Electronic Supporting Information

Base-free regio- and stereoselective photochemical synthesis of enol ethers from 1,3-dicarbonyl compounds

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General Information:

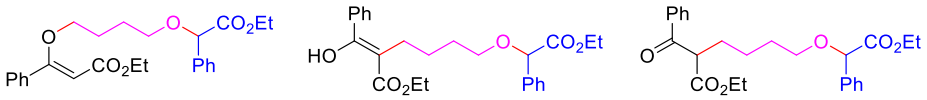
All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 300–400 meshes. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C in $CDCl_3$; 2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C in d_6-DMSO, 3.31 ppm for ^{1}H and 49.0 ppm for ^{13}C in CD_3OD). The HRMS spectra were recorded on a Bruker MicroTOF Q II spectrometer.

The Reaction Equipment and Light Source

We use RLH-18 8-position photo reaction system, which manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor we used have equipped 8 bule light 10W LED. This blue light 10 WLED's energy peak wavelength is 455 nm, peak width at half-height is 25 nm, Iirradiance@10 W is 172 mW/cm^2. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2 cm. No filter between LED and test tube. We conducted the photoreaction in room temperature (about 20°C−30°C). In summer, we controlled the temperature of the reaction mixture to keep in about 25°C using low-temperature cycle.

Figure S1. The Reaction Equipment and Light Source (λ_{max} = 455 nm, $\Delta\lambda$ = 25 nm)

Confirm the Structure of 3aa, 3aa', or 3aa''



3aa **3aa'** **3aa''**

There are two single peaks (5.52 ppm, 4.84 ppm) in the ^{1}H NMR, and the maximum chemical shift of carbon is less than 171 ppm. Because **3aa''** only includes one single peak in the ^{1}H NMR and carbonyl group in the ^{13}C NMR should be more than 190 ppm, **3aa''** should be excluded. In general, OH group chemical shift of **3aa'** should be more than 10 ppm owing to intramolecular hydrogen bond of 1,3-dicarbonyl compound. Additionally, HSQC Spectra (Figure S2) indicated that the two single peaks of hydrogen linked to carbon atoms. Therefore, **3aa'** should be excluded. Based on the above analysis, the structure should be **3aa**.

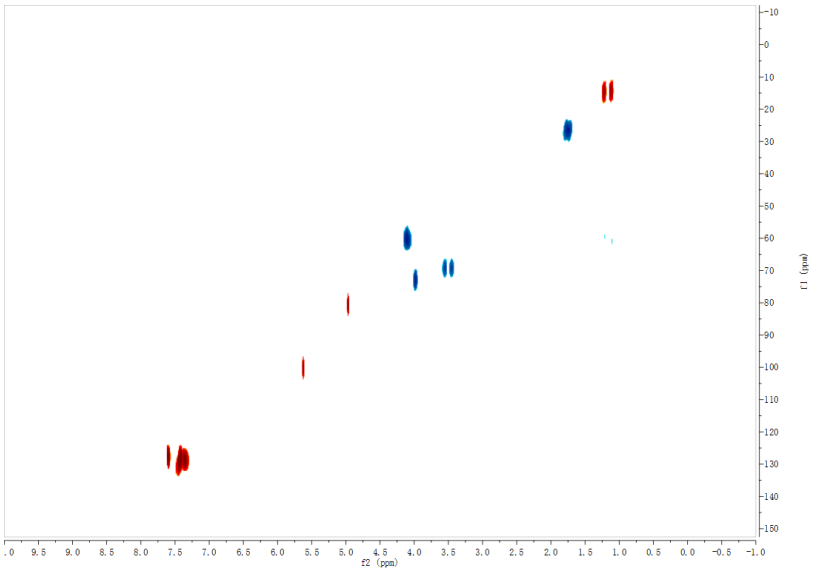
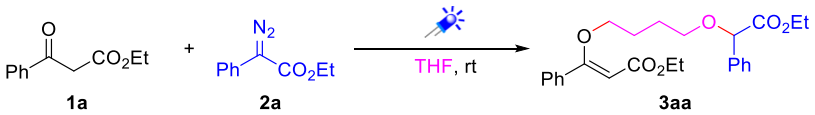


Figure S2. HSQC Spectra

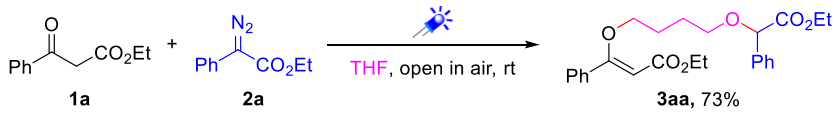
Gram Scale Experiment



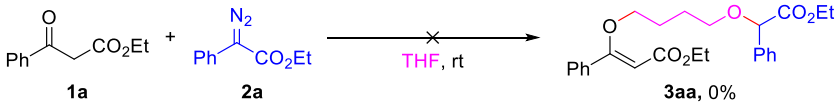
1a **2a** **3aa**

To a 100 mL Schlenk flask was added ethyl 3-oxo-3-phenylpropanoate **1a** (5 mmol, 960 mg) and THF (50 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (7.5 mmol, 1.4 g). Then Schlenk tube was tightly screw capped. The mixture was stirred under the blue LEDs for 18 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **3aa** (1.49 g, 70% yield).

Control Experiments

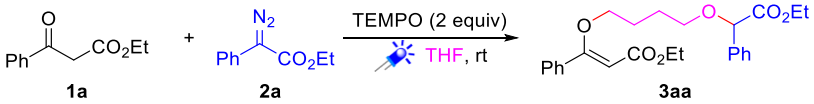


To a 10 mL Schlenk flask was added bethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 77 mg) and THF (2 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (0.6 mmol, 114 mg). Then Schlenk tube was open in air. The mixture was stirred under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **3aa** (124 mg, 73% yield).

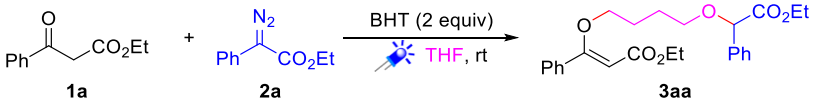


To a 10 mL Schlenk flask was added bethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 77 mg) and THF (2 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (0.6 mmol, 114 mg). Then Schlenk tube was open in air. The mixture was stirred under the without blue LEDs for 6 h. The **3aa** was no detected.

Radical Trapping Experiments



To a 10 mL Schlenk flask was added bethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 77 mg) and THF (2 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (0.6 mmol, 114 mg) and TEMPO (0.8 mmol, 125 mg). Then Schlenk tube was tightly screw capped. The mixture was stirred under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **3aa** (123 mg, 72% yield).



To a 10 mL Schlenk flask was added ethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 77

mg) and THF (2 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (0.6 mmol, 114 mg) and BHT (0.8 mmol, 176 mg). Then Schlenk tube was tightly screw capped. The mixture was stirred under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **3aa** (128 mg, 75% yield).

Computational Details

All the theoretical calculations in the study were performed using Gaussian16 program package.[1] All the geometries were optimized at the M06-2X[2]/6-31G(d, p) level, and the solvent effect was utilized the polarizable continuum model using the integral equation formalism model (IEFPCM) in THF solvent.[3] And the harmonic vibrational frequency calculations were performed at the same level to confirm the local minima and transition state.

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; and Fox, D. J.; *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, **2016**.

(2) Zhao, Y.; Truhlar, D. G. Theor. *Chem. Acc.* **2008***, 120*, 215–241.

(3) Scalmani, G.; Frisch, M. J. *J. Chem. Phys.* **2010**, *132*, 11411–11424.

Table S1. The charges of the enolate species.

	O	C
Mulliken charge	-0.656 e	-0.366 e
NPA charge	-0.731	-0.630

Table S2. The free energies for the species.

Species	G(au)
Carb	-537.071256

THF	-232.258114
TS1	-769.318636
M1	-769.364624
R1	-651.657947
M2	-1421.013908
TS2	-1420.989636
M3	-1421.019177
TS3	-1421.000904
TS3’	-1420.990011
P1	-1421.063405
P2	-1421.091027

Table S3. Reaction Coordinates

Carbene			
C	-3.525404000000	-0.266488000000	-0.667144000000
C	-2.345622000000	-0.986392000000	-0.763591000000
C	-1.156622000000	-0.518641000000	-0.152584000000
C	-1.200667000000	0.704297000000	0.567987000000
C	-2.379090000000	1.420464000000	0.668328000000
C	-3.535463000000	0.932632000000	0.048427000000
H	-4.433429000000	-0.626357000000	-1.137626000000
H	-2.296684000000	-1.923393000000	-1.308602000000
H	-0.296182000000	1.068235000000	1.048176000000
H	-2.412521000000	2.353343000000	1.219844000000
H	-4.459034000000	1.498378000000	0.126404000000
C	0.020126000000	-1.303489000000	-0.317608000000
C	1.218205000000	-0.825735000000	0.348988000000
O	1.500779000000	-1.155955000000	1.488933000000
O	2.010936000000	-0.086601000000	-0.441892000000
C	3.271925000000	0.303682000000	0.135175000000
C	4.014665000000	1.100891000000	-0.913215000000
H	3.818751000000	-0.595772000000	0.430751000000
H	3.080007000000	0.892438000000	1.036812000000
H	4.975618000000	1.432068000000	-0.513243000000
H	4.198857000000	0.492663000000	-1.801493000000
H	3.438576000000	1.981516000000	-1.205934000000
THF			
C	-1.160548000000	0.425737000000	0.137066000000
O	0.000000000000	1.245939000000	-0.000001000000
C	1.160549000000	0.425737000000	-0.137065000000
C	0.726671000000	-0.989757000000	0.237998000000
C	-0.726672000000	-0.989756000000	-0.237999000000
H	-1.512784000000	0.462944000000	1.177209000000

H	-1.950614000000	0.820859000000	-0.508688000000
H	1.512788000000	0.462944000000	-1.177207000000
H	1.950613000000	0.820857000000	0.508692000000
H	1.343272000000	-1.758025000000	-0.232271000000
H	0.768765000000	-1.125415000000	1.323360000000
H	-0.768766000000	-1.125412000000	-1.323361000000
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O	0.017114000000	-2.055980000000	0.179430000000
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C	2.319606000000	-2.040303000000	0.783321000000
C	2.166736000000	-2.037497000000	-0.740824000000
H	0.779269000000	-3.710969000000	-0.820248000000
H	0.274154000000	-2.321501000000	-1.827196000000
H	0.763818000000	-0.675896000000	1.500912000000
H	0.618273000000	-2.331244000000	2.143426000000
H	3.039914000000	-1.304922000000	1.146656000000
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H	2.179875000000	-1.012061000000	-1.120803000000
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H	-3.507298000000	1.800827000000	2.030871000000
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C	0.513194000000	1.514628000000	-0.808547000000
O	0.384400000000	2.633616000000	-1.282266000000
O	1.553596000000	1.139958000000	-0.047847000000
C	2.564693000000	2.145907000000	0.157132000000
H	2.128862000000	2.976480000000	0.719798000000
H	2.882849000000	2.527995000000	-0.816213000000
H	-5.080499000000	0.037075000000	1.303009000000
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H	4.122446000000	0.668657000000	0.320595000000
H	4.491129000000	2.221695000000	1.094100000000
M1			

C	-3.809342000000	1.077330000000	0.065526000000
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C	-2.512747000000	-1.382281000000	-0.016954000000
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C	-4.567295000000	-0.090457000000	0.019664000000
H	-4.303049000000	2.044737000000	0.099542000000
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C	2.854452000000	-2.025692000000	-0.069400000000
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H	4.342597000000	-0.858732000000	0.966833000000
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O	0.345359000000	1.027844000000	0.047020000000
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C	2.266369000000	2.248956000000	0.630578000000
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H	1.524475000000	0.784009000000	-1.633026000000
H	0.049740000000	1.806846000000	-1.834362000000
H	0.401883000000	2.125874000000	1.792697000000
H	1.367478000000	0.602985000000	1.796261000000
H	2.604751000000	3.056348000000	1.280607000000
H	3.093926000000	1.557489000000	0.453159000000
H	1.055415000000	3.623417000000	-0.550234000000
H	2.493059000000	3.034181000000	-1.410576000000
1a			
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O	1.333581000000	2.672760000000	-0.151762000000
C	1.541448000000	0.316254000000	-0.202968000000
C	2.851637000000	0.368524000000	0.283050000000
C	0.972452000000	-0.918693000000	-0.529438000000
C	3.584565000000	-0.799798000000	0.443748000000
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H	3.585066000000	-2.943672000000	0.240329000000
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H	-1.020428000000	2.575886000000	-0.867795000000
H	-0.757708000000	1.077322000000	-1.783347000000
C	-1.497461000000	0.810852000000	0.220330000000
O	-1.330188000000	0.894282000000	1.414388000000
O	-2.441821000000	0.060683000000	-0.352267000000
C	-3.293689000000	-0.668707000000	0.554660000000
C	-4.257768000000	-1.473557000000	-0.286323000000
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H	-4.871196000000	-0.816973000000	-0.906935000000
H	-3.715998000000	-2.164659000000	-0.935956000000
M2			
C	-0.310849000000	-1.795876000000	-2.538487000000
C	0.428094000000	-0.846071000000	-1.841393000000
C	1.428938000000	-1.231013000000	-0.922577000000
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H	-1.083407000000	-1.461590000000	-3.225161000000
H	0.208311000000	0.208447000000	-1.982565000000
H	2.400726000000	-2.933370000000	-0.027939000000
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H	-0.655062000000	-3.896051000000	-2.904478000000
C	2.197162000000	-0.241795000000	-0.209333000000
C	3.281471000000	-0.422483000000	0.672244000000
O	3.654202000000	-1.473248000000	1.194964000000
O	3.922482000000	0.770586000000	0.953383000000
C	5.000123000000	0.678559000000	1.885262000000
C	5.561259000000	2.074172000000	2.057091000000
H	5.754145000000	-0.016575000000	1.503798000000
H	4.629583000000	0.272555000000	2.831592000000
H	6.396700000000	2.061084000000	2.760979000000
H	5.921416000000	2.463965000000	1.101126000000
H	4.795312000000	2.752370000000	2.442965000000
C	2.971694000000	1.550164000000	-1.786722000000
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C	1.605141000000	2.221443000000	0.135810000000

C	2.470181000000	3.371219000000	-0.341018000000
C	2.712651000000	3.040748000000	-1.820959000000
H	3.975988000000	1.292696000000	-1.448229000000
H	2.689150000000	0.991256000000	-2.678130000000
H	0.543849000000	2.341043000000	-0.086640000000
H	1.781257000000	1.905977000000	1.161201000000
H	1.971592000000	4.330740000000	-0.200496000000
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C	-4.321263000000	0.758615000000	1.230889000000
C	-5.546890000000	2.771803000000	-0.260254000000
H	-3.636436000000	2.971770000000	-1.246279000000
C	-5.654197000000	1.081415000000	1.462612000000
H	-3.860232000000	-0.031148000000	1.814599000000
C	-6.267361000000	2.086528000000	0.718250000000
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H	-7.307683000000	2.336333000000	0.900726000000
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C	-1.934857000000	-1.313094000000	0.419624000000
O	-2.827625000000	-1.548048000000	-0.361668000000
O	-1.267214000000	-2.239918000000	1.101923000000
C	-1.665804000000	-3.604677000000	0.864920000000
C	-0.731857000000	-4.484072000000	1.663668000000
H	-1.599123000000	-3.800693000000	-0.207294000000
H	-2.709117000000	-3.719082000000	1.175382000000
H	-0.984098000000	-5.534505000000	1.500712000000
H	0.300427000000	-4.317504000000	1.347550000000
H	-0.811847000000	-4.268714000000	2.731747000000
H	-0.373532000000	0.123440000000	0.595125000000
TS2			
C	1.818193000000	2.160070000000	2.931141000000
C	1.159989000000	1.481647000000	1.907897000000
C	1.545258000000	0.176843000000	1.585042000000
C	2.599174000000	-0.431934000000	2.276009000000
C	3.252075000000	0.250812000000	3.296037000000
C	2.857522000000	1.546575000000	3.626183000000
H	1.524408000000	3.175574000000	3.174667000000

H	0.368035000000	1.977418000000	1.347988000000
H	2.921674000000	-1.433354000000	2.003009000000
H	4.070704000000	-0.223763000000	3.826568000000
H	3.370616000000	2.082118000000	4.418559000000
C	0.813229000000	-0.557447000000	0.512830000000
C	1.627865000000	-1.411337000000	-0.414593000000
O	2.746024000000	-1.121619000000	-0.765403000000
O	0.945779000000	-2.475818000000	-0.855005000000
C	1.626961000000	-3.297796000000	-1.829015000000
C	0.710150000000	-4.453874000000	-2.154069000000
H	2.575370000000	-3.627740000000	-1.397930000000
H	1.845192000000	-2.680996000000	-2.704647000000
H	1.184464000000	-5.101658000000	-2.894151000000
H	0.503691000000	-5.047001000000	-1.259519000000
H	-0.235303000000	-4.092873000000	-2.566029000000
C	-0.093869000000	-2.441497000000	1.983525000000
O	-0.329370000000	-1.296041000000	1.069452000000
C	-1.561958000000	-1.501358000000	0.240359000000
C	-1.940990000000	-2.932502000000	0.551789000000
C	-1.447038000000	-3.123998000000	1.991209000000
H	0.688955000000	-3.053135000000	1.530673000000
H	0.228076000000	-2.011636000000	2.930166000000
H	-2.273522000000	-0.761222000000	0.608833000000
H	-1.281120000000	-1.304959000000	-0.792245000000
H	-3.017610000000	-3.077081000000	0.453771000000
H	-1.420785000000	-3.613643000000	-0.126220000000
H	-2.115809000000	-2.631745000000	2.701333000000
H	-1.350076000000	-4.174146000000	2.268241000000
C	-1.577786000000	2.356777000000	-0.487495000000
O	-1.385112000000	3.210393000000	0.395922000000
C	-2.890542000000	1.590169000000	-0.444164000000
C	-3.569840000000	1.562288000000	0.777670000000
C	-3.405747000000	0.853294000000	-1.515809000000
C	-4.709269000000	0.779602000000	0.943659000000
H	-3.168248000000	2.155106000000	1.592962000000
C	-4.548812000000	0.073999000000	-1.355285000000
H	-2.920397000000	0.888350000000	-2.485925000000
C	-5.196235000000	0.023111000000	-0.121337000000
H	-5.216259000000	0.755444000000	1.903527000000
H	-4.936970000000	-0.492646000000	-2.196133000000
H	-6.081822000000	-0.592088000000	0.004458000000
C	-0.634779000000	1.922415000000	-1.457725000000
H	-0.914857000000	1.189362000000	-2.202341000000
C	0.725374000000	2.396261000000	-1.522272000000

O	1.265787000000	3.285324000000	-0.883201000000
O	1.447410000000	1.628244000000	-2.404291000000
C	2.852525000000	1.871369000000	-2.424107000000
C	3.461408000000	0.906967000000	-3.420166000000
H	3.258466000000	1.712616000000	-1.419144000000
H	3.043176000000	2.914262000000	-2.698526000000
H	4.540771000000	1.065216000000	-3.485942000000
H	3.279518000000	-0.122661000000	-3.102453000000
H	3.028653000000	1.054166000000	-4.413082000000
H	0.139718000000	0.426109000000	-0.344140000000
M3			
C	-1.696003000000	-4.163343000000	-1.492217000000
C	-1.239749000000	-2.930349000000	-1.037690000000
C	-2.144524000000	-1.883280000000	-0.840491000000
C	-3.501656000000	-2.069618000000	-1.107354000000
C	-3.952892000000	-3.304175000000	-1.566621000000
C	-3.052420000000	-4.350398000000	-1.755303000000
H	-0.993452000000	-4.975133000000	-1.648990000000
H	-0.185530000000	-2.752307000000	-0.837166000000
H	-4.201755000000	-1.249659000000	-0.977030000000
H	-5.006978000000	-3.448160000000	-1.779254000000
H	-3.407742000000	-5.310657000000	-2.115080000000
C	-1.595036000000	-0.599258000000	-0.291255000000
C	-2.377028000000	0.665922000000	-0.585033000000
O	-2.818372000000	0.902579000000	-1.680833000000
O	-2.435330000000	1.489079000000	0.459516000000
C	-2.784271000000	2.854365000000	0.146607000000
C	-2.491565000000	3.677800000000	1.378941000000
H	-3.838021000000	2.891970000000	-0.141480000000
H	-2.170280000000	3.155936000000	-0.705605000000
H	-2.706990000000	4.730162000000	1.180248000000
H	-3.104632000000	3.354054000000	2.223984000000
H	-1.436235000000	3.584131000000	1.650711000000
C	-2.540166000000	-1.066270000000	2.029710000000
O	-1.381211000000	-0.776934000000	1.159996000000
C	-0.350506000000	0.060709000000	1.866959000000
C	-1.056424000000	0.425111000000	3.155871000000
C	-1.985600000000	-0.768229000000	3.408051000000
H	-3.340331000000	-0.383136000000	1.737682000000
H	-2.812797000000	-2.103438000000	1.843455000000
H	0.498940000000	-0.609436000000	1.986724000000
H	-0.110765000000	0.878887000000	1.190260000000
H	-0.338995000000	0.574379000000	3.963657000000
H	-1.639236000000	1.339397000000	3.020319000000

H	-1.423139000000	-1.627289000000	3.782417000000
H	-2.789145000000	-0.541097000000	4.109350000000
C	2.299861000000	-0.185751000000	-0.283662000000
O	1.262880000000	-0.901444000000	-0.344162000000
C	3.600882000000	-0.922860000000	-0.032797000000
C	3.539649000000	-2.164749000000	0.606396000000
C	4.849844000000	-0.436528000000	-0.432143000000
C	4.696918000000	-2.891015000000	0.868668000000
H	2.564042000000	-2.546429000000	0.889822000000
C	6.009200000000	-1.166230000000	-0.182185000000
H	4.916966000000	0.506037000000	-0.965802000000
C	5.937821000000	-2.392329000000	0.475820000000
H	4.632251000000	-3.848783000000	1.376410000000
H	6.969695000000	-0.779625000000	-0.508812000000
H	6.842371000000	-2.958756000000	0.674388000000
C	2.371965000000	1.209987000000	-0.390203000000
H	3.328144000000	1.701163000000	-0.277904000000
C	1.272318000000	2.063199000000	-0.693135000000
O	0.074083000000	1.785264000000	-0.814510000000
O	1.677624000000	3.363220000000	-0.849417000000
C	0.654789000000	4.305303000000	-1.156908000000
C	1.327726000000	5.643213000000	-1.384321000000
H	-0.061814000000	4.356373000000	-0.327661000000
H	0.103315000000	3.975727000000	-2.043623000000
H	0.581167000000	6.405509000000	-1.619838000000
H	1.873699000000	5.955945000000	-0.490937000000
H	2.033795000000	5.579529000000	-2.215682000000
H	-0.572736000000	-0.416767000000	-0.653520000000
TS3			
C	-5.828556000000	-0.918891000000	-1.191666000000
C	-4.466377000000	-0.659638000000	-1.296898000000
C	-3.716485000000	-0.363385000000	-0.156423000000
C	-4.339976000000	-0.332064000000	1.091073000000
C	-5.704814000000	-0.588412000000	1.195208000000
C	-6.449227000000	-0.882427000000	0.055848000000
H	-6.405803000000	-1.144655000000	-2.082011000000
H	-3.976944000000	-0.686821000000	-2.266685000000
H	-3.768949000000	-0.093477000000	1.983690000000
H	-6.185285000000	-0.556331000000	2.167368000000
H	-7.513022000000	-1.079520000000	0.138783000000
C	-2.226660000000	-0.167229000000	-0.314478000000
C	-1.593439000000	0.645202000000	0.818580000000
O	-2.004973000000	1.742226000000	1.109327000000
O	-0.550794000000	0.049624000000	1.384580000000

C	0.206942000000	0.849979000000	2.325732000000
C	1.388455000000	0.014451000000	2.758713000000
H	-0.450740000000	1.111964000000	3.158661000000
H	0.508735000000	1.766172000000	1.809915000000
H	1.985767000000	0.573451000000	3.482633000000
H	1.055674000000	-0.914976000000	3.227987000000
H	2.018548000000	-0.221240000000	1.896602000000
C	-1.742741000000	-2.512051000000	0.387046000000
O	-1.585120000000	-1.430334000000	-0.556175000000
C	0.176300000000	-1.373982000000	-1.078850000000
C	0.581754000000	-2.627880000000	-0.353813000000
C	-0.668512000000	-3.476928000000	-0.076249000000
H	-1.561917000000	-2.139648000000	1.399453000000
H	-2.757272000000	-2.905405000000	0.299070000000
H	-0.067032000000	-1.395669000000	-2.131242000000
H	0.327033000000	-0.417779000000	-0.622069000000
H	1.296843000000	-3.175422000000	-0.969169000000
H	1.072929000000	-2.348954000000	0.583779000000
H	-0.998648000000	-3.971586000000	-0.994264000000
H	-0.474662000000	-4.243775000000	0.675536000000
C	2.668232000000	0.000228000000	-0.977848000000
O	2.137489000000	-0.913478000000	-1.690296000000
C	4.040530000000	-0.317637000000	-0.432540000000
C	4.379113000000	-1.659468000000	-0.233987000000
C	4.986287000000	0.667950000000	-0.131742000000
C	5.621794000000	-2.010099000000	0.283708000000
H	3.648966000000	-2.418843000000	-0.494159000000
C	6.234957000000	0.318794000000	0.374988000000
H	4.753253000000	1.711480000000	-0.318791000000
C	6.553692000000	-1.020446000000	0.591217000000
H	5.866177000000	-3.055591000000	0.444924000000
H	6.963668000000	1.093223000000	0.593321000000
H	7.526702000000	-1.291924000000	0.988682000000
C	2.105859000000	1.219288000000	-0.594704000000
H	-2.005584000000	0.410537000000	-1.220200000000
H	2.640179000000	1.822881000000	0.127098000000
C	0.890786000000	1.805605000000	-1.093797000000
O	0.116993000000	1.384936000000	-1.951893000000
O	0.635972000000	2.989894000000	-0.460443000000
C	-0.527930000000	3.701630000000	-0.887415000000
C	-0.775893000000	4.797337000000	0.126426000000
H	-1.378351000000	3.017860000000	-0.939606000000
H	-0.353584000000	4.104213000000	-1.891558000000
H	-1.645214000000	5.390721000000	-0.166986000000

H	-0.971090000000	4.355147000000	1.106508000000
H	0.088551000000	5.461448000000	0.203136000000
TS3'			
C	-4.883139000000	-2.875523000000	-1.421873000000
C	-3.767286000000	-2.045062000000	-1.407921000000
C	-3.644021000000	-1.053187000000	-0.432501000000
C	-4.642981000000	-0.900158000000	0.529724000000
C	-5.760170000000	-1.730699000000	0.512898000000
C	-5.880713000000	-2.718605000000	-0.460754000000
H	-4.976888000000	-3.641010000000	-2.184737000000
H	-2.986213000000	-2.165307000000	-2.153502000000
H	-4.562213000000	-0.126942000000	1.288392000000
H	-6.535341000000	-1.603826000000	1.260926000000
H	-6.753044000000	-3.363591000000	-0.473690000000
C	-2.376012000000	-0.230920000000	-0.397400000000
C	-2.551425000000	1.109645000000	0.322650000000
O	-3.387620000000	1.905972000000	-0.022398000000
O	-1.666601000000	1.300869000000	1.297263000000
C	-1.647764000000	2.607291000000	1.920527000000
C	-0.287208000000	2.762702000000	2.560683000000
H	-2.465576000000	2.648433000000	2.644536000000
H	-1.831989000000	3.358309000000	1.148146000000
H	-0.214394000000	3.743255000000	3.037284000000
H	-0.125958000000	1.996815000000	3.323119000000
H	0.494854000000	2.685598000000	1.798339000000
C	-1.419662000000	-1.697590000000	1.378715000000
O	-1.288167000000	-1.020906000000	0.108098000000
C	0.411848000000	-0.326118000000	0.007980000000
C	0.908177000000	-0.968093000000	1.278680000000
C	0.000817000000	-2.161950000000	1.620648000000
H	-1.762349000000	-0.984013000000	2.133618000000
H	-2.138766000000	-2.510423000000	1.263693000000
H	0.618615000000	-0.763937000000	-0.964413000000
H	0.063264000000	0.693311000000	0.051062000000
H	1.937854000000	-1.305904000000	1.147044000000
H	0.884347000000	-0.229794000000	2.084974000000
H	0.225767000000	-3.003707000000	0.959818000000
H	0.142508000000	-2.486243000000	2.652831000000
C	2.986843000000	-0.327213000000	-1.200281000000
O	2.559178000000	-0.980778000000	-2.166339000000
C	4.139044000000	-0.912041000000	-0.409202000000
C	4.340975000000	-2.294022000000	-0.480218000000
C	5.006974000000	-0.140679000000	0.369957000000
C	5.375868000000	-2.897617000000	0.226049000000

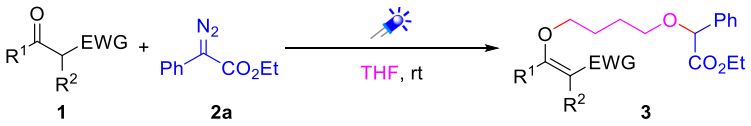
H	3.670933000000	-2.876649000000	-1.104049000000
C	6.052052000000	-0.741389000000	1.067818000000
H	4.884923000000	0.937009000000	0.411704000000
C	6.235141000000	-2.120995000000	1.002567000000
H	5.517318000000	-3.972501000000	0.169227000000
H	6.726215000000	-0.130644000000	1.660093000000
H	7.047513000000	-2.589172000000	1.549603000000
C	2.408066000000	0.875366000000	-0.696825000000
H	2.815170000000	1.331727000000	0.196147000000
C	1.463558000000	1.667252000000	-1.431114000000
O	0.885799000000	1.404821000000	-2.474926000000
O	1.138040000000	2.804653000000	-0.722063000000
C	0.078567000000	3.594571000000	-1.261247000000
C	0.091385000000	4.929714000000	-0.546774000000
H	-0.877282000000	3.070220000000	-1.114770000000
H	0.219335000000	3.713460000000	-2.338344000000
H	-0.725808000000	5.557810000000	-0.909436000000
H	-0.024322000000	4.801089000000	0.533222000000
H	1.036094000000	5.447724000000	-0.727609000000
H	-2.063212000000	0.023772000000	-1.417024000000
3aa			
C	6.102761000000	-0.269036000000	1.214867000000
C	4.715994000000	-0.264668000000	1.090145000000
C	4.115474000000	-0.207641000000	-0.169354000000
C	4.926808000000	-0.119395000000	-1.304254000000
C	6.313164000000	-0.119829000000	-1.177338000000
C	6.906529000000	-0.201723000000	0.080290000000
H	6.553311000000	-0.320756000000	2.201000000000
H	4.087825000000	-0.293040000000	1.974640000000
H	4.477351000000	-0.056031000000	-2.288132000000
H	6.931544000000	-0.057005000000	-2.067178000000
H	7.987621000000	-0.205730000000	0.175138000000
C	2.600859000000	-0.124953000000	-0.258874000000
C	1.982622000000	-0.892563000000	-1.443430000000
O	2.572533000000	-1.496261000000	-2.305751000000
O	0.652133000000	-0.805027000000	-1.377732000000
C	-0.086771000000	-1.556002000000	-2.359857000000
C	-1.549572000000	-1.422802000000	-2.003558000000
H	0.254019000000	-2.595058000000	-2.327897000000
H	0.138772000000	-1.154850000000	-3.352010000000
H	-2.159877000000	-2.006648000000	-2.696159000000
H	-1.727820000000	-1.792894000000	-0.989321000000
H	-1.867608000000	-0.378586000000	-2.046101000000
C	1.941522000000	-1.898248000000	1.208839000000

O	1.948208000000	-0.500257000000	0.933439000000
C	-0.867538000000	-0.507100000000	1.610060000000
C	-0.513039000000	-1.950427000000	1.930623000000
C	0.951045000000	-2.151184000000	2.330476000000
H	1.636956000000	-2.463894000000	0.315056000000
H	2.948014000000	-2.233482000000	1.488388000000
H	-0.522207000000	0.173002000000	2.390386000000
H	-0.444857000000	-0.182347000000	0.656150000000
H	-1.155931000000	-2.277642000000	2.755266000000
H	-0.750719000000	-2.587783000000	1.068401000000
H	1.204528000000	-1.499652000000	3.175455000000
H	1.088092000000	-3.182296000000	2.671636000000
C	-2.916854000000	0.347210000000	0.643745000000
O	-2.303673000000	-0.449015000000	1.528308000000
C	-4.200554000000	-0.241612000000	0.178661000000
C	-4.385801000000	-1.628239000000	0.225303000000
C	-5.236035000000	0.568045000000	-0.302058000000
C	-5.571222000000	-2.195325000000	-0.230495000000
H	-3.593062000000	-2.254737000000	0.620203000000
C	-6.419968000000	-0.000869000000	-0.757476000000
H	-5.123082000000	1.647228000000	-0.296406000000
C	-6.588928000000	-1.384065000000	-0.727408000000
H	-5.700983000000	-3.272113000000	-0.196876000000
H	-7.216843000000	0.637581000000	-1.124331000000
H	-7.514740000000	-1.826139000000	-1.081282000000
C	-2.465670000000	1.526116000000	0.148022000000
H	2.316363000000	0.924887000000	-0.413587000000
H	-2.994557000000	1.946410000000	-0.697728000000
C	-1.384598000000	2.357235000000	0.683641000000
O	-0.912436000000	2.316853000000	1.803449000000
O	-0.995302000000	3.270756000000	-0.229182000000
C	0.005272000000	4.199528000000	0.211381000000
C	0.272401000000	5.150261000000	-0.934349000000
H	0.902870000000	3.643993000000	0.499676000000
H	-0.360638000000	4.721643000000	1.100586000000
H	1.036400000000	5.874946000000	-0.644141000000
H	0.626383000000	4.605202000000	-1.812439000000
H	-0.636239000000	5.693109000000	-1.204251000000
3aa'			
C	-6.531747000000	-1.723571000000	-1.212695000000
C	-5.267533000000	-1.171971000000	-1.390444000000
C	-4.743249000000	-0.275583000000	-0.455313000000
C	-5.501818000000	0.056471000000	0.667100000000
C	-6.769988000000	-0.493712000000	0.845613000000

C	-7.287246000000	-1.383471000000	-0.091458000000
H	-6.928082000000	-2.416632000000	-1.947701000000
H	-4.671349000000	-1.442303000000	-2.258089000000
H	-5.113938000000	0.755803000000	1.400703000000
H	-7.352521000000	-0.225883000000	1.721165000000
H	-8.274931000000	-1.810496000000	0.049463000000
C	-3.316544000000	0.203002000000	-0.678618000000
C	-2.972350000000	1.462472000000	0.122646000000
O	-3.694584000000	2.431917000000	0.163781000000
O	-1.778031000000	1.400842000000	0.709963000000
C	-1.380390000000	2.581244000000	1.435395000000
C	-0.039599000000	2.289487000000	2.068594000000
H	-2.151070000000	2.807945000000	2.177229000000
H	-1.333253000000	3.418924000000	0.733431000000
H	0.294240000000	3.161320000000	2.636670000000
H	-0.113940000000	1.439978000000	2.752432000000
H	0.707091000000	2.069669000000	1.301340000000
C	-2.427958000000	-1.531220000000	0.703510000000
O	-2.369660000000	-0.827462000000	-0.532693000000
C	0.599453000000	-0.904986000000	-0.192299000000
C	0.121588000000	-1.718586000000	1.011699000000
C	-1.213384000000	-2.436589000000	0.802131000000
H	-2.444596000000	-0.821062000000	1.543185000000
H	-3.349715000000	-2.126129000000	0.744397000000
H	0.559190000000	-1.514434000000	-1.100895000000
H	-0.061923000000	-0.046623000000	-0.337151000000
H	0.880198000000	-2.470457000000	1.253797000000
H	0.041539000000	-1.054187000000	1.883373000000
H	-1.166869000000	-3.055166000000	-0.102456000000
H	-1.384216000000	-3.119224000000	1.642106000000
C	3.072071000000	-1.529616000000	-0.158375000000
O	2.734378000000	-2.642203000000	-0.507191000000
C	4.507070000000	-1.216298000000	0.133737000000
C	5.446488000000	-2.240685000000	-0.025197000000
C	4.930193000000	0.049827000000	0.552421000000
C	6.790678000000	-2.005019000000	0.231315000000
H	5.099382000000	-3.214669000000	-0.353101000000
C	6.278371000000	0.284552000000	0.807767000000
H	4.220386000000	0.861856000000	0.680469000000
C	7.207403000000	-0.740730000000	0.648915000000
H	7.515702000000	-2.802244000000	0.105884000000
H	6.602677000000	1.267704000000	1.131637000000
H	8.257605000000	-0.554729000000	0.849825000000
C	2.040666000000	-0.407031000000	-0.010512000000

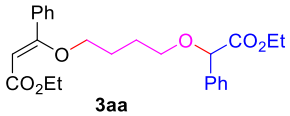
H	2.151882000000	0.054684000000	0.977526000000
C	2.329677000000	0.638545000000	-1.069166000000
O	2.618402000000	0.381781000000	-2.214565000000
O	2.184852000000	1.882060000000	-0.597896000000
C	2.369248000000	2.947350000000	-1.551631000000
C	2.151553000000	4.247786000000	-0.812548000000
H	1.654392000000	2.810187000000	-2.367262000000
H	3.377947000000	2.869569000000	-1.966288000000
H	2.288488000000	5.087900000000	-1.496705000000
H	1.138896000000	4.294980000000	-0.404616000000
H	2.865034000000	4.347998000000	0.008539000000
H	-3.227039000000	0.520243000000	-1.725631000000

Typical Experimental Procedure A and Data of the Enol Ethers



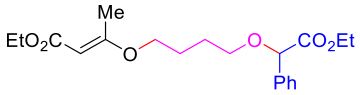
1 2a 3

To a 10 mL Schlenk flask was added ethyl 1,3-dicarbonyl **1** (0.4 mmol) and THF (2 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (0.6 mmol, 114 mg). Then Schlenk tube was tightly screw capped. The mixture was stirred under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **3**.



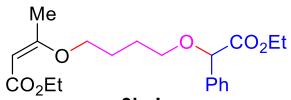
3aa

Ethyl (*Z*)-3-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)-3-phenylacrylate (**3aa,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (133 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.48 (m, 2 H), 7.47 – 7.28 (m, 8 H), 5.52 (s, 1 H), 4.84 (s, 1 H), 4.30 – 4.07 (m, 4 H), 4.01 – 3.97 (m, 2 H), 3.71 – 3.42 (m, 2 H), 2.00 – 1.79 (m, 4 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 170.5, 166.8, 164.3, 136.9, 134.6, 130.4, 128.6, 128.4, 128.3, 127.04, 126.95, 99.8, 80.0, 72.4, 68.7, 60.5, 59.1, 26.3, 25.5, 14.2, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{31}O_6$ 427.2115, found 427.2113**.**



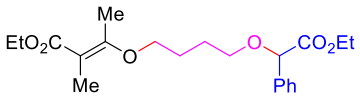
3ba

Ethyl (*E*)-3-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)but-2-enoate (**3ba,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (61 mg, 42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2 H), 7.39 – 7.27 (m, 3 H), 4.98 (s, 1 H), 4.84 (s, 1 H), 4.28 – 4.03 (m, 4 H), 3.77 (dd, *J* = 6.1, 5.2 Hz, 2 H), 3.58 (dt, *J* = 8.9, 6.1 Hz, 1 H), 3.48 (dt, *J* = 8.9, 6.0 Hz, 1 H), 2.26 (s, 3 H), 1.94 – 1.63 (m, 4 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 170.7, 167.8, 136.5, 128.4, 128.3, 126.9, 91.0, 80.9, 69.0, 67.6, 60.9, 59.0, 26.0, 25.3, 18.8, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{28}NaO_6$ 387.1778, found 387.1786**.**



3ba'

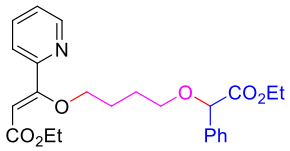
Ethyl (*Z*)-3-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)but-2-enoate (**3ba',** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (61 mg, 42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2 H), 7.39 – 7.30 (m, 3 H), 4.86 (s, 1 H), 4.84 (s, 1 H), 4.21 – 4.03 (m, 6 H), 3.63 – 3.58 (m, 1 H), 3.52 – 3.47 (m, 1 H), 1.96 (s, 3 H), 1.91 – 1.72 (m, 4 H), 1.25 – 1.22 (m, 3 H), 1.21 – 1.18 (m, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 167.4, 165.3, 136.6, 128.4 (2C, overlap), 127.0, 95.7, 80.8, 69.1, 68.4, 60.9, 58.8, 26.4, 25.7, 19.4, 14.3, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{28}NaO_6$ 387.1778, found 387.1788**.**



3ca

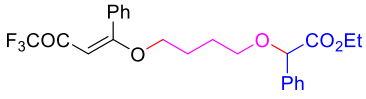
Ethyl (*E*)-3-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)-2-methylbut-2-enoate (**3ca,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (139 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 2 H), 7.40 – 7.29 (m, 3 H), 4.84

(s, 1 H), 4.21 –4.11 (m, 4 H), 3.99 – 3.85 (m, 2 H), 3.66 – 3.54 (m, 1 H), 3.51 – 3.46 (m, 1 H), 2.33 (d, *J* = 1.2 Hz, 3 H), 1.84 – 1.74 (m, 7 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 169.7, 163.9, 136.6, 128.5, 128.4, 127.0, 106.0, 81.0, 69.2, 66.8, 61.0, 59.5, 26.5, 26.0, 15.1, 14.3, 14.0, 11.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{30}NaO_6$ 401.1935, found 401.1930**.**



3da

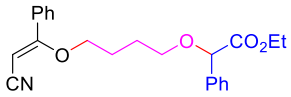
Ethyl (Z)-3-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)-3-(pyridin-2-yl)acrylate (**3da,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (137 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.59 (m, 1 H), 7.72 – 7.71 (m, 2 H), 7.44 (dd, *J* = 7.7, 1.6 Hz, 2 H), 7.40 – 7.27 (m, 4 H), 6.46 (s, 1 H), 4.85 (s, 1 H), 4.22 – 4.11 (m, 6 H), 3.61 (dt, *J* = 8.9, 6.1 Hz, 1 H), 3.51 (dt, *J* = 9.0, 6.1 Hz, 1 H), 2.01 – 1.79 (m, 4 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) δ 170.5, 164.5, 163.7, 151.8, 149.5, 137.5, 136.9, 128.40, 128.36, 127.0, 125.1, 121.1, 99.8, 80.0, 73.5, 68.7, 60.6, 59.5, 26.4, 25.6, 14.1, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{30}NO_6$ 428.2068, found 428.2058**.**



3ea

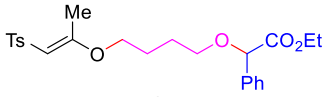
Ethyl (*E*)-2-phenyl-2-(4-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)oxy)butoxy)acetate (**3ea,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (92 mg, 51%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.04 – 7.91 (m, 2 H), 7.82 – 7.62 (m, 1 H), 7.57 – 7.53 (m, 2 H), 7.44 – 7.27 (m, 5 H), 6.63 (s, 1 H), 4.99 (s, 1 H), 4.20 – 4.04 (m, 4 H), 3.57 (dt, *J* = 9.0, 6.3 Hz, 1 H), 3.49 (dt, *J* = 9.1, 6.1 Hz, 1 H), 1.91 – 1.76 (m, 2 H), 1.75 –

1.63 (m, 2 H), 1.13 (t, J = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) δ 189.2, 170.6, 149.6 (q, J = 35.2 Hz), 136.9, 136.8, 133.7, 128.8, 128.7, 128.4, 128.4, 127.0, 119.4 (dd, J = 552.4, 276.2 Hz), 105.2, 80.1, 69.8, 68.6, 60.6, 25.5, 24.8, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}F_3O_5$ 451.1727, found 451.1711**.**



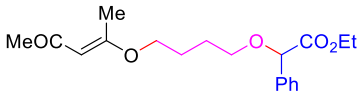
3fa

Ethyl (*Z*)-2-(4-((2-cyano-1-phenylvinyl)oxy)butoxy)-2-phenylacetate (**3fa,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (129 mg, 85%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.68 – 7.60 (m, 2 H), 7.55 – 7.43 (m, 3 H), 7.41 – 7.31 (m, 5 H), 5.53 (s, 1 H), 4.98 (s, 1 H), 4.36 (t, J = 6.2 Hz, 2 H), 4.19 – 3.97 (m, 2 H), 3.58 – 3.44 (m, 2 H), 1.87 – 1.77 (m, 2 H), 1.77 – 1.64 (m, 2 H), 1.12 (t, J = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) δ 170.5, 169.8, 136.9, 133.2, 131.1, 128.7, 128.42, 128.38, 127.0, 126.6, 117.5, 80.0, 73.3, 71.6, 68.6, 60.6, 26.1, 25.4, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}NO_4$ 380.1856, found 380.1830**.**



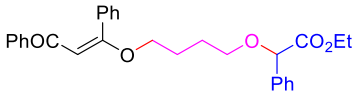
3ga

Ethyl (*E*)-2-phenyl-2-(4-((1-tosylprop-1-en-2-yl)oxy)butoxy)acetate (**3ga,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (91 mg, 51%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.76 (d, J = 8.3 Hz, 2 H), 7.49 – 7.15 (m, 7 H), 5.68 (s, 1 H), 4.89 (s, 1 H), 4.22 – 4.00 (m, 2 H), 3.80 – 3.79 (m, 2 H), 3.61 – 3.40 (m, 2 H), 2.42 – 2.41 (m, 3 H), 2.15 (s, 3 H), 1.79 – 1.70 (m, 4 H), 1.16 (td, J = 7.1, 1.9 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) δ 172.7, 170.9, 144.9, 142.4, 138.2, 130.8, 129.7, 129.6, 128.3, 127.6, 104.1, 82.1, 70.2, 70.0, 62.2, 26.9, 26.5, 21.5, 18.5, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{30}NaO_6S$ 469.1655, found 469.1665**.**



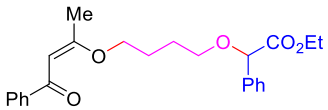
3ha

Ethyl (*E*)-2-(4-((4-oxopent-2-en-2-yl)oxy)butoxy)-2-phenylacetate (**3ha,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (72 mg, 54%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.47 – 7.30 (m, 5 H), 5.60 (s, 1 H), 4.98 (s, 1 H), 4.26 – 4.01 (m, 2 H), 3.84 (t, *J* = 6.3 Hz, 2 H), 3.56 – 3.41 (m, 2 H), 2.16 – 2.13 (m, 3 H), 2.06 (s, 3 H), 1.76 – 1.52 (m, 4 H), 1.13 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 196.0, 170.5, 170.4, 136.9, 128.41, 128.38, 127.0, 100.0, 80.0, 68.6, 67.7, 60.6, 31.7, 25.6, 25.0, 19.1, 13.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{26}NaO_5$ 357.1672, found 357.1671**.**



3ia

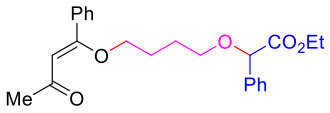
Ethyl (*E*)-2-(4-((3-oxo-1,3-diphenylprop-1-en-1-yl)oxy)butoxy)-2-phenylacetate (**3ia,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (112 mg, 61%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.96 – 7.84 (m, 2 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.42 – 7.30 (m, 10 H), 6.38 (s, 1 H), 4.99 (s, 1 H), 4.19 (t, *J* = 6.3 Hz, 2 H), 4.14 – 4.03 (m, 2 H), 3.58 (dt, *J* = 8.9, 6.2 Hz, 1 H), 3.49 (dt, *J* = 9.0, 6.0 Hz, 1 H), 1.92 – 1.80 (m, 2 H), 1.79 – 1.68 (m, 2 H), 1.12 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 188.9, 170.6, 169.9, 139.2, 136.9, 135.7, 132.1, 129.4, 128.8, 128.40, 128.36 (2C, overlap), 127.9, 127.6, 127.0, 98.6, 80.1, 69.0, 68.7, 60.6, 25.7, 25.3, 13.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{29}H_{31}O_5$ 459.2166, found 459.2176**.**



3ja

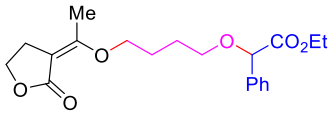
Ethyl (*Z*)-2-(4-((4-oxo-4-phenylbut-2-en-2-yl)oxy)butoxy)-2-phenylacetate (**3ja,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (97

mg, 61%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.98 – 7.80 (m, 2 H), 7.64 – 7.48 (m, 1 H), 7.44 – 7.41 (m, 4 H), 7.35 – 7.26 (m, 3 H), 6.25 (s, 1 H), 4.91 (s, 1 H), 4.21 – 4.07 (m, 2 H), 4.06 – 3.92 (m, 2 H), 3.59 (dt, *J* = 9.0, 6.1 Hz, 1 H), 3.48 (dt, *J* = 9.1, 5.9 Hz, 1 H), 2.36 (s, 3 H), 1.98 – 1.81 (m, 2 H), 1.80 – 1.67 (m, 2 H), 1.14 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 192.4, 176.1, 172.7, 141.6, 138.2, 133.0, 129.6, 129.52, 129.48, 128.7, 128.2, 97.6, 82.1, 70.3, 69.6, 62.2, 27.0, 26.8, 20.8, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}NaO_5$ 419.1829, found 419.1845**.**



3ja'

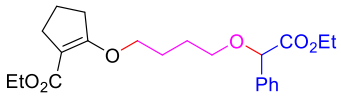
Ethyl (*Z*)-2-(4-((3-oxo-1-phenylbut-1-en-1-yl)oxy)butoxy)-2-phenylacetate (**3ja',** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (54 mg, 34%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.50 – 7.27 (m, 10 H), 5.71 (s, 1 H), 4.91 (s, 1 H), 4.22 – 4.08 (m, 2 H), 4.04 (t, *J* = 6.2 Hz, 2 H), 3.61 (dt, *J* = 9.0, 6.2 Hz, 1 H), 3.50 (dt, *J* = 9.1, 6.0 Hz, 1 H), 2.06 – 1.85 (m, 5 H), 1.85 – 1.70 (m, 2 H), 1.17 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 200.2, 172.8, 172.5, 138.2, 137.1, 131.0, 130.1, 129.7, 129.6, 129.0, 128.3, 104.1, 82.2, 70.4, 70.3, 62.3, 30.9, 27.2, 26.8, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{28}NaO_5$ 419.1829, found 419.1761**.**



3ka

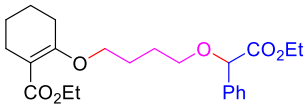
Ethyl (*Z*)-2-(4-(1-(2-oxodihydrofuran-3(2H)-ylidene)ethoxy)butoxy)-2-phenylacetate (**3ka,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (90 mg, 62%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.89 (dd, *J* = 7.8, 1.6 Hz, 2 H), 7.86 – 7.72 (m, 3 H), 5.38 (d, *J* = 7.4 Hz, 1 H), 5.31 (d, *J* = 6.3 Hz, 1 H), 4.79 – 4.51 (m, 6 H), 4.08 (dt, *J* = 9.1, 5.9 Hz, 1 H), 3.97 (dt, *J* = 9.1, 5.7 Hz, 1 H), 3.78 (dt, *J* = 3.2, 1.6 Hz, 1 H), 2.88 (s, 3 H), 2.39 – 2.15

(m, 4 H), 1.65 (td, *J* = 7.1, 1.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) δ 175.1, 172.7, 168.0, 138.2, 129.7, 129.6, 128.3, 100.7, 82.1, 70.4, 68.4, 66.0, 62.2, 27.6, 27.0, 26.6, 14.4, 13.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}NaO_6$ 385.1622, found 385.1620**.**



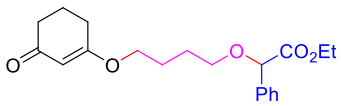
3la

Ethyl 2-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)cyclopent-1-ene-1-carboxylate (**3la,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (151 mg, 97%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.41 (dd, *J* = 7.7, 1.5 Hz, 2 H), 7.38 – 7.25 (m, 3 H), 4.91 (s, 1 H), 4.27 – 3.99 (m, 6 H), 3.56 – 3.63 (m, 1 H), 3.51 – 3.47 (m, 1 H), 2.62 (t, *J* = 7.7 Hz, 2 H), 2.48 (t, *J* = 7.4 Hz, 2 H), 1.91 – 1.65 (m, 6 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 1.17 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) δ 172.5, 171.5, 167.1, 138.2, 129.52, 129.45, 128.2, 104.1, 81.9, 71.2, 70.2, 62.1, 60.2, 32.2, 30.0, 27.6, 26.8, 20.2, 14.8, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{30}NaO_6$ 413.1935, found 413.1945**.**



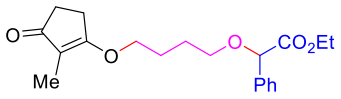
3ma

Ethyl 2-(4-(2-ethoxy-2-oxo-1-phenylethoxy)butoxy)cyclohex-1-ene-1-carboxylate (**3ma,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (89 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.8, 1.5 Hz, 2 H), 7.40 – 7.28 (m, 3 H), 4.84 (s, 1 H), 4.33 – 4.04 (m, 4 H), 3.97 – 3.76 (m, 2 H), 3.61 – 3.56 (m, 1 H), 3.48 (dt, *J* = 8.0, 5.6 Hz, 1 H), 2.38 – 2.17 (m, 4 H), 1.83 – 1.73 (m, 4 H), 1.73 – 1.61 (m, 2 H), 1.60 – 1.49 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 167.9, 161.6, 136.7, 128.3 (2C, overlap), 126.9, 107.8, 80.9, 69.2, 67.6, 60.9, 59.6, 26.5, 26.5, 25.9, 25.3, 22.4, 22.0, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{32}NaO_6$ 427.2091, found 427.2102**.**



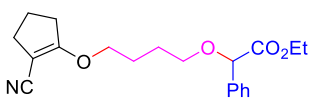
3na

Ethyl 2-(4-((3-oxocyclohex-1-en-1-yl)oxy)butoxy)-2-phenylacetate (**3na,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (129 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2 H), 7.39 – 7.27 (m, 3 H), 5.31 (s, 1 H), 4.82 (s, 1 H), 4.27 – 4.05 (m, 2 H), 3.84 (t, *J* = 6.2 Hz, 2 H), 3.57 (dt, *J* = 8.9, 6.1 Hz, 1 H), 3.47 (dt, *J* = 8.9, 6.0 Hz, 1 H), 2.37 – 2.29 (m, 4 H), 2.06 – 1.90 (m, 2 H), 1.90 – 1.80 (m, 2 H), 1.78 – 1.71 (m, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.3, 177.6, 170.5, 136.3, 128.2 (2C, overlap), 126.8, 102.4, 80.8, 68.8, 67.8, 60.8, 36.4, 28.7, 25.8, 25.1, 20.9, 13.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}NaO_5$ 369.1672, found 369.1682**.**



3oa

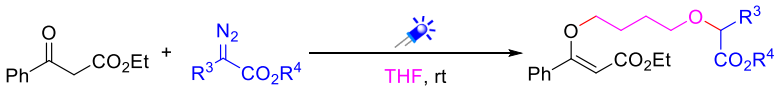
Ethyl 2-(4-((2-methyl-3-oxocyclopent-1-en-1-yl)oxy)butoxy)-2-phenylacetate (**3oa,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (133 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2 H), 7.38 – 7.28 (m, 3 H), 4.83 (s, 1 H), 4.27 – 4.01 (m, 4 H), 3.60 (dt, *J* = 9.0, 6.1 Hz, 1 H), 3.50 (dt, *J* = 9.0, 5.9 Hz, 1 H), 2.66 – 2.47 (m, 2 H), 2.45 – 2.33 (m, 2 H), 1.98 – 1.84 (m, 2 H), 1.83 – 1.74 (m, 2 H), 1.60 (t, *J* = 1.5 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 205.1, 184.0, 170.6, 136.3, 128.32, 128.27, 126.8, 115.6, 80.8, 68.9, 68.8, 60.9, 33.2, 26.4, 25.5, 24.8, 13.8, 5.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}NaO_5$ 369.1672, found 369.1673**.**



3pa

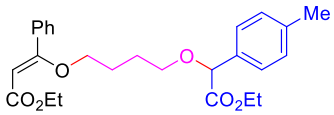
Ethyl 2-(4-((2-cyanocyclopent-1-en-1-yl) voxy) butoxy)-2-phenylacetate (**3pa,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (102 mg, 74%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.43 (dd, *J* = 7.8, 1.5 Hz, 2 H), 7.38 – 7.32 (m, 3 H), 4.92 (s, 1 H), 4.27 – 4.24 (m, 2 H), 4.21 – 4.01 (m, 2 H), 3.62 – 3.57 (m, 1 H), 3.53 – 3.41 (m, 1 H), 2.67 – 2.41 (m, 4 H), 2.11 – 1.56 (m, 6 H), 1.18 (td, *J* = 7.1, 3.6 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD_SPE) δ 174.8, 172.7, 138.2, 129.6, 129.5, 128.3, 118.4, 82.1, 80.2, 72.1, 70.2, 62.2, 33.1, 32.0, 27.4, 26.8, 21.4, 14.4. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{20}H_{25}NNaO_4$ 366.1676, found 366.1677**.**

Typical Experimental Procedure B and Data of the Enol Ethers



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

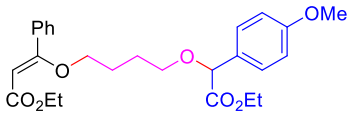
To a 10 mL Schlenk flask was added ethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 77 mg) and THF (2 mL), followed by diazoacetates **2** (0.6 mmol). Then Schlenk tube was tightly screw capped. The mixture was stirred under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **3**.



3ab

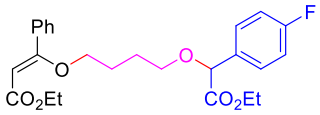
Ethyl (*Z*)-3-(4-(2-ethoxy-2-oxo-1-(p-tolyl)ethoxy)butoxy)-3-phenylacrylate (**3ab,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (141 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.46 (m, 2 H), 7.45 – 7.34 (m, 3 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 7.9 Hz, 2 H), 5.52 (s, 1 H), 4.80 (s, 1 H), 4.34 – 4.08 (m, 4 H), 4.05 – 3.94 (m, 2 H), 3.59 – 3.54 (m, 1 H), 3.50 – 3.44 (m, 1 H), 2.33 (s, 3 H), 1.94 – 1.76 (m, 4 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 167.7, 165.1, 138.1, 135.1, 133.7, 130.1, 129.1, 128.4, 127.3, 126.9, 100.5, 80.7, 72.5, 69.0,

60.9, 59.5, 26.7, 25.9, 21.0, 14.2, 14.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{32}NaO_6$ 463.2091, found 463.2095**.**



3ac

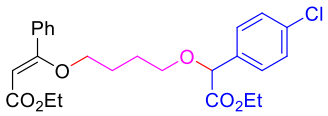
Ethyl (*Z*)-3-(4-(2-ethoxy-1-(4-methoxyphenyl)-2-oxoethoxy)butoxy)-3-phenylacrylate (**3ac,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (137 mg, 75%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.59 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.51 – 7.39 (m, 3 H), 7.30 – 7.28 (m, 2 H), 6.93 – 6.90 (m, 2 H), 5.60 (s, 1 H), 4.88 (s, 1 H), 4.12 – 4.02 (m, 4 H), 3.94 (t, *J* = 6.1 Hz, 2 H), 3.74 (s, 3 H), 3.48 (dt, *J* = 8.9, 6.0 Hz, 1 H), 3.39 (dt, *J* = 9.0, 6.0 Hz, 1 H), 1.98 – 1.55 (m, 4 H), 1.21 (t, *J* = 7.1 Hz, 3 H), 1.12 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 172.9, 169.6, 167.0, 161.3, 136.3, 131.5, 130.2, 129.7, 129.6, 128.5, 114.9, 101.1, 81.6, 73.7, 70.0, 62.1, 60.8, 55.7, 27.8, 27.0, 14.7, 14.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{33}O_7$ 457.2221, found 457.2245**.**



3ad

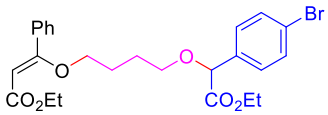
Ethyl (*Z*)-3-(4-(2-ethoxy-1-(4-fluorophenyl)-2-oxoethoxy)butoxy)-3-phenylacrylate (**3ad,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (162 mg, 91%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.72 – 7.55 (m, 2 H), 7.51 – 7.37 (m, 5 H), 7.19 (t, *J* = 8.8 Hz, 2 H), 5.60 (s, 1 H), 4.99 (s, 1 H), 4.19 – 4.01 (m, 4 H), 3.96 – 3.93 (m, 2 H), 3.52 (dt, *J* = 9.0, 6.0 Hz, 1 H), 3.42 (dt, *J* = 9.0, 5.9 Hz, 1 H), 1.86 – 1.61 (m, 4 H), 1.21 (t, *J* = 7.1 Hz, 3 H), 1.12 (t, *J* = 7.1 Hz, 3 H). ^{19}F NMR (376 MHz, d_6-DMSO) δ -113.65. ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 170.4, 166.8, 164.3, 162.0 (d, *J* = 244.5 Hz), 134.6, 133.2 (d, *J* = 3.0 Hz), 130.4, 129.1 (d, *J* = 8.4 Hz), 128.7, 127.1, 115.3 (d, *J* = 21.5 Hz), 99.8, 79.2, 72.4, 68.7, 60.6, 59.1, 26.3, 25.5, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{29}FNaO_6$ 467.1840,

found 467.1840**.**



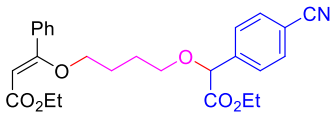
3ae

Ethyl (*Z*)-3-(4-(1-(4-chlorophenyl)-2-ethoxy-2-oxoethoxy)butoxy)-3-phenylacrylate (**3ae,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (138 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 2 H), 7.46 – 7.33 (m, 5 H), 7.33 – 7.27 (m, 2 H), 5.52 (s, 1 H), 4.81 (s, 1 H), 4.35 – 4.08 (m, 4 H), 4.08 – 3.93 (m, 2 H), 3.59 (dt, *J* = 9.0, 5.9 Hz, 1 H), 3.53 – 3.37 (m, 1 H), 1.98 – 1.73 (m, 4 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 170.2, 166.8, 164.3, 135.9, 134.6, 133.0, 130.5, 128.8, 128.7, 128.5, 127.1, 99.8, 79.1, 72.4, 68.8, 60.8, 59.2, 26.3, 25.5, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{29}ClNaO_6$ 483.1545, found 483.1561**.**



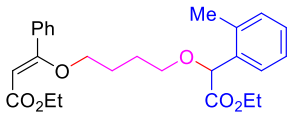
3af

Ethyl (*Z*)-3-(4-(1-(4-bromophenyl)-2-ethoxy-2-oxoethoxy)butoxy)-3-phenylacrylate (**3af,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (187 mg, 93%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.69 – 7.54 (m, 4 H), 7.51 – 7.40 (m, 3 H), 7.38 – 7.28 (m, 2 H), 5.60 (s, 1 H), 4.99 (s, 1 H), 4.18 – 4.02 (m, 4 H), 3.96 – 3.93 (m, 2 H), 3.53 (dt, *J* = 9.0, 6.0 Hz, 1 H), 3.43 (dt, *J* = 9.0, 5.9 Hz, 1 H), 1.85 – 1.51 (m, 4 H), 1.21 (t, *J* = 7.1 Hz, 3 H), 1.11 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 170.1, 166.8, 164.3, 136.3, 134.6, 131.4, 130.4, 129.1, 128.7, 127.1, 121.6, 99.8, 79.2, 72.4, 68.8, 60.7, 59.1, 26.3, 25.5, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{29}BrNaO_6$ 527.1040, found 527.0778**.**



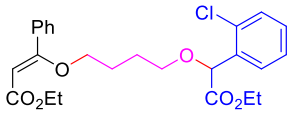
3ag

Ethyl (*Z*)-3-(4-(1-(4-cyanophenyl)-2-ethoxy-2-oxoethoxy)butoxy)-3-phenylacrylate (**3ag,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (130 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.61 (m, 2 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.54 – 7.49 (m, 2 H), 7.45 – 7.33 (m, 3 H), 5.53 (s, 1 H), 4.89 (s, 1 H), 4.26 – 4.09 (m, 4 H), 4.08 – 3.93 (m, 2 H), 3.65 (dt, *J* = 8.9, 5.8 Hz, 1 H), 3.59 – 3.45 (m, 1 H), 1.93 – 1.77 (m, 4 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.21 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, *d*$_6$-DMSO) δ 169.8, 166.8, 164.3, 142.3, 134.6, 132.5, 130.5, 128.7, 127.8, 127.1, 118.5, 111.2, 99.8, 79.2, 72.4, 69.1, 61.0, 59.2, 26.3, 25.5, 14.2, 13.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{29}NNaO_6$ 474.1887, found 474.1907**.**



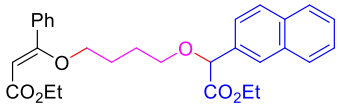
3ah

Ethyl (*Z*)-3-(4-(2-ethoxy-2-oxo-1-(o-tolyl)ethoxy)butoxy)-3-phenylacrylate (**3ah,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (121 mg, 69%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.64 – 7.47 (m, 2 H), 7.46 – 7.37 (m, 3 H), 7.32 (d, *J* = 7.4 Hz, 1 H), 7.17 (t, *J* = 8.3 Hz, 3 H), 5.50 (s, 1 H), 5.10 (s, 1 H), 4.24 – 4.03 (m, 4 H), 3.96 (s, 2 H), 3.60 – 3.56 (m, 1 H), 3.45 (t, *J* = 7.3 Hz, 1 H), 2.38 (s, 3 H), 1.79 – 1.78 (m, 4 H), 1.33 – 1.22 (m, 3 H), 1.21 – 1.10 (m, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 172.8, 169.6, 166.9, 137.7, 136.5, 136.3, 131.6, 131.4, 129.7, 129.4, 128.53, 128.45, 127.1, 101.0, 79.4, 73.7, 70.3, 62.1, 60.7, 27.8, 27.1, 19.6, 14.7, 14.4. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{32}NaO_6$ 463.2091, found 463.2093**.**



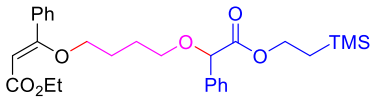
3ai

Ethyl (*Z*)-3-(4-(1-(2-chlorophenyl)-2-ethoxy-2-oxoethoxy)butoxy)-3-phenylacrylate (**3ai,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (155 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.30 (m, 3 H), 7.29 – 7.14 (m, 4 H), 7.17 – 7.03 (m, 2 H), 5.37 (s, 1 H), 5.16 (s, 1 H), 4.32 – 3.93 (m, 4 H), 3.92 – 3.77 (m, 2 H), 3.53 – 3.48 (m, 1 H), 3.39 – 3.34 (m, 1 H), 1.73 – 1.64 (m, 4 H), 1.14 (t, *J* = 7.1 Hz, 3 H), 1.06 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 167.6, 165.1, 135.1, 134.7, 133.5, 130.1, 129.5, 129.4, 128.5, 128.4, 127.2, 127.0, 100.5, 77.2, 72.4, 69.7, 61.1, 59.5, 26.6, 25.9, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{29}ClNaO_6$ 483.1545, found 483.1545**.**



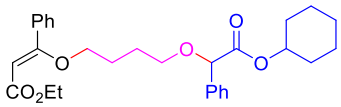
3aj

Ethyl (*Z*)-3-(4-(2-ethoxy-1-(naphthalen-2-yl)-2-oxoethoxy)butoxy)-3-phenylacrylate (**3aj,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (175 mg, 92%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.28 – 8.20 (m, 1 H), 7.99 – 7.88 (m, 2 H), 7.62 – 7.37 (m, 9 H), 5.61 (s, 1 H), 5.58 (s, 1 H), 4.20 – 4.00 (m, 4 H), 3.93 – 3.90 (m, 2 H), 3.64 (dt, *J* = 9.0, 5.8 Hz, 1 H), 3.52 – 3.49 (m, 1 H), 1.72 – 1.67 (m, 4 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 1.06 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 172.8, 169.6, 166.9, 136.2, 135.3, 134.1, 132.3, 131.4, 130.3, 129.6, 128.4, 127.8, 127.3, 126.9, 126.2, 125.3, 101.0, 80.7, 73.6, 70.4, 62.2, 60.7, 27.8, 27.0, 14.74, 14.72, 14.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{33}O_6$ 477.2272, found 477.2258**.**



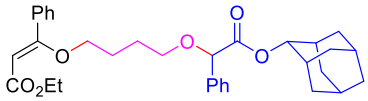
3ak

Ethyl (*Z*)-3-(4-(2-oxo-1-phenyl-2-(2-(trimethylsilyl)ethoxy) ethoxy)butoxy)-3-phenylacrylate (**3ak,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (189 mg, 95%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.50 (d, *J* = 7.0 Hz, 2 H), 7.46 – 7.16 (m, 8 H), 5.50 (s, 1 H), 4.86 (s, 1 H), 4.20 – 4.12 (m, 4 H), 3.97 – 3.96 (m, 2 H), 3.59 – 3.55 (m, 1 H), 3.53 – 3.35 (m, 1 H), 1.79 (d, *J* = 2.6 Hz, 4 H), 1.26 (t, *J* = 7.0 Hz, 3 H), 0.90 (t, *J* = 8.0 Hz, 2 H), -0.03 (d, *J* = 7.0 Hz, 9 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 172.7, 169.6, 166.9, 138.2, 136.3, 131.4, 129.7, 129.6, 129.5, 128.5, 128.3, 101.2, 82.2, 73.7, 70.3, 64.4, 60.7, 27.8, 27.0, 18.0, 14.8, -1.4. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{28}H_{38}NaO_6Si$ 521.2330, found 521.2361**.**



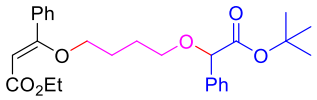
3al

Ethyl (*Z*)-3-(4-(2-(cyclohexyloxy)-2-oxo-1-phenylethoxy)butoxy)-3-phenylacrylate (**3al,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (161 mg, 84%); ^{1}H NMR (400 MHz, *d*$_6$-DMSO) δ 7.75 – 7.53 (m, 2 H), 7.53 – 7.41 (m, 3 H), 7.40 – 7.24 (m, 5 H), 5.60 (s, 1 H), 4.93 (s, 1 H), 4.70 (dt, *J* = 8.1, 4.2 Hz, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.98 – 3.95 (m, 2 H), 3.53 (dt, *J* = 8.9, 6.1 Hz, 1 H), 3.45 (dt, *J* = 9.0, 5.9 Hz, 1 H), 1.94 – 1.66 (m, 5 H), 1.59 (s, 2 H), 1.55 – 1.14 (m, 10 H). ^{13}C{^{1}H} NMR (100 MHz, *d*$_6$-DMSO) δ 169.9, 166.8, 164.3, 137.1, 134.7, 130.4, 128.6, 128.3, 127.0, 126.9, 99.7, 80.2, 72.4, 68.7, 59.1, 30.8, 30.6, 26.4, 25.6, 24.7, 22.8, 22.7, 14.2. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{29}H_{36}NaO_6$ 503.2404, found 503.2401**.**



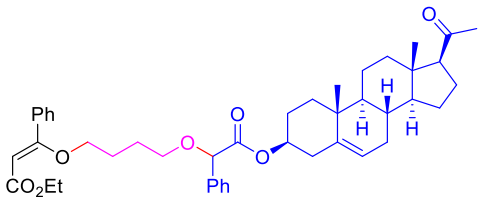
3am

Ethyl (*Z*)-3-(4-(2-(((1R,3S,5r,7r)-adamantan-2-yl)oxy)-2-oxo-1-phenylethoxy)butoxy)-3-phenylacrylate (**3am,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (134 mg, 63%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.55 – 7.49 (m, 2 H), 7.47 – 7.36 (m, 5 H), 7.37 – 7.27 (m, 3 H), 5.50 (s, 1 H), 4.94 (s, 1 H), 4.89 (s, 1 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 4.06 – 3.89 (m, 2 H), 3.63 – 3.58 (m, 1 H), 3.51 – 3.46 (m, 1 H), 1.96 – 1.93 (m, 2 H), 1.89 – 1.74 (m, 9 H), 1.69 (s, 4 H), 1.60 – 1.51 (m, 2 H), 1.42 – 1.31 (m, 1 H), 1.30 – 1.20 (m, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 169.7, 166.7, 164.2, 137.3, 134.6, 130.4, 128.6, 128.3, 128.2, 127.0, 126.8, 99.7, 80.2, 76.8, 72.4, 68.7, 59.1, 36.6, 35.5, 35.4, 31.2, 31.03, 31.00, 30.8, 26.5, 26.4, 26.3, 25.6, 14.1. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{33}H_{40}NaO_6$ 555.2717, found 555.2742**.**



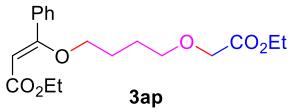
3an

Ethyl (*Z*)-3-(4-(2-(tert-butoxy)-2-oxo-1-phenylethoxy)butoxy)-3-phenylacrylate (**3an,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (120 mg, 66%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.60 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.55 – 7.40 (m, 3 H), 7.40 – 7.23 (m, 5 H), 5.60 (s, 1 H), 4.80 (s, 1 H), 4.09 (q, *J* = 7.1 Hz, 2 H), 3.98 – 3.94 (m, 2 H), 3.52 (dt, *J* = 8.8, 6.1 Hz, 1 H), 3.43 (dt, *J* = 8.9, 5.8 Hz, 1 H), 1.95 – 1.56 (m, 4 H), 1.33 (s, 9 H), 1.21 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 169.8, 166.8, 164.3, 137.2, 134.6, 130.5, 128.7, 128.3, 128.2, 127.1, 126.8, 99.8, 81.0, 80.9, 72.4, 68.6, 59.2, 27.5, 26.4, 25.6, 14.2. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{34}NaO_6$ 477.2248, found 477.2239**.**



3ao

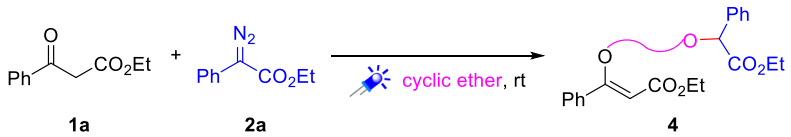
Ethyl (*Z*)-3-(4-(2-(((3S,8S,9S,10R,13S,14S,17S) -17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-2-oxo-1-phenylethoxy)butoxy)-3-phenylacrylate (**3ao,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (195 mg, 70%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.59 (d, *J* = 7.1 Hz, 2 H), 7.52 – 7.17 (m, 8 H), 5.60 (s, 1 H), 5.32 – 5.27 (m, 1 H), 4.93 (s, 1 H), 4.52 – 4.51 (m, 1 H), 4.16 – 3.83 (m, 4 H), 3.61 – 3.40 (m, 2 H), 2.25 (d, *J* = 7.4 Hz, 1 H), 2.13 – 2.11 (m, 1 H), 2.09 – 1.84 (m, 7 H), 1.83 – 1.64 (m, 5 H), 1.65 – 1.45 (m, 5 H), 1.37 (s, 4 H), 1.22 – 1.15 (m, 3 H), 1.11 – 1.02 (m, 3 H), 0.91 (s, 4 H), 0.51 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ 208.4, 170.0, 166.8, 164.3, 139.2, 139.1, 136.9, 134.7, 130.4, 128.7, 128.4, 127.1, 126.9, 122.2, 99.7, 80.1, 73.9, 72.5, 68.8, 62.5, 59.2, 56.0, 49.2, 43.2, 37.9, 37.5, 37.3, 36.4, 36.0, 31.2, 31.1, 27.2, 26.4, 25.6, 24.0, 22.2, 20.5, 18.9, 14.2, 12.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{44}H_{57}O_7$ 697.4099, found 697.4117**.**



3ap

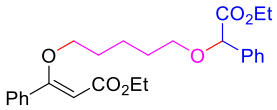
Ethyl (*Z*)-3-(4-(2-ethoxy-2-oxoethoxy)butoxy)-3-phenylacrylate (**3ap,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (52 mg, 37%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.5, 2.0 Hz, 2 H), 7.42 – 7.36 (m, 3 H), 5.53 (s, 1 H), 4.24 – 4.16 (m, 4 H), 4.10 – 3.81 (m, 4 H), 3.59 – 3.55 (m, 2 H), 1.96 – 1.68 (m, 4 H), 1.29 (q, *J* = 7.3 Hz, 6 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 170.5, 167.8, 165.3, 135.2, 130.2, 128.5, 127.4, 100.7, 72.5, 71.3, 68.3, 60.8, 59.7, 26.7, 26.0, 14.4, 14.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{26}NaO_6$ 373.1622, found 373.1620**.**

Typical Experimental Procedure C and Data of the Vinyl Ethers



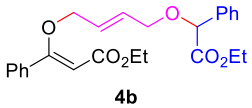
1a **2a** **4**

To a 10 mL Schlenk flask was added ethyl 3-oxo-3-phenylpropanoate **1a** (0.4 mmol, 77 mg) and cyclic ether (2 mL), followed by ethyl 2-diazo-2-phenylacetate **2a** (0.6 mmol, 114 mg). Then Schlenk tube was tightly screw capped. The mixture was stirred under the blue LEDs for 6 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (10:1) to afford the desired product **4**.



4a

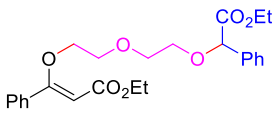
Ethyl (*Z*)-3-((5-(2-ethoxy-2-oxo-1-phenylethoxy)pentyl)oxy)-3-phenylacrylate (**4a,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (157 mg, 89%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.53 (dd, *J* = 7.8, 1.6 Hz, 2 H), 7.48 – 7.37 (m, 5 H), 7.36 – 7.23 (m, 3 H), 5.51 (s, 1 H), 4.89 (s, 1 H), 4.24 – 4.03 (m, 4 H), 3.96 – 3.93 (m, 2 H), 3.54 (dt, *J* = 9.1, 6.3 Hz, 1 H), 3.42 (dt, *J* = 9.1, 6.3 Hz, 1 H), 1.75 – 1.60 (m, 4 H), 1.55 – 1.47 (m, 2 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 1.16 (t, *J* = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD) δ 172.7, 169.6, 167.0, 138.3, 136.4, 131.4, 129.7, 129.6, 129.5, 128.5, 128.3, 101.0, 82.1, 73.9, 70.6, 62.1, 60.8, 30.7, 30.2, 23.5, 14.8, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{32}NaO_6$ 463.2091, found 463.2105**.**



4b

Ethyl (*Z*)-3-(((E)-4-(2-ethoxy-2-oxo-1-phenylethoxy)but-2-en-1-yl)oxy)-3-phenylacrylate (**4b,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (114 mg, 67%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.51 (dd, *J* = 8.1, 1.4 Hz, 2 H), 7.48 – 7.16

(m, 8 H), 5.87 (dt, *J* = 7.3, 6.5 Hz, 1 H), 5.78 – 5.72 (m, 1 H), 5.58 (s, 1 H), 4.83 (s, 1 H), 4.68 – 4.46 (m, 2 H), 4.29 – 4.03 (m, 4 H), 3.98 – 3.86 (m, 2 H), 1.47 – 1.21 (m, 3 H), 1.20 – 1.02 (m, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) δ 172.4, 169.1, 166.9, 137.8, 136.0, 131.6, 130.4, 129.8, 129.7, 129.63, 129.60, 128.6, 128.4, 102.0, 81.3, 69.3, 65.9, 62.3, 60.9, 14.7, 14.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{28}NaO_6$ 447.1778, found 447.1779**.**

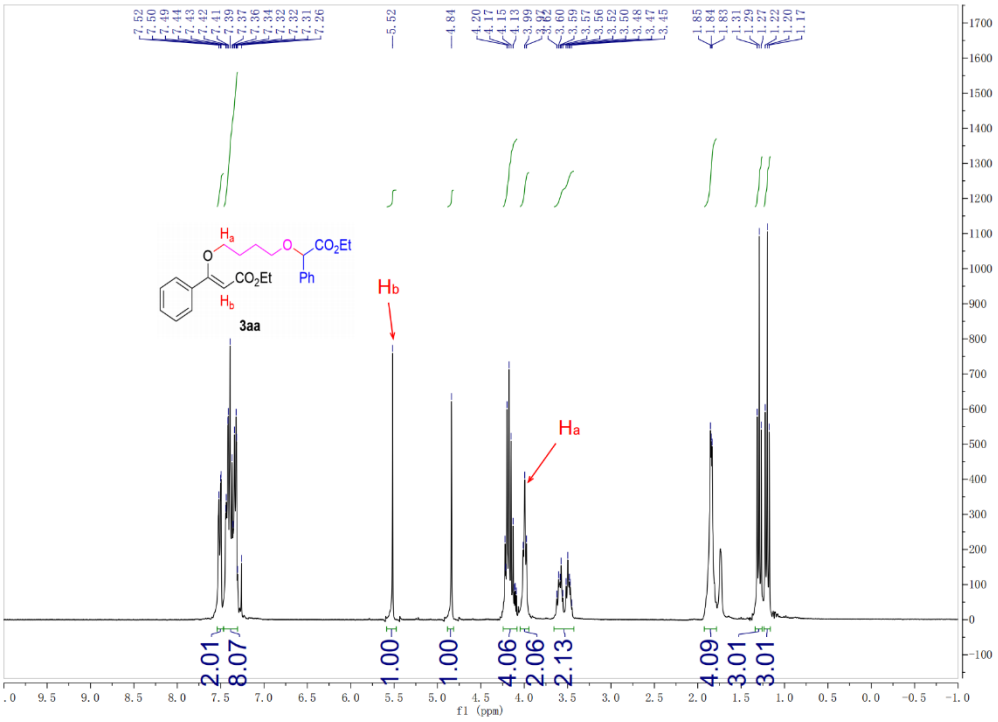


4c

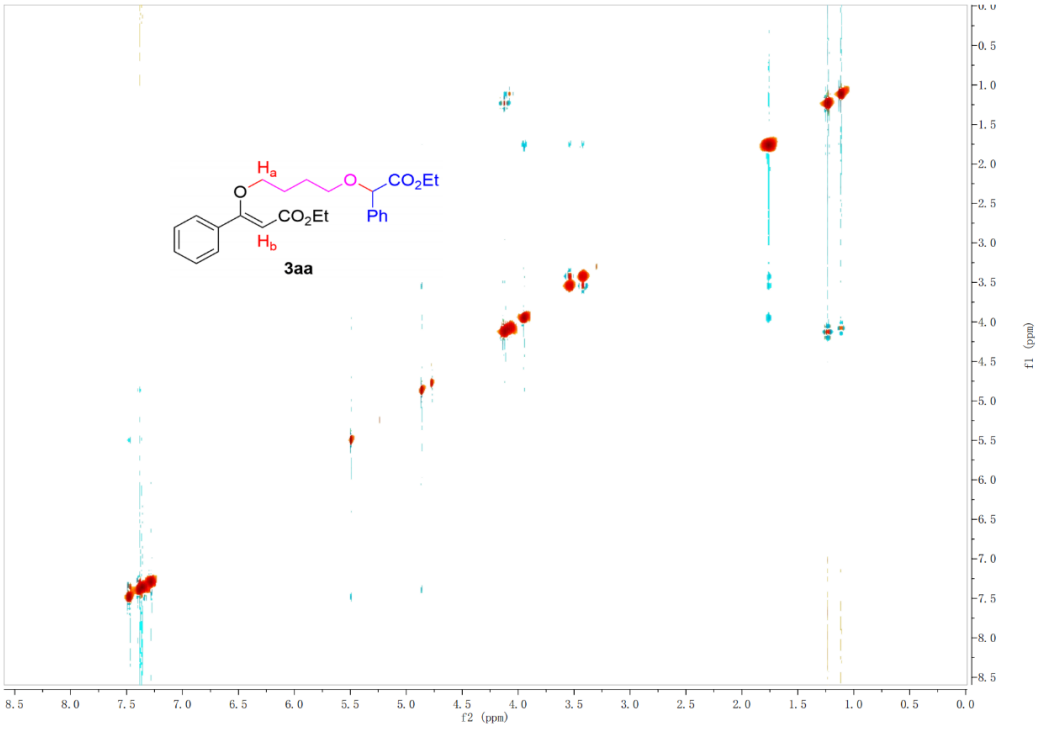
Ethyl (*Z*)-3-(2-(2-(2-ethoxy-2-oxo-1-phenylethoxy)ethoxy)ethoxy)-3-phenylacrylate (**4c,** new compound): The reaction was performed following the general procedure. The residue was purified by flash column chromatography (10:1 PE/EA) to give the product as a colorless oil (53 mg, 30%); ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.69 (d, *J* = 7.5 Hz, 2 H), 7.47 – 7.34 (m, 8 H), 5.69 (s, 1 H), 5.05 (s, 1 H), 4.13 – 4.03 (m, 6 H), 3.89 – 3.48 (m, 6 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.10 (t, *J* = 7.1 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) δ 170.4, 166.9, 164.4, 136.8, 134.8, 130.5, 128.5, 128.4 (2C, overlap), 127.3, 127.1, 98.9, 80.2, 72.7, 69.7, 69.6, 68.5, 60.6, 59.2, 14.2, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{30}NaO_7$ 465.1884, found 465.1891**.**

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of All the Products, NOESY Spectra of Products 3aa, 3ba, 3ca, 3ea, 3fa, 3ga, 3ha, 3ia, 3ja, 3ka and 3ab

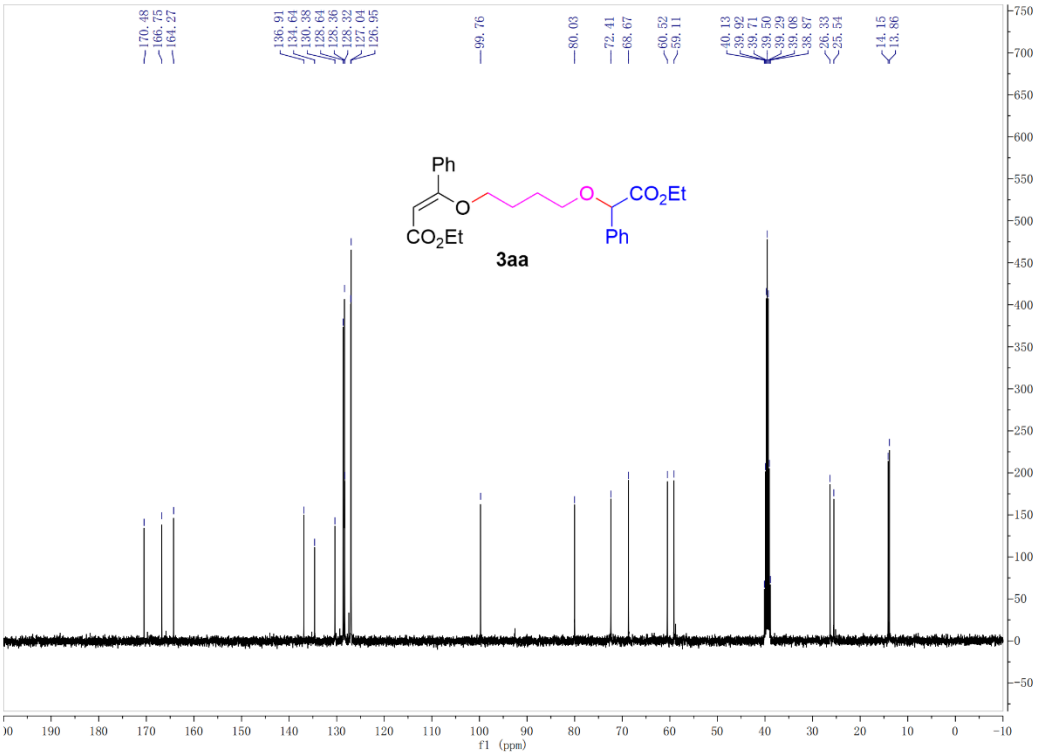
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3aa.



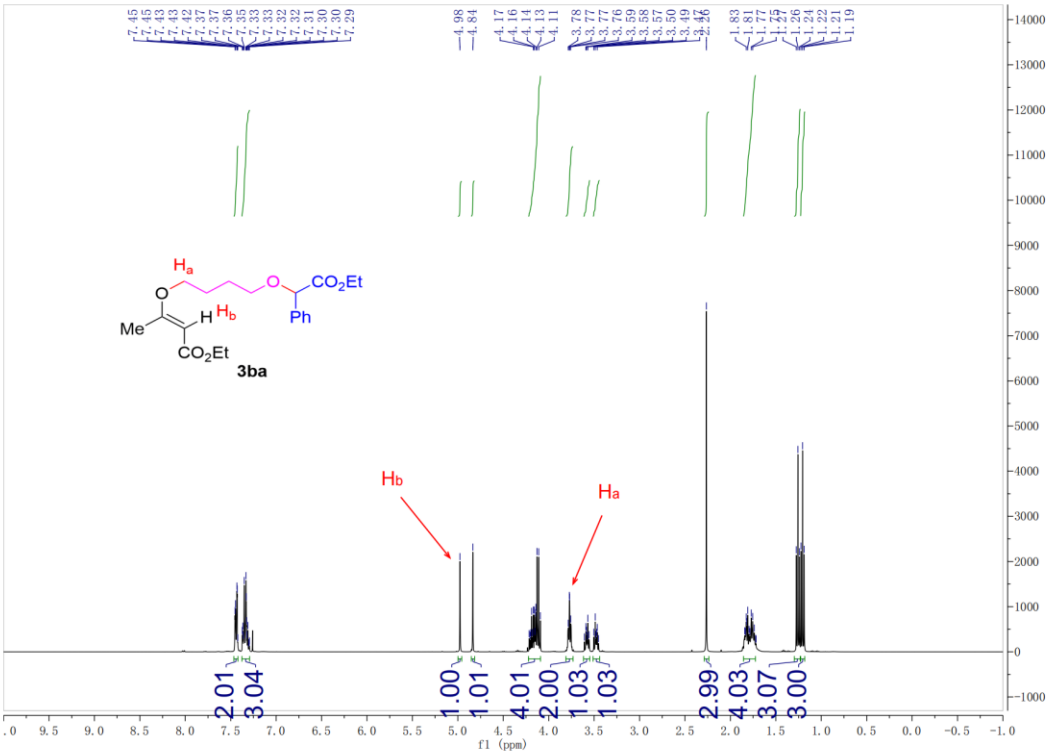
NOESY NMR (400 MHz, $CDCl_3$) Spectrum of 3aa. Based on no NOE effect in H_a and H_b, the stereochemistry is *Z*.



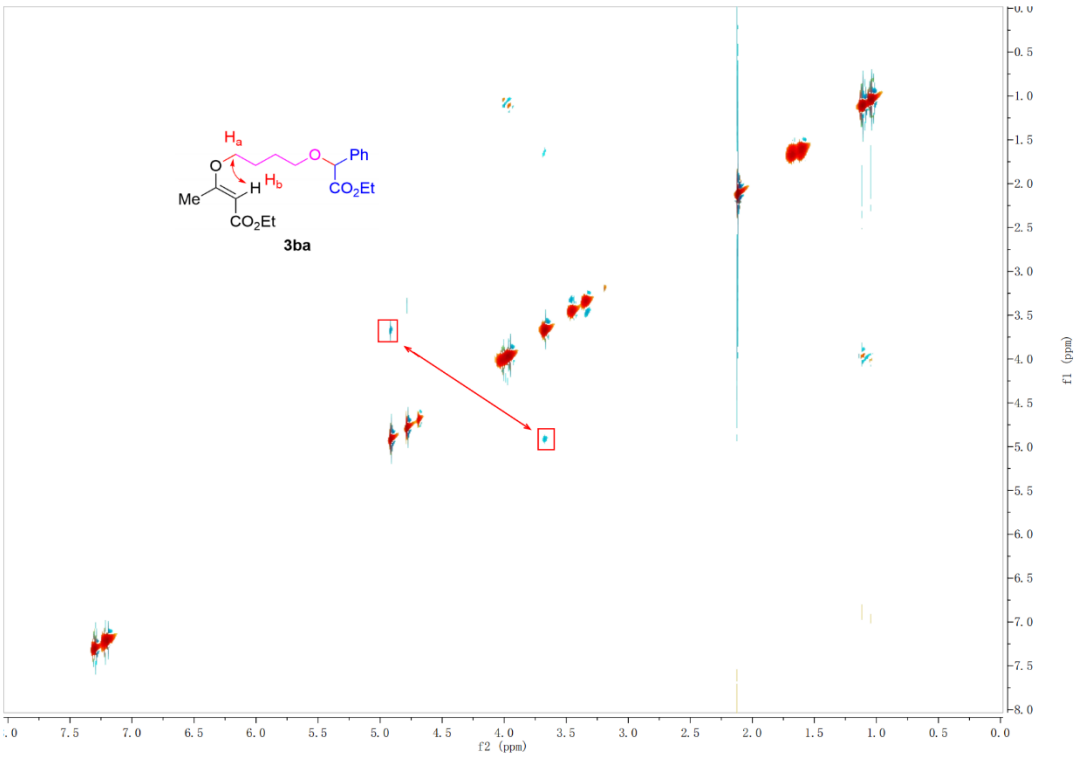
$^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-DMSO) Spectrum of 3aa



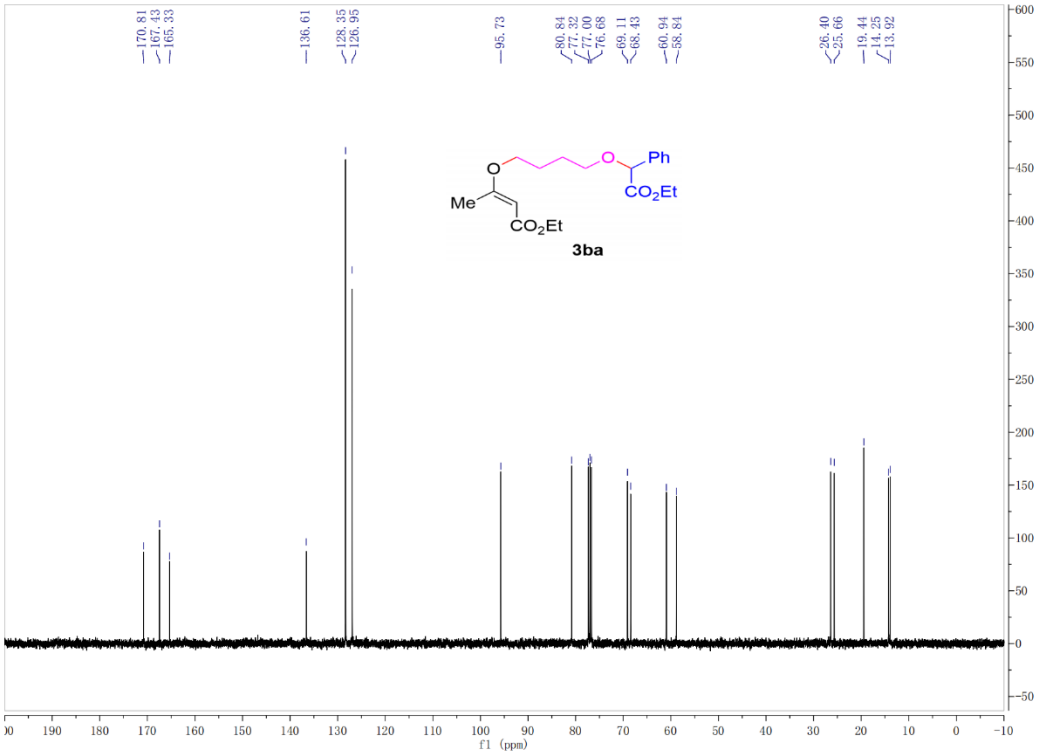
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ba



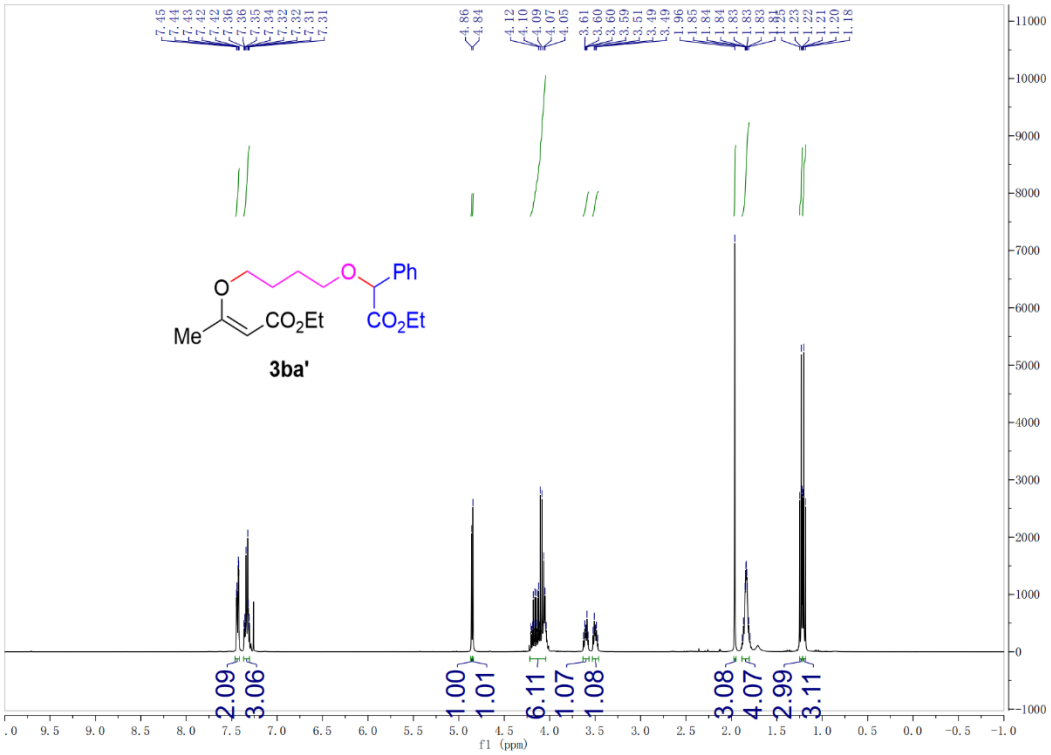
NOESY NMR (400 MHz, $CDCl_3$) Spectrum of 3ba. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



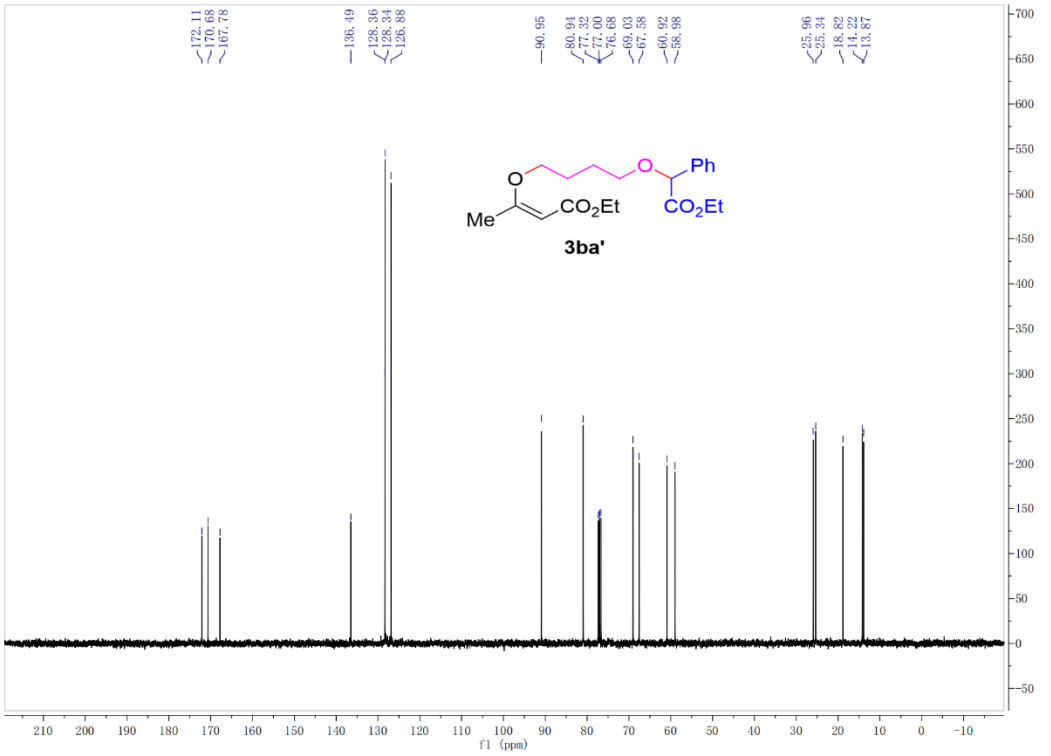
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) Spectrum of 3ba



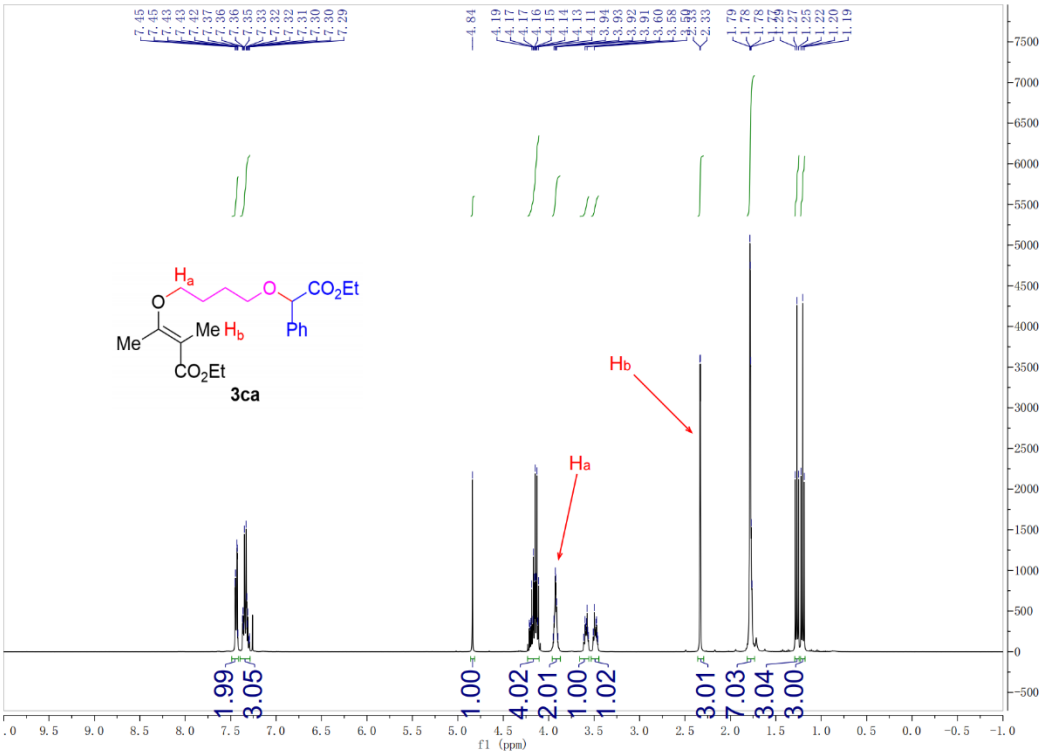
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ba'



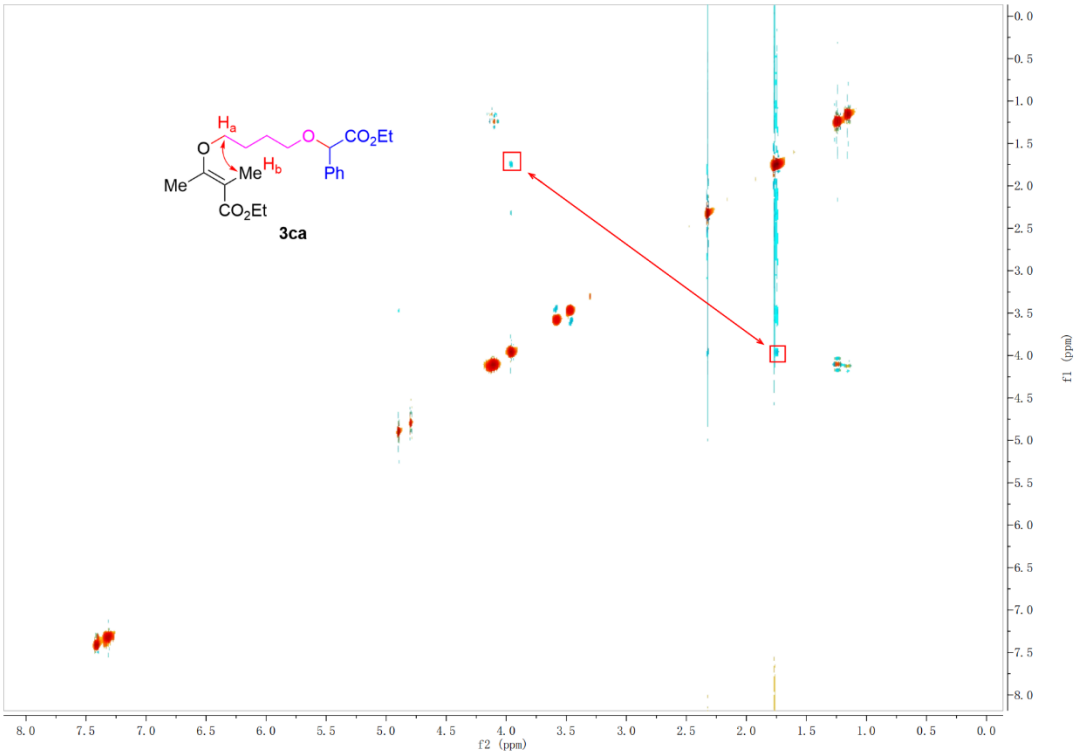
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ba'



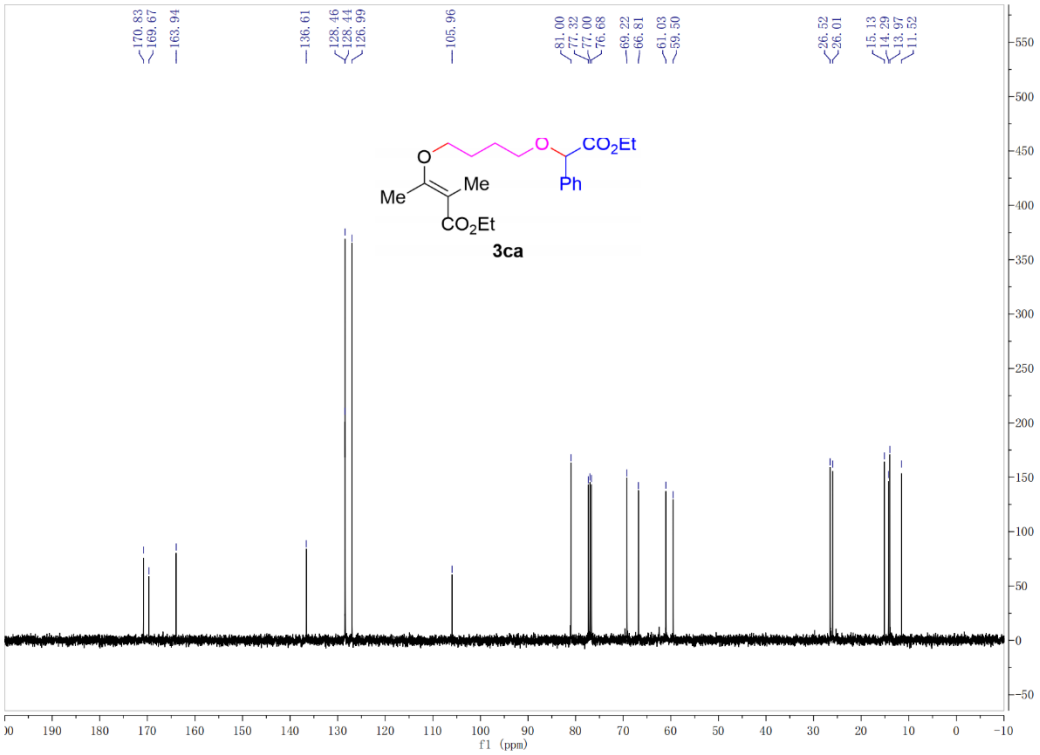
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ca



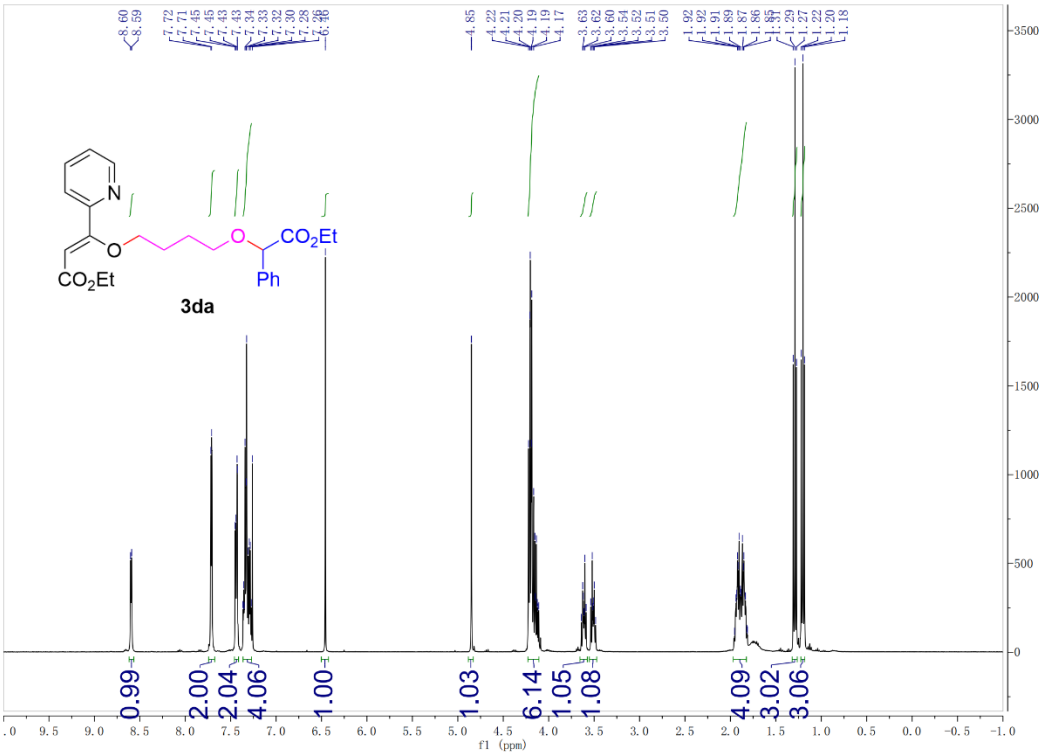
NOESY NMR (400 MHz, $CDCl_3$) Spectrum of 3ca. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



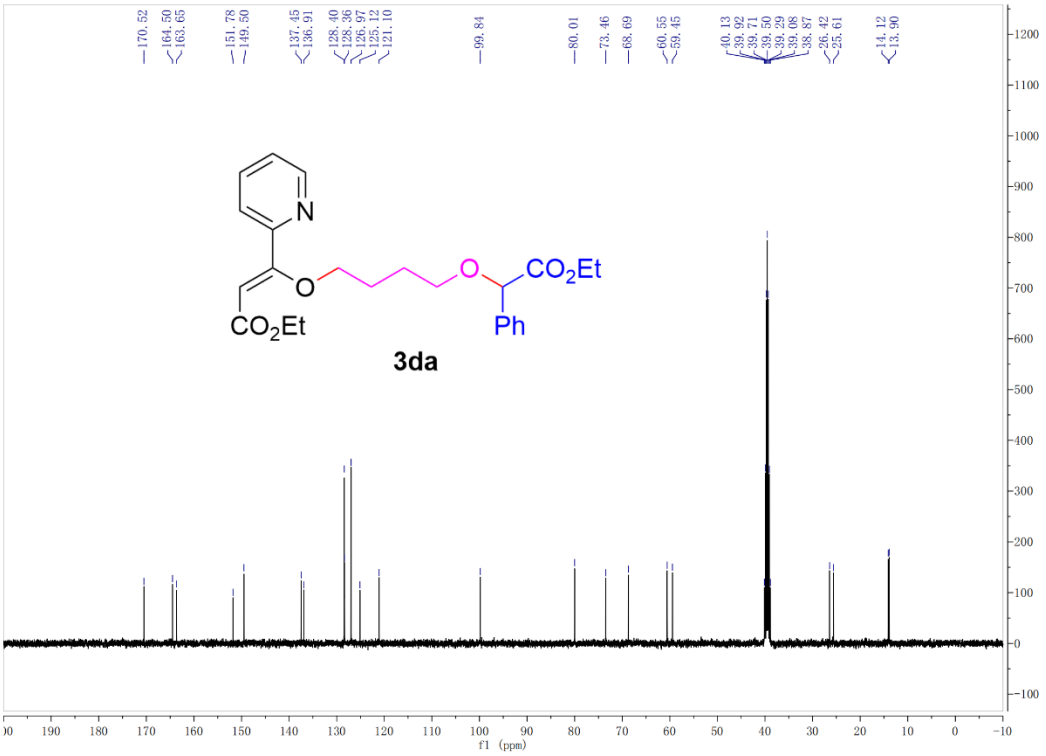
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) Spectrum of 3ca



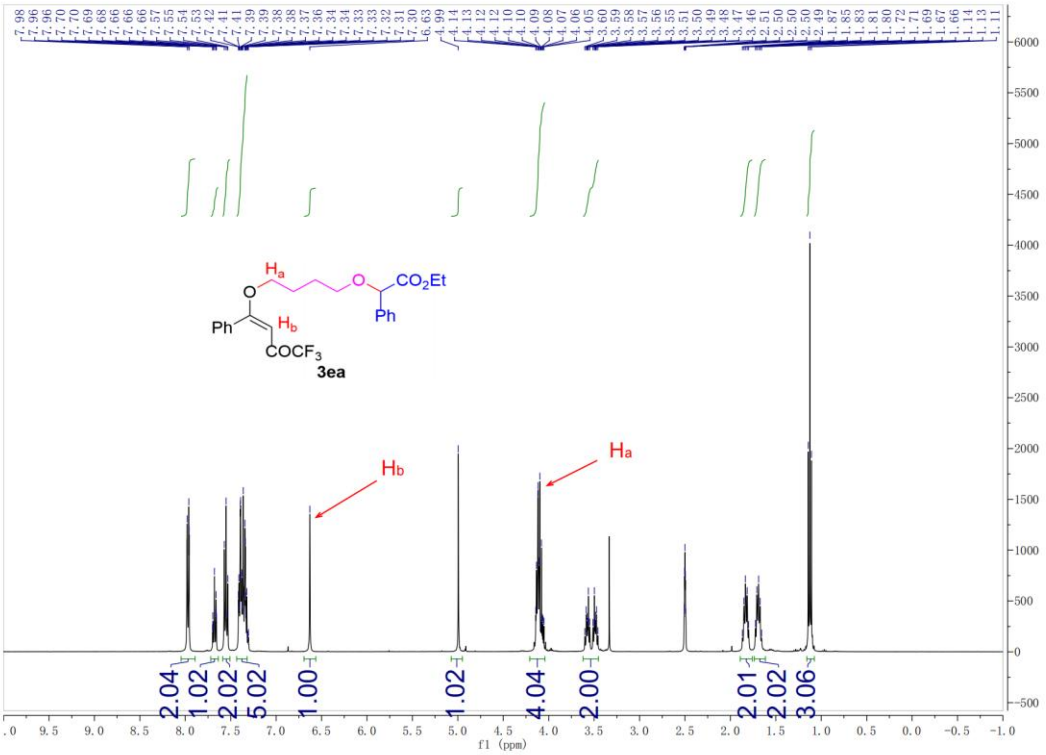
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3da



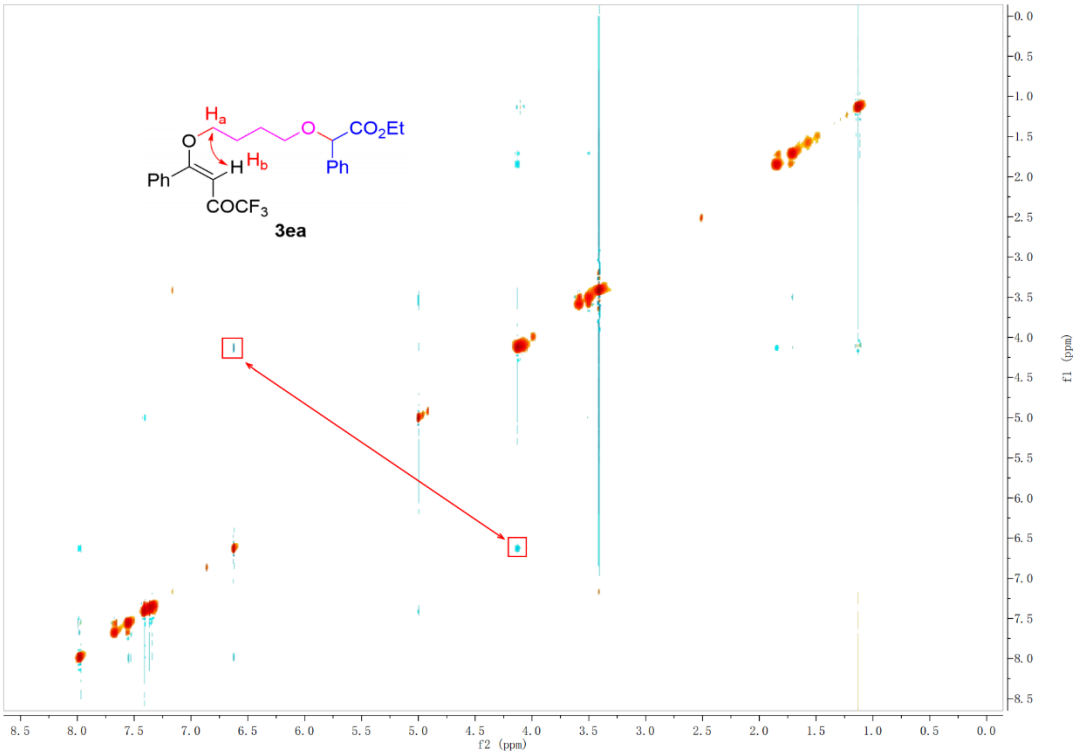
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3da



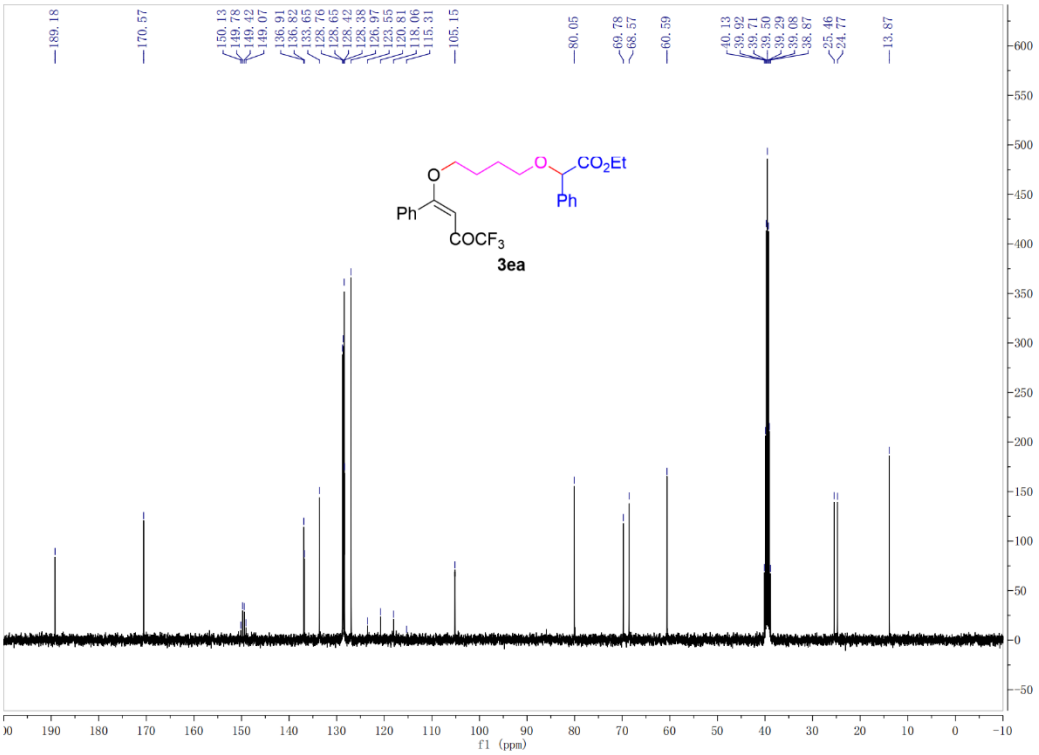
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3ea



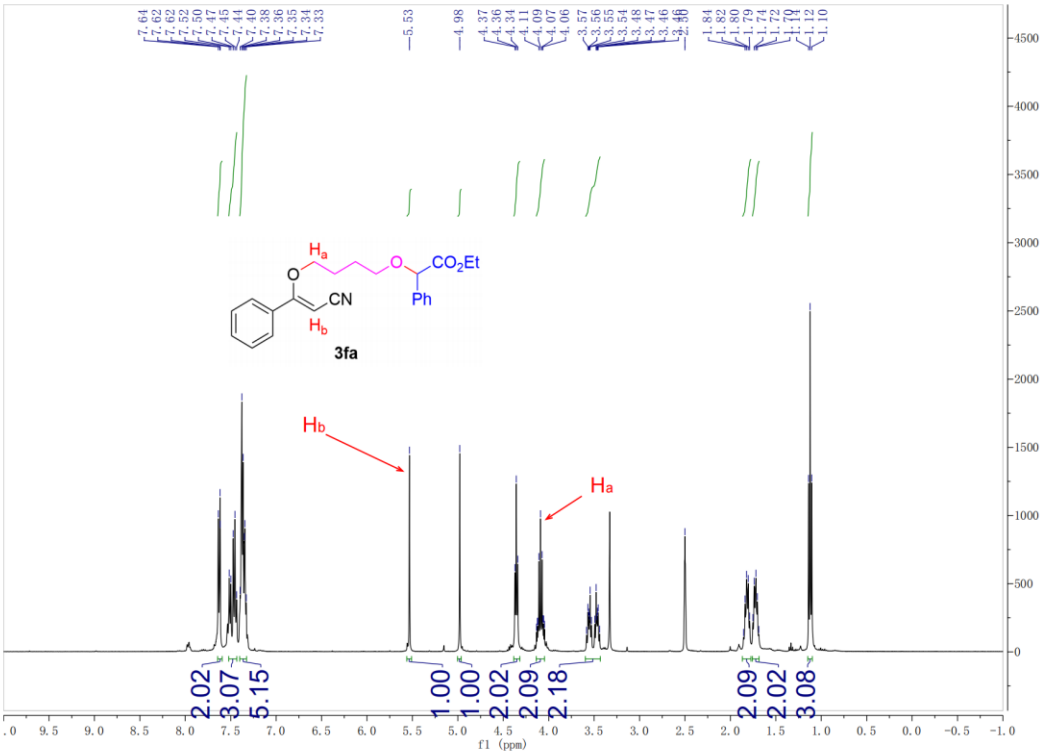
NOESY NMR (400 MHz, d_6-DMSO) Spectrum of 3ea. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



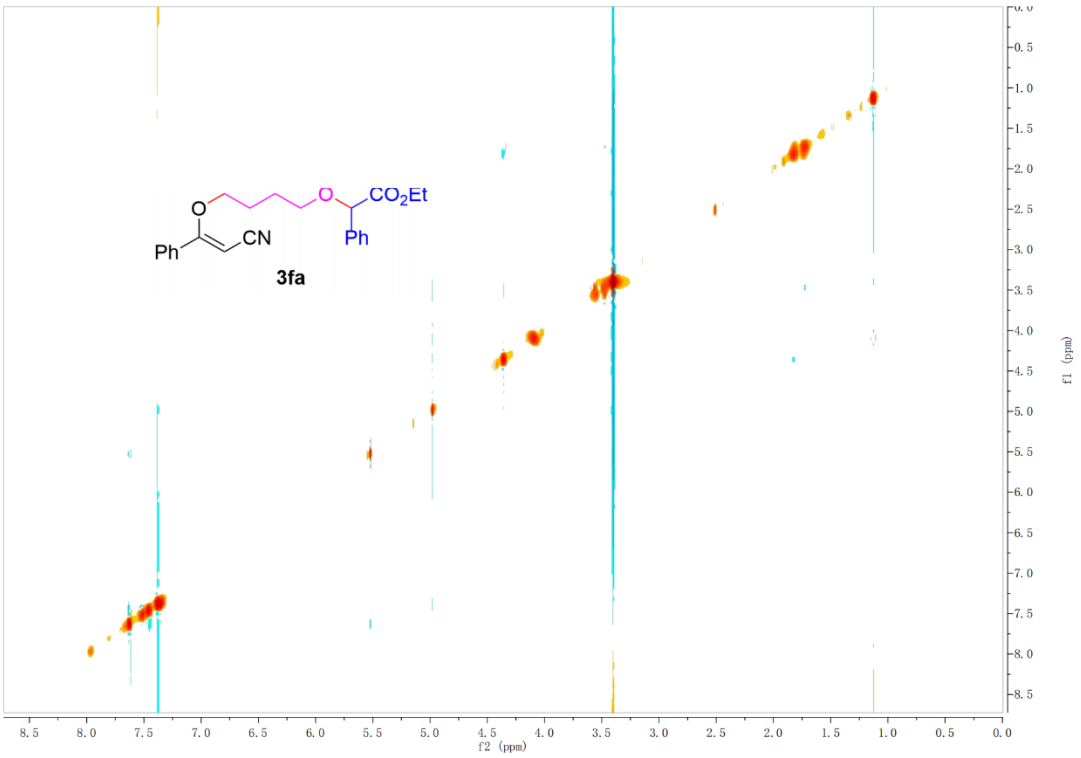
$^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) Spectrum of 3ea



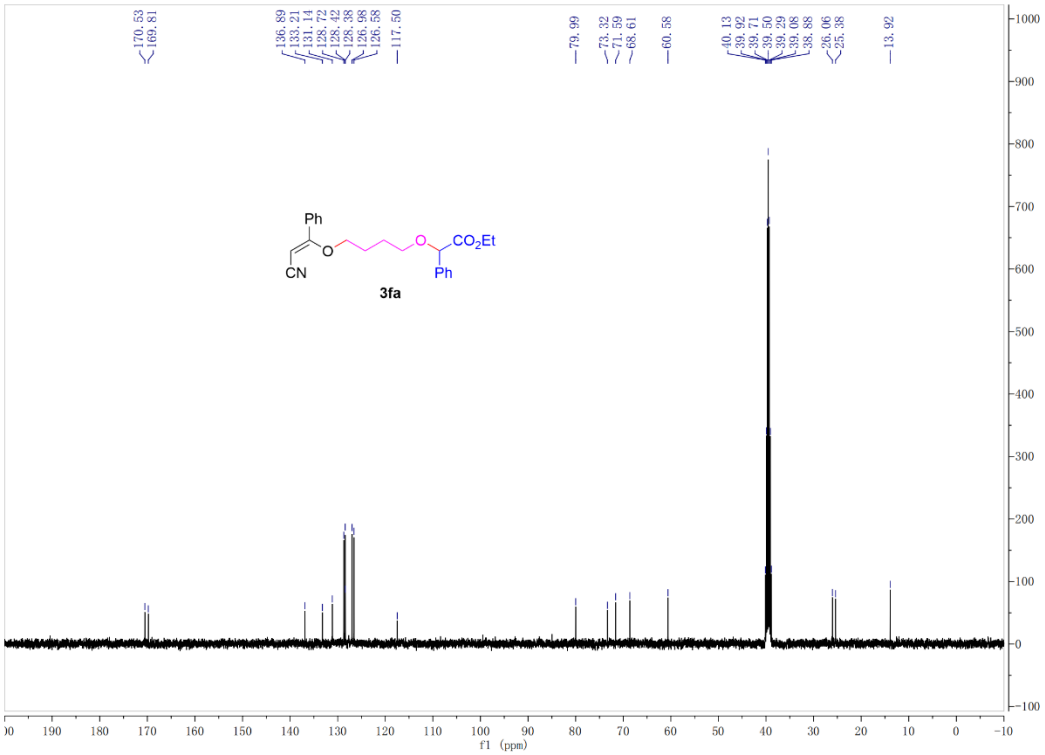
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3fa



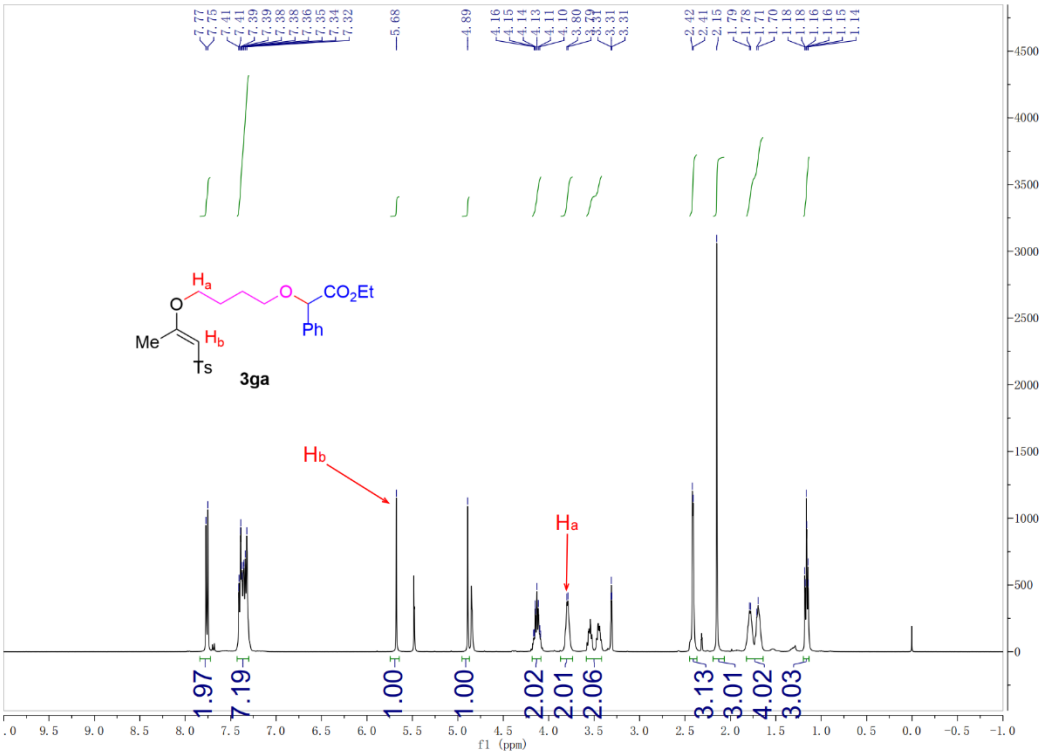
NOESY NMR (400 MHz, d_6-DMSO) Spectrum of 3fa. Based on no NOE effect in H_a and H_b, the stereochemistry is *Z*.



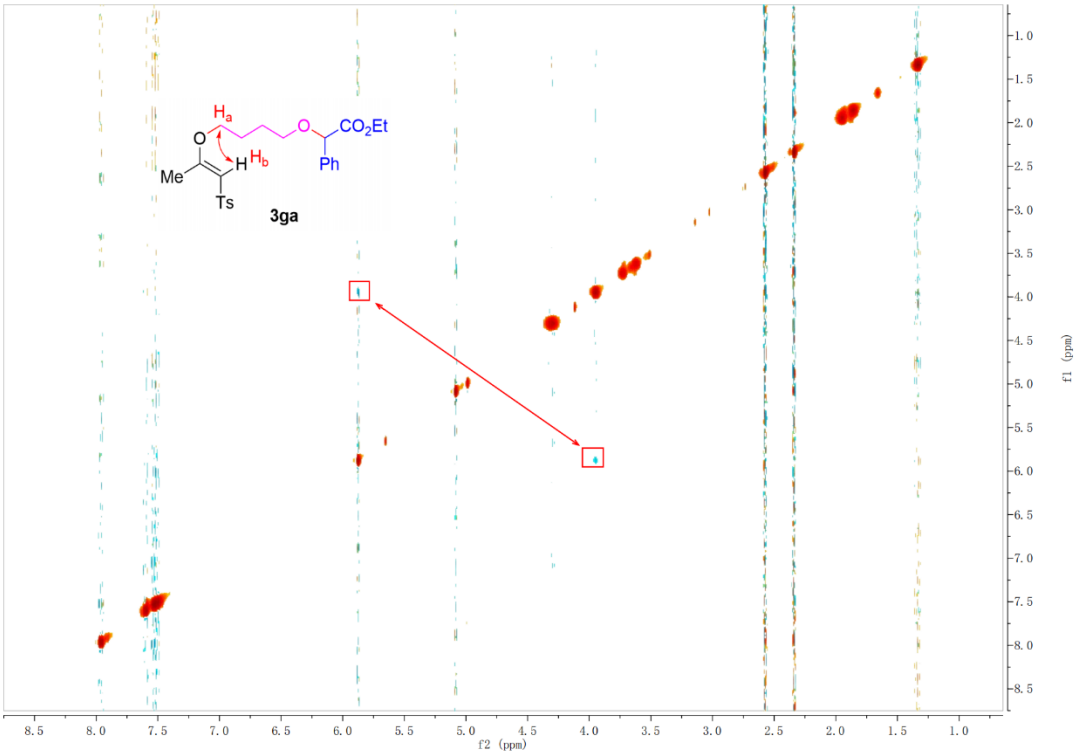
$^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) Spectrum of 3fa



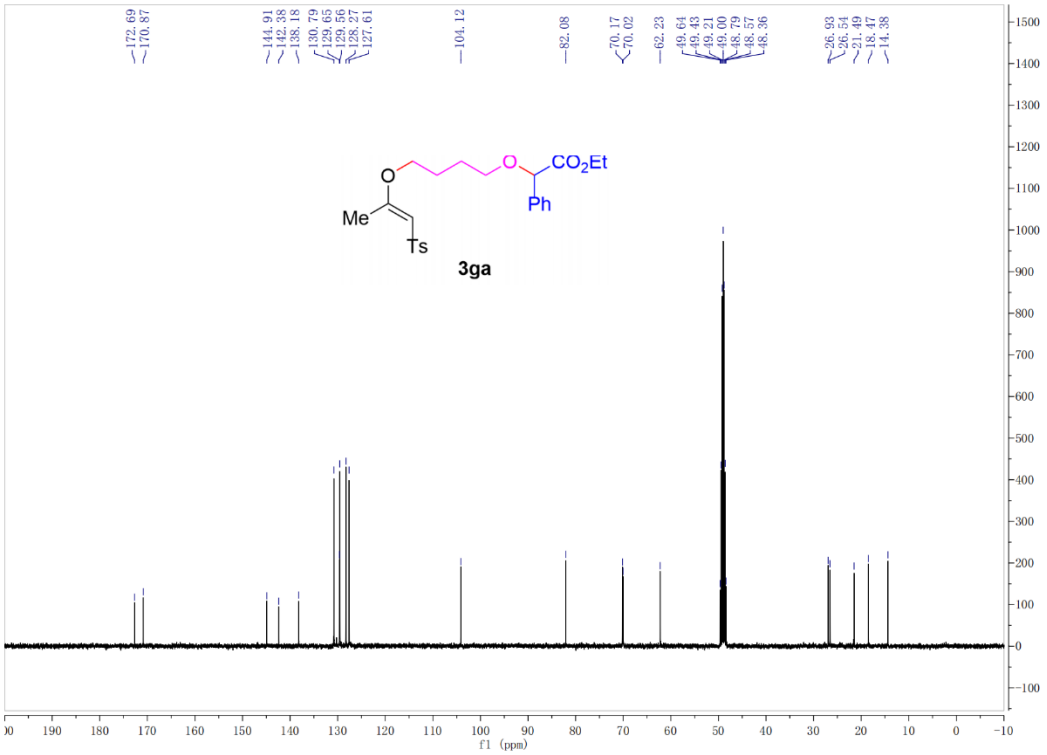
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3ga



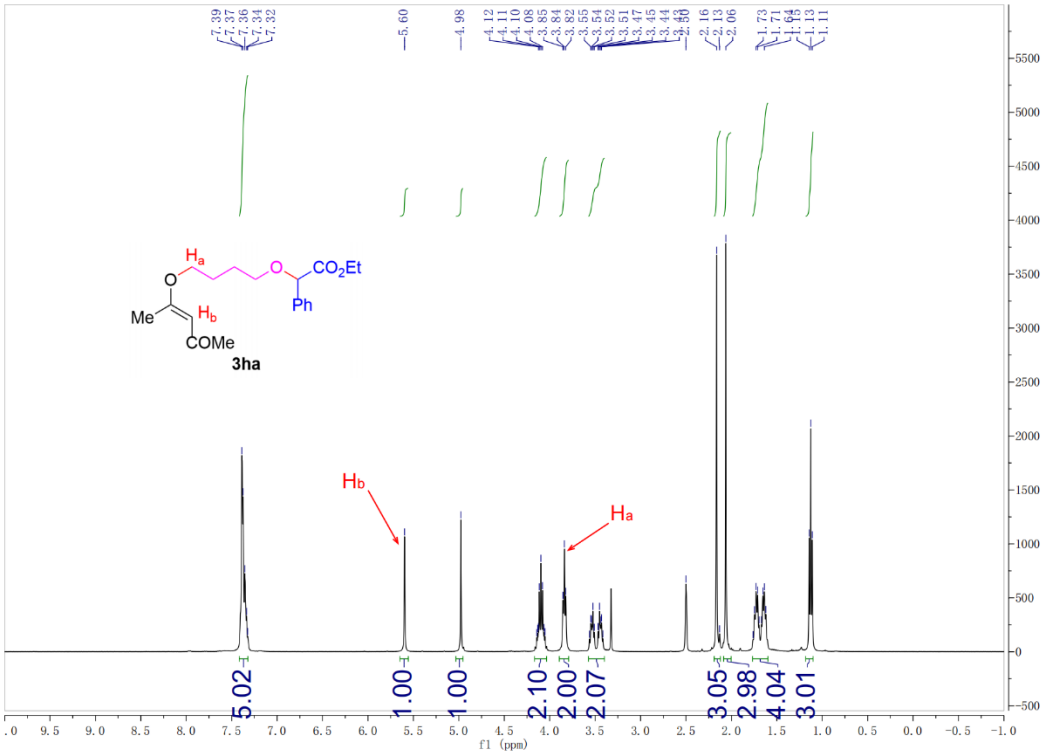
NOESY NMR (400 MHz, CD_3OD) Spectrum of 3ga. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



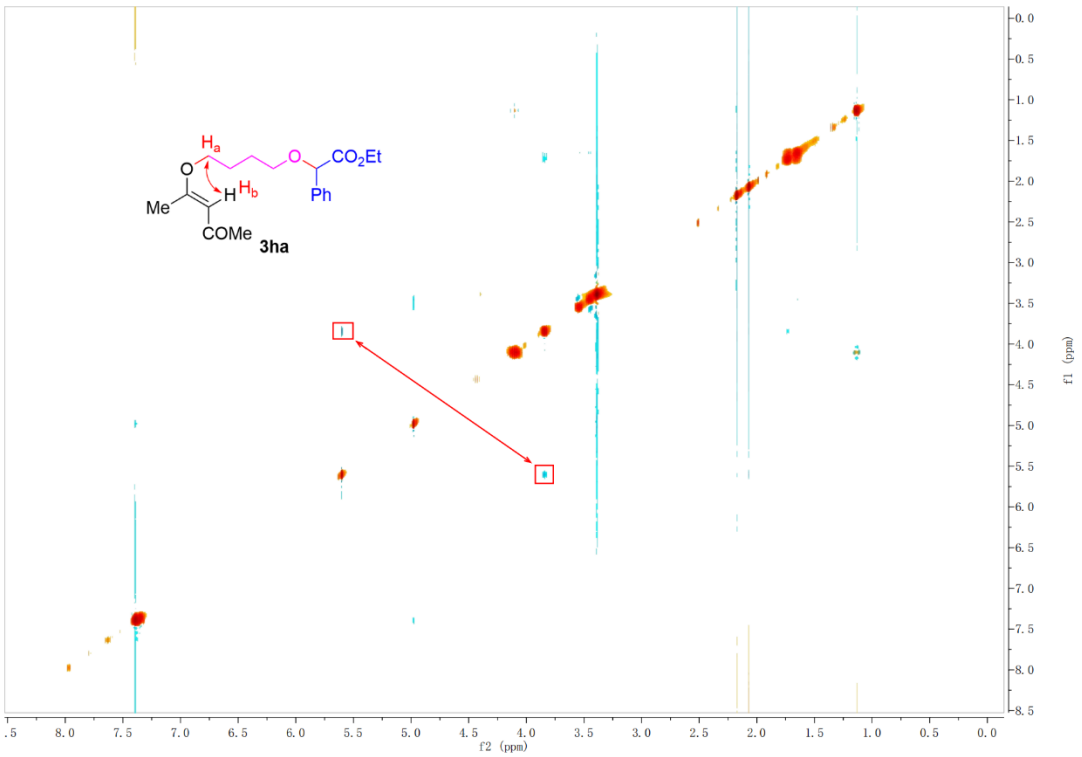
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) Spectrum of 3ga



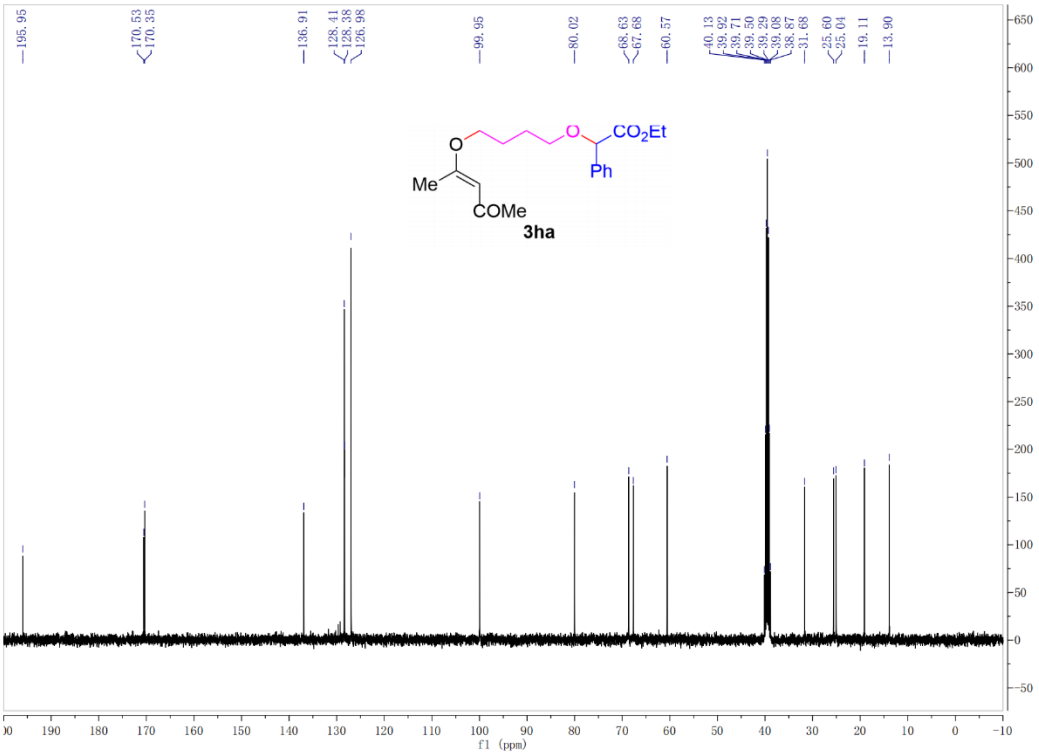
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3ha



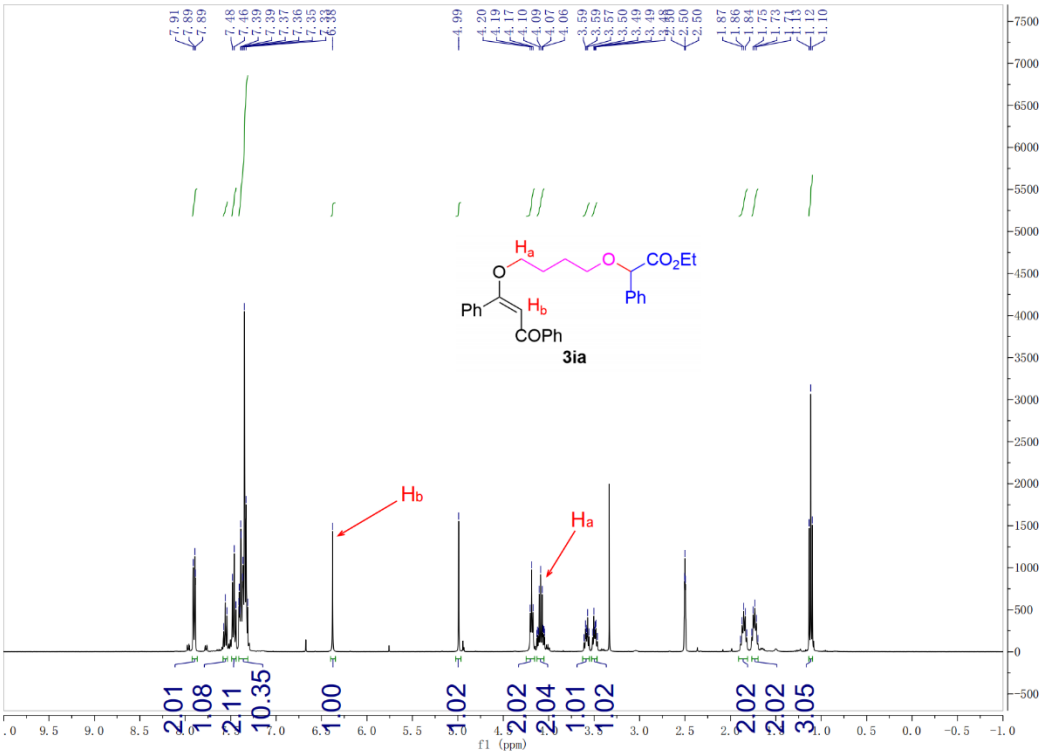
NOESY NMR (400 MHz, d_6-DMSO) Spectrum of 3ha. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



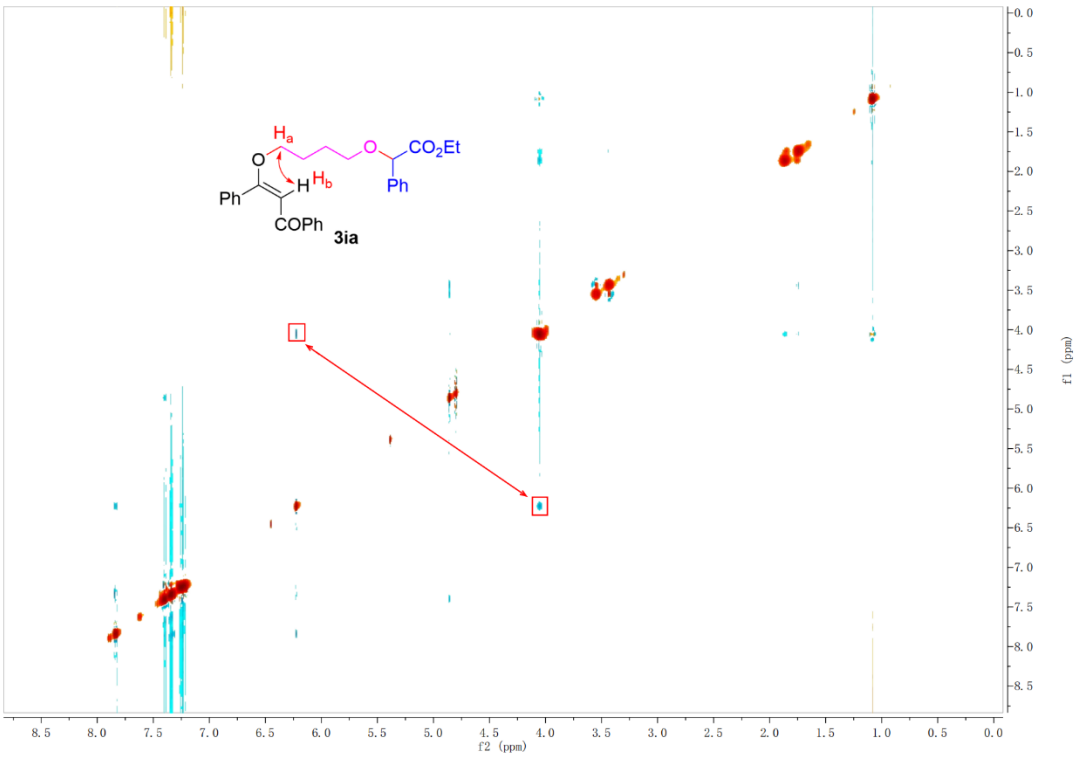
$^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) Spectrum of 3ha



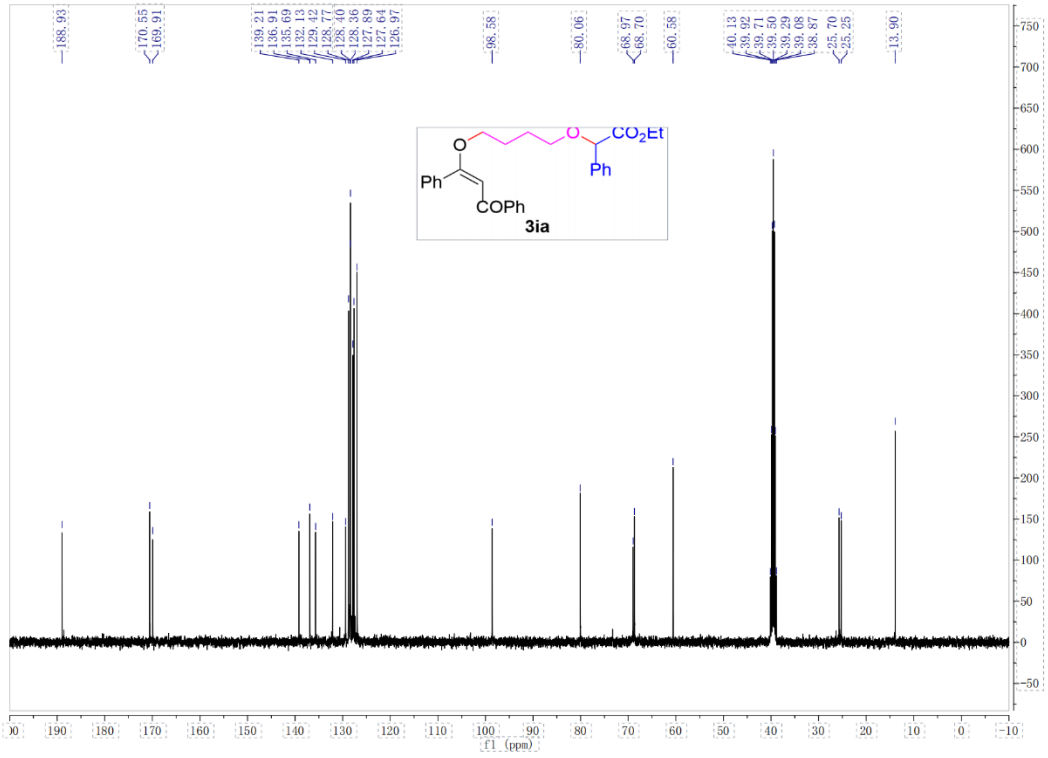
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3ia



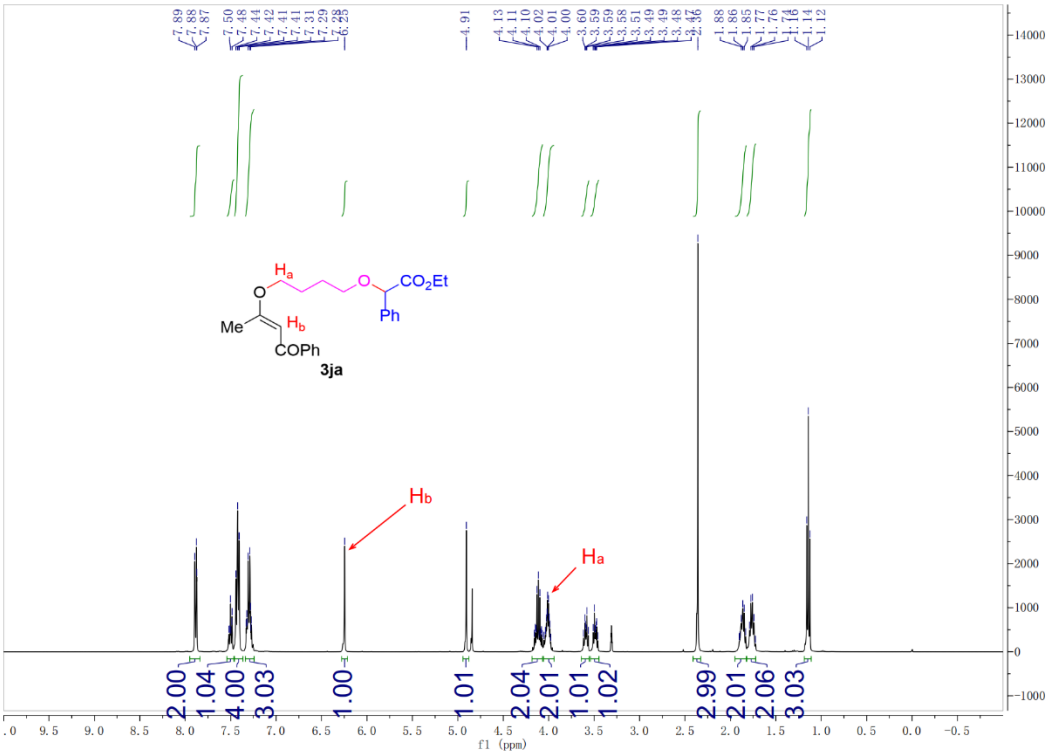
NOESY NMR (400 MHz, d_6-DMSO) Spectrum of 3ia. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



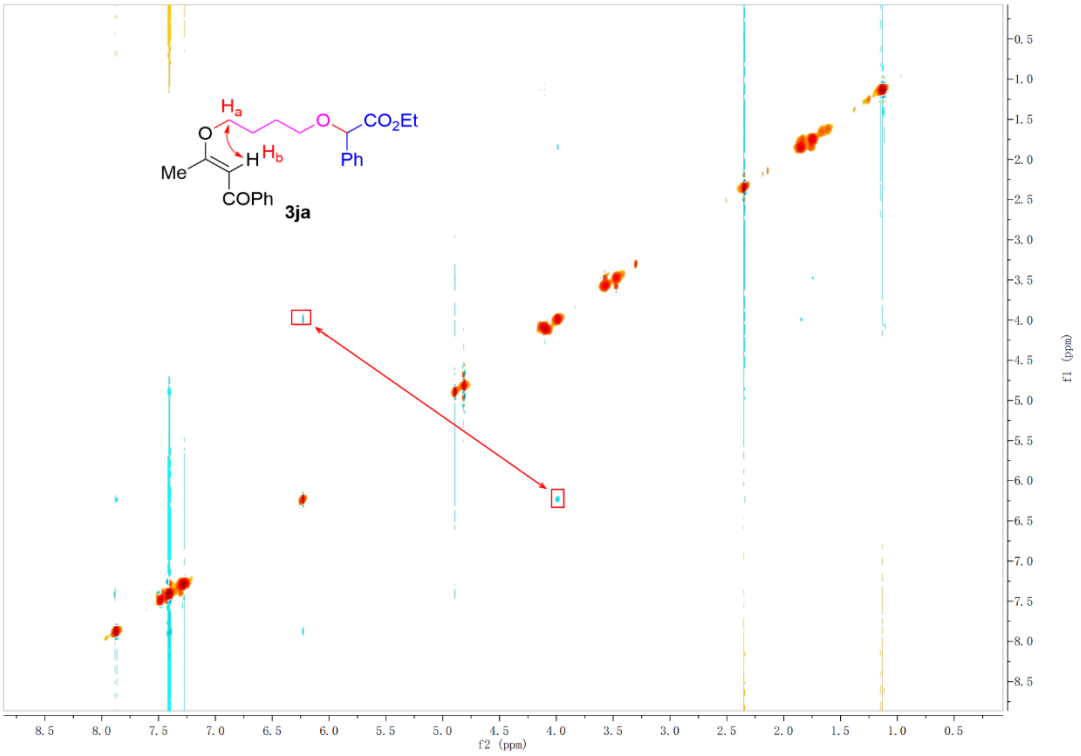
$^{13}C\{^{1}H\}$ NMR (100 MHz, d_6-DMSO) Spectrum of 3ia



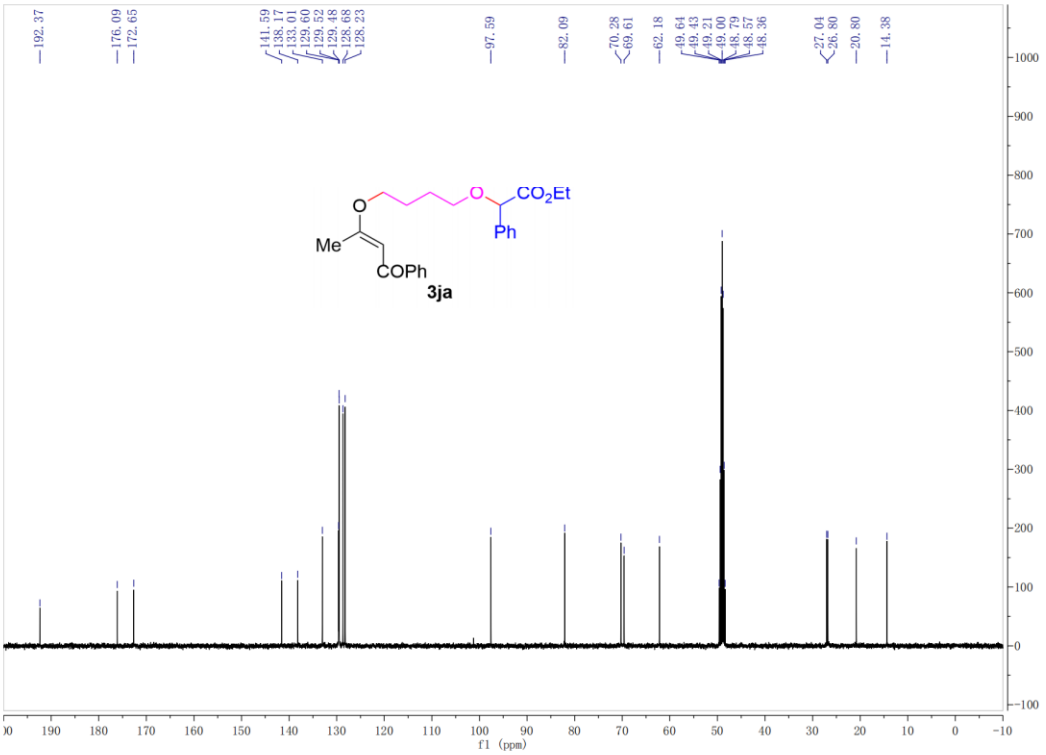
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3ja



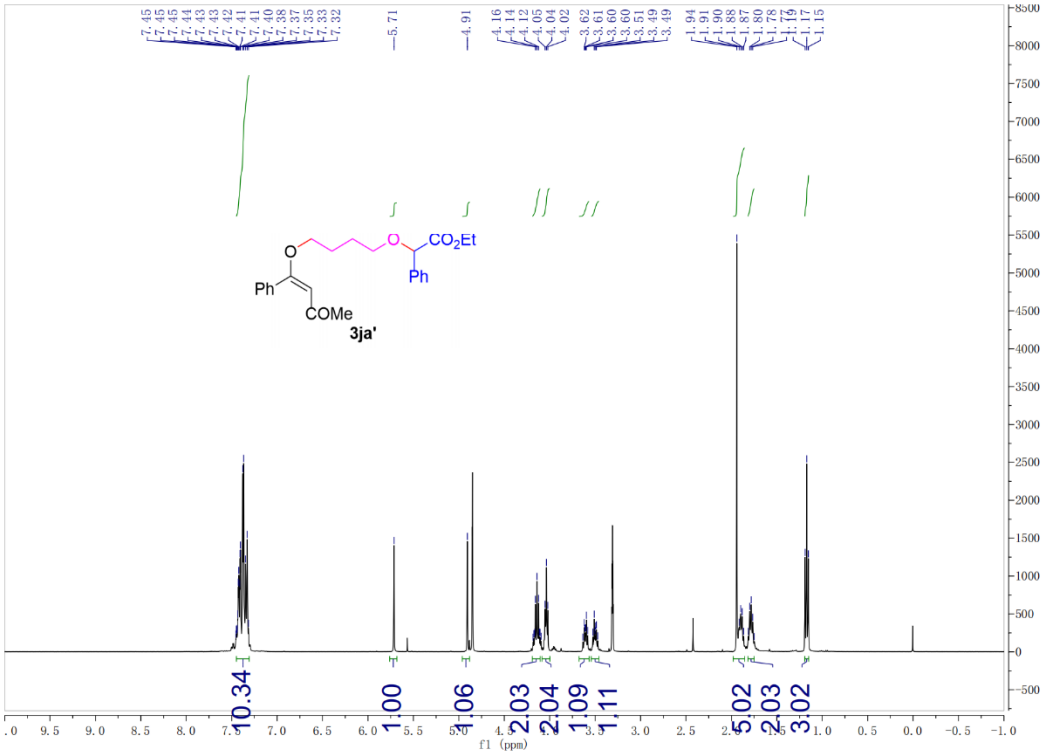
NOESY NMR (400 MHz, CD_3OD) Spectrum of 3ja. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



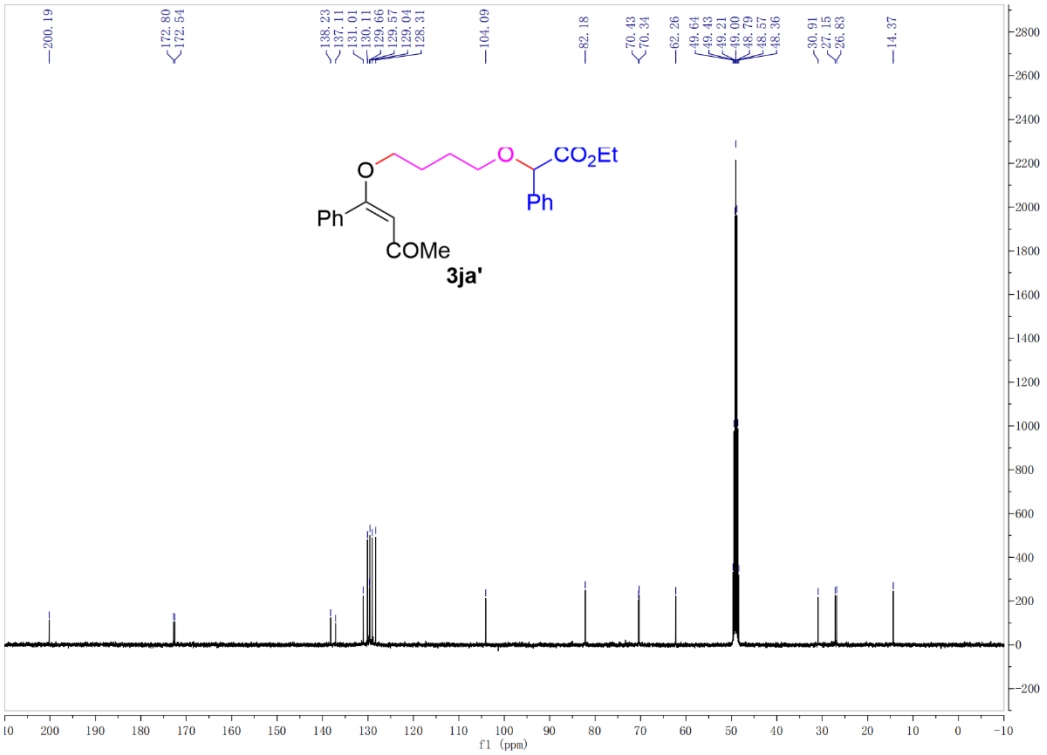
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) Spectrum of 3ja



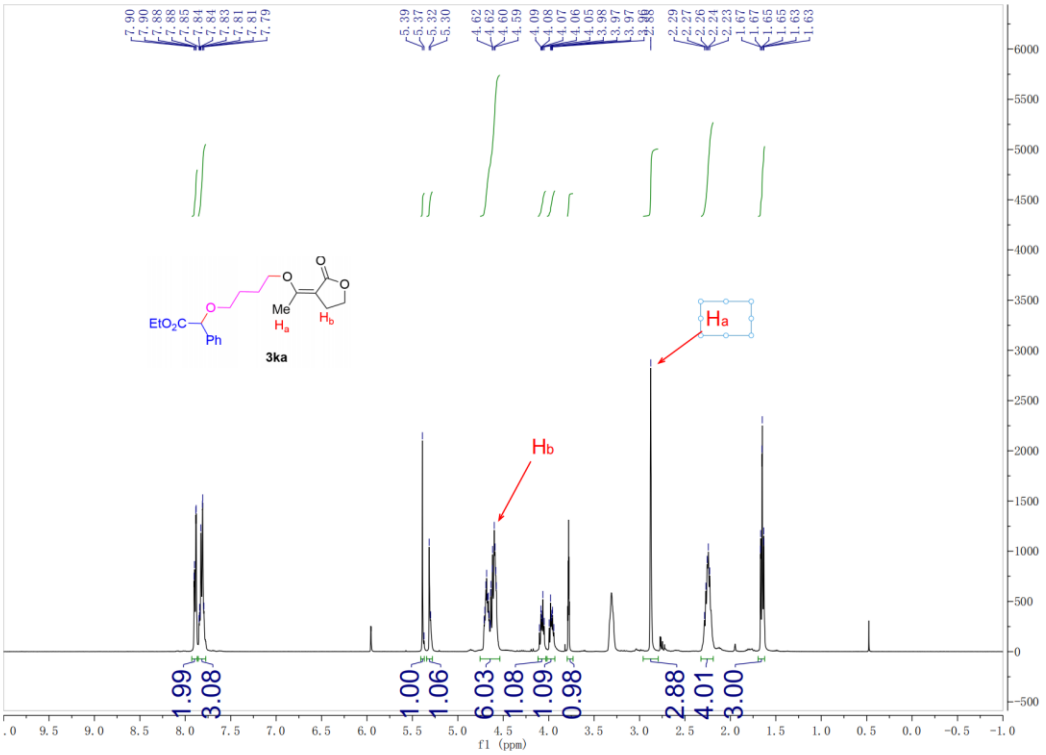
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3ja'



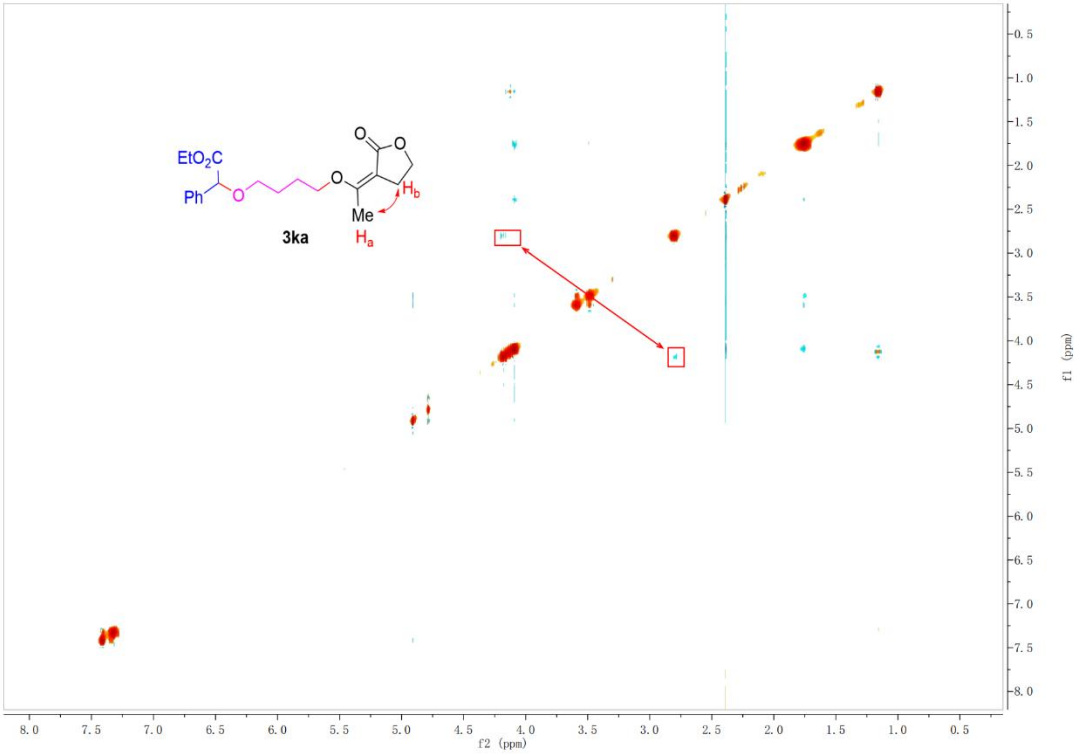
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3ja'



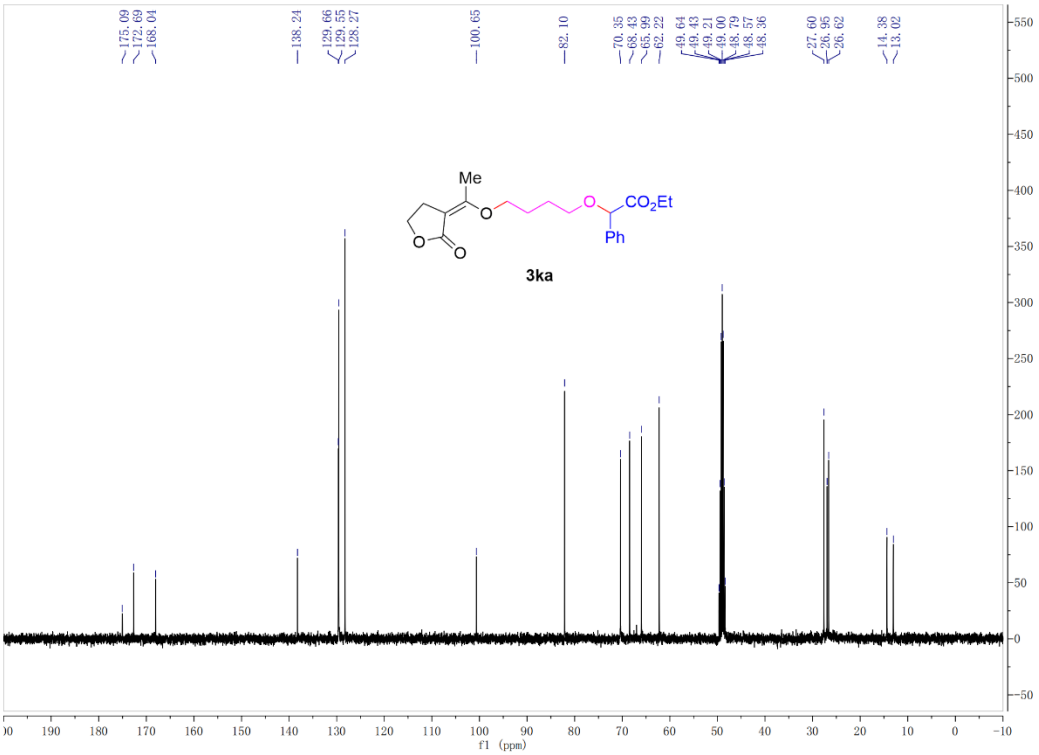
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3ka



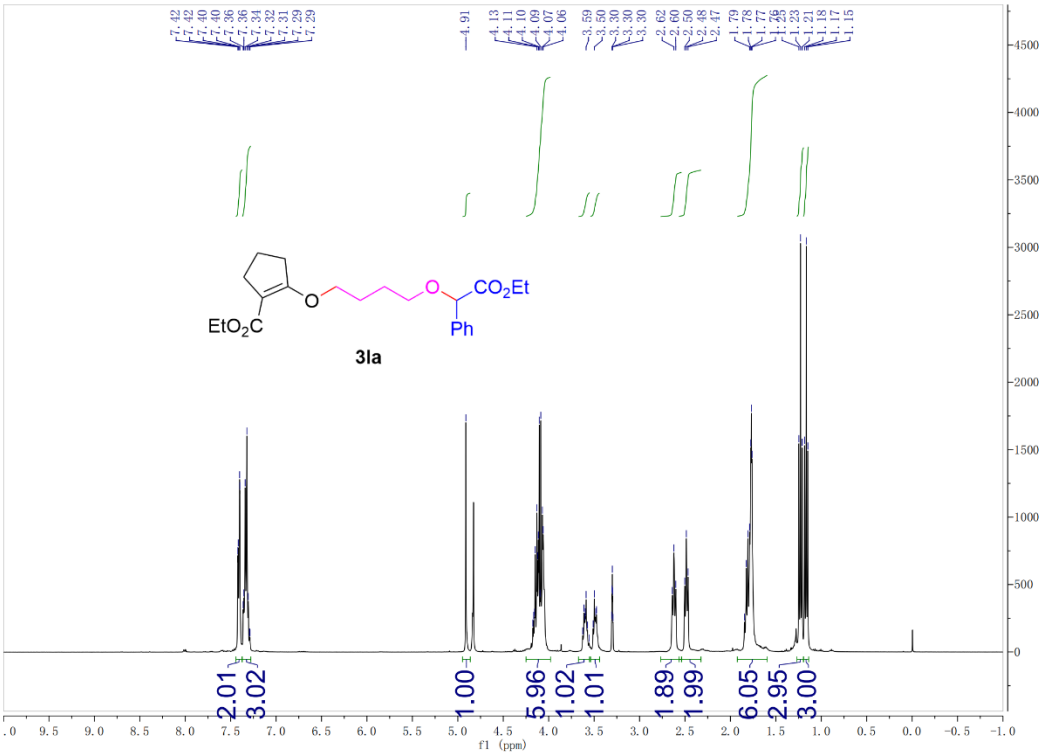
NOESY NMR (400 MHz, CD_3OD) Spectrum of 3ka. Based on the obvious NOE effect in H_a and H_b, the stereochemistry is *E*.



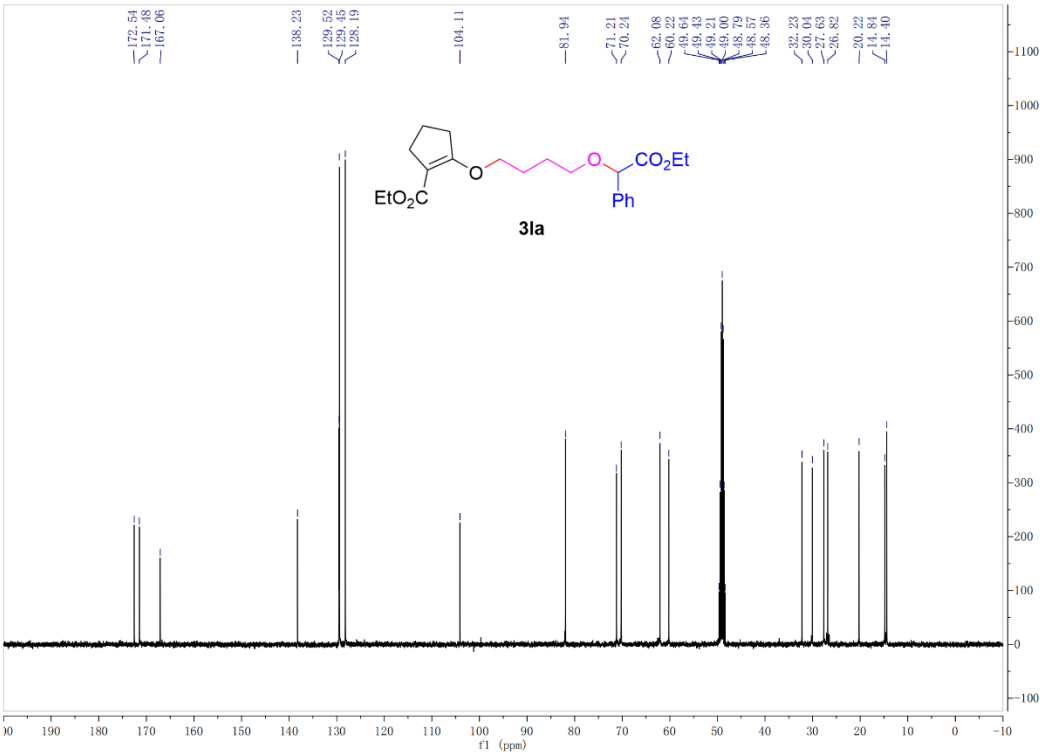
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) Spectrum of 3ka



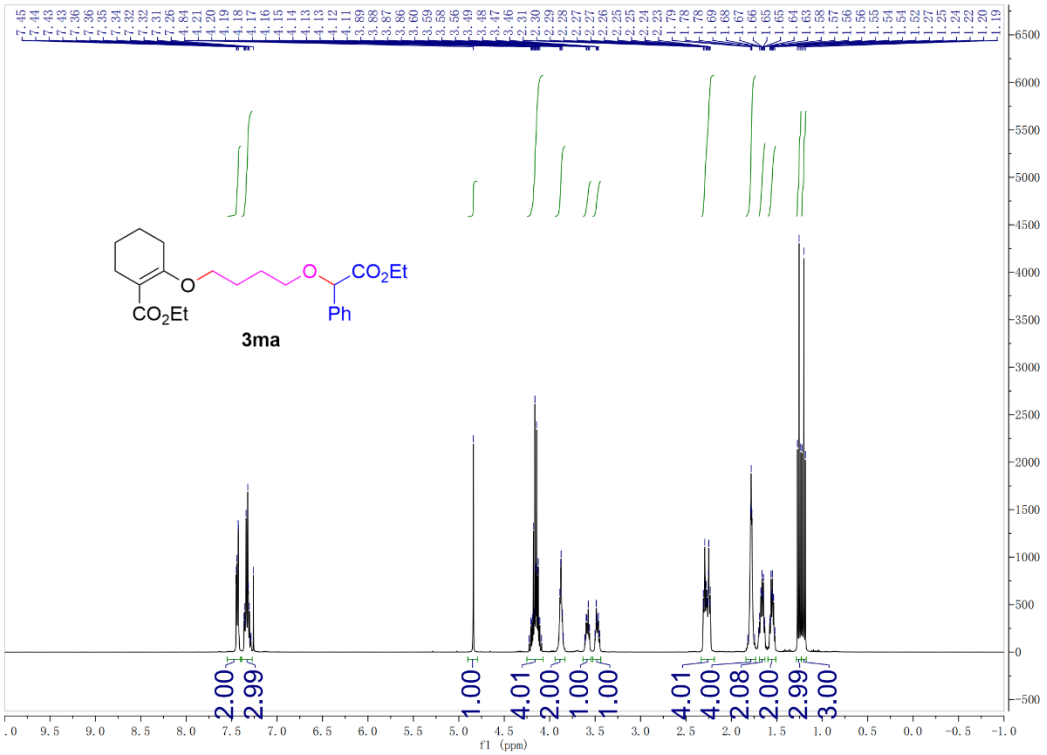
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3la



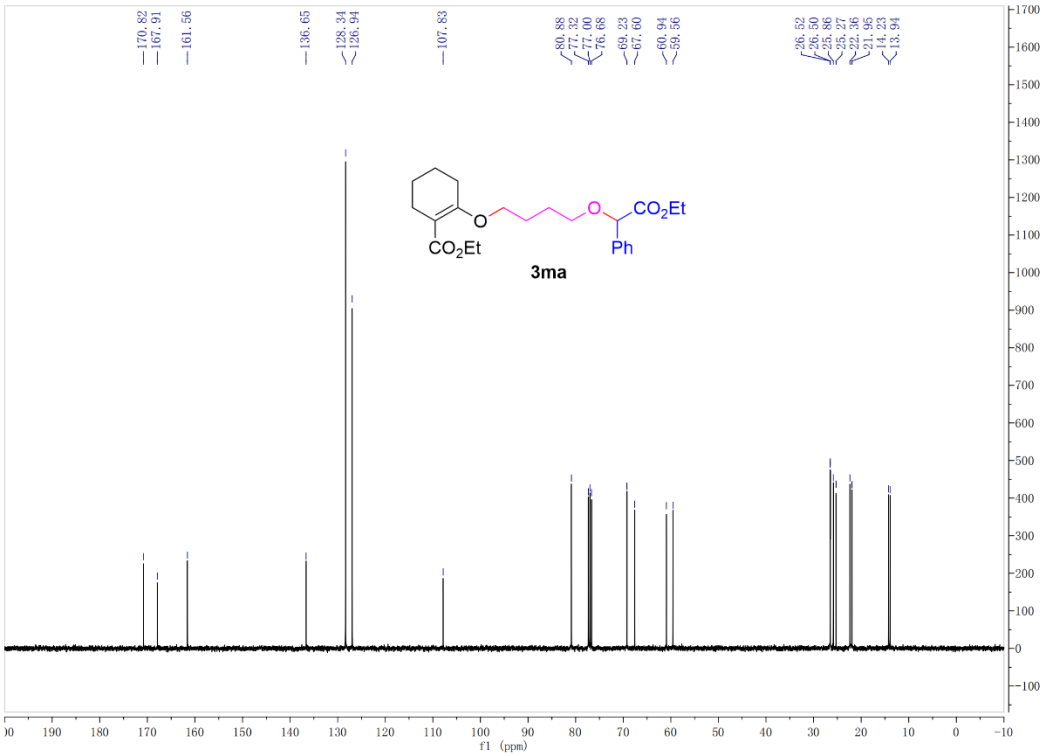
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3la



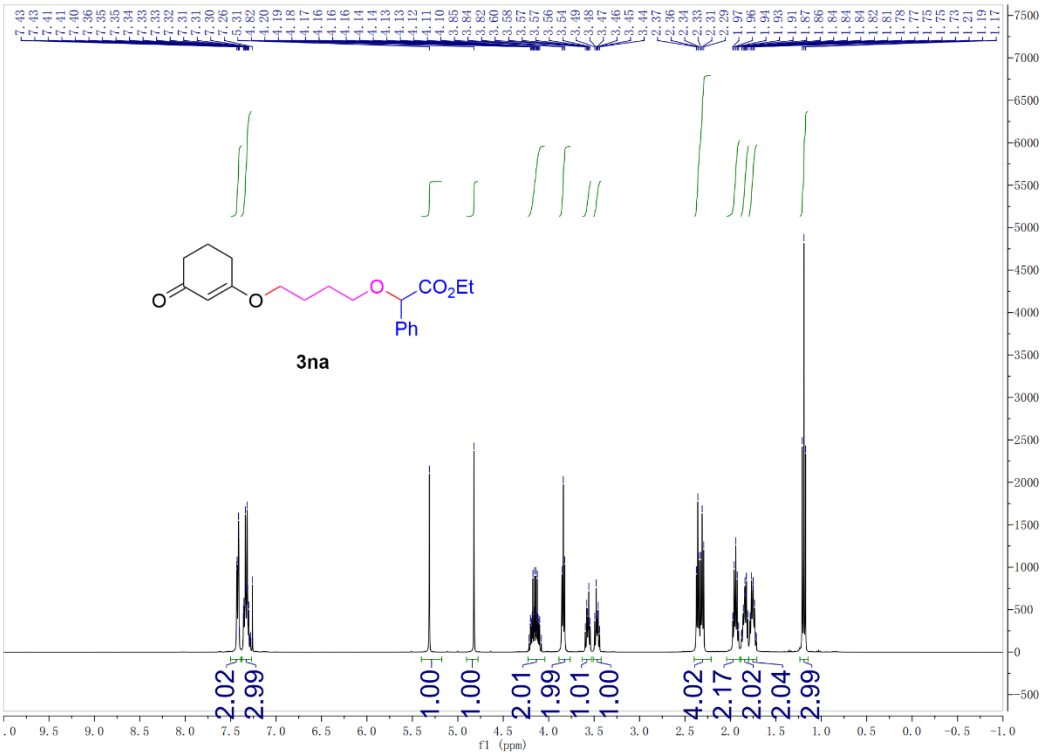
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ma



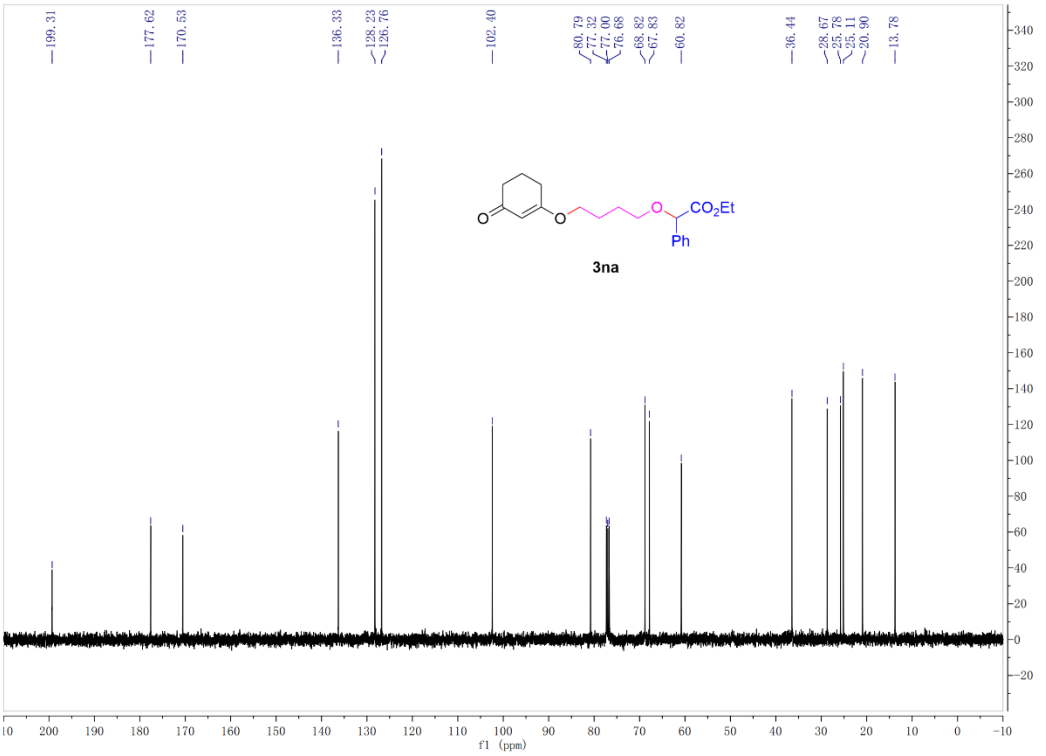
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ma



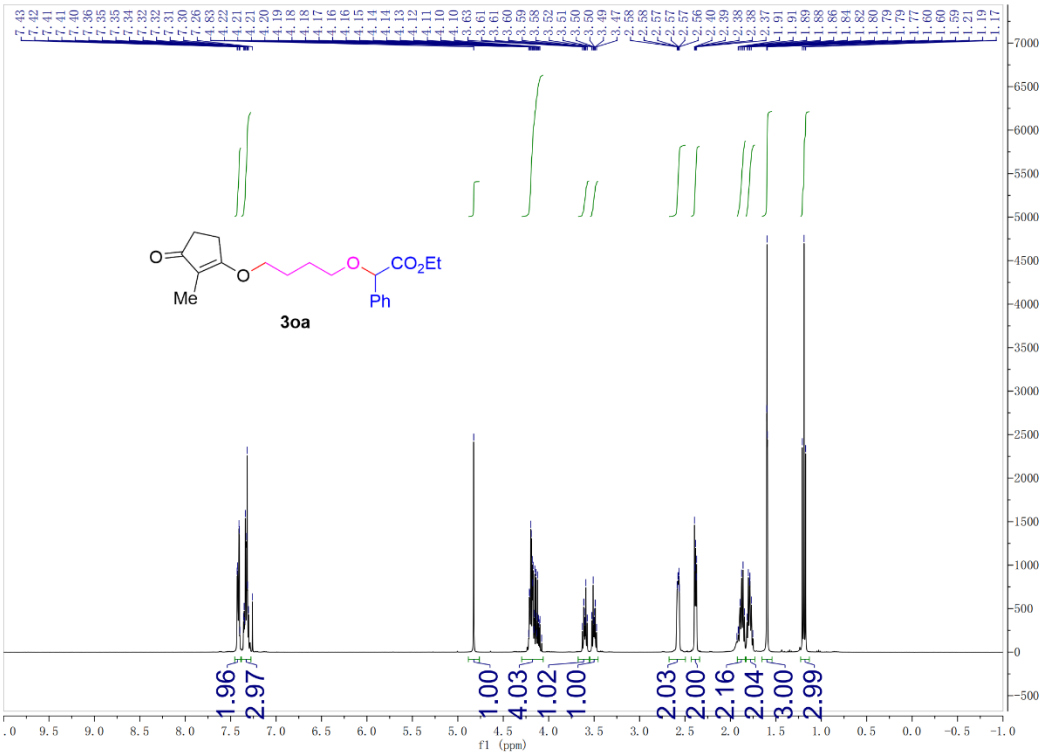
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3na



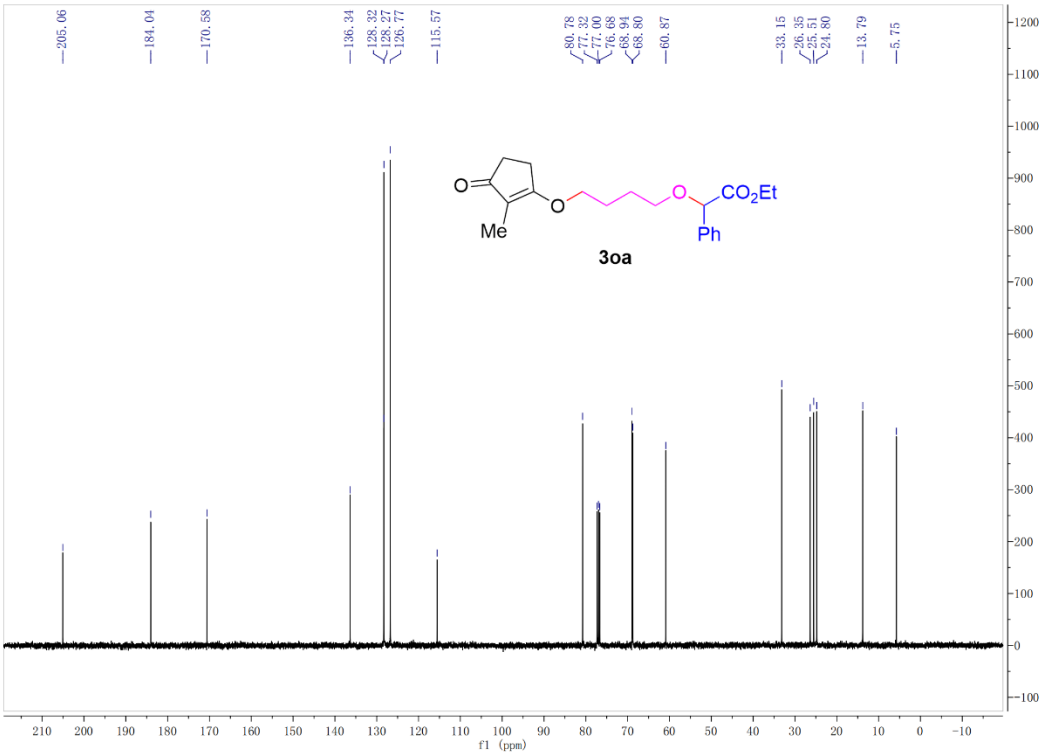
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3na



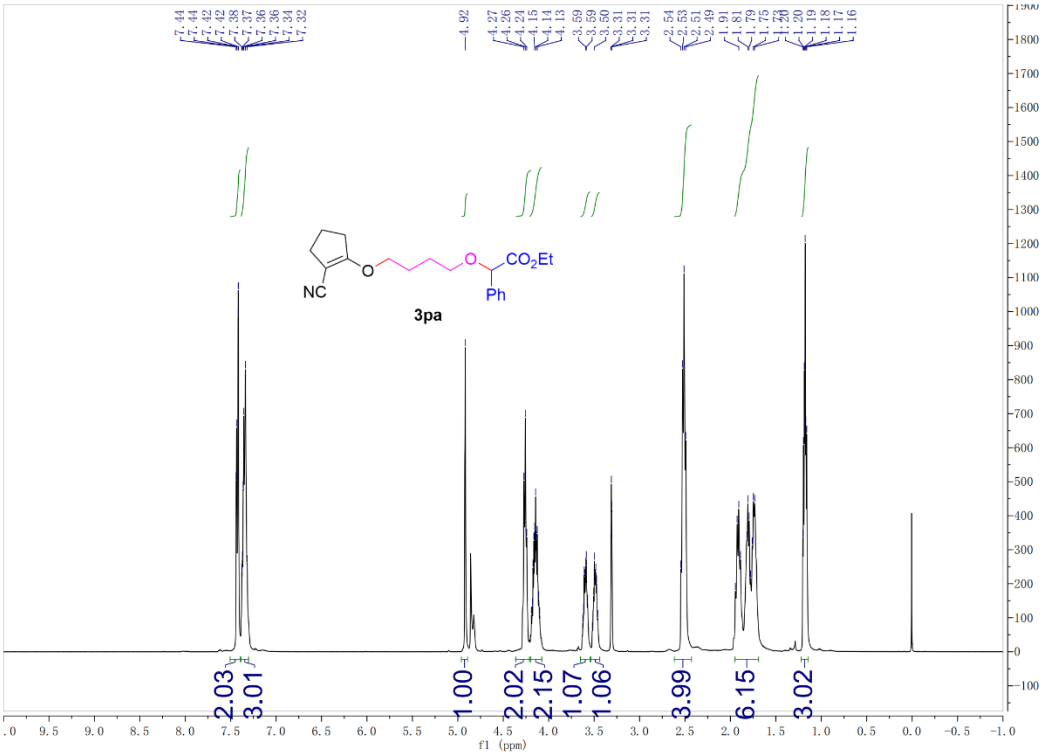
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3oa



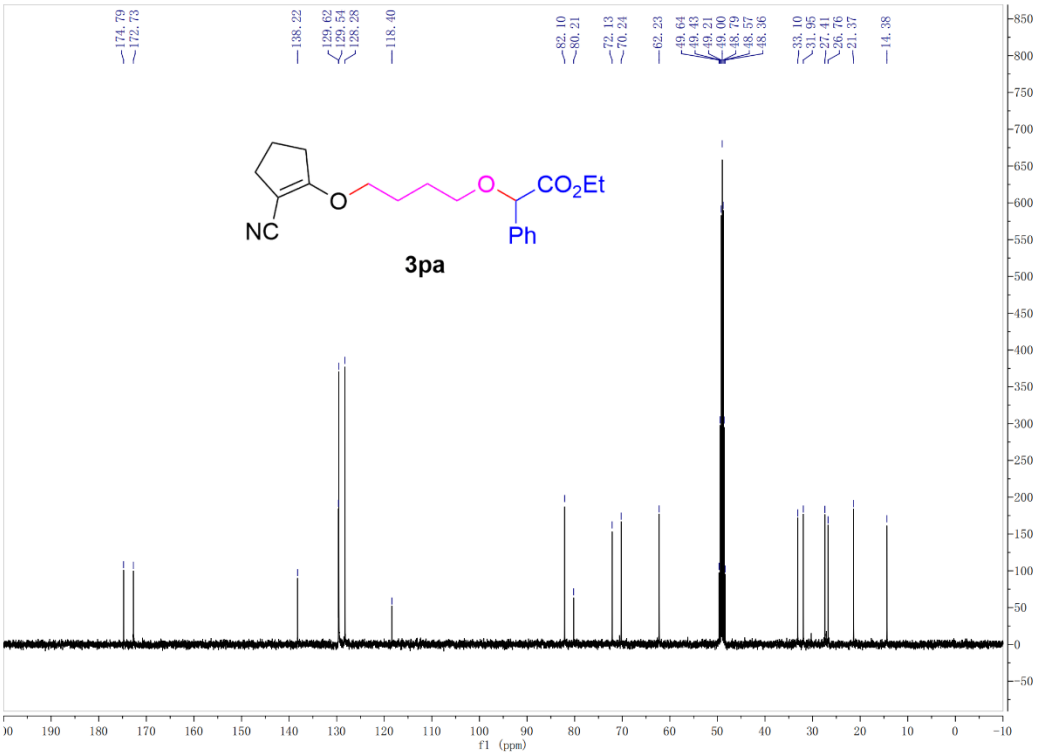
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3oa



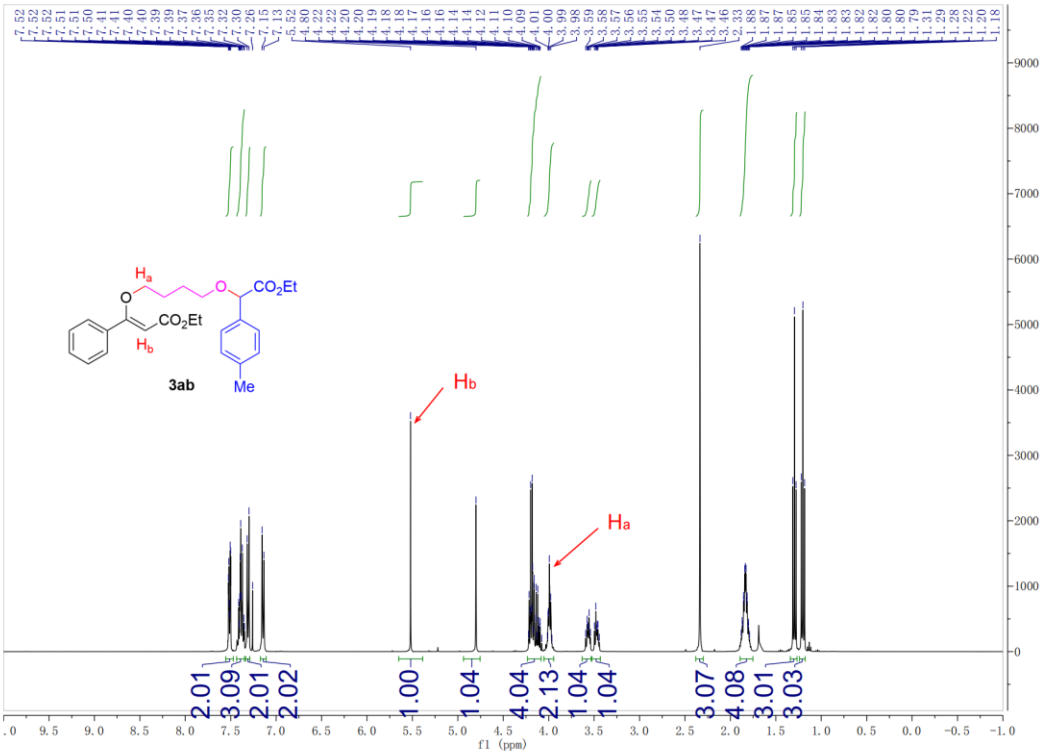
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3pa



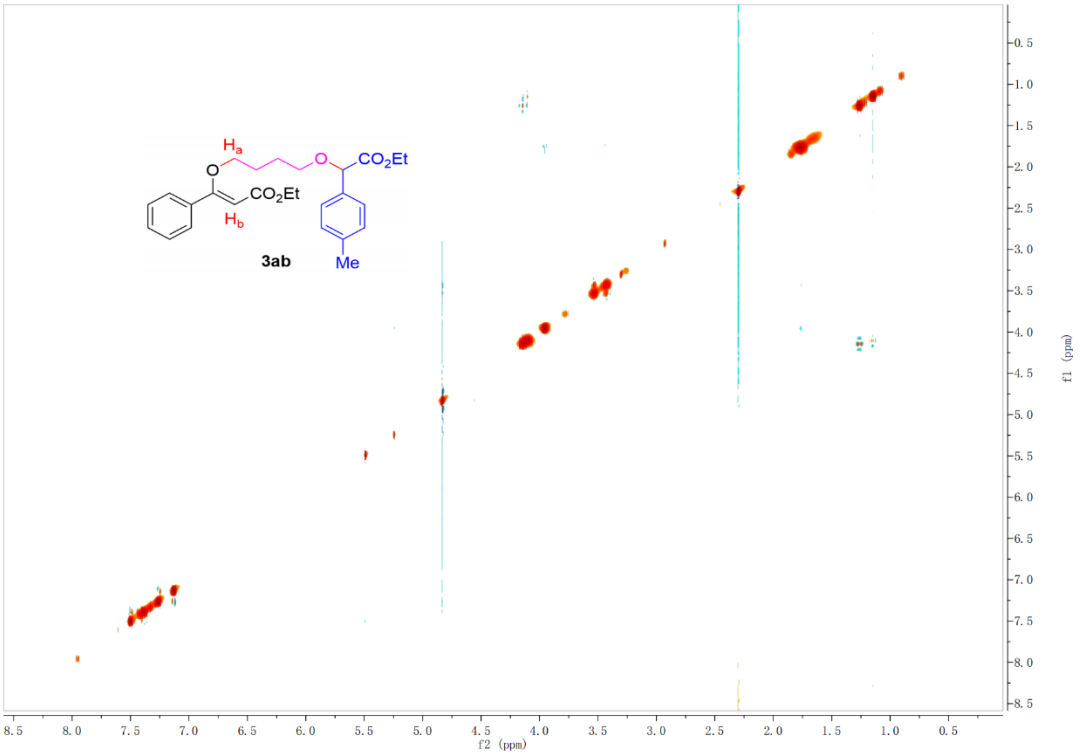
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3pa



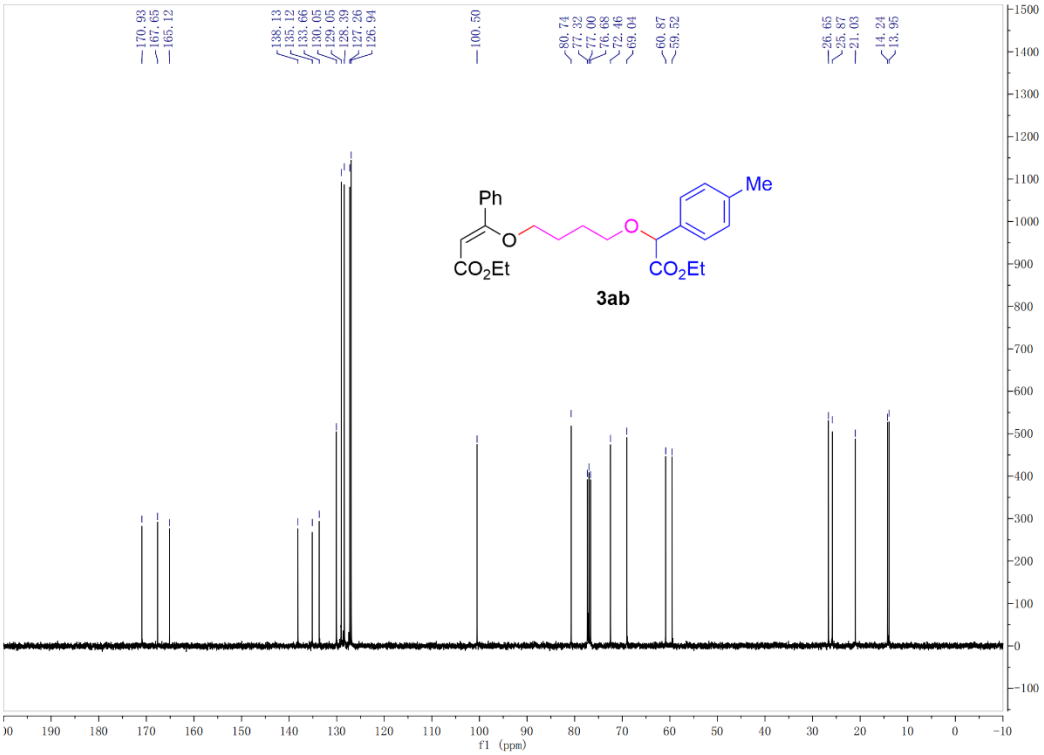
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ab



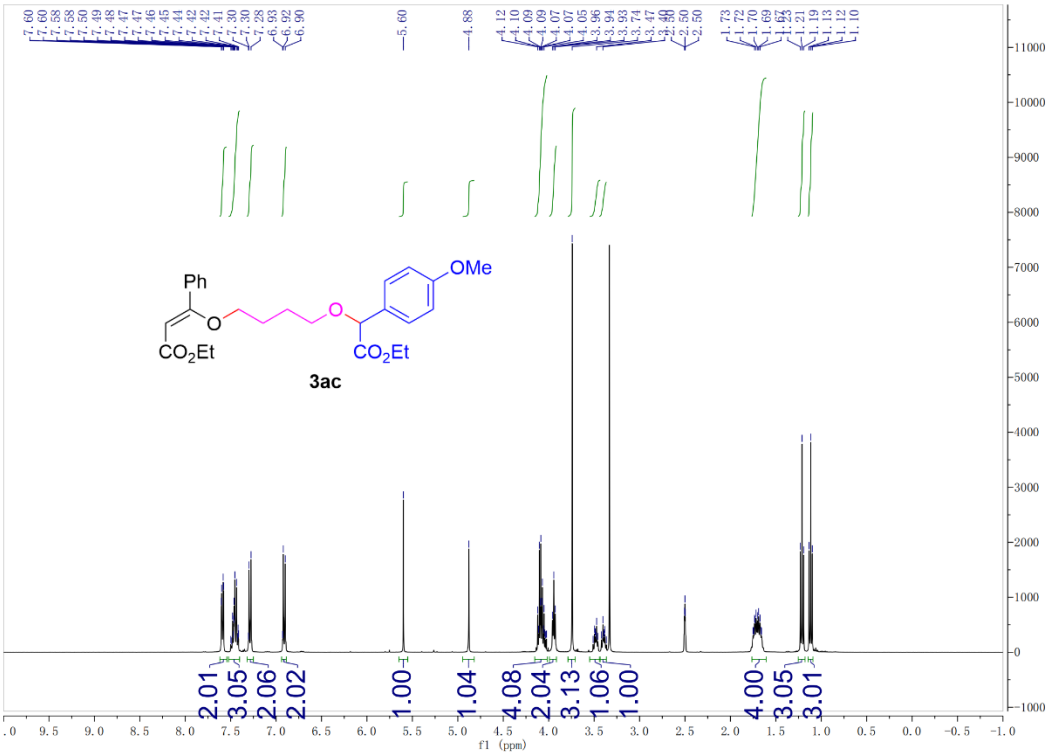
NOESY NMR (400 MHz, $CDCl_3$) Spectrum of 3ab. Based on no NOE effect in H_a and H_b, the stereochemistry is *Z*.



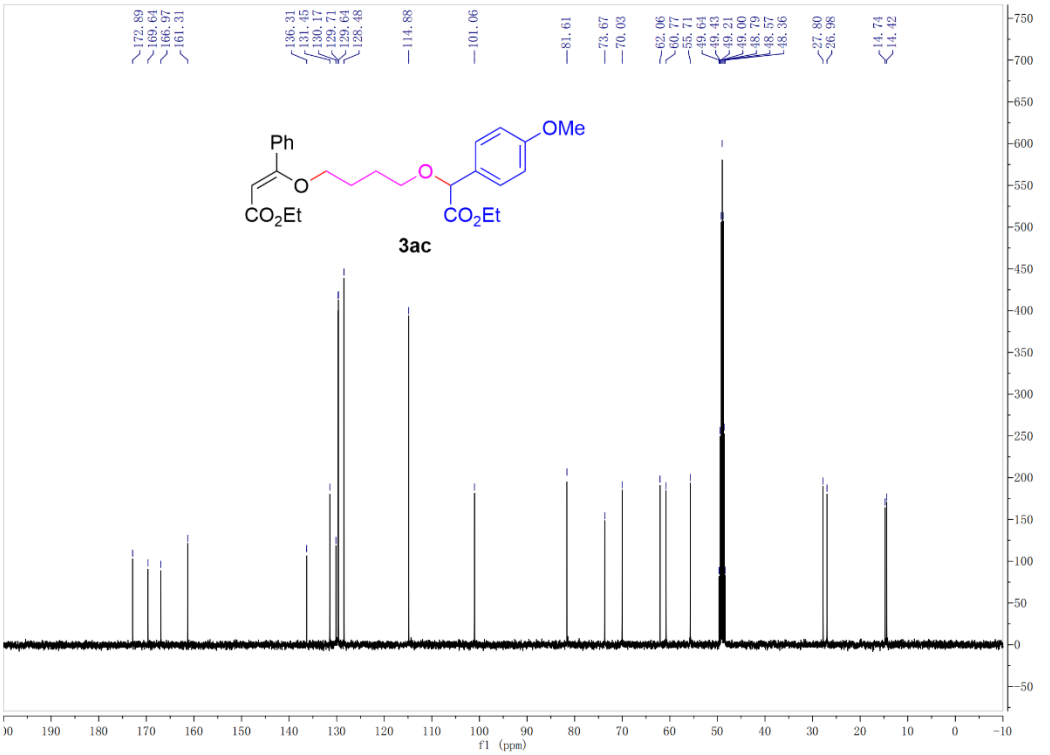
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) Spectrum of 3ab



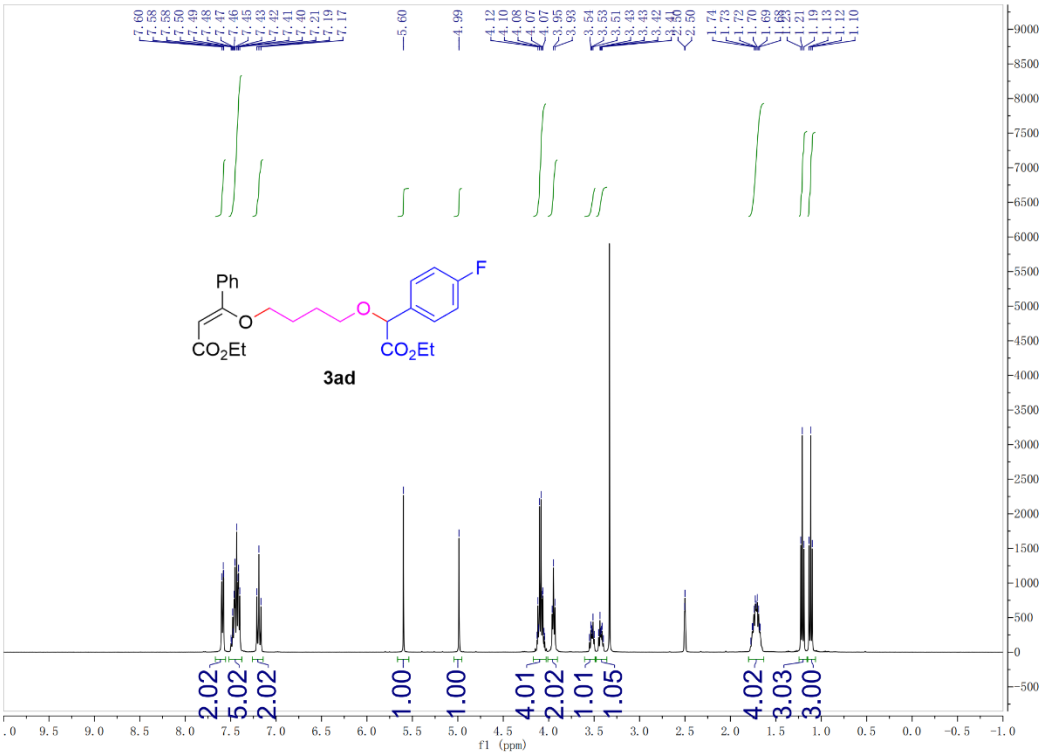
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3ac



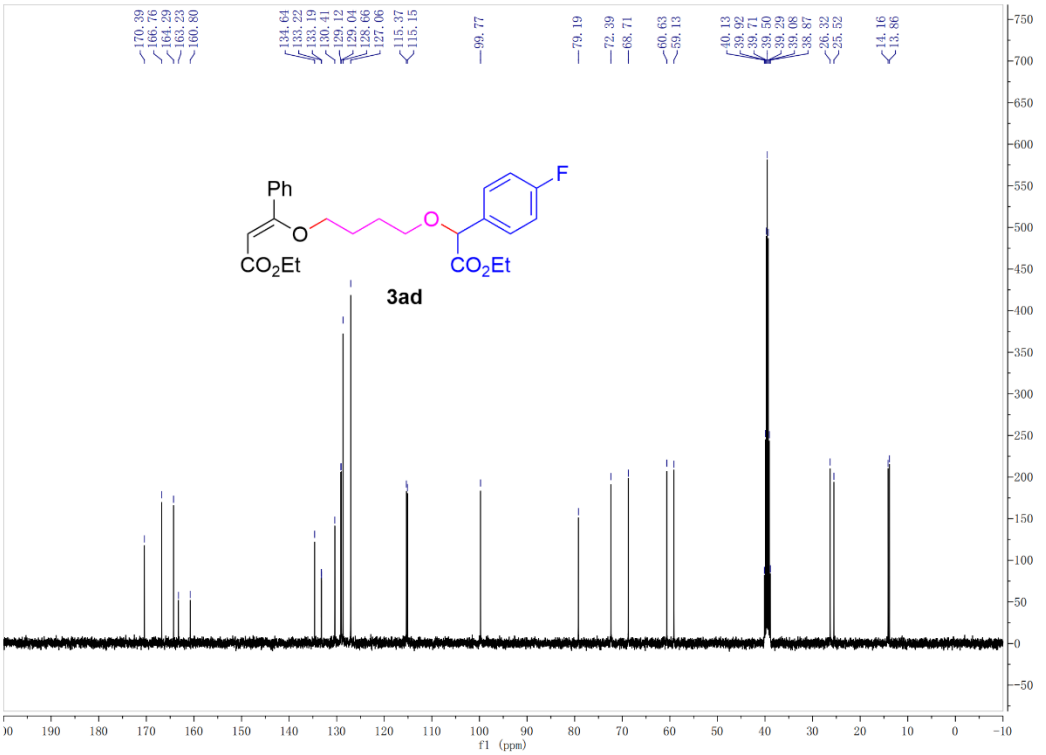
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3ac



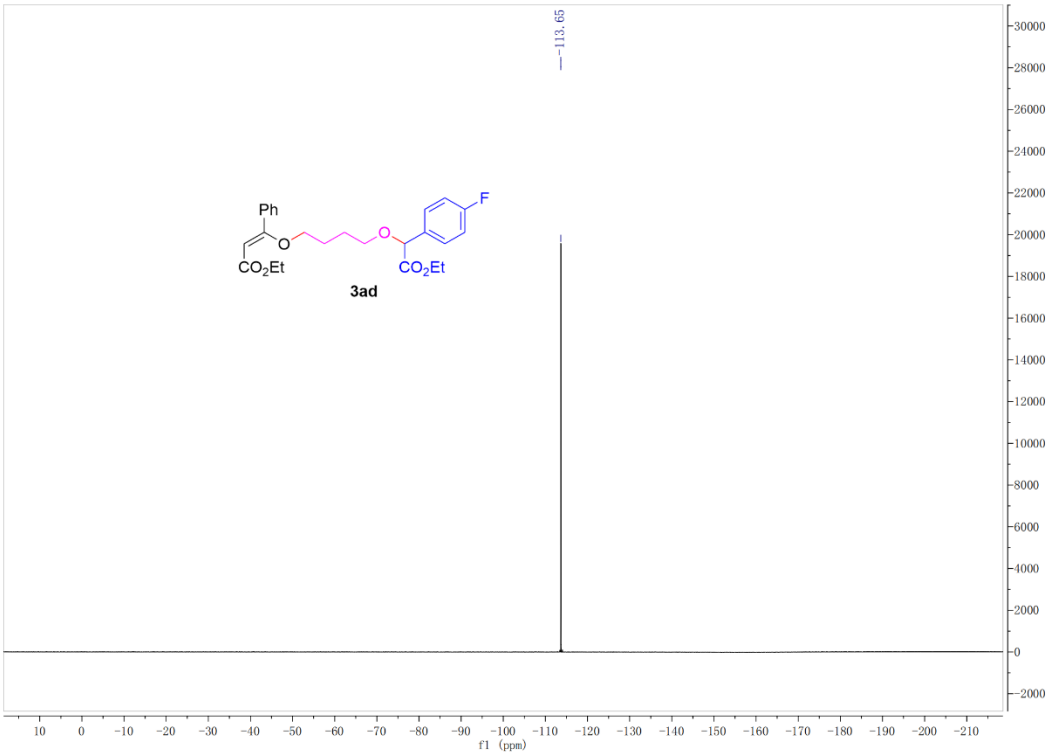
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3ad



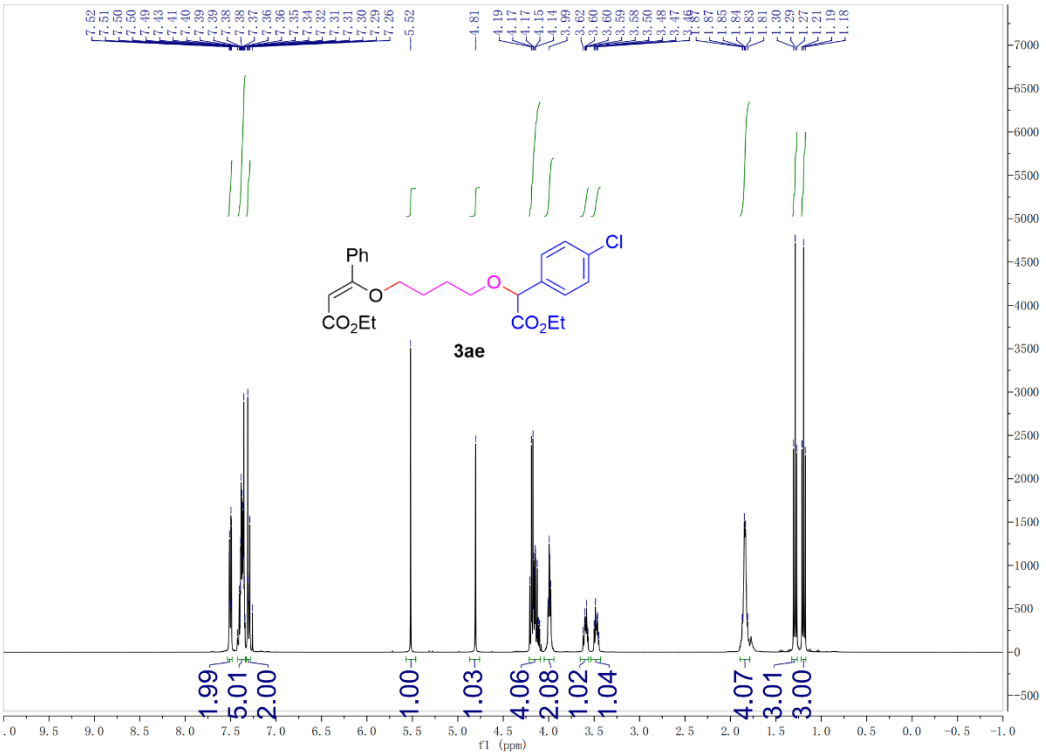
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3ad



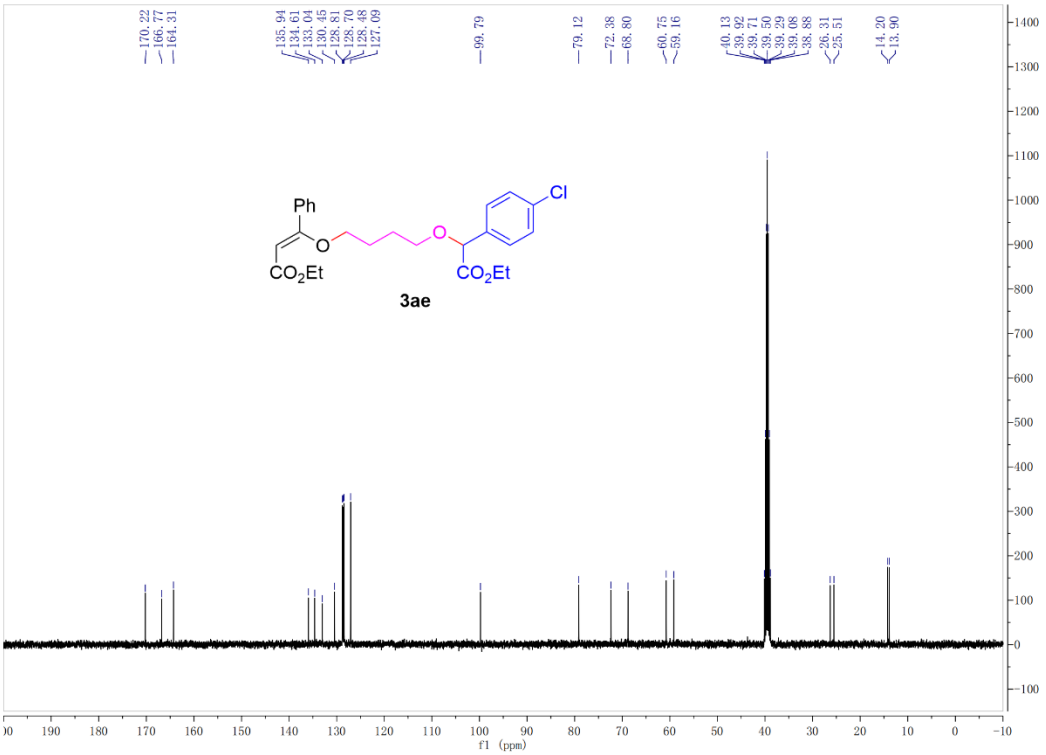
^{19}F NMR (376 MHz, d_6-DMSO) Spectrum of 3ad



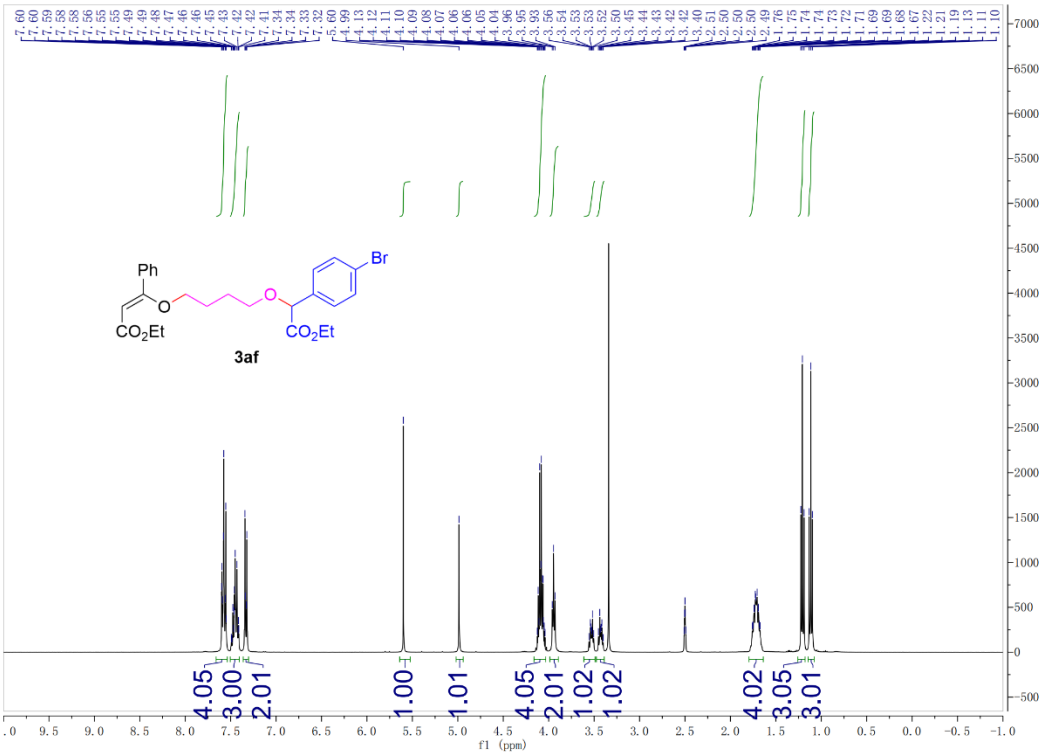
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ae



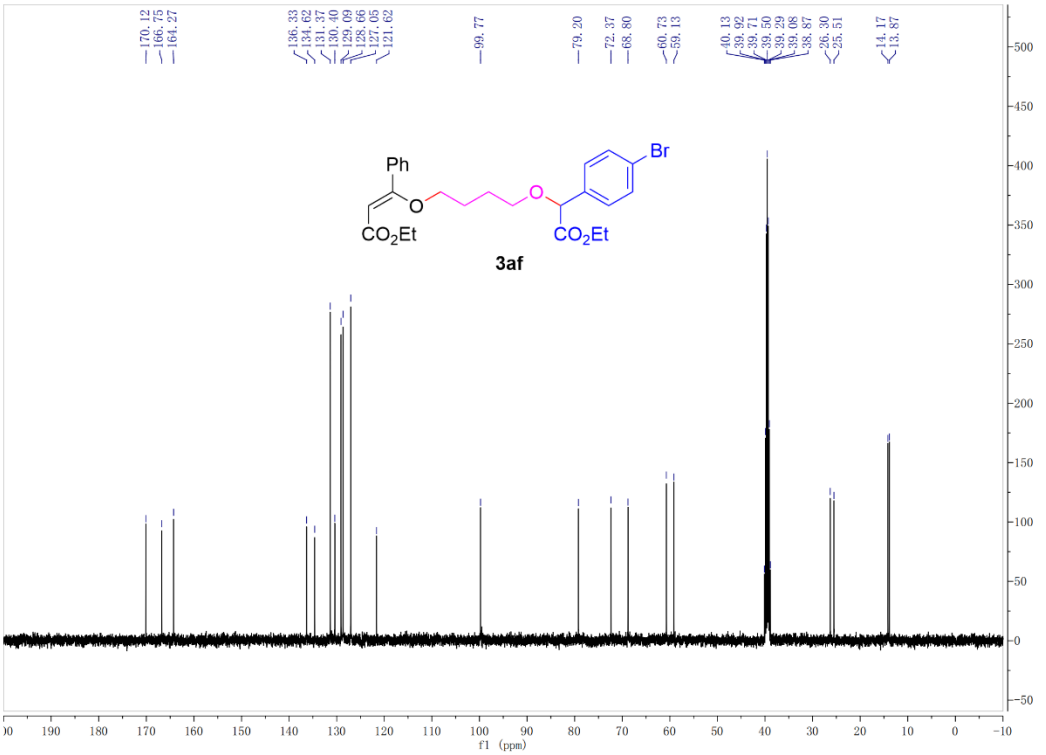
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3ae



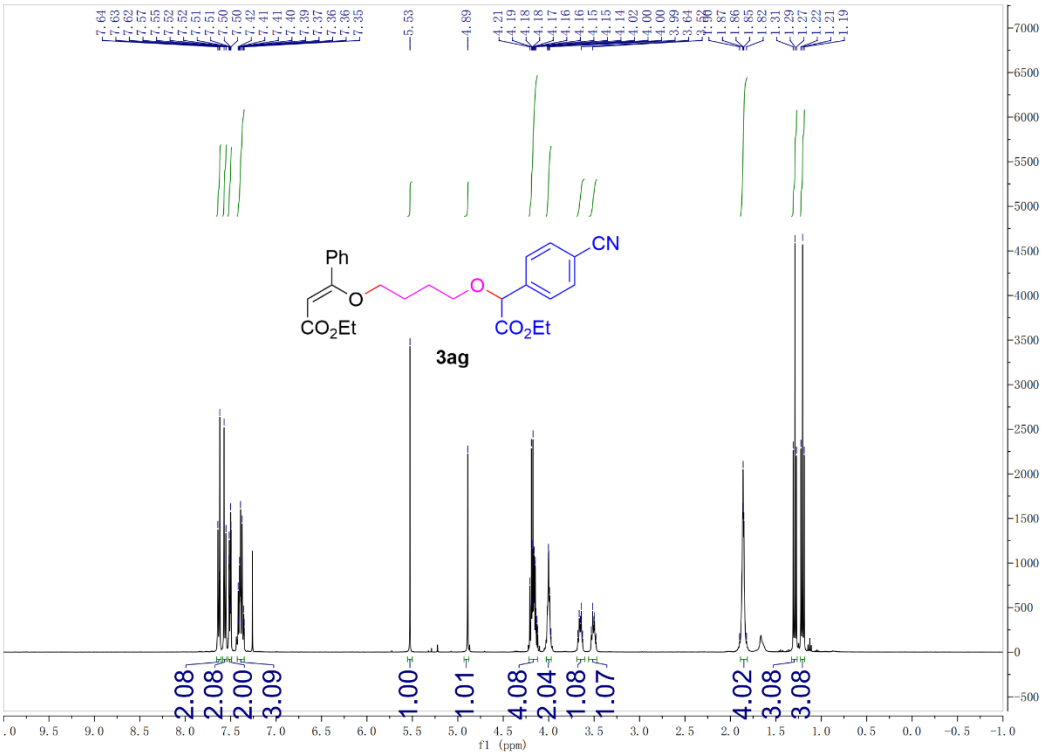
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3af



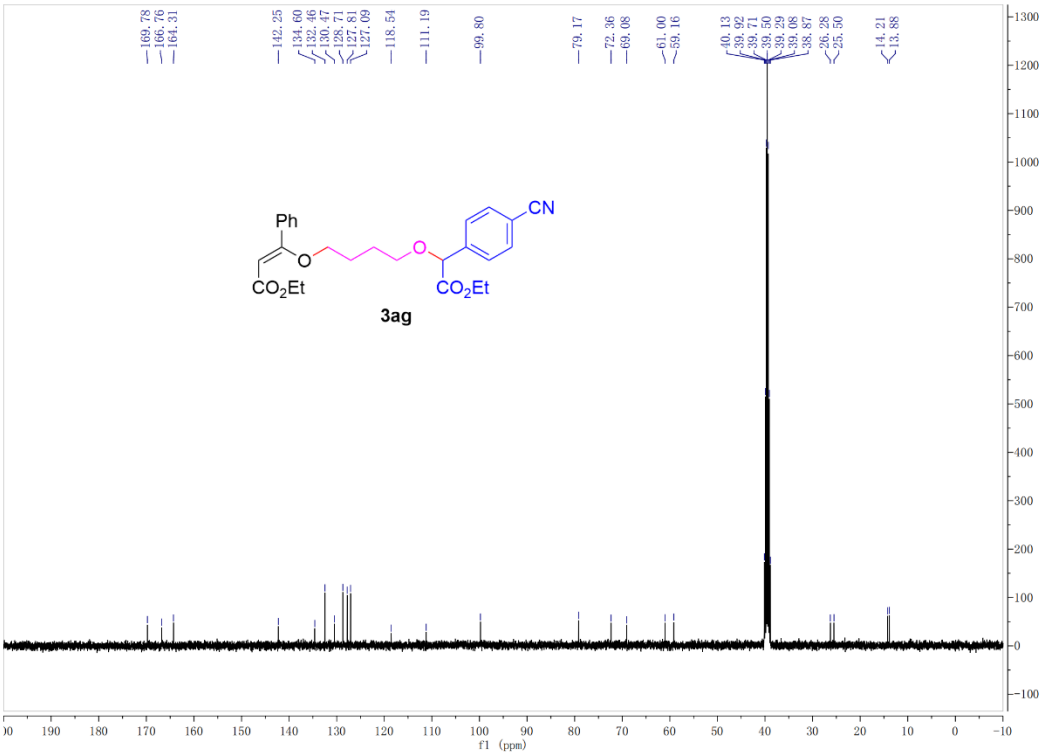
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3af



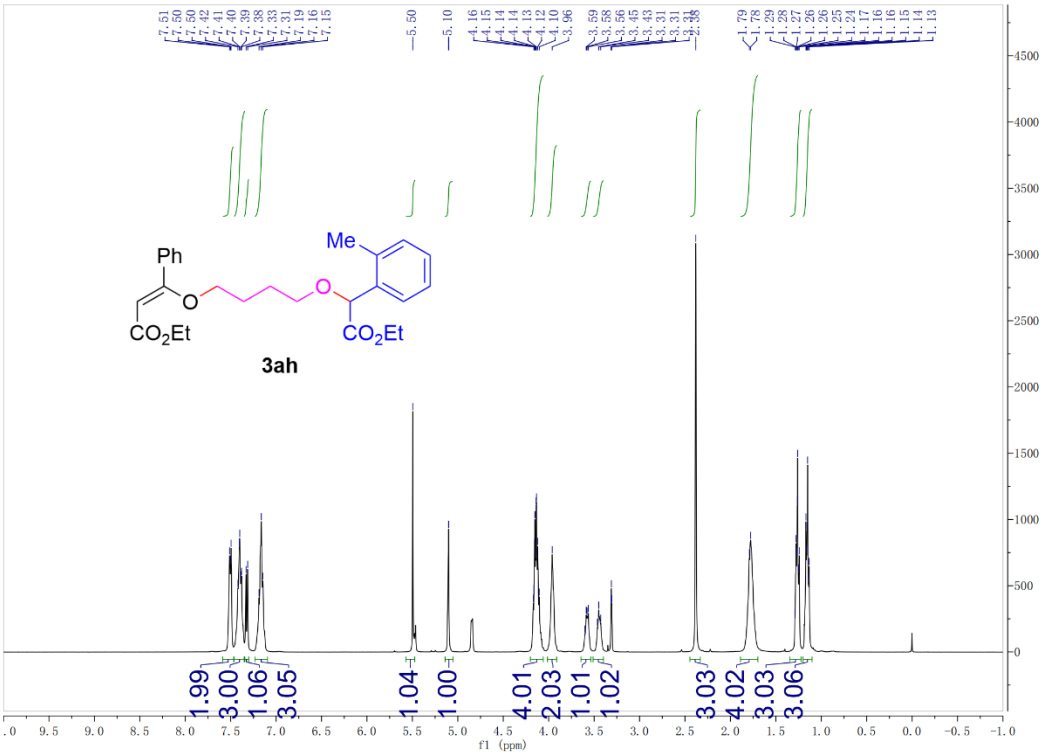
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ag



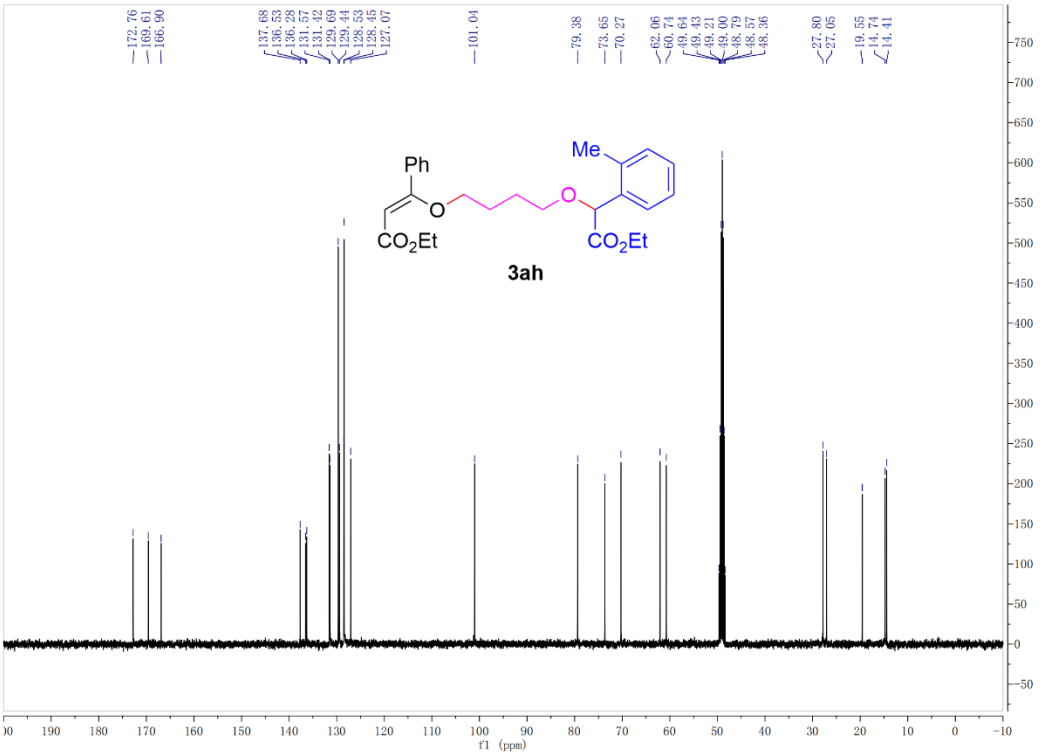
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3ag



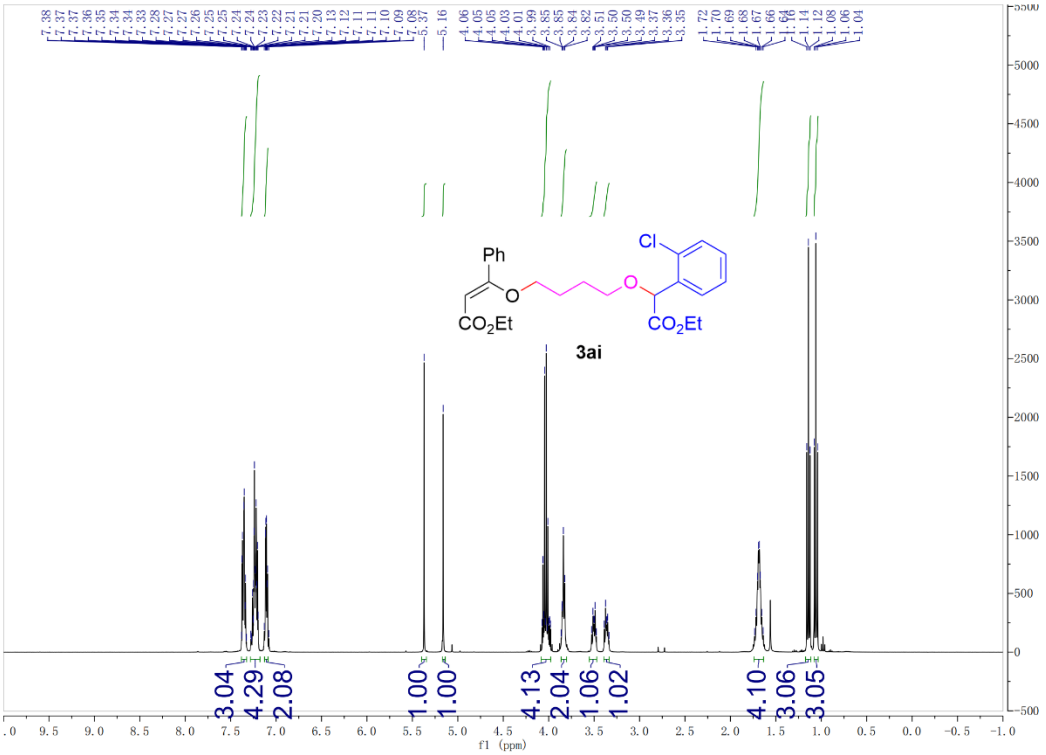
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3ah



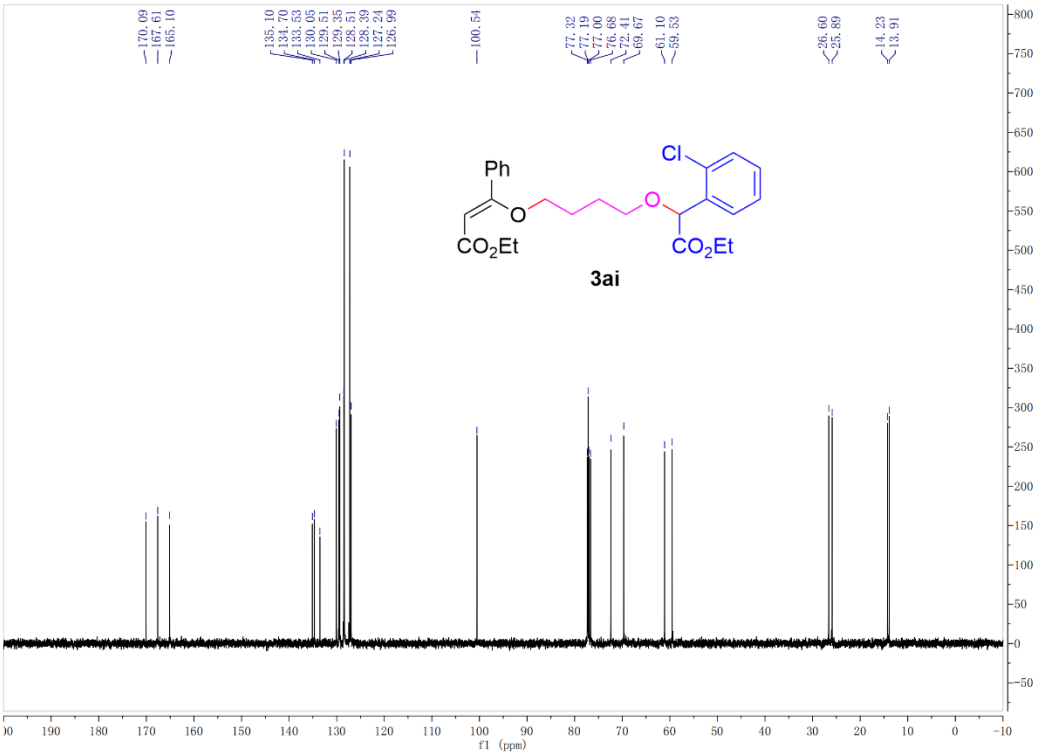
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3ah



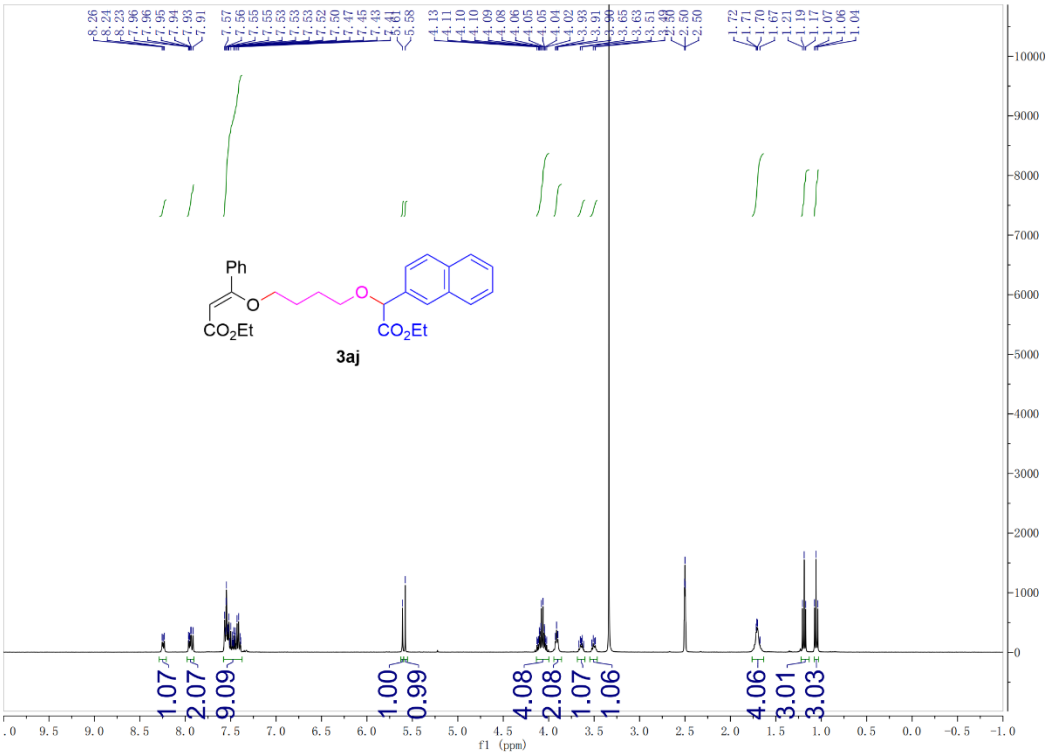
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ai



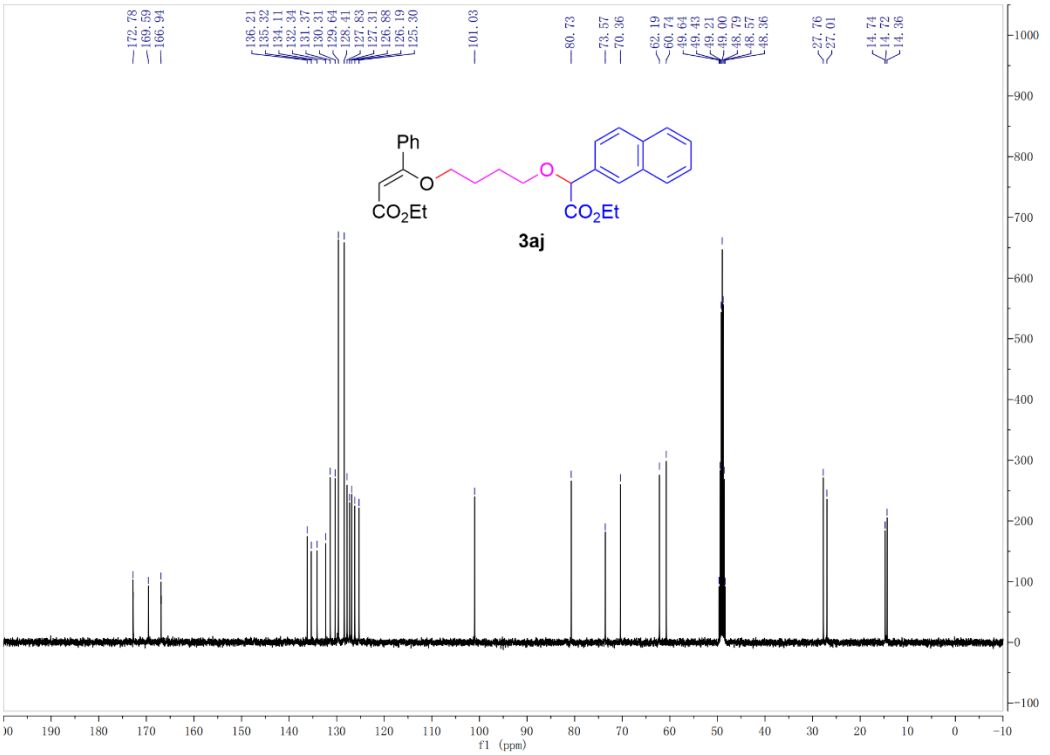
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ai



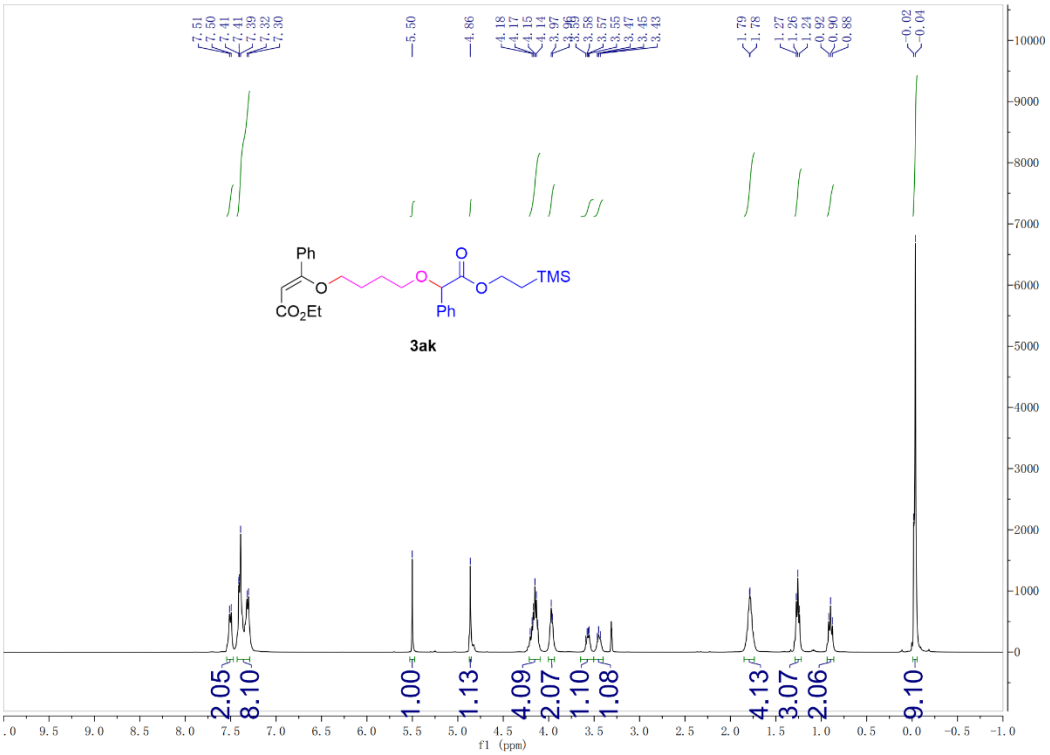
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3aj



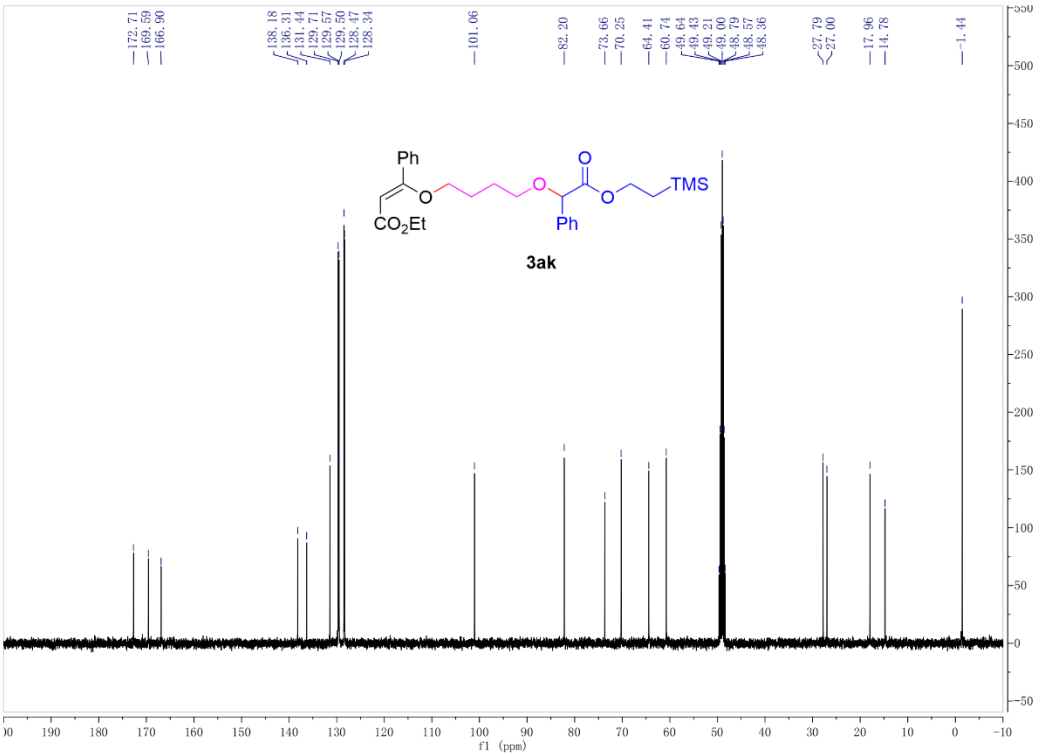
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3aj



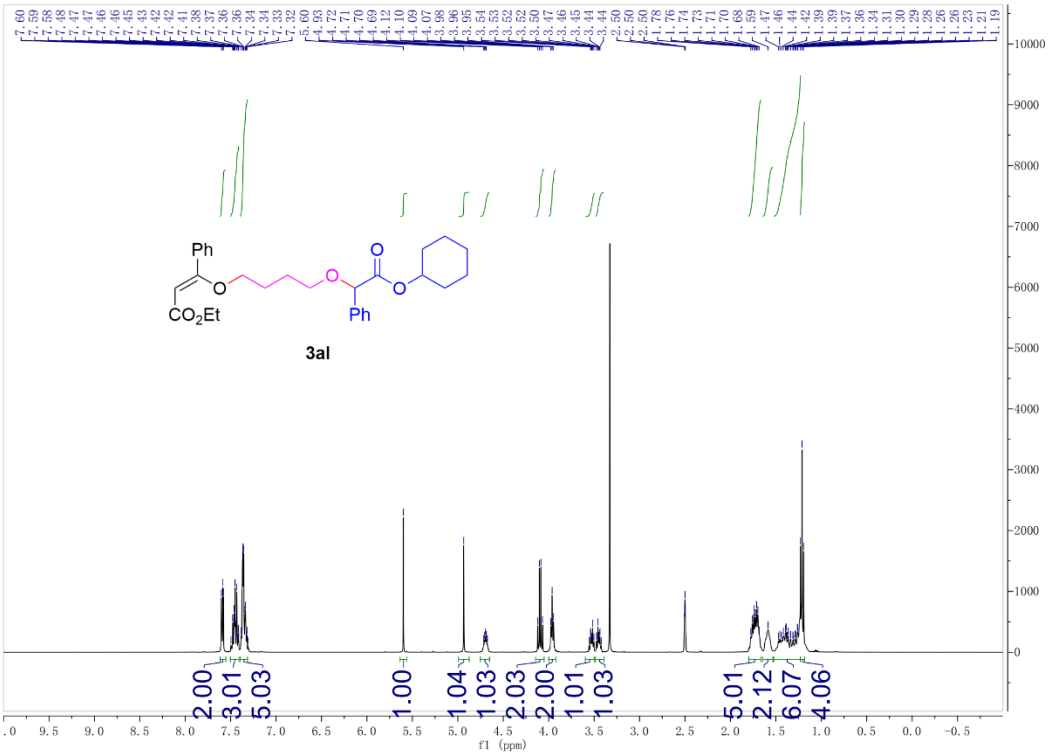
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3ak



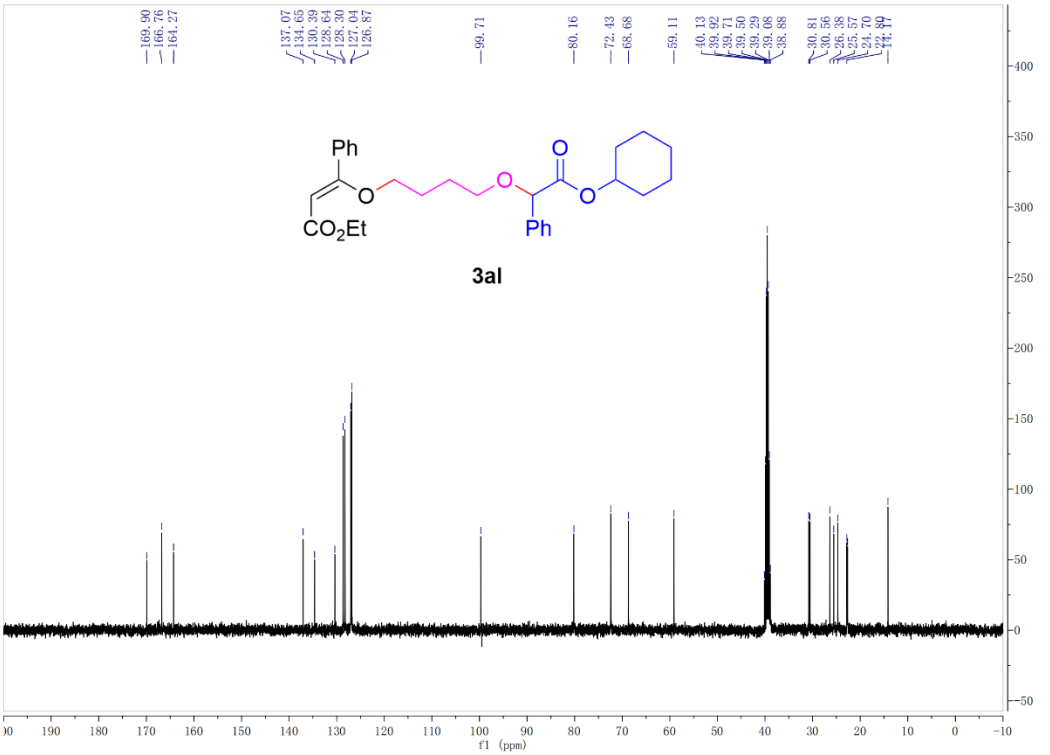
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 3ak



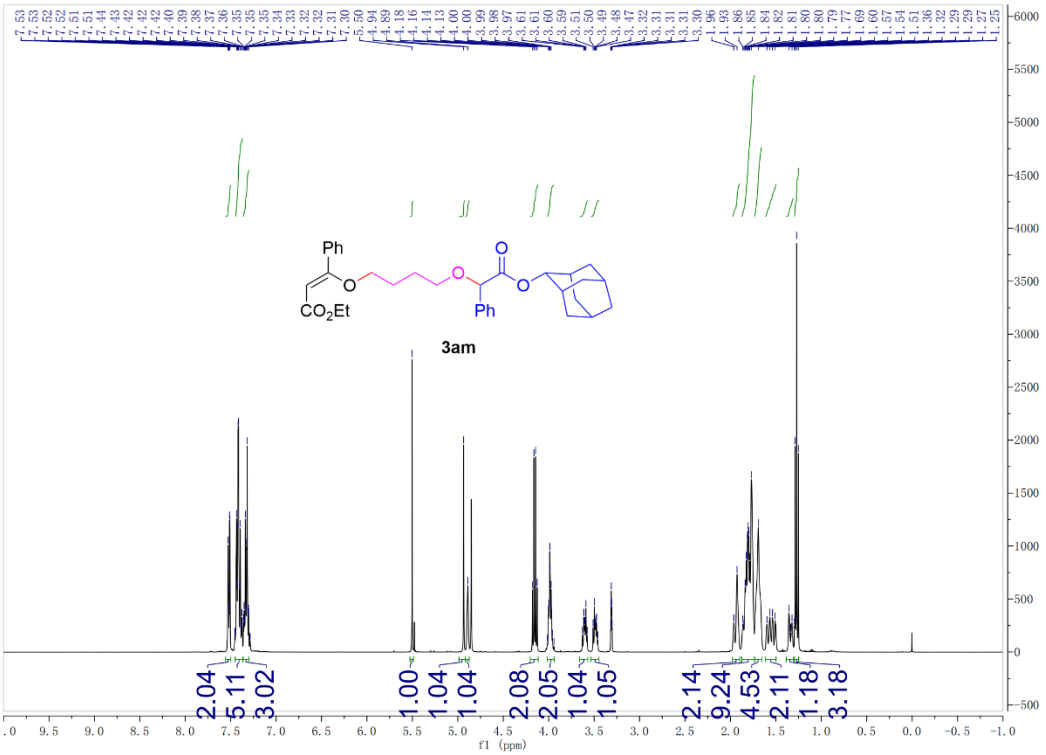
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3al



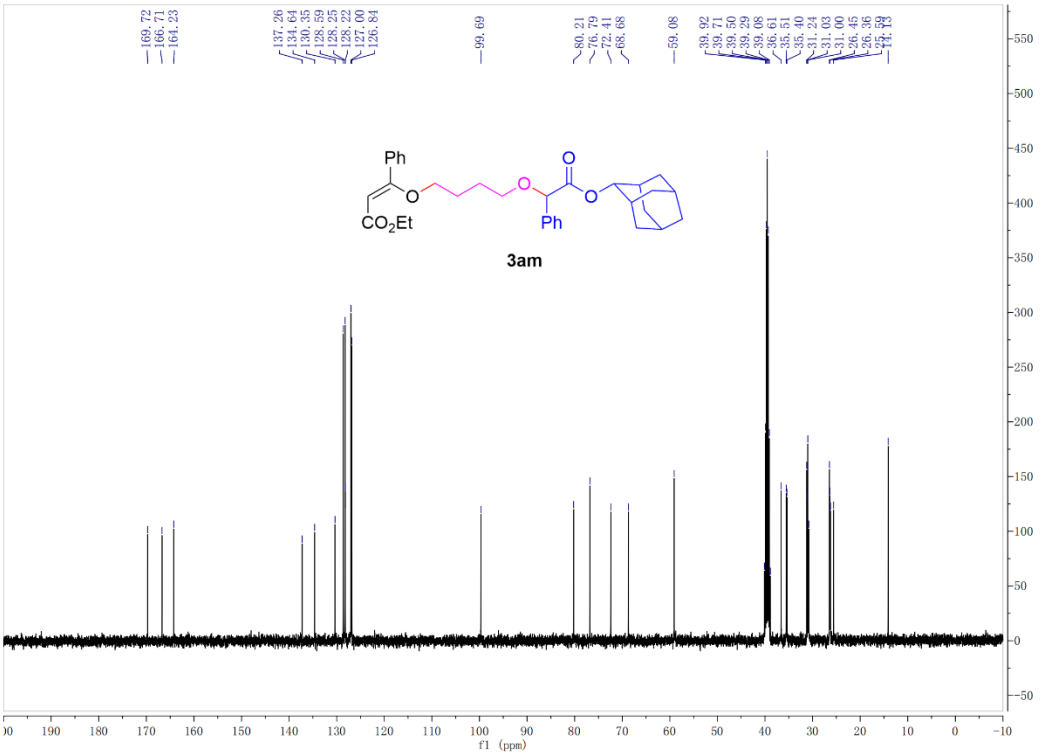
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3al



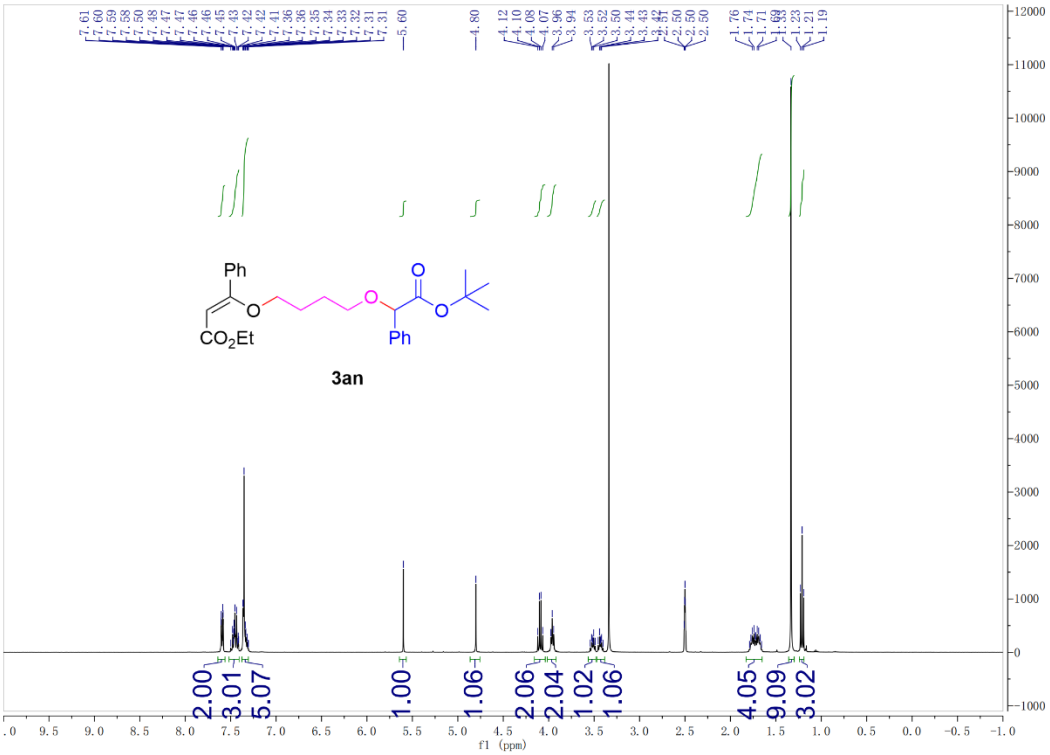
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 3am



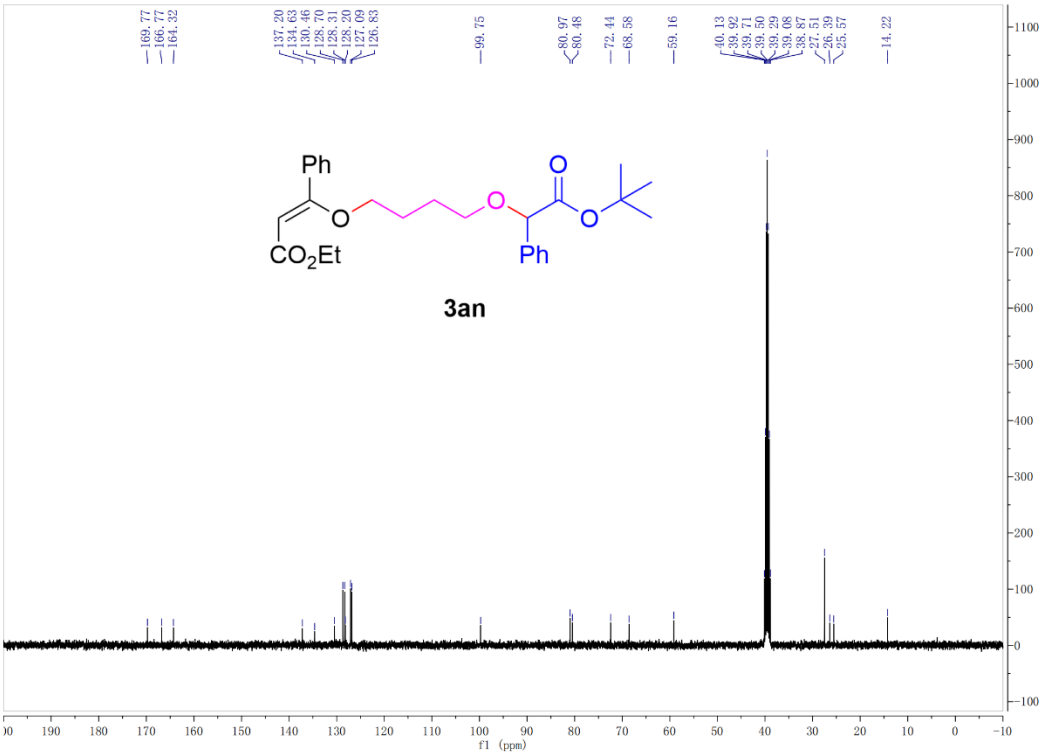
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3am



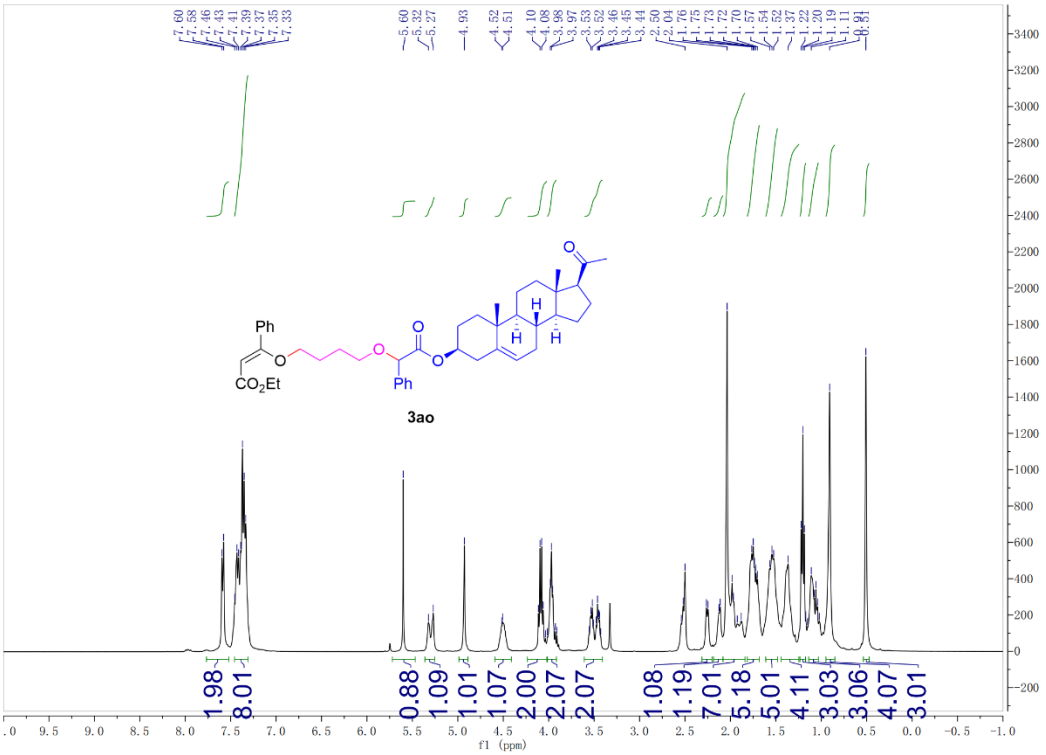
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3an



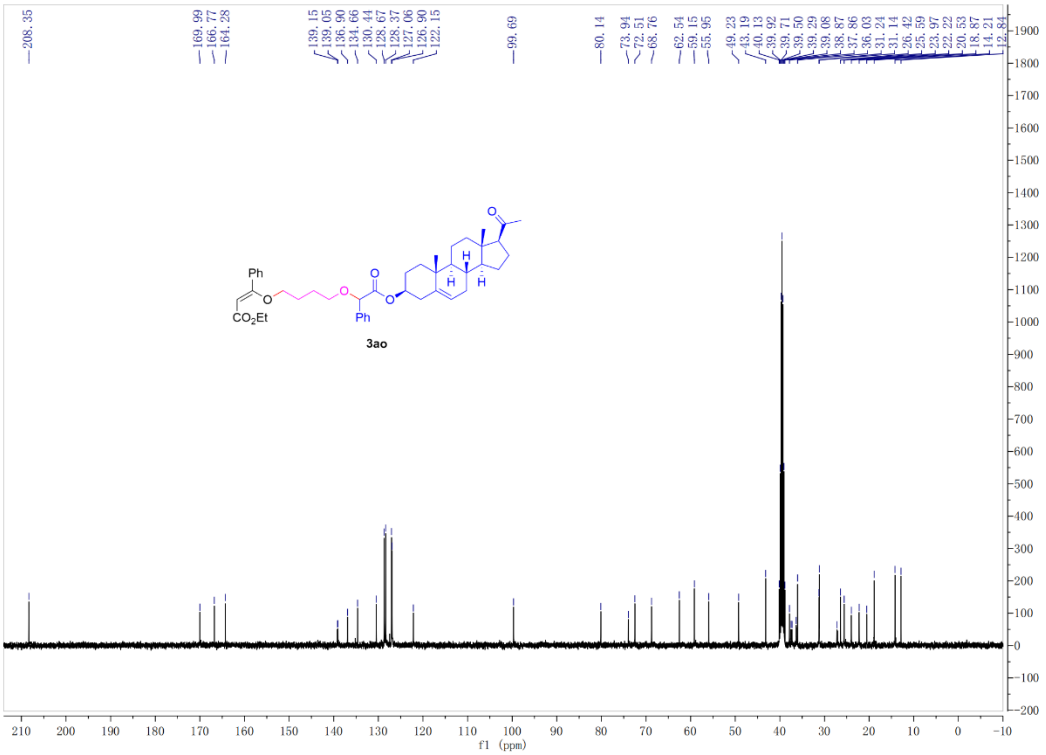
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3an



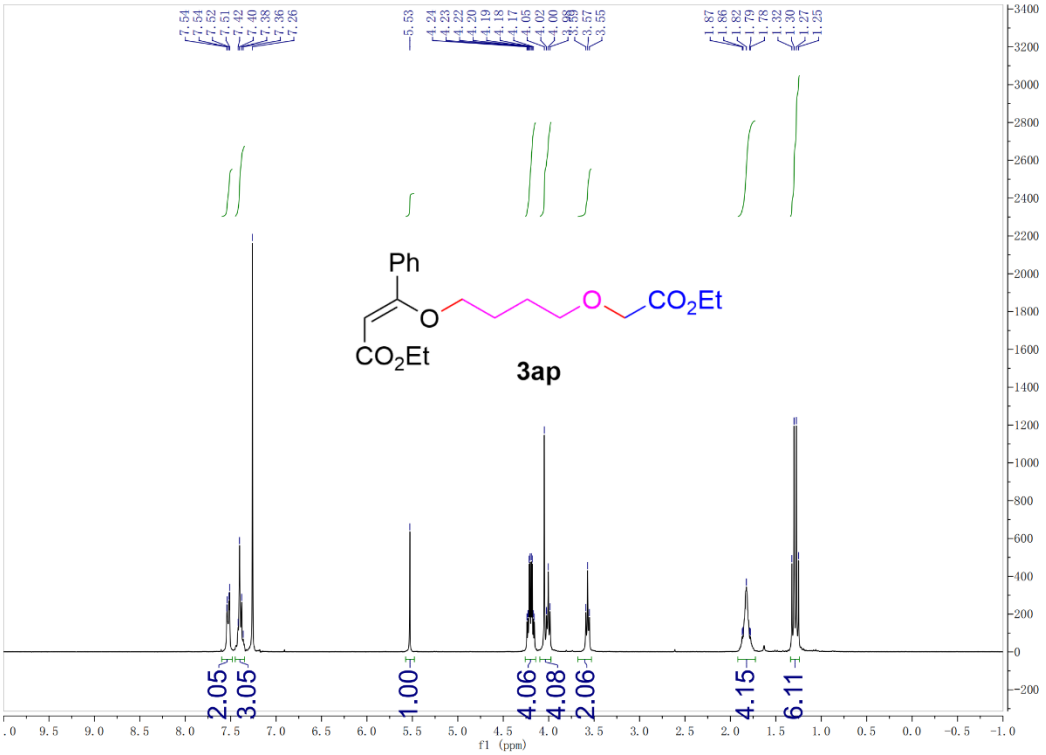
^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 3ao



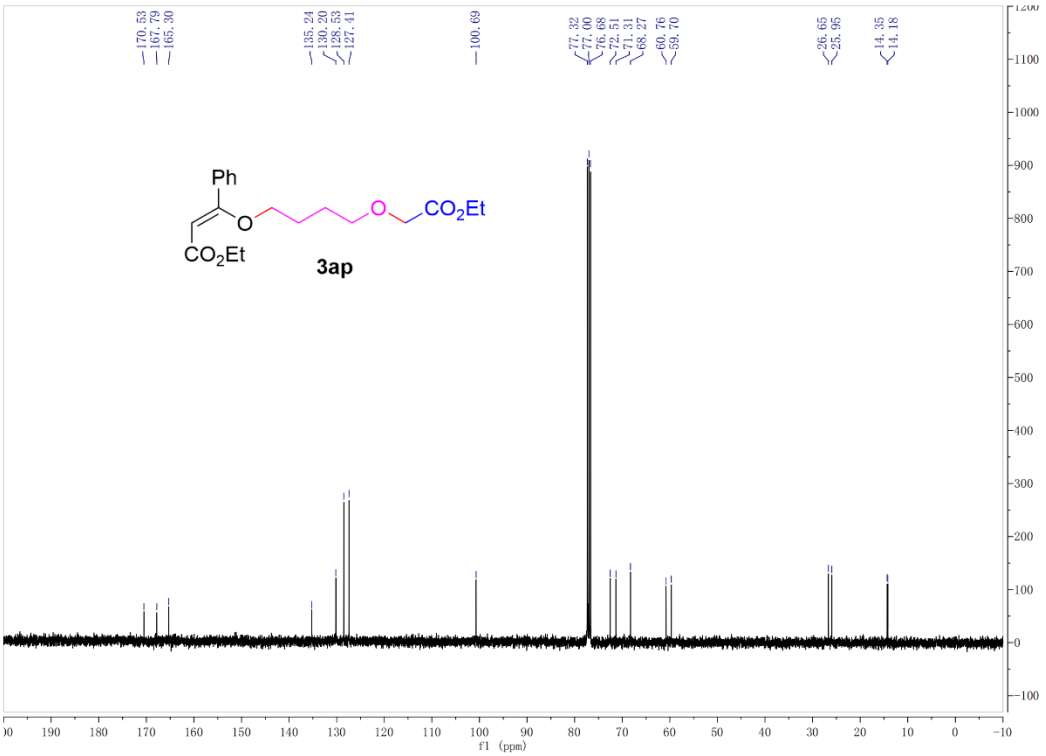
^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 3ao



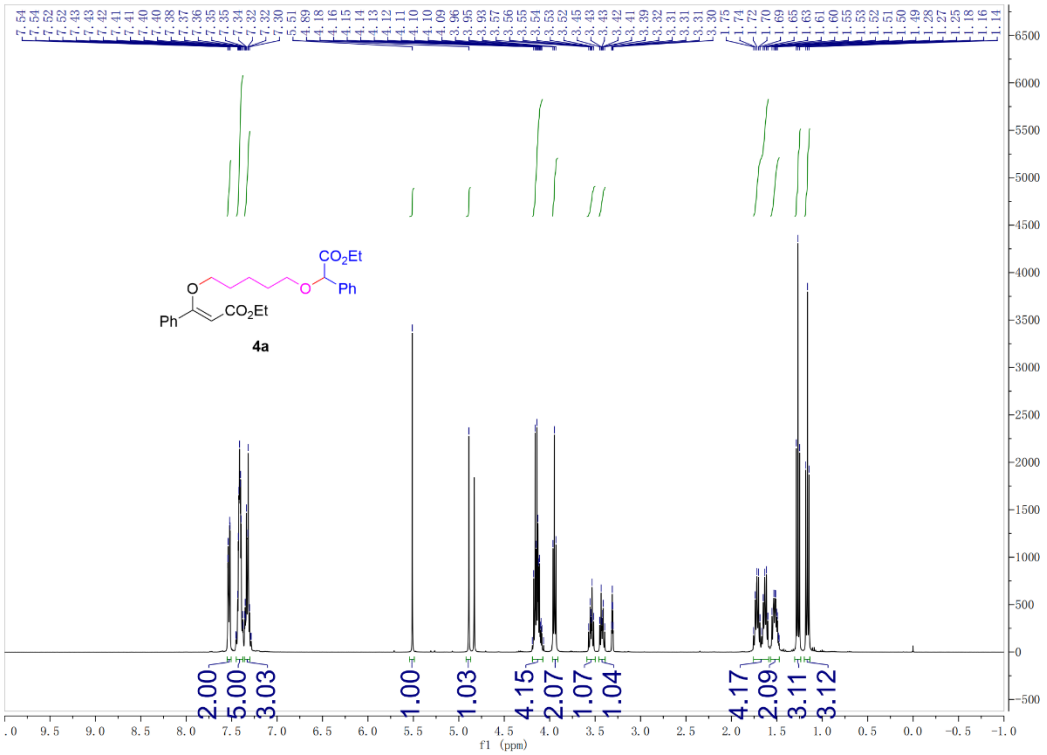
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ap



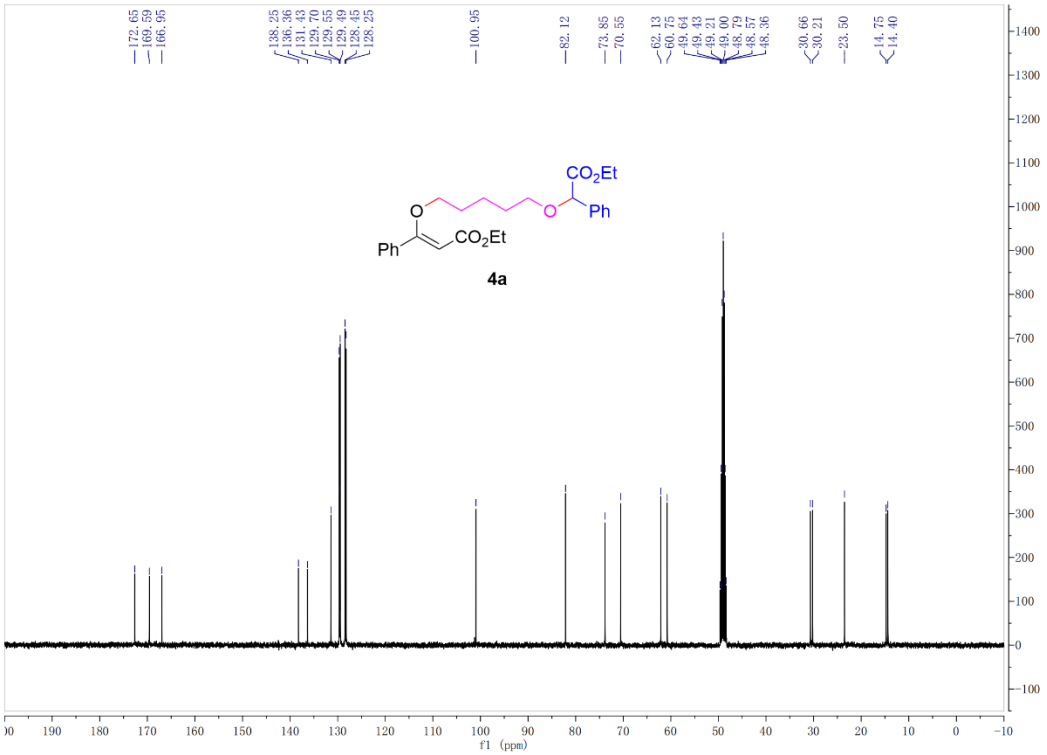
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ap



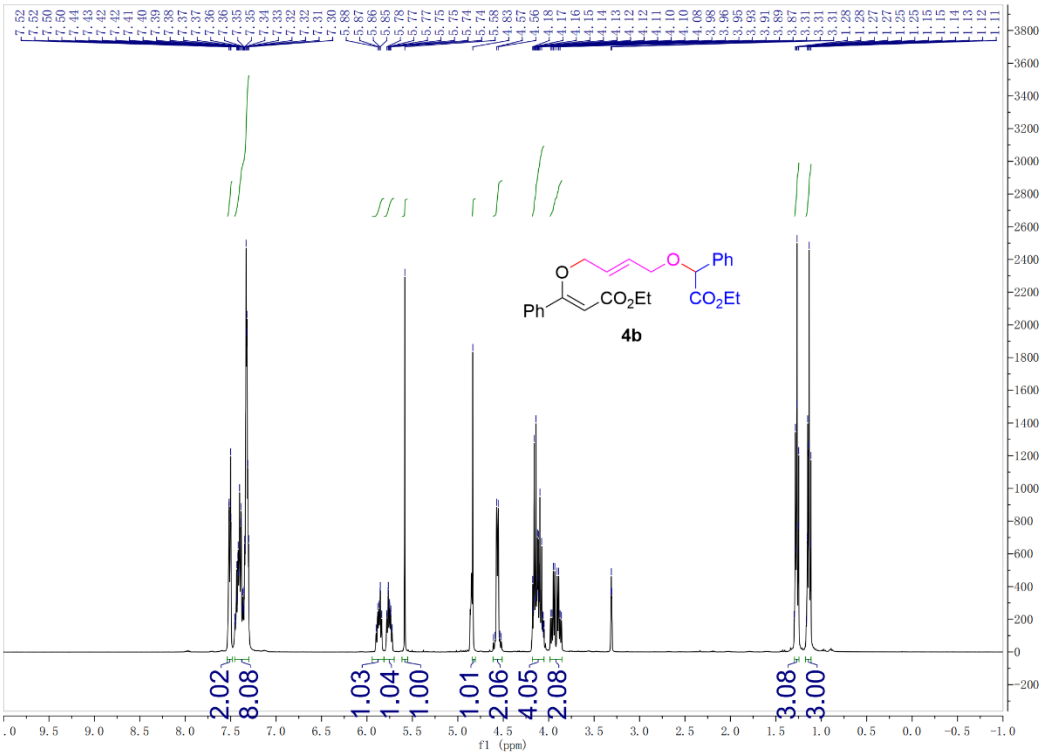
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 4a



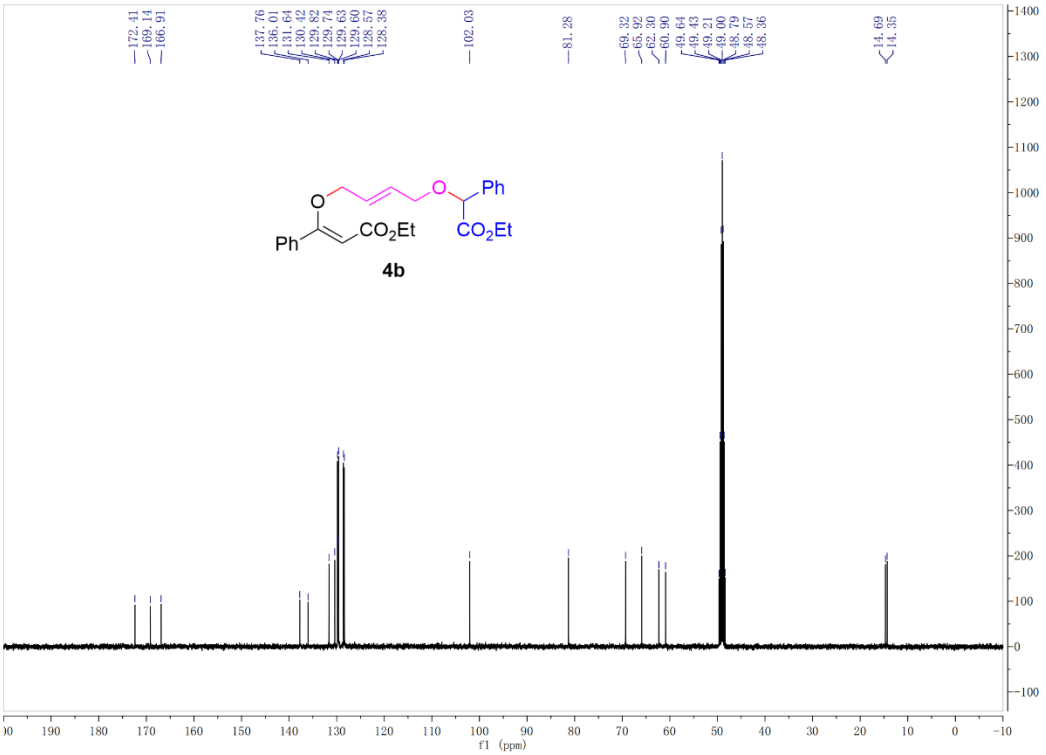
^{13}C{^{1}H} NMR (100 MHz, CD_3OD) Spectrum of 4a



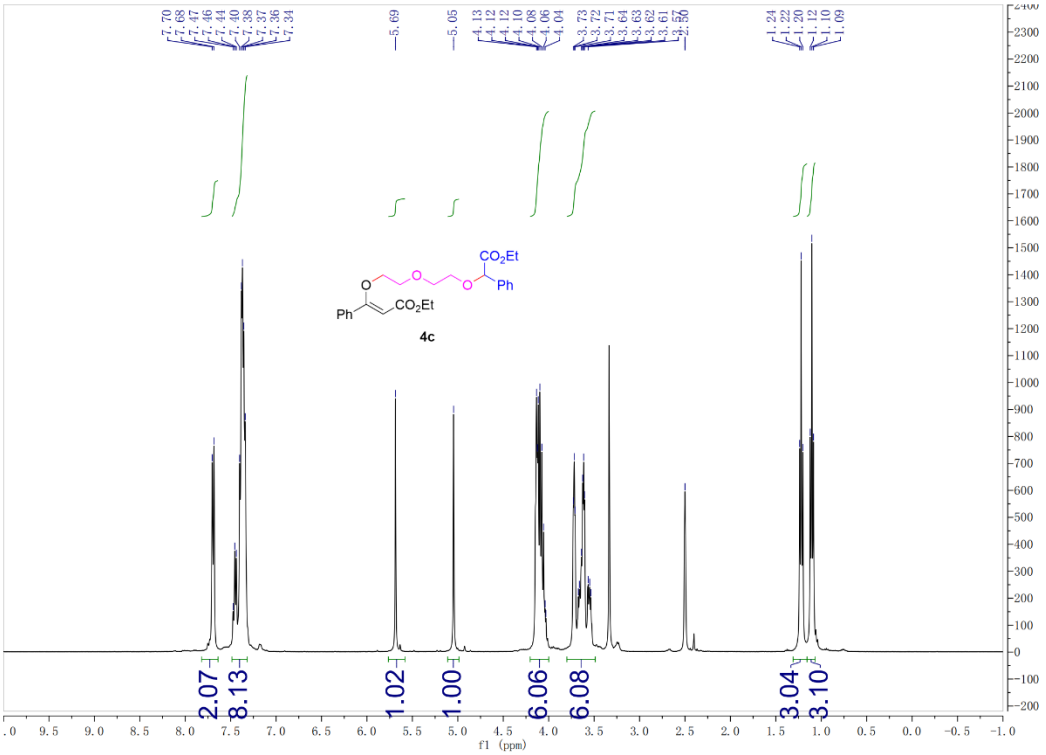
^{1}H NMR (400 MHz, CD_3OD) Spectrum of 4b



$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3OD) Spectrum of 4b



^{1}H NMR (400 MHz, d_6-DMSO) Spectrum of 4c



^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) Spectrum of 4c