Supporting Information

Rh-catalyzed Regioselective *ortho*-C-H Carbenoid Insertion of Diarylazines

Yunliang Yu, Changsheng Kuai, Remi Chauvin,*,† Nian Tian, Shuangshuang Ma and Xiuling Cui*
Engineering Research Center of Molecular Medicine of Ministry of Education, Key Laboratory of Fujian Molecular Medicine, Key Laboratory of Xiamen Marine and Gene Drugs, School of Biomedical Sciences, Huaqiao University, Xiamen 361021, P. R. China
† (a) CNRS, LCC (Laboratoire de Chimie de Coordination), 205, route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4 France. (b) Université de Toulouse, UPS, INPT, F-31077 Toulouse, Cedex 4, France.

Corresponding Author: Xiuling Cui, Email: cuixl@hqu.edu.cn
Tel & Fax: +86-592-6162996
Remi Chauvin, E-mail: remi.chauvin@lcc-toulouse.fr

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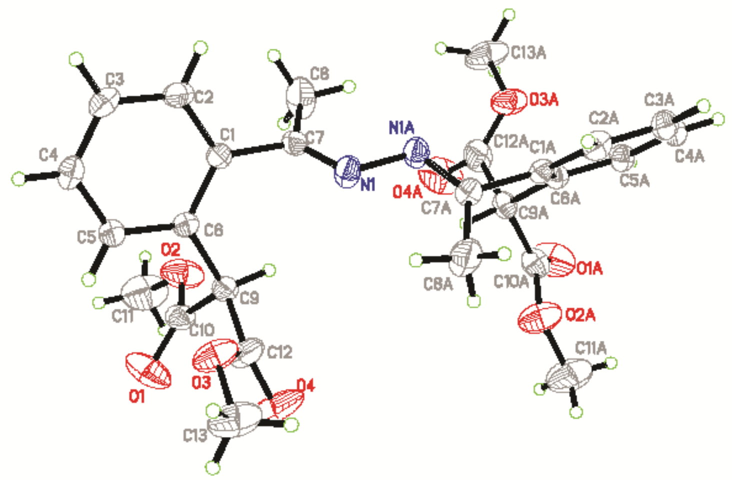


Figure S1. X-Ray structure of product 3aa with the ellipsoid contour 50% probility

Table S1 Crystal data and structure refinement for exp_1605 (3aa).

Identification code	exp_1605
Empirical formula	$C_{13}H_{14}NO_4$
Formula weight	248.25
Temperature/K	293(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	7.9578(3)
b/Å	14.6936(5)
c/Å	24.4705(10)
α/°	90
β/°	97.184(3)
γ/°	90
Volume/Å^3	2838.83(18)
Z	8
ρ_{calc}g/cm^3	1.162
μ/mm^{-1}	0.087
F(000)	1048.0
Crystal size/mm^3	0.25 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.858 to 52.732
Index ranges	$-9 \le h \le 9$, $-18 \le k \le 12$, $-30 \le l \le 29$
Reflections collected	6009

Independent reflections	2632 [R_{int} = 0.0170, R_{sigma} = 0.0220]
Data/restraints/parameters	2632/12/170
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0693, wR_2 = 0.2032
Final R indexes [all data]	R_1 = 0.0820, wR_2 = 0.2149
Largest diff. peak/hole / e Å^{-3}	0.40/-0.30

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_1605. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	4348(2)	1062.7(14)	6137.0(8)	36.3(5)
C2	5268(3)	322.0(16)	6375.2(10)	47.6(6)
C3	5554(3)	215.7(16)	6938.8(11)	51.0(6)
C4	4952(3)	856.3(17)	7273.2(10)	49.7(6)
C5	4067(3)	1602.7(16)	7047.0(9)	43.5(6)
C6	3748(3)	1714.0(14)	6478.4(8)	36.4(5)
C7	4080(3)	1127.9(15)	5521.6(9)	40.8(5)
C8	5601(4)	1262(3)	5237.3(12)	83.1(11)
C9	2811(3)	2559.8(15)	6245.0(9)	43.4(6)
C10	3697(4)	3410.1(16)	6490.5(11)	52.9(7)
C11	6132(5)	4321(3)	6490(2)	108.7(15)
C12	943(3)	2613(2)	6315.9(13)	64.2(8)
C13	-1329(4)	2051(3)	6746(2)	95.7(13)
N1	2577(2)	1035.5(16)	5292.7(7)	51.1(6)
O1	3194(4)	3885.7(15)	6825.0(11)	98.4(9)
O2	5125(3)	3541.4(14)	6286.0(11)	82.5(7)
O3	444(2)	2052.5(14)	6660.6(10)	72.4(7)
O4	105(7)	3312(5)	6154(3)	120(2)
O4A	-144(13)	2781(8)	5928(6)	120(2)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_1605. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	30.2(10)	39.7(11)	38.9(11)	-1.6(8)	4.1(9)	-2.1(8)
C2	40.9(12)	41.5(12)	59.9(14)	-5.6(10)	4.5(11)	5.8(9)
C3	43.6(13)	44.8(13)	61.8(15)	10.0(11)	-4.2(11)	4.9(10)
C4	46.5(13)	59.3(15)	41.5(12)	10.3(11)	-1.5(10)	-1.8(11)
C5	43.5(12)	47.4(13)	39.5(11)	-1.5(9)	4.2(10)	1.6(10)
C6	33.6(10)	35.5(11)	40.3(11)	0.5(8)	5.0(9)	1.1(8)
C7	36.7(12)	45.1(12)	41.1(11)	-5.8(9)	7.6(9)	2.2(9)
C8	45.1(16)	155(3)	51.7(15)	-5.9(18)	14.4(13)	-15.1(18)
C9	50.1(13)	41.3(12)	38.8(11)	2.7(9)	6.3(10)	8.3(10)
C10	66.5(17)	38.5(12)	54.7(14)	2.1(10)	10.6(13)	11.9(11)
C11	88(3)	61(2)	175(4)	-18(2)	13(3)	-15.4(18)
C12	49.6(15)	69.1(18)	72.8(18)	15.2(14)	3.7(14)	19.7(13)
C13	40.9(16)	79(2)	170(4)	-7(2)	23(2)	-5.7(15)
N1	38.0(11)	78.1(15)	37.4(10)	3.9(9)	6.0(9)	-0.6(9)
O1	147(2)	58.4(14)	100.3(19)	-28.2(12)	57.5(17)	-8.0(14)
O2	67.1(14)	57.8(13)	127(2)	-27.2(12)	29.7(14)	-8.6(10)
O3	38.9(10)	60.7(12)	118.7(18)	16.2(11)	13.5(11)	2.0(8)
O4	75(2)	94(4)	194(6)	65(4)	23(3)	43(3)
O4A	75(2)	94(4)	194(6)	65(4)	23(3)	43(3)

Table S4 Bond Lengths for exp_1605.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.398(3)	C9	C10	1.521(3)
C1	C6	1.393(3)	C9	C12	1.520(4)
C1	C7	1.498(3)	C10	O1	1.183(3)
C2	C3	1.378(4)	C10	O2	1.312(4)
C3	C4	1.372(4)	C11	O2	1.450(4)
C4	C5	1.381(3)	C12	O3	1.277(4)
C5	C6	1.392(3)	C12	O4	1.262(6)
C6	C9	1.523(3)	C12	O4A	1.227(12)
C7	C8	1.483(4)	C13	O3	1.452(4)
C7	N1	1.263(3)	N1	N1[1]	1.422(4)

[1]1/2-X,+Y,1-Z

Table S5 Bond Angles for exp_1605.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C7	118.07(19)	C12	C9	C6	116.0(2)
C6	C1	C2	119.1(2)	C12	C9	C10	108.9(2)
C6	C1	C7	122.86(18)	O1	C10	C9	125.4(3)
C3	C2	C1	121.2(2)	O1	C10	O2	124.1(3)
C4	C3	C2	119.5(2)	O2	C10	C9	110.5(2)
C3	C4	C5	120.3(2)	O3	C12	C9	115.6(2)
C4	C5	C6	120.9(2)	O4	C12	C9	119.5(4)
C1	C6	C9	121.60(18)	O4	C12	O3	122.5(4)
C5	C6	C1	119.00(19)	O4A	C12	C9	121.8(6)
C5	C6	C9	119.35(19)	O4A	C12	O3	113.2(6)
C8	C7	C1	117.3(2)	C7	N1	N1[1]	113.8(2)
N1	C7	C1	116.6(2)	C10	O2	C11	116.9(3)
N1	C7	C8	126.1(2)	C12	O3	C13	119.0(3)
C10	C9	C6	109.98(18)				

[1] 1/2-X,+Y,1-Z

Table S6 Torsion Angles for exp_1605.

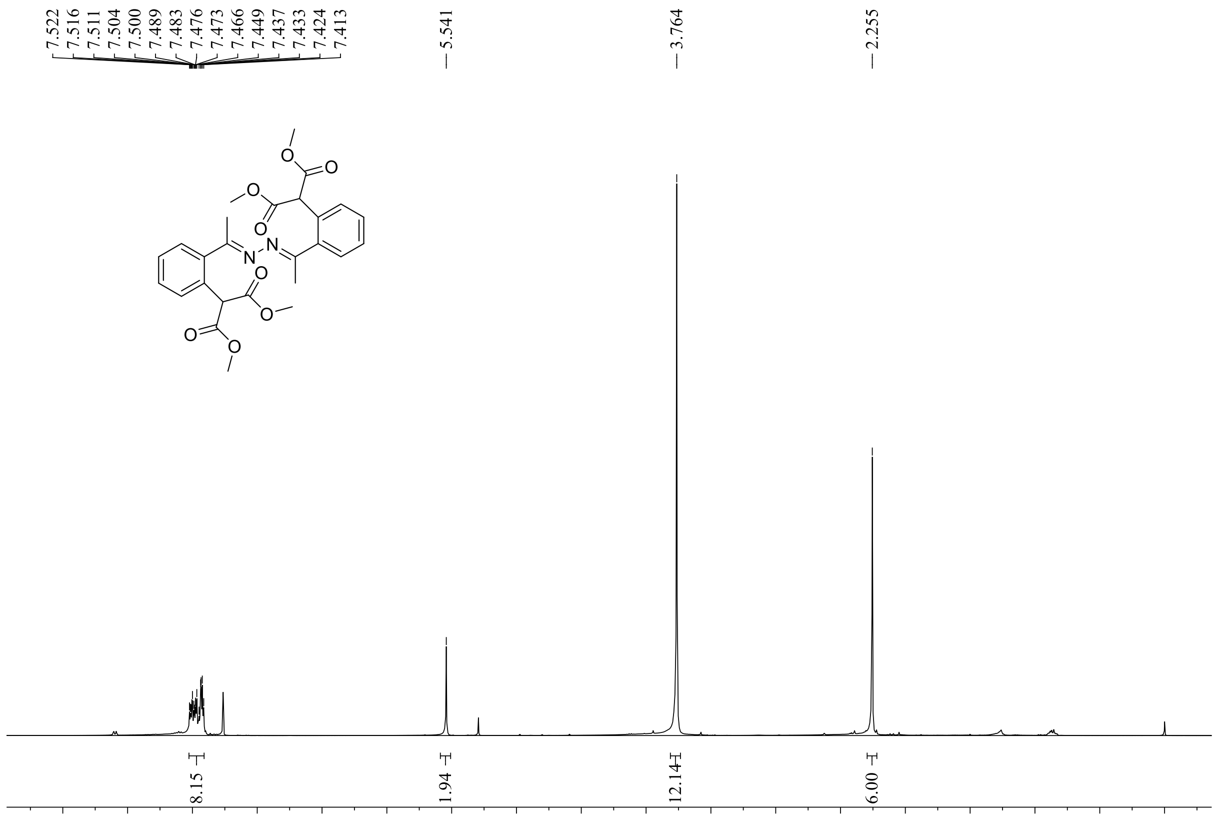
A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-1.1(4)	C6	C9	C10	O2	72.6(3)
C1	C6	C9	C10	-123.8(2)	C6	C9	C12	O3	14.4(4)
C1	C6	C9	C12	112.0(3)	C6	C9	C12	O4	177.0(5)
C1	C7	N1	N1[1]	-175.50(13)	C6	C9	C12	O4A	-129.7(8)
C2	C1	C6	C5	-0.6(3)	C7	C1	C2	C3	-179.6(2)
C2	C1	C6	C9	177.0(2)	C7	C1	C6	C5	-179.49(19)
C2	C1	C7	C8	-65.0(3)	C7	C1	C6	C9	-1.8(3)
C2	C1	C7	N1	113.0(3)	C8	C7	N1	N1[1]	2.2(3)
C2	C3	C4	C5	-0.1(4)	C9	C10	O2	C11	-178.9(3)
C3	C4	C5	C6	0.9(4)	C9	C12	O3	C13	-179.1(3)
C4	C5	C6	C1	-0.5(3)	C10	C9	C12	O3	-110.3(3)
C4	C5	C6	C9	-178.3(2)	C10	C9	C12	O4	52.3(6)
C5	C6	C9	C10	53.8(3)	C10	C9	C12	O4A	105.6(8)
C5	C6	C9	C12	-70.3(3)	C12	C9	C10	O1	21.7(4)
C6	C1	C2	C3	1.5(3)	C12	C9	C10	O2	-159.2(2)
C6	C1	C7	C8	113.9(3)	O1	C10	O2	C11	0.2(5)
C6	C1	C7	N1	-68.2(3)	O4	C12	O3	C13	18.9(7)
C6	C9	C10	O1	-106.4(3)	O4A	C12	O3	C13	-31.9(8)

[1] 1/2-X,+Y,1-Z

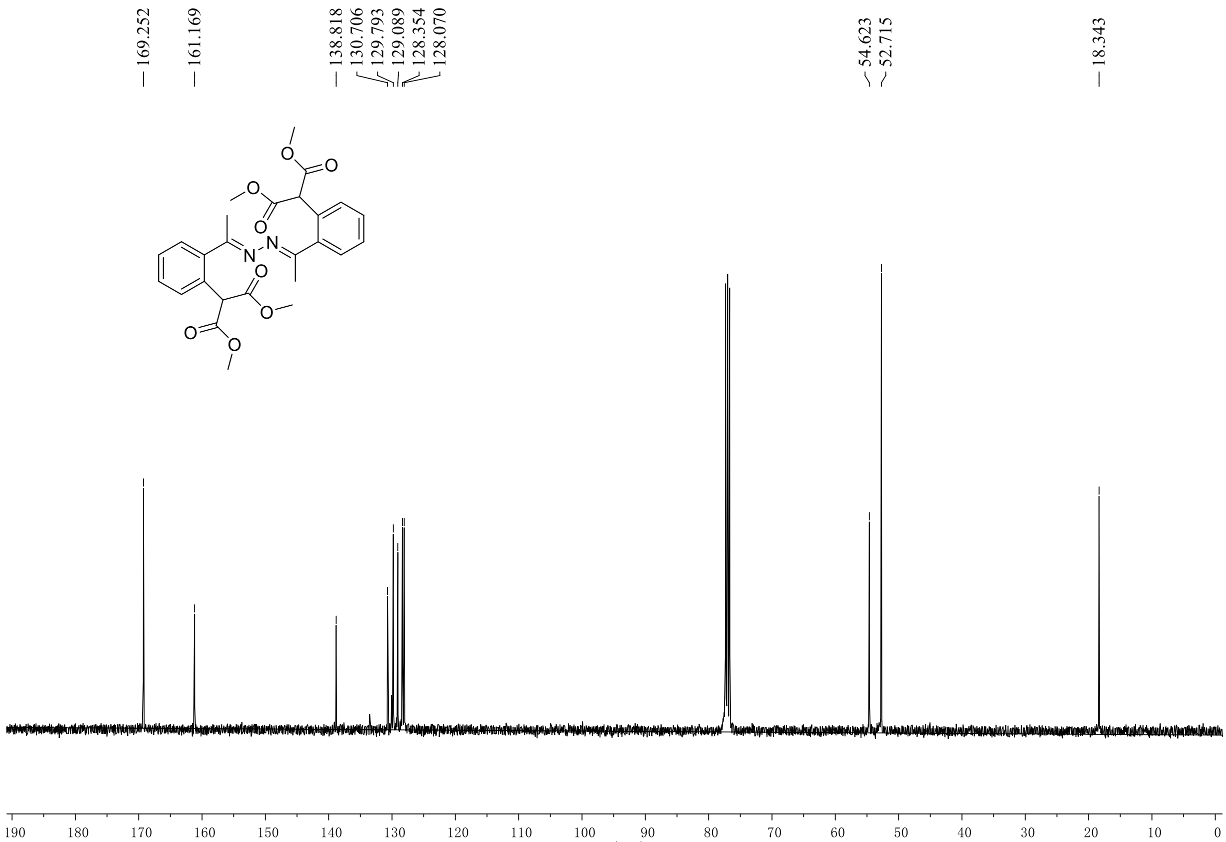
Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_1605.

Atom	*x*	*y*	*z*	U(eq)
H2	5694	-107	6149	57
H3	6151	-286	7091	61
H4	5141	788	7654	60
H5	3679	2037	7278	52
H8A	6017	1871	5301	125
H8B	5308	1167	4849	125
H8C	6462	836	5378	125
H9	2889	2570	5849	52
H11A	6308	4307	6885	163
H11B	5548	4871	6369	163
H11C	7207	4302	6350	163
H13A	-1556	1529	6962	144
H13B	-2024	2027	6396	144
H13C	-1580	2596	6937	144

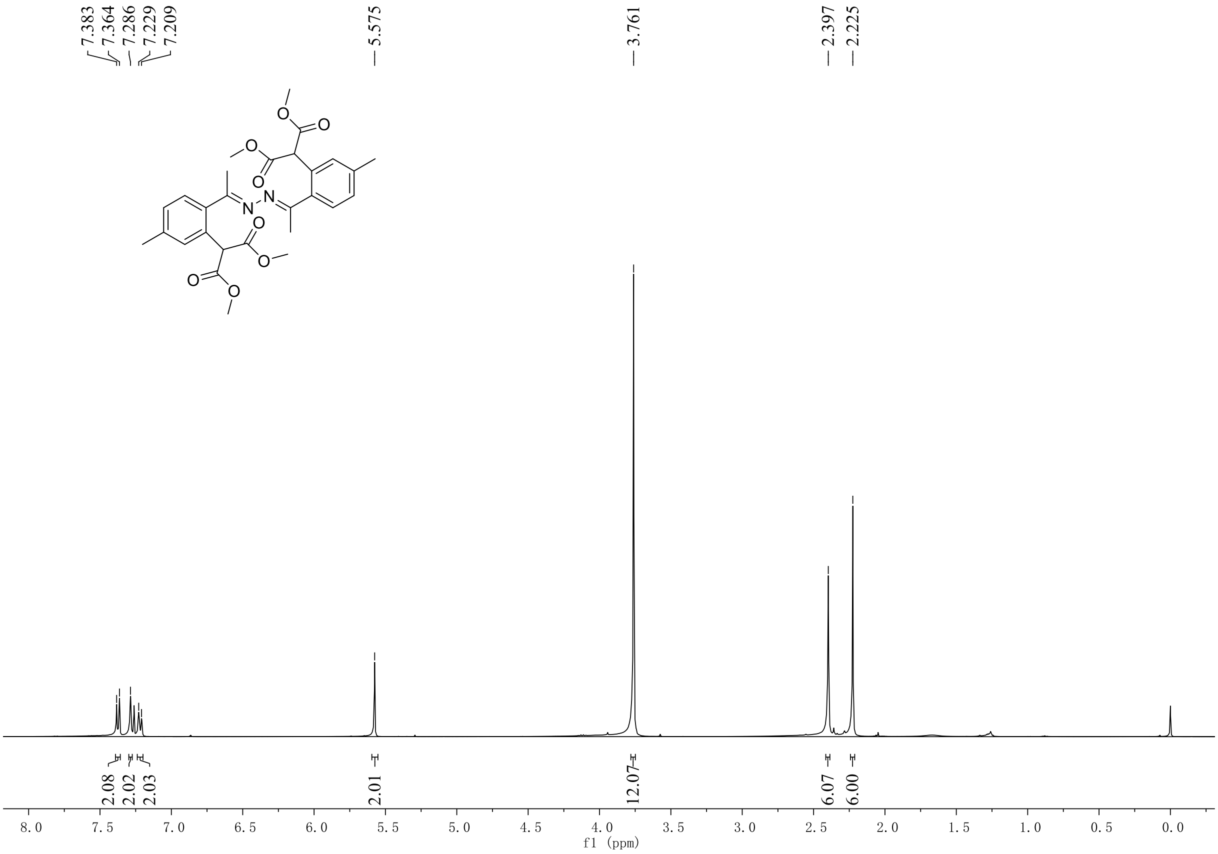
^{1}H NMR spectrum of **3aa**



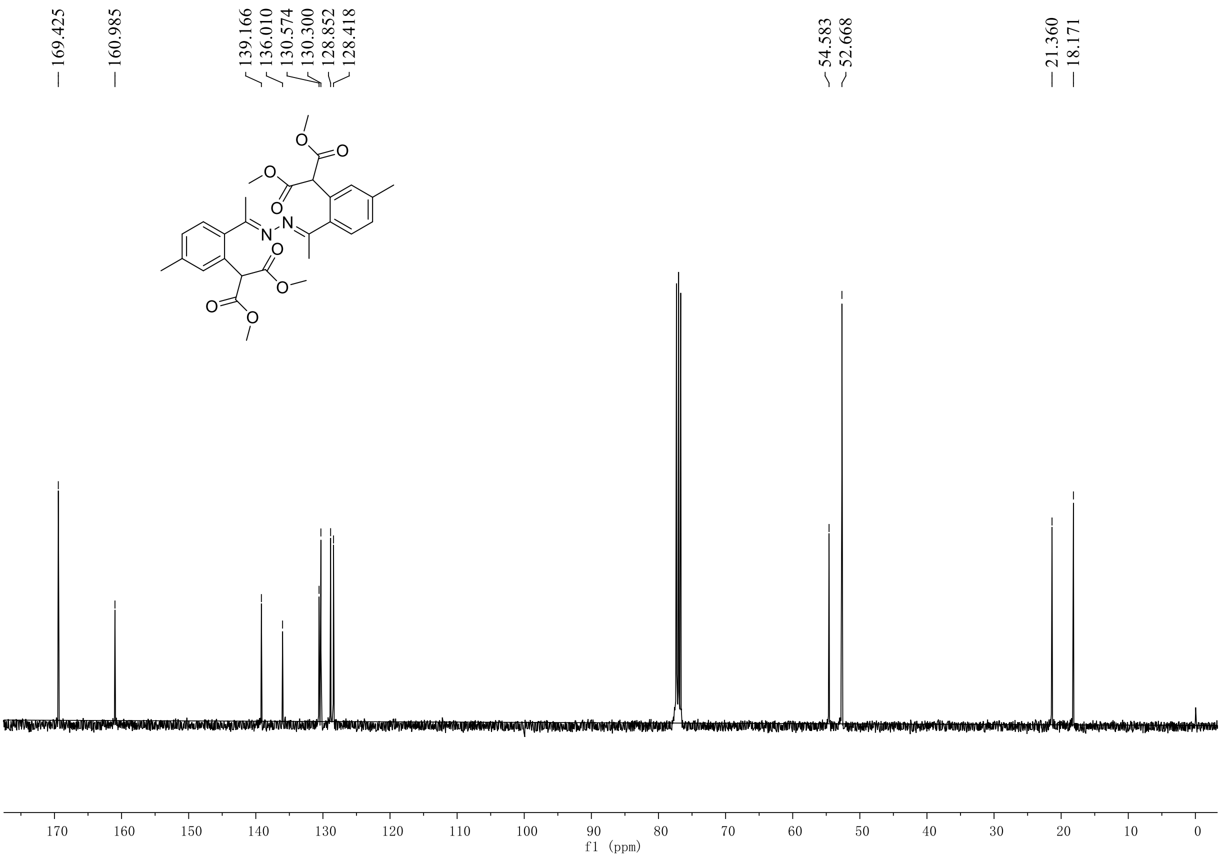
^{13}C NMR spectrum of **3aa**



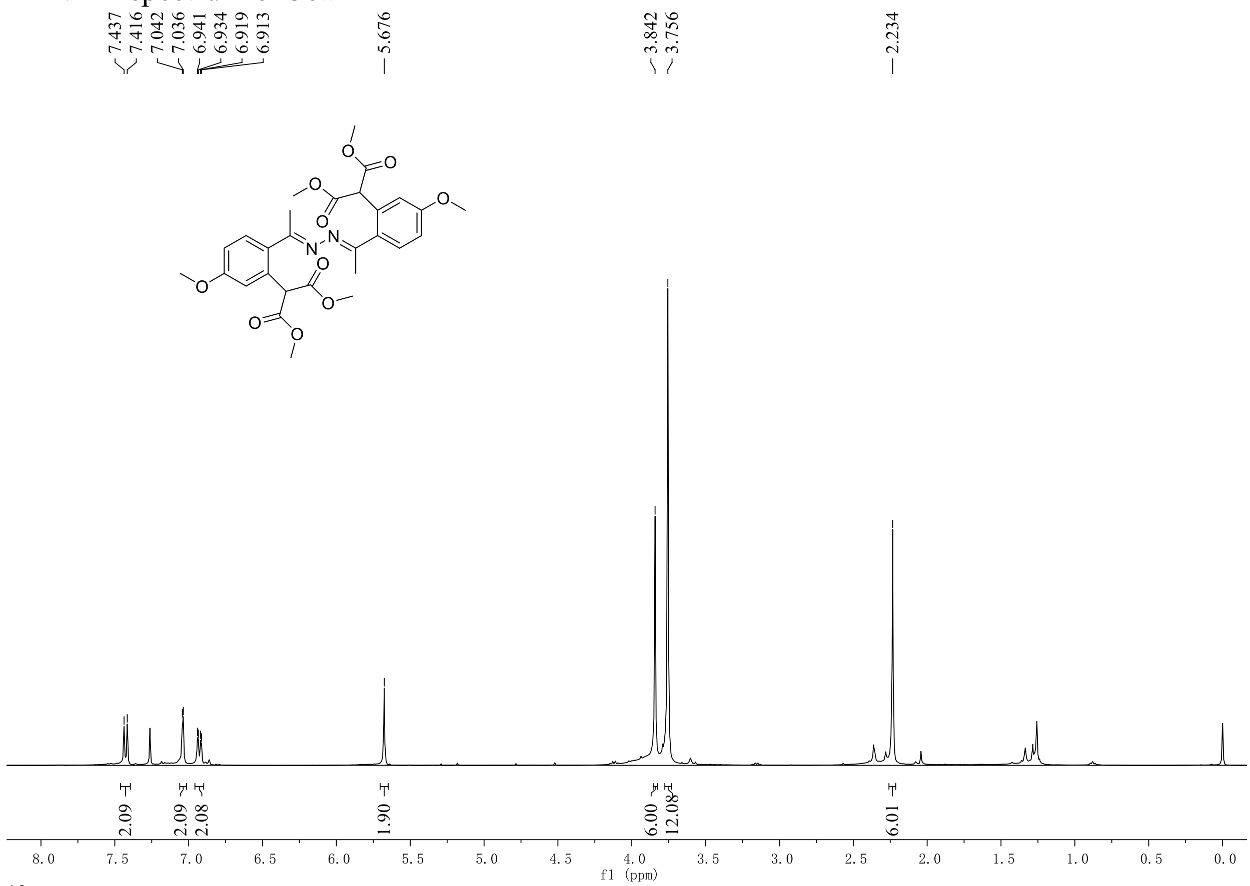
^{1}H NMR spectrum of **3ba**



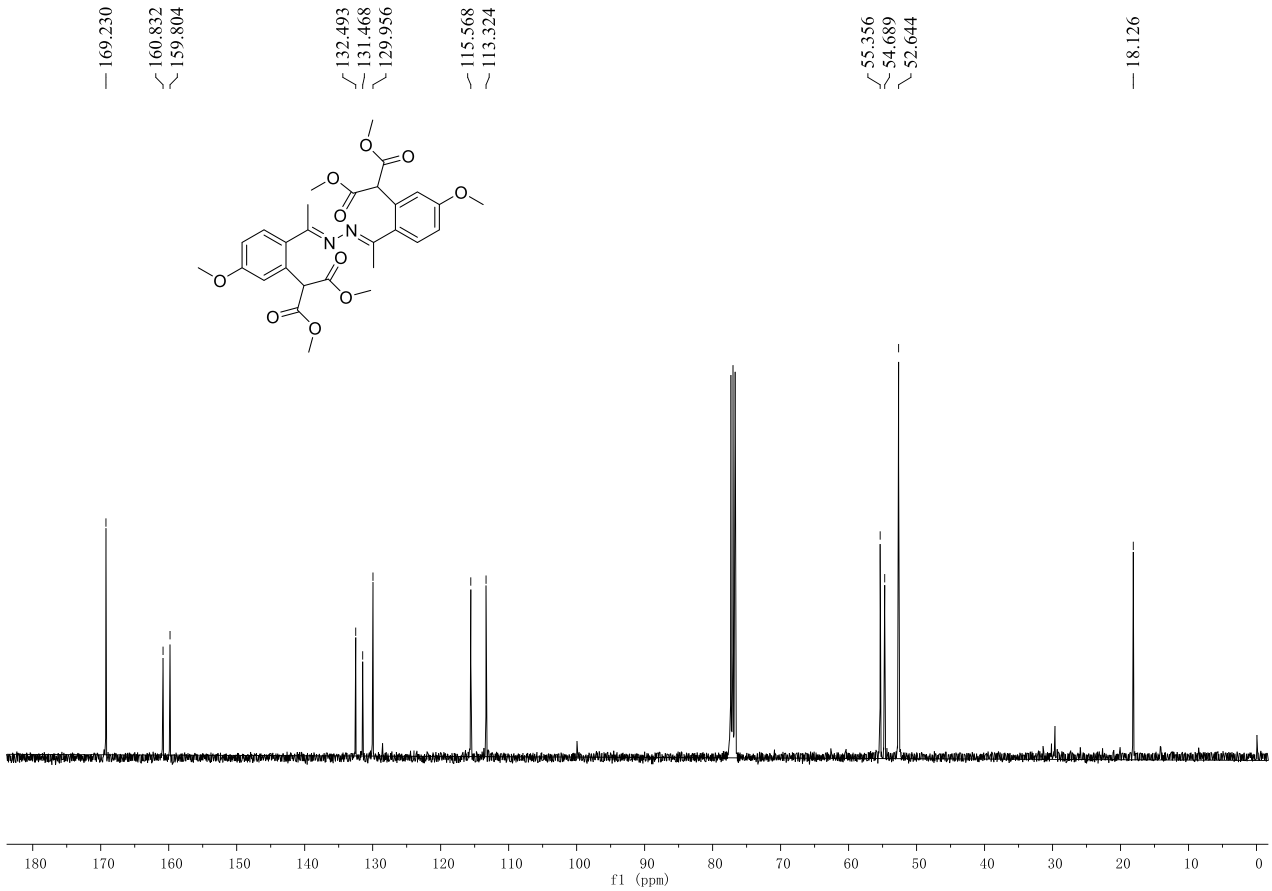
^{13}C NMR spectrum of **3ba**



[1]H NMR spectrum of **3ca**



[13]C NMR spectrum of **3ca**



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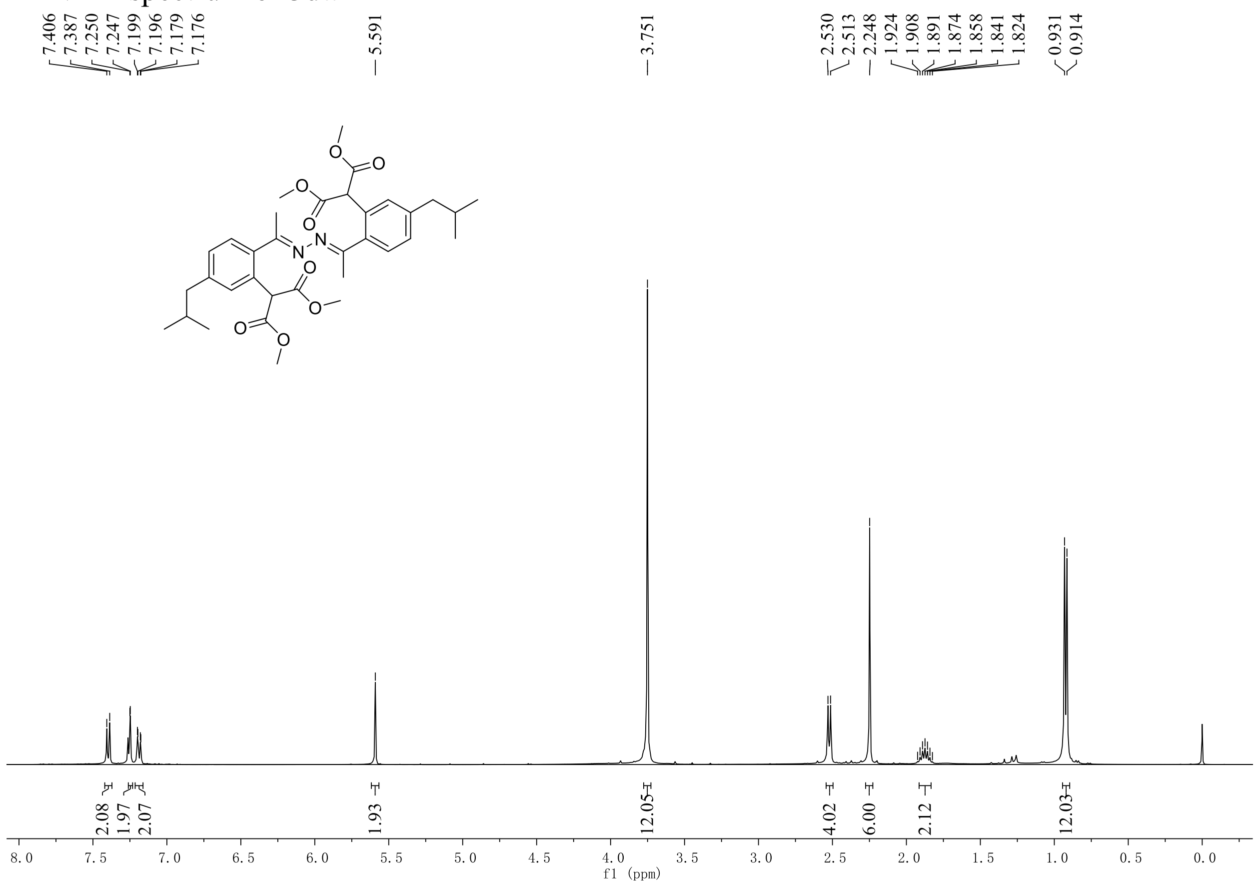

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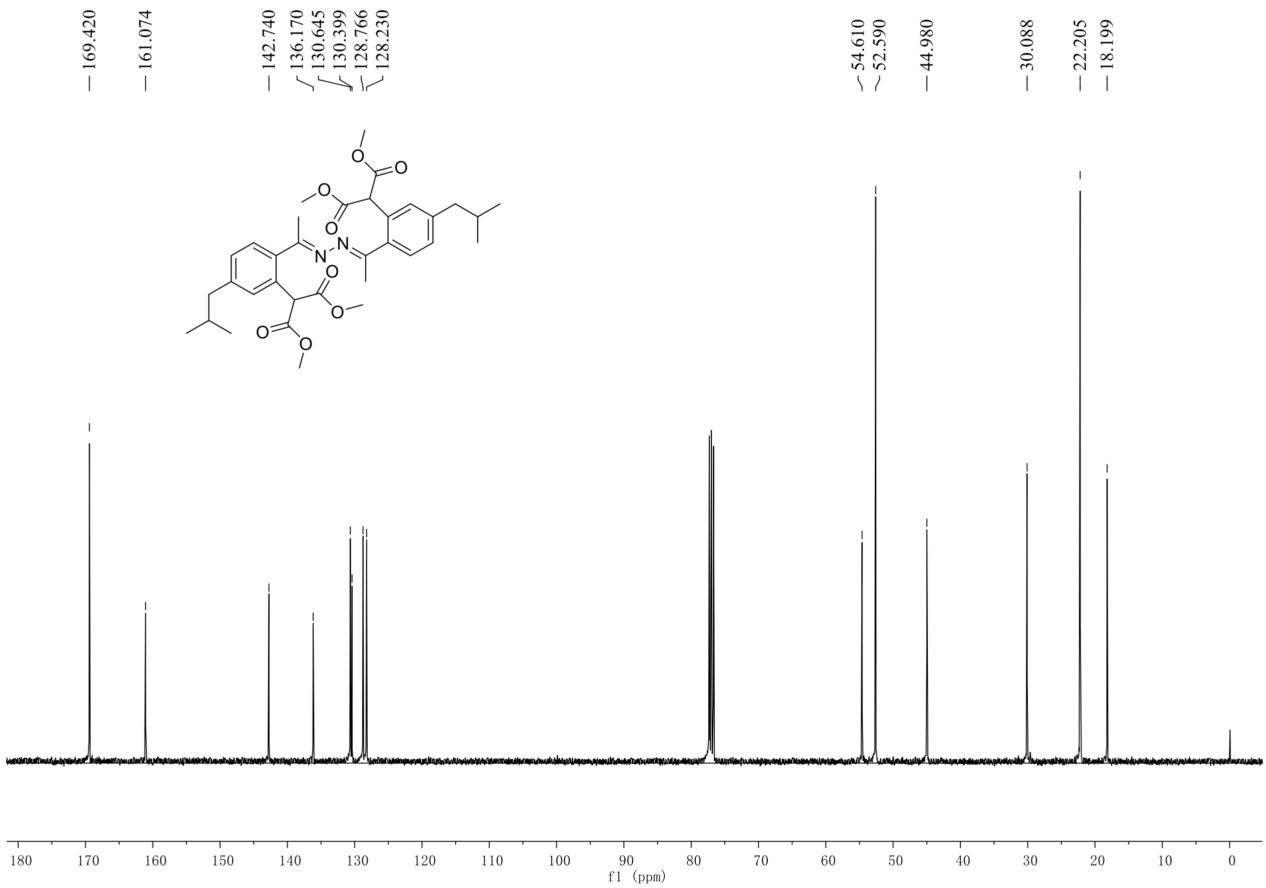

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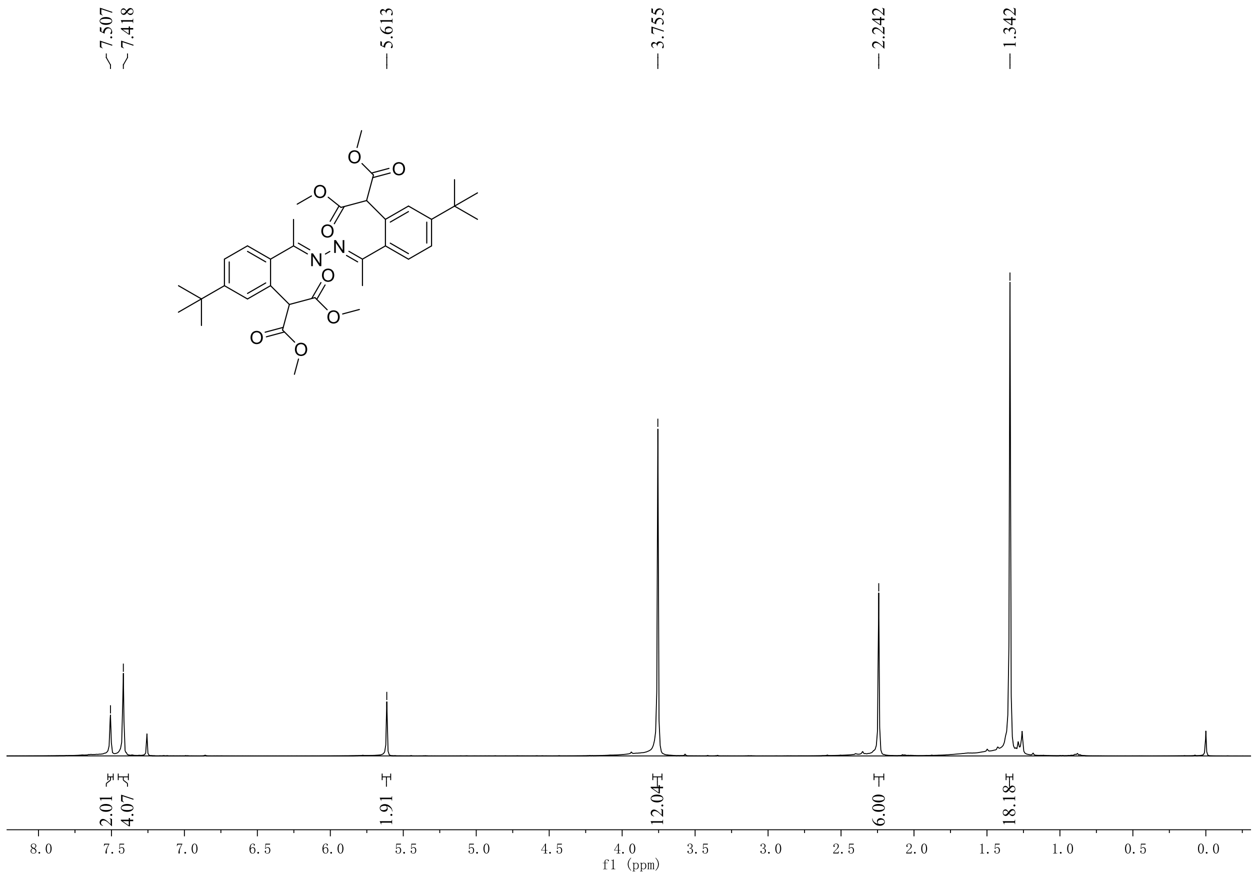

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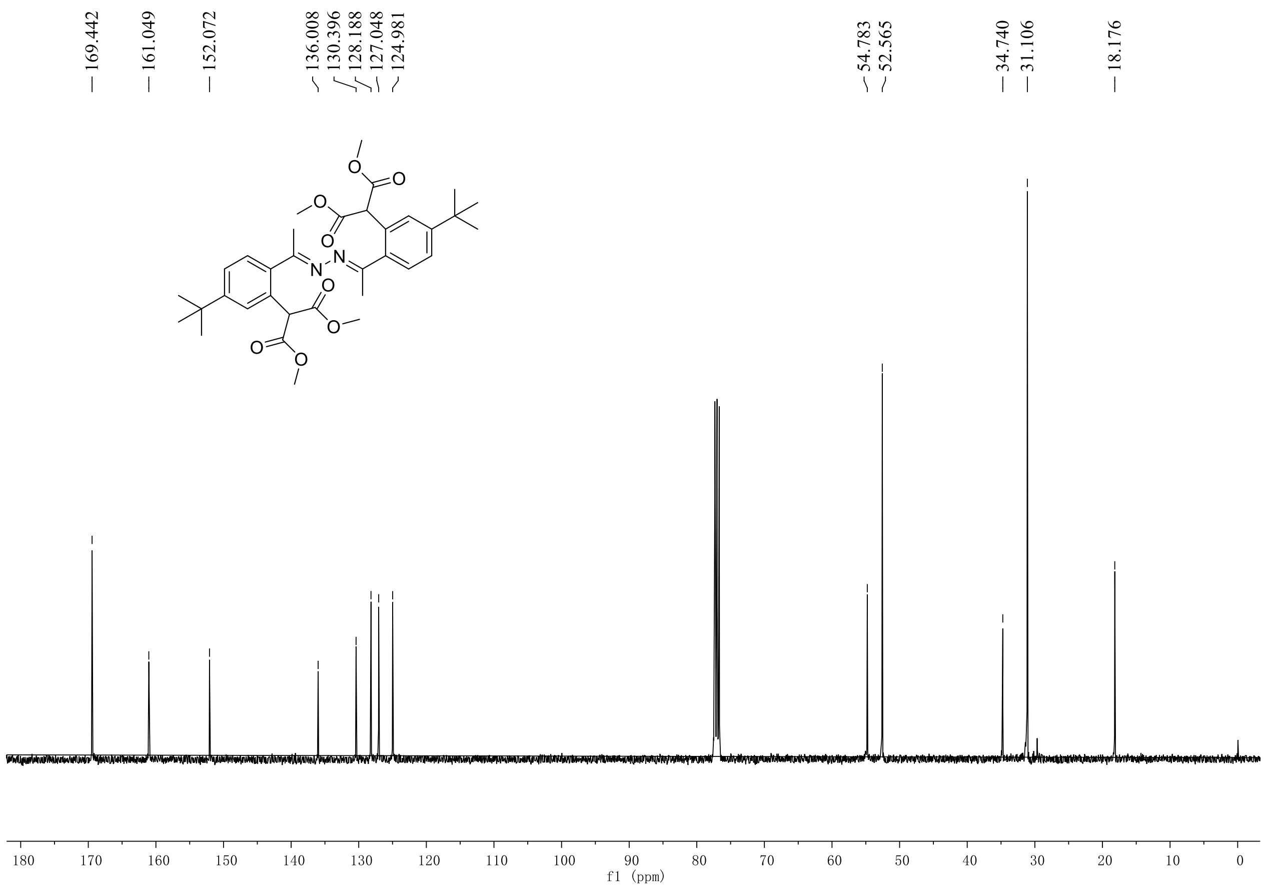

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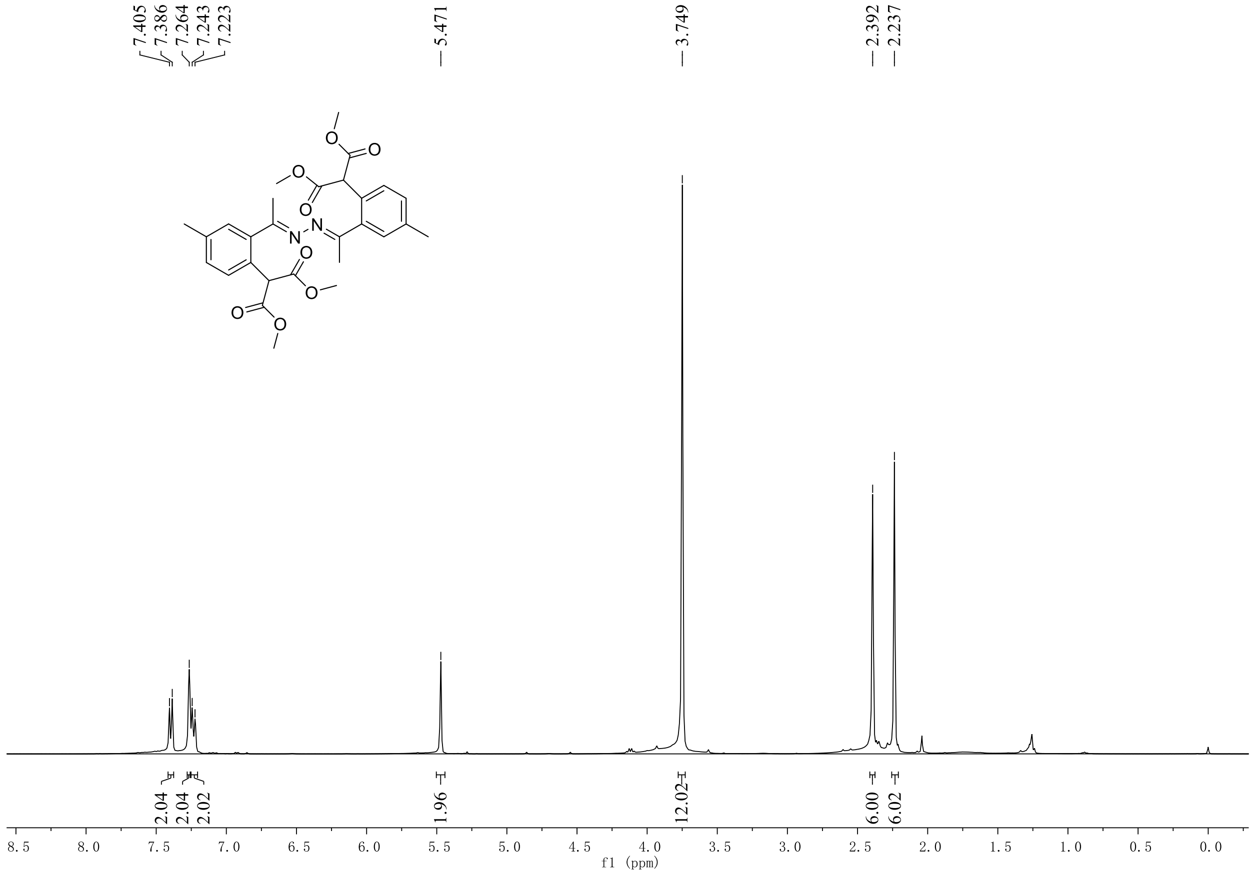

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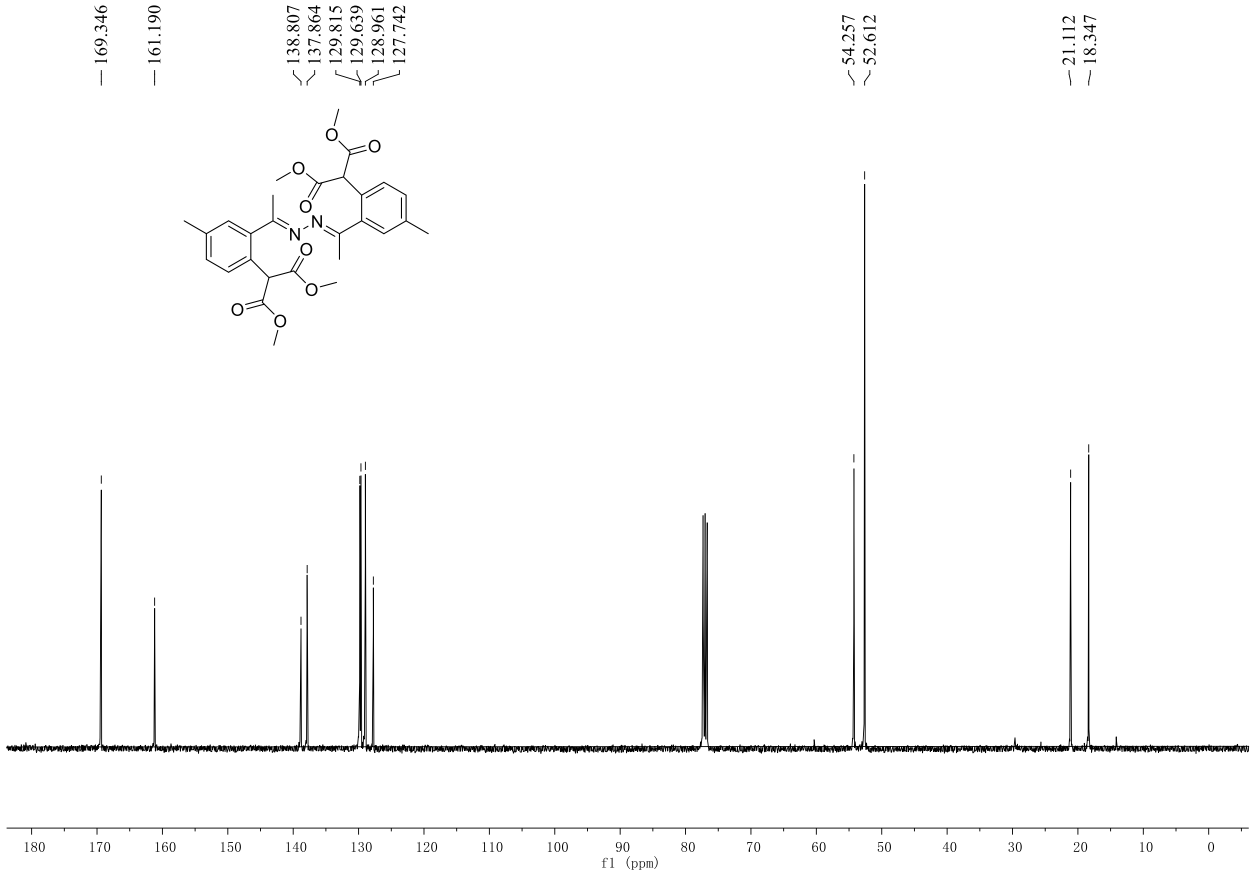
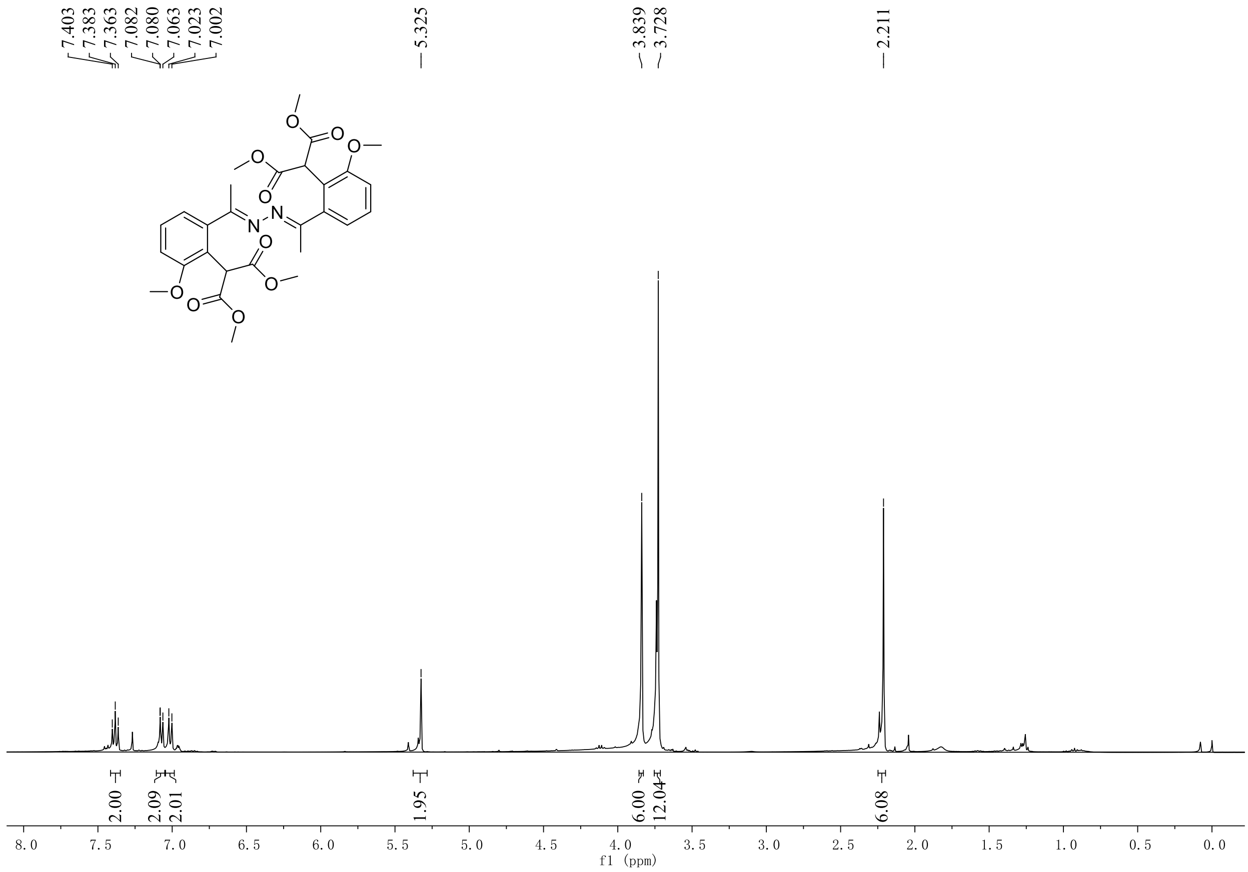


[1]H NMR spectrum of **3ga**



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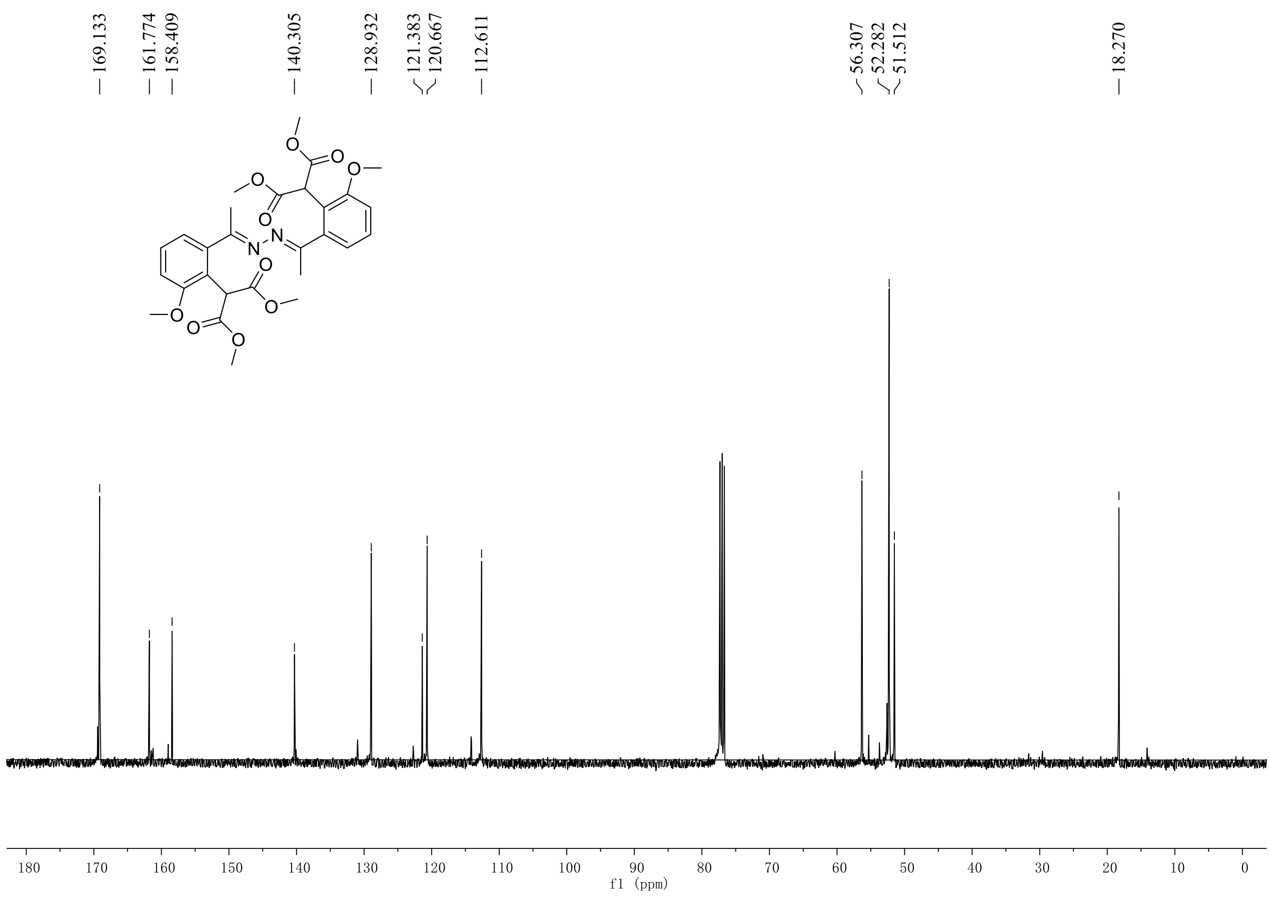
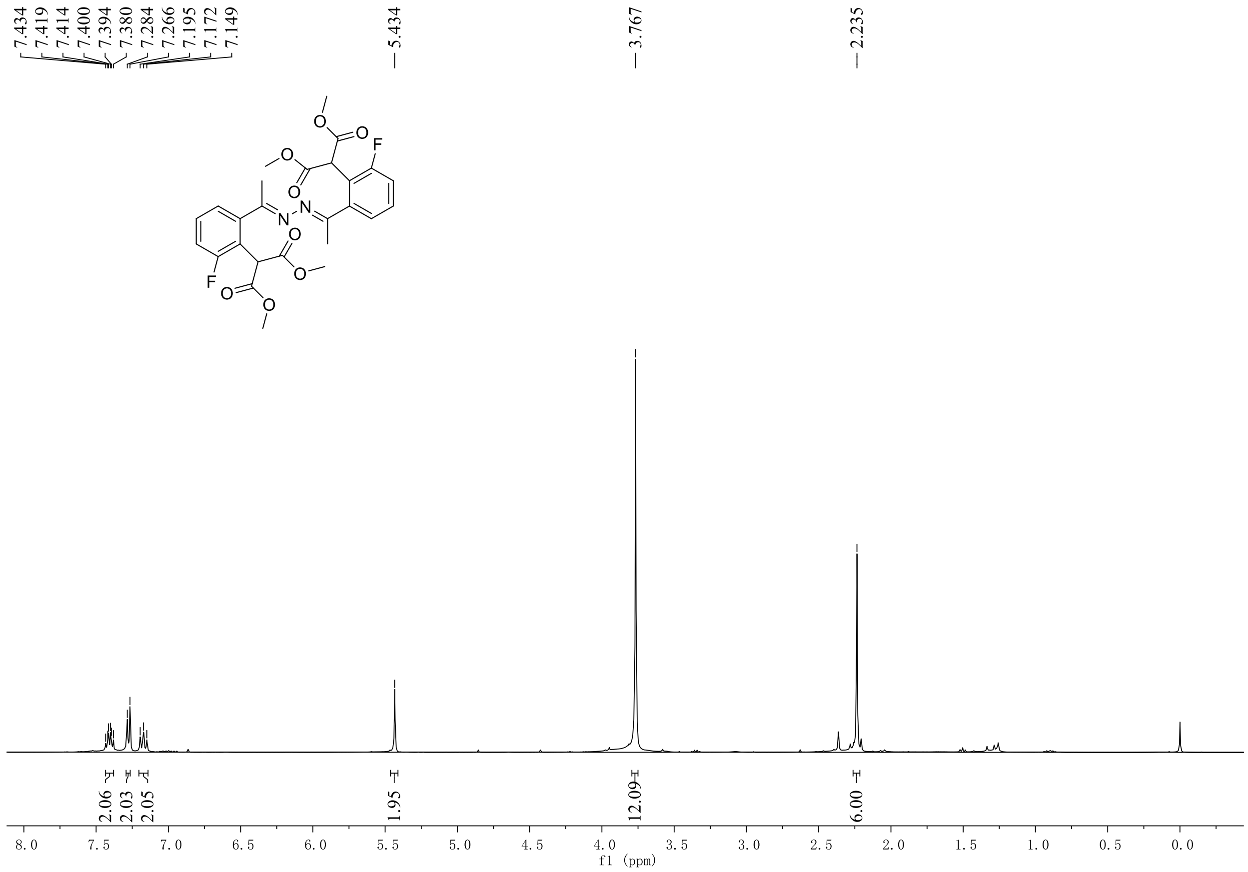
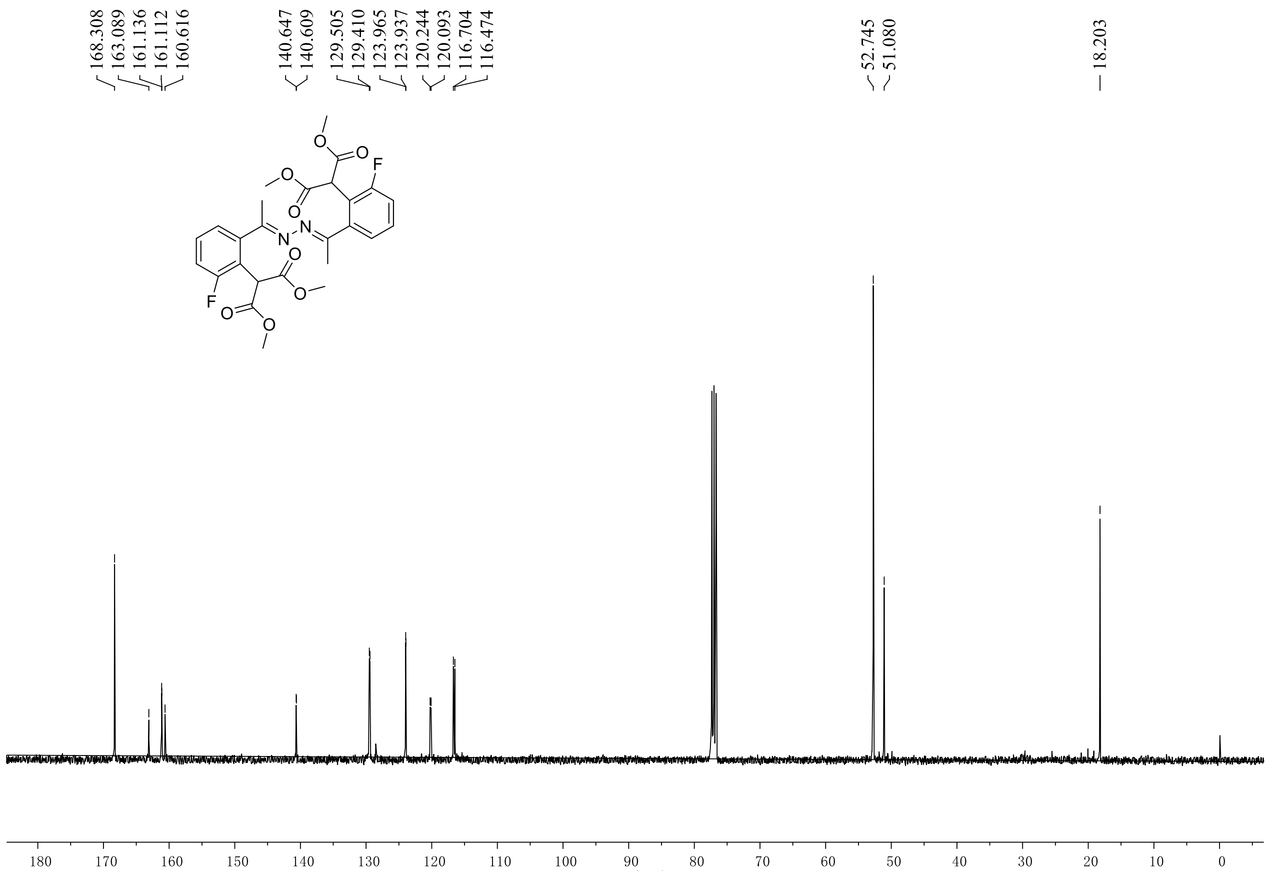


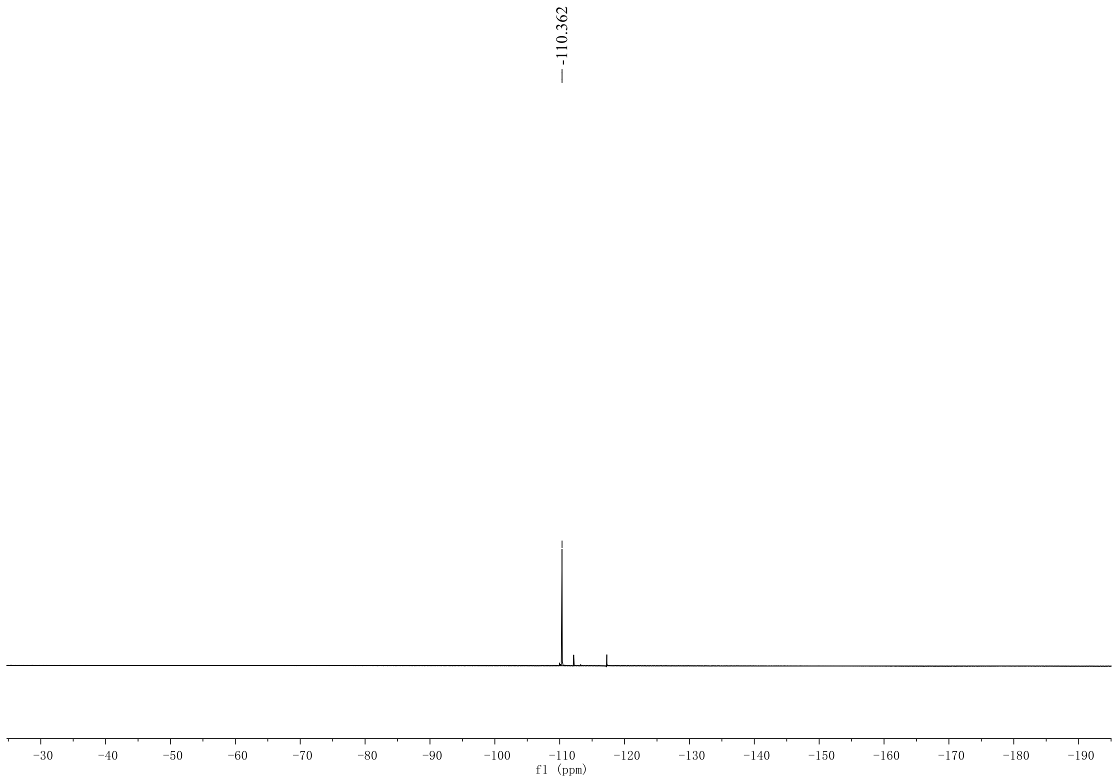
^{1}H NMR spectrum of **3ha**



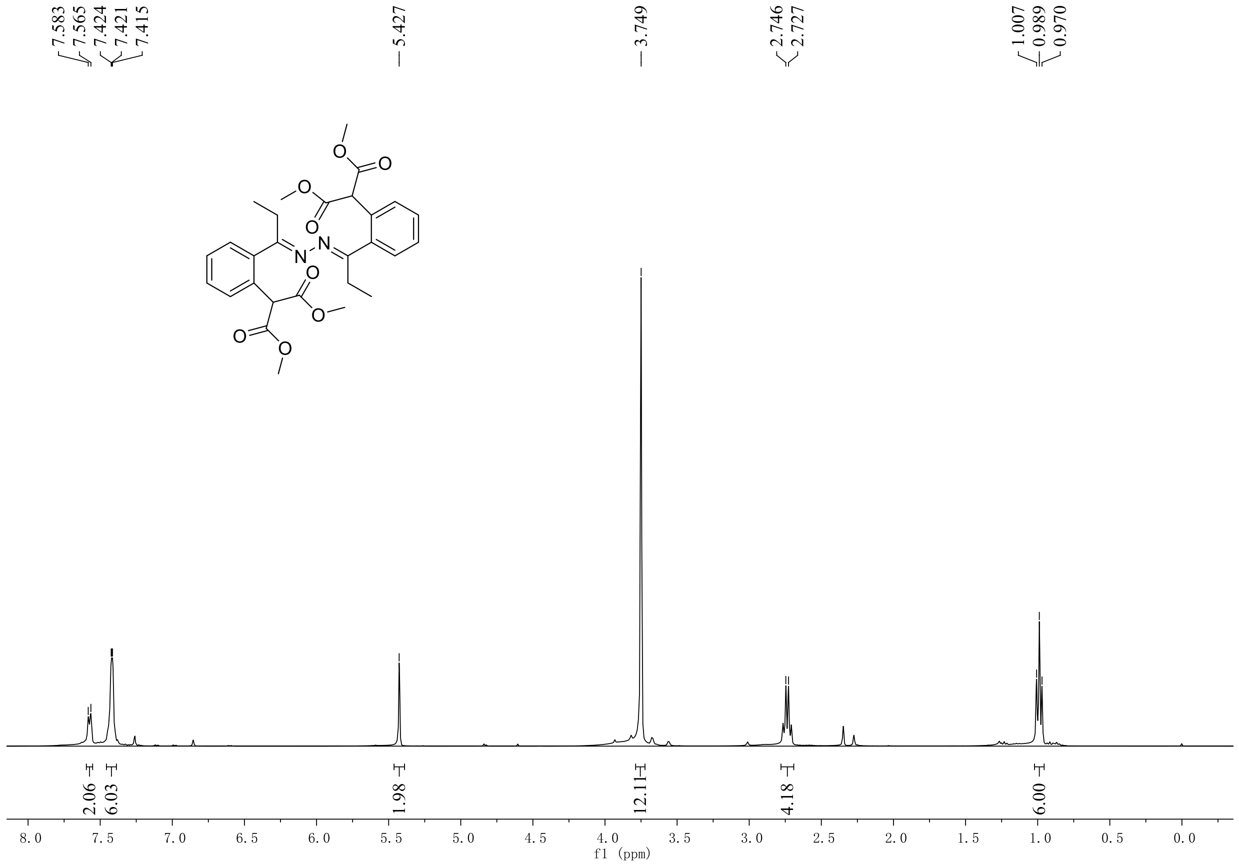
^{13}C NMR spectrum of **3ha**



^{19}F NMR spectrum of **3ha**



^{1}H NMR spectrum of **3ia**



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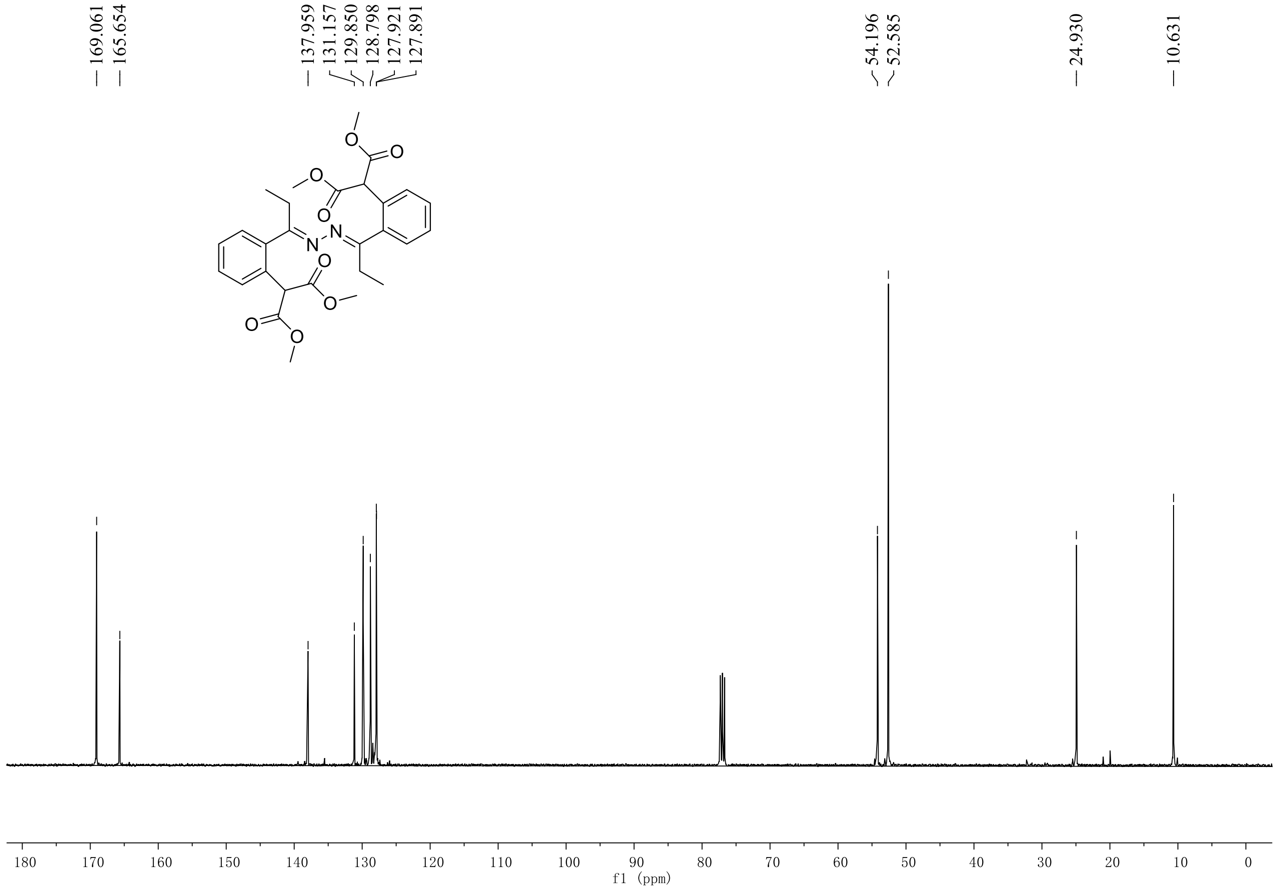

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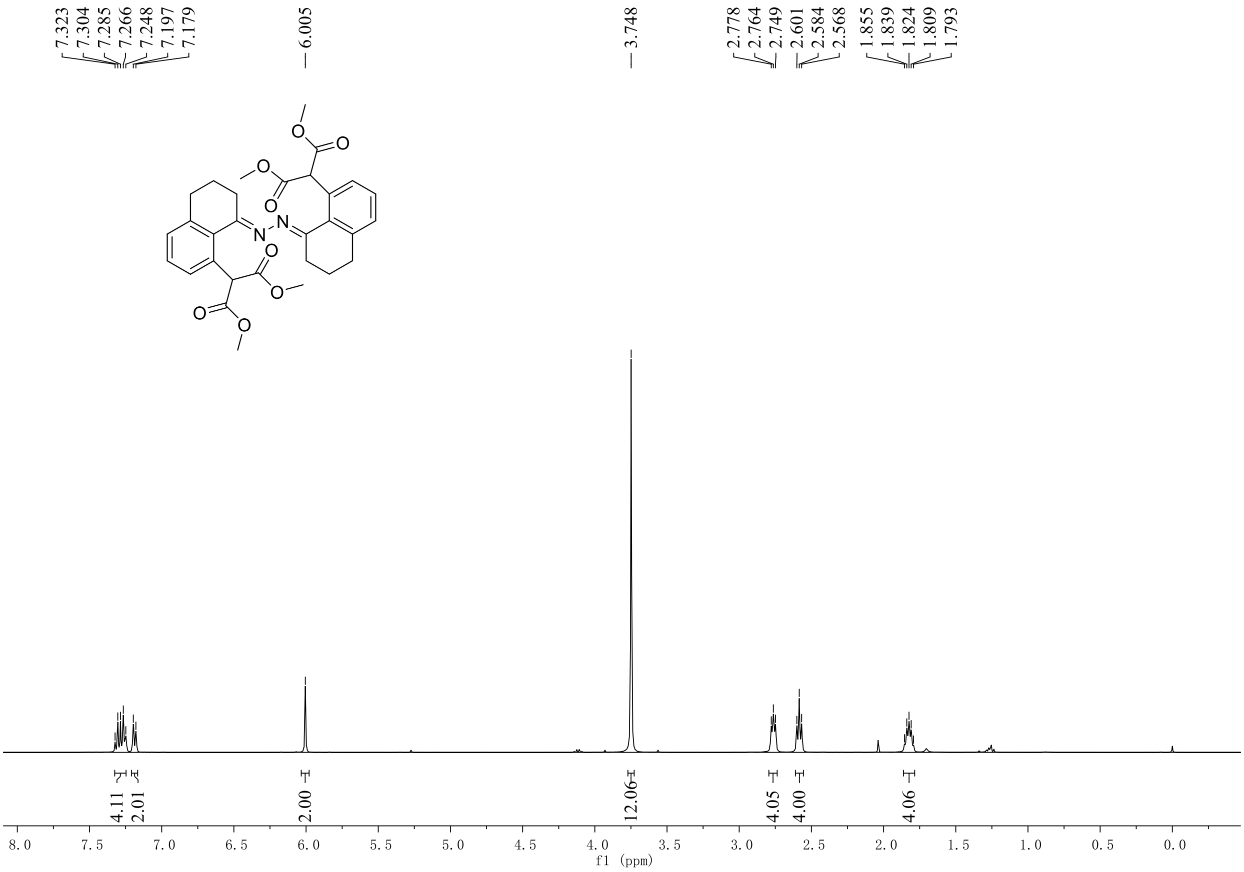

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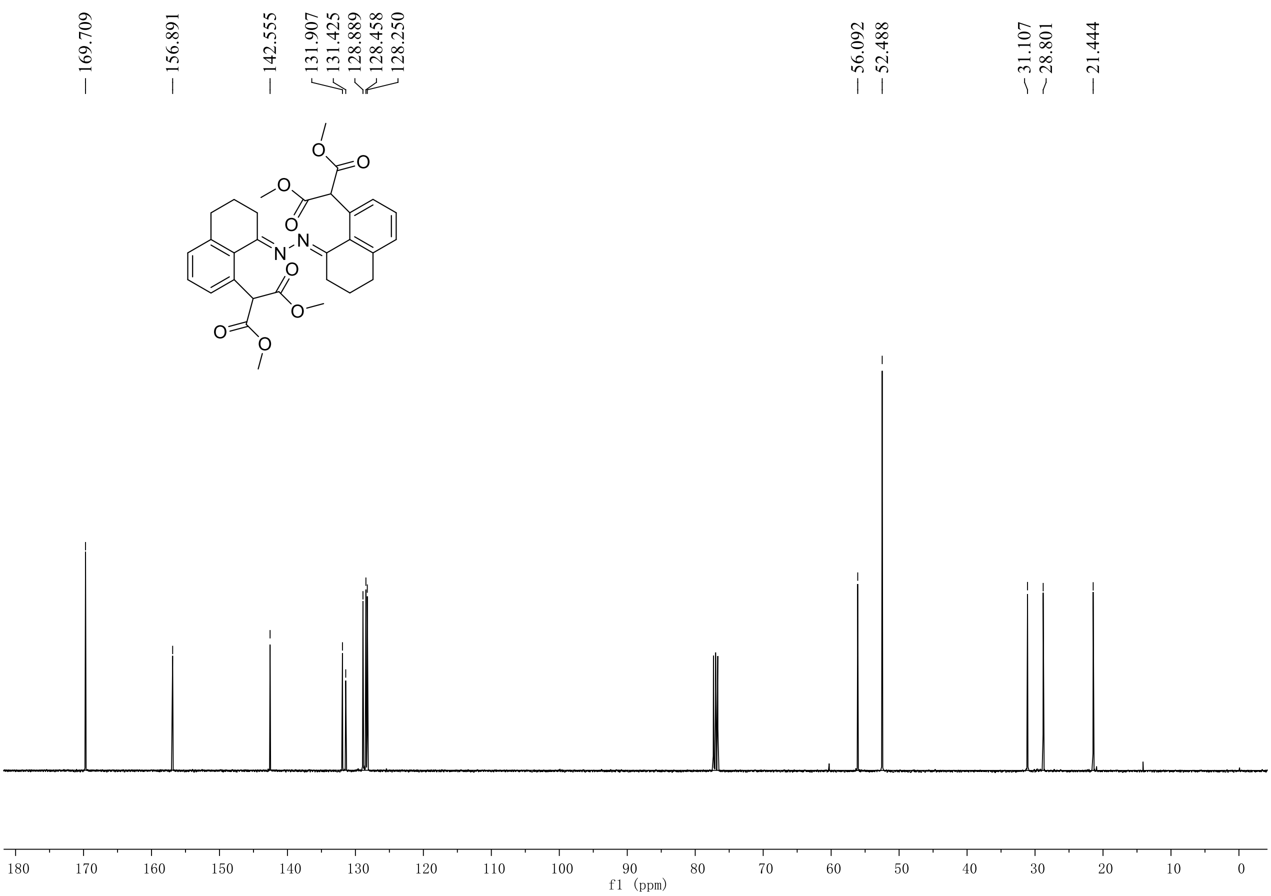

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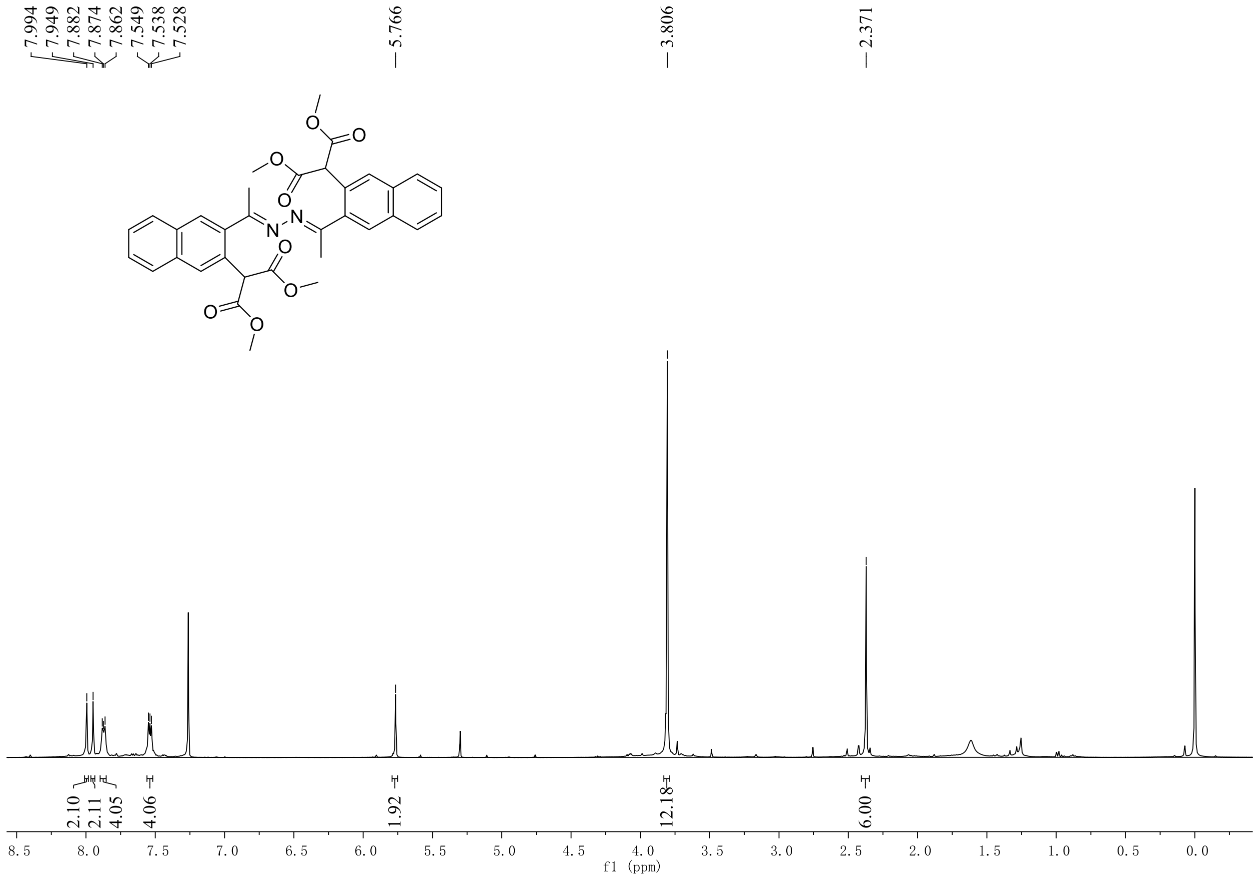
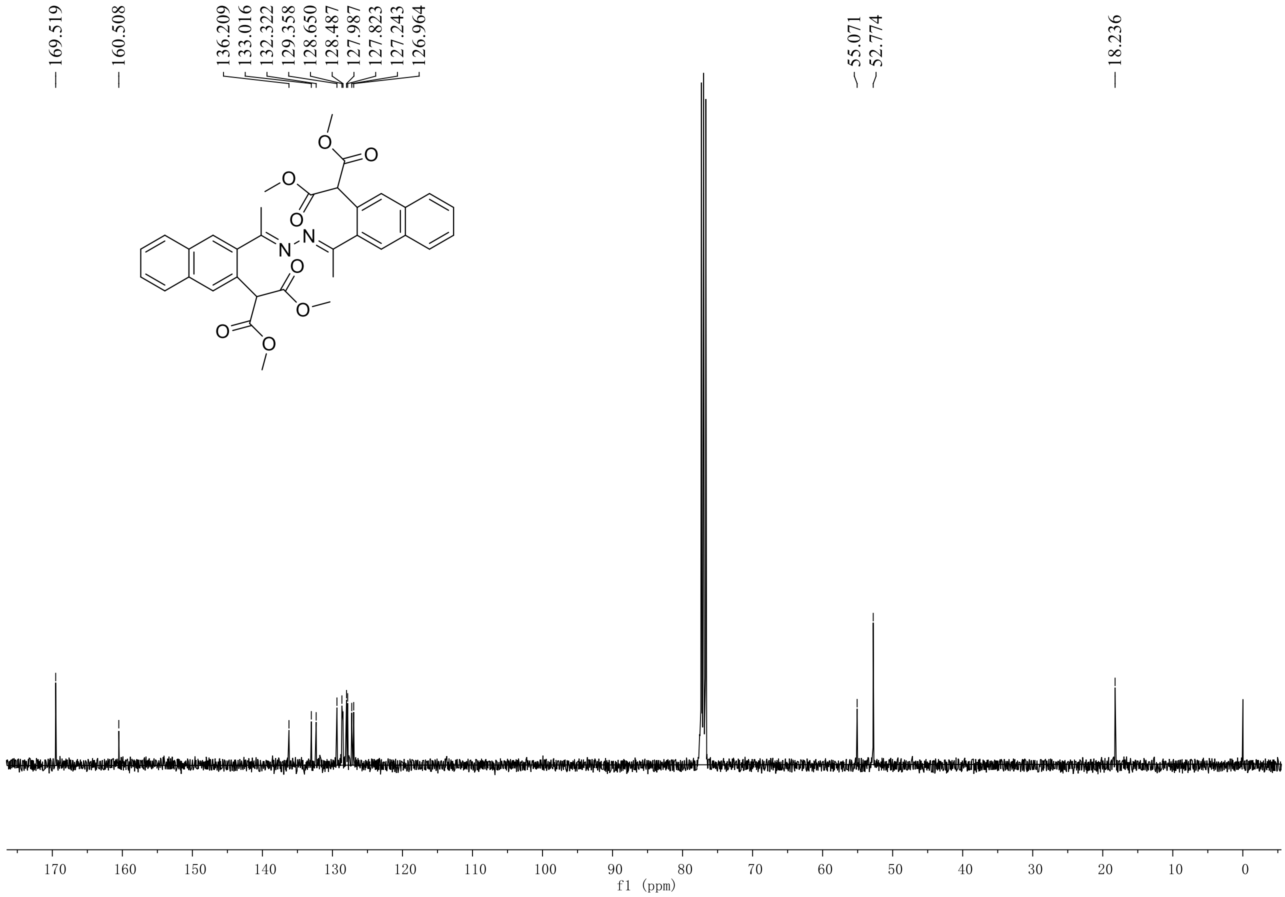
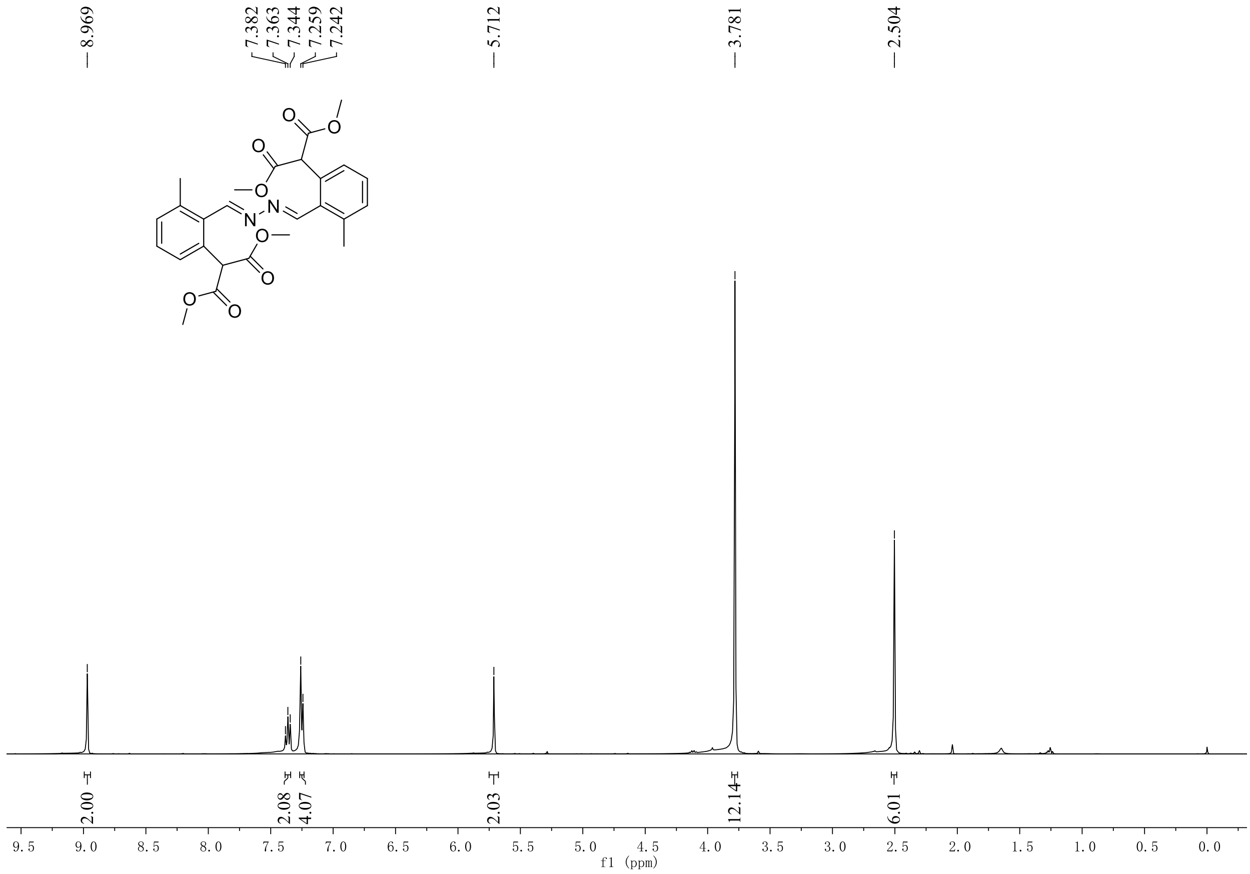


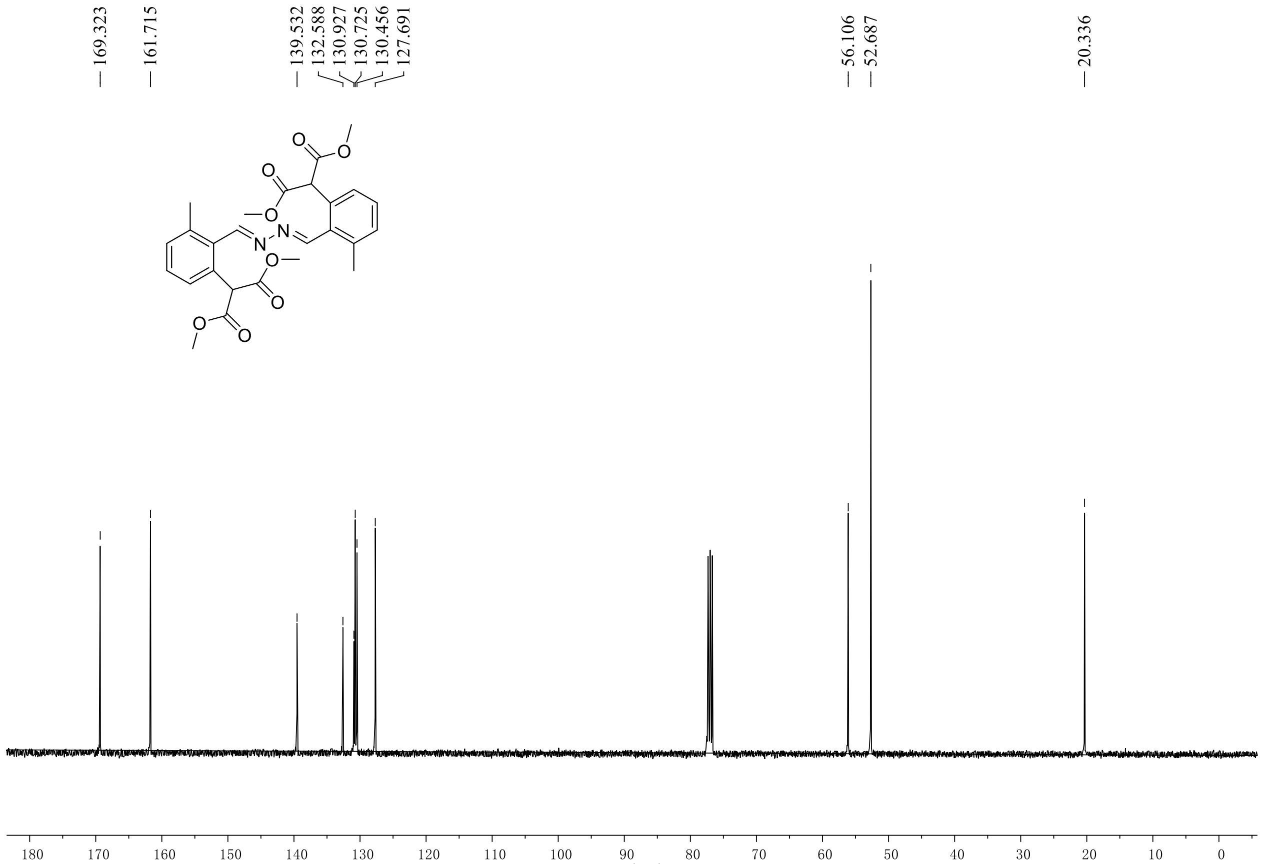
^{13}C NMR spectrum of **3ka**



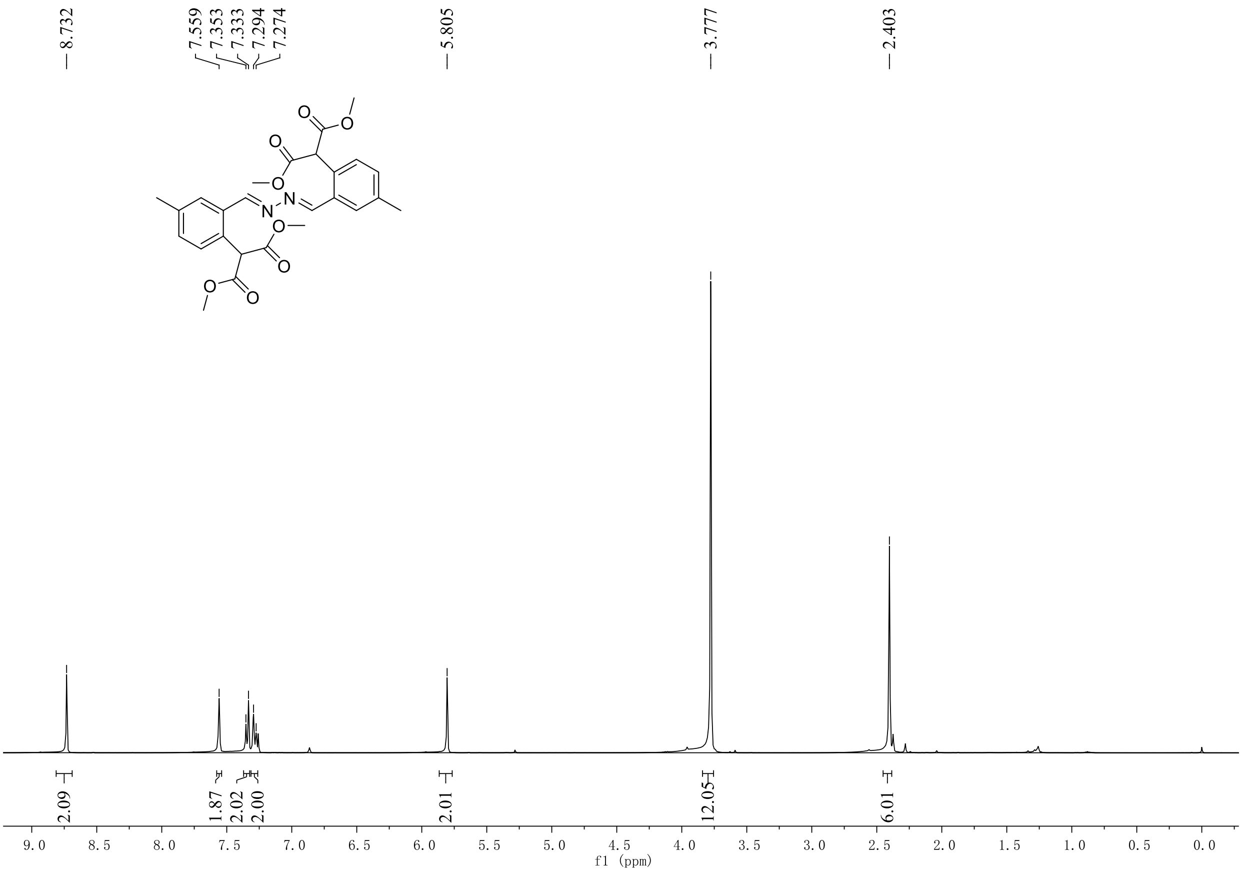
[1]H NMR spectrum of **3la**



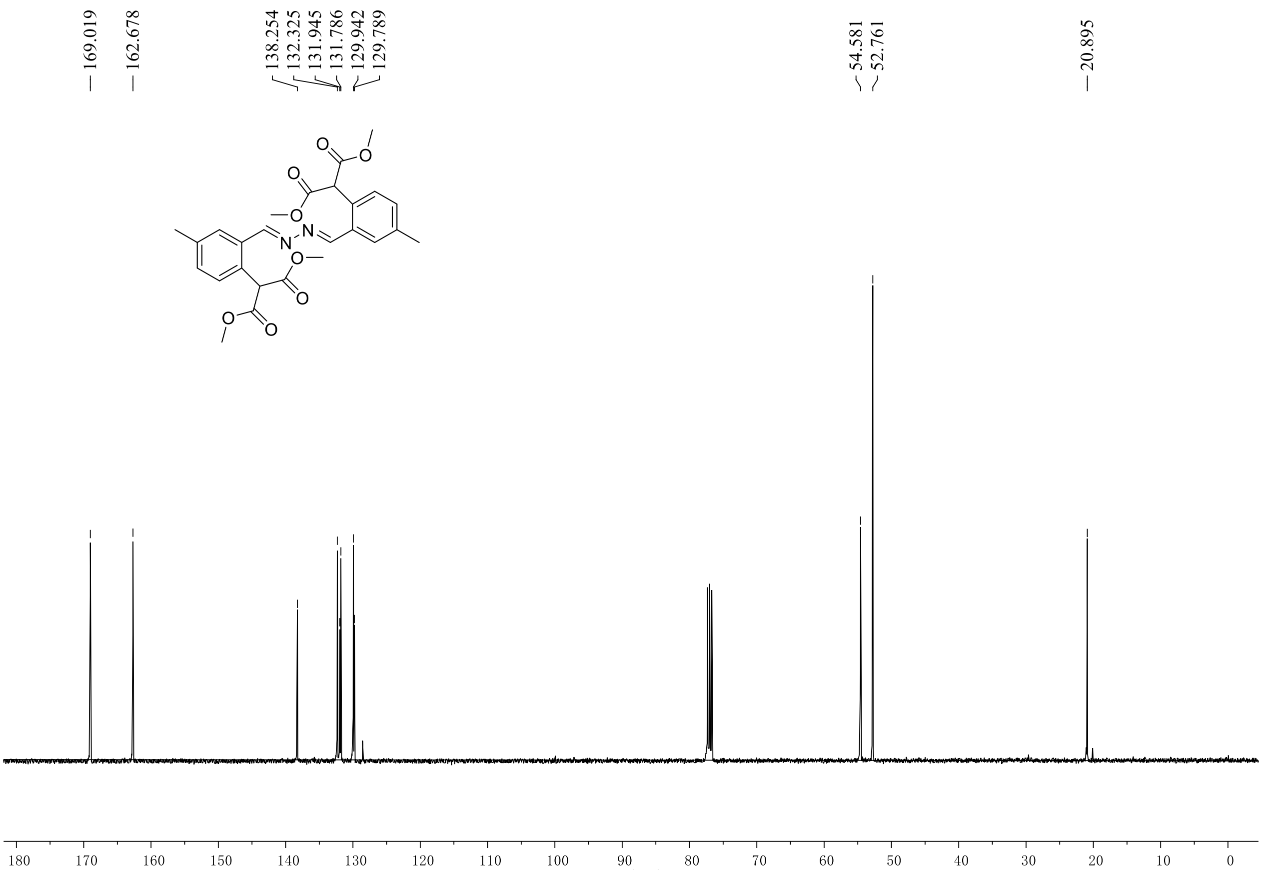
[13]C NMR spectrum of **3la**



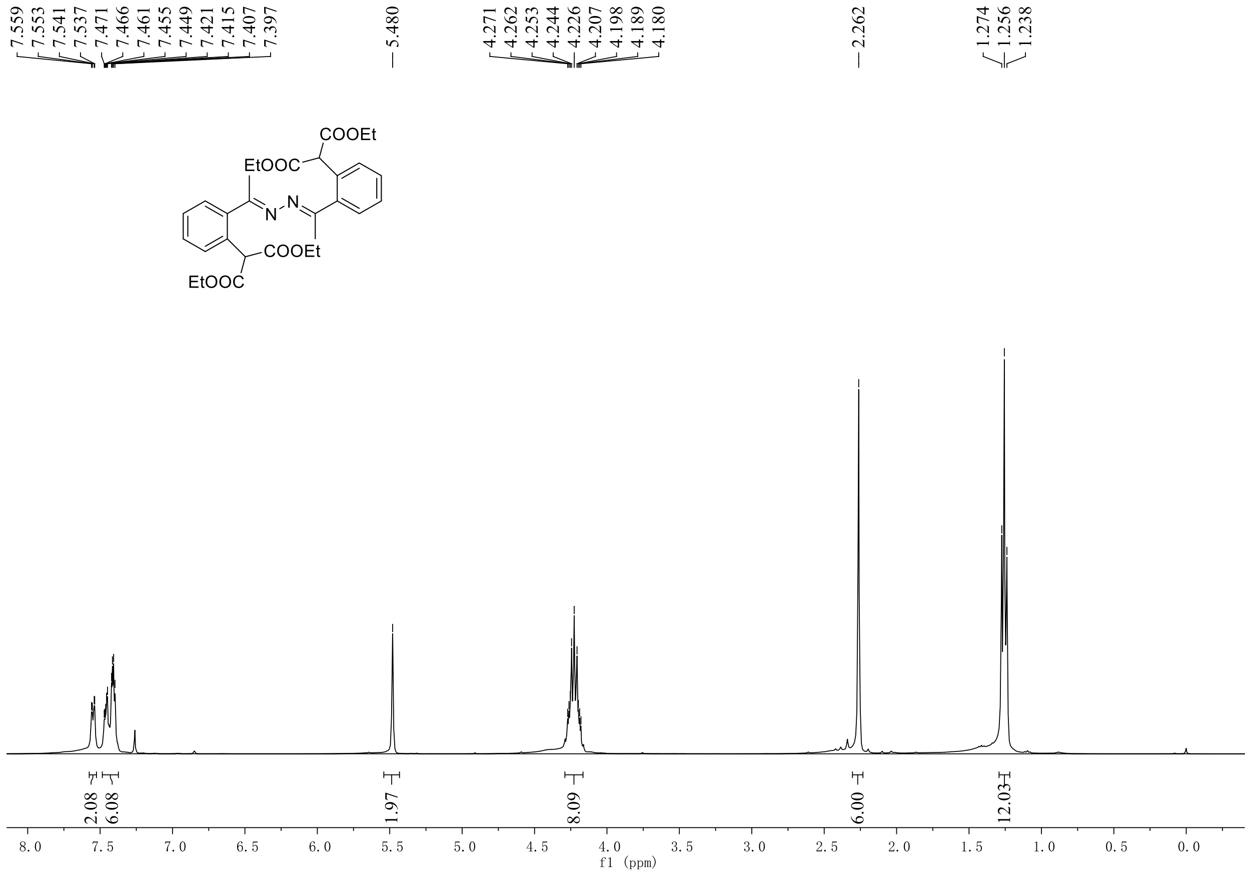
^{1}H NMR spectrum of **3ma**



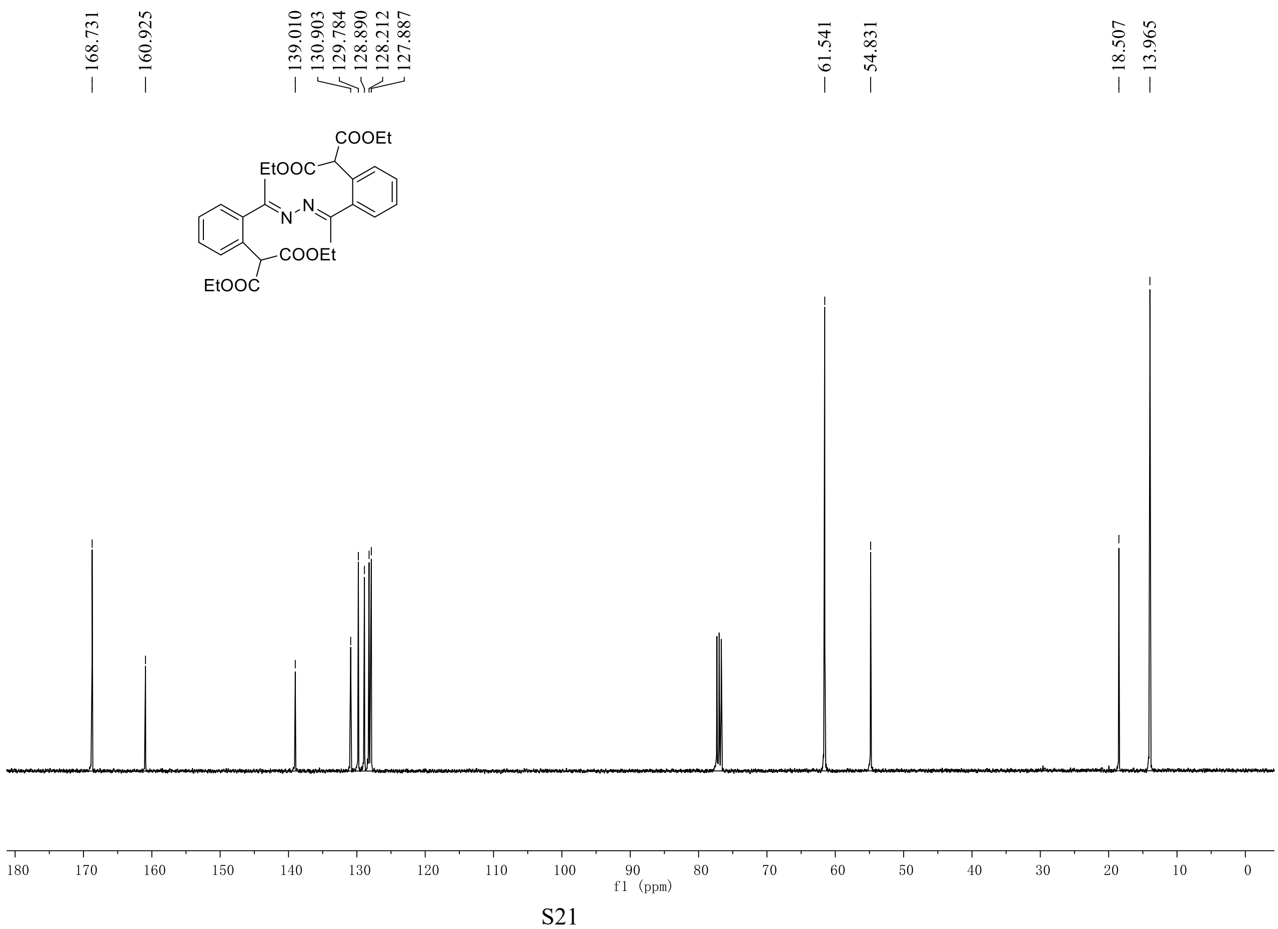
^{13}C NMR spectrum of **3ma**



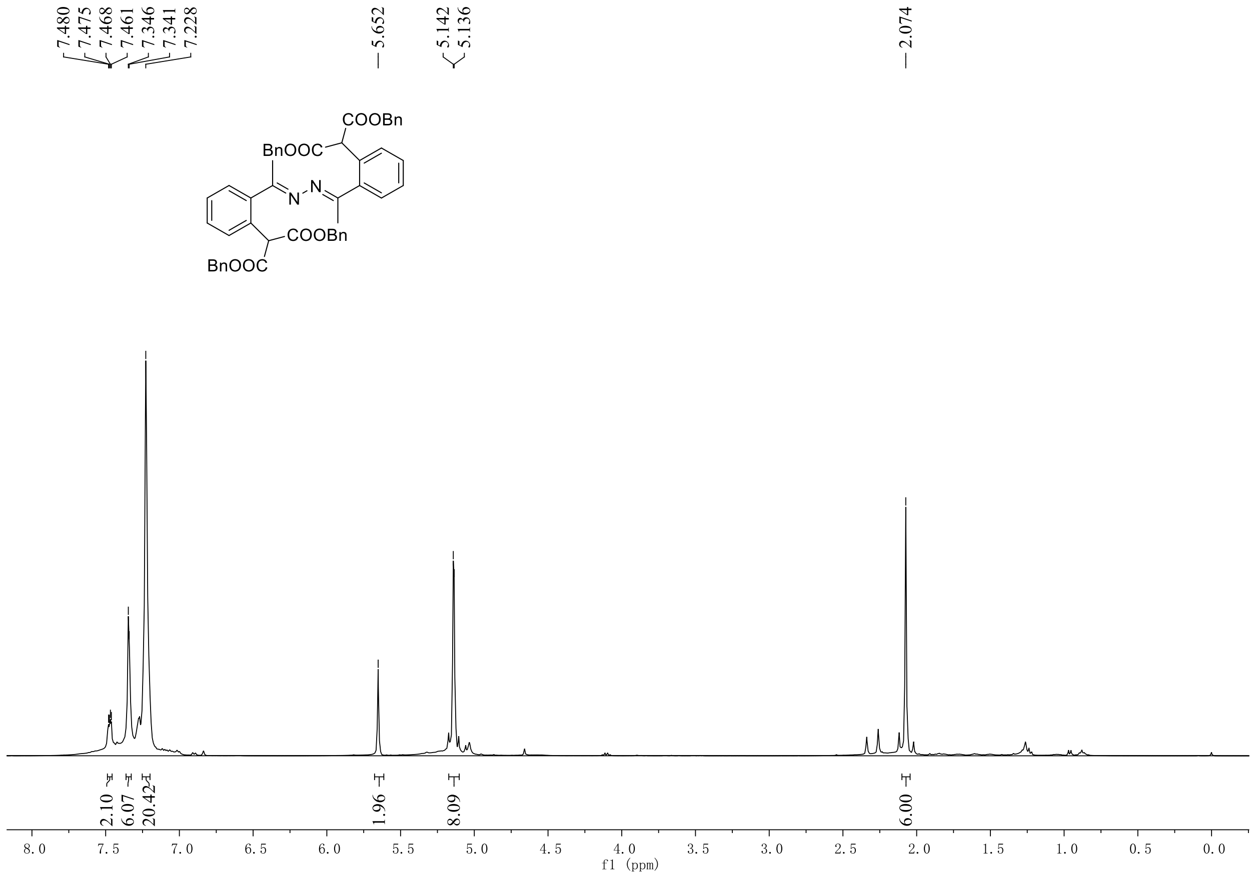
^{1}H NMR spectrum of **3ab**



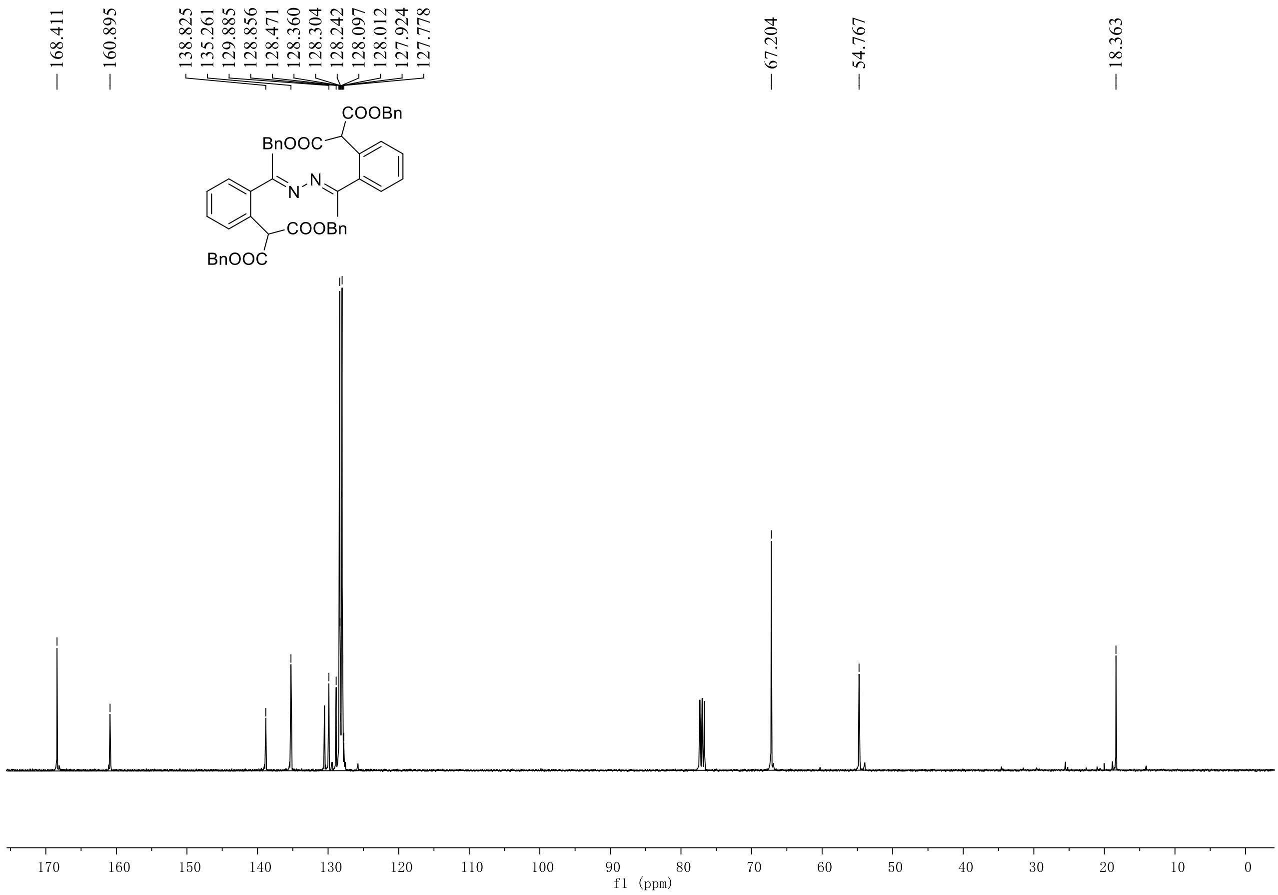
^{13}C NMR spectrum of **3ab**



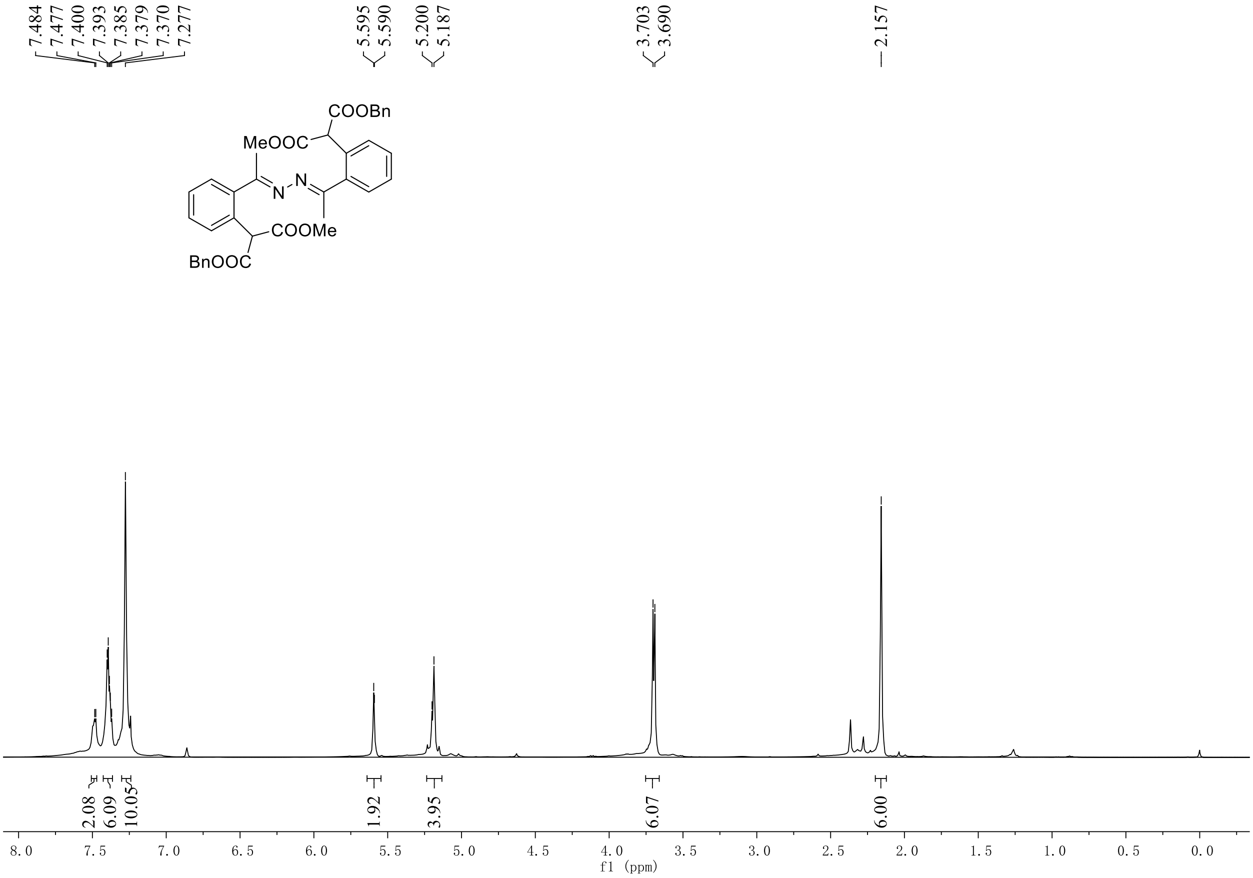
^{1}H NMR spectrum of **3ac**



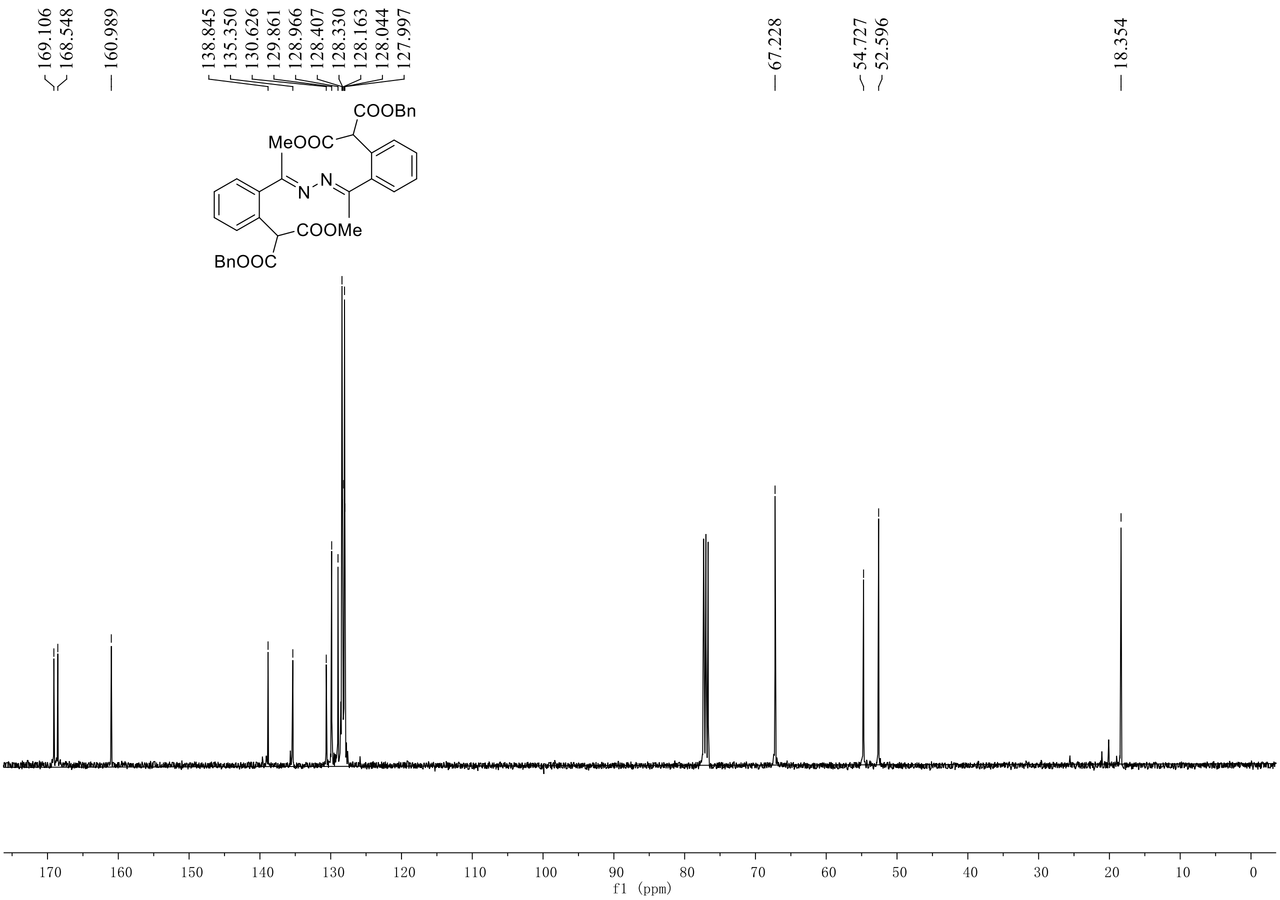
^{13}C NMR spectrum of **3ac**



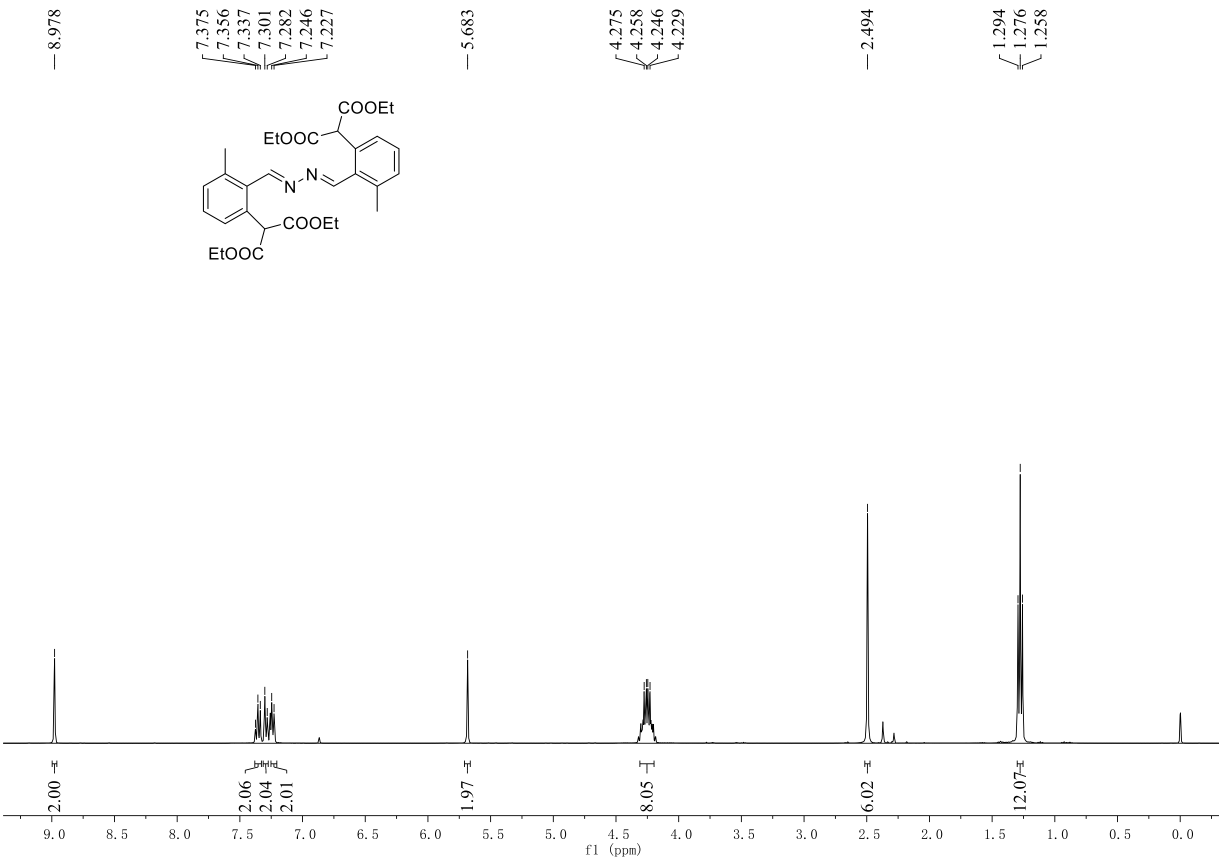
[1]H NMR spectrum of **3ad**



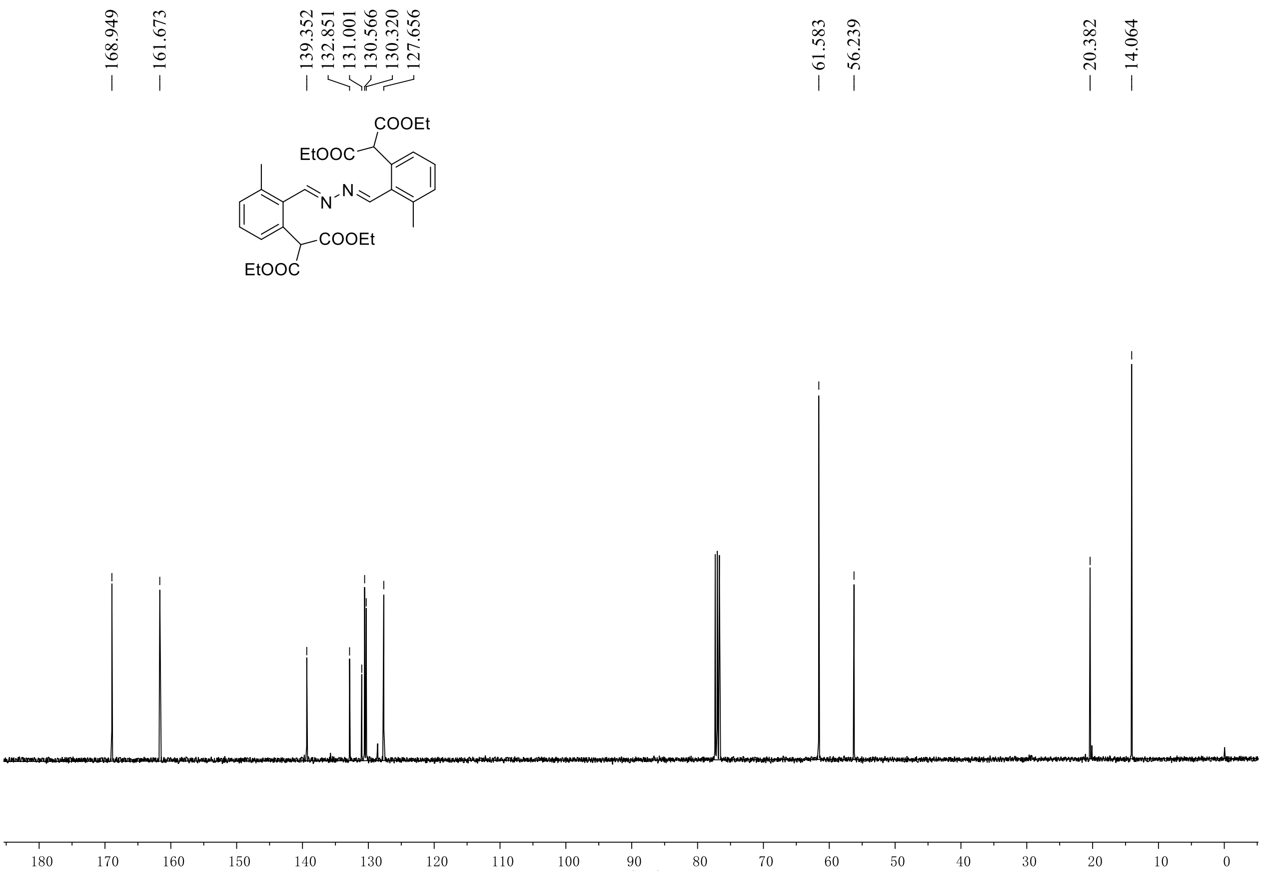
[13]C NMR spectrum of **3ad**



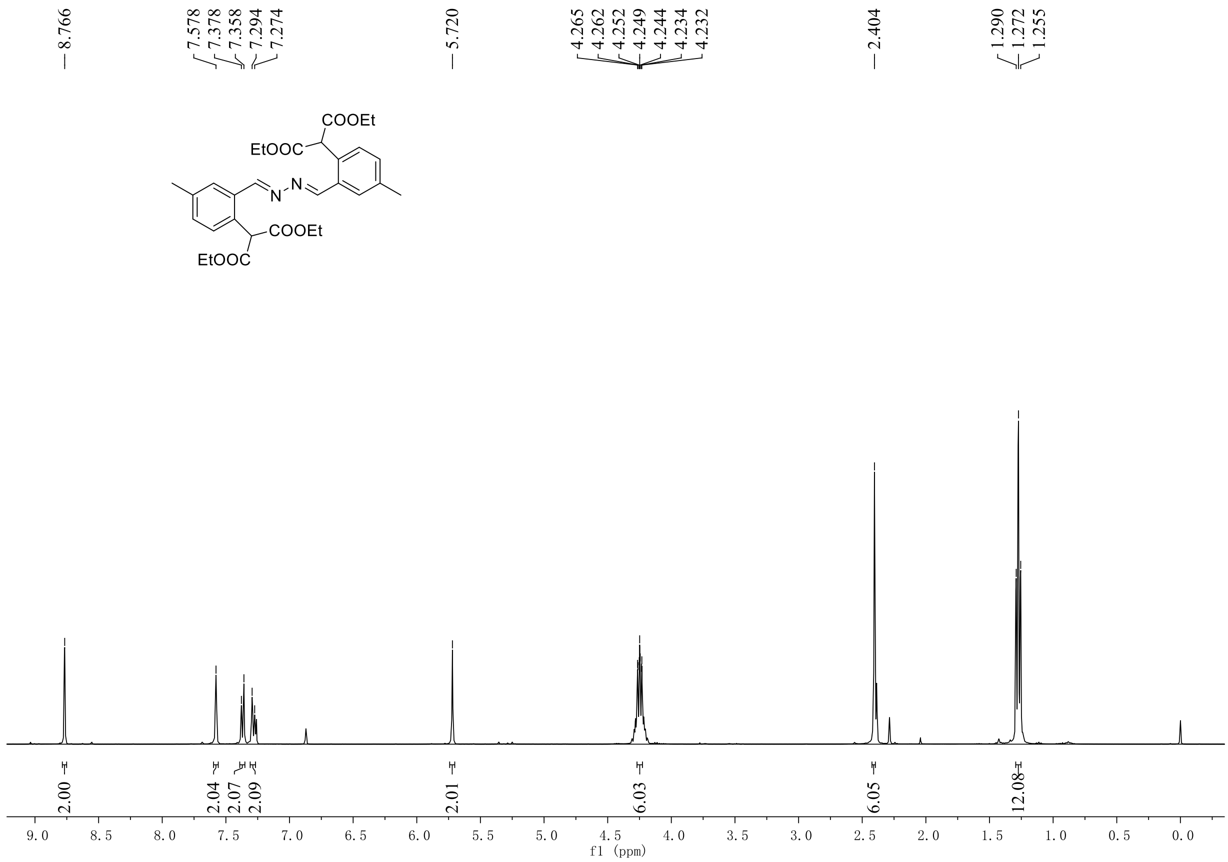
[1]H NMR spectrum of **3lb**



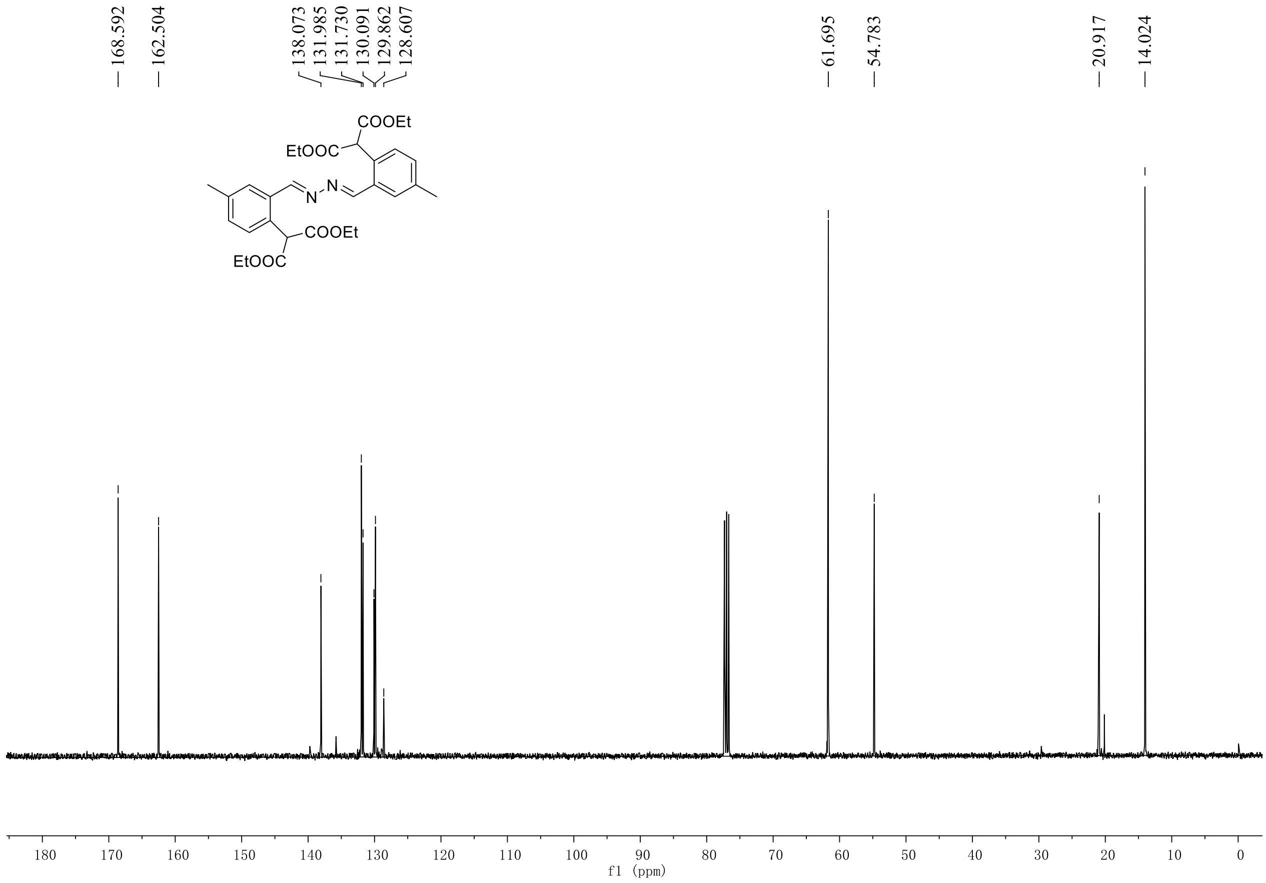
[13]C NMR spectrum of **3lb**



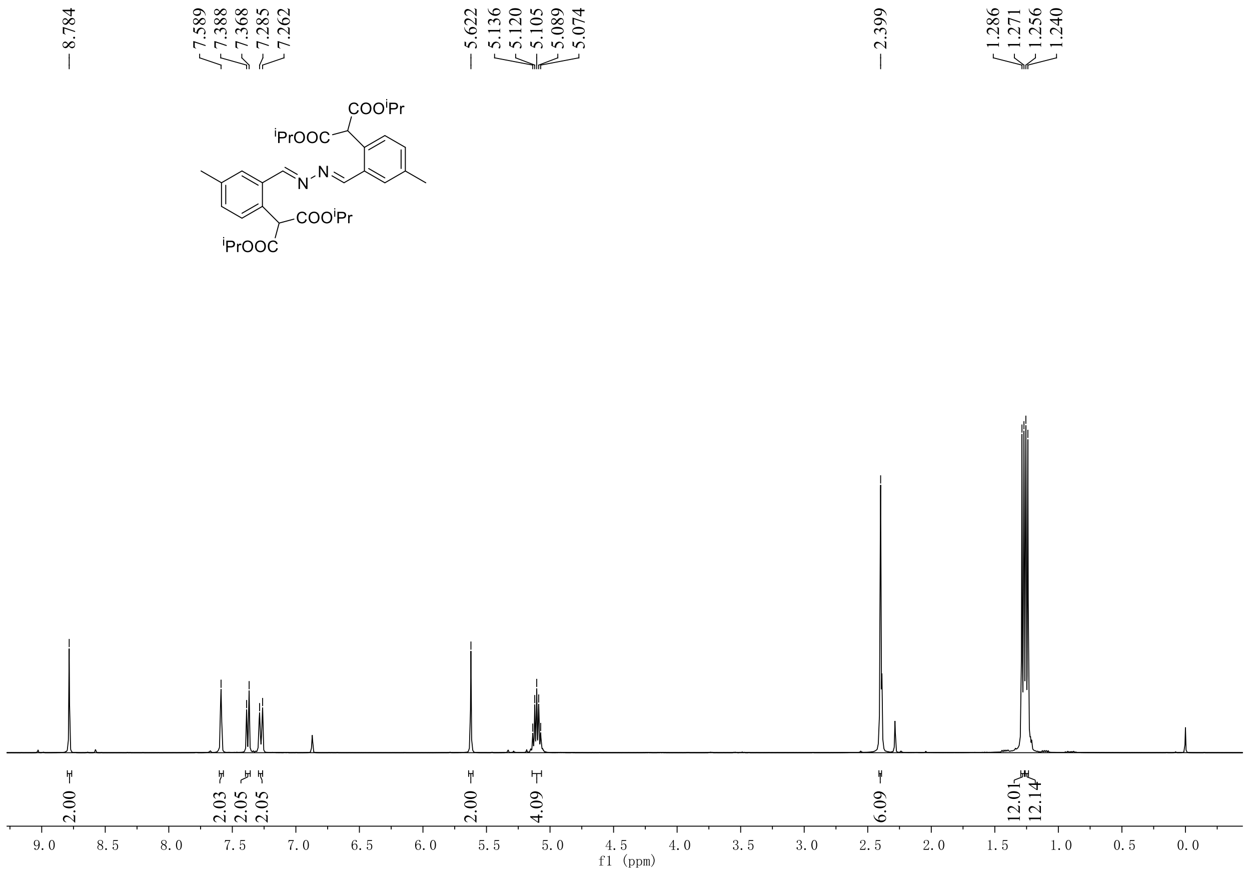
^{1}H NMR spectrum of **3mb**



^{13}C NMR spectrum of **3mb**



^{1}H NMR spectrum of **3me**



^{13}C NMR spectrum of **3me**