

Supporting Information for

Triflic Acid-Catalyzed Cycloisomerization of 1,6-enynes: Facile Access to Carbo- and Azaheterocycles

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School of Chemistry and Chemical Engineering and Guangdong Cosmetics Engineering & Technology Research Center, Guangdong Pharmaceutical University, Zhongshan 528458, P.R. of China

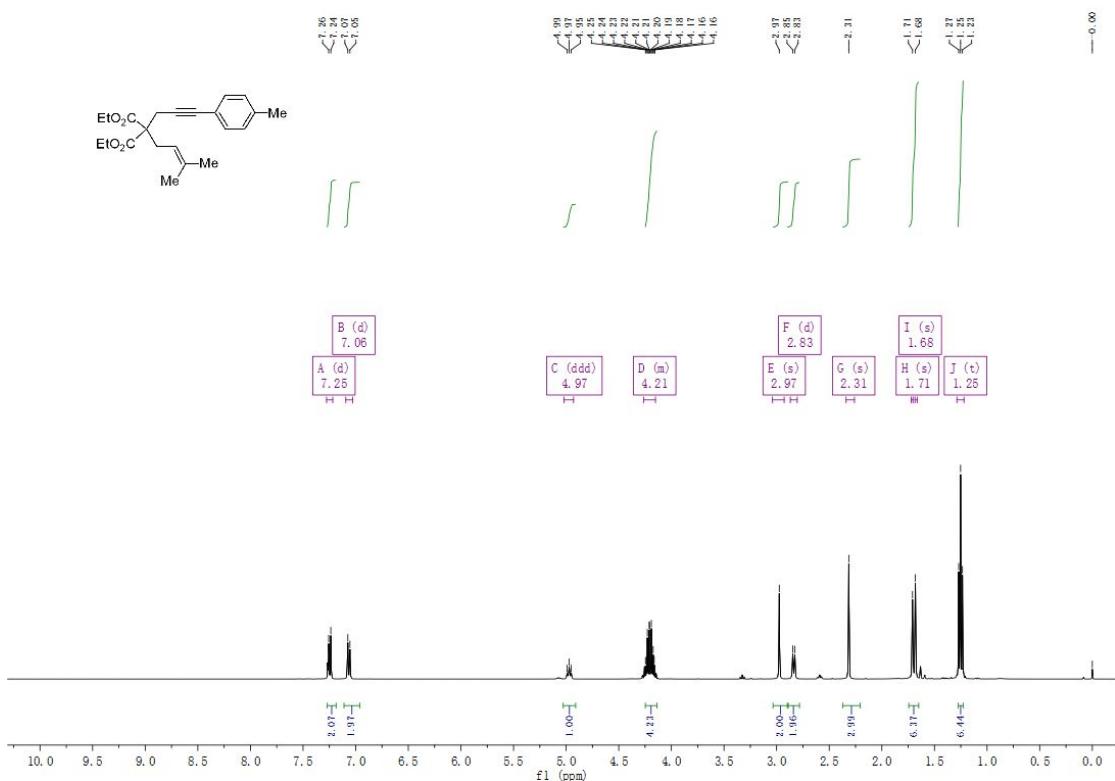
E-mail: yuyue@gdpu.edu.cn.; caohua@gdpu.edu.cn

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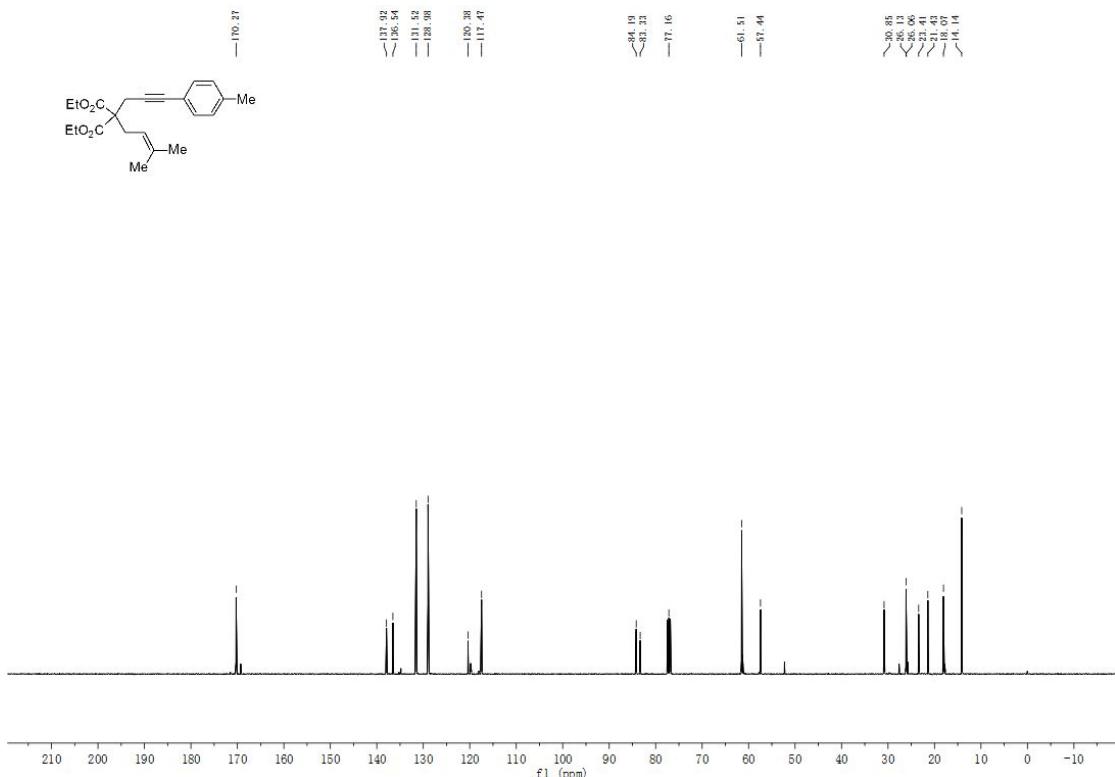
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1. NMR spectra for new compounds

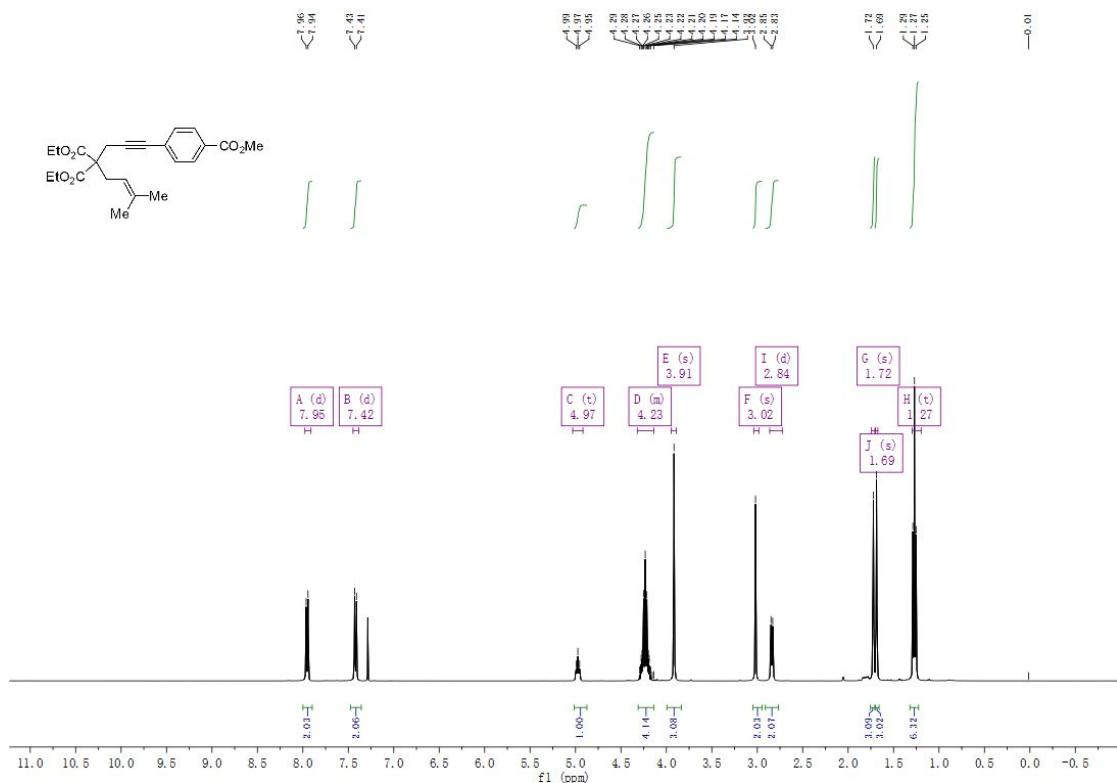
¹H NMR (400 MHz, CDCl₃) spectrum of compound **1b**



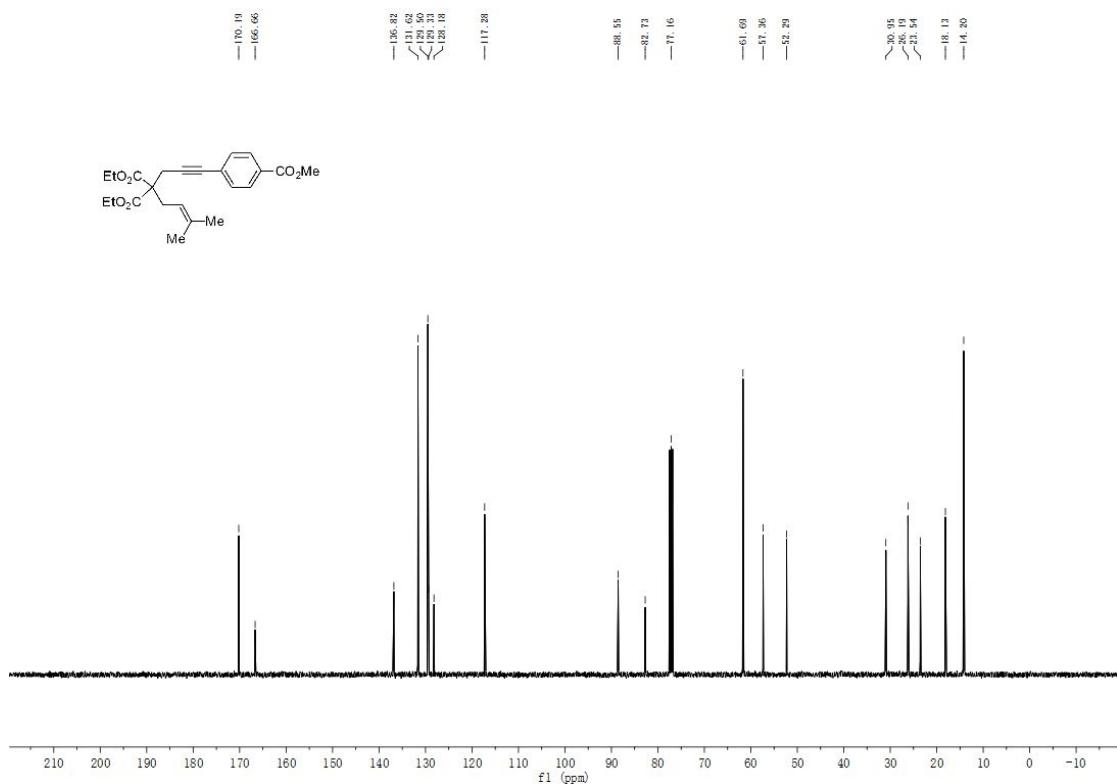
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **1b**



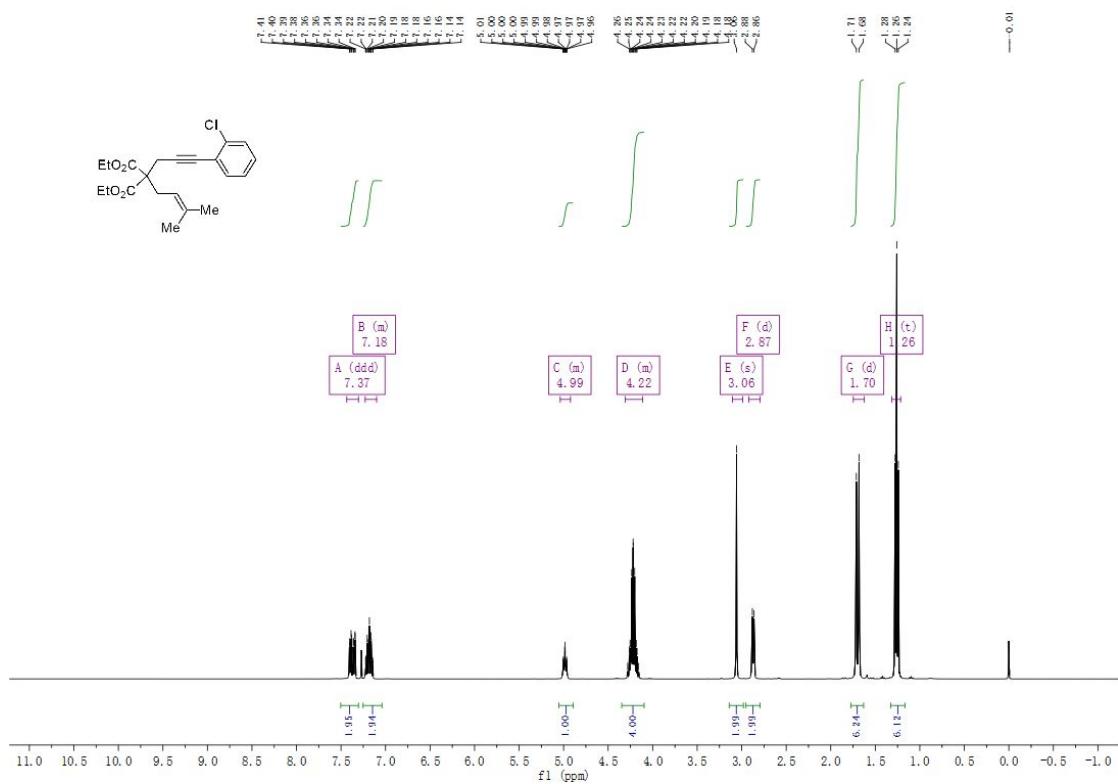
¹H NMR (400 MHz, CDCl₃) spectrum of compound **1f**



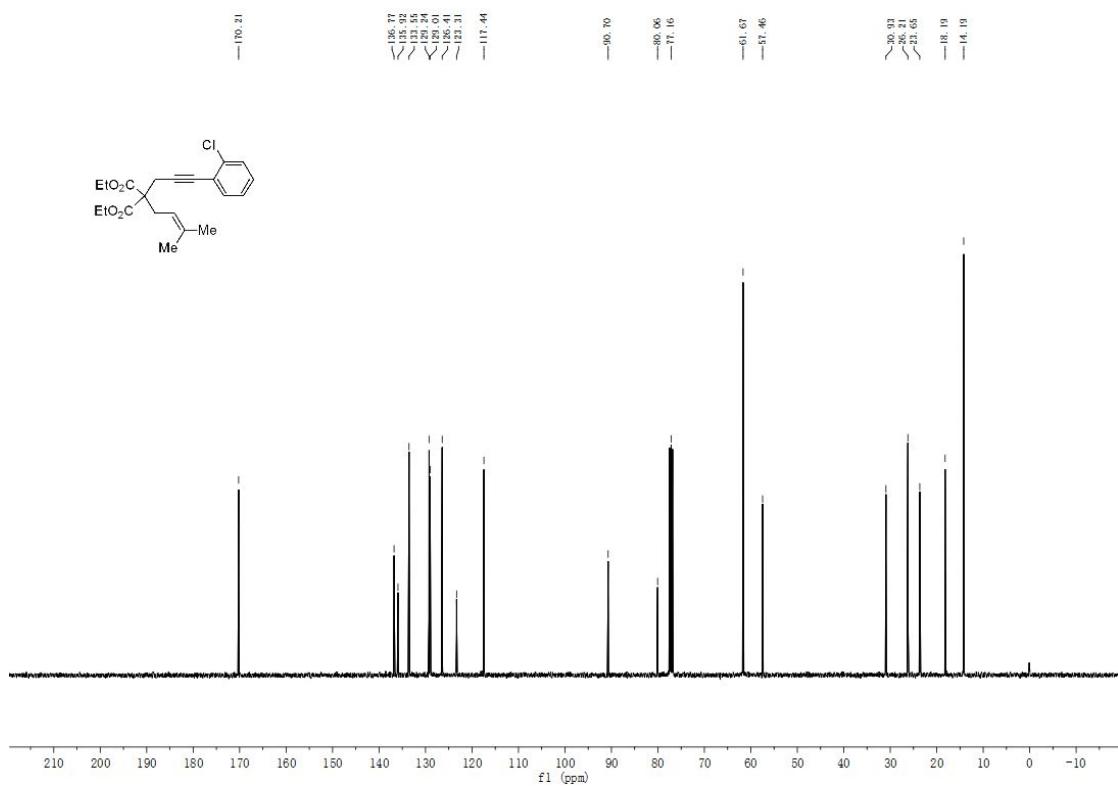
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **1f**



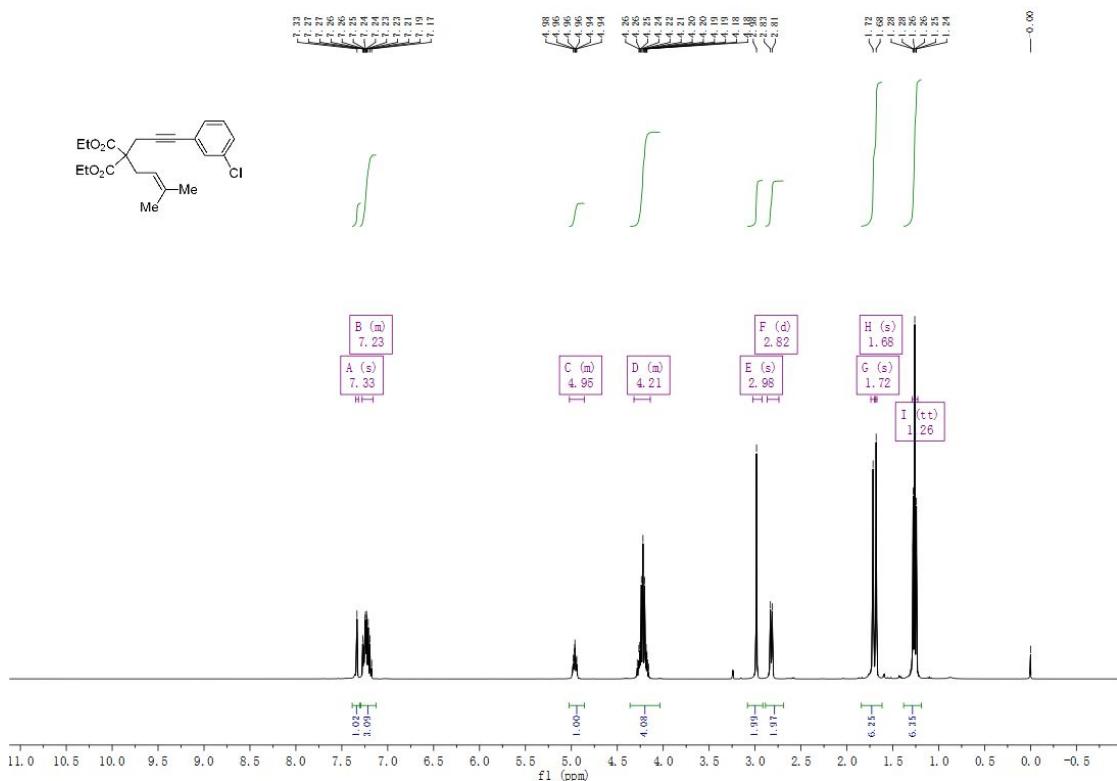
¹H NMR (400 MHz, CDCl₃) spectrum of compound **1g**



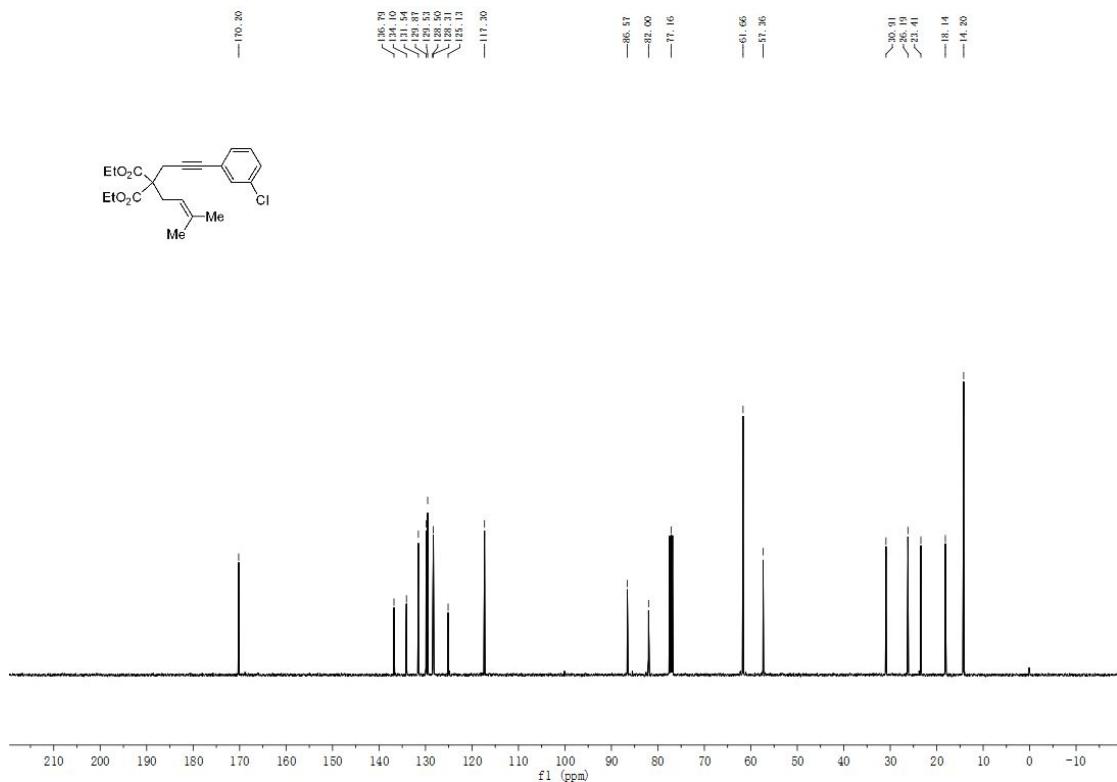
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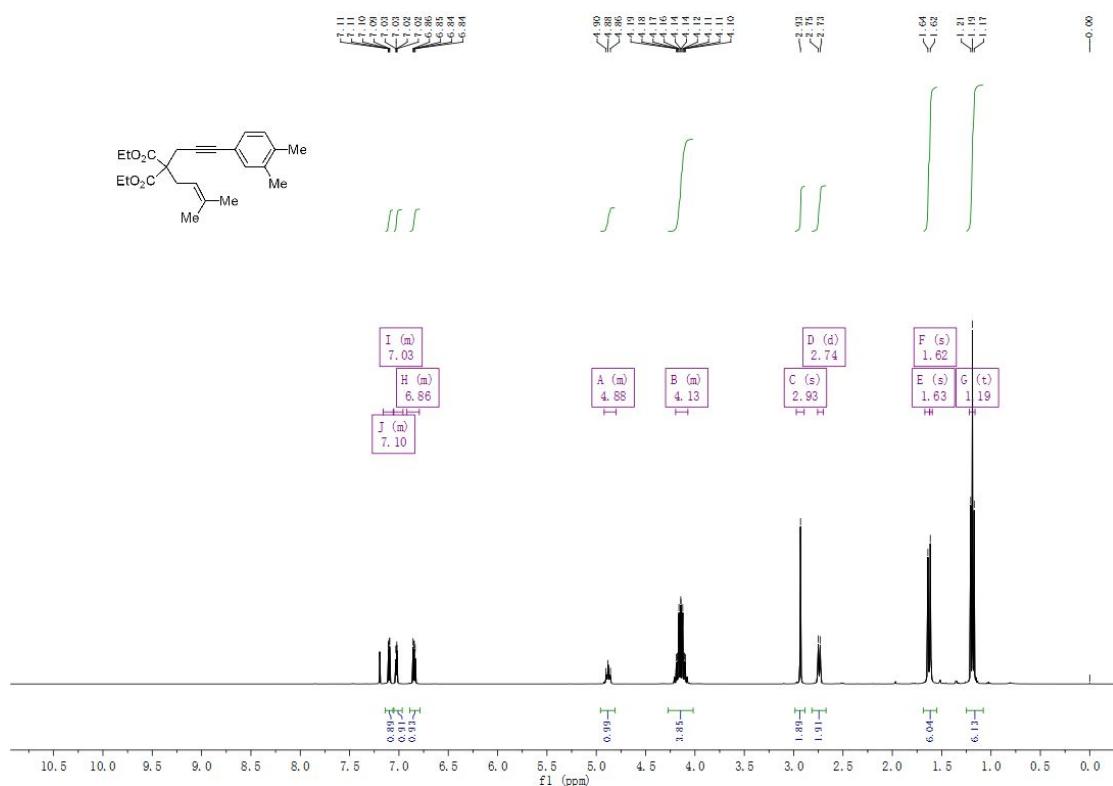
¹H NMR (400 MHz, CDCl₃) spectrum of compound **1h**



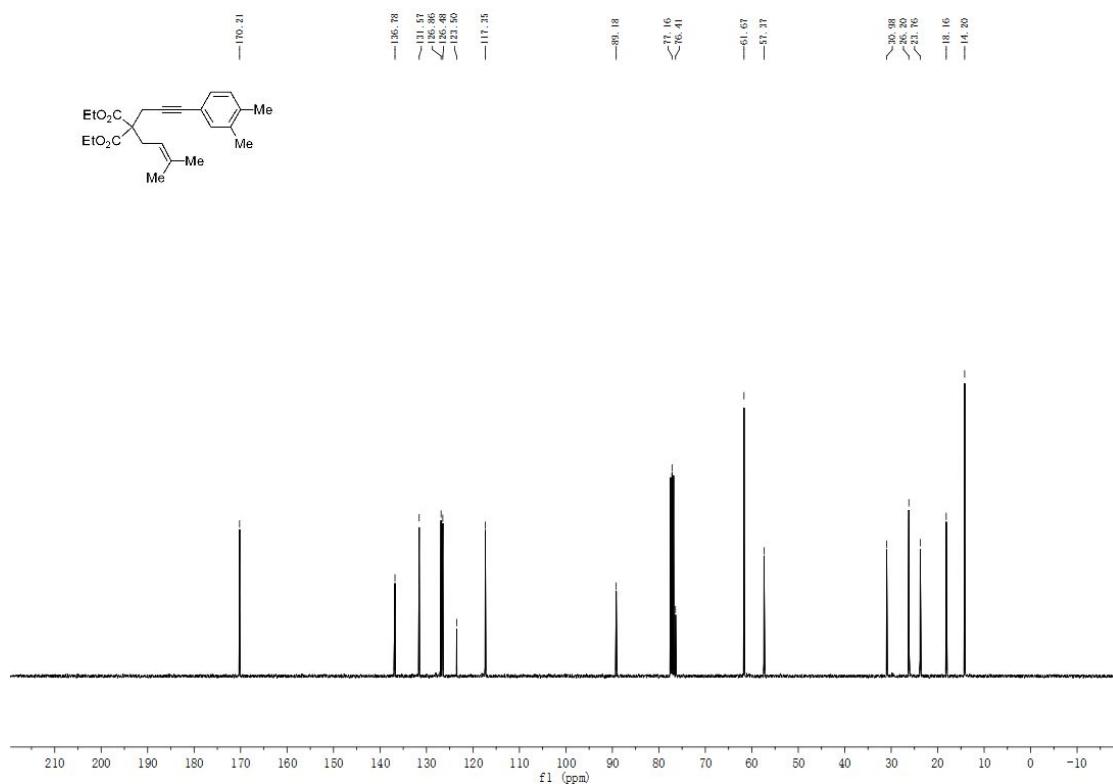
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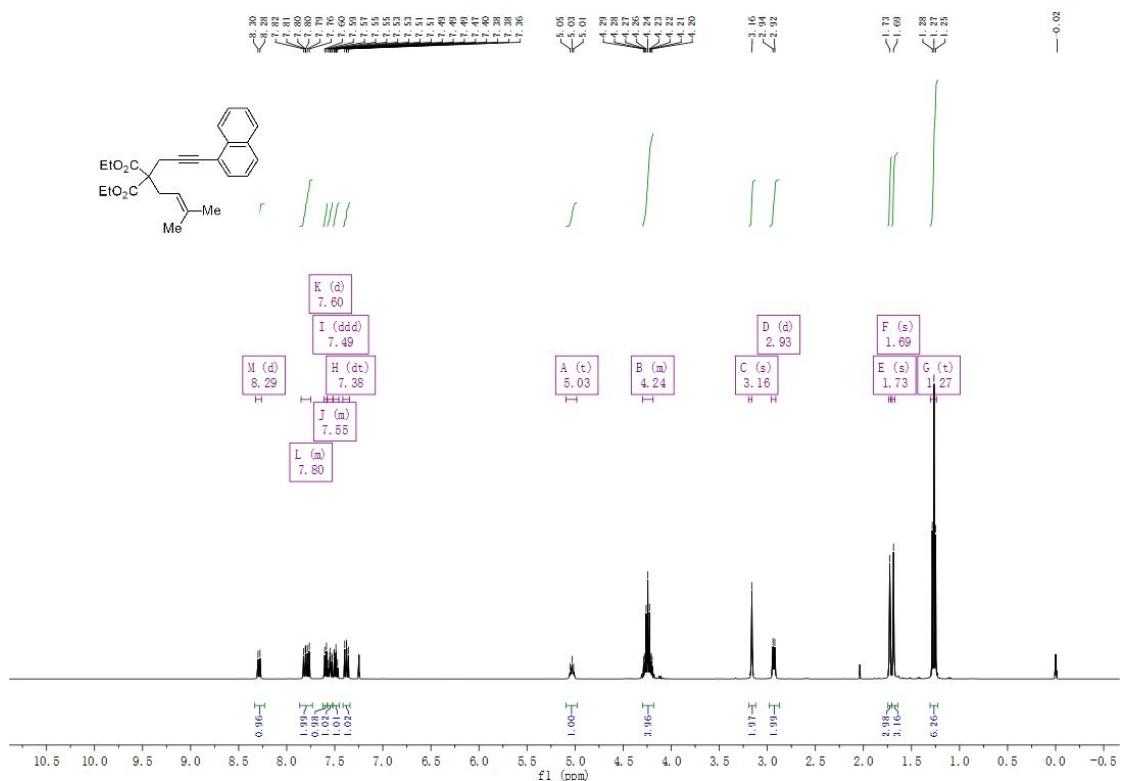
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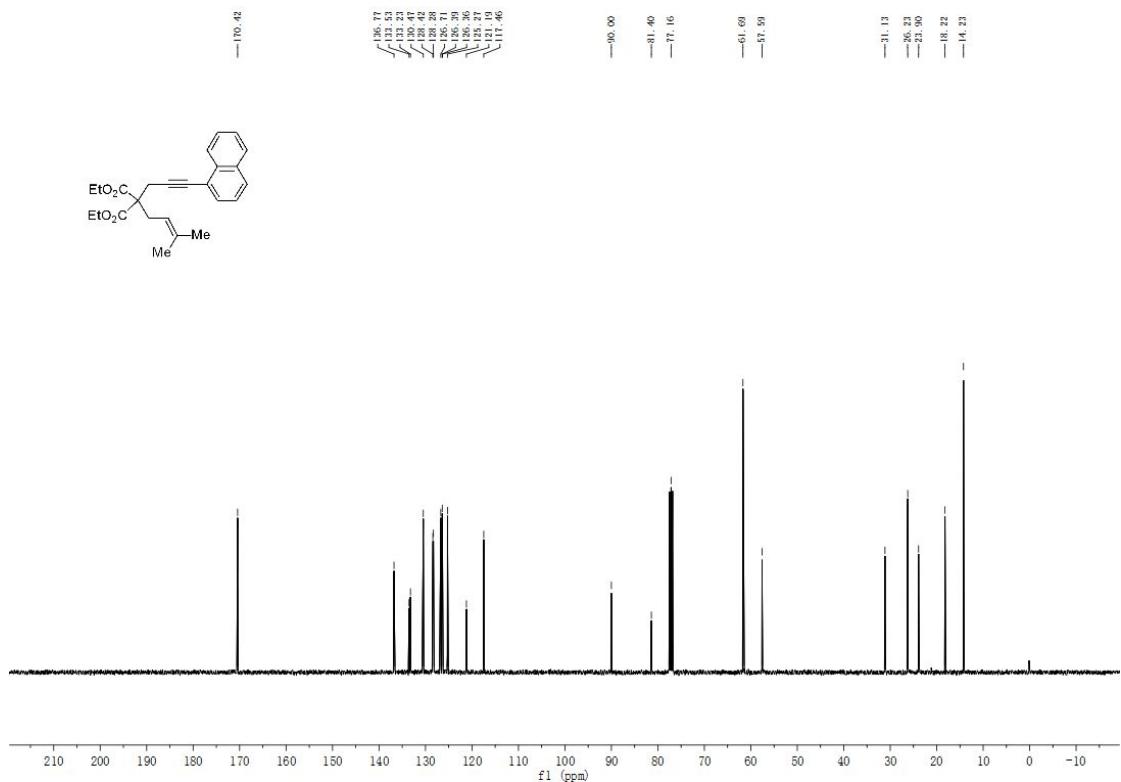
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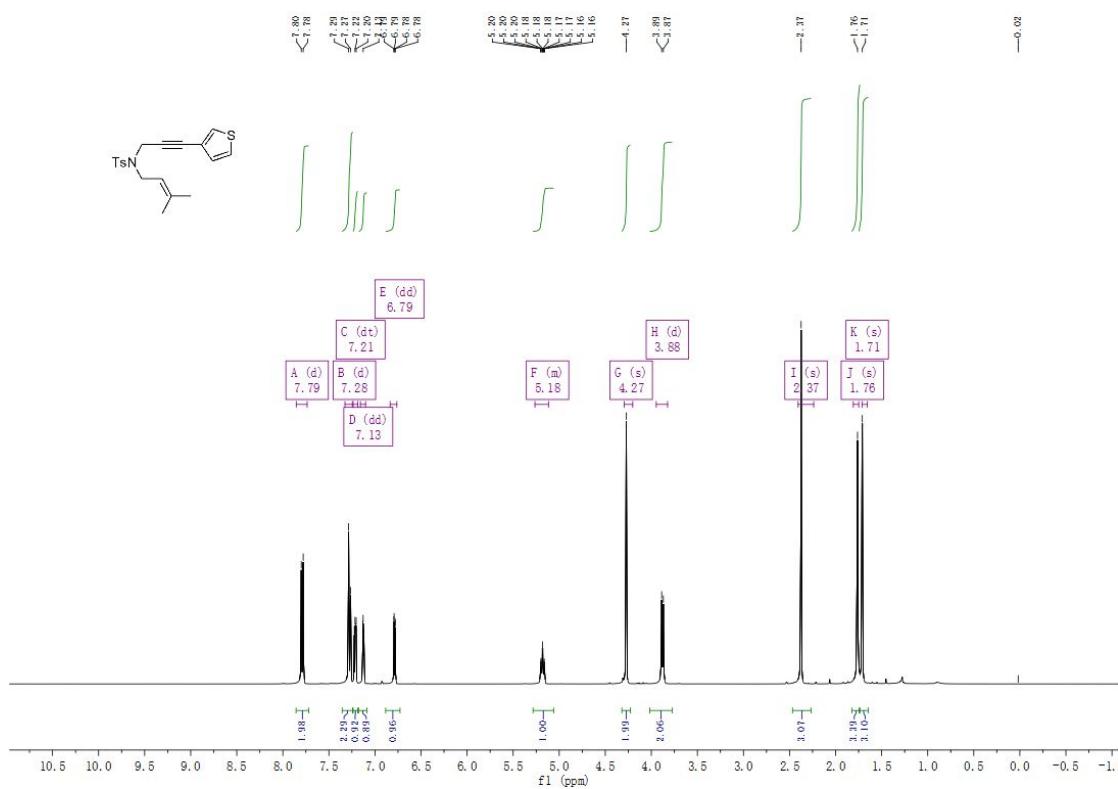
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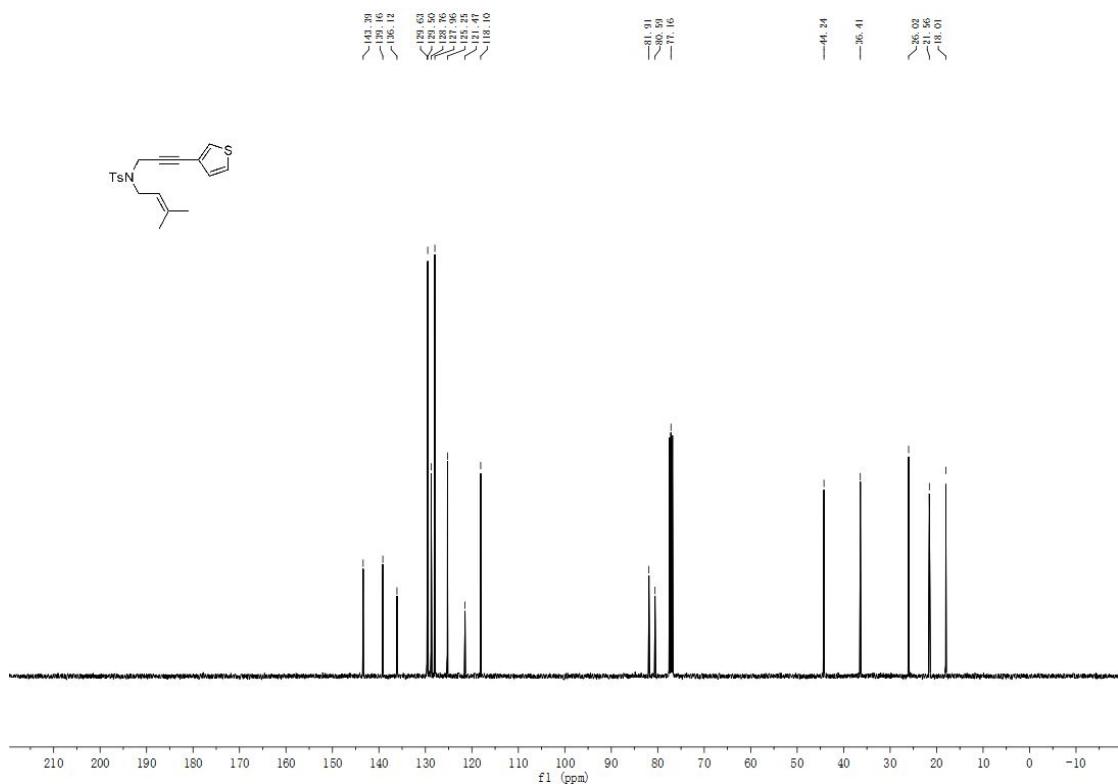
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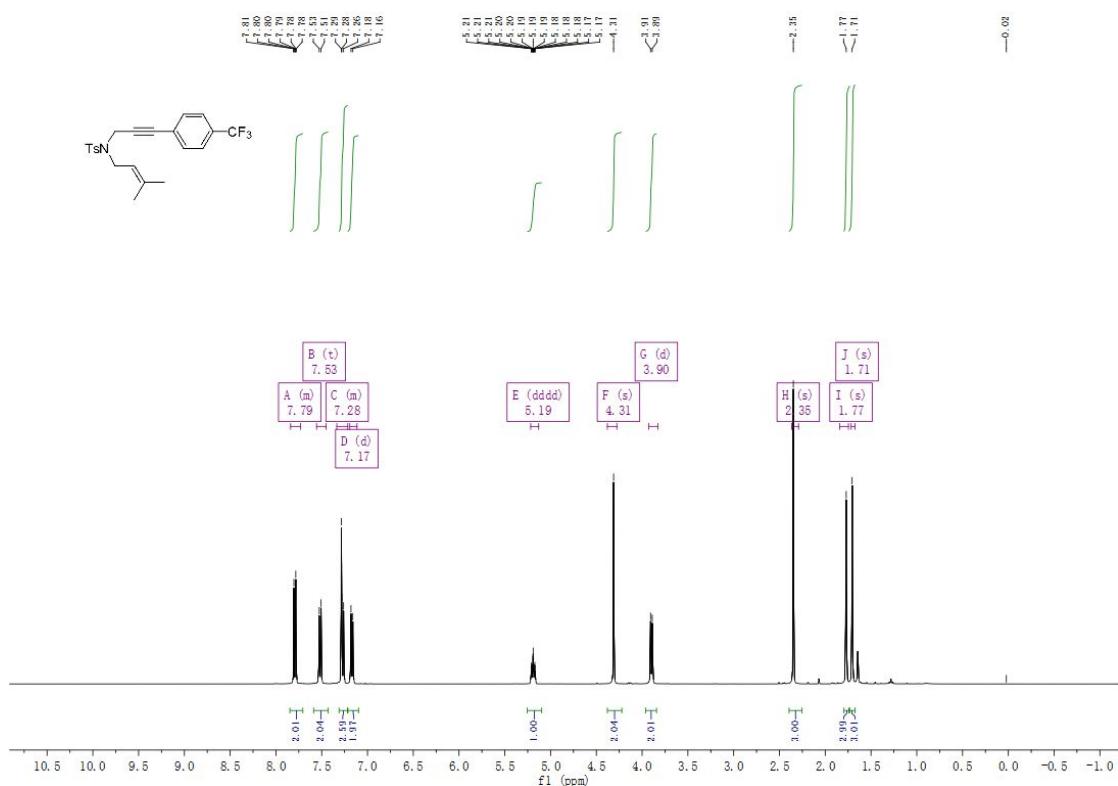
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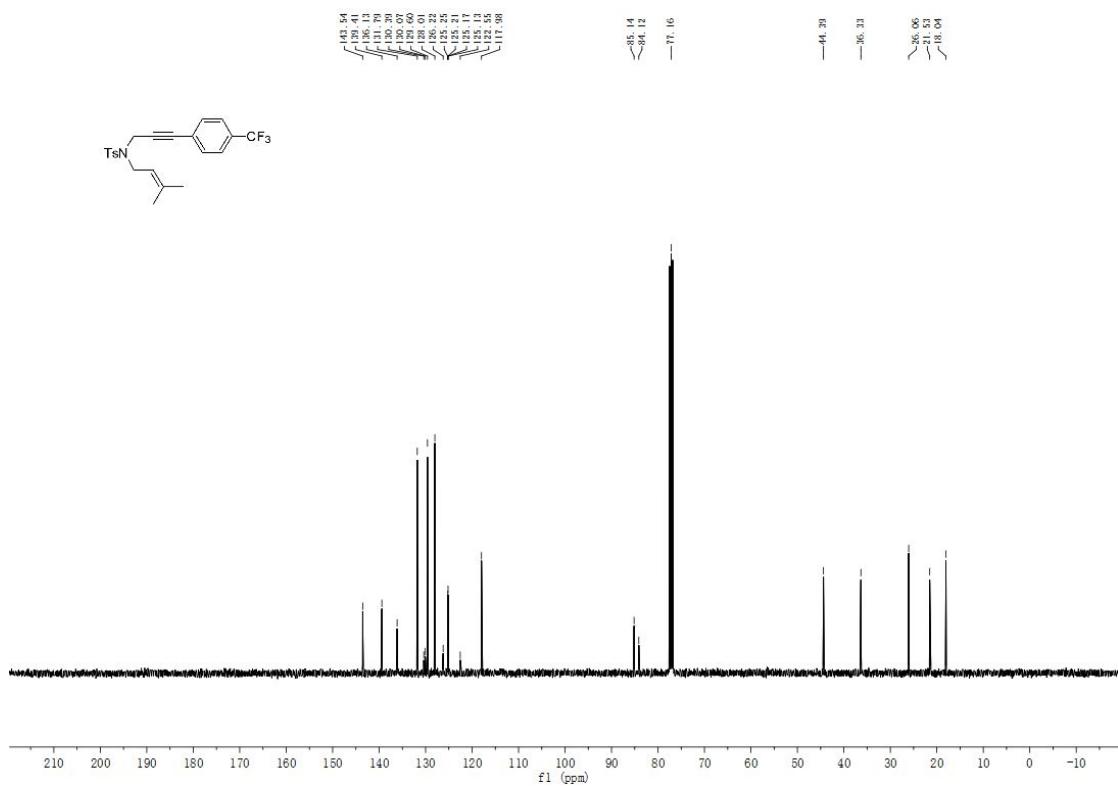
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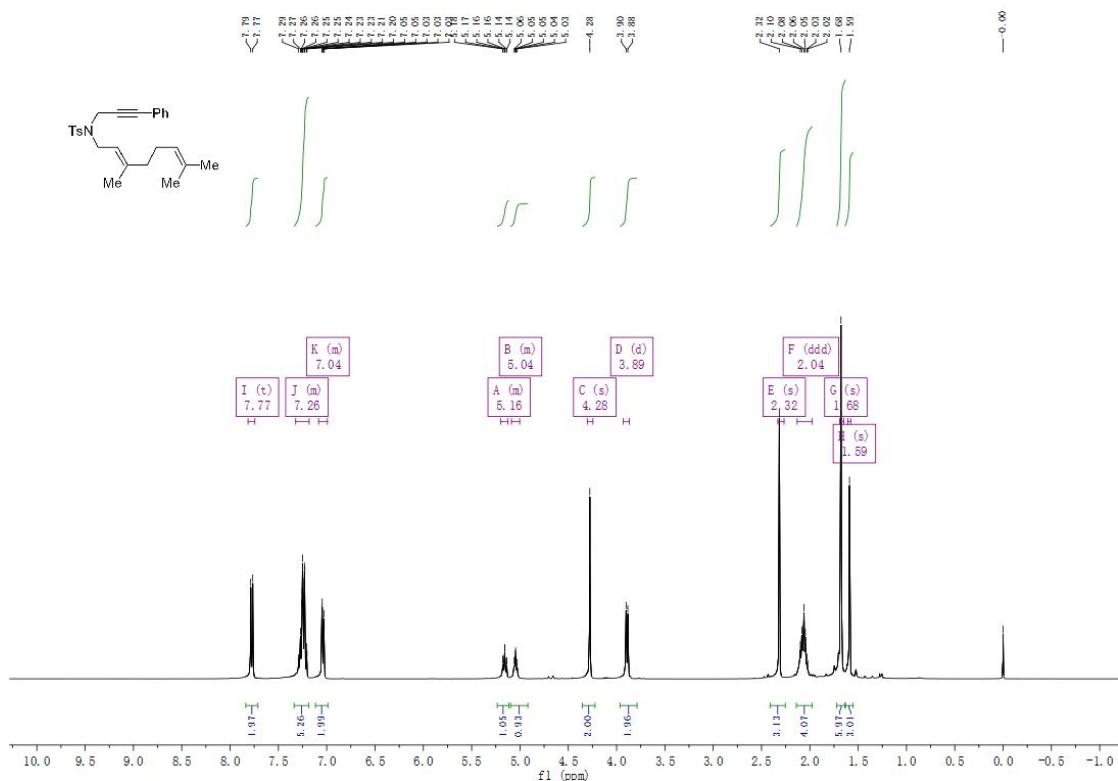
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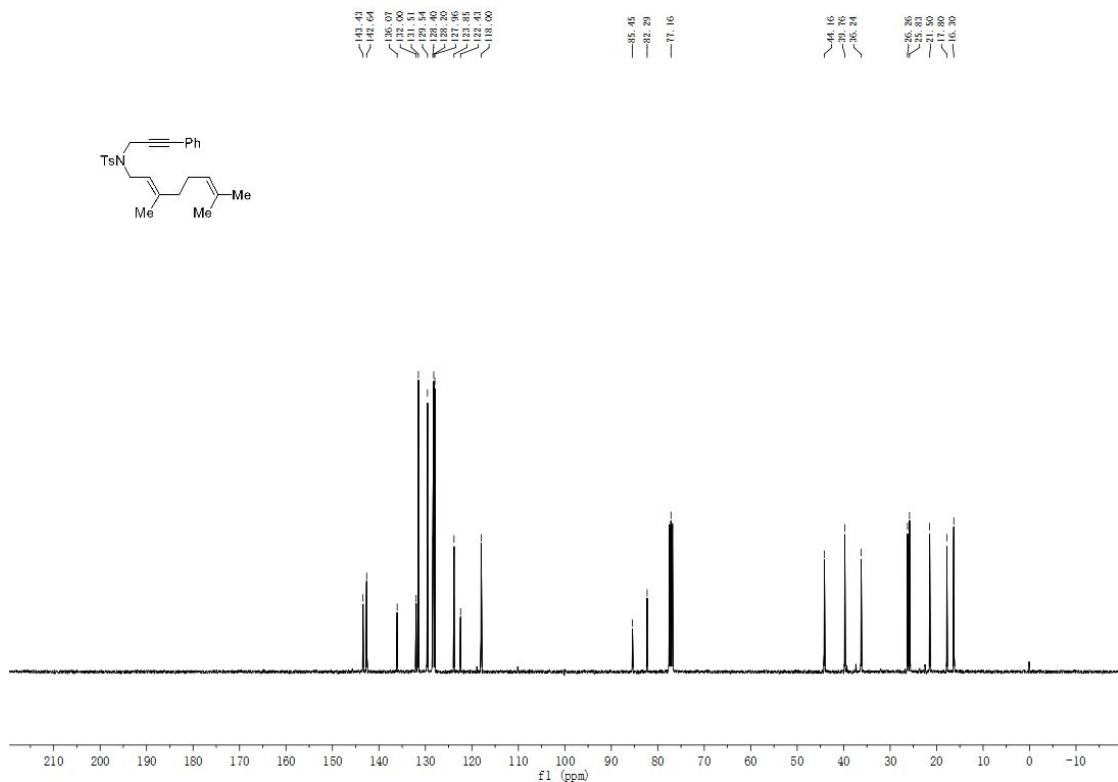
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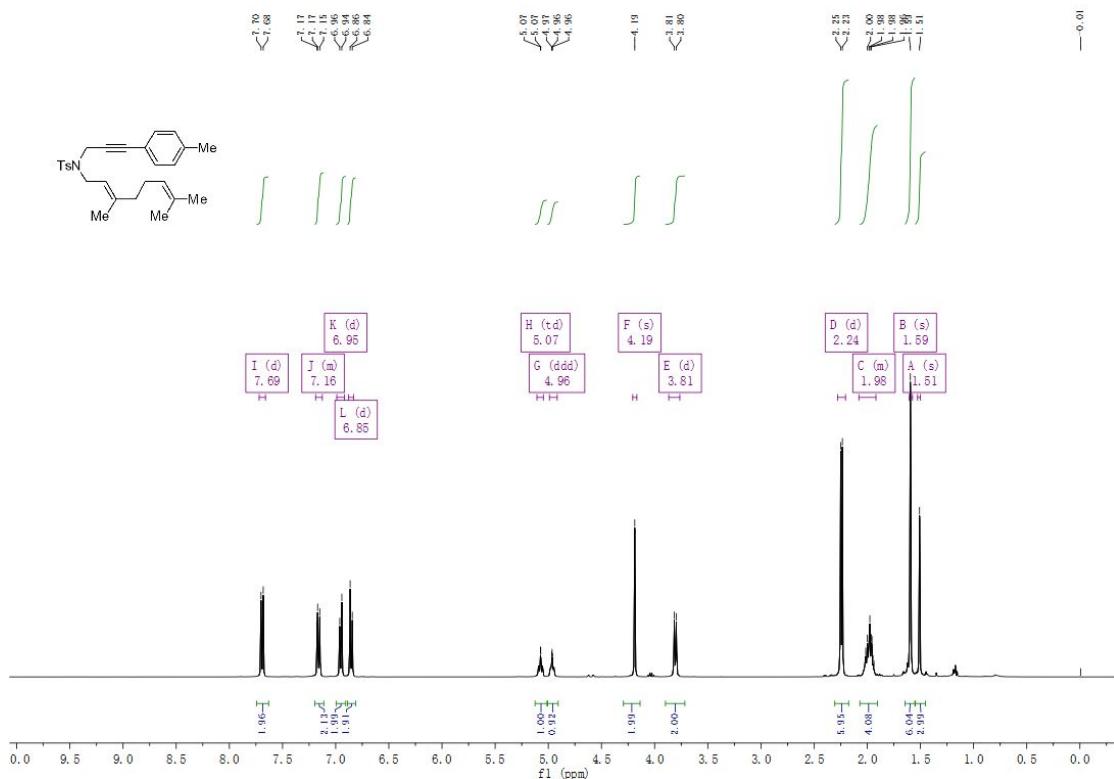
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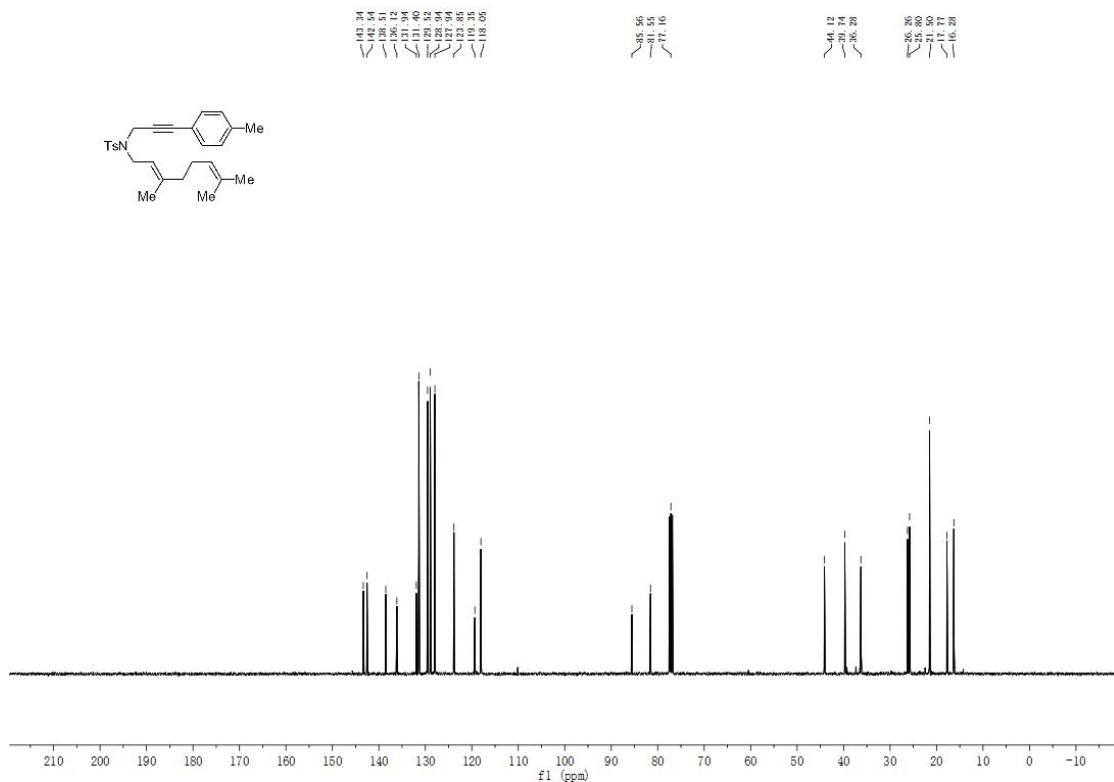
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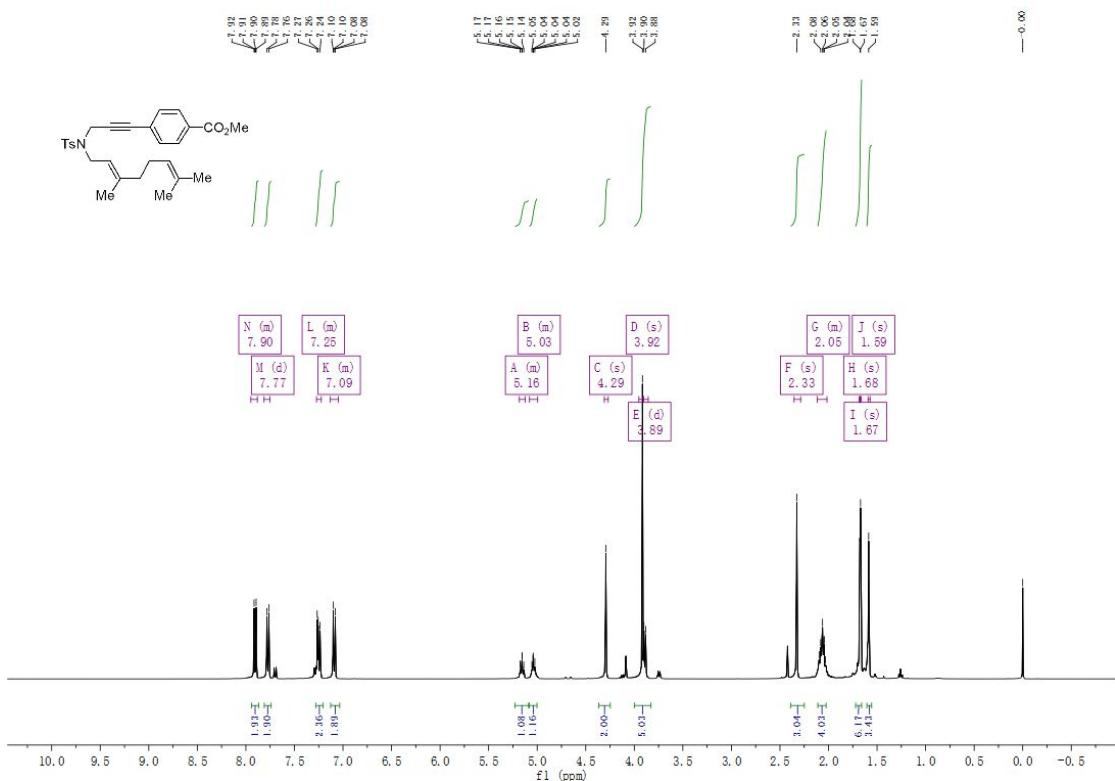
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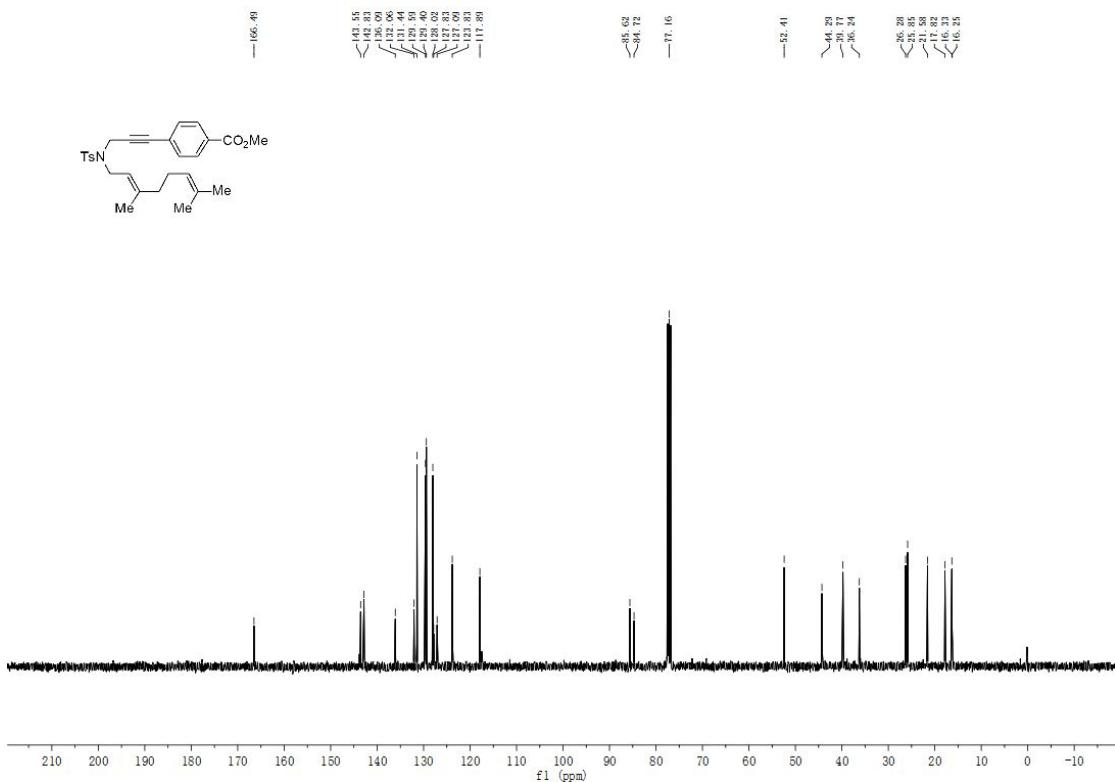
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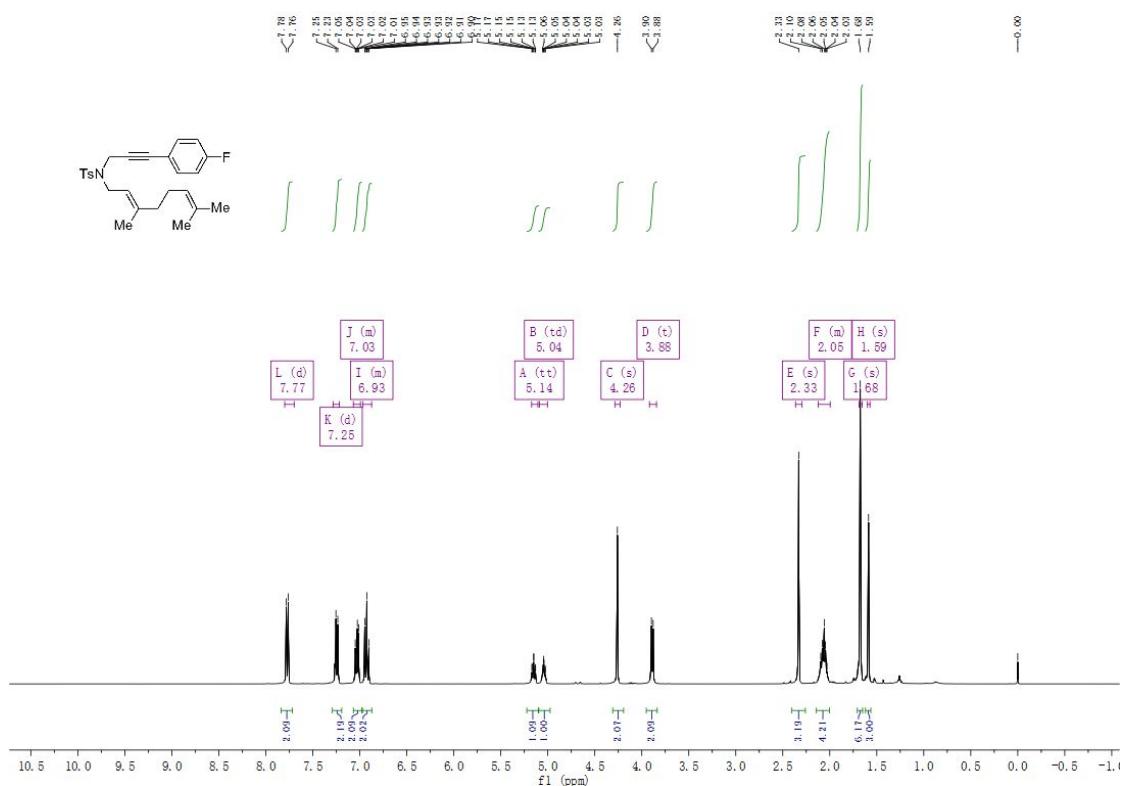
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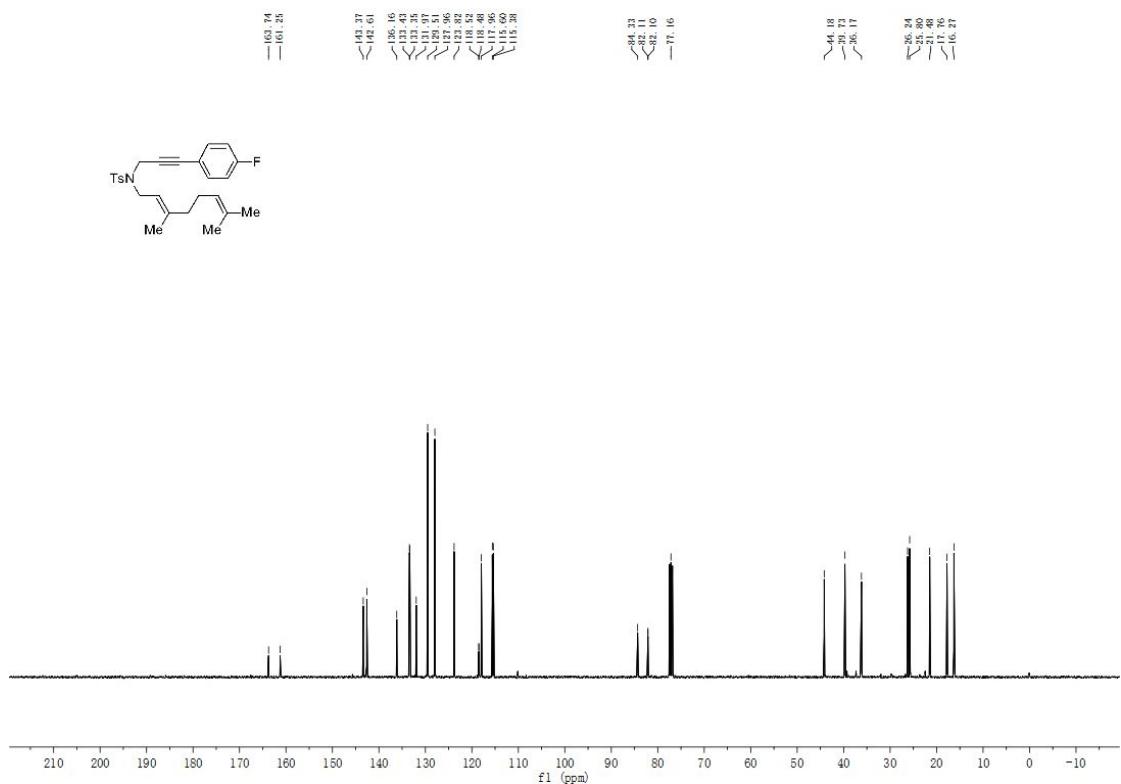
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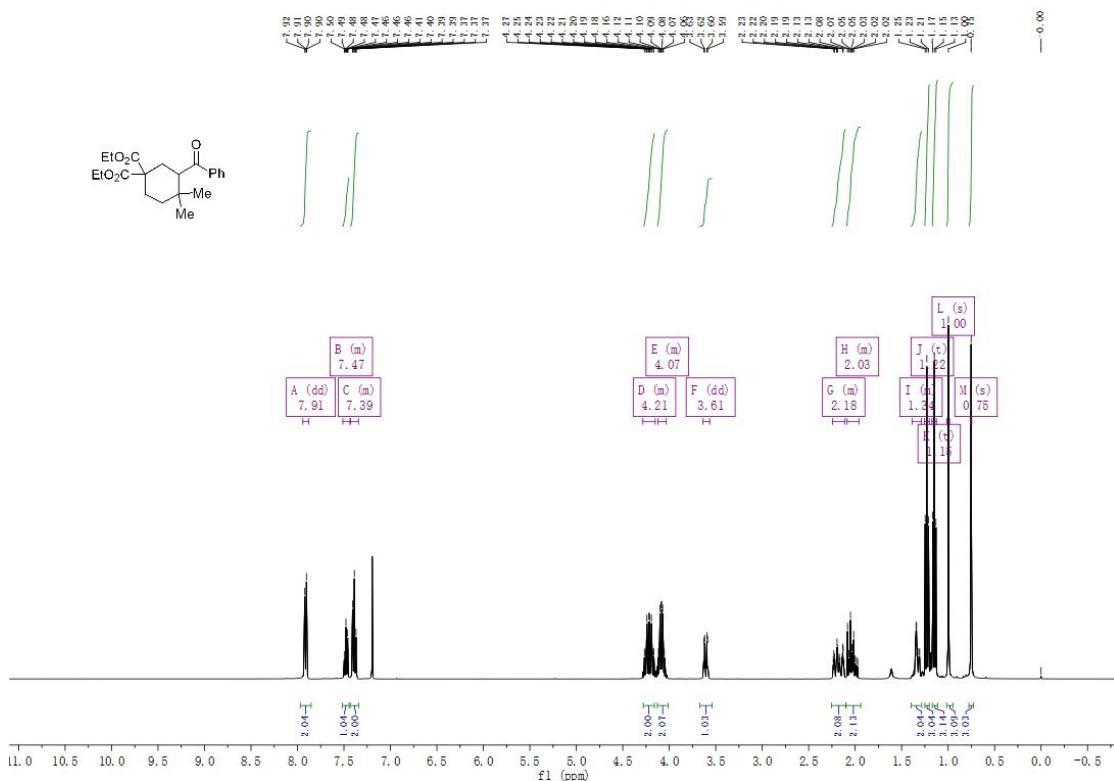
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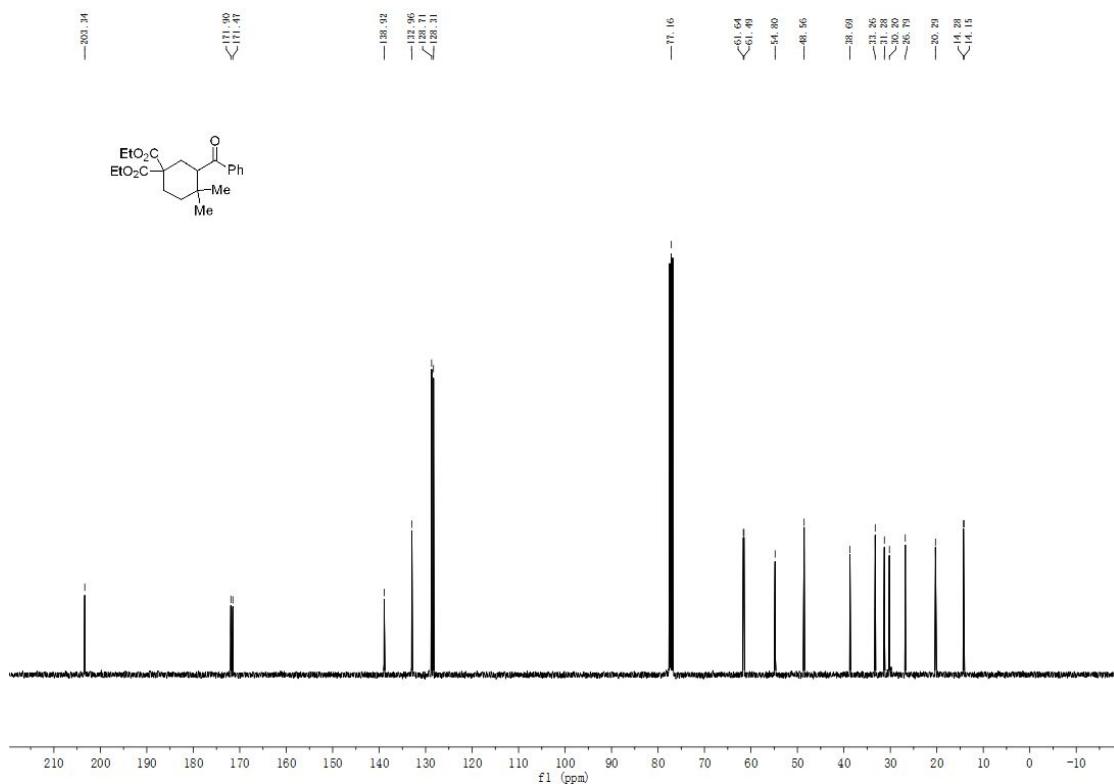
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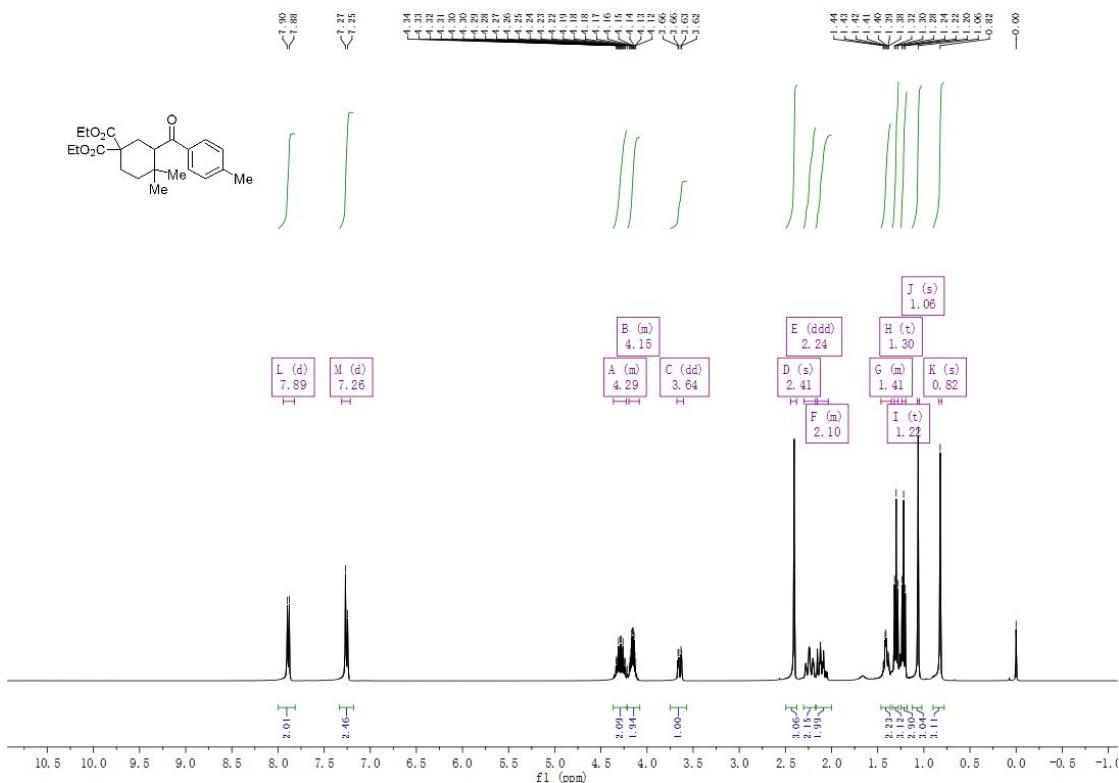
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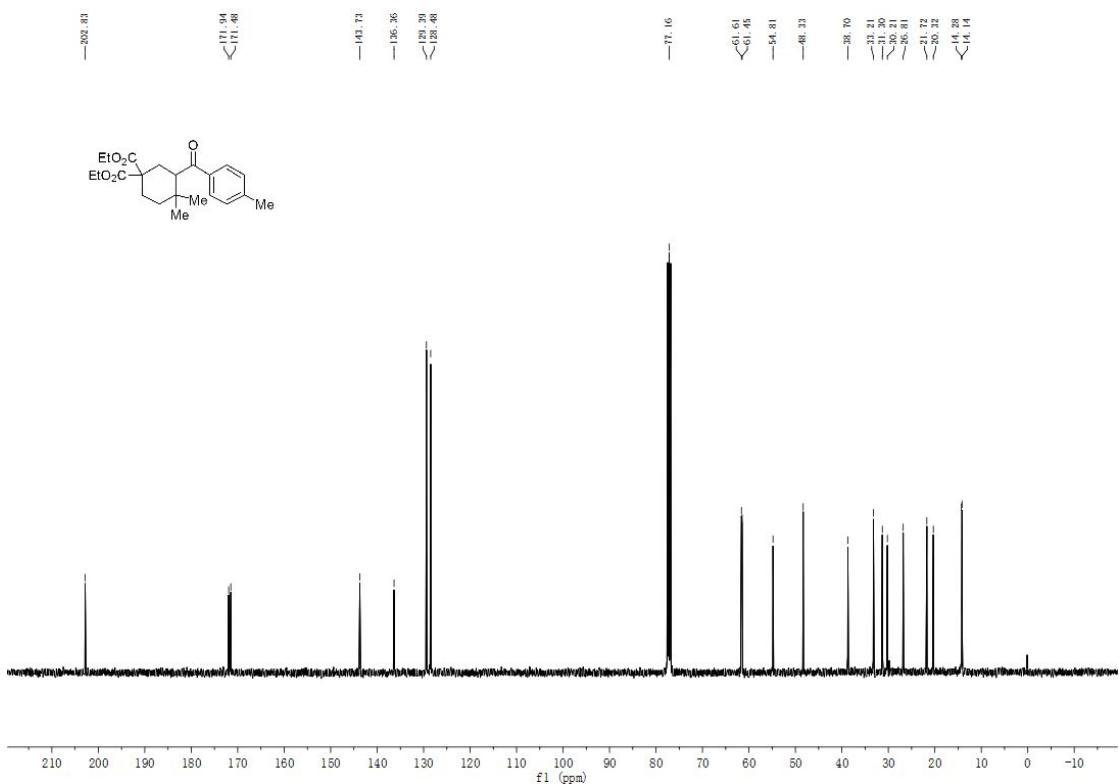
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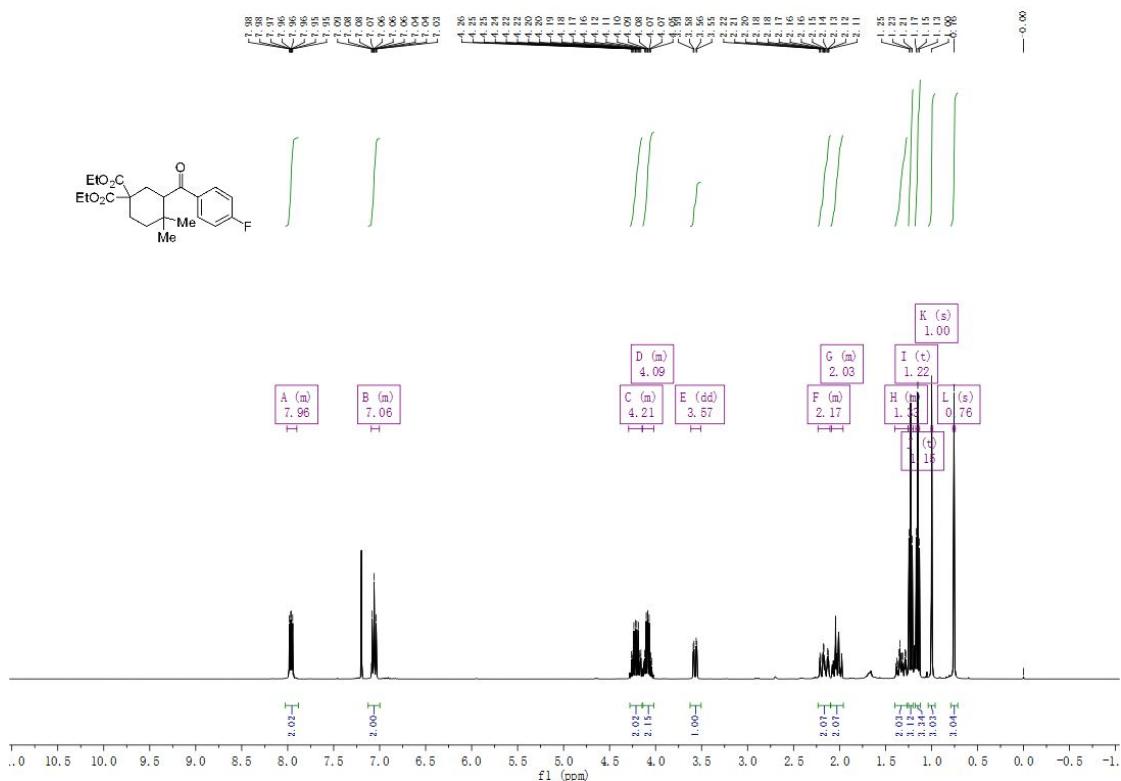
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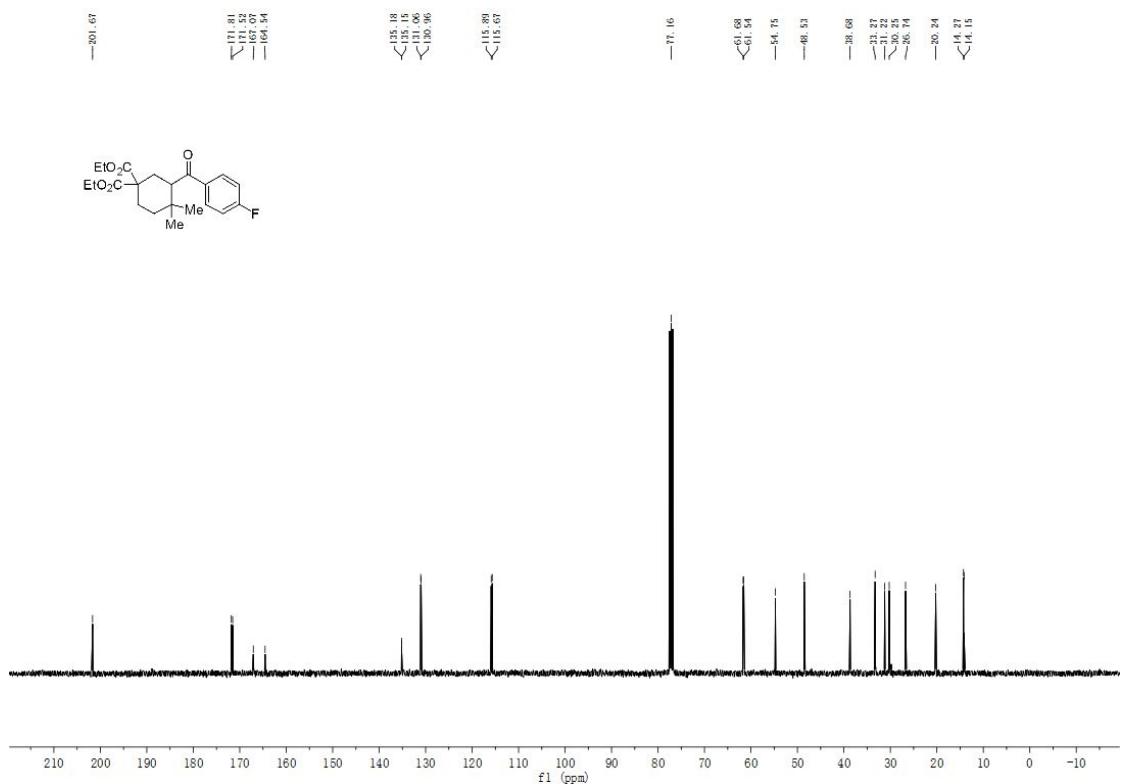
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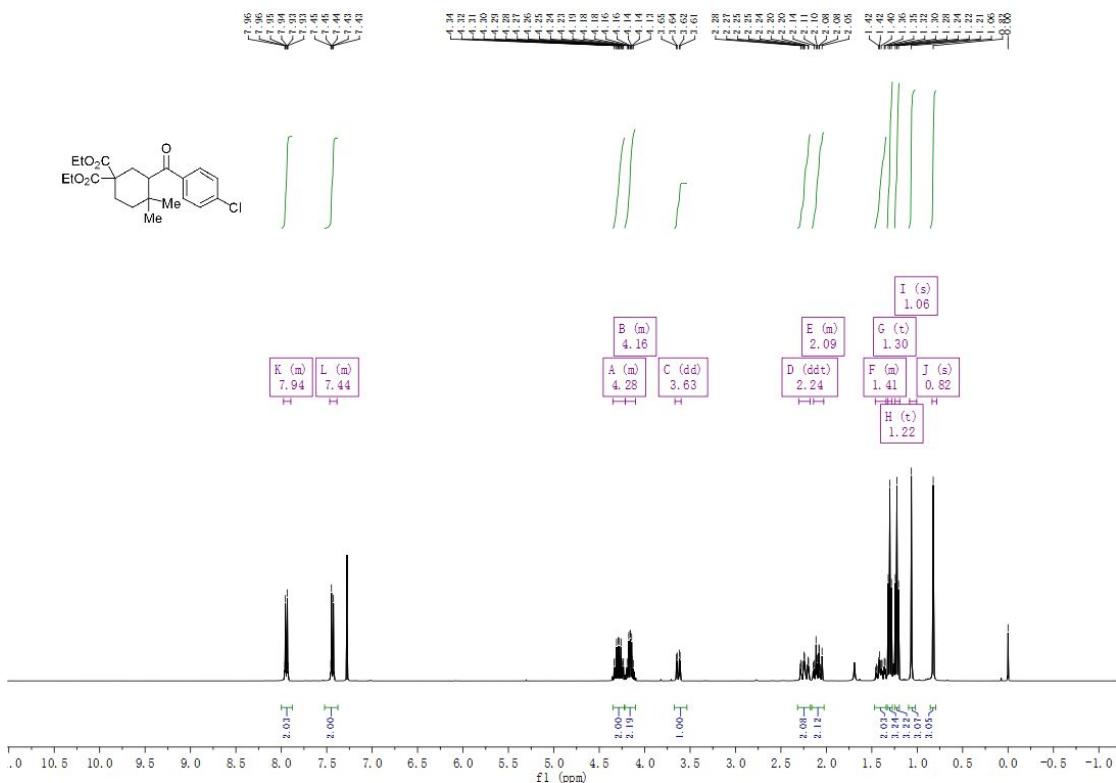
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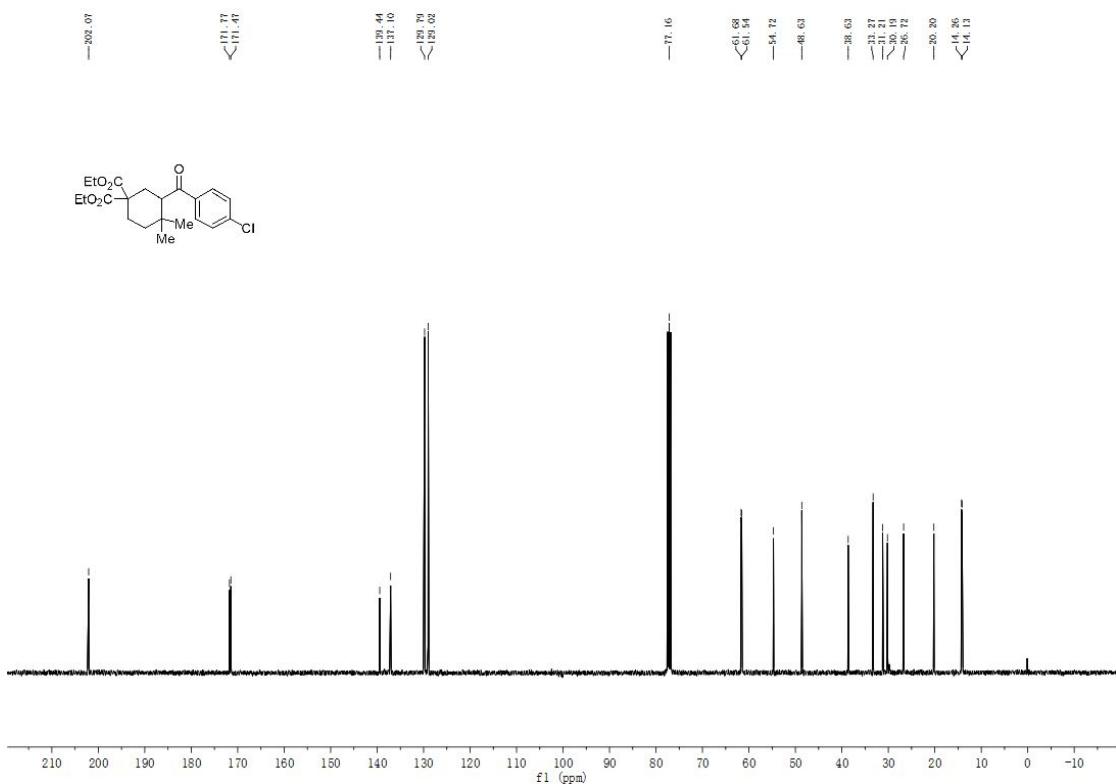
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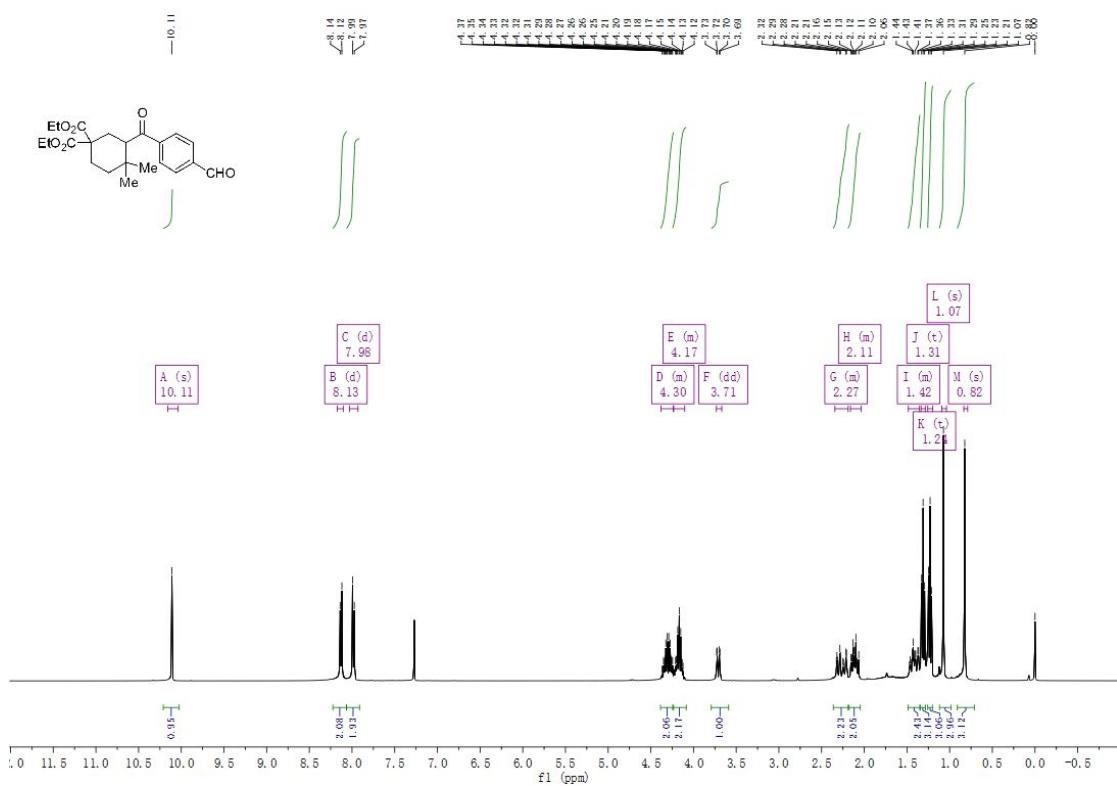
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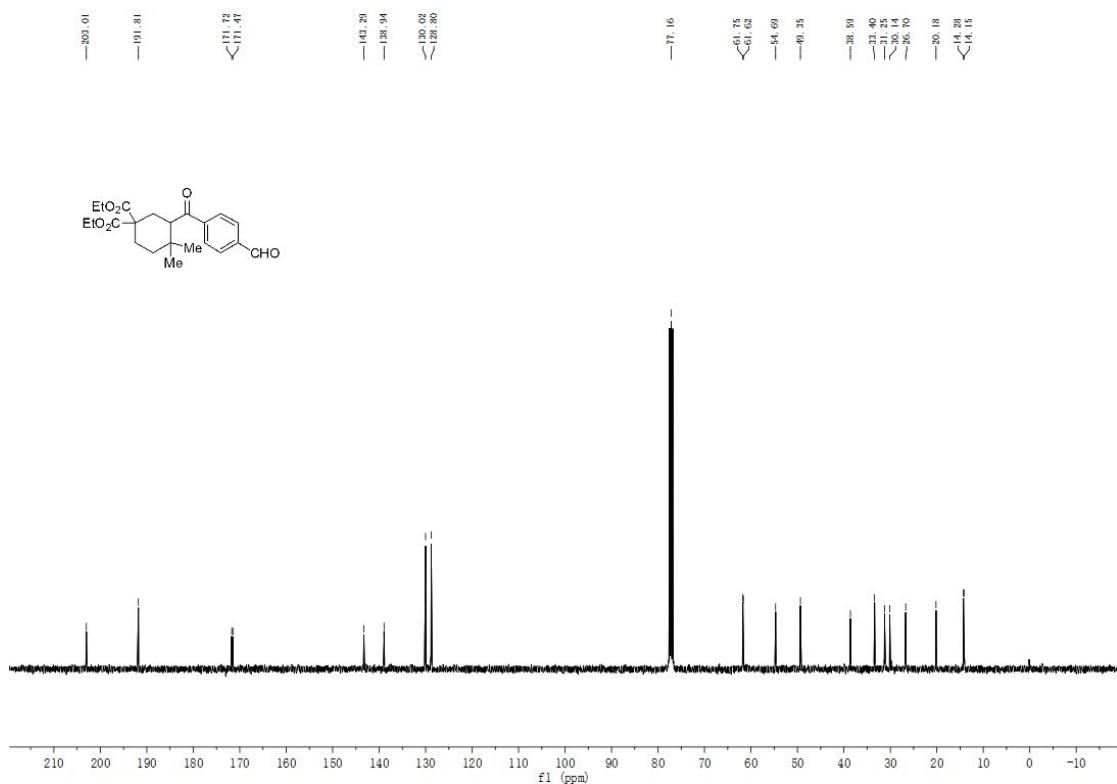
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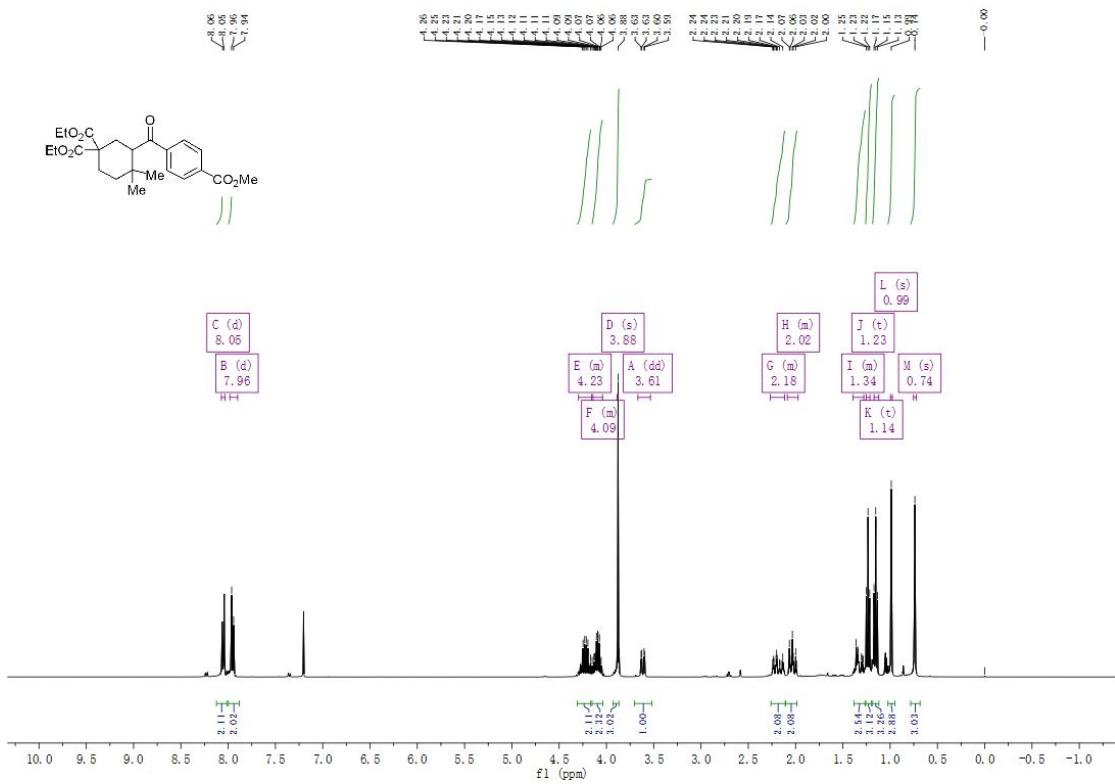
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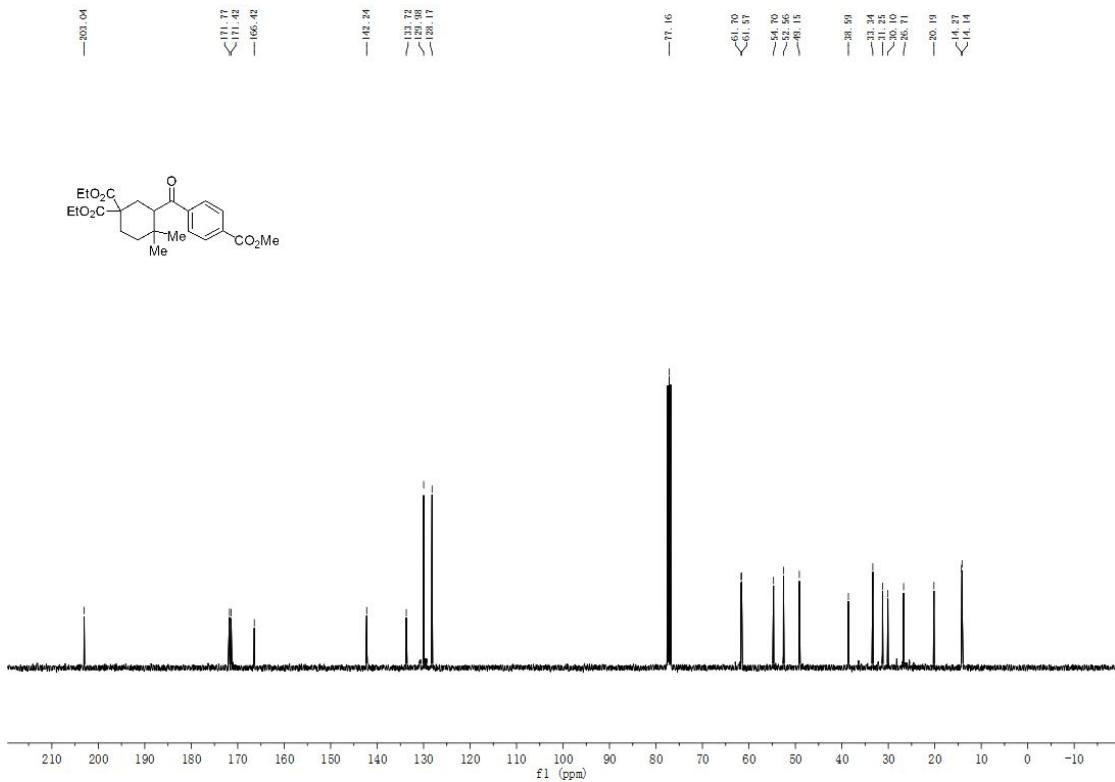
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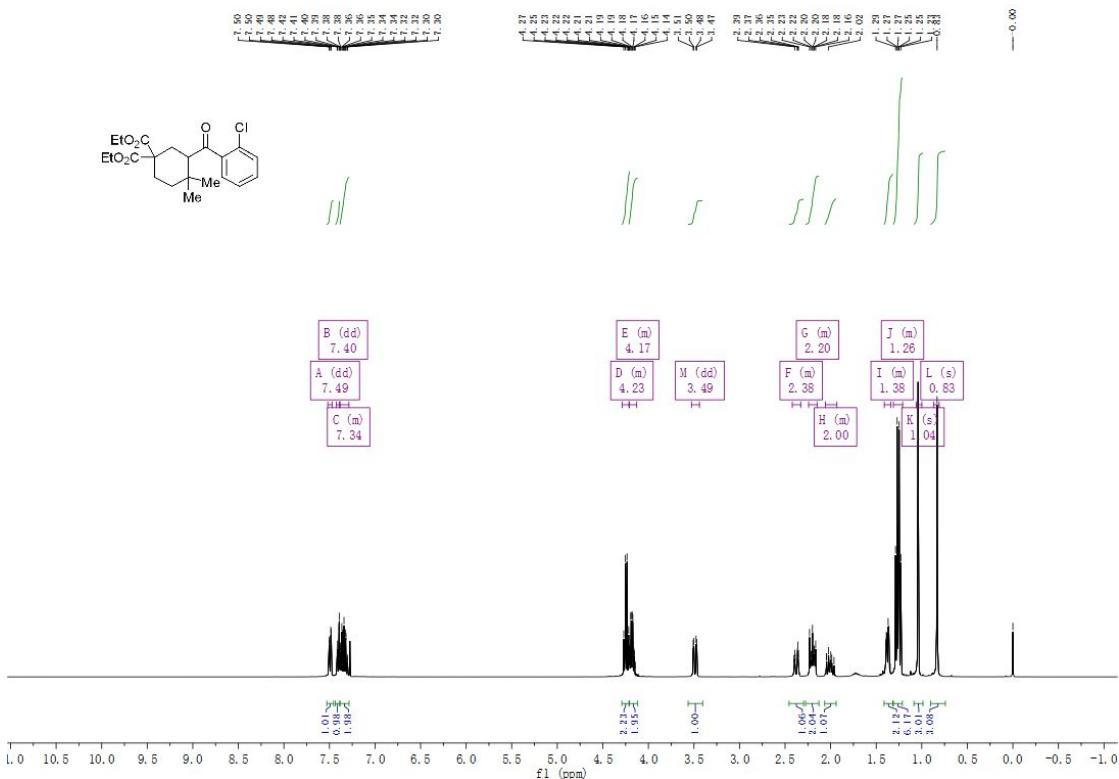
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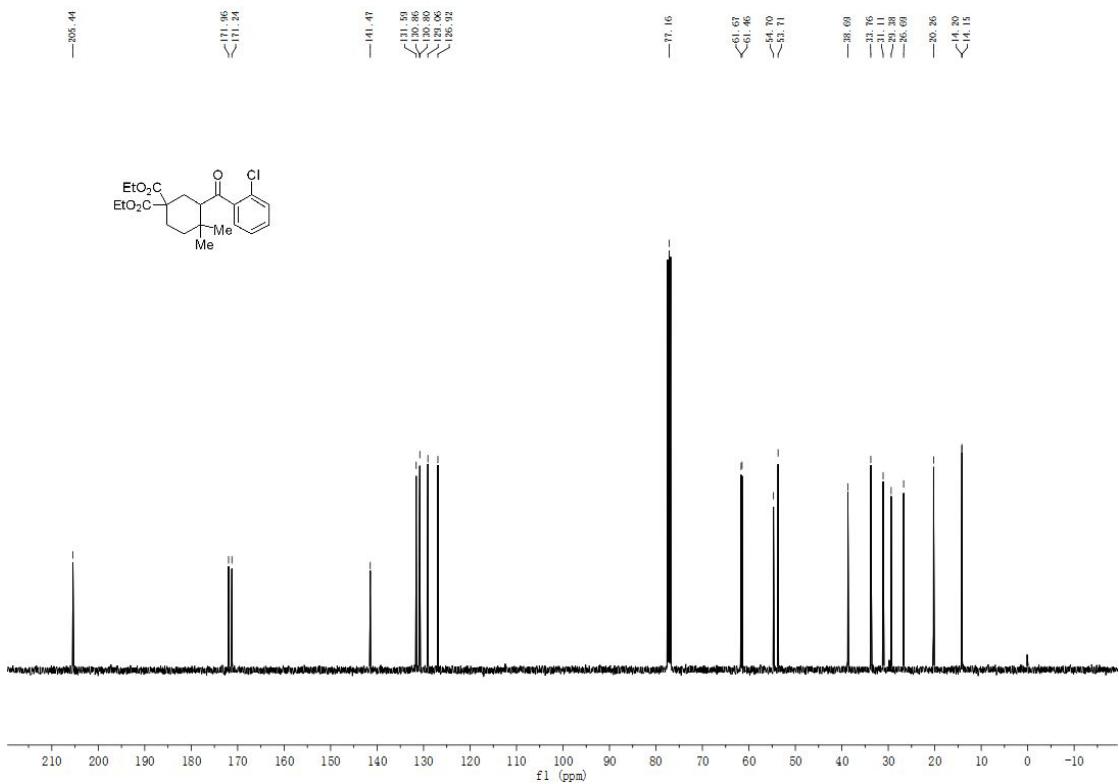
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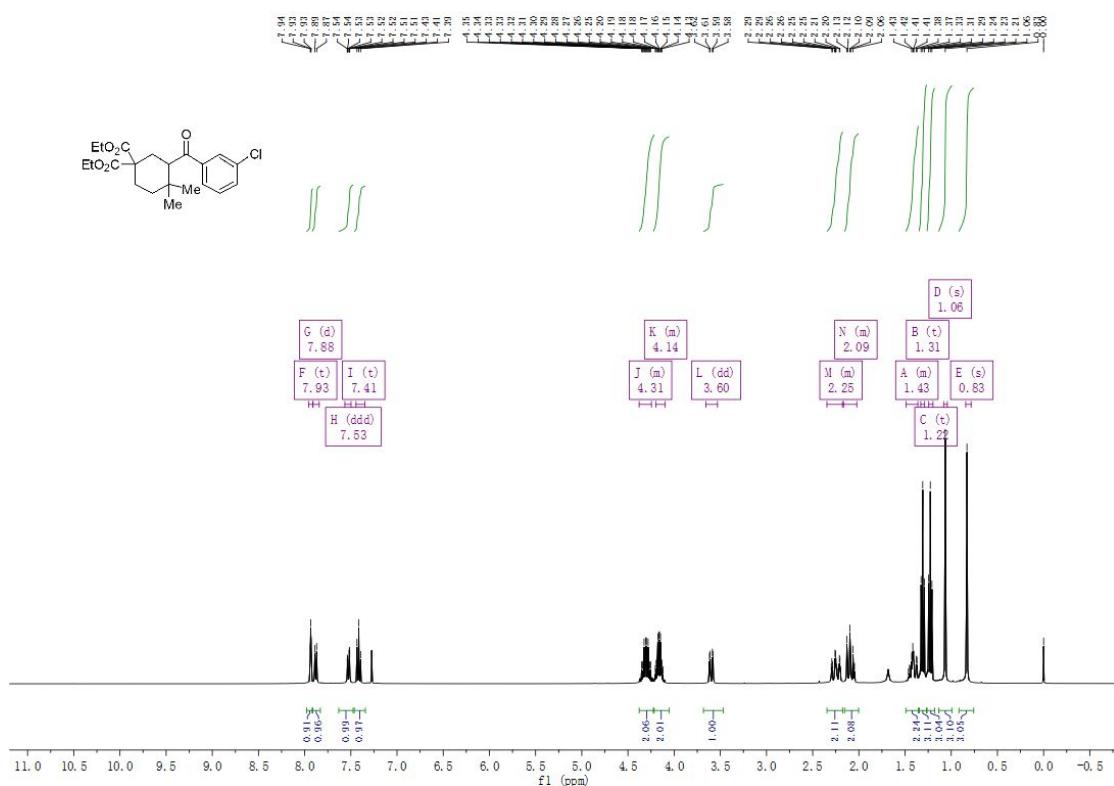
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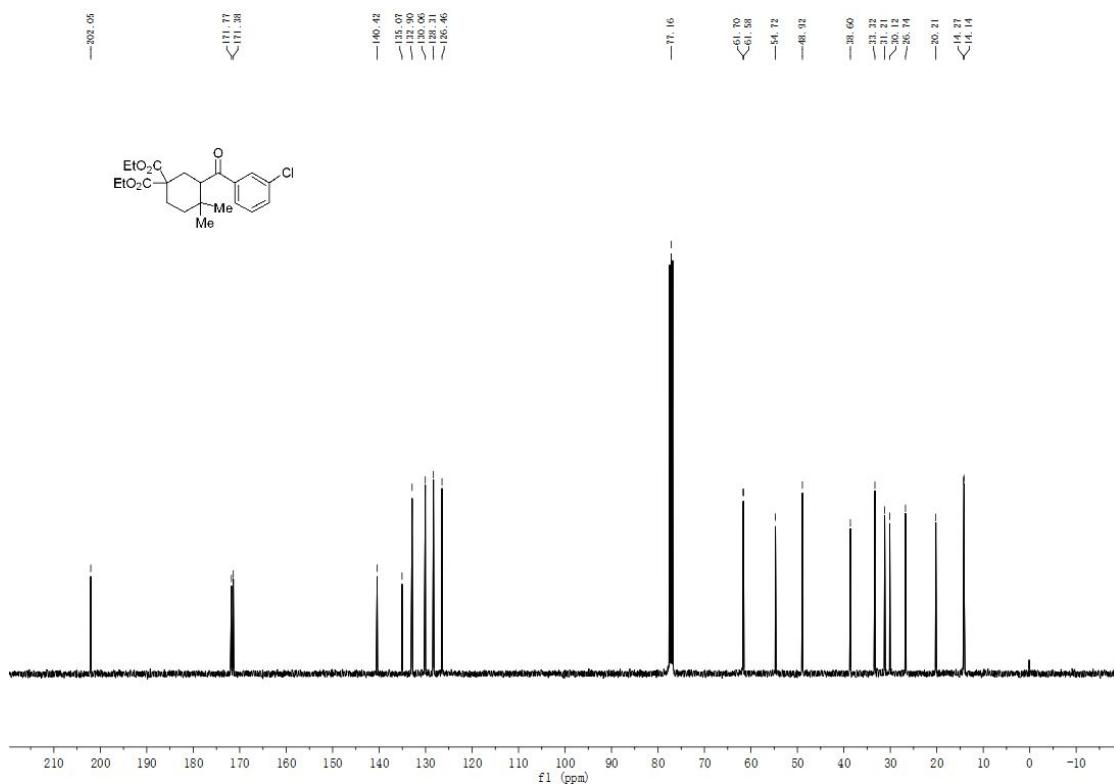
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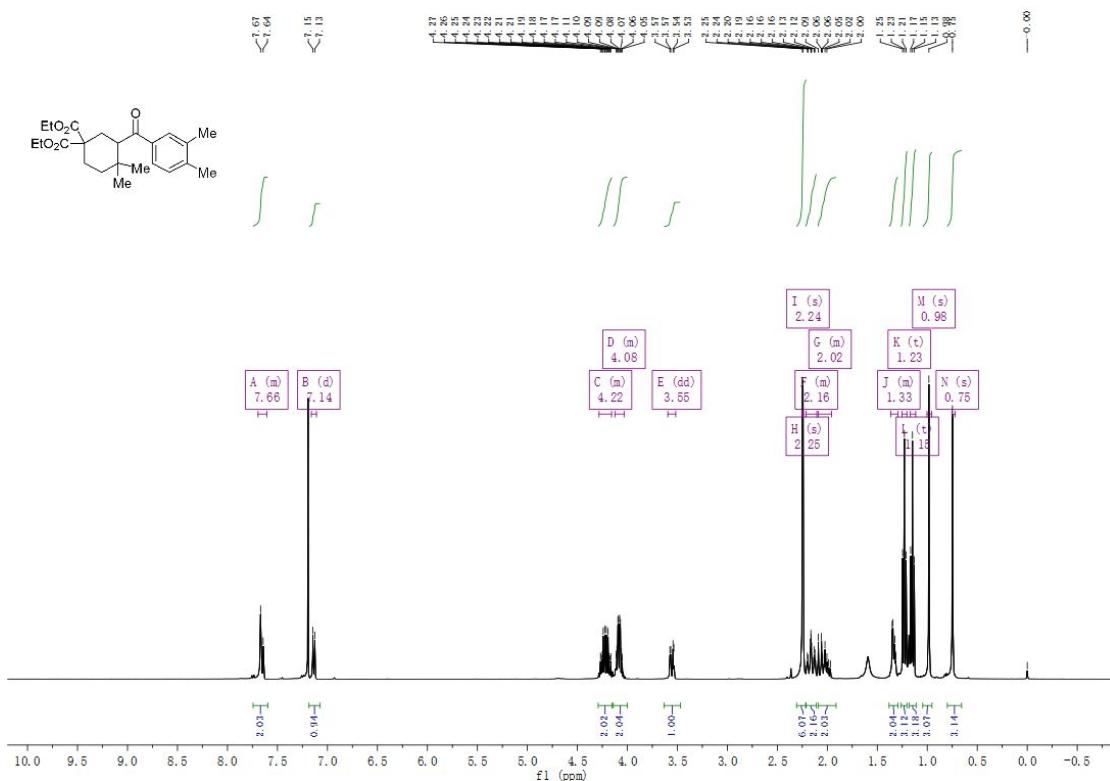
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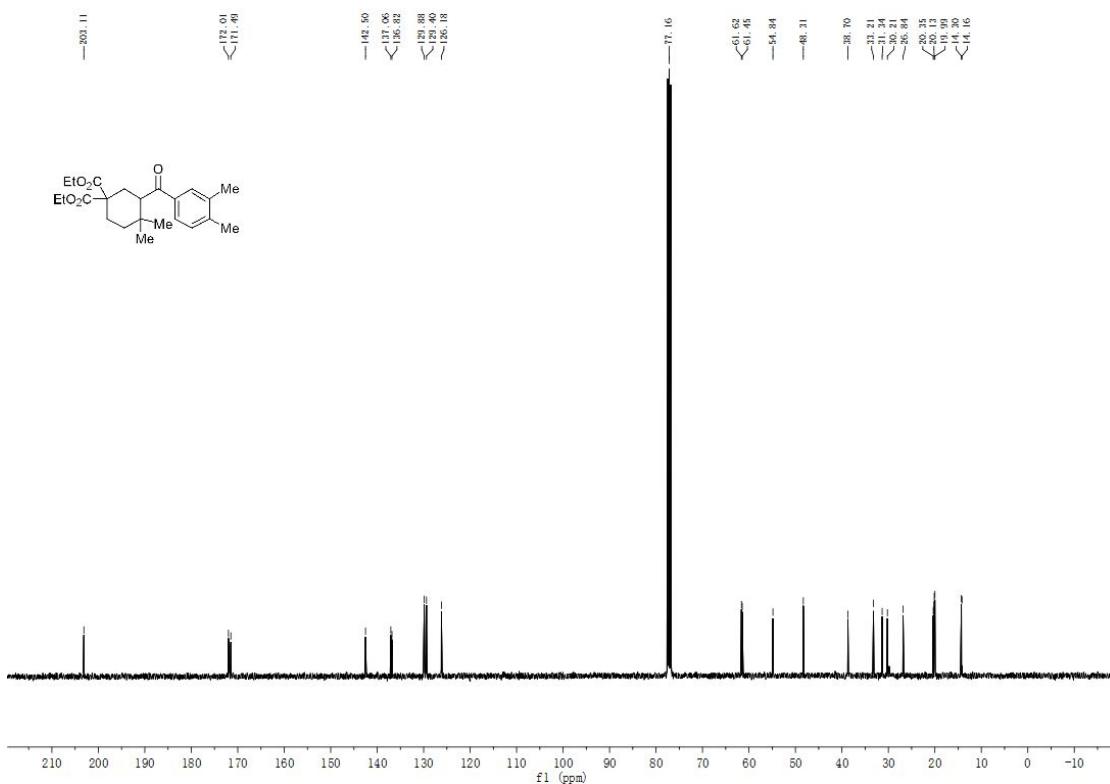
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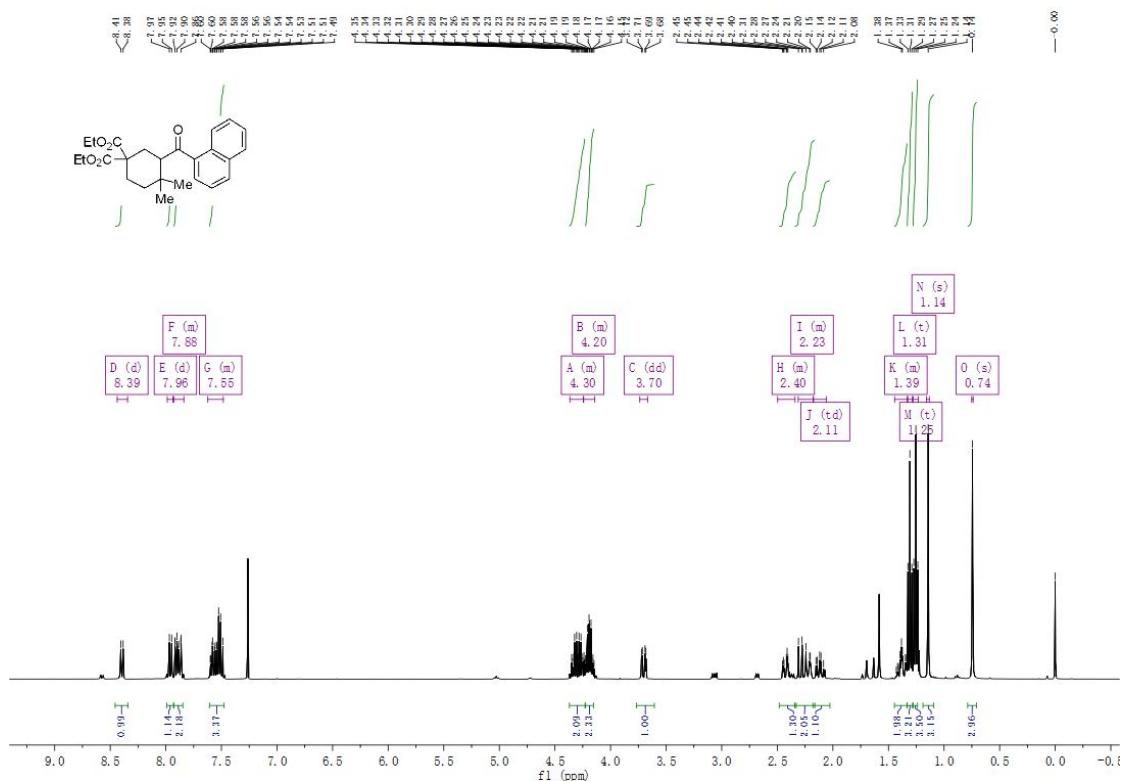
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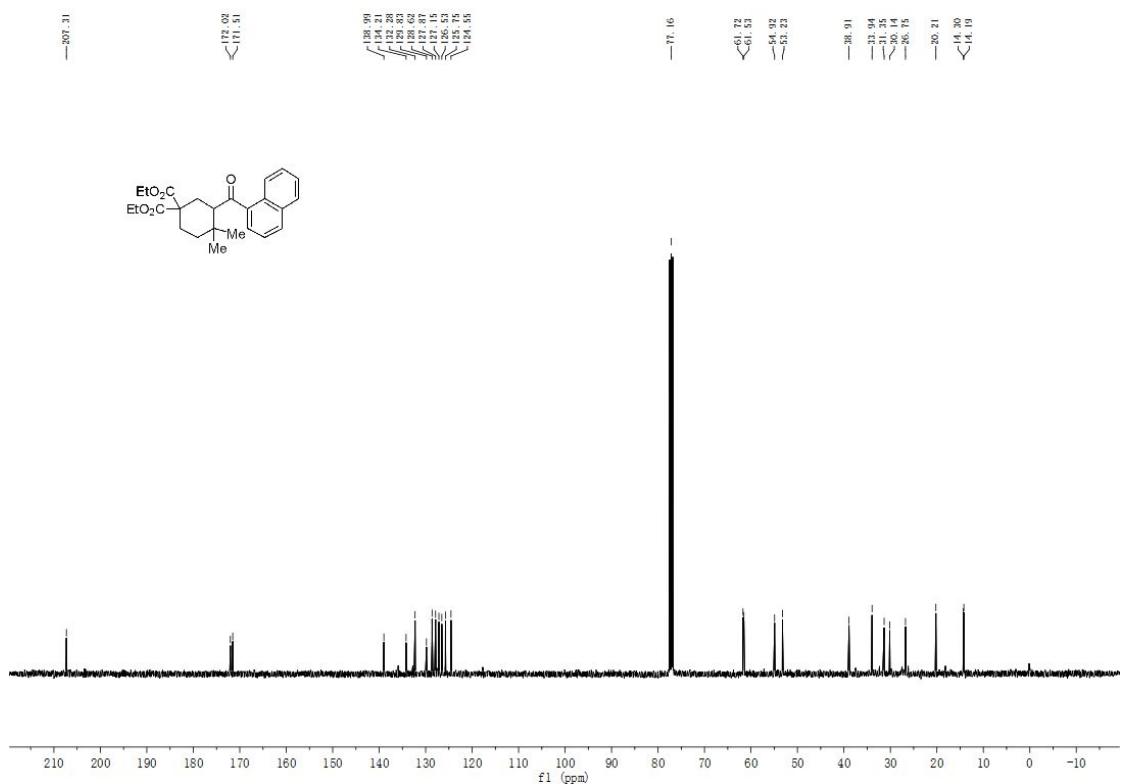
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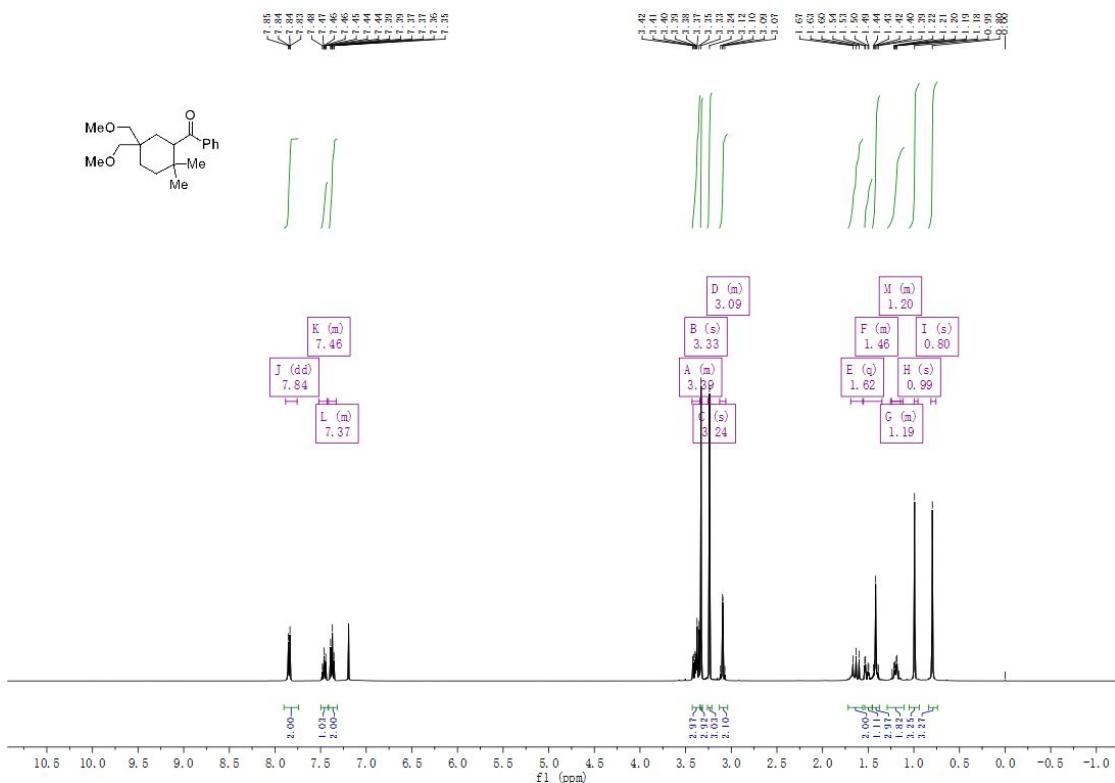
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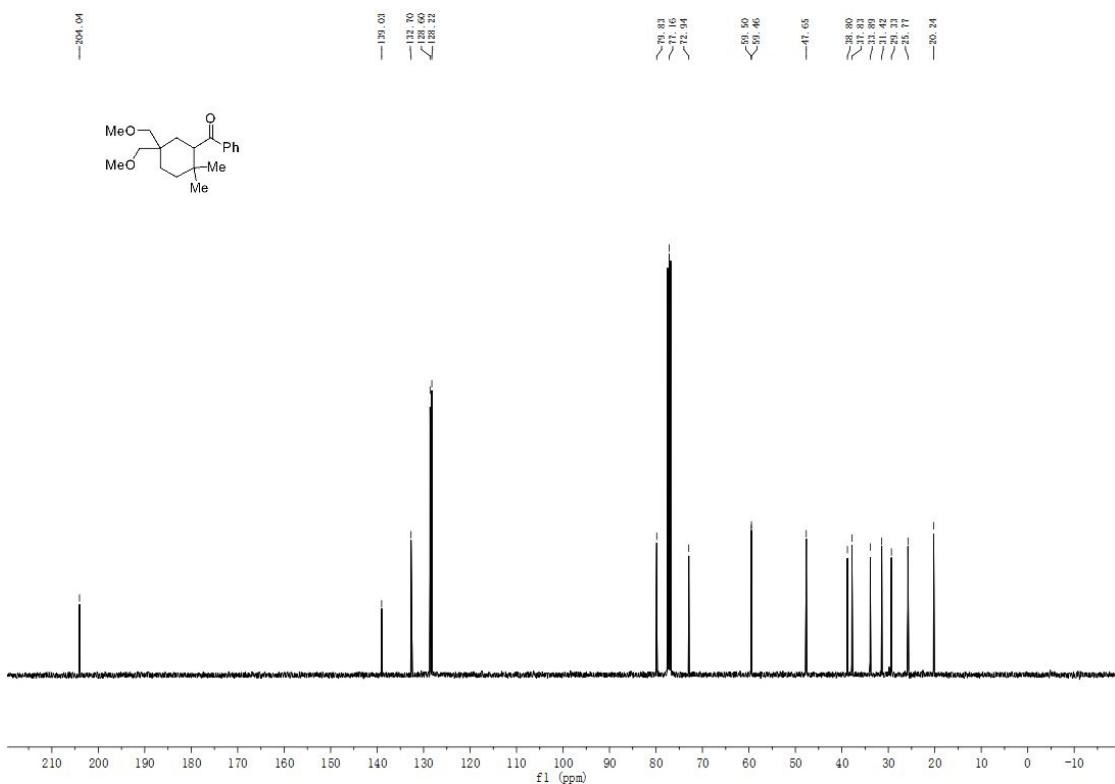
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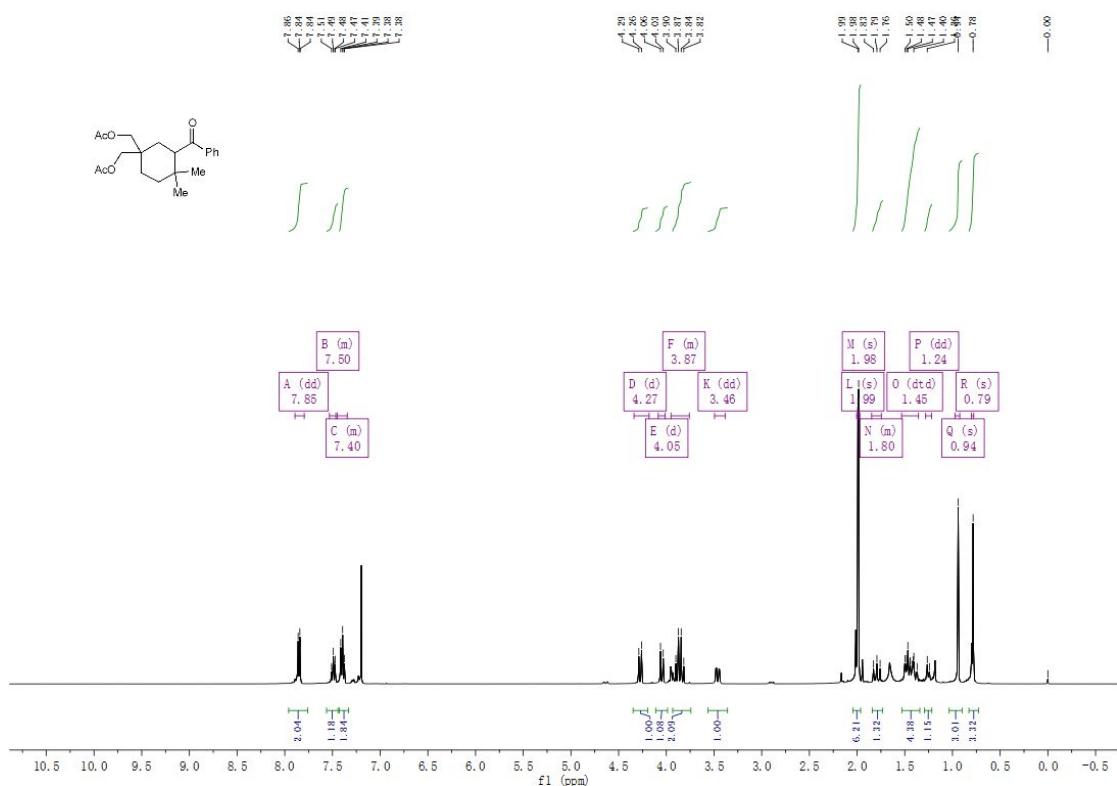
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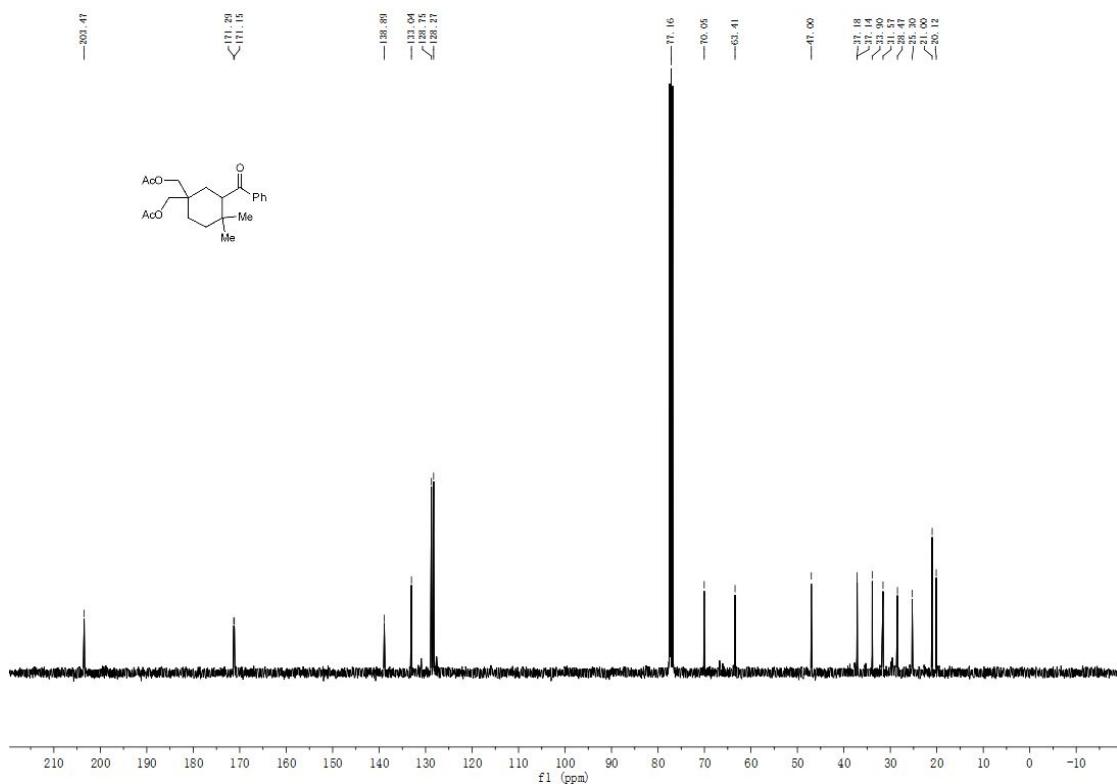
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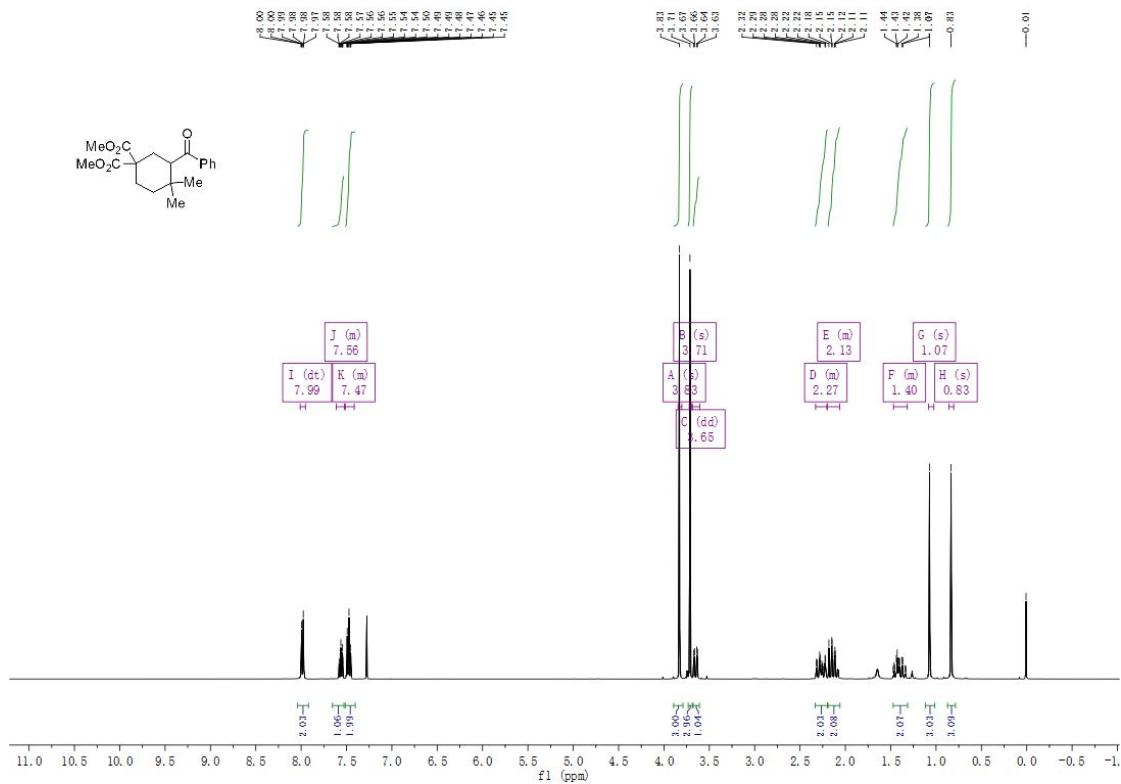
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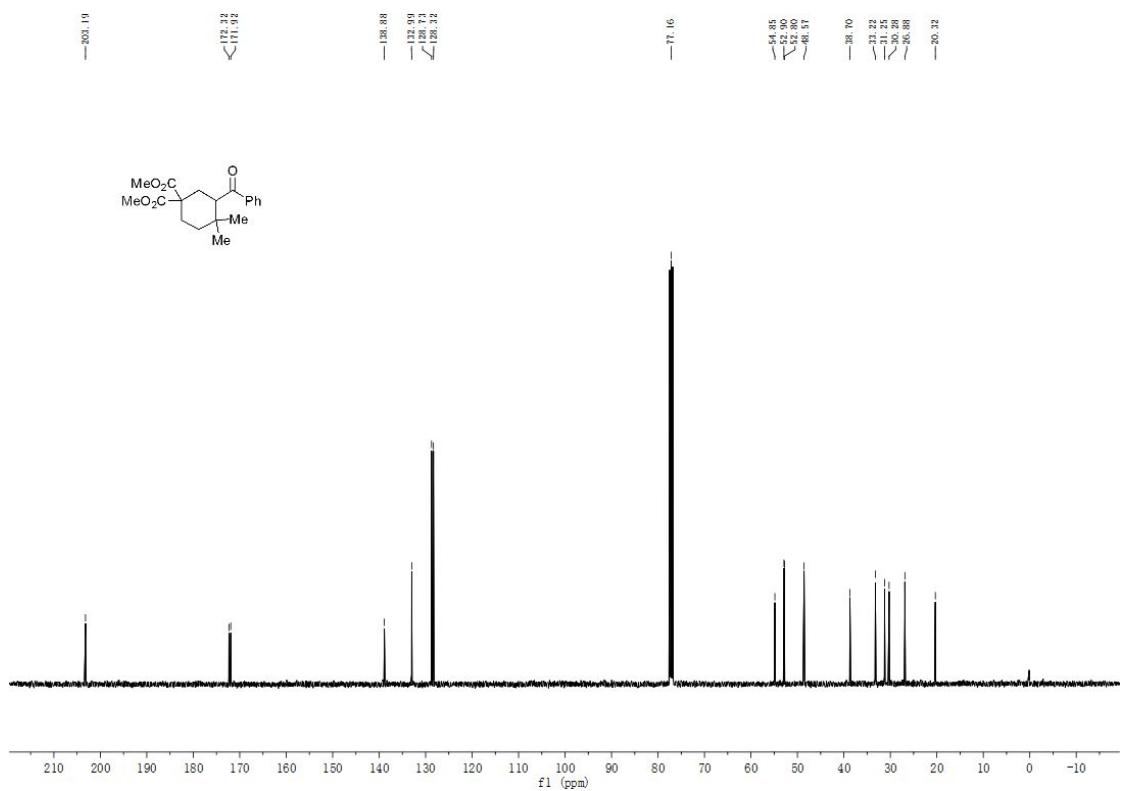
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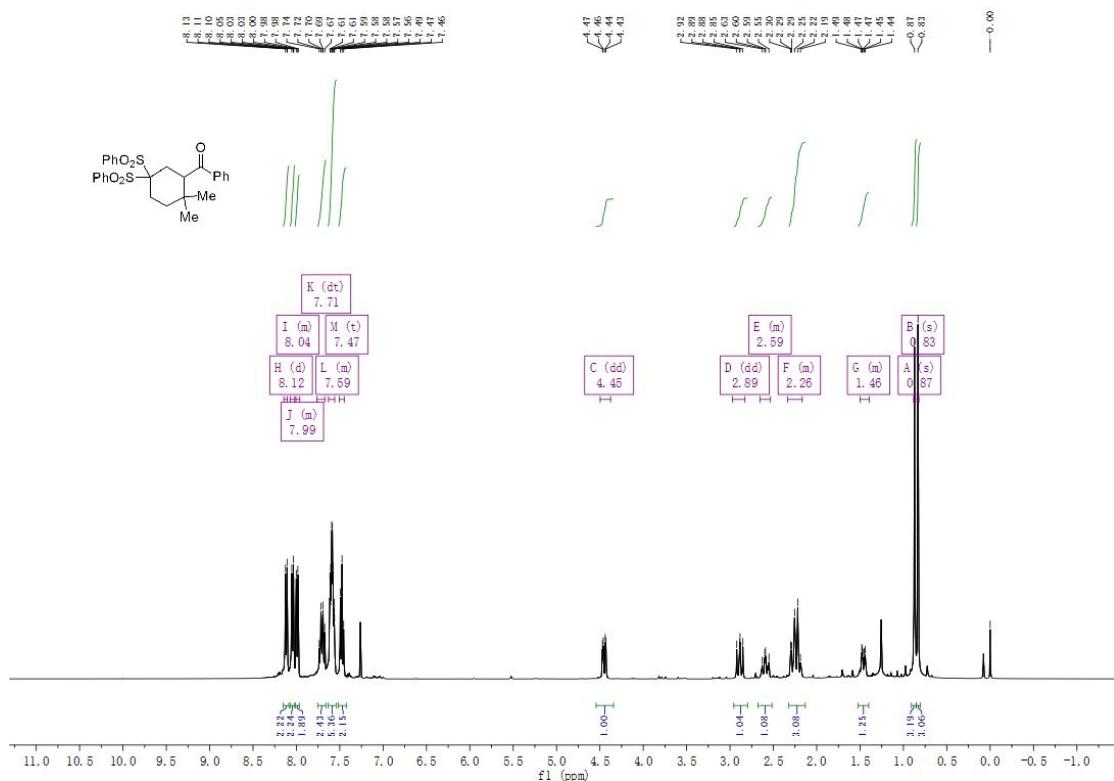
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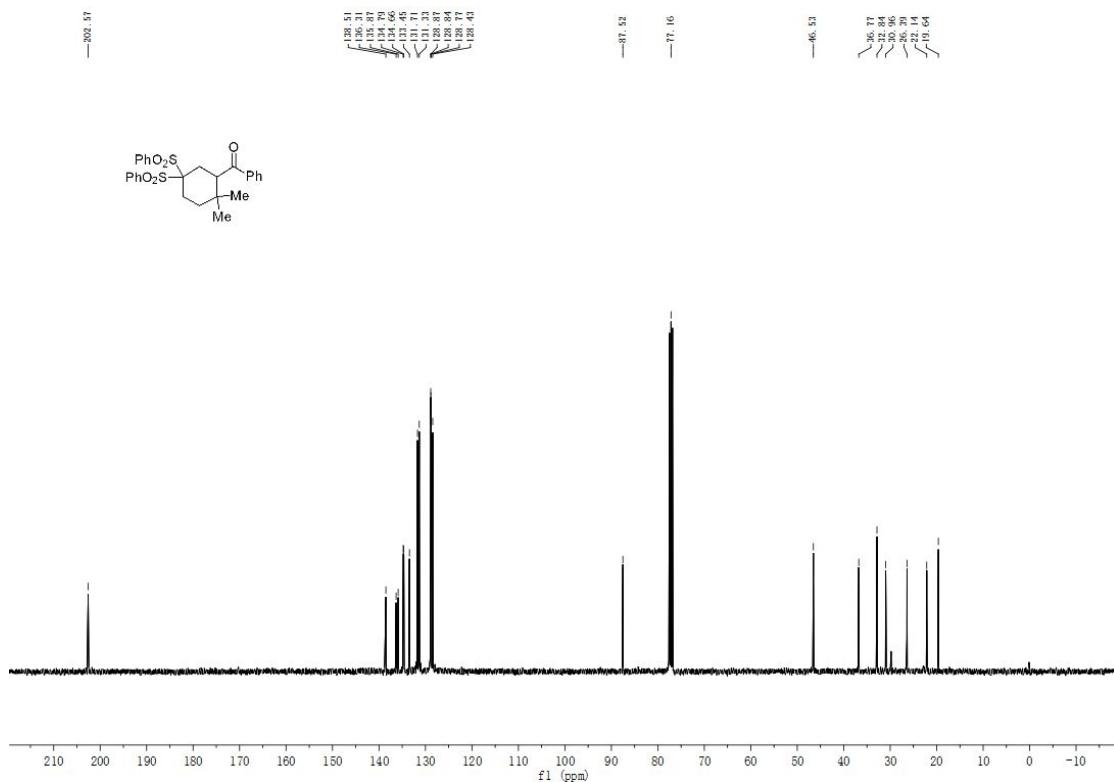
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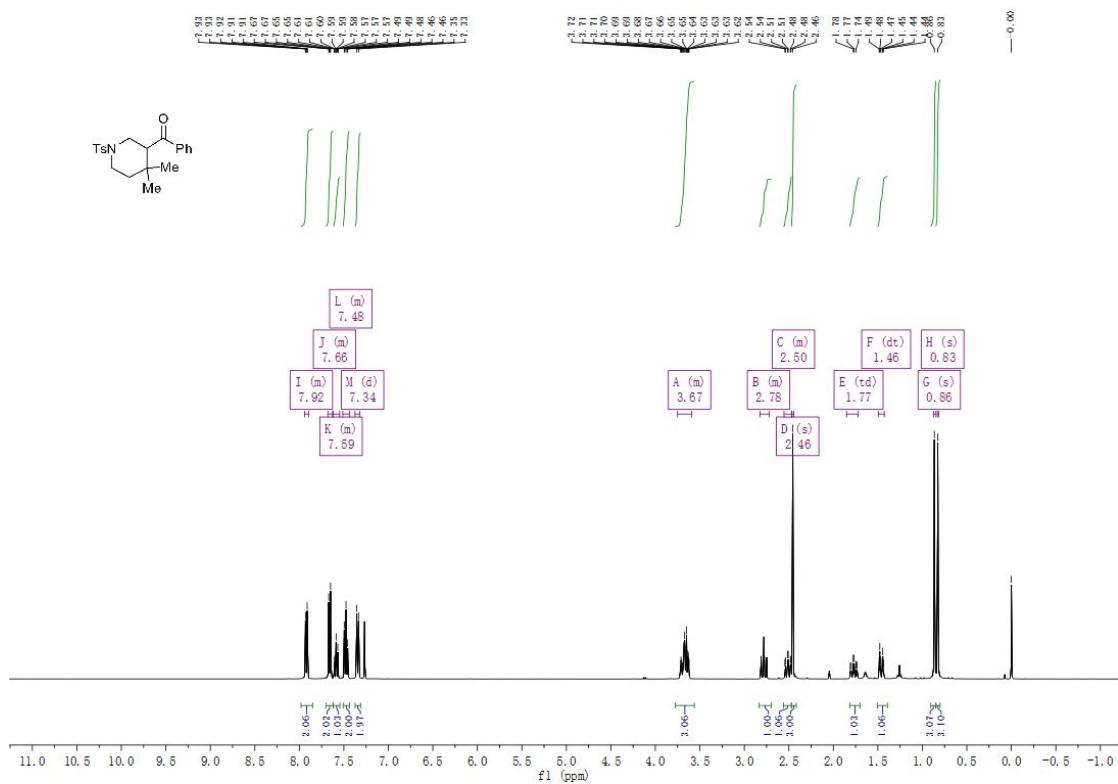
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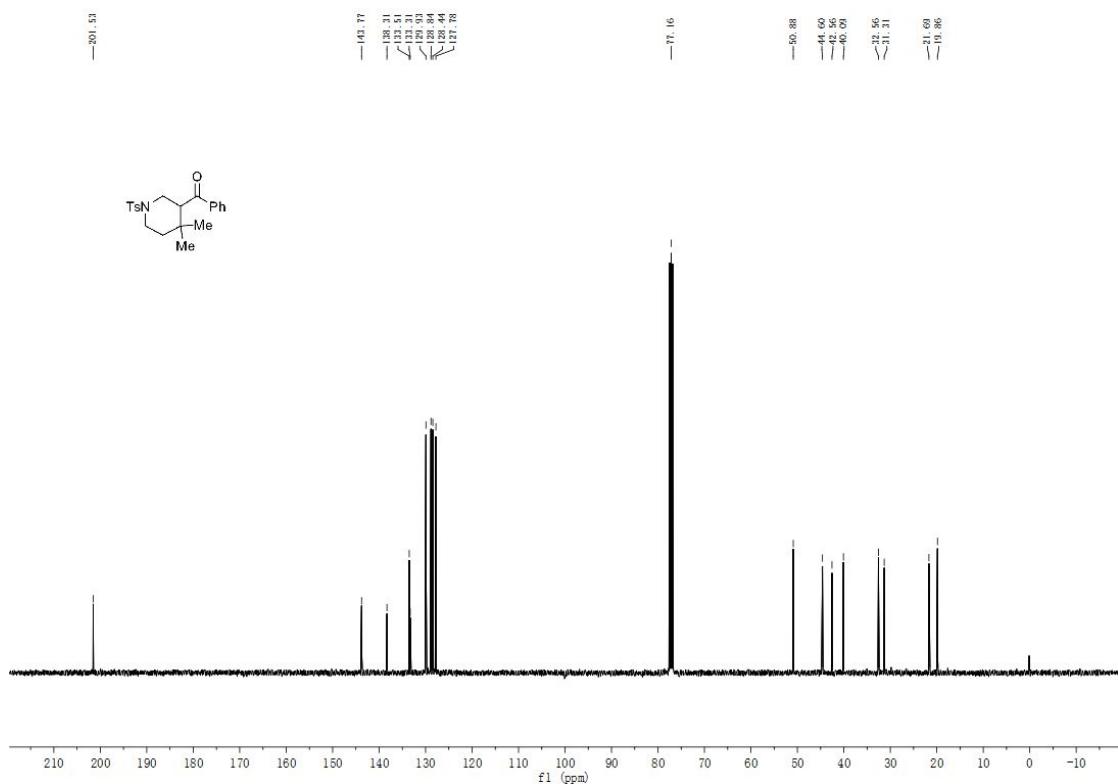
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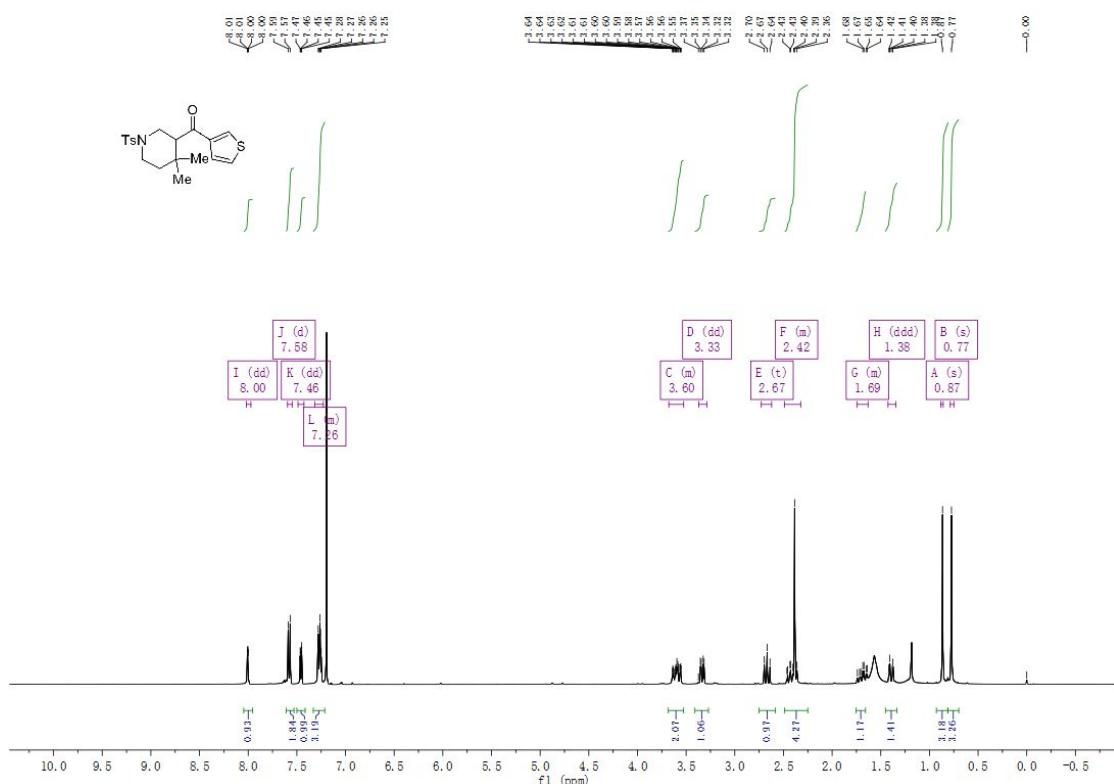
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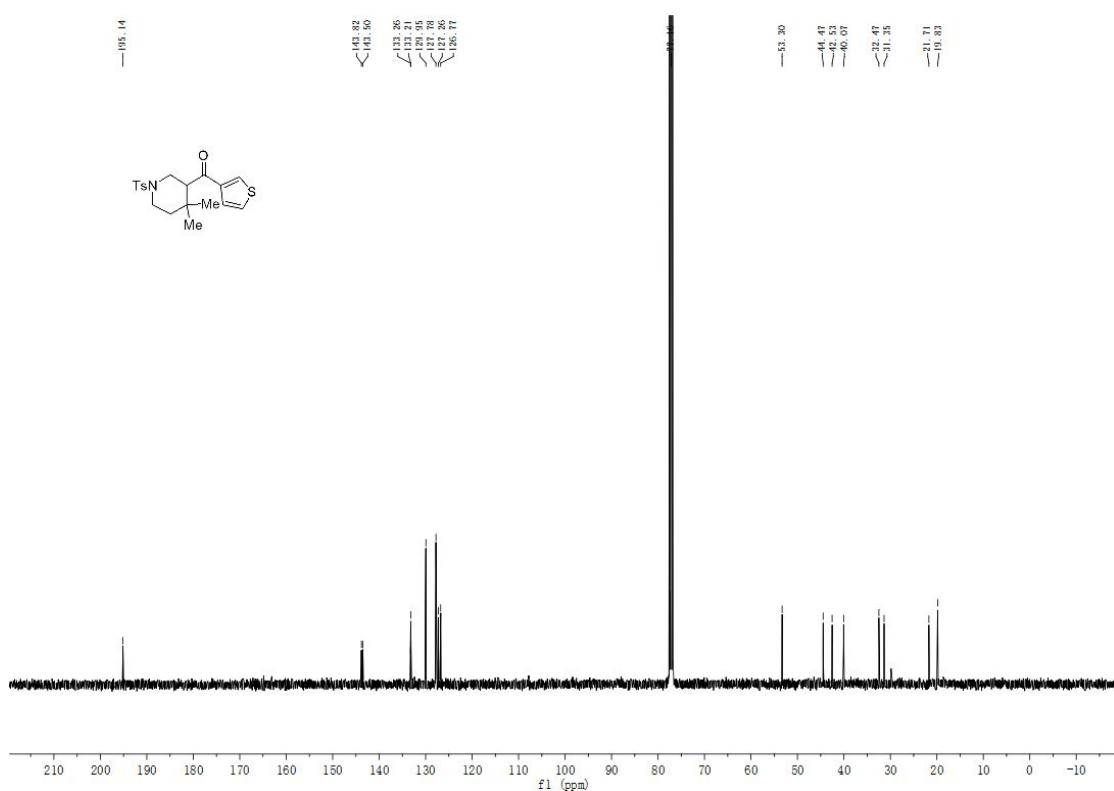
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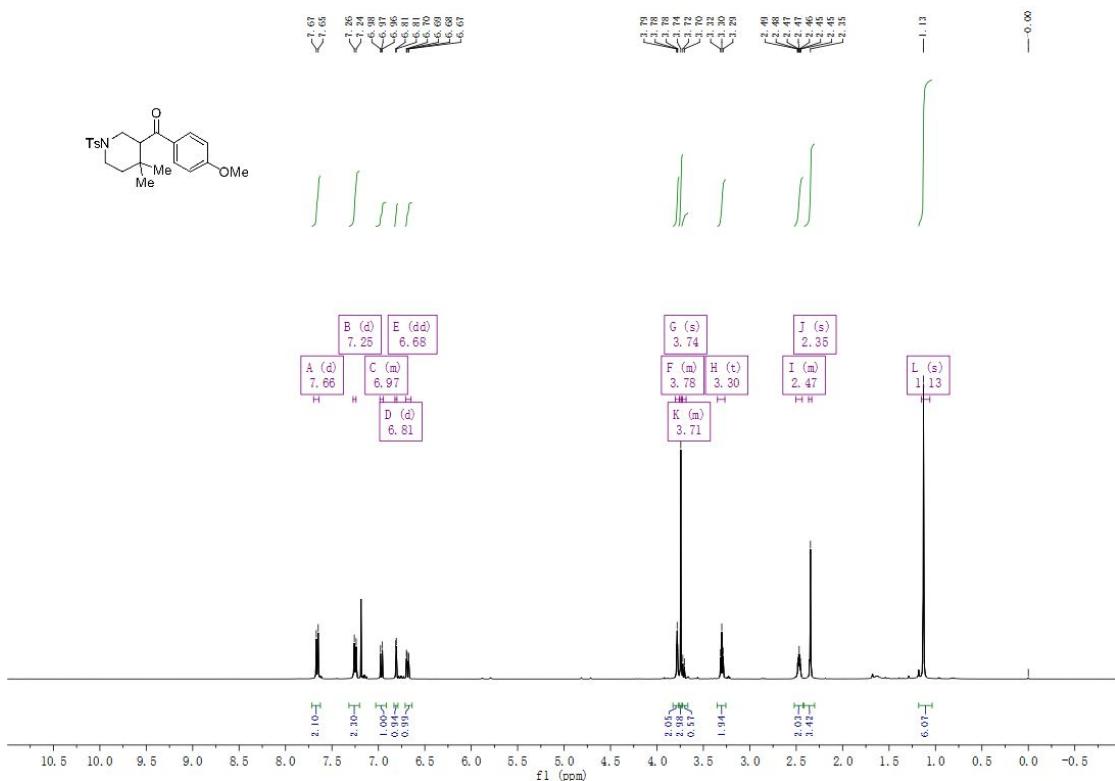
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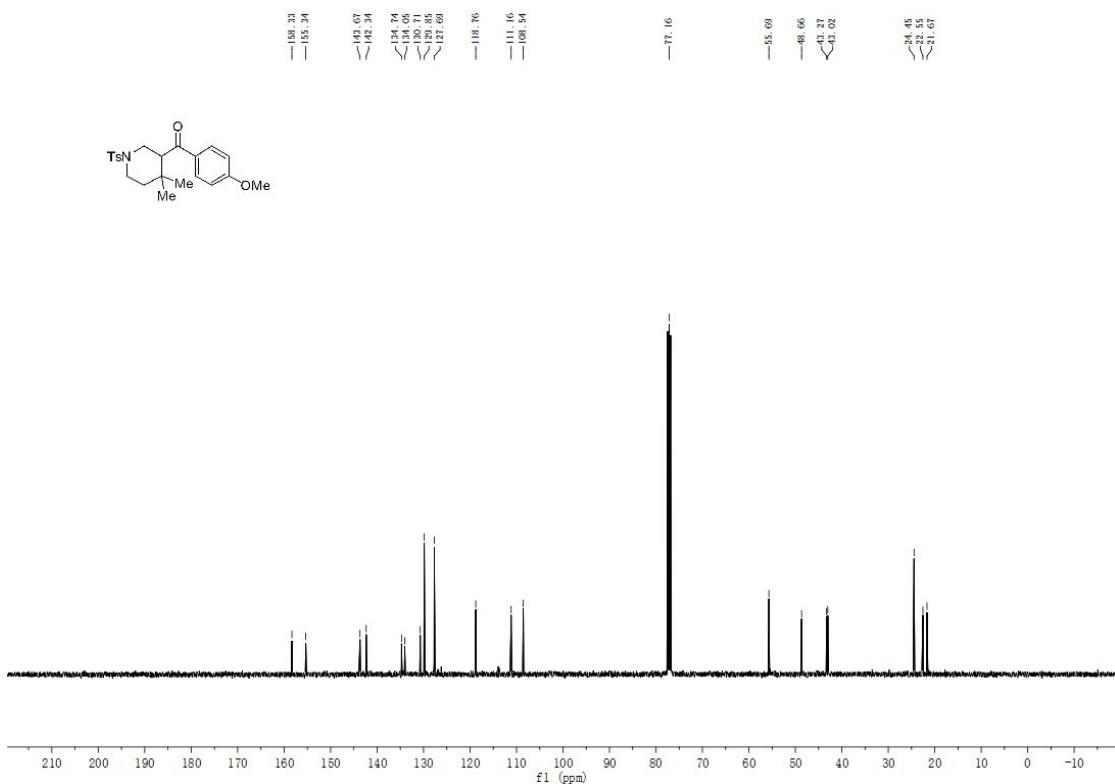
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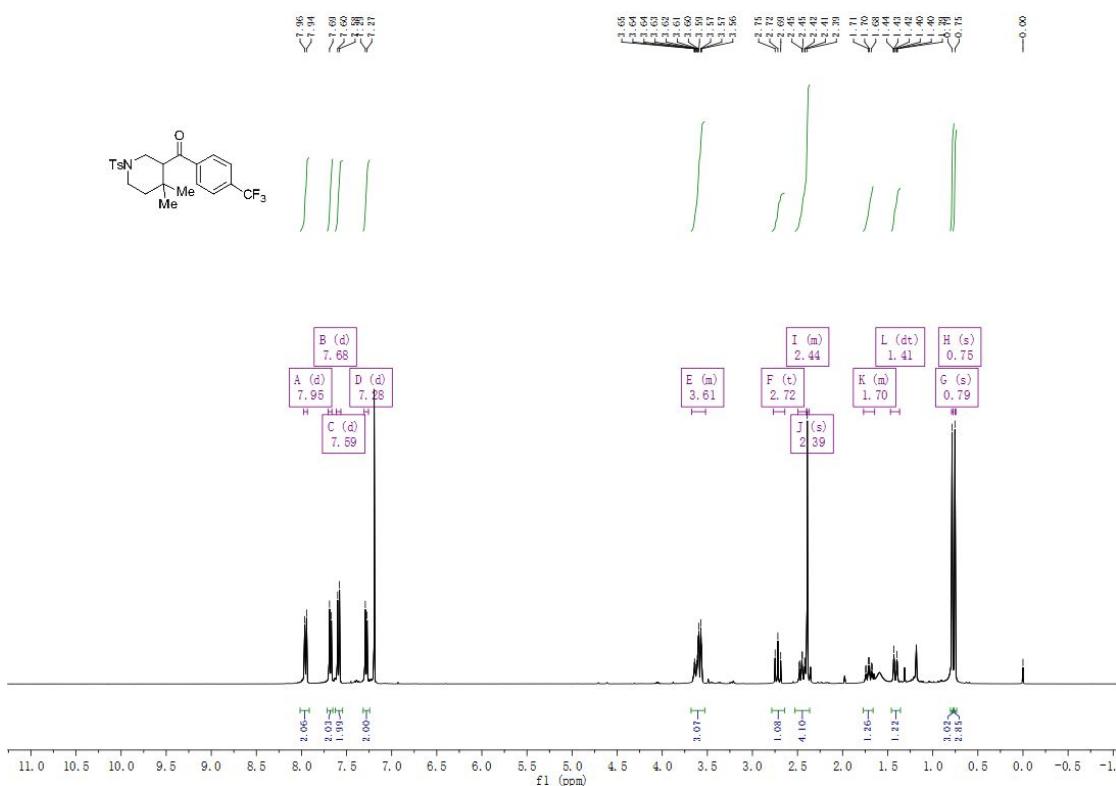
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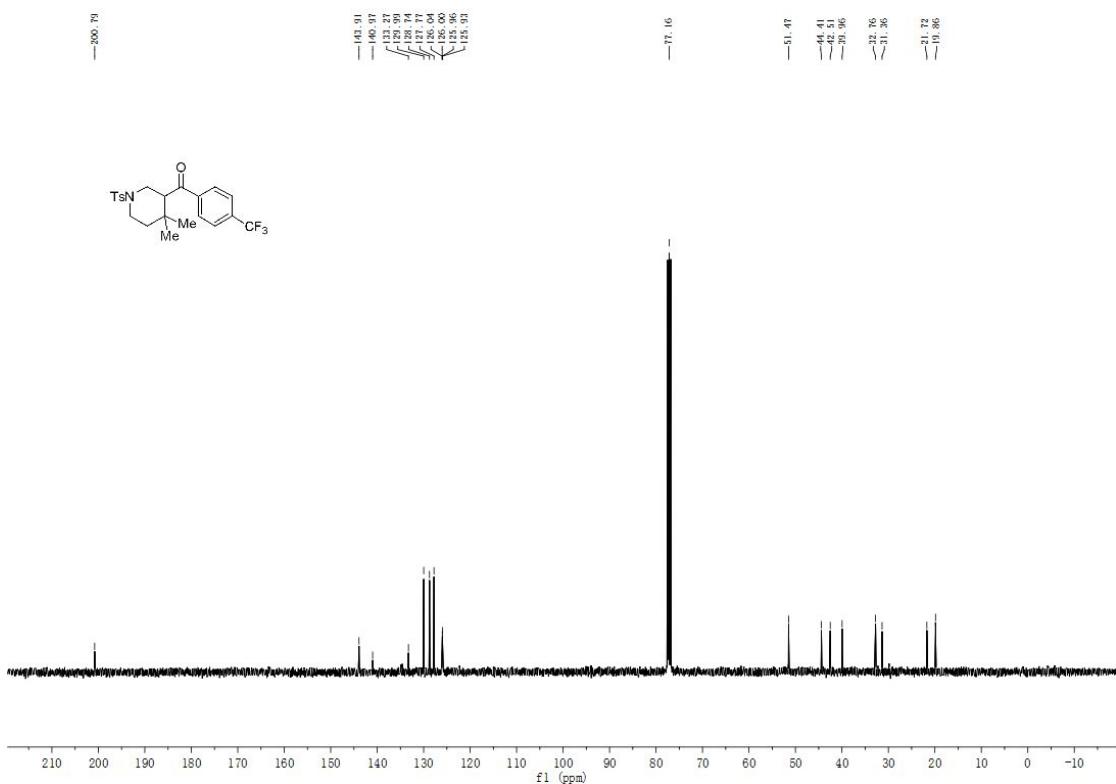
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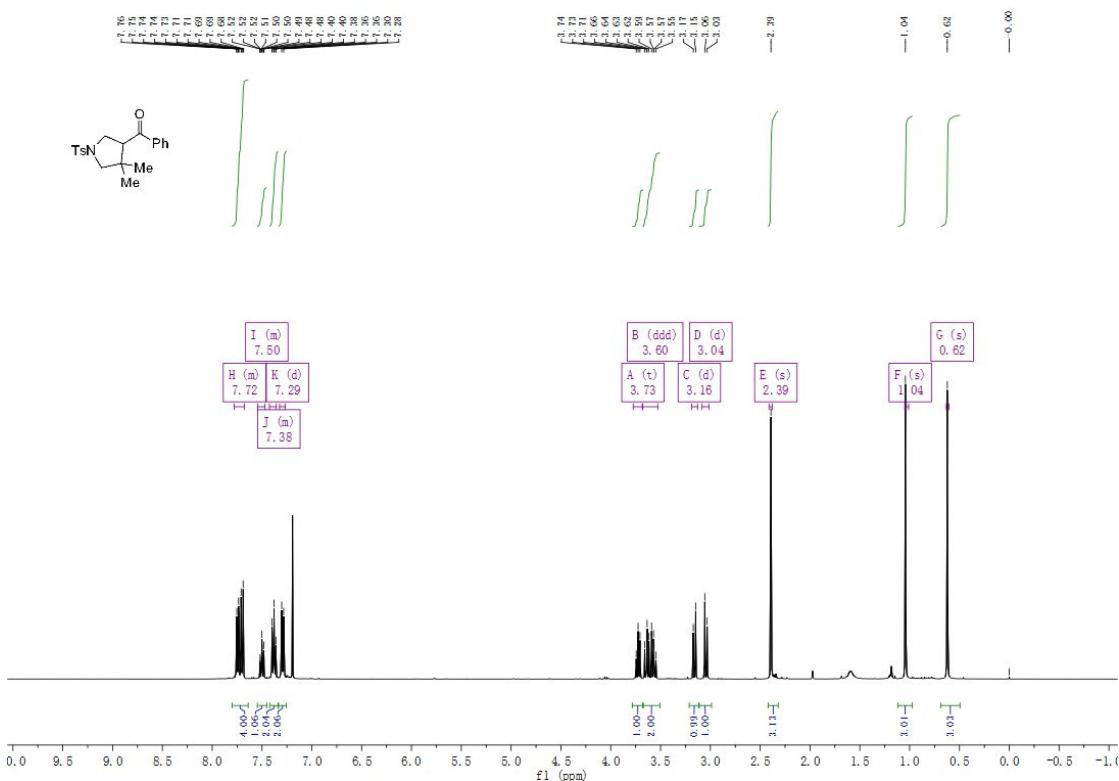
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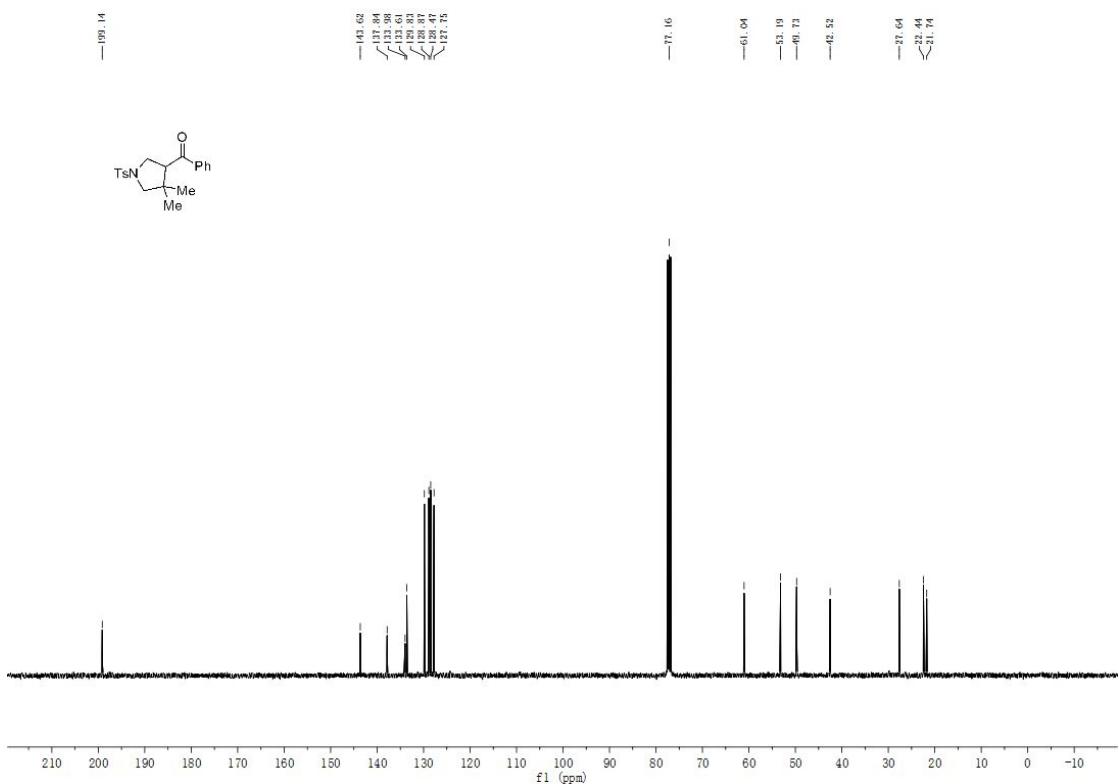
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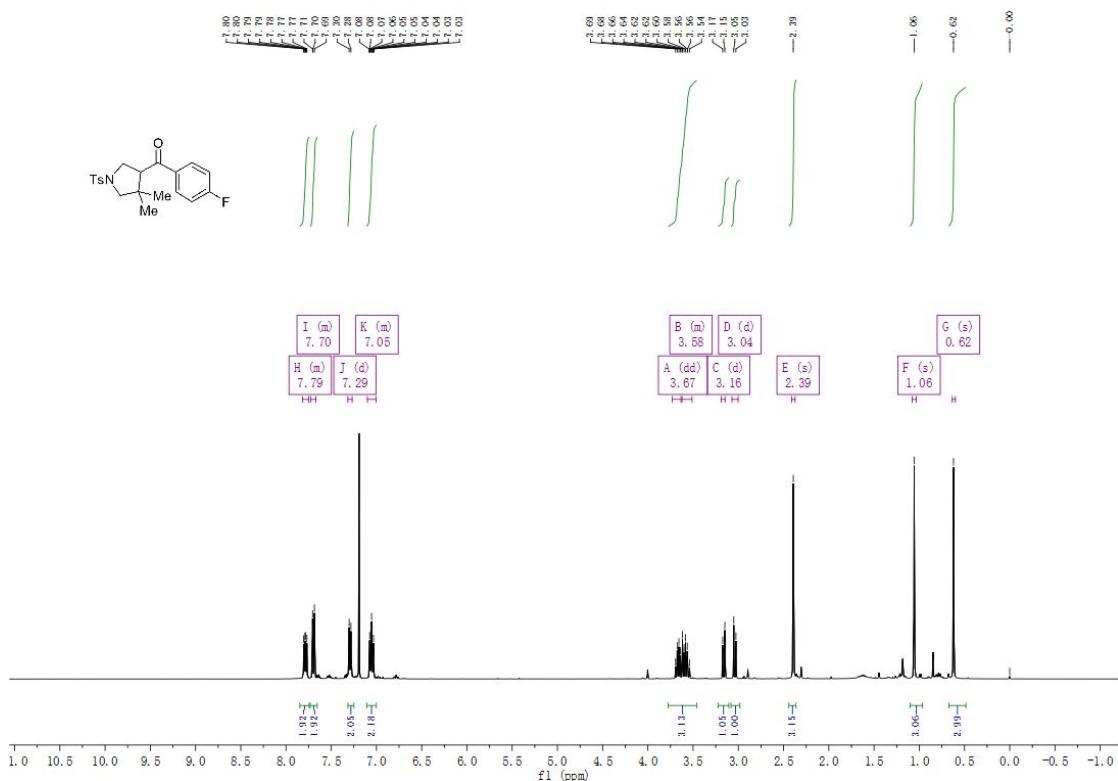
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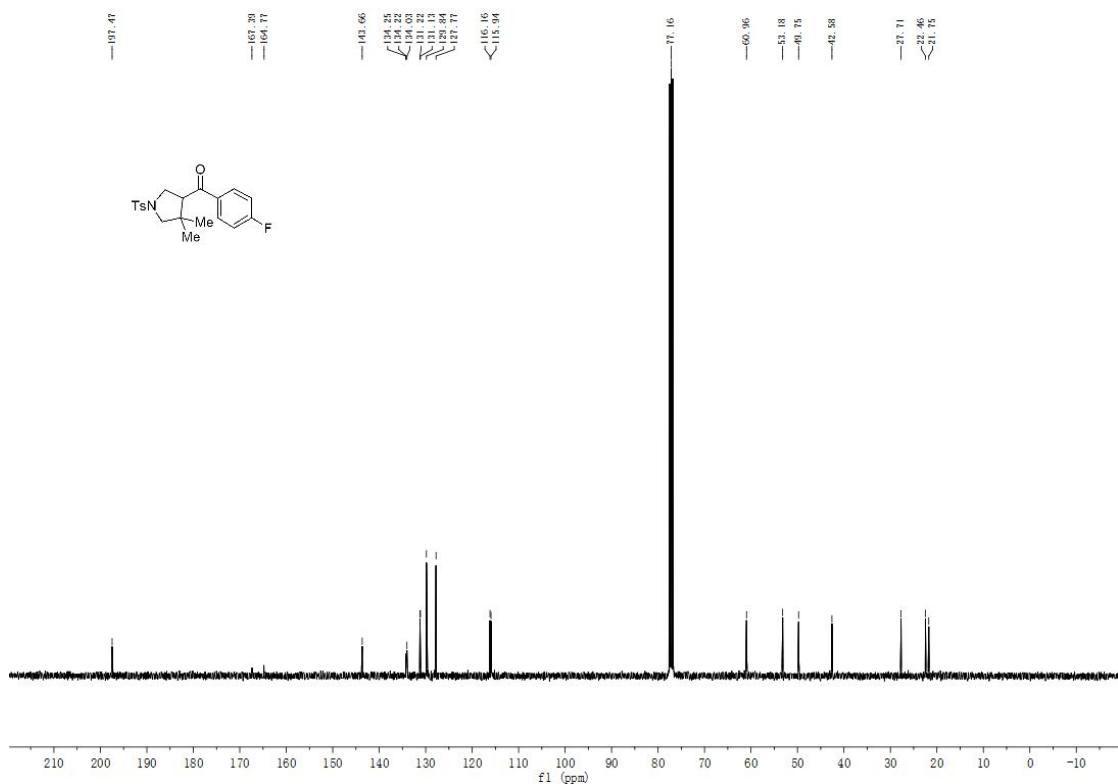
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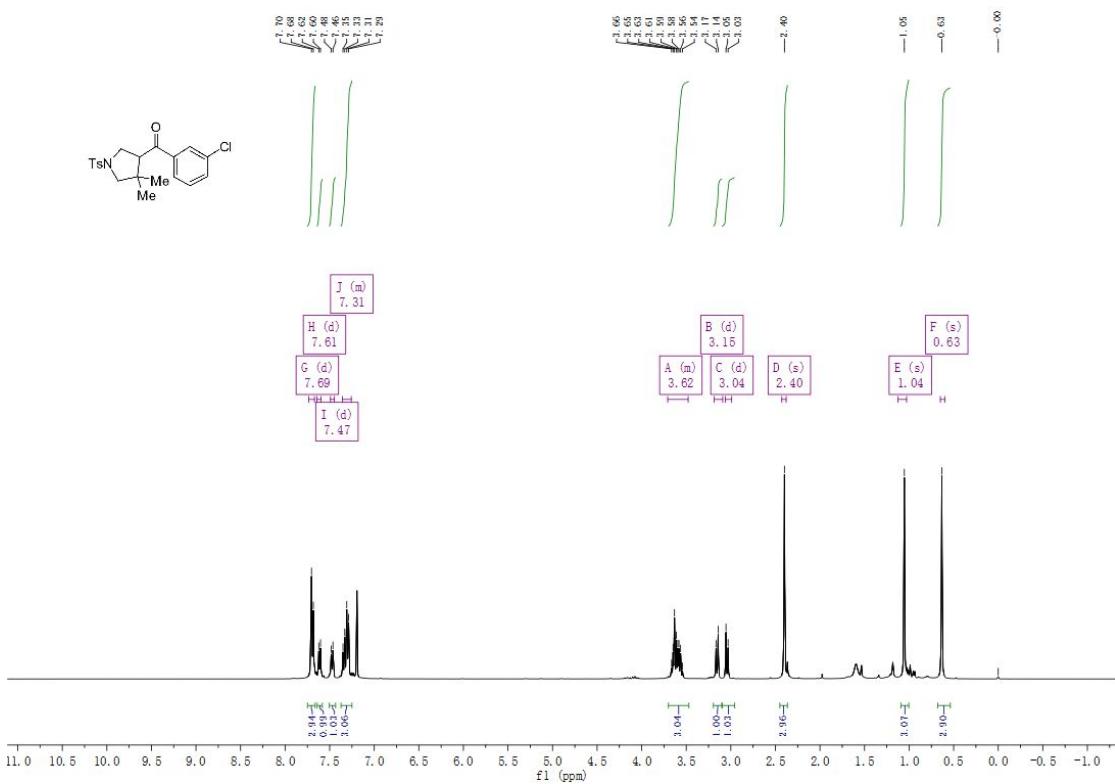
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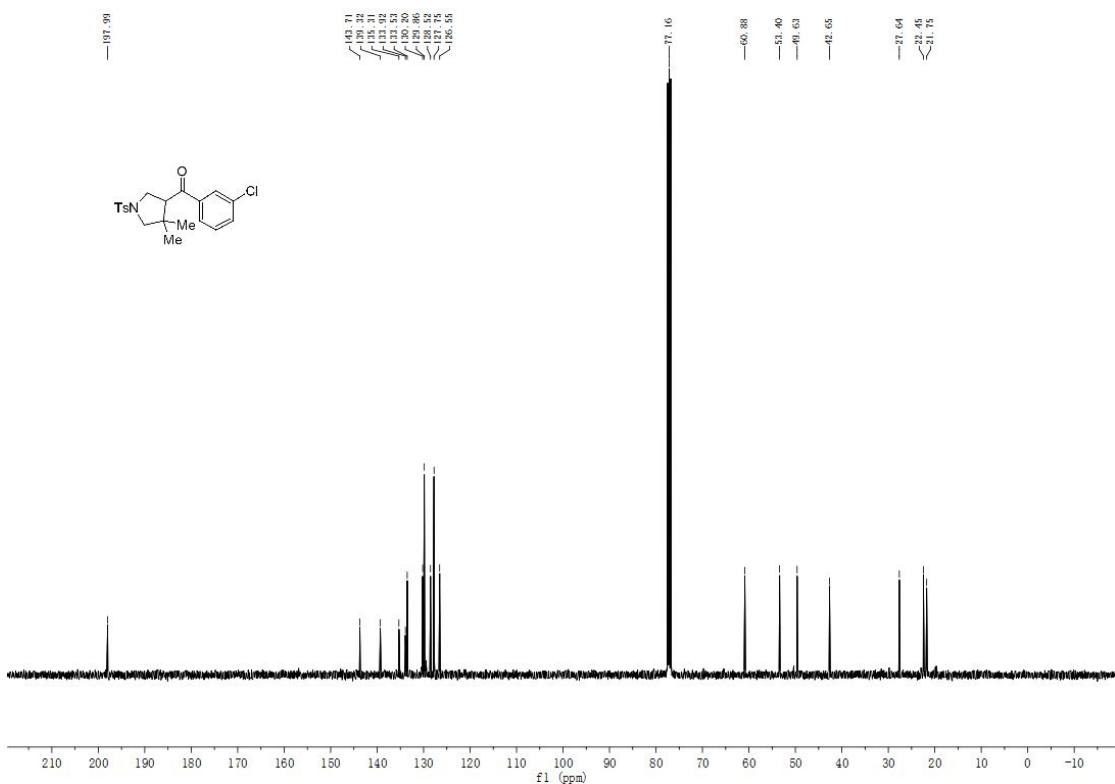
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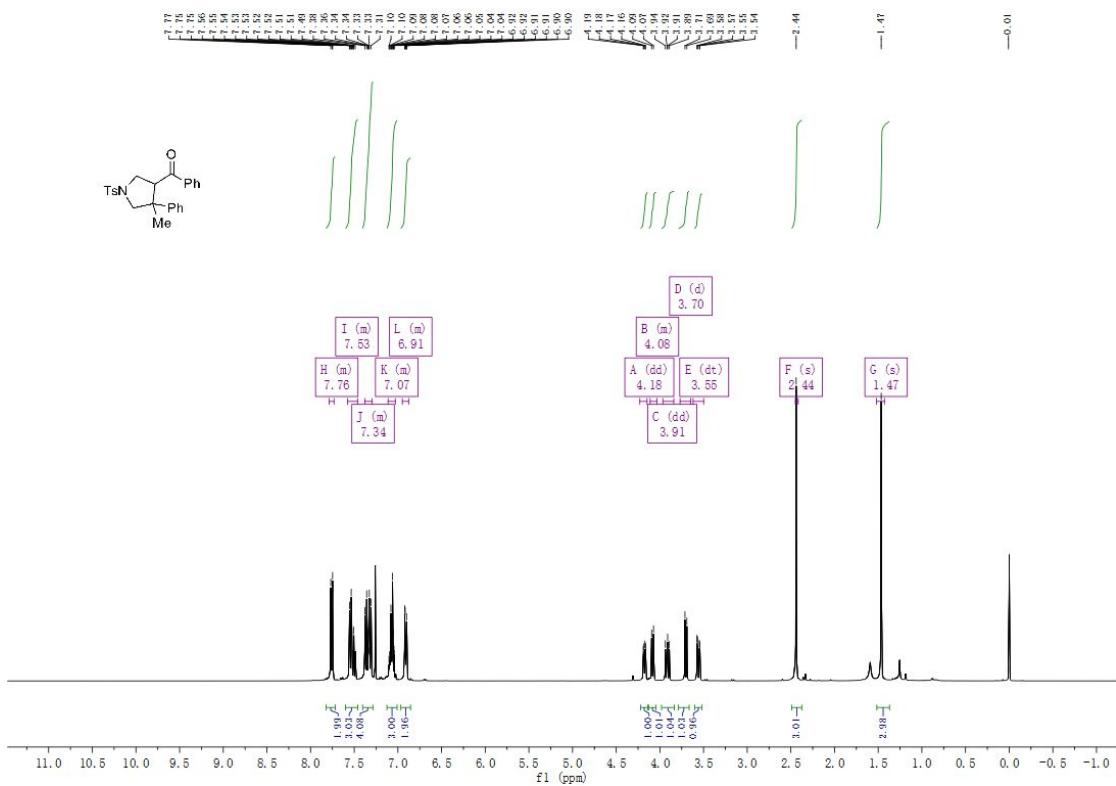
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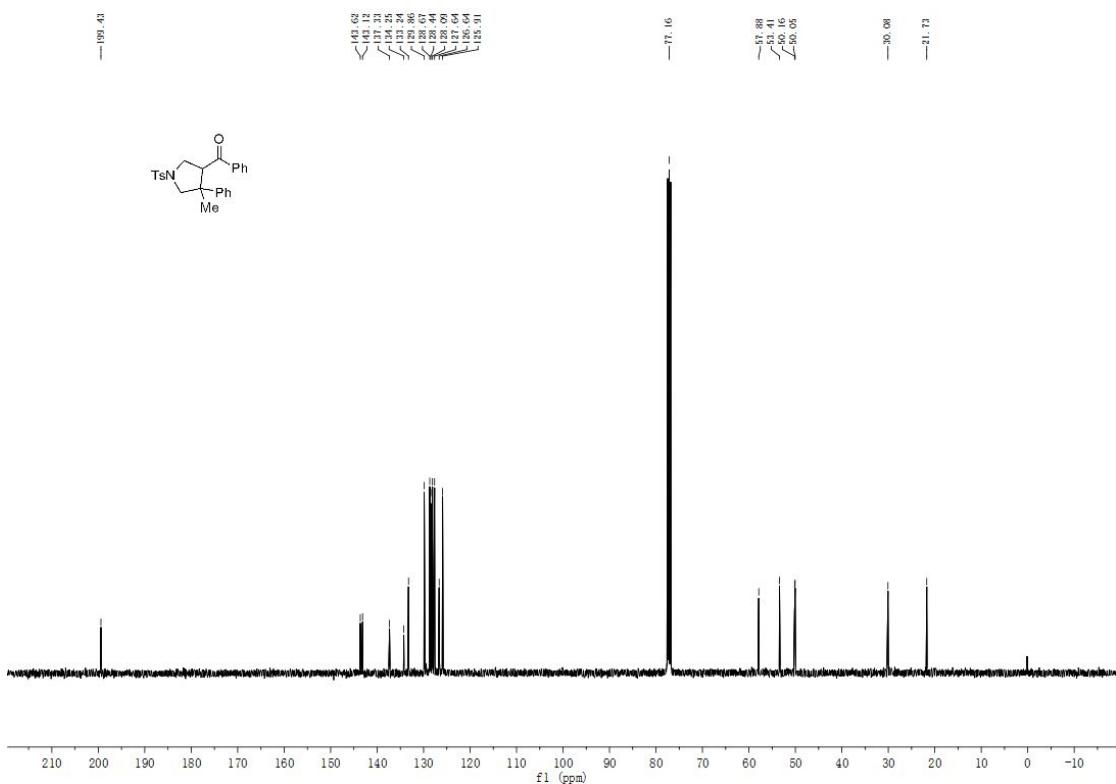
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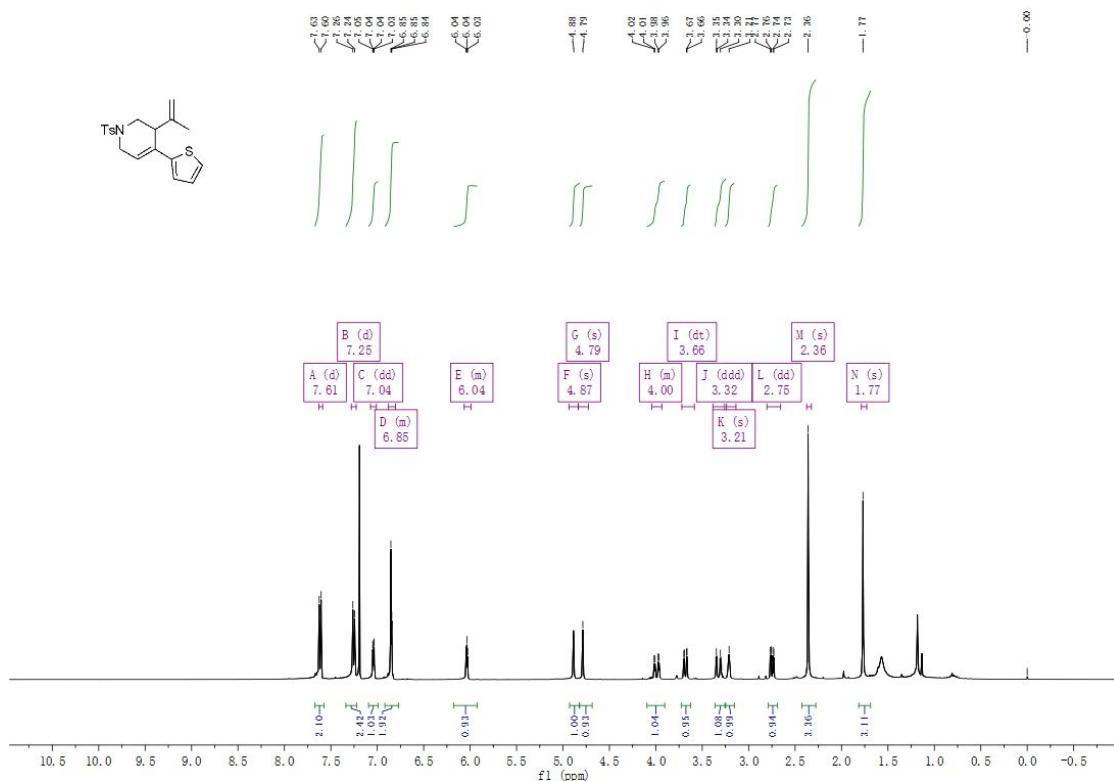
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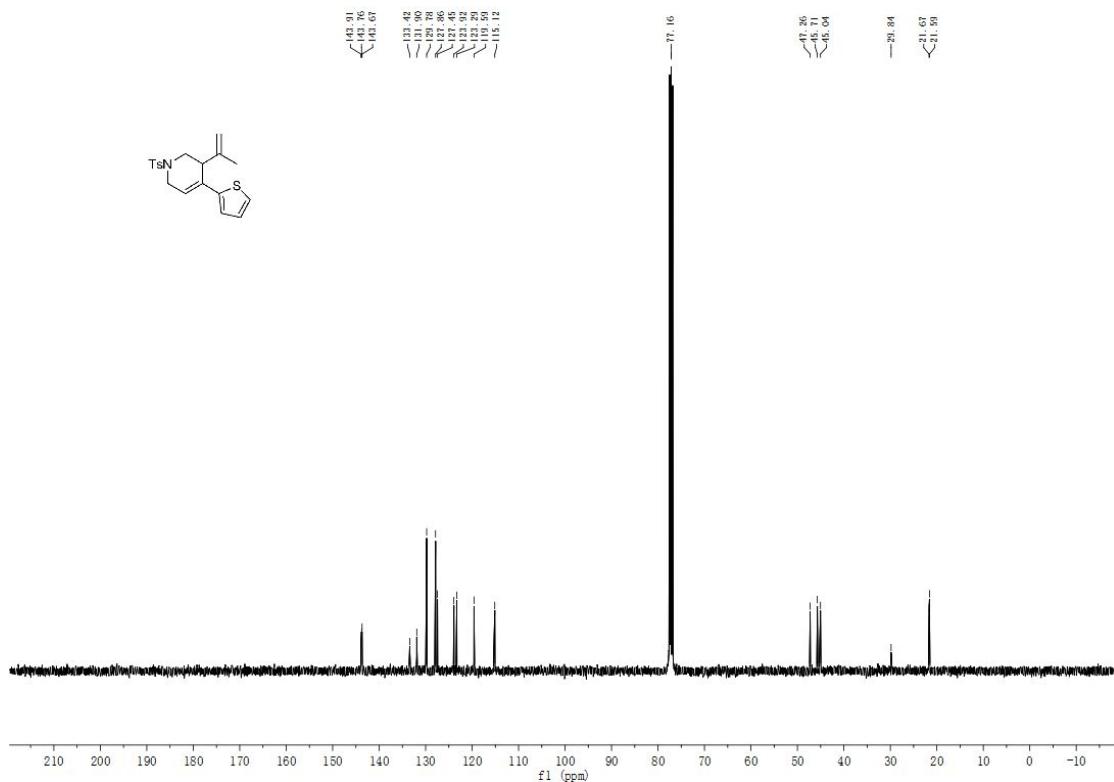
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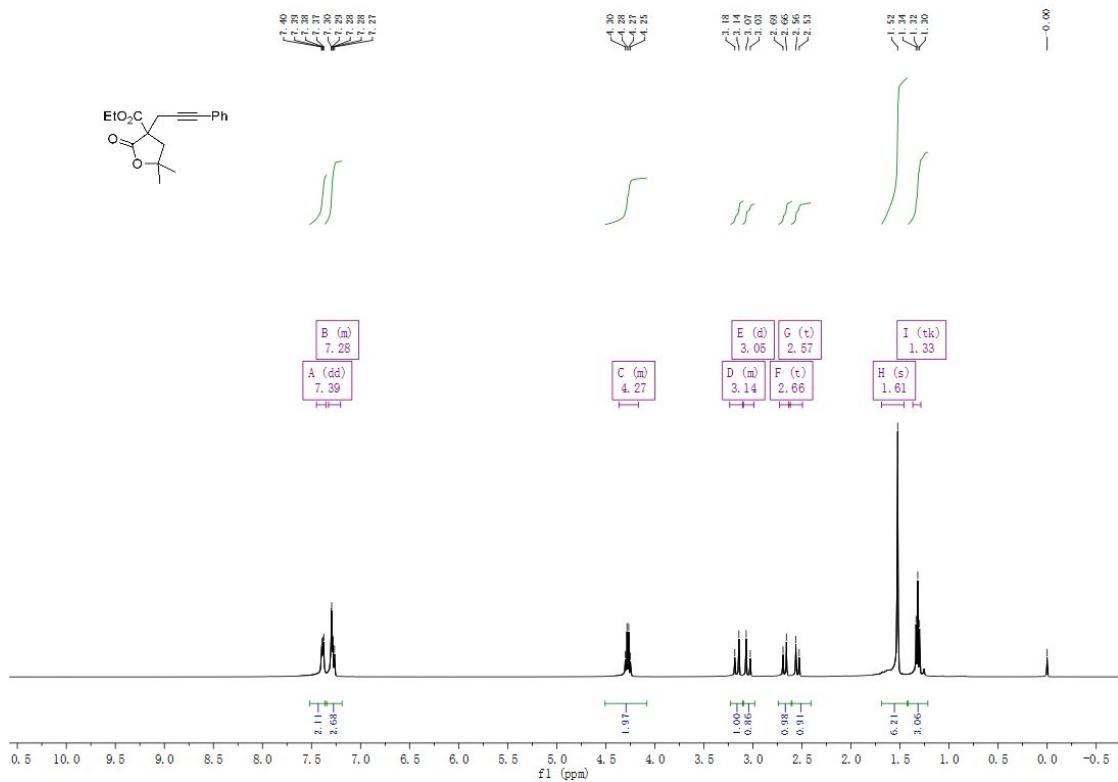
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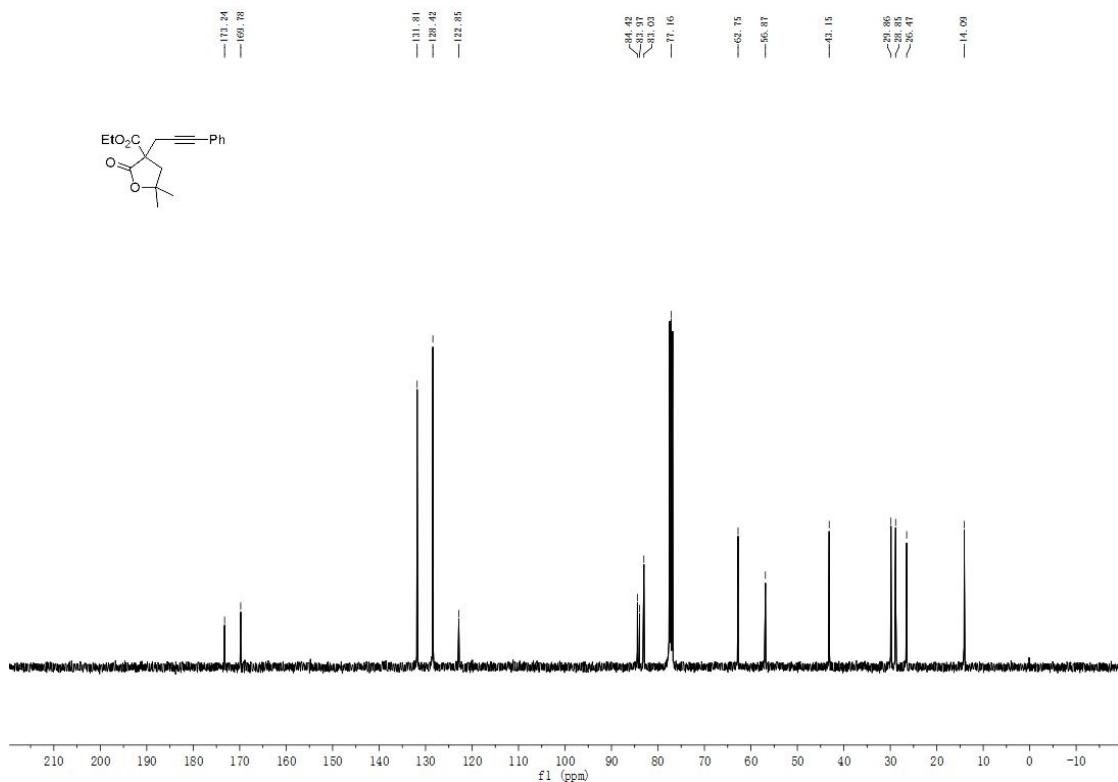
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **6**



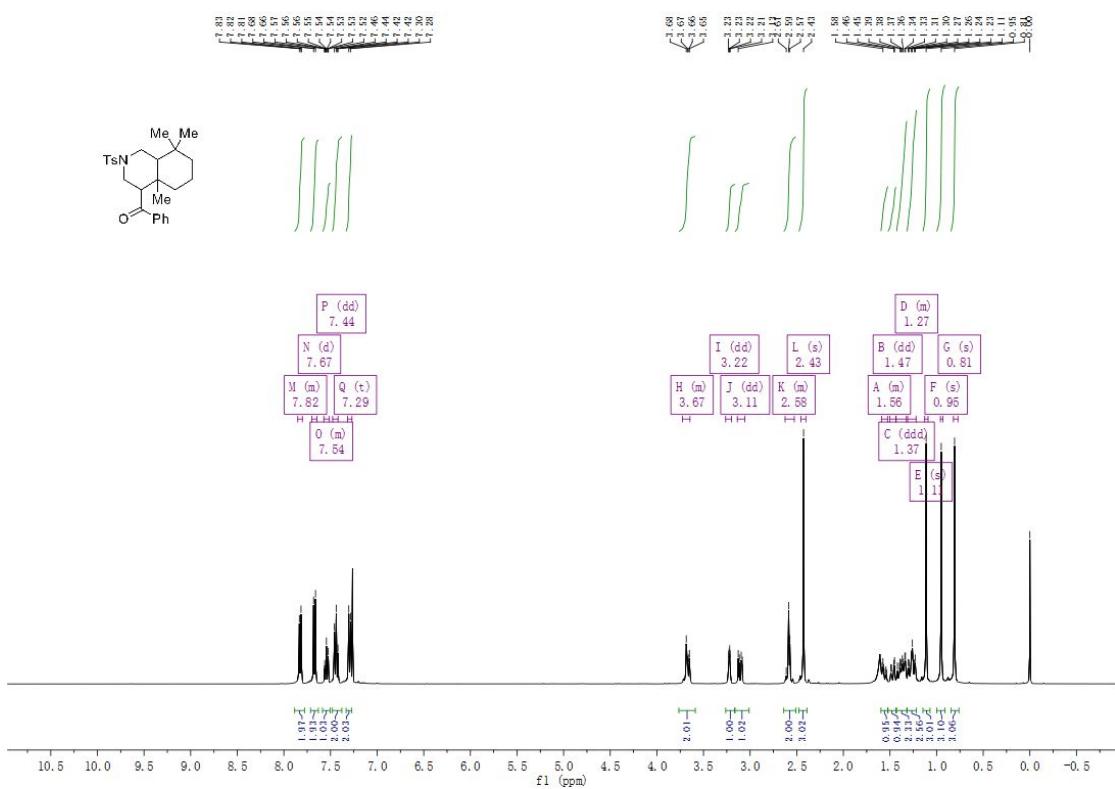
¹H NMR (400 MHz, CDCl₃) spectrum of compound **8**



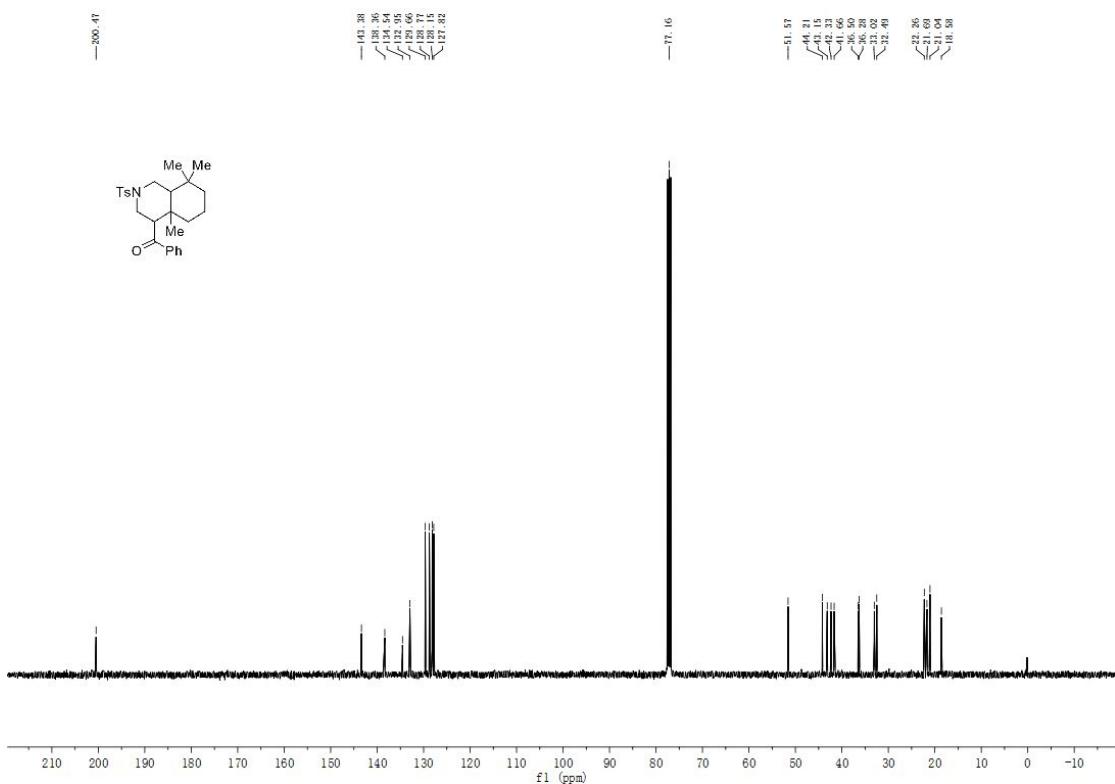
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **8**



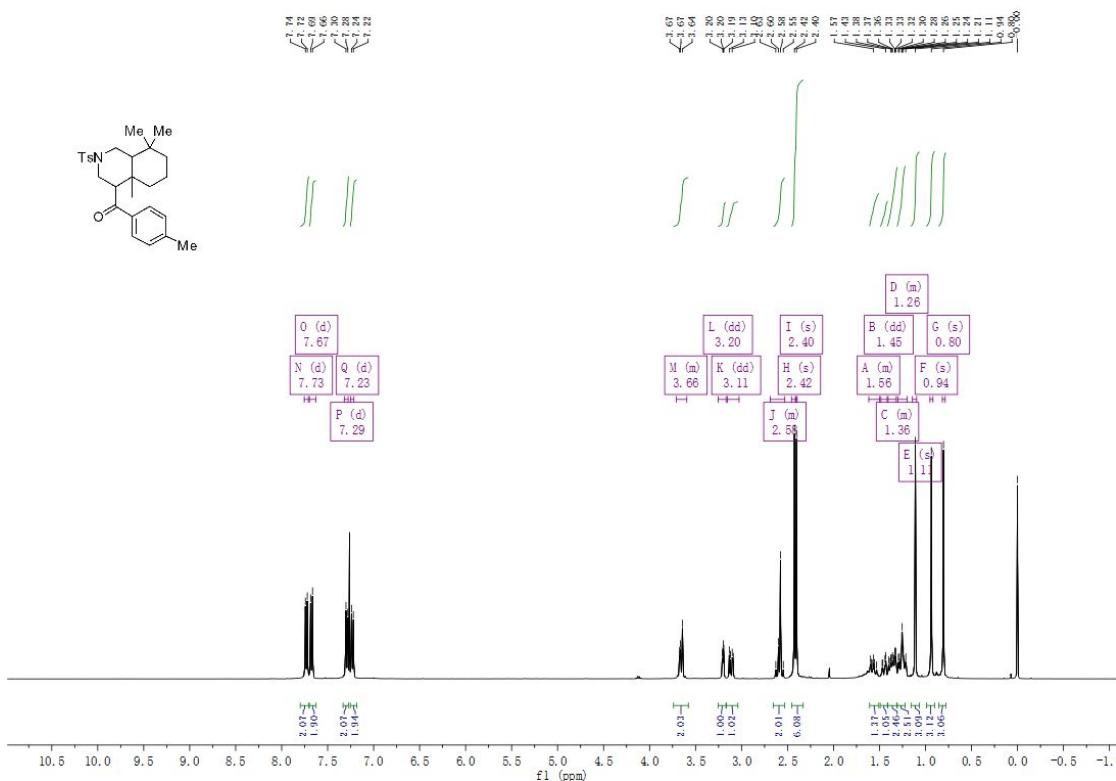
¹H NMR (400 MHz, CDCl₃) spectrum of compound **10a**



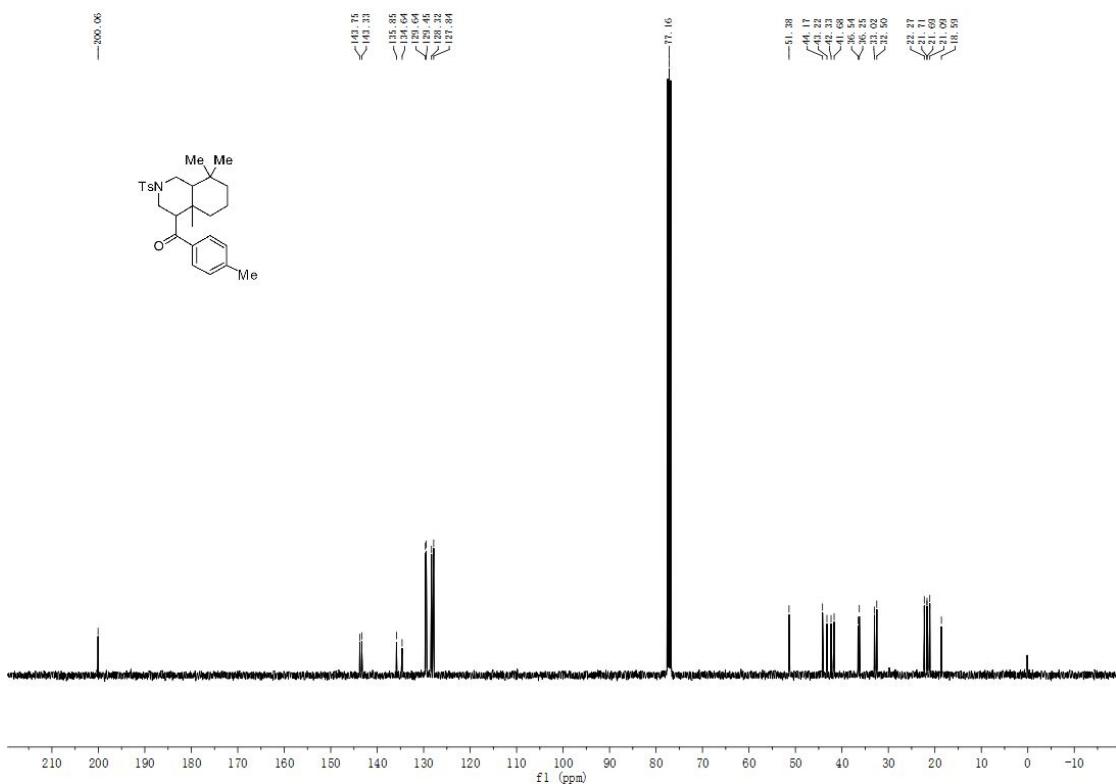
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **10a**



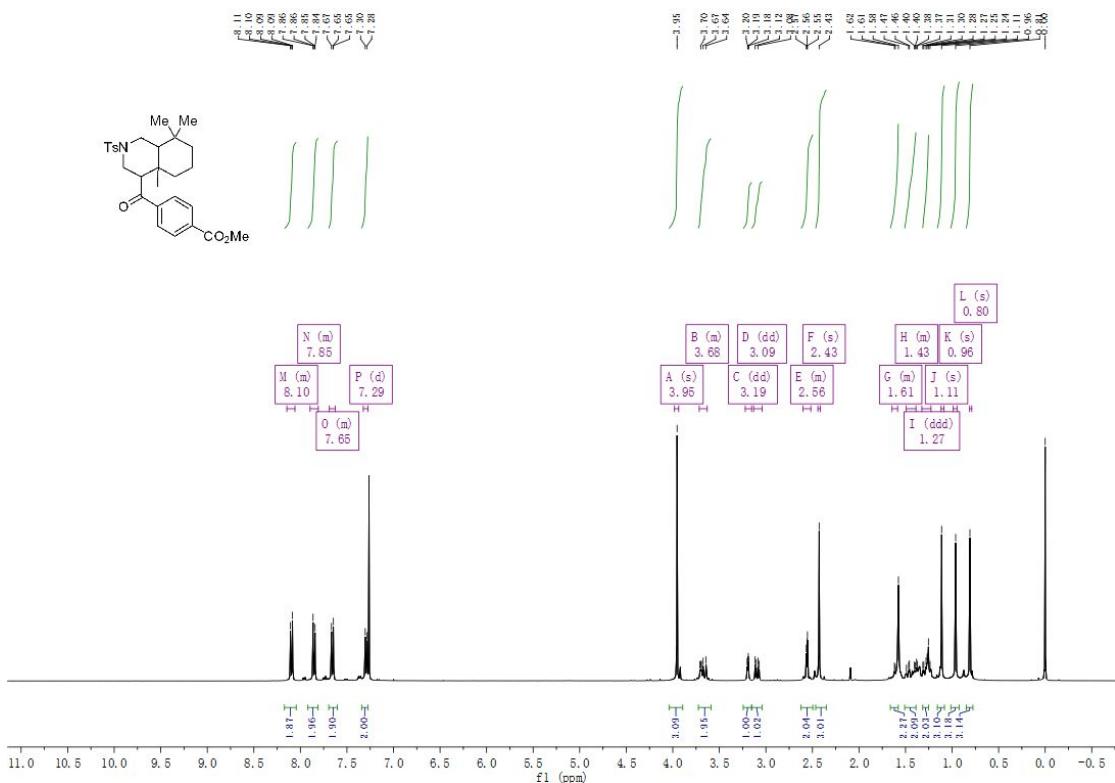
¹H NMR (400 MHz, CDCl₃) spectrum of compound **10b**



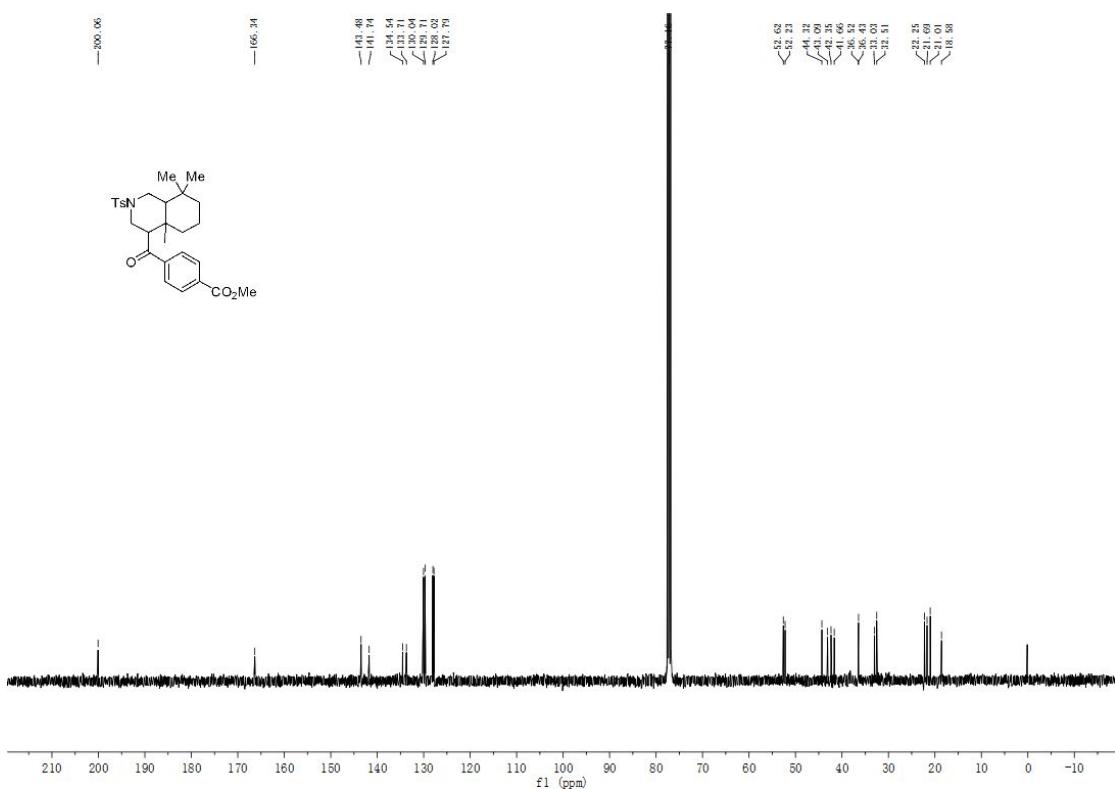
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **10b**



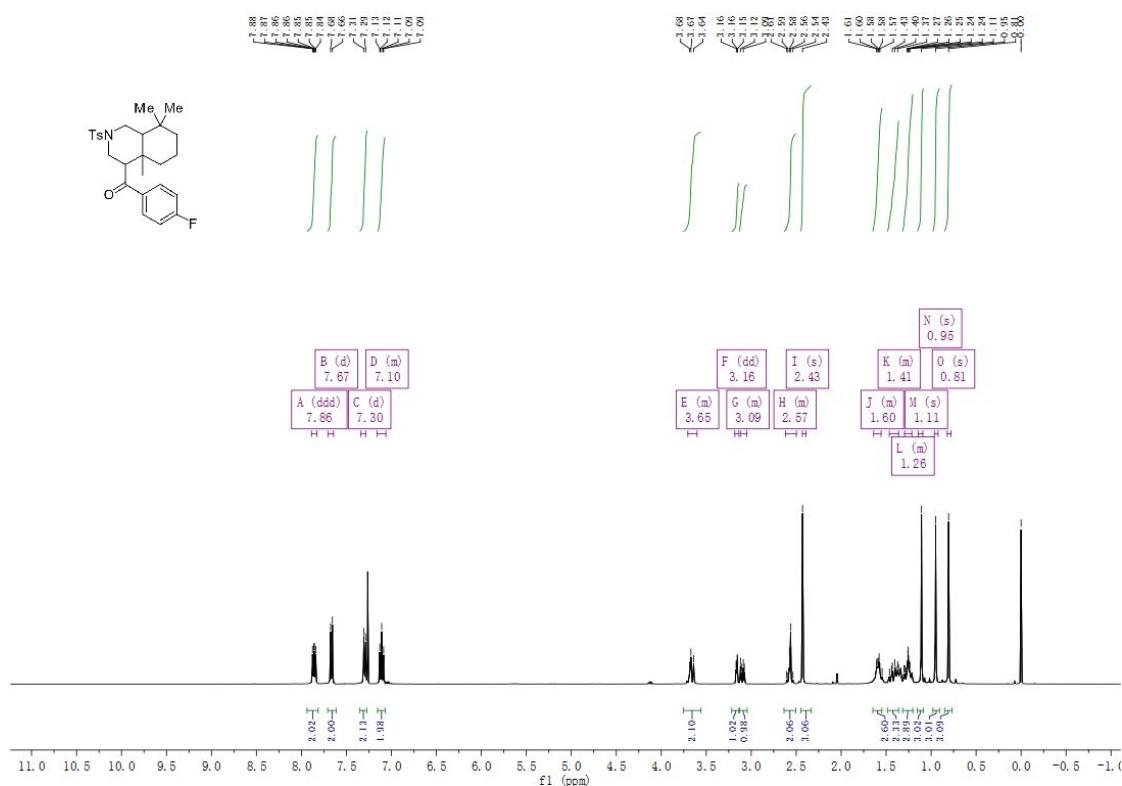
¹H NMR (400 MHz, CDCl₃) spectrum of compound **10c**



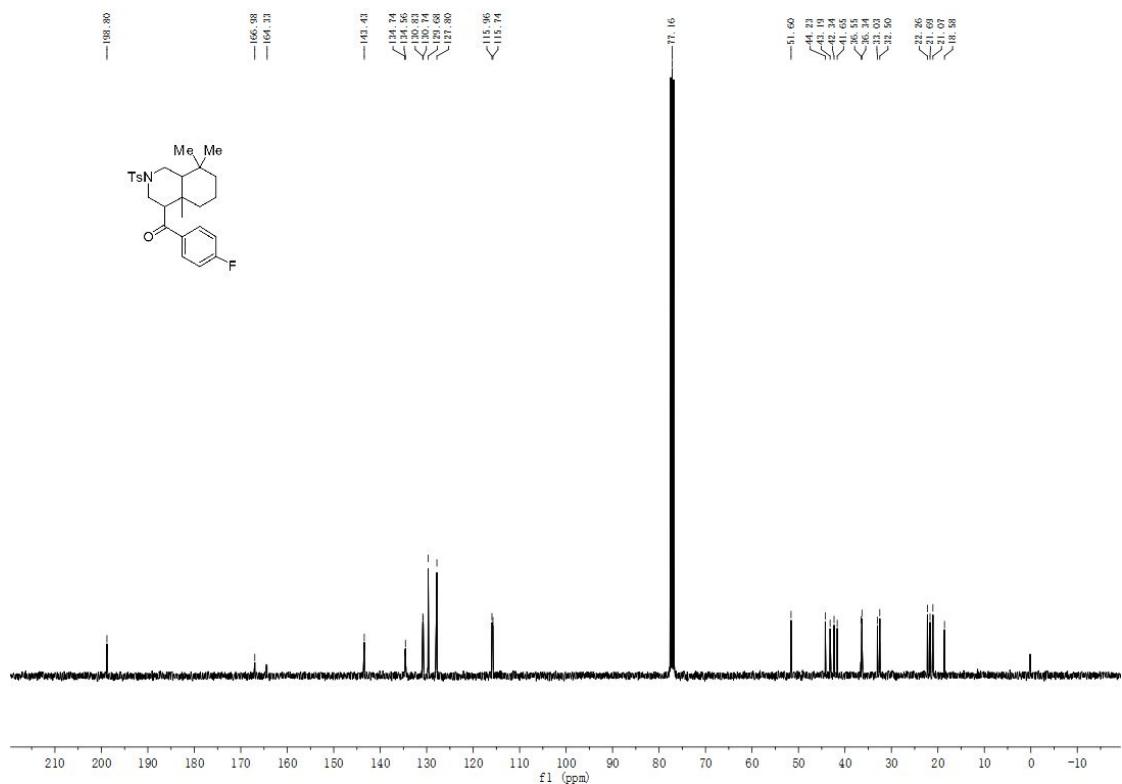
¹³C NMR (101 MHz, CDCl₃) spectrum of compound **10c**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **10d**

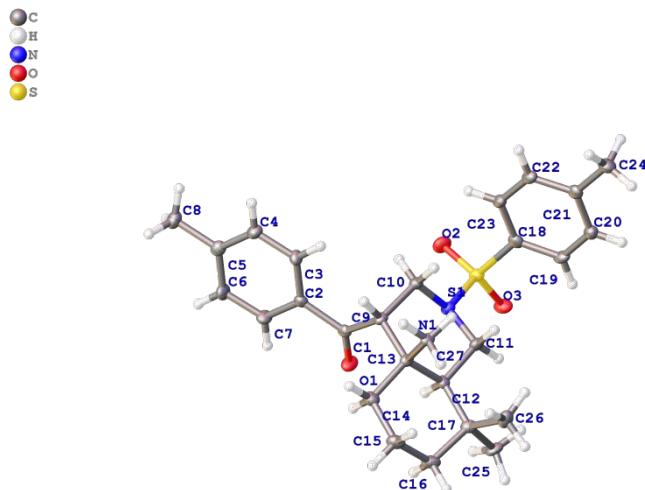


¹³C NMR (101 MHz, CDCl₃) spectrum of compound **10d**



2. X-ray crystallographic data

Figure 1 X-ray single crystal structure of **10b**



Single crystals of **10b** were grown by slow evaporation of its DCM/PE solution. Thermal ellipsoids drawn at the 30 % probability level. Single-crystal X-ray diffraction data were collected with a 'multiwire proportional' diffractometer. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Least Squares minimization. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 1954492).

Table S1 Crystal data and structure refinement for **10b**

Empirical formula	C ₂₇ H ₃₅ NO ₃ S
Formula weight	453.62
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.0850(7)
b/Å	13.7260(12)
c/Å	15.9662(8)
α/°	83.794(6)
β/°	89.703(4)
γ/°	85.423(7)
Volume/Å ³	2407.3(3)
Z	4
ρ _{calc} g/cm ³	1.252
μ/mm ⁻¹	0.163
F(000)	976.0

Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	Mo Kα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.148 to 49.998
Index ranges	-12 ≤ h ≤ 13, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	17358
Independent reflections	8463 [R _{int} = 0.0562, R _{sigma} = 0.1003]
Data/restraints/parameters	8463/0/587
Goodness-of-fit on F ²	1.071
Final R indexes [I>=2σ (I)]	R ₁ = 0.0978, wR ₂ = 0.2215
Final R indexes [all data]	R ₁ = 0.1232, wR ₂ = 0.2363
Largest diff. peak/hole / e Å ⁻³	0.98/-0.51

Table S2 Bond Lengths for **10b**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1B	O1B	1.440(4)	C13B	C17B	1.551(7)
S1B	O2B	1.434(4)	C13B	C11B	1.550(8)
S1B	N1B	1.645(5)	C13B	C18B	1.542(7)
S1B	C20B	1.777(5)	C13B	C14B	1.543(7)
S1	O2	1.437(4)	C19	C20	1.384(8)
S1	O3	1.432(4)	C24B	C23B	1.387(8)
S1	N1	1.649(4)	C4	C5	1.385(8)
S1	C18	1.761(6)	C20B	C21B	1.388(8)
O005	C7B	1.217(6)	C5	C6	1.390(8)
O1	C1	1.216(6)	C5	C8	1.509(8)
N1	C10	1.464(6)	C8B	C9B	1.551(7)
N1	C11	1.483(6)	C22	C21	1.388(8)
N1B	C12B	1.481(7)	C4B	C3B	1.393(8)
N1B	C9B	1.472(7)	C4B	C5B	1.391(8)
C1	C2	1.511(7)	C4B	C19B	1.496(8)
C1	C9	1.520(8)	C2B	C1B	1.405(8)
C23	C18	1.397(8)	C2B	C3B	1.383(8)
C23	C22	1.384(8)	C21	C20	1.409(8)
C25B	C24B	1.394(8)	C21	C24	1.495(8)
C25B	C20B	1.382(8)	C1B	C6B	1.390(7)
C3	C4	1.398(8)	C23B	C22B	1.394(8)
C3	C2	1.393(7)	C23B	C26B	1.511(8)
C13	C27	1.537(7)	C12	C11	1.541(7)
C13	C12	1.556(7)	C12	C17	1.543(7)
C13	C9	1.567(7)	C9	C10	1.551(7)
C13	C14	1.544(7)	C6B	C5B	1.384(8)

C7	C2	1.389(8)	C25	C17	1.542(7)
C7	C6	1.383(8)	C11B	C12B	1.536(7)
C18	C19	1.394(8)	C21B	C22B	1.385(8)
C7B	C8B	1.527(7)	C16B	C15B	1.523(8)
C7B	C1B	1.497(8)	C15B	C14B	1.524(8)
C10B	C8B	1.548(8)	C16	C15	1.541(8)
C10B	C11B	1.551(7)	C16	C17	1.545(8)
C10B	C16B	1.554(7)	C15	C14	1.532(7)
C10B	C01P	1.542(7)	C17	C26	1.530(8)

Table S3 Bond Angles for **10b**

Atom	Atom	Atom	Angle/ [°]	Atom	Atom	Atom	Angle/ [°]
O1B	S1B	N1B	105.5(2)	C4	C5	C6	118.6(5)
O1B	S1B	C20B	108.6(3)	C4	C5	C8	120.9(5)
O2B	S1B	O1B	120.3(2)	C6	C5	C8	120.5(5)
O2B	S1B	N1B	106.8(2)	C7B	C8B	C10B	118.0(4)
O2B	S1B	C20B	108.4(2)	C7B	C8B	C9B	107.0(4)
N1B	S1B	C20B	106.5(2)	C10B	C8B	C9B	111.3(4)
O2	S1	N1	105.9(2)	C3	C2	C1	124.3(5)
O2	S1	C18	108.6(3)	C7	C2	C1	117.4(5)
O3	S1	O2	120.0(2)	C7	C2	C3	118.3(5)
O3	S1	N1	107.1(2)	C23	C22	C21	121.6(5)
O3	S1	C18	108.3(3)	C3B	C4B	C19B	121.0(5)
N1	S1	C18	106.1(2)	C5B	C4B	C3B	117.7(5)
C10	N1	S1	115.7(3)	C5B	C4B	C19B	121.3(5)
C10	N1	C11	112.9(4)	C3B	C2B	C1B	121.4(5)
C11	N1	S1	115.8(3)	C22	C21	C20	118.2(5)
C12B	N1B	S1B	117.2(3)	C22	C21	C24	120.8(5)
C9B	N1B	S1B	115.1(4)	C20	C21	C24	121.0(5)
C9B	N1B	C12B	112.3(4)	C2B	C1B	C7B	123.9(5)
O1	C1	C2	119.7(5)	C6B	C1B	C7B	118.8(5)
O1	C1	C9	123.0(5)	C6B	C1B	C2B	117.3(5)
C2	C1	C9	117.3(4)	C24B	C23B	C22B	119.4(5)
C22	C23	C18	119.2(5)	C24B	C23B	C26B	120.1(5)
C20B	C25B	C24B	120.3(5)	C22B	C23B	C26B	120.5(5)
C2	C3	C4	120.7(5)	C11	C12	C13	111.2(4)
C27	C13	C12	114.7(4)	C11	C12	C17	113.5(4)
C27	C13	C9	105.4(4)	C17	C12	C13	116.2(4)
C27	C13	C14	108.1(4)	C1	C9	C13	117.1(4)
C12	C13	C9	109.6(4)	C1	C9	C10	108.0(4)

C14	C13	C12	108.4(4)	C10	C9	C13	111.6(4)
C14	C13	C9	110.5(4)	N1	C10	C9	109.7(4)
C6	C7	C2	120.9(5)	C5B	C6B	C1B	121.1(5)
C23	C18	S1	119.4(4)	C10B	C11B	C13B	115.7(4)
C19	C18	S1	119.4(4)	C12B	C11B	C10B	111.4(4)
C19	C18	C23	120.7(5)	C12B	C11B	C13B	113.3(4)
O005	C7B	C8B	123.0(5)	N1B	C12B	C11B	108.4(4)
O005	C7B	C1B	119.8(5)	N1B	C9B	C8B	109.9(4)
C1B	C7B	C8B	117.2(4)	C19	C20	C21	121.3(5)
C8B	C10B	C11B	109.8(4)	C22B	C21B	C20B	119.0(5)
C8B	C10B	C16B	109.7(4)	C15B	C16B	C10B	111.9(5)
C11B	C10B	C16B	108.5(4)	C16B	C15B	C14B	111.8(5)
C01P	C10B	C8B	105.6(4)	N1	C11	C12	108.5(4)
C01P	C10B	C11B	114.5(4)	C15	C16	C17	113.7(5)
C01P	C10B	C16B	108.7(4)	C14	C15	C16	109.9(4)
C11B	C13B	C17B	108.9(4)	C12	C17	C16	107.3(4)
C18B	C13B	C17B	106.4(4)	C25	C17	C12	108.4(4)
C18B	C13B	C11B	116.6(4)	C25	C17	C16	105.9(4)
C18B	C13B	C14B	110.2(5)	C26	C17	C12	116.4(5)
C14B	C13B	C17B	106.8(4)	C26	C17	C25	107.0(5)
C14B	C13B	C11B	107.6(4)	C26	C17	C16	111.2(4)
C20	C19	C18	119.0(5)	C7	C6	C5	121.0(6)
C23B	C24B	C25B	119.7(5)	C15	C14	C13	111.9(5)
C5	C4	C3	120.4(5)	C21B	C22B	C23B	121.1(5)
C25B	C20B	S1B	120.1(4)	C2B	C3B	C4B	120.9(5)
C25B	C20B	C21B	120.5(5)	C15B	C14B	C13B	114.3(4)
C21B	C20B	S1B	119.2(4)	C6B	C5B	C4B	121.6(5)