SUPPORTING INFORMATION

Acid-Catalyzed Regioselective Remote Heteroarylation of Alkenes *via* C=C Bond Migration

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1. Materials and instrument equipments

1.1. Glassware, solvents and reagents

Unless otherwise stated, all chemicals and reagents available from commercial sources were directly used without further purification. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in a nitrogen-filled glove box or under nitrogen atmosphere using standard schlenk techniques. All glassware was oven-dried immediately prior to use. All solvents were freshly distilled and degassed according to standard methods.

1.2. Chromatography and instrumentation

Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 TLC silica plates and visualization of the developed chromatogram was performed by UV absorbance (254 nm).

Flash column chromatography (FCC) of product was accomplished using forced-flow chromatography on silica gel (200 – 300 mesh) with the indicated solvent system according to standard techniques.

NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer at ambient temperature. NMR spectra are referred to the referenced $CDCl_3$ (^1H: 7.26 ppm; ^{13}C: 77.16 ppm). The data for ^1H NMR is represented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, coupling constant (s) in Hz, integration).

High-resolution mass spectra (HRMS-ESI/APCI) were obtained with Shimazu LC-20AT mass spectrometer. (HRMS-EI) were obtained with ThermoFisher, Q Exactive GC mass spectrometer.

In situ IR tests used a Mettler-Toledo ReactIR™ 15 with the probe 11 (the interface of probe is an AgX 6 mm × 1.5 m fiber). The absorbance was recorded at the range from 3000 cm^{-1} to 650 cm^{-1}.

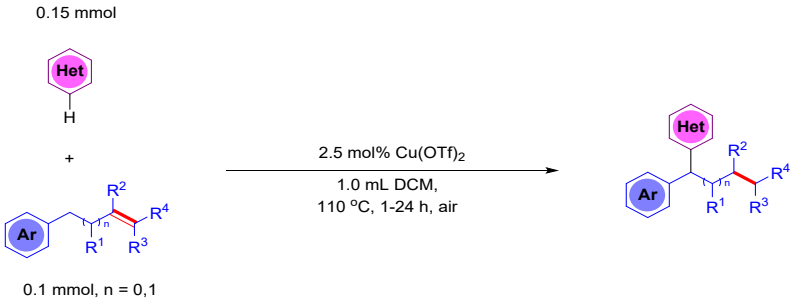
X-ray photoelectron spectroscopy (XPS) was performed on a Thermal Field Emission Scanning Electron Microscope Quanta 400 by depth analysis of photoelectron spectroscopy.

1.3. Naming of compounds

The compound names were generated by the computer program ChemBioDraw Ultra 14.0 software, according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC) nomenclature.

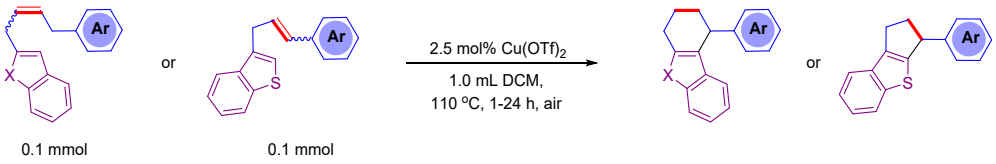
2. General experiment procedures

General Procedure A:



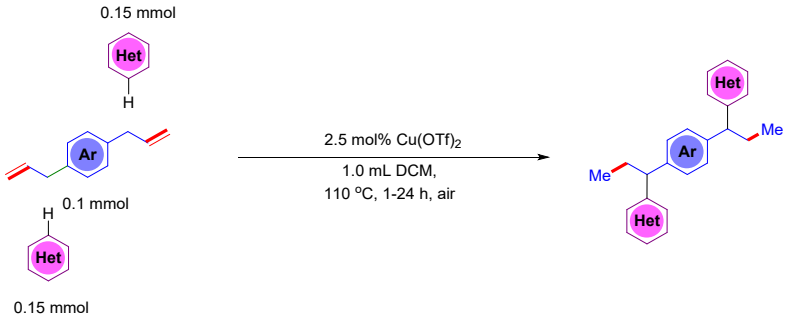
In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol), alkene derivatives (0.1 mmol), and heterocyclic derivatives (0.15 mmol) under air atmosphere. Next, DCM (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature, and the reaction was stirred at 110 °C for 1-24 hours. After the reaction is completed, it was cooled to room temperature, the reaction mixture was then concentrated in vacuo and the residue was further purified by flash column chromatography using petroleum ether and ethyl acetate as eluents to afford the corresponding products.

General Procedure B:



In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol), alkene heterocyclic derivatives (0.1 mmol) under air atmosphere. Next, DCM (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature, and the reaction was stirred at 110 °C for 1-24 hours. After the reaction is completed, it was cooled to room temperature, the reaction mixture was then concentrated in vacuo and the residue was further purified by flash column chromatography using petroleum ether and ethyl acetate as eluents to afford the corresponding products.

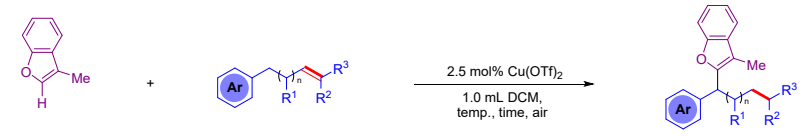
General Procedure C:



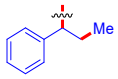
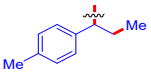
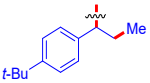
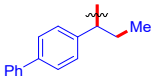
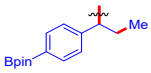
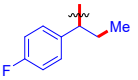
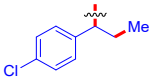
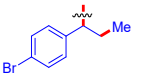
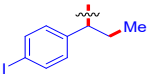
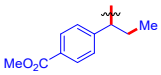
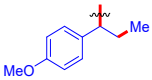
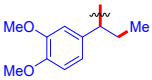
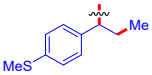
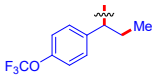
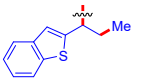
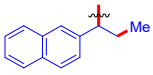
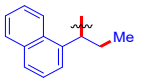
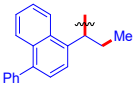
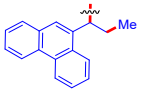
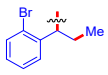
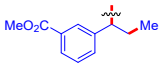
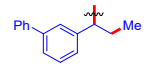
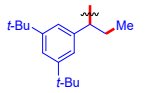
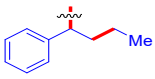
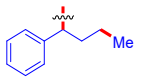
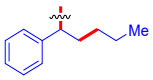
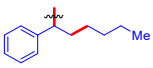
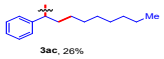
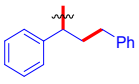
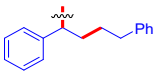
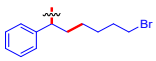
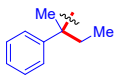
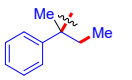
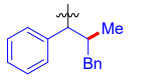
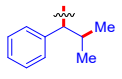
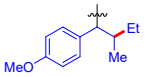
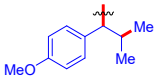
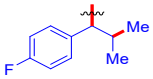
In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol), alkene derivatives (0.1 mmol), and heterocyclic derivatives (0.3 mmol) under air atmosphere. Next, DCM (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature, and the reaction was stirred at 110 °C for 1-24 hours. After the reaction is completed, it was cooled to room temperature, the reaction mixture was then concentrated in vacuo and the residue was further purified by flash column chromatography using petroleum ether and ethyl acetate as eluents to afford the corresponding products.

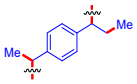
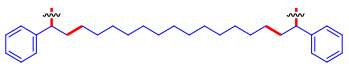
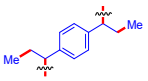
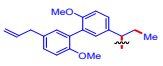
3. Summary of substrate scope exploration

3.1. Exploration of the substrate scope of alkene derivatives[a-b] (for the convenience of reference, the substrate is set with hyperlinks)



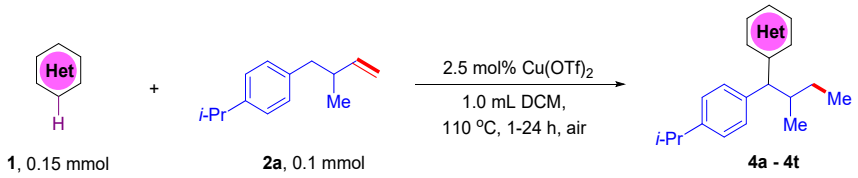
1a, 0.15 mmol + **2**, 0.1 mmol, n = 0,1 → **3a - 3bg**

 **3a**, 64%	 **3b**, 85%	 **3c**, 51%	 **3d**, 77%	 **3e**, 20%	 **3f**, 23%
 **3g**, 58%	 **3h**, 39%	 **3i**, 60%	 **3j**, 55%	 **3k**, 65%	 **3l**, 70%
 **3m**, 45%	 **3n**, 28%	 **3o**, 36%	 **3p**, 93%	 **3q**, 78%	 **3r**, 27%
 **3s**, 63%	 **3t**, 40%	 **3u**, 60%	 **3v**, 40%	 **3w**, 79%	 **3x**, 55%
 **3y**, 71%	 **3z**, 45%	 **3aa**, 60%	 **3ab**, 22%	 **3ac**, 26%	 **3ad**, 23%
 **3ae**, 10%	 **3af**, 20%	 **3ag**, 73%	 **3ah**, 66%	 **3ai**, 56%; 2/1 dr	 **3aj**, 82%
3ae, 10%  **3ak**, 86%; 1.2/1 dr	 **3al**, 99%	 **3am**, 53%	**3an**, 83%	**3ao**, 36%	**3ap**, 75%
3aq, 83%; 1.5/1 dr	**3ar**, 61%; 1/1 dr	**3as**, 84%; 2/1 dr	**3at**, 77%; 1/1 dr	**3au**, 65%; 2/1 dr	**3av**, 79%, 70%[c]
3aw, 32%	**3ax**, 91%; 1.4/1 dr	**3ay**, 86%; 1.6/1 dr	**3az**, 95%; 1/1 dr	**3ba**, 0%	**3bb**,18%

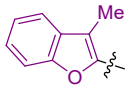
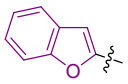
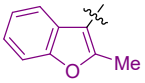
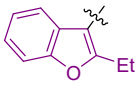
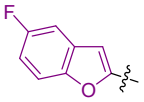
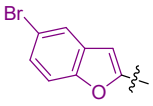
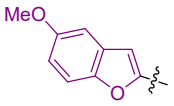
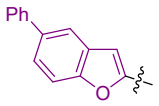
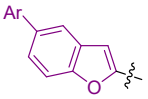
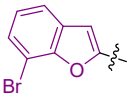
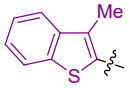
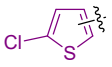
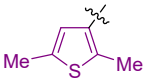
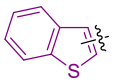
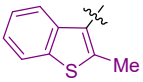
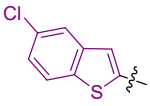
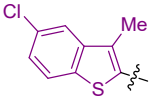
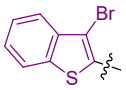
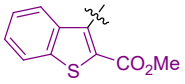
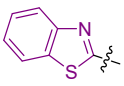
 **3bc**, 53%	 **3bd**, 37%	 **3be**, 18%	 **3bf**, 31%	 **3bg**, 45%[d]

[a]: reactions were conducted with 0.15 mmol **1a**, 0.1 mmol **2** (alkenes), 2.5 mol% $Cu(OTf)_2$, 0.1 M DCM, 110 °C, 1-24 h in a sealed tube under air (when diene was used as reactant, 0.3 mmol of **1a** was added); [b]: isolated yield. [c]: 3-methylbenzothiophene as a heteroaryl reactant; [d]: raw material ratio: **1a**/ diene = 0.15 mmol/ 0.1 mmol. Unless otherwise specified, all internal alkenes used are *E*/*Z* mixtures.

3.2. Exploration of the substrate scope of heteroaryl derivatives[a-b] (for the convenience of reference, the substrate is set with hyperlinks)

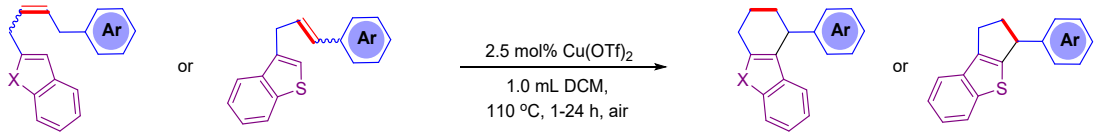


1, 0.15 mmol **2a**, 0.1 mmol **4a - 4t**

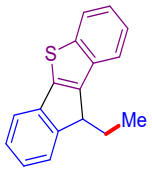
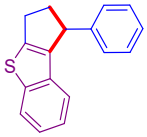
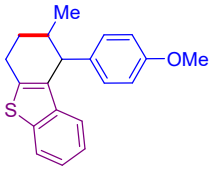
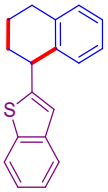
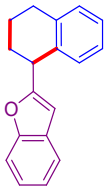
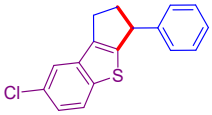
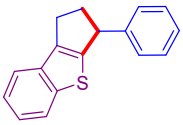
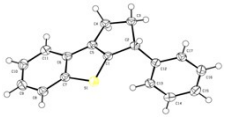
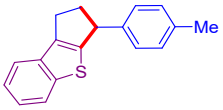
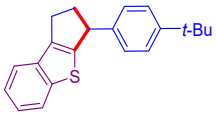
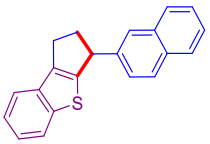
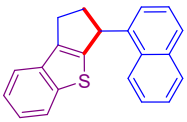
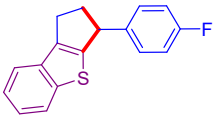
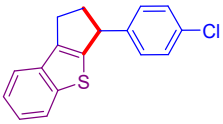
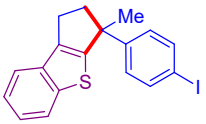
 **4a**, 94%; 1/1 dr	 **4b**, 70%; 1/1 dr	 **4c**, 62%; 1/1 dr	 **4d**, 66%; 3.2/1 dr	 **4e**, 74%; 1/1 dr
 **4f**, 65%; 1/1 dr	 **4g**, 59%; 1/1 dr	 **4h**, 73%[c]	 Ar = 4-CO_2Me-C_6H_4 **4i**, 55%; 1/1 dr	 **4j**, 83%[c]
 **4k**, 84%; 1.2/1 dr	 **4l**, 30%; 1/1 dr	 **4m**, 81%; 1/1 dr	 C2/C3 = 3/1 **4n**, 57%; 1/1 dr	 **4o**, 49%[c]
 **4p**, 62%; 4/1 dr	 **4q**, 91%; 1.8/1 dr	 **4r**, 0%	 **4s**, 0%	 **4t**, 0%

[a]: reactions were conducted with 0.15 mmol **1** (heteroaryls), 0.1 mmol **2az**, 2.5 mol% $Cu(OTf)_2$, 0.1 M DCM, 110 °C, 1-24 h in a sealed tube under air; [b]: isolated yield; [c]: allylbenzene was used as an alkene raw material. Unless otherwise specified, all internal alkenes used are *E*/*Z* mixtures.

3.3. Exploration of the substrate scope of heteroaromatic alkene derivatives[a-b] (for the convenience of reference, the substrate is set with hyperlinks)



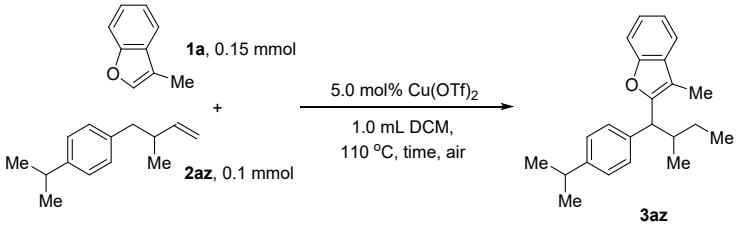
5, 0.1 mmol **6**, 0.1 mmol **7a - 7n**

 five/six ring = 1/2.4 **7a**, 55%[c]	 **7b**, 68%	 **7c**, 70%; 1.5/1 dr	 **7d**, 35%	 **7e**, 48%
 **7f**, 22%	 **7g**, 55%; 30%[d]	 **7g**, CCDC 2308239	 **7h**, 47%	 **7i**, 50%
 **7j**, 32%	 **7k**, 54%	 **7l**, 81%	 **7m**, 57%	 **7n**, 35%

[a]: reactions were conducted with 0.1 mmol heteroaromatic alkenes, 2.5 mol% $Cu(OTf)_2$, 0.1 M DCM, 110 °C, 1-24 h in a sealed tube under air; [b]: isolated yield; [c]: due to the similarity of R_f between substrate and products and the difficulty in column chromatography separation, the yield was measured by ^1H NMR; [d]: one pot reaction between benzothiophene and cinnamyl alcohol. Unless otherwise specified, all internal alkenes used are *E*/*Z* mixtures.

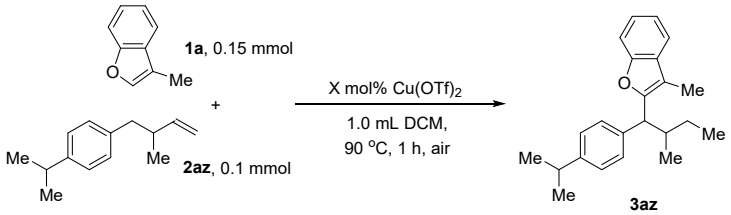
4. Partial optimization details of reaction conditions

Table S1. Optimization of reaction time



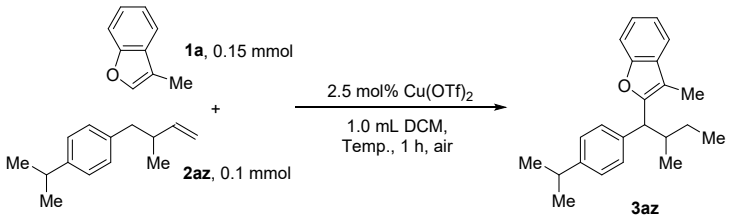
Entry	time/ h	Isolated yield/%
1	0.5	69
2	1.0	96
3	2.0	89
4	4.0	85
5	8.0	83
6	16.0	94

Table S2. Optimization of catalyst dosage



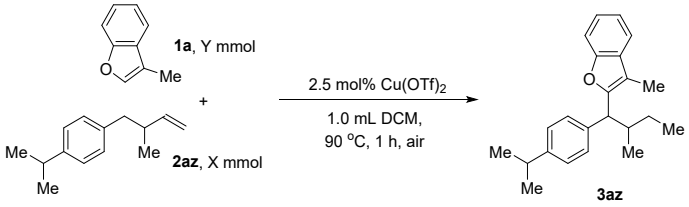
Entry	X	Isolated yield/%
1	10	92
2	2.5	95
3	1.0	67
4	0	0

Table S3. Optimization of reaction temperature



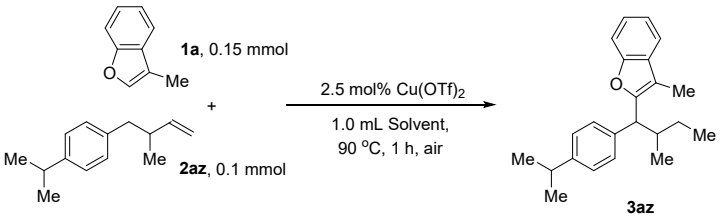
Entry	Temp./ °C	Isolated yield/%
1	70	0
2	90	95
3	130	92

Table S4. Optimization of the molar ratio of reactants



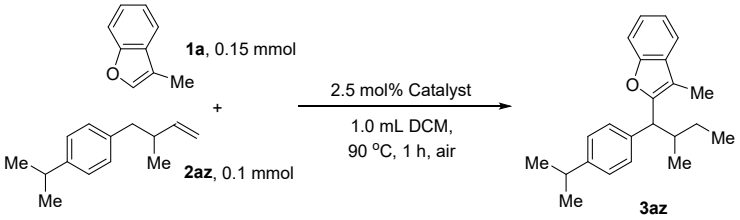
Entry	X mmol	Y mmol	Isolated yield/%
1	0.1	0.1	61
2	0.15	0.1	95

Table S5. Optimization of reaction solvents



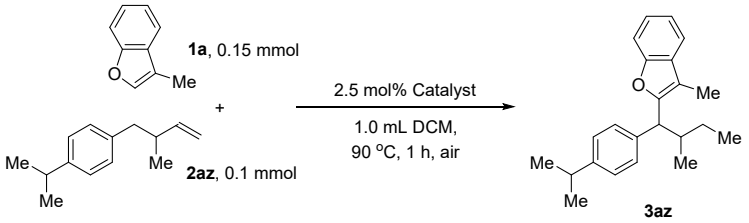
Entry	Solvent	Isolated yield/%
1	EtOAc	0
2	THF	0
3	Dioxane	0
4	Hexane	0
5	Toluene	0
6	DMF	0
7	MeCN	0
8	1,2-DCE	76
9	DMSO	0
10	EtOH	0
11	*t*-BuOH	0
12	PhCl	0

Table S6. Optimization of different types of copper catalysts



Entry	Catalyst	Result
1	$Cu(MeCN)_4PF_6$	N. R.
2	$Cu(NO_3)_2{\cdot}3H_2O$	N. R.
3	CuF_2	N. R.
4	CuCl	N. R.
5	CuI	N. R.
6	$Cu(OAc)_2$	N. R.
7	$Cu(acac)_2$	N. R.

Table S7. Optimization of different types of $M_x(OTf)_y$ catalysts (M = metal)

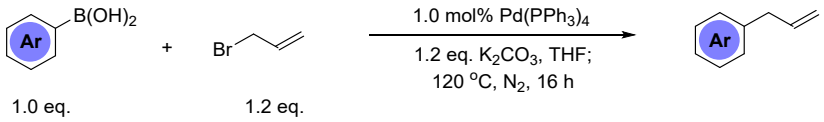


Entry	Catalyst	Isolated yield/%
1	Cu(OTf)	0
2	$Fe(OTf)_3$	89
3	$Fe(OTf)_2$	0
4	$Yb(OTf)_3$	0
5	$Ni(OTf)_2$	0
6	$Bi(OTf)_3$	82
7	$In(OTf)_2$	0
8	Ag(OTf)	0
9	$Zn(OTf)_2$	0

5. Synthesis of materials and unsuccessful substrates

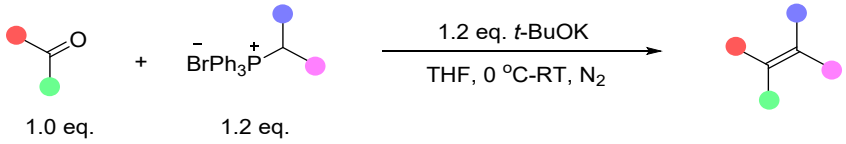
5.1. Synthesis of starting materials

Synthesis of allyl benzene derivatives



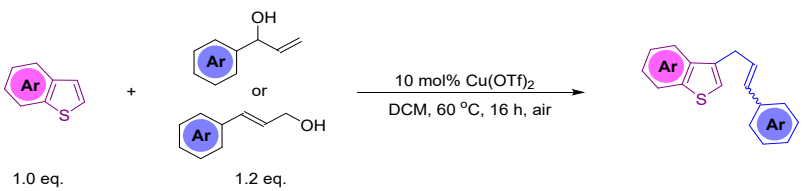
Prepare according to the literature procedure[1]: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with arylboric acids (5.0 mmol, 1.0 equiv.), allyl bromide (1.2 equiv.) and dry THF (10 mL). The mixture was stirred at room temperature for 16 hours. After that, the mixture was concentrated under vacuum. The residue was further purified by flash column chromatography (silica, petroleum ether as the eluent) to give the corresponding products.

Synthesis of polysubstituted alkene derivatives



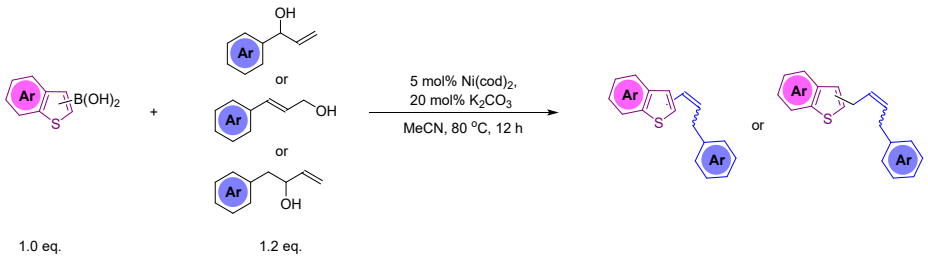
Prepare according to the literature procedure[2]: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with aldehydes or ketone derivatives (10.0 mmol, 1.0 equiv.), phosphine salt compounds (1.2 equiv.), and dry THF. The mixture was then stirred at room temperature for 12 hours. After the reaction is completed, the mixture was concentrated under vacuum. The residue was further purified by flash column chromatography (silica, petroleum ether as the eluent) to give the corresponding products.

Synthesis of 3-cinnamylbenzo[b]thiophene derivatives



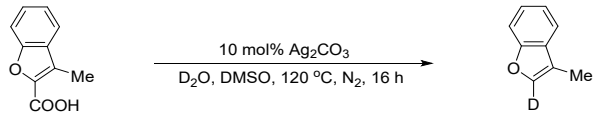
Prepare according to the literature procedure: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with benzothiophene derivatives (0.2 mmol, 1.2 equiv.), allyl alcohol derivatives (1.2 equiv.), 10 mol% $Cu(OTf)_2$, and DCM (1.0 mL). The mixture was then stirred at room temperature for 16 hours. After the reaction is completed, cool it to room temperature, the mixture was concentrated under vacuum. The residue was further purified by flash column chromatography (silica, petroleum ether as the eluent) to give the corresponding products.

Synthesis of heteroaryl alkene derivatives



Prepare according to the literature procedure[3]: In a nitrogen-filled glove box, 5.0 mol% $Ni(cod)_2$, Ph_3P and MeCN were added sequentially to a screw-cap vial, after stirring at room temperature for 10 min, 20 mol% K_2CO_3, boronic acid (1.0 equiv.), allyl alcohol derivatives (1.2 equiv.) were added. Then tighten the vial cap and take the vial outside the glove box. After the reaction mixture was stirred at 80 °C for 12 h, the mixture was cooled down to room temperature. Then the mixture was concentrated under vacuum and the residue was further purified by flash column chromatography (silica, petroleum ether as the eluent) to give the corresponding products.

Synthesis of 3-methylbenzofuran-2-*d*



Prepare according to the literature procedure[4]: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with 3-methylbenzofuran-2-carboxylic acid (17.6 mg, 0.1 mmol, 1.0 equiv.), 10 mol% Ag_2CO_3, DMSO (1.0 mL), and D_2O (0.5 mL). The mixture was stirred at 120 °C for 16 hours. After the reaction is completed, cool to room temperature. The mixture was concentrated under vacuum and then purified by flash column chromatography (silica, petroleum ether as the eluent) to give the corresponding deuterated product with 83% D.

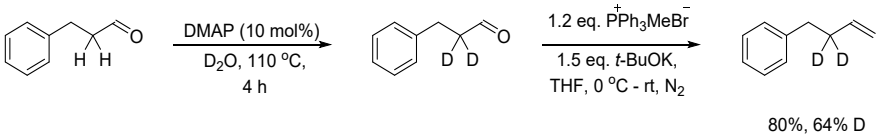
TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 1.1 Hz, 0.17H), 7.32 – 7.21 (m, 2H), 2.25 (s, 3H) ppm.

All recorded spectroscopic data match those previously reported in the literature.[4]

Synthesis of (but-3-en-1-yl-2,2-d_2)benzene



80%, 64% D

***Prepare according to the literature procedure*[5]**:

(i) In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with 3-phenylpropanal (58.8 mg, 0.4 mmol, 1.0 equiv.), DMAP (4.8 mg, 0.04 mmol, 0.01 equiv.) and D_2O (0.5 mL). The mixture was stirred at room temperature for 4 hours. After that, the mixture was concentrated under vacuum to give the product quantitatively.

(ii) In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with methyltriphenylphosphonium bromide (1.2 equiv.), *t*-BuOK (1.5 equiv.) and dry THF (2.0 mL). Stir them in ice/H_2O bath for 1 hour, and then add aldehyde (1.0 equiv.). The mixture was stirred at room temperature for 12 hours. After the reaction is completed, the mixture was concentrated under vacuum and the residue was then purified by flash column chromatography (silica, petroleum ether as the eluent) to give the corresponding product.

TLC: R_f = 0.75 (petroleum ether)

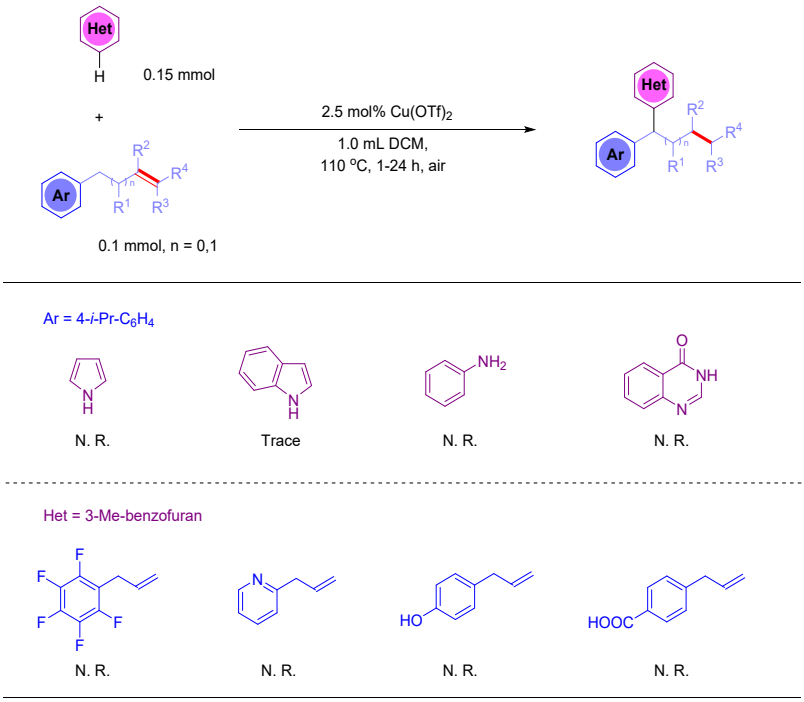
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 9.4, 5.6 Hz, 2H), 7.18 (dd, *J* = 10.1, 4.1 Hz, 3H), 5.95 – 5.78 (m, 1H), 5.08 – 4.96 (m, , 2H), 2.75 – 2.69 (m, 2H), 2.42 – 2.34 (m, 0.72H) ppm.

All recorded spectroscopic data match those previously reported in the literature.[5]

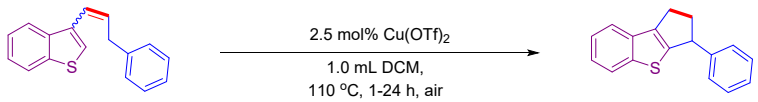
5.2. Some substrates with unsuccessful reactions

5.2.1. Unreactive substrates



5.2.2. Substrates with poor effect

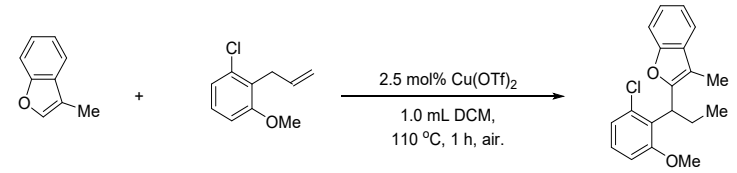
3-phenyl-2,3-dihydro-1*H*-benzo[b]cyclopenta[d]thiophene



0.1 mmol **7G**, complex

The reaction was performed according to **general procedure B** using 3-(3-phenylprop-1-en-1-yl)benzo[b]thiophene (25.0 mg, 0.1 mmol, 1.0 equiv.) After the reaction was completed, cooling it to room temperature, complex spots were found in TLC test.

2-(1-(2-chloro-6-methoxyphenyl)propyl)-3-methylbenzofuran



0.15 mmol 0.1 mmol 12%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-allyl-1-chloro-3-methoxybenzene (18.2 mg, 0.1 mmol, 1.0 equiv.). Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the corresponding product (3.8 mg, 12%) as a colorless liquid.

TLC: R_f = 0.50 (petroleum ether)

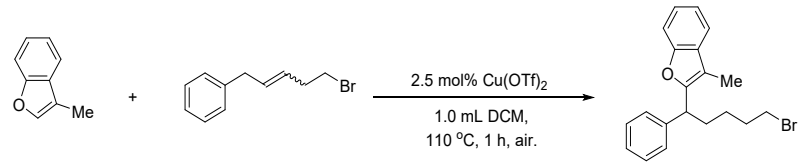
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.36 (m, 2H), 7.22 – 7.12 (m, 2H), 7.10 (t, *J* = 8.1 Hz, 1H), 6.99 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.88 (t, *J* = 7.7 Hz, 1H), 3.67 (s, 3H), 2.57 – 2.38 (m, 1H), 2.33 – 2.15 (m, 1H), 1.99 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.42, 154.79, 153.69, 135.10, 130.95, 128.88, 128.04, 122.86, 122.38, 121.80, 118.51, 110.68, 110.36, 109.94, 56.20, 39.75, 23.51, 12.68, 7.86.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{19}O_2Cl$ $[M]^+$:314.10681, found: 314.10702.

2-(5-bromo-1-phenylpentyl)-3-methylbenzofuran



0.15 mmol 0.1 mmol 25%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and (5-bromopent-2-en-1-yl)benzene (22.5 mg, 0.1 mmol, 1.0 equiv.). Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the corresponding product (10.0 mg, 25%) as a colorless liquid.

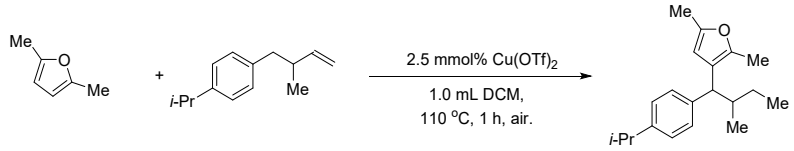
TLC: R_f = 0.70 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.39 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.17 (m, 3H), 4.07 (dd, *J* = 9.4, 6.0 Hz, 1H), 2.37 (ddd, *J* = 12.6, 9.4, 5.9 Hz, 1H), 2.22 – 2.15 (m, 4H), 2.03 – 1.90 (m, 2H), 1.78 (tt, *J* = 9.5, 6.2 Hz, 2H), 1.70 – 1.60 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.93, 154.04, 142.92, 130.46, 128.56, 127.88, 126.54, 123.32, 122.11, 118.93, 110.95, 110.21, 41.57, 41.41, 34.62, 28.40, 28.37, 18.59, 8.09.

3-(1-(4-isopropylphenyl)-2-methylbutyl)-2,5-dimethylfuran



0.15 mmol 0.1 mmol 32%; 1/1 dr

The reaction was performed according to **general procedure A** using 2,5-dimethylfuran (17.3 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.). Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the corresponding product (9.1 mg, 32%) as a colorless liquid.

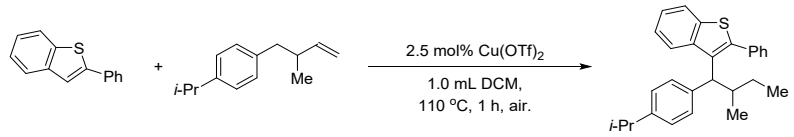
TLC: R_f = 0.70 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 2.1 Hz, 4H), 5.93 (d, *J* = 4.4 Hz, 1H), 3.28 (dd, *J* = 15.6, 10.4 Hz, 1H), 2.88 (dp, *J* = 20.4, 6.8 Hz, 1H), 2.19 (d, *J* = 4.4 Hz, 6H), 2.06 – 1.91 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.11 (td, *J* = 7.6, 3.1 Hz, 1H), 1.03 – 0.92 (m, 1H), 0.91 – 0.73 (m, 6H).

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{28}O$ $[M]^+$: 284.21347, found: 284.21350.

3-(1-(4-isopropylphenyl)-2-methylbutyl)-2-phenylbenzo[b]thiophene



0.15 mmol 0.1 mmol 13%; 1/1 dr

The reaction was performed according to **general procedure A** using 2-phenylbenzo[b]thiophene (31.5 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.). Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the corresponding product (5.2 mg, 13%) as a colorless liquid.

TLC: R_f = 0.70 (petroleum ether)

NMR Spectroscopy (***see spectra***):

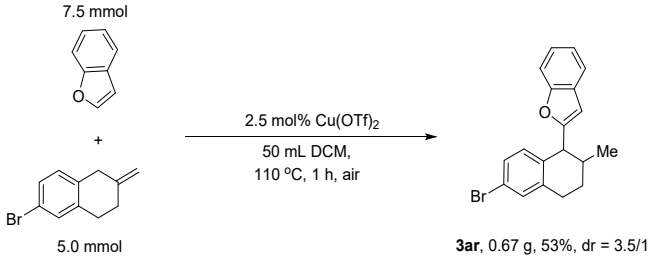
^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (ddd, *J* = 11.5, 10.6, 6.5 Hz, 4H), 7.50 – 7.36 (m, 3H), 7.35 – 7.27 (m, 2H), 7.23 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.17 – 7.07 (m, 2H), 3.60 (d, *J* = 10.8 Hz, 1H), 2.82 (td, *J* = 13.7, 6.8 Hz, 1H), 2.42 – 2.26 (m, 1H), 1.51 – 1.41 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.10 – 1.01 (m, 1H), 0.88 (dt, *J* = 8.2, 7.2 Hz, 6H).

HRMS (EI): m/z Theo. Mass calculated for $C_{28}H_{30}O$ $[M]^+$: 398.20627, found: 398.20621.

6. Gram-scale reactions and product transformations

6.1. Gram-scale reactions (Note: for greater safety, it is recommended to use 1,2-DCE as a solvent for large-scale synthesis under condensate reflux conditions, with no significant change in reaction efficiency)

6.1.1. Gram level reaction for the synthesis of 2-(6-bromo-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran



Preparation procedure: In an oven-dried 150 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (45 mg, 0.125 mmol, 0.025 equiv.), benzofuran (0.89 g, 7.5 mmol, 1.5 equiv.), and 6-bromo-2-methylene-1,2,3,4-tetrahydronaphthalene (3.6 mL, 30 mmol, 3.0 equiv.). Next, DCM (50 mL) was added. Finally, the round bottom flask was installed with a condenser tube under ambient atmosphere and the reaction was stirred and refluxed at 110 °C for 12 hours. After the reaction was completed, it was cooled to room temperature. The reaction mixture was concentrated in vacuo and the residue was further purified by flash column chromatography (silica, petroleum ether as the eluent) to afford product **3ar** (0.67 g, 53%).

TLC: R_f = 0.70 (petroleum ether)

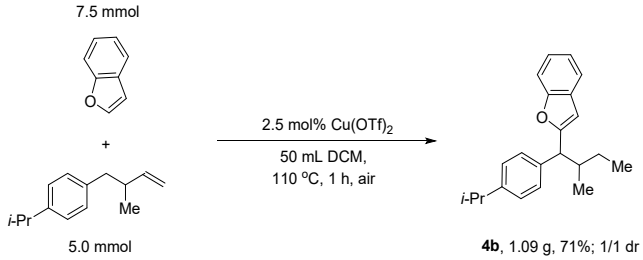
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.42 (m, 1H), 7.38 – 7.30 (m, 2H), 7.25 – 7.06 (m, 3H), 6.99 – 6.84 (m, 1H), 6.42 – 6.19 (m, 1H), 4.00 (m, 1H), 3.02 – 2.75 (m, 2H), 2.41 – 1.77 (m, 2H), 1.76 – 1.55 (m, 1H), 1.02 (dd, *J* = 21.3, 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.45, 155.02, 139.28, 134.98, 132.11, 132.01, 131.89, 131.35, 129.11, 128.96, 128.67, 123.67, 123.50, 122.72, 122.62, 120.56, 120.35, 111.21, 111.14, 105.48, 105.18, 47.15, 44.33, 33.25, 33.04, 29.46, 29.11, 28.27, 26.68, 20.21, 19.49 ppm.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{17}OBr$ $[M]^+$: 340.04573, found: 340.04568.

6.1.2. Gram level reaction for the synthesis of 2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran



Preparation procedure: In an oven-dried 150 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (45 mg, 0.125 mmol, 0.025 equiv.), benzofuran (0.89 g, 7.5 mmol, 1.5 equiv.), and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (0.94 g, 5.0 mmol, 1.0 equiv.). Next, DCM (50 mL) was added. Finally, the round bottom flask was installed with a condenser tube under ambient atmosphere and the reaction was stirred and refluxed at 110 °C for 12 hours. After the reaction was completed, it was cooled to room temperature. The reaction mixture was concentrated in vacuo and the residue was further purified by flash column chromatography (silica, petroleum ether as the eluent) to afford product **4b** (1.09 g, 71%).

TLC: R_f = 0.80 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.41 (m, 2H), 7.38 – 7.28 (m, 2H), 7.25 – 7.13 (m, 4H), 6.52 (d, *J* = 1.3 Hz, 1H), 3.80 (dd, *J* = 9.7, 1.5 Hz, 1H), 2.97 – 2.83 (m, 1H), 2.43 – 2.27 (m, 1H), 1.61 – 1.42 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.22 – 1.05 (m, 1H), 1.02 – 0.85 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.03, 160.98, 154.83, 147.16, 147.13, 138.84, 138.65, 128.94, 128.62, 128.47, 126.54, 126.49, 123.22, 122.52, 120.44, 111.10, 111.09, 102.92, 102.84, 52.19, 52.04, 38.41, 38.35, 33.81, 27.88, 27.22, 24.13, 17.61, 17.32, 11.42, 11.29 ppm.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{26}O$ $[M]^+$: 306.19782, found: 306.19766.

6.2. Synthetic transformation of the products

Incomplete oxidation synthesis of alkene:

2-(6-bromo-2-methyl-3,4-dihydronaphthalen-1-yl)benzofuran (8a)

Prepare according to the modified literature procedure: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged sequentially with 3-(6-bromo-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (34.1 mg, 0.1 mmol, 1.0 equiv.), DDQ (22.7 mg, 0.1 mmol, 1.0 equiv.), and DCM (1.0 mL). The vial was capped under ambient atmosphere, stirred at room temperature for 5 minutes, then placed in an oil bath preheated to 110 °C and stirred for 1 hour.

After the reaction is completed, the reaction mixture was cooled to room temperature, concentrated in vacuo, and the residue was purified by flash column chromatography (silica, petroleum ether as the eluent) to afford a white solid product **8a** (20.7 mg, 61%).

TLC: R_f = 0.60 (petroleum ether)

NMR Spectroscopy (***see spectra***):

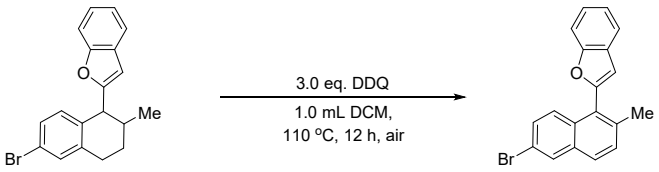
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.58 (m, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.69 (s, 1H), 2.87 (t, *J* = 7.9 Hz, 2H), 2.44 (t, *J* = 7.9 Hz, 2H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.74, 153.63, 142.05, 136.96, 133.92, 130.22, 129.51, 128.72, 126.64, 124.13, 123.83, 122.88, 120.91, 120.14, 111.40, 107.32, 30.62, 27.64, 22.02.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{15}BrO$ $[M]^+$: 338.03008, found: 338.03005.

Complete oxidative aromatization to construct naphthalene ring:

2-(6-bromo-2-methylnaphthalen-1-yl)benzofuran (8a*)



0.1 mmol **8a***, 73%

Prepare according to the modified literature procedure: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged sequentially with 3-(6-bromo-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (34.1 mg, 0.1 mmol, 1.0 equiv.), DDQ (68.1 mg, 0.3 mmol, 3.0 equiv.), and DCM (1.0 mL). The vial was capped under ambient atmosphere, stirred at room temperature for 5 minutes, then placed in an oil bath preheated at 110 °C and stirred for 1 hour. After the reaction is completed, the reaction mixture was cooled to room temperature, concentrated in vacuo, and the residue was purified by flash column chromatography (silica, petroleum ether as the eluent) to afford a white solid product (24.6 mg, 73%).

TLC: R_f = 0.60 (petroleum ether)

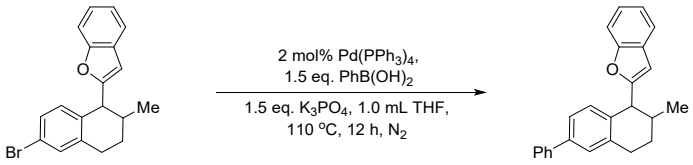
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 1.9 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.41 – 7.30 (m, 2H), 6.86 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.19, 153.25, 137.47, 133.16, 131.82, 130.04, 129.96, 129.79, 128.76, 128.60, 127.57, 127.26, 124.40, 123.10, 121.13, 119.46, 111.52, 107.96, 20.98.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{13}BrO$ $[M]^+$: 336.01443, found: 336.01437.

2-(2-methyl-6-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (8b)



0.1 mmol **8b**, 58%

Prepare according to the modified literature procedure: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with 3-(6-bromo-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (34.1 mg, 0.1 mmol, 1.0 equiv.), 2.0 mol% $Pd(PPh_3)_4$ (18.8 mg, 0.002 mmol), $PhB(OH)_2$ (18.3 mg, 0.15 mmol, 1.5 equiv.), and K_3PO_4 (31.8 mg, 0.15 mmol, 1.5 equiv.), THF (1. 0 mL). The vial was capped under N_2 atmosphere, placed in an oil bath preheated at 110 °C and stirred for 12 hours, After the reaction is completed, the reaction mixture was cooled to room temperature and purified directly by flash column chromatography (silica, petroleum ether as the eluent) to afford the title compound **8b** (19.6 mg, 58%).

TLC: R_f = 0.40 (petroleum ether)

NMR Spectroscopy (***see spectra***):

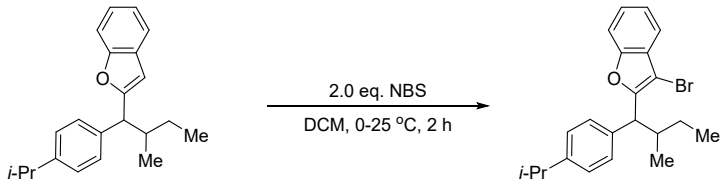
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.50 (m, 3H), 7.50 – 7.38 (m, 4H), 7.38 – 7.27 (m, 2H), 7.25 – 7.15 (m, 2H), 7.12 – 7.01 (m, 1H), 6.50 – 6.26 (m, 1H), 4.33 – 4.19 (m, 1H), 3.14 – 2.90 (m, 2H), 2.49 – 1.85 (m, 2H), 1.83 – 1.58 (m, 1H), 1.07 (dd, *J* = 23.3, 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.07, 161.00, 155.05, 154.86, 141.16, 139.57, 139.47, 137.36, 137.26, 136.02, 135.15, 130.92, 129.97, 128.81, 127.89, 127.86, 127.22, 127.18, 124.87, 124.71, 123.52, 123.34, 122.64, 122.54, 120.52, 120.48, 111.24, 111.15, 105.39, 105.09, 47.47, 44.54, 33.61, 33.27, 30.08, 29.44, 28.78, 27.15, 20.42, 19.57.

HRMS (EI): m/z Theo. Mass calculated for $C_{25}H_{22}O$ $[M]^+$: 338.16652, found: 338.16670.

3-bromo-2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran (8c)

Bromination method I:

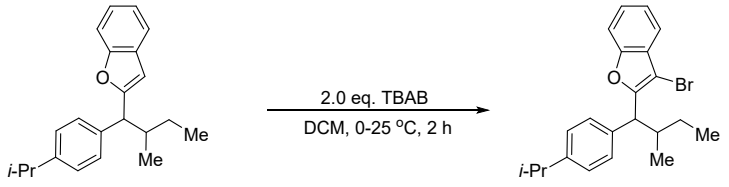


0.2 mmol **8c,** 30%

Prepare according to the modified literature procedure (I): 1-(1-phenylethyl)3-methylbenzofuran (0.2 mmol, 1.0 equiv.) was dissolved in 1 mL DCM and the solution was cooled down to 0 °C. NBS (0.4 mmol, 2.0 equiv.) was added portionwise, and the mixture was stirred at room temperature for 2 h. After the reaction is completed, the mixture was diluted with ethyl acetate, washed three times with saturated aqueous solution of $NaHCO_3$, then washed with brine and dried over anhydrous Na_2SO_4. The organic phase was evaporated under reduced pressure and the residue was purified by silica gel column

chromatography eluting with a gradient of petroleum ether/ ethyl acetate = 10/1, v/v. The fractions containing the product were evaporated under reduced pressure to give the corresponding product **8c** (23.2 mg, 30%) as a white solid.

Bromination method II:



0.2 mmol **8c,** 54%

Prepare according to the modified literature procedure (II): 1-(1-phenylethyl)3-methylbenzofuran (0.2 mmol, 1.0 equiv.) was dissolved in 1 mL DCM and the solution was cooled down to 0 °C. Then tetra butyl ammonium bromide (TBAB) (0.4 mmol, 2.0 equiv.) was added portionwise, and the mixture was stirred at room temperature for 2 h. After the reaction is completed, the mixture was diluted with ethyl acetate, washed three times with saturated aqueous solution of $NaHCO_3$, then washed with brine and dried over anhydrous Na_2SO_4. The organic phase was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (silica, petroleum ether as the eluent) to give the corresponding product **8c** (41.6 mg, 54%) as a white solid.

TLC: R_f = 0.65 (petroleum ether)

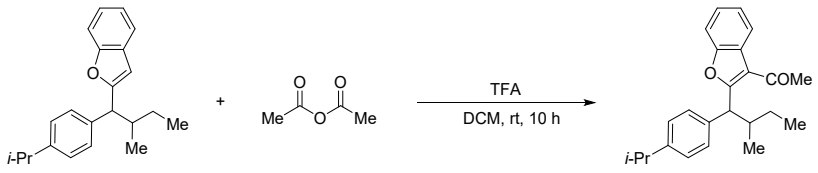
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.31 (m, 4H), 7.29 – 7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.97 (dd, *J* = 16.2, 10.8 Hz, 1H), 2.95 – 2.76 (m, 1H), 2.54 – 2.35 (m, 1H), 1.49 – 1.39 (m, 1H), 1.22 (dd, *J* = 6.9, 0.6 Hz, 6H), 1.17 – 1.06 (m, 1H), 0.92 – 0.83 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.54, 156.47, 153.76, 153.74, 147.37, 137.87, 137.71, 128.50, 128.48, 126.67, 124.53, 123.23, 119.43, 119.39, 111.47, 111.43, 95.09, 95.04, 49.91, 49.77, 37.92, 37.73, 33.82, 27.49, 27.17, 24.10, 17.37, 17.21, 11.09, 10.98 ppm.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{25}BrO$ $[M]^+$: 384.10833, found: 384.10805.

1-(2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran-3-yl)ethan-1-one (8d)



0.2 mmol **8d,** 68%

Prepare according to the modified literature procedure: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with 1-(1-phenylethyl)3-methylbenzofuran (50.2 mg, 0.2 mmol, 1.0 equiv.) and DCM (0.5 mL) under ambient atmosphere. An

aqueous solution of TFA was added dropwise, the reaction was stirred at room temperature for 10 hours. After the reaction is completed, then saturated $NaHCO_3$ (0.3 mL) was added and stirring for approximately 10 minutes, and then the aqueous phase was extracted with ethyl acetate. The combined organic layers were passed through a plug of anhydrous Na_2SO_4 and concentrated in vacuo. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the corresponding product **8d** (47.4 mg, 68%).

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.75 (m, 1H), 7.60 – 7.49 (m, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.30 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.81 (t, *J* = 10.9 Hz, 1H), 2.93 – 2.80 (m, 1H), 2.69 (d, *J* = 3.0 Hz, 3H), 2.59 – 2.44 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.18 – 1.07 (m, 1H), 1.07 – 0.91 (m, 1H), 0.87 (dd, *J* = 12.0, 6.3 Hz, 6H).

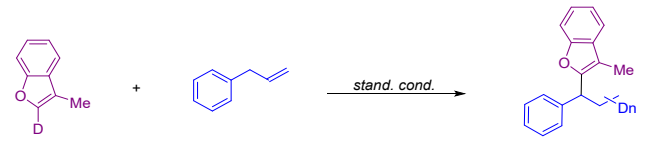
^{13}C NMR (100 MHz, $CDCl_3$): δ 194.45, 194.41, 167.15, 153.95, 153.93, 147.49, 137.89, 137.72, 128.85, 126.67, 126.00, 125.97, 124.44, 123.98, 121.44, 121.42, 117.68, 111.59, 111.54, 50.27, 50.09, 38.26, 38.23, 33.81, 31.85, 27.85, 27.04, 24.06, 17.41, 17.33, 11.07, 10.97.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{28}O_2$ $[M]^+$: 348.20838, found: 348.20830.

7. Preliminary mechanistic investigation

a. Substrate deuterium labeling experiments

a1. Deuterated benzofuran tracking experiments



83% D, 0.15 mmol 0.1 mmol 61% (total < 5% D)

The reaction was performed according to **general procedure A** using 3-methylbenzofuran-2-d (20.0 mg, 0.15 mmol, 1.5 equiv.) and allylbenzene (11.8 mg, 0.10 mmol, 1.0 equiv.) as substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the deuterated product (15.3 mg, 61%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

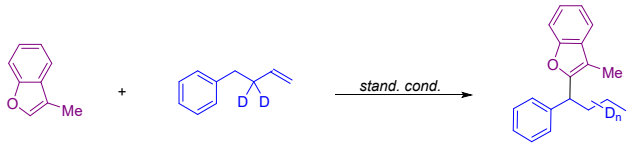
NMR and HRMS Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.33 (m, 4H), 7.33 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 4.02 (dd, *J* = 8.9, 6.8 Hz, 1H), 2.31 – 2.16 (m, 4H), 2.16 – 2.04 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.85, 154.11, 142.85, 130.49, 128.57, 127.92, 126.58, 123.32, 122.10, 118.93, 110.95, 110.52, 45.43, 27.52, 12.77, 8.10 ppm.

HRMS (APCI): m/z Theo. Mass calculated for $C_{18}H_{19}O$ $[M+H]^+$: 521.14304, found: 251.14291. m/z Theo. Mass calculated for $C_{18}H_{18}DO$ $[M+H]^+$: 252.14931, found: 2512.14941.

a2. Deuterated alkene tracking experiments



0.15 mmol 64% D, 0.1 mmol 50% (n = 1-3, mixtures)

The reaction was performed according to **general procedure A** using 3-methylbenzofuran-2-d (14.6 mg, 0.1 mmol, 1.0 equiv.) and allylbenzene (13.4 mg, 0.15 mmol, 1.5 equiv.) as substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the deuterated products (13.2 mg, 50%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

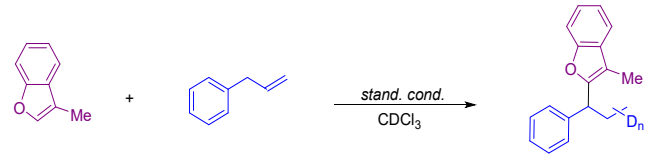
NMR and HRMS Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.38 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.18 (m, 3H), 4.18 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.30 – 2.19 (m, 4H), 2.15 – 2.00 (m, 1H), 1.32 (dq, *J* = 14.5, 7.2 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.02, 154.09, 142.99, 130.48, 128.58, 127.90, 126.55, 123.31, 122.10, 118.93, 110.95, 110.29, 43.27, 43.19, 36.52, 36.43, 21.24, 21.14, 14.03, 14.01, 8.10 ppm.

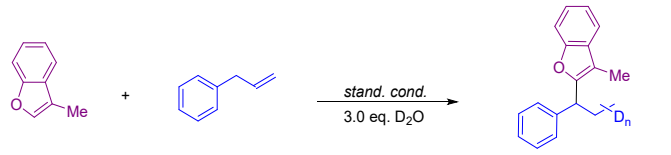
HRMS (ESI): m/z Theo. Mass calculated for $C_{19}H_{21}O$ $[M+H]^+$: 265.15889, found: 265.15833. m/z Theo. Mass calculated for $C_{19}H_{20}DO$ $[M+H]^+$: 266.16497, found: 266.16473. m/z Theo. Mass calculated for $C_{19}H_{19}D_2O$ $[M+H]^+$: 267.17125, found: 267.17099. m/z Theo. Mass calculated for $C_{19}H_{18}D_3O$ $[M+H]^+$: 268.17752, found: 268.17749.

b. Environmental deuterium source experiments



0.15 mmol 0.1 mmol 65% (0% D)

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (14.6 mg, 0.1 mmol, 1.0 equiv.) and allylbenzene (69 μL, 0.15 mmol, 1.5 equiv.) as substrates, 1.0 mL of $CDCl_3$ was added instead of DCM as solvent. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the deuterated product (16.3 mg, 65%) as a colorless liquid. **TLC**: R_f = 0.75 (petroleum ether)



0.15 mmol 0.1 mmol 63% (n = 1-7, mixtures)

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (14.6 mg, 0.1 mmol, 1.0 equiv.), allylbenzene (0.15 mmol, 1.5 equiv.) and D_2O (0.3 mmol, 3.0 equiv.). Purification by flash column chromatography (silica, petroleum ethe as an eluent) afforded multiple deuterium mixed products (15.8 mg, 63%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR and HRMS Spectroscopy (***see spectra***):

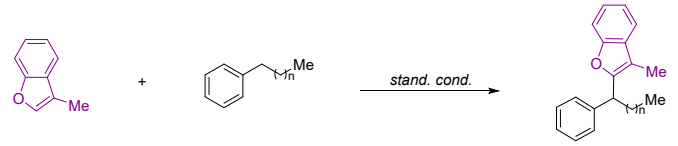
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.27 (m, 6H), 7.20 (q, *J* = 7.2 Hz, 3H), 4.03 (dd, *J* = 8.9, 6.6 Hz, 1H), 2.32 – 2.22 (m, 1H), 2.22 – 2.16 (m, 3H), 2.16 – 2.06 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.86, 154.12, 142.85, 128.57, 127.92, 126.57, 123.32, 123.21, 122.10, 121.99, 118.93, 118.82, 110.95, 110.84, 110.52, 45.44, 45.36, 27.52, 27.43, 12.77, 12.67, 8.10, 7.91 ppm.

HRMS (ESI): m/z Theo. Mass calculated for $C_{18}H_{18}D_1O$ $[M+H]^+$: 252.17931, found: 252.17911. m/z Theo. Mass calculated for $C_{18}H_{17}D_2O$ $[M+H]^+$: 253.15560, found: 253.15530. m/z Theo. Mass calculated for $C_{18}H_{16}D_3O$ $[M+H]^+$: 254.16181, found: 254.16165. m/z Theo. Mass calculated for $C_{18}H_{15}D_4O$ $[M+H]^+$: 255.16815, found: 255.16791. m/z Theo. Mass calculated for $C_{18}H_{14}D_5O$ $[M+H]^+$: 256.17443, found: 256.17426. m/z Theo. Mass calculated for $C_{18}H_{13}D_6O$ $[M+H]^+$: 257.18070, found: 257.18057. m/z Theo. Mass calculated for $C_{18}H_{12}D_7O$ $[M+H]^+$: 258.18698, found: 258.18695.

c. Control and possible intermediate experiments

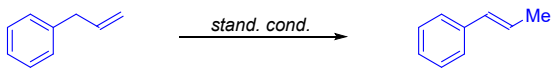
c1. Control experiments of alkylbenzenes



0.15 mmol 0.1 mmol (n = 1, 2) N. D.

In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol), 3-methylbenzofuran (0.15 mmol, 1.5 equiv.), and 1-phenylpropane (or 1-phenylbutane) (0.1 mmol, 1.0 equiv.). Next, DCM (1.0 mL) was added. Finally, the reaction vial was capped under ambient atmosphere and the reaction was stirred at 110 °C for 1 hour. After the reaction is completed, cool it to room temperature. No target reaction product was detected by TLC and HRMS analysis.

c2. Control experiment of alkene isomerization



0.1 mmol NMR yield: 23%

In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol), allylbenzene (0.1 mmol, 1.0 equiv.). Next, the solvent DCM (1.0 mL) was added. Finally, the reaction vial was capped under ambient atmosphere and the reaction was stirred at 110 °C for 1 hour. After the reaction is completed, cool it to room temperature. The reaction mixture was filtrated and concentrated in vacuo. By NMR analysis, 23% of alkene isomerization was detected.

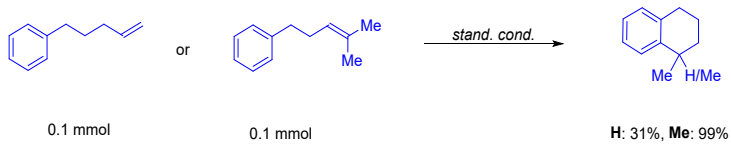
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 10H), 7.21 (t, J = 6.7 Hz, 10H), 6.42 (d, J = 15.8 Hz, 1H), 6.25 (dq, J = 15.6, 6.5 Hz, 1H), 6.04 – 5.94 (m, 3H), 5.16 – 4.98 (m, 5H), 3.41 (d, J = 6.6 Hz, 5H), 1.94 – 1.81 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.30, 137.57, 131.29, 128.83, 128.71, 128.68, 128.66, 126.97, 126.30, 126.07, 125.91, 115.84, 77.58, 77.26, 76.94, 40.49, 18.71 ppm.

All recorded spectroscopic data match those previously reported in the literature.[6]

c3. Friedel-Crafts-type cyclization experiments



In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol) and pent-4-en-1-ylbenzene (or (4-methylpent-3-en-1-yl)benzene) (0.1 mmol, 1.0 equiv.). Next, DCM (1.0 mL) was added. Finally, the reaction vial was capped under ambient atmosphere and the reaction was stirred at 110 °C for 1 hour. After the reaction is completed, cool it to room temperature. The reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography using the specified conditions to afford the products.

TLC: R_f = 0.90 (petroleum ether)

NMR Spectroscopy (***see spectra***):

H: 1-methyl-1,2,3,4-tetrahydronaphthalene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 1H), 7.23 – 7.11 (m, 3H), 2.97 (dt, *J* = 13.3, 6.5 Hz, 1H), 2.91 – 2.74 (m, 2H), 2.07 – 1.88 (m, 2H), 1.86 – 1.73 (m, 1H), 1.68 – 1.57 (m, 1H), 1.37 (d, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.39, 137.07, 129.22, 128.29, 125.83, 125.62, 77.58, 77.26, 76.94, 32.70, 31.74, 30.22, 23.09, 20.68 ppm.

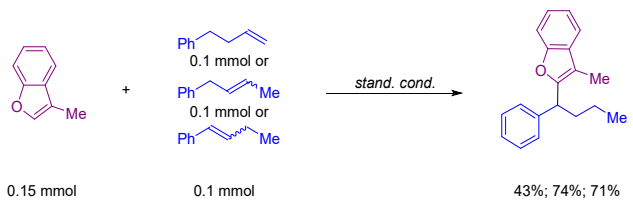
Me: 1,1-dimethyl-1,2,3,4-tetrahydronaphthalene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.21 – 7.13 (m, 1H), 7.13 – 7.03 (m, 2H), 2.80 (t, *J* = 6.3 Hz, 2H), 1.91 – 1.77 (m, 2H), 1.75 – 1.63 (m, 2H), 1.32 (s, 6H) ppm.

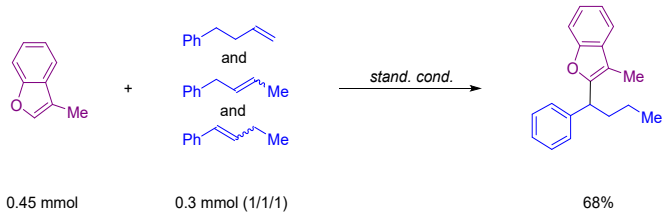
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.94, 136.25, 129.18, 126.75, 125.93, 125.37, 39.49, 33.97, 32.02, 30.90, 19.88 ppm.

All recorded spectroscopic data match those previously reported in the literature.[7]

d. Reaction of mixed alkenes



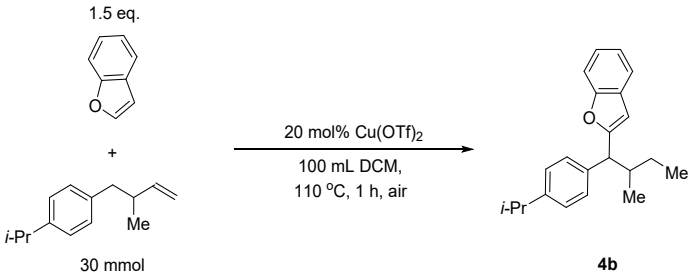
The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and but-3-en-1-ylbenzene (or but-2-en-1-ylbenzene or but-1-en-1-ylbenzene) (14 μL, 0.1 mmol, 1.0 equiv.) as subatrates and $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol). Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the corresponding product (11.4 mg, 43%; 19.5 mg, 74%; 18.4 mg, 71%) as a colorless liquid. **TLC**: R_f = 0.75 (petroleum ether).



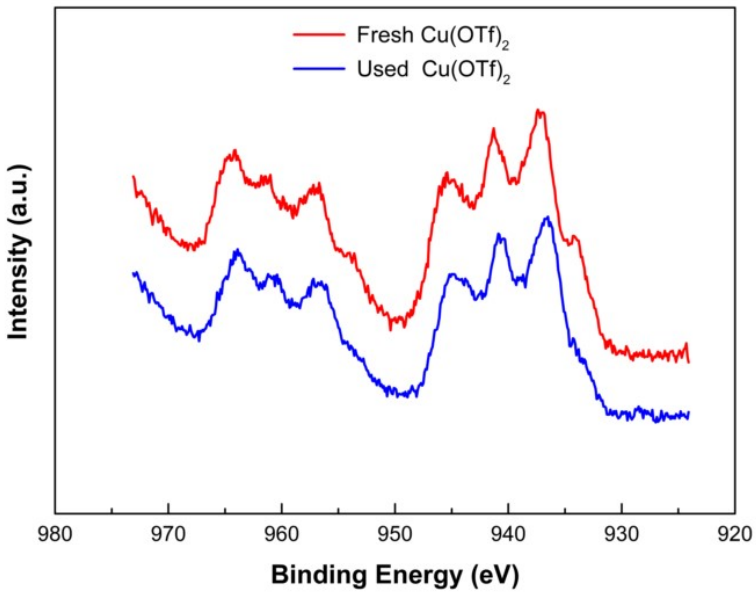
The reaction was performed according to **general procedure A** using 3-methylbenzofuran (59.4 mg, 0.45 mmol, 1.5 equiv.), but-3-en-1-ylbenzene (14 μL, 0.1 mmol, 1.0 equiv.), but-2-en-1-ylbenzene (14 μL, 0.1 mmol, 1.0 equiv.), but-1-en-1-ylbenzene, (14 μL, 0.1 mmol, 1.0 equiv.) and $Cu(OTf)_2$ (2.7 mg, 0.0075 mmol). Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded the product (53.9 mg, 68%) as a colorless liquid. **TLC**: R_f = 0.75 (petroleum ether).

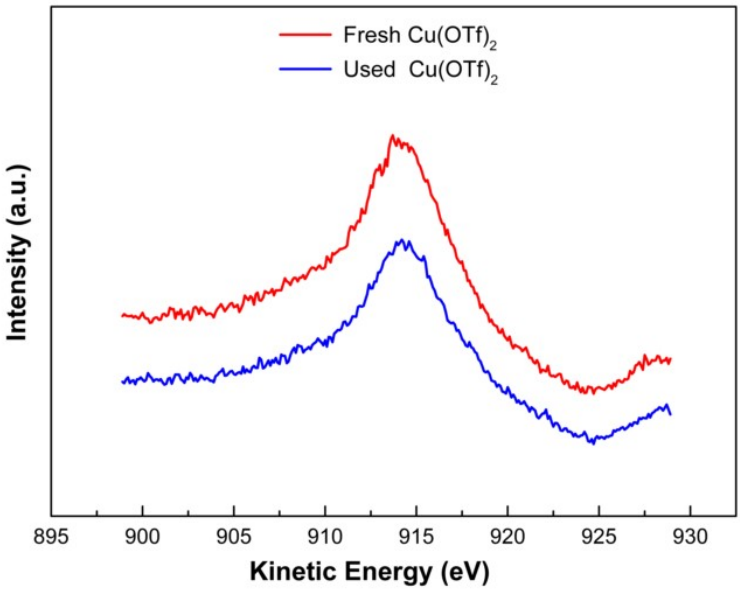
e. The tested XPS spectrogram of Cu2p and CuLMM

Test procedure for the used copper catalyst:

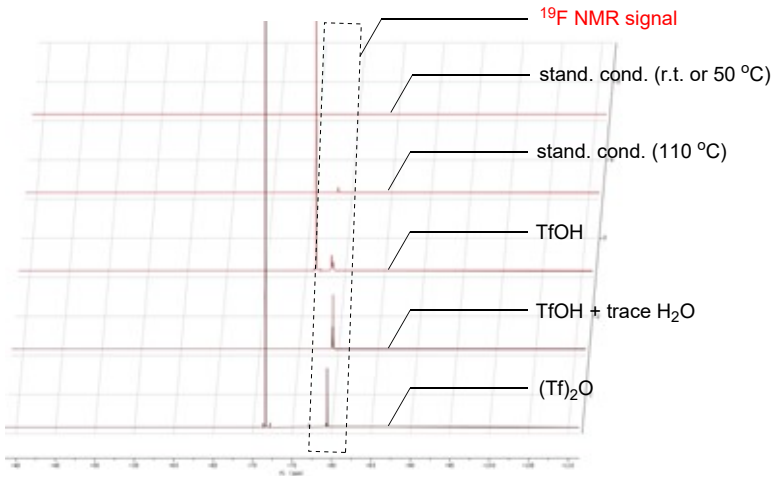


In an oven-dried 250 mL bottomed flask equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (180 mg, 5.0 mmol, 0.2 equiv.), benzofuran (5.3 g, 45 mmol, 1.5 equiv.), and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (3.6 mL, 30 mmol, 1.0 equiv.). Next, DCM (100 mL) was added. Finally, the round bottom flask was installed with a condenser tube under ambient atmosphere. The reaction was stirred and refluxed at 110 °C for 1 hour. After the reaction was completed, it was cooled to room temperature. Filter out the copper catalyst with filter paper for drying, and then immediately take it for XPS testing and the results are as follows:





f. Nuclear magnetic resonance fluorine spectroscopy detection



Sample preparation conditions and spectra testing:

Sample (5) preparation process: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol, 0.025 equiv.), 3-methylbenzofuran (0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (0.1 mmol, 1.0 equiv.) under air atmosphere. Next, DCE (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature and the reaction was stirred at room temperature or 50 °C for 12 hours. After the reaction is completed, cool it to room temperature, and then take a small amount of the reaction solution and filter it through a membrane filtra to prepare the NMR test sample.

Sample (4) preparation process: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol, 0.025 equiv.), 3-methylbenzofuran (0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (0.1 mmol, 1.0 equiv.) under air atmosphere. Next, DCE (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature and the reaction was stirred at 110 °C for 1 hour. After the reaction is completed, cool it to room temperature, and then take a small amount of the reaction solution and filter it through a membrane filtra to prepare the NMR test sample.

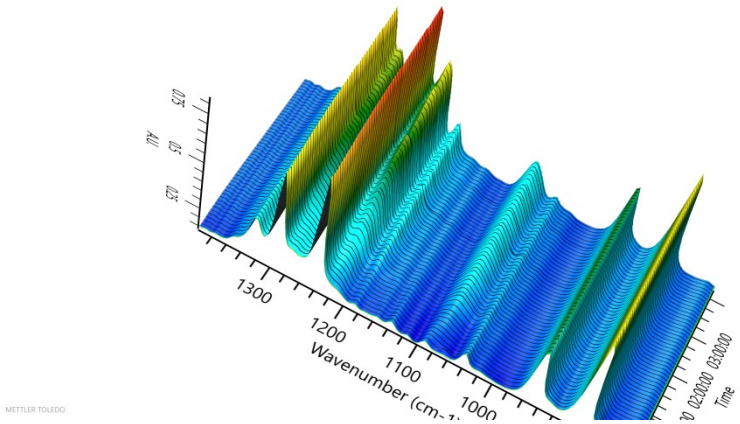
Sample (3) production process: TfOH was charged into a sample tube containing DCE, took a small amount of the resulting solution to a nuclear magnetic resonance tube for testing.

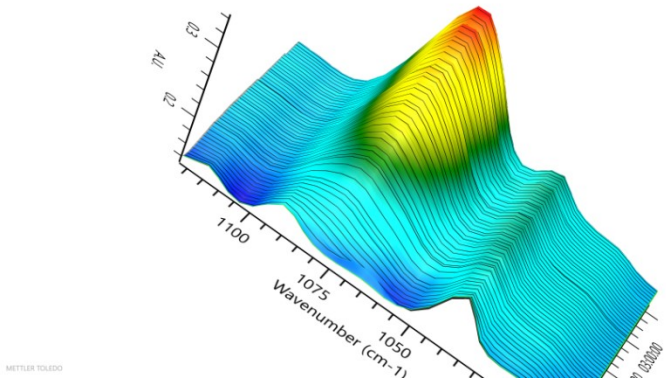
Sample (2) production process: TfOH was charged into a sample tube containing DCE, then trace H_2O was added, eventually a small amount of the resulting solution was taken to a nuclear magnetic resonance tube for testing.

Sample (1) production process: Tf_2O was charged into a sample tube containing DCE, a small amount of the resulting solution was then taken to a nuclear magnetic resonance tube for testing.

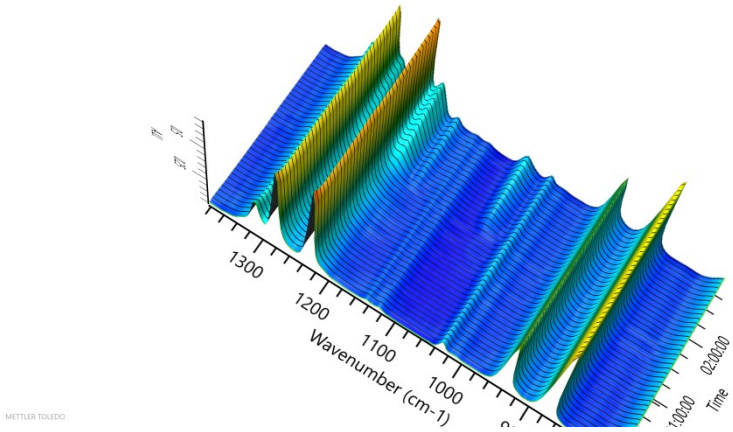
The *in situ* fourier-transform infrared (FT-IR) of 3D spectrogram

(a): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, were charged with $Cu(OTf)_2$, benzofuran, and alkene (1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene) under air atmosphere. Next, DCE was added. One neck was connected to a condenser tube for reflux, and the other was connected to an in-situ infrared test probe. Finally, the flask with a reflux device was put in an oil bath. Detect the reaction process and the recorded in-situ FT-IR spectra are as follows:

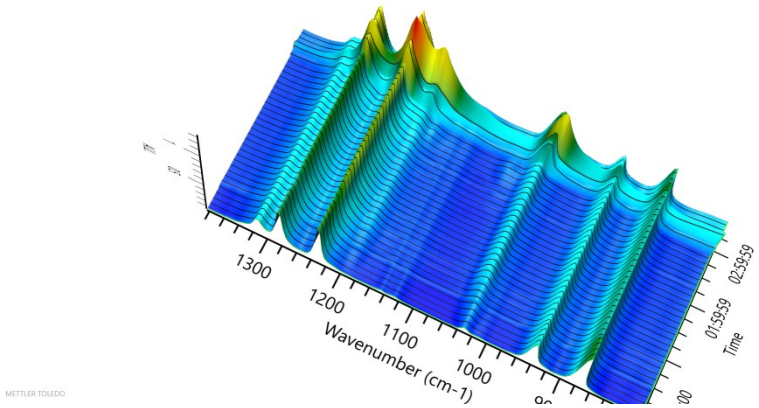




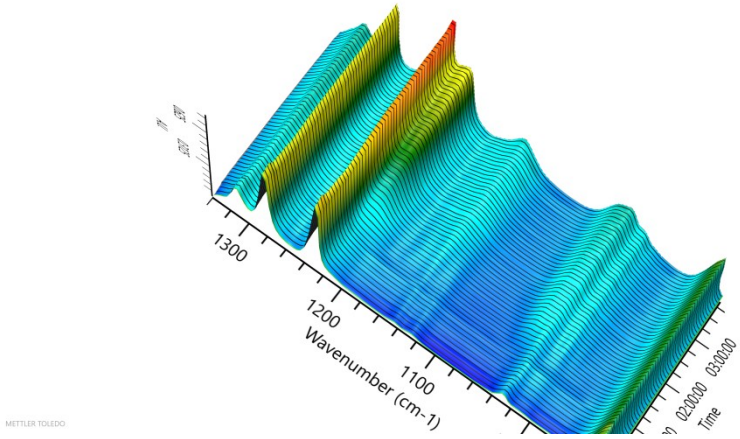
(b): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, was charged with $Cu(OTf)_2$ under air atmosphere. Next, DCE was added. One neck was connected to a condenser tube for reflux, and the other was connected to an in-situ infrared test probe. Finally, the flask was put in an oil bath with a reflux device. The recorded FT-IR spectra are as follows:



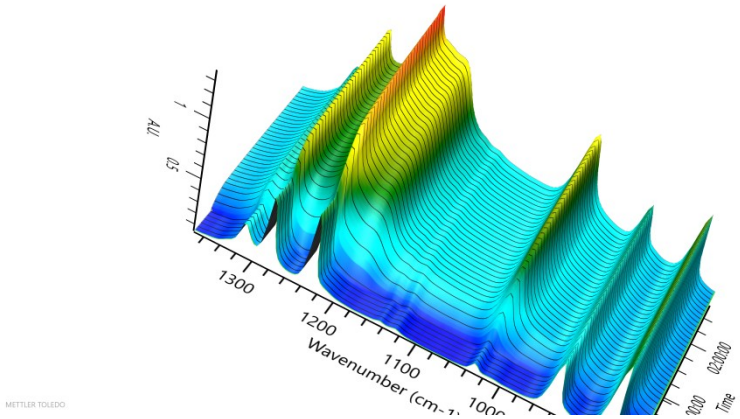
(c): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, was charged with CuOTf under air atmosphere. Next, DCE was added. One neck is connected to a condenser tube for reflux, and the other was connected to an in-situ infrared test probe. Finally, the flask was put in an oil bath with a reflux device. The recorded FT-IR spectra are as follows:



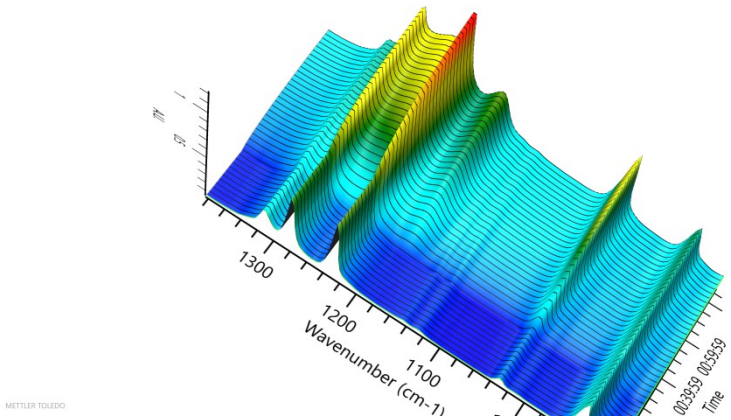
(d): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, was charged with $Bi(OTf)_3$ under air atmosphere. Next, DCE was added. One neck was connected to a condenser tube for reflux, and the other was connected to an in-situ infrared test probe. Finally, the flask was put in an oil bath with a reflux device. The recorded FT-IR spectra are as follows:



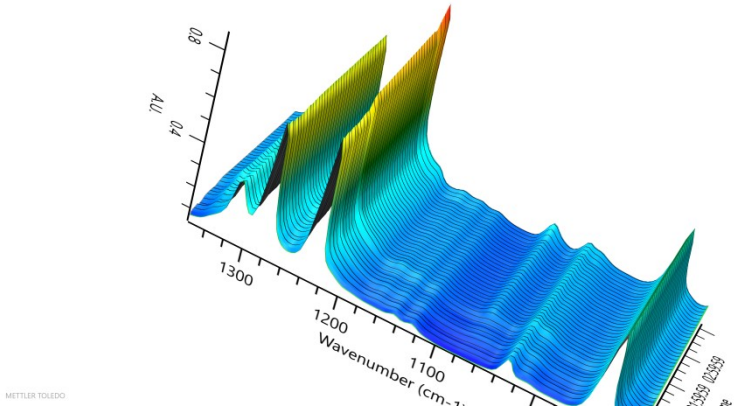
(e): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, was charged with Tf_2O under air atmosphere. Next, DCE was added. One neck was connected to a condenser tube for reflux, and the other was connected to an in-situ infrared test probe. Finally, the flask was put in an oil bath with reflux. The recorded FT-IR spectra are as follows.



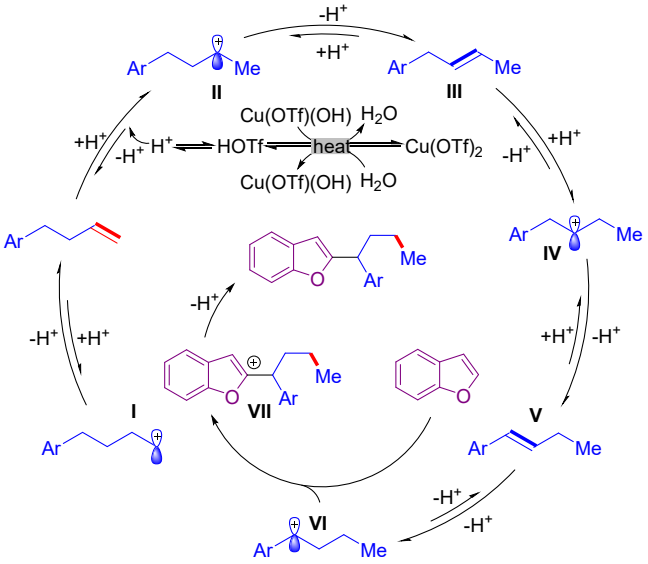
(f): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, was charged with TfOH under air atmosphere. Next, DCE was added. One neck was connected to a condenser tube for reflux, and the other port was connected to an in-situ infrared test probe. Finally, the flask was put in an oil bath with a reflux device. The recorded FT-IR spectra are as follows:



(g): Experiment procedure: In an oven-dried 100 mL two necked round bottomed flask equipped with a magnetic stirring bar, was charged with $Fe(OTf)_3$ under air atmosphere. Next, DCE was added. One neck was connected to a condenser tube for reflux, and the other was connected to an in-situ infrared test probe. Finally, the flask was put in an oil bath with a reflux device. The recorded FT-IR spectra are as follows:



Possible mechanism pathway



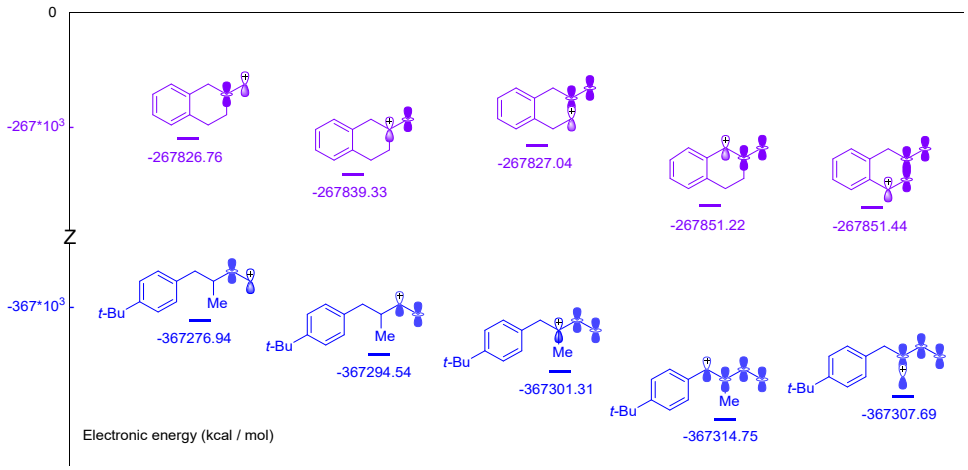
The reaction mechanism is suggested that Initially, $Cu(OTf)_2$ is activated *in situ* to generate TfOH by trace amounts of H_2O in the system, and then the resulting TfOH continues to react with the alkene substrate to form carbocation intermediate Ⅰ and Ⅱ. After undergoing Wagner–Meerwein type rearrangement, a variety of carbocation intermediates (Ⅳ, Ⅵ) and alkene isomers (Ⅲ, Ⅴ) are formed, among which the most stable styrene type Ⅵ is favourable. Then intermediate Ⅵ reacts with benzofuran, similar to the Friedel-Crafts type alkylation, to produce intermediate Ⅶ. Finally, intermediate Ⅶ loses H^+ and aromatizes to obtain the target product, and H^+ continues to participate in the next catalytic cycle.

8. Carbocation electron energy calculation studies

8.1. Computational methods

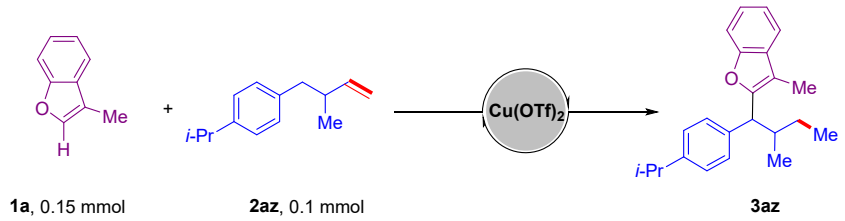
Carbocation electron energy calculations used the Gaussian 09 program. Geometry optimization calculations were performed at the B3LYP-D3 level of theory; the SDD effective core potential basis set was used for Br and Y and the 6-31G (d,p) basis set used for other atoms. Frequency calculations were performed at the same level. Single-point energy calculations were performed at the M06L, SMD (chloroform)/SDD (Br, Y), 6-311+G (d, p) level of theory. The calculation process was linked to The National Supercomputing Center in Guangzhou, Sun Yat-sen University.

8.2. Calculation of carbocation electron energy



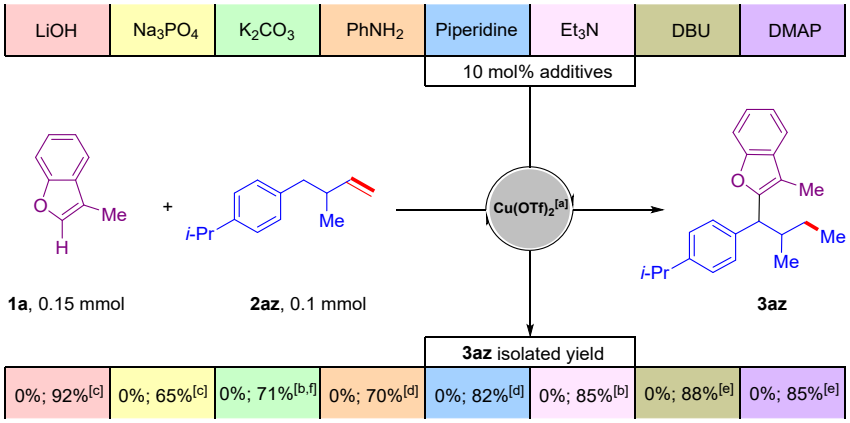
9. In-situ quenching experiments of active intermediates

9.1 Control experiments of quenching



General Procedure: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol, 0.025 equiv.), K_2CO_3 or DMAP (10 mol%, 0.1 equiv.), 3-methylbenzofuran (0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (0.1 mmol, 1.0 equiv.) under air atmosphere. Next, DCM (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature and the reaction was stirred at 110 °C for 48 hours. After the reaction is completed, cool it to room temperature, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography using petroleum ether as an eluent, but no target product was obtained.

9.2 Quenching experiments



[a]: 0.15 mmol **1a**, 0.1 mmol **2az**, 2.5 mol% $Cu(OTf)_2$, 10 mol% additives, 0.1 M DCM, 110 °C, 12 h in a sealed tube under air; [b-e]: supplement [b]100 mol%, or [c]40 mol%, or [d]20 mol%, or [e]12.5 mol% $Cu(OTf)_2$, 110 °C, 4 h; [f]: add trace H_2O, 110 °C, 12 h. (Piperidine = hexahydropyridine; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DMAP = 4-dimethylaminopyridine; unless otherwise specified, all data are isolated yields)

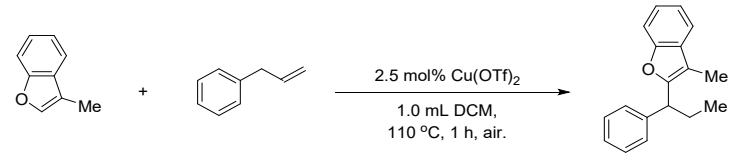
General Procedure **[a]**: In an oven-dried 15 mL pressure-resistant reaction tube equipped with a magnetic stirring bar were charged with $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol, 0.025 equiv.), bases including organic and inorganic bases (10 mol%, as shown in the above scheme), **1a** (0.15 mmol, 1.5 equiv.), and **2az** (0.1 mmol, 1.0 equiv.) under air atmosphere. Next, DCM (1.0 mL) was added. Finally, the tube was closed with a cap and put in an oil bath with preset temperature and the reaction was stirred at 110 °C for 12 hours. After the reaction is completed, cool it to room temperature, the reaction mixture was purified by flash column chromatography using petroleum ether as an eluent, and the target product was not afforded.

General Procedure **[b-e]**: Add [b]100 mol% or [c]40 mol% or [d]20 mol% or [e]12.5 mol% $Cu(OTf)_2$ to the reaction tube treated according to ***General Procedure*** **[a]**, then the tube was closed with a cap and put in an oil bath at preset temperature and the reaction was stirred at 110 °C for 4 hours. After the reaction is completed, cool it to room temperature, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography using petroleum ether and ethyl acetate as an eluent to afford the target product.

General Procedure **[f]**: Add trace H_2O to the reaction tube without reaction in ***General Procedure*** **[b]**, then the tube was closed with a cap and put in an oil bath at preset temperature and the reaction was stirred at 110 °C for 12 hours. After the reaction is completed, cool it to room temperature, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography using petroleum ether and ethyl acetate as eluents to afford the target product.

10. Experimental and characterization details

3-methyl-2-(1-phenylpropyl)benzofuran (3a) (*see substrate list*)



The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and allylbenzene (11.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3a** (16.1 mg, 64%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

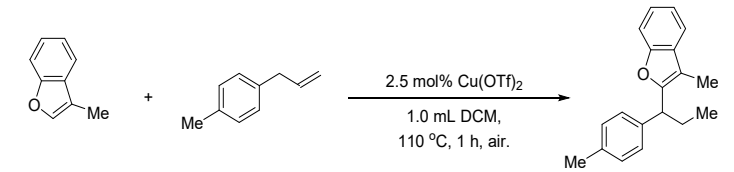
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.42 (m, 2H), 7.43 – 7.38 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 4.05 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.23 (s, 3H), 2.19 – 2.09 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.95, 154.21, 142.94, 130.59, 128.67, 128.02, 126.68, 123.42, 122.21, 119.03, 111.04, 110.62, 45.54, 27.61, 12.87, 8.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{18}O$ $[M]^+$: 250.13522, found: 250.13533.

3-methyl-2-(1-(p-tolyl)propyl)benzofuran (3b) (*see substrate list*)



The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-methylbenzene (13.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3b** (22.4 mg, 85%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

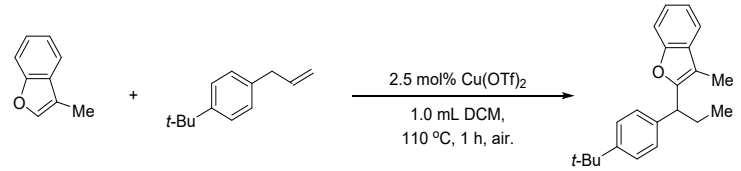
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.37 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.15 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.00 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.31 (s, 3H), 2.29 – 2.21 (m, 1H), 2.20 (s, 3H), 2.16 – 2.02 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.04, 154.06, 139.82, 136.09, 130.49, 129.25, 127.76, 123.23, 122.04, 118.89, 110.93, 110.34, 44.94, 27.51, 21.15, 12.79, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O$ $[M]^+$: 264.15087, found: 264.1514.

2-(1-(4-(tert-butyl)phenyl)propyl)-3-methylbenzofuran (3c) (*see substrate list*)



0.15 mmol 0.1 mmol 51%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-(tert-butyl)benzene (17.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3c** (15.6 mg, 51%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

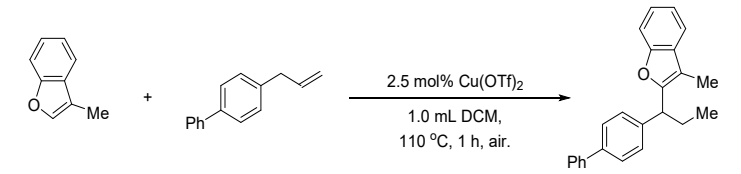
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.39 (m, 2H), 7.35 – 7.28 (m, 4H), 7.25 – 7.15 (m, 2H), 4.01 (dd, *J* = 9.4, 6.3 Hz, 1H), 2.34 – 2.18 (m, 4H), 2.17 – 2.03 (m, 1H), 1.30 (s, 9H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.02, 154.07, 149.26, 139.77, 130.49, 127.47, 125.43, 123.23, 122.04, 118.89, 110.92, 110.43, 44.82, 34.50, 31.50, 27.49, 12.83, 8.15.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{26}O$ $[M]^+$: 306.19782, found: 306.19790.

2-(1-([1,1'-biphenyl]-4-yl)propyl)-3-methylbenzofuran (3d) (*see substrate list*)



0.15 mmol 0.1 mmol 77%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 4-allyl-1,1'-biphenyl (19.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash chromatography (silica, petroleum ether as the eluent) afforded **3d** (25.1 mg, 77%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

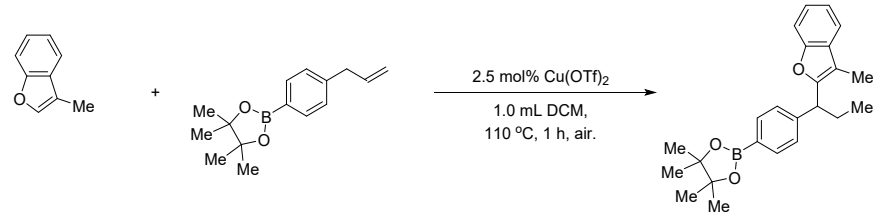
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.52 (m, 4H), 7.51 – 7.40 (m, 6H), 7.38 – 7.31 (m, 1H), 7.30 – 7.18 (m, 2H), 4.11 (dd, *J* = 9.2, 6.5 Hz, 1H), 2.40 – 2.28 (m, 1H), 2.27 (s, 3H), 2.24 – 2.12 (m, 1H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.68, 154.11, 141.90, 141.08, 139.51, 130.44, 128.83, 128.30, 127.32, 127.21, 127.15, 123.37, 122.14, 118.97, 110.97, 110.63, 45.02, 27.53, 12.81, 8.16.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{22}O$ $[M]^+$: 326.16652, found: 326.16656.

4,4,5,5-tetramethyl-2-(4-(1-(3-methylbenzofuran-2-yl)propyl)phenyl)-1,3,2-dioxaborolane (3e) (*see substrate list*)



0.15 mmol 0.1 mmol 20%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-(4-allylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3e** (7.5 mg, 20%) as a colorless liquid.

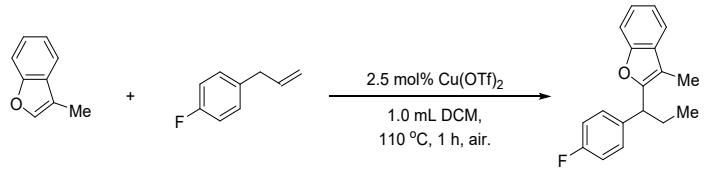
TLC: R_f = 0.35 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.42 (m, 1H), 7.39 (t, *J* = 5.9 Hz, 2H), 7.21 (tdd, *J* = 6.7, 4.7, 1.7 Hz, 3H), 4.04 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.27 – 2.23 (m, 1H), 2.20 – 2.10 (m, 4H), 1.33 (s, 12H), 0.92 (t, *J* = 7.3 Hz, 3H).

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{29}BO_3$ $[M]^+$: 376.22043, found: 376.22014.

2-(1-(4-fluorophenyl)propyl)-3-methylbenzofuran (3f) (*see substrate list*)



0.15 mmol 0.1 mmol 23%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-fluorobenzene (13.6 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3f** (6.2 mg, 23%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

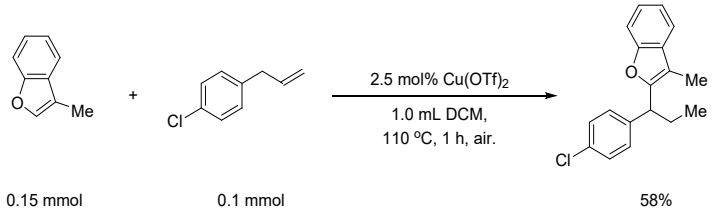
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.25 – 7.16 (m, 2H), 7.02 – 6.91 (m, 2H), 4.00 (dd, *J* = 9.1, 6.7 Hz, 1H), 2.31 – 2.14 (m, 4H), 2.13 – 2.00 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.86, 160.43, 154.52, 154.05, 138.51, 138.48, 130.36, 129.36, 129.28, 123.45, 122.18, 119.00, 115.42, 115.21, 110.95, 110.55, 44.59, 27.68, 12.70, 8.10.

^{19}F NMR (377 MHz, $CDCl_3$): δ -116.81.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{17}FO$ $[M]^+$: 268.12579, found: 268.12607.

2-(1-(4-chlorophenyl)propyl)-3-methylbenzofuran (3g) (*see substrate list*)



0.15 mmol 0.1 mmol 58%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-chlorobenzene (15.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3g** (16.5 mg, 58%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

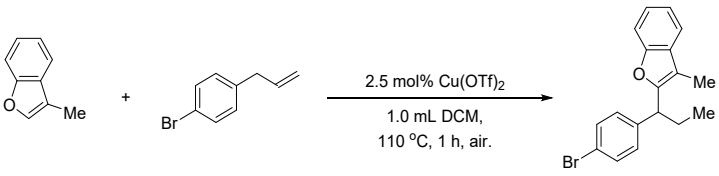
NMR Spectroscopy (***see spectra***):

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 – 7.39 (m, 2H), 7.35 – 7.29 (m, 2H), 7.26 (dt, *J* = 6.4, 1.9 Hz, 2H), 7.24 – 7.15 (m, 2H), 4.00 (dd, *J* = 9.1, 6.7 Hz, 1H), 2.31 – 2.16 (m, 4H), 2.14 – 2.01 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.17, 154.06, 141.26, 132.31, 130.30, 129.27, 128.68, 123.51, 122.21, 119.02, 110.96, 110.74, 44.73, 27.50, 12.69, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{17}ClO$ $[M]^+$: 284.09624, found: 284.09638.

2-(1-(4-bromophenyl)propyl)-3-methylbenzofuran (3h) (*see substrate list*)



0.15 mmol 0.1 mmol 39%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-bromobenzene (19.7 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3h** (12.8 mg, 39%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

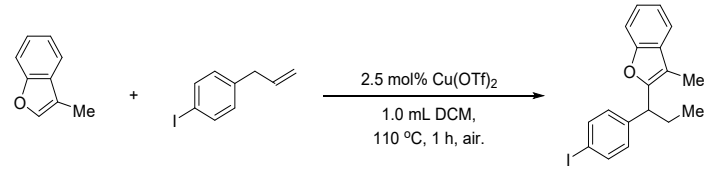
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.36 (m, 4H), 7.28 – 7.16 (m, 4H), 3.98 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.30 – 2.15 (m, 4H), 2.13 – 2.00 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.11, 141.82, 131.66, 130.34, 129.68, 123.54, 122.24, 120.43, 119.03, 110.97, 110.78, 12.67, 8.08.

HRMS (EI): m/z calculated for $C_{18}H_{17}BrO$ $[M]^+$: 328.04573, found: 328.04579.

All recorded spectroscopic data match those previously reported in the literature.[8]

2-(1-(4-iodophenyl)propyl)-3-methylbenzofuran (3i) (*see substrate list*)



0.15 mmol 0.1 mmol 60%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-iodobenzene (24.3 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3i** (22.6 mg, 60%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

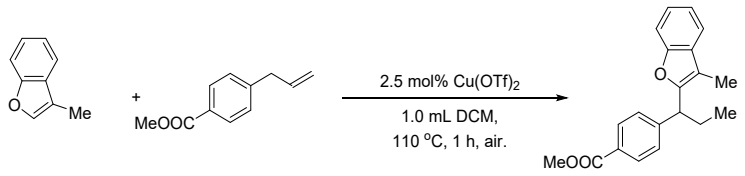
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.36 (m, 2H), 7.21 (qd, *J* = 7.2, 3.5 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.02 – 3.90 (m, 1H), 2.31 – 2.14 (m, 4H), 2.14 – 1.98 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.10, 154.06, 142.51, 137.65, 130.33, 130.01, 123.54, 122.24, 119.02, 110.96, 110.80, 91.84, 44.97, 27.40, 12.67, 8.08.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{17}IO$ $[M]^+$: 376.03186, found: 376.03189.

methyl 4-(1-(3-methylbenzofuran-2-yl)propyl)benzoate (3j) (*see substrate list*)



0.15 mmol 0.1 mmol 55%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and methyl 4-allylbenzoate (17.6 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3j** (16.9 mg, 55%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

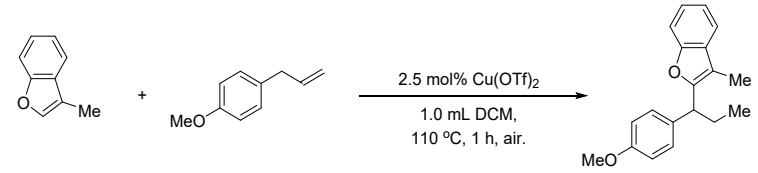
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.25 – 7.16 (m, 2H), 4.08 (dd, *J* = 9.1, 6.6 Hz, 1H), 3.89 (s, 3H), 2.33 – 2.18 (m, 4H), 2.17 – 2.07 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.13, 154.12, 153.82, 148.05, 130.29, 129.97, 128.55, 127.97, 123.58, 122.25, 119.07, 110.99, 52.15, 45.41, 27.38, 12.68, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{20}O_3$ $[M]^+$: 308.14070, found: 308.14088.

2-(1-(4-methoxyphenyl)propyl)-3-methylbenzofuran (3k) (*see substrate list*)



0.15 mmol 0.1 mmol 65%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-methoxybenzene (14.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3k** (18.2 mg, 65%) as a colorless liquid.

TLC: R_f = 0.5 (petroleum ether)

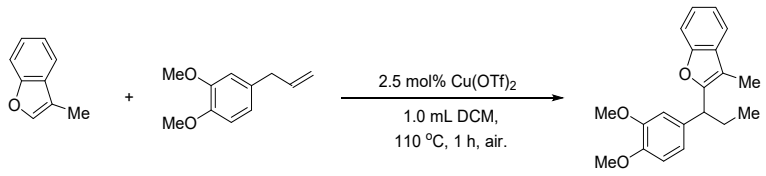
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 7.26 – 7.18 (m, 2H), 6.90 – 6.83 (m, 2H), 4.01 (dd, *J* = 9.1, 6.7 Hz, 1H), 3.79 (s, 3H), 2.33 – 2.19 (m, 4H), 2.18 – 2.03 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.25, 155.16, 154.03, 134.97, 130.48, 128.82, 123.24, 122.06, 118.89, 113.92, 110.91, 110.20, 55.34, 44.49, 27.62, 12.75, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O_2$ $[M]^+$: 280.14578, found: 280.14585.

2-(1-(3,4-dimethoxyphenyl)propyl)-3-methylbenzofuran (3l) (*see substrate list*)



0.15 mmol 0.1 mmol 70%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 4-allyl-1,2-dimethoxybenzene (17.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3l** (21.7 mg, 70%) as a colorless liquid.

TLC: R_f = 0.45 (petroleum ether)

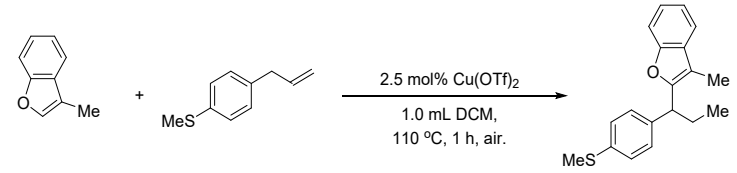
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.41 (m, 2H), 7.26 – 7.16 (m, 2H), 6.98 – 6.89 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 3.98 (dd, *J* = 9.0, 6.7 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.32 – 2.18 (m, 4H), 2.16 – 2.02 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.97, 154.01, 148.95, 147.72, 135.44, 130.44, 123.27, 122.08, 119.86, 118.91, 111.18, 110.85, 110.28, 55.97, 44.92, 27.67, 12.73, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{22}O_3$ $[M]^+$: 310.15635, found: 310.15646.

3-methyl-2-(1-(4-(methylthio)phenyl)propyl)benzofuran (3m) (*see substrate list*)



0.15 mmol 0.1 mmol 45%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and (4-allylphenyl)(methyl)sulfane (16.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3m** (13.3 mg, 45%) as a colorless liquid.

TLC: R_f = 0.65 (petroleum ether)

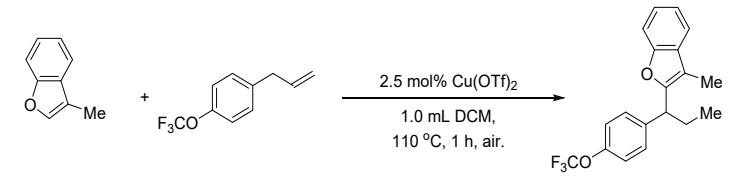
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.36 (m, 3H), 7.34 – 7.27 (m, 2H), 7.22 (ddd, *J* = 8.3, 6.6, 2.9 Hz, 4H), 3.99 (dd, *J* = 9.1, 6.7 Hz, 1H), 2.25 – 2.17 (m, 4H), 2.09 (dt, *J* = 13.7, 7.1 Hz, 1H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.65, 154.07, 139.89, 136.29, 130.42, 128.42, 127.18, 123.37, 122.13, 118.95, 110.93, 110.51, 44.86, 27.46, 16.27, 12.72, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}SO$ $[M]^+$: 296.12294, found: 296.12292.

3-methyl-2-(1-(4-(trifluoromethoxy)phenyl)propyl)benzofuran (3n) (*see substrate list*)



0.15 mmol 0.1 mmol 28%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-(trifluoromethoxy)benzene (20.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3n** (9.4 mg, 28%) as a colorless liquid.

TLC: R_f = 0.55 (petroleum ether)

NMR Spectroscopy (***see spectra***):

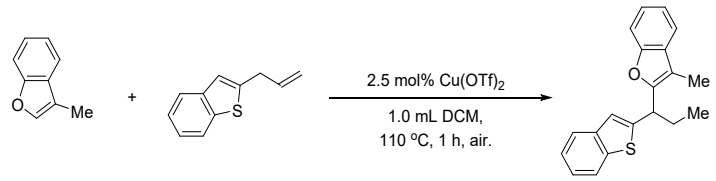
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.38 (m, 4H), 7.26 – 7.19 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.05 (dd, *J* = 8.9, 6.8 Hz, 1H), 2.28 (t, *J* = 3.6 Hz, 1H), 2.22 (s, 3H), 2.16 – 2.03 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.12, 154.08, 147.92, 141.54, 141.48, 130.31, 129.20, 124.19, 123.58, 122.34, 122.27, 121.08, 119.52, 119.06, 111.44, 110.98, 110.85, 44.76, 27.63, 12.68, 8.08.

^{19}F NMR (177 MHz, $CDCl_3$): δ -57.86.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{17}F_3O_2$ $[M]^+$: 334.11752, found: 334.11761.

2-(1-(benzo[b]thiophen-2-yl)propyl)-3-methylbenzofuran (3o) (*see substrate list*)



0.15 mmol 0.1 mmol 36%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-allylbenzo[b]thiophene (17.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3o** (11.0 mg, 36%) as a colorless liquid.

TLC: R_f = 0.50 (petroleum ether)

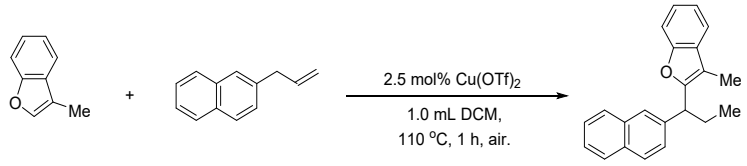
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.35 – 7.26 (m, 2H), 7.22 (dt, *J* = 13.0, 5.4 Hz, 2H), 7.12 (s, 1H), 4.37 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.40 – 2.22 (m, 5H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.12, 153.11, 146.97, 139.95, 139.46, 130.23, 124.24, 123.85, 123.78, 123.24, 122.29, 122.26, 120.73, 119.16, 111.41, 111.12, 41.13, 28.02, 12.58, 8.15.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{18}OS$ $[M]^+$: 306.10729, found: 306.10733.

3-methyl-2-(1-(naphthalen-2-yl)propyl)benzofuran (3p) (*see substrate list*)



0.15 mmol 0.1 mmol 93%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-allylnaphthalene (16.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3p** (27.9 mg, 93%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

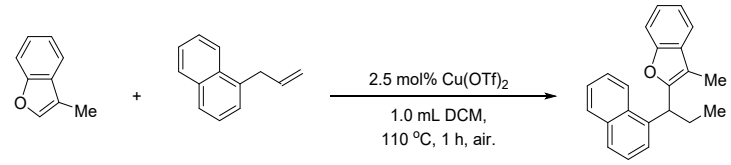
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.75 (m, 4H), 7.56 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.26 (s, 2H), 4.23 (dd, *J* = 8.9, 6.7 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.31 – 2.17 (m, 4H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 181.42, 169.92, 167.34, 158.52, 152.53, 152.39, 137.72, 129.23, 128.35, 128.20, 128.09, 126.72, 114.63, 114.60, 110.71, 110.48, 101.50, 101.22, 50.42, 16.35.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{20}O$ $[M]^+$: 300.15087, found: 300.15097.

3-methyl-2-(1-(naphthalen-1-yl)propyl)benzofuran (3q) (*see substrate list*)



0.15 mmol 0.1 mmol 78%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allylnaphthalene (16.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3q** (23.4 mg, 78%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

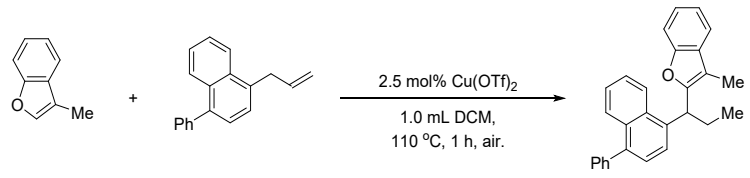
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.55 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.27 – 7.18 (m, 2H), 4.89 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.51 – 2.36 (m, 1H), 2.32 – 2.19 (m, 4H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.78, 154.07, 138.80, 134.03, 131.56, 130.58, 129.17, 127.24, 126.17, 125.76, 125.46, 125.16, 123.34, 123.04, 122.13, 118.94, 110.96, 110.79, 40.65, 27.78, 13.08, 8.32.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{20}O$ $[M]^+$: 300.15087, found: 300.15078.

3-methyl-2-(1-(4-phenylnaphthalen-1-yl)propyl)benzofuran (3r) (*see substrate list*)



0.15 mmol 0.1 mmol 27%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-4-phenylnaphthalene (24.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3r** (10.2 mg,27%) as a colorless liquid.

TLC: R_f = 0.70 (petroleum ether)

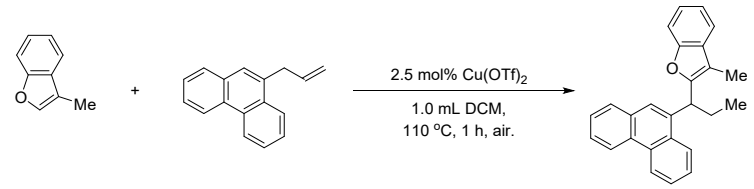
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.22 (dd, *J* = 11.5, 8.4 Hz, 1H), 7.11 – 7.00 (m, 1H), 5.94 – 5.82 (m, 1H), 1.91 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 182.90, 182.88, 158.12, 148.27, 146.61, 139.35, 136.21, 128.70, 127.80, 127.10, 126.96, 126.55, 126.54, 125.03, 124.99, 121.70, 121.68, 121.05, 121.03, 51.75, 17.67, 17.63.

HRMS (EI): m/z Theo. Mass calculated for $C_{28}H_{24}O$ $[M]^+$: 376.18217, found: 376.18211.

3-methyl-2-(1-(phenanthren-9-yl)propyl)benzofuran (3s) (*see substrate list*)



0.15 mmol 0.1 mmol 63%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 9-allylphenanthrene (21.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3s** (22.1 mg, 63%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

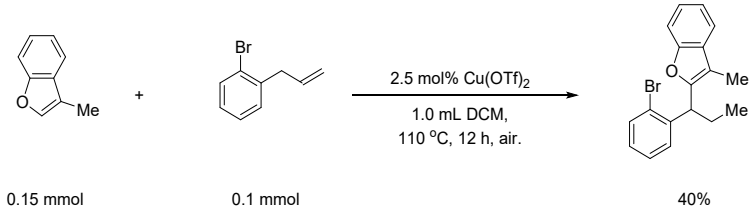
NMR Spectroscopy (***see spectra***):

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.82 – 8.73 (m, 1H), 8.67 (d, *J* = 8.1 Hz, 1H), 8.32 – 8.20 (m, 1H), 7.94 – 7.82 (m, 2H), 7.72 – 7.54 (m, 4H), 7.52 – 7.40 (m, 2H), 7.29 – 7.19 (m, 2H), 4.89 (dd, *J* = 9.6, 5.3 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.42 – 2.28 (m, 1H), 2.24 (s, 3H), 1.11 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.60, 154.11, 136.73, 131.84, 130.99, 130.94, 130.65, 129.81, 128.82, 126.80, 126.76, 126.47, 126.23, 125.90, 123.72, 123.52, 123.39, 122.51, 122.15, 118.96, 111.03, 41.07, 27.43, 13.09, 8.38.

HRMS (EI): m/z Theo. Mass calculated for $C_{26}H_{22}O$ $[M]^+$: 350.16652, found: 350.16653.

2-(1-(2-bromophenyl)propyl)-3-methylbenzofuran (3t) (*see substrate list*)



0.15 mmol 0.1 mmol 40%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-2-bromobenzene (19.7 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3t** (13.1 mg, 40%) as a colorless liquid.

TLC: R_f = 0.70 (petroleum ether)

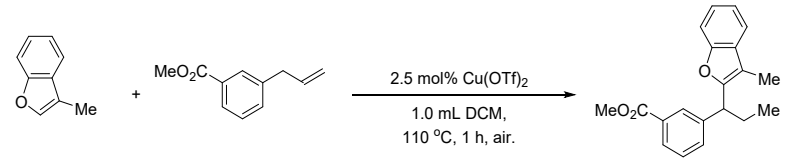
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.44 (ddd, *J* = 9.5, 7.4, 4.1 Hz, 2H), 7.29 (t, *J* = 2.8 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.05 (td, *J* = 7.8, 1.6 Hz, 1H), 4.61 (dd, *J* = 9.2, 6.2 Hz, 1H), 2.27 – 2.15 (m, 4H), 2.12 – 2.00 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.24, 153.66, 142.07, 132.81, 130.41, 129.58, 128.08, 127.85, 124.25, 123.47, 122.20, 119.12, 111.45, 110.93, 43.91, 27.72, 12.57, 8.31.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{17}BrO$ $[M]^+$: 328.04573, found: 328.04579.

methyl 3-(1-(3-methylbenzofuran-2-yl)propyl)benzoate (3u) (*see substrate list*)



0.15 mmol 0.1 mmol 60%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and methyl 3-allylbenzoate (17.6 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3u** (18.5 mg, 60%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

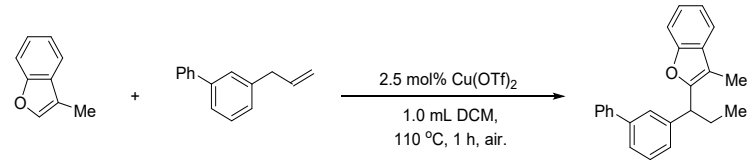
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.92 – 7.86 (m, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.43 (ddd, *J* = 7.2, 3.8, 1.5 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.25 – 7.17 (m, 2H), 4.09 (dd, *J* = 9.0, 6.7 Hz, 1H), 3.91 (s, 3H), 2.35 – 2.23 (m, 1H), 2.21 (s, 3H), 2.16 – 2.08 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.28, 154.14, 143.19, 132.71, 132.55, 130.45, 130.34, 129.13, 128.70, 127.93, 123.51, 122.20, 119.02, 111.01, 110.83, 52.22, 45.24, 27.50, 12.68, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{20}O_3$ $[M]^+$: 308.14070, found: 307.14079.

2-(1-([1,1'-biphenyl]-3-yl)propyl)-3-methylbenzofuran (3v) (*see substrate list*)



0.15 mmol 0.1 mmol 40%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 3-allyl-1,1'-biphenyl (19.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3v** (13.0 mg, 40%) as a colorless oily liquid.

TLC: R_f = 0.60 (petroleum ether)

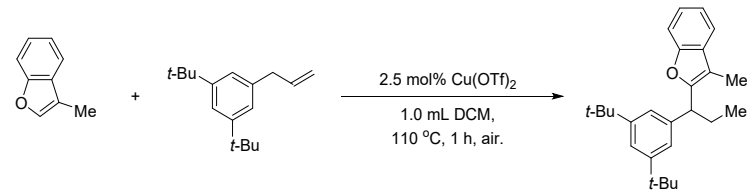
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 3H), 7.49 – 7.41 (m, 5H), 7.41 – 7.32 (m, 3H), 7.26 – 7.17 (m, 2H), 4.11 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.41 – 2.27 (m, 1H), 2.27 – 2.22 (m, 3H), 2.22 – 2.11 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.72, 154.15, 143.33, 141.57, 141.51, 130.48, 129.00, 128.85, 127.39, 127.35, 126.89, 126.85, 125.54, 123.36, 122.13, 118.96, 110.98, 110.61, 45.56, 27.59, 12.81, 8.17.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{22}O$ $[M]^+$: 326.16652, found: 326.16658.

2-(1-(3,5-di-tert-butylphenyl)propyl)-3-methylbenzofuran (3w) (*see substrate list*)



0.15 mmol 0.1 mmol 79%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-allyl-3,5-di-tert-butylbenzene (23.0 mg 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3w** (28.6 mg, 79%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

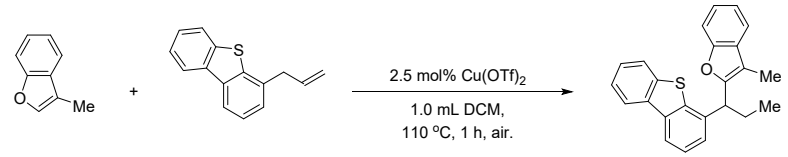
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.39 (m, 2H), 7.28 (d, *J* = 3.0 Hz, 3H), 7.25 – 7.16 (m, 2H), 4.03 (dd, *J* = 9.5, 6.2 Hz, 1H), 2.42 – 2.26 (m, 1H), 2.25 (d, *J* = 7.1 Hz, 3H), 2.18 – 2.04 (m, 1H), 1.34 (s, 19H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.16, 154.12, 150.71, 141.87, 130.59, 123.16, 122.17, 121.97, 120.56, 118.84, 110.83, 110.36, 45.99, 34.96, 31.66, 27.79, 12.84, 8.21.

HRMS (EI): m/z Theo. Mass calculated for $C_{26}H_{34}O$ $[M]^+$: 362.26042, found: 362.26012.

2-(1-(dibenzo[b,d]thiophen-4-yl)propyl)-3-methylbenzofuran (3x) (*see substrate list*)



0.15 mmol 0.1 mmol 55%

The reaction was performed according to **general procedure A** using 2-methylbenzofuran **y** (19.8 mg, 0.15 mmol, 1.5 equiv.) and 4-allyldibenzo[b, d]thiophene (22.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3x** (19.6 mg, 55%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

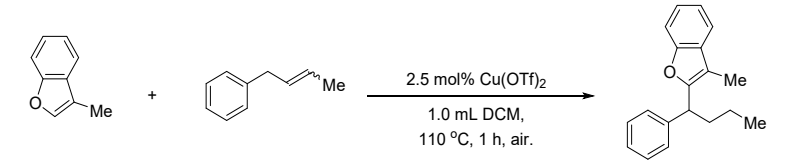
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.10 (m, 1H), 8.04 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.25 – 7.14 (m, 2H), 4.36 (dd, *J* = 8.9, 6.5 Hz, 1H), 2.49 – 2.26 (m, 5H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.15, 153.25, 139.07, 139.01, 137.10, 136.31, 135.86, 130.34, 126.81, 125.35, 125.19, 124.54, 123.51, 122.82, 122.16, 121.79, 119.98, 119.09, 111.59, 110.98, 44.41, 26.90, 12.75, 8.48.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{20}OS$ $[M]^+$: 356.12294, found: 356.12310.

3-methyl-2-(1-phenylbutyl)benzofuran (3y) (*see substrate list*)



0.15 mmol 0.1 mmol 71%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and but-2-en-1-ylbenzene (13.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3y** (18.7 mg, 71%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

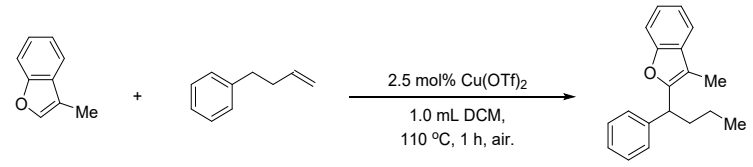
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 4H), 7.31 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.25 – 7.17 (m, 3H), 4.16 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.33 – 2.18 (m, 4H), 2.12 – 2.00 (m, 1H), 1.39 – 1.25 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ155.02, 154.10, 142.99, 130.49, 128.58, 127.90, 126.55, 123.31, 122.11, 118.93, 110.95, 110.29, 43.27, 36.52, 21.24, 14.03, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O$ $[M]^+$: 264.15140, found: 264.15073.

3-methyl-2-(1-phenylbutyl)benzofuran (3z) (*see substrate list*)



0.15 mmol 0.1 mmol 45%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and but-3-en-1-ylbenzene (13.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3z** (11.9 mg, 45%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

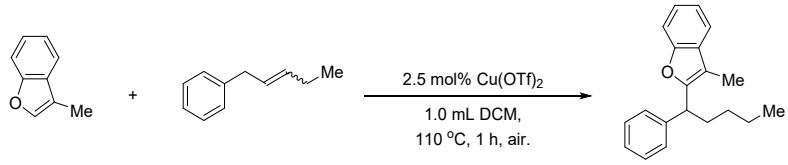
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 4H), 7.31 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.25 – 7.17 (m, 3H), 4.16 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.33 – 2.18 (m, 4H), 2.12 – 2.00 (m, 1H), 1.39 – 1.25 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.02, 154.10, 142.99, 130.49, 128.58, 127.90, 126.55, 123.31, 122.11, 118.93, 110.95, 110.29, 43.27, 36.52, 21.24, 14.03, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O$ $[M]^+$: 264.15087, found: 264.15073.

3-methyl-2-(1-phenylpentyl)benzofuran (3aa) (*see substrate list*)



0.15 mmol 0.1 mmol 60%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and pent-2-en-1-ylbenzene (14.6 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3aa** (16.7 mg, 60%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

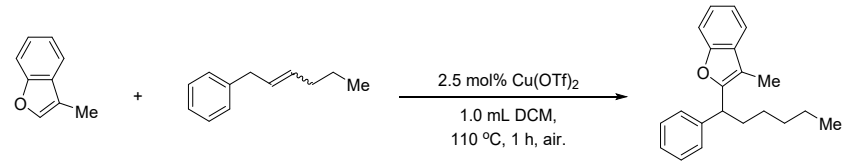
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.34 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.15 (m, 3H), 4.11 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.31 – 2.15 (m, 4H), 2.12 – 1.99 (m, 1H), 1.39 – 1.22 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.03, 154.07, 143.02, 130.48, 128.57, 127.88, 126.54, 123.29, 122.09, 118.93, 110.96, 110.27, 43.52, 34.11, 30.28, 22.69, 14.13, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{22}O$ $[M]^+$: 278.16652, found: 278.16640.

3-methyl-2-(1-phenylhexyl)benzofuran (3ab) (*see substrate list*)



0.15 mmol 0.1 mmol 22%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and hex-2-en-1-ylbenzene (16.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ab** (6.4 mg, 22%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

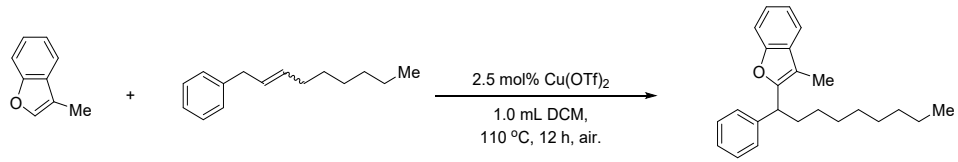
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.39 (m, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 4.11 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.30 – 2.15 (m, 4H), 2.10 – 2.00 (m, 1H), 1.28 (dd, *J* = 6.7, 4.7 Hz, 6H), 0.85 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.05, 154.08, 143.04, 130.49, 128.57, 127.88, 126.54, 123.29, 122.09, 118.93, 110.96, 110.27, 43.55, 34.34, 31.81, 27.74, 22.64, 14.19, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{24}O$ $[M]^+$: 292.18217, found: 292.18213.

3-methyl-2-(1-phenylnonyl)benzofuran (3ac) (*see substrate list*)



0.15 mmol 0.1 mmol 26%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and hept-2-en-1-ylbenzene (20.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ac** (8.0 mg, 26%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

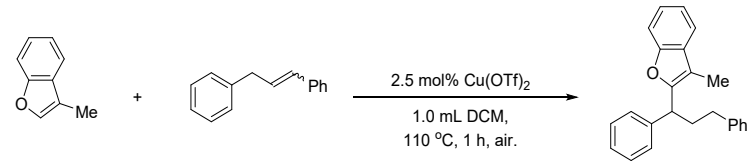
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.17 (m, 3H), 4.12 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.31 – 2.15 (m, 4H), 2.14 – 1.97 (m, 1H), 1.27 (dd, *J* = 15.8, 8.6 Hz, 12H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.06, 154.09, 143.05, 130.50, 128.57, 127.89, 126.54, 123.29, 122.09, 118.93, 110.96, 110.28, 43.55, 34.38, 31.99, 29.60, 29.57, 29.41, 28.07, 22.79, 14.23, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{30}O$ $[M]^+$: 334.22912, found: 334.22885.

2-(1,3-diphenylpropyl)-3-methylbenzofuran (3ad) (*see substrate list*)



0.15 mmol 0.1 mmol 23%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and prop-1-ene-1,3-diyldibenzene (19.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ad** (7.5 mg, 23%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

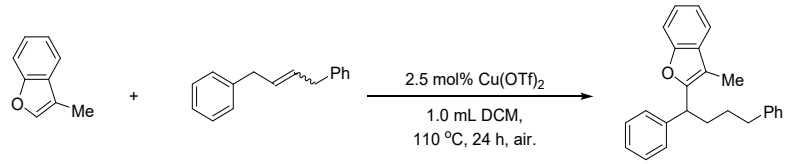
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.1, 1.9 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.29 (m, 4H), 7.25 – 7.12 (m, 6H), 4.12 (dd, *J* = 8.4, 6.3 Hz, 1H), 2.73 – 2.49 (m, 3H), 2.47 – 2.34 (m, 1H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.45, 154.19, 142.66, 141.82, 130.46, 128.66, 128.63, 128.48, 127.87, 126.68, 126.02, 123.45, 122.19, 119.02, 111.01, 110.75, 42.66, 35.84, 34.09, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{22}O$ $[M]^+$: 326.16652, found: 326.16626.

2-(1,4-diphenylbutyl)-3-methylbenzofuran (3ae) (*see substrate list*)



0.15 mmol 0.1 mmol 10%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1,4-diphenylbut-2-ene (20.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ae** (3.4 mg, 10%) as a colorless liquid.

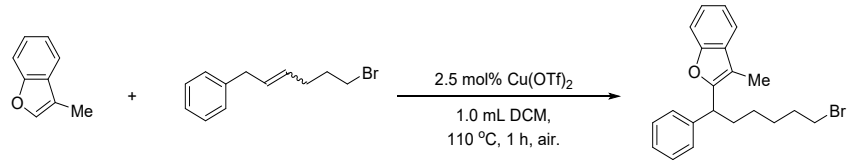
TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.38 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.25 – 7.17 (m, 5H), 7.12 (d, *J* = 7.3 Hz, 2H), 4.13 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.34 – 2.06 (m, 5H), 1.62 (dd, *J* = 15.4, 7.8 Hz, 2H).

HRMS (EI): m/z Theo. Mass calculated for $C_{25}H_{24}O$ $[M]^+$: 340.18217, found: 340.18203.

2-(6-bromo-1-phenylhexyl)-3-methylbenzofuran (3af) (*see substrate list*)



0.15 mmol 0.1 mmol 20%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and (6-bromohex-2-en-1-yl)benzene (23.9 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3af** (7.4 mg, 20%) as a colorless liquid.

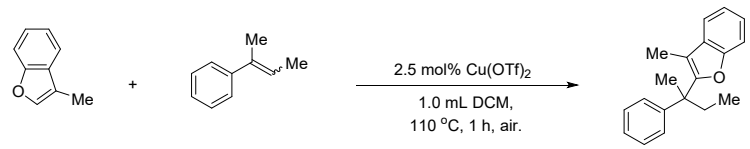
TLC: R_f = 0.70 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.46 (m, 1H), 7.37 – 7.31 (m, 1H), 7.25 – 7.07 (m, 5H), 7.01 (dd, *J* = 13.0, 5.3 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 4.03 (d, *J* = 10.0 Hz, 1H), 3.11 – 2.83 (m, 2H), 2.23 (s, 3H), 2.21 – 2.12 (m, 2H), 1.54 – 1.45 (m, 2H), 0.93 (dt, *J* = 22.0, 7.4 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.52, 154.14, 137.29, 136.68, 130.39, 129.13, 129.01, 126.28, 126.04, 123.45, 122.10, 118.84, 112.49, 111.11, 43.68, 40.28, 29.57, 27.44, 26.86, 11.05, 8.19.

methyl 7-(3-methylbenzofuran-2-yl)-7-phenylheptanoate (3ag) (*see substrate list*)



0.15 mmol 0.1 mmol 73%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and but-2-en-2-ylbenzene (13.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ag** (19.3 mg, 73%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

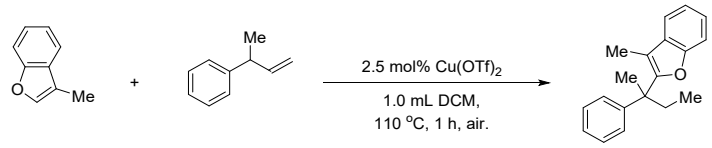
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.39 (m, 2H), 7.35 – 7.28 (m, 4H), 7.27 – 7.18 (m, 3H), 2.37 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.18 (dt, *J* = 14.7, 7.7 Hz, 1H), 1.86 (s, 3H), 1.75 (s, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.54, 153.15, 147.38, 131.47, 128.28, 126.82, 126.20, 123.28, 122.01, 118.72, 110.83, 110.20, 45.66, 33.29, 25.69, 9.34, 8.81.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O$ $[M]^+$: 264.15087, found: 264.15127.

3-methyl-2-(2-phenylbutan-2-yl)benzofuran (3ah) (*see substrate list*)



0.15 mmol 0.1 mmol 66%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and but-3-en-2-ylbenzene (13.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ah** (17.4 mg, 66%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

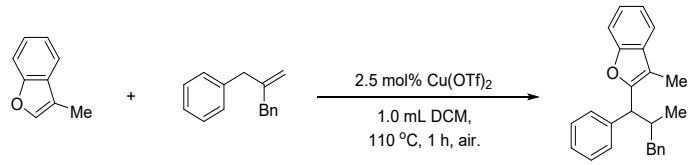
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.39 (m, 2H), 7.35 – 7.28 (m, 4H), 7.27 – 7.18 (m, 3H), 2.37 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.18 (dt, *J* = 14.7, 7.7 Hz, 1H), 1.86 (s, 3H), 1.75 (s, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.54, 153.15, 147.38, 131.47, 128.28, 126.82, 126.20, 123.28, 122.01, 118.72, 110.83, 110.20, 45.66, 33.29, 25.69, 9.34, 8.81.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O$ $[M]^+$: 264.15087, found: 264.15127.

3-methyl-2-(2-methyl-1,3-diphenylpropyl)benzofuran (3ai) (*see substrate list*)



0.15 mmol 0.1 mmol 56%; 2/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and (2-methylenepropane-1,3-diyl)dibenzene (20.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ai** (19.0 mg, 56%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

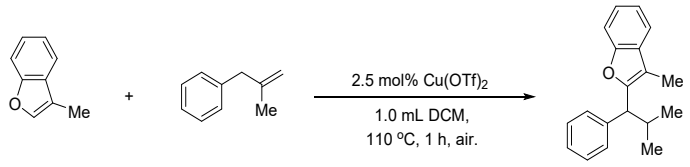
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.39 (m, 4H), 7.39 – 7.08 (m, 10H), 3.86 (dd, *J* = 18.2, 10.2 Hz, 1H), 2.92 – 2.68 (m, 2H), 2.34 – 2.11 (m, 4H), 0.84 (d, *J* = 6.5 Hz, 2H), 0.78 (d, *J* = 6.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.42, 154.33, 154.18, 154.11, 141.63, 141.17, 141.01, 130.34, 130.25, 129.41, 129.24, 128.76, 128.60, 128.47, 128.28, 128.21, 126.78, 126.65, 125.93, 125.89, 123.40, 123.34, 122.20, 122.13, 118.97, 111.03, 110.99, 110.93, 110.79, 50.45, 50.25, 41.66, 41.52, 39.11, 38.82, 17.91, 17.73, 8.18.

HRMS (EI): m/z Theo. Mass calculated for $C_{25}H_{24}O$ $[M]^+$: 340.18217, found: 340.18210.

3-methyl-2-(2-methyl-1-phenylpropyl)benzofuran (3aj) (*see substrate list*)



0.15 mmol 0.1 mmol 82%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and (2-methylallyl)benzene 13.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3aj** (21.6 mg, 82%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

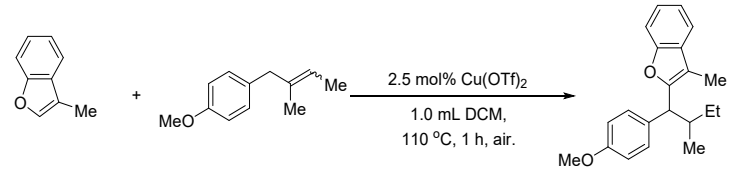
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.38 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.15 (m, 3H), 3.66 (d, *J* = 10.5 Hz, 1H), 2.73 – 2.54 (m, 1H), 2.22 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.92, 154.10, 142.04, 130.35, 130.28, 128.52, 126.56, 123.23, 122.08, 118.90, 110.91, 110.46, 52.02, 32.05, 21.64, 8.13.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{20}O$ $[M]^+$: 264.15087, found: 264.15078.

2-(1-(4-methoxyphenyl)-2-methylbutyl)-3-methylbenzofuran (3ak) (*see substrate list*)



0.15 mmol 0.1 mmol 86%; 1.2/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-methoxy-4-(2-methylbut-2-en-1-yl)benzene (17.6 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ak** (26.5 mg, 86%) as a colorless liquid.

TLC: R_f = 0.55 (petroleum ether)

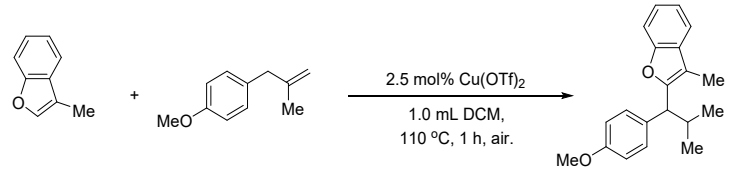
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.38 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.12 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H), 3.72 (dd, *J* = 13.5, 10.7 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.21 (d, *J* = 2.8 Hz, 3H), 1.50 – 1.36 (m, 1H), 1.15 – 0.94 (m, 1H), 0.93 – 0.79 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.23, 155.26, 155.16, 154.04, 134.21, 134.04, 130.39, 130.36, 129.46, 129.45, 123.14, 123.12, 122.04, 118.87, 118.84, 113.91, 110.91, 110.87, 110.17, 110.13, 55.34, 49.31, 49.15, 38.16, 37.97, 27.56, 27.32, 17.47, 17.41, 11.21, 11.10, 8.16.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{24}O_2$ $[M]^+$: 308.17708, found: 308.17734.

2-(1-(4-methoxyphenyl)-2-methylpropyl)-3-methylbenzofuran (3al) (*see substrate list*)



0.15 mmol 0.1 mmol 99%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-methoxy-4-(2-methylallyl)benzene (16.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3al** (29.1 mg, 99%) as a colorless liquid.

TLC: R_f = 0.55 (petroleum ether)

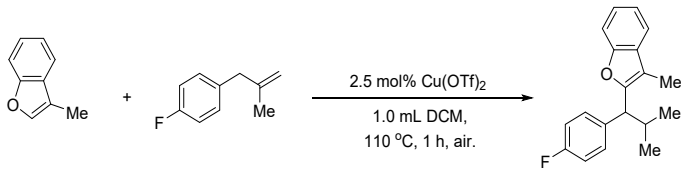
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (td, *J* = 7.6, 1.7 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.25 – 7.15 (m, 2H), 6.90 – 6.80 (m, 2H), 3.78 (s, 3H), 3.62 (d, *J* = 10.5 Hz, 1H), 2.68 – 2.51 (m, 1H), 2.23 (s, 3H), 0.91 (dd, *J* = 9.5, 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.24, 155.23, 154.01, 134.22, 130.35, 129.38, 123.14, 122.04, 118.87, 113.87, 110.87, 110.09, 55.32, 51.05, 32.15, 21.61, 8.13.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{22}O_2$ $[M]^+$: 294.16143, found: 294.16140.

2-(1-(4-fluorophenyl)-2-methylpropyl)-3-methylbenzofuran (3am) (*see substrate list*)



0.15 mmol 0.1 mmol 53%

The reaction was performed according to **general procedure A** using 3-methylbenzo[b]thiophene (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-fluoro-4-(2-methylallyl)benzene (15.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3am** (14.9 mg, 53%) as a colorless oily liquid.

TLC: R_f = 0.80 (petroleum ether)

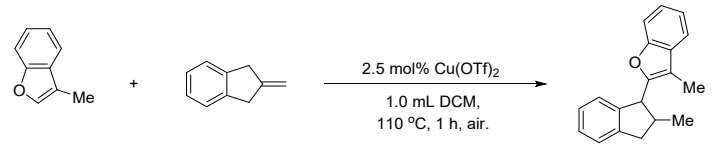
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.35 (m, 4H), 7.25 – 7.15 (m, 2H), 7.03 – 6.92 (m, 2H), 3.64 (d, *J* = 10.5 Hz, 1H), 2.67 – 2.48 (m, 1H), 2.21 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.92, 160.50, 154.60, 154.09, 137.78, 137.75, 130.26, 129.92, 129.84, 123.38, 122.19, 118.98, 115.39, 115.18, 110.92, 110.52, 51.19, 32.26, 21.56, 21.53, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{19}FO$ $[M]^+$: 282.14144, found: 282.14160.

3-methyl-2-(2-methyl-2,3-dihydro-1H-inden-1-yl)benzofuran (3an) (*see substrate list*)



0.15 mmol 0.1 mmol 83%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-methylene-2,3-dihydro-1H-indene (13.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3an** (21.7 mg, 83%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

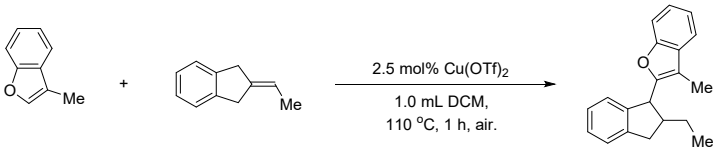
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 1H), 7.40 – 7.36 (m, 1H), 7.32 (dd, *J* = 7.4, 4.3 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.16 (t, *J* = 6.7 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 4.19 (dd, *J* = 9.8, 0.7 Hz, 1H), 3.25 (dd, *J* = 15.3, 7.6 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.73 (ddd, *J* = 15.2, 10.1, 0.7 Hz, 1H), 2.28 (s, 3H), 1.26 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.29, 154.10, 153.98, 153.65, 144.19, 143.90, 143.53, 143.43, 130.53, 130.45, 127.22, 127.16, 126.52, 126.48, 125.36, 124.81, 124.59, 124.35, 123.54, 123.32, 122.13, 122.00, 118.90, 118.83, 112.17, 111.41, 111.06, 111.00, 50.96, 47.35, 42.26, 40.51, 40.34, 39.55, 18.83, 16.65, 8.18.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{18}O$ $[M]^+$: 262.13522, found: 262.13530.

2-(2-ethyl-2,3-dihydro-1H-inden-1-yl)-3-methylbenzofuran (3ao) (*see substrate list*)



0.15 mmol 0.1 mmol 36%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran **x** (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-ethylidene-2,3-dihydro-1H-indene (14.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ao** (9.9 mg, 36%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

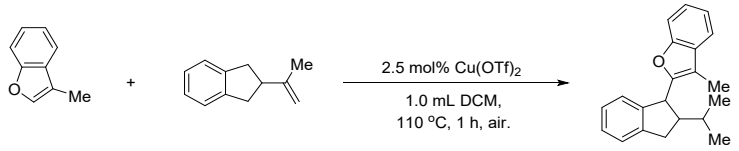
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 4.26 (d, *J* =

9.4 Hz, 1H), 3.26 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.87 – 2.75 (m, 1H), 2.71 (dd, *J* = 14.7, 9.7 Hz, 1H), 2.25 (s, 3H), 1.81 – 1.66 (m, 1H), 1.64 – 1.54 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.29, 154.23, 143.86, 143.25, 130.59, 127.15, 126.54, 124.69, 124.35, 123.51, 122.13, 118.88, 111.78, 111.06, 49.32, 48.76, 37.99, 27.41, 12.57, 8.17.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{20}O$ $[M]^+$: 276.15087, found: 276.15104.

2-(2-isopropyl-2,3-dihydro-1H-inden-1-yl)-3-methylbenzofuran (3ap) (*see substrate list*)



0.15 mmol 0.1 mmol 75%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (15.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ap** (21.8 mg, 75%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

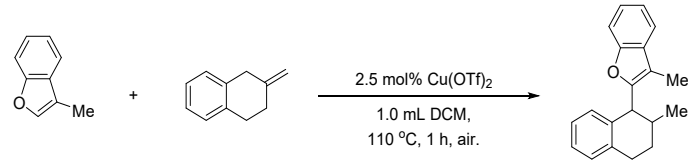
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 5H), 7.45 (dd, *J* = 15.7, 8.1 Hz, 4H), 7.40 – 7.32 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.83 (q, *J* = 7.2 Hz, 1H), 1.91 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.63, 158.30, 149.94, 140.96, 140.34, 138.08, 137.21, 128.96, 127.71, 127.21, 127.13, 125.57, 123.62, 118.19, 112.64, 50.01, 16.52.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{22}O$ $[M]^+$: 290.16652, found: 290.16666.

3-methyl-2-(2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (3aq) (*see substrate list*)



0.15 mmol 0.1 mmol 83%; 1.5/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 2-methylene-1,2,3,4-tetrahydronaphthalene (14.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3aq** (22.9 mg, 83%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

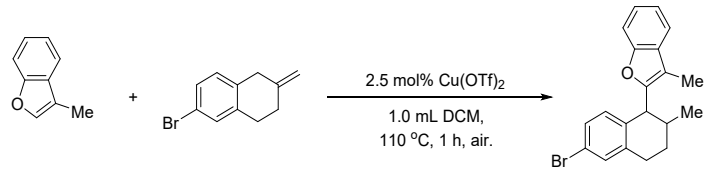
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.43 (m, 1H), 7.40 – 7.28 (m, 1H), 7.26 – 7.14 (m, 4H), 7.07 – 6.80 (m, 2H), 4.36 – 4.35 (m, 1H), 3.17 – 2.84 (m, 2H), 2.41 – 2.17 (m, 4H), 2.17 – 1.99 (m, 1H), 1.86 – 1.57 (m, 1H), 0.98 (dd, J = 24.1, 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.43, 155.28, 154.19, 154.12, 137.33, 137.05, 136.72, 136.56, 130.37, 130.35, 130.14, 129.28, 129.20, 128.79, 126.41, 126.32, 126.04, 125.73, 123.49, 123.30, 122.12, 121.98, 118.89, 118.87, 112.63, 111.58, 111.09, 111.02, 45.75, 42.21, 34.23, 33.80, 31.67, 29.74, 29.47, 28.01, 20.85, 19.23, 8.45, 8.17.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{20}O$ $[M]^+$: 276.15087, found: 276.15094.

2-(6-bromo-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-3-methylbenzofuran (3ar) (*see substrate list*)



0.15 mmol 0.1 mmol 61%; 1/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 6-bromo-2-methylene-1,2,3,4-tetrahydronaphthalene (22.3 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ar** (21.7 mg, 61%) as a colorless liquid.

TLC: R_f = 0.70 (petroleum ether)

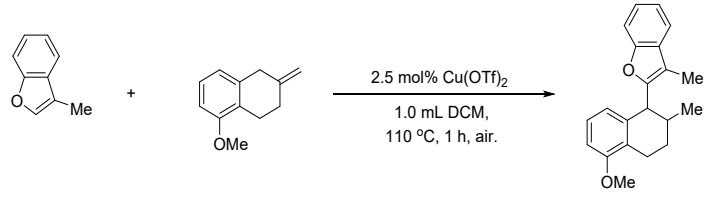
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.41 (m, 1H), 7.39 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 6.85 – 6.68 (m, 1H), 4.28 – 4.26 (m, 1H), 3.12 – 2.80 (m, 2H), 2.35 – 2.13 (m, 4H), 2.11 – 1.95 (m, 1H), 1.84 – 1.57 (m, 1H), 0.95 (dd, J = 25.8, 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.66, 154.52, 154.16, 154.12, 139.67, 139.41, 135.76, 135.65, 132.01, 131.87, 131.73, 130.58, 130.21, 130.16, 129.11, 128.85, 123.70, 123.50, 122.24, 122.10, 120.12, 120.10, 118.98, 118.96, 112.86, 111.79, 111.09, 111.02, 45.29, 41.68, 34.07, 33.61, 31.31, 29.51, 29.27, 27.58, 20.71, 19.08, 8.50, 8.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{19}BrO$ $[M]^+$: 354.06138, found: 354.06149.

2-(5-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-3-methylbenzofuran (3as) (*see substrate list*)



0.15 mmol 0.1 mmol 84%; 2/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 5-methoxy-2-methylene-1,2,3,4-tetrahydronaphthalene (17.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether/ ethyl acetate = 200/1, v/v as the eluent) afforded **3as** (25.7 mg, 84%) as a light yellow liquid.

TLC: R_f = 0.30 (petroleum ether/ ethyl acetate = 40/1, v/v)

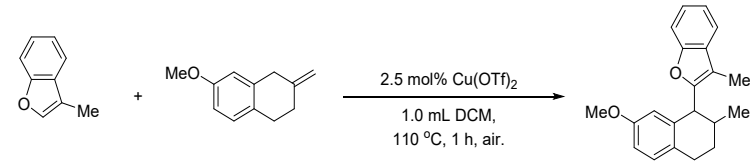
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.44 (m, 1H), 7.41 – 7.29 (m, 1H), 7.29 – 7.17 (m, 2H), 7.11 (dd, *J* = 10.9, 8.6 Hz, 1H), 6.78 – 6.72 (m, 1H), 6.55 – 6.38 (m, 1H), 3.92 (dd, *J* = 16.7, 8.0 Hz, 1H), 3.66 (d, *J* = 22.6 Hz, 3H), 3.09 – 2.78 (m, 2H), 2.39 – 2.17 (m, 4H), 2.14 – 1.98 (m, 1H), 1.84 – 1.51 (m, 2H), 0.97 (dd, *J* = 23.0, 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.94, 157.62, 155.26, 155.06, 154.20, 154.08, 137.72, 130.36, 130.34, 130.08, 130.01, 129.53, 129.33, 123.49, 123.30, 122.08, 121.97, 118.89, 114.74, 114.18, 112.86, 112.66, 112.00, 111.07, 111.01, 55.32, 45.87, 42.50, 34.16, 33.79, 31.85, 28.90, 28.63, 28.22, 20.85, 19.18, 8.46, 8.18.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{22}O_2$ $[M]^+$: 306.16143, found: 306.16146.

2-(7-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-3-methylbenzofuran (3at) (*see substrate list*)



0.15 mmol 0.1 mmol 77%; 1/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 7-methoxy-2-methylene-1,2,3,4-tetrahydronaphthalene (17.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether/ ethyl acetate = 200/1, v/v as the eluent) afforded **3at** (23.6 mg, 77%) as a light yellow liquid.

TLC: R_f = 0.25 (petroleum ether/ ethyl acetate = 40/1, v/v)

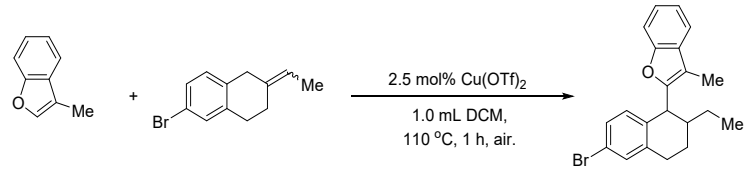
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.41 (m, 2H), 7.37 – 7.28 (m, 2H), 7.24 – 7.15 (m, 4H), 7.07 – 6.93 (m, 2H), 6.69 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 4.31 (d, *J* = 5.5 Hz, 1H), 3.90 (d, *J* = 10.5 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.04 (tdd, *J* = 19.7, 5.6, 2.5 Hz, 2H), 2.78 – 2.56 (m, 2H), 2.33 – 2.15 (m, 8H), 2.15 – 1.93 (m, 2H), 1.80 (m, 1H), 1.67 – 1.56 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.46, 157.33, 155.30, 155.29, 154.16, 154.11, 137.97, 137.79, 130.38, 126.57, 126.29, 126.16, 126.01, 123.43, 123.24, 122.22, 122.08, 121.94, 120.89, 118.86, 118.85, 112.57, 111.60, 111.10, 111.04, 107.63, 107.44, 55.45, 55.39, 45.72, 42.22, 33.59, 33.35, 31.10, 27.44, 23.41, 23.35, 20.78, 19.18, 8.48, 8.16.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{22}O_2$ $[M]^+$: 306.16143, found: 306.16174.

2-(6-bromo-2-ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-3-methylbenzofuran (3au) (*see substrate list*)



0.15 mmol 0.1 mmol 65%; 2/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 6-bromo-2-ethylidene-1,2,3,4-tetrahydronaphthalene (23.7 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3au** (23.9 mg, 65%) as a colorless liquid.

TLC: R_f = 0.80 (petroleum ether)

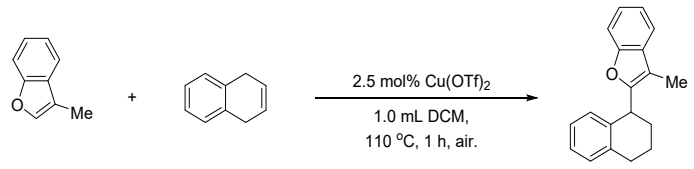
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.42 (m, 1H), 7.39 – 7.28 (m, 2H), 7.27 – 7.18 (m, 2H), 7.16 – 7.10 (m, 1H), 6.87 – 6.67 (m, 1H), 4.30 – 3.94 (m, 1H), 3.12 – 2.79 (m, 2H), 2.25 (d, *J* = 9.4 Hz, 3H), 2.22 – 1.84 (m, 2H), 1.53 – 1.47 (m, 1H), 1.42 – 1.04 (m, 2H), 0.94 (dt, *J* = 21.1, 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.09, 154.81, 154.13, 154.11, 139.90, 139.62, 136.02, 135.78, 131.98, 131.80, 131.73, 130.80, 130.25, 130.13, 129.11, 128.84, 123.67, 123.52, 122.23, 122.11, 120.05, 118.99, 118.93, 112.67, 111.46, 111.10, 111.00, 43.29, 40.87, 40.35, 40.13, 29.54, 29.34, 27.13, 26.75, 26.44, 24.90, 12.09, 11.03, 8.64, 8.20.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{21}BrO$ $[M]^+$: 368.07703, found: 368.07695.

3-methyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (3av) (*see substrate list*)



0.15 mmol 0.1 mmol 79%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1,4-dihydronaphthalene (13.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3av** (20.7 mg, 79%) as a colorless liquid.

TLC: R_f = 0.80 (petroleum ether)

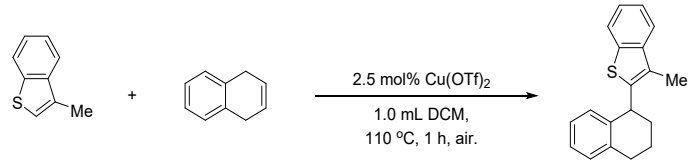
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.45 (m, 1H), 7.40 – 7.32 (m, 1H), 7.26 – 7.20 (m, 2H), 7.20 – 7.11 (m, 2H), 7.09 – 7.01 (m, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.43 – 4.35 (m, 1H), 3.09 – 2.81 (m, 2H), 2.28 – 2.04 (m, 6H), 1.96 – 1.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.43, 154.06, 137.44, 136.44, 130.56, 129.45, 129.04, 126.49, 126.01, 123.49, 122.11, 118.90, 111.01, 110.91, 37.73, 29.76, 29.40, 22.28, 8.07.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{18}O$ $[M]^+$: 262.13522, found: 262.13540.

3-methyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)benzo[b]thiophene (3av*) (*see substrate list*)



0.15 mmol 0.1 mmol 70%

The reaction was performed according to **general procedure A** using 3-methylbenzo[b]thiophene (22.2 mg, 0.15 mmol, 1.5 equiv.) and 1,4-dihydronaphthalene (13.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3av*** (19.5 mg, 70%) as a colorless liquid.

TLC: R_f = 0.80 (petroleum ether)

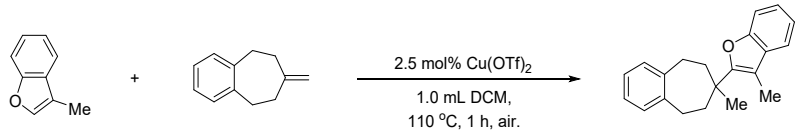
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.55 (m, 2H), 7.38 – 7.29 (m, 2H), 7.24 – 7.11 (m, 2H), 7.12 – 6.94 (m, 2H), 4.68 – 4.24 (m, 1H), 3.08 – 2.84 (m, 2H), 2.45 (s, 3H), 2.36 – 2.21 (m, 1H), 2.19 – 1.80 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.32, 143.97, 140.87, 140.57, 139.51, 138.80, 138.61, 138.13, 137.72, 137.10, 132.03, 130.42, 129.80, 129.20, 129.13, 127.22, 126.53, 126.11, 125.93, 125.84, 125.32, 123.88, 123.79, 122.95, 122.38, 121.57, 121.46, 121.01, 45.80, 39.28, 33.63, 32.53, 29.95, 29.80, 22.09, 21.16, 14.05, 12.01.

HRMS (EI): m/z Theo. Mass calculated for $C_{19}H_{18}S$ $[M]^+$: 278.11237, found: 278.11254.

3-methyl-2-(7-methyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-7-yl)benzofuran (3aw) (*see substrate list*)



0.15 mmol 0.1 mmol 32%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 7-methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (15.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. After the reaction is completed, cooling to room temperature, Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3aw** (9.3 mg, 32%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

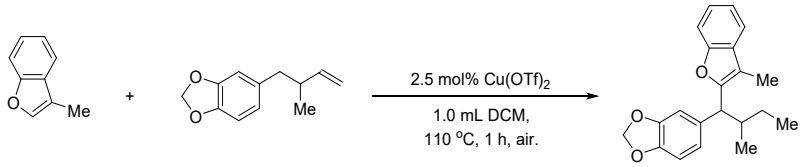
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 5.8, 3.0 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.25 – 7.21 (m, 2H), 7.11 (s, 4H), 2.98 – 2.83 (m, 2H), 2.78 (dd, *J* = 14.0, 8.6 Hz, 2H), 2.70 (d, *J* = 13.0 Hz, 2H), 2.35 (s, 3H), 1.61 (t, *J* = 12.1 Hz, 2H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.33, 153.24, 143.01, 131.78, 128.85, 126.18, 123.30, 121.96, 118.62, 110.66, 109.20, 43.08, 38.25, 36.15, 32.05, 9.38.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{22}O$ $[M]^+$: 290.16652, found: 290.16668.

5-(2-methyl-1-(3-methylbenzofuran-2-yl)butyl)benzo[d][1,3]dioxole (3ax) (*see substrate list*)



0.15 mmol 0.1 mmol 91%; 1.4/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 5-(2-methylbut-3-en-1-yl)benzo[d][1,3]dioxole (19.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether/ ethyl acetate = 200/1, v/v as the eluent) afforded **3ax** (29.3 mg, 91%) as a colorless liquid.

TLC: R_f = 0.15 (petroleum ether/ ethyl acetate = 50/1, v/v)

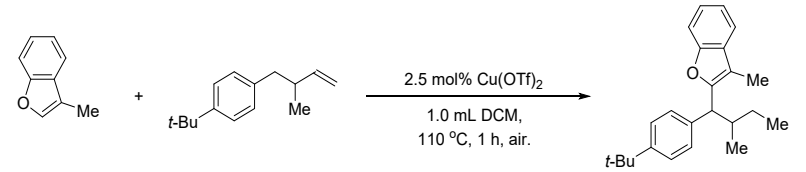
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.39 (m, 2H), 7.22 – 7.15 (m, 2H), 7.00 (d, *J* = 1.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.98 – 5.80 (m, 2H), 3.68 (dd, *J* = 12.7, 10.8 Hz, 1H), 2.43 – 2.27 (m, 1H), 2.20 (d, *J* = 2.7 Hz, 3H), 1.50 – 1.34 (m, 1H), 1.14 – 0.96 (m, 1H), 0.94 – 0.79 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.92, 154.82, 154.05, 147.80, 146.16, 135.98, 135.82, 130.33, 130.30, 123.26, 122.11, 121.65, 118.92, 118.89, 110.97, 110.93, 110.35, 110.33, 108.76, 108.17, 108.15, 100.96, 49.86, 49.73, 38.18, 37.97, 27.55, 27.27, 17.42, 17.38, 11.20, 11.05, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{22}O_3$ $[M]^+$: 322.15635, found: 322.15644.

2-(1-(4-(tert-butyl)phenyl)-2-methylbutyl)-3-methylbenzofuran (3ay) (*see substrate list*)



0.15 mmol 0.1 mmol 86%; 1.6/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-(tert-butyl)-4-(2-methylbut-3-en-1-yl)benzene (20.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3ay** (28.7 mg, 86%) as a colorless liquid.

TLC: R_f = 0.70 (petroleum ether)

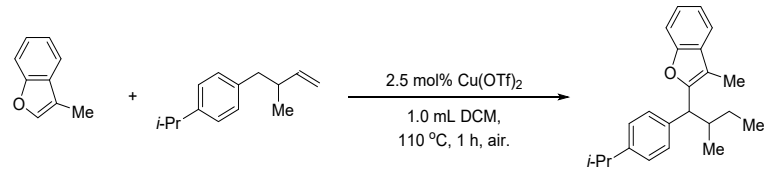
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.38 (m, 2H), 7.36 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.19 (qd, *J* = 7.2, 3.8 Hz, 2H), 3.75 (dd, *J* = 15.7, 10.6 Hz, 1H), 2.42 (qd, *J* = 12.1, 7.1 Hz, 1H), 2.22 (d, *J* = 2.1 Hz, 3H), 1.50 – 1.37 (m, 1H), 1.29 (s, 9H), 1.16 – 0.96 (m, 1H), 0.94 – 0.79 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.24, 155.13, 154.07, 149.17, 138.85, 138.70, 130.41, 130.39, 128.15, 128.12, 125.38, 123.13, 122.03, 118.86, 118.84, 110.92, 110.88, 110.32, 110.27, 49.72, 49.54, 38.06, 37.88, 34.49, 31.52, 27.56, 27.40, 17.57, 17.38, 11.26, 11.08, 8.18.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{30}O$ $[M]^+$: 334.22912, found: 334.22907.

2-(1-(4-isopropylphenyl)-2-methylbutyl)-3-methylbenzofuran (3az) (*see substrate list*)



0.15 mmol 0.1 mmol 95%; 1/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (18.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3az** (30.4 mg, 95%) as a colorless liquid.

TLC: R_f = 0.70 (petroleum ether)

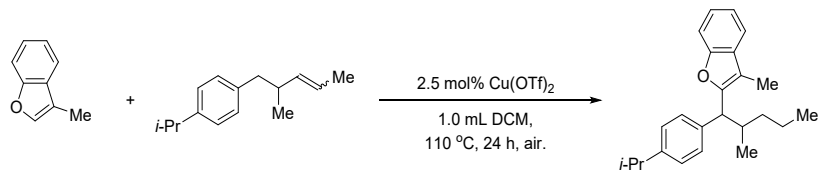
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 10.6, 6.3 Hz, 1H), 3.04 – 2.84 (m, 2H), 2.24 – 2.05 (m, 3H), 2.01 – 1.84 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.84, 158.76, 149.57, 137.87, 132.38, 129.87, 127.76, 126.96, 126.81, 125.50, 123.49, 118.37, 113.43, 51.04, 29.51, 26.90, 22.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{23}H_{28}O$ $[M]^+$: 320.21347, found: 320.21355.

2-(1-(4-isopropylphenyl)-2-methylpentyl)-3-methylbenzofuran (3ba) (*see substrate list*)

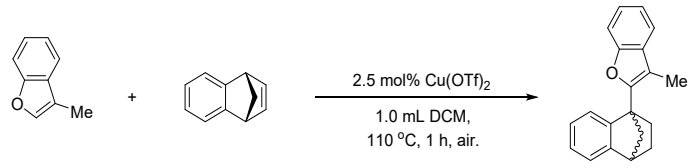


0.15 mmol 0.1 mmol 0%

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylpent-3-en-1-yl)benzene (20.2 mg, 0.1 mmol, 1.0

equiv.) as the substrates. After the reaction is completed, cooling it to room temperature, no new spots were found in TLC test.

2-(3,4-dihydro-1,4-methanonaphthalen-1(2H)-yl)-3-methylbenzofuran (3bb) (*see substrate list*)



0.15 mmol 0.1 mmol 18%; 1/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1,4-dihydro-1,4-methanonaphthalene (14.2 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3bb** (4.9 mg, 18%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

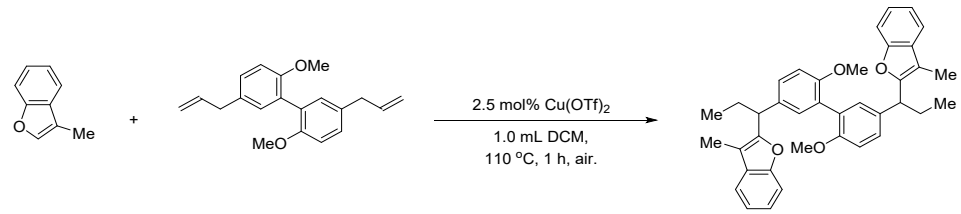
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.38 (m, 2H), 7.31 – 7.19 (m, 4H), 7.18 – 7.09 (m, 2H), 3.54 (s, 1H), 3.43 (s, 1H), 2.97 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.40 (d, *J* = 9.0 Hz, 1H), 2.30 (ddd, *J* = 10.4, 9.4, 4.8 Hz, 1H), 2.18 (s, 3H), 1.89 (d, *J* = 9.0 Hz, 1H), 1.80 – 1.67 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.25, 153.91, 148.59, 148.56, 130.65, 126.11, 125.81, 123.25, 122.17, 121.20, 120.67, 118.76, 110.79, 109.64, 50.16, 48.01, 43.99, 37.74, 33.97, 8.15.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{18}O$ $[M]^+$: 274.13522, found: 274.13543.

2,2'-((6,6'-dimethoxy-[1,1'-biphenyl]-3,3'-diyl)bis(propane-1,1-diyl))bis(3-methylbenzofuran) (3bc) (*see substrate list*)



0.3 mmol 0.1 mmol 53%

The reaction was performed according to **general procedure C** using 3-methylbenzofuran (39.6 mg, 0.3 mmol, 3.0 equiv.) and 5,5'-diallyl-2,2'-dimethoxy-1,1'-biphenyl (29.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether/ ethyl acetate = 200/1, v/v, as the eluent) afforded **3bc** (29.6 mg, 53%) as a colorless liquid.

TLC: R_f = 0.20 (petroleum ether/ ethyl acetate = 40/1, v/v)

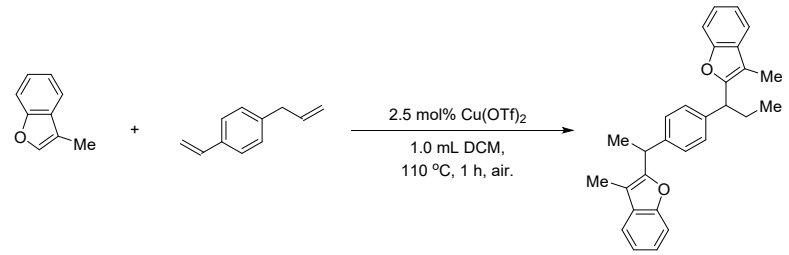
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (ddd, *J* = 7.0, 6.5, 3.8 Hz, 4H), 7.35 – 7.28 (m, 4H), 7.21 (dd, *J* = 6.2, 2.8 Hz, 4H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.02 (dd, *J* = 9.2, 6.5 Hz, 2H), 3.70 (s, 6H), 2.31 – 2.21 (m, 8H), 2.13 (ddd, *J* = 15.8, 9.9, 3.9 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.75, 155.24, 154.11, 134.44, 134.43, 131.44, 131.40, 130.58, 127.71, 127.67, 127.63, 123.17, 122.01, 118.86, 111.33, 110.91, 110.29, 110.27, 55.84, 44.54, 44.51, 27.55, 27.52, 12.76, 8.12.

HRMS (EI): m/z Theo. Mass calculated for $C_{38}H_{38}O_4$ $[M]^+$: 558.27646, found: 558.27746.

3-methyl-2-(1-(4-(1-(3-methylbenzofuran-2-yl)ethyl)phenyl)propyl)benzofuran (3bd) (*see substrate list*)



The reaction was performed according to **general procedure C** using 3-methylbenzofuran (39.6 mg, 0.3 mmol, 3.0 equiv.) and 1-allyl-4-vinylbenzene (14.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3bd** (15.1 mg, 37%) as a colorless liquid.

TLC: R_f = 0.45 (petroleum ether)

Melting point:

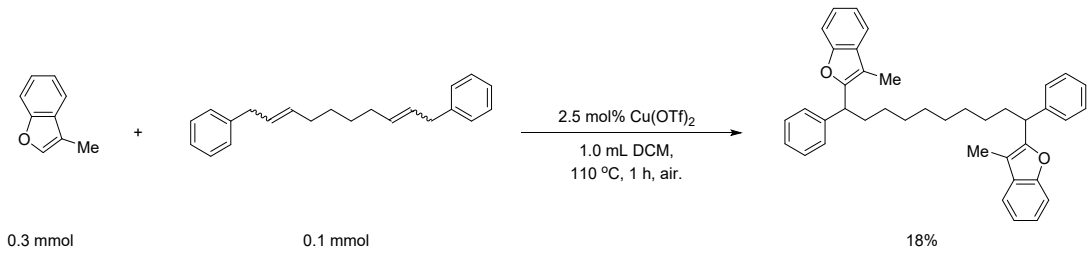
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, *J* = 9.1, 7.0 Hz, 4H), 7.34 – 7.26 (m, 4H), 7.22 – 7.12 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 1H), 3.98 (dd, *J* = 9.2, 6.5 Hz, 1H), 2.27 – 2.17 (m, 4H), 2.15 (d, *J* = 1.2 Hz, 3H), 2.12 – 2.03 (m, 1H), 1.69 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.42, 158.06, 150.33, 138.05, 134.05, 133.55, 131.57, 129.73, 129.19, 127.40, 126.35, 125.51, 125.30, 124.96, 123.45, 123.04, 118.25, 112.35, 48.04, 16.83.

HRMS (EI): m/z Theo. Mass calculated for $C_{29}H_{28}O_2$ $[M]^+$: 408.20838, found: 408.20867.

1,10-bis(3-methylbenzofuran-2-yl)-1,10-diphenyldecane (3be) (*see substrate list*)



The reaction was performed according to **general procedure C** using 3-methylbenzofuran (39.6 mg, 0.3 mmol, 3.0 equiv.) and 1,10-diphenyldeca-2,8-diene (29.0 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3be** (10 mg, 18%) as a colorless liquid.

TLC: R_f = 0.45 (petroleum ether)

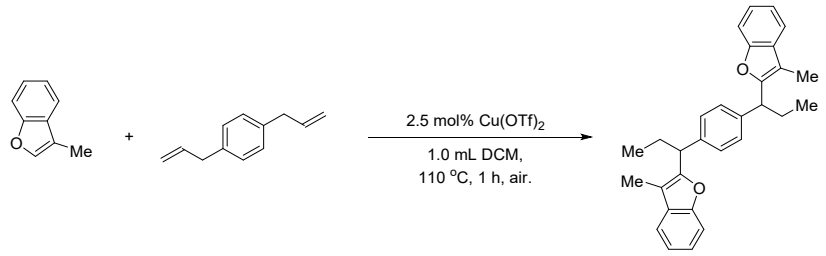
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.34 (m, 7H), 7.29 (t, *J* = 7.5 Hz, 5H), 7.23 – 7.16 (m, 6H), 4.10 (dd, *J* = 9.3, 6.6 Hz, 2H), 2.20 (m, 8H), 2.04 (m, 2H), 1.33 – 1.18 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.00, 154.05, 143.00, 130.46, 128.56, 127.86, 126.53, 123.28, 122.08, 118.92, 110.95, 110.26, 43.51, 34.33, 29.53, 28.01, 8.13.

HRMS (ESI): m/z Theo. Mass calculated for $C_{40}H_{42}NaO_2$ $[M+Na]^+$: 577.30770, found: 577.30820.

1,4-bis(1-(3-methylbenzofuran-2-yl)propyl)benzene (3bf) (*see substrate list*)



0.3 mmol 0.1 mmol 31%

The reaction was performed according to **general procedure C** using 3-methylbenzofuran (39.6 mg, 0.3 mmol, 3.0 equiv.) and 1,4-diallylbenzene (15.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **3bf** (13.1 mg, 31%) as a colorless liquid.

TLC: R_f = 0.35 (petroleum ether)

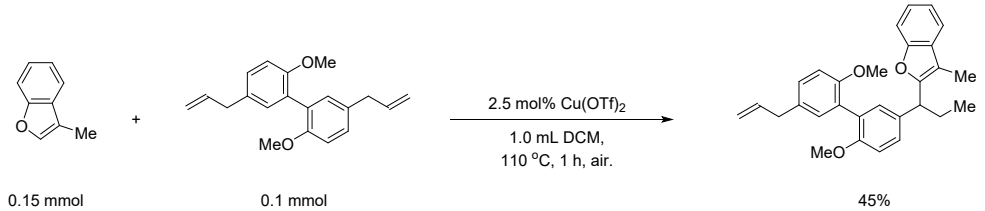
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (td, *J* = 6.2, 2.6 Hz, 4H), 7.29 (s, 4H), 7.23 – 7.14 (m, 4H), 3.98 (dd, *J* = 9.2, 6.5 Hz, 2H), 2.29 – 2.15 (m, 9H), 2.13 – 1.98 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.89, 154.08, 140.91, 130.47, 127.92, 123.26, 122.06, 118.90, 110.92, 110.46, 100.13, 44.99, 27.49, 12.77, 8.10.

HRMS (EI): m/z Theo. Mass calculated for $C_{30}H_{30}O_2$ $[M]^+$: 422.22403, found: 422.22452.

2-(1-(5'-allyl-2',6-dimethoxy-[1,1'-biphenyl]-3-yl)propyl)-3-methylbenzofuran (3bg) (*see substrate list*)



0.15 mmol 0.1 mmol 45%

The reaction was performed according to **general procedure C** using 3-methylbenzofuran (39.6 mg, 0.3 mmol, 3.0 equiv.) and 5,5'-diallyl-2,2'-dimethoxy-1,1'-biphenyl (29.4 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether/ ethyl acetate = 200/1, v/v, as the eluent) afforded **3bg** (19.2 mg, 45%) as a colorless liquid.

TLC: R_f = 0.25 (petroleum ether/ ethyl acetate = 40/1, v/v)

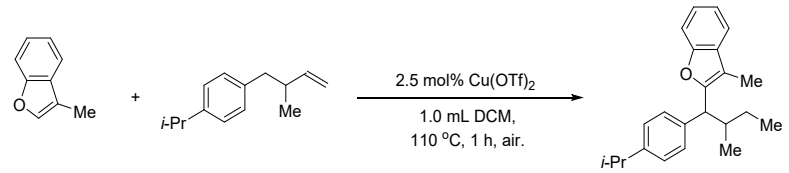
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.26 – 7.09 (m, 4H), 7.07 (d, *J* = 2.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 4.3 Hz, 2H), 6.06 – 5.89 (m, 1H), 5.14 – 5.02 (m, 2H), 4.00 (dd, *J* = 9.2, 6.5 Hz, 1H), 3.78 – 3.69 (m, 6H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.31 – 2.17 (m, 4H), 2.16 – 2.07 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.21, 155.76, 155.66, 155.24, 154.10, 137.97, 134.48, 134.46, 131.93, 131.90, 131.75, 131.25, 130.58, 128.69, 128.53, 127.76, 127.73, 123.17, 122.01, 120.47, 118.86, 115.61, 111.51, 111.41, 111.22, 110.92, 110.27, 56.00, 55.92, 55.90, 55.81, 44.56, 39.55, 29.85, 27.59, 27.56, 12.77, 8.14.

HRMS (EI): m/z Theo. Mass calculated for $C_{29}H_{30}O_3$ $[M]^+$: 426.21895, found: 426.21919.

2-(1-(4-isopropylphenyl)-2-methylbutyl)-3-methylbenzofuran (4a) (*see substrate list*)



0.15 mmol 0.1 mmol 95%; 1.1/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (18.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4a** (30.4 mg, 95%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

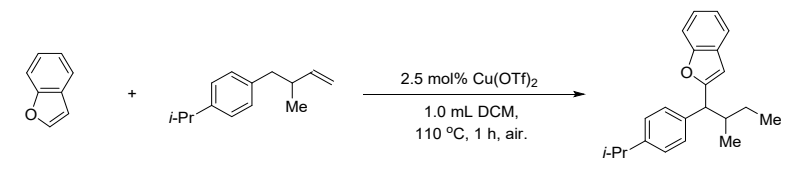
NMR and HSQC Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.38 (m, 2H), 7.36 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.24 – 7.11 (m, 4H), 3.76 (dd, *J* = 15.6, 10.6 Hz, 1H), 2.96 – 2.77 (m, 1H), 2.54 – 2.32 (m, 1H), 2.22 (d, *J* = 2.3 Hz, 3H), 1.49 – 1.35 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.06 (m, 1H), 0.96 – 0.78 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.25, 155.15, 154.09, 146.92, 139.26, 139.11, 130.42, 130.40, 128.44, 128.41, 126.54, 126.53, 123.14, 122.03, 118.86, 118.84, 110.92, 110.88, 110.32, 110.27, 49.85, 49.67, 38.09, 37.90, 33.80, 27.58, 27.40, 24.13, 17.56, 17.40, 11.24, 11.08, 8.17.

HRMS (EI): m/z Theo. Mass calculated for $C_{23}H_{28}O$ $[M]^+$: 320.21347, found: 320.21355.

2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran (4b) (*see substrate list*)



0.15 mmol 0.1 mmol 70%; 1/1 dr

The reaction was performed according to **general procedure A** using benzofuran (17.7 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4b** (21.4 mg, 70%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

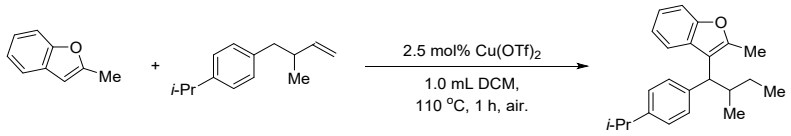
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.12 (m, 4H), 6.49 (d, *J* = 1.9 Hz, 1H), 3.78 (dd, *J* = 9.7, 1.9 Hz, 1H), 2.96 – 2.78 (m, 1H), 2.40 – 2.24 (m, 1H), 1.54 – 1.37 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.20 – 1.00 (m, 1H), 1.00 – 0.81 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.04, 160.99, 154.83, 147.17, 147.13, 138.84, 138.65, 128.94, 128.62, 128.47, 126.54, 126.49, 123.21, 122.52, 120.44, 111.11, 111.09, 102.91, 102.84, 52.18, 52.04, 38.41, 38.34, 33.80, 27.87, 27.22, 24.12, 17.61, 17.31, 11.42, 11.28.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{26}O$ $[M]^+$: 306.19782, found: 306.19766.

3-(1-(4-isopropylphenyl)-2-methylbutyl)-2-methylbenzofuran (4c) (*see substrate list*)



0.15 mmol 0.1 mmol 62%; 1/1 dr

The reaction was performed according to **general procedure A** using 2-methylbenzofuran (19.8 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4c** (19.8 mg, 62%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

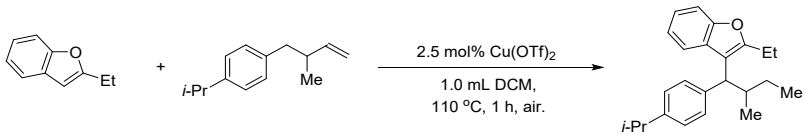
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.65 (m, 1H), 7.39 – 7.32 (m, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.11 (dd, *J* = 8.1, 1.5 Hz, 2H), 3.65 (t, *J* = 11.4 Hz, 1H), 2.93 – 2.74 (m, 1H), 2.67 – 2.51 (m, 1H), 2.47 (d, *J* = 1.9 Hz, 3H), 1.63 – 1.52 (m, 1H), 1.21 (dd, *J* = 6.9, 0.8 Hz, 6H), 1.16 – 0.99 (m, 1H), 0.98 – 0.82 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.84, 158.76, 149.57, 137.87, 132.38, 129.87, 127.76, 126.96, 126.81, 125.50, 123.49, 118.37, 113.43, 51.04, 29.51, 26.90, 22.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{23}H_{28}O$ $[M]^+$: 320.21347, found: 320.21347.

2-ethyl-3-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran (4d) (*see substrate list*)



0.15 mmol 0.1 mmol 66%; 3.2/1 dr

The reaction was performed according to **general procedure A** using 2-ethylbenzofuran (21.9 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4d** (22.0 mg, 66%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

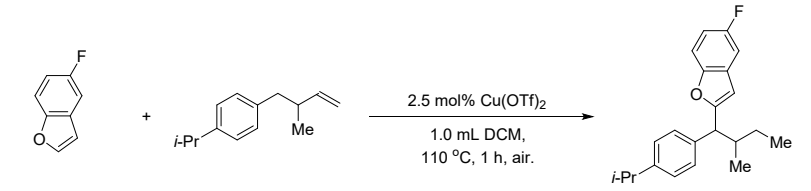
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 10.6, 6.3 Hz, 1H), 3.04 – 2.84 (m, 2H), 2.24 – 2.05 (m, 3H), 2.01 – 1.84 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.84, 158.76, 149.57, 137.87, 132.38, 129.87, 127.76, 126.96, 126.81, 125.50, 123.49, 118.37, 113.43, 51.04, 29.51, 26.90, 22.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{24}H_{30}O$ $[M]^+$: 334.22912, found: 334.22897.

5-fluoro-2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran (4e) (*see substrate list*)



0.15 mmol 0.1 mmol 74%; 1/1 dr

The reaction was performed according to **general procedure A** using 5-fluorobenzofuran (20.4 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4e** (24.0 mg, 74%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

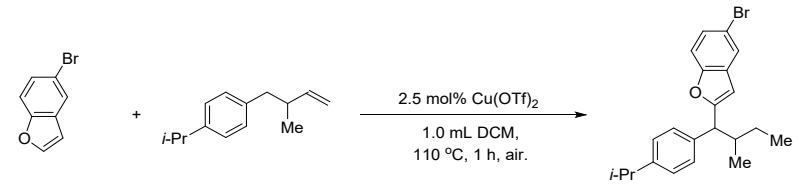
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.9, 4.1 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.20 – 7.14 (m, 2H), 7.11 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.90 (td, *J* = 9.1, 2.6 Hz, 1H), 6.45 (d, *J* = 1.8 Hz, 1H), 3.75 (dd, *J* = 9.7, 3.0 Hz, 1H), 2.91 – 2.84 (m, 1H), 2.36 – 2.22 (m, 1H), 1.52 – 1.37 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.18 – 1.07 (m, 1H), 0.98 – 0.91 (m, 3H), 0.88 – 0.80 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.04, 163.00, 160.45, 158.10, 151.06, 147.33, 147.30, 138.53, 138.36, 129.79, 129.68, 128.59, 128.44, 126.62, 126.56, 111.62, 111.60, 111.52, 111.50, 110.83, 110.57, 106.12, 105.87, 103.23, 103.19, 103.16, 103.12, 52.28, 52.13, 38.42, 38.36, 33.81, 27.87, 27.18, 24.11, 17.59, 17.28, 11.39, 11.23.

^{19}F NMR (177 MHz, $CDCl_3$): δ -121.80, -121.84.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{25}FO$ $[M]^+$: 324.18840, found: 324.18834.

5-bromo-2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran (4f) (*see substrate list*)



0.15 mmol 0.1 mmol 65%; 1/1 dr

The reaction was performed according to **general procedure A** using 5-bromobenzofuran (29.6 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4f** (25.0 mg, 65%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

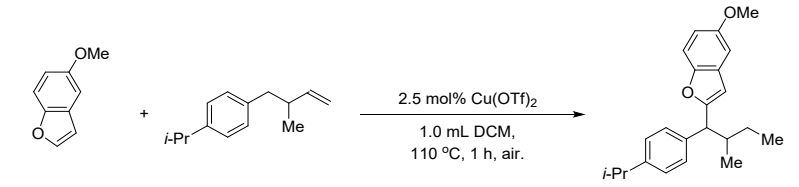
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, *J* = 1.2 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.23 – 7.13 (m, 2H), 7.12 – 7.00 (m, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 3.77 (dd, *J* = 9.8, 4.3 Hz, 1H), 2.97 – 2.82 (m, 1H), 2.36 – 2.28 (m, 1H), 1.25 (dd, *J* = 6.9, 3.9 Hz, 6H), 1.15 – 1.00 (m, 2H), 0.99 – 0.91 (m, 3H), 0.87 (dd, *J* = 12.2, 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.53, 162.50, 153.56, 147.35, 147.32, 138.38, 138.20, 130.94, 128.57, 128.42, 126.63, 126.57, 126.08, 123.09, 115.60, 112.52, 112.51, 102.48, 102.42, 52.17, 52.00, 38.36, 38.32, 33.80, 27.85, 27.14, 24.11, 17.58, 17.26, 11.39, 11.23.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{25}BrO$ $[M]^+$: 384.10833, found: 384.10836.

2-(1-(4-isopropylphenyl)-2-methylbutyl)-5-methoxybenzofuran (4g) (*see substrate list*)



0.15 mmol 0.1 mmol 59%; 1/1 dr

The reaction was performed according to **general procedure A** using 5-methoxybenzofuran (22.2 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4g** (19.8 mg, 59%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

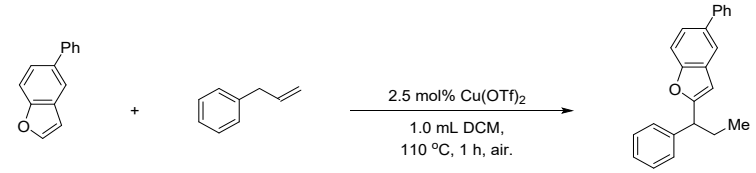
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.79 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.42 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H), 3.73 (dd, *J* = 9.8, 1.6

Hz, 1H), 2.93 – 2.80 (m, 1H), 2.34 – 2.22 (m, 1H), 1.53 – 1.40 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.15 – 1.00 (m, 1H), 0.93 (dd, *J* = 10.7, 7.0 Hz, 3H), 0.84 (dd, *J* = 14.1, 7.1 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.94, 161.89, 155.88, 149.81, 147.15, 147.11, 138.83, 138.65, 129.48, 128.58, 128.43, 126.53, 126.48, 111.62, 111.46, 111.44, 103.35, 103.10, 103.02, 56.10, 52.24, 52.11, 38.41, 38.35, 33.79, 27.86, 27.20, 24.12, 17.59, 17.30, 11.42, 11.27.

HRMS (EI): m/z Theo. Mass calculated for $C_{23}H_{28}O_2$ $[M]^+$: 336.20838, found: 336.20828.

5-phenyl-2-(1-phenylpropyl)benzofuran (4h) (*see substrate list*)



0.15 mmol 0.1 mmol 73%

The reaction was performed according to **general procedure A** using 5-phenylbenzofuran (29.1 mg, 0.15 mmol, 1.5 equiv.) and allylbenzene (11.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4h** (22.8 mg, 73%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

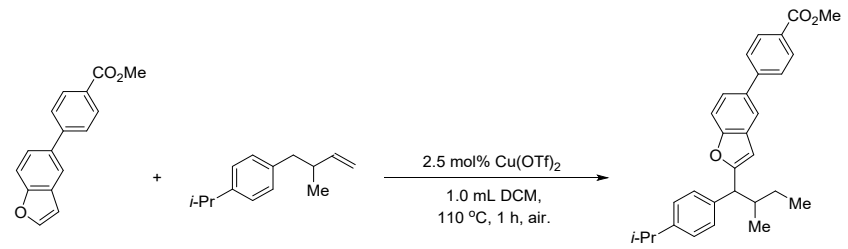
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.54 – 7.38 (m, 5H), 7.37 – 7.29 (m, 5H), 6.51 (s, 1H), 3.98 (t, *J* = 7.7 Hz, 1H), 2.40 – 2.18 (m, 1H), 2.13 – 1.93 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.13, 154.56, 142.01, 136.38, 129.36, 128.83, 128.67, 128.62, 128.17, 128.12, 127.57, 126.92, 126.88, 123.20, 119.16, 111.19, 102.74, 47.77, 27.73, 12.56.

HRMS (EI): m/z Theo. Mass calculated for $C_{28}H_{30}O$ $[M]^+$: 382.22912, found: 382.22919.

methyl 4-(2-(1-(4-isopropylphenyl)-2-methylbutyl)benzofuran-5-yl)benzoate (4i) (*see substrate list*)



0.15 mmol 0.1 mmol 55%; 1/1 dr

The reaction was performed according to **general procedure A** using methyl 4-(benzofuran-5-yl)benzoate (37.8 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22

μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4i** (24.2 mg, 55%) as a colorless liquid.

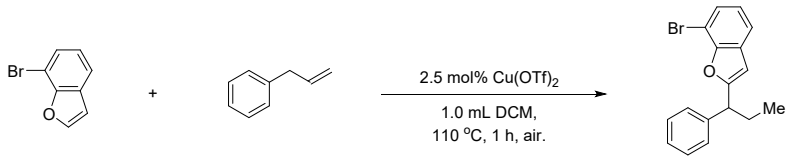
TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.47 (dt, *J* = 8.5, 5.1 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 1.8 Hz, 1H), 3.95 (s, 3H), 3.80 (dd, *J* = 9.7, 1.9 Hz, 1H), 2.96 – 2.80 (m, 1H), 2.40 – 2.26 (m, 1H), 1.32 (d, *J* = 8.0 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.02 – 0.83 (m, 7H).

HRMS (EI): m/z Theo. Mass calculated for $C_{30}H_{32}O_3$ $[M]^+$: 440.23460, found: 440.23467.

7-bromo-2-(1-phenylpropyl)benzofuran (4j) (*see substrate list*)



0.15 mmol 0.1 mmol 83%

The reaction was performed according to **general procedure A** using 7-bromobenzofuran (29.6 mg, 0.15 mmol, 1.5 equiv.) and allylbenzene (11.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4j** (26.1 mg, 83%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

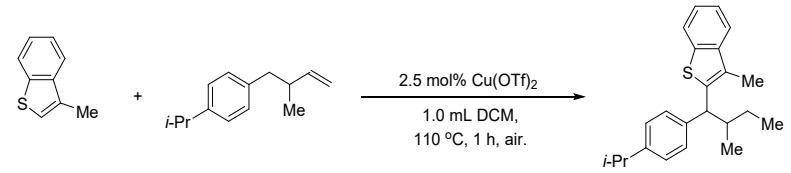
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.37 (m, 2H), 7.34 (d, *J* = 4.3 Hz, 4H), 7.29 (dd, *J* = 7.9, 4.1 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.46 (s, 1H), 4.01 (t, *J* = 7.7 Hz, 1H), 2.38 – 2.24 (m, 1H), 2.10 – 1.98 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.50, 152.02, 141.55, 130.14, 128.71, 128.23, 127.02, 126.58, 123.87, 119.71, 103.88, 103.30, 47.69, 27.90, 12.55.

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{15}BrO$ $[M]^+$: 314.03008, found: 314.03033.

2-(1-(4-isopropylphenyl)-2-methylbutyl)-3-methylbenzo[b]thiophene (4k) (*see substrate list*)



0.15 mmol 0.1 mmol 84%; 1.2/1 dr

The reaction was performed according to **general procedure A** using 3-methylbenzo[b]thiophene (22.2 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol,

1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4k** (28.2 mg, 84%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

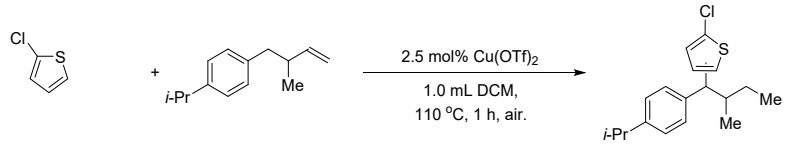
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 7.9, 2.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 3H), 7.29 – 7.24 (m, 1H), 7.21 – 7.11 (m, 2H), 4.05 (dd, *J* = 15.0, 10.9 Hz, 1H), 2.95 – 2.80 (m, 1H), 2.42 (d, *J* = 6.6 Hz, 3H), 2.26 (qdd, *J* = 12.9, 6.6, 3.4 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.14 – 0.76 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.84, 146.81, 144.08, 143.95, 140.76, 140.72, 140.70, 140.60, 138.66, 138.57, 128.24, 128.19, 126.66, 126.63, 123.78, 123.64, 122.28, 121.51, 121.46, 51.87, 40.40, 40.18, 33.76, 27.81, 27.67, 24.11, 24.10, 17.91, 17.68, 12.21, 12.16, 11.40, 11.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{23}H_{28}S$ $[M]^+$: 336.19062, found: 336.19083.

2-chloro-5-(1-(4-isopropylphenyl)-2-methylbutyl)thiophene and other isomer mixtures (4l) (*see substrate list*)



0.15 mmol 0.1 mmol 30%; 1/1 dr

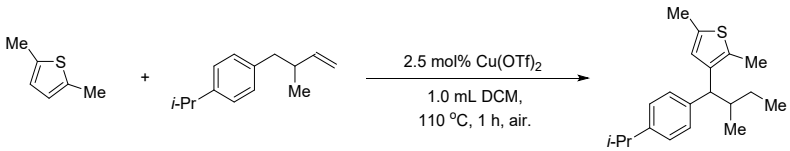
The reaction was performed according to **general procedure A** using 2,5-dimethylfuran (17.3 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded mixtures **4l** (9.1 mg, 32%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{23}ClS$ $[M]^+$: 306.12035, found: 306.12042.

3-(1-(4-isopropylphenyl)-2-methylbutyl)-2,5-dimethylthiophene (4m) (*see substrate list*)



0.15 mmol 0.1 mmol 32%; 1/1 dr

The reaction was performed according to **general procedure A** using 2,5-dimethylthiophene (17.2 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4m** (9.6 mg, 32%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

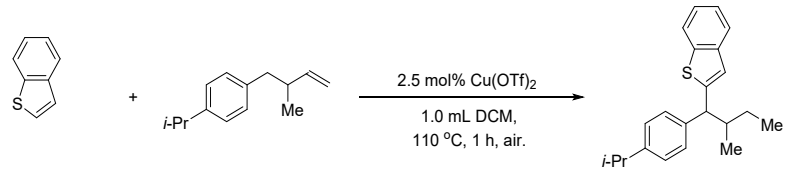
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 10.6, 6.3 Hz, 1H), 3.04 – 2.84 (m, 2H), 2.24 – 2.05 (m, 3H), 2.01 – 1.84 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.84, 158.76, 149.57, 137.87, 132.38, 129.87, 127.76, 126.96, 126.81, 125.50, 123.49, 118.37, 113.43, 51.04, 29.51, 26.90, 22.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{28}S$ $[M]^+$: 300.19062, found: 300.19008.

2-(1-(4-isopropylphenyl)-2-methylbutyl)benzo[b]thiophene (4n) (*see substrate list*)



0.15 mmol 0.1 mmol 57%, C2/C3 = 3/1; 1/1 dr

The reaction was performed according to **general procedure A** using benzo[b]thiophene (20.1 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4n** (18.4 mg, 57%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

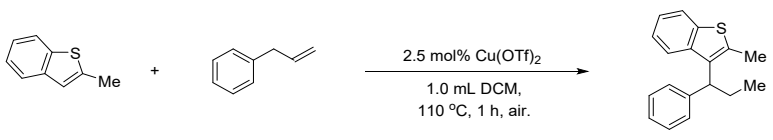
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.29 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.13 – 7.05 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 10.6, 6.3 Hz, 1H), 3.04 – 2.84 (m, 2H), 2.24 – 2.05 (m, 3H), 2.01 – 1.84 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 183.84, 158.76, 149.57, 137.87, 132.38, 129.87, 127.76, 126.96, 126.81, 125.50, 123.49, 118.37, 113.43, 51.04, 29.51, 26.90, 22.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{26}S$ $[M]^+$: 322.17497, found: 322.17519.

2-methyl-3-(1-phenylpropyl)benzo[b]thiophene (4o) (*see substrate list*)



0.15 mmol 0.1 mmol 49%

The reaction was performed according to **general procedure A** using 2-methylbenzo[b]thiophene (22.2 mg, 0.15 mmol, 1.5 equiv.) and allylbenzene (11.8 mg, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4o** (16.5 mg, 49%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

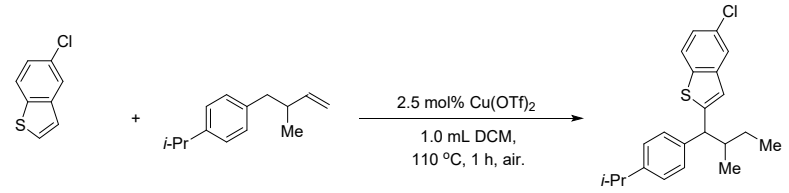
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.50 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.35 – 7.23 (m, 5H), 7.23 – 7.12 (m, 3H), 4.37 (dd, *J* = 10.2, 5.6 Hz, 1H), 2.53 (s, 3H), 2.47 – 2.34 (m, 1H), 2.34 – 2.21 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.61, 148.59, 133.95, 131.58, 129.49, 127.90, 127.77, 126.66, 125.77, 121.36, 118.64, 34.36, 27.21, 22.45, 13.89.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{18}S$ $[M]^+$: 266.11237, found: 266.11244.

5-chloro-2-(1-(4-isopropylphenyl)-2-methylbutyl)benzo[b]thiophene (4p) (*see substrate list*)



0.15 mmol 0.1 mmol 62%; 4/1 dr

The reaction was performed according to **general procedure A** using 5-chlorobenzo[b]thiophene (25.2 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4p** (22.0 mg, 62%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

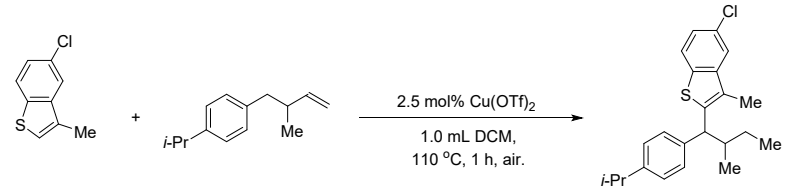
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.71 (m, 1H), 7.63 (dd, *J* = 20.5, 18.3 Hz, 1H), 7.36 (d, *J* = 3.7 Hz, 1H), 7.25 – 7.03 (m, 6H), 3.95 – 3.82 (m, 1H), 2.88 – 2.79 (m, 1H), 2.31 – 2.21 (m, 1H), 1.51 – 1.32 (m, 1H), 1.20 (d, *J* = 7.0 Hz, 6H), 1.06 – 0.99 (m, 1H), 0.93 – 0.82 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 146.86, 146.83, 140.87, 140.83, 140.06, 139.98, 139.37, 139.24, 138.56, 130.35, 128.32, 128.21, 128.06, 126.72, 126.67, 126.58, 126.53, 124.68, 124.65, 123.93, 123.79, 123.22, 122.78, 122.56, 121.95, 121.94, 119.94, 51.31, 50.92, 39.51, 39.44, 33.71, 28.09, 27.57, 24.17, 24.08, 17.97, 17.86, 11.69, 11.42.

HRMS (EI): m/z Theo. Mass calculated for $C_{22}H_{25}ClS$ $[M]^+$: 356.13600, found: 356.13606.

5-chloro-2-(1-(4-isopropylphenyl)-2-methylbutyl)-3-methylbenzo[b]thiophene (4q) (*see substrate list*)



0.15 mmol 0.1 mmol 91%; 1.8/1 dr

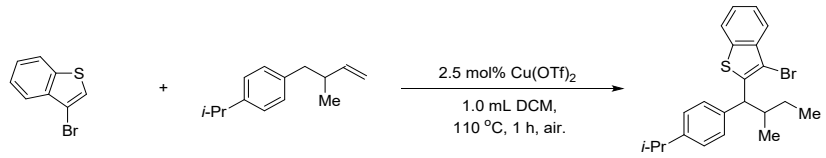
The reaction was performed according to **general procedure A** using 5-chloro-3-methylbenzo[b]thiophene (27.2 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **4q** (33.7 mg, 91%) as a colorless liquid.
TLC: R_f = 0.75 (petroleum ether)
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.27 (s, 2H), 7.23 – 7.05 (m, 4H), 4.01 (dd, *J* = 14.4, 11.2 Hz, 1H), 2.87 (dt, *J* = 13.6, 5.7 Hz, 1H), 2.36 (d, *J* = 7.1 Hz, 3H), 2.26 – 2.15 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.15 – 1.03 (m, 2H), 0.97 – 0.84 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 147.06, 147.03, 146.42, 146.28, 142.08, 142.04, 140.35, 140.27, 136.76, 136.67, 130.20, 130.18, 128.21, 128.15, 126.76, 126.72, 126.58, 126.45, 123.95, 123.25, 121.31, 121.26, 51.96, 40.48, 40.23, 33.76, 27.82, 27.62, 24.09, 24.07, 17.86, 17.64, 12.18, 12.12, 11.39, 11.14.

HRMS (EI): m/z Theo. Mass calculated for $C_{23}H_{27}ClS$ $[M]^+$: 370.15165, found: 370.15155.

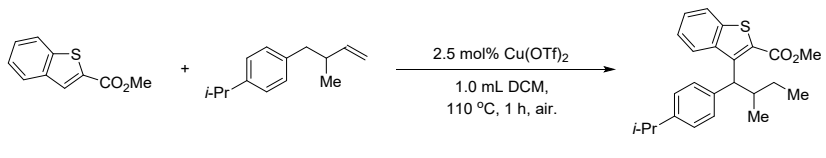
3-bromo-2-(1-(4-isopropylphenyl)-2-methylbutyl)benzo[b]thiophene (4r) (*see substrate list*)



0.15 mmol 0.1 mmol 0%

The reaction was performed according to **general procedure A** using 3-bromobenzo[b]thiophene (32.4 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. After the reaction is completed, cooling it to room temperature, no new spots were found in TLC test.

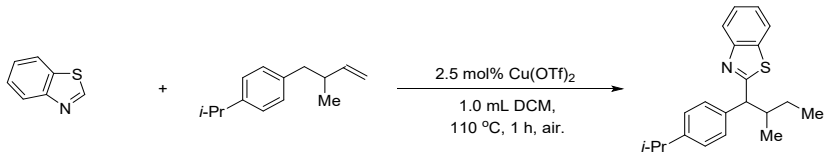
methyl 3-(1-(4-isopropylphenyl)-2-methylbutyl)benzo[b]thiophene-2-carboxylate (4s) (*see substrate list*)



0.15 mmol 0.1 mmol 0%

The reaction was performed according to **general procedure A** using methyl benzo[b]thiophene-2-carboxylate (28.8 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. After the reaction is completed, cooling it to room temperature, no new spots were found in TLC test.

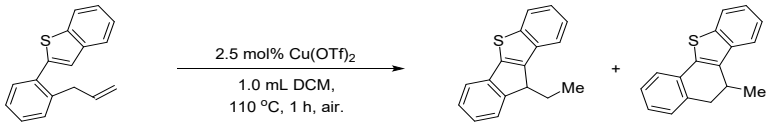
2-(1-(4-isopropylphenyl)-2-methylbutyl)benzo[d]thiazole (4t) (*see substrate list*)



0.15 mmol 0.1 mmol 0%

The reaction was performed according to **general procedure A** using benzo[d]thiazole (20.1 mg, 0.15 mmol, 1.5 equiv.) and 1-isopropyl-4-(2-methylbut-3-en-1-yl)benzene (22 μL, 0.1 mmol, 1.0 equiv.) as the substrates. After the reaction is completed, cooling it to room temperature, no new spots were found in TLC test.

10-ethyl-10H-benzo[b]indeno[2,1-d]thiophene (7a) and 6-methyl-5,6-dihydrobenzo[b]naphtho[2,1-d]thiophene (*see substrate list*)



0.1 mmol

1 / 2.4

55% (five rings and six rings mixture)

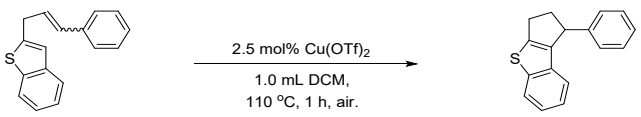
The reaction was performed according to **general procedure B** using 2-(2-allylphenyl)benzo[b]thiophene (23.4 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7a** mixtures as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (*see spectra*):

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{14}S$ $[M]^+$: 250.08100, found: 250.08099.

1-phenyl-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7b) (*see substrate list*)



0.1 mmol 69%

The reaction was performed according to **general procedure B** using 2-(3-phenylallyl)benzo[b]thiophene (25.0 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7b** (17.3 mg, 69%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 13.8, 6.4 Hz, 2H), 7.25 – 7.09 (m, 6H), 4.52 – 4.43 (m, 1H), 3.27 – 3.00 (m, 3H), 2.52 – 2.37 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.33, 144.79, 144.56, 142.42, 134.91, 128.70, 127.64, 126.55, 124.14, 123.45, 123.27, 121.83, 77.48, 77.16, 76.84, 47.35, 40.65, 29.46.

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{14}S$ $[M]^+$: 250.08107, found: 250.08141.

3-phenyl-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7c) (*see substrate list*)

0.1 mmol 70%; 1.5/1 dr

The reaction was performed according to **general procedure B** using 3-(3-phenylprop-1-en-1-yl)benzo[b]thiophene (25.0 mg, 0.10 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7c** (21.6 mg, 70%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

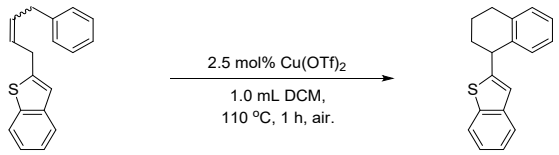
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.23 – 6.96 (m, 5H), 6.83 – 6.73 (m, 2H), 3.76 (d, *J* = 8.0 Hz, 4H), 3.13 – 2.86 (m, 2H), 2.09 – 1.59 (m, 3H), 1.11 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.07, 139.72, 138.93, 138.42, 137.16, 130.80, 130.68, 129.51, 123.86, 123.65, 123.35, 122.44, 122.23, 122.17, 113.75, 113.26, 55.31, 48.60, 37.90, 28.53, 24.27, 19.39.

HRMS (EI): m/z Theo. Mass calculated for $C_{20}H_{20}SO$ $[M]^+$: 308.12294, found: 308.12311.

2-(1,2,3,4-tetrahydronaphthalen-1-yl)benzo[b]thiophene (7d) (*see substrate list*)



0.1 mmol 35%

The reaction was performed according to **general procedure B** using 2-(4-phenylbut-2-en-1-yl)benzo[b]thiophene (26.4 mg, 0.10 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7d** (9.2 mg, 35%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

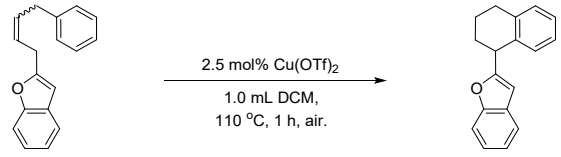
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.72 (m, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.30 (ddd, *J* = 13.6, 6.6, 1.4 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.16 – 7.07 (m, 2H), 6.89 (s, 1H), 4.47 (t, *J* = 6.0 Hz, 1H),

2.88 (tdd, *J* = 24.3, 13.7, 6.9 Hz, 2H), 2.32 – 2.19 (m, 1H), 2.19 – 2.05 (m, 1H), 2.05 – 1.89 (m, 1H), 1.86 – 1.78 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.07, 139.94, 139.67, 138.01, 137.19, 129.34, 128.68, 126.73, 125.85, 124.21, 123.72, 123.07, 122.37, 122.17, 41.30, 32.86, 29.51, 20.51.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{16}S$ $[M]^+$: 264.09672, found: 264.09705.

2-(1,2,3,4-tetrahydronaphthalen-1-yl)benzofuran (7e) (*see substrate list*)



The reaction was performed according to **general procedure B** using 3-(4-phenylbut-2-en-1-yl)benzo[b]thiophene (26.4 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7e** (11.9 mg, 48%) as a colorless liquid.

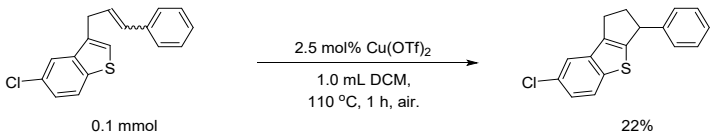
TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.09 (m, 6H), 6.18 (s, 1H), 4.33 (t, *J* = 5.7 Hz, 1H), 2.97 – 2.77 (m, 2H), 2.36 – 2.19 (m, 1H), 2.19 – 2.06 (m, 1H), 1.96 – 1.78 (m, 2H).

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{16}O$ $[M]^+$: 248.11957, found: 248.11955.

7-chloro-3-phenyl-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7f) (*see substrate list*)



The reaction was performed according to **general procedure B** using 5-chloro-3-(3-phenylallyl)benzo[b]thiophene (28.4 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7f** (6.2 mg, 22%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

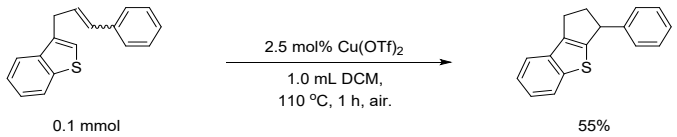
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 16.9, 5.2 Hz, 2H), 7.32 (dd, *J* = 12.9, 5.9 Hz, 2H), 7.25 – 7.15 (m, 3H), 4.56 (dt, *J* = 9.6, 5.7 Hz, 1H), 3.13 – 2.99 (m, 2H), 2.98 – 2.84 (m, 1H), 2.53 – 2.38 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.65, 144.56, 143.63, 140.99, 136.36, 130.60, 128.81, 127.35, 126.95, 124.60, 123.94, 121.61, 49.06, 39.82, 26.84.

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{13}ClS$ $[M]^+$: 284.04210, found: 284.04224.

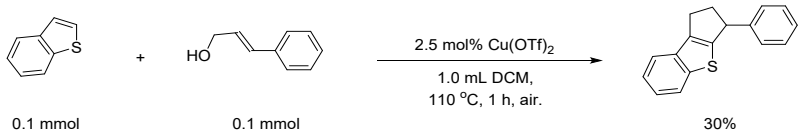
3-phenyl-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7g) (*see substrate list*)

Intramolecular cyclization:



The reaction was performed according to **general procedure B** using 3-(3-phenylallyl)benzo[b]thiophene (25.0 mg, 0.10 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7g** (13.8 mg, 55%) as a colorless liquid.

Intermolecular cyclization:



The reaction was performed using benzo[b]thiophene (13.4 mg, 0.10 mmol, 1.0 equiv.), (*E*)-3-phenylprop-2-en-1-ol (13.4 mg, 0.10 mmol, 1.0 equiv.) as the substrates. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7g** (7.5 mg, 30%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

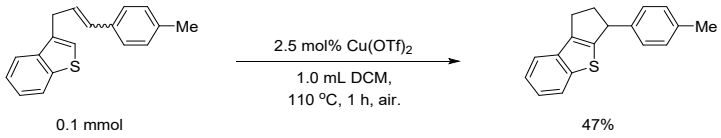
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 14.4, 7.6 Hz, 3H), 7.29 – 7.24 (m, 3H), 4.60 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.17 – 3.03 (m, 2H), 3.03 – 2.91 (m, 1H), 2.56 – 2.43 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.31, 145.65, 144.95, 141.62, 135.23, 128.73, 127.38, 126.80, 124.32, 123.71, 123.63, 121.85, 49.01, 39.94, 26.93.

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{14}S$ $[M]^+$: 250.08160, found: 250.08143.

3-(p-tolyl)-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7h) (*see substrate list*)



The reaction was performed according to **general procedure B** using 3-(3-(p-tolyl)allyl)benzo[b]thiophene (26.4 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7h** (12.4 mg, 47%) as a colorless liquid.

TLC: R_f = 0.75 (petroleum ether)

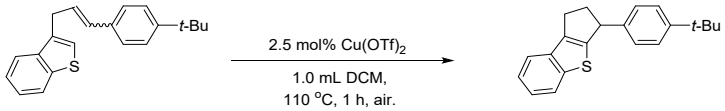
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.18 – 7.09 (m, 4H), 4.61 – 4.48 (m, 1H), 3.16 – 3.00 (m, 2H), 2.99 – 2.88 (m, 1H), 2.51 – 2.40 (m, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.62, 145.63, 141.96, 141.48, 136.37, 135.27, 129.42, 127.27, 124.29, 123.72, 123.57, 121.82, 48.63, 40.02, 26.93, 21.19.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{16}S$: 264.09672, found: 264.09700.

3-(4-(tert-butyl)phenyl)-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7i) (*see substrate list*)



0.1 mmol 50%

The reaction was performed according to **general procedure B** using 3-(3-(4-(tert-butyl)phenyl)allyl)benzo[b]thiophene (30.6 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7i** (15.3 mg, 50%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

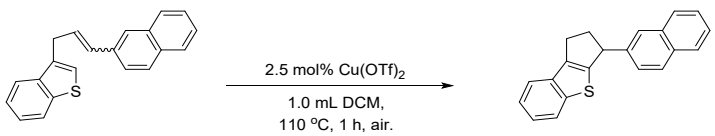
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.31 – 7.26 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.63 – 4.50 (m, 1H), 3.16 – 3.00 (m, 2H), 3.00 – 2.86 (m, 1H), 2.55 – 2.38 (m, 1H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.70, 146.65, 145.73, 141.93, 141.60, 135.39, 127.10, 125.71, 124.39, 123.81, 123.67, 121.92, 48.63, 40.00, 31.64, 27.03.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{22}S$ $[M]^+$: 306.14367, found: 306.14379.

3-(naphthalen-2-yl)-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7j) (*see substrate list*)



0.1 mmol 32%

The reaction was performed according to **general procedure B** using 3-(3-(naphthalen-2-yl)allyl)benzo[b]thiophene (30.0 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash

column chromatography (silica, petroleum ether as the eluent) afforded **7j** (9.6 mg, 32%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

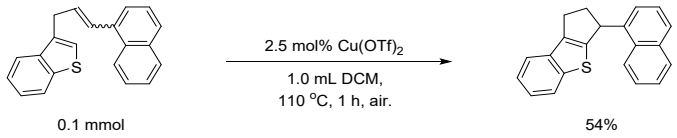
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dt, *J* = 8.1, 5.0 Hz, 4H), 7.73 – 7.66 (m, 2H), 7.48 – 7.28 (m, 5H), 4.76 (dd, *J* = 7.4, 4.9 Hz, 1H), 3.22 – 3.08 (m, 2H), 3.07 – 2.94 (m, 1H), 2.62 – 2.48 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.26, 145.71, 142.36, 141.78, 135.26, 133.65, 132.63, 128.58, 127.86, 127.78, 126.23, 125.95, 125.67, 124.37, 123.78, 123.70, 121.92, 49.16, 39.84, 27.03.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{16}S$ $[M]^+$: 300.09672, found: 300.09691.

3-(naphthalen-1-yl)-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7k) (*see substrate list*)



0.1 mmol 54%

The reaction was performed according to **general procedure B** using 3-(3-(naphthalen-1-yl)allyl)benzo[b]thiophene (30.0 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7k** (16.2 mg, 54%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

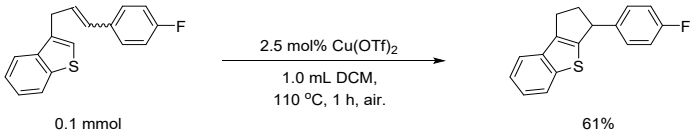
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.50 (m, 2H), 7.37 (ddt, *J* = 20.3, 13.2, 7.7 Hz, 4H), 5.42 – 5.31 (m, 1H), 3.37 – 3.22 (m, 1H), 3.18 – 2.96 (m, 2H), 2.54 (ddt, *J* = 11.0, 8.4, 5.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.76, 145.32, 142.14, 140.61, 135.30, 134.14, 131.56, 129.07, 127.36, 126.22, 125.76, 125.73, 124.35, 124.06, 123.72, 123.58, 121.86, 44.96, 38.93, 26.77.

HRMS (EI): m/z Theo. Mass calculated for $C_{21}H_{16}S$ $[M]^+$: 300.09672, found: 300.09680.

3-(4-fluorophenyl)-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7l) (*see substrate list*)



0.1 mmol 61%

The reaction was performed according to **general procedure B** using 3-(3-(4-fluorophenyl)allyl)benzo[b]thiophene (26.8 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by

flash column chromatography (silica, petroleum ether as the eluent) afforded **7l** (16.3 mg, 61%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

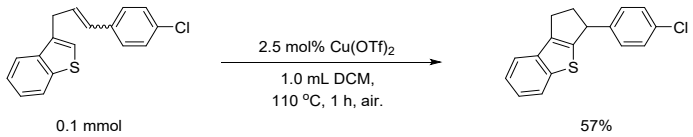
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.99 (dd, *J* = 12.0, 5.4 Hz, 2H), 4.56 (dd, *J* = 7.7, 6.0 Hz, 1H), 3.15 – 3.01 (m, 2H), 3.01 – 2.88 (m, 1H), 2.50 – 2.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.08, 160.65, 146.10, 145.62, 141.68, 140.68, 140.65, 135.18, 128.86, 128.78, 124.41, 123.77, 123.75, 121.91, 115.61, 115.40, 48.28, 40.04, 26.87.

^{19}F NMR (177 MHz, $CDCl_3$): δ -116.44, -116.83.

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{13}FS$ $[M]^+$: 268.07165, found: 268.07186.

3-(4-chlorophenyl)-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7m) (*see substrate list*)



0.1 mmol 57%

The reaction was performed according to **general procedure B** using 3-(3-(4-chlorophenyl)allyl)benzo[b]thiophene (28.4 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column chromatography (silica, petroleum ether as the eluent) afforded **7m** (16.2 mg, 57%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

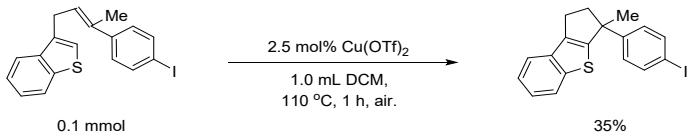
NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.32 – 7.25 (m, 3H), 7.20 – 7.13 (m, 2H), 4.55 (dd, *J* = 7.4, 5.5 Hz, 1H), 3.18 – 3.01 (m, 2H), 3.01 – 2.89 (m, 1H), 2.50 – 2.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.78, 145.73, 143.58, 141.97, 135.23, 132.64, 129.08, 128.97, 128.90, 128.86, 124.53, 124.35, 123.92, 123.86, 123.64, 123.52, 122.03, 121.79, 48.49, 46.83, 40.71, 40.04, 29.49, 26.98.

HRMS (EI): m/z Theo. Mass calculated for $C_{17}H_{13}ClS$ $[M]^+$: 284.04210, found: 284.04234.

1-methyl-3-phenyl-2,3-dihydro-1H-benzo[b]cyclopenta[d]thiophene (7n) (*see substrate list*)



0.1 mmol 35%

The reaction was performed according to **general procedure B** using (Z)-3-(3-(4-iodophenyl)but-2-en-1-yl)benzo[b]thiophene (39.0 mg, 0.1 mmol, 1.0 equiv.) as the substrate. Purification by flash column

chromatography (silica, petroleum ether as the eluent) afforded **7n** (13.7 mg, 35%) as a colorless oily liquid.

TLC: R_f = 0.75 (petroleum ether)

NMR Spectroscopy (***see spectra***):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.55 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.73 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.30, 143.73, 141.00, 138.25, 131.68, 129.15, 126.90, 124.07, 123.91, 122.40, 121.52, 120.35, 38.60, 22.80, 11.93.

HRMS (EI): m/z Theo. Mass calculated for $C_{18}H_{15}IS$ $[M]^+$: 389.99337, found: 389.99355.

11. Supplementary references

(1) (a) Gerbino, D. C.; Mandolesi, S. D.; Schmalz, H. G.; Podestá, J. C., Introduction of Allyl and Prenyl Side-Chains into Aromatic Systems by Suzuki Cross-Coupling Reactions. *Eur. J. Org. Chem.* **2009,** *2009*, 3964−3972. (b) Wu, S.; Zhang, Y.; Jiang, H.; Ding, N.; Wang, Y.; Su, Q.; Zhang, H.; Wu, L.; Yang, Q., Manganese Catalyzed Dehydrogenative Silylation of Alkenes: Direct Access to Allylsilanes. *Tetrahedron Lett.* **2020,** *61*, 152053. (c) Jin, Y.; Jing, Y.; Li, C.; Li, M.; Wu, W.; Ke, Z.; Jiang, H., Palladium-Catalysed Selective Oxidative Amination of Olefins with Lewis Basic Amines. *Nat. Chem.* **2022,** *14*, 1118−1125.

(2) (a) Xiao, J.; He, Y.; Ye, F.; Zhu, S., Remote sp^3 C−H Amination of Alkenes with Nitroarenes. *Chem.* **2018,** *4*, 1645–1657. (b) Zhang, S.; Bedi, D.; Cheng, L.; Unruh, D. K.; Li, G.; Findlater, M., Cobalt(II)-Catalyzed Stereoselective Olefin Isomerization: Facile Access to Acyclic Trisubstituted Alkenes. *J. Am. Chem. Soc.* **2020,** *142*, 8910−8917. (c) Chen, W.; Chen, Y.; Gu, X.; Chen, Z.; Ho, C. Y., (NHC)Pd(II) Hydride-Catalyzed Dehydroaromatization by Olefin Chain-Walking Isomerization and Transfer-dehydrogenation. *Nat. Commun.* **2022,** *13*, 5507.

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(6) Lee, W. C.; Wang, C. H.; Lin, Y. H.; Shih, W. C.; Ong, T. G., Tandem Isomerization and C–H Activation: Regioselective Hydroheteroarylation of Allylarenes. *Org. Lett.* **2013,** *15*, 5358–5361.

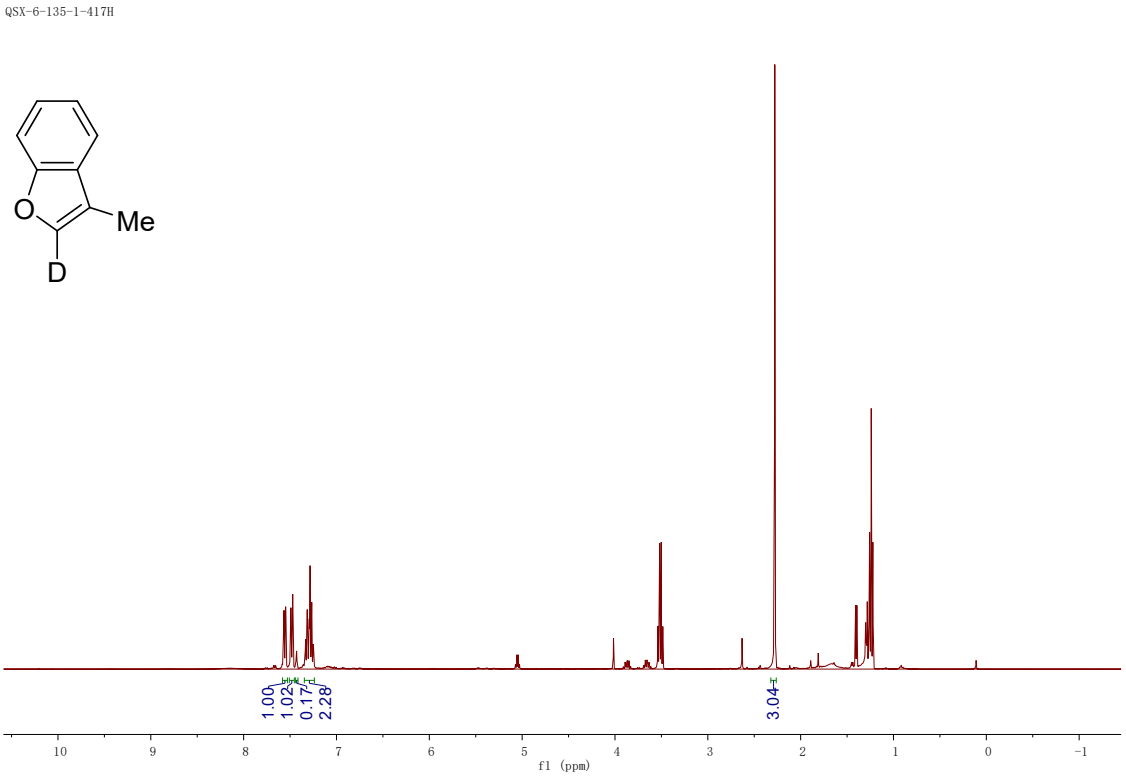
(7) (a) Zhang, D.; Iwai, T.; Sawamura, M., Iridium-Catalyzed Alkene-Selective Transfer Hydrogenation with 1,4-Dioxane as Hydrogen Donor. *Org. Lett.* **2019,** *21*, 5867–5872. (b) Chou, T. H.; Yu, B. H.; Chein, R. J., ZnI_2/$Zn(OTf)_2$-TsOH: A Versatile Combined-acid System for Catalytic Intramolecular Hydrofunctionalization and Polyene Cyclization. *Chem. Commun.* **2019,** *55*, 13522–13525.

(8) Hajra, S.; Maity, S.; Roy, S.; Maity, R.; Samanta, S., Brønsted Acid Promoted Regioselective C-3 Arylation and Heteroarylation of Spiro-epoxyoxindoles for the Construction of All Carbon Quaternary Centres: A Detailed Study. *Eur. J. Org. Chem.* **2019,** *2019*, 969−987.

12. Measured spectrograms and single crystal structure

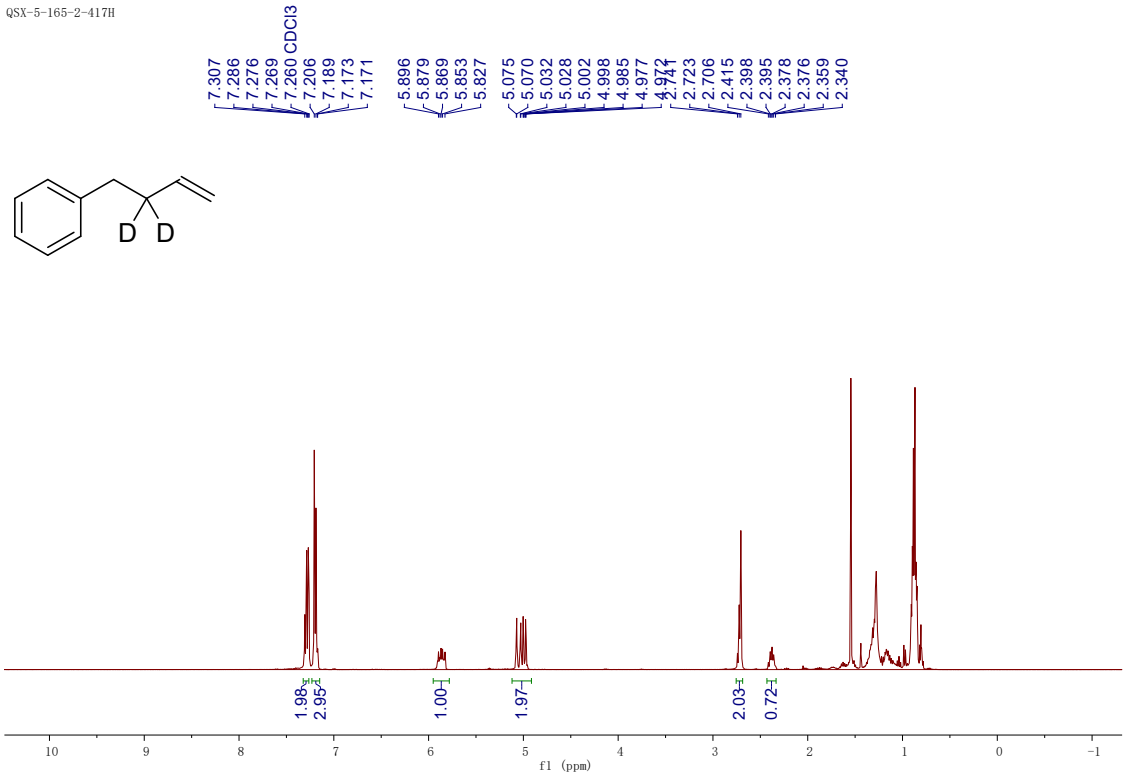
12.1. Measured spectrograms (NMR and HRMS spectra)

^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)

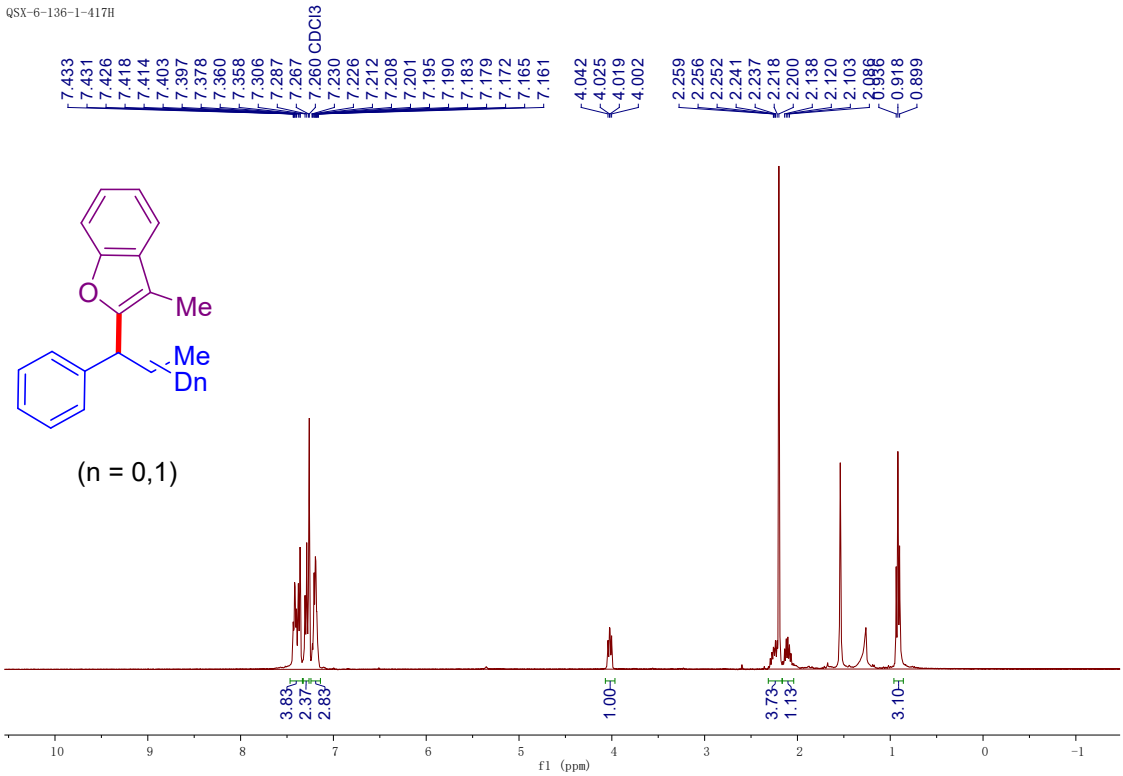


The impurity peaks around 3.5 ppm and 1.2 ppm in the figure are the methylene and methyl peaks of ether.

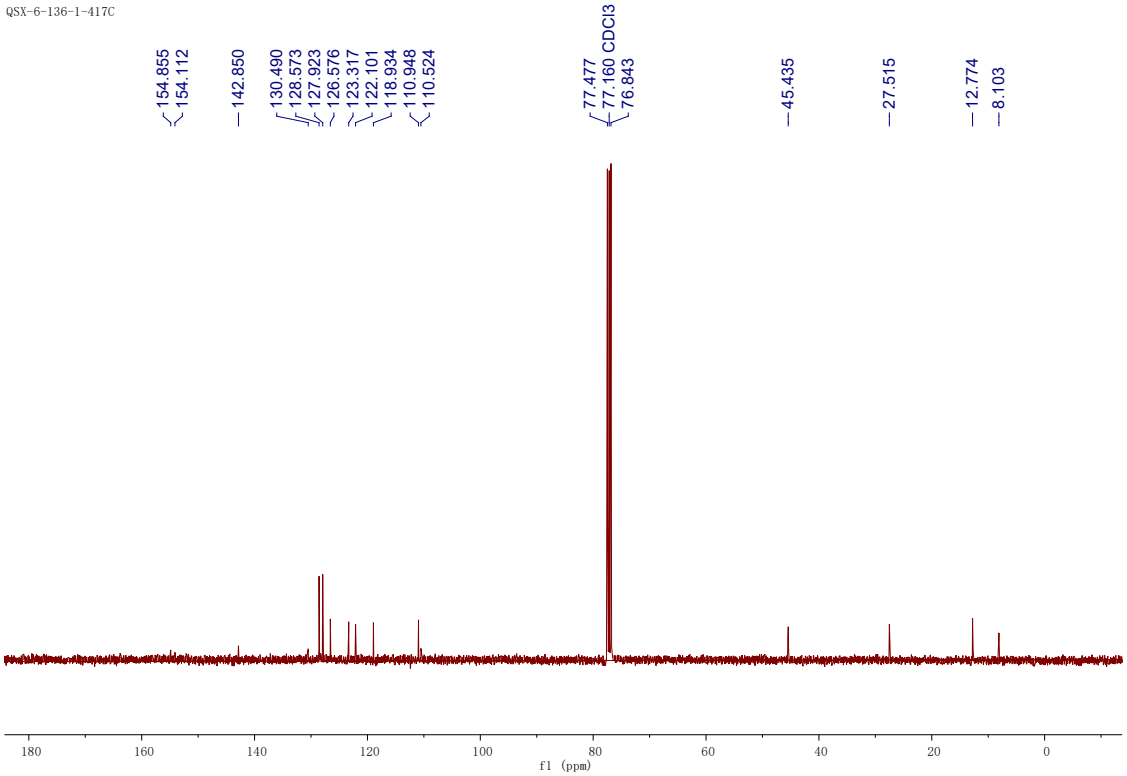
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



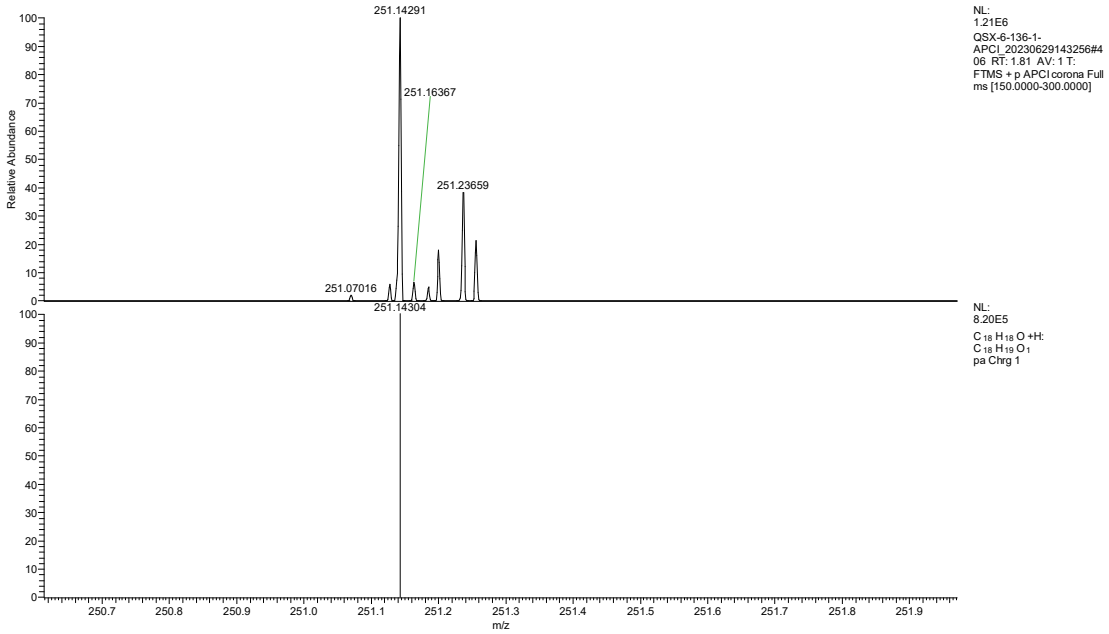
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)

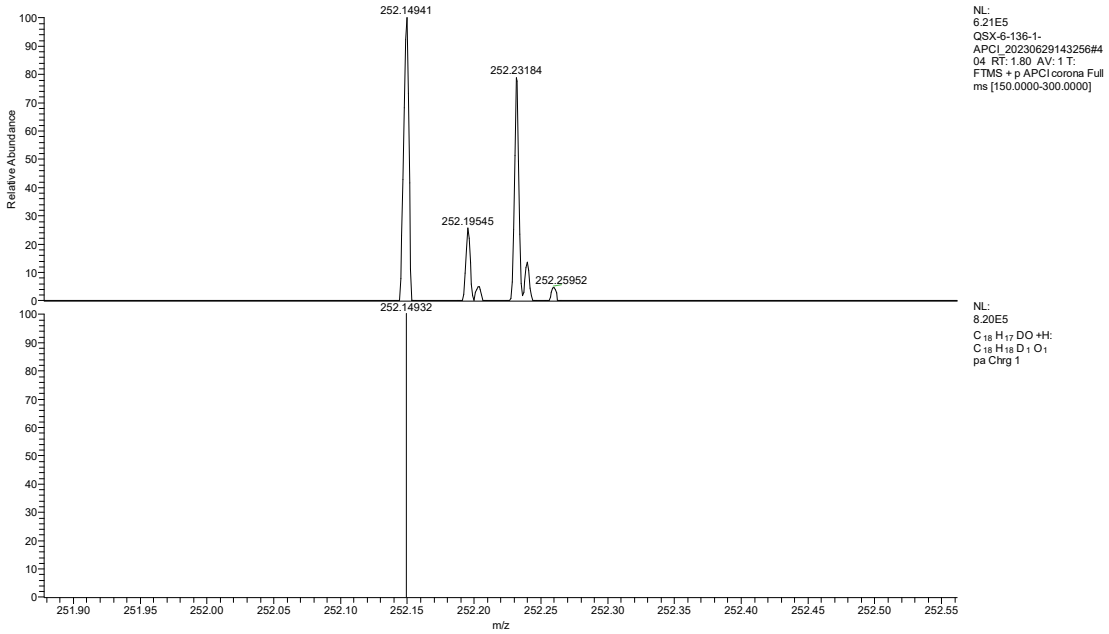


^{13}C NMR (100 MHz, $CDCl_3$) spectrum

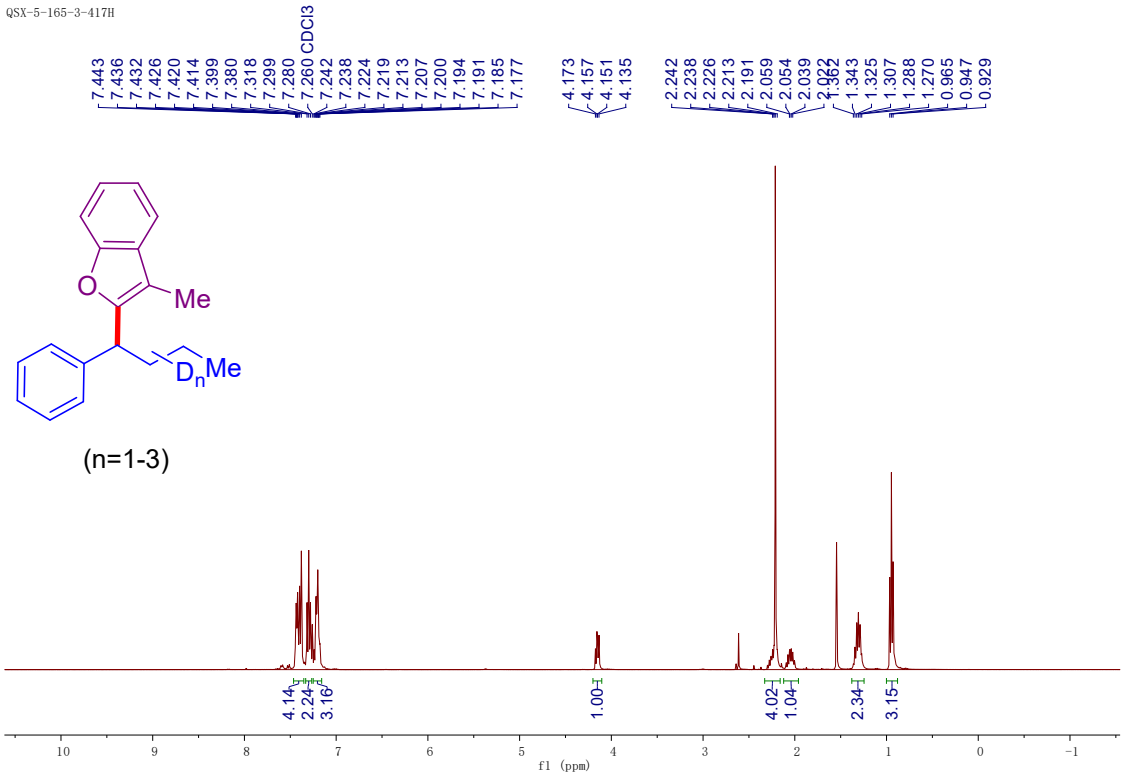


HRMS (APCI) analysis spectrum

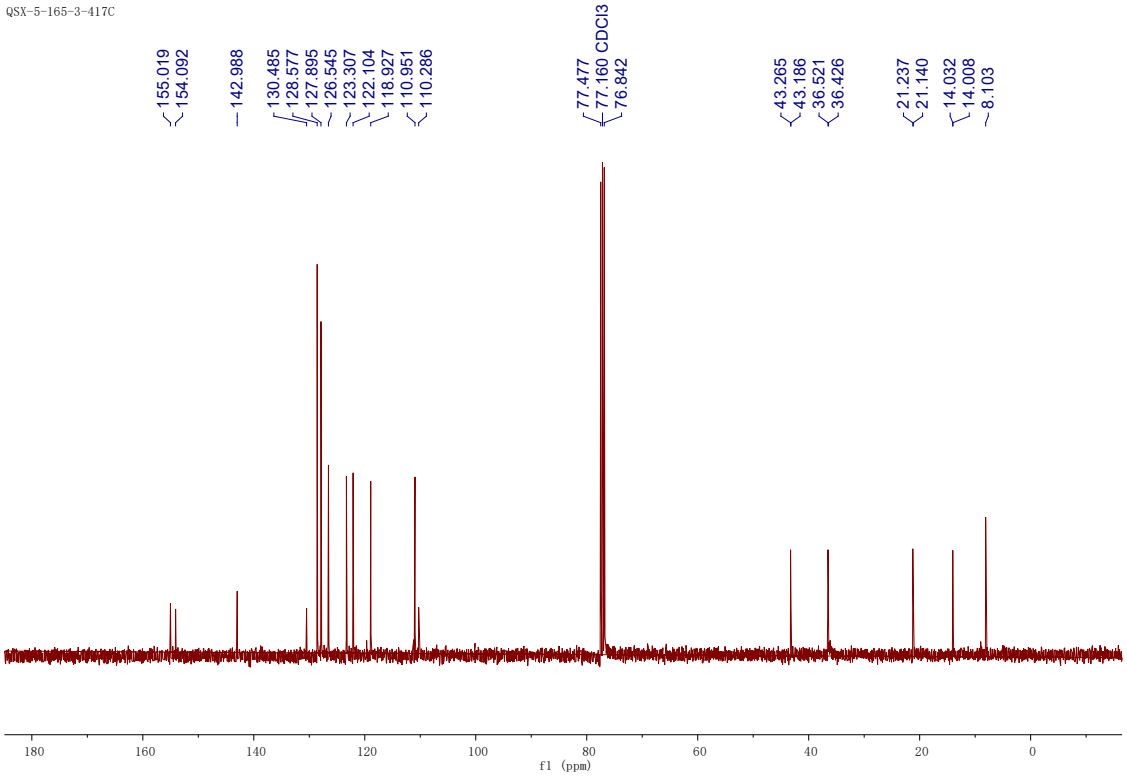




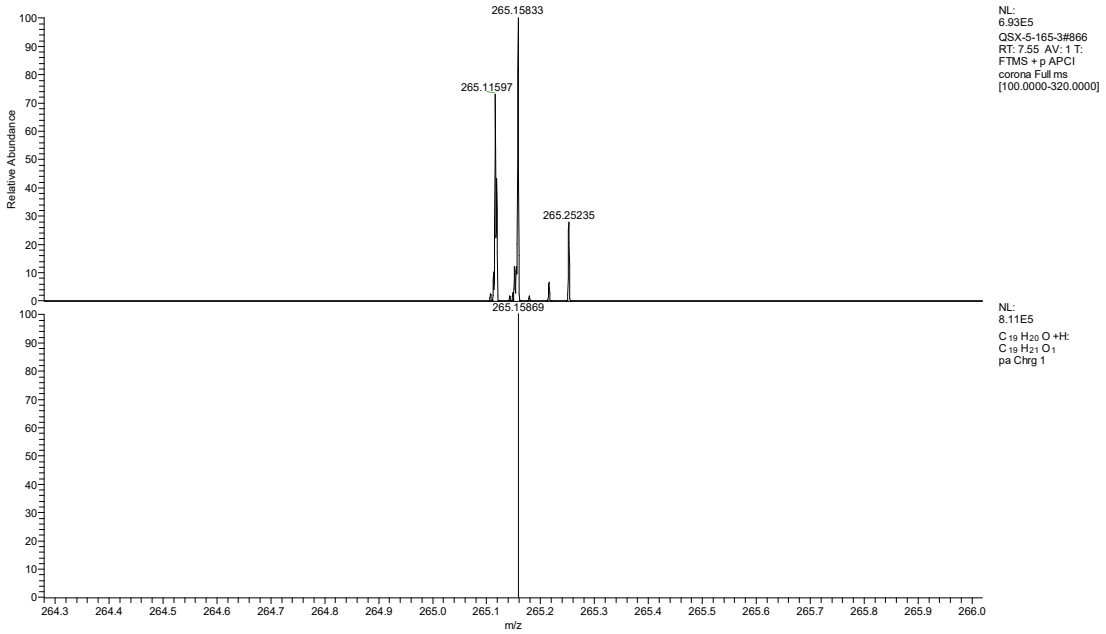
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)

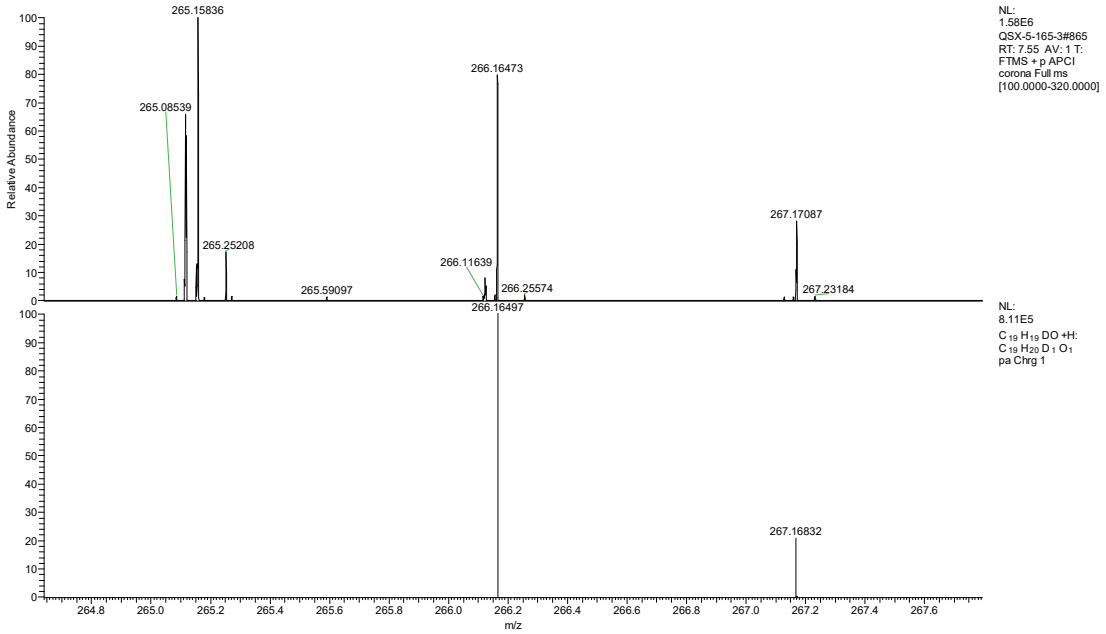


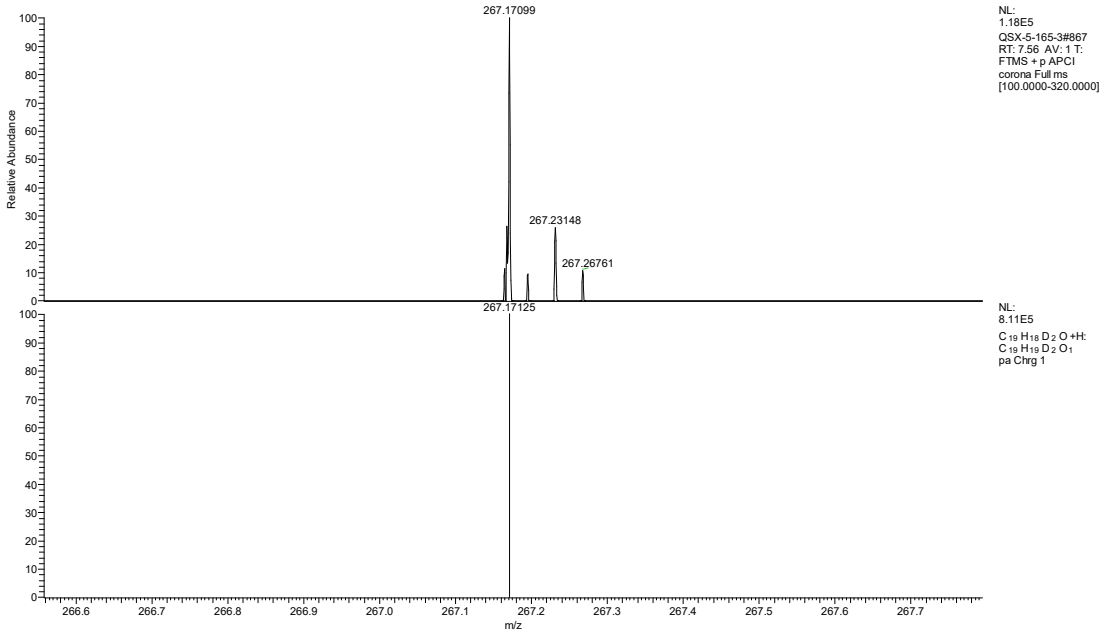
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



HRMS (ESI) analysis spectrum






267.17099
267.23148
267.26761
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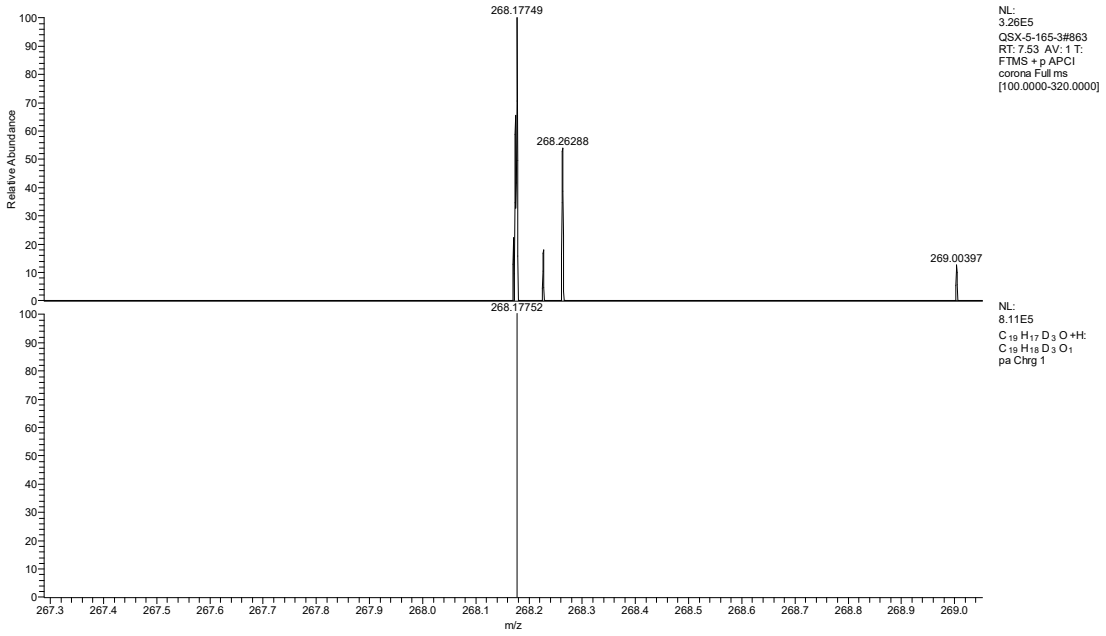
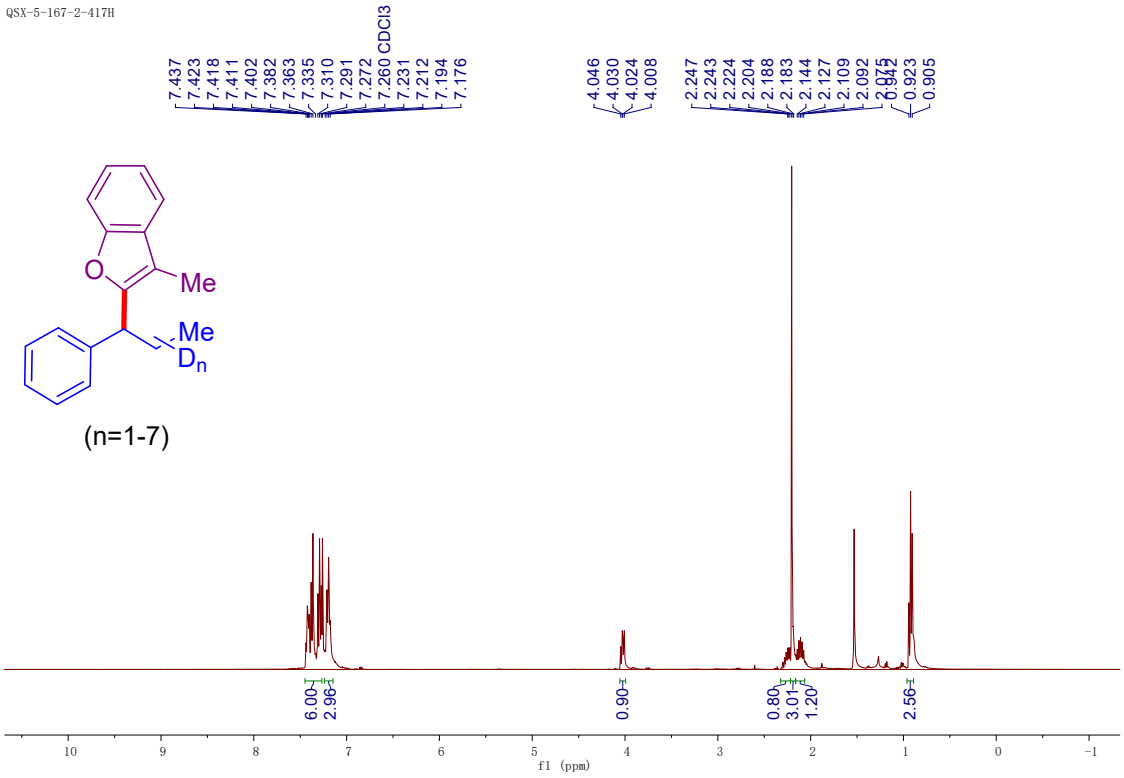
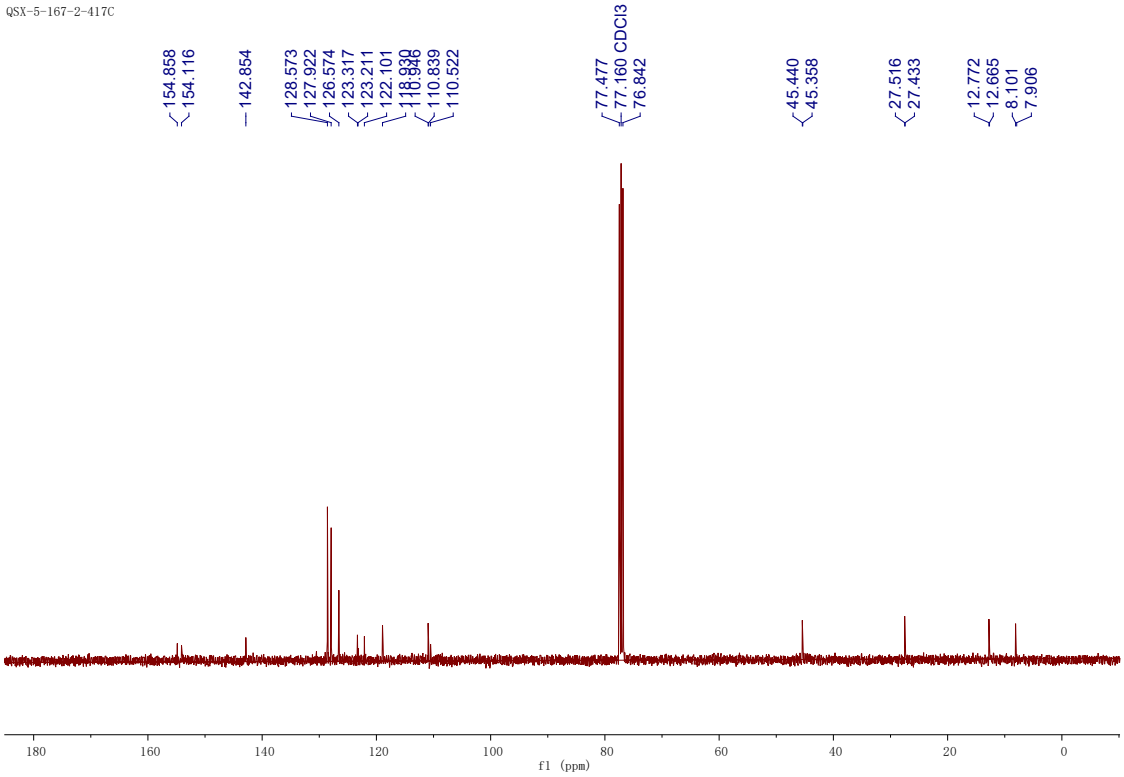
1.18E5
QSX-5-165-3#867
RT: 7.56 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
Relative Abundance
267.17125
NL:
8.11E5
C 19 H 18 D 2 O +H:
C 19 H 19 D 2 O 1
pa Chrg 1
m/z


268.17749
268.26288
269.00397
NL:
3.26E5
QSX-5-165-3#863
RT: 7.53 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
Relative Abundance
268.17752
NL:
8.11E5
C 19 H 17 D 3 O +H:
C 19 H 18 D 3 O 1
pa Chrg 1
m/z

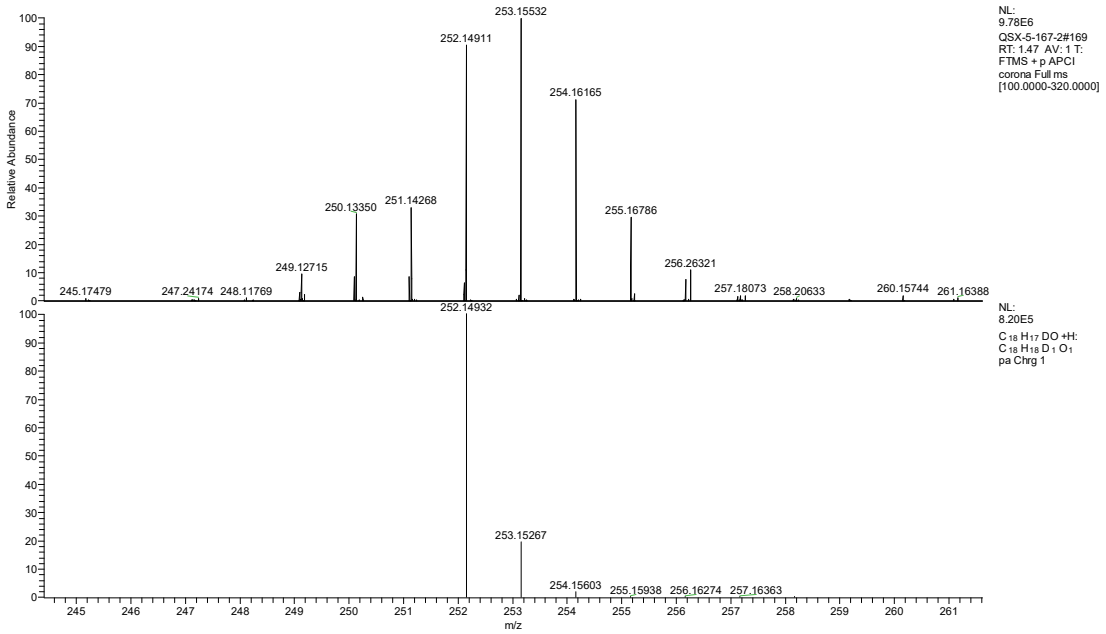
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)

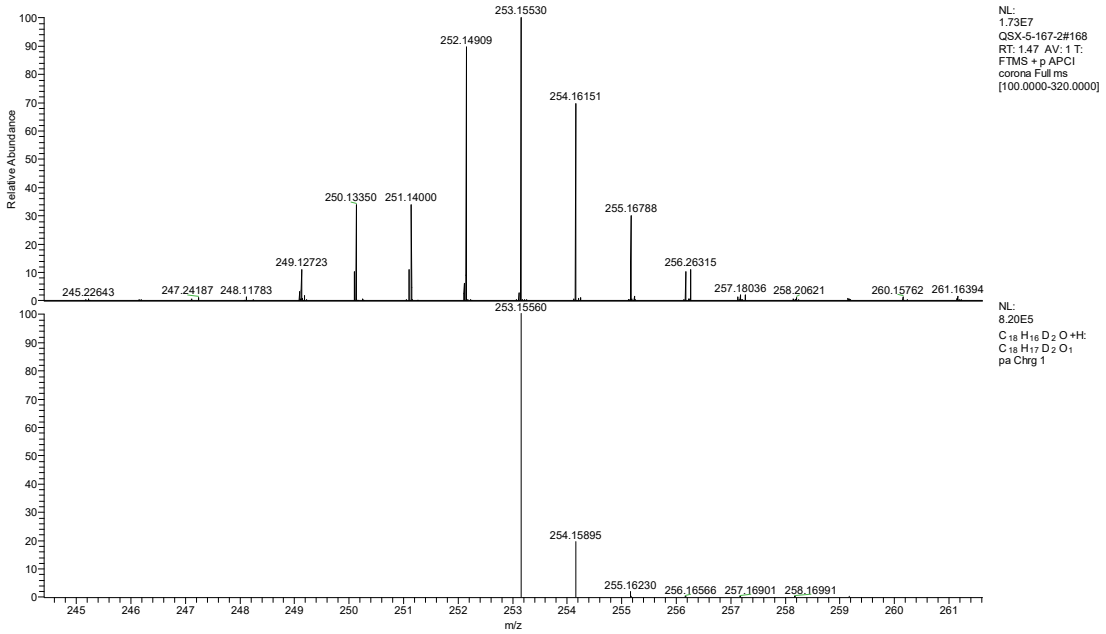


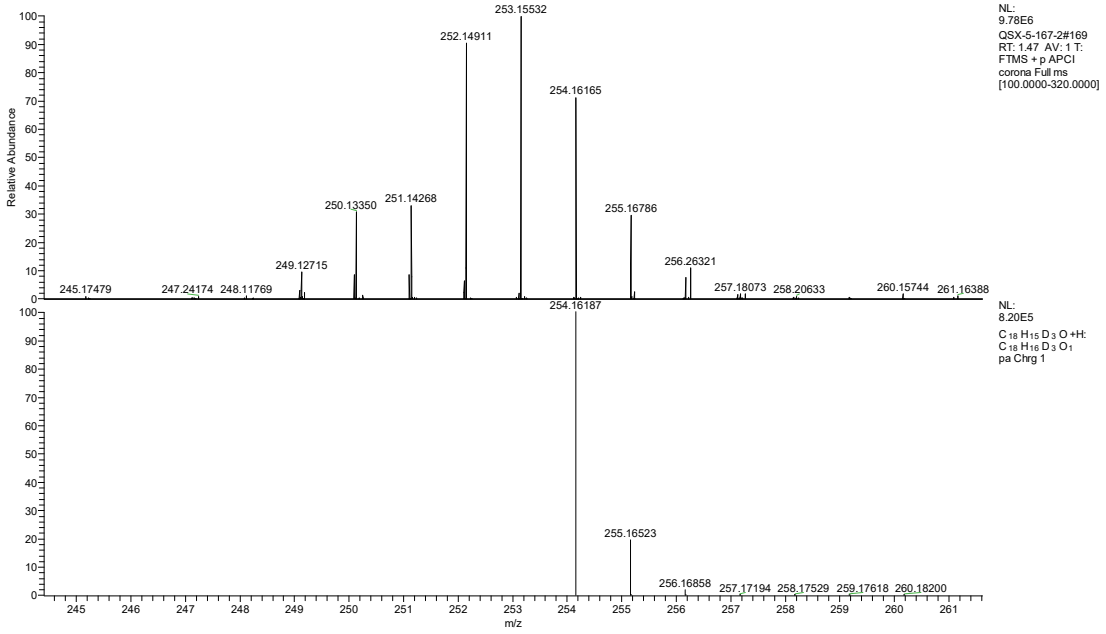
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



HRMS (ESI) analysis spectrum



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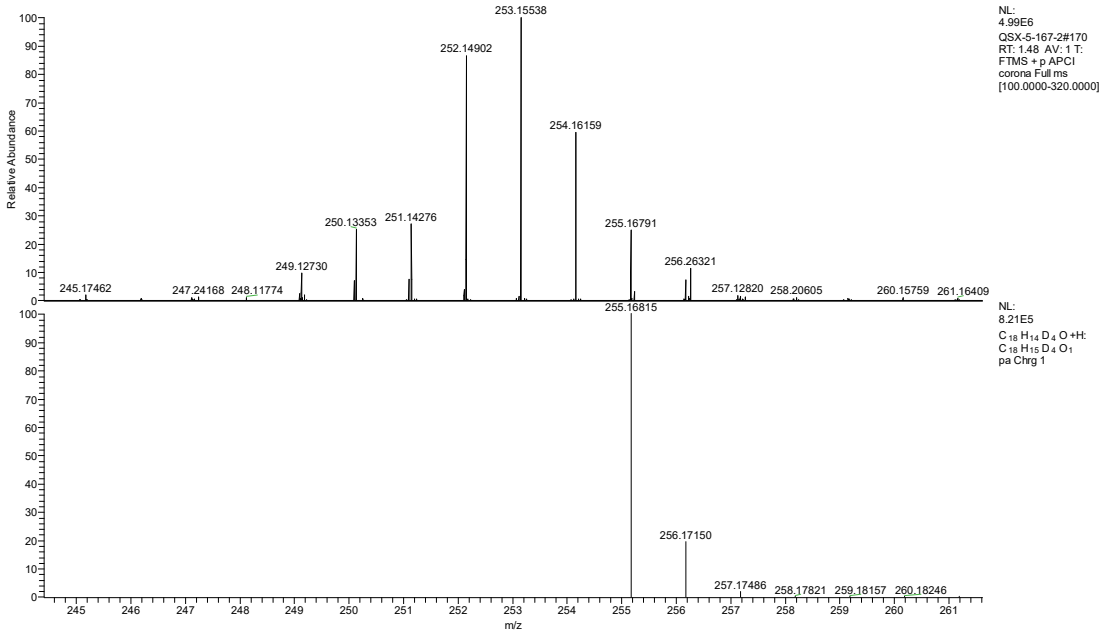
254.16165
250.13350
251.14268
255.16786
249.12715
256.26321
245.17479
247.24174
248.11769
257.18073
258.20633
260.15744
261.16388
NL:
9.78E6
QSX-5-167-2#169
RT: 1.47 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
254.16187
255.16523
256.16858
257.17194
258.17529
259.17618
260.18200
NL:
8.20E5
C 18 H15 D 3 O +H:
C 18 H16 D 3 O 1
pa Chrg 1
Relative Abundance
m/z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252.14902
254.16159
250.13353
251.14276
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249.12730
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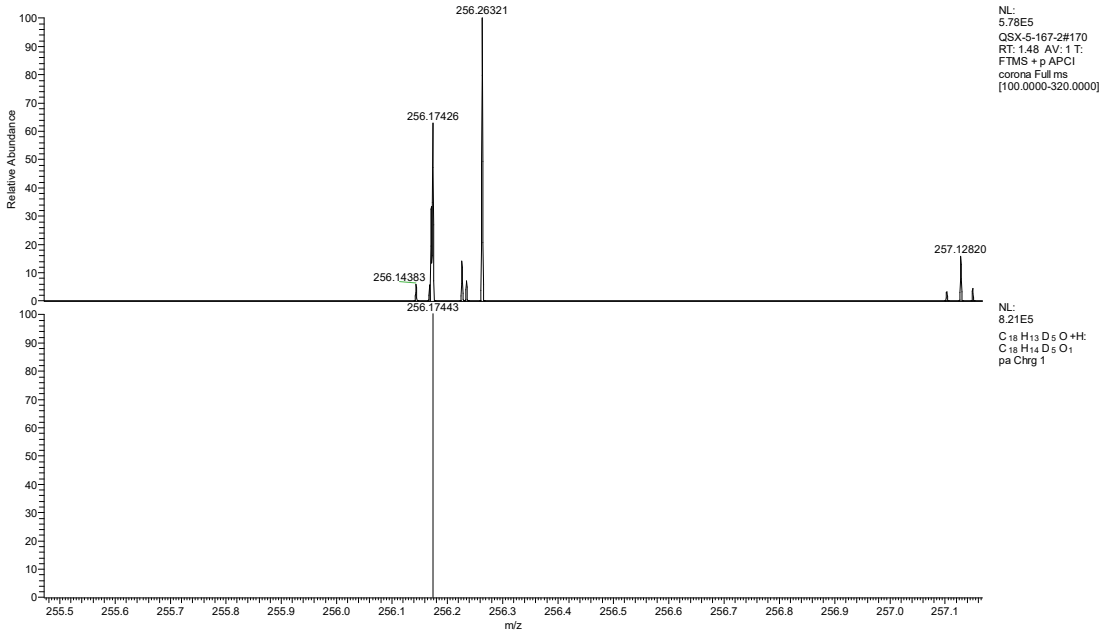
245.17462
247.24168
248.11774
257.12820
258.20605
260.15759
261.16409
NL:
4.99E6
QSX-5-167-2#170
RT: 1.48 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
255.16815
256.17150
257.17486
258.17821
259.18157
260.18246
NL:
8.21E5
C 18 H14 D 4 O +H:
C 18 H15 D 4 O 1
pa Chrg 1
Relative Abundance
m/z


256.26321
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257.12820
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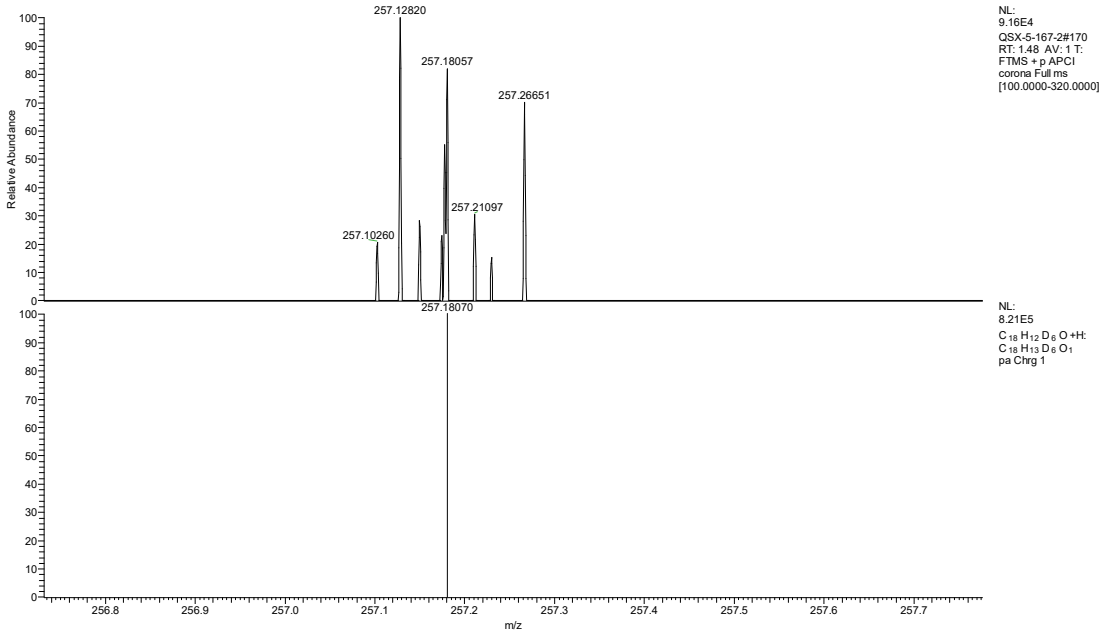
256.17443
NL:
5.78E5
QSX-5-167-2#170
RT: 1.48 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
NL:
8.21E5
C 18 H 13 D 5 O +H:
C 18 H 14 D 5 O 1
pa Chrg 1
Relative Abundance
m/z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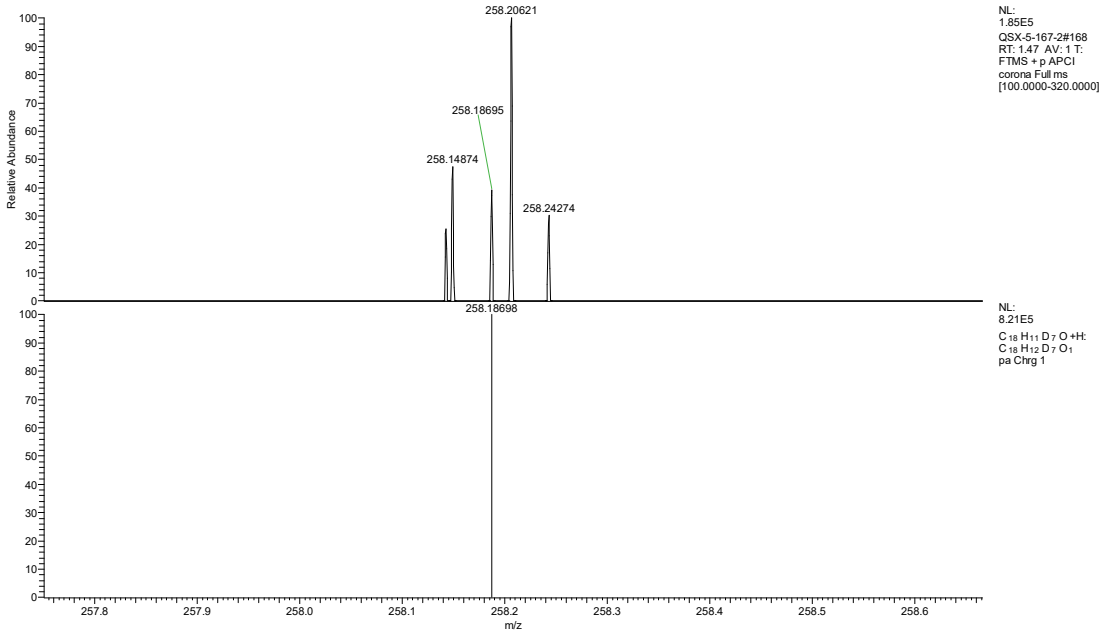
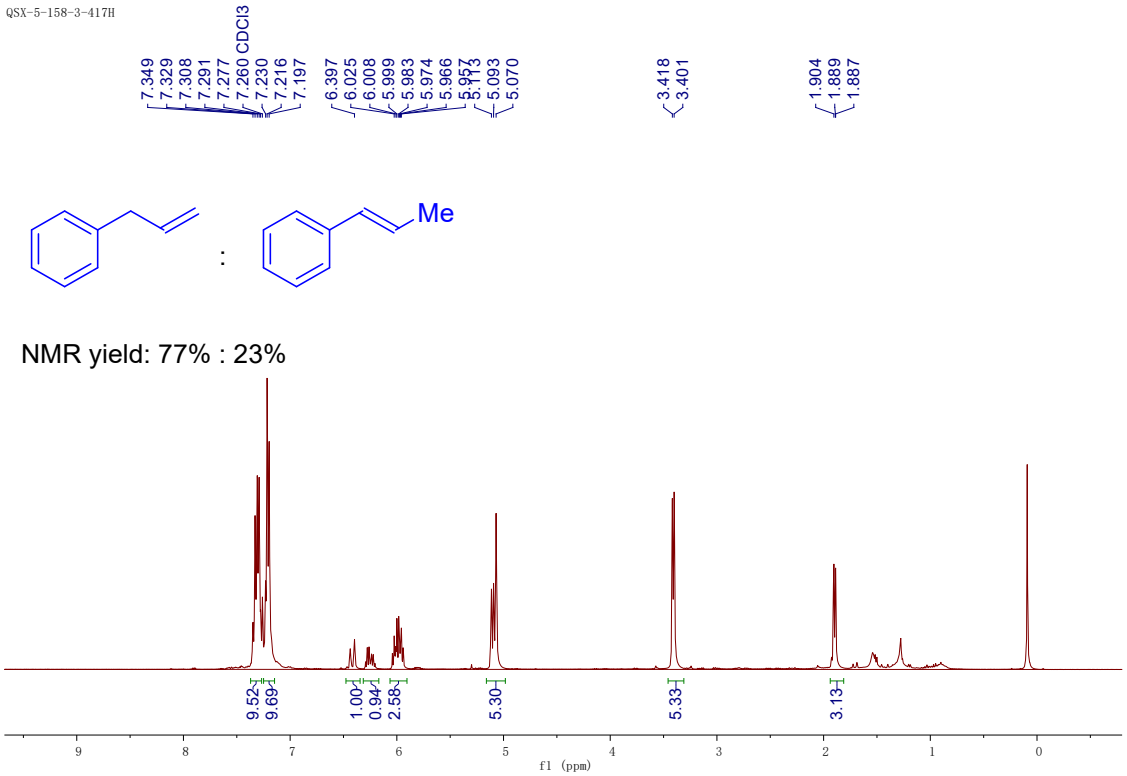
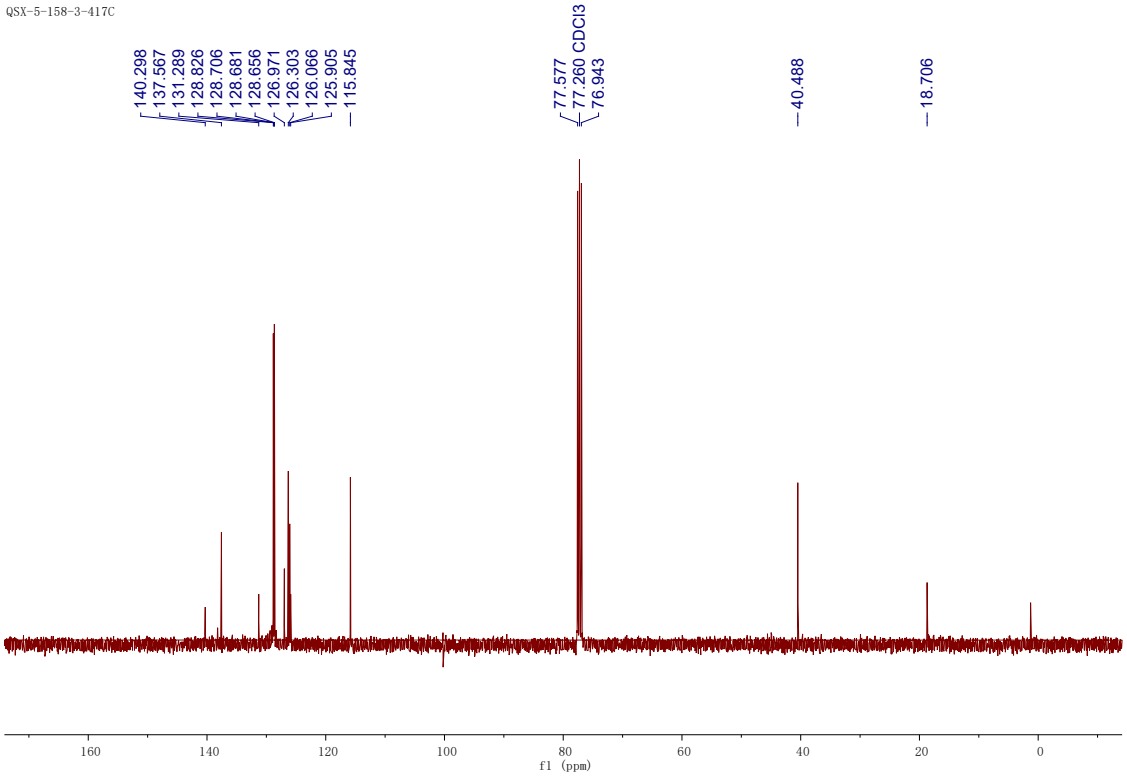
257.18057
257.26651
257.21097
257.10260
257.18070
NL:
9.16E4
QSX-5-167-2#170
RT: 1.48 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
NL:
8.21E5
C 18 H 12 D 6 O +H:
C 18 H 13 D 6 O 1
pa Chrg 1
Relative Abundance
m/z


258.20621
258.18695
258.14874
258.24274
NL:
1.85E5
QSX-5-167-2#168
RT: 1.47 AV: 1 T:
FTMS + p APCI
corona Full ms
[100.0000-320.0000]
Relative Abundance
258.18698
NL:
8.21E5
C 18 H 11 D 7 O +H:
C 18 H 12 D 7 O 1
pa Chrg 1
m/z

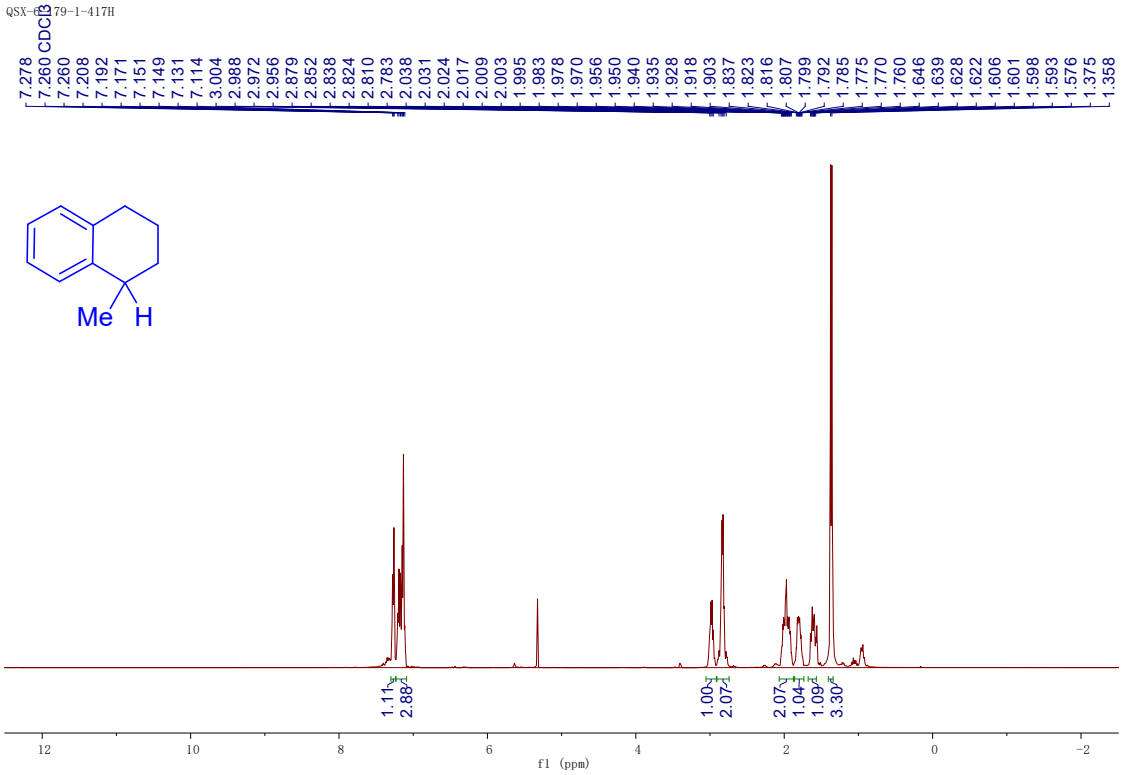
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



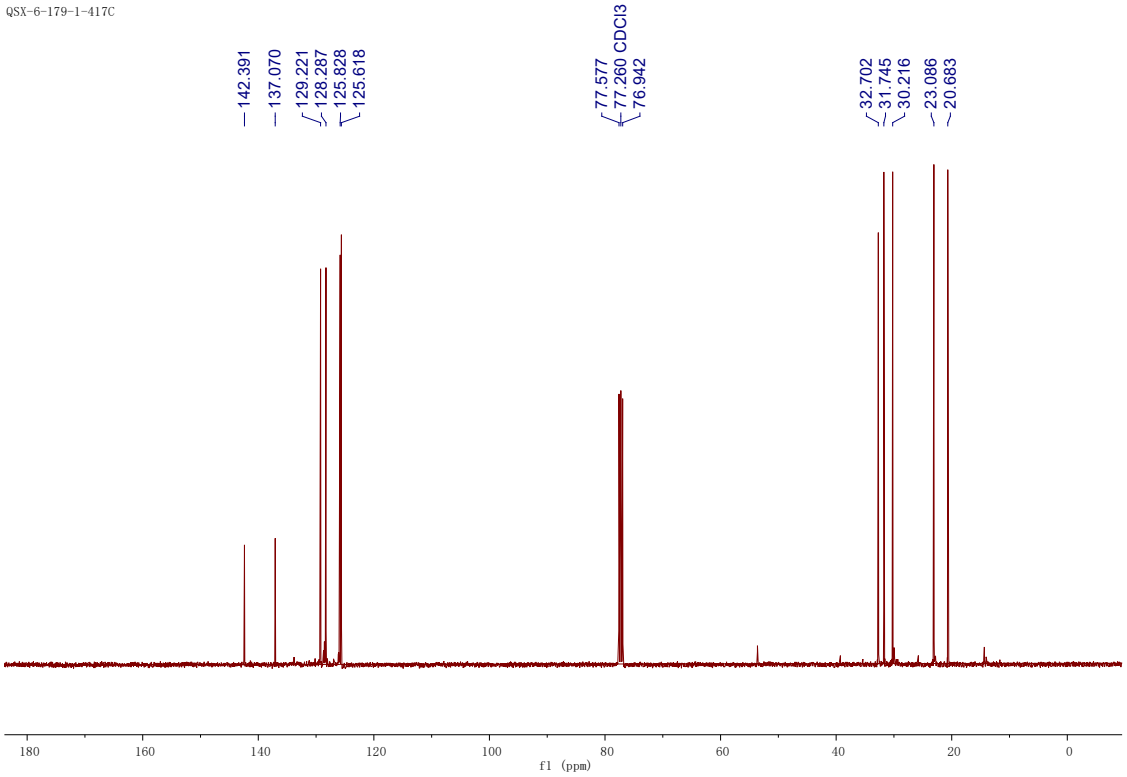
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



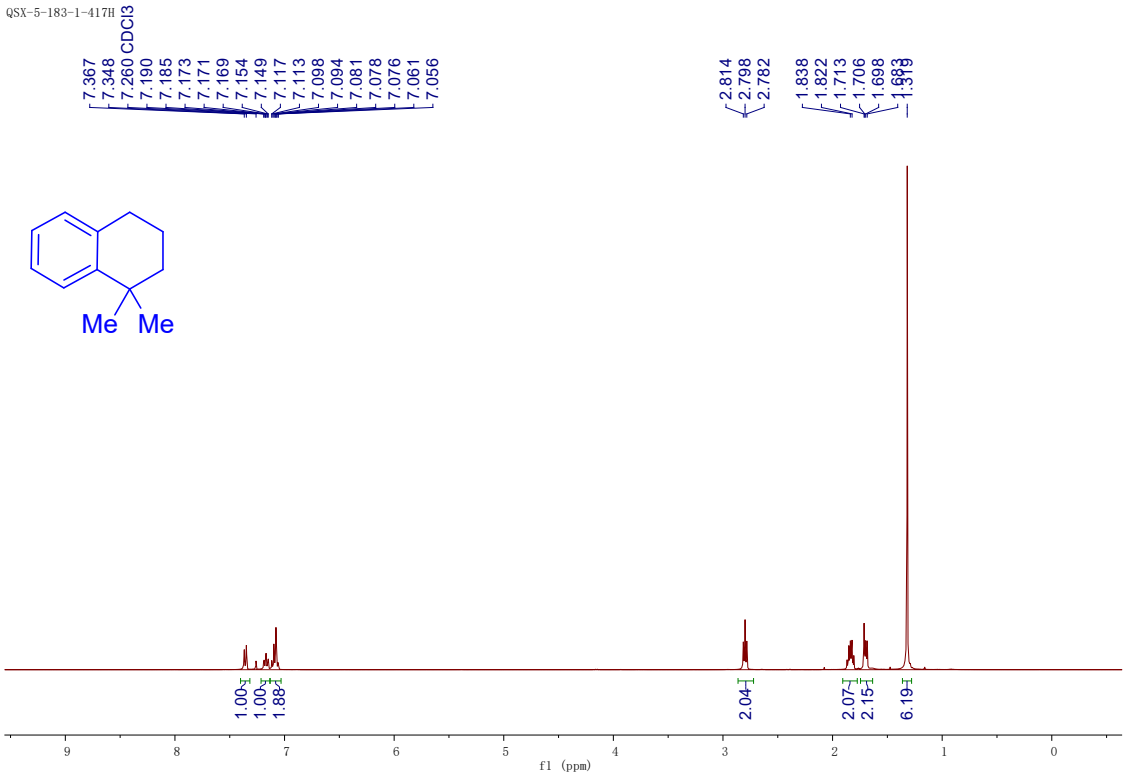
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



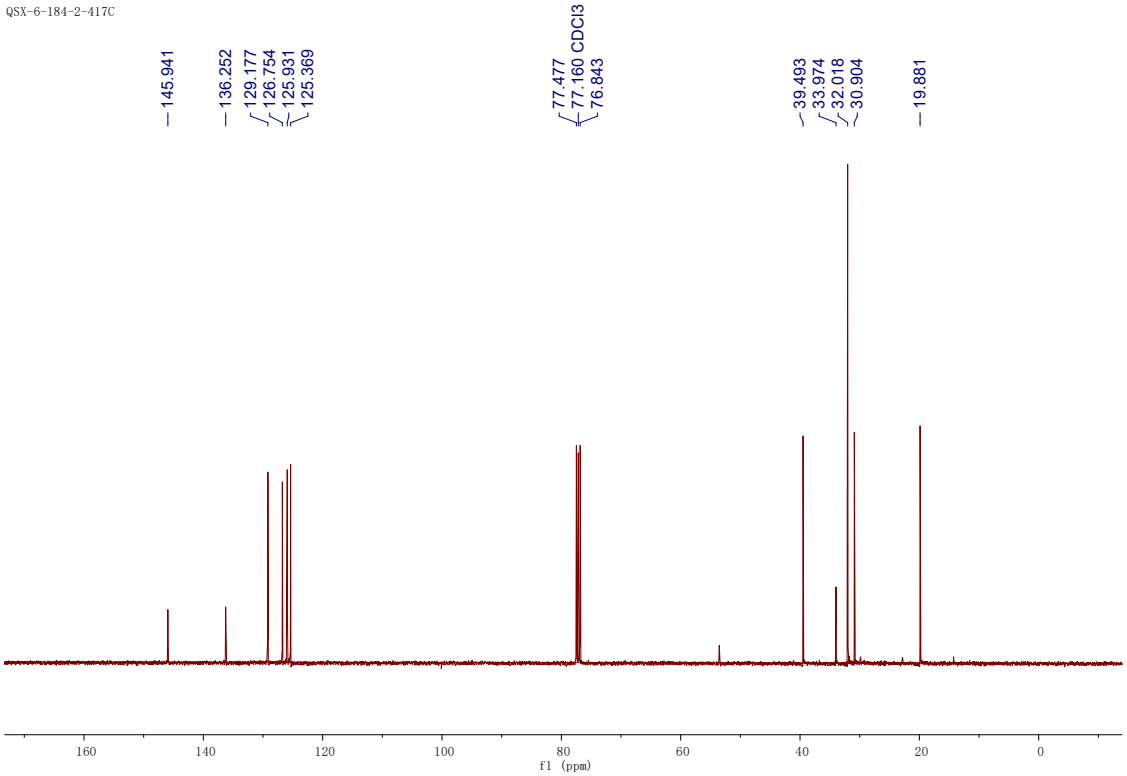
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



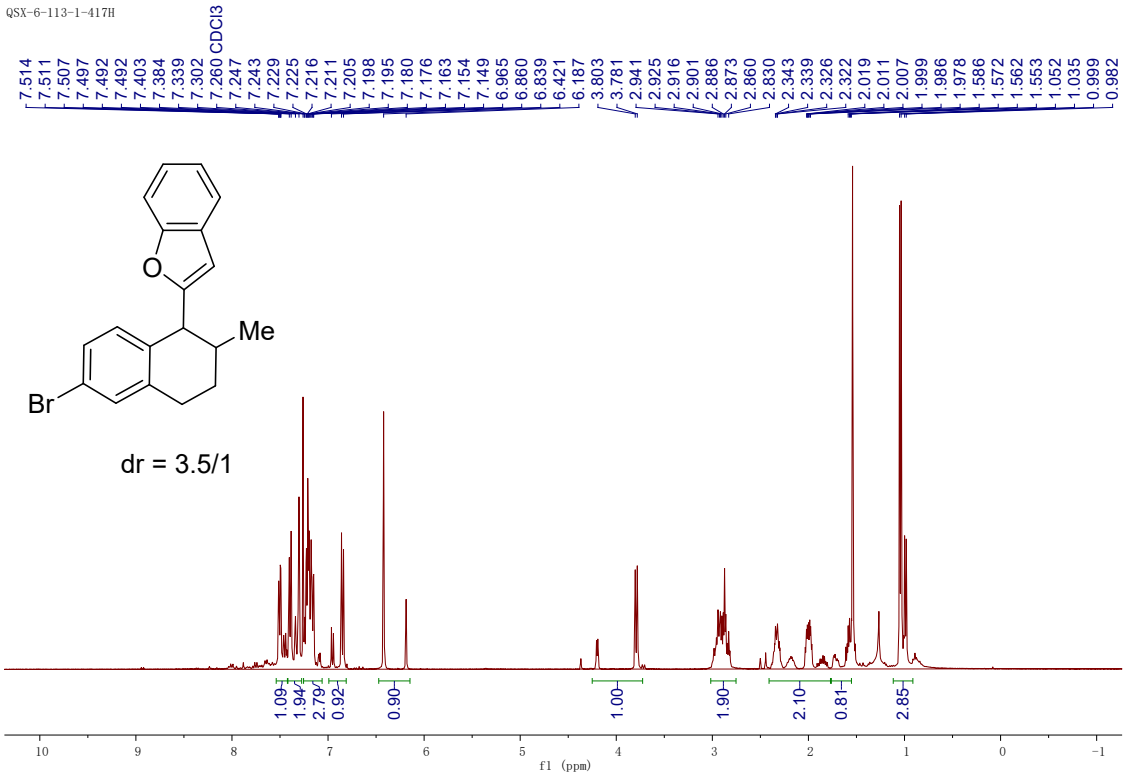
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



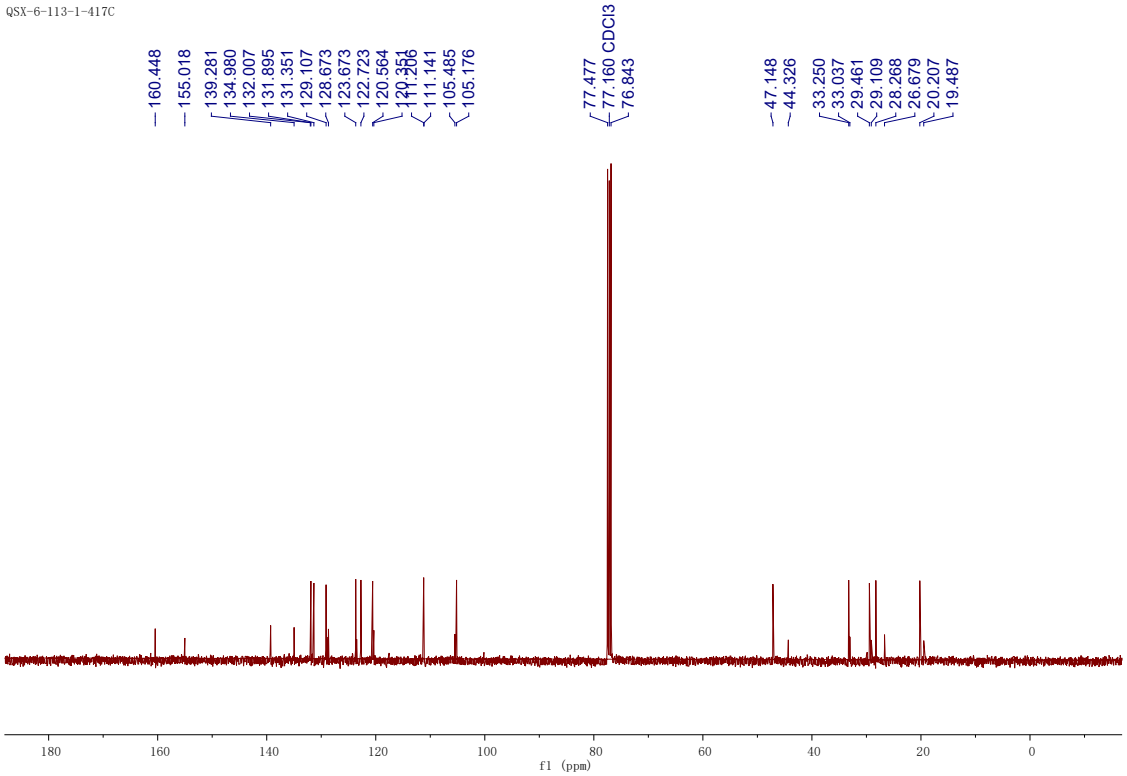
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



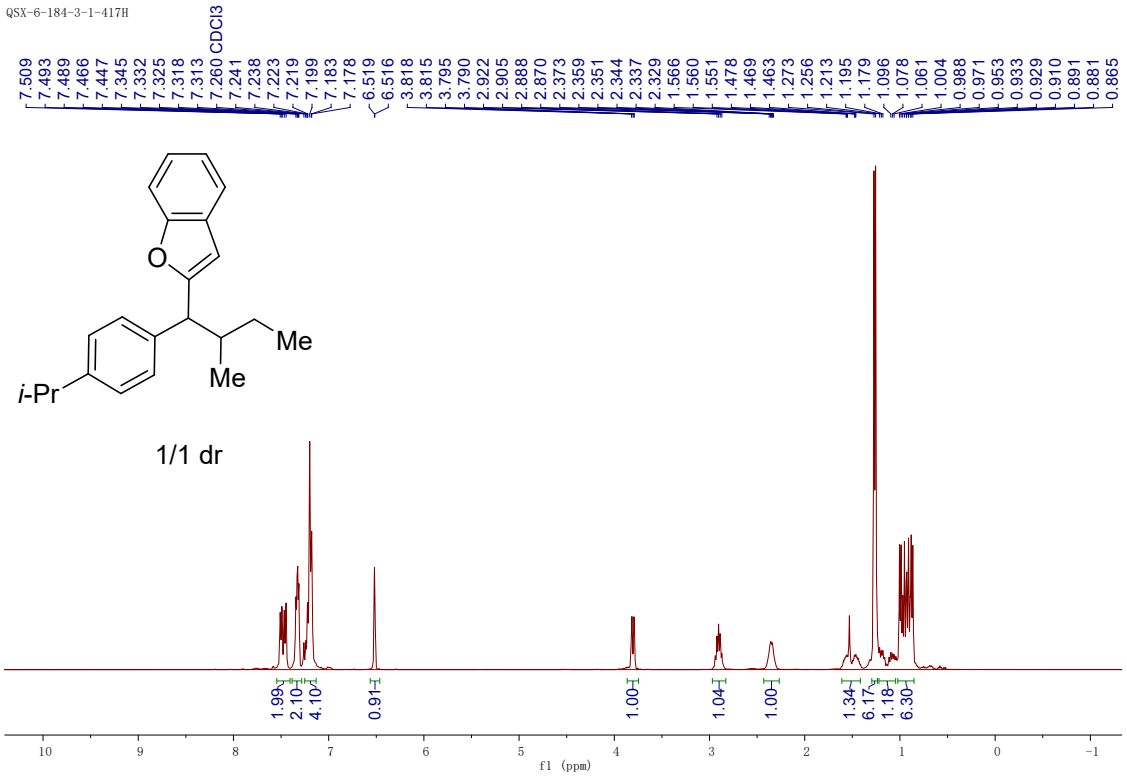
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ar (*see procedure*)



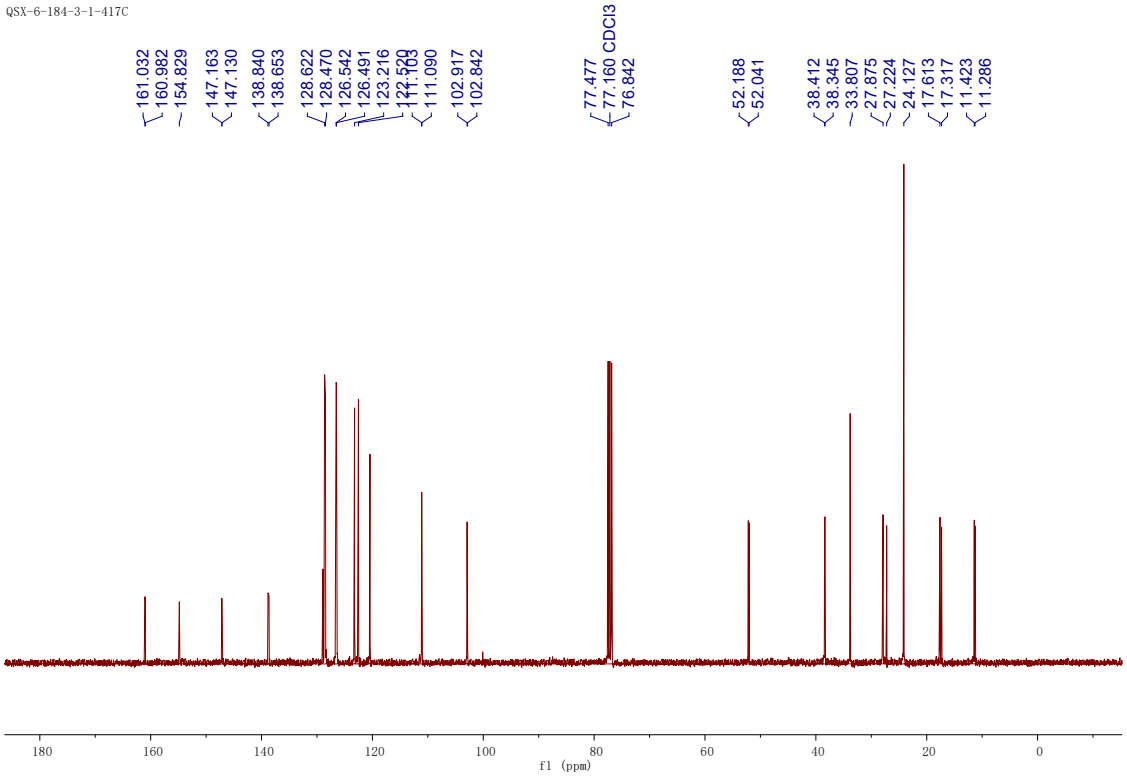
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ar



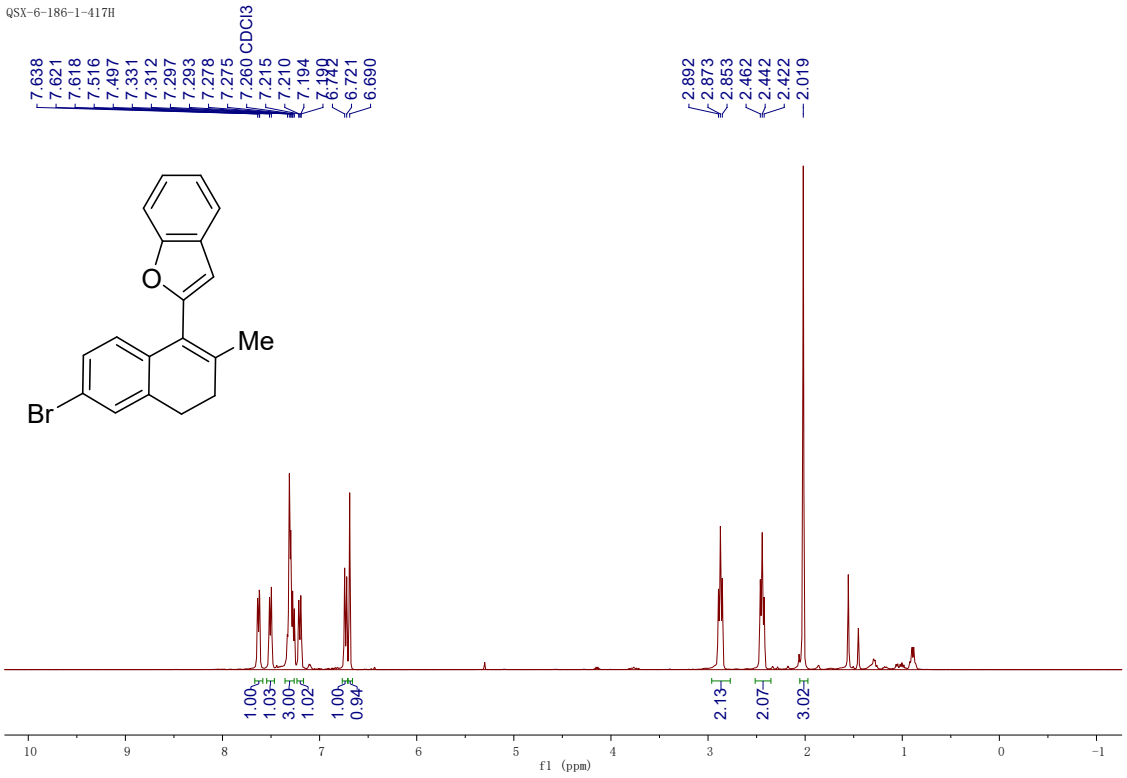
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4b (*see procedure*)



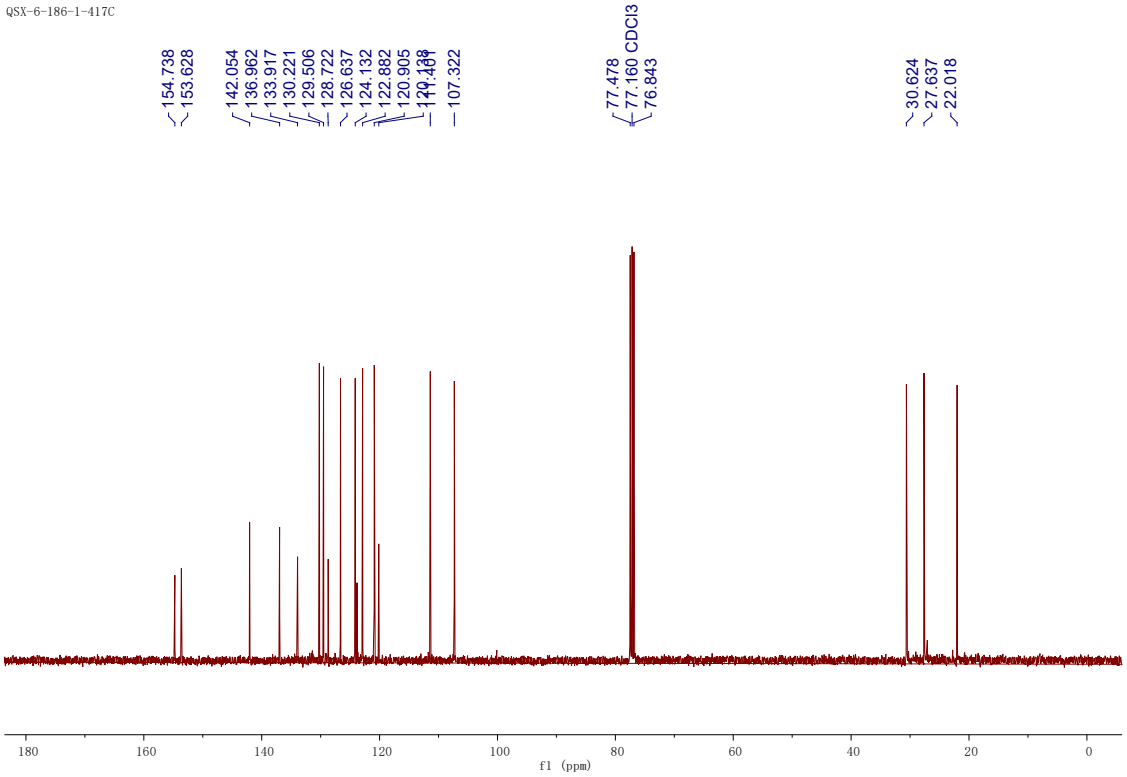
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4b



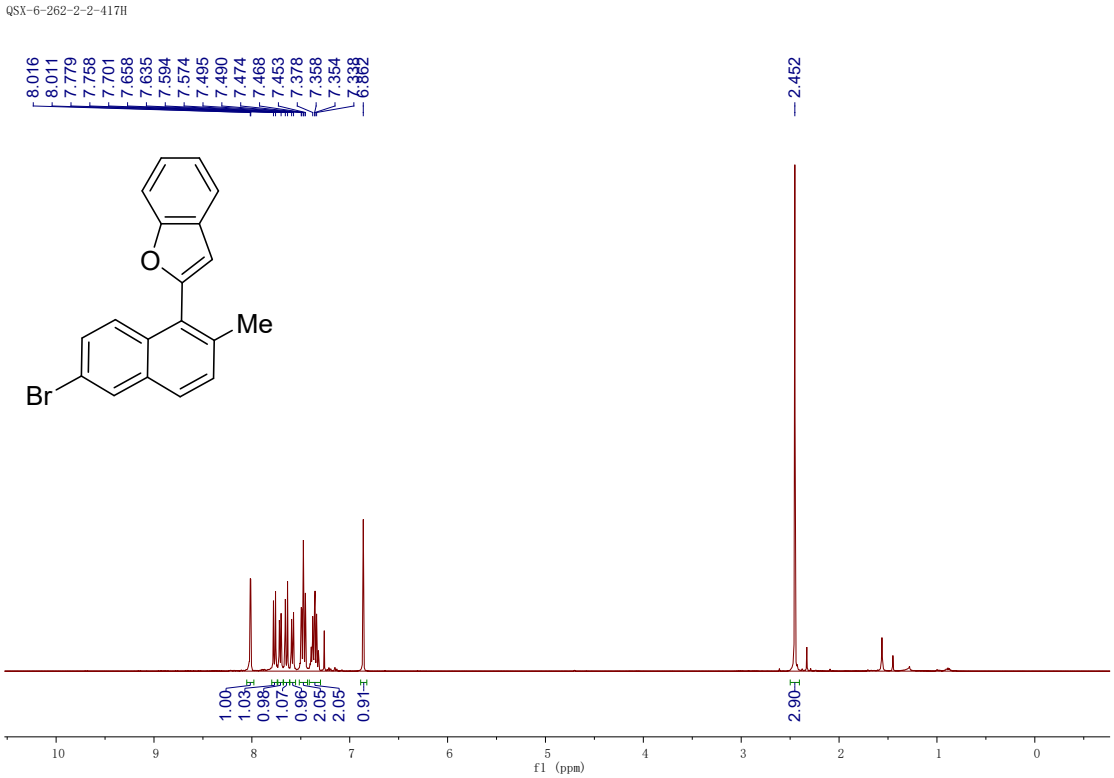
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8a (*see procedure*)



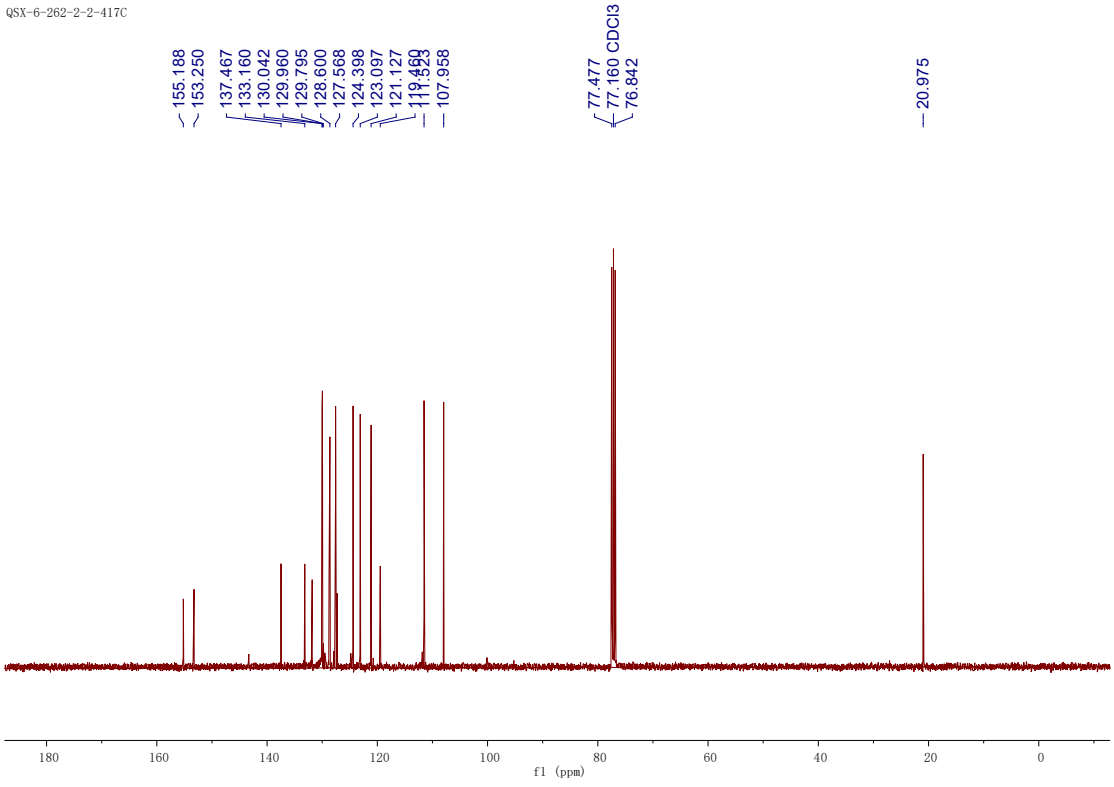
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8a



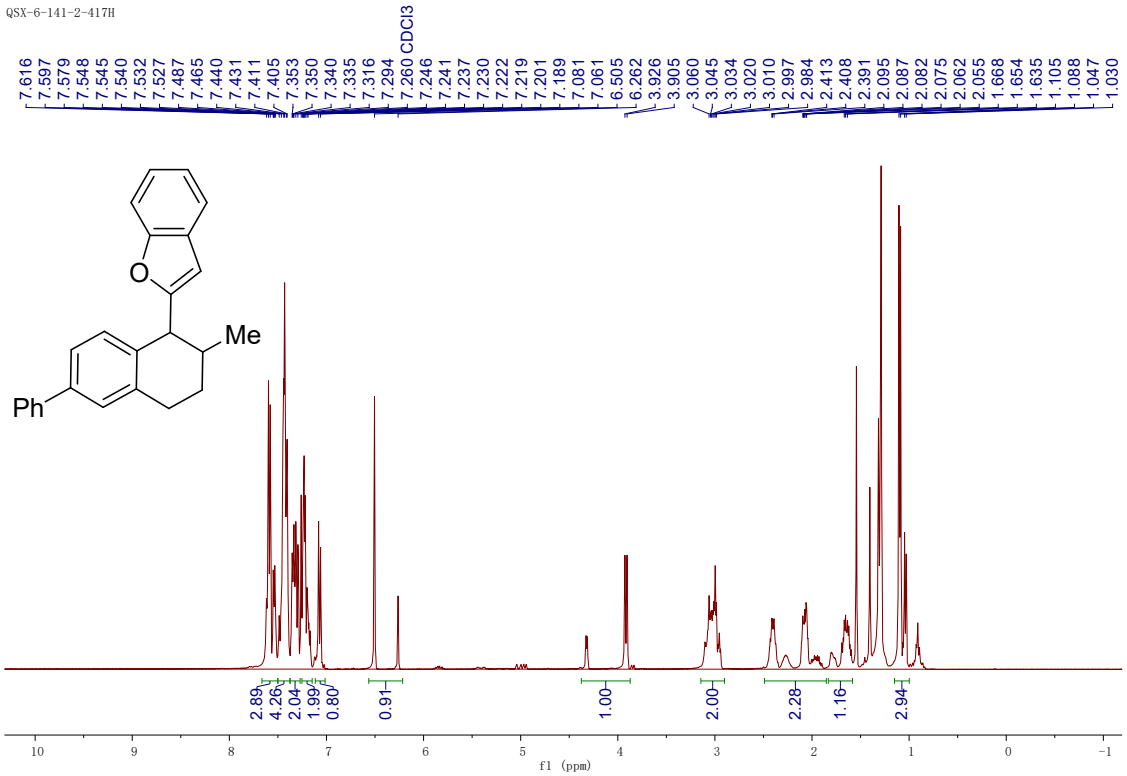
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8a* (*see procedure*)



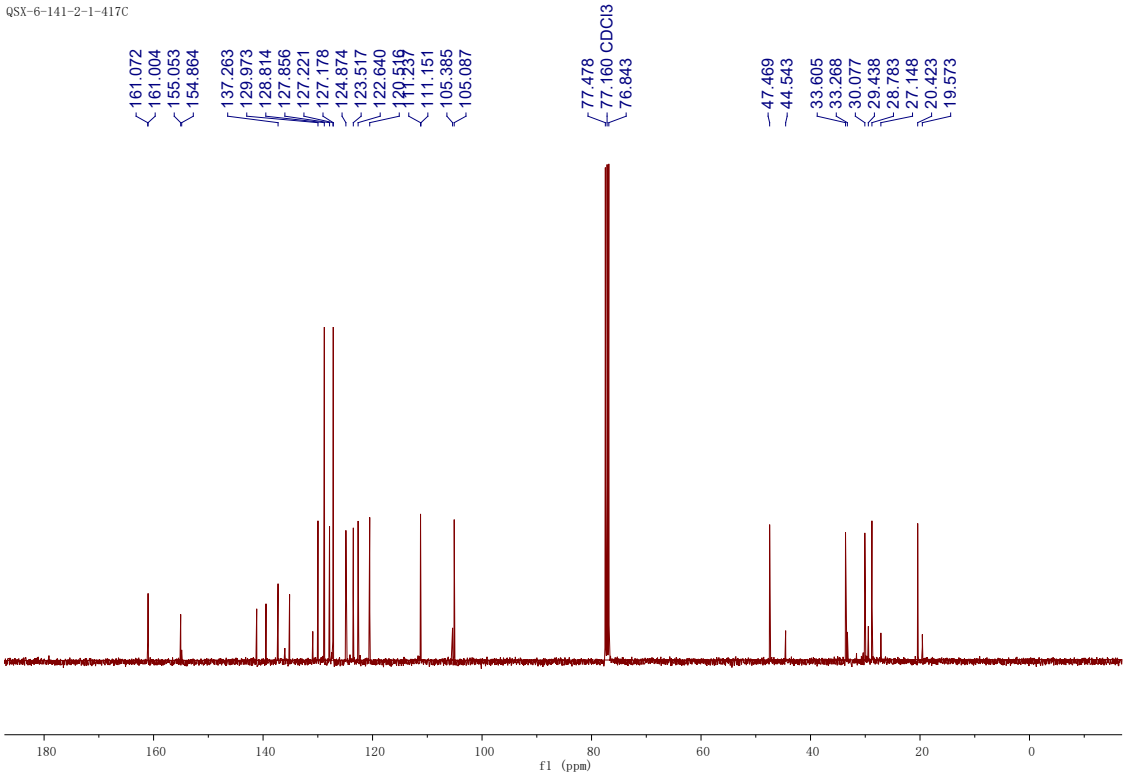
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8a*



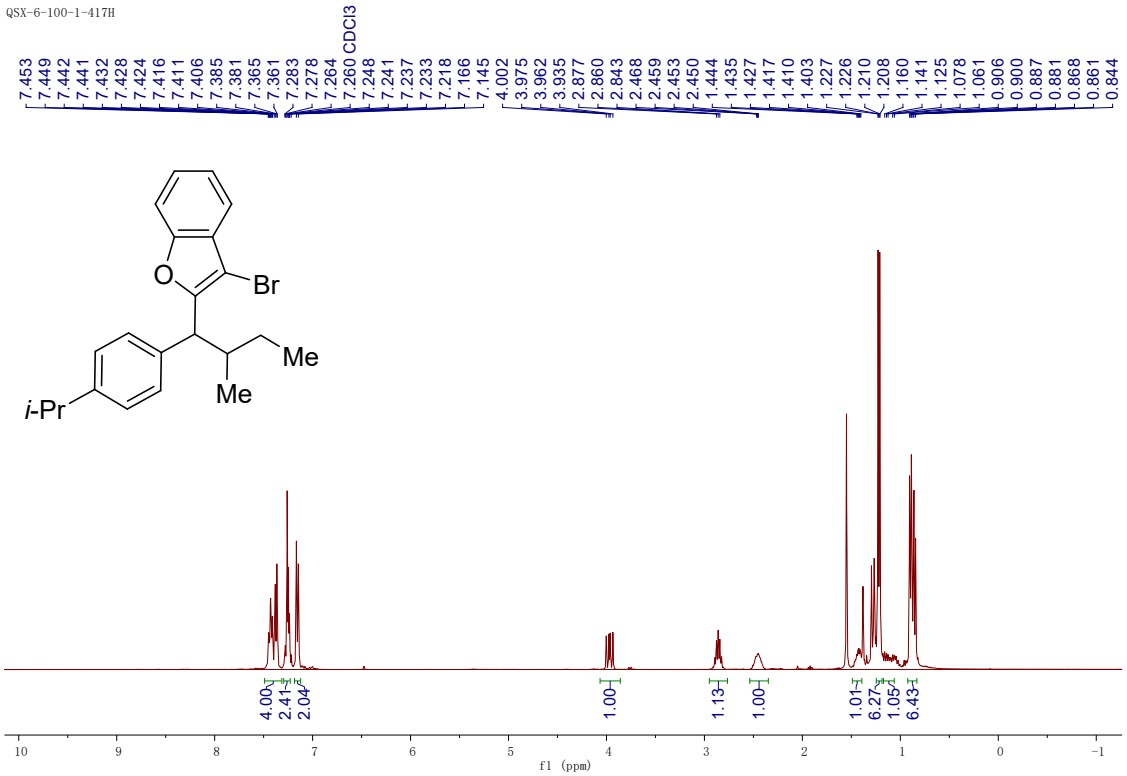
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8b (*see procedure*)



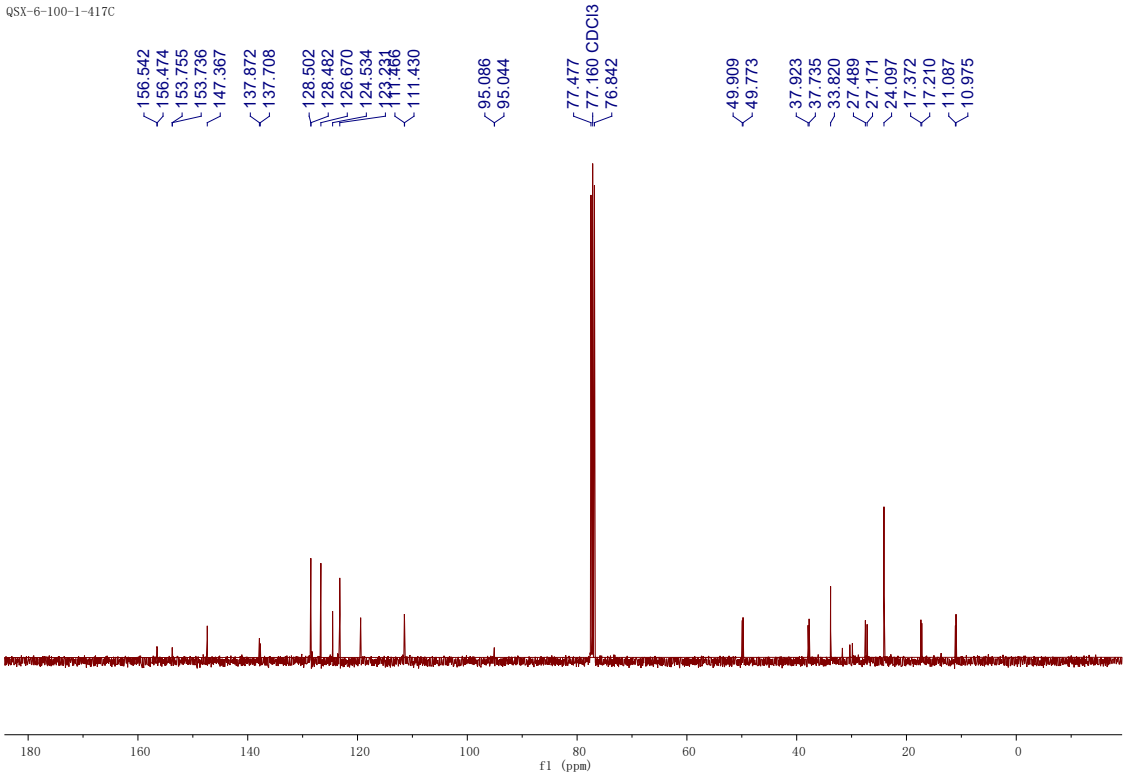
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8b



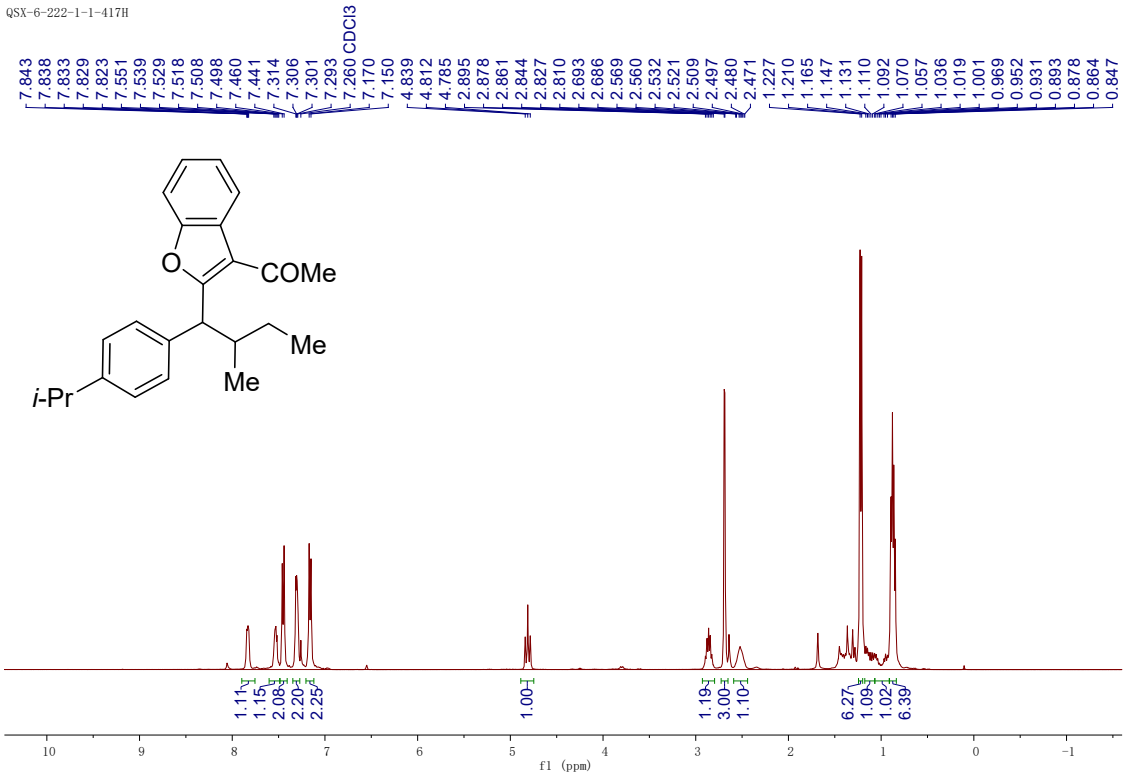
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8c (*see procedure*)



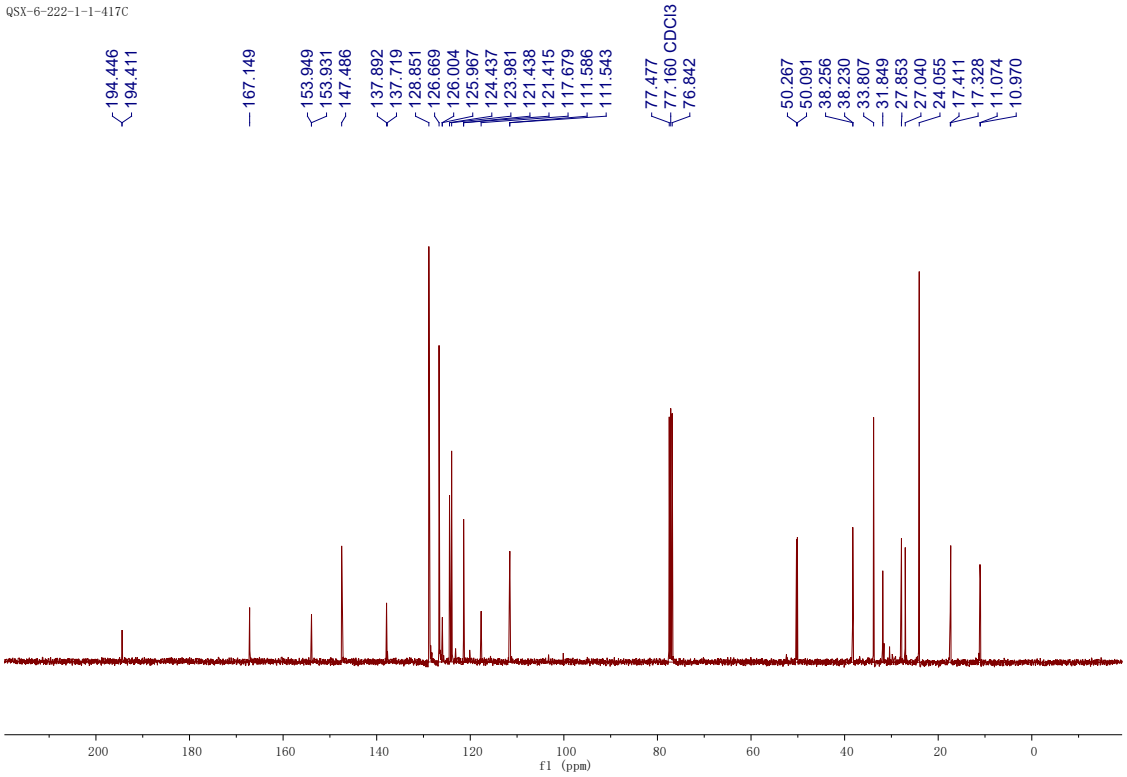
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8c



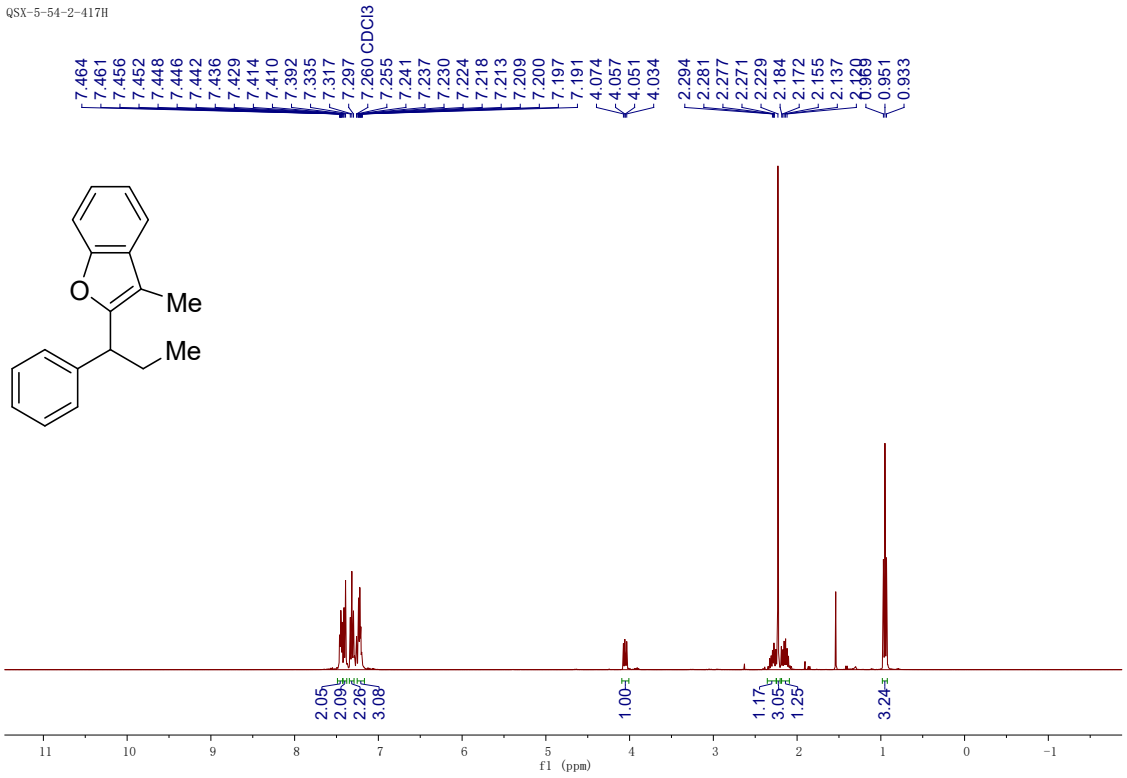
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8d (*see procedure*)



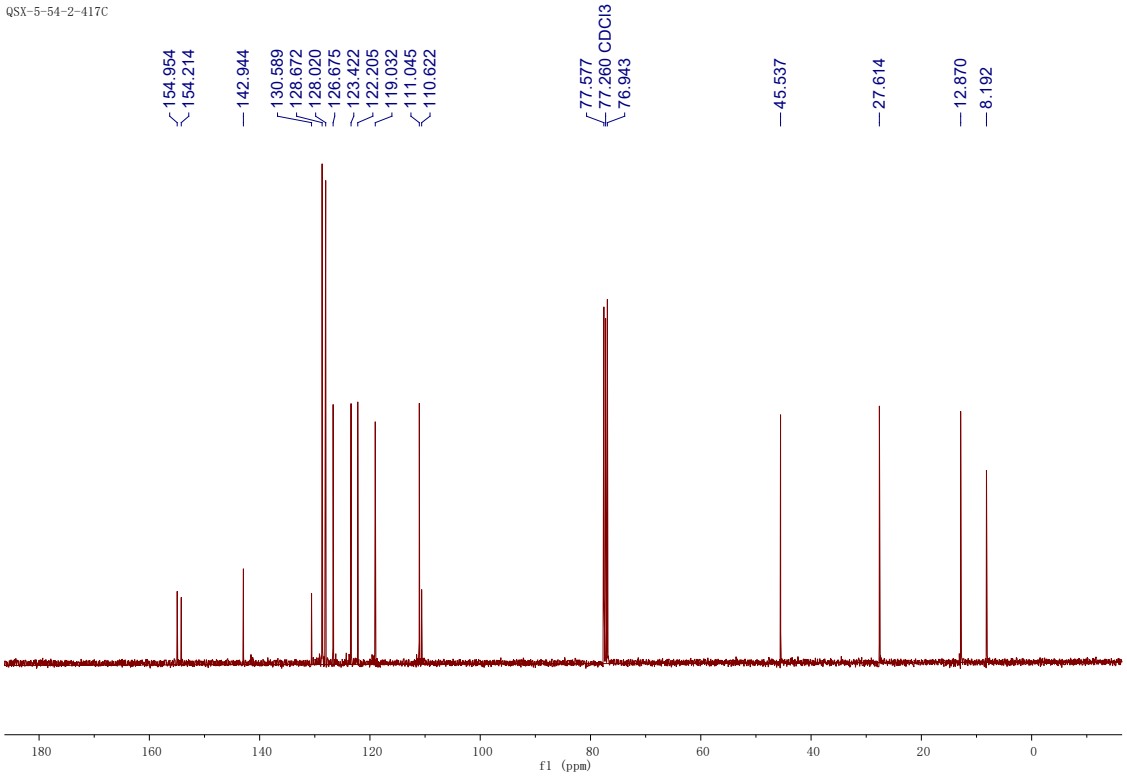
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8d



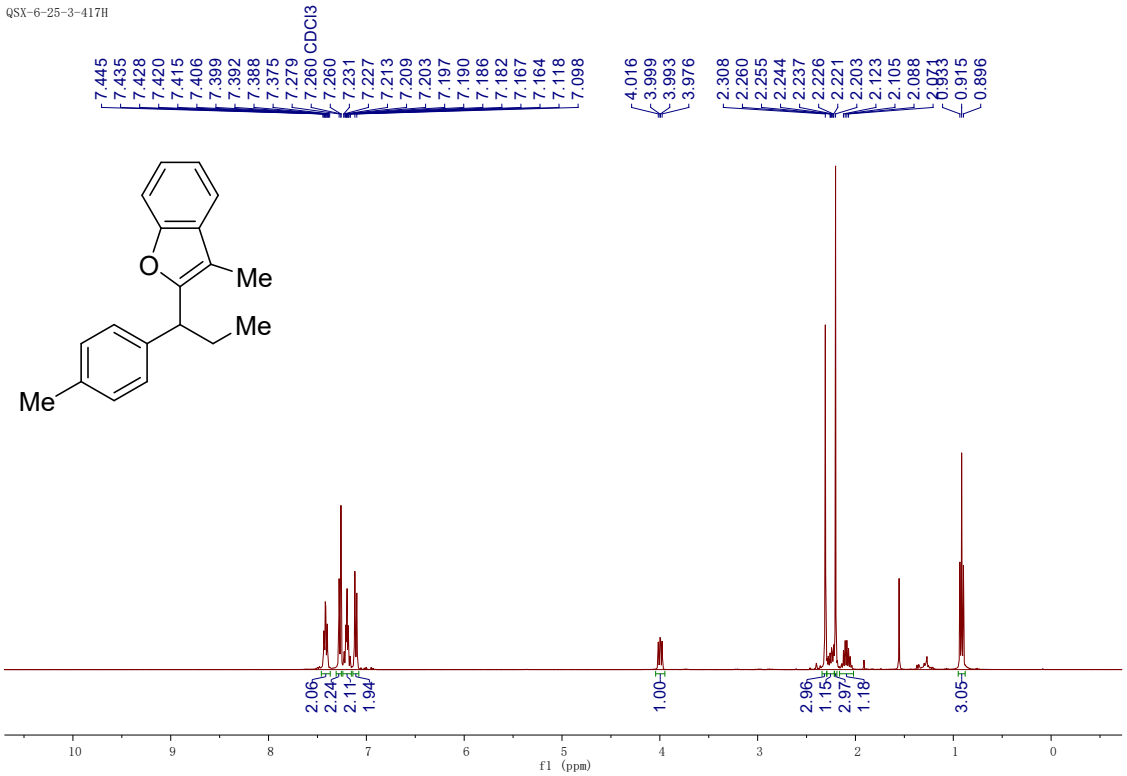
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a (*see procedure*)



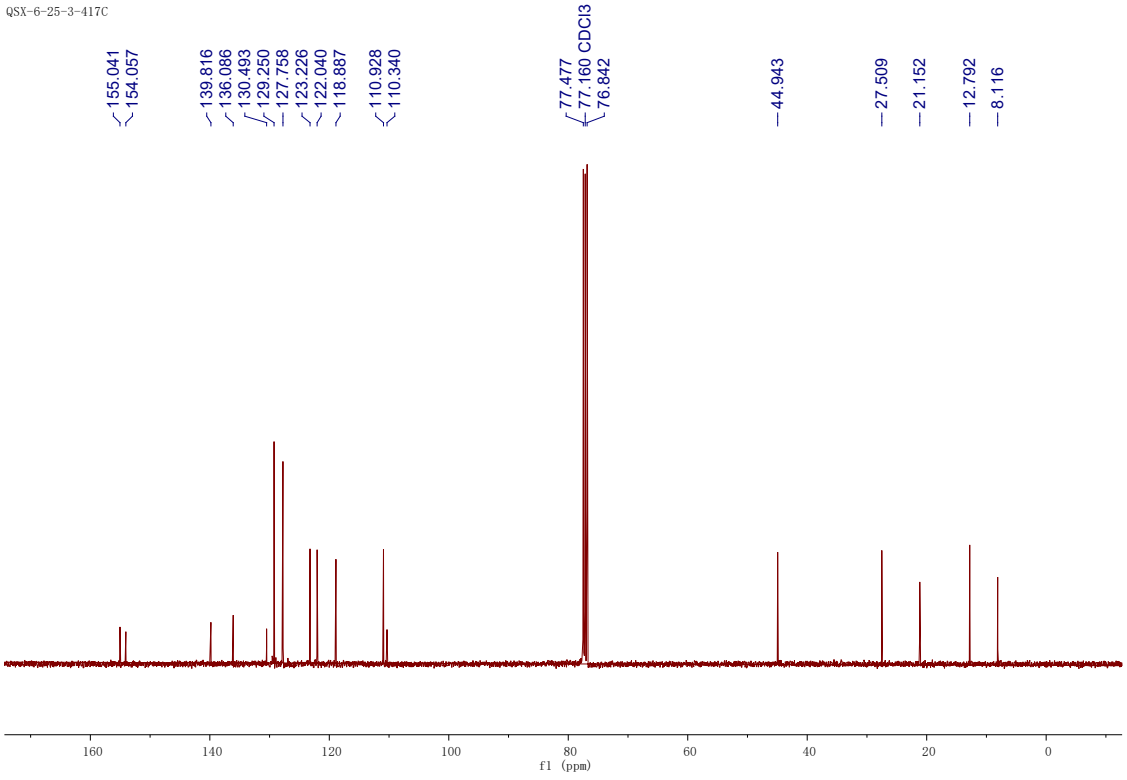
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3a



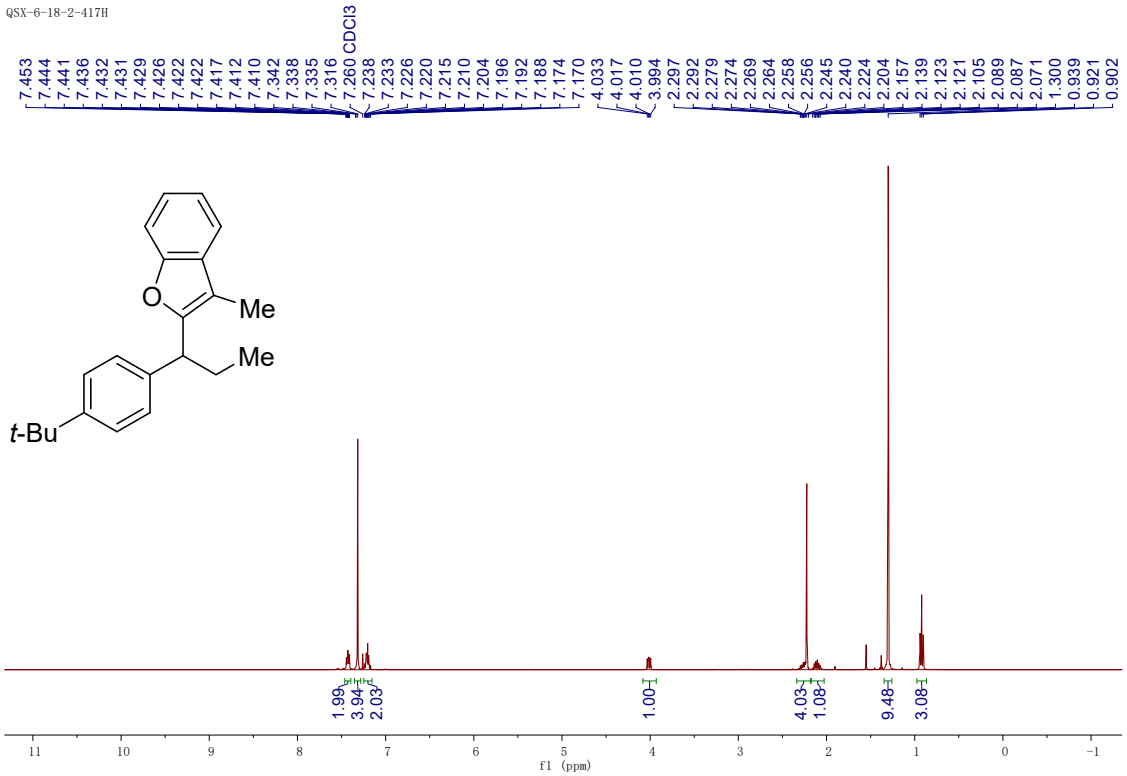
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b (*see procedure*)



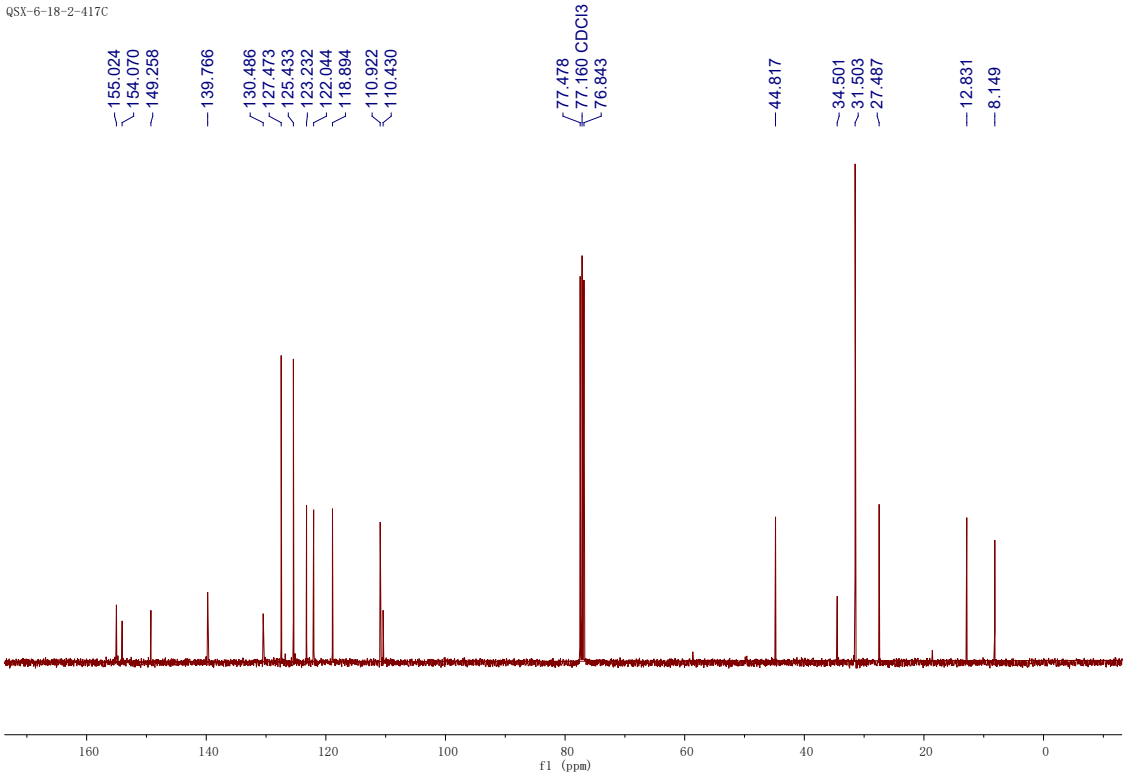
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3b



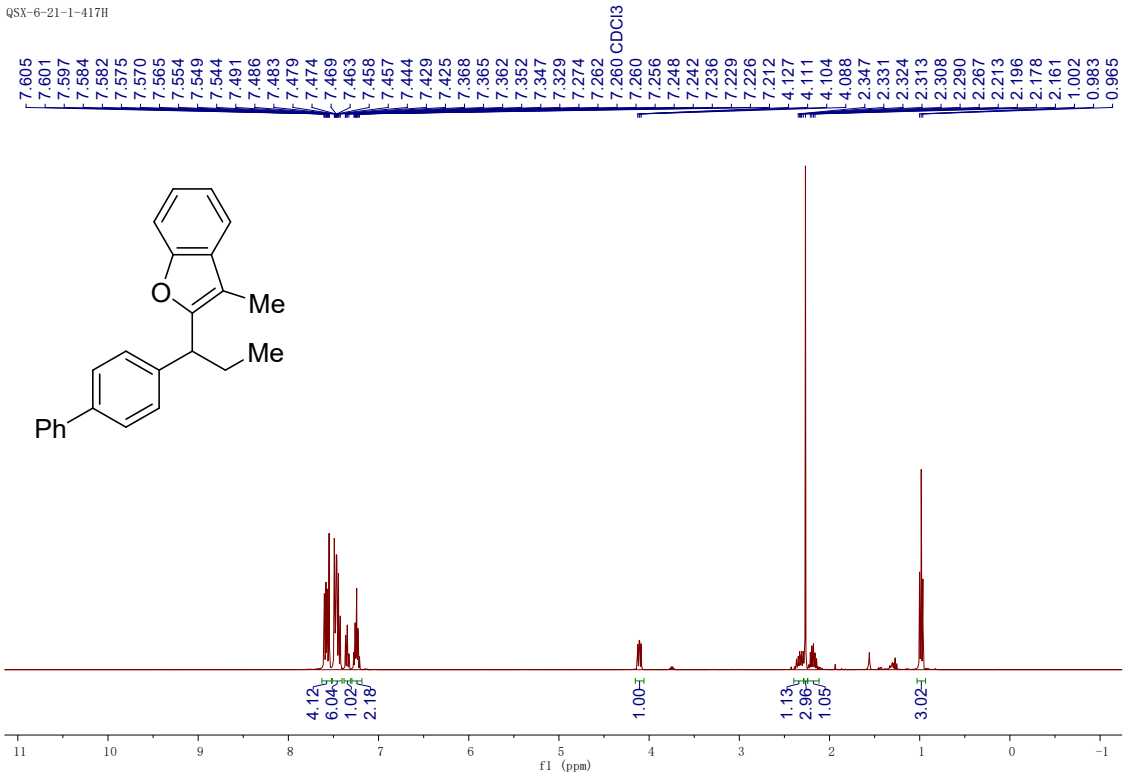
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c (*see procedure*)



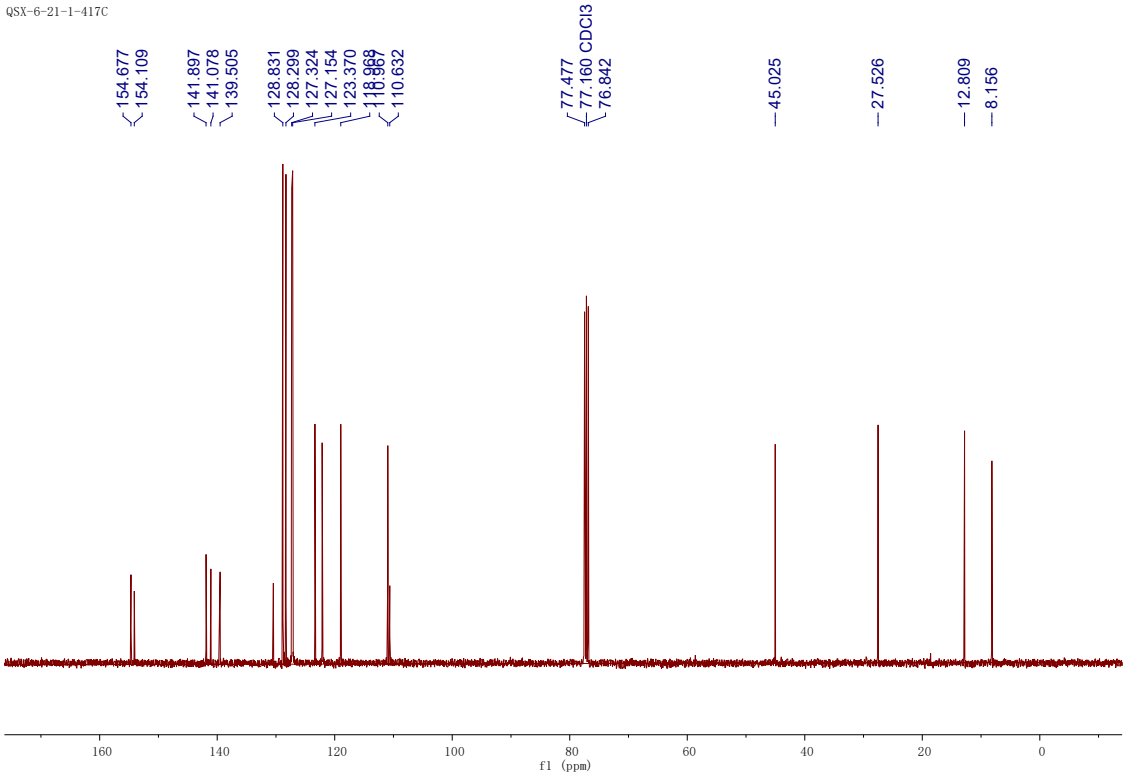
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3c



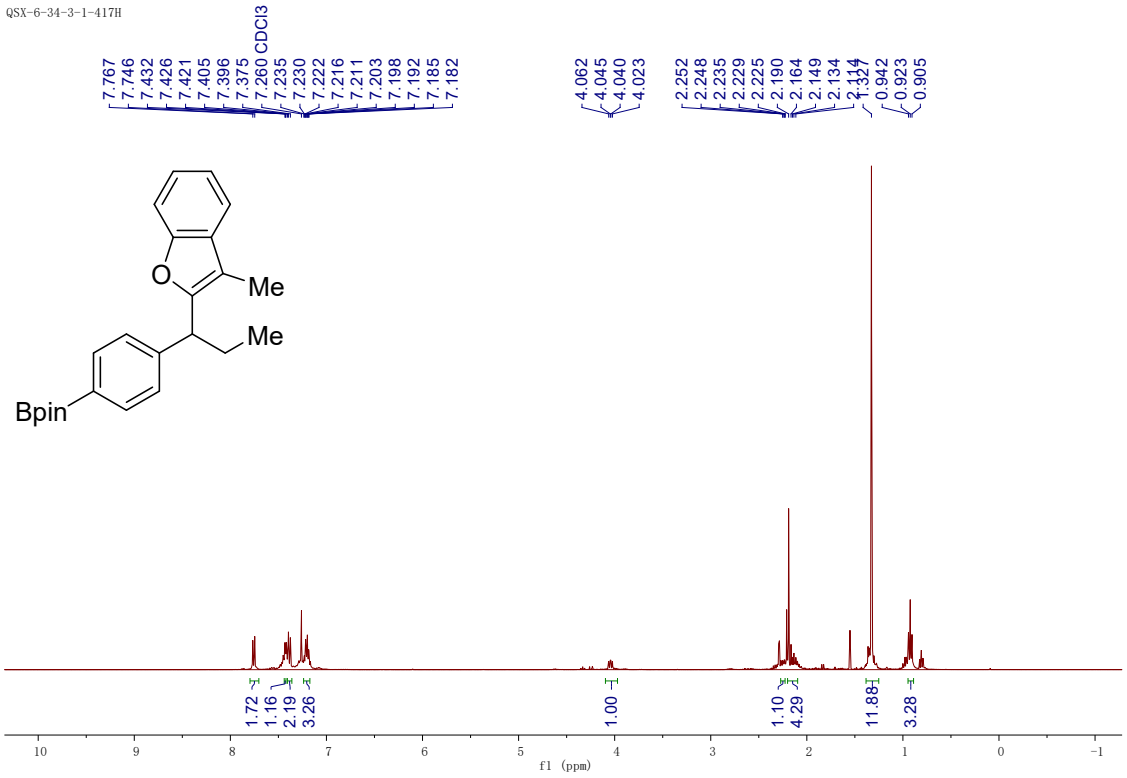
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3d (*see procedure*)



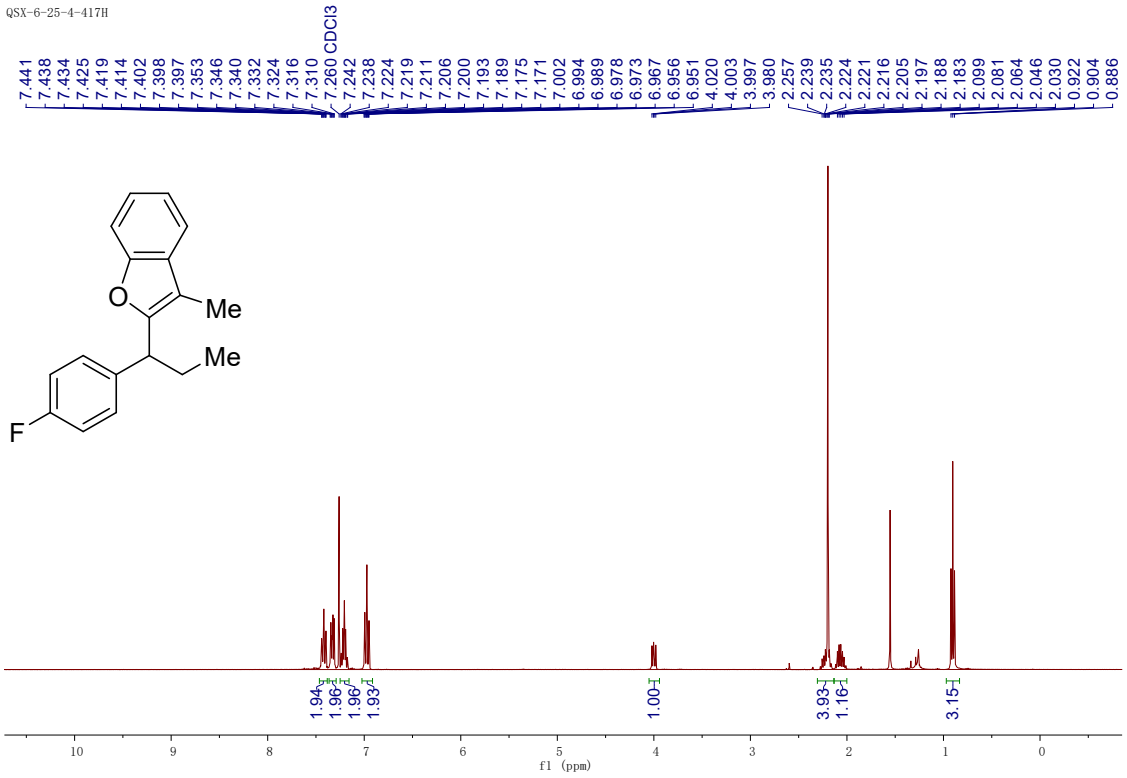
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3d



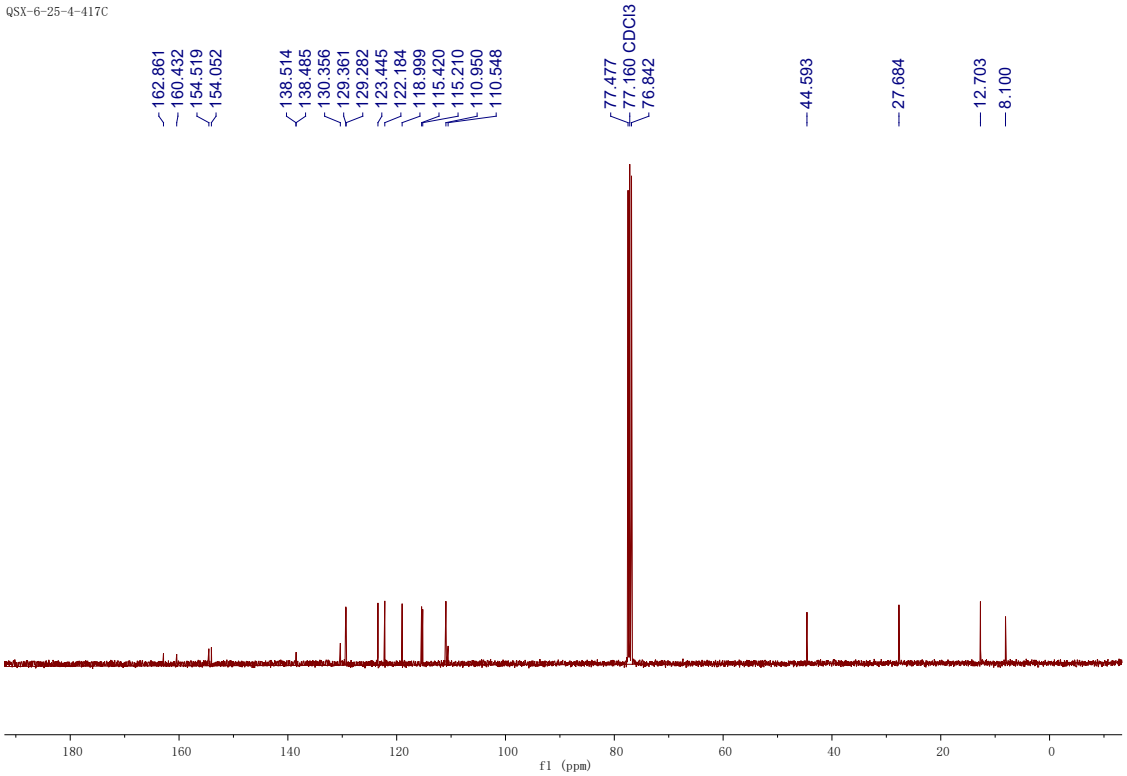
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3e (*see procedure*)



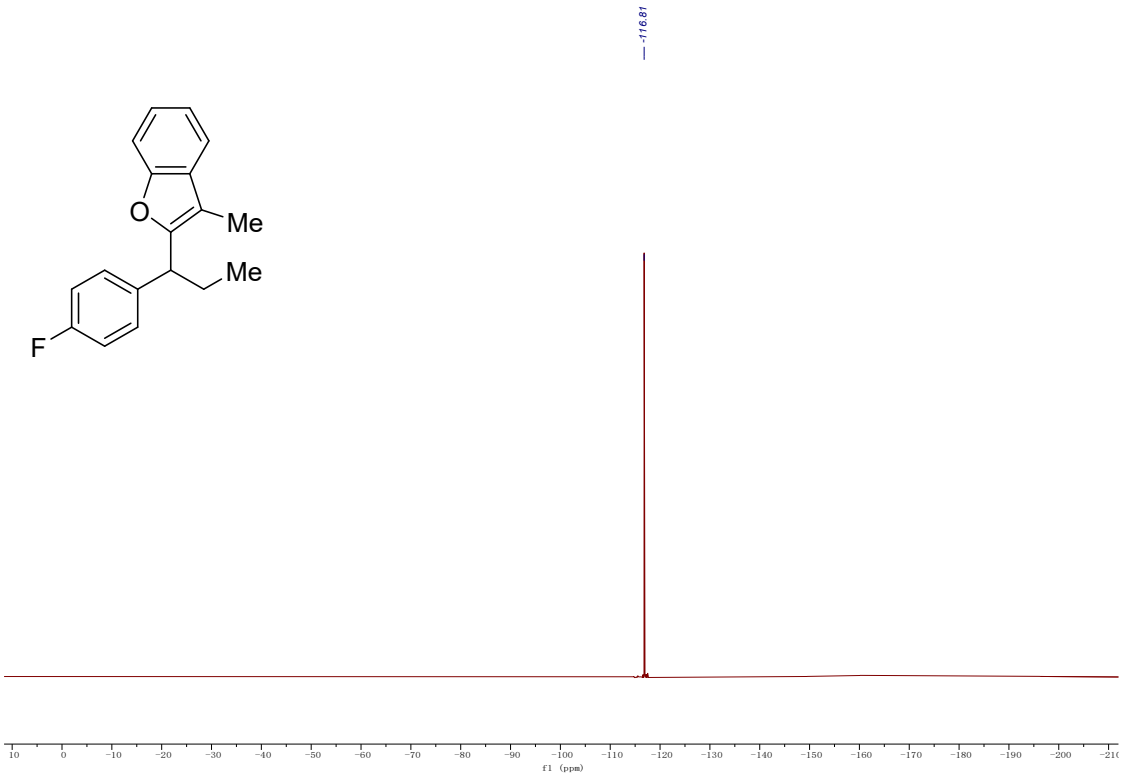
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3f (*see procedure*)



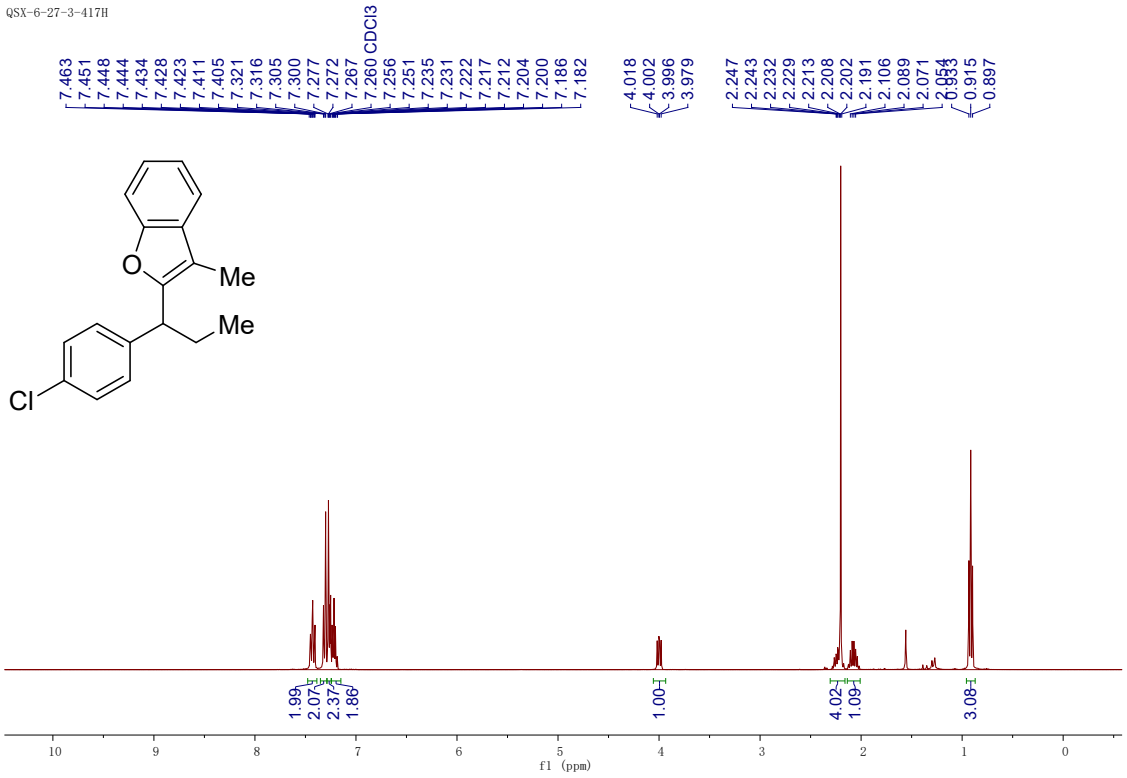
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f



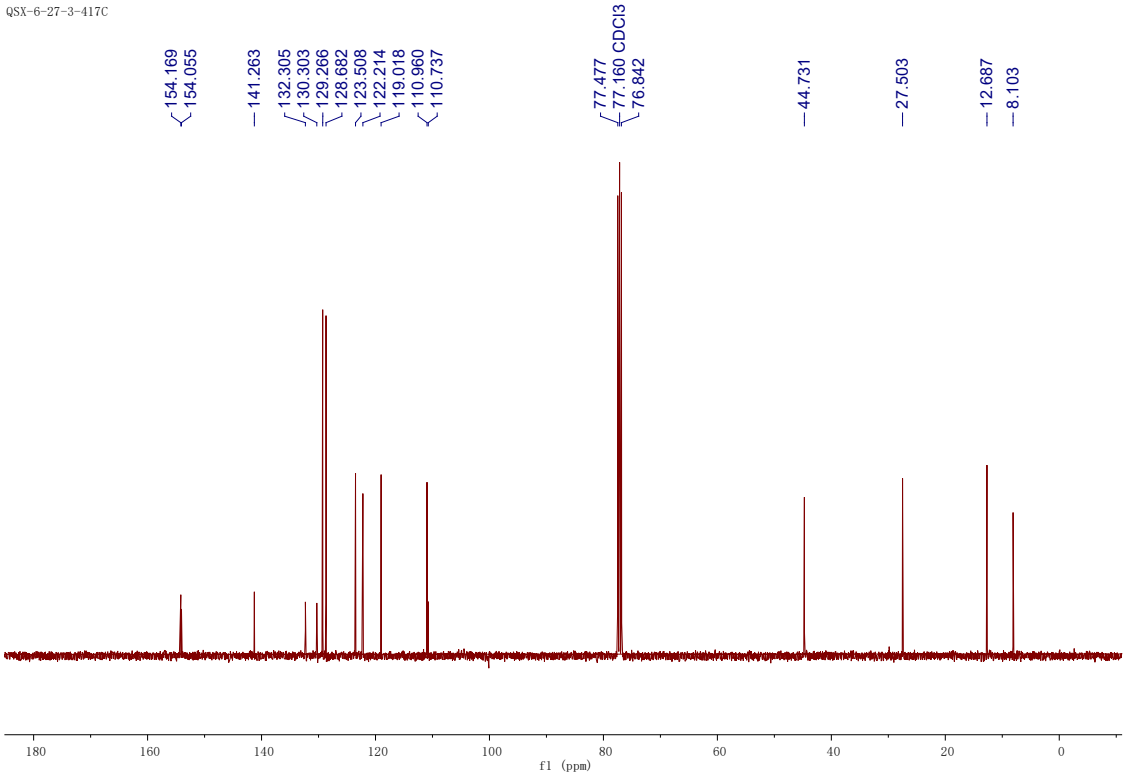
^{19}F NMR (177 MHz, $CDCl_3$) spectrum of 3f



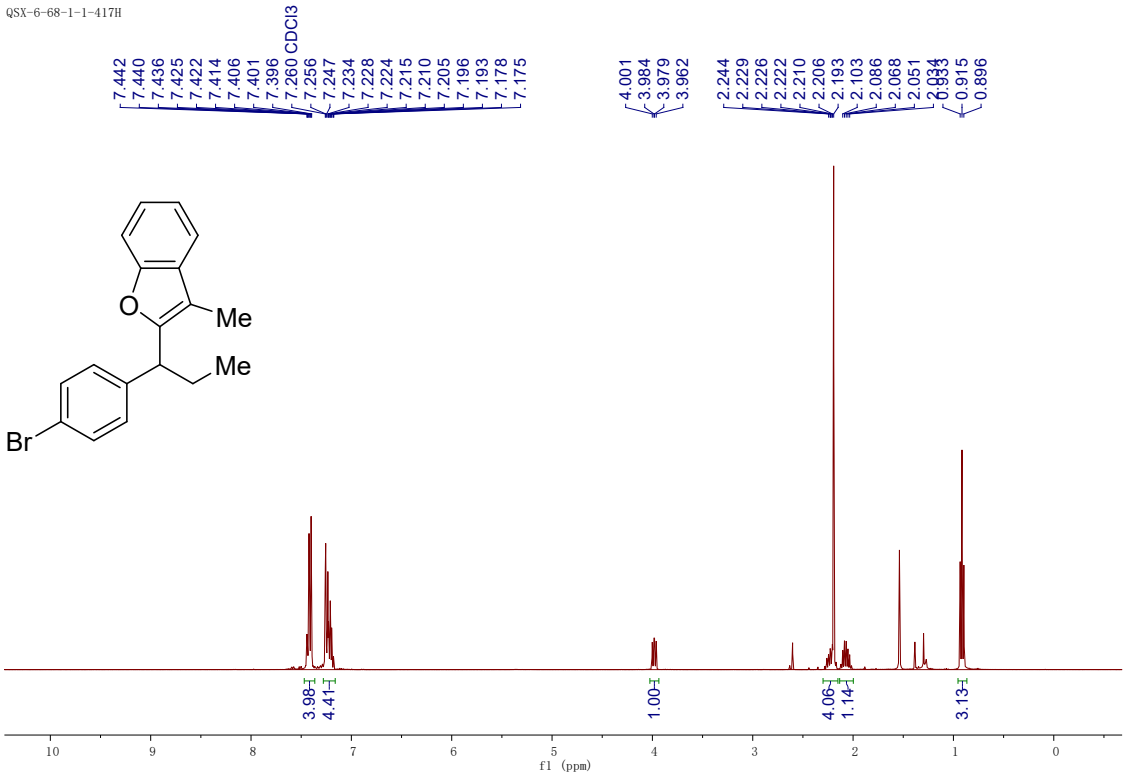
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3g (*see procedure*)



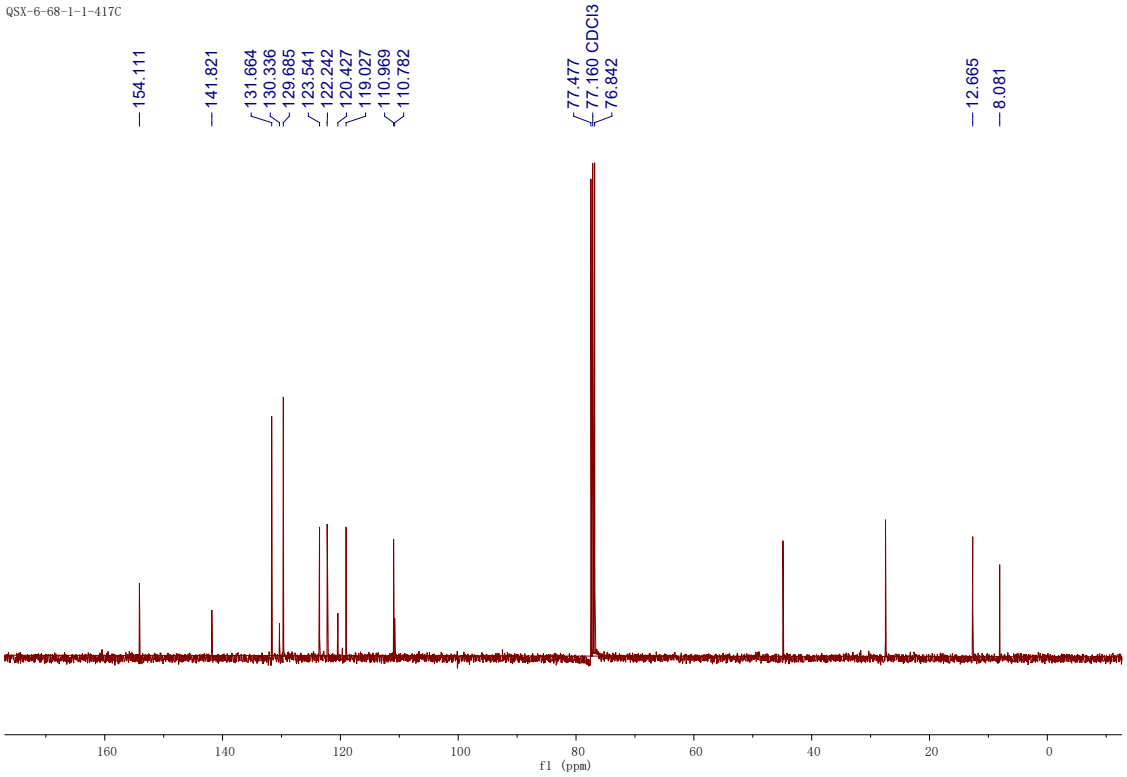
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



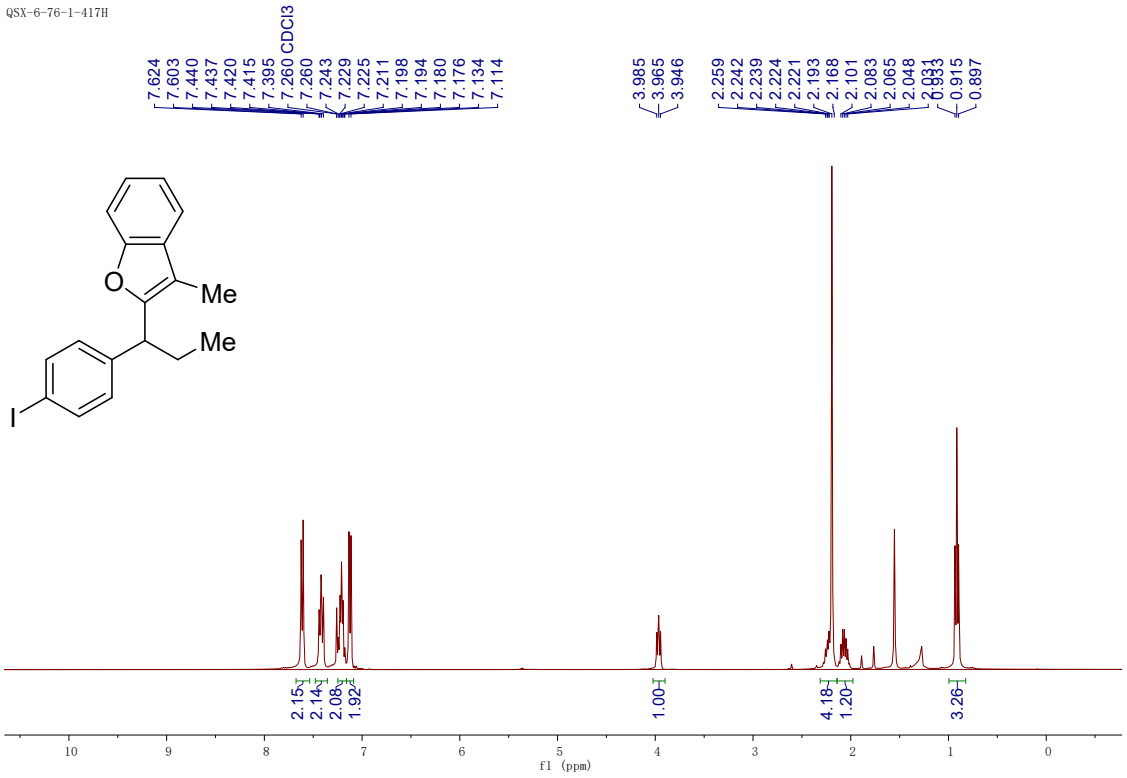
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3h (*see procedure*)



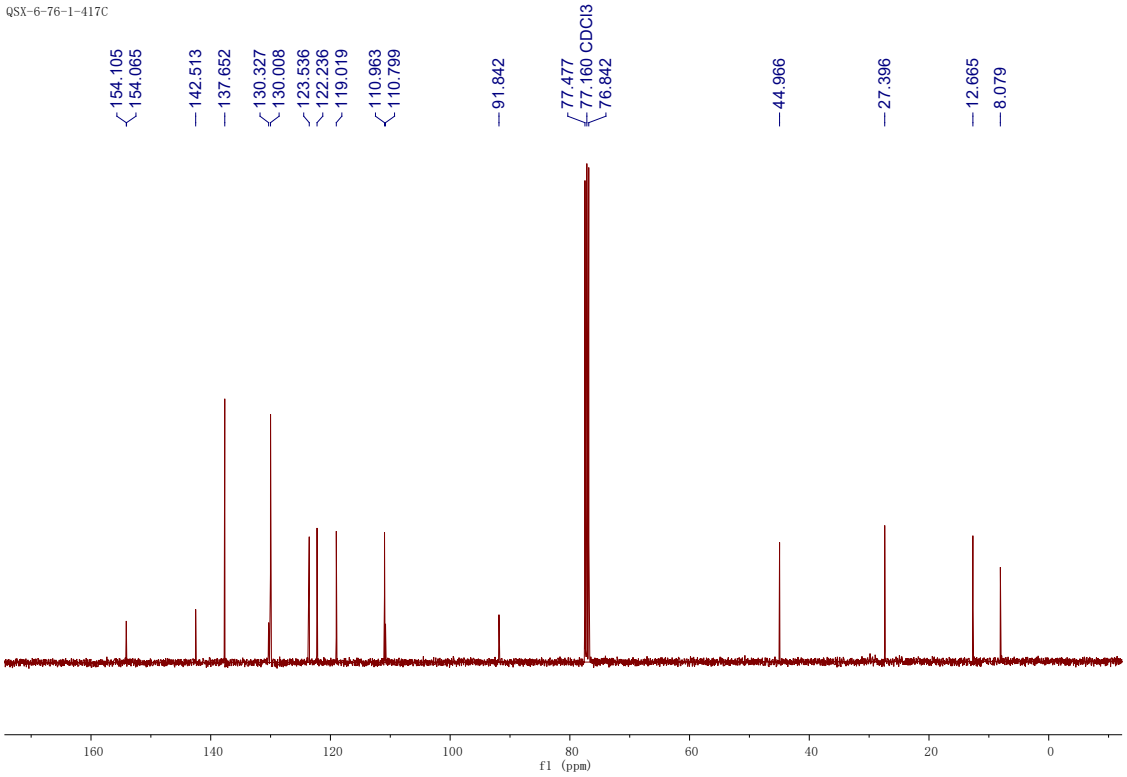
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3h



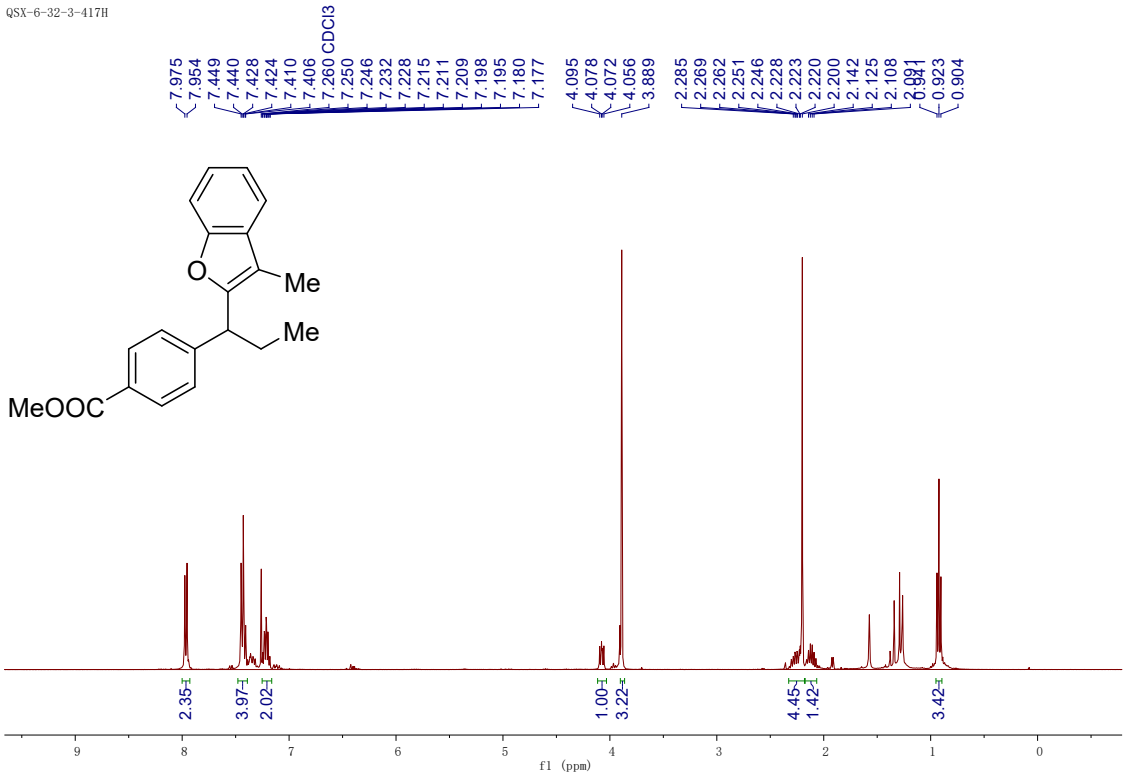
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3i (*see procedure*)



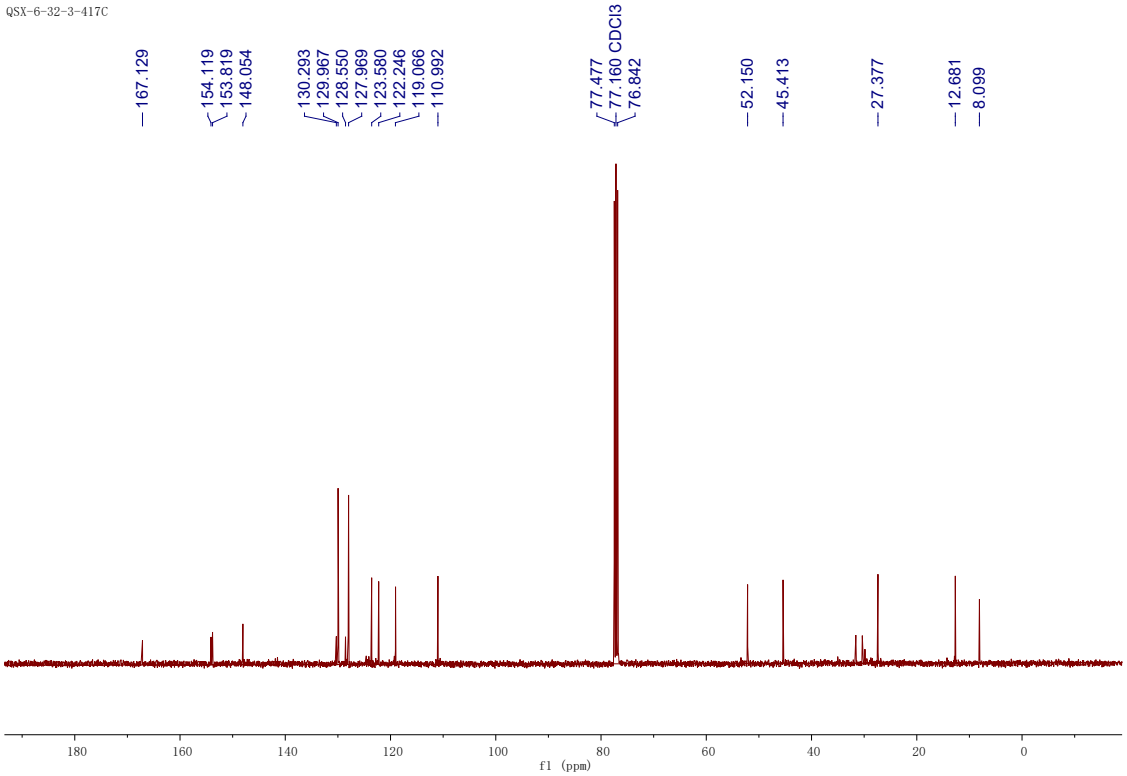
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3i



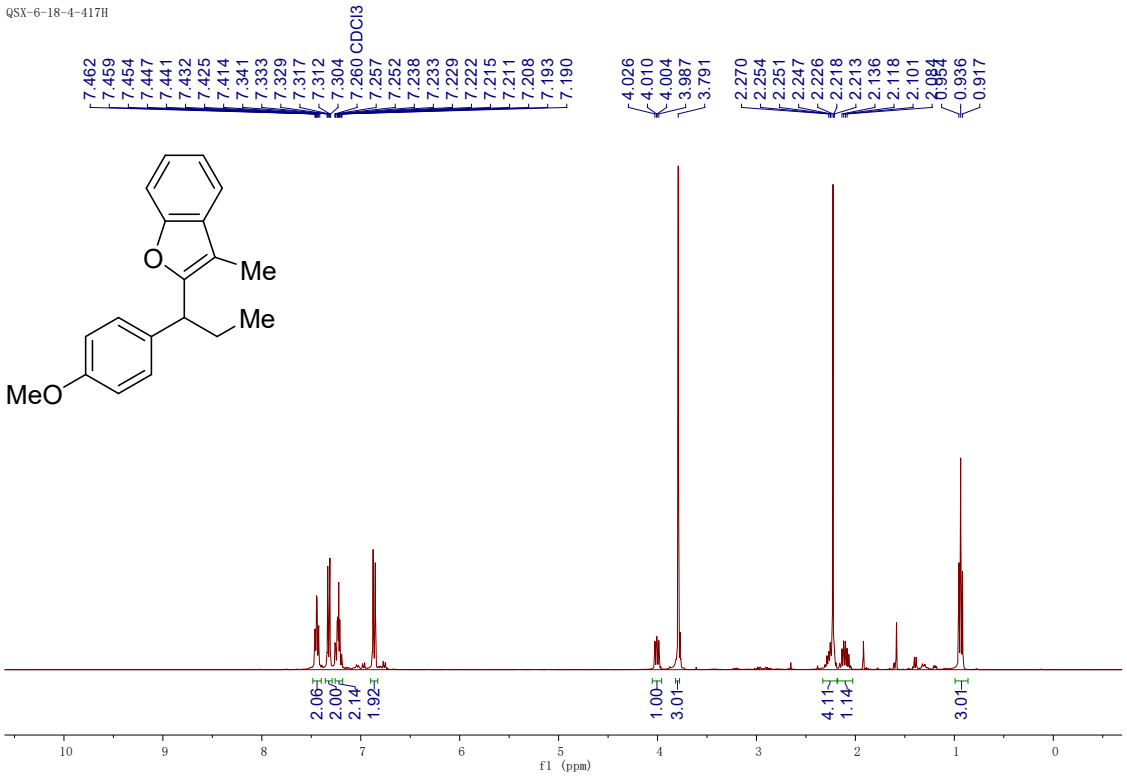
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3j (*see procedure*)



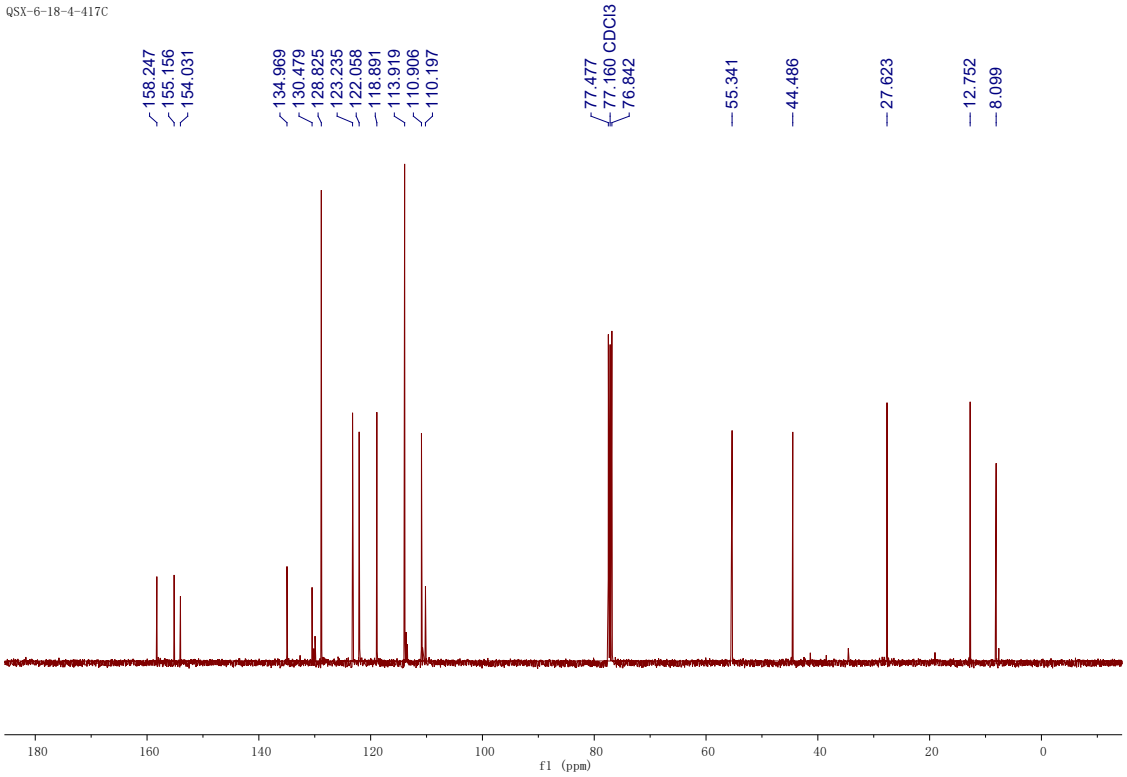
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3j



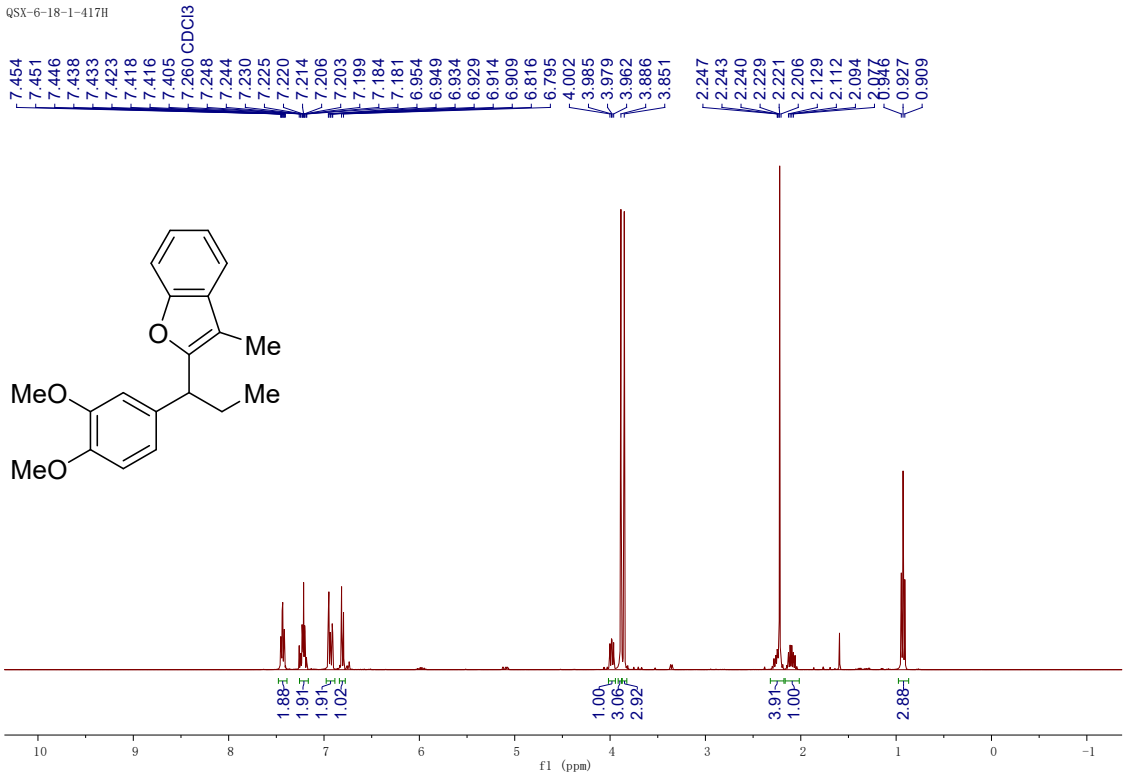
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k (*see procedure*)



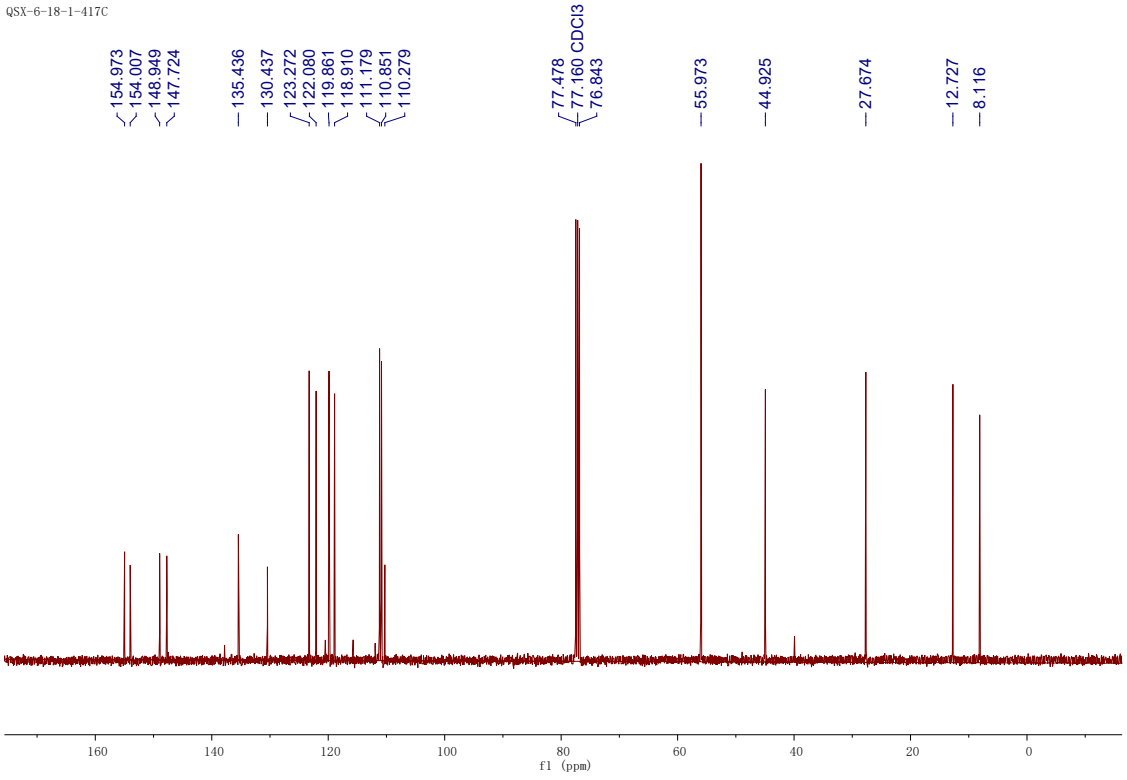
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3k



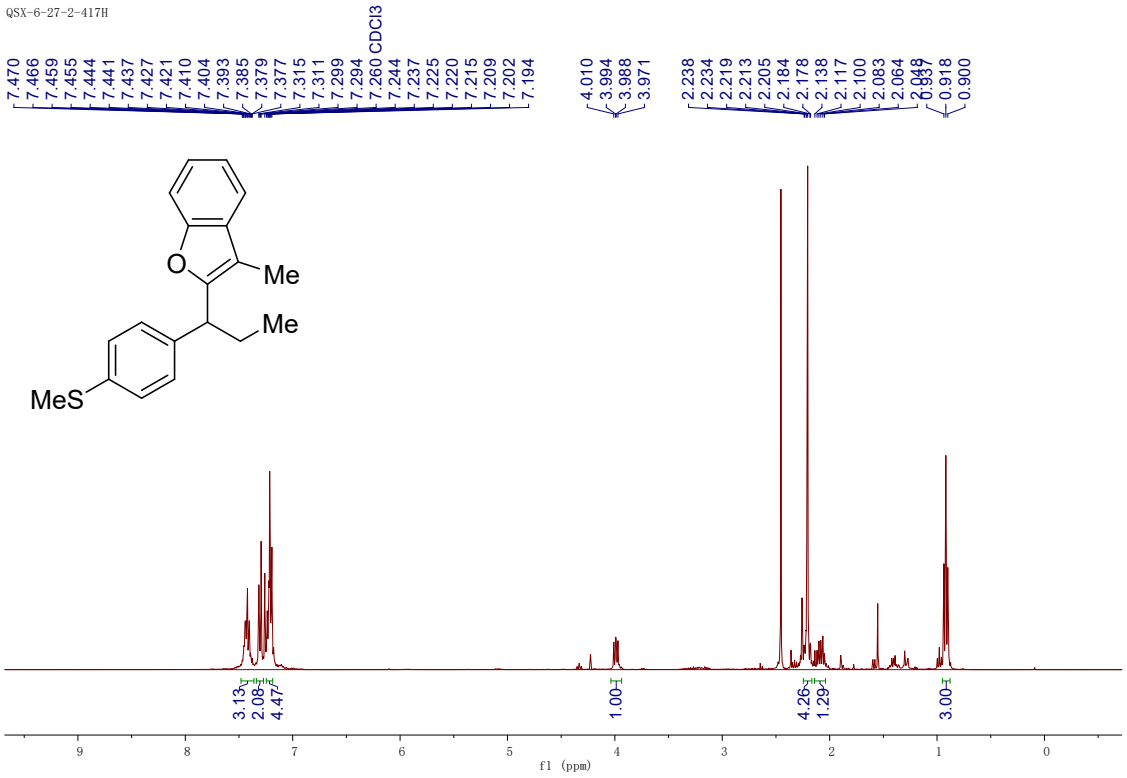
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3l (*see procedure*)



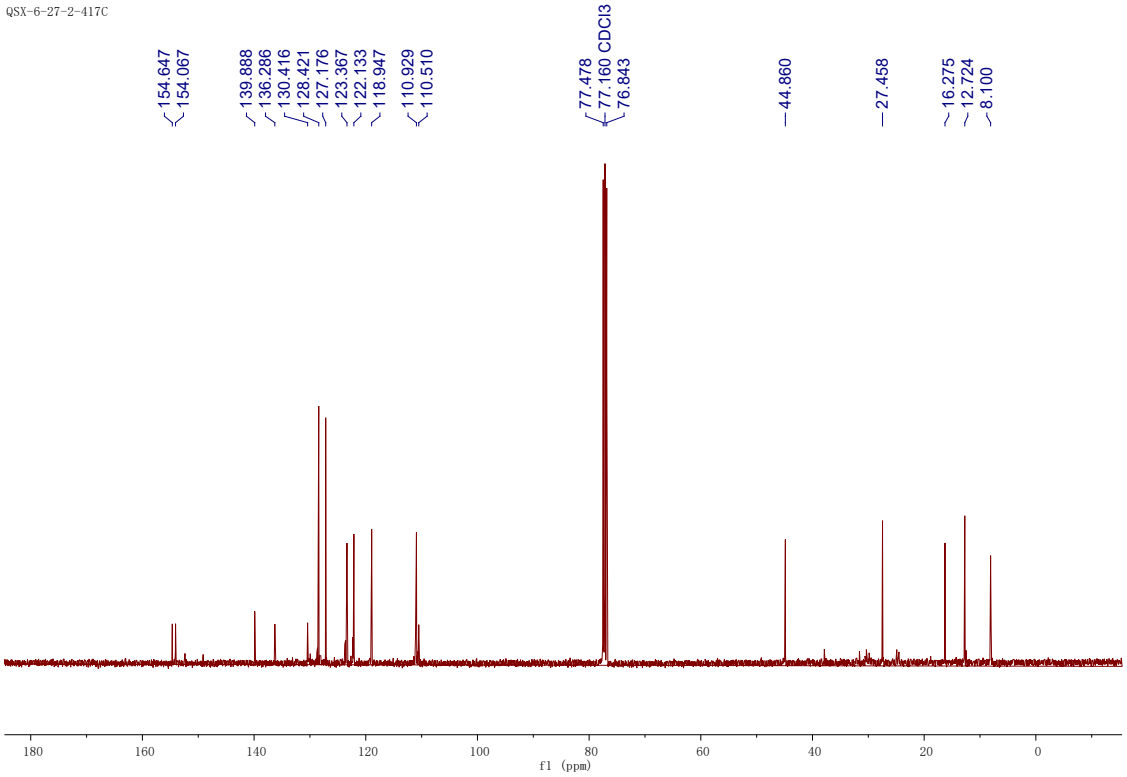
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3l



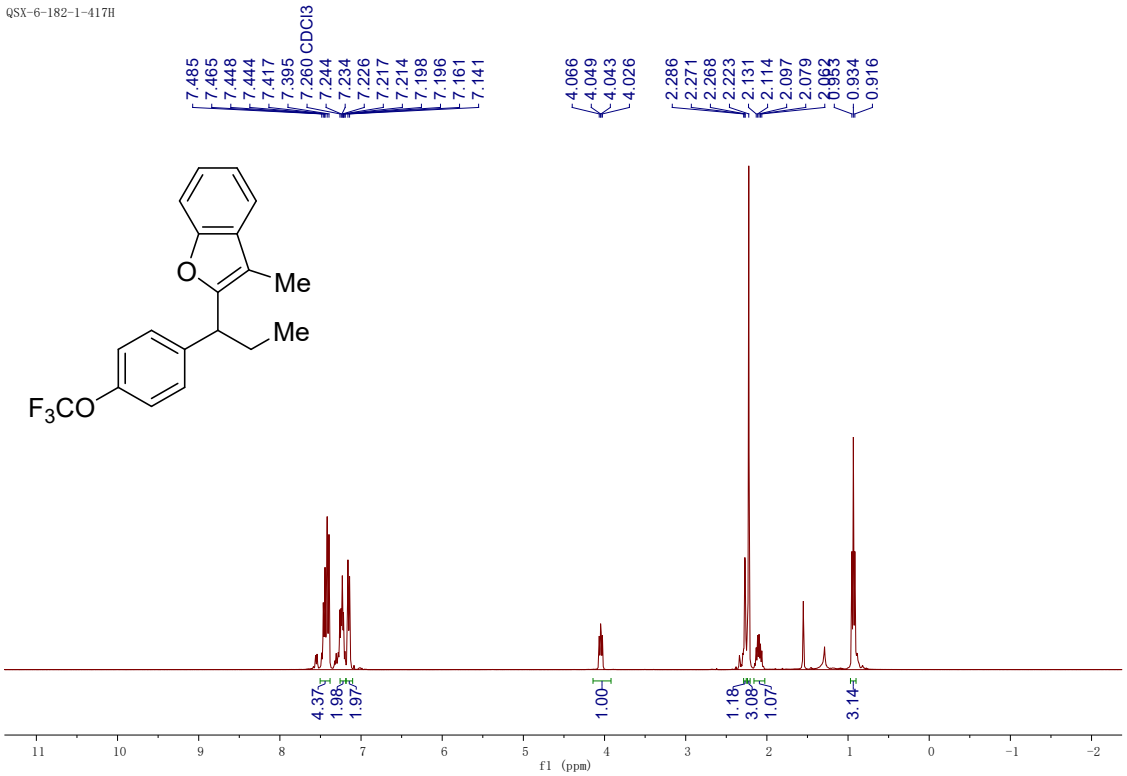
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3m (*see procedure*)



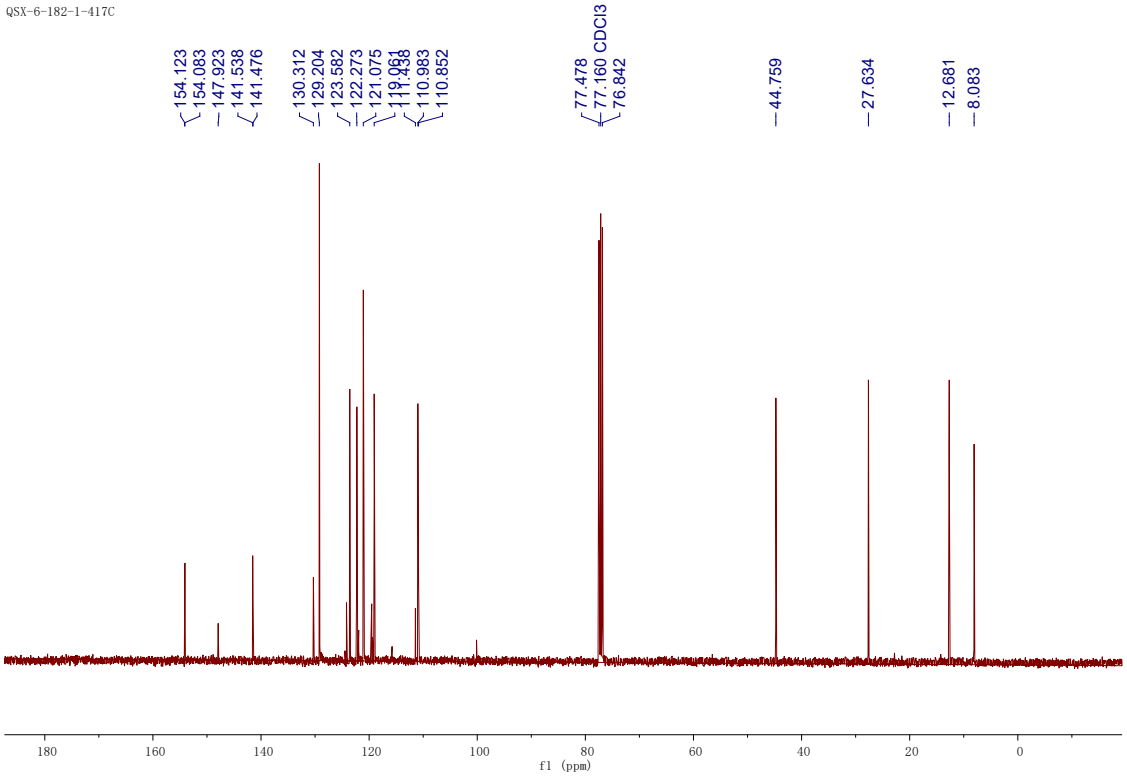
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3m



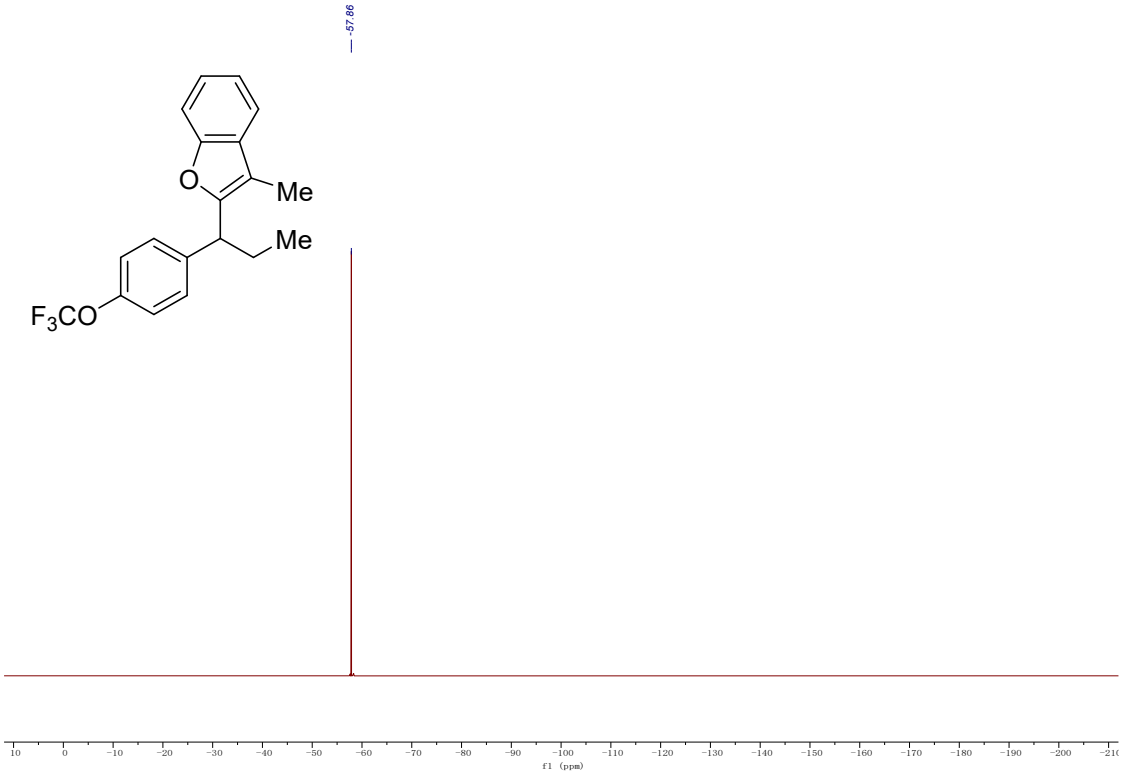
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3n (*see procedure*)



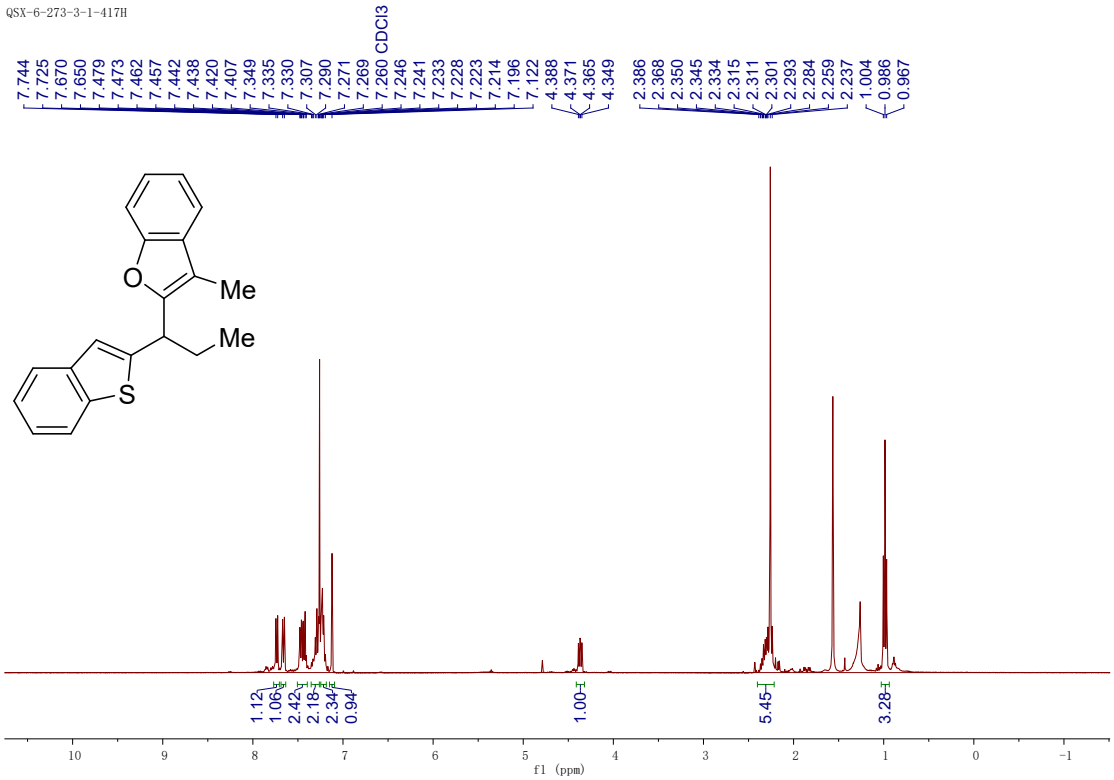
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3n



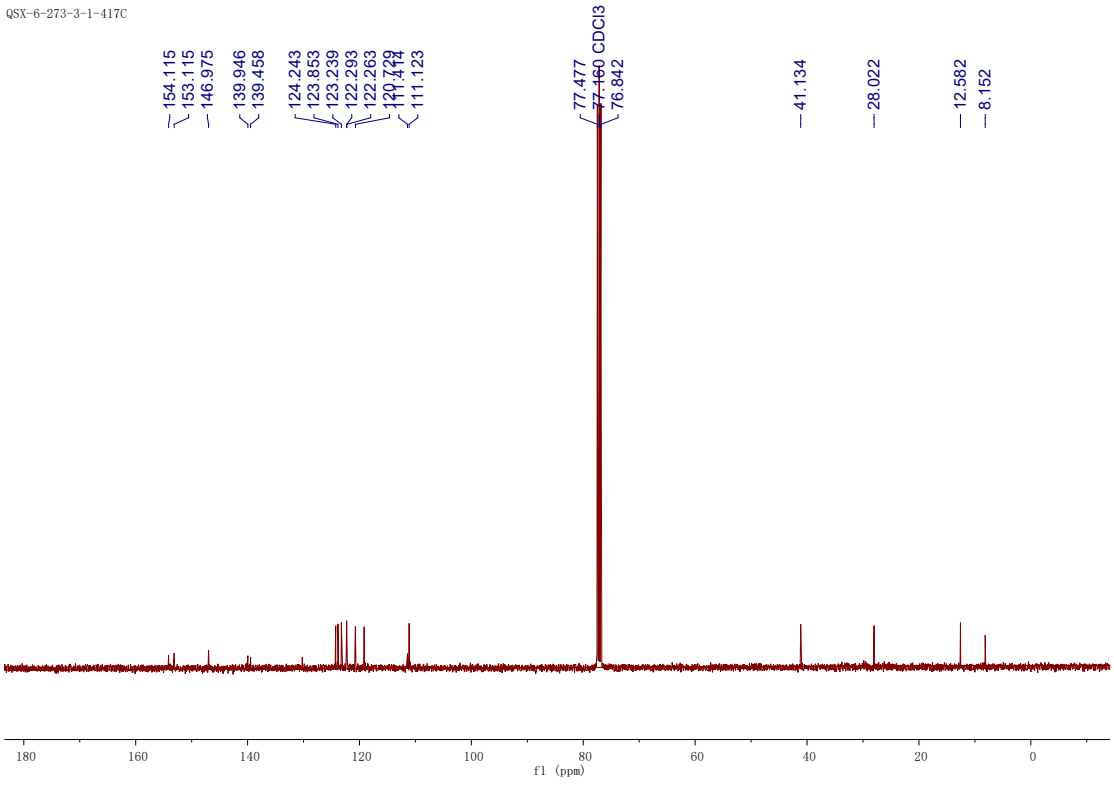
^{19}F NMR (177 MHz, $CDCl_3$) spectrum of 3o



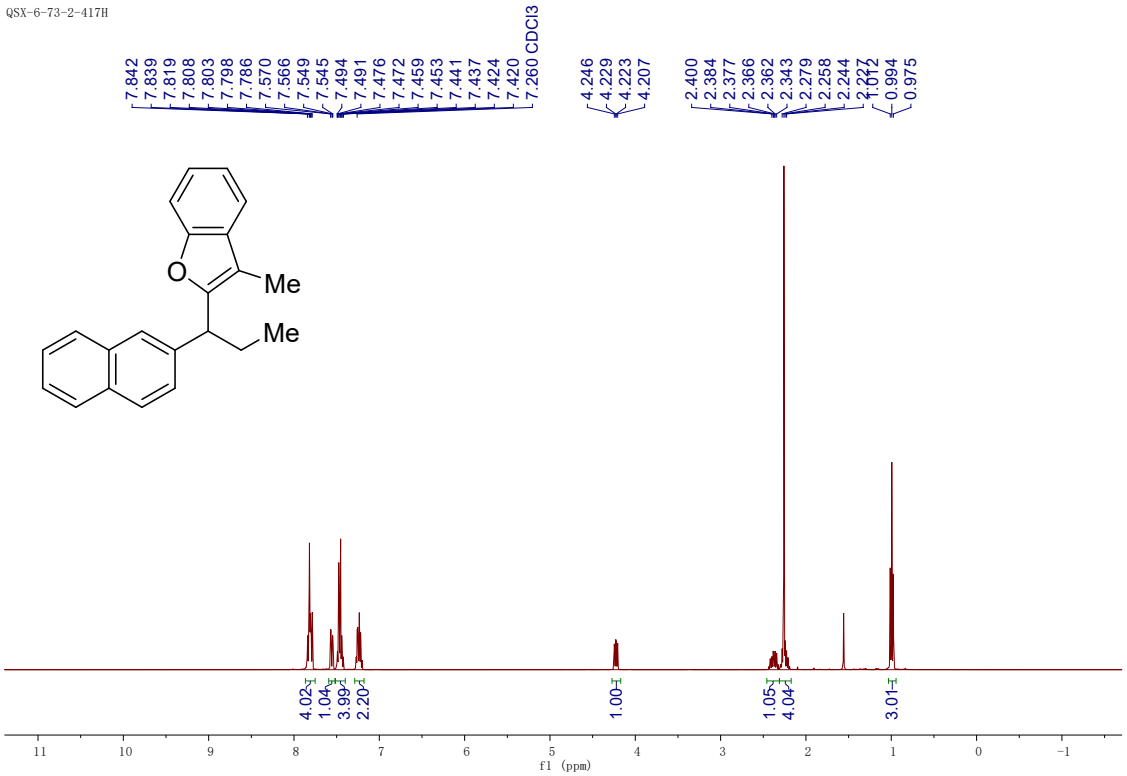
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3o (*see procedure*)



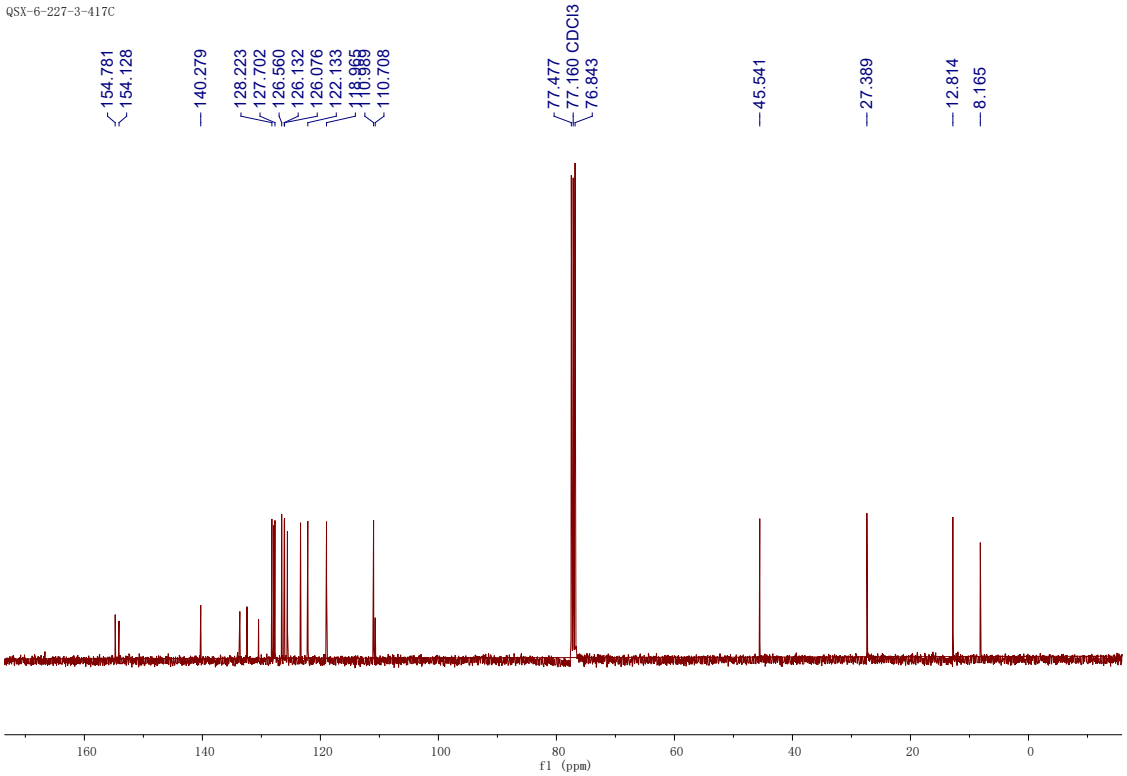
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3o



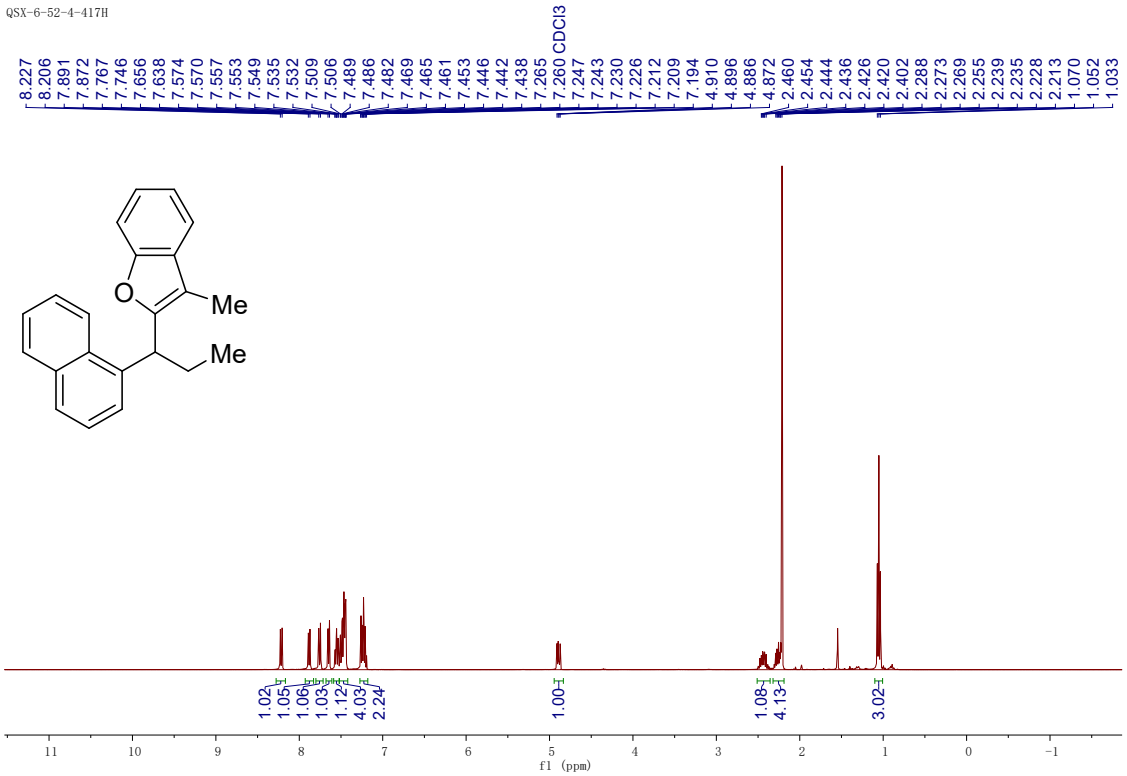
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p (*see procedure*)



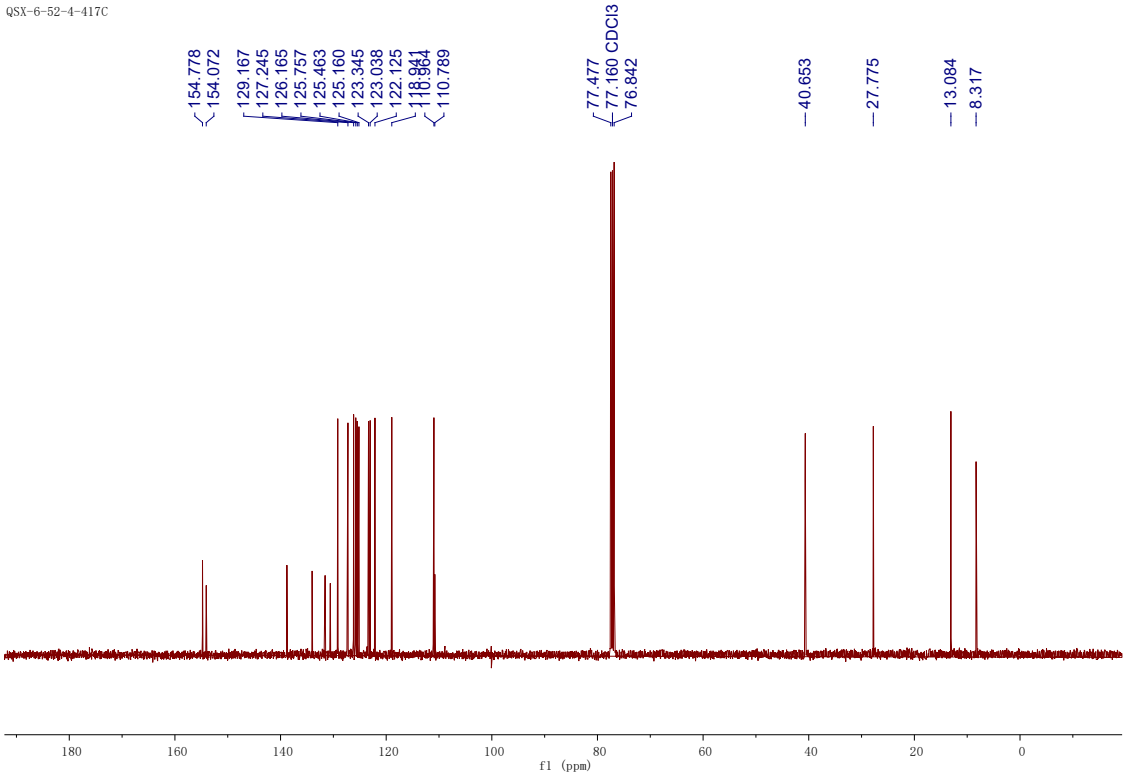
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3p



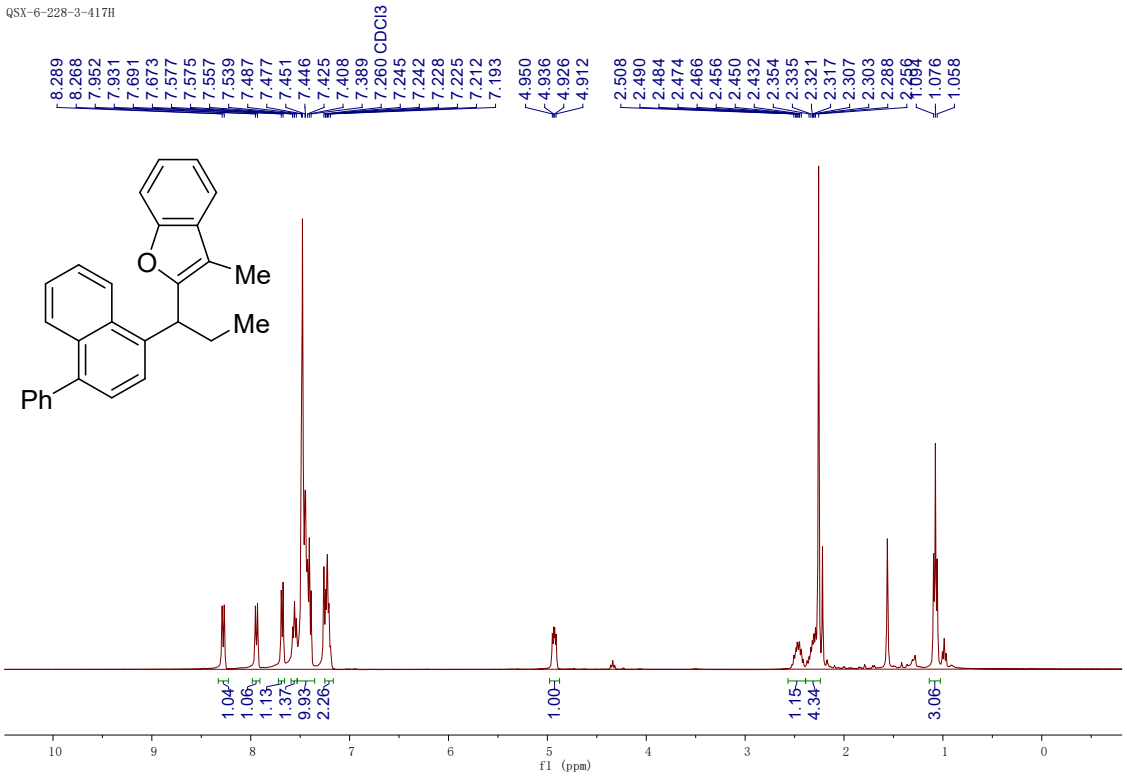
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3q (*see procedure*)



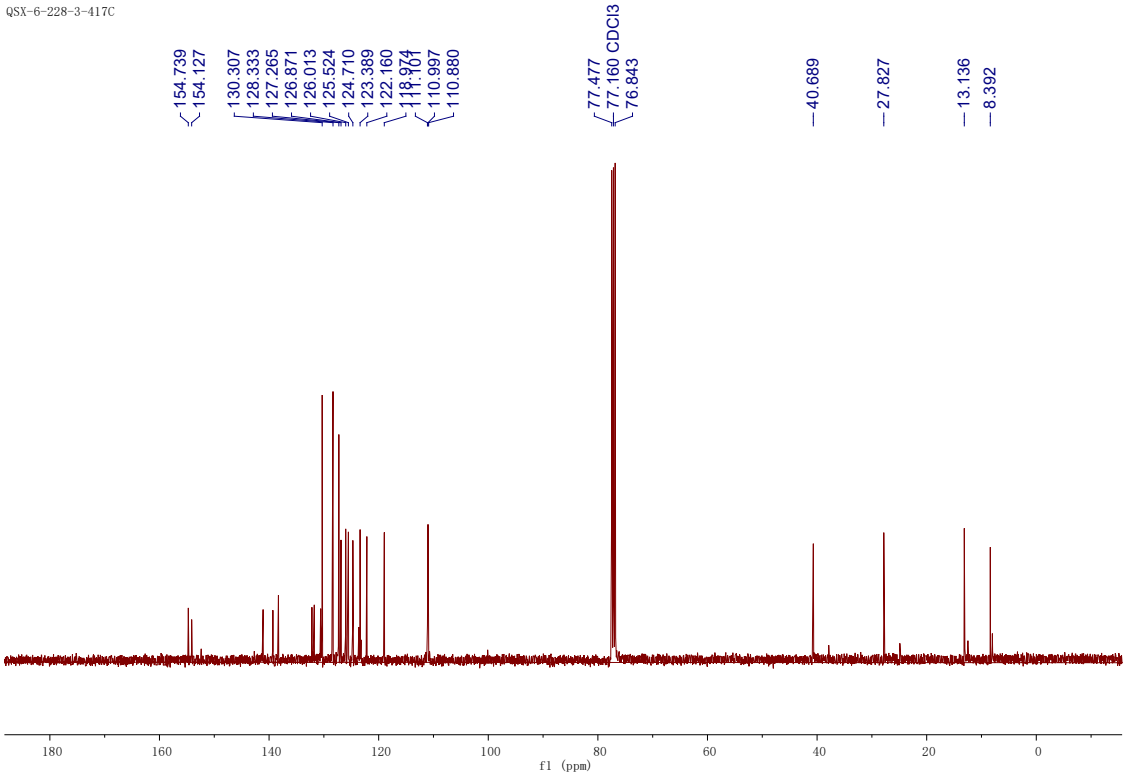
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3q



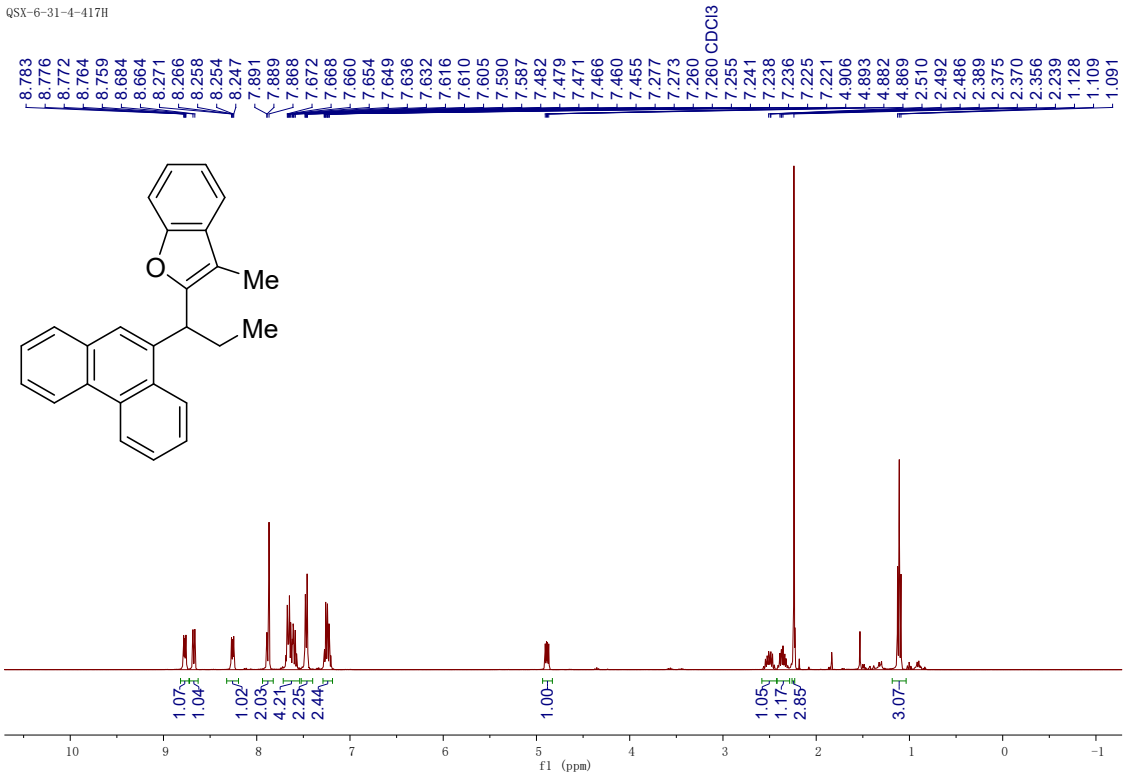
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3r (*see procedure*)



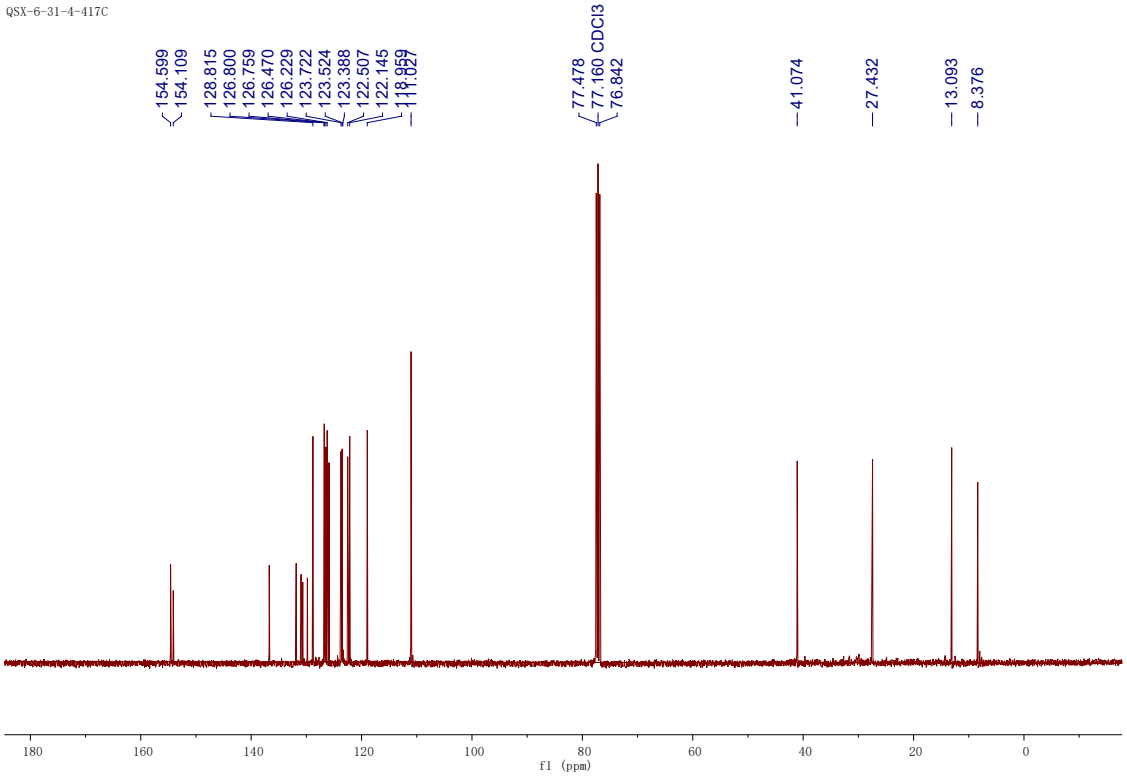
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3r



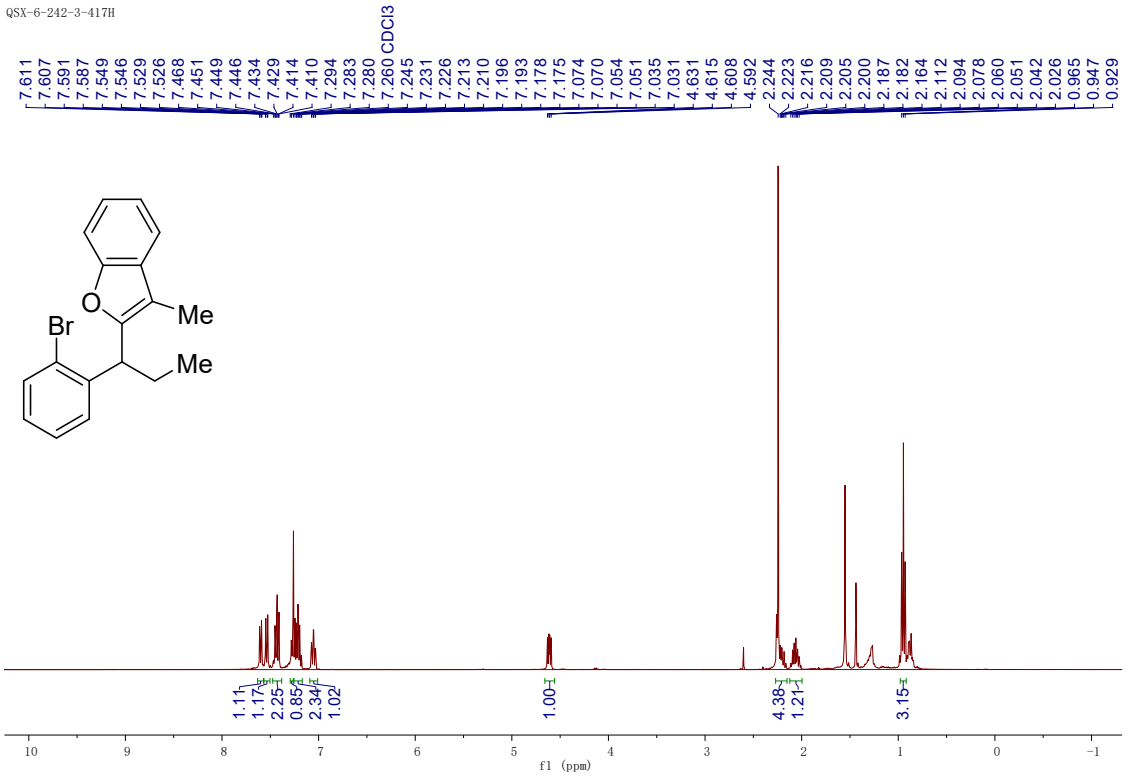
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3s (*see procedure*)



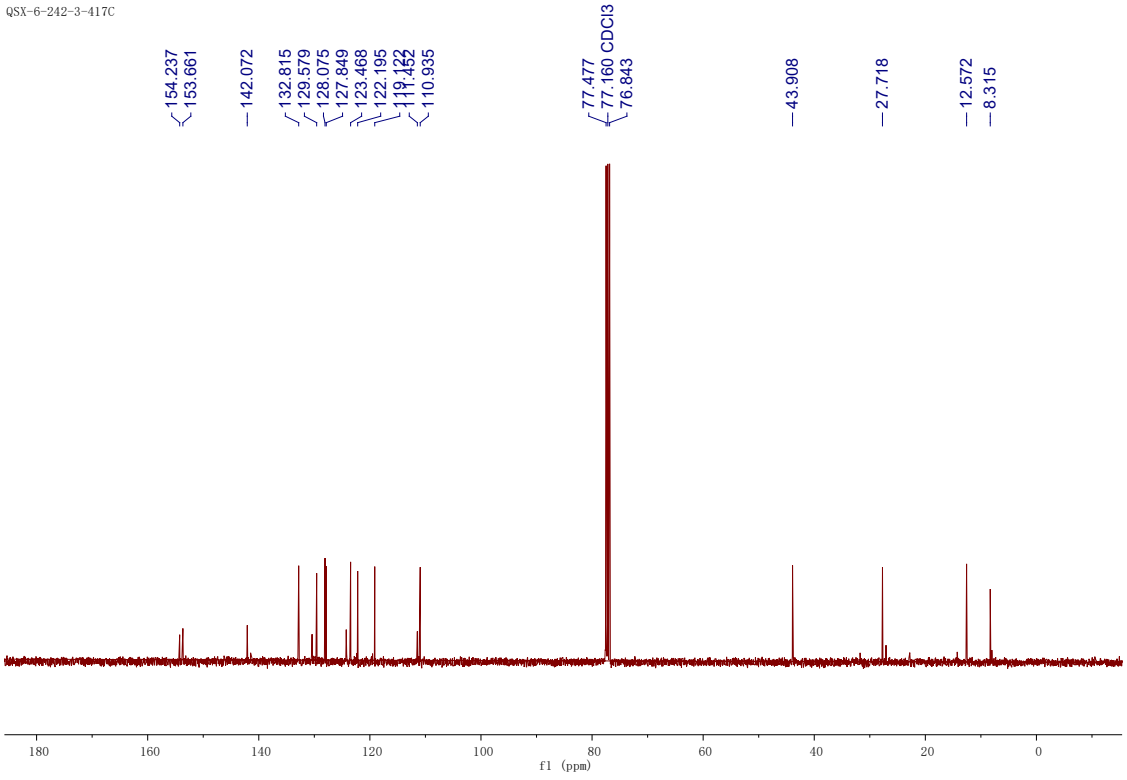
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3s



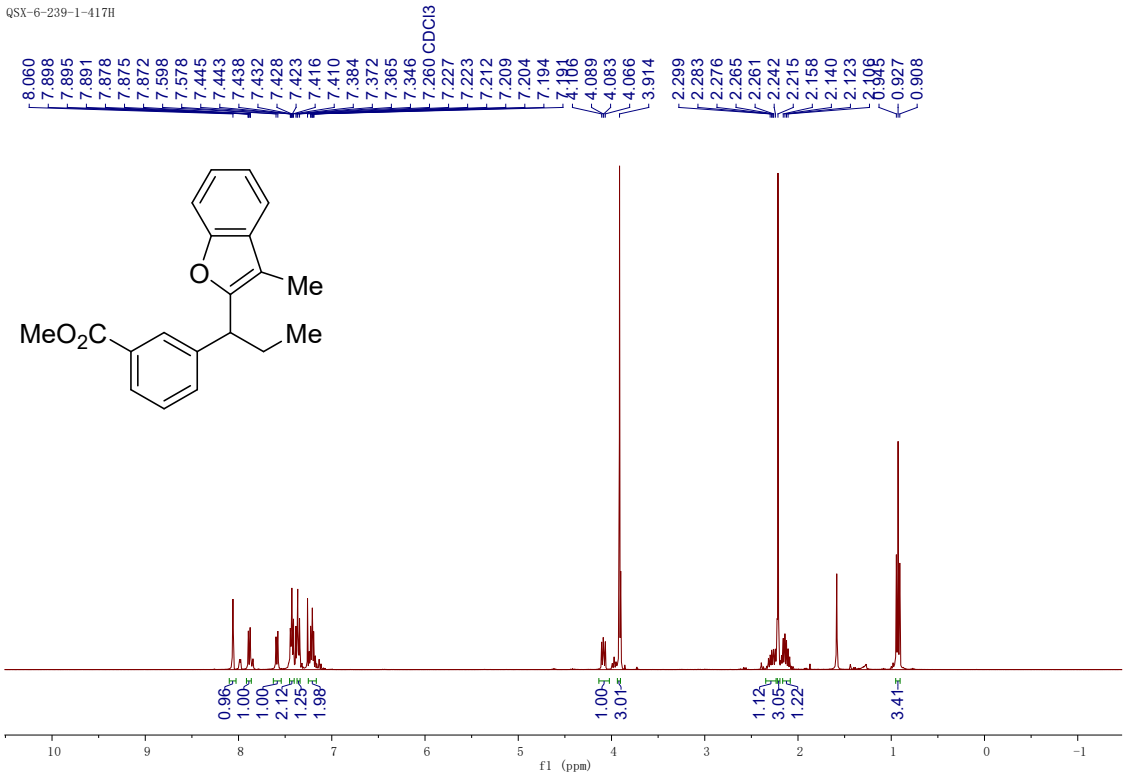
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3t (*see procedure*)



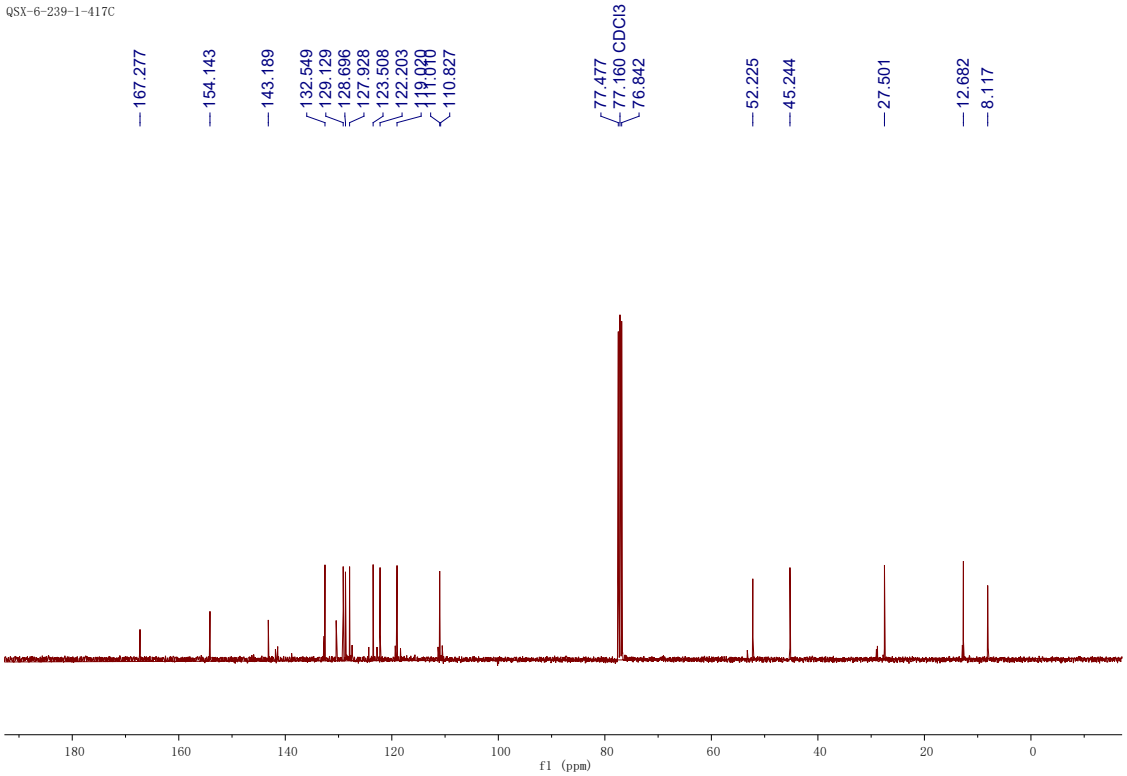
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3t



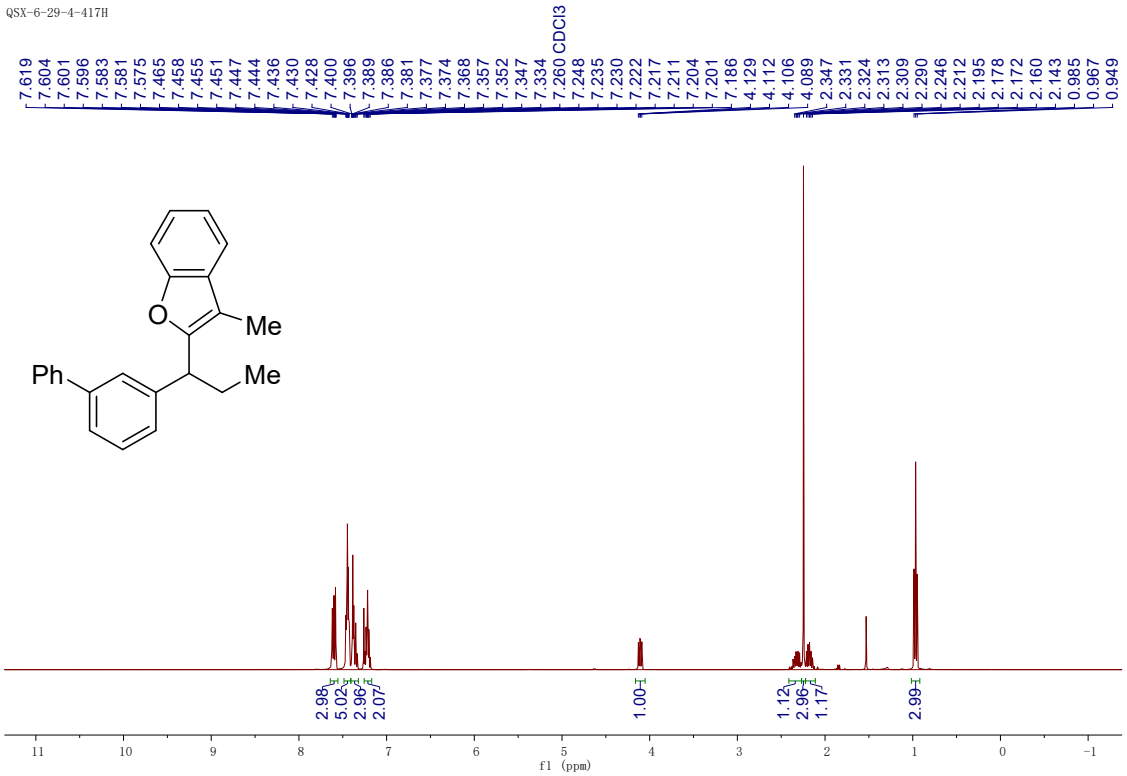
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3u (*see procedure*)



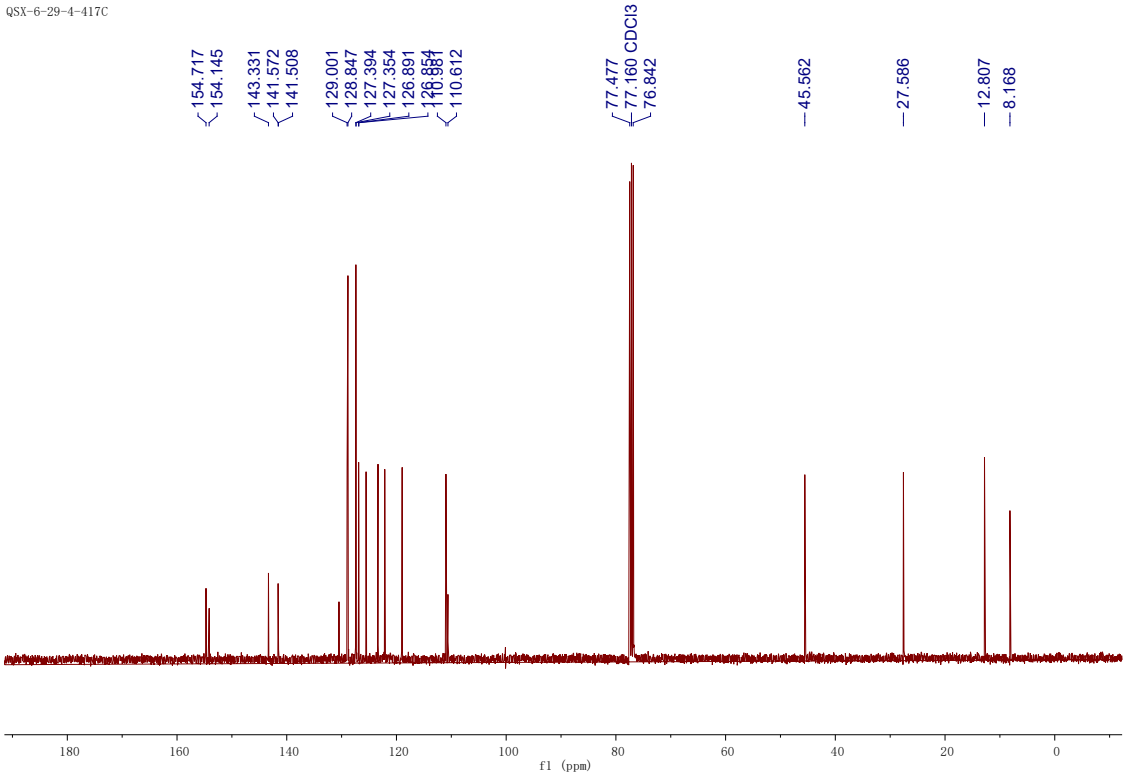
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3u



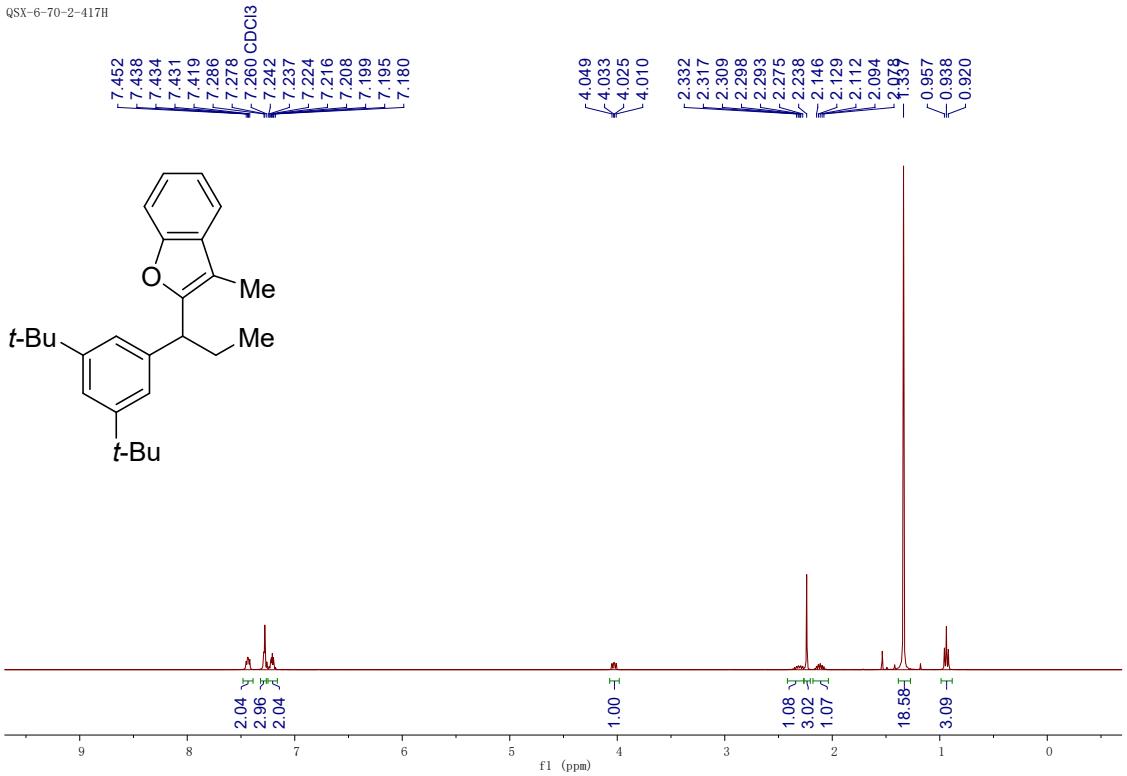
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3v (*see procedure*)



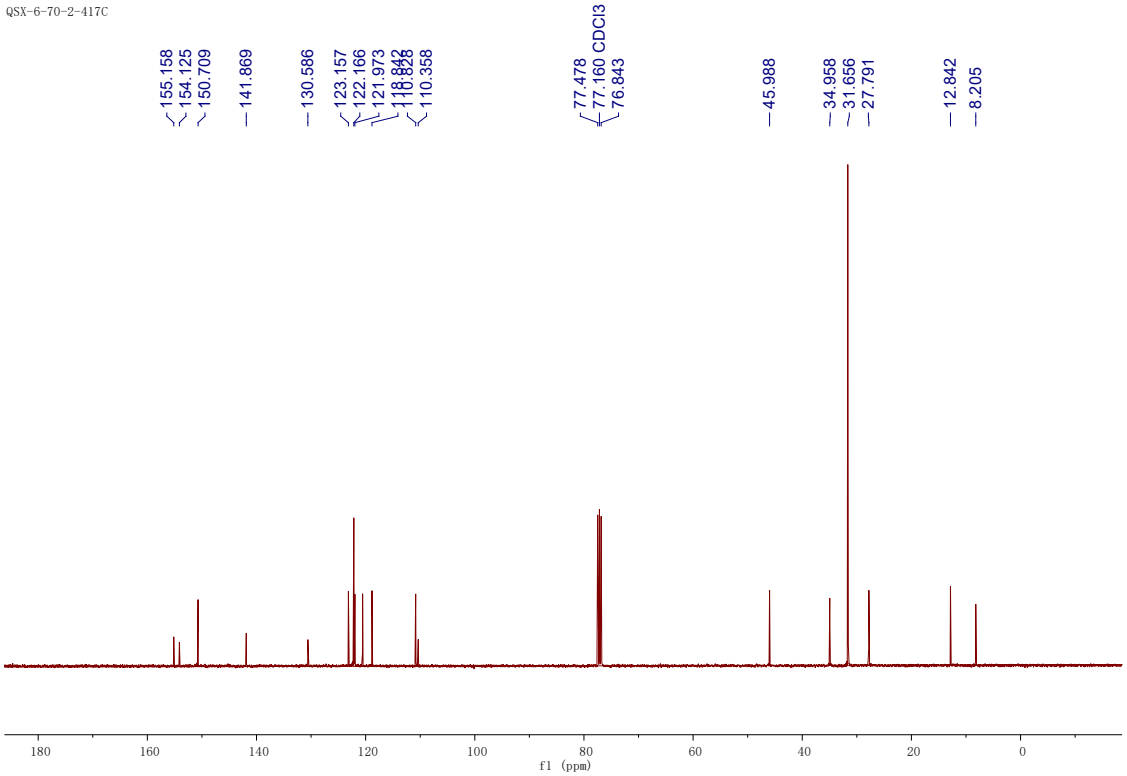
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3v



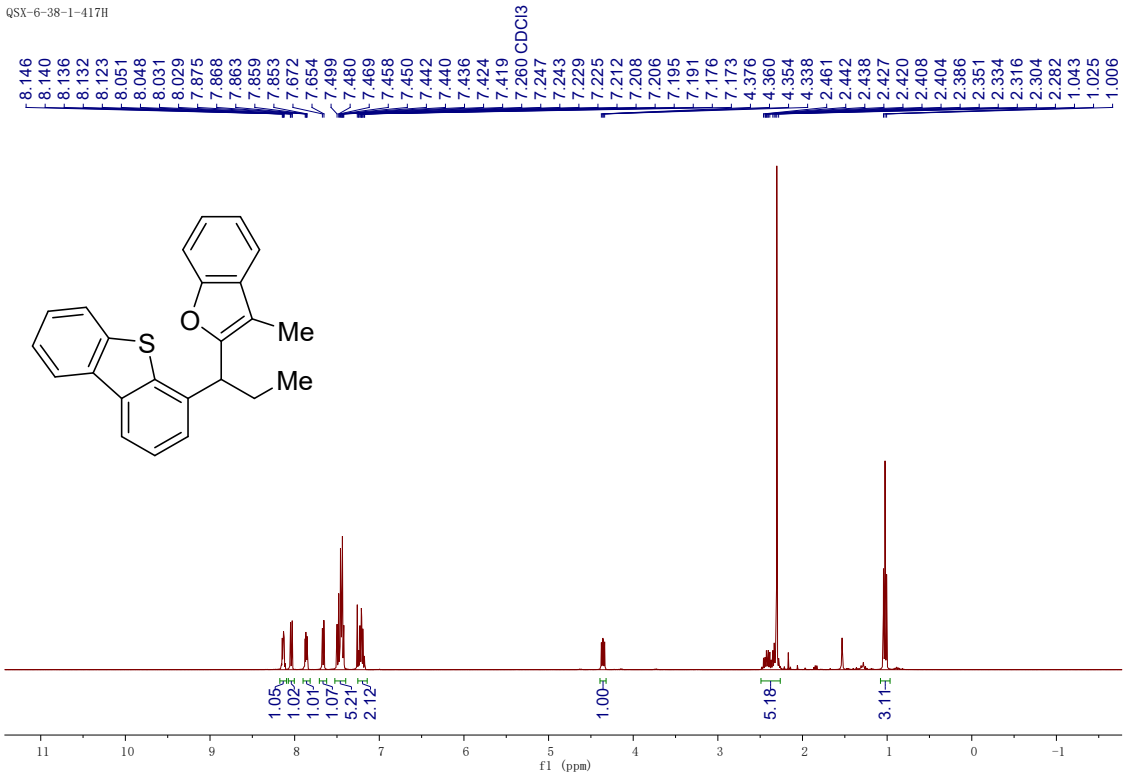
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3w (*see procedure*)



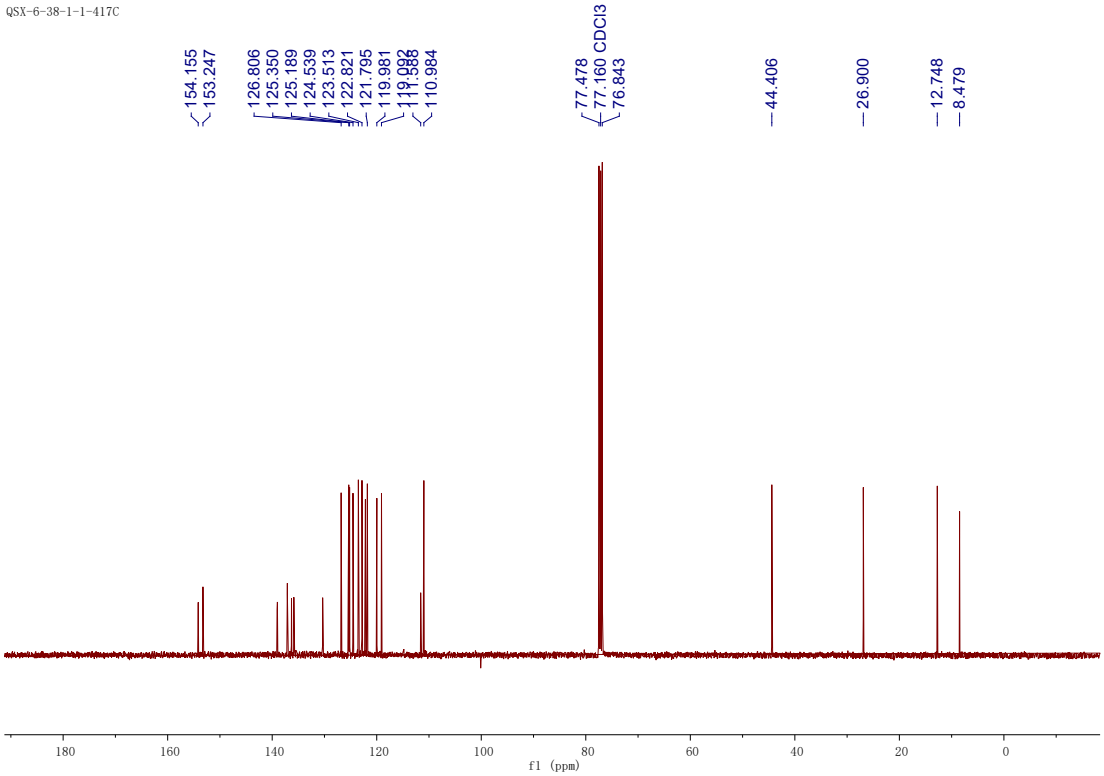
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3w



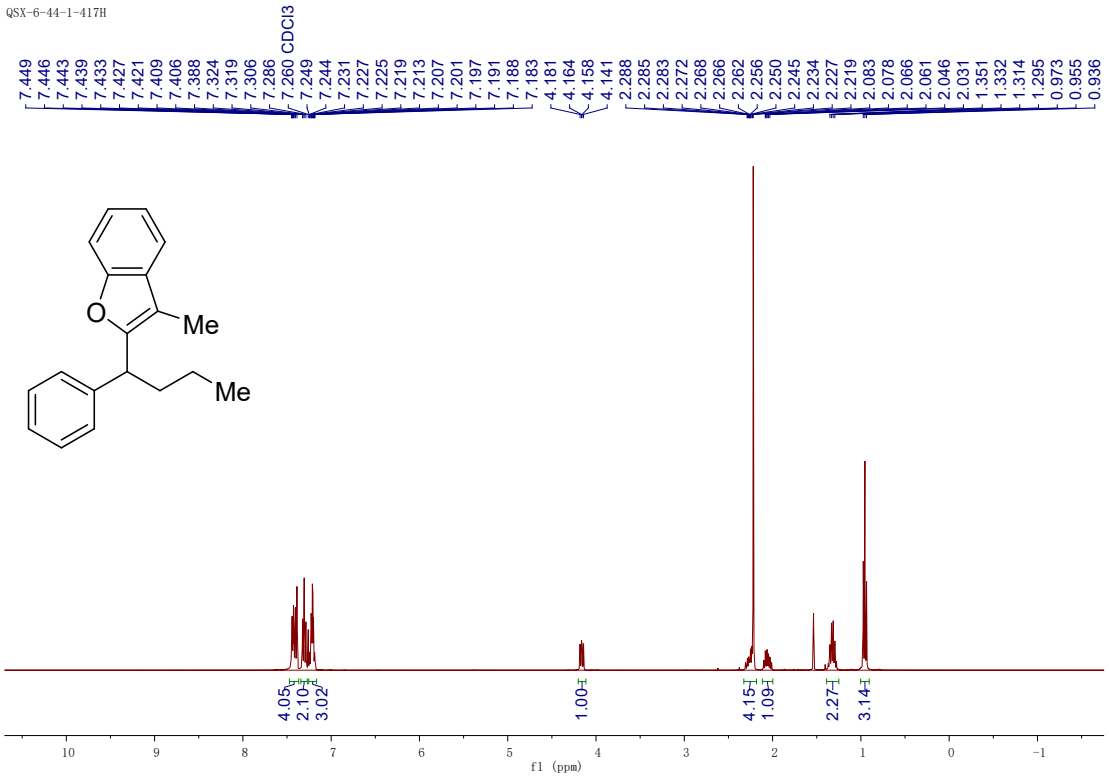
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3x (*see procedure*)



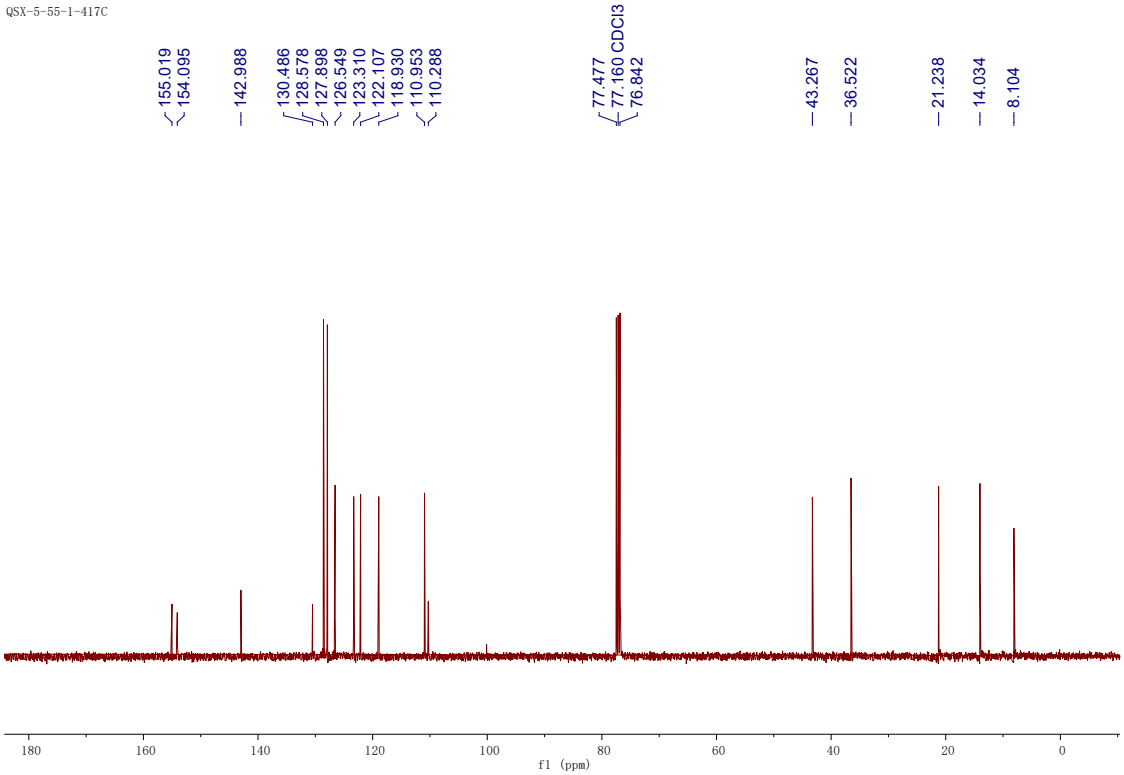
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3x



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3y (*see procedure*)

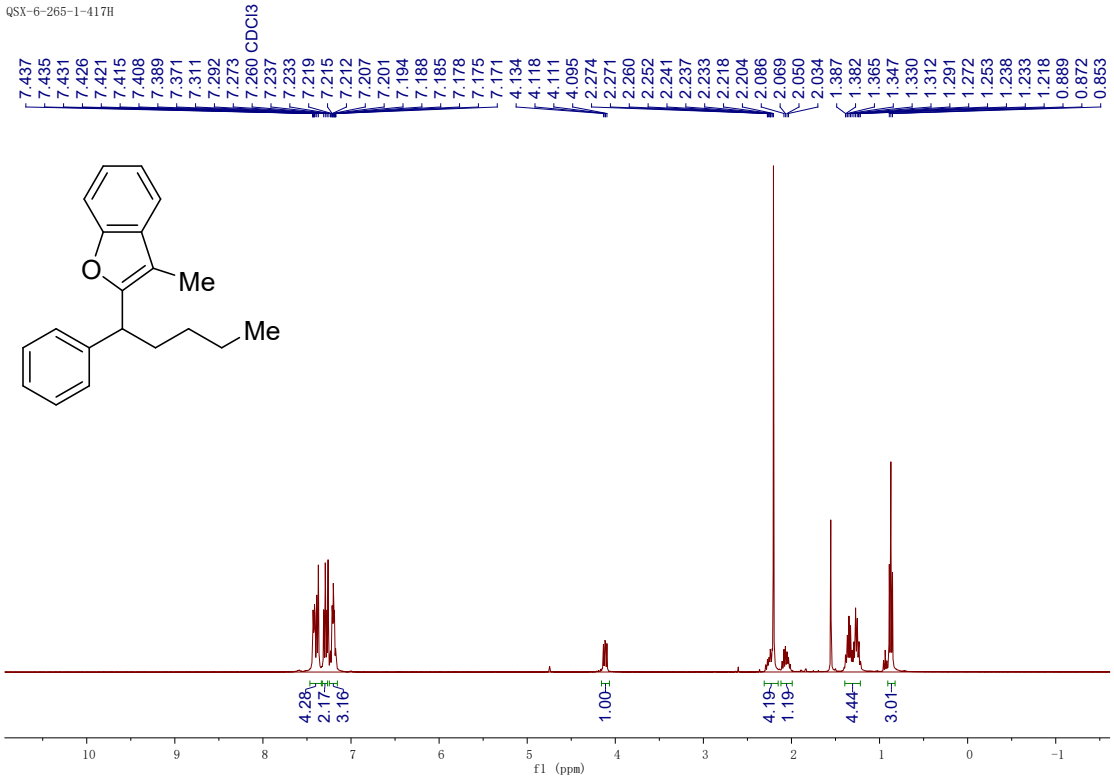


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3y

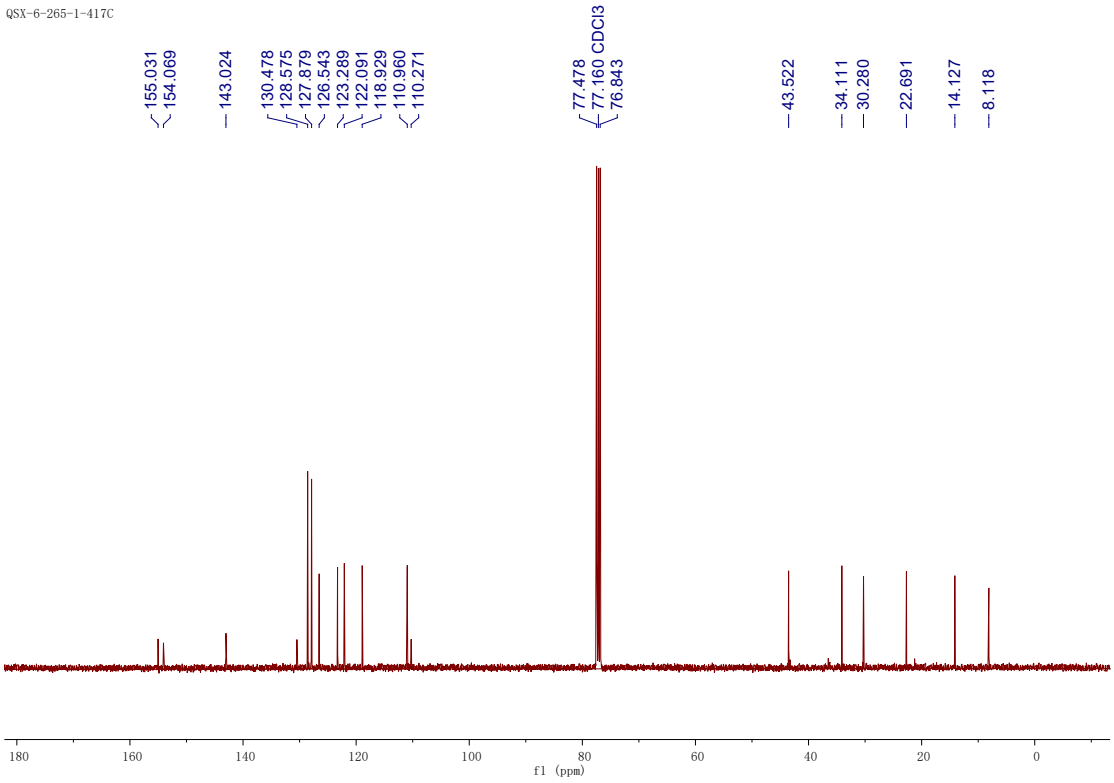


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3z same as above (*see procedure*)

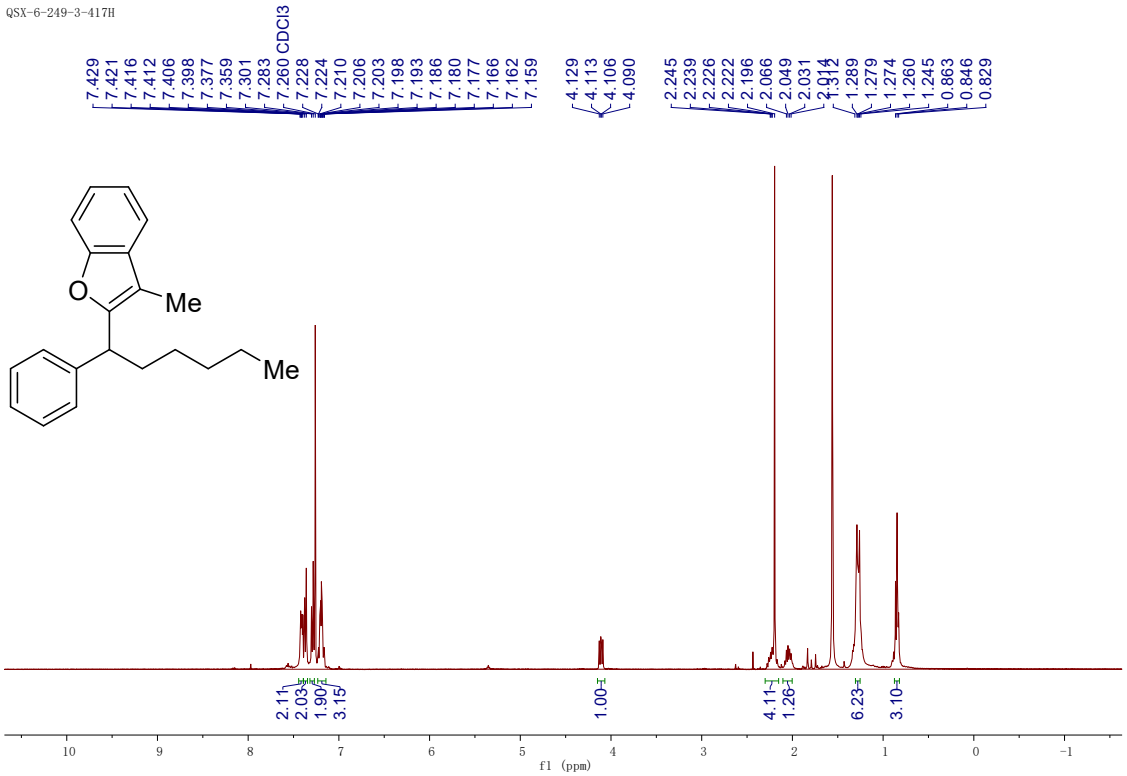
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aa (*see procedure*)



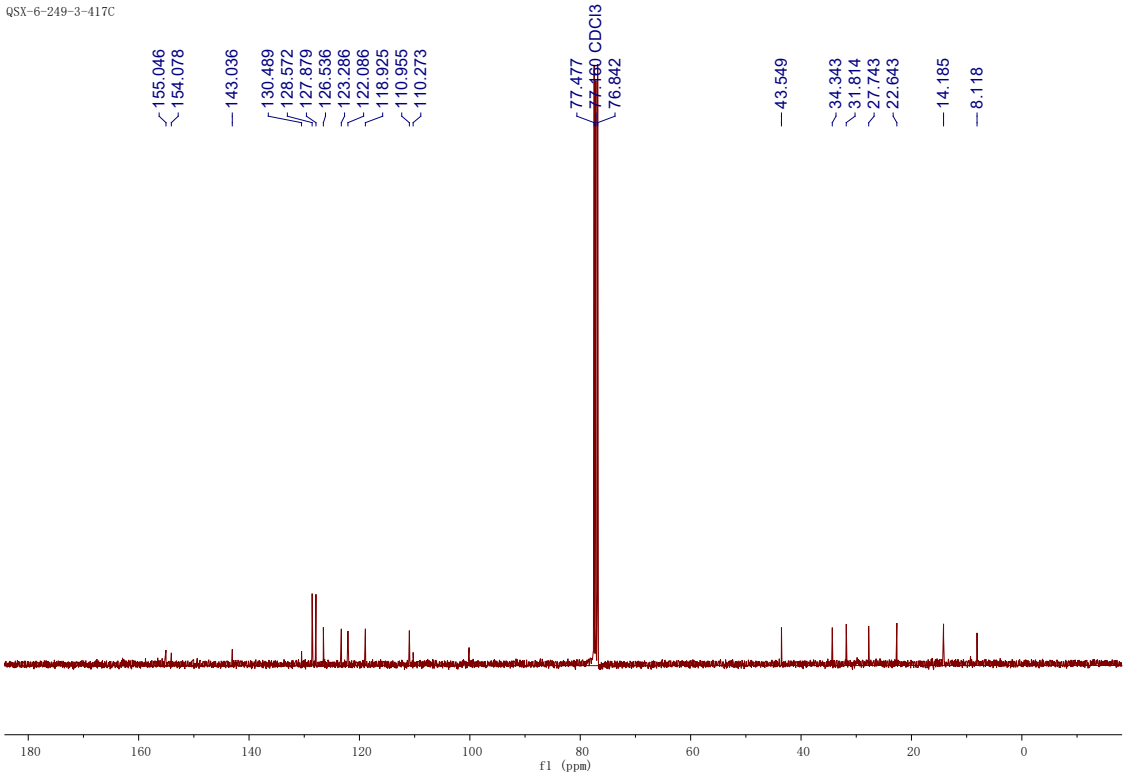
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aa



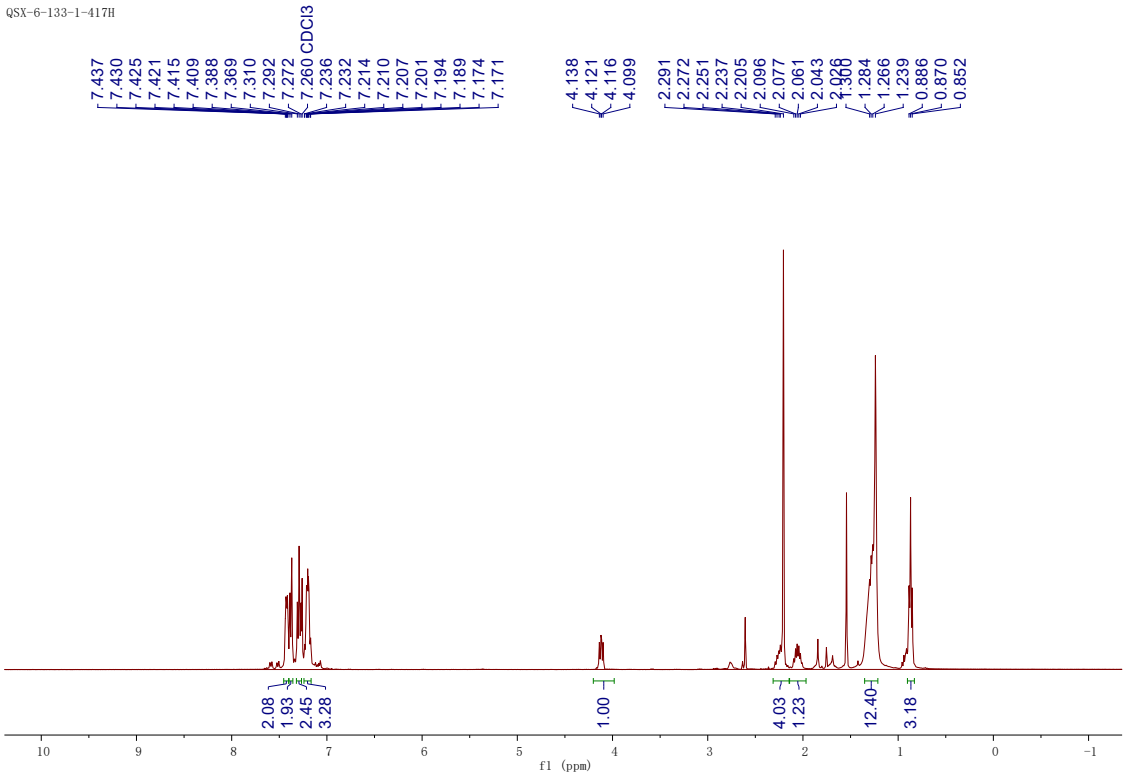
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ab (*see procedure*)



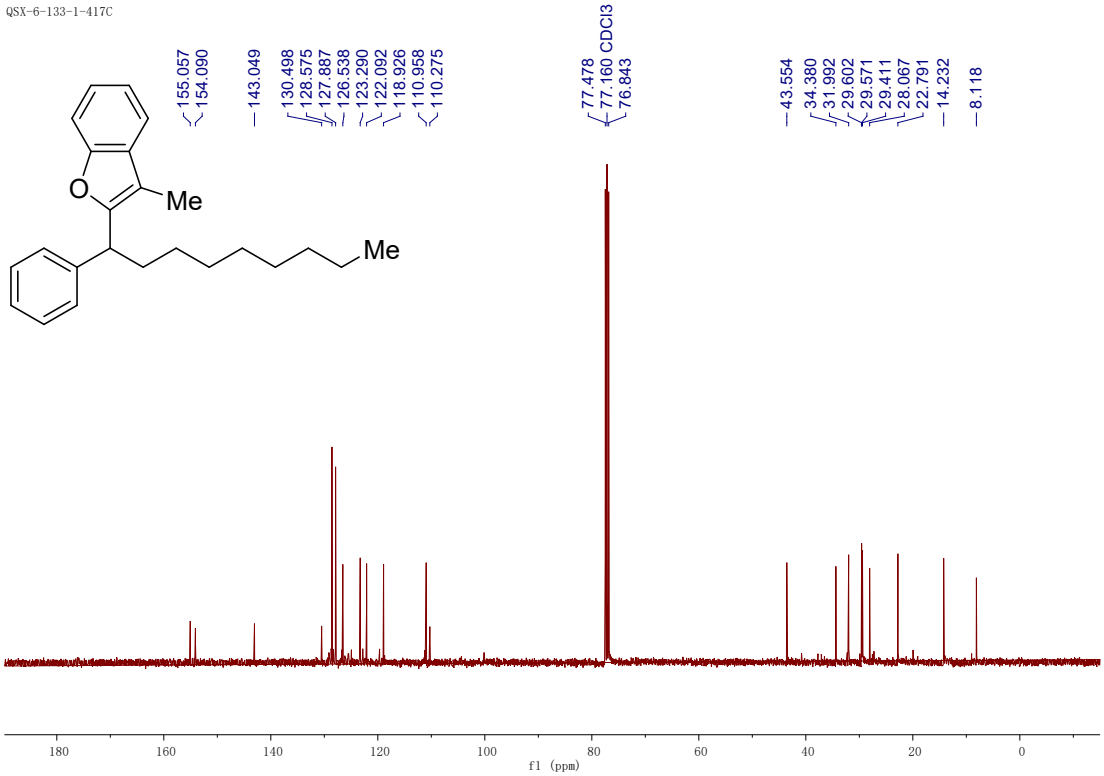
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ab



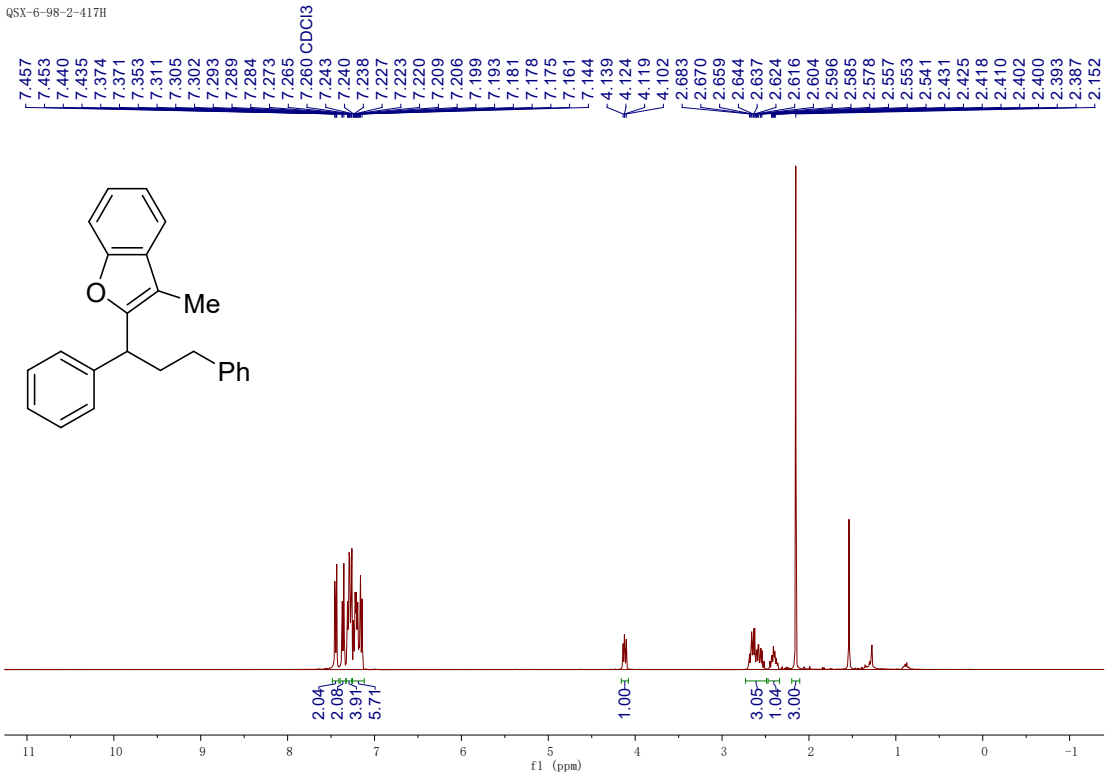
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ac (*see procedure*)



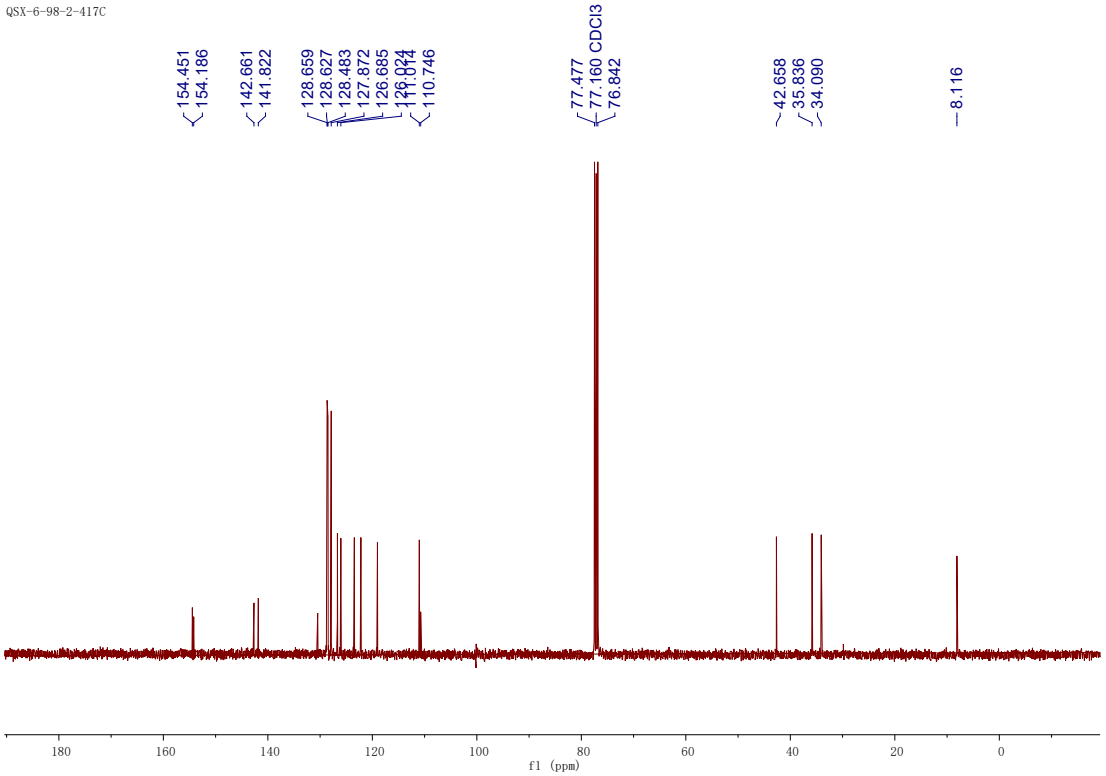
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ac



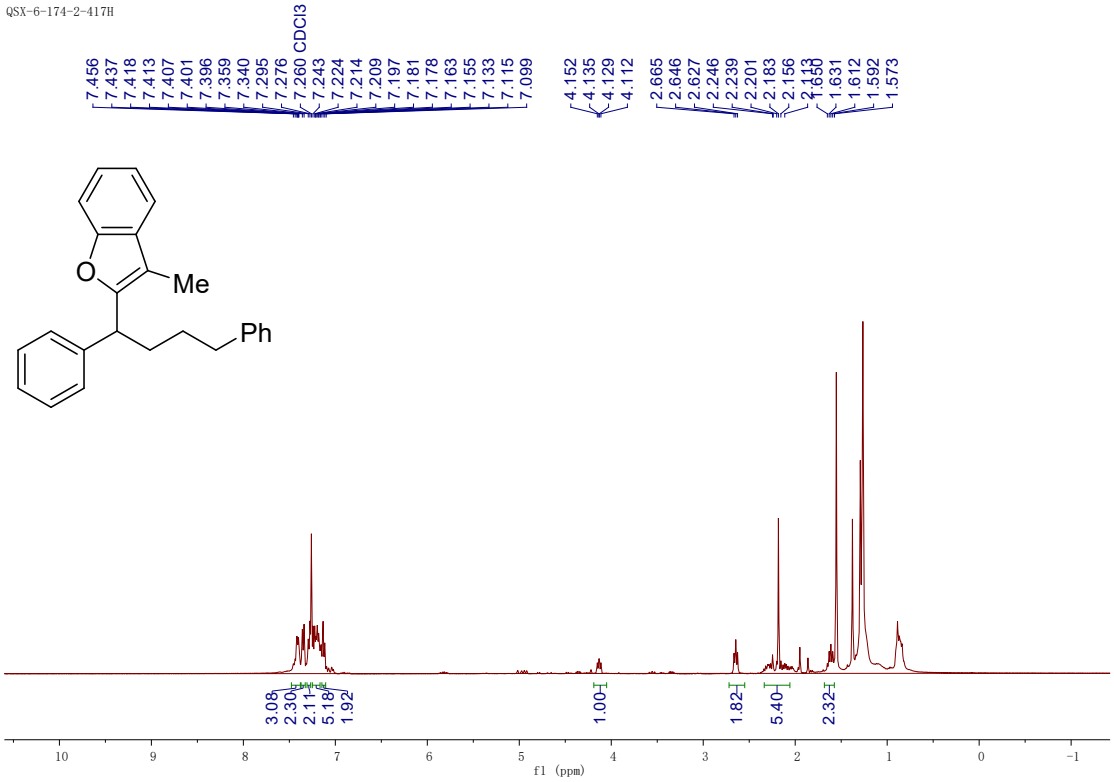
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ad (*see procedure*)



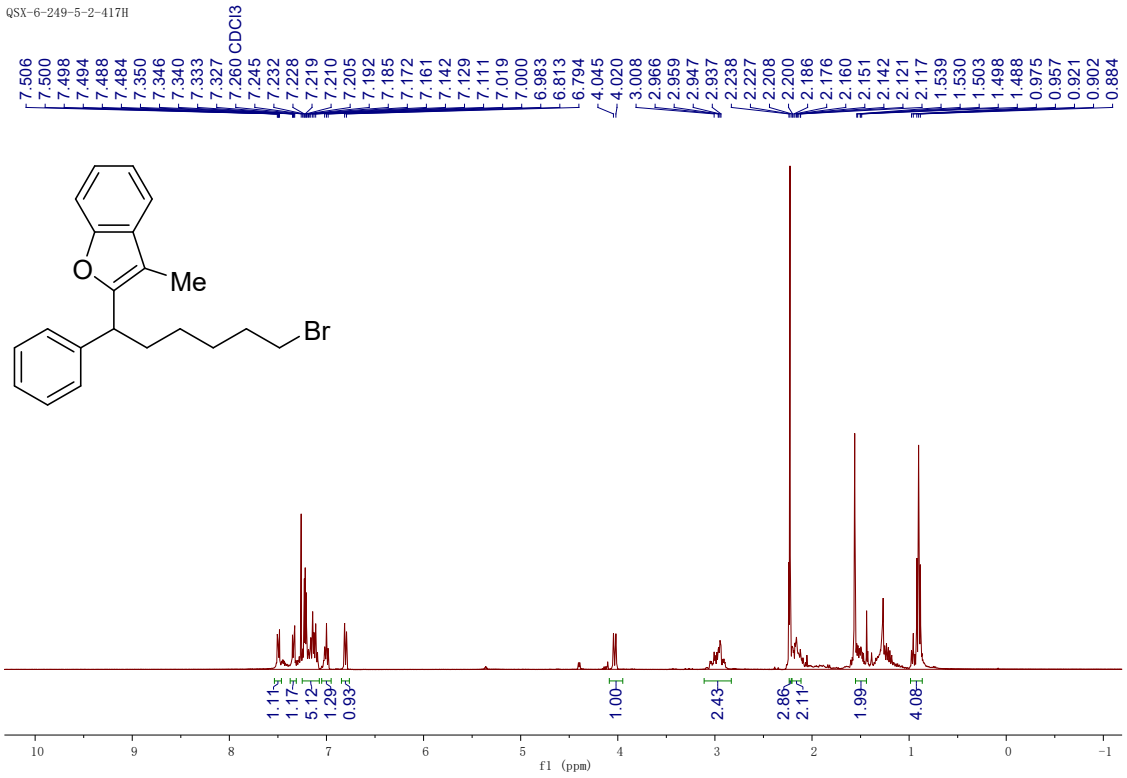
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ad



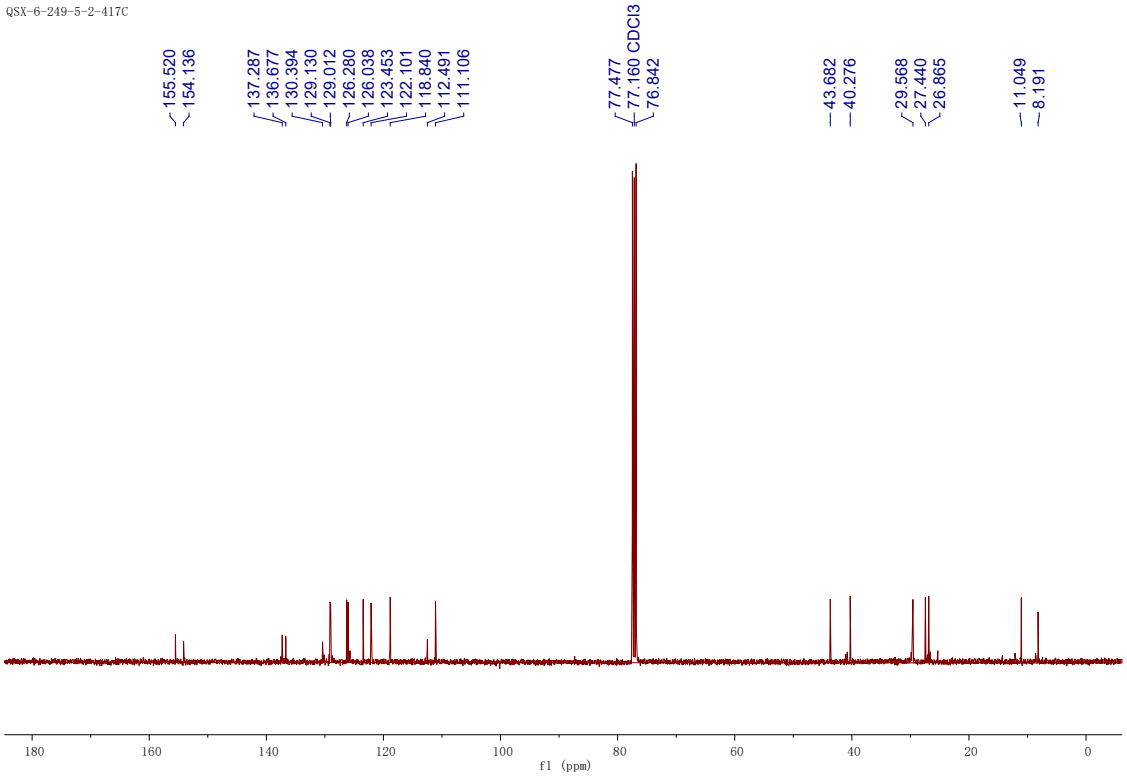
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ae (*see procedure*)



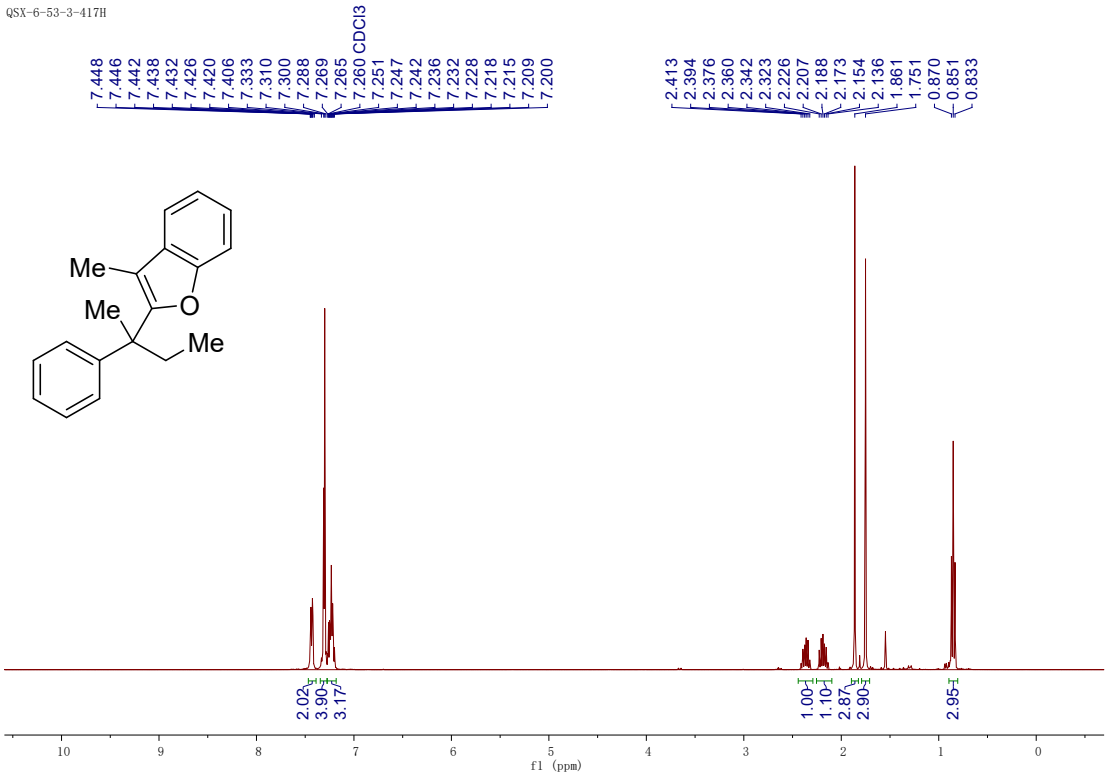
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3af (*see procedure*)



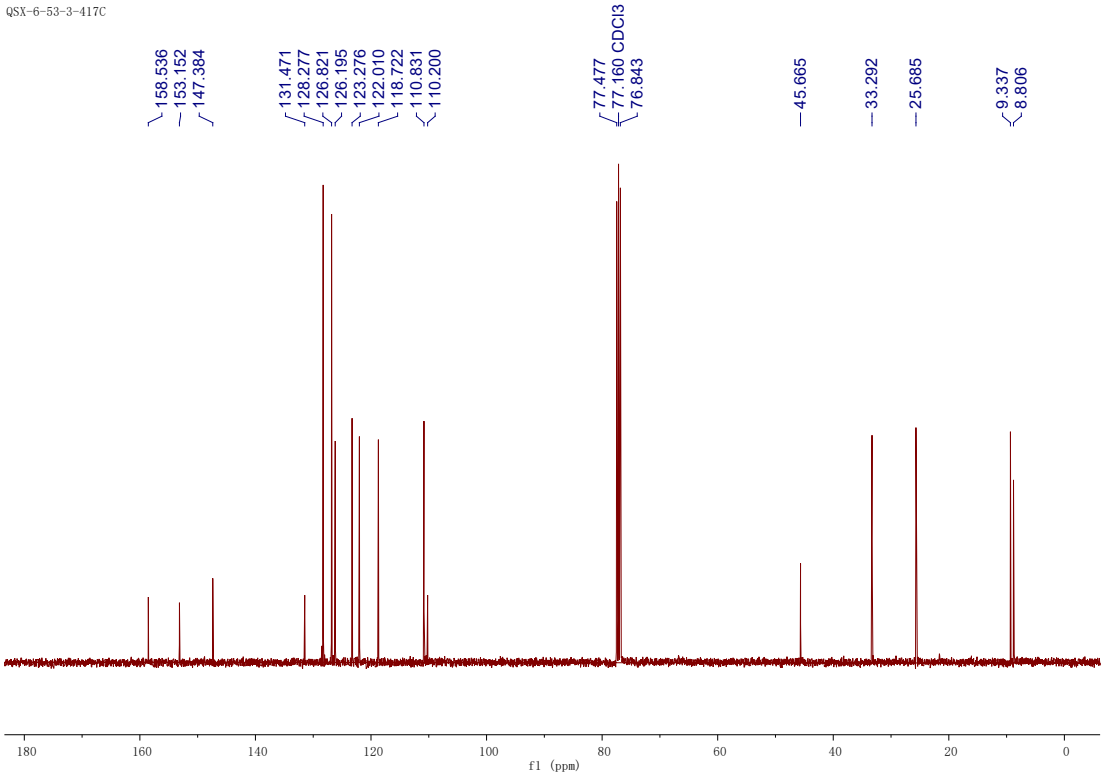
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3af



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ah (*see procedure*)

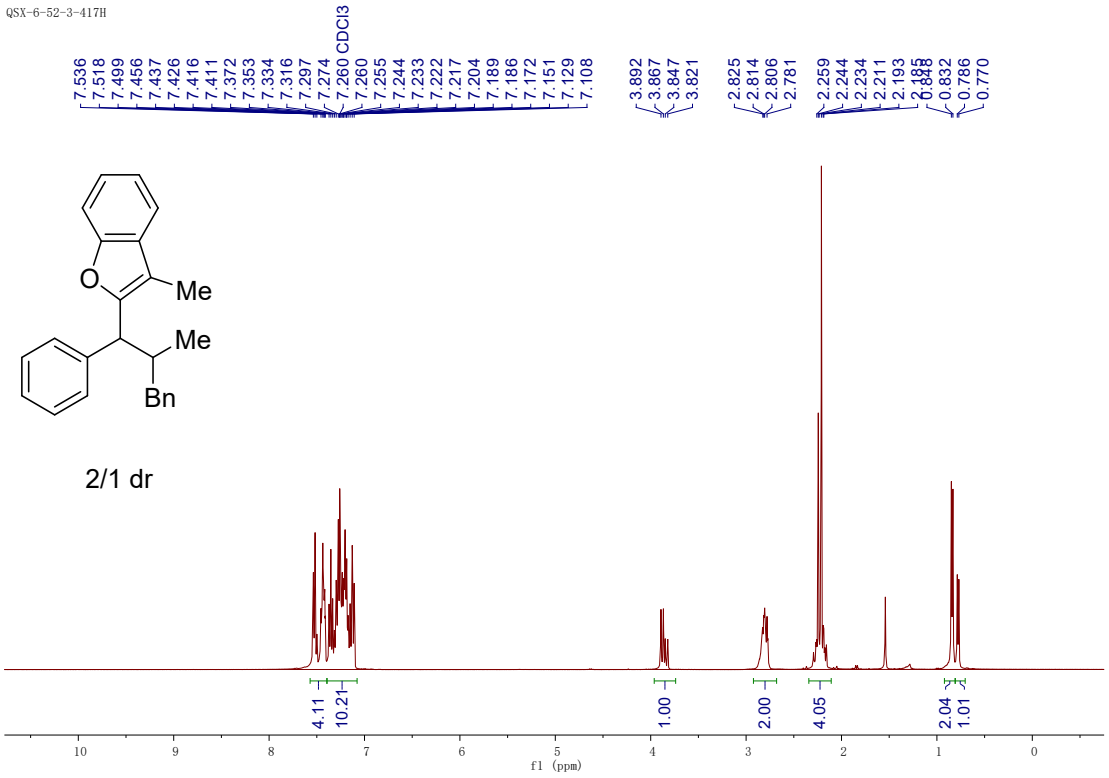


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ah

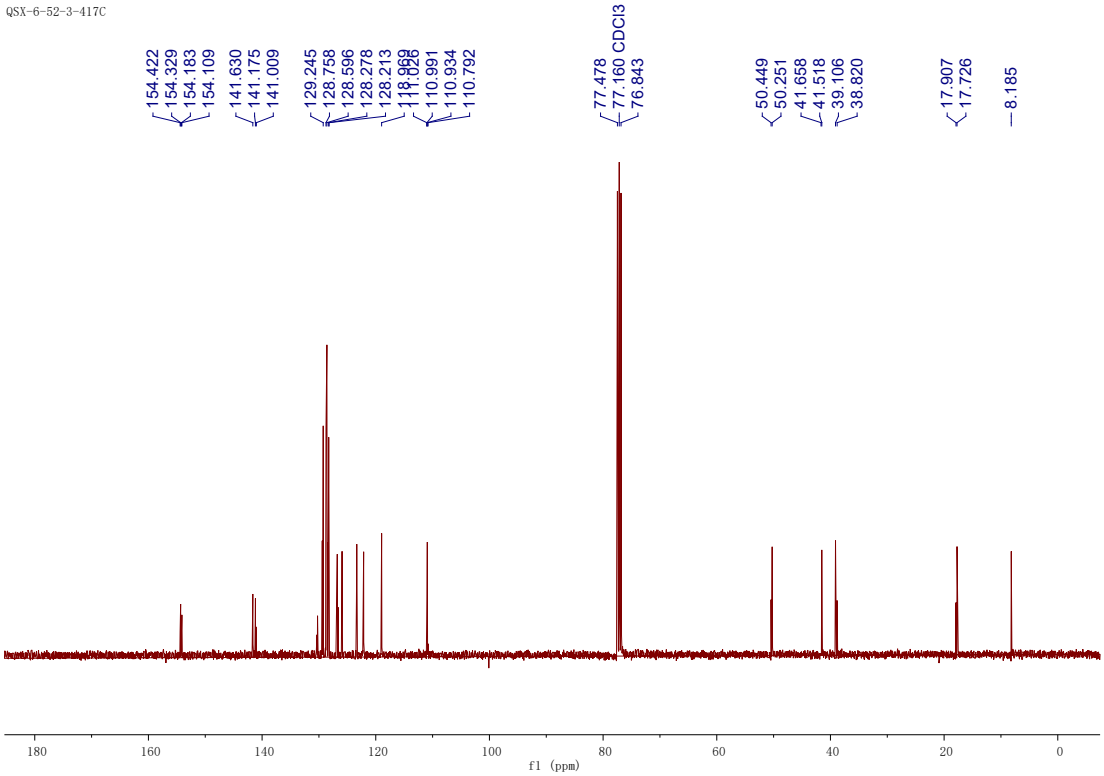


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ag same as above (*see procedure*)

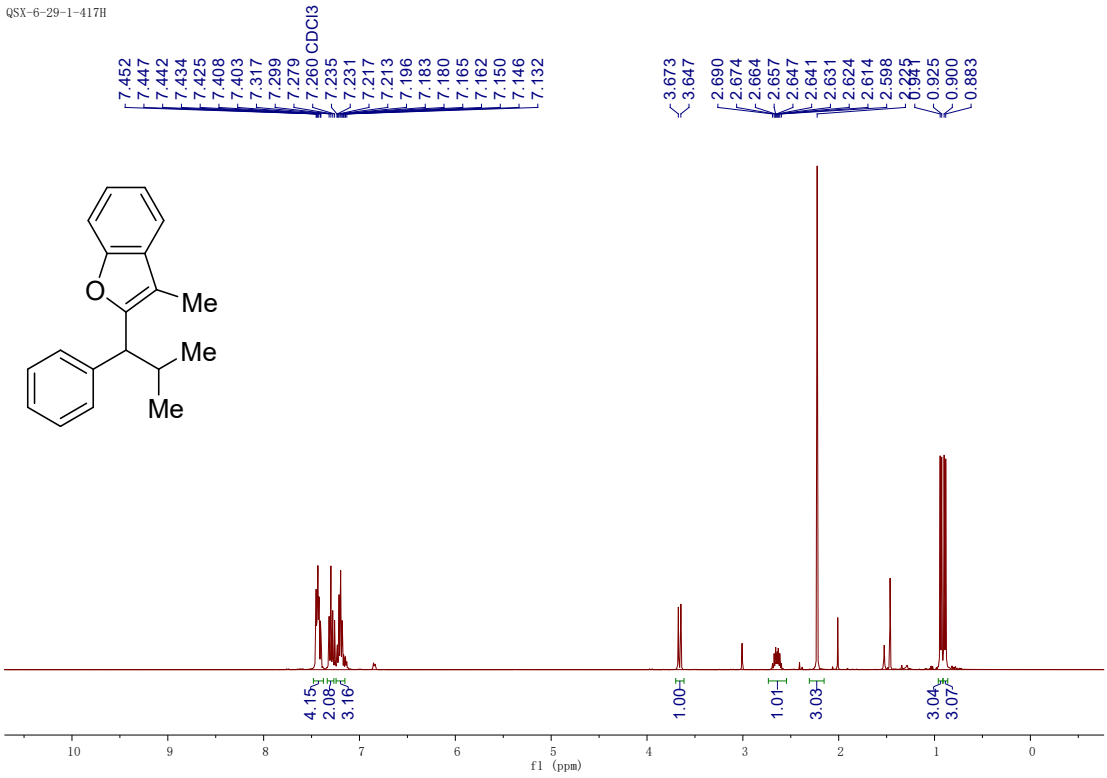
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ai (*see procedure*)



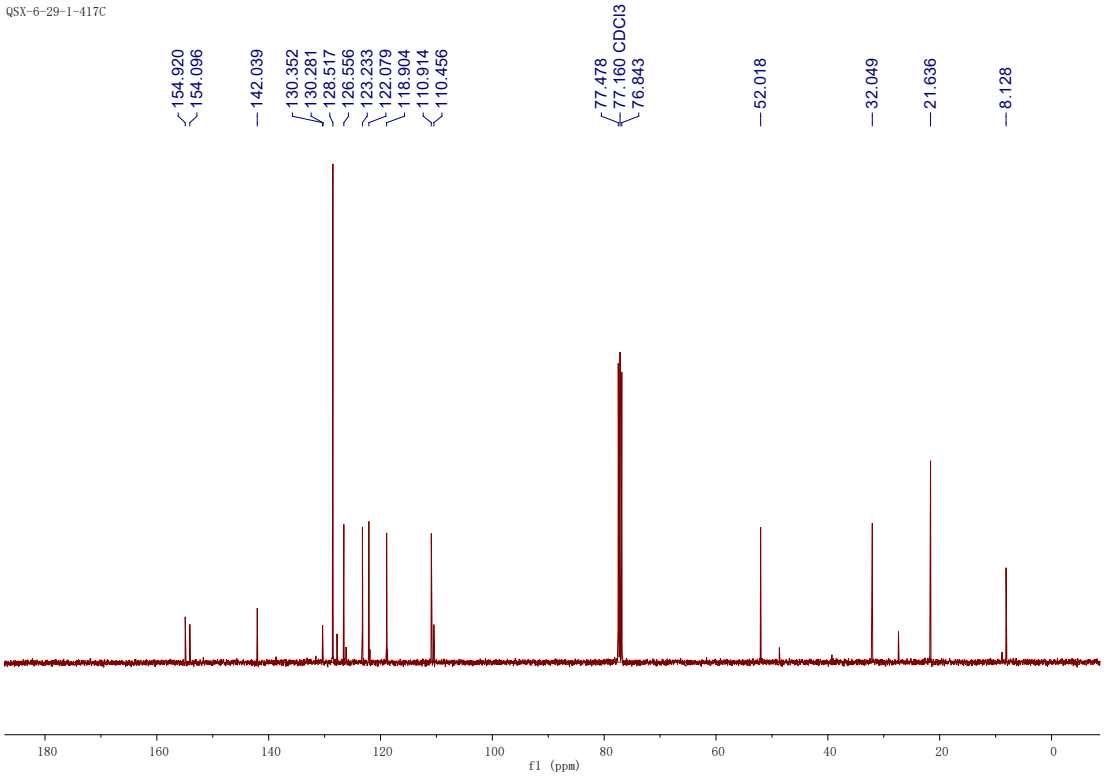
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ai



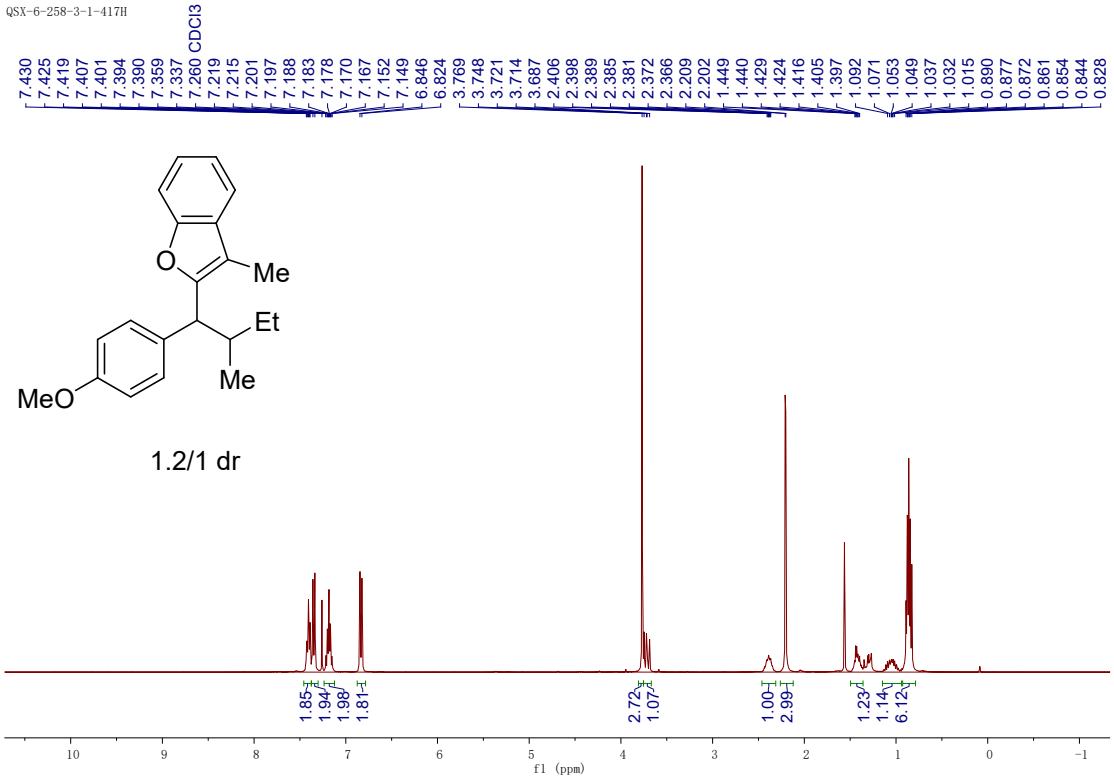
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aj (*see procedure*)



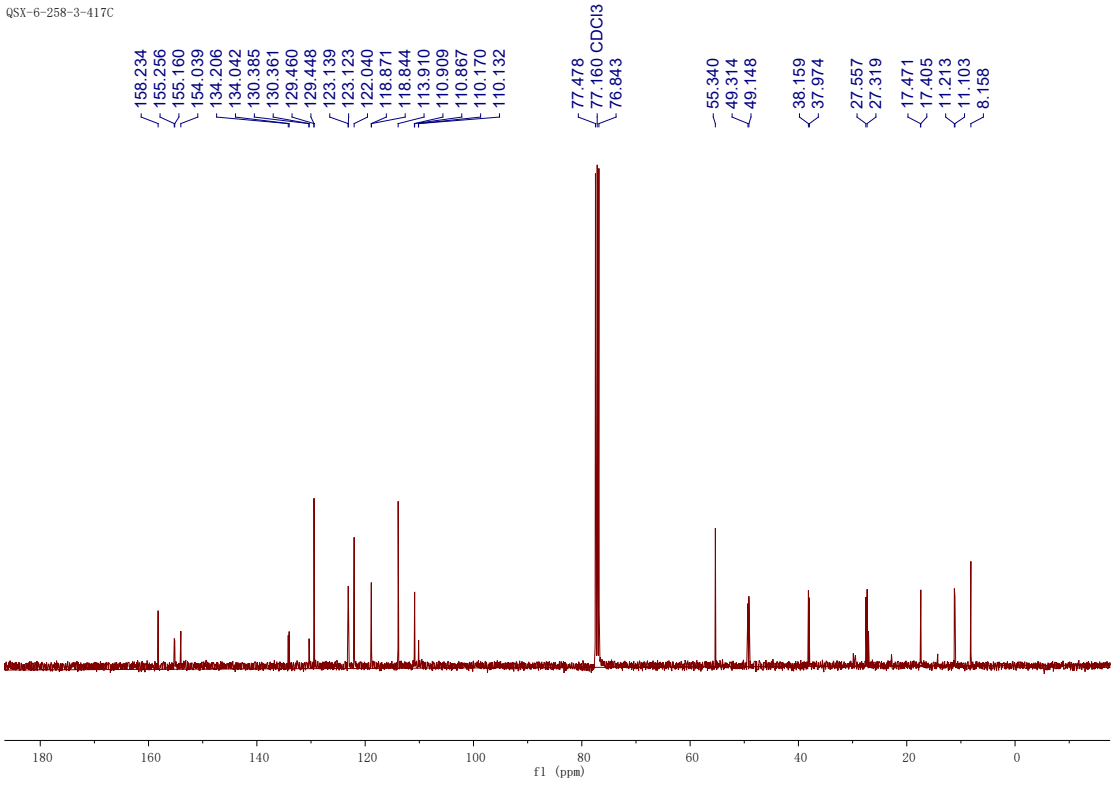
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aj



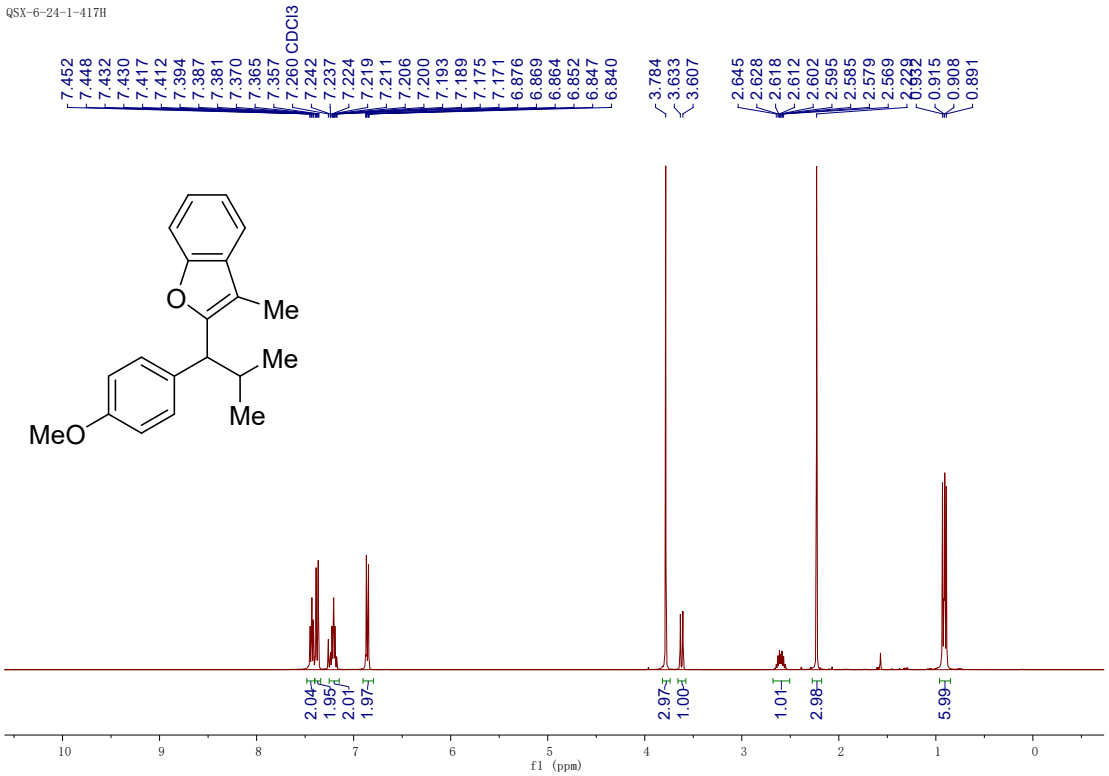
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ak (*see procedure*)



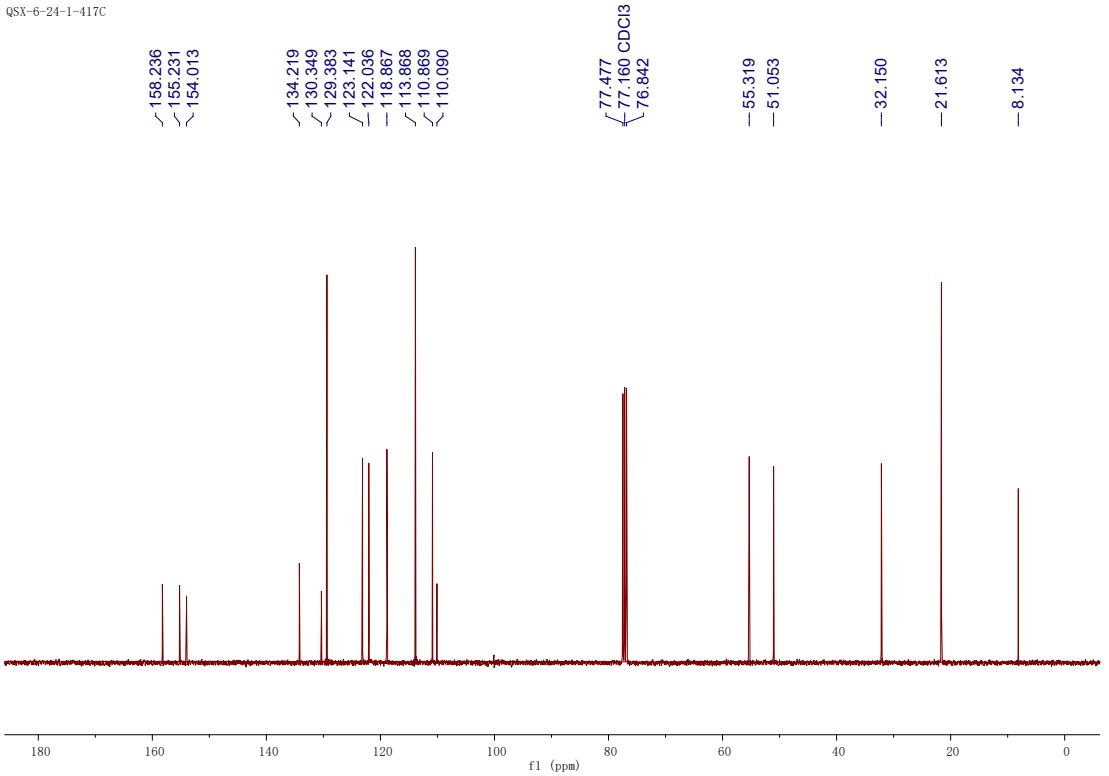
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ak



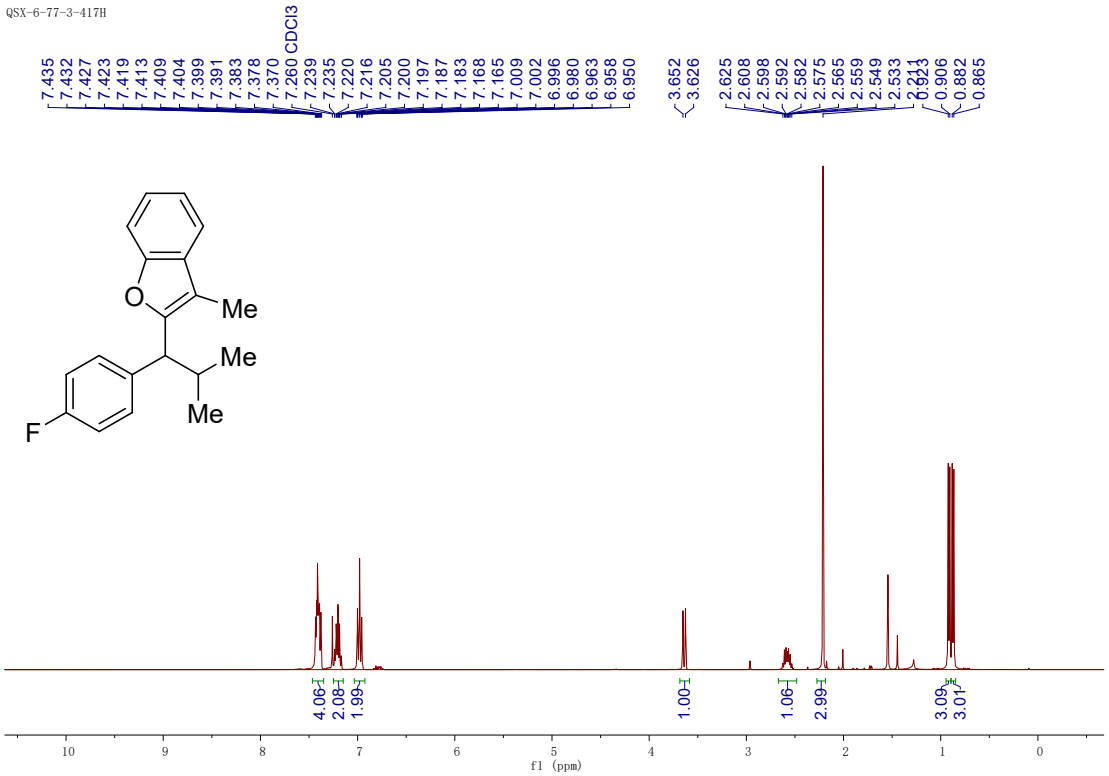
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3al (*see procedure*)



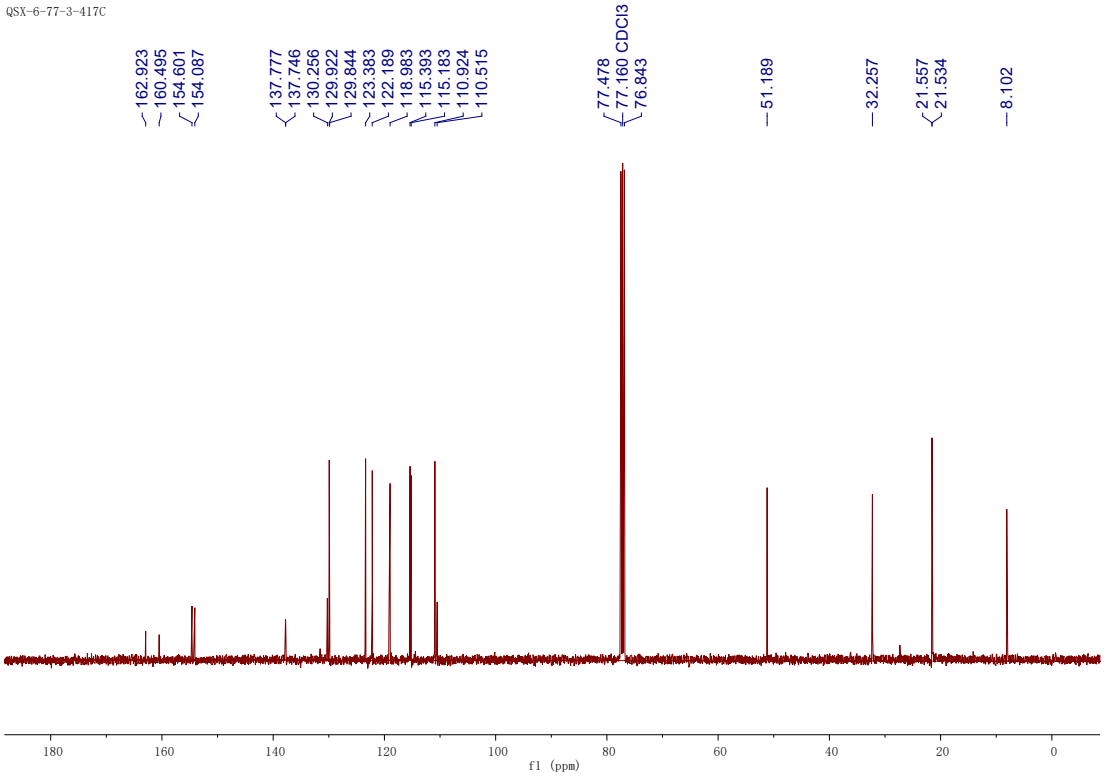
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3al



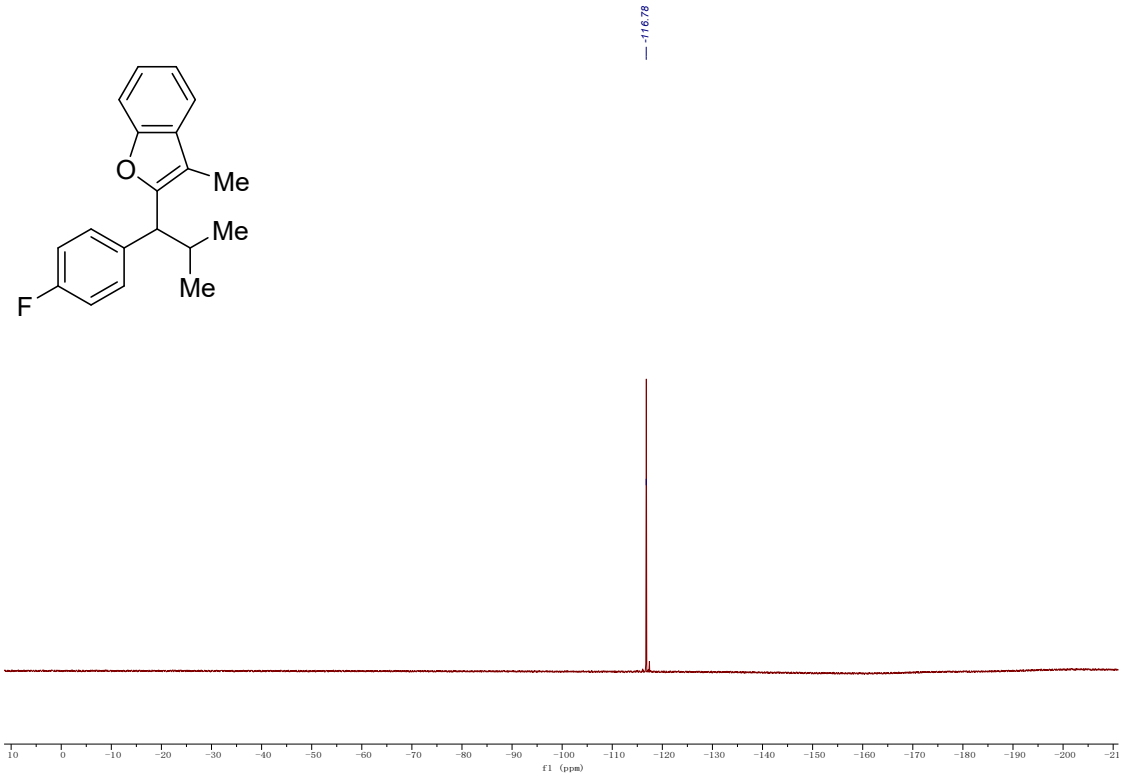
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3am (*see procedure*)



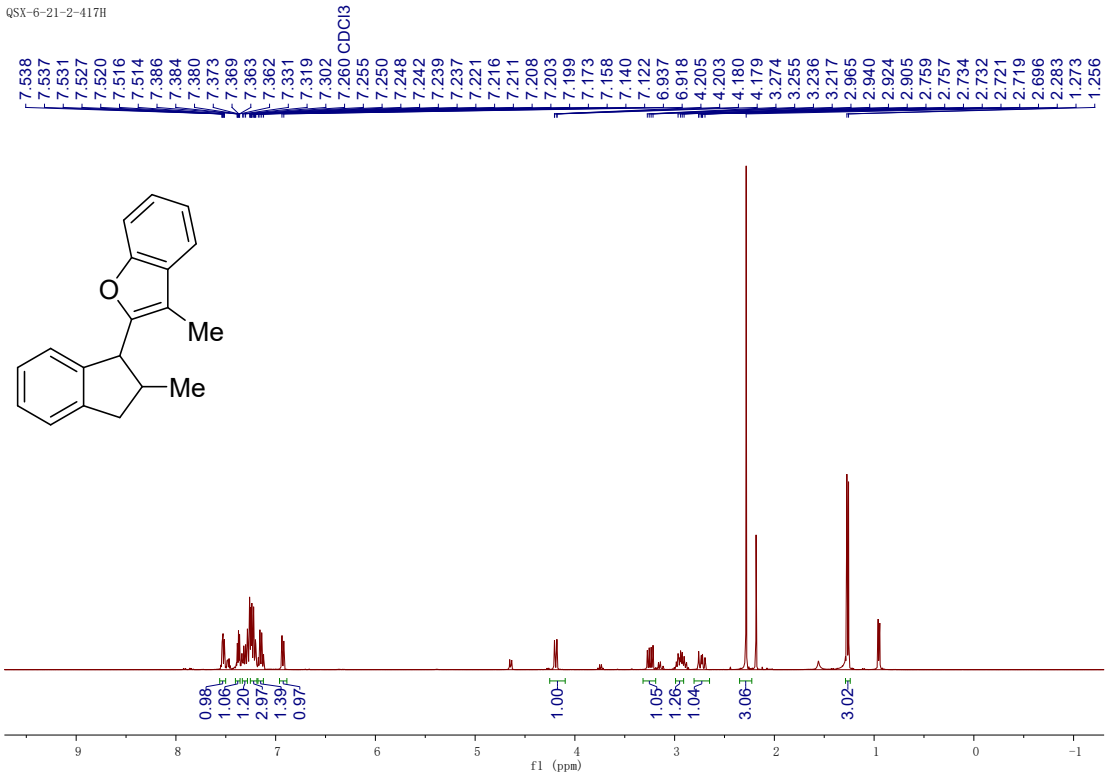
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3am



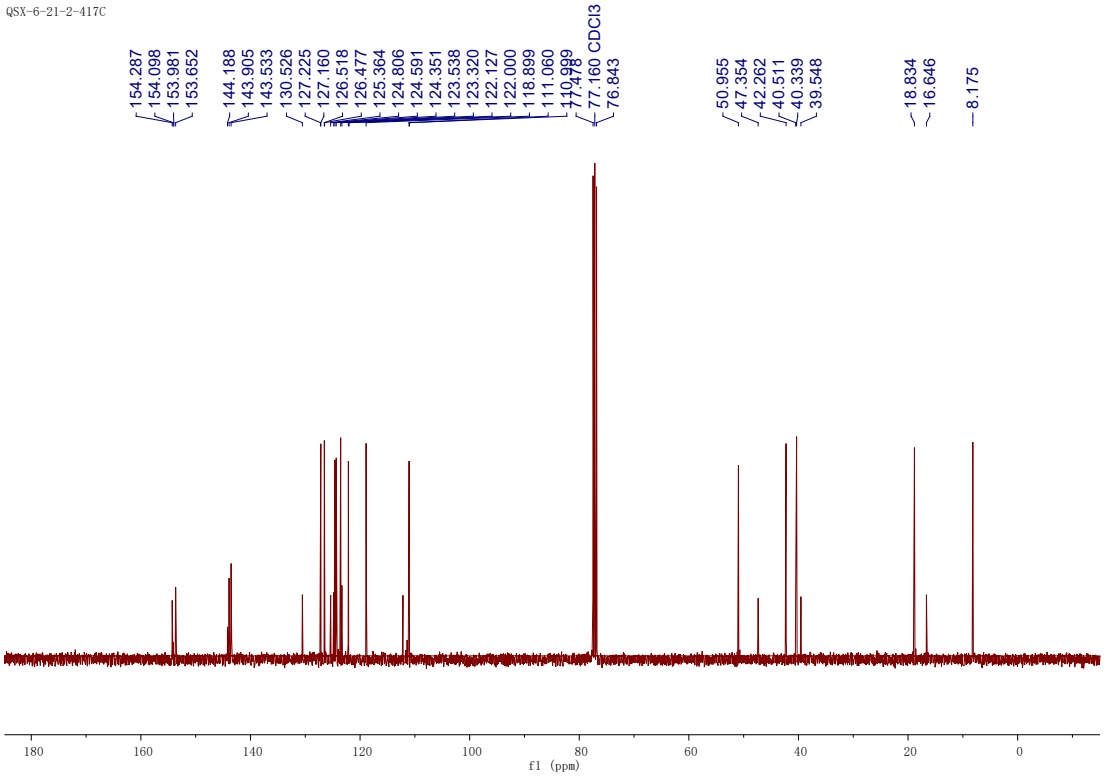
^{19}F NMR (177 MHz, $CDCl_3$) spectrum of 3am



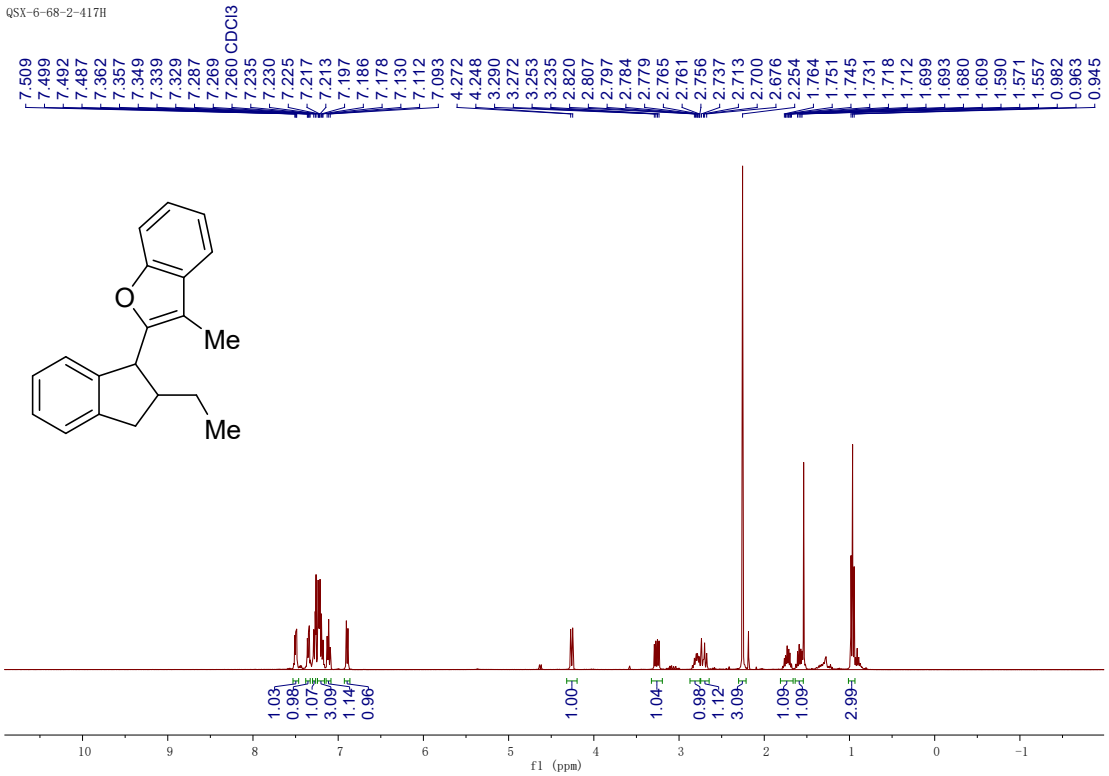
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3an (*see procedure*)



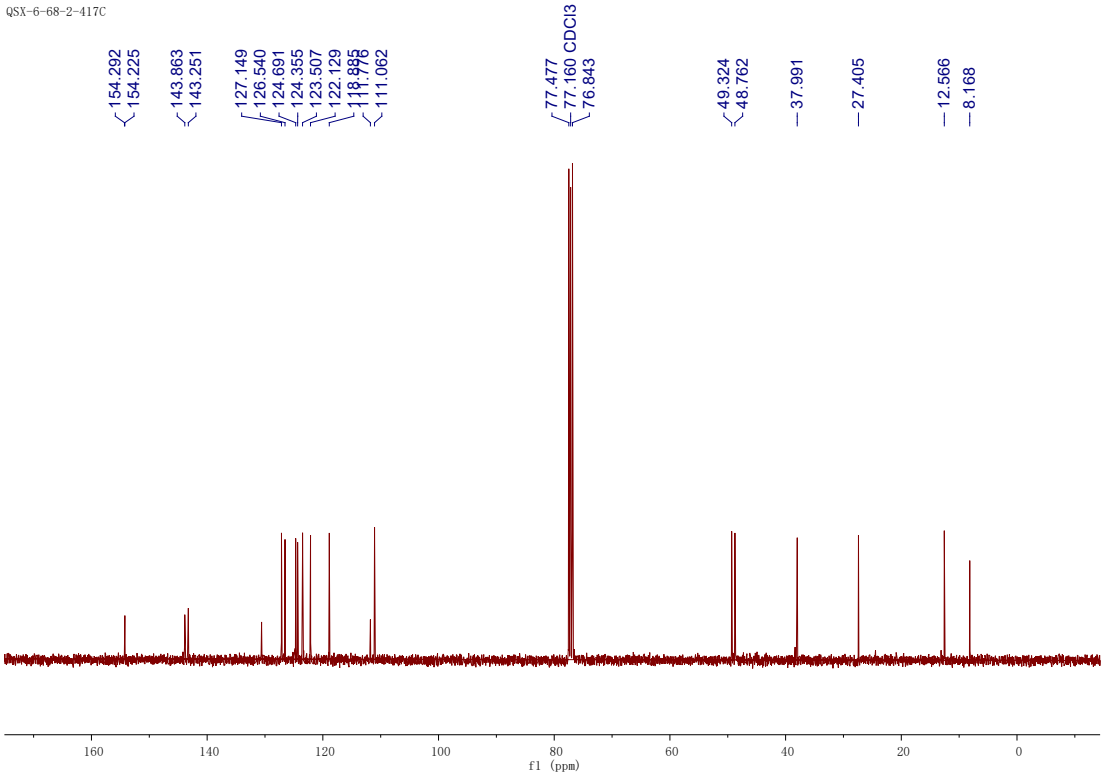
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3an



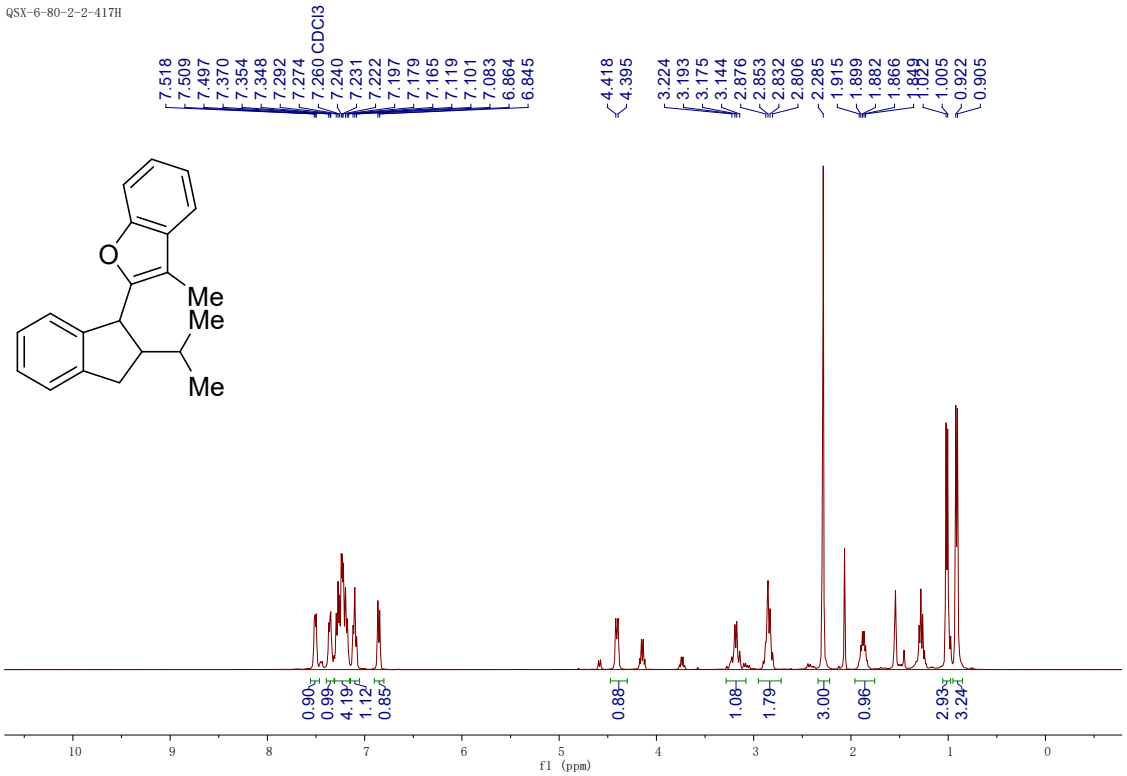
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ao (*see procedure*)



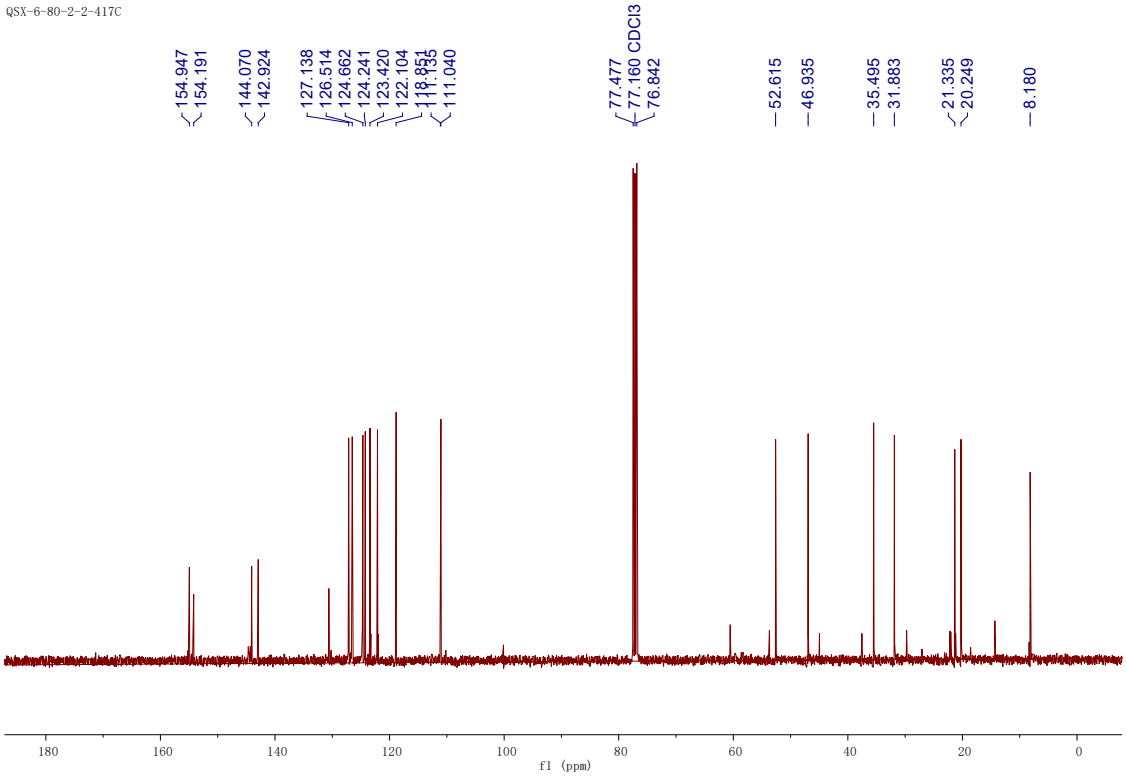
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ao



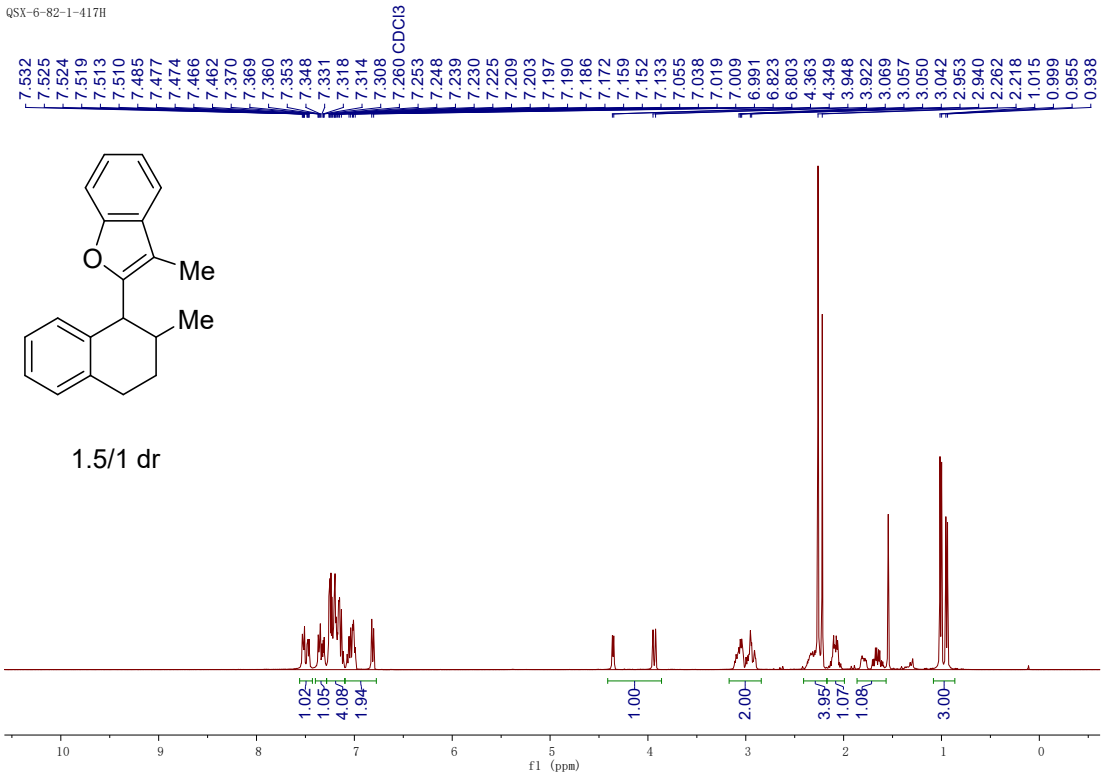
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ap (*see procedure*)



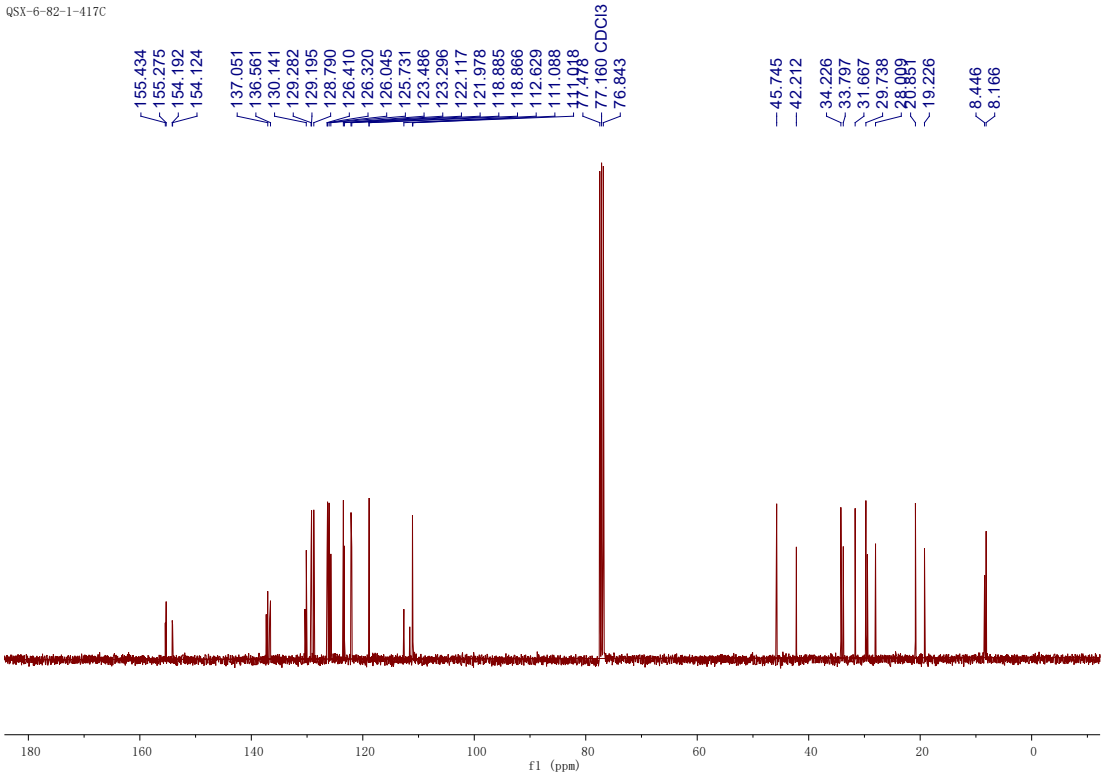
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ap



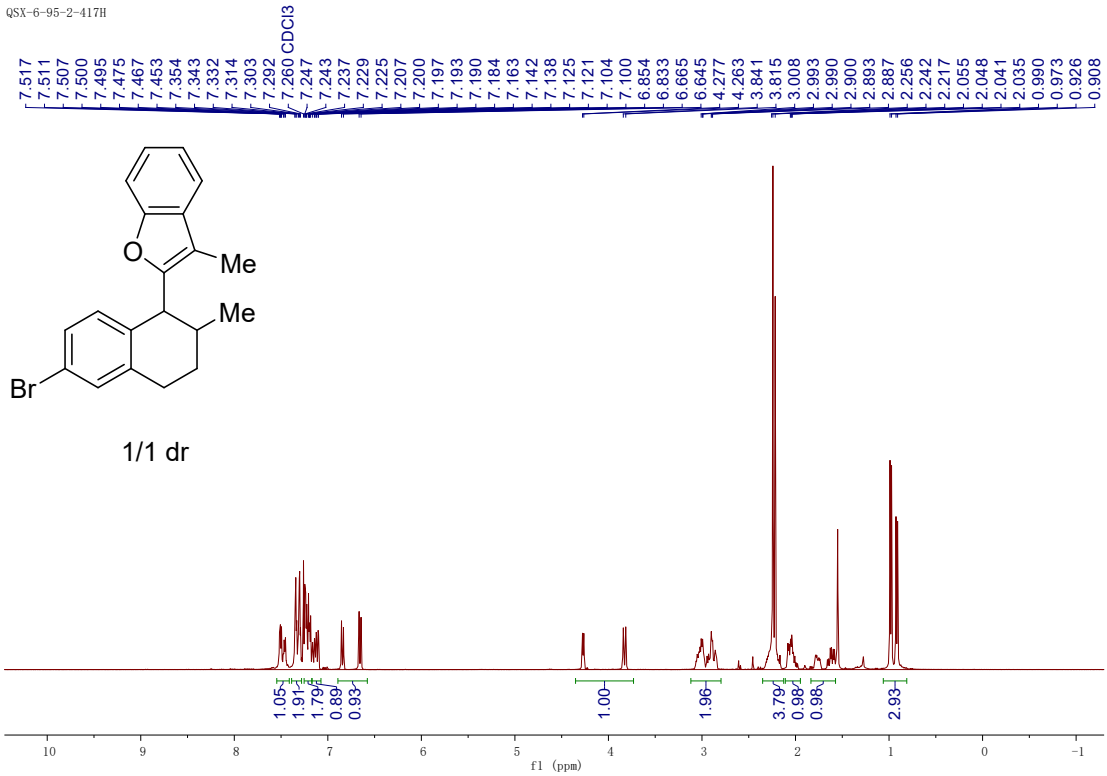
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aq (*see procedure*)



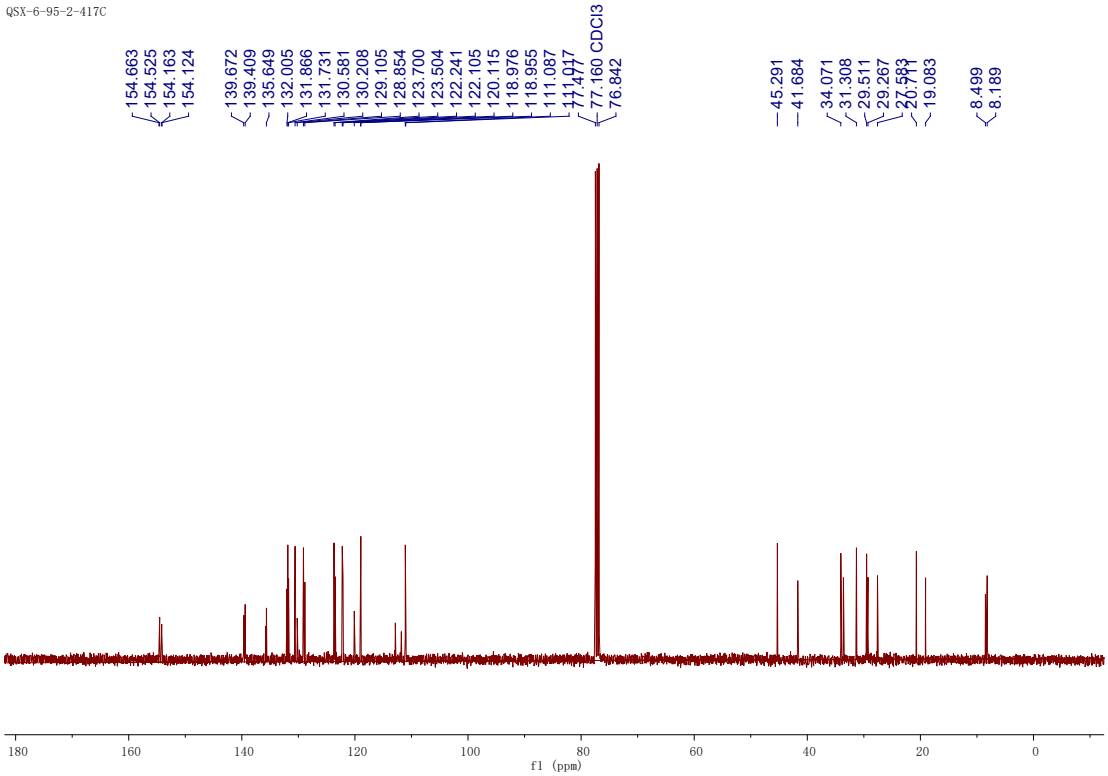
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aq



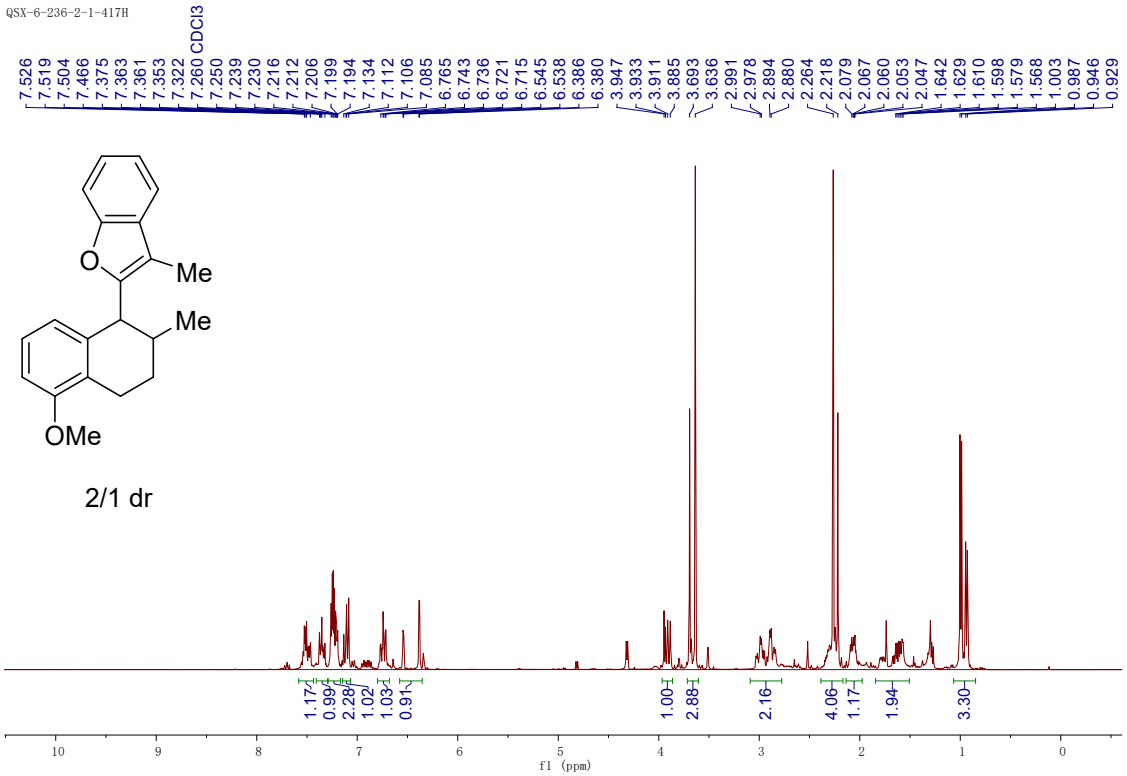
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ar (*see procedure*)



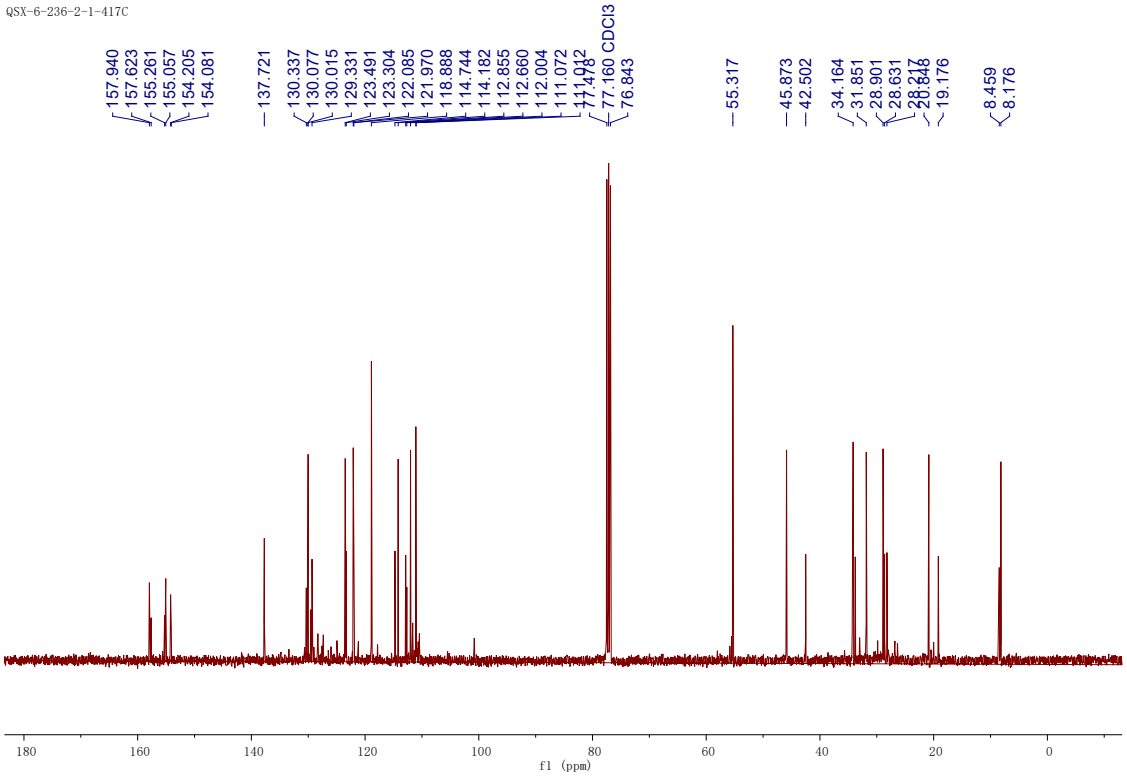
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ar



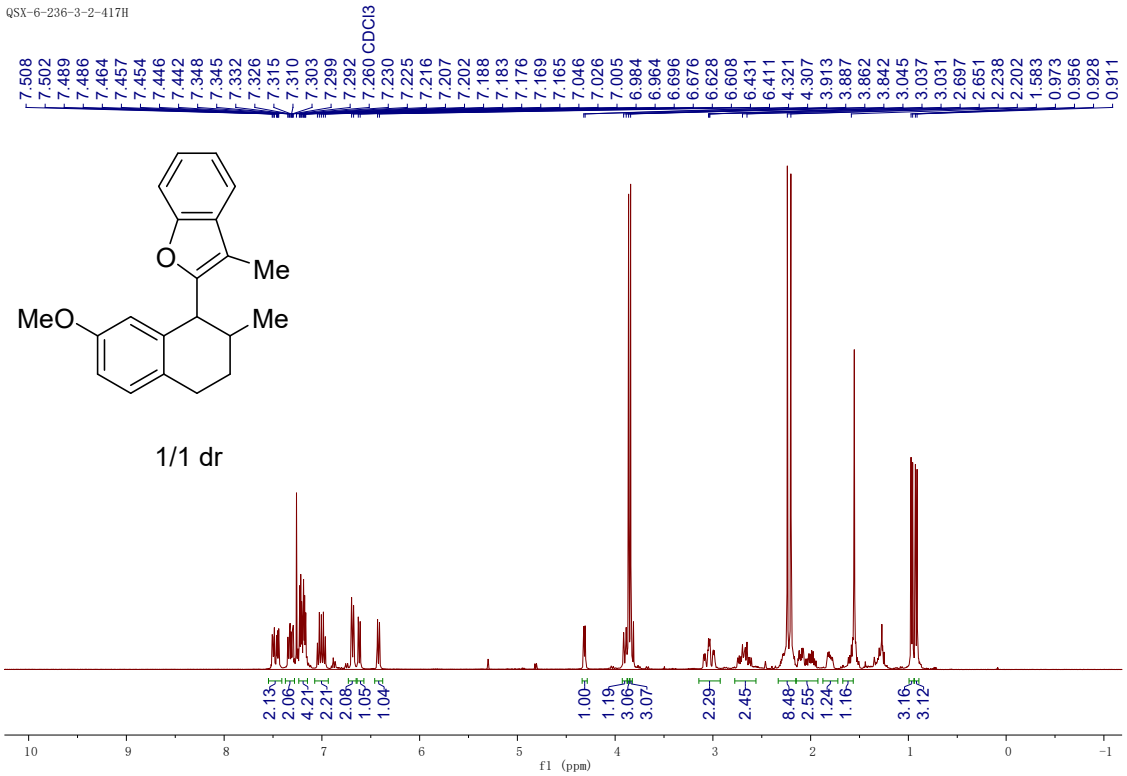
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3as (*see procedure*)



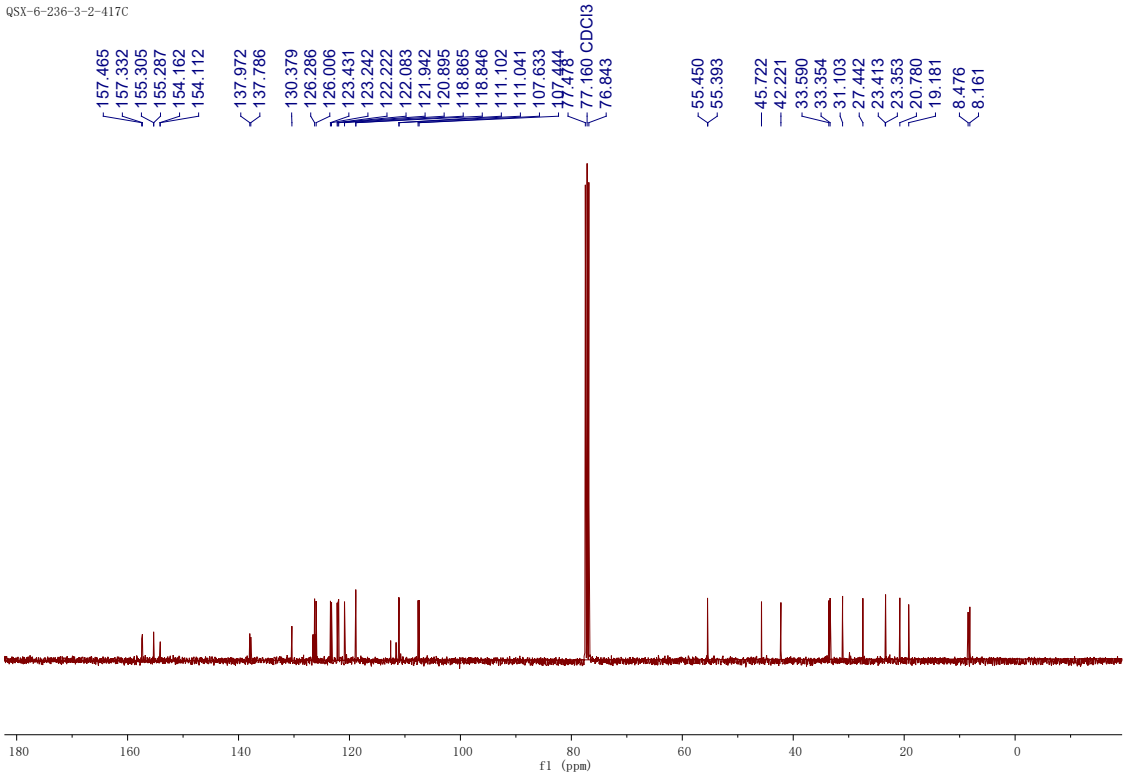
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3as



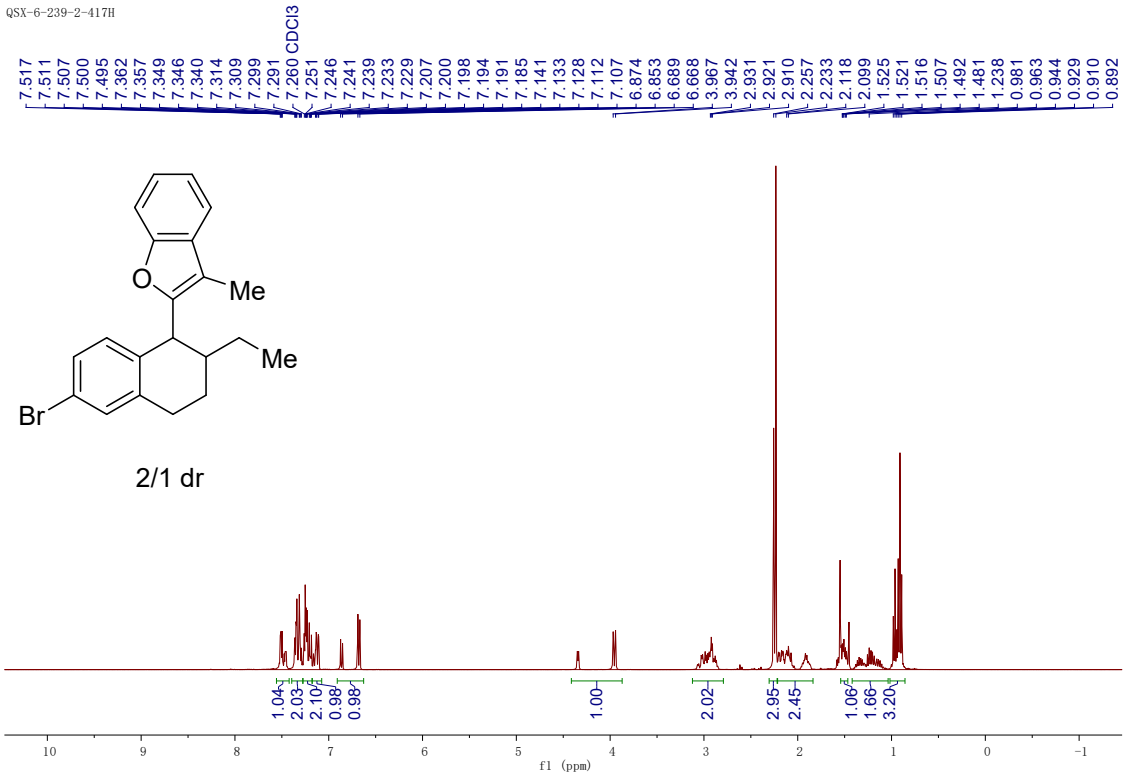
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3at (*see procedure*)



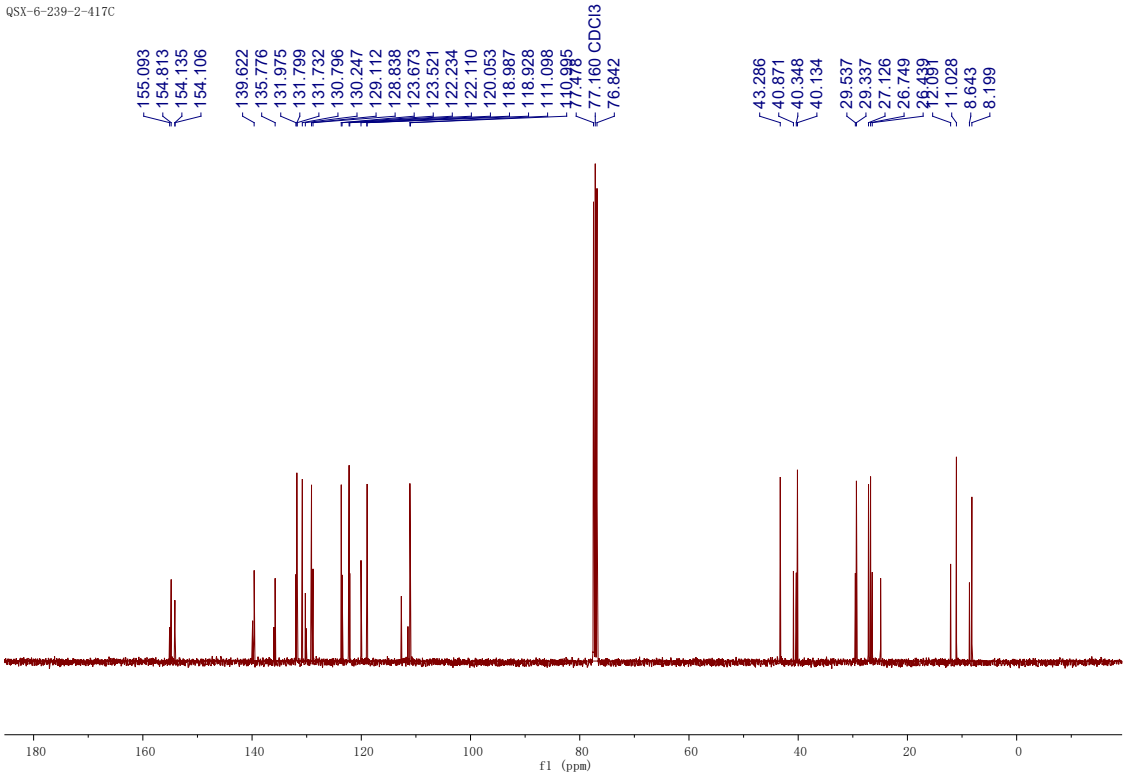
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3at



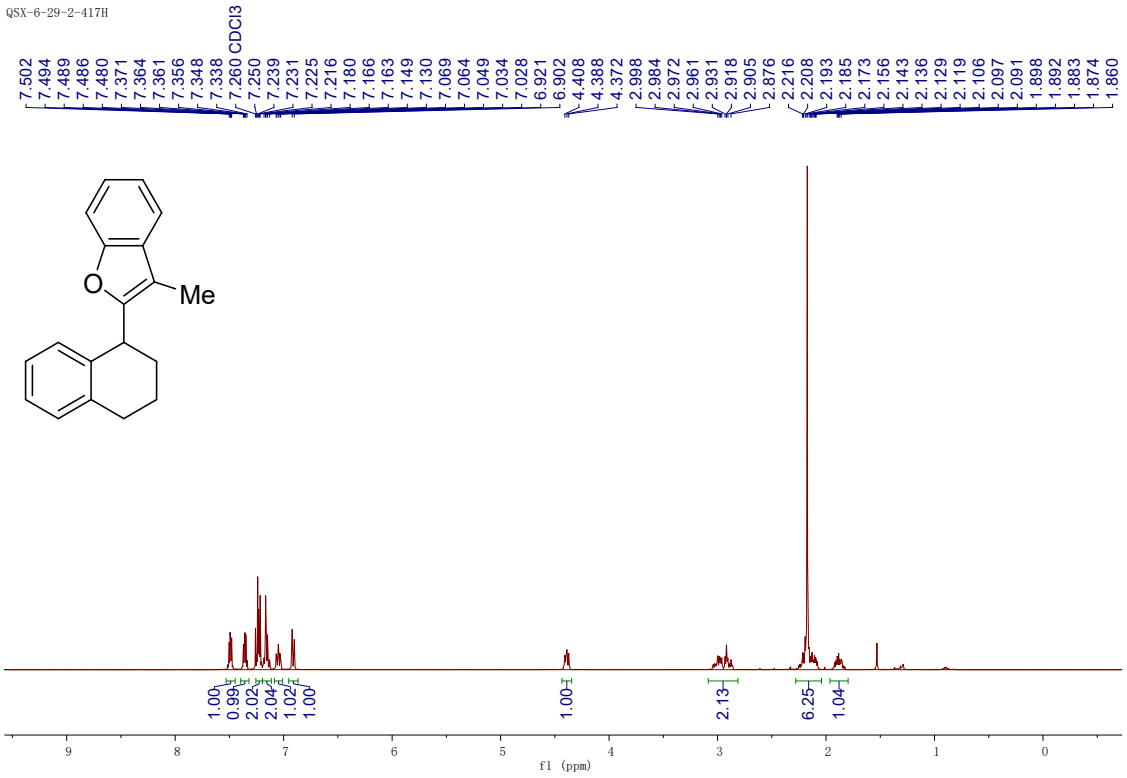
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3au (*see procedure*)



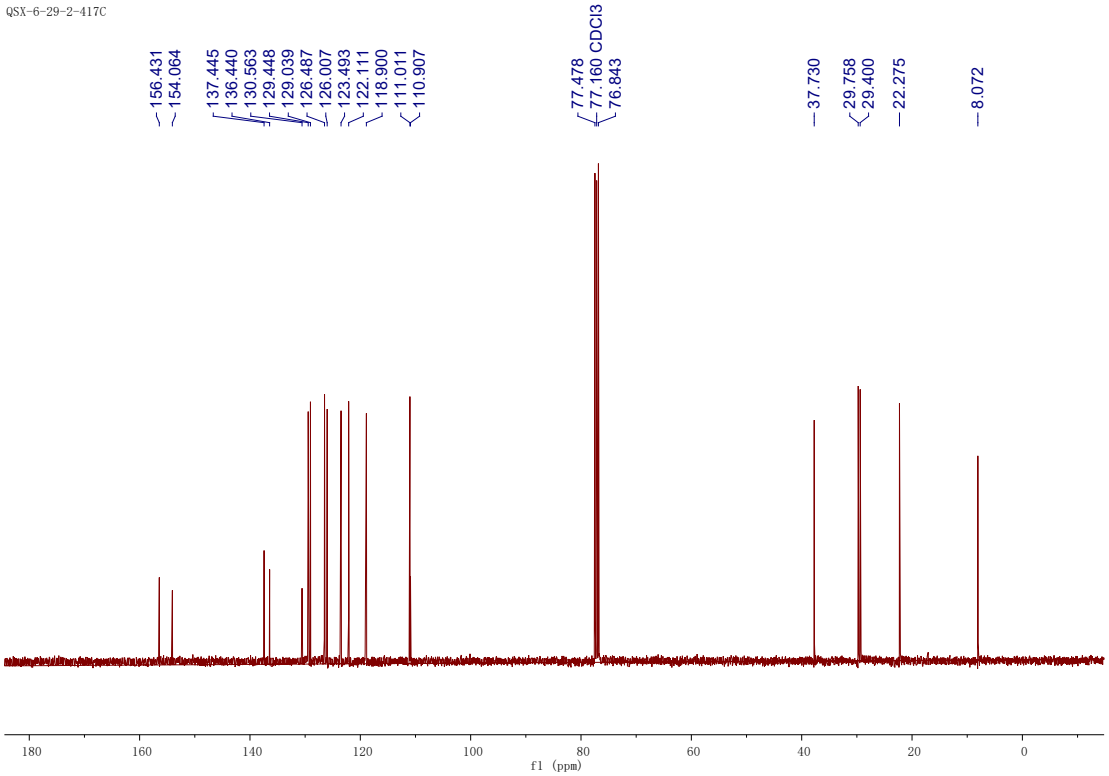
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3au



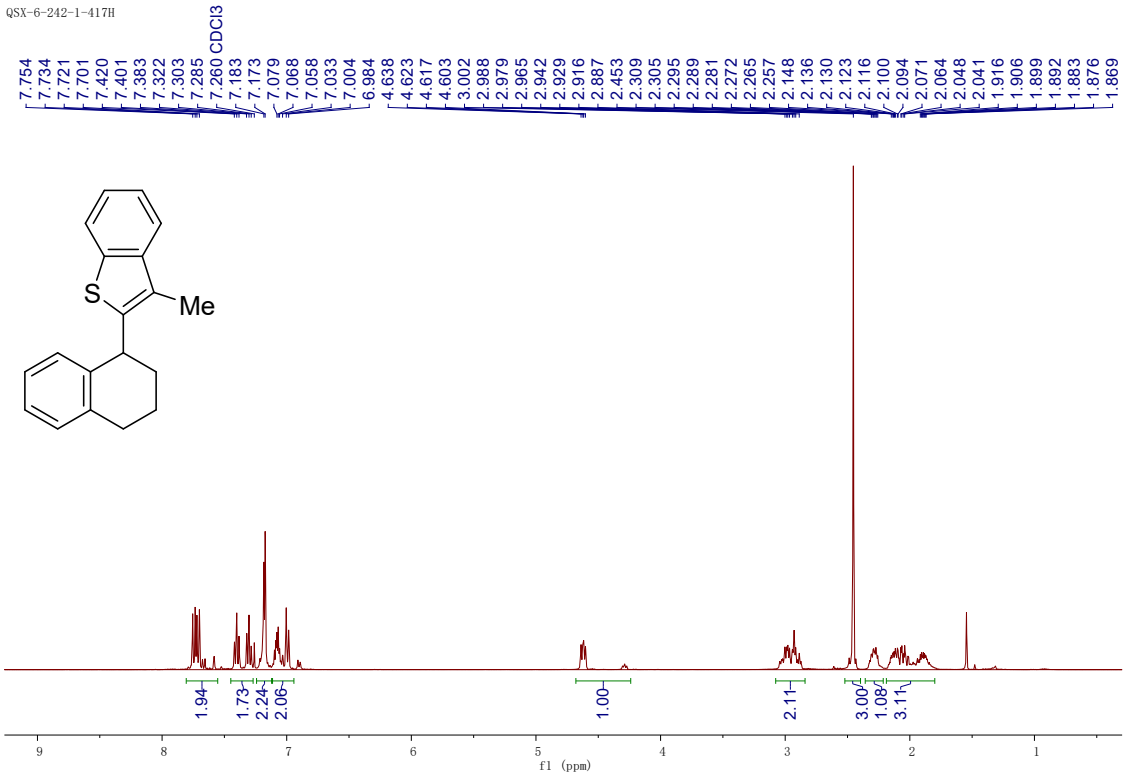
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3av (*see procedure*)



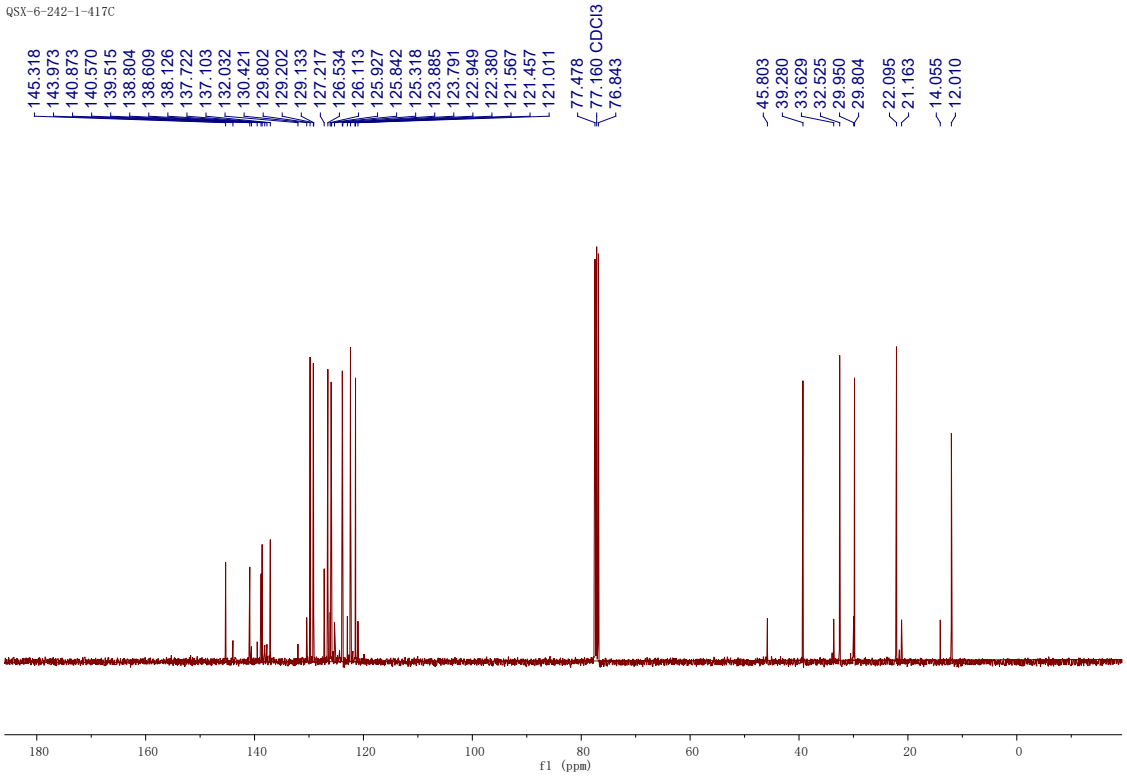
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3av



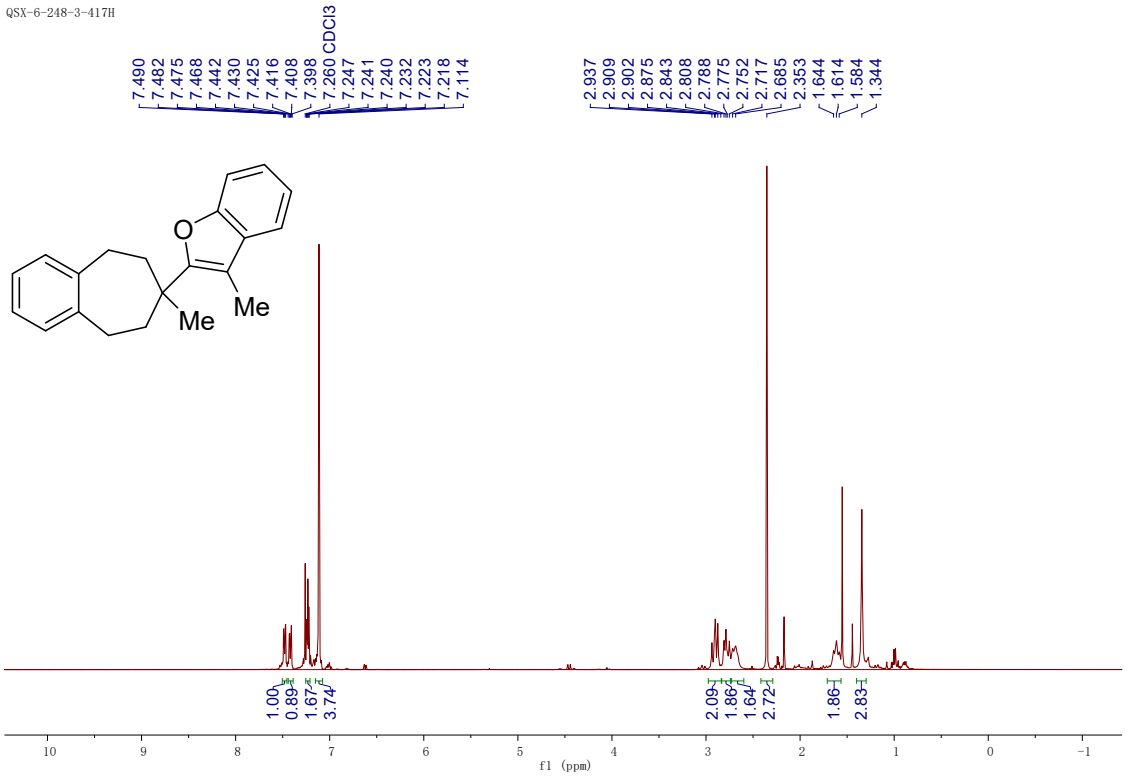
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3av* (*see procedure*)



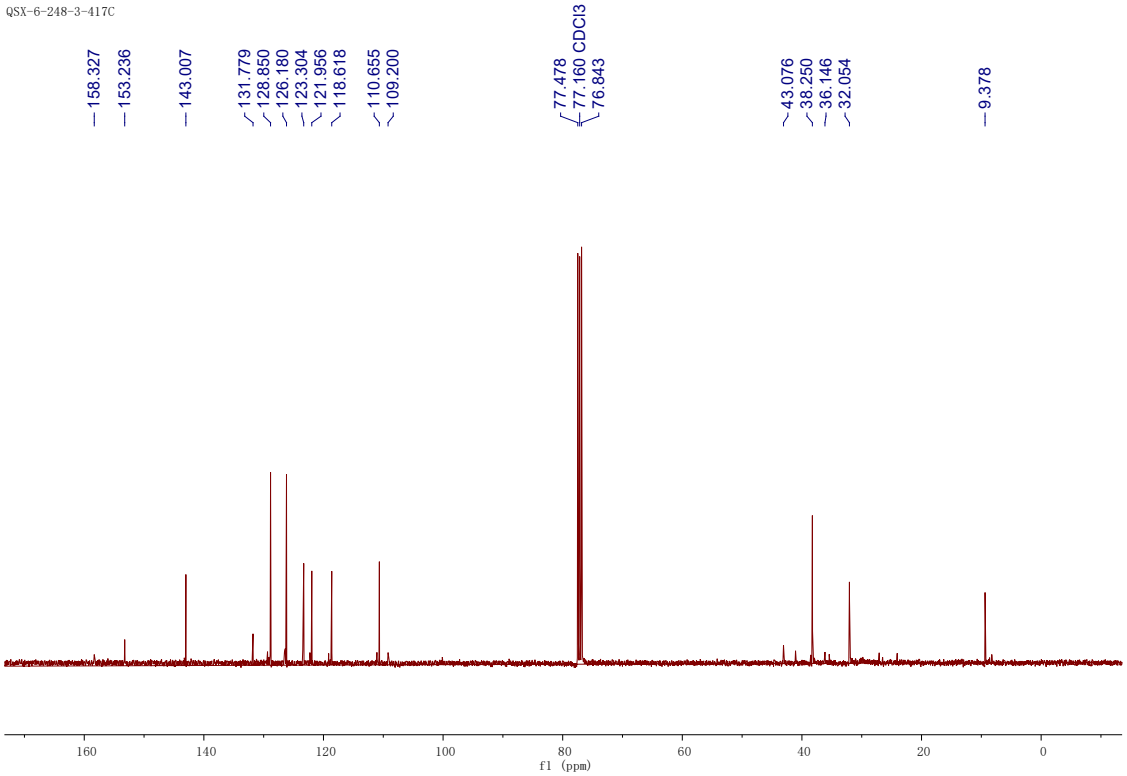
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3av*



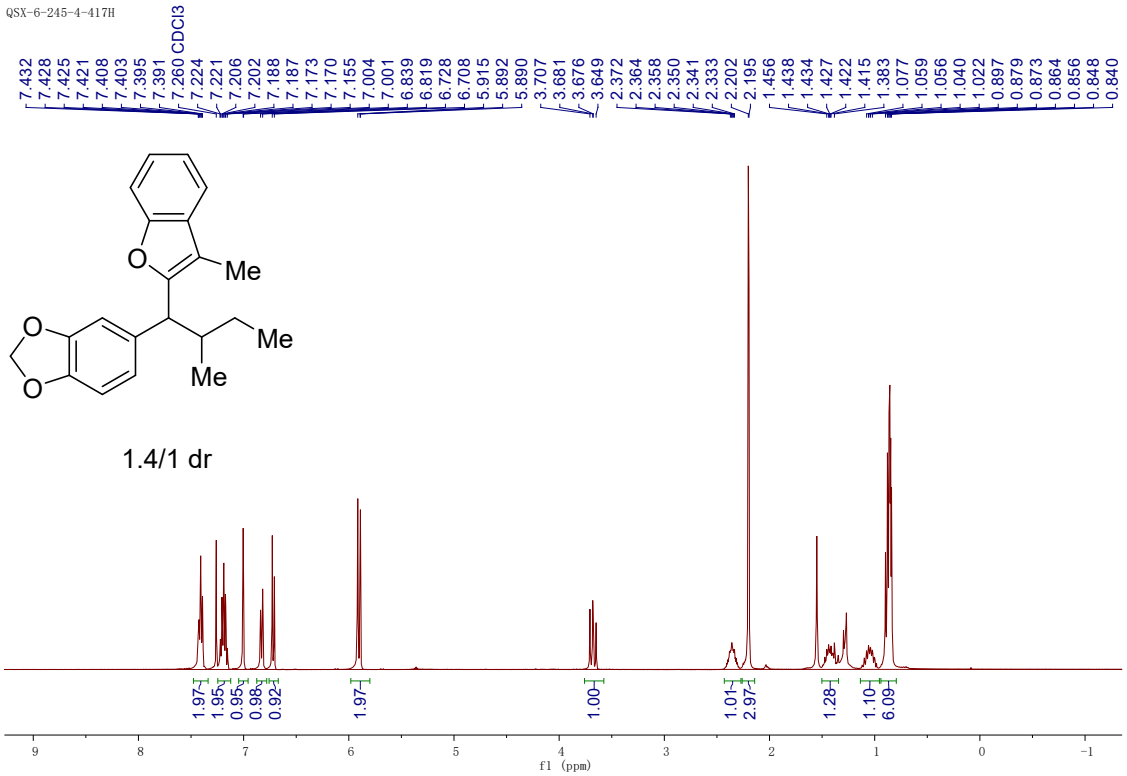
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aw (*see procedure*)



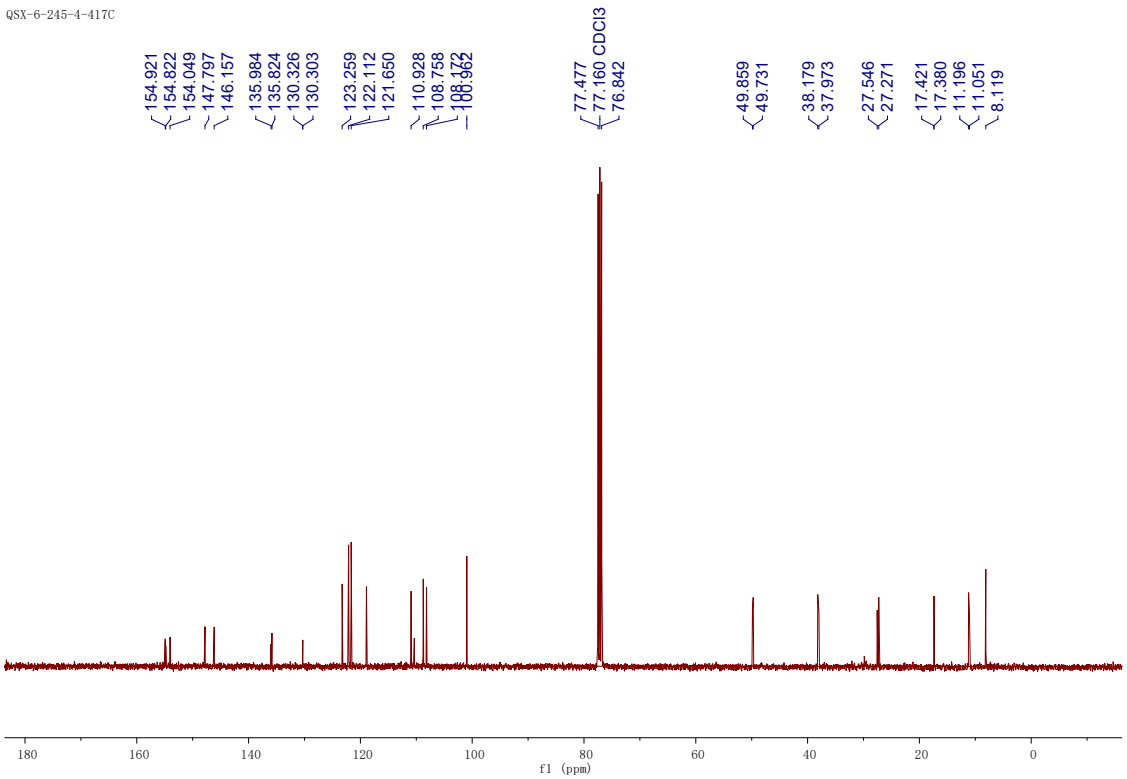
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3aw



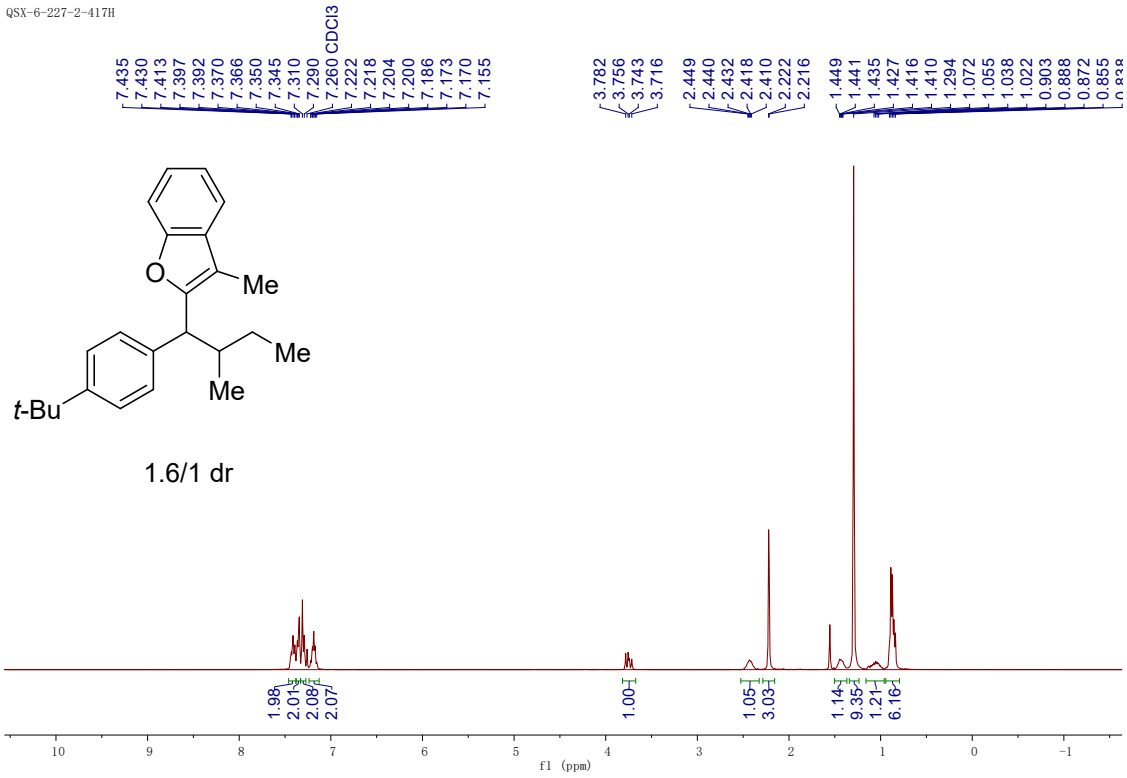
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ax (*see procedure*)



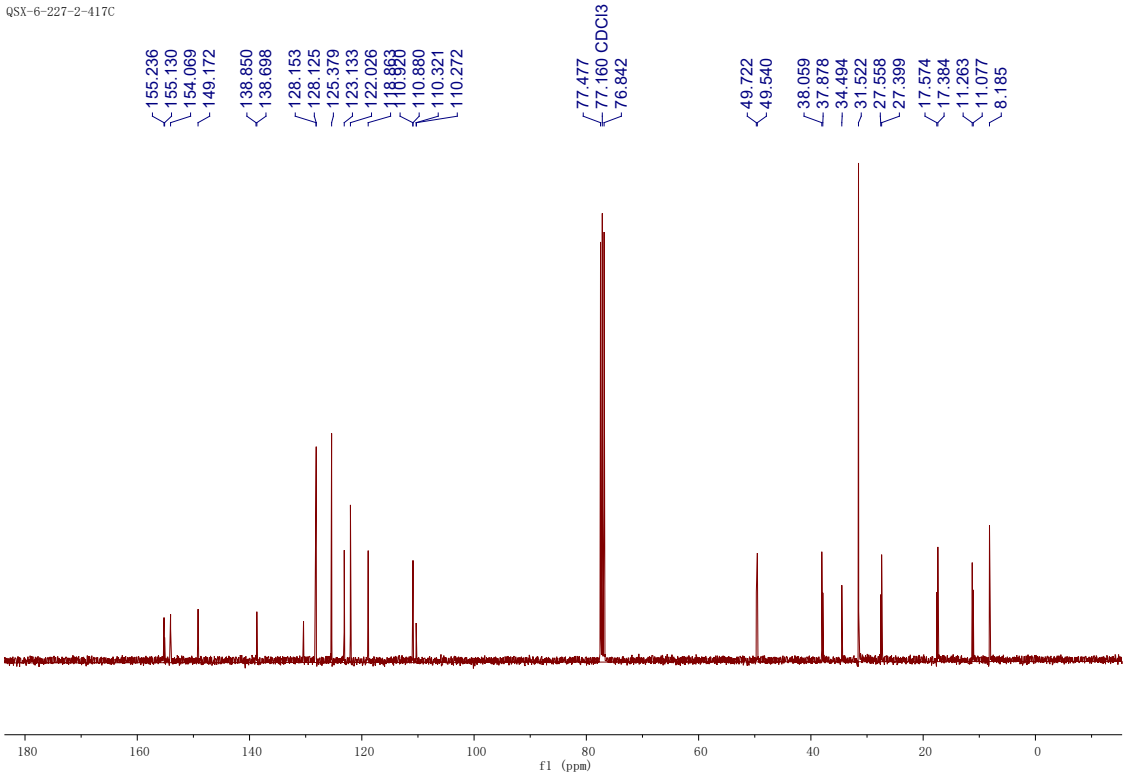
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ax



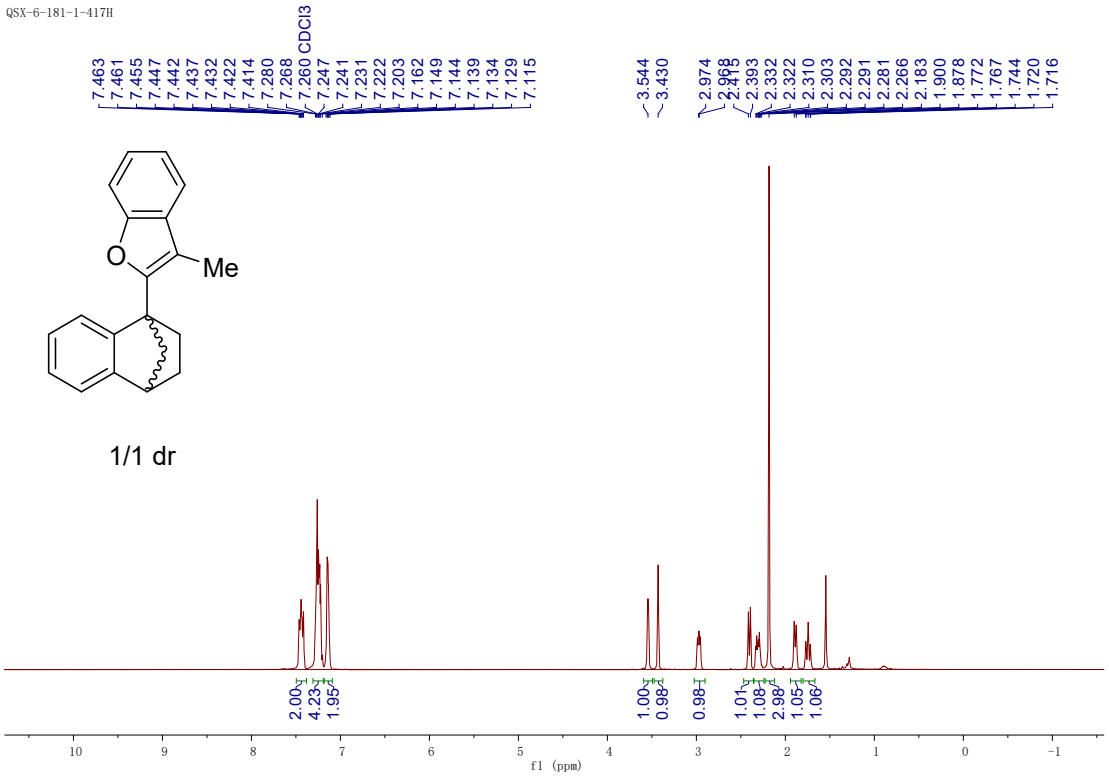
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ay (*see procedure*)



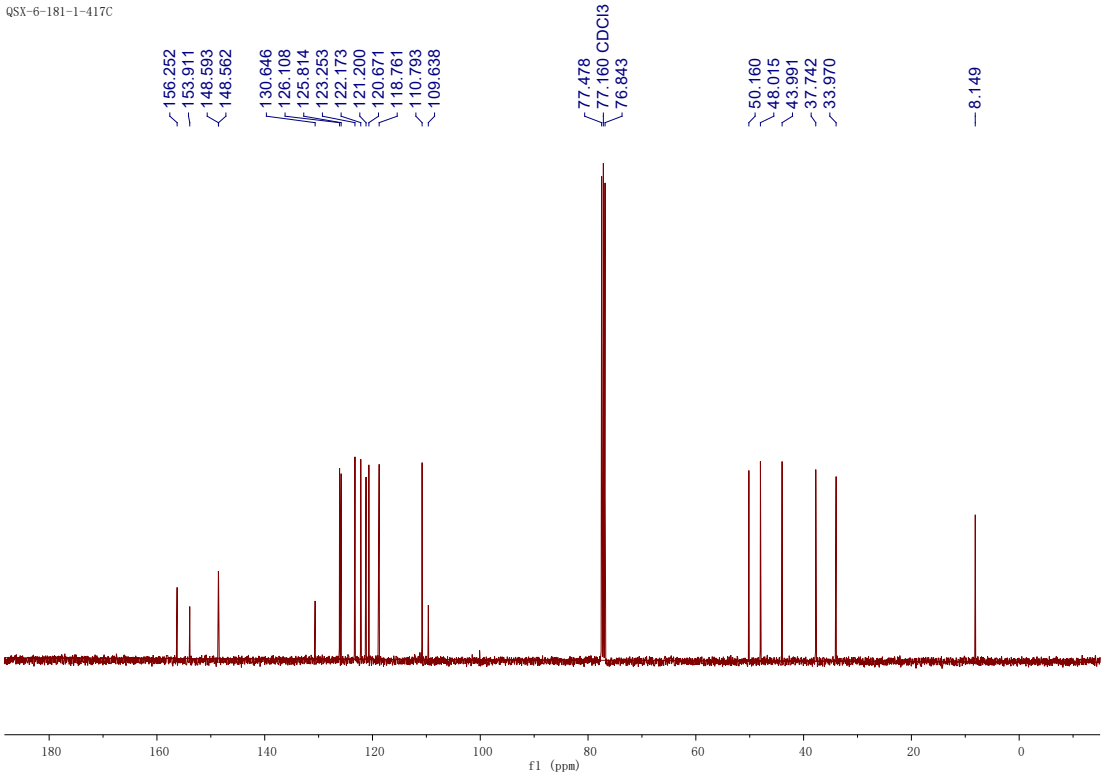
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3ay



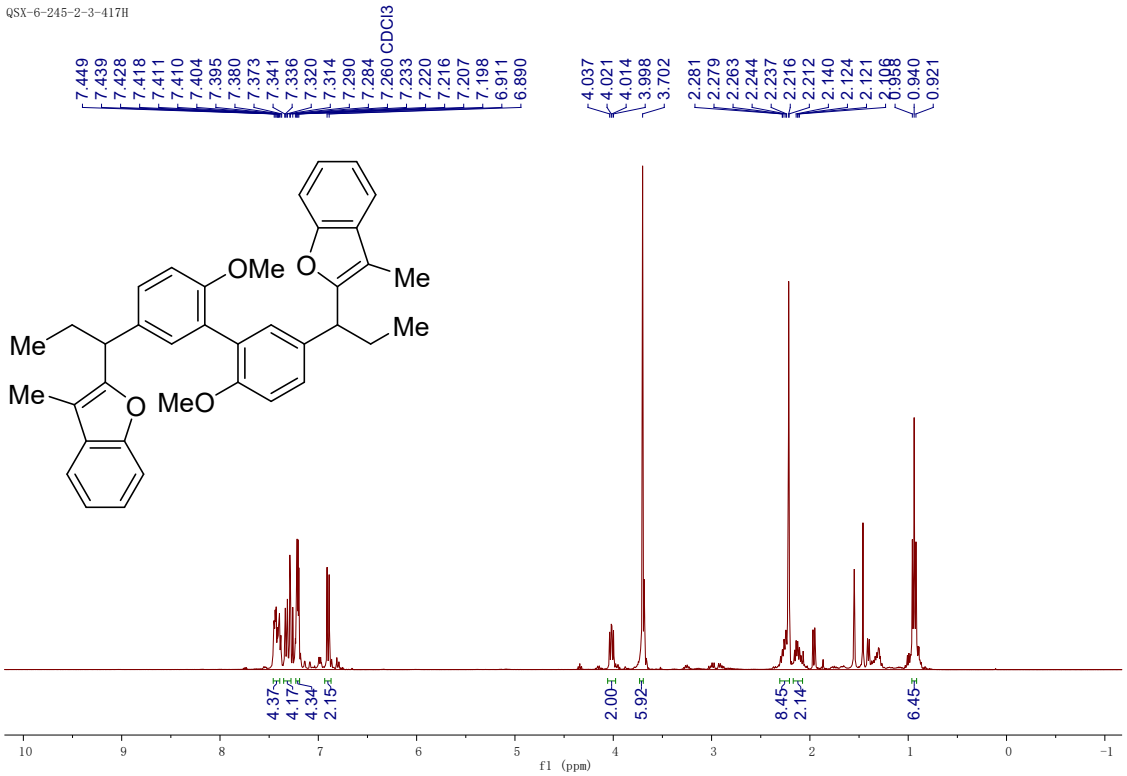
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3bb (*see procedure*)



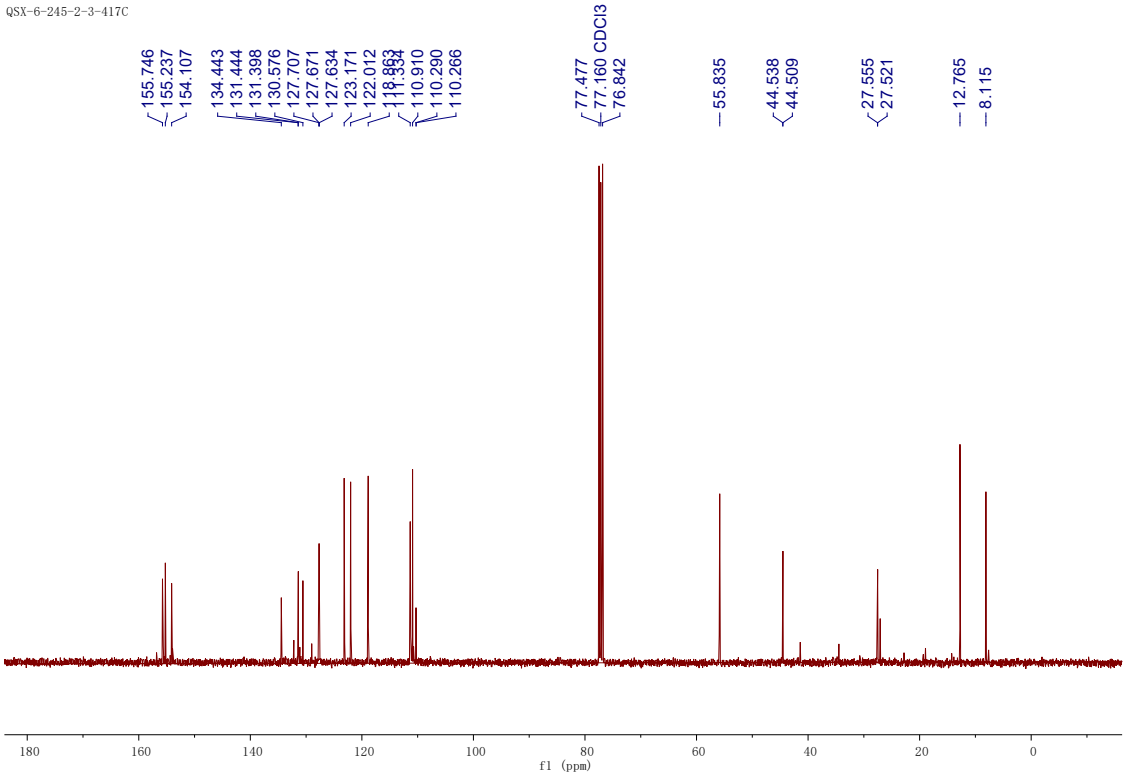
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3bb



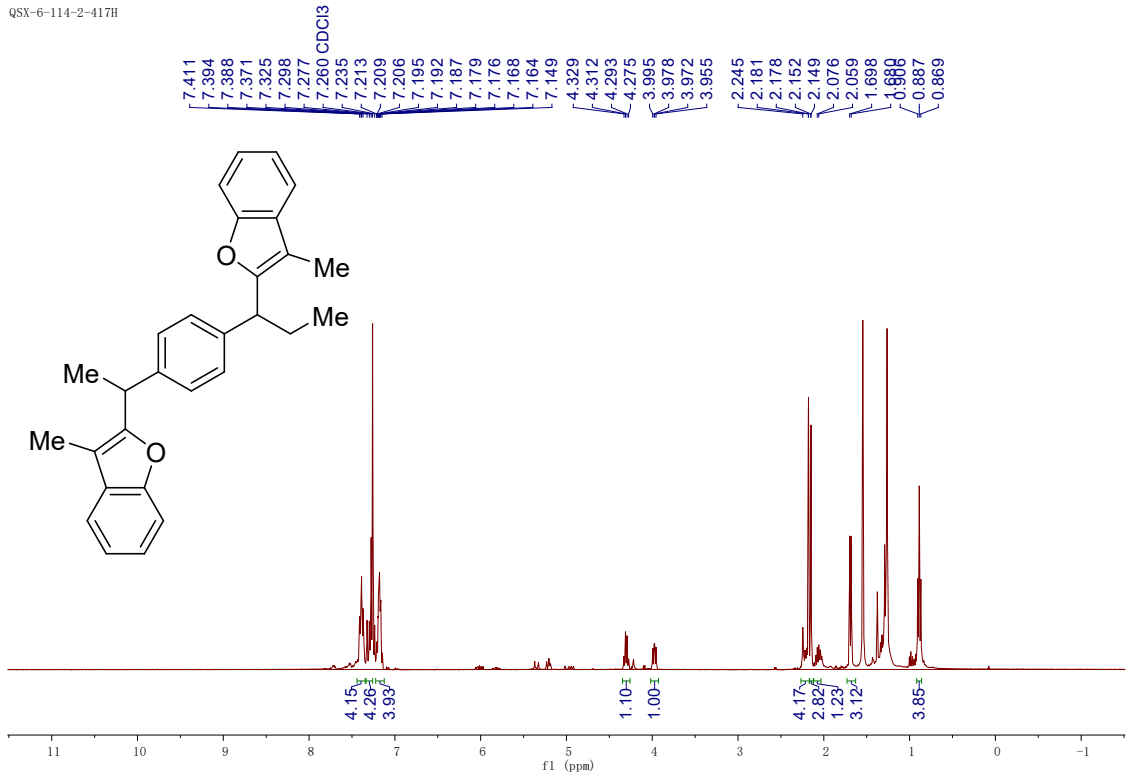
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3bc (*see procedure*)



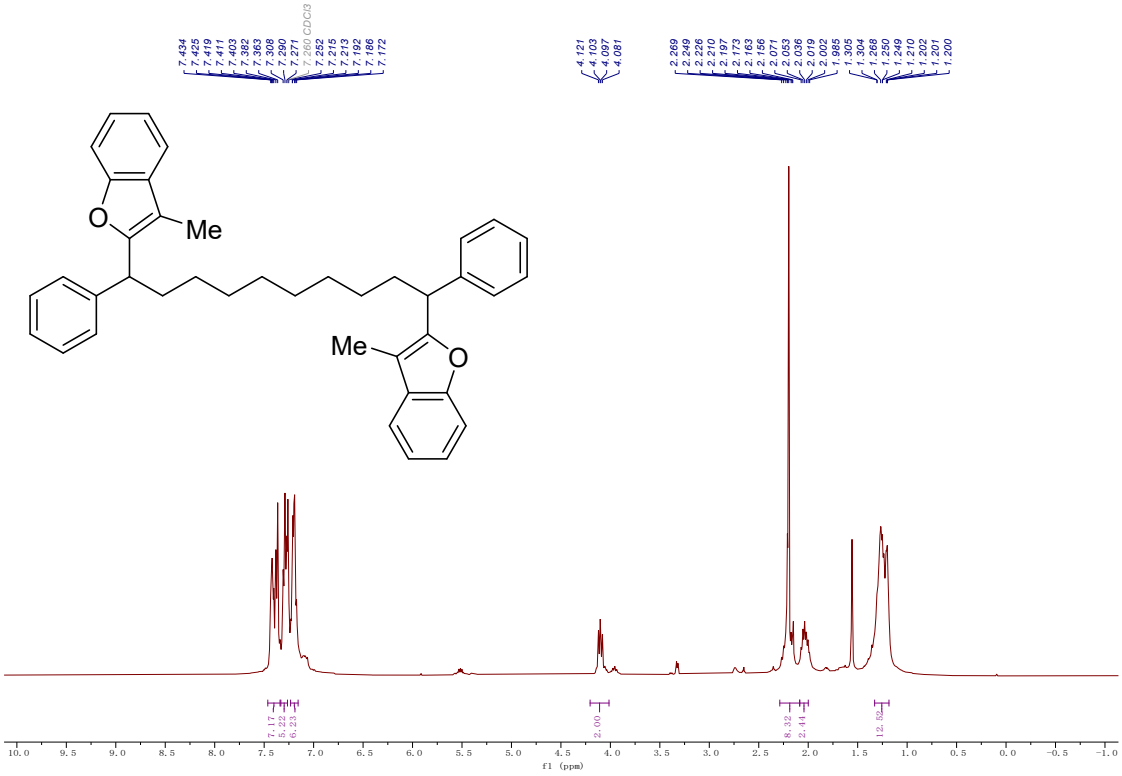
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3bc



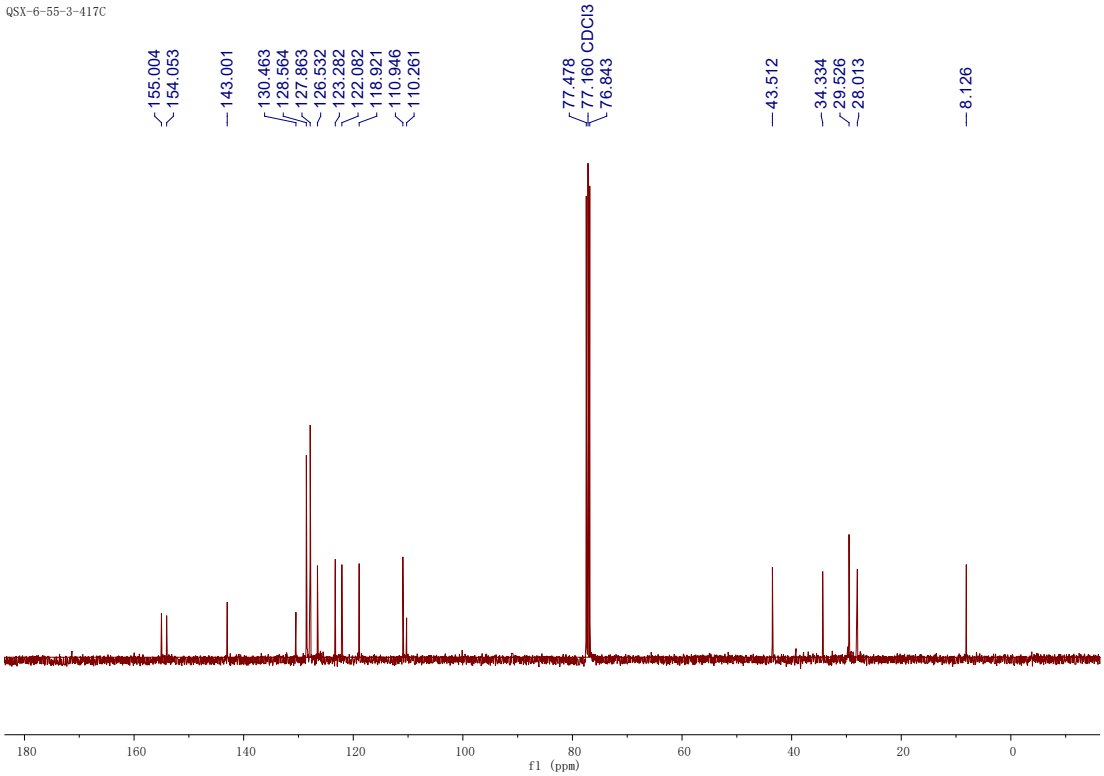
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3bd (*see procedure*)



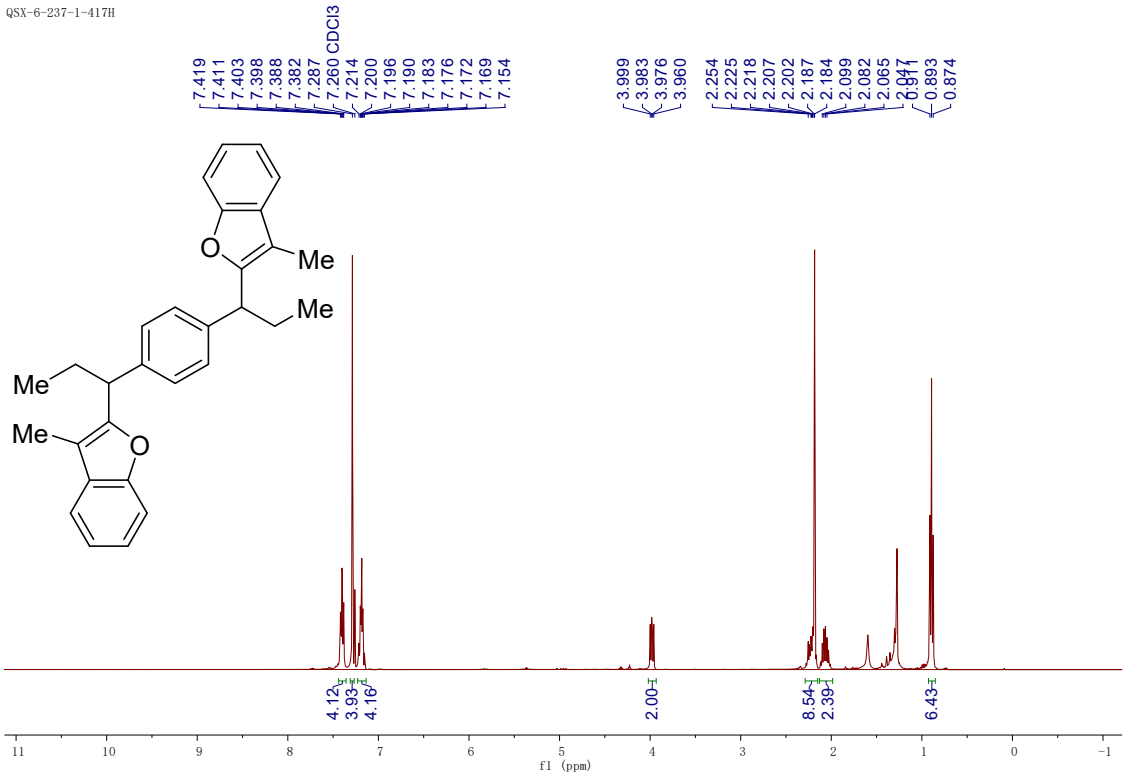
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3be (*see procedure*)



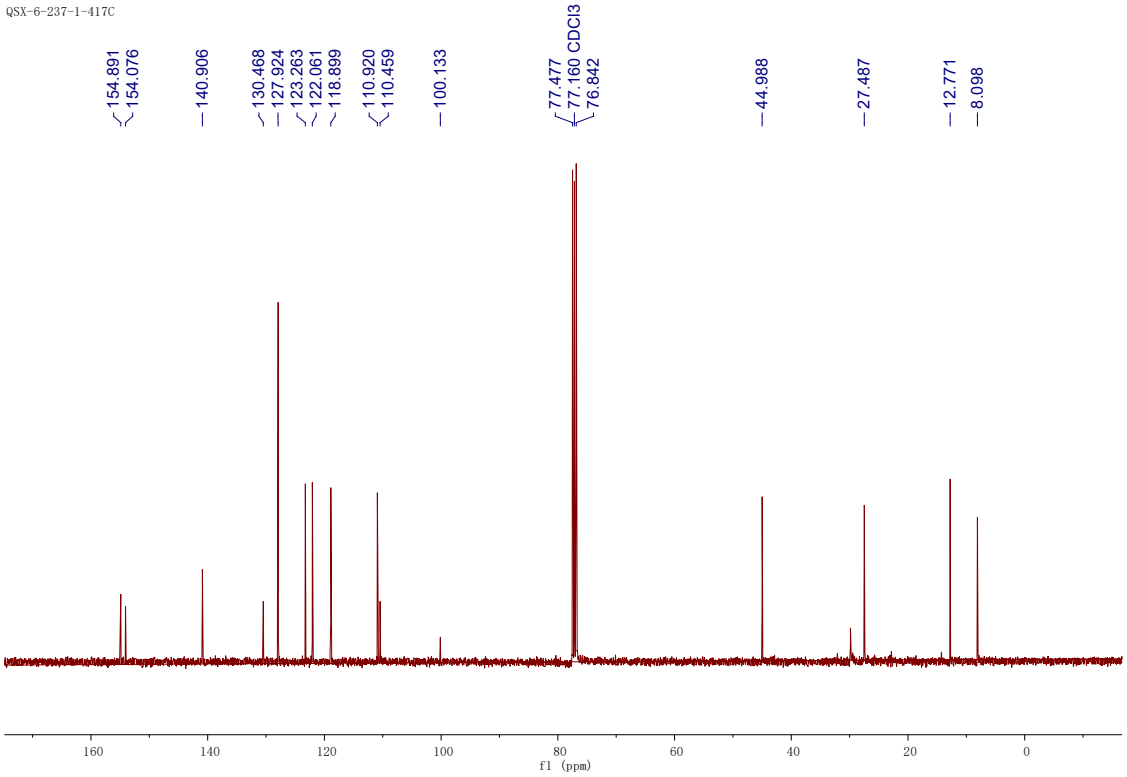
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3be



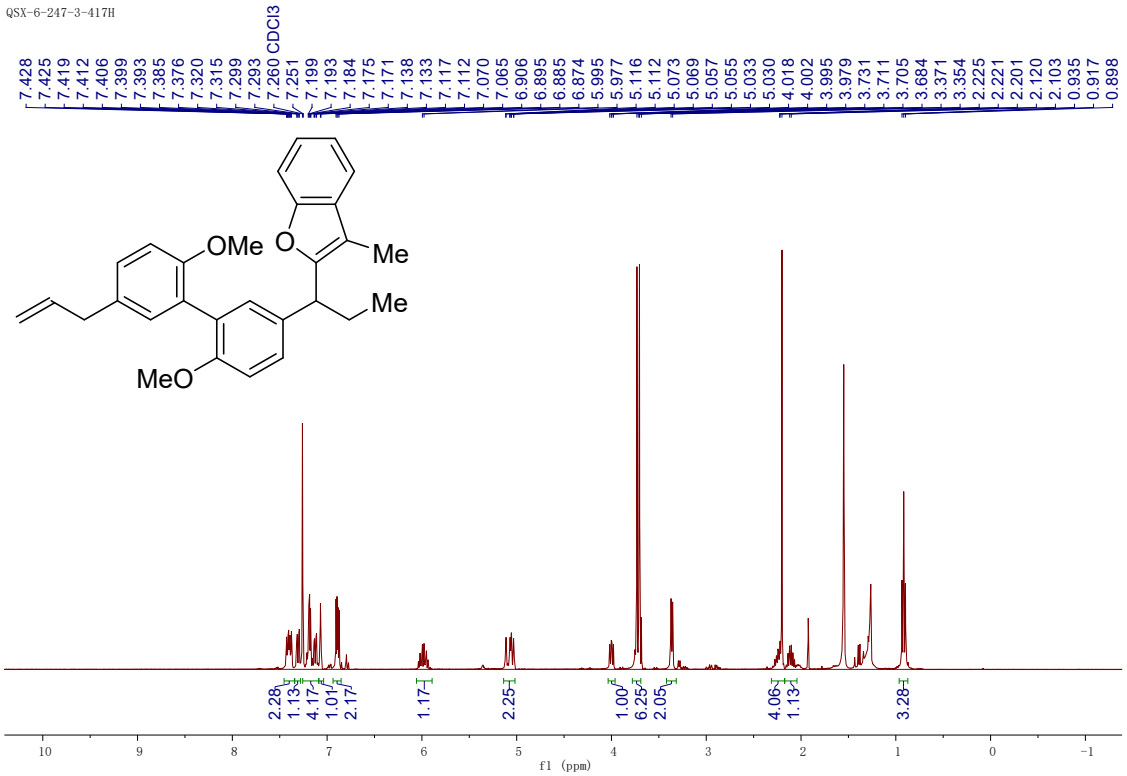
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3bf (*see procedure*)



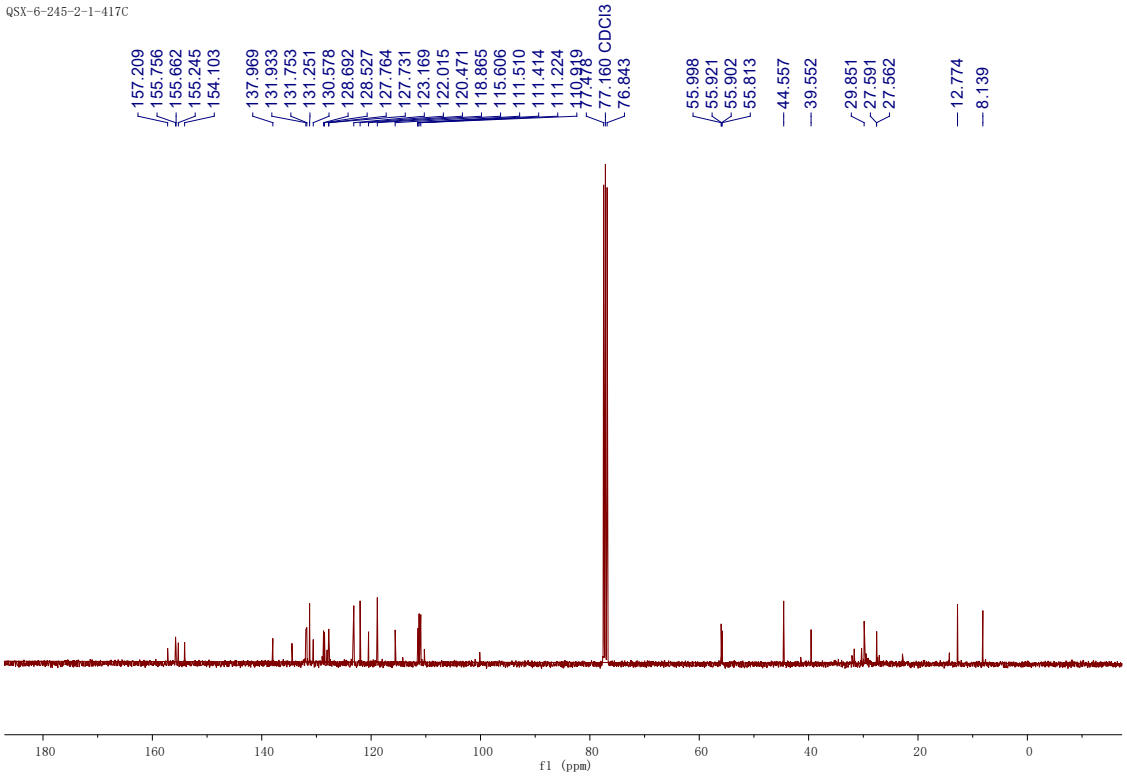
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3bf



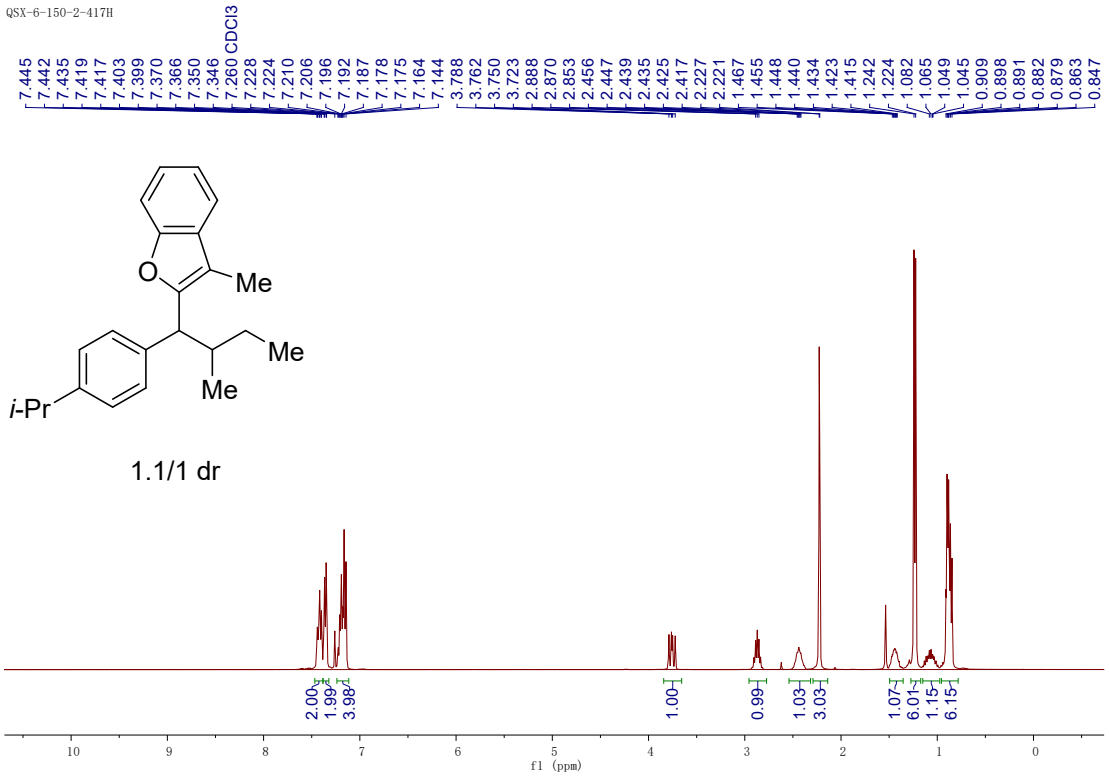
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3bg (*see procedure*)



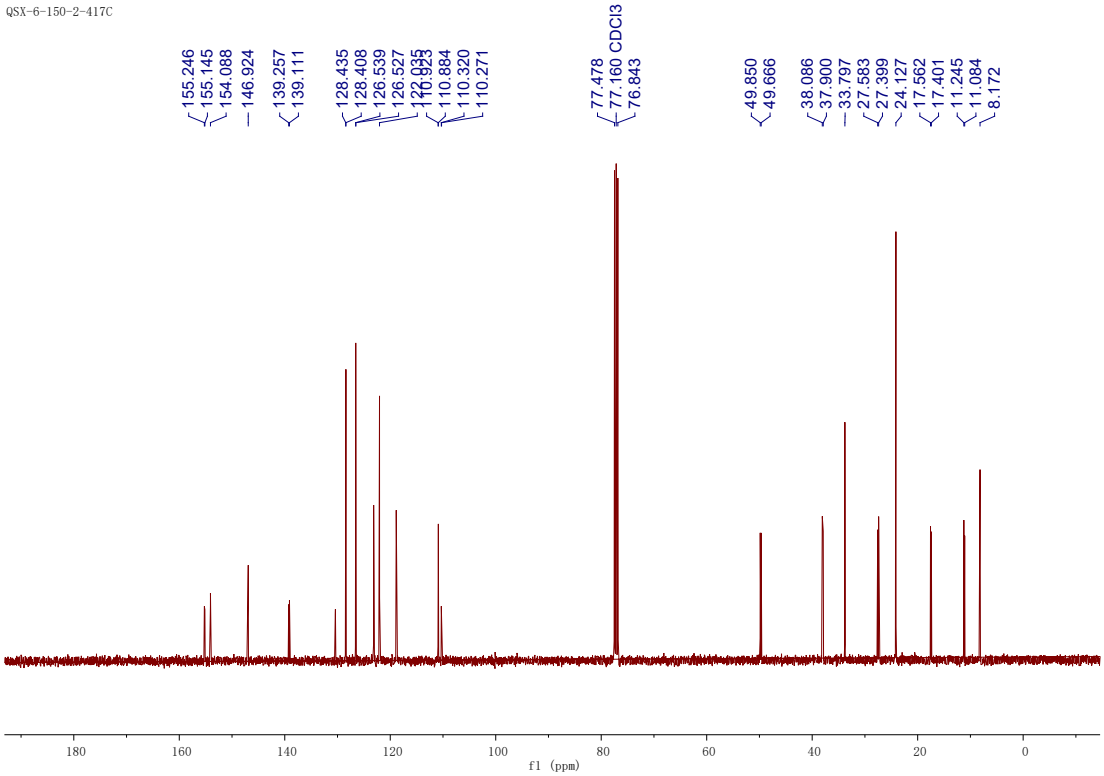
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3bg



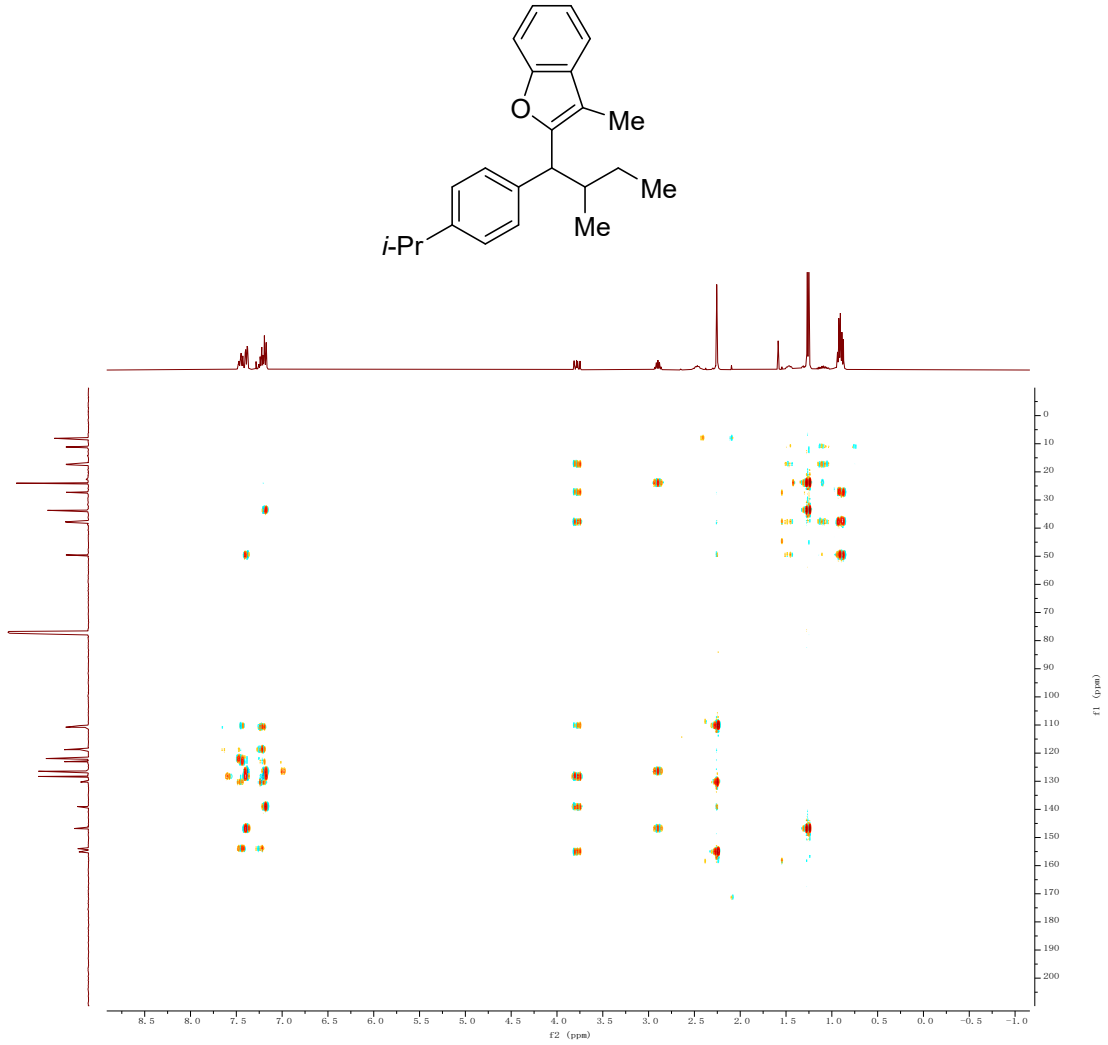
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a (*see procedure*)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4a

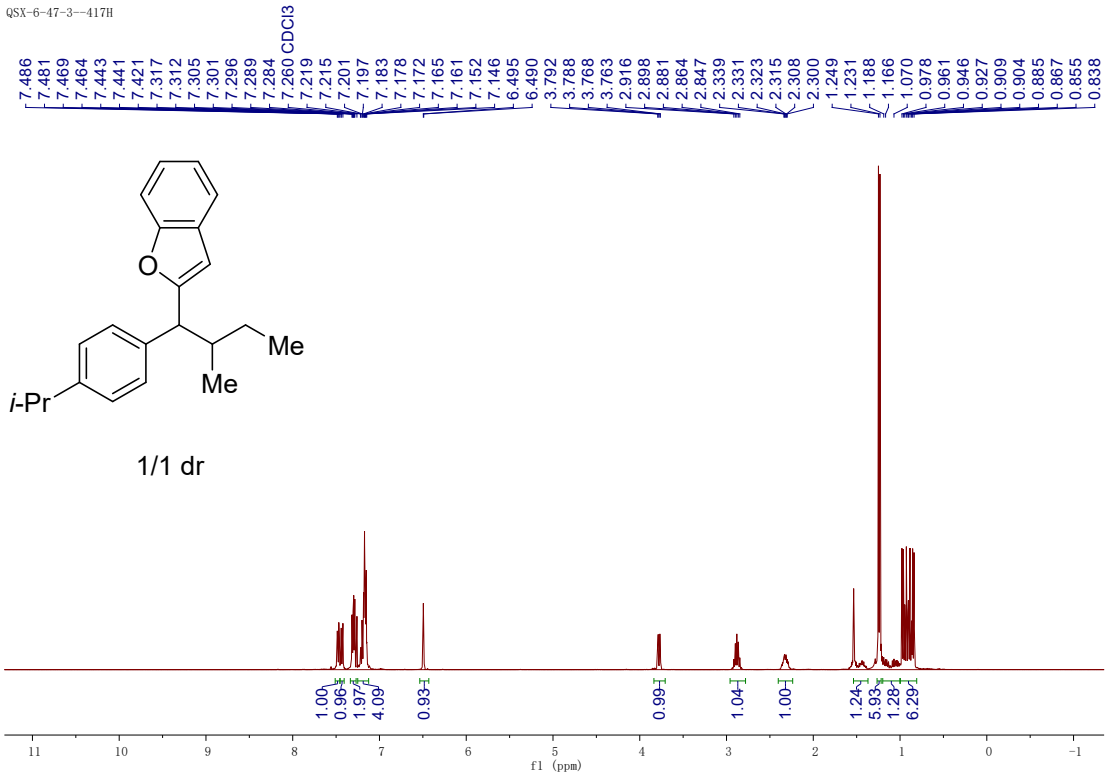


HSQC (400 MHz, $CDCl_3$) spectrum of 4a

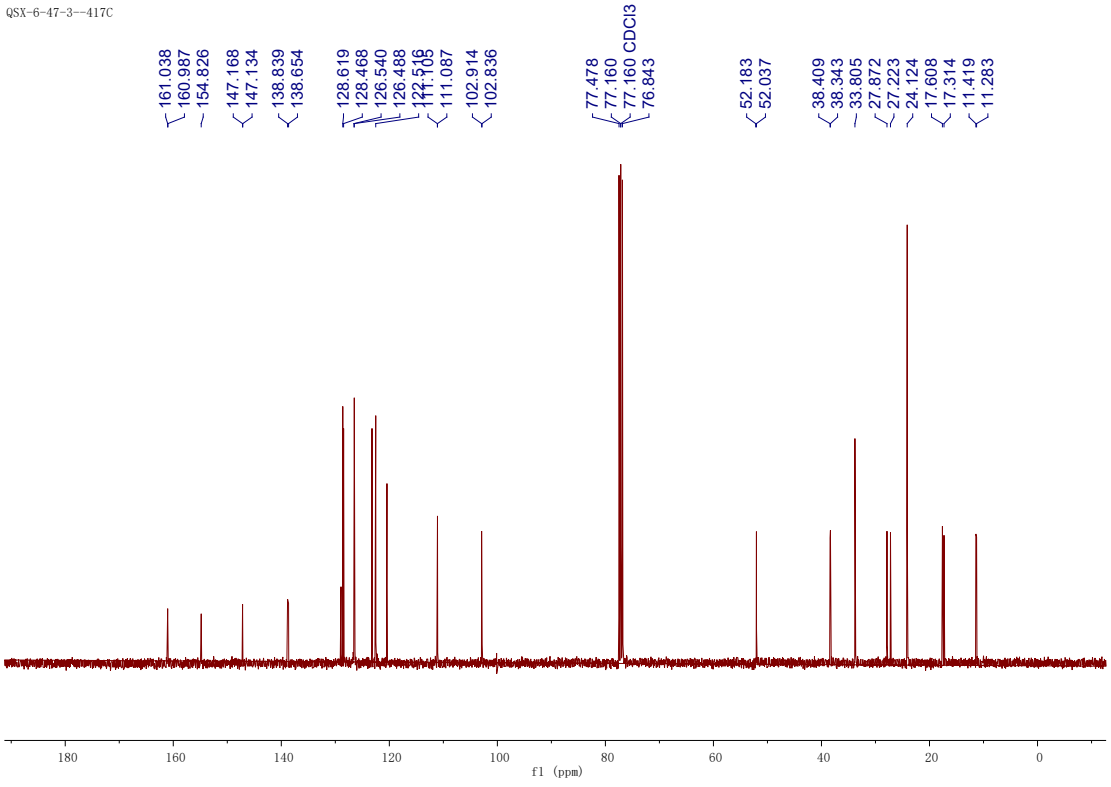


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3az same as above (*see procedure*)

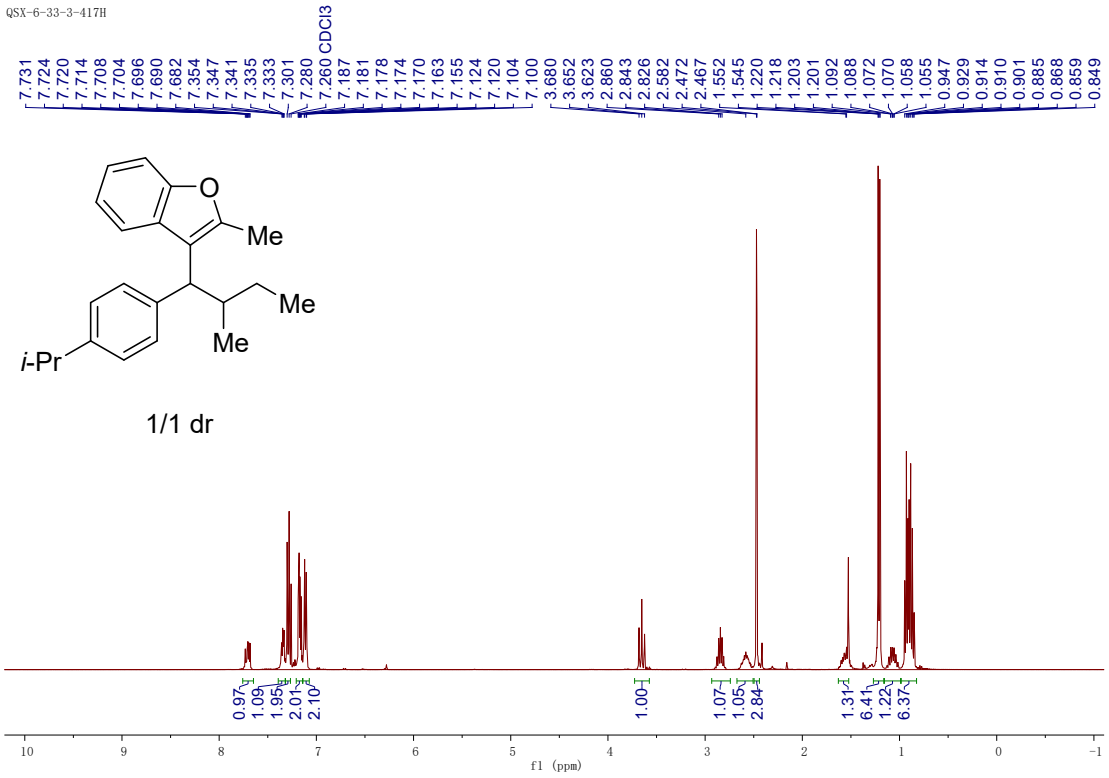
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4b (*see procedure*)



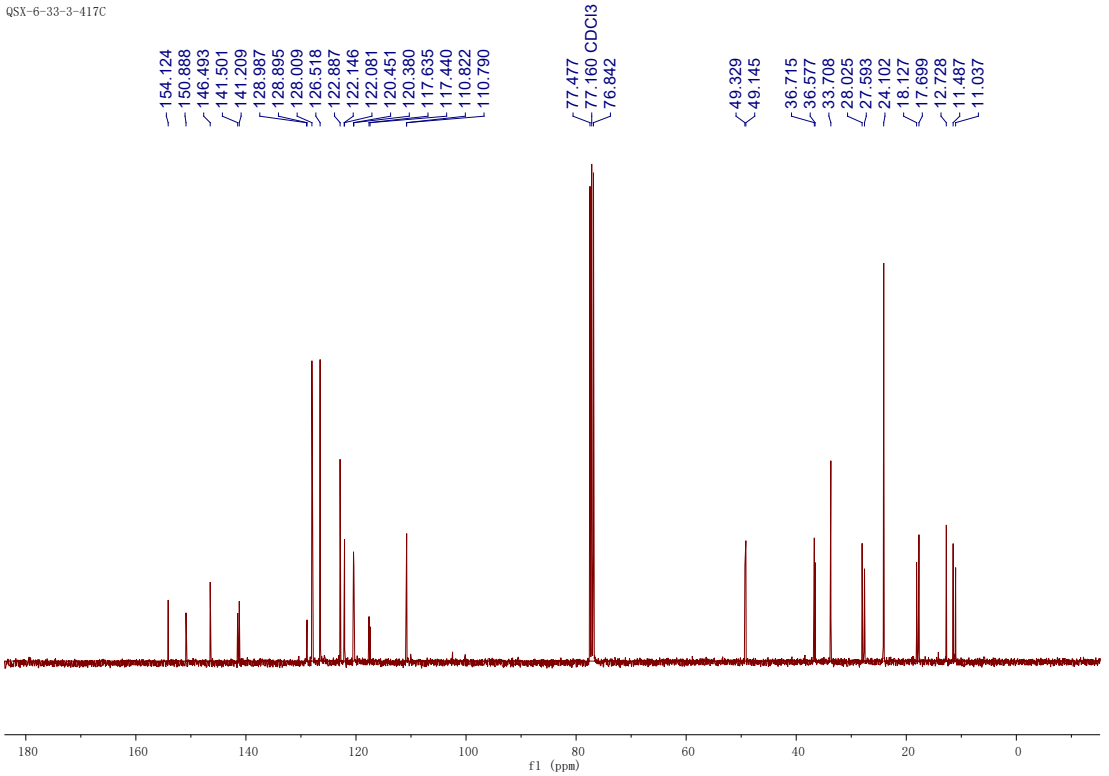
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4b



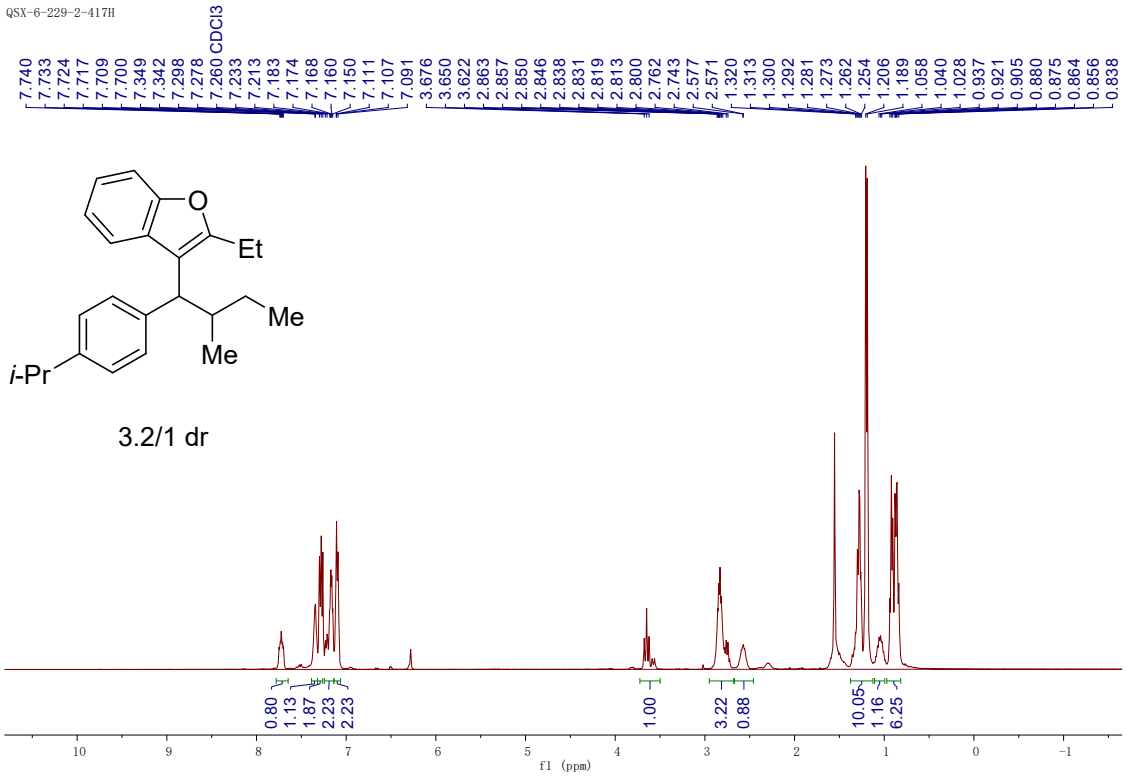
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4c (*see procedure*)



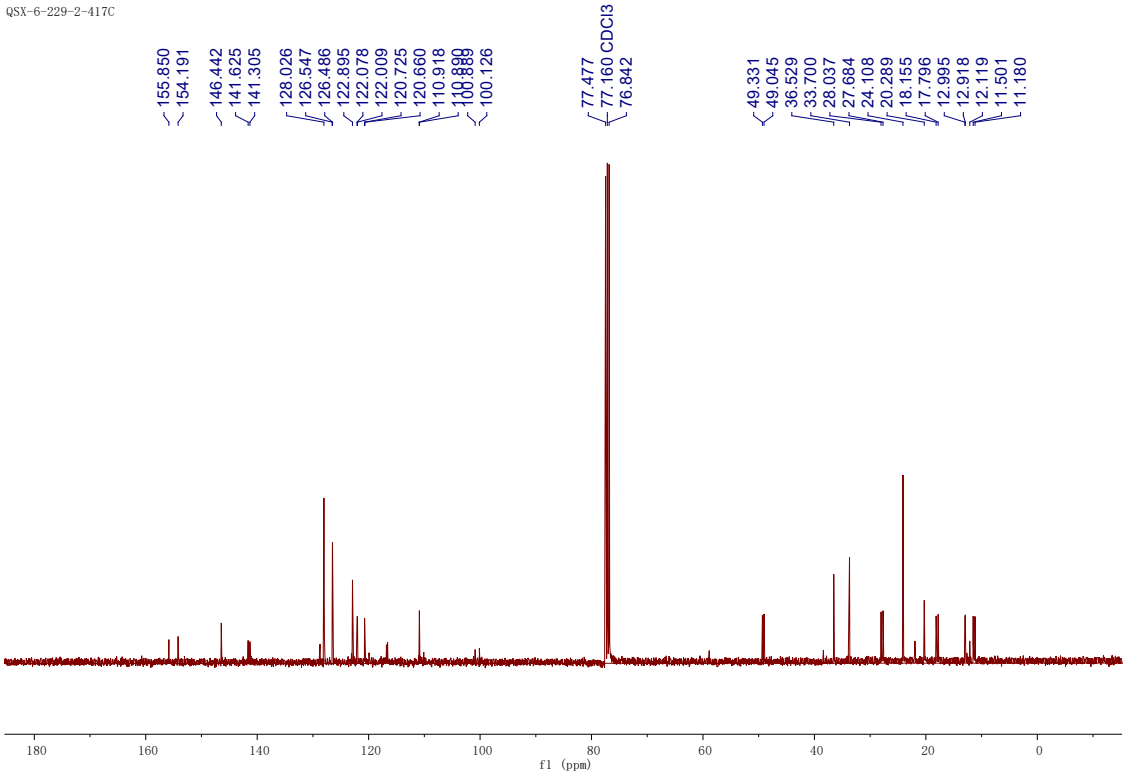
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4c



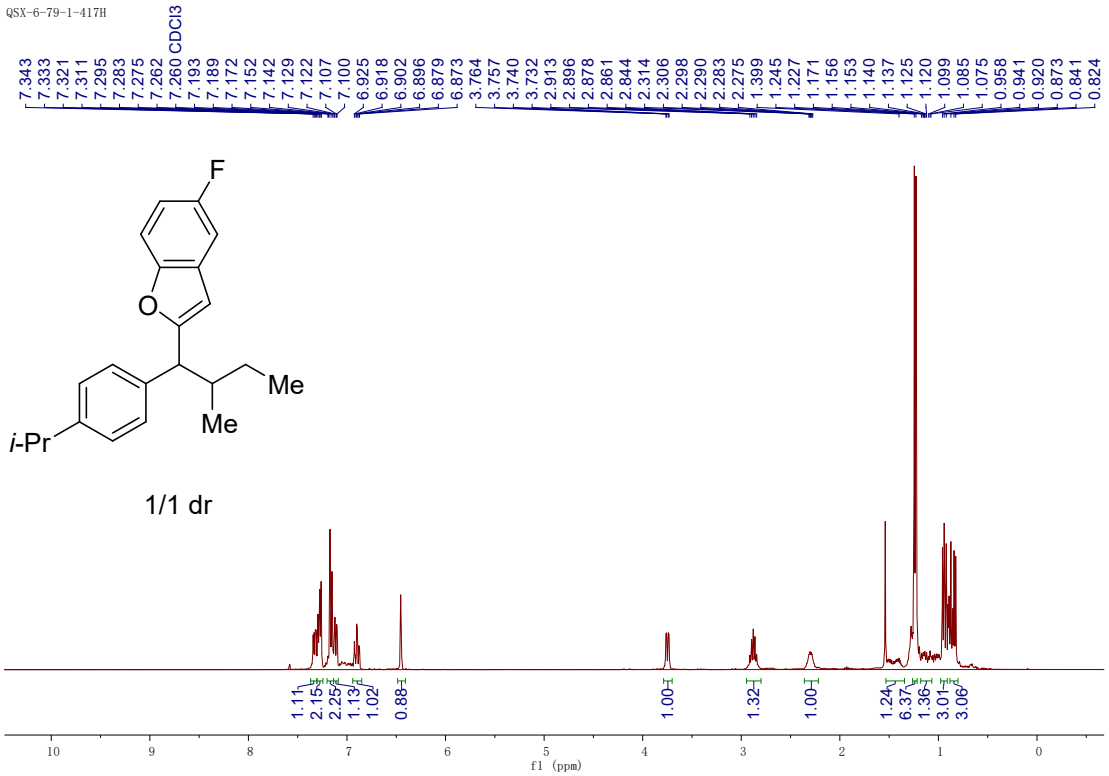
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4d (*see procedure*)



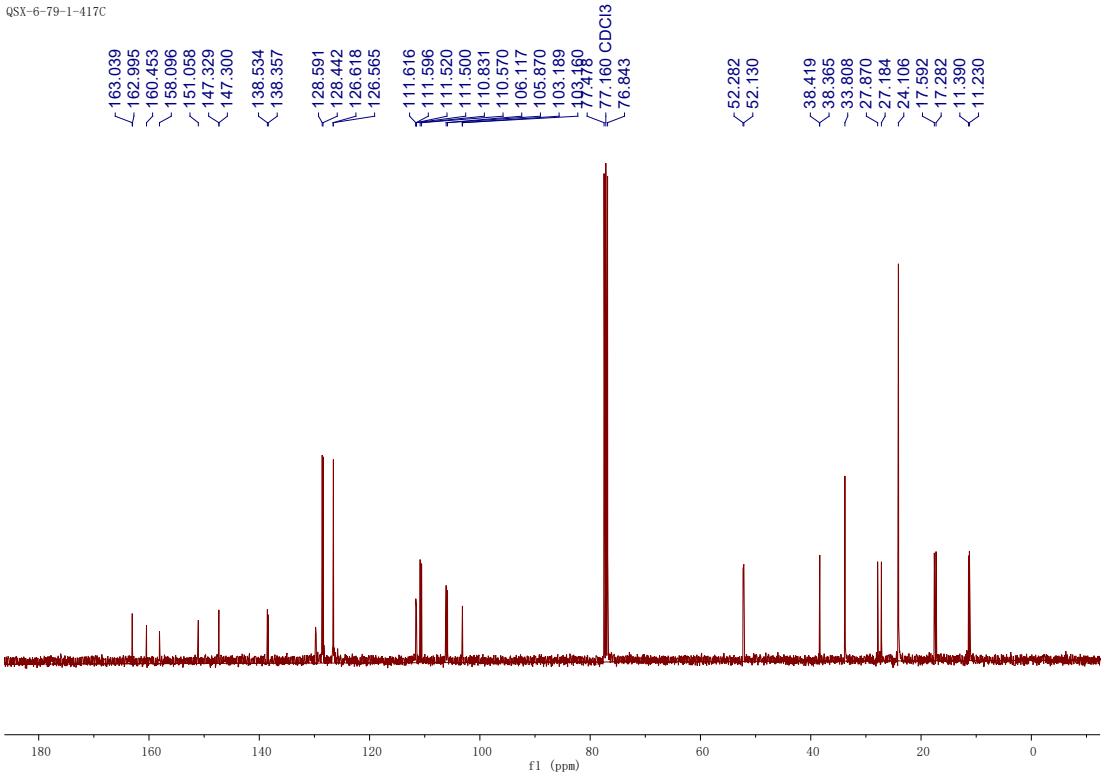
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4d



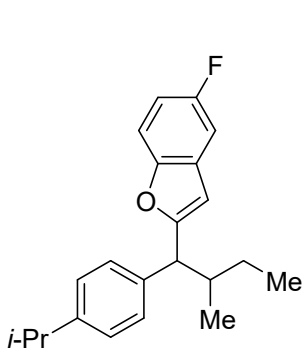
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4e (*see procedure*)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4e

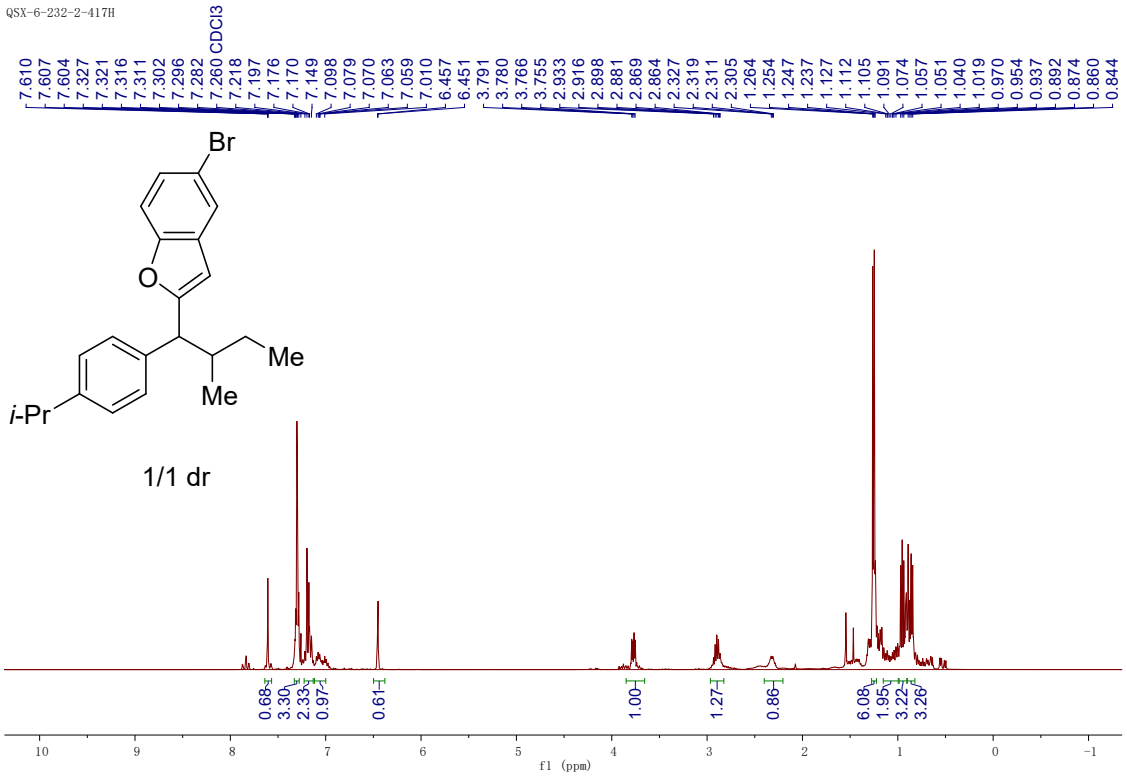


^{19}F NMR (177 MHz, $CDCl_3$) spectrum of 4e

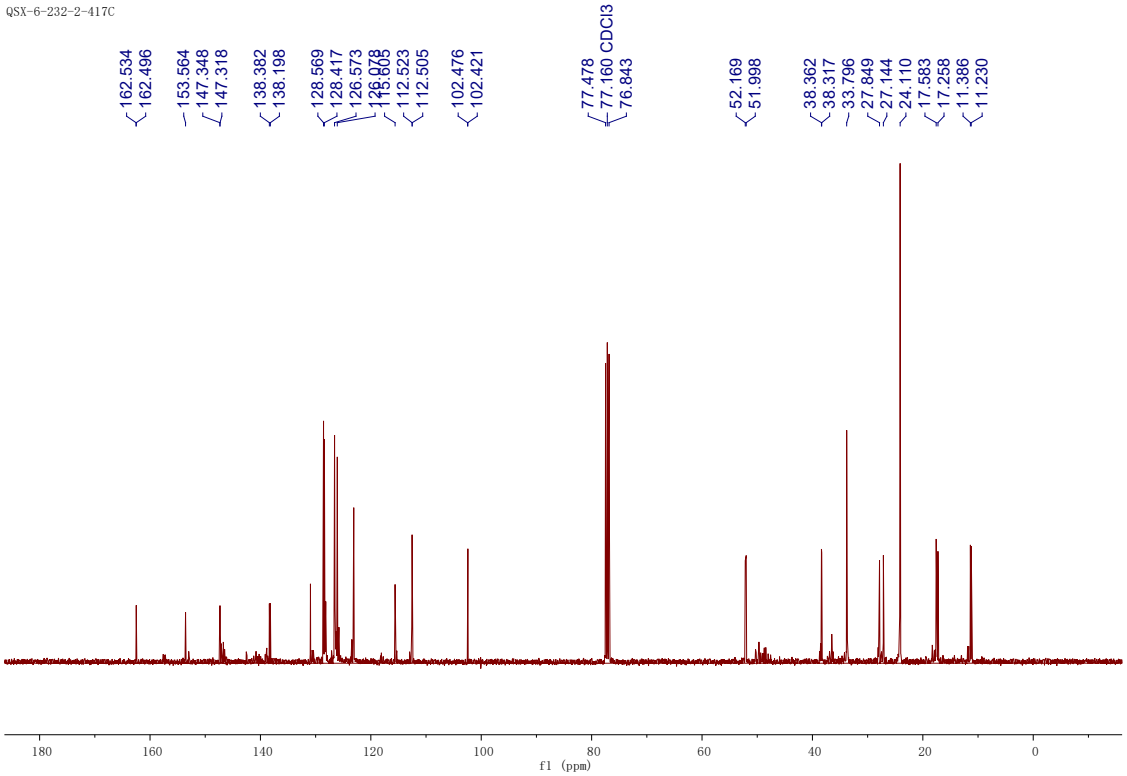


1/1 dr

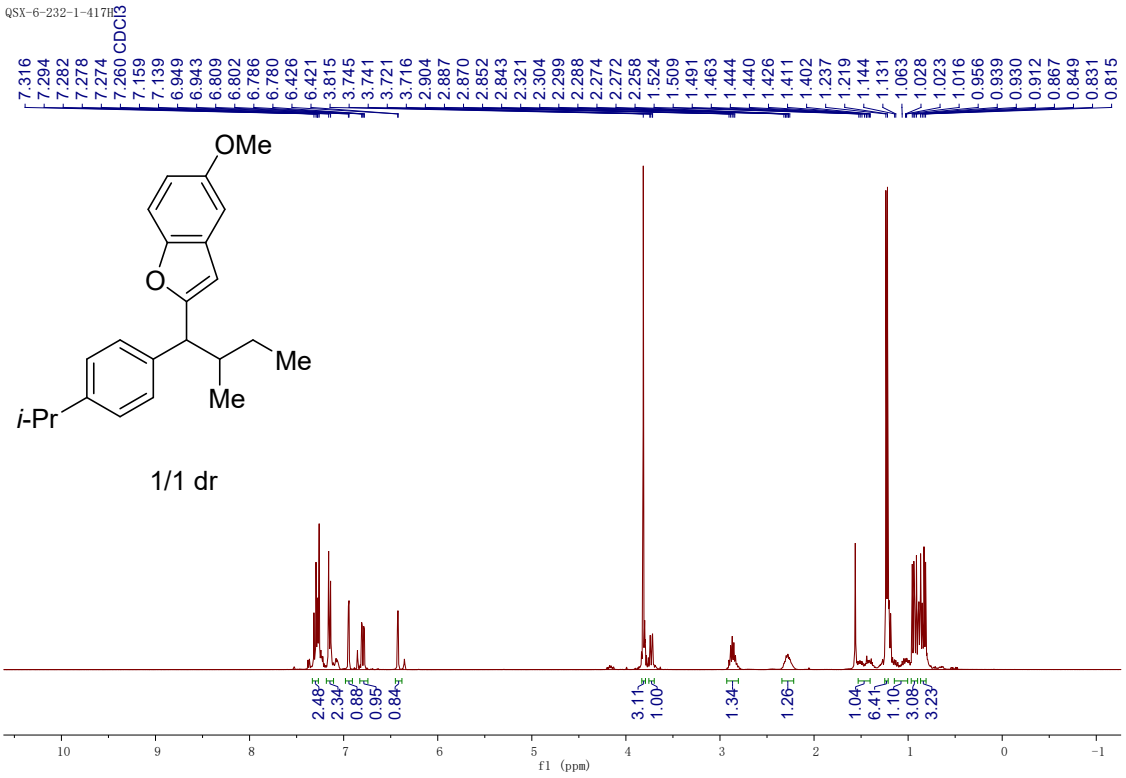
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4f (*see procedure*)



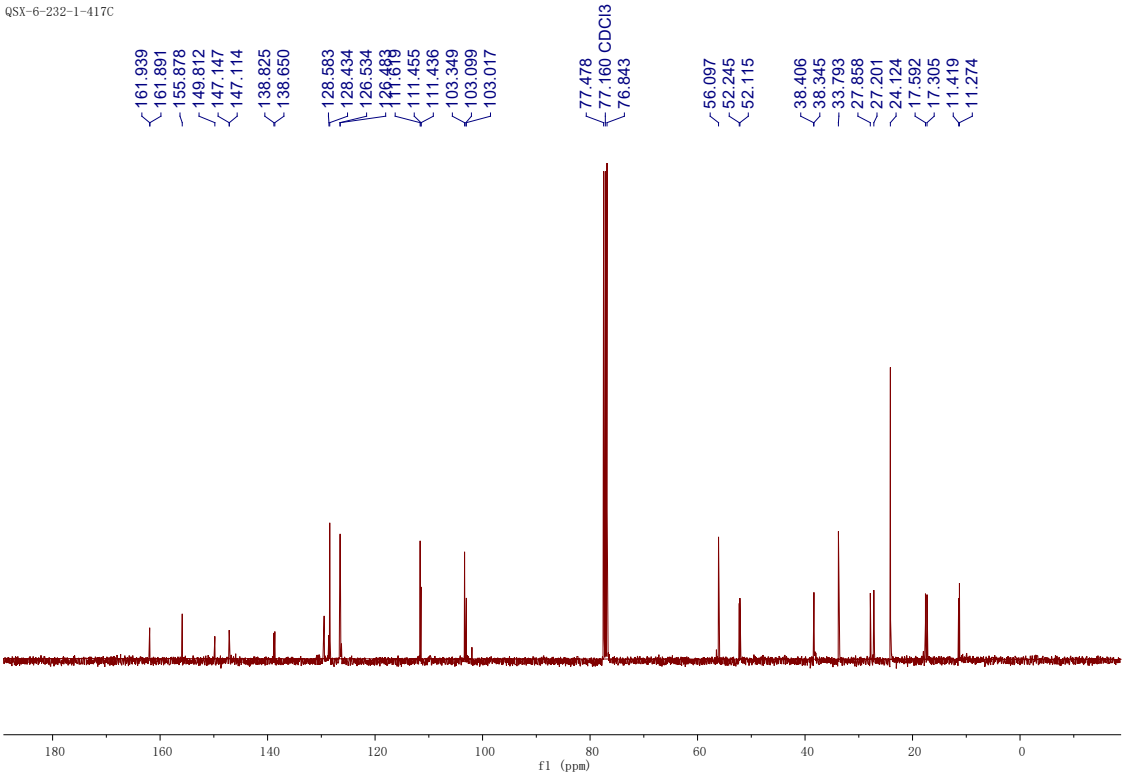
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4f



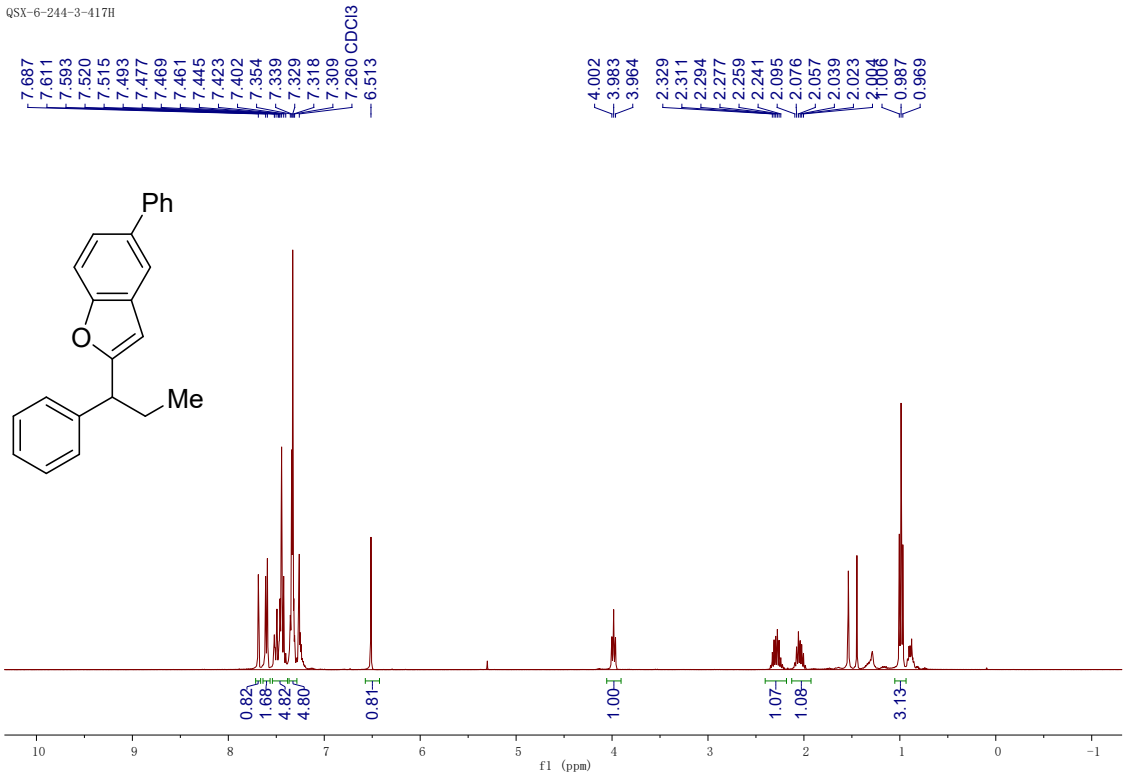
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4g (*see procedure*)



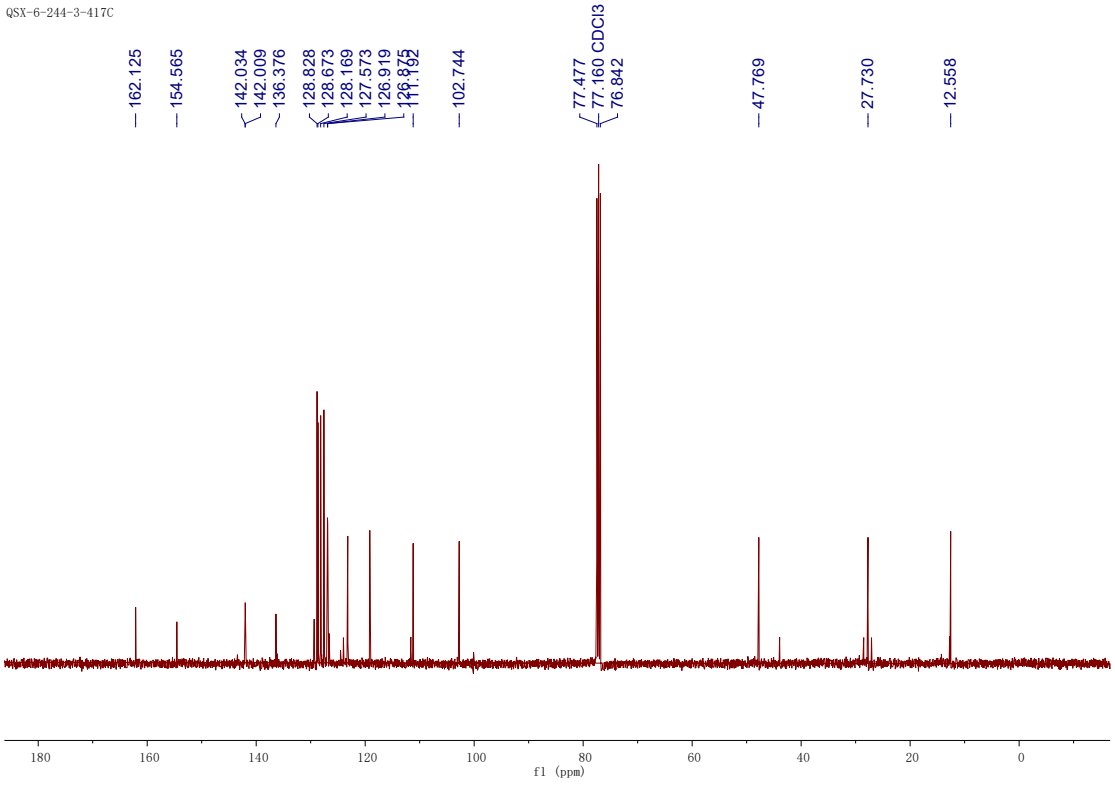
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4g



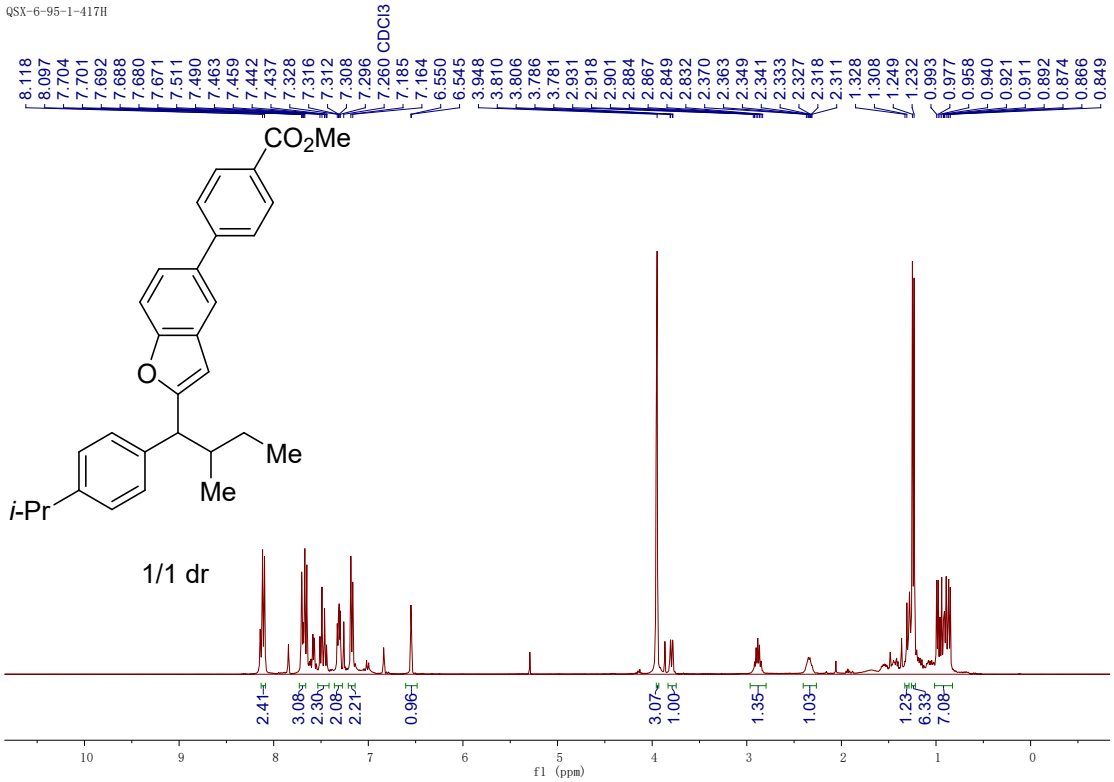
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4h (*see procedure*)



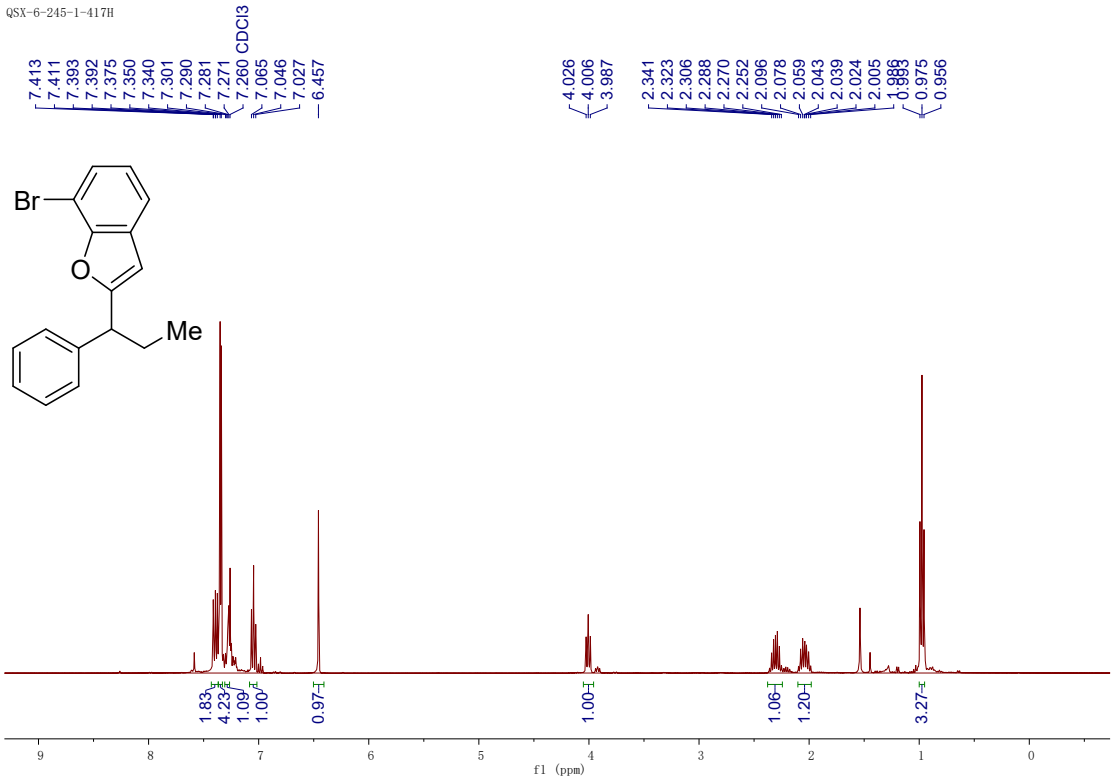
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4h



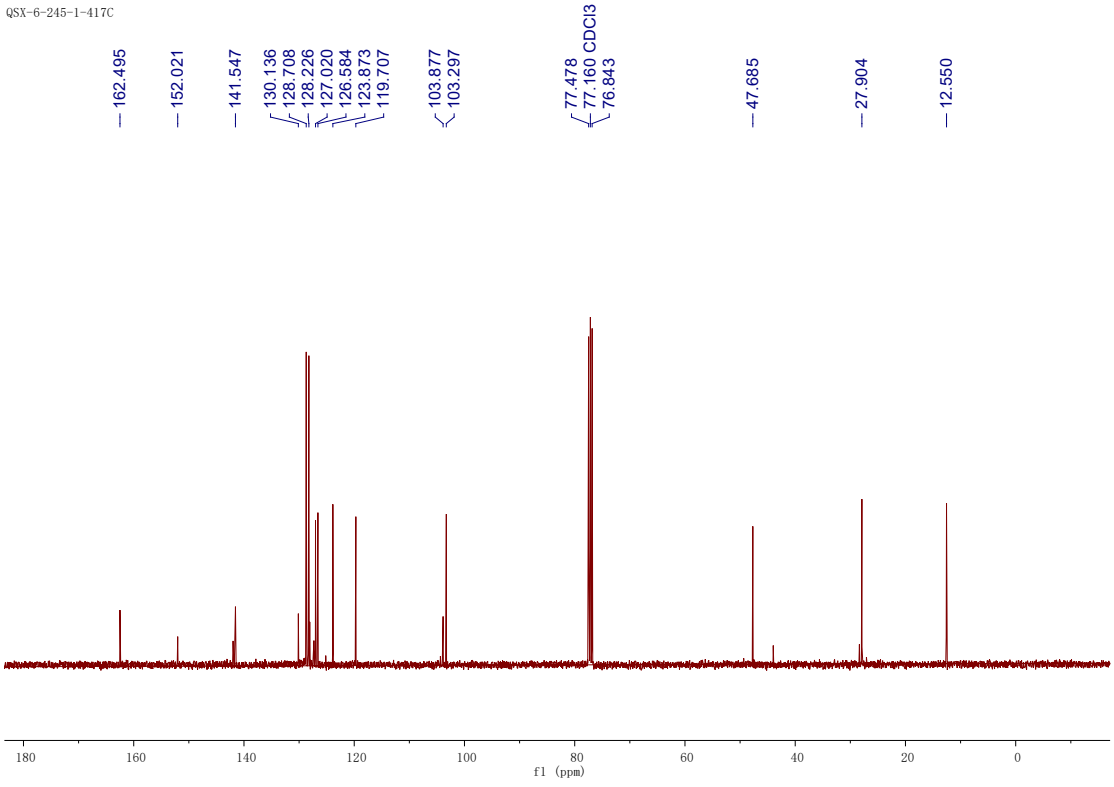
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4i (*see procedure*)



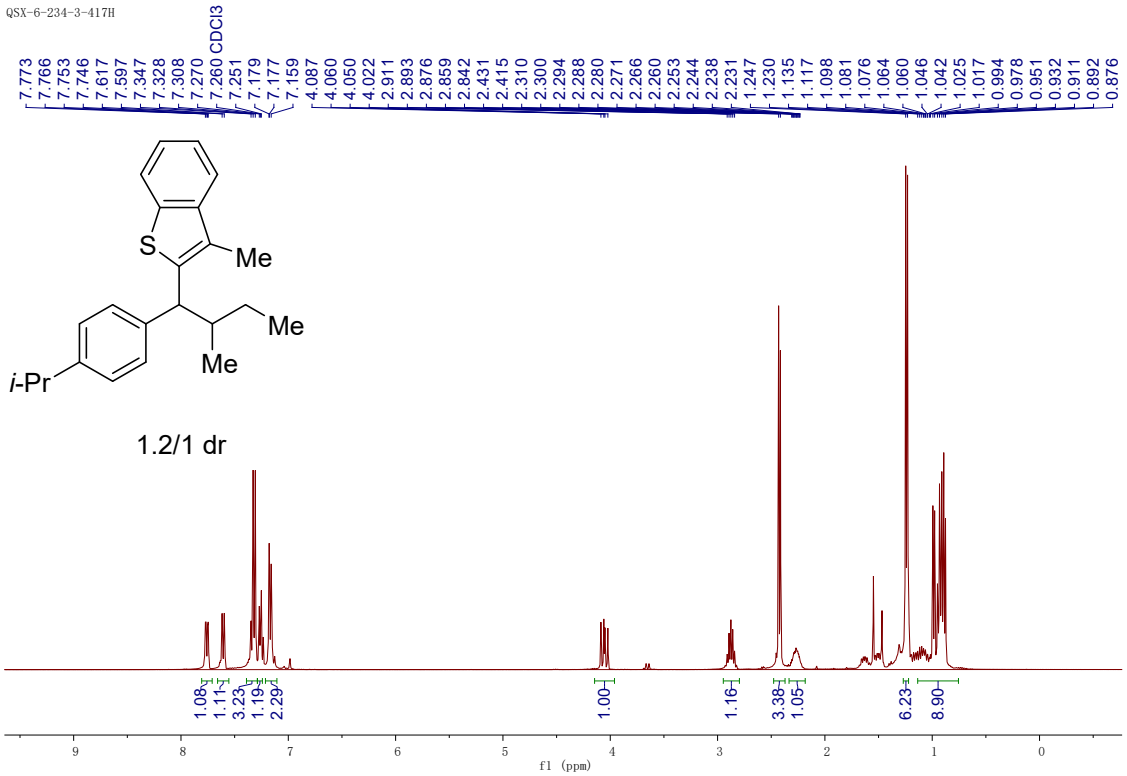
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4j (*see procedure*)



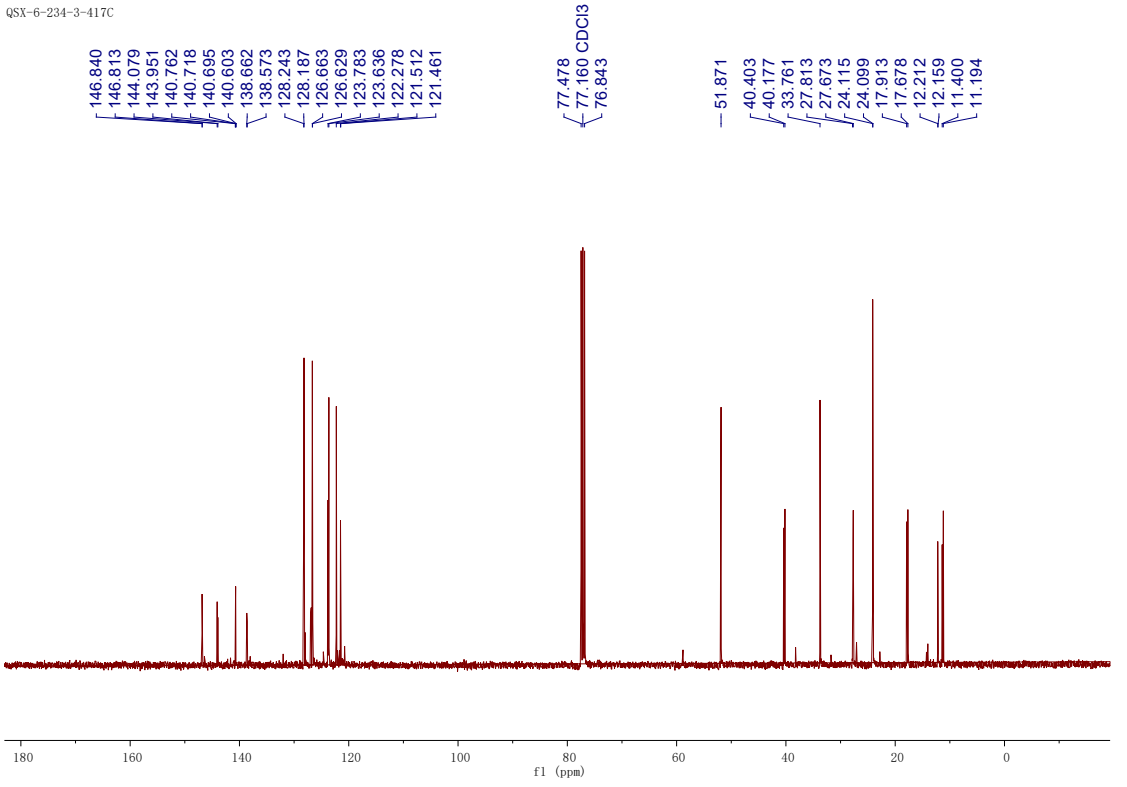
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4j



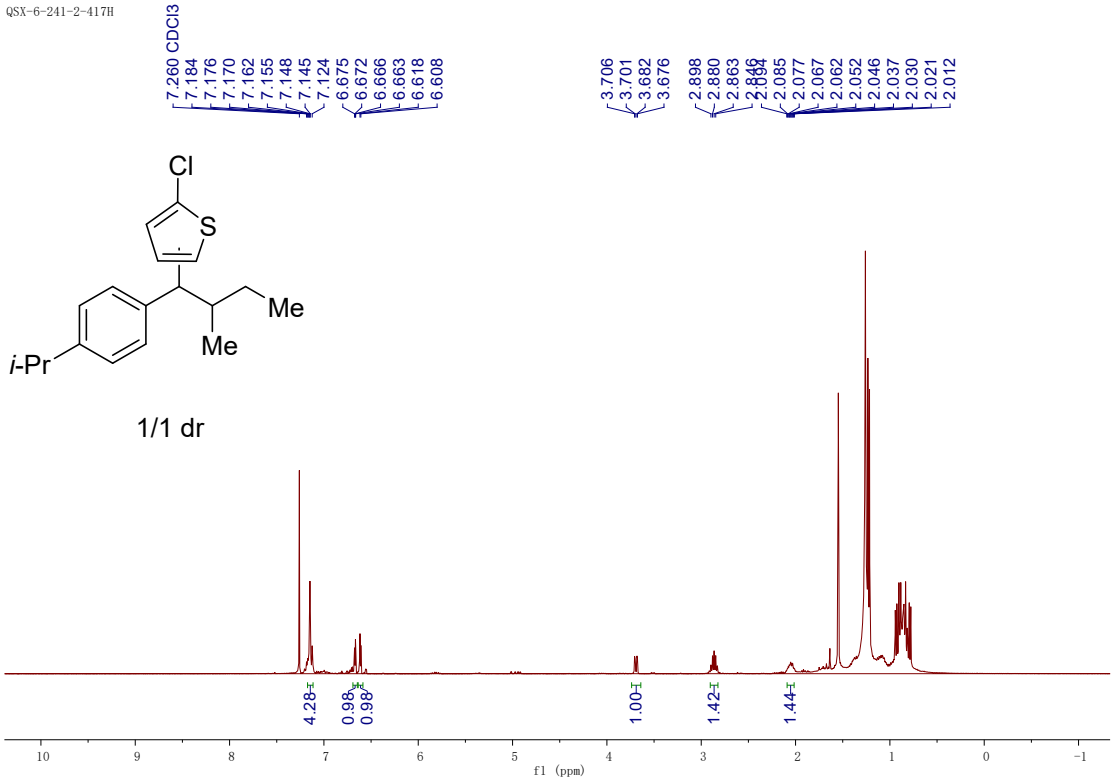
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4k (*see procedure*)



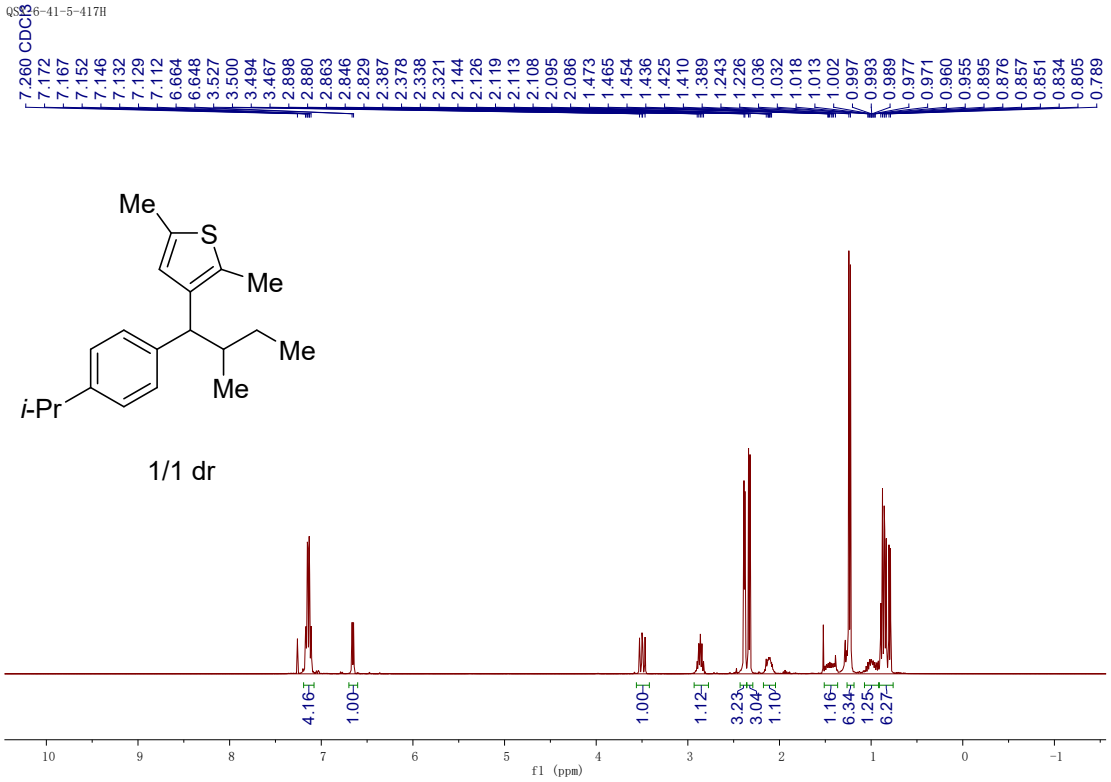
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4k



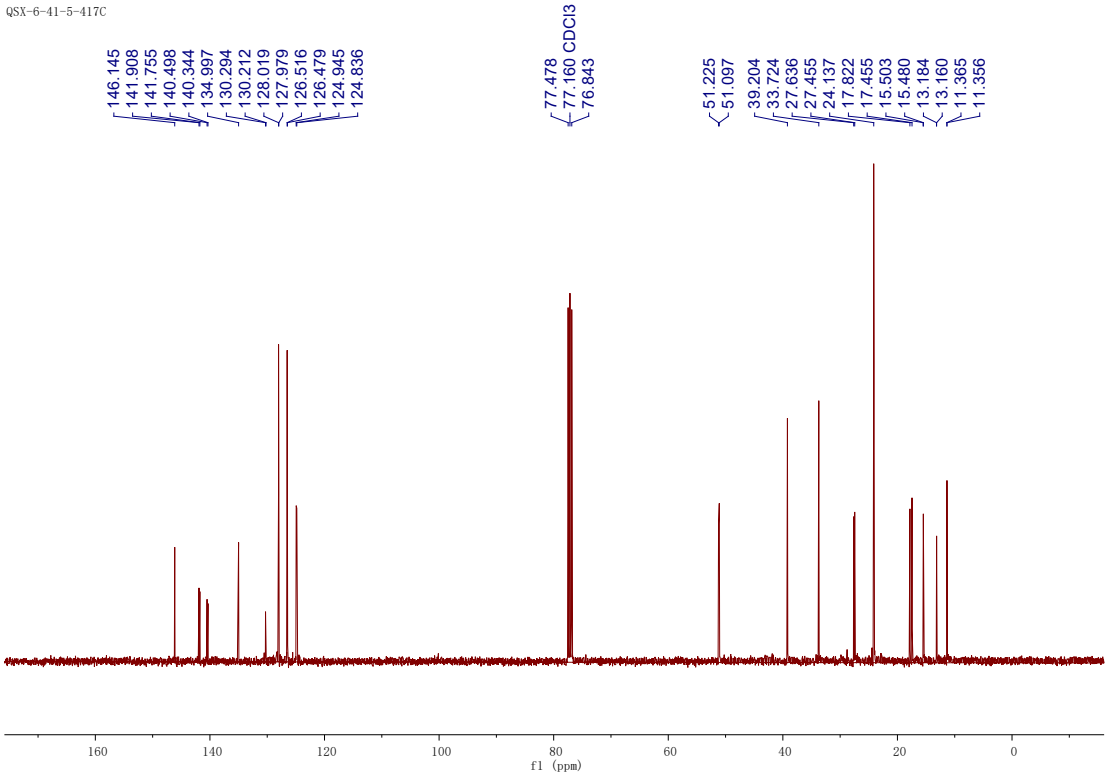
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4l (*see procedure*)



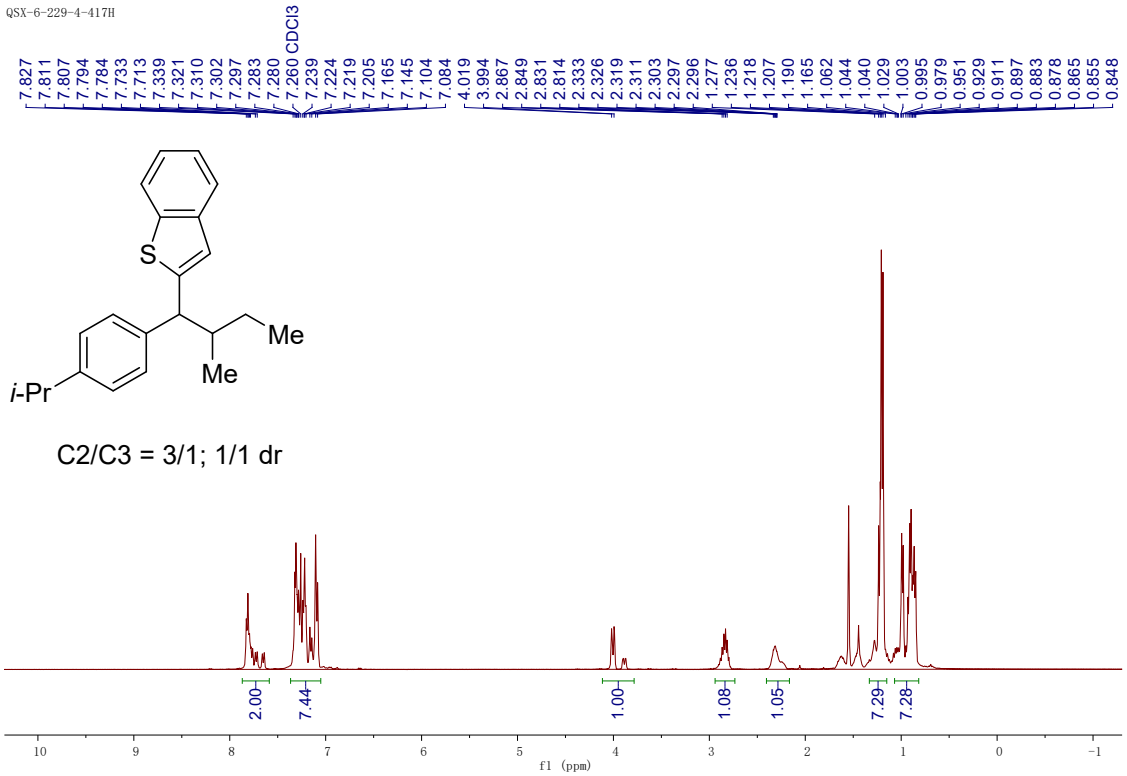
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4m (*see procedure*)



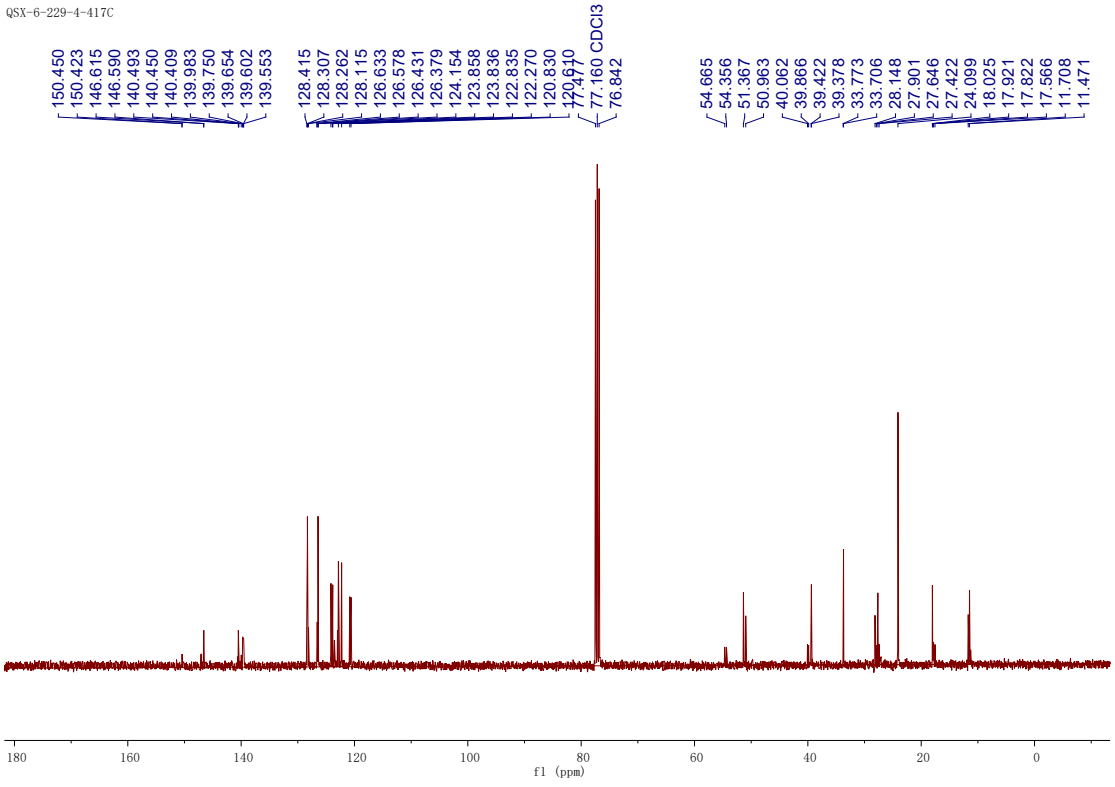
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4m



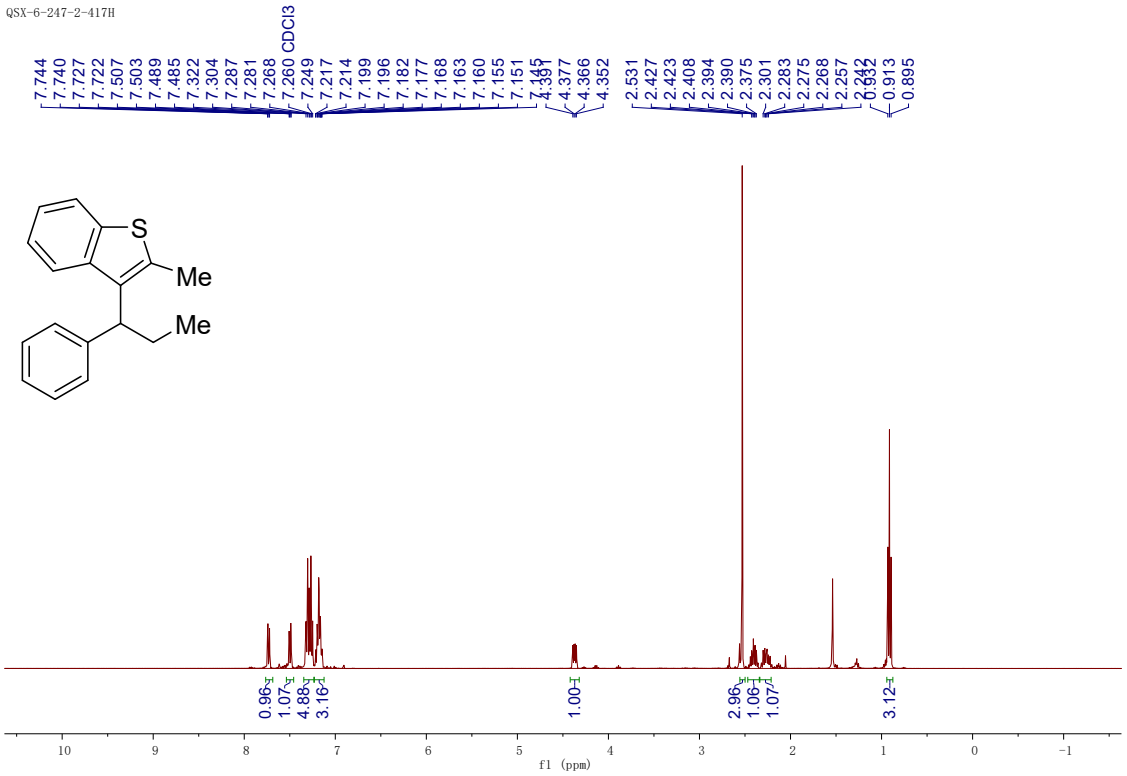
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4n (*see procedure*)



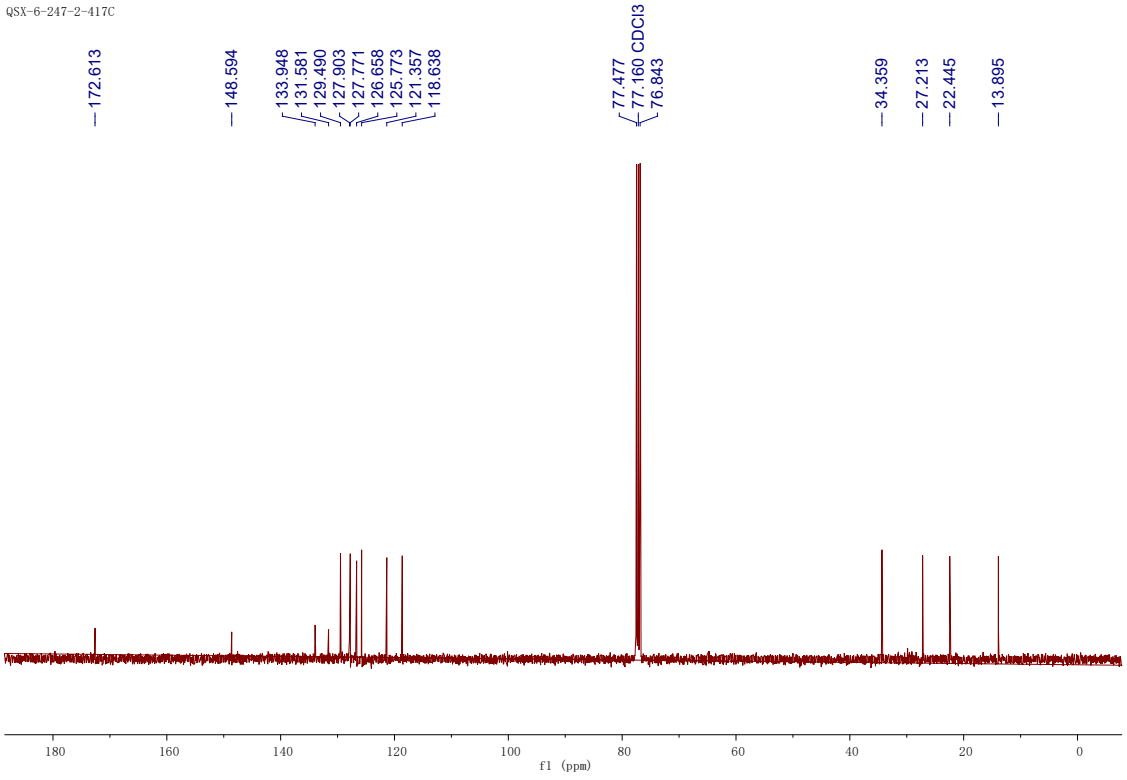
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4n



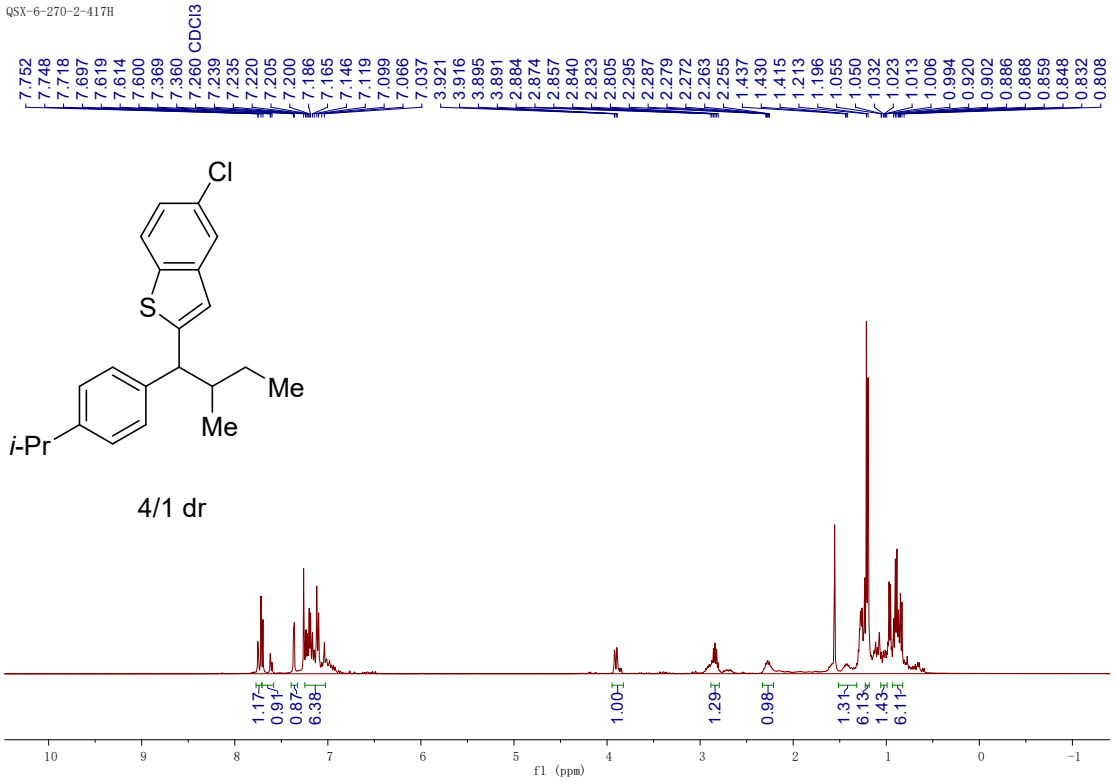
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4o (*see procedure*)



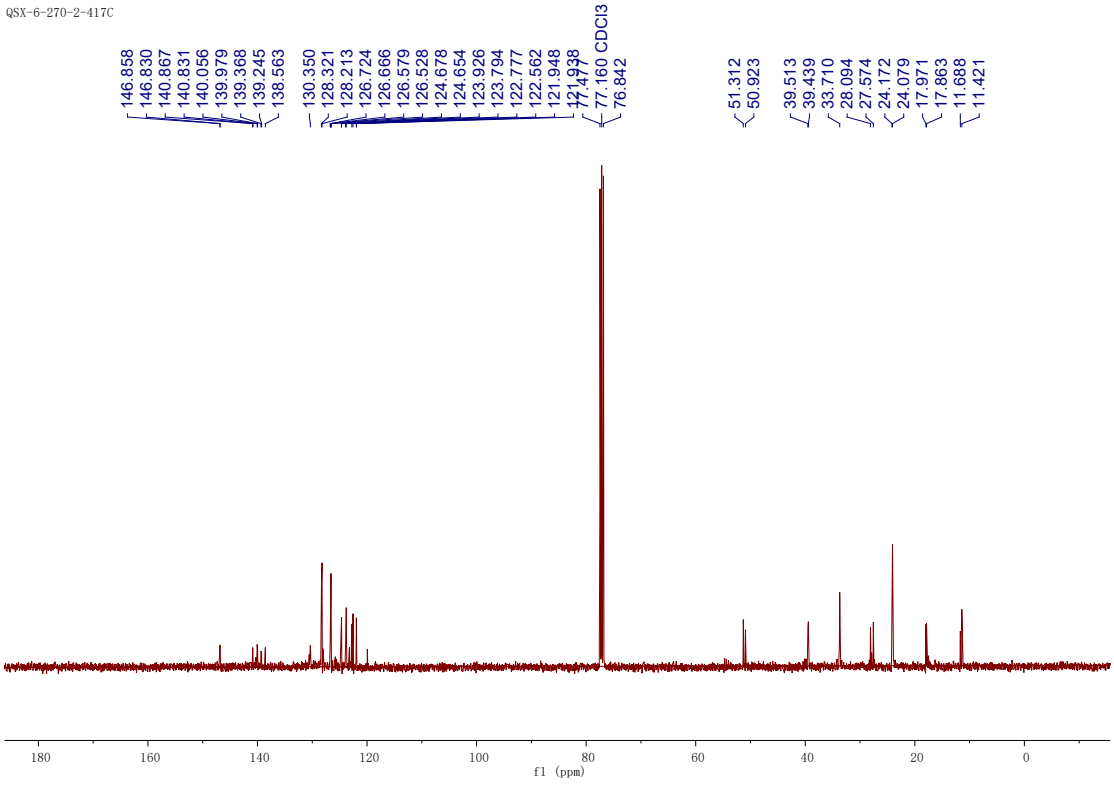
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4o



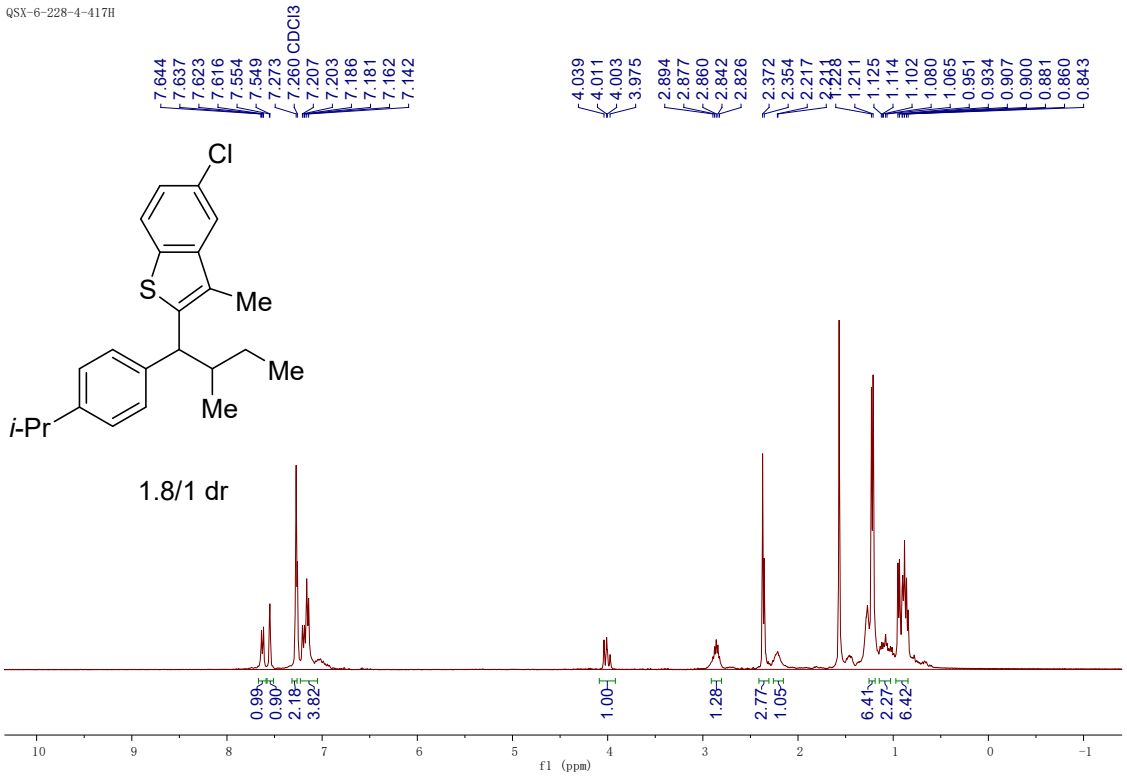
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4p (*see procedure*)



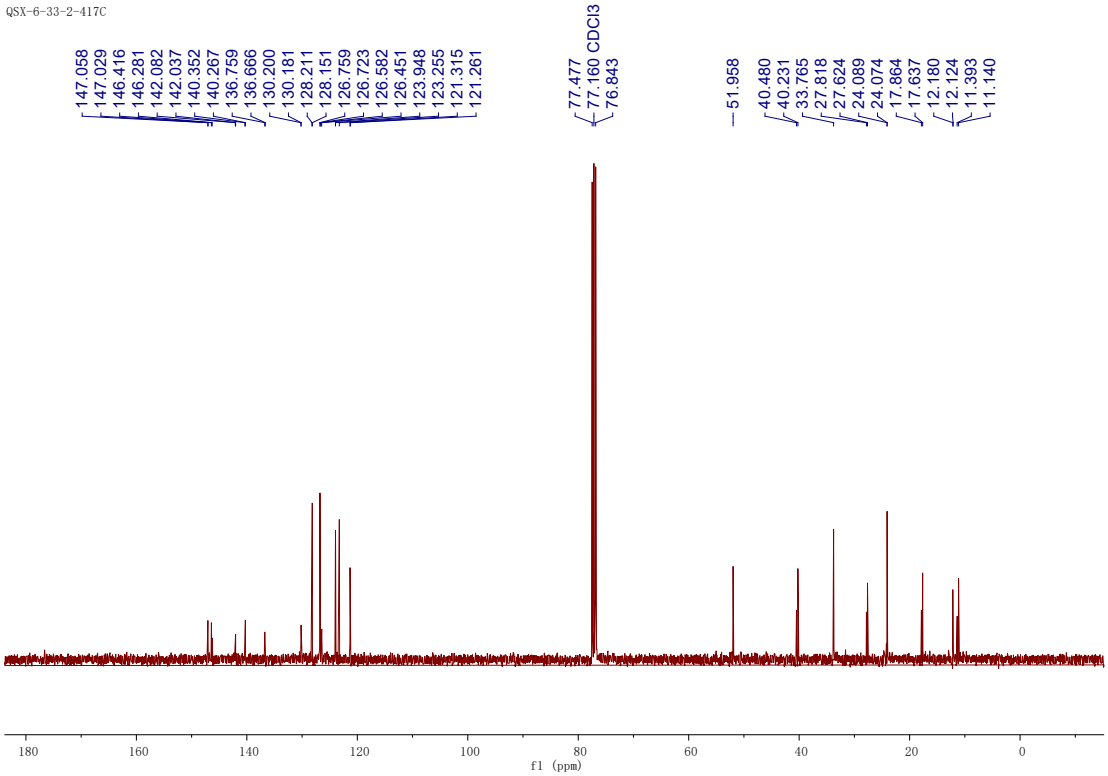
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4p



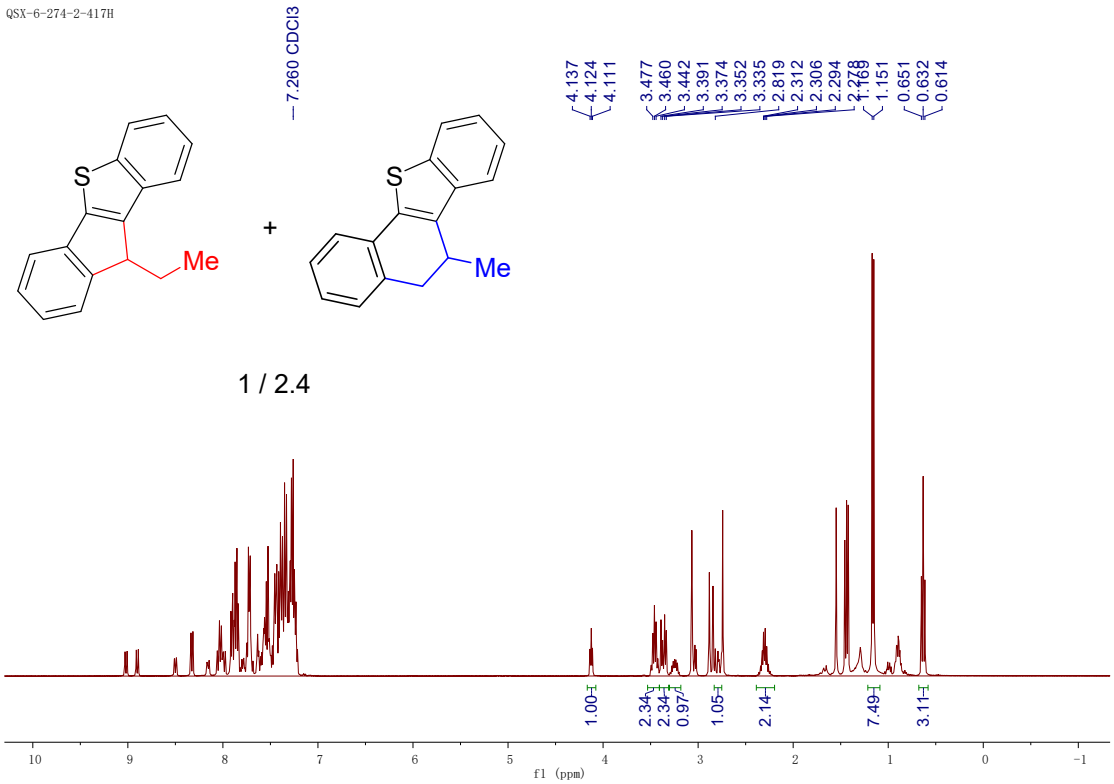
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4q (*see procedure*)



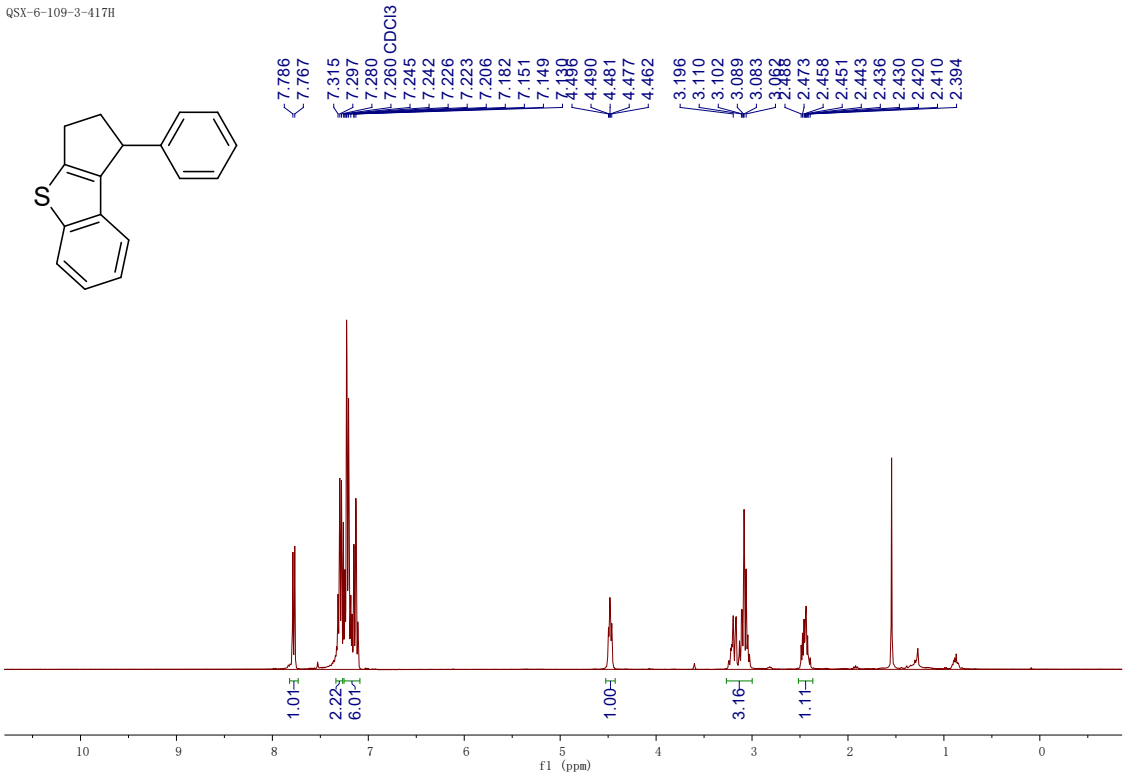
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4q



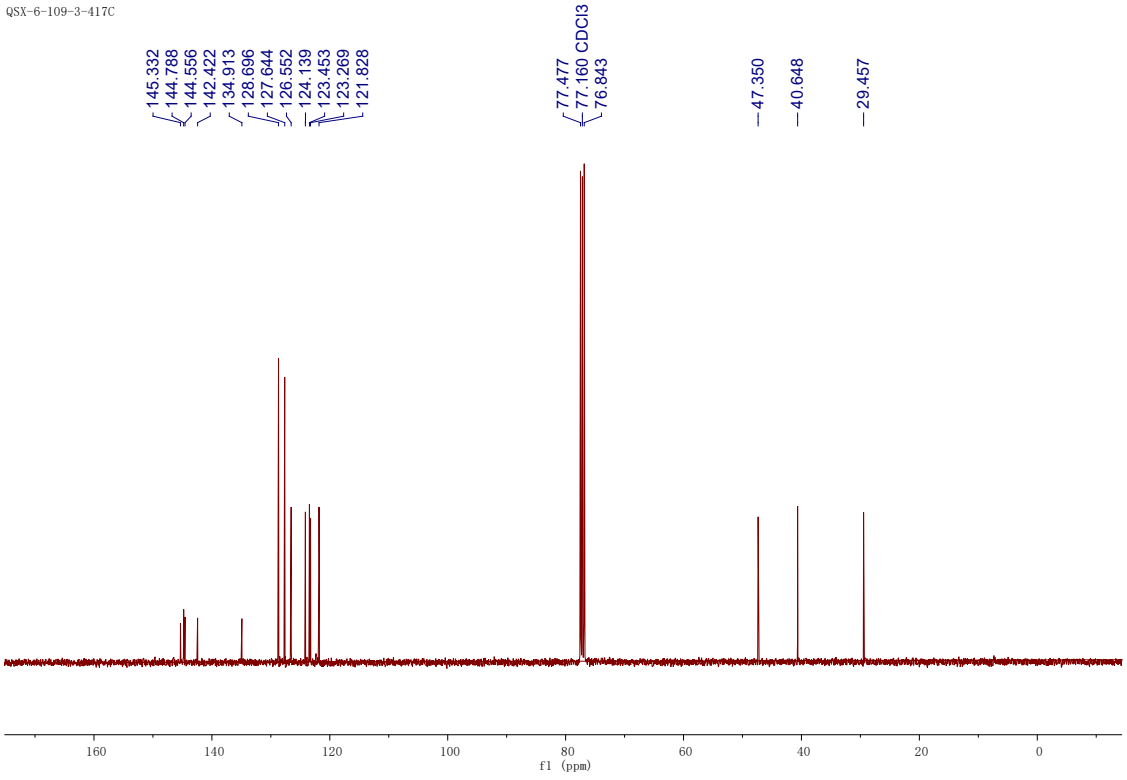
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7a (*see procedure*)



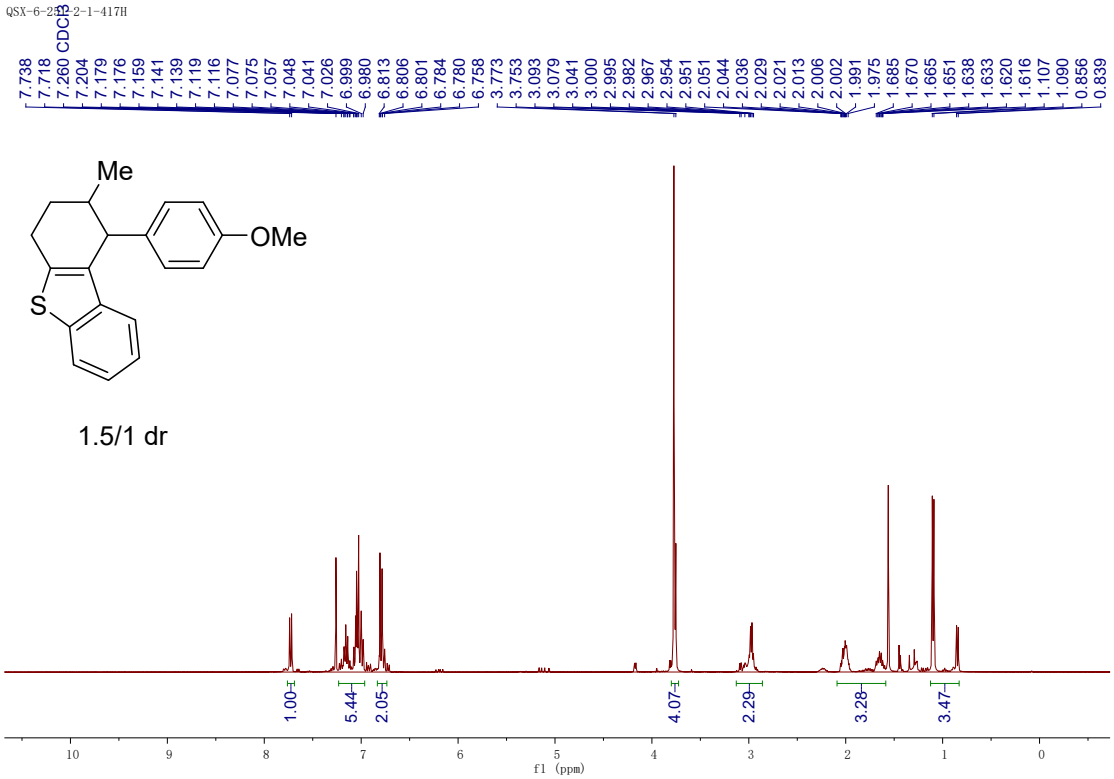
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7b (*see procedure*)



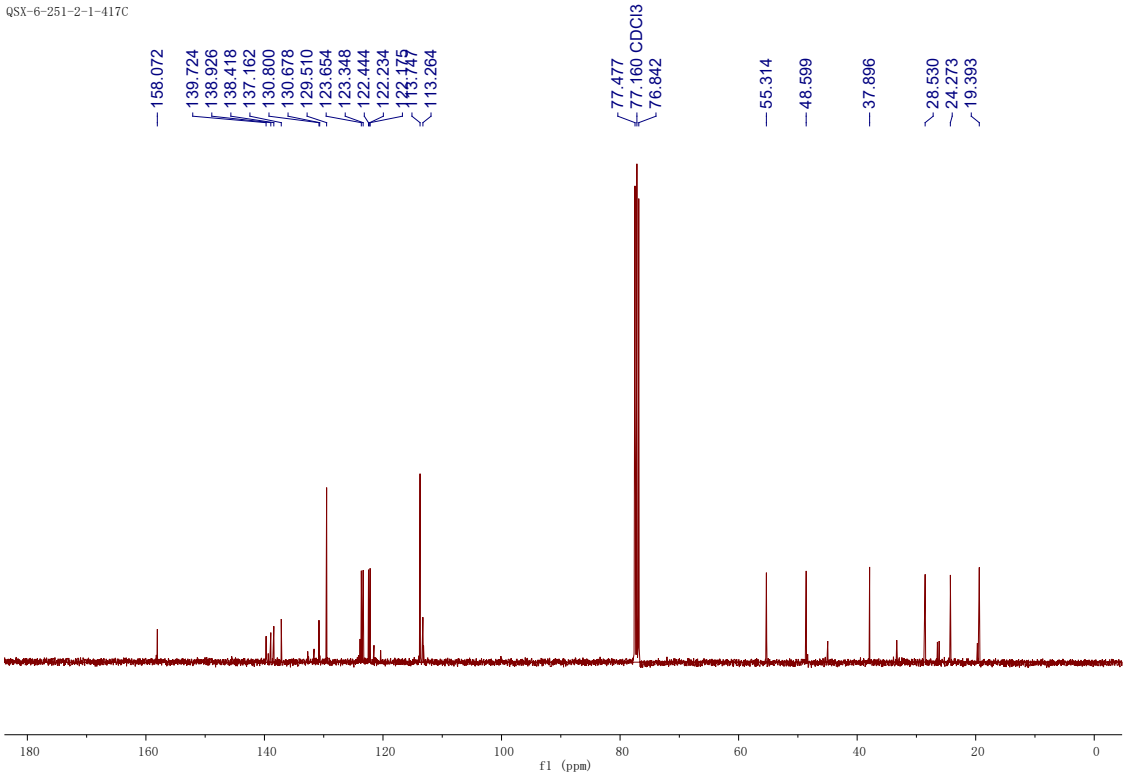
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7b



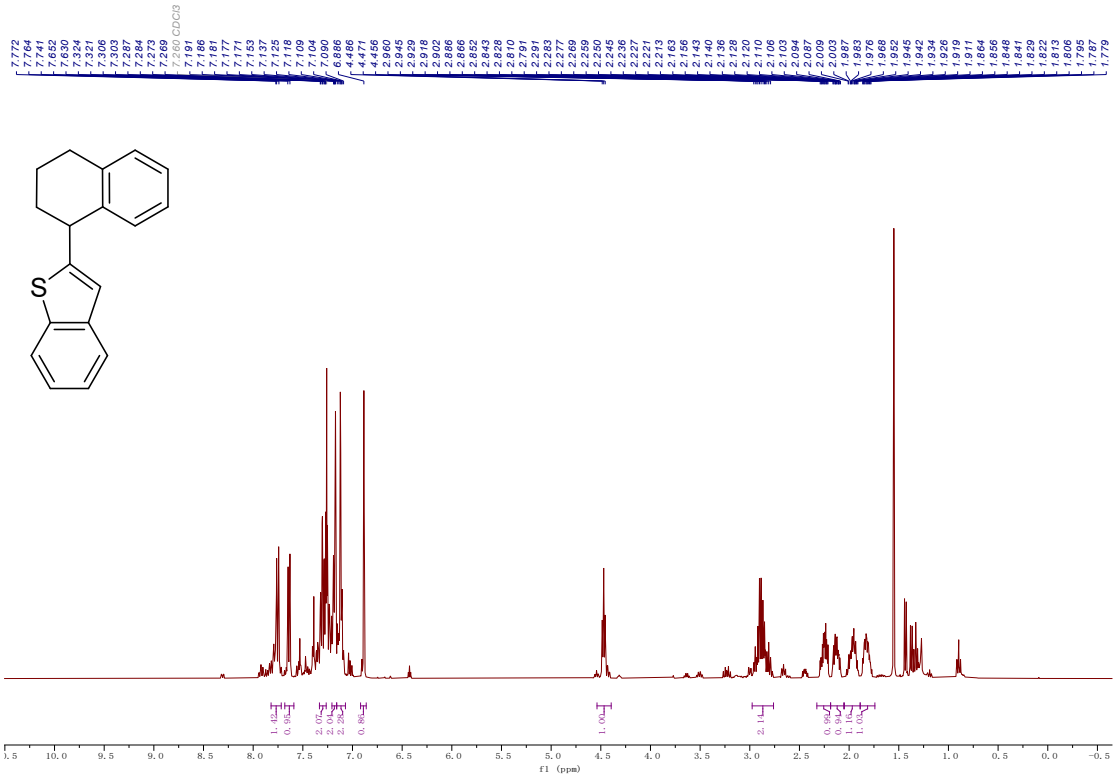
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7c (*see procedure*)



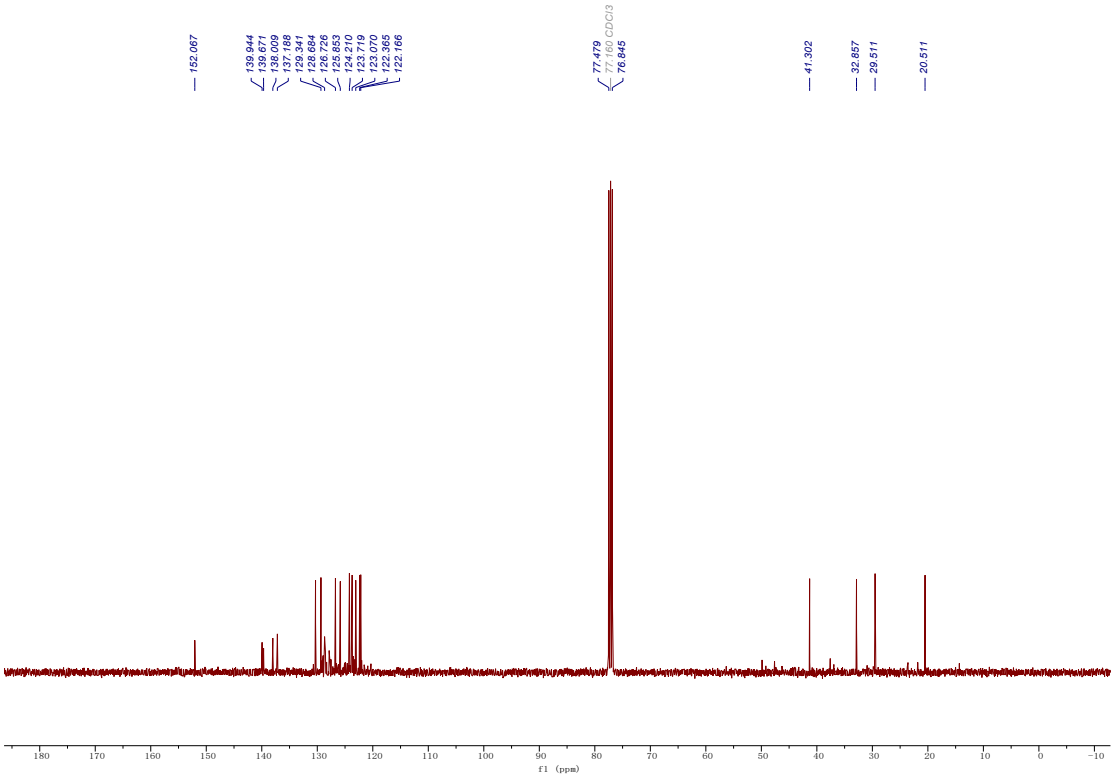
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7c



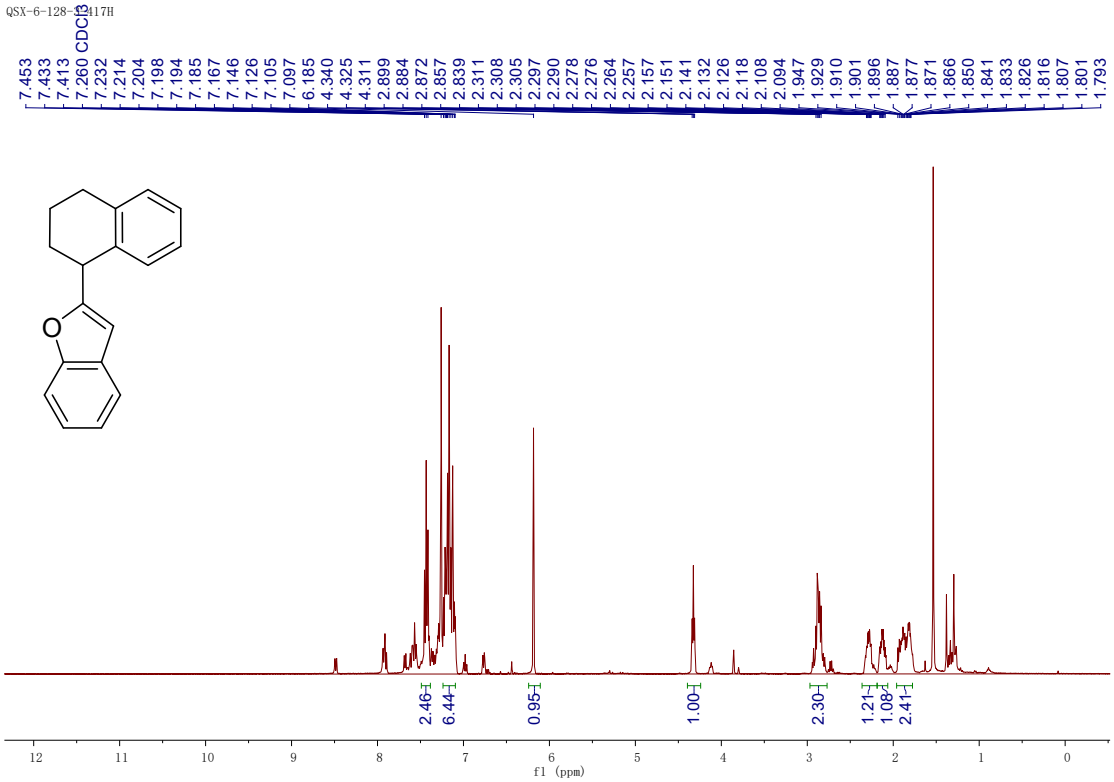
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7d (*see procedure*)



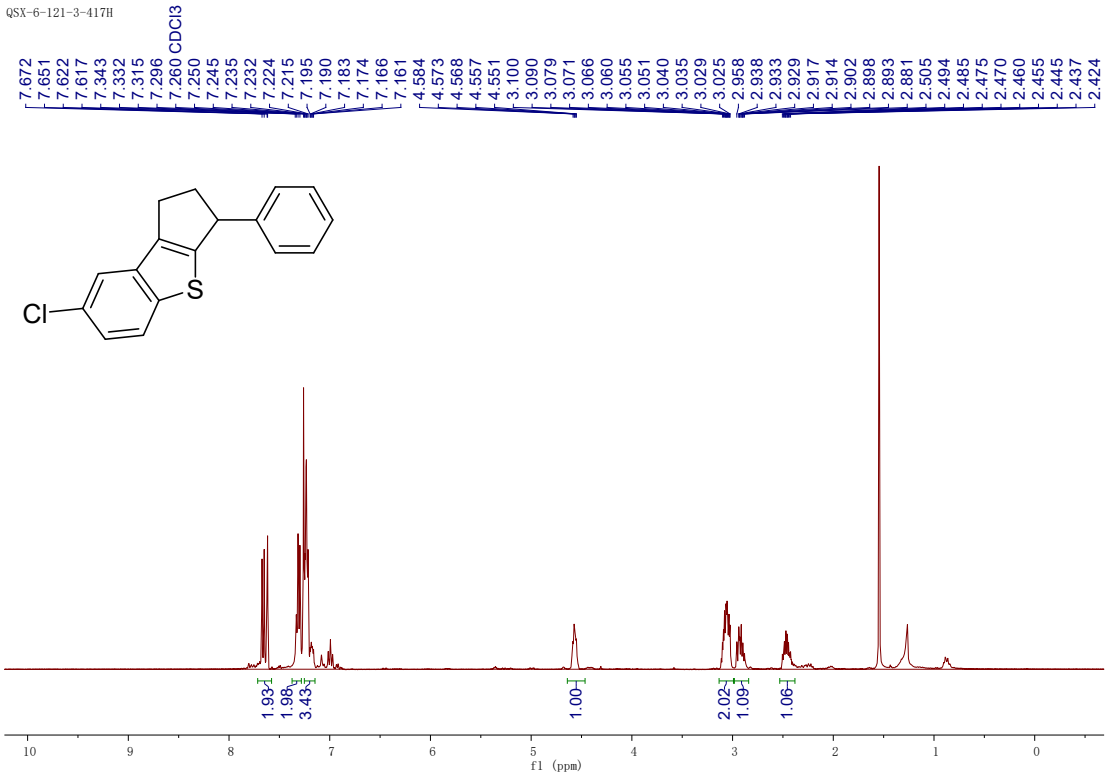
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7d



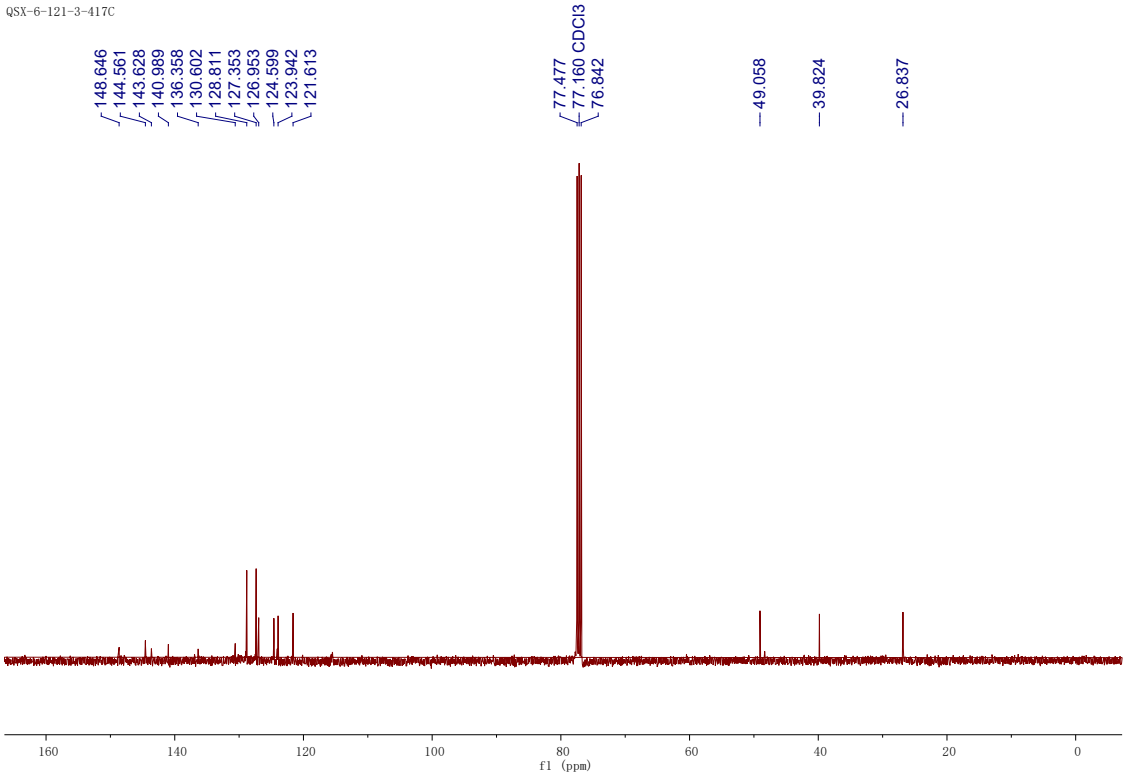
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7e (*see procedure*)



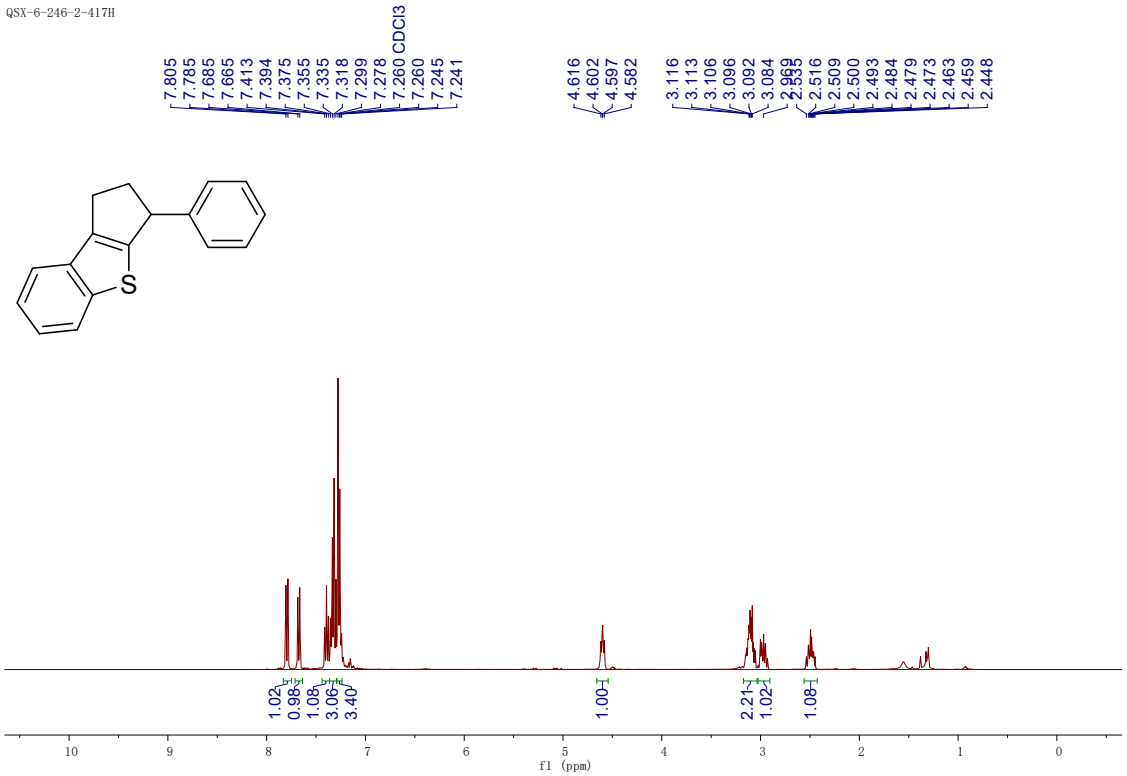
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7f (*see procedure*)



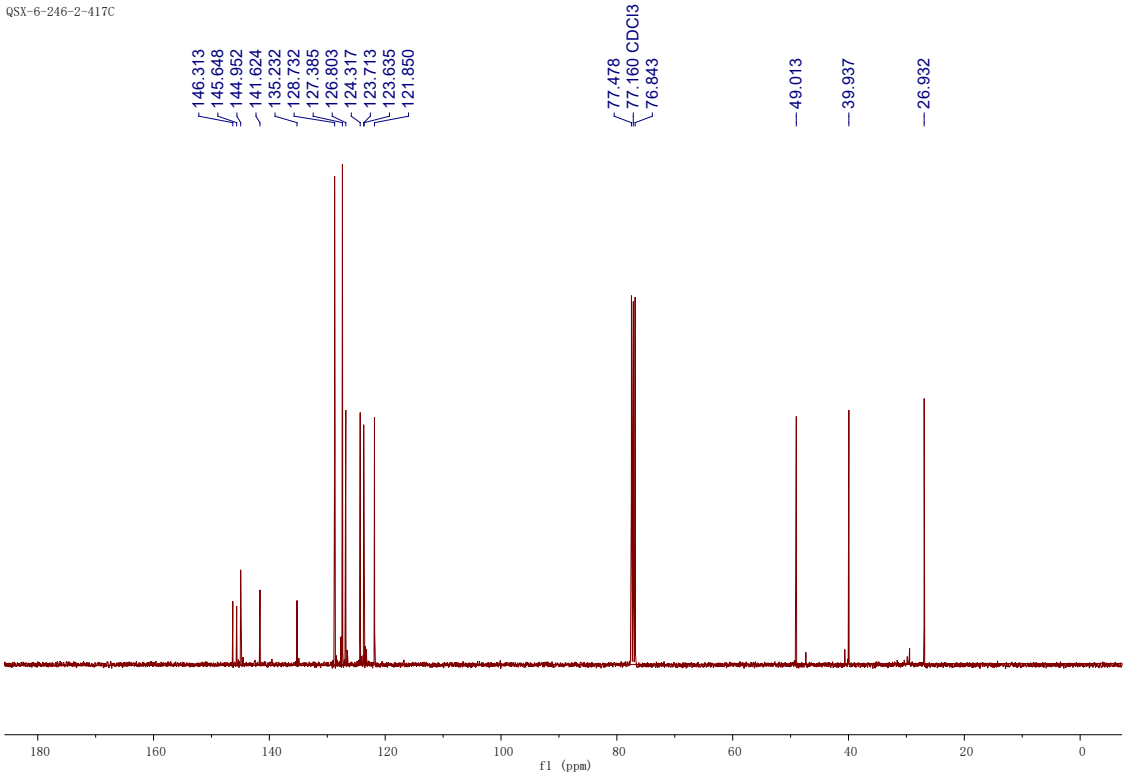
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7f



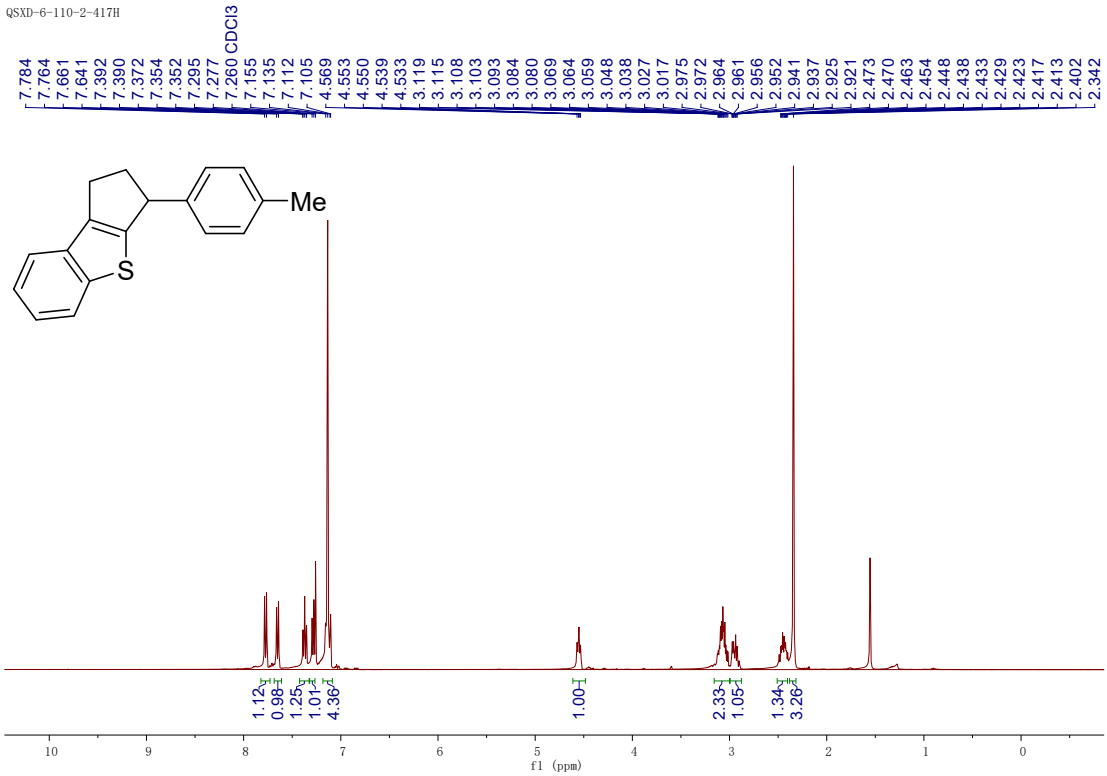
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7g (*see procedure*)



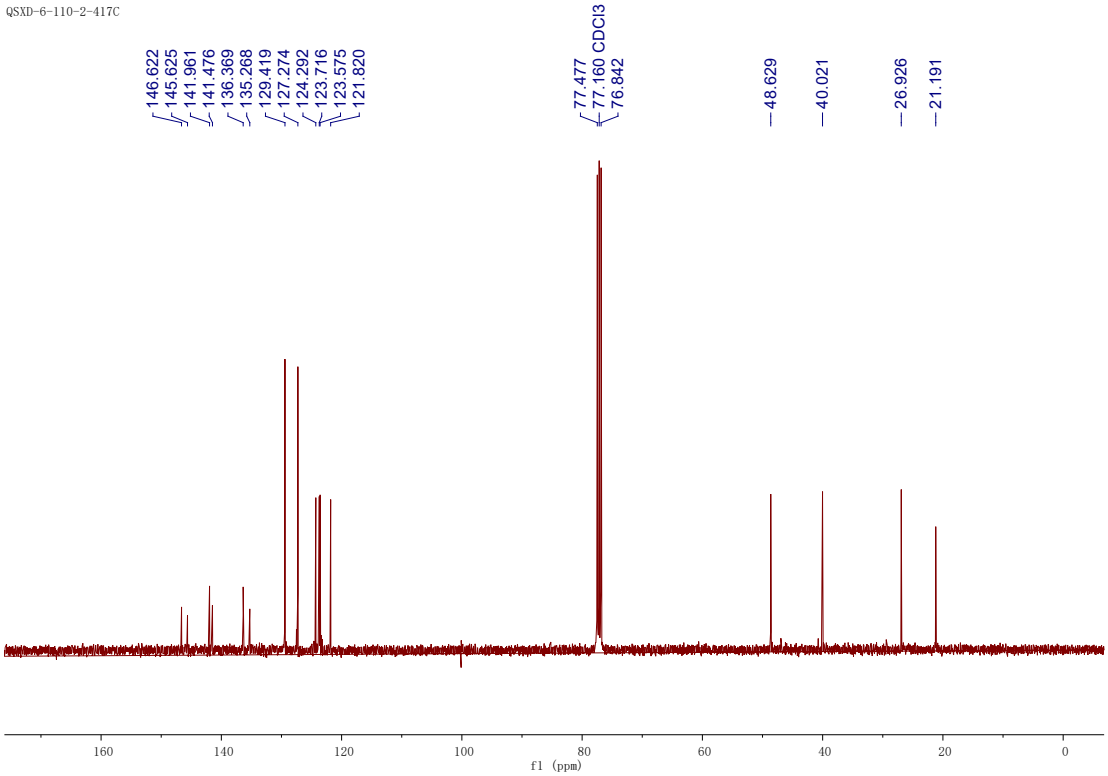
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7g



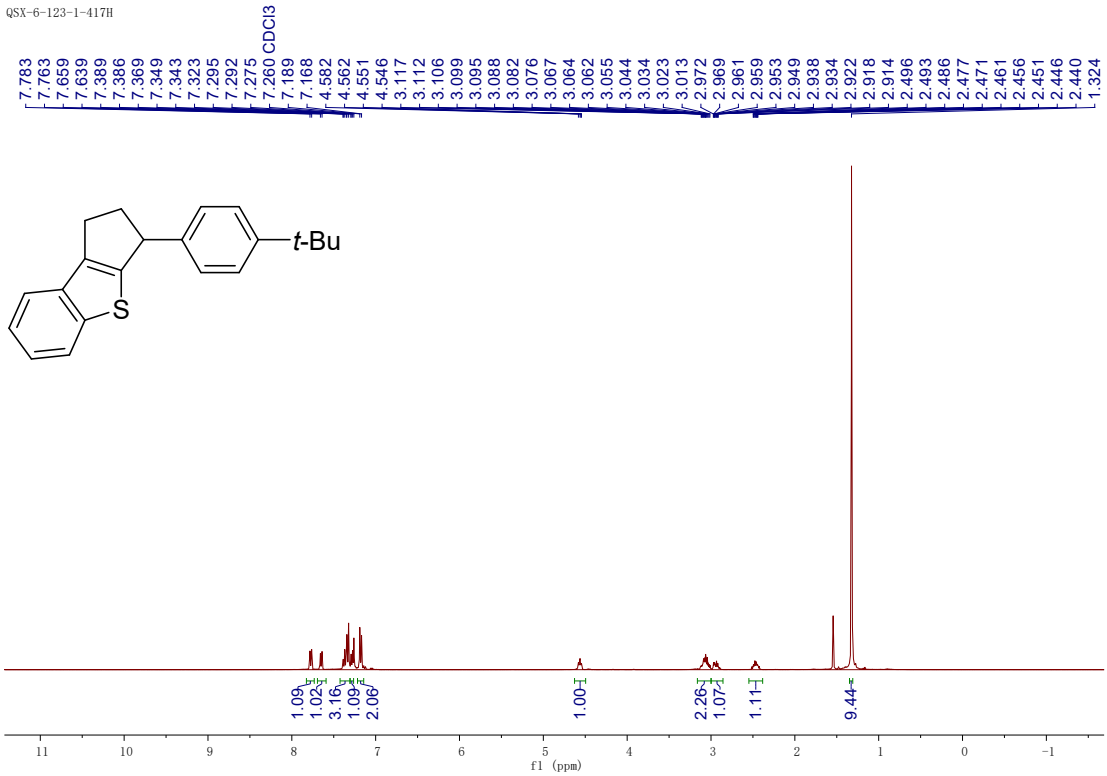
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7h (*see procedure*)



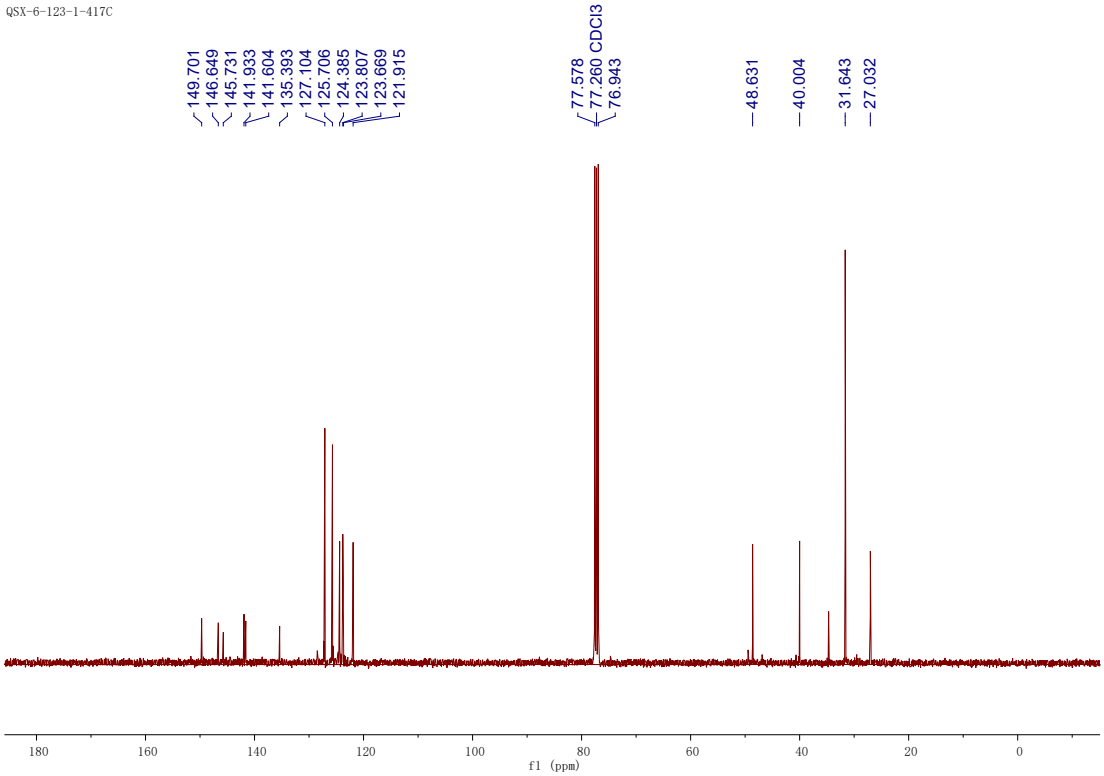
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7h



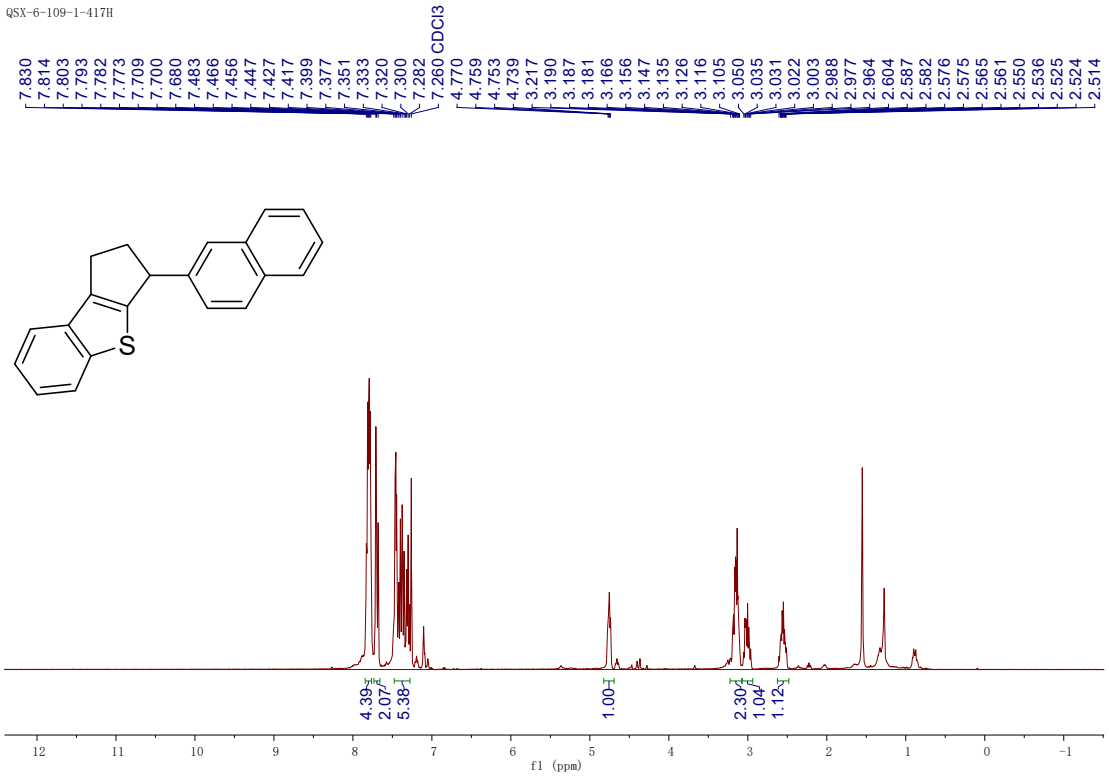
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7i (*see procedure*)



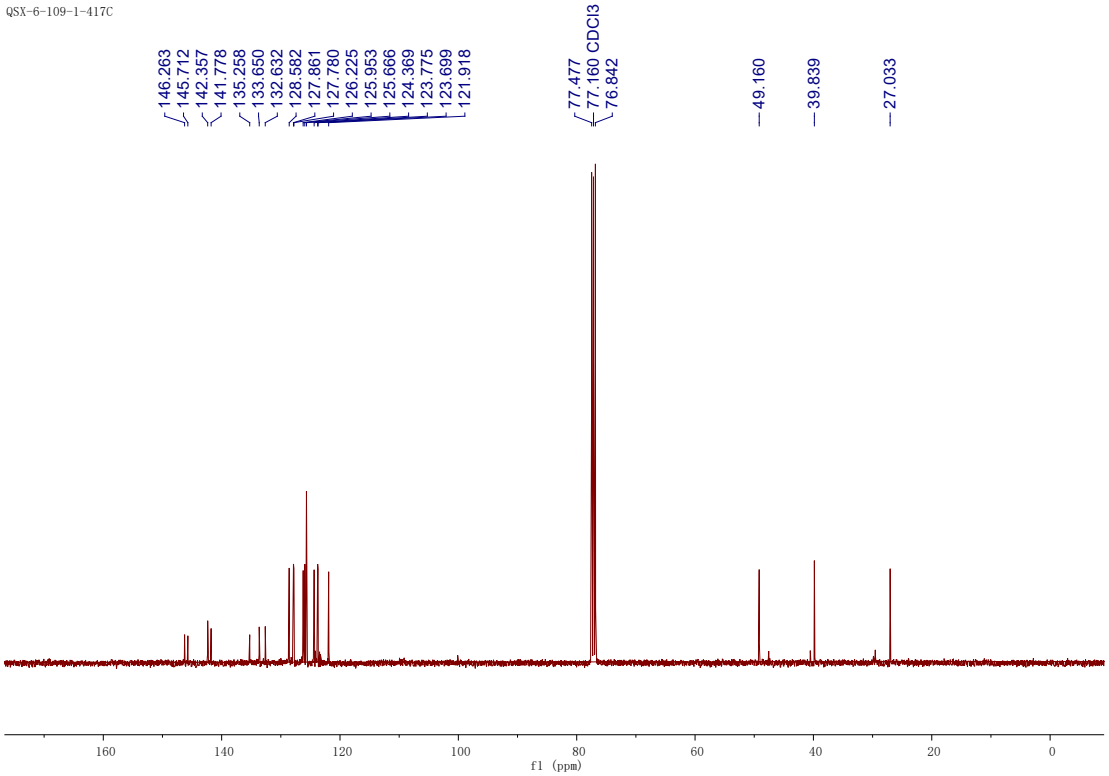
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7i



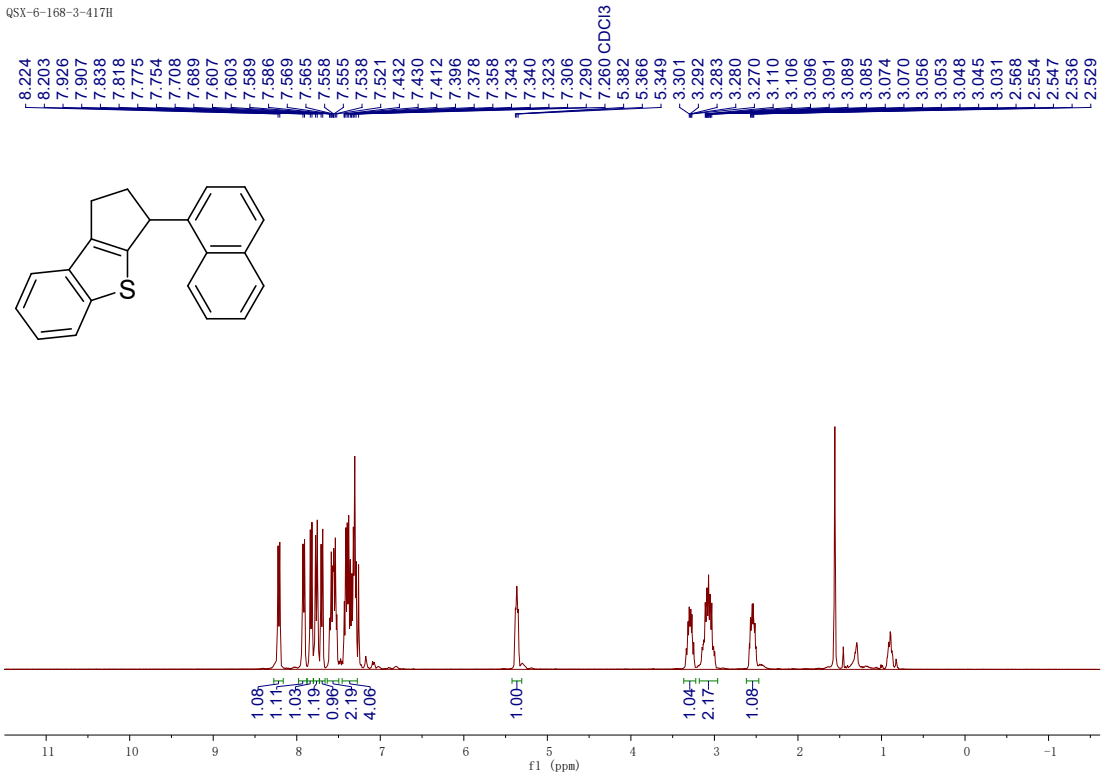
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7j (*see procedure*)



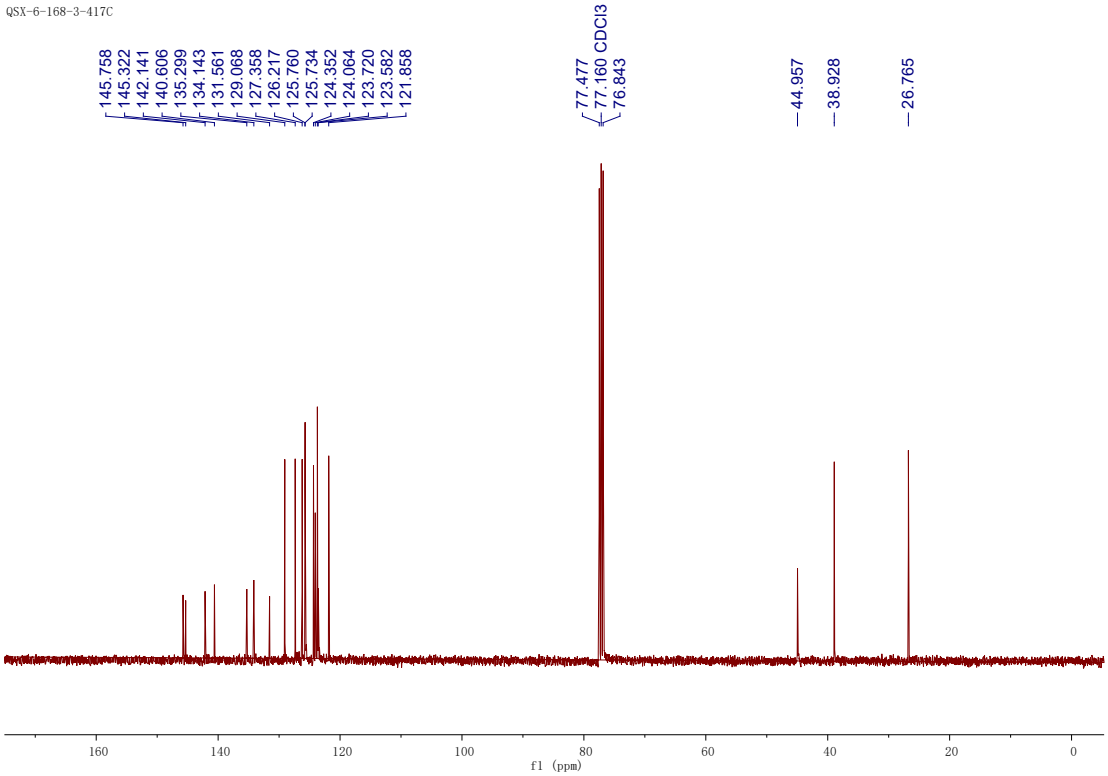
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7j



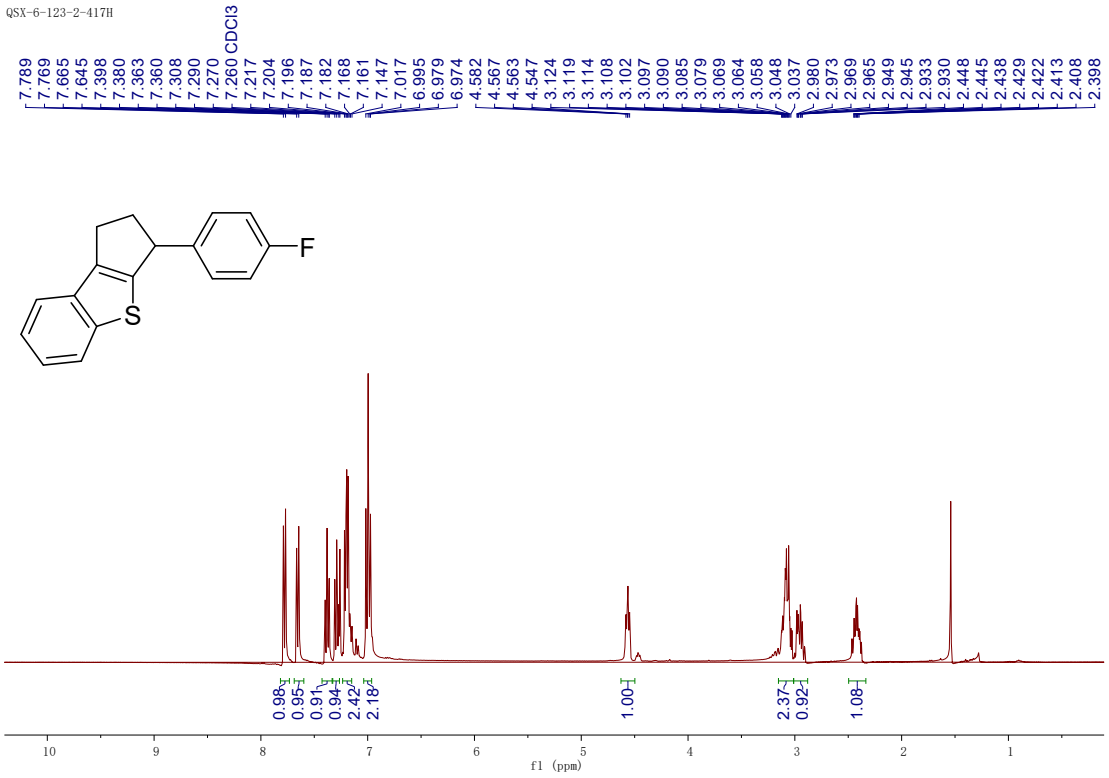
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7k (*see procedure*)



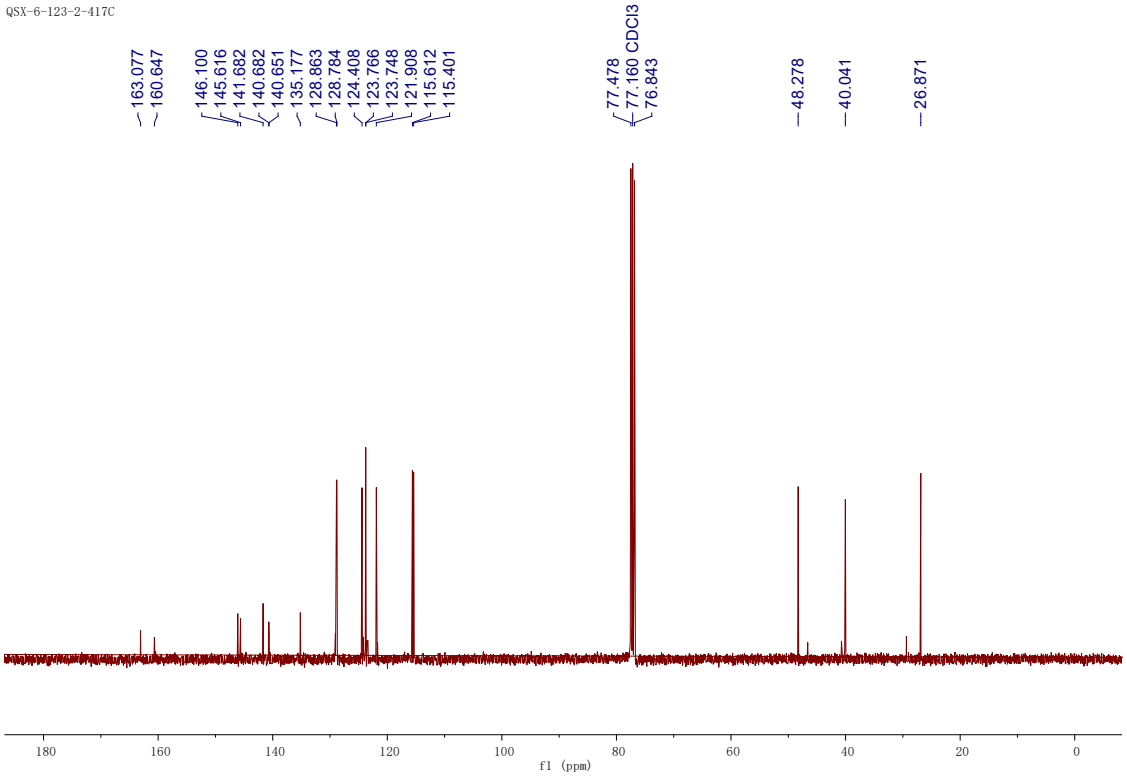
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7k



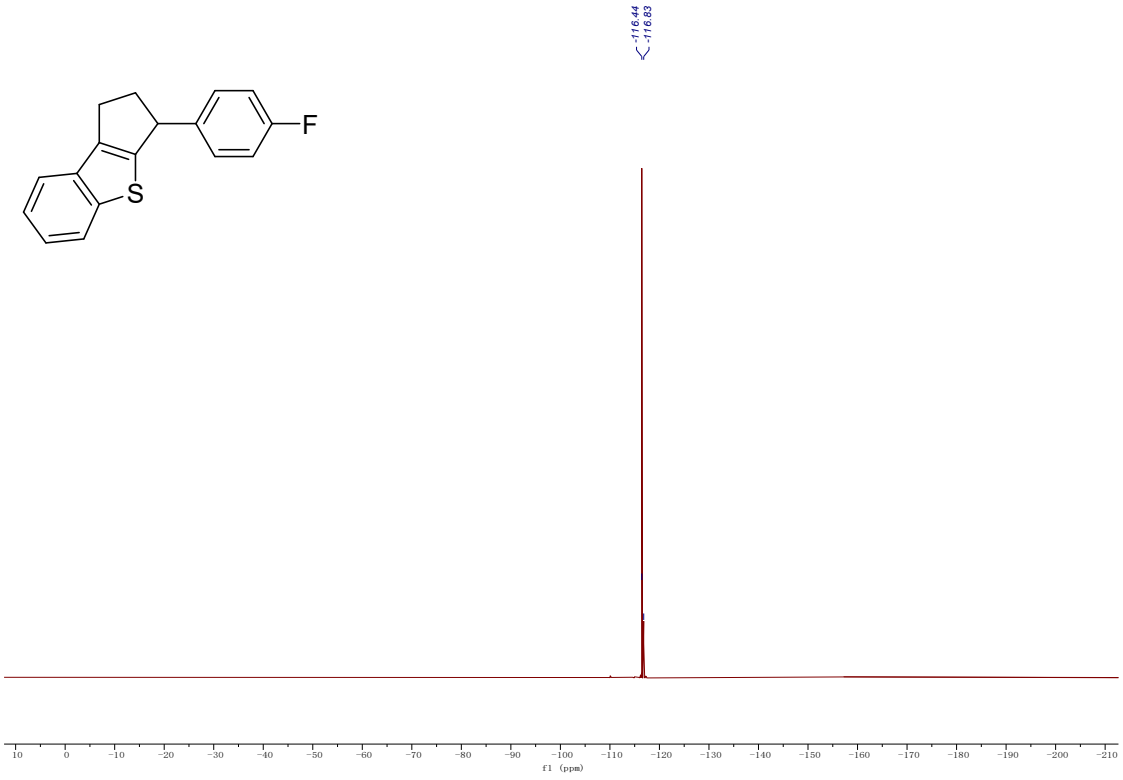
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7l (*see procedure*)



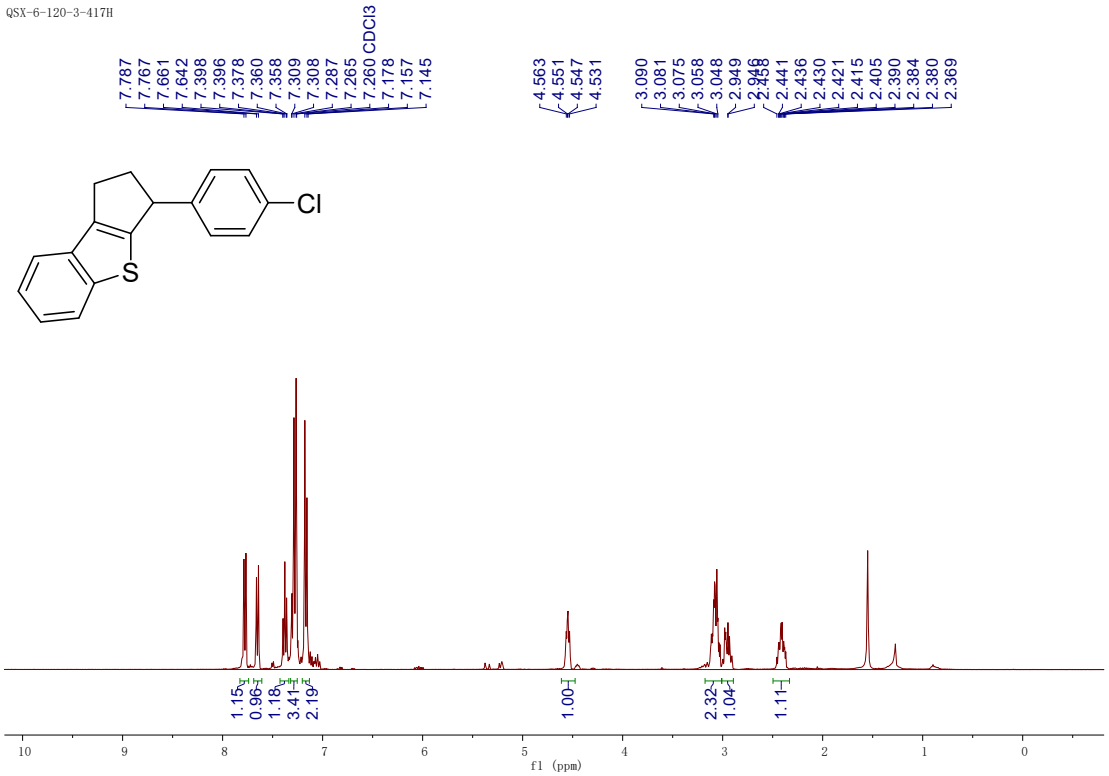
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7l



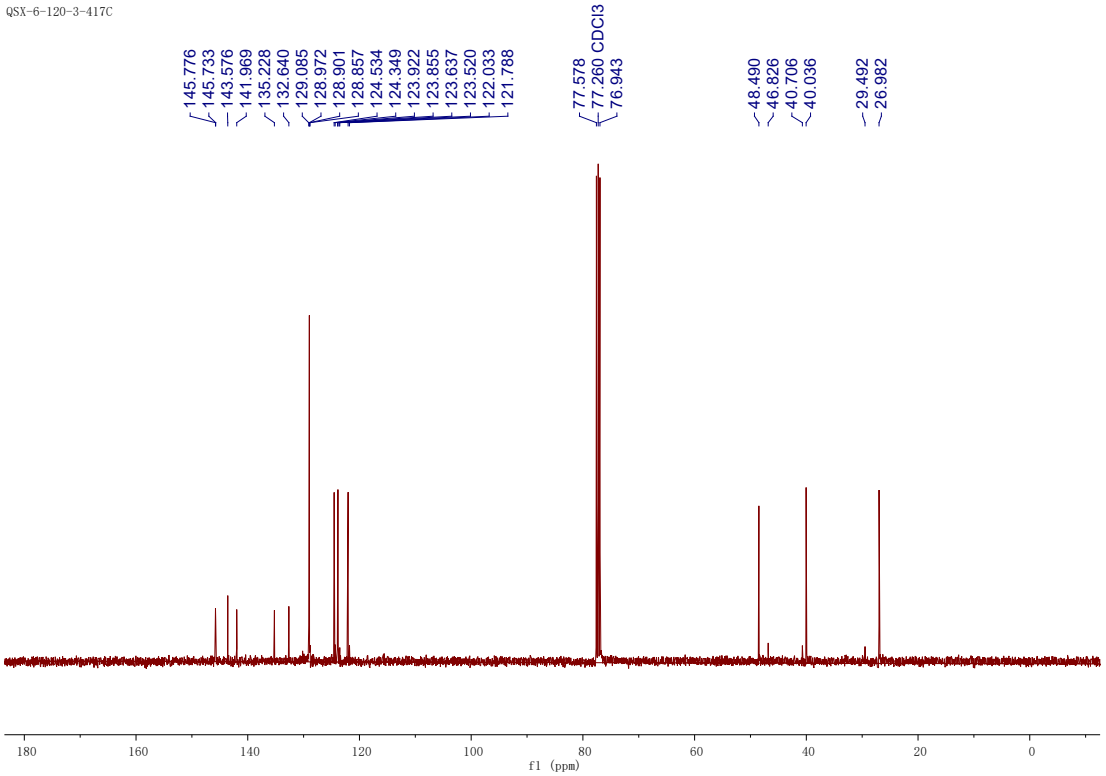
^{19}F NMR (177 MHz, $CDCl_3$) spectrum of 7l



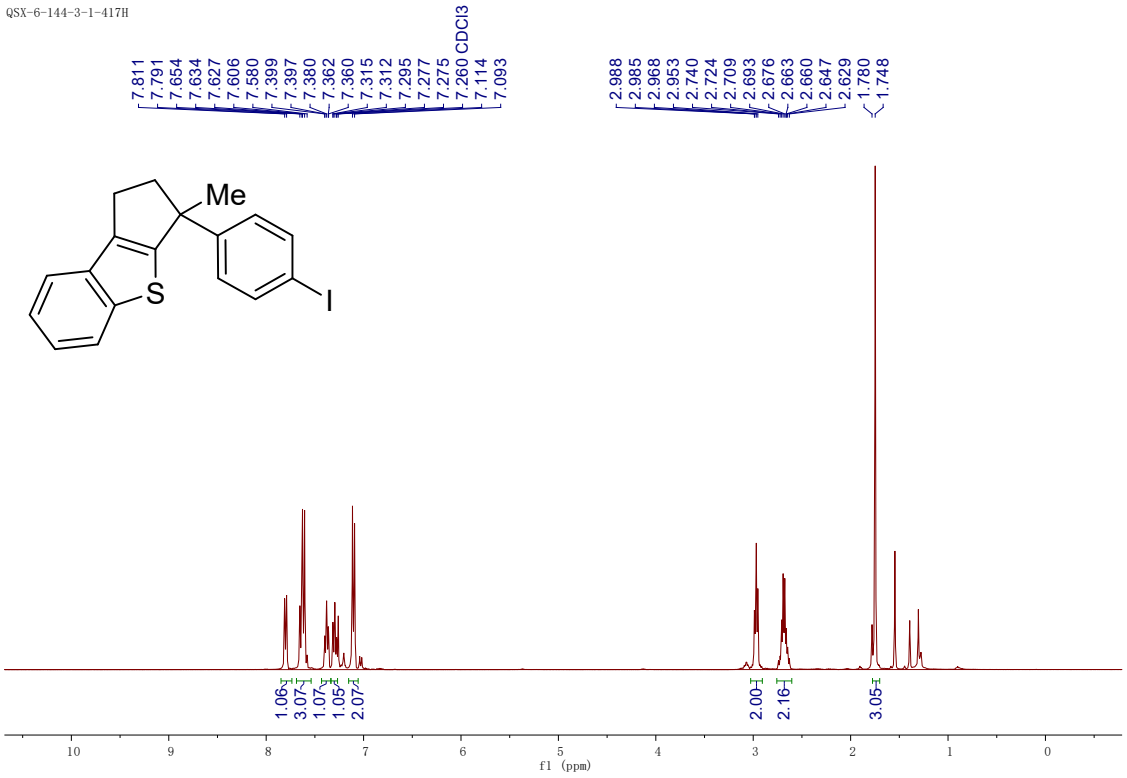
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7m (*see procedure*)



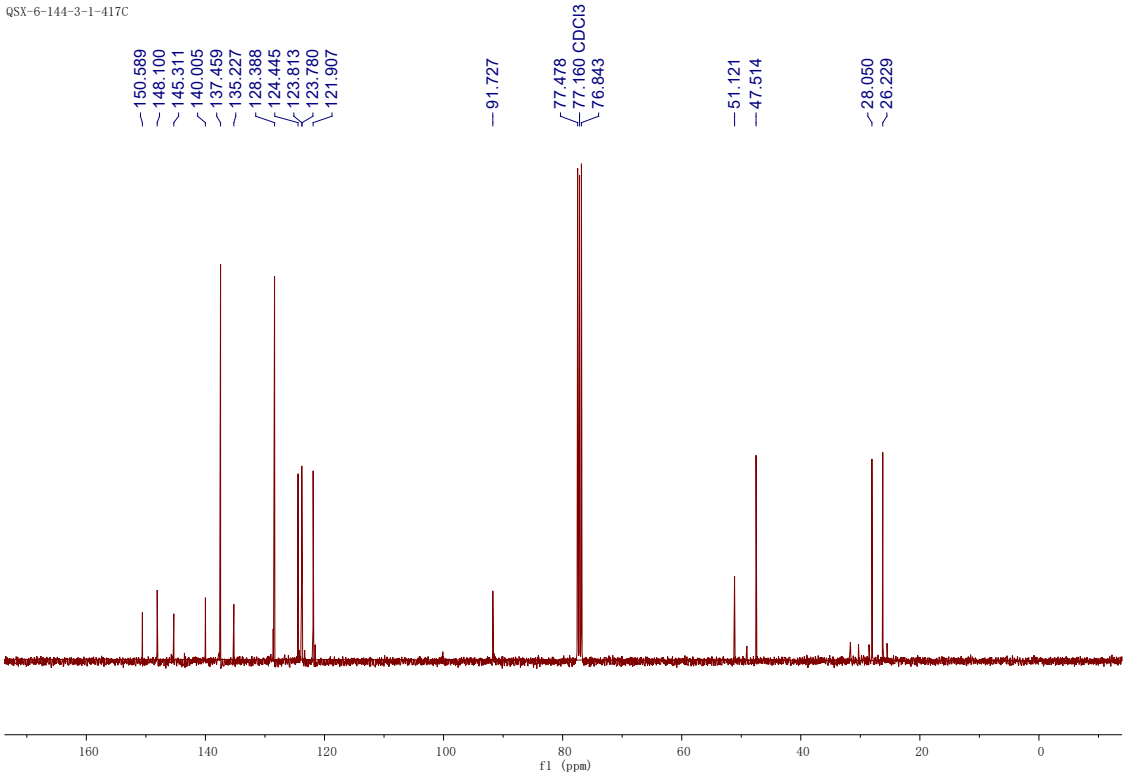
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7m



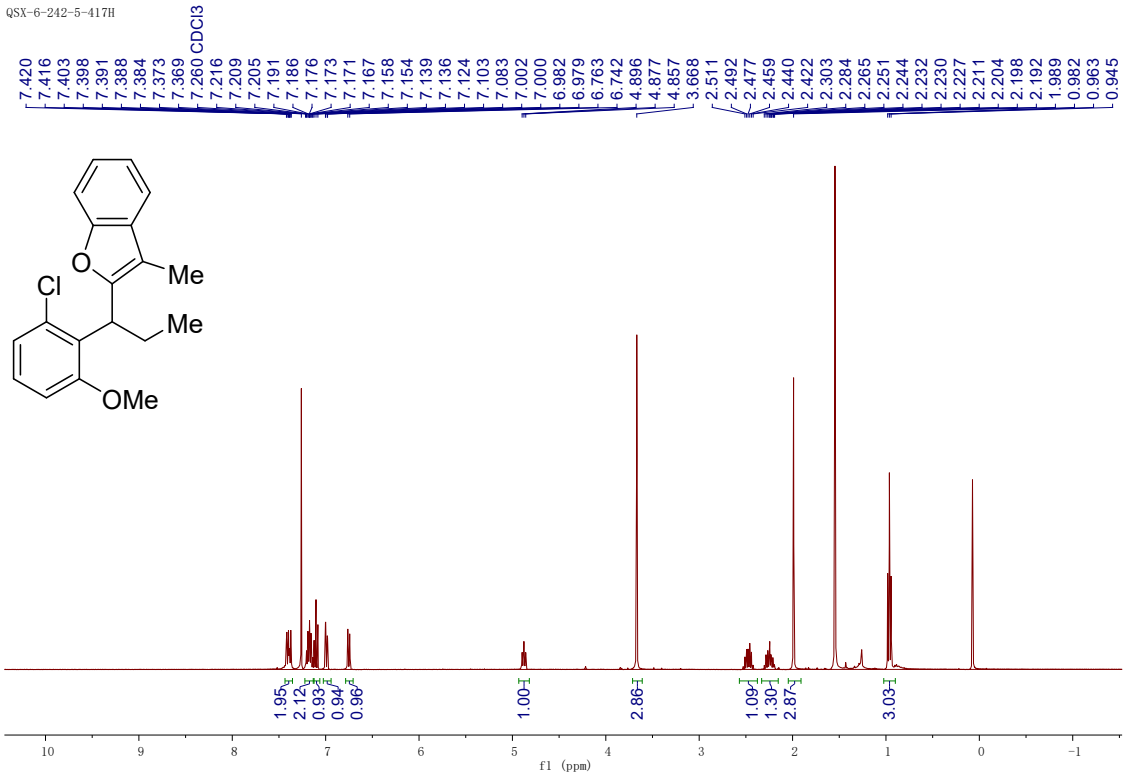
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 7n (*see procedure*)



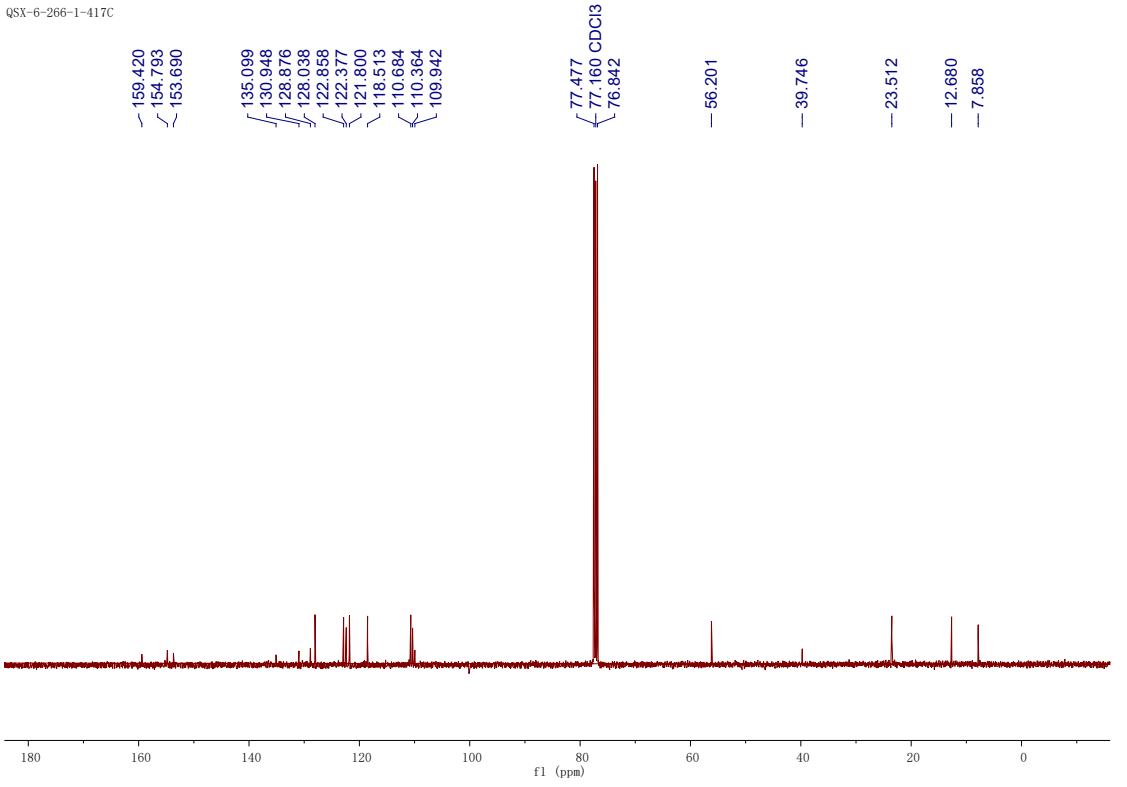
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 7n



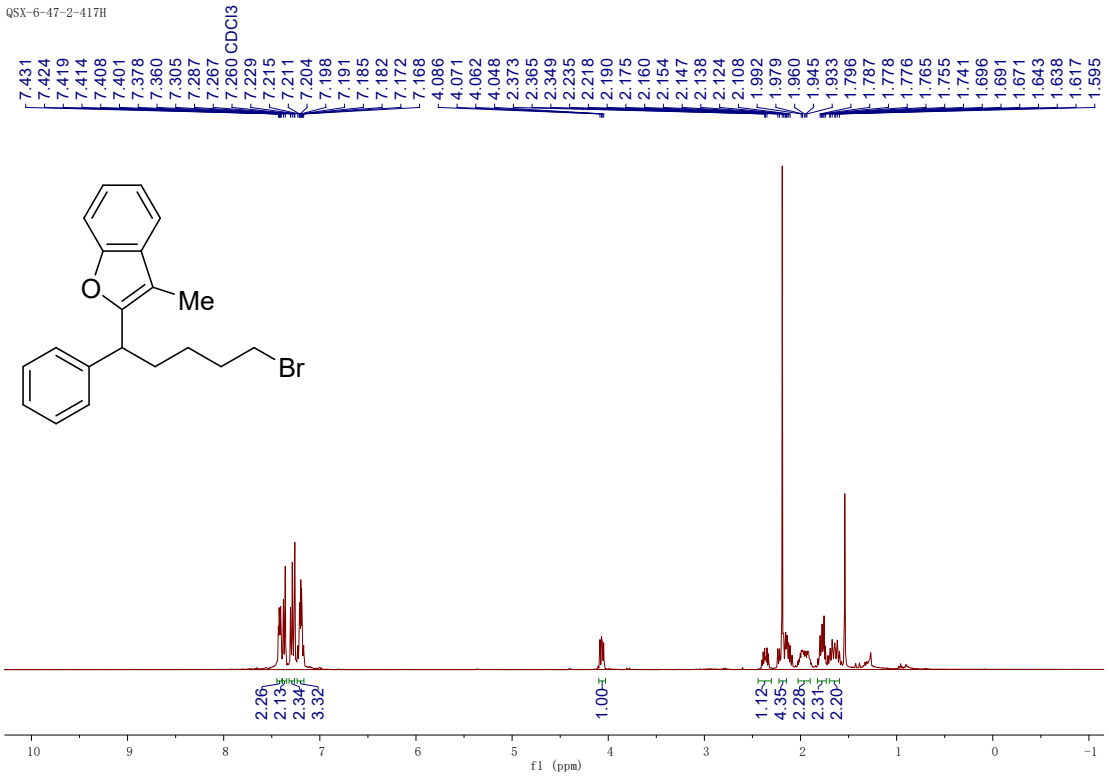
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



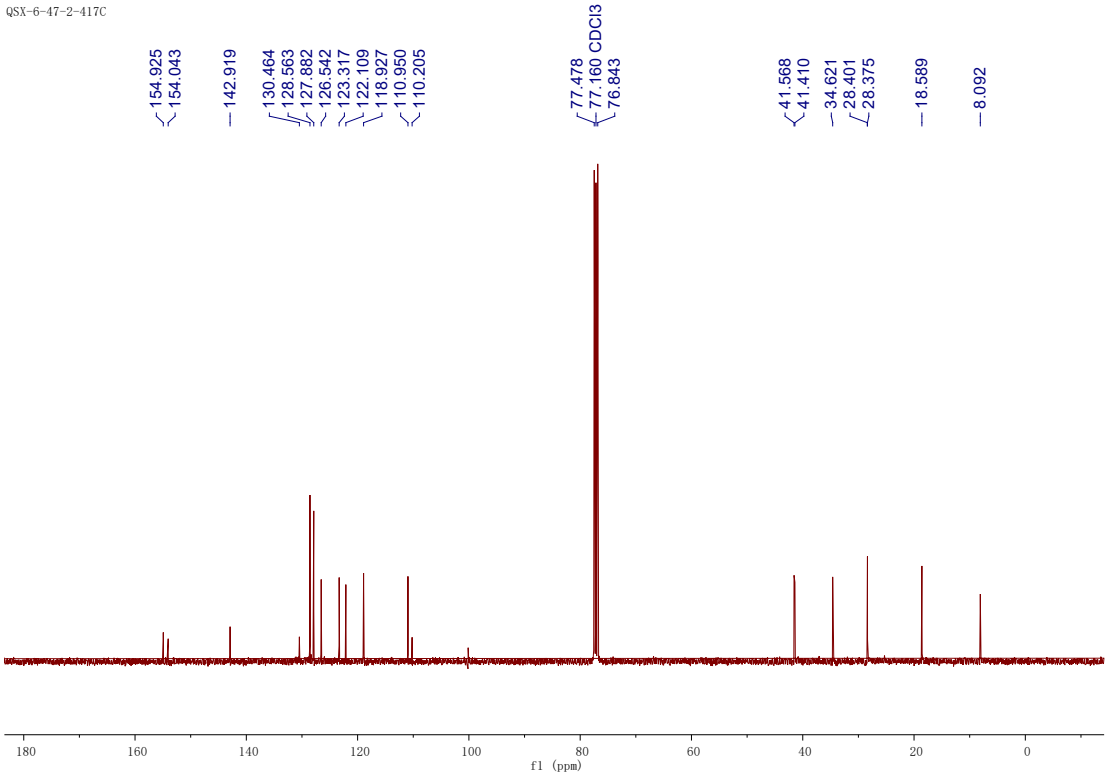
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



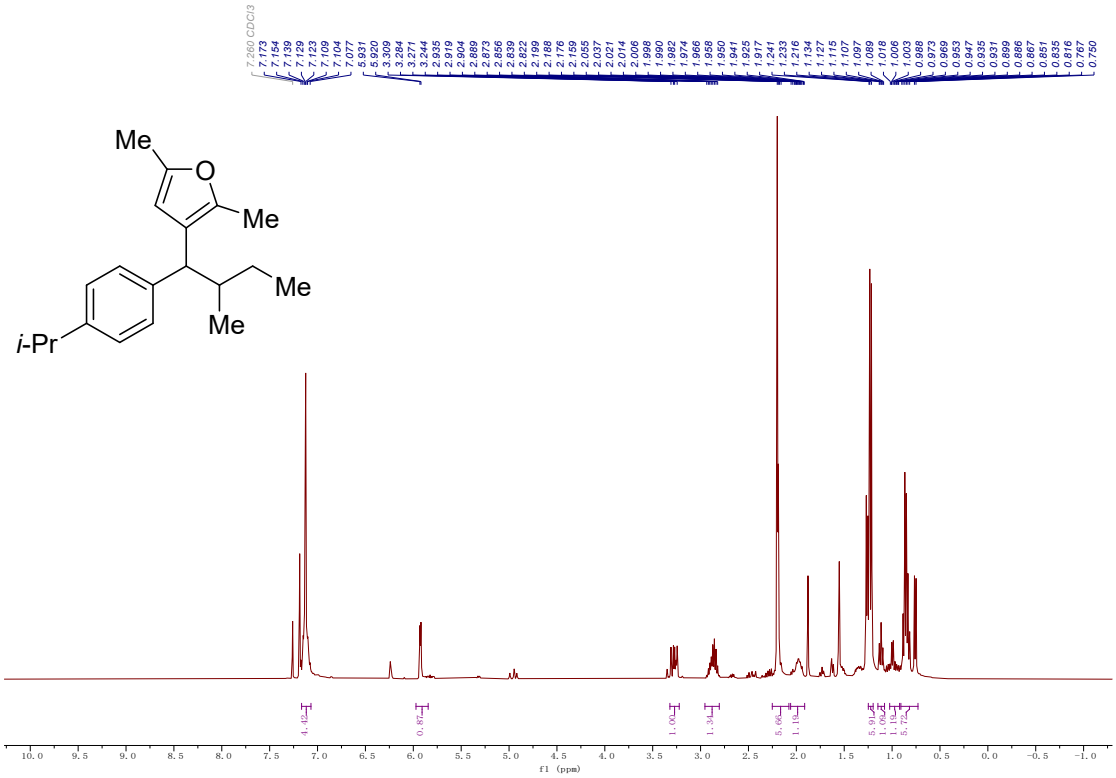
^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



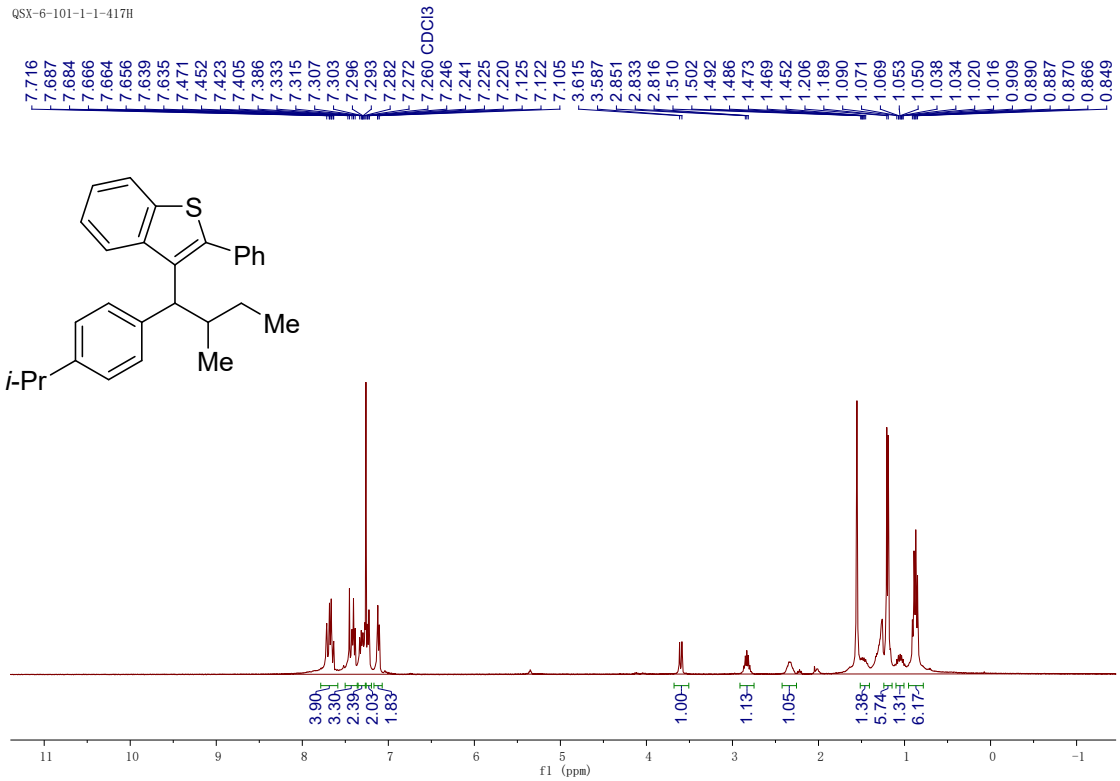
^{13}C NMR (100 MHz, $CDCl_3$) spectrum



^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum (*see procedure*)



12.2. Single crystal x-ray structure 7g (*see substrate list*)

Single crystal acquisition process: Single crystal suitable for X-ray diffraction of compound was obtained from a solution of compound in DCM layered with cyclohexane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre with a reference CCDC 2308239. Diffraction data were collected on a Super Nova, Dual, Cu at home/near, AtlasS2 diffract meter employing Cu-Kα radiation (λ = 1.54184 Å). The crystal structure and detailed information were shown as follows.

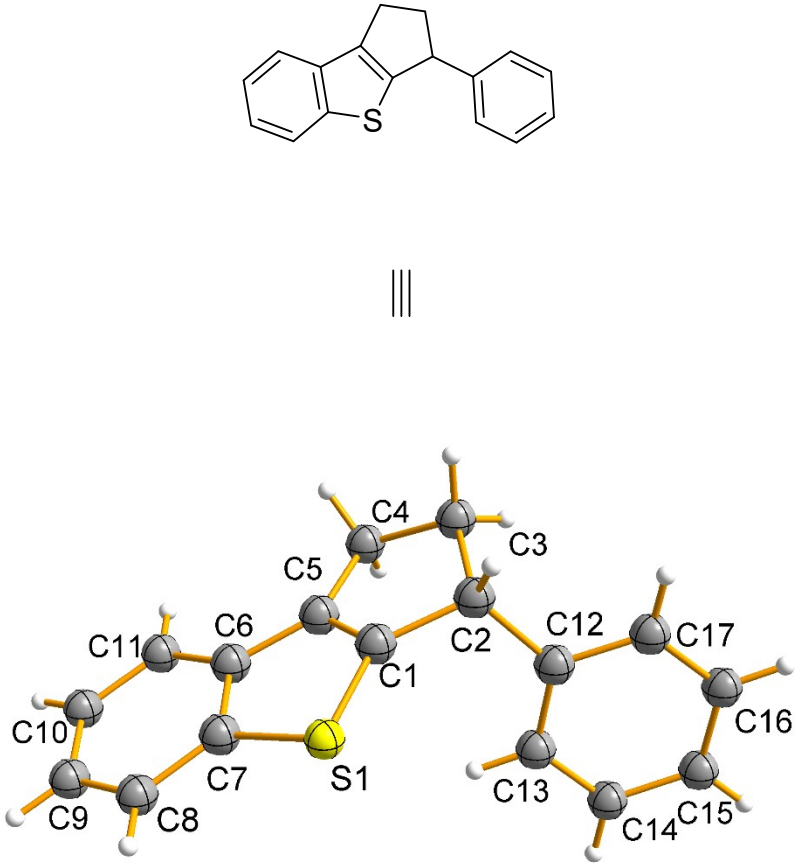


Table S8. Crystal data and structure refinement for A21060801AQLQ1.

Identification code	A21060801AQLQ1
Empirical formula	$C_{17}H_{14}S$
Formula weight	250.34
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.2038(9)

b/Å	8.2643(9)
c/Å	10.5638(10)
α/°	105.060(9)
β/°	106.146(9)
γ/°	103.841(10)
Volume/Å^3	625.75(12)
Z	2
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	2.080
F(000)	264.0
Crystal size/mm^3	0.150 × 0.070 × 0.060
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.304 to 146.028
Index ranges	-8 ≤ h ≤ 9, -9 ≤ k ≤ 10, -13 ≤ l ≤ 12
Reflections collected	3942
Independent reflections	2387 [R_{int} = 0.0320, R_{sigma} = 0.0452]
Data/restraints/parameters	2387/0/163
Goodness-of-fit on F^2	0.986
Final R indexes [I>=2σ (I)]	R_1 = 0.0436, wR_2 = 0.1285
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1400
Largest diff. peak/hole / e Å^{-3}	0.28/-0.39

Table S9. Fractional Atomic Coordinates (×10^4) and Equiv.alent Isotropic Displacement Parameters (Å^2×10^3) for A21060801AQLQ1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	3883(2)	6526(3)	3457(2)	23.1(4)
C2	2788(2)	7522(2)	4027.5(19)	23.3(4)
C3	1714(3)	6132(3)	4529(2)	25.5(4)
C4	1883(3)	4314(3)	3845(2)	26.0(4)
C5	3394(2)	4807(3)	3328(2)	23.2(4)
C6	4378(2)	3848(3)	2690.8(19)	23.5(4)
C7	5642(3)	4986(3)	2344(2)	25.1(4)
C8	6745(3)	4367(3)	1696(2)	29.0(4)
C9	6586(3)	2592(3)	1395(2)	31.6(5)
C10	5356(3)	1438(3)	1734(2)	30.1(5)
C11	4257(3)	2063(3)	2377(2)	26.8(4)
C12	1530(2)	8029(2)	2963(2)	22.5(4)

C13	1064(3)	7262(3)	1518(2)	26.5(4)
C14	-197(3)	7674(3)	586(2)	31.2(5)
C15	-1008(3)	8855(3)	1092(2)	32.2(5)
C16	-545(3)	9642(3)	2531(2)	29.6(5)
C17	734(3) 9246(3)	3456(2)	25.5(4)	
S1	5578.2(6) 7158.9(6)	2819.7(5)	28.2(2)	

Table S10. Anisotropic Displacement Parameters ($Å^2×10^3$) for A21060801AQLQ1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	20.0(9)	26.2(9)	26.2(9)	12.9(8)	10.1(7)	6.8(7)
C2	20.9(9)	23.9(9)	24.0(9)	9.1(7)	9.0(7)	4.0(7)
C3	24.7(9)	30.2(10)	26.3(10)	14.6(8)	12.6(7)	8.4(8)
C4	23.1(9)	26.8(10)	30.1(10)	13.5(8)	12.3(8)	5.1(7)
C5	19.5(9)	25.4(9)	24.0(9)	11.2(7)	7.0(7)	4.7(7)
C6	20.2(9)	27.6(10)	21.4(9)	10.3(8)	6.4(7)	5.5(7)
C7	22.3(9)	27.5(10)	27.3(10)	12.1(8)	10.5(7)	7.0(7)
C8	23.5(9)	34.9(11)	31.8(11)	14.8(9)	12.7(8)	8.5(8)
C9	28.1(10)	39.8(12)	29.0(11)	10.1(9)	12.2(8)	14.9(9)
C10	31.2(11)	26.7(10)	28.6(10)	7.0(8)	6.4(8)	11.3(8)
C11	24.8(9)	24.8(9)	27.0(10)	9.9(8)	6.3(7)	4.6(7)
C12	17.9(9)	21.9(9)	29.0(10)	12.0(7)	10.7(7)	3.0(7)
C13	26.8(10)	24.5(9)	29.5(10)	10.6(8)	12.5(8)	7.1(7)
C14	33.1(11)	35.0(11)	25.4(10)	13.8(9)	10.4(8)	7.9(9)
C15	25.0(10)	35.8(11)	40.1(12)	22.8(9)	9.5(8)	10.1(8)
C16	24.4(10)	26.9(10)	44.5(12)	17.4(9)	17.3(9)	9.8(8)
C17	24.2(9)	25.6(9)	29.0(10)	11.0(8)	13.7(8)	6.0(7)
S1	23.9(3)	26.8(3)	41.0(3)	17.5(2)	17.8(2)	7.3(2)

Table S11. Bond Lengths for A21060801AQLQ1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.498(3)	C7	S1	1.752(2)
C1	C5	1.340(3)	C8	C9	1.383(3)
C1	S1	1.7371(19)	C9	C10	1.404(3)
C2	C3	1.570(2)	C10	C11	1.387(3)
C2	C12	1.520(3)	C12	C13	1.391(3)
C3	C4	1.546(3)	C12	C17	1.393(3)

C4	C5	1.500(3)	C13	C14	1.390(3)
C5	C6	1.436(3)	C14	C15	1.385(3)
C6	C7	1.421(3)	C15	C16	1.387(3)
C6	C11	1.397(3)	C16	C17	1.387(3)
C7	C8	1.390(3)			

Table S12. Bond Angles for A21060801AQLQ1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	S1	131.54(14)	C8	C7	C6	121.75(18)
C5	C1	C2	114.54(17)	C8	C7	S1	126.69(15)
C5	C1	S1	113.76(16)	C9	C8	C7	118.01(19)
C1	C2	C3	100.75(15)	C8	C9	C10	121.5(2)
C1	C2	C12	114.77(16)	C11	C10	C9	120.22(19)
C12	C2	C3	111.60(14)	C10	C11	C6	119.77(18)
C4	C3	C2	107.63(15)	C13	C12	C2	122.99(18)
C5	C4	C3	102.98(15)	C13	C12	C17	118.55(18)
C1	C5	C4	111.61(18)	C17	C12	C2	118.37(17)
C1	C5	C6	113.66(17)	C14	C13	C12	120.72(19)
C6	C5	C4	134.68(17)	C15	C14	C13	120.0(2)
C7	C6	C5	110.61(17)	C14	C15	C16	119.94(19)
C11	C6	C5	130.64(17)	C17	C16	C15	119.75(19)
C11	C6	C7	118.75(18)	C16	C17	C12	120.99(19)
C6	C7	S1	111.56(15)	C1	S1	C7	90.41(9)

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for A21060801AQLQ1.

Atom	*x*	*y*	*z*	U(eq)
H2	3586	8588	4840	28
H3A	2208	6494	5546	31
H3B	457	6050	4243	31
H4A	2178	3740	4528	31
H4B	777	3530	3073	31
H8	7566	5124	1472	35
H9	7309	2152	959	38
H10	5279	251	1526	36
H11	3442	1297	2599	32
H13	1602	6466	1172	32

H14	-497	7156	-379	37
H15	-1863	9120	468	39
H16	-1090	10433	2874	36
H17	1065	9801	4420	31