Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Visible-Light Photocatalytic Preparation of Alkenyl Thioethers from 1,2,3-Thiadiazoles and Hantzsch Esters: Synthetic and Mechanistic Investigations

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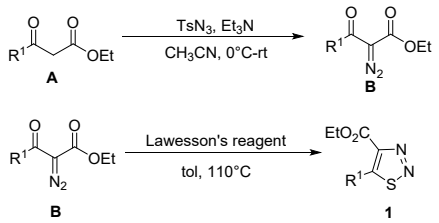
1. General Information

The commercially available reagents were used without further purification unless otherwise noted. Dry solvents were distilled over CaH_2 and stored under argon in Schlenk tubes. All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in preheated glassware under an argon atmosphere using standard Schlenk techniques. Flash column chromatography was performed with silica gel (300–400 mesh). NMR spectra were recorded on Varian Inova–600 MHz, Inova–400 MHz, Bruker DRX–400 spectrometer. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C, respectively. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^{19}F-NMR spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer. Mass spectra were measured with an Agilent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT PremierTM and BRUKERmicrOTF-Q III. X-ray crystal structure analyses were measured on a Bruker D8 Venture instrument. Melting points were measured using INESA WRR and values are uncorrected.

2. Experimental Section

2.1 General procedure for the synthesis of 1,2,3-thiadiazoles

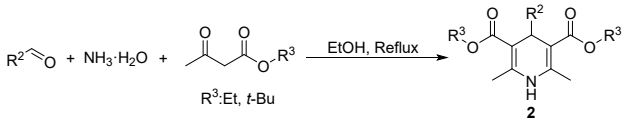
Thiadiazoles (1) were prepared by reported methods.[1]



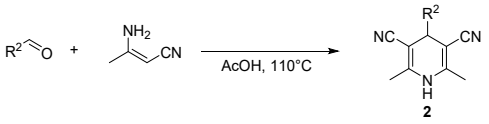
To a solution of ethyl benzoylacetate **A** (10 mmol) and 4-acetamidobenzenesulfonyl azide (11 mmol) in CH_3CN (20 mL) Et_3N (12 mmol) was added slowly at 0 ºC. The reaction mixture was stirred at room temperature overnight and concentrated in vacuo. The resulting crude product was purified by flash chromatography (EA:PE (1:30, v/v)) to yield compound **B**. Then **B** was dissolved in toluene (50 mL) and treated with Lawesson's reagent (12 mmol, 1.2 equiv). The reaction was heated at reflux for 4 hours, then cooled to room temperature and concentrated in vacuo. The resulting oil was purified by column chromatography (EA:PE (1:30, v/v)) to give **1a-1n**.

2.2 General procedure for the synthesis of DHPs

DHPs (2) were prepared by reported methods.[2]



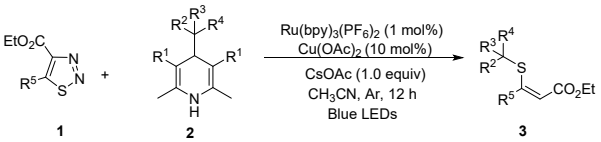
To a flask charged with *t*-butyl acetoacetate (20 mmol) (or methyl acetoacetateand ethyl acetoacetate), the aldehyde (10 mmol) and ethanol (20 mL) was added ammonia aqueous solution (4.0 mL, 28%, 60 mmol). The mixture was heated at 80 ºC under an argon atmosphere for 8 hours. The reaction was allowed to cool to room temperature. The solution was concentrated under reduced pressure. A mixture of water and EA were added to the concentrated residue and the layers were separated. The aqueous layer was extracted with EA for 3 times. The combined organic layers were washed with brine, dried ($MgSO_4$), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel. Obtained solid product could be washed with EA:PE (5: 95, v/v) as further purification. **2a**-2q are known compounds.



A reaction flask was charged with 3-Aminocrotononitrile (20 mmol), the aldehyde (10 mmol), AcOH (10 mL). The reaction was heated at 110 ºC under an argon atmosphere with stirring for 3 hours. The crude reaction mixture was allowed to cool to room temperature. The reaction was diluted with water and extracted with EtOAc for three times. The combined organic layers were neutralized

with saturated solution of $NaHCO_3$ until the removal of acetic acid was achieved, washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel. The obtained solid product could be washed with EA:PE (5: 95, v/v) as further purification. **2s-2t** are known compounds.

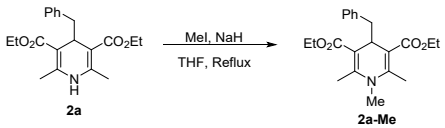
2.3 General procedure for visible-light induced photoredox alkylation reaction with Hantzsch ester



A reaction tube was charged with the $Ru(bpy)_3(PF_6)_2$ (0.86 mg, 1 mol %), $Cu(OAc)_2$ (1.8mg, 10 mol %), CsOAc (19.1 mg, 0.1 mmol, 1.0 equiv), Hantzsch ester **2** (0.15 mmol, 1.5 equiv), 1,2,3-thadiadole **1** (0.1 mmol, 1.0 equiv) and CH_3CN (1 mL). The mixture was stirred under irradiation of 6 W Blue LEDs under an argon atmosphere at room temperature for 12 hours. Then the mixture was diluted with H_2O and the resulting mixture was extracted with dichloromethane for 3 times. The combined organic layers were washed with brine, dried ($MgSO_4$), and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on silica gel.

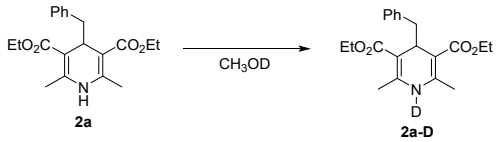
2.4 General procedure for the synthesis of 2a-Me

2a-Me were prepared by reported methods.[3]



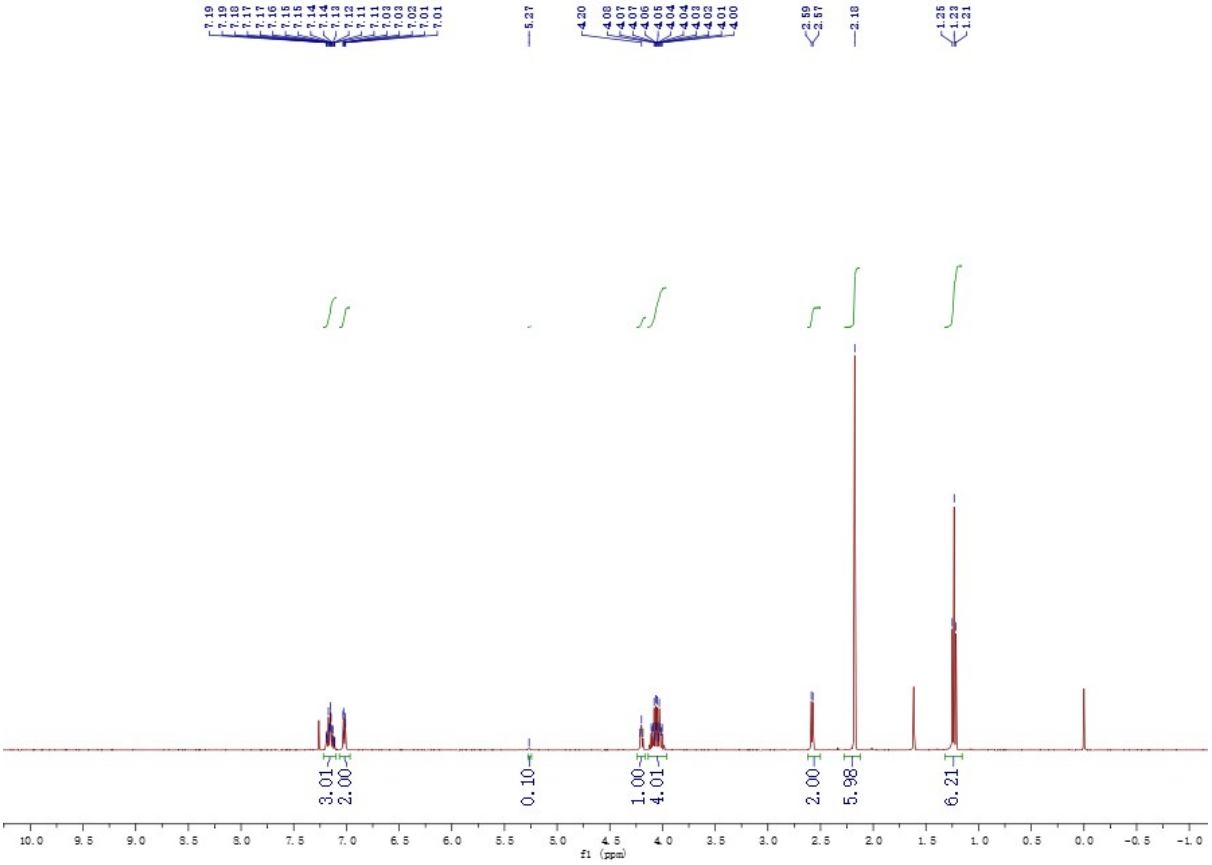
To a 100 mL round-bottomed flask with a stir bar was added **2a**, then added the solution of NaH (3 mmol) in THF (35 mL), the mixture was stirred at 70 ºC under an argon atmosphere for 0.5 hours. The solution of MeI (5 mmol) in THF (15 mL) was added to the reaction mixture, which was refluxed for 2 hours in oil bath, then poured into brine and extracted with EtOAc. The combined extracts were dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography (EA:PE(1:3, v/v)) to afford the desired **2a-Me**.

2.5 General procedure for the synthesis of 2a-D



N-deuterium labeled indole **2a-D** was synthesized as following procedure: In a dried 10 mL schlenk tube, **2a** (1.5 g, 4.37 mmol) was dissolved in MeOD (6 mL, 230 mmol) and the mixture was stirred in room temperature under an argon atmosphere for 12 hours. Then the mixture was

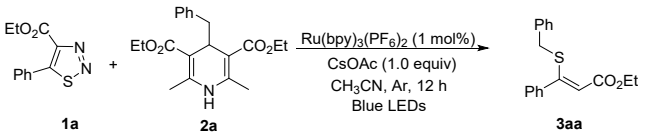
concentrated under vacuum to remove the solvent. MeOD (6 mL) was added into the schlenk tube again and the mixture was stirred in room temperature for another 12 hours. After that, the mixture was concentrated under vacuum to give quantitative yield of the product **2a-D** with 90% D.



^{1}H NMR of **2a-D**(400 MHz, $CDCl_3$)

3. Optimization of Reaction Conditions

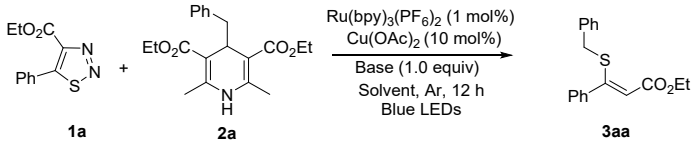
Table S1. Optimization of reaction conditions



Entry[a]	Variation from optimized conditions	Yield of **3aa** (%)[b]
1	none	88(*Z*:*E*=3:1)
2	10 mol% $Cu(OTf)_2$	83
3	10 mol% CuI	84
4	10 mol% $Cu(CH_3CN)_4BF_4$	81
5	10 mol% $CuCl_2$	85
6	10 mol% $Cu(OAc)_2$	89 (82)[c]
7	10 mol% $NiCl_2$	0
8	10 mol% $PdCl_2$	4(*Z*:*E*=1:1)

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol%), CsOAc (0.1 mmol), CH_3CN (1 mL), Ar atmosphere, irradiation with 6 W blue LEDs (450~465 nm), 12 h. [b] ^1H NMR yields determined using dibromomethane as an internal standard; *Z*/*E* is greater than 99/1 unless other specified. [c] Isolated yield.

Table S2. Optimization of reaction conditions



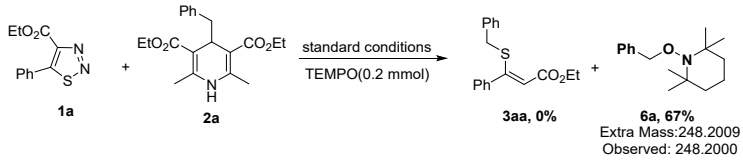
1a **2a** **3aa**

Entry[a]	Variation from optimized conditions	Base	Yield of **3aa** (%)[b]
1	MeCN	CsOAc	89
2	DCM	CsOAc	trace
3	THF	CsOAc	trace
4	DCE	CsOAc	trace
5	DMF	CsOAc	54
6	$PhCF_3$	CsOAc	5
7	1,4-Dioxane	CsOAc	trace
8	MeCN	Cs_2CO_3	10
9	MeCN	K_3PO_4	54
10	MeCN	NEt_3	47
11	MeCN	KOAc	55
12[c]	MeCN	CsOAc	90
13[d]	MeCN	CsOAc	58
14[e]	MeCN	CsOAc	0

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol%), $Cu(OAc)_2$ (10 mol%), Base (0.1 mmol), Solvent (1 mL), Ar atmosphere, irradiation with 6 W blue LEDs (450-465 nm), 12 h. [b] ^1H NMR yields determined using dibromomethane as an internal standard; *Z/E* is greater than 99/1 unless other specified. [c] Under 6W Blue LEDs (415~430 nm). [d] Under 6W Purple LEDs (385~400 nm).[e] Under dark.

4. Mechanistic Experiments

4.1 Radical trapping experiment



General procedure: A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol) in 1 mL CH_3CN was added **2a** (0.15 mmol), TEMPO (0.2 mmol, 2 equiv.), $Ru(bpy)_3(PF_6)_2$ (1 mol %), $Cu(OAc)_2$ (10 mol %), CsOAc (0.1 mmol), under an argon atmosphere, 6W Blue LEDs. The reaction mixture was then stirred for 12 hours. According to the detected result by ESI-HRMS, the benzyl radical could be trapped by TEMPO produce the 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine, $[M+H^+]$ 248.2009, found: 248.2000.

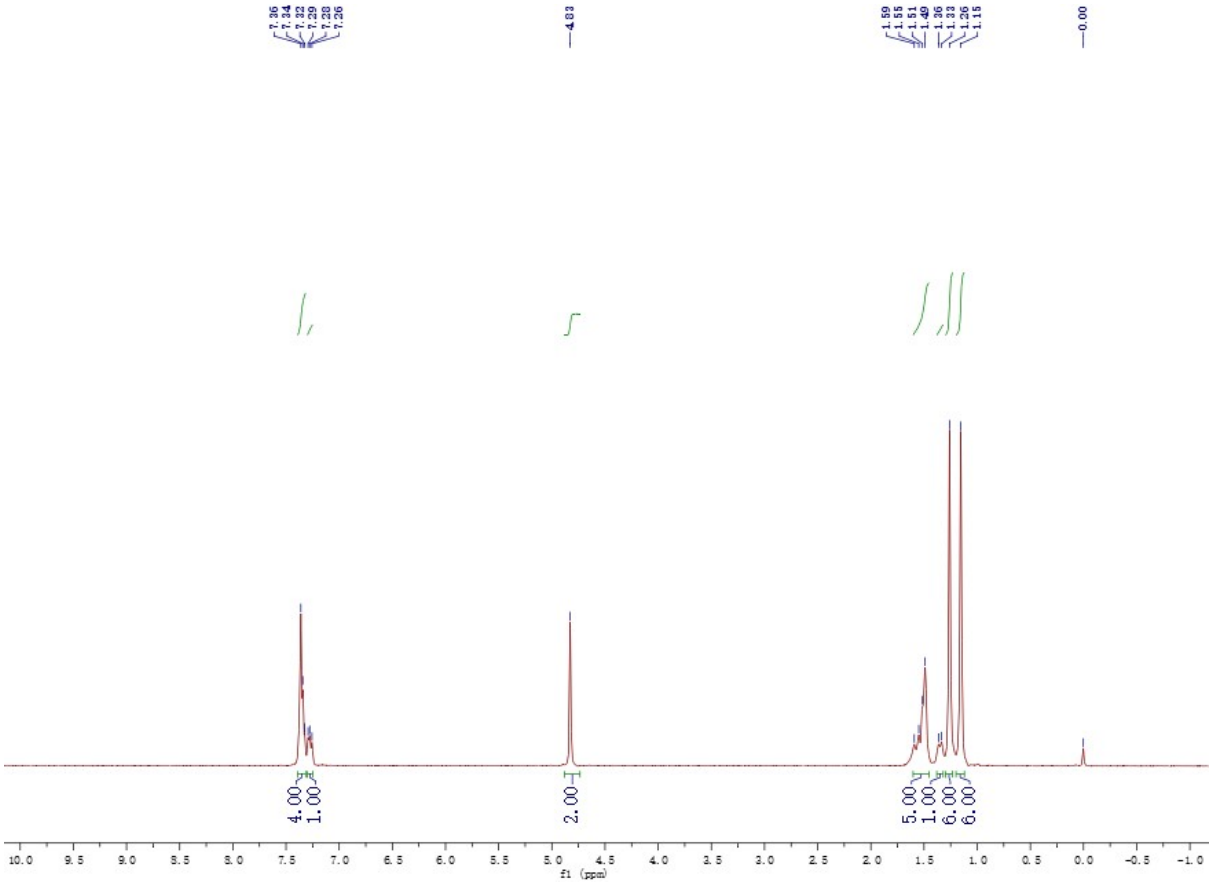


Fig. S1 ^1H NMR spectrum of **6a** (400 MHz, $CDCl_3$)

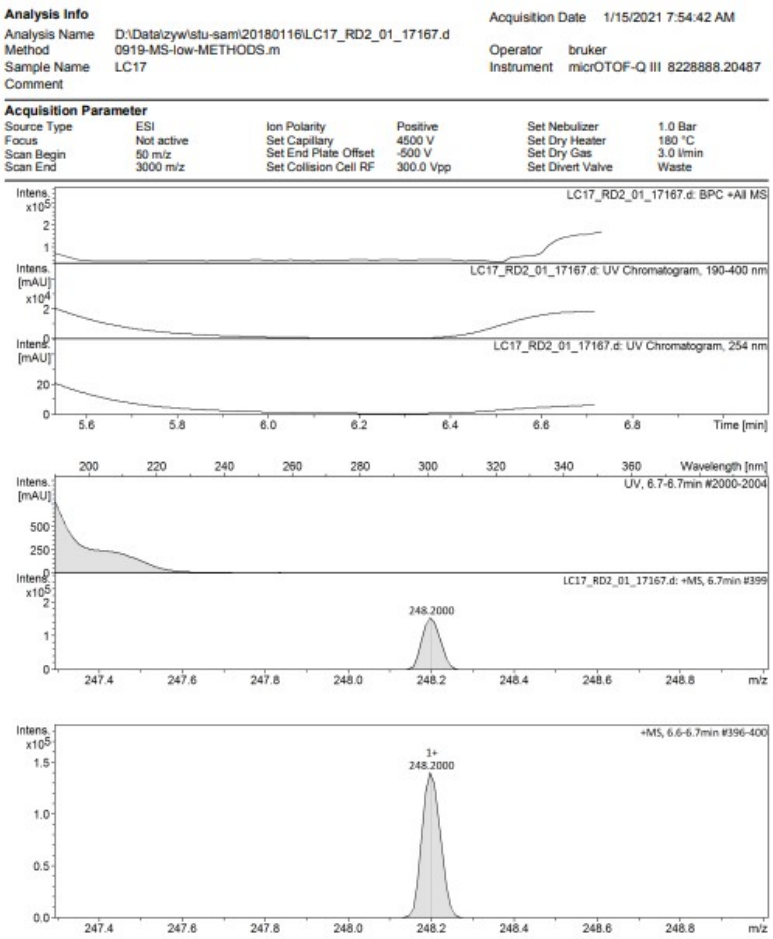
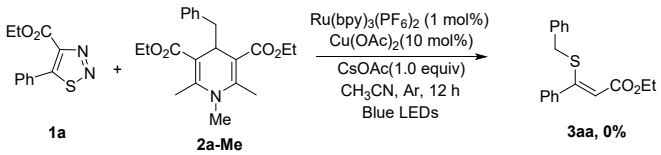


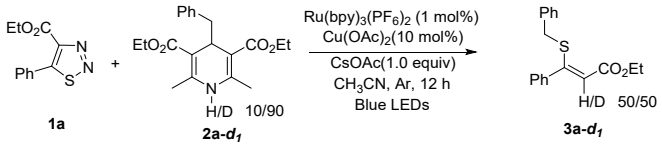
Fig. S2 ESI-HRMS of **6a**

4.2 The reaction of 1,2,3-thiadiazole with 2a-Me



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol) in 1 mL CH_3CN was added **2a-Me** (0.15 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol %), $Cu(OAc)_2$ (10 mol %), CsOAc (0.1 mmol), under an argon atmosphere, 6W Blue LEDs. The reaction mixture was then stirred for 12 hours. The solvent was then removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography. The desired **3a** could not be obtained.

4.3 The reaction of 1,2,3-thiadiazole with 2a-D



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol) in 1 mL CH_3CN was added **2a-D** (0.15 mmol), $Ru(bpy)_3(PF_6)_2$ (1 mol %), $Cu(OAc)_2$ (10 mol %), CsOAc (0.1 mmol), under an argon atmosphere, 6W Blue LEDs. The reaction mixture was then stirred for 12 hours. The solvent was then removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography. The desired **3a-D** could be obtained in 82% yield with 50% D.

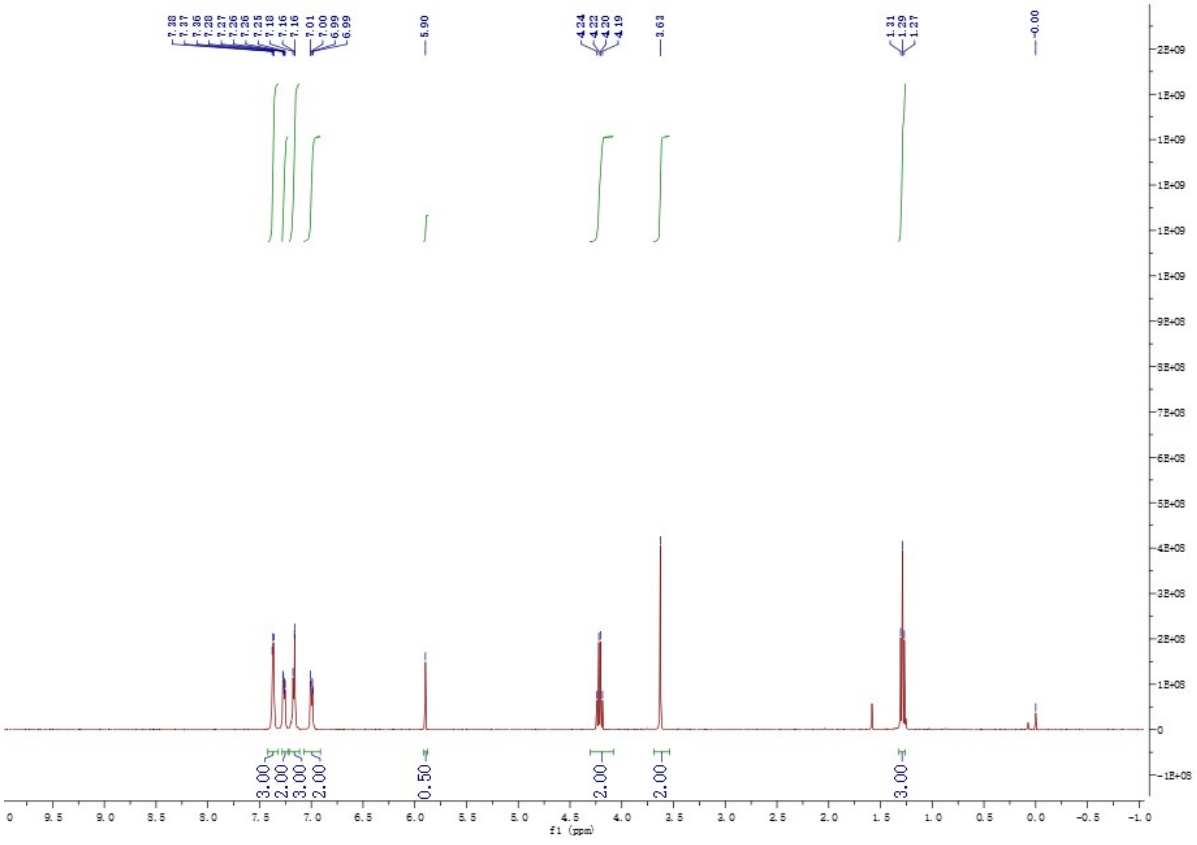


Fig. S3 ^1H NMR spectrum of **3a-D** (400 MHz, $CDCl_3$)

4.4 Light on-off experiments

Following the standard procedure, the reaction between **1a** (0.1 mmol, 1.0 eq.) and **2a** (0.15 mmol, 1.5 eq.) was conducted for light on-off experiment.

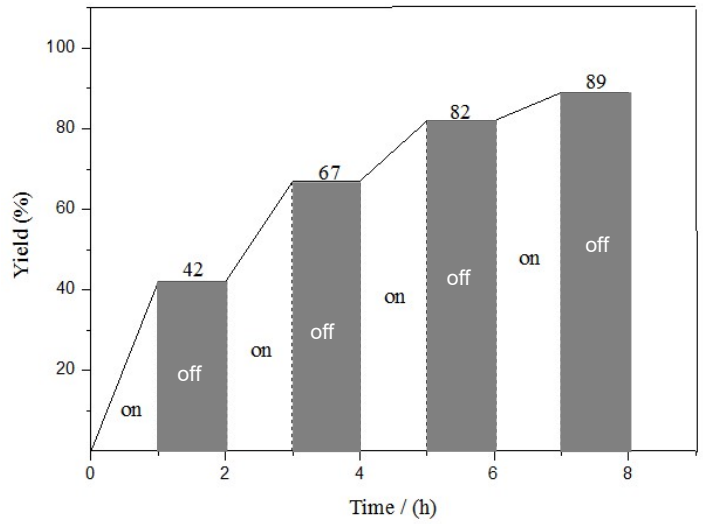


Fig. S4 Profile of the yield with light on-off over time. The yield was determined by ^{1}H NMR.

4.5 Fluorescence quenching experiments

$Ru(bpy)_3(PF_6)_2$ (4.0 mg 5.0 μmol) was dissolved in 1.0 mL CH_3CN to prepare a 5×10^{-3} M solution. 100 μL of this solution was added to each of a set of 6 volumetric flasks (10 mL). Subsequently, the solution of quencher $Cu(OAc)_2$ in CH_3CN(5×10^{-3} M) or the solution of quencher **1a** or **2a** in CH_3CN(5×10^{-2} M) was added in increasing amounts(0, 100 μL, 200 μL, 300 μL, 400 μL, 500 μL) to the volumetric flasks and the volumetric flasks were adjusted to 10 mL by adding CH_3CN. All $Ru(bpy)_3(PF_6)_2$ solutions were irradiated at 390 nm and the emission intensity from 400 to 780 nm was recorded by FLS920 Spectrophotometer.

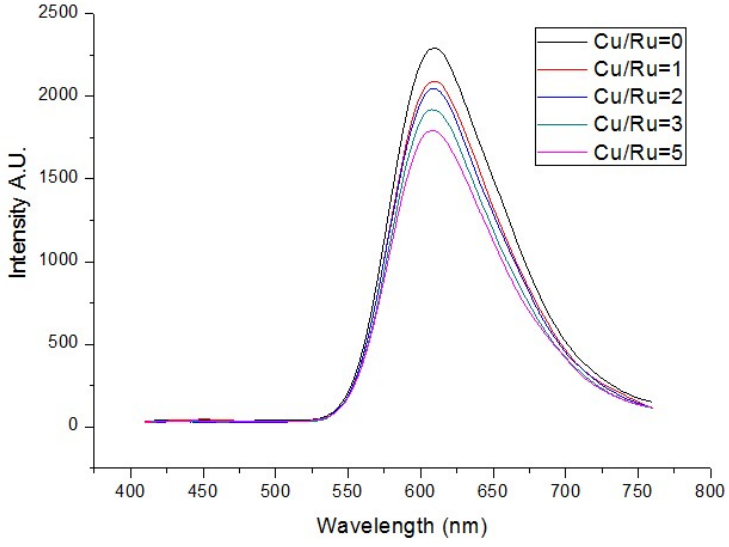


Fig. S5 The emission quenching spectrum of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) by various concentration of $Cu(OAc)_2$.

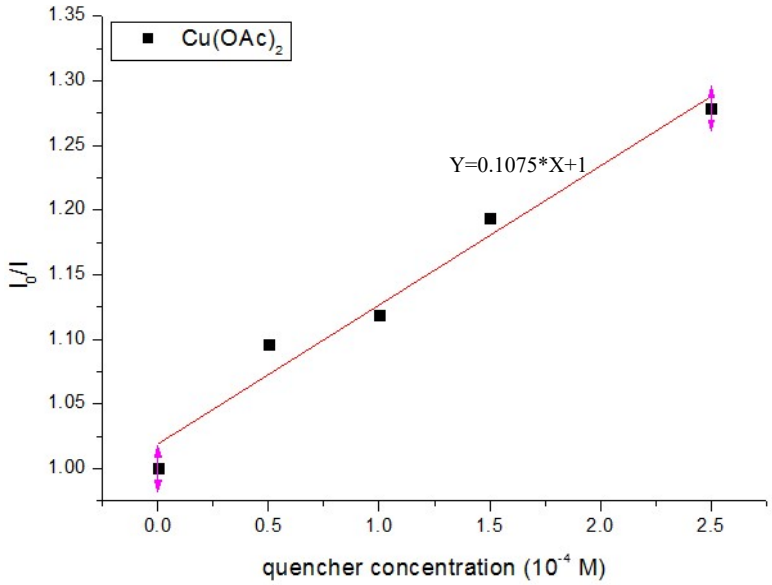


Fig. S6 Stern-Volmer plot for the emission quenching of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) with various concentration of $Cu(OAc)_2$.

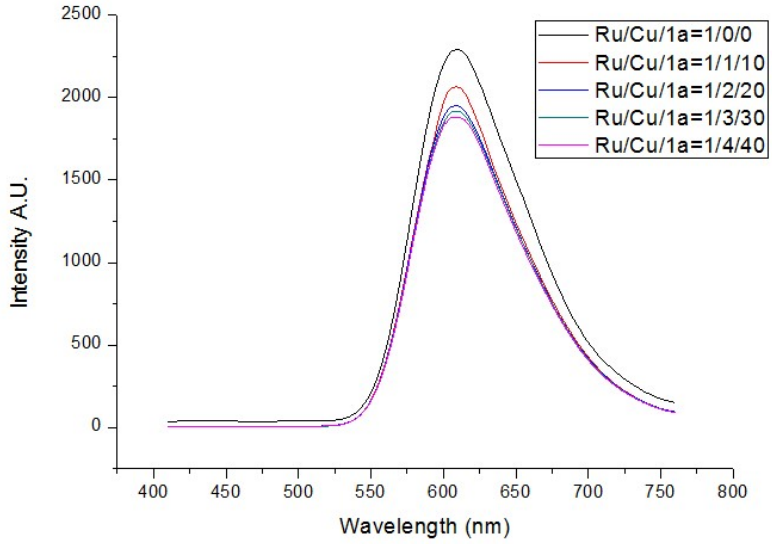


Fig. S7 The emission quenching spectrum of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) by various concentration of **1a** and $Cu(OAc)_2$.

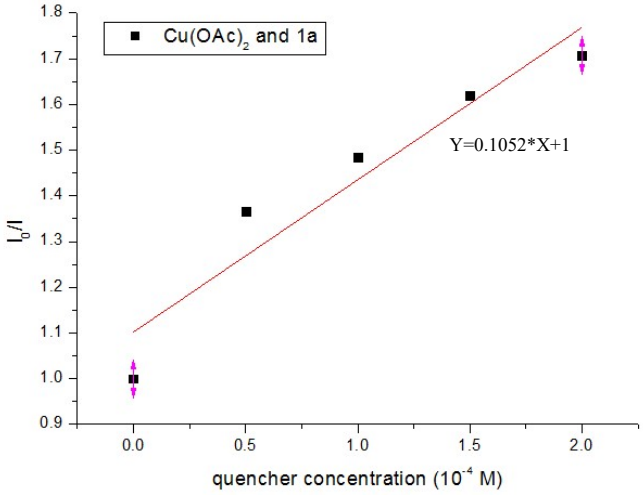


Fig. S8 Stern-Volmer plot for the emission quenching of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) with various concentration of **1a** and $Cu(OAc)_2$.

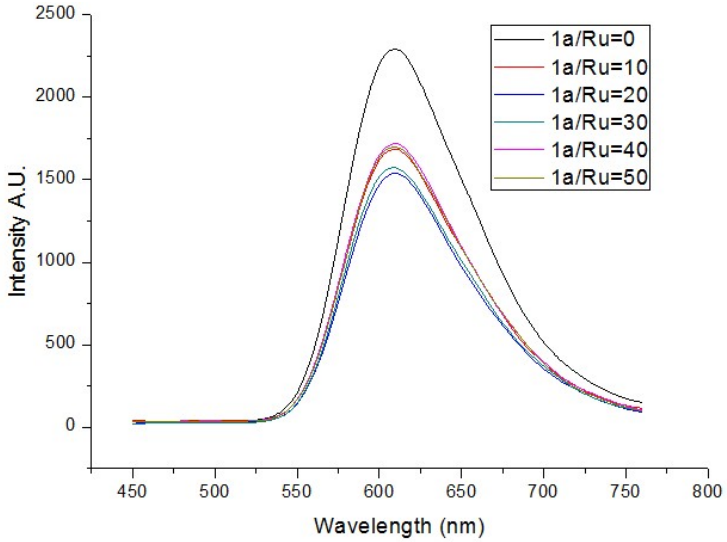


Fig. S9 The emission quenching spectrum of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) by various concentration of **1a**.

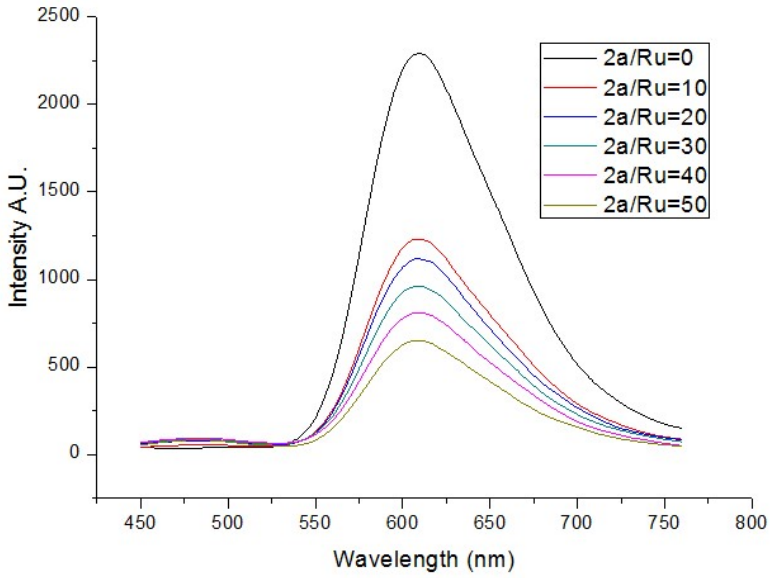


Fig. S10 The emission quenching spectrum of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) by various concentration of **2a**.

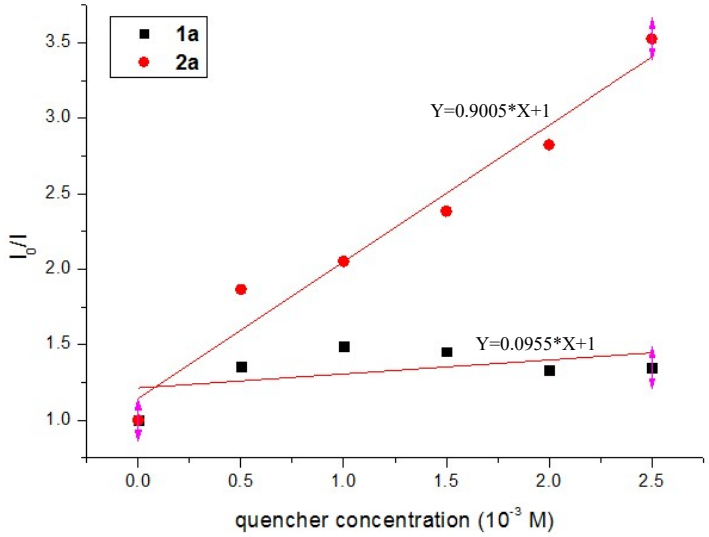
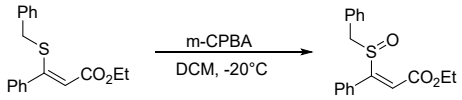


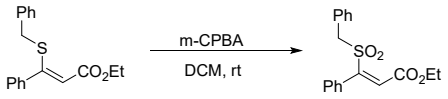
Fig. S11 Stern-Volmer plot for the emission quenching of $Ru(bpy)_3(PF_6)_2$ (5×10^{-5} M) with various concentration of **1a** or **2a**.

5. Oxidation Experiments



3a **4a, 89%**

A mixture of **3a** (0.1 mmol) and an excess of 75% m-CPBA (0.2 mmol) was stirred at -20 ºC for 4 hours. The mixture was poured into saturated $NaHCO_3$ (aq.) and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (EA:PE(1:4, v/v)) to afford **5a** as yellow oil in 89% yield.



3a **5a, 95%**

A mixture of **3a** (0.1 mmol) and an excess of 75% m-CPBA (0.3 mmol) was stirred at room temperature for 12 h. The mixture was poured into saturated $NaHCO_3$ (aq.) and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (EA:PE(1:3, v/v)) to afford **6a** as yellow oil in 95% yield.

6. Computational Studies

6.1 Computational methods

The B3LYP density functional method with Grimme-D3 correction[4] was employed to carry out the computational studies. For geometry optimizations, the LANL2DZ basis set in conjunction with the LANL2DZ pseudopotential[5] was used for Cu and Ru atoms. The 6-31+G(d)[6] basis set was used for other atoms. Vibrational frequency analyses at the same level of theory were performed on all the optimized geometries to characterize stationary points as local minima (no imaginary frequency) or transition states (one imaginary frequency). In addition, intrinsic reaction coordinate (IRC) calculations[7] were used to verify that the transition state connects with appropriate reactant and product. The gas-phase Gibbs free energies for all species were obtained at 298.15 K and 1 atm at their respective optimized structures. To consider the effect of solvation, B3LYP-D3 functional with the SMD[8] continuum solvation model (in acetonitrile solvent) was used in single-point energy calculations. A larger basis set, SDD[9] for Cu and Ru atoms and 6-311++G(d,p) for the remaining atoms, was utilized for such single-point energy calculation. The solvation Gibbs free energy was used for discussion and its value was obtained from the addition of solvation single-point energy and gas-phase thermal correction to Gibbs free energy. The translational entropy in solution was corrected using the method proposed by Whitesides et al. [10] All calculations were carried out with the Gaussian 09 suite of programs[11]. The 3D structures of

optimized intermediates or transition states were demonstrated using the software of CYLView.[12]

The Marcus Theory[13] was applied to calculate the kinetic barrier of single electron transfer (SET). For a SET reaction below,

$$*[Ru]^{2+} + R_1 \xrightarrow{\text{SET}} [Ru]^{3+} + P_1$$

according to the Marcus-Hush equation, the solvent outer-sphere reorganization energy λ_o could be calculated from Equations S1 and S2.

$$\lambda_0 = (332 \text{ kcal/mol})\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}\right) \quad \text{Equation S1}$$

$$R = a_1 + a_2 \quad \text{Equation S2}$$

a_1 and a_2 are the radii of the excited-state photoredox ***Ru^{II}** and reactant **R$_1$**, respectively. ε_{op} and ε are the optical dielectric constant (2.25) and the static dielectric constant (35.7) of acetonitrile solvent, respectively. The radius of a molecule can be derived by calculating molecular volume via a Monte-Carlo integration as implemented in the Gaussian 09 program. For a single electron transfer reaction, the inner reorganization energies of the reactants are usually small enough and thus are neglected. Therefore, the total reorganization energy λ is approximately equal to λ_o. Next, the $\Delta G^{\neq}$ of a single electron transfer process could be calculated from Equations S3 and S4. ΔG_r is the Gibbs energy change for a SET reaction (Equation S5).

$$\Delta G_{ET}^{\neq} = \Delta G_0^{\neq}\left(1 + \frac{\Delta G_r}{4\Delta G_0^{\neq}}\right)^2 \quad \text{Equation S3}$$

$$\Delta G_0^{\neq} = \frac{\lambda}{4} \quad \text{Equation S4}$$

$$\Delta G_r = G([Ru]^{3+}) + G(P_1) - G(*[Ru]^{2+}) - G(R_1) \quad \text{Equation S5}$$

Table S3. Estimated activation barriers for SET/PCET steps.

steps	a_1 (Å)	a_2 (Å)	R (Å)	λ (kcal/mol)	ΔG_r (kcal/mol)	$\Delta G_{SET}^{\neq}$ (kcal/mol)
SET-1	6.39(***[Ru]^{II}**)	5.84(^{2}**INT7**)	12.23	11.3	-8.6	0.2
PCET-1	6.39(***[Ru]^{II}**)	6.21(^{1}**INT1**)	12.60	11.0	-1.8	1.9
SET-2	6.18(**[Ru]^{I}**)	5.84(^{2}**INT7**)	12.02	11.5	-20.1	1.6
PCET-2	6.21(**[Ru]^{III}**)	6.21(^{1}**INT1**)	12.42	11.1	-13.3	0.1

6.2 More computational results and discussion

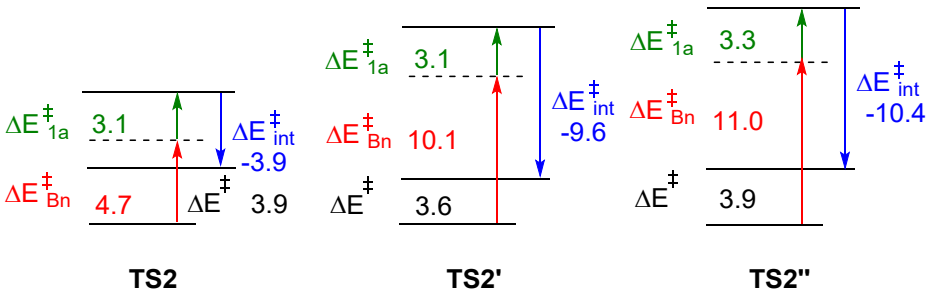
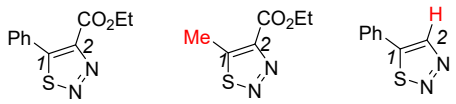


Fig. S12 Distortion, interaction and activation energies for **TS2, TS2'** and **TS2''** (green arrow: distortion energy of substrate **1a**; red arrow: distortion energy of benzyl radical; blue arrow: interaction energy; black: activation energy, in kcal/mol).

Table S4. The Fukui nucleophilicity indexes of **1a**, **1p**, and **1n**.



1a **1p** **1n**

Entry	Reaction sites	Fukui nucleophilicity index
1a	S	0.20
	C^1	0.12
	C^2	0.05
1p	S	0.26
	C^1	0.54
	C^2	0.06
1n	S	-0.11
	C^1	-0.01
	C^2	-0.13

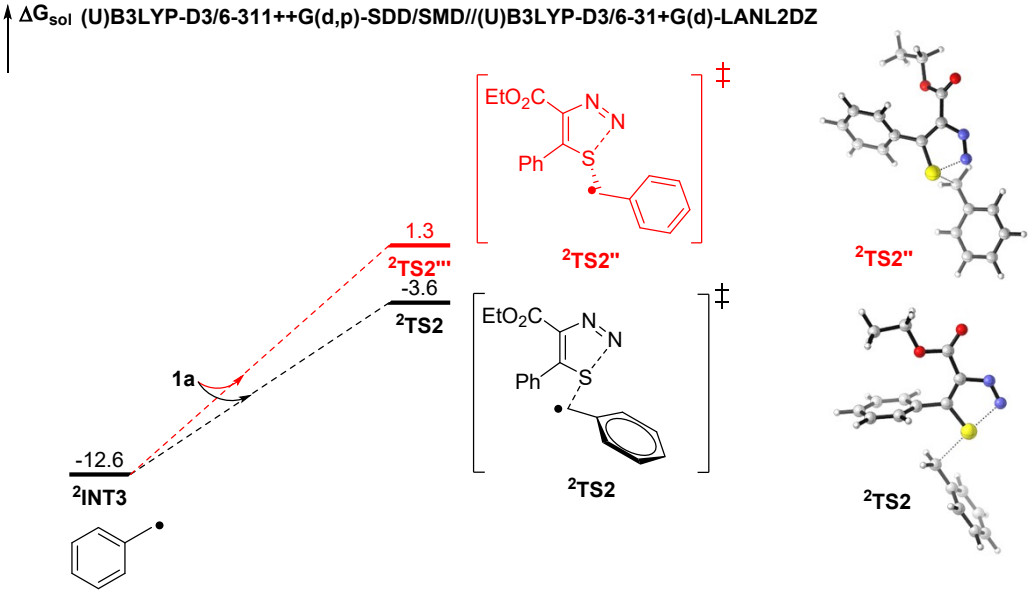


Fig. S13 Energy profiles (in kcal/mol) for two transtion states of benzyl radical attack to S-site of **1a**.

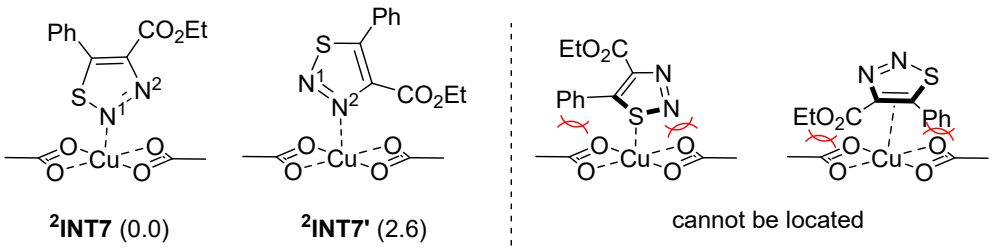


Fig. S14 Possible modes of coordination for 1,2,3-thiadiazoles with $Cu(OAc)_2$. The numbers in parenthesis are ΔΔG (in kcal/mol).

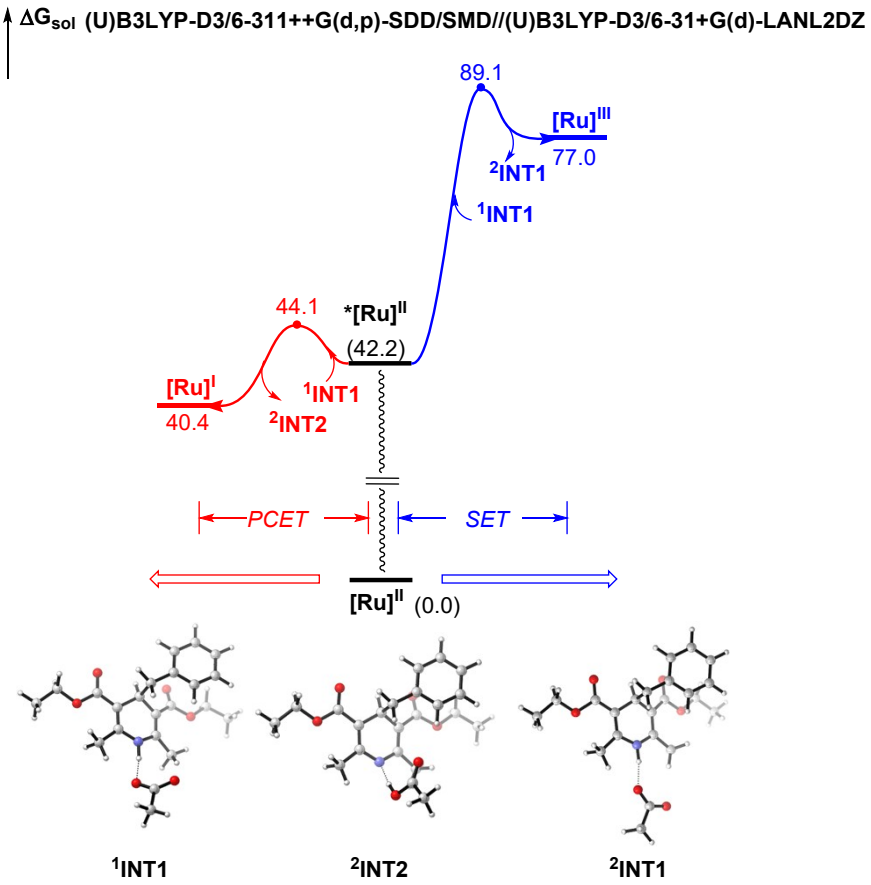


Fig. S15 Comparisons of the possible quenching paths of ***Ru^{II}** by **^{1}INT1** (in kcal/mol).

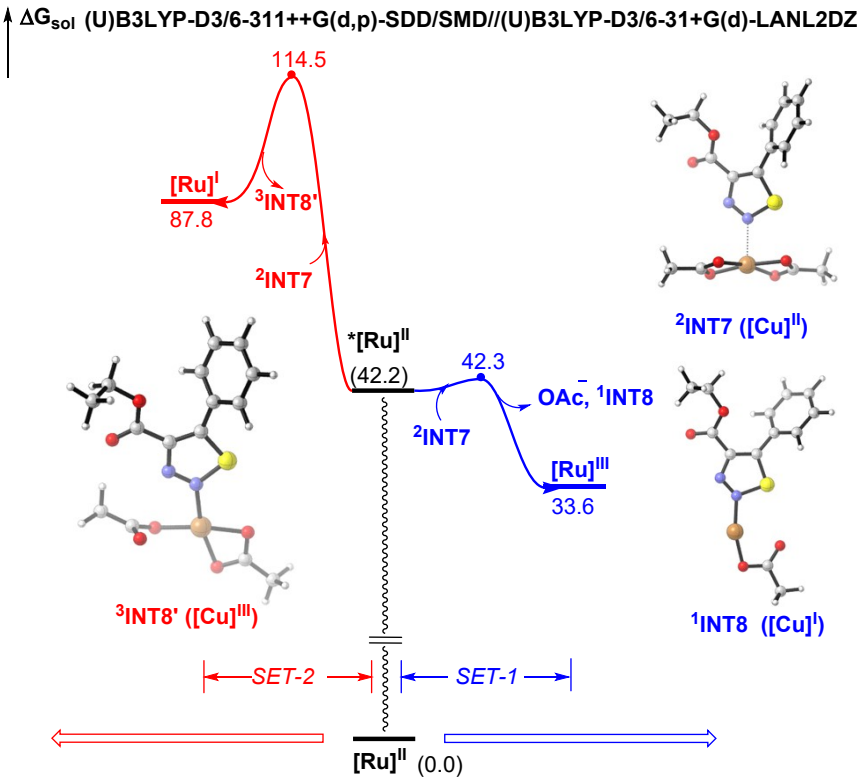


Fig. S16 Comparisons of the possible quenching paths of ***Ru^{II}** by Cu^{II} species **^{2}INT7** (in kcal/mol).

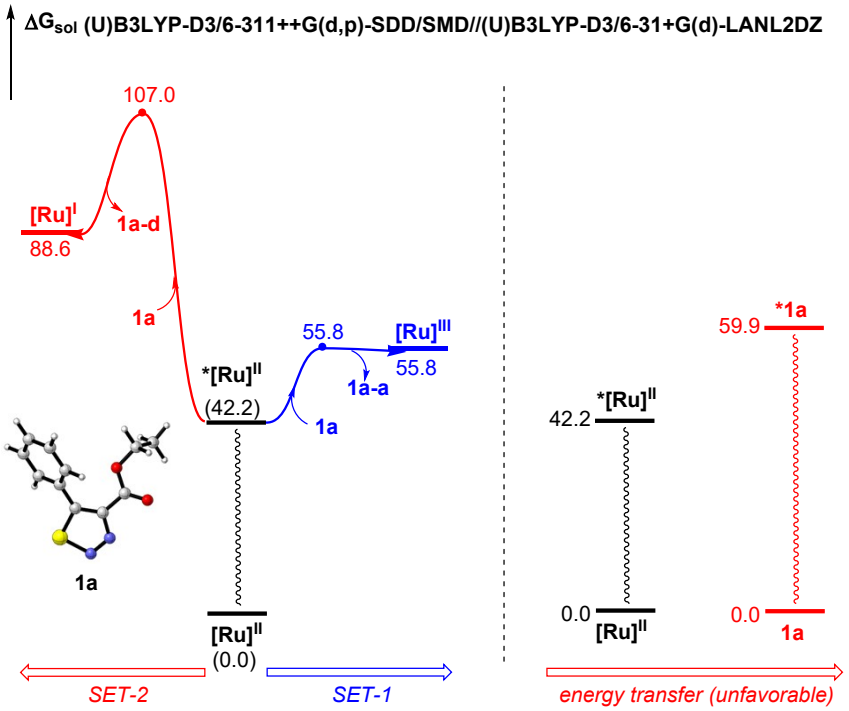


Fig. S17 (a) Comparisons of the possible quenching paths of ***Ru^{II}** by **1a** (in kcal/mol). (b) The calculated singlet−triplet energy gap (in kcal/mol) for the **1a** and comparison with the **Ru^{II}** photocatalyst.

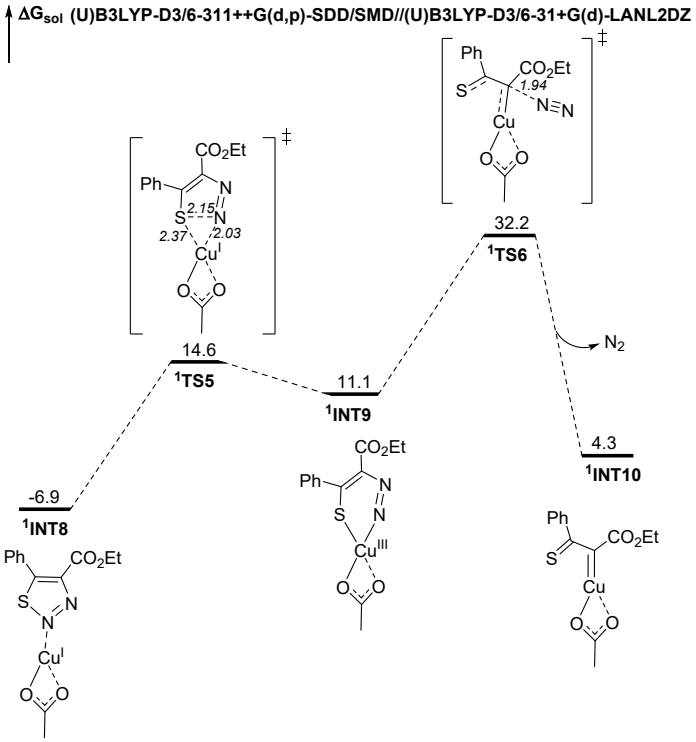


Fig. S18 Energy profiles (in kcal/mol) for the oxidative addition of **1a** to Cu center and the subsequent denitrogenation.

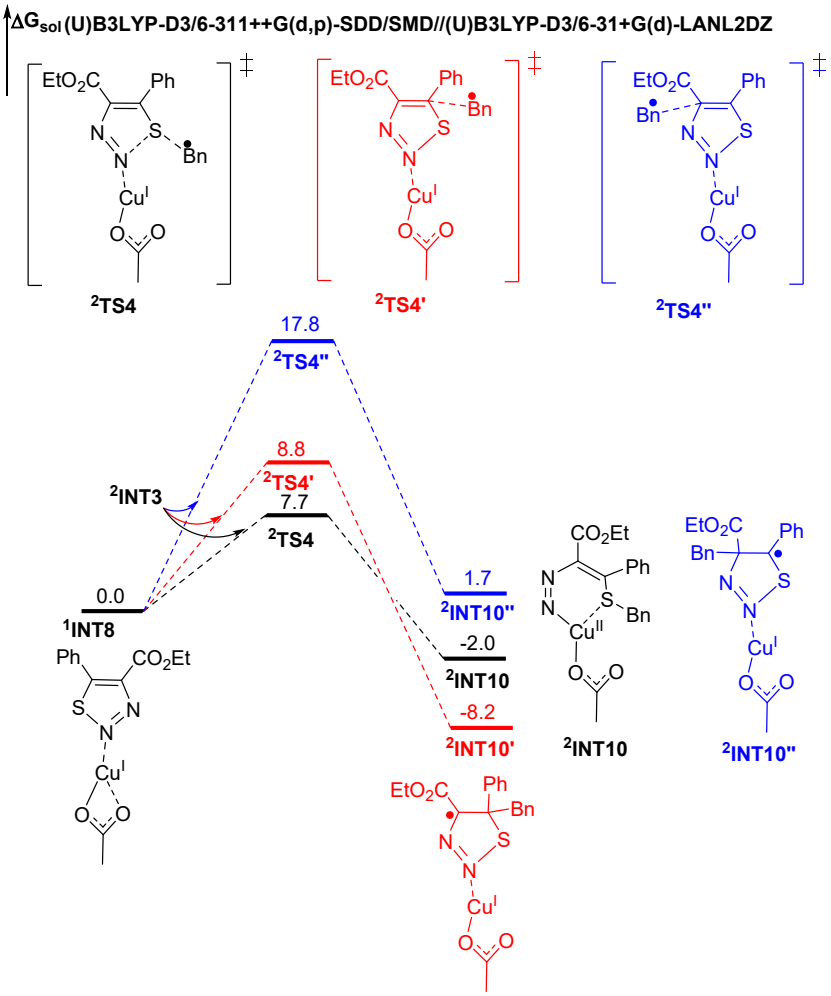


Fig. S19 Energy profiles (in kcal/mol) for possible benzyl radical attack to **^{1}INT8**.

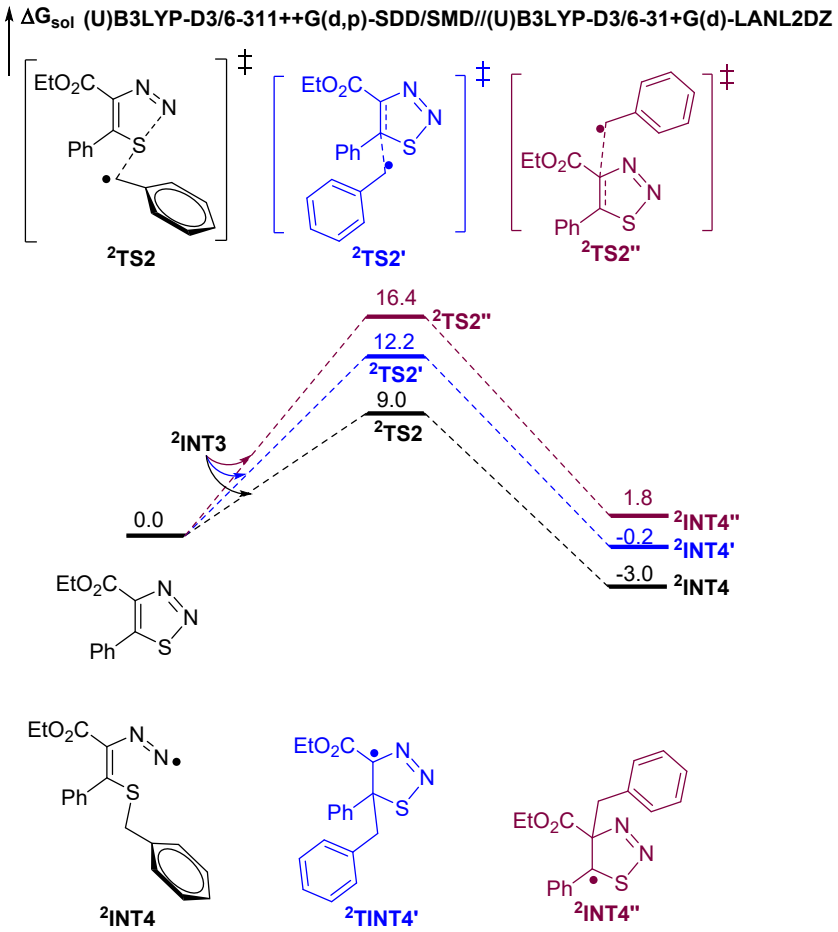


Fig. S20 Energy profiles (in kcal/mol) for possible benzyl radical attack to **1a**.

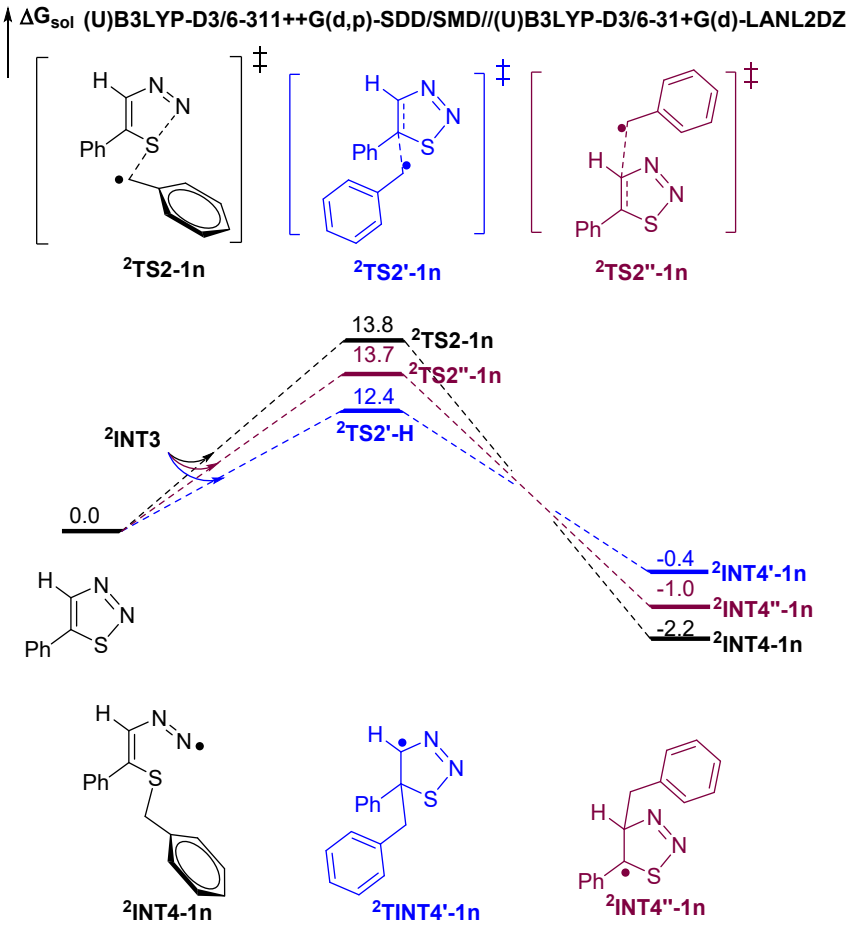


Fig. S21 Energy profiles (in kcal/mol) for possible benzyl radical attack to **1n**.

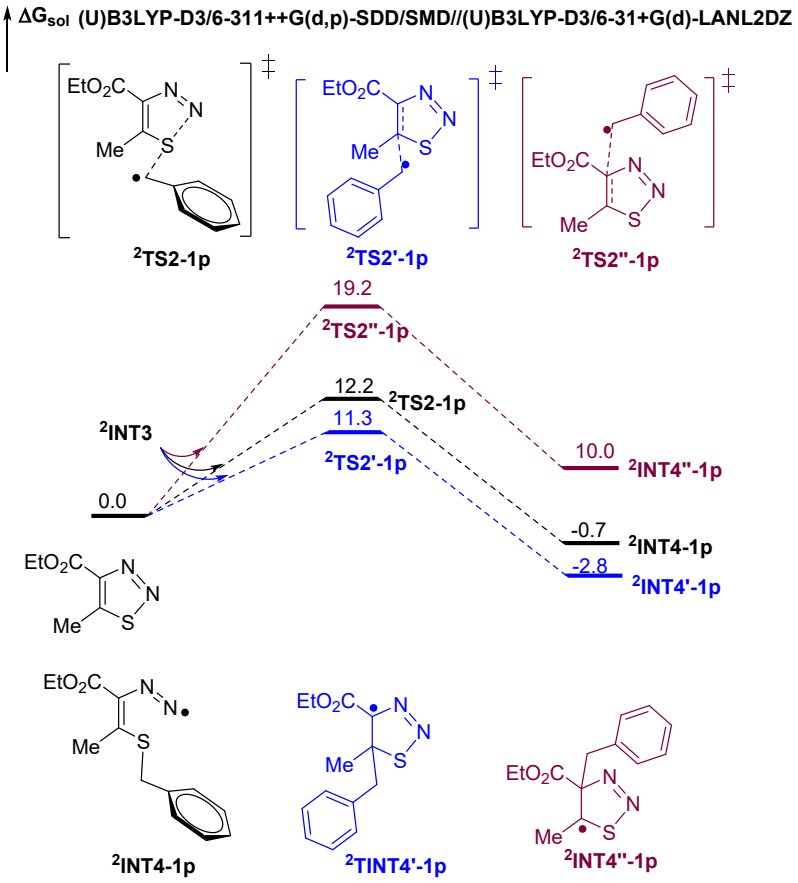


Fig. S22 Energy profiles (in kcal/mol) for possible benzyl radical attack to **1p**.

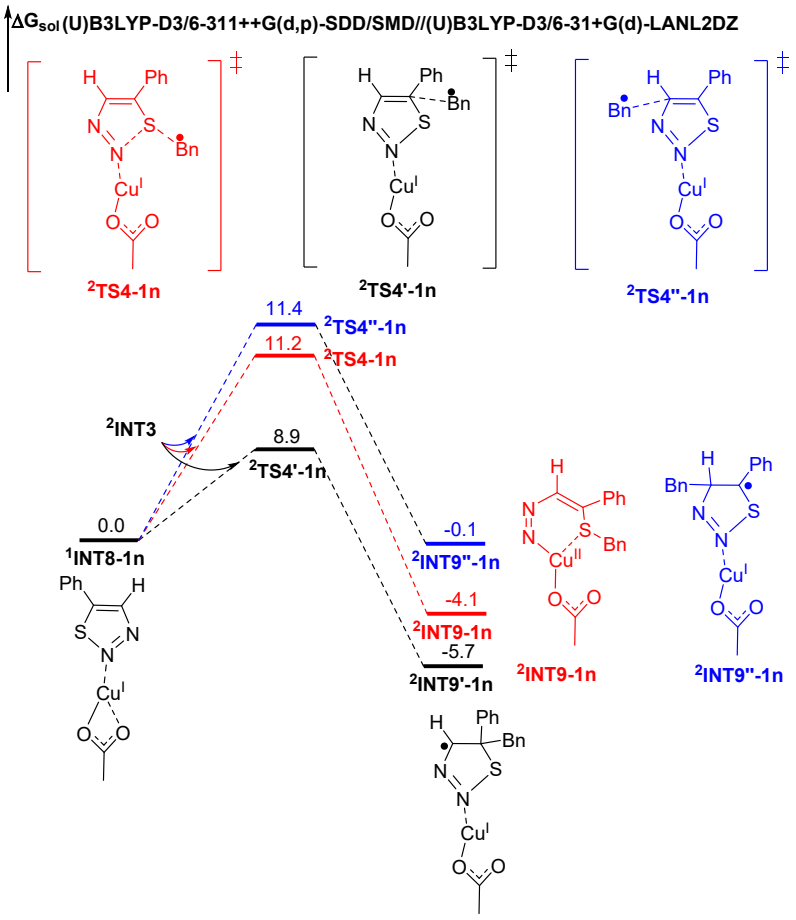


Fig. S23 Energy profiles (in kcal/mol) for possible benzyl radical attack to **^{1}INT8-1n**.

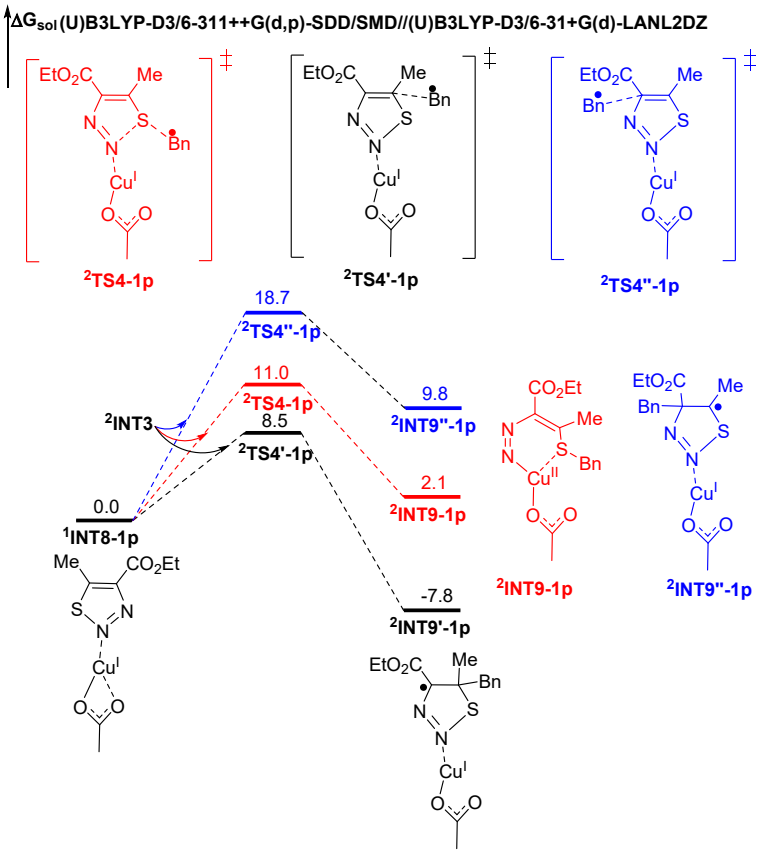


Fig. S24 Energy profiles (in kcal/mol) for possible benzyl radical attack to **^{1}INT8-1p.**

7. Cartesian Coordinates and Energies

$Ru(bpy)_3^{2+}$

C	2.58000600	-1.30432200	0.58396200
C	3.80540400	-1.58926800	1.19424500
C	4.21890700	-0.84260400	2.29548100
C	3.39341400	0.17966300	2.76685700
C	2.18630800	0.41583500	2.11724800
H	4.43600600	-2.38464100	0.81570100
H	5.16863800	-1.05605900	2.77530000
H	3.67484400	0.78659200	3.62066700
H	1.51033800	1.19656500	2.44516100
C	2.05183600	-2.03700100	-0.58289600
C	2.70969400	-3.10943500	-1.19307600
C	2.13107800	-3.73942000	-2.29286900
H	3.66435000	-3.45506700	-0.81527100
C	0.29340500	-2.21044300	-2.11348000
C	0.89894400	-3.28133100	-2.76260800
H	2.63387200	-4.57302600	-2.77252800
H	-0.66199100	-1.81751700	-2.44027800
H	0.41099900	-3.74179800	-3.61492400
N	1.78216900	-0.30431100	1.05418700
N	0.85009900	-1.59721300	-1.05229500
C	0.74010300	2.79410200	-0.58346300
C	1.34148400	3.89920600	-1.19360500
C	2.17565000	3.71198300	-2.29377400
C	2.39244900	2.41567100	-2.76417600
C	1.76641800	1.35667300	-2.11497900
H	1.16519500	4.89901700	-0.81563000
H	2.64739400	4.56357100	-2.77339000
H	3.03431700	2.22253700	-3.61697300
H	1.90154600	0.33261500	-2.44214300
C	-0.15886200	2.88617200	0.58309000
C	-0.52379900	4.09030100	1.19312900
C	-1.37848900	4.07612800	2.29336800
H	-0.14864500	5.03362400	0.81501600
C	-1.45513000	1.68675600	2.11481300
C	-1.85347600	2.85073200	2.76395400
H	-1.66777700	5.00570300	2.77293600
H	-1.79505700	0.71141600	2.44218700
H	-2.52108700	2.79185200	3.61682300
N	0.95815300	1.53331200	-1.05313500
N	-0.62782100	1.69577600	1.05297600
C	-2.79078700	-0.75525500	-0.58410200
C	-4.04832500	-0.78616700	-1.19476000
C	-4.30176400	0.02891800	-2.29597000
C	-3.28630100	0.86305500	-2.76688000
C	-2.05655900	0.84984100	-2.11693000
H	-4.82701100	-1.43740500	-0.81646200
H	-5.27492100	0.01227200	-2.77603700
H	-3.43877900	1.51458300	-3.62058900
H	-1.23635100	1.47760100	-2.44426200
C	-2.42195200	-1.57980900	0.58272900
C	-3.28312600	-2.49724200	1.19258200
C	-2.84416200	-3.23104900	2.29260400
H	-4.28777900	-2.64296400	0.81443300
C	-0.73538600	-2.10491700	2.11406000
C	-1.54510200	-3.03130300	2.76292400
H	-3.50521700	-3.94583700	2.77204300
H	0.27960800	-1.91318500	2.44128500
H	-1.16063700	-3.58083100	3.61543000
N	-1.80688400	0.06247500	-1.05407800
N	-1.15632000	-1.39198200	1.05262900
Ru	-0.00020200	-0.00042800	0.00033300

Zero-point correction= 0.486171 (Hartree/Particle)
Thermal correction to Energy= 0.514793
Thermal correction to Enthalpy= 0.515737
Thermal correction to Gibbs Free Energy= 0.426475
Sum of electronic and zero-point Energies= -1579.456208
Sum of electronic and thermal Energies= -1579.427587
Sum of electronic and thermal Enthalpies= -1579.426642
Sum of electronic and thermal Free Energies= -1579.515904
B3LYP-D3/6-311++G(d,p)-SDD/SMD//B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1581.59433037

***$Ru(bpy)_3^{2+}$**

C	2.97974600	-1.00475800	0.48518500
C	4.35870300	-0.98441700	0.73227200
C	4.85832200	-0.14403500	1.72659600
C	3.97392300	0.66312800	2.44500300

C	2.61828100	0.59934100	2.12787200
H	5.03889600	-1.59730800	0.15236400
H	5.92402000	-0.11595100	1.93127600
H	4.32322000	1.32745500	3.22836600
H	1.88777300	1.21371800	2.64794900
C	2.36356400	-1.86908300	-0.55201700
C	3.03136300	-2.96633400	-1.10859900
C	2.40826500	-3.73628200	-2.08781500
H	4.02409700	-3.23088700	-0.76486100
C	0.49683400	-2.30958000	-1.89020500
C	1.11560500	-3.39885300	-2.49217700
H	2.92113700	-4.58931200	-2.52081600
H	-0.51084500	-2.00887300	-2.15559100
H	0.59072300	-3.96823100	-3.25158800
N	2.13379500	-0.21455300	1.18090400
N	1.10017500	-1.55880100	-0.94782000
C	0.52111400	2.90052700	-0.51857700
C	1.07165100	4.05852900	-1.07596800
C	2.05652300	3.95160600	-2.05512700
C	2.47709000	2.68268300	-2.45939400
C	1.89646200	1.56803700	-1.86615600
H	0.73640400	5.03673500	-0.75303500
H	2.48805400	4.84500800	-2.49502400
H	3.24041300	2.55467000	-3.21921900
H	2.18946500	0.56179800	-2.14164600
C	-0.52218800	2.90032500	0.51865600
C	-1.07337000	4.05818100	1.07574800
C	-2.05811600	3.95097300	2.05499700
H	-0.73872600	5.03650200	0.75253800
C	-1.89667300	1.56746000	1.86677100
C	-2.47792500	2.68195100	2.45971400
H	-2.49013800	4.84426300	2.49464200
H	-2.18904500	0.56112900	2.14259100
H	-3.24110400	2.55376500	3.21965200
N	0.94130600	1.66645200	-0.92124200
N	-0.94167700	1.66614700	0.92176000
C	-2.97929400	-1.00545300	-0.48539400
C	-4.35822800	-0.98530200	-0.73263600
C	-4.85784100	-0.14508700	-1.72710200
C	-3.97346100	0.66210800	-2.44549600
C	-2.61784700	0.59852500	-2.12820100
H	-5.03841500	-1.59820700	-0.15273800
H	-5.92352000	-0.11715500	-1.93190200
H	-4.32274900	1.32630600	-3.22897200
H	-1.88736000	1.21293900	-2.64826300
C	-2.36310700	-1.86958100	0.55197200
C	-3.03080900	-2.96689100	1.10856500
C	-2.40769400	-3.73668400	2.08789200
H	-4.02346700	-3.23161700	0.76475100
C	-0.49644900	-2.30972300	1.89036900
C	-1.11511700	-3.39905000	2.49234600
H	-2.92048200	-4.58976200	2.52090000
H	0.51115900	-2.00885100	2.15584100
H	-0.59022100	-3.96831100	3.25183500
N	-2.13336200	-0.21520600	-1.18109200
N	-1.09980700	-1.55908000	0.94788800
Ru	0.00003900	0.03140700	0.00008200

Zero-point correction= 0.483664 (Hartree/Particle)
Thermal correction to Energy= 0.513579
Thermal correction to Enthalpy= 0.514524
Thermal correction to Gibbs Free Energy= 0.419332
Sum of electronic and zero-point Energies= -1579.384550
Sum of electronic and thermal Energies= -1579.354634
Sum of electronic and thermal Enthalpies= -1579.353690
Sum of electronic and thermal Free Energies= -1579.448882
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1581.519862

$Ru(bpy)_3^{3+}$

C	-2.85979600	-0.45926600	0.56888800
C	-4.01607200	-0.96353600	1.16816700
C	-3.90799500	-1.85355400	2.23736300
C	-2.63984100	-2.22851100	2.68727600
C	-1.52272200	-1.69962400	2.05021700
H	-4.99549200	-0.67125100	0.80873800
H	-4.80214400	-2.24925900	2.70930300
H	-2.51367800	-2.91827600	3.51508800
H	-0.51784800	-1.96028400	2.36055200
C	-2.85694300	0.47735200	-0.56868800
C	-4.01011300	0.98899800	-1.16769400
C	-3.89660100	1.87823100	-2.23697800

H	-4.99129800	0.70301100	-0.80801000
C	-1.51232300	1.70894800	-2.05052300
C	-2.62619200	2.24493900	-2.68733700
H	-4.78832100	2.27963800	-2.70869700
H	-0.50583900	1.96289800	-2.36120300
H	-2.49583600	2.93375300	-3.51529000
N	-1.62745900	-0.83204700	1.02398000
N	-1.62236500	0.84224000	-1.02412400
C	1.01484500	-2.71293700	-0.56835600
C	1.14824500	-3.96751600	-1.16721300
C	0.32122200	-4.31400000	-2.23630900
C	-0.63167400	-3.39723100	-2.68658700
C	-0.72431400	-2.16449600	-2.04995500
H	1.88657700	-4.67419700	-0.80755800
H	0.41938300	-5.28701900	-2.70791300
H	-1.29355900	-3.62887000	-3.51436500
H	-1.44767600	-1.42003200	-2.36069100
C	1.82761400	-2.24695600	0.56900000
C	2.84258900	-2.99608500	1.16818500
C	3.55970500	-2.45719700	2.23698200
H	3.07902500	-3.99053500	0.80894600
C	2.23380400	-0.46845100	2.04971500
C	3.25059100	-1.17131300	2.68662500
H	4.34960200	-3.03360500	2.70881700
H	1.95716200	0.53222200	2.35976600
H	3.78519200	-0.71695600	3.51410700
N	0.08150100	-1.82623800	-1.02375000
N	1.53445600	-0.99322500	1.02389600
C	1.84215800	2.23529800	-0.56858300
C	2.86203700	2.97797800	-1.16747400
C	3.57562000	2.43483000	-2.23647600
C	3.25808500	1.15117900	-2.68663100
C	2.23676300	0.45471300	-2.04996100
H	3.10490800	3.97077100	-0.80794700
H	4.36923500	3.00626300	-2.70812500
H	3.78964800	0.69367900	-3.51433700
H	1.95357500	-0.54396700	-2.36055300
C	1.03215900	2.70633400	0.56866900
C	1.17357100	3.95987200	1.16787400
C	0.34829400	4.31159800	2.23660600
H	1.91673900	4.66172900	0.80873300
C	-0.71136200	2.16911300	2.04925500
C	-0.61093600	3.40109700	2.68615600
H	0.45266600	5.28383900	2.70848100
H	-1.43980100	1.42935500	2.35934300
H	-1.27176300	3.63698300	3.51357900
N	1.54088600	0.98362500	-1.02387800
N	0.09281200	1.82570900	1.02348500
Ru	-0.00004100	0.00001800	-0.00025700

Zero-point correction= 0.486553 (Hartree/Particle)
Thermal correction to Energy= 0.515288
Thermal correction to Enthalpy= 0.516232
Thermal correction to Gibbs Free Energy= 0.426559
Sum of electronic and zero-point Energies= -1579.008317
Sum of electronic and thermal Energies= -1578.979582
Sum of electronic and thermal Enthalpies= -1578.978637
Sum of electronic and thermal Free Energies= -1579.068311
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1581.39955

$Ru(bpy)_3^+$

C	-1.48958900	2.46638700	-0.59564700
C	-1.89498500	3.63713200	-1.26282600
C	-1.21087800	4.06677200	-2.38908600
C	-0.11322600	3.31826800	-2.84736000
C	0.23686700	2.16640000	-2.15849800
H	-2.74446300	4.20250200	-0.89775500
H	-1.52117300	4.96888100	-2.90673000
H	0.45684400	3.62168200	-3.71854400
H	1.06955000	1.54852600	-2.47430400
C	-2.13332900	1.93636700	0.59670100
C	-3.20432100	2.55907100	1.26403300
C	-3.75706000	1.97031700	2.39049200
H	-3.59614000	3.50126300	0.89896000
C	-2.17010900	0.18457500	2.15970900
C	-3.23311500	0.74943900	2.84880100
H	-4.58269600	2.44810200	2.90826300
H	-1.72354500	-0.75121300	2.47552400
H	-3.64009900	0.24835200	3.72016500
N	-0.42733600	1.73517900	-1.06838100
N	-1.61969800	0.75346500	1.06935400

C	2.74414900	0.87874800	0.59619100
C	3.81925700	1.49422600	1.26358500
C	3.58614800	2.26734500	2.39009600
C	2.26695000	2.42471700	2.84839600
C	1.24592500	1.78711900	2.15928400
H	4.83105800	1.36195400	0.89848800
H	4.41299100	2.74299600	2.90790700
H	2.03681000	3.02781300	3.71978000
H	0.21224500	1.86881900	2.47502900
C	2.88081000	0.05652400	-0.59643400
C	4.09722100	-0.17805900	-1.26381900
C	4.12672200	-0.98472800	-2.39053600
H	5.01183800	0.27429500	-0.89860900
C	1.75694500	-1.28723200	-2.15985100
C	2.92932700	-1.56016100	-2.84900800
H	5.06297500	-1.16726900	-2.90836800
H	0.80528400	-1.69875000	-2.47584000
H	2.90660600	-2.20502800	-3.72057600
N	1.46299900	1.02593100	1.06889900
N	1.71613600	-0.49705100	-1.06924300
C	-0.61073600	-2.81582100	0.59565800
C	-0.61485200	-4.05493500	1.26253300
C	0.17159100	-4.23998800	2.38872100
C	0.96744600	-3.17627600	2.84724800
C	0.92544800	-1.97298800	2.15861900
H	-1.23533400	-4.86495000	0.89729100
H	0.17038300	-5.19409600	2.90613600
H	1.60501400	-3.27874900	3.71845700
H	1.51298800	-1.11872000	2.47464900
C	-1.39170000	-2.52265900	-0.59645600
C	-2.20354600	-3.45853900	-1.26367000
C	-2.91750200	-3.08034500	-2.38984700
H	-2.26904000	-4.47688600	-0.89869400
C	-1.99417100	-0.87699200	-2.15911300
C	-2.81719800	-1.75554500	-2.84806100
H	-3.54412100	-3.79966400	-2.90750600
H	-1.87474100	0.15300400	-2.47487500
H	-3.36470300	-1.41315800	-3.71927000
N	0.15746700	-1.78004200	1.06845700
N	-1.28896800	-1.23707600	-1.06892800
Ru	0.00014400	0.00005900	0.00000400

Zero-point correction= 0.481412 (Hartree/Particle)
Thermal correction to Energy= 0.510326
Thermal correction to Enthalpy= 0.511270
Thermal correction to Gibbs Free Energy= 0.420810
Sum of electronic and zero-point Energies= -1579.705365
Sum of electronic and thermal Energies= -1579.676451
Sum of electronic and thermal Enthalpies= -1579.675507
Sum of electronic and thermal Free Energies= -1579.765967
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1581.696181

1a

C	-0.41521100	1.09774900	-0.01666100
C	0.96457600	1.11147100	-0.17072400
S	-0.93913100	2.72285500	0.18175700
N	0.71562400	3.32862800	0.06393800
N	1.52057900	2.37000200	-0.12219000
C	-1.37443700	-0.01573700	-0.05614500
C	-1.31535400	-0.97178100	-1.08194100
C	-2.38862300	-0.10978600	0.90845200
C	-2.24525000	-2.00534100	-1.13157400
H	-0.54801000	-0.89091500	-1.84389900
C	-3.31329400	-1.15077300	0.85946000
H	-2.43542200	0.62334700	1.70818900
C	-3.24425000	-2.10067300	-0.15982900
H	-2.19366700	-2.73544000	-1.93389200
H	-4.08700500	-1.21823500	1.61836300
H	-3.96762300	-2.90970600	-0.20043400
C	1.90212700	-0.03417400	-0.32812800
O	3.00973400	0.05968600	-0.80804700
O	1.36203500	-1.17536300	0.14469200
C	2.16834000	-2.37002800	0.01383800
C	3.14787500	-2.49700300	1.16853000
H	2.68861400	-2.33883700	-0.94655200
H	1.43772100	-3.18208200	0.00898400
H	3.69203300	-3.44500900	1.09177800
H	3.87304300	-1.67948000	1.14515000
H	2.61984900	-2.47787000	2.12713500

Zero-point correction= 0.195638 (Hartree/Particle)

Thermal correction to Energy= 0.209943
Thermal correction to Enthalpy= 0.210887
Thermal correction to Gibbs Free Energy= 0.152204
Sum of electronic and zero-point Energies= -1083.164805
Sum of electronic and thermal Energies= -1083.150500
Sum of electronic and thermal Enthalpies= -1083.149556
Sum of electronic and thermal Free Energies= -1083.208238
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1083.589869

2a

C	-0.11859900	-2.09923700	-0.32928300
C	-0.41648700	-0.92576500	0.27411100
C	0.51686500	0.25931500	0.10083600
C	1.94984300	-0.19583500	-0.08173200
C	2.19725800	-1.38292300	-0.69863400
H	1.33973600	-3.12377600	-1.35302900
C	0.07348800	1.13705800	-1.11228600
H	0.20605200	0.55011400	-2.02888900
H	0.75676600	1.99154700	-1.16104200
C	-1.35543700	1.60445700	-0.99926900
C	-1.68283800	2.70130000	-0.19199000
C	-2.39266400	0.90498700	-1.62661800
C	-3.00935500	3.08636400	-0.01315800
H	-0.88657800	3.24221800	0.31297600
C	-3.72387700	1.28734200	-1.45322800
H	-2.15302900	0.04428800	-2.24547400
C	-4.03676800	2.37897500	-0.64294100
H	-3.24394600	3.93684200	0.62103000
H	-4.51480600	0.73296800	-1.95199200
H	-5.07189400	2.67998000	-0.50580600
C	-1.61018900	-0.65587200	1.10454800
O	-1.62651300	0.17062500	1.99738500
O	-2.71313800	-1.36808900	0.75757700
C	2.96628100	0.76590700	0.35418500
O	2.70302000	1.88563500	0.76427100
O	4.24790000	0.31026000	0.28245600
C	-3.92560600	-0.99581600	1.44715000
C	-5.06946100	-1.70433700	0.74939500
H	-4.02843700	0.09094300	1.39870000
H	-3.84152800	-1.28182200	2.50091100
H	-6.01812500	-1.45007500	1.23444600
H	-5.12359600	-1.39673600	-0.29959600
H	-4.94510400	-2.79184600	0.78641800
C	5.26058200	1.24853900	0.69486300
C	6.60349900	0.56502100	0.52362800
H	5.07550800	1.53604400	1.73458800
H	5.17866000	2.15446400	0.08578700
H	7.40881500	1.23847900	0.83591600
H	6.65831800	-0.34354600	1.13201400
H	6.77204200	0.28963300	-0.52275800
C	-0.92150600	-3.36869400	-0.37179800
H	-1.85880500	-3.26386100	0.16660100
H	-1.15333400	-3.63140900	-1.41276100
H	-0.34676200	-4.19997000	0.05763300
C	3.52681500	-1.95305700	-1.11816200
H	4.17385700	-1.18470200	-1.53825000
H	4.05630600	-2.38360600	-0.26133900
H	3.38329100	-2.74169900	-1.86583600
N	1.12029800	-2.21579000	-0.96937700
H	0.45327500	0.88223400	0.99418100

Zero-point correction= 0.421528 (Hartree/Particle)
Thermal correction to Energy= 0.447286
Thermal correction to Enthalpy= 0.448230
Thermal correction to Gibbs Free Energy= 0.363790
Sum of electronic and zero-point Energies= -1132.543311
Sum of electronic and thermal Energies= -1132.517553
Sum of electronic and thermal Enthalpies= -1132.516609
Sum of electronic and thermal Free Energies= -1132.601049
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1133.308922

3aa

C	-1.31033200	-0.15637000	0.20526900
C	-1.65501700	1.11382000	-0.14006100
S	0.24413200	-0.71305900	0.82639500
C	-2.31175000	-1.24458900	0.06433200
C	-3.65180500	-1.00204600	0.41339100
C	-1.96045800	-2.51838600	-0.41212300
C	-4.61452400	-1.99767700	0.27308800
H	-3.92426400	-0.03304300	0.81907900
C	-2.92627100	-3.51201700	-0.55460700

H	-0.92923800	-2.71675700	-0.68240300
C	-4.25519200	-3.25606400	-0.21374800
H	-5.64363400	-1.79539400	0.55580900
H	-2.63987700	-4.48813300	-0.93548700
H	-5.00554700	-4.03434000	-0.32010600
C	-0.97130800	2.36014000	0.20832700
O	-0.04513800	2.51067200	0.98991300
O	-1.57066100	3.40232800	-0.43091600
C	-1.03574100	4.71133100	-0.14761000
C	0.19859700	4.99819100	-0.98926600
H	-0.80827200	4.77929300	0.91920500
H	-1.85238300	5.39611700	-0.38901600
H	0.54002900	6.02514300	-0.81638700
H	1.00916800	4.31568900	-0.72073000
H	-0.02484300	4.88301000	-2.05486000
C	1.51954900	0.32826700	-0.01847900
H	1.62529100	1.26175700	0.53135100
H	1.12630500	0.55303400	-1.01431000
C	2.80136100	-0.45344200	-0.07997700
C	3.01849400	-1.40061800	-1.08896800
C	3.79099300	-0.25980600	0.89017600
C	4.20467200	-2.12948800	-1.13482400
H	2.24935800	-1.56314300	-1.84009900
C	4.97841200	-0.99118600	0.84948600
H	3.62681000	0.47050200	1.67832700
C	5.18829200	-1.92655500	-0.16390200
H	4.36306800	-2.85601500	-1.92694500
H	5.73919900	-0.82864300	1.60776100
H	6.11348200	-2.49485800	-0.19866800
H	-2.59220500	1.24970000	-0.66983800

Zero-point correction= 0.317507 (Hartree/Particle)
Thermal correction to Energy= 0.337193
Thermal correction to Enthalpy= 0.338137
Thermal correction to Gibbs Free Energy= 0.265468
Sum of electronic and zero-point Energies= -1245.160999
Sum of electronic and thermal Energies= -1245.141314
Sum of electronic and thermal Enthalpies= -1245.140370
Sum of electronic and thermal Free Energies= -1245.213038
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1245.755571

^{1}INT1

C	0.02863200	1.20378100	-0.74344400
C	-0.62205700	0.00375300	-0.79851000
C	0.02608000	-1.20491600	-0.14507400
C	1.53532800	-1.12230200	-0.22082000
C	2.12138600	0.12062800	-0.16839400
H	1.80643000	2.18322600	-0.19870100
C	-0.41806900	-1.31984100	1.35325100
H	0.00882400	-0.46814300	1.89527000
H	0.02966600	-2.23505100	1.75676600
C	-1.91373400	-1.33929000	1.52554100
C	-2.63506800	-2.53428000	1.40746900
C	-2.62812000	-0.14951100	1.71853800
C	-4.02648900	-2.54357700	1.47576200
H	-2.09214000	-3.46079500	1.23700000
C	-4.02218800	-0.15196900	1.78447400
H	-2.08324500	0.78701400	1.79427500
C	-4.72786500	-1.34962900	1.66220500
H	-4.56663100	-3.48201200	1.37453800
H	-4.55577600	0.78459400	1.92866500
H	-5.81421800	-1.35395600	1.71229900
C	-1.93726400	-0.26076400	-1.38683300
O	-2.31768200	-1.36792900	-1.74118900
O	-2.77143800	0.82073500	-1.47358400
C	2.22881600	-2.39453900	-0.21184900
O	1.68203000	-3.48949000	-0.11544700
O	3.59723400	-2.31032900	-0.33279300
C	-4.11145300	0.52301700	-1.88220200
C	-4.93610300	1.77492300	-1.64400000
H	-4.48204800	-0.32270200	-1.29600200
H	-4.11871200	0.22452300	-2.93767500
H	-5.97804200	1.60568700	-1.94084700
H	-4.91540700	2.04444100	-0.58313300
H	-4.54405300	2.62055000	-2.21912300
C	4.28937200	-3.55951000	-0.29512200
C	5.77263900	-3.25335900	-0.40881400
H	3.94325800	-4.19732700	-1.11664600
H	4.05379700	-4.08488000	0.63771200
H	6.35601100	-4.18154100	-0.39178200
H	5.98763800	-2.72480000	-1.34347400

H	6.10238000	-2.62032600	0.42169800
C	-0.44260500	2.56155000	-1.18246500
H	-1.50312500	2.56949700	-1.41334300
H	-0.20602000	3.28674500	-0.38967800
H	0.12655500	2.87810700	-2.06678300
C	3.58957100	0.43309700	-0.00820700
H	4.03085900	-0.16560500	0.79111600
H	4.13394900	0.18081600	-0.92455900
H	3.71866000	1.49869800	0.19718700
N	1.33496700	1.23331100	-0.28725300
H	-0.31380500	-2.10800500	-0.65319600
C	2.15425500	4.39262700	0.71974700
O	0.95015900	4.45831800	1.03855300
O	2.71622100	3.50696100	-0.01086300
C	3.10885100	5.48878100	1.23949700
H	3.90426300	5.03381900	1.84293200
H	3.59801700	5.98750800	0.39361900
H	2.57247100	6.22859400	1.84072200

Zero-point correction= 0.471533 (Hartree/Particle)
Thermal correction to Energy= 0.502793
Thermal correction to Enthalpy= 0.503738
Thermal correction to Gibbs Free Energy= 0.404547
Sum of electronic and zero-point Energies= -1361.070767
Sum of electronic and thermal Energies= -1361.039506
Sum of electronic and thermal Enthalpies= -1361.038562
Sum of electronic and thermal Free Energies= -1361.137753
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1362.025687

^{2}INT2

C	-0.09444300	1.12246000	-1.38281500
C	-0.39833600	-0.20086800	-1.12355300
C	0.55646800	-1.01398400	-0.32361400
C	1.95646900	-0.50736000	-0.39109100
C	2.15738900	0.84068800	-0.65805700
H	1.00018300	3.20505800	-0.35882600
C	0.11769600	-0.93090400	1.22480600
H	0.28643900	0.09995200	1.54598200
H	0.80636800	-1.59294600	1.75530500
C	-1.31267800	-1.31998100	1.46961000
C	-1.69144100	-2.66714500	1.51943700
C	-2.29565900	-0.33138400	1.61093500
C	-3.02522100	-3.02372400	1.70553100
H	-0.93434600	-3.43737400	1.39627100
C	-3.63114000	-0.68771700	1.80304900
H	-2.00544300	0.71480600	1.57095300
C	-4.00048300	-2.03346500	1.84722400
H	-3.30503500	-4.07294500	1.73799400
H	-4.38338900	0.08779700	1.92190600
H	-5.04084200	-2.31008200	1.99600600
C	-1.64992200	-0.89763800	-1.50298100
O	-1.70445400	-2.10327700	-1.66646900
O	-2.71569700	-0.08386800	-1.62629900
C	2.99065700	-1.48414500	-0.00012100
O	2.72731300	-2.59476800	0.43356100
O	4.25842700	-1.05648400	-0.18854000
C	-3.98299300	-0.74750500	-1.83781100
C	-5.06271600	0.30482500	-1.69060200
H	-4.08023100	-1.54304500	-1.09499400
H	-3.97939000	-1.20657700	-2.83175000
H	-6.04793900	-0.14820900	-1.84454700
H	-5.03393500	0.74026900	-0.68711600
H	-4.93367400	1.10876100	-2.42241700
C	5.29468500	-1.99640800	0.17226900
C	6.62505300	-1.32588000	-0.10655400
H	5.15942400	-2.90985600	-0.41505900
H	5.17683200	-2.26243500	1.22727200
H	7.44469500	-2.00610800	0.14785000
H	6.71309600	-1.05964600	-1.16459200
H	6.73580600	-0.41430400	0.48929300
C	-1.03792300	2.12117700	-2.00046400
H	-1.56523200	1.70468100	-2.86039700
H	-1.79452600	2.41456600	-1.26620400
H	-0.47809200	3.00681300	-2.30773200
C	3.47141200	1.57133200	-0.52859700
H	3.99377500	1.30652400	0.39225700
H	4.14136000	1.31725300	-1.35657100
H	3.28360500	2.64678300	-0.54902800
N	1.12771900	1.63056600	-1.06292900
H	0.49457100	-2.06808400	-0.59927800
C	-0.01136100	3.74481500	1.17442000

O	-0.56012000	2.66238300	1.30102900
O	0.86900000	4.02856400	0.20901000
C	-0.24968000	4.92543100	2.08685400
H	0.69317800	5.23407100	2.55021400
H	-0.61848900	5.77664800	1.50517400
H	-0.97356500	4.65754800	2.85695900

Zero-point correction= 0.471268 (Hartree/Particle)
Thermal correction to Energy= 0.502711
Thermal correction to Enthalpy= 0.503656
Thermal correction to Gibbs Free Energy= 0.404328
Sum of electronic and zero-point Energies= -1360.971255
Sum of electronic and thermal Energies= -1360.939812
Sum of electronic and thermal Enthalpies= -1360.938868
Sum of electronic and thermal Free Energies= -1361.038195
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1361.853363

^{2}TS1

C	-0.12487300	1.07025500	-1.39088000
C	-0.39666200	-0.27689500	-1.16504500
C	0.60416100	-1.06654400	-0.50188800
C	1.94760900	-0.55389700	-0.47218900
C	2.13080500	0.81040800	-0.71807100
H	1.00153900	3.14313100	-0.43358200
C	0.09910600	-0.92956800	1.45385000
H	0.38387900	0.10637000	1.61633600
H	0.81800800	-1.66957600	1.79488100
C	-1.30950600	-1.23239600	1.62709400
C	-1.75780500	-2.56176900	1.76260300
C	-2.26353500	-0.19289300	1.60492800
C	-3.11291100	-2.84436300	1.88067700
H	-1.02900400	-3.36768600	1.75923000
C	-3.61914800	-0.48169300	1.72664300
H	-1.92098700	0.83253200	1.50402700
C	-4.04948400	-1.80542300	1.86222900
H	-3.44447200	-3.87366700	1.98212100
H	-4.34497500	0.32709700	1.71896800
H	-5.10911700	-2.02695600	1.95609100
C	-1.66364400	-0.98764500	-1.45579500
O	-1.75864700	-2.20231000	-1.43863900
O	-2.70782800	-0.17460600	-1.71810500
C	2.98566200	-1.51008100	-0.03695700
O	2.73038700	-2.59801900	0.45519900
O	4.25051900	-1.08478400	-0.24743600
C	-3.98239400	-0.83405700	-1.88008400
C	-5.04239300	0.24863700	-1.89726500
H	-4.11858600	-1.52997200	-1.04883400
H	-3.96445100	-1.41401500	-2.80873700
H	-6.03321400	-0.20068300	-2.02389300
H	-5.03257700	0.80643800	-0.95548100
H	-4.87491200	0.95291500	-2.71848000
C	5.29351100	-1.99348800	0.16833800
C	6.61884700	-1.32215200	-0.13228100
H	5.17430100	-2.93637700	-0.37419000
H	5.16975700	-2.20860100	1.23422000
H	7.44402900	-1.97943300	0.16161000
H	6.71281300	-1.10681300	-1.20133900
H	6.71413500	-0.38119500	0.41893200
C	-1.11393400	2.07004600	-1.92792500
H	-1.60366500	1.70628400	-2.83341900
H	-1.90020300	2.25256400	-1.18950800
H	-0.59887700	3.00830800	-2.14158200
C	3.43572800	1.54806900	-0.55485400
H	3.93292600	1.28745900	0.38178700
H	4.13053900	1.29103200	-1.36095700
H	3.24664400	2.62284300	-0.58308800
N	1.09888600	1.58601600	-1.11620900
H	0.48118700	-2.14245700	-0.54631200
C	0.08094200	3.73345900	1.14251000
O	-0.44279400	2.64995800	1.34858900
O	0.89442100	3.98892500	0.11524100
C	-0.12114400	4.94671600	2.02098700
H	0.84368700	5.29288000	2.40591000
H	-0.54674700	5.76545600	1.43138500
H	-0.78595500	4.69834600	2.84882000

Zero-point correction= 0.469291 (Hartree/Particle)
Thermal correction to Energy= 0.500630
Thermal correction to Enthalpy= 0.501574
Thermal correction to Gibbs Free Energy= 0.402466
Sum of electronic and zero-point Energies= -1360.963047
Sum of electronic and thermal Energies= -1360.931708

Sum of electronic and thermal Enthalpies= -1360.930764
Sum of electronic and thermal Free Energies= -1361.029872
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1361.843184

^{2}INT3

C	2.39934700	0.00000500	0.00000600
H	2.96087100	0.92827400	0.00008500
H	2.96085800	-0.92827400	-0.00004700
C	0.99408500	0.00000200	-0.00000900
C	0.25222300	-1.21763300	-0.00001500
C	0.25221400	1.21763300	0.00003700
C	-1.13280700	-1.21150500	-0.00002200
H	0.79485300	-2.15940300	-0.00002000
C	-1.13281700	1.21150200	0.00001400
H	0.79483900	2.15940600	0.00004700
C	-1.83831600	-0.00000300	-0.00001500
H	-1.67540700	-2.15298500	-0.00002600
H	-1.67541700	2.15298300	0.00002000
H	-2.92418100	-0.00001300	-0.00003600

Zero-point correction= 0.115060 (Hartree/Particle)
Thermal correction to Energy= 0.120725
Thermal correction to Enthalpy= 0.121670
Thermal correction to Gibbs Free Energy= 0.085393
Sum of electronic and zero-point Energies= -270.823414
Sum of electronic and thermal Energies= -270.817748
Sum of electronic and thermal Enthalpies= -270.816804
Sum of electronic and thermal Free Energies= -270.853081
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -271.019269

^{2}TS2

C	-0.60923200	-0.72618900	-0.04313800
C	-1.53660200	-1.74966700	-0.00778900
S	1.03858600	-1.24580600	-0.11466800
N	0.22062300	-3.16683700	-0.09476200
N	-0.98190000	-3.02901700	-0.03057900
C	-0.96461600	0.71270200	-0.00309400
C	-1.08637100	1.44383800	-1.18917100
C	-1.18320000	1.34490900	1.22543000
C	-1.43443100	2.79266900	-1.14606900
H	-0.92121100	0.94743900	-2.14065100
C	-1.52748700	2.69516200	1.26531700
H	-1.09168700	0.77212500	2.14335700
C	-1.65660000	3.42149500	0.08025700
H	-1.53323200	3.35236400	-2.07165600
H	-1.69651800	3.17897000	2.22301600
H	-1.92629800	4.47299200	0.11232400
C	-3.01646300	-1.67951500	0.05534100
O	-3.73537400	-2.64287300	0.21388500
O	-3.46001700	-0.41626400	-0.08831100
C	-4.88616300	-0.21948300	0.00278600
C	-5.12631200	1.27200700	-0.12853300
H	-5.23696200	-0.61582500	0.96086400
H	-5.37351800	-0.79281600	-0.79216300
H	-6.19785700	1.48720100	-0.05942700
H	-4.60495100	1.81749000	0.66386300
H	-4.75650300	1.63981000	-1.09051700
C	2.08915500	0.88509800	-0.03427000
H	1.62195900	1.25103800	0.87465000
H	1.67756100	1.29541000	-0.95093500
C	3.49621200	0.56352400	-0.00009800
C	4.23289500	0.40476700	-1.19350300
C	4.16071500	0.34585100	1.22600700
C	5.57927400	0.06104700	-1.16024700
H	3.73204000	0.55634800	-2.14626600
C	5.50712300	0.00252700	1.25632300
H	3.60347800	0.45099400	2.15333900
C	6.22369600	-0.14051000	0.06411700
H	6.13077100	-0.05197800	-2.08938900
H	6.00248800	-0.15621600	2.21007200
H	7.27556100	-0.40975600	0.08899200

Zero-point correction= 0.311359 (Hartree/Particle)
Thermal correction to Energy= 0.333078
Thermal correction to Enthalpy= 0.334022
Thermal correction to Gibbs Free Energy= 0.254095
Sum of electronic and zero-point Energies= -1353.982512
Sum of electronic and thermal Energies= -1353.960794
Sum of electronic and thermal Enthalpies= -1353.959849
Sum of electronic and thermal Free Energies= -1354.039776
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1354.600557

^{2}TS2'

C	0.42928900	-0.89833200	0.59081500
C	1.74957100	-1.33780800	0.19594200
S	-0.31646800	-2.32816000	1.32015300
N	1.02119900	-3.36694100	0.82040600
N	1.96097300	-2.67277200	0.29918500
C	0.06751500	0.42045500	1.18055400
C	1.04312700	1.37347500	1.51422400
C	-1.27366000	0.70891000	1.48327700
C	0.68266000	2.59039300	2.08717700
H	2.09028500	1.15757700	1.35035600
C	-1.63201400	1.92571100	2.05873300
H	-2.04531300	-0.02052600	1.26498900
C	-0.65723700	2.87756300	2.35318800
H	1.45626700	3.30939900	2.34137800
H	-2.67746400	2.12478600	2.27444000
H	-0.93519300	3.82715100	2.80121300
C	2.81030900	-0.55235000	-0.47314900
O	3.97862100	-0.86851000	-0.53056400
O	2.31081300	0.58071800	-1.03011900
C	3.27512100	1.48063400	-1.61616700
C	2.52159700	2.73664900	-2.00762700
H	3.74290300	0.98819500	-2.47436400
H	4.06046700	1.68021200	-0.88060800
H	3.21122900	3.46791800	-2.44203600
H	1.74720200	2.51236900	-2.74862600
H	2.04115700	3.18493200	-1.13219300
C	-0.40292600	-0.86786900	-1.37842100
H	-0.19063500	-1.91319600	-1.58396700
H	0.31397000	-0.16295600	-1.78200500
C	-1.78240400	-0.46218300	-1.33014600
C	-2.13090600	0.90123300	-1.45305500
C	-2.81114300	-1.39938800	-1.08563000
C	-3.45420700	1.30983600	-1.34193900
H	-1.34426500	1.63050100	-1.62347900
C	-4.13167100	-0.98462500	-0.96236900
H	-2.55466100	-2.44994800	-0.98702900
C	-4.45853200	0.37058000	-1.08926800
H	-3.70557900	2.36176200	-1.44144500
H	-4.91236000	-1.71544500	-0.77202900
H	-5.49213200	0.69084200	-0.99555000

Zero-point correction= 0.312969 (Hartree/Particle)
Thermal correction to Energy= 0.333566
Thermal correction to Enthalpy= 0.334510
Thermal correction to Gibbs Free Energy= 0.261083
Sum of electronic and zero-point Energies= -1353.983325
Sum of electronic and thermal Energies= -1353.962729
Sum of electronic and thermal Enthalpies= -1353.961785
Sum of electronic and thermal Free Energies= -1354.035212
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1354.602360

^{2}TS2''

C	-1.41192200	0.73337800	-0.12219400
C	-1.55680700	-0.68634700	-0.23648700
S	-2.75001900	1.45709400	-0.95940500
N	-3.55111800	-0.12028100	-1.15797400
N	-2.84097100	-1.04965700	-0.71464300
C	-0.34139000	1.51951800	0.45246400
C	0.91301900	0.95473600	0.77062600
C	-0.52173400	2.89939300	0.70159900
C	1.93040800	1.73180000	1.30684100
H	1.10760200	-0.08638400	0.55927900
C	0.50017400	3.67217200	1.23938300
H	-1.48212200	3.36033400	0.48911100
C	1.73445100	3.09461400	1.54697100
H	2.88991800	1.26972200	1.51996100
H	0.33069900	4.72910600	1.42375100
H	2.53393500	3.69960300	1.96429400
C	-1.01205400	-1.68276600	0.76358800
O	-0.77510400	-2.84542600	0.51716300
O	-0.88220300	-1.12099500	1.97619800
C	-0.31184600	-1.95604300	3.01513300
C	1.20698100	-1.92961900	2.95599800
H	-0.70231300	-2.96945500	2.90264400
H	-0.68744800	-1.51868600	3.94211900
H	1.61980700	-2.52626600	3.77697500
H	1.56340300	-2.35118900	2.01165500
H	1.57901800	-0.90506800	3.04768500
C	-0.56886000	-1.33978100	-1.99478900
H	-1.17887000	-0.75713900	-2.68002700

H	-0.86191200	-2.37592800	-1.87428000
C	0.82946500	-1.00274800	-1.90444400
C	1.75136000	-1.87464500	-1.27981100
C	1.29769200	0.24609700	-2.36854200
C	3.07826900	-1.49670600	-1.11084000
H	1.40058900	-2.83617400	-0.91884900
C	2.62697600	0.61521800	-2.20270800
H	0.59728900	0.92672900	-2.84482100
C	3.52139700	-0.24874400	-1.56500800
H	3.77473600	-2.17605500	-0.62687600
H	2.96680500	1.58383400	-2.55765300
H	4.55877900	0.04329700	-1.42974100

Zero-point correction= 0.313256 (Hartree/Particle)
Thermal correction to Energy= 0.333622
Thermal correction to Enthalpy= 0.334566
Thermal correction to Gibbs Free Energy= 0.262375
Sum of electronic and zero-point Energies= -1353.984655
Sum of electronic and thermal Energies= -1353.964289
Sum of electronic and thermal Enthalpies= -1353.963345
Sum of electronic and thermal Free Energies= -1354.035536
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1354.596995

^{2}TS2'''

C	-0.62159200	0.01737000	-0.50122400
C	-0.91032400	-1.36523800	-0.49168600
S	1.05377900	0.30211900	-0.73428100
N	1.27843100	-1.65332200	-0.97493500
N	0.15972200	-2.14648300	-0.81633800
C	-1.56976900	1.13272600	-0.42512400
C	-2.79584500	1.07273300	-1.11237700
C	-1.26448100	2.29655300	0.29972700
C	-3.69131800	2.13488200	-1.05736400
H	-3.03049000	0.19542500	-1.70539200
C	-2.16436300	3.35831900	0.35519600
H	-0.32343500	2.35664800	0.83837800
C	-3.38322500	3.28109100	-0.31893400
H	-4.62923600	2.07357100	-1.60209400
H	-1.91294100	4.24567100	0.92896700
H	-4.08463900	4.10918300	-0.27743100
C	-2.17405900	-2.05385200	-0.15365600
O	-2.47016800	-3.17572800	-0.50933400
O	-2.95392700	-1.27584800	0.62848700
C	-4.26515200	-1.79345800	0.93164600
C	-5.01180100	-0.69743200	1.66692300
H	-4.15748600	-2.70098700	1.53442700
H	-4.75881700	-2.07576700	-0.00386400
H	-6.02500200	-1.03359900	1.91192500
H	-4.49889700	-0.43552600	2.59768100
H	-5.07891000	0.20329500	1.04910500
C	2.20520400	0.15142700	1.15351100
H	1.77299900	-0.77081800	1.53227400
H	1.84569000	1.04648200	1.65695100
C	3.60236900	0.13129200	0.76063300
C	4.33901500	1.33028800	0.66682300
C	4.23505100	-1.07823800	0.40442200
C	5.66584600	1.31789800	0.25246400
H	3.85859900	2.26963200	0.92915000
C	5.56157100	-1.08486100	-0.01121600
H	3.66730100	-2.00217700	0.44406400
C	6.28321900	0.11021600	-0.08683000
H	6.22227400	2.24895900	0.19324200
H	6.03628800	-2.02404200	-0.28008400
H	7.31984700	0.10109200	-0.41071500

Zero-point correction= 0.311897 (Hartree/Particle)
Thermal correction to Energy= 0.333252
Thermal correction to Enthalpy= 0.334196
Thermal correction to Gibbs Free Energy= 0.256869
Sum of electronic and zero-point Energies= -1353.975827
Sum of electronic and thermal Energies= -1353.954473
Sum of electronic and thermal Enthalpies= -1353.953529
Sum of electronic and thermal Free Energies= -1354.030856
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1354.595561

^{2}INT4

C	-0.58944500	-0.22544000	-0.14855400
C	-1.67195600	-1.05260400	-0.01038400
S	1.01437700	-0.89580200	-0.42835600
N	-0.58519300	-3.10999500	-0.23806900
N	-1.51861200	-2.46773100	0.12026600
C	-0.70730700	1.24826800	-0.02672200

C	-0.48340100	2.07183100	-1.13670300
C	-0.98371900	1.82689200	1.21756600
C	-0.55461800	3.45656800	-1.00567800
H	-0.26887900	1.61915700	-2.10033900
C	-1.04334300	3.21271400	1.34739900
H	-1.15532600	1.18485400	2.07628700
C	-0.83110600	4.03051700	0.23681700
H	-0.39468100	4.08830700	-1.87461900
H	-1.25881600	3.65351800	2.31638500
H	-0.88098400	5.11067300	0.33837200
C	-3.07112500	-0.56183100	0.07104700
O	-3.43136400	0.55951300	-0.23045800
O	-3.90493300	-1.53164900	0.50195700
C	-5.30684300	-1.18241100	0.55038800
C	-5.95569200	-1.32353300	-0.81727400
H	-5.40401900	-0.16315200	0.93203500
H	-5.73015800	-1.88496400	1.27159900
H	-7.03215400	-1.13296000	-0.74022000
H	-5.52736800	-0.60323600	-1.51913900
H	-5.81032000	-2.33453800	-1.21079000
C	2.13186700	0.50239400	0.09653200
H	1.81967900	0.82945300	1.09031200
H	2.01070700	1.33508000	-0.59692700
C	3.54068800	-0.02060100	0.09352400
C	4.34884600	0.12805200	-1.03931700
C	4.05485400	-0.68963400	1.21100700
C	5.65093600	-0.37085600	-1.05210200
H	3.95367500	0.63974500	-1.91334400
C	5.35595100	-1.18833300	1.20118500
H	3.42844500	-0.81963400	2.08986800
C	6.15740300	-1.02939000	0.06895400
H	6.26909700	-0.24482600	-1.93635300
H	5.74431600	-1.70149900	2.07621600
H	7.17184000	-1.41758600	0.06087000

Zero-point correction= 0.313502 (Hartree/Particle)
Thermal correction to Energy= 0.335450
Thermal correction to Enthalpy= 0.336395
Thermal correction to Gibbs Free Energy= 0.257172
Sum of electronic and zero-point Energies= -1354.002341
Sum of electronic and thermal Energies= -1353.980393
Sum of electronic and thermal Enthalpies= -1353.979449
Sum of electronic and thermal Free Energies= -1354.058672
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1354.6226976

^{2}TS3

C	-0.15550600	-0.45567700	-1.02110400
C	-1.06205900	-1.12040500	-0.29177100
S	1.16000900	-1.28988400	-1.88725200
N	-0.77081100	-3.53325000	-1.25215600
N	-1.51041000	-2.80933300	-0.78234300
C	-0.20383800	1.02316700	-1.08682400
C	-1.44065100	1.67515300	-1.22542200
C	0.96600700	1.79001500	-0.96993500
C	-1.50817400	3.06523900	-1.23145600
H	-2.34286100	1.08261500	-1.34246900
C	0.89171000	3.18003500	-0.96954200
H	1.92190500	1.29198100	-0.85729300
C	-0.34191500	3.82187200	-1.10004300
H	-2.46921900	3.55789800	-1.34820300
H	1.80116600	3.76433300	-0.86347500
H	-0.39361100	4.90695400	-1.10515300
C	-1.98927000	-0.66207400	0.74138900
O	-1.62456800	-0.06404400	1.73975300
O	-3.26606600	-1.00692800	0.48101600
C	-4.24366700	-0.59215500	1.46590600
C	-4.65281300	0.85525900	1.24414600
H	-3.82208300	-0.73755700	2.46327900
H	-5.08038400	-1.27819000	1.31861400
H	-5.43098300	1.13766000	1.96200900
H	-3.79564600	1.51945100	1.38361600
H	-5.05000900	0.99369300	0.23324900
C	2.02388000	-2.10273700	-0.44826700
H	2.80560200	-2.70486500	-0.92080100
H	1.31903200	-2.77794100	0.03866400
C	2.59114100	-1.07913000	0.49157000
C	1.83510100	-0.60298300	1.57012300
C	3.84948400	-0.51438200	0.24376400
C	2.32323700	0.42660500	2.37447900
H	0.84835500	-1.00732600	1.76612500
C	4.34122400	0.50842200	1.05243300

H	4.43827600	-0.87141800	-0.59790800
C	3.57533600	0.98528100	2.11905600
H	1.71479700	0.79519000	3.19489100
H	5.31978800	0.93471000	0.84942900
H	3.95396400	1.78778200	2.74578800

Zero-point correction= 0.311403 (Hartree/Particle)
Thermal correction to Energy= 0.333339
Thermal correction to Enthalpy= 0.334283
Thermal correction to Gibbs Free Energy= 0.257110
Sum of electronic and zero-point Energies= -1353.994094
Sum of electronic and thermal Energies= -1353.972159
Sum of electronic and thermal Enthalpies= -1353.971215
Sum of electronic and thermal Free Energies= -1354.048388
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1354.6079026

^{2}INT5

C	0.81070100	-0.55032100	-0.05736500
C	1.07538800	0.74657000	-0.02171900
S	-0.89047100	-1.10489600	-0.14912300
C	1.82193100	-1.64162100	-0.02242300
C	3.09753700	-1.43509100	-0.57256700
C	1.51838700	-2.88590700	0.55344800
C	4.04373800	-2.45623900	-0.54507400
H	3.33826800	-0.47378600	-1.01176400
C	2.47069400	-3.90238700	0.57656100
H	0.54348300	-3.05133500	1.00012300
C	3.73540200	-3.69234800	0.02613800
H	5.02596300	-2.28490400	-0.97620400
H	2.22343600	-4.85806300	1.02987700
H	4.47649100	-4.48649600	0.04343500
C	2.06450200	1.78381100	0.02475500
O	3.15394200	1.73658000	-0.53322200
O	1.63189800	2.84703600	0.74082900
C	2.53487800	3.97556200	0.81429100
C	2.43361500	4.84577300	-0.42866100
H	3.55313100	3.60641800	0.95828800
H	2.21461200	4.51353400	1.70938100
H	3.06478500	5.73425900	-0.31388300
H	2.77127800	4.29450900	-1.31008200
H	1.40128500	5.17361400	-0.58758500
C	-1.77809600	0.50642900	-0.03455000
H	-1.47244100	1.12176700	-0.88563300
H	-1.45069200	1.00538600	0.88190200
C	-3.25954800	0.24860000	-0.03721300
C	-3.94340100	0.02316700	1.16340100
C	-3.97076200	0.20295900	-1.24196800
C	-5.31345500	-0.23357800	1.16118600
H	-3.39532000	0.05011100	2.10176900
C	-5.34102200	-0.05439600	-1.24692600
H	-3.44443300	0.37040800	-2.17823800
C	-6.01560800	-0.27258300	-0.04473400
H	-5.83300900	-0.40208500	2.10020100
H	-5.88171800	-0.08331500	-2.18865000
H	-7.08359700	-0.47102300	-0.04729900

Zero-point correction= 0.304177 (Hartree/Particle)
Thermal correction to Energy= 0.324269
Thermal correction to Enthalpy= 0.325213
Thermal correction to Gibbs Free Energy= 0.249806
Sum of electronic and zero-point Energies= -1244.492450
Sum of electronic and thermal Energies= -1244.472358
Sum of electronic and thermal Enthalpies= -1244.471414
Sum of electronic and thermal Free Energies= -1244.546821
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1245.0722161

^{2}INT5'

C	1.35104900	-0.16894800	-0.19603500
C	1.39822000	1.15310600	-0.12241000
S	-0.14647100	-1.11142800	-0.48852800
C	2.57653700	-0.99612400	-0.04603200
C	3.80620900	-0.48321400	-0.49220400
C	2.54360600	-2.27278800	0.53421200
C	4.97333800	-1.22774400	-0.35684900
H	3.82735500	0.49835100	-0.95494500
C	3.71476500	-3.01745500	0.66416800
H	1.60268100	-2.67260800	0.89647900
C	4.93162800	-2.49929700	0.22057800
H	5.91595400	-0.82001900	-0.71061600
H	3.67527600	-4.00305900	1.11898600
H	5.84244400	-3.08252700	0.32167800
C	0.70709300	2.38648800	-0.35541400

O	-0.11453500	2.55460900	-1.25002200
O	1.09873400	3.35756800	0.49974700
C	0.46145100	4.64501500	0.33011900
C	-0.90298900	4.67693900	1.00107600
H	0.38281100	4.86457300	-0.73756600
H	1.15509100	5.34869700	0.79570200
H	-1.33054000	5.68343800	0.93040100
H	-1.58570700	3.97763100	0.51125500
H	-0.81899800	4.41077900	2.05963300
C	-1.48898800	0.07406100	-0.04924300
H	-1.51348800	0.86760000	-0.79722400
H	-1.22499100	0.51500000	0.91733100
C	-2.78697300	-0.68223300	0.01458500
C	-3.14635900	-1.39191400	1.16725500
C	-3.64495600	-0.70482200	-1.09071200
C	-4.34511400	-2.10043000	1.21846400
H	-2.47944500	-1.38567700	2.02578700
C	-4.84436800	-1.41509400	-1.04286700
H	-3.36862700	-0.15996100	-1.98964700
C	-5.19738500	-2.11358900	0.11227400
H	-4.61505500	-2.64188800	2.12078900
H	-5.50298600	-1.42145100	-1.90673900
H	-6.13241500	-2.66520500	0.15156200

Zero-point correction= 0.304298 (Hartree/Particle)
Thermal correction to Energy= 0.324301
Thermal correction to Enthalpy= 0.325245
Thermal correction to Gibbs Free Energy= 0.250425
Sum of electronic and zero-point Energies= -1244.493859
Sum of electronic and thermal Energies= -1244.473856
Sum of electronic and thermal Enthalpies= -1244.472912
Sum of electronic and thermal Free Energies= -1244.547732
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1245.0744482

[1]INT6

C	1.55377800	0.12622300	-0.15072900
C	1.35281600	1.42559100	-0.21066000
S	0.19842300	-1.19886600	-0.23845400
C	2.89786300	-0.48974900	-0.01961000
C	4.03570000	0.33818300	-0.11074000
C	3.11757100	-1.86197500	0.19423600
C	5.32001500	-0.17743400	0.00579100
H	3.85933300	1.39712400	-0.27286300
C	4.40925400	-2.38106600	0.30988800
H	2.27073100	-2.53429800	0.28556300
C	5.52145800	-1.54702800	0.21681700
H	6.17542000	0.49168600	-0.07112900
H	4.54131400	-3.44855600	0.47729100
H	6.52719500	-1.95225800	0.30581300
C	0.34563000	2.37044800	-0.40240300
O	-0.05857100	2.86298000	-1.46627800
O	-0.14606000	2.87268300	0.83029400
C	-1.10435400	3.91615900	0.71057000
C	-2.51280100	3.37686900	0.47340900
H	-0.82288000	4.58666500	-0.10783100
H	-1.05705800	4.46766500	1.65835700
H	-3.24732600	4.19383000	0.45627600
H	-2.54565100	2.85677200	-0.48725200
H	-2.79773600	2.67192700	1.26295500
C	-1.26861300	-0.10138300	-0.19789800
H	-1.27508100	0.51562400	-1.09900900
H	-1.15573600	0.56728200	0.65784800
C	-2.52403300	-0.91895800	-0.08832500
C	-2.96176300	-1.39673100	1.15475800
C	-3.28599500	-1.22416000	-1.22264800
C	-4.12861400	-2.15105500	1.26234400
H	-2.36990000	-1.17294200	2.03845900
C	-4.45439800	-1.98029300	-1.12087800
H	-2.95289500	-0.86073300	-2.19143100
C	-4.88162200	-2.44641700	0.12311200
H	-4.45287500	-2.50913600	2.23684200
H	-5.03267500	-2.20394200	-2.01449700
H	-5.79327000	-3.03349600	0.20553200

Zero-point correction= 0.302478 (Hartree/Particle)
Thermal correction to Energy= 0.322539
Thermal correction to Enthalpy= 0.323483
Thermal correction to Gibbs Free Energy= 0.249066
Sum of electronic and zero-point Energies= -1244.565526
Sum of electronic and thermal Energies= -1244.545465
Sum of electronic and thermal Enthalpies= -1244.544521
Sum of electronic and thermal Free Energies= -1244.618938

(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1245.2242404

^{2}INT7

Cu	-3.17935500	0.05676900	0.08542800
C	-3.56288600	-2.20981400	-0.50853800
O	-2.93801200	-1.91925800	0.56950200
O	-3.99867100	-1.25483400	-1.22529500
C	-3.73952600	-3.64228400	-0.92652700
H	-2.78833700	-4.01641200	-1.32300200
H	-4.00229700	-4.25441200	-0.05969400
H	-4.50371200	-3.72415200	-1.70125400
C	-3.18544400	2.29004300	0.83096900
O	-2.75480300	1.36335000	1.59136200
O	-3.67533500	1.95264500	-0.29924900
C	-3.08064700	3.73524900	1.22098900
H	-3.01978100	3.83433000	2.30666600
H	-2.16783300	4.14965000	0.77714300
H	-3.93242100	4.29509600	0.82755300
C	1.47357800	-0.64161500	-0.09223300
C	1.22290500	0.63621300	-0.58428000
S	-0.03590400	-1.42800000	0.14036800
N	-0.89629300	-0.02913500	-0.42423900
N	-0.10983900	0.91509500	-0.74861500
C	2.73445000	-1.34386600	0.18773800
C	3.77179300	-1.35694600	-0.75802700
C	2.89070000	-2.05475200	1.38774200
C	4.94465300	-2.05964300	-0.50026600
H	3.64761200	-0.82578100	-1.69491500
C	4.07076000	-2.75007900	1.64476900
H	2.09497100	-2.04009800	2.12665200
C	5.09948300	-2.75463100	0.70218200
H	5.73834600	-2.06911100	-1.24136300
H	4.18468700	-3.28678400	2.58169100
H	6.01748700	-3.29973100	0.90088300
C	2.17827500	1.74004600	-0.88439700
O	1.89321800	2.71800100	-1.53863900
O	3.37956000	1.51266800	-0.32077300
C	4.39804200	2.51584700	-0.54879300
C	4.27056500	3.65829800	0.44535100
H	4.31417700	2.87270000	-1.57807200
H	5.33639600	1.97098100	-0.42395700
H	5.09674100	4.36464500	0.30693200
H	3.32971300	4.19371400	0.29328300
H	4.30505300	3.28236100	1.47279000

Zero-point correction= 0.299941 (Hartree/Particle)
Thermal correction to Energy= 0.327475
Thermal correction to Enthalpy= 0.328419
Thermal correction to Gibbs Free Energy= 0.233298
Sum of electronic and zero-point Energies= -1736.250817
Sum of electronic and thermal Energies= -1736.223282
Sum of electronic and thermal Enthalpies= -1736.222338
Sum of electronic and thermal Free Energies= -1736.317459

(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1738.1620298

^{1}INT8

Cu	-3.09220600	1.00490400	-0.09511300
C	-4.99467300	-0.58139800	0.16837400
O	-3.98525000	-1.31308800	0.18742000
O	-4.94700700	0.71065700	0.03556800
C	-6.38989900	-1.16526200	0.30161100
H	-6.98045800	-0.91125500	-0.58508100
H	-6.34460400	-2.24930500	0.41822200
H	-6.89555200	-0.71823500	1.16401300
C	0.93694400	-0.43278900	-0.12866500
C	1.01087800	0.95338800	-0.25809700
S	-0.72025000	-0.87544700	-0.05275700
N	-1.19560900	0.78524500	-0.17441600
N	-0.19947900	1.58222400	-0.28338300
C	1.98847900	-1.45666400	-0.10544400
C	3.04314800	-1.41879500	-1.03198500
C	1.91950300	-2.51424500	0.81547200
C	4.01353700	-2.41543800	-1.02655400
H	3.08662700	-0.61949700	-1.76328800
C	2.89813500	-3.50574400	0.82089900
H	1.11237400	-2.54330200	1.54162300
C	3.94643000	-3.45853600	-0.09888300
H	4.82063100	-2.38230500	-1.75211400
H	2.84053000	-4.31313800	1.54426600
H	4.70696300	-4.23356900	-0.09687800
C	2.22020700	1.82776300	-0.32305700
O	2.22247000	2.93057800	-0.82058400

O	3.27806500	1.23127800	0.25217200
C	4.52566100	1.96974900	0.22963600
C	4.59833400	2.95095200	1.38745400
H	4.61111200	2.48079400	-0.73225400
H	5.29042600	1.19370500	0.30311300
H	5.57854000	3.44037700	1.39644900
H	3.82939100	3.72122900	1.28540100
H	4.46130000	2.43388700	2.34235800

Zero-point correction= 0.248664 (Hartree/Particle)
Thermal correction to Energy= 0.270550
Thermal correction to Enthalpy= 0.271494
Thermal correction to Gibbs Free Energy= 0.192056
Sum of electronic and zero-point Energies= -1507.804652
Sum of electronic and thermal Energies= -1507.782767
Sum of electronic and thermal Enthalpies= -1507.781822
Sum of electronic and thermal Free Energies= -1507.861260
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1509.5906275

^{2}INT9

Cu	-2.89146900	0.65494200	0.58131100
C	-4.57863400	-1.08878600	0.93420000
O	-3.40444700	-1.46577900	1.20151600
O	-4.82268500	0.10178300	0.52334200
C	-5.75120100	-2.02893300	1.11352900
H	-6.41037000	-1.97775000	0.24208000
H	-5.40450100	-3.05221300	1.26892700
H	-6.33560000	-1.71090600	1.98447400
C	1.16945100	-0.70401300	0.57749000
C	1.21563000	0.66193600	0.83998500
S	-0.44844600	-1.23367000	0.76978400
N	-0.95464000	0.37507000	1.18991300
N	0.01248600	1.21197600	1.16163000
C	2.22498200	-1.61070400	0.10940500
C	3.05102800	-1.23101800	-0.96063200
C	2.38680600	-2.87758700	0.68907900
C	4.03006300	-2.10129700	-1.42959900
H	2.89838000	-0.26855900	-1.43567600
C	3.37289200	-3.74302000	0.21905500
H	1.75341200	-3.17175000	1.52082500
C	4.19668500	-3.35689100	-0.83910300
H	4.65937800	-1.80303100	-2.26289200
H	3.49678100	-4.71786900	0.68072000
H	4.96253700	-4.03327500	-1.20691400
C	2.38450100	1.58020200	0.74417500
O	2.29865200	2.73921600	0.39798300
O	3.52524500	0.95313700	1.07420000
C	4.74668600	1.72091400	0.93769000
C	5.00167200	2.56493100	2.17518200
H	4.67005200	2.34162000	0.04157900
H	5.51888300	0.96235200	0.79367900
H	5.96723100	3.07465800	2.08337300
H	4.22110700	3.32163300	2.28944500
H	5.02528100	1.93860100	3.07247200
C	-2.75137100	2.08383000	-0.89819200
H	-3.77965700	1.99634800	-1.24762400
H	-2.52075200	3.02938700	-0.40773500
C	-1.71331200	1.51620200	-1.73774300
C	-1.97899300	0.39901500	-2.57022800
C	-0.38484800	2.00392700	-1.69930900
C	-0.96769200	-0.20363400	-3.30741300
H	-2.99303100	0.00872300	-2.61179600
C	0.62076500	1.40162900	-2.44750400
H	-0.14524500	2.84728800	-1.06001100
C	0.34184900	0.29059600	-3.24984300
H	-1.19619000	-1.06293300	-3.93197100
H	1.62879300	1.80554400	-2.39795000
H	1.13045000	-0.18243800	-3.82804900

Zero-point correction= 0.365762 (Hartree/Particle)
Thermal correction to Energy= 0.394853
Thermal correction to Enthalpy= 0.395797
Thermal correction to Gibbs Free Energy= 0.298716
Sum of electronic and zero-point Energies= -1778.654646
Sum of electronic and thermal Energies= -1778.625555
Sum of electronic and thermal Enthalpies= -1778.624611
Sum of electronic and thermal Free Energies= -1778.721692
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1780.631355

^{2}TS4

Cu	2.80597200	-0.11215700	-1.29088500
C	4.91426400	-0.87029700	-0.05916300

O	4.02937800	-1.34952500	0.67652900
O	4.67203300	-0.19177100	-1.13724900
C	6.38582100	-1.05132700	0.26905900
H	6.86162300	-0.07116200	0.38023000
H	6.50832900	-1.62930200	1.18643300
H	6.88772000	-1.55971400	-0.56092600
C	-1.43852500	-0.92199500	-0.49713700
C	-1.21403000	0.44424000	-0.80055700
S	0.06840300	-1.80039500	-0.46621800
N	0.92935800	-0.11493700	-1.19499900
N	0.02421000	0.73719700	-1.25669500
C	-2.69438100	-1.63543400	-0.33415700
C	-3.87248000	-1.19731600	-0.97464600
C	-2.75908600	-2.80639300	0.44985700
C	-5.06124200	-1.89900400	-0.82485400
H	-3.84488600	-0.31169700	-1.59586700
C	-3.95247000	-3.50754400	0.59367500
H	-1.86834500	-3.15909900	0.96140900
C	-5.11078300	-3.05586000	-0.04022700
H	-5.95545100	-1.54619100	-1.33004300
H	-3.97731900	-4.40442000	1.20550200
H	-6.04350800	-3.60034800	0.07228000
C	-2.14284100	1.56335400	-0.52576700
O	-3.17371800	1.45462000	0.11068100
O	-1.67383400	2.72766500	-1.00703600
C	-2.43778200	3.89884200	-0.64653800
C	-1.70033400	5.10075400	-1.20230300
H	-2.52563300	3.93431200	0.44383800
H	-3.44748600	3.80326500	-1.05865900
H	-2.24306200	6.01854400	-0.95175900
H	-0.69292100	5.16536800	-0.77964200
H	-1.61340700	5.03550500	-2.29128400
C	0.85572200	-1.53750000	1.27938900
H	0.41833500	-2.36031400	1.85078100
H	1.92099400	-1.71132100	1.09524800
C	0.56802600	-0.19082100	1.83871700
C	-0.70802100	0.12825500	2.32726500
C	1.56206100	0.79953700	1.81161100
C	-0.99747600	1.42384900	2.75044900
H	-1.48470300	-0.63092200	2.35036100
C	1.27236900	2.09261500	2.24206000
H	2.55642900	0.53545200	1.46412100
C	-0.00968600	2.40996400	2.69817800
H	-1.99591000	1.66392800	3.10167700
H	2.04670800	2.85381900	2.21778300
H	-0.23575300	3.42193300	3.02266300

Zero-point correction= 0.366204 (Hartree/Particle)
Thermal correction to Energy= 0.394559
Thermal correction to Enthalpy= 0.395503
Thermal correction to Gibbs Free Energy= 0.300974
Sum of electronic and zero-point Energies= -1778.631639
Sum of electronic and thermal Energies= -1778.603284
Sum of electronic and thermal Enthalpies= -1778.602339
Sum of electronic and thermal Free Energies= -1778.696869
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1780.6102994

^{2}INT10

Cu	2.39839200	-0.23698700	-1.14172600
C	4.31874600	-1.65375300	0.04853000
O	3.58908000	-1.53649000	1.05030600
O	4.07242500	-1.11931900	-1.10389400
C	5.60449700	-2.46335600	0.11341500
H	6.45097200	-1.84058700	-0.19448700
H	5.77035200	-2.84560700	1.12211700
H	5.54683100	-3.29872000	-0.59294900
C	-1.00395900	-0.67292500	-0.13949500
C	-1.13449700	0.56882200	-0.73888200
S	0.56793900	-1.32072000	0.34294500
N	1.00990500	0.90926300	-1.71132000
N	-0.15202200	1.09705300	-1.59863900
C	-2.17133400	-1.54589600	0.04187700
C	-3.19464700	-1.56299900	-0.92599700
C	-2.29080800	-2.38497900	1.16505600
C	-4.31489600	-2.36993100	-0.75898000
H	-3.09053700	-0.95684600	-1.82033900
C	-3.41628700	-3.18527100	1.33248000
H	-1.50305500	-2.39247600	1.91046700
C	-4.43352100	-3.17874000	0.37433500
H	-5.08976200	-2.37852000	-1.51975900
H	-3.50038500	-3.81709600	2.21162000

H	-5.30712100	-3.81088600	0.50340500
C	-2.36774800	1.40244300	-0.74651600
O	-2.67478300	2.17090900	-1.63338600
O	-3.04601500	1.25343300	0.41177500
C	-4.29507200	1.97736000	0.51765300
C	-5.42624500	1.22481100	-0.16395900
H	-4.15985500	2.97192800	0.08632600
H	-4.45948000	2.06461000	1.59358800
H	-6.37180700	1.75448600	-0.00250100
H	-5.24917400	1.16080400	-1.24123400
H	-5.51729700	0.21228100	0.23954000
C	0.97953500	-0.20321700	1.81089400
H	0.13039600	-0.30650500	2.48907700
H	1.85705800	-0.71657500	2.20395800
C	1.26404100	1.21903700	1.46148300
C	0.23810100	2.17286100	1.43579600
C	2.56670000	1.59992000	1.09851700
C	0.49910500	3.47712400	1.01180500
H	-0.76680200	1.89069300	1.73494600
C	2.82427100	2.90486700	0.67997500
H	3.36363100	0.86442900	1.16150200
C	1.78861300	3.84147800	0.62219900
H	-0.30564800	4.20605300	0.98328600
H	3.83380000	3.18962300	0.39824000
H	1.98907400	4.85465900	0.28630700

Zero-point correction= 0.367266 (Hartree/Particle)
Thermal correction to Energy= 0.396073
Thermal correction to Enthalpy= 0.397017
Thermal correction to Gibbs Free Energy= 0.303238
Sum of electronic and zero-point Energies= -1778.652366
Sum of electronic and thermal Energies= -1778.623559
Sum of electronic and thermal Enthalpies= -1778.622615
Sum of electronic and thermal Free Energies= -1778.716394
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1780.6280641

^{2}INT11

C	1.22023900	0.49432600	0.59048300
C	2.58856100	0.54696300	0.17196000
S	0.37870100	-1.05099400	0.73449500
N	3.38297200	2.72420500	-0.69249300
N	3.02955300	1.70490500	-0.32999500
C	0.49070200	1.73165500	0.87610300
C	-0.78974000	1.97673900	0.33600300
C	1.06699200	2.71516700	1.70644800
C	-1.47706200	3.14759100	0.64290800
H	-1.21853200	1.27788300	-0.37459200
C	0.37549800	3.88465700	2.00737300
H	2.04565500	2.53677600	2.14239100
C	-0.90184600	4.10323900	1.48365600
H	-2.46045700	3.31376200	0.21410600
H	0.82843300	4.62090600	2.66489300
H	-1.44205400	5.01338700	1.72620600
C	3.65483700	-0.48370800	0.10767700
O	4.77299400	-0.25115100	-0.31086300
O	3.23658900	-1.67619600	0.55246700
C	4.21954100	-2.74149600	0.53385400
C	3.50919500	-4.00513900	0.97484500
H	5.03770700	-2.46659500	1.20611300
H	4.62819500	-2.82067300	-0.47755100
H	4.21737500	-4.84010900	0.99254500
H	3.08706600	-3.88509800	1.97704700
H	2.69615200	-4.25696200	0.28651200
C	0.33432800	-1.72964300	-1.02277300
H	-0.27601500	-2.63037900	-0.91807500
H	1.36305700	-2.00885100	-1.25763800
C	-0.24935200	-0.74375900	-1.98292100
C	0.57639800	0.18231800	-2.63244400
C	-1.63965700	-0.66967400	-2.15925400
C	0.02451000	1.18328100	-3.43231000
H	1.65421000	0.11889500	-2.51107100
C	-2.18736000	0.33084900	-2.96200000
H	-2.28840000	-1.37641600	-1.64624900
C	-1.35973000	1.26357900	-3.59281100
H	0.67468000	1.89886600	-3.92724500
H	-3.26476900	0.38265800	-3.08998700
H	-1.79098000	2.04555200	-4.21118900
C	-4.12437400	-1.47230700	0.63311700
O	-3.36773000	-2.28445900	0.05784700
O	-3.69681300	-0.43494800	1.27537000
C	-5.63137500	-1.66388800	0.61669400

H	-5.98501700	-1.84817900	1.63716900
H	-6.12072600	-0.74905900	0.26698200
H	-5.90747200	-2.50484000	-0.02182900
Cu	-1.79955700	-0.59102900	1.06030100

Zero-point correction= 0.366038 (Hartree/Particle)
Thermal correction to Energy= 0.395791
Thermal correction to Enthalpy= 0.396735
Thermal correction to Gibbs Free Energy= 0.298957
Sum of electronic and zero-point Energies= -1778.644433
Sum of electronic and thermal Energies= -1778.614680
Sum of electronic and thermal Enthalpies= -1778.613736
Sum of electronic and thermal Free Energies= -1778.711515
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1780.6222353

^{2}TS5

C	1.29524400	0.24969300	-0.36406100
C	2.63348600	0.35232600	-0.97406400
S	0.12077000	-0.66993100	-1.34396500
N	2.97315000	2.11187800	-2.64671300
N	2.83496100	1.28969800	-1.87203100
C	1.04391200	0.75795300	0.94762200
C	-0.22912100	0.72011500	1.57712300
C	2.11064200	1.36357900	1.67366900
C	-0.42198600	1.24948100	2.84184300
H	-1.08149600	0.31084300	1.04956700
C	1.90964900	1.88546400	2.94080900
H	3.09322400	1.41659700	1.21954900
C	0.64330100	1.83289100	3.53779000
H	-1.41260100	1.21464600	3.28413100
H	2.74215100	2.33868600	3.47091600
H	0.48862100	2.24608000	4.52986900
C	3.75839200	-0.56268700	-0.73424700
O	4.85599500	-0.47461000	-1.24990000
O	3.38546300	-1.51111700	0.14803300
C	4.39548500	-2.48749000	0.48902300
C	3.76953000	-3.44138700	1.48680600
H	5.26310400	-1.96394700	0.90263300
H	4.71606000	-2.99416900	-0.42637400
H	4.49920100	-4.20288700	1.78181200
H	3.44394200	-2.90583700	2.38411700
H	2.90048900	-3.94446800	1.05110800
C	-0.83501600	0.67516800	-2.27356700
H	-1.58379500	0.09445800	-2.81793200
H	-0.12291400	1.10384800	-2.98198400
C	-1.44116100	1.69670500	-1.36854700
C	-0.72205400	2.84947000	-1.03005400
C	-2.69878600	1.47159800	-0.78834200
C	-1.23986900	3.76101200	-0.11090700
H	0.25076900	3.02876600	-1.48087400
C	-3.21320300	2.38581500	0.12985100
H	-3.25719100	0.57202700	-1.03817800
C	-2.48406600	3.52658800	0.47605000
H	-0.67022800	4.64793000	0.15037400
H	-4.18642200	2.20422700	0.57694600
H	-2.88673700	4.23311500	1.19623100
C	-3.94340000	-2.14756100	-0.00623700
O	-3.77373700	-1.58643000	-1.11149200
O	-2.98399300	-2.34499100	0.83750900
C	-5.31330500	-2.64786100	0.41457600
H	-5.29163300	-3.74044800	0.49287700
H	-5.56488700	-2.25875200	1.40639800
H	-6.07284100	-2.34993200	-0.31017900
Cu	-1.51144000	-1.57762000	-0.12035900

Zero-point correction= 0.365901 (Hartree/Particle)
Thermal correction to Energy= 0.394816
Thermal correction to Enthalpy= 0.395760
Thermal correction to Gibbs Free Energy= 0.299807
Sum of electronic and zero-point Energies= -1778.636506
Sum of electronic and thermal Energies= -1778.607591
Sum of electronic and thermal Enthalpies= -1778.606647
Sum of electronic and thermal Free Energies= -1778.702600
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1780.6170158

^{2}INT12

Cu	1.80734300	-0.47868900	1.65170600
C	4.25647000	-0.37748900	0.88667000
O	3.68523600	-0.48756200	2.03241900
O	3.62728600	-0.25814100	-0.19027100
C	5.77588300	-0.38688200	0.89784800
H	6.17329200	-0.33063900	-0.11738500

H	6.14325100	0.46229400	1.48435000
H	6.13621400	-1.29658700	1.38886500
C	-0.88648500	-0.33801800	-0.18953600
C	-0.20243600	0.44631800	-1.05842400
S	-0.42858600	-0.53239800	1.54997500
N	-0.43142000	1.15715300	-3.29971900
N	-0.56808400	0.32769300	-2.46549600
C	-2.06942600	-1.11934800	-0.58722400
C	-3.07800700	-0.52480900	-1.36365200
C	-2.22085700	-2.45361000	-0.16800500
C	-4.21115400	-1.25137300	-1.72004500
H	-2.99648800	0.51954300	-1.63638900
C	-3.34493200	-3.17976400	-0.54626100
H	-1.44110300	-2.91916500	0.42413900
C	-4.34506400	-2.58052500	-1.31839300
H	-4.99256300	-0.77350600	-2.30321000
H	-3.44377900	-4.21531400	-0.23472200
H	-5.22836500	-3.14752600	-1.59831100
C	0.92306800	1.37286500	-0.71685500
O	1.00645800	1.95948100	0.35075200
O	1.78057100	1.49426300	-1.71979400
C	2.92439800	2.36415100	-1.49653900
C	3.95064700	2.02993100	-2.55677100
H	3.30142400	2.17140500	-0.49347000
H	2.56671200	3.39708300	-1.56125200
H	4.80338400	2.71181700	-2.46644800
H	4.30511900	1.00723000	-2.40720600
H	3.53131500	2.13123800	-3.56288200
C	-1.13243200	1.03456300	2.29932700
H	-1.23230000	0.77440700	3.35680600
H	-0.37917500	1.80716500	2.16755100
C	-2.44111700	1.41108500	1.67401200
C	-3.61851800	0.72059300	1.98686300
C	-2.48046600	2.43179000	0.71605000
C	-4.81689800	1.04789600	1.35684200
H	-3.58845400	-0.08585400	2.71490100
C	-3.68200300	2.76426100	0.08892500
H	-1.56358300	2.95650200	0.46476900
C	-4.85145000	2.07154100	0.40682500
H	-5.72289700	0.50205900	1.60275600
H	-3.70321400	3.56209300	-0.64804900
H	-5.78630800	2.32689100	-0.08380200
C	1.58274900	-2.56301800	-0.86366500
N	1.15839700	-2.91430200	0.15915200
C	2.11769400	-2.08002700	-2.13009600
H	1.32055300	-1.61383500	-2.71719000
H	2.88827400	-1.33762500	-1.90031600
H	2.54649400	-2.90824600	-2.70236800

Zero-point correction= 0.413530 (Hartree/Particle)
Thermal correction to Energy= 0.448176
Thermal correction to Enthalpy= 0.449120
Thermal correction to Gibbs Free Energy= 0.341128
Sum of electronic and zero-point Energies= -1911.379082
Sum of electronic and thermal Energies= -1911.344436
Sum of electronic and thermal Enthalpies= -1911.343492
Sum of electronic and thermal Free Energies= -1911.451484
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1913.4387078

^{2}TS6

Cu	1.79780700	0.14890300	-1.75006600
C	4.24748600	0.12464100	-0.98171300
O	3.67299000	0.03784900	-2.12749700
O	3.62103000	0.23195500	0.09826400
C	5.76607600	0.07531400	-0.99314800
H	6.16810900	0.22380600	0.01092600
H	6.09674000	-0.89473400	-1.38044400
H	6.15722800	0.84198700	-1.66943000
C	-0.88080000	0.36771800	0.10396100
C	-0.17423800	-0.24591300	1.05298600
S	-0.43457800	0.22207300	-1.66268100
N	-0.41720300	-0.29717700	3.63539900
N	-0.53518900	0.35357700	2.70601200
C	-2.07119200	1.19590300	0.36340300
C	-3.05582800	0.73911100	1.25340800
C	-2.24919200	2.42633400	-0.29094700
C	-4.19695200	1.50180600	1.48900300
H	-2.94618200	-0.23556200	1.71261800
C	-3.38338900	3.19141700	-0.03731000
H	-1.48531900	2.78484400	-0.97210800
C	-4.36161500	2.73054200	0.84882300

H	-4.96150300	1.12895100	2.16407700
H	-3.50641200	4.14883900	-0.53484300
H	-5.25190900	3.32520500	1.03270300
C	0.93130600	-1.21569900	1.00213000
O	1.00853600	-2.07713100	0.13644700
O	1.77714900	-1.07341700	2.01537200
C	2.92151600	-1.96957900	2.03222300
C	3.93570300	-1.37729000	2.98632200
H	3.31210900	-2.03436800	1.01785300
H	2.56402900	-2.95474900	2.35003300
H	4.78863500	-2.05816500	3.08187900
H	4.29358500	-0.42459600	2.58840600
H	3.50427500	-1.22181900	3.98048200
C	-1.10475800	-1.48262000	-2.04605300
H	-1.17290000	-1.48021600	-3.13783000
H	-0.35223200	-2.19519900	-1.71618700
C	-2.42944900	-1.72175200	-1.38620400
C	-3.59501000	-1.10173900	-1.85333100
C	-2.49564900	-2.53367900	-0.24751800
C	-4.80788000	-1.29314000	-1.19591100
H	-3.54440300	-0.45465800	-2.72517800
C	-3.71216300	-2.73191600	0.40715700
H	-1.58715500	-2.99950000	0.12235800
C	-4.86932600	-2.10999100	-0.06420200
H	-5.70447300	-0.80247800	-1.56291000
H	-3.75434500	-3.36920700	1.28601300
H	-5.81563600	-2.25964200	0.44770900
C	1.59662900	2.70404300	0.26334800
N	1.14224600	2.84352800	-0.79672800
C	2.17227900	2.48398500	1.58365400
H	1.39515300	2.14494400	2.27495700
H	2.93712200	1.70709600	1.48463700
H	2.61439000	3.40936300	1.96513800

Zero-point correction= 0.411098 (Hartree/Particle)
Thermal correction to Energy= 0.446071
Thermal correction to Enthalpy= 0.447015
Thermal correction to Gibbs Free Energy= 0.337588
Sum of electronic and zero-point Energies= -1911.373270
Sum of electronic and thermal Energies= -1911.338297
Sum of electronic and thermal Enthalpies= -1911.337353
Sum of electronic and thermal Free Energies= -1911.446780
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1913.4312121

^{2}INT13

Cu	1.75474300	0.16781000	-1.64034500
C	4.19706600	0.09331400	-0.85834900
O	3.62851800	0.02950700	-2.00877900
O	3.56525000	0.20755900	0.21785800
C	5.71402900	0.00951500	-0.86015300
H	6.11198900	0.13239300	0.14898900
H	6.02536000	-0.96105600	-1.26167000
H	6.12723000	0.77849600	-1.52060300
C	-0.87778200	0.36288800	0.25380900
C	-0.14208800	-0.28950800	1.12594300
S	-0.47382500	0.21722800	-1.54114400
C	-2.07561500	1.15968500	0.57728500
C	-2.91268300	0.73872800	1.62289800
C	-2.40159400	2.31658400	-0.14568100
C	-4.06202700	1.45927900	1.93320700
H	-2.67164900	-0.17413100	2.15609000
C	-3.54807500	3.03878300	0.17660300
H	-1.74631500	2.65404800	-0.94102900
C	-4.38354800	2.61066000	1.21090700
H	-4.71385400	1.11486400	2.73082400
H	-3.78981000	3.93785900	-0.38260700
H	-5.28329400	3.17013500	1.45065000
C	0.94276500	-1.24749000	1.22178600
O	1.04049200	-2.19981600	0.45710400
O	1.75533200	-0.99295800	2.24423700
C	2.93187300	-1.83991000	2.35449900
C	3.91308600	-1.12540500	3.25863300
H	3.34003400	-1.98122500	1.35455300
H	2.61047000	-2.80666400	2.75702100
H	4.79067100	-1.76075200	3.42128200
H	4.23803900	-0.19891800	2.77896800
H	3.46699000	-0.89744700	4.23227700
C	-1.10534300	-1.51730400	-1.83766600
H	-1.14484400	-1.58971400	-2.92882100
H	-0.35220700	-2.19918500	-1.44512700
C	-2.44134300	-1.72561700	-1.18860900

C	-3.59064100	-1.09062300	-1.67579700
C	-2.52979900	-2.50480600	-0.02939200
C	-4.80846000	-1.23195100	-1.01515100
H	-3.52258900	-0.46783500	-2.56406500
C	-3.75136200	-2.65258900	0.62887200
H	-1.63314500	-2.98005100	0.35730000
C	-4.89115100	-2.01314600	0.14006100
H	-5.69170300	-0.72823800	-1.39663300
H	-3.81018400	-3.26192700	1.52643100
H	-5.84051500	-2.12054900	0.65685900
C	1.48994700	2.71443100	0.32062500
N	1.03508400	2.88262200	-0.73523300
C	2.06585800	2.45699100	1.63385700
H	1.34060000	1.91885600	2.25196400
H	2.94154600	1.81528300	1.49565400
H	2.33984100	3.39584900	2.12413700

Zero-point correction= 0.403979 (Hartree/Particle)
Thermal correction to Energy= 0.436814
Thermal correction to Enthalpy= 0.437758
Thermal correction to Gibbs Free Energy= 0.332896
Sum of electronic and zero-point Energies= -1801.876503
Sum of electronic and thermal Energies= -1801.843669
Sum of electronic and thermal Enthalpies= -1801.842724
Sum of electronic and thermal Free Energies= -1801.947586
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1803.8972953

^{1}INT14

Cu	1.86676500	-0.10902500	-1.06929600
C	4.59709000	0.19213200	-0.81336600
O	3.68421800	-0.59906500	-1.27081400
O	4.41375200	1.28586800	-0.25825200
C	6.01768900	-0.35443200	-0.96018500
H	6.75370800	0.43544900	-0.79258300
H	6.17077900	-1.14425700	-0.21415500
H	6.15961400	-0.80458200	-1.94742000
C	-0.96985700	0.29465100	0.56710400
C	-0.42850200	-0.40913000	1.53870600
S	-0.34090000	0.14167300	-1.25771500
C	-2.19401600	1.12188200	0.64731800
C	-3.12963300	0.82349700	1.65510900
C	-2.47807900	2.18311200	-0.22652700
C	-4.30807600	1.55225900	1.77788400
H	-2.90312600	0.00020100	2.32347800
C	-3.65808800	2.91634000	-0.09755300
H	-1.76415800	2.44937600	-0.99721700
C	-4.58337400	2.60398000	0.89882700
H	-5.02207000	1.29129700	2.55635900
H	-3.84979200	3.73980100	-0.78172600
H	-5.50701500	3.17110200	0.99052700
C	0.64198600	-1.33197800	1.49126100
O	0.55941800	-2.55694900	1.32946100
O	1.86583400	-0.73063400	1.73550400
C	2.99271800	-1.60948100	1.87938300
C	4.10967600	-0.80314000	2.52069200
H	3.29097900	-1.97464600	0.89143500
H	2.69897700	-2.46985900	2.48872000
H	5.00404600	-1.42811500	2.63934300
H	4.36590600	0.05802600	1.89737700
H	3.80658800	-0.44236300	3.51024800
C	-0.90737200	-1.61882500	-1.54453200
H	-0.75512200	-1.79341100	-2.61428600
H	-0.26020800	-2.27741200	-0.96694600
C	-2.34180300	-1.79204900	-1.13815200
C	-3.38103700	-1.25298200	-1.90545100
C	-2.64434500	-2.43281900	0.06973400
C	-4.70353300	-1.35244900	-1.47751500
H	-3.14469600	-0.72937500	-2.82876800
C	-3.96888900	-2.53427100	0.49588300
H	-1.82876000	-2.80917100	0.68071900
C	-5.00050900	-1.99378000	-0.27305300
H	-5.50052400	-0.91796900	-2.07558900
H	-4.19247300	-3.02185600	1.44147900
H	-6.03049000	-2.06067600	0.06870900
C	1.13073700	3.17029000	-0.12957900
N	0.61413300	3.63159500	-1.06260800
C	1.78706400	2.58135300	1.03237500
H	1.14790400	1.80518000	1.46331800
H	2.73370800	2.12415900	0.71647300
H	1.98065200	3.35418900	1.78441500

Zero-point correction= 0.403091 (Hartree/Particle)

Thermal correction to Energy= 0.435633
Thermal correction to Enthalpy= 0.436578
Thermal correction to Gibbs Free Energy= 0.333998
Sum of electronic and zero-point Energies= -1801.974552
Sum of electronic and thermal Energies= -1801.942010
Sum of electronic and thermal Enthalpies= -1801.941065
Sum of electronic and thermal Free Energies= -1802.043645
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1804.0639065

^{2}INT12'

Cu	1.87992000	-0.62378700	-0.26653000
C	3.87491300	0.55511200	0.87842500
O	3.97559300	0.84672800	-0.34306500
O	2.94341200	-0.17879400	1.35449400
C	4.87516700	1.12025900	1.87734500
H	4.39645100	1.92859100	2.44334800
H	5.17144300	0.35243900	2.59798600
H	5.75276100	1.52308000	1.36733300
C	-1.17867500	-0.49286800	-0.84007500
C	-2.41796400	-0.14427300	-1.23603900
S	0.25376100	-0.21575200	-1.90456000
N	-3.61255100	0.83763600	-2.99268900
N	-2.59013500	0.42488200	-2.55002100
C	-0.85832900	-1.00098200	0.51026100
C	-1.21236500	-0.25177500	1.64000300
C	-0.09745500	-2.17520100	0.66237400
C	-0.81202000	-0.67374000	2.90705900
H	-1.75202500	0.68068500	1.51792400
C	0.28856200	-2.59356800	1.93447100
H	0.16982100	-2.76827800	-0.20742300
C	-0.06188100	-1.83990500	3.05717500
H	-1.06950700	-0.07427900	3.77512500
H	0.87650100	-3.49934400	2.04315500
H	0.26166500	-2.15572200	4.04430300
C	-3.62183000	-0.19015700	-0.34026300
O	-4.30908800	0.78495600	-0.12416000
O	-3.82132700	-1.41565800	0.15982900
C	-4.90035300	-1.54809000	1.12193000
C	-6.23746200	-1.72662800	0.42278400
H	-4.89874600	-0.66558100	1.76622500
H	-4.62278400	-2.42707400	1.70662000
H	-7.02309400	-1.90087400	1.16651500
H	-6.49412600	-0.83081300	-0.14841900
H	-6.20756200	-2.58532000	-0.25529500
C	0.23925600	1.66290800	-2.05441000
H	1.23865400	1.86548400	-2.44883600
H	-0.51106900	1.90393800	-2.80746100
C	-0.00798800	2.34578800	-0.74621500
C	1.03496200	2.48146800	0.18064200
C	-1.29358100	2.78715500	-0.40657000
C	0.78653500	3.02914900	1.43735400
H	2.03543500	2.15383900	-0.08700300
C	-1.53804400	3.34252600	0.85041600
H	-2.10770900	2.69391200	-1.11814000
C	-0.49988800	3.45580100	1.77724800
H	1.59899100	3.11662700	2.15243200
H	-2.54046400	3.67597700	1.10226700
H	-0.69099300	3.88065500	2.75881700
C	3.97260800	-2.09142600	-1.52793000
N	2.89695600	-2.44893700	-1.26701600
C	5.29908000	-1.56155400	-1.81308400
H	5.31628900	-0.53224100	-1.43310500
H	6.06448900	-2.15981400	-1.30971200
H	5.48965100	-1.56694400	-2.89040900

Zero-point correction= 0.412755 (Hartree/Particle)
Thermal correction to Energy= 0.447829
Thermal correction to Enthalpy= 0.448774
Thermal correction to Gibbs Free Energy= 0.337867
Sum of electronic and zero-point Energies= -1911.377198
Sum of electronic and thermal Energies= -1911.342124
Sum of electronic and thermal Enthalpies= -1911.341180
Sum of electronic and thermal Free Energies= -1911.452086
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1913.4359034

^{2}TS6'

Cu	1.91595600	-0.66333300	-0.17548800
C	3.96255200	0.67616900	0.66203200
O	3.97483500	0.81044800	-0.59042000
O	3.08055000	-0.00177000	1.29132300
C	5.01935400	1.36987100	1.51046800

H	4.55279400	2.19678200	2.05897400
H	5.42282500	0.67738100	2.25554700
H	5.82335100	1.76731600	0.88763900
C	-1.17149200	-0.63350800	-0.64619500
C	-2.41872200	-0.40507200	-1.02704300
S	0.23139400	-0.50080300	-1.78955300
N	-3.62598300	0.47384100	-3.17207000
N	-2.64165400	0.04874300	-2.79550000
C	-0.80452800	-0.91590100	0.76438600
C	-1.17540300	-0.02461100	1.77760500
C	-0.00783000	-2.03400200	1.07319100
C	-0.74558200	-0.24311600	3.08617500
H	-1.75146900	0.85926800	1.52862900
C	0.41026600	-2.24727700	2.38576300
H	0.26402600	-2.74273600	0.29598700
C	0.04828400	-1.34836100	3.39196400
H	-1.01598500	0.46655800	3.86247200
H	1.02976600	-3.10833500	2.61567500
H	0.39408500	-1.50566500	4.40914400
C	-3.67286600	-0.25631900	-0.27776100
O	-4.35205600	0.75129700	-0.33255600
O	-3.97131100	-1.36347700	0.42250500
C	-5.17636100	-1.30208400	1.22878500
C	-6.40903100	-1.60347300	0.39240200
H	-5.23763000	-0.31312700	1.68935000
H	-5.01292100	-2.05525200	2.00194300
H	-7.29589400	-1.62789900	1.03562000
H	-6.55458400	-0.83129500	-0.36744300
H	-6.31318100	-2.57595300	-0.10074700
C	0.20139300	1.34054600	-2.17396900
H	1.19101300	1.49969600	-2.61080900
H	-0.56167600	1.48309800	-2.93974300
C	-0.02937800	2.19330700	-0.96590500
C	1.03300100	2.47852100	-0.09730700
C	-1.31464500	2.65853500	-0.65913300
C	0.80538200	3.20097900	1.07214000
H	2.03220600	2.13168600	-0.34411600
C	-1.53814000	3.38961700	0.50856600
H	-2.14667500	2.44245500	-1.32148700
C	-0.47978300	3.65453600	1.37997900
H	1.63351400	3.40556100	1.74409900
H	-2.54017800	3.74165800	0.73597200
H	-0.65445500	4.21725200	2.29287100
C	3.95566300	-2.29214500	-1.32949700
N	2.90571300	-2.62700200	-0.95767200
C	5.25000100	-1.78526800	-1.76524300
H	5.26002100	-0.71021000	-1.54506700
H	6.05726500	-2.28602800	-1.22235800
H	5.38328000	-1.94942500	-2.83869000

Zero-point correction= 0.410126 (Hartree/Particle)
Thermal correction to Energy= 0.445557
Thermal correction to Enthalpy= 0.446502
Thermal correction to Gibbs Free Energy= 0.334206
Sum of electronic and zero-point Energies= -1911.367359
Sum of electronic and thermal Energies= -1911.331928
Sum of electronic and thermal Enthalpies= -1911.330984
Sum of electronic and thermal Free Energies= -1911.443280
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1913.4247617

^{2}INT13'

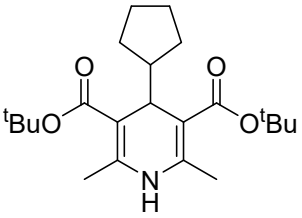
Cu	1.78088700	-0.64430600	0.03241200
C	3.98974800	0.62391000	-0.25685300
O	3.78406200	0.03009900	-1.34965500
O	3.20658600	0.53448300	0.74872300
C	5.20330400	1.52816200	-0.10001900
H	4.87177500	2.57337200	-0.09298300
H	5.69584400	1.34043000	0.85876800
H	5.90694300	1.38644900	-0.92290100
C	-1.40472300	-0.83150200	0.12452200
C	-2.65281600	-0.90358900	-0.25176600
S	-0.13108800	-1.32280100	-1.09421300
C	-0.92626000	-0.31209300	1.42949300
C	-1.47328100	0.87054200	1.94315800
C	0.10728700	-0.96482000	2.12379700
C	-0.96742500	1.41208700	3.12383900
H	-2.26294500	1.37320700	1.39643600
C	0.60549200	-0.41542000	3.30482500
H	0.50093300	-1.91161700	1.76354400
C	0.07567100	0.77729300	3.80082200
H	-1.37895900	2.34196100	3.50538900

H	1.41197800	-0.91902500	3.82829900
H	0.47644000	1.21140000	4.71203900
C	-4.02826400	-0.51564400	-0.15161800
O	-4.39538600	0.65069700	-0.25102000
O	-4.85041700	-1.56696300	0.02305400
C	-6.26571000	-1.26357100	0.09981400
C	-6.86741400	-1.09004800	-1.28583900
H	-6.40151300	-0.36625300	0.70837400
H	-6.69041900	-2.12399700	0.62063100
H	-7.95034200	-0.94450200	-1.20323400
H	-6.43978000	-0.21586300	-1.78377800
H	-6.68371800	-1.97683200	-1.90064700
C	-0.36814400	0.05578600	-2.34229600
H	0.41583300	-0.14561500	-3.07810600
H	-1.34265200	-0.11457500	-2.80455800
C	-0.24767100	1.41926100	-1.73572800
C	1.02039000	1.96766400	-1.49737300
C	-1.39008800	2.12277200	-1.33598000
C	1.14127900	3.19310600	-0.84523700
H	1.91070600	1.42779400	-1.80877400
C	-1.26468100	3.35352300	-0.69054700
H	-2.37743000	1.70299200	-1.50152200
C	-0.00015700	3.88674100	-0.43686900
H	2.12864900	3.60110400	-0.65113100
H	-2.15762800	3.88883400	-0.38022000
H	0.09626700	4.84055300	0.07429600
C	3.55049400	-2.92662900	-0.21530400
N	2.57826400	-2.87272800	0.41993700
C	4.75605900	-2.90795600	-1.03291300
H	4.83676600	-1.89941900	-1.45748800
H	5.63516100	-3.12734800	-0.41953100
H	4.68463500	-3.64822300	-1.83537900

Zero-point correction= 0.403123 (Hartree/Particle)
Thermal correction to Energy= 0.436322
Thermal correction to Enthalpy= 0.437267
Thermal correction to Gibbs Free Energy= 0.329025
Sum of electronic and zero-point Energies= -1801.869594
Sum of electronic and thermal Energies= -1801.836395
Sum of electronic and thermal Enthalpies= -1801.835450
Sum of electronic and thermal Free Energies= -1801.943692
(U)B3LYP-D3/6-311++G(d,p)-SDD/SMD//(U)B3LYP-D3/6-31+G(d)-LANL2DZ energy = -1803.8888567

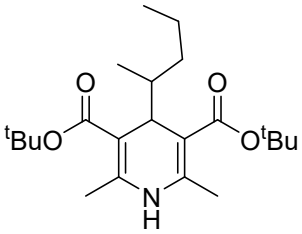
8. Syntheses and Characterization of Compounds

Di-tert-butyl 4-cyclopentyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate(2n)



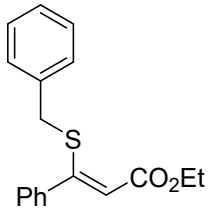
With general procedure 2.2, reaction of benzyloxyacetaldehyde (10 mmol) and tert-butyl acetoacetate (20 mmol) provided **2n** after flash column chromatography (10 vol % EtOAc in petroleum ether) as a white solid (1.6 g, 42%). R_f = 0.3 (10 vol % EtOAc in petroleum ether). M.P. 149-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H), 3.92 (d, J = 7.5 Hz, 1H), 2.26 (s, 6H), 1.68 (s, 1H), 1.60 – 1.54 (m, 2H), 1.49 (s, 20H), 1.41 (dt, J = 9.7, 4.0 Hz, 2H), 1.20 (tt, J = 9.6, 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 143.3, 104.2, 79.2, 48.0, 36.4, 28.6, 28.3, 24.0, 19.2. HRMS (ESI): calcd. for $C_{22}H_{35}NNaO_4$([M+Na]+): 400.2458, found: 400.2461.

Di-tert-butyl 2,6-dimethyl-4-(pentan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate(2q)



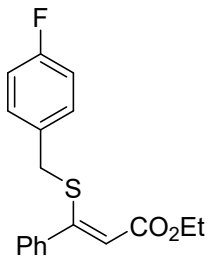
With general procedure 2.2, reaction of benzyloxyacetaldehyde (10 mmol) and tert-butyl acetoacetate (20 mmol) provided **2q** after flash column chromatography (10 vol % EtOAc in petroleum ether) as a white solid (1.7 g, 45%). R_f = 0.3 (10 vol % EtOAc in petroleum ether). M.P. 143-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (s, 1H), 3.93 (d, J = 4.8 Hz, 1H), 2.25 (d, J = 4.5 Hz, 6H), 1.49 (s, 6H), 1.39 – 1.32 (m, 18H), 1.31 – 1.15 (m, 2H), 1.03 – 0.91 (m, 2H), 0.85 (t, J = 7.0 Hz, 3H), 0.72 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.0, 143.4, 143.1, 103.6, 102.8, 79.3, 79.2, 40.8, 38.7, 35.2, 28.3, 28.2, 20.7, 19.2, 19.1, 15.0, 14.4. HRMS (ESI): calcd. for $C_{22}H_{37}NNaO_4$([M+Na]+): 402.2615, found: 402.2621.

Ethyl (Z)-3-(benzylthio)-3-phenylacrylate(3aa)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3aa** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (24.4 mg, 82%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.32 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 7.03 (dd, J = 7.2, 2.1 Hz, 2H), 5.93 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.66 (s, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.8, 138.4, 136.7, 128.8, 128.7, 128.3, 128.2, 128.0, 126.9, 116.0, 60.0, 37.2, 14.2. HRMS (APCI): calcd. for $C_{18}H_{18}NaO_2S$([M+Na]$^+$): 321.0920, found: 321.0925.

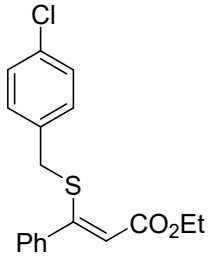
Ethyl (Z)-3-((4-fluorobenzyl)thio)-3-phenylacrylate(3ba)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2b** (0.15 mmol) provided the product **3ba** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (25.6 mg, 81%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 3H), 7.25 (d, J = 3.3 Hz, 2H), 6.96 – 6.90 (m, 2H), 6.85 (t, J = 8.5 Hz, 2H), 5.91 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 3.61 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 161.8 (d, J = 245 Hz), 159.3, 138.3,

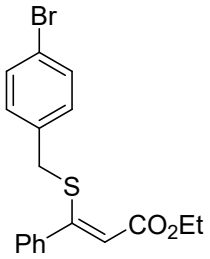
132.6 (d, J = 3.0 Hz), 130.3 (d, J = 8.0 Hz), 128.8, 128.4, 128.0, 115.7 (d, J = 120.8 Hz), 114.9, 60.0, 36.4, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.38 (s, 1F). HRMS (APCI): calcd. for $C_{18}H_{17}FNaO_2S([M+Na]^+)$: 339.0825, found: 339.0825.

Ethyl (Z)-3-((4-chlorobenzyl)thio)-3-phenylacrylate(3ca)



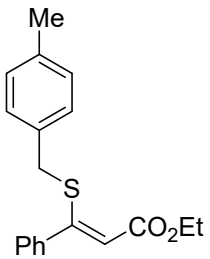
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2c** (0.15 mmol) provided the product **3ca** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (27.2 mg, 82%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 3H), 7.28 – 7.18 (m, 2H), 7.16 – 7.06 (m, 2H), 6.88 (d, J = 8.5 Hz, 2H), 5.90 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.0, 138.2, 135.5, 132.7, 130.1, 128.8, 128.4, 128.3, 128.0, 116.5, 60.0, 36.4, 14.2. HRMS (APCI): calcd. for $C_{18}H_{17}ClNaO_2S([M+Na]^+)$: 355.0530, found: 355.0538.

Ethyl (Z)-3-((4-bromobenzyl)thio)-3-phenylacrylate(3da)



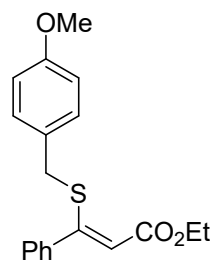
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2d** (0.15 mmol) provided the product **3da** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (34.5 mg, 79%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 5.0, 1.7 Hz, 3H), 7.30 – 7.26 (m, 2H), 7.23 (dd, J = 6.6, 3.0 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 5.90 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.0, 138.1, 136.0, 131.2, 130.4, 128.8, 128.4, 128.0, 120.8, 116.5, 60.1, 36.4, 14.2. HRMS (APCI): calcd. for $C_{18}H_{17}BrNaO_2S([M+Na]^+)$: 399.0025, found: 399.0029.

Ethyl (Z)-3-((4-methylbenzyl)thio)-3-phenylacrylate(3ea)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2e** (0.15 mmol) provided the product **3ea** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (29.8 mg, 89%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 4.1, 2.0 Hz, 3H), 7.27 (dd, J = 6.6, 3.0 Hz, 2H), 6.98 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 5.89 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 2.26 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.9, 138.5, 136.6, 133.5, 128.9, 128.7, 128.3, 128.0, 115.9, 59.9, 37.0, 20.9, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_2S([M+Na]^+)$: 335.1076, found: 335.1080.

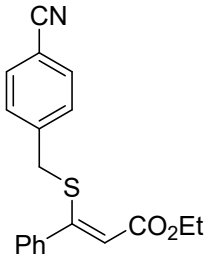
Ethyl (Z)-3-((4-methoxybenzyl)thio)-3-phenylacrylate(3fa)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2f** (0.15 mmol) provided the product **3fa** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (34.5 mg, 79%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 3H), 7.31 – 7.24 (m, 2H), 6.95 – 6.88 (m, 2H), 6.74 – 6.66 (m, 2H), 5.98 – 5.80 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.74 (s, 3H), 3.58 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.9, 158.5, 138.5,

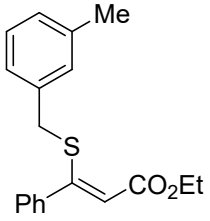
129.9, 128.7, 128.6, 128.3, 128.0, 115.9, 113.6, 59.9, 55.1, 36.7, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_3S([M+Na]^+)$: 355.0530, found: 355.0538.

Ethyl (Z)-3-((4-cyanobenzyl)thio)-3-phenylacrylate(3ga)



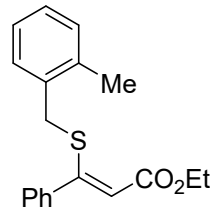
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2g** (0.15 mmol) provided the product **3ga** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a white solid (24.9 mg, 70%). M.P. 52-53 °C. R_f = 0.45 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 6.3 Hz, 3H), 7.19 (d, J = 6.4 Hz, 2H), 7.03 (d, J = 7.7 Hz, 2H), 5.92 (s, 1H), 4.22 (q, J = 6.9 Hz, 2H), 3.69 (s, 2H), 1.30 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 158.1, 142.8, 137.8, 131.9, 129.4, 129.0, 128.5, 128.0, 118.5, 117.1, 110.7, 60.1, 36.5, 14.2. HRMS (APCI): calcd. for $C_{19}H_{17}NNaO_2S([M+Na]^+)$: 346.0872, found: 346.0875.

Ethyl (Z)-3-((3-methylbenzyl)thio)-3-phenylacrylate(3ha)



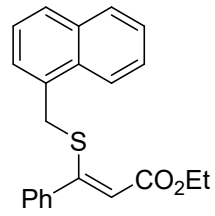
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2h** (0.15 mmol) provided the product **3ha** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (25.9 mg, 83%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 2.5 Hz, 3H), 7.27 (s, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 7.4 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 6.76 (s, 1H), 5.89 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.59 (s, 2H), 2.23 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.0, 138.4, 137.7, 136.5, 129.6, 128.7, 128.3, 128.1, 128.0, 127.7, 125.8, 115.8, 60.0, 37.2, 21.1, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_2S([M+Na]^+)$: 335.1076, found: 335.1077.

Ethyl (Z)-3-((2-methylbenzyl)thio)-3-phenylacrylate(3ia)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2i** (0.15 mmol) provided the product **3ia** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (27.1 mg, 87%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 6.2 Hz, 3H), 7.34 (d, J = 7.0 Hz, 2H), 7.13 – 7.01 (m, 3H), 6.97 (d, J = 7.2 Hz, 1H), 5.91 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.57 (s, 2H), 2.23 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.3, 138.6, 136.7, 134.2, 130.2, 129.8, 128.8, 128.5, 127.9, 127.4, 125.9, 115.7, 60.0, 35.6, 19.0, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_2S([M+Na]^+)$: 335.1076, found: 335.1076.

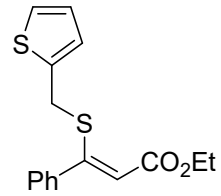
Ethyl (Z)-3-((naphthalen-1-ylmethyl)thio)-3-phenylacrylate(3ja)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2j** (0.15 mmol) provided the product **3ja** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (28.9 mg, 83%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 1H), 7.83 – 7.74 (m, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.54 – 7.37 (m, 7H), 7.30 – 7.18 (m, 1H), 7.08 (d, J = 7.0 Hz, 1H), 5.93 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.04 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 160.0, 138.6, 133.7, 132.2, 131.4, 128.9, 128.6, 128.6, 128.2, 128.0, 127.5, 126.1,

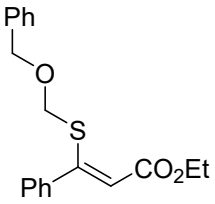
125.6, 125.1, 123.7, 115.8, 60.0, 35.3, 14.2. HRMS (APCI): calcd. for $C_{22}H_{20}NaO_2S([M+Na]^+)$: 371.1076, found: 371.1078.

Ethyl (Z)-3-phenyl-3-((thiophen-2-ylmethyl)thio)acrylate(3ka)



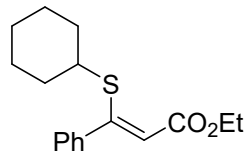
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2k** (0.15 mmol) provided the product **3ka** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (23.7 mg, 78%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 3H), 7.29 (s, 2H), 7.11 (d, J = 4.7 Hz, 1H), 6.79 (s, 1H), 6.60 (s, 1H), 5.93 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 3.84 (s, 2H), 1.29 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 158.9, 139.8, 138.1, 128.9, 128.4, 128.0, 126.5, 126.3, 125.0, 116.6, 60.1, 31.7, 14.3. HRMS (APCI): calcd. for $C_{16}H_{16}NaO_2S_2$ ($[M+Na]^+$): 327.0484, found: 327.0475.

Ethyl (Z)-3-(((benzyloxy)methyl)thio)-3-phenylacrylate(3la)



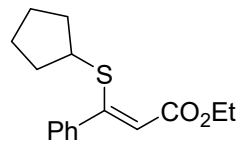
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2l** (0.15 mmol) provided the product **3ja** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (19.4 mg, 59%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 5H), 7.33 – 7.26 (m, 3H), 7.21 (d, J = 6.9 Hz, 2H), 6.02 (s, 1H), 4.56 (s, 2H), 4.47 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 157.6, 137.8, 136.9, 128.9, 128.3, 128.2, 127.9, 127.7, 118.2, 71.5, 70.1, 60.1, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_3S([M+Na]^+)$: 351.1025, found: 351.1028.

Ethyl (Z)-3-(cyclohexylthio)-3-phenylacrylate(3ma)



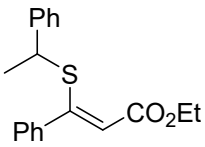
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2m** (0.15 mmol) provided the product **3ma** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (15.4 mg, 53%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 5H), 5.91 (s, 1H), 4.22 (q, J = 6.9 Hz, 2H), 2.63 (t, J = 10.7 Hz, 1H), 1.74 – 1.57 (m, 5H), 1.45 (d, J = 11.9 Hz, 1H), 1.30 (t, J = 7.1 Hz, 5H), 1.15 – 1.05 (m, 1H), 0.97 (dd, J = 24.0, 11.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.4, 139.0, 128.7, 128.2, 127.9, 116.8, 59.9, 44.4, 33.6, 25.8, 25.2, 14.3. HRMS (APCI): calcd. for $C_{17}H_{22}NaO_2S([M+Na]^+)$: 313.1233, found: 313.0770.

Ethyl (Z)-3-(cyclopentylthio)-3-phenylacrylate(3na)



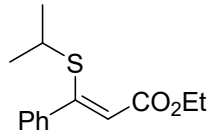
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2n** (0.15 mmol) provided the product **3na** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (22.4 mg, 81%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 5H), 5.90 (s, 1H), 4.22 (q, J = 7.0 Hz, 2H), 3.11 – 2.99 (m, 1H), 1.64 (s, 4H), 1.47 (d, J = 5.3 Hz, 2H), 1.36 (s, 2H), 1.30 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.8, 139.4, 128.5, 128.2, 127.9, 116.1, 59.9, 44.2, 33.9, 25.0, 14.3. HRMS (APCI): calcd. for $C_{16}H_{20}NaO_2S([M+Na]^+)$: 299.1076, found: 299.1079.

Ethyl (Z)-3-phenyl-3-((1-phenylethyl)thio)acrylate(3oa)



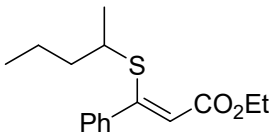
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2o** (0.15 mmol) provided the product **3oa** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (26.2 mg, 84%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 3H), 7.17 (dt, J = 3.6, 2.0 Hz, 2H), 7.15 – 7.10 (m, 2H), 6.96 – 6.88 (m, 2H), 5.85 (s, 1H), 4.22 (qd, J = 7.1, 1.0 Hz, 2H), 4.05 – 3.96 (m, 1H), 1.45 (d, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 159.0, 143.1, 138.8, 128.6, 128.1, 128.1, 128.0, 127.1, 126.7, 117.0, 60.0, 45.3, 23.2, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_2S([M+Na]^+)$: 335.1076, found: 335.1086.

Ethyl (Z)-3-(isopropylthio)-3-phenylacrylate(3pa)



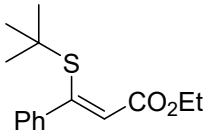
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2p** (0.15 mmol) provided the product **3pa** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (18.5 mg, 74%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 5H), 5.93 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.94 (dt, J = 13.5, 6.7 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.10 (d, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.4, 139.0, 128.8, 128.3, 128.0, 117.1, 60.0, 36.3, 23.4, 14.3. HRMS (APCI): calcd. for $C_{14}H_{18}NaO_2S([M+Na]^+)$: 273.0920, found: 273.0910.

Ethyl (Z)-3-(isopropylthio)-3-phenylacrylate(3qa)



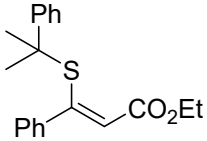
With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2q** (0.15 mmol) provided the product **3qa** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (25.6 mg, 92%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 5H), 5.94 (s, 1H), 4.23 (q, J = 6.8 Hz, 2H), 2.77 (dd, J = 13.0, 6.5 Hz, 1H), 1.42 (ddd, J = 23.5, 14.8, 7.1 Hz, 2H), 1.29 (dd, J = 16.1, 9.1 Hz, 5H), 1.07 (d, J = 6.5 Hz, 3H), 0.73 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.8, 139.1, 128.7, 128.3, 128.0, 117.0, 59.9, 41.0, 39.2, 21.7, 20.0, 14.3, 13.5. HRMS (APCI): calcd. for $C_{16}H_{22}NaO_2S([M+Na]^+)$: 301.1233, found: 301.1225.

Ethyl (Z)-3-(pentan-2-ylthio)-3-phenylacrylate(3ra)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2r** (0.15 mmol) provided the product **3ra** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (15.3 mg, 58%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.35 (dd, J = 4.1, 2.4 Hz, 3H), 6.24 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 151.8, 141.6, 129.0, 128.4, 128.0, 125.6, 60.3, 48.1, 31.8, 14.2. HRMS (APCI): calcd. for $C_{15}H_{20}NaO_2S([M+Na]^+)$: 287.1076, found: 287.1080.

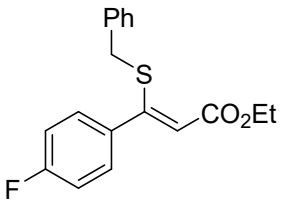
Ethyl (Z)-3-phenyl-3-((2-phenylpropan-2-yl)thio)acrylate(3sa)



With general procedure 2.3, reaction of **1a** (0.1 mmol) and **2s** (0.15 mmol) provided the product **3sa** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (18.3 mg, 56%). R_f = 0.70 (10

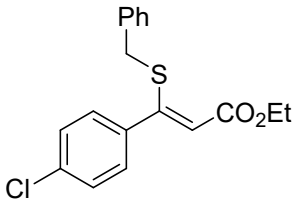
vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 3H), 7.12 – 7.07 (m, 3H), 7.01 (t, J = 7.7 Hz, 2H), 6.98 – 6.93 (m, 2H), 5.93 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.57 (s, 6H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 155.1, 146.3, 139.6, 128.2, 127.6, 127.4, 126.4, 126.0, 122.8, 60.1, 52.2, 31.3, 14.2. HRMS (APCI): calcd. for $C_{20}H_{22}NaO_2S([M+Na]^+$): 349.1233, found: 349.1235.

Ethyl (Z)-3-(benzylthio)-3-(4-fluorophenyl)acrylate(3ab)



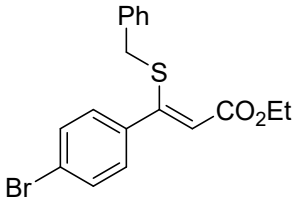
With general procedure 2.3, reaction of **1b** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ab** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (25.9 mg, 82%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.18 (d, J = 5.7 Hz, 3H), 7.05 (t, J = 8.5 Hz, 2H), 7.02 – 6.96 (m, 2H), 5.88 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.64 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 162.9 (d, J = 249 Hz), 158.3, 136.6, 134.5 (d, J = 3.5 Hz), 129.9 (d, J = 8.3 Hz), 128.7, 128.2, 127.0, 116.2 (d, J = 113.4 Hz), 115.3, 60.1, 37.2, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68 (s, 1F). HRMS (APCI): calcd. for $C_{18}H_{17}FNaO_2S([M+Na]^+$): 339.0825, found: 339.0830.

Ethyl (Z)-3-(benzylthio)-3-(4-chlorophenyl)acrylate(3ac)



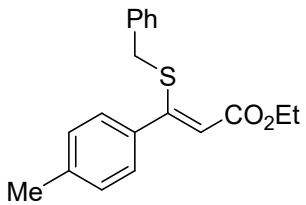
With general procedure 2.3, reaction of **1c** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ac** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (24.2 mg, 73%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.22 – 7.15 (m, 5H), 7.03 – 6.97 (m, 2H), 5.88 (s, 1H), 4.26 – 4.16 (m, 2H), 3.61 (d, J = 13.7 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 158.1, 136.8, 136.5, 134.8, 129.3, 128.7, 128.6, 128.3, 127.1, 116.8, 60.1, 37.2, 14.2. HRMS (APCI): calcd. for $C_{18}H_{17}ClNaO_2S([M+Na]^+$): 355.0530, found: 355.0529.

Ethyl (Z)-3-(benzylthio)-3-(4-bromophenyl)acrylate(3ad)



With general procedure 2.3, reaction of **1d** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ad** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (30.1 mg, 80%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 5.7 Hz, 3H), 7.12 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 5.5 Hz, 2H), 5.87 (s, 1H), 4.21 (q, J = 7.0 Hz, 2H), 3.62 (s, 2H), 1.28 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 158.1, 137.3, 136.5, 131.6, 129.6, 128.8, 128.7, 128.3, 127.1, 123.0, 116.7, 60.1, 37.2, 14.2. HRMS (APCI): calcd. for $C_{18}H_{17}BrNaO_2S([M+Na]^+$): 399.0025, found: 399.0032.

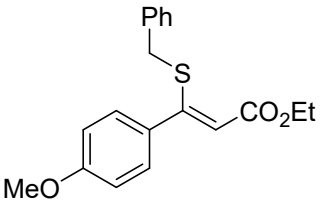
Ethyl (Z)-3-(benzylthio)-3-(p-tolyl)acrylate(3ae)



With general procedure 2.3, reaction of **1e** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ae** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (23.1 mg, 74%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 7H), 7.02 (d, J = 6.0 Hz, 2H), 5.89 (s,

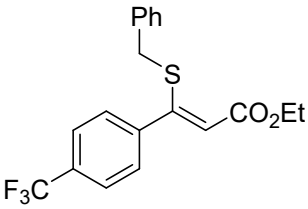
1H), 4.20 (q, J = 7.1 Hz, 2H), 3.63 (s, 2H), 2.38 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 159.9, 138.8, 136.8, 135.6, 129.0, 128.8, 128.2, 127.9, 126.9, 115.8, 59.9, 37.3, 21.1, 14.2. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_2S$([M+Na]$^+$): 335.1076, found: 335.1079.

Ethyl (Z)-3-(benzylthio)-3-(4-methoxyphenyl)acrylate(3af)



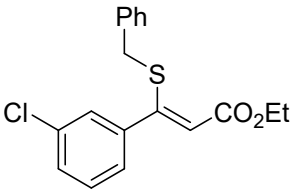
With general procedure 2.3, reaction of **1f** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3af** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (21.7 mg, 66%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 6.2 Hz, 3H), 7.03 (d, J = 6.3 Hz, 2H), 6.89 (d, J = 8.1 Hz, 2H), 5.89 (s, 1H), 4.20 (q, J = 6.9 Hz, 2H), 3.84 (s, 3H), 3.67 (s, 2H), 1.28 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.1, 159.3, 136.9, 130.9, 129.4, 128.8, 128.2, 126.9, 115.8, 113.7, 59.9, 55.3, 37.4, 14.3. HRMS (APCI): calcd. for $C_{19}H_{20}NaO_3S$([M+Na]$^+$): 351.1025, found: 351.1022.

Ethyl (Z)-3-(benzylthio)-3-(4-(trifluoromethyl)phenyl)acrylate(3ag)



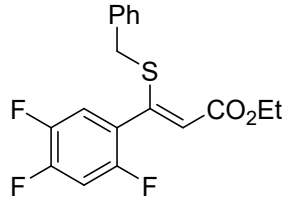
With general procedure 2.3, reaction of **1g** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ag** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (28.6 mg, 78%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.19 – 7.13 (m, 3H), 6.96 (dd, J = 6.5, 2.9 Hz, 2H), 5.90 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.62 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 157.8, 141.9, 136.4, 130.8 (d, J = 32.8 Hz), 128.7, 128.3(q, J =51.1 Hz) 127.1, 125.4 (q, J = 3.7 Hz), 123.7 (q, J = 272.4 Hz), 117.2, 60.3, 37.2, 14.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.68 (s, 3F). HRMS (APCI): calcd. for $C_{19}H_{17}F_3NaO_2S$([M+Na]$^+$): 389.0794, found: 389.0794.

Ethyl (Z)-3-(benzylthio)-3-(3-chlorophenyl)acrylate(3ah)



With general procedure 2.3, reaction of **1h** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ah** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (28.2 mg, 85%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 3H), 7.18 (dd, J = 7.9, 1.6 Hz, 4H), 7.02 – 6.95 (m, 2H), 5.88 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.64 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 157.8, 140.0, 136.5, 134.3, 129.6, 128.8, 128.7, 128.2, 128.1, 127.1, 126.2, 116.9, 60.1, 37.2, 14.2. HRMS (APCI): calcd. for $C_{18}H_{17}ClNaO_2S$([M+Na]$^+$): 355.0530, found: 355.0533.

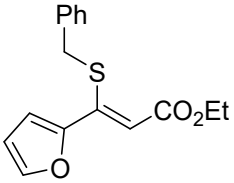
Ethyl (Z)-3-(benzylthio)-3-(2,4,5-trifluorophenyl)acrylate(3ai)



With general procedure 2.3, reaction of **1n** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3an** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (23.6 mg, 67%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^{1}H NMR (400

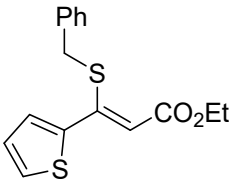
MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.20 (s, 2H), 7.05 (s, 2H), 6.99 – 6.82 (m, 2H), 5.94 (s, 0.2H, *Z*), 5.85 (s, 0.8H, *E*), 4.22 (q, J = 6.7 Hz, 1.6H, *E*), 4.06 (s, 0.4H, *Z*), 4.02 (d, J = 6.9 Hz, 0.4H, *Z*), 3.64 (s, 1.6H, *E*), 1.29 (t, J = 6.9 Hz, 2.3H, *E*), 1.15 (t, J = 6.9 Hz, 0.7H, *Z*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 151.7, 135.9, 128.8 (d, J = 4.0 Hz), 128.5 (d, J = 21.7 Hz), 127.8, 127.3, 118.2 (d, J = 2.6 Hz), 118.0 (d, J = 4.2 Hz), 117.5, 114.1, 106.1 (d, J = 21.1 Hz), 105.8 (d, J = 21.1 Hz), 60.3, 36.8, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.66 (dd, J = 14.9, 4.7 Hz, 1F), -131.41 (dd, J = 21.5, 4.7 Hz, 1F), -141.55 (dd, J = 21.6, 14.9 Hz, 1F). HRMS (APCI): calcd. for $C_{18}H_{15}F_3NaO_2S([M+Na]^+$): 375.0637, found: 375.0640.

Ethyl (Z)-3-(benzylthio)-3-(furan-2-yl)acrylate(3aj)



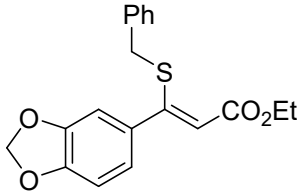
With general procedure 2.3, reaction of **1j** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3aj** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (13.5 mg, 47%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.25 – 7.15 (m, 5H), 6.72 (s, 1H), 6.44 (s, 1H), 6.40 (s, 1H), 4.22 (q, J = 6.8 Hz, 2H), 4.07 (s, 2H), 1.30 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 152.0, 144.2, 142.7, 137.1, 128.9, 128.3, 127.2, 116.6, 113.1, 111.9, 60.2, 38.8, 14.3. HRMS (APCI): calcd. for $C_{16}H_{16}NaO_3S([M+Na]^+$): 311.0712, found: 311.0704.

Ethyl (Z)-3-(benzylthio)-3-(thiophen-2-yl)acrylate(3ak)



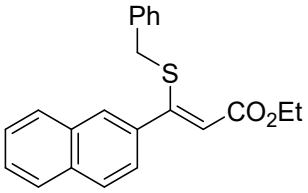
With general procedure 2.3, reaction of **1k** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3ak** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (12.8 mg, 42%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 4.3 Hz, 1H), 7.32 (s, 4H), 7.28 (s, 2H), 7.03 (s, 1H), 5.87 (s, 1H), 4.12 – 4.05 (m, 2H), 4.03 (s, 2H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 150.1, 137.1, 134.9, 129.4, 128.9, 128.7, 128.1, 127.6, 126.8, 112.7, 60.0, 38.2, 14.0. HRMS (APCI): calcd. for $C_{16}H_{16}NaO_2S_2([M+Na]^+$): 327.0484, found: 327.0480.

Ethyl (Z)-3-(benzo[d][1,3]dioxol-5-yl)-3-(benzylthio)acrylate(3al)



With general procedure 2.3, reaction of **1m** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3al** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (26.8 mg, 77%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.1 Hz, 3H), 7.06 (d, J = 6.6 Hz, 2H), 6.82 – 6.73 (m, 3H), 6.00 (s, 2H), 5.89 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.70 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.0, 148.1, 147.6, 136., 132.4, 128.8, 128.2, 127.0, 122.0, 116.1, 108.6, 108.1, 101.3, 60.0, 37.4, 14.2. HRMS (APCI): calcd. for $C_{22}H_{20}NaO_2S([M+Na]^+$): 365.0818, found: 365.0816.

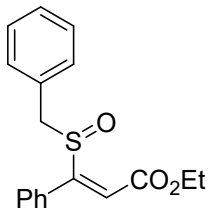
Ethyl (Z)-3-(benzylthio)-3-(naphthalen-2-yl)acrylate(3am)



With general procedure 2.3, reaction of **1m** (0.1 mmol) and **2a** (0.15 mmol) provided the product **3am** after flash column chromatography (1 vol % EtOAc in petroleum ether) as a colorless oil (26.8 mg, 77%). R_f = 0.70 (10 vol % EtOAc in petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 2H), 7.81 (d, J

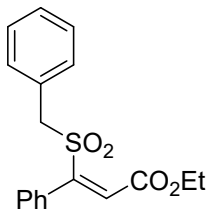
= 4.2 Hz, 1H), 7.70 (s, 1H), 7.53 (s, 2H), 7.43 (d, J = 8.3 Hz, 1H), 7.12 (s, 3H), 6.95 (s, 2H), 6.01 (s, 1H), 4.23 (q, J = 6.5 Hz, 2H), 3.64 (s, 2H), 1.30 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 159.7, 136.7, 135.9, 133.1, 132.8, 128.8, 128.2, 128.1, 128.1, 127.6, 127.2, 127.0, 126.8, 126.6, 125.7, 116.5, 60.0, 37.3, 14.3. HRMS (APCI): calcd. for $C_{22}H_{20}NaO_2S([M+Na]^+$): 371.1076, found: 371.1081.

Ethyl (Z)-3-(benzylsulfinyl)-3-phenylacrylate(4a)



A mixture of **3a** (0.1 mmol) and an excess of 75% m-CPBA (0.2 mmol) was stirred at -20 ºC for 4 h. The mixture was poured into saturated $NaHCO_3$ (aq.) and extracted with DCM. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (EA:PE(1:4, v/v)) to afford **4a** as yellow oil in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 1H), 7.26 – 7.21 (m, 6H), 7.19 – 7.15 (m, 2H), 6.44 (s, 1H), 4.35 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 146.8, 132.7, 132.2, 131.2, 129.7, 129.0, 128.9, 128.6, 128.4, 126.5, 62.0, 61.2, 13.9. HRMS (APCI): calcd. for $C_{18}H_{18}NaO_3S([M+Na]^+$): 337.0869, found: 337.0875.

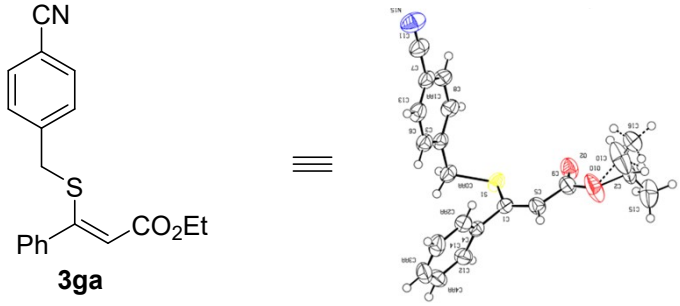
Ethyl (Z)-3-(benzylsulfonyl)-3-phenylacrylate(5a)



A mixture of 3a (0.1 mmol) and an excess of 75% m-CPBA (0.3 mmol) was stirred at room temperature for 12 h. The mixture was poured into saturated $NaHCO_3$ (aq.) and extracted with DCM. The combined extracts were dried over MgSO4, filtered, and evaporated. The residue was purified by column chromatography (EA:PE(1:3, v/v)) to afford **5a** as yellow oil in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 4H), 7.35 – 7.27 (m, 5H), 6.36 (s, 1H), 4.37 – 4.20 (m, 3H), 4.16 (d, J = 12.4 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.3, 131.5, 131.2, 130.4, 129.7, 129.3, 128.6, 128.2, 128.0, 122.7, 61.3, 61.1, 14.1. HRMS (APCI): calcd. for $C_{18}H_{18}NaO_4S([M+Na]^+$): 353.0818, found: 353.0817.

9. X-ray Crystal Structures

X-ray Crystal Structures for **3ga**



3ga

Identification code	**3ga**
Empirical formula	$C_{19}H_{17}NO_2S$
Formula weight	323.40
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	7.0402(6)
b/Å	7.1269(6)
c/Å	17.5281(8)
α/°	79.600(6)
β/°	84.651(5)
γ/°	84.242(7)
Volume/Å^3	858.12(11)
Z	2
ρ_{calc}g/cm^3	1.252
μ/mm^{-1}	1.741
F(000)	340.0
Crystal size/mm^3	0.35 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.292 to 145.298
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 8, -22 ≤ l ≤ 18
Reflections collected	8458
Independent reflections	3609 [R_{int} = 0.0495, R_{sigma} = 0.0495]
Data/restraints/parameters	3609/0/228
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R1 = 0.0676, wR2 = 0.1766
Final R indexes [all data]	R1 = 0.0803, wR2 = 0.1958
Largest diff. peak/hole / e Å^{-3}	0.41/-0.51

10. References

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Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford CT, **2010**.

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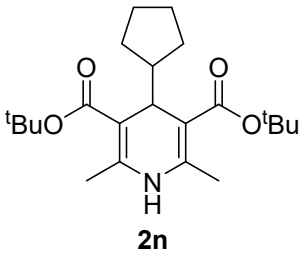
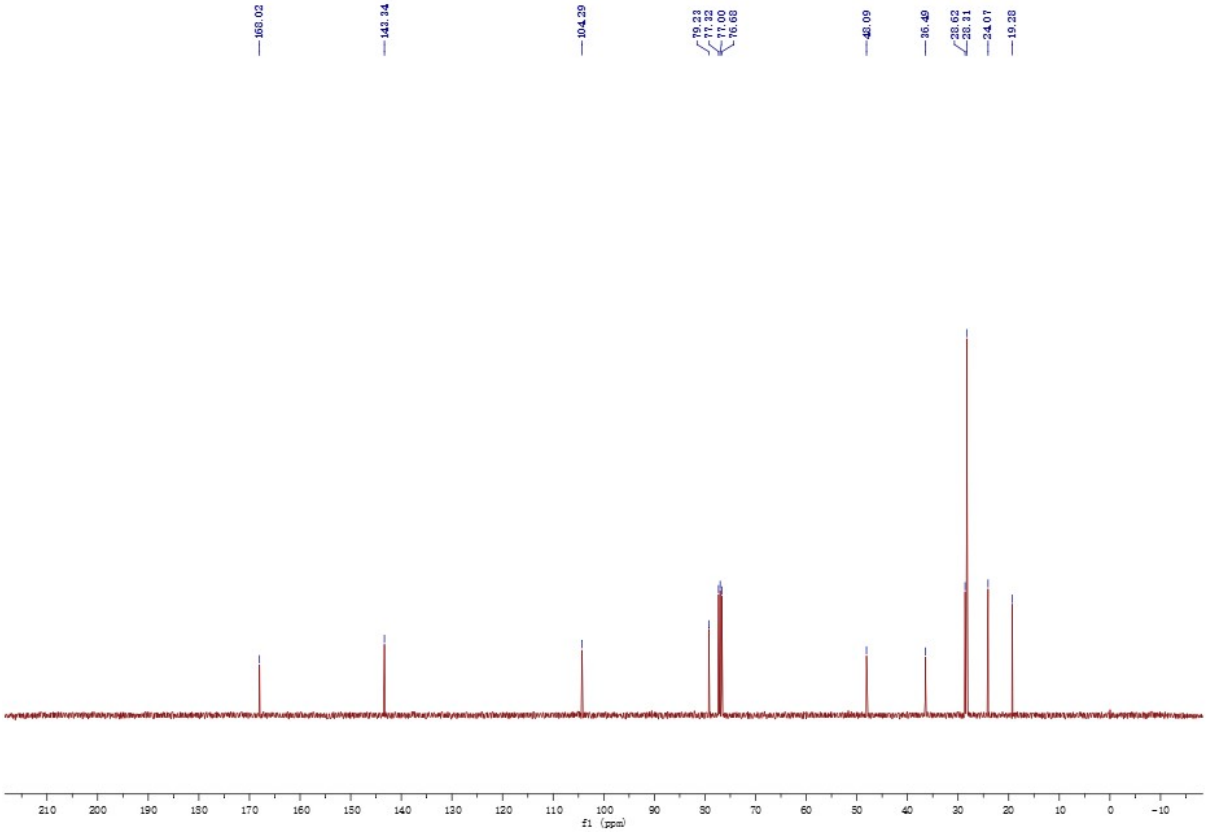
11. NMR spectra

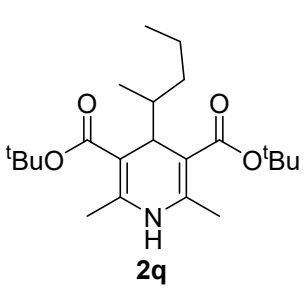


2n

^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$)

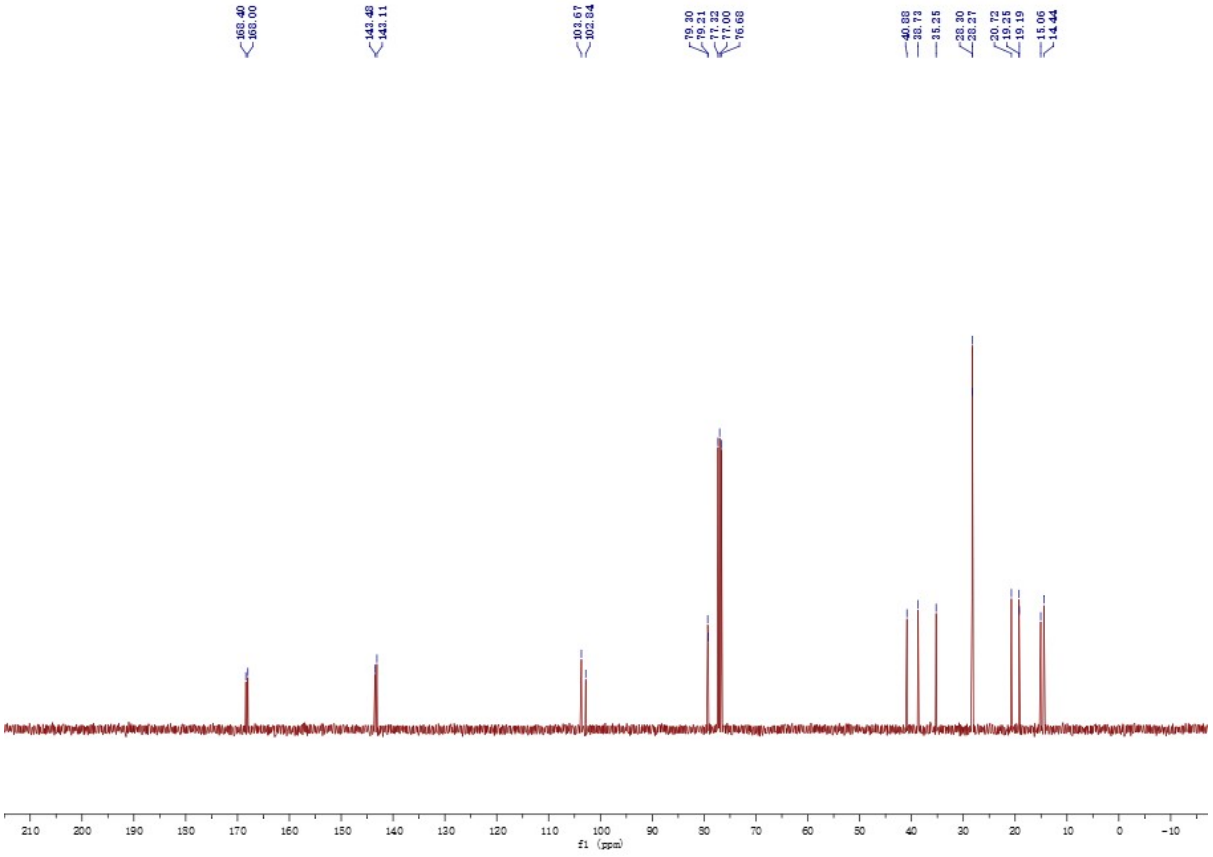


^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$)



2q

^{1}H NMR spectrum of **2q** (400 MHz, $CDCl_3$)



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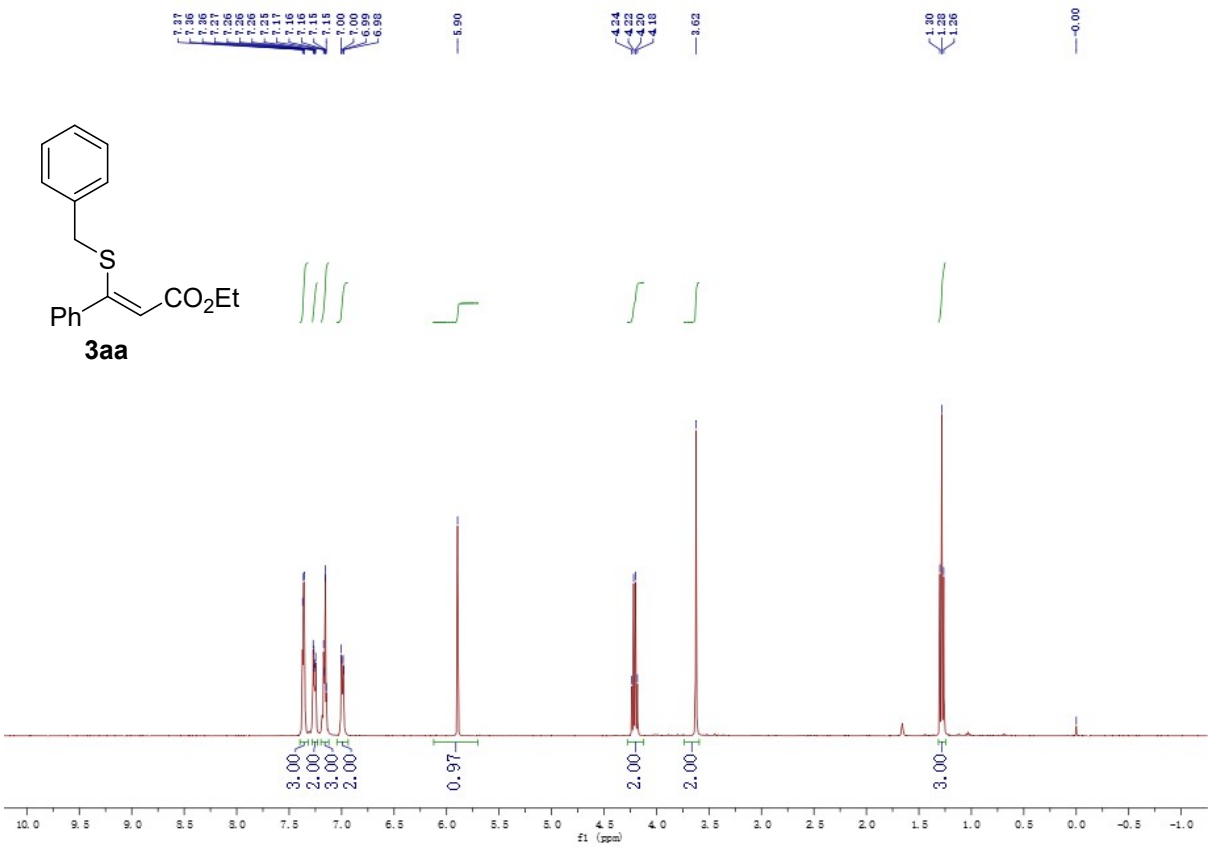
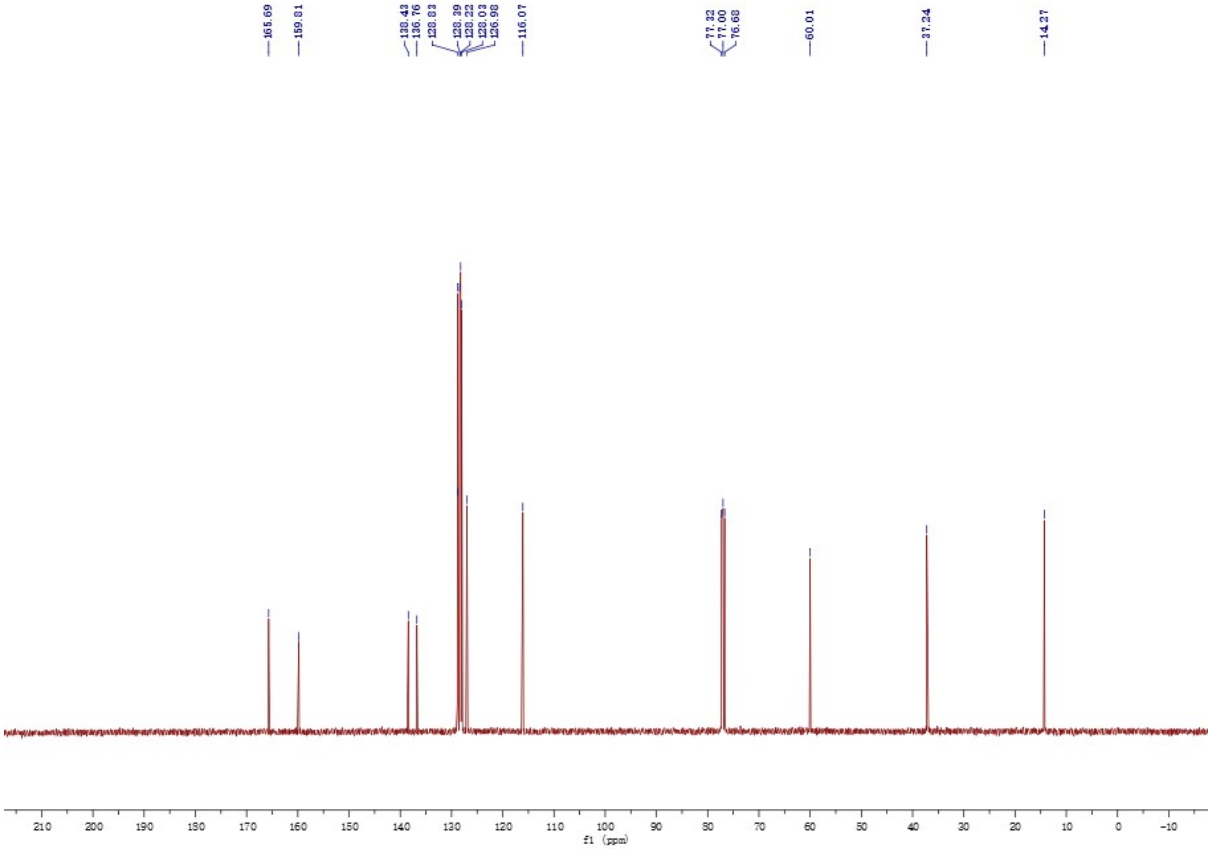
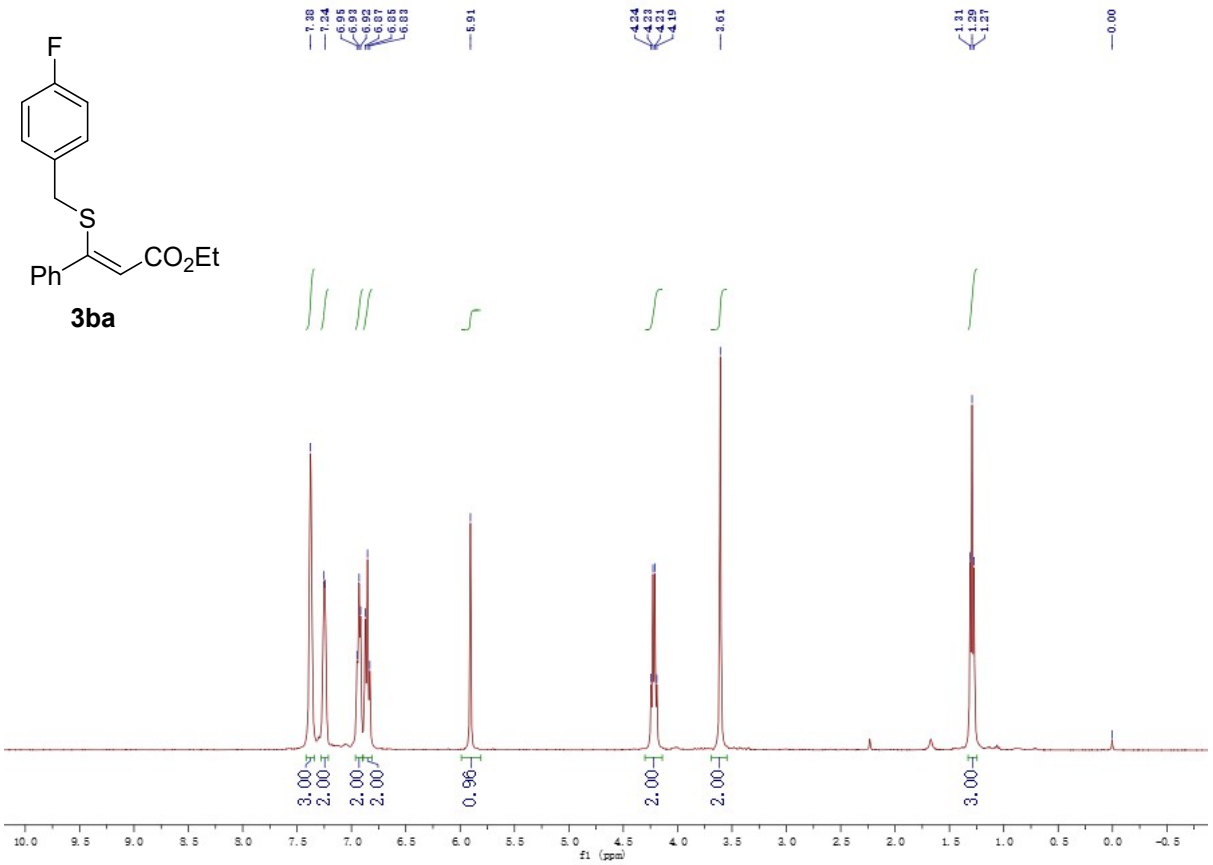


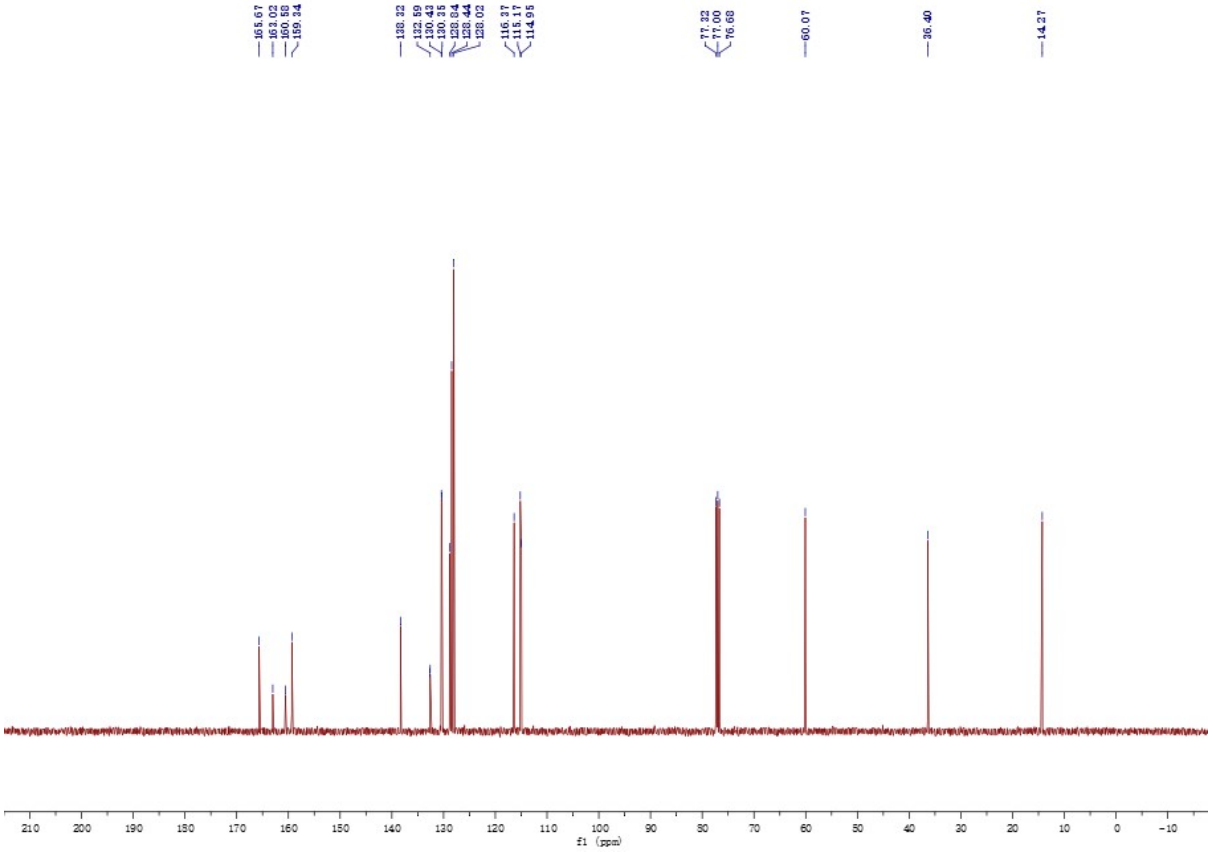
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



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



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



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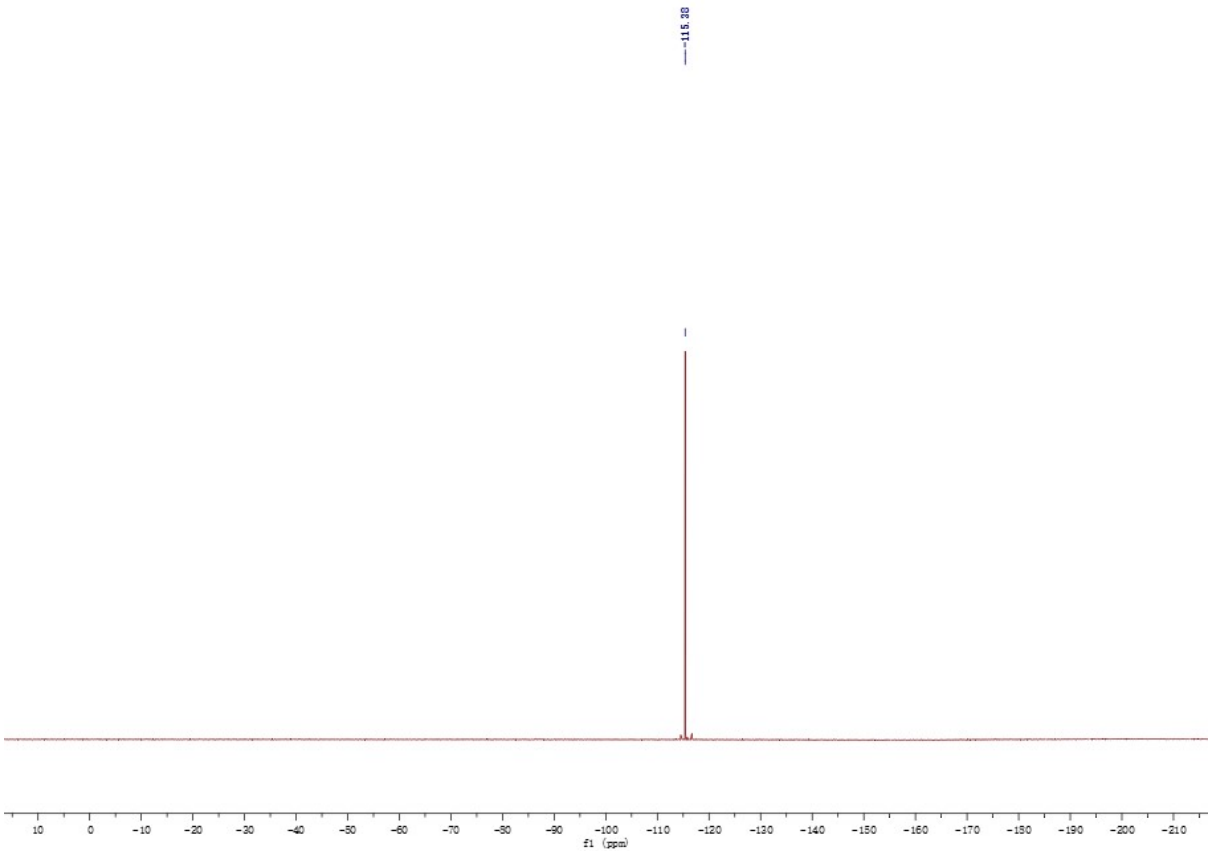
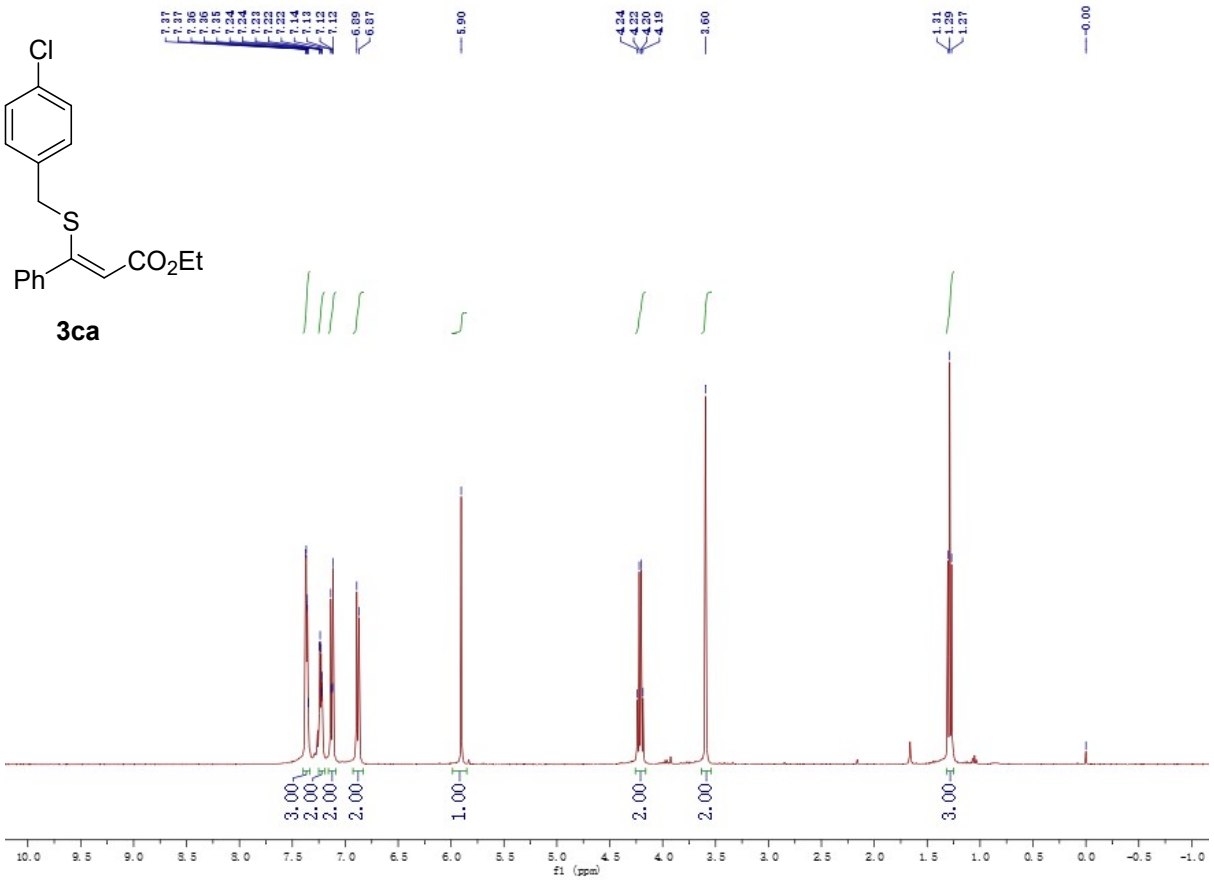
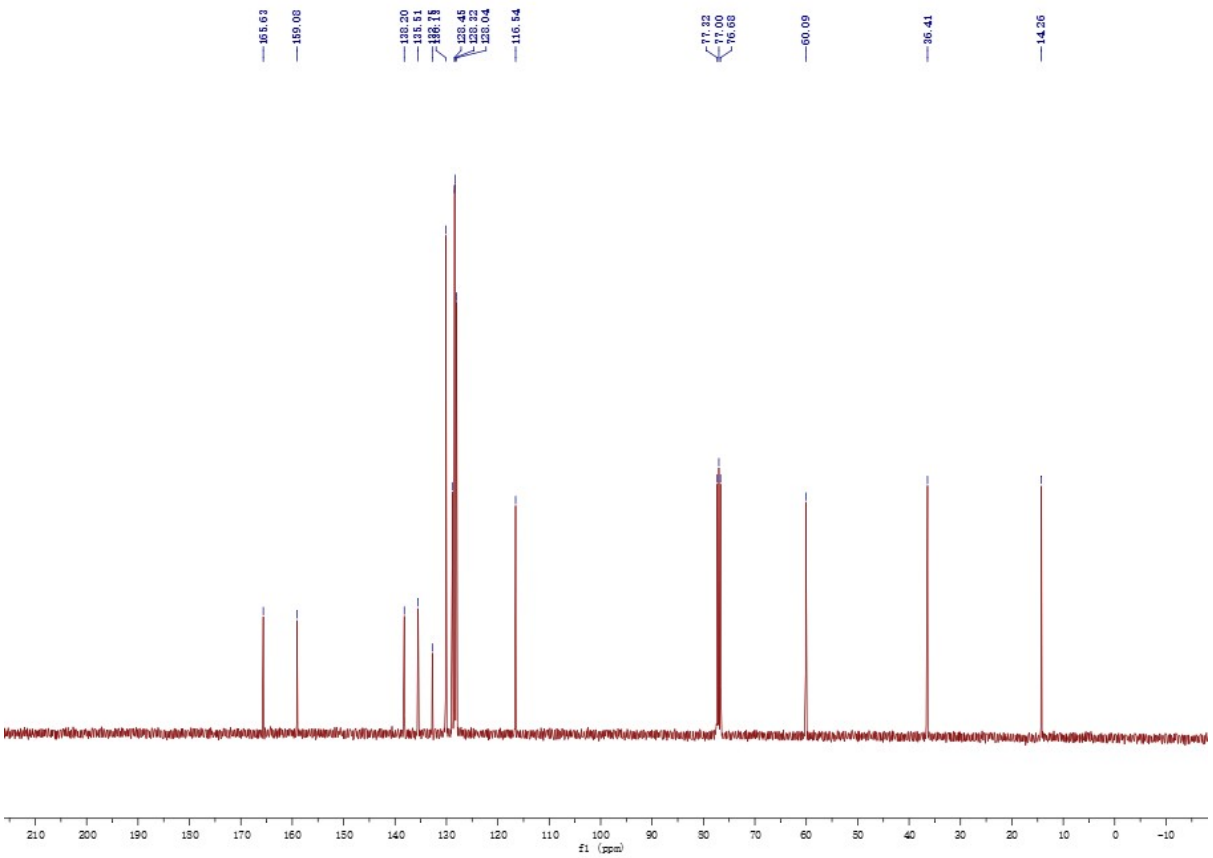


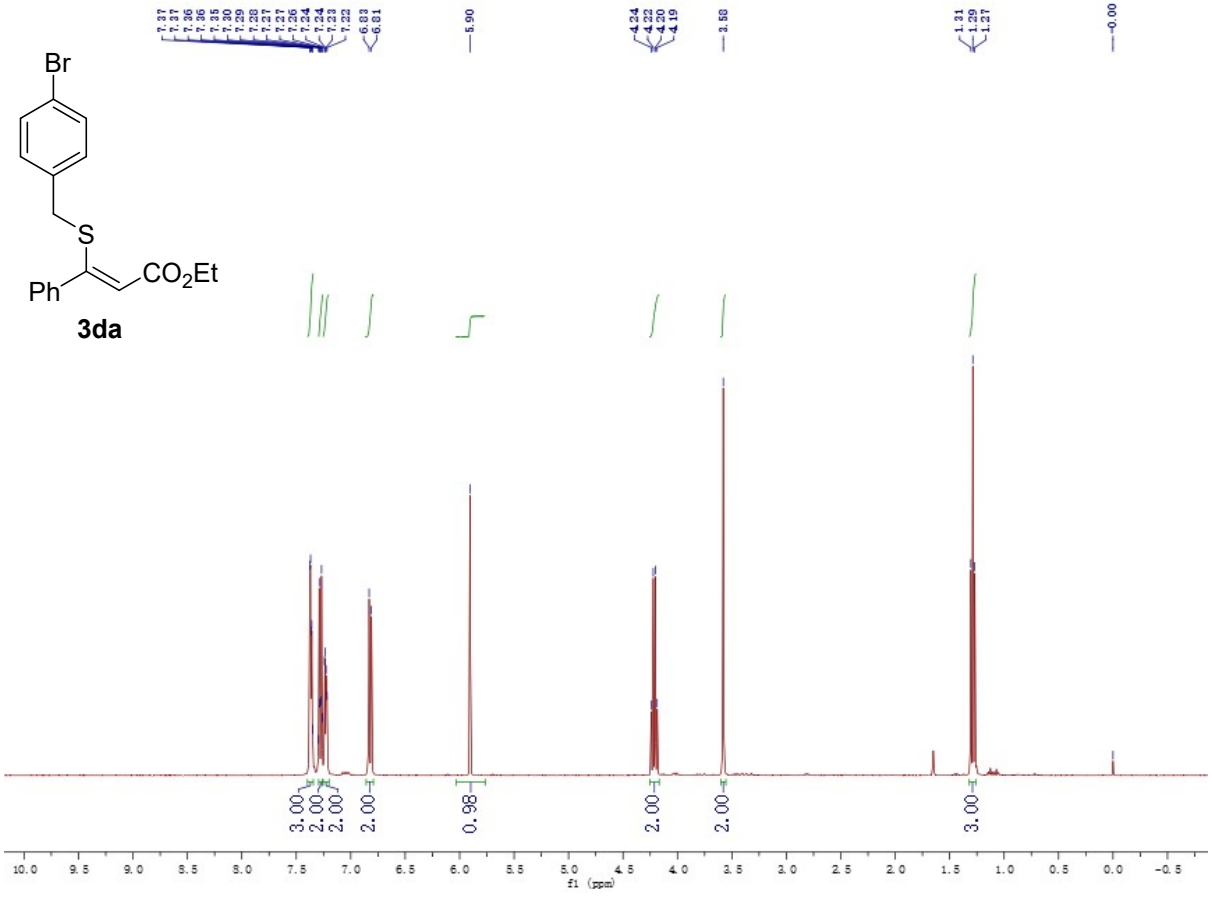
^{19}F NMR spectrum of **3ba** (376 MHz, $CDCl_3$)



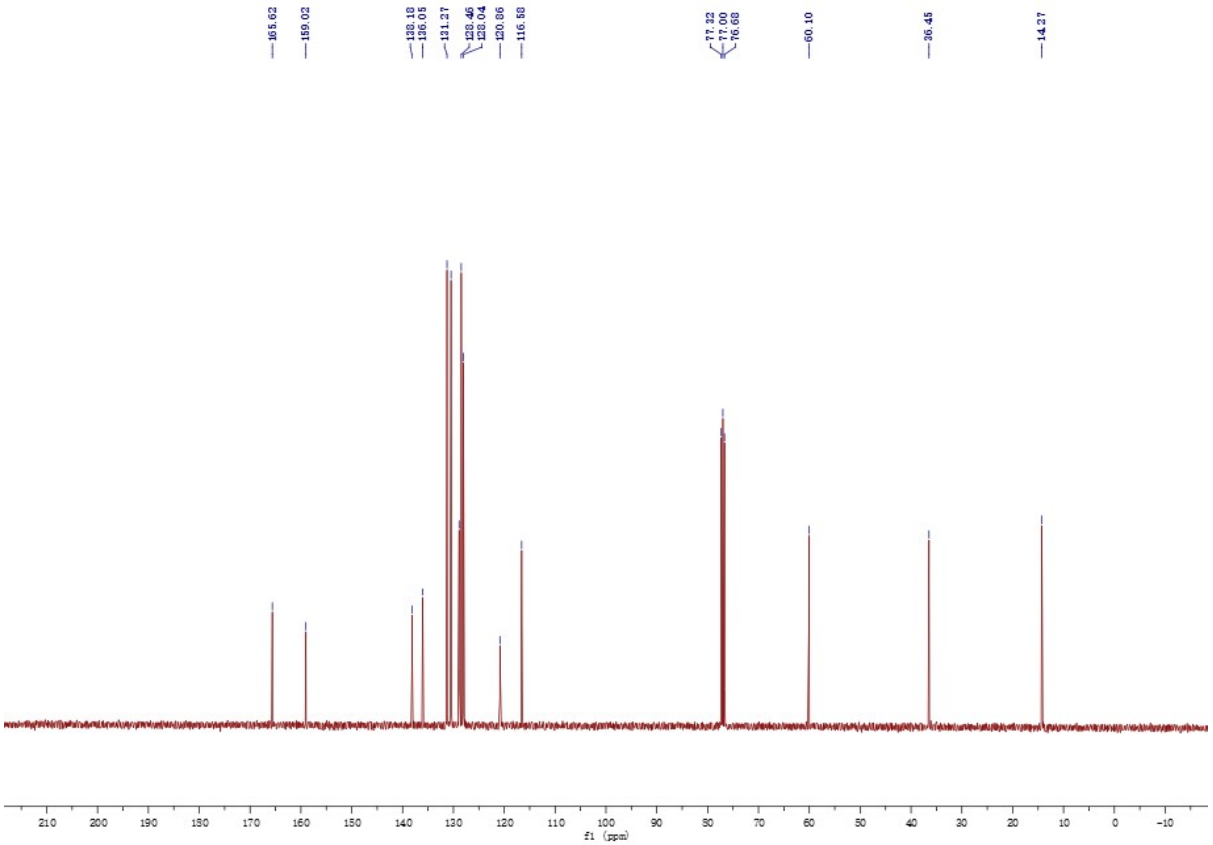
^{1}H NMR spectrum of **3ca** (400 MHz, $CDCl_3$)



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



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



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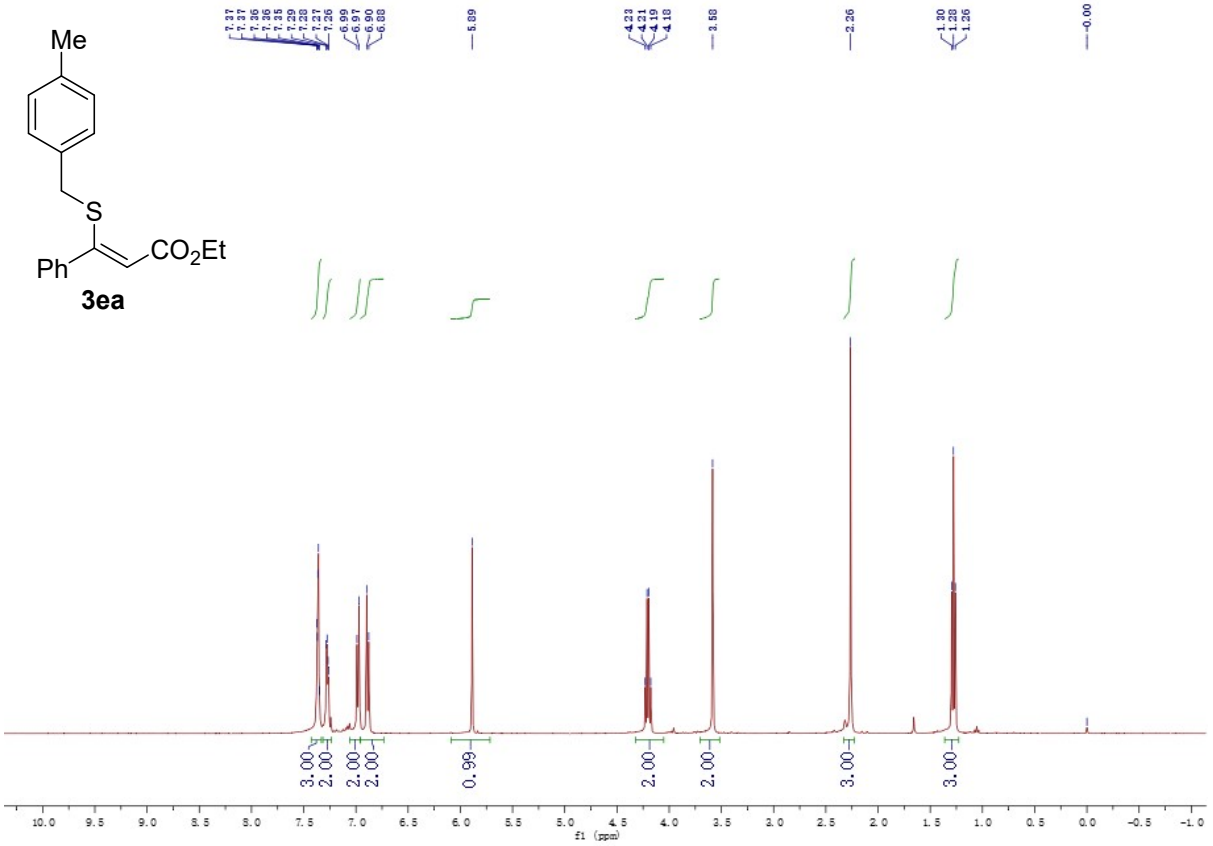

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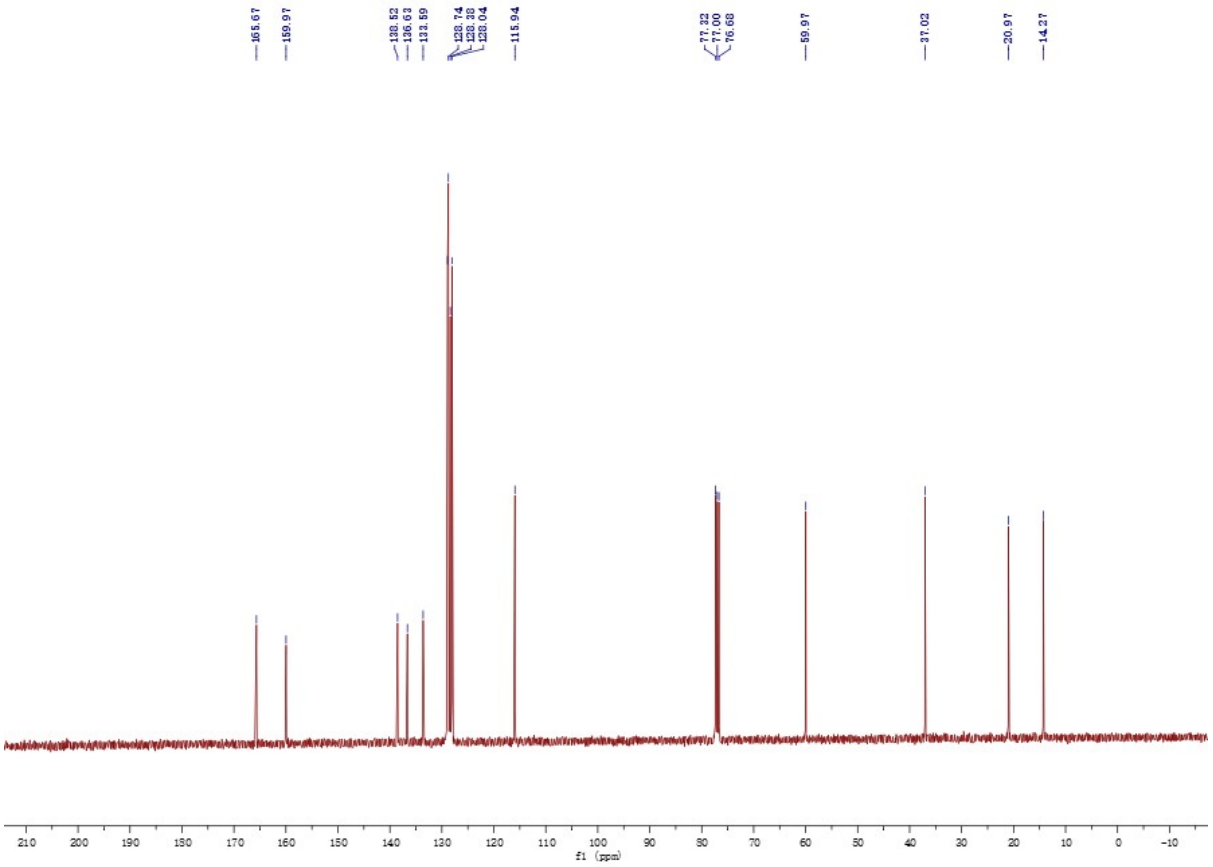
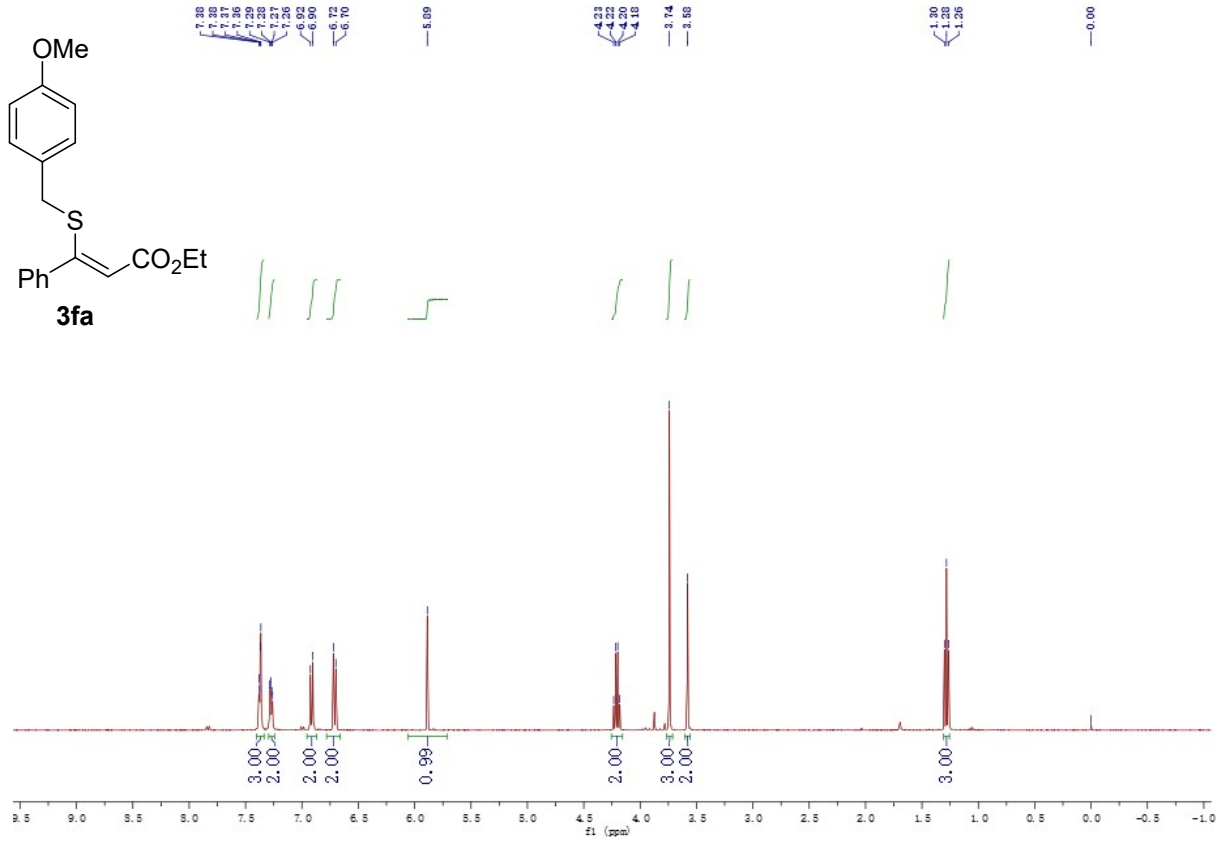
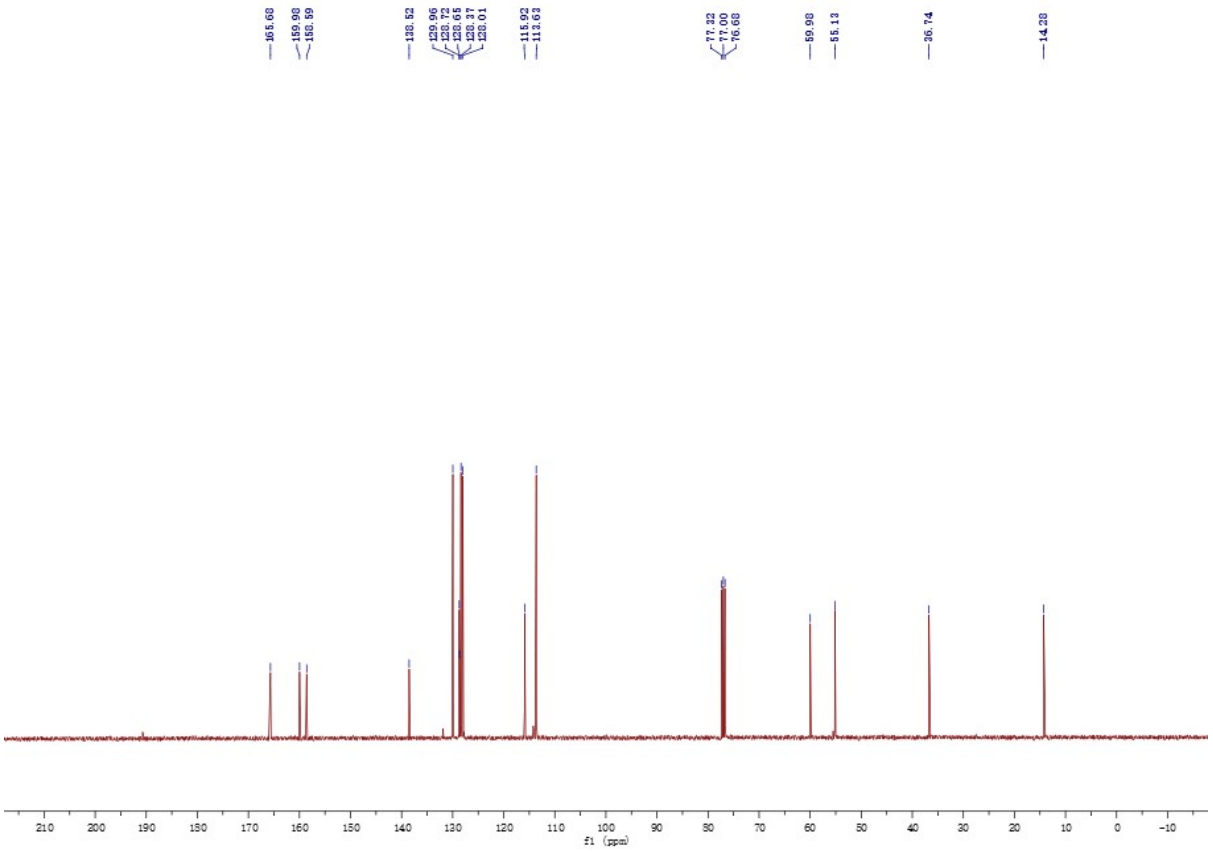


^{13}C NMR spectrum of **3ea** (100 MHz, $CDCl_3$)



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



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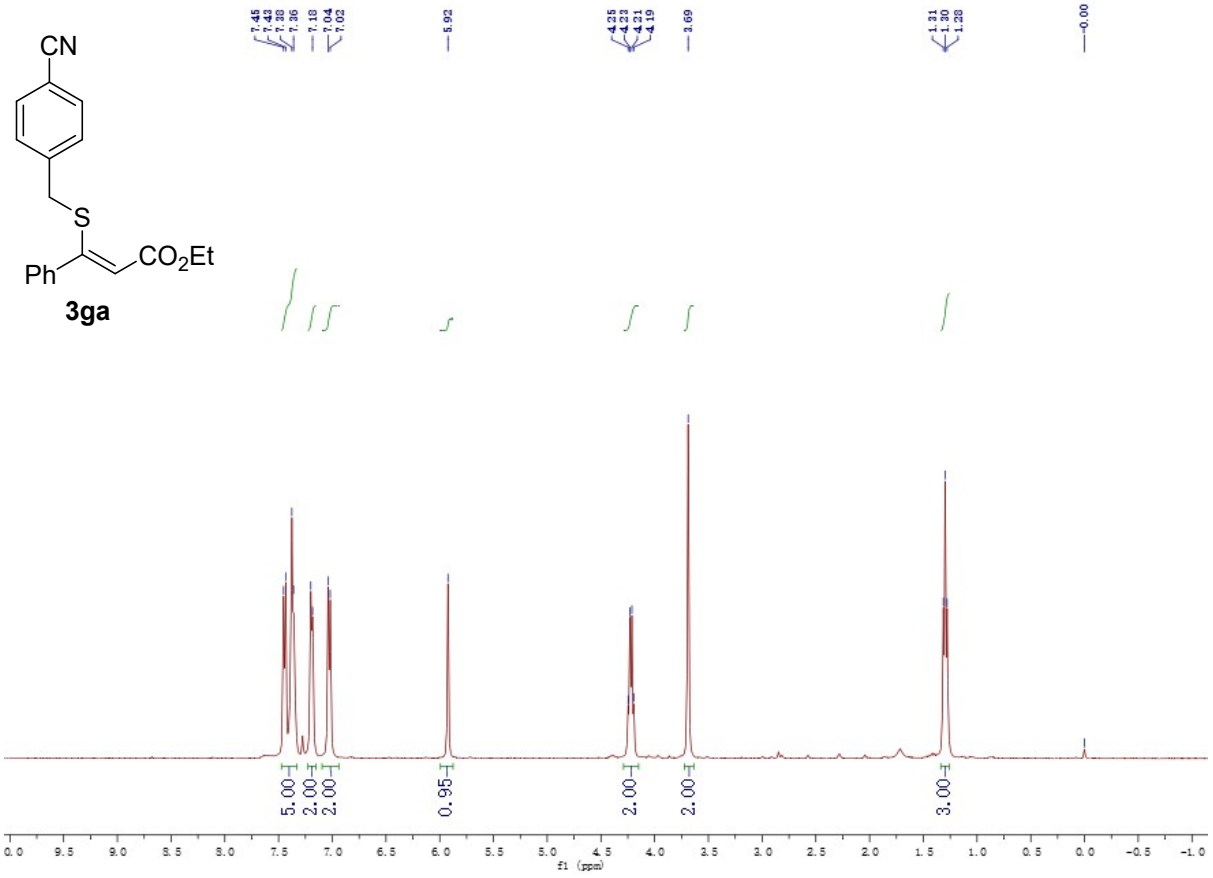
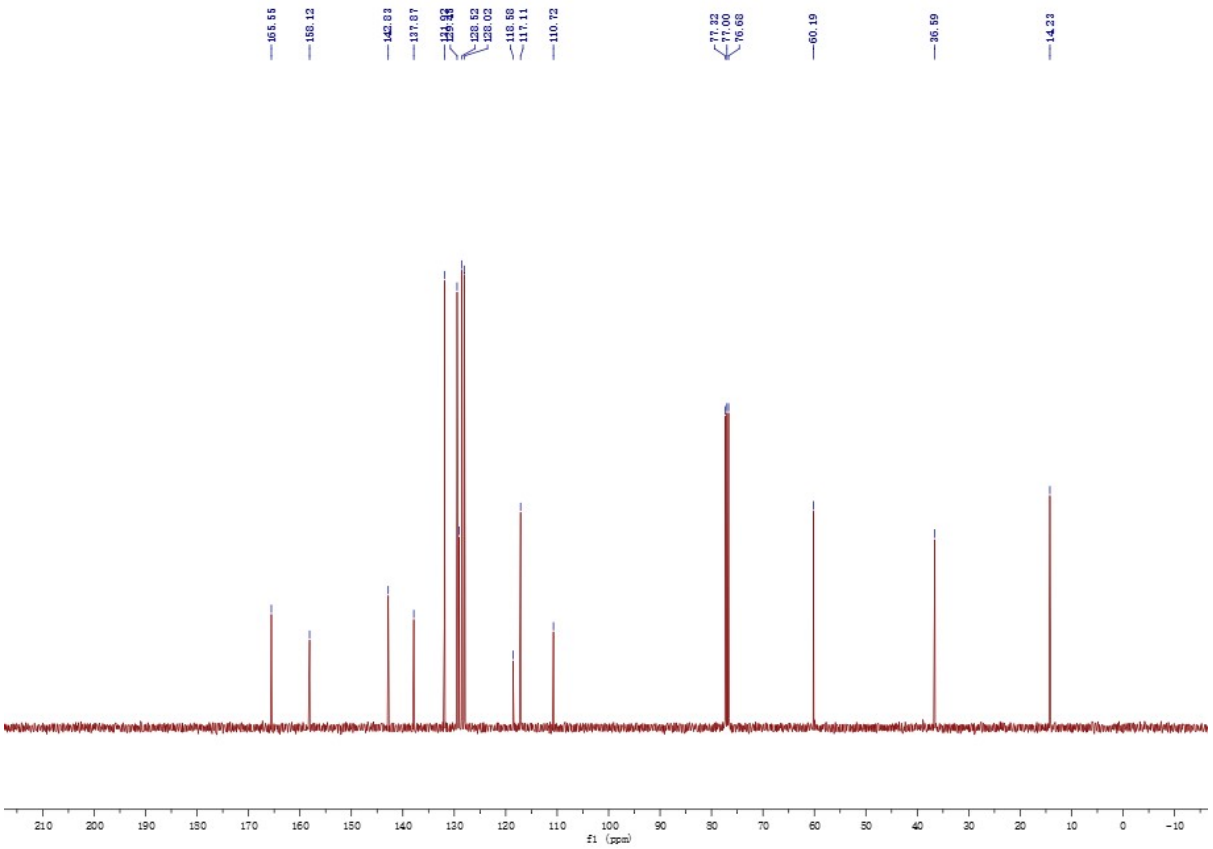


3ga

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



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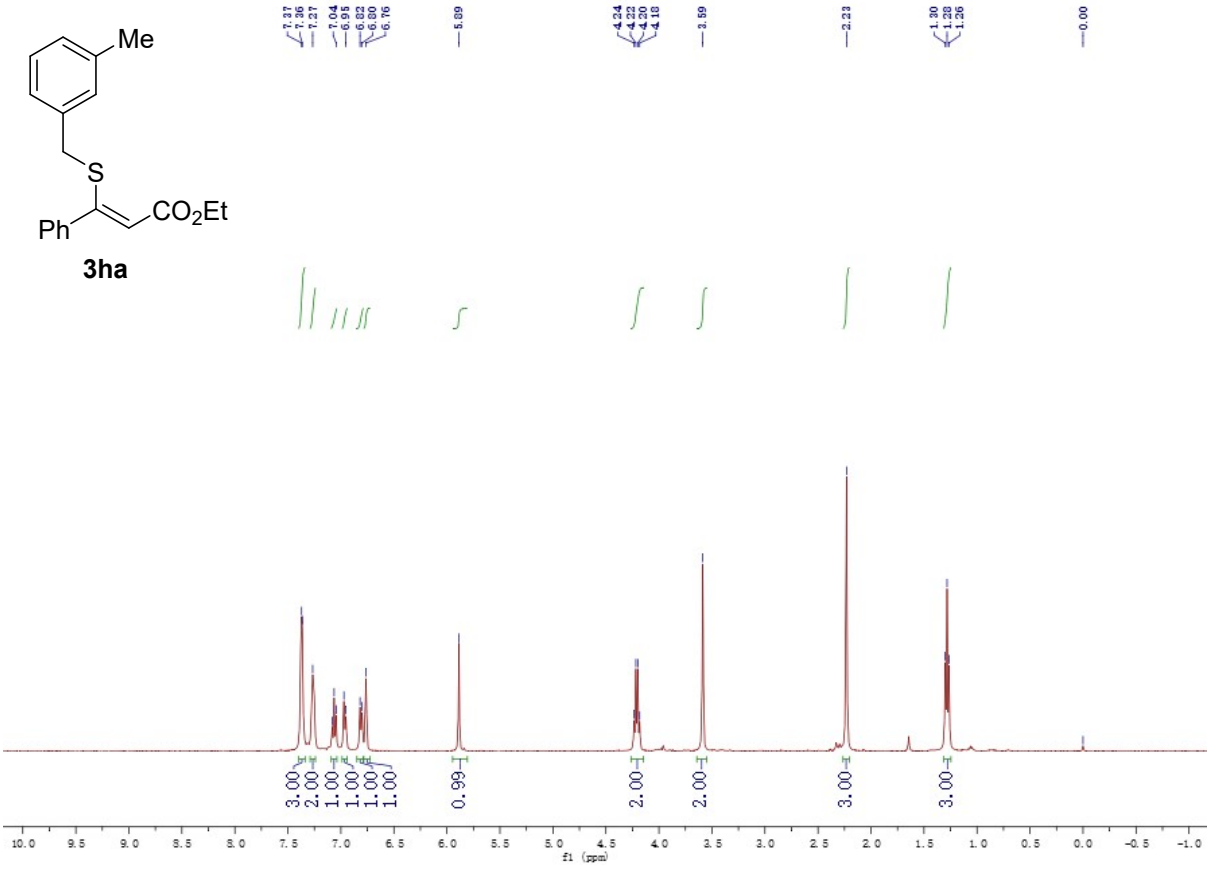
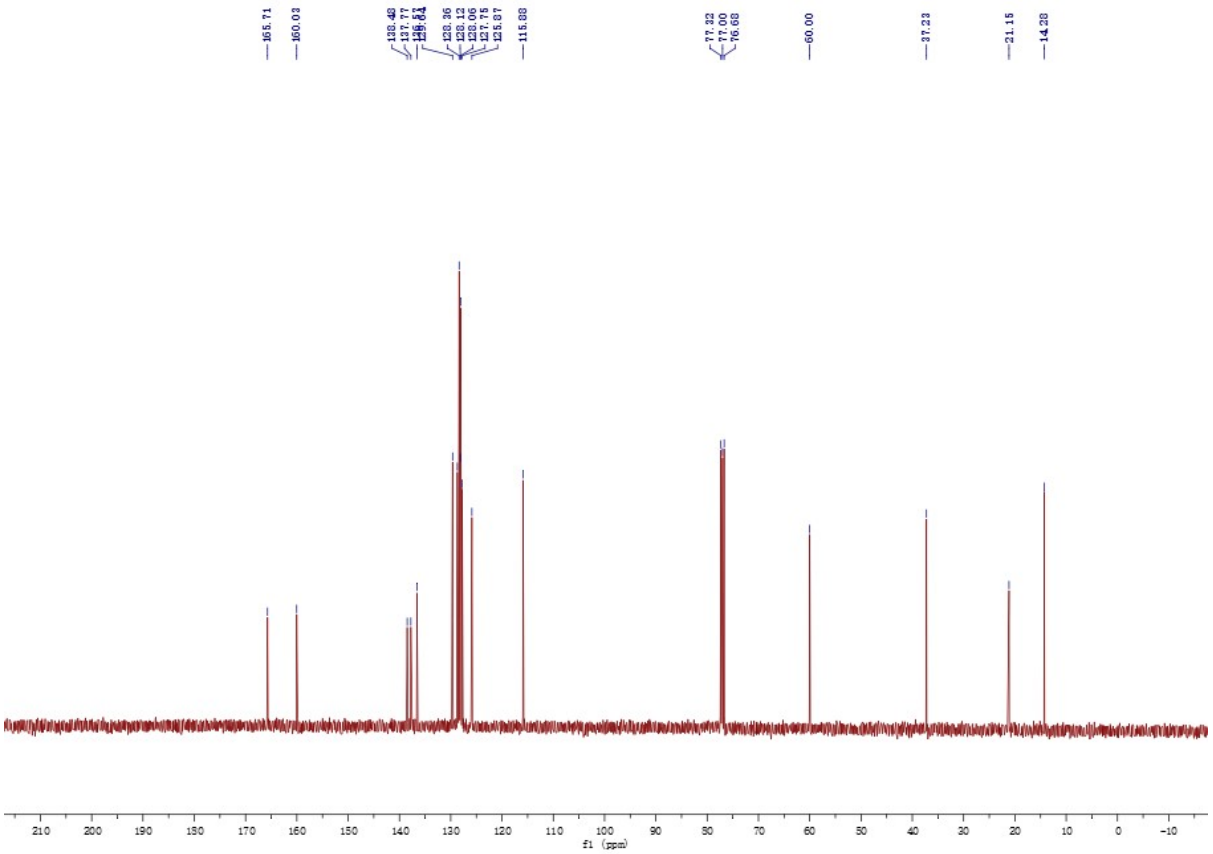
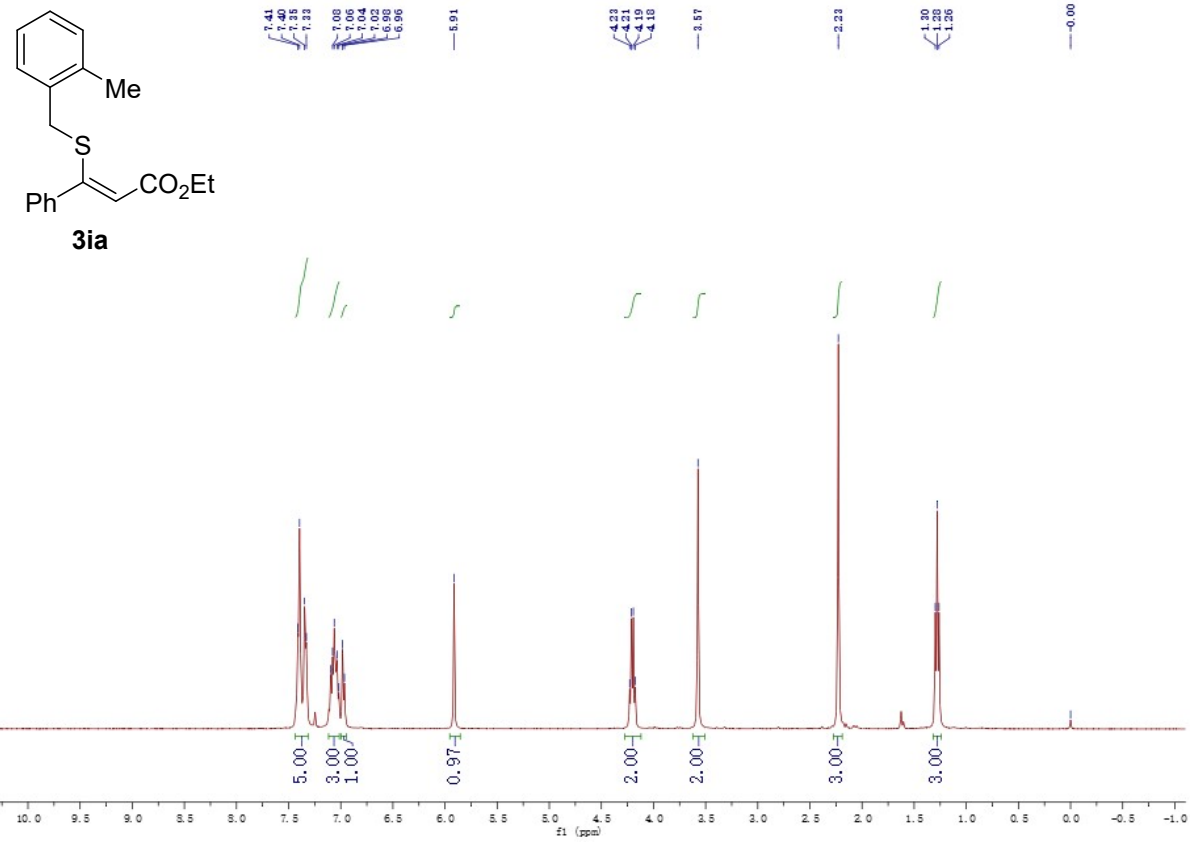


3ha

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



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



3ia

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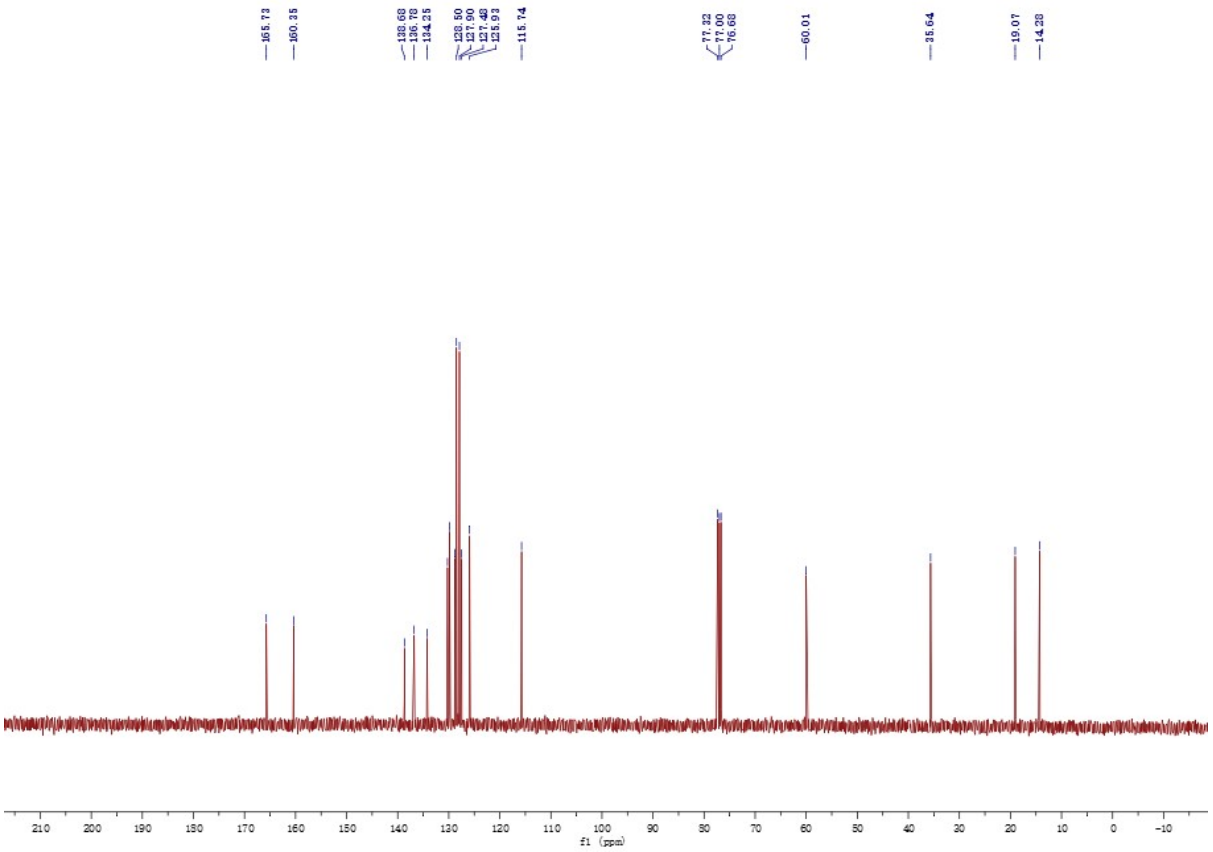

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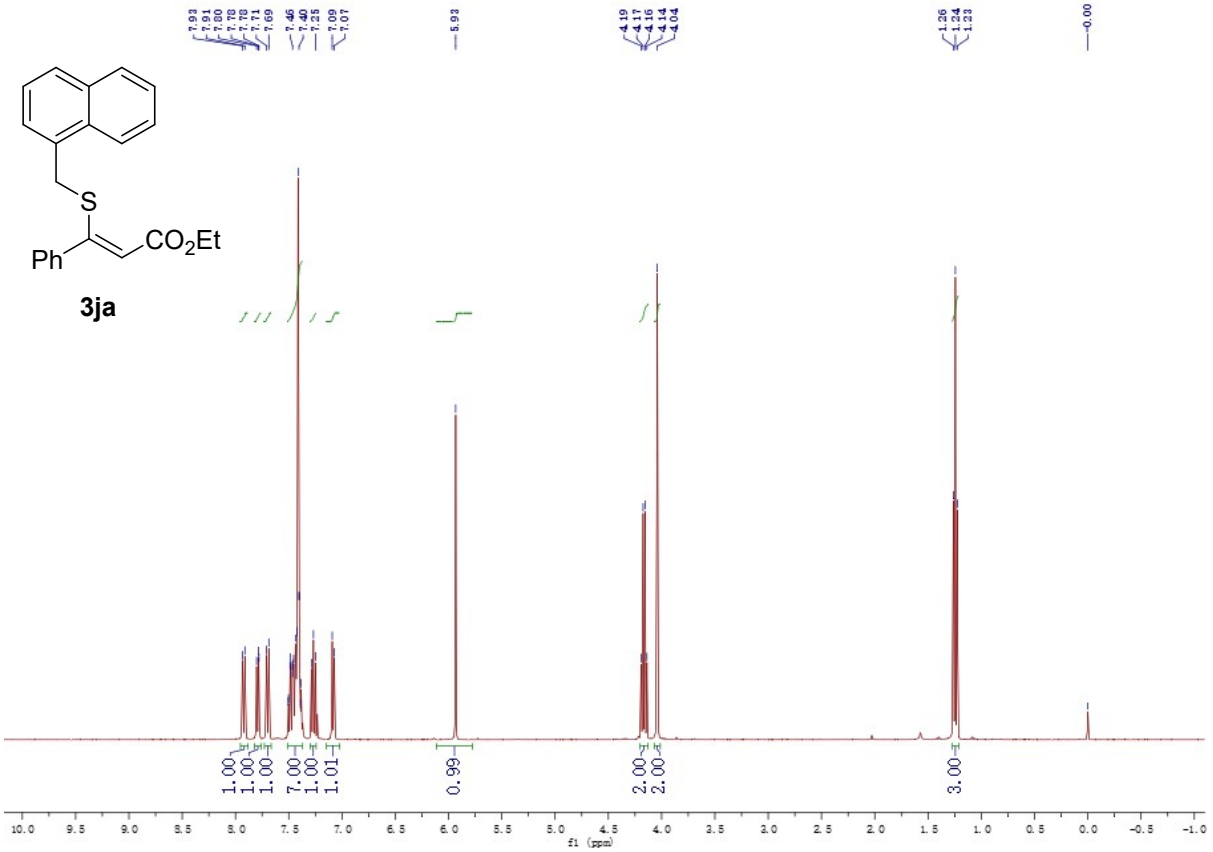

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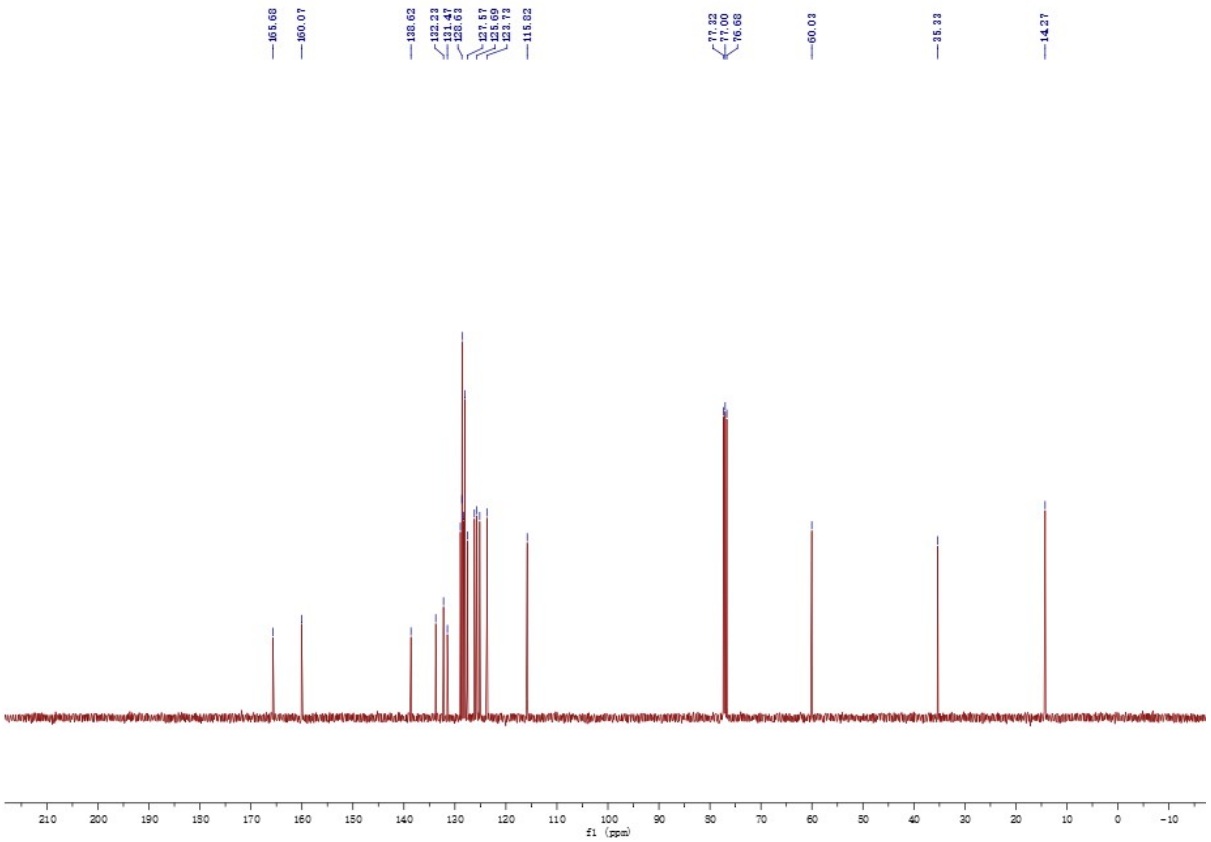

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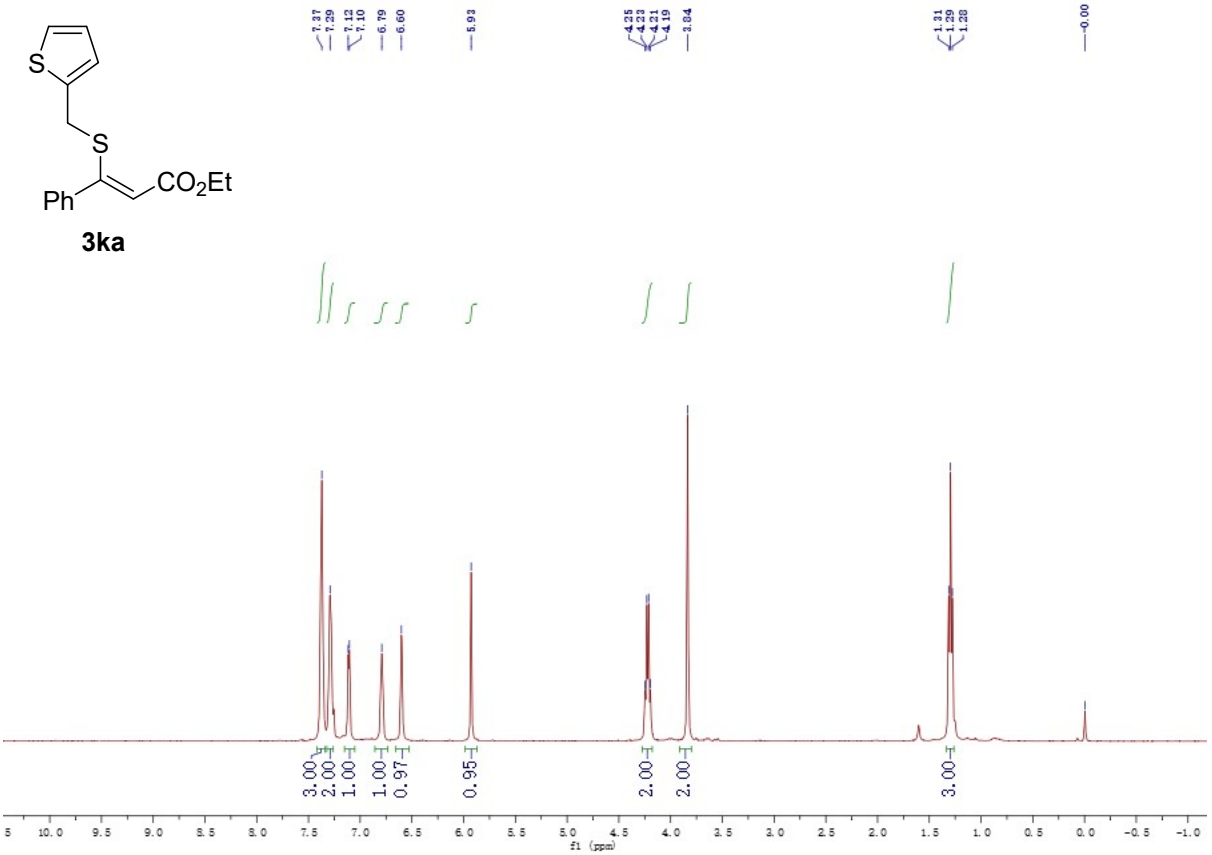
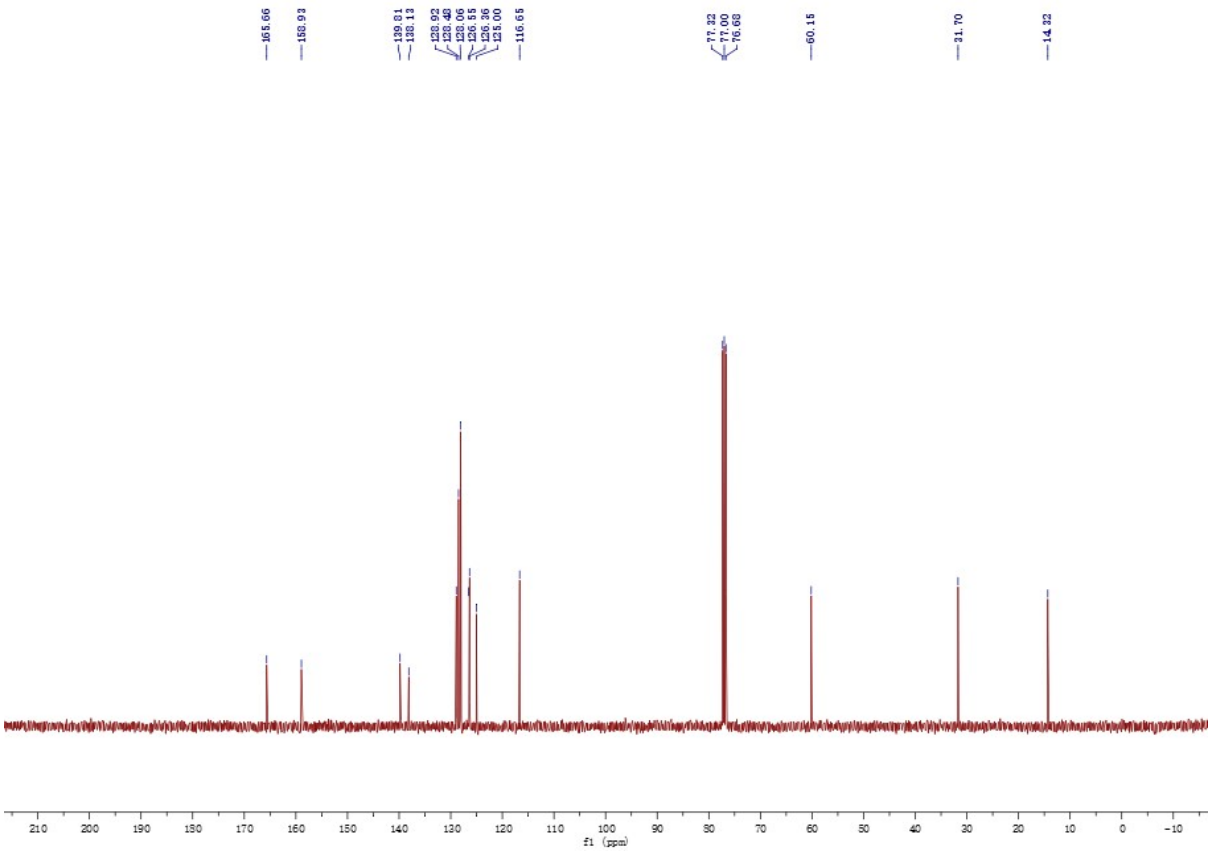


3ka

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



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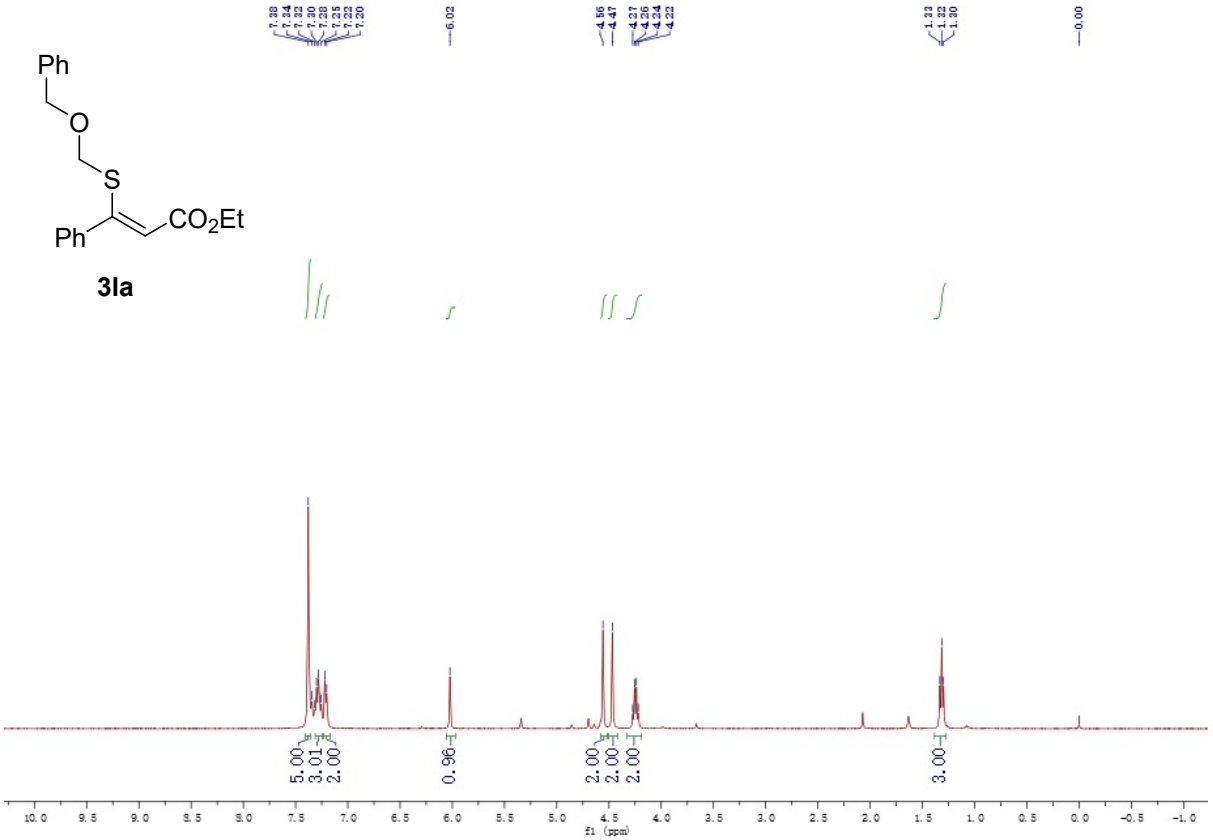
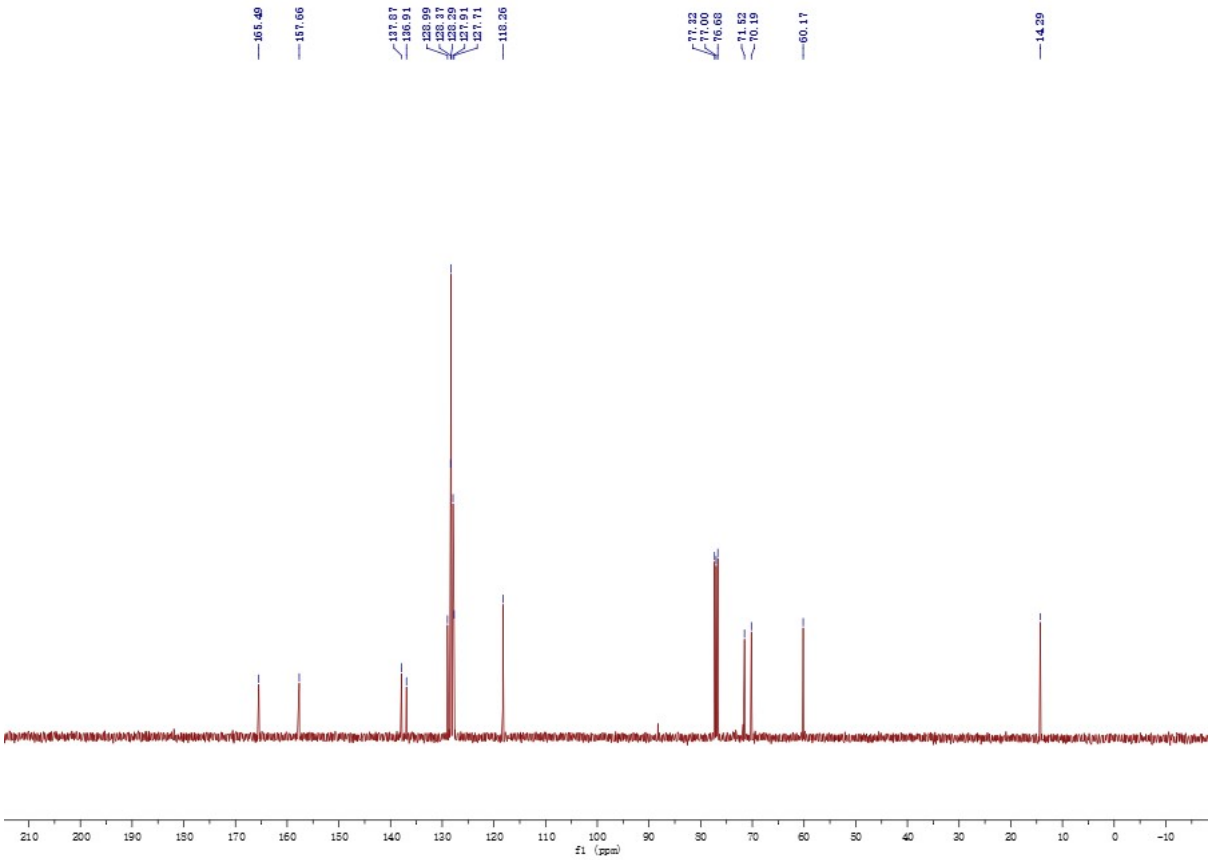


3la

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



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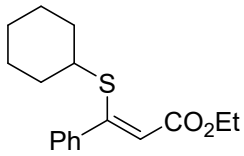
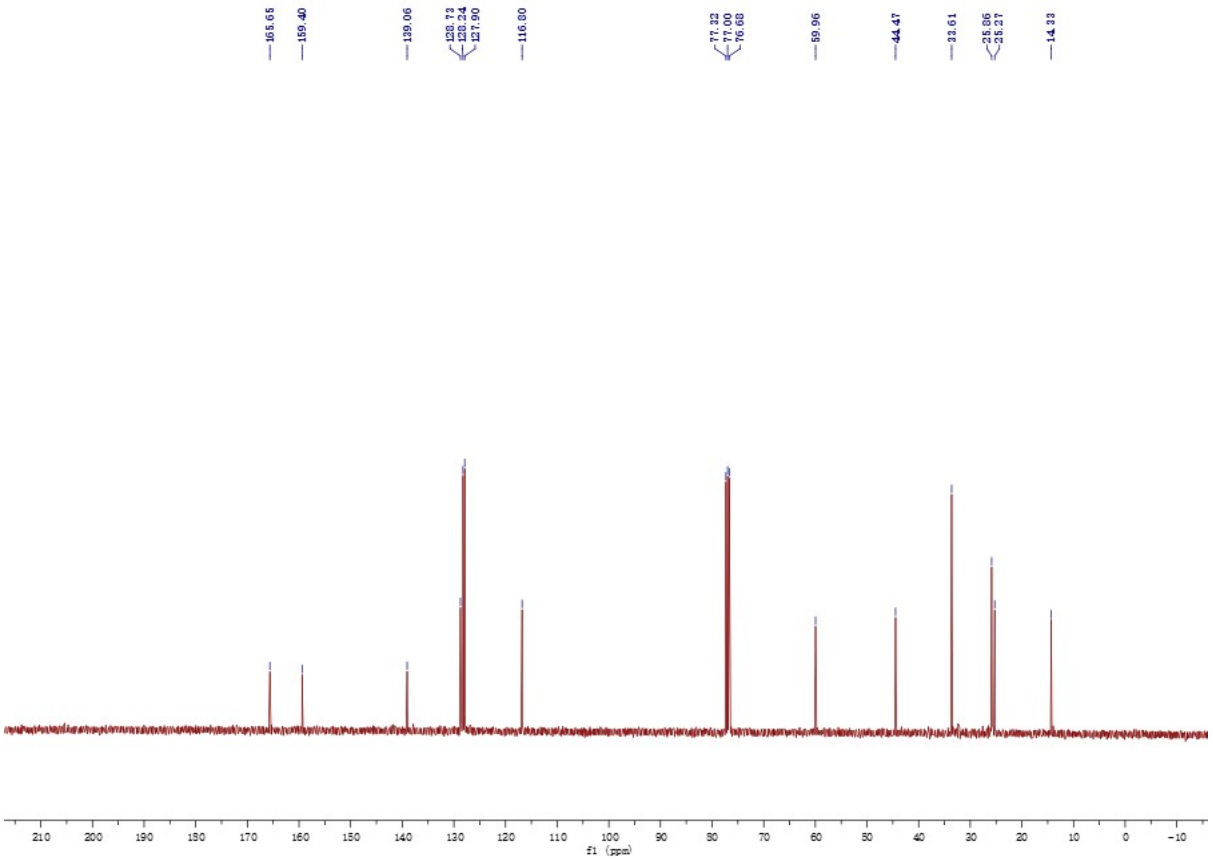


3ma

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



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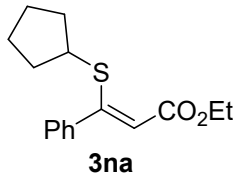
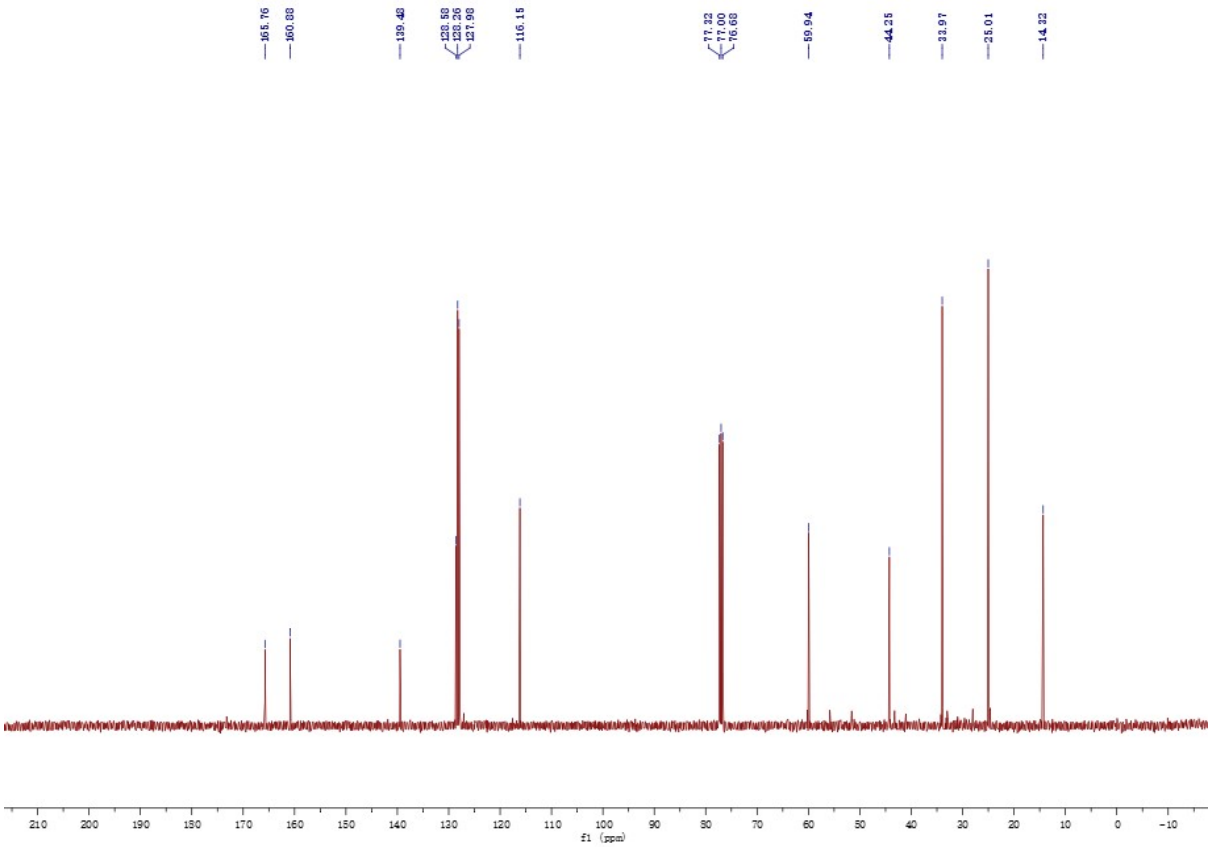
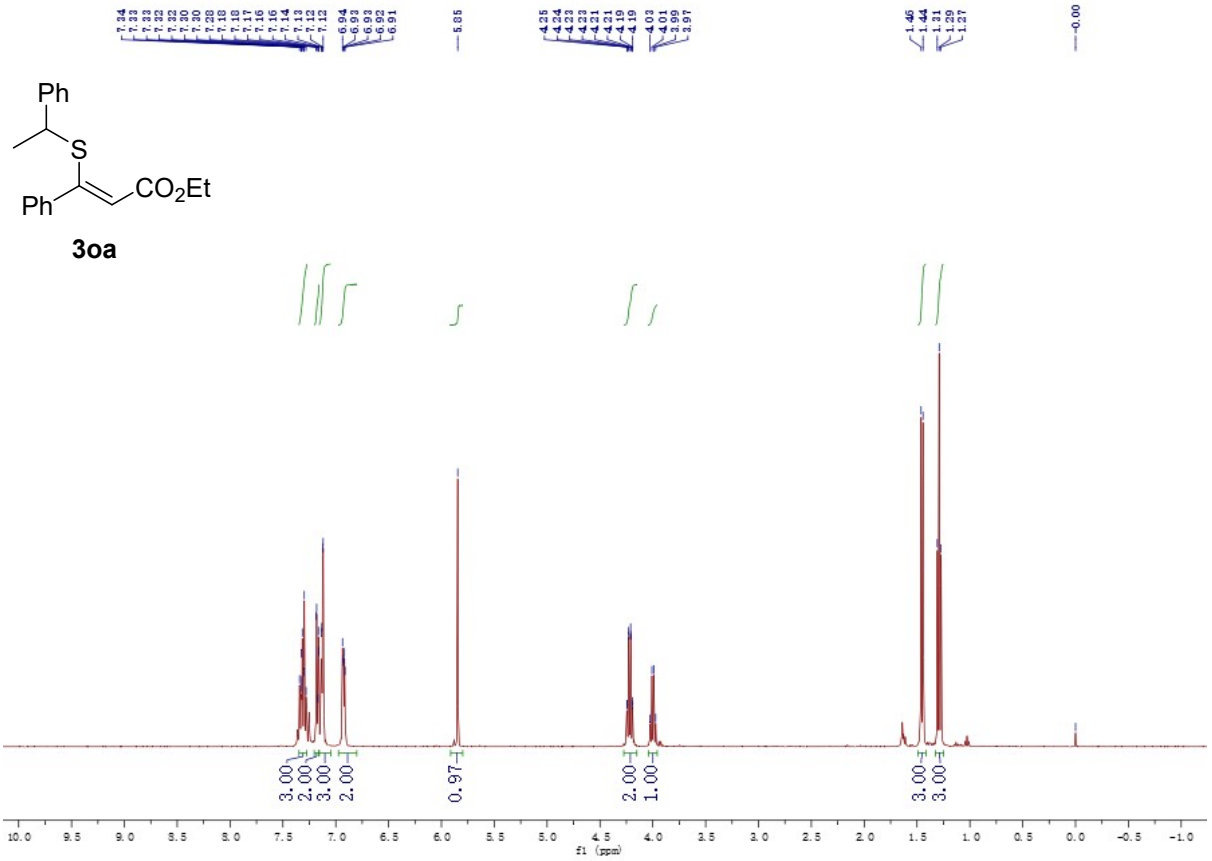


3na

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

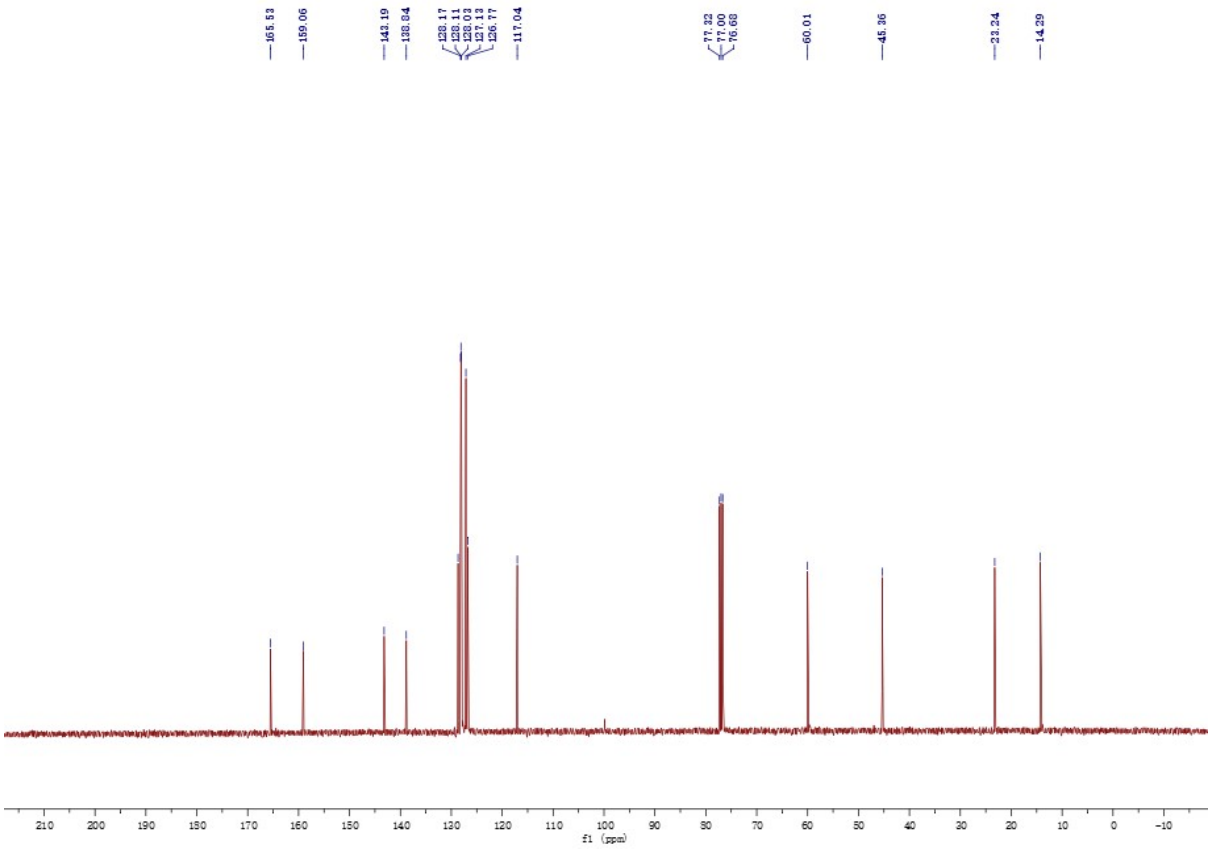


^{13}C NMR spectrum of **3na** (100 MHz, $CDCl_3$)

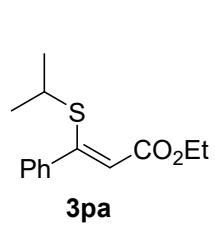


3oa

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

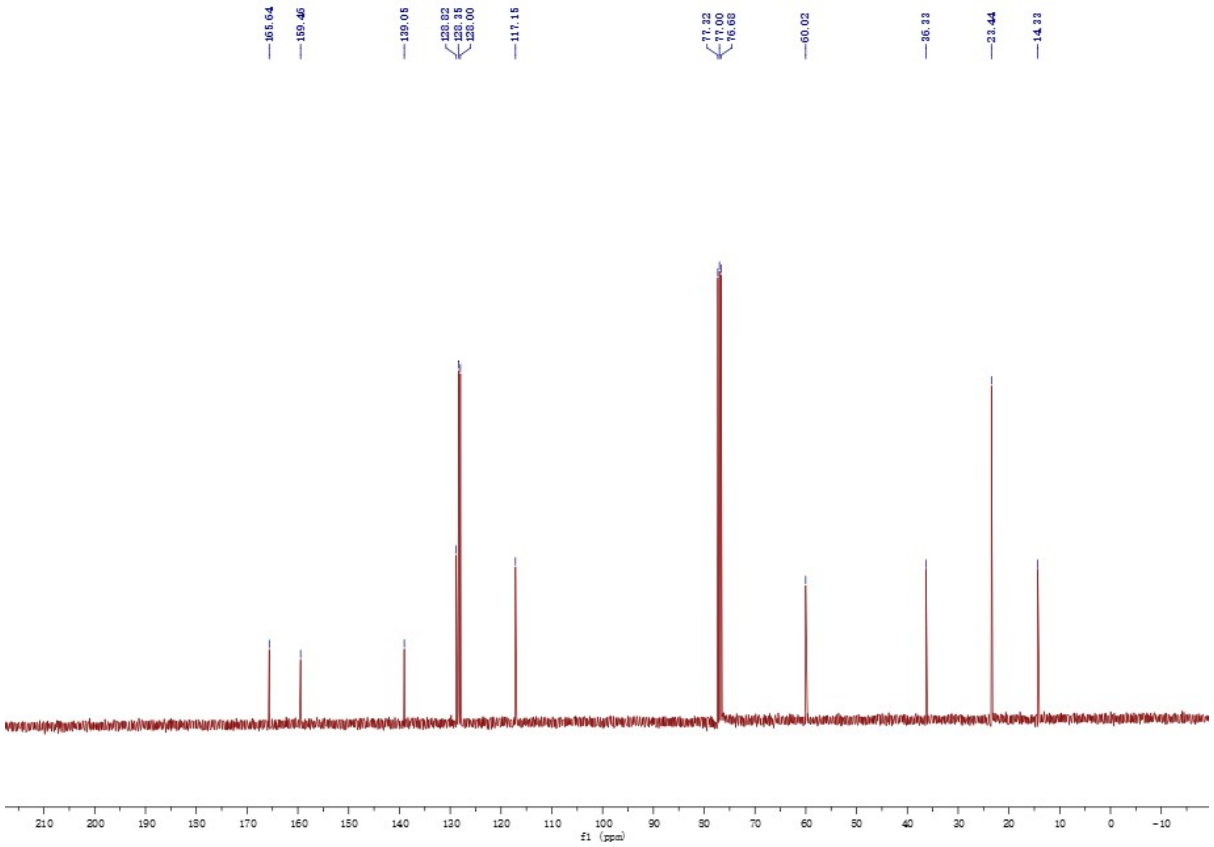


^{13}C NMR spectrum of **3oa** (100 MHz, $CDCl_3$)

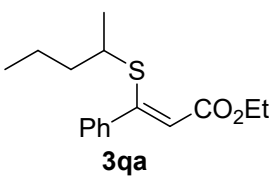


3pa

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

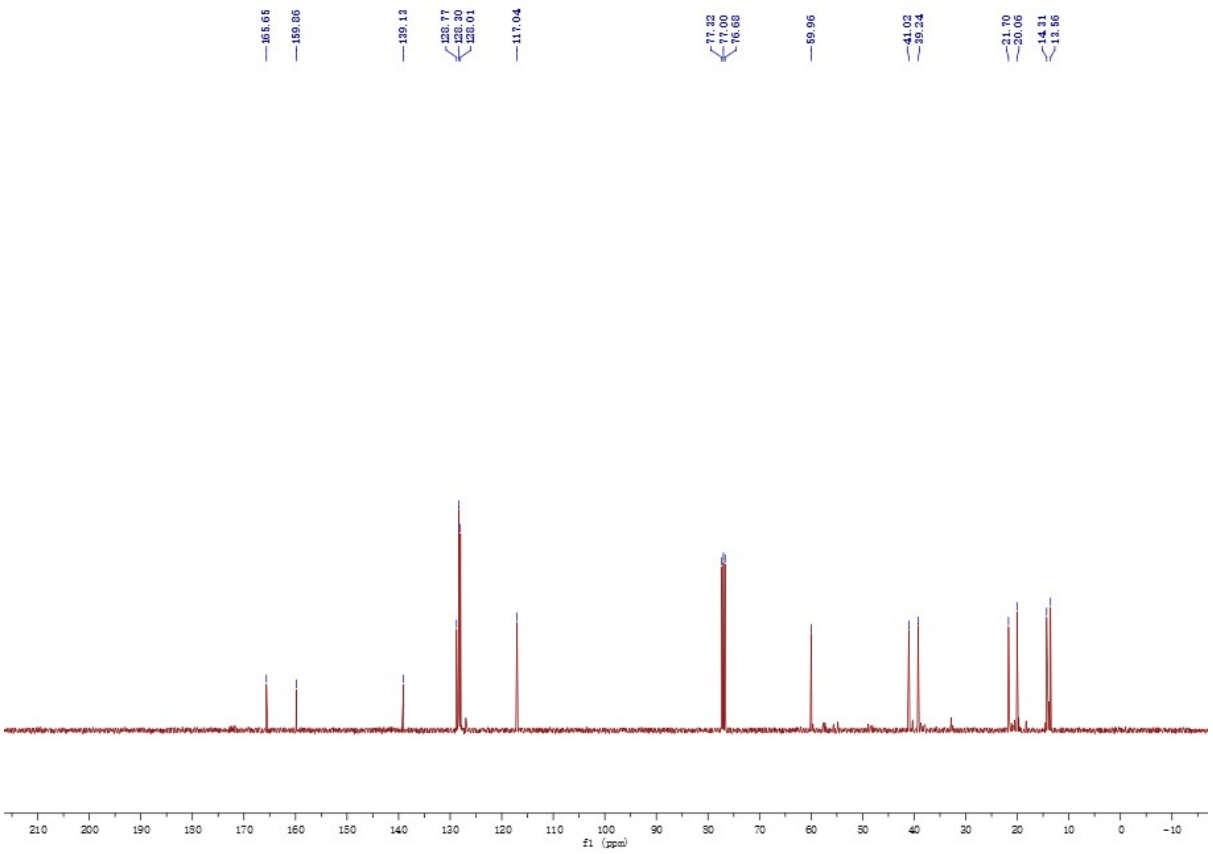


^{13}C NMR spectrum of **3pa** (100 MHz, $CDCl_3$)

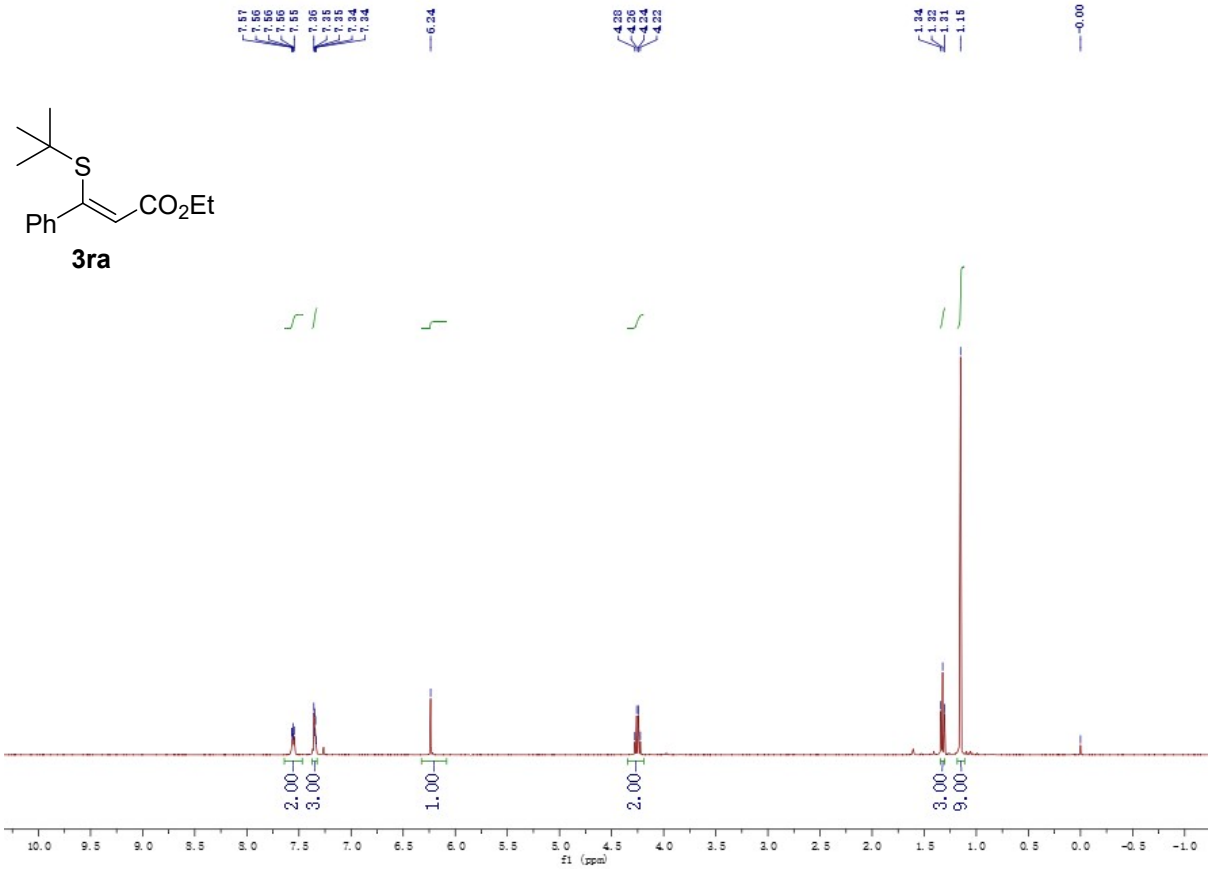


3qa

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

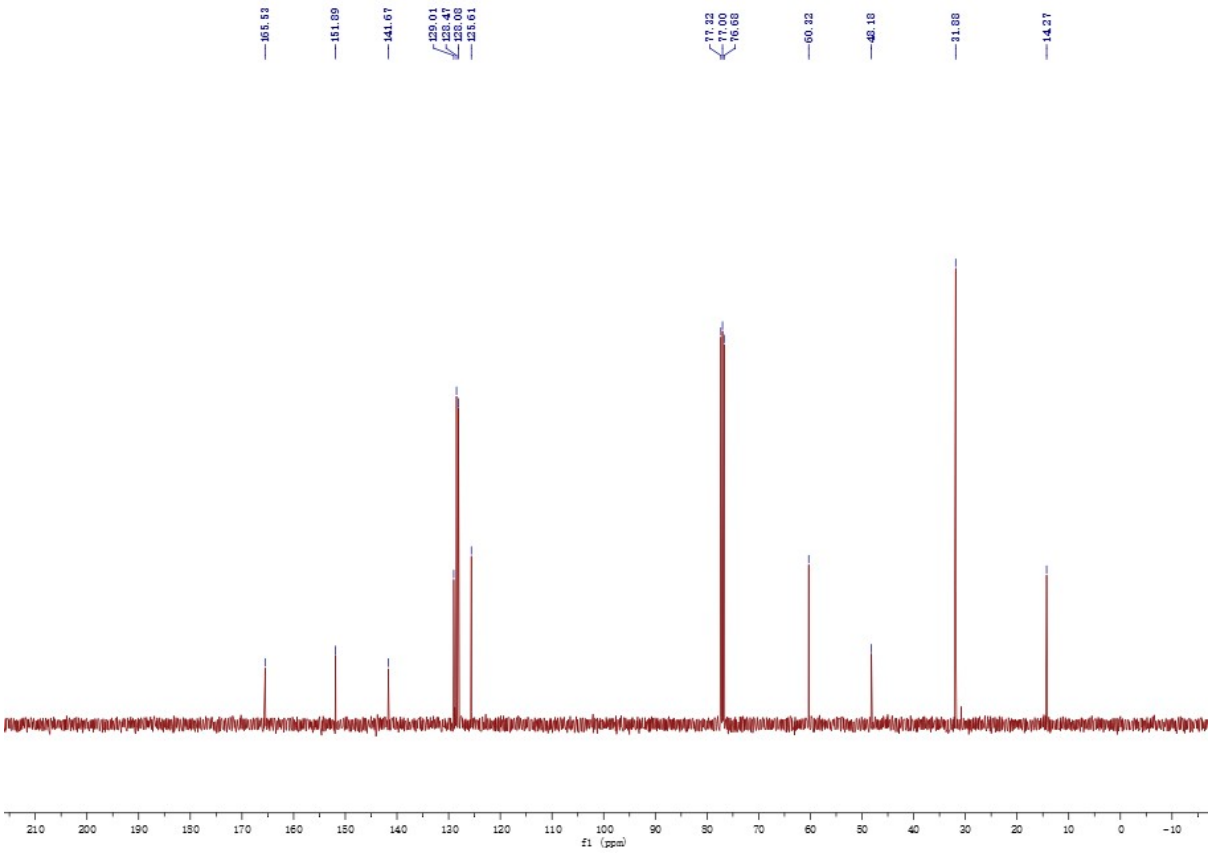


^{13}C NMR spectrum of **3qa** (100 MHz, $CDCl_3$)

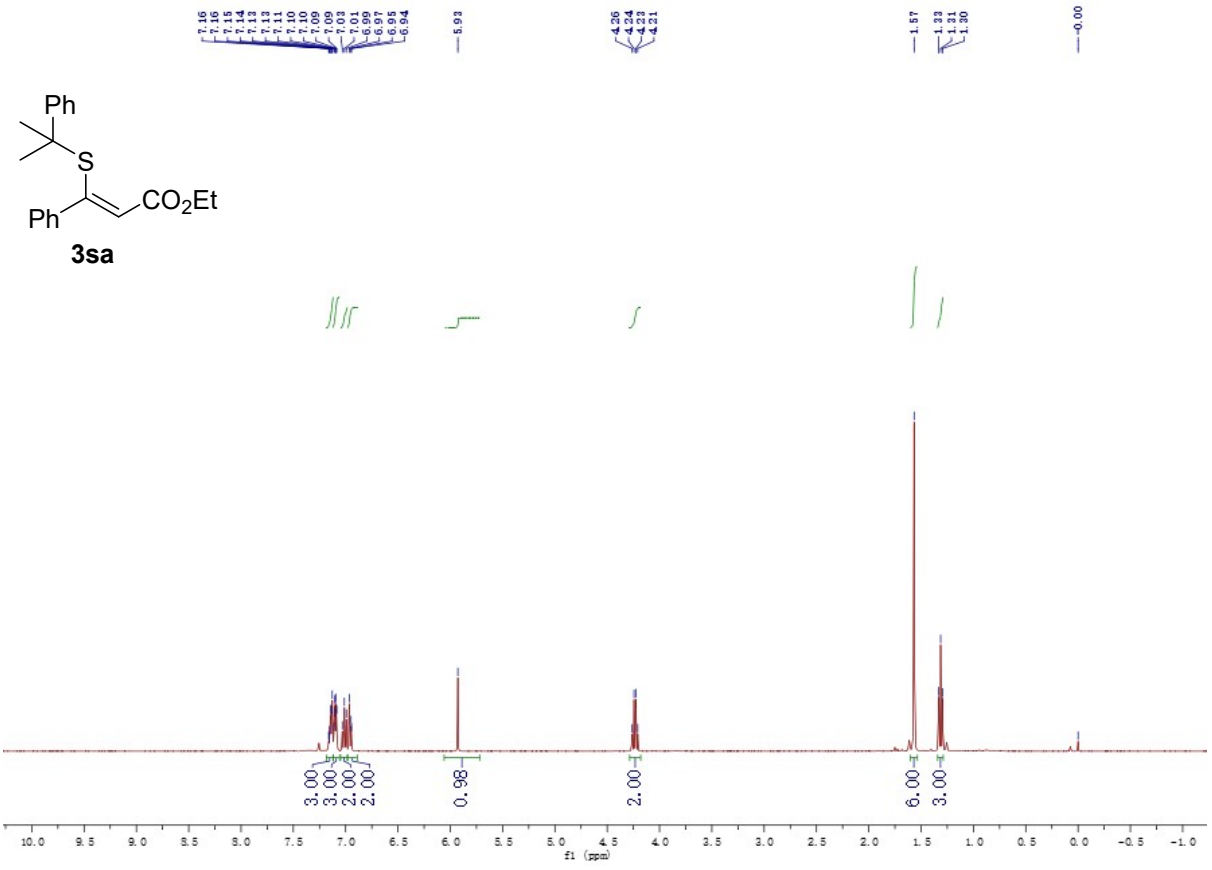


3ra

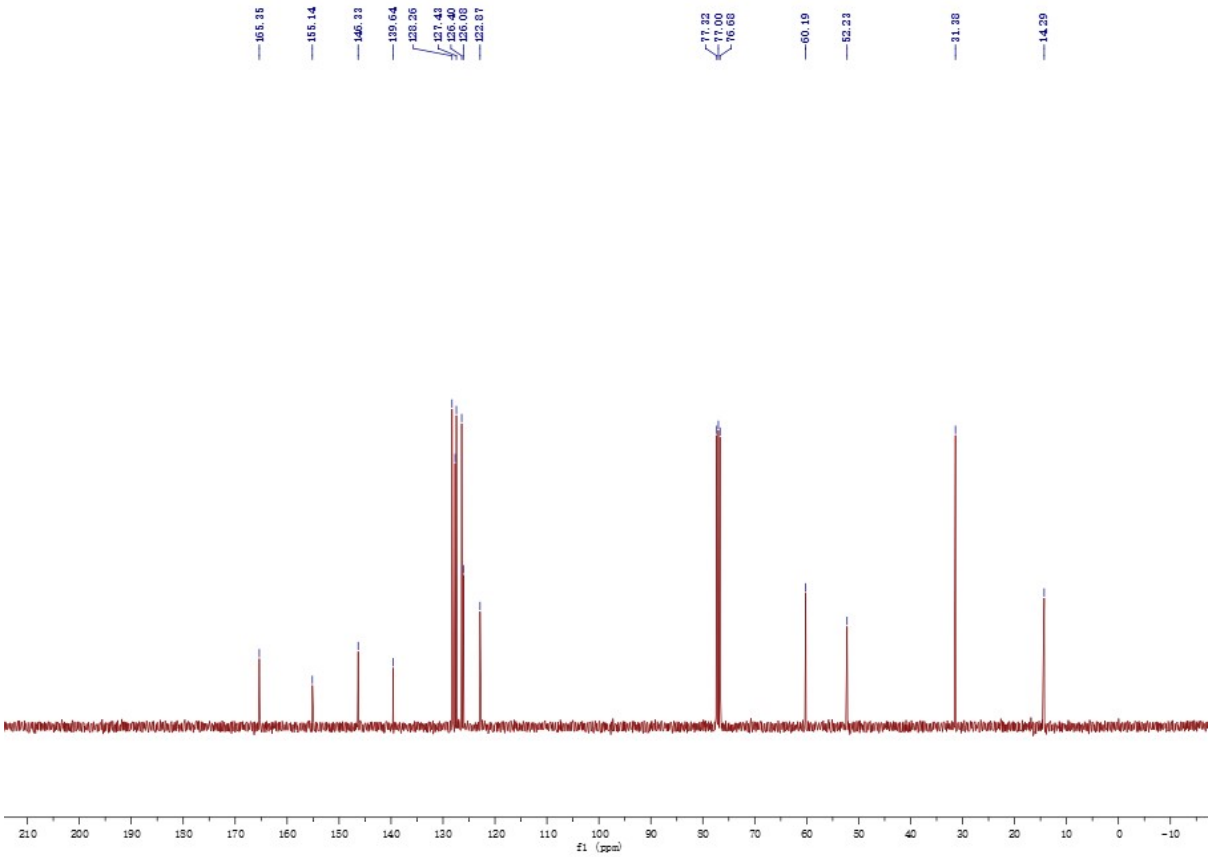
^{1}H NMR spectrum of **3ra** (400 MHz, $CDCl_3$)



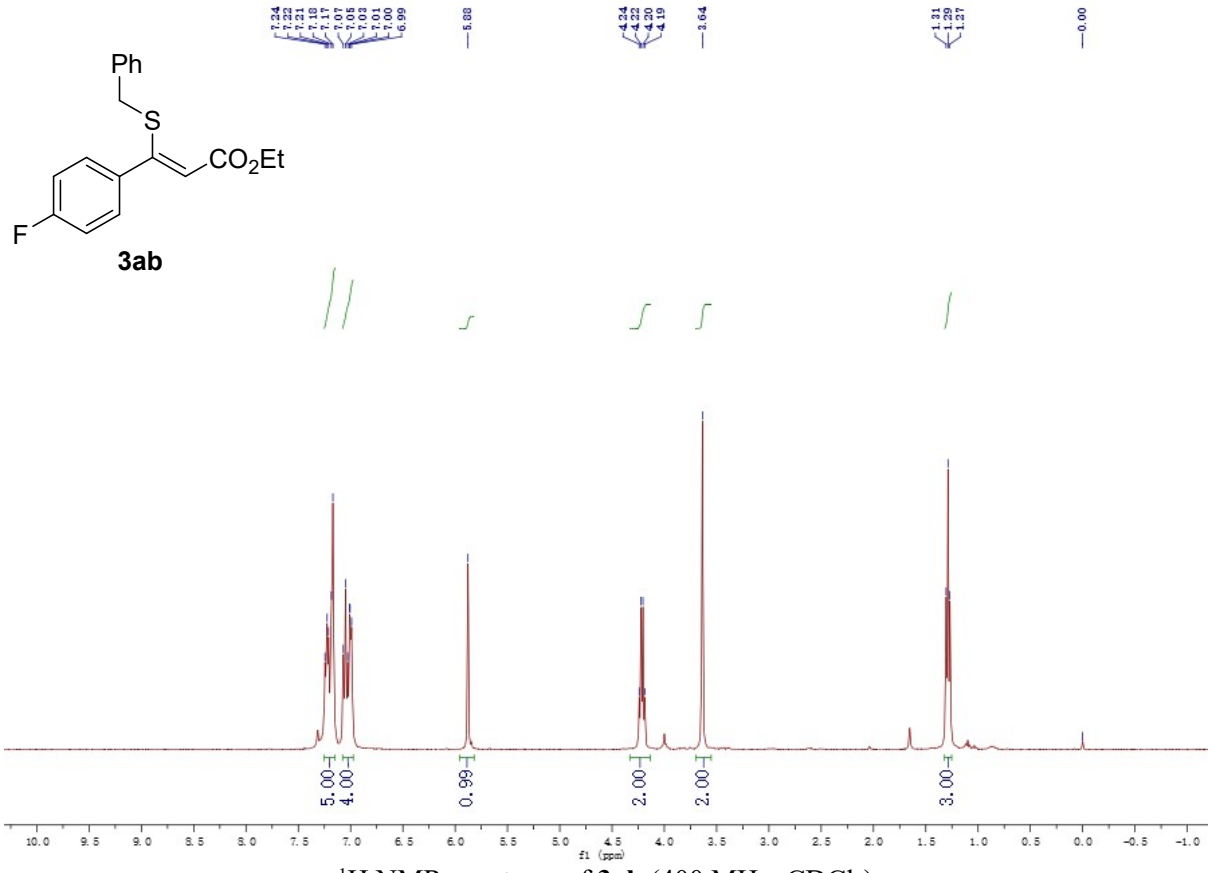
^{13}C NMR spectrum of **3ra** (100 MHz, $CDCl_3$)



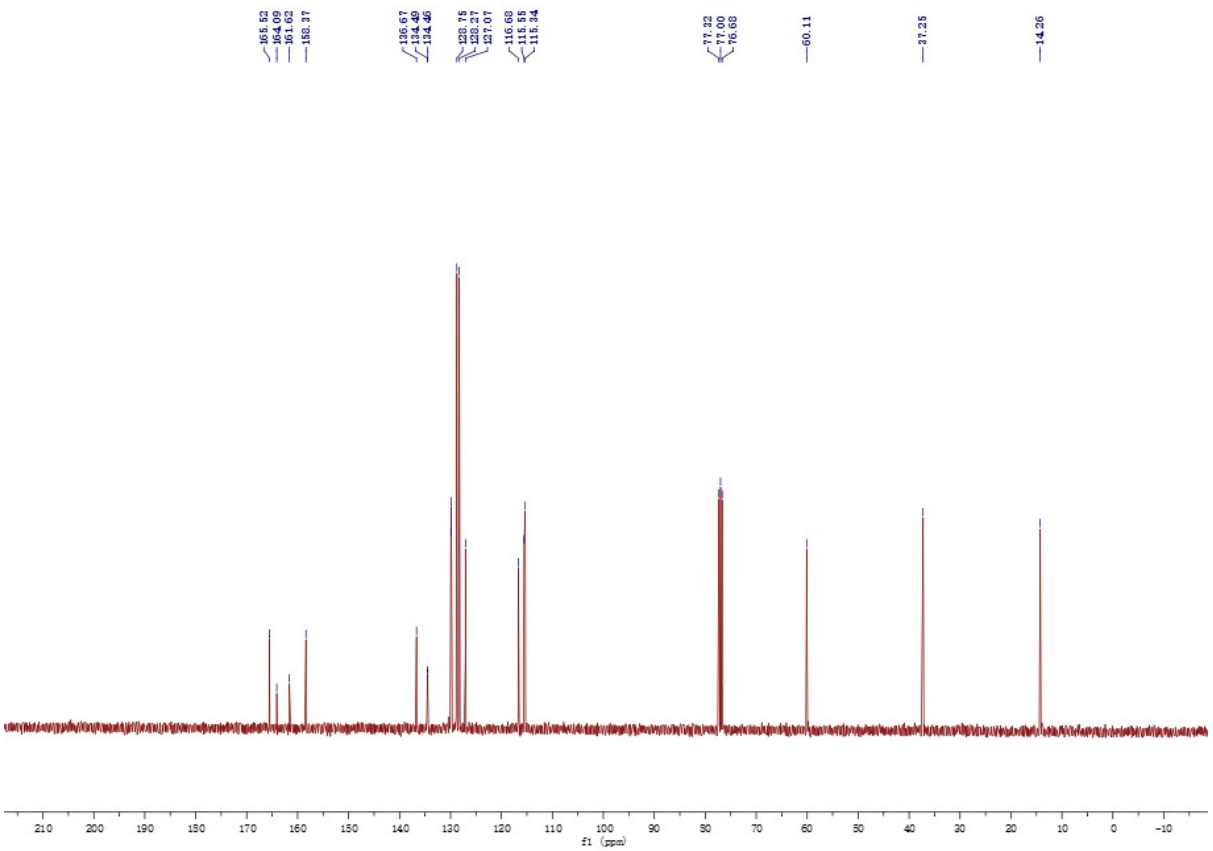
^{1}H NMR spectrum of **3sa** (400 MHz, $CDCl_3$)



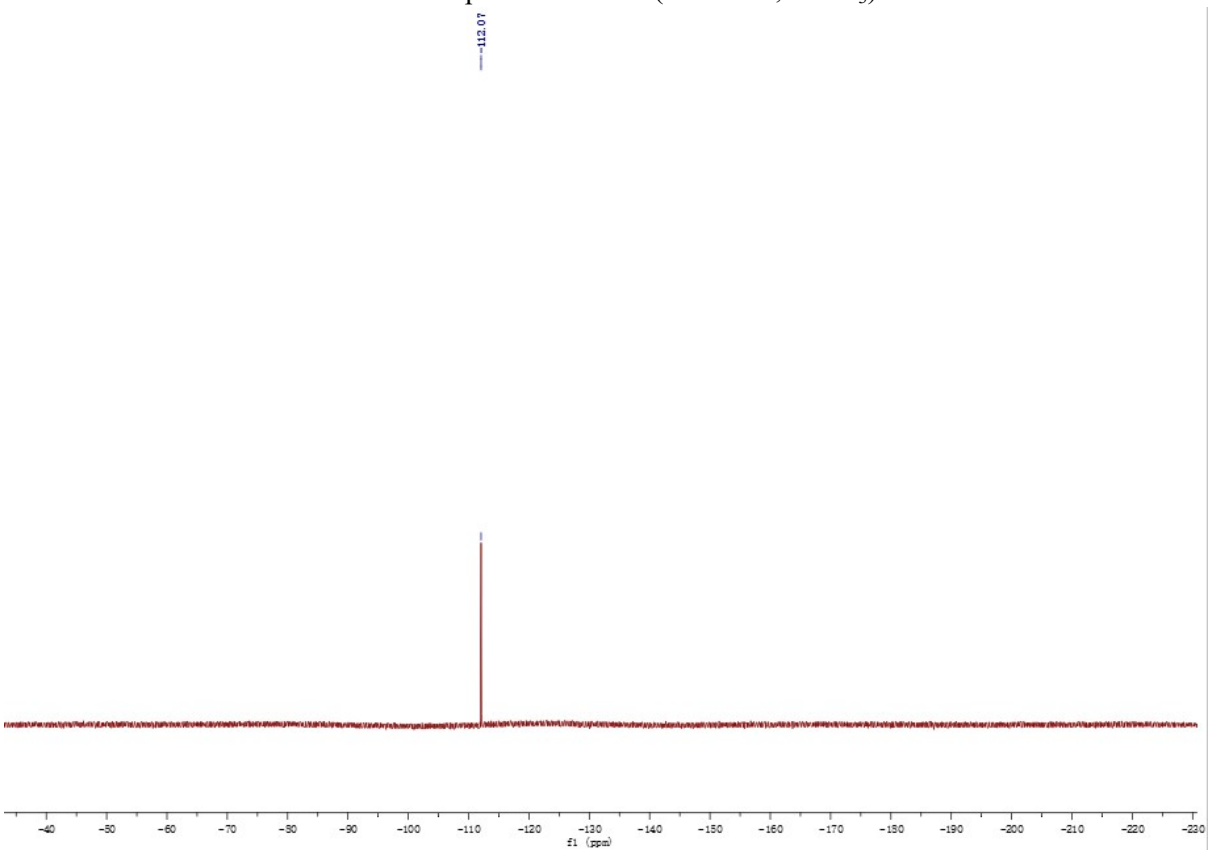
^{13}C NMR spectrum of **3sa** (100 MHz, $CDCl_3$)



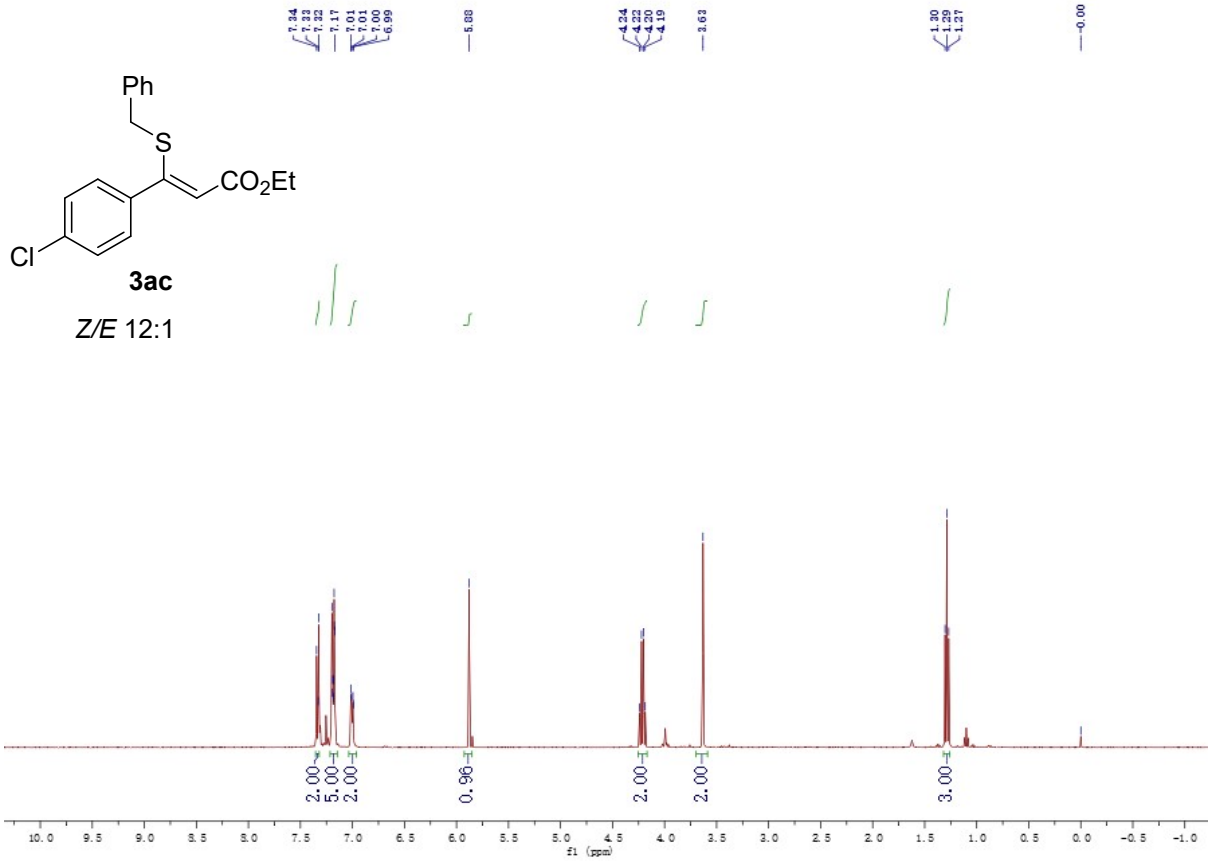
^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$)



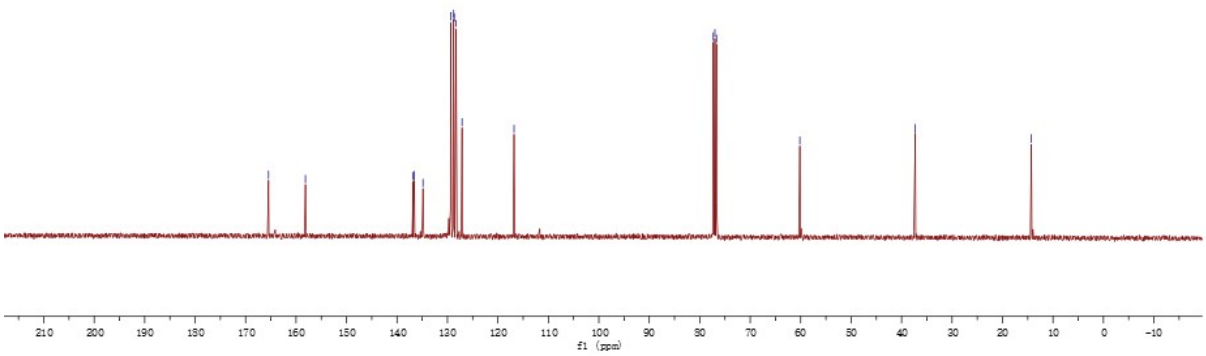
^{13}C NMR spectrum of **3ab** (100 MHz, $CDCl_3$)



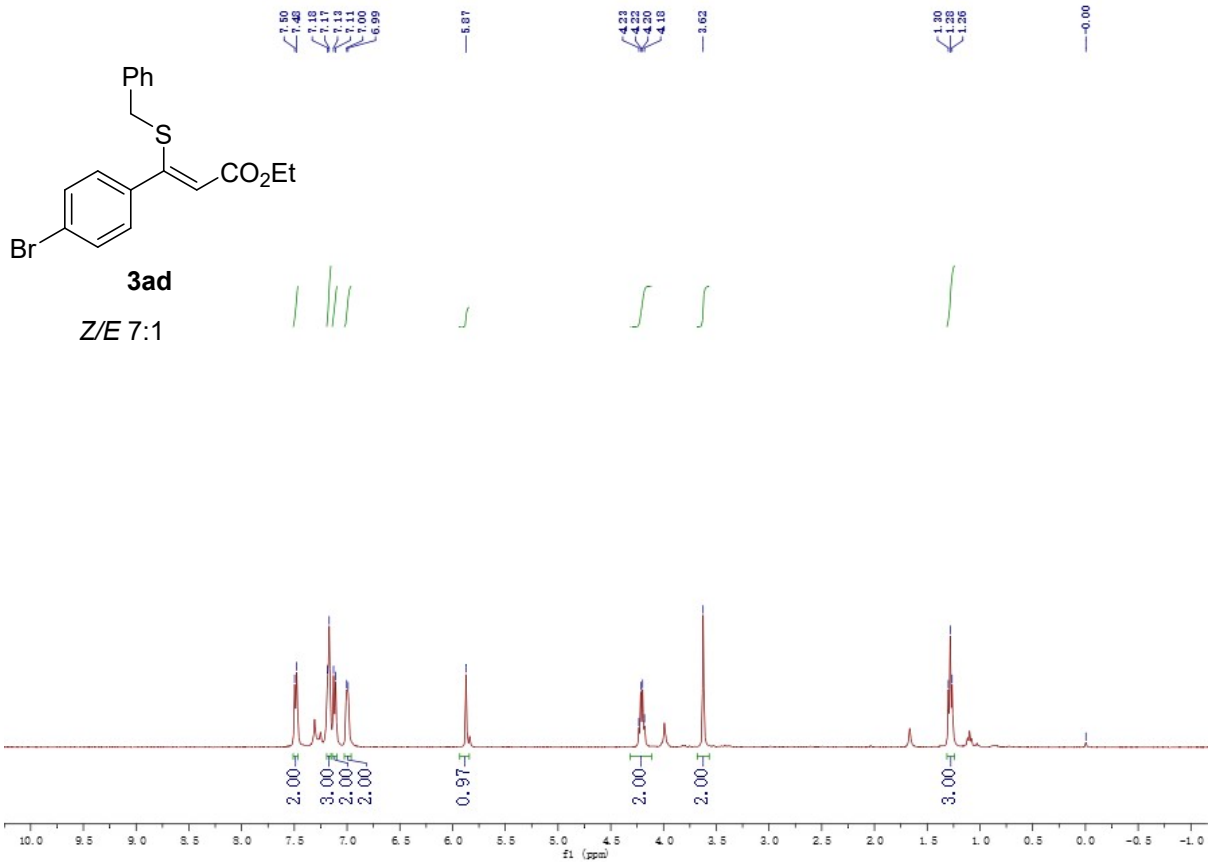
^{19}F NMR spectrum of **3ab** (376 MHz, $CDCl_3$)



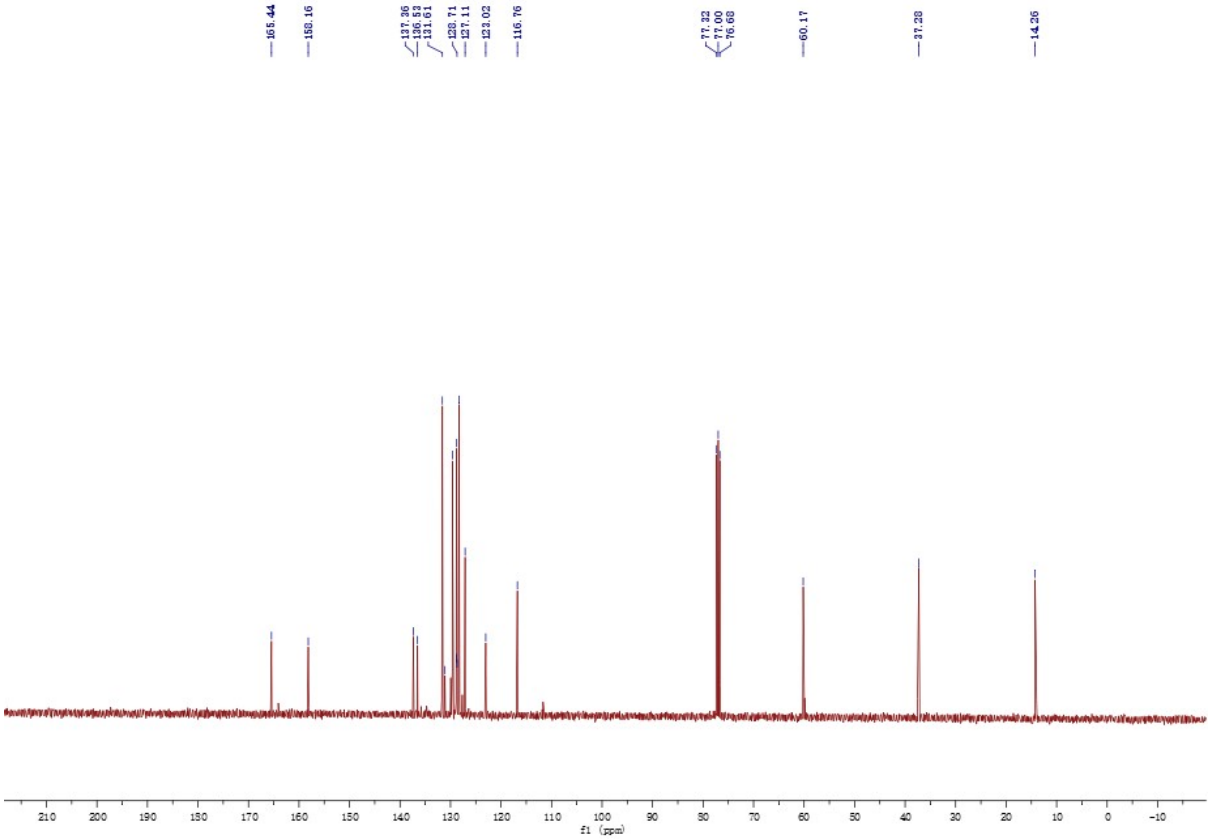
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



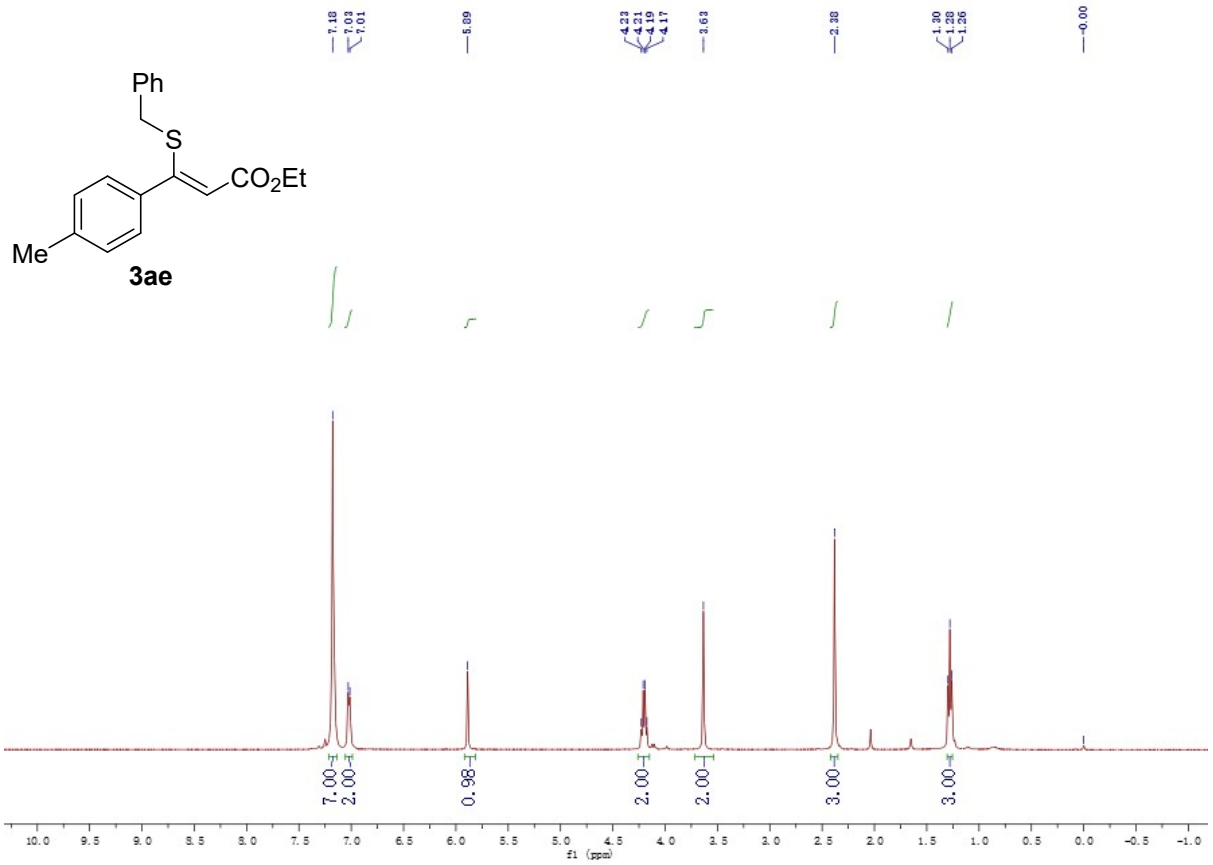
^{13}C NMR spectrum of **3ac** (100 MHz, $CDCl_3$)



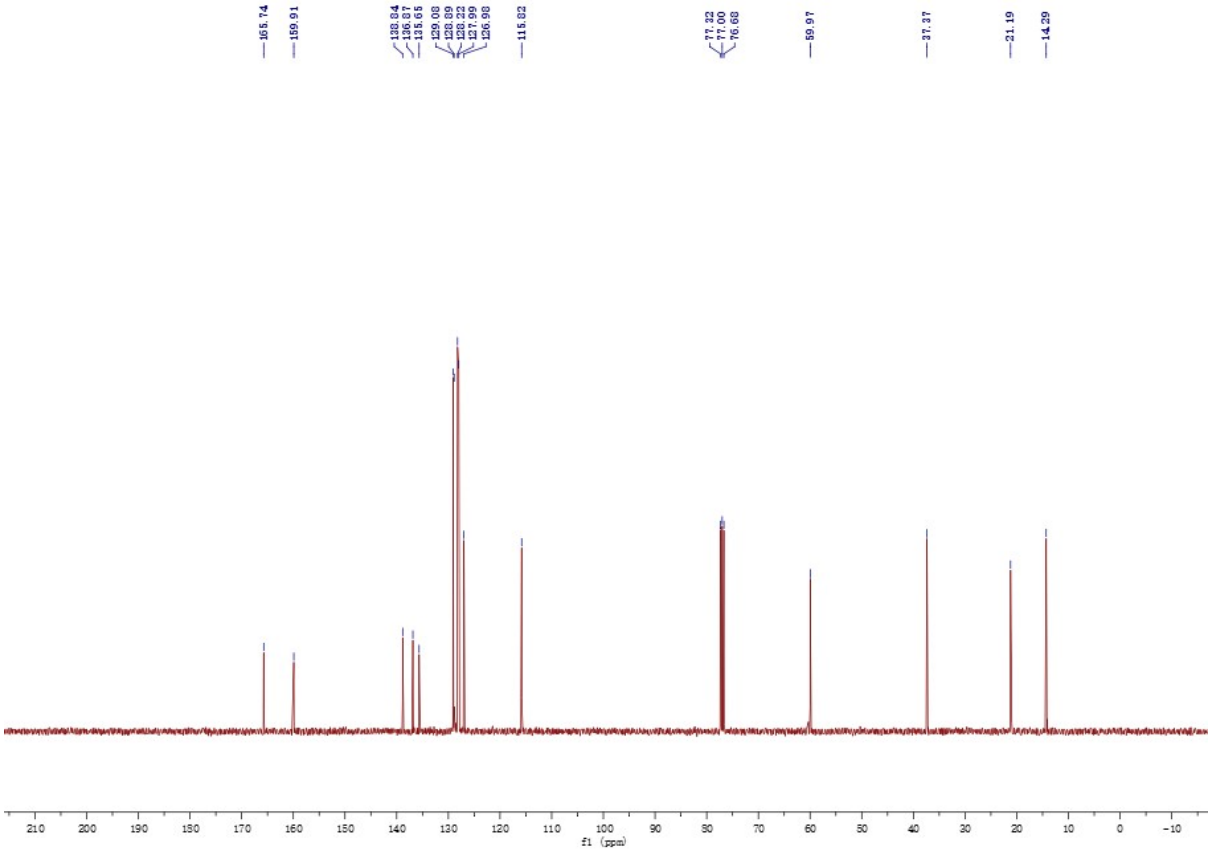
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)



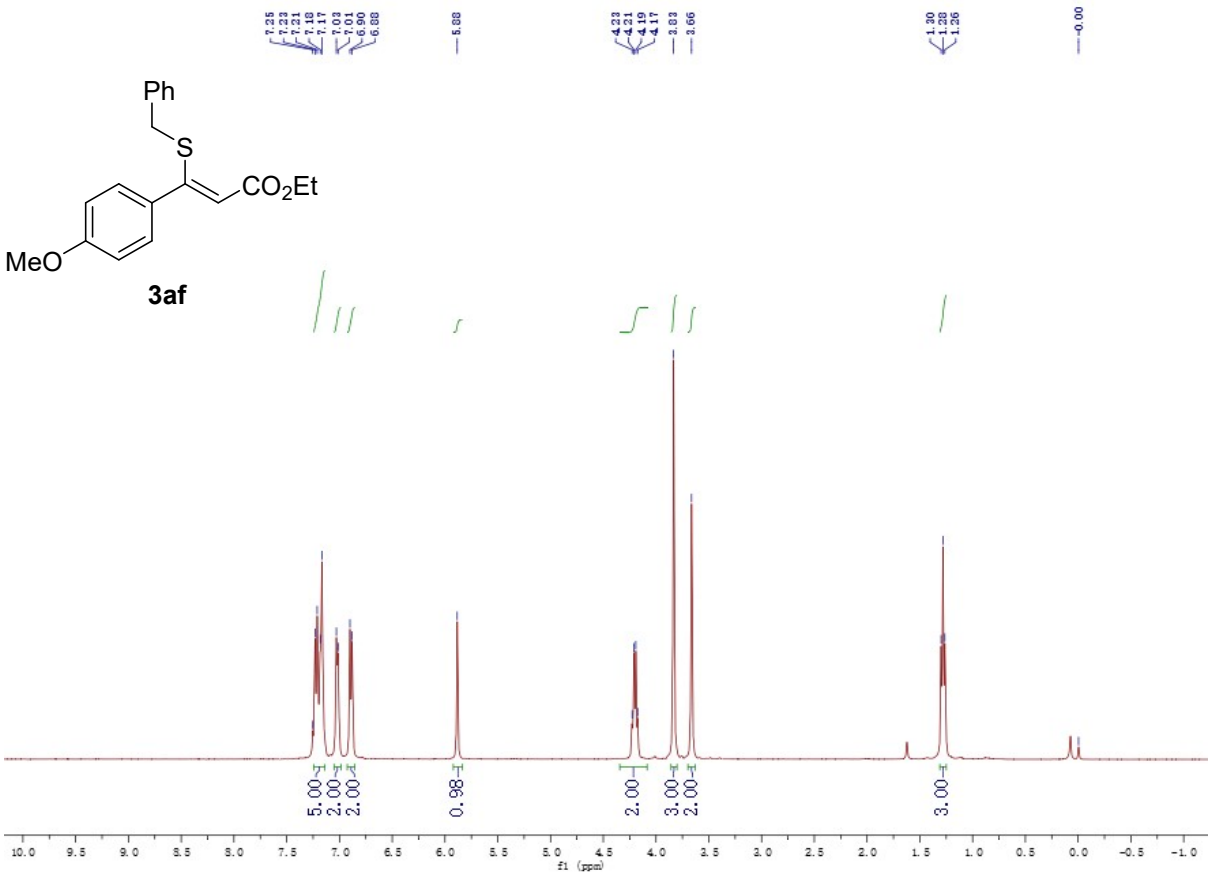
^{13}C NMR spectrum of **3ad** (100 MHz, $CDCl_3$)



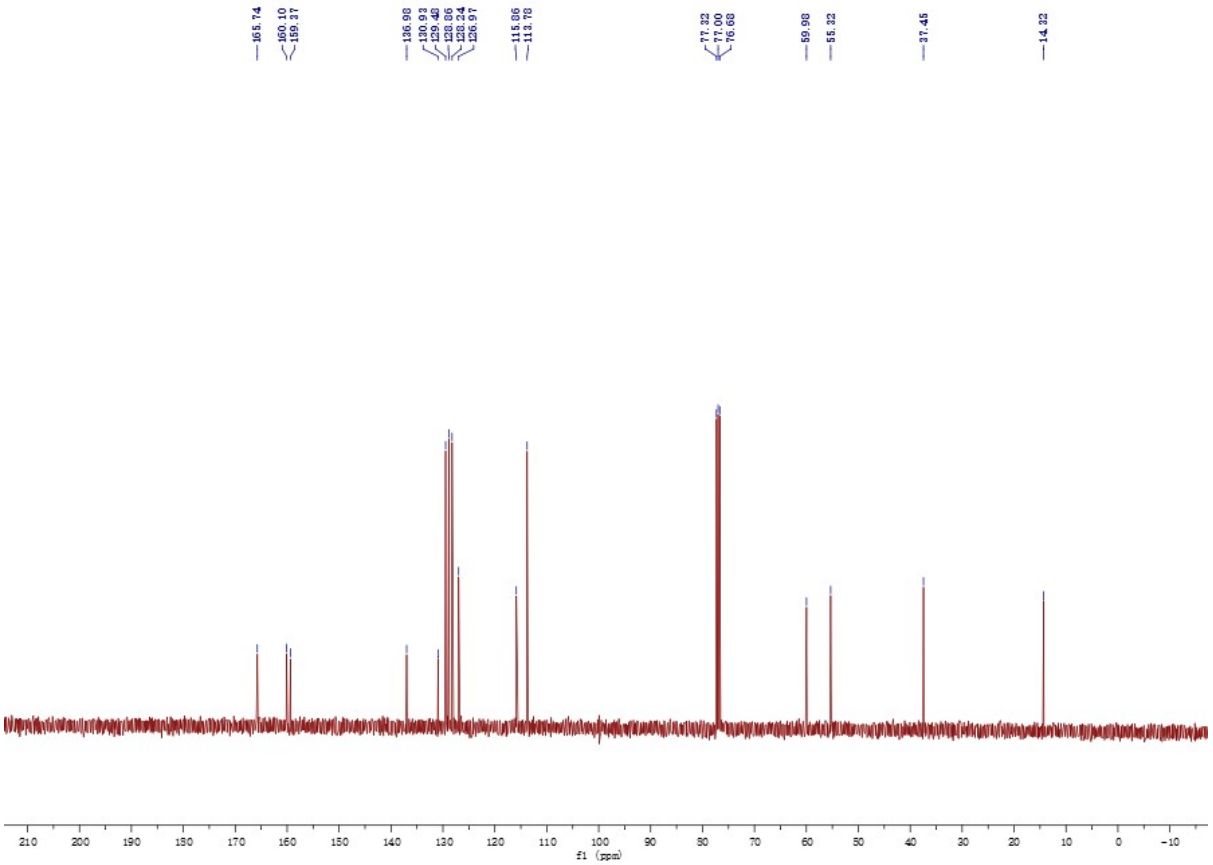
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



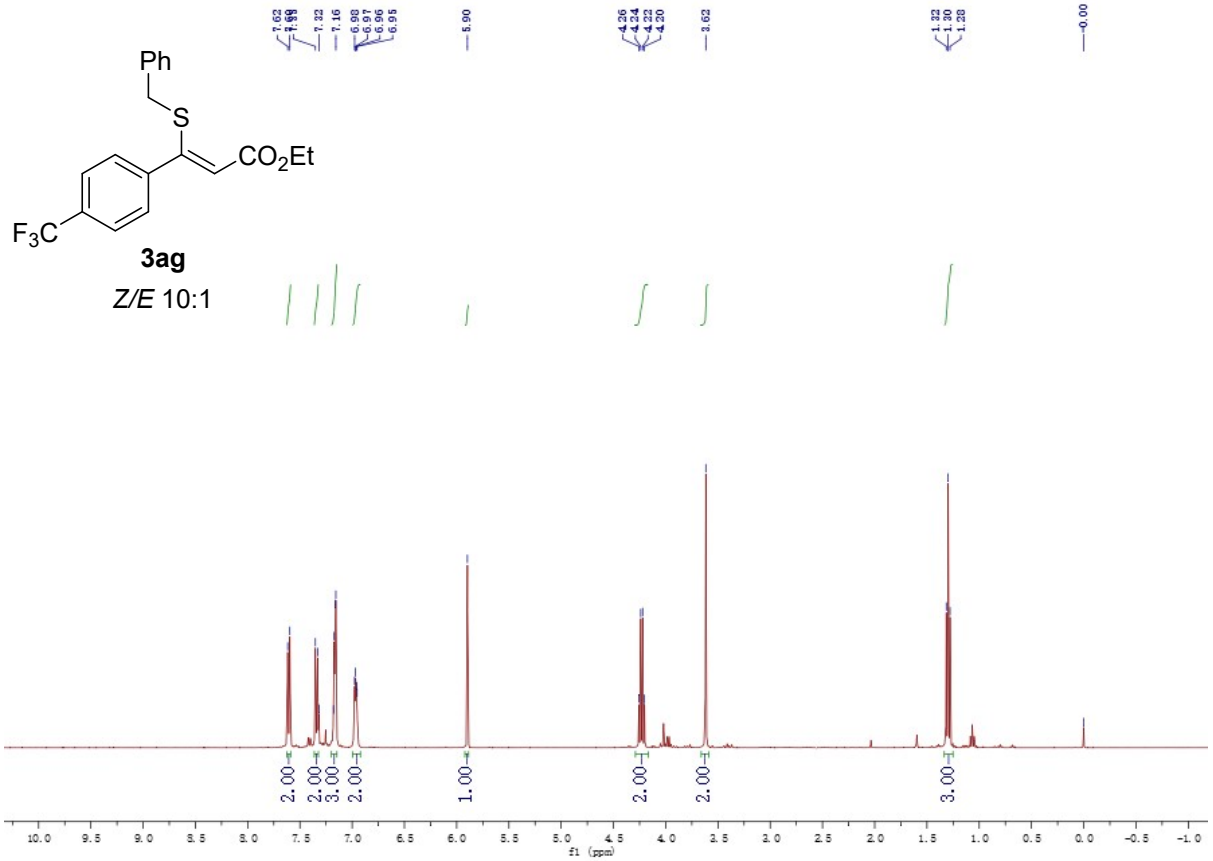
^{13}C NMR spectrum of **3ae** (100 MHz, $CDCl_3$)



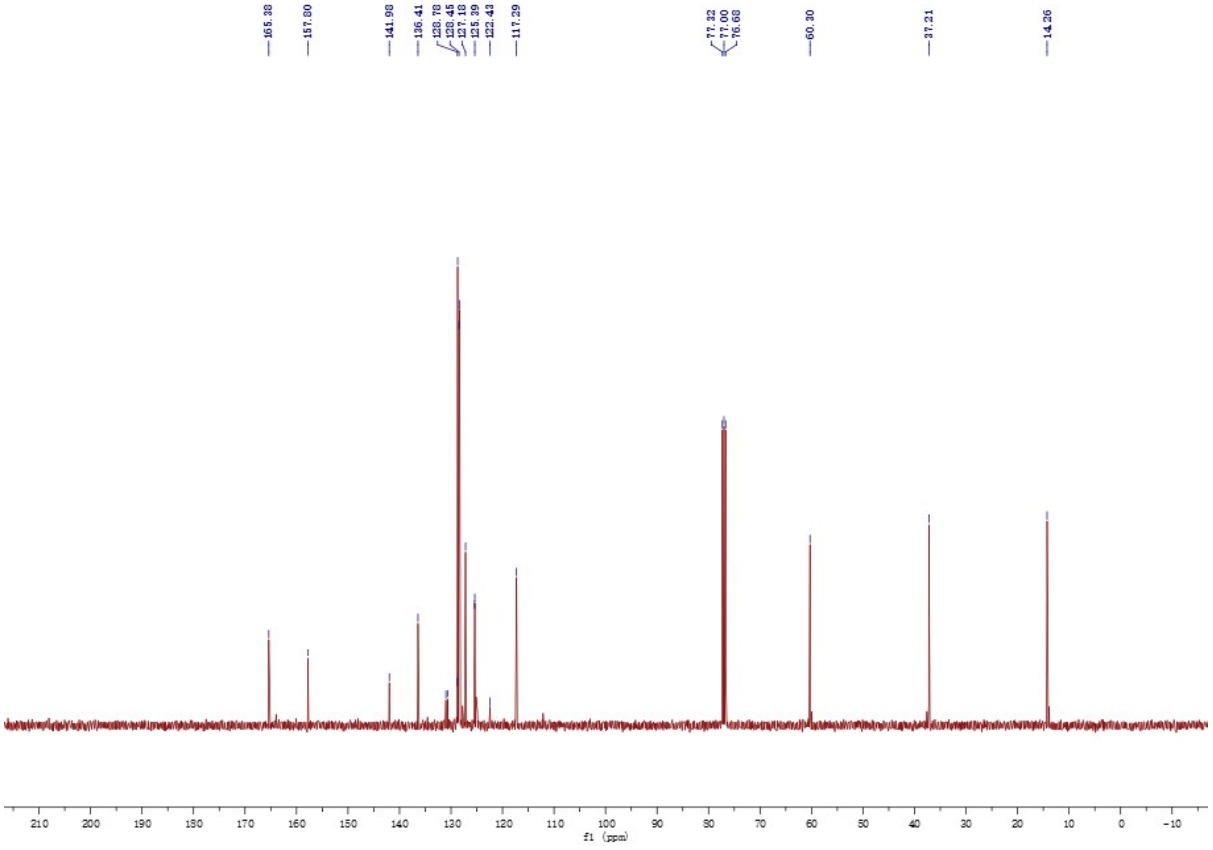
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



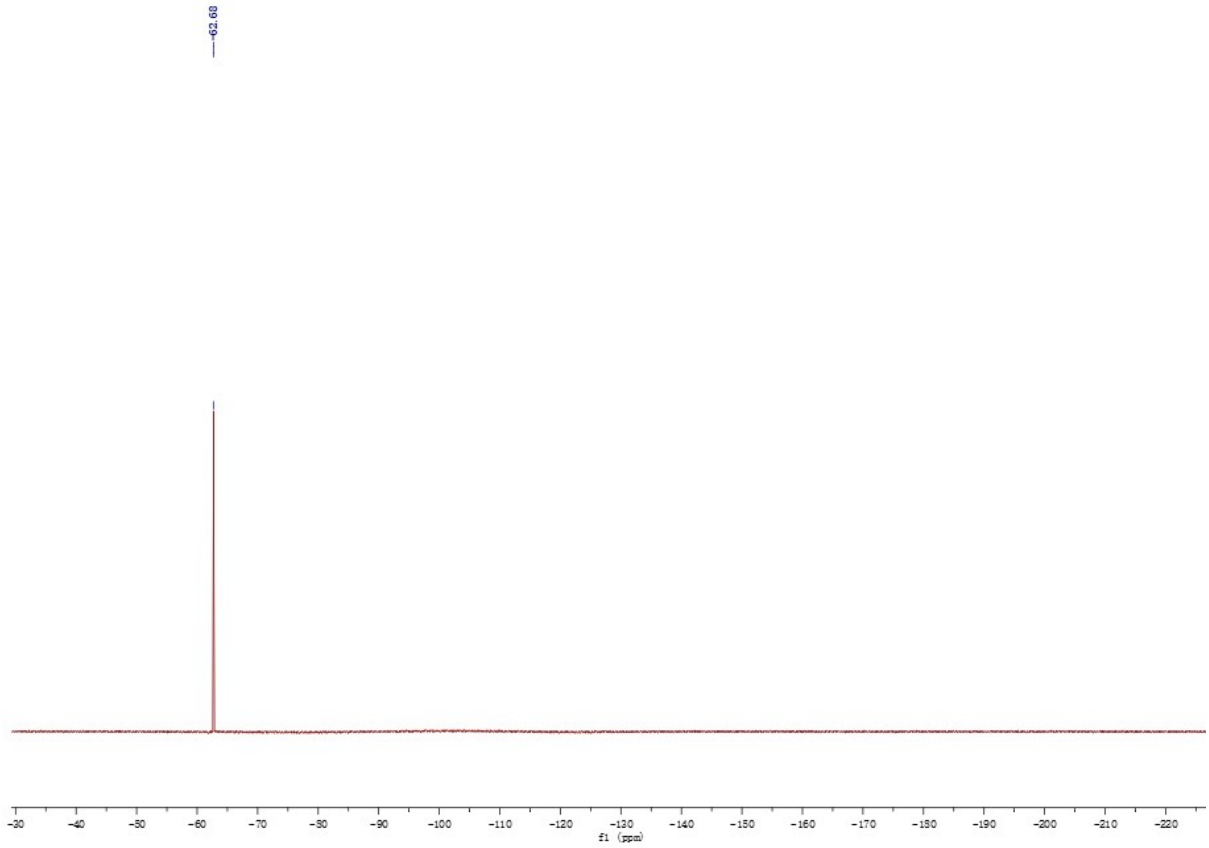
^{13}C NMR spectrum of **3af** (100 MHz, $CDCl_3$)



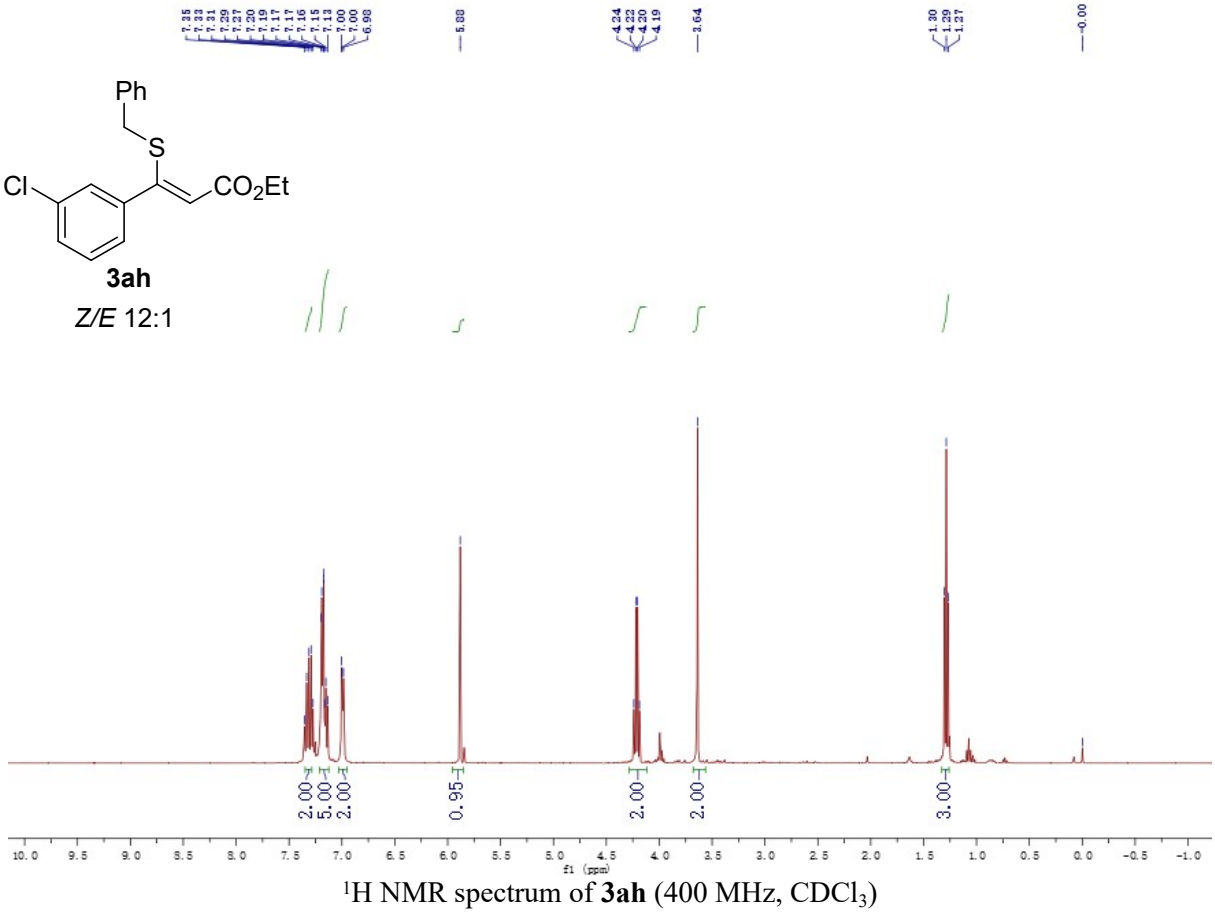
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)



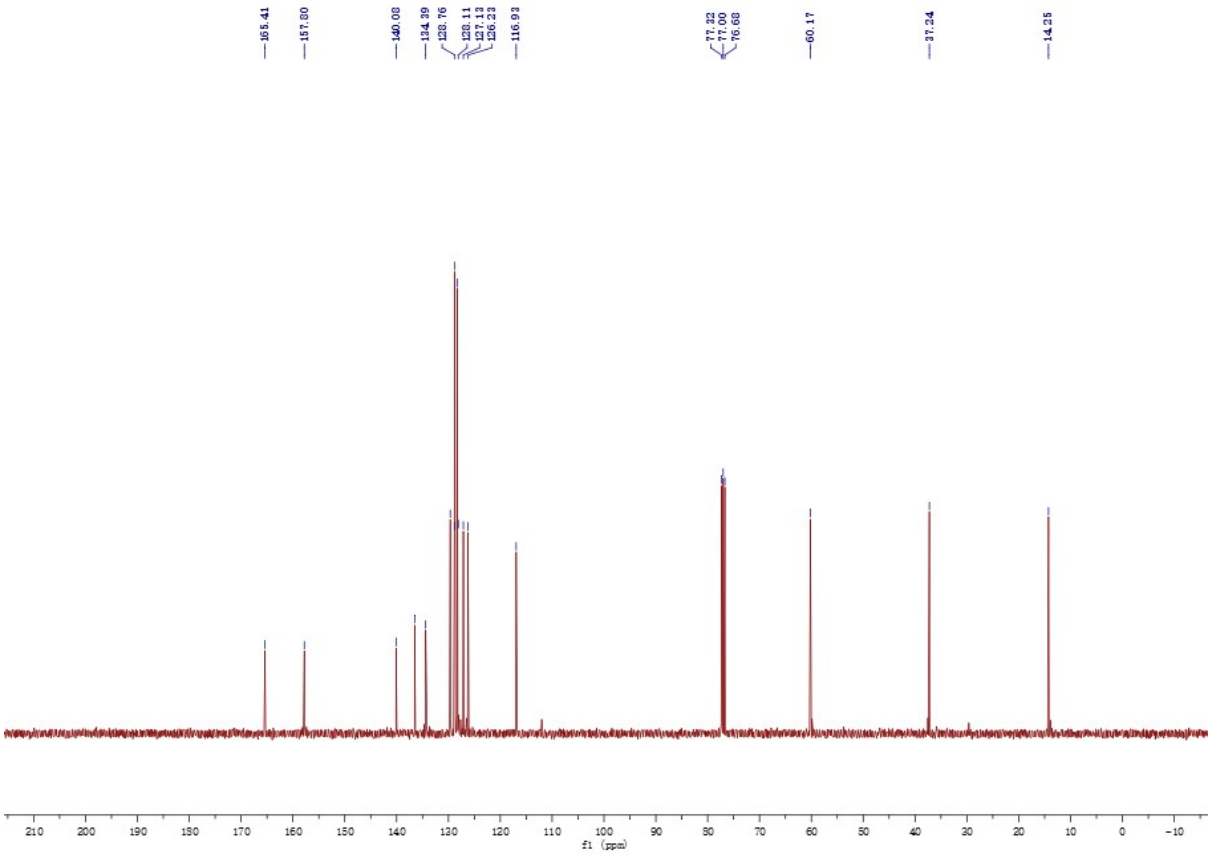
^{13}C NMR spectrum of **3ag** (100 MHz, $CDCl_3$)



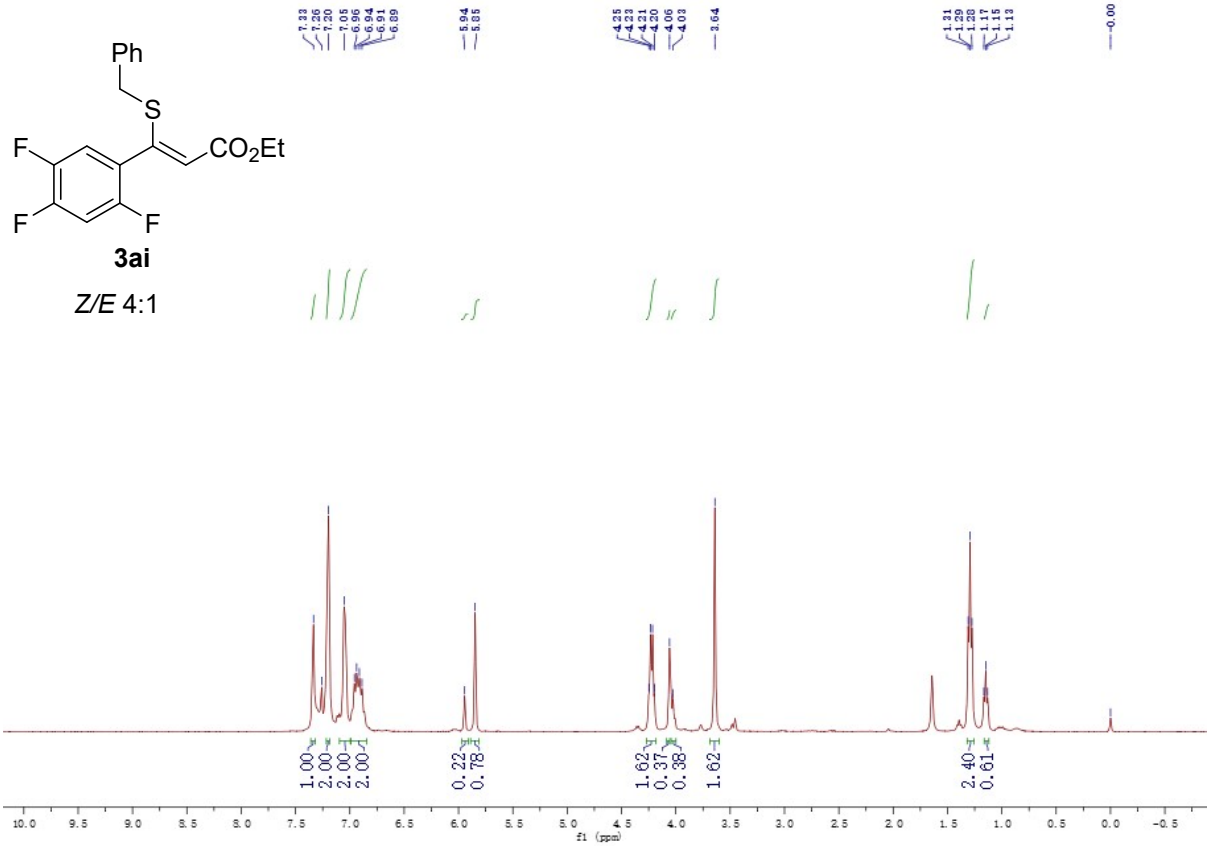
^{19}F NMR spectrum of **3ag** (376 MHz, $CDCl_3$)



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



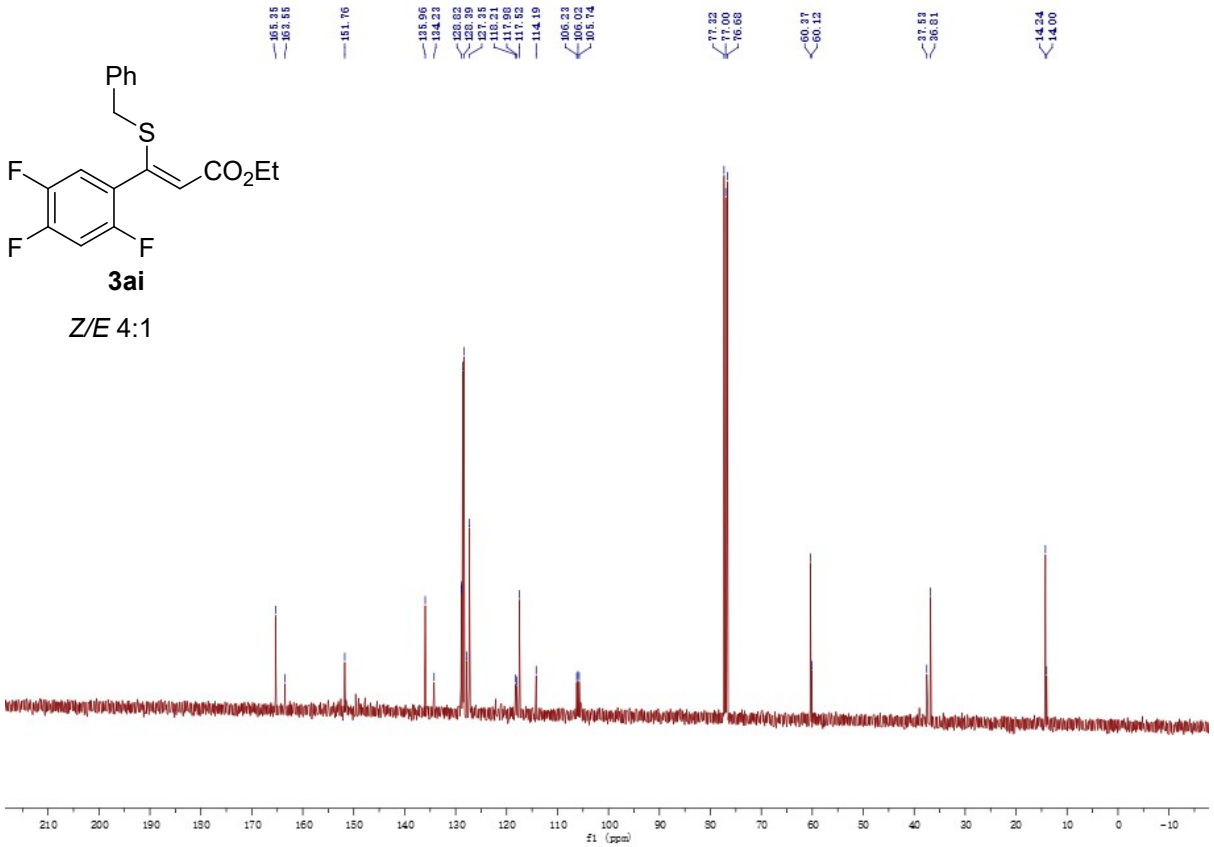
^{13}C NMR spectrum of **3ah** (100 MHz, $CDCl_3$)



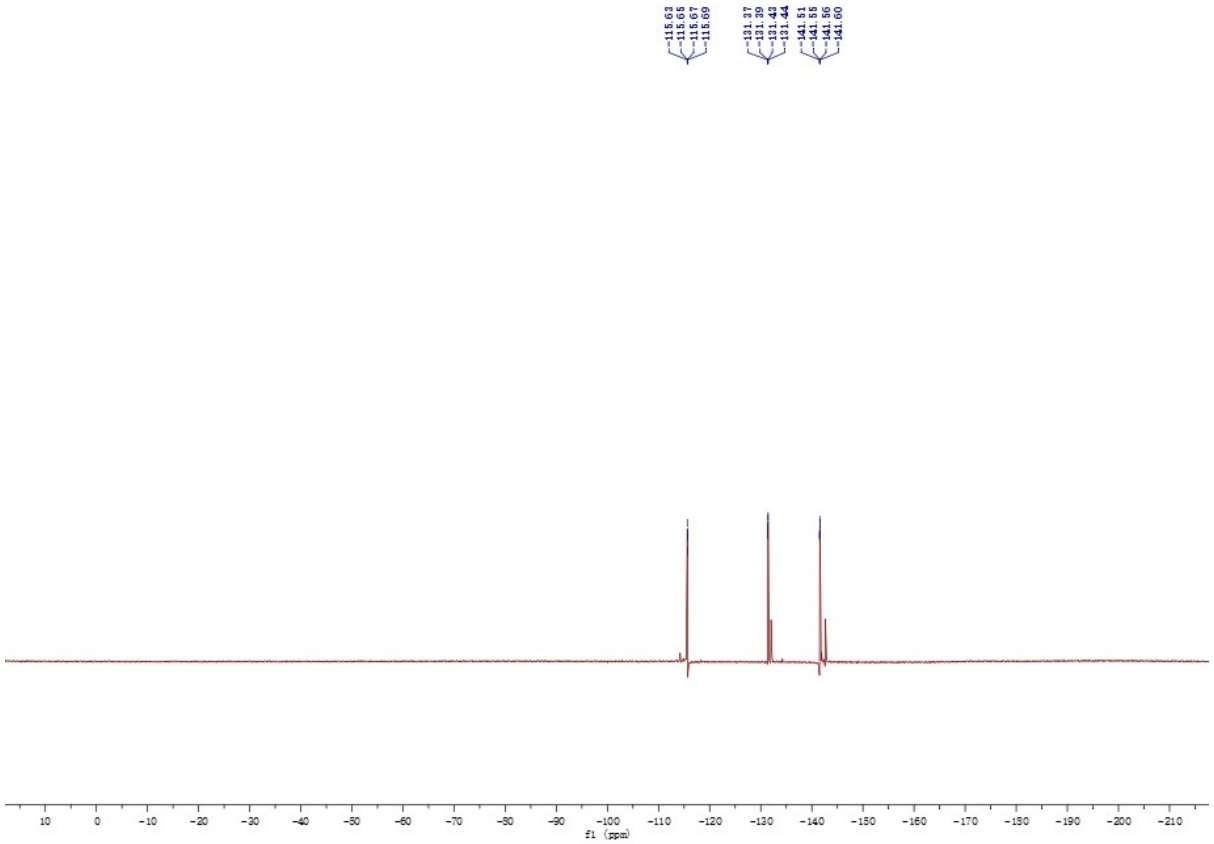
3ai

Z/*E* 4:1

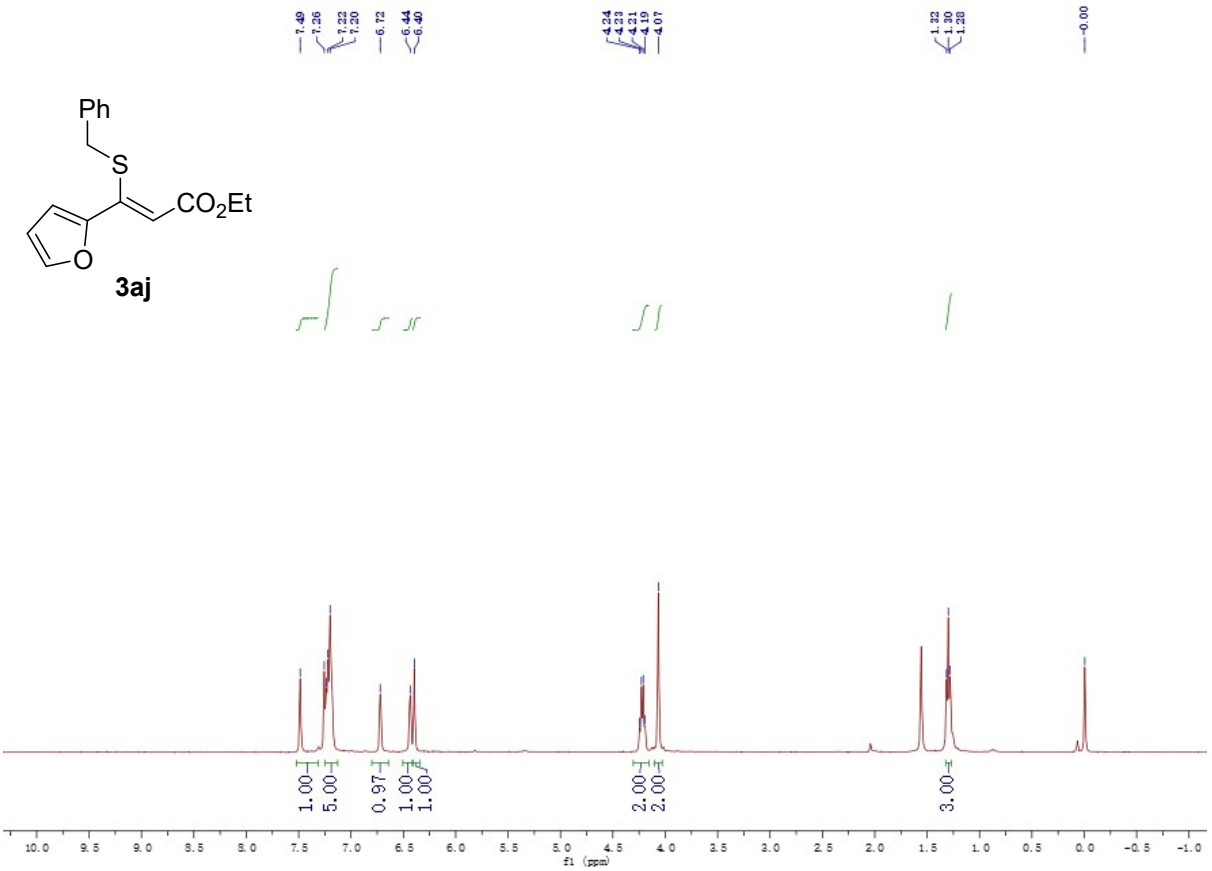
^{1}H NMR spectrum of **3ai (*E*:*Z*=3:1)** (400 MHz, $CDCl_3$)



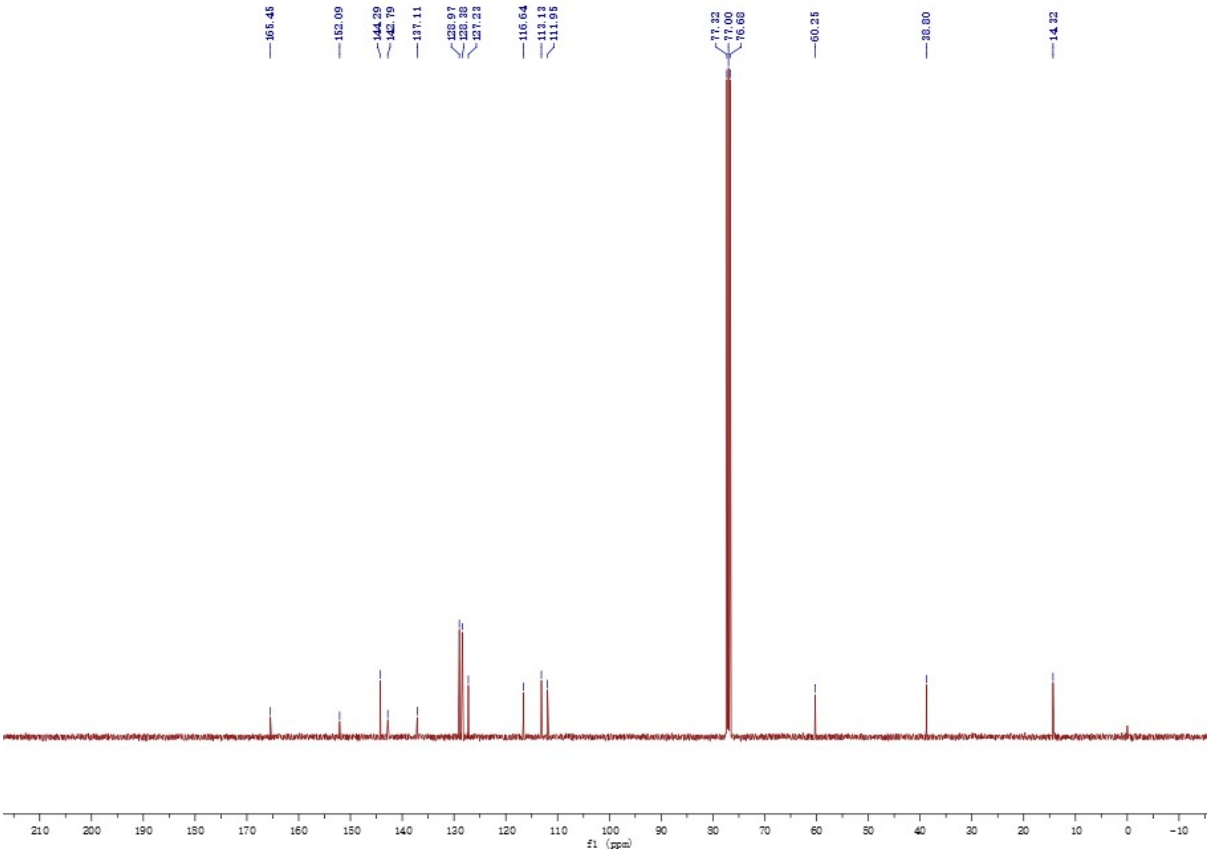
^{13}C NMR spectrum of **3ai** (100 MHz, $CDCl_3$)



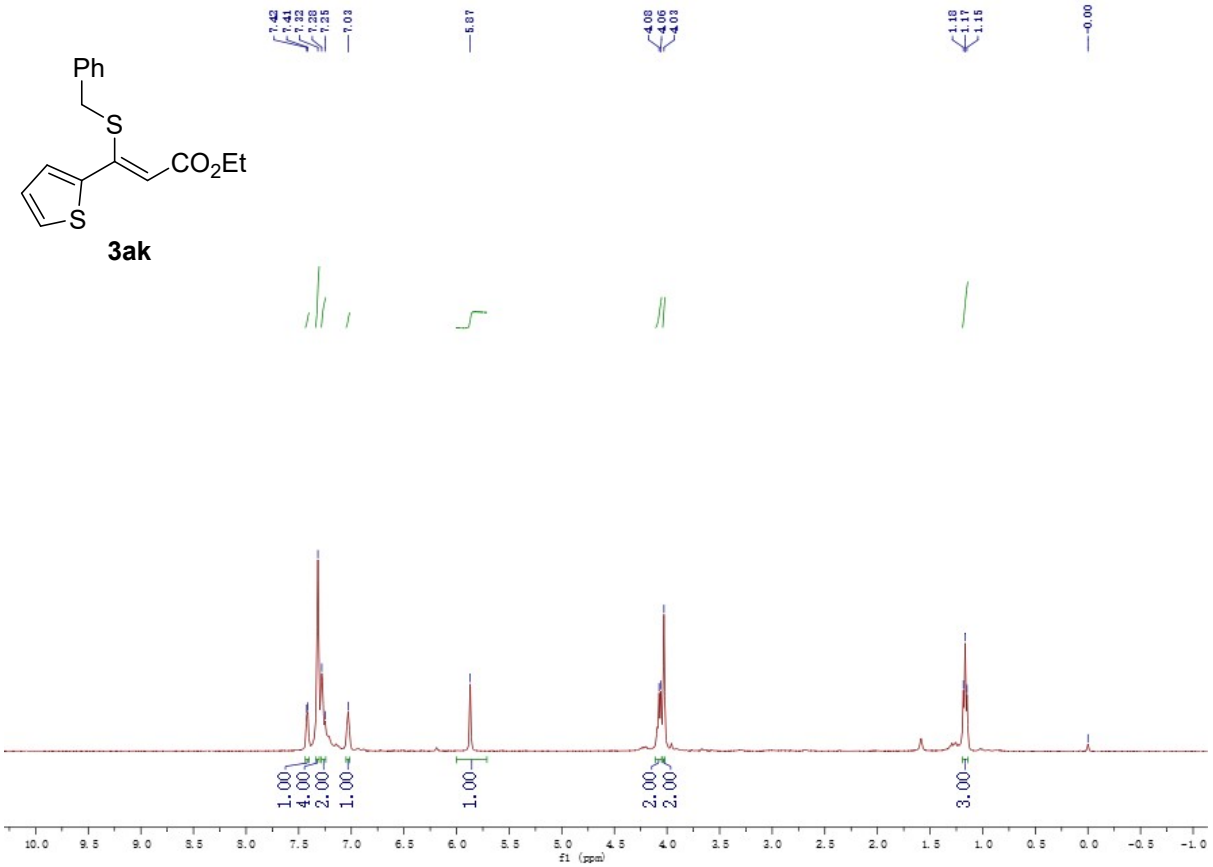
^{19}F NMR spectrum of **3ai** (376 MHz, $CDCl_3$)



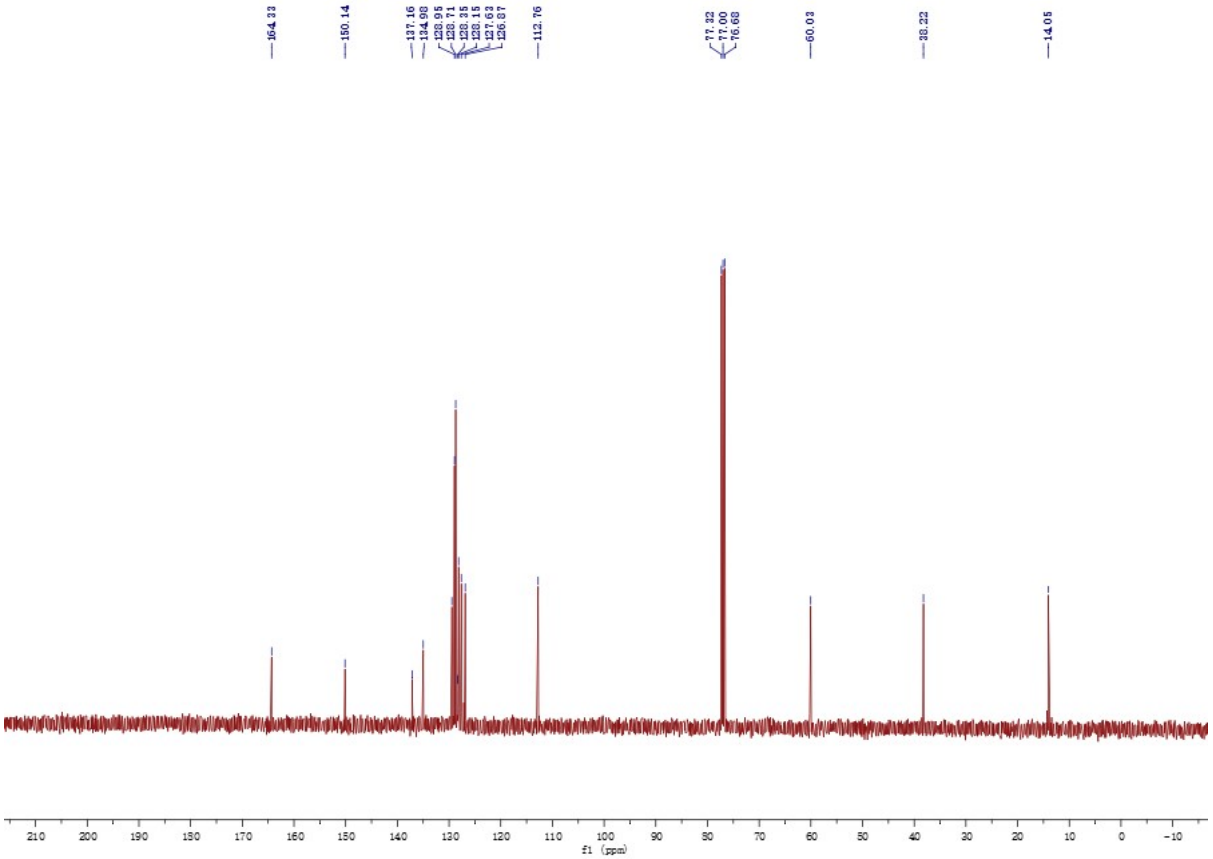
^{1}H NMR spectrum of **3aj** (400 MHz, $CDCl_3$)



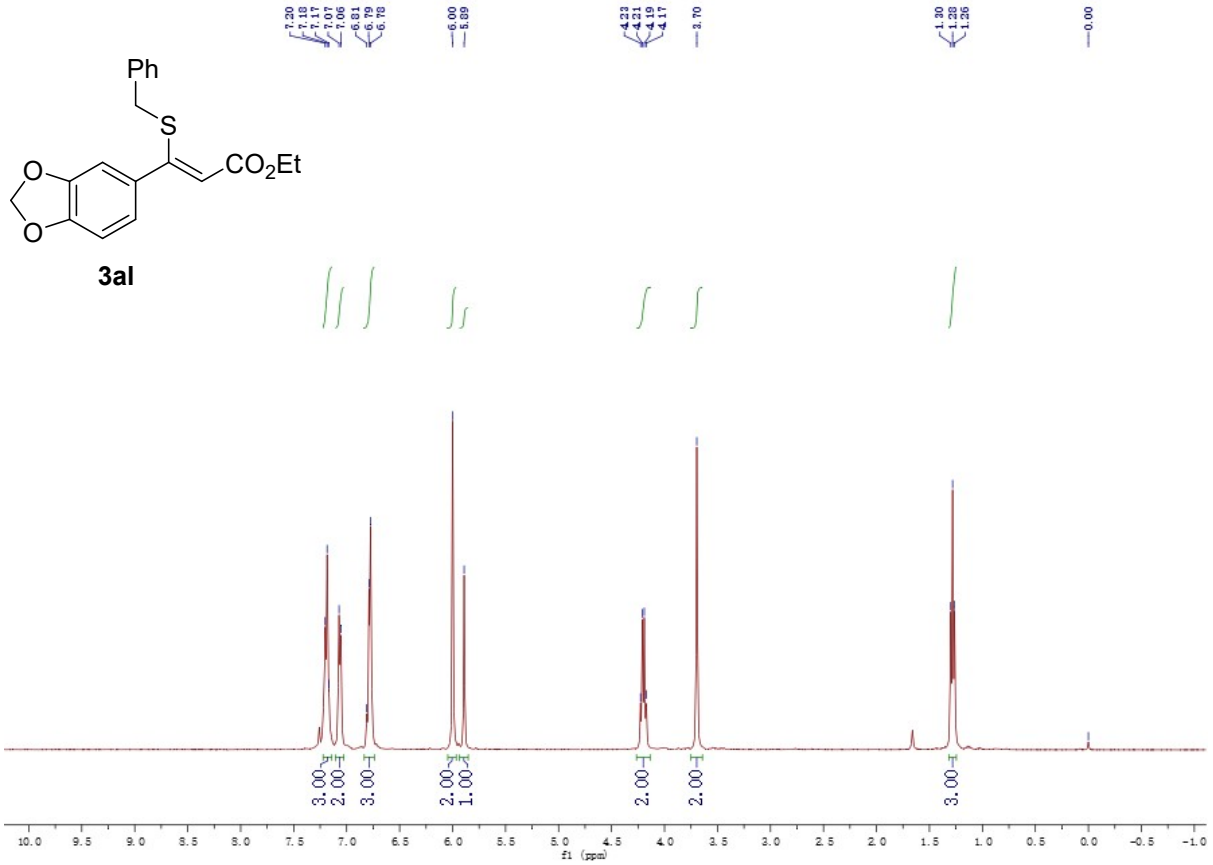
^{13}C NMR spectrum of **3aj** (100 MHz, $CDCl_3$)



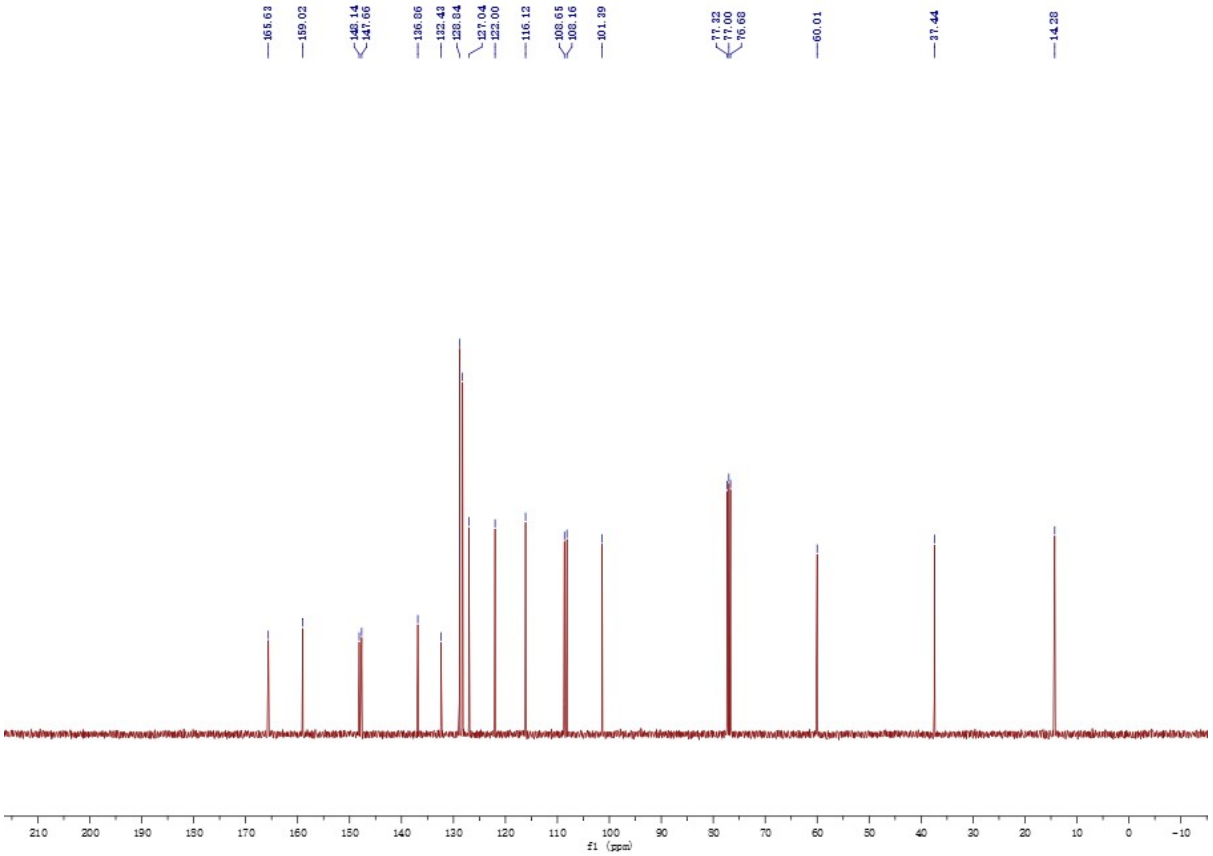
^{1}H NMR spectrum of **3ak** (400 MHz, $CDCl_3$)



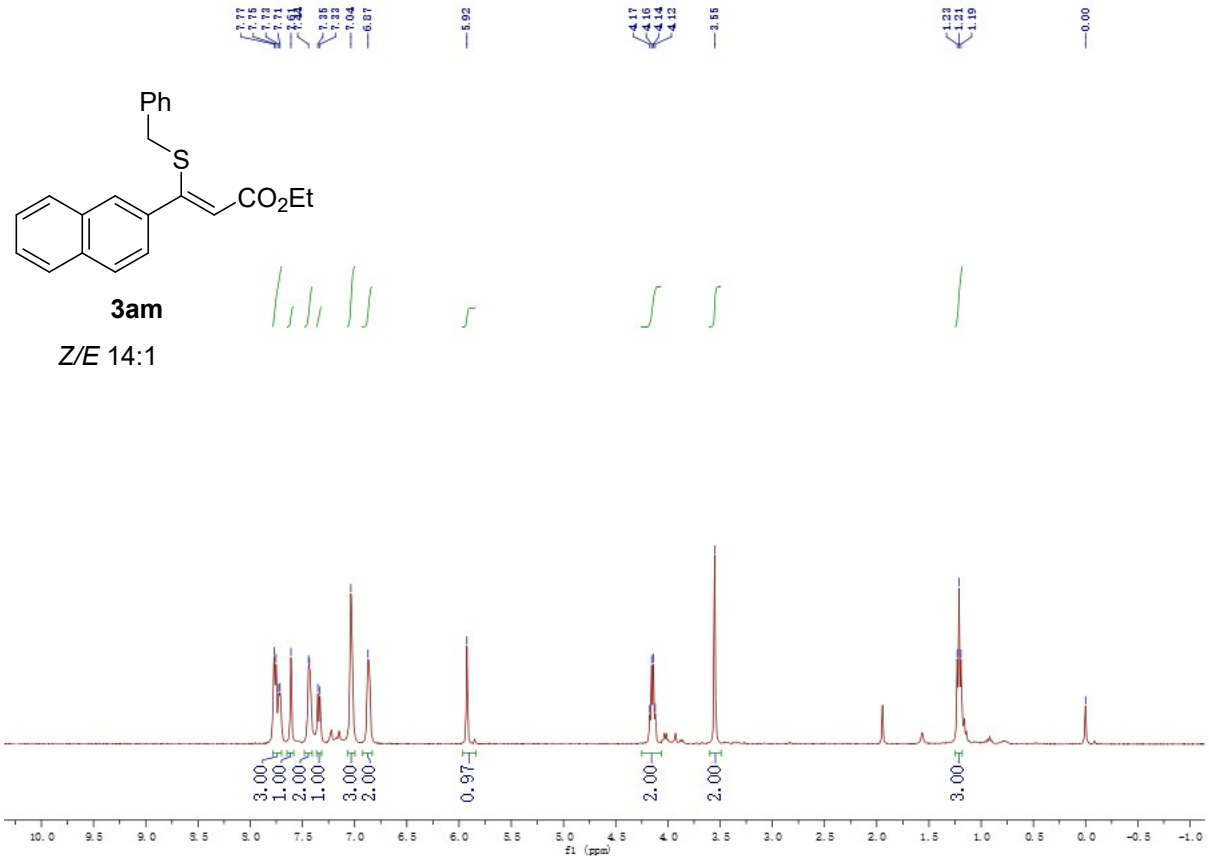
^{13}C NMR spectrum of **3ak** (100 MHz, $CDCl_3$)



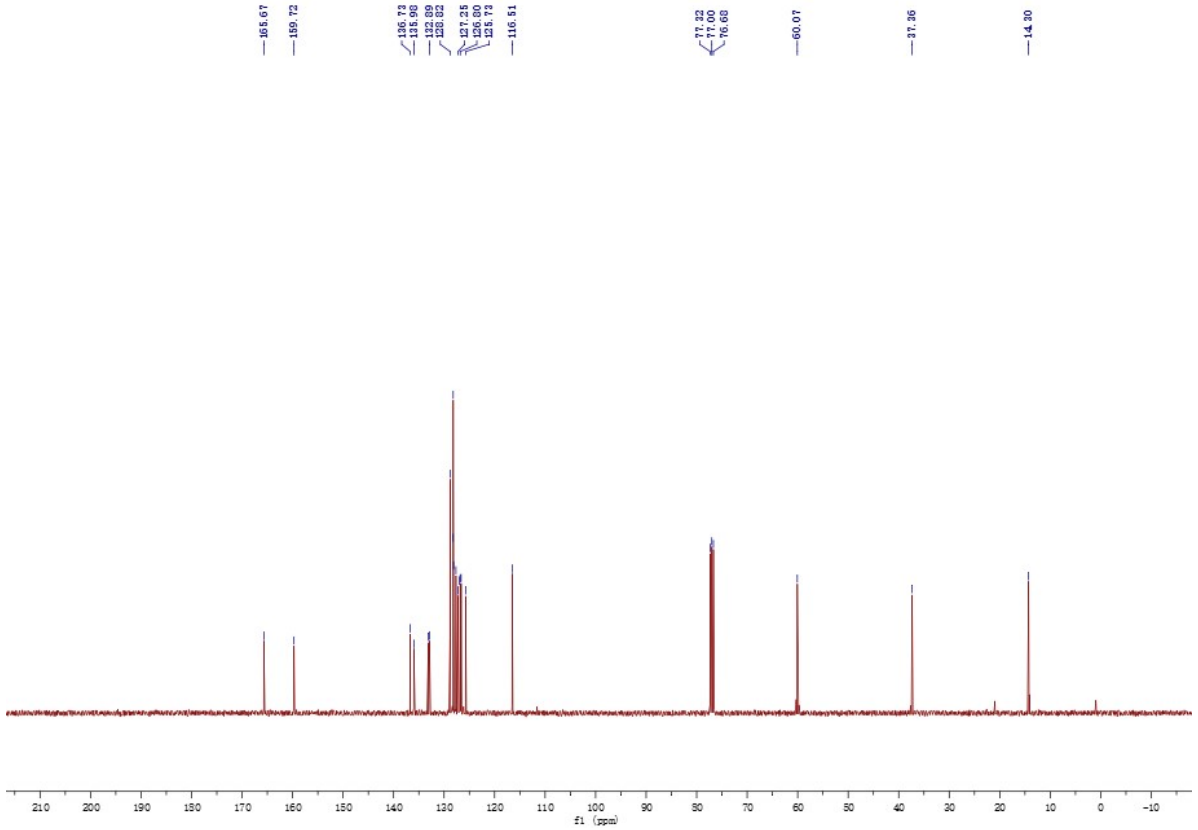
^{1}H NMR spectrum of **3al** (400 MHz, $CDCl_3$)



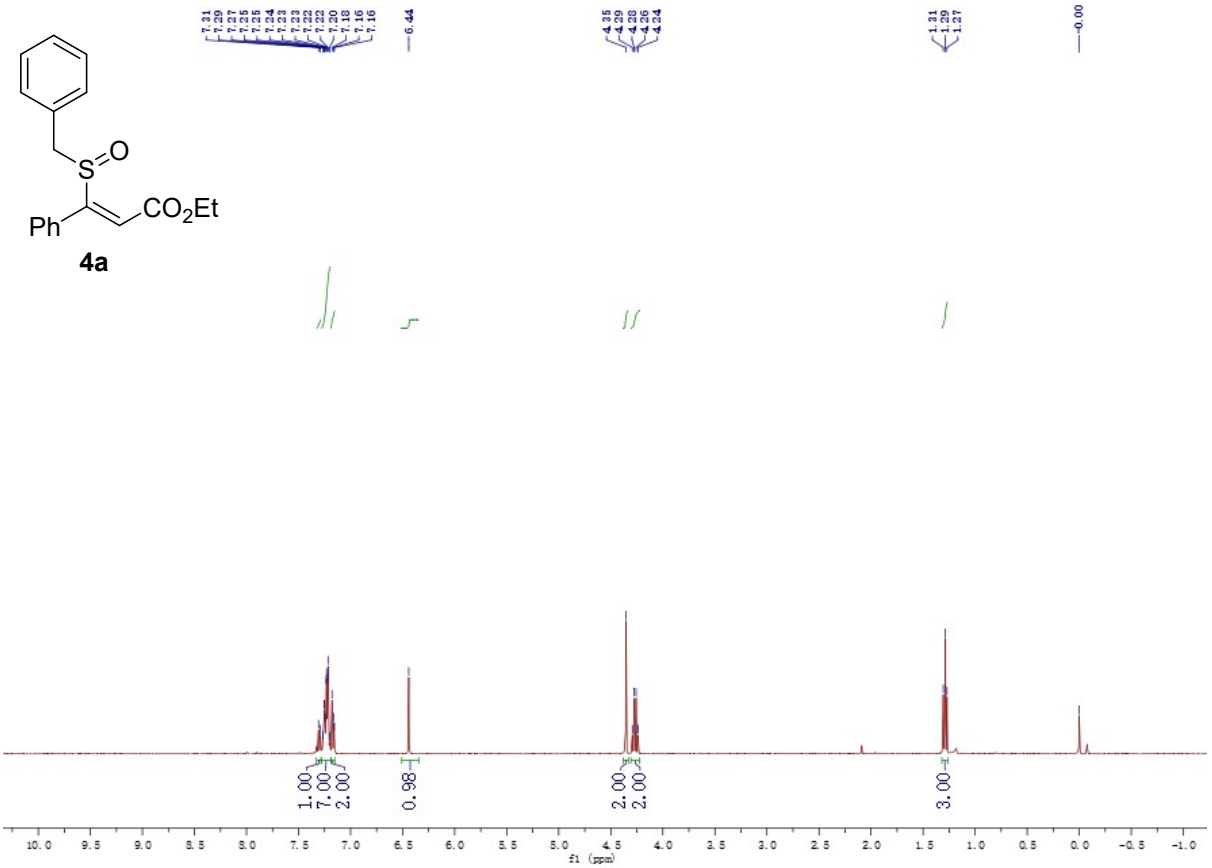
^{13}C NMR spectrum of **3al** (100 MHz, $CDCl_3$)



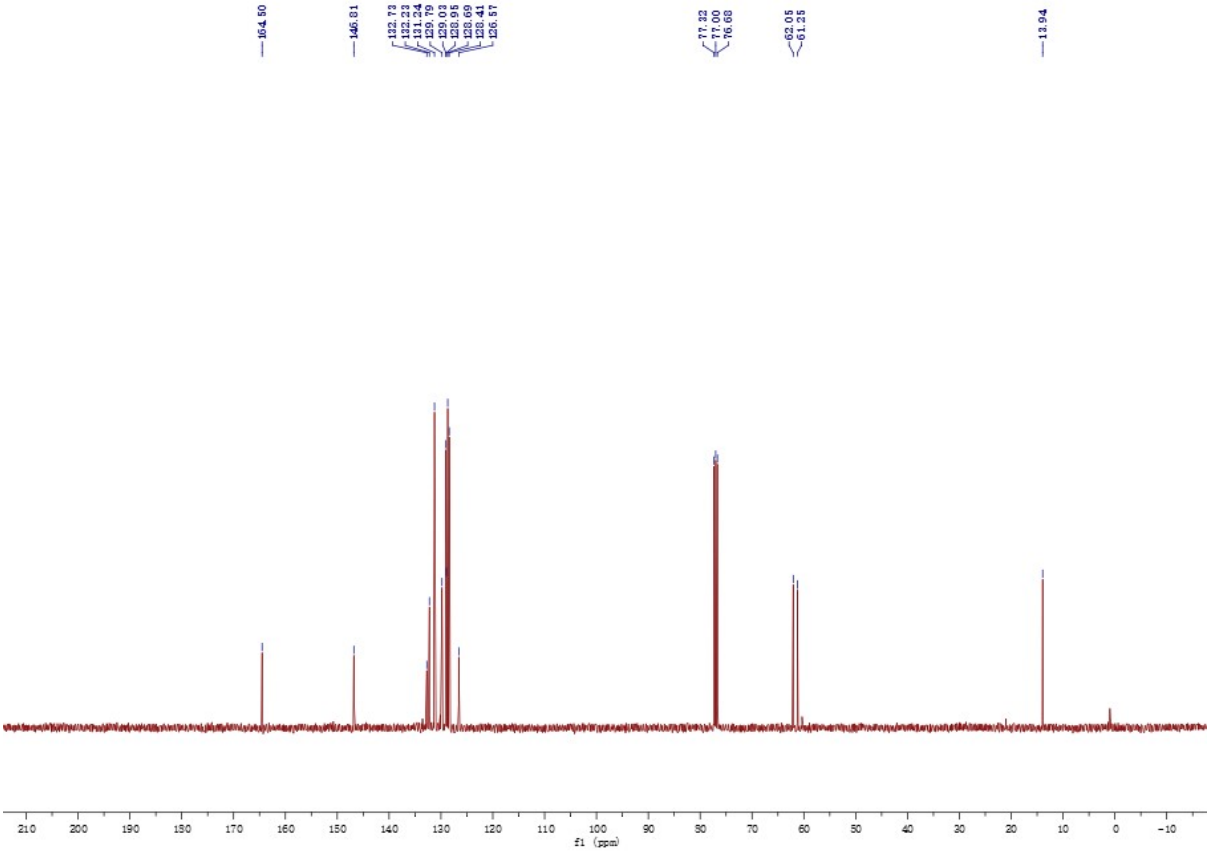
^{1}H NMR spectrum of **3am** (400 MHz, $CDCl_3$)



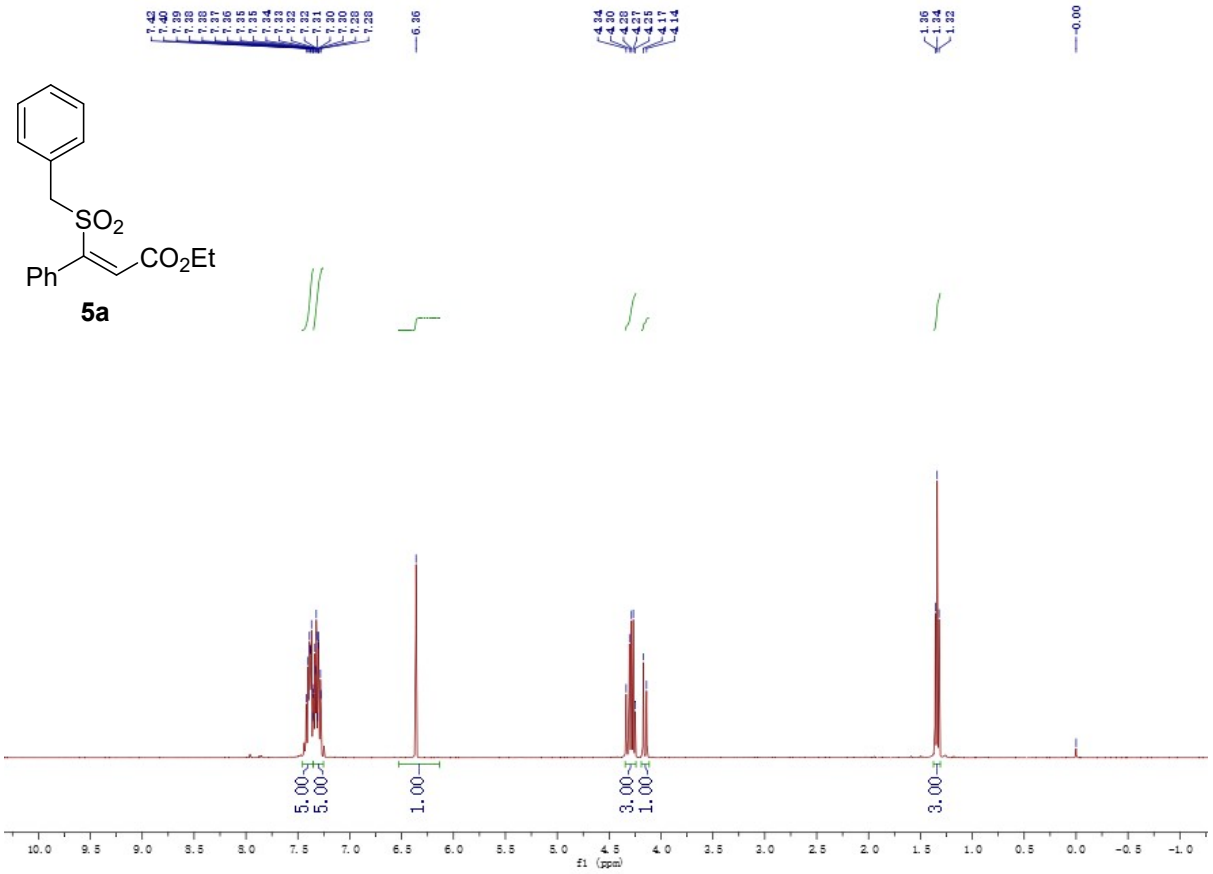
^{13}C NMR spectrum of **3am** (100 MHz, $CDCl_3$)



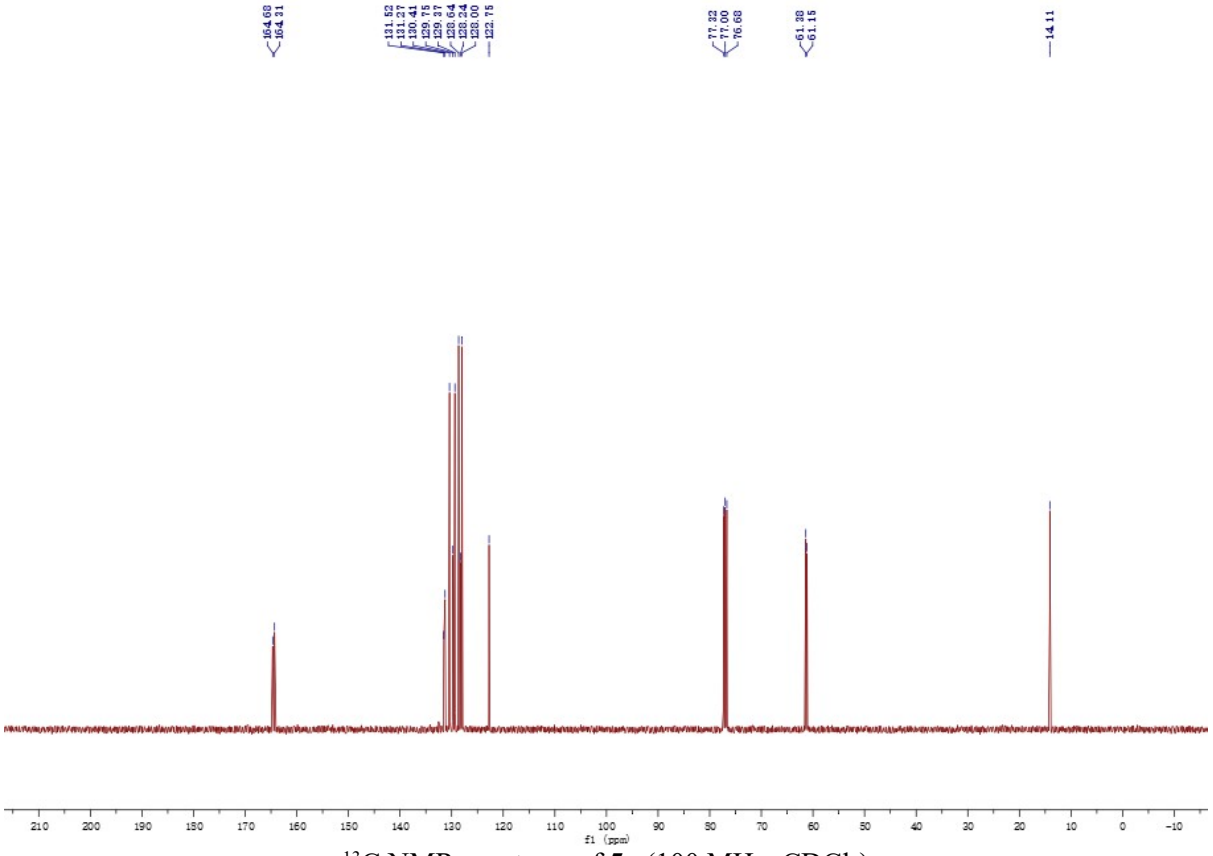
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



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



^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **5a** (100 MHz, $CDCl_3$)