Supporting Information for

Dual Effects of Cyclopentadienyl Ligands on Rh(III)-Catalyzed Dehydrogenative Arylation of Electron-Rich Alkenes

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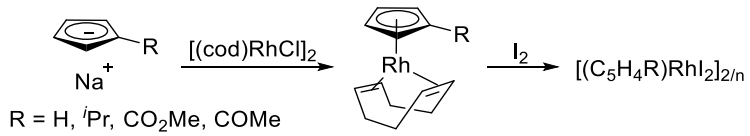
Contents:

1) General Information

Unless otherwise noted, all the reactions were carried out under argon atmosphere using standard Schlenk technique. TLC was performed on glass-backed silica plates. Column chromatography was performed on 200-300 mesh silica gel, eluting with petroleum ether and ethyl acetate. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectra (HRMS) were obtained on Bruker En Apex ultra 7.0T FT-MS by the Public Instrument Platform of College of Chemistry and Chemical Engineering at Xiamen University. NMR data were obtained on a Bruker AV-400 spectrometer and a Bruker AV-500 Spectrometer in DMSO-d_6, acetone-d_6 or $CDCl_3$. $[Cp^*RhCl_2]_2$[1] and $[Cp^{CF3}RhCl_2]_2$[2] were prepared from $RhCl_3{\cdot}xH_2O$ following literature procedures. $NaCp^{CO2Me}$ and $NaCp^{COMe}$ were prepared through the reaction of CpNa with dimethyl carbonate and methyl acetate respectively.[3] Most benzamide derivatives **1** and anilide derivatives **4** were prepared following the previous literatures.[4,5] All other compounds have been reported in the literature are commercially available and used without any further purification.

2) Preparation of $[X\text{-}CpRhI_2]_{2/n}$ Complexes and Evaluation of the Electronic Effects of X-Cp Ligands



General Procedures for the Preparation of $[X\text{-}CpRhI_2]_{2/n}$. To a solution of X-CpNa (2.0 M in THF, 2.2 equiv) was added $[(cod)RhCl]_2$ (1.0 mmol, 493.1 mg) under argon atmosphere. The resultant mixture was stirred at room temperature for 5 hours. After removing the solvent in vacuo, suitable amount of toluene or hexane was added. The resulting solution was filtered and the filtrate was concentrated to afford the crude X-CpRh(cod) complex as a yellow solid. The X-CpRh(cod) was then dissolved in toluene (10 mL) under argon atmosphere and cooled to 0 °C. Then 1.1 equiv of I_2 (558.3 mg) in 15 mL of toluene was added dropwise. The resulting solution was stirred at room temperature overnight. The precipitate that formed was filtered off and washed three times with toluene to give the corresponding polymeric or dimeric $[X\text{-}CpRhI_2]_{2/n}$ complexes.

$[CpRhI_2]_n$: black solid; yield 93% (785.2 mg); ^{1}H NMR (500 MHz, DMSO-d6) δ 6.07 (s, 5H); ^{13}C NMR (126 MHz, DMSO-d6) δ 89.6 (d, J = 5.9 Hz).

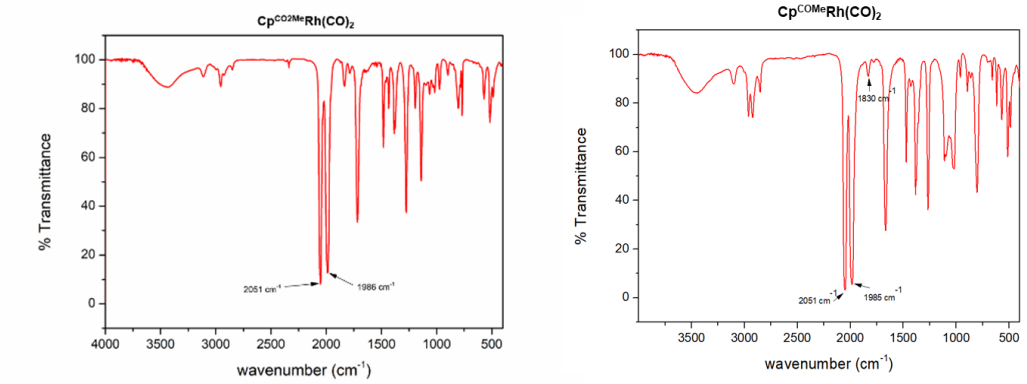
$[Cp^{iPr}RhI_2]_2$: brown solid; yield 88% (817.3 mg); ^{1}H NMR (500 MHz, DMSO-d6) δ 6.01 (s, 2H), 5.90 (s, 2H), 3.01-2.94 (m, 1H), 1.18 (d, J = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d6) δ 117.8 (d, J = 5.4 Hz), 88.1 (d, J = 5.8 Hz), 87.6 (d, J = 6.6 Hz), 27.1, 22.2.

$[Cp^{CO2Me}RhI_2]_2$: black solid; yield 81% (777.5 mg); ^{1}H NMR (500 MHz, DMSO-d6) δ 6.50 (s, 2H), 6.16 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 162.4, 93.3 (d, J = 5.1 Hz), 91(d, J = 5.4 Hz), 89.7 (d, J = 4.7 Hz), 52.7.

$[Cp^{COMe}RhI_2]_2$: black solid; yield 85% (785.3 mg); ^{1}H NMR (500 MHz, DMSO) δ 6.60 (t, J = 2.1 Hz, 2H), 6.19 (t, J = 2.1 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 193.5, 93.8 (d, J = 6.4 Hz), 93.6 (d, J = 5.2 Hz), 91.1 (d, J = 5.8 Hz), 28.7.

Table S1. CO stretching frequencies of [X-Cp^{x}Rh(CO)$_2$] and ^{31}P chemical shifts of [X-CpRhP(OEt)$_3$X$_2$]

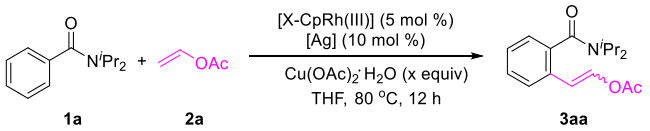
Cp* and X-Cp ligands	υ_A and υ_S (cm) of [X-CpRh(CO)$_2$]	δ^{31}P (ppm) of [X-CpRhP(OEt)$_3$X$_2$] in CD_2Cl_2
Cp*	2016/1948 (C_6D_6)[6]	114.2 (J = 215.9 Hz, X = Cl)[6]
Cp	2048/1985 (*n*-hexane)[7], 2051/1987 (as liquid)[8]	109.5 (J = 206.9 Hz, X = I)
Cp^{CF3}	2040/1977 (C_6D_6)[6]	104.5 (J = 205.8 Hz, X = Cl)[6]
Cp^{iPr}	2036/1968 (C_6D_6)[6]	110.6 (J = 209.1 Hz, X = I) 110.5 (J = 201.6 Hz, X = Cl)[6]
Cp^{CO2Me}	2051/1986 (as liquid)	106.6 (J = 203.0 Hz, X = I)
Cp^{COMe}	2051/1985 (as liquid)	--
Cp^{E}	2044/1984 (C_6D_6)[6]	99.1 (J = 197.1 Hz, X = Cl)[6]



To evaluate the electronic effects of X-Cp ligands, the collected data for antisymmetric and symmetric CO stretching frequencies (υ_A and υ_S) of [X-CpRh(CO)$_2$] were shown in Table S1. Moreover, corresponding [X-CpRhP(OEt)$_3$I$_2$] complexes were prepared following the previous literature.[6] Their ^{31}P chemical shifts were also included in Table S1.

3) Reaction Optimization

Table S2 Details for optimization of the reaction conditions[a]



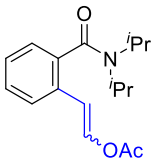
Entry	[Cp^{x}Rh(III)]	[Ag]	Cu(OAc)$_2$·H$_2$O (equiv)	Additive (equiv)	Solvent	Yield (%)[b]
1	[Cp*RhCl$_2$]$_2$	AgSbF$_6$	1.1	-	THF	21 (13:1)
2	**[Cp^{CF3}RhCl$_2$]$_2$**	**AgSbF$_6$**	1.1	-	**THF**	**82 (14:1)**
3	**[CpRhI$_2$]$_2$**	**AgSbF$_6$**	1.1	-	**THF**	**86 (10:1)**
4	[Cp^{iPr}RhI$_2$]$_2$	AgSbF$_6$	1.1	-	THF	79 (6:1)
5	[Cp^{CO2Me}RhI$_2$]$_2$	AgSbF$_6$	1.1	-	THF	37 (19:1)
6[c]	[CpRhI$_2$]$_2$	AgSbF$_6$	1.1	-	THF	81 (6:1)
7	[CpRhI$_2$]$_2$	AgSbF$_6$	0.5	-	THF	62 (22:1)

8	$[CpRhI_2]_2$	$AgSbF_6$	0	-	THF	22 (16:1)
9	$[CpRhI_2]_2$	$AgSbF_6$	0	HOAc (2)	THF	31
10	$[CpRhI_2]_2$	$AgSbF_6$	0	PivOH (2)	THF	31
11	$[CpRhI_2]_2$	$AgSbF_6$	0	CF_3CO_2H (2)	THF	12
12	$[CpRhI_2]_2$	$AgSbF_6$	CuO (1.1)	-	THF	39 (21:1)
13[d]	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	THF	40 (25:1)
14[e]	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	THF	70 (22:1)
15[f]	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	THF	84 (9:1)
16	$[CpRh(MeCN)_3](SbF_6)_2$	-	1.1	-	THF	87 (10:1)
17	$[CpRhI_2]_2$	-	1.1	-	THF	0
18	$[CpRhI_2]_2$	AgOAc	1.1	-	THF	0
19	$[CpRhI_2]_2$	$AgNO_3$	1.1	-	THF	trace
20	$[CpRhI_2]_2$	$AgBF_4$	1.1	-	THF	10 (9:1)
21	$[CpRhI_2]_2$	$AgNTf_2$	1.1	-	THF	88 (10:1)
22	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	acetone	87 (11:1)
23	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	DME	87 (8:1)
24	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	1,4-dioxane	85 (10:1)
25	$[CpRhI_2]_2$	$AgSbF_6$	1.1.	-	DCE	60 (21:1)
26	$[CpRhI_2]_2$	$AgSbF_6$	1.1	-	*t*-AmylOH	52 (18:1)

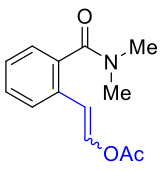
[a]Reaction Conditions: **1a** (0.2 mmol), **2a** (2.0 mmol), [X-CpRh(III)] (5 mol %), [Ag] (10 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.1 equiv), THF (1 mL), 80 °C, in air for 12 h. [b]Isolated yields (E/Z ratios are shown in parentheses). [c]**2a** (5 equiv). [d]60 °C. [e]2.5 mol % of [Rh]. [f]8 h.

4) Procedures and Characterization Data

General Procedures for the Arylation of Electron-Rich Alkenes with Benzamides. To a 15 mL Schlenk tube, benzamide derivative **1** (0.2 mmol), alkene **2** (2.0 mmol), $[CpRhI_2]_n$ or $[Cp^{CF3}RhCl_2]_2$ (5 mol % of [Rh]), $AgSbF_6$ (10 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.1 equiv) and THF (1.0 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography to afford the product **3** (PE:EA = 5:1-1:1).

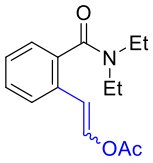


2-(diisopropylcarbamoyl)styryl acetate (**3aa**): colorless solid; yield 86% (49.8 mg; [CpRh]), 82% (47.5 mg; $[Cp^{CF3}Rh]$); ^{1}H NMR (500 MHz, DMSO) δ 7.98 (d, *J* = 7.8 Hz, 0.1H), 7.84 (d, *J* = 12.8 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.39 (td, *J* = 7.8, 1.1 Hz, 0.1H), 7.35 – 7.26 (m, 2.2H), 7.16 (d, *J* = 1.1 Hz, 0.1H), 7.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.30 (d, *J* = 12.8 Hz, 1H), 5.66 (d, *J* = 7.3 Hz, 0.1H), 3.60 – 3.51 (m, 1.1H), 3.51 – 3.42 (m, 1.1H), 2.26 (s, 0.3H), 2.18 (s, 3H), 1.47 (t, *J* = 6.6 Hz, 6.6H), 1.02 (d, *J* = 6.7 Hz, 6.6H); ^{13}C NMR (126 MHz, DMSO) δ 168.9, 167.7, 137.7, 137.2, 135.3, 129.4, 129.3, 128.4, 128.1, 127.5, 127.4, 126.1, 125.2, 111.8, 99.5, 50.6, 44.8, 20.6, 20.4, 20.3, 20.2, 20.19, 20.1, 19.9; HRMS m/z (ESI) calcd. for $C_{17}H_{23}NNaO_3^+$ $(M+Na)^+$ 312.1570, found 312.1563.

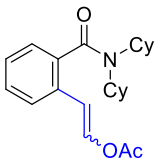


2-(dimethylcarbamoyl)styryl acetate (**3ba**): colorless liquid; yield 91% (42.5 mg; [CpRh]), 87% (40.5 mg; $[Cp^{CF3}Rh]$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 0.3H), 7.78 (d, *J* = 12.7 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.32 (m, 0.6H), 7.31 – 7.27 (m, 1.3H), 7.25 (dd, *J* = 7.3, 0.6 Hz, 1H), 7.22 (dd, *J* = 5.1, 1.1 Hz, 0.3H), 7.18 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.36 (d, *J* = 12.7 Hz, 1H), 5.67 (d, *J* = 7.4 Hz, 0.3H), 3.11 (s, 3H), 3.09 (s, 0.9H), 2.77 (s, 3.9H), 2.21 (s, 0.9H), 2.15 (s, 3H); ^{13}C NMR

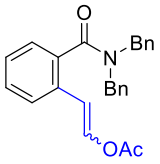
(126 MHz, $CDCl_3$) δ 171.0, 170.9, 167.9, 167.4, 137.8, 136.4, 135.8, 135.2, 130.8, 130.4, 129.7, 129.2, 128.8, 128.4, 127.6, 127.5, 127.1, 126.6, 126.3, 125.8, 112.3, 108.2, 38.6, 34.8, 20.9, 20.7; HRMS m/z (ESI) calcd. for $C_{13}H_{15}NNaO_3^+$ $(M+Na)^+$ 256.0944, found 256.0939.



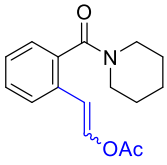
2-(diethylcarbamoyl)styryl acetate (**3ca**): colorless liquid; yield 78% (40.8 mg; [CpRh]), 84% (43.9 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 0.3H), 7.75 (d, *J* = 12.7 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 0.3H), 7.27 – 7.22 (m, 1.3H), 7.21 – 7.17 (m, 1.3H), 7.16 – 7.11 (m, 1.3H), 6.32 (d, *J* = 12.7 Hz, 1H), 5.64 (d, *J* = 7.4 Hz, 0.3H), 3.51 (s, 2.6H), 3.06 – 3.01 (m, 2.6H), 2.17 (s, 0.9H), 2.11 (s, 3H), 1.23 – 1.18 (m, 3.9H), 0.97 – 0.82 (m, 3.9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 170.3, 168.0, 167.5, 137.7, 136.8, 136.1, 135.1, 130.7, 130.2, 129.8, 129.0, 128.7, 127.5, 127.4, 126.3, 125.9, 125.7, 112.1, 108.0, 43.0, 39.1, 39.0, 21.0, 20.8, 14.1, 13.0, 12.9; HRMS m/z (ESI) calcd. for $C_{15}H_{19}NNaO_3^+$ $(M+Na)^+$ 284.1257, found 284.1251.



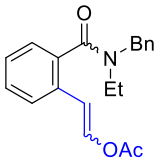
2-(dicyclohexylcarbamoyl)styryl acetate (**3da**): colorless liquid; yield 88% (65.0 mg; [CpRh]), 75% (55.5 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 0.2H), 7.78 (d, *J* = 12.7 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.27 (m, 0.2H), 7.25 – 7.21 (m, 1.2H), 7.20 – 7.16 (m, 1.2H), 7.09 – 7.05 (m, 1.2H), 6.38 (d, *J* = 12.7 Hz, 1H), 5.73 (d, *J* = 7.4 Hz, 0.2H), 3.11 – 2.97 (m, 2.4H), 2.68 – 2.59 (m, 2.4H), 2.20 (s, 0.6H), 2.13 (s, 3H),1.64 – 1.56 (m, 7.2H), 1.50 – 1.33 (m, 4.8H), 1.29 – 1.20 (m, 4.8H), 1.04 – 0.76 (m, 4.8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 168.0, 137.8, 137.3, 134.9, 130.3, 129.8, 128.5, 127.5, 125.6, 125.4, 124.9, 112.4, 108.4, 60.0, 56.2, 31.4, 31.2, 30.0, 26.8, 25.7, 25.6, 25.4, 25.2, 20.8; HRMS m/z (ESI) calcd. for $C_{23}H_{31}NNaO_3^+$ $(M+Na)^+$ 392.2196, found 392.2194.



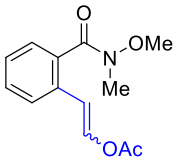
2-(dibenzylcarbamoyl)styryl acetate (**3ea**): colorless liquid; yield 94% (72.5 mg; [CpRh]), 67% (51.6 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 0.1H), 7.67 (dd, *J* = 12.7, 2.3 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1.1H), 7.31 – 7.11 (m, 12.1H), 6.98 (d, *J* = 6.9 Hz, 2.2H), 6.43 (d, *J* = 12.7 Hz, 1H), 5.73 (d, *J* = 7.3 Hz, 0.1H), 4.93 (s, 1.1H), 4.32 (s, 1.1H), 4.10 (s, 2.2H), 2.10 (s, 3.3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 171.2, 167.9, 167.4, 137.9, 136.9, 136.8, 136.1, 135.7, 135.3, 135.2, 131.3, 130.7, 130.0, 129.4, 129.0, 128.9, 128.8, 128.79, 128.7, 128.6, 127.8, 127.7, 127.6, 127.5, 126.6, 126.3, 125.8, 112.3, 108.1, 51.1, 51.0, 46.6, 46.5, 20.9, 20.8; HRMS m/z (ESI) calcd. for $C_{25}H_{23}NNaO_3^+$ $(M+Na)^+$ 408.1570, found 408.1562.



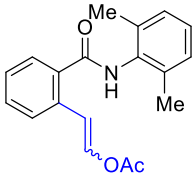
2-(piperidine-1-carbonyl)styryl acetate (**3fa**): colorless liquid; yield 73% (39.9 mg; [CpRh]), 88% (48.0 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 0.3H), 7.74 (d, *J* = 12.7 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 0.3H), 7.26 – 7.22 (m, 1.3H), 7.20 (d, *J* = 7.9 Hz, 1.3H), 7.16 (dd, *J* = 9.2, 1.0 Hz, 0.3H), 7.13 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.35 (d, *J* = 12.7 Hz, 1H), 5.68 (d, *J* = 7.4 Hz, 0.3H), 3.78 – 3.61 (m, 2.6H), 3.09 – 3.04 (m, 2.6H), 2.17 (s, 0.9H), 2.11 (s, 3H), 1.59 (s, 5.2H), 1.39 – 1.35 (m, 2.6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 169.2, 168.0, 167.5, 137.6, 136.5, 135.8, 135.1, 130.9, 130.4, 129.8, 129.1, 128.7, 127.6, 127.5, 126.5, 126.1, 125.7, 112.3, 108.2, 48.1, 42.6, 26.5, 25.8, 24.6, 24.5, 21.0, 20.8; HRMS m/z (ESI) calcd. for $C_{16}H_{19}NNaO_3^+$ $(M+Na)^+$ 296.1257, found 296.1252.



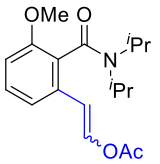
2-(benzyl(ethyl)carbamoyl)styryl acetate (**3ga**): colorless liquid; yield 98% (63.4 mg; [CpRh]), 83% (53.7 mg; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 11.1, 8.0 Hz, 0.2H), 7.71 (t, *J* = 12.5 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1.2H), 7.31 – 7.27 (m, 2H), 7.25 (s, 0.4H), 7.24 – 7.12 (m, 6H), 7.11 (d, *J* = 7.2 Hz, 0.2H), 7.01 (d, *J* = 7.0 Hz, 1H), 6.38 (t, *J* = 12.7 Hz, 1H), 5.69 (dd, *J* = 34.5, 7.4 Hz, 0.2H), 4.70 (s, 1.2H), 4.20 (s, 1.2H), 3.45 (d, *J* = 235.0 Hz, 1.2H), 2.97 – 2.91 (m, 1.2H), 2.13 (d, *J* = 3.4 Hz, 0.6H), 2.09 (d, *J* = 10.1 Hz, 3H), 1.12 (dd, *J* = 13.2, 6.1 Hz, 1.6H), 0.88 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 171.0, 170.9, 170.8, 168.0, 167.9, 167.5, 167.4, 137.9, 137.7, 137.5, 137.4, 136.6, 135.9, 135.6, 135.3, 135.2, 131.1, 130.8, 130.6, 130.4, 129.9, 129.8, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.58, 127.5, 127.4, 127.36, 127.3, 126.6, 126.3, 126.2, 126.0, 125.8, 125.7, 112.3, 112.1, 108.1, 108.0, 51.7, 46.7, 42.4, 39.2, 39.1, 21.0, 20.9, 20.8, 20.7, 13.5, 13.4, 12.3, 12.2; HRMS m/z (ESI) calcd. for $C_{20}H_{21}NNaO_3^+$ $(M+Na)^+$ 346.1414, found 346.1406.



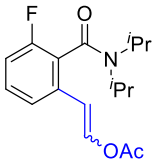
2-(methoxy(methyl)carbamoyl)styryl acetate (**3ha**): colorless liquid; yield 65% (32.4 mg; [CpRh]), 62% (30.8 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, Acetone) δ 8.01 (d, *J* = 8.0 Hz, 0.36H), 7.82 (d, *J* = 12.8 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 5.4 Hz, 0.36H), 7.42 – 7.37 (m, 1.36H), 7.33 – 7.29 (m, 2.72H), 6.45 (d, *J* = 12.8 Hz, 1H), 5.79 (d, *J* = 7.4 Hz, 0.36H), 3.50 (s, 4.08H), 3.28 (s, 4.08H), 2.25 (s, 1.08H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, Acetone) δ 168.4, 168.1, 138.6, 136.8, 136.1, 135.9, 132.2, 131.8, 130.4, 130.1, 129.7, 127.8, 127.7, 127.6, 127.4, 126.4, 113.1, 109.0, 61.4, 20.7, 20.5; HRMS m/z (ESI) calcd. for $C_{13}H_{15}NNaO_4^+$ $(M+Na)^+$ 272.0893, found 272.0887.



2-((2,6-dimethylphenyl)carbamoyl)styryl acetate (**3ia**): colorless solid; yield 69% (42.7 mg; [CpRh]), 66% (40.7 mg; [Cp^{CF3}Rh]); ^{1}H NMR (400 MHz, DMSO) δ 9.79 (s, 1H), 9.77 (s, 0.2H), 8.00 (d, *J* = 7.8 Hz, 0.2H), 7.86 (d, *J* = 12.7 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.59 (m, 1.2H), 7.53 (td, *J* = 7.7, 1.2 Hz, 0.2H), 7.47 (td, *J* = 7.5, 1.2 Hz, 1H), 7.43 – 7.37 (m, 1.2H), 7.34 (d, *J* = 7.4 Hz, 0.2H), 7.12 (s, 3.6H), 6.79 (d, *J* = 12.8 Hz, 1H), 6.17 (d, *J* = 7.4 Hz, 0.2H), 2.25 (s, 7.2H), 2.19 (s, 3.6H); ^{13}C NMR (126 MHz, DMSO) δ 167.8, 167.1, 137.4, 136.0, 135.3, 134.9, 131.6, 129.86, 127.7, 127.6, 127.2, 126.7, 125.7, 112.6, 20.4, 18.1; HRMS m/z (ESI) calcd. for $C_{19}H_{19}NNaO_3^+$ $(M+Na)^+$ 332.1257, found 332.1250.

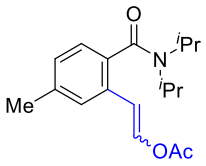


2-(diisopropylcarbamoyl)-3-methoxystyryl acetate (**3ja**): colorless solid; yield 62% (39.6 mg; [CpRh]), 41% (26.2 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 12.7 Hz, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.38 (d, *J* = 12.7 Hz, 1H), 3.78 (s, 3H), 3.62 – 3.56 (m, 1H), 3.52 – 3.46 (m, 1H), 2.16 (s, 3H), 1.60 (d, *J* = 6.8 Hz, 3H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 167.5, 155.7, 137.8, 132.0, 129.1, 127.3, 117.9, 112.3, 109.7, 55.7, 51.2, 46.1, 21.1, 20.8, 20.7, 20.6; HRMS m/z (ESI) calcd. for $C_{18}H_{25}NNaO_4^+$ $(M+Na)^+$ 342.1676, found 342.1670.

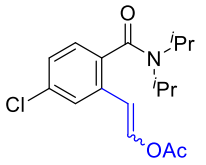


2-(diisopropylcarbamoyl)-3-fluorostyryl acetate (**3ka**): colorless solid; yield 54% (33.3 mg; [CpRh]), 75% (46.1 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 12.7 Hz, 1H), 7.25 – 7.19 (m, 2H), 6.96 – 6.90 (m, 1H), 6.36 (d, *J* = 12.7 Hz, 1H), 3.64 – 3.58 (m, 1H), 3.55 – 3.49 (m, 1H), 2.16 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 164.8 (d, *J* = 1.3 Hz), 158.6 (d, *J* = 244.6 Hz), 138.4, 133.3

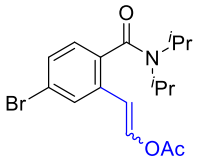
(d, *J* = 4.8 Hz), 129.6 (d, *J* = 8.5 Hz), 125.5 (d, *J* = 20.9 Hz), 121.4 (d, *J* = 2.9 Hz), 114.3 (d, *J* = 21.7 Hz), 111.5 (d, *J* = 2.9 Hz), 51.4, 46.3, 21.1, 20.7, 20.66, 20.6, 20.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.95; HRMS m/z (ESI) calcd. for $C_{17}H_{22}FNNaO_3^+$ $(M+Na)^+$ 330.1476, found 330.1470.



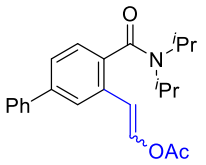
2-(diisopropylcarbamoyl)-5-methylstyryl acetate (**3la**): colorless solid; yield 89% (54.0 mg; [CpRh]), 80% (48.5 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 12.7 Hz, 1H), 7.73 (s, 0.16H), 7.28 (d, *J* = 7.4 Hz, 0.16H), 7.26 (s, 1H), 7.08 – 6.97 (m, 2.32H), 6.39 (d, *J* = 12.7 Hz, 1H), 5.74 (d, *J* = 7.4 Hz, 0.16H), 3.65 – 3.58 (m, 1.16H), 3.52 – 3.45 (m, 1.16H), 2.36 (s, 0.48H), 2.33 (s, 3H), 2.24 (s, 0.48H), 2.16 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3.48H), 1.54 (d, *J* = 6.8 Hz, 3.48H), 1.07 (d, *J* = 6.7 Hz, 3.48H), 1.04 (d, *J* = 6.7 Hz, 3.48H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 170.3, 168.0, 167.4, 138.3, 137.7, 137.4, 135.9, 135.1, 134.8, 130.4, 130.3, 129.9, 128.4, 128.3, 126.3, 125.5, 125.0, 112.5, 108.5, 51.0, 46.0, 21.6, 21.3, 20.9, 20.88, 20.8, 20.75, 20.7; HRMS m/z (ESI) calcd. for $C_{18}H_{25}NNaO_3^+$ $(M+Na)^+$ 326.1727, found 326.1717.



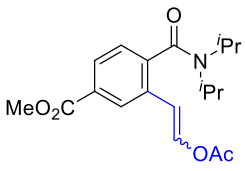
5-chloro-2-(diisopropylcarbamoyl)styryl acetate (**3ma**): colorless solid; yield 86% (55.7 mg; [CpRh]), 70% (45.5 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.7 Hz, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.20 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.35 (d, *J* = 12.7 Hz, 1H), 3.59 – 3.53 (m, 1H), 3.52 – 3.46 (m, 1H), 2.17 (s, 3H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 167.8, 138.5, 136.0, 134.4, 132.5, 127.6, 126.9, 125.8, 111.4, 51.2, 46.1, 20.9, 20.7, 20.6, 20.5; HRMS m/z (ESI) calcd. for $C_{17}H_{22}ClNNaO_3^+$ $(M+Na)^+$ 346.1180, found 346.1173.



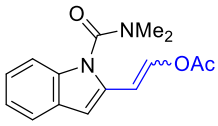
5-bromo-2-(diisopropylcarbamoyl)styryl acetate (**3na**): colorless solid; yield 77% (56.7 mg; [CpRh]), 74% (54.2 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.7 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.36 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.34 (d, *J* = 12.8 Hz, 1H), 3.60 – 3.54 (m, 1H), 3.53 – 3.47 (m, 1H), 2.18 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 167.8, 138.5, 136.5, 132.8, 130.5, 128.7, 127.1, 122.5, 111.3, 51.2, 46.2, 20.9, 20.7, 20.69, 20.6; HRMS m/z (ESI) calcd. for $C_{17}H_{22}BrNNaO_3^+$ $(M+Na)^+$ 390.0675, found 390.0671.



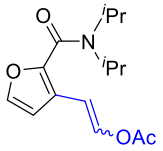
2-(4-(diisopropylcarbamoyl)-[1,1'-biphenyl]-3-yl)vinyl acetate (**3oa**): colorless solid; yield 92% (67.2 mg; [CpRh]), 67% (48.9 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.7 Hz, 0.17H), 7.91 (d, *J* = 12.7 Hz, 1H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.61 (d, *J* = 1.3 Hz, 0.17H), 7.60 – 7.56 (m, 2.34H), 7.48 – 7.42 (m, 3.51H), 7.38 – 7.34 (m, 1.17H), 7.23 (d, *J* = 7.8 Hz, 0.17H), 7.21 (d, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 12.7 Hz, 1H), 5.84 (d, *J* = 7.4 Hz, 0.17H), 3.74 – 3.67 (m, 1.17H), 3.57 – 3.49 (m, 1.17H), 2.24 (s, 0.51H), 2.18 (s, 3H), 1.63 (d, *J* = 6.8 Hz, 3.51H), 1.59 (d, *J* = 6.8 Hz, 3.51H), 1.12 (d, *J* = 6.6 Hz, 3.51H), 1.10 (d, *J* = 6.5 Hz, 3.51H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 170.00, 167.9, 167.3, 141.6, 141.0, 140.8, 140.4, 137.7, 137.3, 136.5, 135.2, 130.9, 130.4, 129.0, 128.9, 128.7, 127.8, 127.6, 127.2, 127.1, 126.4, 126.3, 126.0, 125.5, 124.6, 112.5, 108.3, 51.1, 46.0, 20.9, 20.89, 20.8, 20.77, 20.7, 20.63, 20.6; HRMS m/z (ESI) calcd. for $C_{23}H_{27}NNaO_3^+$ $(M+Na)^+$ 388.1883, found 388.1882.



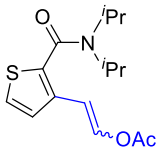
methyl 3-(2-acetoxyvinyl)-4-(diisopropylcarbamoyl)benzoate (**3pa**): colorless solid; yield 81% (56.3 mg; [CpRh]), 73% (50.7 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.2 Hz, 0.11H), 8.13 (d, *J* = 1.1 Hz, 1H), 7.94 – 7.87 (m, 2.11H), 7.37 (d, *J* = 7.3 Hz, 0.11H), 7.20 (d, *J* = 7.9 Hz, 1.11H), 6.41 (d, *J* = 12.7 Hz, 1H), 5.76 (d, *J* = 7.3 Hz, 0.11H), 3.91 (s, 3.33H), 3.56 – 3.46 (m, 2.22H), 2.27 (s, 0.33H), 2.18 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3.33H), 1.55 (d, *J* = 6.8 Hz, 3.33H), 1.08 (d, *J* = 6.7 Hz, 3.33H), 1.05 (d, *J* = 6.6 Hz, 3.33H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 167.8, 166.4, 141.5, 138.5, 135.9, 131.5, 130.9, 130.4, 128.6, 128.5, 127.1, 125.7, 125.2, 111.5, 107.4, 52.4, 51.2, 46.2, 20.9, 20.8, 20.73, 20.7, 20.67, 20.6, 20.5; HRMS m/z (ESI) calcd. for $C_{19}H_{25}NNaO_5^+$ $(M+Na)^+$ 370.1625, found 370.1621.



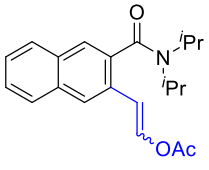
2-(1-(dimethylcarbamoyl)-1H-indol-2-yl)vinyl acetate (**3qa**): colorless liquid; yield 56% (30.5 mg; [CpRh]), 58% (31.4 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, DMSO) δ 7.81 (d, *J* = 12.8 Hz, 0.75H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 0.75H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.32 – 7.27 (m, 1.75H), 7.23 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 0.75H), 7.16 – 7.11 (m, 1.75H), 7.09 (s, 1H), 6.85 (s, 0.75H), 6.47 (dd, *J* = 12.8, 0.6 Hz, 0.75H), 5.92 (d, *J* = 7.1 Hz, 1H), 3.17 – 2.72 (m, 10.50H), 2.34 (s, 3H), 2.20 (s, 2.25H); ^{13}C NMR (126 MHz, DMSO) δ 167.6, 167.3, 152.7, 152.6, 137.6, 135.5, 135.4, 134.4, 132.7, 131.5, 128.1, 127.8, 123.3, 123.0, 121.3, 121.2, 120.7, 120.4, 111.0, 110.9, 106.3, 105.2, 102.4, 100.9, 20.6, 20.3; HRMS m/z (ESI) calcd. for $C_{15}H_{16}N_2NaO_3^+$ $(M+Na)^+$ 295.1053, found 295.1052.



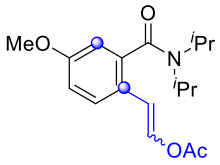
2-(2-(diisopropylcarbamoyl)furan-3-yl)vinyl acetate (**3ra**): colorless solid; yield 47% (26.3 mg; [CpRh]), 46% (25.6 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 12.9 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 6.71 (d, *J* = 12.9 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 6.16 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 4H), 2.24 (s, 3H), 2.15 (s, 3H), 1.35 (s, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.2, 161.0, 160.9, 145.9, 145.5, 142.0, 141.4, 137.3, 134.6, 123.1, 122.0, 112.4, 108.8, 106.5, 102.6, 48.4, 21.1, 21.0, 20.8; HRMS m/z (ESI) calcd. for $C_{15}H_{21}NNaO_4^+$ $(M+Na)^+$ 302.1363, found 302.1359.



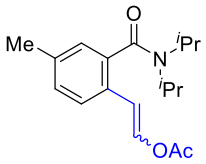
2-(2-(diisopropylcarbamoyl)thiophen-3-yl)vinyl acetate (**3sa**): colorless solid; yield 91% (53.8 mg; [CpRh]), 76% (44.9 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 12.8 Hz, 1H), 7.52 (d, *J* = 5.2 Hz, 0.41H), 7.24 (d, *J* = 5.2 Hz, 0.41H), 7.22 (d, *J* = 7.3 Hz, 0.41H), 7.21 (d, *J* = 5.2 Hz, 1H), 7.05 (d, *J* = 5.2 Hz, 1H), 6.34 (d, *J* = 12.8 Hz, 1H), 5.73 (d, *J* = 7.1 Hz, 0.41H), 3.69 (s, 2.82H), 2.24 (s, 1.23H), 2.16 (s, 3H), 1.33 (s, 16.92H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 167.2, 164.2, 164.1, 137.6, 135.6, 133.8, 133.5, 133.0, 132.5, 128.1, 125.1, 124.6, 124.4, 108.5, 104.7, 49.1, 21.0, 20.9, 20.8; HRMS m/z (ESI) calcd. for $C_{15}H_{21}NNaO_3S^+$ $(M+Na)^+$ 318.1134, found 318.1133.



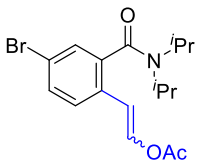
2-(3-(diisopropylcarbamoyl)naphthalen-2-yl)vinyl acetate (**3ta**): colorless solid; yield 87% (59.2 mg; [CpRh]), 71% (48.2 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 12.7 Hz, 1H), 7.92 (s, 1H), 7.81 – 7.76 (m, 2H), 7.61 (s, 1H), 7.50 – 7.43 (m, 2H), 6.57 (d, *J* = 12.7 Hz, 1H), 3.66 (dt, *J* = 13.3, 6.7 Hz, 1H), 3.55 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.20 (s, 3H), 1.64 (t, *J* = 7.0 Hz, 6H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 168.0, 137.8, 136.0, 133.2, 132.4, 128.7, 127.8, 126.9, 126.6, 125.1, 124.4, 112.7, 51.2, 46.1, 20.8, 20.8, 20.7; HRMS m/z (ESI) calcd. for $C_{21}H_{25}NNaO_3^+$ $(M+Na)^+$ 362.1727, found 362.1723.



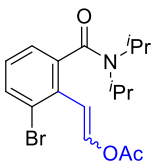
2-(diisopropylcarbamoyl)-4/6-methoxystyryl acetates (**3ua**): colorless solid; yield 78% (49.8 mg; [CpRh]), 59% (37.6 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (C2, d, *J* = 12.6 Hz, 1H), 7.71 (C6, d, *J* = 12.7 Hz, 0.51H), 7.37 (C6, d, *J* = 8.7 Hz, 0.51H), 7.18 (C2, t, *J* = 7.9 Hz, 1H), 6.85 (C2, d, *J* = 8.3 Hz, 1H), 6.82 (C6, dd, *J* = 8.7, 2.7 Hz, 0.51H), 6.74 (C2, dd, *J* = 7.5, 0.7 Hz, 1H), 6.64 (C6, d, *J* = 2.7 Hz, 0.51H), 6.38 (C2, d, *J* = 12.6 Hz, 1H), 6.35 (C6, d, *J* = 12.8 Hz, 0.51H), 3.88 (C2, s, 3H), 3.78 (C6, s, 1.53H), 3.60 (C2+C6, dt, *J* = 13.3, 6.6 Hz, 1.51H), 3.48 (C2+C6, dt, *J* = 13.6, 6.8 Hz, 1.51H), 2.15 (C6, s, 1.53H), 2.14 (C2, s, 3H), 1.60 – 1.53 (C2+C6, m, 9.06H), 1.10 – 1.02 (C2+C6, m, 9.06H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 169.7, 168.1, 167.9, 159.2, 157.6, 140.3, 139.4, 138.8, 136.3, 128.2, 127.3, 122.8, 119.0, 117.9, 114.8, 112.1, 110.6, 110.5, 109.0, 55.7, 55.5, 51.0, 46.0, 45.9, 20.8, 20.79, 20.74, 20.72, 20.7, 20.6, 20.4; HRMS m/z (ESI) calcd. for $C_{18}H_{25}NNaO_4^+$ $(M+Na)^+$ 342.1676, found 342.1671.



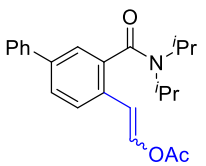
2-(diisopropylcarbamoyl)-4-methylstyryl acetate (**3va**): colorless solid; yield 89% (54.2 mg; [CpRh]), 82% (49.9 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 0.25H), 7.77 (d, *J* = 12.7 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 0.25H), 7.14 (d, *J* = 8.8 Hz, 0.25H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 0.25H), 6.93 (s, 1H), 6.38 (d, *J* = 12.7 Hz, 1H), 5.72 (d, *J* = 7.4 Hz, 0.25H), 3.64 – 3.58 (m, 1.25H), 3.52 – 3.46 (m, 1.25H), 2.33 (s, 0.75H), 2.31 (s, 3H), 2.23 (s, 0.75H), 2.15 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3.75H), 1.55 (d, *J* = 6.8 Hz, 3.75H), 1.08 (d, *J* = 6.7 Hz, 3.75H), 1.05 (d, *J* = 6.7 Hz, 3.75H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 170.2, 168.0, 167.4, 138.4, 137.6, 137.6, 137.5, 137.0, 134.4, 129.7, 129.3, 129.0, 127.4, 127.1, 126.0, 125.7, 125.6, 112.4, 108.3, 51.1, 51.0, 46.0, 21.2, 21.2, 20.9, 20.8, 20.74, 20.7, 20.6, 20.5; HRMS m/z (ESI) calcd. for $C_{18}H_{25}NNaO_3^+$ $(M+Na)^+$ 326.1727, found 326.1720.



4-bromo-2-(diisopropylcarbamoyl)styryl acetate (**3wa-C6**): colorless solid; yield 52% (38.2 mg of C6; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.7 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 2.1 Hz, 1H), 6.34 (d, *J* = 12.8 Hz, 1H), 3.63 – 3.55 (m, 1H), 3.55 – 3.47 (m, 1H), 2.18 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 4.2 Hz, 3H), 1.09 (d, *J* = 4.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 167.9, 139.3, 138.0, 131.7, 129.6, 128.5, 127.4, 121.4, 111.5, 51.2, 46.2, 20.9, 20.8, 20.77, 20.7, 20.6; HRMS m/z (ESI) calcd. for $C_{17}H_{22}BrNNaO_3^+$ $(M+Na)^+$ 390.0675, found 390.0674.

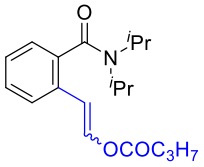


2-bromo-6-(diisopropylcarbamoyl)styryl acetate (**3wa-C2**): colorless solid; yield 45% (33.1 mg of C6+C2; [CpRh]);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 12.8 Hz, 1H), 7.56 (t, *J* = 6.7 Hz, 1H), 7.11 (d, *J* = 1.0 Hz, 1H), 7.10 (d, *J* = 1.0 Hz, 1H), 6.48 (d, *J* = 12.8 Hz, 1H), 3.61 – 3.52 (m, 1H), 3.50 – 3.41 (m, 1H), 2.16 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 167.4, 140.3, 139.5, 132.9, 130.6, 128.7, 125.2, 125.1, 112.0, 51.1, 46.0, 20.8, 20.7, 20.68, 20.6, 20.0; HRMS m/z (ESI) calcd. for $C_{17}H_{22}BrNNaO_3^+$ $(M+Na)^+$ 390.0675, found 390.0672.

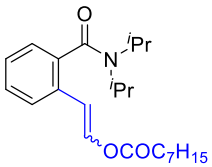


2-(3-(diisopropylcarbamoyl)-[1,1'-biphenyl]-4-yl)vinyl acetate (**3xa**): yield 91% (66.4 mg; [CpRh]), 87% (63.5 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 0.14H), 7.89 (d, *J* = 12.7 Hz, 1H), 7.61 – 7.58 (m, 1.14H), 7.57 (d, *J* = 0.7 Hz, 1.14H), 7.56 (s, 0.14H), 7.54 (s, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 0.14H), 7.46 – 7.41 (m, 2.28H), 7.37 – 7.33 (m, 2.28H),

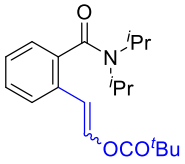
6.46 (d, *J* = 12.7 Hz, 1H), 5.81 (d, *J* = 7.4 Hz, 0.14H), 3.73 – 3.67 (m, 1.14H), 3.57 – 3.51 (m, 1.14H), 2.28 (s, 0.42H), 2.19 (s, 3H), 1.63 (d, *J* = 6.8 Hz, 3.42H), 1.60 (d, *J* = 6.8 Hz, 3.42H), 1.12 (d, *J* = 6.7 Hz, 3.42H), 1.08 (d, *J* = 6.7 Hz, 3.42H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 170.0, 168.0, 167.4, 140.5, 140.3, 140.27, 140.2, 138.9, 138.2, 137.6, 135.1, 130.3, 129.4, 129.0, 127.8, 127.7, 127.3, 127.1, 127.0, 126.9, 126.3, 124.1, 123.6, 112.1, 108.0, 51.2, 51.1, 46.1, 21.0, 20.9, 20.88, 20.8, 20.7, 20.6; HRMS m/z (ESI) calcd. for $C_{23}H_{27}NNaO_3^+$ $(M+Na)^+$ 388.1883, found 388.1877.



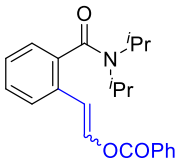
2-(diisopropylcarbamoyl)styryl butyrate (**3ab**): colorless solid; yield 92% (58.4 mg; [CpRh]), 76% (48.2 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 12.7 Hz, 1H), 7.46 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (td, *J* = 7.4, 1.2 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.42 (d, *J* = 12.7 Hz, 1H), 3.64 – 3.56 (m, 1H), 3.54 – 3.46 (m, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.1, 137.7, 137.6, 130.5, 128.5, 127.5, 125.8, 125.5, 112.3, 51.1, 46.0, 36.0, 20.9, 20.8, 20.6, 18.3, 13.7; HRMS m/z (ESI) calcd. for $C_{19}H_{27}NNaO_3^+$ $(M+Na)^+$ 340.1883, found 340.1880.



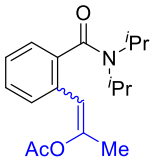
2-(diisopropylcarbamoyl)styryl octanoate (**3ac**): colorless solid; yield 93% (69.4 mg; [CpRh]), 86% (64.2 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 12.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.27 (td, *J* = 7.6, 1.6 Hz, 1H), 7.23 (td, *J* = 7.4, 1.1 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.42 (d, *J* = 12.7 Hz, 1H), 3.64 – 3.56 (m, 1H), 3.54 – 3.46 (m, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.35 – 1.24 (m, 8H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.1, 137.7, 137.7, 130.5, 128.5, 127.5, 125.8, 125.5, 112.3, 51.1, 46.0, 34.1, 31.7, 29.1, 29.0, 24.8, 22.7, 20.9, 20.8, 20.6, 14.1; HRMS m/z (ESI) calcd. for $C_{23}H_{35}NNaO_3^+$ $(M+Na)^+$ 396.2509, found 396.2490.



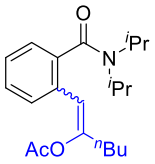
2-(diisopropylcarbamoyl)styryl pivalate (**3ad**): colorless solid; yield 81% (53.6 mg; [CpRh]), 70% (46.4 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 12.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (td, *J* = 7.4, 1.1 Hz, 1H), 7.13 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.44 (d, *J* = 12.7 Hz, 1H), 3.64 – 3.55 (m, 1H), 3.54 – 3.46 (m, 1H), 1.58 (d, *J* = 7.0 Hz, 3H), 1.57 (d, *J* = 6.9 Hz, 3H), 1.25 (s, 9H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 170.2, 138.0, 137.7, 130.6, 128.6, 127.5, 125.8, 125.5, 112.3, 51.1, 46.0, 38.9, 27.0, 20.8, 20.7, 20.5; HRMS m/z (ESI) calcd. for $C_{20}H_{29}NNaO_3^+$ $(M+Na)^+$ 354.2040, found 354.2038.



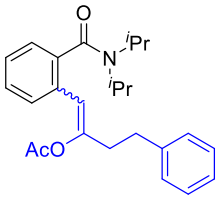
2-(diisopropylcarbamoyl)styryl benzoate (**3ae**): colorless liquid; yield 91% (63.9 mg; [CpRh]), 74% (52.3 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 8.07 (d, *J* = 12.7 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.32 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27 (td, *J* = 7.5, 1.2 Hz, 1H), 7.16 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.64 (d, *J* = 12.7 Hz, 1H), 3.70 – 3.59 (m, 1H), 3.57 – 3.48 (m, 1H), 1.64 (d, *J* = 6.8 Hz, 3H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 163.7, 137.9, 137.8, 133.8, 130.5, 130.2, 128.7, 128.6, 127.7, 126.0, 125.6, 113.1, 51.1, 46.1, 20.9, 20.8, 20.7; HRMS m/z (ESI) calcd. for $C_{22}H_{25}NNaO_3^+$ $(M+Na)^+$ 374.1727, found 374.1723.



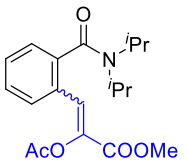
1-(2-(diisopropylcarbamoyl)phenyl)prop-1-en-2-yl acetate (**3af**): colorless solid; yield 98% (59.4 mg; [CpRh]), 85% (51.7 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, DMSO) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 6.9, 1.1 Hz, 0.19H), 7.36 (d, *J* = 1.5 Hz, 0.19H), 7.35 – 7.31 (m, 1.19H), 7.26 (td, *J* = 7.5, 1.1 Hz, 1H), 7.16 (dd, *J* = 7.4, 0.8 Hz, 0.19H), 7.12 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.13 (s, 0.19H), 5.87 (s, 1H), 3.57 – 3.51 (m, 1.19H), 3.44 – 3.39 (m, 1.19H), 2.15 (s, 3H), 2.12 (s, 0.57H), 1.98 (s, 3.57H), 1.48 – 1.40 (m, 7.14H), 1.06 – 0.98 (m, 7.14H); ^{13}C NMR (126 MHz, DMSO) δ 169.0, 168.9, 168.8, 168.3, 148.8, 147.3, 138.7, 138.0, 130.3, 129.7, 128.9, 128.1, 128.0, 127.5, 127.4, 127.3, 124.8, 124.7, 115.2, 112.3, 50.5, 44.9, 44.8, 20.8, 20.7, 20.5, 20.2, 20.1, 19.7, 16.8; HRMS m/z (ESI) calcd. for $C_{18}H_{25}NNaO_3^+$ $(M+Na)^+$ 326.1727, found 326.1724.



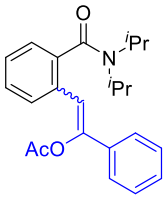
1-(2-(diisopropylcarbamoyl)phenyl)hex-1-en-2-yl acetate (**3ag**): colorless liquid; yield 68% (46.9 mg; [CpRh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 3.7 Hz, 0.45H), 7.31 (d, *J* = 3.9 Hz, 1H), 7.25 (d, *J* = 1.3 Hz, 0.45H), 7.25 – 7.24 (m, 0.45H), 7.20 (td, *J* = 7.5, 1.1 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 0.45H), 7.11 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.30 (s, 0.45H), 6.07 (s, 1H), 3.68 – 3.55 (m, 1.45H), 3.54 – 3.43 (m, 1.45H), 2.47 – 2.29 (m, 2.90H), 2.14 (s, 1.35H), 2.13 (s, 3H), 1.58 – 1.53 (m, 8.70H), 1.52 – 1.46 (m, 2.90H), 1.39 – 1.34 (m, 2.90H), 1.14 – 1.11 (m, 4.35H), 1.04 (t, *J* = 6.9 Hz, 4.35H), 0.93 – 0.88 (m, 4.35H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 168.5, 151.2, 138.4, 131.4, 130.8, 130.7, 128.6, 128.3, 128.0, 127.9, 127.4, 127.1, 126.0, 125.7, 125.1, 112.5, 51.1, 45.9, 34.2, 33.2, 30.3, 29.0, 22.4, 22.3, 21.2, 20.9, 20.83, 20.8, 20.7, 20.6, 20.5, 14.0, 13.9; HRMS m/z (ESI) calcd. for $C_{21}H_{31}NNaO_3^+$ $(M+Na)^+$ 368.2196, found 368.2194.



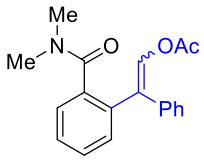
1-(2-(diisopropylcarbamoyl)phenyl)-4-phenylbut-1-en-2-yl acetate (**3ah**): colorless liquid; yield 84% (66.0 mg; [CpRh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 1.8 Hz, 0.16H), 7.29 – 7.26 (m, 3H), 7.24 (dd, *J* = 3.1, 1.9 Hz, 0.48H), 7.22 (d, *J* = 1.2 Hz, 0.64H), 7.21 – 7.17 (m, 4H), 7.13 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.03 – 7.01 (m, 0.16H), 6.38 (s, 0.16H), 6.14 (s, 1H), 3.64 – 3.57 (m, 1.16H), 3.55 – 3.47 (m, 1.16H), 2.88 – 2.83 (m, 2.32H), 2.71 – 2.61 (m, 2.32H), 2.11 (s, 0.48H), 2.10 (s, 3H), 1.59 (d, *J* = 2.5 Hz, 3H), 1.57 (d, *J* = 2.5 Hz, 3H), 1.54 (t, *J* = 6.9 Hz, 0.96H), 1.12 (d, *J* = 6.7 Hz, 3.48H), 1.05 (d, *J* = 6.7 Hz, 3.48H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 170.0, 169.2, 168.4, 151.4, 150.3, 141.1, 140.9, 138.9, 138.4, 130.9, 130.5, 129.3, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.5, 127.3, 126.3, 126.2, 125.1, 125.0, 117.1, 113.0, 51.1, 51.0, 46.0, 36.3, 33.4, 33.1, 31.9, 21.1, 21.0, 20.8, 20.7, 20.6, 20.5, 20.4; HRMS m/z (ESI) calcd. for $C_{25}H_{31}NNaO_3^+$ $(M+Na)^+$ 416.2196, found 416.2193.



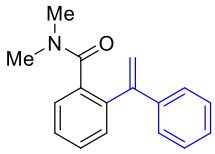
methyl 2-acetoxy-3-(2-(diisopropylcarbamoyl)phenyl)acrylate (**3ai**): colorless solid; yield 69% (47.8 mg; [CpRh]), 82% (56.9 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.41 (s, 1H), 7.37 – 7.34 (m, 2H), 7.23 – 7.20 (m, 1H), 3.80 (s, 3H), 3.56 – 3.50 (m, 2H), 2.29 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 168.4, 162.8, 140.3, 137.9, 130.0, 129.1, 128.5, 128.0, 125.5, 124.1, 52.7, 51.3, 46.2, 20.9, 20.8, 20.7, 20.4, 20.2; HRMS m/z (ESI) calcd. for $C_{19}H_{25}NNaO_5^+$ $(M+Na)^+$ 370.1625, found 370.1620.



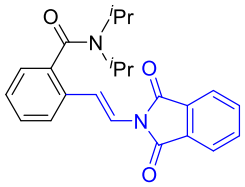
2-(2-(diisopropylcarbamoyl)phenyl)-1-phenylvinyl acetate (**3aj**): colorless solid; yield 69% (50.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.27 (td, *J* = 7.5, 0.9 Hz, 1H), 7.19 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.86 (s, 1H), 3.65 (hept, *J* = 6.6 Hz, 1H), 3.54 – 3.46 (m, 1H), 2.27 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 6H), 1.07 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 168.3, 147.5, 139.1, 135.3, 130.5, 130.0, 128.9, 128.8, 128.2, 128.1, 127.8, 125.3, 124.8, 113.4, 51.2, 46.0, 21.2, 20.8, 20.77, 20.7, 20.6; HRMS m/z (ESI) calcd. for $C_{23}H_{27}NNaO_3^+$ $(M+Na)^+$ 388.1883, found 388.1880.



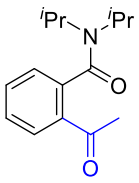
2-(2-(dimethylcarbamoyl)phenyl)-2-phenylvinyl acetate (**3bk**): colorless liquid; yield 23% (14.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.38 – 7.33 (m, 3H), 7.32 – 7.28 (m, 4H), 7.26 – 7.21 (m, 2H), 2.69 (s, 3H), 2.60 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 167.8, 137.3, 136.8, 136.2, 133.6, 131.0, 129.8, 129.1, 127.9, 127.8, 127.6, 127.1, 125.8, 38.8, 34.3, 20.9; HRMS m/z (ESI) calcd. for C19H19NNaO3+ (M+Na)+ 332.1257, found 332.1253.



N,*N*-dimethyl-2-(1-phenylvinyl)benzamide (**3bk'**): colorless solid; yield 59% (29.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.47 (m, 2H), 7.40 – 7.34 (m, 3H), 7.31 – 7.24 (m, 3H), 7.10 (s, 2H), 3.16 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 137.3, 136.1, 134.2, 131.4, 129.2, 128.8, 128.1, 127.8, 126.9, 126.7, 125.7, 125.4, 38.7, 34.9.

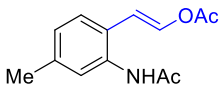


(*E*)-2-(2-(1,3-dioxoisoindolin-2-yl)vinyl)-*N*,*N*-diisopropylbenzamide (**3al**): yellow solid; mp 202-204 °C; yield 89% (66.9 mg; [CpRh]), 88% (66.3 mg; [Cp^{CF3}Rh]), 28% (21.2 mg; [Cp*Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.76 – 7.70 (m, 3H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 15.0 Hz, 1H), 7.33 (td, *J* = 7.7, 1.1 Hz, 1H), 7.27 (td, *J* = 7.4, 1.0 Hz, 1H), 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 3.68 (hept, *J* = 6.7 Hz, 1H), 3.55 (hept, *J* = 6.8 Hz, 1H), 1.72 (d, *J* = 6.8 Hz, 3H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 166.3, 138.3, 134.7, 132.2, 131.8, 128.5, 127.9, 125.6, 124.7, 123.8, 119.2, 116.9, 51.2, 46.1, 20.92, 20.9, 20.8, 20.5; HRMS m/z (ESI) calcd. for $C_{23}H_{24}N_2NaO_3^+$ $(M+Na)^+$ 399.1679, found 399.1674.



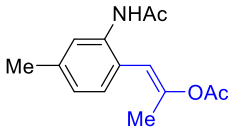
2-acetyl-*N*,*N*-diisopropylbenzamide (**3am'**): colorless solid; mp 112-114 °C; yield 45% (22.2 mg; [Cp^{CF3}Rh]), 29% (14.2 mg; [Cp*Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.51 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (td, *J* = 7.7, 1.3 Hz, 1H), 7.21 (dd, *J* = 7.5, 0.9 Hz, 1H), 3.58 – 3.46 (m, 2H), 2.59 (s, 3H), 1.58 (d, *J* = 6.3 Hz, 6H), 1.11 (d, *J* = 5.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 170.5, 139.5, 135.1, 132.4, 129.6, 128.2, 126.6, 51.2, 45.8, 28.0, 20.4; HRMS m/z (ESI) calcd. for $C_{15}H_{21}NNaO_2^+$ $(M+Na)^+$ 270.1465, found 270.1463.

General Procedures for the Arylation of Electron-Rich Alkenes with Acetanilides. To a 15 mL Schlenk tube, acetanilide derivative **4** (0.2 mmol), alkene **2** (2.0 mmol), $[CpRhI_2]_n$ or $[Cp^{CF3}RhCl_2]_2$ (5 mol% of [Rh]), $AgSbF_6$ (10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (0.3 or 1.1 equiv) and THF (1.0 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography to afford the product **5** (PE:EA = 2:1-1:2).

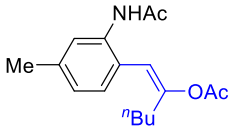


(*E*)-2-acetamido-4-methylstyryl acetate (**5ba**): colorless solid; yield 81% (37.9 mg; [CpRh]), 88% (41.0 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, DMSO)

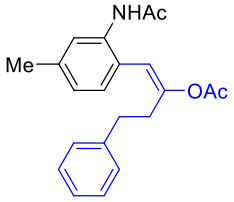
δ 9.44 (s, 1H), 7.70 (d, *J* = 12.7 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.23 (s, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 12.7 Hz, 1H), 2.26 (s, 3H), 2.19 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 168.5, 167.8, 137.0, 136.4, 135.2, 126.6, 126.3, 125.5, 125.2, 111.2, 23.2, 20.7, 20.4.



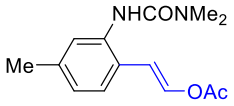
(*E*)-1-(2-acetamido-4-methylphenyl)prop-1-en-2-yl acetate (**5bf**): colorless liquid; yield 79% (39.1 mg; [CpRh]), 66% (32.6 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, DMSO) δ 9.14 (s, 1H), 7.41 (s, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.21 (s, 1H), 2.28 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 169.1, 168.1, 147.8, 136.9, 136.0, 129.1, 125.3, 125.0, 114.7, 23.3, 20.7, 16.6; HRMS m/z (ESI) calcd. for $C_{14}H_{17}NNaO_3^+$ $(M+Na)^+$ 270.1101, found 270.1094.



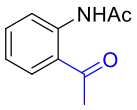
(*E*)-1-(2-acetamido-4-methylphenyl)hex-1-en-2-yl acetate (**5bg**): colorless liquid; yield 60% (34.7 mg; [CpRh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.07 (s, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 5.96 (s, 1H), 2.35 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H), 2.06 (t, *J* = 7.5 Hz, 2H), 1.38 – 1.31 (m, 2H), 1.25 – 1.19 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 168.9, 153.5, 138.7, 136.4, 128.8, 124.2, 120.9, 120.8, 115.1, 29.7, 28.5, 24.7, 22.2, 21.7, 21.0, 13.8; HRMS m/z (ESI) calcd. for $C_{17}H_{23}NNaO_3^+$ $(M+Na)^+$ 312.1570, found 312.1566.



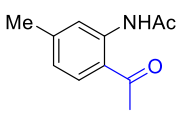
(*E*)-1-(2-acetamido-4-methylphenyl)-4-phenylbut-1-en-2-yl acetate (**5bh**): colorless liquid; yield 66% (44.6 mg; [CpRh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.82 (s, 1H), 7.25 – 7.22 (m, 2H), 7.20 – 7.17 (m, 1H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.96 (s, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 168.8, 152.1, 140.3, 138.7, 136.2, 128.8, 128.6, 128.5, 126.3, 124.3, 120.9, 120.8, 116.0, 32.5, 31.5, 24.7, 21.7, 21.0; HRMS m/z (ESI) calcd. for $C_{21}H_{23}NNaO_3^+$ $(M+Na)^+$ 360.1570, found 360.1564.



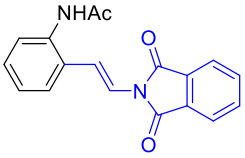
(*E*)-2-(3, 3-dimethylureido)-4-methylstyryl acetate (**5ca**): colorless solid; mp 147-149 °C; yield 55% (28.9 mg; [CpRh]), 55% (28.9 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, DMSO) δ 7.91 (s, 1H), 7.67 (d, *J* = 12.8 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.01 (s, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.45 (d, *J* = 12.8 Hz, 1H), 2.91 (s, 6H), 2.25 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 168.0, 156.6, 137.0, 136.8, 135.9, 128.1, 126.9, 126.0, 125.4, 111.9, 36.2, 20.6, 20.5; HRMS m/z (ESI) calcd. for $C_{14}H_{18}N_2NaO_3^+$ $(M+Na)^+$ 285.1210, found 285.1205.



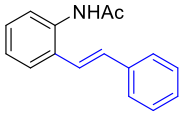
N-(2-acetylphenyl)acetamide (**5am'**): colorless solid; mp 74-76 °C; yield 39% (13.8 mg; [CpRh]), 77% (27.3 mg; [Cp^{CF3}Rh]); ^{1}H NMR (400 MHz, CDCl3) δ 11.69 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.13 – 7.07 (m, 1H), 2.65 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 202.9, 169.6, 141.1, 135.2, 131.7, 122.4, 121.8, 120.8, 28.7, 25.7.



N-(2-acetyl-5-methylphenyl)acetamide (**5bm'**): colorless solid; mp 74-76 °C; yield 54% (20.8 mg; [CpRh]), 90% (34.3 mg; [Cp^{CF3}Rh]), 36% (13.7 mg; [Cp*Rh]); ^{1}H NMR (400 MHz, CDCl3) δ 11.73 (s, 1H), 8.55 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 2.60 (s, 3H), 2.37 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 202.4, 169.5, 146.6, 141.2, 131.8, 123.3, 120.9, 119.4, 28.5, 25.7, 22.2; HRMS m/z (ESI) calcd. for $C_{11}H_{13}NNaO_2^+$ $(M+Na)^+$ 214.0838, found 214.0839.

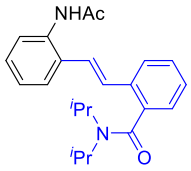


N-(2-(2-(1,3-dioxoisoindolin-2-yl)vinyl)phenyl)acetamide (**5al**): yellow solid; mp 245-247 °C; yield 67% (41.1 mg; [CpRh]), 72% (44.2 mg; [Cp^{CF3}Rh]), 24% (14.7 mg; [Cp^{*}Rh]); ^{1}H NMR (500 MHz, DMSO) δ 9.64 (s, 1H), 7.94 (dt, *J* = 6.9, 3.5 Hz, 2H), 7.90 (dt, *J* = 6.9, 3.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 15.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 168.6, 166.2, 135.5, 135.1, 131.3, 131.1, 127.8, 127.0, 126.1, 125.1, 123.6, 118.7, 116.0, 23.1; HRMS m/z (ESI) calcd. for $C_{18}H_{14}N_2NaO_3^+$ $(M+Na)^+$ 329.0897, found 329.0894.



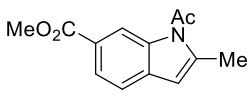
(*E*)-*N*-(2-styrylphenyl)acetamide (**6ak**): colorless solid; yield 72% (34.2 mg; [CpRh]), 12% (5.6 mg; [Cp^{*}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.29 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 16.2 Hz, 1H), 6.99 (d, *J* = 16.1 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 137.2, 134.9, 132.8, 130.5, 128.9, 128.5, 128.3, 127.1, 126.9, 125.7, 124.4, 123.7, 24.4.

Procedure for the Synthesis of 1,2-Diarylethene 7. To a 15 mL Schlenk tube, **3aa** (0.2 mmol), acetanilide derivative **4a** (0.6 mmol), $[CpRhI_2]_n$ (5 mol% of [Rh]), $AgSbF_6$ (10 mol%), $Cu(OAc)_2·H_2O$ (0.3 equiv) and THF (1.0 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography to afford the product **7** (PE:EA = 1:2).



(*E*)-2-(2-acetamidostyryl)-*N*,*N*-diisopropylbenzamide (**7**): colorless solid; mp 192-194 °C; yield 58% (42.2 mg; [CpRh]), 55% (40.1 mg; [Cp^{CF3}Rh]); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.11 (d, *J* = 12.7 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.05 (t, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 16.2 Hz, 1H), 3.67 – 3.58 (m, 1H), 3.56 – 3.48 (m, 1H), 2.24 (s, 3H), 1.60 (d, *J* = 6.7 Hz, 6H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 169.3, 137.6, 135.4, 133.6, 130.1, 128.6, 128.5, 128.4, 127.9, 126.4, 126.3, 126.2, 125.4, 125.3, 124.7, 51.3, 46.1, 24.3, 20.9, 20.8, 20.7, 20.6; HRMS m/z (ESI) calcd. for $C_{23}H_{28}N_2NaO_2^+$ $(M+Na)^+$ 387.2043, found 387.2039.

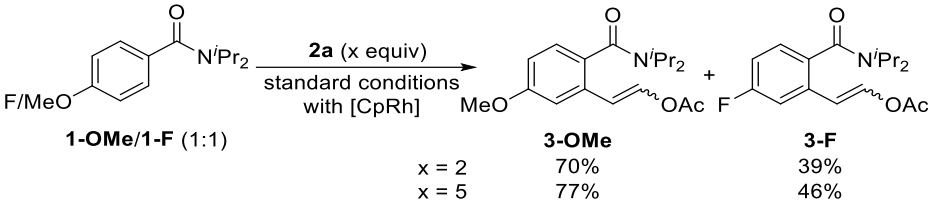
Procedure for the Synthesis of *N*-Acylindoles 8. To a 15 mL Schlenk tube, acetanilide derivative **4d** (0.2 mmol), alkene **2f** (2.0 mmol), $[CpRhI_2]_n$ (5 mol% of [Rh]), $AgNTf_2$ (10 mol%), $Cu(OAc)_2·H_2O$ (1.1 equiv) and THF (1.0 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was filtrated through a short pad of Al_2O_3 to remove the inorganic salts and the filtrate was concentrated under vacuum. Then, $FeCl_3$ (10 mol %) and MeCN (1.0 mL) were added under air and the reaction mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography to afford the product **8** (PE:EA = 4:1).



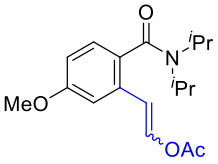
methyl 1-acetyl-2-methyl-1*H*-indole-6-carboxylate (**8**):[10a] colorless solid; yield 69% (32.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.90 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 6.38 (s, 1H), 3.92 (s, 3H), 2.76 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 167.8, 141.2, 136.0, 133.8, 125.3, 124.5, 119.5, 116.8, 109.6, 52.2, 27.5, 17.8.

5) Mechanistic Studies

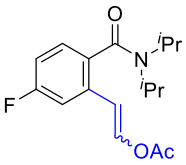
Competition Experiments



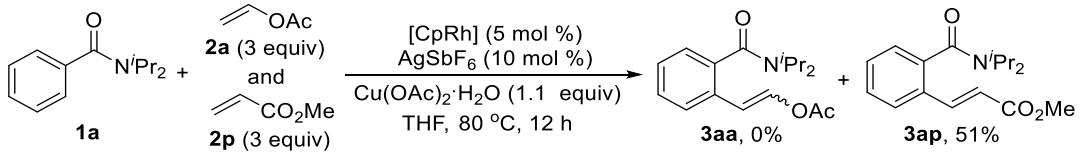
To a 15 mL Schlenk tube, benzamide **1-OMe** (0.2 mmol), benzamide **1-F** (0.2 mmol), vinyl acetate **2a** (0.4 mmol or 1.0 mmol), $[CpRhI_2]_n$ (5 mol% of [Rh]), $AgSbF_6$ (10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (1.1 equiv), and THF (1 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography to afford the products **3-OMe** and **3-F** (PE/EA = 4:1).



2-(diisopropylcarbamoyl)-5-methoxystyryl acetate (**3-OMe**): colorless liquid; yield 70% (44.7 mg, 1 equiv of **2a**), 77% (49.2 mg, 2.5 equiv of **2a**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 12.7 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 0.13H), 7.30 (d, *J* = 7.4 Hz, 0.13H), 7.06 (d, *J* = 7.3 Hz, 0.13H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 0.13H), 6.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.40 (d, *J* = 12.7 Hz, 1H), 5.74 (d, *J* = 7.4 Hz, 0.13H), 3.81 (s, 0.39H), 3.80 (s, 3H), 3.66 – 3.59 (m, 1.13H), 3.51 – 3.44 (m, 1.13H), 2.24 (s, 0.39H), 2.16 (s, 3H), 1.57 (d, *J* = 6.3 Hz, 3.39H), 1.53 (d, *J* = 6.3 Hz, 3.39H), 1.06 (d, *J* = 6.9 Hz, 3.39H), 1.04 (d, *J* = 6.1 Hz, 3.39H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 170.0, 167.9, 167.1, 159.5, 159.1, 137.6, 135.0, 131.9, 131.4, 131.3, 130.7, 126.8, 126.2, 115.1, 113.5, 113.1, 112.5, 110.5, 108.3, 77.4, 77.2, 76.9, 55.4, 55.2, 51.0, 45.9, 20.8, 20.7; HRMS m/z (ESI) calcd. for $C_{18}H_{25}NNaO_4^+$ $(M+Na)^+$ 342.1676, found 342.1673.

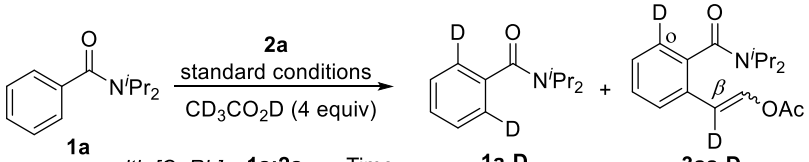


2-(diisopropylcarbamoyl)-5-fluorostyryl acetate (**3-F**): colorless solid; yield 39% (24.1 mg, 1 equiv of **2a**), 46% (28.4 mg, 2.5 equiv of **2a**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 12.7 Hz, 1H), 7.67 (dd, *J* = 10.8, 2.4 Hz, 0.08H), 7.35 (d, *J* = 7.4 Hz, 0.08H), 7.14 (dd, *J* = 10.1, 2.4 Hz, 1H), 7.10 (dd, *J* = 8.4, 5.8 Hz, 1.08H), 6.96 (d, *J* = 2.5 Hz, 0.08H), 6.93 (td, *J* = 8.3, 2.4 Hz, 1H), 6.38 (d, *J* = 12.9 Hz, 1H), 5.73 (d, *J* = 7.4 Hz, 0.08H), 3.62 – 3.53 (m, 1.08H), 3.54 – 3.45 (m, 1.08H), 2.26 (s, 0.24H), 2.17 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3.24H), 1.54 (d, *J* = 6.7 Hz, 3.24H), 1.08 (d, *J* = 6.7 Hz, 3.24H), 1.05 (d, *J* = 6.7 Hz, 3.24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 169.3, 167.8, 167.1, 162.5 (d, *J* = 247.0 Hz), 138.4, 135.9, 133.9 (d, *J* = 3.3 Hz), 133.1 (d, *J* = 8.1 Hz), 127.4 (d, *J* = 8.6 Hz), 126.7 (d, *J* = 8.6 Hz), 116.6 (d, *J* = 23.4 Hz), 114.6 (d, *J* = 21.9 Hz), 112.3 (d, *J* = 22.6 Hz), 111.7 (d, *J* = 2.3 Hz), 107.3 (d, *J* = 2.0 Hz), 51.1, 46.1, 20.9, 20.71, 20.68, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.76, -112.72; HRMS m/z (ESI) calcd. for $C_{17}H_{22}FNNaO_3^+$ $(M+Na)^+$ 330.1476, found 330.1469.



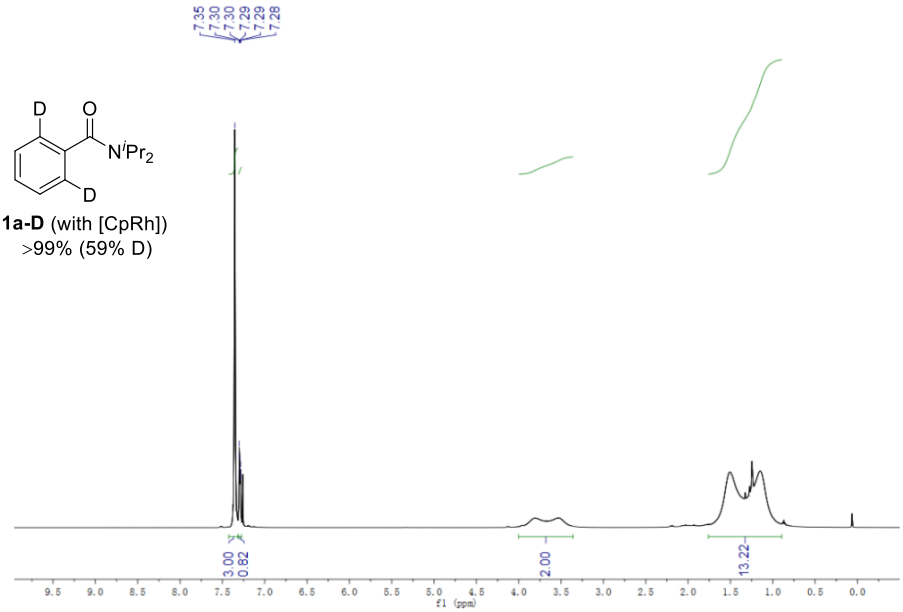
To a 15 mL Schlenk tube, benzamide **1a** (0.2 mmol), vinyl acetate **2a** (0.6 mmol), methyl acrylate **2p** (0.6 mmol), $[CpRhI_2]_n$ (5 mol% of [Rh]), $AgSbF_6$ (10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (1.1 equiv), and THF (1 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography to afford the product **3ap** (PE/EA = 5:1).

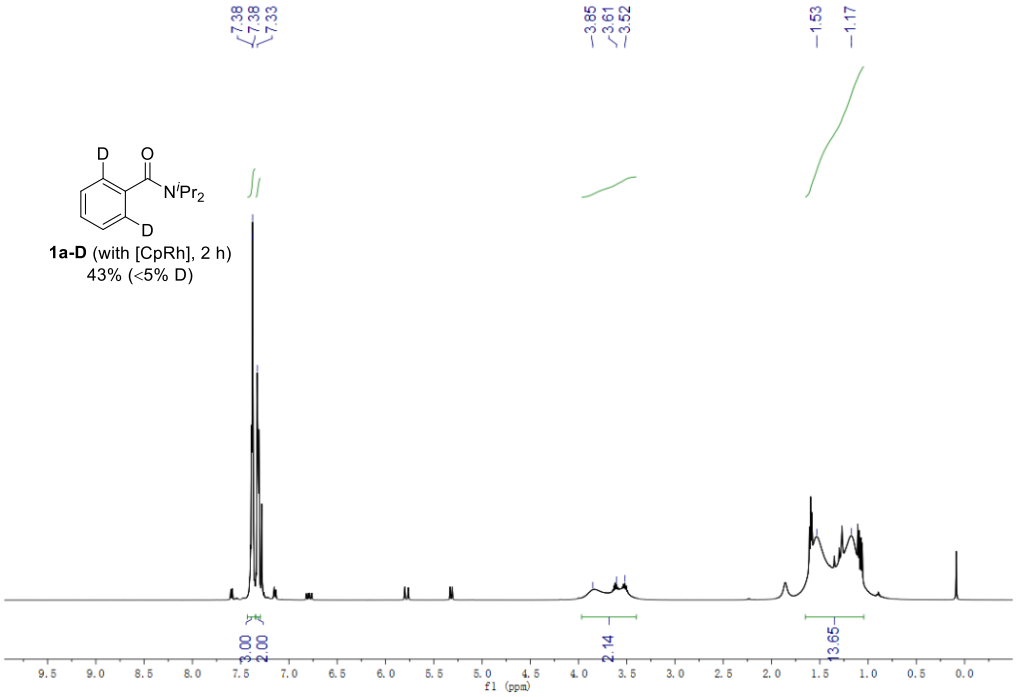
Ortho Deuteration Experiments



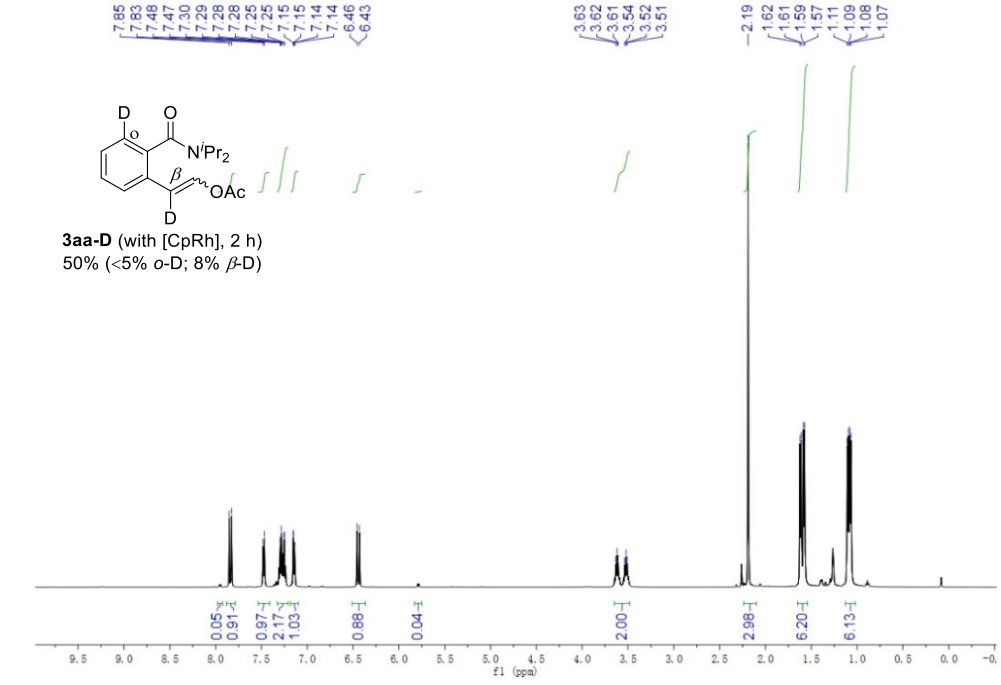
	1a:2a	Time	1a-D	3aa-D
with [CpRh]:	1:0	6 h	>99% (59% D)	-
	1:2	2 h	43% (<5% D)	50% (<5% *o*-D; 8% *β*-D)
		6 h	-	87% (10% *o*-D; 26% *β*-D)
*with [Cp*Rh]:*	1:2	6 h	90% (22% D)	8% (25% *o*-D; 31% *β*-D)
		12 h	82% (31% D)	16% (26% *o*-D; 38% *β*-D)

To a 15 mL Schlenk tube, benzamide **1a** (0.2 mmol), vinyl acetate **2a** (0 mmol or 0.4 mmol), $[CpRhI_2]_n$ or $[Cp^*RhCl_2]_2$ (5 mol% of [Rh]), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (1.1 equiv), CD_3CO_2D (4 equiv) and THF (1 mL) were added under air. Then the tube was sealed with a Teflon lined cap, and the mixture was stirred at 80 °C. After cooling to room temperature, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography to afford the products **1a-D** and **3aa-D** (PE/EA = 5:1-4:1).

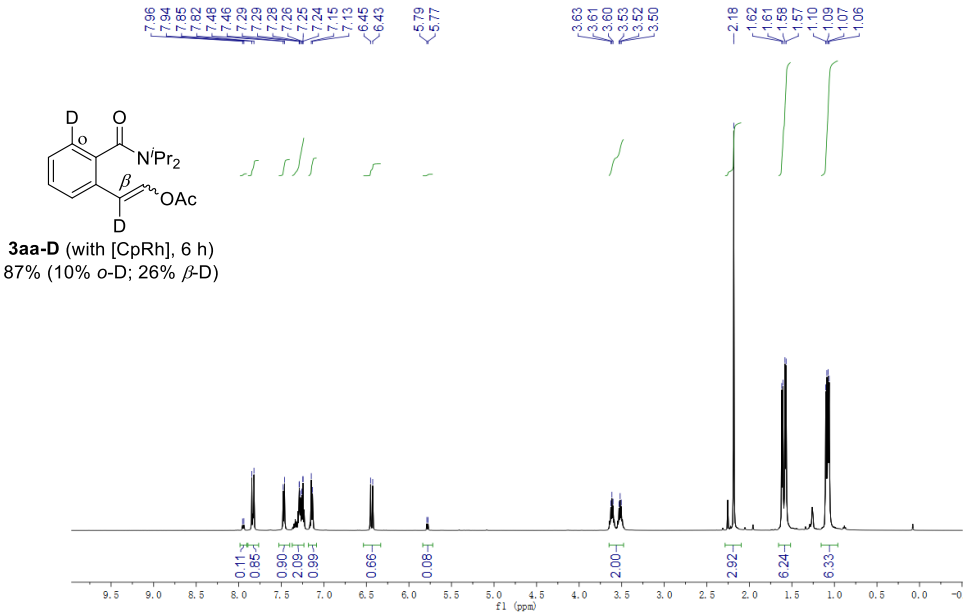




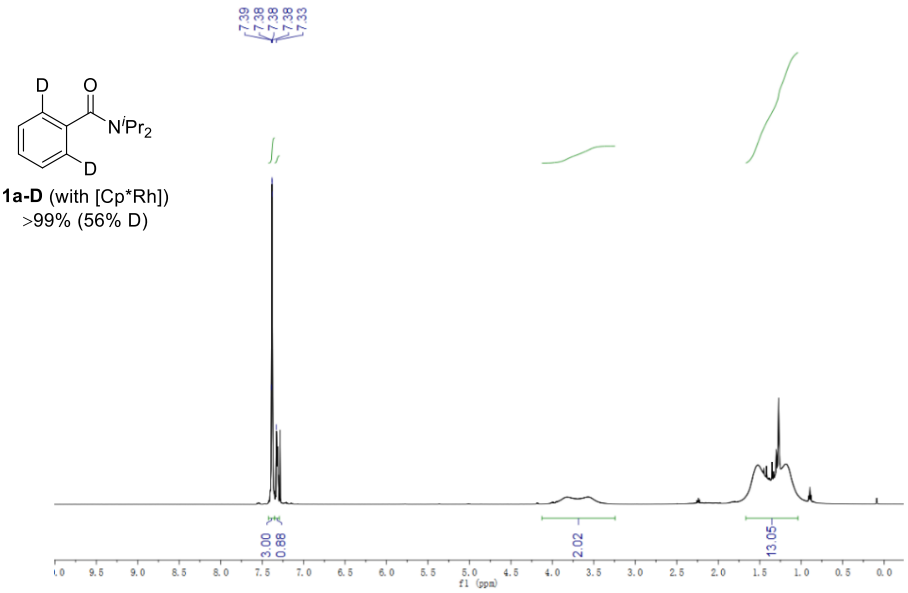
1a-D (with [CpRh], 2 h)
43% (<5% D)



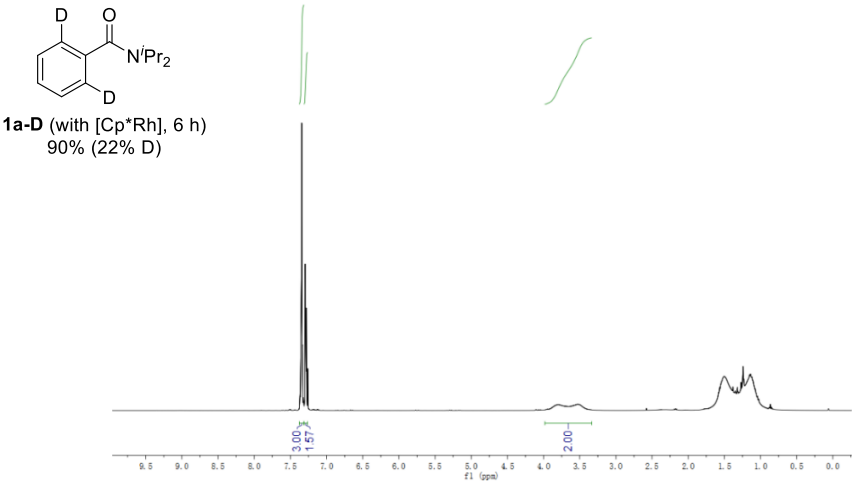
3aa-D (with [CpRh], 2 h)
50% (<5% *o*-D; 8% *β*-D)



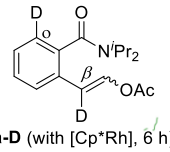
3aa-D (with [CpRh], 6 h)
87% (10% *o*-D; 26% *β*-D)



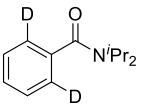
1a-D (with [Cp*Rh])
>99% (56% D)



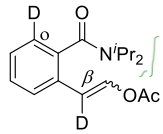
1a-D (with [Cp*Rh], 6 h)
90% (22% D)



3aa-D (with [Cp*Rh], 6 h)
8% (25% *o*-D; 31% *β*-D)

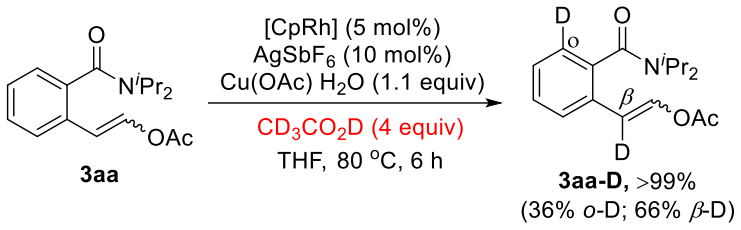


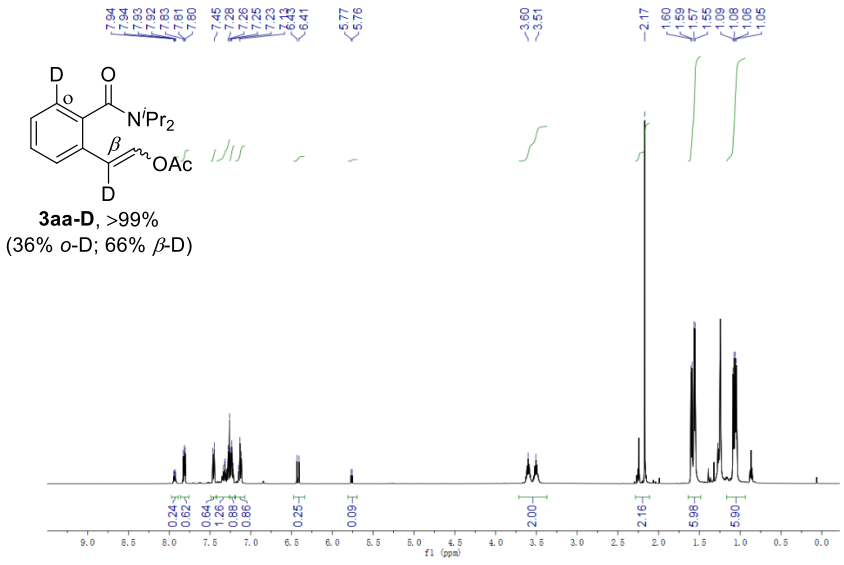
1a-D (with [Cp*Rh], 12 h)
82% (31% D)

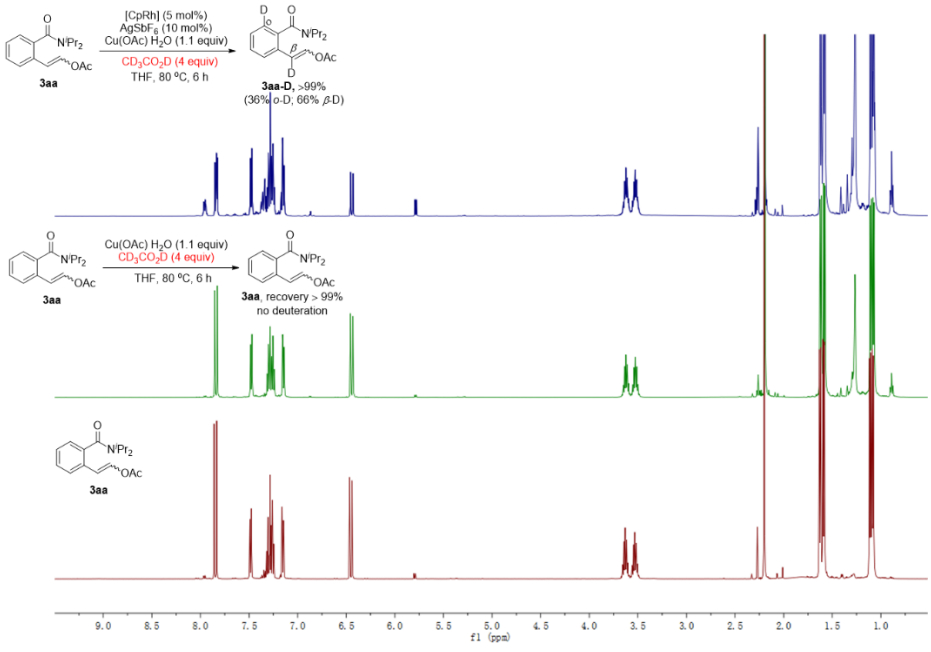


3aa-D (with [Cp*Rh], 12 h)
16% (26% *o*-D; 38% *β*-D)

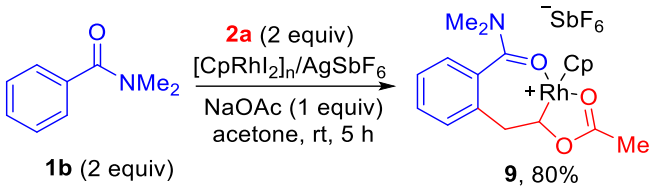
Treatment of **3aa** with CD_3CO_2D under standard reaction conditions for 6 h also afforded the corresponding **3aa-D** with 66% deuterium incorporation at *β*-position and 36% deuterium incorporation at *o*-position. In addition, treatment of **3aa** with CD_3CO_2D in the presence of $Cu(OAc)_2$ for 6 h gave **3aa** with no deuteration. These results indicated that the H/D exchange at *β*-position of **3aa** may proceed via a carbonyl-directed C-H rhodation/protonation process. For ^1H NMR spectra, see below.



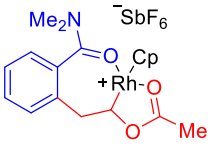




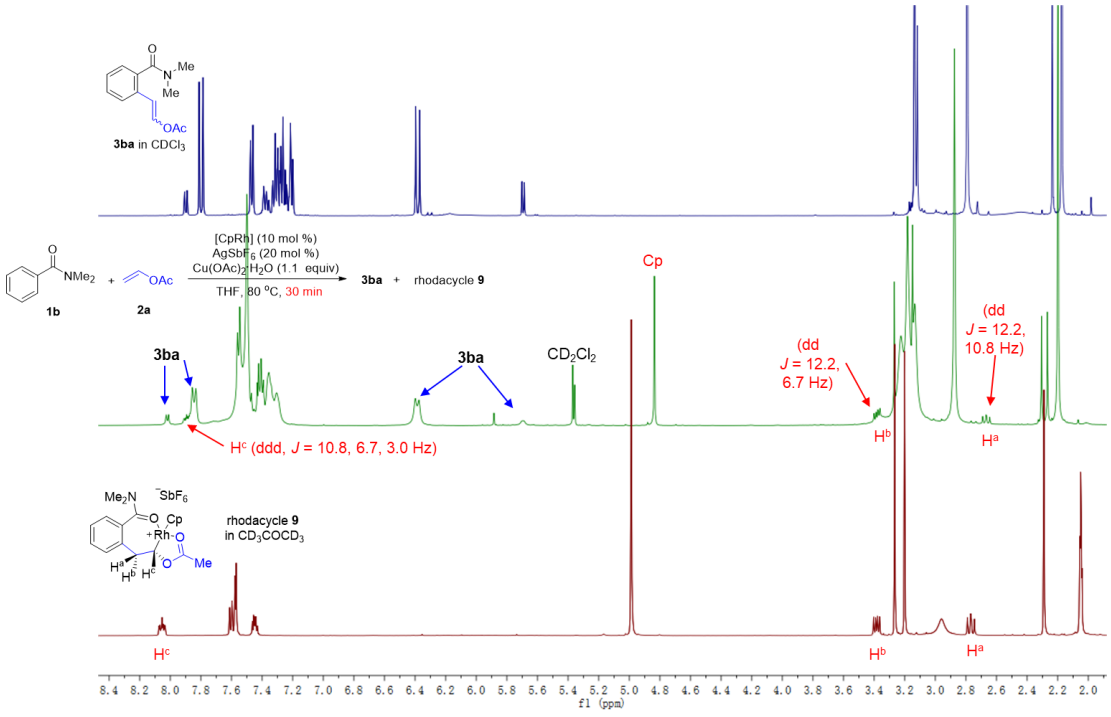
Preparation of Rhodacycle Intermediate 9



To a 25 mL Schlenk tube, $[CpRhI_2]_n$ (84.4 mg, 0.2 mmol of [Rh]), benzamide **1b** (59.6 mg, 0.4 mmol), $AgSbF_6$ (171.9 mg, 0.5 mmol), NaOAc (16.4 mg, 0.2 mmol), vinyl acetate **2a** (34.4 mg, 0.4 mmol) and acetone (5 mL) were added under argon atmonsphere. The reaction mixture was stirred at room temperature for 5 hours. After removing the solvent in vacuo, the residue was dissolved in 5 mL of DCM. The resulting solution was filetered through a pad of Celite and washed with DCM (3*1 mL). The filtrate was concentrated in vacuo to a small volume and diluted with ethyl ether (4 mL) to form a precipitate. The precipitate was collected, washed with ethyl ether (4*4 mL), and dried under vacuum to give complex **9**.



rhodacycle **9**: yellow solid; yield 80% (101.3 mg); ^{1}H NMR (500 MHz, acetone-d6) δ 8.05 (ddd, *J* = 10.1, 6.8, 3.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 4.0 Hz, 2H), 7.48 – 7.42 (m, 1H), 4.99 (s, 5H), 3.38 (dd, *J* = 12.5, 6.8 Hz, 1H), 3.27 (s, 3H), 3.20 (s, 3H), 2.77 (dd, *J* = 12.2, 10.8 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, acetone-d6) δ 186.8, 176.8, 139.4, 135.2, 132.3, 131.5, 128.6, 127.7, 97.5 (d, *J* = 25.6 Hz), 85.1 (d, *J* = 7.0 Hz), 42.1, 40.3, 36.9, 18.5.



6) References

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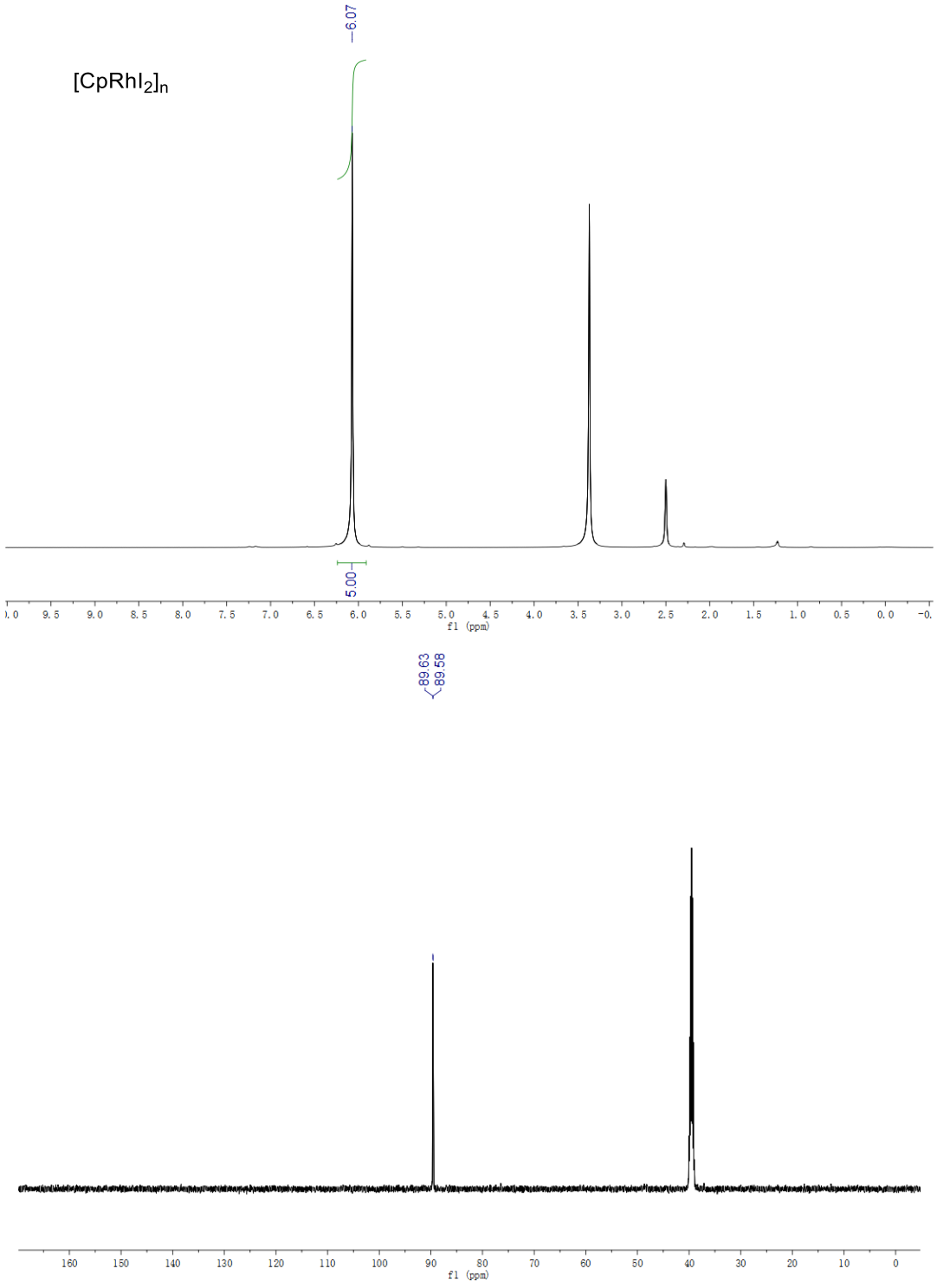
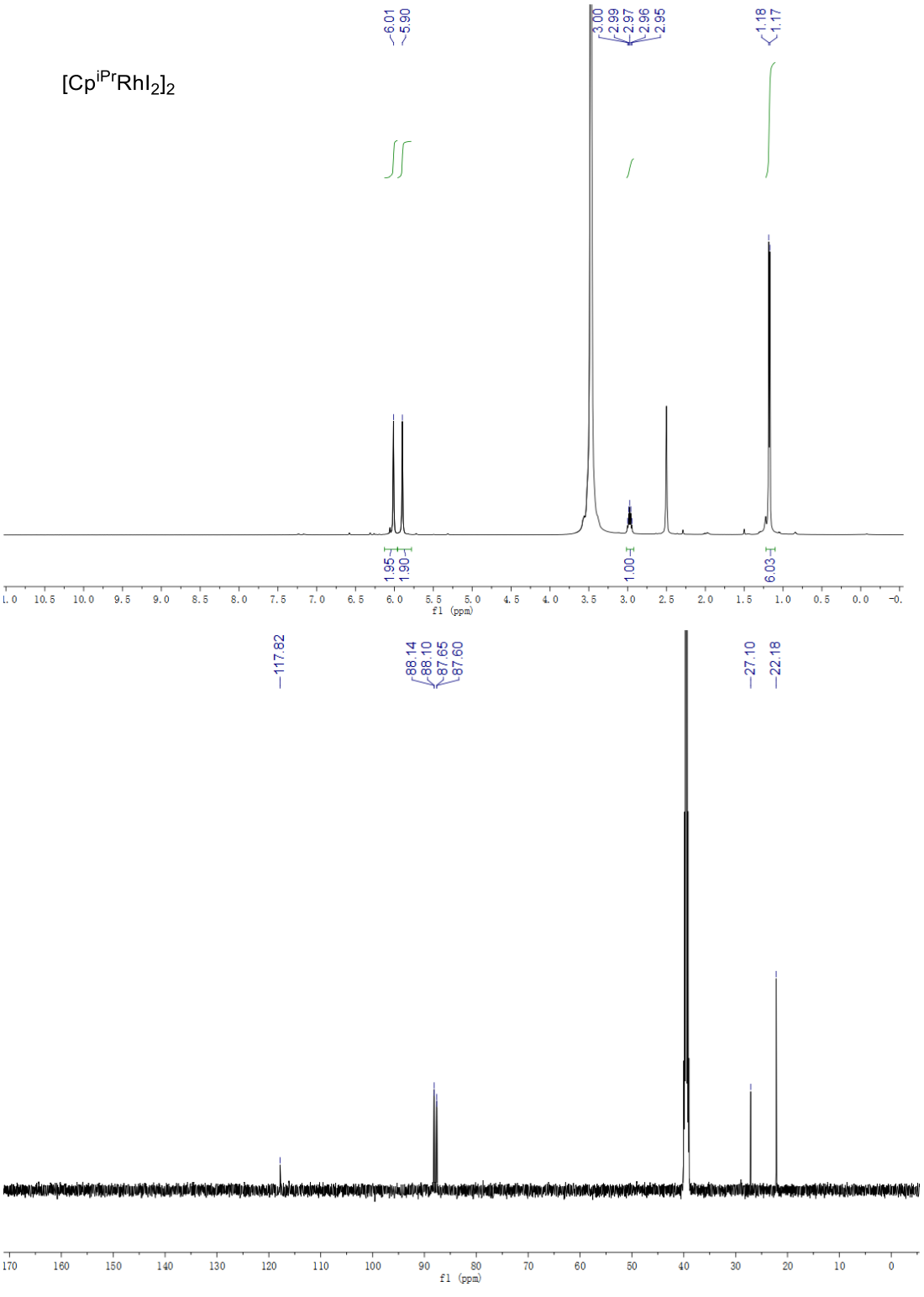
7) ^{1}H, ^{13}C and ^{19}F NMR Spectra



$[Cp^{iPr}RhI_2]_2$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1.95
1.90
1.00
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f1 (ppm)
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88.14
88.10
87.65
87.60
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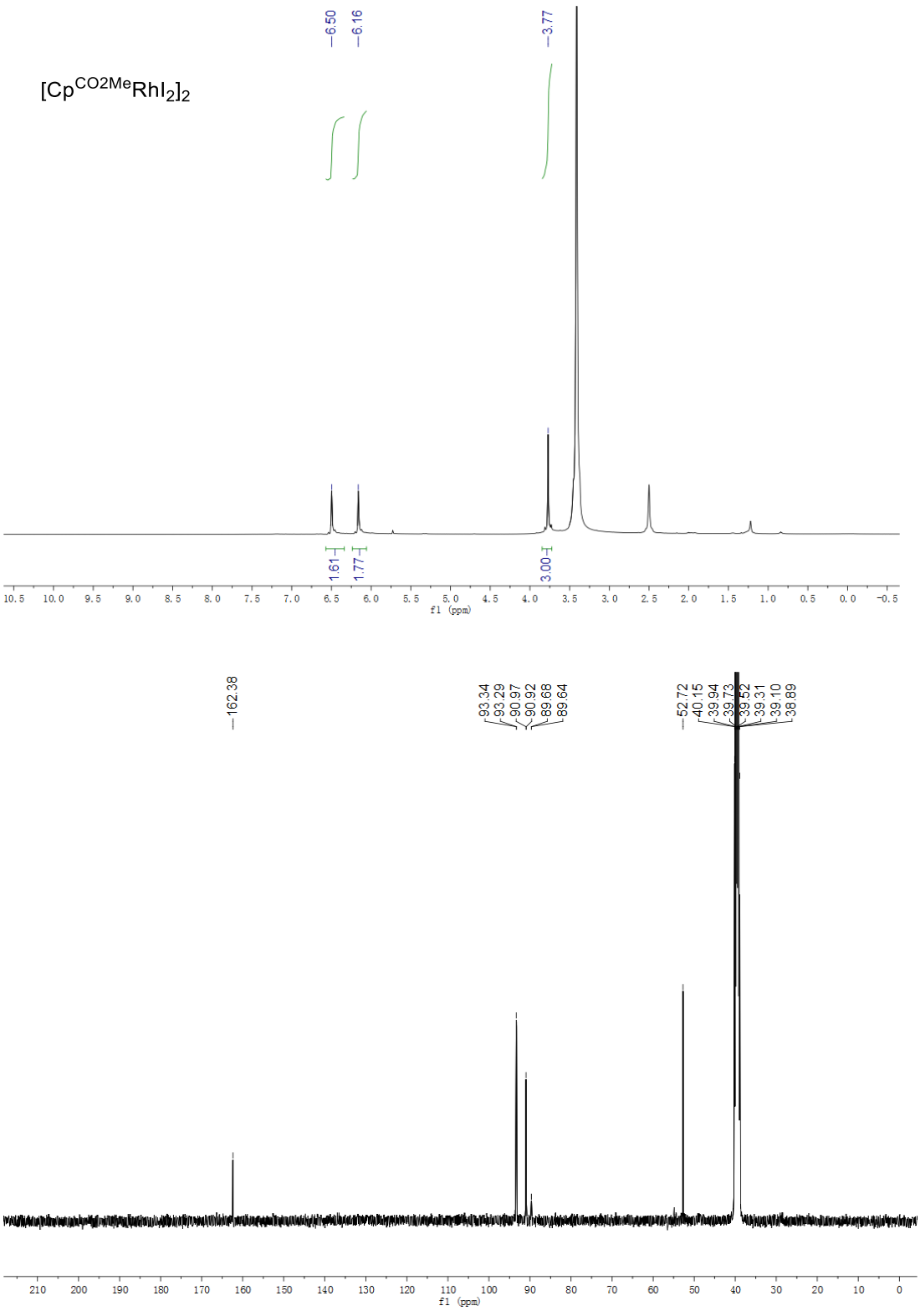
f1 (ppm)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f1 (ppm)
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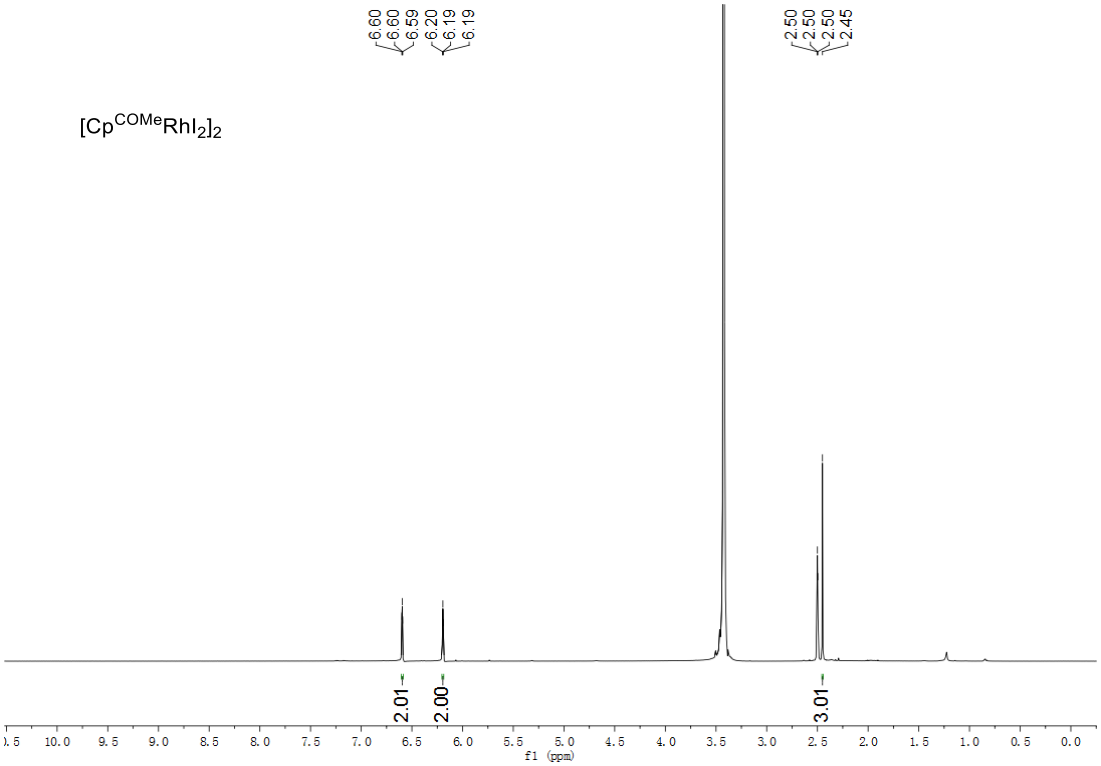
93.34
93.29
90.97
90.92
89.68
89.64
52.72
40.15
39.94
39.73
39.52
39.31
39.10
38.89
f1 (ppm)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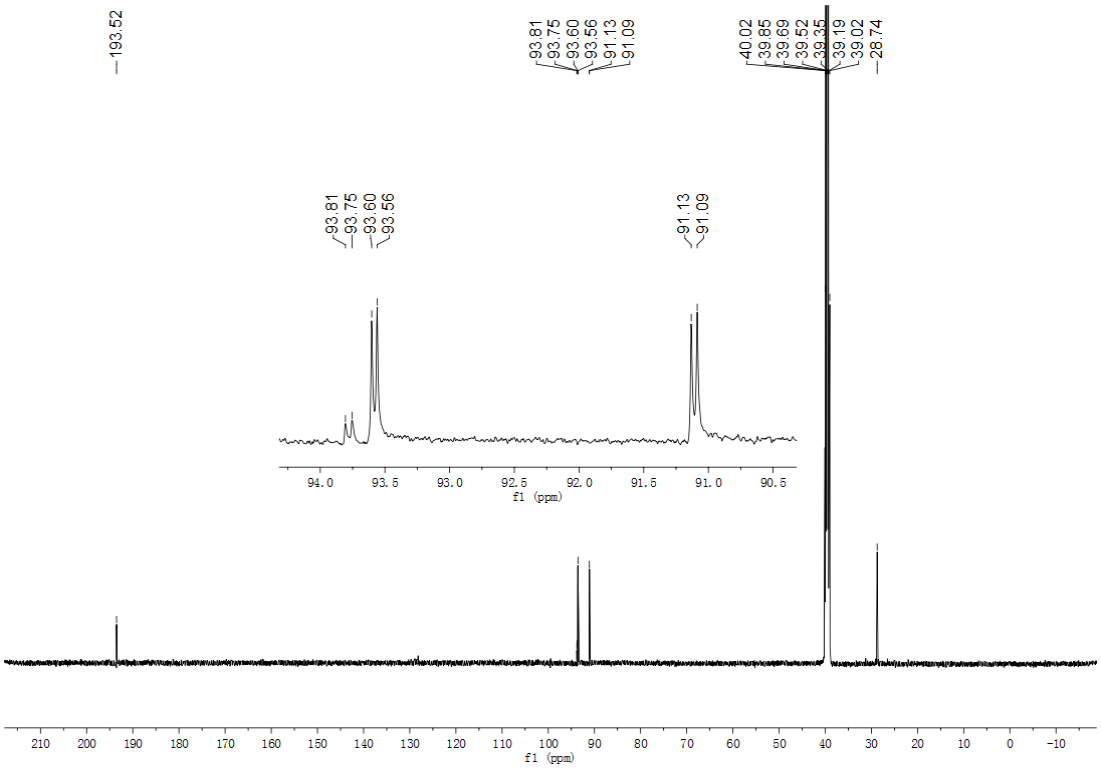
3.01
f1 (ppm)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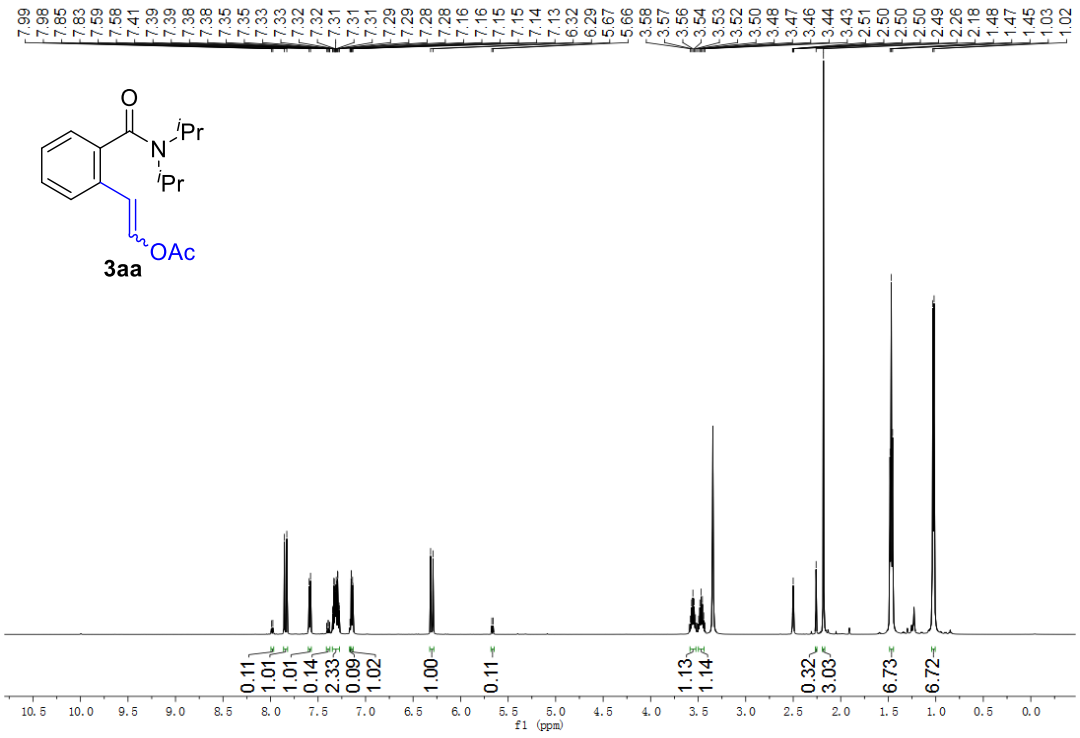
f1 (ppm)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N
iPr
iPr
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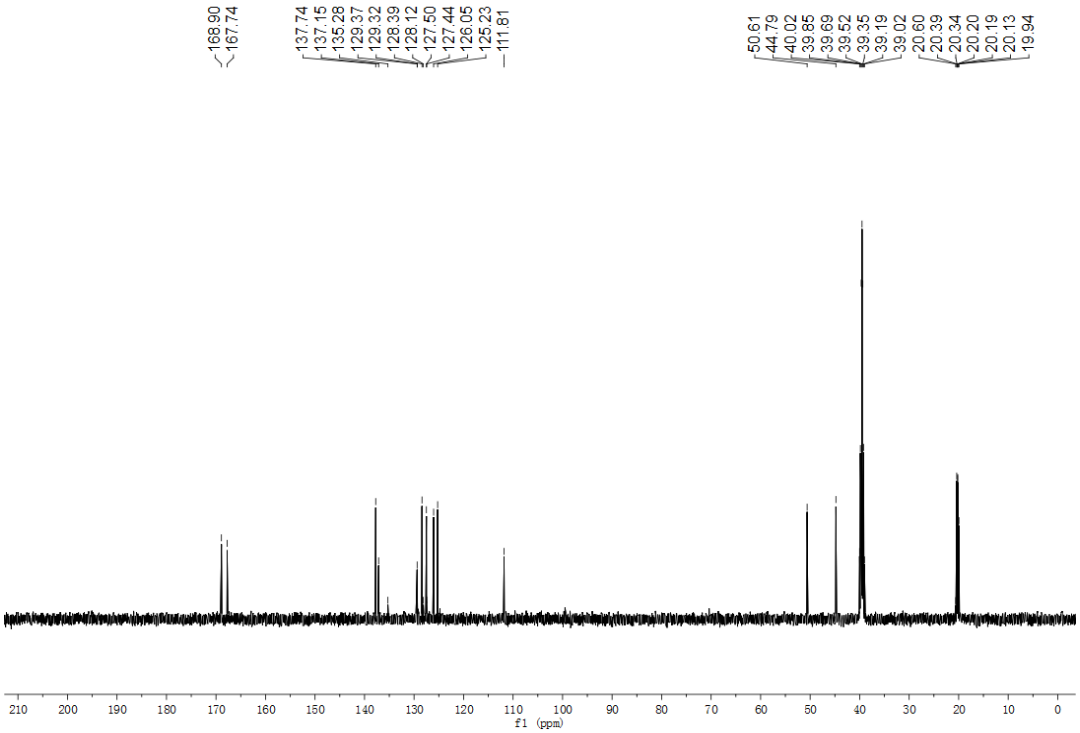
f1 (ppm)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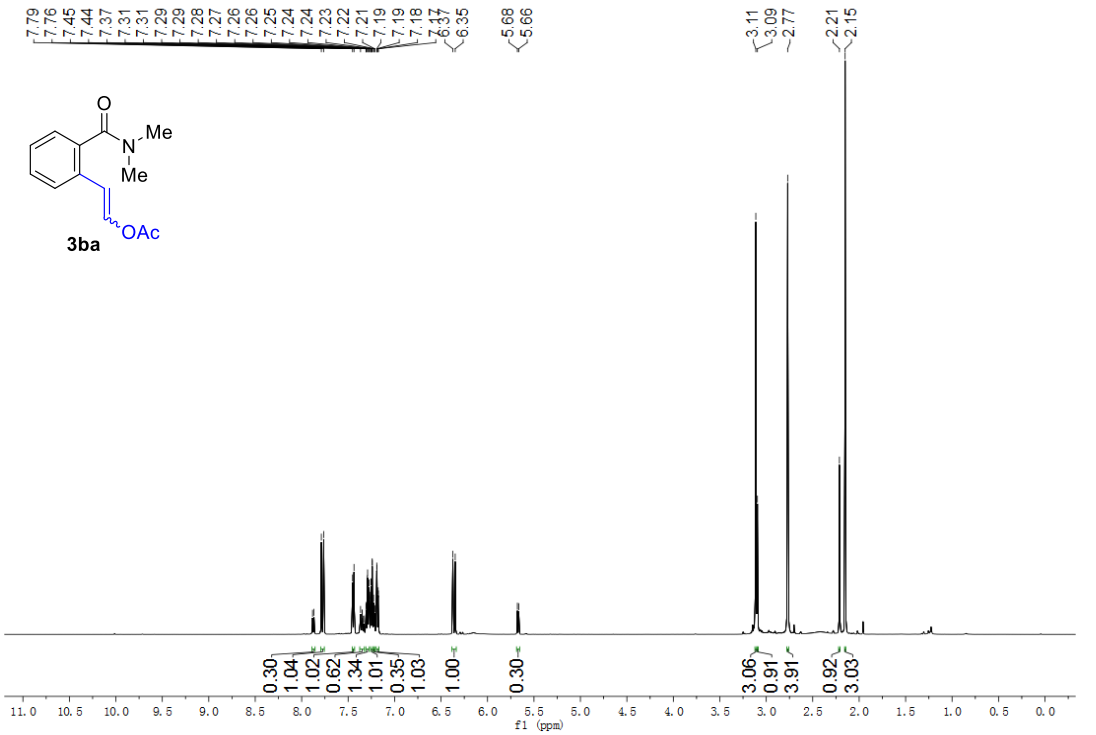
f1 (ppm)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7.19
7.19
7.18
7.17
6.37
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2.15
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Me
Me
OAc
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1.02
0.62
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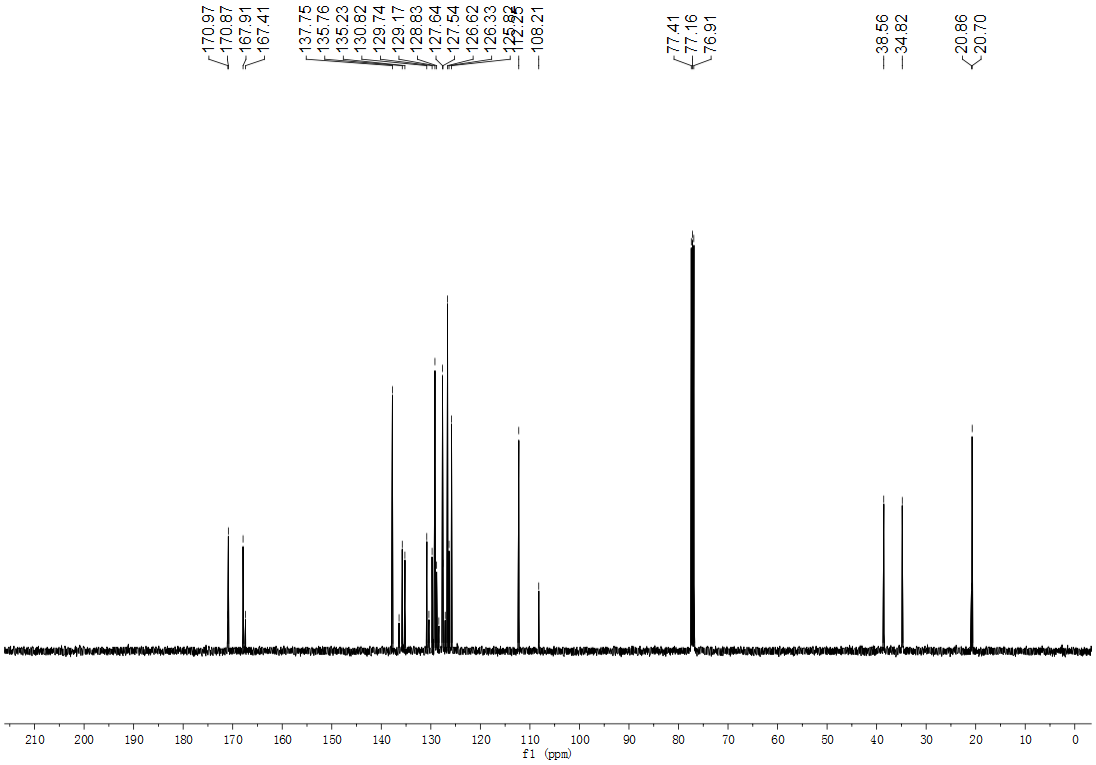
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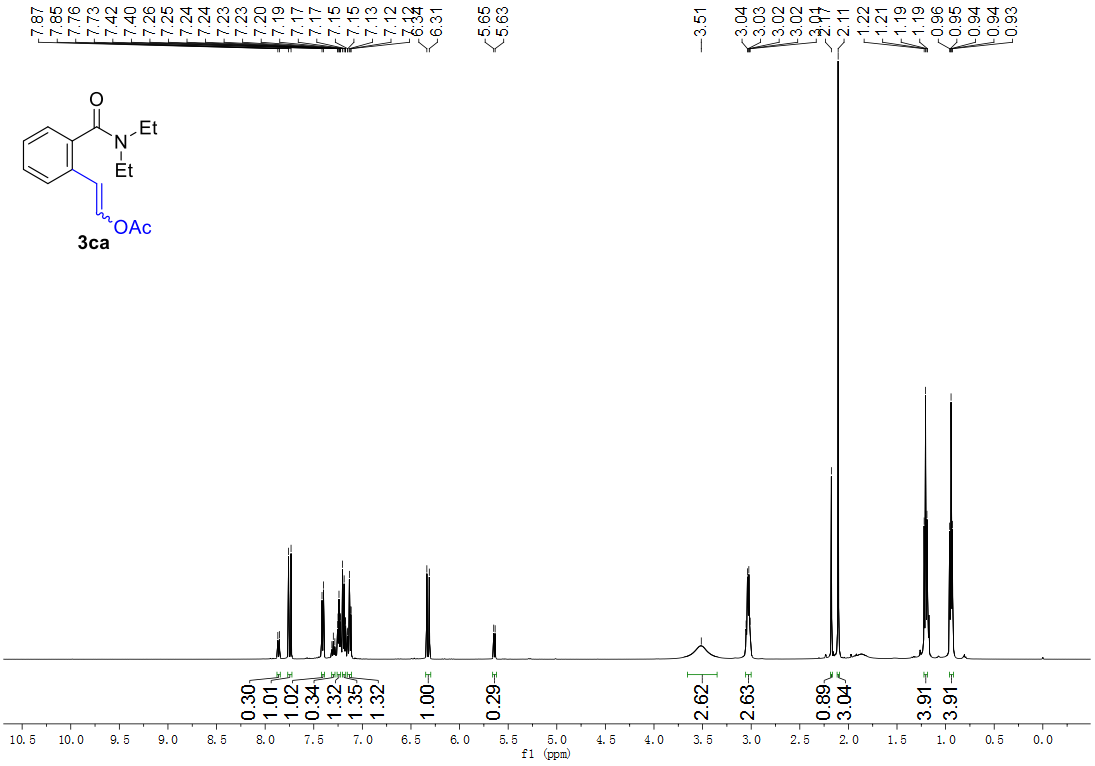
20.70
f1 (ppm)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7.12
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6.31
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5.63
3.51
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3.03
3.02
3.01
2.17
2.11
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1.21
1.19
1.19
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0.95
0.94
0.94
0.93
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Et
Et
OAc
3ca
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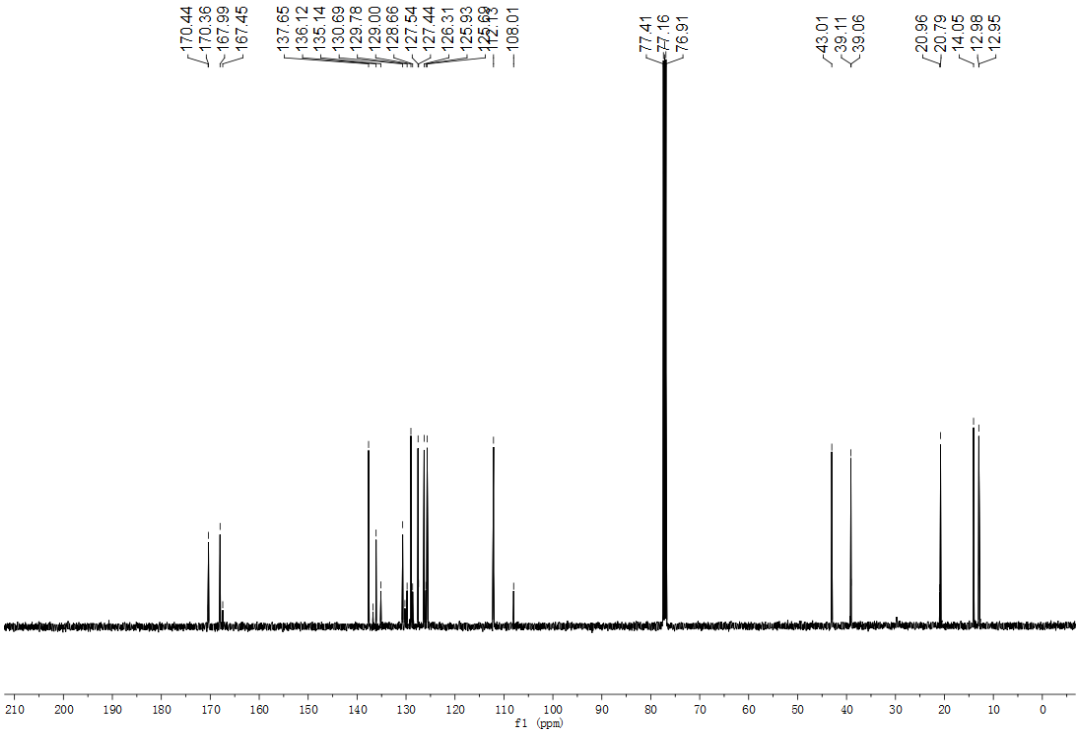
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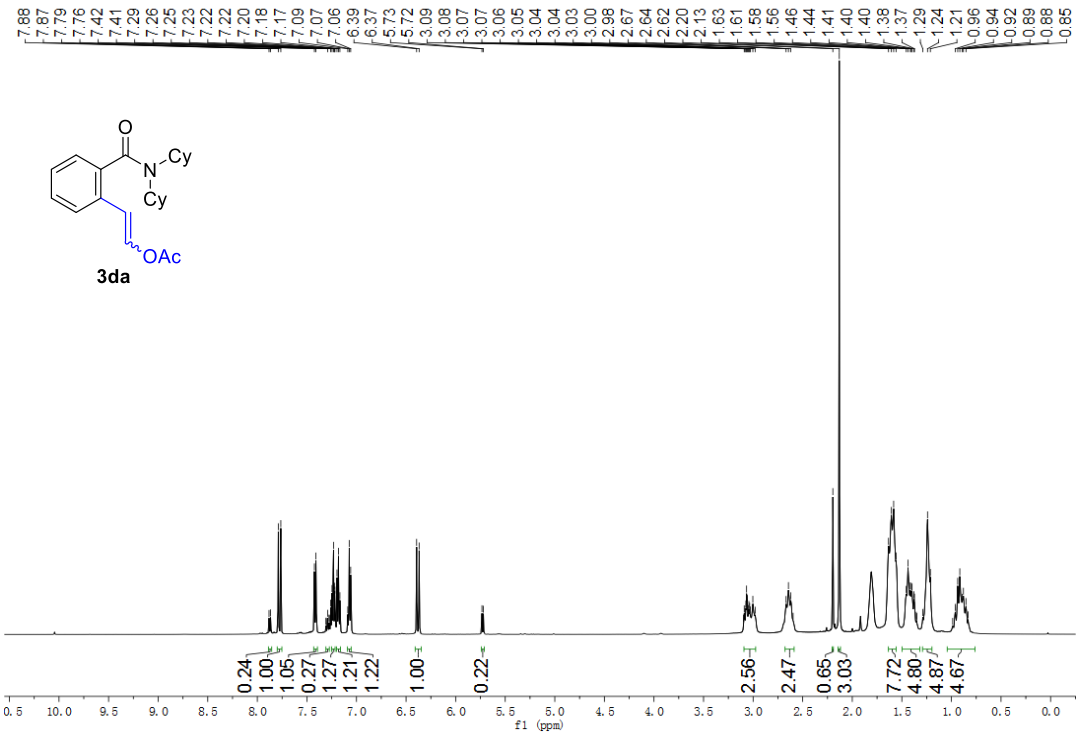
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7.07
7.06
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5.72
3.09
3.08
3.07
3.07
3.06
3.05
3.04
3.04
3.03
3.00
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1.58
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1.41
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1.40
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1.37
1.29
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1.21
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N
Cy
Cy
OAc
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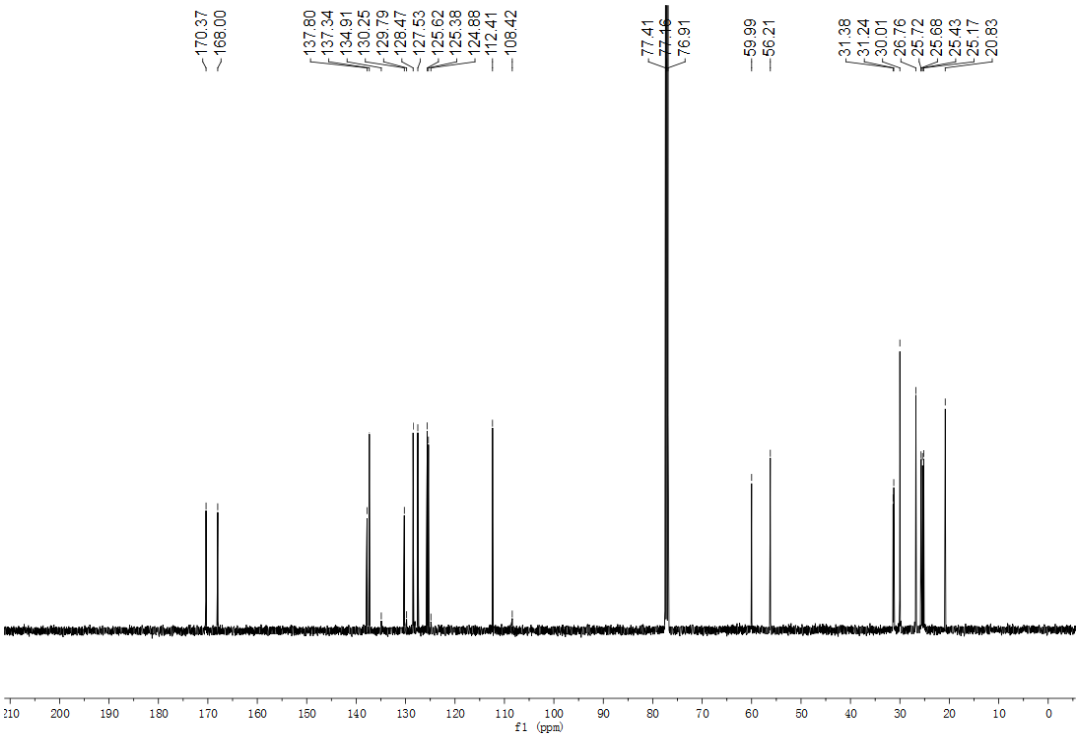
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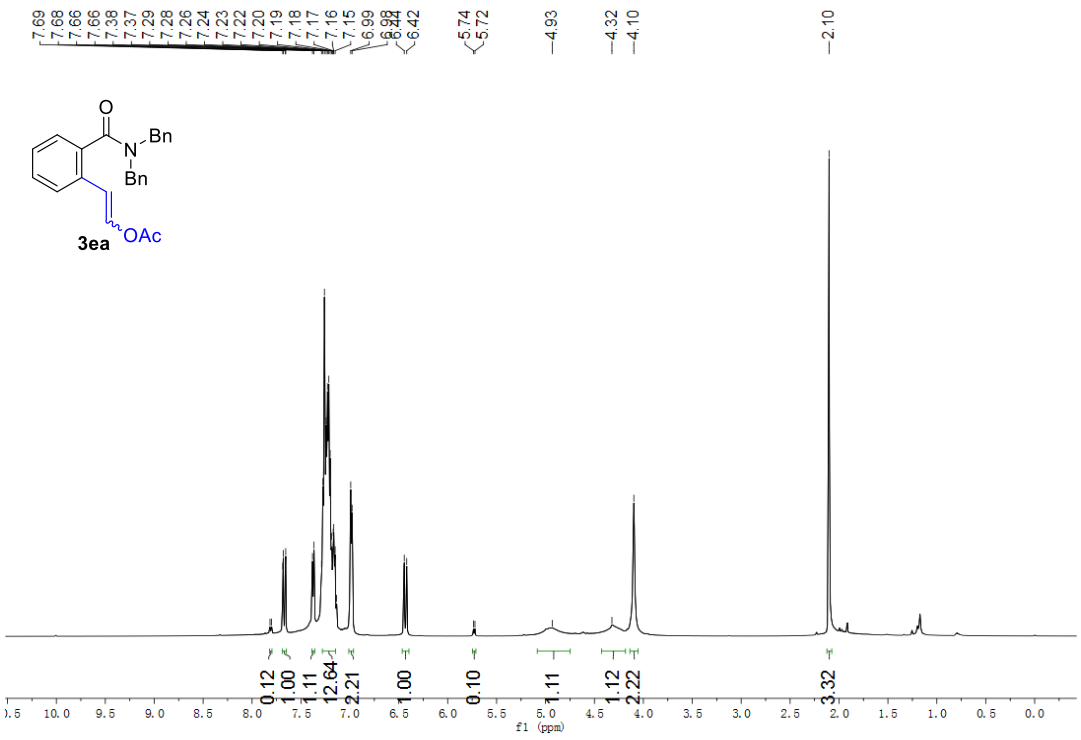
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5.72
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Bn
Bn
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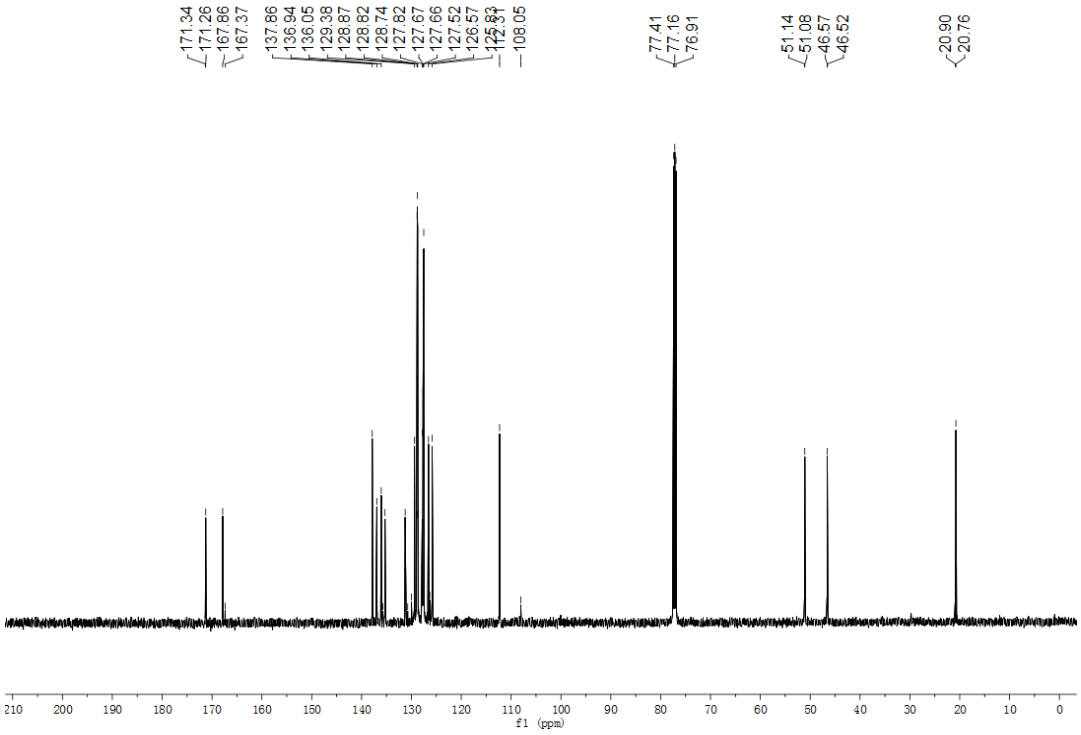
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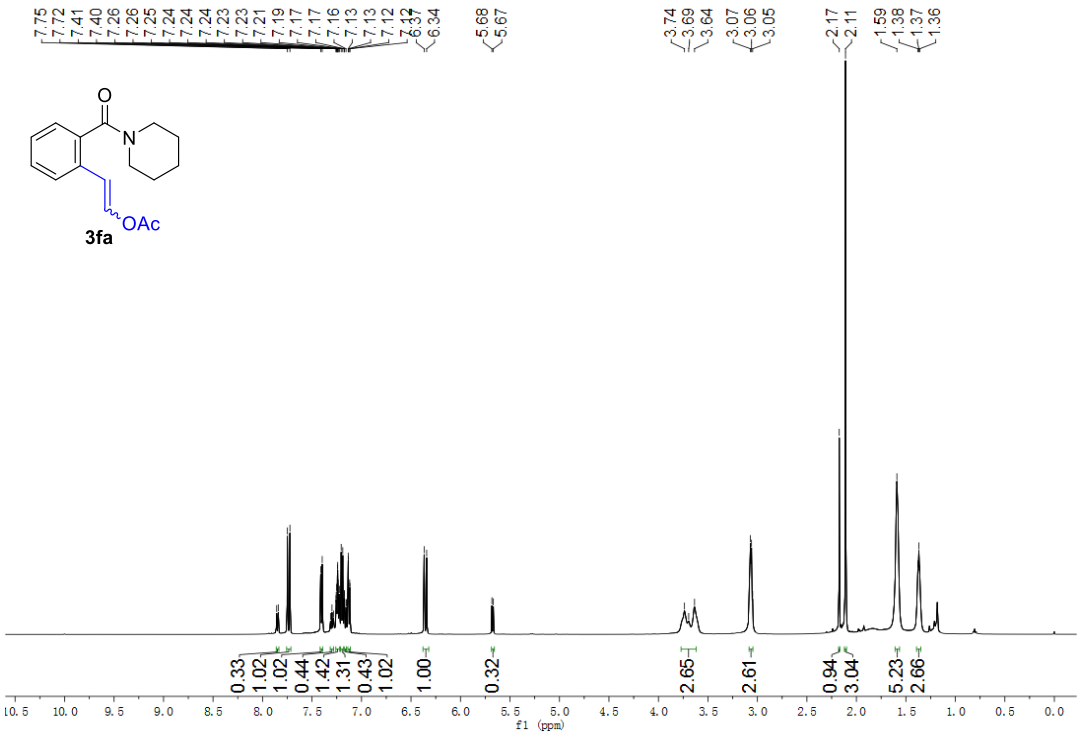
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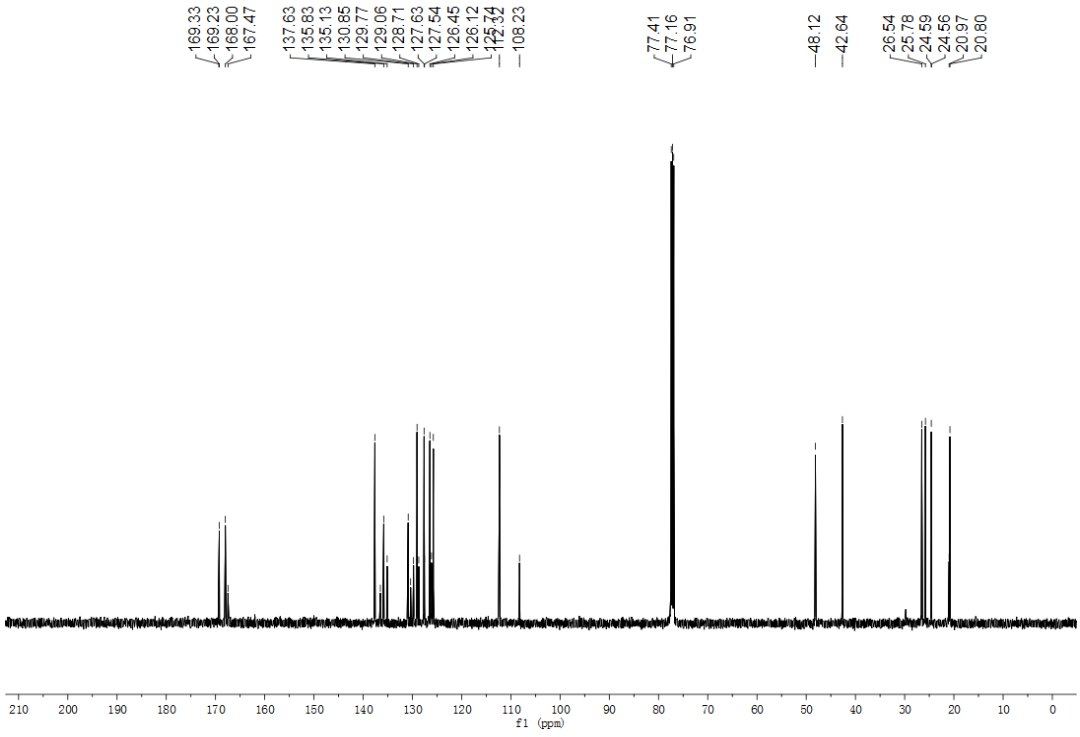
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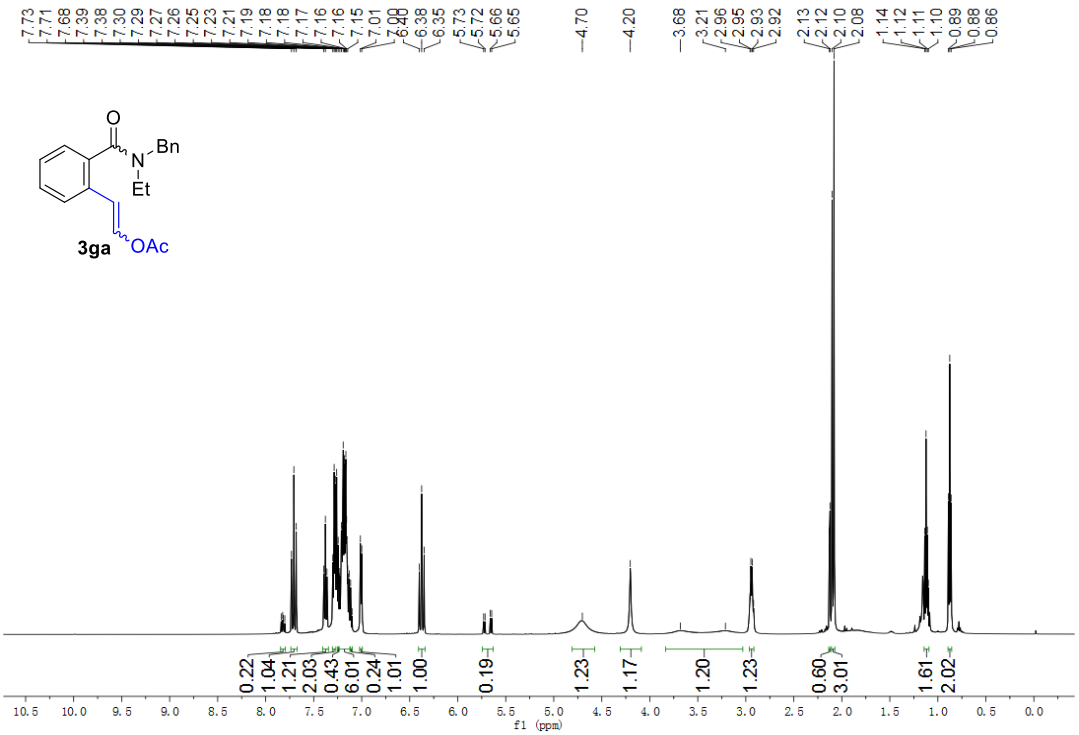
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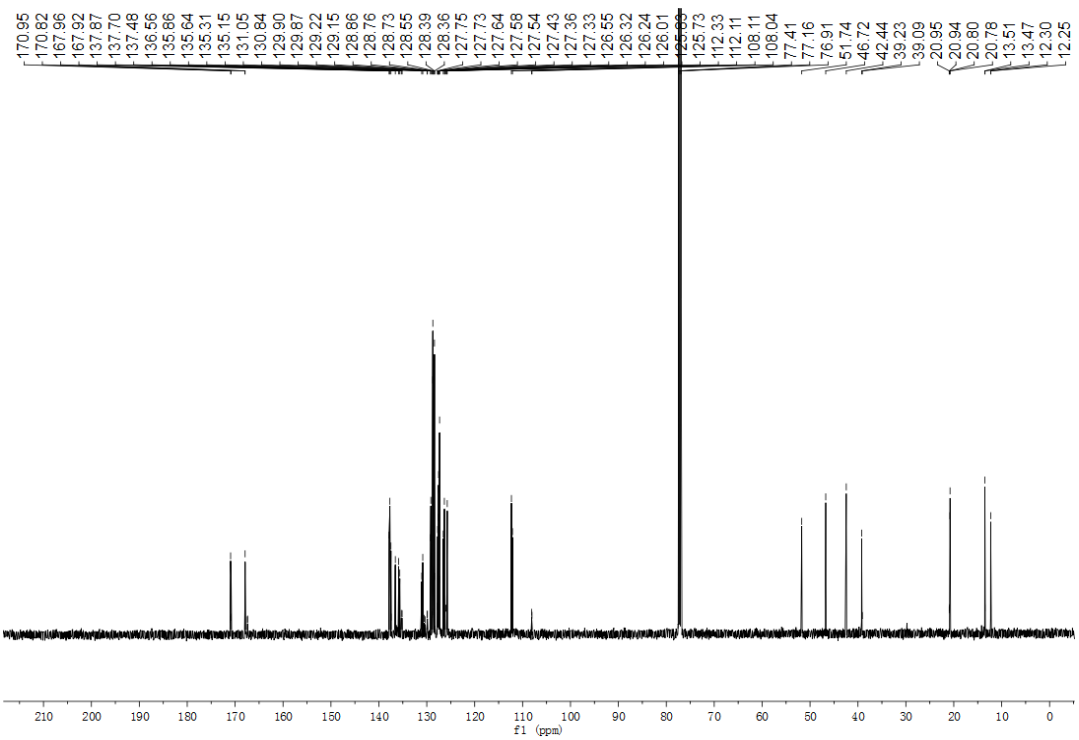

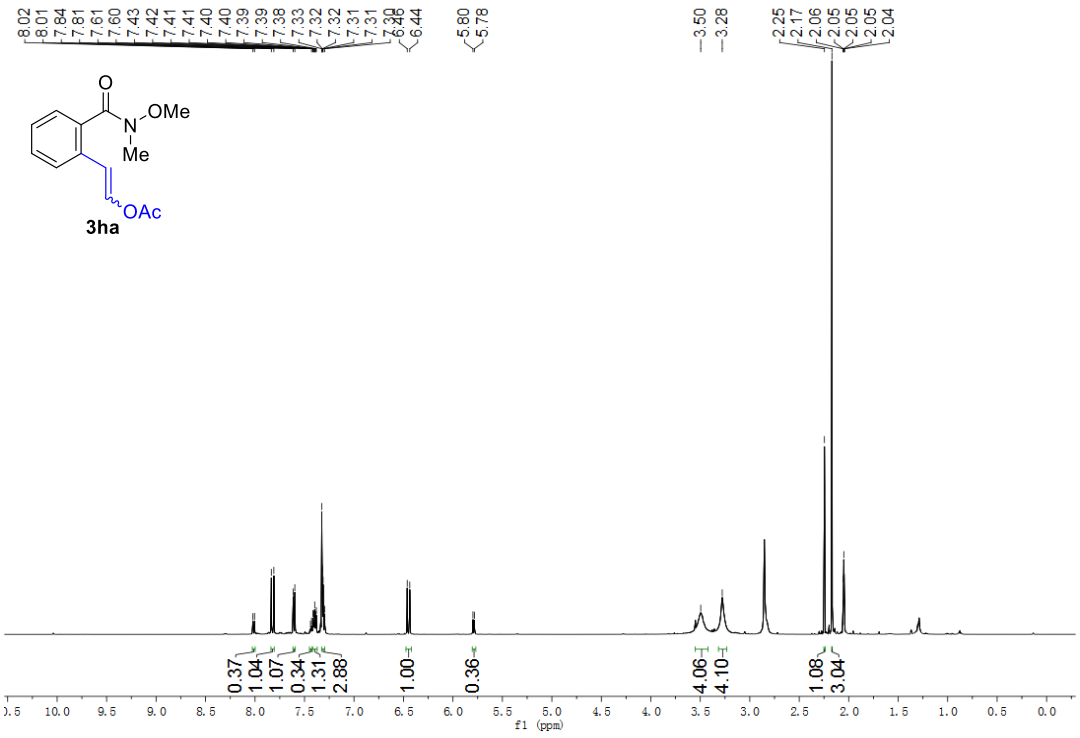
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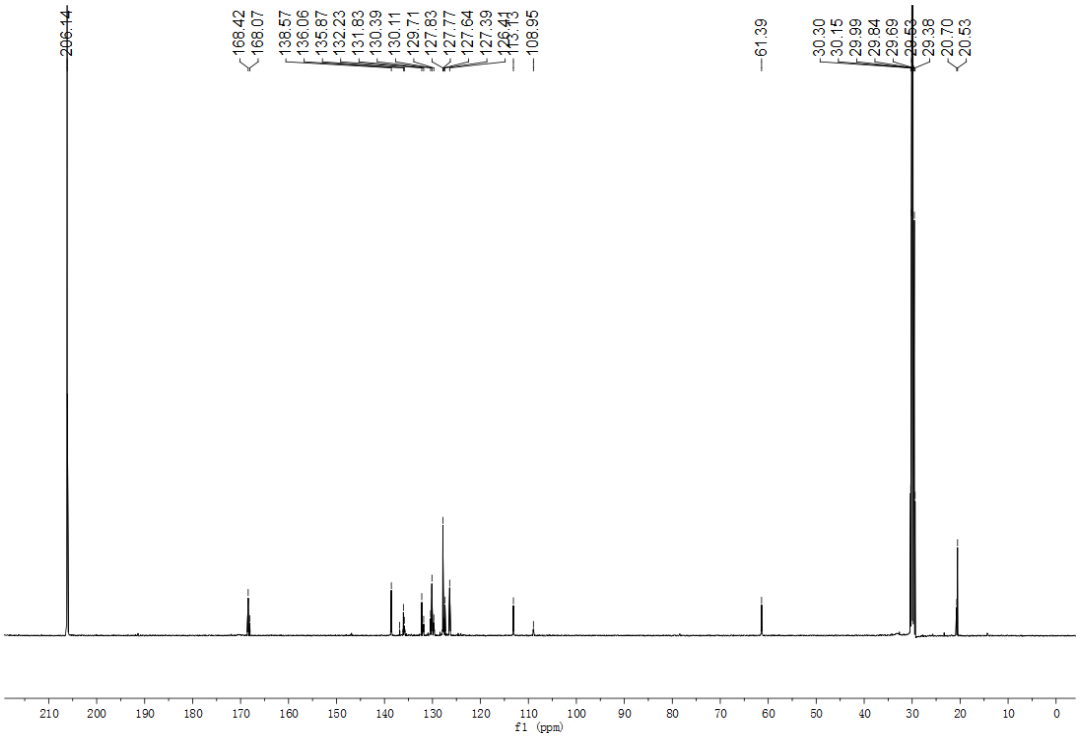
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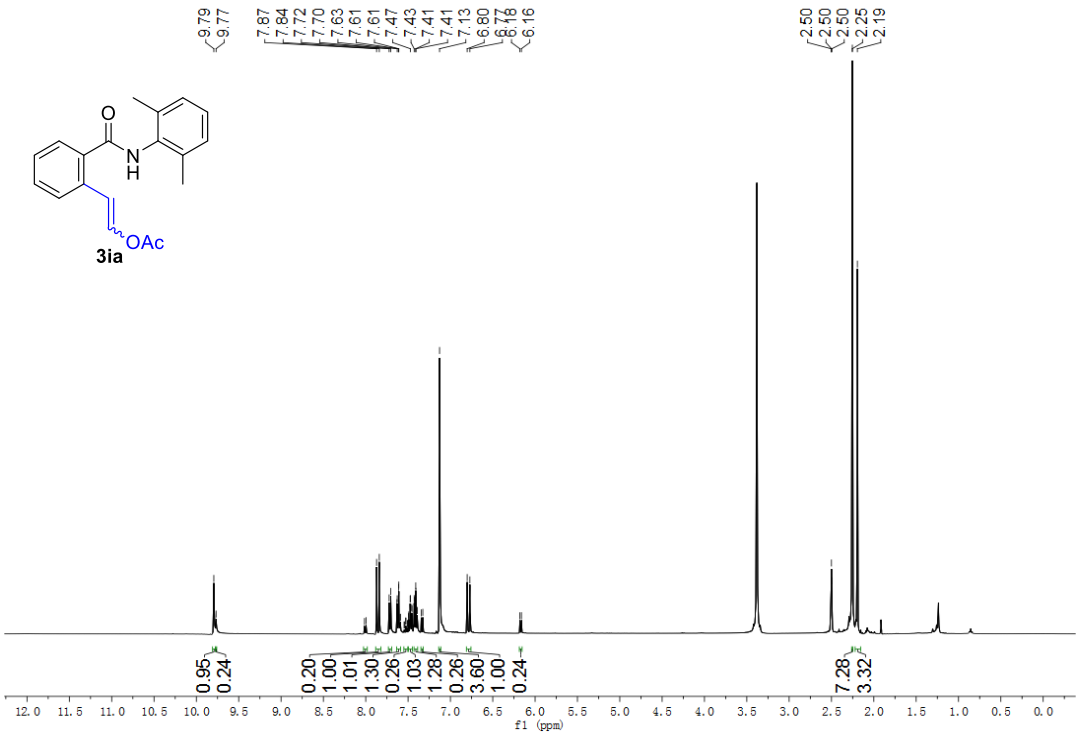
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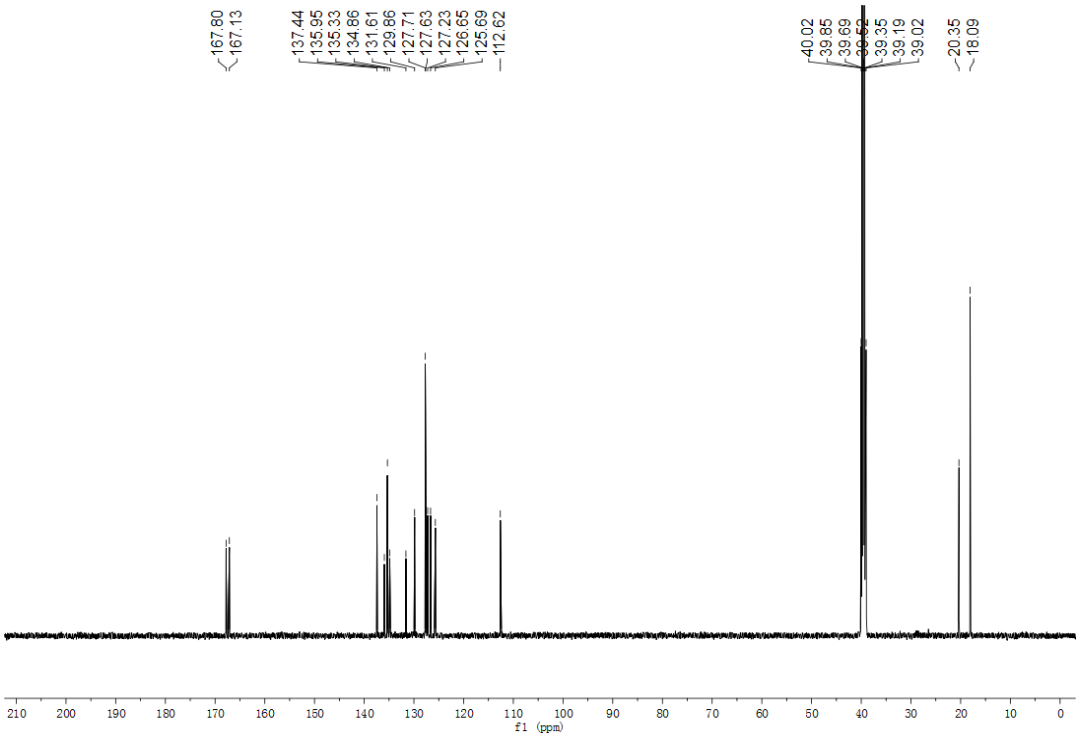
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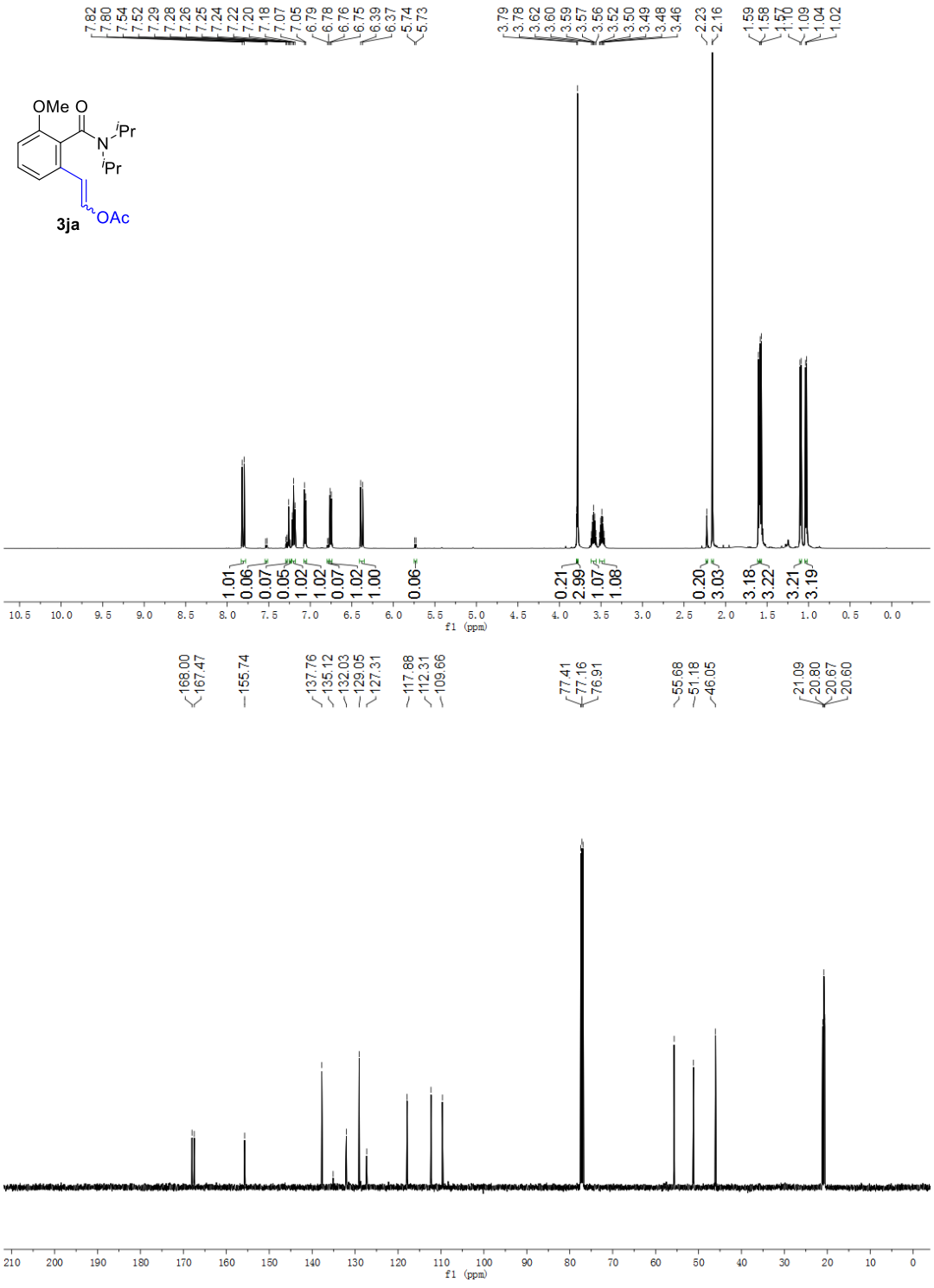
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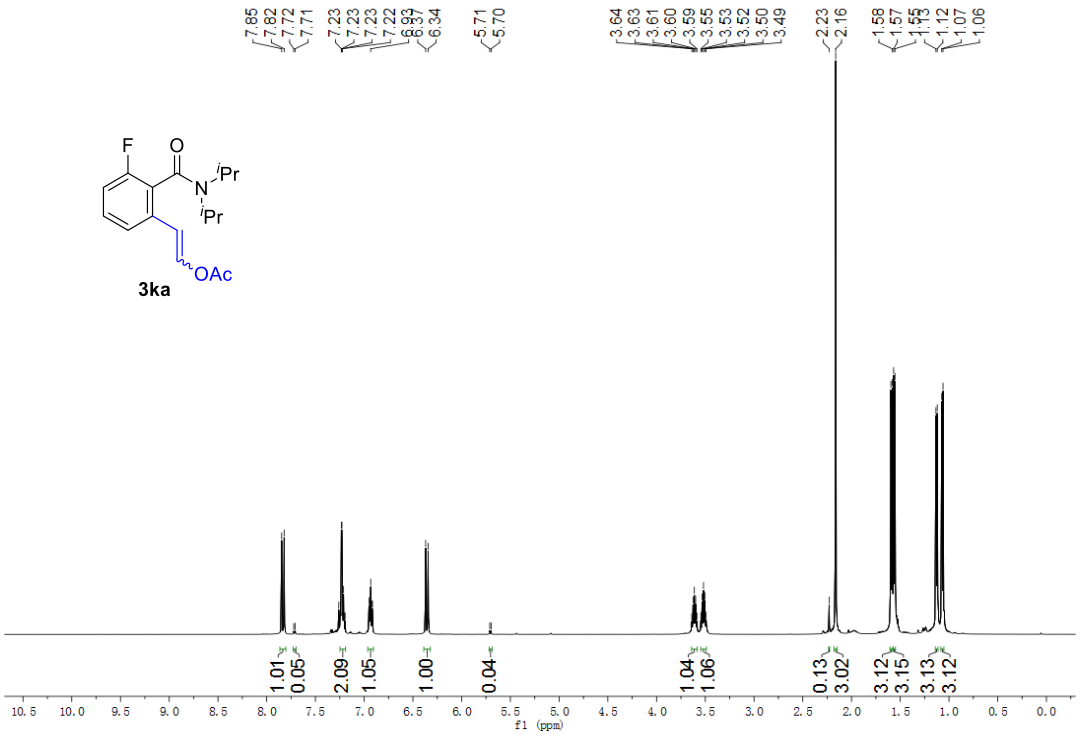
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3.53
3.52
3.50
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2.16
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1.57
1.55
1.53
1.12
1.07
1.06
1.01
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2.09
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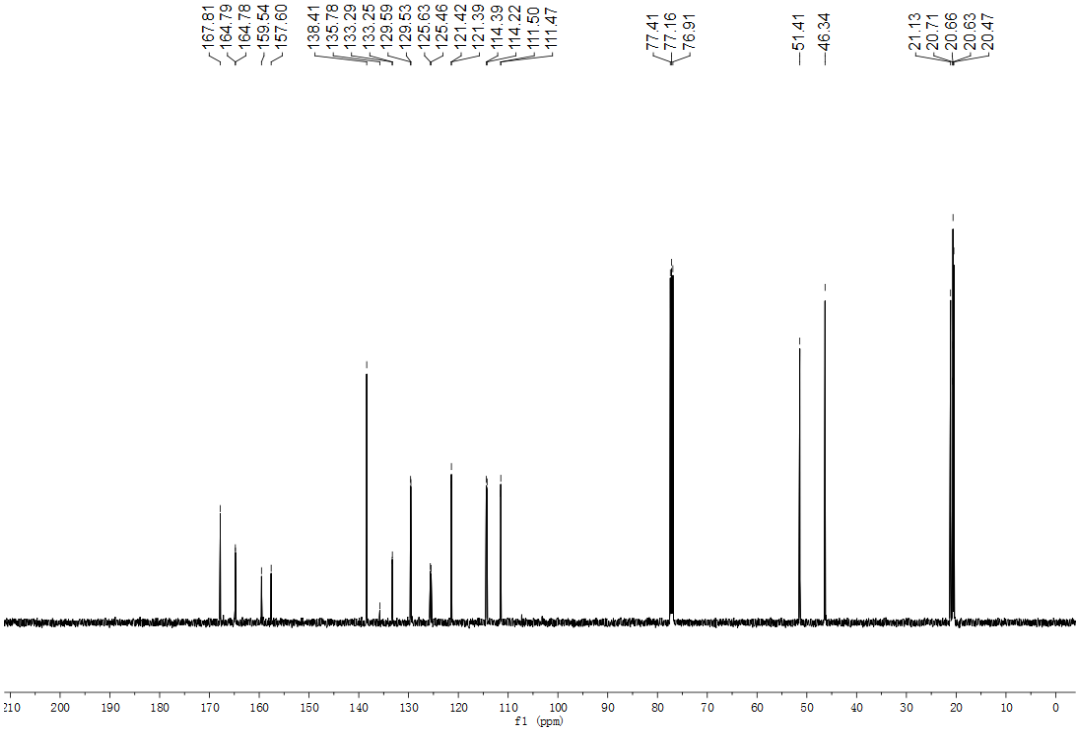
3.12
f1 (ppm)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121.39
114.39
114.22
111.50
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51.41
46.34
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20.66
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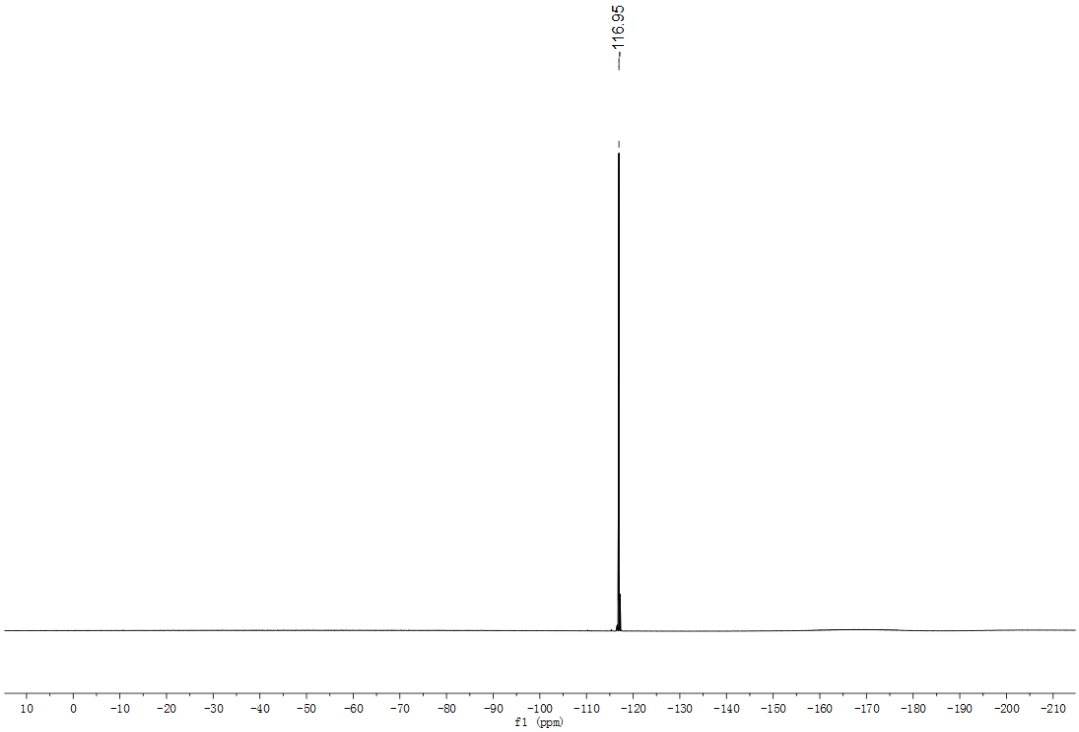
20.47
f1 (ppm)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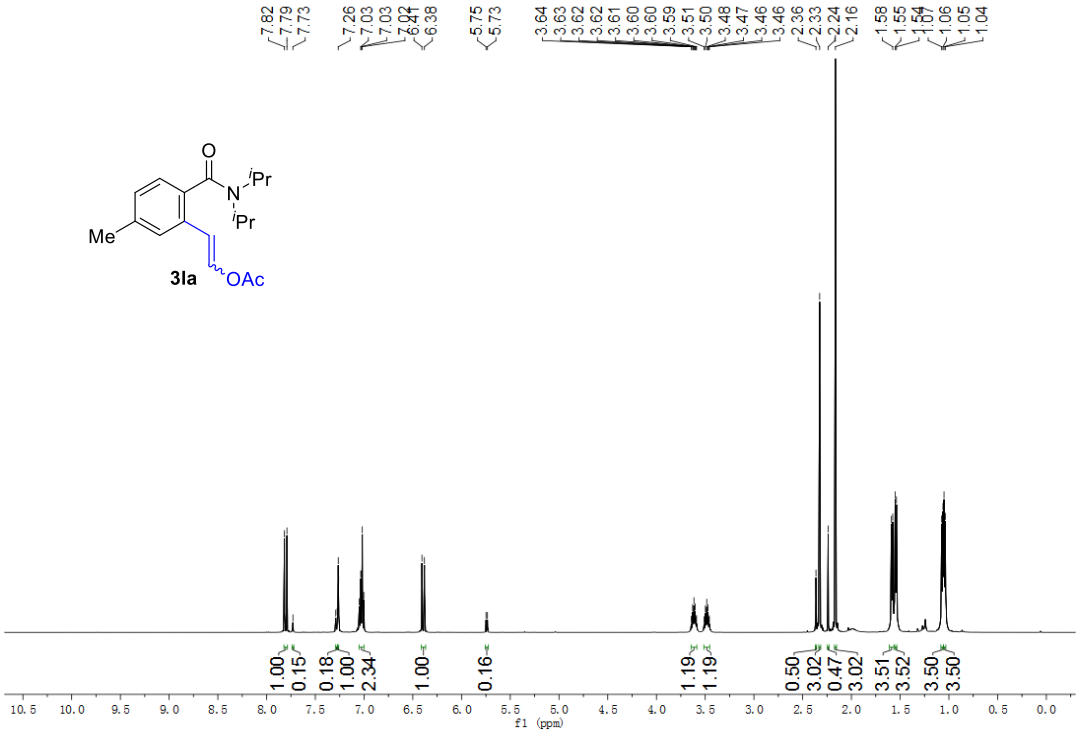
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5.73
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3.63
3.62
3.61
3.60
3.60
3.59
3.51
3.50
3.48
3.47
3.46
3.46
2.36
2.33
2.24
2.16
1.58
1.55
1.54
1.07
1.06
1.05
1.04
O
N
iPr
iPr
Me
3la
OAc
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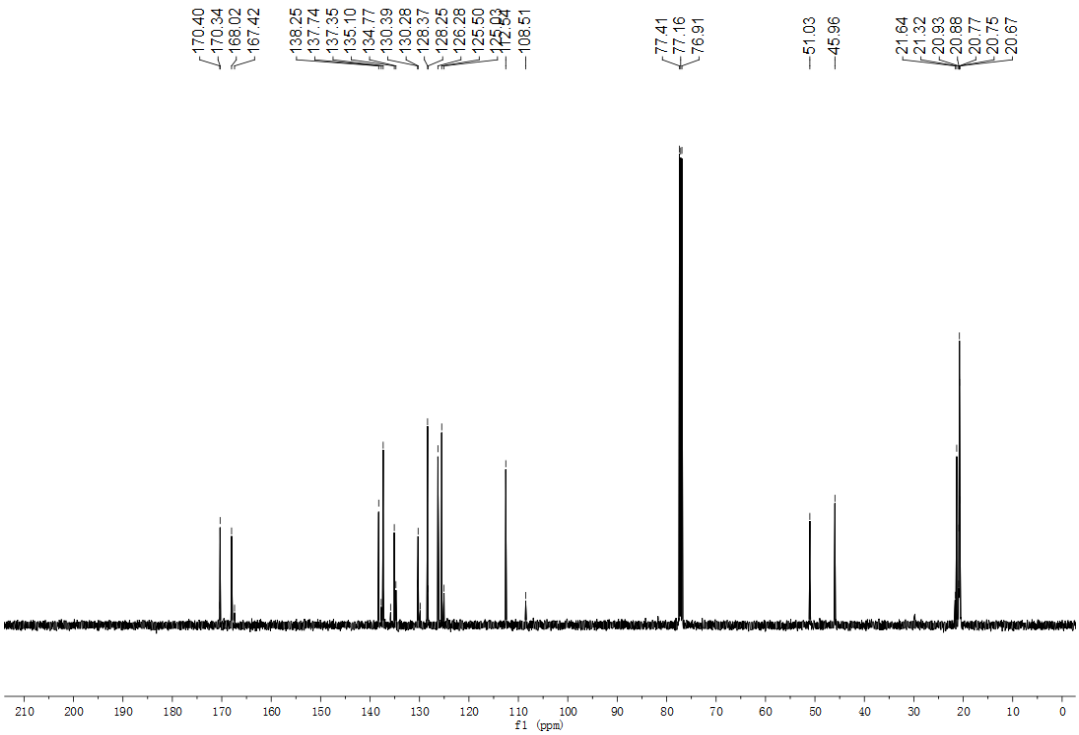
0.15
0.18
1.00
2.34
1.00
0.16
1.19
1.19
0.50
3.02
0.47
3.02
3.51
3.52
3.50
3.50
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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112.54
108.51
77.41
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20.77
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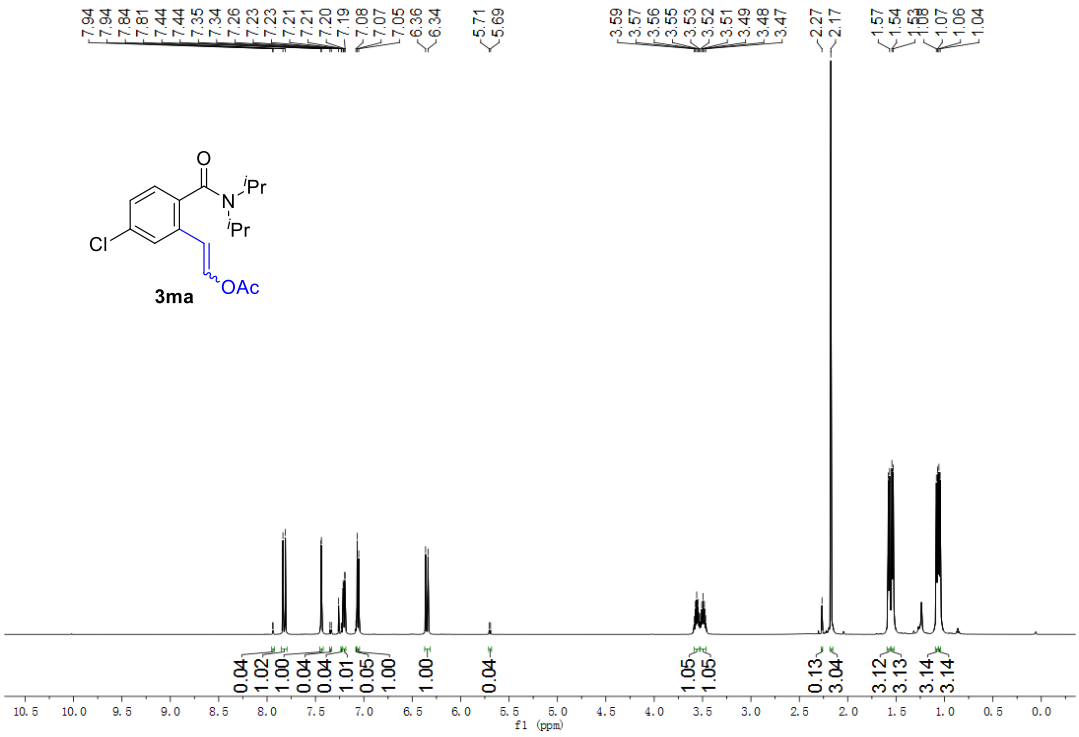
20.67
f1 (ppm)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7.21
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7.19
7.08
7.07
7.05
6.36
6.34
5.71
5.69
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3.57
3.56
3.55
3.53
3.52
3.51
3.49
3.48
3.47
2.27
2.17
1.57
1.54
1.53
1.08
1.07
1.06
1.04
O
N
iPr
iPr
Cl
OAc
3ma
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1.00
0.04
0.04
1.01
0.05
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1.05
0.13
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3.13
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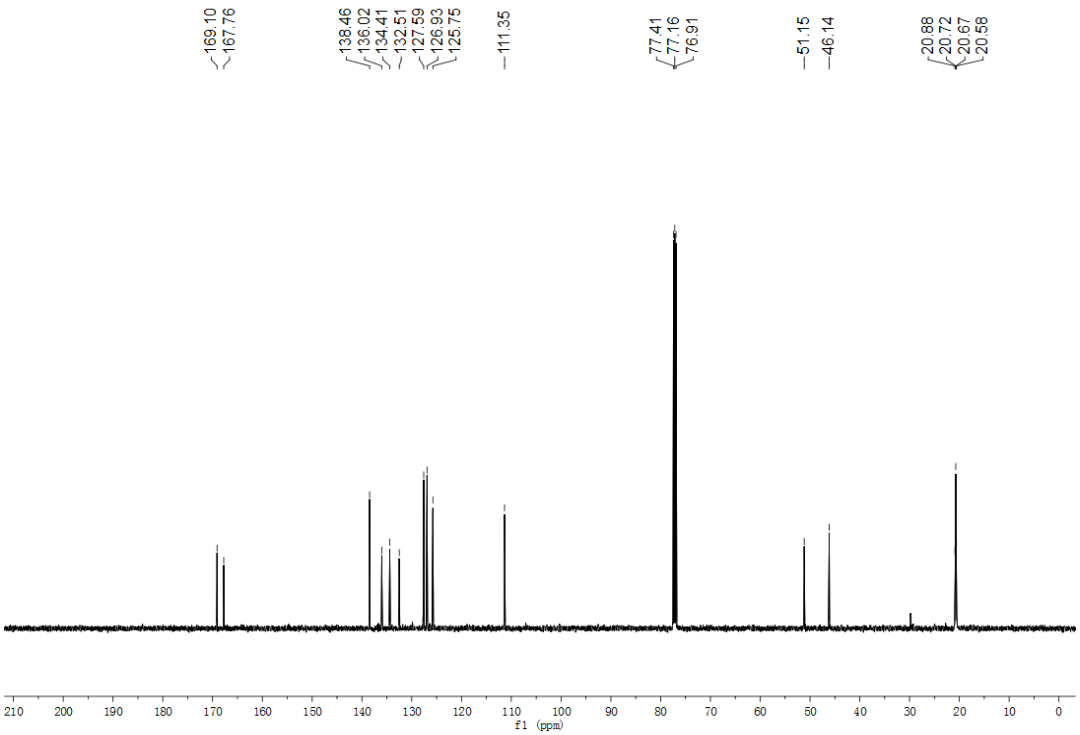
f1 (ppm)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51.15
46.14
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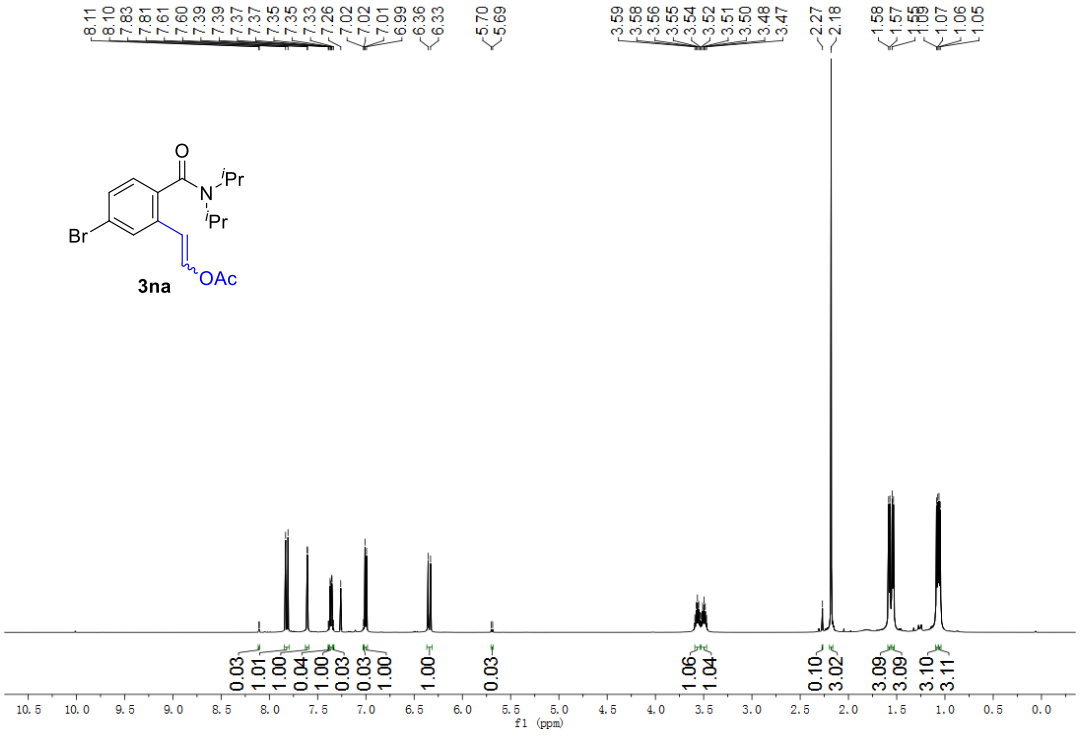
20.72
20.67
20.58
f1 (ppm)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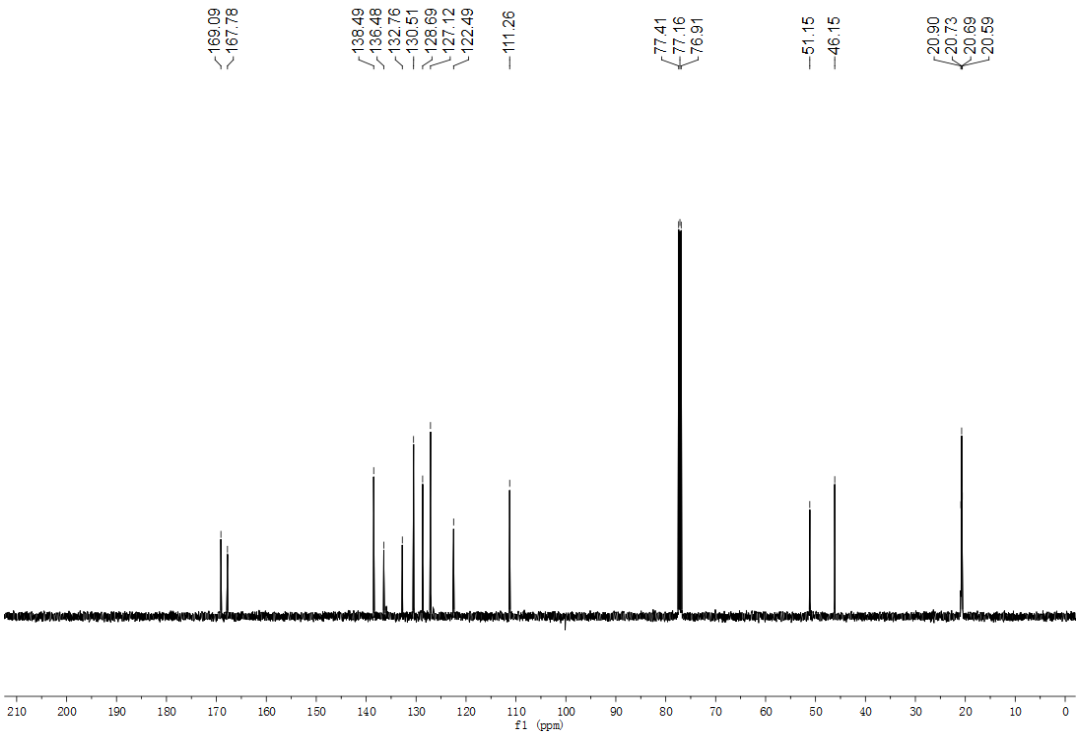
7.35
7.35
7.33
7.26
7.02
7.02
7.01
6.99
6.36
6.33
5.70
5.69
3.59
3.58
3.56
3.55
3.54
3.52
3.51
3.50
3.48
3.47
2.27
2.18
1.58
1.57
1.07
1.06
1.05
O
N
iPr
iPr
Br
OAc
3na
0.03
1.01
1.00
0.04
1.00
0.03
0.03
1.00
1.00
0.03
1.06
1.04
0.10
3.02
3.09
3.09
3.10
3.11
f1 (ppm)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127.12
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111.26
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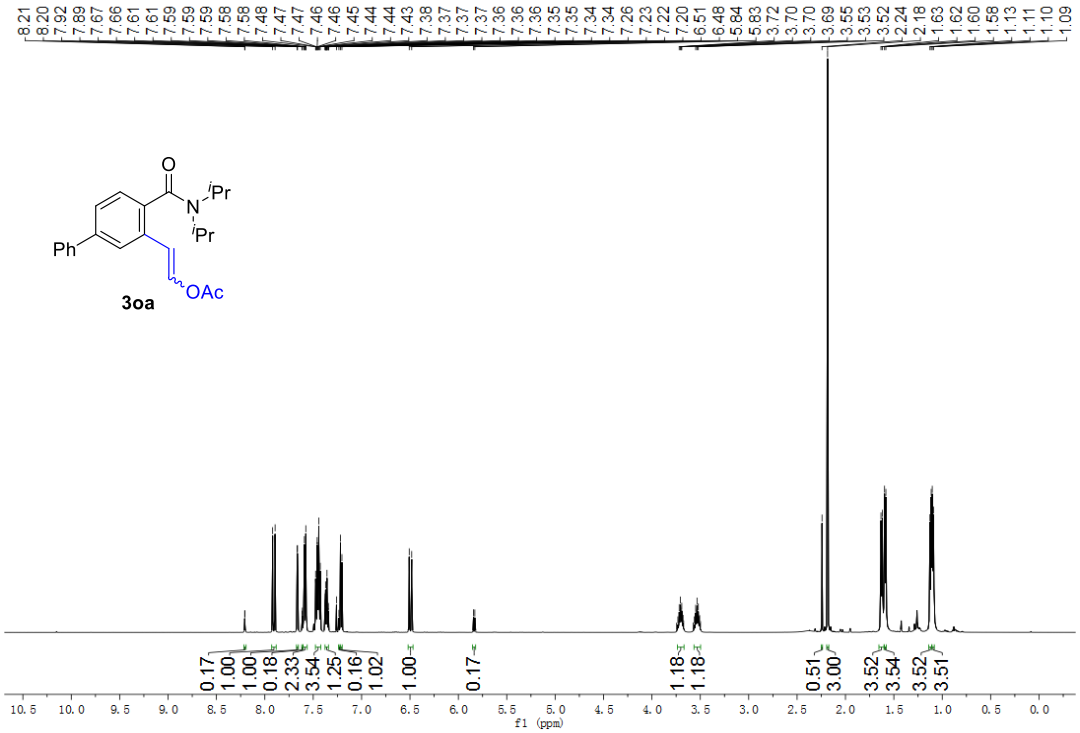
77.16
76.91
51.15
46.15
20.90
20.73
20.69
20.59
f1 (ppm)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7.35
7.35
7.34
7.34
7.26
7.23
7.22
7.20
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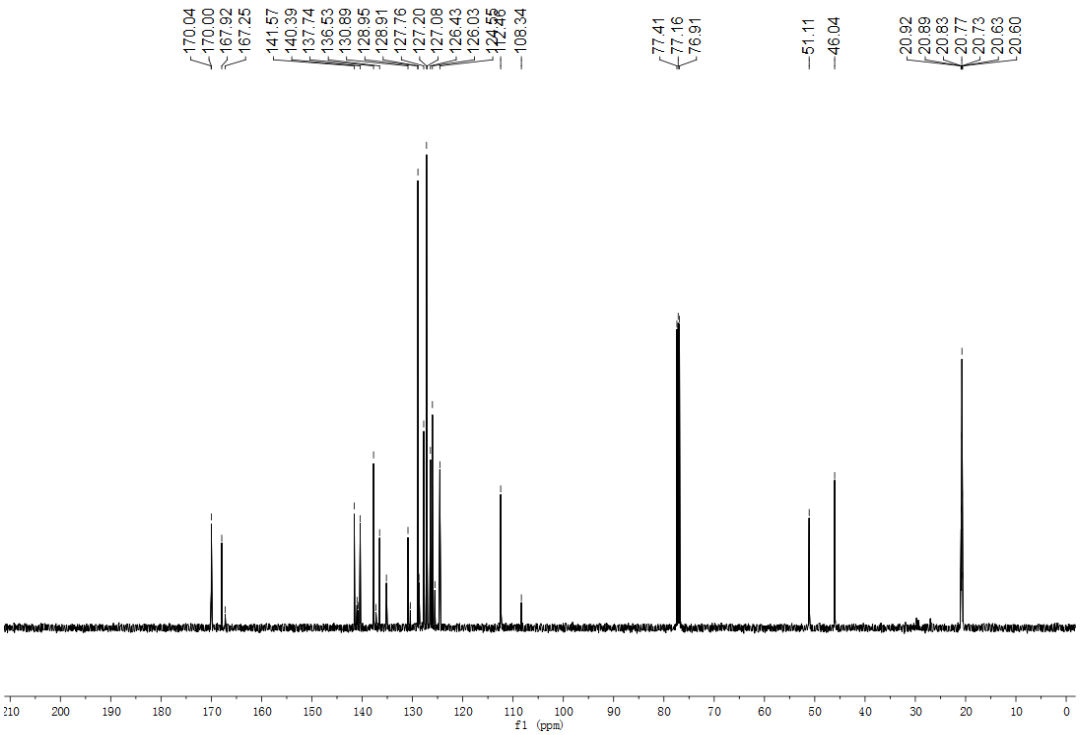
6.48
5.84
5.83
3.72
3.70
3.70
3.69
3.55
3.53
3.52
2.24
2.18
1.63
1.62
1.60
1.58
1.13
1.11
1.10
1.09
0.17
1.00
1.00
0.18
2.33
3.54
1.25
0.16
1.02
1.00
0.17
1.18
1.18
0.51
3.00
3.52
3.54
3.52
3.51
f1 (ppm)

O
N
iPr
iPr
Ph
OAc

3oa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127.08
126.43
126.03
124.55
112.46
108.34
77.41
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46.04
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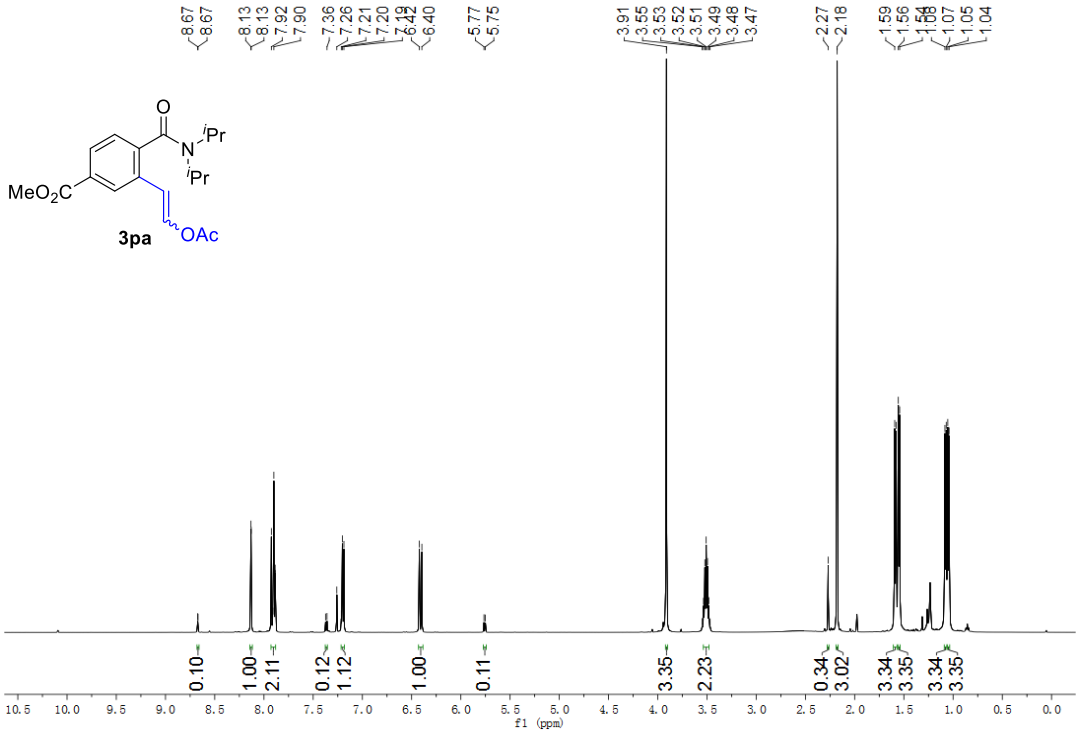
20.89
20.83
20.77
20.73
20.63
20.60
f1 (ppm)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7.20
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5.75
3.91
3.55
3.53
3.52
3.51
3.49
3.48
3.47
2.27
2.18
1.59
1.56
1.54
1.08
1.07
1.05
1.04
0.10
1.00
2.11
0.12
1.12
1.00
0.11
3.35
2.23
0.34
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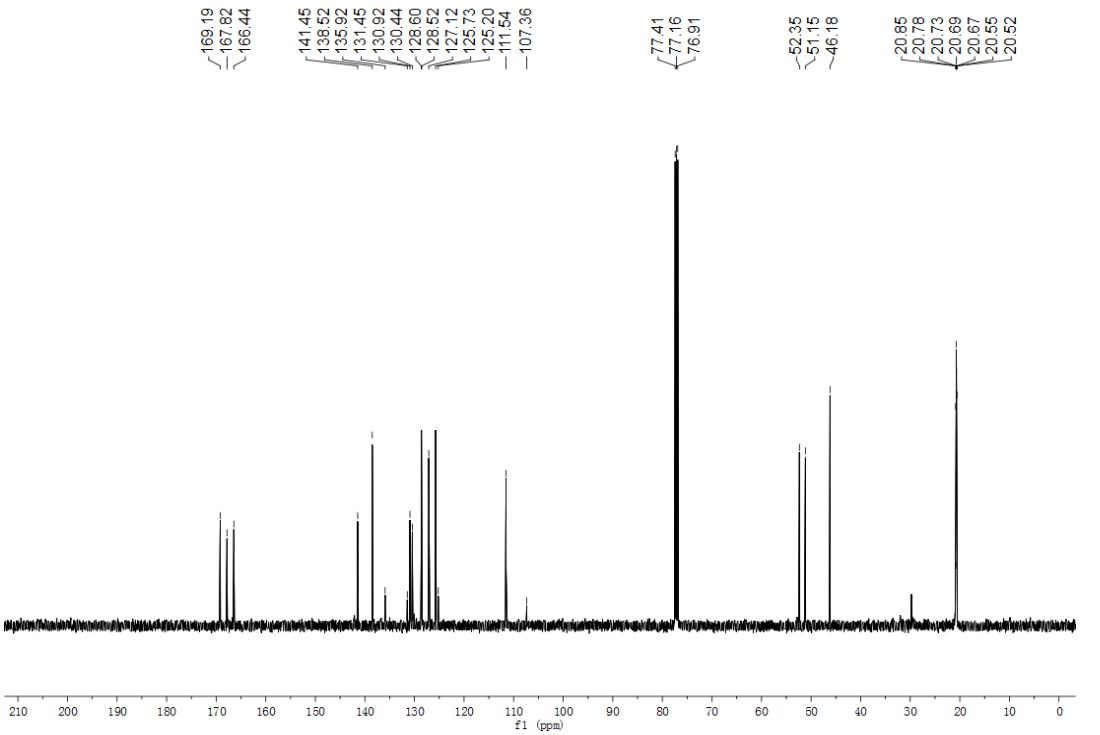
3.34
3.35
f1 (ppm)

O
N
iPr
iPr
MeO2C
OAc

3pa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130.92
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128.52
127.12
125.73
125.20
111.54
107.36
77.41
77.16
76.91
52.35
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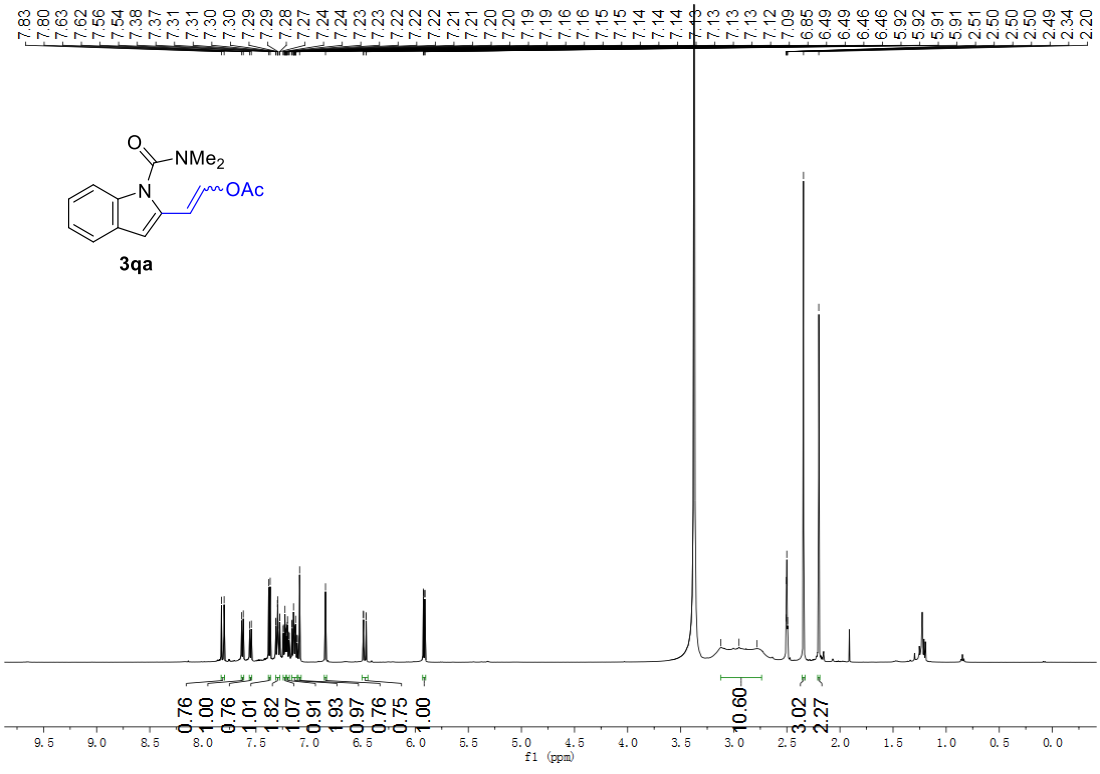
46.18
20.85
20.78
20.73
20.69
20.67
20.55
20.52
f1 (ppm)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7.19
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7.16
7.15
7.15
7.14
7.14
7.14
7.13
7.13
7.13
7.12
7.09
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6.46
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5.91
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2.49
2.34
2.20
O
NMe2
N
OAc
3qa
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0.76
1.01
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0.97
0.76
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10.60
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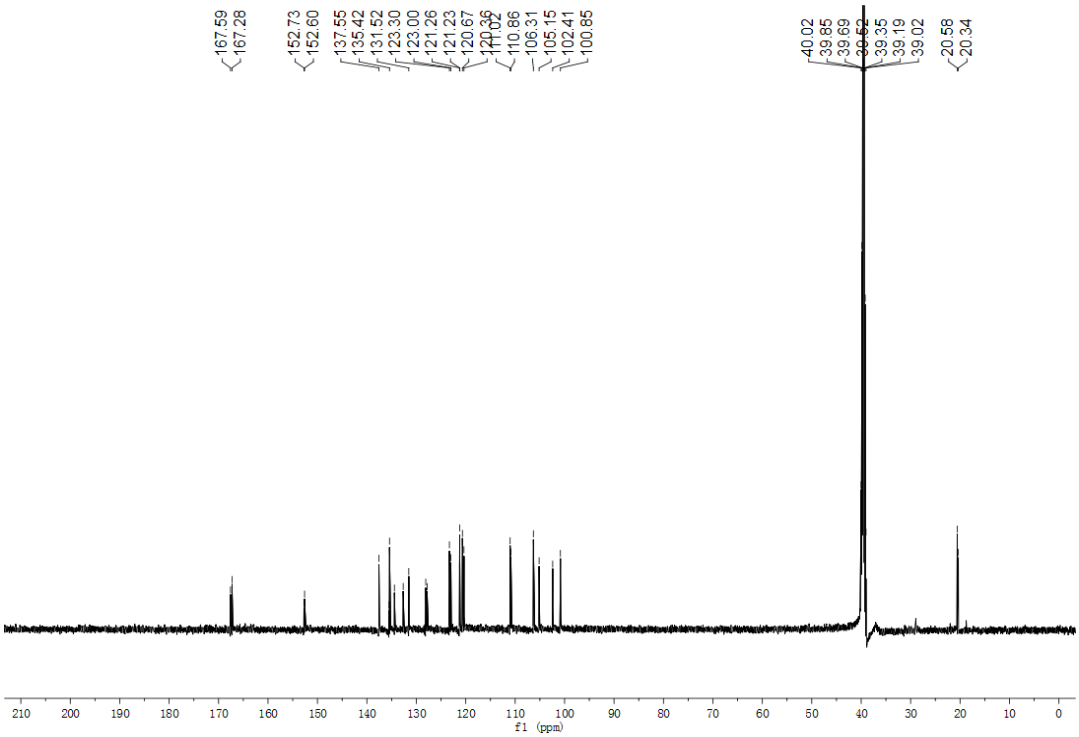
2.27
f1 (ppm)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120.36
111.02
110.86
106.31
105.15
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39.52
39.35
39.19
39.02
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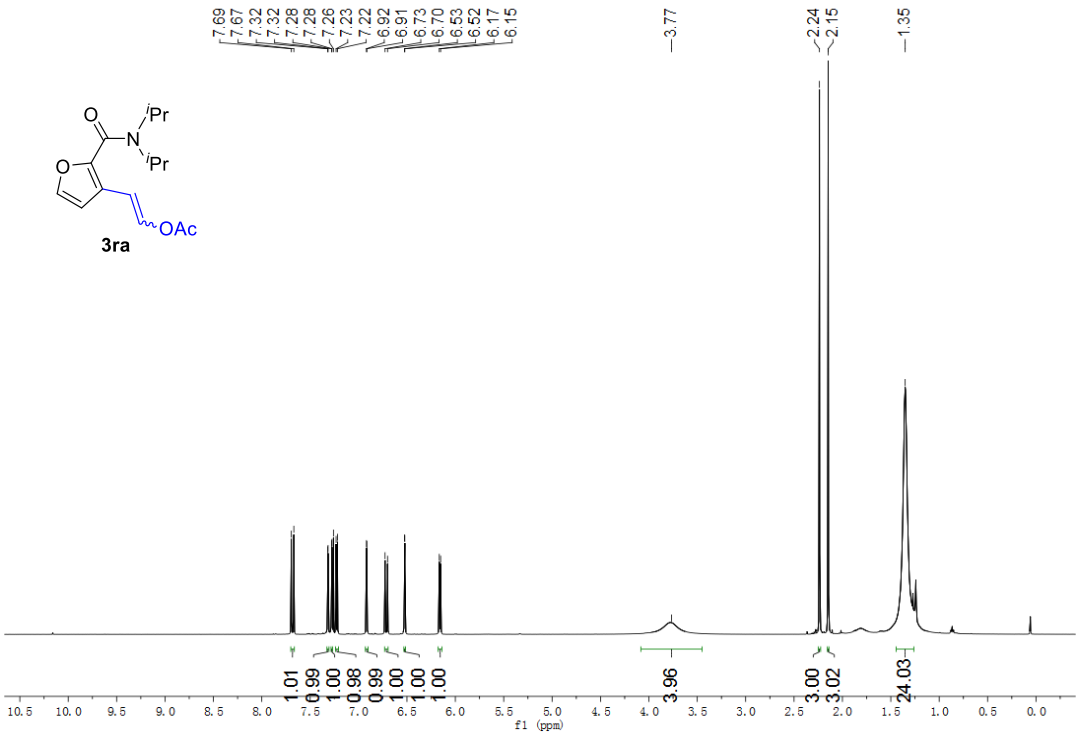
20.34
f1 (ppm)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7.22
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6.70
6.53
6.52
6.17
6.15
3.77
2.24
2.15
1.35
1.01
0.99
1.00
0.98
0.99
1.00
1.00
1.00
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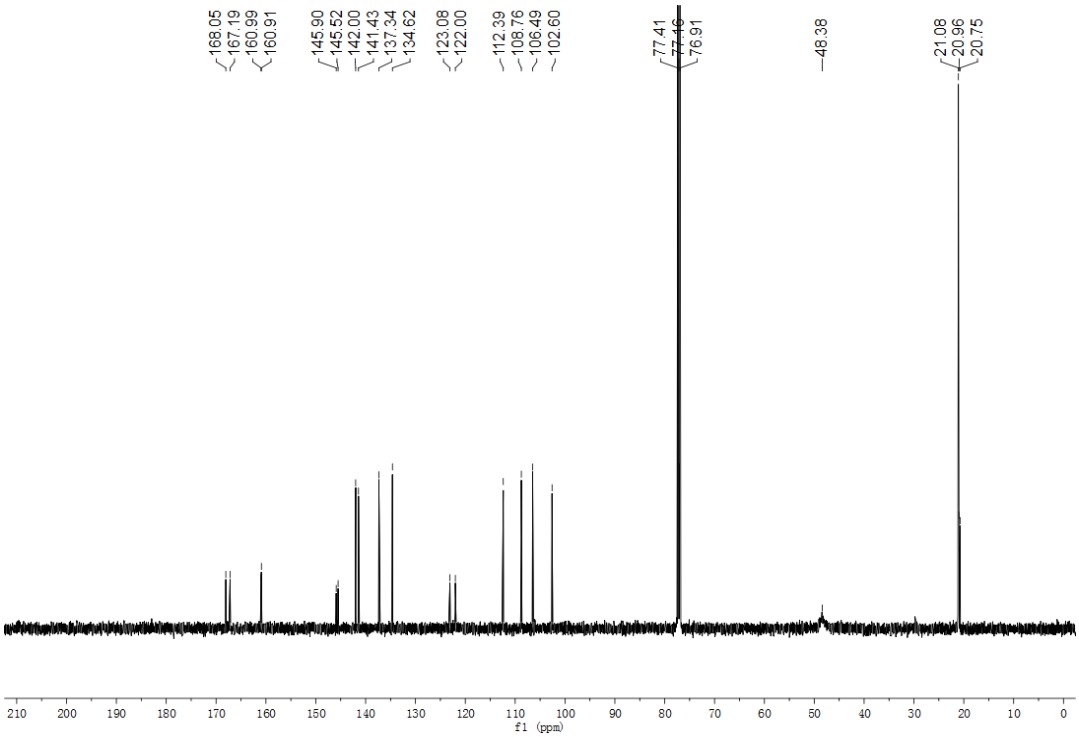
3.00
3.02
24.03
f1 (ppm)

O
N
iPr
iPr
O
OAc

3ra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134.62
123.08
122.00
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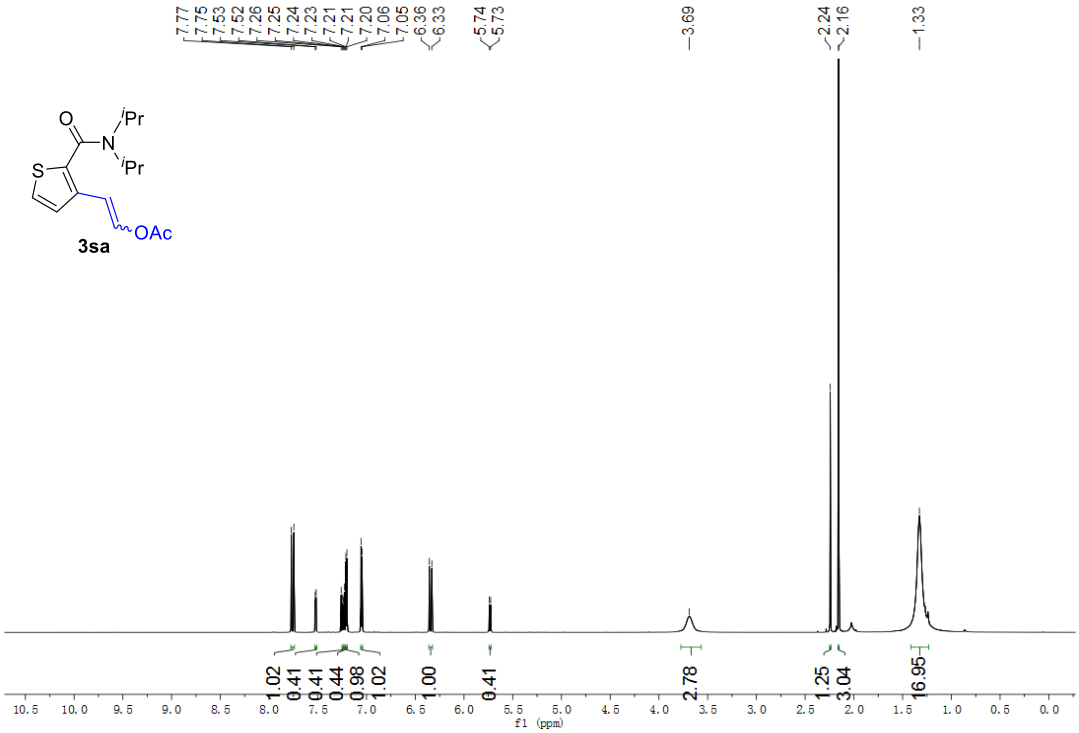
102.60
77.41
77.16
76.91
48.38
21.08
20.96
20.75
f1 (ppm)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7.21
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7.05
6.36
6.33
5.74
5.73
3.69
2.24
2.16
1.33
1.02
0.41
0.41
0.44
0.98
1.02
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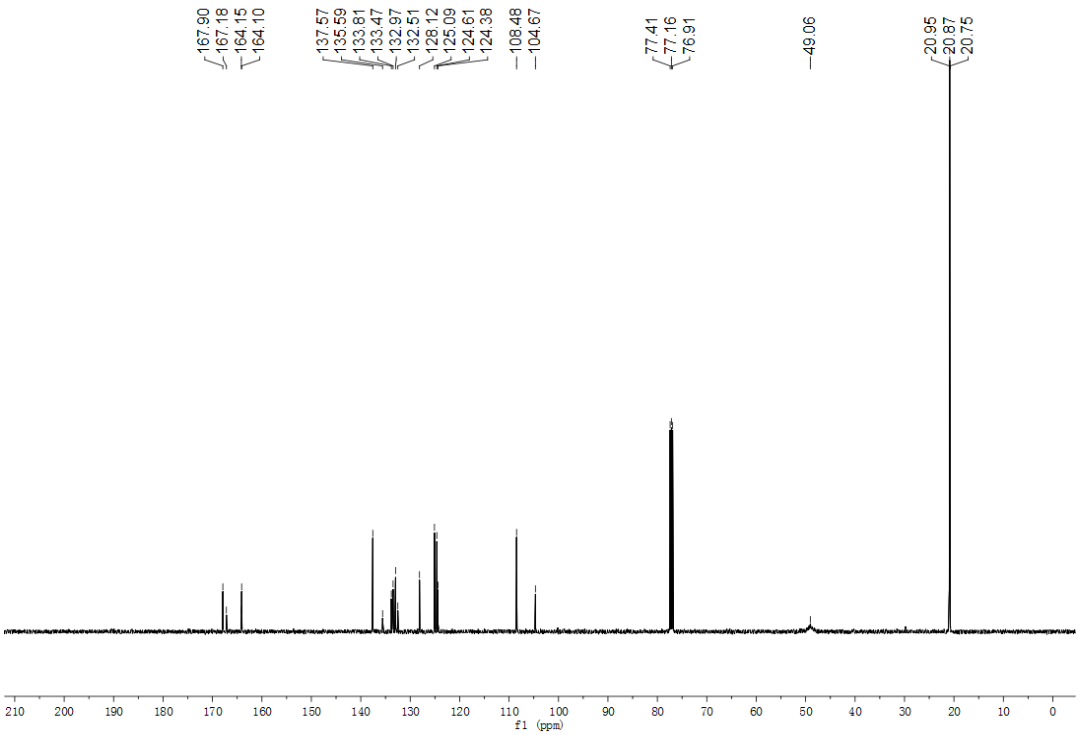
1.25
3.04
16.95
f1 (ppm)

O
N
iPr
iPr
S
OAc

3sa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133.47
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132.51
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125.09
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77.16
76.91
49.06
20.95
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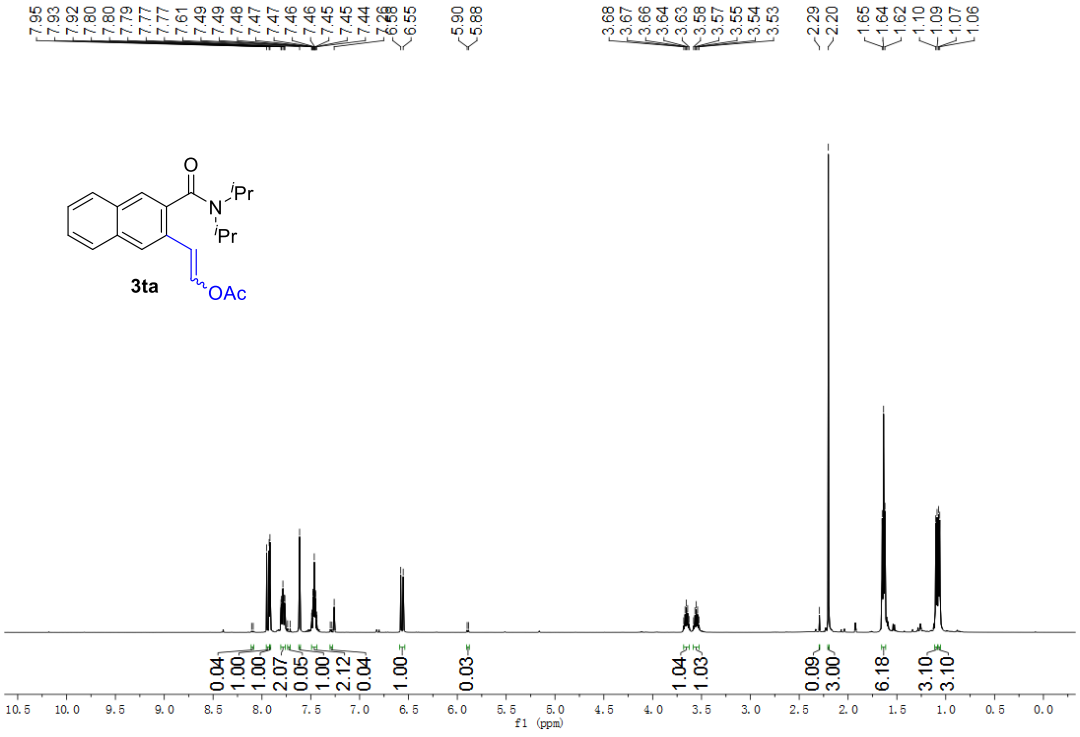
20.75
f1 (ppm)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7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
6.55
5.90
5.88
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3.66
3.64
3.63
3.58
3.57
3.55
3.54
3.53
2.29
2.20
1.65
1.64
1.62
1.10
1.09
1.07
1.06
O
N
iPr
iPr
3ta
OAc
0.04
1.00
1.00
2.07
0.05
1.00
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0.03
1.04
1.03
0.09
3.00
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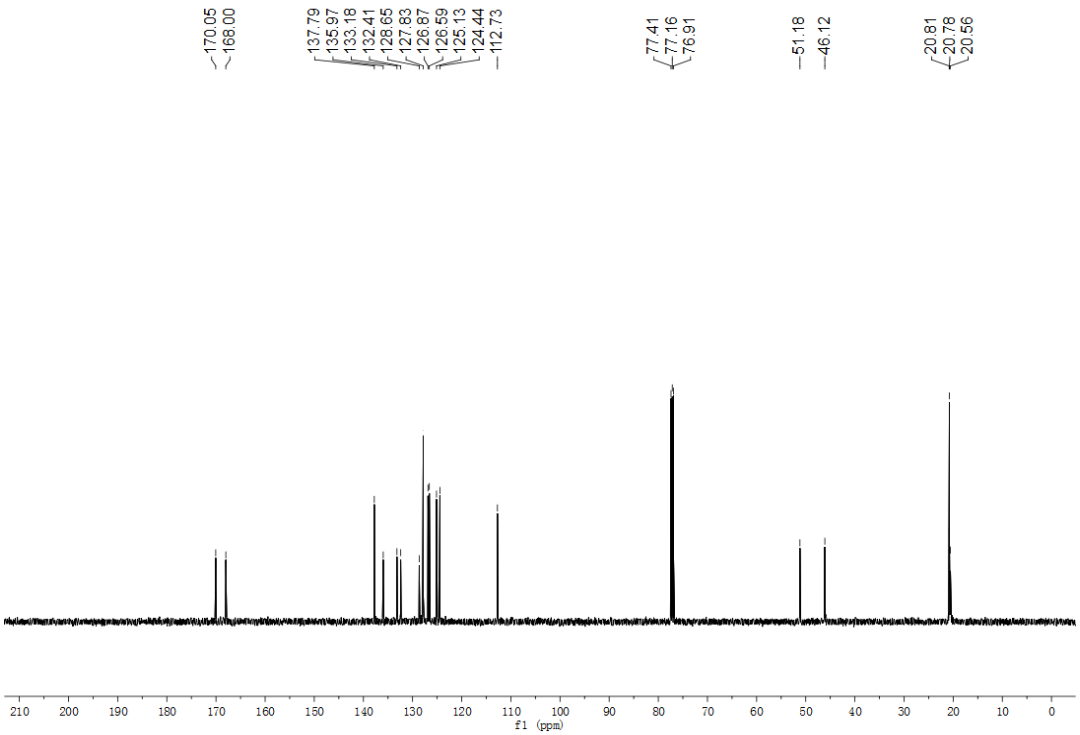
3.10
f1 (ppm)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132.41
128.65
127.83
126.87
126.59
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124.44
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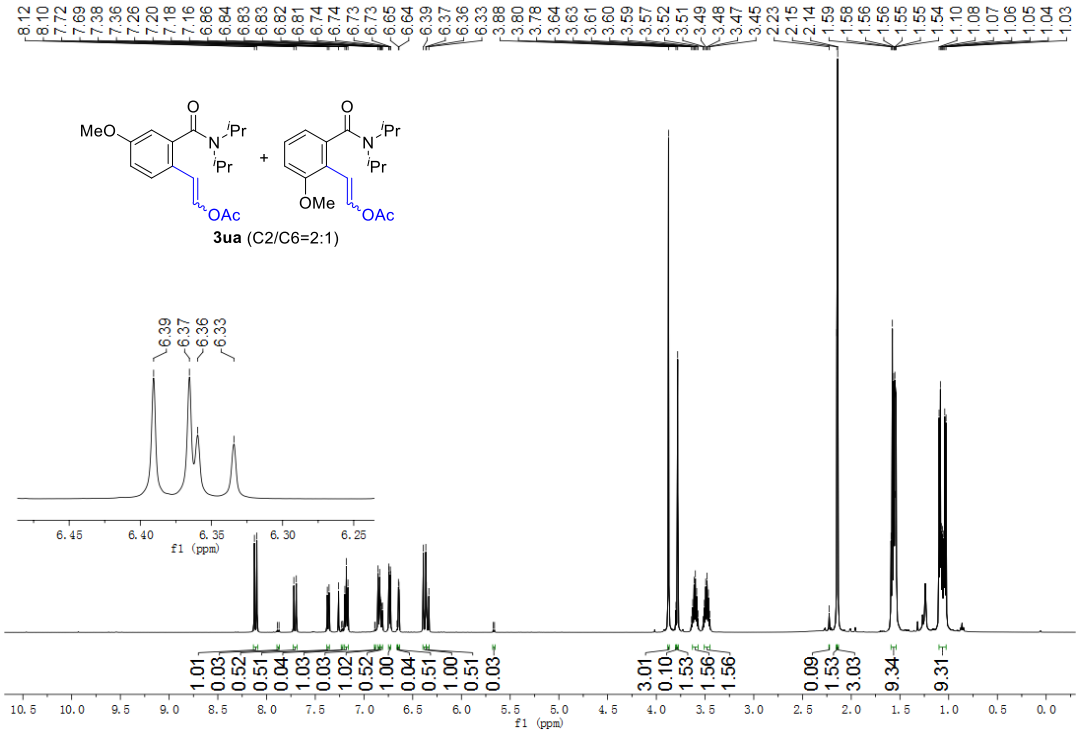
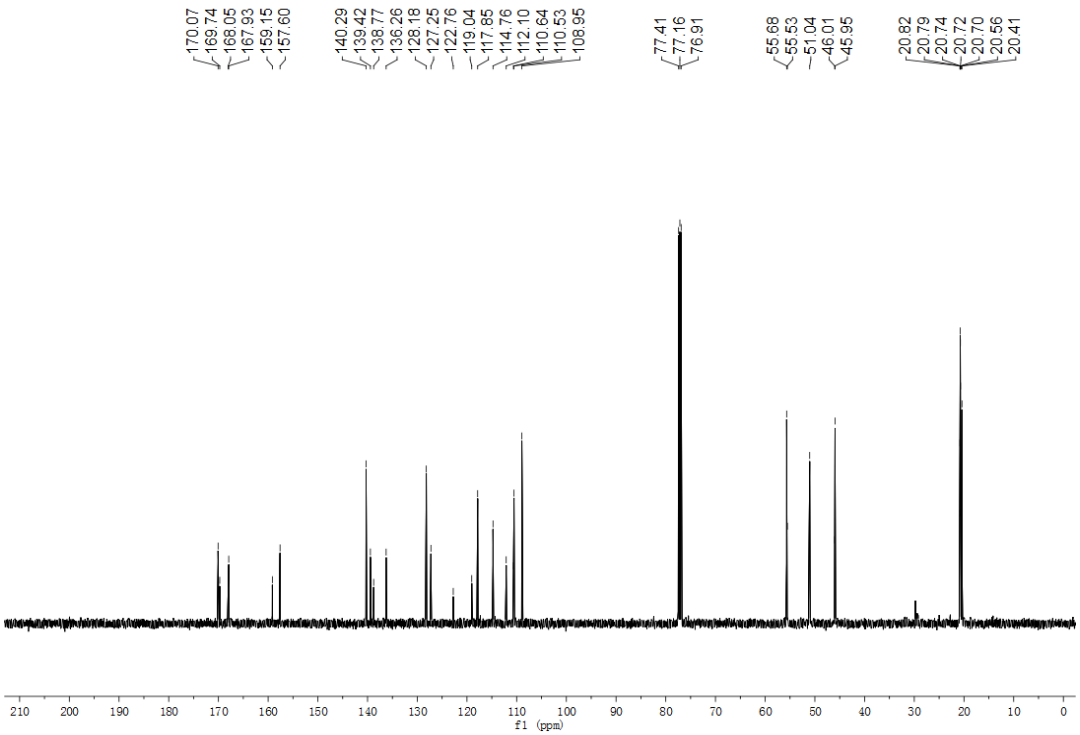
77.41
77.16
76.91
51.18
46.12
20.81
20.78
20.56
f1 (ppm)


MeO
OMe
OAc
3ua (C2/C6=2:1)
6.39
6.37
6.36
6.33
f1 (ppm)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139.42
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136.26
128.18
127.25
122.76
119.04
117.85
114.76
112.10
110.64
110.53
108.95
77.41
77.16
76.91
55.68
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51.04
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45.95
20.82
20.79
20.74
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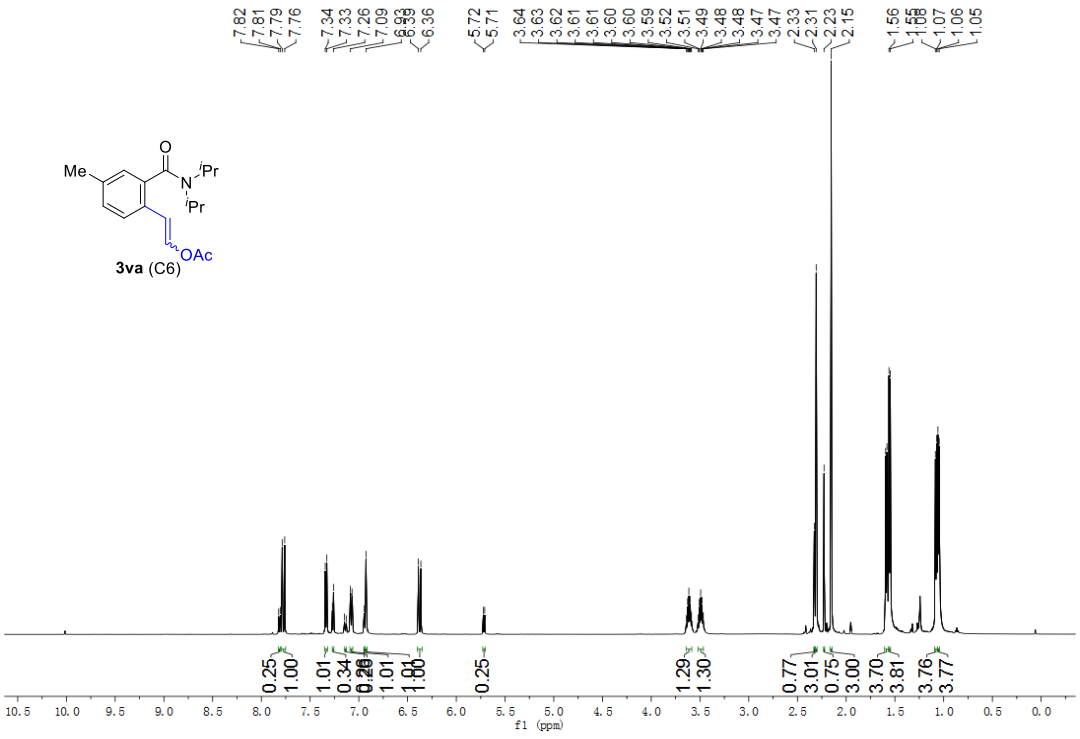
20.70
20.56
20.41
f1 (ppm)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3.63
3.62
3.61
3.61
3.60
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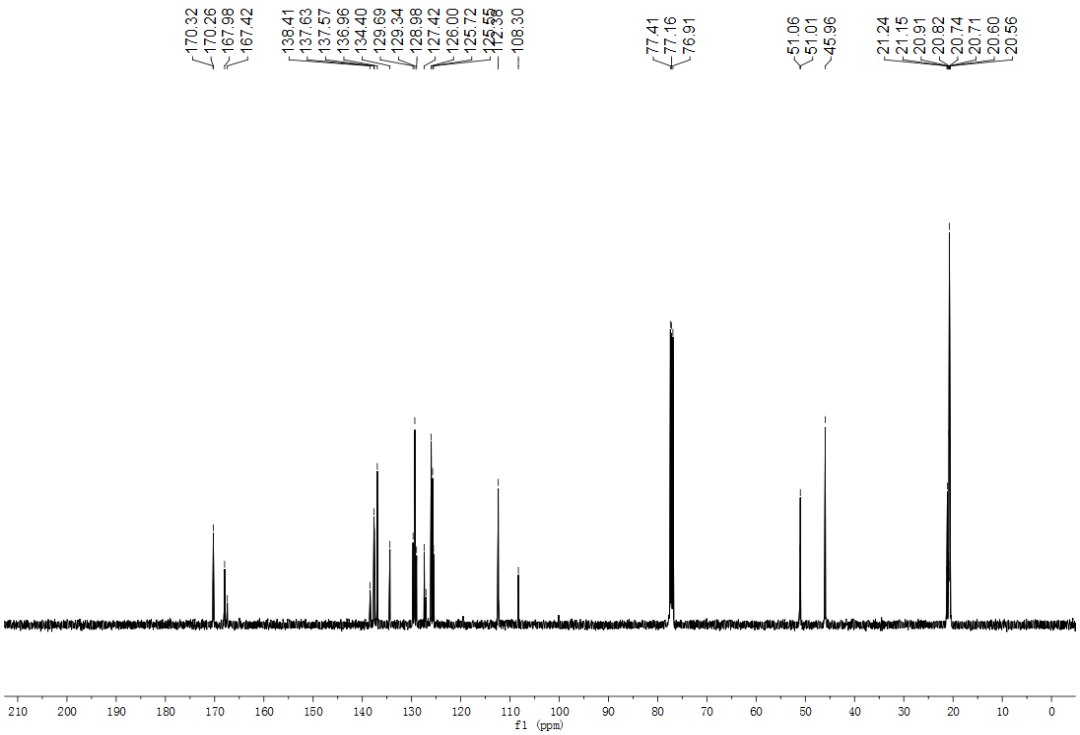
3.52
3.51
3.49
3.48
3.48
3.47
2.33
2.31
2.23
2.15
1.56
1.07
1.06
1.05
0.25
1.00
1.01
1.01
1.01
1.00
0.25
1.29
1.30
0.77
3.01
0.75
3.00
3.70
3.81
3.76
3.77
f1 (ppm)

Me
O
N
iPr
iPr
OAc

3va (C6)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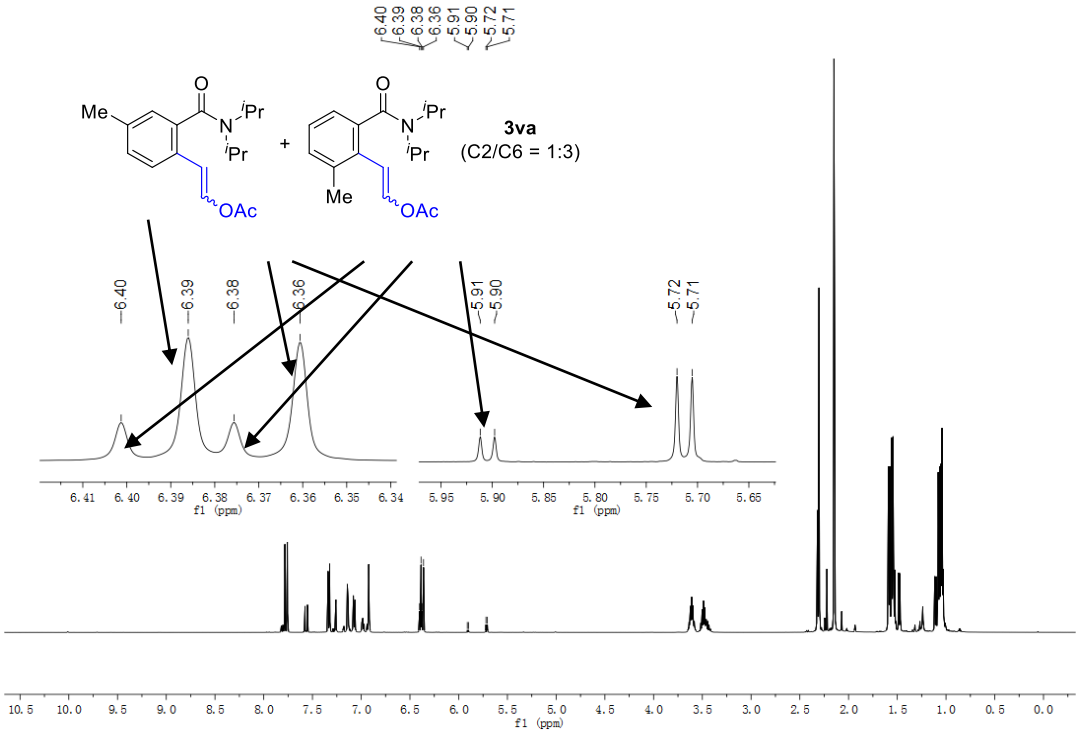
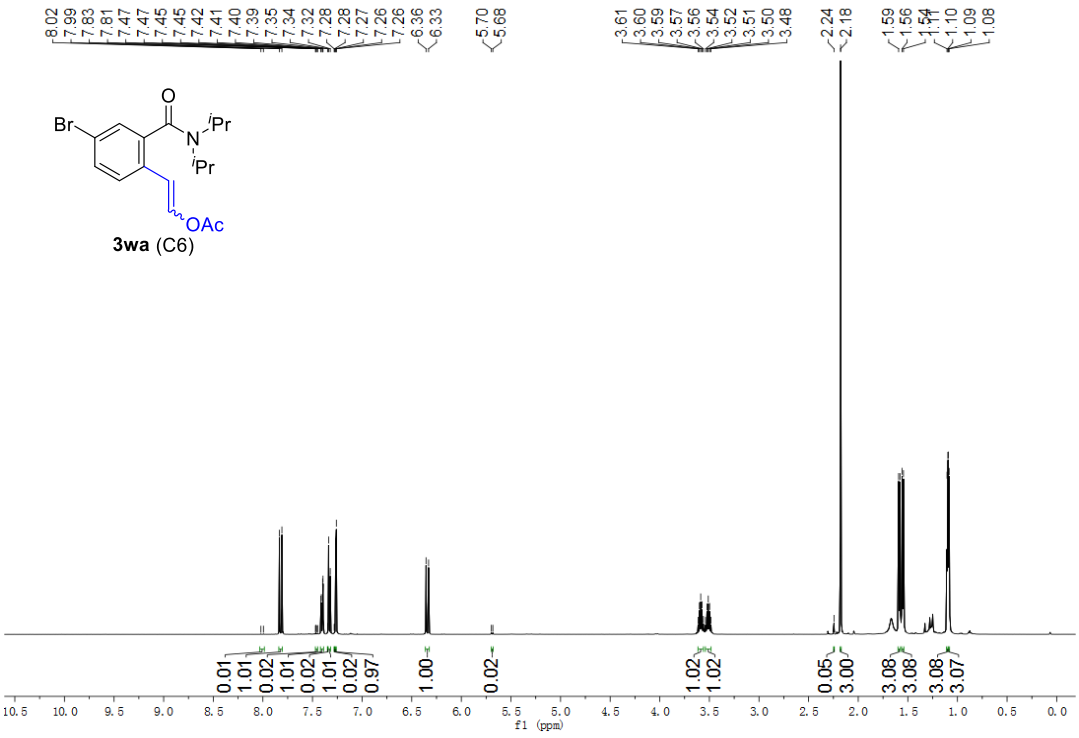
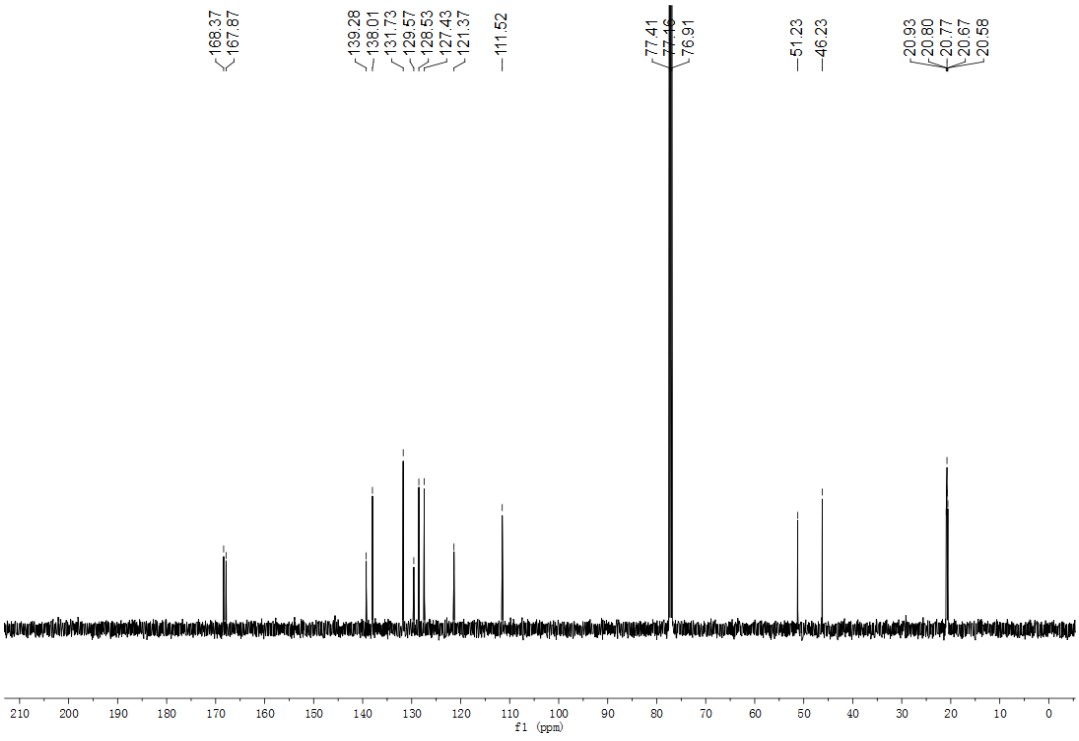
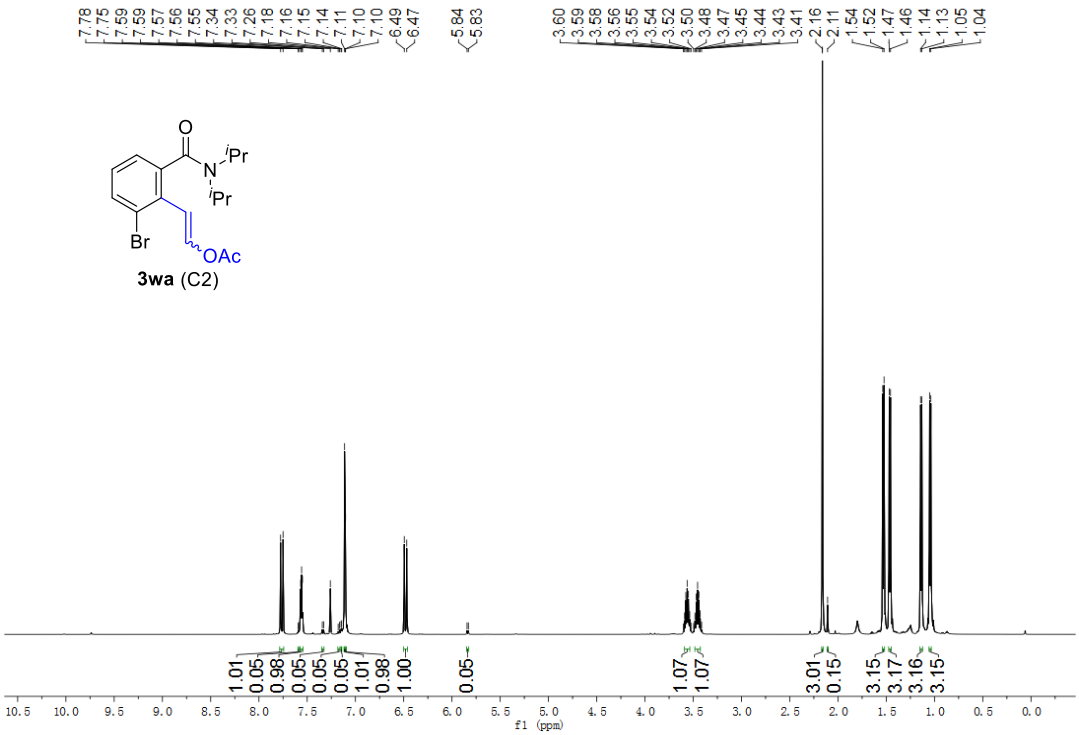
129.34
128.98
127.42
126.00
125.72
125.55
112.38
108.30
77.41
77.16
76.91
51.06
51.01
45.96
21.24
21.15
20.91
20.82
20.74
20.71
20.60
20.56
f1 (ppm)

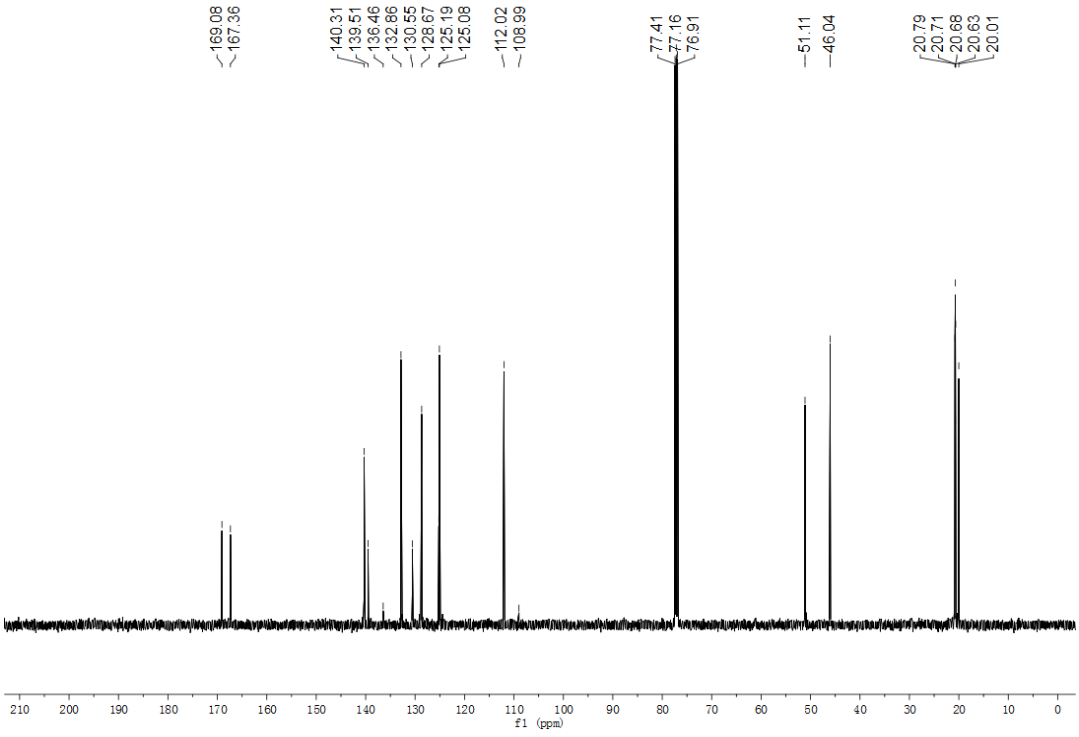

6.40
6.39
6.38
6.36
5.91
5.90
5.72
5.71
Me
O
N
iPr
iPr
OAc
+
Me
3va
(C2/C6 = 1:3)
f1 (ppm)

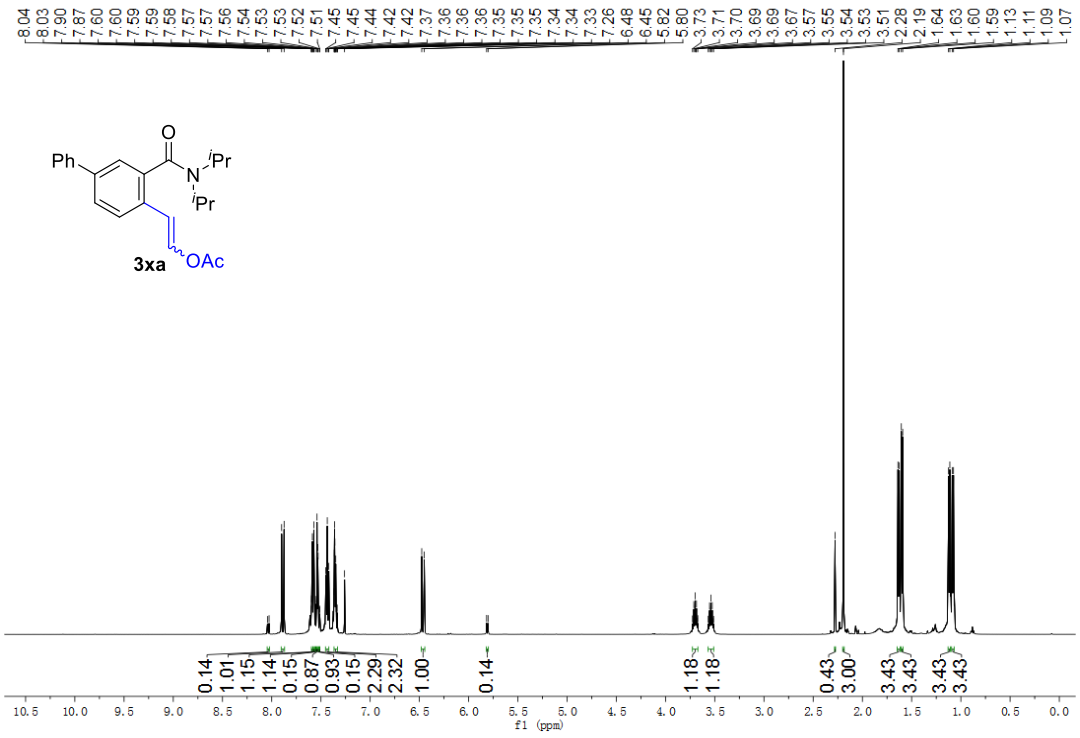

8.02
7.99
7.83
7.81
7.47
7.47
7.45
7.45
7.42
7.41
7.40
7.39
7.35
7.34
7.32
7.28
7.28
7.27
7.26
7.26
6.36
6.33
5.70
5.68
3.61
3.60
3.59
3.57
3.56
3.54
3.52
3.51
3.50
3.48
2.24
2.18
1.59
1.56
1.54
1.11
1.10
1.09
1.08
Br
O
N
iPr
iPr
OAc
3wa (C6)
0.01
1.01
0.02
1.01
0.02
1.01
0.02
0.97
1.00
0.02
1.02
1.02
0.05
3.00
3.08
3.08
3.08
3.07
f1 (ppm)

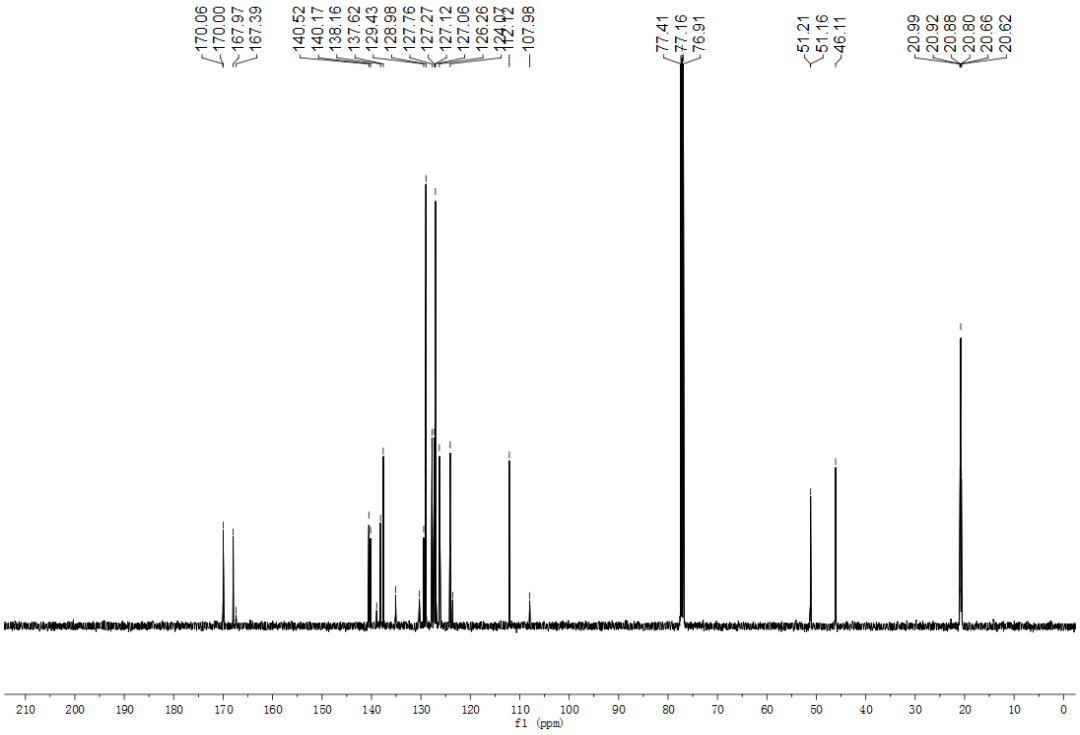

168.37
167.87
139.28
138.01
131.73
129.57
128.53
127.43
121.37
111.52
77.41
77.16
76.91
51.23
46.23
20.93
20.80
20.77
20.67
20.58
f1 (ppm)

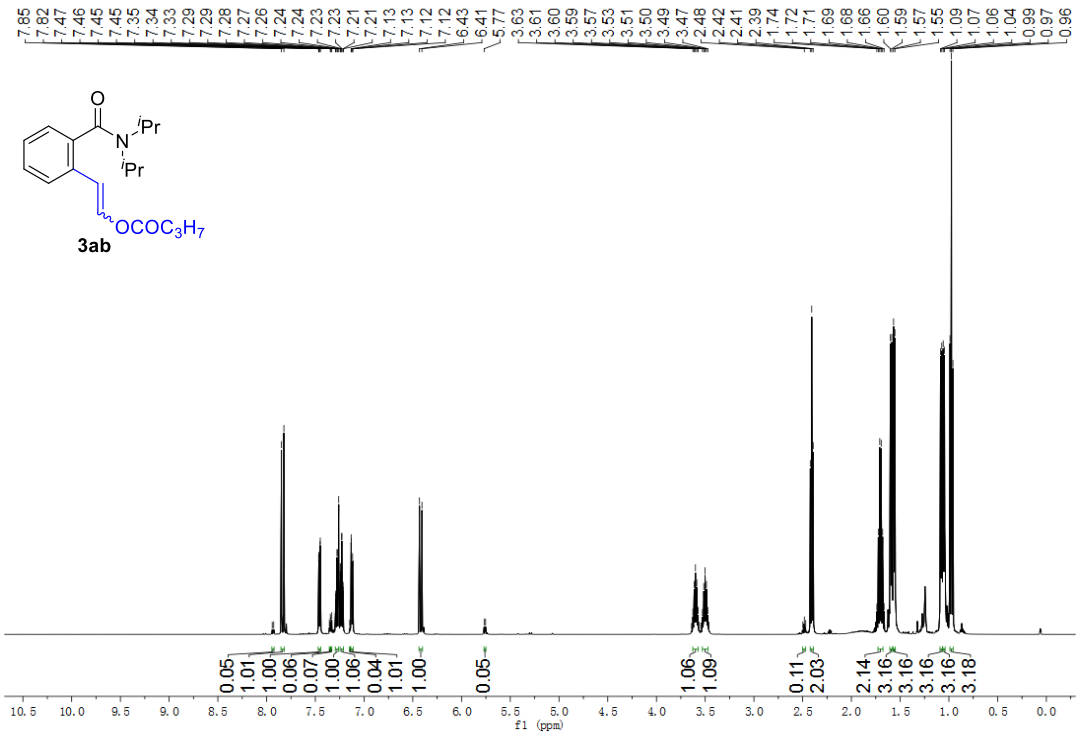

7.78
7.75
7.59
7.59
7.57
7.56
7.55
7.34
7.33
7.26
7.18
7.16
7.15
7.14
7.11
7.10
7.10
6.49
6.47
5.84
5.83
3.60
3.59
3.58
3.56
3.55
3.54
3.52
3.50
3.48
3.47
3.45
3.44
3.43
3.41
2.16
2.11
1.54
1.52
1.47
1.46
1.14
1.13
1.05
1.04
O
N
iPr
iPr
Br
OAc
1.01
0.05
0.98
0.05
0.05
0.05
1.01
0.98
1.00
0.05
1.07
1.07
3.01
0.15
3.15
3.17
3.16
3.15
f1 (ppm)

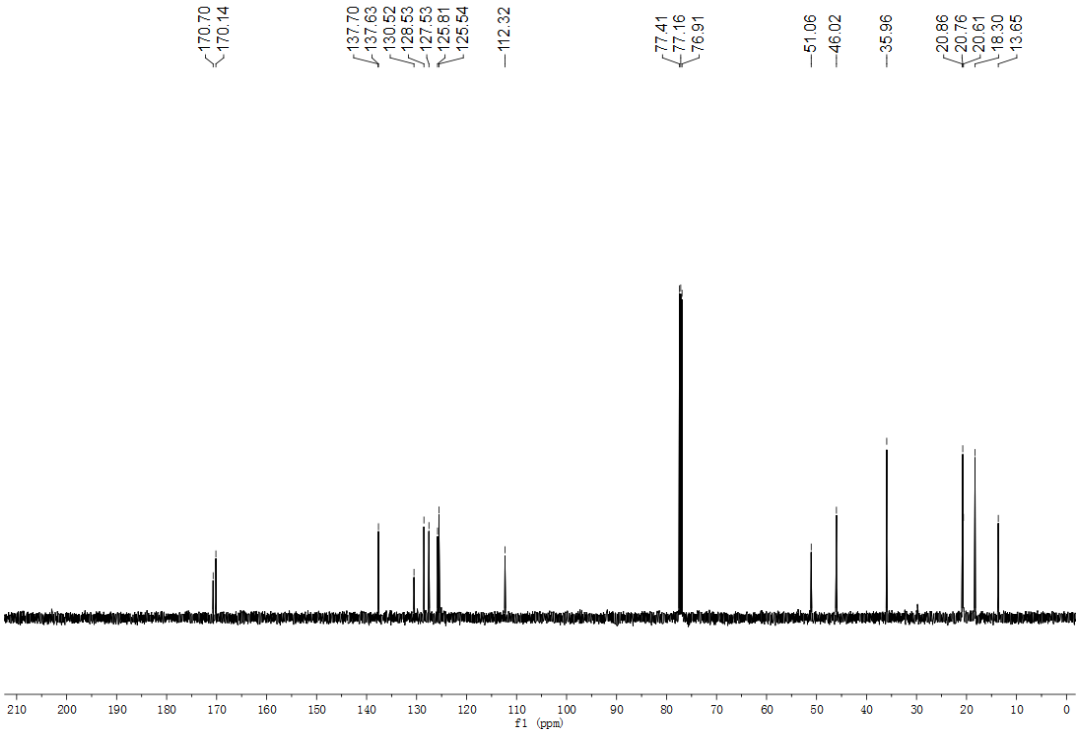
3wa (C2)

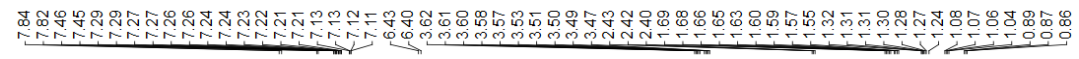

169.08
167.36
140.31
139.51
136.46
132.86
130.55
128.67
125.19
125.08
112.02
108.99
77.41
77.16
76.91
51.11
46.04
20.79
20.71
20.68
20.63
20.01
f1 (ppm)

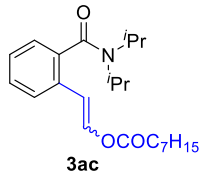

Ph
O
N
iPr
iPr
OAc
3xa
f1 (ppm)


f1 (ppm)

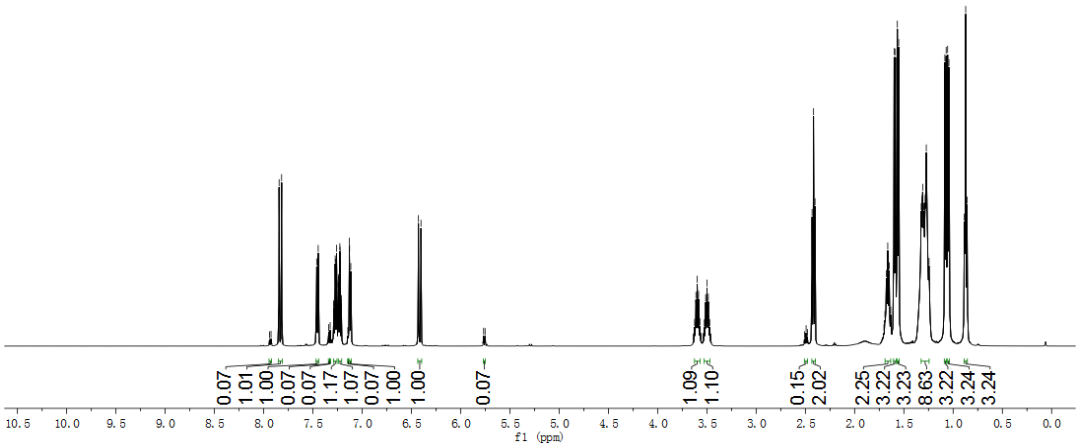

7.85 7.82 7.47 7.46 7.45 7.45 7.35 7.34 7.33 7.29 7.29 7.28 7.27 7.26 7.24 7.24 7.23 7.23 7.21 7.21 7.13 7.13 7.12 7.12 6.43 6.41 5.77
3.63 3.61 3.60 3.59 3.57 3.53 3.51 3.50 3.49 3.47 2.48 2.42 2.41 2.39 1.74 1.72 1.71 1.69 1.68 1.66 1.60 1.59 1.57 1.55 1.09 1.07 1.06 1.04 0.99 0.97 0.96
O
N
iPr
iPr
OCOC3H7
3ab
0.05 1.01 1.00 0.06 0.07 1.00 1.06 0.04 1.01 1.00 0.05 1.06 1.09 0.11 2.03 2.14 3.16 3.16 3.16 3.16 3.18
f1 (ppm)

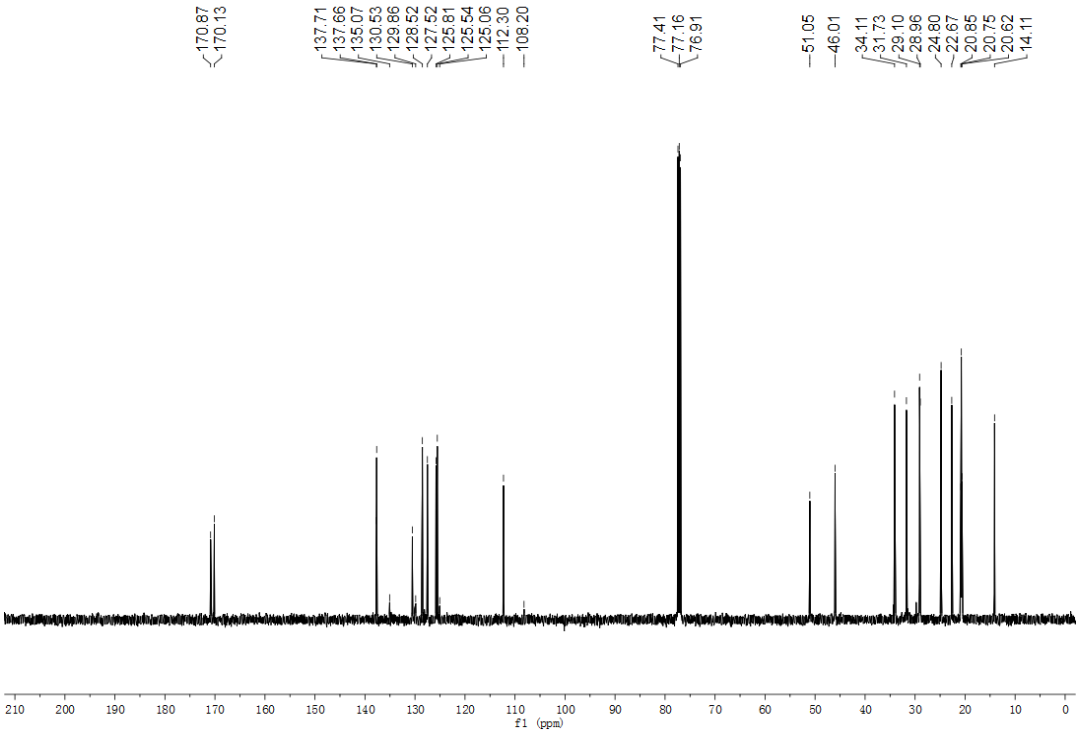

170.70 170.14 137.70 137.63 130.52 128.53 127.53 125.81 125.54 112.32 77.41 77.16 76.91 51.06 46.02 35.96 20.86 20.76 20.61 18.30 13.65
f1 (ppm)

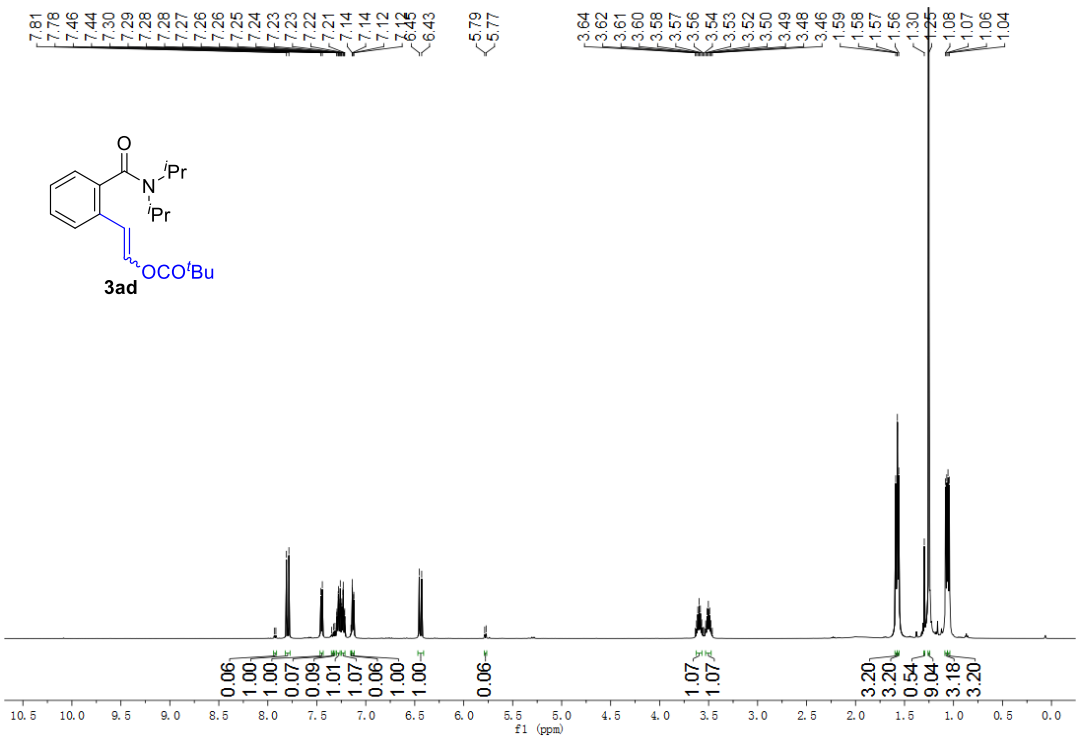


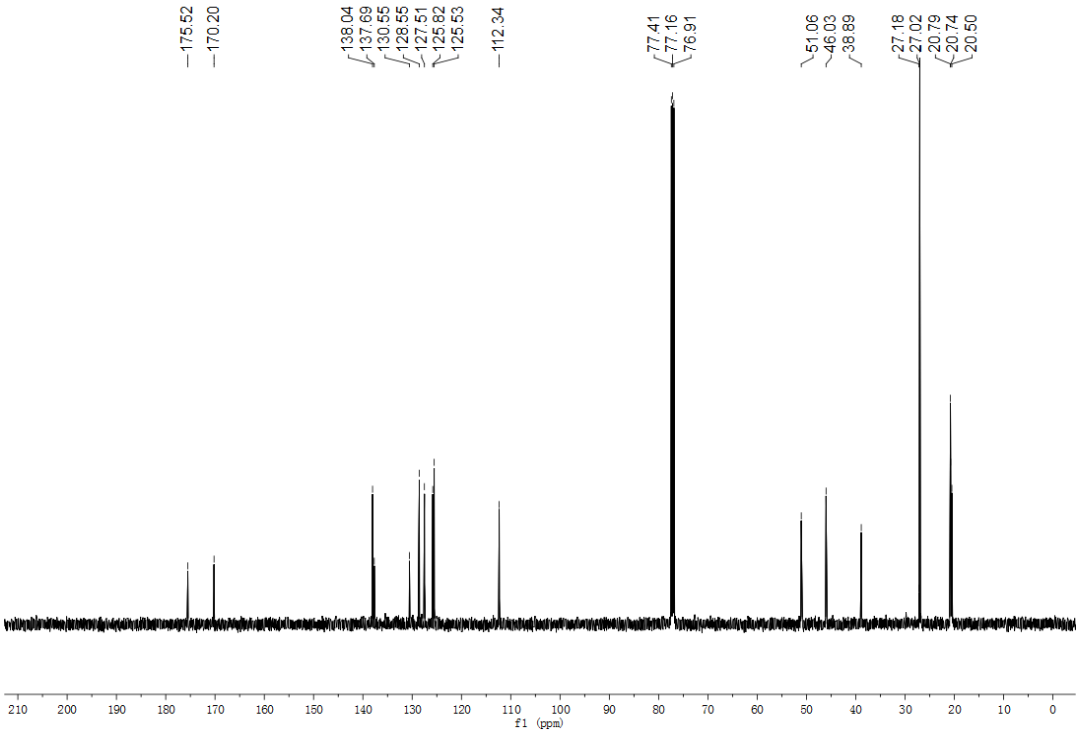


3ac






7.81
7.78
7.46
7.44
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.14
7.14
7.12
6.45
6.43
5.79
5.77
3.64
3.62
3.61
3.60
3.58
3.57
3.56
3.54
3.53
3.52
3.50
3.49
3.48
3.46
1.59
1.58
1.57
1.56
1.30
1.25
1.08
1.07
1.06
1.04
O
N
iPr
iPr
OCOtBu
3ad
0.06
1.00
1.00
0.07
0.09
1.01
1.07
0.06
1.00
1.00
0.06
1.07
1.07
3.20
3.20
0.54
9.04
3.18
3.20
f1 (ppm)


175.52
170.20
138.04
137.69
130.55
128.55
127.51
125.82
125.53
112.34
77.41
77.16
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51.06
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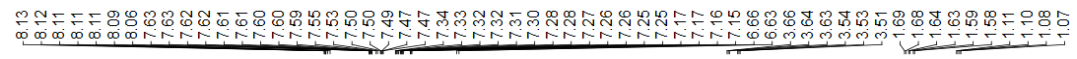
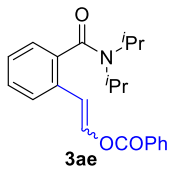
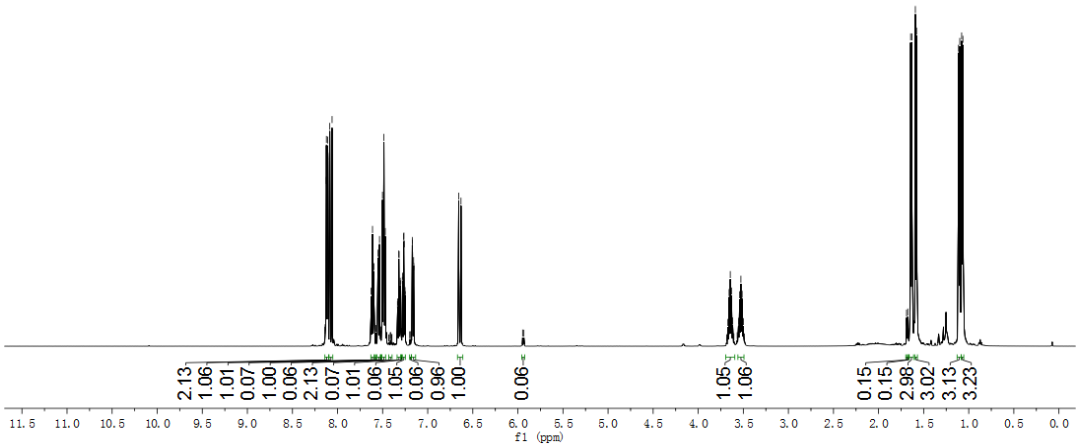
27.18
27.02
20.79
20.74
20.50
f1 (ppm)

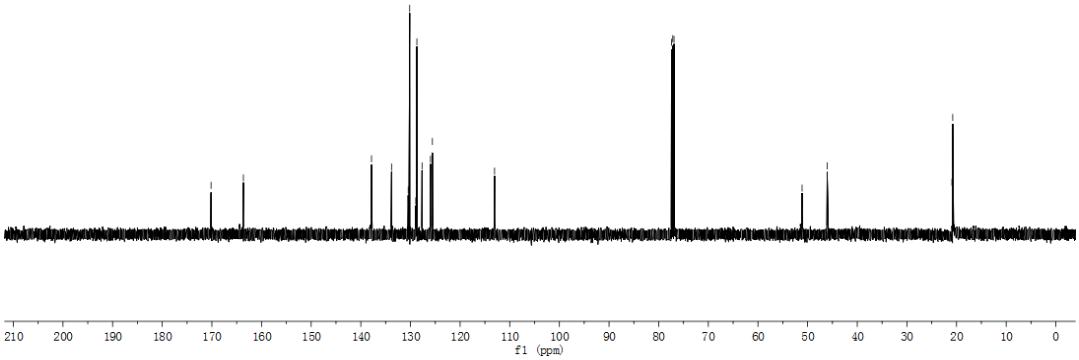


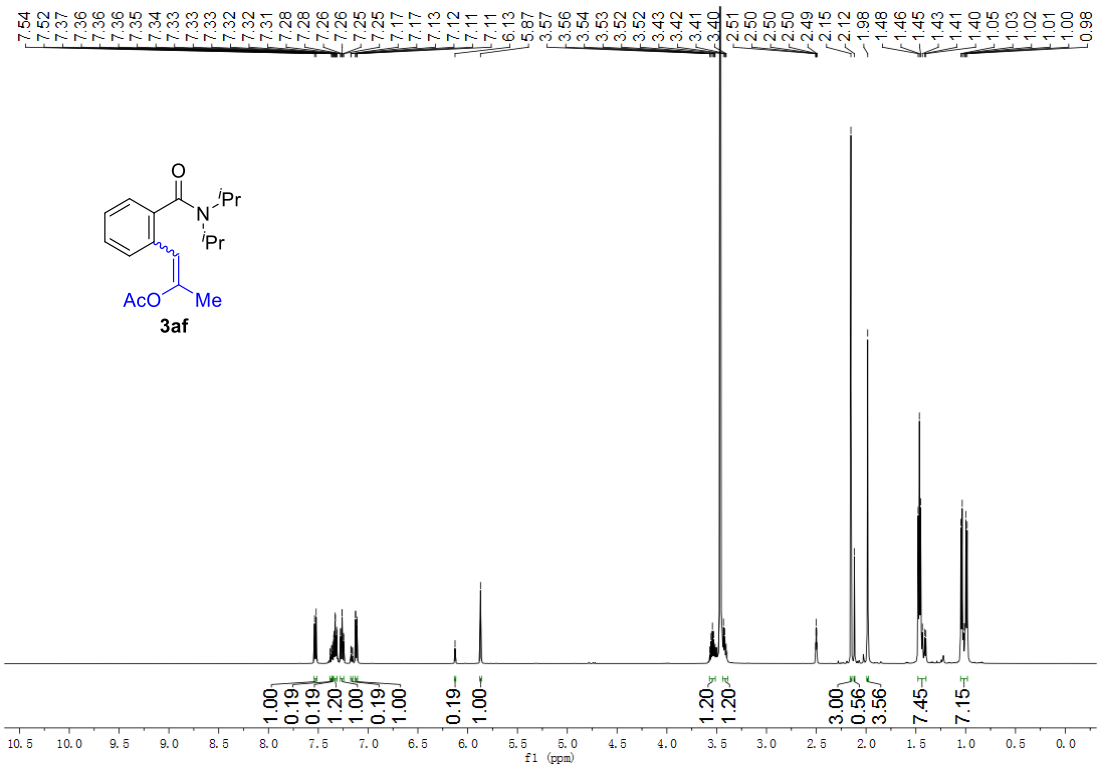

O
N
iPr
iPr
OCOPh

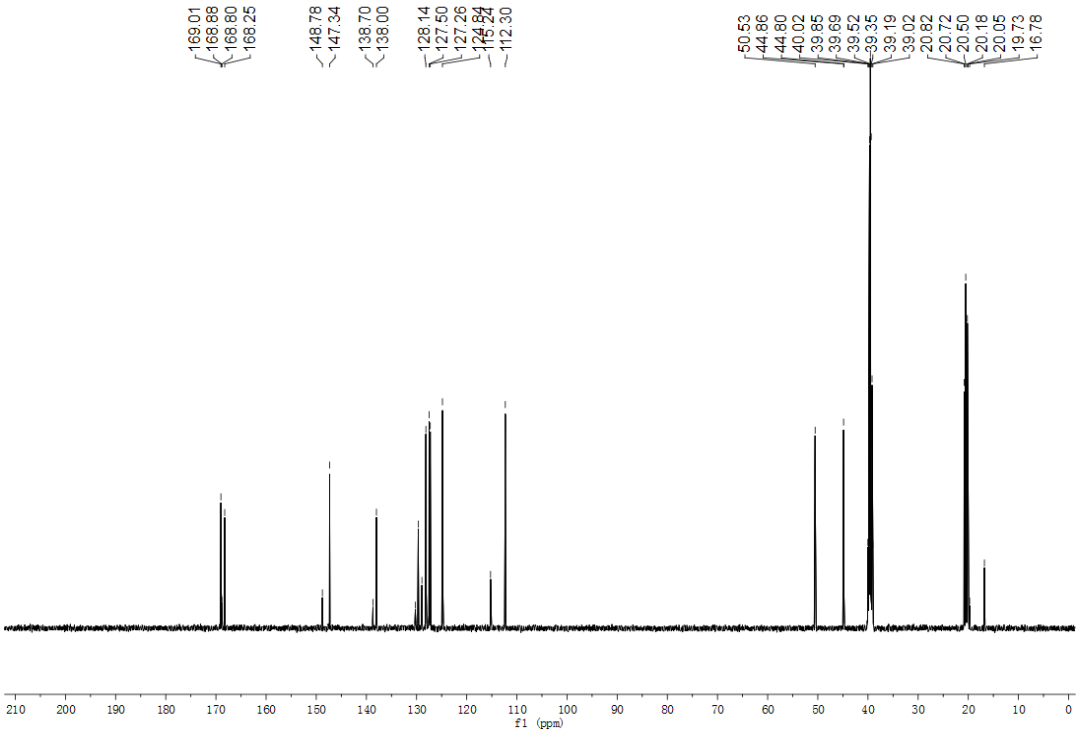
3ae


2.13
1.06
1.01
0.07
1.00
0.06
2.13
0.07
1.01
0.06
1.05
0.06
0.96
1.00
0.06
1.05
1.06
0.15
0.15
2.98
3.02
3.13
3.23
f1 (ppm)


170.16
163.65
137.85
137.77
133.81
130.45
130.26
130.16
128.93
128.73
128.71
128.60
127.66
125.97
125.58
113.06
77.41
77.16
76.91
51.12
46.06
20.93
20.77
20.68


f1 (ppm)


7.54
7.52
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.28
7.26
7.26
7.25
7.25
7.17
7.13
7.12
7.11
6.13
5.87
3.57
3.56
3.54
3.53
3.52
3.43
3.42
3.41
3.40
2.51
2.50
2.50
2.50
2.49
2.15
2.12
1.98
1.48
1.46
1.45
1.43
1.41
1.40
1.05
1.03
1.02
1.01
1.00
0.98
O
N
iPr
iPr
AcO
Me
3af
1.00
0.19
0.19
1.20
1.00
0.19
1.00
0.19
1.00
1.20
1.20
3.00
0.56
3.56
7.45
7.15
f1 (ppm)


169.01
168.88
168.80
168.25
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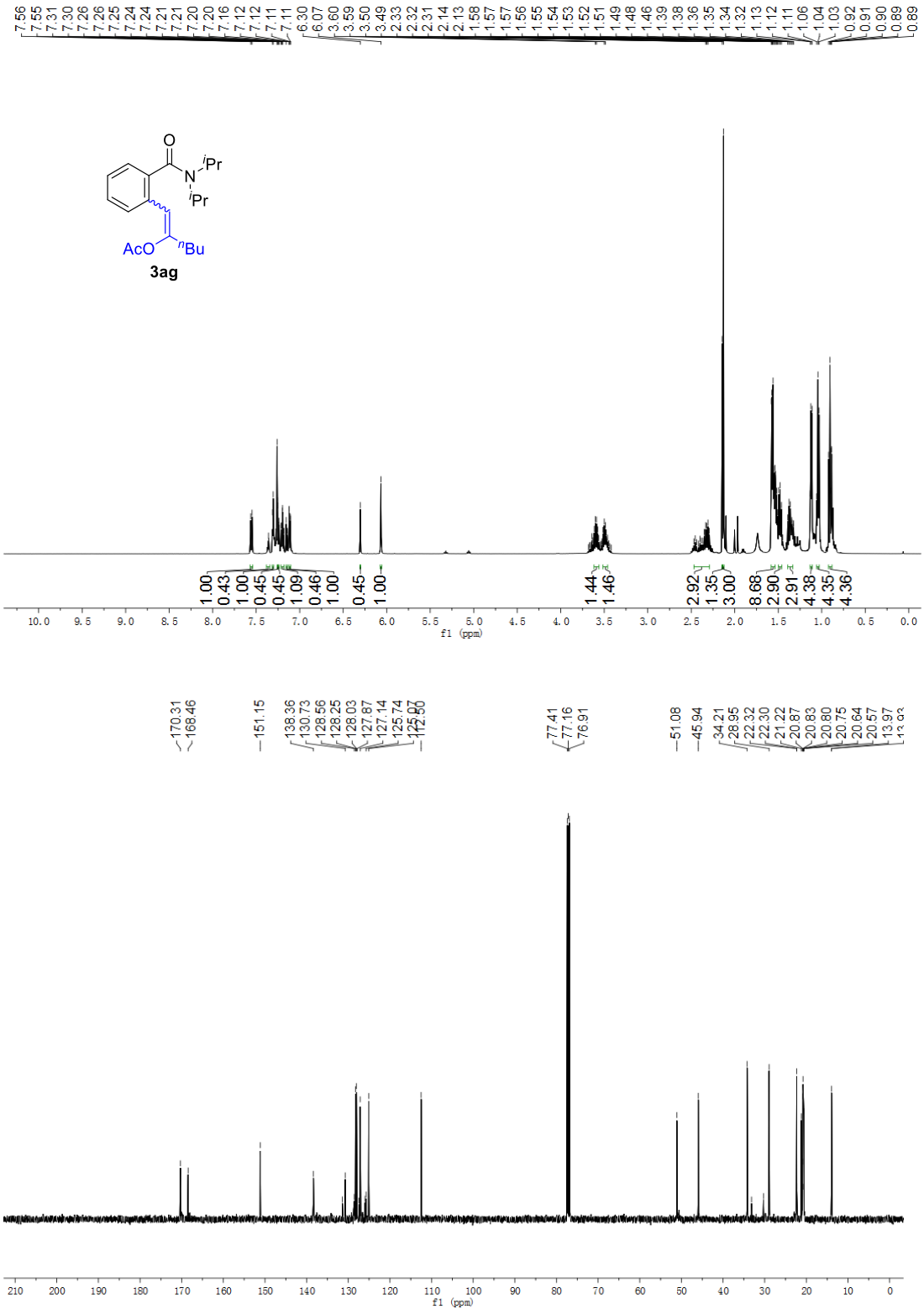
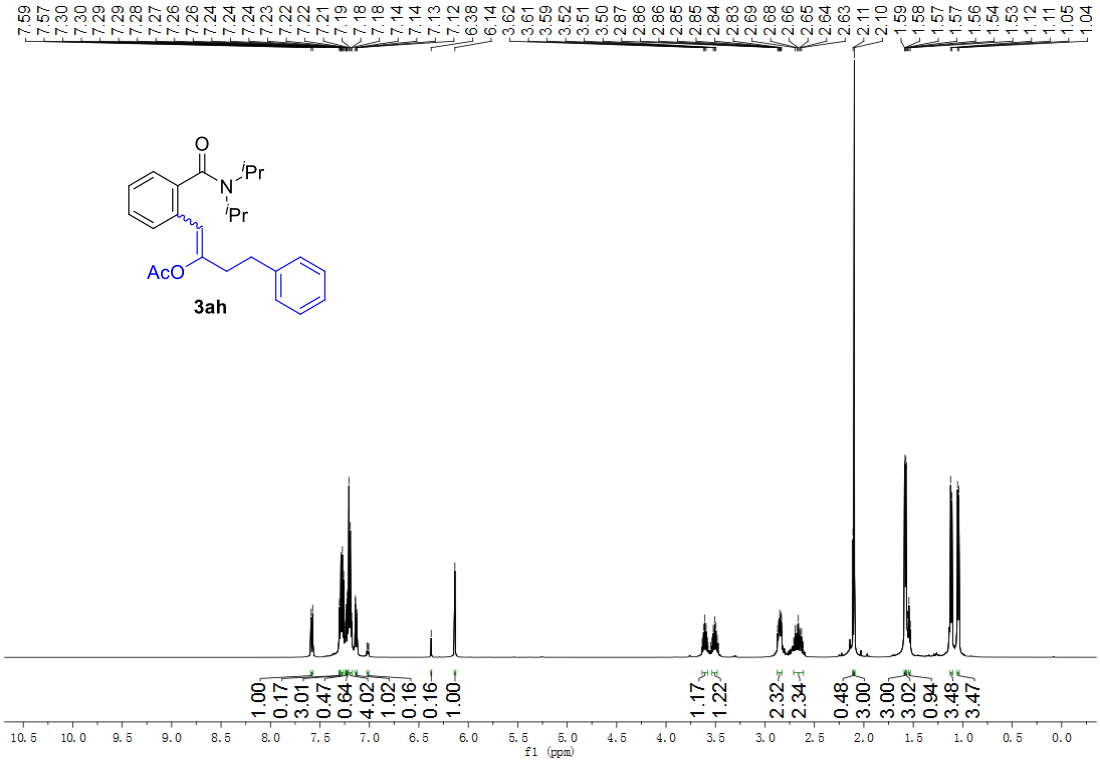
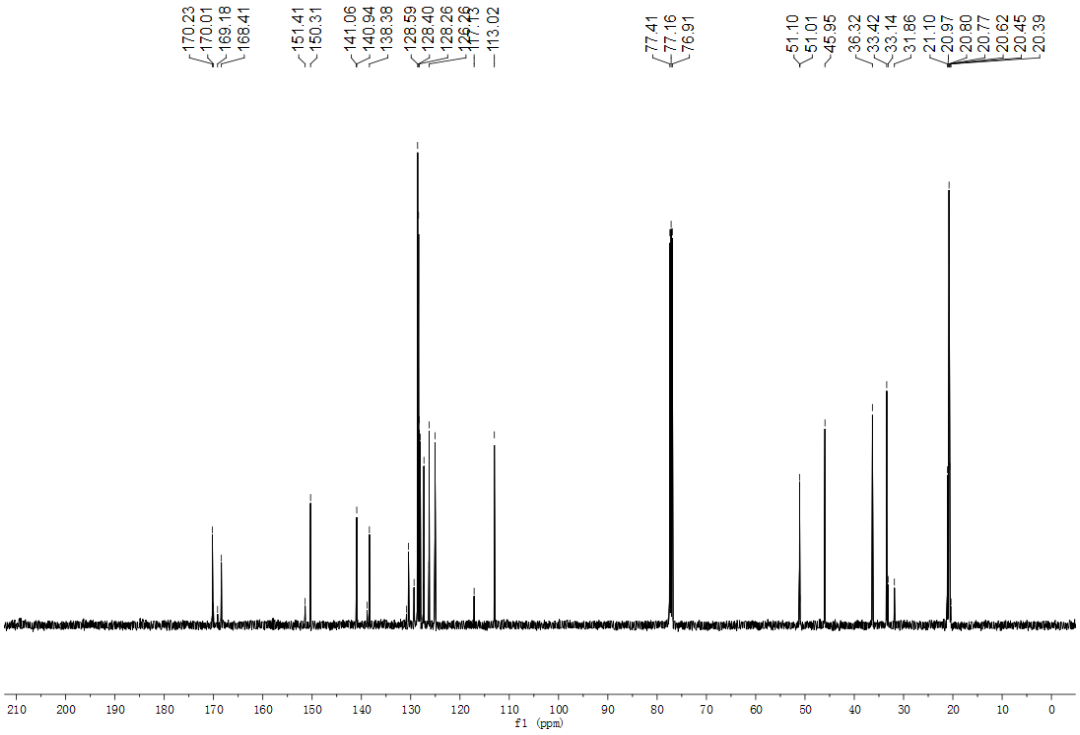
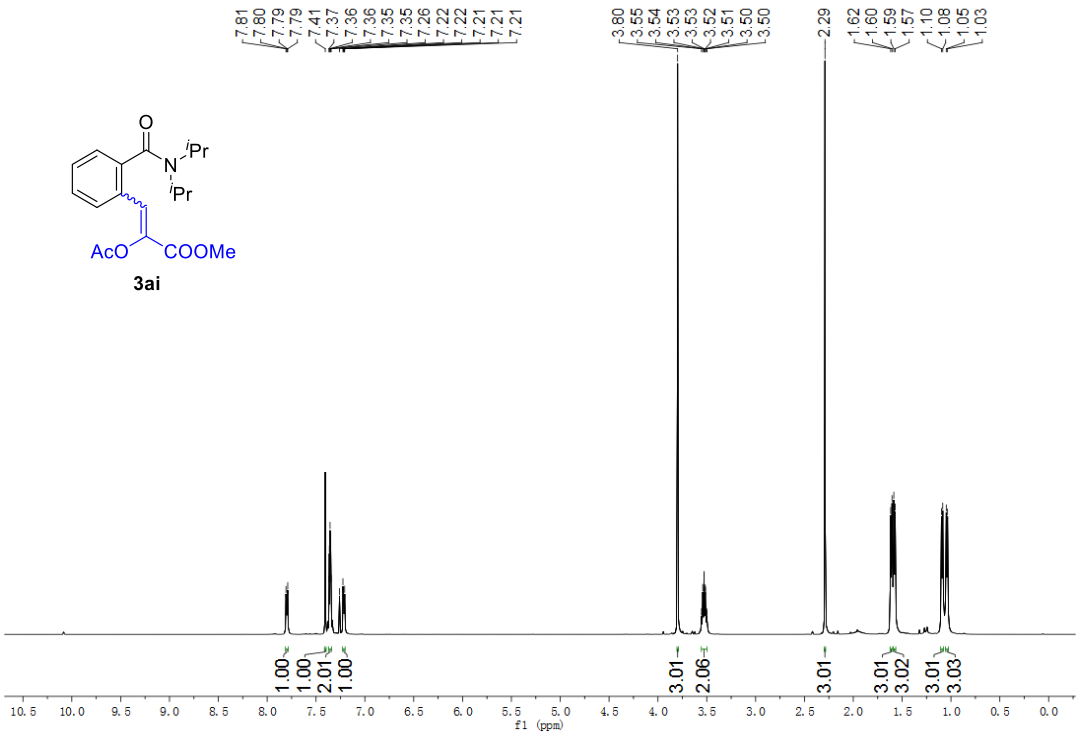
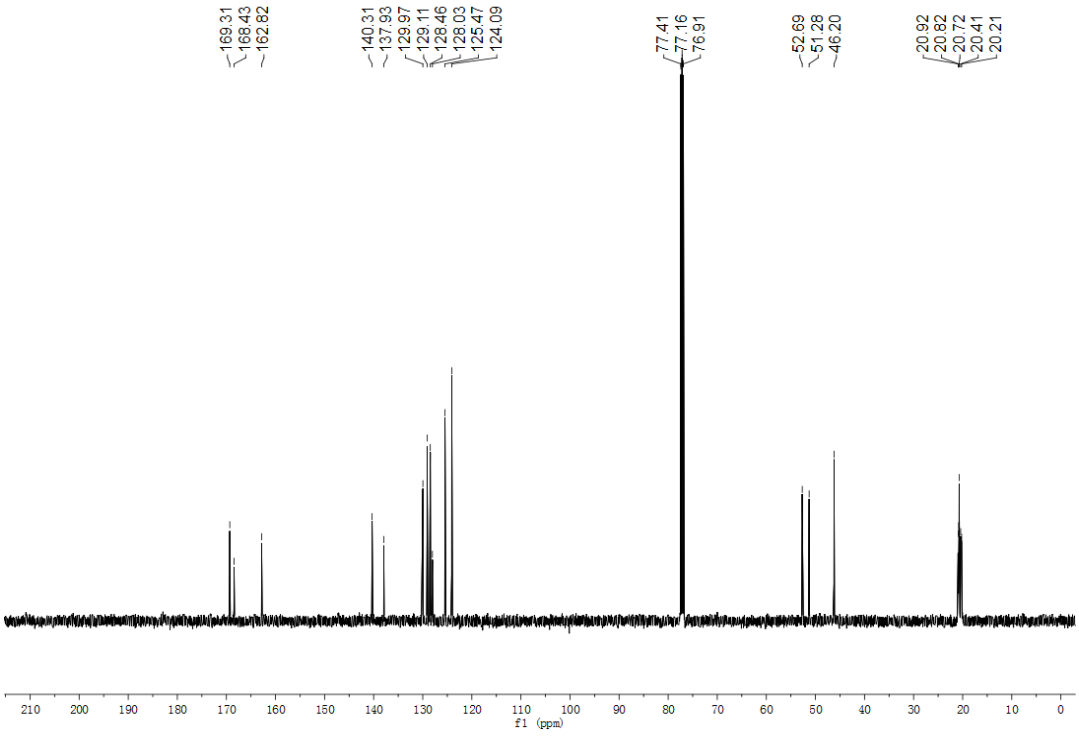
147.34
138.70
138.00
128.14
127.50
127.26
124.84
112.30
50.53
44.86
44.80
40.02
39.85
39.69
39.52
39.35
39.19
39.02
20.82
20.72
20.50
20.18
20.05
19.73
16.78
f1 (ppm)

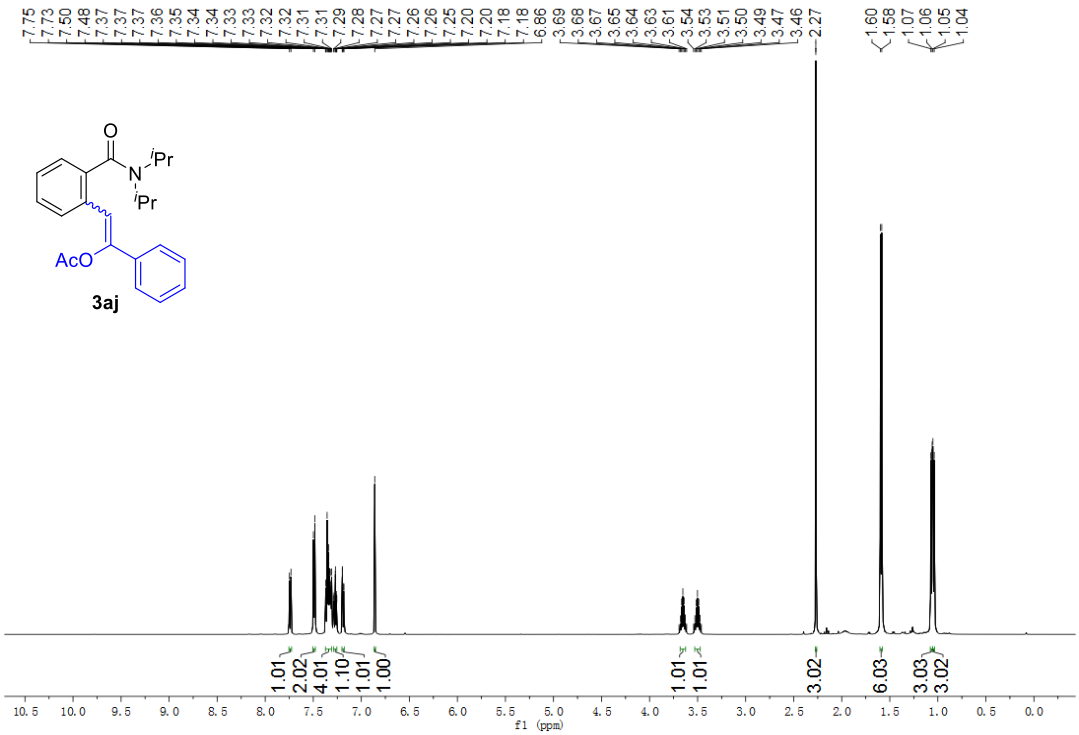

7.56 7.55 7.31 7.30 7.26 7.26 7.25 7.24 7.24 7.21 7.21 7.20 7.20 7.16 7.12 7.12 7.11 7.11 6.30 6.07 3.60 3.59 3.50 3.49 2.33 2.32 2.31 2.14 2.13 1.58 1.57 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.49 1.48 1.46 1.39 1.38 1.36 1.35 1.34 1.32 1.13 1.12 1.11 1.06 1.04 1.03 0.92 0.91 0.90 0.89 0.89
O
N
iPr
iPr
AcO
nBu
3ag
1.00 0.43 1.00 0.45 0.45 1.09 0.46 1.00 0.45 1.00 1.44 1.46 2.92 1.35 3.00 8.68 2.90 2.91 4.38 4.35 4.36
f1 (ppm)
170.31 168.46 151.15 138.36 130.73 128.56 128.25 128.03 127.87 127.14 125.74 125.07 112.50 77.41 77.16 76.91 51.08 45.94 34.21 28.95 22.32 22.30 21.22 20.87 20.83 20.80 20.75 20.64 20.57 13.97
f1 (ppm)

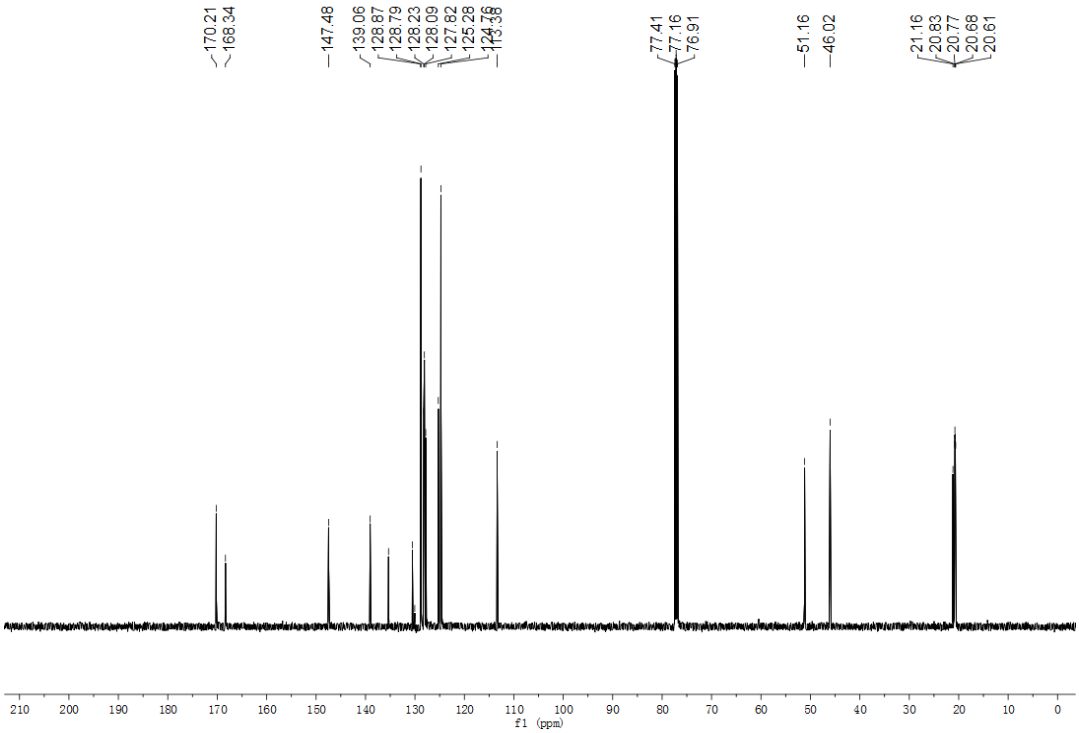

7.59 7.57 7.30 7.29 7.29 7.28 7.27 7.26 7.26 7.24 7.24 7.23 7.22 7.22 7.21 7.19 7.18 7.18 7.14 7.13 7.12 6.38 6.14
3.62 3.61 3.59 3.52 3.51 3.50 2.87 2.86 2.86 2.85 2.85 2.84 2.83 2.69 2.68 2.66 2.65 2.64 2.63 2.11 2.10 1.59 1.58 1.57 1.57 1.56 1.54 1.53 1.12 1.11 1.05 1.04
O
N
iPr
iPr
AcO
3ah
1.00 0.17 3.01 0.47 0.64 4.02 1.02 0.16 0.16 1.00 1.17 1.22 2.32 2.34 0.48 3.00 3.00 3.02 0.94 3.48 3.47
f1 (ppm)

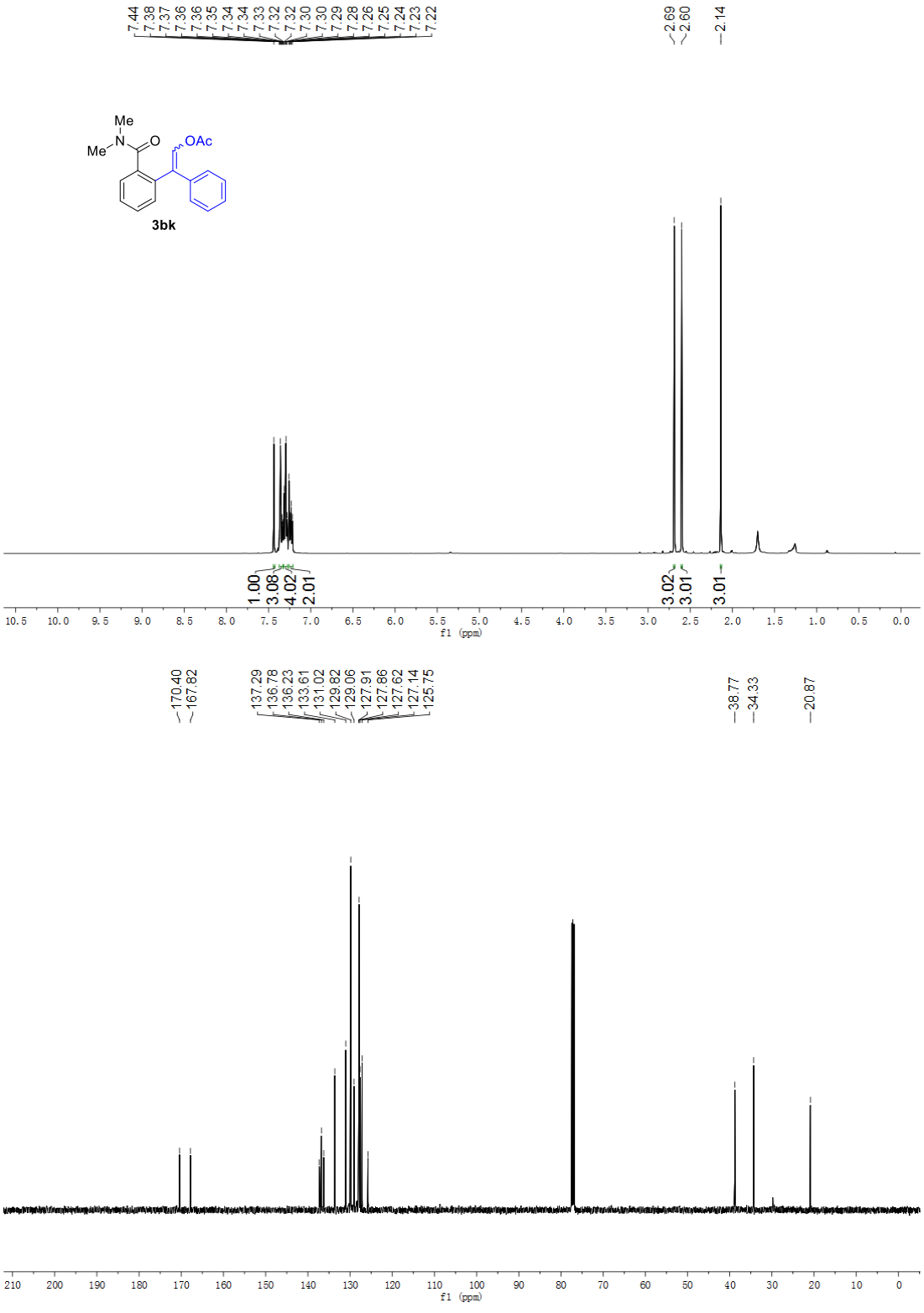

170.23 170.01 169.18 168.41 151.41 150.31 141.06 140.94 138.38 128.59 128.40 128.26 113.02 77.41 77.16 76.91 51.10 51.01 45.95 36.32 33.42 33.14 31.86 21.10 20.97 20.80 20.77 20.62 20.45 20.39
f1 (ppm)


7.81
7.80
7.79
7.79
7.41
7.37
7.36
7.36
7.35
7.35
7.26
7.22
7.22
7.21
7.21
7.21
3.80
3.55
3.54
3.53
3.53
3.52
3.51
3.50
3.50
2.29
1.62
1.60
1.59
1.57
1.10
1.08
1.05
1.03
O
N
iPr
iPr
AcO
COOMe
3ai
1.00
1.00
2.01
1.00
3.01
2.06
3.01
3.01
3.02
3.01
3.03
f1 (ppm)


169.31
168.43
162.82
140.31
137.93
129.97
129.11
128.46
128.03
125.47
124.09
77.41
77.16
76.91
52.69
51.28
46.20
20.92
20.82
20.72
20.41
20.21
f1 (ppm)


7.75 7.73 7.50 7.48 7.37 7.37 7.37 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.20 7.18 7.18 6.86 3.69 3.68 3.67 3.65 3.64 3.63 3.61 3.54 3.53 3.51 3.50 3.49 3.47 3.46 2.27 1.60 1.58 1.07 1.06 1.05 1.04
O
N
iPr
iPr
AcO
3aj
1.01 2.02 4.01 1.10 1.01 1.00 1.01 1.01 3.02 6.03 3.03 3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.21 168.34 147.48 139.06 128.87 128.79 128.23 128.09 127.82 125.28 124.76 113.38 77.41 77.16 76.91 51.16 46.02 21.16 20.83 20.77 20.68 20.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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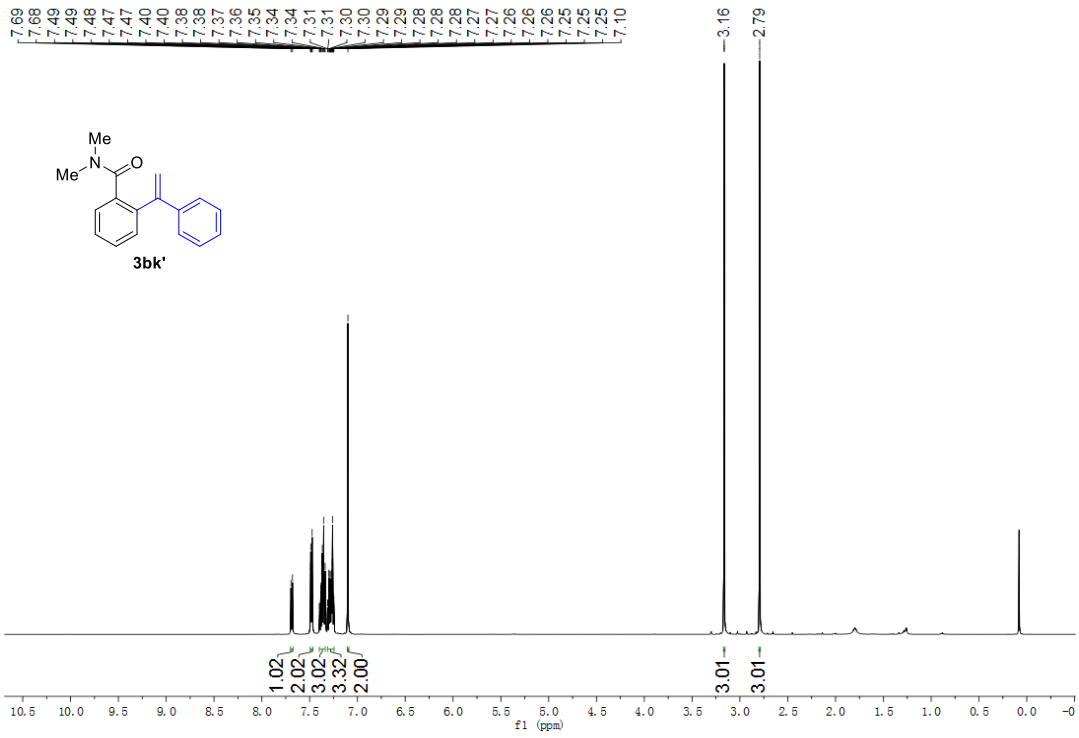
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.28
7.26
7.25
7.24
7.23
7.22
2.69
2.60
2.14
Me
N
Me
O
OAc
3bk
1.00
3.08
4.02
2.01
3.02
3.01
3.01
f1 (ppm)
170.40
167.82
137.29
136.78
136.23
133.61
131.02
129.82
129.06
127.91
127.86
127.62
127.14
125.75
38.77
34.33
20.87
f1 (ppm)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7.34
7.34
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7.31
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7.25
7.10
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2.79
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O
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3.02
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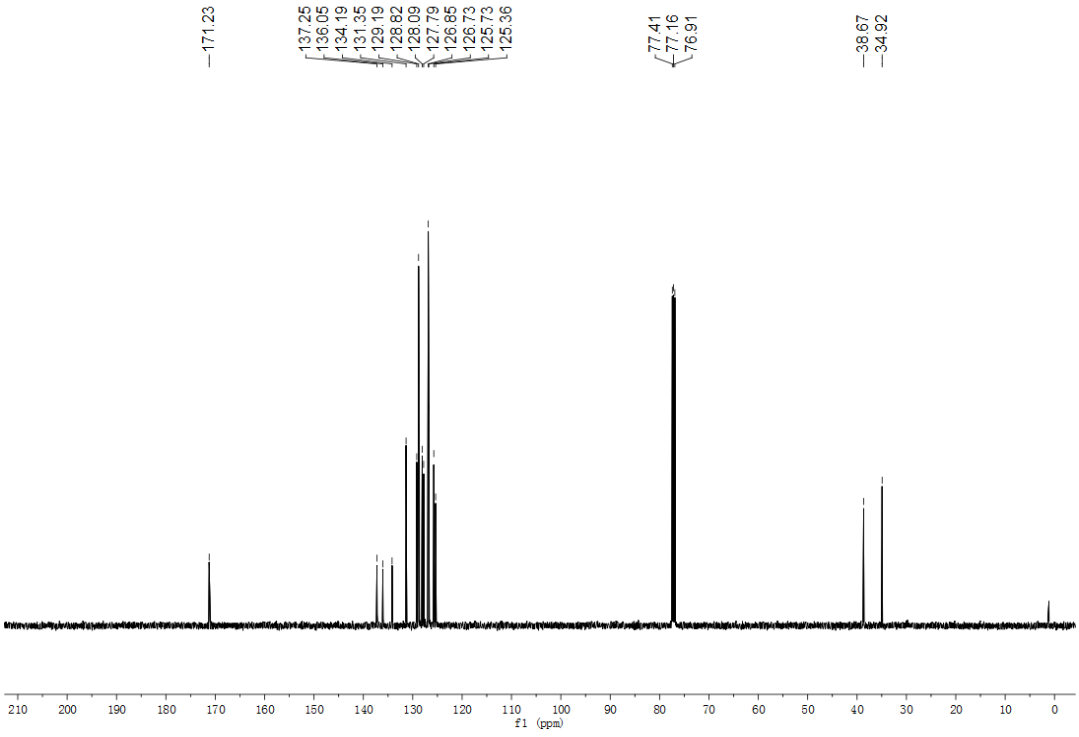
3.01
f1 (ppm)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76.91
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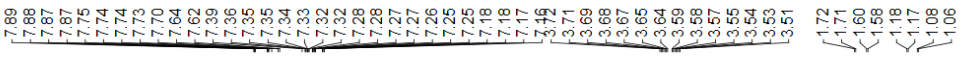
34.92
f1 (ppm)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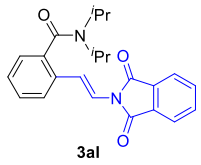
1.08
1.06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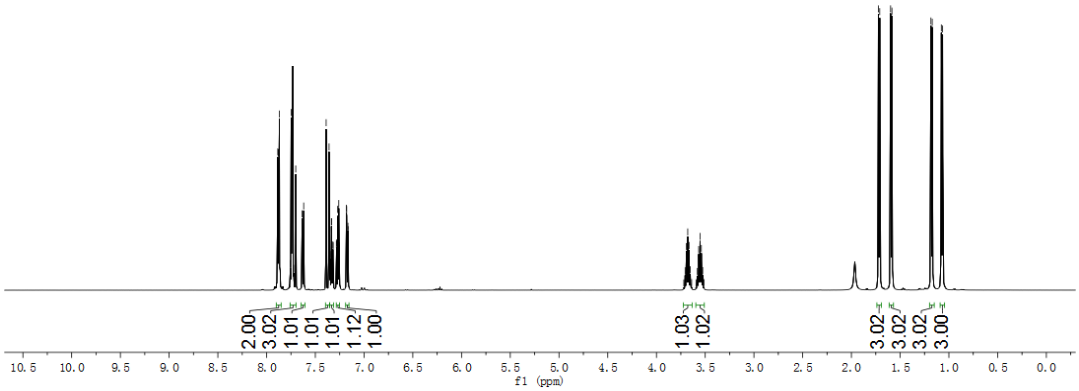
O
N
O

3al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9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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1.5
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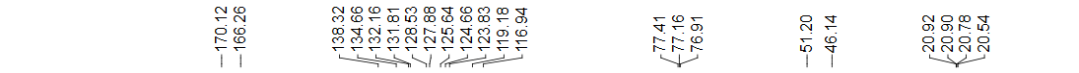
f1 (ppm)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124.66
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76.91
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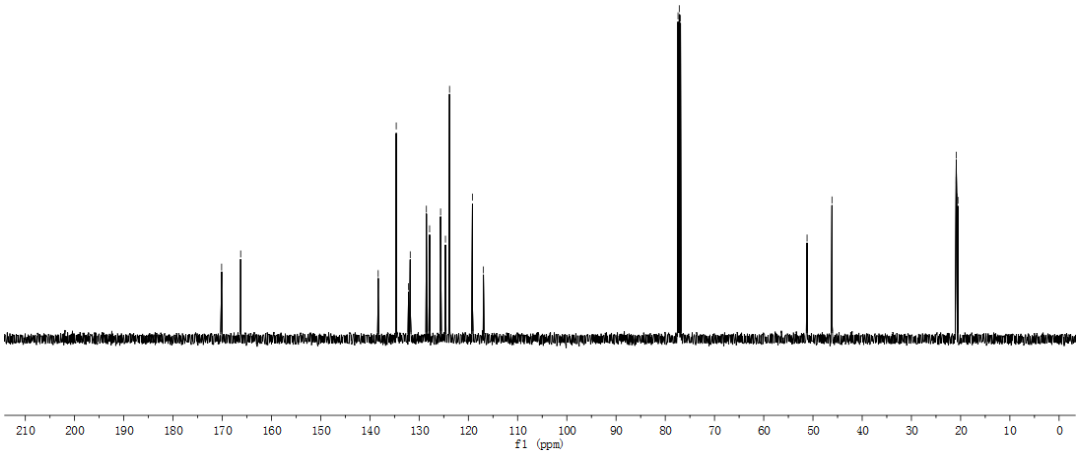
20.54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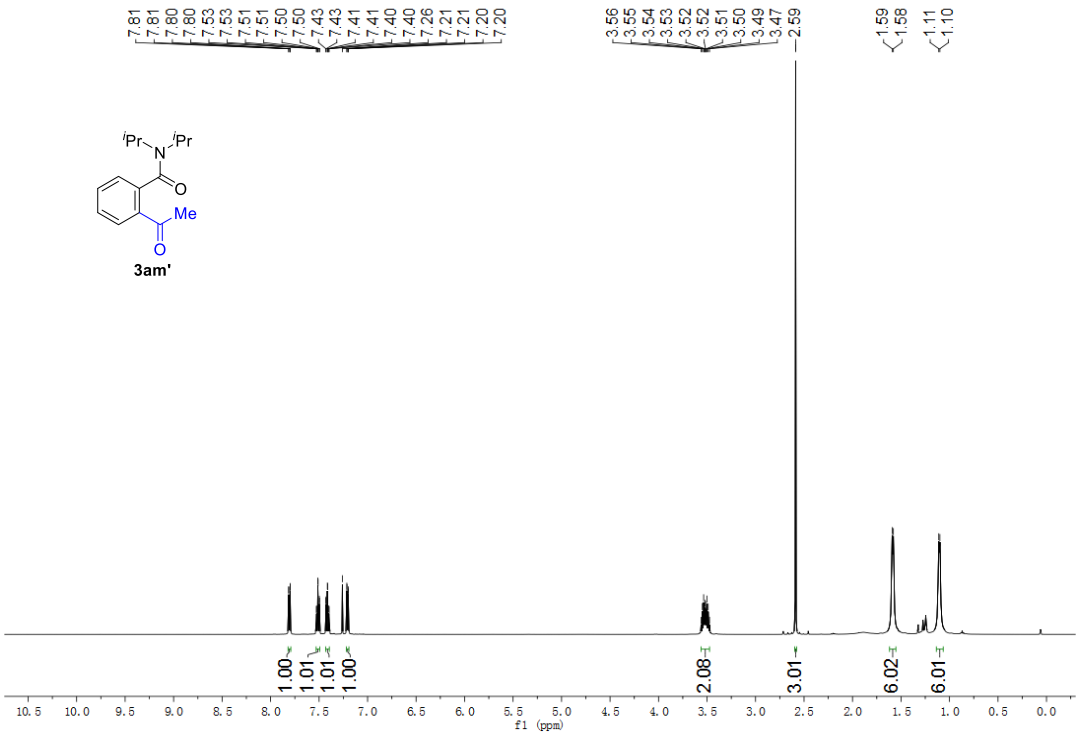
f1 (ppm)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7.41
7.41
7.40
7.40
7.26
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7.21
7.20
7.20
3.56
3.55
3.54
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3.52
3.52
3.51
3.50
3.49
3.47
2.59
1.59
1.58
1.11
1.10
iPr
N
iPr
O
Me
O
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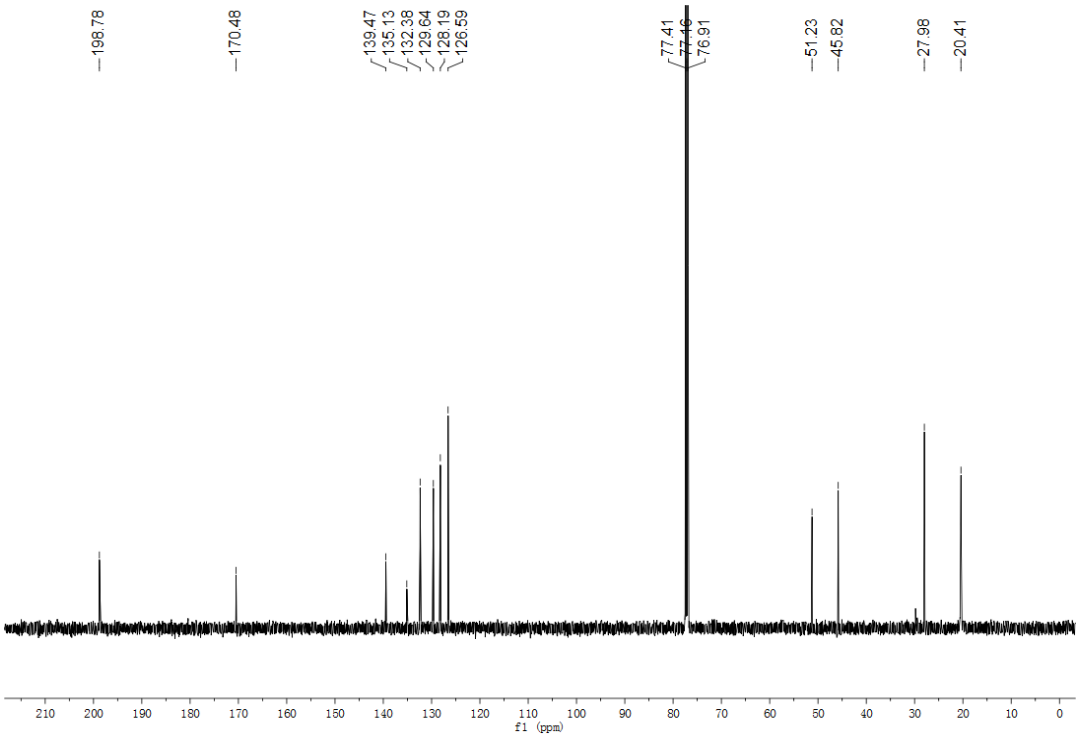
1.01
1.01
1.00
2.08
3.01
6.02
6.01
f1 (ppm)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77.16
76.91
51.23
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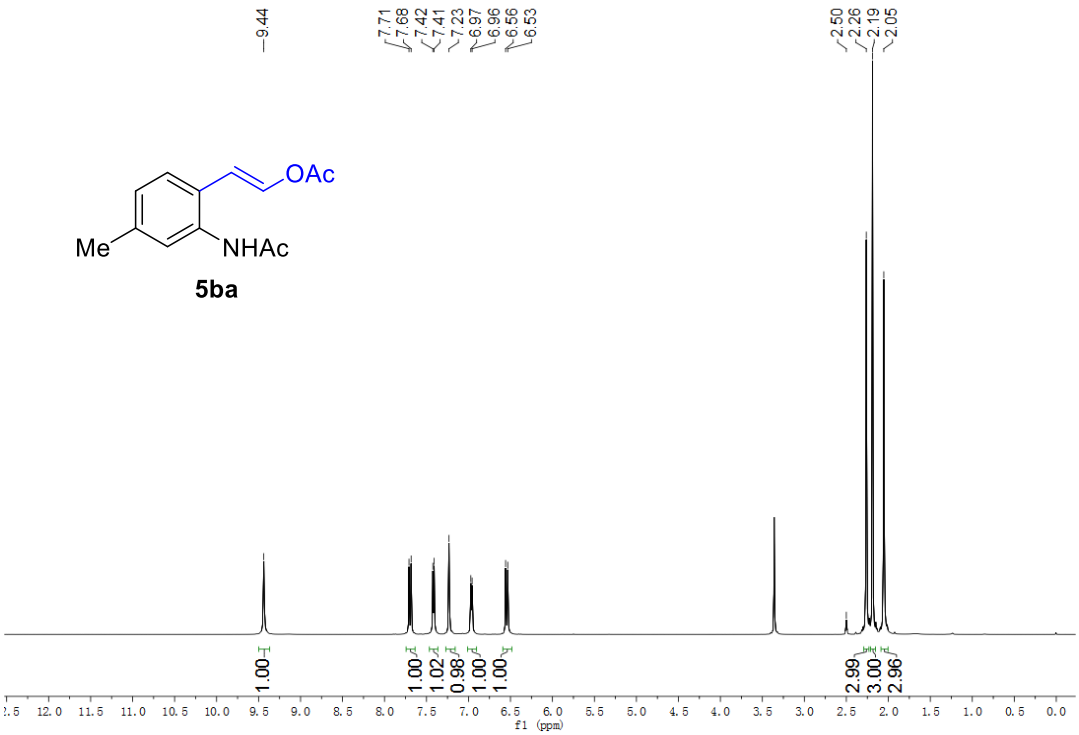
27.98
20.41
f1 (ppm)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6.96
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6.53
2.50
2.26
2.19
2.05
OAc
Me
NHAc
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1.00
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1.00
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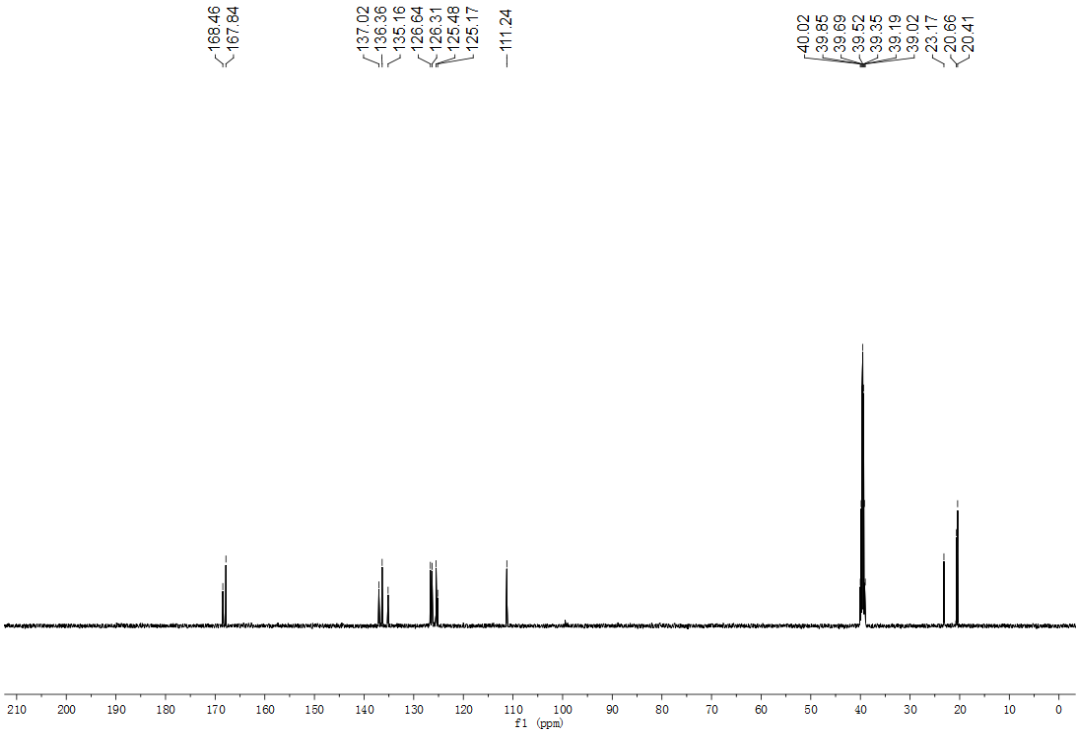
3.00
2.96
f1 (ppm)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125.48
125.17
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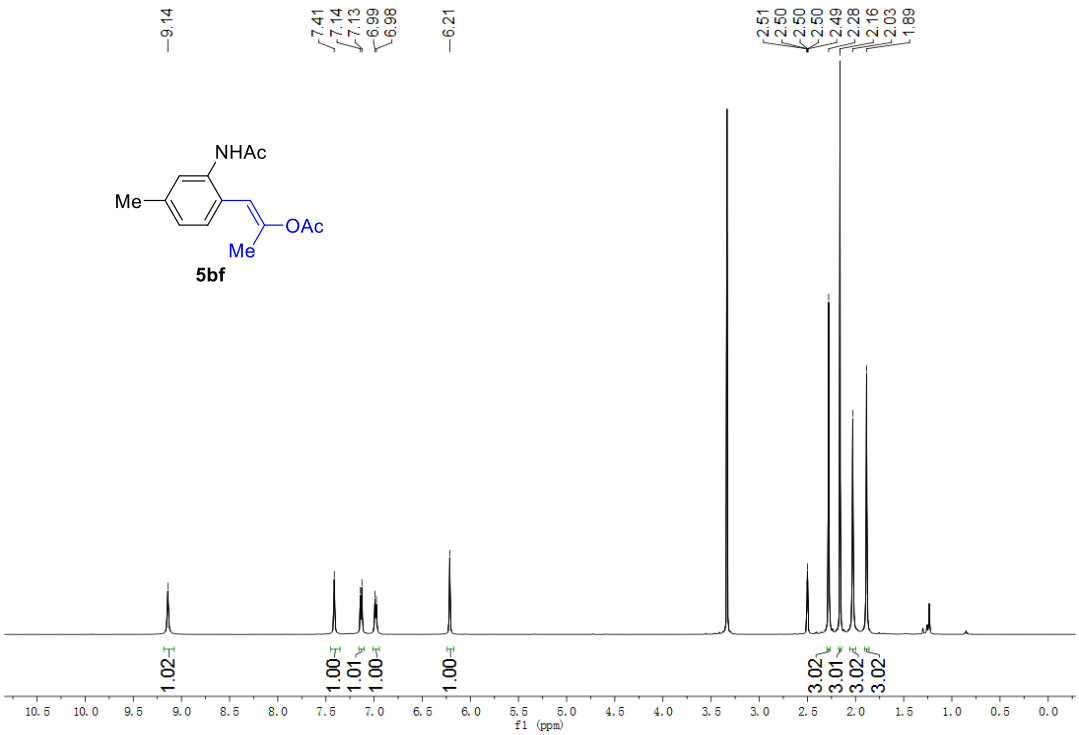
39.35
39.19
39.02
23.17
20.66
20.41
f1 (ppm)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6.98
6.21
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2.49
2.28
2.16
2.03
1.89
NHAc
Me
OAc
Me
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1.00
1.00
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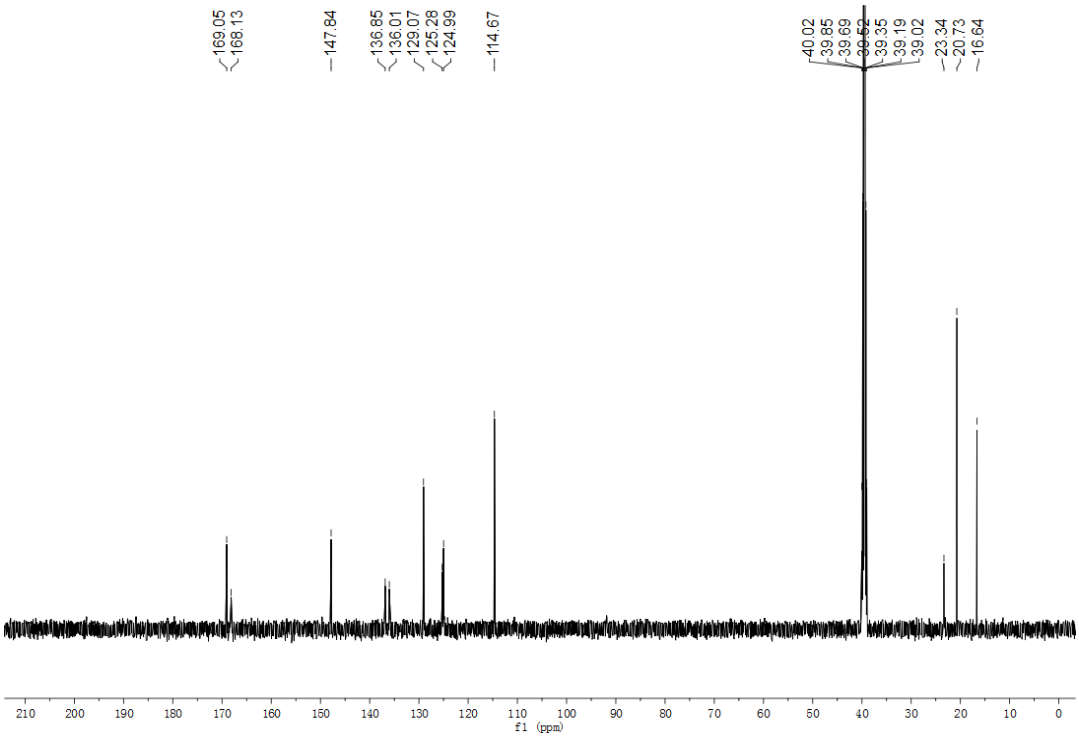
3.01
3.02
3.02
f1 (ppm)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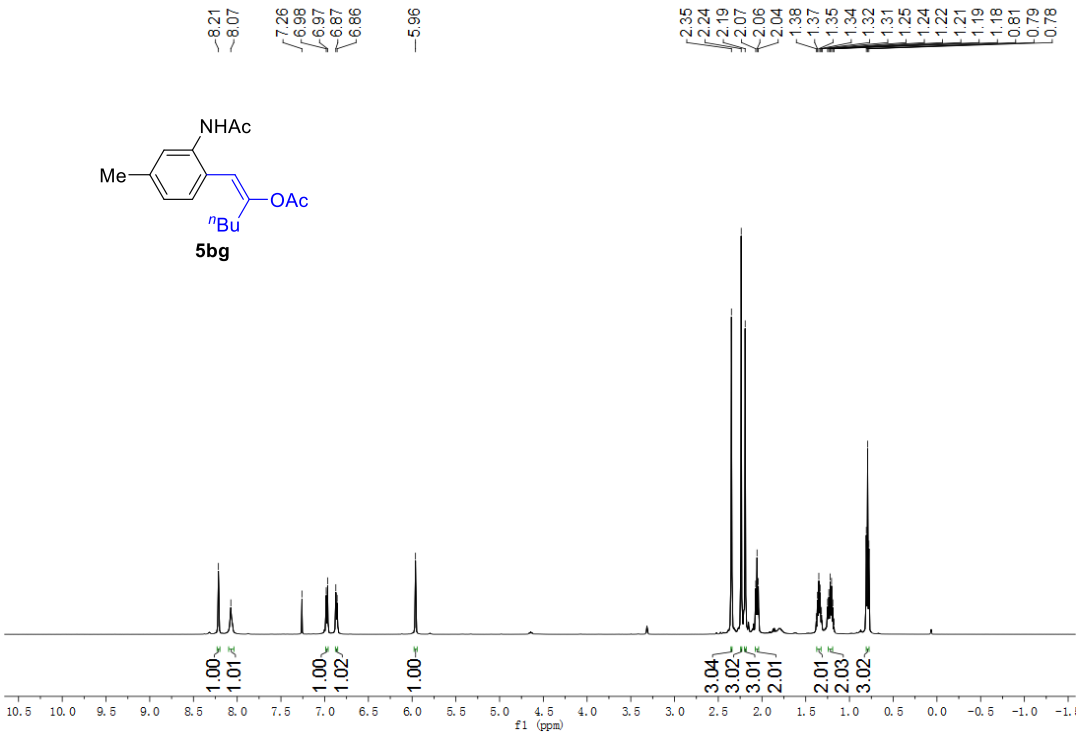
39.02
23.34
20.73
16.64
f1 (ppm)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2.07
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1.37
1.35
1.34
1.32
1.31
1.25
1.24
1.22
1.21
1.19
1.18
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0.79
0.78
NHAc
Me
OAc
nBu
5bg
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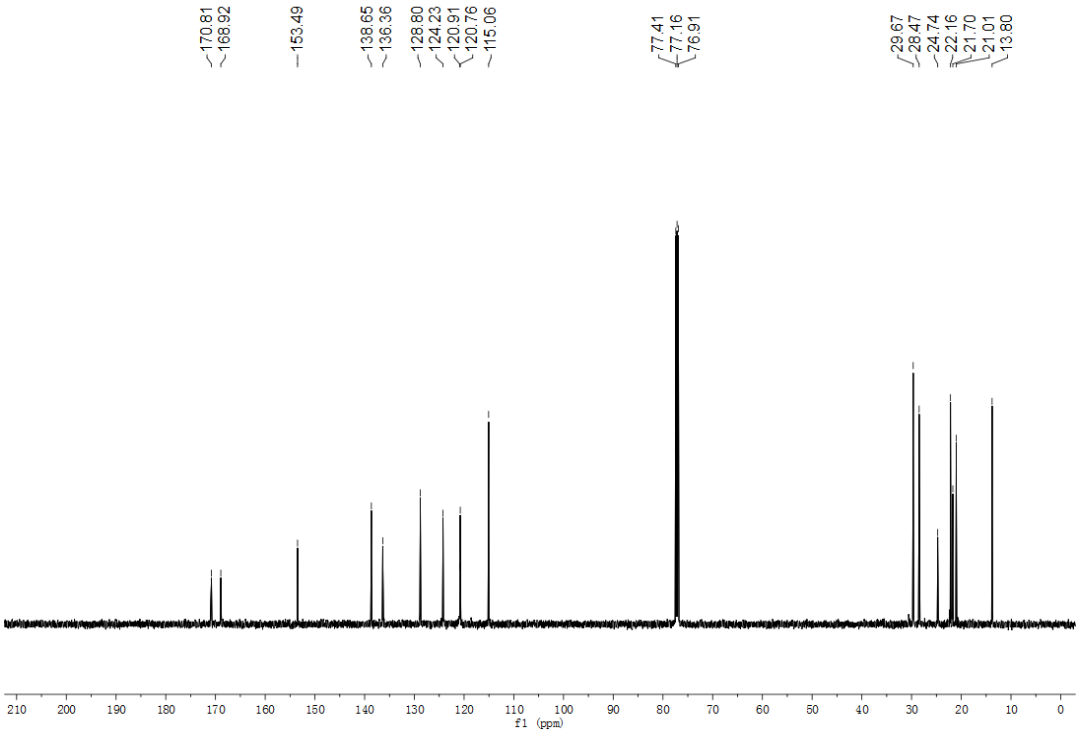
1.00
3.04
3.02
3.01
2.01
2.01
2.03
3.02
f1 (ppm)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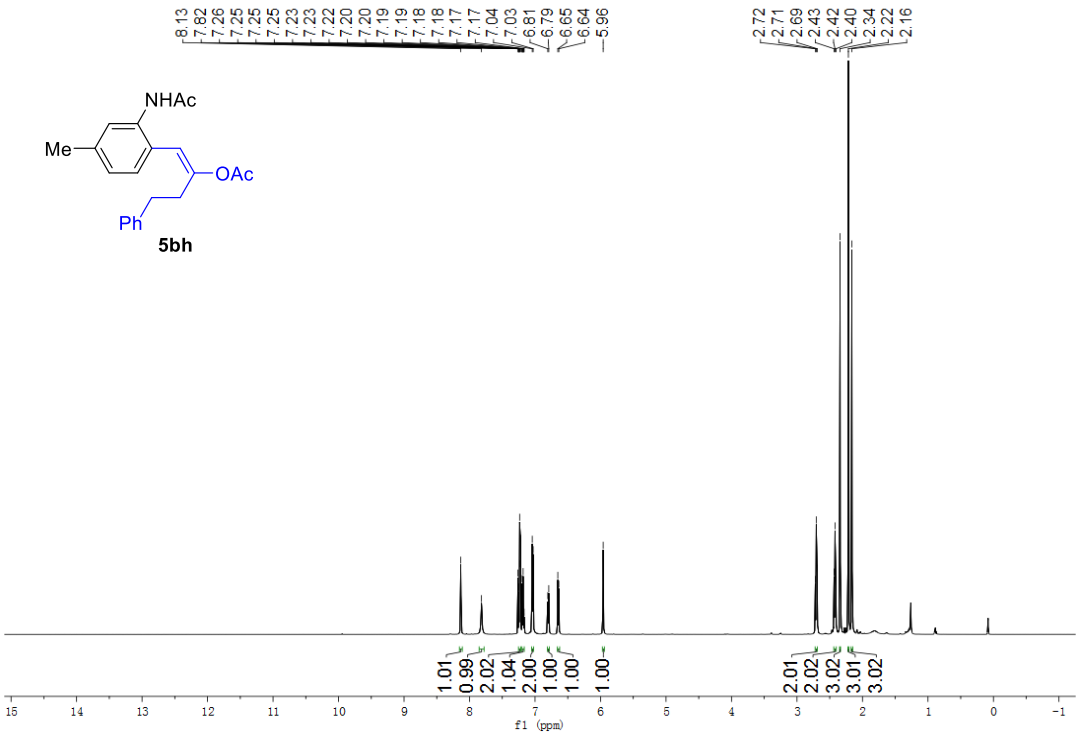
21.70
21.01
13.80
f1 (ppm)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OAc
Ph
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7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.04
7.03
6.81
6.79
6.65
6.64
5.96
2.72
2.71
2.69
2.43
2.42
2.40
2.34
2.22
2.16
1.01
0.99
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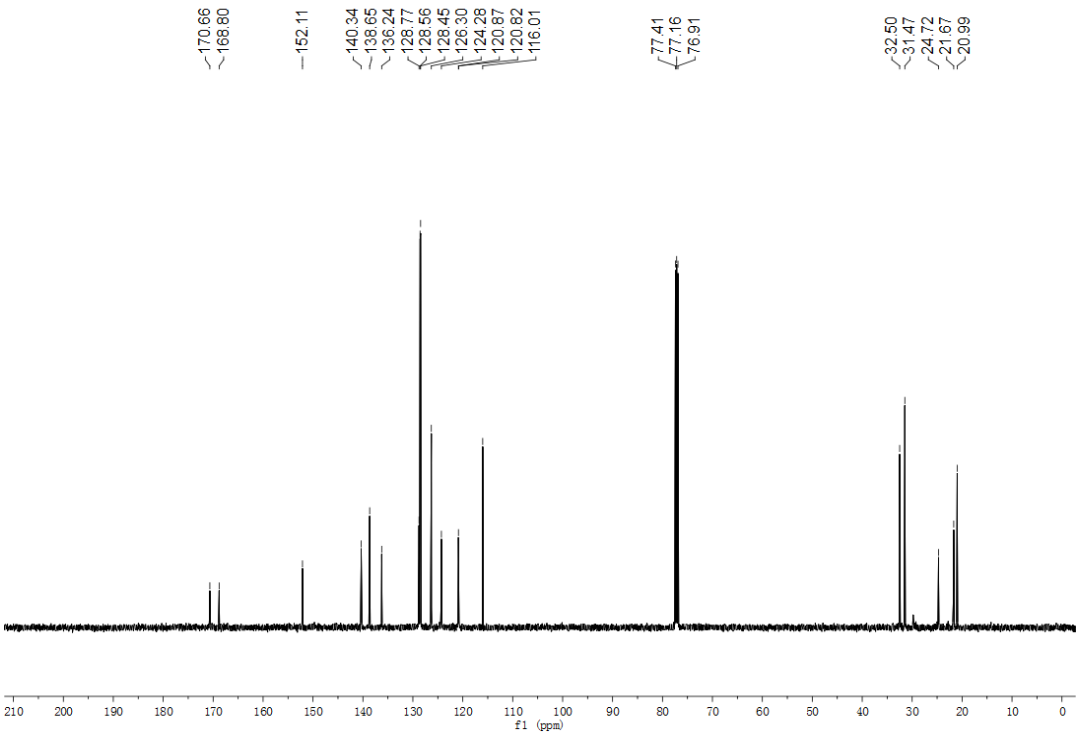
1.00
1.00
1.00
2.01
2.02
3.02
3.01
3.02
f1 (ppm)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128.56
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126.30
124.28
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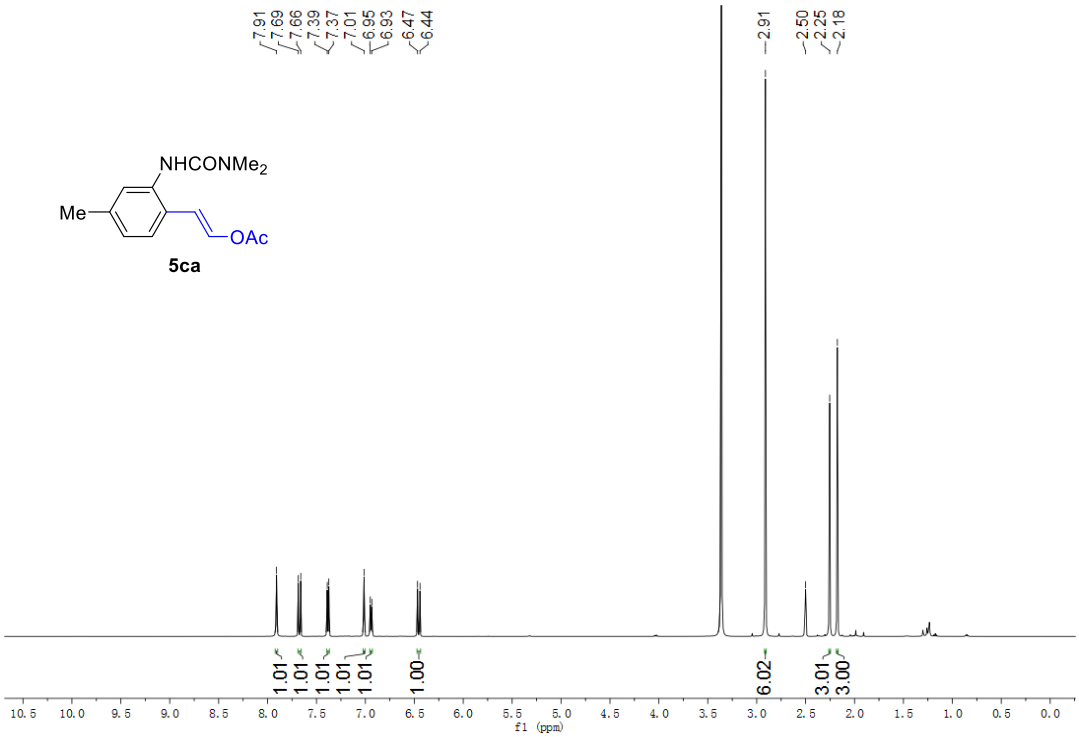
76.91
32.50
31.47
24.72
21.67
20.99
f1 (ppm)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6.93
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6.44
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2.25
2.18
NHCONMe2
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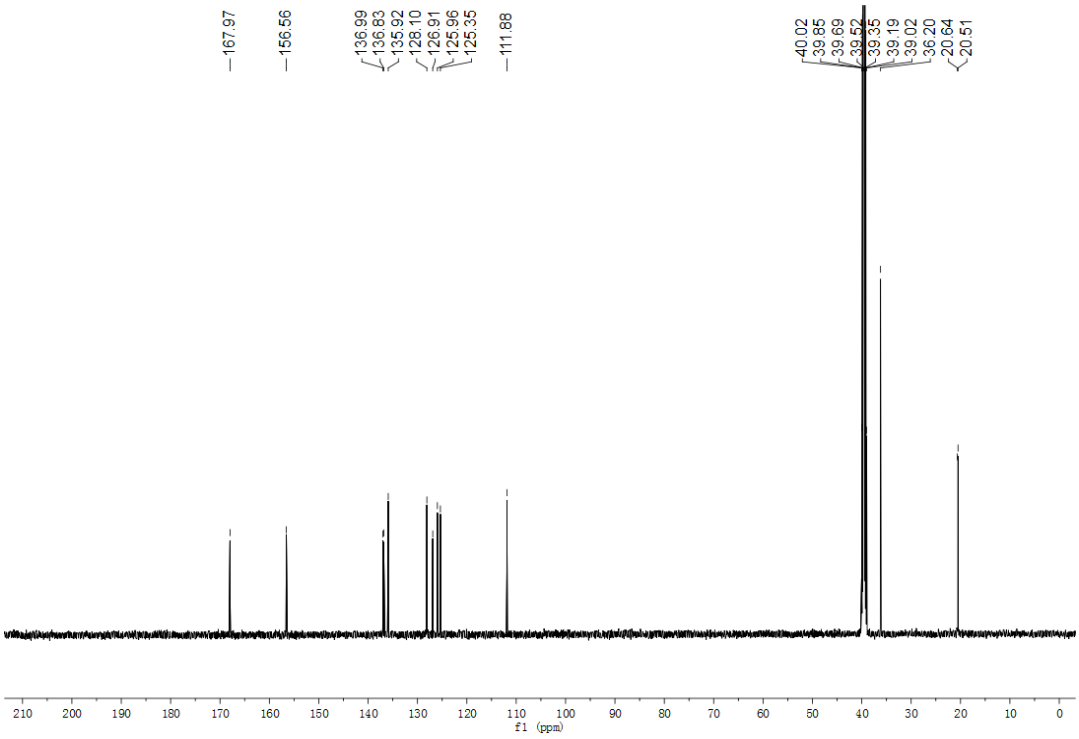
1.01
1.01
1.01
1.01
1.00
6.02
3.01
3.00
f1 (ppm)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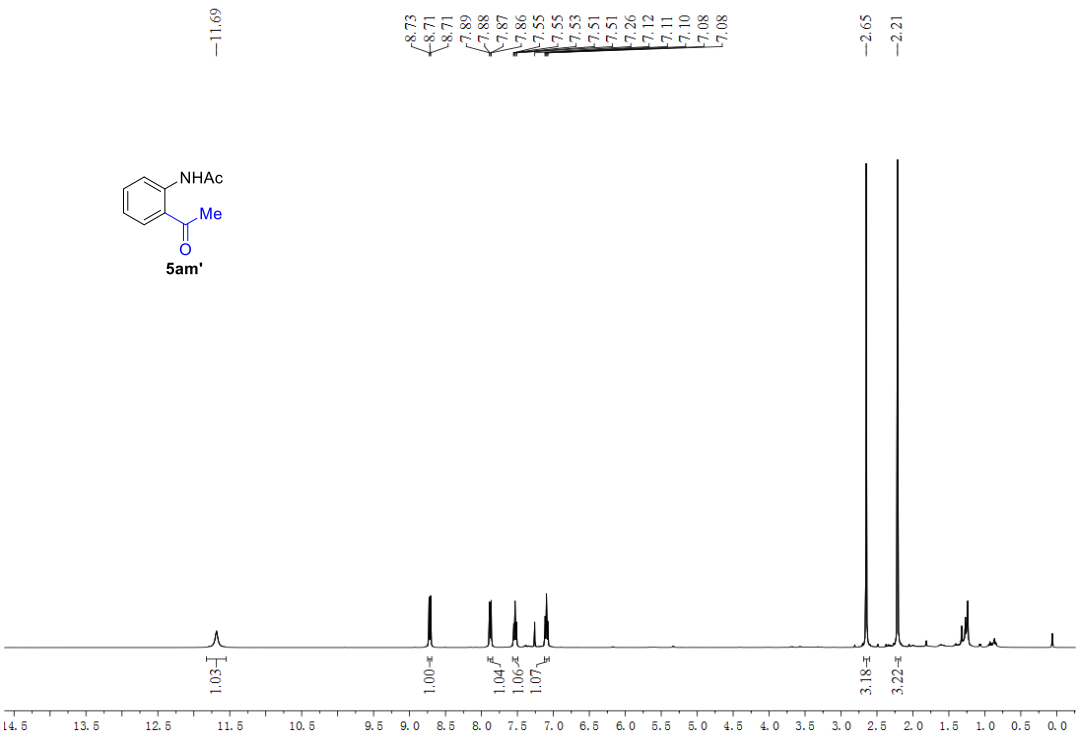
20.51
f1 (ppm)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7.53
7.51
7.51
7.26
7.12
7.11
7.10
7.08
7.08
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Me
O
5am'
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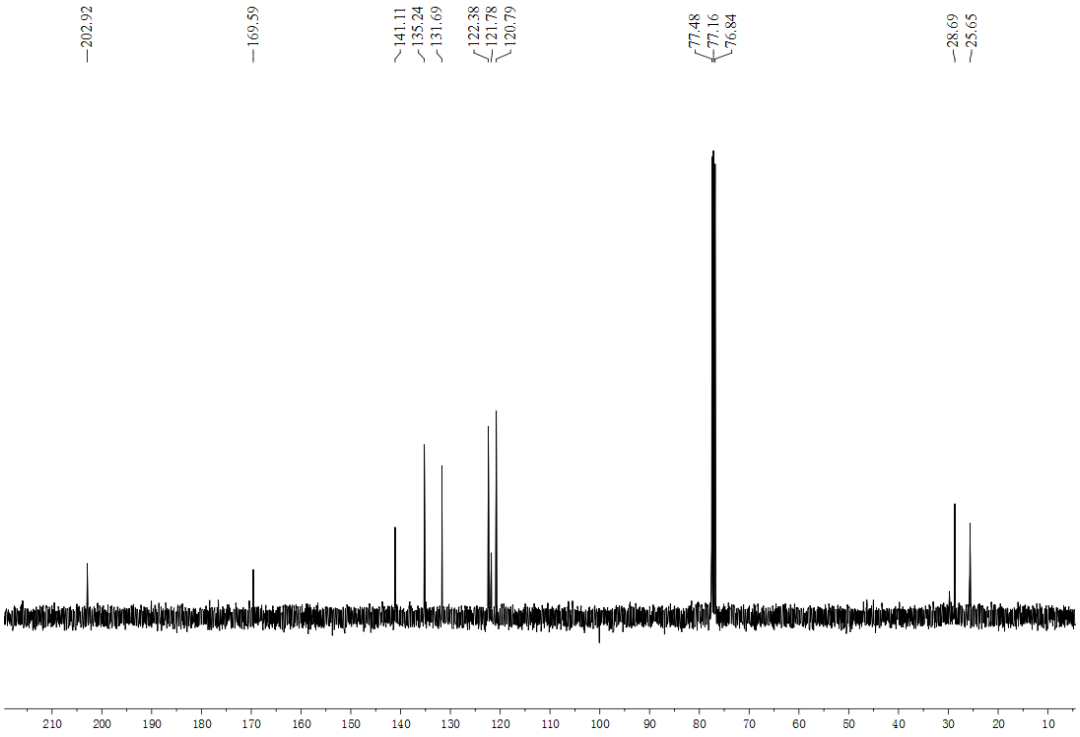
1.00
1.04
1.06
1.07
3.18
3.22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76.84
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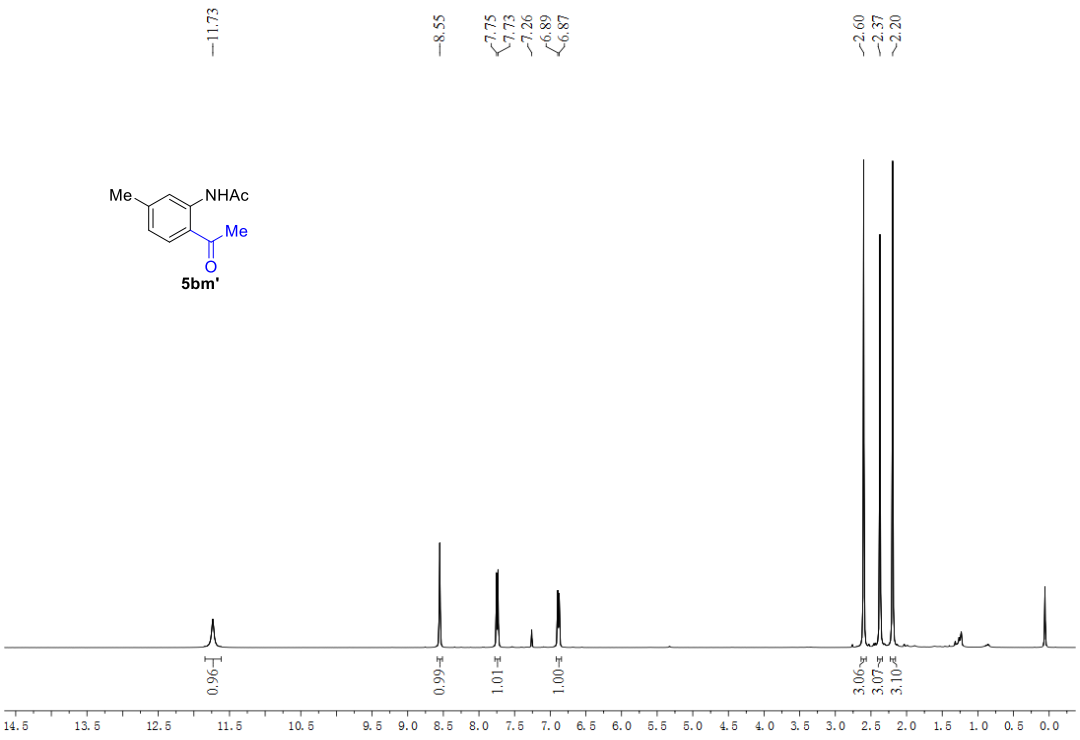
25.65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Me
O
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1.01
1.00
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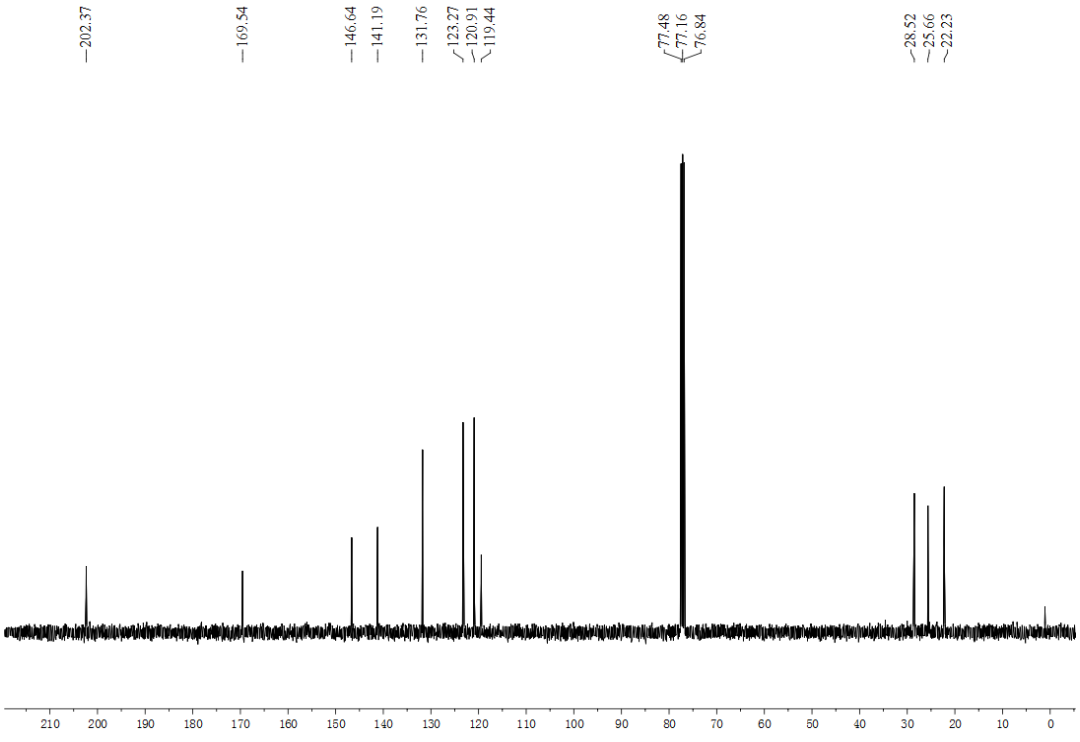
3.07
3.10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77.16
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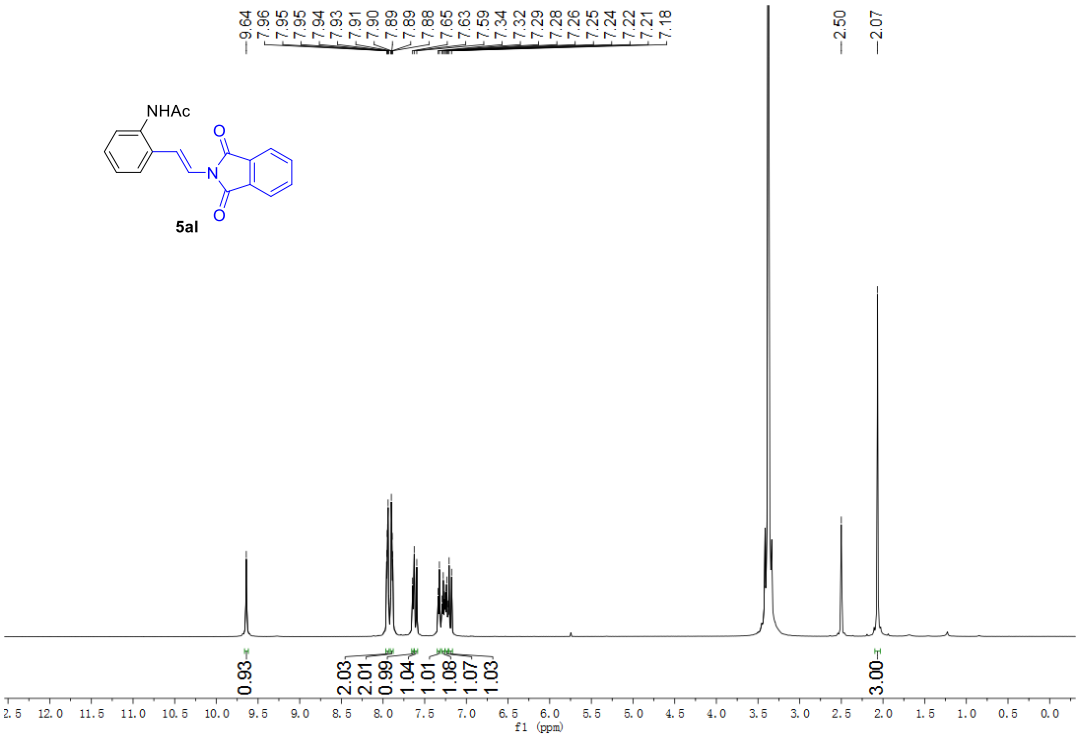
25.66
22.23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7.63
7.59
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7.32
7.29
7.28
7.26
7.25
7.24
7.22
7.21
7.18
2.50
2.07
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O
N
O
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0.99
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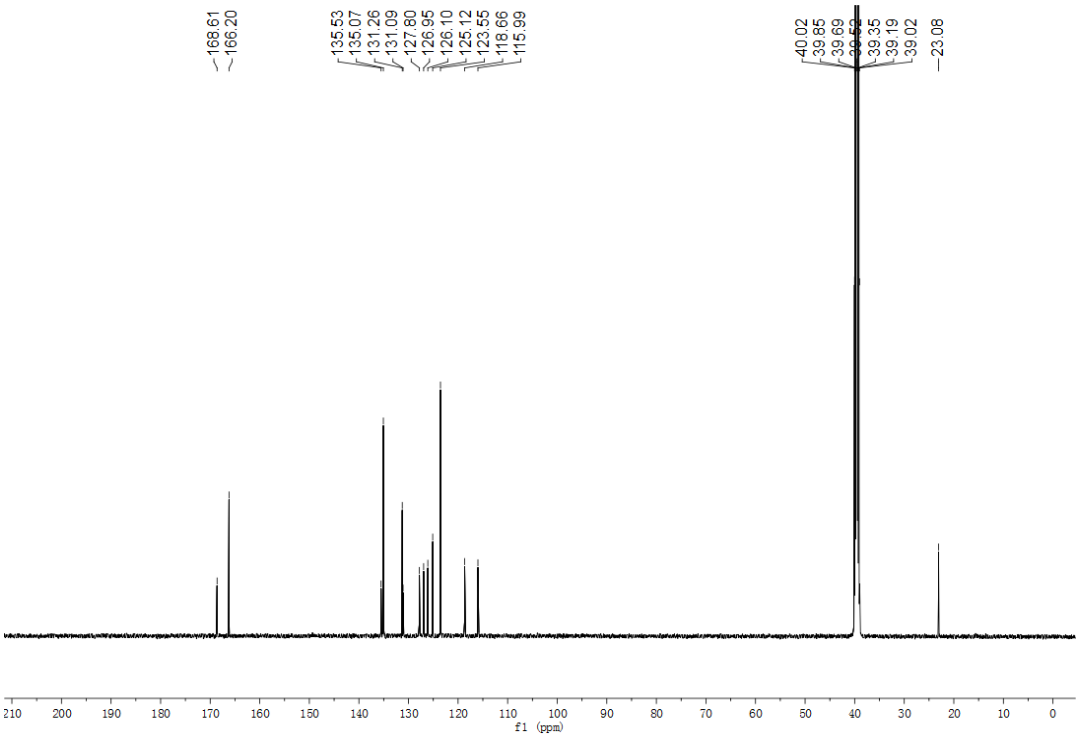
1.01
1.08
1.07
1.03
3.00
f1 (ppm)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39.69
39.52
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39.19
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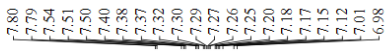
23.08
f1 (ppm)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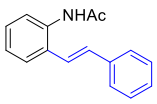
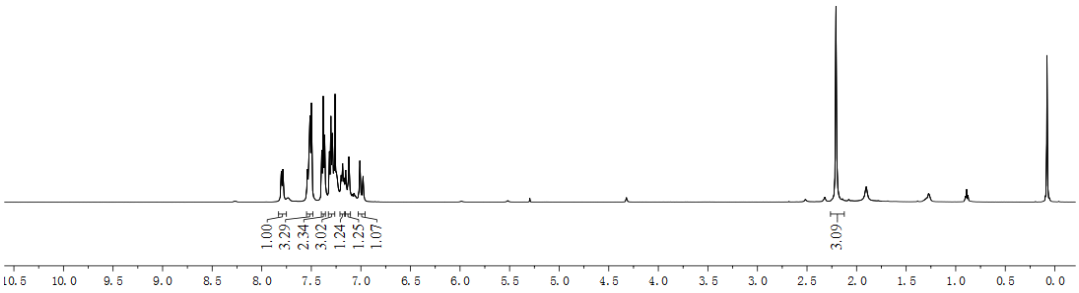
2.21


NHAc

6ak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8.5
8.0
7.5
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6.5
6.0
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2.0
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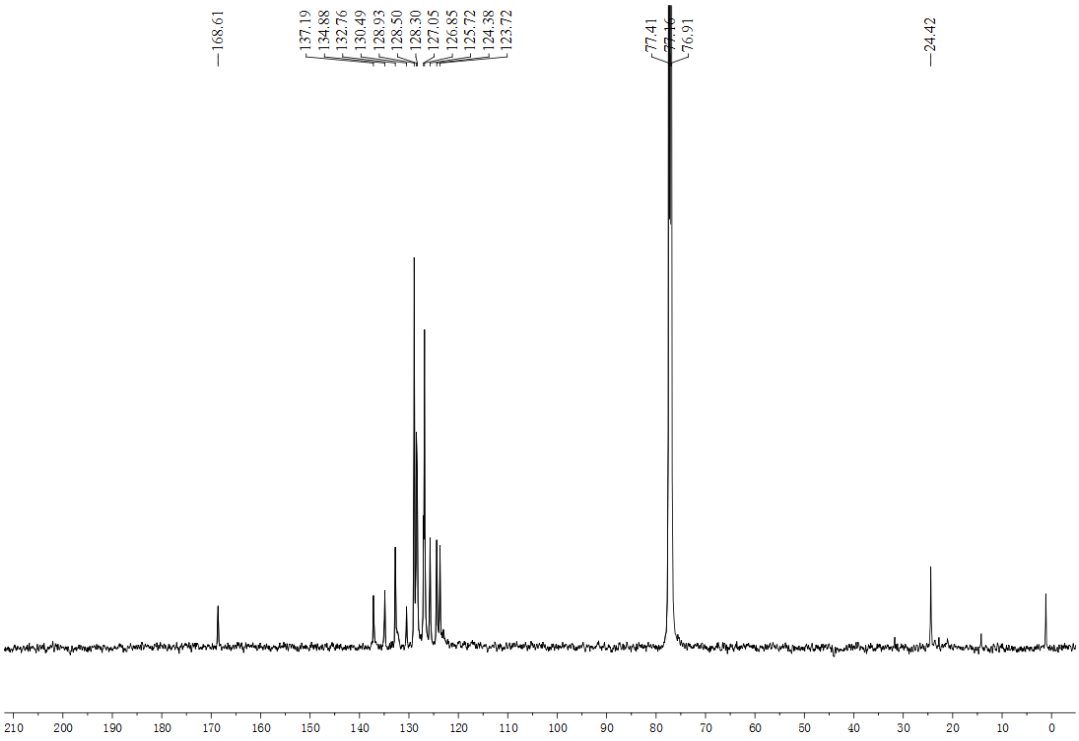
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123.72
77.41
77.16
76.91
24.42
210
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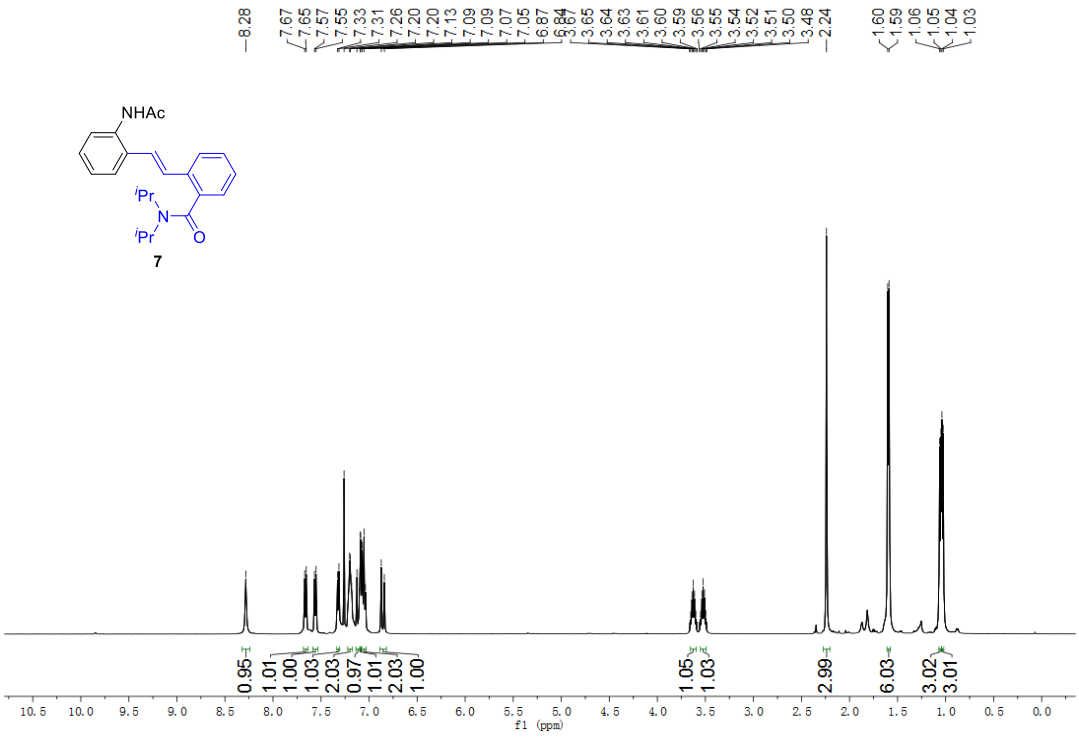
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iPr
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7.09
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7.07
7.05
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1.03
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1.01
1.00
1.03
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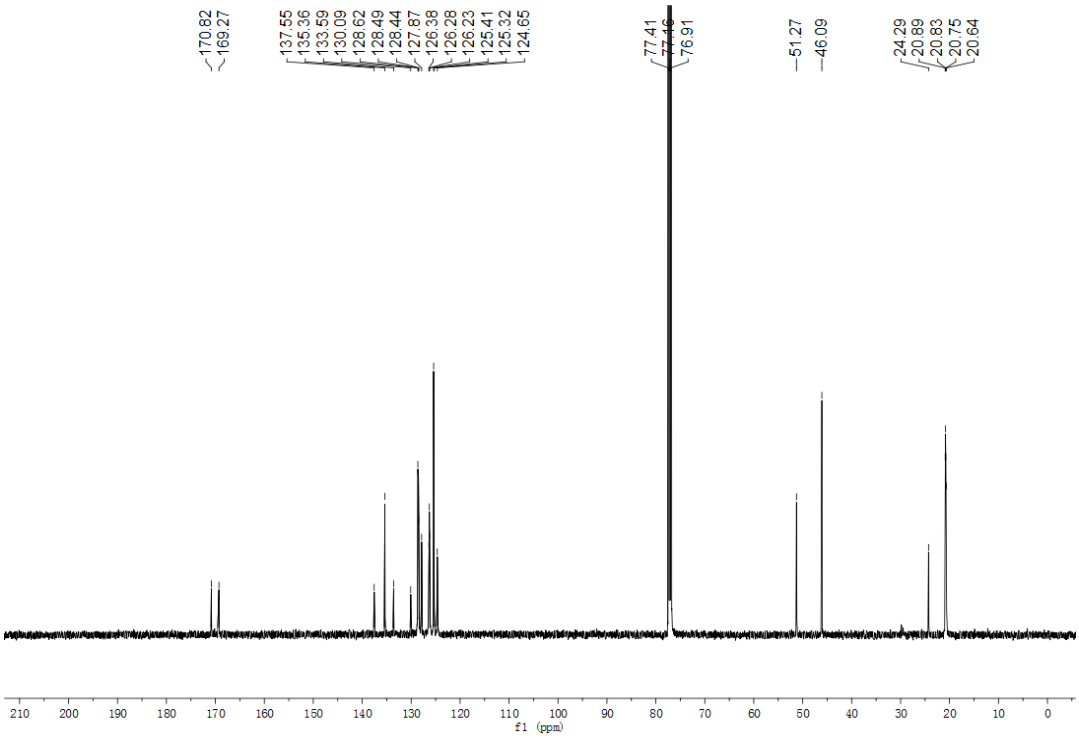
1.05
1.03
2.99
6.03
3.02
3.01
f1 (ppm)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125.32
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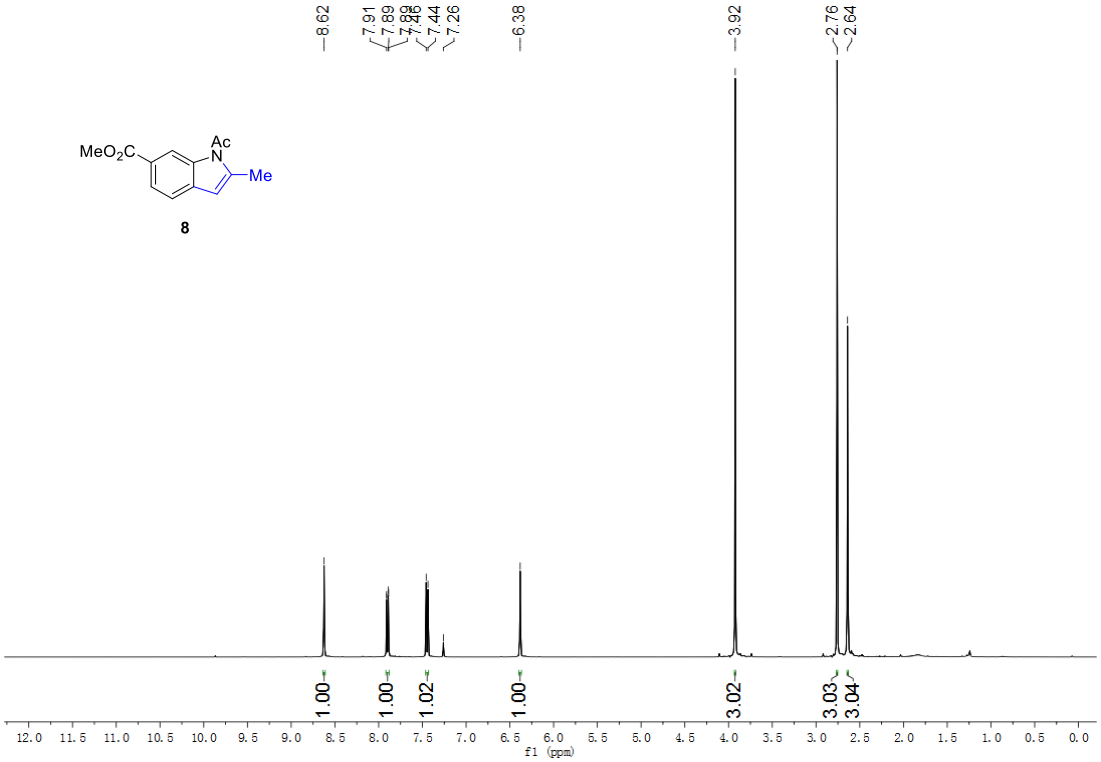
20.75
20.64
f1 (ppm)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Ac
N
Me
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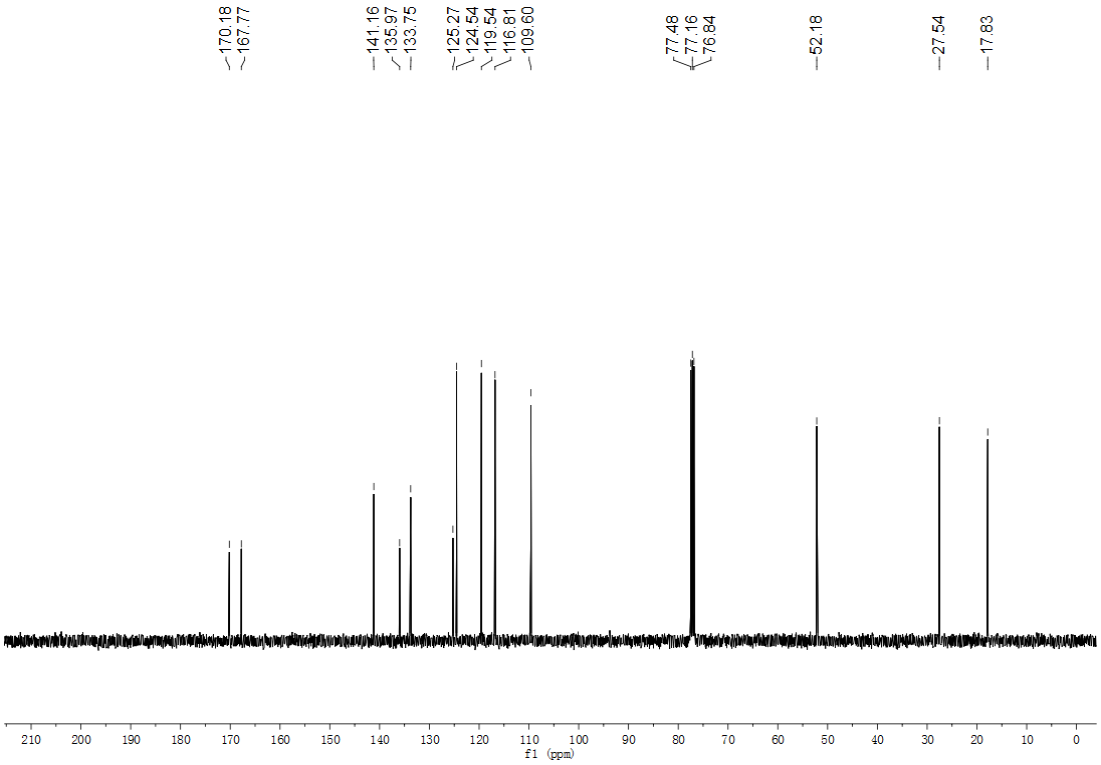
1.00
1.02
1.00
3.02
3.03
3.04
f1 (ppm)

8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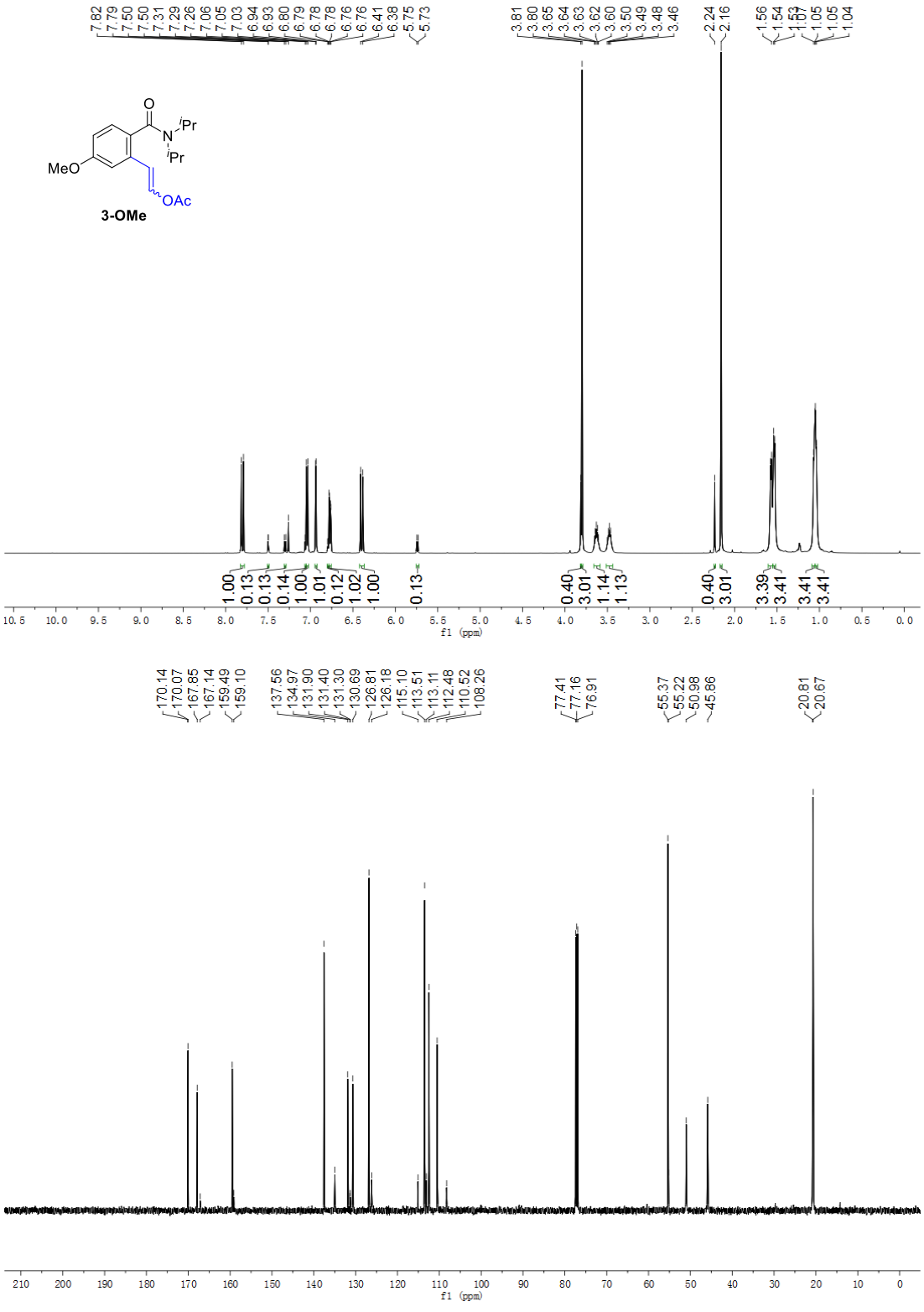
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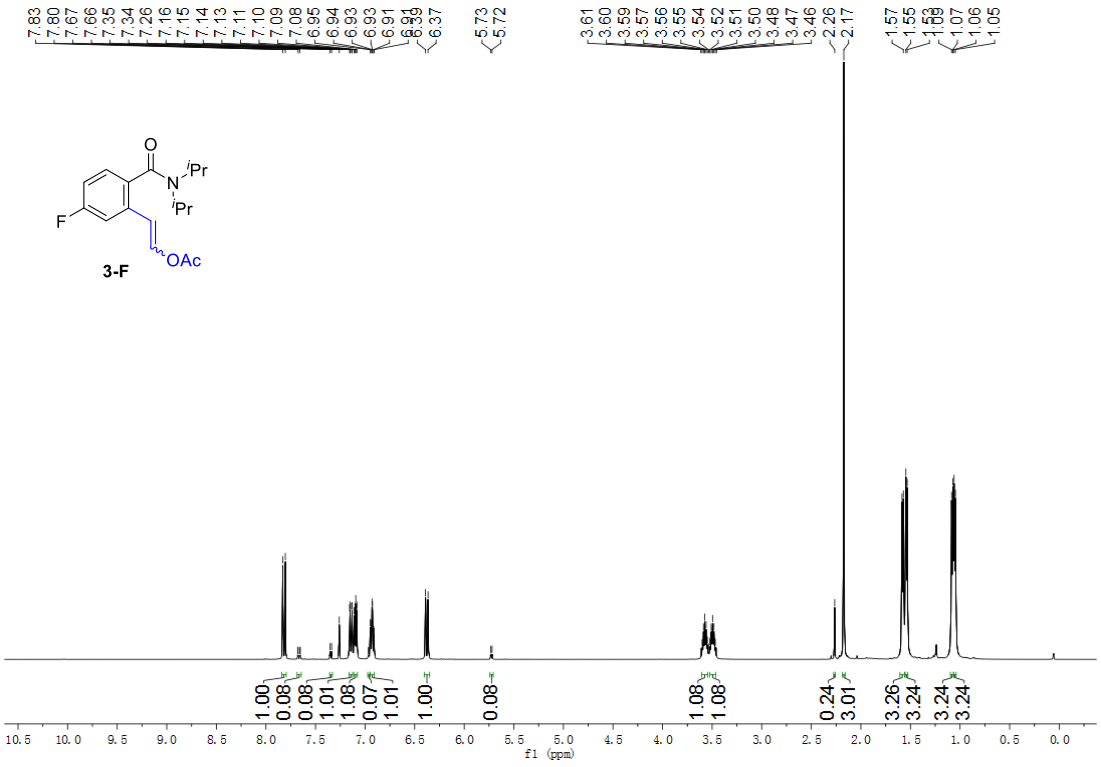
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1.08
0.07
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1.00
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1.08
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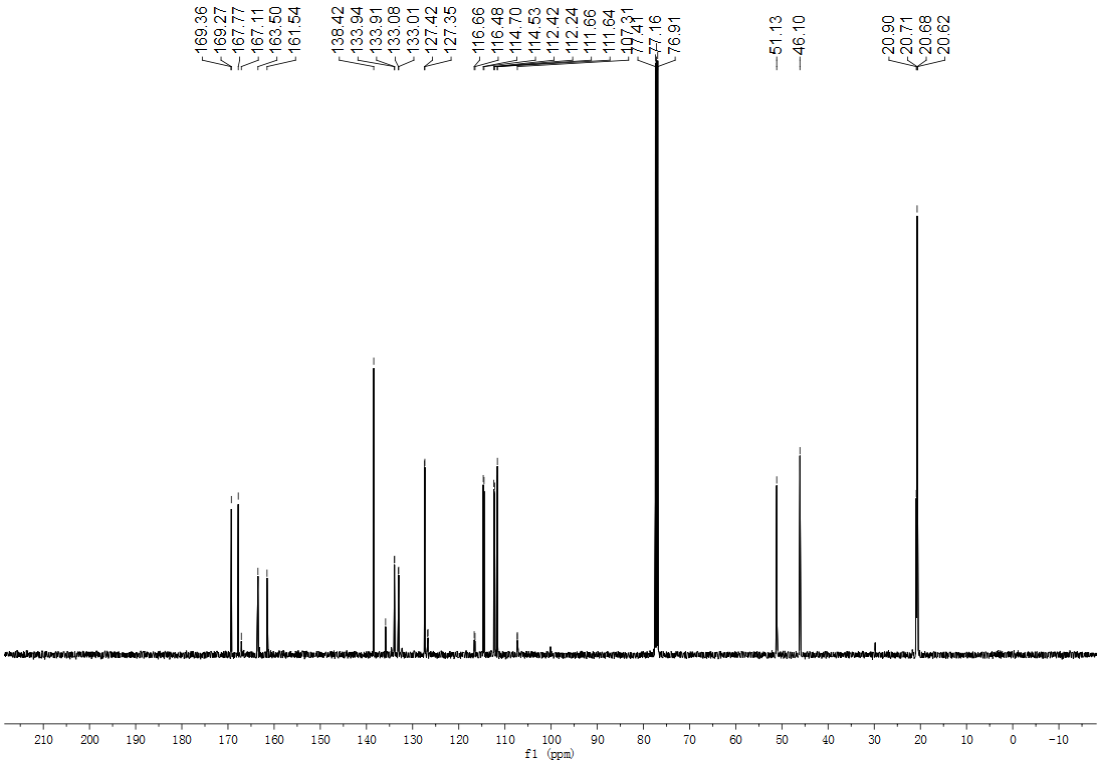
f1 (ppm)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133.94
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133.08
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114.53
112.42
112.24
111.66
111.64
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77.16
76.91
51.13
46.10
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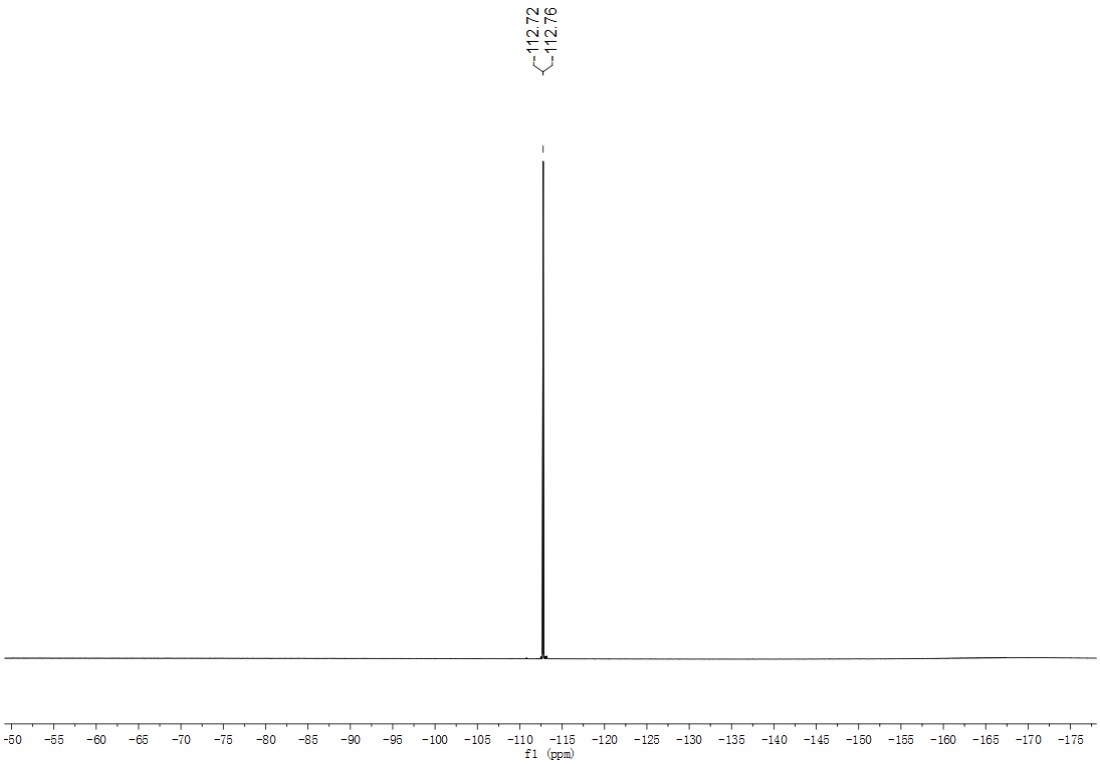
20.71
20.68
20.62
f1 (ppm)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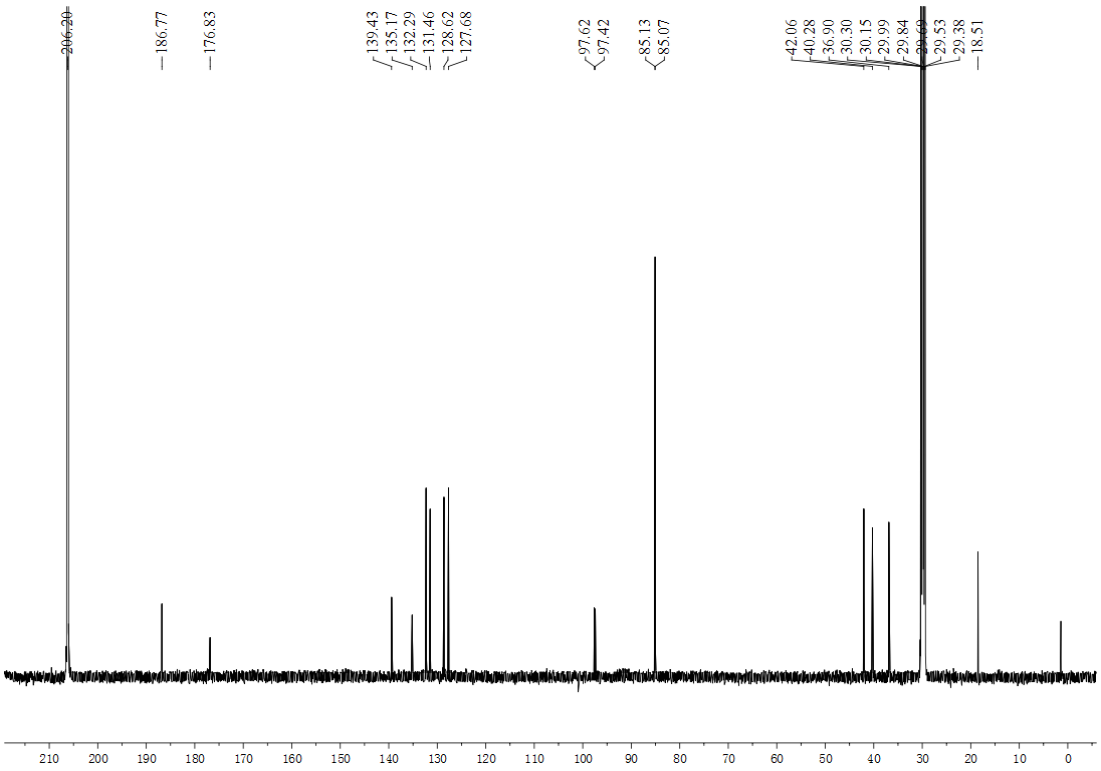
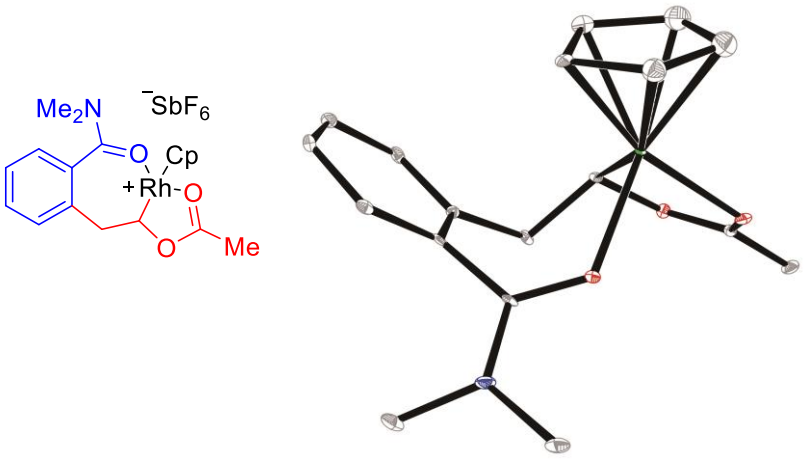
112.76
f1 (ppm)
rhodacycle 9



8) X-ray Single-Crystal Structure of Rhodacycle 9 (CCDC 1829538)



ORTEP drawings of rhodacylcle **9** with 30% thermal ellipsoids (for clarity, hydrogens and SbF_6^- counterion have been omitted).

Table S3 Crystal data and structure refinement for 9.

Identification code	**9**
Empirical formula	$C_{18}H_{21}F_6NO_3RhSb$
Formula weight	638.02
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	9.4938(2)
b/Å	18.0857(5)
c/Å	12.3668(3)
α/°	90
β/°	97.385(2)
γ/°	90
Volume/Å^3	2105.79(9)
Z	4
ρ_{calc}g/cm^3	2.012
μ/mm^{-1}	17.192
F(000)	1240.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.712 to 149.578
Index ranges	-8 ≤ h ≤ 11, -21 ≤ k ≤ 22, -15 ≤ l ≤ 15
Reflections collected	7975
Independent reflections	4221 [R_{int} = 0.0314, R_{sigma} = 0.0322]
Data/restraints/parameters	4221/42/274
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1303
Final R indexes [all data]	R_1 = 0.0493, wR_2 = 0.1314
Largest diff. peak/hole / e Å^{-3}	2.71/-1.33

Table S4 Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for 9. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Sb1	-2810.1(3)	9319.7(2)	8089.8(3)	14.34(14)
Rh1	1594.7(3)	8617.1(2)	4895.1(2)	4.82(13)
F2	-1578(4)	9214(2)	7021(3)	29.4(9)
O1	3426(4)	9213.9(19)	4699(3)	9.7(7)
O3	2025(4)	8902.8(19)	6567(3)	8.7(6)
O2	4483(4)	8110.9(19)	4821(3)	8.9(6)
F3	-3264(4)	8307(2)	7939(4)	33.2(9)
F4	-4033(4)	9433(3)	9161(3)	35.6(10)
F1	-4320(4)	9539(3)	7002(3)	38.1(10)
F5	-2304(5)	10326(2)	8237(4)	40(1)
F6	-1330(4)	9064(2)	9182(3)	32.2(9)
N1	1948(5)	8790(2)	8363(4)	12.2(8)
C4	-618(5)	8337(3)	4793(4)	11.2(9)
C7	3121(5)	7804(3)	5107(4)	6.8(8)

C6	4496(5)	8825(3)	4668(4)	8.5(9)
C15	1771(5)	8508(3)	7361(4)	7.0(9)
C5	-610(6)	9099(3)	4478(5)	19.5(10)
C10	1585(6)	6533(3)	6378(4)	11.5(9)
C12	-558(6)	6804(3)	7141(4)	13.9(10)
C13	-37(5)	7502(3)	7444(4)	9.7(9)
C11	257(6)	6318(3)	6616(4)	15.8(11)
C2	556(7)	8413(4)	3286(5)	26.2(13)
C14	1280(5)	7728(3)	7180(4)	8.4(9)
C16	5875(5)	9136(3)	4465(4)	13.4(10)
C9	2112(5)	7242(3)	6644(4)	7.9(9)
C17	1862(6)	8370(3)	9352(4)	15.8(10)
C3	33(6)	7913(3)	4032(4)	17.1(10)
C8	3469(5)	7496(3)	6260(4)	8.9(9)
C18	2301(6)	9573(3)	8526(4)	18.0(11)
C1	119(7)	9153(4)	3569(5)	25.5(13)

Table S5 Anisotropic displacement parameters ($Å^2×10^3$) for 9. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb1	15.5(2)	15.7(2)	12.8(2)	8.73(11)	5.76(14)	6.95(12)
Rh1	3.5(2)	6.8(2)	3.4(2)	0.60(11)	-2.18(13)	-0.65(11)
F2	39(2)	20.7(17)	34(2)	6.2(15)	26.2(17)	6.5(15)
O1	8.3(16)	9.7(15)	10.4(16)	-2.6(13)	-1.7(12)	-1.9(13)
O3	10.5(10)	8.9(10)	6.5(10)	-1.1(8)	0.3(8)	-1.1(8)
O2	9.1(16)	9.0(16)	9.4(15)	-1.1(12)	3.6(12)	0.7(13)
F3	34(2)	22.1(19)	43(2)	11.7(16)	6.2(17)	-8.6(16)
F4	30(2)	62(3)	17.5(18)	11.9(17)	12.6(15)	19.4(19)
F1	37(2)	61(3)	15.5(17)	16.8(18)	-0.6(15)	24(2)
F5	51(3)	17.7(18)	54(3)	-4.5(17)	18(2)	7.0(18)
F6	23.1(19)	43(2)	28.1(19)	7.5(17)	-4.7(15)	12.4(17)
N1	17(2)	9.7(19)	9(2)	-4.3(16)	-1.1(16)	-0.7(17)
C4	4(2)	19(3)	11(2)	0.7(19)	-0.5(17)	-4.2(18)
C7	4(2)	10(2)	6(2)	-0.6(16)	0.0(15)	0.9(16)
C6	9.0(12)	9.3(12)	7.0(11)	0.0(9)	-0.1(9)	0.0(9)
C15	8(2)	10(2)	3(2)	-1.3(16)	0.9(16)	3.9(17)
C5	19.5(10)	19.5(10)	19.5(10)	0.01(10)	2.48(17)	0.0(1)
C10	20(3)	7(2)	8(2)	1.1(17)	3.2(19)	1.8(19)
C12	16(2)	17(2)	9(2)	3.2(19)	2.1(18)	-7(2)
C13	14(2)	7(2)	7(2)	1.6(17)	-1.7(17)	4.0(18)

C11	27(3)	10(2)	9(2)	-0.1(18)	-1(2)	-8(2)
C2	24.6(15)	29.5(15)	24.3(15)	-1(1)	2.6(10)	-1.2(10)
C14	13(2)	9(2)	3.0(19)	1.9(16)	-1.6(16)	0.0(17)
C16	9(2)	15(2)	15(2)	-2(2)	-0.6(18)	-4.5(19)
C9	8.5(12)	7.8(12)	7.0(12)	0.8(9)	-0.3(9)	0.7(9)
C17	20(3)	18(3)	7(2)	0.6(19)	-1.9(19)	3(2)
C3	16.0(13)	17.5(13)	17.3(13)	-2.3(9)	-0.1(9)	-0.5(9)
C8	11(2)	7(2)	7(2)	3.3(17)	-0.4(17)	3.9(17)
C18	26(3)	16(3)	11(2)	-7(2)	1(2)	-3(2)
C1	23.9(15)	26.7(15)	25.3(15)	4.1(10)	0.4(9)	-1.7(10)

Table S6 Bond lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Sb1	F2	1.884(4)	N1	C15	1.331(6)
Sb1	F3	1.886(4)	N1	C17	1.450(7)
Sb1	F4	1.882(4)	N1	C18	1.464(7)
Sb1	F1	1.878(4)	C4	C5	1.432(8)
Sb1	F5	1.886(4)	C4	C3	1.416(7)
Sb1	F6	1.877(4)	C7	C8	1.527(6)
Rh1	O1	2.087(3)	C6	C16	1.476(7)
Rh1	O3	2.119(3)	C15	C14	1.494(7)
Rh1	C4	2.149(5)	C5	C1	1.397(9)
Rh1	C7	2.058(5)	C10	C11	1.387(8)
Rh1	C5	2.264(6)	C10	C9	1.400(7)
Rh1	C2	2.136(6)	C12	C13	1.390(7)
Rh1	C3	2.133(5)	C12	C11	1.386(8)
Rh1	C1	2.236(6)	C13	C14	1.393(7)
O1	C6	1.240(6)	C2	C3	1.426(9)
O3	C15	1.262(6)	C2	C1	1.456(9)
O2	C7	1.491(6)	C14	C9	1.404(7)
O2	C6	1.306(6)	C9	C8	1.501(7)

Table S7 Bond angles for 9.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F2	Sb1	F3	89.24(18)	C1	Rh1	C5	36.2(2)
F2	Sb1	F5	89.55(18)	C6	O1	Rh1	114.1(3)
F3	Sb1	F5	178.43(19)	C15	O3	Rh1	126.0(3)
F4	Sb1	F2	179.5(2)	C6	O2	C7	115.4(4)
F4	Sb1	F3	91.3(2)	C15	N1	C17	124.8(4)
F4	Sb1	F5	90.0(2)	C15	N1	C18	119.9(4)

F1	Sb1	F2	90.24(18)	C17	N1	C18	115.3(4)
F1	Sb1	F3	89.5(2)	C5	C4	Rh1	75.5(3)
F1	Sb1	F4	89.89(18)	C3	C4	Rh1	70.1(3)
F1	Sb1	F5	91.5(2)	C3	C4	C5	108.7(5)
F6	Sb1	F2	90.27(19)	O2	C7	Rh1	108.7(3)
F6	Sb1	F3	88.38(19)	O2	C7	C8	105.5(4)
F6	Sb1	F4	89.62(18)	C8	C7	Rh1	116.3(3)
F6	Sb1	F1	177.8(2)	O1	C6	O2	122.2(4)
F6	Sb1	F5	90.6(2)	O1	C6	C16	122.5(5)
O1	Rh1	O3	85.87(13)	O2	C6	C16	115.3(4)
O1	Rh1	C4	159.71(17)	O3	C15	N1	119.6(4)
O1	Rh1	C5	122.28(18)	O3	C15	C14	120.4(4)
O1	Rh1	C2	105.8(2)	N1	C15	C14	120.0(4)
O1	Rh1	C3	141.86(18)	C4	C5	Rh1	66.8(3)
O1	Rh1	C1	98.25(19)	C1	C5	Rh1	70.8(4)
O3	Rh1	C4	100.32(16)	C1	C5	C4	107.9(5)
O3	Rh1	C5	100.68(17)	C11	C10	C9	120.9(5)
O3	Rh1	C2	163.5(2)	C11	C12	C13	120.1(5)
O3	Rh1	C3	131.91(18)	C12	C13	C14	120.1(5)
O3	Rh1	C1	129.3(2)	C12	C11	C10	120.0(5)
C4	Rh1	C5	37.8(2)	C3	C2	Rh1	70.4(3)
C4	Rh1	C1	62.8(2)	C3	C2	C1	107.0(6)
C7	Rh1	O1	78.52(16)	C1	C2	Rh1	74.3(4)
C7	Rh1	O3	90.33(16)	C13	C14	C15	120.9(4)
C7	Rh1	C4	120.4(2)	C13	C14	C9	120.3(4)
C7	Rh1	C5	156.8(2)	C9	C14	C15	118.5(4)
C7	Rh1	C2	103.2(2)	C10	C9	C14	118.6(4)
C7	Rh1	C3	94.0(2)	C10	C9	C8	120.1(4)
C7	Rh1	C1	140.1(2)	C14	C9	C8	121.0(4)
C2	Rh1	C4	64.8(2)	C4	C3	Rh1	71.3(3)
C2	Rh1	C5	63.4(2)	C4	C3	C2	107.8(5)
C2	Rh1	C1	38.8(2)	C2	C3	Rh1	70.6(3)
C3	Rh1	C4	38.6(2)	C9	C8	C7	108.4(4)
C3	Rh1	C5	63.4(2)	C5	C1	Rh1	73.0(4)
C3	Rh1	C2	39.0(2)	C5	C1	C2	108.3(6)
C3	Rh1	C1	64.0(2)	C2	C1	Rh1	66.9(4)

Table S8 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for 9.

Atom	***x***	***y***	***z***	**U(eq)**

H4	-990	8151	5398	13
H7	2826	7394	4610	8
H5	-1017	9488	4818	23
H10	2134	6201	6038	14
H12	-1455	6662	7291	17
H13	-569	7819	7824	12
H11	-87	5848	6423	19
H2	1078	8291	2725	31
H16A	5716	9544	3967	20
H16B	6418	8763	4155	20
H16C	6386	9305	5140	20
H17A	1068	8540	9692	24
H17B	2721	8436	9843	24
H17C	1742	7855	9174	24
H3	107	7401	4021	21
H8A	4126	7085	6262	11
H8B	3910	7876	6744	11
H18A	2404	9797	7837	27
H18B	3176	9618	9006	27
H18C	1556	9817	8843	27
H1	295	9587	3207	31

Crystal structure determination of 9.

Crystal Data for $C_{18}H_{21}F_6NO_3RhSb$ (M =638.02 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 9.4938(2) Å, b = 18.0857(5) Å, c = 12.3668(3) Å, β = 97.385(2)°, V = 2105.79(9) Å^3, Z = 4, T = 100.00(10) K, μ(CuKα) = 17.192 mm^{-1}, *Dcalc* = 2.012 g/cm^3, 7975 reflections measured (8.712° ≤ 2Θ ≤ 149.578°), 4221 unique (R_{int} = 0.0314, R_{sigma} = 0.0322) which were used in all calculations. The final R_1 was 0.0484 (I > 2σ(I)) and wR_2 was 0.1314 (all data).