Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Three-Component Acyloxylation of Diazo Compounds with Carboxylic Acids and Azadienes

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Table of Contents

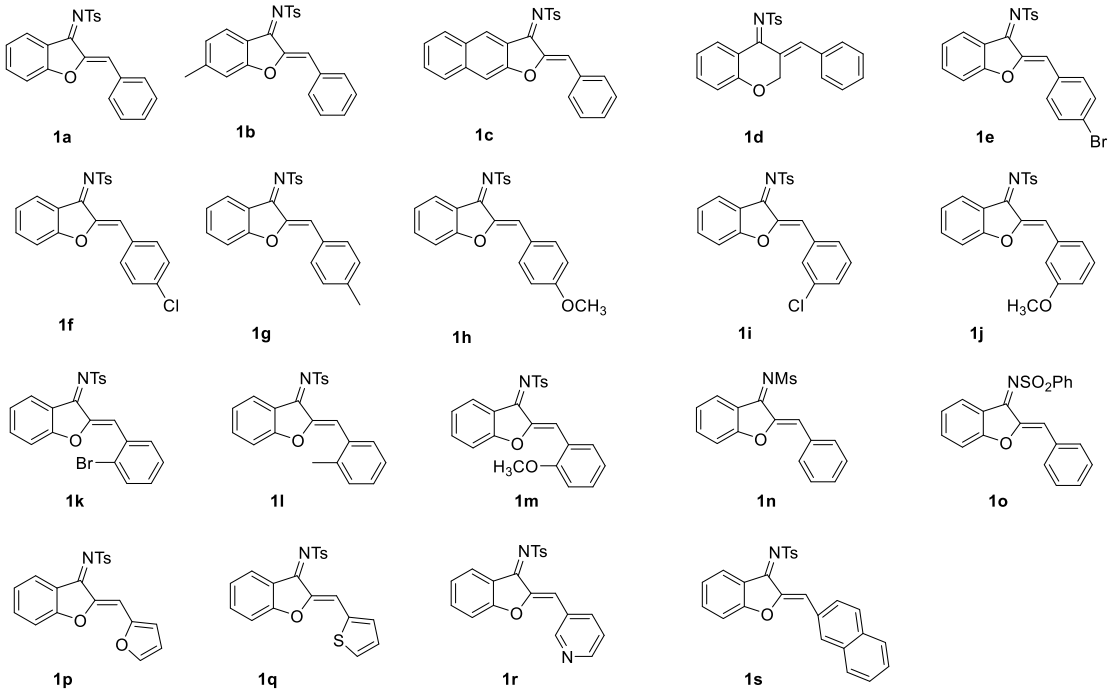
1. General Information

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz and for ^{13}C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, sep: septet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 254 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether, dichloromethane and petroleum ether.

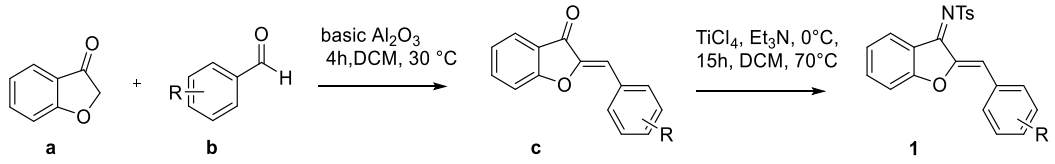
Unless otherwise noted, all starting materials were purchased from commercial sources and used without any further purification. Azadiene **1** compound and its derivatives and diethyl 2-diazomalonate **2** compound and its derivatives were prepared according to literature methods. The cesium salts used in the article were synthesized according to literature methods except cesium acetate. The acids used in the article were purchased commercially.

2. General Procedure for Synthesis of Model Substrates

(1) General procedure for synthesis of azadiene **1a** units



Procedure A:



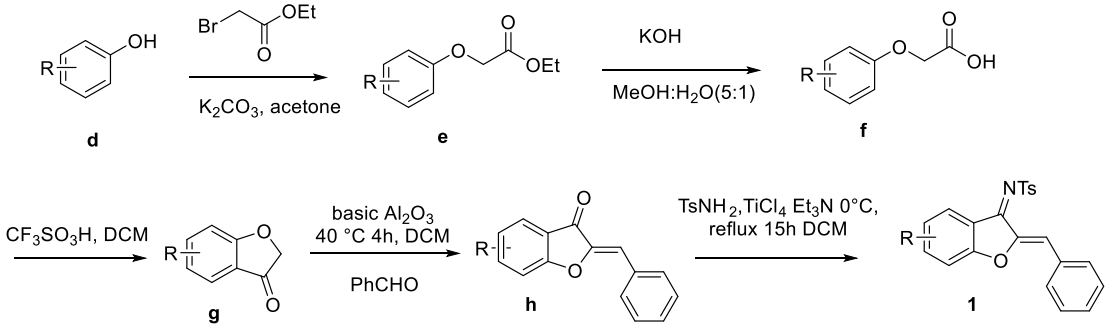
Step 1: To a solution of benzofuran-3(2H)-one (1.34 g, 10 mmol, 1 equiv) in CH_2Cl_2 (0.1 M) was successively added Al_2O_3 (activated at 140°C for 3 h, 5.1 g, 25 mmol, 5 equiv) and **b** (12 mmol, 1.2 equiv). After 4 h stirring at rt, the reaction mixture was filtered over diatomite (CH_2Cl_2) and concentrated under reduced pressure. The resulting crude solid was column chromatography purification

(PE/EA=30:1-20:1) 50%-95% of c as a yellow solid. The NMR spectra match with the data reported in the literature[1].

Step 2: To a solution of **c** (5.0 mmol, 1 equiv) and $TsNH_2$ (1.3 g, 7.5 mmol, 1.5 equiv) in toluene or CH_2Cl_2 (0.1M) was added NEt_3 (1.2 g, 12 mmol, 2.4 equiv). The reaction was cooled to 0 °C and $TiCl_4$ (0.66 mL, 6 mmol, 1.2 equiv) was added dropwise. After 16 h stirring under reflux, the mixture was quenched with H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Petroleum ether/ethyl acetate = 30:1-10:1) then recrystallized to afford 40%-88% of azadiene **1** as a yellow solid. The NMR spectra match with the data reported in the literature[2].

1a,1d-1s were prepared according to the procedure A.

Procedure B:



Step 1: To a 10 mL dry round-bottom flask equipped with a stir bar were added **d** (10 mmol) and dried acetone (30 mL). After the solid was completely dissolved, anhydrous K_2CO_3 (30 mmol) was added. Then ethyl bromoacetate (12 mmol) was dropwise added into the reaction mixture and the resulting mixture was stirred at reflux for 4 h. After the reaction was completed by TLC monitoring, the reaction mixture was cooled to room temperature, filtered and concentrated in-vacuo to obtained the desired ester b. The crude product was used for the next step without further purification.

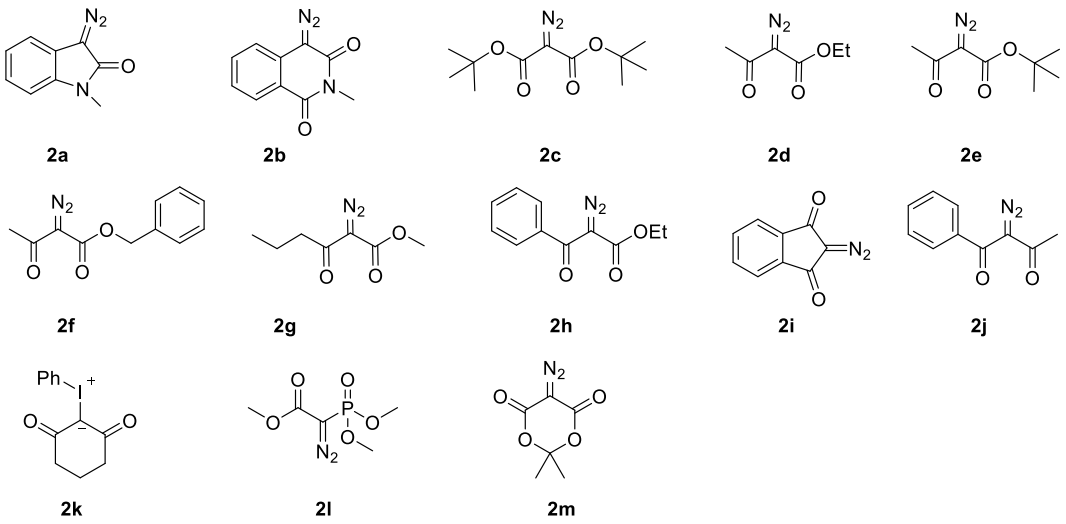
Step 2: A solution of compound **e** and potassium hydroxide (30 mmol) in methanol (25 mL) and water (5 mL) was stirred at room temperature for 5 h. After the reaction was completed by TLC monitoring, the mixture was adjusted to acidic (pH = 2-3) with 35% HCl aq. Then the reaction mixture was diluted with H_2O (30 mL), followed by extraction with ethyl acetate (25 mL × 3). The extracted organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to obtain the crude acid, which was further recrystallized in ethanol to provide pure acid **f**.

Step 3: In a dry round-bottom flask, acid **f** (5 mol) was dissolved with CH_2Cl_2 (25 mL). The mixture was cooled to 0°C and T_fOH (25 mmol) was slowly added into the reaction. After stirring at 0°C for 15 min, the reaction was warmed to room temperature. After the reaction was completed by TLC monitoring, and then quenched with ice water. The final mixture was adjusted with 35% Na_2CO_3 solution to the neutral (pH = 7-8) and extracted with dichloromethane (50 mL × 3). The organic layer was dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 10:1) to obtain the desired ketone **g**.

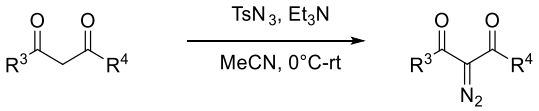
Step 4-5: Same as above procedure A step 1-2.

1b-1c were also prepared according to the procedure B and the literature procedures [3,4].

(2) General procedure for synthesis of Diazo compounds **2a** units



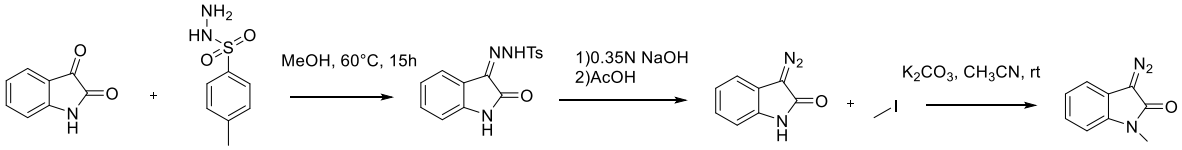
Procedure A[·]:



To a round bottom flask charged with ketoester (10 mmol) and TsN_3 (13 mmol) in acetonitrile (25 mL) was added triethylamine (4.2 mL, 13 mmol) dropwise at 0 °C. Upon stirring at room temperature for 4h-14 h, the reaction mixture was concentrated under reduced pressure. After the reaction was completed by TLC monitoring, The reaction mixture was filtered through a pad of Celite and washed with EtOAc (10 mL x 3). The solvent was evaporated under reduce pressure and the residue was purified by flash column chromatography using EtOAc/petroleum ether as eluent to furnish the pure diazo compound.

2c-2j, 2l-2m were prepared according to the procedure A[5,6].

Procedure B:



Step 1: In a 200 mL round bottom flask, $TsNHNH_2$ (2.05 g, 11 mmol) in methanol (60 mL) were added and kept at 60 °C followed by the corresponding isatin (10 mmol) was added to a hot solution. The reaction mixture was refluxed for 10 h (TLC monitoring), followed by filtration of the crude reaction mixture gave the p-tosylhydrazone derivative as yellow solid (95% yield). The obtained p-tosylhydrazone derivative was used for the next step without any further purification.

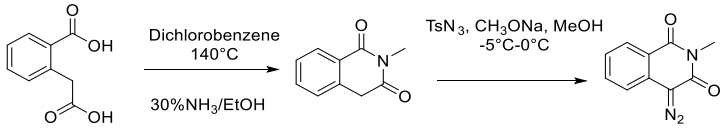
Step 2: In a 100 mL round bottom flask, p-tosylhydrazone (6 mmol, 1 equiv) was added followed by 45 mL of 0.35M aqueous solution of NaOH (0.617 g, 15.42 mmol, 2.57 equiv) was added. The reaction mixture was stirred for 3 h at 50 °C, then allowed to cool to room temperature. The reaction mixture was neutralized by addition of ice and glacial acetic acid (10 mL) and extracted in dichloromethane. The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure to afford the diazo compound as orange solid (90% yield), which was employed in the next step without any further purification.

Step 3: A mixture of diazo compound (5 mmol), K_2CO_3 (1.38 g, 10 mmol) and alkyl halide (10 mmol) in CH_3CN (10 mL) was stirred at room temperature for 15 h. Then, the reaction mixture was diluted with CH_2Cl_2 and washed with water (60 mL × 3). The organic phase was dried by Na_2SO_4 and the solvent was

removed under reduced pressure. The resulting residue was purified by flash chromatography to give N-alkylated diazo compound as an orange solid (71 % yield).

2a were prepared according to the procedure B.[7]

Procedure C.:

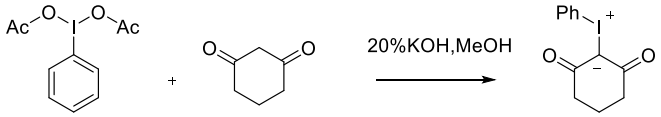


Step 1: In a dry round-bottom flask, homophthalic acid (10.0 mmol, 1.8 g) and methylamine (5 mL of 40% solution in water). The solution of homophthalic acid in aqueous methylamine was evaporated at atmospheric pressure (bath temperature 180 °C) and then dried in vacuo. The residue was heated at reflux in 1.2-dichlorobenzene (10 mL) for 6 hours. The target compound was obtained after removal of the solvent under reduced pressure and recrystallization. Yield 1.1g (66%).

Step 2: The product obtained in the previous step (1 mmol, 1 equiv) and TsN_3 (2 mmol, 2 equiv) in 4 ml of methanol were added to -5 °C with sodium methoxide (2 mmol, 2 equiv). Then, react at 0 °C for 4 h. After the reaction is completed, the reaction was quenched by adding water, extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated in vacuo. Then the residue was purified by flash column chromatography using EtOAc/petroleum ether as eluent to furnish the pure diazo compound. Yield 110mg (54%), pale yellow crystals.

2b were prepared according to the procedure C.[8]

Procedure D.:



In a 100 mL round bottom flask equipped with a magnetic stirrer, add a solution of 1,3-cyclohexanedione (1.0 equiv) in 30 mL methanol, 20 mL 10% KOH aq at room temperature, and then diacetoxy iodobenzene (1.2 equiv) in 40 mL of methanol. The reaction mixture was stirred at room temperature for 2 hours and then quenched with ice cold water. The resulting white precipitate was filtered, and the mother liquor was extracted with dichloromethane, then washed three times with water, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting white solid was recrystallized from DCM/hexane to give the compound as a white solid.

2k were prepared according to the procedure D.[9]

References:

[1] Liu, C.; Zhang, Z.; Zhang, J.; Liu, X.; Xie, M. Regioselective Synthesis of Aurone Derivatives via PBu3-Catalyzed Cyclization of 2-Alkynoylphenols. *Chin. J. Chem.* **2014**, 32, 1233–1237.

[2] Fang, Q. Y.; Yi, M. H.; Wu, X. X.; and Zhao, L. M. Regio- and Diastereoselective Spirocyclopropanation of Benzofuran-Derived Azadienes through 1,4-Addition-Induced Dearomatization Reaction under Mild Conditions. *Org. Lett.* **2020**, 22, 5266−5270.

[3] Y. Su et al. Regioselective synthesis of spiro naphthofuranone-pyrazoline via a [3+2] cycloaddition of benzoaurones with nitrile imines. *Tetrahedron 76* **(2020)** 131355.

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compounds: modular and regiocontrolled synthesis of multisubstituted pyrroles. *Chem. Sci.*, **2015**, 6, 6448.

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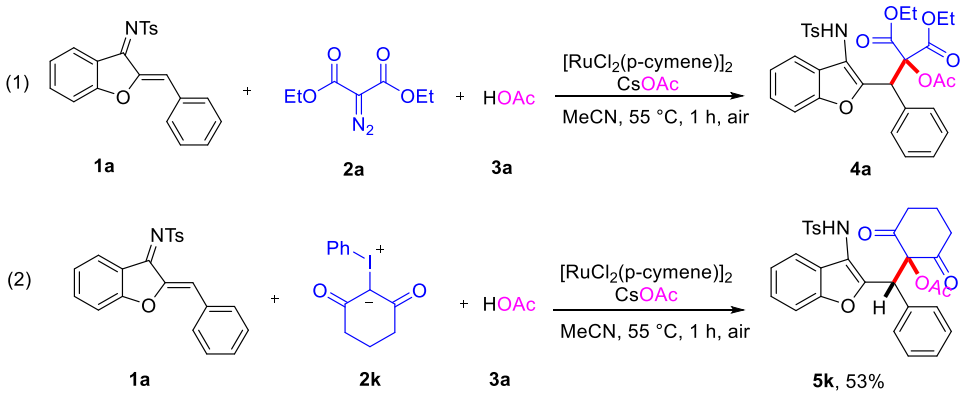
[7] Reddy, A. C. S.; Reddy, P. M.; Anbarasan, P. Diastereoselective Palladium Catalyzed Carbenylative Amination of ortho-Vinylanilines with 3-Diazoindolin-2-ones. *Adv. Synth. Catal.* **2020**, 362, 801 – 806.

[8] Kantin, G.; Darin, D.; Krasavin, M. Rh^{II}-Catalyzed Cycloaddition of α-Diazo Homophthalimides and Nitriles Delivers Oxazolo[5,4-c]isoquinolin-5(4H)-one Scaffold. *Eur. J. Org. Chem.* **2018**, 4857–4859.

[9] Mayakrishnan, S.; Tamizmani, M.; Maheswari, N. U. Harnessing hypervalent iodonium ylides as carbene precursors: C–H activation of N-methoxybenzamides with a Rh(III)-catalyst. *Chem. Commun.*, **2020**, 56, 15462.

3. General Procedure for the Model Reaction

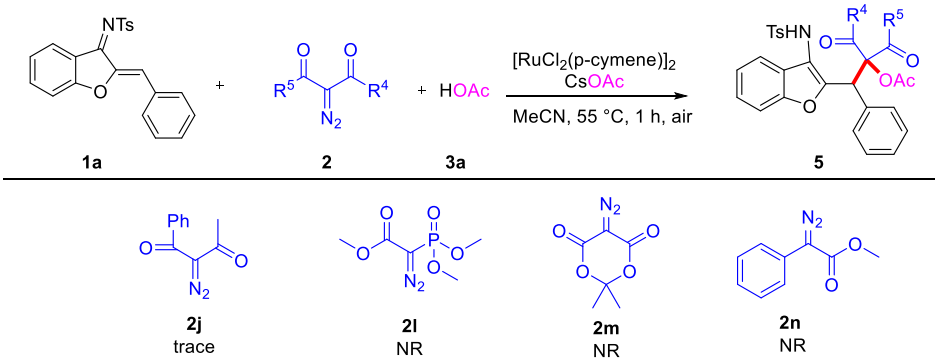


The eq 1： To a flame dried screw-cap tube equipped with magnetic stir bar were introduced azadiene **1a** (37.6 mg, 0.1 mmol), and diethyl 2-diazomalonate **2a** (46.5 mg, 2.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %), CsOAc (38.4 mg, 2 equiv), AcOH (14.3μL, 2.5 equiv), MeCN (1 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 hour. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give the product **4a** as a white solid or yellowish clear liquid (52.8 mg, 89%).

The eq 2: Same as above steps. **2k** (3 equiv), after the completion of the reaction, diatomaceous earth filter, vacuum dry coarse product in acetonitrile recrystallization get **5k** in 53% yield.

4. Scope of Diazo Compounds and Anions Units

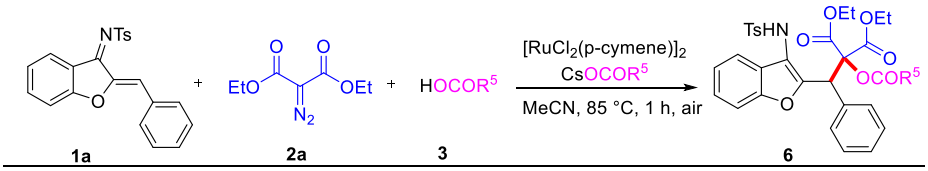
(1) Scheme S3 Scope of Diazo Compounds

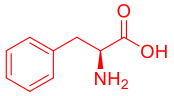


When the substrate **2j** reacts with **1a**, the reaction system is chaotic and the product is less. However, lowering the temperature did not improve the yield, probably because the reactivity of **2j** is too low.

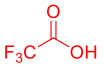
Under standard conditions, **2m** and **1a** failed to react, so we tried to replace **2m** with **2k**. Disappointingly, **2l** and **2n** also failed to react under the optimal reaction conditions.

(2) Scheme S4 Scope of Anions Units





3h, ND

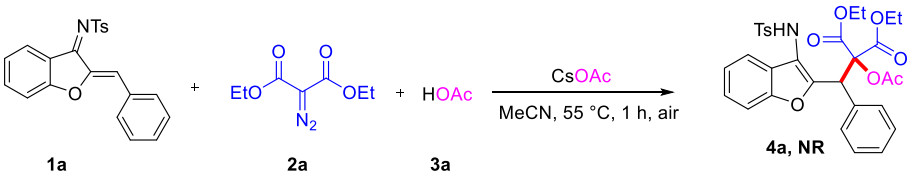


3i, NR

Under standard conditions, during the reaction between **3h** and **1a**, the product **6h** was not found. And the reaction material is destroyed. In addition, under standard conditions, during the reaction of **3i** and **1a**, by TLC found that **1a** and **3i** no reaction and were not destroyed.

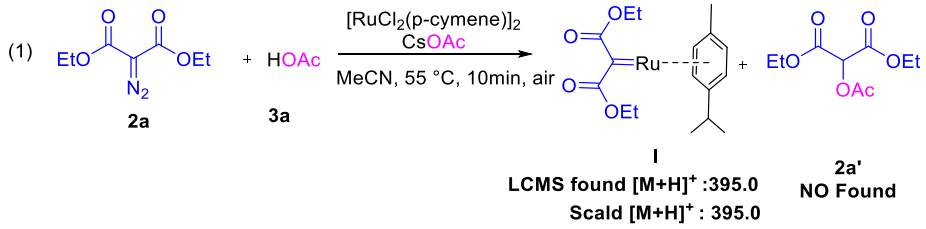
5. Control Experiments and Mechanistic Studies

(1) The model reaction in the absence of catalyst



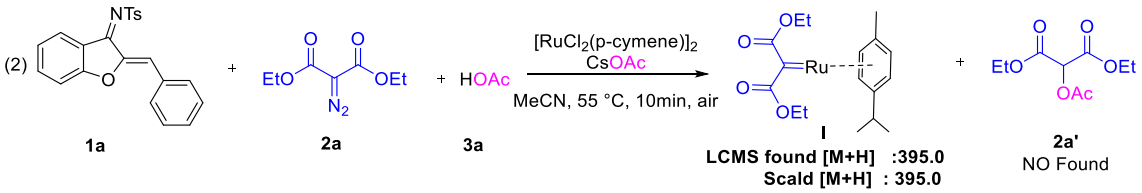
To a flame dried screw-cap tube equipped with magnetic stir bar were introduced azadiene **1a** (37.6 mg, 0.1 mmol), and diethyl 2-diazomalonate **2a** (46.5 mg, 2.5 equiv), CsOAc (38.4 mg, 2 equiv), AcOH (14.3 μL, 2.5 equiv), MeCN (1 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 hour. No product formation was observed by TLC.

(2) Detection of intermediate I and 2a' by LCMS data



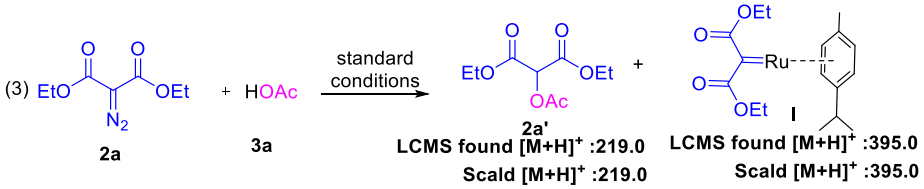
LCMS found $[M+H]^+$:395.0
Scald $[M+H]^+$: 395.0

2a'
NO Found



LCMS found [M+H] :395.0
Scald [M+H] : 395.0

2a'
NO Found



LCMS found $[M+H]^+$:219.0
Scald $[M+H]^+$:219.0

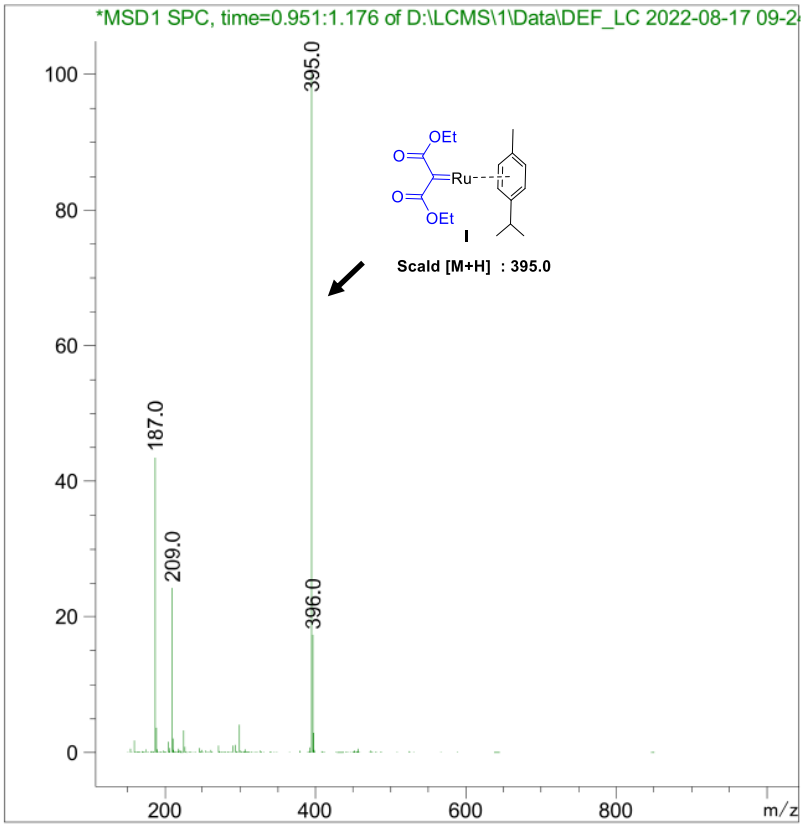
LCMS found $[M+H]^+$:395.0
Scald $[M+H]^+$:395.0

The eq 1： To a flame dried screw-cap tube equipped with magnetic stir bar were introduced diethyl 2-diazomalonate **2a** (23.3 mg, 2.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (1.5 mg, 5 mol %), CsOAc (19.2 mg, 2 equiv), AcOH (7.3μL, 2.5 equiv), MeCN (0.5 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 10min. After completion, the reaction mixture was then tested by LCMS. Different ionic forms of intermediate **I** was detected by LCMS and **2a'** was not found.

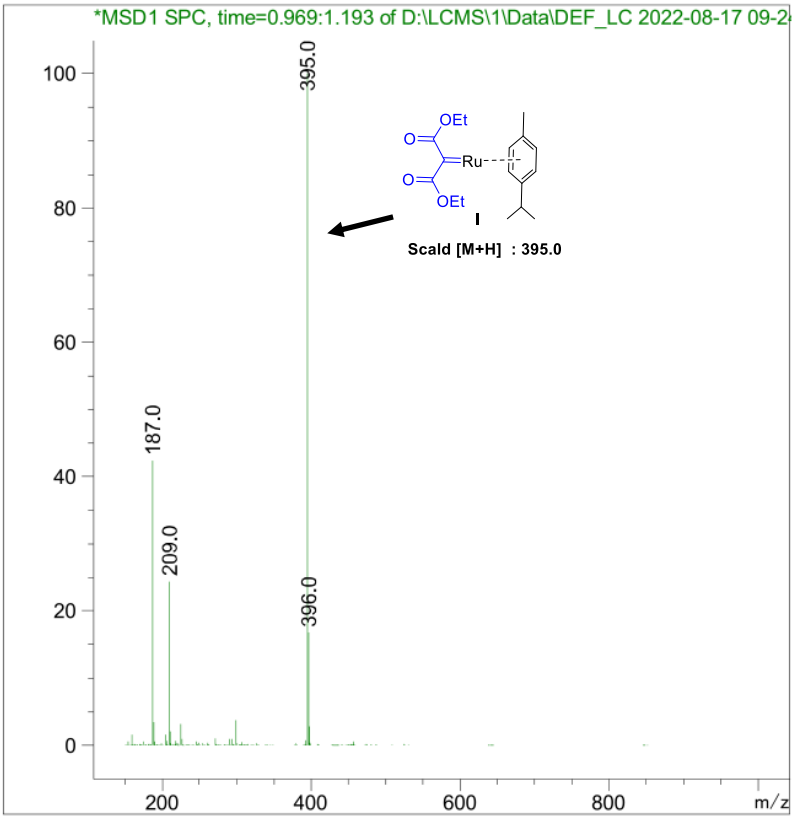
The eq 2：As above. **1a** (18.8 mg, 0.05 mmol), The reaction mixture was stirred in preheated oil bath at 55 C under air atmosphere for 0.5h. After completion, the reaction mixture was then tested by LCMS. Different ionic forms of intermediate **I** was detected by LCMS.

The eq 3：As above. The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1h. After completion, the reaction mixture was then tested by LCMS. Different ionic forms of intermediate **I** was detected by LCMS and **2a'** was found.

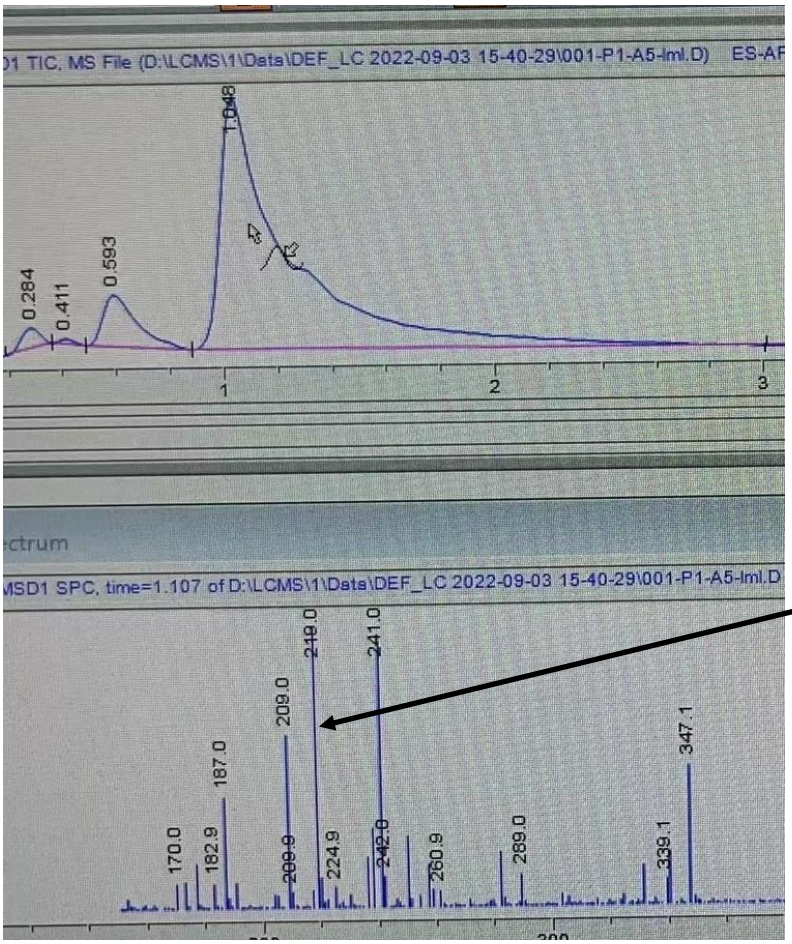
eq 1 LCMS:

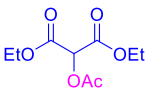


eq 2 LCMS:



eq 3 LCMS:

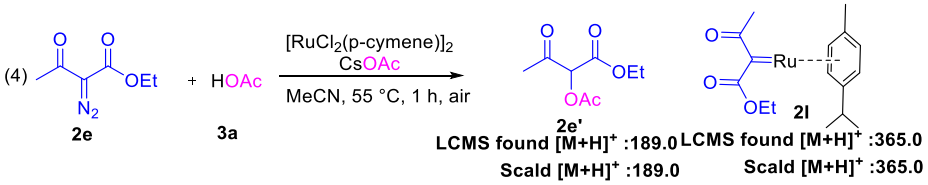




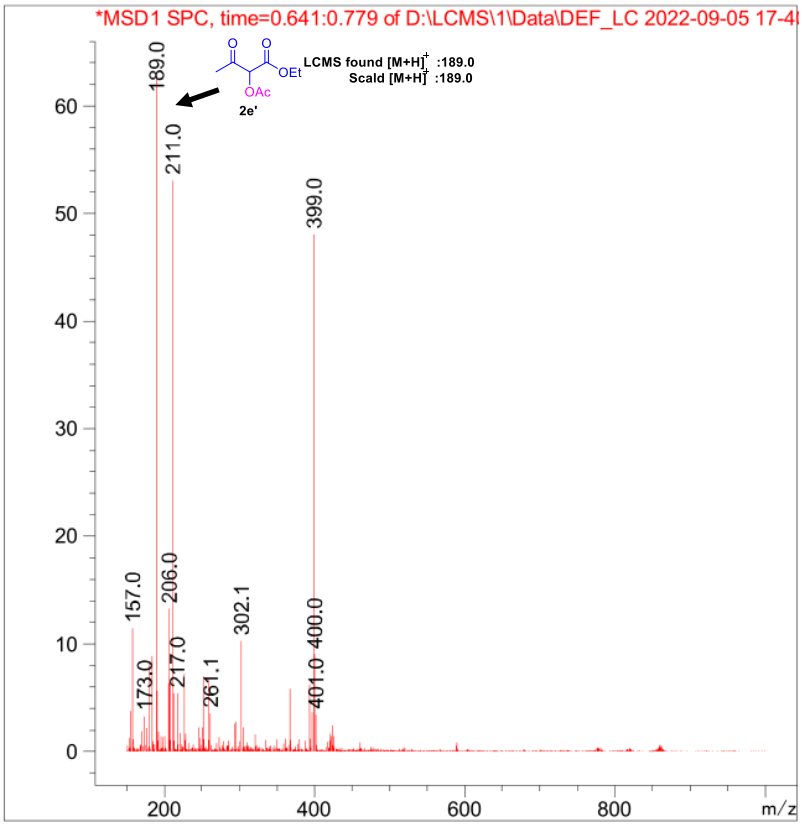
2a'
LCMS found $[M+H]^+$:219.0
Scald $[M+H]^+$:219.0

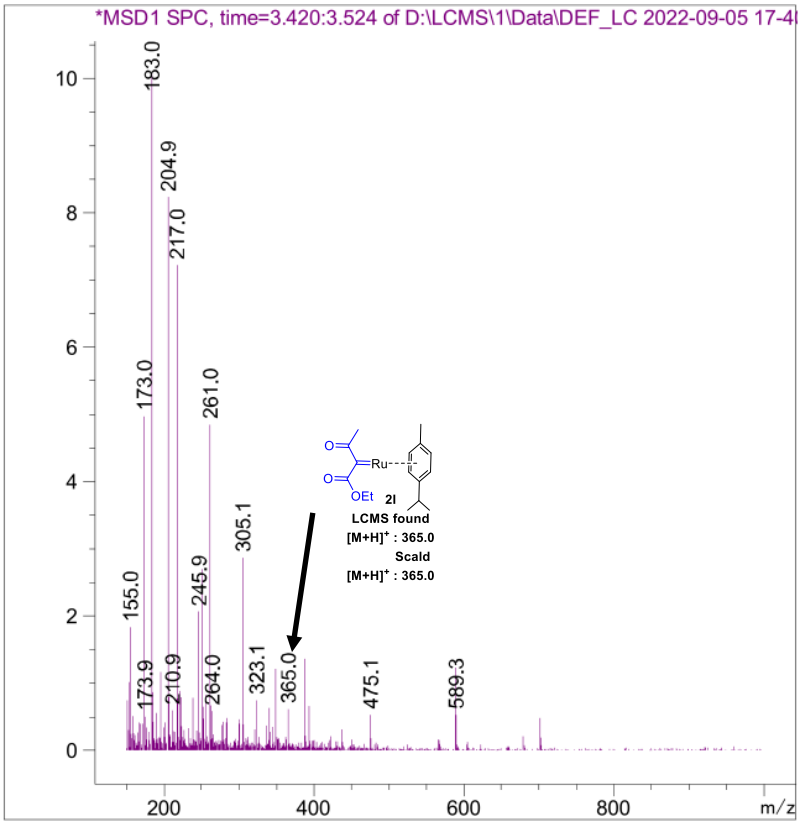
(3) Detection of intermediate 2I and 2e' by LCMS data

The eq 4 : As above **the eq 1**. ethyl 2-diazo-3-oxobutanoate 2e (23.3 mg, 2.5 equiv), AcOH (11.6 μL, 4 equiv). The reaction mixture was stirred in preheated oil bath at 55℃ under air atmosphere for 1h. After completion, the reaction mixture then tested by LCMS. Different ionic forms of intermediate **2I** and **2e'** were detected by LCMS.



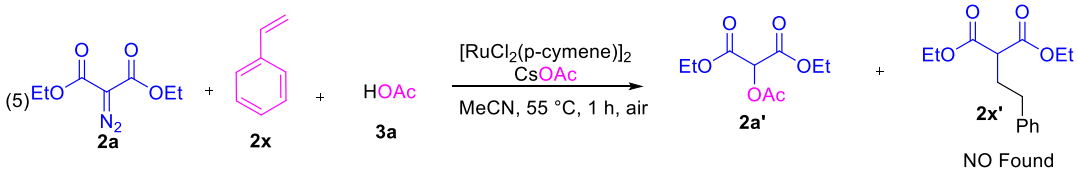
eq 4 LCMS:

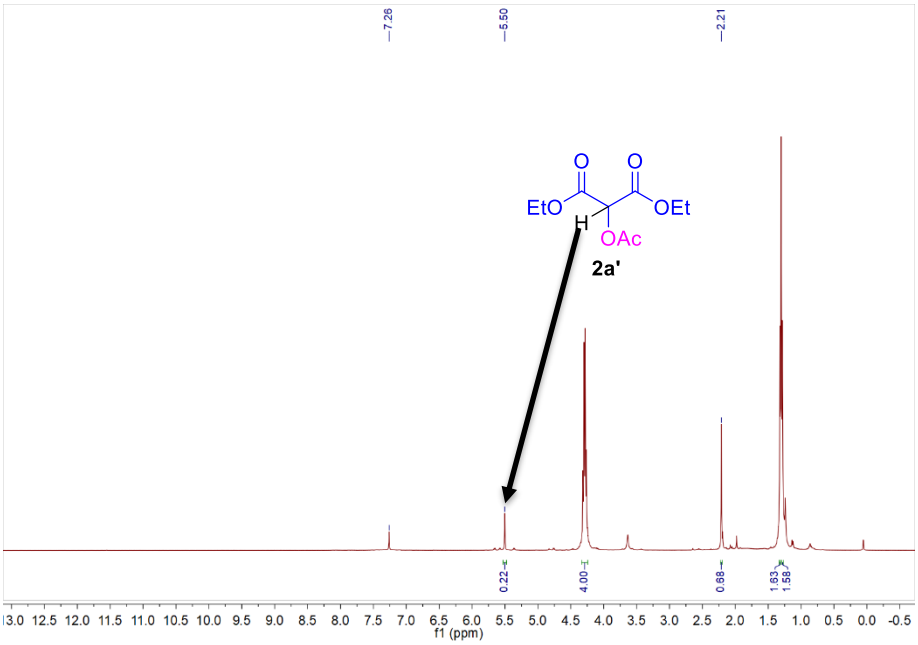




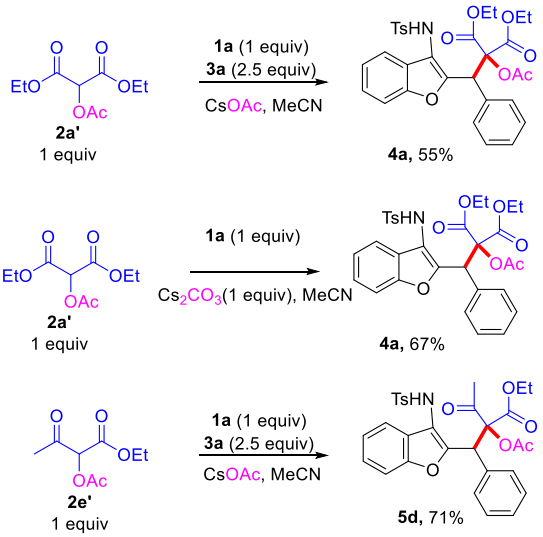
(4) Styrene capture experiment

The eq 5 : As above **the eq 1**, **2a** (0.125mmol), styrene **2x** (13 mg, 1 equiv), AcOH (7.3μL, 1 equiv). The reaction mixture was stirred in preheated oil bath at 55℃ under air atmosphere for 1 h. After completion, the reaction mixture fast through diatomite, low temperature vacuum spin drying then tested by crude NMR.





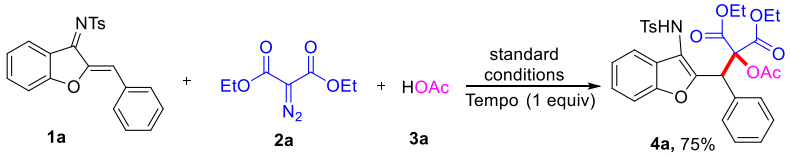
(5) Intermediate 2a' and 2e' transformation

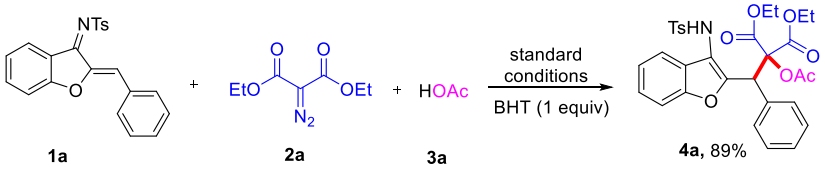


To a flame dried screw-cap tube equipped with magnetic stir bar were introduced diethyl 2-diazomalonate **2a'** (9.5 mg, 1 equiv), **1a** (18.8 mg, 1 equiv), CsOAc (19.2 mg, 2 equiv), AcOH (7.3μL, 2.5 equiv), MeCN (0.5 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 h. Monitored by TLC, after the completion of the reaction, spin-dried silica gel column chromatography to obtain the product **4a** (16.3 mg, 55%).

Diethyl 2-diazomalonate **2a'** (9.5 mg, 1 equiv), Cs_2CO_3(1 equiv), without **3a,** the reaction also gave the product **4a** (19.8 mg, 67%).

(6) Radical trapping experiment

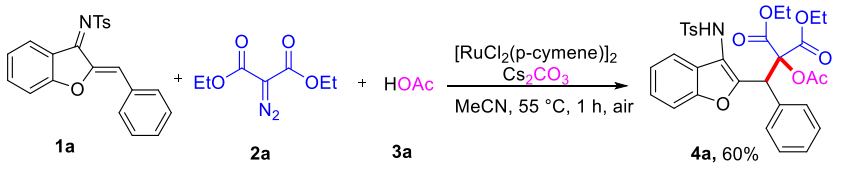




The TEMPO: To a flame dried screw-cap tube equipped with magnetic stir bar were introduced azadiene **1a** (18.8 mg, 0.05 mmol), and diethyl 2-diazomalonate **2a** (23.3 mg, 2.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (1.5 mg, 5 mol %), CsOAc (19. 2 mg, 2 equiv), AcOH (7.3μL, 2.5 equiv), TEMPO (7.8mg, 1equiv), MeCN (0.5 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 hour. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give the product **4a** (75%).

The BHT: As above, BHT (1equiv). The product **4a** (89%).

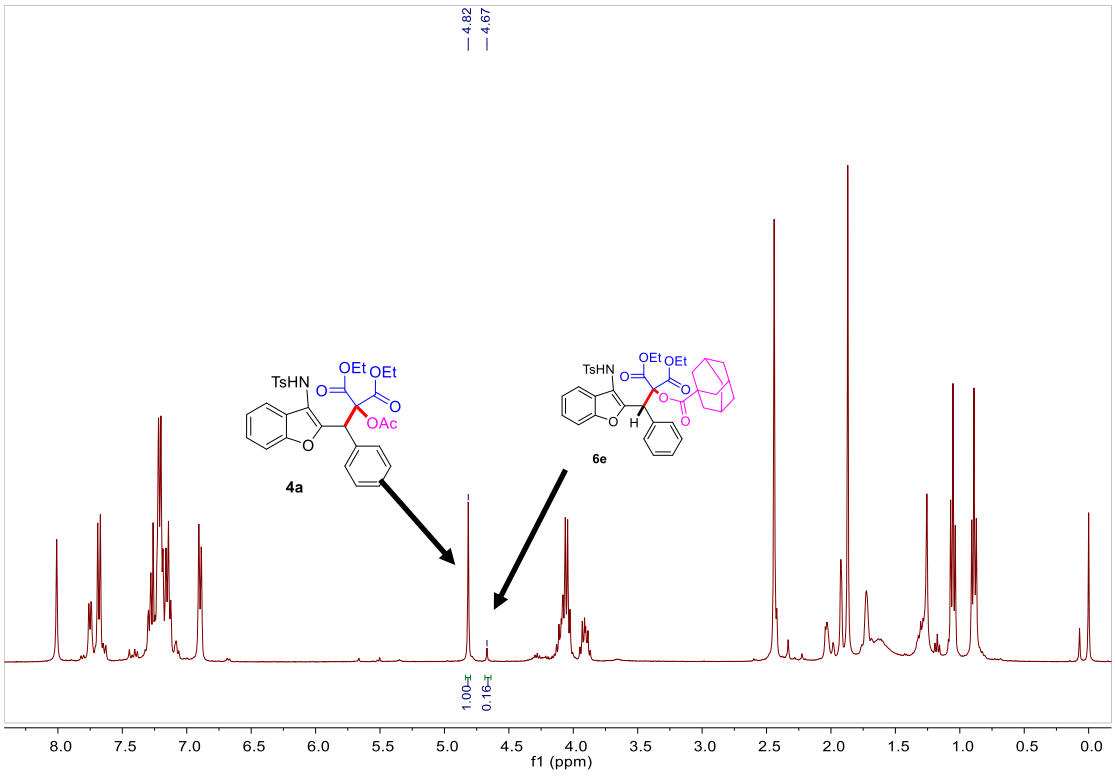
(7) Explore the source of acetate groups



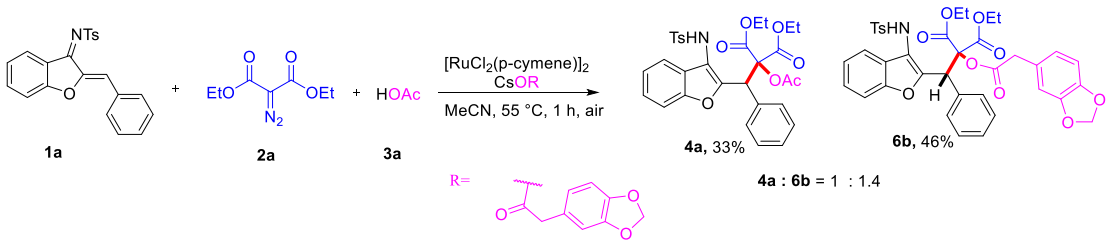
To a flame dried screw-cap tube equipped with magnetic stir bar were introduced azadiene **1a** (18.8 mg, 0.05 mmol), and diethyl 2-diazomalonate **2a** (23.3 mg, 2.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (1.5 mg, 5 mol %), Cs_2CO_3 (32.5 mg, 2 equiv), AcOH (7.3μL, 2.5 equiv), MeCN (0.5 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 hour. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give the product **4a** (60%).

As above, 1-AdCOOCs (31.2mg, 2 equiv). After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give the product **4a** (69%) and **6e** (11%). It can be seen from the crude NMR **4a**:**6e** = 6.3 :1.

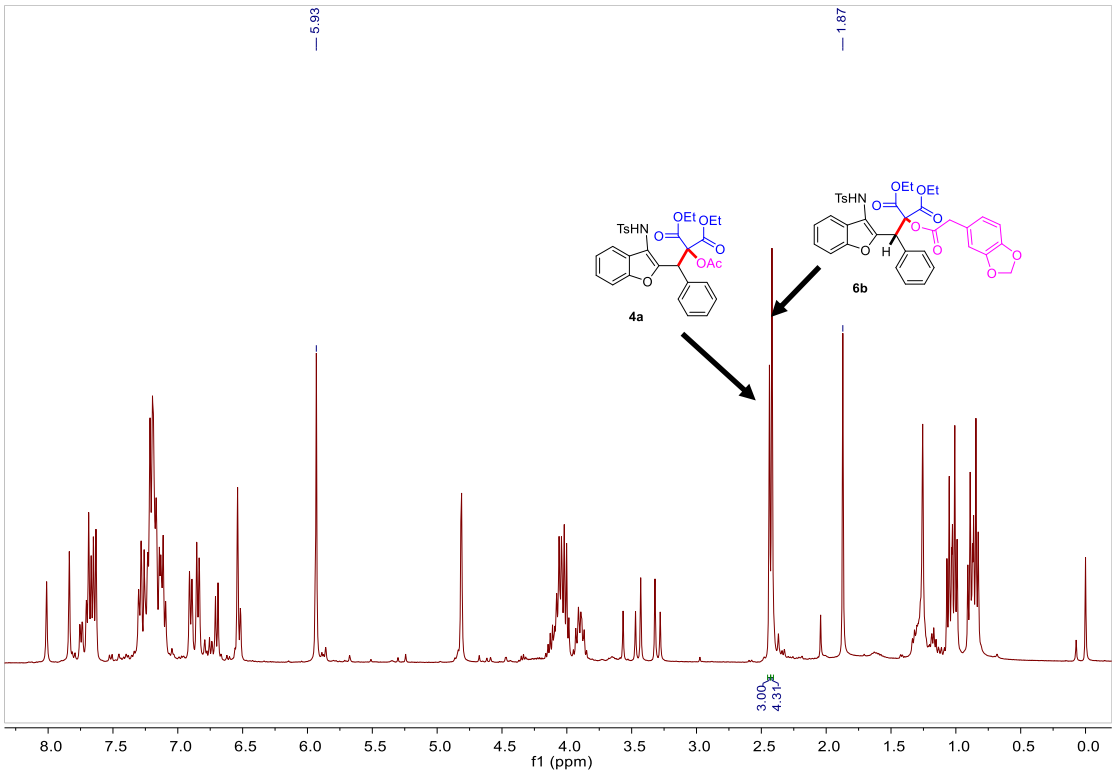
the crude NMR 4a:6e = 6.3 :1:



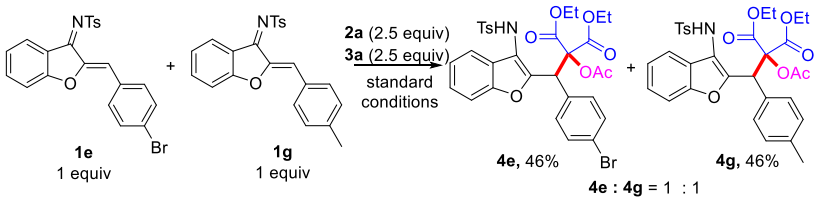
As above, CsOR (31.2 mg, 2 equiv). After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give the product **4a** (33%) and **6b** (46%). It can be seen from the crude NMR **4a**:**6b** = 1 :1.4.



the crude NMR 4a:6b = 1 :1.4:

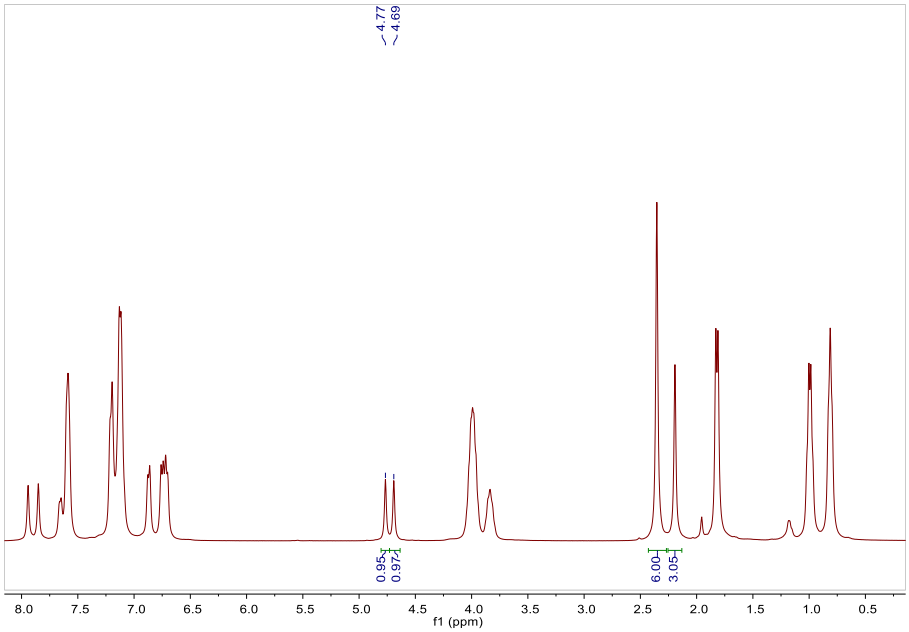


(8) 4e and 4g competition experiment

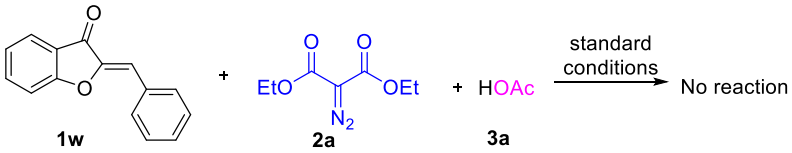


To a flame dried screw-cap tube equipped with magnetic stir bar were introduced azadiene **1e** (45.3 mg, 0.1 mmol), **1g** (38.9 mg, 0.1 mmol) and diethyl 2-diazomalonate **2a** (46.5 mg, 2.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %), CsOAc (38.4 mg, 2 equiv), AcOH (14.3μL, 2.5 equiv), MeCN (1 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 hour. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5) to give crude product **4e** and **4g** by crude NMR got **4e:4g = 1:1.**

Product 4e and 4g mixed crude NMR:



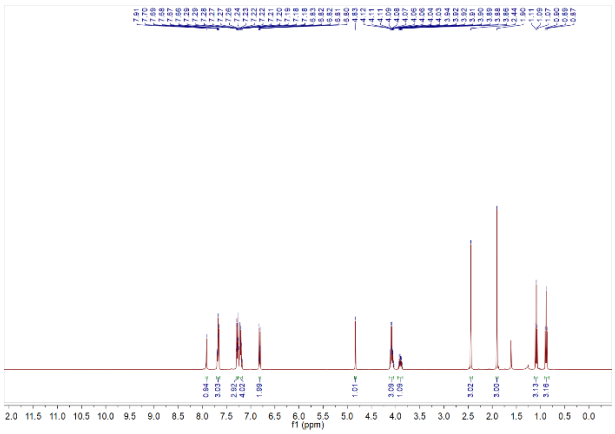
(9) The model reaction without imine group



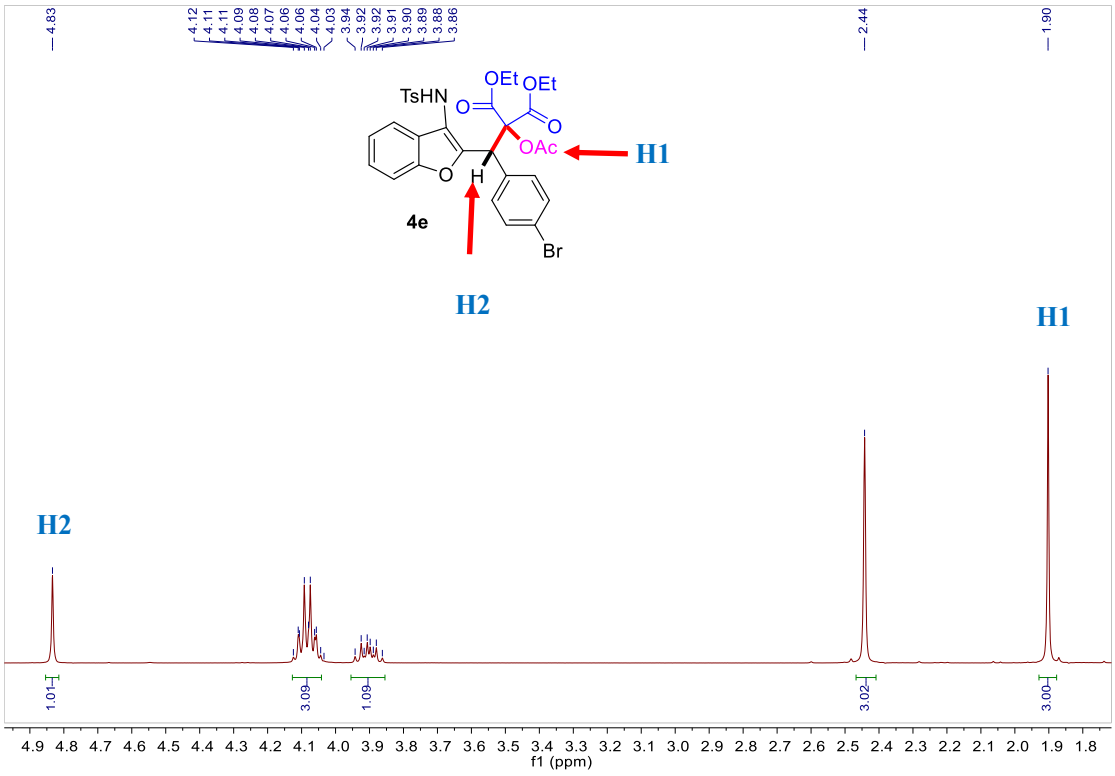
To a flame dried screw-cap tube equipped with magnetic stir bar were introduced (Z)-2-benzylidenebenzofuran-3(2H)-one **1w** (11.1 mg, 0.05 mmol), and diethyl 2-diazomalonate **2a** (23.3mg, 2.5 equiv), $[RuCl_2(p\text{-cymene})]_2$ (1.5 mg, 5 mol %), CsOAc (19.2 mg, 2 equiv), AcOH (7.3μL, 2.5 equiv), MeCN (0.5 mL). The reaction mixture was stirred in preheated oil bath at 55 °C under air atmosphere for 1 hour. No product formation was observed by TLC.

6. NOE Spectra of compound 4e, 5a and 5a'

^{1}H-NMR Spectra of compound 4e:

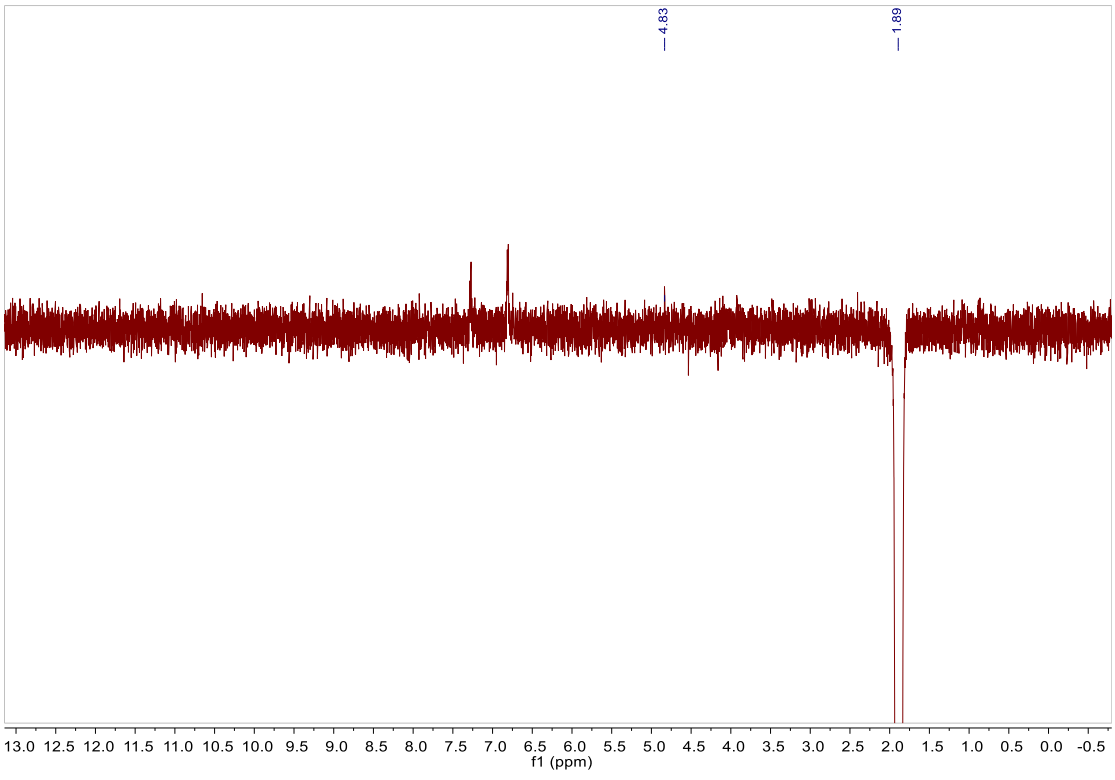


Partially magnified ^{1}H-NMR Spectra of compound 4e:

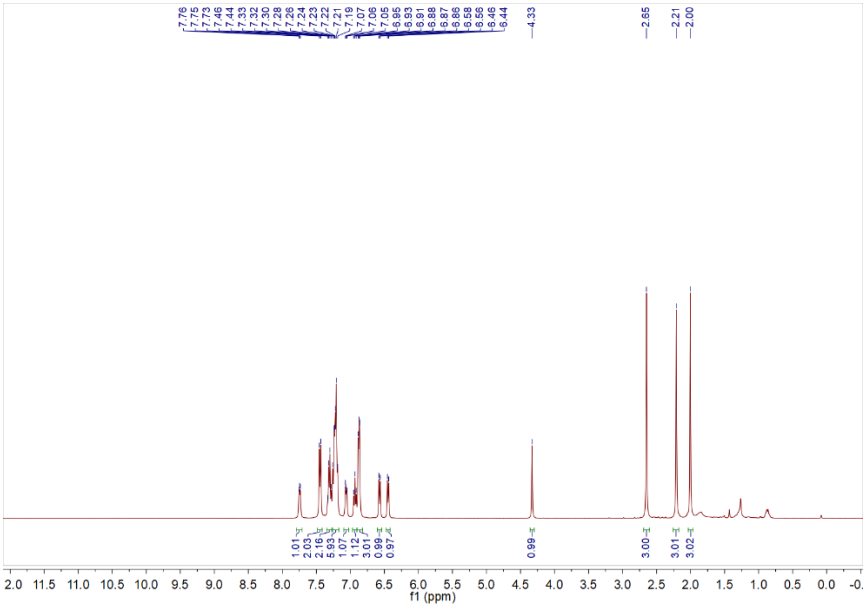


Irradiate 1.90 ppm (H1) of compound 4e:

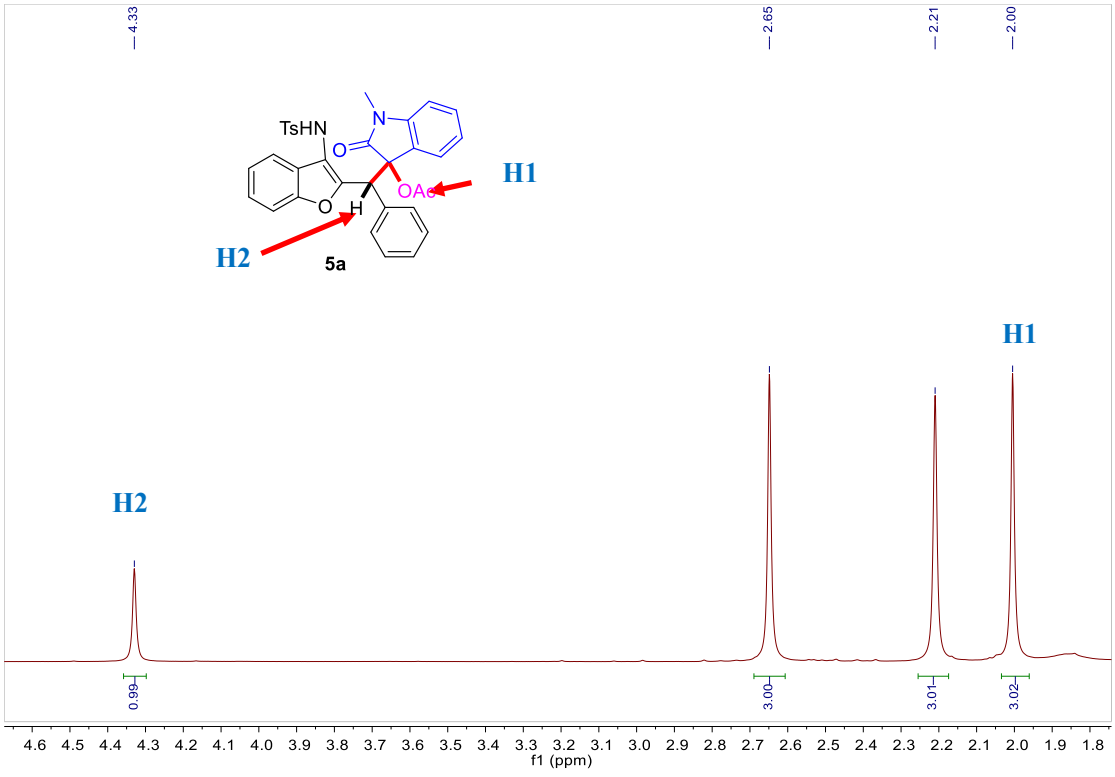
H1 and H2 are responsive:



^{1}H-NMR Spectra of compound 5a:

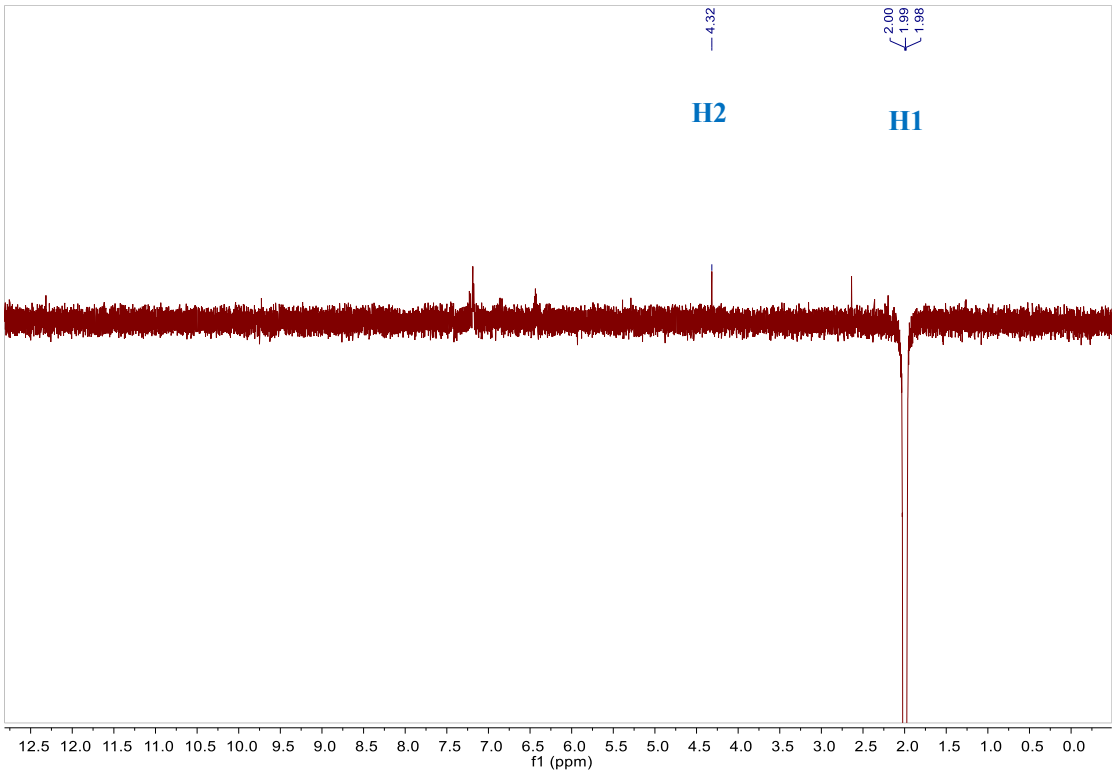


Partially magnified ^{1}H-NMR Spectra of compound 5a:

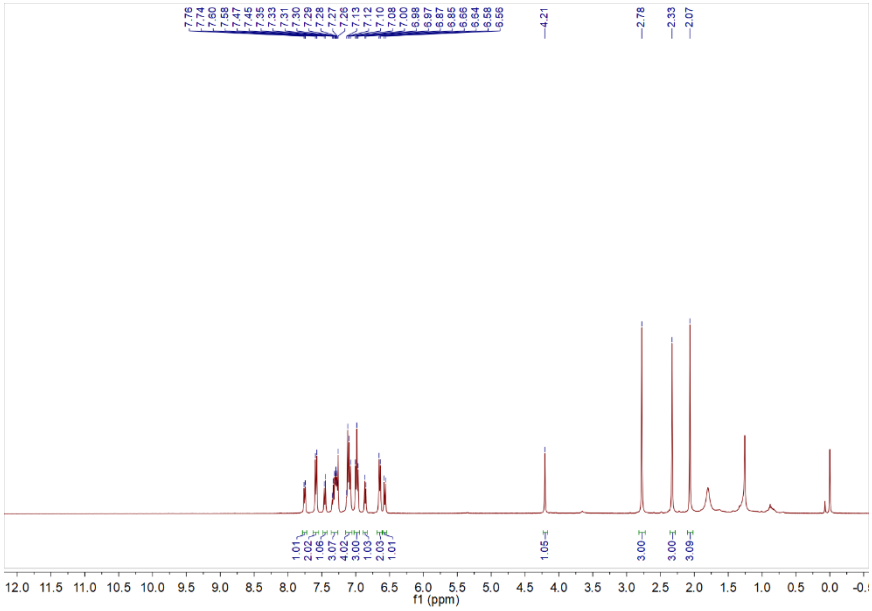


Irradiate 2.00 ppm (H1) of compound 5a:

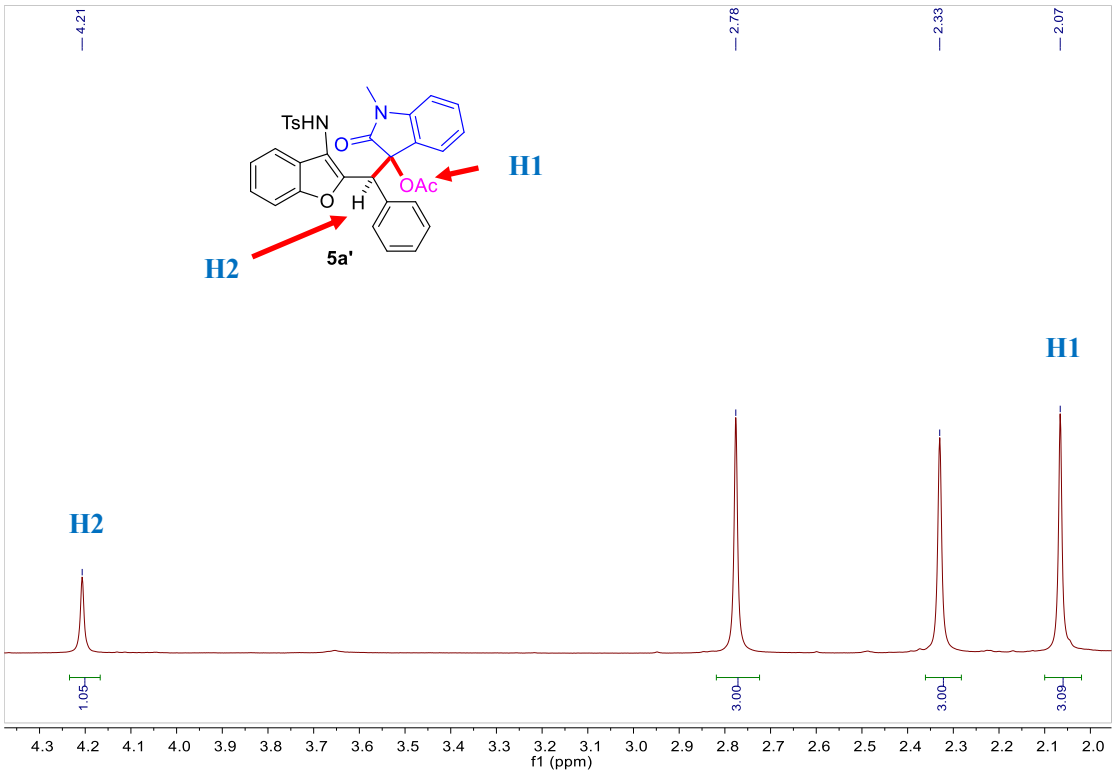
H1, H2 are responsive.



^{1}H-NMR Spectra of compound 5a':

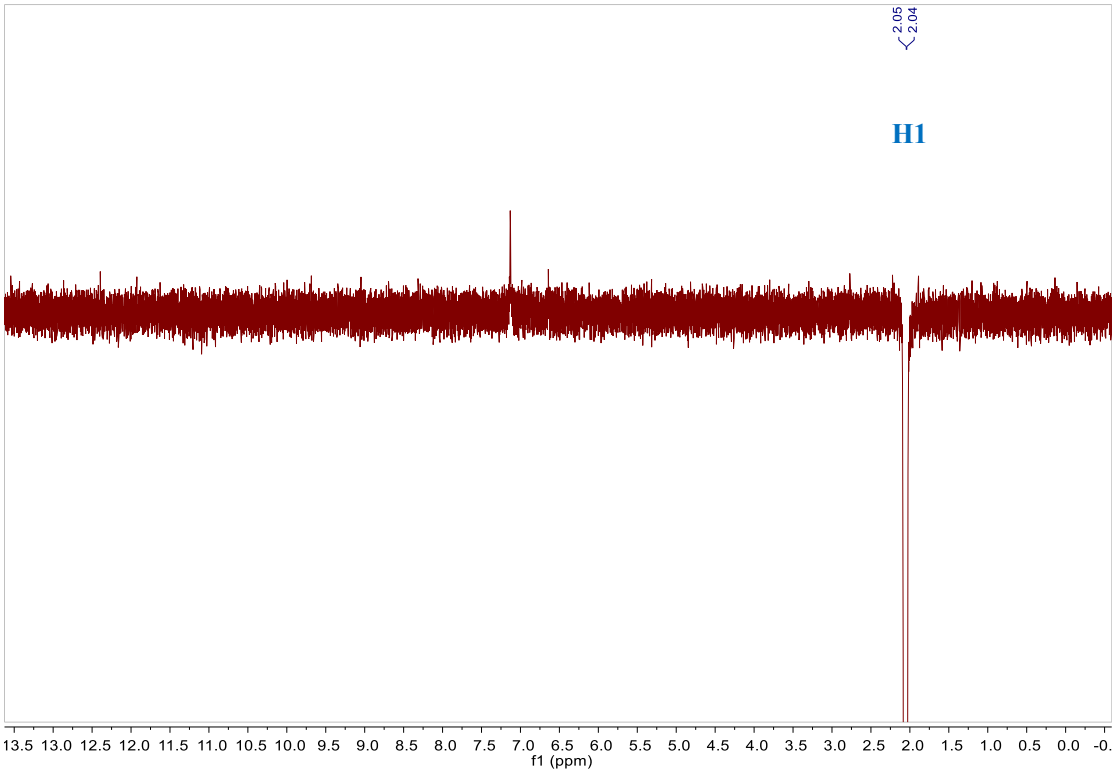


Partially magnified ^{1}H-NMR Spectra of compound 5a':

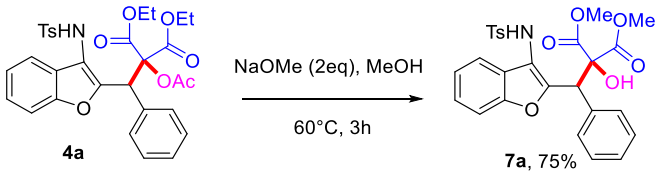


Irradiate 2.07 ppm (H1) of compound 5a':

H1, H2 are no responsive.



7. Synthetic application



To a flame dried screw-cap tube equipped with magnetic stir bar were introduced azadiene **4a** (56.3 mg, 0.1 mmol), NaOMe (16.2 mg, 3 equiv), MeOH (1.2 mL). The reaction mixture was stirred in preheated oil bath at 60°C under air atmosphere for 3 hours. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:3) to give the product **7a** (75%).[1]

References:

[1] Kanemitsu, T.; Sato, M.; Yoshida, M.; Ozasa, E.; Miyazaki, M.; Odanaka, Y.; Nagata, K.; Itoh, T. Enantioselectiveα-Benzoyloxylation of Malonic Diesters by Phase-Transfer Catalysis. *Org. Lett.* **2016**, 18, 5484−5487.

8. X-ray Data of Compound 4e and Sample Preparation

8.1 Sample Preparation and Crystal Measurement

Single crystals suitable for X-ray diffraction experiments were obtained by slowly evaporating a saturated solution of the corresponding compound 3ea in DCM/petroleum ether. Single crystals of C31H30BrNO9S [exp_2928_auto] were []. A suitable crystal was selected and [] on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 298.3(3) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

8.2 X-ray Data of Compound 4e

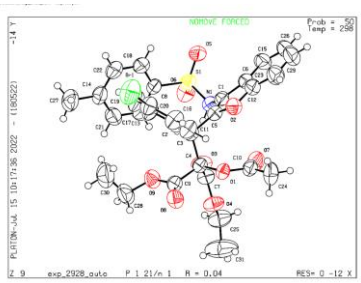


Figure S1. X-ray structure of 4e.

CCDC 2190884 contains the crystal data and supplementary crystallographic data as following: X-ray data of compound **4e** (C31H30BrNO9S): CCDC 2190884

Table S1. Crystal data of 4e

Empirical formula	C31H30BrNO9S
Formula weight	672.53
Temperature/K	298.3(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.09350(10)
b/Å	13.22240(10)
c/Å	28.2845(2)
α/°	90
β/°	93.9010(10)
γ/°	90
Volume/Å^3	3766.11(5)
Z	4
ρ_{calc}g/cm^3	1.186
μ/mm^{-1}	2.388
F(000)	1384.0
Crystal size/mm^3	0.18 × 0.16 × 0.15
Radiation	CuKα (λ = 1.54184
2Θ range for data collection/°	9.122 to 153.772
Index ranges	-12 ⩽ h ⩽ 12, -16 ⩽ k ⩽ 15, -35 ⩽ l ⩽ 31
Reflections collected	50245
Independent reflections	7730 [R_{int} = 0.0242, R_{sigma} = 0.0159]
Data/restraints/parameters	7730/0/392
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.1258
Largest diff. peak/hole / e Å^{-3}	0.57/-0.71

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_2928_auto. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	555.9(3)	7857.1(3)	5121.9(2)	105.71(14)
S1	4656.7(4)	7324.7(3)	2383.0(2)	54.88(12)
O1	6118.5(10)	5178.5(9)	4326.0(4)	50.1(2)
O2	6142.1(13)	7431.6(10)	4040.1(4)	60.5(3)
O3	5711.8(16)	4783.3(10)	3099.3(4)	67.7(3)
O4	6356.8(15)	3678.3(10)	3669.1(4)	67.5(3)

N1	5676.5(13)	6845.4(11)	2794.2(5)	51.3(3)
O5	4823.3(14)	8392.0(11)	2397.6(6)	74.0(4)
O6	4891.8(15)	6776.4(14)	1963.3(5)	75.4(4)
O7	7805.0(14)	5517.0(13)	3870.8(5)	74.8(4)
O8	4079.9(14)	3990.9(12)	4457.8(5)	72.1(4)
O9	3214.3(14)	4244.7(11)	3716.2(5)	70.3(4)
C1	5929.7(16)	7290.5(12)	3245.7(6)	50.2(3)
C2	3586.5(16)	6499.8(12)	4118.3(5)	49.3(3)
C3	4562.3(16)	6112.9(12)	3769.0(5)	47.3(3)
C4	5200.2(16)	5085.7(12)	3920.4(5)	47.6(3)
C5	5531.9(16)	6919.4(12)	3661.1(6)	49.9(3)
C6	6835.9(18)	8106.4(13)	3359.7(7)	58.6(4)
C7	5816.8(18)	4527.7(13)	3508.2(6)	55.3(4)
C8	3028.8(16)	7029.0(13)	2527.5(6)	52.4(4)
C9	4104.9(17)	4369.1(13)	4078.7(6)	52.4(4)
C10	7398.2(17)	5423.2(15)	4255.3(7)	58.8(4)
C11	3921.6(19)	6615.2(16)	4597.2(6)	62.6(4)
C12	6940.4(19)	8149.1(15)	3848.5(8)	63.2(4)
C13	2319.2(19)	6774.3(17)	3945.5(7)	65.2(5)
C14	459.9(18)	6505.4(18)	2723.5(7)	66.9(5)
C15	7575(2)	8783.9(15)	3102.2(9)	72.9(5)
C16	3022(2)	7005.3(17)	4897.7(7)	69.4(5)
C17	2639(2)	6032.8(16)	2514.8(9)	71.7(5)
C18	2156(2)	7766.3(15)	2648.2(9)	69.0(5)
C19	1408(2)	7166(2)	4242.1(8)	76.4(6)
C20	1785(2)	7284.3(17)	4713.7(7)	67.6(5)
C21	1366(2)	5779.3(17)	2613.5(9)	75.2(5)
C22	879(2)	7495.4(18)	2745.3(10)	77.9(6)
C23	7757(3)	8820.0(19)	4107.6(10)	84.1(6)
C24	8183(2)	5538(2)	4716.5(9)	86.5(7)
C25	6974(3)	3026.9(18)	3329.5(9)	85.8(7)
C26	8388(3)	9460.4(19)	3352.4(13)	90.7(8)
C27	-933(2)	6203(3)	2829.9(12)	98.1(8)
C28	2070(3)	3591(2)	3786.8(11)	95.0(8)
C29	8470(3)	9480(2)	3844.1(13)	96.9(8)
C30	892(3)	4181(3)	3861.8(14)	118.5(11)
C31	7232(6)	2067(3)	3549.3(18)	151.5(19)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_2928_auto. 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}
Br1	81.56(19)	142.6(3)	96.2(2)	-29.05(17)	29.97(15)	25.16(16)
S1	49.7(2)	64.2(2)	51.2(2)	14.38(17)	6.58(16)	5.11(17)
O1	43.4(5)	62.9(6)	43.9(5)	2.0(4)	1.4(4)	3.2(5)
O2	63.6(7)	62.7(7)	54.5(6)	-5.1(5)	-1.0(5)	-2.4(6)
O3	94.5(9)	64.5(7)	45.0(6)	1.8(5)	10.8(6)	16.1(7)
O4	88.3(9)	59.4(7)	56.5(7)	4.9(5)	16.2(6)	23.0(6)
N1	49.0(7)	54.7(7)	50.5(7)	6.8(6)	6.3(5)	6.9(6)
O5	66.6(8)	64.3(8)	90.5(10)	29.7(7)	1.4(7)	-1.2(6)
O6	69.3(8)	109.9(11)	48.2(6)	3.9(7)	12.3(6)	9.4(8)
O7	57.1(7)	99.7(11)	69.2(8)	13.1(7)	17.1(6)	4.8(7)
O8	69.5(8)	87.7(9)	58.2(7)	18.9(6)	-1.3(6)	-17.0(7)
O9	69.4(8)	77.8(8)	61.1(7)	1.8(6)	-13.6(6)	-15.1(7)
C1	43.7(7)	52.4(8)	54.7(8)	4.8(6)	5.2(6)	6.5(6)
C2	48.9(8)	53.7(8)	45.6(7)	1.9(6)	5.0(6)	4.5(6)
C3	47.8(7)	53.4(8)	40.7(7)	0.8(6)	2.3(6)	5.1(6)
C4	48.9(7)	54.3(8)	39.4(7)	1.2(6)	1.0(6)	3.3(6)
C5	48.6(8)	52.7(8)	48.0(8)	0.1(6)	0.7(6)	5.5(6)
C6	49.8(9)	52.4(9)	74.2(11)	3.1(8)	8.4(8)	4.2(7)
C7	63.2(10)	55.0(9)	48.2(8)	1.2(7)	8.1(7)	8.6(7)
C8	45.8(8)	58.4(9)	53.3(8)	6.1(7)	4.0(6)	6.3(7)
C9	53.2(8)	55.8(9)	48.1(8)	0.3(7)	1.3(6)	0.9(7)
C10	47.2(8)	66.8(10)	62.6(10)	6.1(8)	5.0(7)	4.8(7)
C11	58.7(10)	82.6(12)	46.5(8)	-2.5(8)	2.3(7)	16.4(9)
C12	55.1(9)	57.6(10)	76.4(12)	-4.8(8)	1.2(8)	1.2(8)
C13	55.7(9)	86.5(13)	52.7(9)	-3.8(9)	-0.4(7)	12.5(9)
C14	49.1(9)	85.4(13)	66.4(10)	10.2(9)	4.9(8)	3.4(9)
C15	64.3(11)	58.3(10)	98.1(15)	8.0(10)	19.9(10)	-1.5(9)
C16	71.1(12)	87.3(13)	50.3(9)	-6.9(9)	8.7(8)	14.4(10)
C17	61.7(10)	59.1(10)	96.1(14)	-6.9(10)	19.3(10)	4.0(8)
C18	58.6(10)	58.1(10)	90.8(14)	2.7(9)	9.8(10)	9.8(8)
C19	51.7(10)	105.0(17)	72.3(12)	-7.2(11)	3.7(9)	19.6(10)
C20	60.2(10)	78.6(12)	66.0(11)	-8.3(9)	17.9(9)	9.7(9)
C21	63.6(11)	65.3(11)	98.0(15)	-5.9(10)	16.0(10)	-8.0(9)
C22	55.5(11)	76.0(13)	103.6(16)	1.4(12)	15.3(10)	18.7(10)
C23	77.7(14)	76.2(14)	96.4(16)	-18.6(12)	-6.9(12)	-6.6(11)
C24	56.3(11)	124(2)	77.6(13)	0.8(13)	-8.0(10)	-12.9(12)
C25	110.2(19)	74.9(13)	75.4(13)	-3.2(10)	29.4(13)	31.4(13)

C26	73.3(14)	63.7(12)	136(2)	0.5(13)	16.7(14)	-13.2(10)
C27	55.5(12)	122(2)	119(2)	18.3(17)	20.1(12)	-0.6(13)
C28	89.3(17)	89.7(16)	101.7(18)	4.7(14)	-24.7(14)	-34.2(14)
C29	74.2(14)	72.7(14)	143(3)	-18.3(15)	0.7(15)	-16.3(11)
C30	74.3(16)	149(3)	132(3)	15(2)	7.2(16)	-23.3(18)
C31	214(5)	91(2)	160(3)	23(2)	92(3)	66(3)

Table S4. Bond Lengths for exp_2928_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C20	1.9080(19)	C3	C5	1.493(2)
S1	N1	1.6282(14)	C4	C7	1.546(2)
S1	O5	1.4215(16)	C4	C9	1.545(2)
S1	O6	1.4246(15)	C6	C12	1.381(3)
S1	C8	1.7639(18)	C6	C15	1.401(3)
O1	C4	1.4301(18)	C8	C17	1.374(3)
O1	C10	1.359(2)	C8	C18	1.373(3)
O2	C5	1.377(2)	C10	C24	1.487(3)
O2	C12	1.379(2)	C11	C16	1.385(3)
O3	C7	1.203(2)	C12	C23	1.386(3)
O4	C7	1.316(2)	C13	C19	1.387(3)
O4	C25	1.461(2)	C14	C21	1.376(3)
N1	C1	1.414(2)	C14	C22	1.376(3)
O7	C10	1.195(2)	C14	C27	1.511(3)
O8	C9	1.185(2)	C15	C26	1.377(4)
O9	C9	1.327(2)	C16	C20	1.371(3)
O9	C28	1.467(3)	C17	C21	1.375(3)
C1	C5	1.359(2)	C18	C22	1.383(3)
C1	C6	1.437(3)	C19	C20	1.371(3)
C2	C3	1.530(2)	C23	C29	1.381(4)
C2	C11	1.382(2)	C25	C31	1.429(4)
C2	C13	1.386(2)	C26	C29	1.388(4)
C3	C4	1.551(2)	C28	C30	1.449(5)

Table S5. Bond Angles for exp_2928_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	S1	C8	107.57(8)	O4	C7	C4	108.97(13)
O5	S1	N1	107.33(8)	C17	C8	S1	118.40(14)

O5	S1	O6	120.23(10)	C18	C8	S1	121.61(14)
O5	S1	C8	108.87(9)	C18	C8	C17	119.99(17)
O6	S1	N1	105.32(8)	O8	C9	O9	126.29(17)
O6	S1	C8	106.91(9)	O8	C9	C4	125.49(15)
C10	O1	C4	118.23(13)	O9	C9	C4	108.22(13)
C5	O2	C12	105.95(14)	O1	C10	C24	110.51(16)
C7	O4	C25	117.45(15)	O7	C10	O1	123.18(17)
C1	N1	S1	123.36(11)	O7	C10	C24	126.30(19)
C9	O9	C28	117.78(16)	C2	C11	C16	121.04(17)
N1	C1	C6	126.06(15)	O2	C12	C6	111.00(16)
C5	C1	N1	125.79(15)	O2	C12	C23	125.1(2)
C5	C1	C6	107.34(16)	C6	C12	C23	123.9(2)
C11	C2	C3	122.99(15)	C2	C13	C19	121.23(18)
C11	C2	C13	118.37(16)	C21	C14	C27	120.2(2)
C13	C2	C3	118.61(14)	C22	C14	C21	117.84(18)
C2	C3	C4	112.82(13)	C22	C14	C27	122.0(2)
C5	C3	C2	110.67(13)	C26	C15	C6	117.9(2)
C5	C3	C4	114.61(13)	C20	C16	C11	119.05(18)
O1	C4	C3	112.37(12)	C8	C17	C21	119.86(19)
O1	C4	C7	111.94(13)	C8	C18	C22	119.22(19)
O1	C4	C9	104.93(12)	C20	C19	C13	118.67(18)
C7	C4	C3	112.99(12)	C16	C20	Br1	119.35(15)
C9	C4	C3	108.98(13)	C16	C20	C19	121.62(18)
C9	C4	C7	104.98(13)	C19	C20	Br1	119.04(15)
O2	C5	C3	117.18(14)	C17	C21	C14	121.4(2)
C1	C5	O2	110.64(15)	C14	C22	C18	121.67(19)
C1	C5	C3	132.15(15)	C29	C23	C12	115.6(3)
C12	C6	C1	105.05(16)	C31	C25	O4	108.1(2)
C12	C6	C15	119.17(19)	C15	C26	C29	121.3(2)
C15	C6	C1	135.8(2)	C30	C28	O9	111.4(2)
O3	C7	O4	125.42(16)	C23	C29	C26	122.1(2)
O3	C7	C4	125.28(15)				

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_2928_auto.

Atom	***x***	***y***	***z***	**U(eq)**
H1	5505	6213	2827	62
H3	4034	5983	3472	57
H11	4764	6428	4720	75

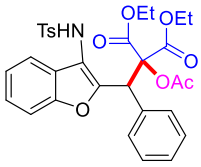
H13	2076	6694	3625	78
H15	7518	8777	2773	88
H16	3254	7077	5220	83
H17	3236	5531	2440	86
H18	2419	8440	2664	83
H19	558	7344	4124	92
H21	1112	5103	2606	90
H22	288	7995	2827	94
H23	7821	8825	4437	101
H24A	7788	6052	4901	130
H24B	9077	5729	4661	130
H24C	8192	4908	4885	130
H25A	6384	2945	3047	103
H25B	7796	3327	3239	103
H26	8893	9913	3189	109
H27A	-1047	5490	2779	147
H27B	-1562	6566	2624	147
H27C	-1075	6363	3154	147
H28A	1901	3163	3511	114
H28B	2271	3158	4059	114
H29	9023	9952	4001	116
H30A	687	4606	3592	178
H30B	1050	4593	4139	178
H30C	160	3734	3904	178
H31A	7727	1652	3345	227
H31B	6407	1742	3604	227
H31C	7738	2163	3846	227

Table S7. Solvent masks information for exp_2928_auto.

Number	X	Y	Z	Volume	Electron count	Content
1	-0.494	0.000	0.500	450.1	96.4	?
2	-0.384	0.500	0.000	450.1	96.4	?

9. Characterization Data and NMR Spectra

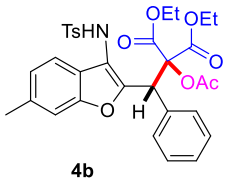
Diethyl(S)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl) malonate (4a)



4a

52.8 mg, 89% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1NH), 7.75 (dd, J = 6.7, 2.3 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.20 (qd, J = 5.9, 5.5, 1.6 Hz, 5H), 7.14 (t, J = 7.3 Hz, 2H), 6.94 – 6.85 (m, 2H), 4.82 (s, 1H), 4.14 – 4.01 (m, 3H), 3.91 (dq, J = 10.7, 7.2 Hz, 1H), 2.44 (s, 3H), 1.87 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.2, 166.1, 153.6, 147.0, 143.6, 136.8, 133.6, 130.4, 129.8, 127.8, 127.8, 127.5, 125.8, 124.9, 123.3, 121.5, 116.3, 110.7, 83.1, 63.2, 62.9, 45.7, 21.6, 20.2, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{31}NNaO_9S^+$ 616.1612; Found 616.1612.

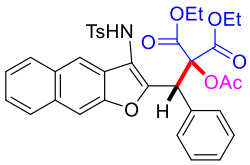
Diethyl(R)-2-acetoxy-2-((6-methyl-3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl) methyl)malonate (4b)



4b

45.7mg, 75% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1NH), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 7.8, 6.3 Hz, 3H), 7.16 – 7.09 (m, 3H), 7.03 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.91 – 6.85 (m, 2H), 4.77 (s, 1H), 4.13 – 4.01 (m, 3H), 3.92 (dd, *J* = 10.7, 7.1 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 1.88 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.2, 165.9, 151.4, 148.6, 143.7, 137.6, 133.7, 130.8, 130.6, 129.9, 128.3, 127.9, 127.8, 127.5, 126.5, 126.1, 124.8, 124.4, 117.6, 111.6, 83.6, 63.1, 62.8, 45.7, 21.6, 20.3, 13.7, 13.4. RMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{34}NO_9S$ 608.1949; Found 608.1955.

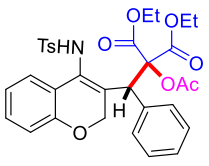
Diethyl(R)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)naphtho[2,3-b]furan-2-yl)(phenyl) methyl) malonate (4c)



4c

59.8 mg, 93% yield; White powder; eluent (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.5 Hz, 1H), 7.98 (s, 1NH), 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.25 – 7.18 (m, 5H), 7.06 (dt, *J* = 6.6, 1.6 Hz, 2H), 5.05 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 3H), 3.90 (dd, *J* = 10.7, 7.1 Hz, 1H), 2.43 (s, 3H), 1.91 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl^3$) δ 168.8, 166.2, 154.0, 146.1, 143.5, 136.8, 135.3, 133.7, 130.4, 129.8, 127.8, 127.7, 127.5, 124.8, 120.9, 116.1, 110.9, 83.2, 63.2, 62.8, 45.7, 21.6, 21.6, 20.2, 13.6, 13.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{33}NNaO_9S^+$ 666.1768; Found 666.1771 .

Diethyl(R)-2-acetoxy-2-((4-((4-methylphenyl)sulfonamido)-2H-chromen-3-yl)(phenyl)methyl) malonate (4d)

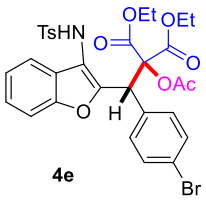


4d

31.7 mg, 52% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.04 (td, *J* = 7.7, 1.5 Hz, 1H), 6.88 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.72 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.63 (td, *J* = 7.6, 1.2 Hz, 1H), 6.50 (s, 1NH), 5.22 (s, 1H), 4.87 – 4.72 (m, 2H), 4.21 (qd, *J* = 7.1, 2.2 Hz, 2H), 3.98 (qd, *J* = 7.1, 1.2 Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 166.4, 165.3, 154.8, 143.9, 137.4, 135.9, 129.7, 129.7, 129.4, 129.0, 128.4, 128.0, 127.7, 127.4, 124.9, 121.0, 115.6, 85.2, 66.5, 63.0, 62.6, 49.4,

21.5, 21.0, 13.7, 13.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{33}NO_9S$ 608.1949; Found 608.1954.

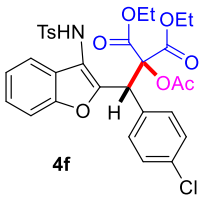
Diethyl(R)-2-acetoxy-2-((4-bromophenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl) methyl)malonate (4e)



4e

54.3 mg, 80% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1NH), 7.68 (dd, *J* = 8.4, 6.6 Hz, 3H), 7.28 (dd, *J* = 8.8, 2.2 Hz, 3H), 7.25 – 7.17 (m, 4H), 6.84 – 6.79 (m, 2H), 4.83 (s, 1H), 4.08 (qd, *J* = 7.2, 3.3 Hz, 3H), 3.90 (dq, *J* = 10.6, 7.1 Hz, 1H), 2.44 (s, 3H), 1.90 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 166.1, 165.9, 153.6, 146.5, 143.7, 136.8, 132.6, 132.1, 131.0, 129.8, 127.6, 125.7, 125.1, 123.4, 122.1, 121.4, 116.4, 110.7, 82.9, 63.3, 63.0, 45.1, 21.6, 20.3, 13.7, 13.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{30}BrNO_9S$ 672.0897; Found 672.0890.

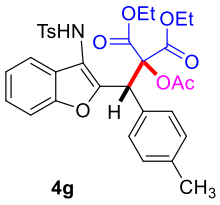
Diethyl(R)-2-acetoxy-2-((4-chlorophenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl) methyl)malonate (4f)



4f

55.8 mg, 89% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1NH), 7.68 (dd, *J* = 8.4, 6.7 Hz, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.17 (m, 4H), 7.15 – 7.10 (m, 2H), 6.90 – 6.85 (m, 2H), 4.85 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 3H), 3.90 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.44 (s, 3H), 1.90 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.1, 153.6, 146.6, 143.7, 136.8, 133.9, 132.1, 131.8, 129.8, 128.0, 127.6, 125.7, 125.1, 123.4, 121.4, 116.4, 110.7, 82.9, 63.3, 63.0, 45.1, 21.6, 20.3, 13.7, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}ClNNaO_9S^+$ 650.1222; Found 650.1219.

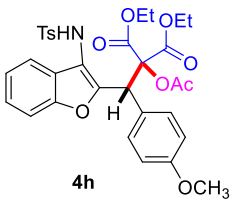
Diethyl(R)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(p-tolyl)methyl) malonate (4g)



4g

55.8 mg, 92% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1NH), 7.77 – 7.71 (m, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.21 (dt, *J* = 9.1, 2.6 Hz, 4H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 4.77 (s, 1H), 4.07 (dq, *J* = 14.3, 7.1 Hz, 3H), 3.91 (dq, *J* = 10.6, 7.2 Hz, 1H), 2.44 (s, 3H), 2.27 (s, 3H), 1.89 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 153.6, 147.3, 143.5, 137.6, 136.9, 130.5, 130.3, 129.8, 128.5, 127.5, 125.8, 124.9, 123.3, 121.4, 116.1, 110.7, 83.3, 76.7, 63.2, 62.8, 45.3, 21.6, 21.1, 20.3, 13.7, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{33}NNaO_9S^+$ 630.1768; Found 630.1767.

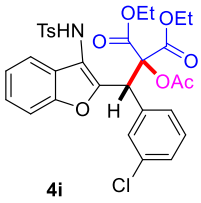
Diethyl(R)-2-acetoxy-2-((4-methoxyphenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl) methyl)malonate (4h)



4h

57.3 mg, 92% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1NH), 7.76 – 7.70 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.17 (m, 4H), 6.87 – 6.80 (m, 2H), 6.70 – 6.65 (m, 2H), 4.76 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 3H), 3.90 (dq, *J* = 10.6, 7.2 Hz, 1H), 3.76 (s, 3H), 2.44 (s, 3H), 1.89 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.2, 159.1, 153.6, 147.4, 143.5, 136.8, 131.6, 129.8, 127.5, 125.8, 125.6, 124.9, 123.3, 121.4, 116.0, 113.1, 110.7, 83.3, 63.2, 62.8, 55.2, 44.9, 21.6, 20.3, 13.7, 13.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{34}NNaO_{10}S^+$ 646.1717; Found 646.1716.

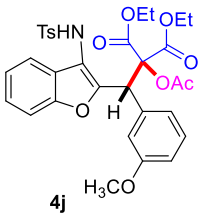
diethyl(R)-2-acetoxy-2-((3-chlorophenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl) methyl)malonate (4i)



4i

57.0 mg, 91% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1NH), 7.76 – 7.72 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.26 – 7.18 (m, 5H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.03 (dt, *J* = 7.8, 1.5 Hz, 1H), 6.81 (t, *J* = 1.8 Hz, 1H), 4.83 (s, 1H), 4.08 (qd, *J* = 7.2, 6.2, 1.5 Hz, 3H), 3.93 (dd, *J* = 10.7, 7.1 Hz, 1H), 2.43 (s, 3H), 1.92 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.0, 165.9, 153.6, 146.2, 143.9, 136.9, 135.5, 133.5, 130.3, 129.9, 129.1, 128.7, 128.1, 127.4, 125.8, 125.2, 123.5, 121.5, 116.7, 110.8, 83.0, 63.4, 63.0, 45.4, 21.8, 20.2, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{30}ClNNaO_9S^+$ 650.1222 ; Found 650.1227.

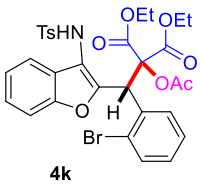
Diethyl(R)-2-acetoxy-2-((3-methoxyphenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)methyl)malonate(4j)



4j

58.0mg, 93% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1NH), 7.72 – 7.64 (m, 3H), 7.30 – 7.27 (m, 1H), 7.21 (pt, *J* = 7.5, 3.6 Hz, 4H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.77 – 6.72 (m, 1H), 6.69 (t, *J* = 2.1 Hz, 1H), 6.45 – 6.40 (m, 1H), 4.81 (s, 1H), 4.12 – 4.03 (m, 3H), 3.93 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 1.91 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.0, 159.0, 153.6, 147.1, 143.8, 136.8, 134.9, 129.8, 128.6, 127.5, 125.8, 124.9, 123.3, 122.8, 121.4, 117.0, 116.3, 112.5, 110.8, 83.2, 63.2, 62.8, 55.2, 45.5, 21.6, 20.3, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{33}NNaO_{10}S^+$ 646.1717 ; Found 646.1712.

Diethyl(R)-2-acetoxy-2-((2-bromophenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl) methyl)malonate (4k)

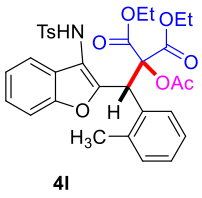


4k

61.1 mg, 91% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.84 (s, 1NH), 7.72 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.41 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.22 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.07 (m, 2H), 5.92 (s, 1H), 4.05 (dtt, *J* = 17.5, 7.3, 3.6 Hz, 4H), 2.38 (s, 3H), 2.05 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 153.6, 144.5, 143.6, 137.6, 133.5, 132.7, 132.3, 129.7, 129.4, 127.5, 127.2, 125.8, 125.0, 124.9, 123.1, 121.8, 117.4,

110.8, 83.6, 63.3, 62.9, 44.2, 21.6, 20.4, 13.5, 13.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{31}H_{30}BrNNaO_9S^+$ 694.0717 ; Found 694.0714.

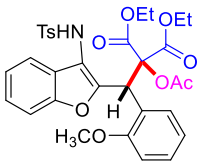
Diethyl(R)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(o-tolyl)methyl) malonate (4l)



4l

55.2 mg, 91% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.95 (s, 1NH), 7.73 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.13 (dt, *J* = 12.8, 7.7 Hz, 2H), 7.04 – 6.96 (m, 2H), 5.59 (s, 1H), 4.10 – 3.90 (m, 4H), 2.39 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 166.7, 165.9, 153.5, 146.3, 143.7, 137.9, 137.3, 132.3, 130.9, 130.3, 129.7, 127.9, 127.5, 125.8, 125.2, 124.8, 123.0, 121.1, 116.6, 110.9, 83.8, 63.2, 62.8, 40.6, 21.6, 20.3, 19.3, 13.5, 13.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{32}H_{33}NNaO_9S^+$ 630.1768 ; Found 630.1760.

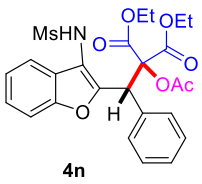
Diethyl(R)-2-acetoxy-2-((2-methoxyphenyl)(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl) methyl)malonate (4m)



4m

56.1 mg, 90% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.51 (s, 1NH), 7.43 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.21 (td, *J* = 7.7, 3.6 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 5.81 (s, 1H), 4.06 – 3.94 (m, 4H), 3.71 (s, 3H), 2.32 (s, 3H), 2.06 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 166.3, 165.3, 156.7, 153.6, 147.5, 137.1, 131.4, 129.3, 129.1, 127.3, 125.0, 124.7, 123.0, 122.3, 121.2, 120.2, 110.9, 109.9, 83.6, 62.8, 62.4, 55.4, 37.1, 21.6, 20.5, 13.5, 13.4. HRMS (ESI-TOF) m/z: [M +Na]$^+$ Calcd for $C_{32}H_{33}NNaO_{10}S^+$ 646.1717 ; Found 646.1720.

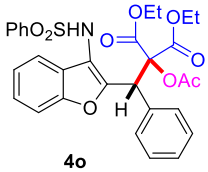
Diethyl (R)-2-acetoxy-2-((3-(methylsulfonamido)benzofuran-2-yl)(phenyl)methyl)malonate (4n)



4n

47.6mg, 92% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.66 – 7.61 (m, 2H), 7.50 (s, 1NH), 7.39 – 7.29 (m, 4H), 7.28 (d, *J* = 5.4 Hz, 1H), 7.24 (d, *J* = 1.7 Hz, 1H), 5.42 (s, 1H), 4.16 – 3.96 (m, 4H), 3.04 (s, 3H), 2.01 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 166.1, 165.8, 153.6, 148.1, 133.8, 130.5, 128.5, 128.3, 125.5, 125.2, 123.5, 120.7, 116.1, 111.1, 83.4, 63.2, 62.9, 46.1, 39.7, 20.4, 13.7, 13.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{27}NNaO_9S^+$ 540.1299 ; Found 540.1299.

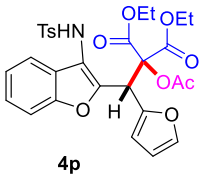
Diethyl (R)-2-acetoxy-2-(phenyl(3-(phenylsulfonamido)benzofuran-2-yl)methyl)malonate (4o)



4o

55.6 mg, 96% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1NH), 7.85 – 7.80 (m, 2H), 7.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.12 (m, 5H), 6.90 – 6.85 (m, 2H), 4.84 (s, 1H), 4.13 – 4.02 (m, 3H), 3.92 (dq, *J* = 10.7, 7.1 Hz, 1H), 1.87 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 166.2, 147.3, 139.9, 133.5, 132.8, 130.4, 129.3, 127.9, 127.5, 125.7, 125.0, 123.3, 121.3, 116.0, 110.8, 83.1, 63.2, 62.9, 45.7, 20.2, 13.6, 13.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{30}H_{29}NNaO_9S^+$ 602.1455; Found 602.1457.

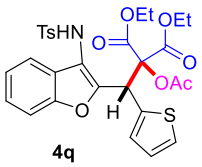
Diethyl(R)-2-acetoxy-2-(furan-2-yl(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)methyl) malonate (4p)



4p

38.5mg, 66% yield; light yellow oil; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.76 (s, 1NH), 7.63 – 7.54 (m, 2H), 7.35 – 7.26 (m, 3H), 7.19 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.24 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.20 (d, *J* = 3.3 Hz, 1H), 4.78 (s, 1H), 4.22 – 4.07 (m, 3H), 3.92 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.34 (s, 3H), 2.01 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.9, 153.6, 146.8, 145.2, 143.4, 141.8, 136.0, 129.6, 127.2, 125.9, 125.2, 123.5, 121.5, 117.0, 110.8, 110.6, 110.5, 82.2, 63.1, 62.9, 39.5, 21.6, 20.4, 13.7, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{29}NNaO_{10}S^+$ 606.1404 ; Found 606.1407.

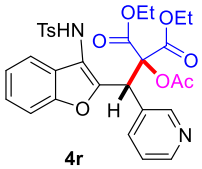
Diethyl(R)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(thiophen-2-yl)methyl) malonate (4q)



4q

49.7 mg, 83% yield; light yellow powder; eluent (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1NH), 7.73 – 7.68 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.80 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.48 (d, *J* = 3.5 Hz, 1H), 5.12 (s, 1H), 4.11 (qd, *J* = 7.3, 4.5 Hz, 3H), 4.00 (dd, *J* = 10.7, 7.1 Hz, 1H), 2.39 (s, 3H), 2.03 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 165.8, 165.5, 153.5, 146.3, 143.7, 136.5, 134.0, 129.8, 129.1, 127.3, 126.5, 125.8, 125.4, 125.1, 123.4, 121.3, 116.2, 110.8, 83.3, 63.2, 62.9, 41.4, 21.6, 20.4, 13.7, 13.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{29}NNaO_9S_2^+$ 622.1176; Found 622.1172.

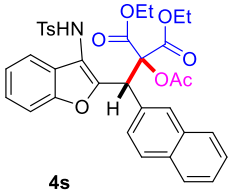
Diethyl(R)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(pyridin-3-yl)methyl) malonate (4r)



4r

33.8 mg, 57% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.93 (d, *J* = 2.3 Hz, 1H), 7.90 (s, 1H), 7.70 (dt, *J* = 8.1, 1.8 Hz, 1H), 7.64 (dd, *J* = 8.5, 2.1 Hz, 3H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.17 (m, 5H), 4.89 (s, 1H), 4.08 (qd, *J* = 7.2, 3.2 Hz, 3H), 3.93 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.44 (s, 3H), 1.92 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.8, 153.6, 150.5, 148.6, 146.1, 144.2, 138.5, 136.5, 130.0, 129.8, 127.4, 125.3, 123.5, 123.0, 121.3, 116.9, 110.8, 82.9, 63.4, 63.1, 43.6, 21.6, 20.2, 13.7, 13.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{31}N_2O_9S^+$ 595.1745; Found 595.1742.

Diethyl(R)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(naphthalen-2-yl) methyl)malonate (4s)

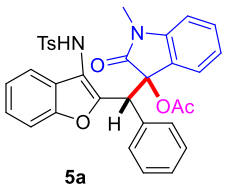


4s

53.3 mg, 83% yield; whiter powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1NH), 7.79 – 7.64 (m, 6H), 7.49 – 7.43 (m, 2H), 7.33 – 7.16 (m, 7H), 5.07 (s, 1H), 4.12 (dq, *J* = 10.6, 7.2 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.94 (dq, *J* = 10.6, 7.2 Hz, 1H), 2.35 (s, 3H), 1.85 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 166.2, 166.1, 153.6, 147.1, 143.6, 136.9, 132.7, 132.6, 131.2, 129.8,

129.6, 128.1, 127.9, 127.5, 127.5, 127.3, 126.3, 126.0, 125.7, 125.0, 123.3, 121.4, 116.4, 110.8, 83.4, 63.3, 62.9, 45.9, 21.6, 20.3, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{33}NNaO_9S^+$ 666.1768; Found 666.1769.

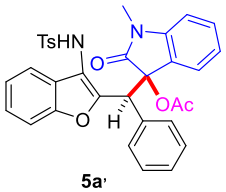
1-methyl-3-((R)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-2-oxoindolin-3-yl acetate (5a)



5a

32.5mg, 56% yield; light yellow powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.17 (m, 6H), 7.10 – 7.03 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.90 – 6.82 (m, 3H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 4.33 (s, 1H), 2.65 (s, 3H), 2.21 (s, 3H), 2.00 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 153.5, 148.0, 144.1, 143.4, 135.9, 132.9, 130.8, 130.2, 129.5, 127.7, 127.4, 127.0, 125.0, 124.5, 123.5, 122.3, 121.1, 116.6, 110.8, 108.0, 80.8, 47.0, 26.0, 21.6, 20.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{28}N_2NaO_6S^+$ 603.1560; Found 603.1562.

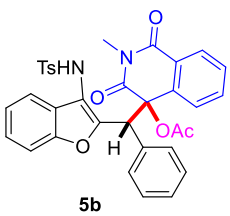
1-methyl-3-((S)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-2-oxoindolin-3-yl acetate (5a')



5a'

16.2 mg, 28% yield; light yellow powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.11 (q, *J* = 8.1, 7.4 Hz, 4H), 6.98 (t, *J* = 7.6 Hz, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.21 (s, 1H), 2.78 (s, 3H), 2.33 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 168.0, 153.5, 148.4, 143.9, 135.7, 131.1, 130.4, 130.3, 129.8, 127.9, 127.4, 127.3, 124.9, 124.6, 124.3, 123.4, 122.4, 121.0, 117.2, 111.3, 108.1, 82.8, 47.9, 25.9, 21.5, 20.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{28}N_2NaO_6S^+$ 603.1560; Found 603.1562.

2-methyl-4-((R)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl acetate (5b)

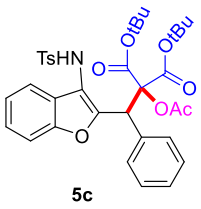


5b

29.2 mg, 62% yield (1:1); colorless oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.68 (dd, *J* = 14.4, 7.8 Hz, 3H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.37 (q, *J* = 6.9, 5.4 Hz, 5H), 7.31 (dd, *J* = 11.9, 5.3 Hz, 5H), 7.21 (d, *J* = 7.8 Hz, 4H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.55 – 6.46 (m, 3H), 6.27 (d, *J* = 7.8 Hz, 1H), 4.69 (s, 1H), 4.39 (s, 1H), 2.92 (s, 3H), 2.80 (s, 3H), 2.41 (s, 3H), 2.26 (d, *J* = 4.9 Hz, 6H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 153.7, 153.3, 148.1, 146.1, 143.7, 135.5, 135.4, 133.0, 132.5, 132.2, 130.8, 130.3, 130.1, 129.9, 129.5, 129.5, 129.1, 128.9, 128.2, 128.1, 128.0, 127.9, 127.6, 127.4, 127.0, 126.6, 126.1, 125.8, 125.7, 125.4, 125.1, 124.8, 124.7, 123.9, 123.7, 121.3, 120.6, 118.4, 116.7, 111.4, 111.3, 81.9, 80.0, 52.4, 51.2, 26.8, 26.6, 21.6, 21.5, 21.0, 20.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{28}N_2NaO_7S^+$ 631.1509; Found 631.1505.

Di-tert-butyl(S)-2-acetoxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)

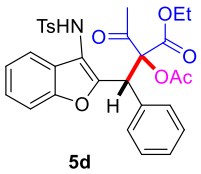
malonate(5c)



5c

37.6 mg, 58% yield; white powder; eluent (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1NH), 7.86 – 7.80 (m, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.08 (m, 8H), 6.77 (d, *J* = 7.4 Hz, 2H), 4.68 (s, 1H), 2.47 (s, 3H), 1.88 (s, 3H), 1.26 (s, 9H), 1.22 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ 168.5, 165.3, 164.6, 153.5, 146.9, 143.5, 137.1, 134.3, 130.4, 129.8, 127.7, 127.6, 127.6, 125.9, 124.7, 123.2, 121.6, 116.0, 110.8, 84.4, 83.9, 83.9, 45.4, 27.4, 27.3, 21.6, 20.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{39}NNaO_9S^+$ 672.2238; Found 672.2237.

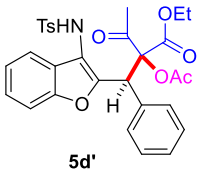
Ethyl-2-acetoxy-2-((R)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxobutanoate (5d)



5d

27.6 mg, 49% yield; white powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.49 – 7.45 (m, 1H), 7.35 (s, 1NH), 7.31 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.24 – 7.12 (m, 7H), 7.10 – 7.06 (m, 2H), 4.85 (s, 1H), 3.96 (dd, *J* = 7.2, 1.4 Hz, 2H), 2.40 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 169.4, 165.7, 153.5, 148.0, 143.7, 136.7, 133.6, 130.4, 129.8, 128.0, 127.5, 125.5, 124.9, 123.3, 120.8, 116.1, 110.9, 88.9, 62.7, 45.2, 26.6, 21.6, 20.5, 13.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NNaO_8S^+$ 586.1506; Found 586.1511.

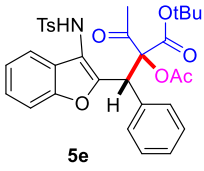
Ethyl2-acetoxy-2-((S)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxobutanoate (5d')



5d'

27.6 mg, 49% yield; white powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1NH), 7.83 – 7.76 (m, 1H), 7.69 – 7.63 (m, 2H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.25 – 7.17 (m, 5H), 7.14 (dd, *J* = 8.2, 6.4 Hz, 2H), 6.88 (dt, *J* = 7.1, 1.4 Hz, 2H), 4.66 (s, 1H), 4.13 – 3.96 (m, 2H), 2.43 (s, 3H), 2.05 (s, 3H), 1.96 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 168.5, 153.6, 147.0, 143.5, 136.8, 133.4, 130.6, 129.9, 128.0, 127.9, 127.4, 125.9, 124.9, 123.4, 121.6, 116.0, 110.6, 88.4, 63.1, 45.2, 26.7, 21.6, 20.4, 13.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NNaO_8S^+$ 586.1506; Found 586.1513.

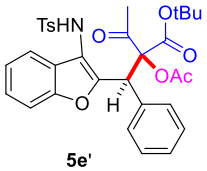
Tert-butyl 2-acetoxy-2-((R)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxobutanoate (5e)



5e

33.6 mg, 57% yield; white powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.64 (s, 1NH), 7.57 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.23 – 7.13 (m, 7H), 6.99 – 6.94 (m, 2H), 4.80 (s, 1H), 2.44 (s, 3H), 2.12 (d, *J* = 2.9 Hz, 6H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 169.3, 163.7, 147.7, 143.6, 137.1, 134.3, 130.3, 129.8, 128.0, 127.8, 127.6, 124.8, 123.2, 121.1, 115.8, 110.7, 89.6, 84.3, 44.4, 27.1, 25.8, 21.6, 20.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{33}NNaO_8S^+$ 614.1819; Found 614.1822.

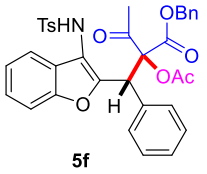
Tert-butyl 2-acetoxy-2-((S)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxobutanoate (5e')



5e'

16.6 mg, 28% yield; white powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1NH), 7.87 – 7.81 (m, 1H), 7.69 – 7.63 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 3H), 7.18 (d, *J* = 7.1 Hz, 2H), 7.15 – 7.10 (m, 2H), 6.86 – 6.80 (m, 2H), 4.60 (s, 1H), 2.43 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 168.3, 165.5, 153.5, 147.0, 143.5, 136.8, 133.7, 130.6, 129.9, 127.9, 127.7, 127.5, 124.8, 123.3, 121.7, 116.0, 110.7, 89.0, 84.7, 44.9, 27.4, 26.6, 21.6, 20.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{33}NNaO_8S^+$ 614.1819; Found 614.1816.

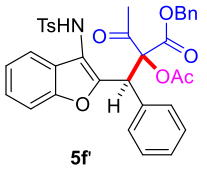
Benzyl2-acetoxy-2-((R)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxobutanoate (5f)



5f

31.3 mg, 50% yield; light yellow powder; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.37 (s, 1NH), 7.30 (d, *J* = 6.6 Hz, 3H), 7.07 (ddt, *J* = 46.8, 18.3, 7.5 Hz, 12H), 4.85 (s, 2H), 4.81 (s, 1H), 2.33 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 169.5, 165.5, 147.9, 143.7, 136.6, 134.1, 133.4, 130.3, 129.8, 128.7, 128.6, 128.5, 128.0, 127.4, 125.0, 123.3, 120.8, 116.1, 110.9, 89.1, 68.4, 45.2, 26.6, 21.6, 20.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{31}NNaO_8S^+$ 648.1663; Found 648.1667.

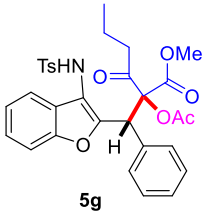
Benzyl2-acetoxy-2-((S)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxobutanoate (5f')



5f'

23.8 mg, 38% yield; colorless oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.24 – 7.12 (m, 7H), 7.08 – 7.02 (m, 2H), 6.97 – 6.91 (m, 2H), 5.03 – 4.93 (m, 2H), 4.72 (s, 1H), 2.42 (s, 3H), 2.06 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 168.7, 167.0, 153.6, 147.4, 143.5, 136.8, 134.1, 133.3, 130.6, 129.9, 128.7, 128.6, 128.4, 128.0, 128.0, 127.4, 125.8, 124.9, 123.4, 121.5, 116.0, 110.7, 88.4, 68.7, 45.3, 26.9, 21.6, 20.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{31}NNaO_8S^+$ 648.1663; Found 648.1668.

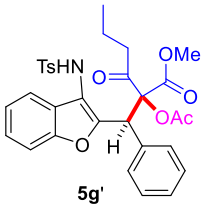
Methyl 2-acetoxy-2-((R)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-3-oxohexanoate (5g)



5g

30.0 mg, 52% yield; colorless oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.49 (s, 1NH), 7.36 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.20 (dd, *J* = 23.5, 8.1 Hz, 6H), 7.10 (d, *J* = 7.3 Hz, 2H), 4.88 (s, 1H), 3.54 (s, 3H), 2.53 – 2.31 (m, 5H), 2.10 (s, 3H), 1.53 (q, *J* = 7.4 Hz, 2H), 0.83 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 169.4, 166.6, 153.5, 147.9, 143.7, 136.5, 133.6, 130.3, 129.8, 127.9, 127.5, 125.5, 124.9, 123.3, 120.9, 116.2, 110.9, 88.7, 53.1, 45.5, 40.9, 21.6, 20.5, 17.1, 13.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{31}NNaO_8S^+$ 600.1663; Found 600.1660.

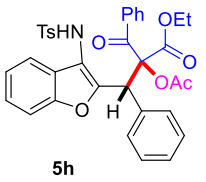
Methyl 2-acetoxy-2-((S)-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl) -3-oxohexanoate (5g')



5g'

23.1 mg, 40% yield; colorless oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1NH), 7.86 – 7.78 (m, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.31-7.27 (m, 1H), 7.25 – 7.16 (m, 5H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 4.63 (s, 1H), 3.58 (s, 3H), 2.43 (s, 4H), 2.11 (s, 4H), 1.31 (dd, *J* = 14.1, 7.1 Hz, 1H), 1.18 (dq, *J* = 14.1, 7.2 Hz, 1H), 0.57 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 168.4, 168.1, 153.5, 147.0, 143.5, 136.9, 133.3, 130.7, 129.9, 127.9, 127.9, 127.4, 125.9, 124.9, 123.3, 121.7, 116.0, 110.5, 88.4, 53.5, 45.3, 40.9, 21.6, 20.6, 16.0, 13.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{31}NNaO_8S^+$ 600.1663; Found 600.1667.

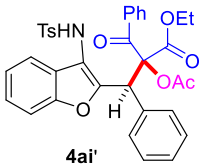
Ethyl (3R)-2-acetoxy-2-benzoyl-3-(3-((4-methylphenyl)sulfonamido)benzofura-2-yl)-3-phenylpropanoate (5h)



5h

23.1 mg, 37% yield; colorless oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1NH), 8.00 – 7.94 (m, 2H), 7.79 – 7.72 (m, 3H), 7.51 – 7.45 (m, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.13 (m, 8H), 7.02 – 6.96 (m, 2H), 5.01 (s, 1H), 3.76 (qd, *J* = 7.1, 4.9 Hz, 2H), 2.46 (s, 3H), 2.07 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 168.5, 153.5, 147.1, 143.5, 137.2, 134.2, 133.8, 133.7, 130.4, 129.8, 128.7, 128.2, 128.0, 127.8, 127.6, 125.9, 124.8, 123.3, 121.6, 116.1, 110.5, 89.2, 62.8, 45.3, 21.6, 20.7, 13.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{31}NNaO_8S^+$ 648.1663; Found 648.1665.

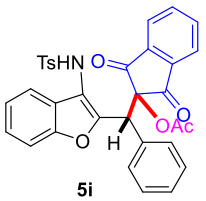
Ethyl (3S)-2-acetoxy-2-benzoyl-3-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-3-phenylpropanoate (4ai')



4ai'

18.2mg, 29% yield; colorless oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1NH), 7.98 – 7.92 (m, 1H), 7.89 – 7.80 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.29 (dt, *J* = 8.2, 2.9 Hz, 1H), 7.26 – 7.16 (m, 5H), 7.13 (dd, *J* = 8.0, 6.5 Hz, 2H), 6.88 – 6.80 (m, 2H), 5.10 (s, 1H), 3.96 (dq, *J* = 10.6, 7.1 Hz, 1H), 3.61 – 3.49 (m, 1H), 2.44 (s, 3H), 1.40 (s, 3H), 0.45 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 168.8, 146.6, 143.5, 136.6, 133.9, 133.8, 133.6, 131.0, 129.9, 128.8, 128.6, 127.6, 127.5, 125.0, 123.3, 121.9, 116.4, 110.7, 85.9, 63.6, 45.6, 21.6, 20.0, 12.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{31}NNaO_8S^+$ 648.1663; Found 648.1667.

(R)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-1,3-dioxo-2,3-dihydro-1H-inden-2-yl acetate (5i)

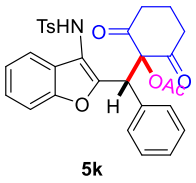


5i

9.3 mg, 16% yield; light yellow oil; eluent (dichloromethane/petroleum ether = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.52 – 7.46 (m, 3H), 7.29 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.23 – 7.13 (m, 7H), 7.09 – 7.04 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.39 (s, 1NH), 4.55 (s, 1H), 2.28 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 148.1, 143.9, 140.3, 138.8, 135.8, 135.7, 135.3, 131.9, 130.4, 129.7, 128.0, 127.8, 127.3, 125.1, 124.7, 123.4, 123.0, 122.7, 120.2, 116.5, 111.1, 81.9, 46.0, 21.6, 19.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{25}NNaO_7S^+$ 602.1244; Found 602.1244.

(R)-1-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-2,6-dioxocyclohexyl

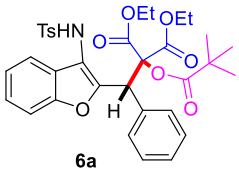
acetate (5k)



5k

28.9 mg, 53% yield; light yellow powder; eluent (recrystallization from acetonitrile). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.36 (dd, *J* = 8.0, 4.1 Hz, 4H), 7.12 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.85 (td, *J* = 7.6, 1.7 Hz, 1H), 6.70 (s, 1NH), 6.56 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 1H), 3.15 (ddd, *J* = 16.5, 13.0, 6.0 Hz, 1H), 2.87 (dq, *J* = 16.6, 3.2 Hz, 1H), 2.75 – 2.68 (m, 1H), 2.68 – 2.57 (m, 1H), 2.30 (s, 3H), 2.17 (s, 3H), 2.07 (qt, *J* = 5.8, 2.8 Hz, 1H), 2.00 – 1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 199.8, 169.3, 153.6, 150.0, 144.1, 135.9, 132.4, 130.7, 129.6, 128.5, 128.5, 127.4, 124.8, 122.9, 118.4, 115.7, 111.7, 91.6, 45.5, 39.7, 39.2, 21.5, 20.3, 17.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{27}NNaO_7S^+$ 568.1400; Found 568.1405.

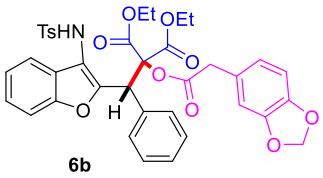
Diethyl(R)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-2-(pivaloyloxy) malonate (6a)



6a

27.3 mg, 43% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1NH), 7.71 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.16 (m, 5H), 7.13 (t, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 4.84 (s, 1H), 4.04 (dq, *J* = 13.1, 7.5, 6.4 Hz, 3H), 3.87 (dq, *J* = 14.3, 7.5 Hz, 1H), 2.42 (s, 3H), 1.02 (s, 12H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.1, 147.4, 143.5, 136.8, 133.6, 130.6, 129.8, 127.8, 127.7, 127.5, 124.9, 123.2, 121.3, 116.1, 110.8, 82.9, 63.0, 62.6, 46.0, 38.6, 26.5, 21.6, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{37}NNaO_9S^+$ 658.2081; Found 658.2081.

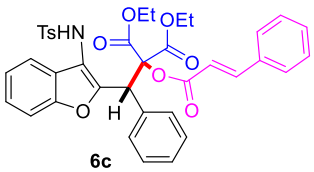
Diethyl(R)-2-(2-(benzo[d][1,3]dioxol-5-yl)acetoxy)-2-((3-((4-methylphenyl)sulfonamido) benzofuran-2-yl)(phenyl)methyl)malonate (6b)



6b

50.6 mg, 71% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1NH), 7.70 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.16 (m, 5H), 7.12 (t, *J* = 7.6 Hz, 2H), 6.88 – 6.82 (m, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 2H), 5.93 (s, 2H), 4.82 (s, 1H), 4.09 – 3.96 (m, 3H), 3.89 (dd, *J* = 10.7, 7.1 Hz, 1H), 3.46 (d, *J* = 16.0 Hz, 1H), 3.31 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 165.9, 153.6, 147.1, 143.6, 136.8, 133.4, 130.5, 129.8, 127.9, 127.7, 127.5, 126.0, 125.7, 124.9, 123.3, 122.7, 121.3, 116.2, 110.9, 110.0, 108.2, 101.1, 83.5, 63.2, 62.9, 45.9, 40.0, 21.6, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{35}NNaO_{11}S^+$ 722.1667; Found 722.1667.

Diethyl(R)-2-(cinnamoyloxy)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl) methyl)malonate (6c)

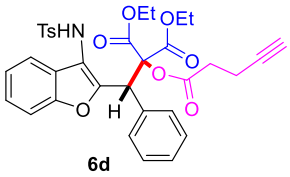


6c

35.4 mg, 52% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1NH), 7.79 – 7.74 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.37 (m, 6H), 7.23 – 7.18 (m, 5H), 7.15 (q, *J* = 6.8, 6.1 Hz, 3H), 7.00 – 6.93 (m, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 4.87 (s, 1H), 4.18 – 3.98 (m, 4H), 2.43 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 165.9, 164.5, 153.6, 147.1, 146.9, 143.5, 136.9, 133.9, 133.6, 130.8, 130.4, 129.8, 129.0, 128.3, 127.9, 127.8, 127.5, 125.9, 124.8, 123.2, 121.4,

116.2, 116.0, 110.9, 83.4, 63.2, 62.8, 45.8, 21.6, 13.6, 13.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{35}NNaO_9S^+$ 704.1925; Found 704.1920.

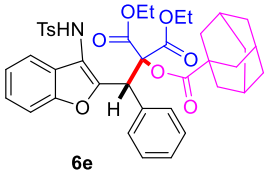
Diethyl(R)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-2-(pent-4-ynoyloxy)malonate (6d)



6d

15.8 mg, 25% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1NH), 7.72 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (dd, *J* = 8.1, 6.3 Hz, 5H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.94 – 6.87 (m, 2H), 4.83 (s, 1H), 4.12 – 4.00 (m, 3H), 3.97 – 3.87 (m, 1H), 2.51 (dt, *J* = 16.7, 7.6 Hz, 1H), 2.43 (s, 3H), 2.35 (ddd, *J* = 16.7, 8.5, 6.5 Hz, 1H), 2.20 (ddd, *J* = 10.8, 5.6, 3.3 Hz, 2H), 1.91 (t, *J* = 2.6 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.9, 147.0, 143.6, 136.8, 133.5, 130.4, 129.8, 127.9, 127.8, 127.5, 125.0, 123.3, 121.4, 116.3, 110.7, 83.3, 81.9, 69.2, 63.3, 62.9, 45.7, 32.7, 21.6, 13.8, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{33}NNaO_9S^+$ 654.1768; Found 654.1764.

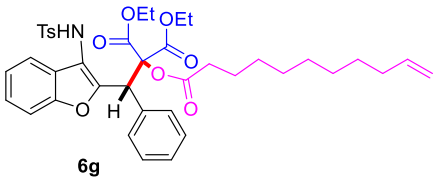
Diethyl (R)-2-((adamantane-1-carbonyl)oxy)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)malonate (6e)



6e

19.3 mg, 27% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1NH), 7.75 – 7.70 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.16 (m, 5H), 7.14 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 7.1 Hz, 2H), 4.84 (s, 1H), 4.04 (dp, *J* = 21.8, 7.2 Hz, 3H), 3.92 – 3.83 (m, 1H), 2.43 (s, 3H), 1.99 – 1.90 (m, 3H), 1.74 – 1.58 (m, 12H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 147.4, 143.5, 136.8, 133.7, 130.6, 129.8, 127.8, 127.7, 127.5, 124.8, 123.2, 121.4, 116.1, 110.8, 82.7, 63.0, 62.6, 45.9, 40.5, 38.1, 36.3, 27.7, 21.6, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{43}NNaO_9S^+$ 736.2551; Found 736.2553.

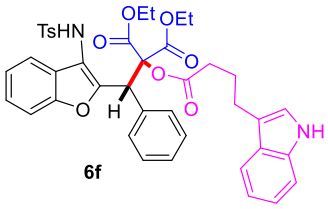
Diethyl (R)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)-2-(undec-10-enoyloxy)malonate (6g)



6g

52.4 mg, 73% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1NH), 7.78 – 7.71 (m, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 6.5 Hz, 1H), 7.19 (t, *J* = 8.3 Hz, 5H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 2H), 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 4.96 (dd, *J* = 23.1, 13.6 Hz, 2H), 4.83 (s, 1H), 4.06 (dq, *J* = 18.6, 7.2 Hz, 3H), 3.89 (dd, *J* = 10.7, 7.0 Hz, 1H), 2.43 (s, 3H), 2.20 (dt, *J* = 15.3, 7.4 Hz, 1H), 2.07 (dq, *J* = 28.0, 7.3 Hz, 3H), 1.39 – 1.16 (m, 12H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 147.2, 143.6, 136.8, 136.4, 133.6, 130.5, 129.9, 127.8, 127.8, 127.5, 124.9, 123.3, 122.0, 121.6, 121.4, 119.2, 118.8, 116.2, 115.2, 111.1, 110.8, 83.1, 63.2, 62.8, 45.9, 33.1, 24.6, 24.1, 21.6, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{47}NNaO_9S^+$ 740.2865; Found 740.2866.

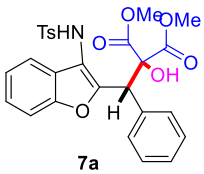
Diethyl (R)-2-((4-(1H-indol-3-yl)butanoyl)oxy)-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)malonate (6f).



6f

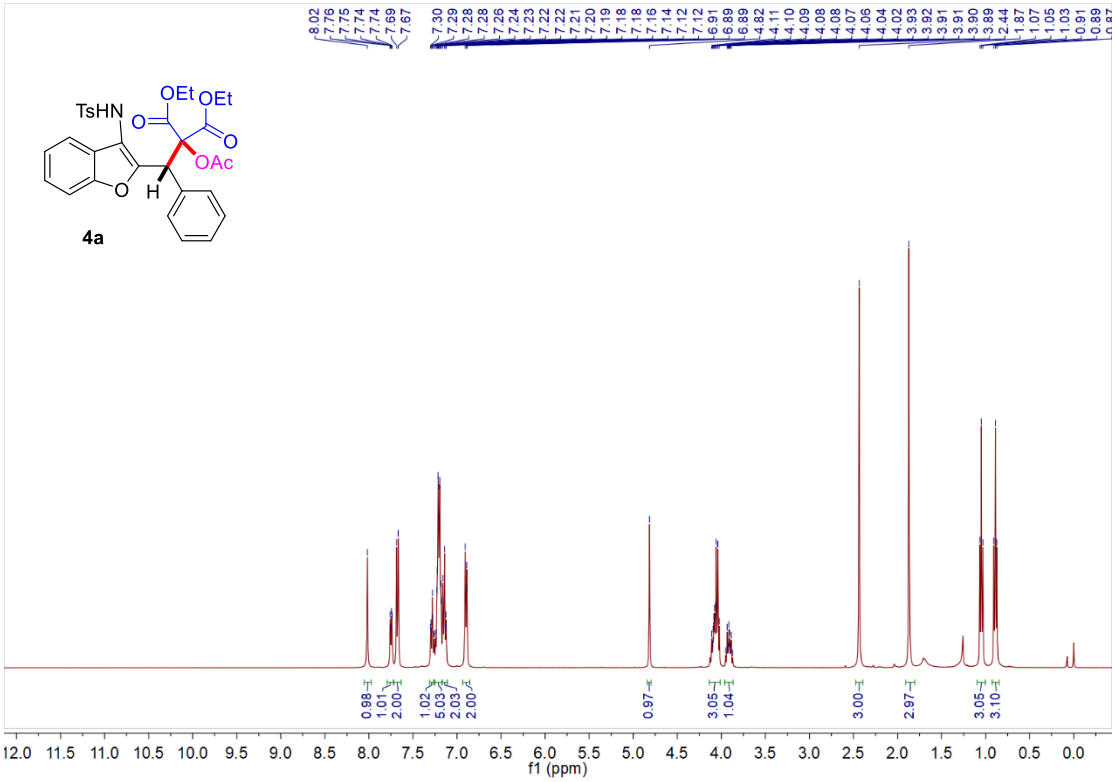
21.4 mg, 29% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2NH), 7.76 – 7.70 (m, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.07 (m, 10H), 6.95 – 6.84 (m, 3H), 4.85 (s, 1H), 4.07 (dq, *J* = 14.2, 7.2 Hz, 3H), 3.92 (dd, *J* = 10.7, 7.1 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.24 (ddd, *J* = 39.1, 16.2, 8.4 Hz, 2H), 1.78 (p, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 143.5, 139.1, 136.8, 133.6, 130.5, 129.8, 127.8, 127.7, 127.5, 124.9, 123.3, 121.4, 116.2, 114.2, 110.8, 83.0, 63.2, 62.8, 45.8, 33.8, 33.5, 29.2, 29.1, 29.0, 28.9, 28.8, 24.2, 21.6, 13.6, 13.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{41}H_{40}N_2O_9SNa^+$ 759.2347; Found 759.2353.

dimethyl (S)-2-hydroxy-2-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)malonate (7a).



7a

19.7 mg, 75% yield; colorless oil; eluent (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.28 (s, 1NH), 7.23 (dd, *J* = 12.5, 7.0 Hz, 2H), 7.15 (dd, *J* = 21.7, 10.2 Hz, 7H), 4.73 (d, *J* = 2.9 Hz, 1H), 4.05 (s, 1OH), 3.72 (d, *J* = 3.0 Hz, 3H), 3.58 (d, *J* = 3.0 Hz, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.2, 153.8, 148.6, 143.7, 136.6, 133.8, 130.0, 129.7, 128.0, 128.0, 127.4, 125.4, 124.8, 123.1, 120.8, 115.7, 111.5, 82.0, 54.0, 53.9, 46.2, 21.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}NO_8S^+$ 524.1374; Found 524.1375.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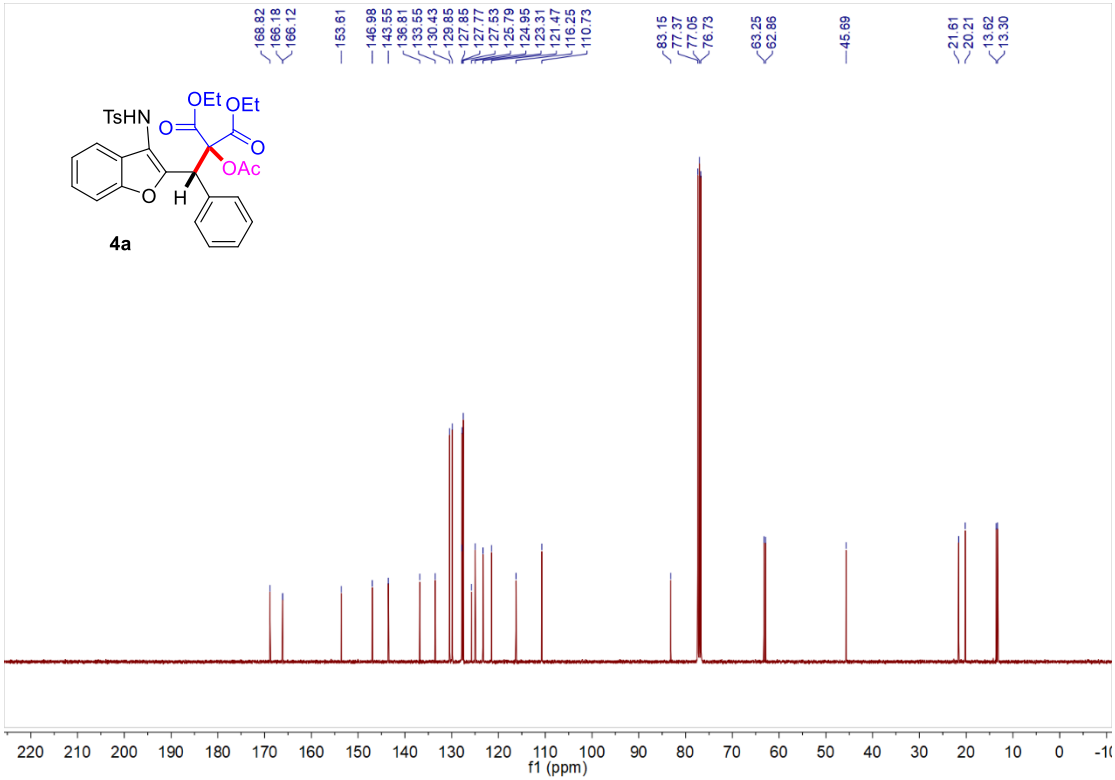
OEt
O
O
O
OAc
H
O
4a
f1 (ppm)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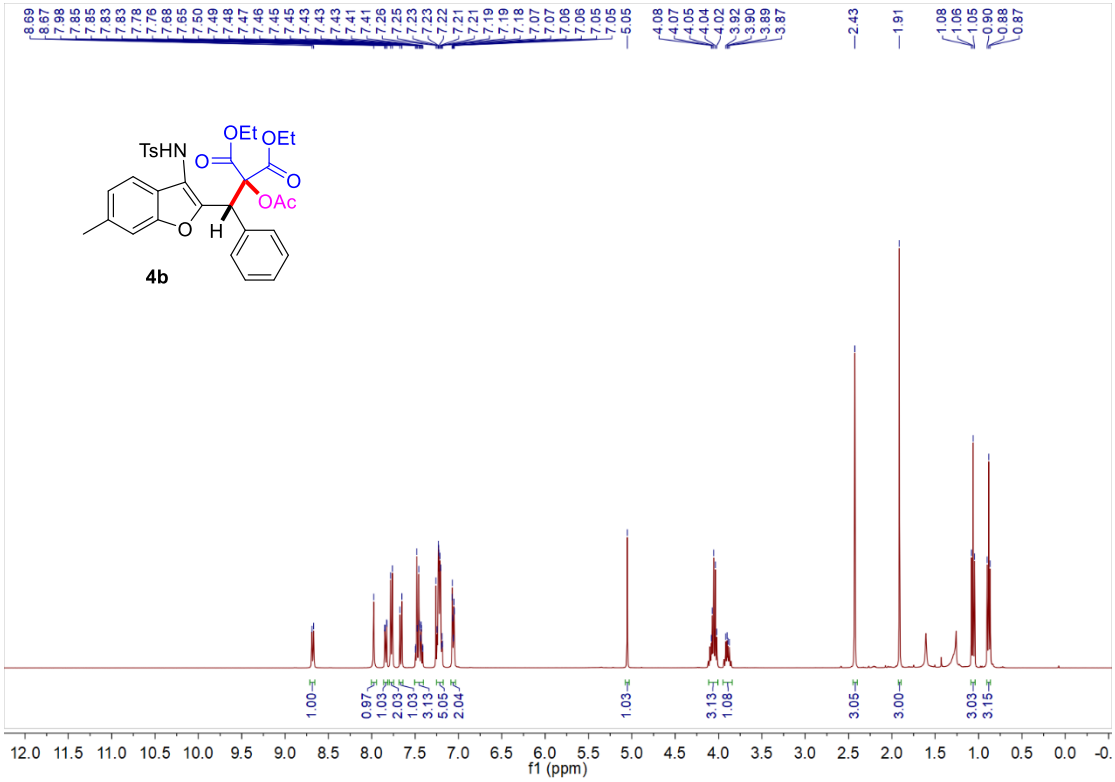
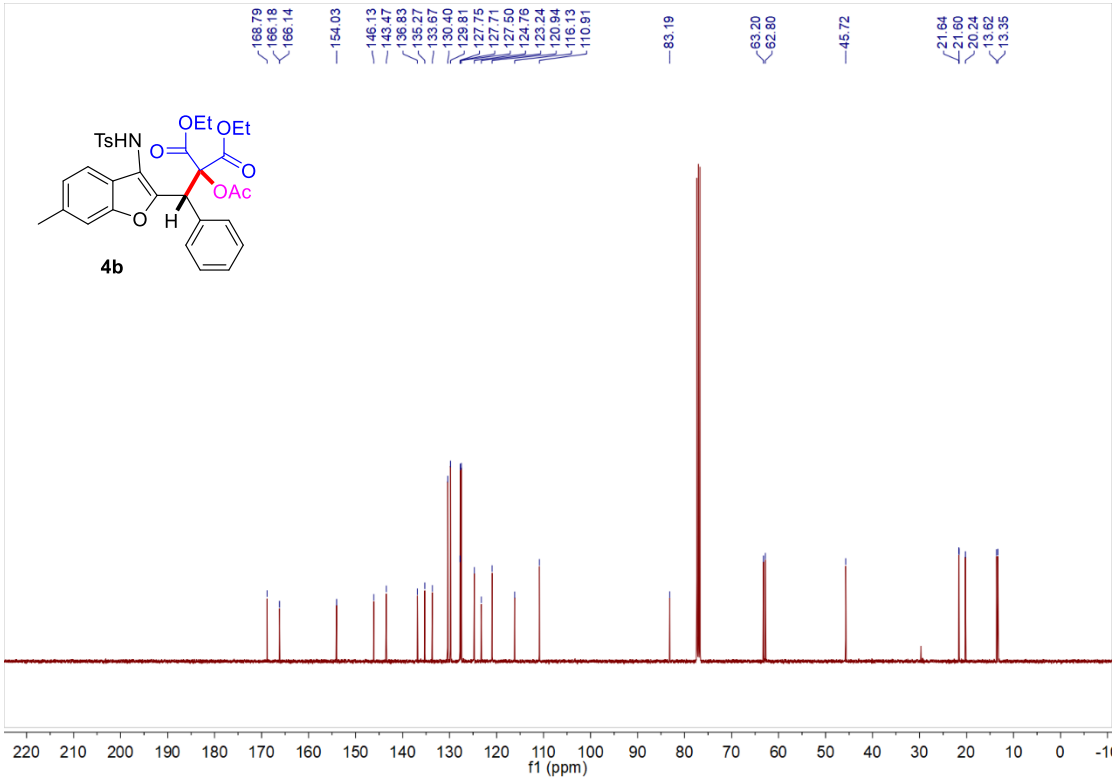
OEt
O
O
O
OAc
H
O
4a
f1 (ppm)


TsHN
OEt
OEt
O
O
OAc
O
H
4b
f1 (ppm)


TsHN
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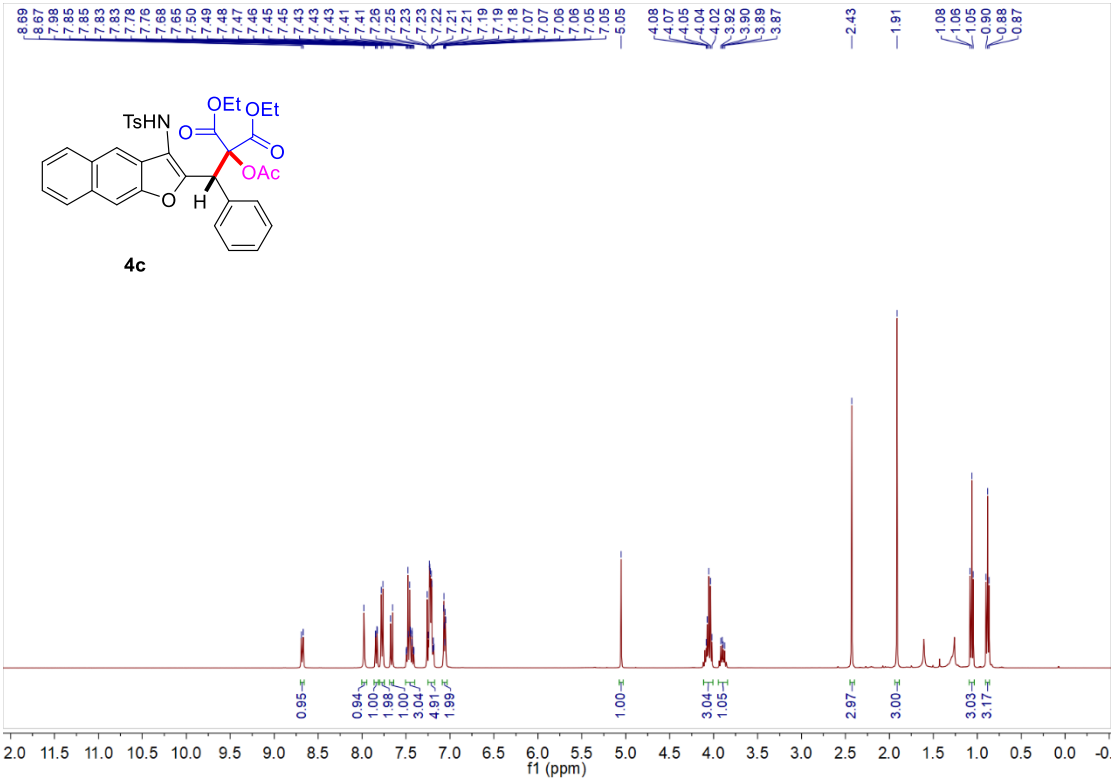
O
OAc
O
H
4b
f1 (ppm)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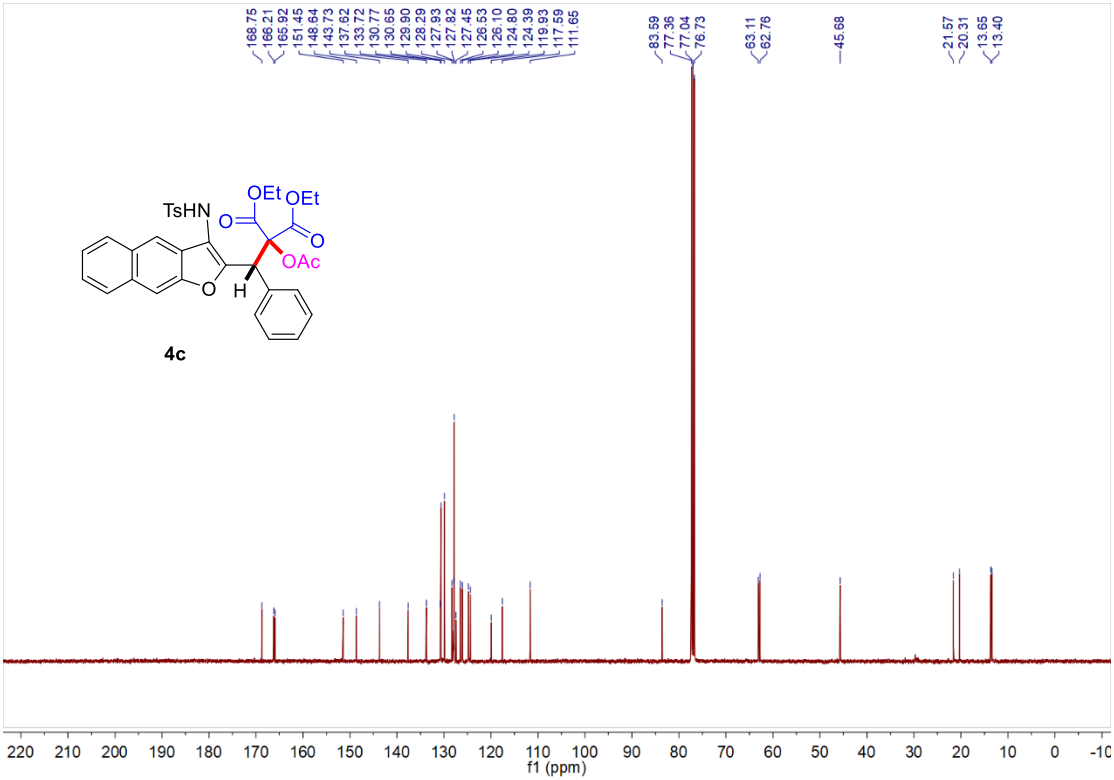
OEt
O
O
OAc
O
H
4c
f1 (ppm)


TsHN
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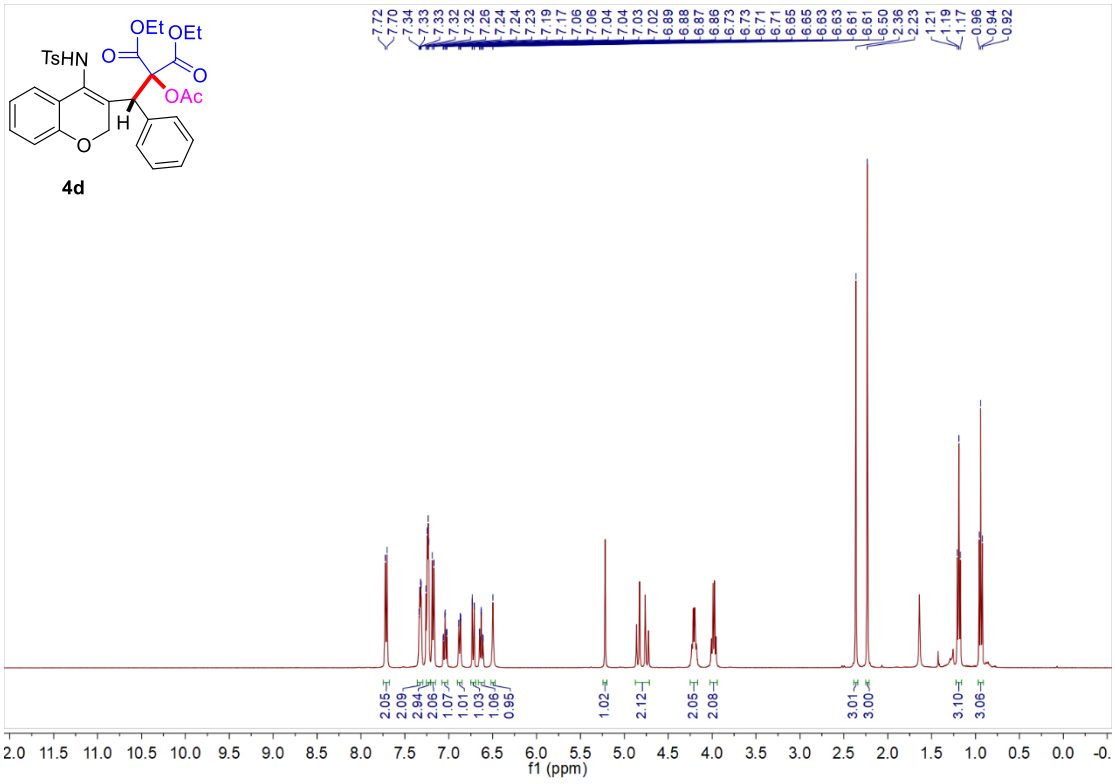
O
OAc
O
H
4c
f1 (ppm)


OEt
OEt
TsHN
O
O
OAc
H
O
4d
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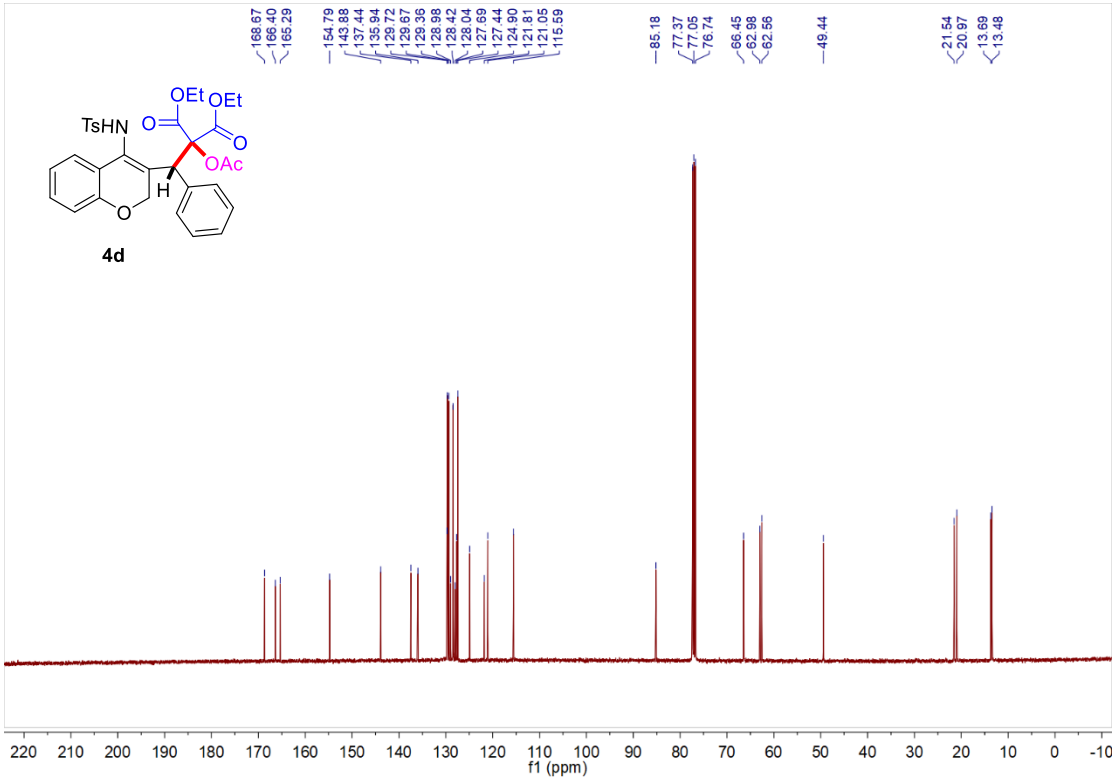
7.70
7.34
7.33
7.33
7.32
7.32
7.26
7.24
7.24
7.23
7.19
7.17
7.06
7.06
7.04
7.04
7.03
7.02
6.89
6.88
6.87
6.86
6.73
6.73
6.71
6.71
6.65
6.65
6.63
6.63
6.61
6.61
6.50
2.36
2.23
1.21
1.19
1.17
0.96
0.94
0.92
2.05
2.09
2.94
2.06
1.07
1.01
1.03
1.06
0.95
1.02
2.12
2.05
2.08
3.01
3.00
3.10
3.06
f1 (ppm)


OEt
OEt
TsHN
O
O
OAc
H
O
4d
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166.40
165.29
154.79
143.88
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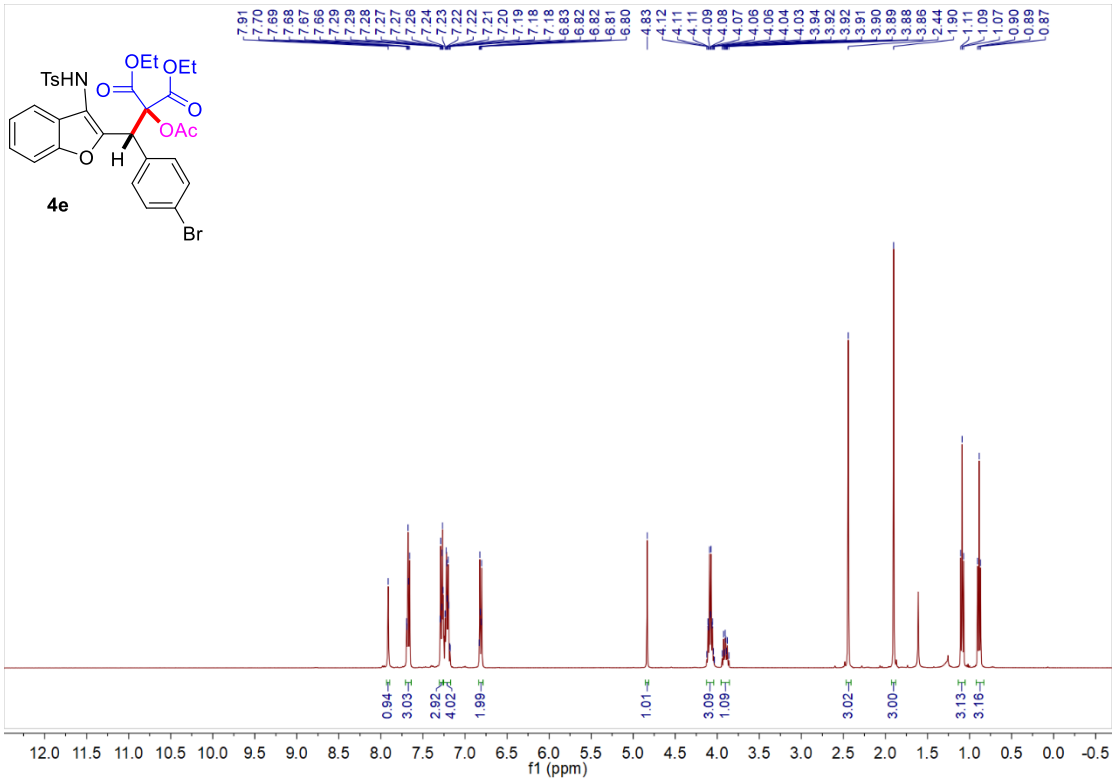
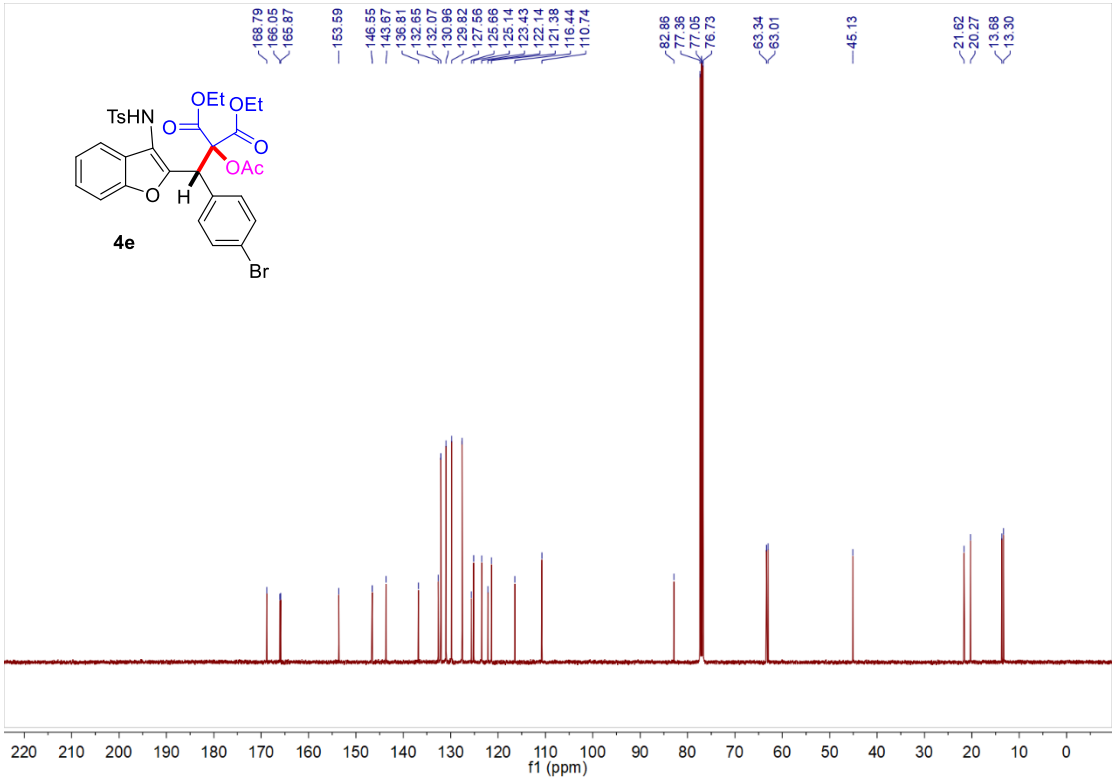
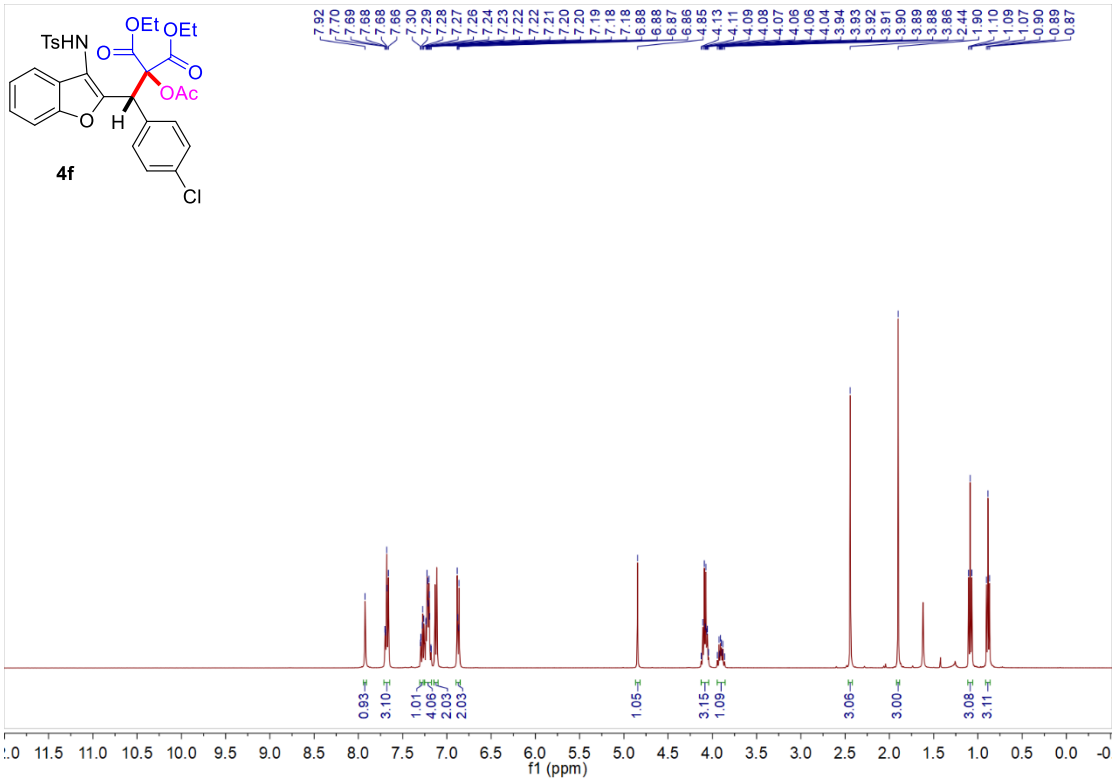
135.94
129.72
129.67
129.36
128.98
128.42
128.04
127.69
127.44
124.90
121.81
121.05
115.59
85.18
77.37
77.05
76.74
66.45
62.98
62.56
49.44
21.54
20.97
13.69
13.48
f1 (ppm)


TsHN
OEt
OEt
O
O
O
OAc
H
O
4e
Br
f1 (ppm)


TsHN
OEt
OEt
O
O
O
OAc
H
O
4e
Br
f1 (ppm)


TsHN
OEt
OEt
O
O
OAc
O
H
Cl
4f
7.92
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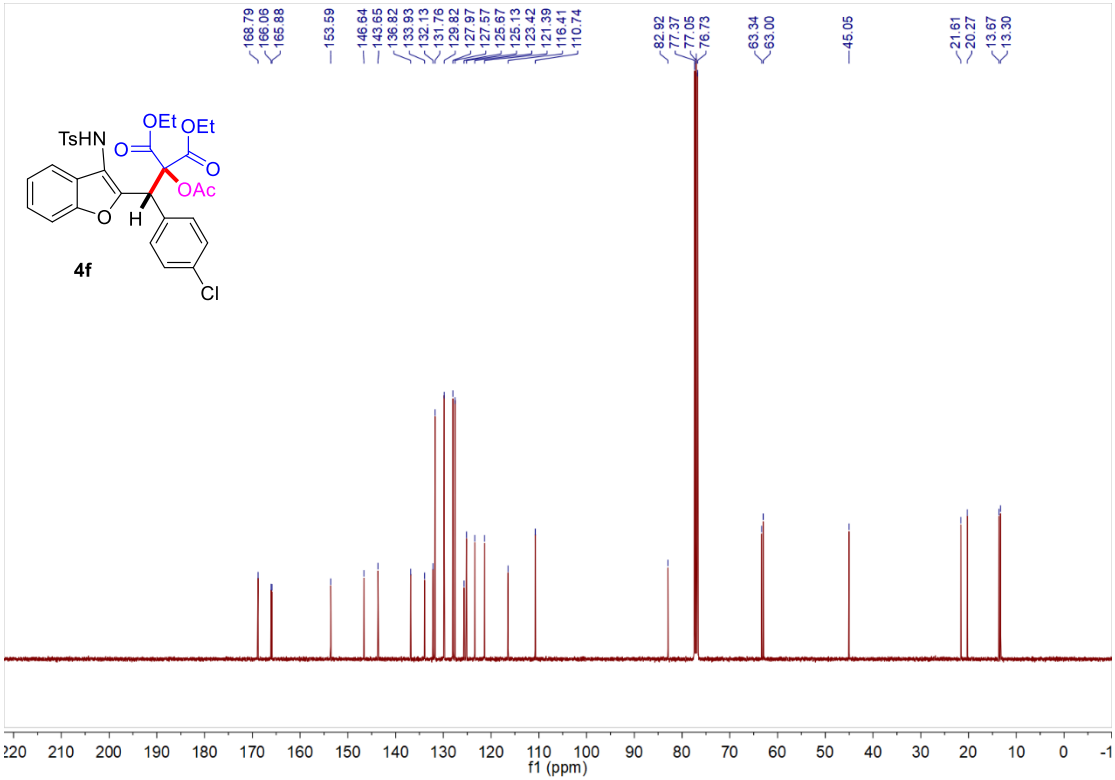
7.69
7.68
7.66
7.30
7.29
7.28
7.27
7.26
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.18
6.88
6.88
6.87
6.86
4.85
4.13
4.11
4.09
4.08
4.07
4.06
4.06
4.04
3.94
3.93
3.92
3.91
3.90
3.89
3.88
3.86
2.44
1.90
1.10
1.09
1.07
0.90
0.89
0.87
0.93
3.10
1.01
4.06
2.03
2.03
1.05
3.15
1.09
3.06
3.00
3.08
3.11
f1 (ppm)


TsHN
OEt
OEt
O
O
OAc
O
H
Cl
4f
168.79
166.06
165.88
153.59
146.64
143.65
136.82
133.93
132.13
131.76
129.82
127.97
127.57
125.67
125.13
123.42
121.39
116.41
110.74
82.92
77.37
77.05
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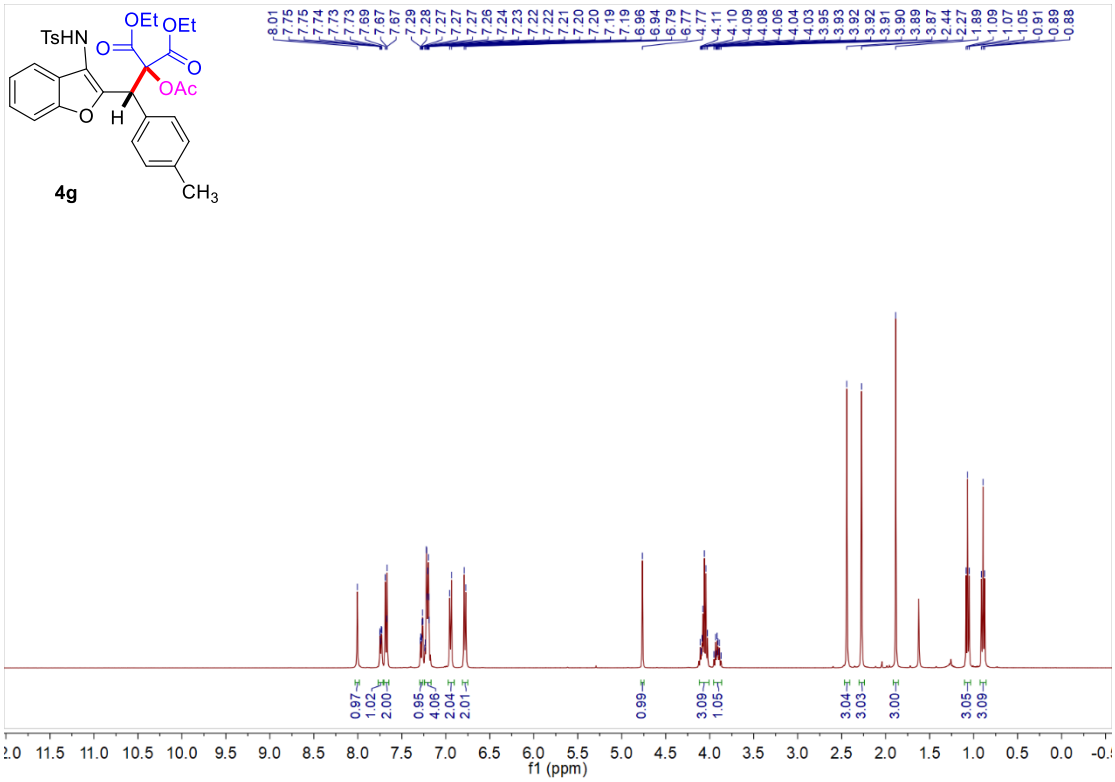
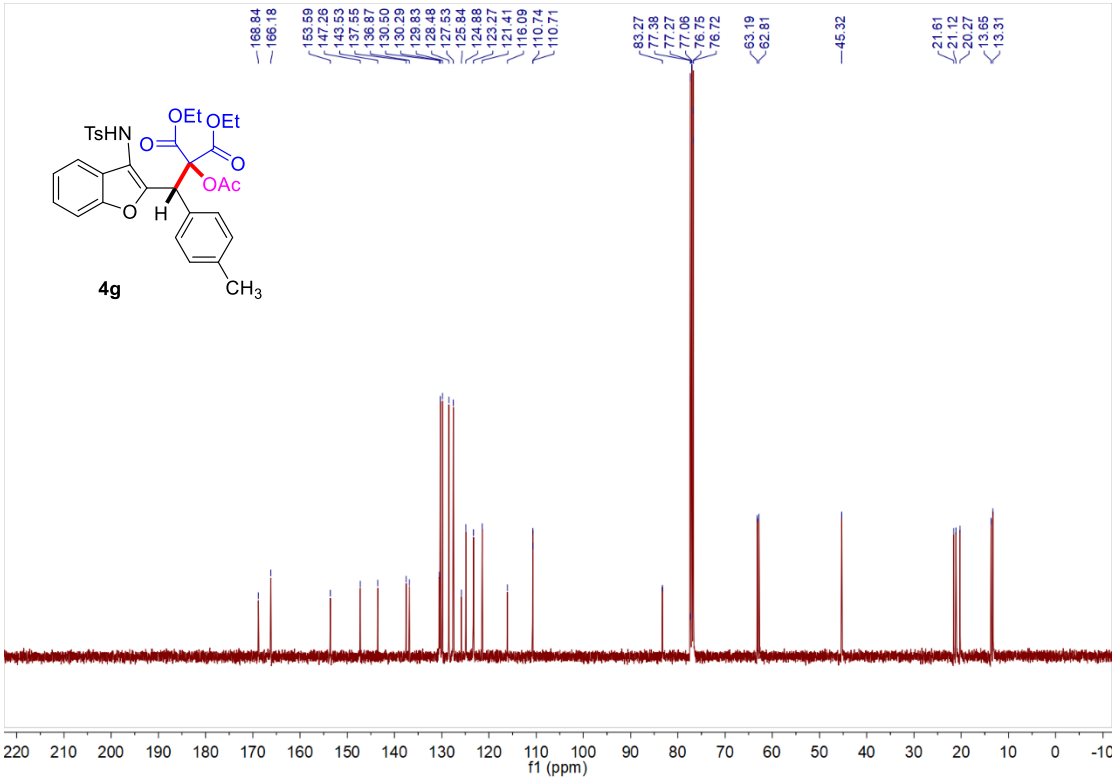
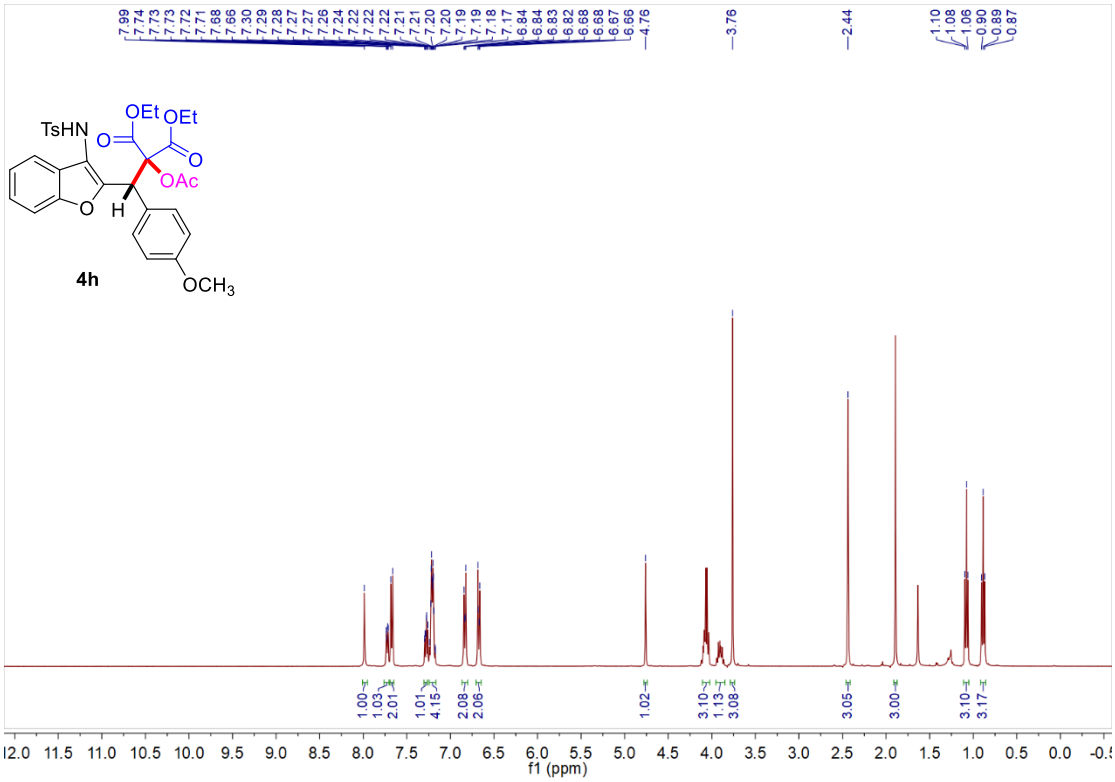
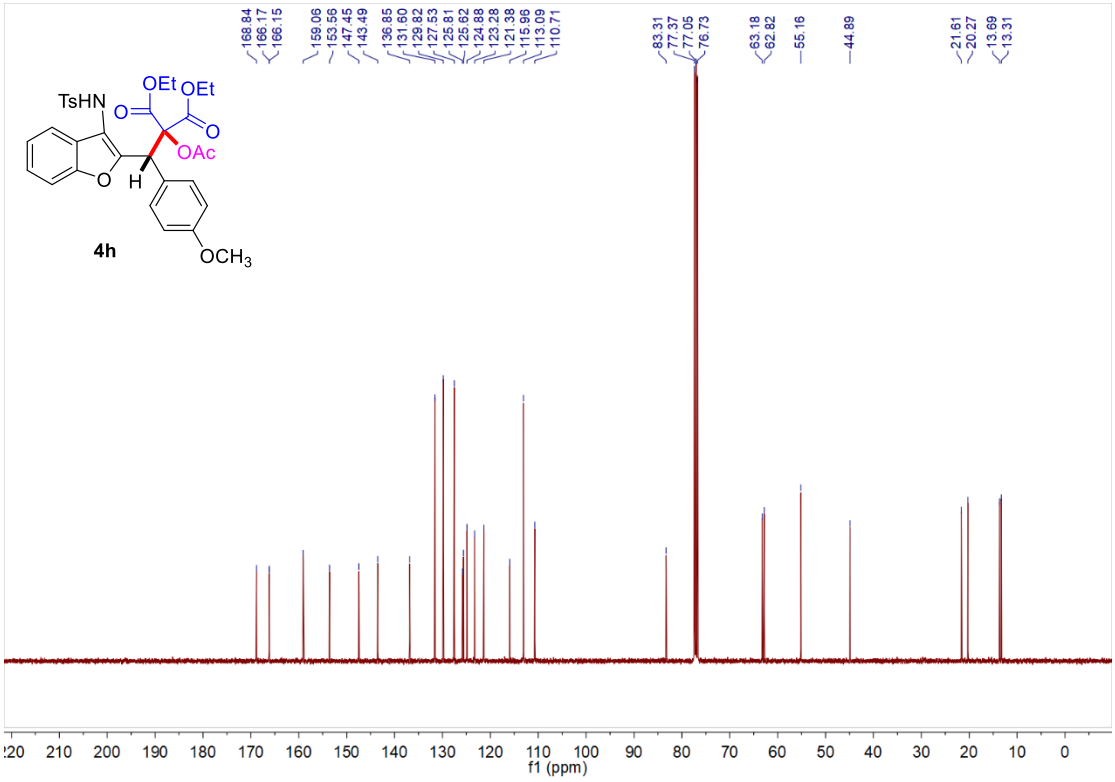
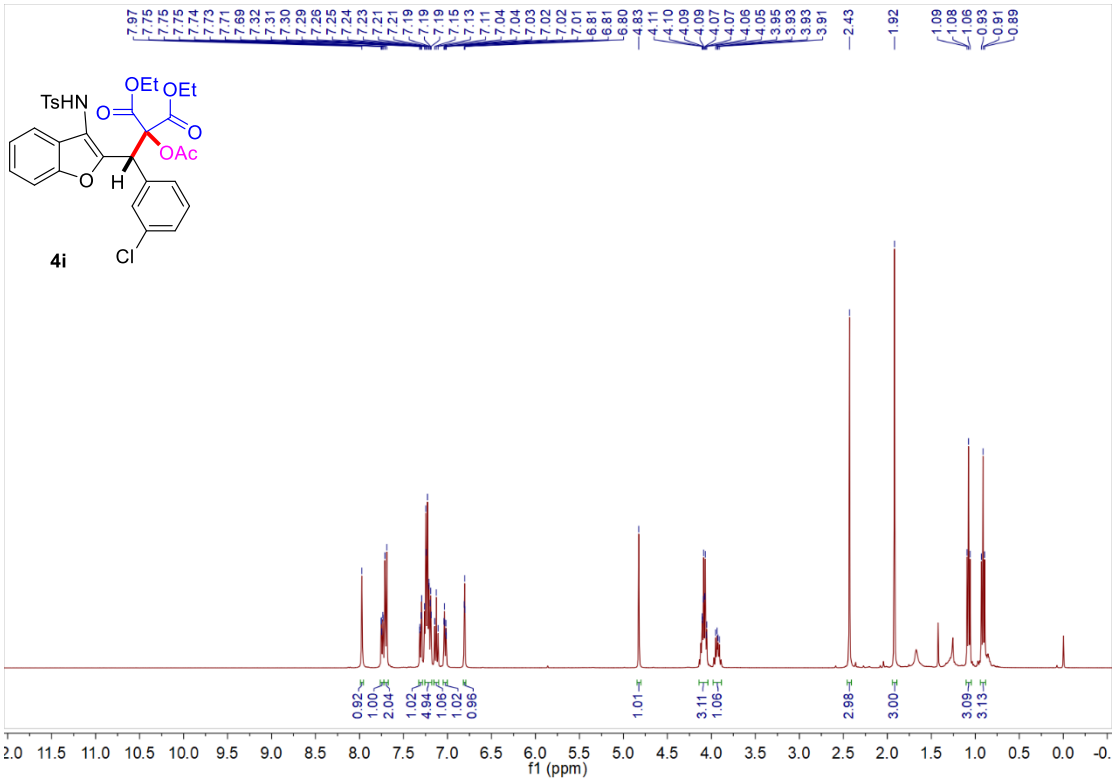
21.61
20.27
13.67
13.30
f1 (ppm)

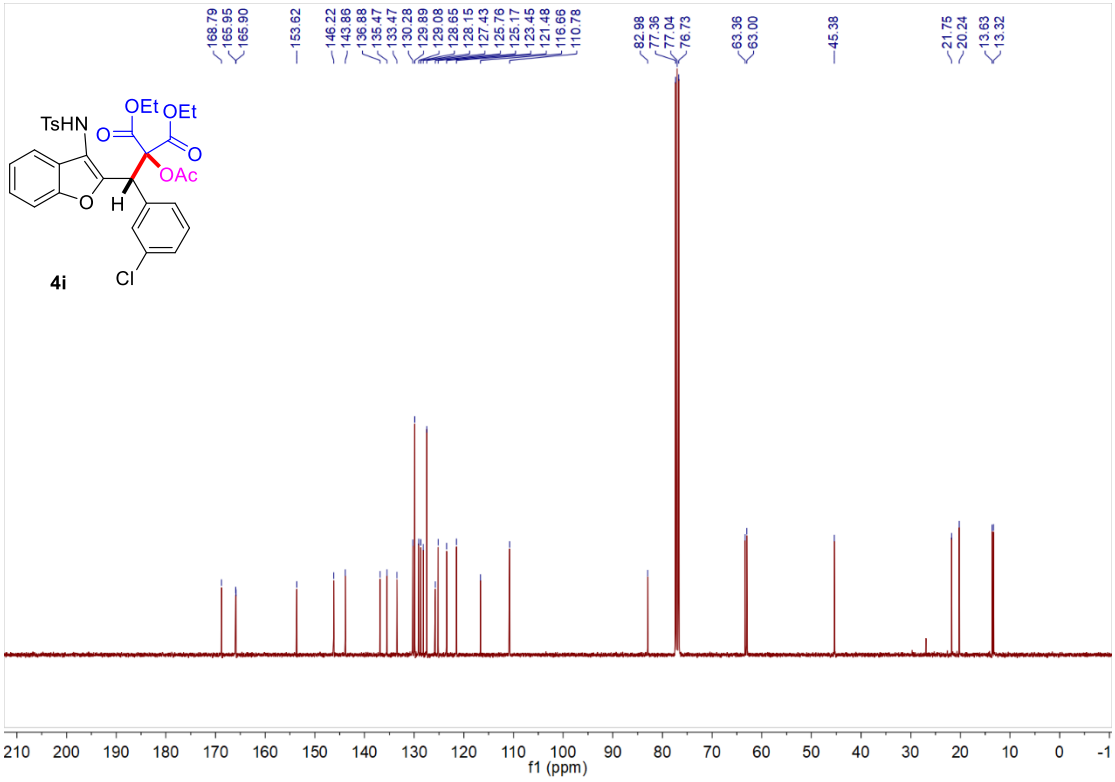

TsHN
OEt
OEt
O
O
OAc
O
H
CH3
4g
f1 (ppm)

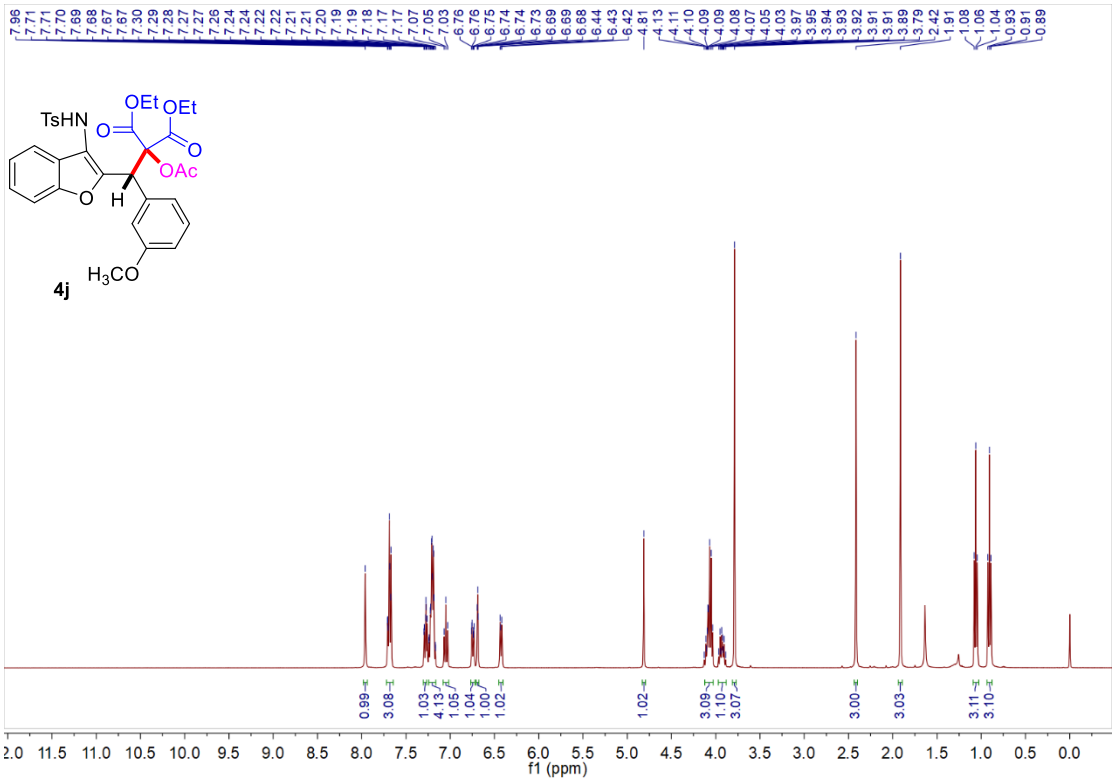

TsHN
OEt
OEt
O
O
OAc
O
H
CH3
4g
f1 (ppm)

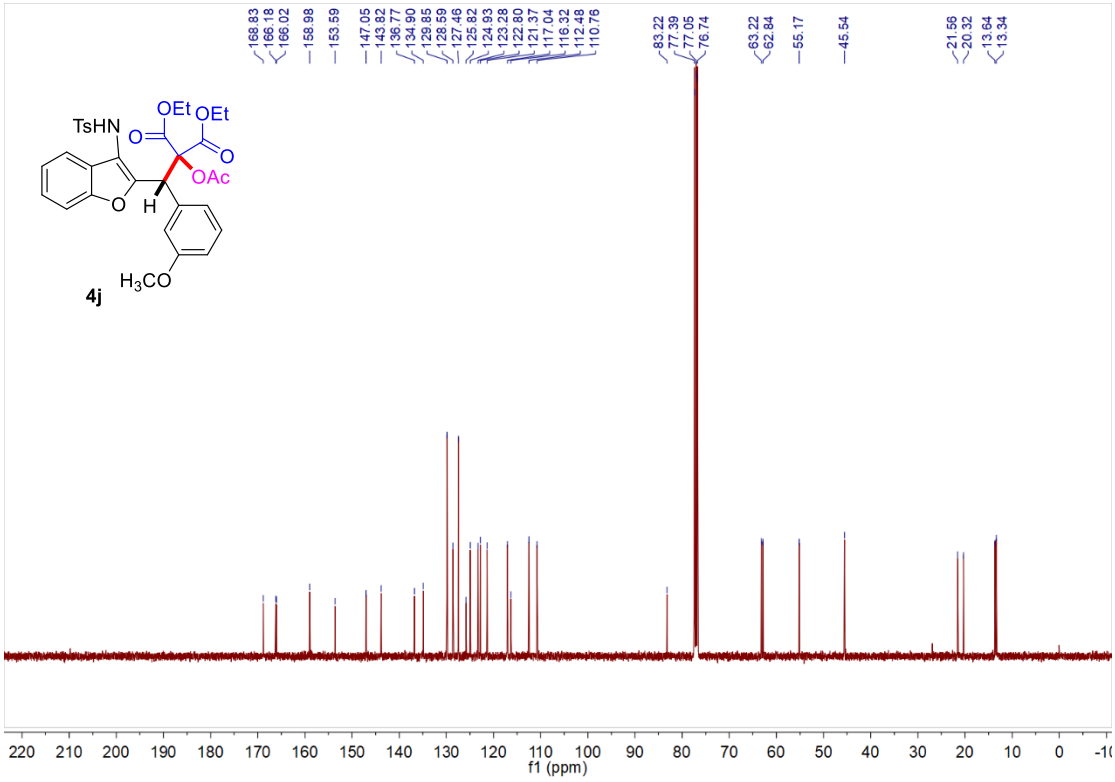

TsHN
OEt
OEt
O
O
O
OAc
H
O
4h
OCH3
f1 (ppm)

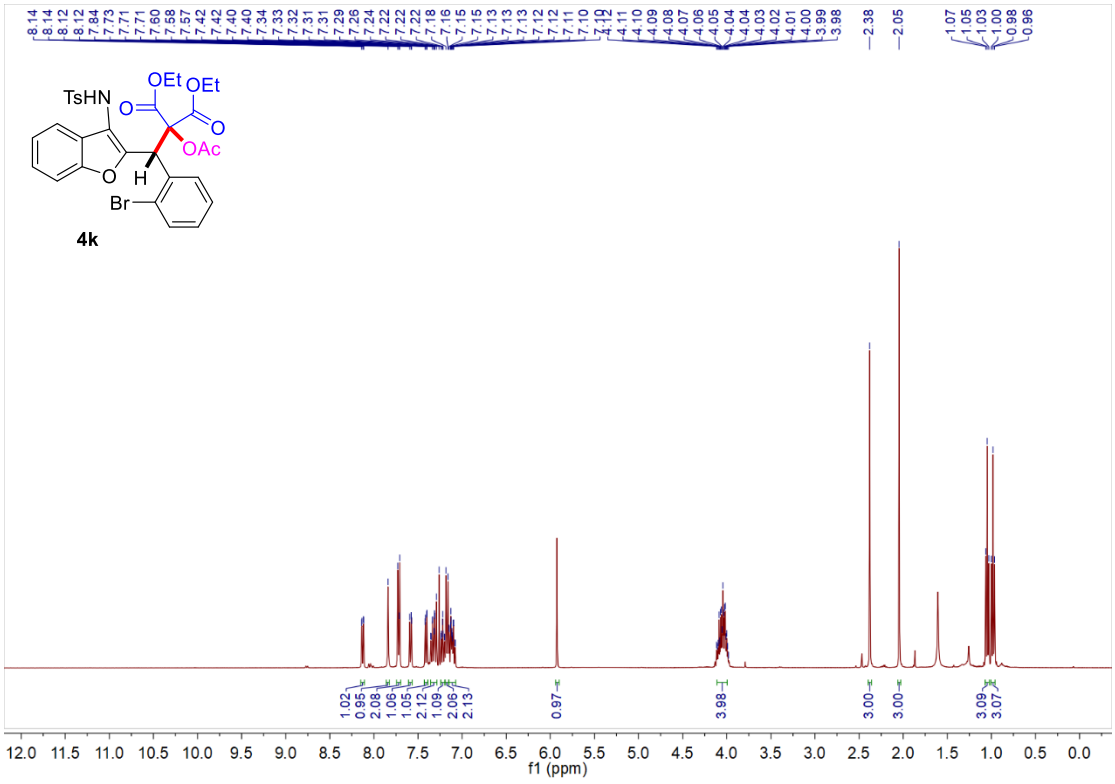

TsHN
OEt
OEt
O
O
O
OAc
H
O
4h
OCH3
f1 (ppm)

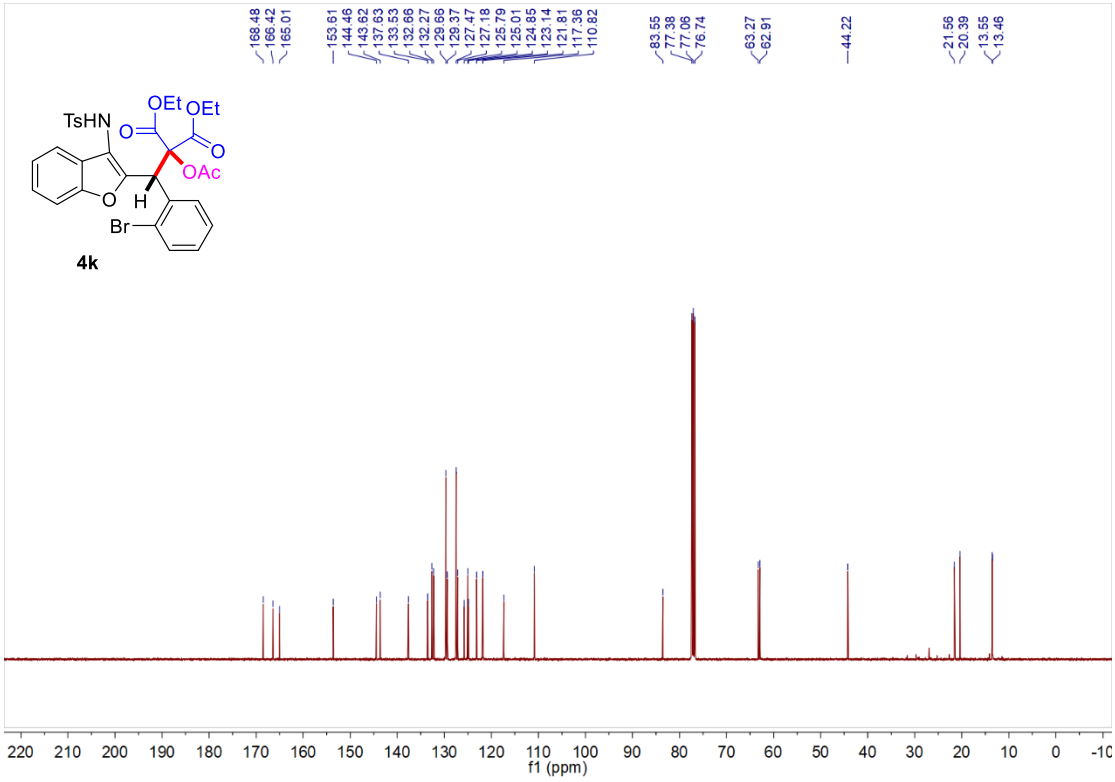

TsHN
OEt
OEt
O
O
O
OAc
H
O
Cl
4i
f1 (ppm)

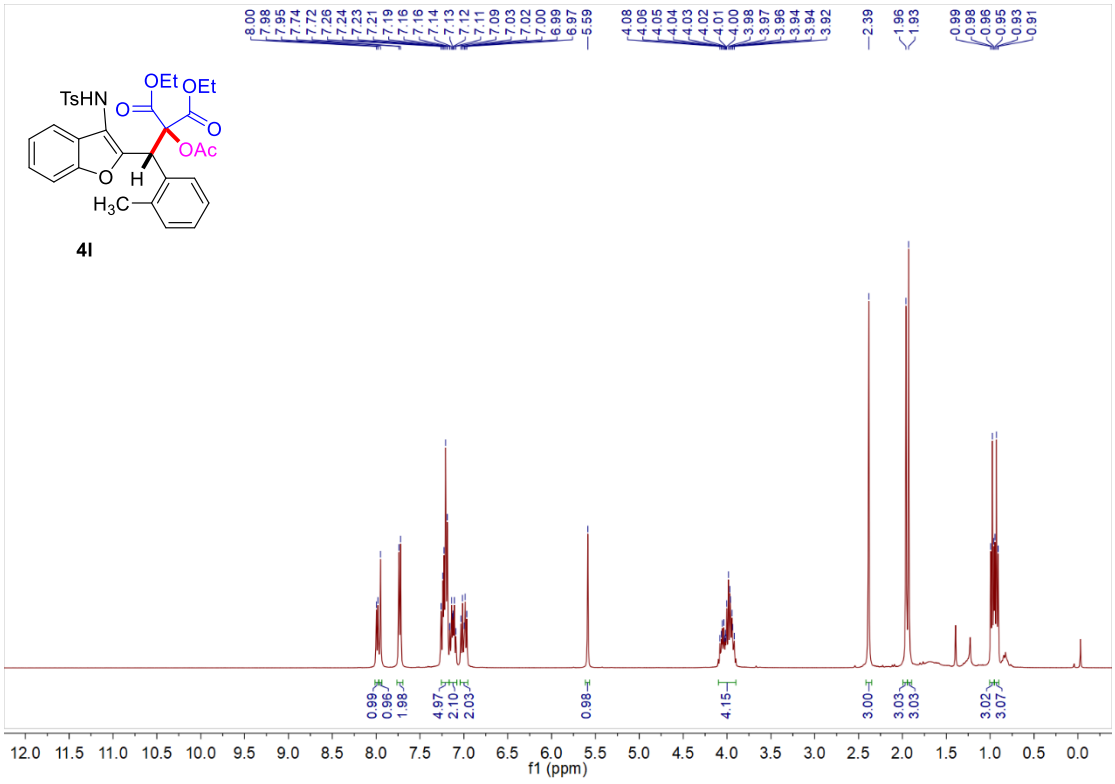

TsHN
OEt
OEt
O
O
O
OAc
H
O
Cl
4i
f1 (ppm)

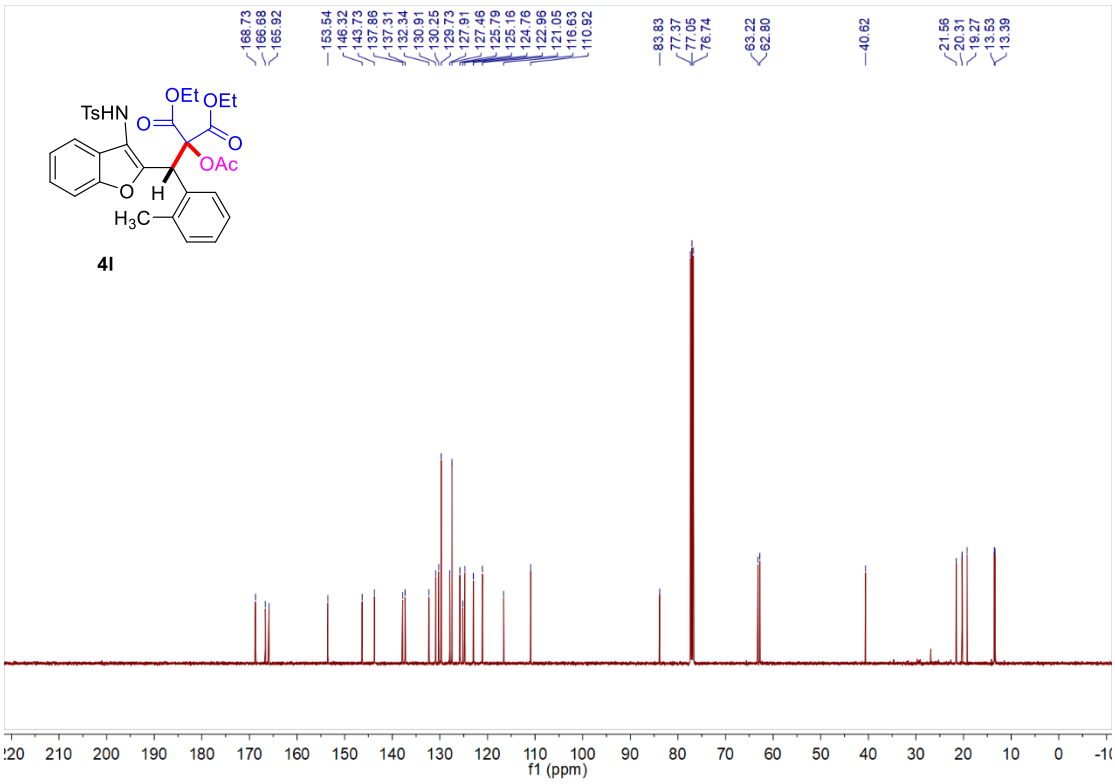

TsHN
OEt
OEt
O
O
OAc
H
O
H3CO
4j
f1 (ppm)

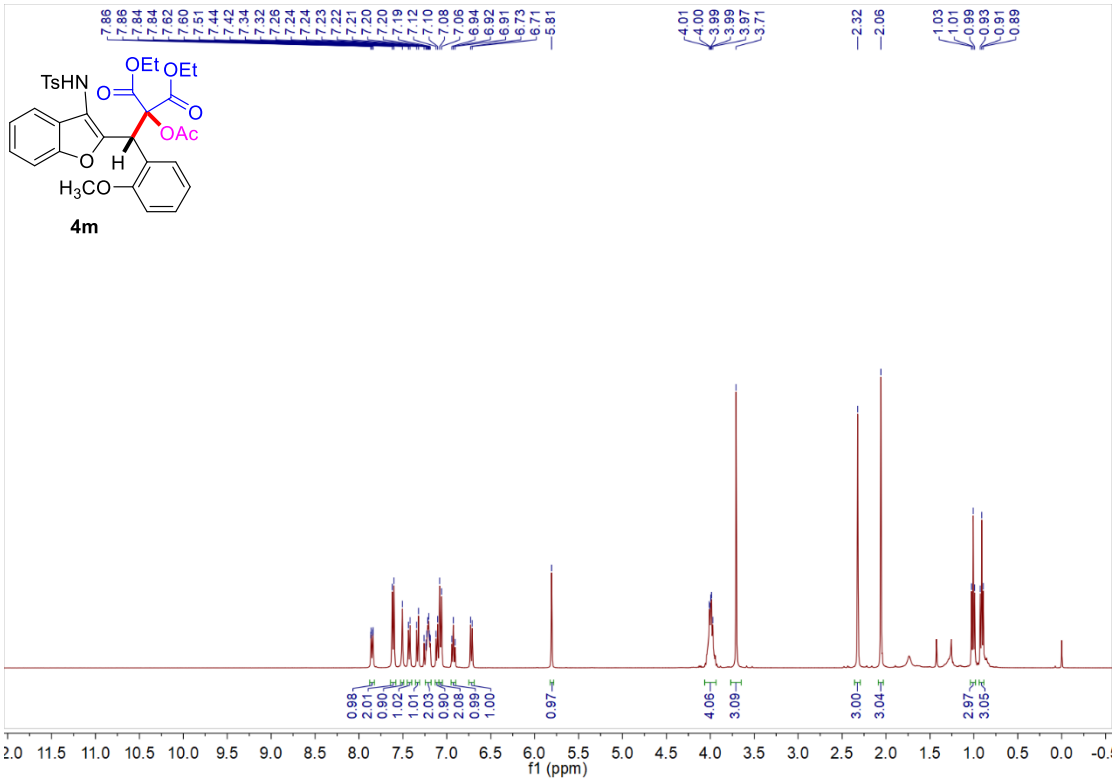

TsHN
OEt
OEt
O
O
OAc
H
O
H3CO
4j
f1 (ppm)

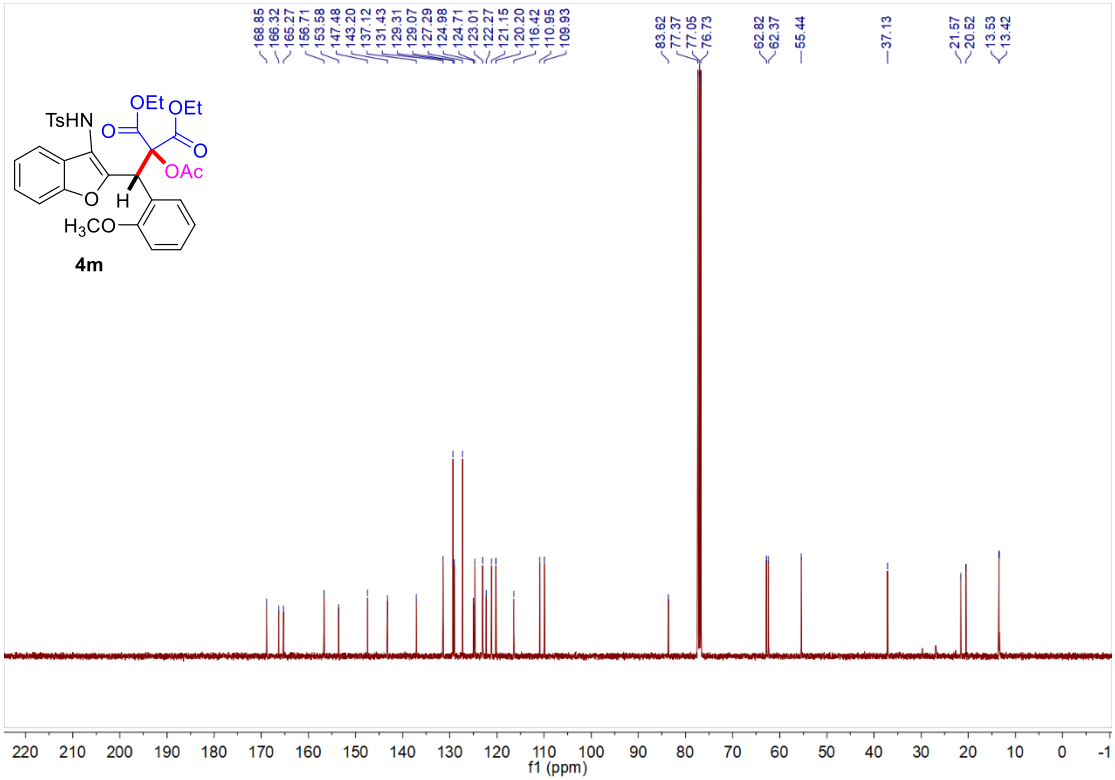

TsHN
OEt
OEt
O
O
O
OAc
H
Br
4k
f1 (ppm)

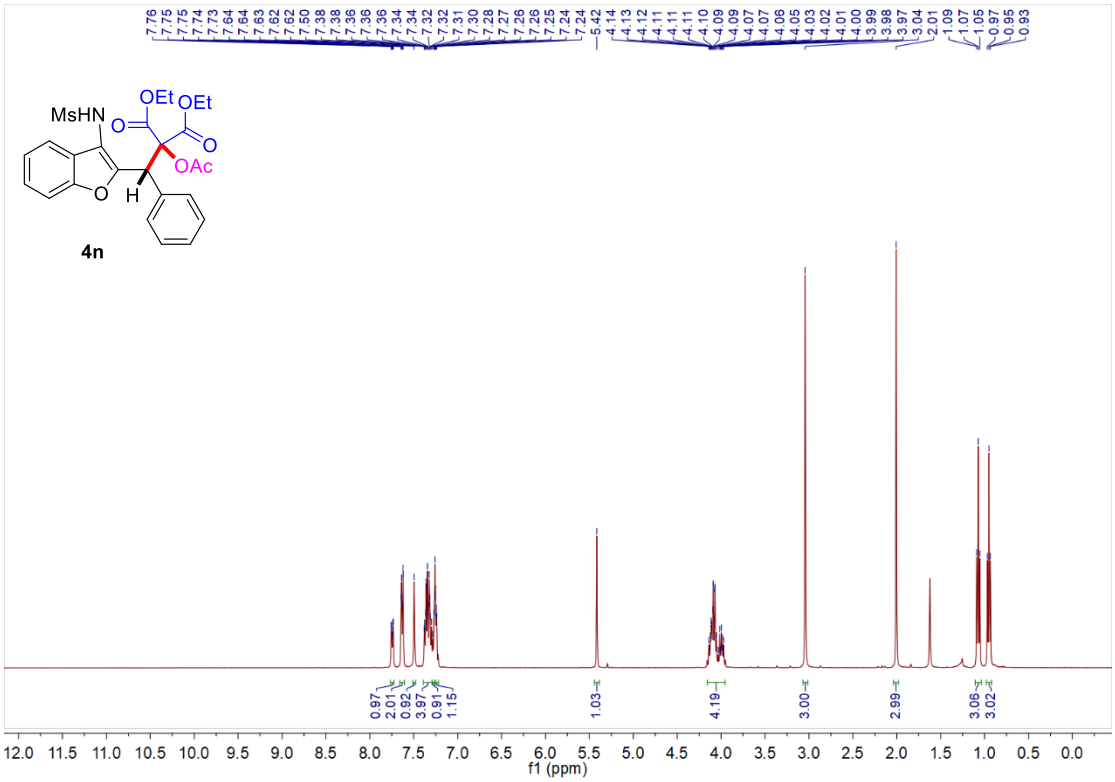

TsHN
OEt
OEt
O
O
O
OAc
H
Br
4k
f1 (ppm)

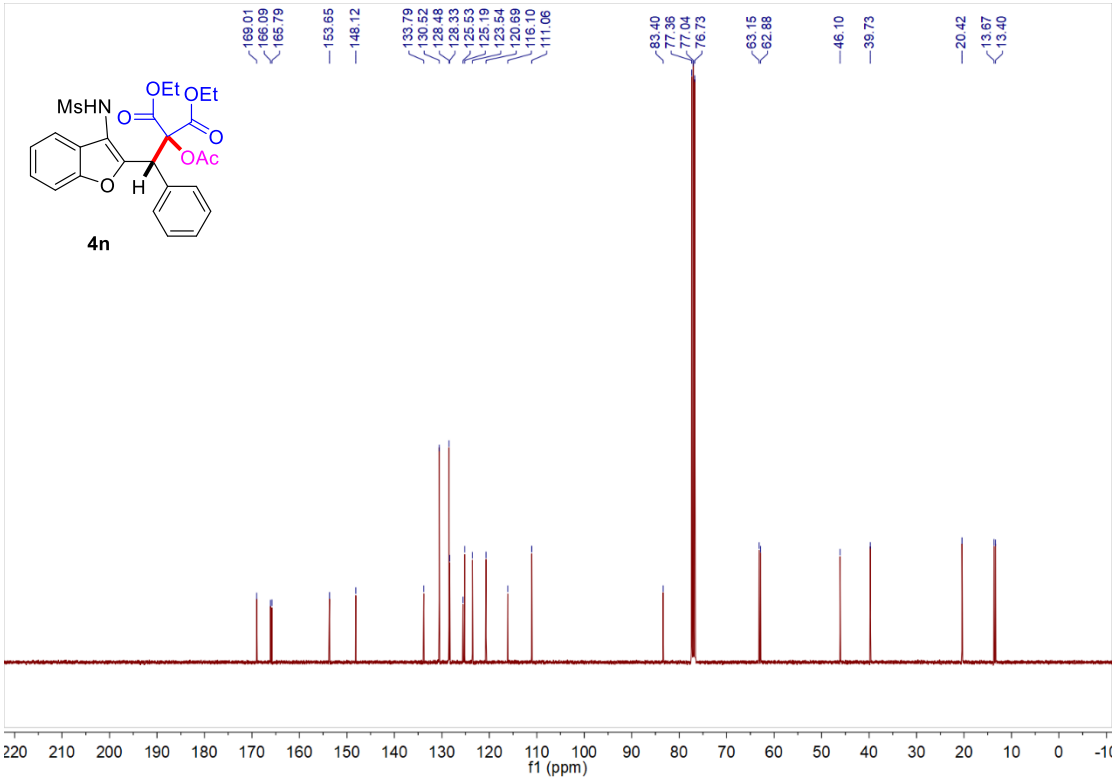

TsHN
OEt
OEt
O
O
O
OAc
O
H
H3C
4l
f1 (ppm)

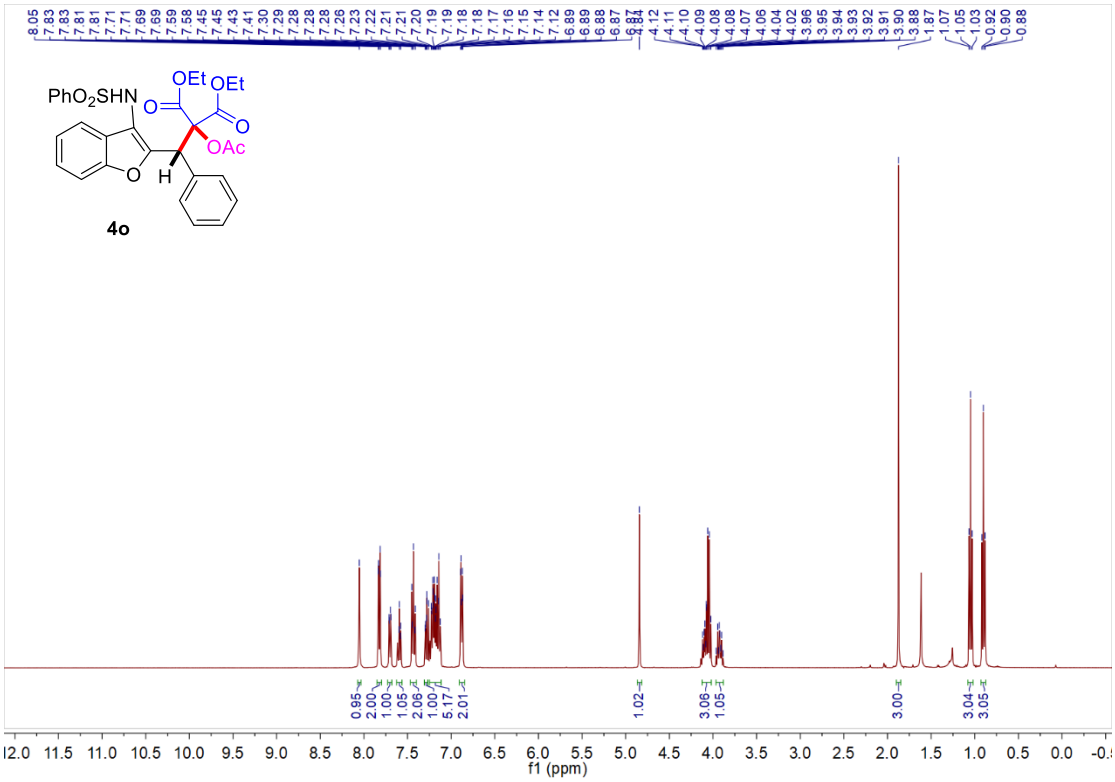

TsHN
OEt
OEt
O
O
O
OAc
O
H
H3C
4l
f1 (ppm)

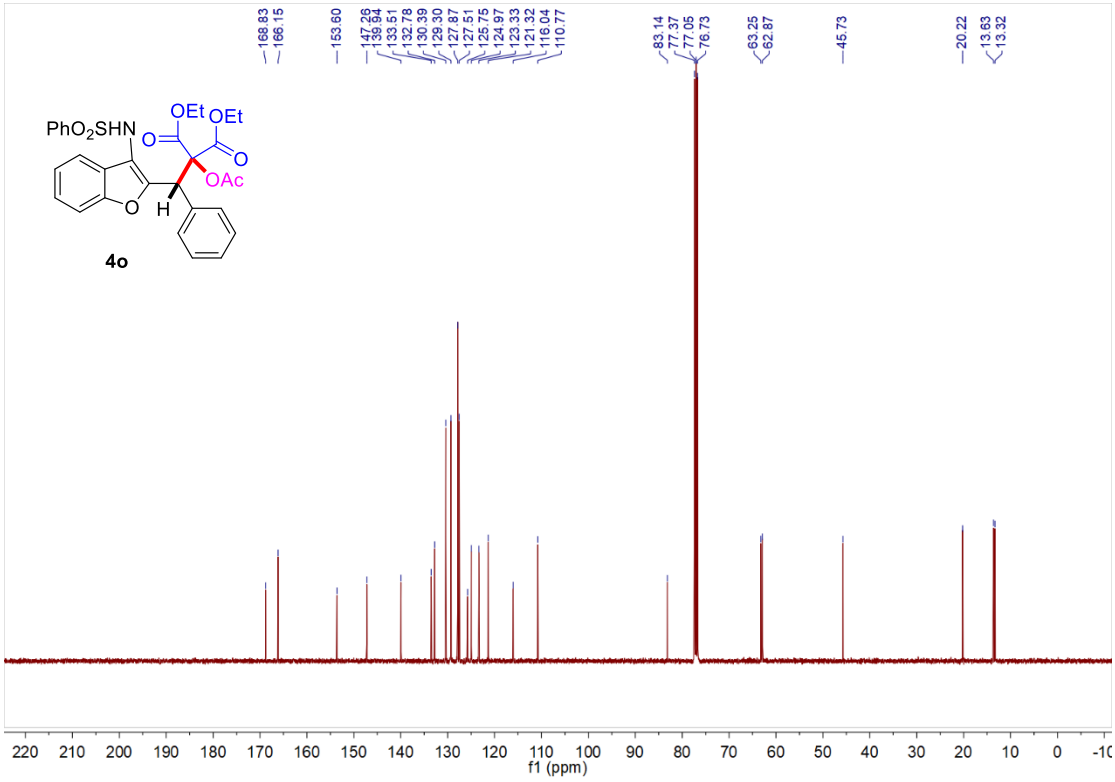

TsHN
OEt
OEt
O
O
OAc
O
H
H3CO
4m
f1 (ppm)

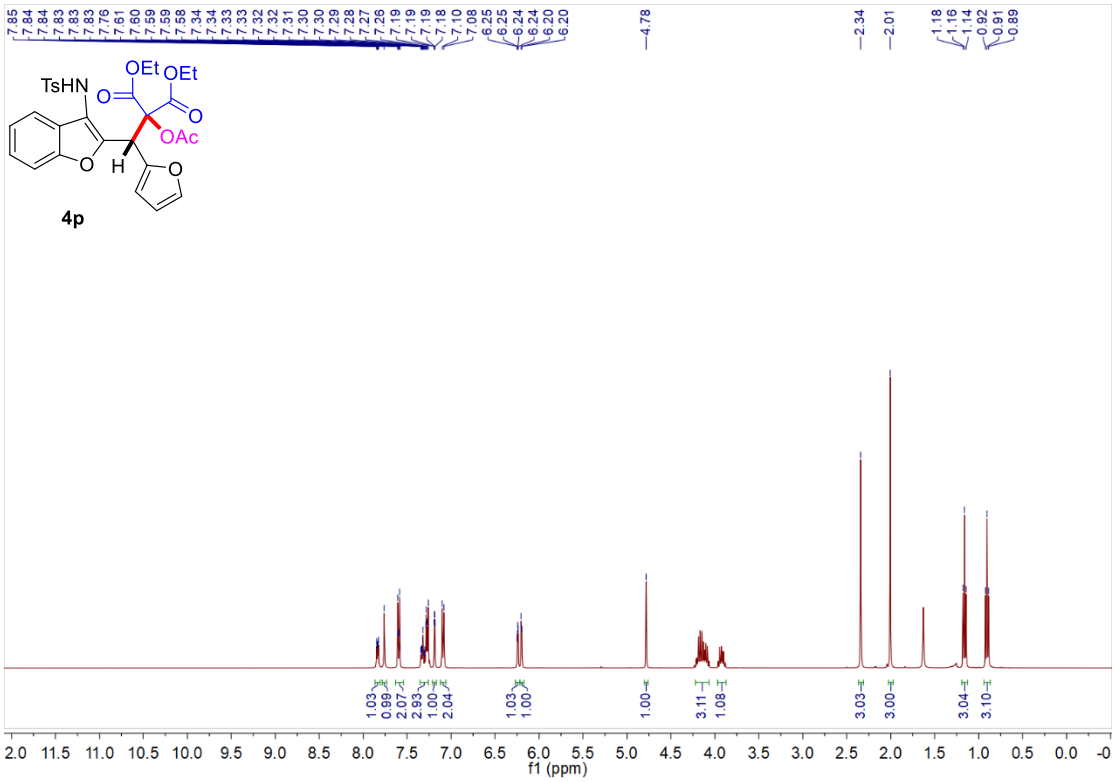

TsHN
OEt
OEt
O
O
OAc
O
H
H3CO
4m
f1 (ppm)

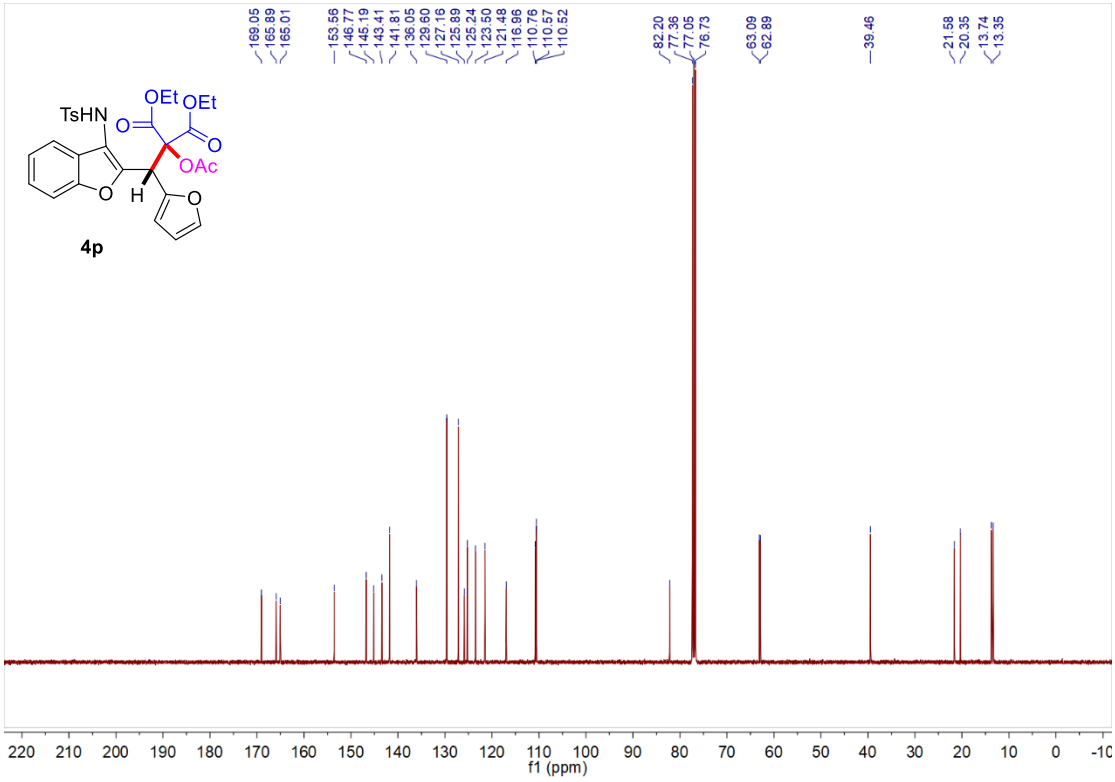

MsHN
OEt
OEt
O
O
O
OAc
H
4n
f1 (ppm)

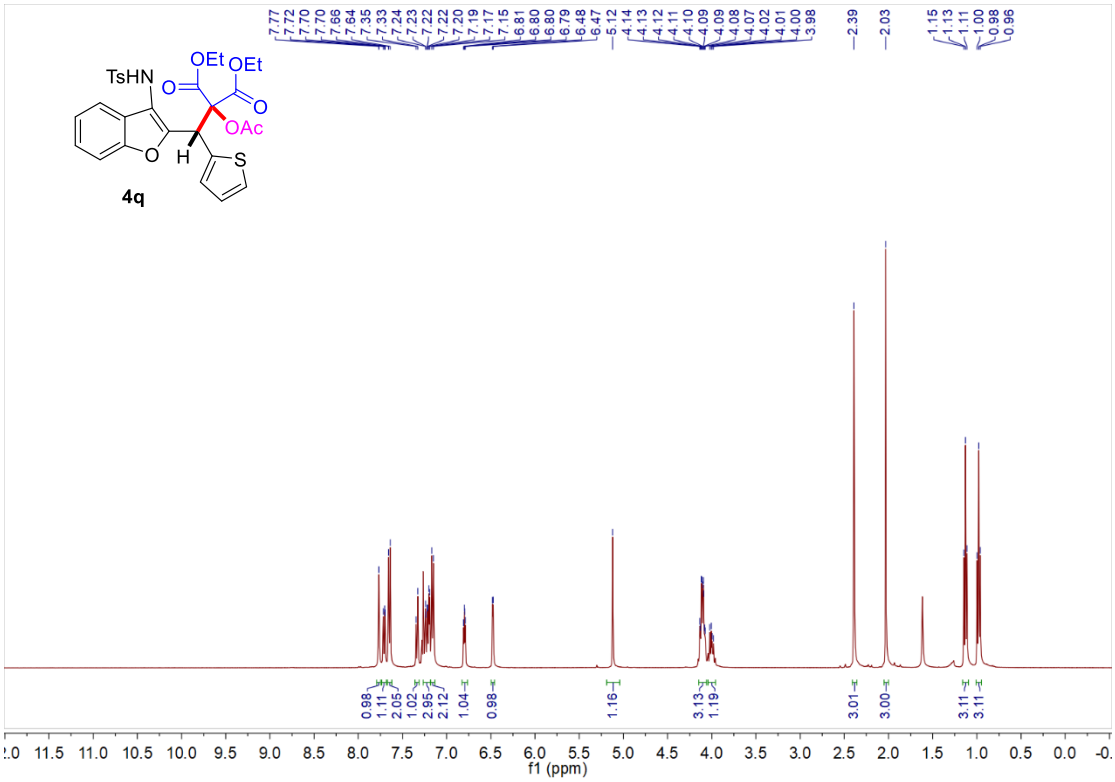

MsHN
OEt
OEt
O
O
O
OAc
H
4n
f1 (ppm)

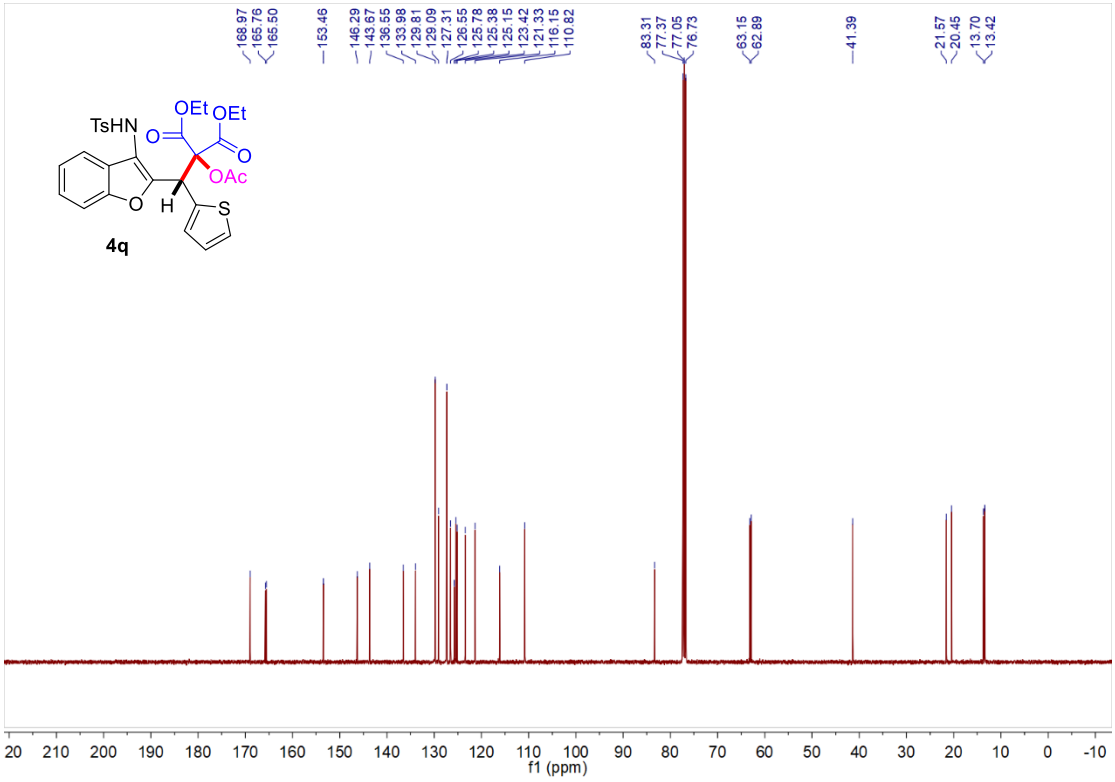

PhO2SHN
OEt
OEt
O
O
OAc
O
H
4o
f1 (ppm)

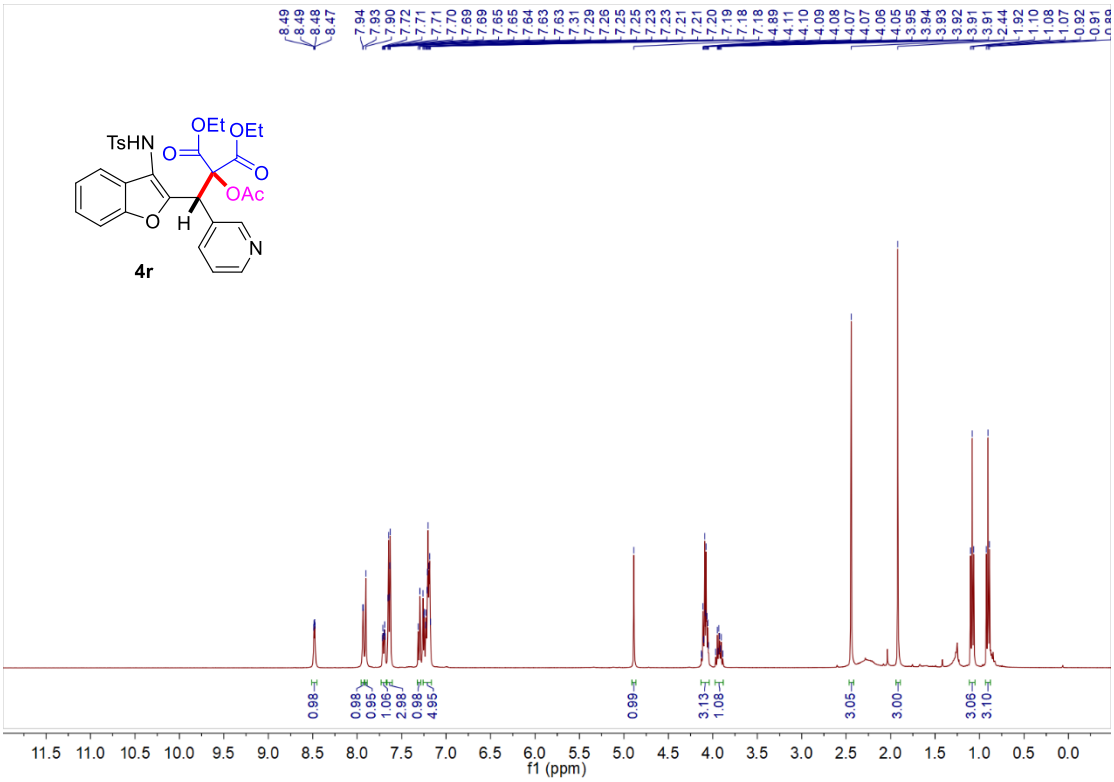

PhO2SHN
OEt
OEt
O
O
OAc
O
H
4o
f1 (ppm)

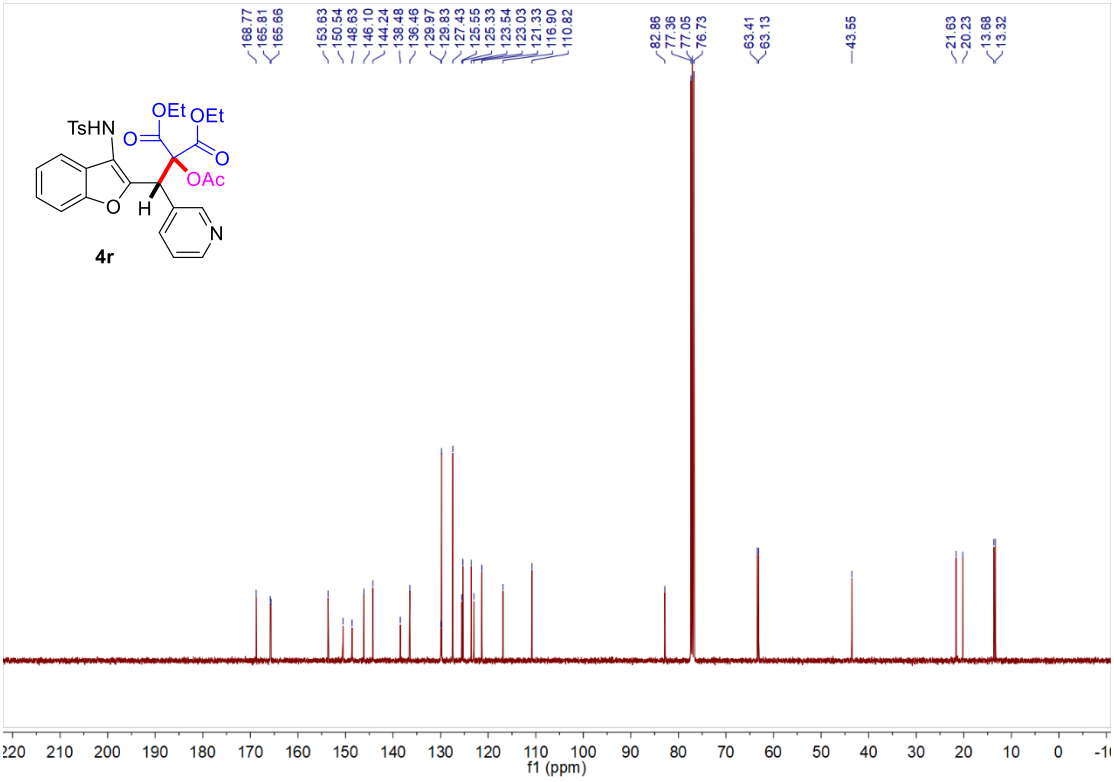

TsHN
OEt
OEt
O
O
OAc
O
H
O
4p
f1 (ppm)

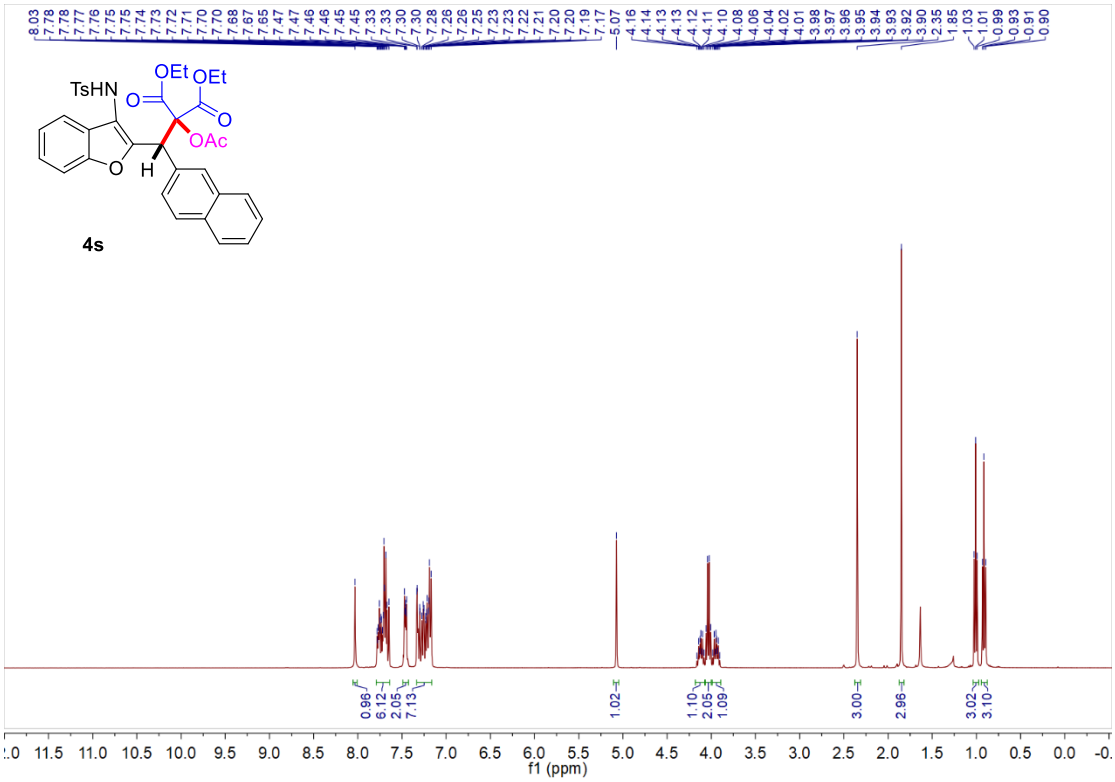

TsHN
OEt
OEt
O
O
OAc
O
H
O
4p
f1 (ppm)

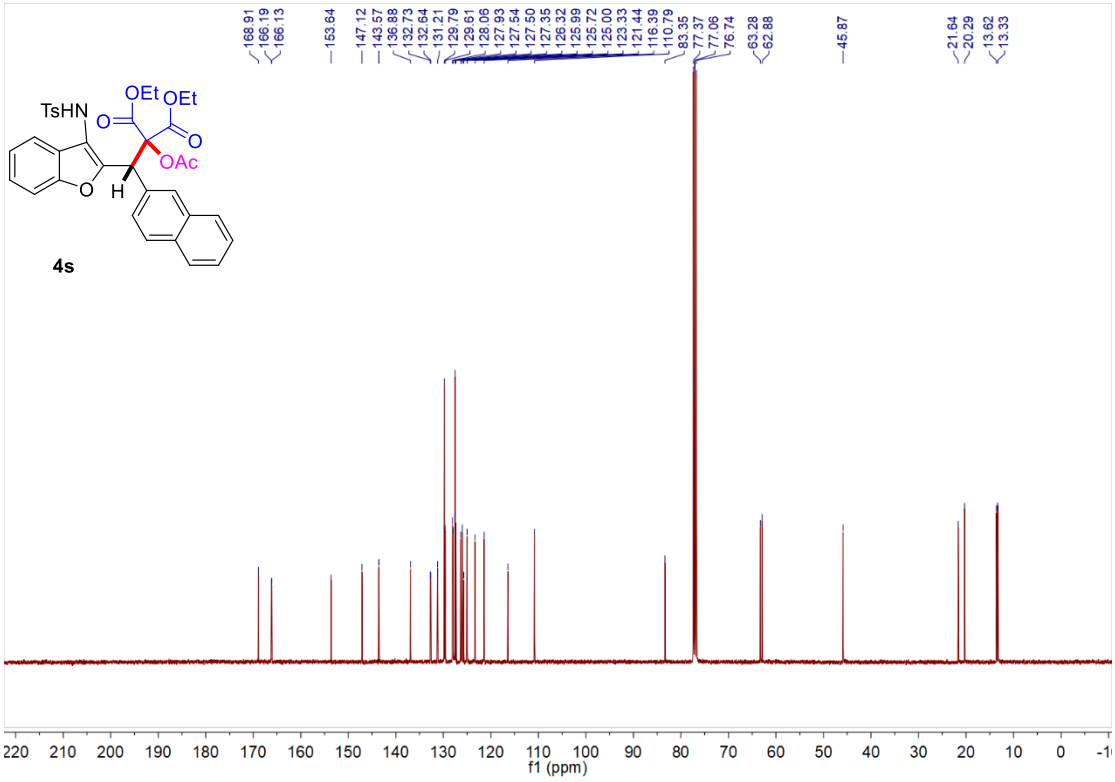

TsHN
OEt
OEt
O
O
O
OAc
H
S
O
4q
f1 (ppm)

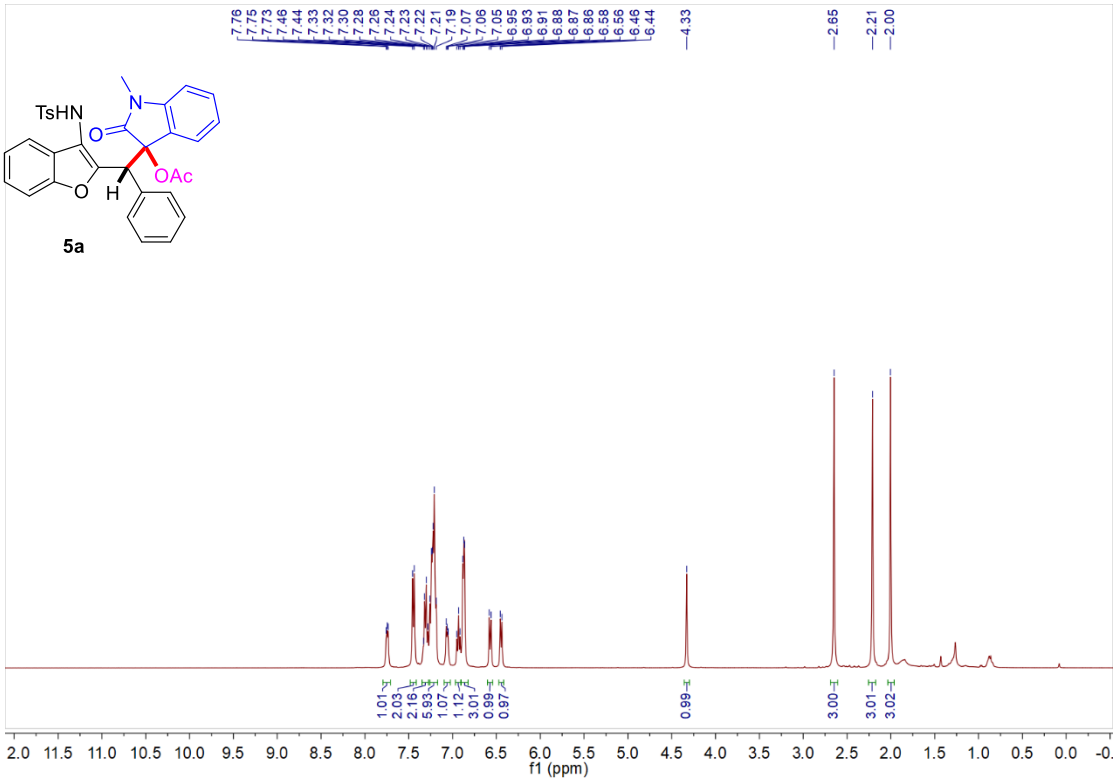

TsHN
OEt
OEt
O
O
O
OAc
H
S
O
4q
f1 (ppm)

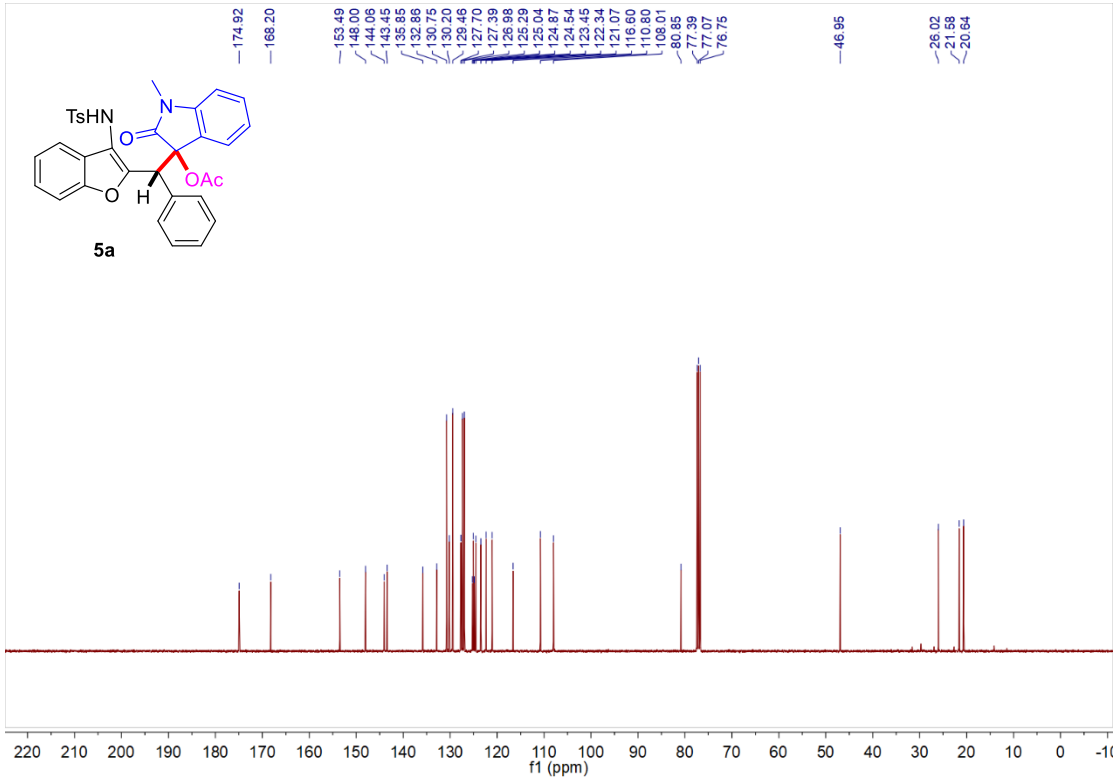

TsHN
OEt
OEt
O
O
OAc
O
H
N
4r
f1 (ppm)


TsHN
OEt
OEt
O
O
OAc
O
H
N
4r
f1 (ppm)


TsHN
OEt
OEt
O
O
O
OAc
H
4s
f1 (ppm)


TsHN
OEt
OEt
O
O
O
OAc
H
4s
f1 (ppm)


7.76
7.75
7.73
7.46
7.44
7.33
7.32
7.30
7.28
7.26
7.24
7.23
7.22
7.21
7.19
7.07
7.06
7.05
6.95
6.93
6.91
6.88
6.87
6.86
6.58
6.56
6.46
6.44
4.33
2.65
2.21
2.00
TsHN
N
O
O
H
OAc
5a
1.01
2.03
2.16
5.93
1.07
1.12
3.01
0.99
0.97
0.99
3.00
3.01
3.02
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.92
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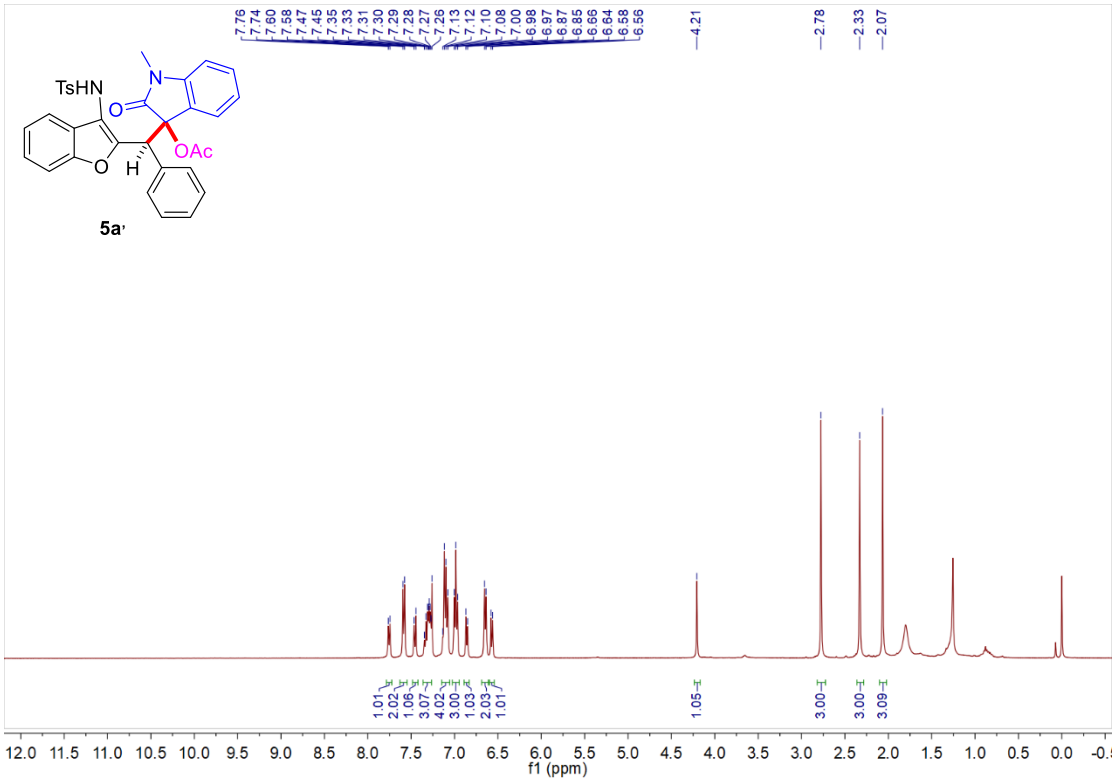
148.00
144.06
143.45
135.85
132.86
130.75
130.20
129.46
127.70
127.39
126.98
125.29
125.04
124.87
124.54
123.45
122.34
121.07
116.60
110.80
108.01
80.85
77.39
77.07
76.75
46.95
26.02
21.58
20.64
TsHN
N
O
O
H
OAc
5a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


TsHN
N
O
OAc
O
H
5a'
7.76
7.74
7.60
7.58
7.47
7.45
7.35
7.33
7.31
7.30
7.29
7.28
7.27
7.26
7.13
7.12
7.10
7.08
7.00
6.98
6.97
6.87
6.85
6.66
6.64
6.58
6.56
4.21
2.78
2.33
2.07
1.01
2.02
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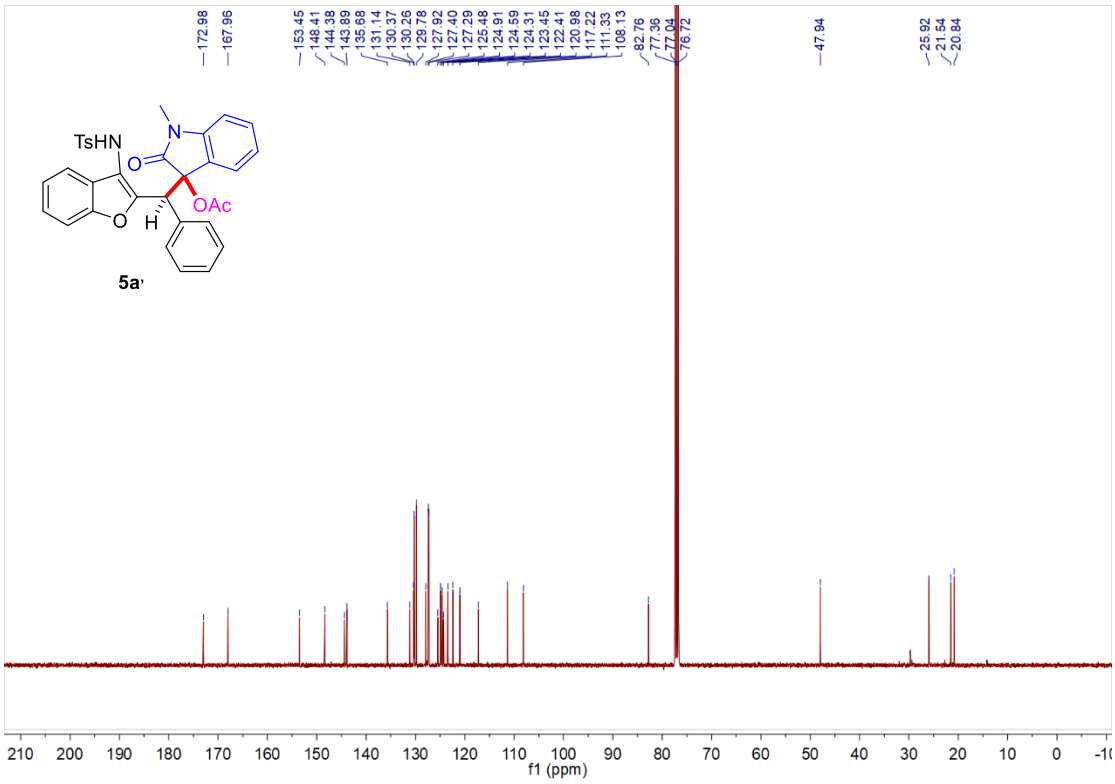
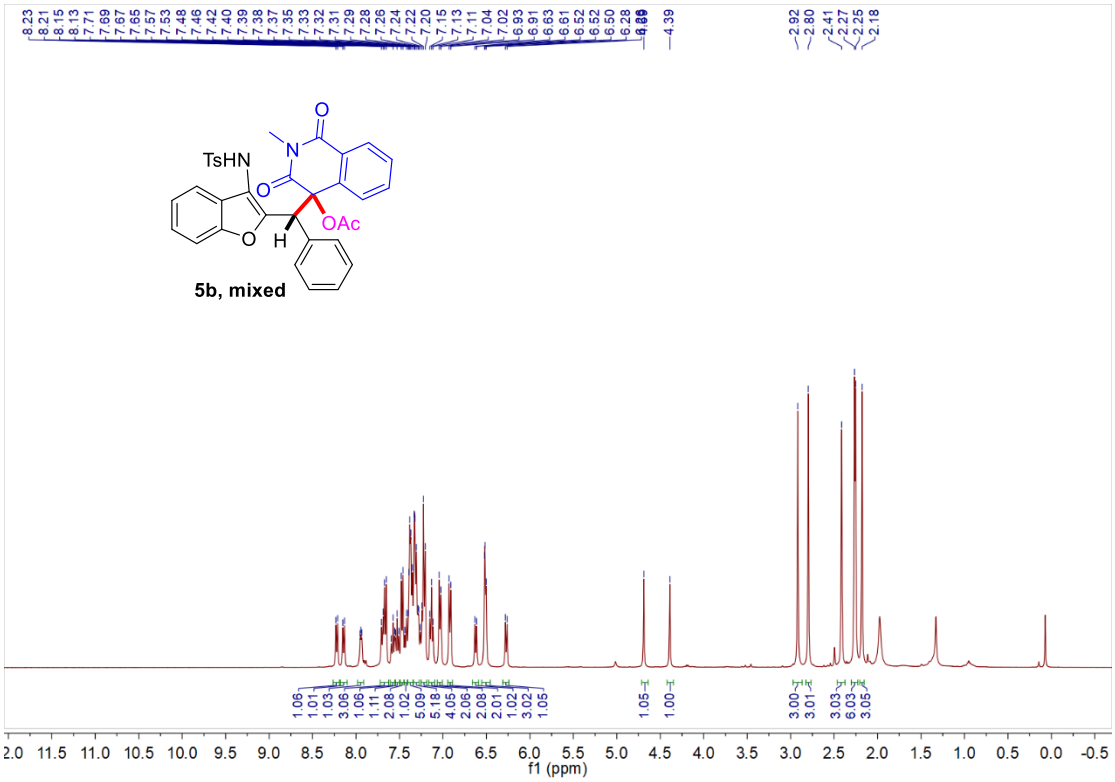
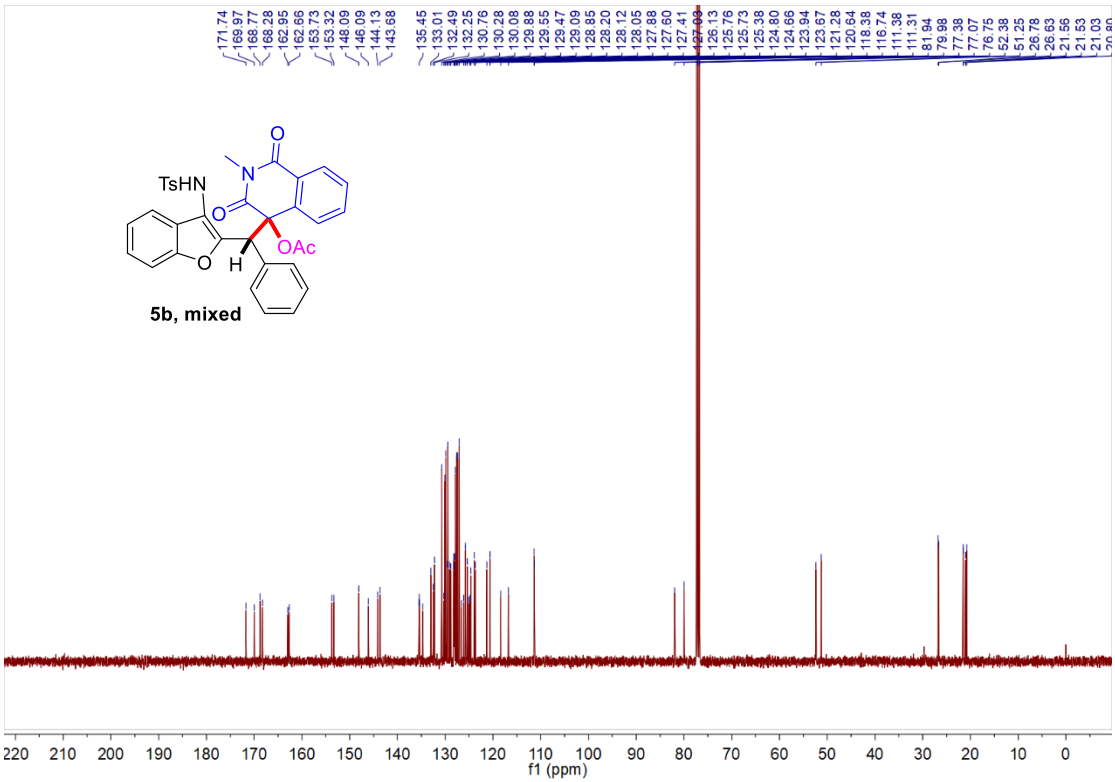
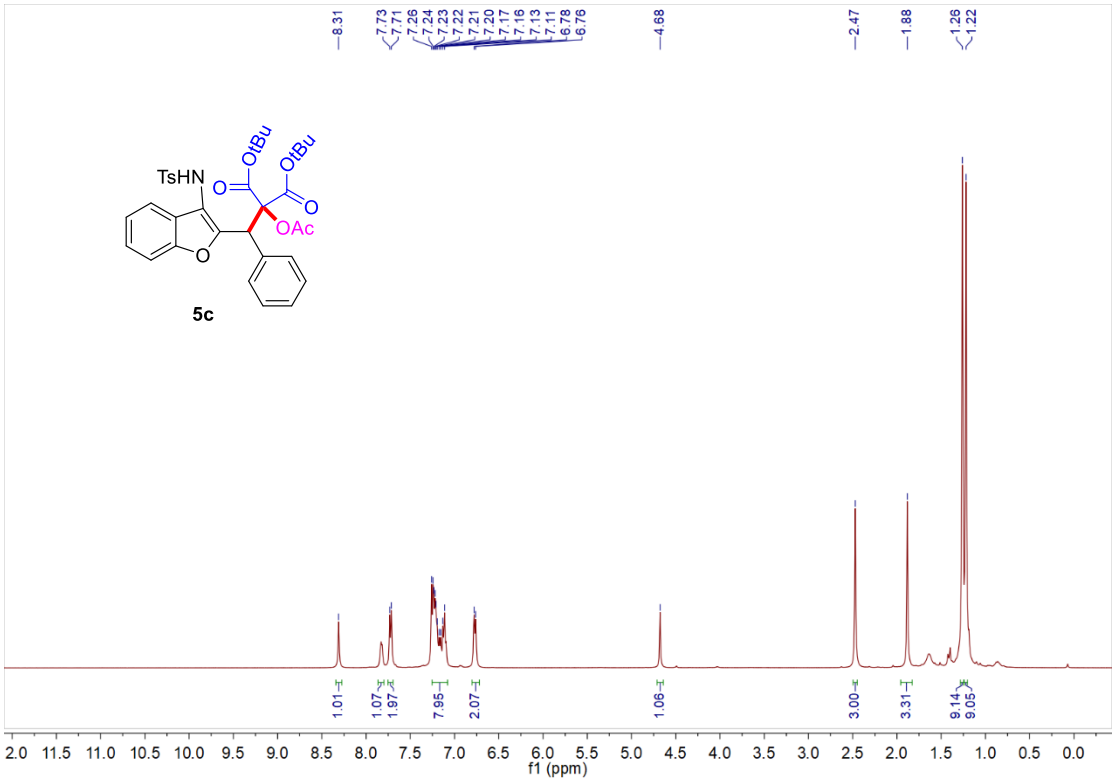
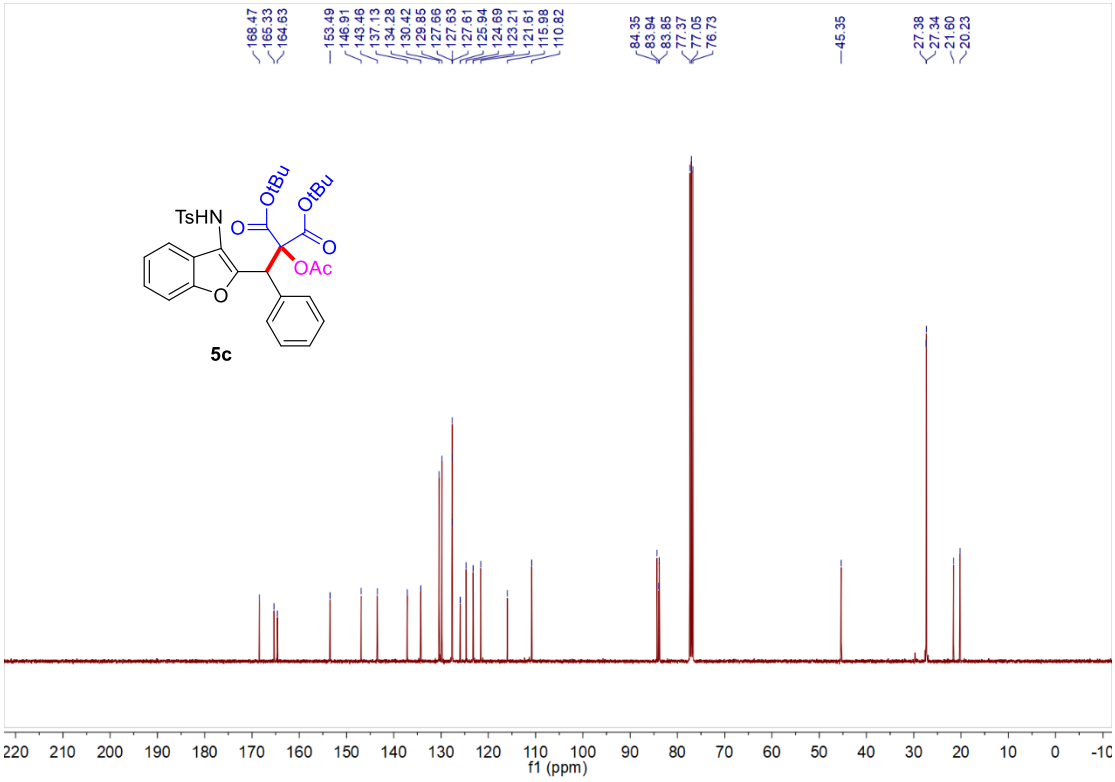
1.05
3.00
3.00
3.09
f1 (ppm)


TsHN
N
O
OAc
O
H
5a'
172.98
167.96
153.45
148.41
144.38
143.89
135.68
131.14
130.37
130.26
129.78
127.92
127.40
127.29
125.48
124.91
124.59
124.31
123.45
122.41
120.98
117.22
111.33
108.13
82.76
77.36
77.04
76.72
47.94
25.92
21.54
20.84
f1 (ppm)


TsHN
O
N
O
OAc
O
H
5b, mixed
f1 (ppm)


TsHN
O
N
O
OAc
O
H
5b, mixed
f1 (ppm)


8.31
7.73
7.71
7.26
7.24
7.23
7.22
7.21
7.20
7.17
7.16
7.13
7.11
6.78
6.76
4.68
2.47
1.88
1.26
1.22
TsHN
OtBu
OtBu
O
O
O
OAc
O
5c
1.01
1.07
1.97
7.95
2.07
1.06
3.00
3.31
9.14
9.05
f1 (ppm)


168.47
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164.63
153.49
146.91
143.46
137.13
134.28
130.42
129.85
127.66
127.63
127.61
125.94
124.69
123.21
121.61
115.98
110.82
84.35
83.94
83.85
77.37
77.05
76.73
45.35
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21.60
20.23
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OtBu
OtBu
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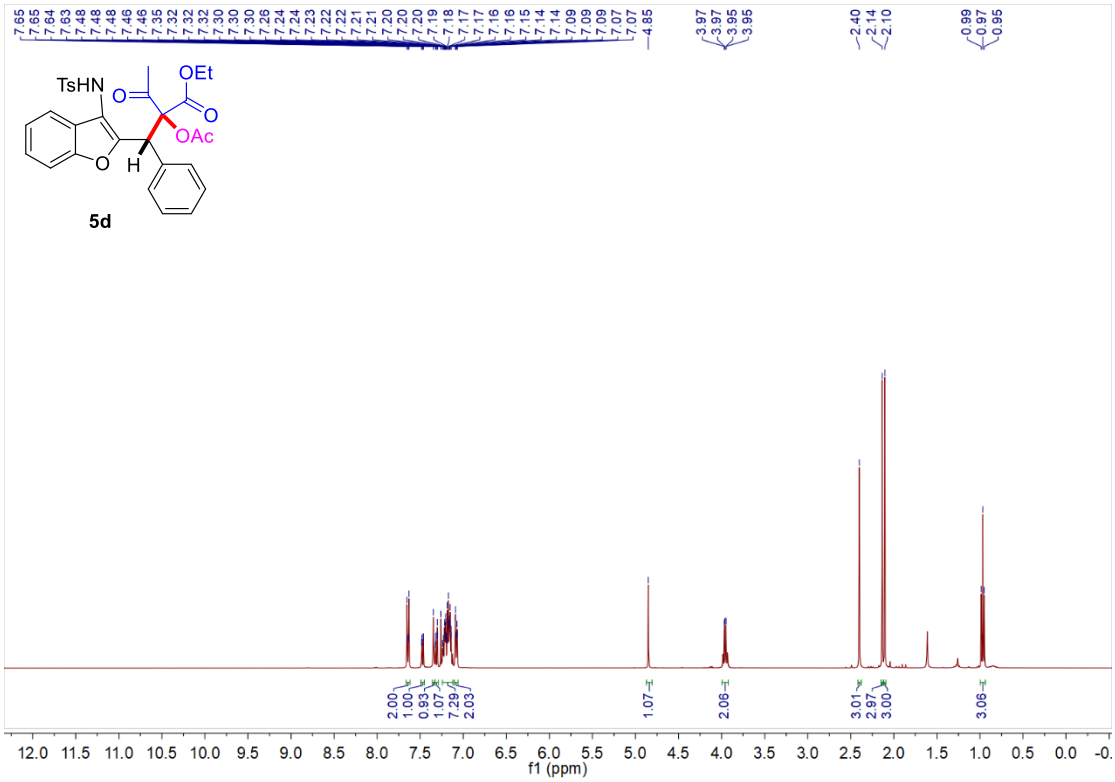
O
O
OAc
O
5c
f1 (ppm)


TsHN
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OAc
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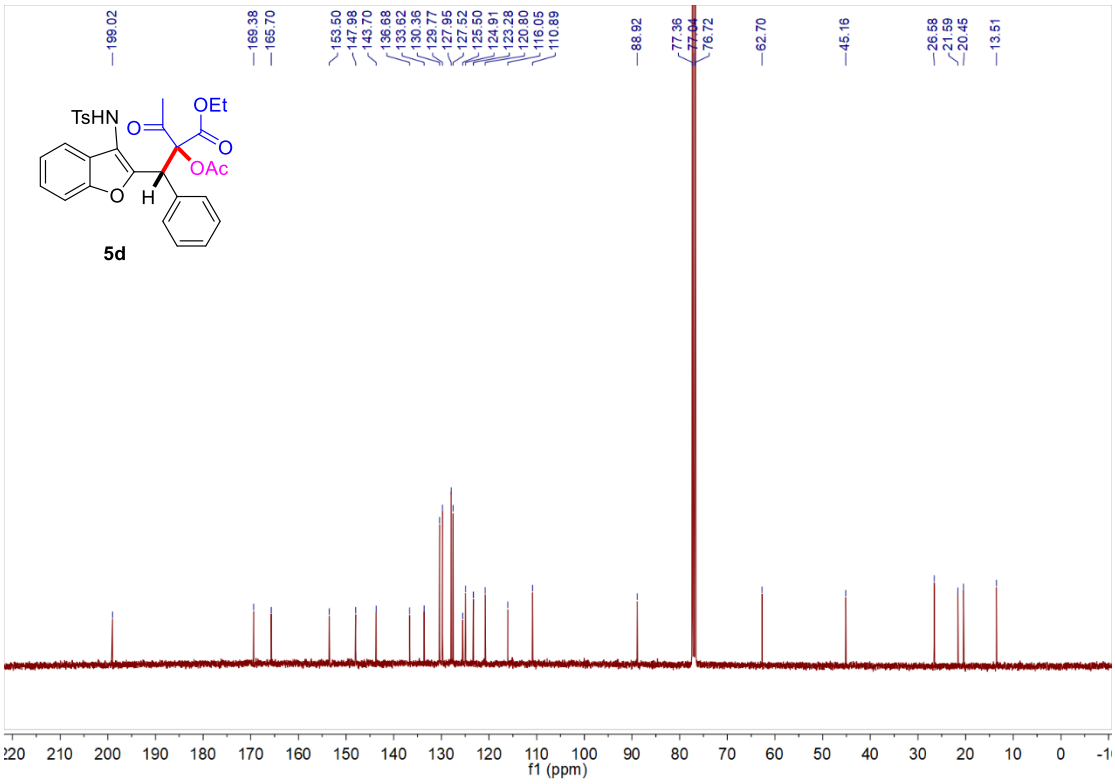
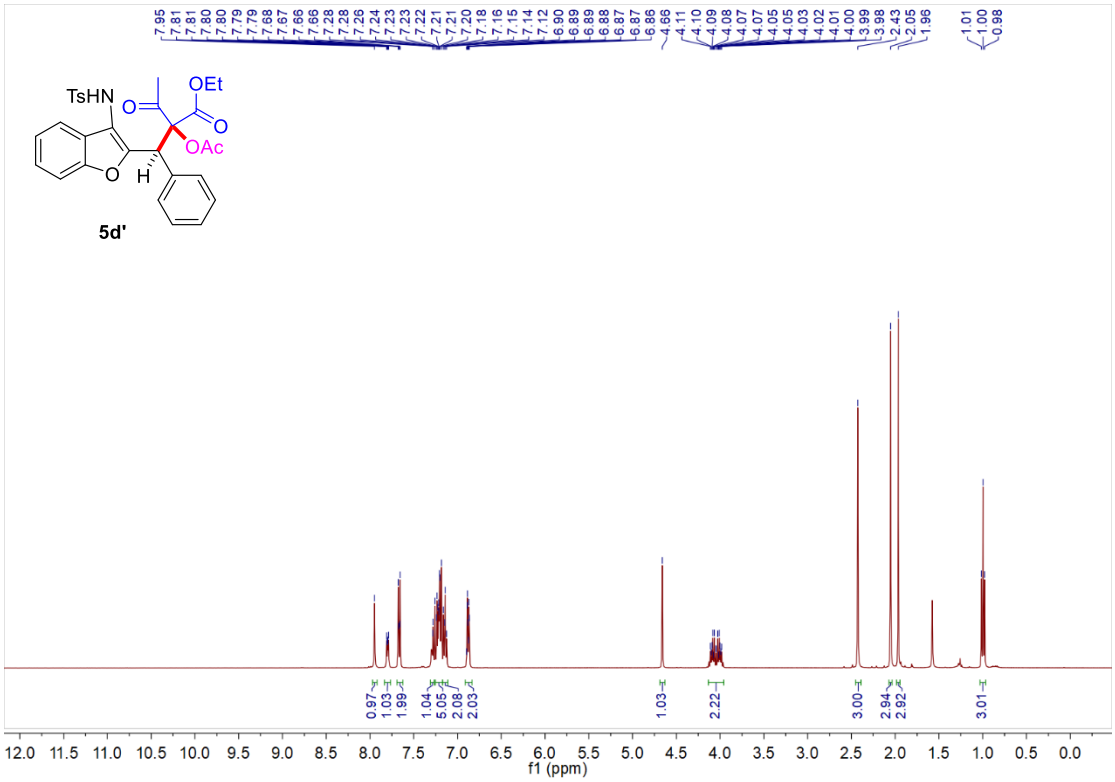
5d
f1 (ppm)


TsHN
OEt
OAc
H
5d
f1 (ppm)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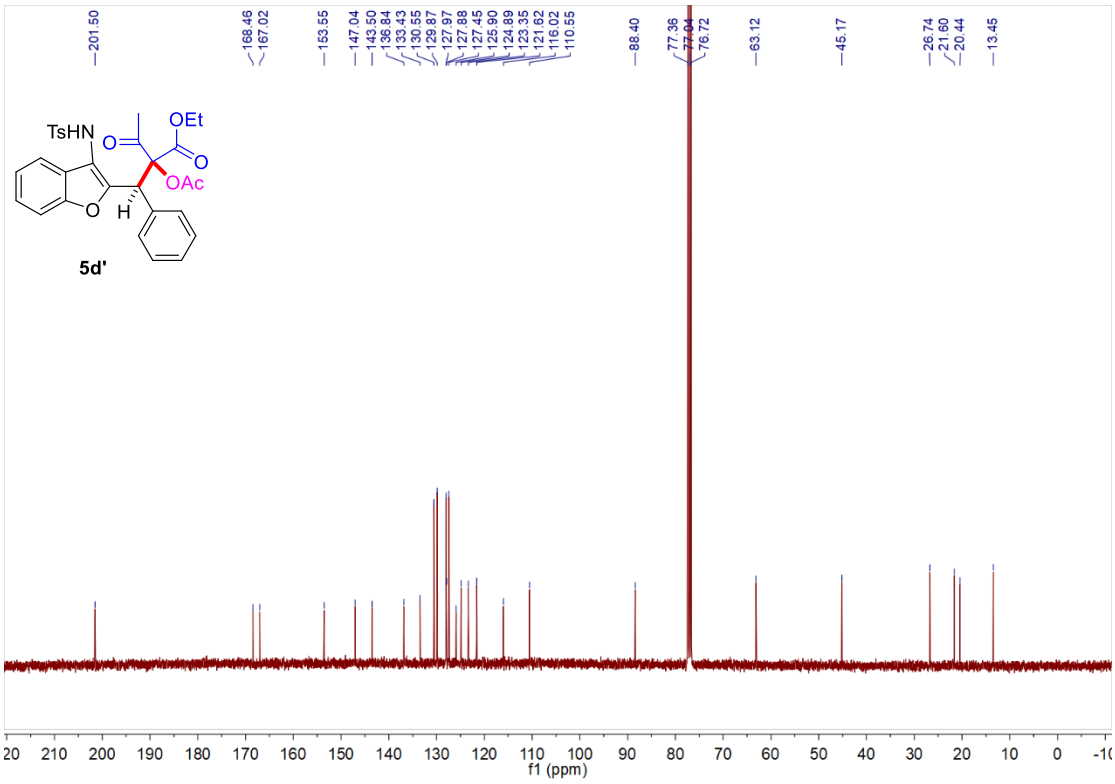
OEt
O
OAc
O
H
5d'
f1 (ppm)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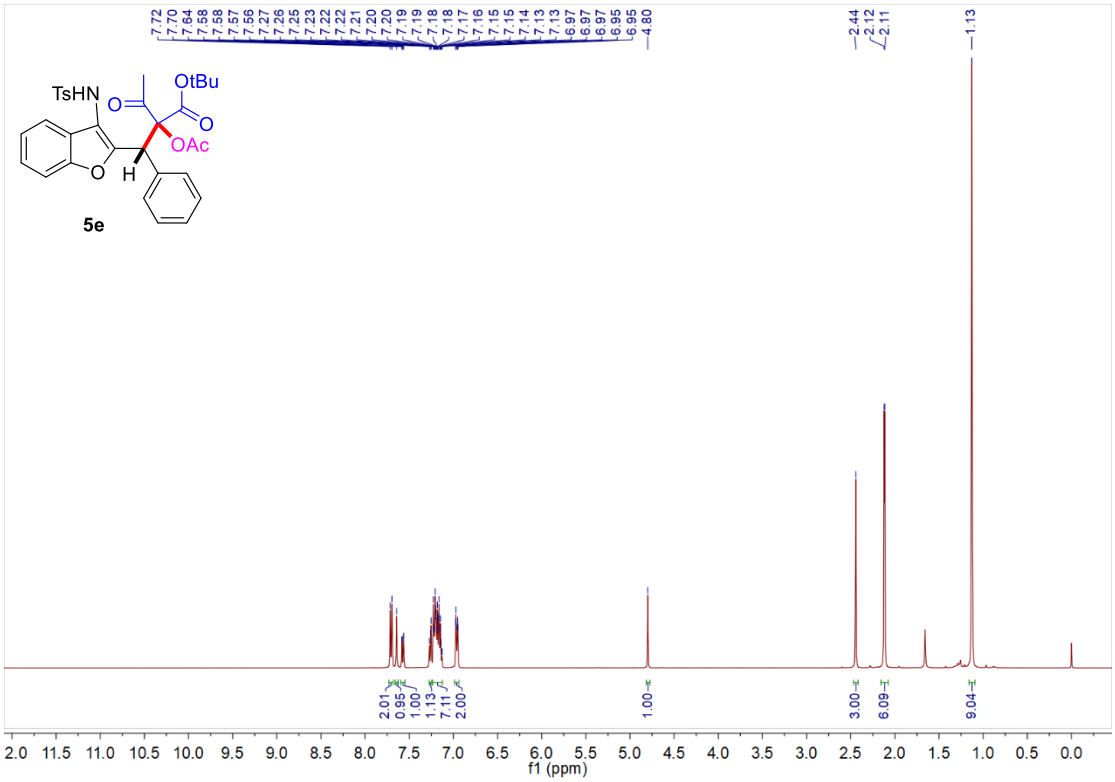
OEt
O
OAc
O
H
5d'
f1 (ppm)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OtBu
O
OAc
O
H
5e
7.72
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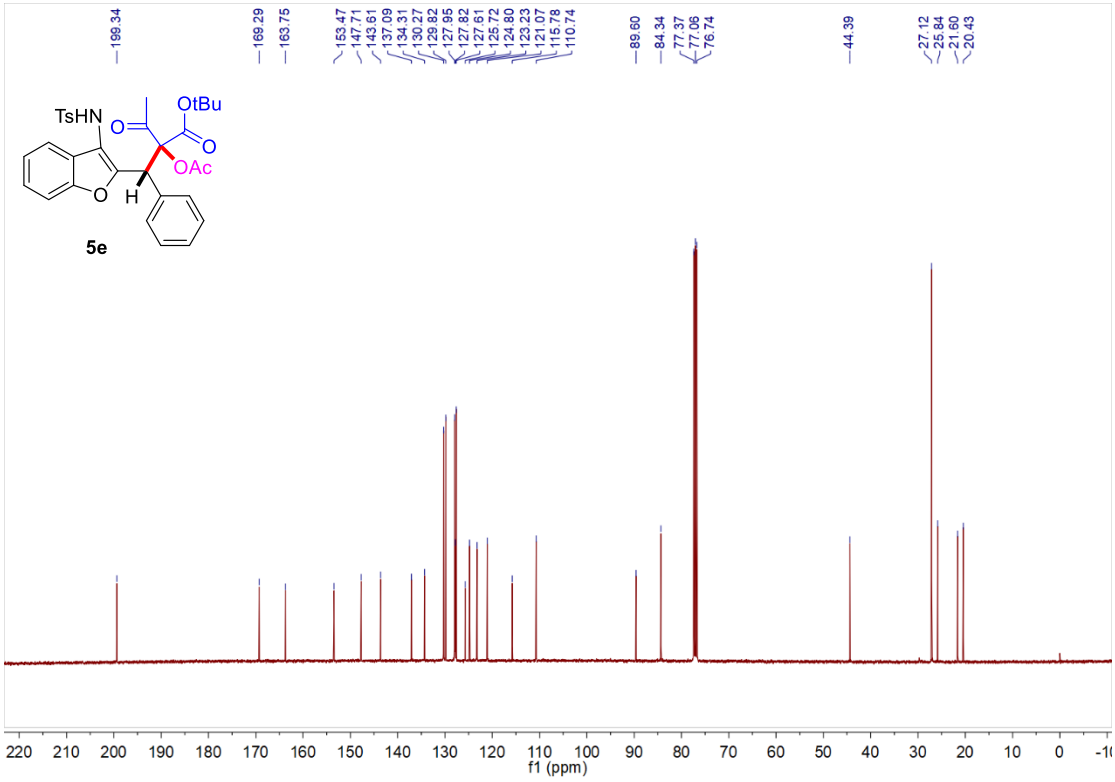
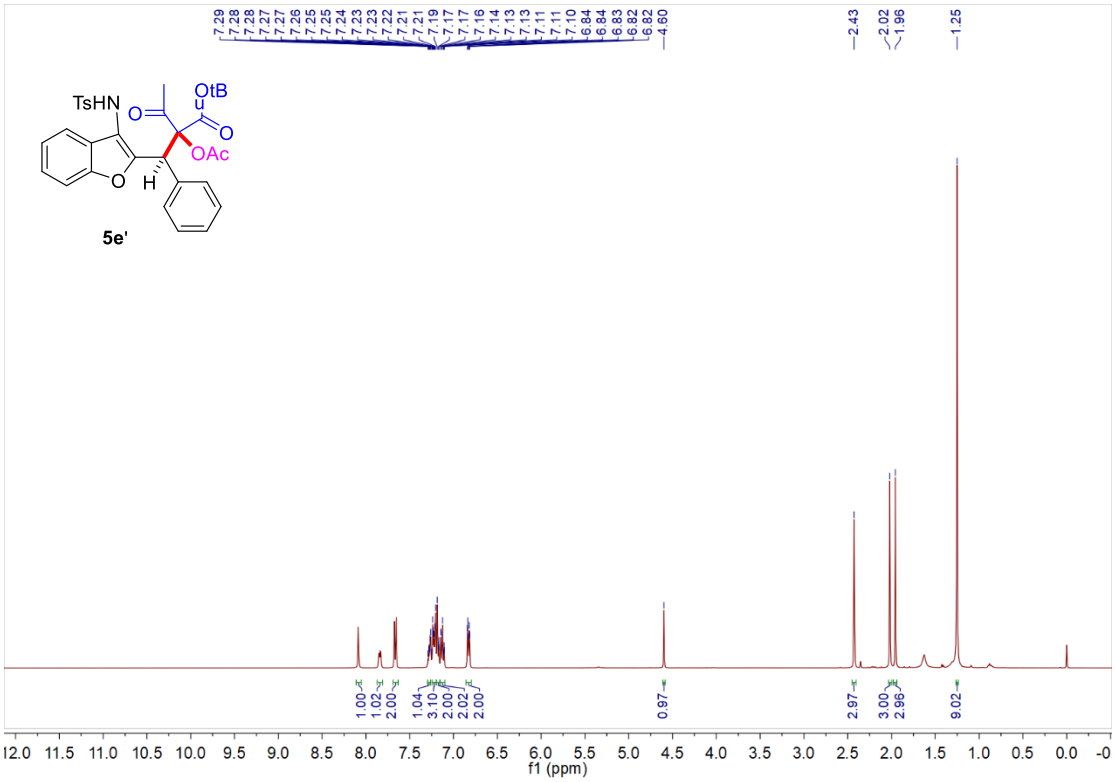
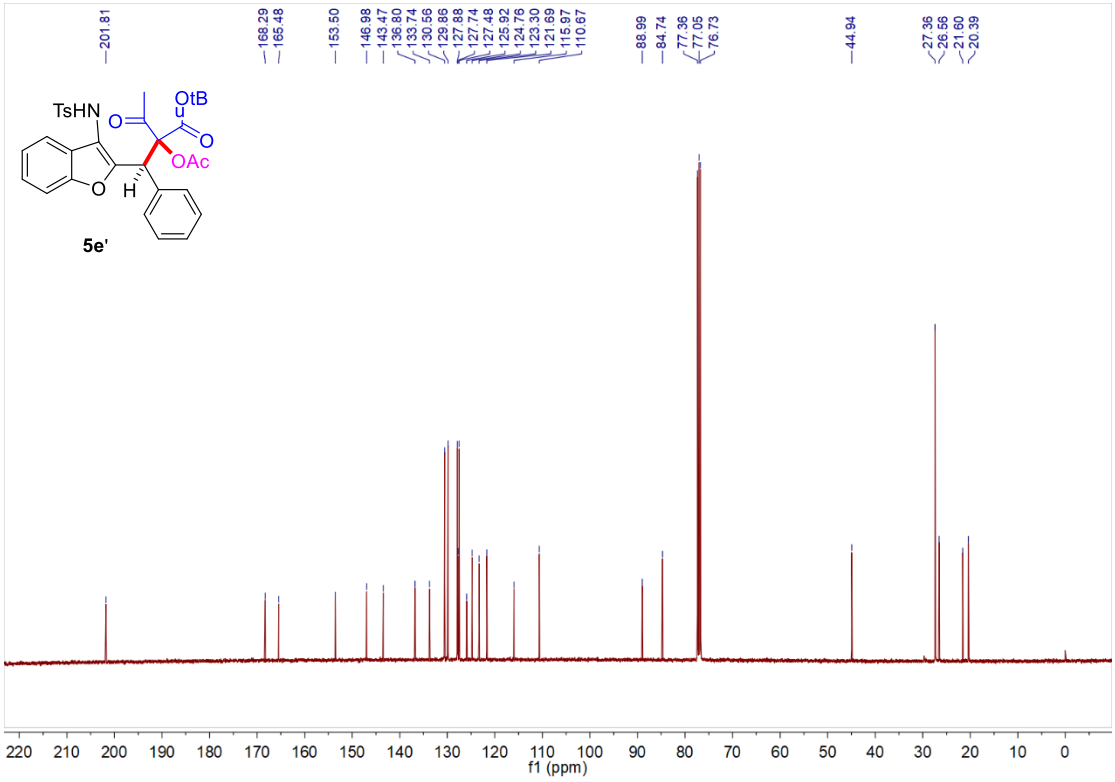
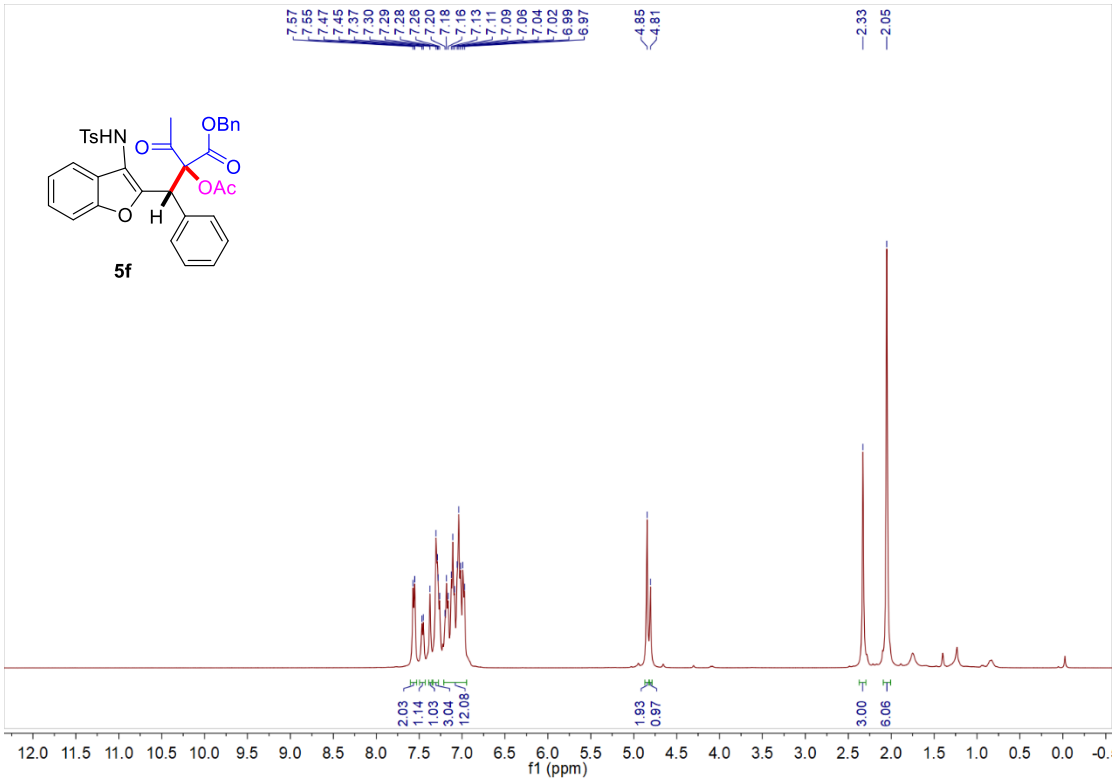
7.58
7.57
7.56
7.27
7.26
7.25
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.15
7.15
7.14
7.13
7.13
6.97
6.97
6.97
6.95
6.95
4.80
2.44
2.12
2.11
1.13
2.01
0.95
1.00
1.13
7.11
2.00
1.00
3.00
6.09
9.04
f1 (ppm)


TsHN
O
OtBu
O
OAc
O
H
5e
199.34
169.29
163.75
153.47
147.71
143.61
137.09
134.31
130.27
129.82
127.95
127.82
127.61
125.72
124.80
123.23
121.07
115.78
110.74
89.60
84.34
77.37
77.06
76.74
44.39
27.12
25.84
21.60
20.43
f1 (ppm)


TsHN
OtBu
OAc
5e'
f1 (ppm)


TsHN
OtBu
OAc
5e'
f1 (ppm)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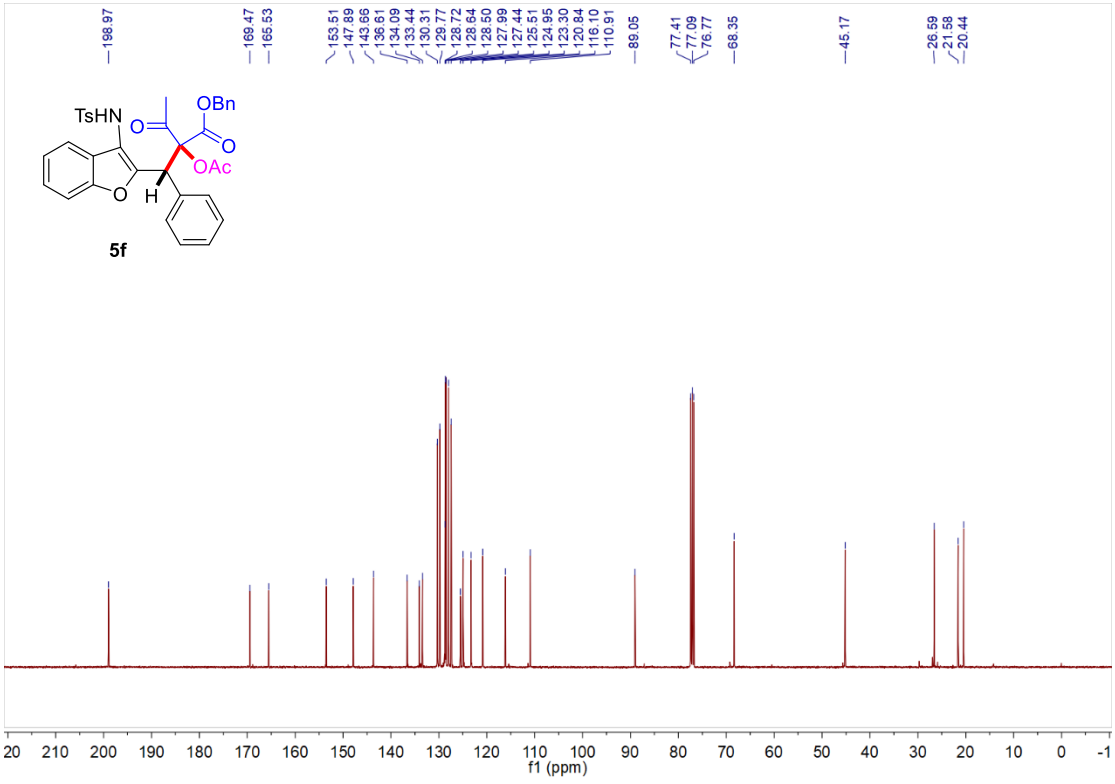
7.55
7.47
7.45
7.37
7.30
7.29
7.28
7.26
7.20
7.18
7.16
7.13
7.11
7.09
7.06
7.04
7.02
6.99
6.97
4.85
4.81
2.33
2.05
TsHN
O
OBn
O
OAc
O
H
5f
2.03
1.14
1.03
3.04
12.08
1.93
0.97
3.00
6.06
f1 (ppm)


198.97
169.47
165.53
153.51
147.89
143.66
136.61
134.09
133.44
130.31
129.77
128.72
128.64
128.50
127.99
127.44
125.51
124.95
123.30
120.84
116.10
110.91
89.05
77.41
77.09
76.77
68.35
45.17
26.59
21.58
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TsHN
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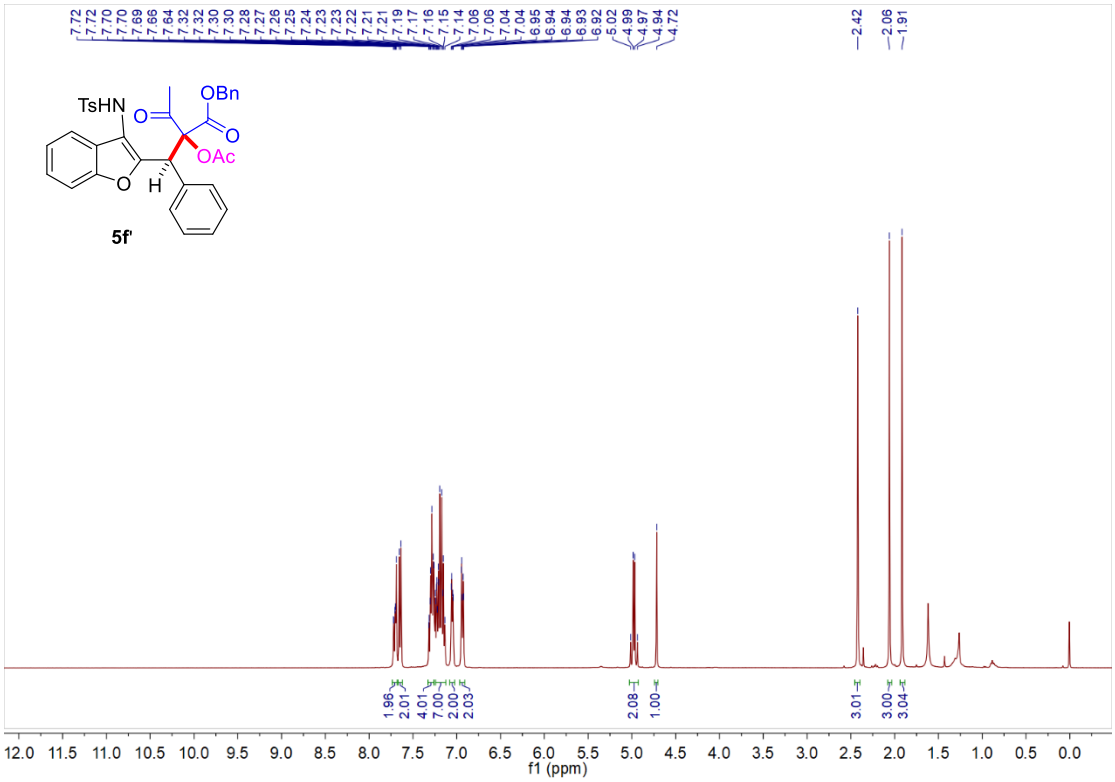
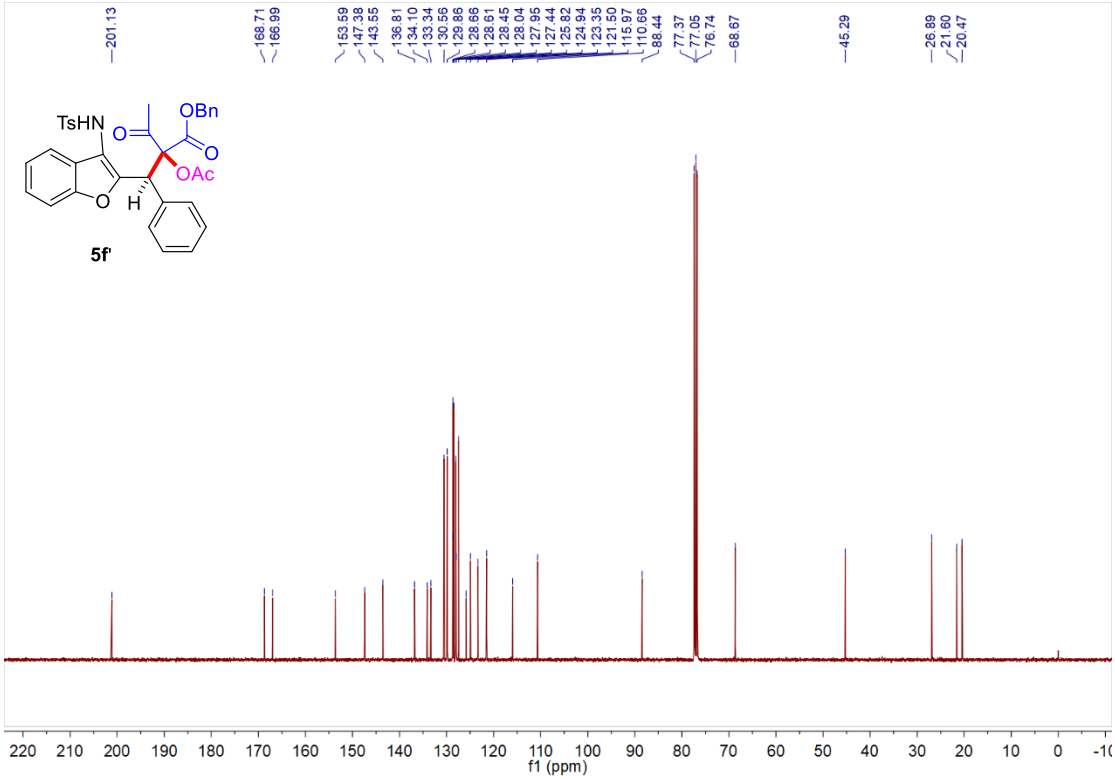
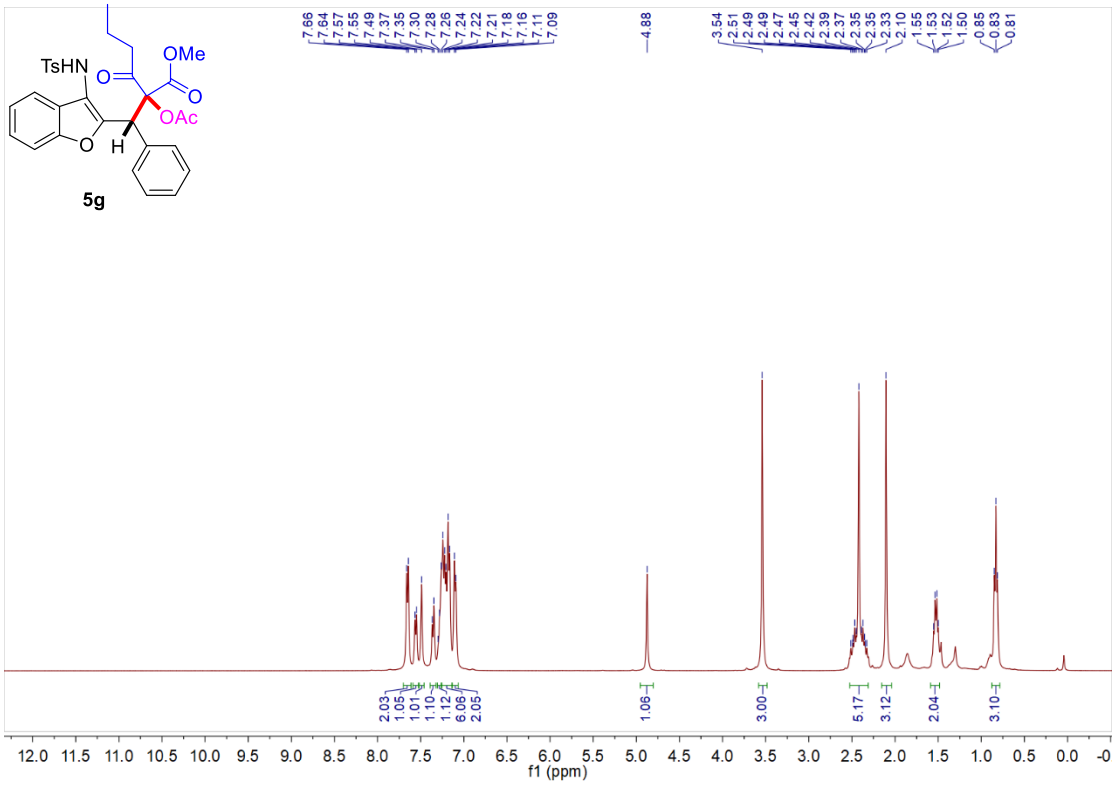
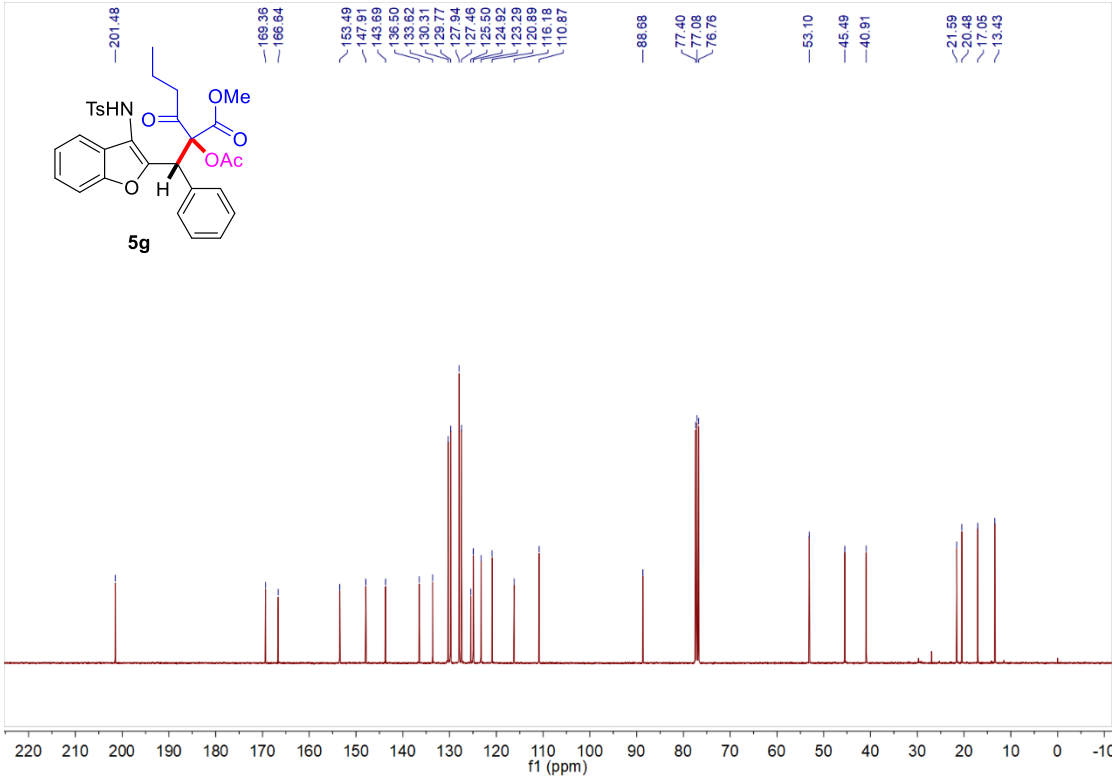
OBn
O
OAc
O
H
5f
f1 (ppm)


TsHN
OBn
OAc
5f'
f1 (ppm)


TsHN
OBn
OAc
5f'
f1 (ppm)


TsHN
O
OMe
O
OAc
O
H
5g
7.66
7.64
7.57
7.55
7.49
7.37
7.35
7.30
7.28
7.26
7.24
7.22
7.21
7.18
7.16
7.11
7.09
4.88
3.54
2.51
2.49
2.49
2.47
2.45
2.42
2.39
2.37
2.35
2.35
2.33
2.10
1.55
1.53
1.52
1.50
0.85
0.83
0.81
2.03
1.05
1.01
1.10
1.12
6.06
2.05
1.06
3.00
5.17
3.12
2.04
3.10
f1 (ppm)


TsHN
O
OMe
O
OAc
O
H
5g
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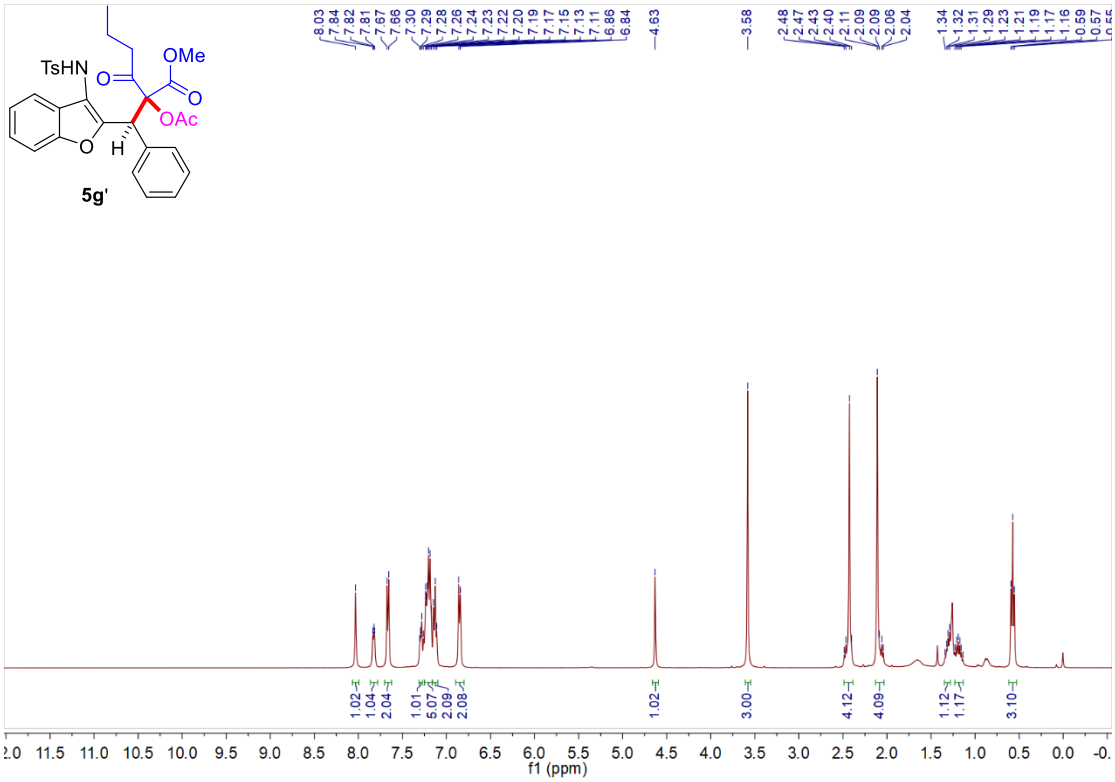
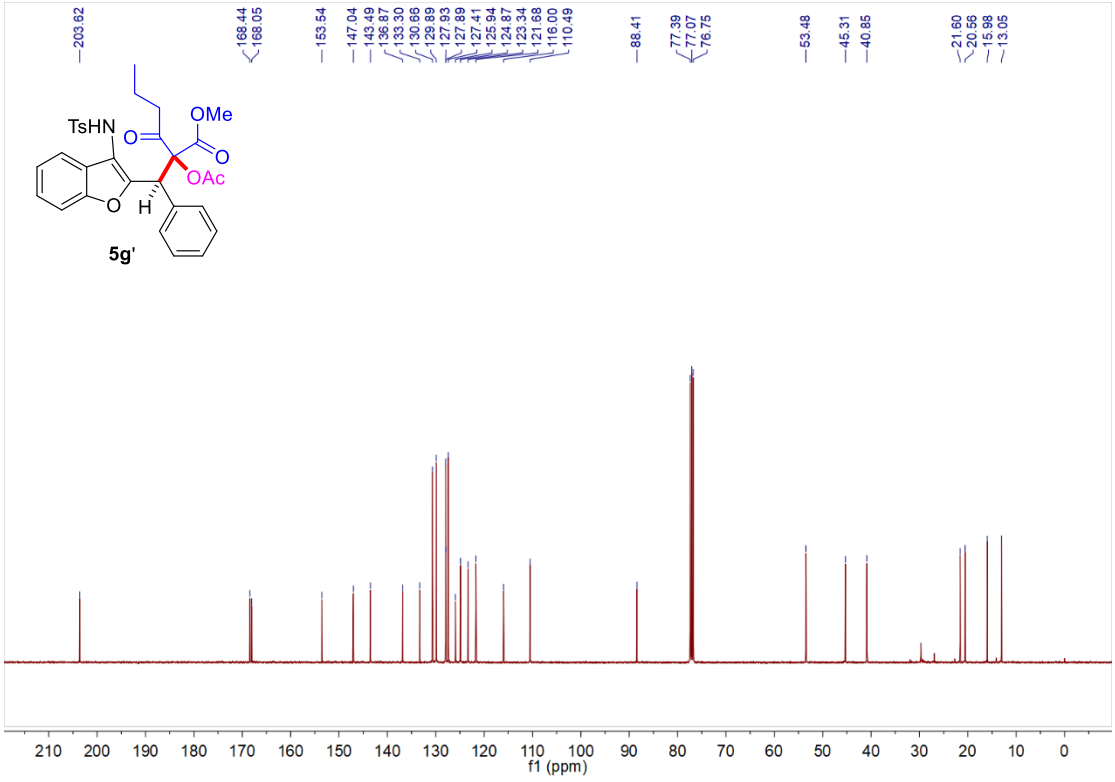
169.36
166.64
153.49
147.91
143.69
136.50
133.62
130.31
129.77
127.94
127.46
125.50
124.92
123.29
120.89
116.18
110.87
88.68
77.40
77.08
76.76
53.10
45.49
40.91
21.59
20.48
17.05
13.43
f1 (ppm)


TsHN
O
OMe
O
OAc
O
H
5g'
8.03
7.84
7.82
7.81
7.67
7.66
7.30
7.29
7.28
7.26
7.24
7.23
7.22
7.20
7.19
7.17
7.15
7.13
7.11
6.86
6.84
4.63
3.58
2.48
2.47
2.43
2.40
2.11
2.09
2.09
2.06
2.04
1.34
1.32
1.31
1.29
1.23
1.21
1.19
1.17
1.16
1.02
1.04
2.04
1.01
5.07
2.09
2.08
1.02
3.00
4.12
4.09
1.12
1.17
3.10
f1 (ppm)


TsHN
O
OMe
O
OAc
O
H
5g'
203.62
168.44
168.05
153.54
147.04
143.49
136.87
133.30
130.66
129.89
127.93
127.89
127.41
125.94
124.87
123.34
121.68
116.00
110.49
88.41
77.39
77.07
76.75
53.48
45.31
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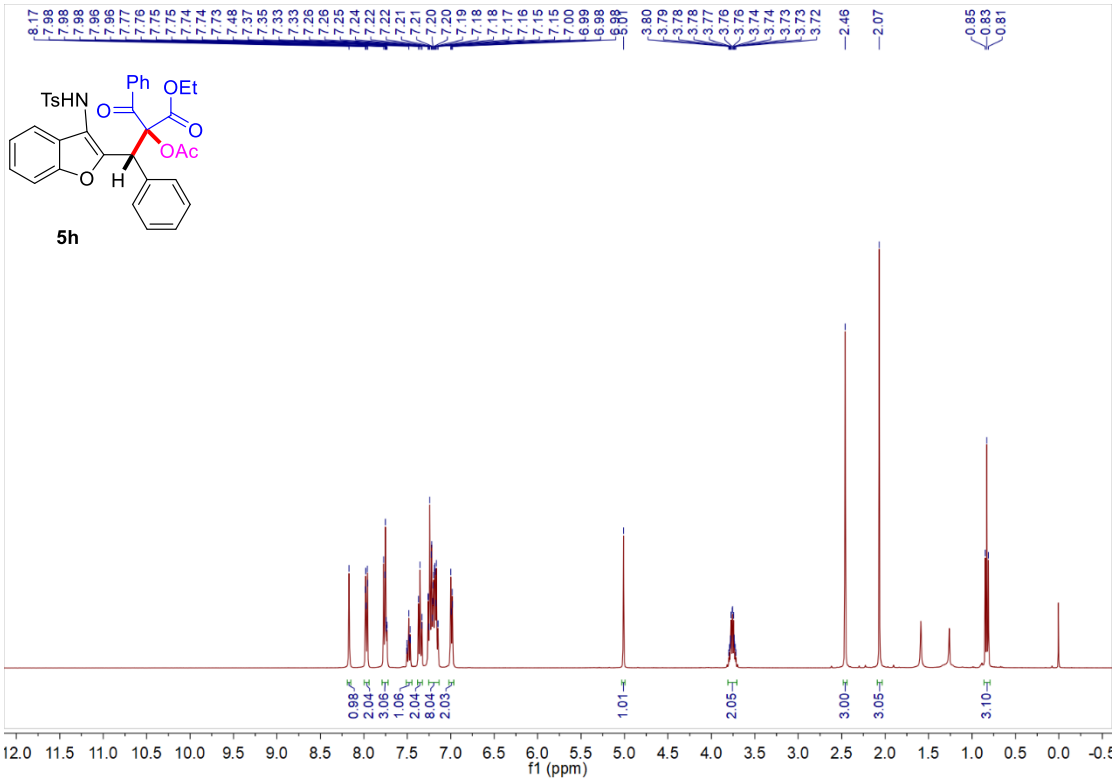
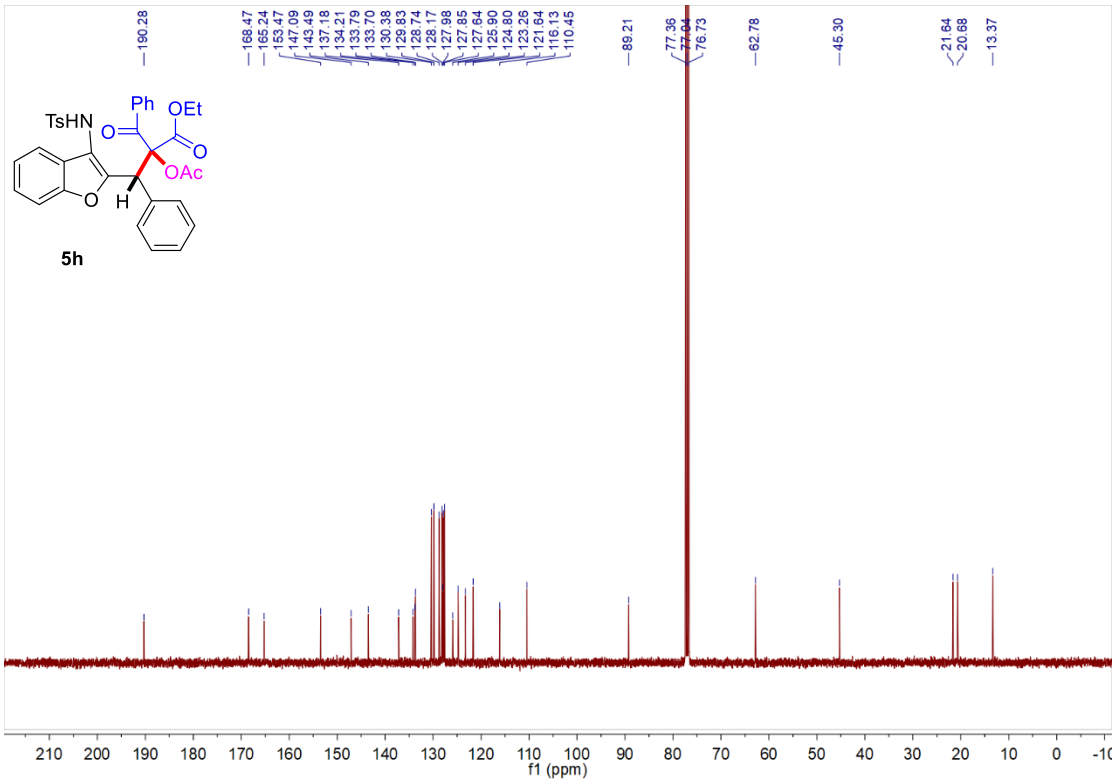
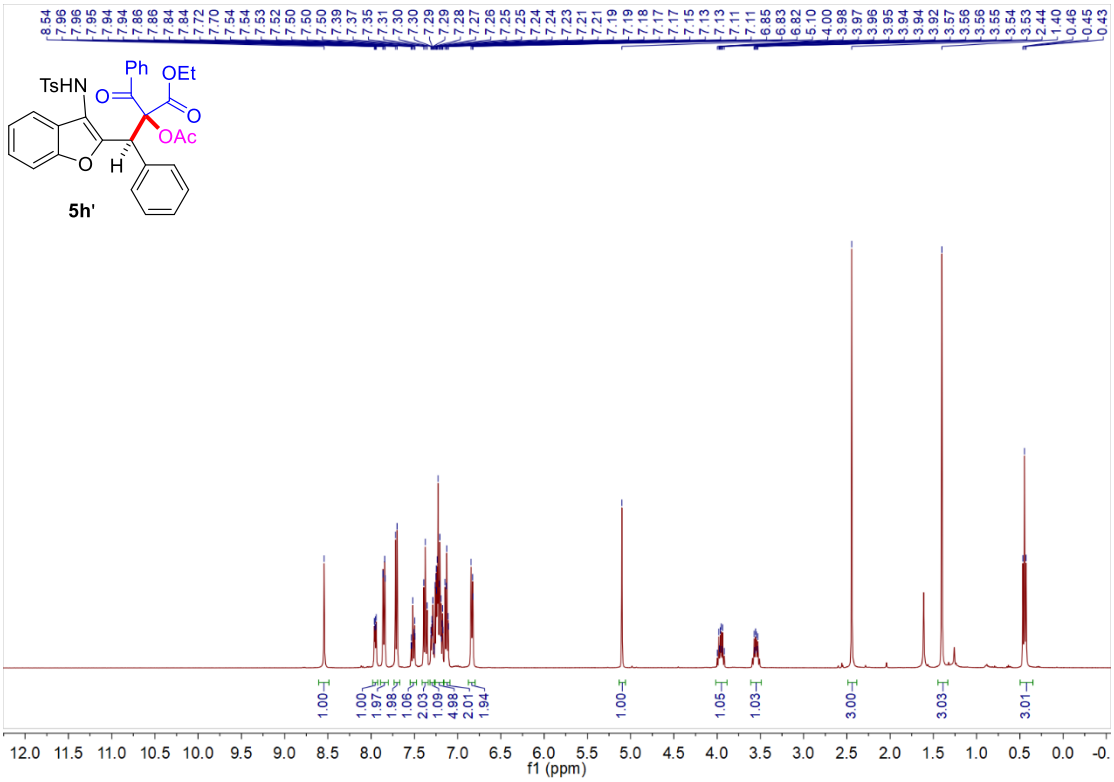
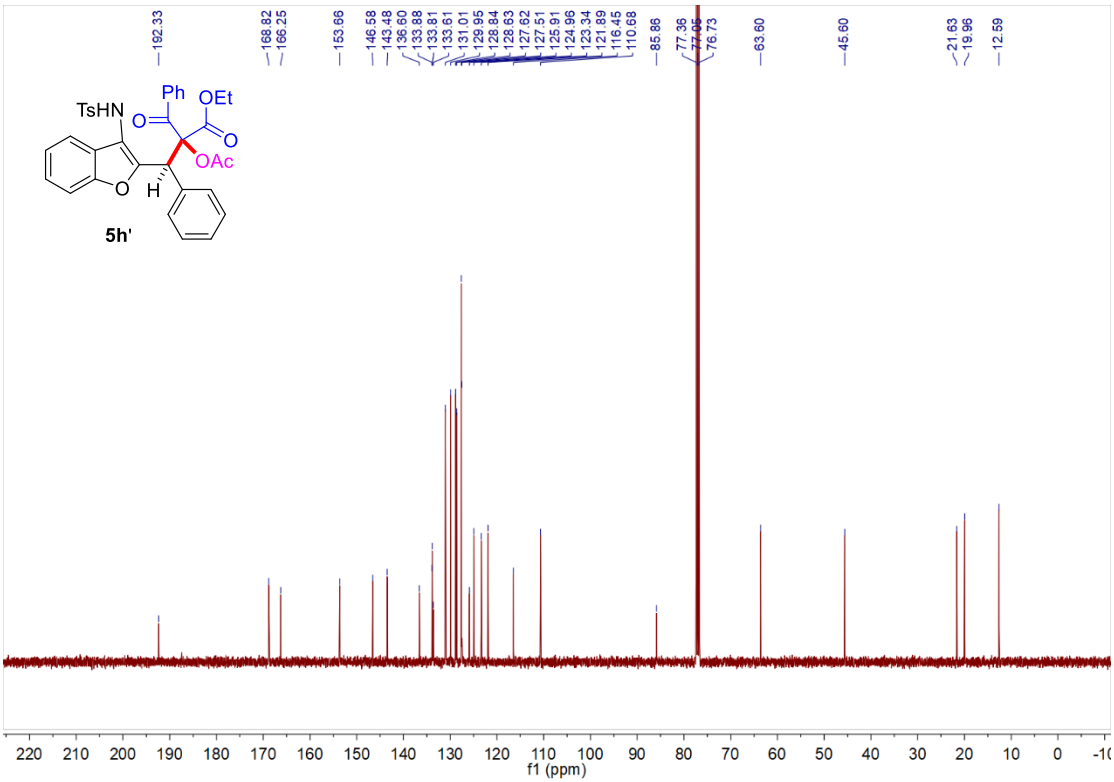
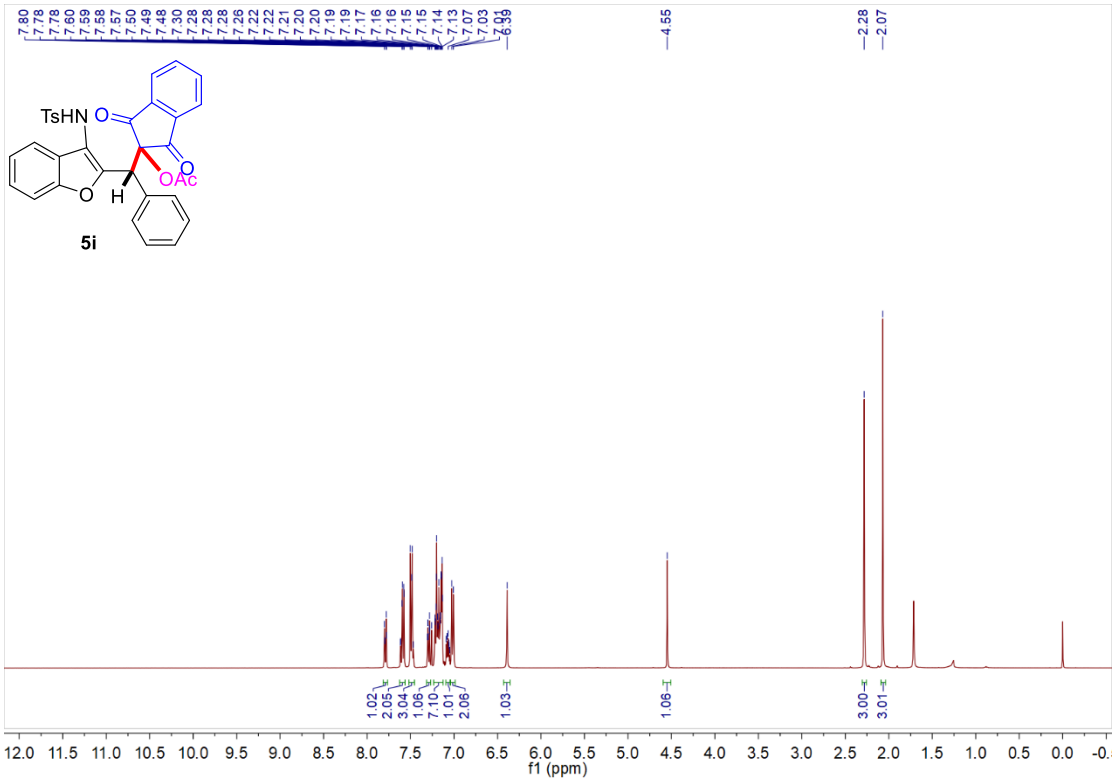
21.60
20.56
15.98
13.05
f1 (ppm)

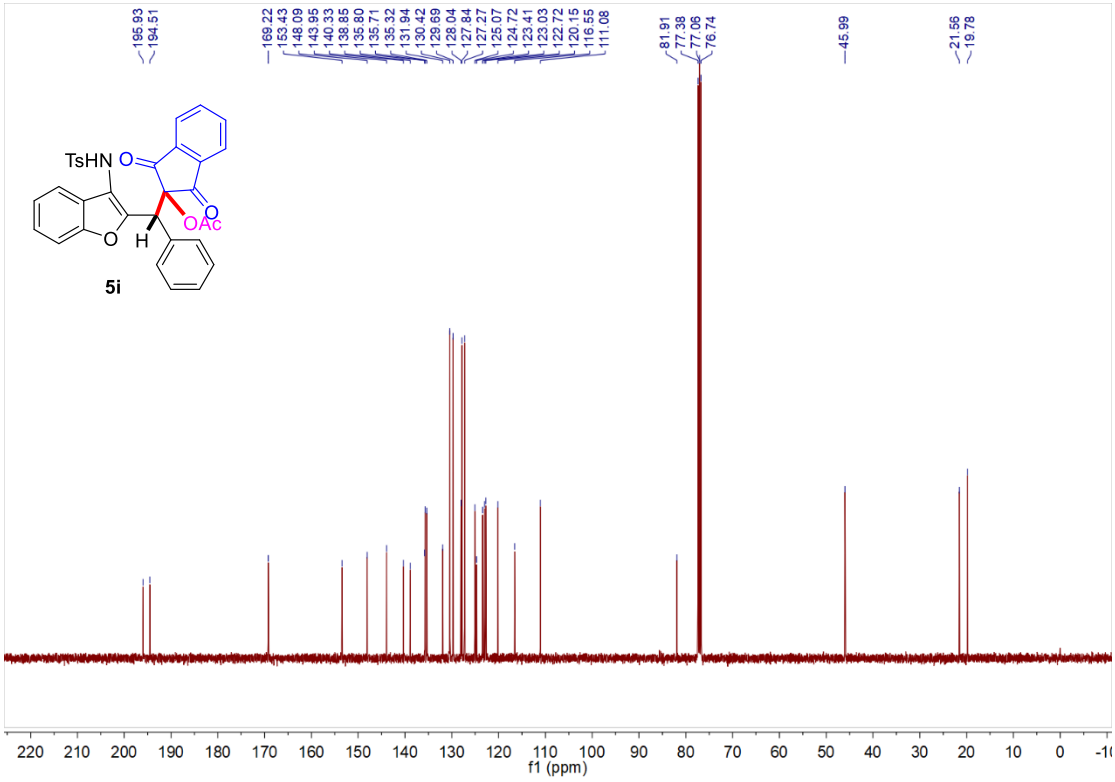

TsHN
Ph
OEt
O
O
OAc
O
H
5h
f1 (ppm)

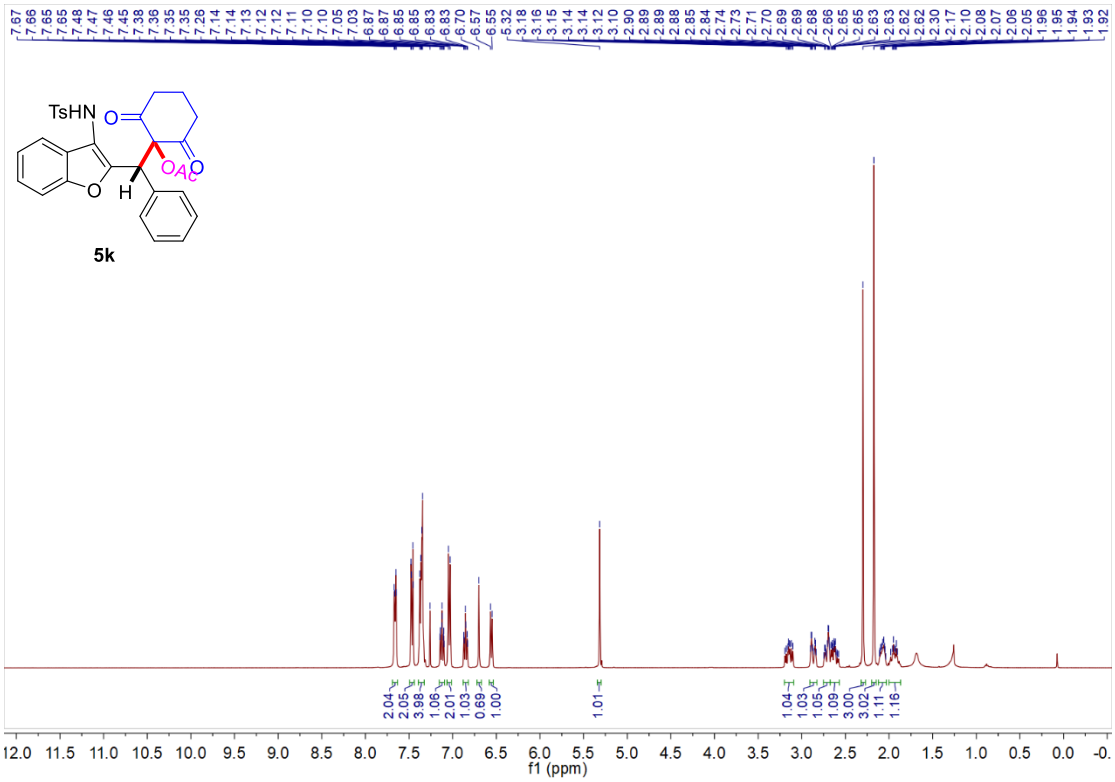

TsHN
Ph
OEt
O
O
OAc
O
H
5h
f1 (ppm)


TsHN
Ph
OEt
O
O
OAc
O
H
5h'
f1 (ppm)


TsHN
Ph
OEt
O
O
OAc
O
H
5h'
f1 (ppm)


TsHN
O
O
OAc
H
O
5i
f1 (ppm)


TsHN
O
O
OAc
H
O
5i
f1 (ppm)


TsHN
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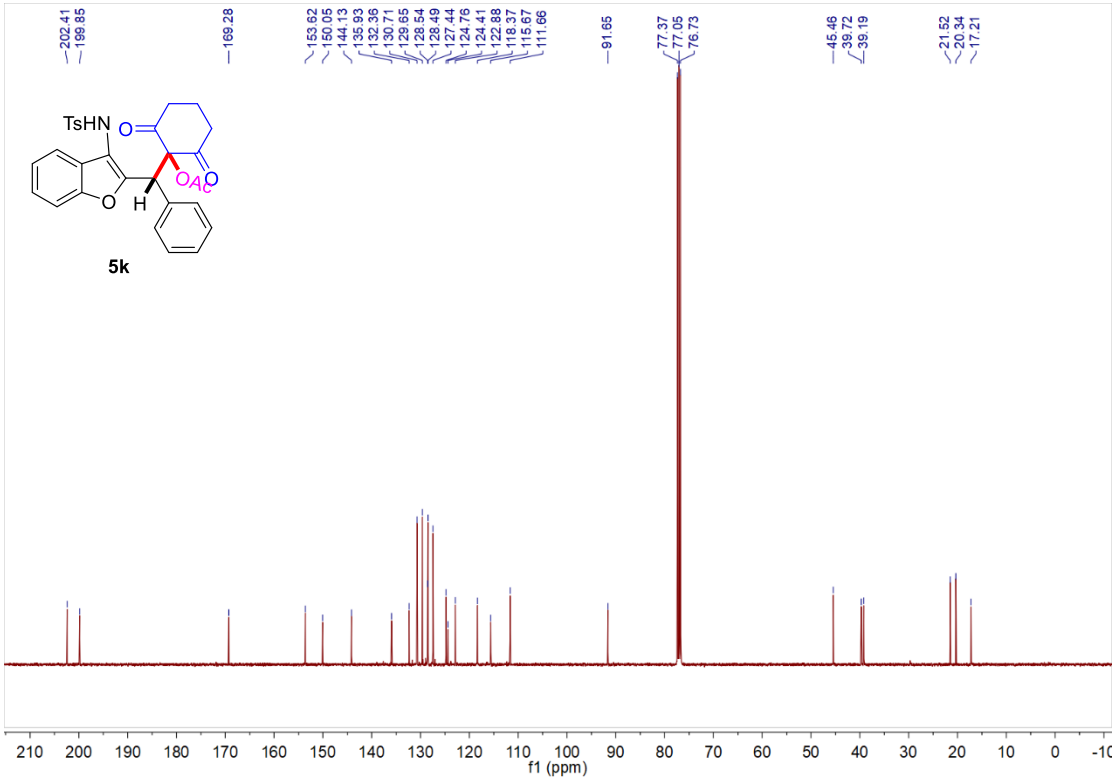
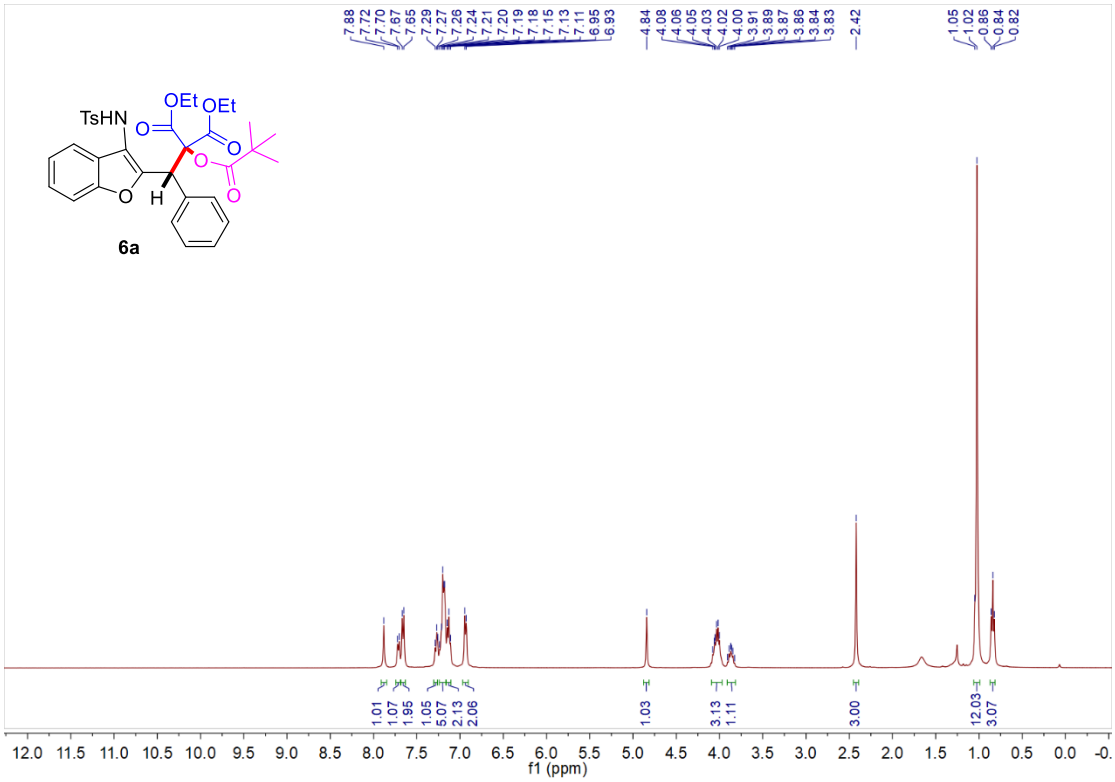
OAc
O
H
O
5k
f1 (ppm)


TsHN
O
OAc
O
H
O
5k
f1 (ppm)


7.88
7.72
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7.67
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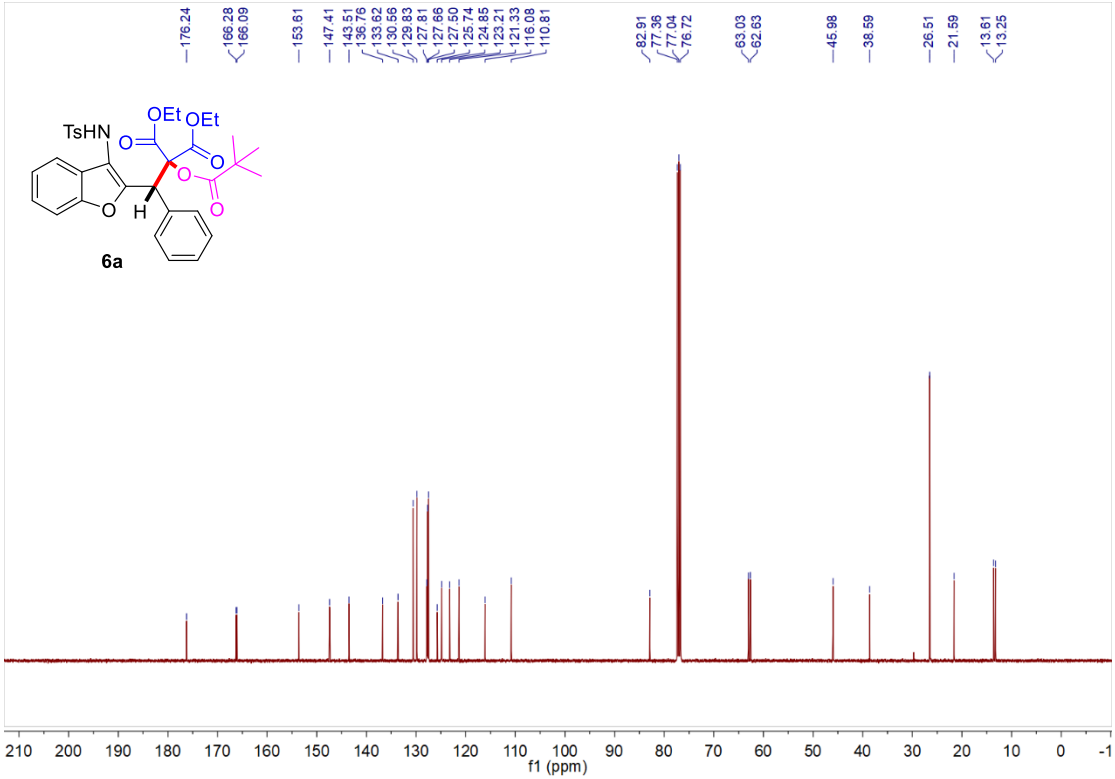
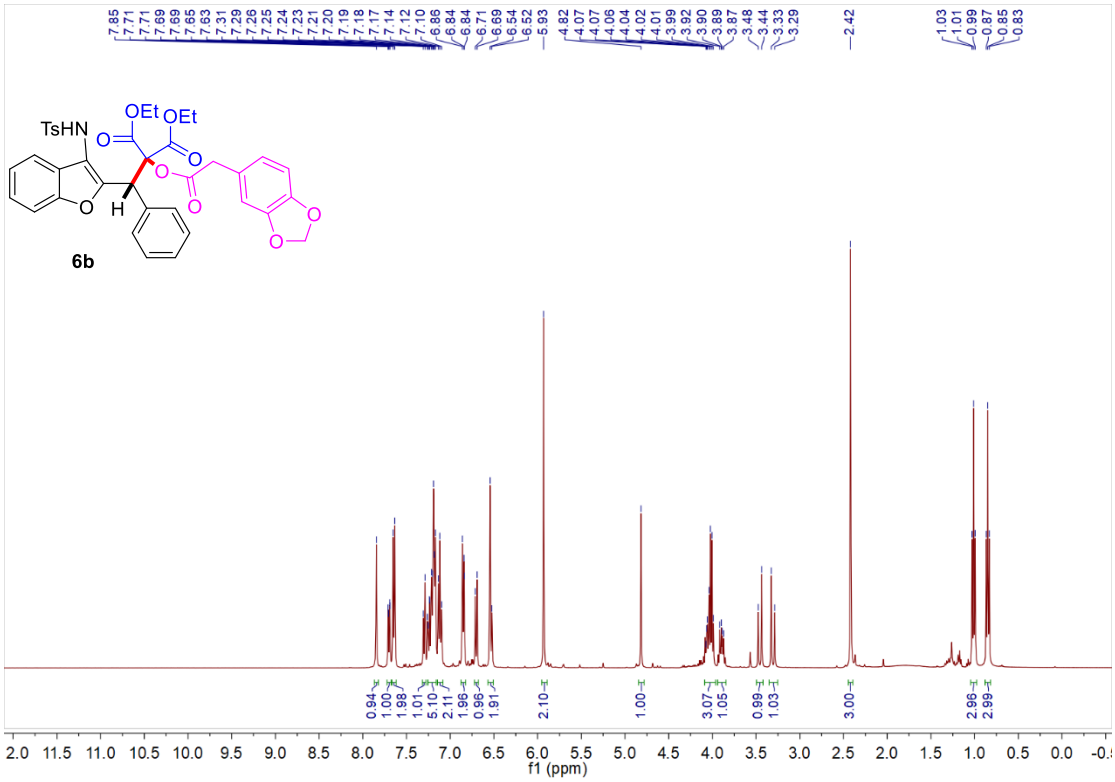
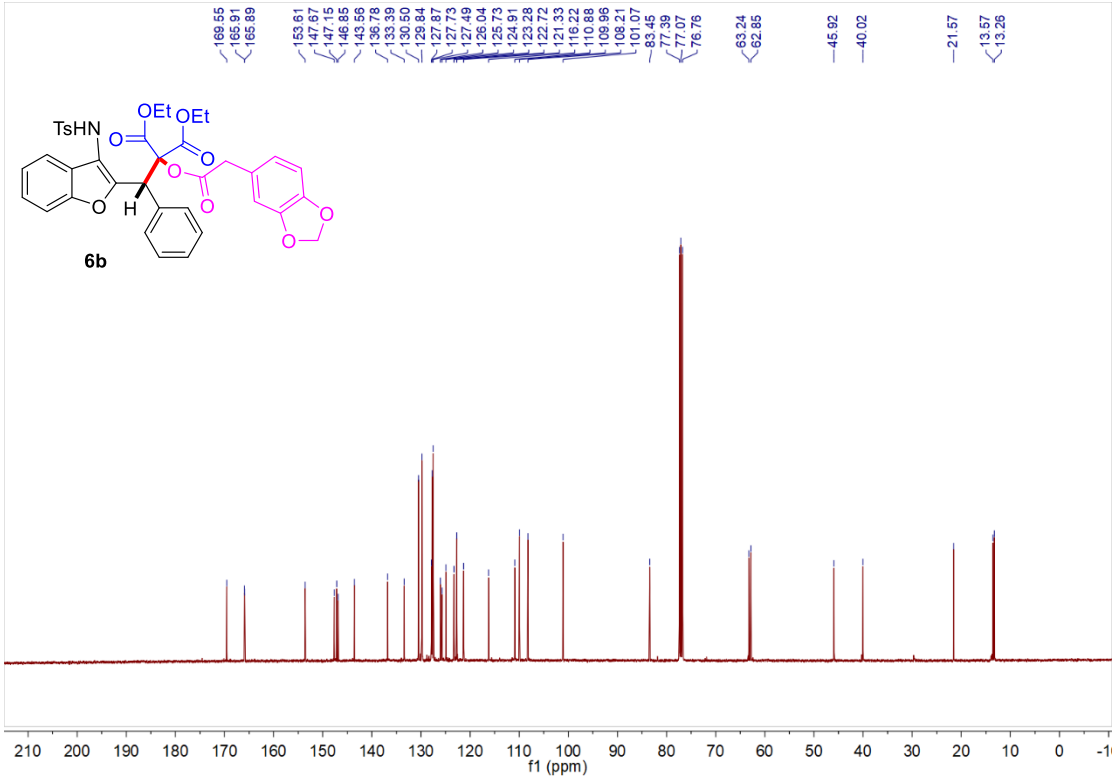
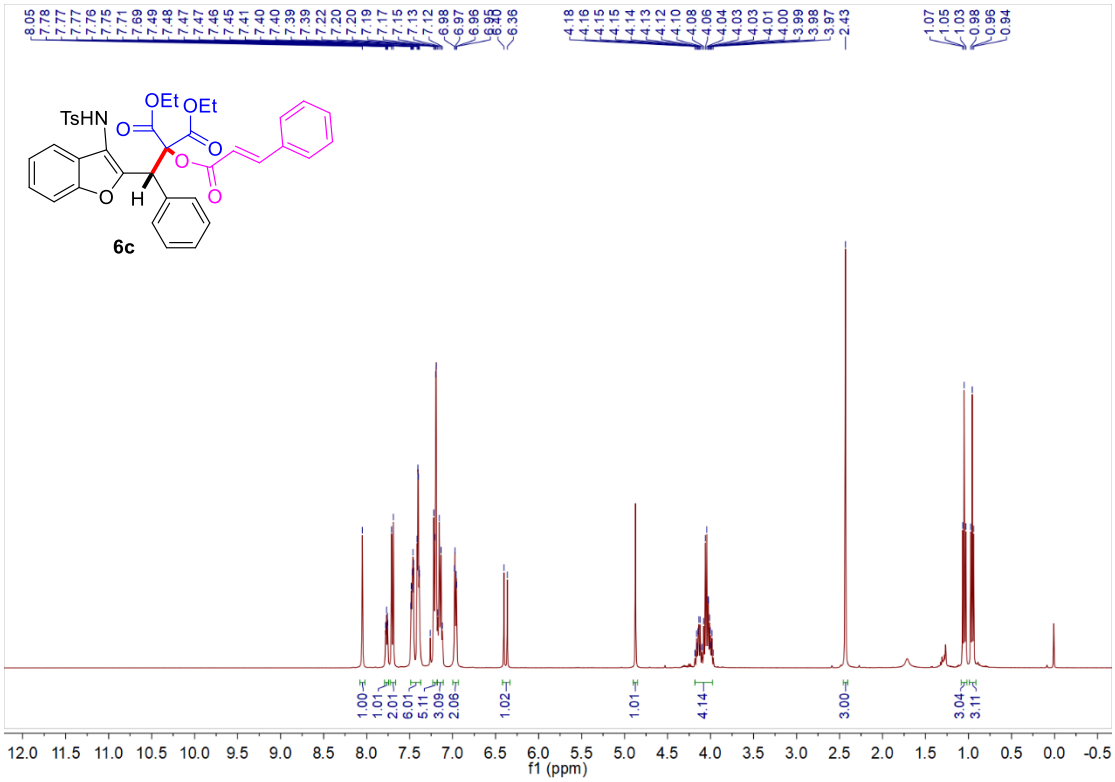
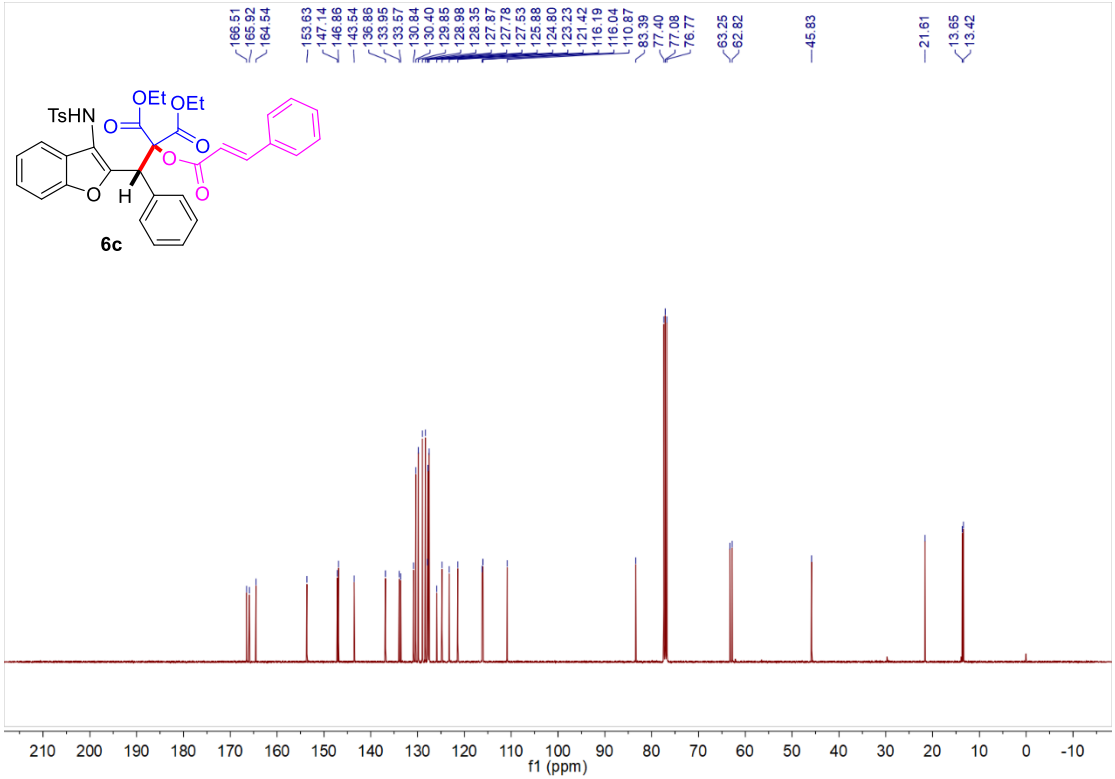
7.27
7.26
7.24
7.21
7.20
7.19
7.18
7.15
7.13
7.11
6.95
6.93
4.84
4.08
4.06
4.05
4.03
4.02
4.00
3.91
3.89
3.87
3.86
3.84
3.83
2.42
1.05
1.02
0.86
0.84
0.82
TsHN
OEt
OEt
O
O
O
O
O
H
6a
1.01
1.07
1.95
1.05
5.07
2.13
2.06
1.03
3.13
1.11
3.00
12.03
3.07
f1 (ppm)

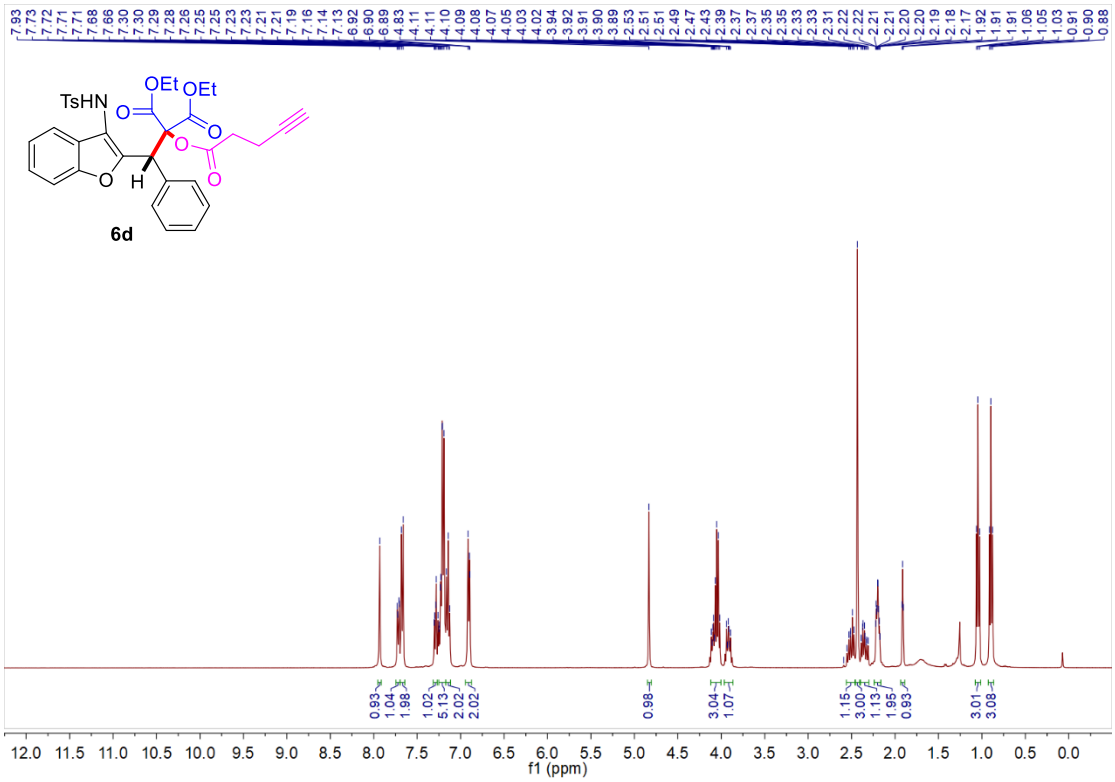

176.24
166.28
166.09
153.61
147.41
143.51
136.76
133.62
130.56
129.83
127.81
127.66
127.50
125.74
124.85
123.21
121.33
116.08
110.81
82.91
77.36
77.04
76.72
63.03
62.63
45.98
38.59
26.51
21.59
13.61
13.25
TsHN
OEt
OEt
O
O
O
O
O
H
6a
f1 (ppm)

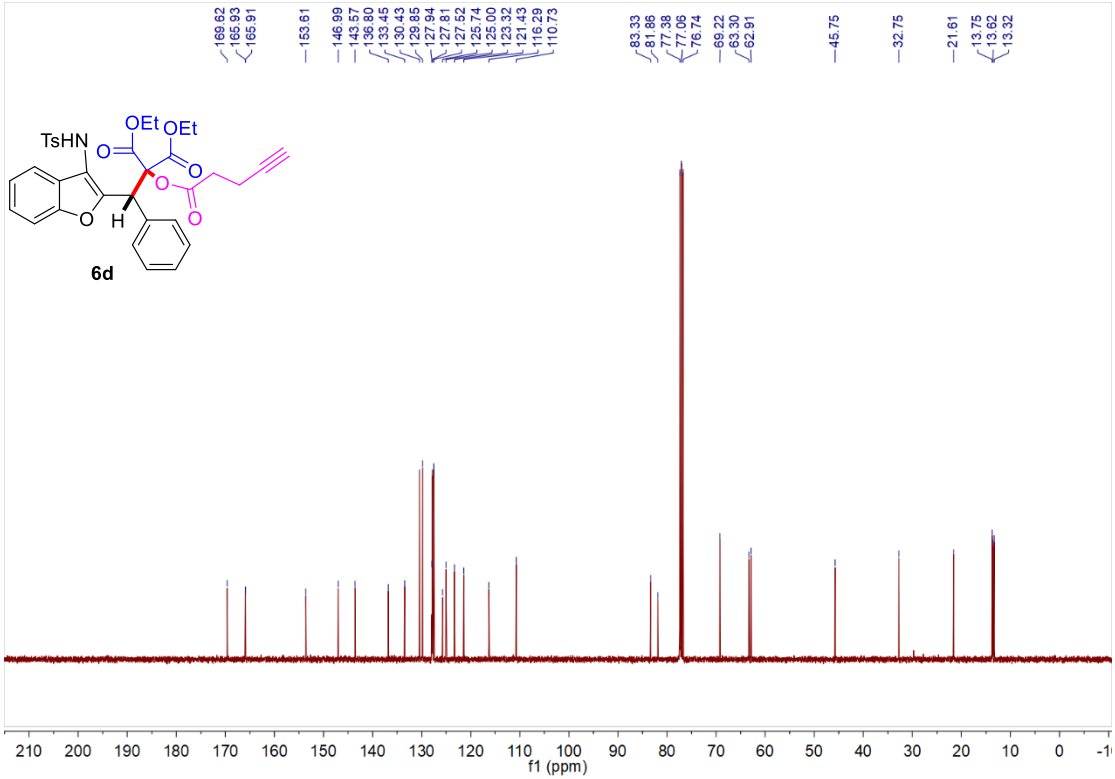

TsHN
OEt
OEt
O
O
O
O
O
O
O
H
6b
f1 (ppm)

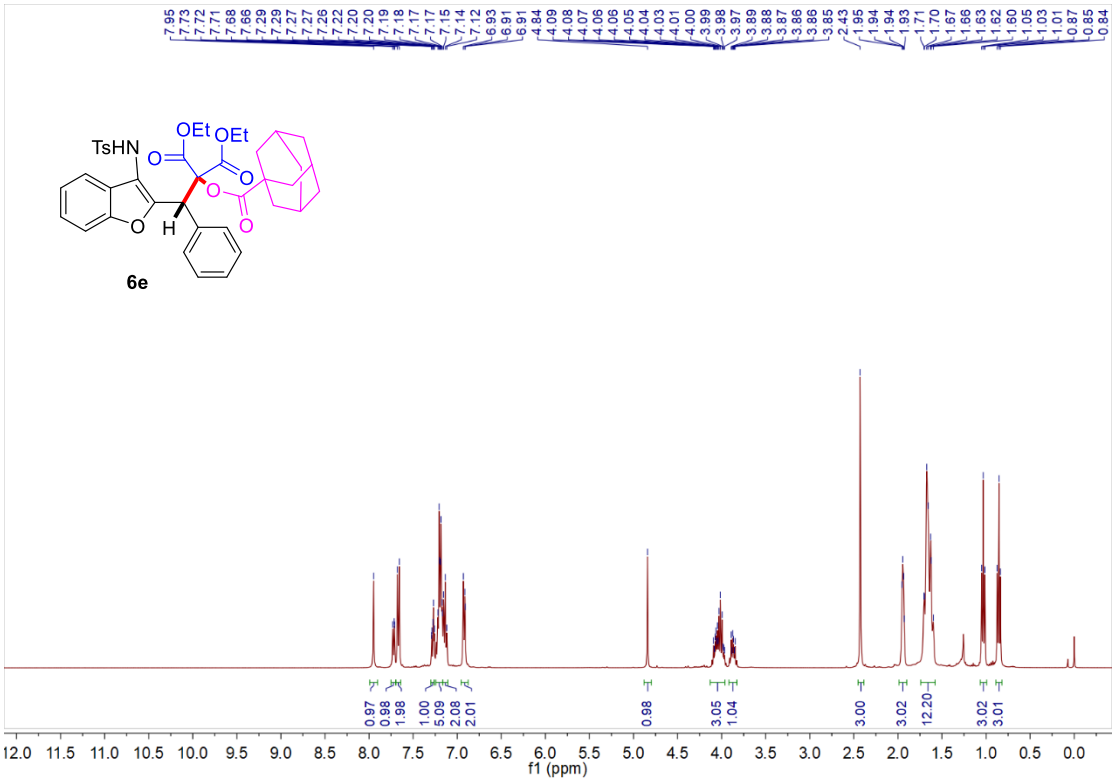

TsHN
OEt
OEt
O
O
O
O
O
O
O
H
6b
f1 (ppm)

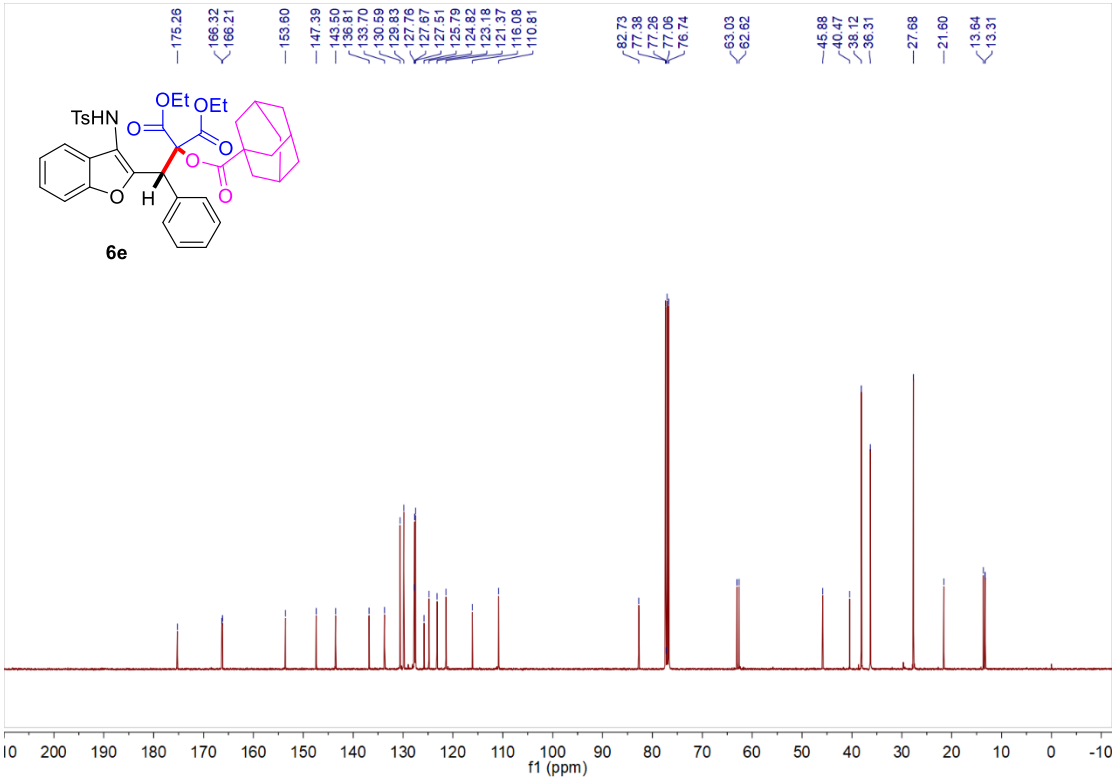

TsHN
OEt
OEt
O
O
O
O
O
H
6c
f1 (ppm)

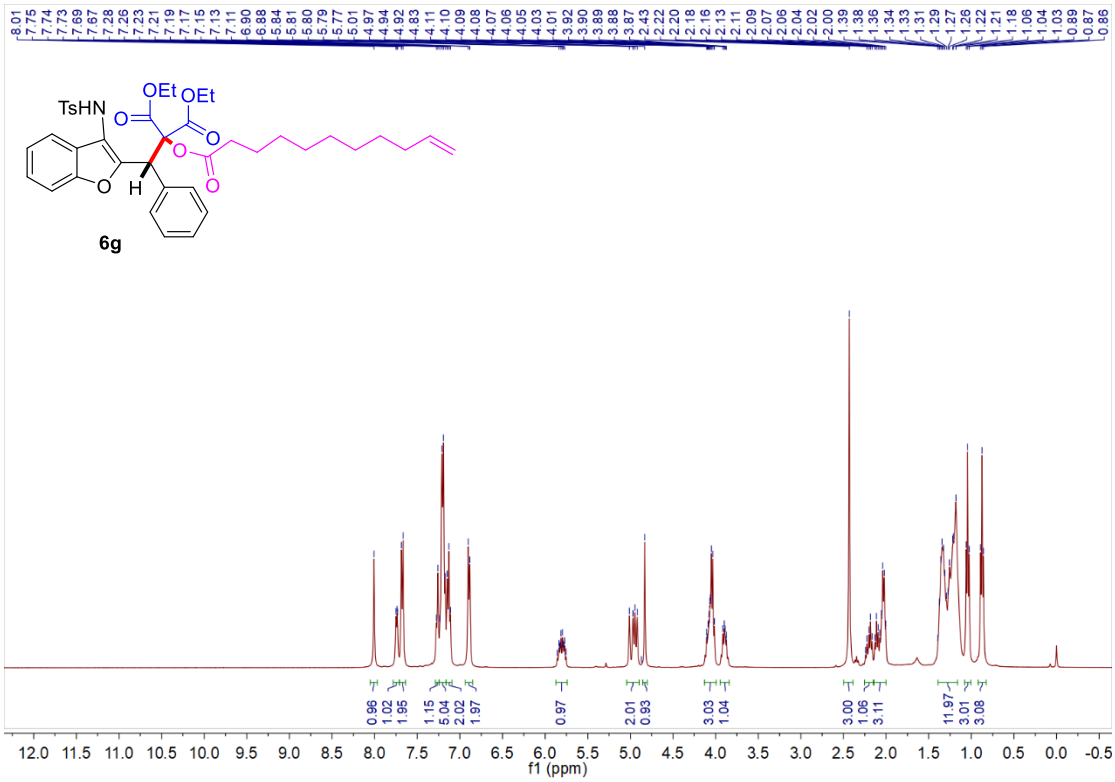

TsHN
OEt
OEt
O
O
O
O
O
H
6c
f1 (ppm)

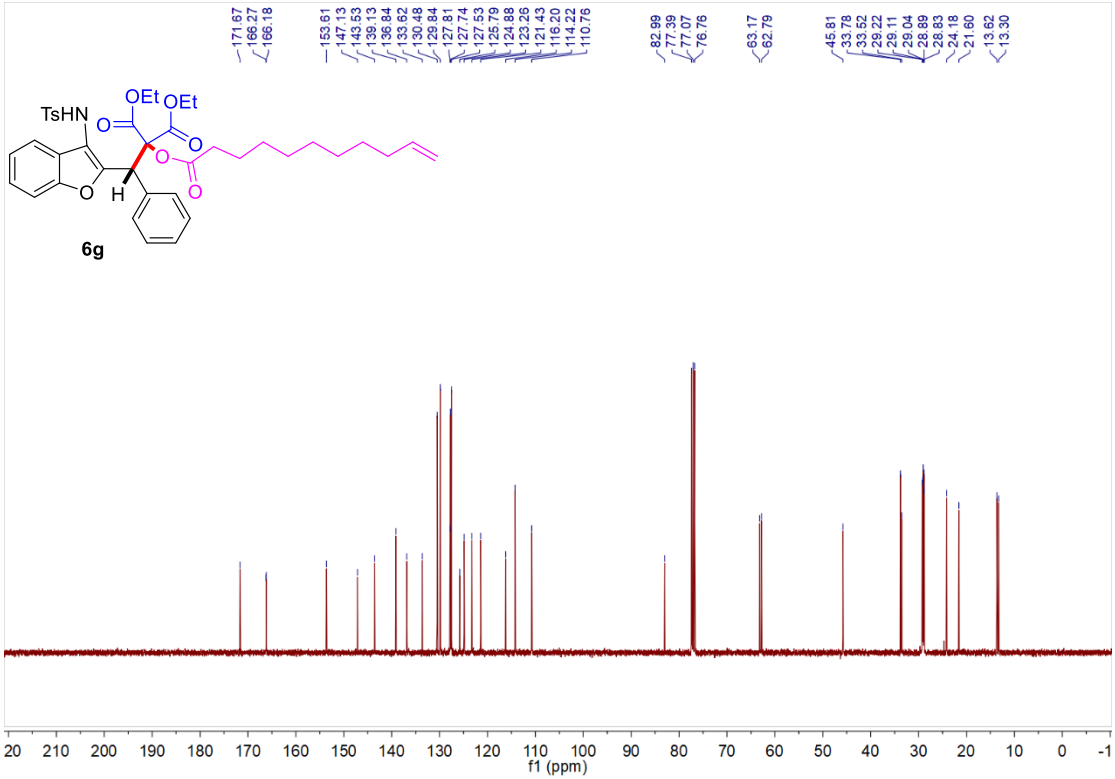

TsHN
OEt
OEt
O
O
O
O
O
H
6d
f1 (ppm)

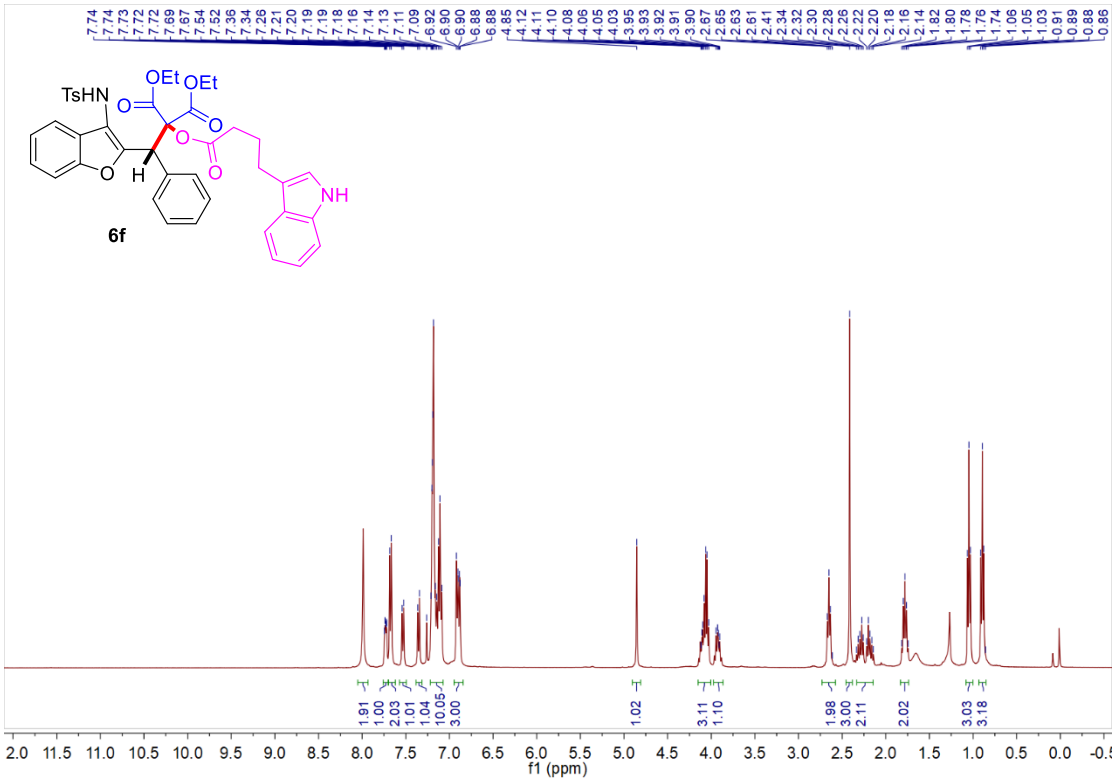

TsHN
OEt
OEt
O
O
O
O
O
H
6d
f1 (ppm)

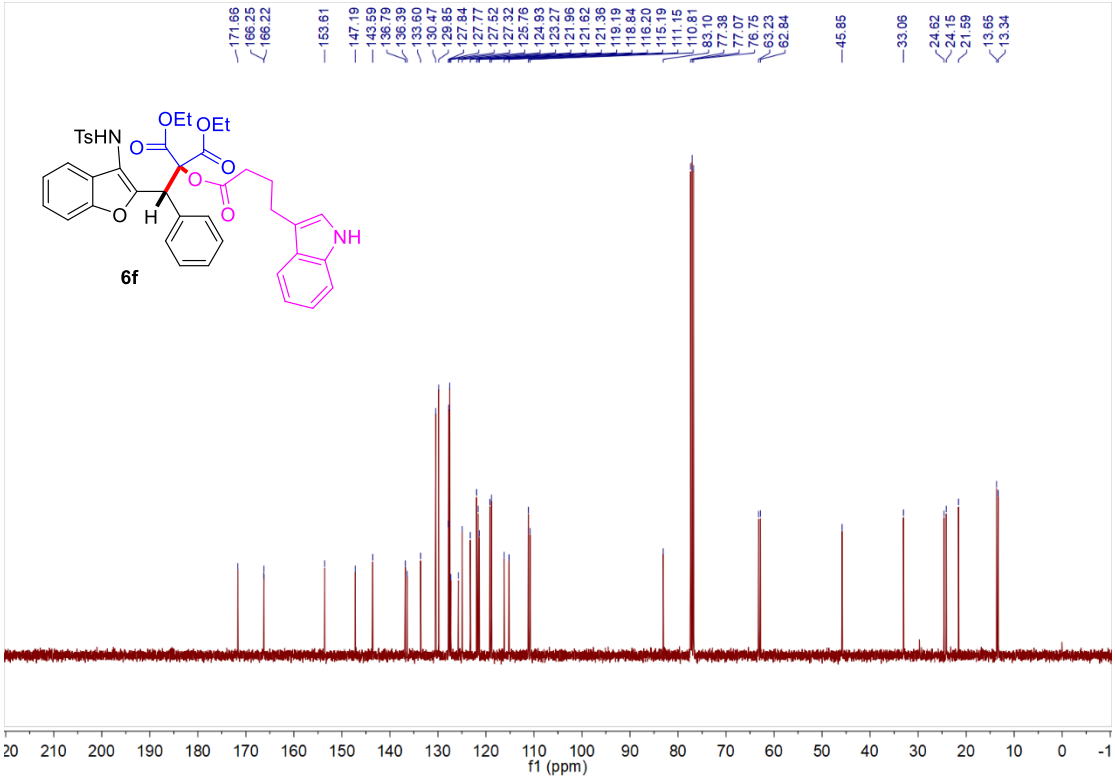

TsHN
OEt
OEt
O
O
O
O
O
H
6e
f1 (ppm)

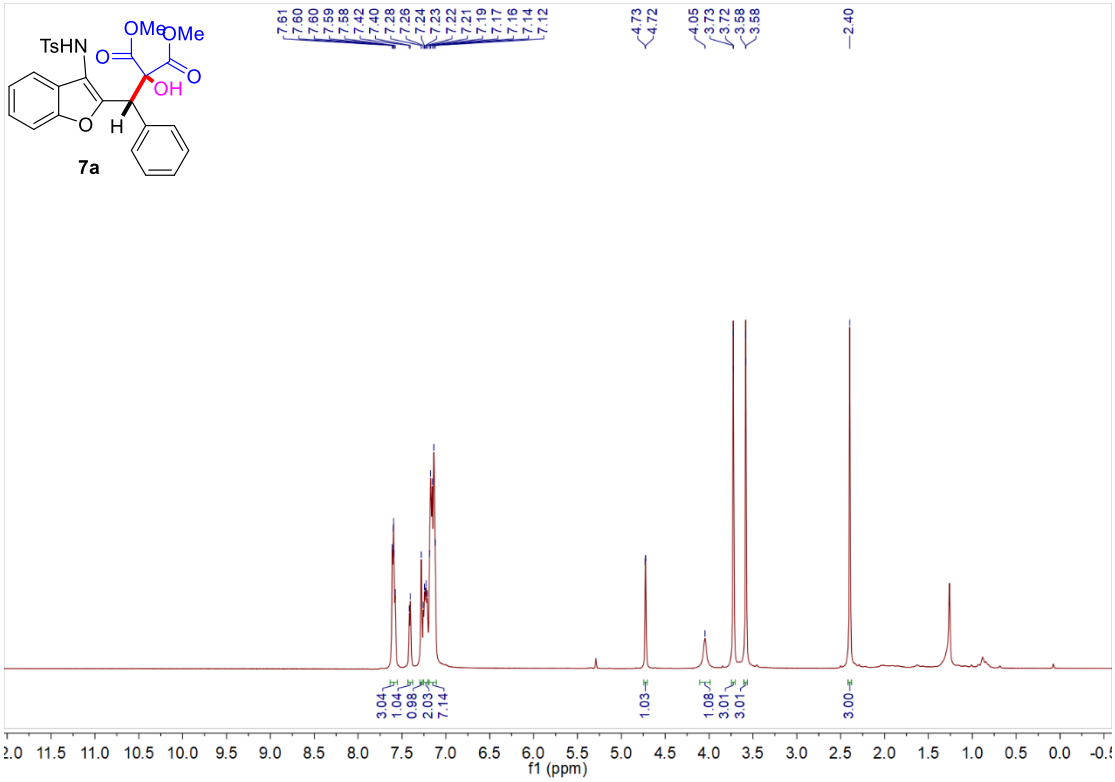

TsHN
OEt
OEt
O
O
O
O
O
H
6e
f1 (ppm)

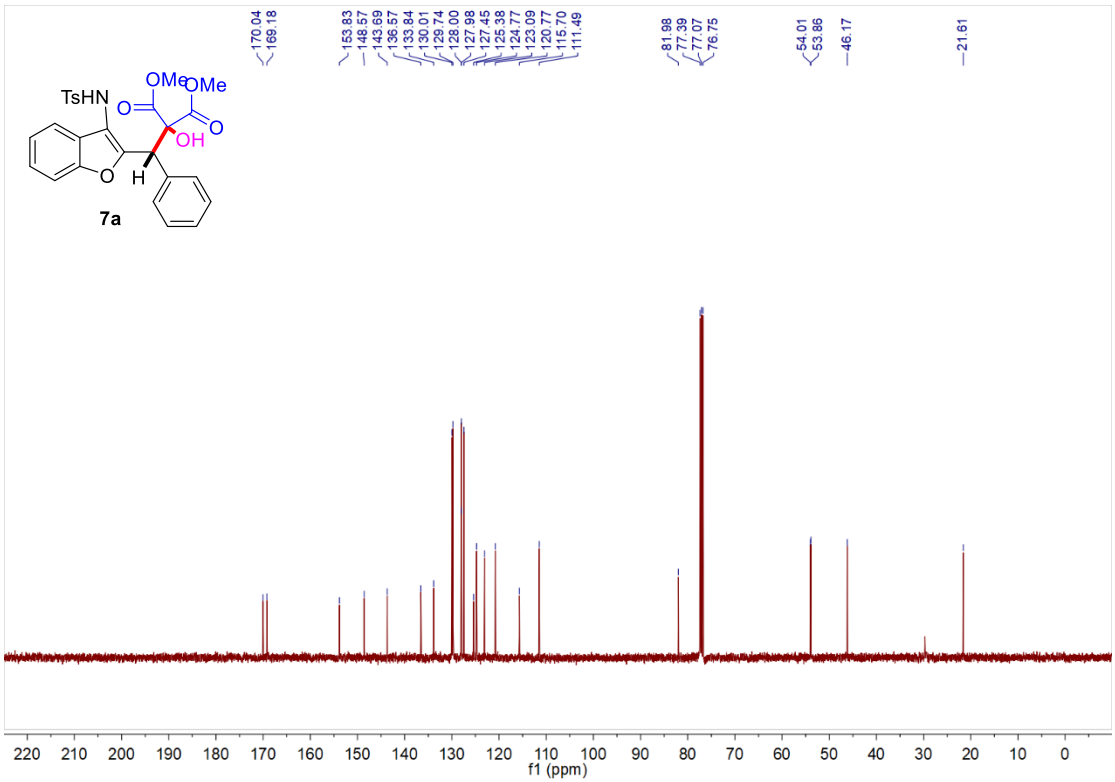

TsHN
OEt
OEt
O
O
O
O
O
H
6g
f1 (ppm)


TsHN
OEt
OEt
O
O
O
O
O
H
6g
f1 (ppm)


TsHN
OEt
OEt
O
O
O
O
O
H
NH
6f
f1 (ppm)


TsHN
OEt
OEt
O
O
O
O
O
H
NH
6f
f1 (ppm)


TsHN
OMe
OMe
O
O
OH
O
H
7a
7.61
7.60
7.60
7.59
7.58
7.42
7.40
7.28
7.26
7.24
7.23
7.22
7.21
7.19
7.17
7.16
7.14
7.12
4.73
4.72
4.05
3.73
3.72
3.58
3.58
2.40
3.04
1.04
0.98
2.03
7.14
1.03
1.08
3.01
3.01
3.00
f1 (ppm)


TsHN
OMe
OMe
O
O
OH
O
H
7a
170.04
169.18
153.83
148.57
143.69
136.57
133.84
130.01
129.74
128.00
127.98
127.45
125.38
124.77
123.09
120.77
115.70
111.49
81.98
77.39
77.07
76.75
54.01
53.86
46.17
21.61
f1 (ppm)