Supporting Information

Practical Metal-Free Synthesis of Chalcone Derivatives via a Tandem Cross-Dehydrogenative-Coupling/Elimination Reaction

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1. Materials and Methods

General. All reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen or air. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.[1] NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS, LC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer or Waters TDQ/UPLC H-CLASS-SQ Detector 2. High resolution mass spectra (HRMS) were recorded by ESI-TOF.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., and other commercial suppliers and used as received. Solvents were dried over CaH_2 (for DCE and DCM) or sodium (for dioxane and THF) by refluxing for overnight and freshly distilled prior to use. *tert*-Amyl-OH was purchased from commercial suppliers and used directly without further purification.

2. Investigation of the Key Reaction Parameters

The reactions were performed according to the General Procedure, with the corresponding modifications shown in Table S1-S5. The crude mixture was analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

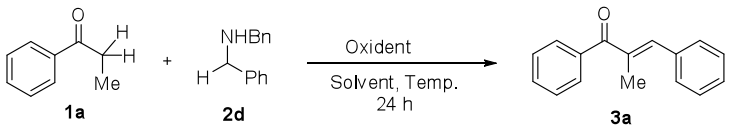


Table S1: Investigation of the Effect of Oxidants for the Reaction[a]

Entry	Oxidant	solvent	Temp. (^{o}C)	**3a** (%)[b]
1	DDQ	*tert*-Amyl-OH	120	64
2	DCP	*tert*-Amyl-OH	120	-
3	TBHP	*tert*-Amyl-OH	120	-
4	Ag_2CO_3	*tert*-Amyl-OH	120	-
5	$K_2S_2O_8$	*tert*-Amyl-OH	120	81
6	$Na_2S_2O_8$	*tert*-Amyl-OH	120	74
7	KHS_2O_8	*tert*-Amyl-OH	120	50
8	**$(NH_4)_2S_2O_8$**	***tert*-Amyl-OH**	**120**	**94 (95)[c]**

[a] Reaction conditions: **1a** (0.25 mmol), **2d** (1.25 mmol), and oxidant (3.0 equiv) in *tert*-Amyl-OH (0.5 mL) at 120 ^{o}C for 24 h. [b] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield in parentheses for 1.0 g scale synthesis. *tert*-Amyl-OH = *tert*-Amyl alcohol.

Table S2: Investigation of the Effect of Solvent for the Reaction[a]

Entry	Oxidant	solvent	Temp. (^{o}C)	**3a** (%)[b]
1	**$(NH_4)_2S_2O_8$**	***tert*-Amyl-OH**	**120**	**94 (95)[c]**
2	$(NH_4)_2S_2O_8$	MeOH	120	46
3	$(NH_4)_2S_2O_8$	*i*-PrOH	120	44
4	$(NH_4)_2S_2O_8$	*n*-BuOH	120	60
5	$(NH_4)_2S_2O_8$	CH_3CN	120	74
6	$(NH_4)_2S_2O_8$	toluene	120	71
7	$(NH_4)_2S_2O_8$	THF	120	66
8	$(NH_4)_2S_2O_8$	DCM	120	75
9	$(NH_4)_2S_2O_8$	DCE	120	83
10	$(NH_4)_2S_2O_8$	Pyridine	120	68

[a] Reaction conditions: **1a** (0.25 mmol), **2d** (1.25 mmol), and $(NH_4)_2S_2O_8$ (3.0 equiv) in solvent (0.5 mL) at 120 ^{o}C for 24 h. [b] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield in parentheses for 1.0 g scale synthesis. *tert*-Amyl-OH = *tert*-Amyl alcohol; DCM =dichloromethane; DCE = 1,2-dichloroethane.

Table S3: Investigation of the Effect of Temperature for the Reaction[a]

Entry	Oxidant	Solvent	Temp. (ºC)	**3a** (%)[b]
1	$(NH_4)_2S_2O_8$	*tert*-Amyl-OH	100	86
2	$(NH_4)_2S_2O_8$	*tert*-Amyl-OH	110	91
3	**$(NH_4)_2S_2O_8$**	***tert*-Amyl-OH**	**120**	**94 (95)[c]**
4	$(NH_4)_2S_2O_8$	*tert*-Amyl-OH	130	97
5	$(NH_4)_2S_2O_8$	*tert*-Amyl-OH	140	88

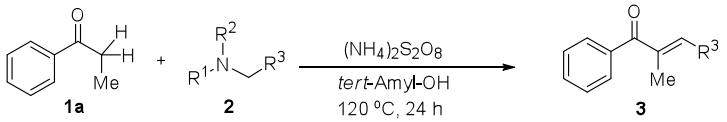
[a] Reaction conditions: **1a** (0.25 mmol), **2d** (1.25 mmol), and $(NH_4)_2S_2O_8$ (3.0 equiv) in solvent (0.5 mL) at intend temperature for 24 h. [b] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield in parentheses for 1.0 g scale synthesis.

Table S4: Investigation of the Effect of the Amount of Dibenzylamine and Oxidant for the Reaction[a]

Entry	**2d** (equiv)	$(NH_4)_2S_2O_8$ (equiv)	**3a** (%)[b]
1	2.0	3.0	Trace
2	3.0	3.0	3
3	4.0	3.0	45
4	4.5	3.0	87
5	**5.0**	**3.0**	**94 (95)[c]**
6	5.5	3.0	93
7	6.0	3.0	77
8	5.0	-	None
9	5.0	2.0	35
10	5.0	2.5	70
11	5.0	3.5	68
12	5.0	4.0	16

[a] Reaction conditions: **1a** (0.25 mmol), **2d** (1.25 mmol), and $(NH_4)_2S_2O_8$ (3.0 equiv) in solvent (0.5 mL) at 120 °C for 24 h. [b] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield in parentheses for 1.0 g scale synthesis.

Table S5: Investigation of the Source of Amines for the Reaction[a]



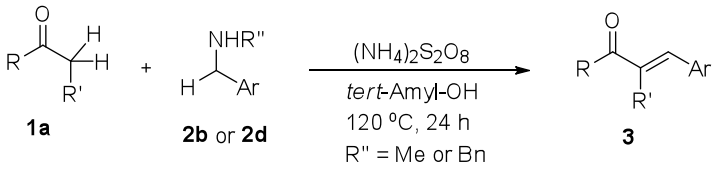
Entry	**2**	R^1	R^2	R^3	**3a** (%)[b]
1	**2a**	H	H	Ph	5
2	**2b**	H	Me	Ph	83
3	**2c**	H	Ph	Ph	7
4	**2d**	H	Bn	Ph	94 (95)[c]
5	**2e**	Me	Me	Ph	11
6	**2f**	H	Et	Me	-

7	**2g**	Et	Et	Me	-

[a] Reaction conditions: **1a** (0.5 mmol), **2** (2.5 mmol), and $(NH_4)_2S_2O_8$ (1.5 mmol) in *tert*-Amyl-OH (1.0 mL) at 120 °C for 24 h. [b] ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield in parentheses for 1.0 g scale synthesis.

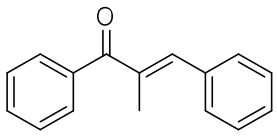
3. General Procedure for Metal-Free Synthesis of Chalcone Derivatives

General Procedure



In a dried Schlenk flask were placed with ketone **1** (0.5 mmol), benzylamine **2** (2.5 mmol), $(NH_4)_2S_2O_8$ (1.5 mmol). Then 1.0 mL of *tert*-Amyl-OH was added with a syringe under nitrogen atmosphere. The resulting mixture was stirred at 120 ºC for 24 h. After cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate and filtered through a plug of celite, followed by with 10.0 mL of ethyl acetate. The combined organic residue was concentrated and then purified by column chromatography on silica gel to give chalcone derivative **3** (using petroleum ether/ CH_2Cl_2 or petroleum ether/ ethyl acetate as mobile phase).

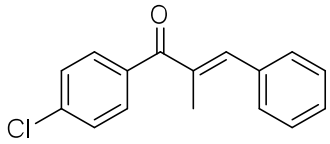
1.0 Gram Scale Synthesis



(*E*)-2-methyl-1,3-diphenylprop-2-en-1-one (Table 2, 3a)[2]

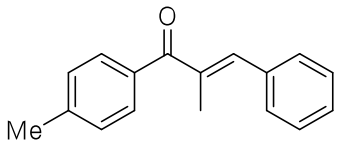
The general procedure was applied to propiophenone (1.00 g, 7.46 mmol), dibenzylamine (7.2 mL, 37.3 mmol), and $(NH_4)_2S_2O_8$ (5.11 g, 22.4 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 10:1~5:1) to afford the title compound as a colorless oil (1.57 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.47-7.38 (m, 6H), 7.34-7.33 (m, 1H), 7.18 (s, 1H), 2.27

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 142.3, 138.7, 137.0, 136.0, 131.8, 129.8, 129.6, 128.7, 128.6, 128.3, 14.6. GC-MS (EI): calcd for $C_{16}H_{14}O$ [M] 222.10, found 222.16.



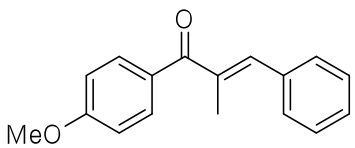
(*E*)-1-(4-chlorophenyl)-2-methyl-3-phenylprop-2-en-1-one (Table 2, 3b)

The general procedure was applied to 1-(4-chlorophenyl)propan-1-one (73 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1) to afford the title compound as a light yellow solid (113 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (dt, *J* = 9.2, 2.4 Hz, 2H), 7.46-7.41 (m, 6H), 7.37-7.33 (m, 1H), 7.14 (d, *J* = 1.2 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) HRMS (ESI$^+$): calcd for $C_{16}H_{13}ClO$ $[M+Na]^+$ 279.0553, found 279.0554.



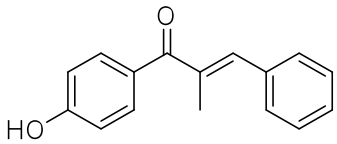
(*E*)-2-methyl-3-phenyl-1-(p-tolyl)prop-2-en-1-one (Table 2, 3c)[3]

The general procedure was applied to 1-(*p*-tolyl)propan-1-one (74 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1) to afford the title compound as a colorless oil (98 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.2 Hz, 2H), 7.40 (m, 4H), 7.33 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.16 (s, 1H), 2.41 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 142.4, 141.4, 137.0, 135.9, 135.6, 129.8 (2C), 129.7 (2C), 128.9 (2C), 128.5 (3C), 21.6, 14.7. GC-MS (EI): calcd for $C_{17}H_{16}O$ [M] 236.12, found 236.15.



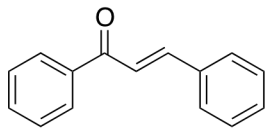
(*E*)-1-(4-methoxyphenyl)-2-methyl-3-phenylprop-2-en-1-one (Table 2, 3d) [3]

The general procedure was applied to 1-(4-methoxyphenyl)propan-1-one (88 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1) to afford the title compound as a light yellow solid (110 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.8 Hz, 2H), 7.44-7.39 (m, 4H), 7.35-7.31 (m, 1H), 7.12 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 198.3, 162.8, 140.1, 137.0, 136.0, 132.0, 130.7, 129.7, 128.5, 128.4, 113.6, 55.5, 15.0. GC-MS (EI): calcd for $C_{17}H_{16}O_2$ [M] 252.12, found 252.16.



(*E*)-1-(4-hydroxyphenyl)-2-methyl-3-phenylprop-2-en-1-one (Table 2, 3e)

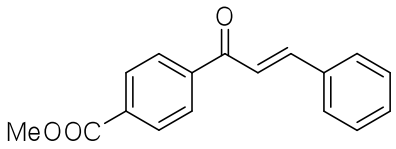
The general procedure was applied to 1-(4-hydroxyphenyl)propan-1-one (75 mg, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a white solid (89 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.8 Hz, 2H), 7.42-7.39 (m, 4H), 7.36-7.31 (m, 1H), 7.12 (s, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.24 (brs, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.1, 159.8, 140.7, 137.0, 136.0, 132.5, 130.7, 129.8, 128.62, 128.59, 115.2, 15.1. HRMS (ESI^+): calcd for $C_{16}H_{14}O_2$ $[M+Na]^+$ 261.0891, found 261.0900.



(*E*)- 1,3-diphenylprop-2-en-1-one (Table 2, 3f)[4,5]

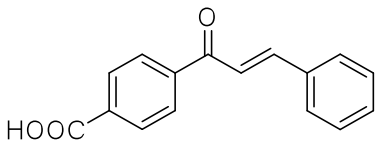
The general procedure was applied to acetophenone (58 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 10:1 ~ 5:1) to afford the title compound as a light yellow solid (65 mg, 62% yield). ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 16.0 Hz, 1H), 7.67-7.64 (m, 2H), 7.58 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.57-7.49 (m, 3H), 7.44-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 190.7, 145.0, 138.4, 135.1, 132.9, 130.7, 129.1, 128.8, 128.7, 128.6, 122.3. GC-MS (EI): calcd for $C_{15}H_{12}O$ [M] 208.09, found 208.14.



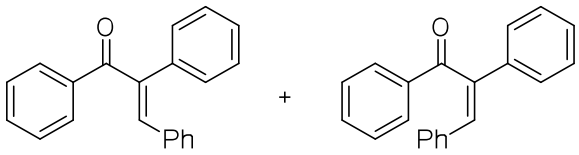
Methyl 4-cinnamoylbenzoate (Table 2, 3g)[6]

The general procedure was applied to methyl 4-acetylbenzoate (89 mg, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1) to afford the title compound as a light yellow solid (60 mg, 43% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 16.0 Hz, 1H), 7.67-7.65 (m, 2H), 7.49 (d, *J* = 15.6 Hz, 1H), 7.45-7.43 (m, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 190.3, 166.5, 146.0, 141.9, 134.8, 133.7, 131.0, 130.0, 129.2, 128.7, 128.5, 122.1, 52.6. GC-MS (EI): calcd for $C_{17}H_{14}O_3$ [M] 266.09, found 266.14.



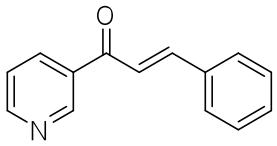
4-Cinnamoylbenzoic acid (Table 2, 3h)[7]

The general procedure was applied to methyl 4-acetylbenzoic acid (82 mg, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a white solid (72 mg, 54% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.68-7.65 (m, 2H), 7.50 (d, *J* = 15.6 Hz, 1H), 7.45-7.44 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* = 194.2, 171.9, 150.0, 146.0, 139.7, 139.6, 136.1, 134.8, 134.3, 134.2, 133.9, 127.2. GC-MS (EI): calcd for $C_{16}H_{12}O_3$ [M] 252.08, found 252.16.



1,2,3-Triphenylprop-2-en-1-one (Table 2, 3i and 3i')[8]

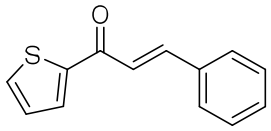
The general procedure was applied to 1,2-diphenylethanone (91 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was analyzed by GC-MS using tridecane as an internal standard to get the stereoisomeric ratio (**3i** : **3i**' = 4:1). Then, it was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:2) to afford the product as a white solid (**3i**: 27 mg, 19% yield; **3i'**: 7 mg, 5% yield.). **3i**: δ = 7.86 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.54 (t, *J* = 4.4 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.35-7.32 (m, 3H), 7.29-7.28 (m, 2H), 7.23-7.16 (m, 4H), 7.09 (dd, *J* =7.2, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 197.7, 140.8, 140.2, 138.2, 136.5, 134.8, 132.2, 130.4, 129.8, 129.7, 129.0, 128.8, 128.32, 128.29, 127.9. **3i'**: ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.45-7.47 (m, 3H), 7.37-7.33 (m, 4H), 7.31-7.28 (m, 3H), 7.20–7.15 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.4, 140.9, 138.0, 136.4, 135.4, 133.7, 130.2, 129.7, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 126.4. GC-MS (EI): calcd for $C_{21}H_{16}O$ [M] 284.12, found 284.18. GC-MS (EI): calcd for $C_{21}H_{16}O$ [M] 284.12, found 284.17.



(*E*)-3-phenyl-1-(pyridin-3-yl)prop-2-en-1-one (Table 2, 3j)[9]

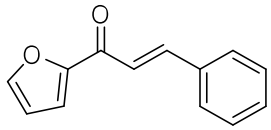
The general procedure was applied to 1-(pyridin-3-yl)ethanone (55 mg, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate 10:1~5:1) to afford the title compound as a yellow solid (58 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (d, *J* = 1.6 Hz, 1H), 8.80 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.28 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.83 (d, *J* = 15.6 Hz, 1H), 7.67-7.65 (m, 2H), 7.51-7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 189.3, 153.3, 149.9, 146.2, 136.1, 134.6,

133.7, 131.2, 129.2, 128.8, 123.8, 121.6. GC-MS (EI): calcd for $C_{14}H_{11}NO$ [M] 209.08, found 209.10.



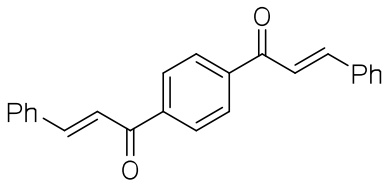
(*E*)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (Table 2, 3k)[10]

The general procedure was applied to 1-(thiophen-2-yl)ethanone (54 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:2~1:1) to afford the title compound as a yellow solid (79 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.84 (d, *J* = 11.6 Hz, 1H), 7.70-7.64 (m, 3H), 7.45-7.41 (m, 4H), 7.18 (t, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 182.2, 145.7, 144.2, 134.9, 134.0, 131.9, 130.7, 129.1, 128.6, 128.4, 121.9. GC-MS (EI): calcd for $C_{13}H_{10}OS$ [M] 214.05, found 214.10.



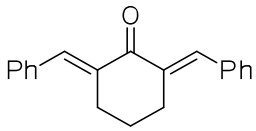
(*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (Table 2, 3l)[9]

The general procedure was applied to 1-(furan-2-yl)ethanone (50 μL, 0.5 mmol), dibenzylamine (480 μL, 2.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:2~1:1) to afford the title compound as a yellow solid (53 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.47-7.38 (m, 5H), 7.34 (m, 1H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.5, 142.2, 138.5, 136.9, 135.8, 131.7, 129.7 (2C), 129.5 (2C), 128.6, 128.5 (2C). GC-MS (EI): calcd for $C_{13}H_{10}O_2$ [M] 198.07, found 198.12.



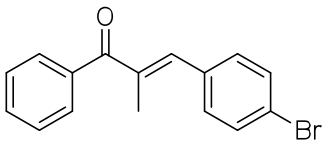
(2*E*,2'*E*)-1,1'-(1,4-phenylene)bis(3-phenylprop-2-en-1-one) (Table 2, 3m)[10]

The general procedure was applied to 1,1'-(1,4-phenylene)diethanone **1d** (81 mg, 0.5 mmol), dibenzylamine **2d** (960 μL, 5.0 mmol), and $(NH_4)_2S_2O_8$ (685 mg, 3.0 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel to provide the desired product (using petroleum ether/CH_2Cl_2 10:1~5:1 as mobile phase) as a yellow solid (51 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 4H), 7.85 (d, *J* = 15.6 Hz, 2H), 7.68–7.66 (m, 4H), 7.54 (d, *J* = 15.6 Hz, 2H), 7.46–7.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 190.1, 145.9, 141.3, 134.6, 130.9, 129.1, 128.7, 128.6, 121.9. LC-MS (ESI$^+$): calcd for $C_{24}H_{18}O_2$ $[M+H]^+$ 339.14, found 339.24.



(2*E*, 6*E*)-2,6-dibenzylidenecyclohexanone (Table 2, 3n)[11]

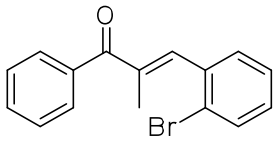
The general procedure was applied to cyclohexanone (52 μL, 0.5 mmol), dibenzylamine (480 μL, 5.0 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a yellow solid (71 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 2H), 7.45 (d, *J* = 7.2 Hz, 4H), 7.38 (t, *J* = 7.6 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 5.2 Hz, 4H), 1.80-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 190.5, 137.0, 136.3, 136.1, 130.5, 128.7, 128.5, 28.6, 23.1. GC-MS (EI): calcd for $C_{20}H_{18}O$ [M] 274.14, found 274.19.



(*E*)-3-(4-bromophenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3o)[12]

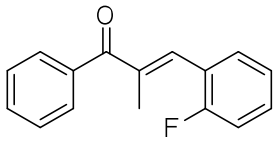
The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 1-(4-bromophenyl)-N-methylmethanamine (250 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a light yellow solid

(67 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.2 Hz, 2H), 7.55-7.53 (m, 3H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.09 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.2, 140.6, 138.2, 137.5, 134.7, 131.8, 131.7, 131.2, 129.5, 128.3, 122.8, 14.5. GC-MS (EI): calcd for $C_{16}H_{13}BrO$ [M] 300.01, found 300.07.



(*E*)-3-(2-bromophenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3p)

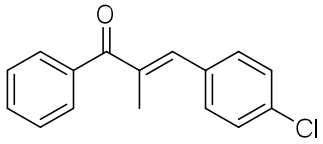
The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 1-(2-bromophenyl)-N-methylmethanamine (184 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a light yellow solid (39 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.42 (m, 2H), 7.32 (s, 1H), 7.26 (m, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.1, 140.7, 138.1, 137.9, 136.3, 132.8, 130.4, 129.74 (2C), 129.67 (2C), 128.3 (2C), 127.1, 124.2, 14.2. HRMS (ESI^+): calcd for $C_{16}H_{13}BrO$ $[M+Na]^+$ 323.0047, found 323.0056.



(*E*)-3-(2-fluorophenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3q)

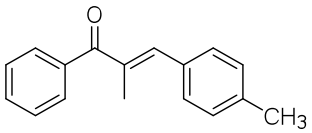
The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 1-(2-fluorophenyl)-N-methylmethanamine (166 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a light yellow oil (30 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49-7.42 (m, 3H), 7.36-7.31 (m, 1H), 7.21-7.17 (m, 2H), 7.10 (t, *J* = 8.1 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.0, 161.5, 159.0, 138.9, 138.1, 134.3 (*J* = 12 Hz), 132.0, 130.4, 129.6 (3C), 128.3 (2C), 123.9 (*J* = 12

Hz), 115.7 (J = 22 Hz), 14.6. HRMS (ESI^+): calcd for $C_{16}H_{13}FO$ $[M+Na]^+$ 268.0848, found 263.0844.



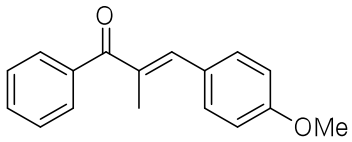
(*E*)-3-(4-chlorophenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3r)[13]

The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 1-(4-chlorophenyl)-N-methylmethanamine (179 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a light yellow oil (50 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.39-7.33 (m, 4H), 7.11 (s, 1H), 2.24 (d, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 140.6, 138.3, 137.4, 134.5, 134.2, 131.8, 130.9, 129.5, 128.7, 128.3, 14.5. GC-MS (EI): calcd for $C_{16}H_{13}ClO$ [M] 256.07, found 256.12.



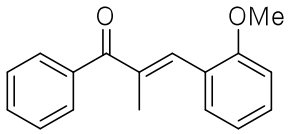
(*E*)-2-methyl-1-phenyl-3-(p-tolyl)prop-2-en-1-one (Table 3, 3s)[14]

The general procedure was applied to propiophenone (33 μL, 0.25 mmol), N-methyl-1-(p-tolyl)methanamine (184 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a colorless oil (45 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 6.8 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 16 Hz, 2H), 7.21 (d, J = 16 Hz, 2H), 7.17 (s, 1H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 142.6, 138.9, 138.7, 136.0, 133.0, 131.5, 129.8, 129.5, 129.2, 128.2, 21.4, 14.4. GC-MS (EI): calcd for $C_{17}H_{16}O$ [M] 236.12, found 236.17.



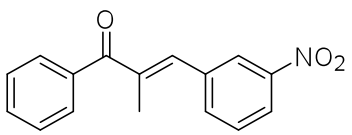
(*E*)-3-(4-methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3t)

The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 1-(4-methoxyphenyl)-N-methylmethanamine (195 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a light yellow solid (43 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.52 (t, *J* = 5.6 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.15 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.28 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.6, 160.0, 142.7, 138.9, 134.9, 131.6, 131.4, 129.4, 128.4, 128.2, 114.0, 55.4, 14.4. HRMS (ESI$^+$): calcd for $C_{17}H_{16}O_2$ $[M+Na]^+$ 275.1048, found 275.1052.



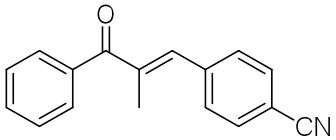
(*E*)-3-(2-methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3u)

The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 1-(2-methoxyphenyl)-N-methylmethanamine (188 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as light yellow oil (35 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.47-7.40 (m, 3H), 7.38 (s, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 2.18 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.4, 157.4, 138.7, 138.5, 136.4, 131.6, 130.1,130.0, 129.7, 128.1, 124.9, 120.2, 110.5, 55.5, 14.4. HRMS (ESI$^+$): calcd for $C_{17}H_{16}O_2$ $[M+Na]^+$ 275.1048, found 275.1047.



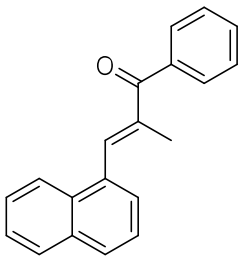
(*E*)-2-methyl-3-(3-nitrophenyl)-1-phenylprop-2-en-1-one (Table 3, 3v)

The general procedure was applied to propiophenone (33 μL, 0.25 mmol), N-methyl-1-(3-nitrophenyl)methanamine (179 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a white solid (46 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (t, *J* = 2.0 Hz, 1H), 7.78 (td, *J* = 8.0, 0.8 Hz, 1H), 7.77 (td, *J* = 8.4, 2.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62-7.56 (m, 2H), 7.48 (t, *J* = 5.6 Hz, 2H), 7.16 (s, 1H), 2.28 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 198.7, 148.3, 139.5, 138.1, 137.7, 137.4, 135.2, 132.2, 129.5 (3C), 128.4 (2C), 124.1, 123.1, 14.6. HRMS (ESI$^+$): calcd for $C_{16}H_{13}NO_3$ $[M+Na]^+$ 290.0793, found 290.0789.



(*E*)-3-(4-cyanophenyl)-2-methyl-1-phenylprop-2-en-1-one (Table 3, 3w)

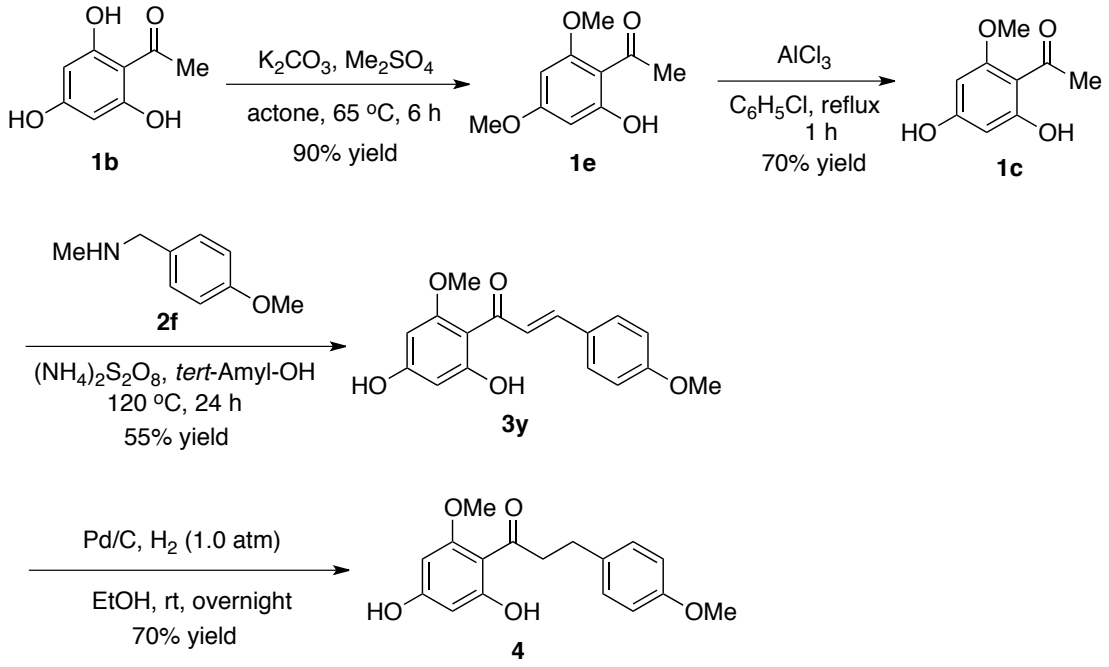
The general procedure was applied to propiophenone (33 μL, 0.25 mmol), 4-((methylamino)methyl)benzonitrile (176 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a white solid (56 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51-7.46 (m, 4H), 7.11 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 198.7, 140.3, 139.7, 138.7, 137.6, 132.25, 132.22, 130.0, 129.6, 128.4, 118.6, 111.8, 14.7. HRMS (ESI$^+$): calcd for $C_{17}H_{13}NO$ $[M+Na]^+$ 270.0895, found 270.0933.



(*E*)-2-methyl-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one (Table 3, 3x)

The general procedure was applied to propiophenone (33 μL, 0.25 mmol), *N*-methyl-1-(naphthalen-1-yl)methanamine (204 μL, 1.25 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 5:1~5:2) to afford the title compound as a white solid (33 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (m, 4H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.58 (t, *J* = 6.4 Hz, 1H), 7.52 (m, 6H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.3, 140.3, 139.0, 138.5, 133.6, 133.0, 131.9, 131.4, 129.5, 128.9, 128.7, 128.4, 126.8, 126.5, 126.2, 125.2, 124.5, 14.6. HRMS (ESI$^+$): calcd for $C_{20}H_{16}O$ [M+Na]$^+$ 295.1099, found 295.1093.

4. Concise Synthesis of Bioactive Cytotoxic Dihydrochalcone 4[15]



Compound **1e**, **1c** were prepared according to the literature.[15]

1-(2-Hydroxy-4,6-dimethoxyphenyl)ethanone **1e**: 947 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.03 (s, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 5.91 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 203.2, 167.6, 166.1, 162.9, 106.0, 93.5, 90.8, 55.6 (2C), 32.9.

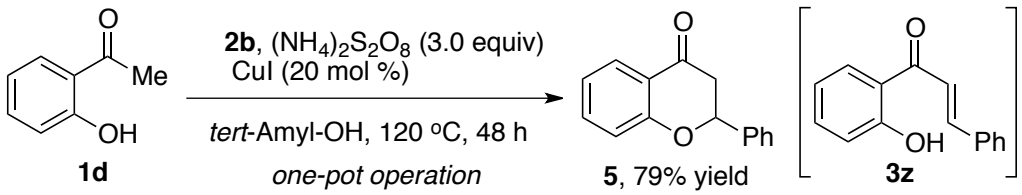
1-(2,4-Dihydroxy-6-methoxyphenyl)ethanone **1c**: 357 mg, 70% yield. ^{1}H NMR (400 MHz, DMSO-*d*^{6}): δ = 13.82 (s, 1H), 5.97 (d, *J* = 2.0 Hz, 1H), 5.86 (d, *J* = 2.0 Hz, 1H),

3.82 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d^6): δ = 202.2, 166.3, 165.2, 163.4, 104.6, 95.6, 91.3, 55.8, 32.6.

Synthesis of compound 3y: The general procedure was applied to compound **1c** (91mg, 0.5 mmol), 1-(4-methoxyphenyl)-*N*-methylmethanamine **2f** (390 μL, 2.5 mmol), and $(NH_4)_2S_2O_8$ (342.3 mg, 1.5 mmol) at 120 ºC for 24 h under N_2. The crude product was purified by column chromatography on silica gel to provide the desired product **3y** as a yellow solid (80 mg, 55% yield) (using petroleum ether/ ethyl acetate 5:1~5:2 as mobile phase). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.04 (s, 1H), 9.89 (s, 1H), 7.97 (d, J = 15.6 Hz, 1H), 7.84 (d, J = 15.6 Hz, 1H), 7.61 (d, J = 6.8 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.05 (d, J = 2.4 Hz, 1H), 5.91 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8, 166.6, 165.1, 163.6, 161.9, 131.0 (2C), 128.9, 113.3 (2C), 105.0, 92.4 (2C), 89.7 (2C), 54.6, 54.5.

Synthesis of cytotoxic dihydrochalcone 4: In a dried Schlenk tube, compound (45 mg, 0.15 mmol), Pd/C (5 wt%, 20 mg) and ethanol (2.0 mL) were added under a hydrogen atmosphere (1.0 atm). The mixture was stirred at room temperature for overnight. After evaporation of the solvent under vacuum, the resulting residue was purified by chromatography (PE/EtOAc = 5:2) to provide the desired product **4** as a white solid (32 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.96 (s, 1H), 7.15 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 5.99 (d, J = 2.4 Hz, 1H), 5.90 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.26 (t, J = 7.6 Hz, 2H), 2.93 (t, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.2, 167.6, 166.1, 162.9, 159.2, 133.1, 128.7, 114.0, 106.0, 93.5, 90.8, 55.6, 55.3, 45.1, 32.9.

5. Synthesis of Flavonoid Derivative 5[16] via a One-Pot Operation

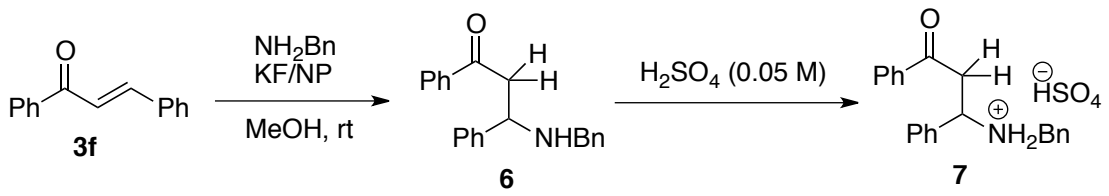


In a dried Schlenk tube, 1-(2-hydroxyphenyl)ethanone **1d** (136 mg, 1.0 mmol), *N*-methyl-1-phenylmethanamine **2b** (682 μL, 5.0 mmol), CuI (38.2 mg, 0.2 mmol),

$(NH_4)_2S_2O_8$ (684 mg, 3.0 mmol) and *tert*-Amyl alcohol (2.0 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at 120 °C for 48 h. Then the crude product was purified by column chromatography (PE/EtOAc = 5:2) (177 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.0 Hz, 1H), 7.54-7.48 (m, 3H), 7.46-7.39 (m, 3H), 7.08-7.05 (m, 2H), 5.49 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.10 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.90 (dd, *J* = 14.0, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 192.0, 161.6, 138.7, 136.2, 128.9, 128.8, 127.1, 126.2, 121.7, 120.9, 118.2, 79.6, 44.7. GC-MS (EI): calcd for $C_{15}H_{12}O_2$ [M] 224.08, found 224.15.

6. Synthesis of Compounds 6 and 7 for Mechanistic Studies

Synthesis of *β*-Amino Ketone 6 and the Related Ammonium Salt 7



In a dried Schlenk, chalcone **3f** (936 mg, 4.5 mmol), benzylamine (492 μL, 4.5 mmol), KF/NP phosphate catalyst[17,18] and methanol (4.5 mL) was added under a nitrogen atmosphere. Then the mixture was stirred at room temperature for 24 h. The desired *β*-amino ketone **6** was obtained as a white solid through recrystallization from a PE/EtOAc solution (850 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43-7.39 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30-7.25 (m, 5H), 7.23-7.21 (m, 1H), 4.34 (dd, *J* = 4.4, 4.0 Hz, 1H), 3.62 (q, *J* = 13.6, 13.2 Hz, 2H), 3.38-3.28 (m, 2H), 2.26 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 198.9, 143.3, 140.4, 136.9, 133.2, 128.7, 128.6, 128.3, 128.2, 128.1, 127.41, 127.37, 126.8, 58.6, 51.6, 47.4. LC-MS (ESI^+): calcd for $C_{22}H_{21}NO$ $[M+H]^+$ 316.17, found 316.27.

A Schlenk tube was loaded with *β*-amino ketone **6** (470 mg, 1.5 mmol) and EtOAc (5 mL). When 0.05 M H_2SO_4 (4 mL) was dropped into the solution, a colorless solid was produced at the boundary phase. After filtration and dry under vacuum, the desired ammonium salt **7** was obtained as a colorless solid (607 mg, 98%)[19]. ^{1}H NMR (400

MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 2H), 7.45-7.27 (m, 11H), 4.64 (s, 1H), 7.24 (d, *J* = 16.4 Hz, 1H), 4.07-4.03 (m, 1H), 3.95 (d, *J* = 13.6 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 1.61 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 199.0, 143.2, 140.4, 136.9, 133.2, 128.7, 128.6, 128.3, 128.2, 128.1, 127.43, 127.38, 126.8, 57.7, 48.4, 42.8. LC-MS (ESI^+): calcd for $C_{22}H_{21}NO$ $[M\text{-}HSO_4^-]^+$ 316.17, found 316.21.

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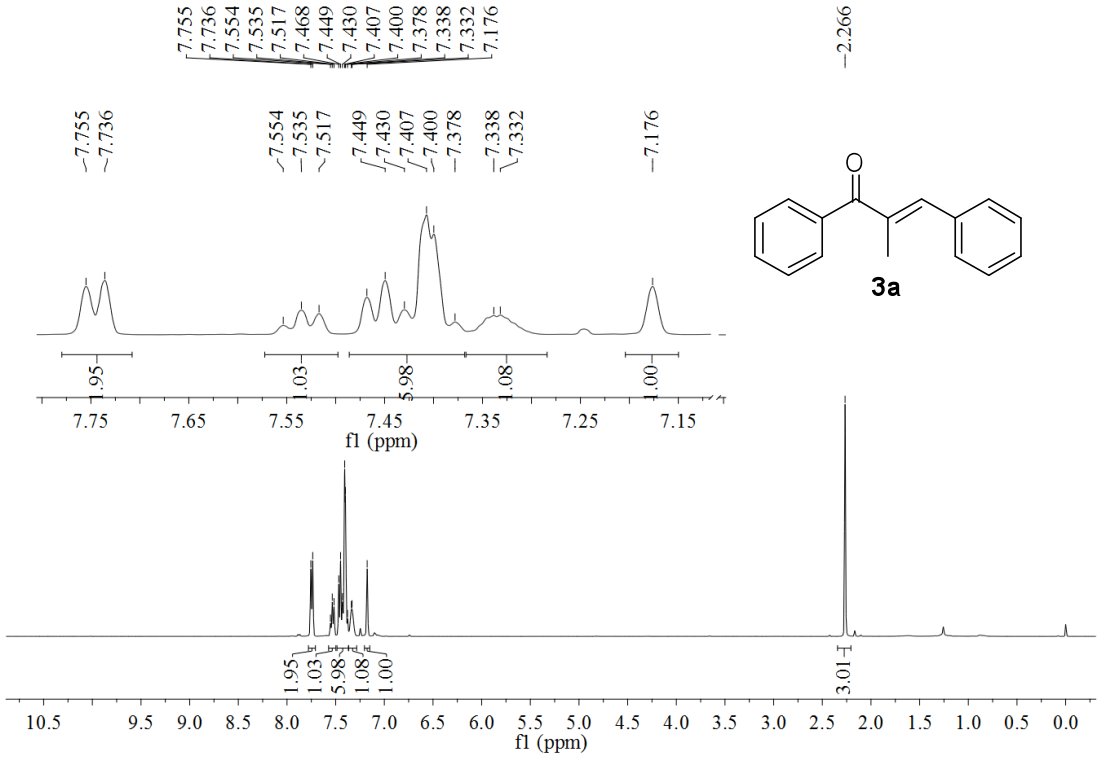
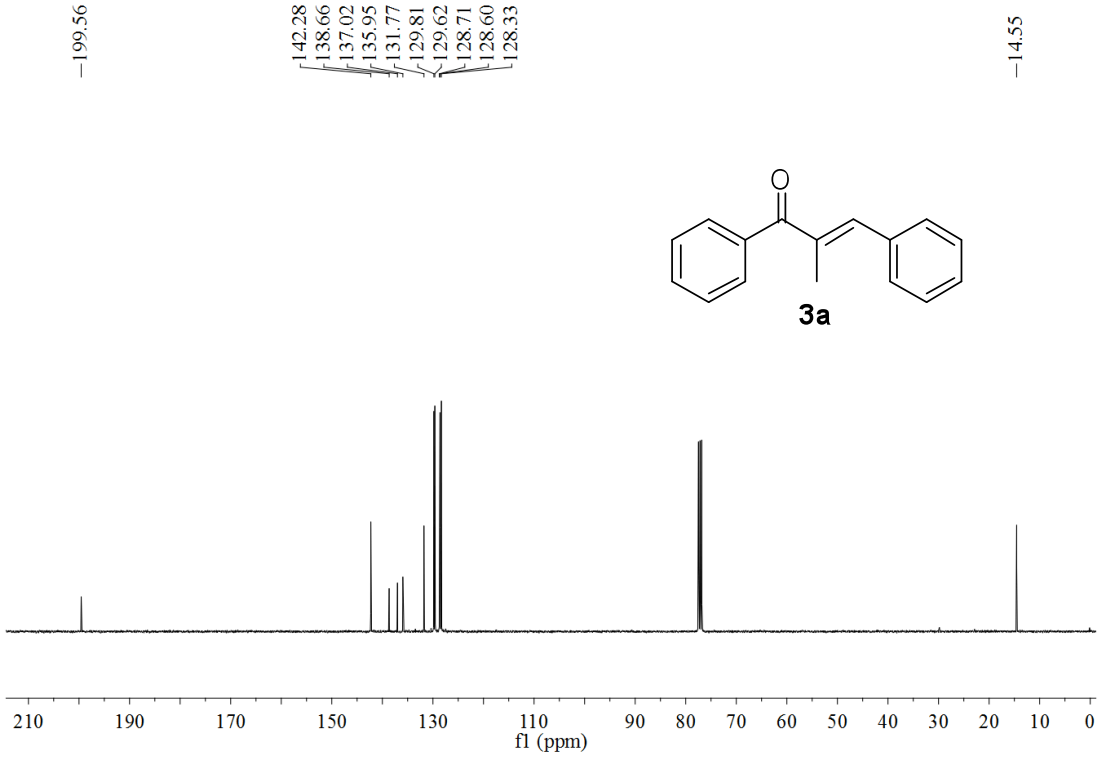
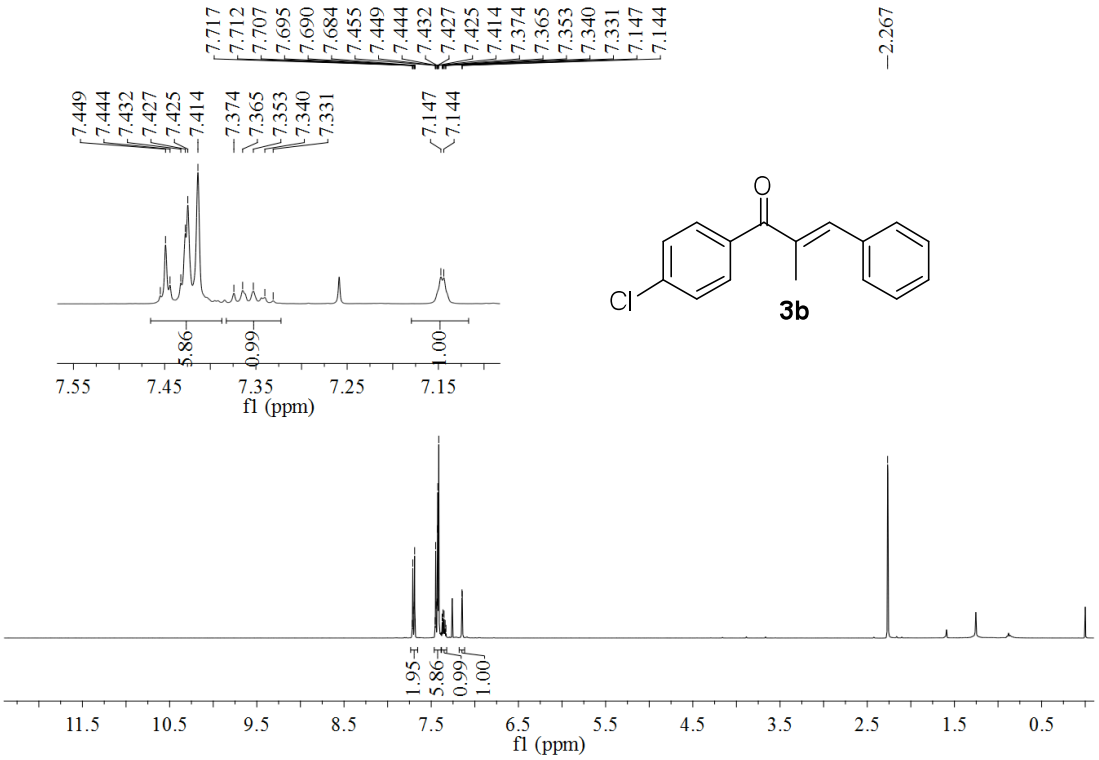
(19) Wilson, S. D.; Sun, L. H. *Journal of the Chinese Chemical Society* (Peking) **1934**, *V2*, 243.

7. Copies of ^{1}H and ^{13}C NMR spectra



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7.427
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7.414
7.374
7.365
7.353
7.340
7.331
7.147
7.144
2.267
5.86
0.99
1.00
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
Cl
O
3b
1.95
5.86
0.99
1.00
11.5
10.5
9.5
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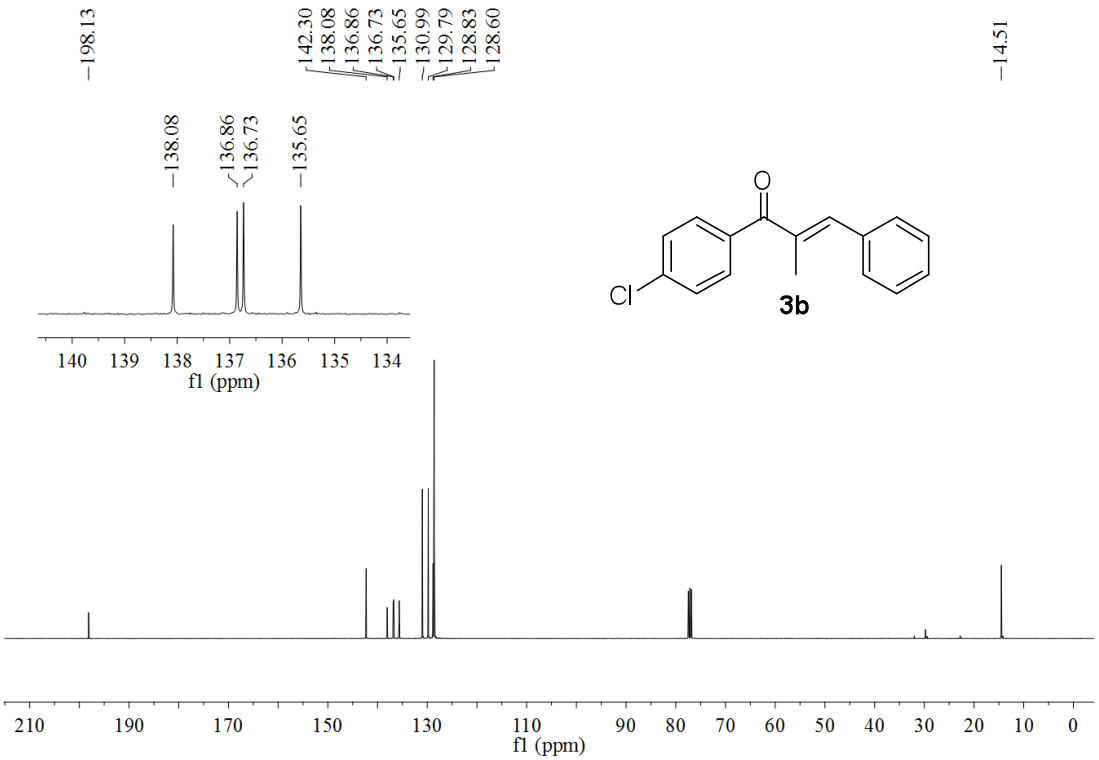
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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136.73
135.65
140
139
138
137
136
135
134
f1 (ppm)
Cl
O
3b
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90
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50
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30
20
10
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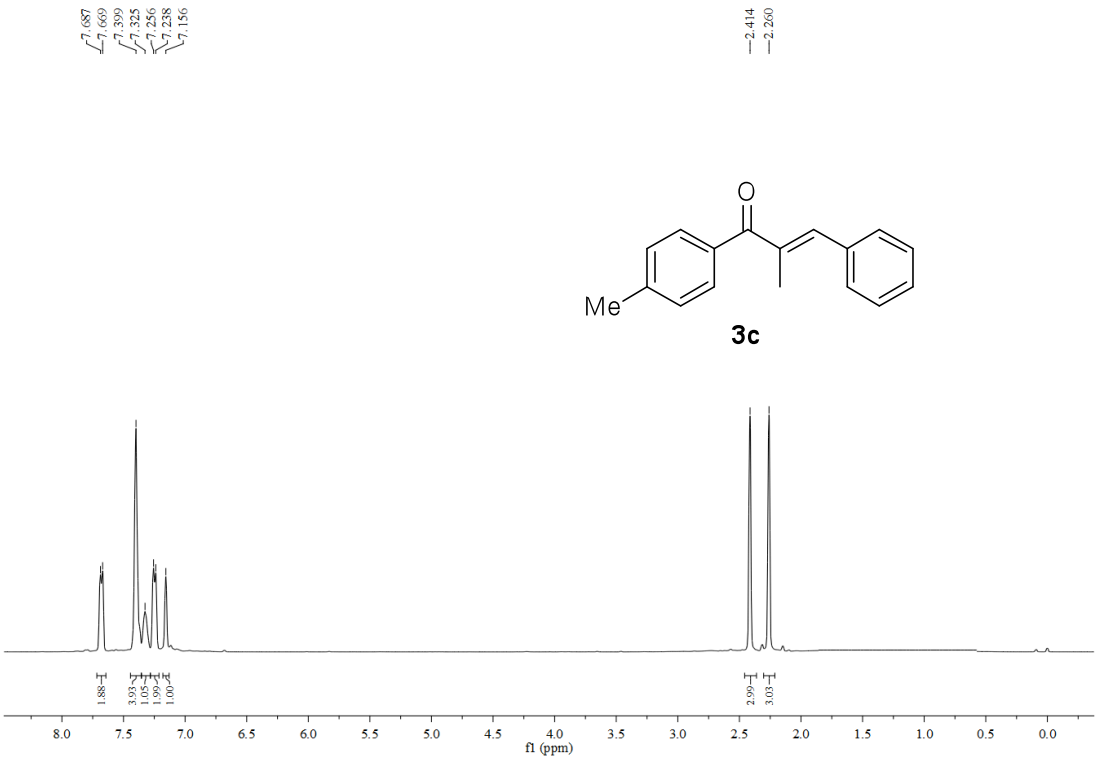
f1 (ppm)



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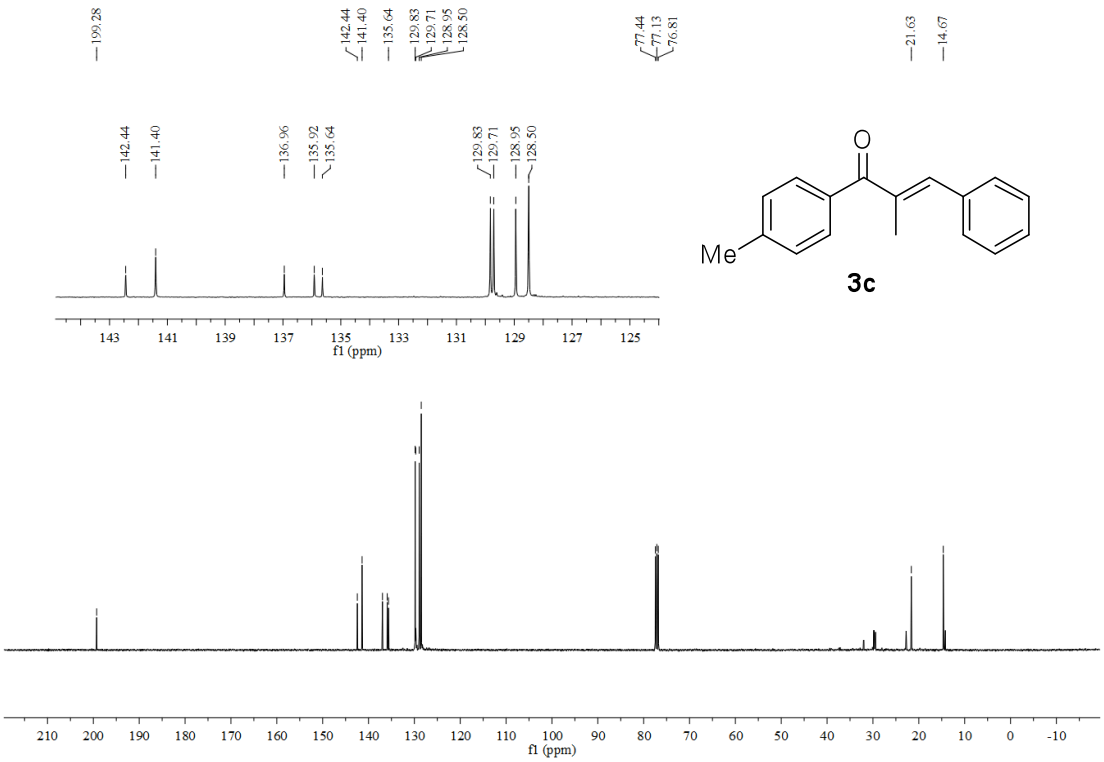

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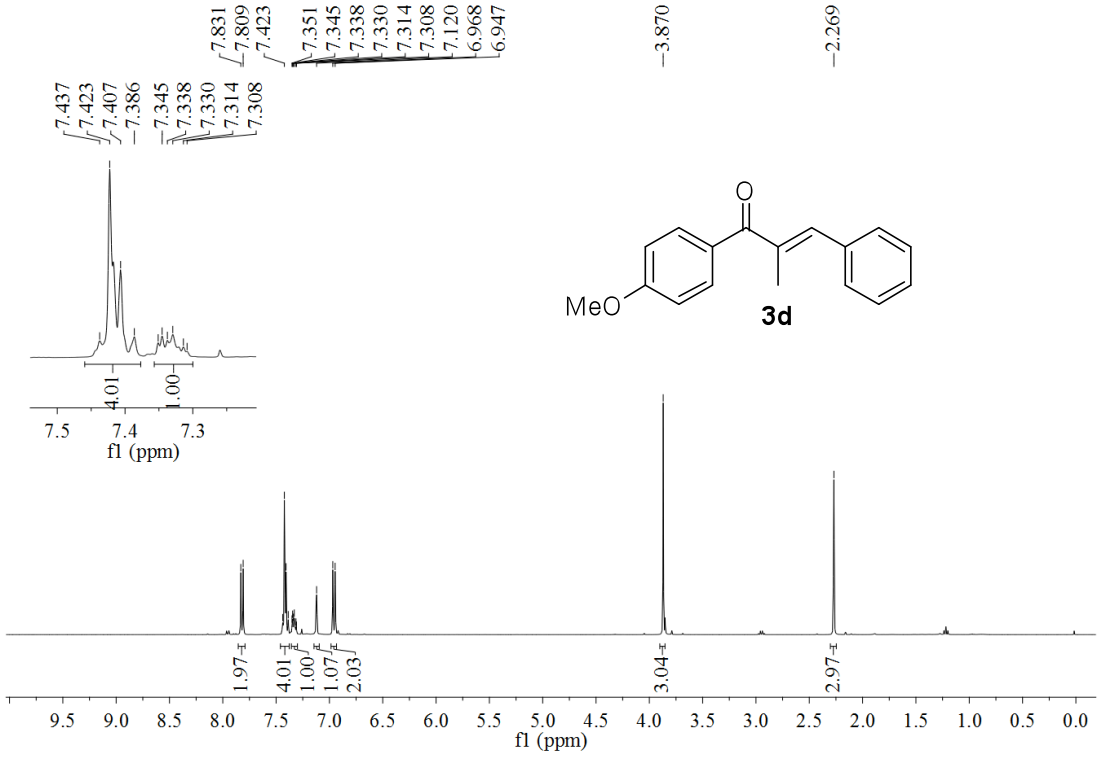
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3.870
2.269
7.437
7.423
7.407
7.386
7.345
7.338
7.330
7.314
7.308
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7.5
7.4
7.3
f1 (ppm)
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4.01
1.00
1.07
2.03
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2.97
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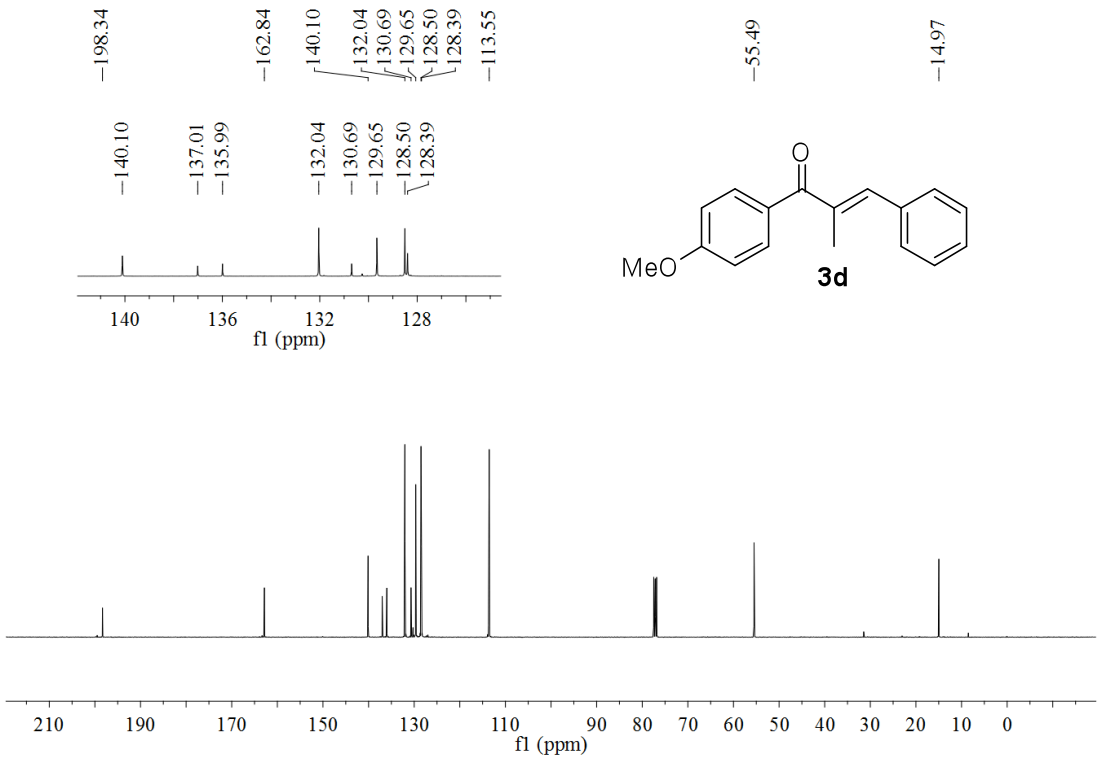
f1 (ppm)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128.39
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135.99
132.04
130.69
129.65
128.50
128.39
MeO
3d
140
136
132
128
f1 (ppm)
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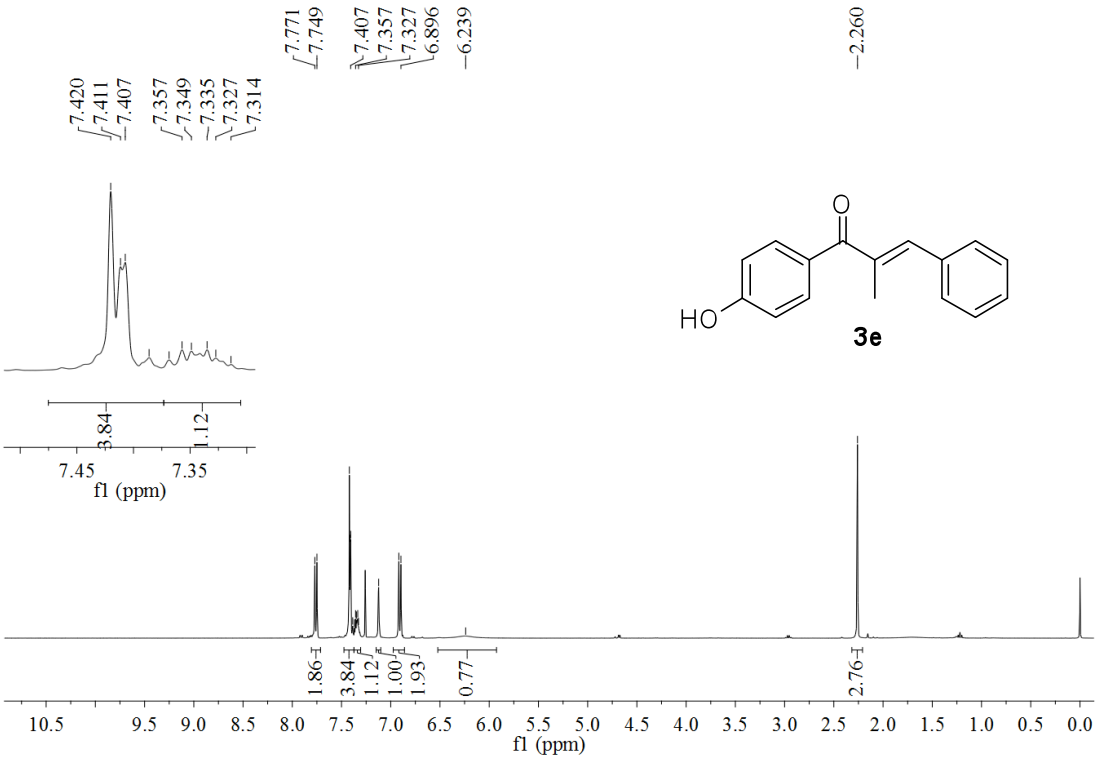
f1 (ppm)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O
HO
3e
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7.45
7.35
f1 (ppm)
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3.84
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10.5
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
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4.5
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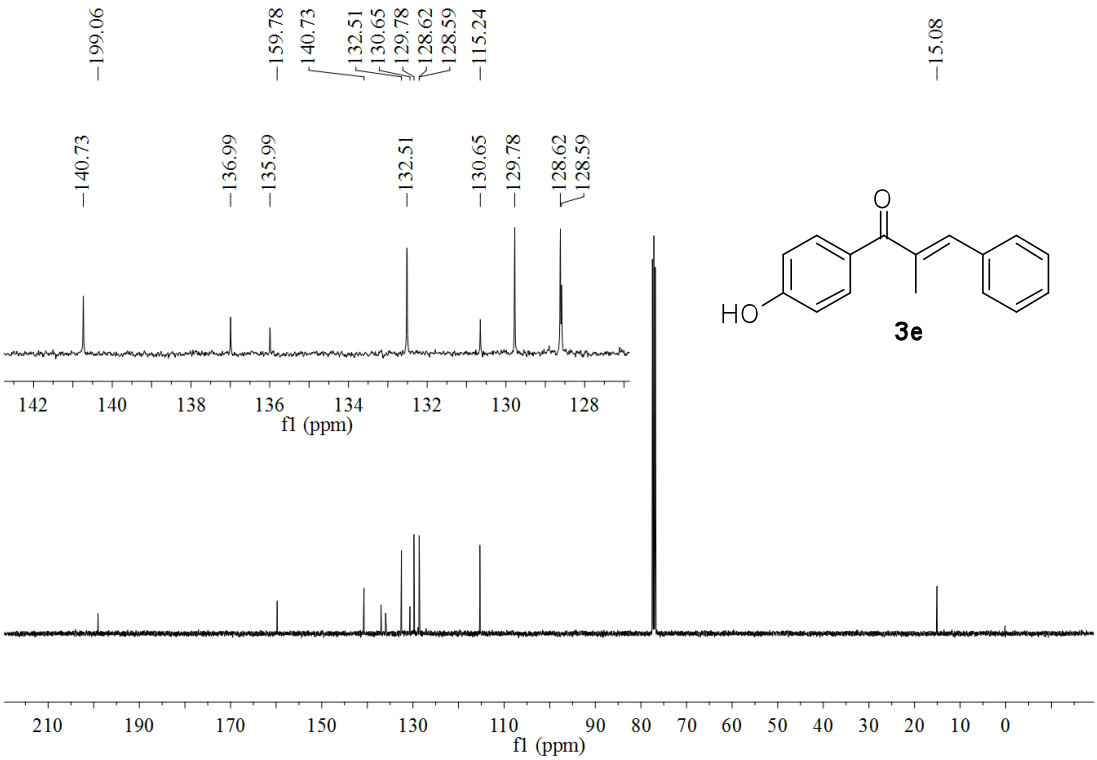
f1 (ppm)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132
130
128
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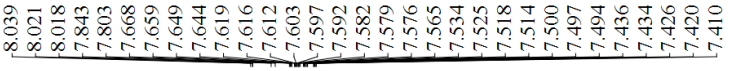
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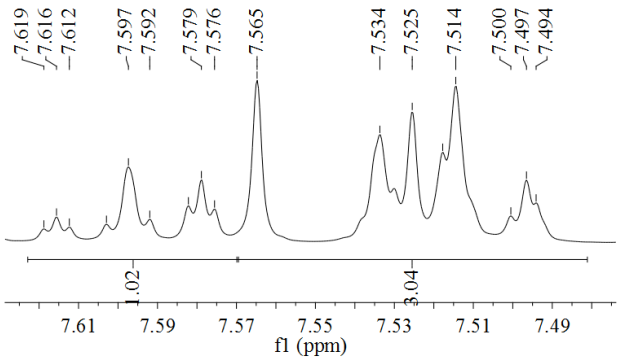
7.420
7.410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7.579
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7.565
7.534
7.525
7.514
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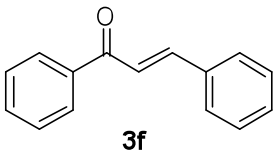
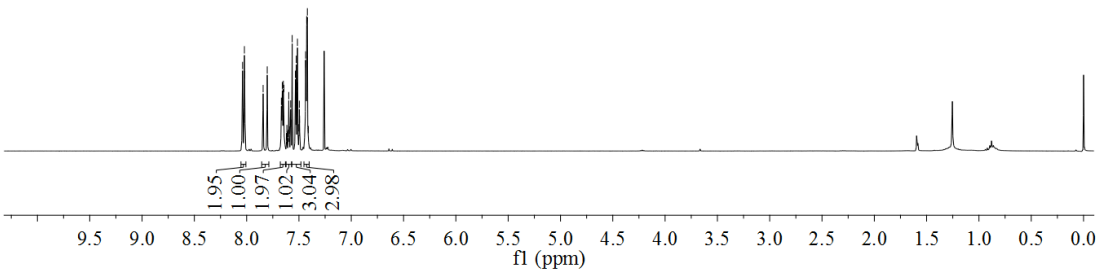
7.55
7.53
7.51
7.49
f1 (ppm)


O
3f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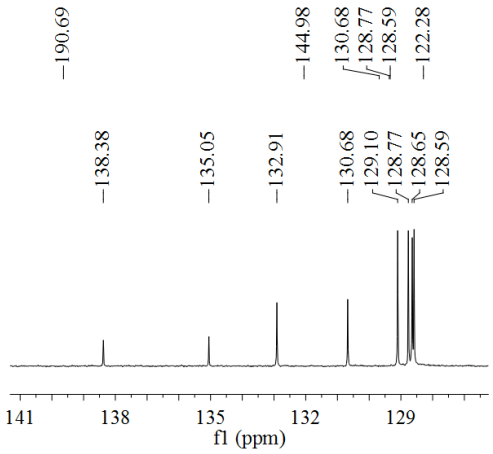
f1 (ppm)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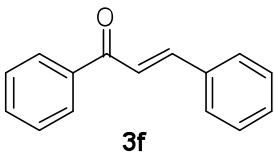
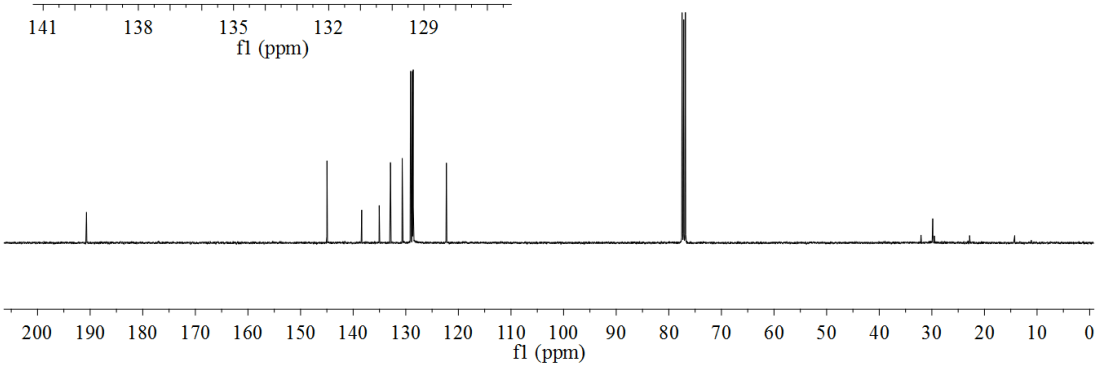
128.59
141
138
135
132
129
f1 (ppm)


O
3f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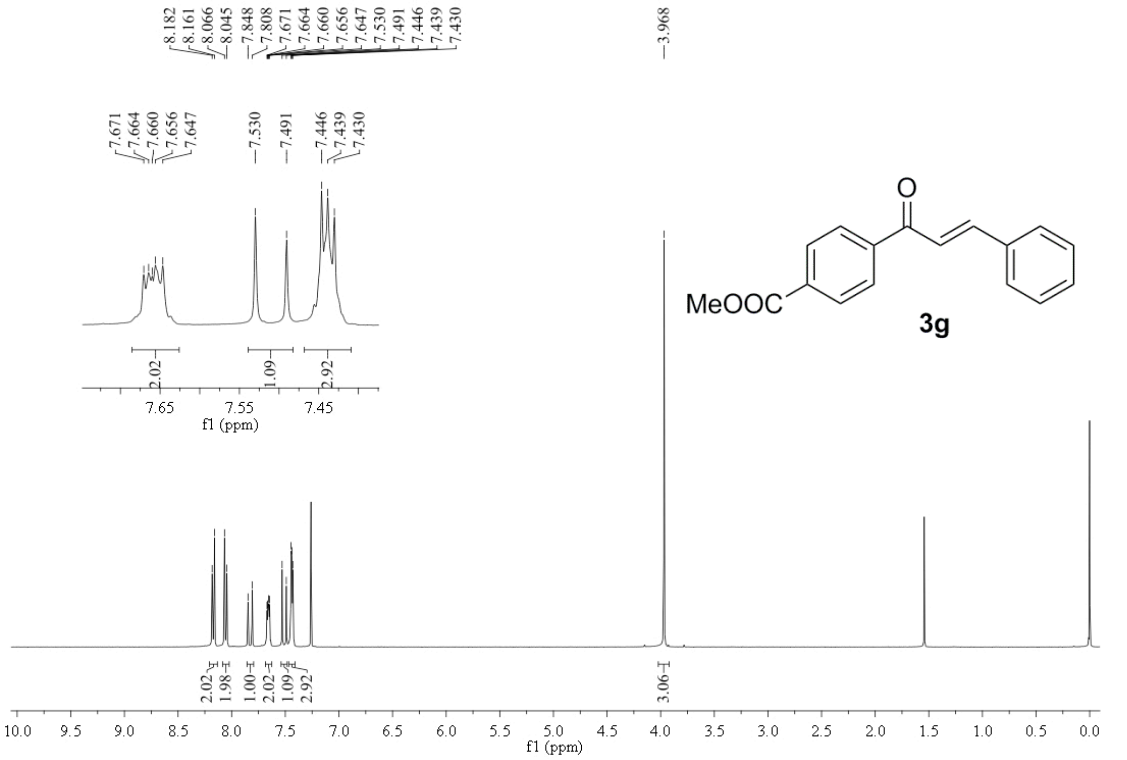
40
30
20
10
0
f1 (ppm)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7.446
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7.430
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1.09
2.92
7.65
7.55
7.45
f1 (ppm)
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O
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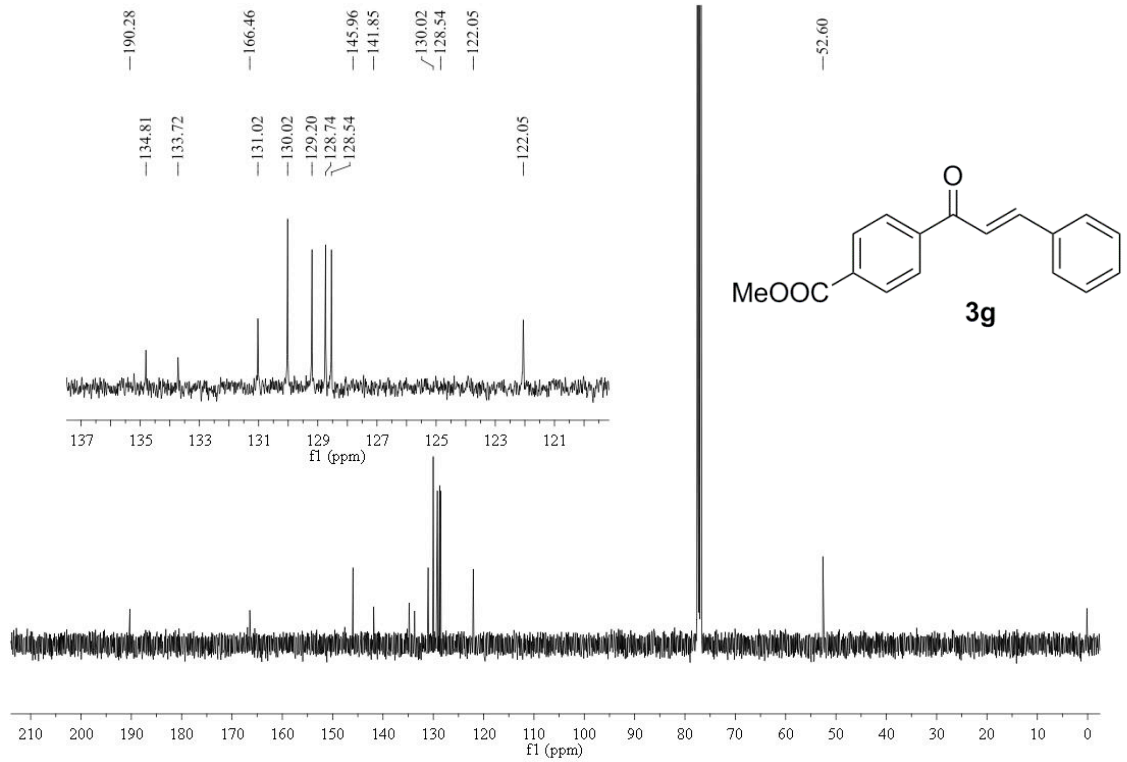
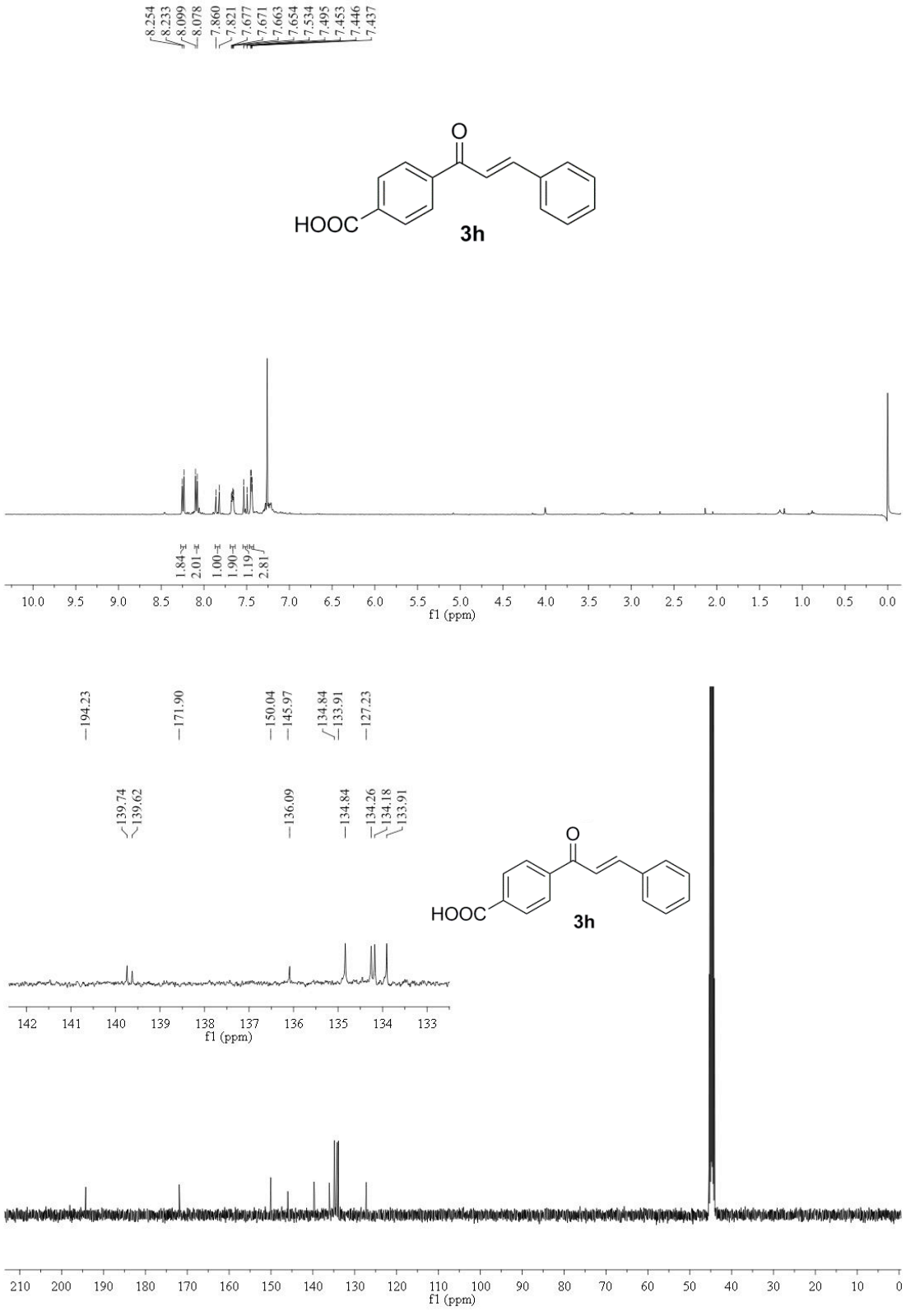
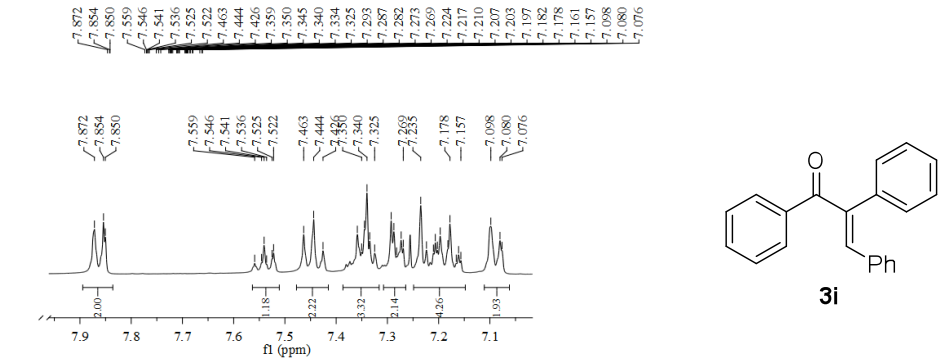
2.02
1.98
1.00
2.02
1.09
2.92
3.06
f1 (ppm)


190.28
166.46
145.96
141.85
130.02
128.54
122.05
52.60
134.81
133.72
131.02
130.02
129.20
128.74
128.54
122.05
137
135
133
131
129
127
125
123
121
f1 (ppm)
MeOOC
O
3g
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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7.444
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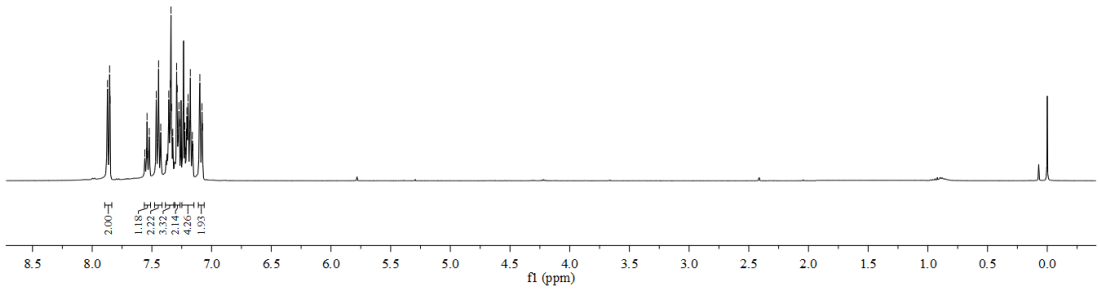
7.359
7.350
7.345
7.340
7.334
7.325
7.293
7.287
7.282
7.273
7.269
7.224
7.217
7.210
7.207
7.203
7.197
7.182
7.178
7.161
7.157
7.098
7.080
7.076
2.00
1.18
2.22
3.32
2.14
4.26
1.93
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)

O
Ph

3i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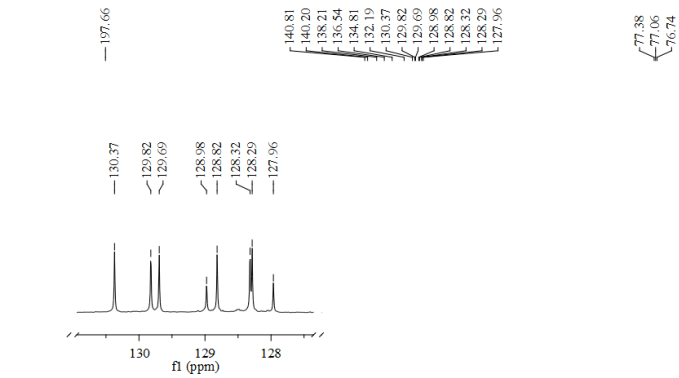
1.18
2.22
3.32
2.14
4.26
1.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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140.81
140.20
138.21
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134.81
132.19
130.37
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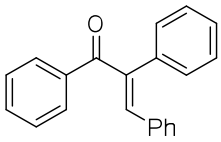
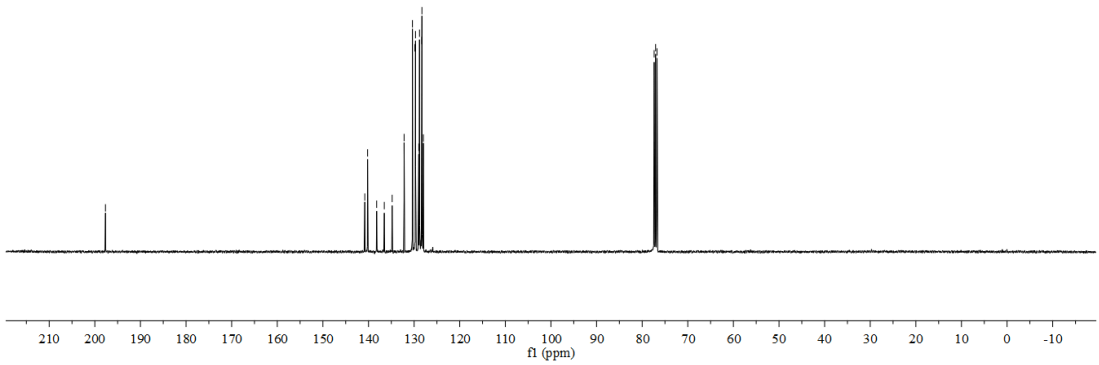
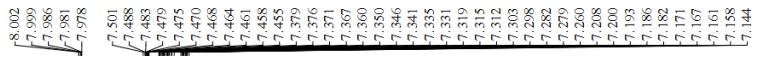
129.69
128.98
128.82
128.32
128.29
127.96
77.38
77.06
76.74
130.37
129.82
129.69
128.98
128.82
128.32
128.29
127.96
130
129
128
f1 (ppm)


O
Ph

3i


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.002
7.999
7.986
7.981
7.978
7.501
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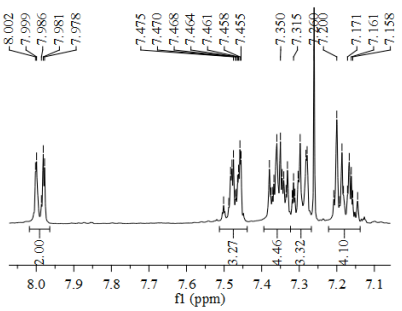
7.483
7.479
7.475
7.470
7.468
7.464
7.461
7.458
7.455
7.379
7.376
7.371
7.367
7.360
7.350
7.346
7.341
7.335
7.331
7.319
7.315
7.312
7.303
7.298
7.282
7.279
7.260
7.208
7.200
7.193
7.186
7.182
7.171
7.167
7.161
7.158
7.144


8.002
7.999
7.986
7.981
7.978
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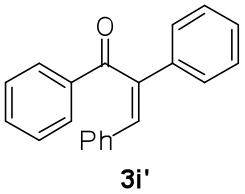
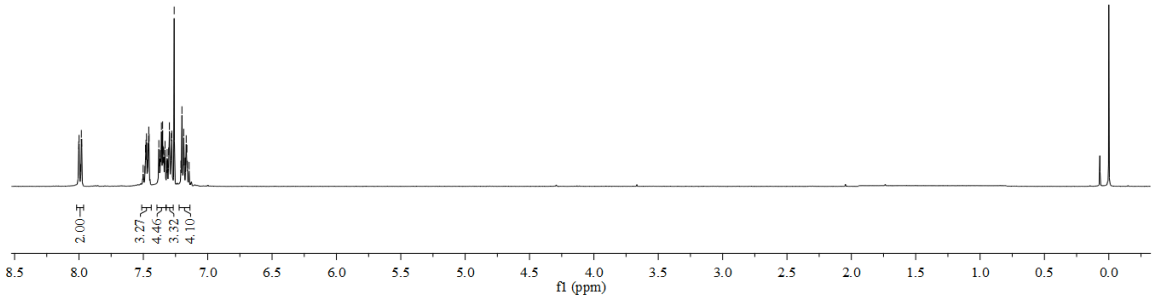
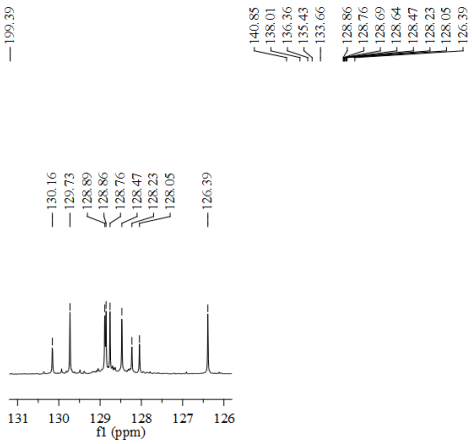
7.470
7.468
7.464
7.461
7.458
7.455
7.350
7.315
7.200
7.171
7.161
7.158
2.00
3.27
4.46
3.32
4.10
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)


O
Ph

3i'


2.00
3.27
4.46
3.32
4.10
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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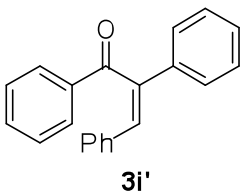
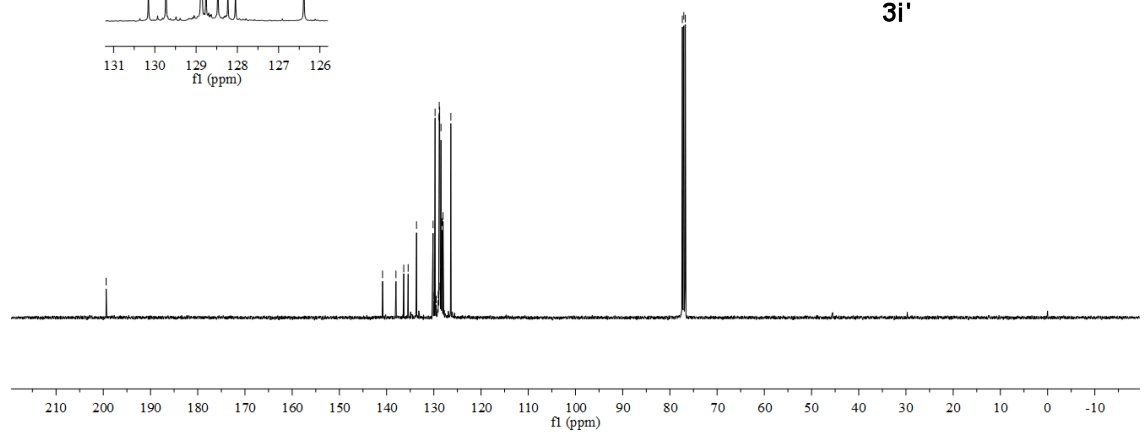
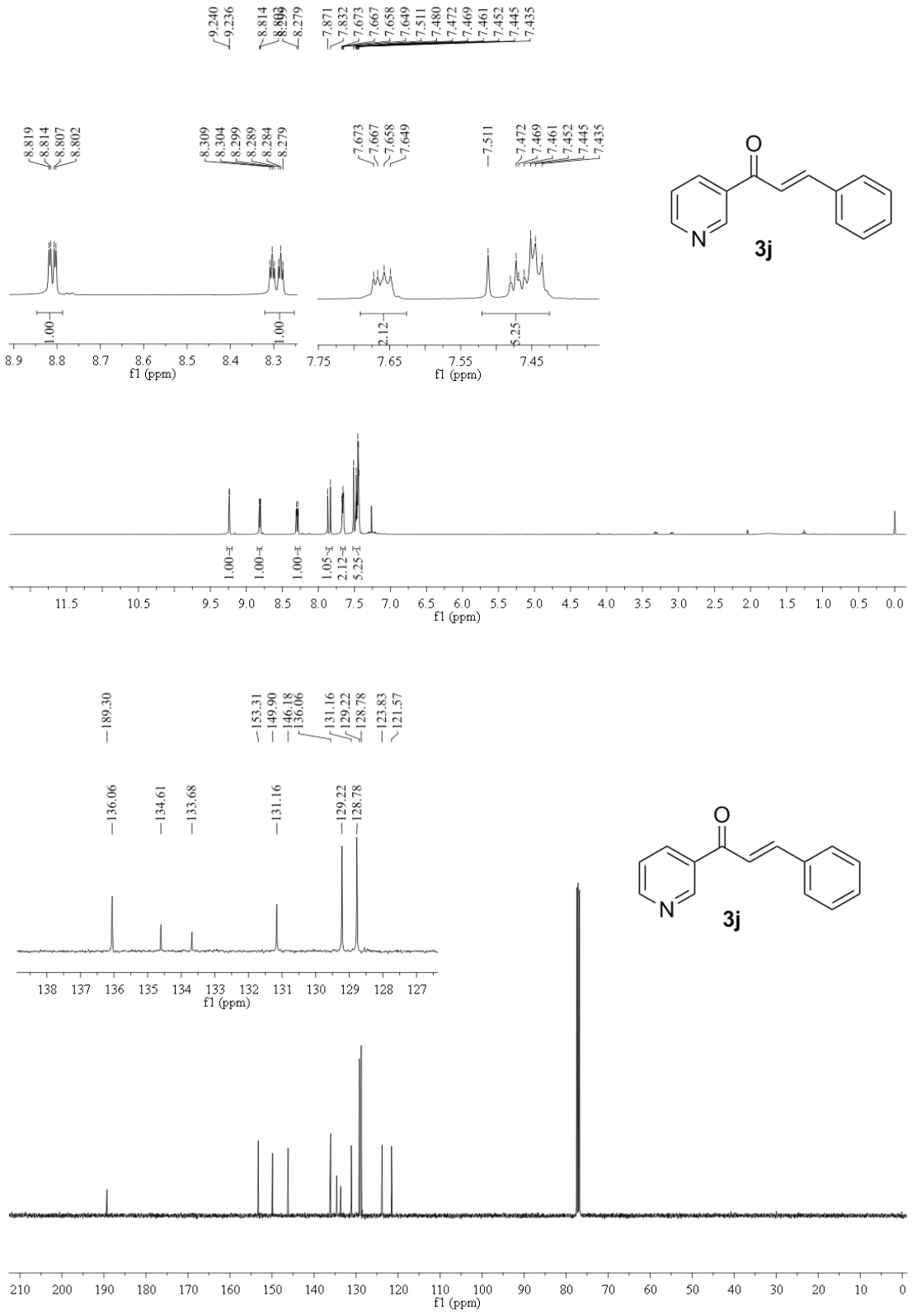
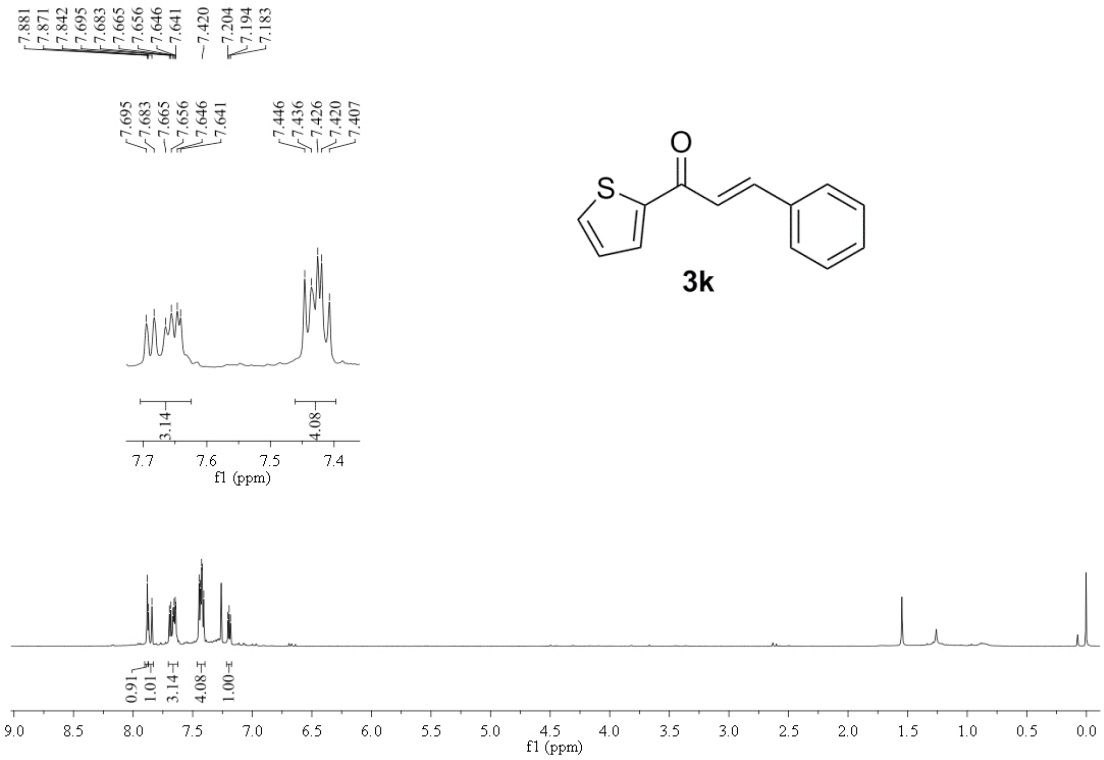
140.85
138.01
136.36
135.43
133.66
128.86
128.76
128.69
128.64
128.47
128.23
128.05
126.39
77.36
77.05
76.73
130.16
129.73
128.89
128.86
128.76
128.47
128.23
128.05
126.39
131
130
129
128
127
126
f1 (ppm)

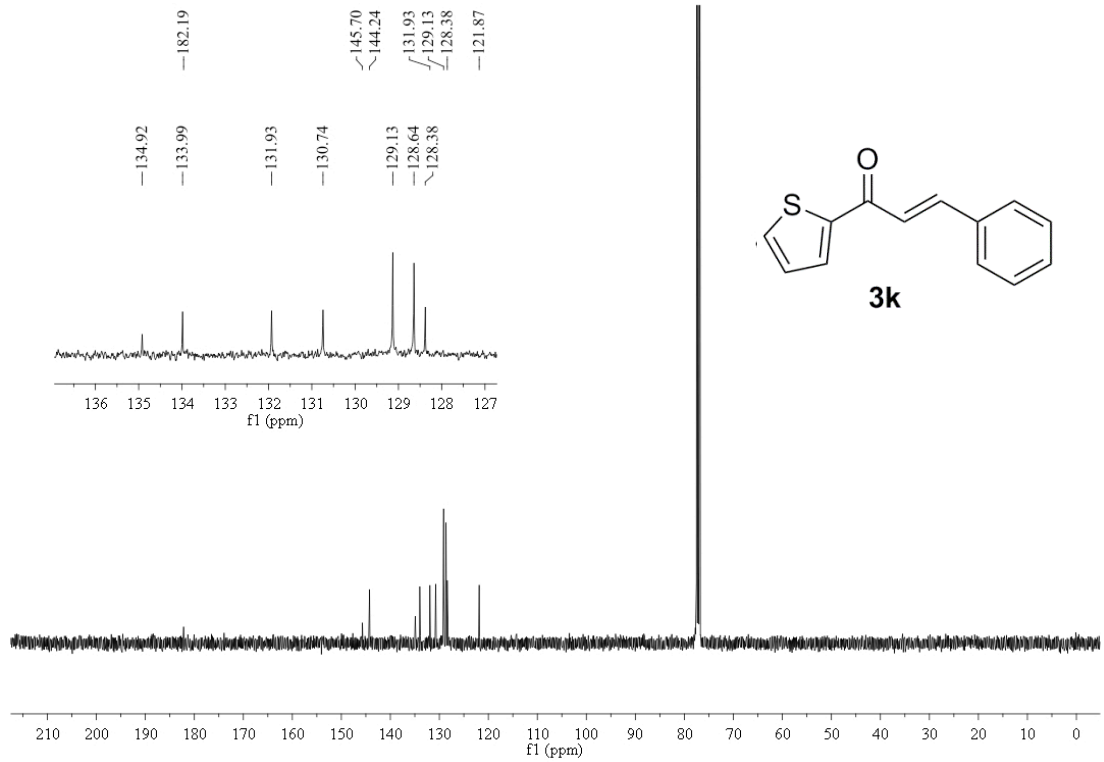

O
Ph

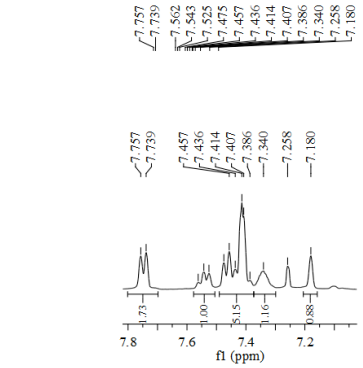
3i'


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)





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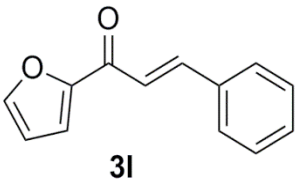
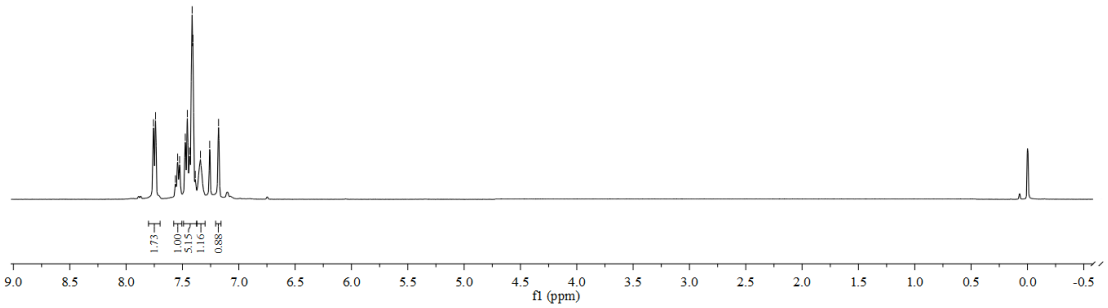
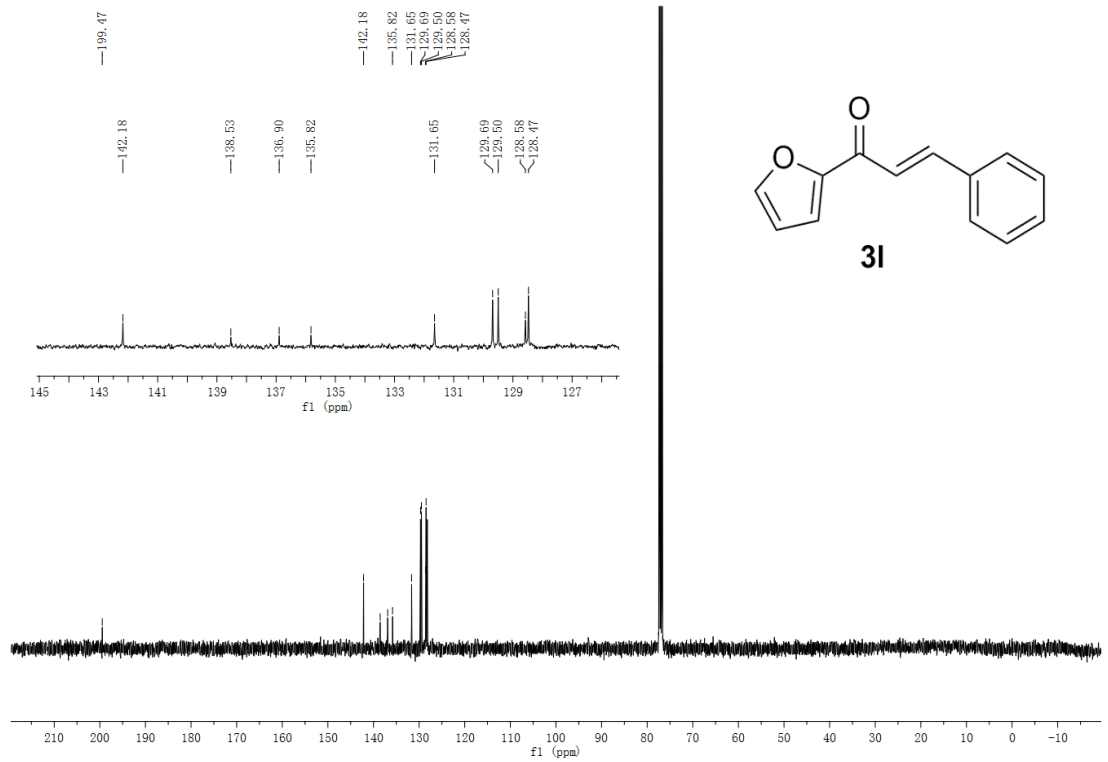
7.543
7.525
7.475
7.457
7.436
7.414
7.407
7.386
7.340
7.258
7.180
1.73
1.00
5.15
1.16
0.88
f1 (ppm)


O
O

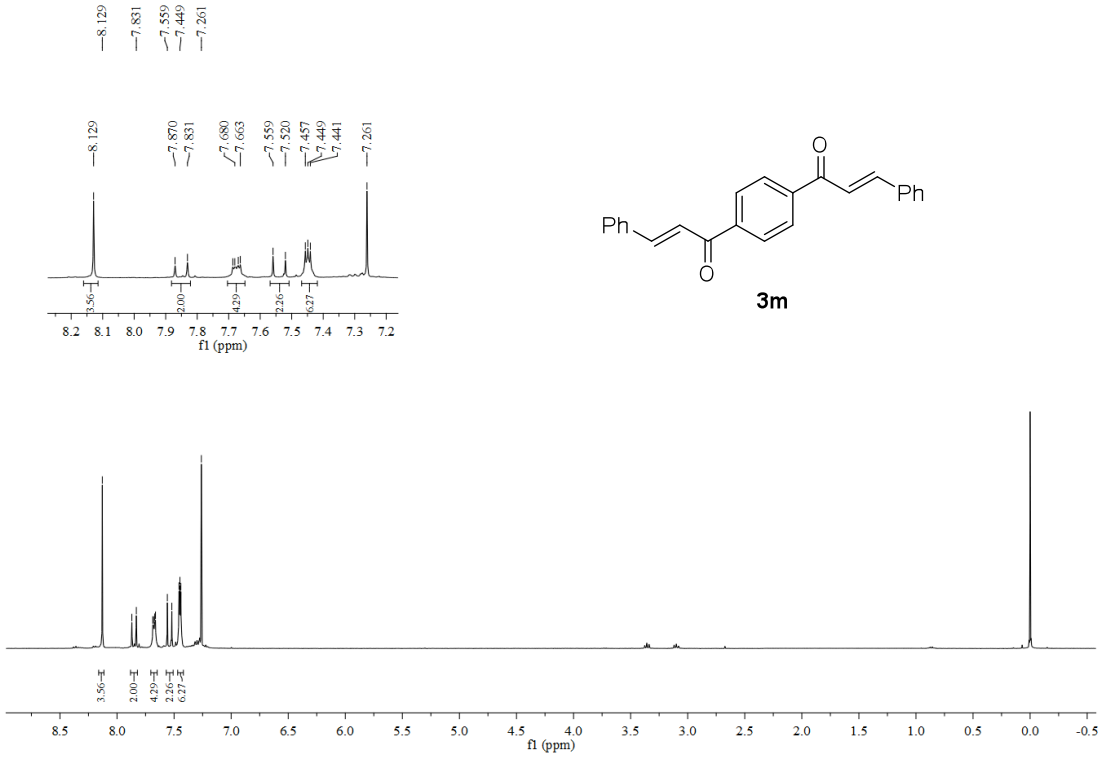
3l


1.73
1.00
5.15
1.16
0.88
f1 (ppm)


199.47
142.18
135.82
131.65
129.69
129.50
128.58
128.47
138.53
136.90
f1 (ppm)

O
O

3l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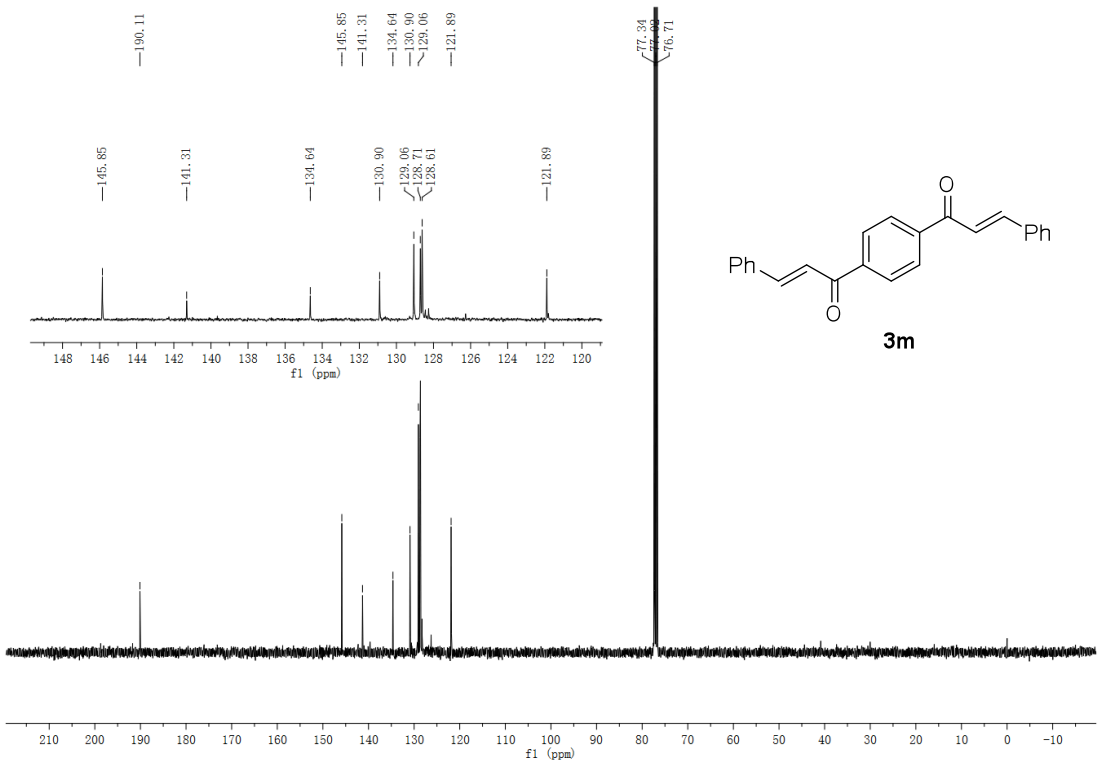
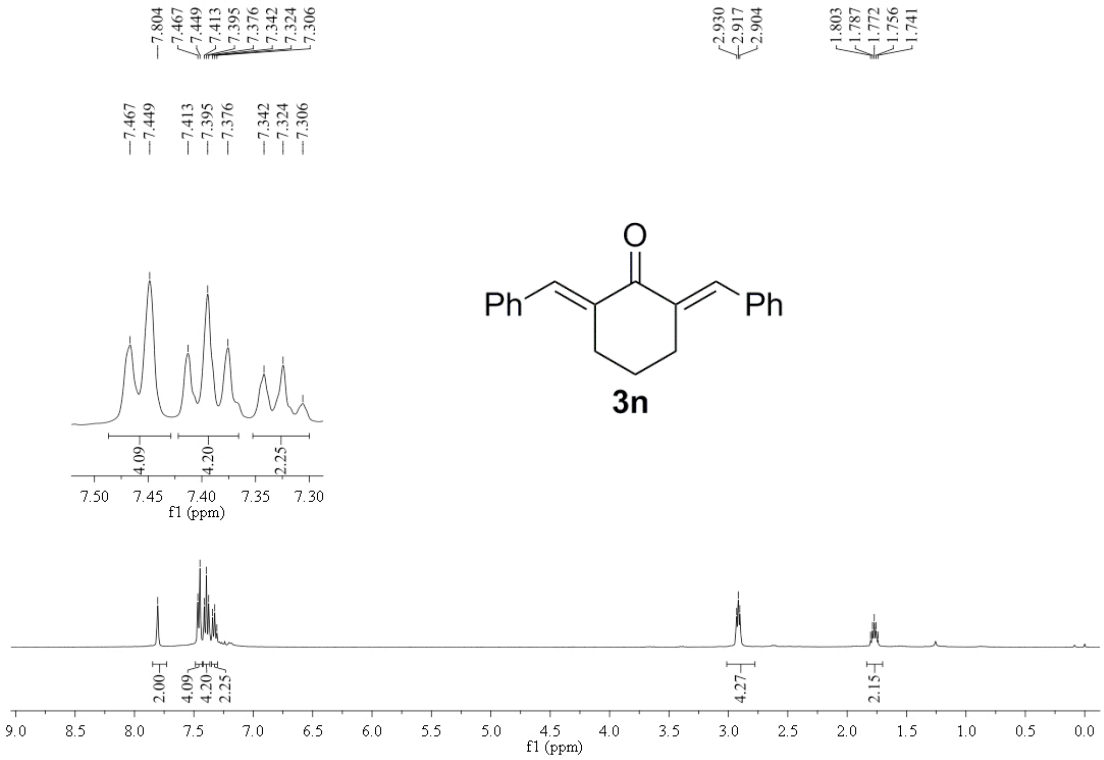
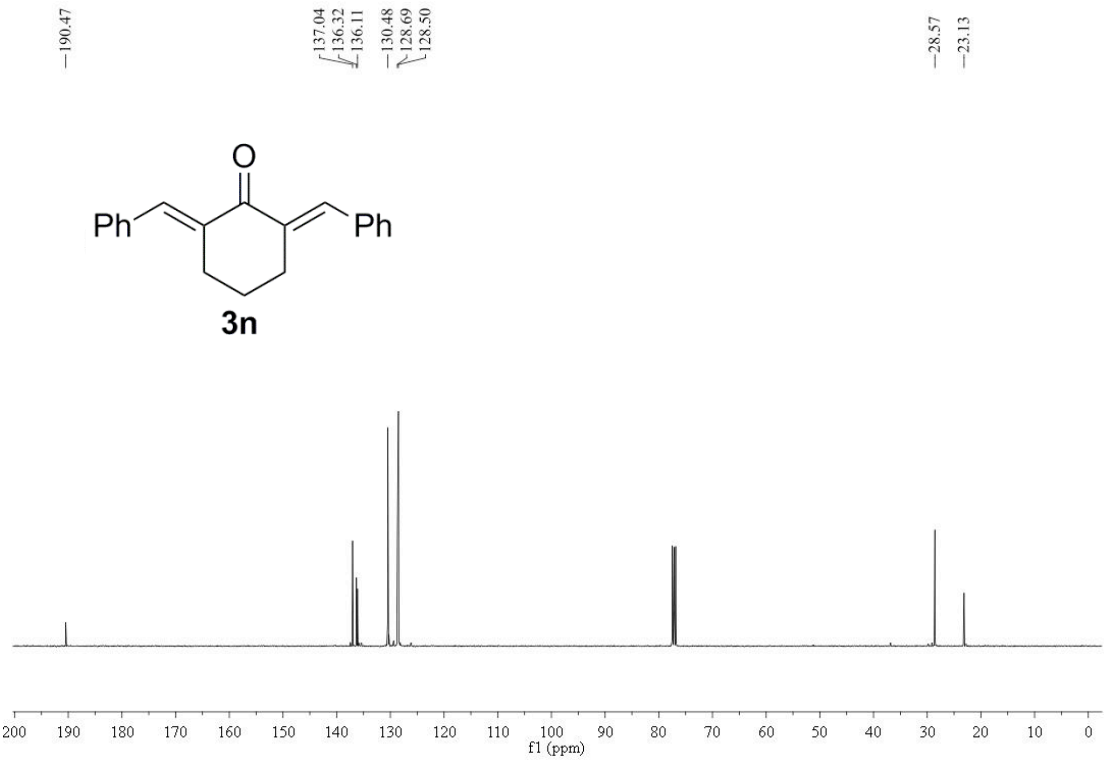
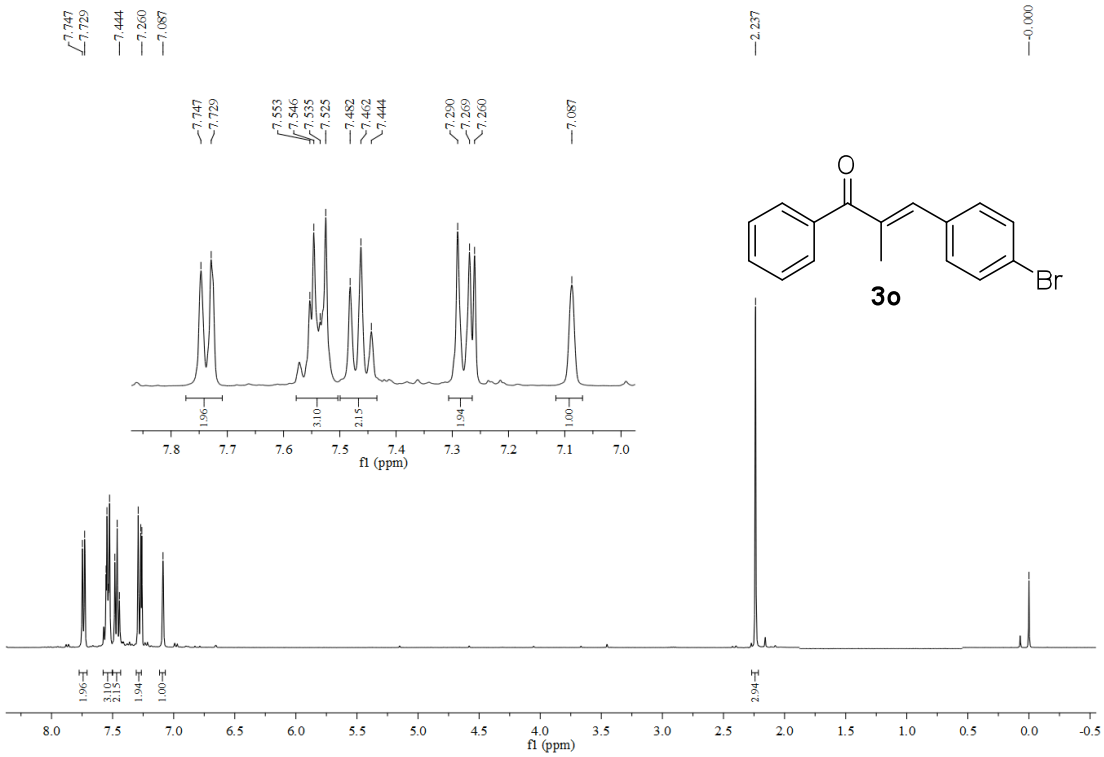
7.449
7.261
7.870
7.680
7.663
7.520
7.457
7.441
3.56
2.00
4.29
2.26
6.27
f1 (ppm)
Ph
O
3m

f1 (ppm)


190.11
145.85
141.31
134.64
130.90
129.06
121.89
77.34
76.71
128.71
128.61
f1 (ppm)
Ph
O
3m



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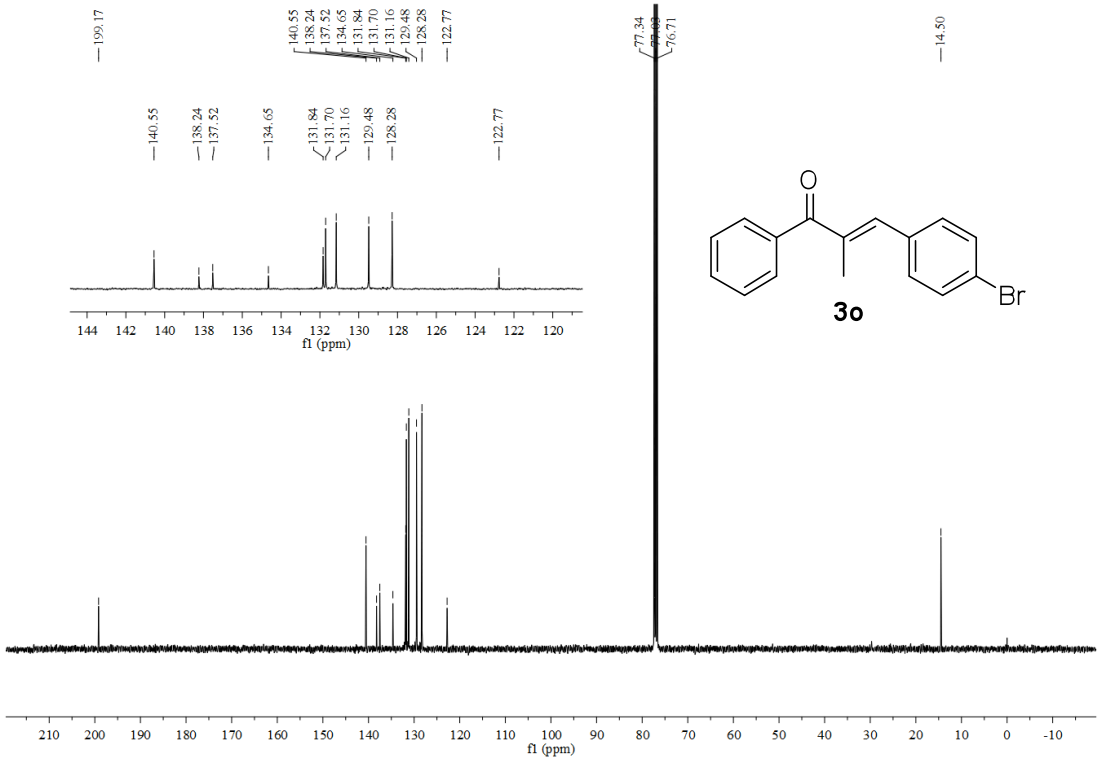
7.444
7.260
7.087
2.237
0.000
O
Br
3o
f1 (ppm)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137.52
134.65
131.84
131.70
131.16
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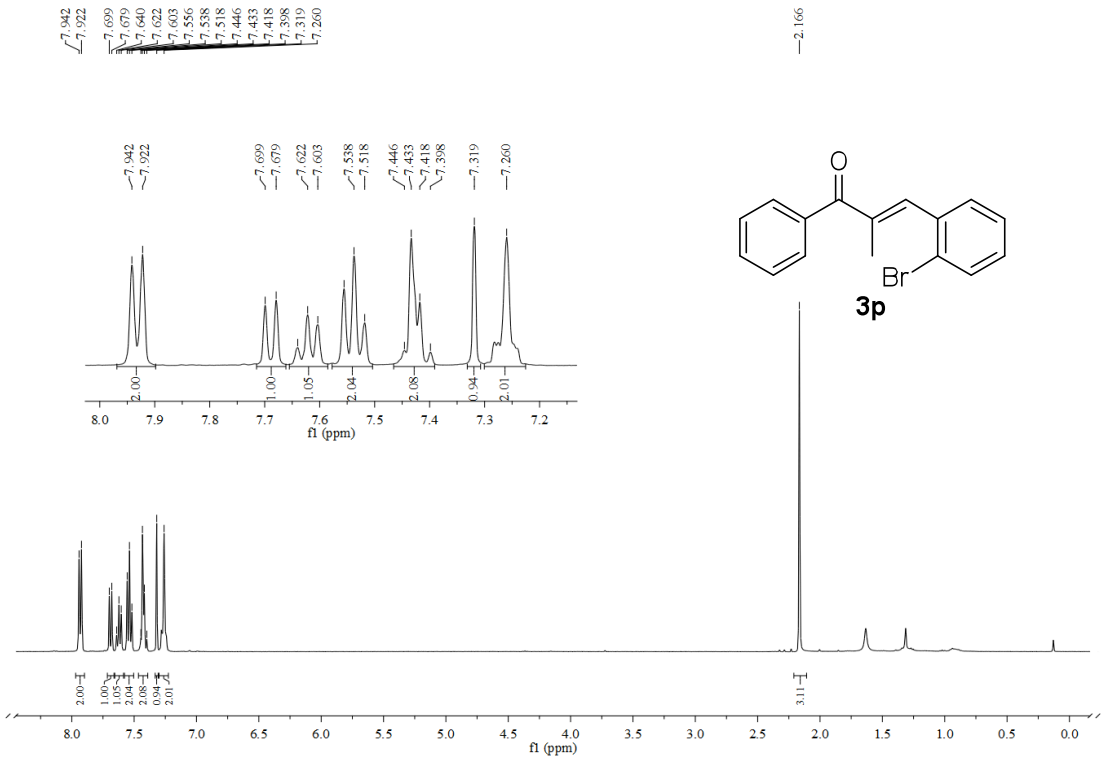
128.28
122.77
77.34
77.03
76.71
14.50
O
Br
3o
f1 (ppm)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7.699
7.679
7.640
7.622
7.603
7.556
7.538
7.518
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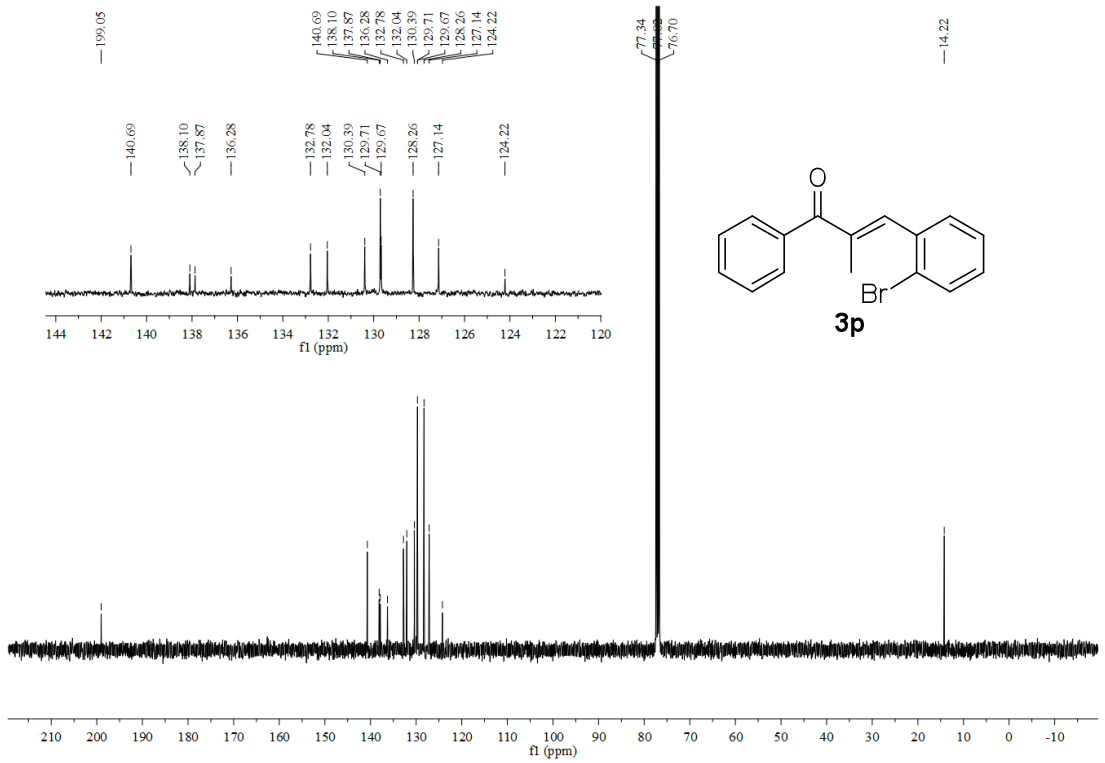
7.433
7.418
7.398
7.319
7.260
2.166
O
Br
3p
f1 (ppm)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136.28
132.78
132.04
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129.71
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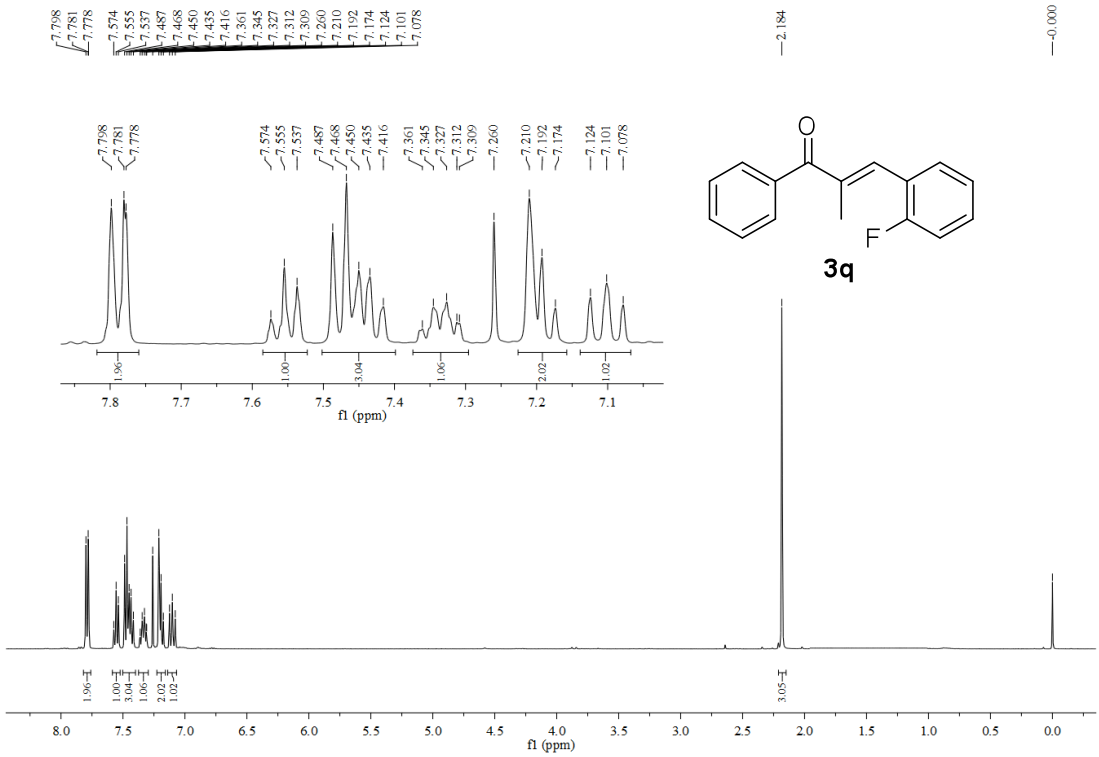
128.26
127.14
124.22
77.34
76.70
14.22
O
Br
3p
f1 (ppm)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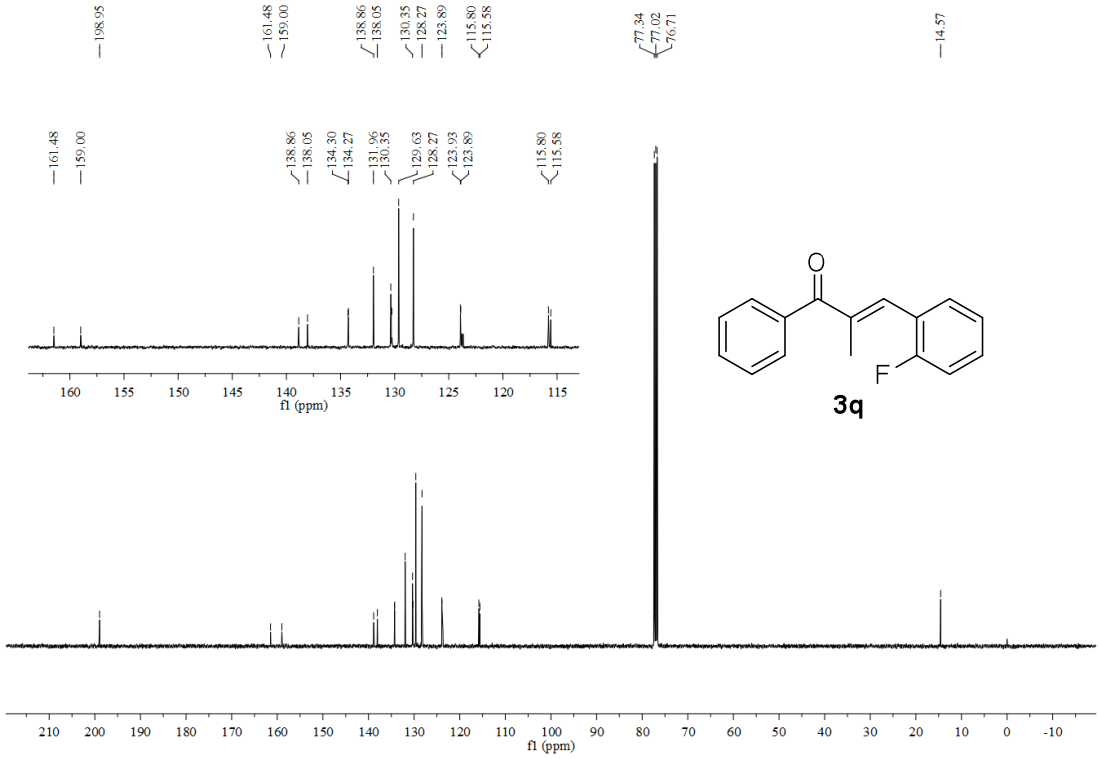
7.555
7.537
7.487
7.468
7.450
7.435
7.416
7.361
7.345
7.327
7.312
7.309
7.260
7.210
7.192
7.174
7.124
7.101
7.078
2.184
-0.000
1.96
1.00
3.04
1.06
2.02
1.02
3.05
fl (ppm)
O
F
3q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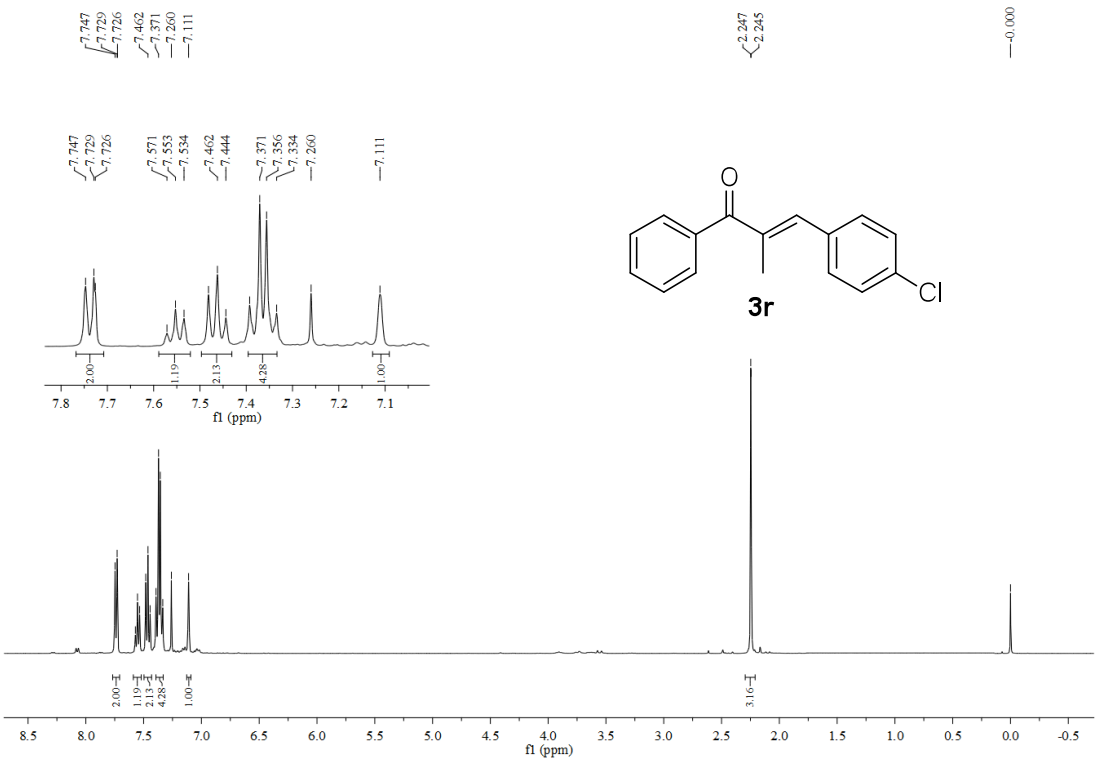
130.35
128.27
123.89
115.80
115.58
77.34
77.02
76.71
14.57
134.30
134.27
131.96
129.63
123.93
fl (ppm)
O
F
3q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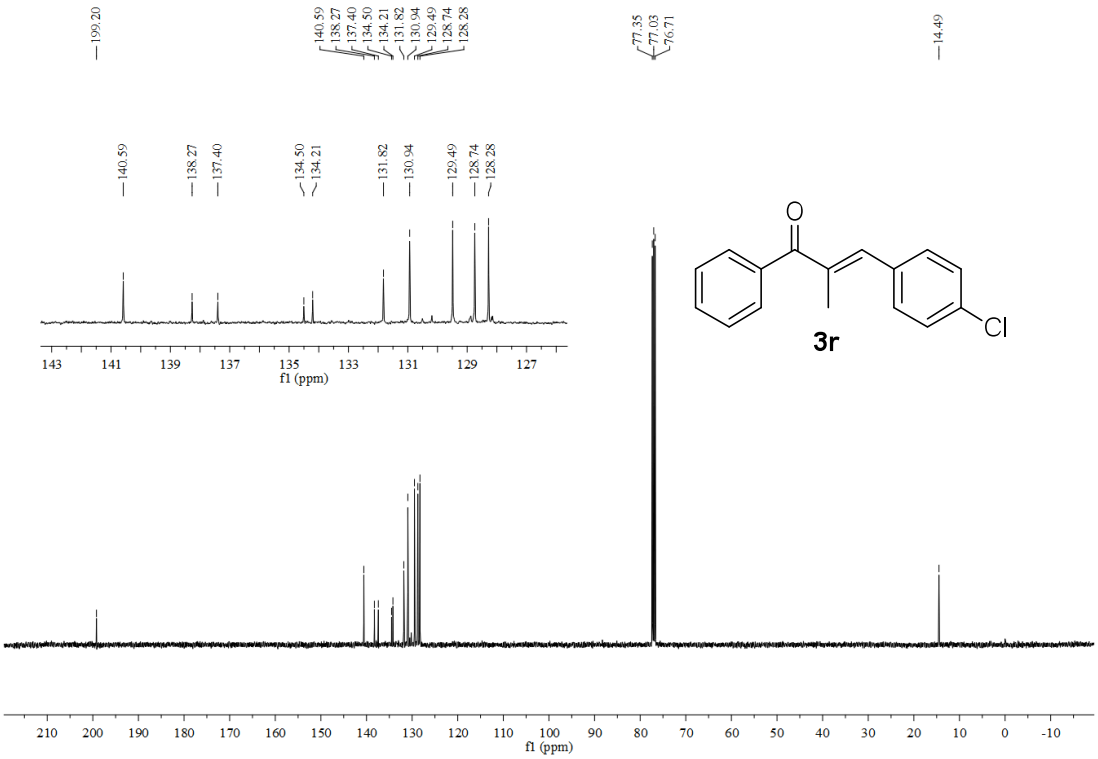
7.726
7.462
7.371
7.260
7.111
2.247
2.245
-0.000
7.571
7.553
7.534
7.462
7.444
7.371
7.356
7.334
7.260
7.111
O
Cl
3r
2.00
1.19
2.13
4.28
1.00
3.16
fl (ppm)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140.59
138.27
137.40
134.50
134.21
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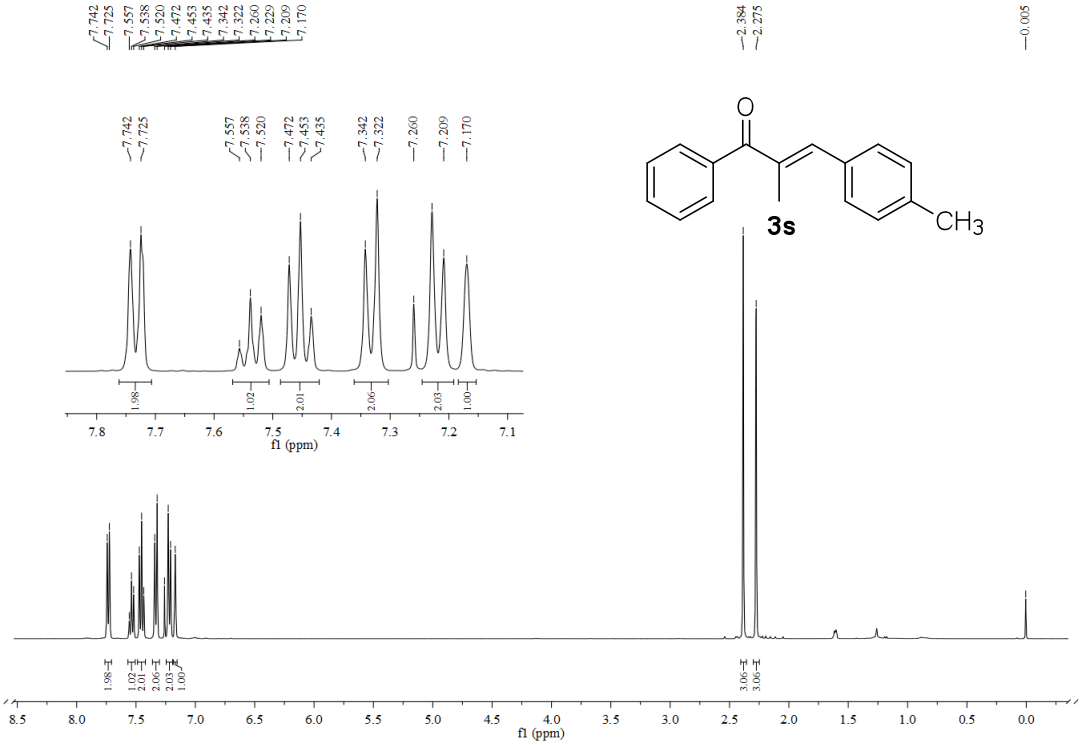
130.94
129.49
128.74
128.28
77.35
77.03
76.71
14.49
O
Cl
3r
fl (ppm)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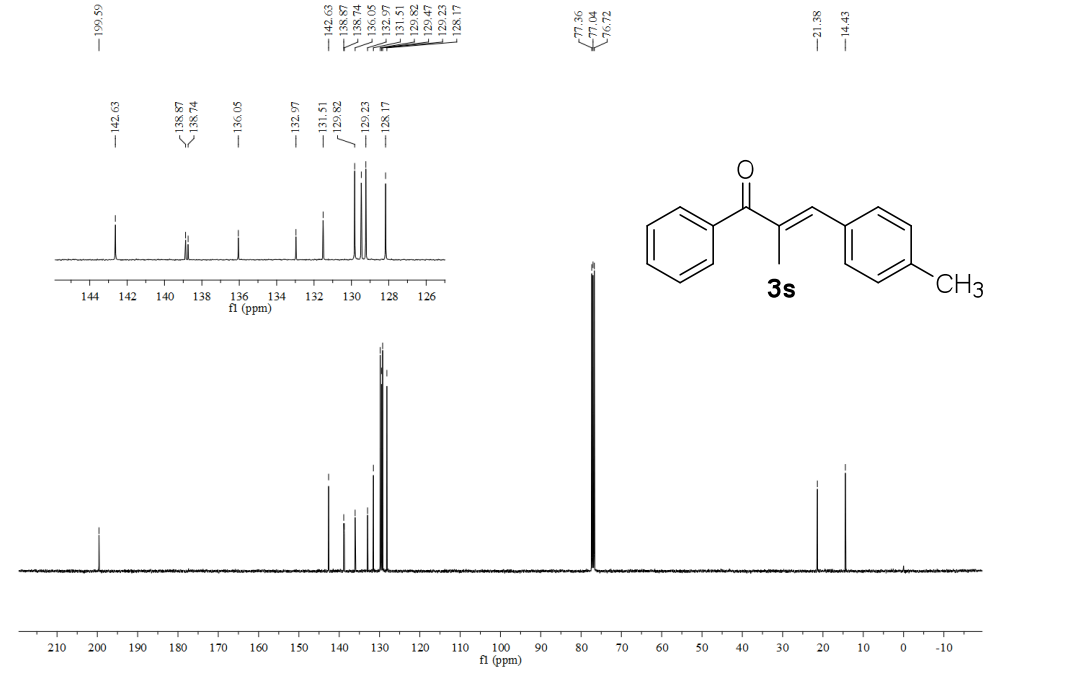
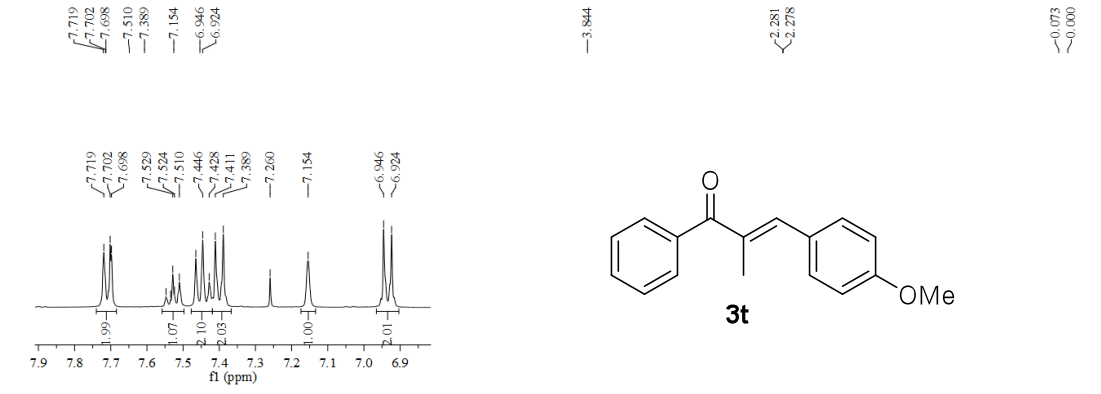
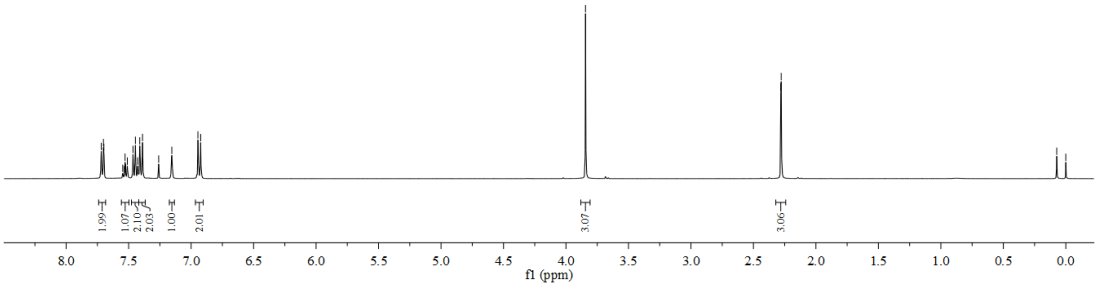
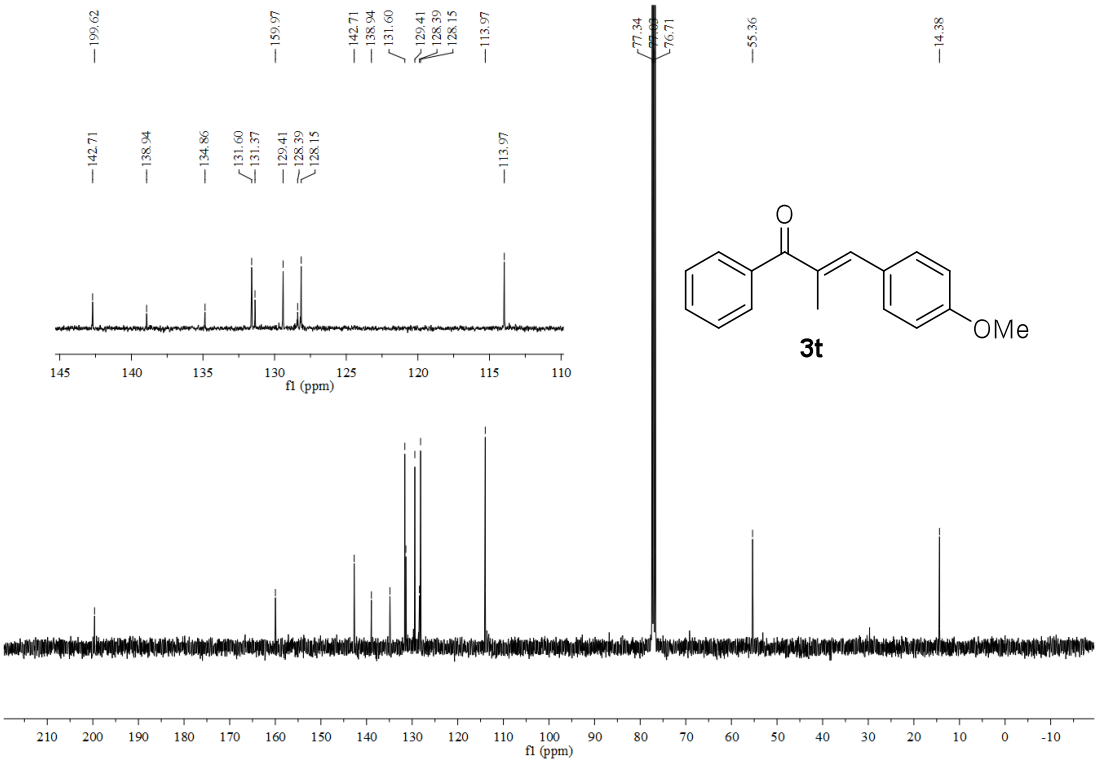
7.557
7.538
7.520
7.472
7.453
7.435
7.342
7.322
7.260
7.209
7.170
2.384
2.275
0.005
O
CH3
3s
f1 (ppm)

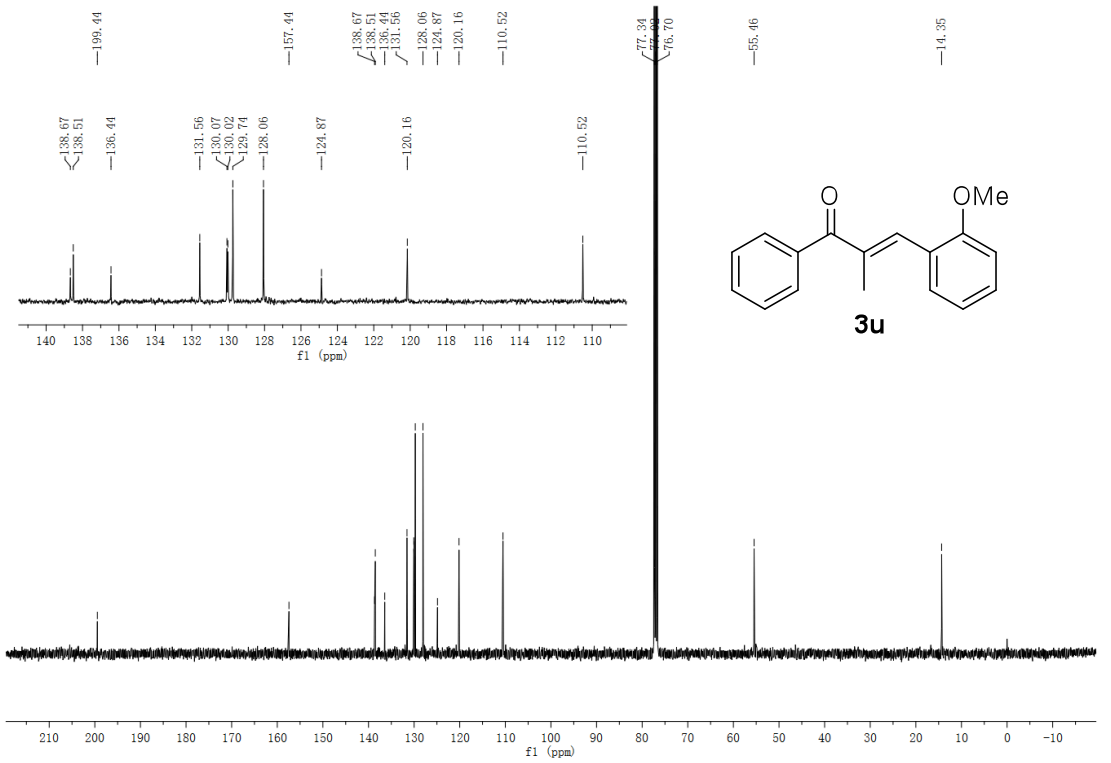

199.59
142.63
138.87
138.74
136.05
132.97
131.51
129.82
129.47
129.23
128.17
77.36
77.04
76.72
21.38
14.43
O
CH3
3s
f1 (ppm)

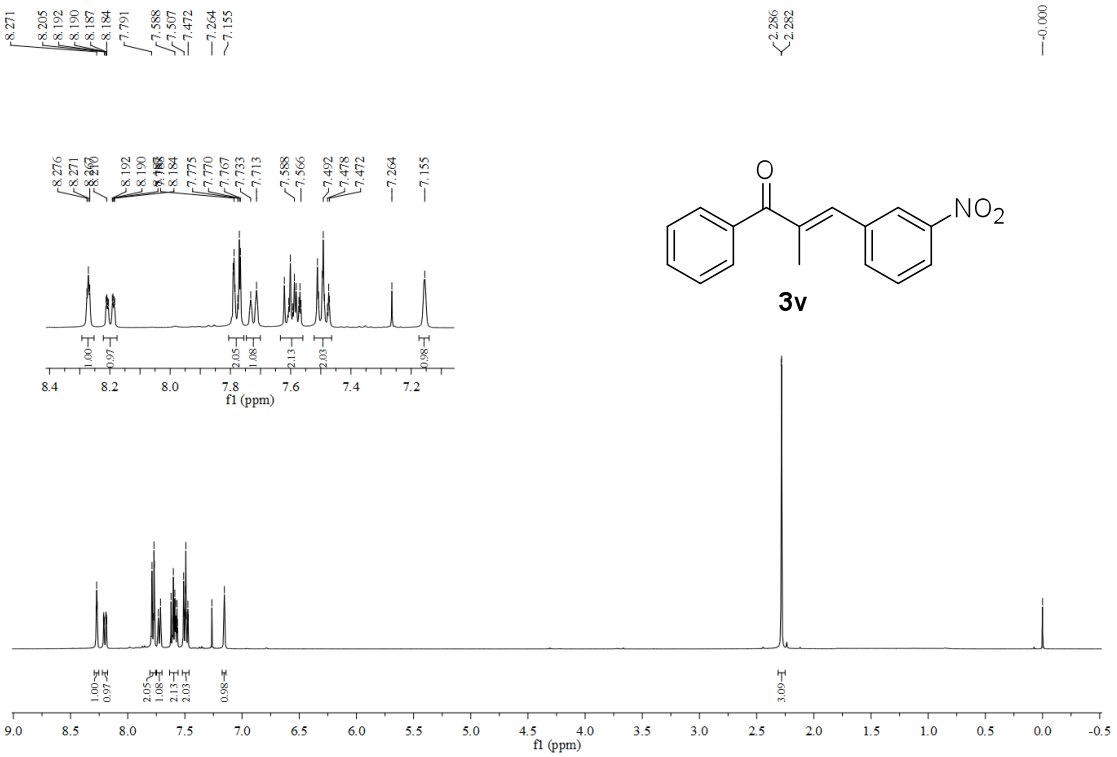

7.719
7.702
7.698
7.510
7.389
7.154
6.946
6.924
3.844
2.281
2.278
0.073
0.000
7.529
7.524
7.446
7.428
7.411
7.260
1.99
1.07
2.10
2.03
1.00
2.01
f1 (ppm)
O
OMe
3t

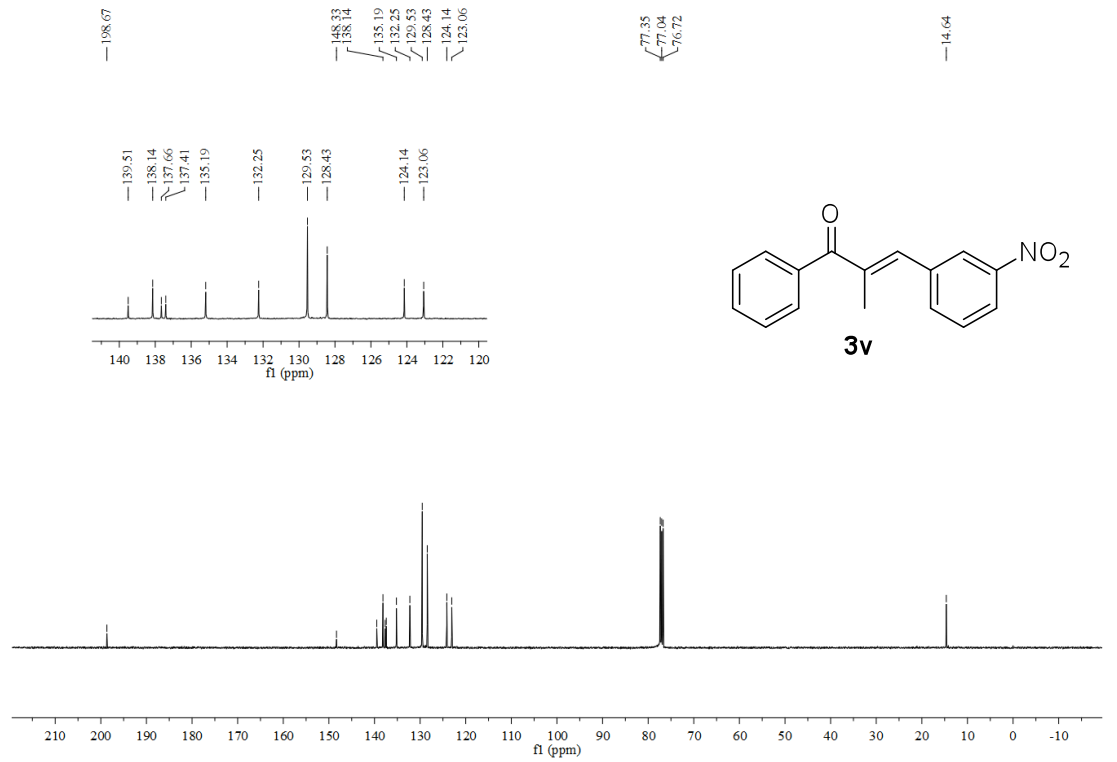

1.99
1.07
2.10
2.03
1.00
2.01
3.07
3.06
f1 (ppm)

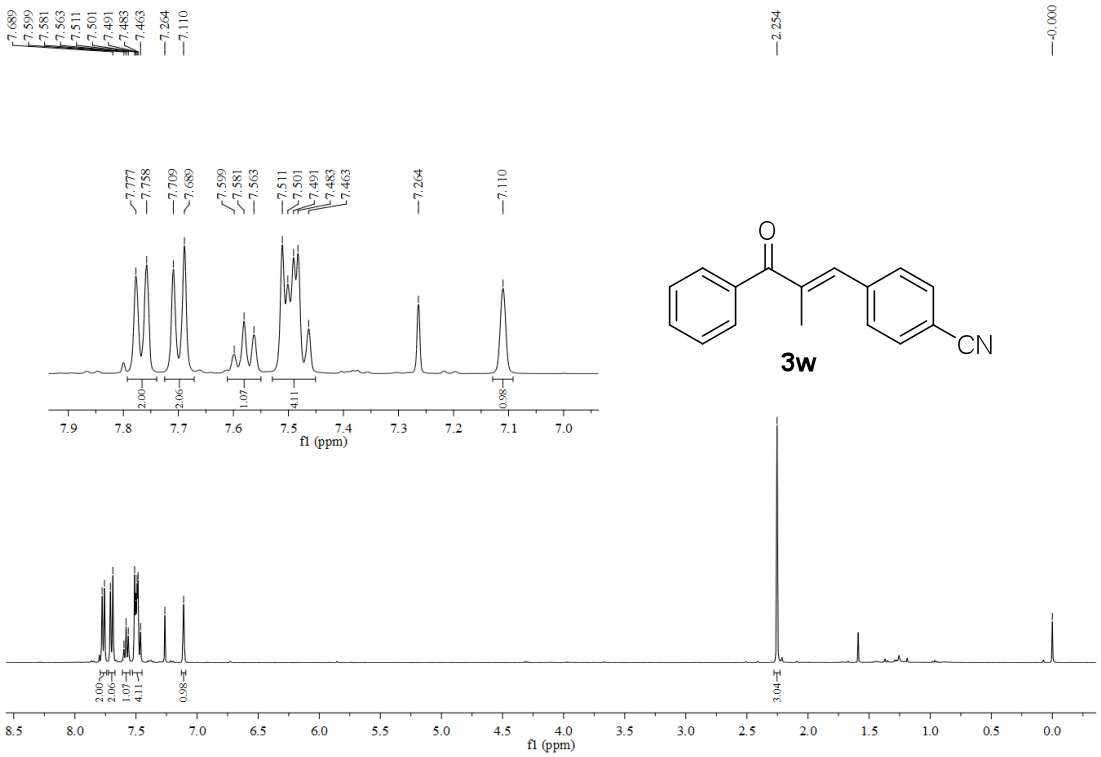

199.62
159.97
142.71
138.94
131.60
129.41
128.39
128.15
113.97
77.34
77.03
76.71
55.36
14.38
134.86
131.37
f1 (ppm)
O
OMe
3t

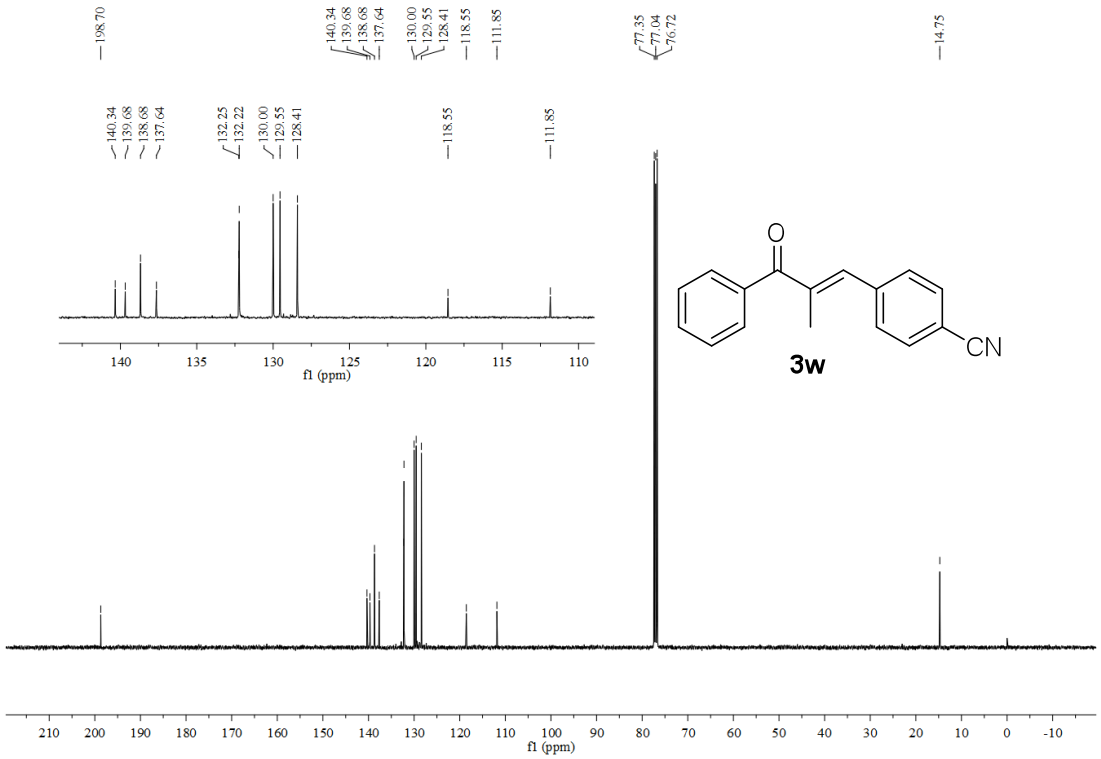

7.802
7.799
7.787
7.782
7.778
7.465
7.398
7.260
7.026
7.007
6.989
6.912
6.892
3.795
2.182
2.179
-0.000
O
OMe
3u
f1 (ppm)

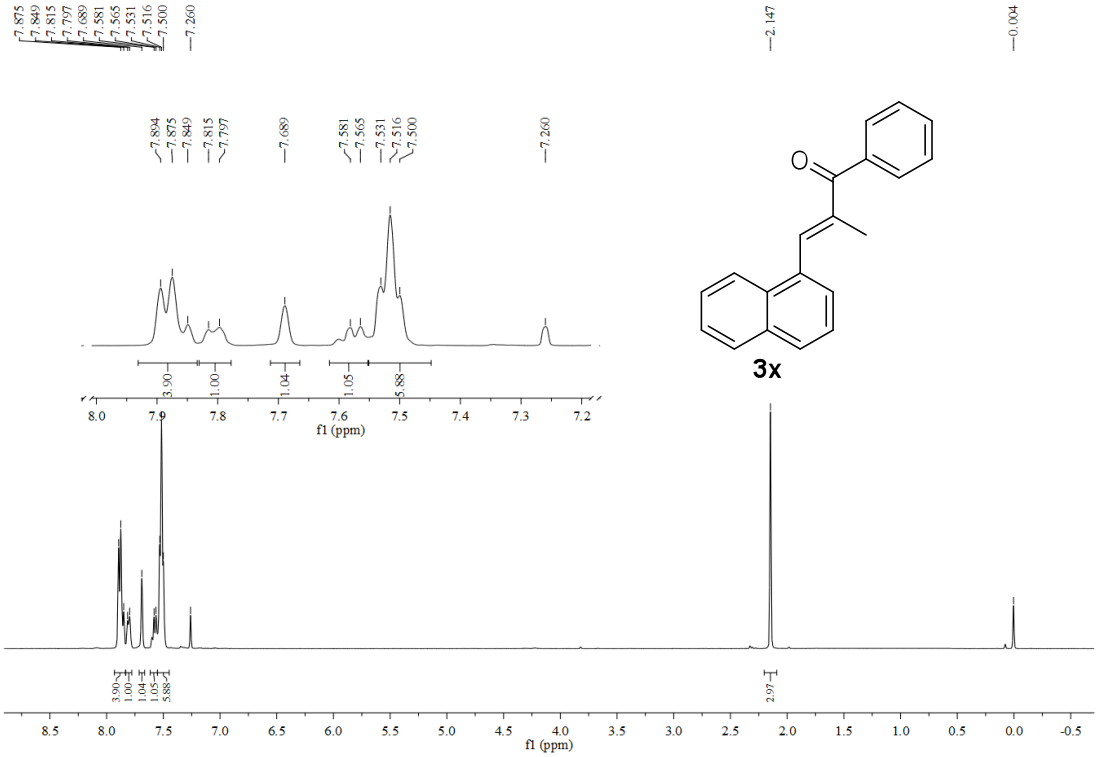

199.44
157.44
138.67
138.51
136.44
131.56
128.06
124.87
120.16
110.52
77.34
77.02
76.70
55.46
14.35
O
OMe
3u
f1 (ppm)

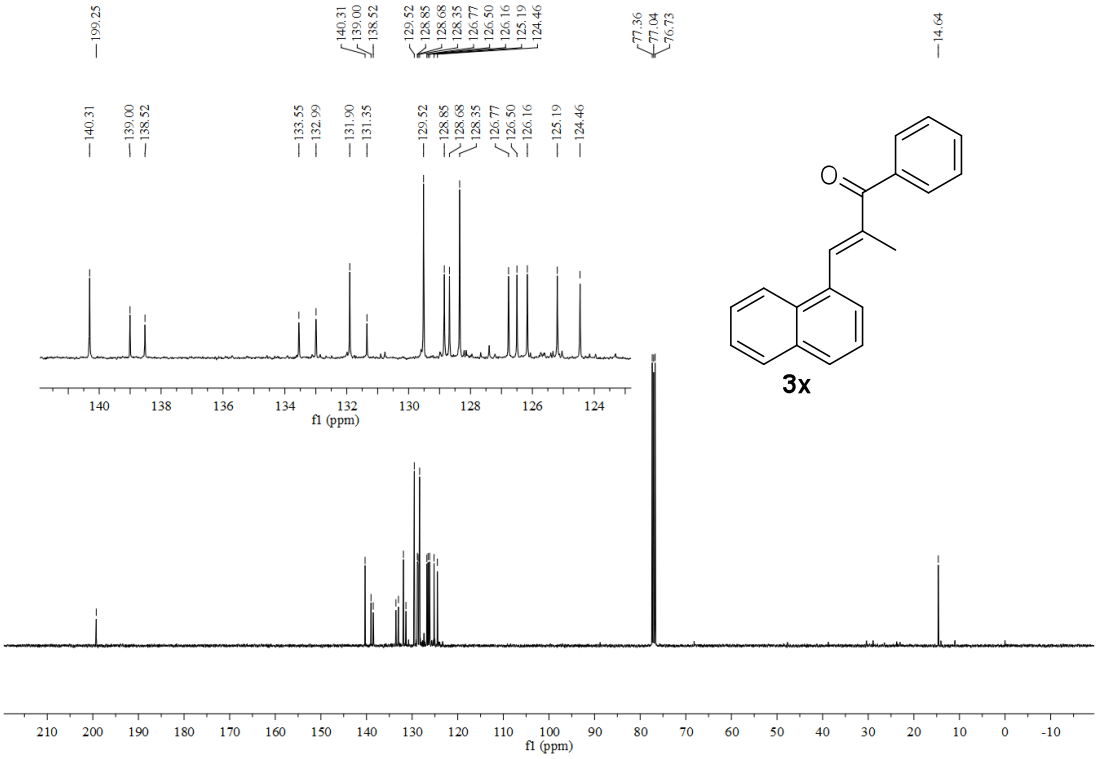

8.271
8.205
8.192
8.190
8.187
8.184
7.791
7.588
7.507
7.472
7.264
7.155
2.286
2.282
-0.000
f1 (ppm)
O
NO2
3v

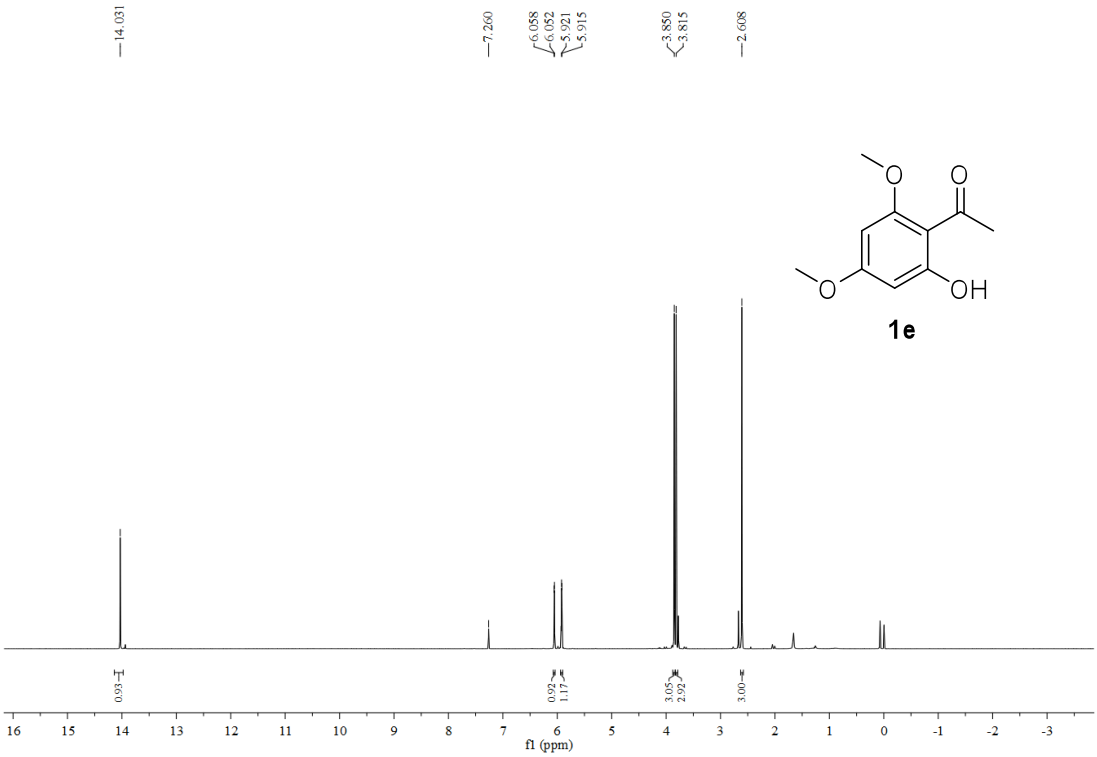

198.67
148.33
138.14
135.19
132.25
129.53
128.43
124.14
123.06
77.35
77.04
76.72
14.64
139.51
138.14
137.66
137.41
135.19
132.25
129.53
128.43
124.14
123.06
f1 (ppm)
O
NO2
3v


7.689
7.599
7.581
7.563
7.511
7.501
7.491
7.483
7.463
7.264
7.110
2.254
-0.000
O
CN
3w
f1 (ppm)

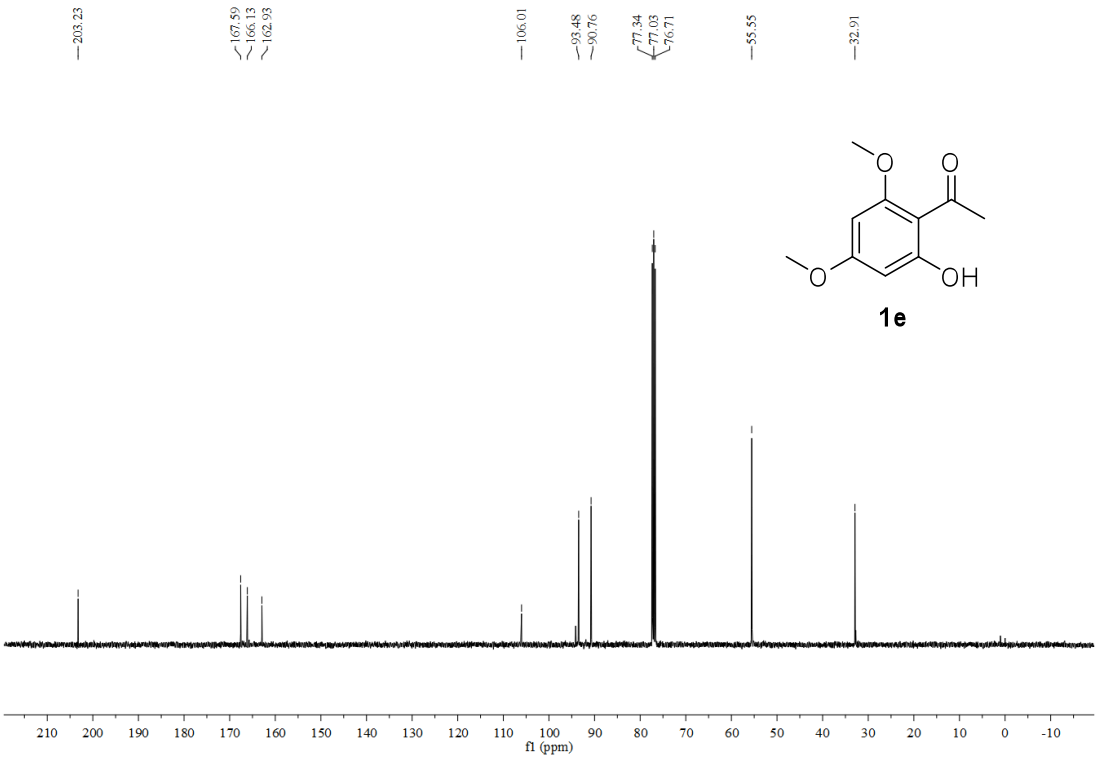

198.70
140.34
139.68
138.68
137.64
130.00
129.55
128.41
118.55
111.85
77.35
77.04
76.72
14.75
132.25
132.22
O
CN
3w
f1 (ppm)


7.875
7.849
7.815
7.797
7.689
7.581
7.565
7.531
7.516
7.500
7.260
2.147
0.004
3.90
1.00
1.04
1.05
5.88
2.97
f1 (ppm)
3x

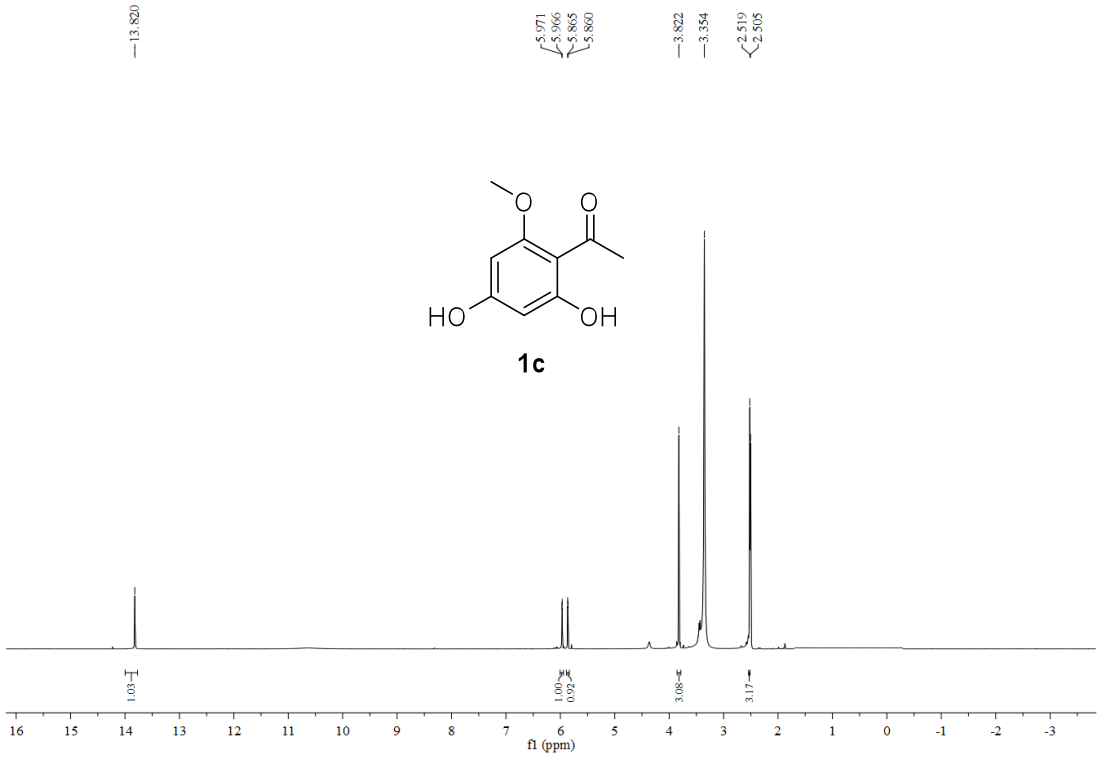

199.25
140.31
139.00
138.52
133.55
132.99
131.90
131.35
129.52
128.85
128.68
128.35
126.77
126.50
126.16
125.19
124.46
77.36
77.04
76.73
14.64
f1 (ppm)
3x

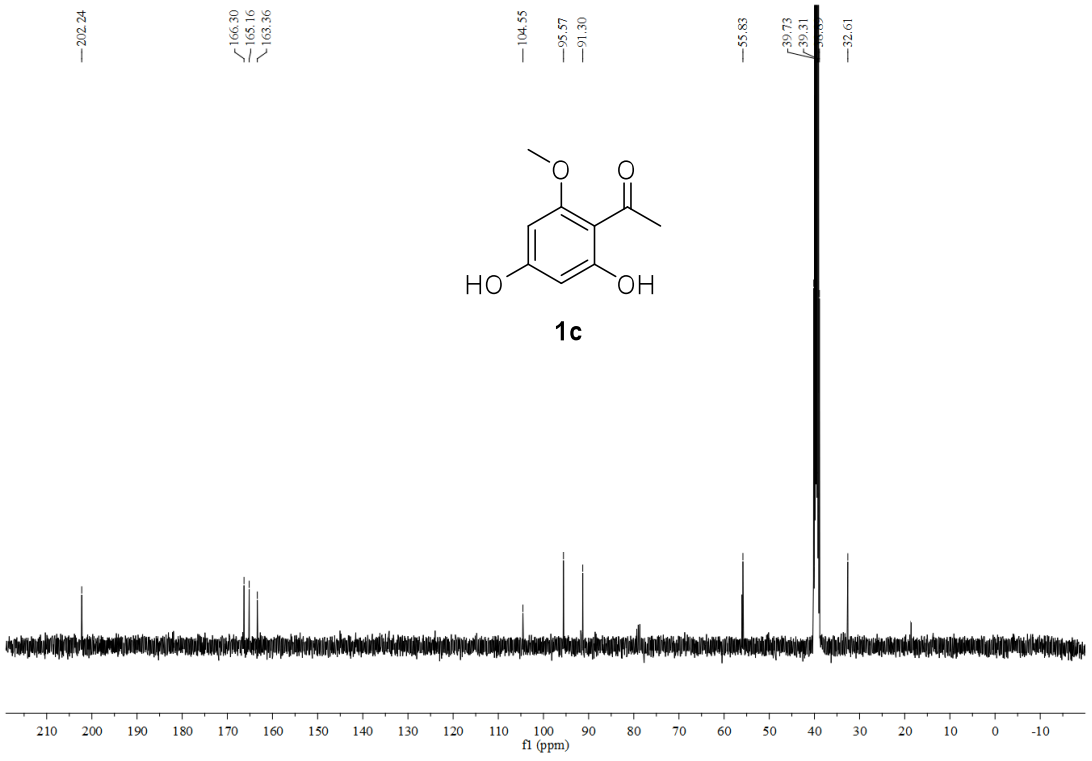


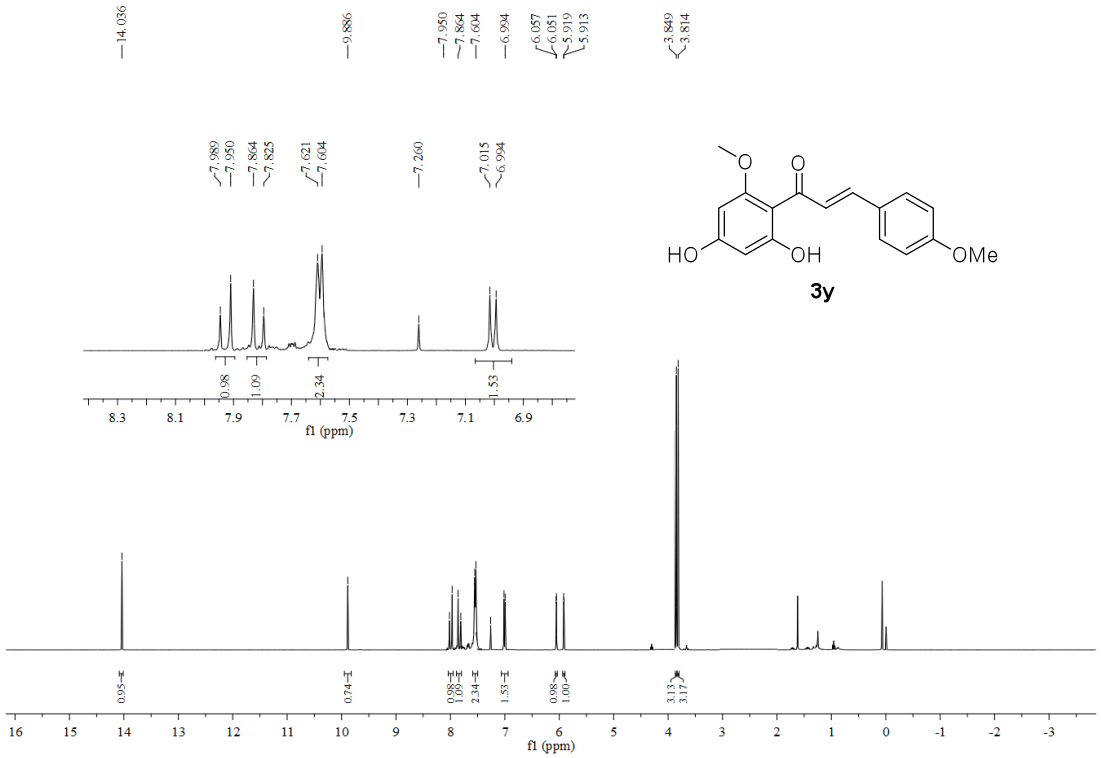
1e

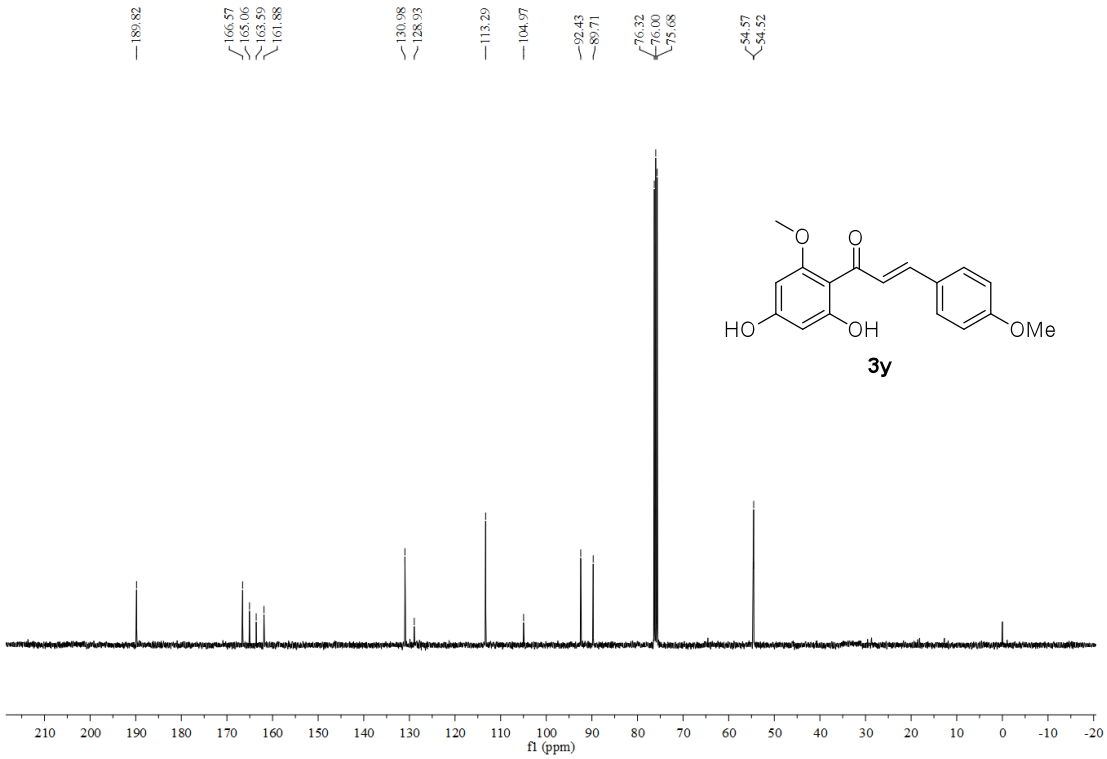


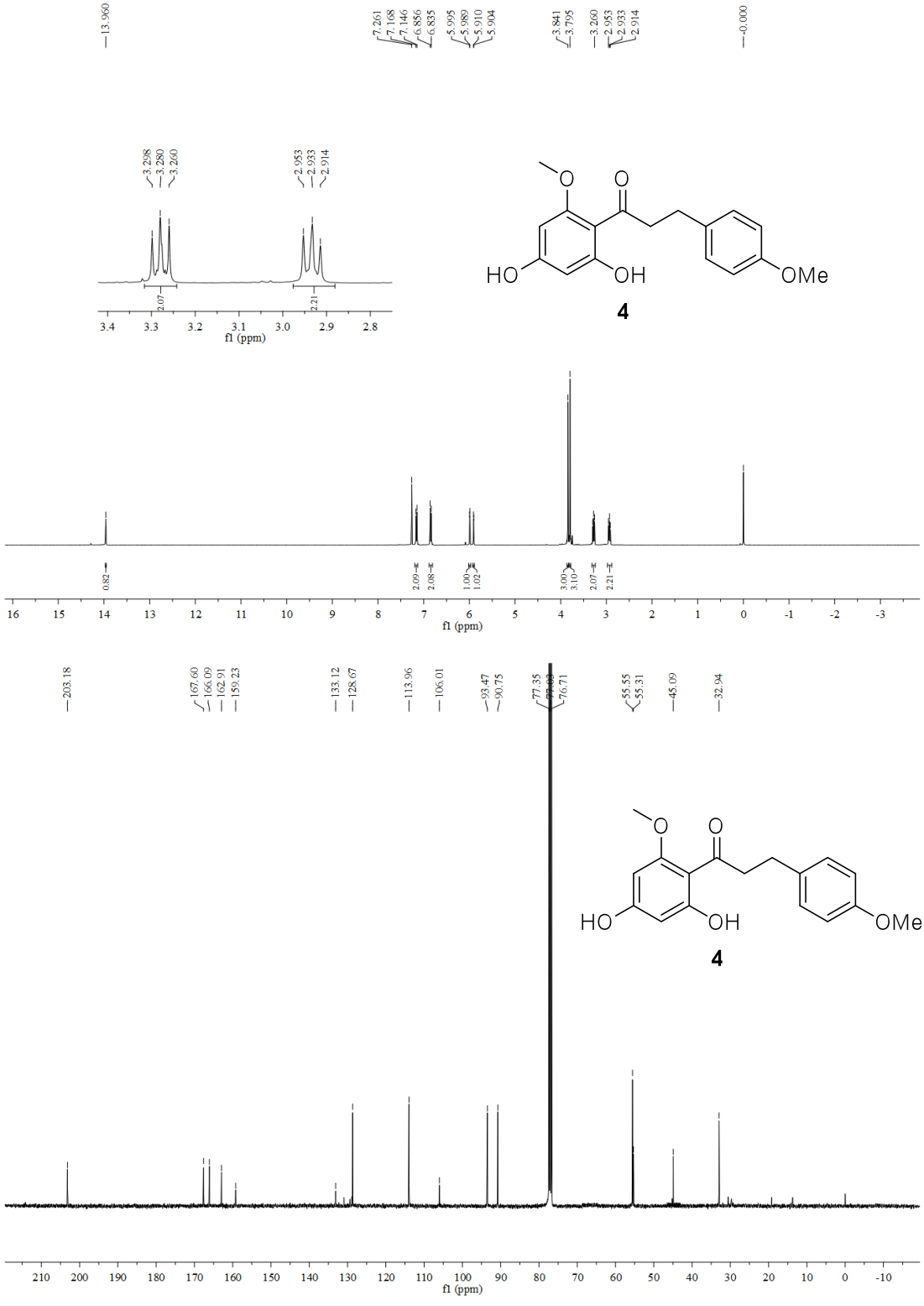
1e

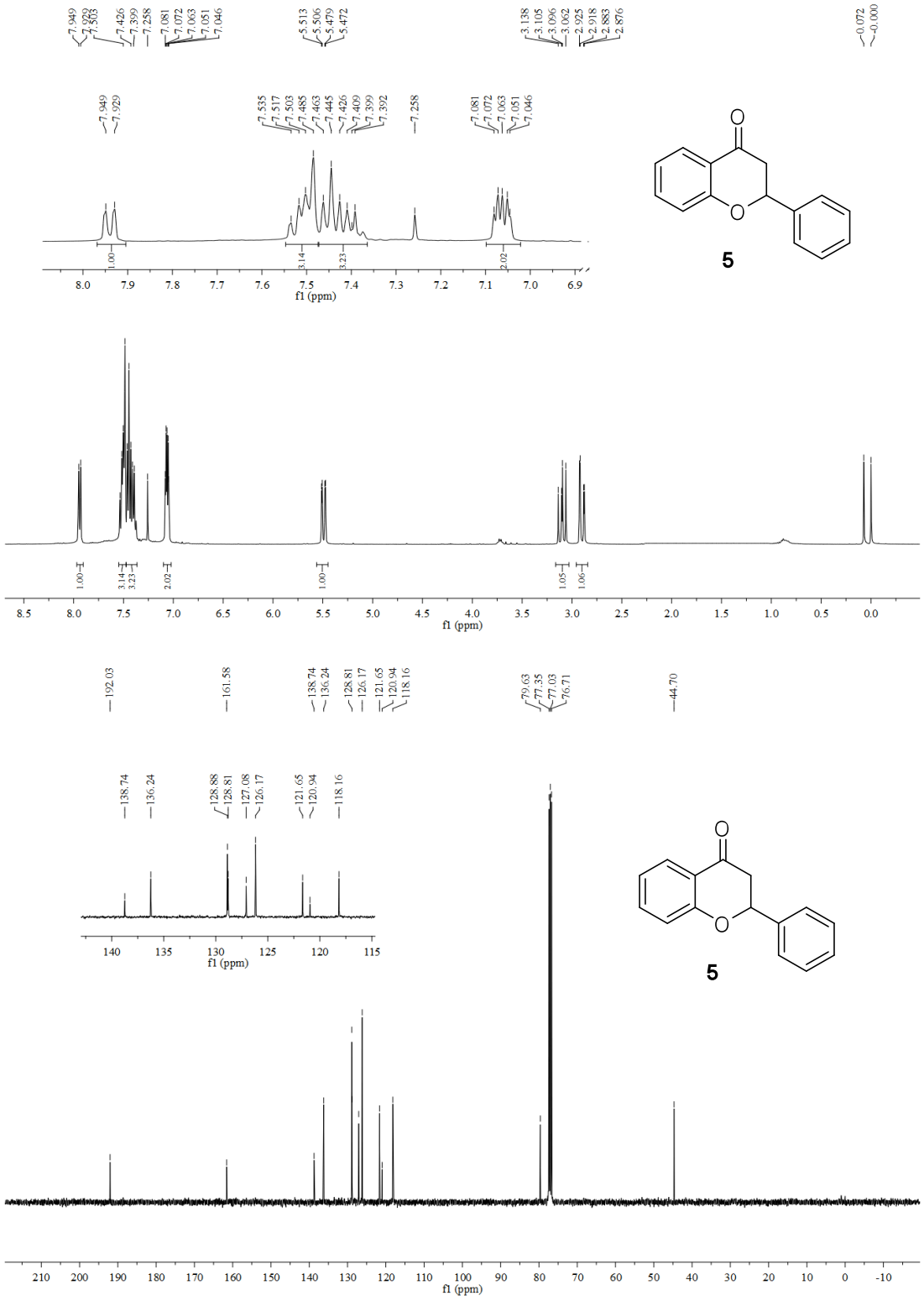


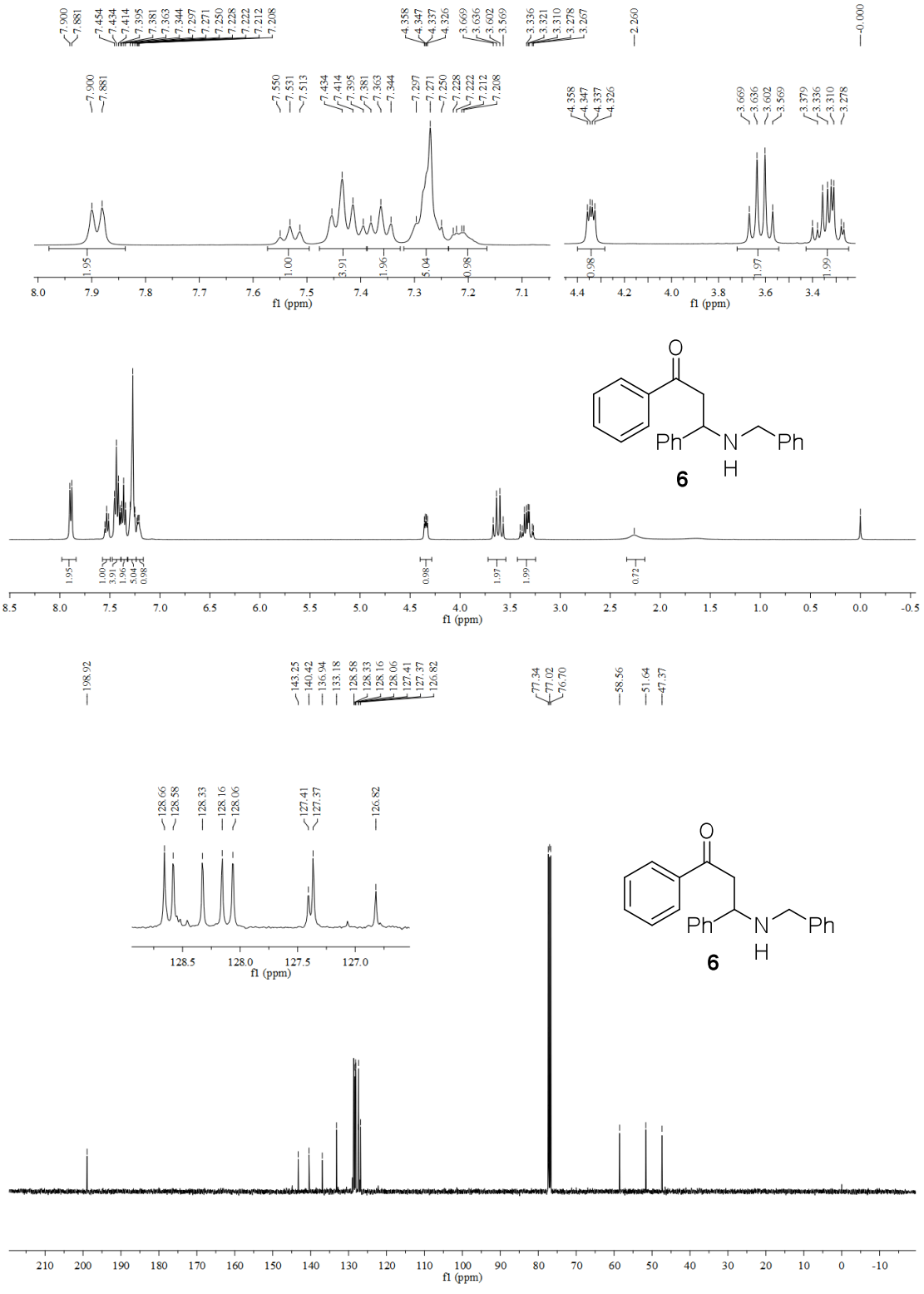


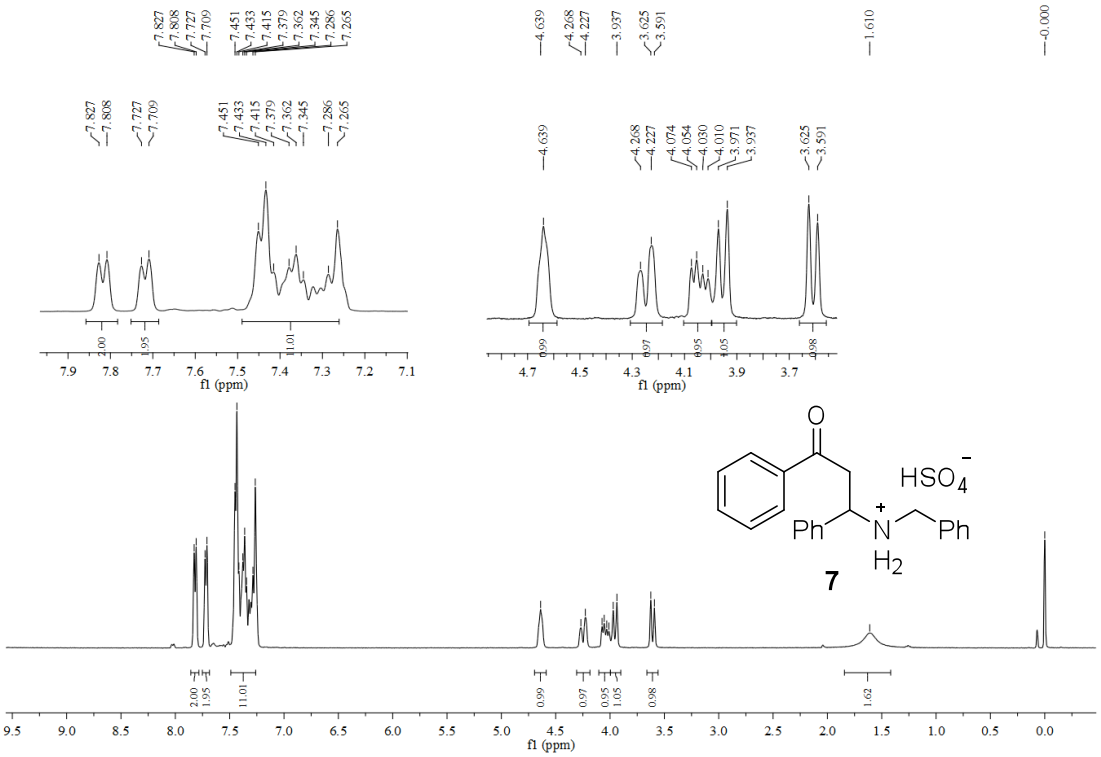

14.036
9.886
7.950
7.864
7.604
6.994
6.057
6.051
5.919
5.913
3.849
3.814
7.989
7.950
7.864
7.825
7.621
7.604
7.260
7.015
6.994
0.98
1.09
2.34
1.53
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
HO
OH
OMe
3y
0.95
0.74
0.98
1.09
2.34
1.53
0.98
1.00
3.13
3.17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

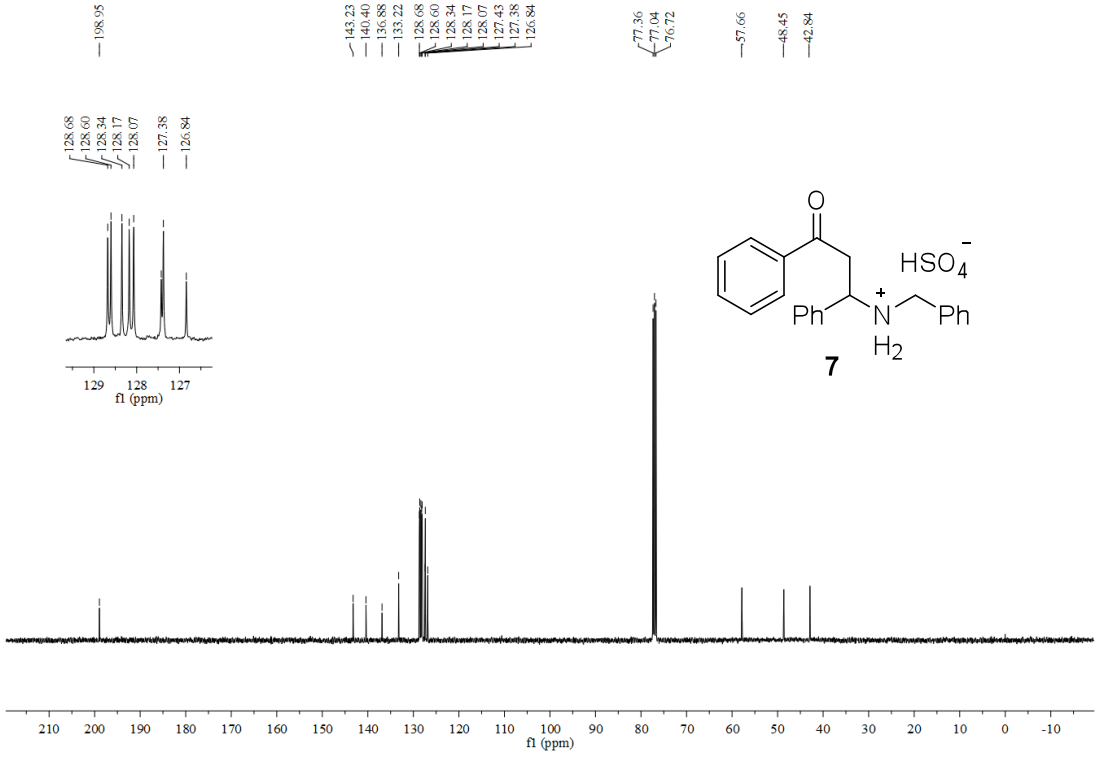

189.82
166.57
165.06
163.59
161.88
130.98
128.93
113.29
104.97
92.43
89.71
76.32
76.00
75.68
54.57
54.52
HO
OH
OMe
3y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


13.960
7.261
7.168
7.146
6.856
6.835
5.995
5.989
5.910
5.904
3.841
3.795
3.260
2.953
2.933
2.914
0.000
3.298
3.280
3.260
2.953
2.933
2.914
2.07
2.21
3.4
3.3
3.2
3.1
3.0
2.9
2.8
f1 (ppm)
HO
OH
OMe
4
0.82
2.09
2.08
1.00
1.02
3.00
3.10
2.07
2.21
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)
203.18
167.60
166.09
162.91
159.23
133.12
128.67
113.96
106.01
93.47
90.75
77.35
77.03
76.71
55.55
55.31
45.09
32.94
HO
OH
OMe
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.949
7.929
7.503
7.426
7.399
7.258
7.081
7.072
7.063
7.051
7.046
5.513
5.506
5.479
5.472
3.138
3.105
3.096
3.062
2.925
2.918
2.883
2.876
0.072
-0.000
7.535
7.517
7.503
7.485
7.463
7.445
7.426
7.409
7.399
7.392
1.00
3.14
3.23
2.02
f1 (ppm)
5
1.00
3.14
3.23
2.02
1.00
1.05
1.06
f1 (ppm)
192.03
161.58
138.74
136.24
128.81
126.17
121.65
120.94
118.16
79.63
77.35
77.03
76.71
44.70
128.88
127.08
f1 (ppm)
5
f1 (ppm)


7.900
7.881
7.454
7.434
7.414
7.395
7.381
7.363
7.344
7.297
7.271
7.250
7.228
7.222
7.212
7.208
4.358
4.347
4.337
4.326
3.669
3.636
3.602
3.569
3.336
3.321
3.310
3.278
3.267
2.260
0.000
f1 (ppm)
Ph
N
H
Ph
6
198.92
143.25
140.42
136.94
133.18
128.58
128.33
128.16
128.06
127.41
127.37
126.82
77.34
77.02
76.70
58.56
51.64
47.37


7.827
7.808
7.727
7.709
7.451
7.433
7.415
7.379
7.362
7.345
7.286
7.265
4.639
4.268
4.227
3.937
3.625
3.591
1.610
0.000
fl (ppm)
HSO4
Ph
N
H2
Ph
O
7


198.95
143.23
140.40
136.88
133.22
128.68
128.60
128.34
128.17
128.07
127.43
127.38
126.84
77.36
77.04
76.72
57.66
48.45
42.84
fl (ppm)
HSO4
Ph
N
H2
Ph
O
7