d, J = 7.9 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.40 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 5.38 (s, 1H), 5.20 (s, 1H), 4.09 (t, J = 6.8 Hz, 2H), 2.83 (t, J = 6.7 Hz, 2H), 2.44 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 144.9, 141.1, 141.0, 132.6, 131.1, 130.3, 129.8, 129.5, 129.3, 127.7, 118.5, 117.6, 112.5, 67.9, 34.3, 21.6 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{17}NNaO_3$ $[M+Na]^+$ 350.0821, found 350.0822.

5. Product Characterization

Methyl 1-[(1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl]cyclopropanecarboxylate (3a)



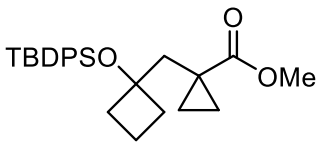
Prepared following the General Procedure A using **1a** (41 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.005 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3a** (29 mg, 0.09 mmol, 90%), as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.56 (m, 2H), 7.40 – 7.33 (m, 3H), 3.59 (s, 3H), 2.16 – 2.06 (m, 2H), 2.12 (s, 2H), 2.05 – 1.94 (m, 2H), 1.62 – 1.44 (m, 2H), 1.20 – 1.13 (m, 2H), 1.00 – 0.91 (m, 2H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 176.1, 139.8, 133.3, 129.2, 127.7, 77.6, 51.7, 42.2, 37.0, 21.1, 14.6, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{26}NaO_3Si$ $[M+Na]^+$ 341.1543, found 341.1544.

Methyl 1-[(1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl]cyclopropanecarboxylate (3aa)



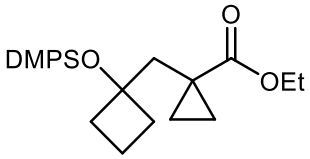
Prepared following the General Procedure A using **1aa** (59 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.005 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **3aa** (37 mg, 0.09mmol, 88%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.75 – 7.70 (m, 4H), 7.44 – 7.35 (m, 6H), 3.62 (s, 3H), 2.23 (s, 2H), 2.07 – 1.99 (m, 2H), 1.91 – 1.84 (m, 2H), 1.40 – 1.32 (m, 1H), 1.28 – 1.25 (m, 2H), 1.21 – 1.14 (m, 1H), 1.13 – 1.09 (m, 2H), 1.02 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 176.3, 135.9, 135.4, 129.4, 127.4, 78.3, 51.7, 42.6, 37.1, 27.1, 21.1, 19.0, 15.6, 12.2 ppm.

HRMS (ESI$^+$) calcd. for $C_{26}H_{34}NaO_3Si$ $[M+Na]^+$ 445.2169, found 445.2168.

Ethyl 1-[(1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl]cyclopropanecarboxylate (3b)



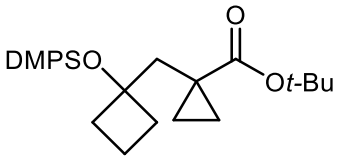
Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2b** (90 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3b** (67 mg, 0.20 mmol, 67%), as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64 – 7.58 (m, 2H), 7.40 – 7.34 (m, 3H), 4.07 (q, J = 6.8 Hz, 2H), 2.17 – 2.07 (m, 2H), 2.14 (s, 2H), 2.07 – 2.00 (m, 2H), 1.62 – 1.50 (m, 2H), 1.22 (t, 3H), 1.20 – 1.15 (m, 2H), 1.01 – 0.95 (m, 2H), 0.40 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.7, 139.8, 133.3, 129.2, 127.7, 77.6, 60.4, 41.9, 37.0, 21.0, 14.7, 14.1, 12.6, 0.6 ppm.

HRMS (ESI$^+$) calcd. for $C_{19}H_{28}NaO_3Si$ $[M+Na]^+$ 355.1700, found 355.1701.

Butyl 1-[(1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl]cyclopropanecarboxylate (3c)



Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2c** (98 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue

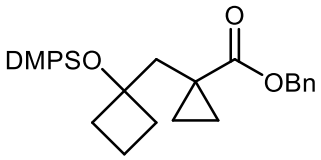
LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3c** (68 mg, 0.19 mmol, 63%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.58 (m, 2H), 7.41 – 7.34 (m, 3H), 2.16 – 2.02 (m, 4H), 2.10 (s, 2H), 1.62 – 1.53 (m, 2H), 1.43 (s, 9H), 1.15 – 1.09 (m, 2H), 0.97 – 0.92 (m, 2H), 0.40 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.9, 139.8, 133.3, 129.2, 127.7, 79.8, 77.9, 41.9, 36.9, 27.9, 21.8, 14.9, 12.7, 0.7 ppm.

HRMS (ESI^+) calcd. for $C_{21}H_{32}NaO_3Si$ $[M+Na]^+$ 383.2013, found 383.2012.

Benzyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (3d)



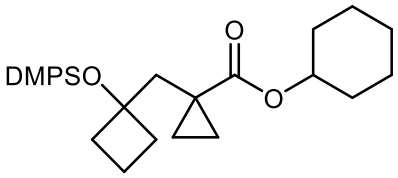
Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2d** (108 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3d** (95 mg, 0.24 mmol, 80%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.59 (m, 2H), 7.43 – 7.30 (m, 8H), 5.07 (s, 2H), 2.20 – 2.09 (m, 2H), 2.19 (s, 2H), 2.08 – 2.01 (m, 2H), 1.59 – 1.52 (m, 1H), 1.52 – 1.45 (m, 1H), 1.28 – 1.23 (m, 2H), 1.07 – 1.00 (m, 2H), 0.42 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.4, 139.7, 136.2, 133.3, 129.2, 128.4, 127.9, 127.9, 127.7, 77.6, 66.2, 42.0, 37.0, 21.2, 14.8, 12.6, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{24}H_{30}NaO_3Si$ $[M+Na]^+$ 417.1856, found 417.1855.

Cyclohexyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (3e)



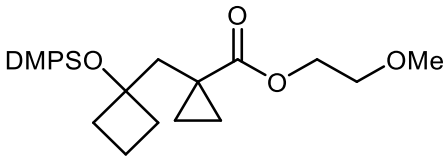
Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2e** (106 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3e** (103 mg, 0.20 mmol, 67%), as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.66 – 7.59 (m, 2H), 7.43 – 7.37 (m, 4H), 4.82 – 4.64 (m, 1H), 2.18 – 2.03 (m, 4H), 2.16 (s, 2H), 1.85 – 1.77 (m, 2H), 1.75 – 1.67 (m, 2H), 1.62 – 1.50 (m, 3H), 1.47 – 1.34 (m, 4H), 1.33 – 1.27 (m, 1H), 1.22 – 1.17 (m, 2H), 1.03 – 0.98 (m, 2H), 0.41 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.2, 139.9, 133.4, 129.3, 127.8, 77.9, 72.5, 41.9, 37.1, 31.6, 25.5, 23.8, 21.3, 15.0, 12.8, 0.8 ppm.

HRMS (ESI^+) calcd. for $C_{23}H_{34}NaO_3Si$ $[M+Na]^+$409.2169, found 409.2170.

2-methoxyethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (3f)



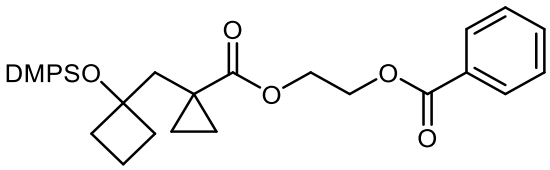
Prepared following the General Procedure A using **1a** (124 mg, 0.6 mmol, 2.0 equiv), **2f** (132 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3f** (71 mg, 0.19 mmol, 65%), as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.53 (m, 2H), 7.43 – 7.30 (m, 3H), 4.19 – 4.08 (m, 2H), 3.58 – 3.48 (m, 2H), 3.35 (s, 3H), 2.17 – 1.98 (m, 4H), 2.14 (s, 2H), 1.59 – 1.48 (m, 2H), 1.35 – 1.24 (m, 1H), 1.23 – 1.16 (m, 2H), 1.02 – 0.95 (m, 2H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.7, 139.8, 133.3, 129.2, 127.7, 77.7, 70.5, 63.5, 58.9, 41.9, 37.0, 21.1, 14.9, 12.6, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{20}H_{30}NaO_4Si$ $[M+Na]^+$385.1806, found 385.1806.

2-((1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carbonyl)oxy)ethyl benzoate (3g)



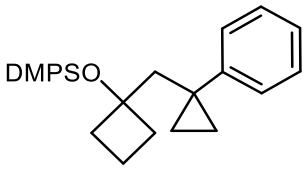
Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2g** (134 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (11.8 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol, 2.0 equiv), s-collidine (0.10 mL, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (20% EtOAc/ hexane) gave the title compound **3g** (81 mg, 0.18 mmol, 60%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.03 (dd, J = 8.2, 1.4 Hz, 2H), 7.62 – 7.52 (m, 3H), 7.48 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 4.52 – 4.44 (m, 2H), 4.36 – 4.29 (m, 2H), 2.13 (s, 2H), 2.11 – 1.96 (m, 4H), 1.55 – 1.43 (m, 2H), 1.23 – 1.16 (m, 2H), 1.04 – 0.97 (m, 2H), 0.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.5, 166.3, 139.7, 133.3, 133.1, 129.8, 129.7, 129.2, 128.4, 127.7, 77.6, 62.7, 62.2, 41.9, 37.0, 21.1, 15.0, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{26}H_{32}NaO_5Si$ $[M+Na]^+$ 475.1911, found 475.1911.

Dimethyl(phenyl)(1-((1-phenylcyclopropyl)methyl)cyclobutoxy)silane (3h)



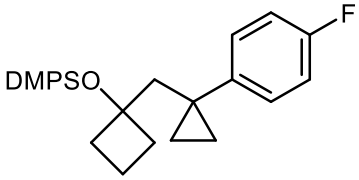
Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2h** (91 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3h** (52 mg, 0.16 mmol, 52%), as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.60 (m, 2H), 7.44 – 7.37 (m, 6H), 7.29 – 7.21 (m, 1H), 7.20 – 7.13 (m, 1H), 2.02 – 1.92 (m, 2H), 2.00 (s, 2H), 1.75 – 1.65 (m, 2H), 1.51 – 1.43 (m, 1H), 1.36 – 1.27 (m, 1H), 0.85 – 0.79 (m, 4H), 0.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 146.2, 140.2, 133.4, 129.8, 129.1, 127.8, 127.6, 125.7, 77.9, 50.1, 36.6, 23.1, 12.7, 12.7, 0.7 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{28}NaOSi$ $[M+Na]^+$ 359.1802, found359.1802.

(1-((1-(4-fluorophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3i)



Prepared following the General Procedure A using **1a** (83 mg, 0.40 mmol, 2.0 equiv), **2i** (64 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3i** (41 mg, 0.11 mmol, 57%), as a pale yellow liquid.

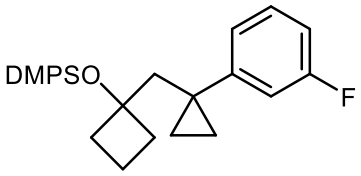
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.57 (m, 2H), 7.41 – 7.37 (m, 3H), 7.35 – 7.30 (m, 2H), 6.96 – 6.87 (m, 2H), 2.02 – 1.89 (m, 2H), 1.92 (s, 2H), 1.72 – 1.62 (m, 2H), 1.52 – 1.43 (m, 1H), 1.36 – 1.29 (m, 1H), 0.82 – 0.72 (m, 4H), 0.35 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.1 (d, J = 245.0 Hz), 141.9, 140.1, 133.3, 133.0, 131.4 (d, J = 7.9 Hz) ,129.1, 127.6, 114.5 (d, J = 21.1 Hz), 77.8, 50.3, 36.7, 22.5, 12.8, 12.7, 0.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -117.5 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{27}FNaOSi$ $[M+Na]^+$ 377.1707, found 377.1706.

(1-((1-(3-fluorophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3j)



Prepared following the General Procedure A using **1a** (83 mg, 0.40 mmol, 2.0 equiv), **2j** (64 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound (55 mg, 0.15 mmol, 77%), as a pale yellow liquid.

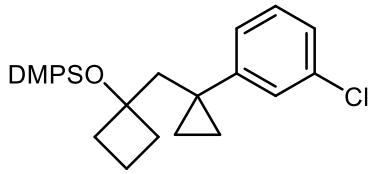
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 – 7.57 (m, 2H), 7.41 – 7.37 (m, 4H), 7.23 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 6.89 – 6.81 (m, 1H), 2.05 – 1.92 (m, 2H), 1.97 (s, 2H), 1.79 – 1.68 (m, 2H), 1.58 – 1.44 (m, 1H), 1.41 – 1.28 (m, 1H), 0.87 – 0.77 (m, 4H), 0.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.5 (d, J = 245.3 Hz), 149.0, 140.0, 133.3, 133.0, 129.1, 127.6, 125.4, 116.7 (d, J = 20.8 Hz), 112.6 (d, J = 21.3 Hz), 77.8, 49.9, 36.6, 23.0, 12.9, 12.7, 0.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -114.5 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{27}FNaOSi$ $[M+Na]^+$ 377.1707, found 377.1706.

(1-((1-(3-chlorophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3k)



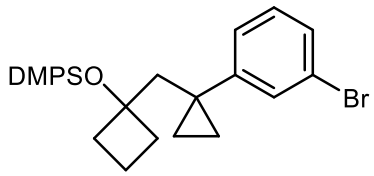
Prepared following the General Procedure A using **1a** (41 mg, 0.2 mmol, 2.0 equiv), **2k** (34 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3k** (31 mg, 0.08 mmol, 83%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.60 – 7.53 (m, 2H), 7.40 – 7.33 (m, 4H), 7.26 – 7.23 (m, 1H), 7.17 – 7.08 (m, 2H), 2.00 – 1.89 (m, 2H), 1.92 (s, 2H), 1.74 – 1.65 (m, 2H), 1.51 – 1.42 (m, 1H), 1.36 – 1.28 (m, 1H), 0.81 – 0.73 (m, 4H), 0.31 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.5, 140.0, 133.4, 133.3, 130.1, 129.1, 129.1, 128.1, 127.7, 125.9, 77.8, 49.9, 36.6, 23.1, 12.7, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{27}ClNaOSi$ $[M+Na]^+$ 393.1412, found 393.1411.

(1-((1-(3-bromophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3l)



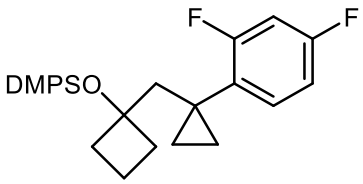
Prepared following the General Procedure A using **1a** (41 mg, 0.2 mmol, 2.0 equiv), **2l** (38 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3l** (19 mg, 0.05 mmol, 46%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 – 7.55 (m, 2H), 7.55 – 7.51 (m, 1H), 7.40 – 7.34 (m, 3H), 7.31 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.92 (s,2H), 1.74 – 1.65 (m, 2H), 1.52 – 1.41 (m, 1H), 1.36 – 1.27 (m, 1H), 0.80 – 0.76 (m, 4H), 0.32 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.8, 140.0, 133.3, 133.0, 129.4, 129.1, 128.8, 128.6, 127.7, 121.8, 77.8, 50.0, 36.6, 23.1, 12.8, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{27}BrNaOSi$ $[M+Na]^+$ 437.0907, found 437.0908.

(1-((1-(2,4-difluorophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3m)



Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2m** (102 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3m** (59 mg, 0.16 mmol, 53%), as a pale yellow liquid.

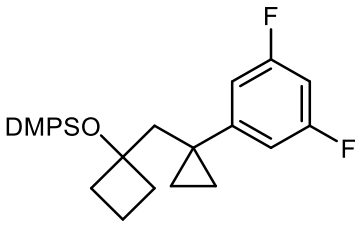
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 – 7.54 (m, 2H), 7.39 – 7.35 (m, 3H), 7.28 – 7.19 (m, 1H), 6.76 – 6.62 (m, 2H), 2.02 – 1.89 (m, 2H), 1.92 (s, 2H), 1.82 – 1.73 (m, 2H), 1.56 – 1.47 (m, 1H), 1.38 – 1.33 (m, 1H), 0.84 – 0.79 (m, 2H), 0.78 – 0.73 (m, 2H), 0.31 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.2 (dd, *J* = 101.8, 12.0 Hz), 160.7 (dd, *J* = 98.5, 11.9 Hz), 140.0, 133.3, 133.0, 132.8 (dd, *J* = 9.3, 6.4 Hz), 129.1, 127.6, 110.2 (dd, *J* = 20.7, 3.6 Hz), 103.3 (t, *J* = 25.6 Hz), 77.8, 48.5, 36.5, 17.9, 12.8, 12.5, 0.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -111.05 (d, *J* = 7.5 Hz), -113.75 (d, *J* = 7.5 Hz) ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{26}F_2NaOSi$ $[M+Na]^+$ 395.1613, found 395.1614.

(1-((1-(3,5-difluorophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3n)



Prepared following the General Procedure A using **1a** (21 mg, 0.10 mmol, 2.0 equiv), **2n** (17 mg, 0.050 mmol, 1.0 equiv), 4CzIPN (2 mg, 0.0025 mmol, 5.0 mol%), Cs_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv), s-collidine (16 mg, 0.13 mmol, 2.5 equiv) and MeCN (1.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3n** (16 mg, 0.043 mmol, 85%), as a pale yellow liquid.

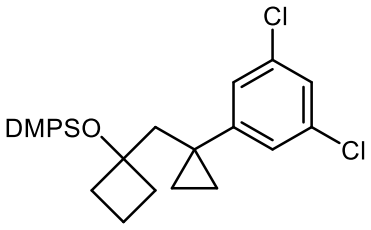
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.60 – 7.53 (m, 2H), 7.41 – 7.34 (m, 3H), 6.91 – 6.84 (m, 2H), 6.60 – 6.51 (m, 1H), 2.05 – 1.89 (m, 2H), 1.92 (s, 2H), 1.76 – 1.67 (m, 2H), 1.53 – 1.43 (m, 1H), 1.36 – 1.29 (m, 1H), 0.82 – 0.73 (m, 4H), 0.32 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.6 (d, J = 247.8 Hz), 150.5, 139.9, 133.3, 129.2, 127.7, 112.5 (dd, J = 18.3, 6.3 Hz), 101.2 (t, J = 25.7 Hz), 77.7, 49.7, 36.6, 23.1, 13.0, 12.7, 0.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -111.4 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{26}F_2NaOSi$ $[M+Na]^+$ 395.1613, found 395.1613.

(1-((1-(3,5-dichlorophenyl)cyclopropyl)methyl)cyclobutoxy)dimethyl(phenyl)silane (3o)



Prepared following the General Procedure A using **1a** (413 mg, 2.0 mmol, 2.0 equiv), **2o** (371 mg, 1.0 mmol, 1.0 equiv), 4CzIPN (39 mg, 0.050 mmol, 5.0 mol%), Cs_2CO_3 (652 mg, 2.0 mmol, 2.0 equiv), s-

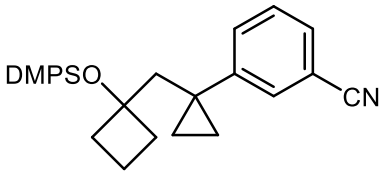
collidine (303 mg, 2.5 mmol, 2.5 equiv) and MeCN (20.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3o** (36 mg, 0.90 mmol, 90%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 – 7.51 (m, 2H), 7.43 – 7.33 (m, 4H), 7.27 – 7.24 (m, 2H), 7.12 (t, J = 1.9 Hz, 1H), 2.06 – 1.89 (m, 2H), 1.92 (s, 2H), 1.80 – 1.71 (m, 2H), 1.55 – 1.43 (m, 1H), 1.39 – 1.31 (m, 1H), 0.84 – 0.73 (m, 4H), 0.32 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 149.9, 139.8, 134.0, 133.3, 129.2, 128.5, 127.7, 125.9, 77.7, 49.8, 36.6, 23.1, 12.8, 12.7, 0.5 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{26}Cl_2NaOSi$ $[M+Na]^+$ 427.1022, found 427.1022.

3-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropyl)benzonitrile (3p)



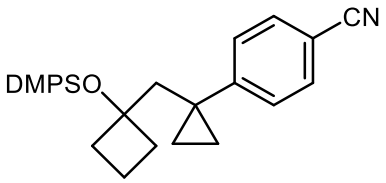
Prepared following the General Procedure A using **1a** (41 mg, 0.20 mmol, 2.0 equiv), **2p** (33 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **3p** (35 mg, 0.097 mmol, 97%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.66 – 7.62 (m, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.50 (m, 2H), 7.41 – 7.34 (m, 4H), 7.31 – 7.28 (m, 1H), 1.98 – 1.91 (m, 2H), 1.92 (s, 2H), 1.73 – 1.64 (m, 2H), 1.51 – 1.41 (m, 1H), 1.35 – 1.29 (m, 1H), 0.84 – 0.80 (m, 2H), 0.78 – 0.74 (m, 2H), 0.28 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 147.8, 139.7, 134.7, 133.7, 133.3, 129.4, 129.2, 128.6, 127.7, 119.2, 111.7, 77.6, 49.9, 36.6, 23.0, 12.7, 0.5 ppm.

HRMS (ESI^+) calcd. for $C_{23}H_{27}NNaOSi$ $[M+Na]^+$ 384.1754, found 384.1754.

4-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropyl)benzonitrile (3q)



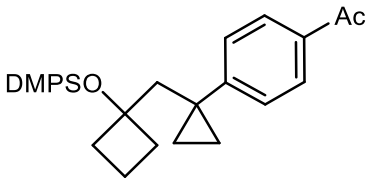
Prepared following the General Procedure A using **1a** (41 mg, 0.20 mmol, 2.0 equiv), **2q** (33 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **3q** (37 mg, 0.070 mmol, 70%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 – 7.48 (m, 3H), 7.47 – 7.42 (m, 3H), 7.40 – 7.33 (m, 3H), 2.02 – 1.90 (m, 2H), 1.96 (s, 2H), 1.76 – 1.65 (m, 2H), 1.55 – 1.43 (m, 1H), 1.34 – 1.28 (m, 1H), 0.87 – 0.82 (m, 2H), 0.82 – 0.75 (m, 2H), 0.28 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 152.3, 139.8, 133.3, 131.8, 130.7, 129.4, 127.8, 119.3, 77.8, 49.9, 36.7, 23.6, 13.0, 12.8, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{23}H_{27}NNaOSi$ $[M+Na]^+$ 384.1754, found 384.1754.

1-(4-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropyl)phenyl)ethan-1-one (3r)



Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2r** (103 mg, 0.3 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue

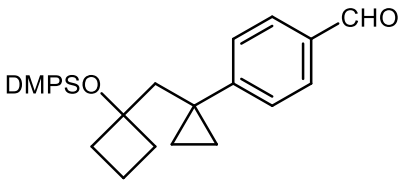
LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **3r** (81 mg, 0.21 mmol, 70%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.74 – 7.69 (m, 2H), 7.47 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.26 – 7.22 (m, 3H), 2.45 (s, 3H), 1.92 – 1.80 (m, 2H), 1.89 (s, 2H), 1.65 – 1.56 (m, 2H), 1.40 – 1.32 (m, 1H), 1.24 – 1.17 (m, 1H), 0.78 – 0.67 (m, 4H), 0.20 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 197.8, 152.2, 139.8, 134.7, 133.3, 129.8, 129.1, 128.0, 127.6, 77.8, 49.8, 36.6, 26.5, 23.2, 12.9, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{24}H_{30}NaO_2Si$ $[M+Na]^+$ 401.1907, found 401.1908.

4-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropyl)benzaldehyde (3s)



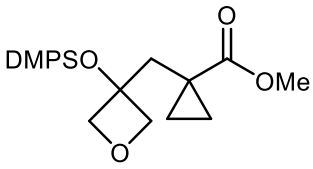
Prepared following the General Procedure A using **1a** (41 mg, 0.20 mmol, 2.0 equiv), **2s** (33 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **3s** (31 mg, 0.086 mmol, 86%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.93 (s, 1H), 7.77 – 7.65 (m, 2H), 7.56 – 7.48 (m, 4H), 7.38 – 7.33 (m, 3H), 2.04 – 1.90 (m, 2H), 2.00 (s, 2H), 1.75 – 1.65 (m, 2H), 1.52 – 1.40 (m, 1H), 1.31 – 1.25 (m, 1H), 0.90 – 0.77 (m, 4H), 0.28 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 192.1, 154.1, 139.9, 134.3, 133.4, 130.5, 129.6, 129.3, 127.7, 77.9, 49.9, 36.7, 23.6, 13.1, 12.8, 0.7 ppm.

HRMS (ESI^+) calcd. for $C_{23}H_{28}NaO_2Si$ $[M+Na]^+$ 387.1751, found 387.1750.

Methyl 1-((3-((dimethyl(phenyl)silyl)oxy)oxetan-3-yl)methyl)cyclopropane-1-carboxylate (3t)



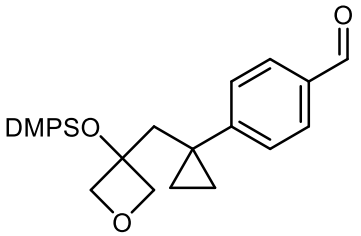
Prepared following the General Procedure A using **1g** (42 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3t** (25 mg, 0.077 mmol, 77%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64 – 7.56 (m, 2H), 7.43 – 7.34 (m, 4H), 4.66 – 4.59 (m, 2H), 4.53 – 4.46 (m, 2H), 3.57 (s, 3H), 2.26 (s, 2H), 1.24 – 1.20 (m, 2H), 0.84 – 0.80 (m, 2H), 0.45 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.3, 138.7, 133.2, 129.6, 127.9, 84.1, 76.8, 51.7, 42.1, 20.5, 14.9, 0.2 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{24}NaO_4Si$ $[M+Na]^+$ 343.1336, found 343.1336.

4-(1-((3-((dimethyl(phenyl)silyl)oxy)oxetan-3-yl)methyl)cyclopropyl)benzaldehyde (3u)



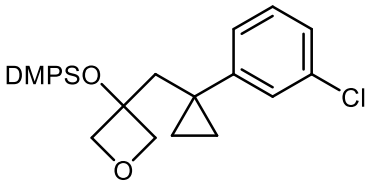
Prepared following the General Procedure A using **1g** (21 mg, 0.10 mmol, 2.0 equiv), **2s** (17 mg, 0.05 mmol, 1.0 equiv), 4CzIPN (2 mg, 0.0025 mmol, 5.0 mol%), Cs_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv), s-collidine (16 mg, 0.13 mmol, 2.5 equiv) and MeCN (1.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3u** (12 mg, 0.032 mmol, 64%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.95 (s, 1H), 7.77 – 7.69 (m, 2H), 7.61 – 7.54 (m, 2H), 7.52 – 7.45 (m, 2H), 7.43 – 7.33 (m, 3H), 4.44 – 4.33 (m, 2H), 3.99 – 3.88 (m, 2H), 2.17 (s, 2H), 0.86 – 0.82 (m, 4H), 0.42 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 191.9, 152.4, 138.6, 134.7, 133.2, 130.4, 129.7, 129.6, 128.0, 83.5, 76.6, 49.2, 23.1, 12.7, 0.3 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{26}NaO_3Si$ $[M+Na]^+$ 389.1543, found 389.1544.

((3-((1-(3-chlorophenyl)cyclopropyl)methyl)oxetan-3-yl)oxy)dimethyl(phenyl)silane (3v)



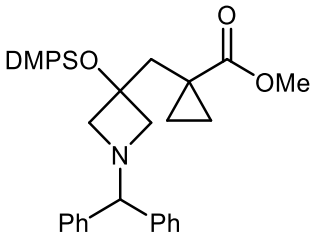
Prepared following the General Procedure A using **1g** (42 mg, 0.20 mmol, 2.0 equiv), **2k** (34 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3v** (23 mg, 0.062 mmol, 62%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64 – 7.57 (m, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.33 (m, 1H), 7.25 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 4.42 – 4.36 (m, 2H), 3.98 – 3.91 (m, 2H), 2.11 (s, 2H), 0.82 – 0.74 (m, 4H), 0.45 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 147.0, 138.8, 133.7, 133.2, 130.1, 129.6, 129.4, 128.0, 128.0, 126.6, 83.6, 76.6, 49.4, 22.7, 12.4, 0.3 ppm.

HRMS (ESI^+) calcd. for $C_{21}H_{25}ClNaO_2Si$ $[M+Na]^+$ 395.1205, found 395.1206.

Methyl 1-((1-benzhydryl-3-((dimethyl(phenyl)silyl)oxy)azetidin-3-yl)methyl)cyclopropane-1-carboxylate (3w)



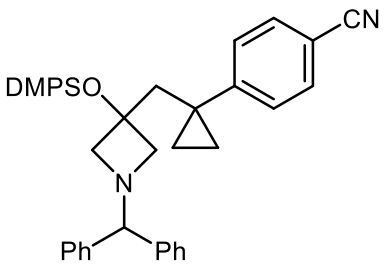
Prepared following the General Procedure A using **1h** (75 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3w** (14 mg, 0.029 mmol, 29%), as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67 – 7.62 (m, 2H), 7.45 – 7.39 (m, 3H), 7.27 – 7.12 (m, 10H), 3.99 (s, 1H), 3.59 (s, 3H), 3.17 – 3.10 (m, 2H), 3.05 – 2.99 (m, 2H), 2.19 (s, 2H), 1.22 – 1.17 (m, 2H), 0.86 – 0.80 (m, 2H), 0.41 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.5, 142.5, 139.5, 133.6, 129.5, 128.3, 127.8, 127.3, 126.9, 77.8, 72.6, 66.0, 51.7, 43.1, 21.0, 14.6, 0.3 ppm.

HRMS (ESI^+) calcd. for $C_{30}H_{35}NNaO_3Si$ $[M+Na]^+$ 508.2278, found 508.2277.

4-(1-((1-benzhydryl-3-((dimethyl(phenyl)silyl)oxy)azetidin-3-yl)methyl)cyclopropyl)benzonitrile (3x)



Prepared following the General Procedure A using **1h** (75 mg, 0.20 mmol, 2.0 equiv), **2q** (33 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED

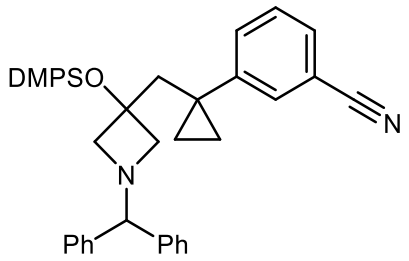
for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **3x** (12 mg, 0.022 mmol, 22%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 – 7.51 (m, 2H), 7.48 – 7.38 (m, 8H), 7.21 – 7.14 (m, 9H), 3.94 (s, 1H), 2.83 (s, 4H), 2.15 (s, 2H), 0.88 – 0.83 (m, 2H), 0.83 – 0.77 (m, 2H), 0.28 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 151.7, 142.2, 139.0, 133.5, 131.7, 130.1, 129.5, 128.3, 127.8, 127.2, 119.0, 109.5, 72.6, 65.6, 49.9, 22.5, 13.1, 0.3 ppm.

HRMS (ESI^+) calcd. for $C_{30}H_{36}N_2NaOSi$ $[M+Na]^+$ 551.2489, found 551.2489.

3-(1-((1-benzhydryl-3-((dimethyl(phenyl)silyl)oxy)azetidin-3-yl)methyl)cyclopropyl)benzonitrile (3y)



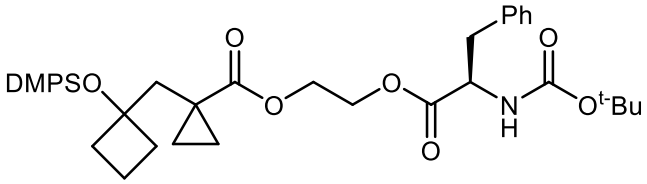
Prepared following the General Procedure A using **1h** (187 mg, 0.50 mmol, 2.5 equiv), **2p** (66 mg, 0.20 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (20% EtOAc/ hexane) gave the title compound **3y** (57 mg, 0.11 mmol, 55%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67 – 7.63 (m, 1H), 7.62 – 7.56 (m, 3H), 7.49 – 7.42 (m, 3H), 7.41 – 7.36 (m, 1H), 7.31 – 7.27 (m, 1H), 7.23 – 7.12 (m, 10H), 3.97 (s, 1H), 2.84 (s, 4H), 2.14 (s, 2H), 0.91 – 0.84 (m, 2H), 0.83 – 0.76 (m, 2H), 0.32 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 147.3, 142.2, 139.2, 134.2, 133.5, 133.3, 129.5, 128.6, 128.2, 127.8, 127.2, 126.9, 119.1, 111.7, 72.6, 65.5, 50.0, 22.7, 12.7, 0.3 ppm.

HRMS (ESI^+) calcd. for $C_{30}H_{36}N_2NaOSi$ $[M+Na]^+$ 551.2489, found 551.2489.

2-(((tert-butoxycarbonyl)-D-phenylalanyl)oxy)ethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (4a)



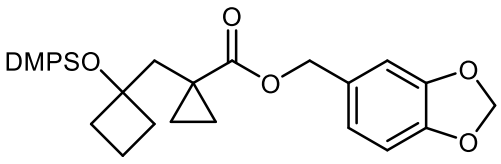
Prepared following the General Procedure A using **1a** (84 mg, 0.40 mmol, 2.0 equiv), **2v** (112 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.25 mmol, 2.5 equiv) and MeCN (4.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **4a** (66 mg, 0.11 mmol, 55%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.61 – 7.56 (m, 2H), 7.39 – 7.34 (m, 3H), 7.31 – 7.23 (m, 3H), 7.15 – 7.10 (m, 2H), 5.00 – 4.92 (m, 1H), 4.65 – 4.55 (m, 1H), 4.30 – 4.23 (m, 2H), 4.17 – 4.10 (m, 2H), 3.16 – 3.00 (m, 2H), 2.16 – 2.08 (m, 4H), 2.04 – 1.96 (m, 2H), 1.57 – 1.51 (m, 1H), 1.42 (s, 9H), 1.38 – 1.36 (m, 1H), 1.21 – 1.16 (m, 2H), 1.03 – 0.99 (m, 2H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.4, 171.6, 155.0, 139.6, 135.8, 133.3, 133.0, 129.2, 128.5, 127.7, 127.1, 79.9, 77.5, 63.0, 61.9, 54.3, 41.8, 38.2, 37.0, 28.3, 21.1, 15.0, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{33}H_{45}NNaO_7Si$ $[M+Na]^+$ 618.2858, found 618.2857.

Benzo[*d*][1,3]dioxol-5-ylmethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (4b)



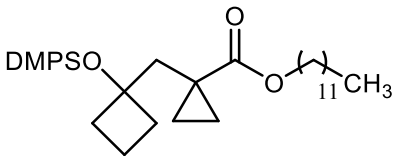
Prepared following the General Procedure A using **1a** (114 mg, 0.40 mmol, 2.0 equiv), **2u** (81 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.25 mmol, 2.5 equiv) and MeCN (4.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **4b** (31 mg, 0.07 mmol, 35%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.54 (m, 2H), 7.40 – 7.31 (m, 3H), 6.82 – 6.74 (m, 3H), 5.96 (s, 2H), 4.92 (s, 2H), 2.16 – 2.05 (m, 2H), 2.13 (s, 2H), 2.04 – 1.94 (m, 2H), 1.58 – 1.41 (m, 2H), 1.22 – 1.15 (m, 2H), 1.01 – 0.95 (m, 2H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.5, 147.6, 147.4, 139.7, 133.3, 130.0, 129.2, 127.7, 122.0, 108.8, 108.1, 101.1, 77.6, 77.3, 77.0, 76.7, 66.2, 41.9, 37.0, 21.2, 14.8, 12.6, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{25}H_{30}NaO_5Si$ $[M+Na]^+$ 461.1755, found 461.1755.

Dodecyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (4c)



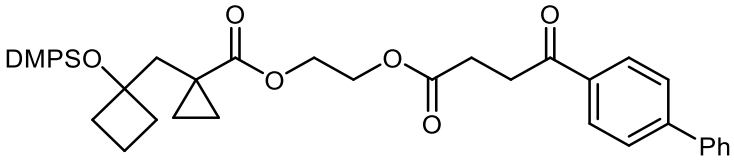
Prepared following the General Procedure A using **1a** (124 mg, 0.60 mmol, 2.0 equiv), **2t** (132 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (12 mg, 0.015 mmol, 5.0 mol%), Cs_2CO_3 (196 mg, 0.60 mmol, 2.0 equiv), s-collidine (91 mg, 0.75 mmol, 2.5 equiv) and MeCN (6.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **4c** (87 mg, 0.18 mmol, 61%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.57 (m, 2H), 7.39 – 7.35 (m, 3H), 3.99 (t, J = 6.7 Hz, 2H), 2.16 – 2.07 (m, 2H), 2.13 (s, 2H), 2.06 – 1.99 (m, 2H), 1.57 – 1.51 (m, 2H), 1.36 – 1.23 (m, 20H), 1.19 – 1.15 (m, 2H), 1.00 – 0.95 (m, 2H), 0.89 (t, J = 6.7 Hz, 3H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.8, 139.8, 133.3, 133.0, 129.2, 127.7, 77.7, 64.6, 42.0, 37.0, 31.9, 29.6, 29.6, 29.5, 29.3, 29.2, 28.6, 25.9, 22.7, 21.1, 14.8, 14.1, 12.7, 0.6 ppm.

HRMS (ESI$^+$) calcd. for $C_{29}H_{48}NaO_3Si$ [M+Na]$^+$ 495.3265, found 495.3266.

2-((4-([1,1'-biphenyl]-4-yl)-4-oxobutanoyl)oxy)ethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (4d)



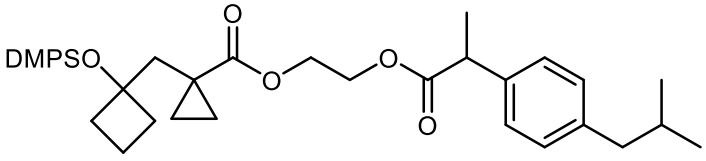
Prepared following the General Procedure A using **1a** (41 mg, 0.20 mmol, 2.0 equiv), **2w** (55 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (20% EtOAc/ hexane) gave the title compound **4d** (40 mg, 0.068mmol, 68%), as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.06 (d, J = 8.4 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.66 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.48 (dd, J = 8.3, 6.6 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.38 – 7.33 (m, 3H), 4.32 – 4.25 (m, 2H), 4.25 – 4.17 (m, 2H), 3.35 (t, J = 6.7 Hz, 2H), 2.79 (t, J = 6.6 Hz, 2H), 2.19 – 2.07 (m, 4H), 2.07 – 1.96 (m, 2H), 1.59 – 1.50 (m, 2H), 1.22 – 1.17 (m, 2H), 1.03 – 0.98 (m, 2H), 0.39 (s, 6H). ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 197.4, 175.5, 172.6, 145.9, 139.8, 139.7, 135.1, 133.3, 129.2, 128.9, 128.6, 128.2, 127.7, 127.2, 77.6, 62.4, 62.1, 41.9, 37.0, 33.3, 28.1, 21.0, 15.0, 12.7, 0.6 ppm.

HRMS (ESI$^+$) calcd. for $C_{35}H_{40}NaO_6Si$ [M+Na]$^+$ 607.2486, found 607.2486.

2-((2-(4-isobutylphenyl)propanoyl)oxy)ethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclobutyl)methyl)cyclopropane-1-carboxylate (4e)



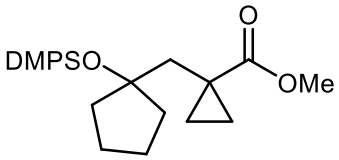
Prepared following the General Procedure A using **1a** (41 mg, 0.20 mmol, 2.0 equiv), **2x** (50 mg, 0.1 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **4e** (26 mg, 0.048 mmol, 48%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.56 (m, 2H), 7.39 – 7.34 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 4.28 – 4.17 (m, 2H), 4.16 – 4.11 (m, 2H), 3.69 (q, J = 7.3 Hz, 1H), 2.44 (d, J = 7.2 Hz, 2H), 2.13 – 2.04 (m, 2H), 2.09 (s, 2H), 2.03 – 1.96 (m, 2H), 1.88 – 1.80 (m, 1H), 1.58 – 1.50 (m, 2H), 1.48 (d, J = 7.2 Hz, 3H), 1.14 – 1.09 (m, 2H), 0.99 – 0.94 (m, 2H), 0.90 (d, J = 6.6 Hz, 6H), 0.38 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.4, 174.4, 140.6, 139.7, 137.4, 133.3, 129.3, 129.2, 127.7, 127.1, 77.6, 62.4, 62.1, 45.0, 45.0, 41.8, 37.0, 30.2, 22.4, 21.0, 18.5, 14.9, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{32}H_{44}NaO_5Si$ $[M+Na]^+$ 559.2850, found 559.2851.

Methyl 1-((1-(((dimethyl(phenyl)silyl)oxy)cyclopentyl)methyl)cyclopropane-1-carboxylate (5a)



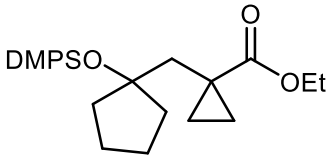
Prepared following the General Procedure A using **1b** (44 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **5a** (21 mg, 0.063 mmol, 63%), as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.54 (m, 2H), 7.39 – 7.32 (m, 3H), 3.58 (s, 3H), 2.04 (s, 2H), 1.76 – 1.65 (m, 2H), 1.65 – 1.61 (m, 1H), 1.58 – 1.49 (m, 4H), 1.32 – 1.24 (m, 1H), 1.21 – 1.12 (m, 2H), 0.95 – 0.85 (m, 2H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.9, 140.1, 133.3, 129.1, 127.6, 86.4, 51.7, 43.5, 39.6, 22.8, 21.4, 14.9, 1.0 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{28}NaO_3Si$ $[M+Na]^+$ 355.1700, found 355.1700.

Ethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclopentyl)methyl)cyclopropane-1-carboxylate (5b)



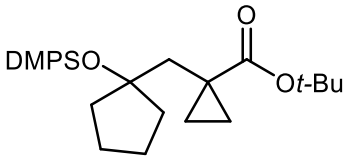
Prepared following the General Procedure A using **1b** (44 mg, 0.20 mmol, 2.0 equiv), **2b** (30 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **5b** (28 mg, 0.081 mmol, 81%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.54 (m, 2H), 7.39 – 7.30 (m, 3H), 4.04 (q, J = 7.1 Hz, 2H), 2.04 (s, 2H), 1.72 – 1.64 (m, 2H), 1.64 – 1.58 (m, 4H), 1.55 – 1.51 (m, 1H), 1.35 – 1.29 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H), 1.17 – 1.14 (m, 2H), 0.90 – 0.87 (m, 2H), 0.37 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.5, 140.1, 133.3, 129.1, 127.6, 86.5, 60.4, 43.3, 39.5, 22.8, 21.4, 15.0, 14.1, 1.0 ppm.

HRMS (ESI^+) calcd. for $C_{20}H_{30}NaO_3Si$ $[M+Na]^+$ 369.1856, found 369.1856.

***Tert*-butyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclopentyl)methyl)cyclopropane-1-carboxylate (5c)**



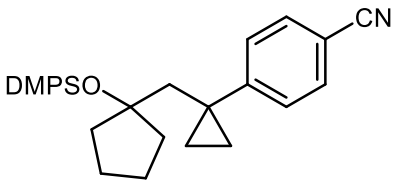
Prepared following the General Procedure A using **1b** (44 mg, 0.20 mmol, 2.0 equiv), **2c** (33 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **5c** (17 mg, 0.045 mmol, 45%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.54 (m, 2H), 7.40 – 7.32 (m, 3H), 2.02 (s, 2H), 1.70 – 1.55 (m, 8H), 1.41 (s, 9H), 1.13 – 1.07 (m, 2H), 0.87 – 0.82 (m, 2H), 0.38 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.6, 140.2, 133.3, 129.1, 127.6, 86.7, 79.9, 43.2, 39.4, 27.9, 22.9, 22.2, 14.9, 1.1 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{34}NaO_3Si$ $[M+Na]^+$ 397.2169, found 397.2169.

4-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclopentyl)methyl)cyclopropyl)benzonitrile (5d)



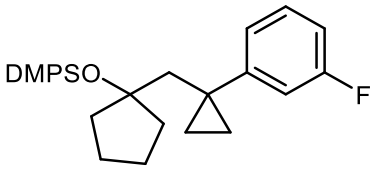
Prepared following the General Procedure A using **1b** (44 mg, 0.20 mmol, 2.0 equiv), **2q** (33 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/ hexane) gave the title compound **5d** (36 mg, 0.095 mmol, 95%), as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 – 7.43 (m, 4H), 7.42 – 7.31 (m, 5H), 1.97 (s, 2H), 1.55 – 1.52 (m, 1H), 1.51 – 1.44 (m, 2H), 1.43 – 1.33 (m, 4H), 1.27 – 1.24 (m, 1H), 0.84 – 0.75 (m, 4H), 0.22 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 152.3, 139.8, 133.2, 131.7, 130.2, 129.1, 127.6, 119.2, 109.1, 86.4, 50.7, 39.8, 23.7, 23.0, 13.5, 0.7 ppm.

HRMS (ESI$^+$) calcd. for $C_{24}H_{29}NNaOSi$ [M+Na]$^+$ 398.1911, found 398.1911.

((1-((1-(3-fluorophenyl)cyclopropyl)methyl)cyclopentyl)oxy)dimethyl(phenyl)silane (5e)



Prepared following the General Procedure A using **1b** (44 mg, 0.20 mmol, 2.0 equiv), **2j** (32 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/ hexane) gave the title compound **5e** (36 mg, 0.098 mmol, 98%), as a pale yellow oil.

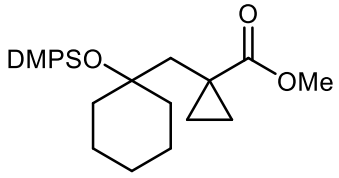
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 – 7.49 (m, 2H), 7.39 – 7.31 (m, 3H), 7.20 – 7.13 (m, 1H), 7.13 – 7.08 (m, 1H), 7.06 – 6.99 (m, 1H), 6.85 – 6.75 (m, 1H), 1.97 (s, 2H), 1.55 – 1.43 (m, 4H), 1.40 – 1.32 (m, 4H), 0.81 – 0.71 (m, 4H), 0.27 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.6 (d, J = 245.4 Hz), 149.1, 140.2, 133.3, 129.3, 129.0z, 127.5, 124.9, 116.2 (d, J = 10.1 Hz), 112.5 (d, J = 10.9 Hz), 86.6, 50.7, 39.6, 23.2, 23.0, 13.4, 0.8 ppm

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -114.3 ppm

HRMS (ESI$^+$) calcd. for $C_{23}H_{29}FNaO_3Si$ [M+Na]$^+$ 391.1864, found 391.1865.

Methyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclohexyl)methyl)cyclopropane-1-carboxylate (5f)



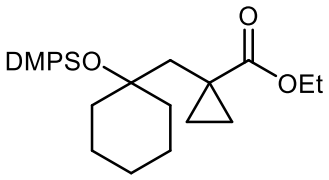
Prepared following the General Procedure A using **1c** (47 mg, 0.20 mmol, 2.0 equiv) and **2a** (28 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5f** (21 mg, 0.062 mmol, 62%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.56 (m, 2H), 7.39 – 7.31 (m, 3H), 3.56 (s, 3H), 1.97 (s, 2H), 1.62 – 1.55 (m, 4H), 1.53 – 1.45 (m, 2H), 1.39 – 1.30 (m, 4H), 1.17 – 1.12 (m, 2H), 0.82 – 0.74 (m, 2H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.7, 140.5, 133.4, 129.0, 127.6, 77.5, 51.6, 44.2, 38.7, 25.6, 22.8, 20.9, 14.7, 1.6 ppm.

HRMS (ESI^+) calcd. for $C_{20}H_{30}NaO_3Si$ $[M+Na]^+$ 369.1856, found 369.1856.

Ethyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclohexyl)methyl)cyclopropane-1-carboxylate (5g)



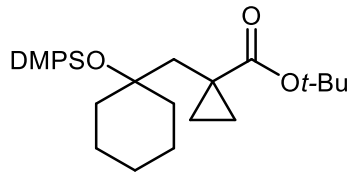
Prepared following the General Procedure A using **1c** (47 mg, 0.20 mmol, 2.0 equiv) and **2b** (30 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5g** (29 mg, 0.081 mmol, 81%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.65 – 7.57 (m, 2H), 7.39 – 7.31 (m, 3H), 4.03 (q, J = 7.2 Hz, 2H), 1.97 (s, 2H), 1.62 – 1.54 (m, 4H), 1.53 – 1.45 (m, 2H), 1.43 – 1.34 (m, 2H), 1.33 – 1.25 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 1.16 – 1.11 (m, 2H), 0.80 – 0.75 (m, 2H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.2, 140.5, 133.3, 129.0, 127.6, 77.6, 60.4, 44.5, 38.7, 25.6, 22.8, 21.0, 14.8, 14.1, 1.6 ppm.

HRMS (ESI$^+$) calcd. for $C_{21}H_{32}NaO_3Si$ $[M+Na]^+$ 383.2013, found 383.2013.

***Tert*-butyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclohexyl)methyl)cyclopropane-1-carboxylate (5h)**



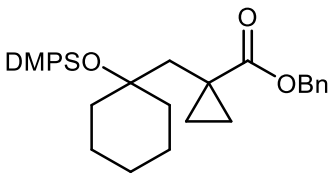
Prepared following the General Procedure A using **1c** (47 mg, 0.20 mmol, 2.0 equiv) and **2c** (33 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5h** (16 mg, 0.042 mmol, 42%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.55 (m, 2H), 7.39 – 7.30 (m, 3H), 1.93 (s, 2H), 1.56 – 1.51 (m, 4H), 1.48 – 1.42 (m, 2H), 1.42 – 1.37 (m, 2H), 1.40 (s, 9H), 1.30 – 1.24 (m, 2H), 1.10 – 1.04 (m, 2H), 0.76 – 0.70 (m, 2H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.3, 140.6, 133.3, 129.0, 127.6, 79.9, 77.8, 45.5, 38.5, 27.9, 25.6, 22.5, 21.8, 18.4, 14.8, 1.7, 1.0 ppm.

HRMS (ESI$^+$) calcd. for $C_{23}H_{36}NaO_3Si$ $[M+Na]^+$ 411.2326, found 411.2326.

Benzyl 1-((1-((dimethyl(phenyl)silyl)oxy)cyclohexyl)methyl)cyclopropane-1-carboxylate (5i)



Prepared following the General Procedure A using **1c** (94 mg, 0.40 mmol, 2.0 equiv) and **2d** (72 mg, 0.20 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL), which was irradiated with 30W blue

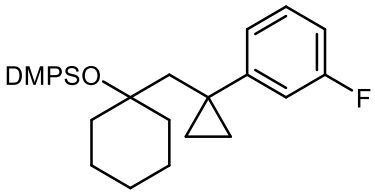
LED for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5i** (60 mg, 0.14 mmol, 71%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.67 – 7.61 (m, 2H), 7.40 – 7.33 (m, 8H), 5.04 (s, 2H), 2.03 (s, 2H), 1.65 – 1.57 (m, 4H), 1.55 – 1.48 (m, 2H), 1.39 – 1.32 (m, 4H), 1.25 – 1.19 (m, 2H), 0.87 – 0.81 (m, 2H), 0.41 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.9, 140.5, 136.2, 133.3, 133.0, 129.0, 128.4, 128.0, 127.6, 77.5, 66.1, 44.3, 38.7, 25.6, 22.8, 21.1, 14.8, 1.5 ppm.

HRMS (ESI^+) calcd. for $C_{26}H_{34}NaO_3Si$ $[M+Na]^+$ 445.2169, found 445.2169.

((1-((1-(3-fluorophenyl)cyclopropyl)methyl)cyclohexyl)oxy)dimethyl(phenyl)silane (5j)



Prepared following the General Procedure A using **1c** (47 mg, 0.20 mmol, 2.0 equiv) and **2j** (32 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **5j** (31 mg, 0.080 mmol, 80%) as a pale yellow liquid.

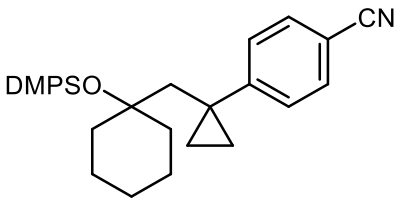
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 – 7.54 (m, 2H), 7.38 – 7.33 (m, 3H), 7.21 – 7.13 (m, 1H), 7.12 – 7.08 (m, 1H), 7.04 – 6.98 (m, 1H), 6.85 – 6.76 (m, 1H), 1.95 (s, 2H), 1.54 – 1.45 (m, 2H), 1.43 – 1.33 (m, 3H), 1.29 – 1.19 (m, 4H), 1.16 – 1.08 (m, 1H), 0.82 – 0.76 (m, 2H), 0.76 – 0.71 (m, 2H), 0.31 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.6 (d, J = 245.9 Hz), 149.1, 140.7, 133.3, 129.3 (d, J = 8.7 Hz), 129.0, 127.5, 124.7 (d, J = 2.5 Hz), 115.9 (d, J = 21.0 Hz), 112.5 (d, J = 21.0 Hz), 78.1, 52.4, 30.4, 25.5, 22.7, 13.7, 1.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -114.2 ppm.

HRMS (ESI^+) calcd. for $C_{24}H_3FNaOSi$ $[M+Na]^+$ 405.2020, found 405.2020.

4-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclohexyl)methyl)cyclopropyl)benzonitrile (5k)



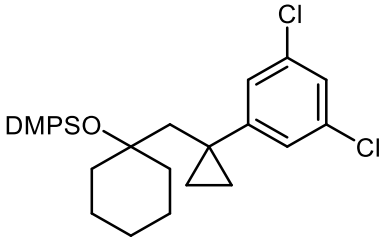
Prepared following the General Procedure A using **1c** (47 mg, 0.20 mmol, 2.0 equiv) and **2q** (33 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 0.0050 mmol, 5.0 mol%), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv), s-collidine (30 mg, 0.25 mmol, 2.5 equiv) and MeCN (2.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **5k** (37 mg, 0.095 mmol, 95%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 – 7.47 (m, 2H), 7.47 – 7.42 (m, 2H), 7.40 – 7.31 (m, 5H), 1.97 (s, 2H), 1.54 – 1.47 (m, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.28 (m, 2H), 1.23 – 1.15 (m, 4H), 0.82 – 0.77 (m, 4H), 0.24 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 152.4, 140.3, 133.2, 131.7, 129.7, 129.1, 127.6, 119.2, 109.0, 77.9, 50.1, 38.8, 25.5, 23.0, 22.9, 13.7, 1.4 ppm.

HRMS (ESI^+) calcd. for $C_{25}H_{31}NNaOSi$ $[M+Na]^+$ 412.2067, found 412.2068.

((1-((1-(3,5-dichlorophenyl)cyclopropyl)methyl)cyclohexyl)oxy)dimethyl(phenyl)silane (5l)



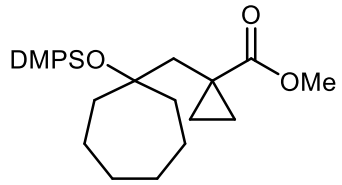
Prepared following the General Procedure A using **1c** (30 mg, 0.13 mmol, 2.0 equiv) and **2o** (19 mg, 0.05 mmol, 1.0 equiv), 4CzIPN (2 mg, 0.0025 mmol, 5.0 mol%), Cs_2CO_3 (33 mg, 0.10 mmol, 2.0 equiv), s-collidine (15 mg, 0.13 mmol, 2.5 equiv) and MeCN (1.0 mL), which was irradiated with 30W blue LED for 24 h. Purification by flash column chromatography (10% EtOAc/Petroleum ether) gave the title compound **5l** (18 mg, 0.043 mmol, 85%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.53 – 7.47 (m, 2H), 7.37 – 7.33 (m, 3H), 7.18 (d, 2H), 7.05 (t, J = 1.9 Hz, 1H), 1.91 (s, 2H), 1.54 – 1.43 (m, 4H), 1.33 – 1.29 (m, 2H), 1.24 – 1.17 (m, 4H), 0.79 – 0.72 (m, 4H), 0.26 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 150.3, 140.4, 134.2, 133.2, 129.0, 127.7, 127.6, 125.7, 77.8, 38.9, 29.7, 25.6, 23.1, 22.5, 13.6, 1.4 ppm.

HRMS (ESI^+) calcd. for $C_{24}H_{30}Cl_2NaOSi$ $[M+Na]^+$ 455.1335, found 455.1335.

Methyl 1-((1-((dimethyl(phenyl)silyl)oxy)cycloheptyl)methyl)cyclopropane-1-carboxylate (5m)



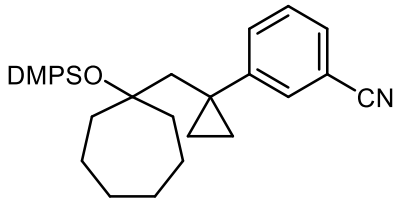
Prepared following the General Procedure A using **1d** (99 mg, 0.40 mmol, 2.0 equiv) and **2a** (57 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL). Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5m** (70 mg, 0.19 mmol, 97%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.57 (m, 2H), 7.38 – 7.34 (m, 3H), 3.57 (s, 3H), 1.95 (s, 2H), 1.79 – 1.68 (m, 4H), 1.54 – 1.44 (m, 6H), 1.36 – 1.31 (m, 1H), 1.29 – 1.26 (m, 1H), 1.18 – 1.14 (m, 2H), 0.92 – 0.87 (m, 2H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 150.4, 140.5, 134.2, 133.3, 129.1, 127.8, 127.7, 125.8, 77.9, 38.9, 29.8, 25.6, 23.2, 22.6, 13.6, 1.5, 1.1 ppm.

HRMS (ESI$^+$) calcd. for $C_{21}H_{32}NaO_3Si$ $[M+Na]^+$ 383.2013, found 383.2013.

Methyl 1-((1-(((dimethyl(phenyl)silyl)oxy)cyclooctyl)methyl)cyclopropane-1-carboxylate (5n)



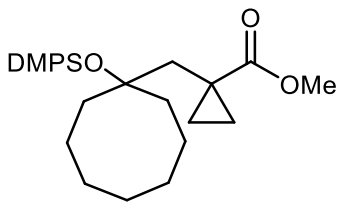
Prepared following the General Procedure A using **1d** (99 mg, 0.40 mmol, 2.0 equiv) and **2p** (66 mg, 0.2 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL). Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5n** (83 mg, 0.18 mmol, 91%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.60 – 7.53 (m, 2H), 7.47 – 7.43 (m, 2H), 7.37 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 1.91 (s, 2H), 1.68 – 1.52 (m, 4H), 1.46 – 1.32 (m, 6H), 1.20 – 1.09 (m, 2H), 0.83 – 0.73 (m, 4H), 0.19 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.3, 140.2, 134.0, 133.2, 132.9, 129.1, 129.0, 128.6, 127.5, 119.2, 111.7, 81.6, 52.8, 42.0, 29.9, 22.6, 22.5, 13.5, 1.2 ppm.

HRMS (ESI$^+$) calcd. for $C_{26}H_{33}NNaOSi$ $[M+Na]^+$ 426.2224, found 426.2223.

Methyl 1-((1-(((dimethyl(phenyl)silyl)oxy)cyclooctyl)methyl)cyclopropane-1-carboxylate (5o)



Prepared following the General Procedure A using **1e** (105 mg, 0.40 mmol, 2.0 equiv) and **2a** (57 mg, 0.20 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv),

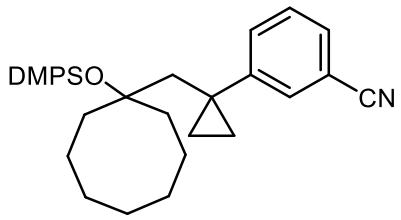
s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL). Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5o** (71 mg, 0.19 mmol, 95%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.56 (m, 2H), 7.39 – 7.35 (m, 3H), 3.57 (s, 3H), 1.93 (s, 2H), 1.84 – 1.76 (m, 2H), 1.70 – 1.62 (m, 2H), 1.61 – 1.52 (m, 2H), 1.50 – 1.39 (m, 7H), 1.20 – 1.14 (m, 2H), 0.93 – 0.88 (m, 2H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 176.1, 140.5, 133.5, 129.1, 127.7, 81.2, 51.8, 44.7, 36.6, 28.3, 25.0, 22.8, 20.8, 15.1, 1.7 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{34}NaO_3Si$ $[M+Na]^+$ 397.2169, found 397.2169.

3-(1-((1-((dimethyl(phenyl)silyl)oxy)cyclooctyl)methyl)cyclopropyl)benzonitrile (5p)



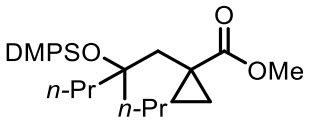
Prepared following the General Procedure A using **1e** (105 mg, 0.40 mmol, 2.0 equiv) and **2p** (66 mg, 0.20 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL). Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5p** (82 mg, 0.17 mmol, 87%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 – 7.54 (m, 3H), 7.48 – 7.43 (m, 2H), 7.39 – 7.35 (m, 3H), 7.30 (dt, J = 7.7, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 1.91 (s, 2H), 1.80 – 1.69 (m, 2H), 1.53 – 1.49 (m, 2H), 1.47 – 1.25 (m, 10H), 0.85 – 0.76 (m, 4H), 0.23 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.5, 140.4, 134.2, 133.3, 133.1, 129.2, 129.1, 128.7, 127.6, 119.3, 111.8, 81.2, 51.9, 37.4, 28.2, 24.5, 22.6, 22.5, 13.7, 1.5 ppm.

HRMS (ESI$^+$) calcd. for $C_{27}H_{35}NNaOSi$ $[M+Na]^+$ 440.2380, found 440.2380.

Methyl 1-(2-((dimethyl(phenyl)silyl)oxy)-2-isopropyl-3-methylbutyl)cyclopropane-1-carboxylate (5q)



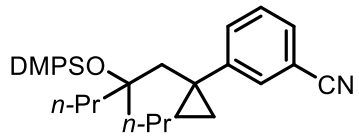
Prepared following the General Procedure A using **1f** (100 mg, 0.40 mmol, 2.0 equiv) and **2a** (57 mg, 0.20 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL). Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **5q** (67 mg, 0.18 mmol, 92%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.64 – 7.57 (m, 2H), 7.39 – 7.35 (m, 3H), 3.54 (s, 3H), 1.93 (s, 2H), 1.52 – 1.44 (m, 4H), 1.36 – 1.25 (m, 5H), 1.19 – 1.14 (m, 2H), 0.89 – 0.82 (m, 8H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 175.8, 140.3, 133.3, 129.0, 127.5, 80.1, 51.6, 42.4, 41.8, 20.8, 17.3, 14.6, 1.5 ppm.

HRMS (ESI$^+$) calcd. for $C_{21}H_{34}NaO_3Si$ $[M+Na]^+$ 385.2169, found 385.2169.

3-(1-(2-((dimethyl(phenyl)silyl)oxy)-2-isopropyl-3-methylbutyl)cyclopropyl)benzonitrile (5r)



Prepared following the General Procedure A using **1f** (100 mg, 0.40 mmol, 2.0 equiv) and **2p** (66 mg, 0.20 mmol, 1.0 equiv), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv), s-collidine (61 mg, 0.50 mmol, 2.5 equiv) and MeCN (4.0 mL). Purification by flash column

chromatography (5% EtOAc/Petroleum ether) gave the title compound **5r** (75 mg, 0.19 mmol, 93%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.59 – 7.51 (m, 2H), 7.46 – 7.41 (m, 2H), 7.37 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 1.87 (s, 2H), 1.36 – 1.29 (m, 4H), 1.20 – 1.10 (m, 4H), 0.79 – 0.75 (m, 4H), 0.71 (t, J = 7.2 Hz, 6H), 0.23 (s, 6H) ppm.

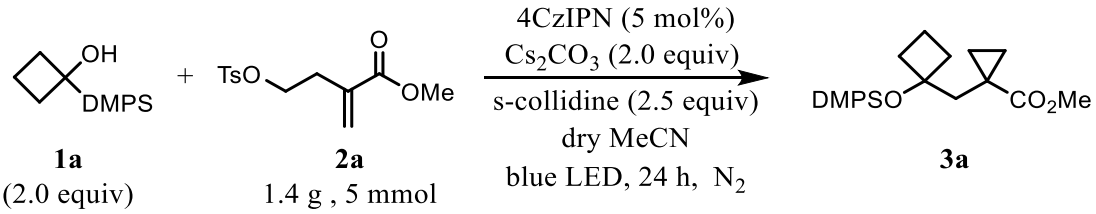
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 148.3, 140.1, 134.2, 133.3, 133.1, 129.2, 129.1, 128.6, 127.6, 119.2, 111.8, 80.5, 47.9, 43.0, 22.5, 17.3, 14.5, 13.5, 1.5 ppm.

HRMS (ESI^+) calcd. for $C_{26}H_{35}NNaOSi$ $[M+Na]^+$ 428.2380, found 428.2379.

6. Follow-up chemistry

(a) Gram-scale synthesis

a) Gram-scale synthesis of **3a**:



1a (2.0 equiv)

2a 1.4 g , 5 mmol

3a

Prepared following the modified General Procedure A. 4CzIPN (197 mg, 0.25 mmol, 5.0 mol%) was added to a solution of **1a** (1.55 g, 7.5 mmol, 2.0 equiv), **2a** (1.42 g, 5.0 mmol, 1.0 equiv), s-collidine (1.51 g, 12.5 mmol, 2.5 equiv) and dry MeCN (40 mL) under N_2 at rt. The mixture was irradiated with 2×30 W blue LED for 24 h. Water (20 mL) was added to the reaction mixture. The phases were separated and the aqueous phase was extracted into DCM (2 ×30 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAc/hexane) gave the title compound **3a** (1.33 g, 4.2 mmol, 84%), as a colorless liquid.

b) Reaction set-up:

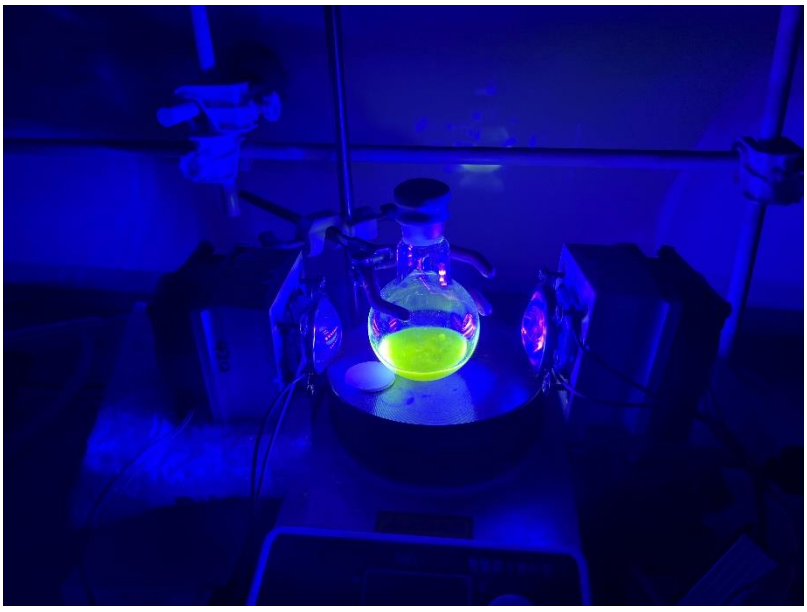
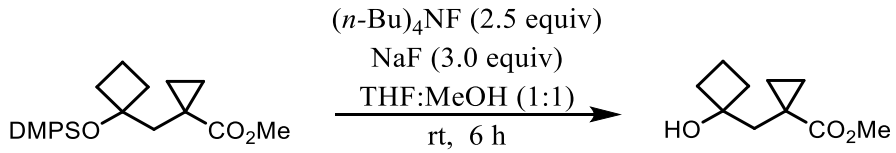


Figure S2. Photoredox reaction setup for scale up.

(b) Reprehensive product transformations

a) Removal of **3a** silicon group:



3a **6a**

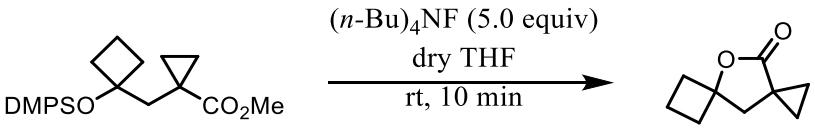
The solution of **3a** (80 mg, 0.25 mmol, 1.0 equiv.), NaF (32 mg, 0.75 mmol, 3.0 equiv), THF and MeOH (1:1, 5.0 mL) was added (*n*-Bu)$_4$NF (2.5 equiv) sequently and stirred at room temperature for 6 h. Water (30 mL) was added to the reaction mixture. The phases were separated and the aqueous phase was extracted into DCM (3 × 30 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (20% EtOAc/hexane) gave the corresponding compound **6a** (39 mg, 0.21 mmol, 85%) as a pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.33 (s, 1H), 3.62 (s, 3H), 2.10 – 2.00 (m, 4H), 1.95 (s, 2H), 1.77 – 1.68 (m, 1H), 1.48 – 1.37 (m, 1H), 1.34 – 1.28 (m, 2H), 0.90 – 0.83 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 177.7, 75.6, 52.2, 43.2, 36.2, 21.3, 15.7, 12.5 ppm.

HRMS (ESI^+) calcd. for $C_{10}H_{16}NaO_3$ $[M+Na]^+$ 207.0992, found 207.0991.

b) Intramolecular ester exchange of **3a**:



3a **6b**

To **3a** (32 mg, 0.10 mmol, 1.0 equiv.) in dry THF (2 mL) was added (*n*-Bu)$_4$NF (0.11 mL, 1M) and stirred at room temperature for 10 min. Water (30 mL) was added to the reaction mixture. The phases were separated and the aqueous phase was extracted into EA (3 × 30 mL). The combined

organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (20% EtOAc/hexane) gave the corresponding compound **6b** (12 mg, 0.080 mmol, 80%) as a yellow oil with strong fruity aroma.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.33 (s, 1H), 3.62 (s, 3H), 2.10 – 2.00 (m, 4H), 1.95 (s, 2H), 1.77 – 1.68 (m, 1H), 1.48 – 1.37 (m, 1H), 1.34 – 1.28 (m, 2H), 0.90 – 0.83 (m, 2H) ppm.

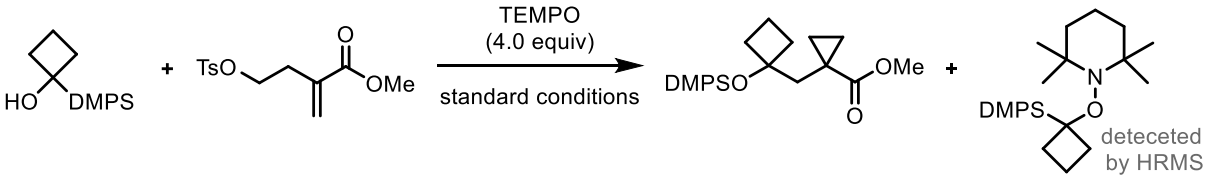
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 179.4, 82.8, 41.6, 35.6, 20.8, 14.6, 12.3 ppm.

HRMS (ESI^+) calcd. for $C_9H_{12}NaO_2$ $[M+Na]^+$ 175.0730, found 175.0730.

7. Mechanistic Studies

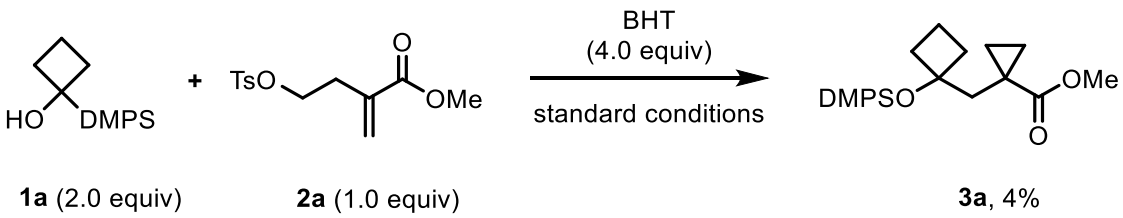
(a) Radical quenching experiments:

To further investigate the cascade reaction of this new photocatalyzed radical tandem/polar crossover cyclization, the control experiments were carried out with radical scavengers.



1a (2.0 equiv) **2a** (1.0 equiv) **3a**, 0% **3aa**

To a 5 mL vial equipped with a magnetic stir bar was added **1a** (42 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 5.0 mol%), s-collidine (31 mg, 0.25 mmol, 2.5 equiv) and Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv). Then anhydrous MeCN (2 mL) and TEMPO (63 mg, 0.40 mmol, 4.0 equiv) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for 20 h. HRMS analysis of this reaction crude mixture showed that **3aa** was formed and no product **3a** was observed, the reaction was completely inhibited.

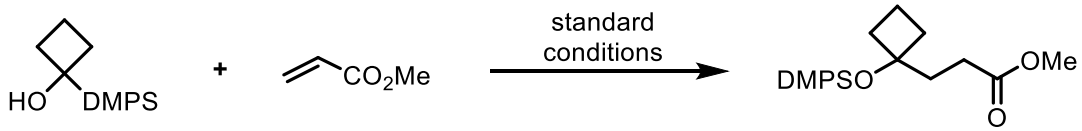


1a (2.0 equiv) **2a** (1.0 equiv) **3a**, 4%

To a 5 mL vial equipped with a magnetic stir bar was added **1a** (42 mg, 0.20 mmol, 2.0 equiv), **2a** (28 mg, 0.10 mmol, 1.0 equiv), 4CzIPN (4 mg, 5.0 mol%), s-collidine (31 mg, 0.25 mmol, 2.5 equiv) and Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv). Then anhydrous MeCN (2 mL) and BHT (88 mg, 0.40 mmol, 4.0 equiv) was added to the mixture. The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for 20 h. After reaction, 4% of **3a** was observed from crude reaction mixture.

Both of these results supported the speculation that the reaction proceeded via a radical pathway.

(b) Radical and anion trapping experiments:



1a (2.0 equiv) (1.0 equiv) **7b**, 50%

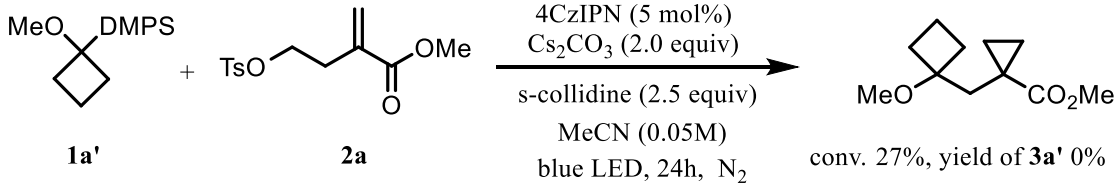
To a 7 mL vial equipped with a magnetic stir bar was added **1a** (82 mg, 0.4 mmol, 2.0 equiv), methyl acrylate (17 mg, 0.10 mmol, 1.0 equiv.), 4CzIPN (8 mg, 0.010 mmol, 5.0 mol%), s-collidine (61 mg, 0.50 mmol, 2.5 equiv), Cs_2CO_3 (130 mg, 0.40 mmol, 2.0 equiv) and MeCN (4.0 mL). The vial was sealed with a septum and the reaction mixture degassed by sparging with nitrogen for 15 min. The nitrogen inlet was removed, and the vial further sealed with parafilm. The reaction mixture was stirred at 800 rpm and irradiated with a 30 W blue LED lamp with fan cooling for 20 h. Then partitioned between DCM (20 mL) and water (30 mL). The phases were separated and the aqueous phase was extracted into DCM (2 ×20 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAc/hexane) gave the title compound **7b** (29 mg, 0.10 mmol, 50%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.62 – 7.57 (m, 2H), 7.40 – 7.34 (m, 3H), 3.65 (s, 3H), 2.42 – 2.36 (m, 2H), 2.18 – 2.07 (m, 2H), 1.99 – 1.89 (m, 4H), 0.39 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.7, 133.3, 129.3, 127.8, 76.2, 51.5, 36.0, 35.1, 28.9, 12.7, 0.6 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{24}NaO_3$ $[M+Na]^+$ 315.1387, found 315.1388.

(c) Transfer of alkoxyl radical experiments:



1a' **2a** conv. 27%, yield of **3a'** 0%

In a glovebox, to an oven-dried 10 mL tube equipped with a magnetic stir bar was added **1a′** (66 mg, 0.30 mmol, 2.0 equiv), **2a** (43 mg, 0.15 mmol, 1.0 equiv.), 4CzIPN (6 mg, 0.0075 mmol, 0.5 mol%), s-collidine (45mg, 0.38 mmol, 2.5 equiv), Cs2CO3 (98 mg, 0.30 mmol, 2.0 equiv) and dry MeCN (4 mL) sequentially. The tube was sealed, then irradiated with a 30 W blue LED lamp. The mixture was stirred under blue light irradiation at ambient temperature for the 24 h. Then the blue light was turned off. The reaction mixture was filtered through a thin silica gel plug with EA (30 mL) as the eluent. The filtrate was concentrated under reduced pressure. The conversion of **2a** and yield of **3a′** were determined by ^{1}H NMR analysis of the unpurified mixture with 1,3,5-trimethoxybenzene as an internal standard. The failure of the reaction with **1a′** indicated the importance of OH group of compound **1a**.

(d) Light-dark experiments:

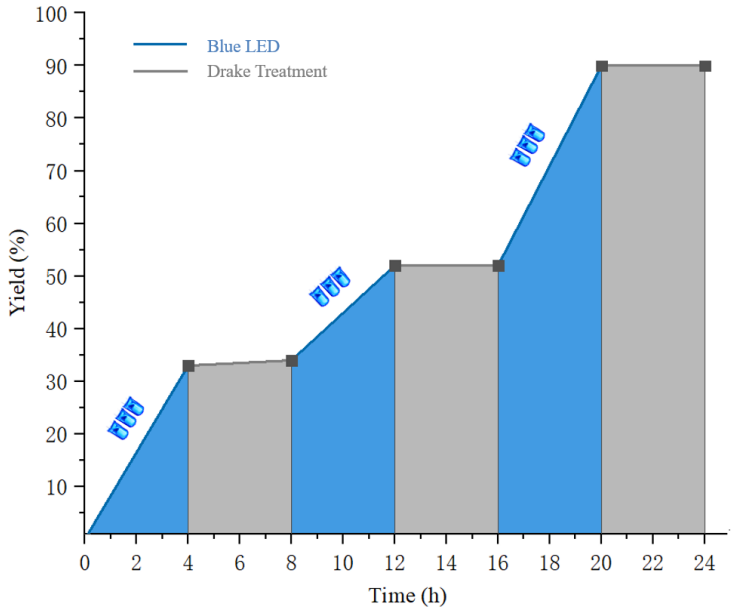


Figure S3. light-dark experiments

(e) Fluorescence quenching experiments:

Emission intensities were recorded using an F-4600 FL Spectrophotometer. First, the emission intensity of 4CzIPN solutions was observed at 500 nm. The solutions were irradiated at 378 nm (Maximum absorption wavelength of 4CzIPN) and fluorescence was measured from 450 nm to 793 nm. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of 4CzIPN with different concentration of **1a**, **1b** and s-collidine in degassed anhydrous CH_3CN in 10 mm path length quartz cuvette was collected. Figure S4 to Figure S6: the emission spectra of 5×10^{-5} M solutions of 4CzIPN with reactants (**1a**, **2a** or s-collidine) in degassed anhydrous CH_3CN in 10 mm path length quartz cuvette were collected. Figure S7: the emission spectra of 5×10^{-5} M solutions of 4CzIPN with reactants (**1a** and s-collidine) in degassed anhydrous CH_3CN in 10 mm path length quartz cuvette was collected. Figure S8: the emission spectra of 5×10^{-5} M solutions of 4CzIPN with reactants (**1a,** $Cs_2CO_3$and s-collidine) in degassed anhydrous CH_3CN in 10 mm path length quartz cuvette was collected. The linear relationship between I_0/I and the increasing concentration was collected in Figure S9 (I_0 and I are the fluorescence intensities before and after the increasing of the concentration)

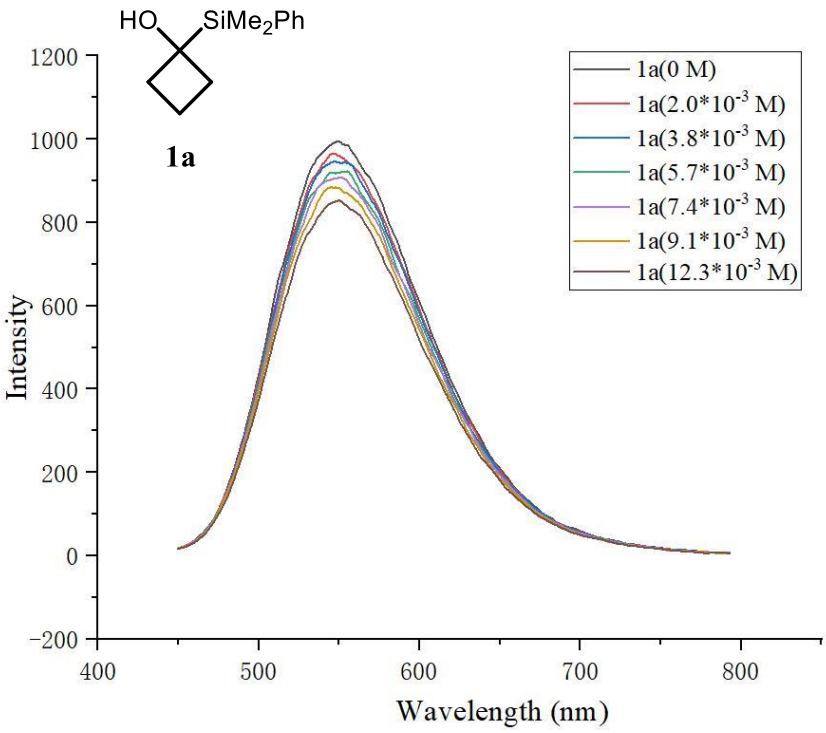


Figure S4. fluorescence quenching experiment of **1a**

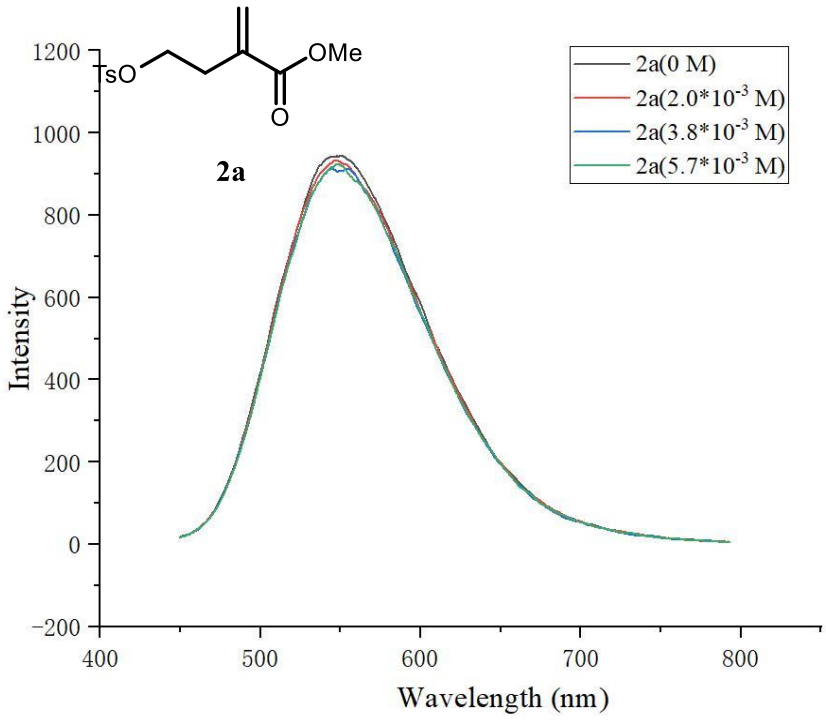


Figure S5. fluorescence quenching experiment of **2a**

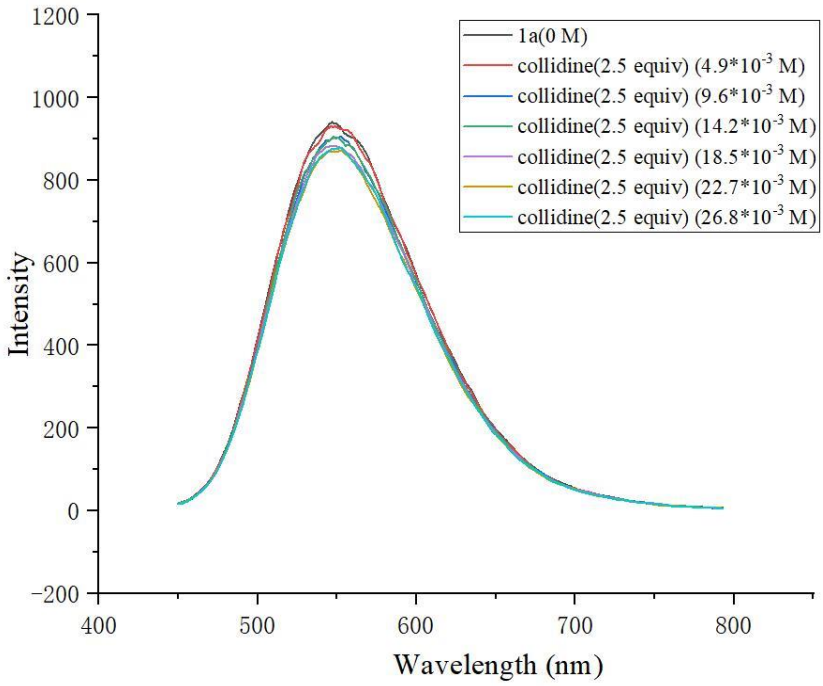


Figure S6. fluorescence quenching experiment of s-collidine

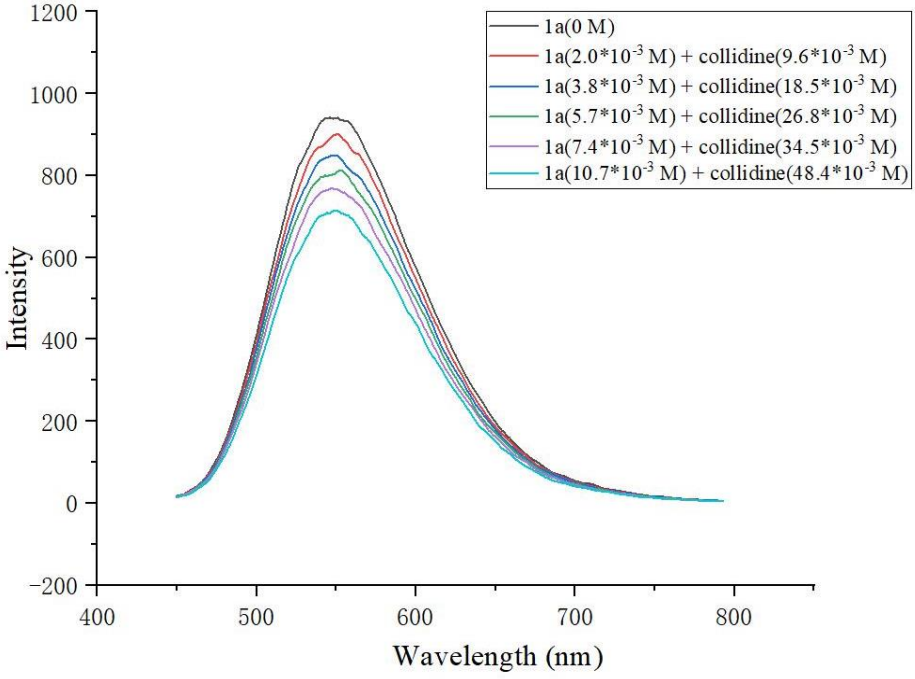


Figure S7. fluorescence quenching experiment of **1a** and collidine

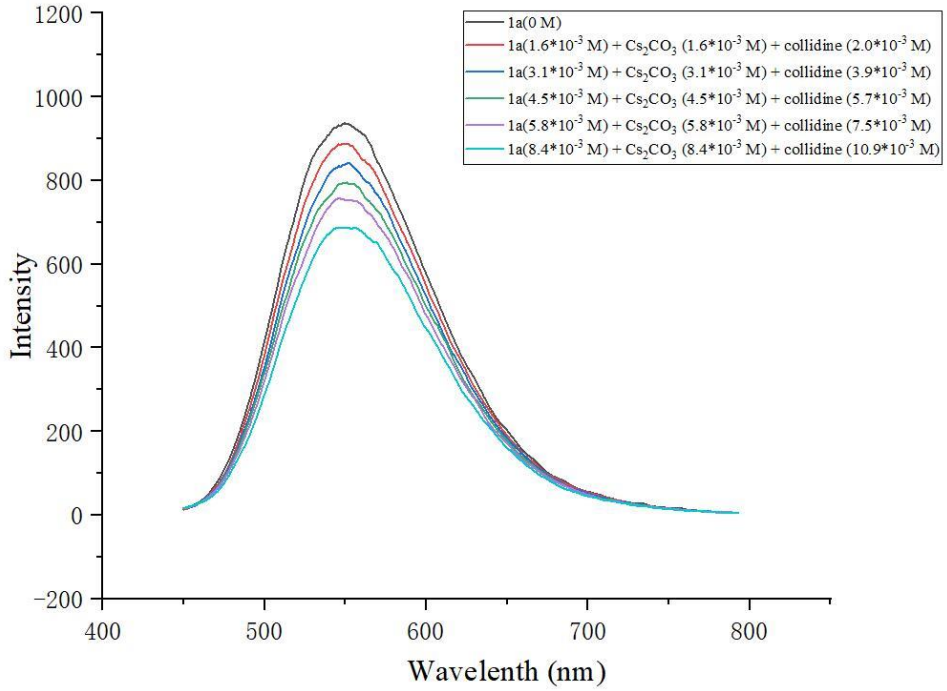


Figure S8. fluorescence quenching experiment of **1a**, Cs_2CO_3 and collidine

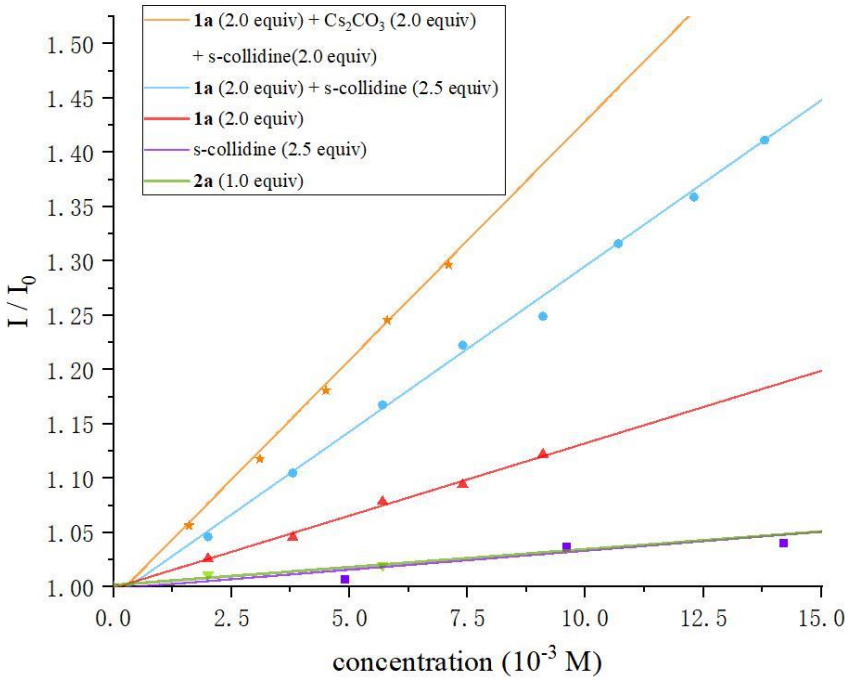


Figure S9. the linear relationship between I_0/I and concentration

8. Reference

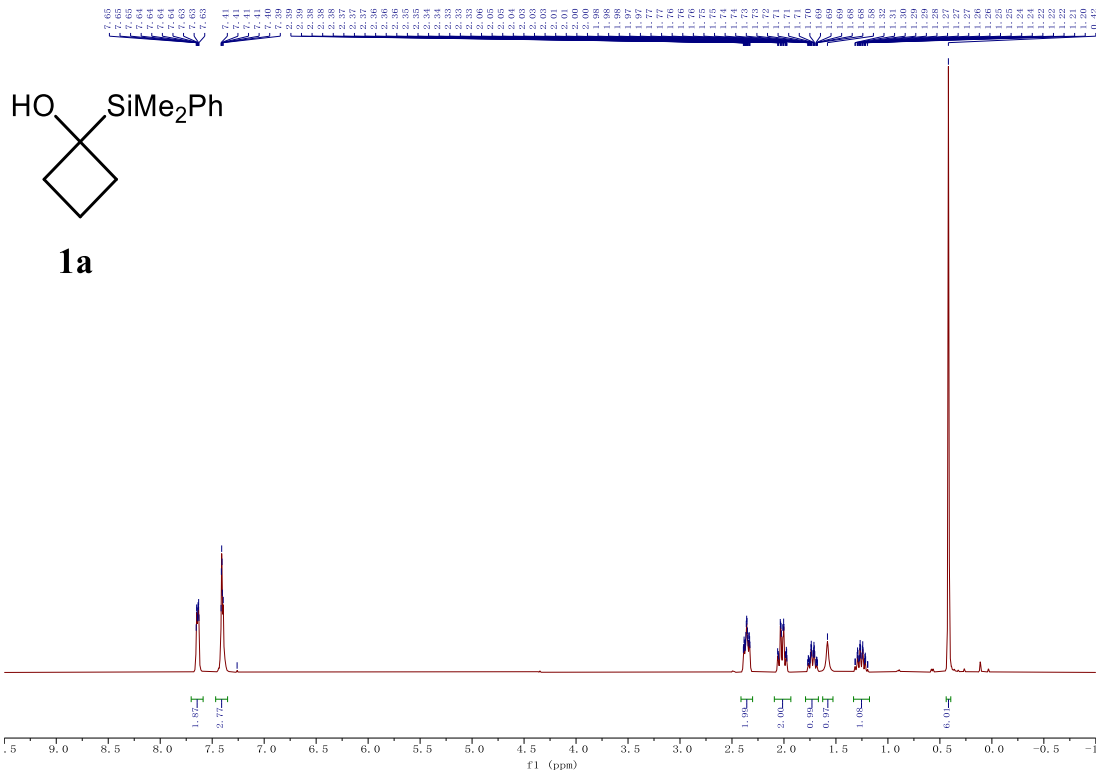
1. Luo, J.; Zhang, J. *ACS Catal.* **2016**, *6*, 873; b) Zheng, Z.; van der Werf, A.; Deliaval, M.; Selander, N. *Org. Lett.* **2020**, *22*, 2791.

2. Zhang, Y.; Zhang, Y.; Shen, X. *Chem Catal.* **2021,** *2*, 423.

3. a) H. Li, Y. Zhang, X. Yang, Z. Deng, Z. Zhu, P. Zhou, X. Ouyang, Y. Yuan, X. Chen, L. Yang, M. Liu, C. Shu, *Angew. Chem.* **2023**, *135*, e202300159; b) Shu, C.; Mega, R. S.; Andreassen, B. J.; Noble, A.; Aggarwal, V. K., *Angew. Chem., Int. Ed*. **2018***, 57,* 15430.

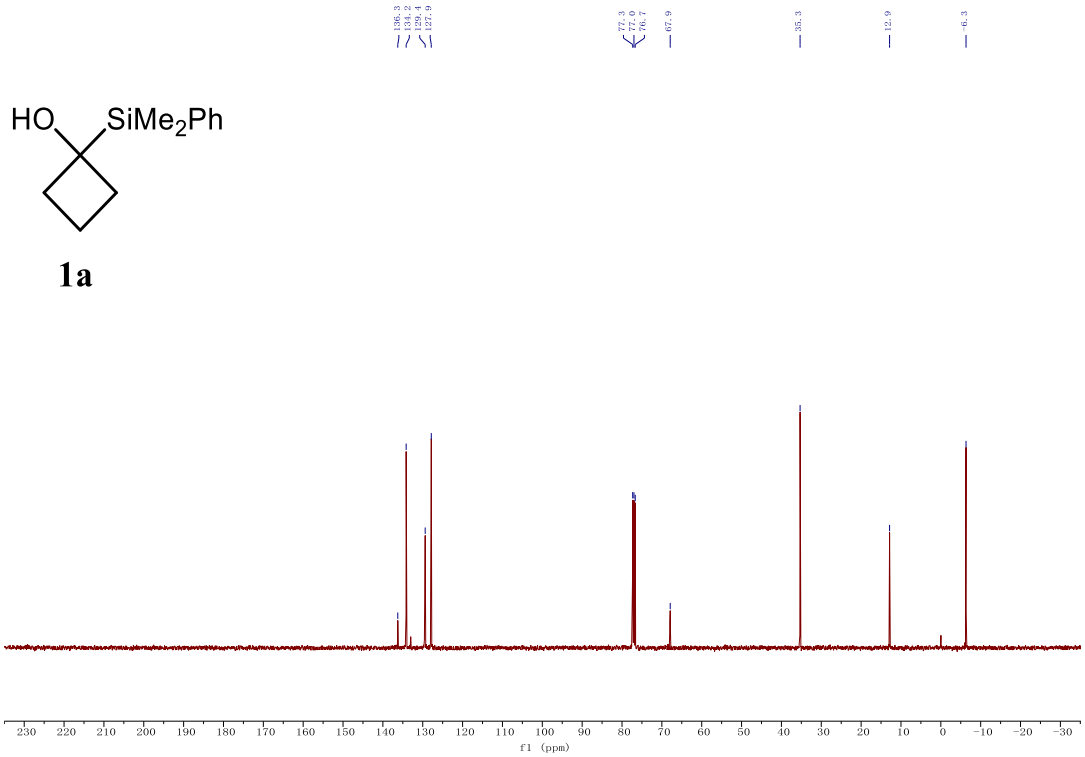
9. NMR Spectra

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



1a

^{13}C NMR (101 MHz, $CDCl_3$)



1a

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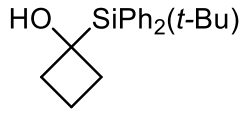

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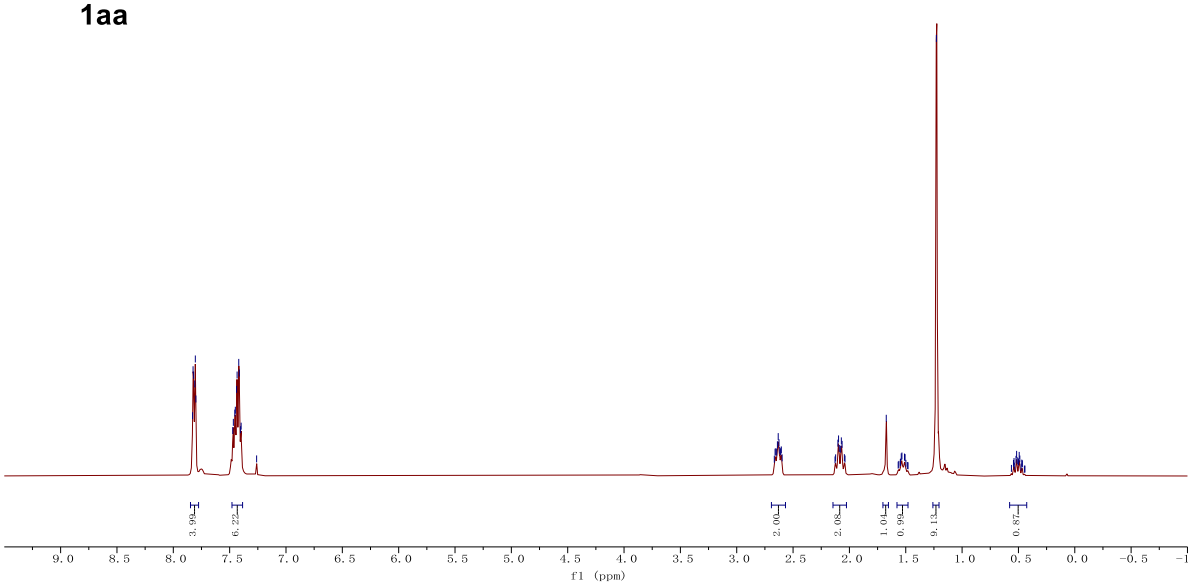
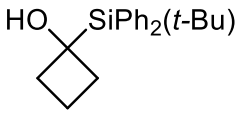


^{13}C NMR (101 MHz, $CDCl_3$)



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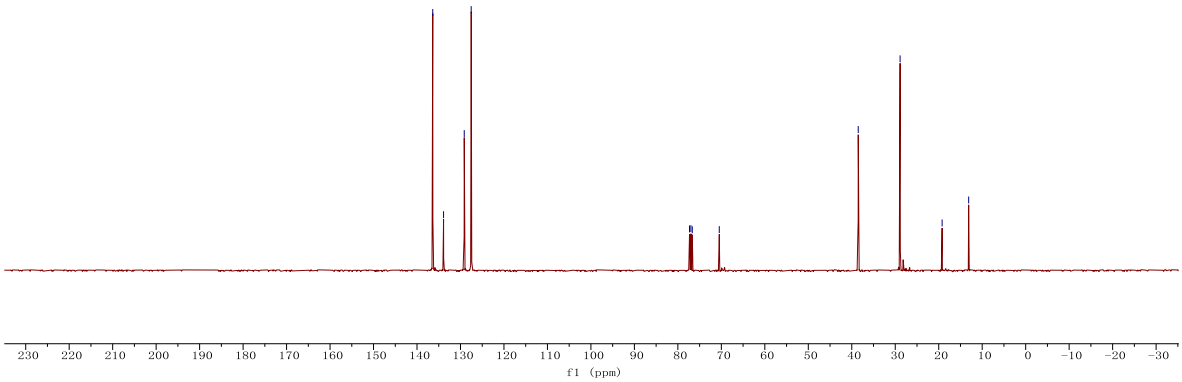

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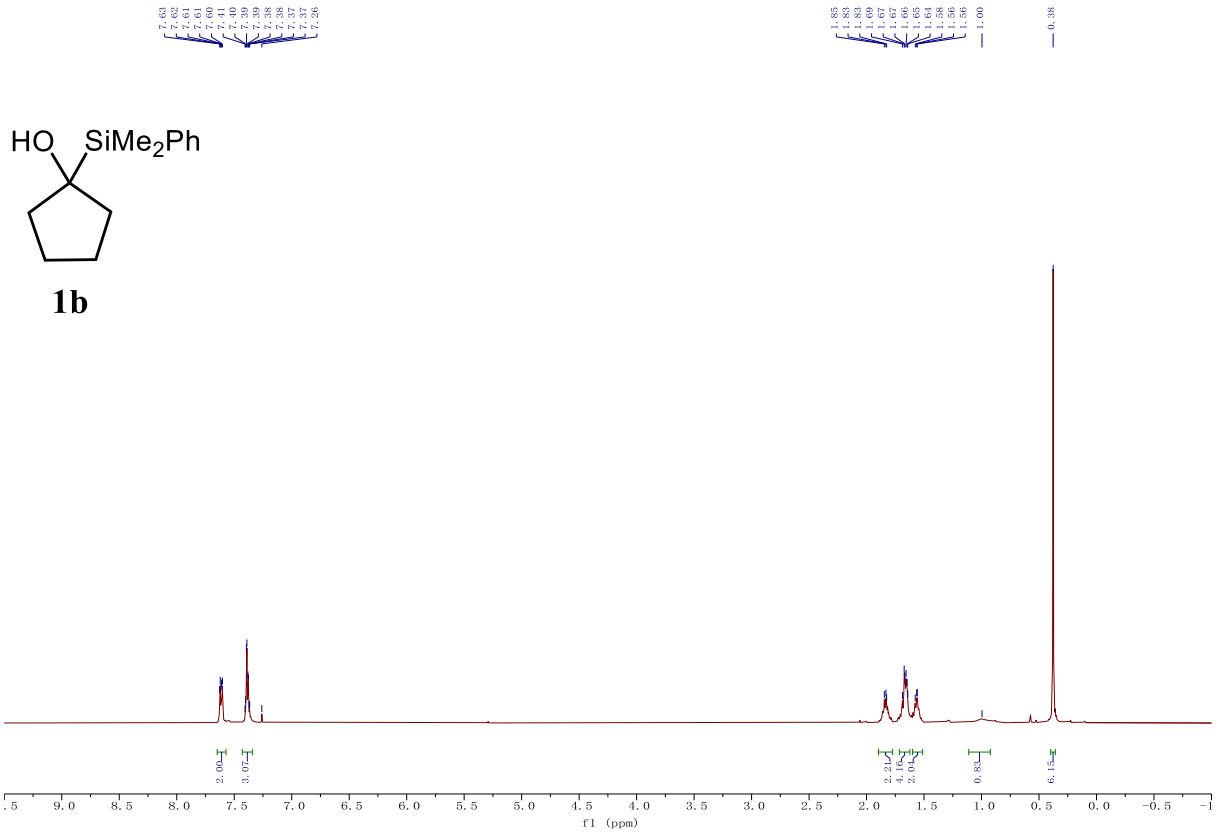

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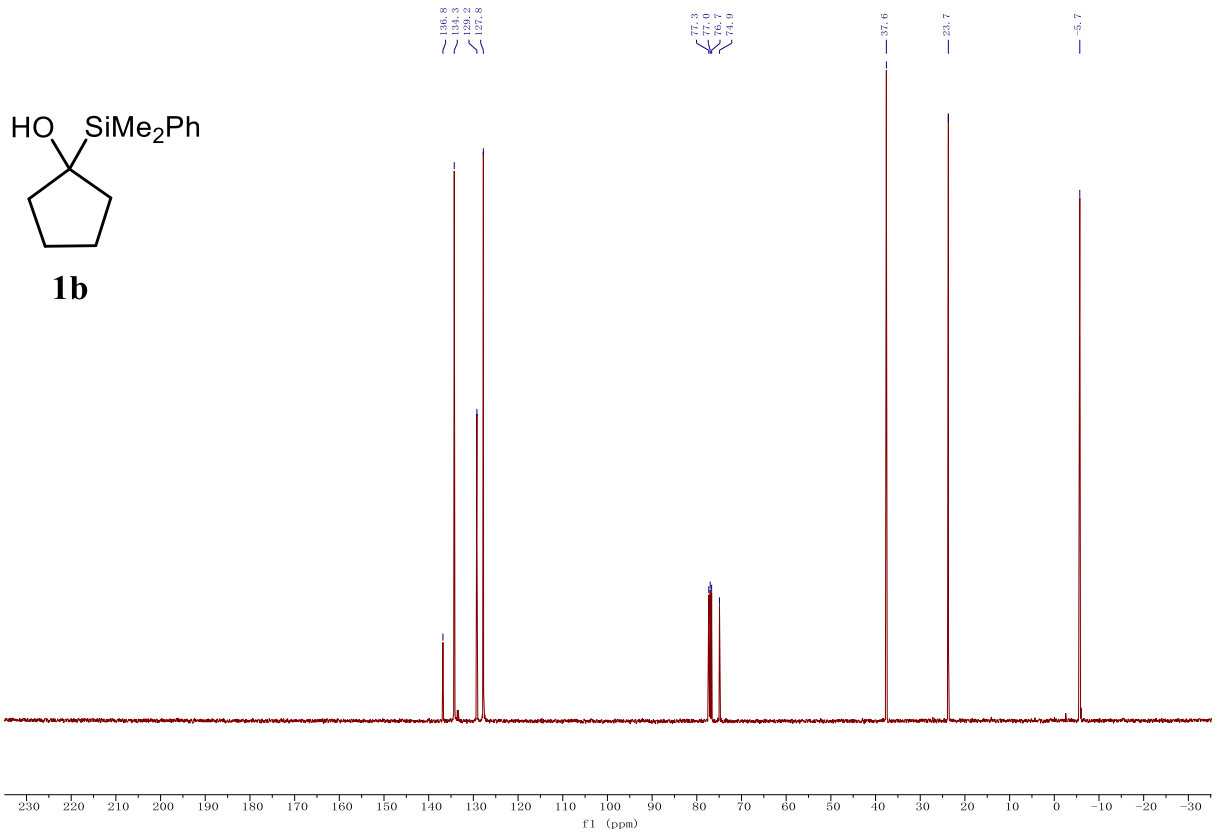

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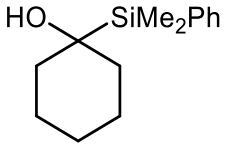

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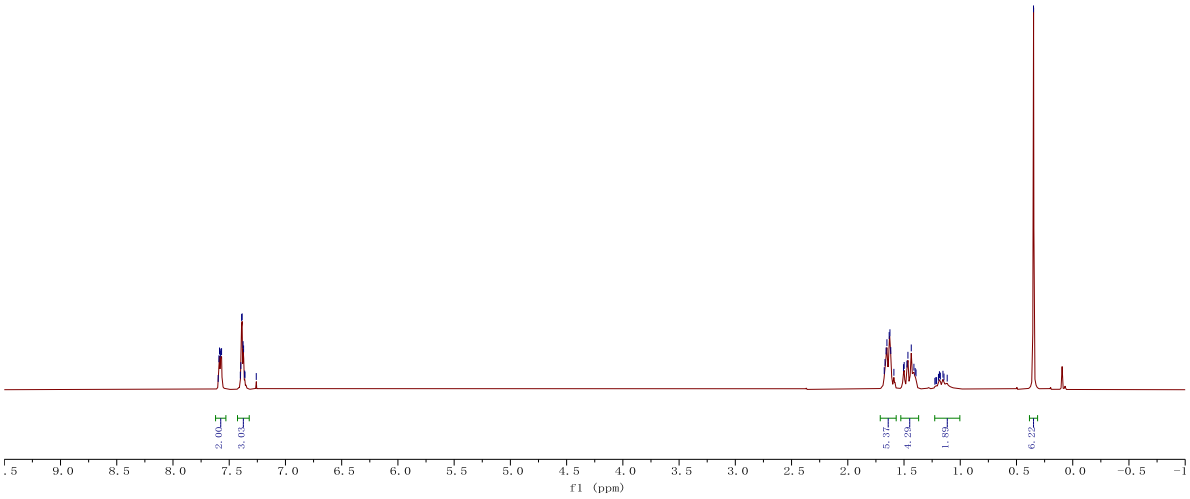
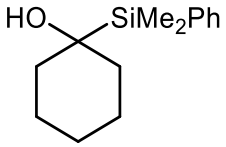


^{13}C NMR (101 MHz, $CDCl_3$)



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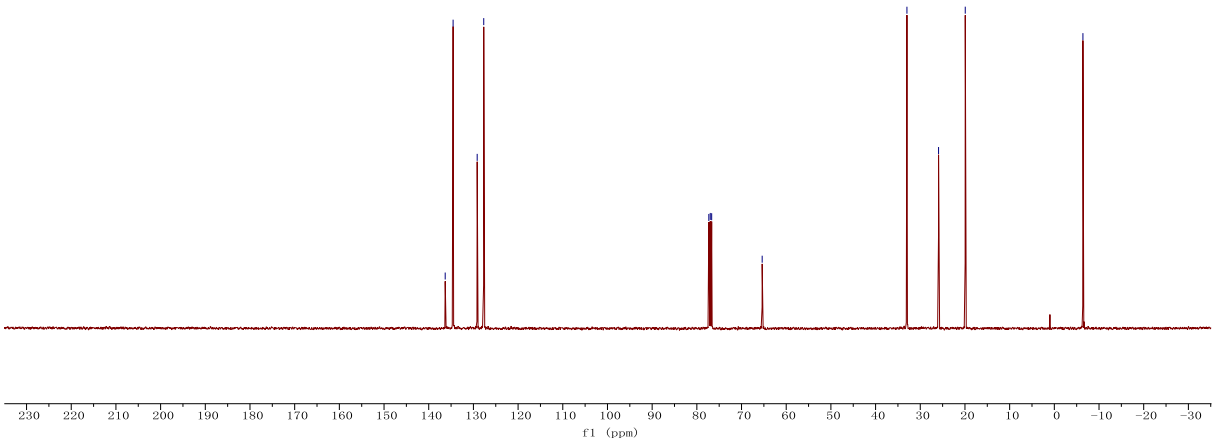

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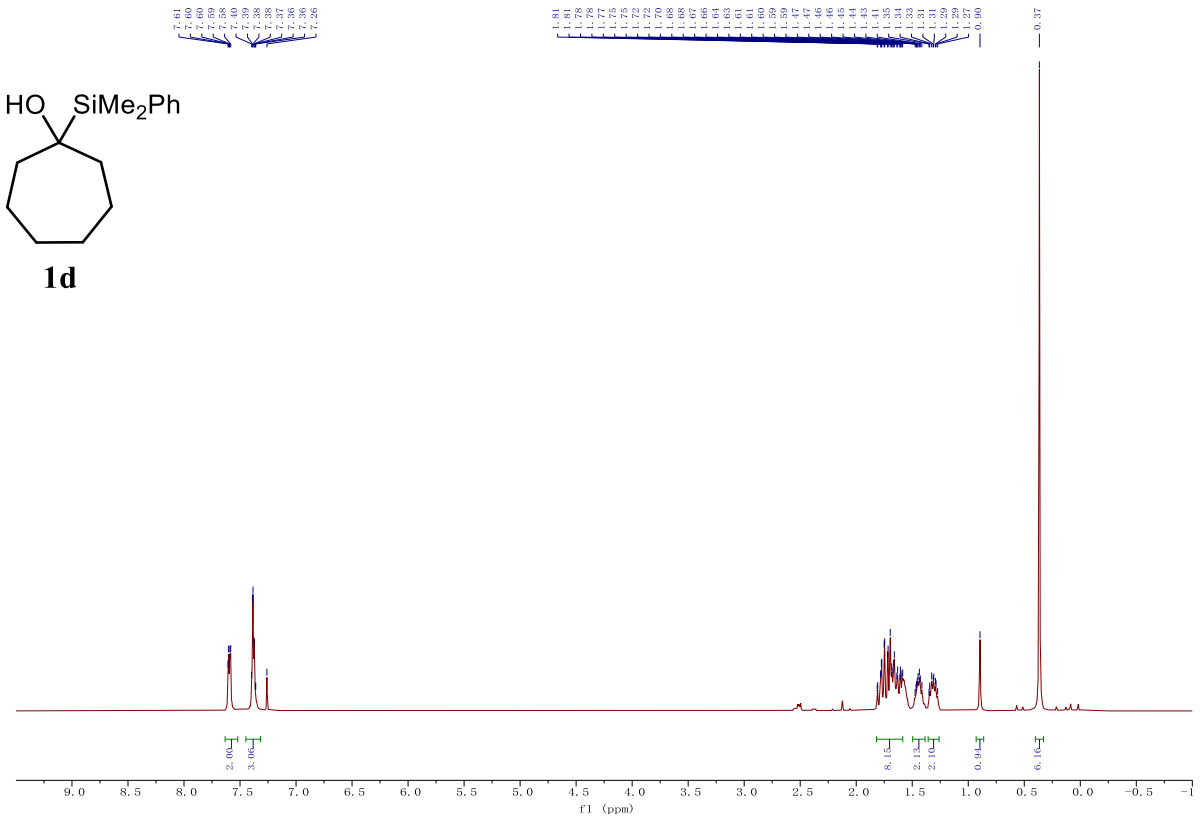

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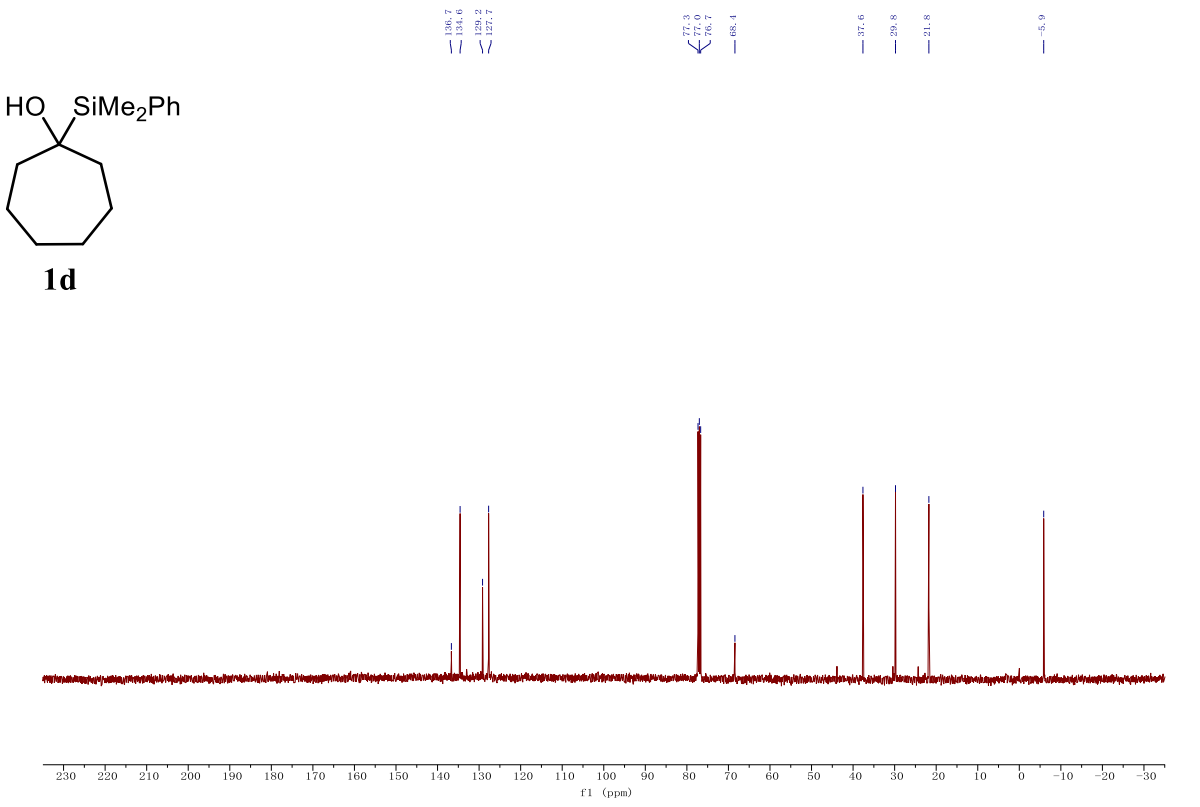

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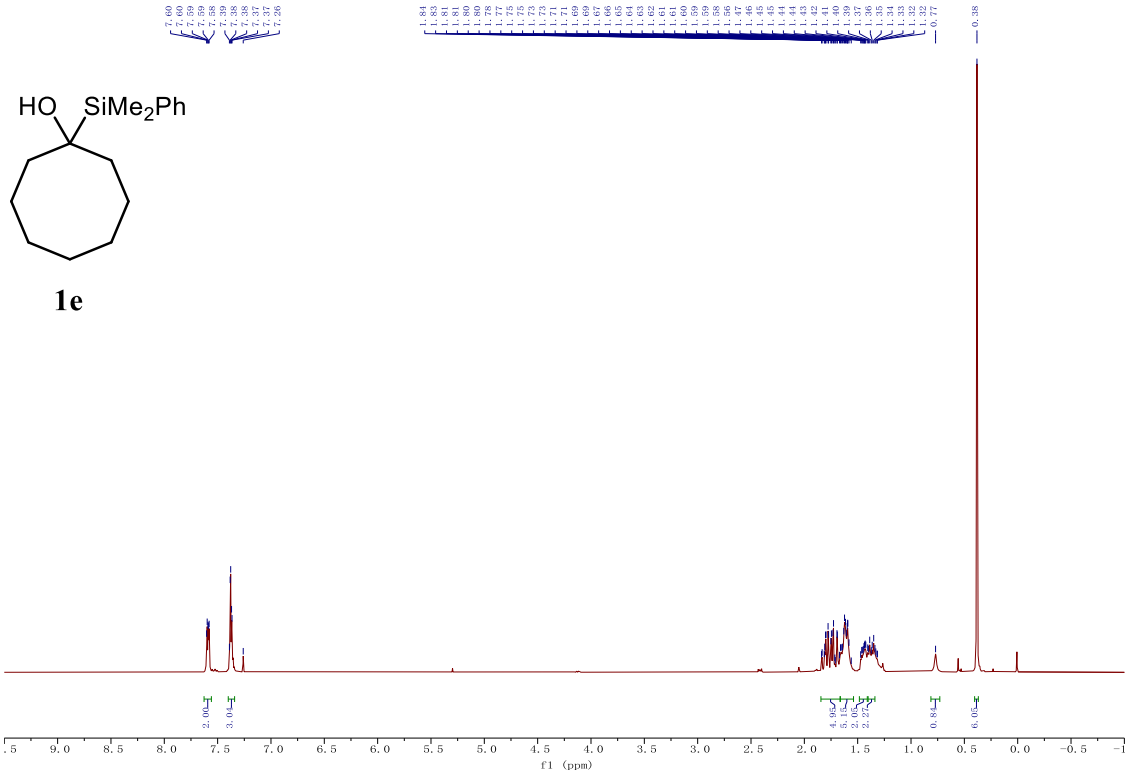

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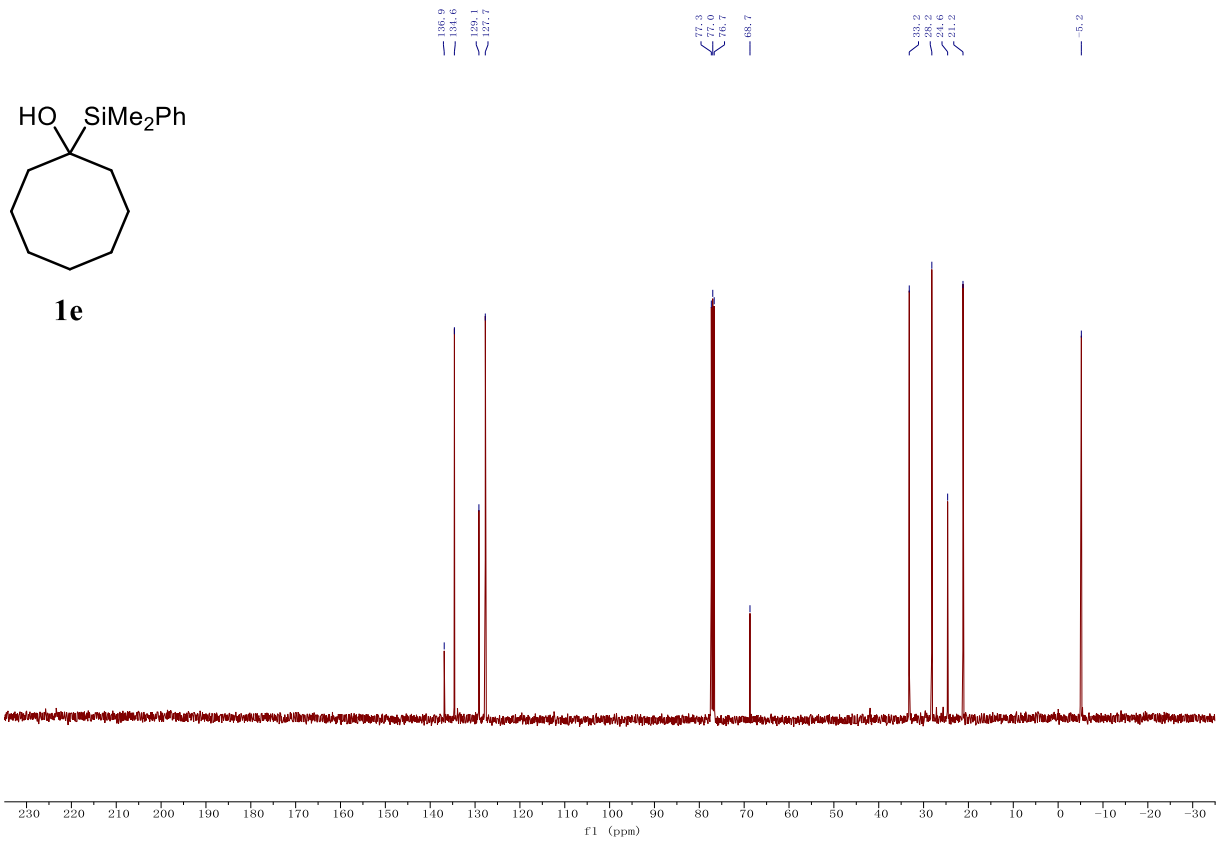

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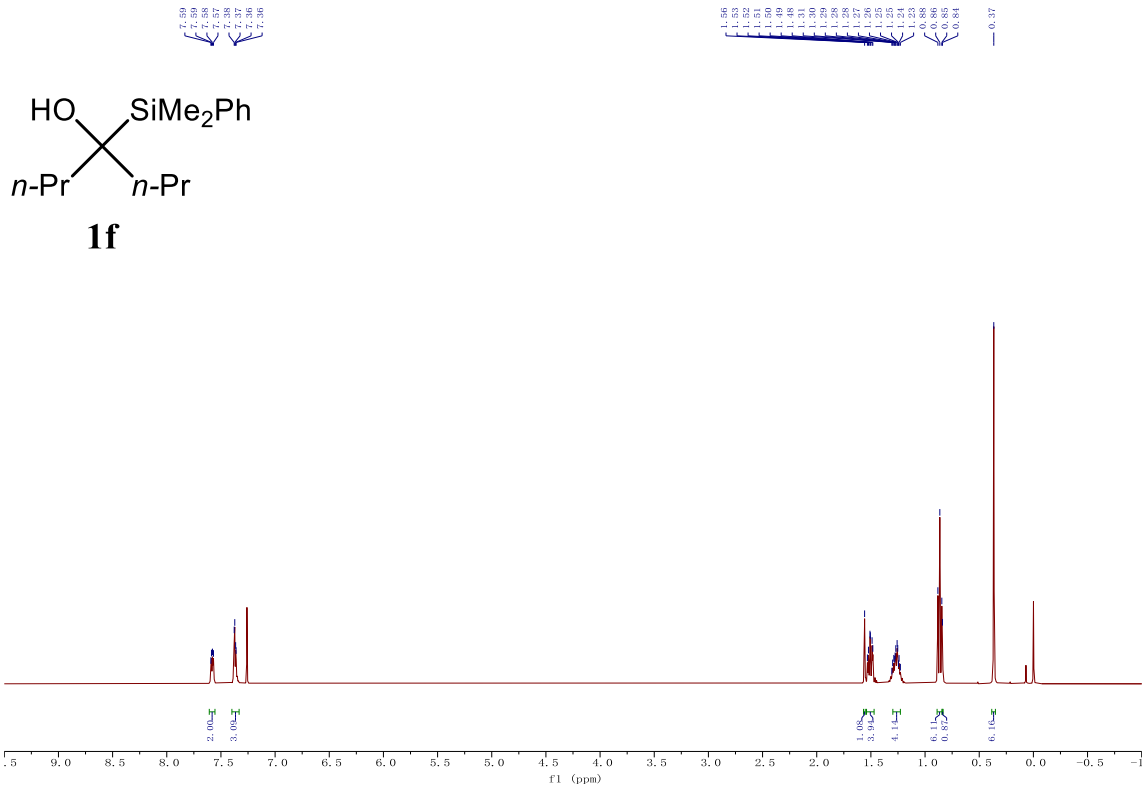

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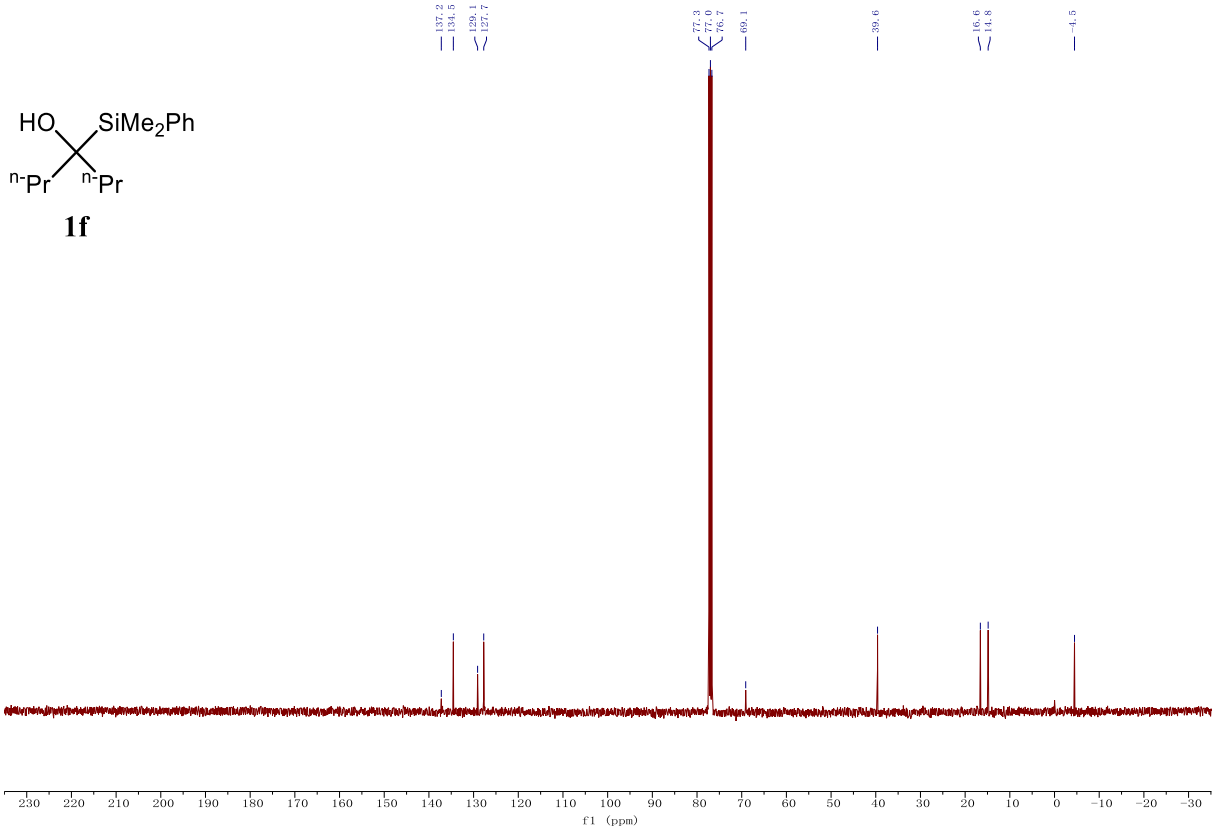

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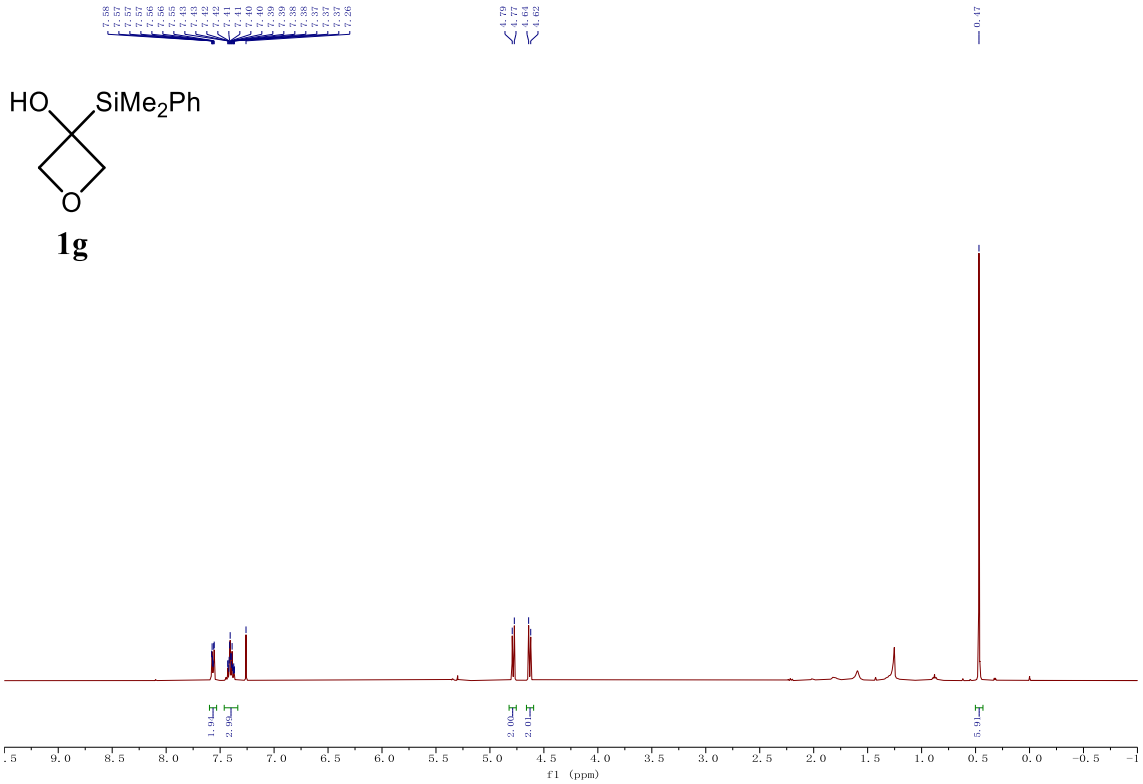

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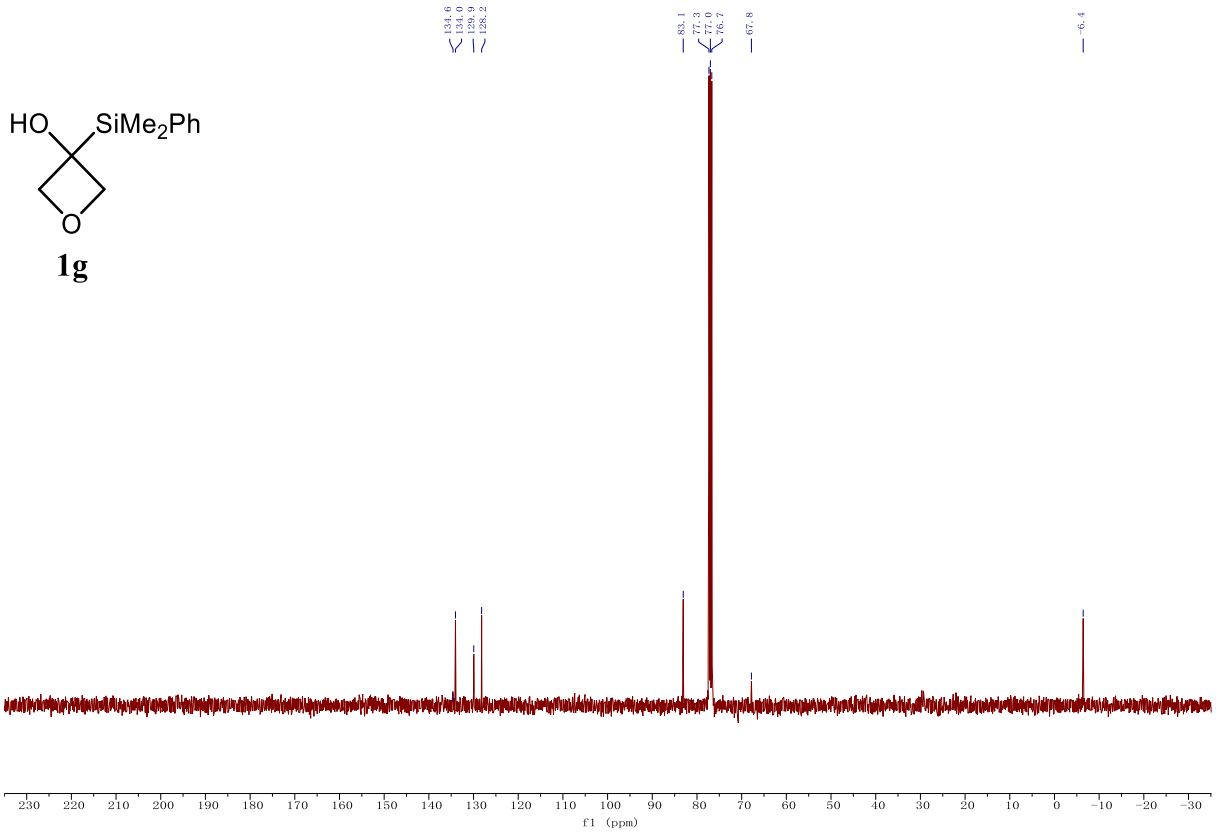

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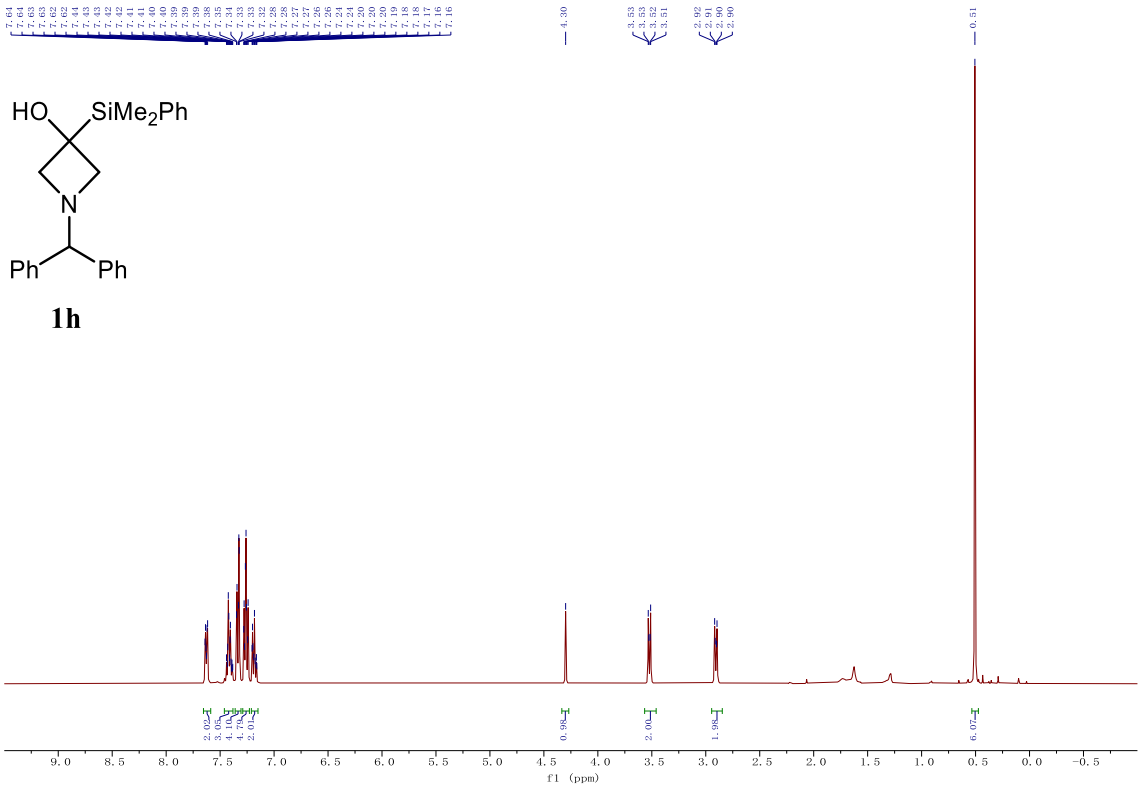

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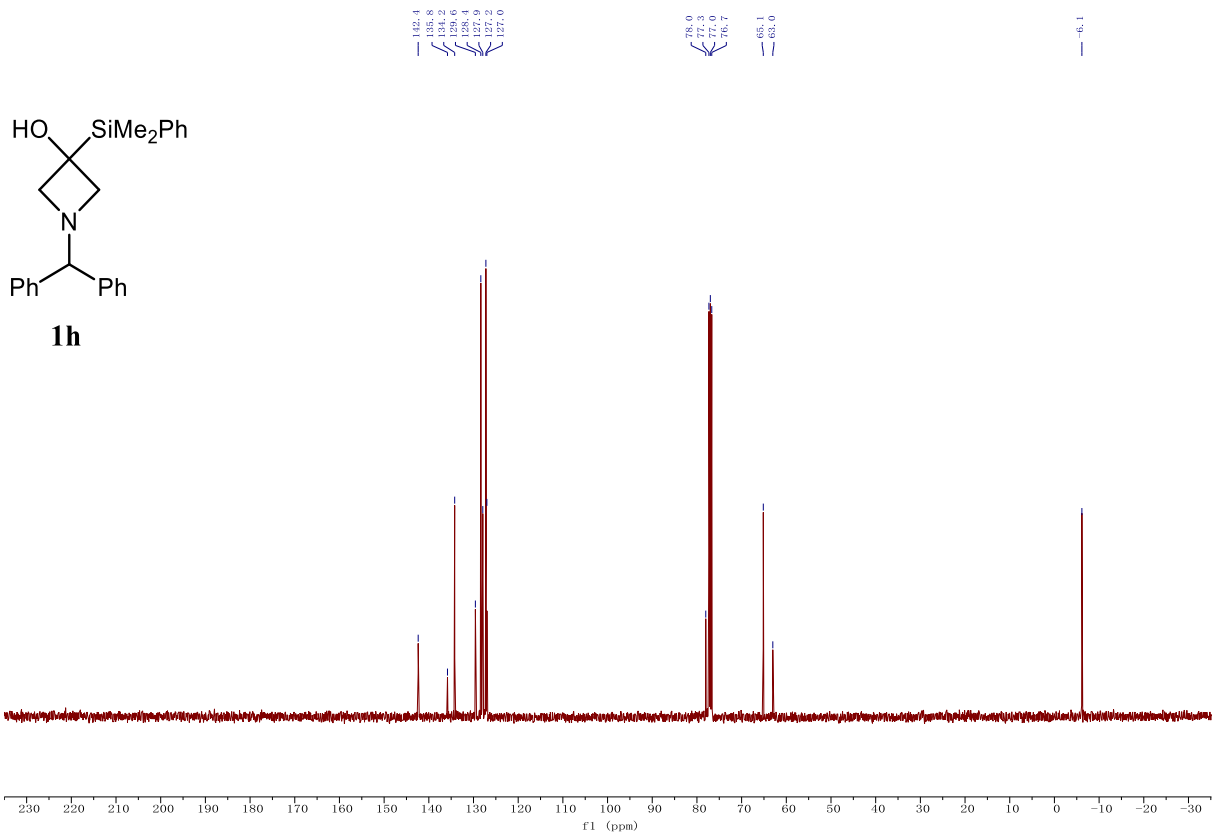

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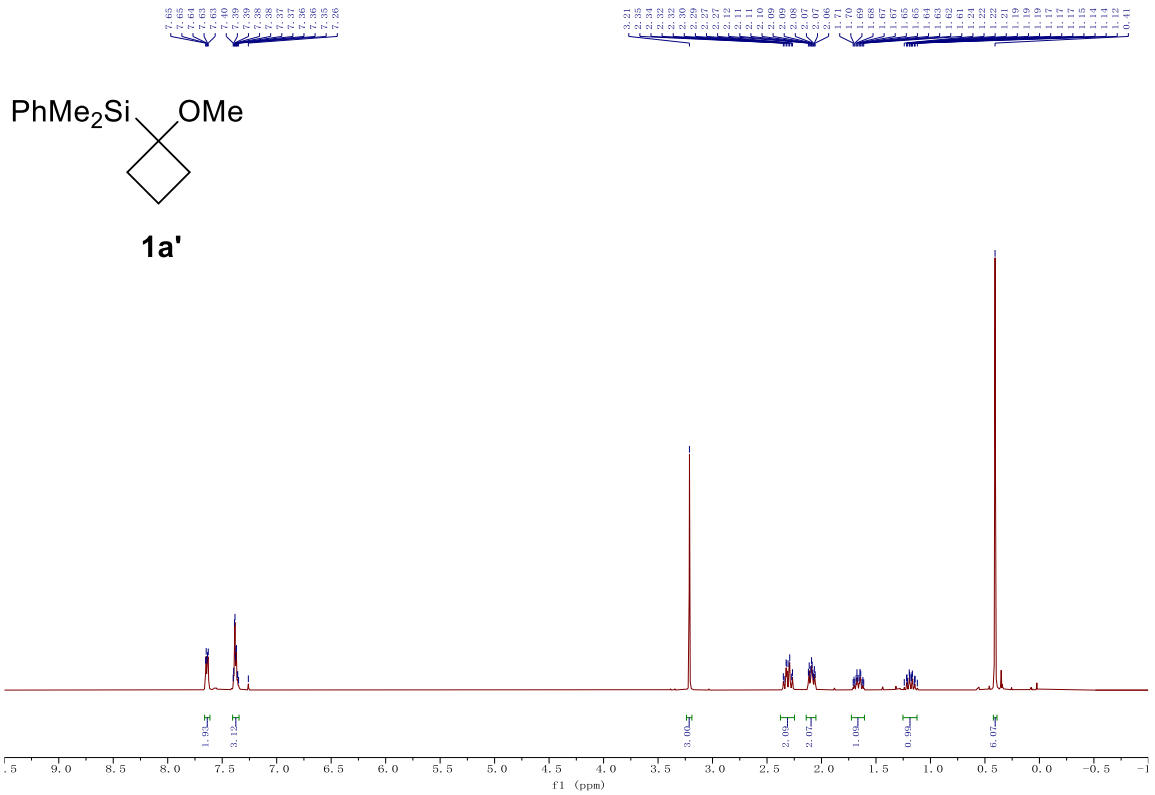

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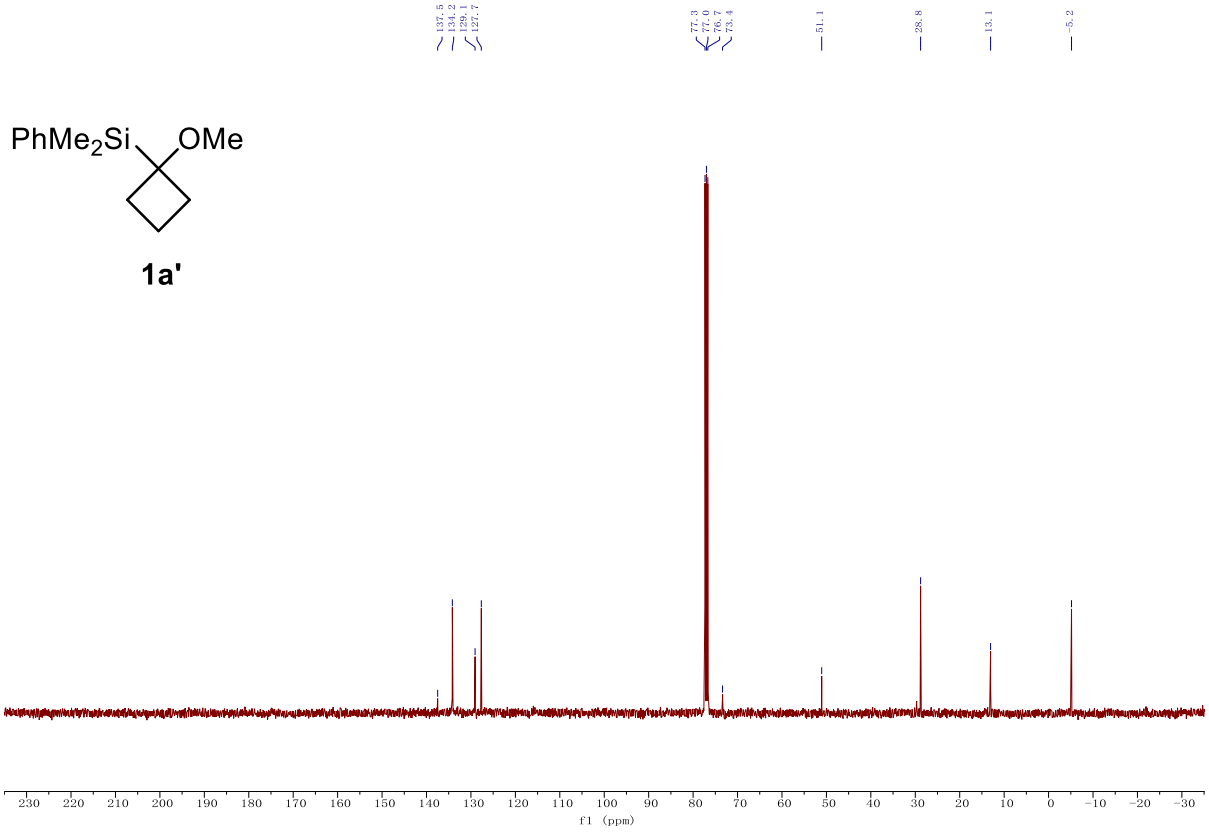

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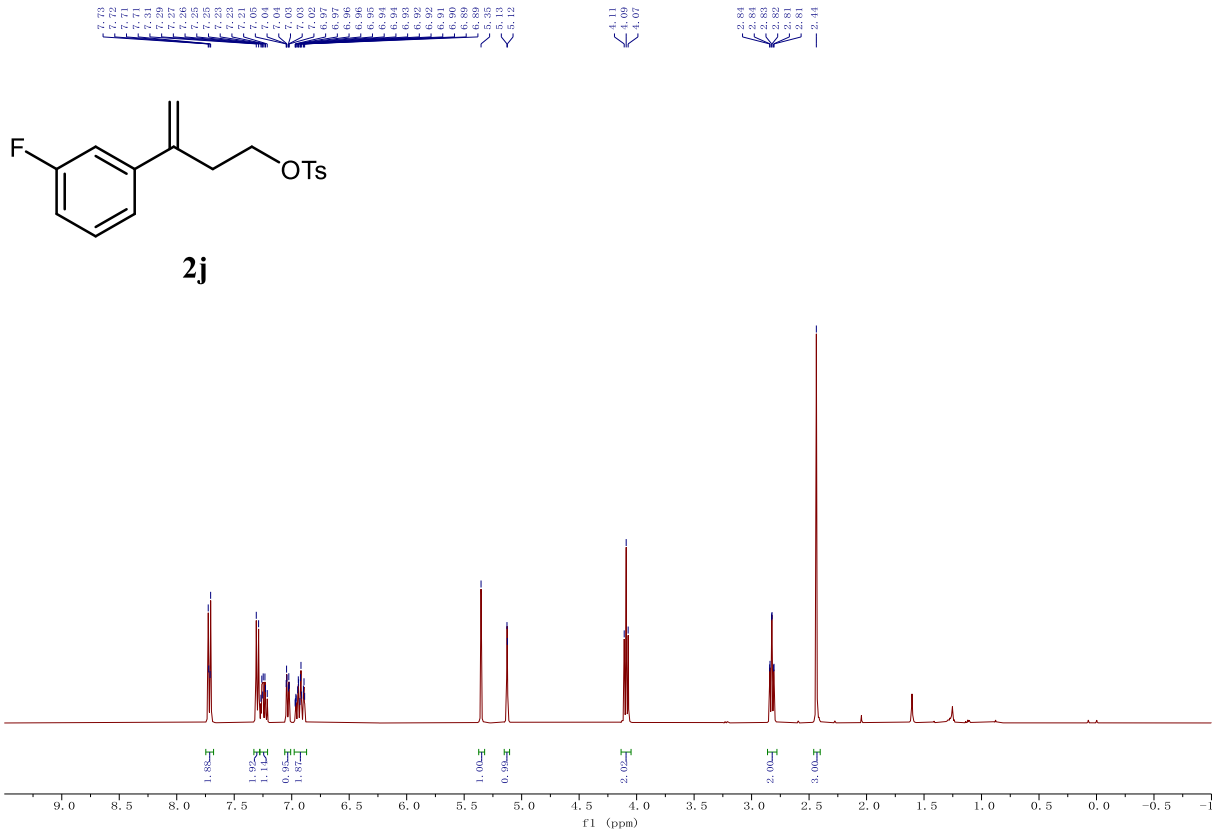

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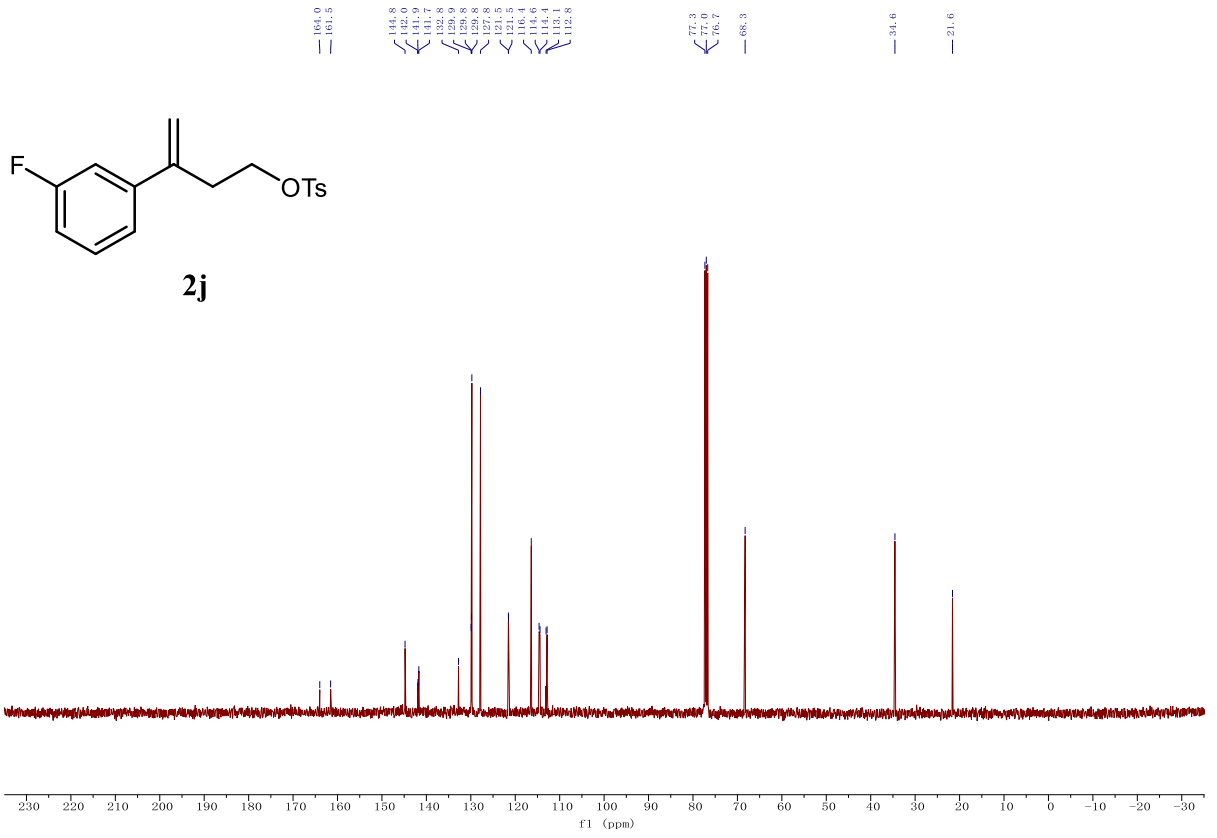
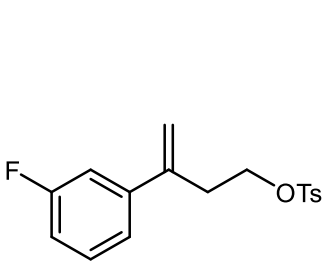


^{19}F NMR (376 MHz, $CDCl_3$)



2j

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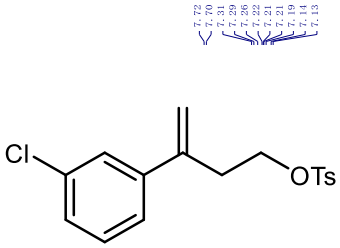

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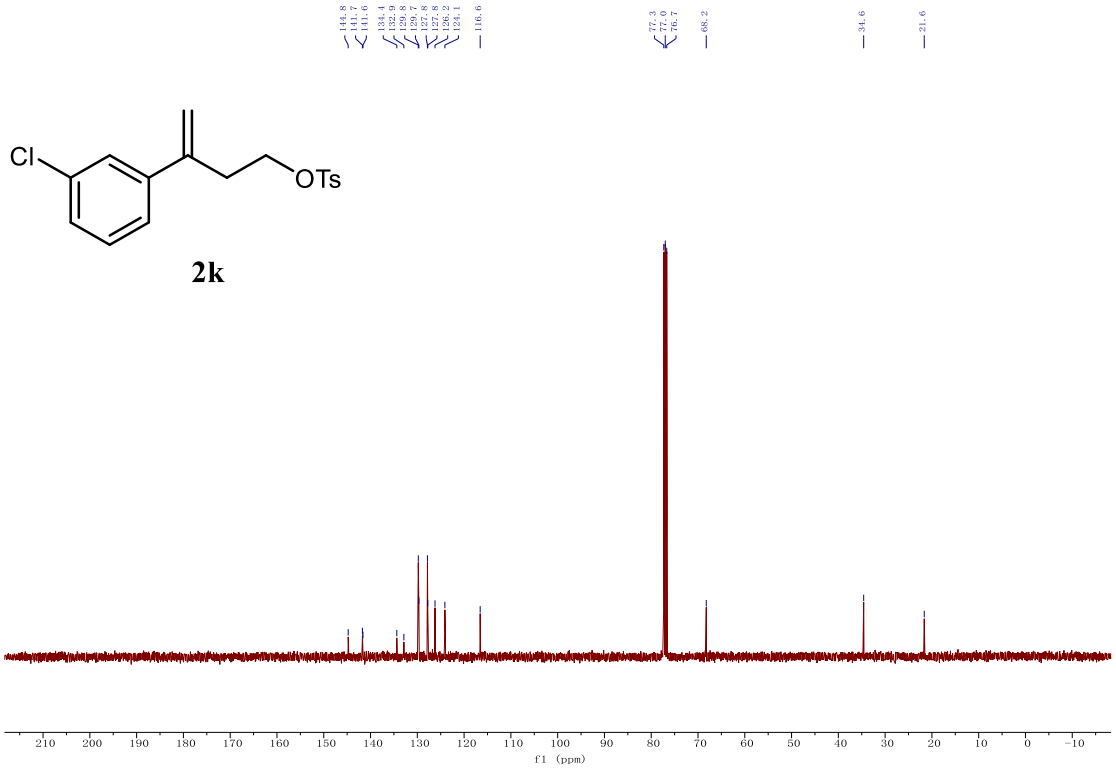

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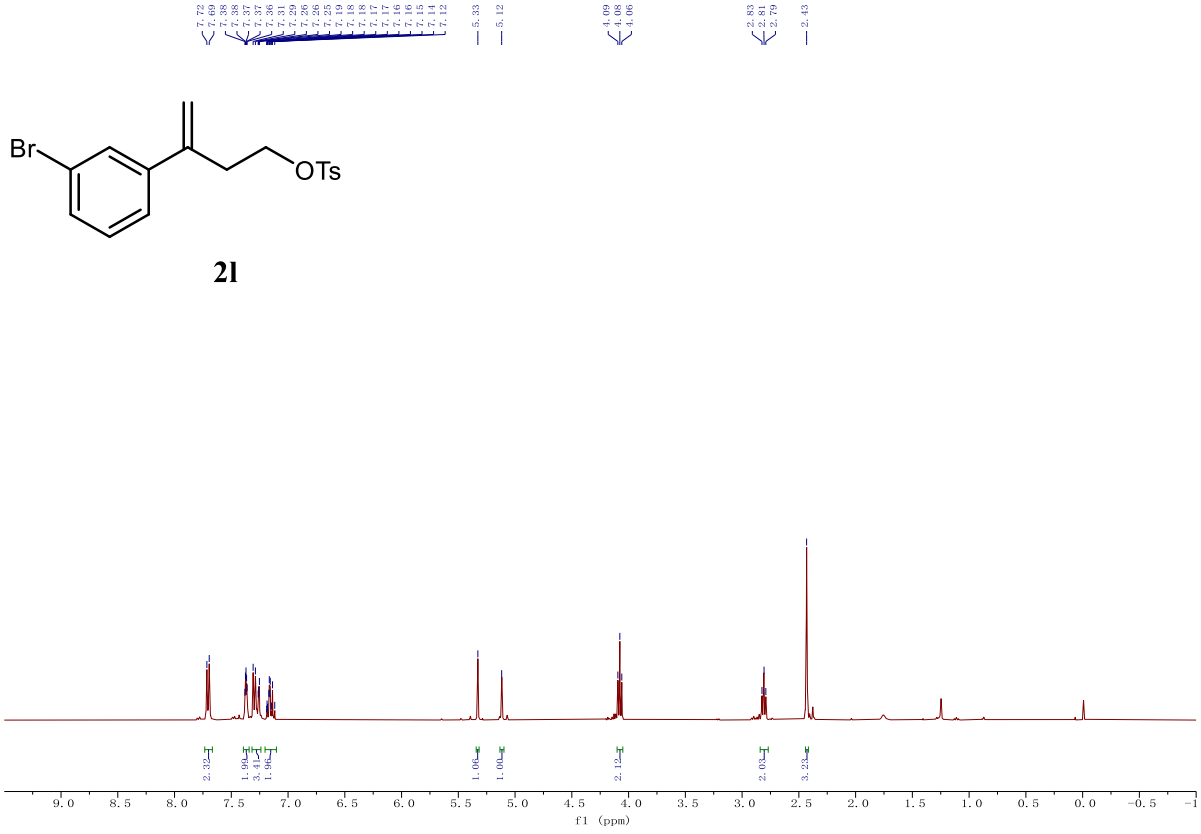

2l

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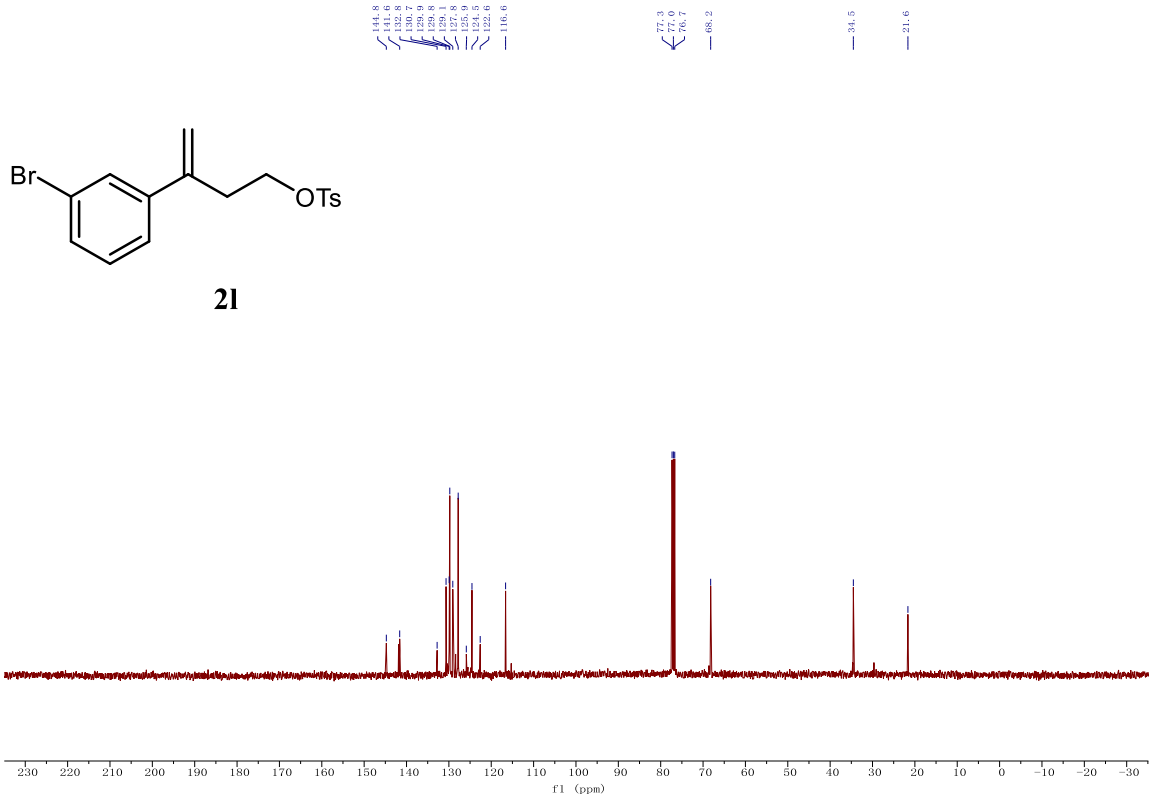

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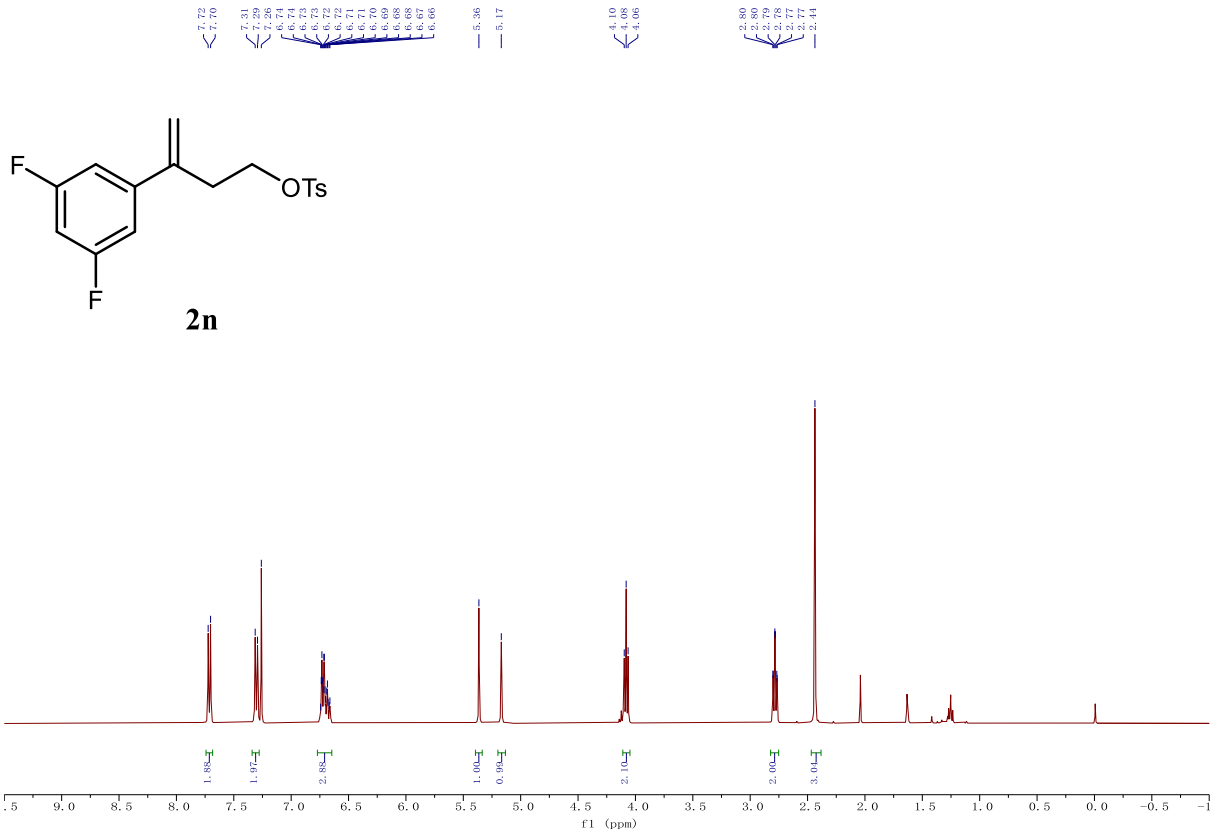
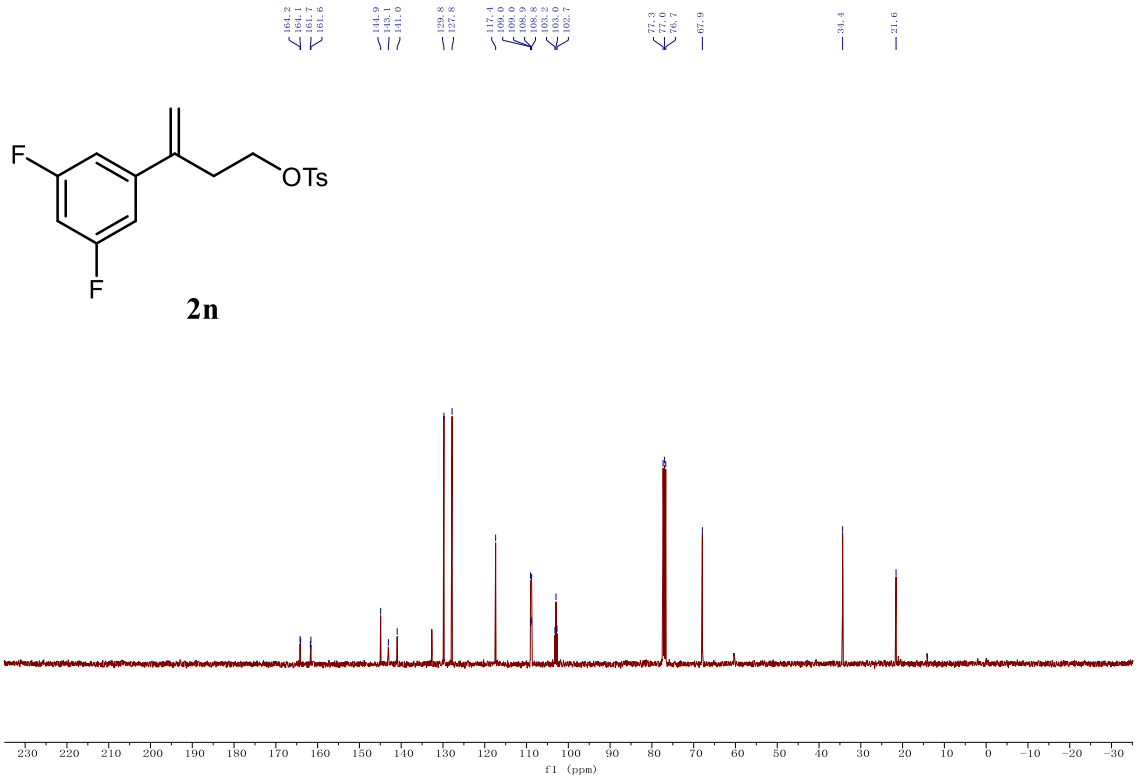
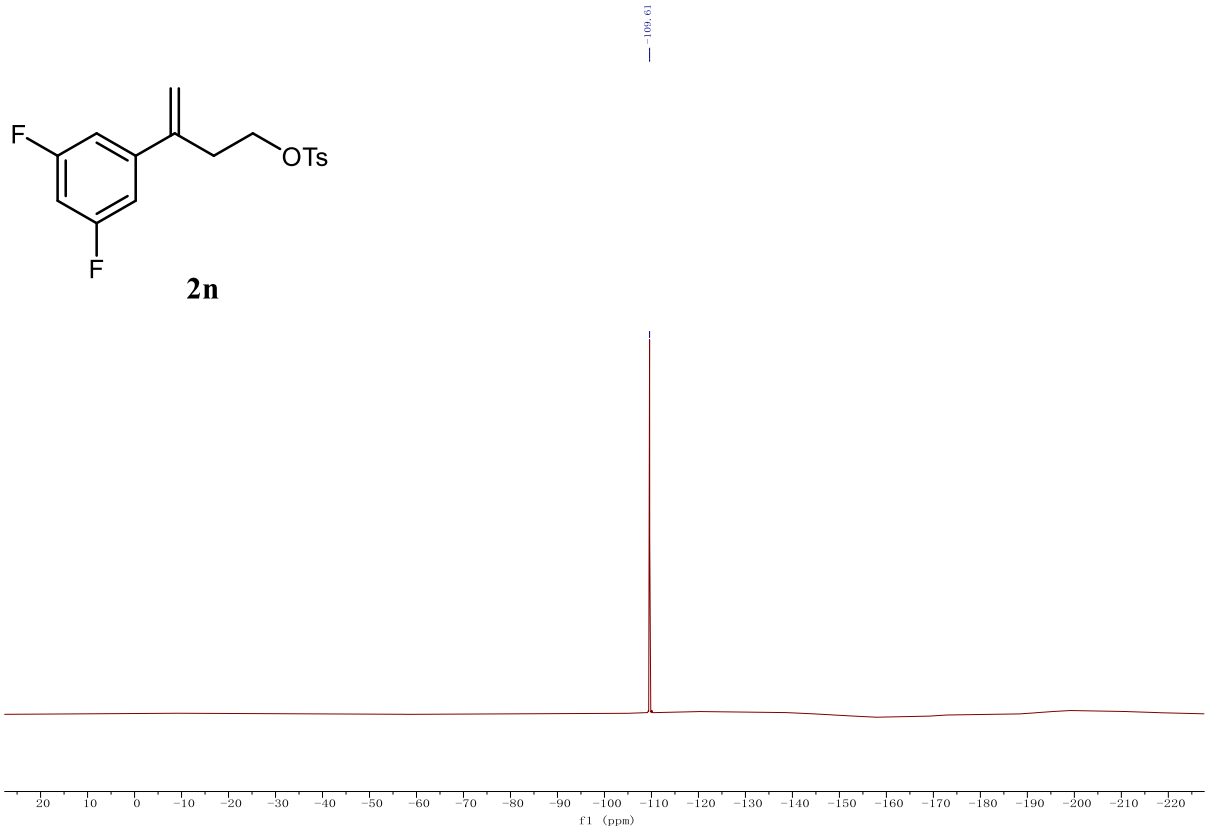


2n

^{13}C NMR (101 MHz, $CDCl_3$)



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



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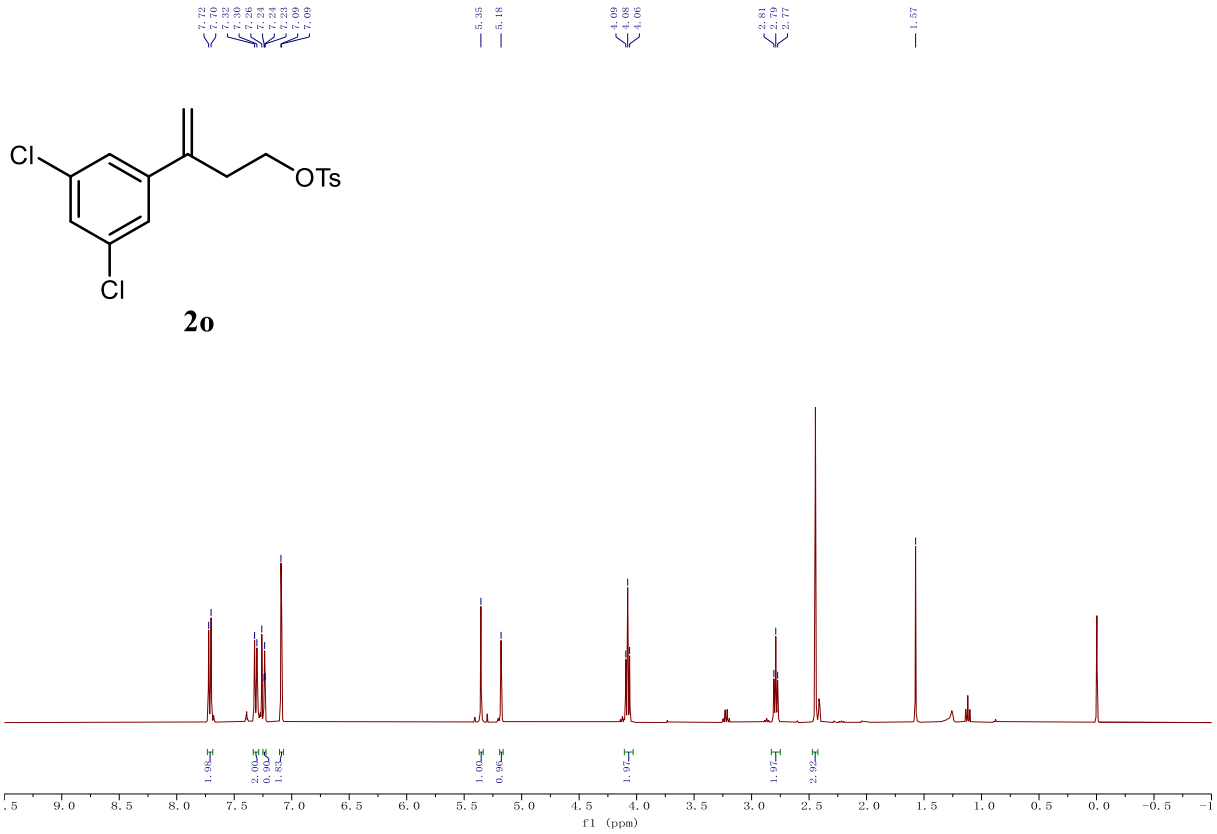

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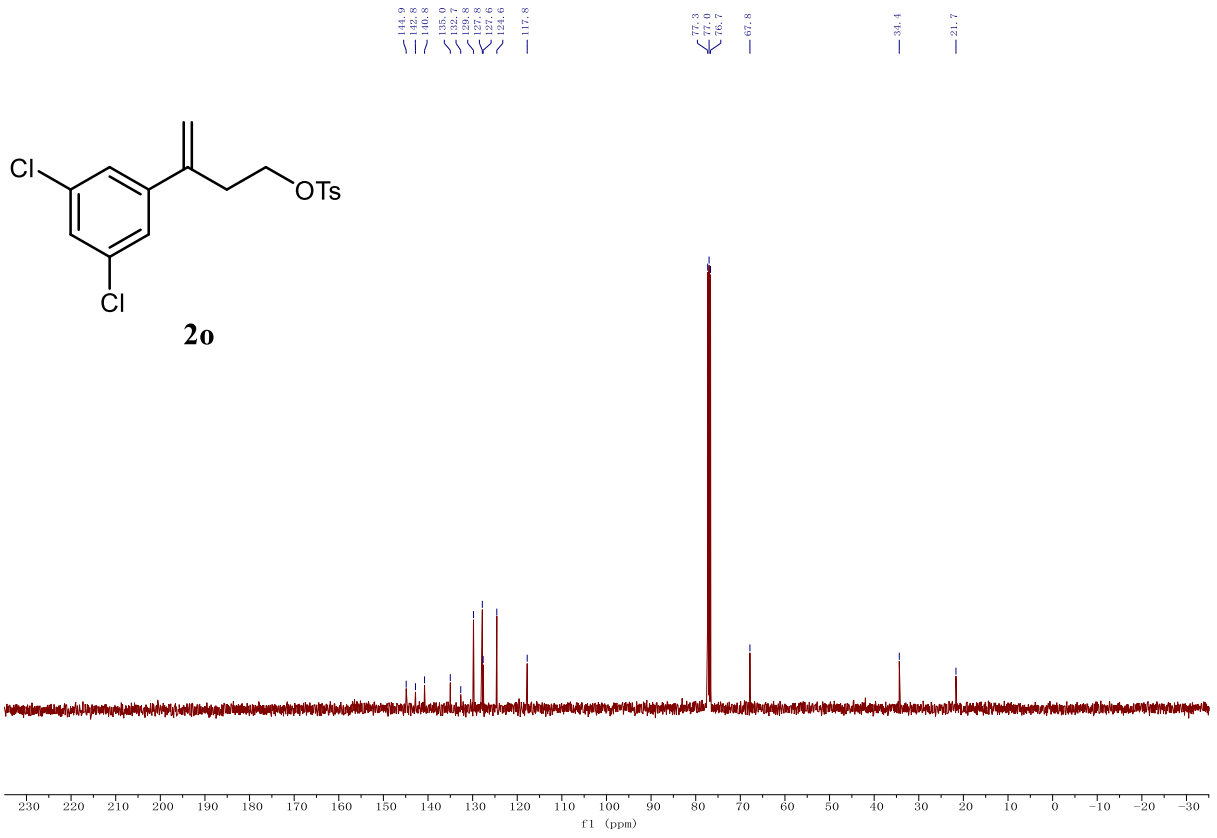
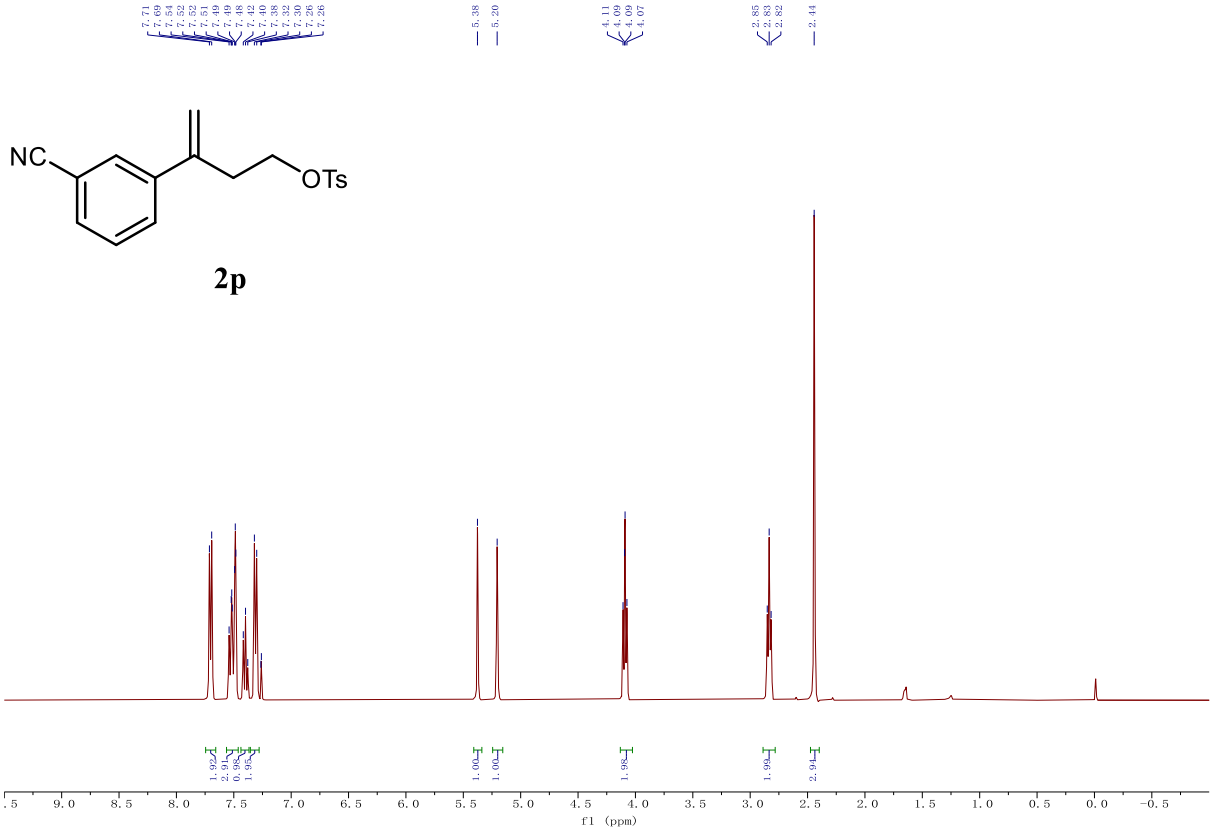
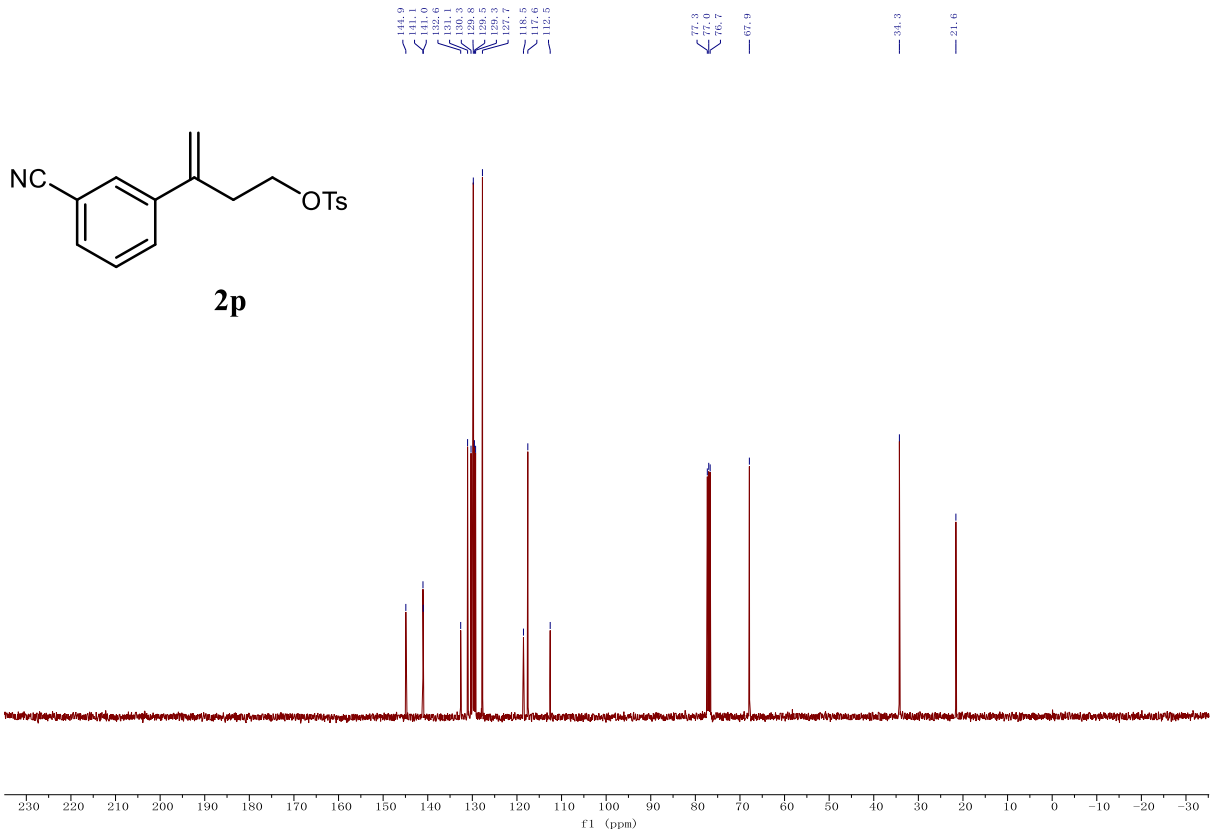


2o

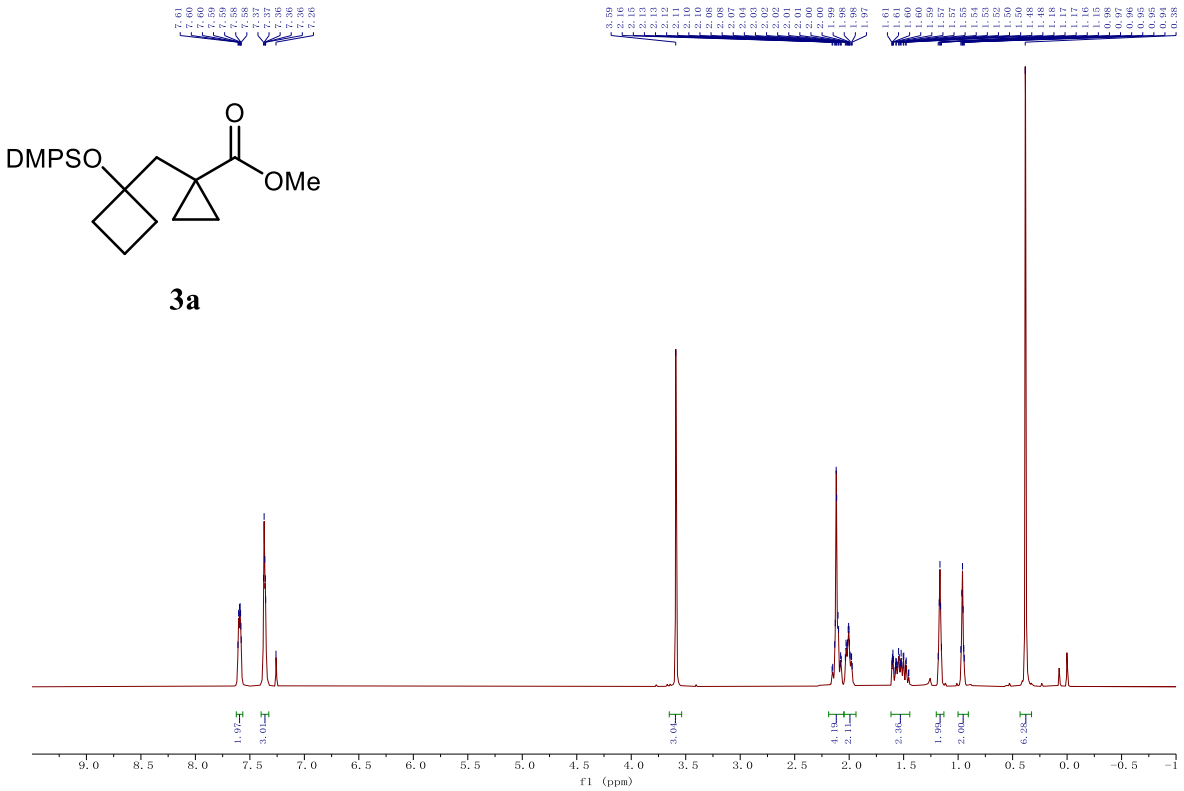
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

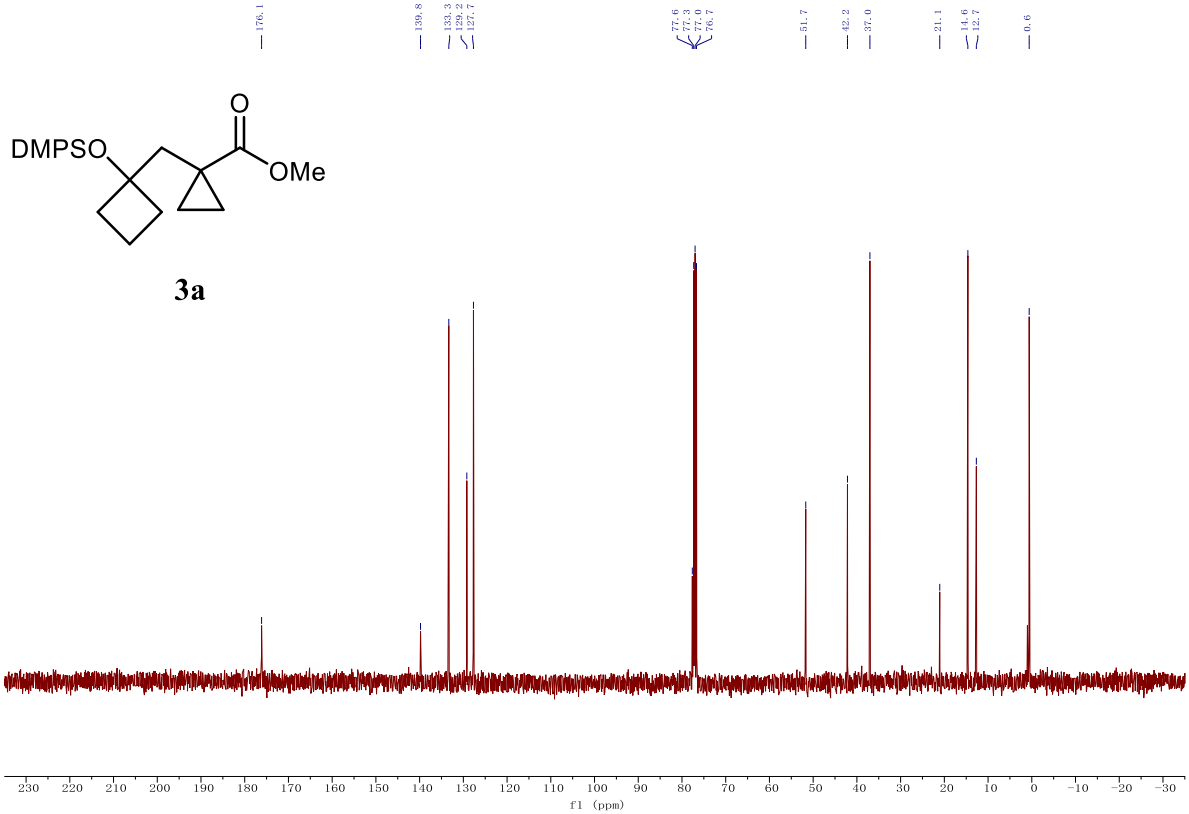


^{1}H NMR (400 MHz, $CDCl_3$)



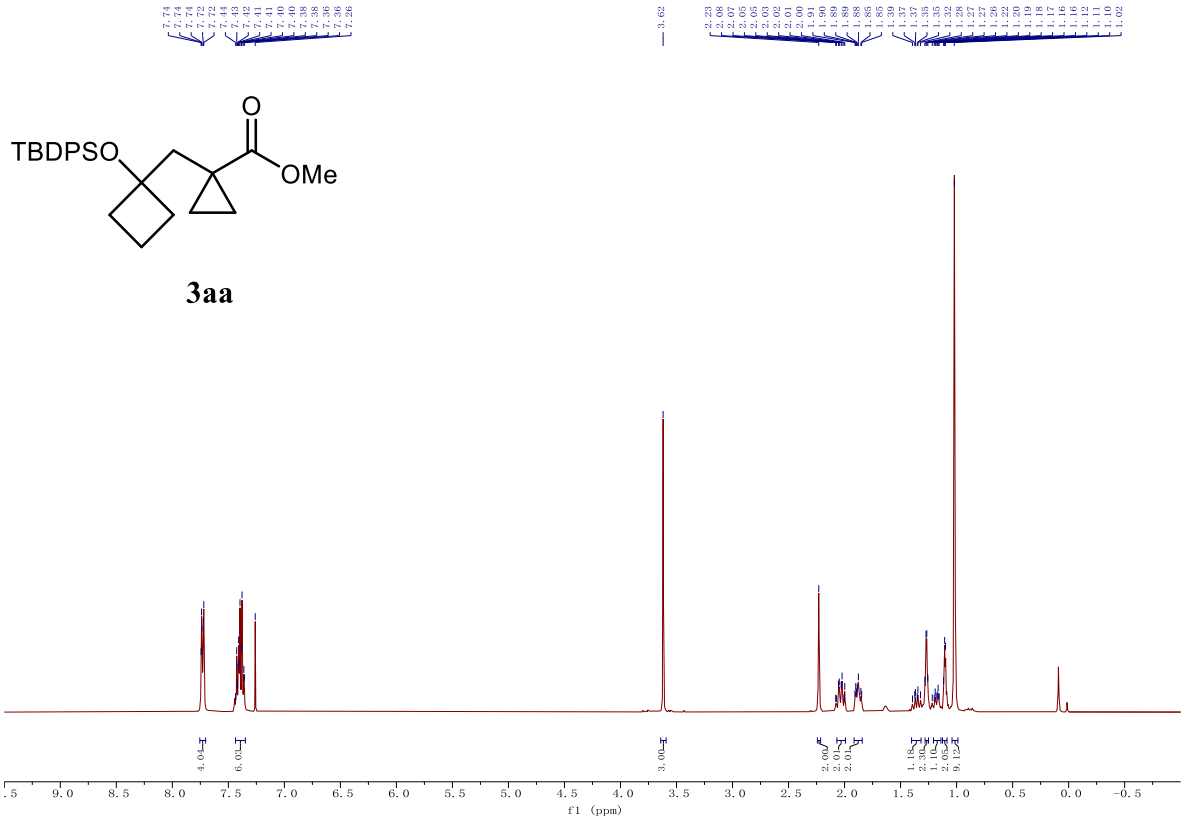
3a

^{13}C NMR (101 MHz, $CDCl_3$)



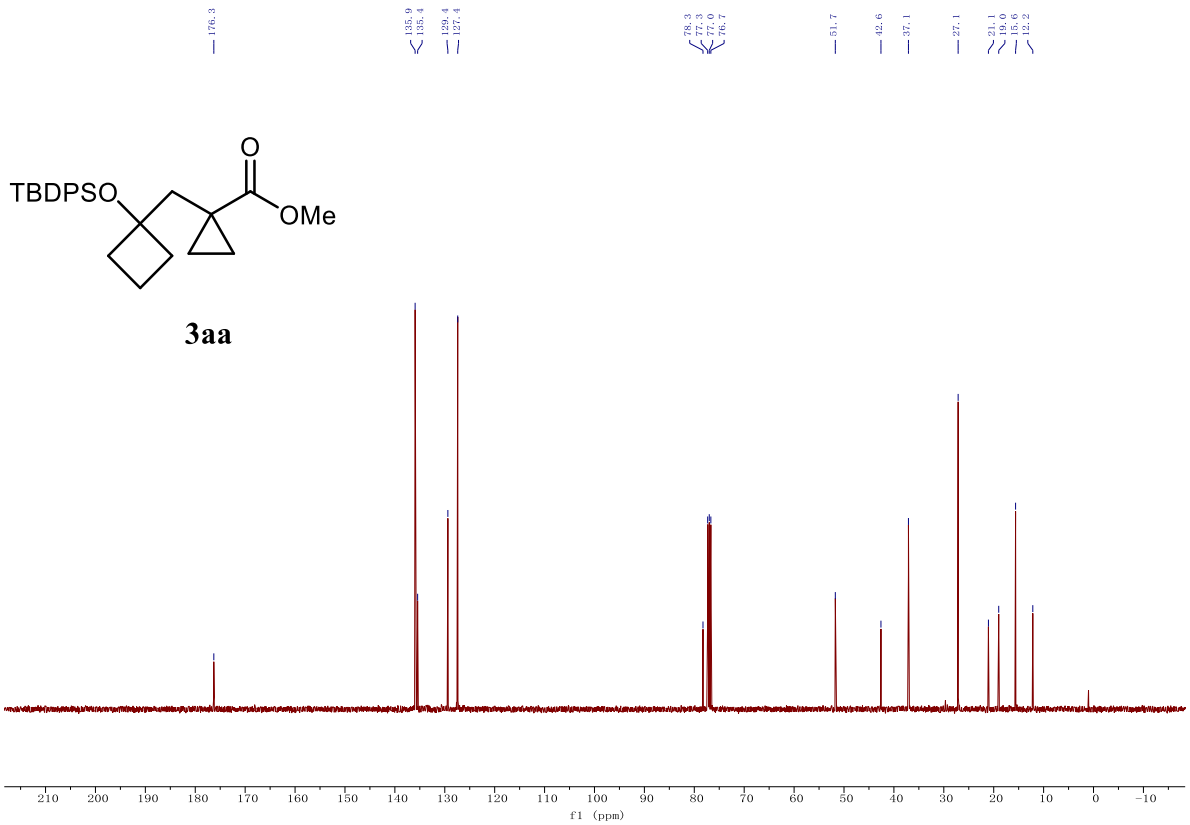
3a

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



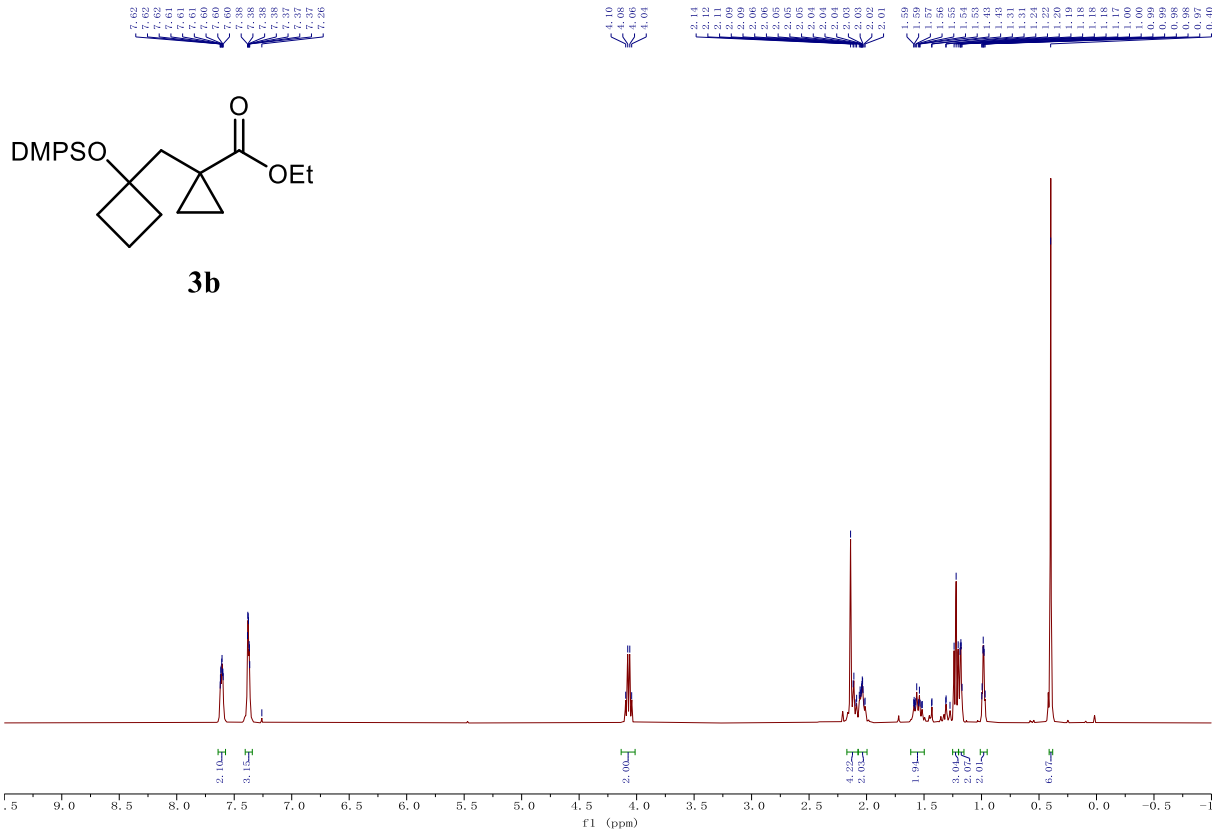
3aa

^{13}C NMR (101 MHz, $CDCl_3$)



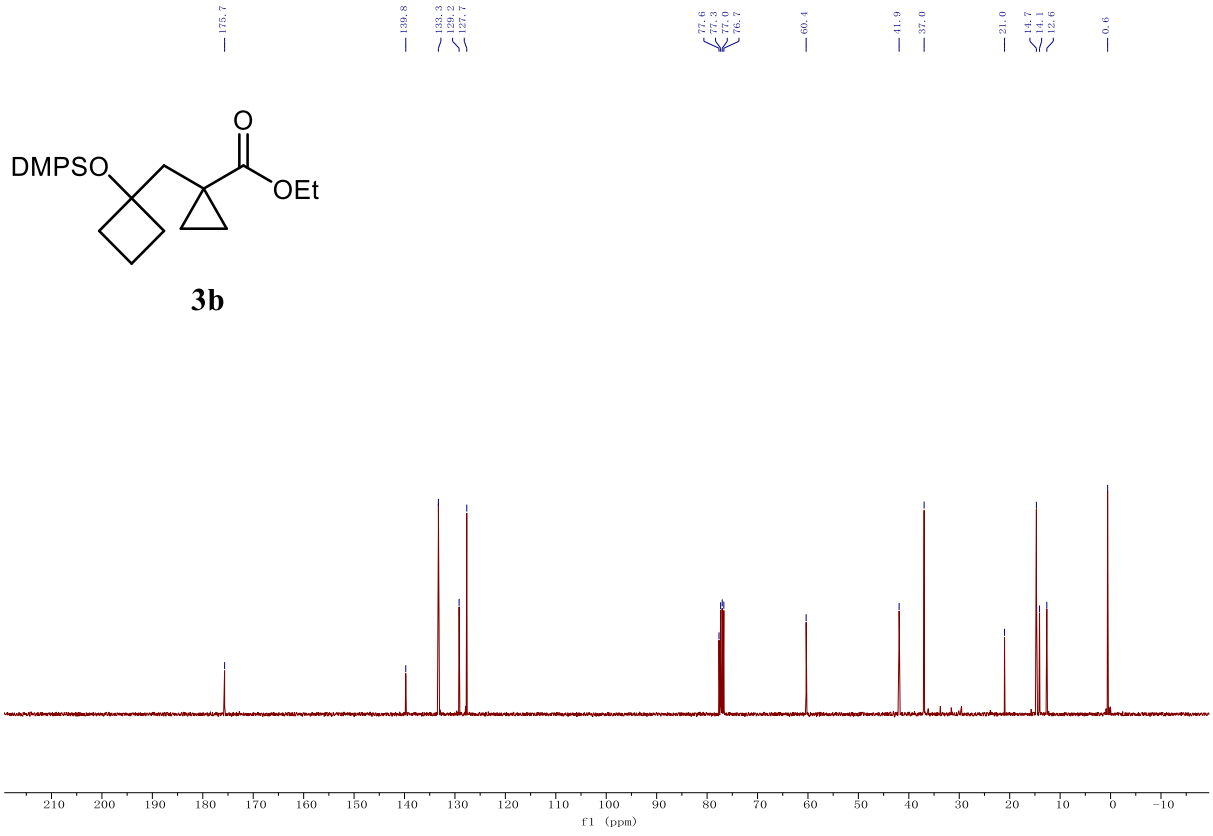
3aa

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



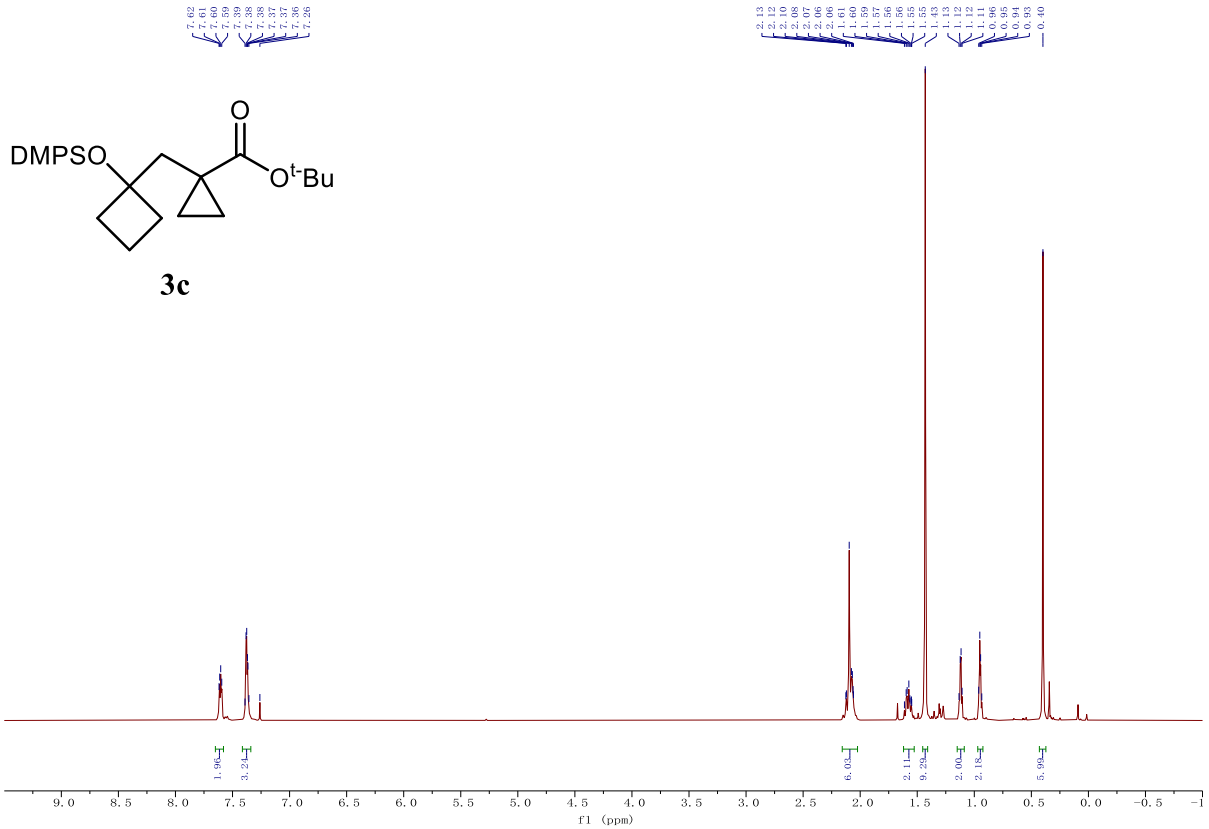
3b

^{13}C NMR (101 MHz, $CDCl_3$)



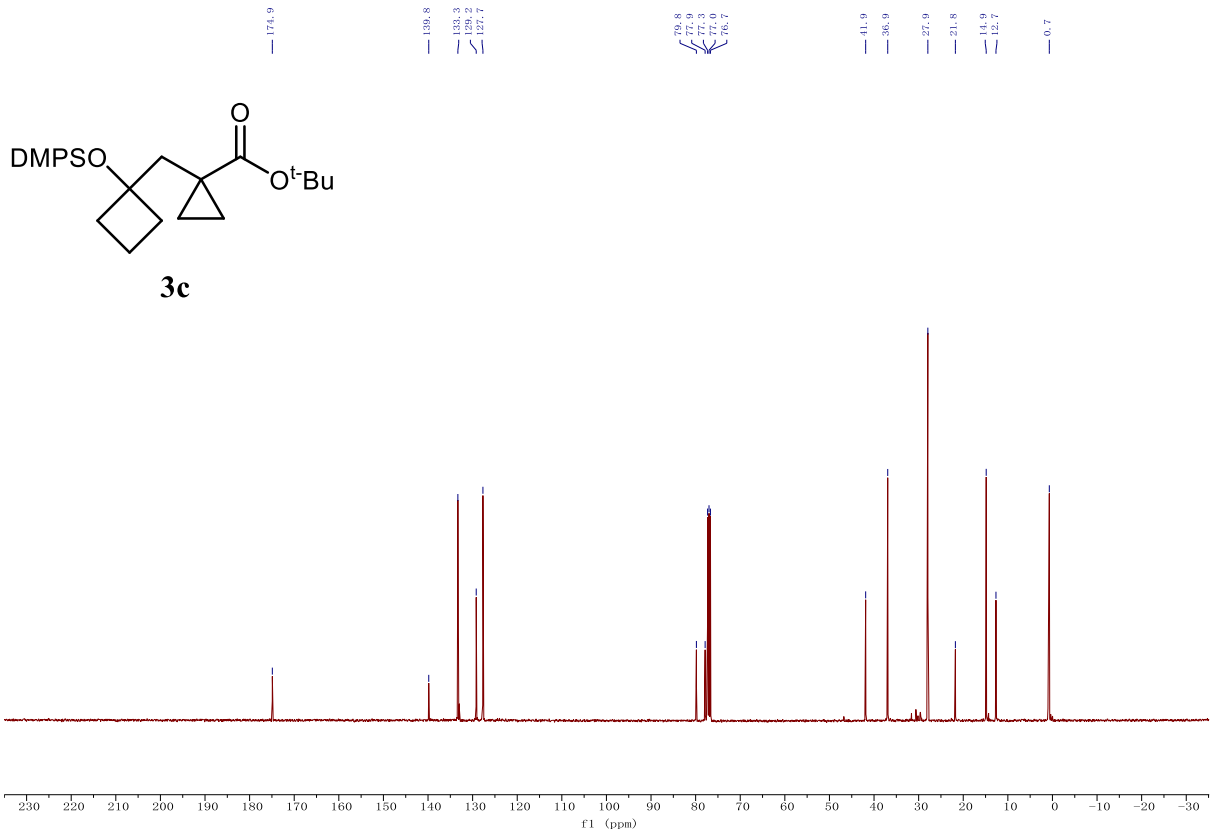
3b

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



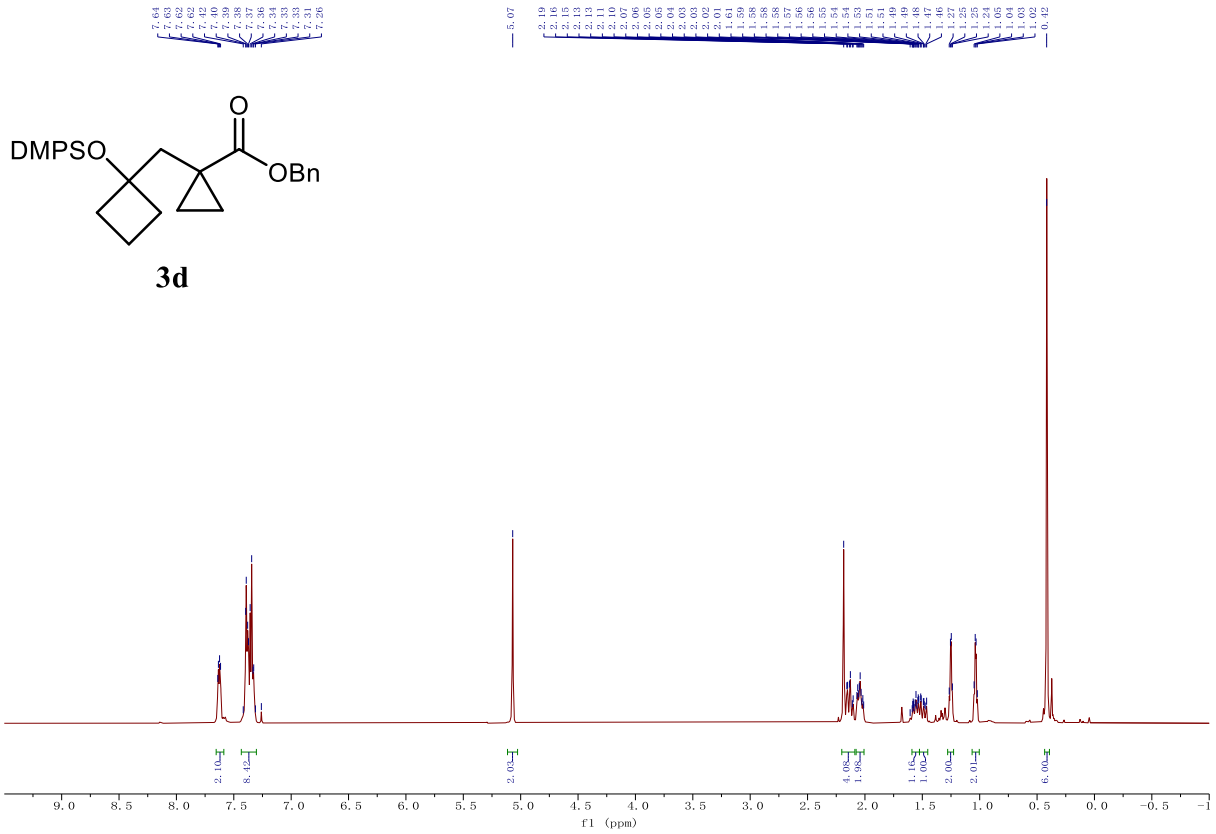
3c

^{13}C NMR (101 MHz, $CDCl_3$)



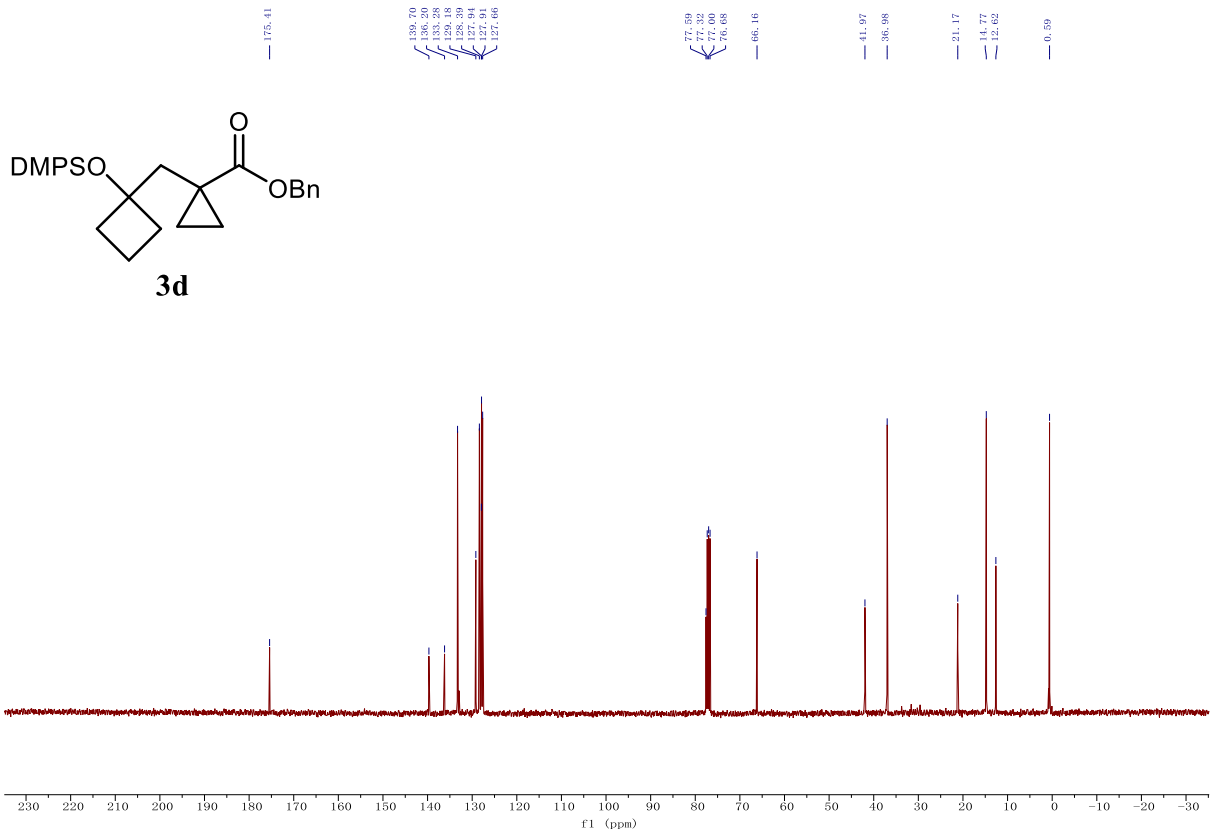
3c

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



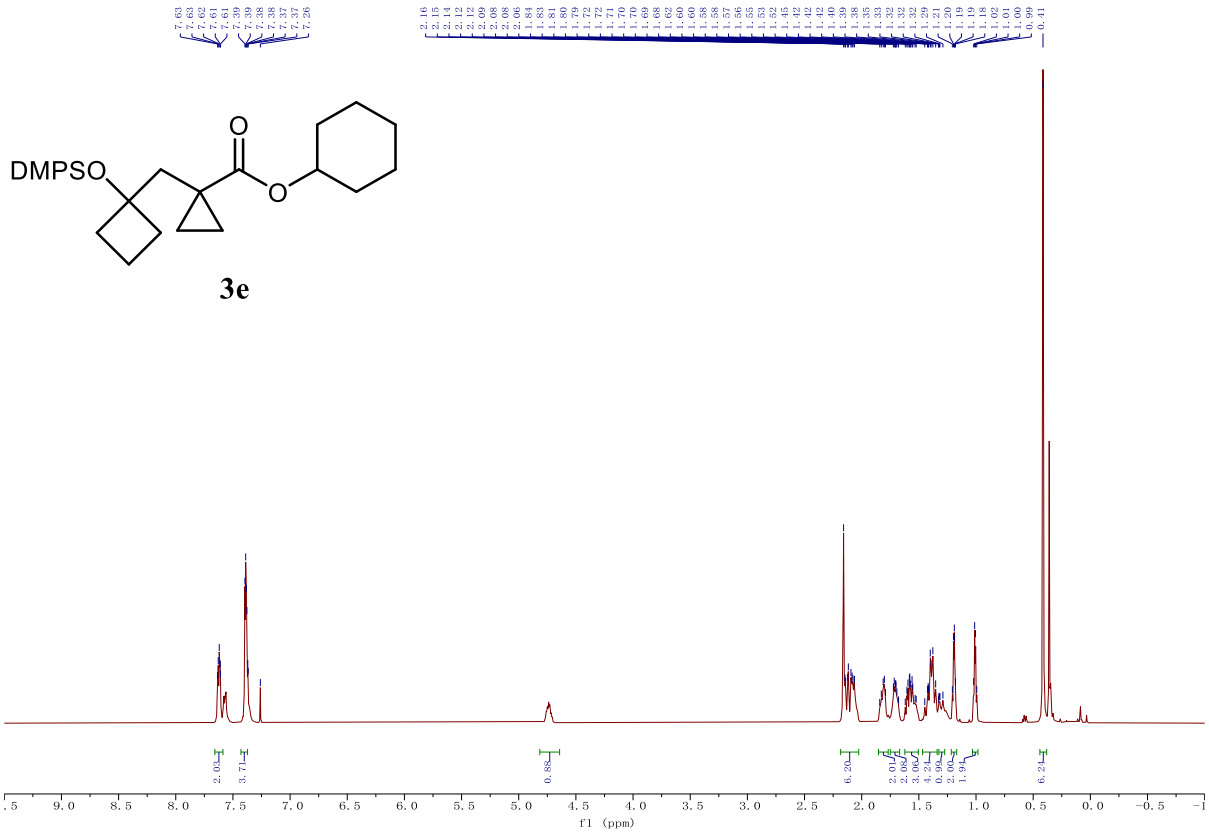
3d

^{13}C NMR (101 MHz, $CDCl_3$)

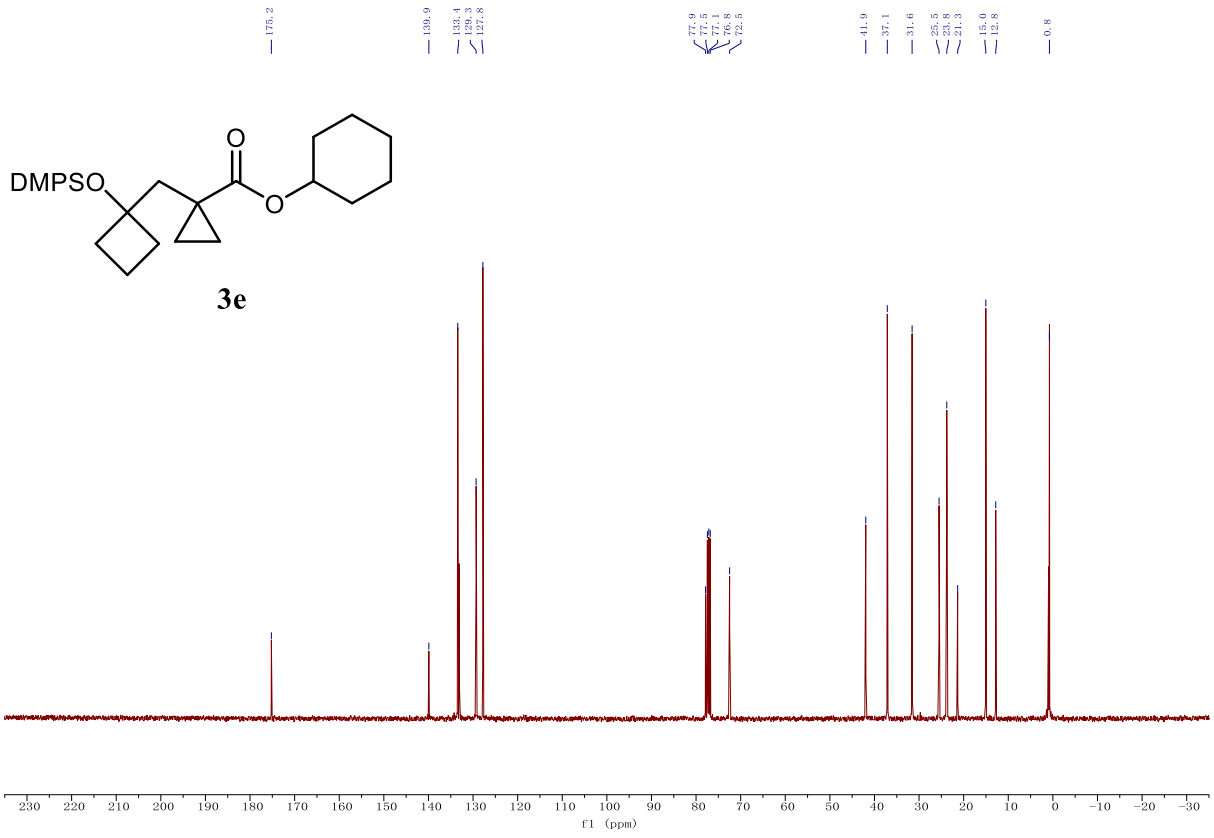


3d

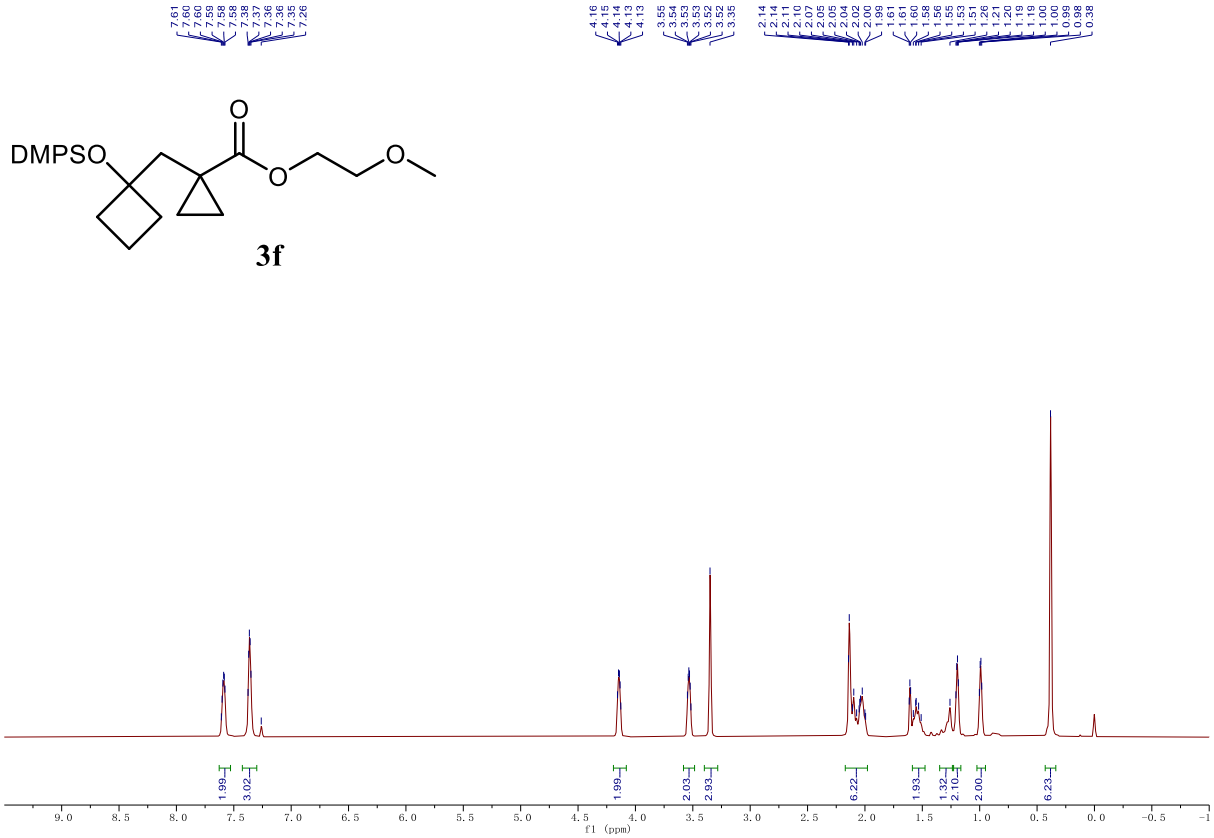
^{1}H NMR (400 MHz, $CDCl_3$)



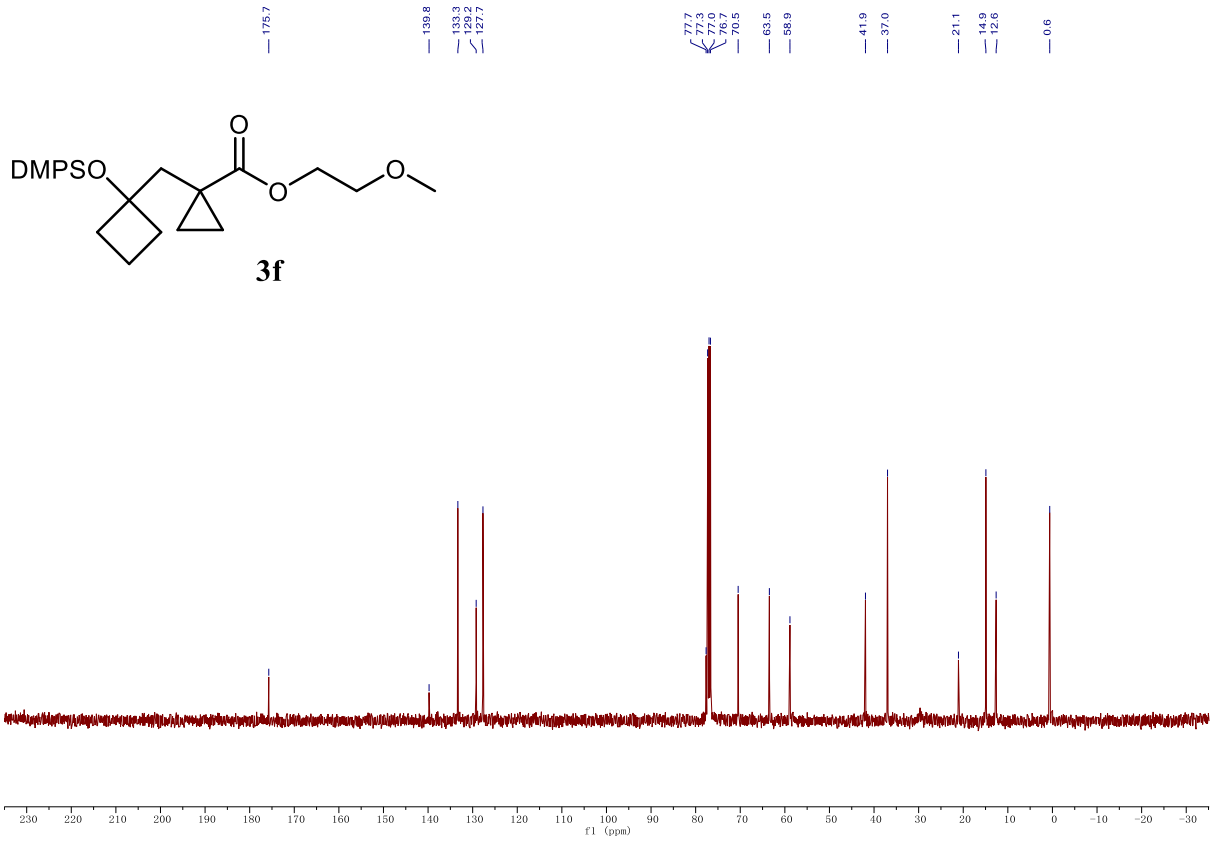
^{13}C NMR (101 MHz, $CDCl_3$)



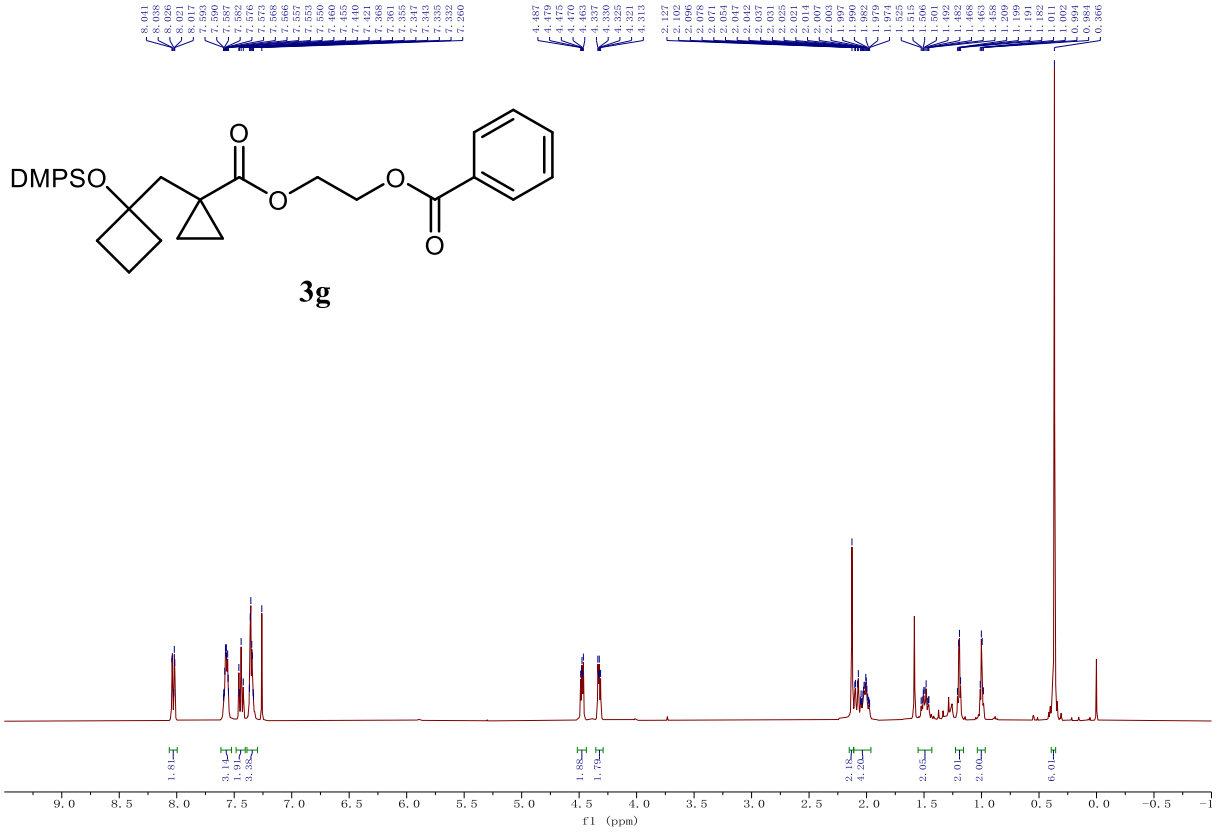
^{1}H NMR (400 MHz, $CDCl_3$)



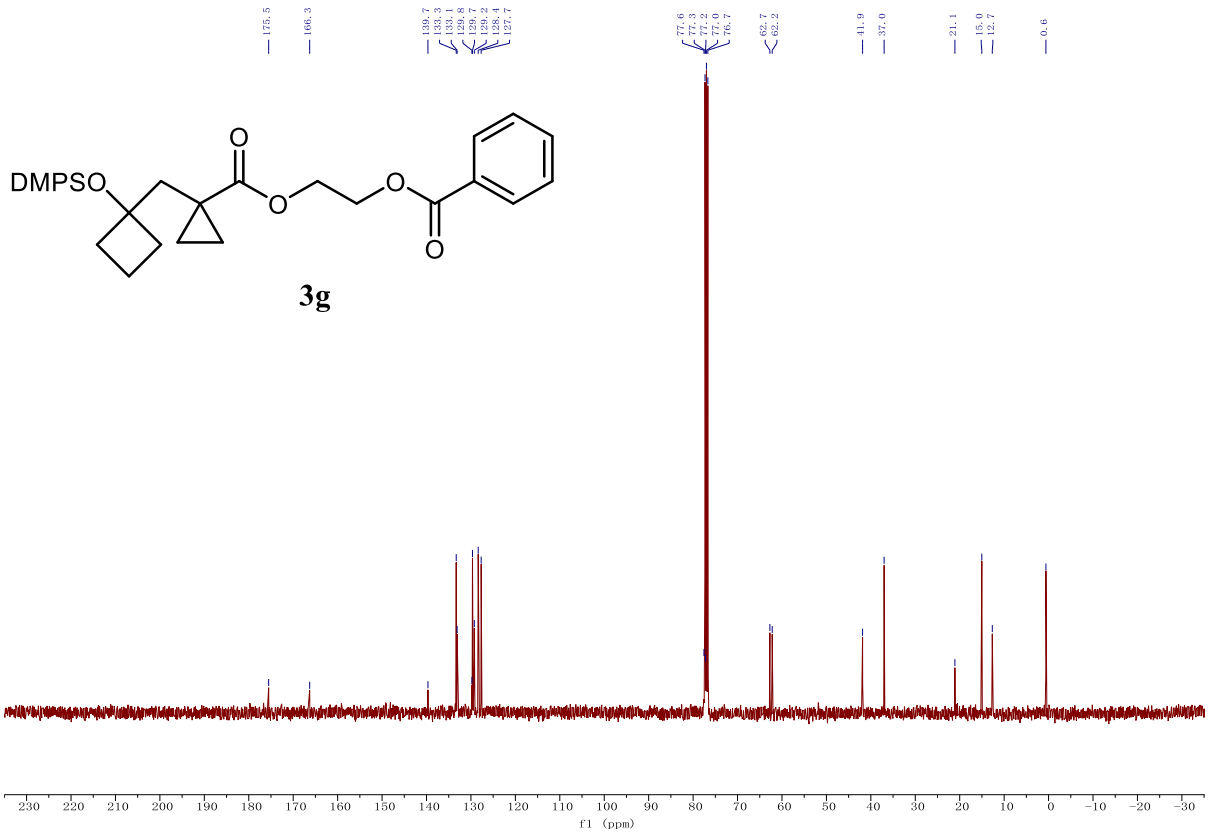
^{13}C NMR (101 MHz, $CDCl_3$)



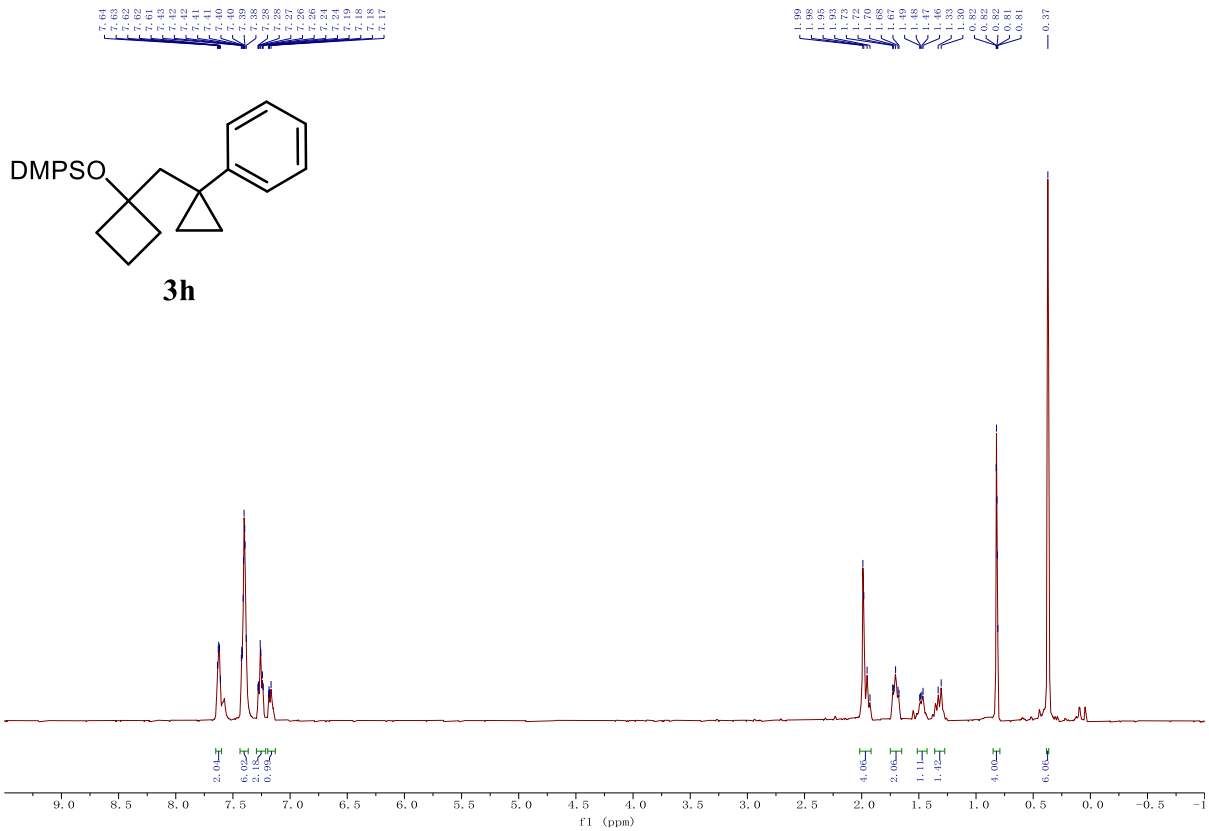
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

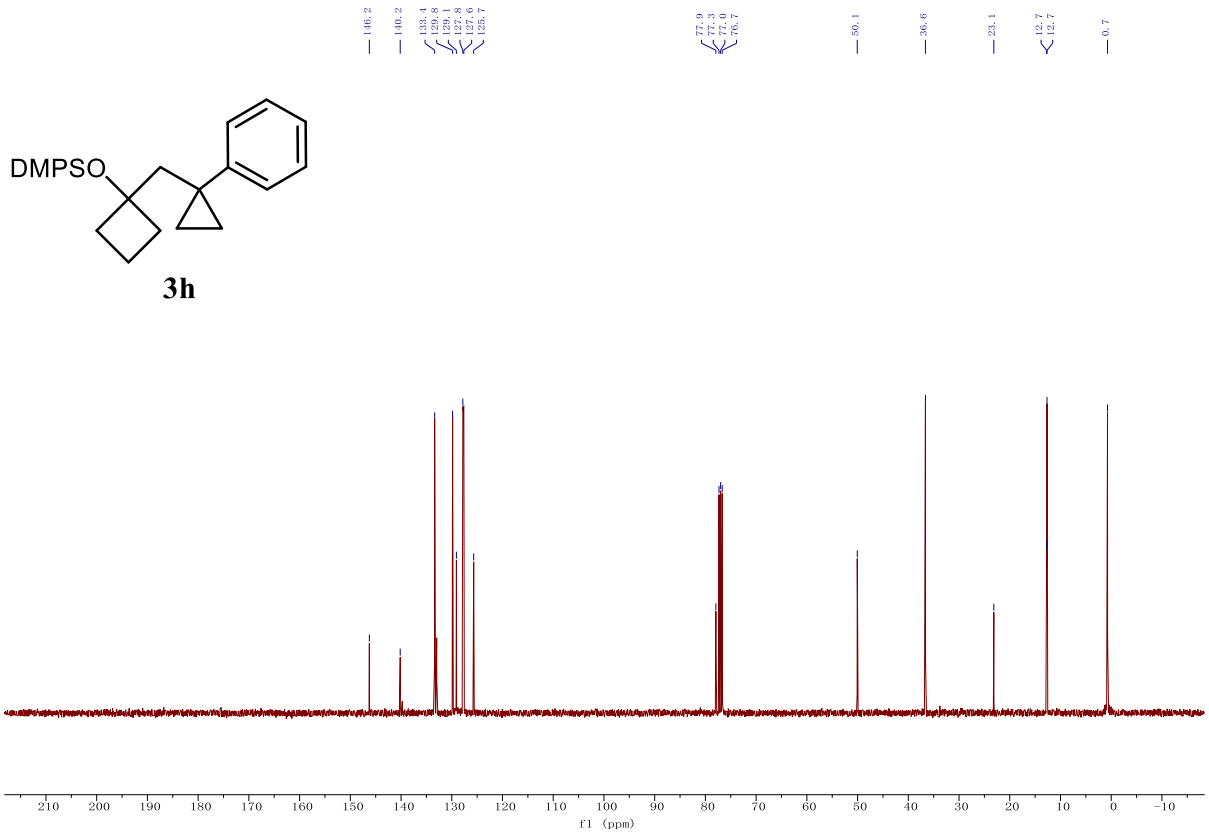


^{1}H NMR (400 MHz, $CDCl_3$)



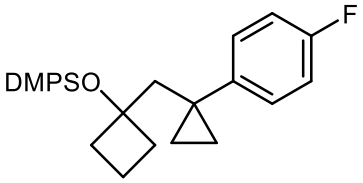
3h

^{13}C NMR (101 MHz, $CDCl_3$)

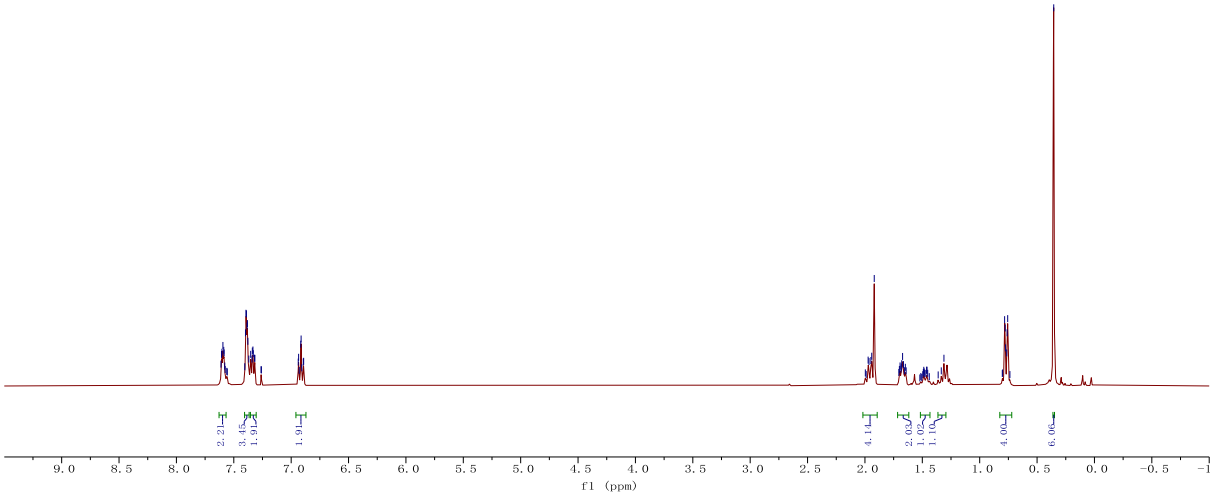


3h

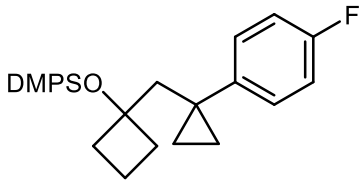
^{1}H NMR (400 MHz, $CDCl_3$)



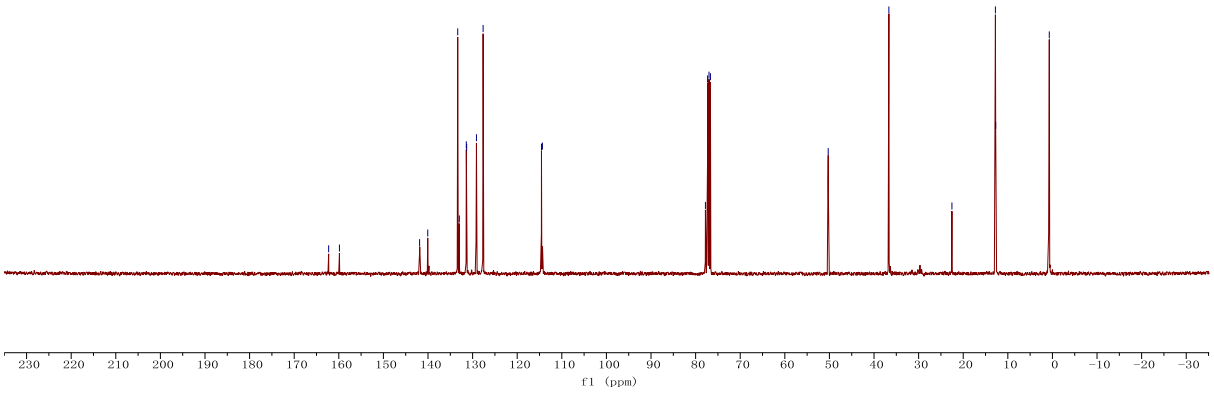
3i



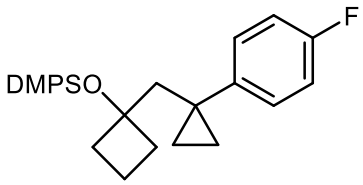
^{13}C NMR (101 MHz, $CDCl_3$)



3i

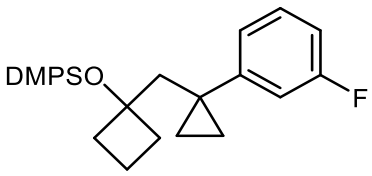


^{19}F NMR (101 MHz, $CDCl_3$)



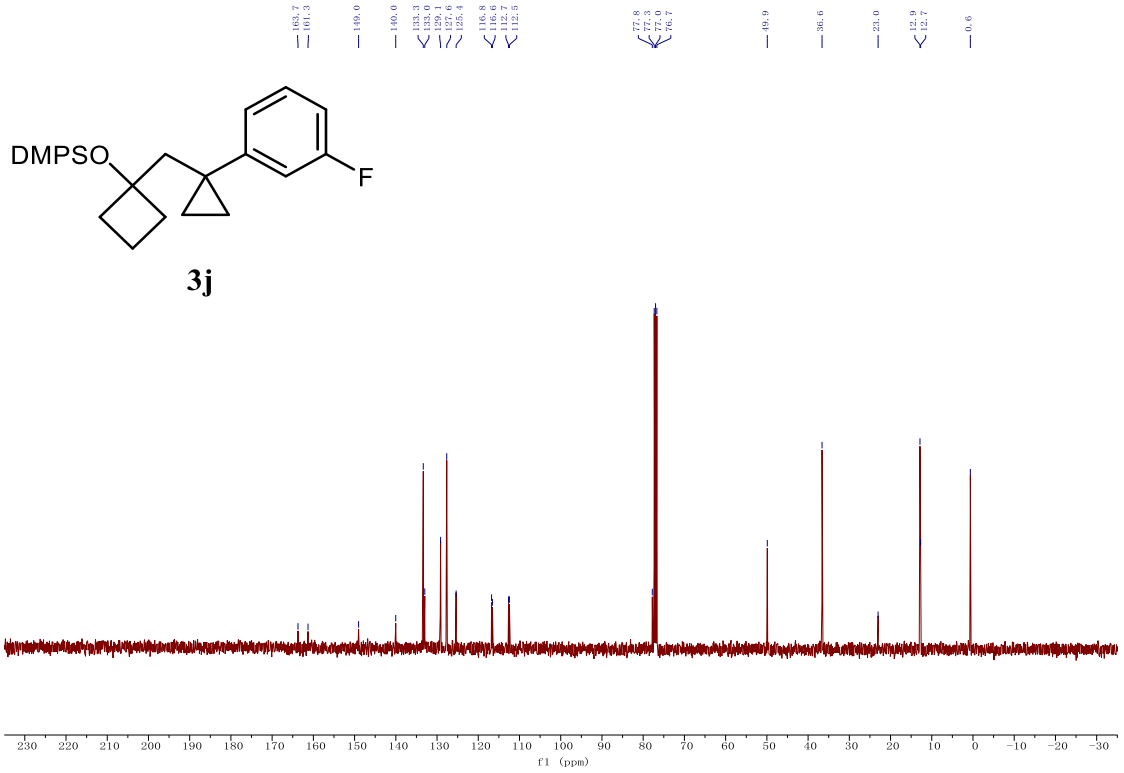
3i

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



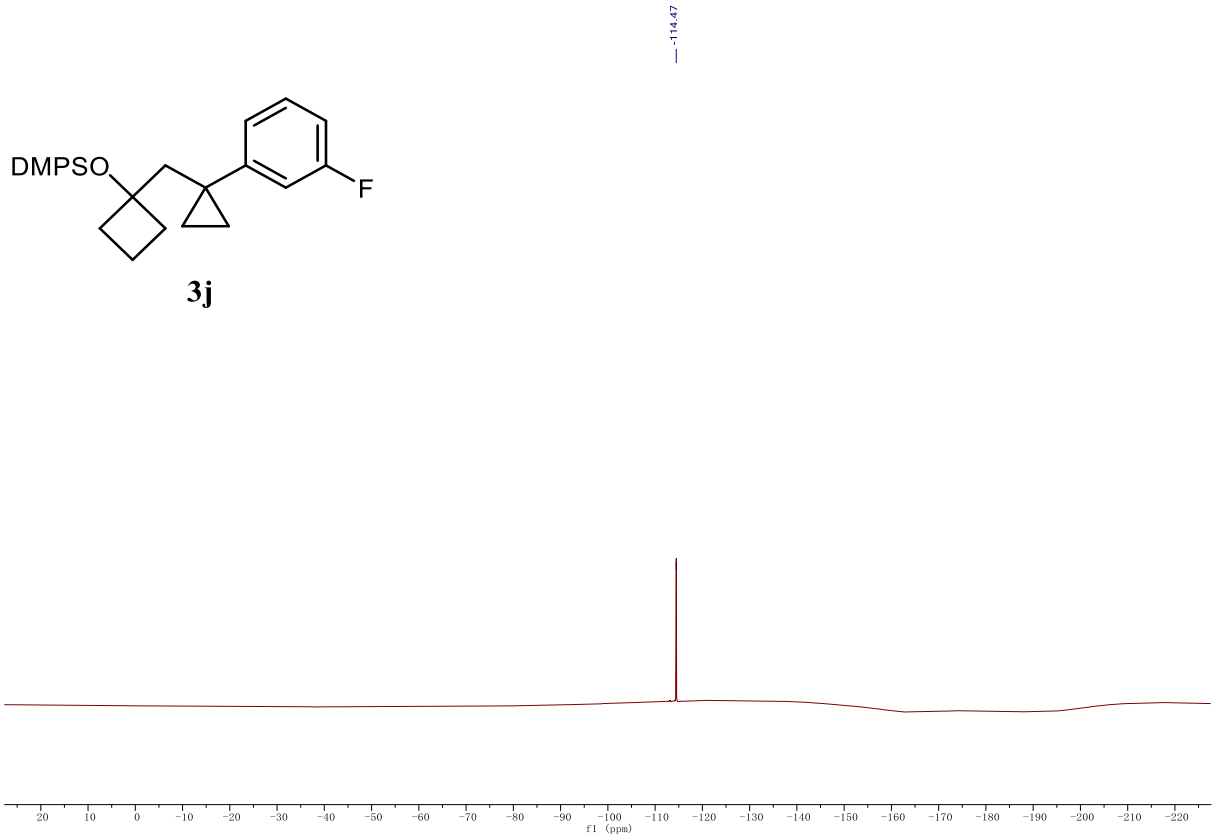
3j

^{13}C NMR (101 MHz, $CDCl_3$)



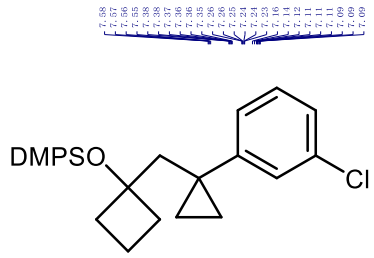
3j

^{19}F NMR (400 MHz, $CDCl_3$)

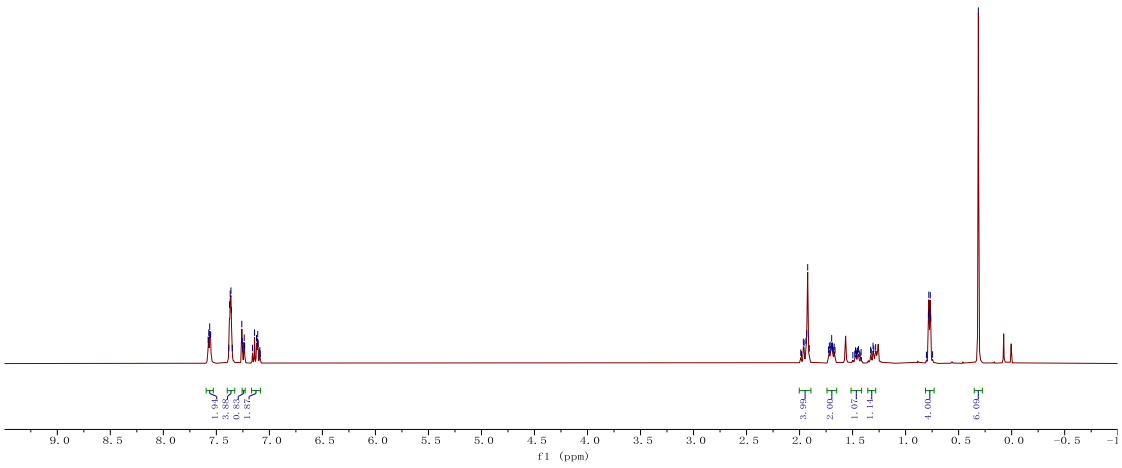


3j

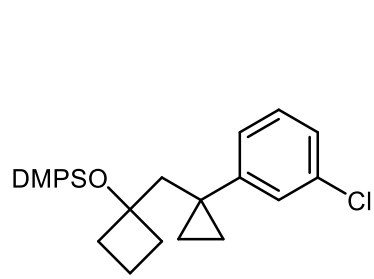
^{1}H NMR (400 MHz, $CDCl_3$)



3k



^{13}C NMR (101 MHz, $CDCl_3$)



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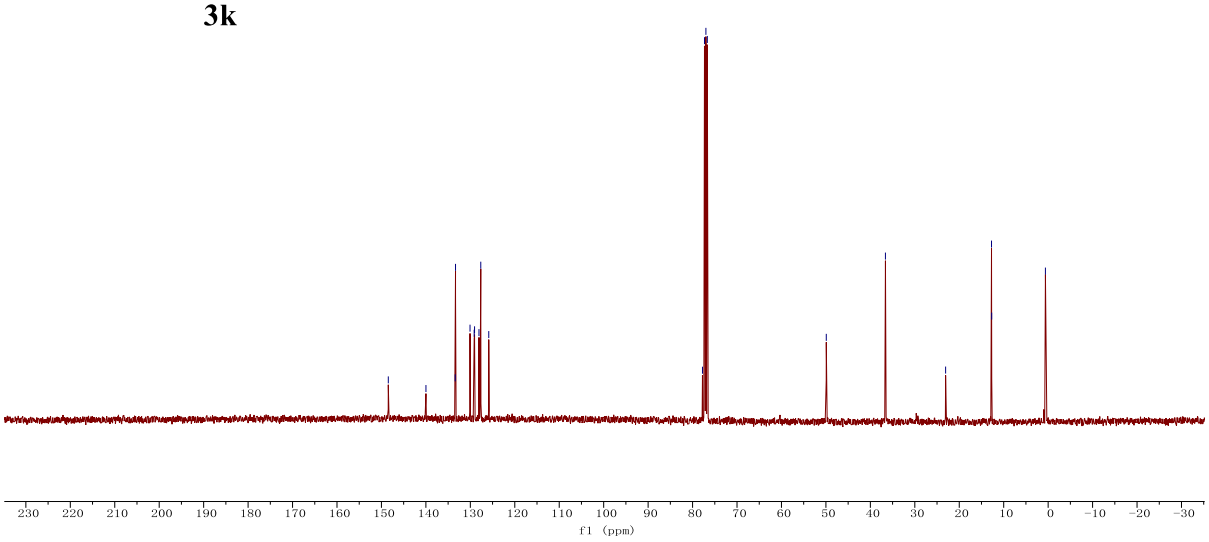
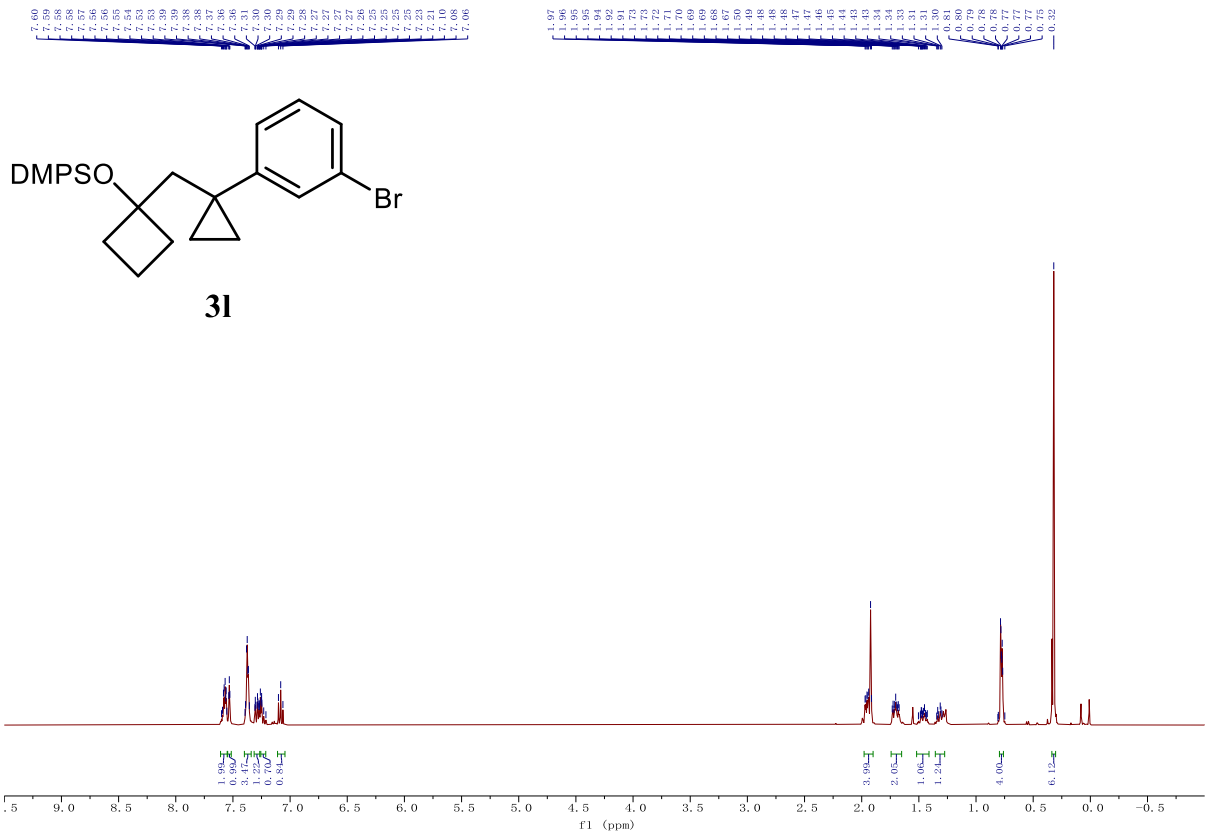
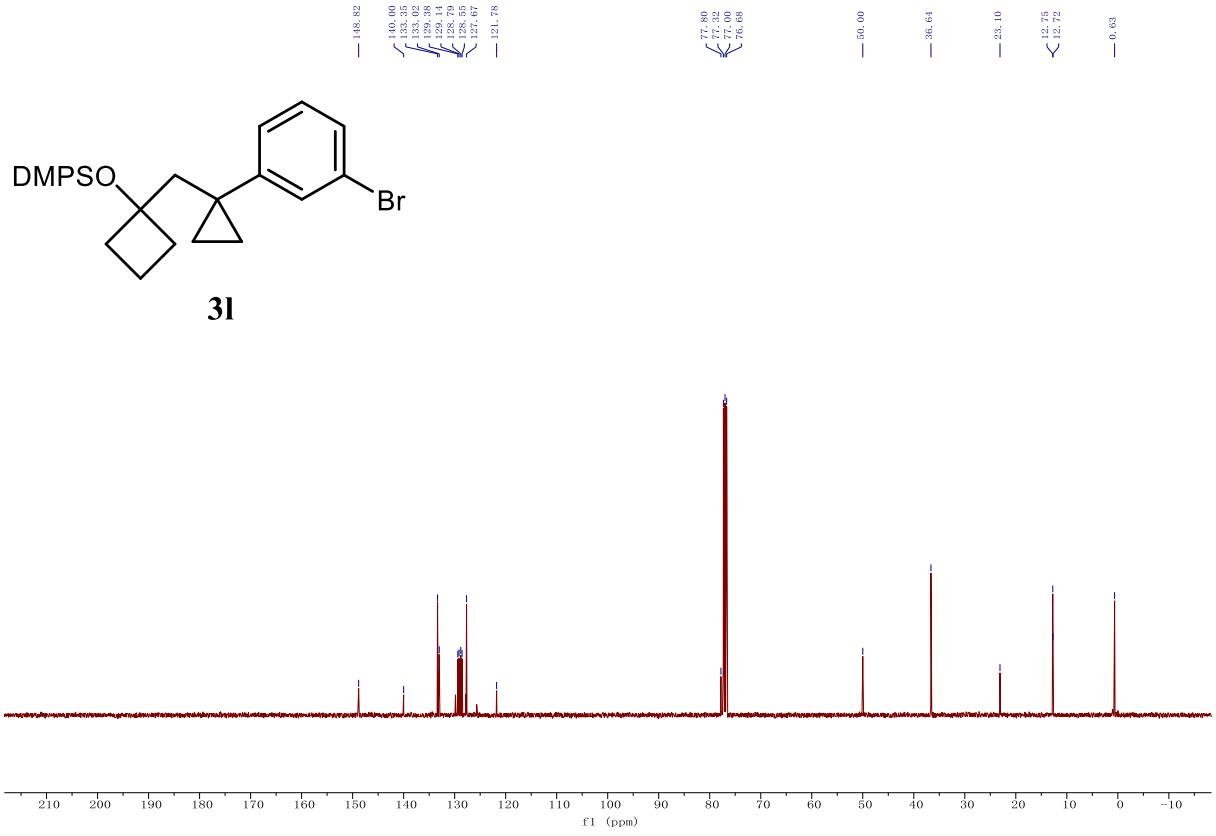


^{1}H NMR (400 MHz, $CDCl_3$)



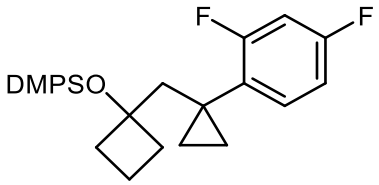
3l

^{13}C NMR (101 MHz, $CDCl_3$)

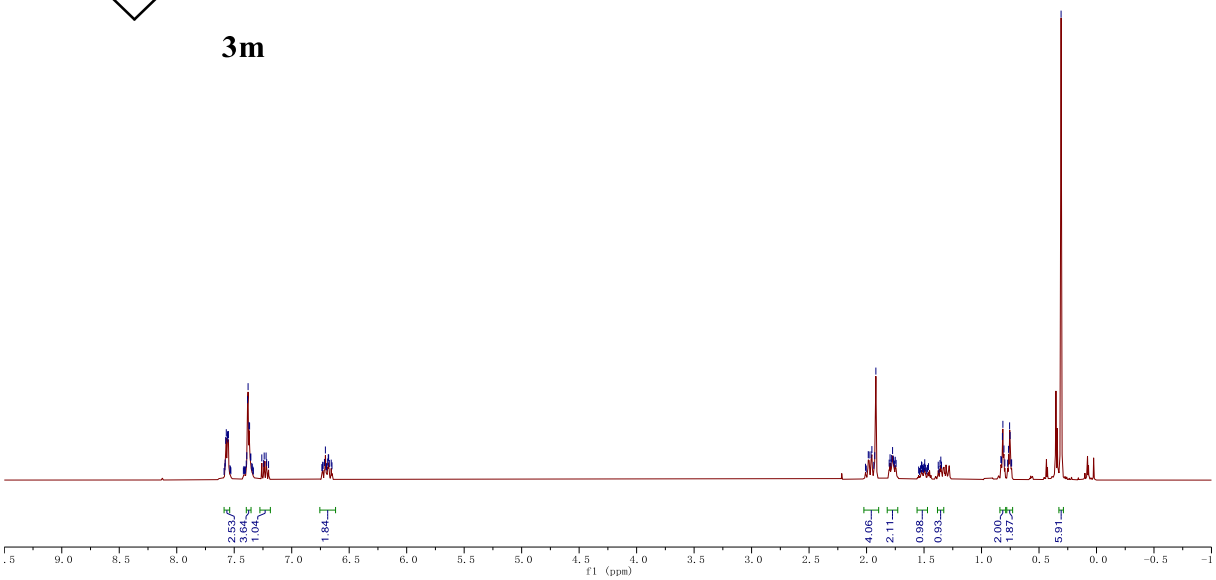


3l

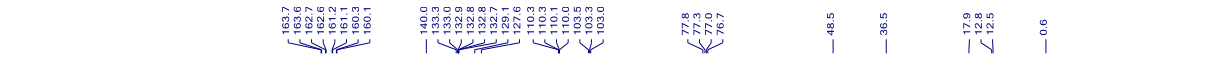
^{1}H NMR (400 MHz, $CDCl_3$)

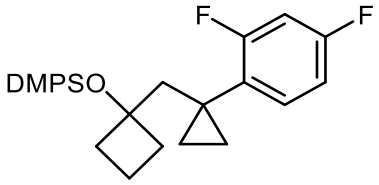


3m

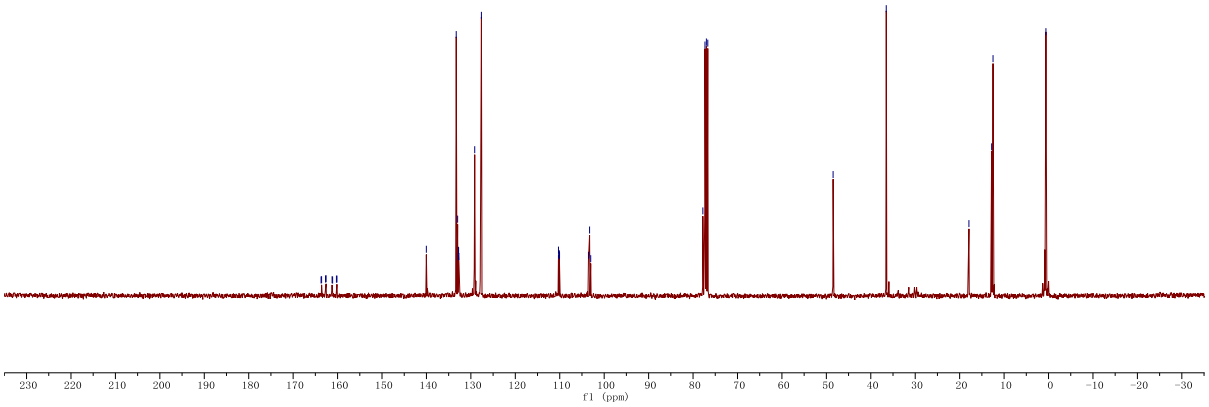


^{13}C NMR (101 MHz, $CDCl_3$)

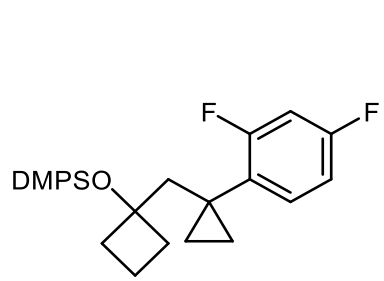




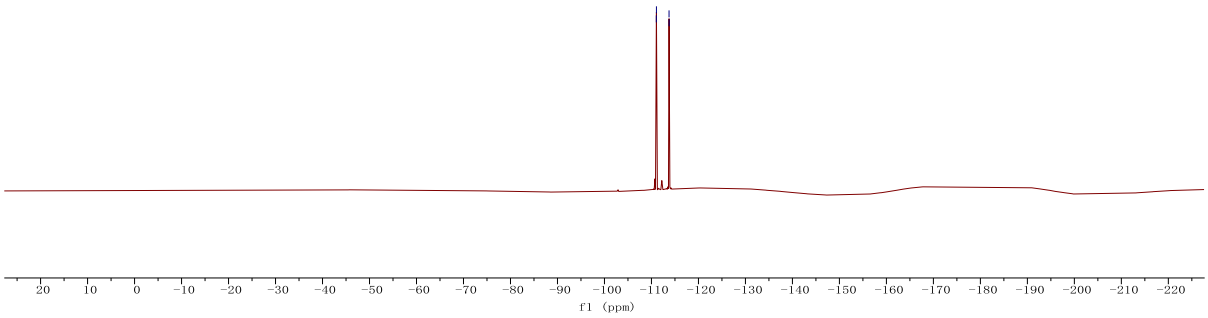
3m



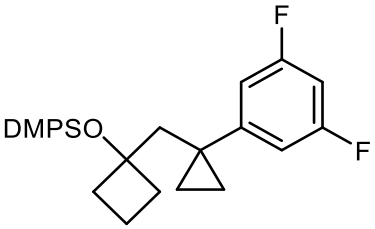
^{19}F NMR (376 MHz, $CDCl_3$)



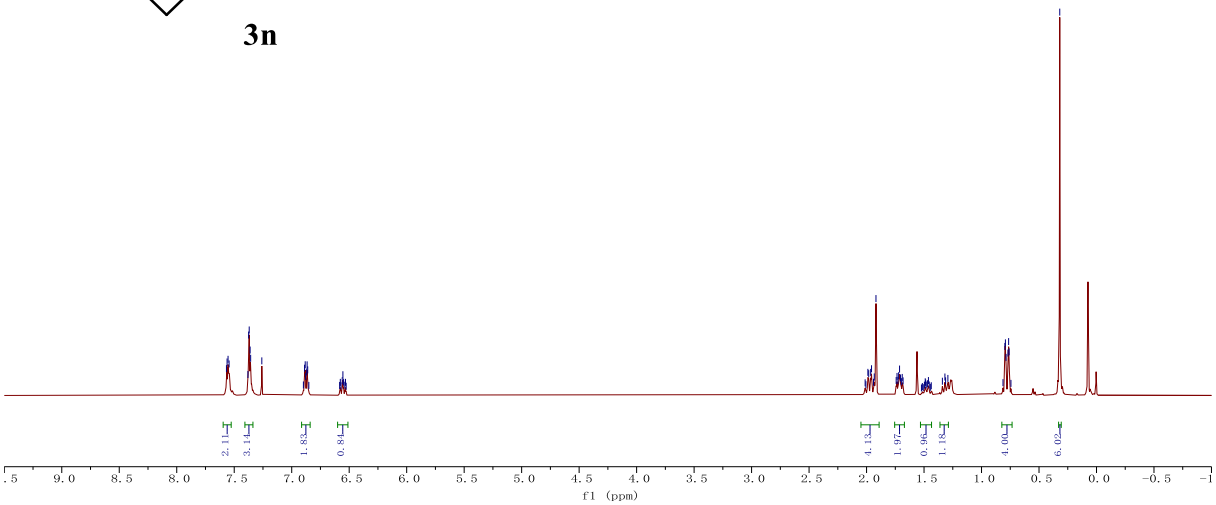
3m



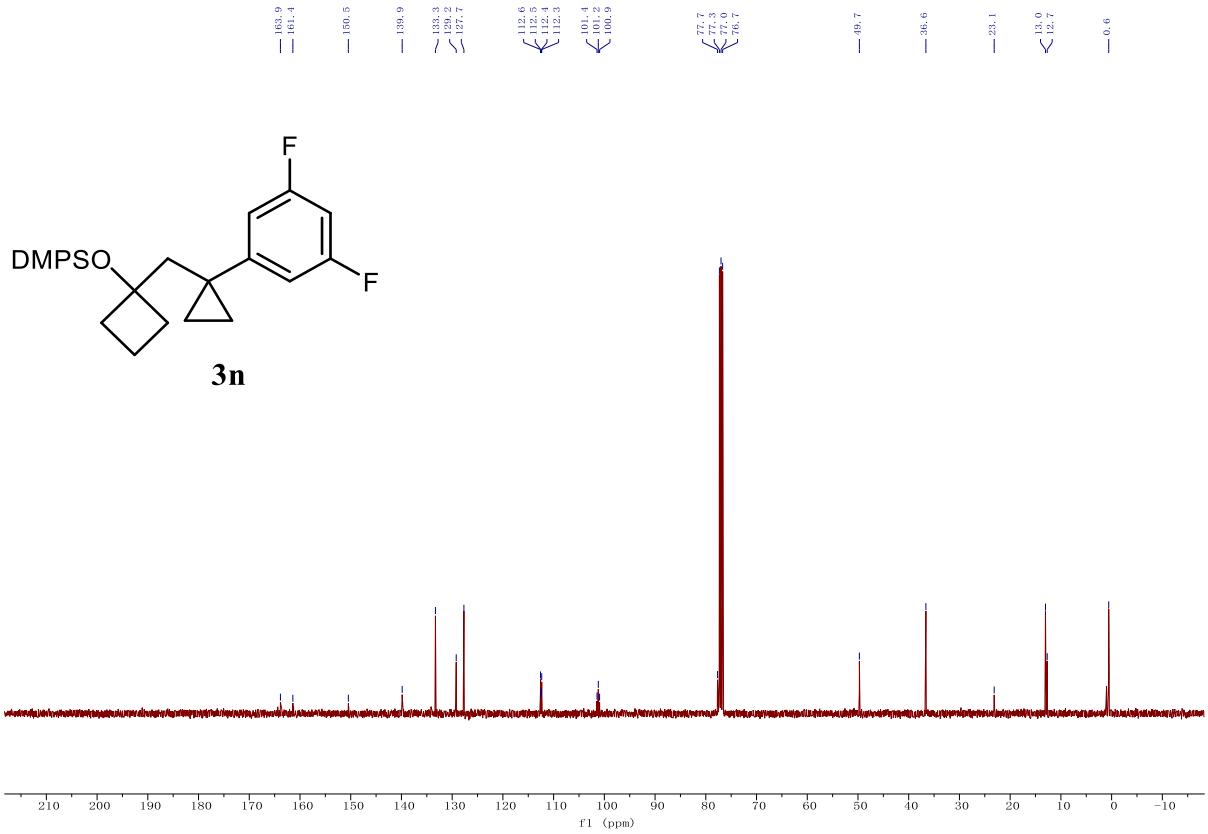
^{1}H NMR (400 MHz, $CDCl_3$)



3n

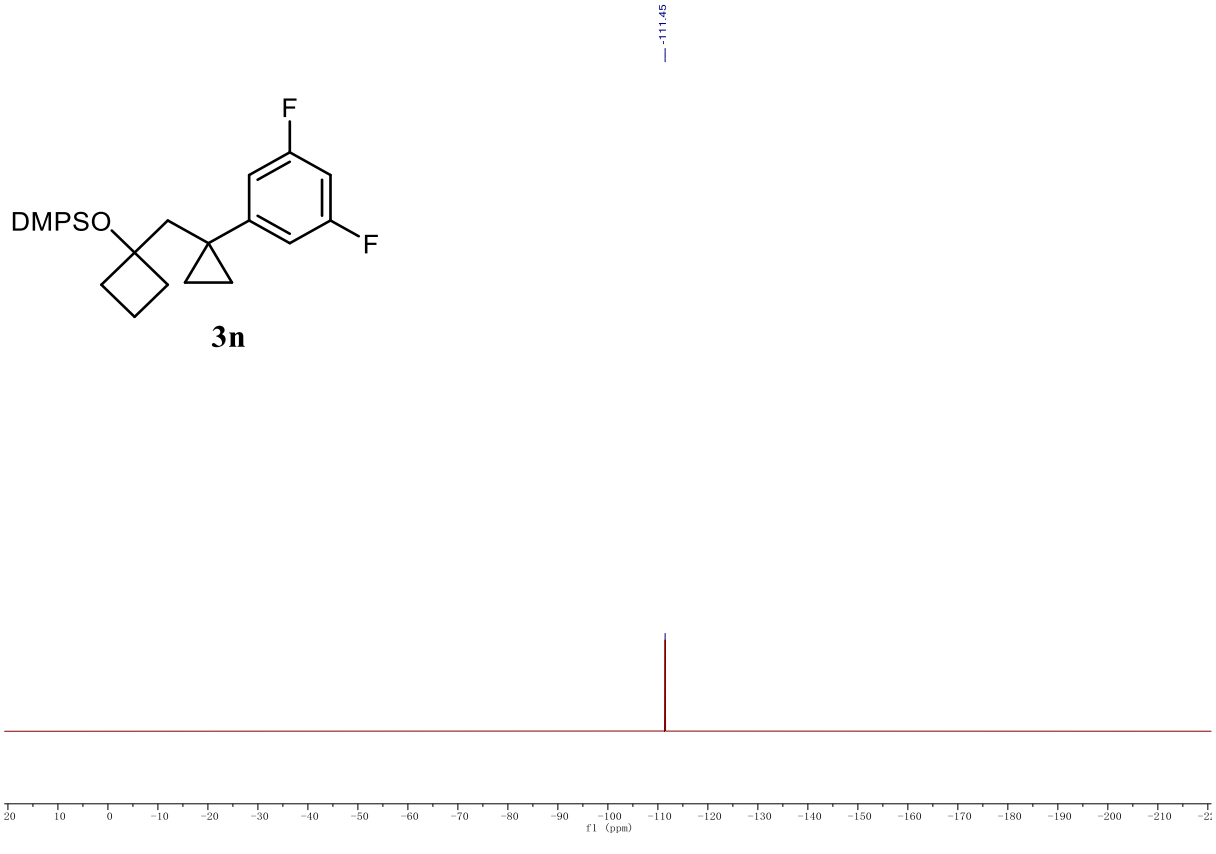


^{13}C NMR (400 MHz, $CDCl_3$)



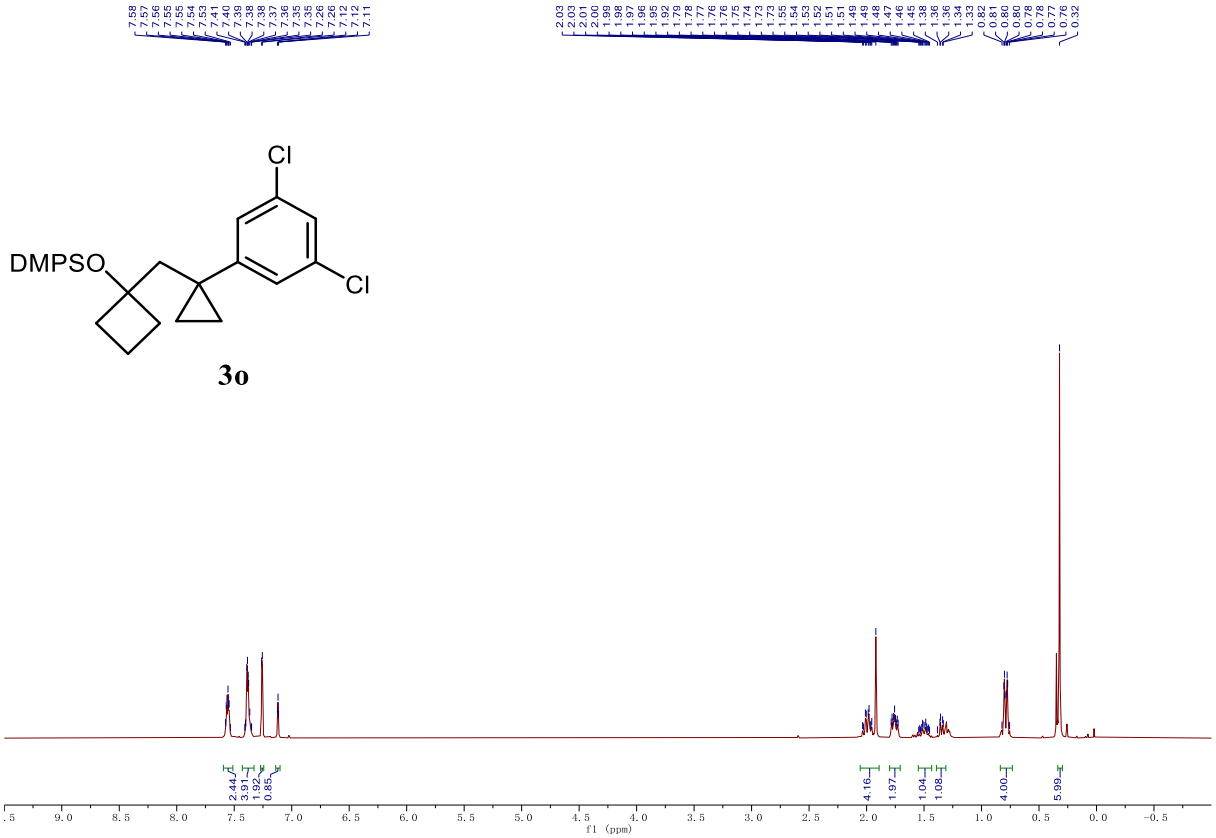
3n

^{19}F NMR (400 MHz, $CDCl_3$)

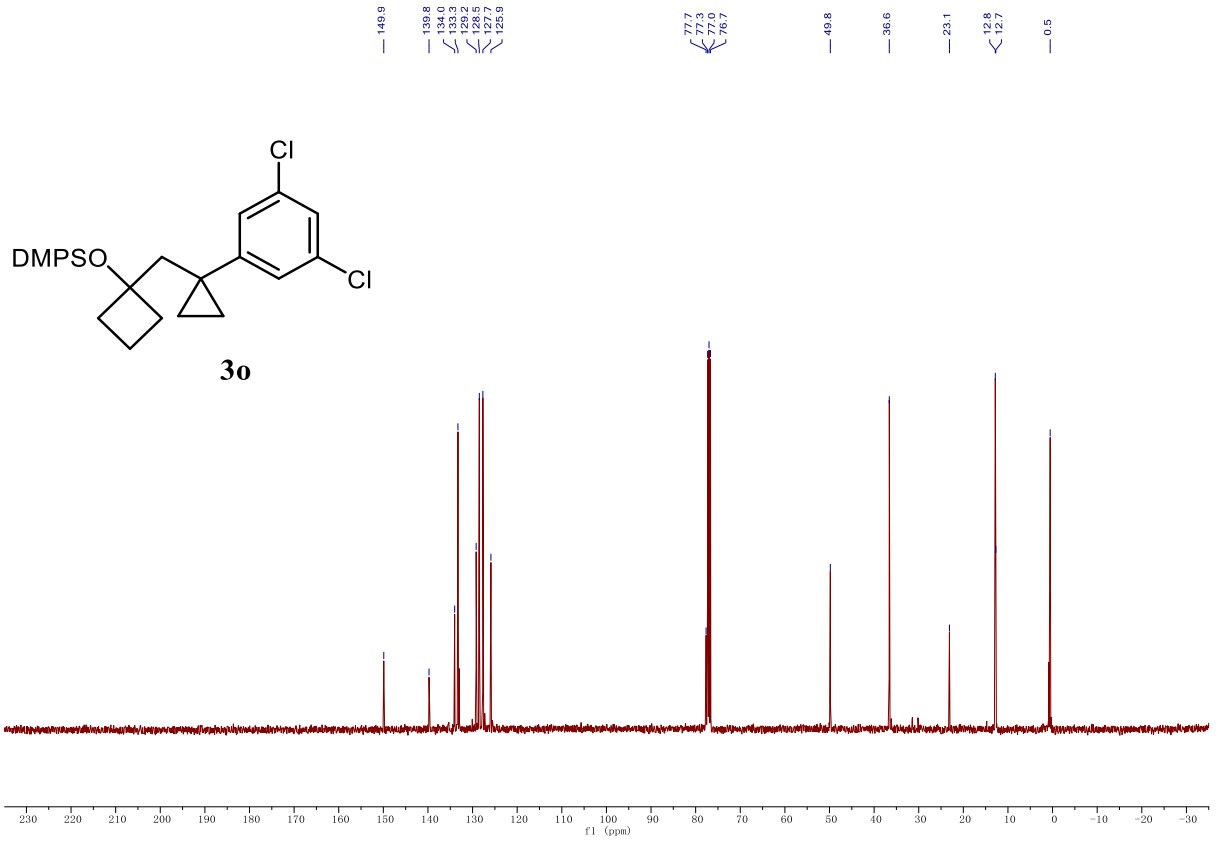


3n

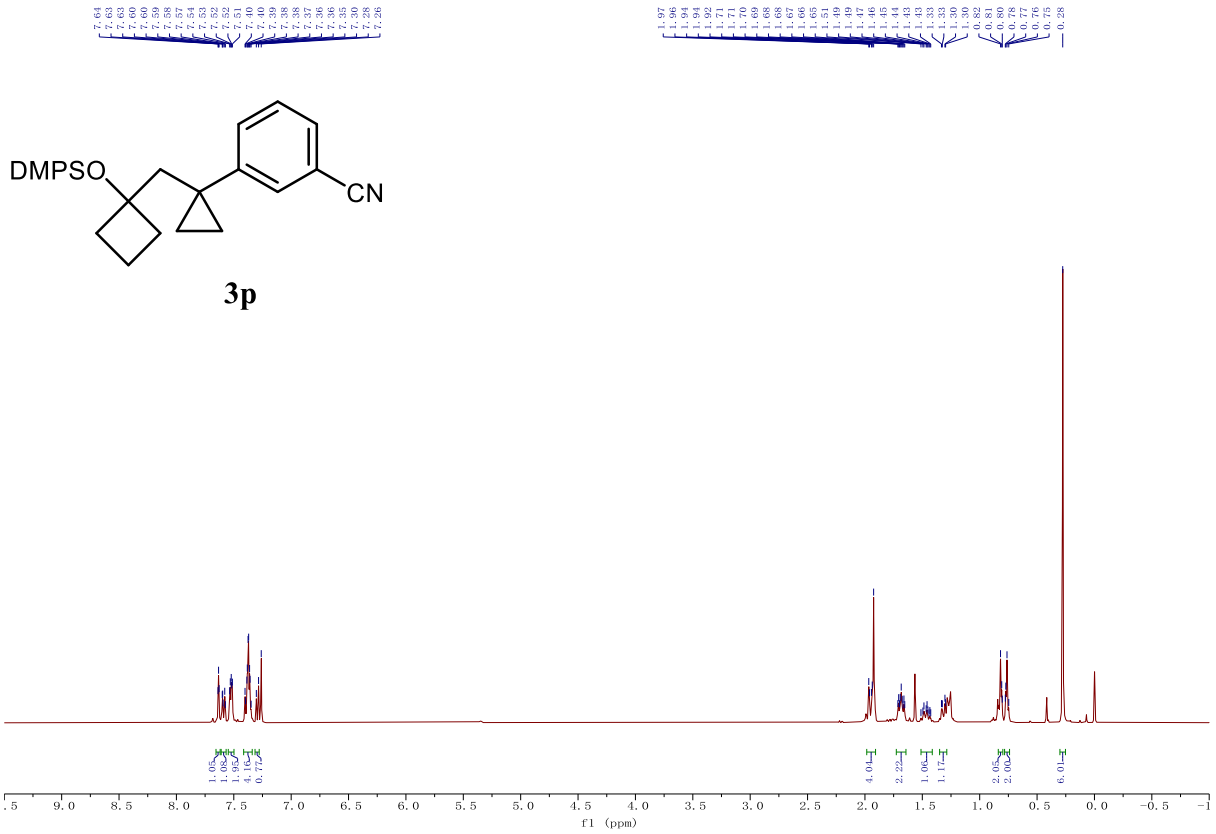
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

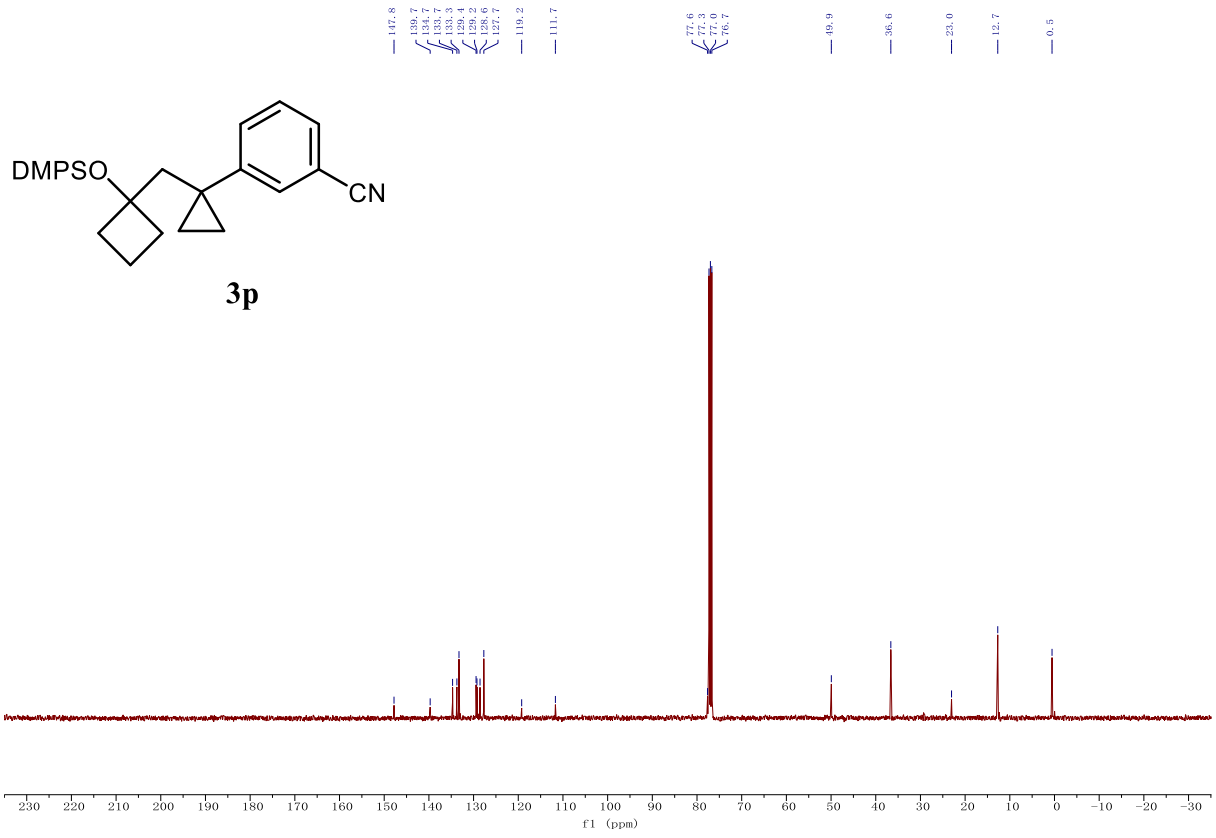


^{1}H NMR (400 MHz, $CDCl_3$)



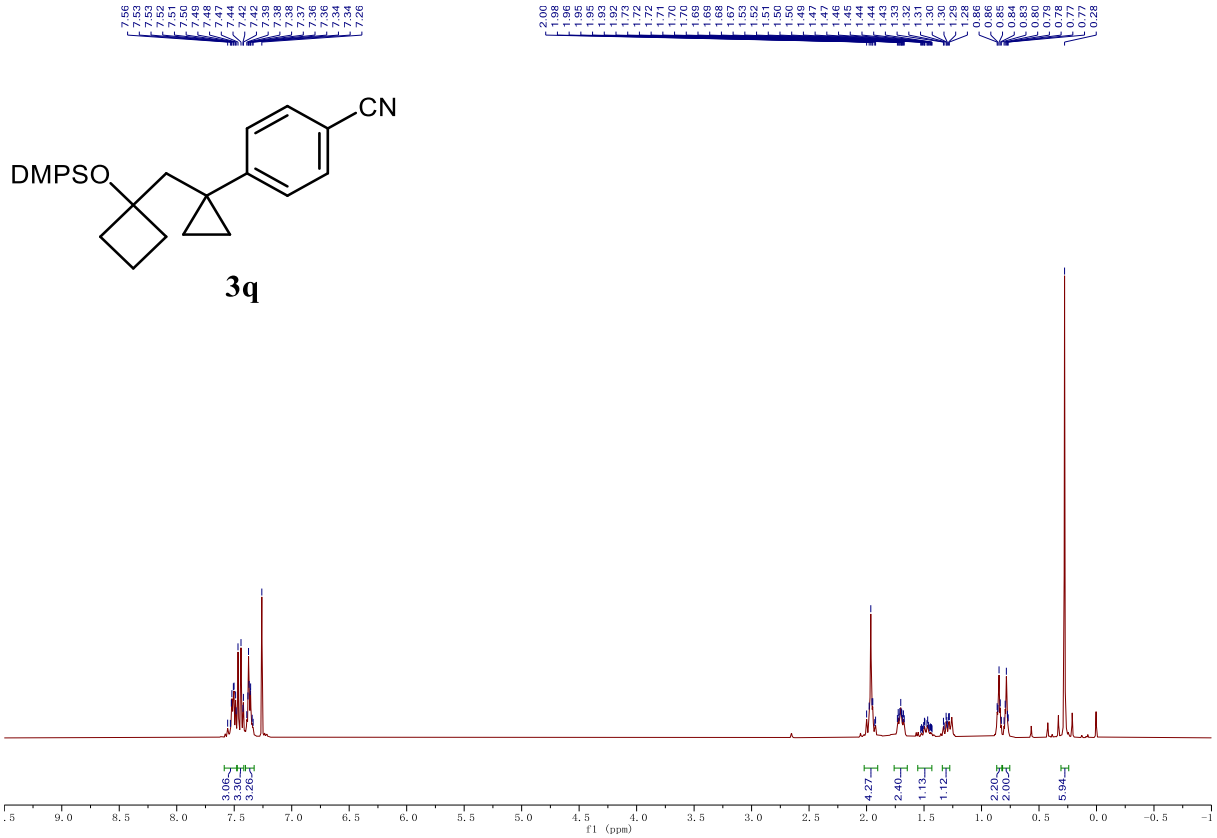
3p

^{13}C NMR (101 MHz, $CDCl_3$)

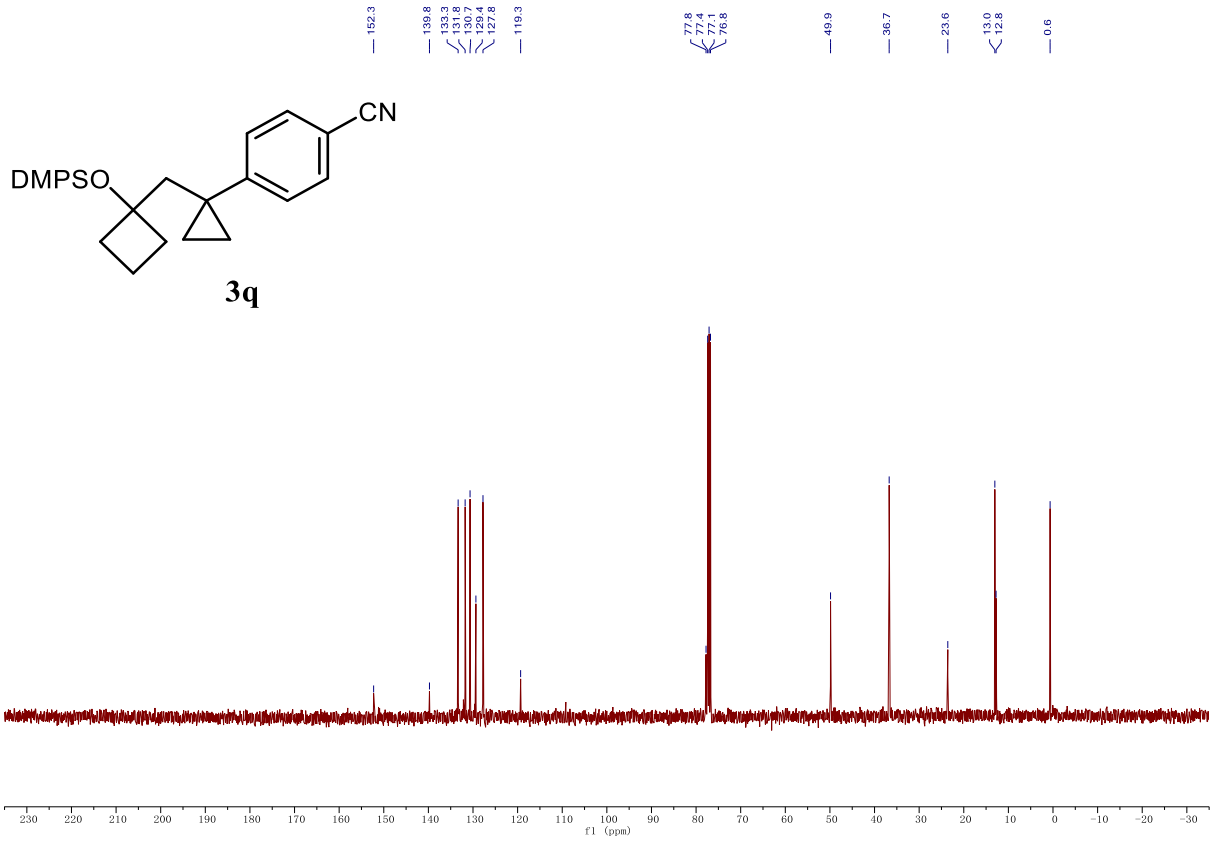


3p

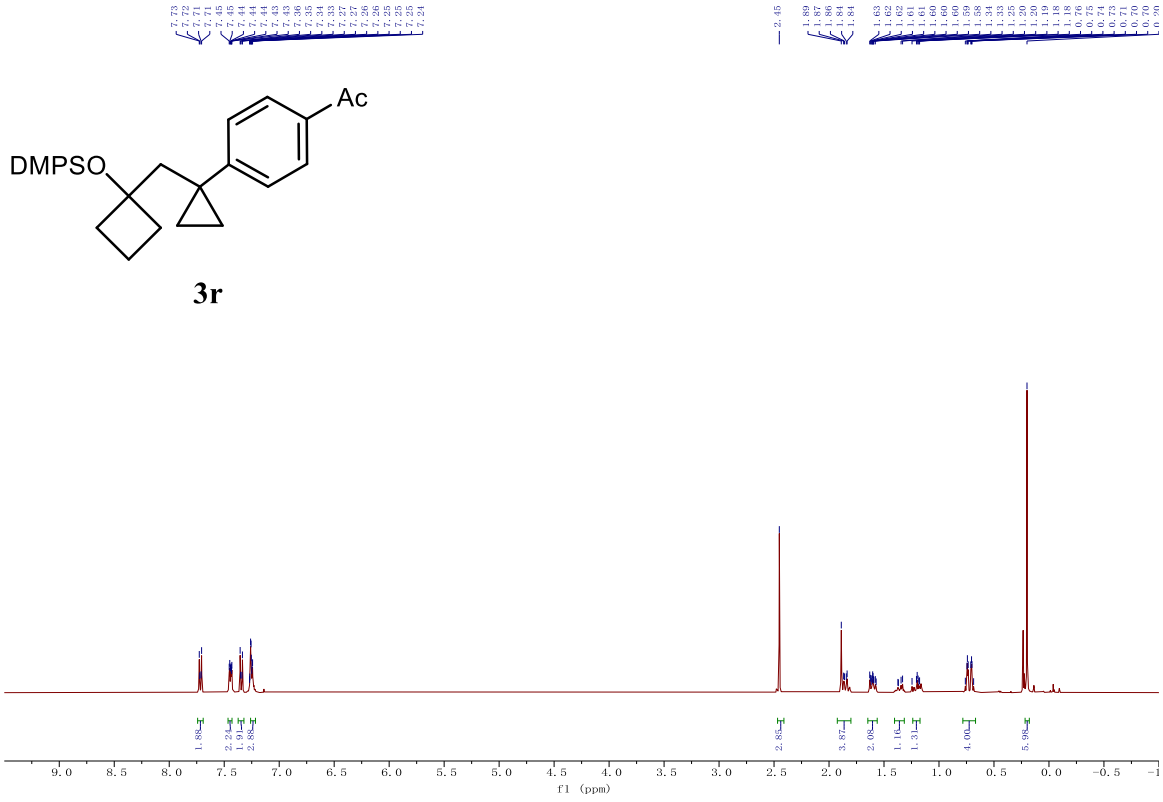
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

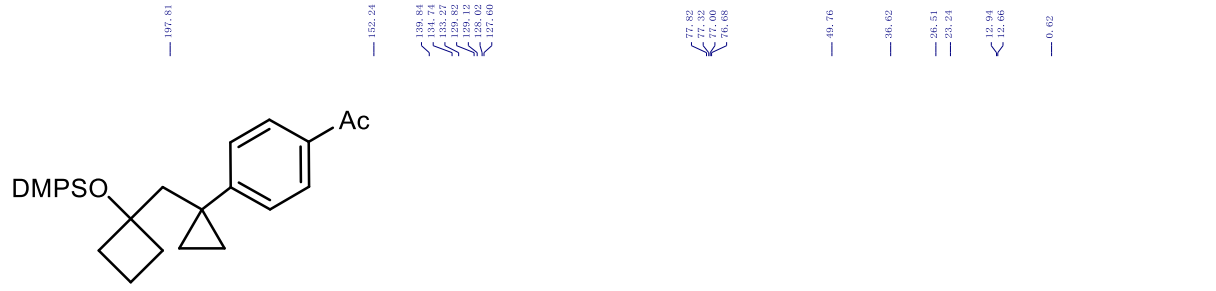


^{1}H NMR (400 MHz, $CDCl_3$)

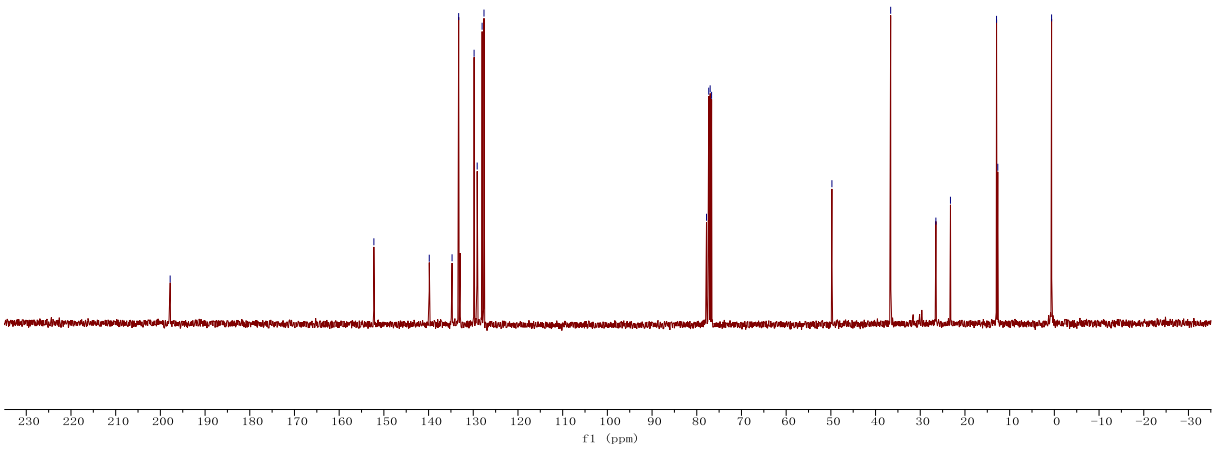


3r

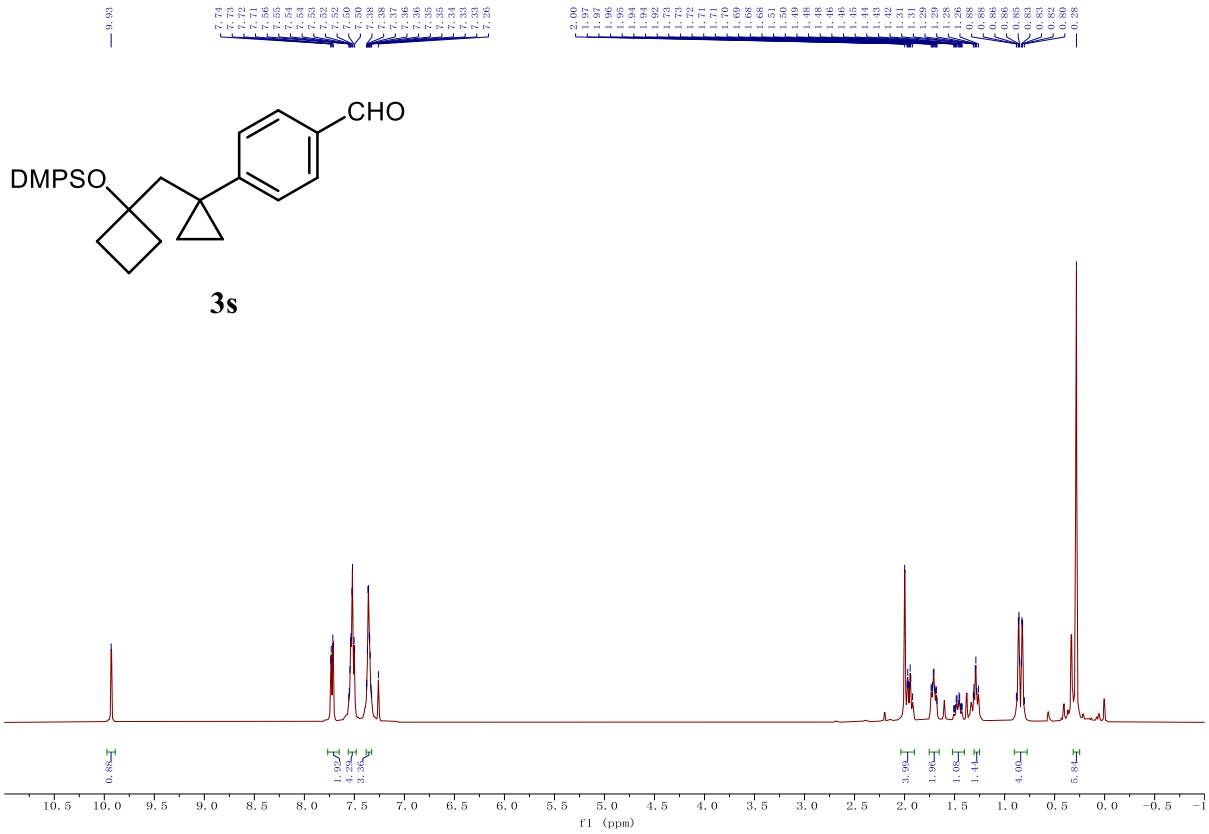
^{13}C NMR (101 MHz, $CDCl_3$)



3r

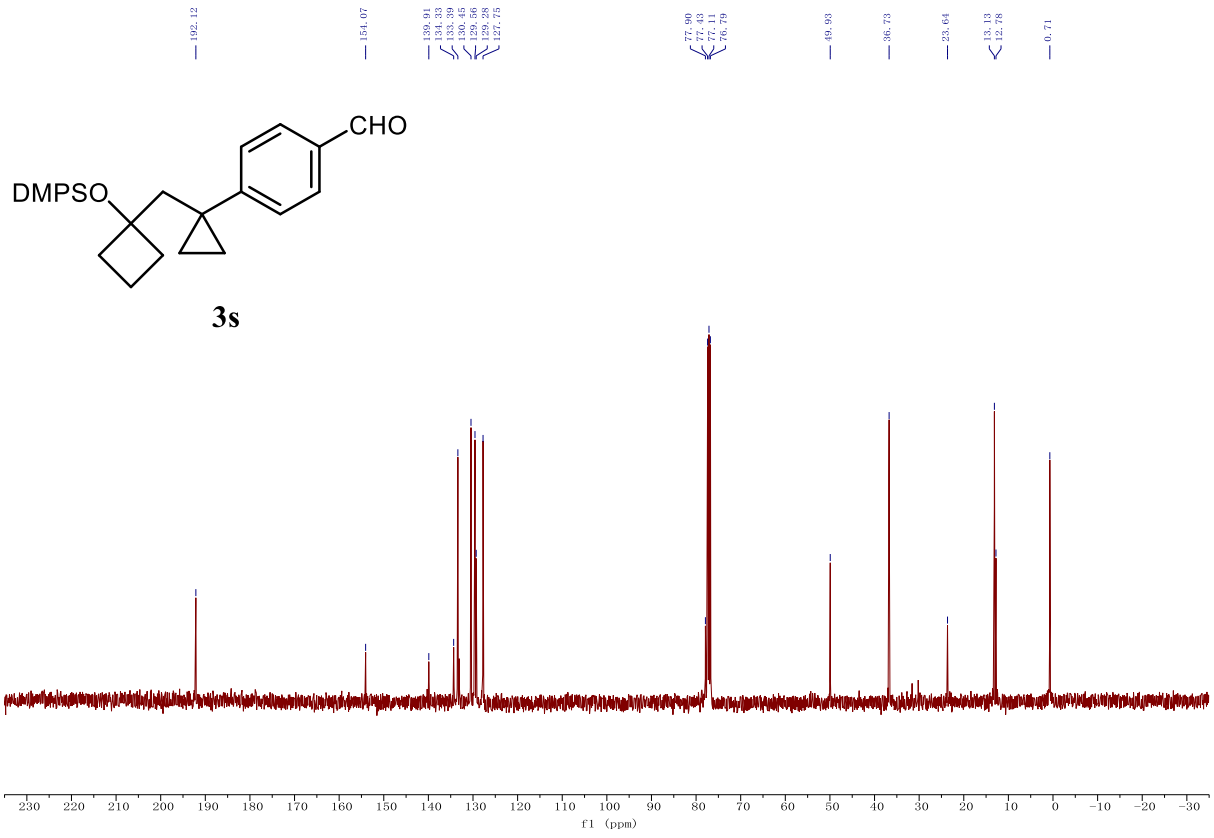


^{1}H NMR (400 MHz, $CDCl_3$)



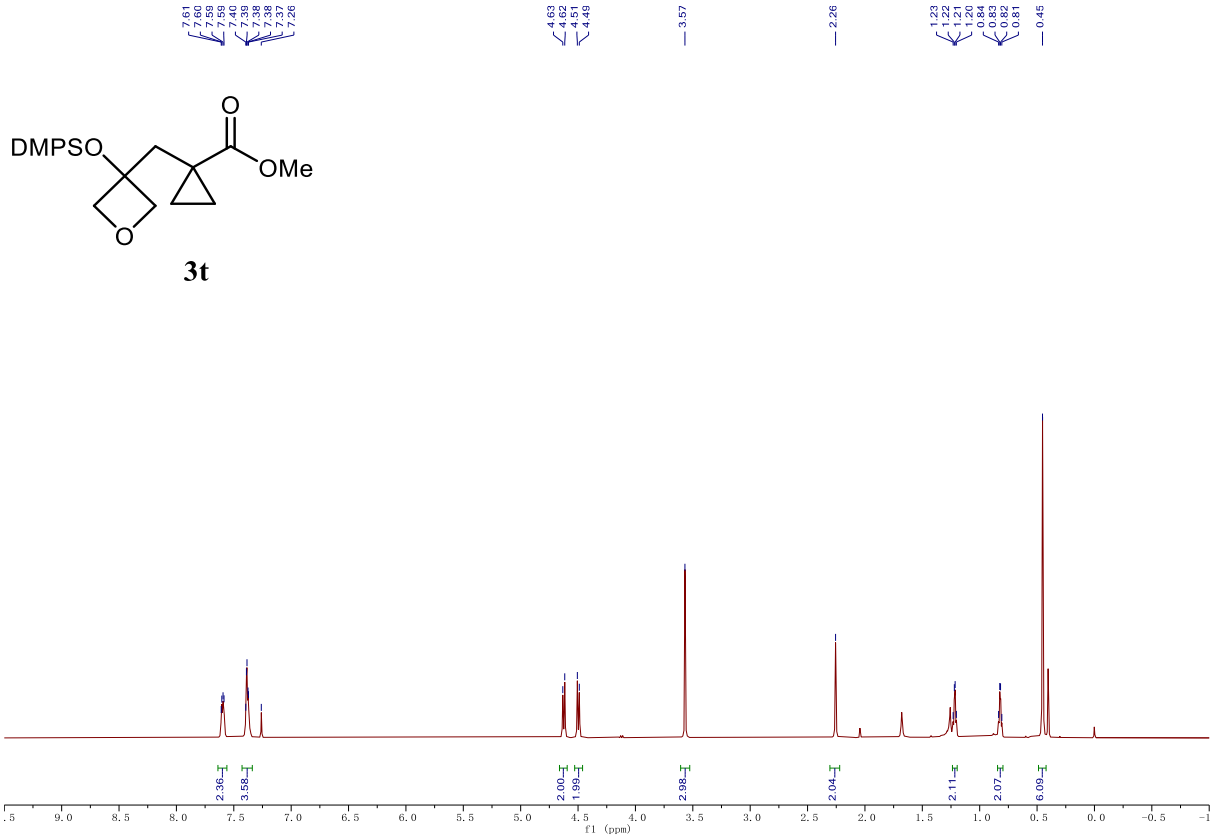
3s

^{13}C NMR (101 MHz, $CDCl_3$)



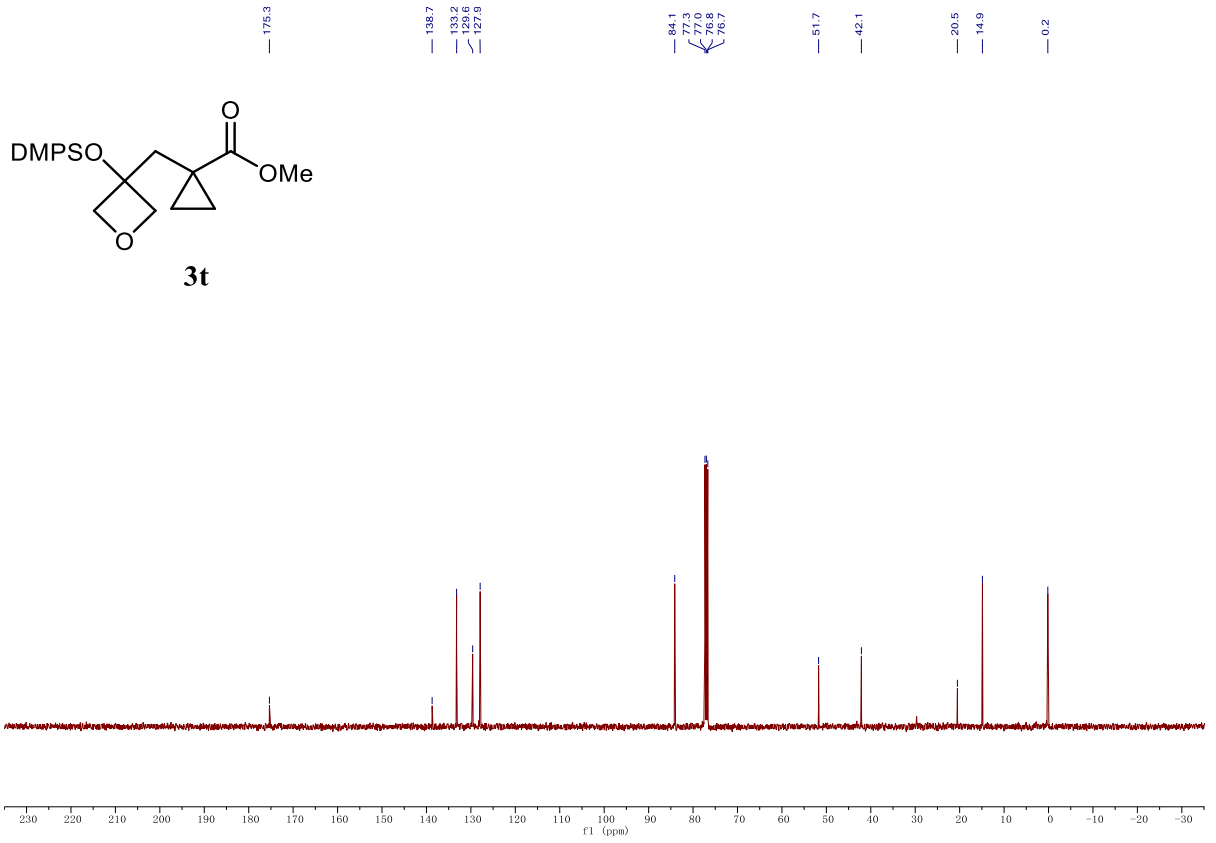
3s

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



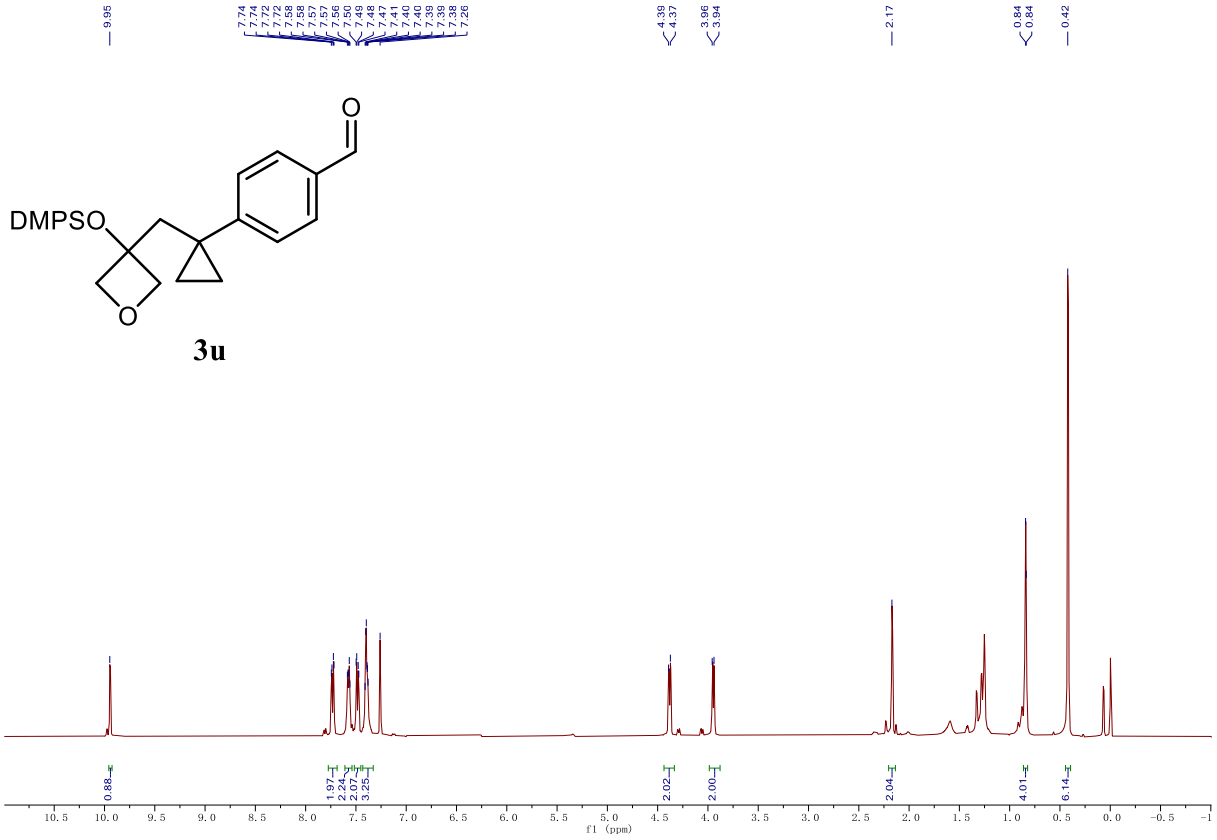
3t

^{13}C NMR (101 MHz, $CDCl_3$)

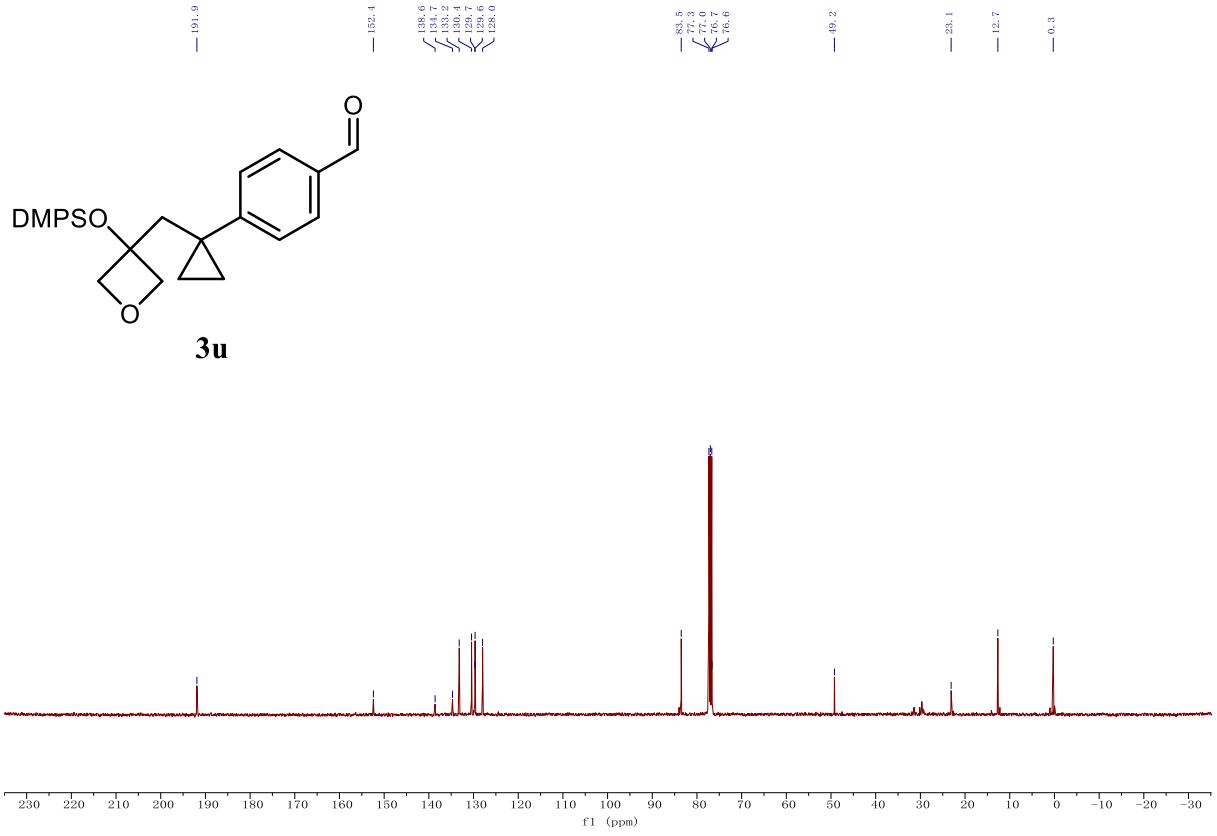


3t

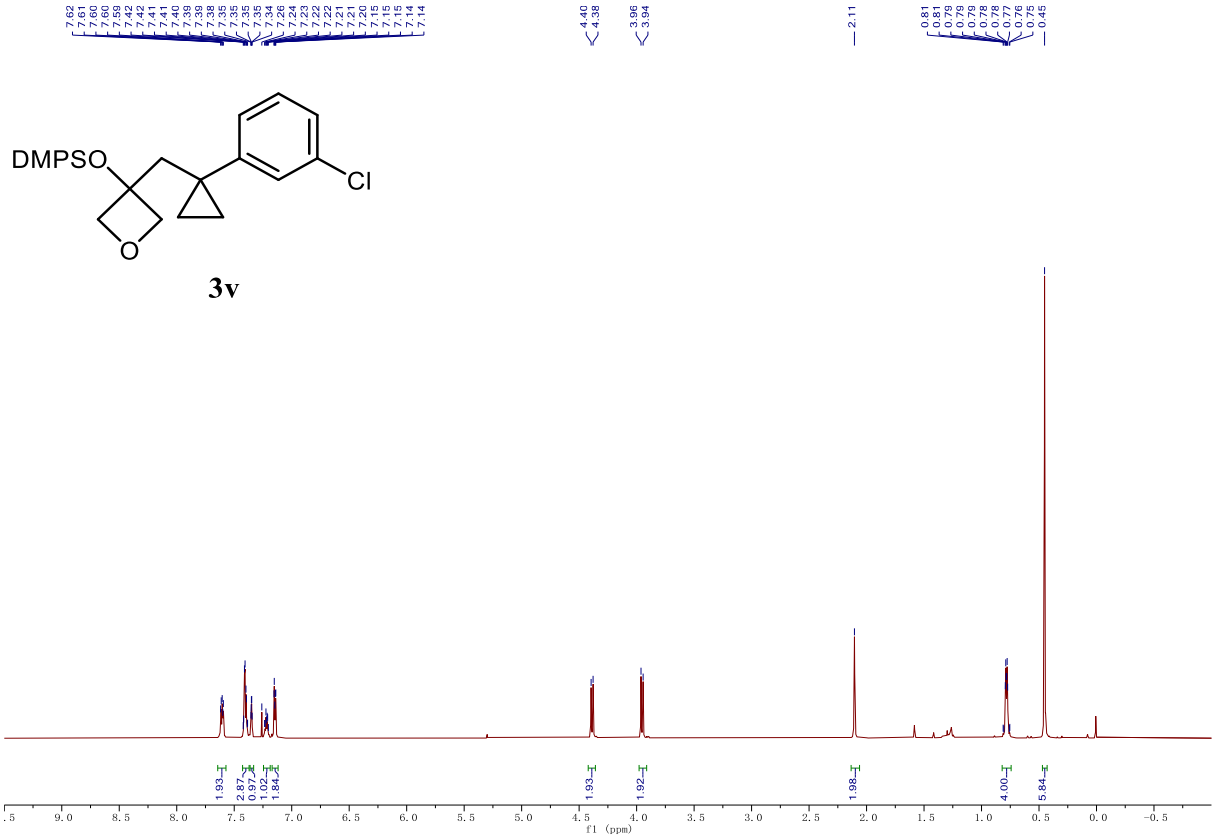
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

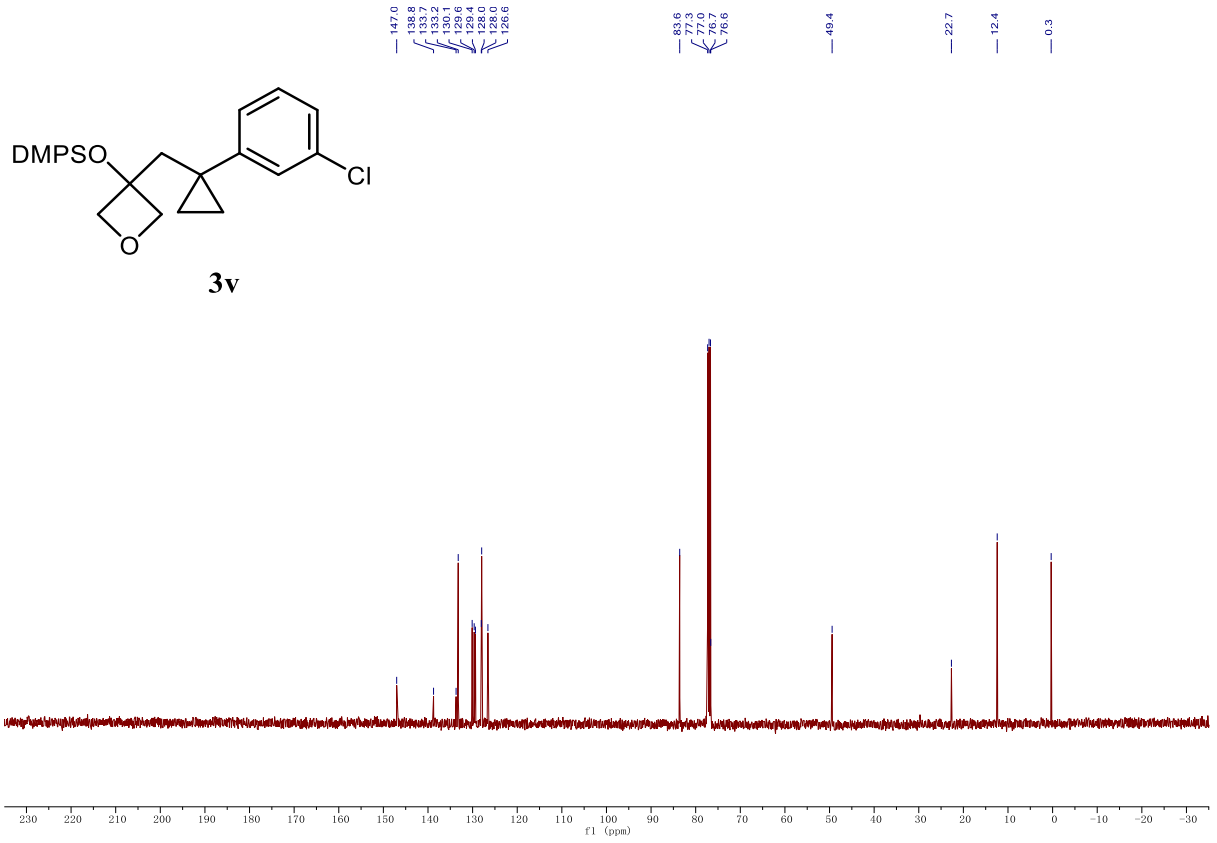


^{1}H NMR (400 MHz, $CDCl_3$)



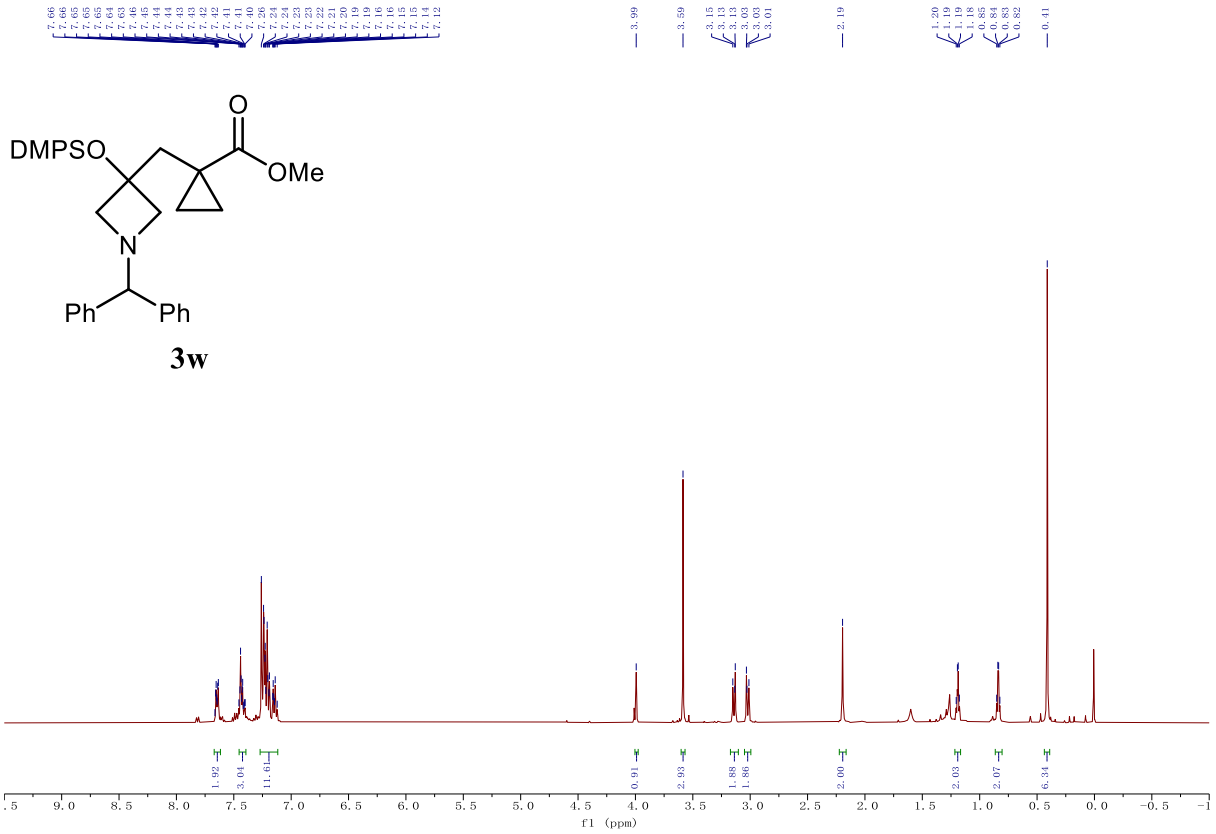
3v

^{13}C NMR (101 MHz, $CDCl_3$)



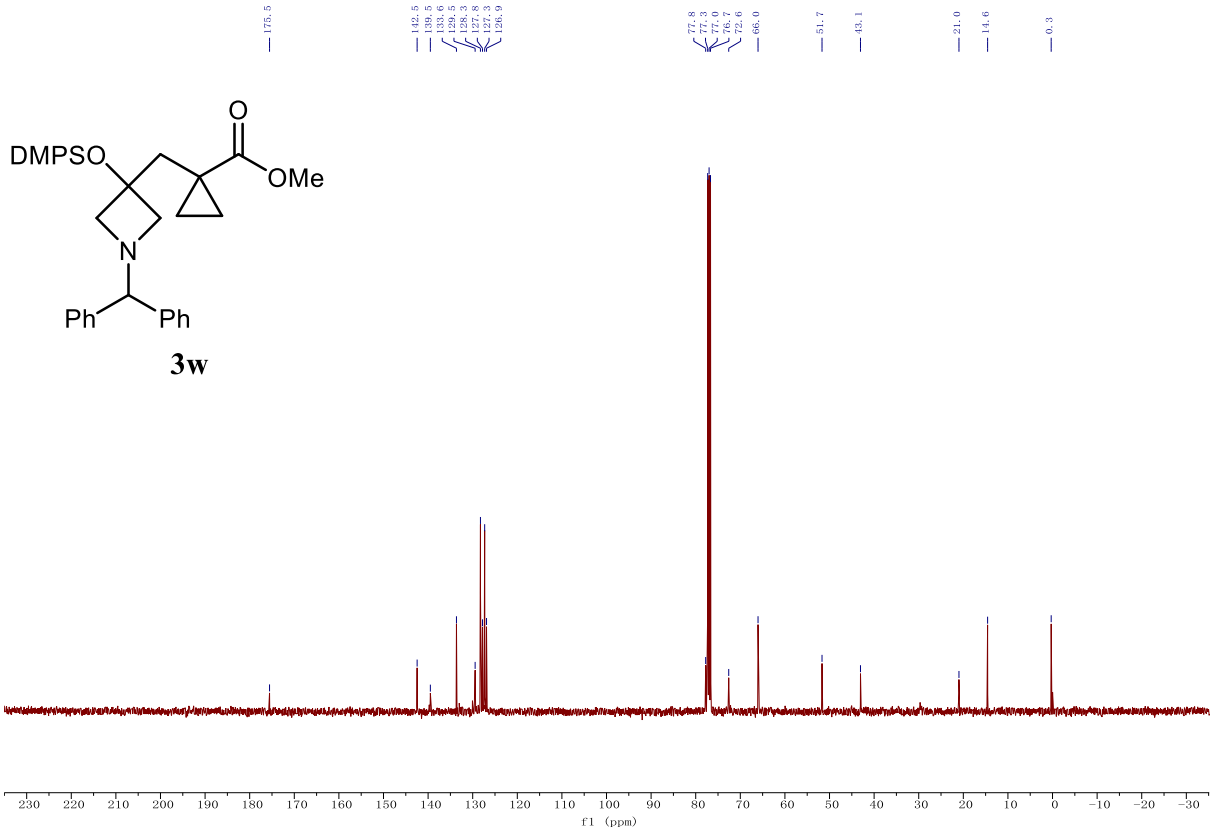
3v

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



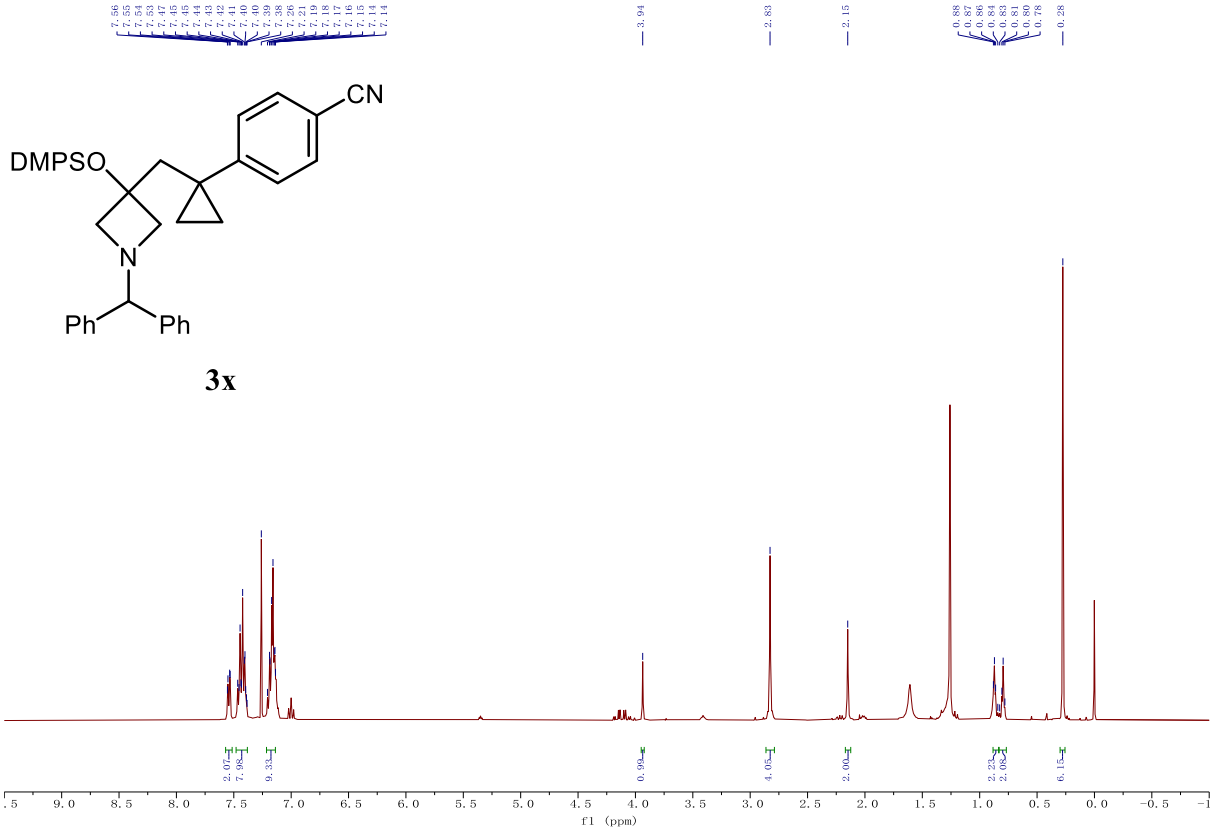
3w

^{13}C NMR (101 MHz, $CDCl_3$)



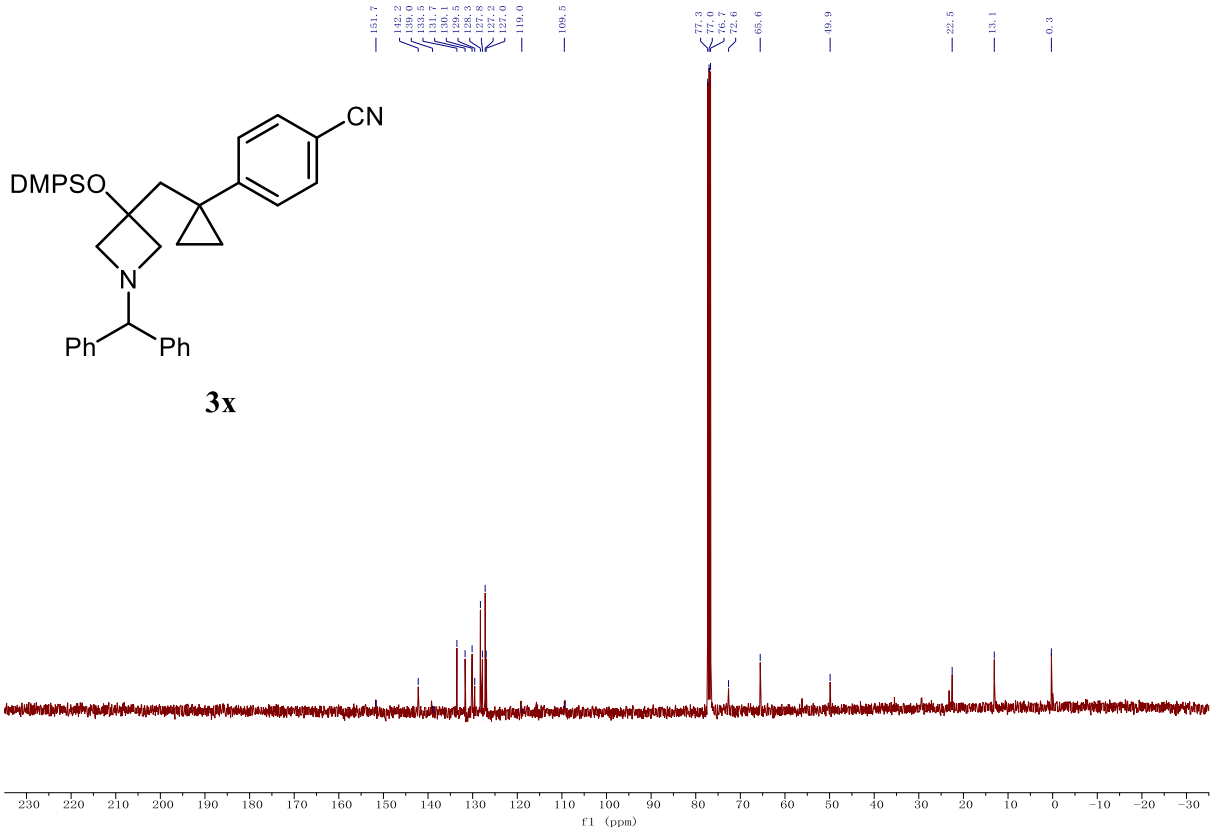
3w

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



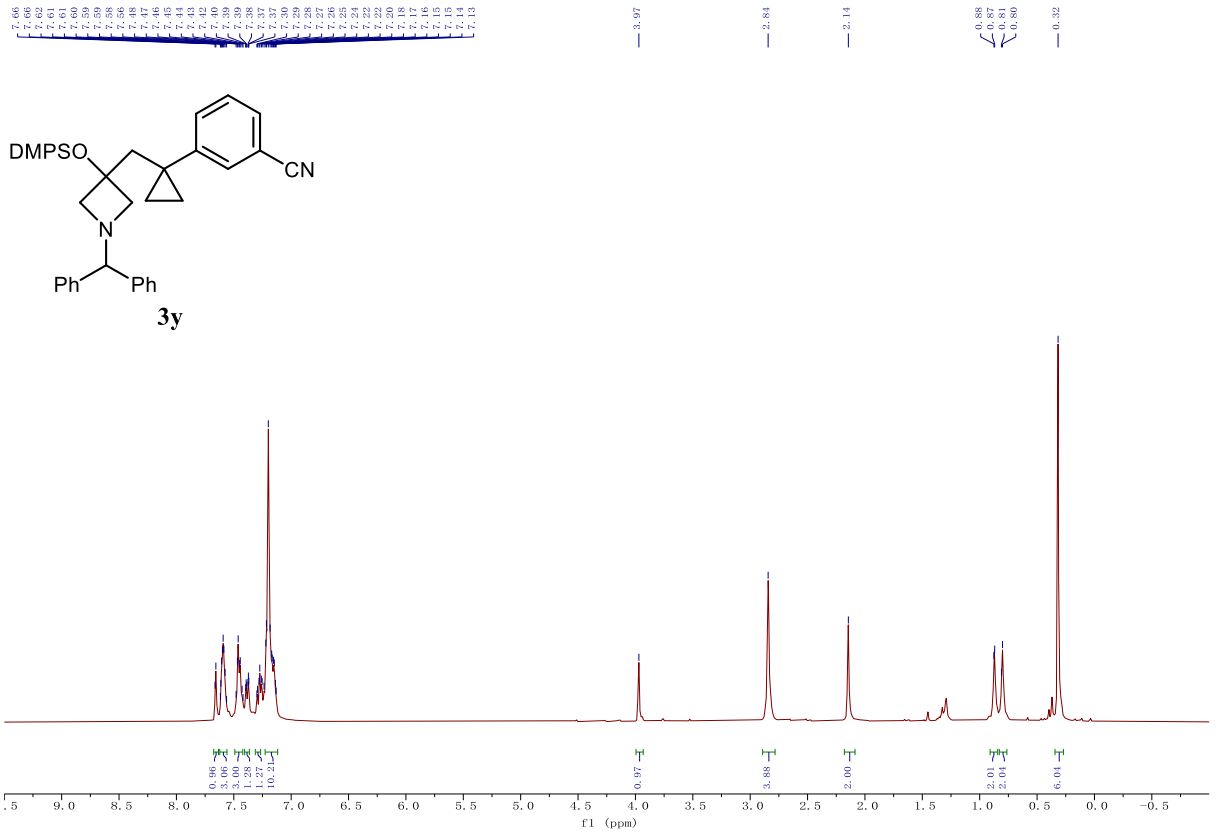
3x

^{13}C NMR (101 MHz, $CDCl_3$)

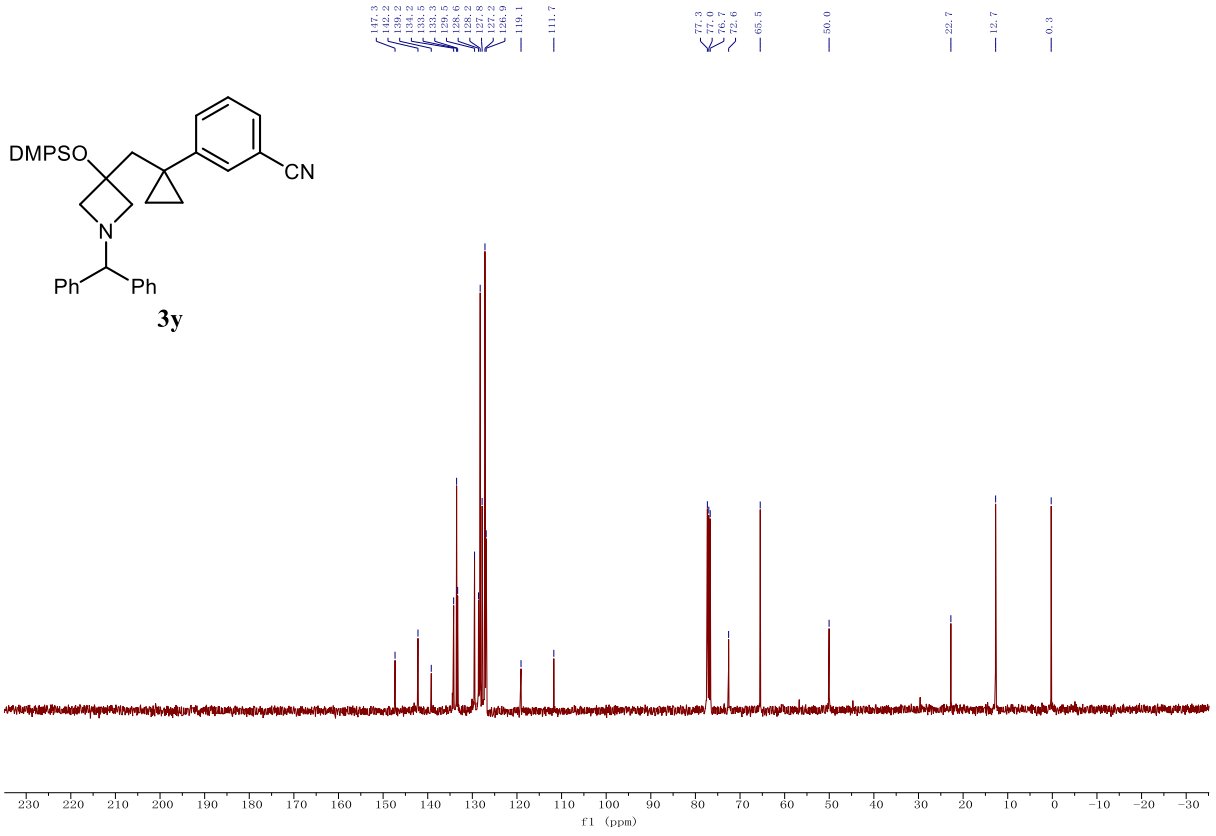


3x

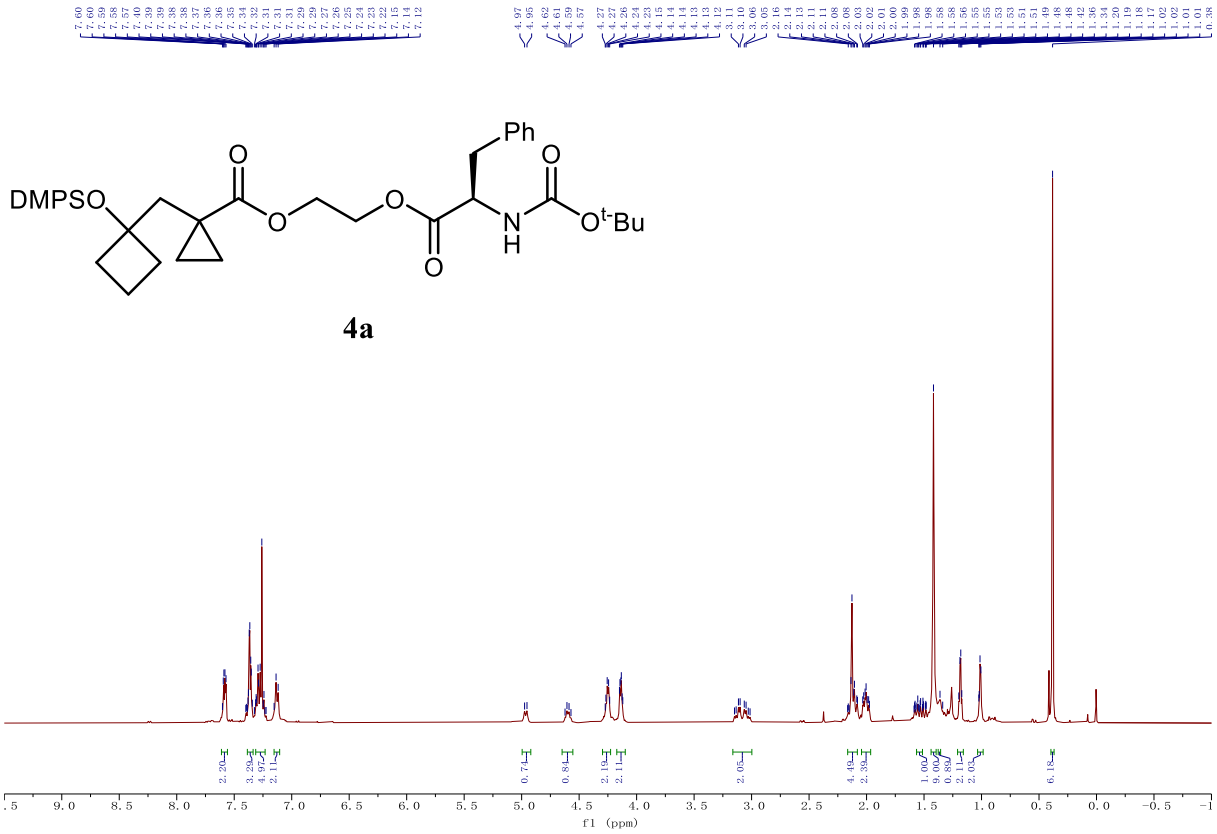
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

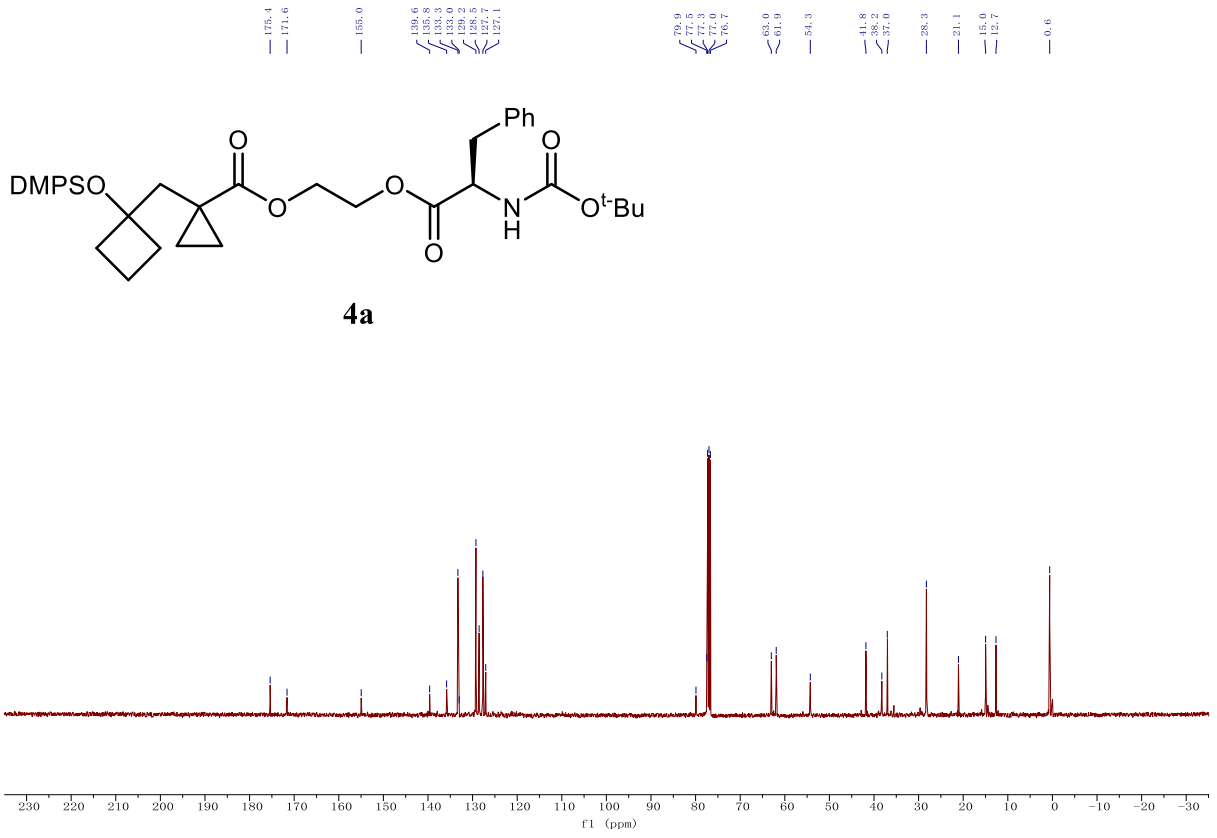


^{1}H NMR (400 MHz, $CDCl_3$)



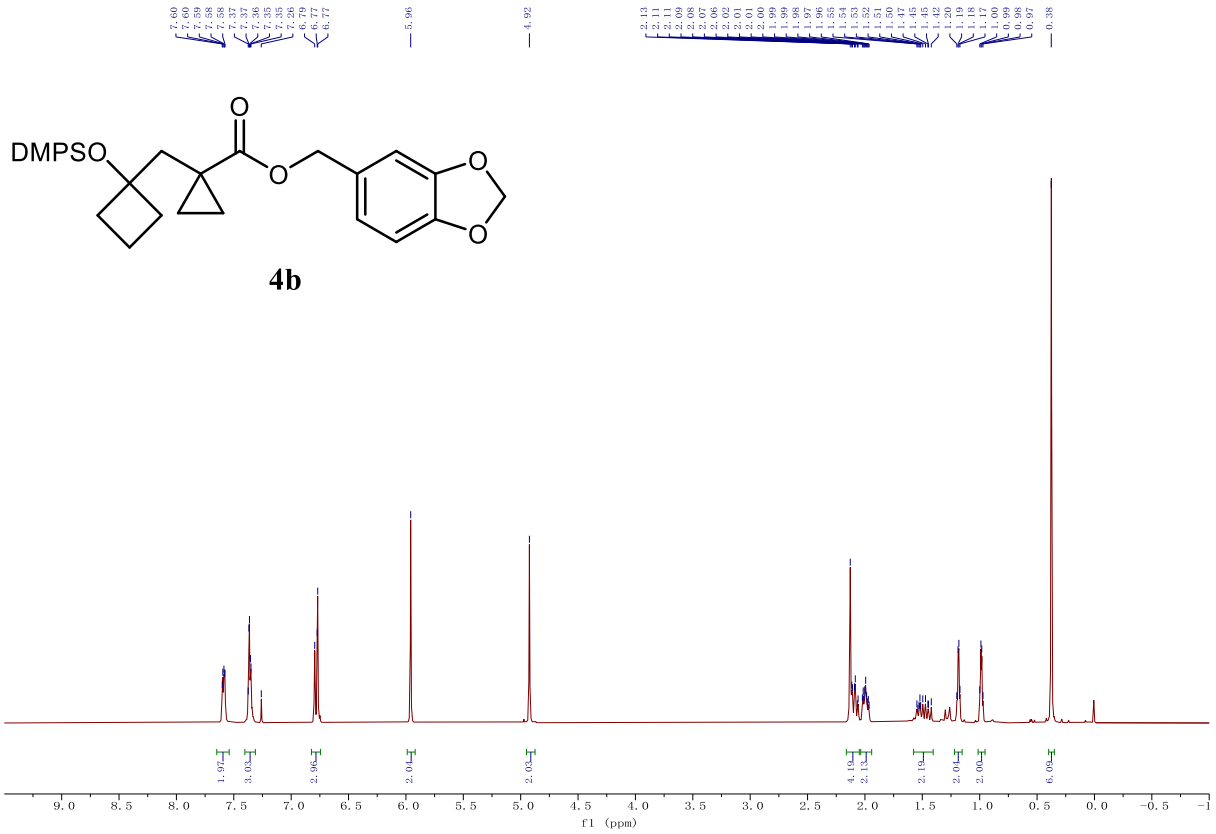
4a

^{13}C NMR (101 MHz, $CDCl_3$)

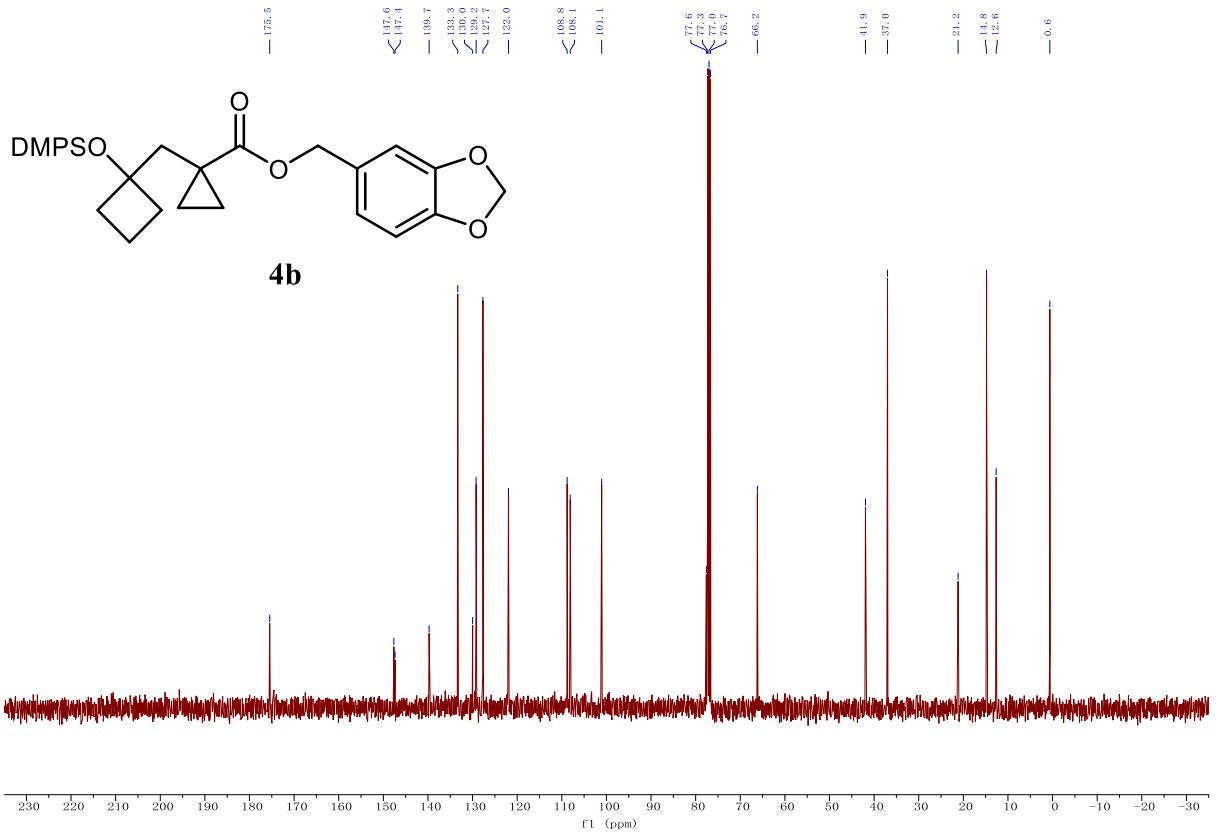


4a

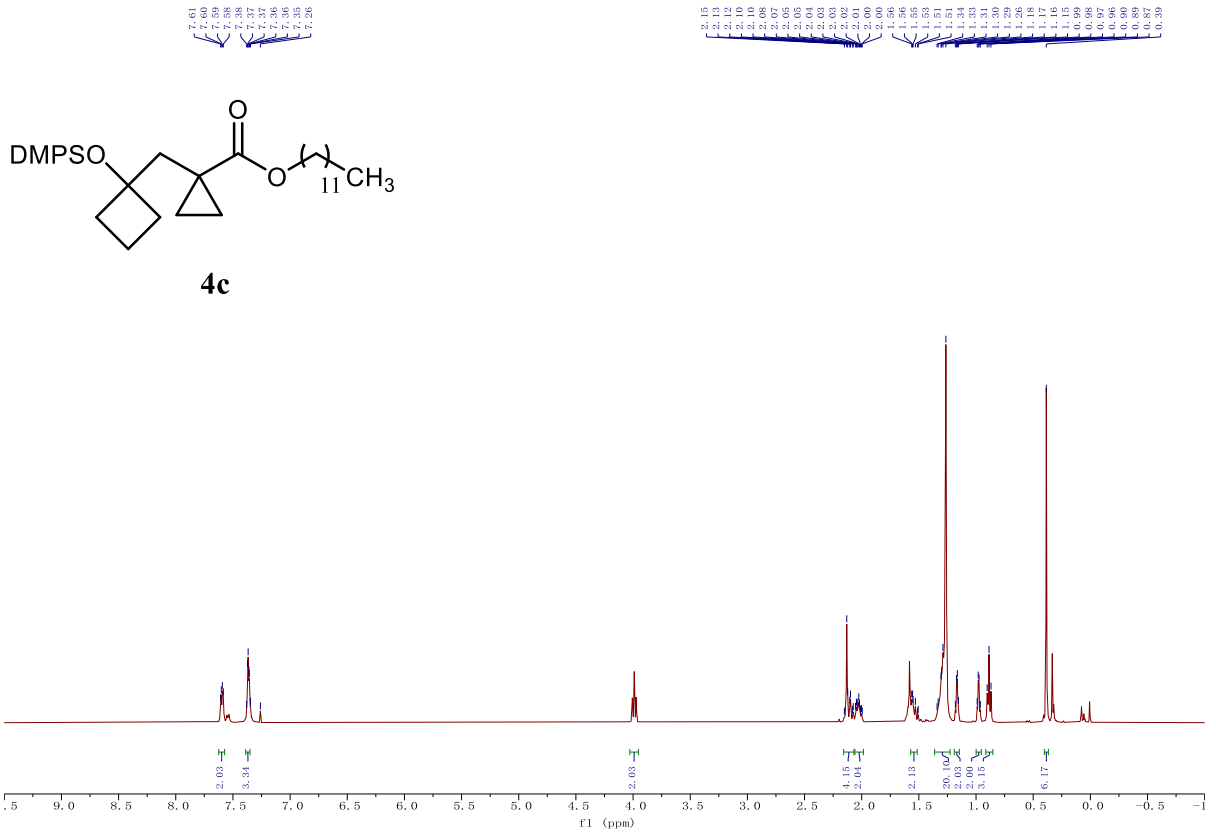
^{1}H NMR (400 MHz, $CDCl_3$)



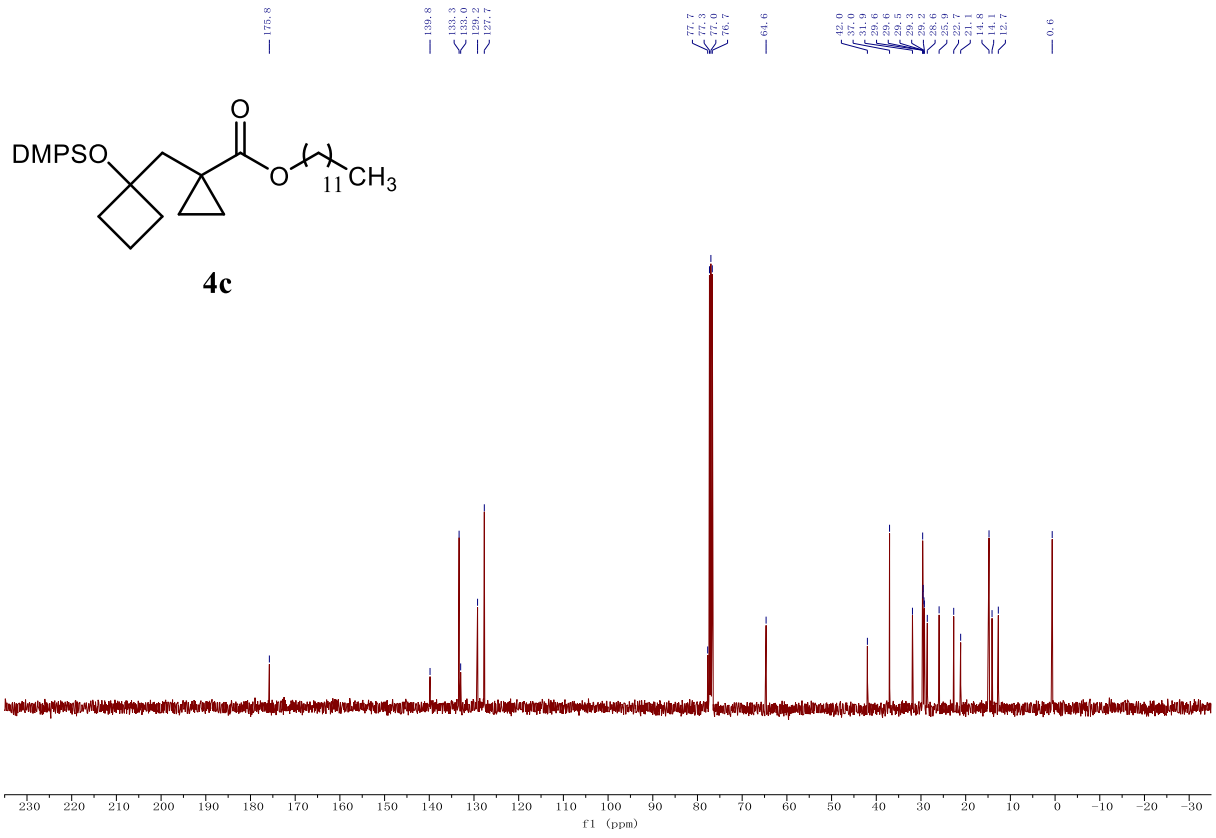
^{13}C NMR (101 MHz, $CDCl_3$)



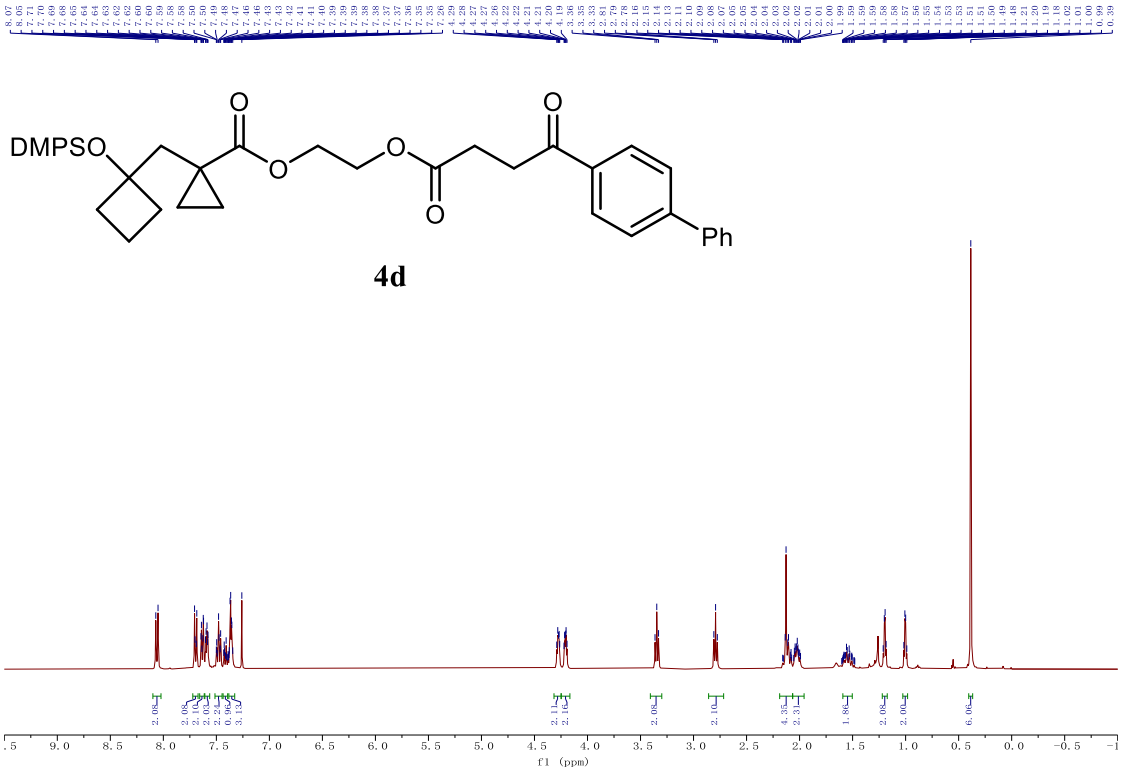
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

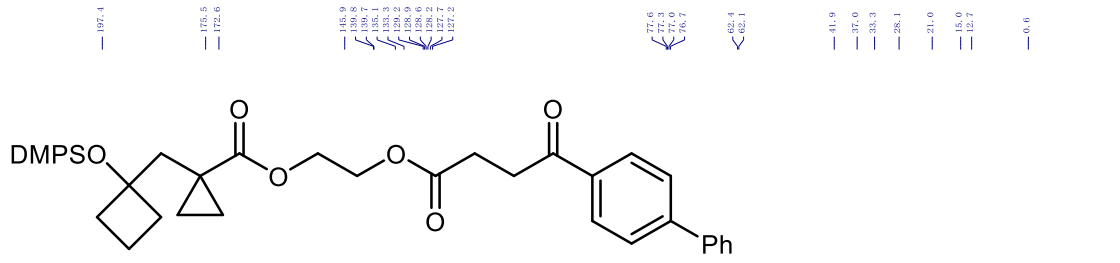


^{1}H NMR (400 MHz, $CDCl_3$)

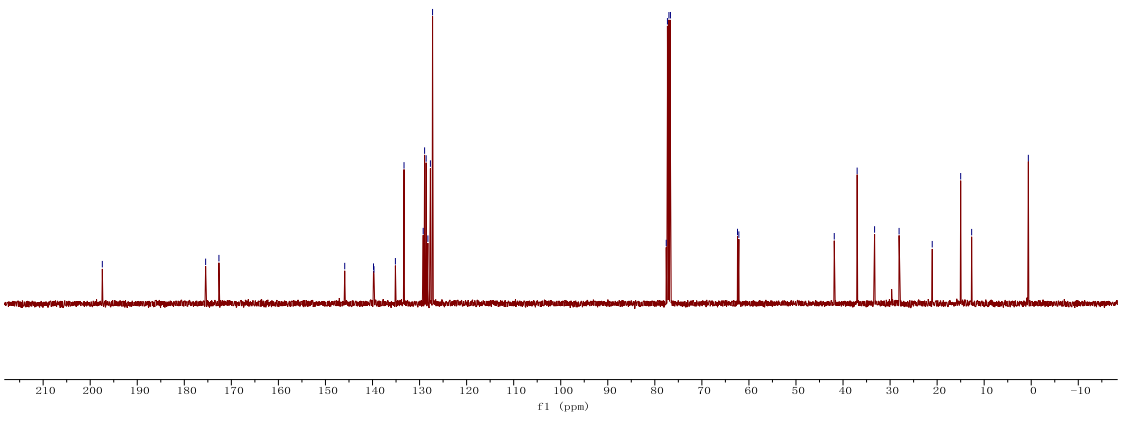


4d

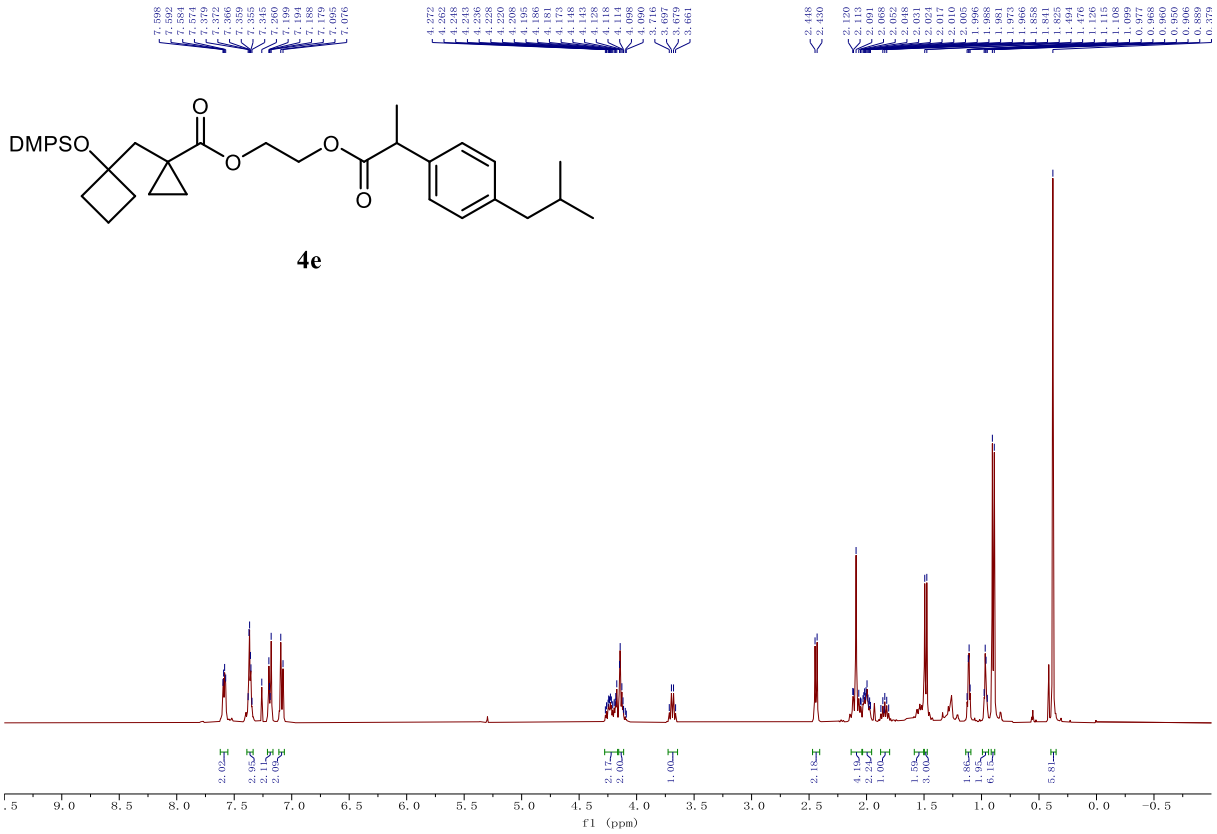
^{13}C NMR (101 MHz, $CDCl_3$)



4d

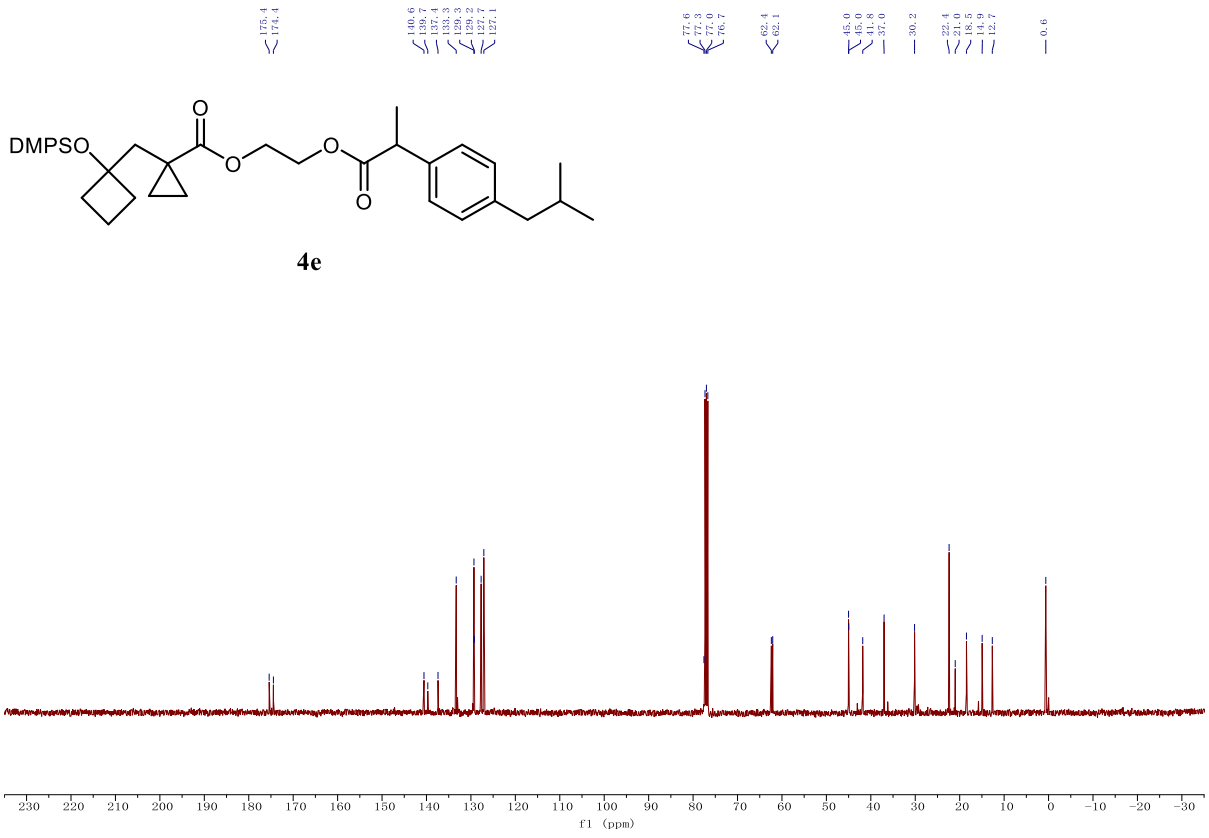


^{1}H NMR (400 MHz, $CDCl_3$)



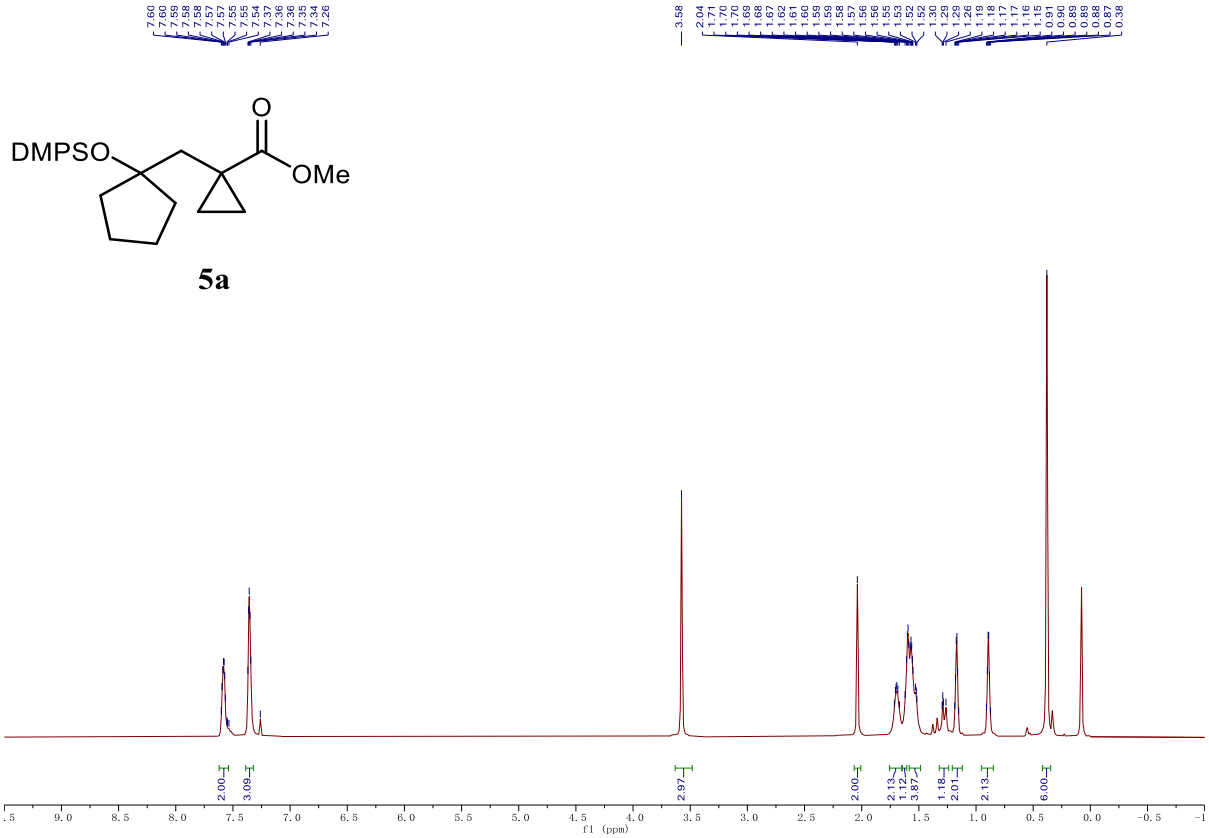
4e

^{13}C NMR (101 MHz, $CDCl_3$)



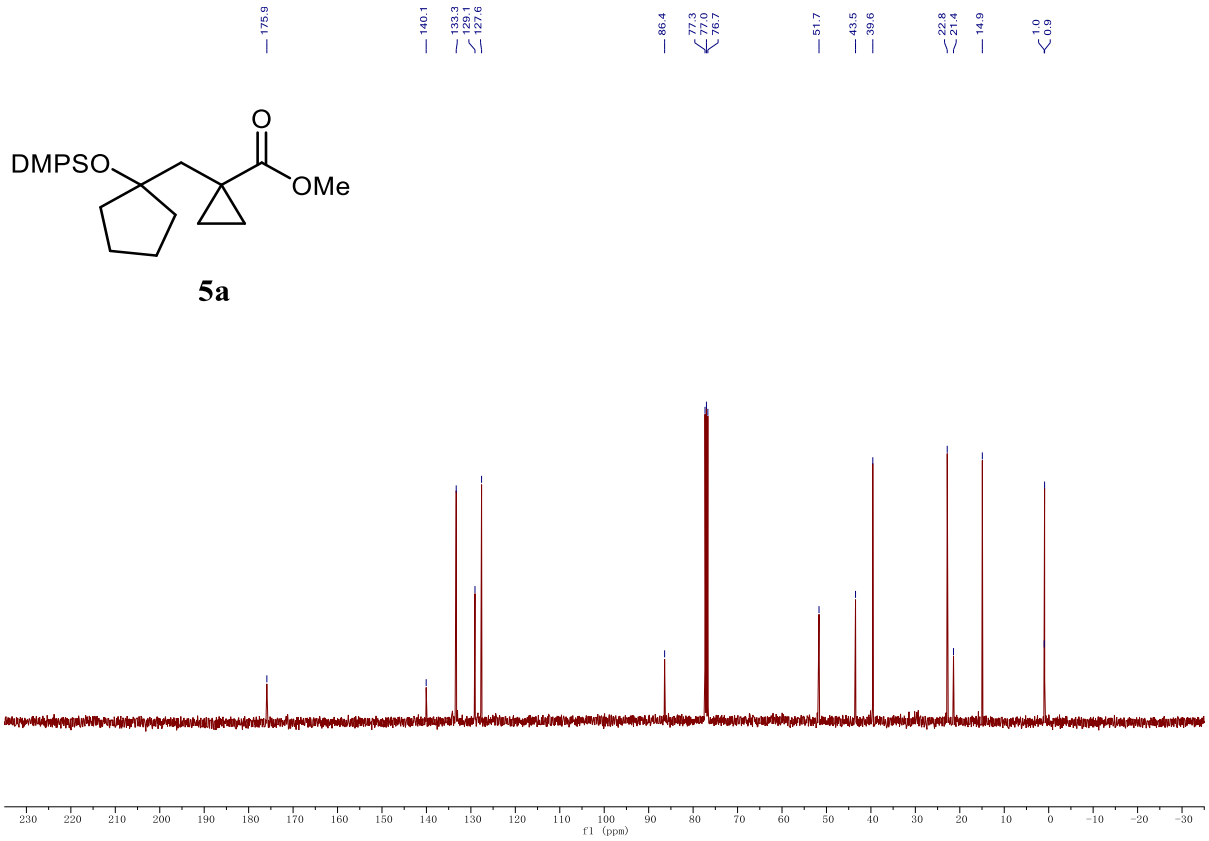
4e

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



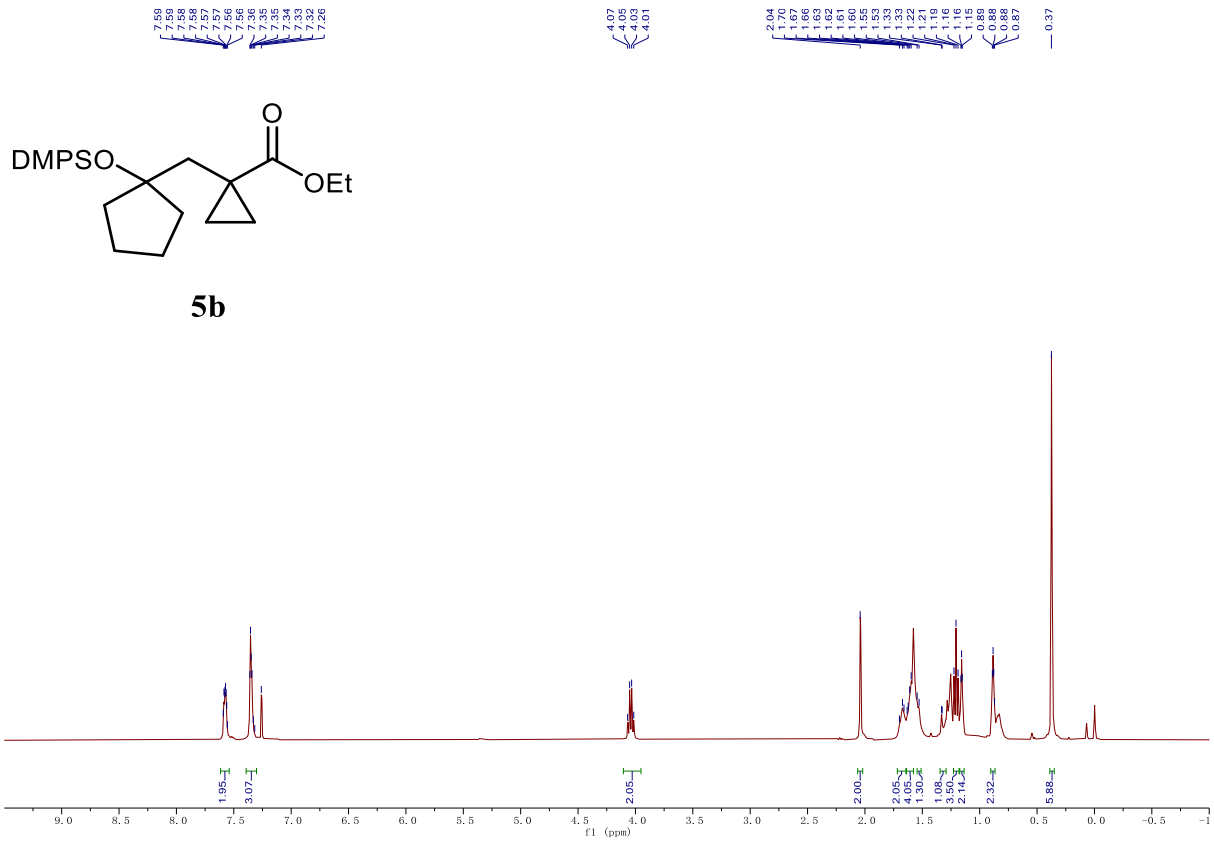
5a

^{13}C NMR (101 MHz, $CDCl_3$)



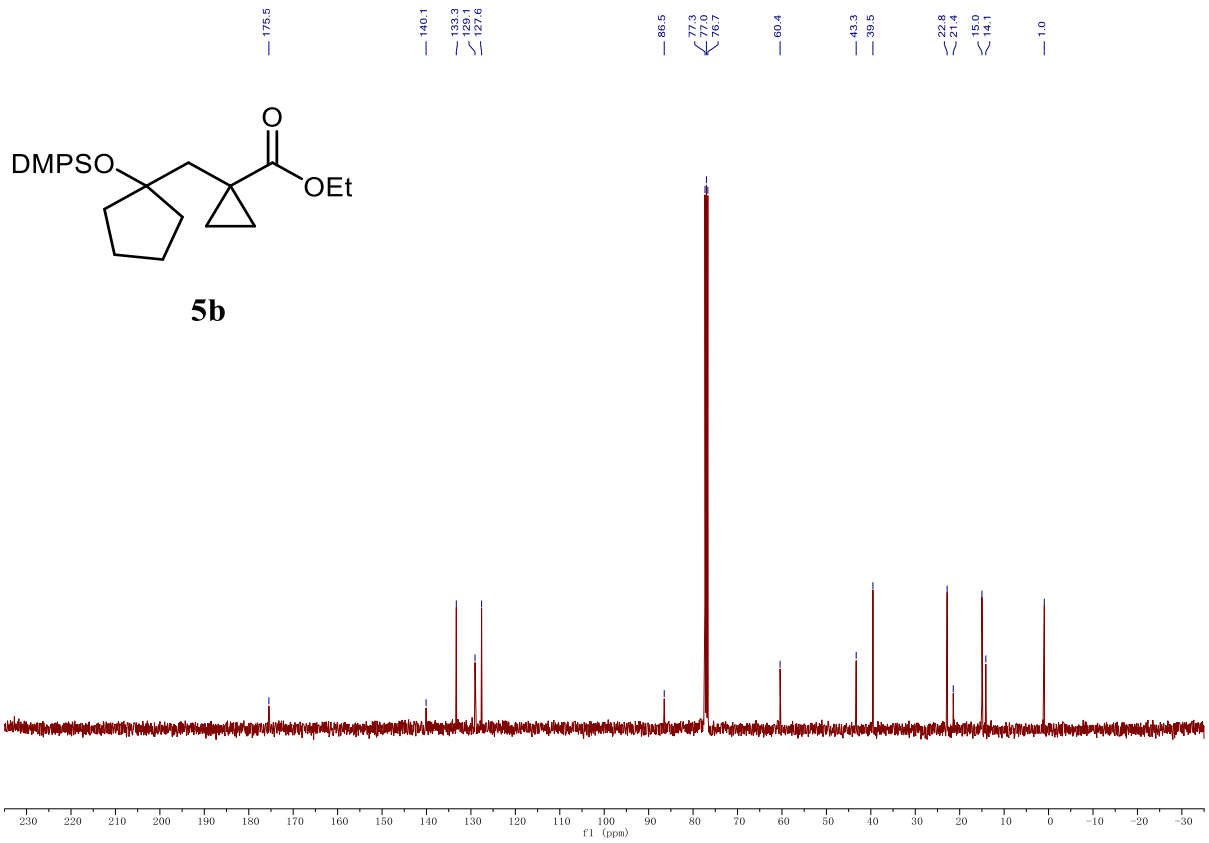
5a

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



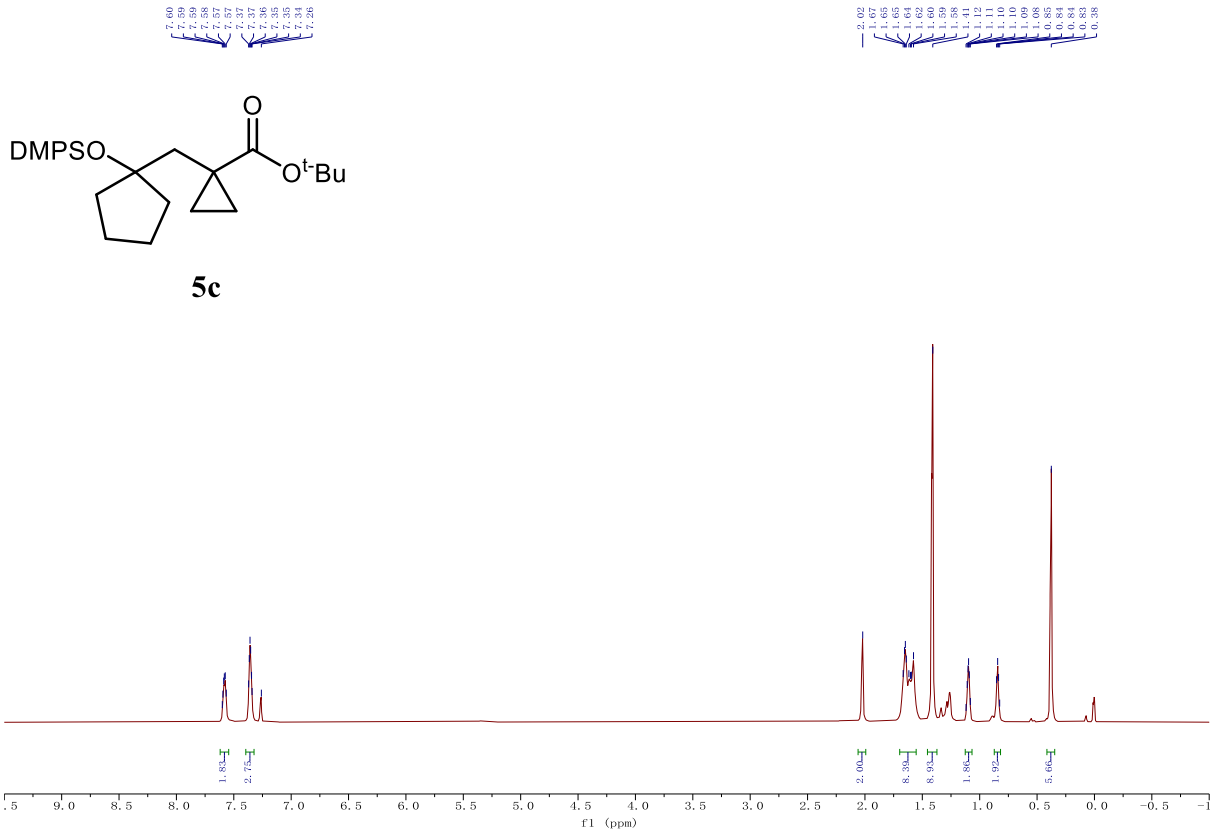
5b

^{13}C NMR (101 MHz, $CDCl_3$)



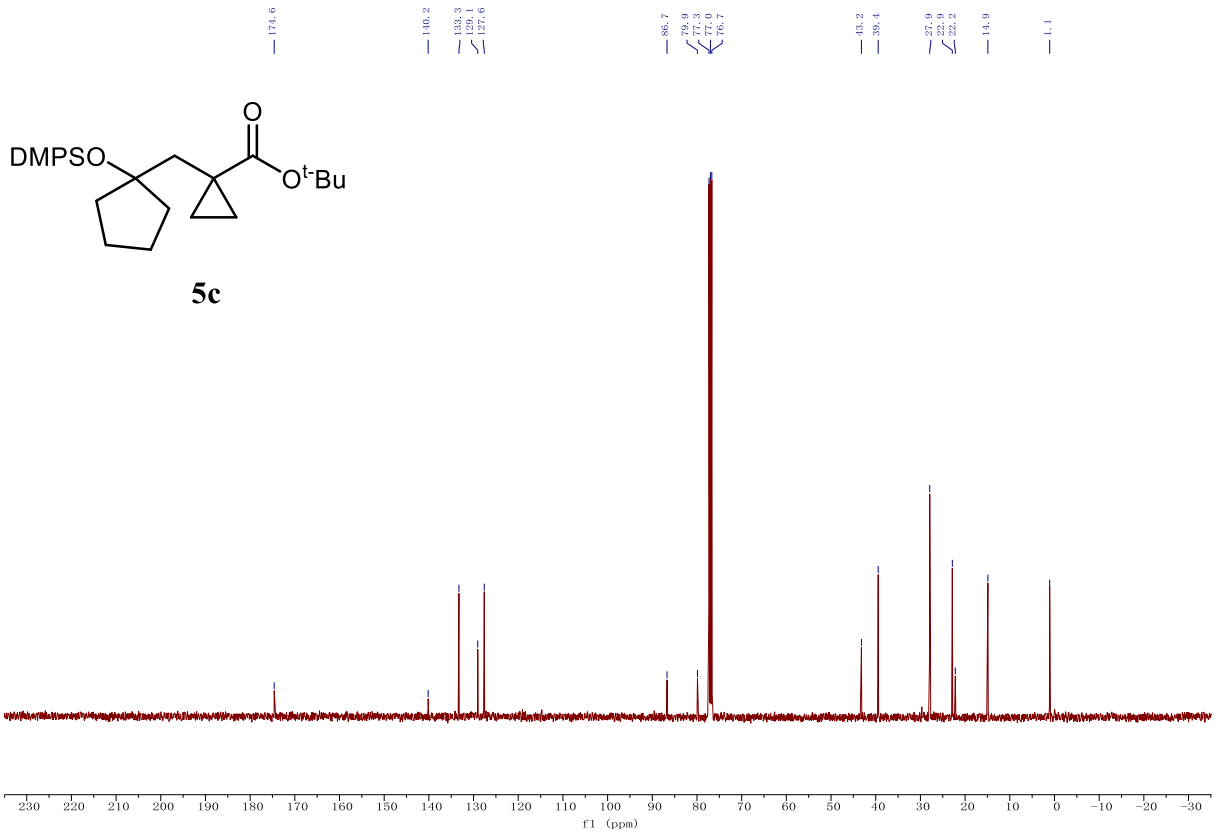
5b

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



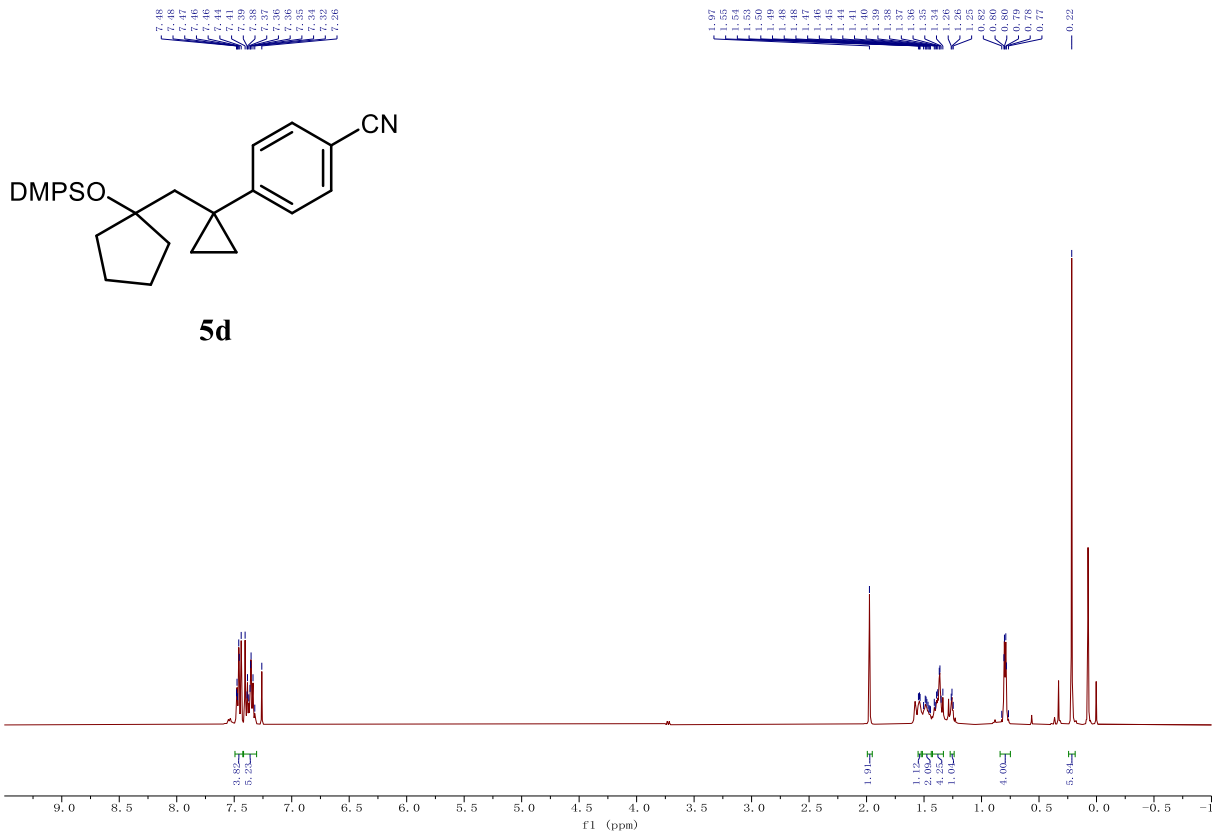
5c

^{13}C NMR (101 MHz, $CDCl_3$)



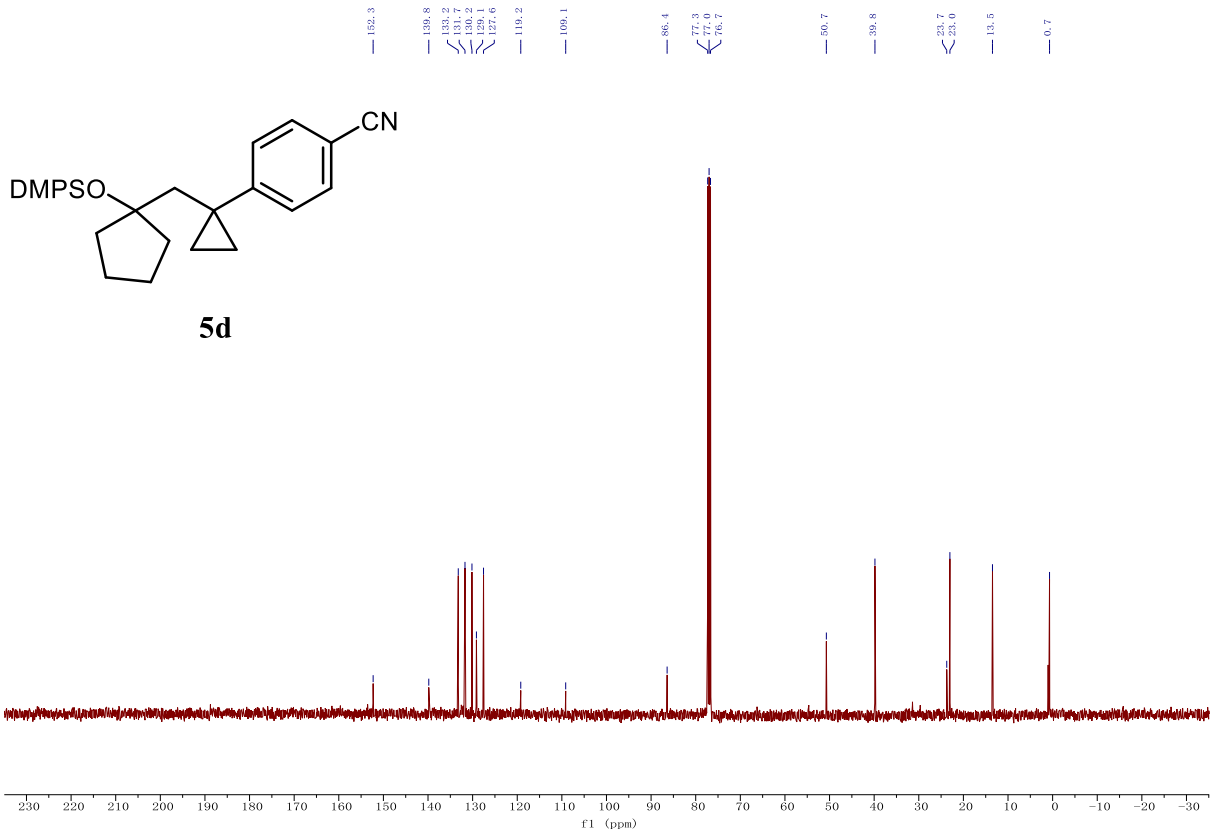
5c

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



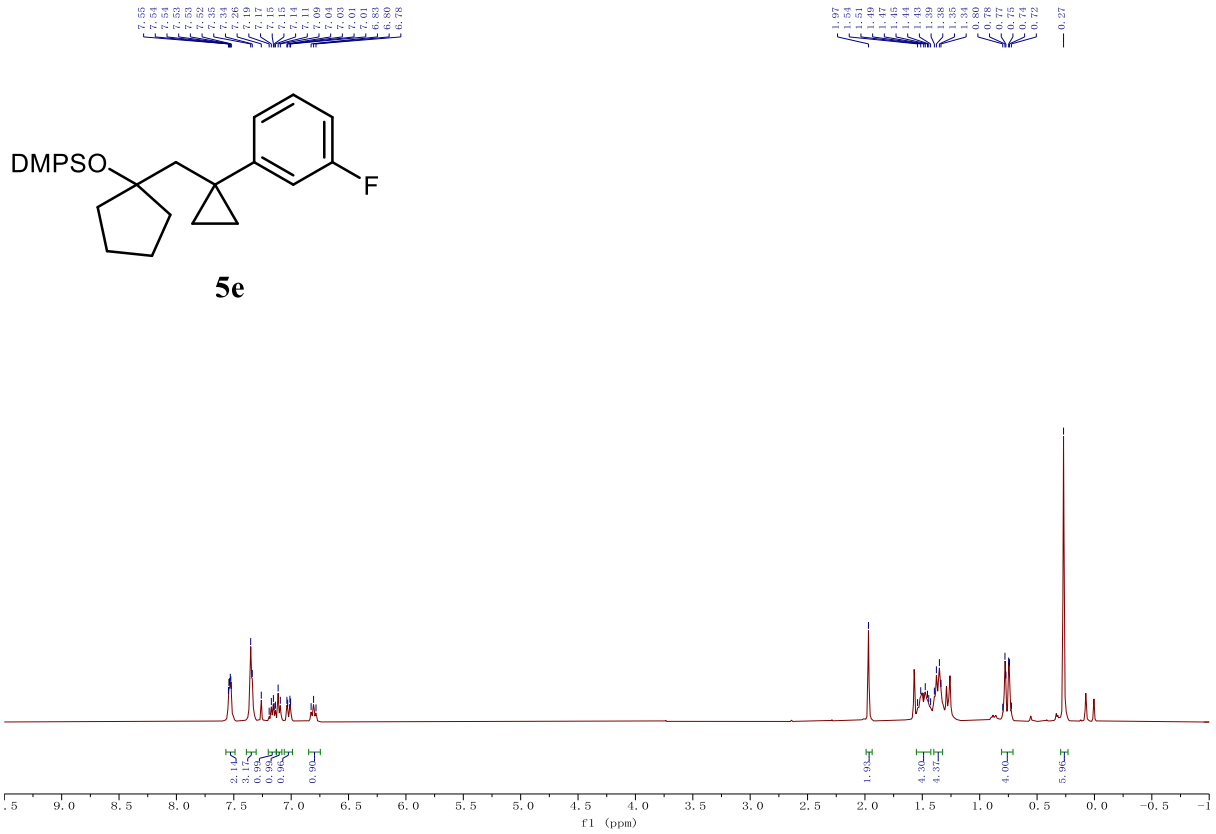
5d

^{13}C NMR (101 MHz, $CDCl_3$)

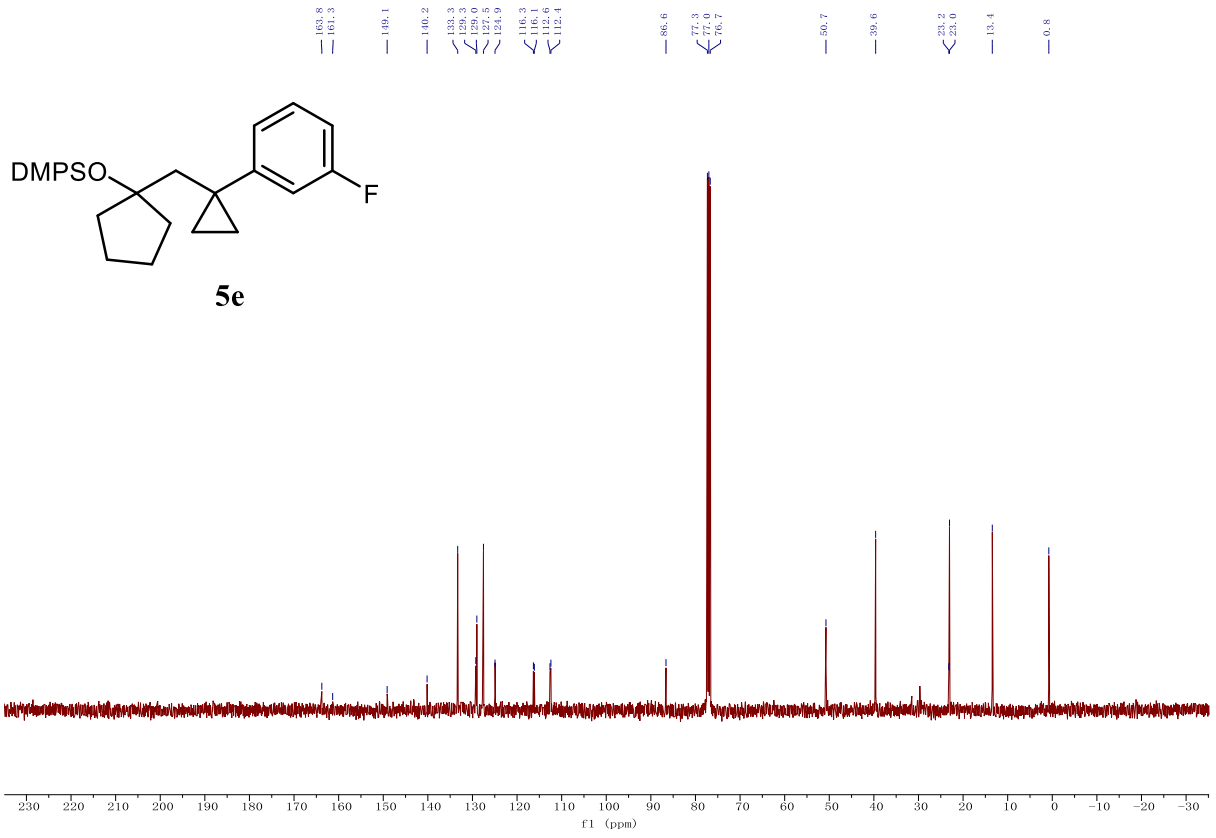


5d

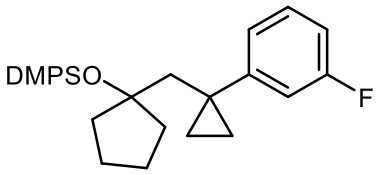
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

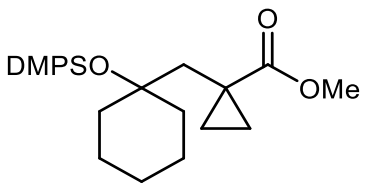


^{19}F NMR (400 MHz, $CDCl_3$)

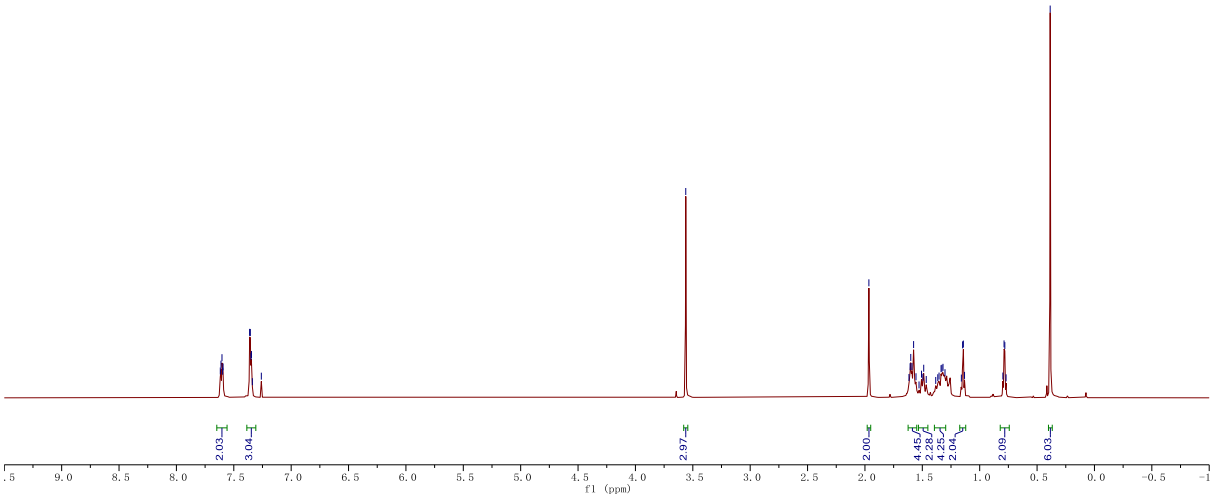


5e

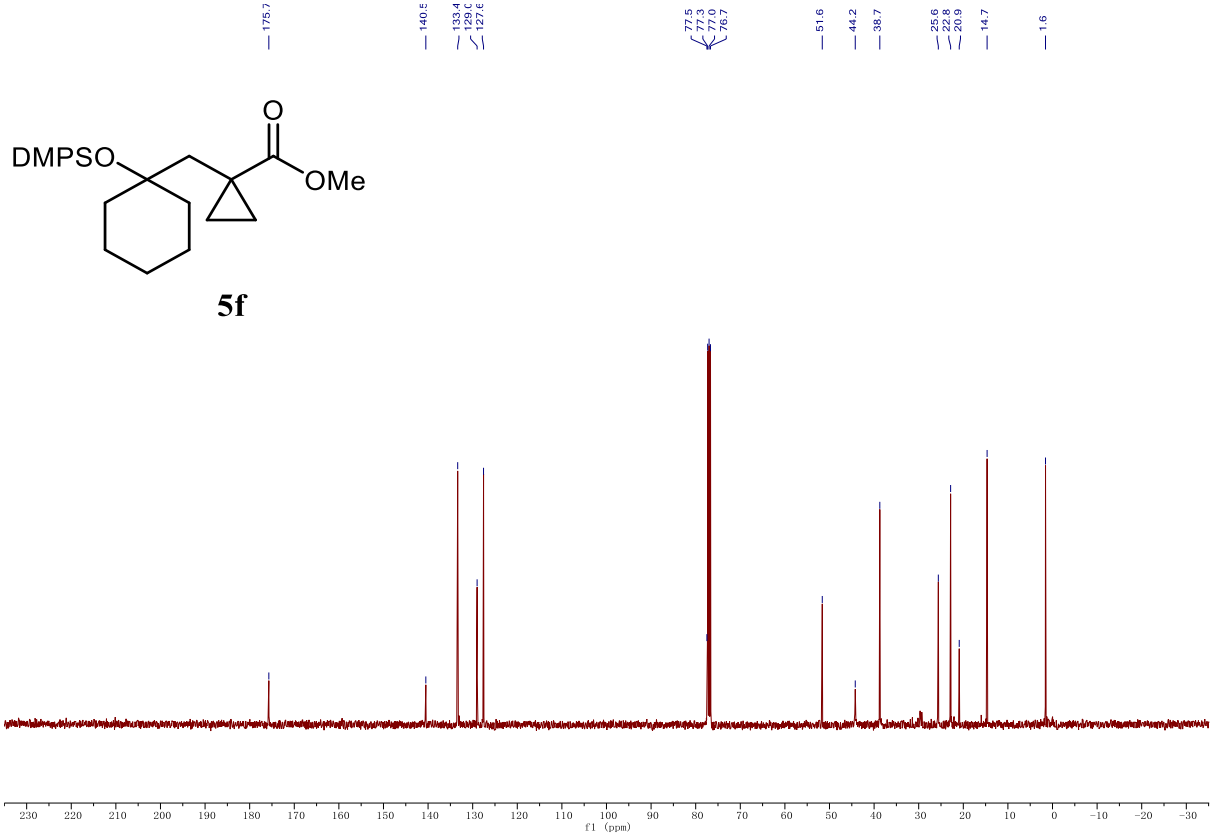
^{1}H NMR (400 MHz, $CDCl_3$)



5f

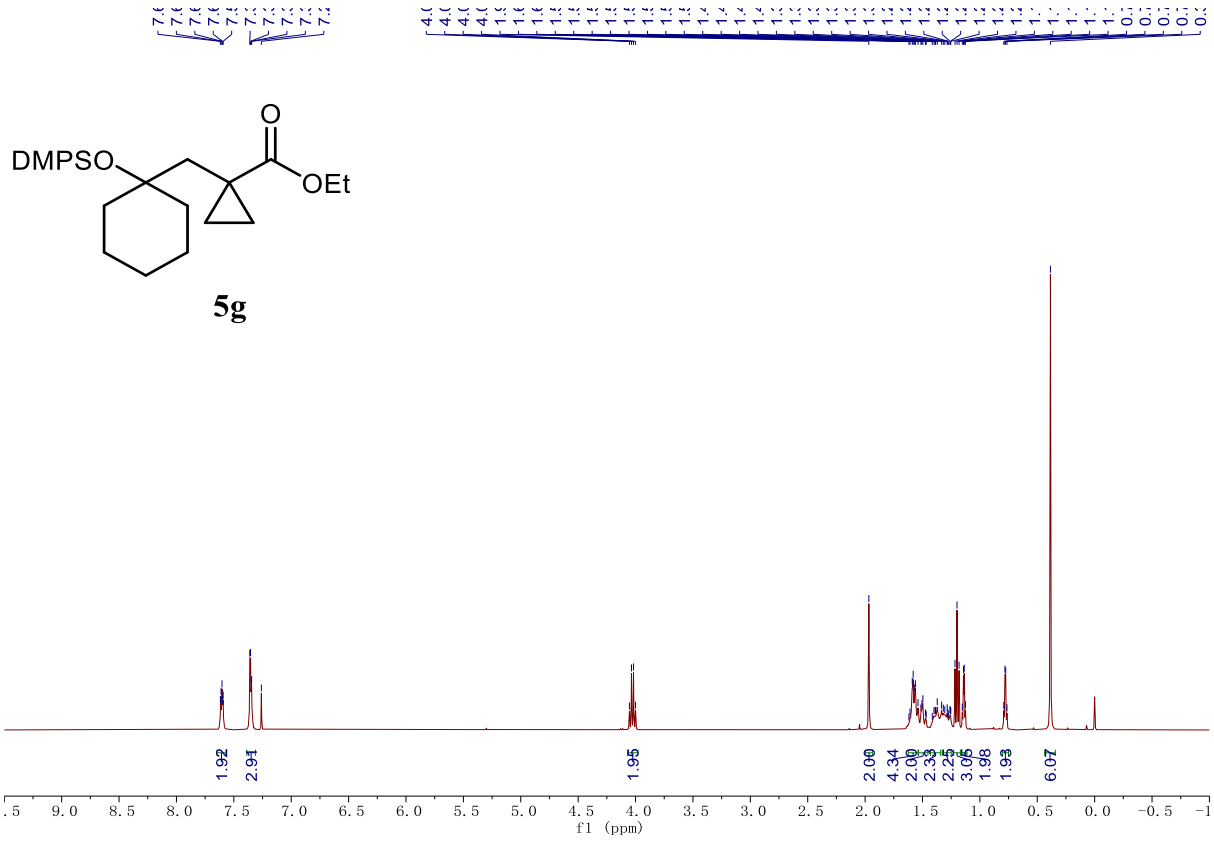


^{13}C NMR (101 MHz, $CDCl_3$)



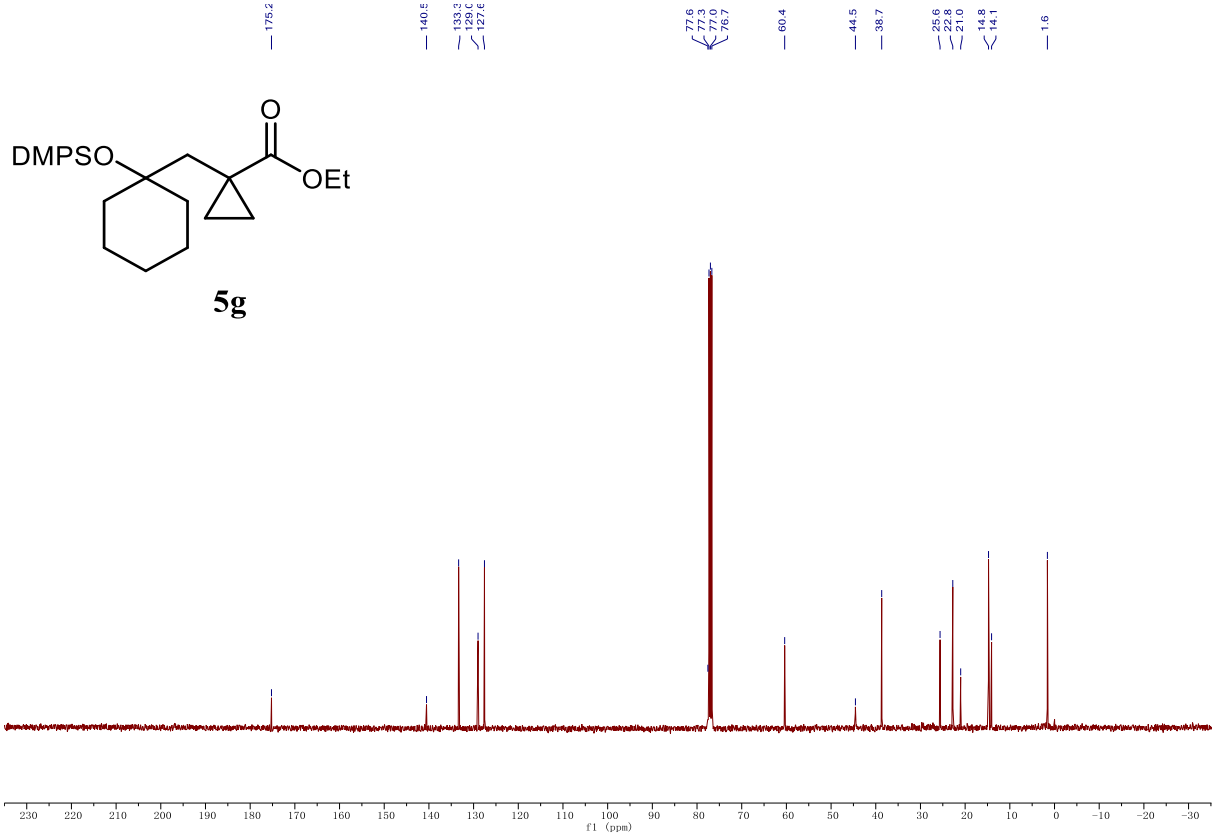
5f

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



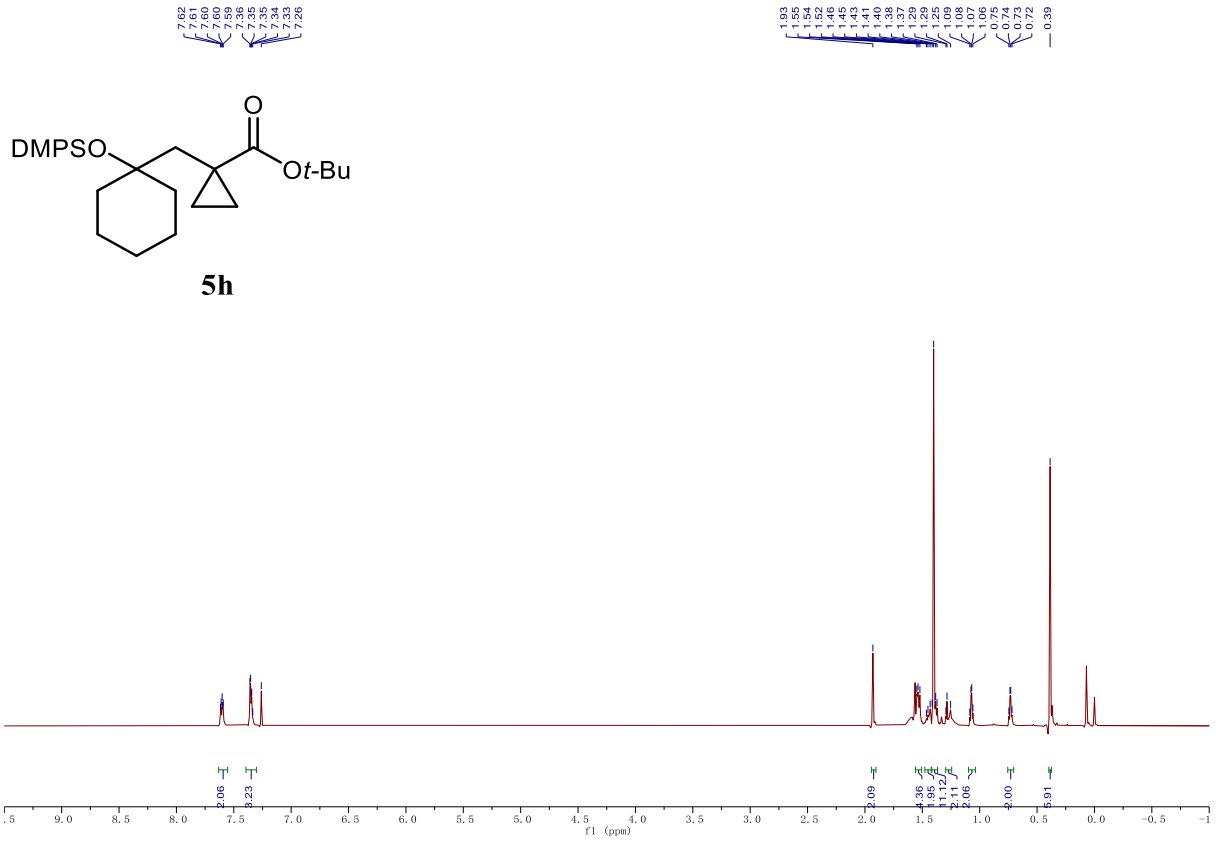
5g

^{13}C NMR (101 MHz, $CDCl_3$)



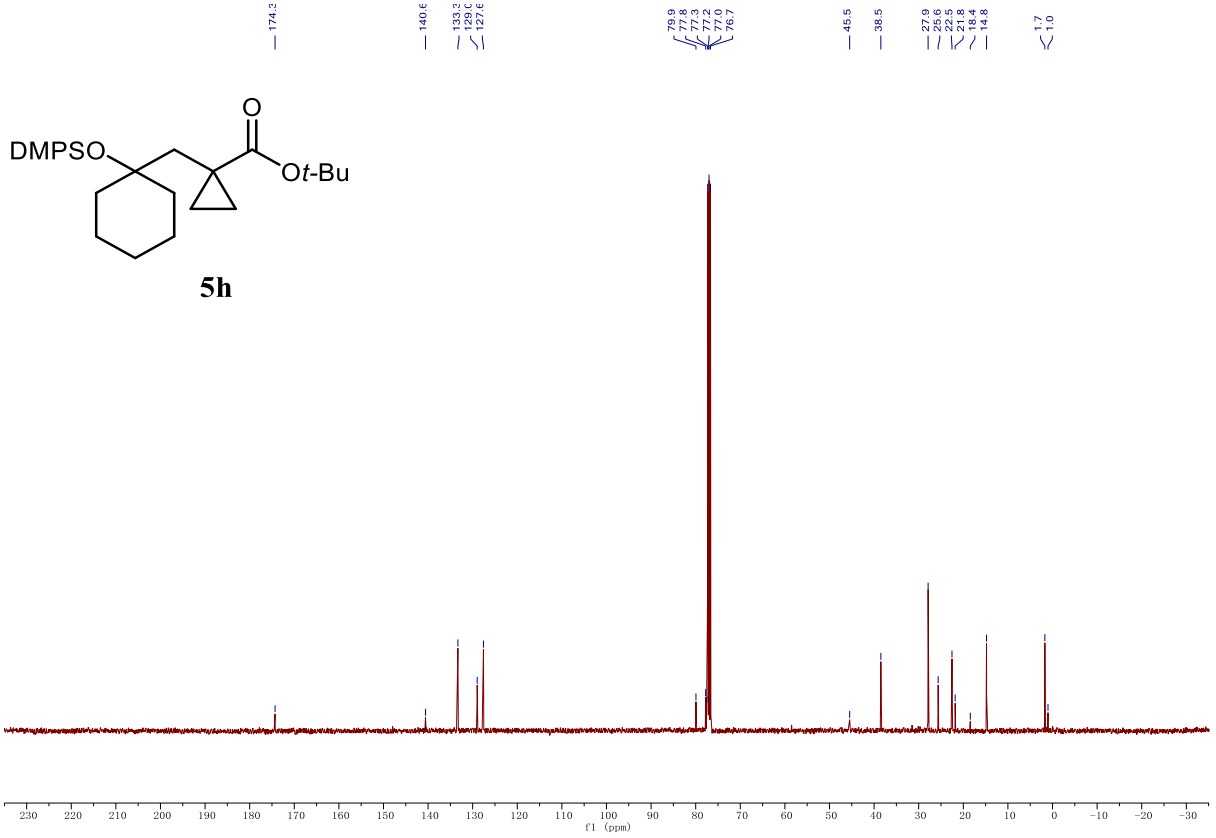
5g

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



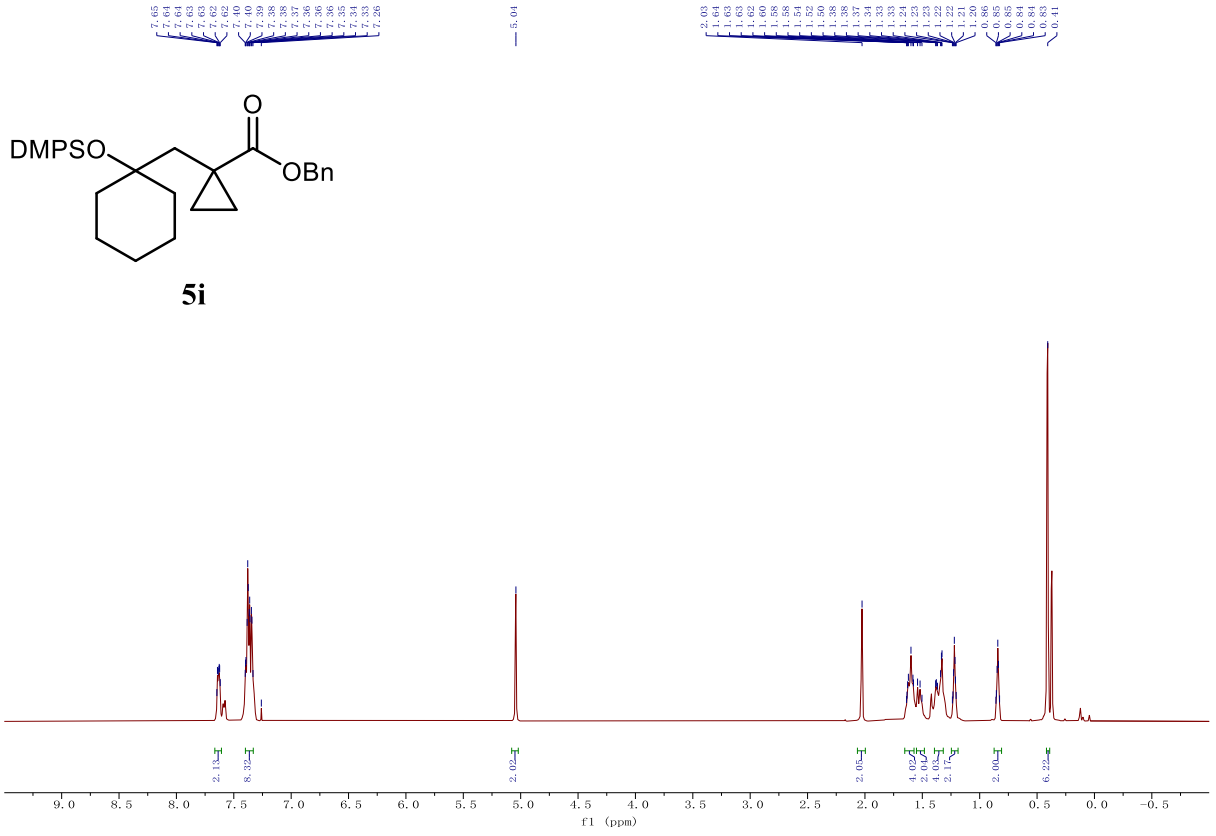
5h

^{13}C NMR (101 MHz, $CDCl_3$)



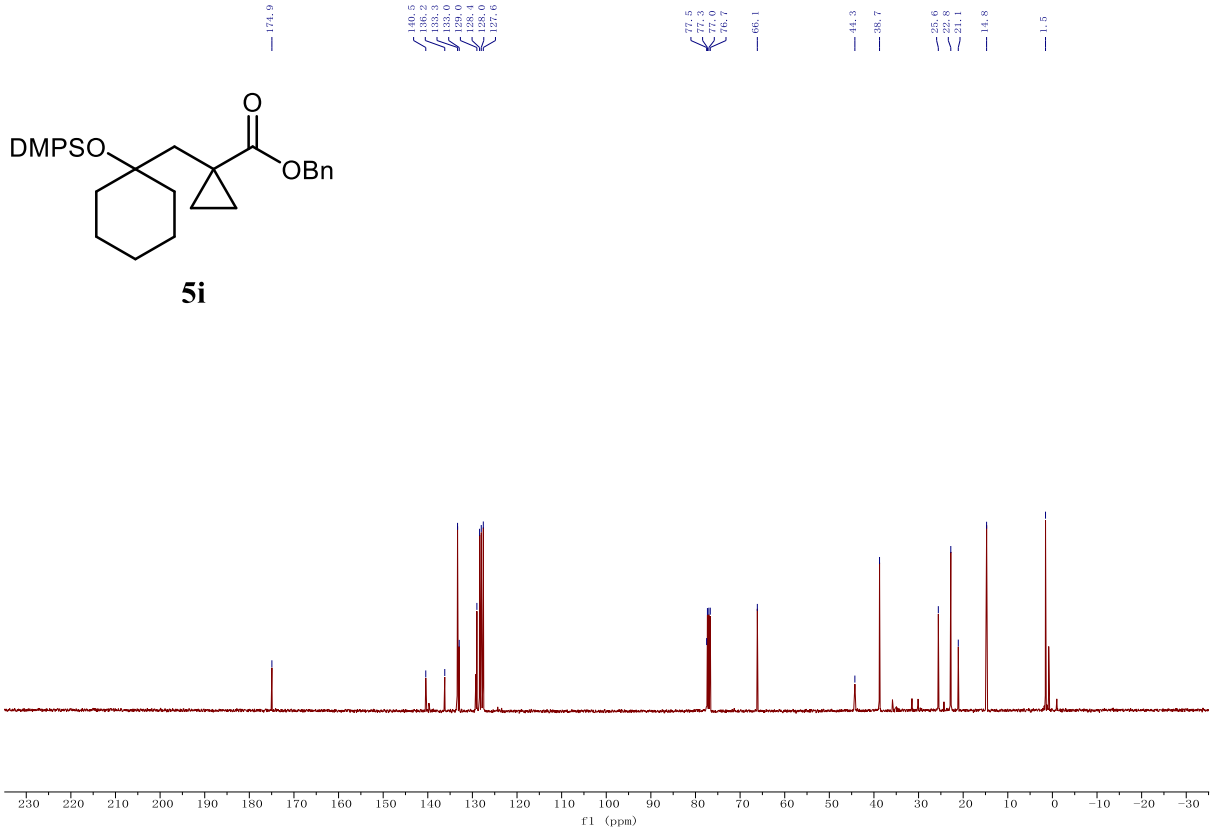
5h

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



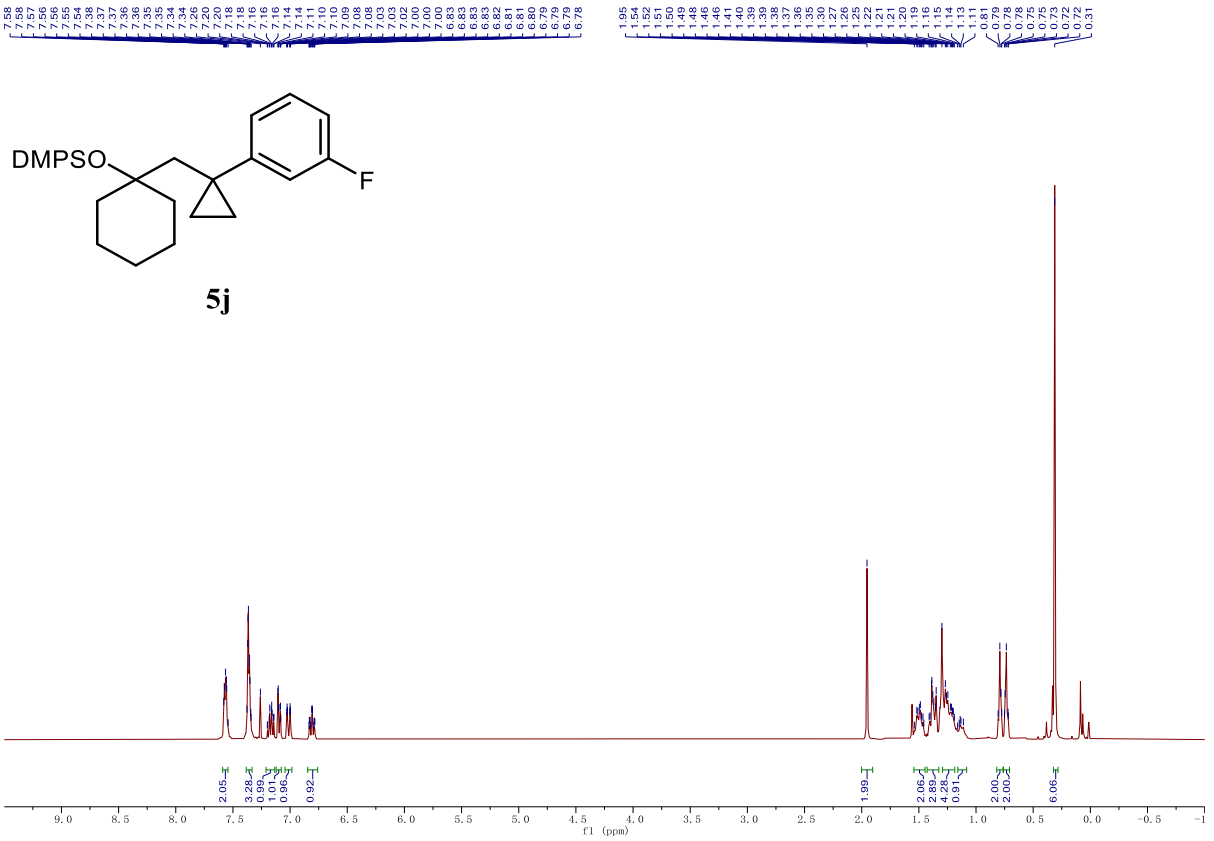
5i

^{13}C NMR (101 MHz, $CDCl_3$)



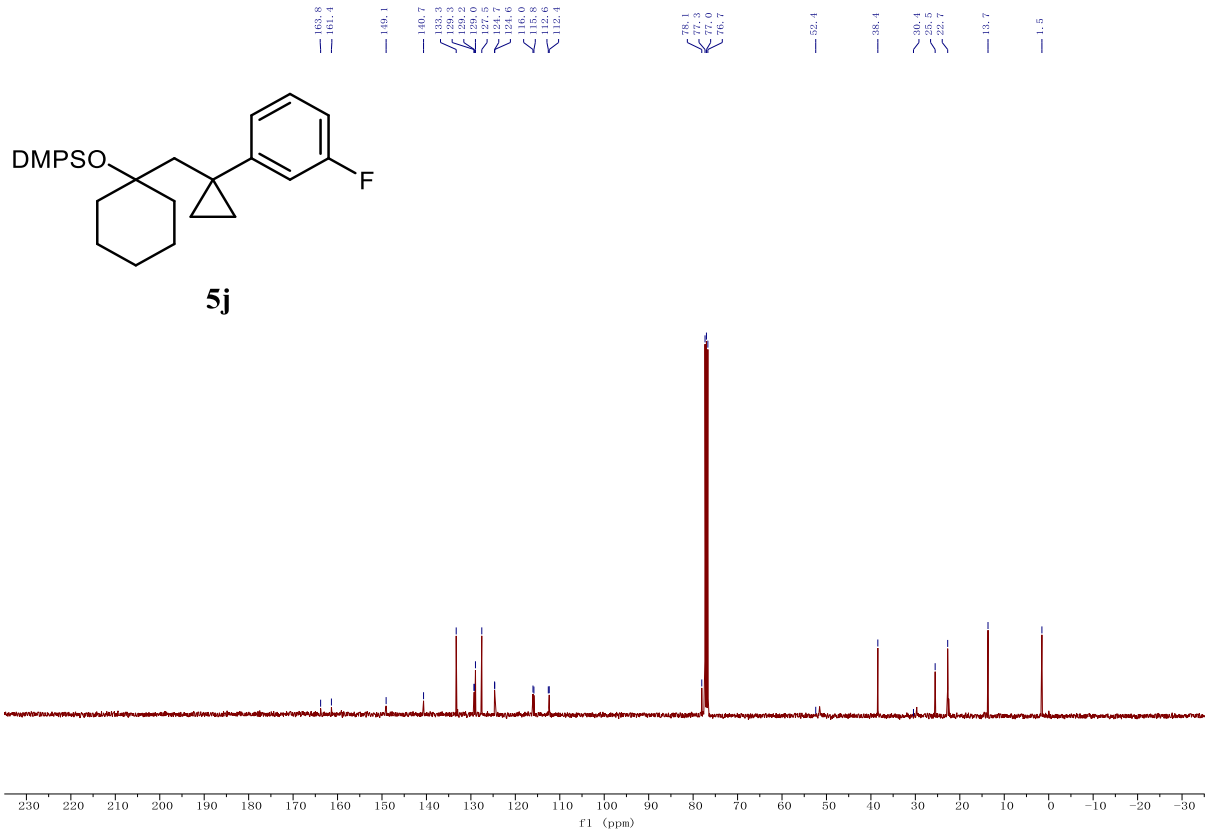
5i

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



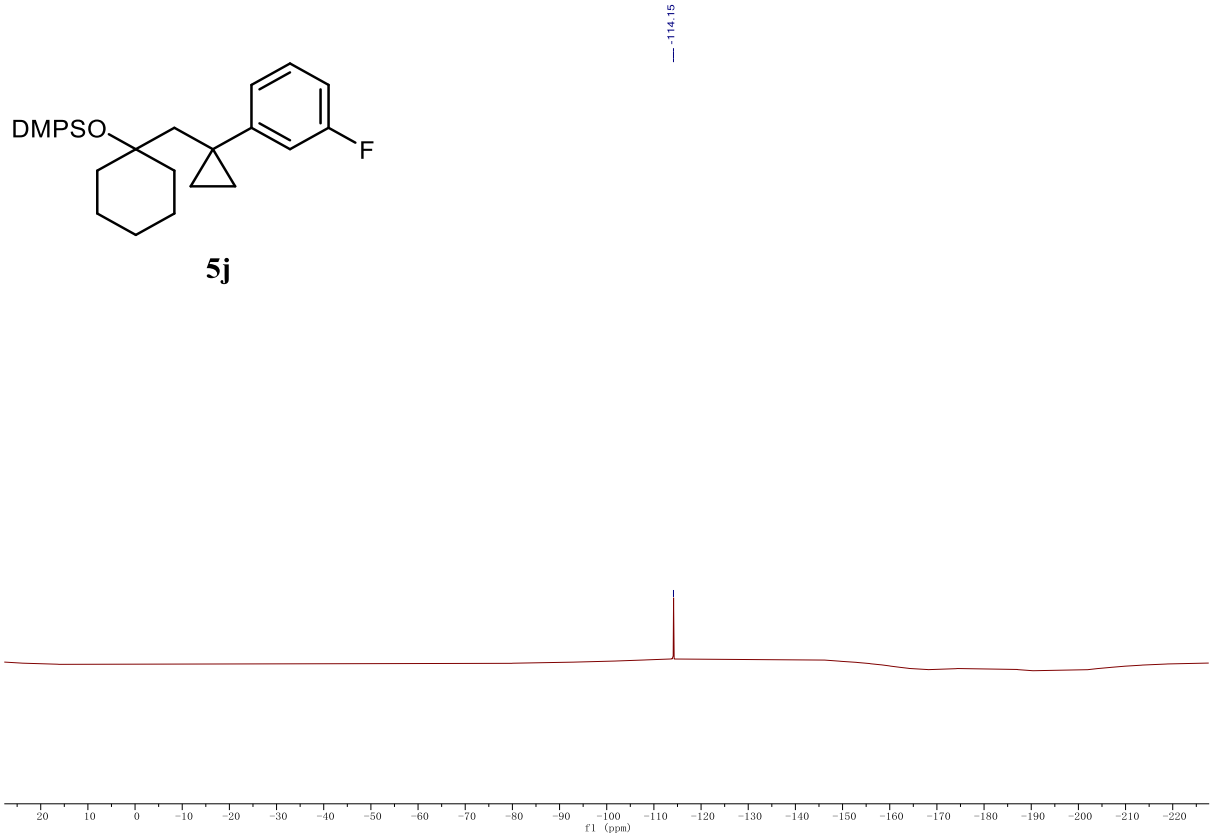
5j

^{13}C NMR (101 MHz, $CDCl_3$)



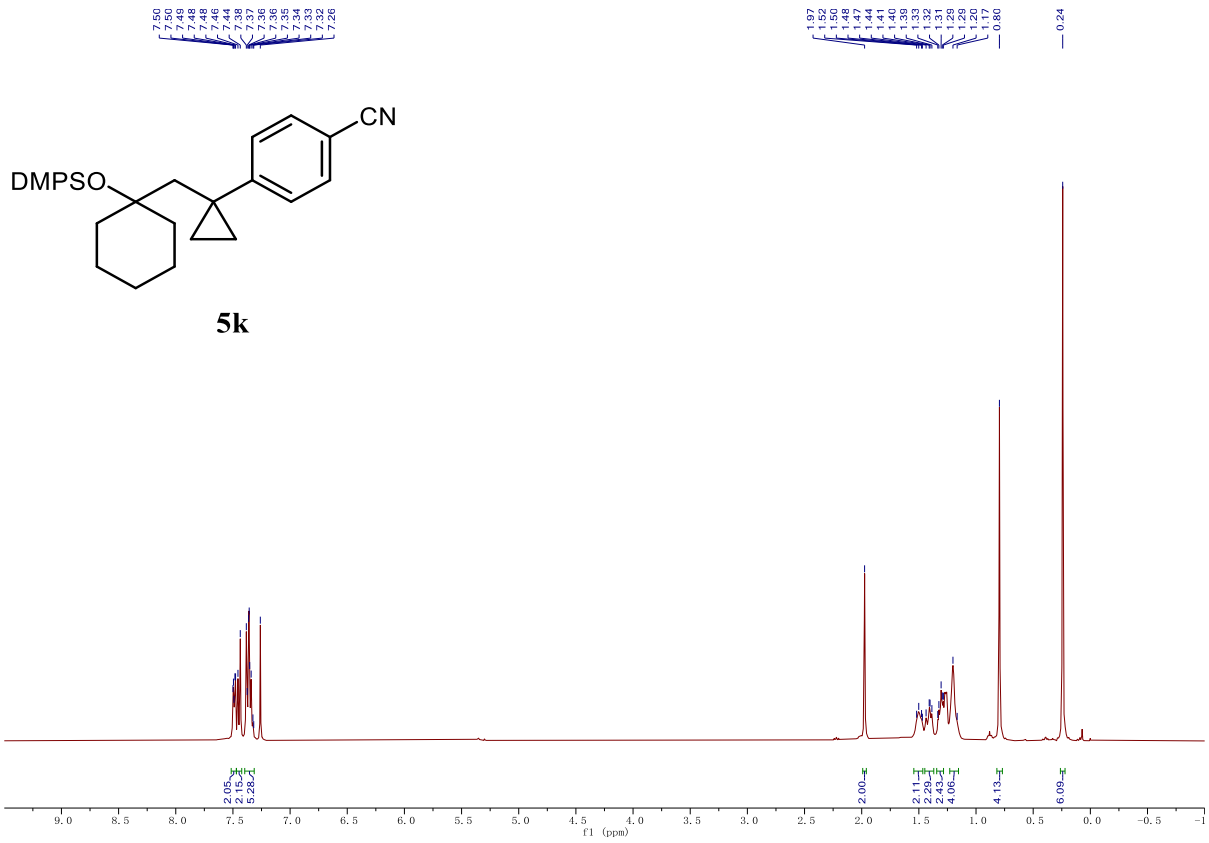
5j

^{19}F NMR (400 MHz, $CDCl_3$)



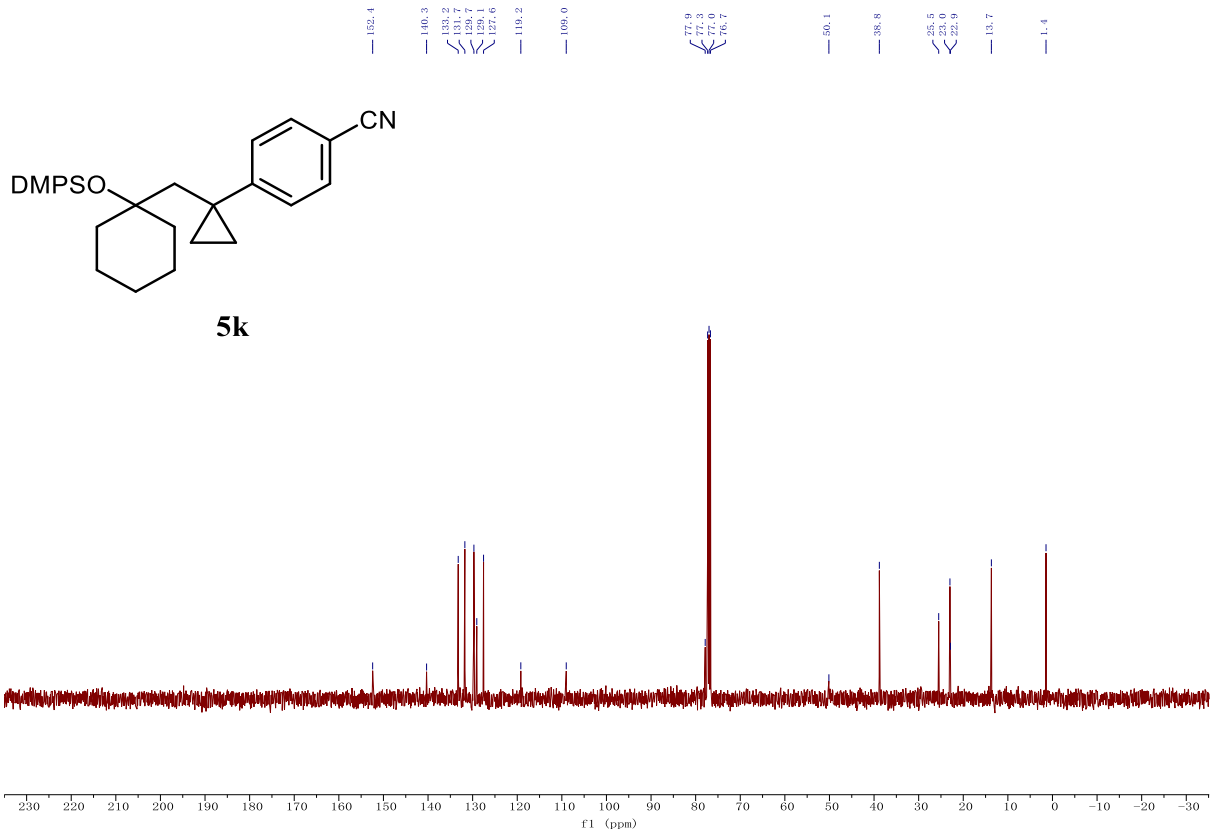
5j

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



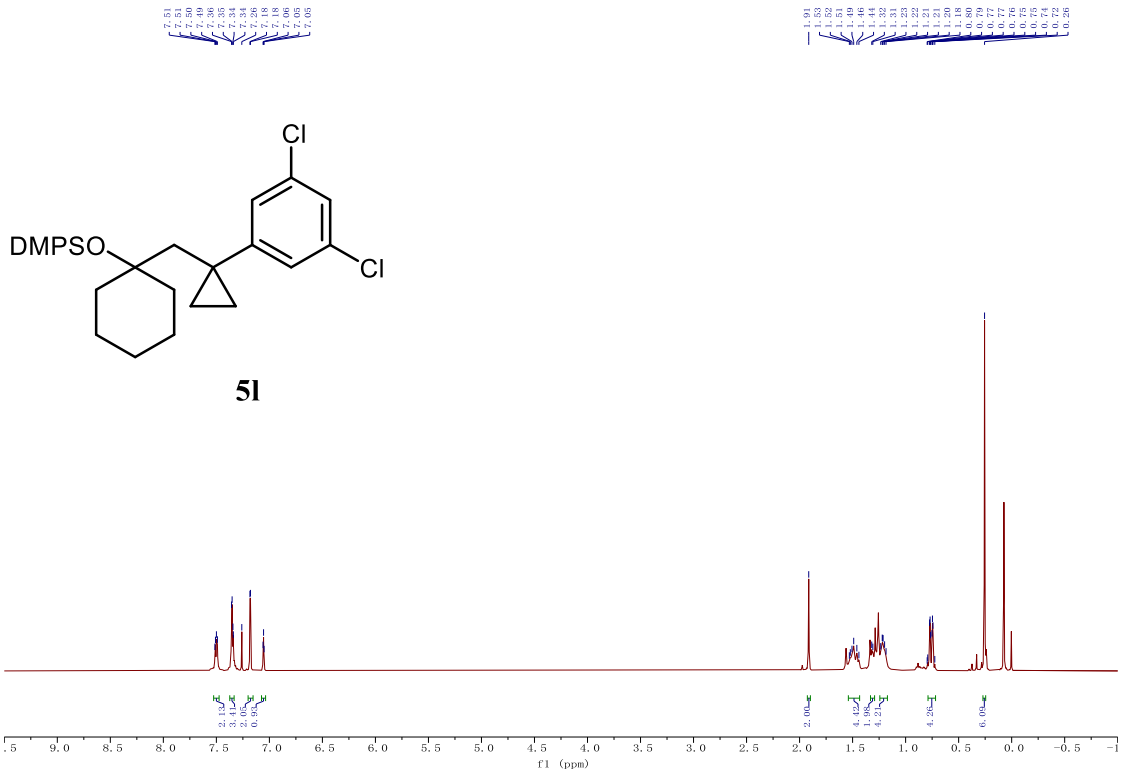
5k

^{13}C NMR (101 MHz, $CDCl_3$)



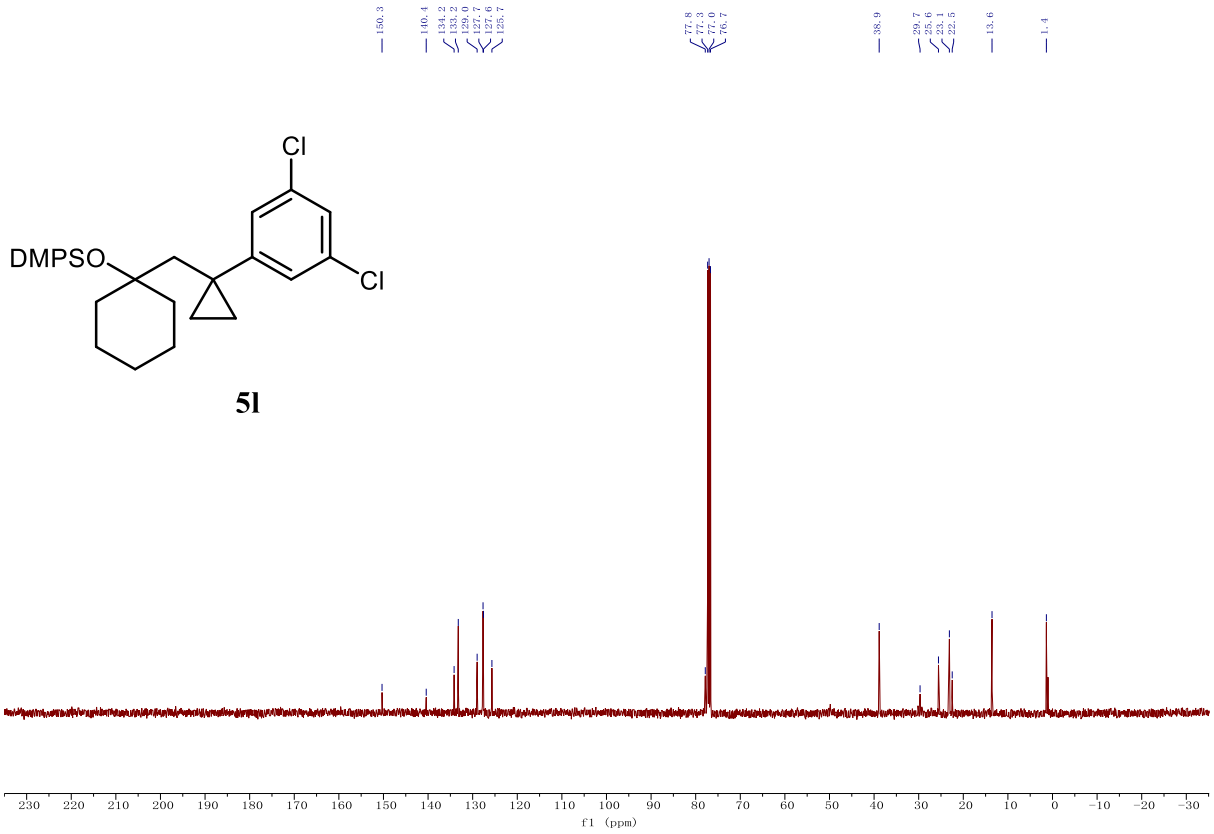
5k

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



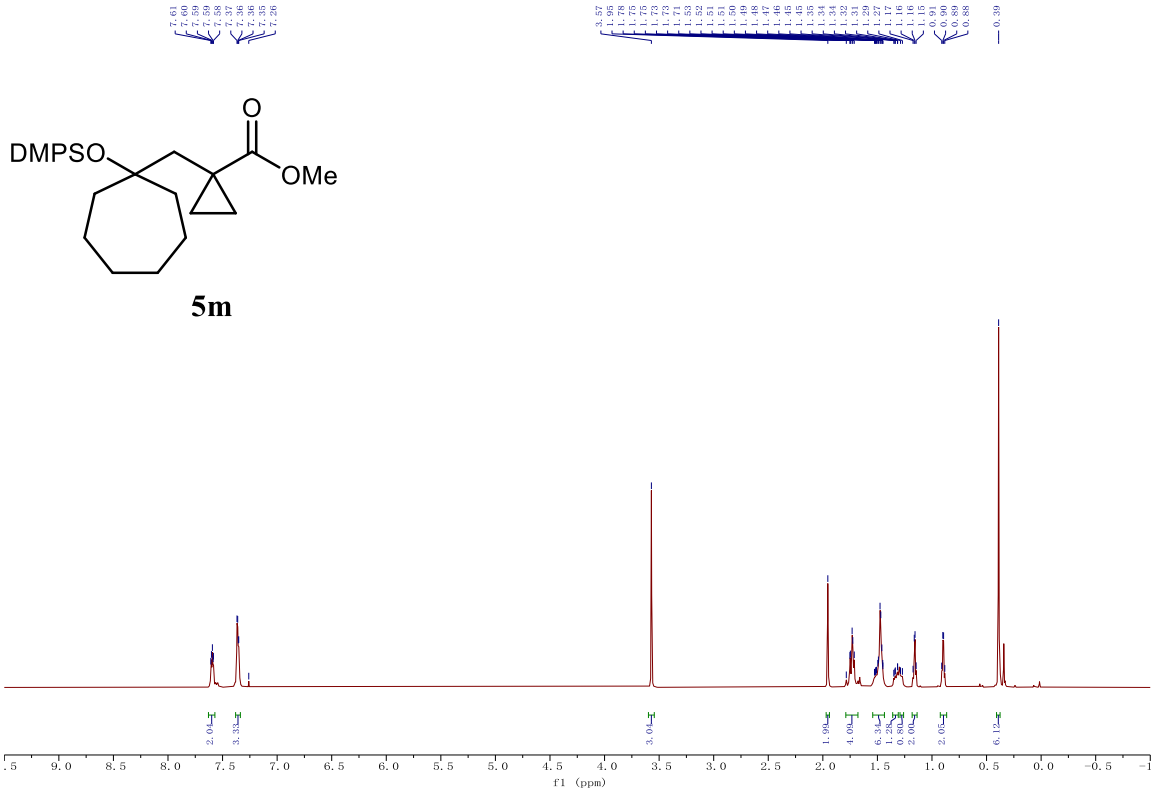
5l

^{13}C NMR (101 MHz, $CDCl_3$)



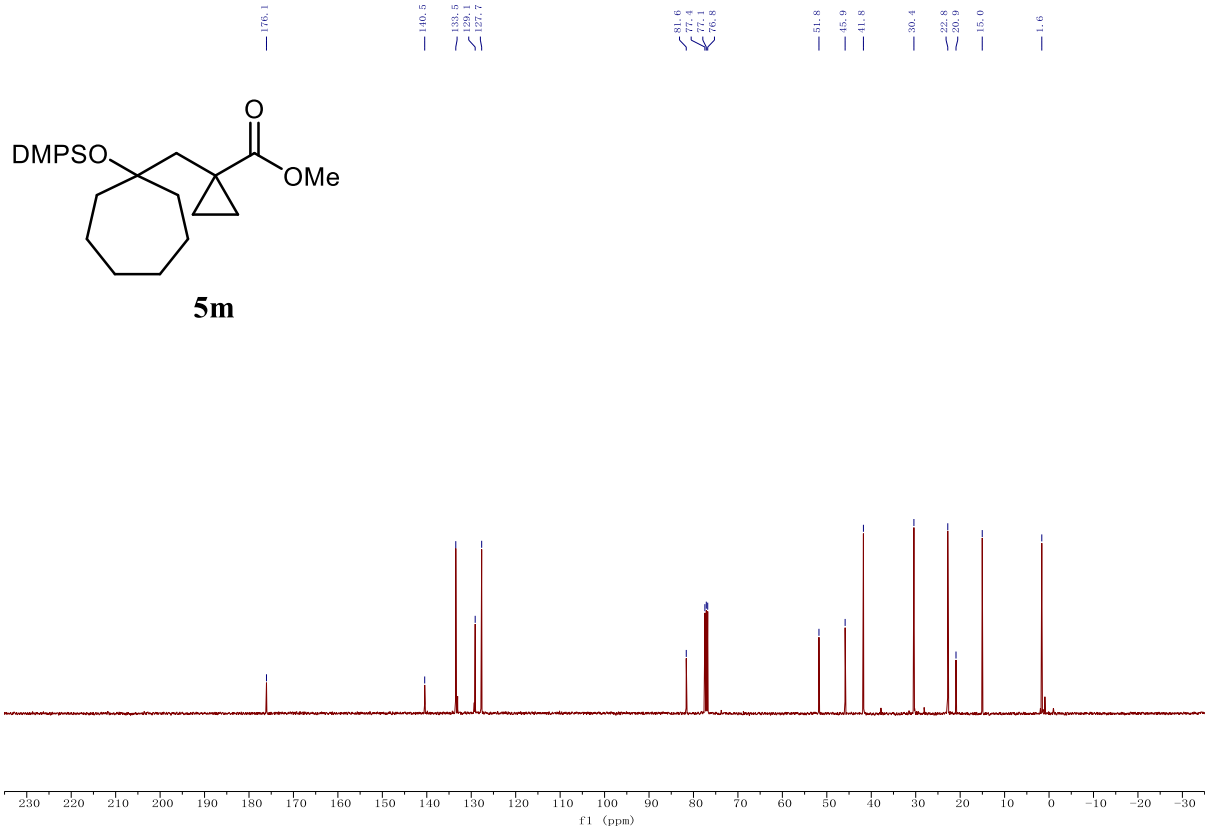
5l

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



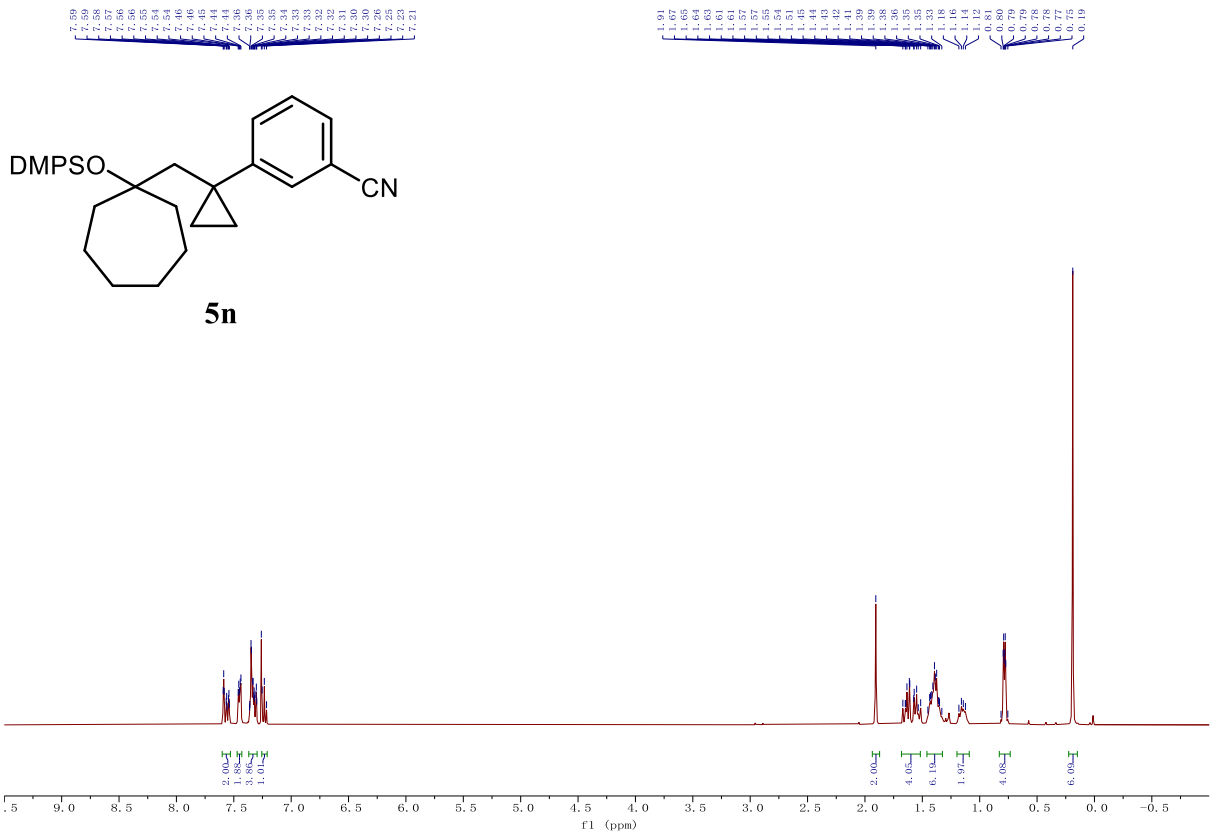
5m

^{13}C NMR (101 MHz, $CDCl_3$)

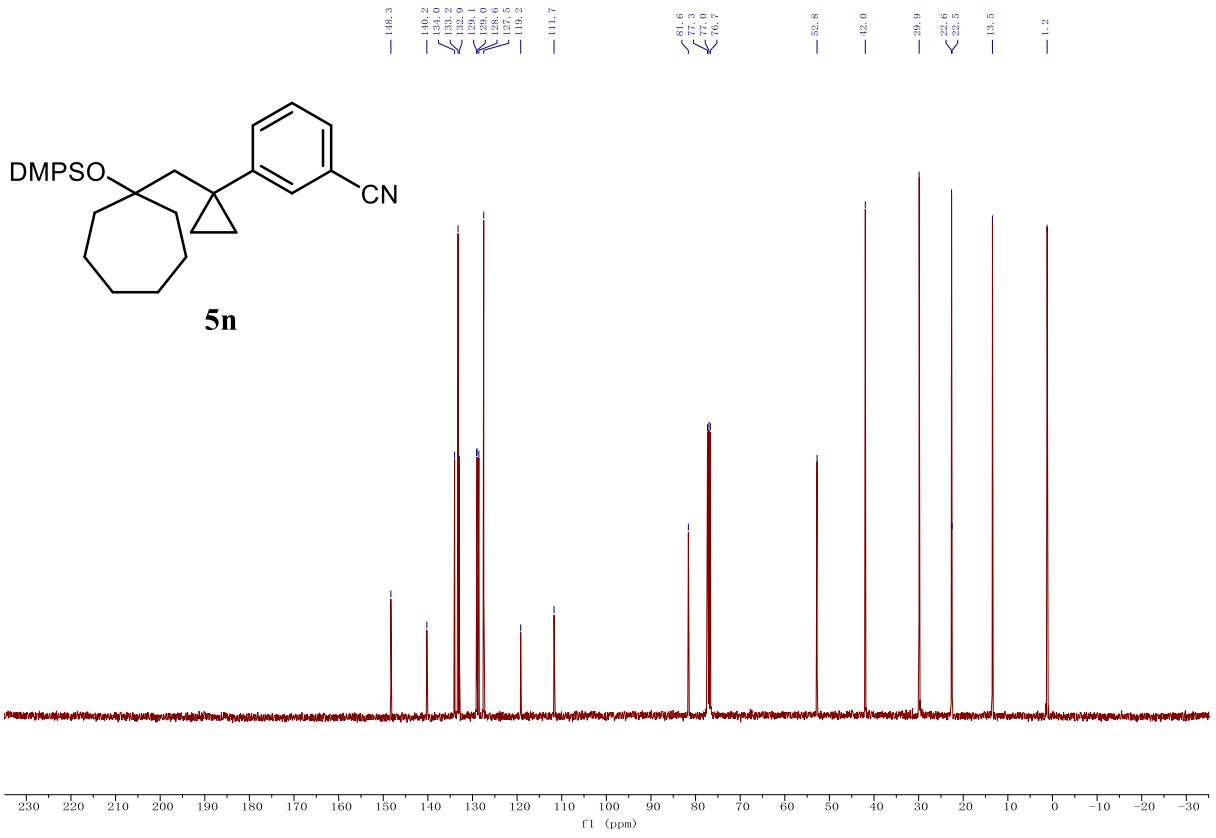


5m

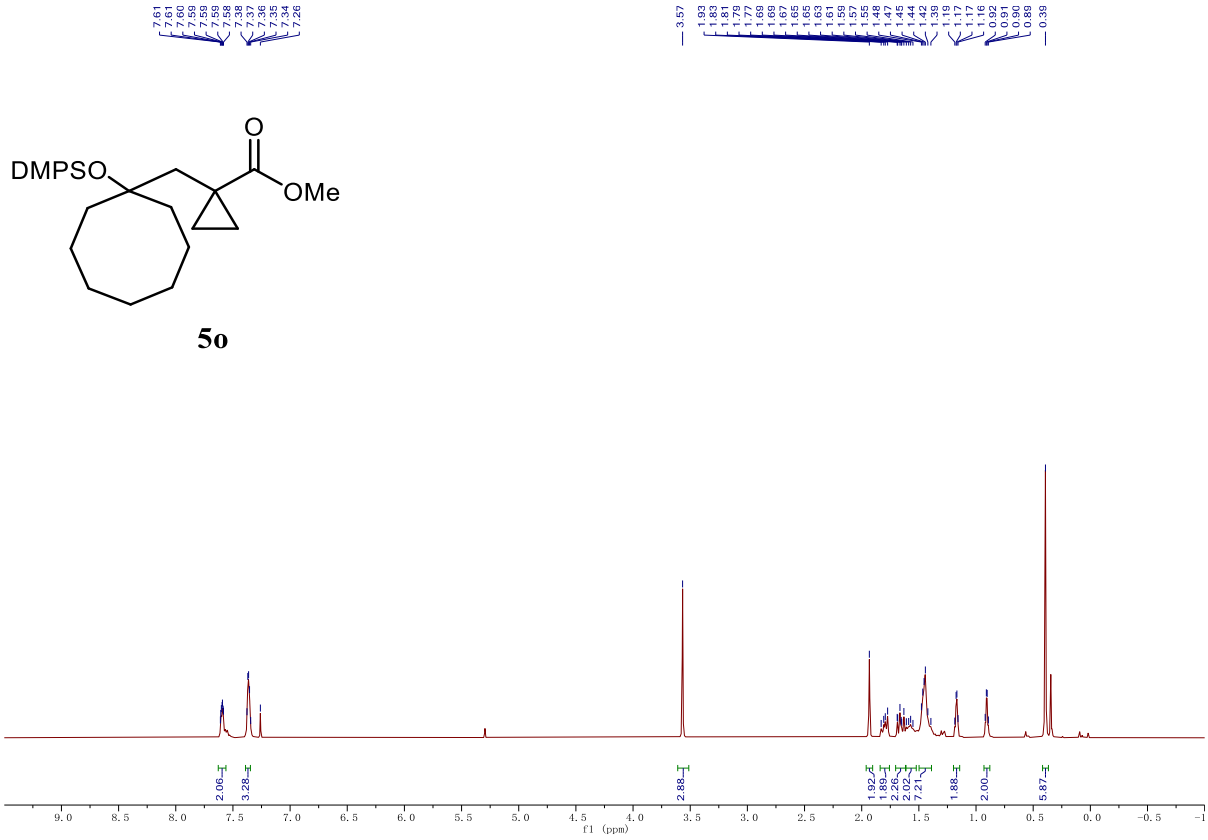
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

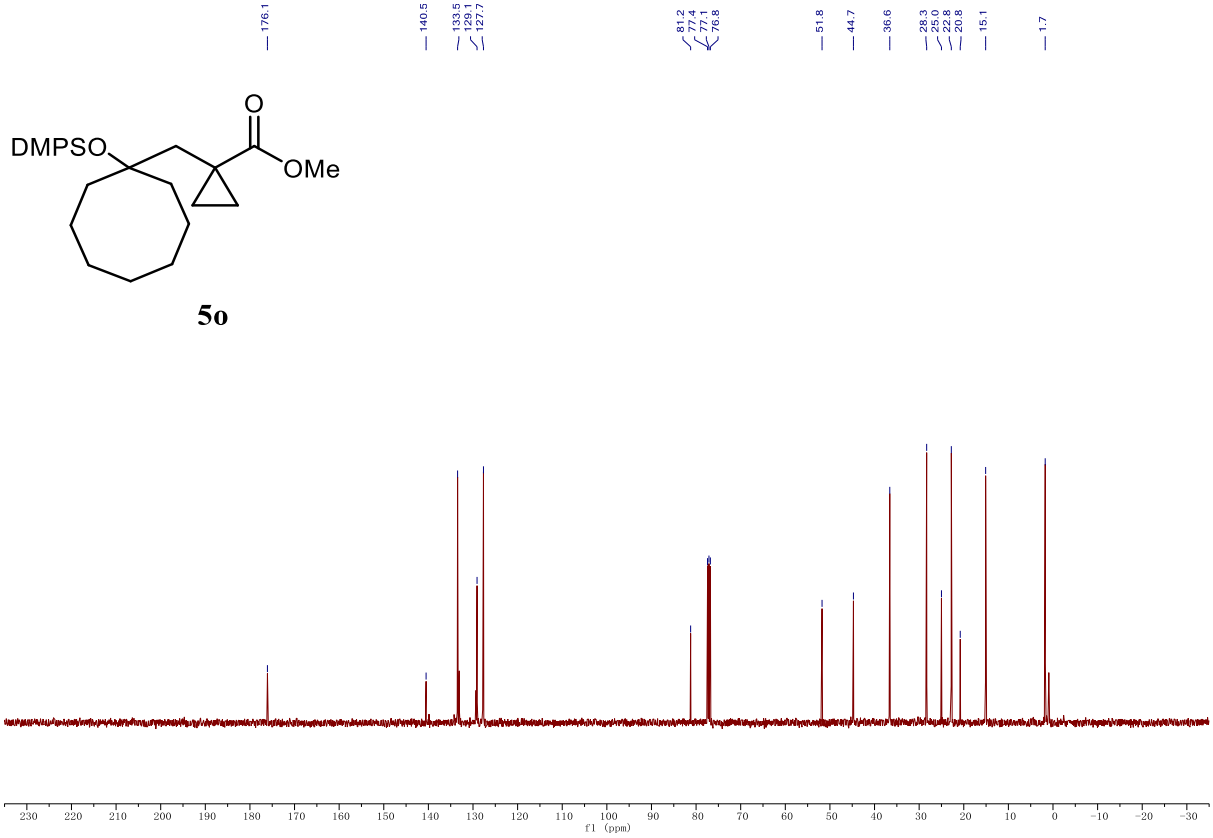


^{1}H NMR (400 MHz, $CDCl_3$)



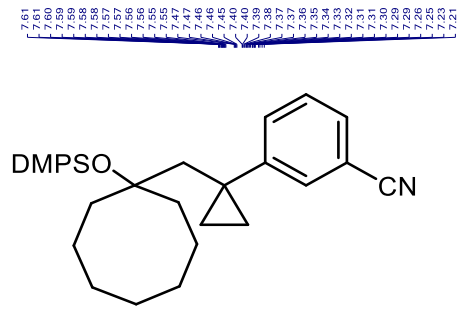
5o

^{13}C NMR (101 MHz, $CDCl_3$)

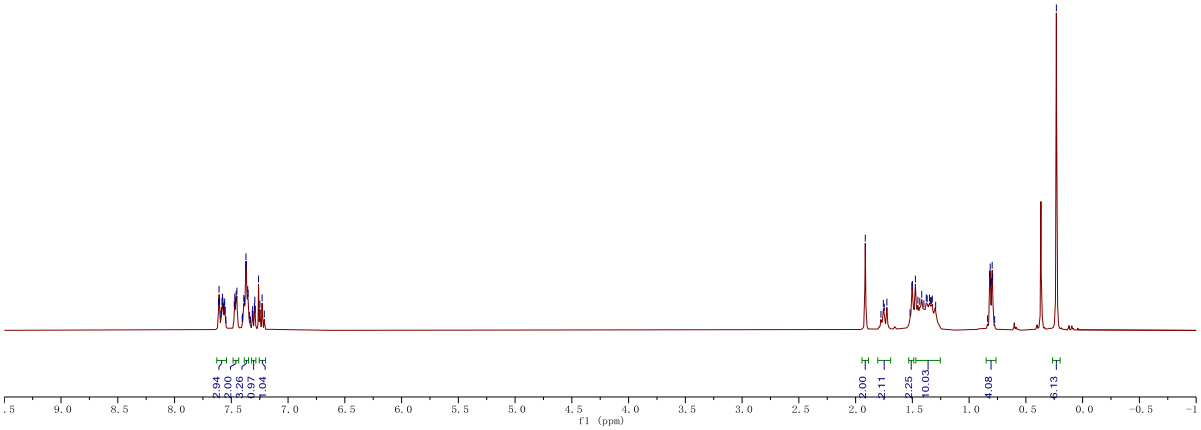


5o

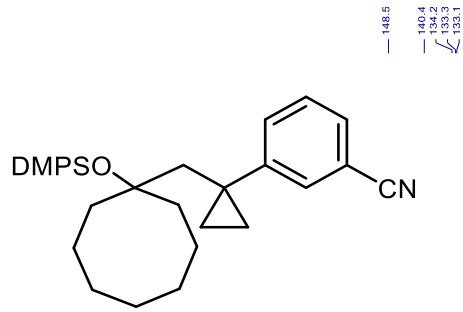
^{1}H NMR (400 MHz, $CDCl_3$



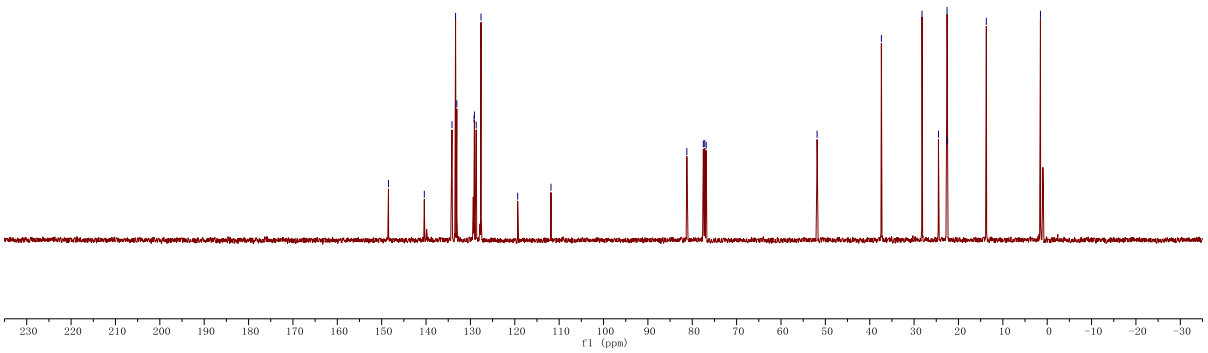
5p



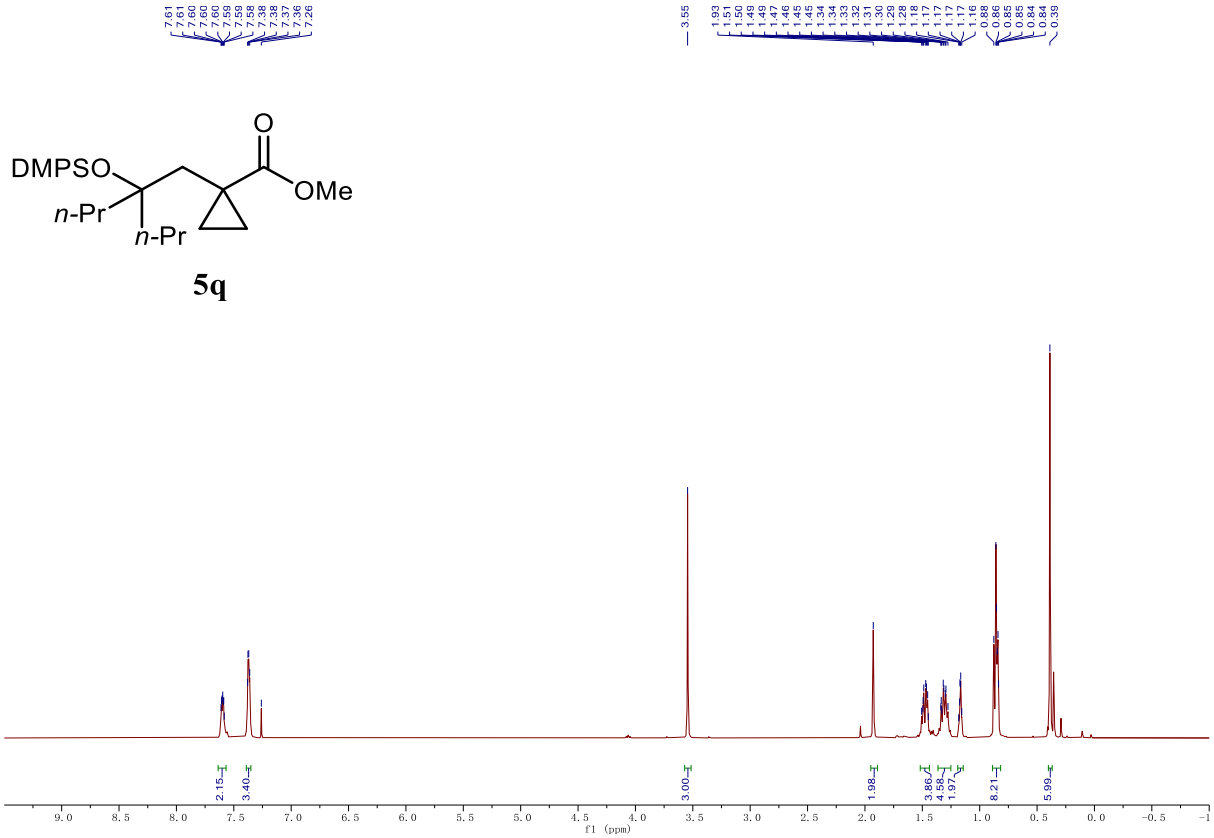
^{13}C NMR (101 MHz, $CDCl_3$)



5p

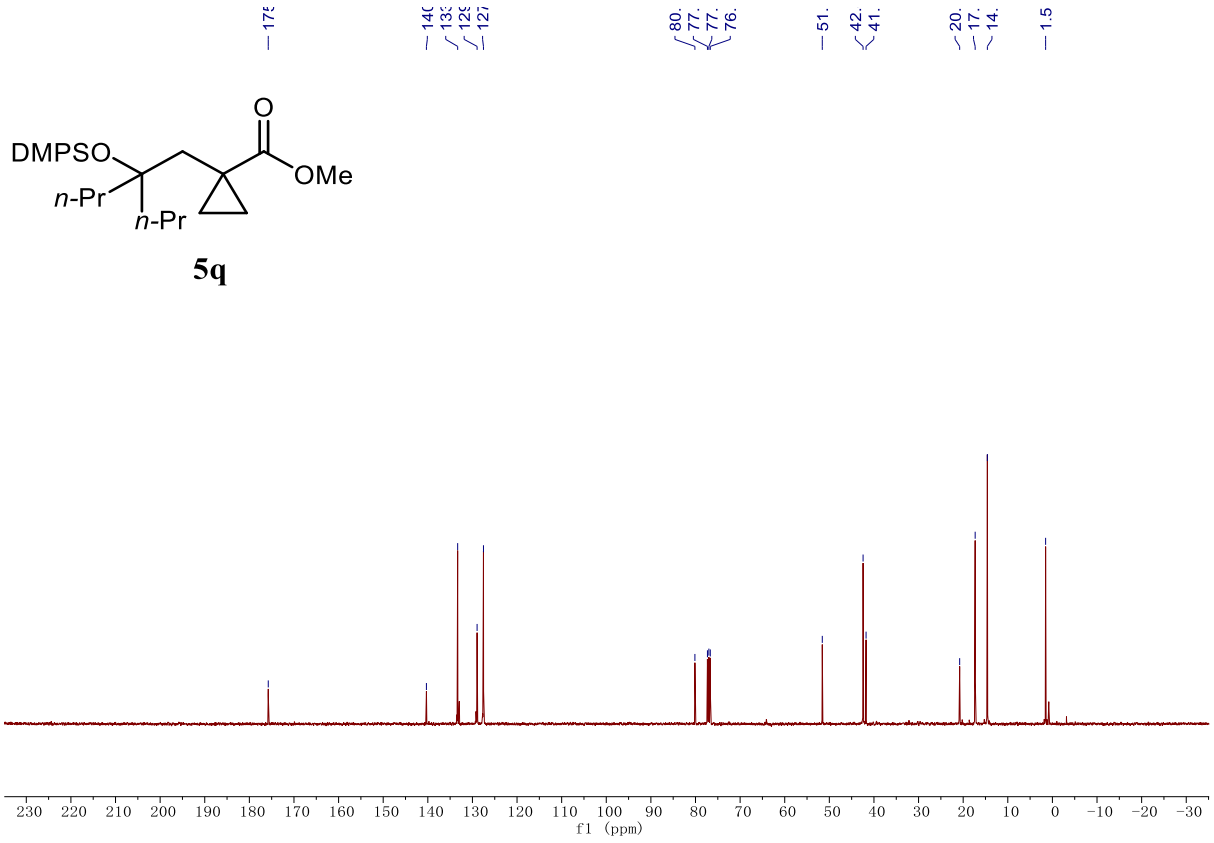


^{1}H NMR (400 MHz, $CDCl_3$)



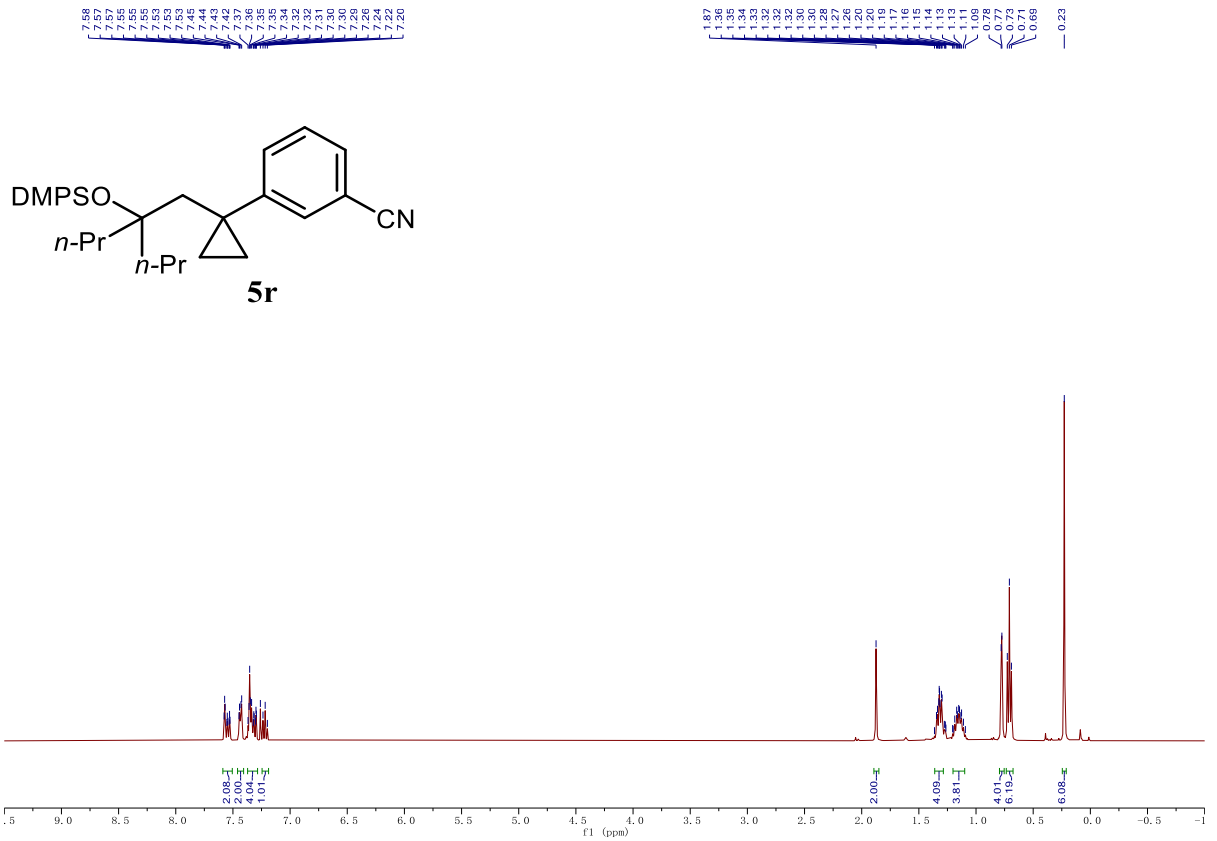
5q

^{13}C NMR (101 MHz, $CDCl_3$)

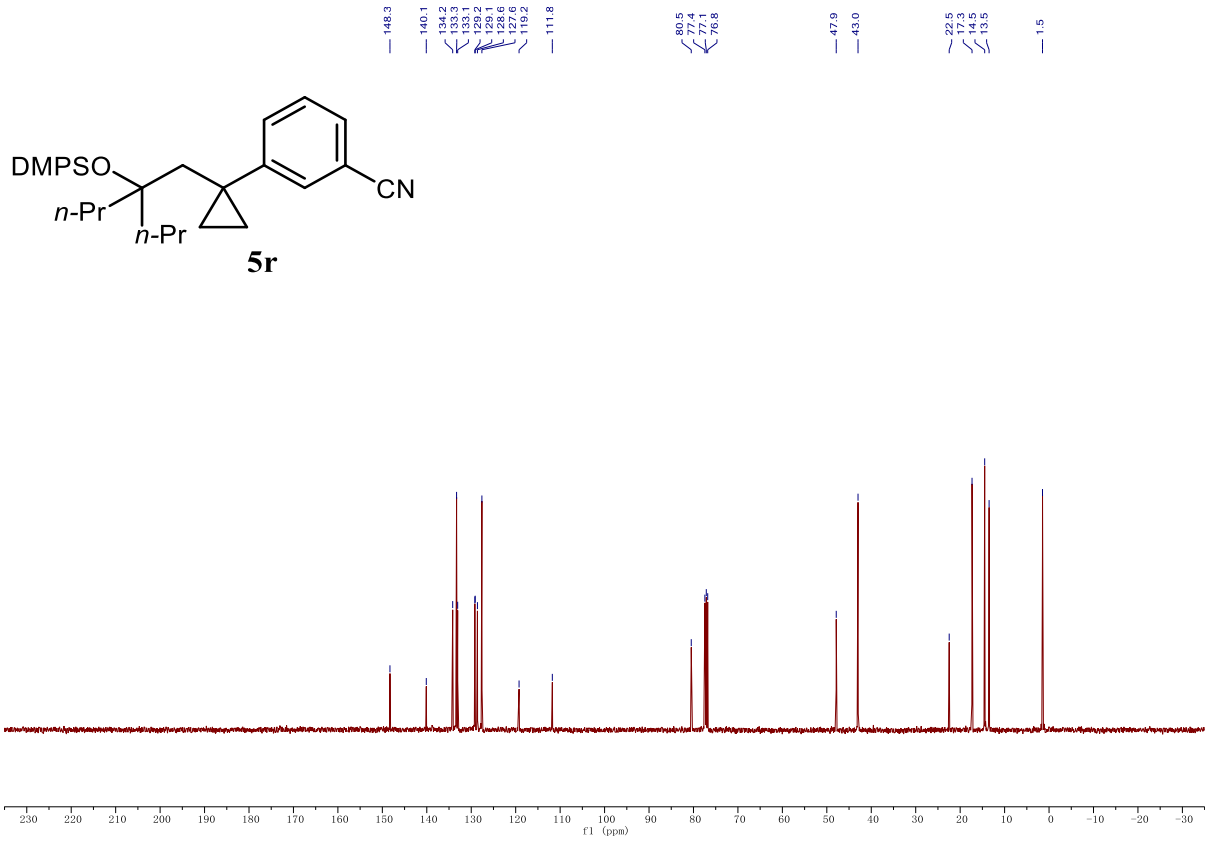


5q

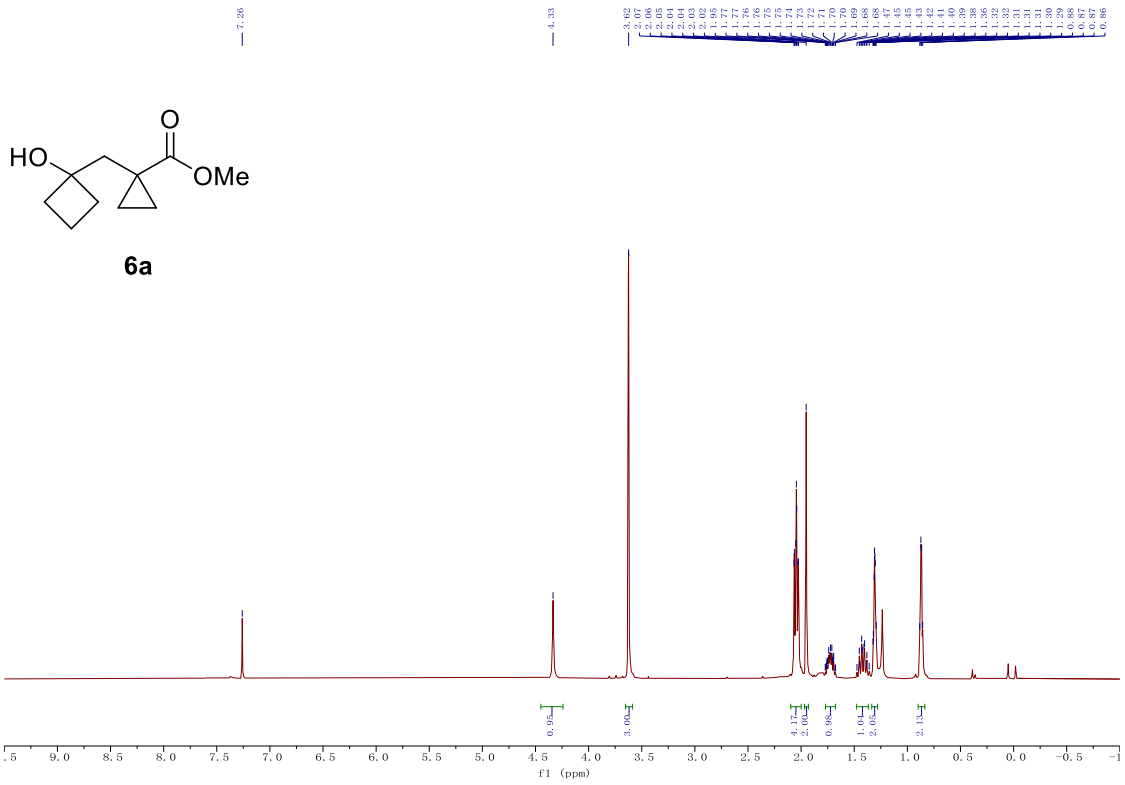
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

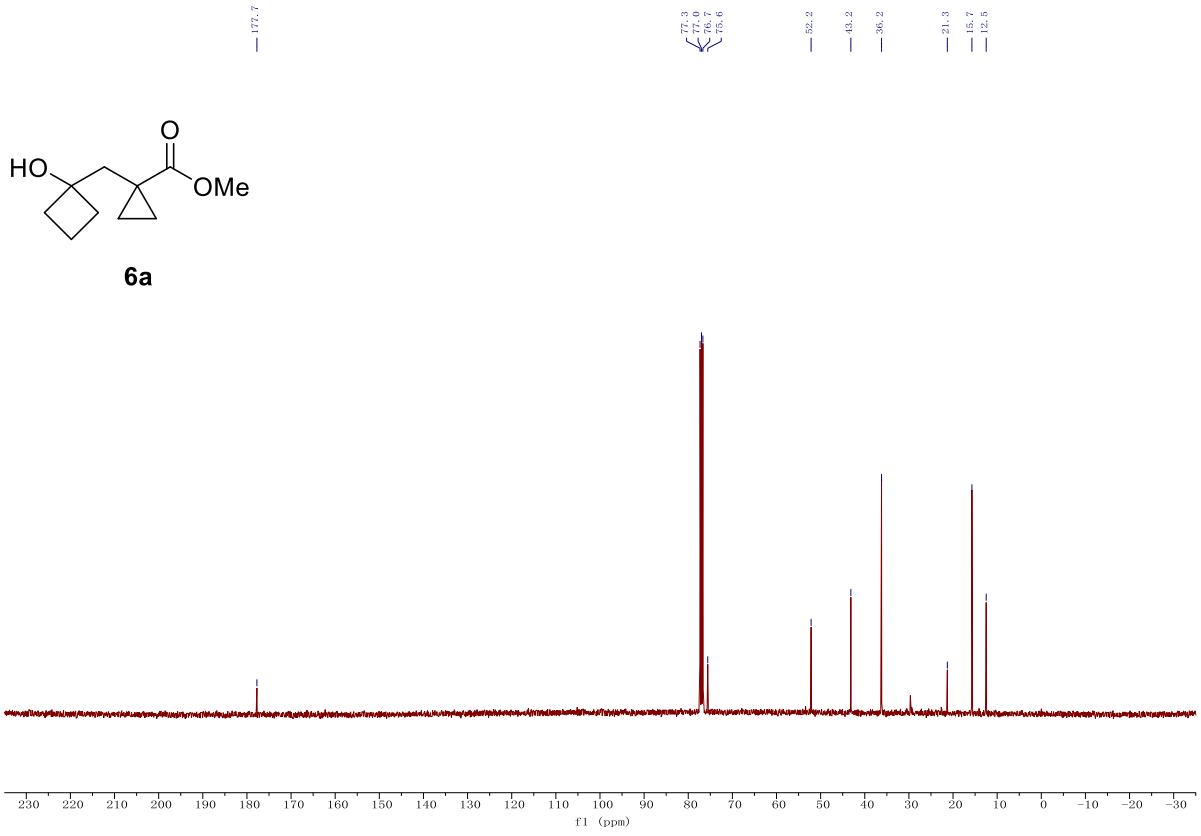


^{1}H NMR (400 MHz, $CDCl_3$)



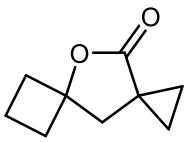
6a

^{13}C NMR (101 MHz, $CDCl_3$)

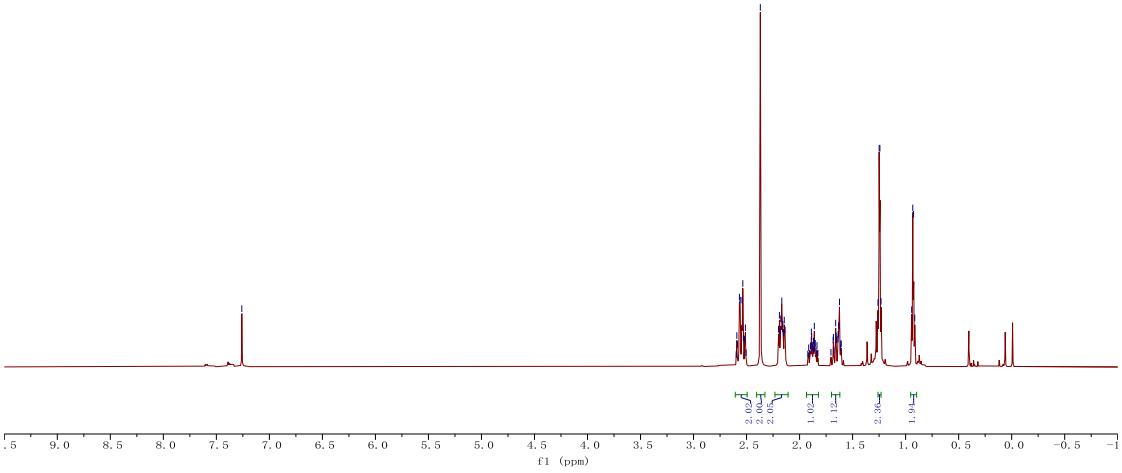


6a

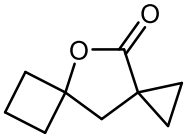
^{1}H NMR (400 MHz, $CDCl_3$)



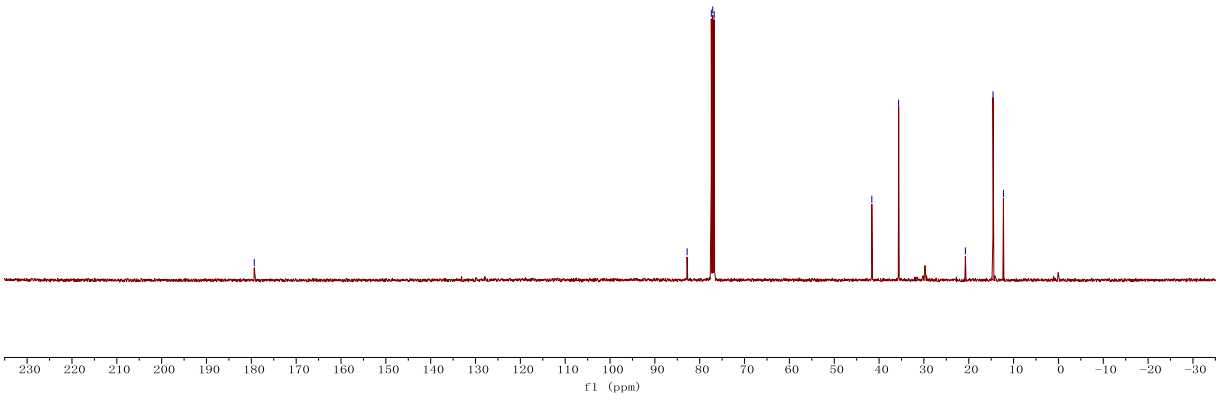
6b



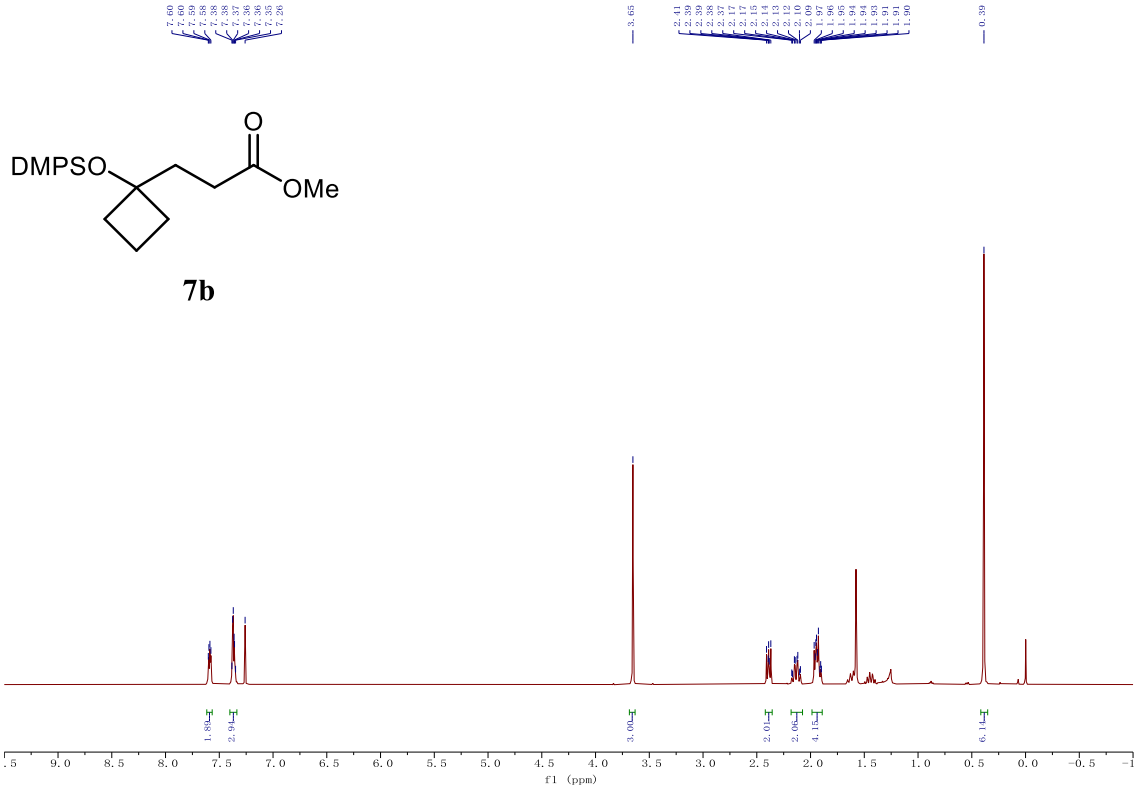
^{13}C NMR (101 MHz, $CDCl_3$)



6b

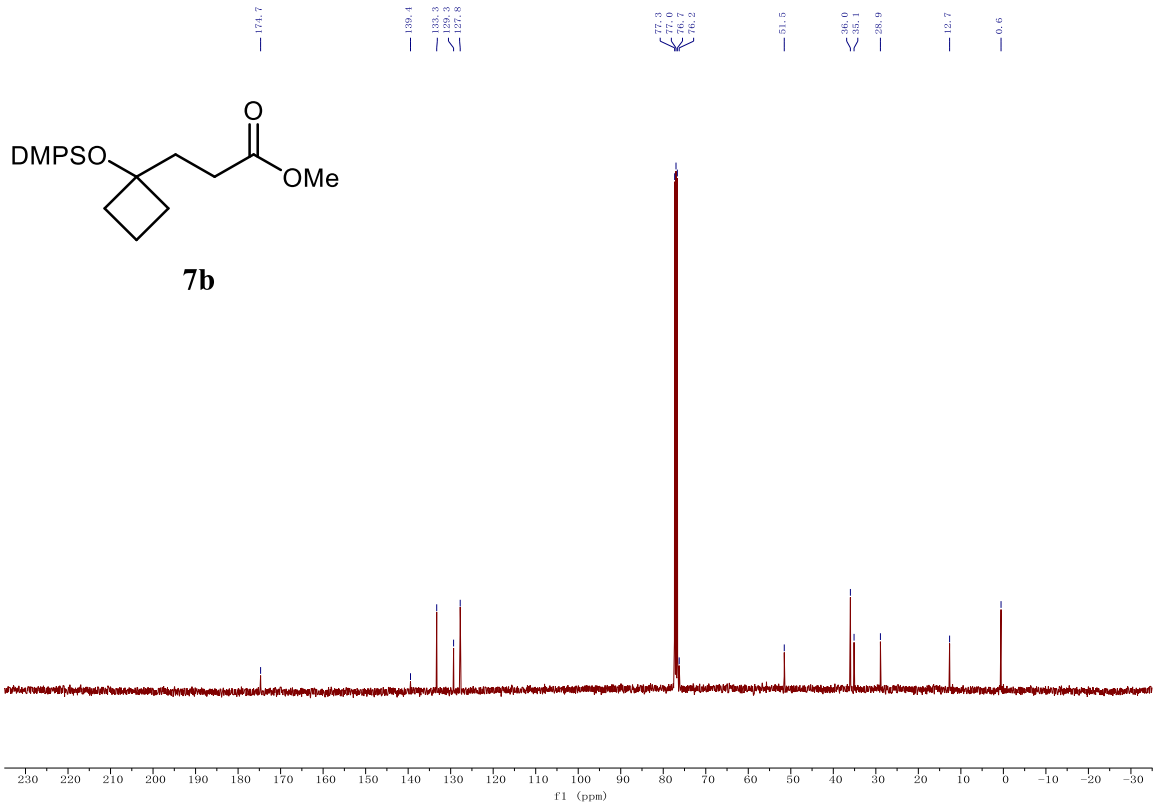


^{1}H NMR (400 MHz, $CDCl_3$)



7b

^{13}C NMR (101 MHz, $CDCl_3$)



7b