Supporting Information

Versatile palladium-catalyzed C–H olefination of (hetero)arenes at room temperature

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Table of contents

I. General Remarks

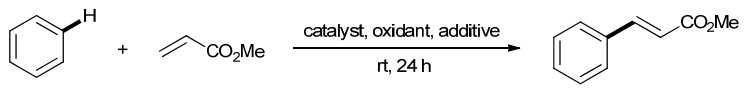
NMR spectra were obtained on a Bruker AV II-400 (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz). The ^{1}H NMR chemical shifts were measured using $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). High resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected.

All reactions were carried out under an air atmosphere. All reagents were obtained from commercial suppliers and were used without further purification. Arenes, olefins, trifluoroacetic acid, $K_2S_2O_8$, $(NH_4)_2S_2O_8$ and $Na_2S_2O_8$ were purchased from Chengdu Kelong Chemical Engineering Reagent (China) CO., Ltd. $Pd(OAc)_2$ and $PdCl_2$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd.

II. Optimization of the Pd-catalyzed direct C–H bond olefination of arenes at room temperature

A sealed Schlenk tube with a magnetic stir bar was charged with palladium catalyst (0.03 mmol), oxidant (0.6 mmol), TFA, benzene **1a** (2.0 mL, 22.5 mmol) and methyl acrylate **2a** (27.0 μL, 0.3 mmol) under air. After being stirred at room temperature for 12h or 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) on silica gel to provide the desired product **3a**.

Table S1. Optimization of the oxidative cross-coupling of benzene **1a** with methyl acrylate **2a** [a]



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

Entry	Catalyst	Oxidant	Additive (equiv)	Yield (%)[b]
1	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	none	trace

2	$Pd(TFA)_2$	$(NH_4)_2S_2O_8$	none	trace
3	**$Pd(OAc)_2$**	**$(NH_4)_2S_2O_8$**	**TFA (5.0)**	**81**
4	$Pd(TFA)_2$	$(NH_4)_2S_2O_8$	TFA (5.0)	72
5	$PdCl_2$	$(NH_4)_2S_2O_8$	TFA (5.0)	trace
6	$Pd(OAc)_2$	$K_2S_2O_8$	TFA (5.0)	75
7	$Pd(OAc)_2$	$Na_2S_2O_8$	TFA (5.0)	61
8	$Pd(OAc)_2$	NFSI	TFA (5.0)	57
9	$Pd(OAc)_2$	O_2 (1.0 atm)	TFA (5.0)	44
10[c]	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA (5.0)	51
11	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA (2.5)	42
12	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA (10.0)	63
13[d]	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA (5.0)	57
14[e]	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA (5.0)	50
15[f]	$Pd(OAc)_2$	$(NH_4)_2S_2O_8$	TFA (5.0)	n. r.

[a] Reaction conditions: methyl acrylate (0.30 mmol), arene (22.5 mmol, 75.0 equiv), Pd catalyst (0.03 mmol, 10 mol%), oxidant (2.0 equiv) and TFA at room temperature for 24 h under air. [b] Isolated yield. [c] The reaction time was 12 h. [d] $Pd(OAc)_2$ (0.015 mmol, 5 mol%) was used. [e] Arene (15 mmol, 50.0 equiv) was used.[f] Arene (0.9 mmol, 3.0 equiv) and CH_2Cl_2 (2.0 mL) were used. n.r. = no reaction.

III. General procedure for the Pd-catalyzed oxidative C–H/C–H cross-coupling of arenes with alkenes at room temperature

A sealed Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), olefin (0.3 mmol) and arene (22.5 mmol) under air. After being stirred at room temperature for 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography on silica gel to provide the desired product.

IV. Typical procedure for the synthesis of 3a

A sealed Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature

under air. After being stirred at room temperature for 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide **3a** as colorless liquid (39.3 mg, 81% yield).

V. General procedure for the Pd-catalyzed direct C–H bond olefination of heteroarenes at room temperature

A sealed Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), olefin (0.6 mmol), heteroarene (0.3 mmol) and CH_2Cl_2 (2.0 mL) under air. After being stirred at room temperature for 48 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography on silica gel to provide the desired product.

VI. General procedure for the Pd-catalyzed regioselective arylation of coumarins at room temperature

A sealed Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), coumarin (0.3 mmol), and arene (22.5 mmol) under air. After being stirred at room temperature for 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography on silica gel to provide the desired product.

VII. General procedure for the Pd-catalyzed oxidative C–H/C–H cross-coupling

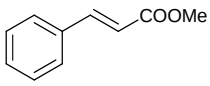
of arenes with quinones at room temperature

A sealed Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), quinone (0.3 mmol), and arene (22.5 mmol) under air. After being stirred at room temperature for 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography on silica gel to provide the desired product.

VIII. Typical procedure for the synthesis of 7b

A sealed Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), 1,4-naphthoquinone **5b** (47.4 mg, 0.3 mmol), and benzene (2.0 mL, 22.5 mmol) under air. After being stirred at room temperature for 24 h, the mixture was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10 mL of CH_2Cl_2. The filtrate was collected and evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2/1, v/v) to provide **7b** as a yellow solid (66.1 mg, 94% yield).

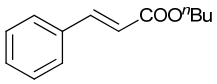
IX. Characterization of substances 3, 6, and 7



trans-Methyl cinnamate (3a)[1]

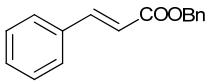
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3a** as colorless liquid (39.3 mg,

81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 6.45 (d, J = 16.0 Hz, 1H), 7.39 (t, J = 3.2 Hz, 3H), 7.52-7.54 (m, 2H), 7.70 (d, J = 16.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.8, 118.0, 128.2, 129.0, 130.4, 134.6, 145.0, 167.6 ppm.



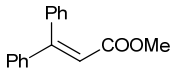
trans-Butyl cinnamate (3b)[1]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), *n*-butyl acrylate (43.0 μL, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3b** as colorless liquid (50.1 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.2 Hz, 3H), 1.40-1.49 (m, 2H), 1.66-1.73 (m, 2H), 4.22 (t, J = 6.8 Hz, 2H), 6.44 (d, J = 16.0 Hz, 1H), 7.38-7.39 (m, 3H), 7.52-7.54 (m, 2H), 7.68 (d, J = 16.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.4, 31.0, 64.6, 118.5, 128.2, 129.0, 130.4, 134.7, 144.7, 167.3 ppm.



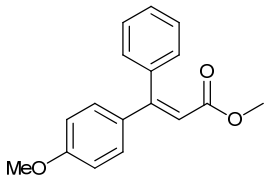
trans-Benzyl cinnamate (3c)[2]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), benzyl acrylate (45.0 μL, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3c** as colorless liquid (60.3 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (s, 2H), 6.49 (d, J = 16.0 Hz, 1H), 7.34-7.43 (m, 8H), 7.51-7.54 (m, 2H), 7.74 (d, J = 16.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.5, 118.0, 128.3, 128.40, 128.42, 128.7, 129.0, 130.5, 134.5, 136.2, 145.3, 167.0 ppm.



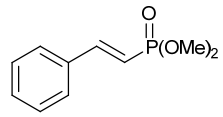
Methyl 3,3-diphenylacrylate (3d)[1]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl cinnamate (48.7 mg, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3d** as colorless liquid (47.6 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.53 (s, 3H), 6.29 (s, 1H), 7.13-7.17 (m, 2H), 7.21-7.28 (m, 5H), 7.31-7.32 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.4, 116.9, 128.0, 128.3, 128.4, 128.5, 129.2, 129.6, 138.9, 140.9, 157.2, 166.5 ppm.



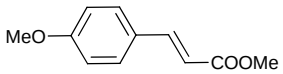
(*E*)-Methyl 3-(4-methoxyphenyl)-3-phenylacrylate (3e)[3]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), (*E*)-methyl 3-(4-methoxyphenyl)acrylate (57.6 mg, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3e** as a white solid (36.2 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (s, 3H), 3.82 (s, 3H), 6.32 (s, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.19-7.26 (m, 4H), 7.38-7.40 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.3, 55.5, 113.9, 114.8, 128.0, 128.2, 129.2, 129.9, 133.3, 139.2, 157.0, 161.0, 166.7 ppm. HRMS (ESI^+): calcd for $C_{17}H_{16}NaO_3$ $[M+Na]^+$ 291.0997, found 291.1001.



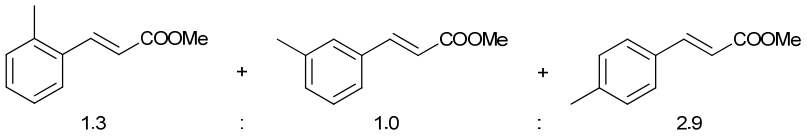
(*E*)-Dimethyl styrylphosphonate (3f)[4]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), dimethyl vinylphosphonate (36.0 μL, 0.3 mmol) and benzene (2 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) afforded **3f** as pale yellow liquid (46.2 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3H), 3.79 (s, 3H), 6.22 (t, J = 18.0 Hz, 1H), 7.38-7.40 (m, 3H), 7.49-7.59 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.7 (d, J = 6.0 Hz), 112.4 (d, J = 192.0 Hz), 127.9, 129.0, 130.6, 134.8 (d, J = 23.0 Hz), 150.0 (d, J = 7.0 Hz) ppm.



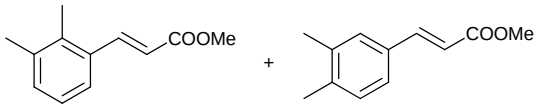
(*E*)-Methyl 3-(4-methoxyphenyl)acrylate (3g)[5]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and anisole (2.4 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3g** as a pale yellow solid (36.5 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 3.84 (s, 3H), 6.31 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 16.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.7, 55.5, 114.5, 115.4, 127.3, 129.9, 144.7, 161.5, 167.9 ppm.



Methyl (*E*)-3-(*x*-tolyl)acrylate (3h)[6a,6b]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and methylbenzene (2.4 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3h** as pale yellow liquid (41.4 mg, 78% yield). The ratio of *o*/*m*/*p* was 1.3/1.0/2.9 as determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of three isomers): δ = 2.37 (s, ArC<u>H</u>$_3$), 2.44 (s, ArC<u>H</u>$_3$), 3.799 (s, OC<u>H</u>$_3$), 3.804 (s, OC<u>H</u>$_3$), 3.81 (s, OC<u>H</u>$_3$), 6.37 (d, *J* = 16.0 Hz, =C<u>H</u>), 6.40 (d, *J* = 16.0 Hz, =C<u>H</u>), 6.43 d, *J* = 16.0 Hz, =C<u>H</u>), 7.18-7.33 (m, Ar<u>H</u>), 7.42 (d, *J* = 8.0 Hz, Ar<u>H</u>), 7.55 (d, *J* = 7.6 Hz, Ar<u>H</u>), 7.67 (d, *J* = 16.0 Hz, =C<u>H</u>), 7.99 (d, *J* = 16.0 Hz, =C<u>H</u>) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 21.4, 21.5, 51.70, 51.74, 51.8, 116.8, 117.7, 119.0, 125.4, 126.4, 126.5, 128.2, 128.8, 128.9, 129.7, 130.1, 130.9, 131.2, 131.8, 133.5, 134.5, 137.7, 138.6, 140.8, 142.6, 145.0, 145.1, 167.55, 167.57, 167.7 ppm.

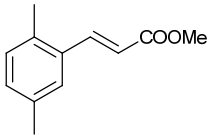


1.0 : 5.0

(*E*)-Methyl 3-(2,3-dimethylphenyl)acrylate (3i-1) and (*E*)-methyl 3-(3,4-dimethylphenyl)acrylate (3i-2)[7]

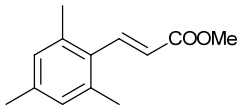
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and 1,2-dimethylbenzene (2.7 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product as colorless liquid (42.2 mg, 74% yield). The ratio of **3i-1**/**3i-2** was 1.0/5.0 as determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers): δ = 2.28 (s, C<u>H</u>$_3$, major isomer), 2.31 (s, C<u>H</u>$_3$, minor isomer), 2.33 (s, C<u>H</u>$_3$, minor isomer), 3.80 (s, OC<u>H</u>$_3$, major isomer), 3.82 (s, OC<u>H</u>$_3$, minor isomer), 6.32 (d, *J* = 15.6 Hz, =C<u>H</u>, minor isomer), 6.40 (d, *J* = 16.0 Hz, =C<u>H</u>, major isomer), 7.09-7.19 (m, Ar<u>H</u>, major+ minor isomer), 7.28 (d, *J* = 1.6 Hz, Ar<u>H</u>, major isomer), 7.30 (s, Ar<u>H</u>, major isomer),

7.39 (d, J = 7.6 Hz, ArH, minor isomer), 7.66 (d, J = 16.0 Hz, =CH, major isomer), 8.09 (d, J = 15.6 Hz, =CH, minor isomer) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4, 19.85, 19.91, 20.7, 51.7, 116.6, 119.4, 124.6, 124.8, 125.8, 125.9, 129.1, 129.4, 129.9, 130.3, 131.7, 132.2, 133.8, 134.7, 136.2, 136.7, 137.2, 137.5, 139.6, 141.4, 143.8, 145.2, 167.6, 167.8 ppm.



(*E*)-Methyl 3-(2,5-dimethylphenyl)acrylate (3j)[8]

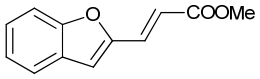
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and 1,4-dimethylbenzene (2.8 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3j** as colorless liquid (37.7 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.39 (s, 3H), 3.81 (s, 3H), 6.35 (d, J = 16.0 Hz, 1H), 7.090 (s, 1H), 7.093 (s, 1H), 7.36 (s, 1H), 7.96 (d, J = 16.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4, 21.1, 51.8, 118.7, 127.1, 130.9., 131.1, 133.3, 134.8, 135.9, 142.9, 167.7 ppm.



(*E*)-Methyl 3-mesitylacrylate (3k)[9]

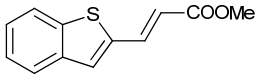
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (27.0 μL, 0.3 mmol) and mesitylene (3.1 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3k** as a pale yellow solid (38.1 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.33 (s, 6H), 3.82 (s, 3H),

6.06 (d, J = 16.4 Hz, 1H), 6.90 (s, 2H), 7.85 (d, J = 16.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.18, 21.20, 51.8, 123.0, 129.3, 131.1, 137.0, 138.5, 143.6, 167.6 ppm.



(*E*)-Methyl 3-(benzofuran-2-yl)acrylate (3l)[10]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (54.0 μL, 0.6 mmol), 2,3-benzofuran (33.1 μL, 0.3 mmol) and CH_2Cl_2 (2.0 mL) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3l** as a pale yellow solid (40.5 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.58 (d, J = 15.6 Hz, 1H), 6.94 (s, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 15.6 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0, 111.3, 111.6, 118.7, 121.9, 123.5, 126.6, 128.5, 131.6, 152.5, 155.7, 167.3 ppm.



(*E*)-Methyl 3-(benzo[*b*]thiophen-2-yl)acrylate (3m)[10]

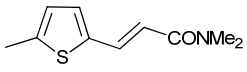
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (54.0 μL, 0.6 mmol), benzo[*b*]thiophene (40.3 mg, 0.3 mmol) and CH_2Cl_2 (2.0 mL) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3m** as a white solid (41.7 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.30 (d, J = 15.6 Hz, 1H), 7.33-7.39 (m, 2H), 7.46 (s, 1H), 7.75-7.80 (m, 2H), 7.88 (d, J = 15.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0, 119.2, 122.6, 124.6, 125.0, 126.4, 128.8, 138.0, 139.6, 139.7, 140.4, 167.1 ppm.

(*E*)-Methyl 3-(thiophen-2-yl)acrylate (3n-1)[11]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (54.0 μL, 0.6 mmol), thiophene (23.8 μL, 0.3 mmol) and CH_2Cl_2 (2.0 mL) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3n-1** (13.4 mg, 27% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 6.24 (d, J = 16.0 Hz, 1H), 7.05 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 7.25 (d, J = 4.8 Hz, 1H), 7.37 (d, J = 5.2 Hz, 1H), 7.79 (d, J = 15.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.8, 116.7, 128.2, 128.6, 131.1, 137.4, 139.7, 167.4 ppm. Product **3n-2** was also obtained as a yellow solid (45.4 mg, 60% yield).

(2*E*,2'*E*)-Dimethyl 3,3'-(thiophene-2,5-diyl)diacrylate (3n-2)[11]

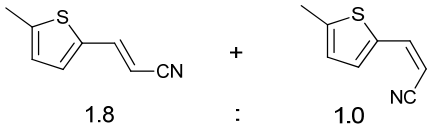
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 6H), 6.26 (d, J = 16.0 Hz, 2H), 7.17 (s, 2H), 7.71 (d, J = 16.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0, 118.5, 131.8, 136.7, 141.9, 167.0 ppm.



(*E*)-*N*,*N*-Dimethyl-3-(5-methylthiophen-2-yl)acrylamide (3o)[12]

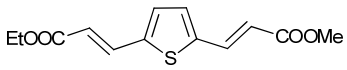
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), *N*,*N*-dimethylacrylamide (61.8 μL, 0.6 mmol), 2-methylthiophene (26.7 μL, 0.3 mmol) and CH_2Cl_2 (2.0 mL) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) afforded **3o** as a yellow solid (31.7 mg, 54% yield). M.p.: 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 3.05 (s, 3H), 3.13 (s, 3H), 6.54 (d, J = 14.8 Hz, 1H), 6.67-6.68 (m, 1H), 7.00 (d, J = 3.6 Hz, 1H), 7.70 (d, J = 15.2 Hz, 1H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 15.9, 36.1, 37.5, 114.8, 126.5, 131.0, 135.8, 138.6, 142.6, 166.8 ppm. HRMS (ESI^+): calcd for $C_{10}H_{14}NOS$ $[M+H]^+$ 196.0796, found 196.0794.



3-(5-Methylthiophen-2-yl)acrylonitrile (3p)[13]

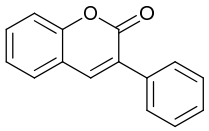
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), selectfluor (212.6 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), acrylonitrile (98.7 μL, 1.5 mmol), 2-methylthiophene (26.7 μL, 0.3 mmol) and CH_2Cl_2 (2.0 mL) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3p** as yellow liquid (a mixture of (*E*)- and (*Z*)-isomers, 23.4 mg, 59% yield). The ratio of (*E*)-**3p**/(*Z*)-**3p** was 1.8:1.0 as determined by ^1H NMR. ^1H NMR (400 MHz, $CDCl_3$, a mixture of two isomers): δ = 2.50 (s, C<u>H</u>$_3$, major isomer), 2.54 (s, C<u>H</u>$_3$, minor isomer), 5.14 (d, *J* = 12.0 Hz, =C<u>H</u>, minor isomer), 5.48 (d, *J* = 16.4 Hz, =C<u>H</u>, major isomer), 6.72-6.73 (m, major isomer), 6.76-6.77 (m, minor isomer), 7.03 (d, *J* = 3.6 Hz, major isomer), 7.13 (d, *J* = 12.0 Hz, minor isomer), 7.30 (d, *J* = 3.6 Hz, minor isomer), 7.37 (d, *J* = 16.4 Hz, major isomer) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9, 16.0, 90.0, 92.8, 118.1, 118.5, 126.1, 126.9, 132.1, 133.4, 136.0, 136.6, 141.3, 143.1, 145.2, 146.2 ppm. HRMS (ESI^+): calcd for C_8H_8NS $[M+H]^+$ 150.0377, found 150.0377.



(*E*)-Ethyl 3-(5-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)thiophen-2-yl)acrylate (3q)[14]

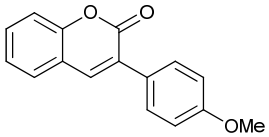
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), methyl acrylate (54.0 μL, 0.6 mmol), (*E*)-ethyl 3-(thiophen-2-yl)acrylate (54.6 mg, 0.3 mmol) and CH_2Cl_2 (2.0 mL) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v)

afforded **3q** as a yellow solid (40.5 mg, 51% yield). M.p.: 56-58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.2 Hz, 3H), 3.80 (s, 3H), 4.25 (q, J = 7.2 Hz, 2H), 6.25 (d, J = 15.6 Hz, 2H), 7.17 (s, 2H), 7.69 (d, J = 4.0 Hz, 1H), 7.73 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 52.0, 60.9, 118.4, 119.0, 131.7, 131.8, 136.4, 136.7, 141.8, 142.0, 166.6, 167.0 ppm. HRMS (ESI^+): calcd for $C_{13}H_{14}NaO_4S$ $[M+H]^+$ 289.0510, found 289.0514.



3-Phenylcoumarin (6a)[15]

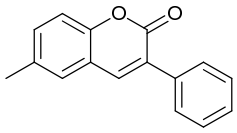
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), coumarin (43.8 mg, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **6a** as a white solid (49.2 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (td, J = 7.6 Hz, 0.8 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.41-7.48 (m, 3H), 7.52-7.56 (m, 2H), 7.70-7.72 (m, 2H), 7.82 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.6, 119.8, 124.6, 128.0, 128.5, 128.6, 128.7, 129.0, 131.5, 134.9, 140.0, 153.7, 160.7 ppm.



3-(4-Methoxyphenyl)-2*H*-chromen-2-one (6b)[15]

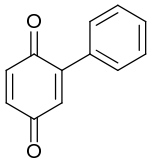
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), coumarin (43.8 mg, 0.3 mmol) and anisole (2.4 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **6b** as a white solid (60.1 mg, 79%

yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 6.98 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.49-7.54 (m, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.76 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 114.1, 116.5, 120.0, 124.6, 127.2, 127.8, 128.0, 130.0, 131.2, 138.6, 153.5, 160.3, 160.9 ppm.



6-Methyl-3-phenyl-2*H*-chromen-2-one (6c)[15]

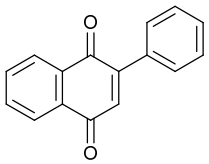
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), 6-methylcoumarin (48.1 mg, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded **6c** as a white solid (52.3 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.25-7.27 (m, 1H), 7.33 (s, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.40-7.47 (m, 3H), 7.70 (d, J = 6.8 Hz, 2H), 7.76 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 116.3, 119.6, 127.8, 128.4, 128.6, 128.7, 128.9, 132.6, 134.3, 135.0, 140.0, 151.8, 160.9 ppm.



2-Phenyl-1,4-benzoquinone (7a)[16]

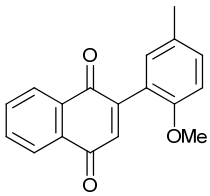
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), 1,4-benzoquinone (32.4 mg, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 1/1, v/v) afforded **7a** as a yellow solid (34.8 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82-6.89 (m, 3H), 7.42-7.49 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.6, 129.3, 130.2, 132.8, 136.3, 137.1, 146.0,

186.7, 187.7 ppm.



2-Phenyl-1,4-naphthoquinone (7b)[16]

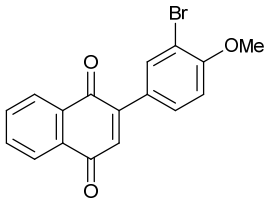
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), 1,4-naphthoquinone (47.4 mg, 0.3 mmol) and benzene (2.0 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2/1, v/v) afforded **7b** as a yellow solid (66.1 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (s, 1H), 7.48-7.49 (m, 3H), 7.57-7.58 (m, 2H), 7.79 (t, *J*= 4.4 Hz, 2H), 8.11-8.14 (m, 1H), 8.18-8.20 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.1, 127.2, 128.6, 129.6, 130.2, 132.2, 132.6, 133.5, 133.95, 134.02, 135.3, 148.2, 184.5, 185.3 ppm.



2-(2-Methoxy-5-methylphenyl)naphthalene-1,4-dione (7c)[16]

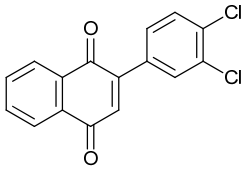
$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), 1,4-naphthoquinone (47.4 mg, 0.3 mmol) and 4-methylanisole (2.8 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2/1-1/1, v/v) afforded **7c** as a yellow solid (78.2 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.76 (s, 3H), 6.89 (d, *J* = 8.4 Hz, 1H), 7.01 (s, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.73-7.77 (m, 2H), 8.10-8.16 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5, 56.0, 111.4, 123.2, 126.1, 127.0, 130.0, 131.1, 131.5, 132.3, 132.7, 133.6, 133.8,

136.7, 148.4, 155.3, 183.7, 185.4 ppm.



2-(3-Bromo-4-methoxyphenyl)naphthalene-1,4-dione (7d)

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (111.4 μL, 1.5 mmol), 1,4-naphthoquinone (47.4 mg, 0.3 mmol) and 2-bromoanisole (2.8 mL, 22.5 mmol) at room temperature for 24 h. Purification via column chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1, v/v) afforded **7d** as a yellow solid (42.4 mg, 41% yield). M.p.: 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (s, 3H), 7.00 (d, J = 8.8 Hz, 1H), 7.05 (s, 1H), 7.57 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.77-7.79 (m, 2H), 7.85 (d, J = 2.4 Hz, 1H), 8.11-8.13 (m, 1H), 8.17-8.19 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.6, 111.7, 112.0, 126.1, 127.0, 127.2, 130.2, 132.2, 132.5, 134.05, 134.07, 134.5, 146.2, 157.6, 184.5, 185.1 ppm. HRMS (ESI^+): calcd for $C_{17}H_{11}BrNaO_3$ $[M+Na]^+$ 364.9789, found 364.9788.



2-(3,4-Dichlorophenyl)naphthalene-1,4-dione (7e)[16]

$Pd(OAc)_2$ (6.7 mg, 0.03 mmol), $(NH_4)_2S_2O_8$ (137.0 mg, 0.6 mmol), TFA (222.8 μL, 3.0 mmol), 1,4-naphthoquinone (47.4 mg, 0.3 mmol) and 1,2-dichlorobenzene (2.5 mL, 22.5 mmol) at room temperature for 48 h. Purification via column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 1/1, v/v) afforded **7e** as a yellow solid (48.3 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (s, 1H),

7.42 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.80 (t, J = 4.4 Hz, 2H), 8.11-8.14 (m, 1H), 8.17-8.19 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.3, 127.3, 128.7, 130.7, 131.4, 132.1, 132.3, 133.0, 133.3, 134.3, 134.7, 135.8, 145.9, 183.9, 184.8 ppm.

X. References

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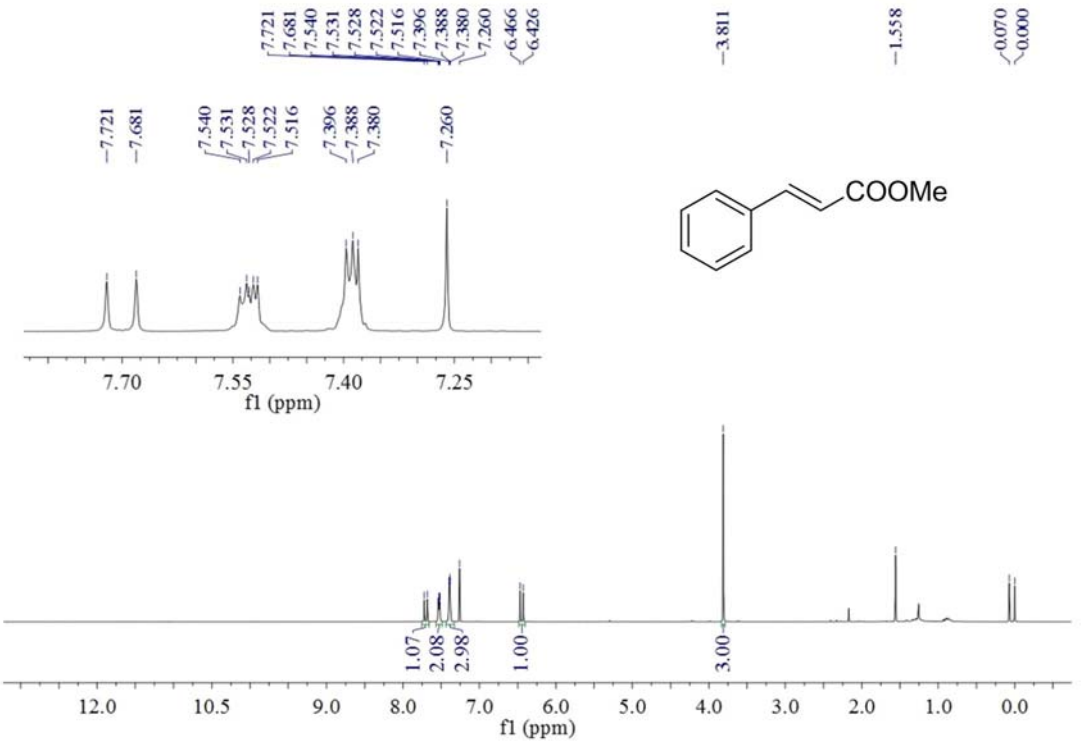
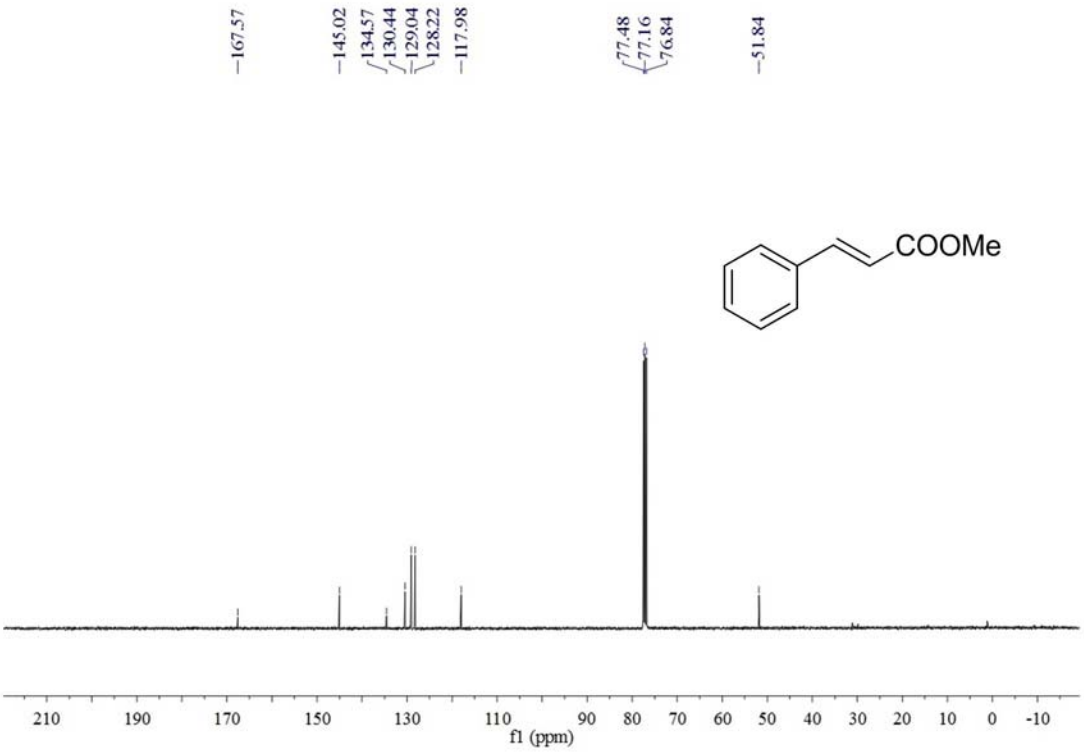
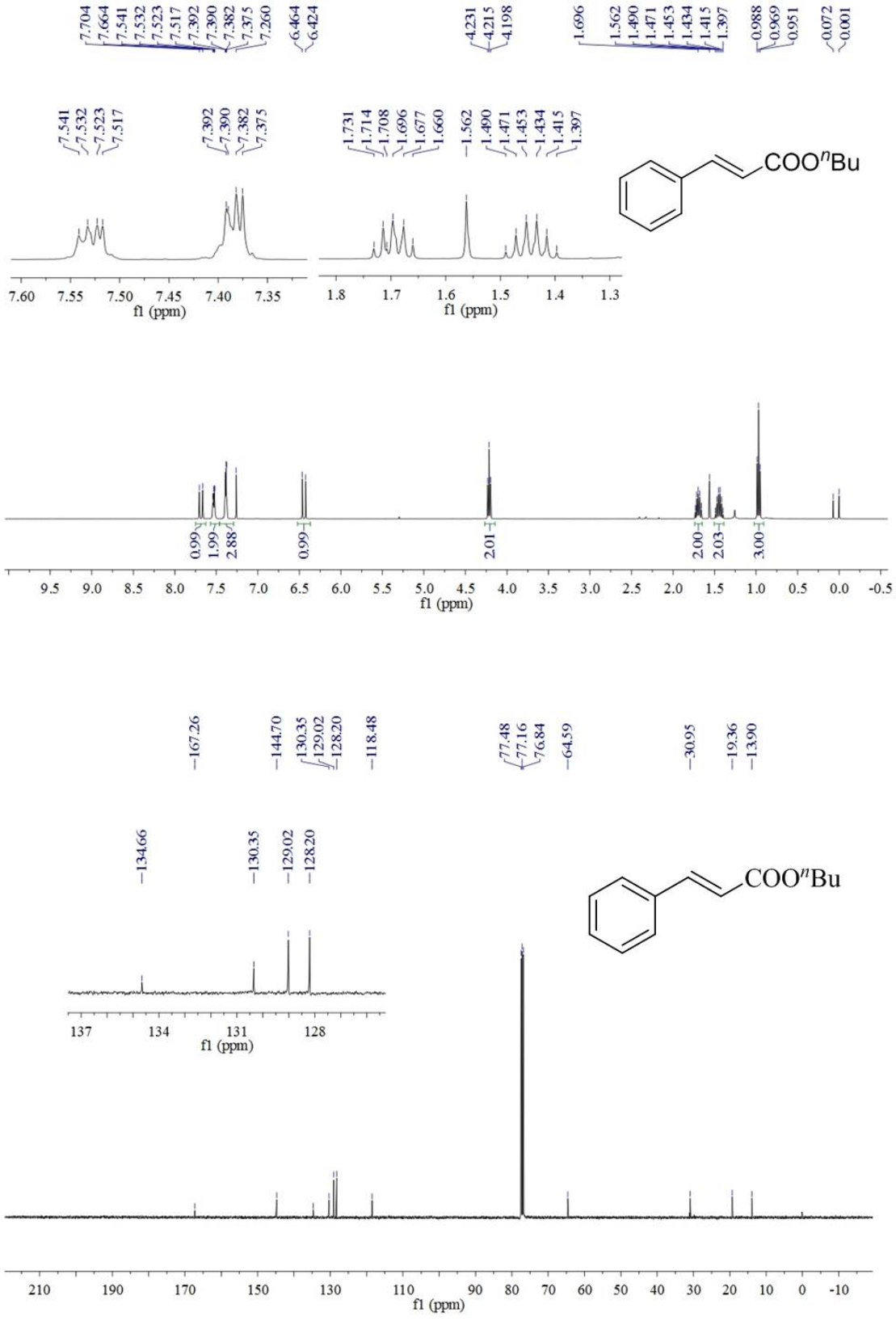
XI. Copies of ^{1}H, ^{13}C NMR and ^{1}H-^{1}H NOESY spectra



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7.375
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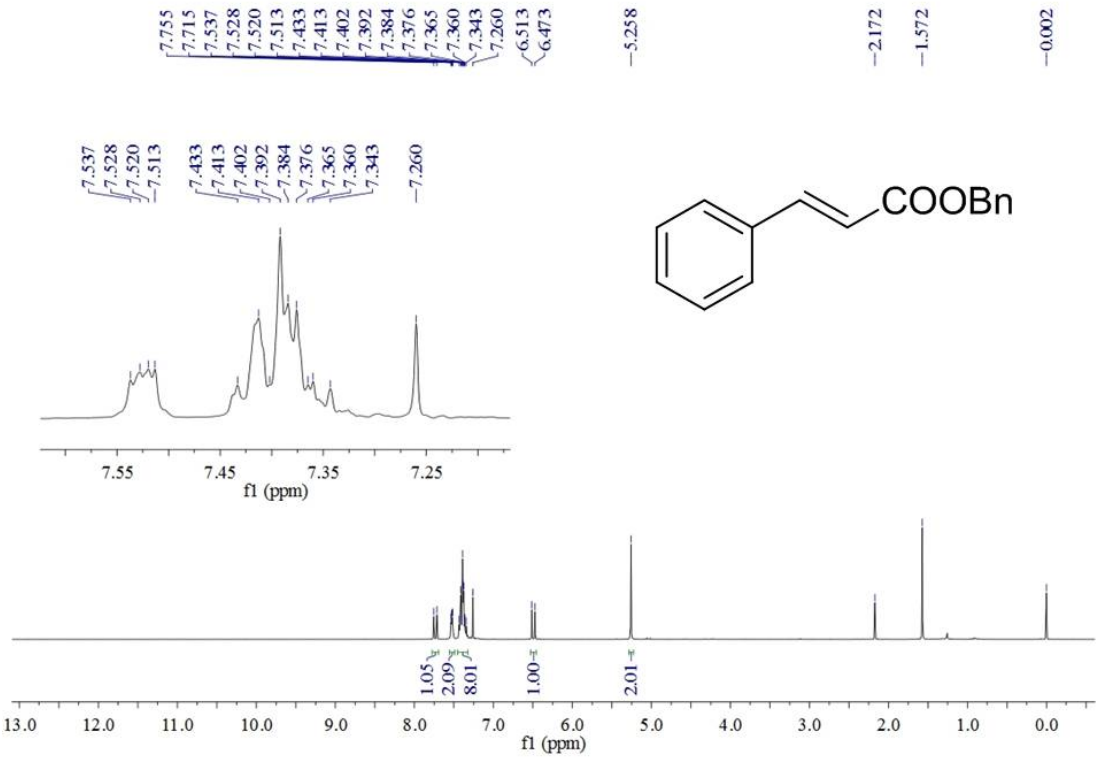
6.464
6.424
4.231
4.215
4.198
1.696
1.562
1.490
1.471
1.453
1.434
1.415
1.397
0.988
0.969
0.951
0.072
0.001
COO^{n}Bu
f1 (ppm)
0.99
1.99
2.88
0.99
2.01
2.00
2.03
3.00
167.26
144.70
130.35
129.02
128.20
118.48
77.48
77.16
76.84
64.59
30.95
19.36
13.90
134.66
f1 (ppm)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7.513
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7.392
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7.365
7.360
7.343
7.260
6.513
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COOBn
f1 (ppm)
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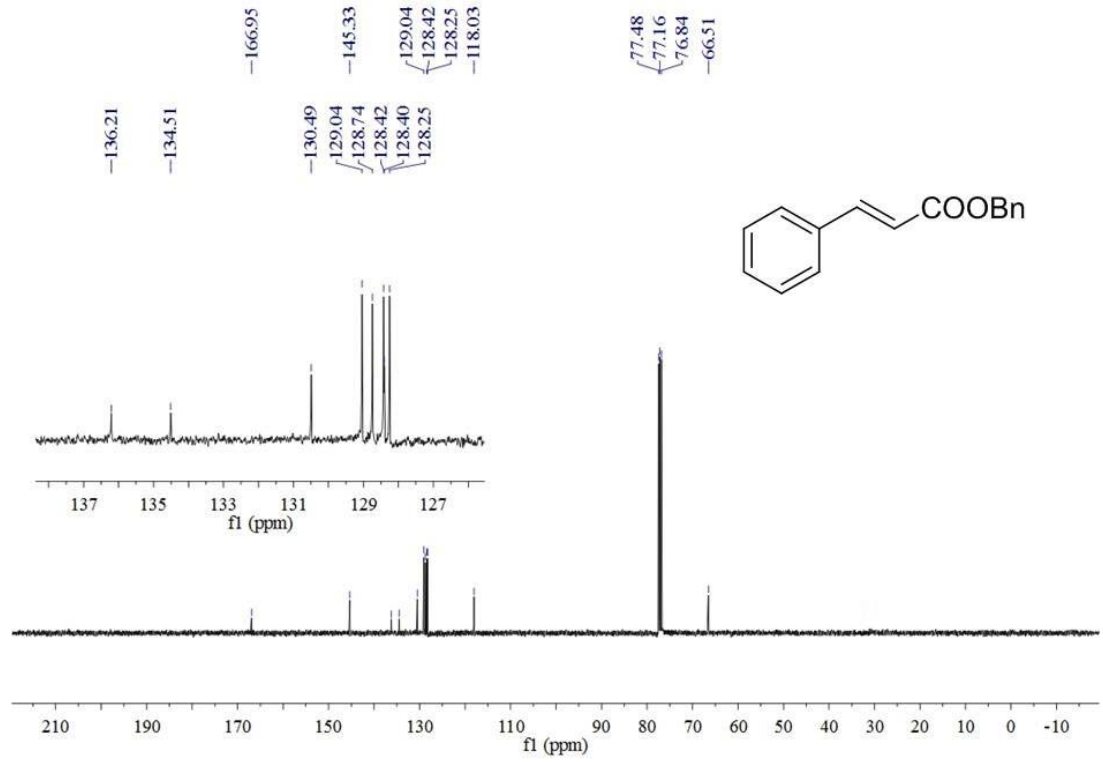
2.09
8.01
1.00
2.01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129.04
128.42
128.25
118.03
77.48
77.16
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128.40
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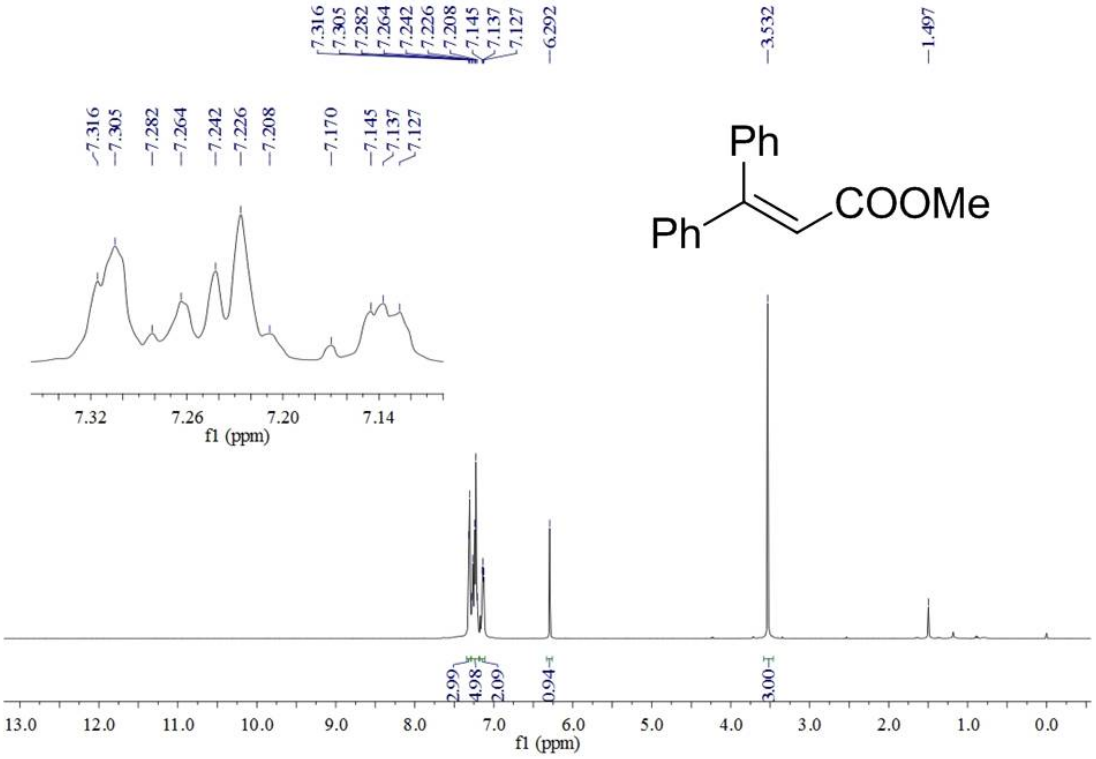
f1 (ppm)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7.127
6.292
3.532
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7.170
Ph
Ph
COOMe
7.32
7.26
7.20
7.14
f1 (ppm)
2.99
4.98
2.09
0.94
3.00
13.0
12.0
11.0
10.0
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8.0
7.0
6.0
5.0
4.0
3.0
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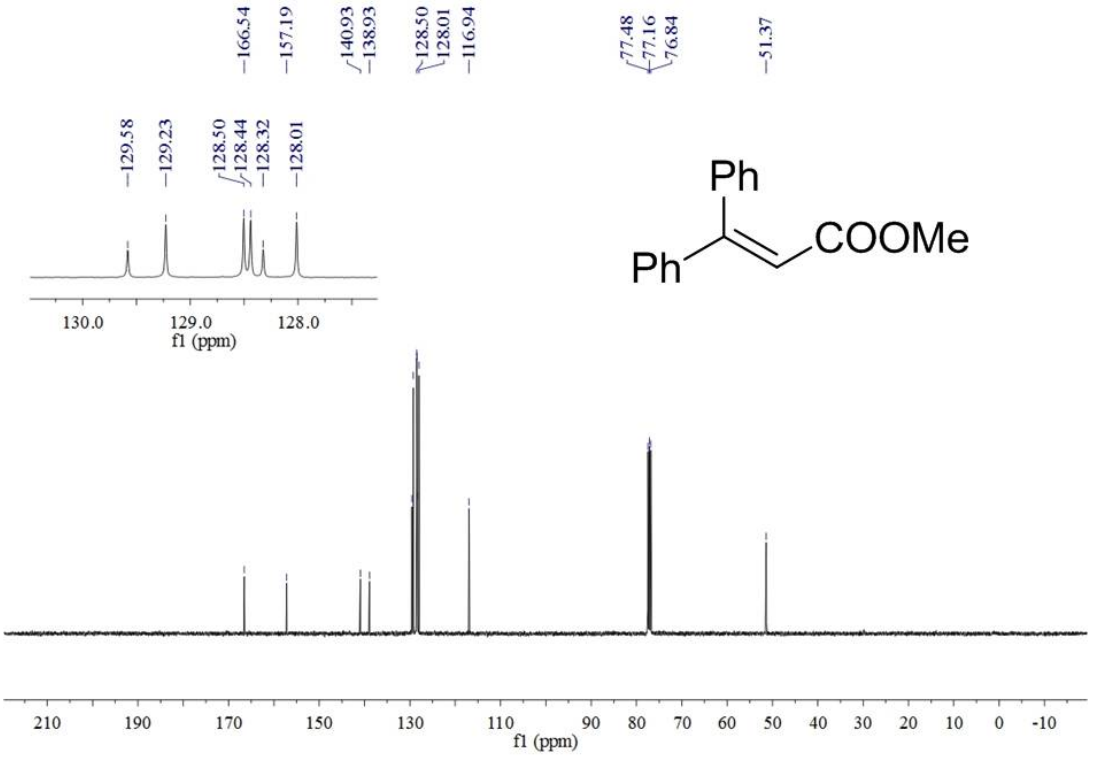
f1 (ppm)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128.50
128.44
128.32
128.01
Ph
Ph
COOMe
130.0
129.0
128.0
f1 (ppm)
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170
150
130
110
90
80
70
60
50
40
30
20
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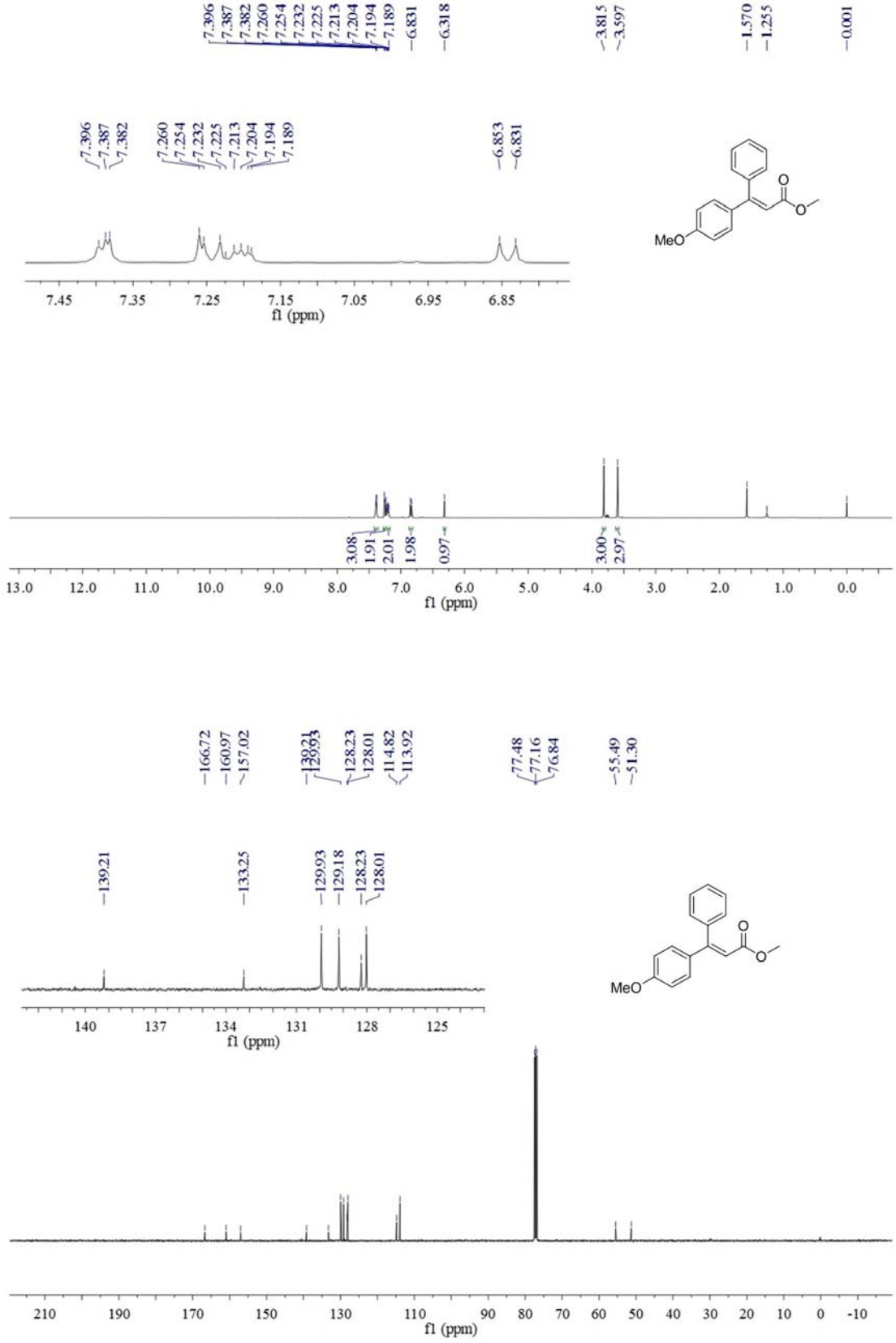
0
-10
f1 (ppm)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7.232
7.225
7.213
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7.194
7.189
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6.318
3.815
3.597
1.570
1.255
0.001
6.853
6.831
MeO
O
O
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7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
3.08
1.91
2.01
1.98
0.97
3.00
2.97
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
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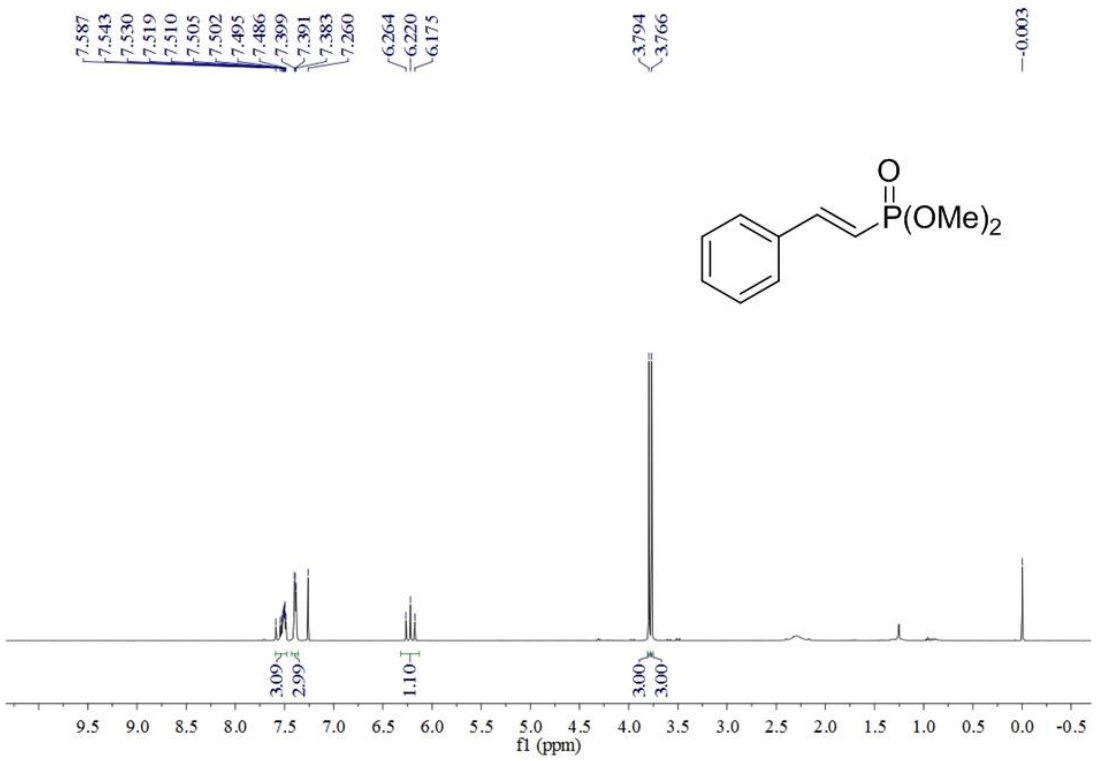
160.97
157.02
139.21
129.93
128.23
128.01
114.82
113.92
77.48
77.16
76.84
55.49
51.30
139.21
133.25
129.93
129.18
128.23
128.01
MeO
O
O
140
137
134
131
128
125
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.391
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6.264
6.220
6.175
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O
P(OMe)2
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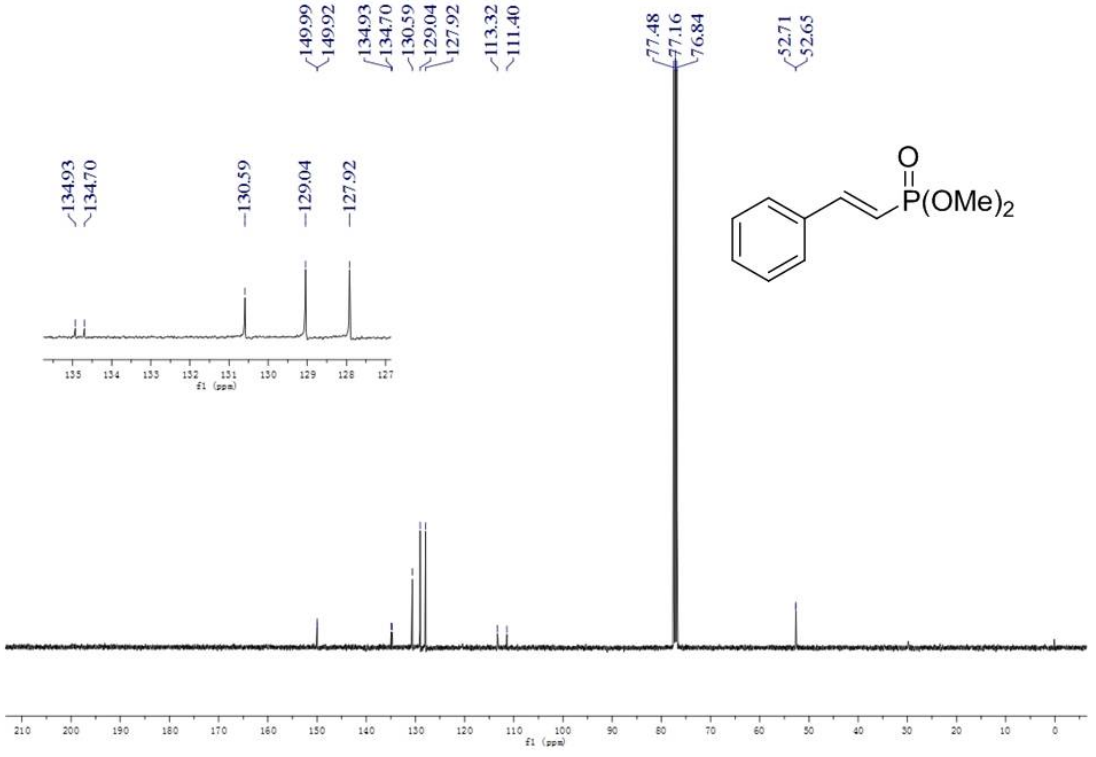
2.99
1.10
3.00
3.00
f1 (ppm)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134.70
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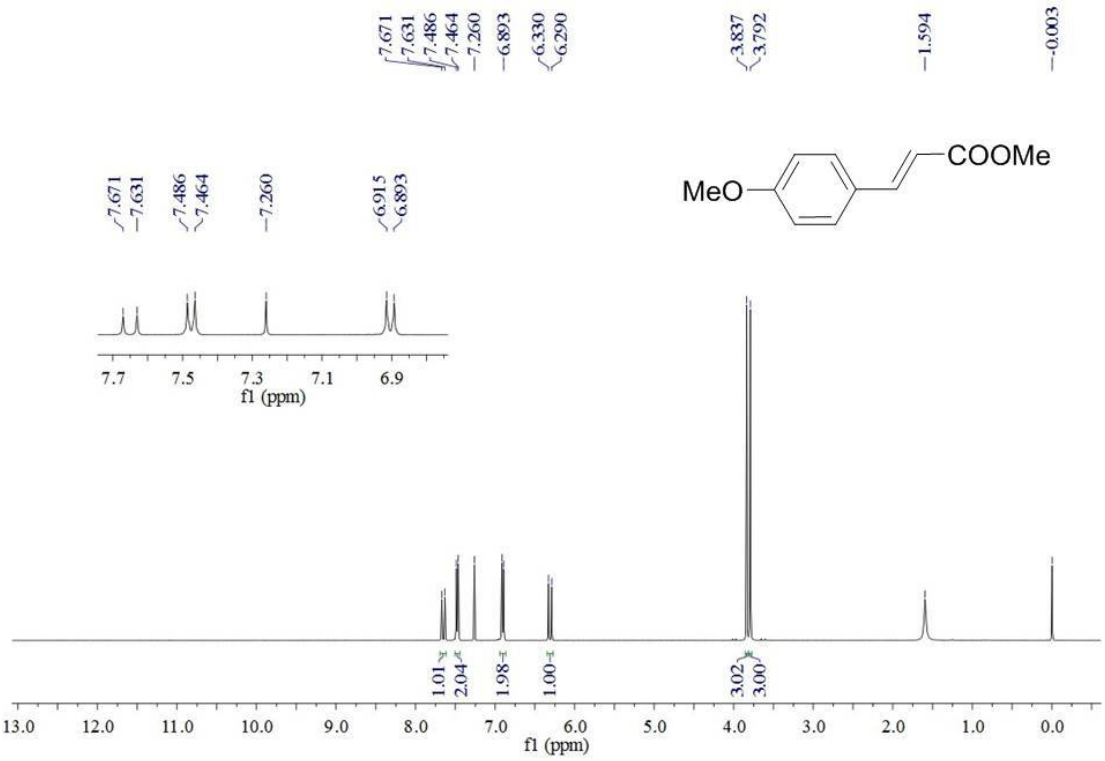
O
P(OMe)2
f1 (ppm)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MeO
COOMe
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
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2.04
1.98
1.00
3.02
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12.0
11.0
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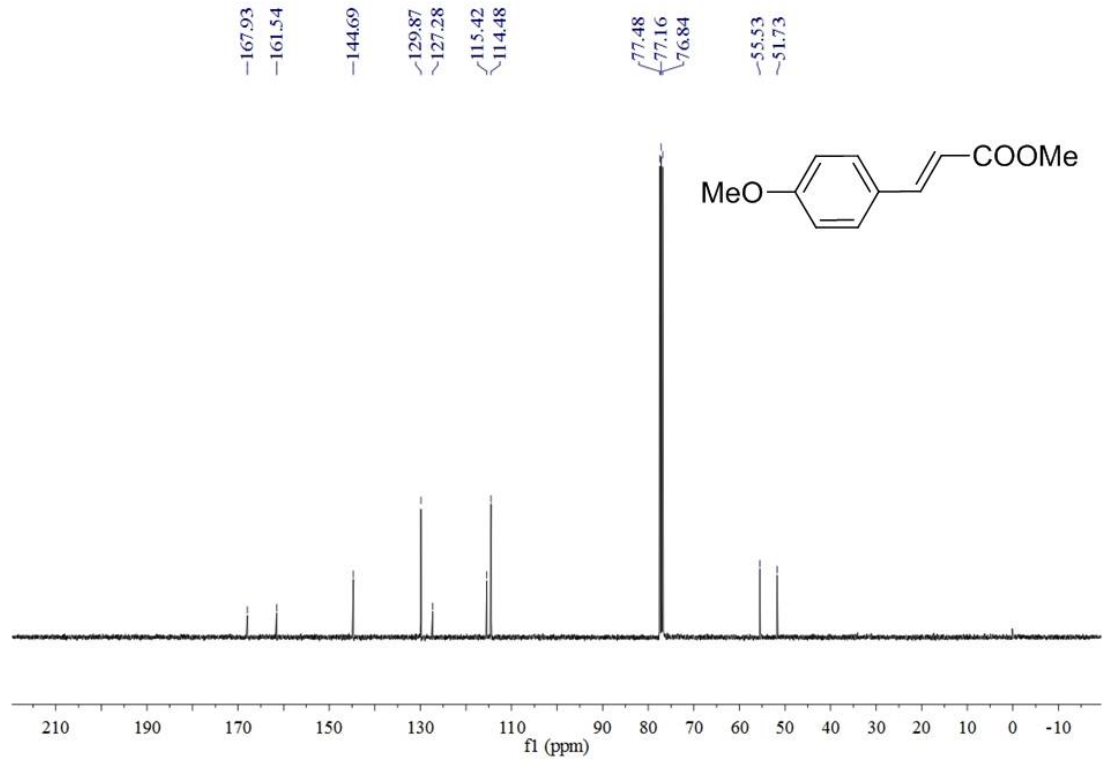
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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127.28
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77.48
77.16
76.84
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51.73
MeO
COOMe
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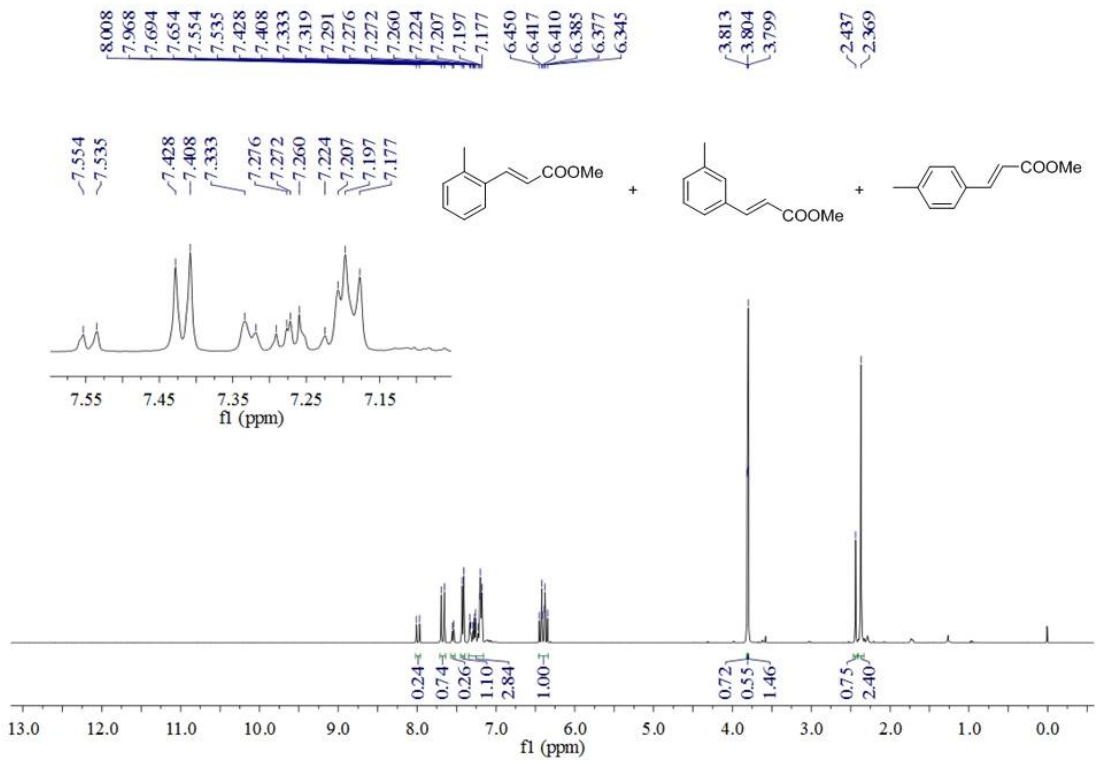
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.177
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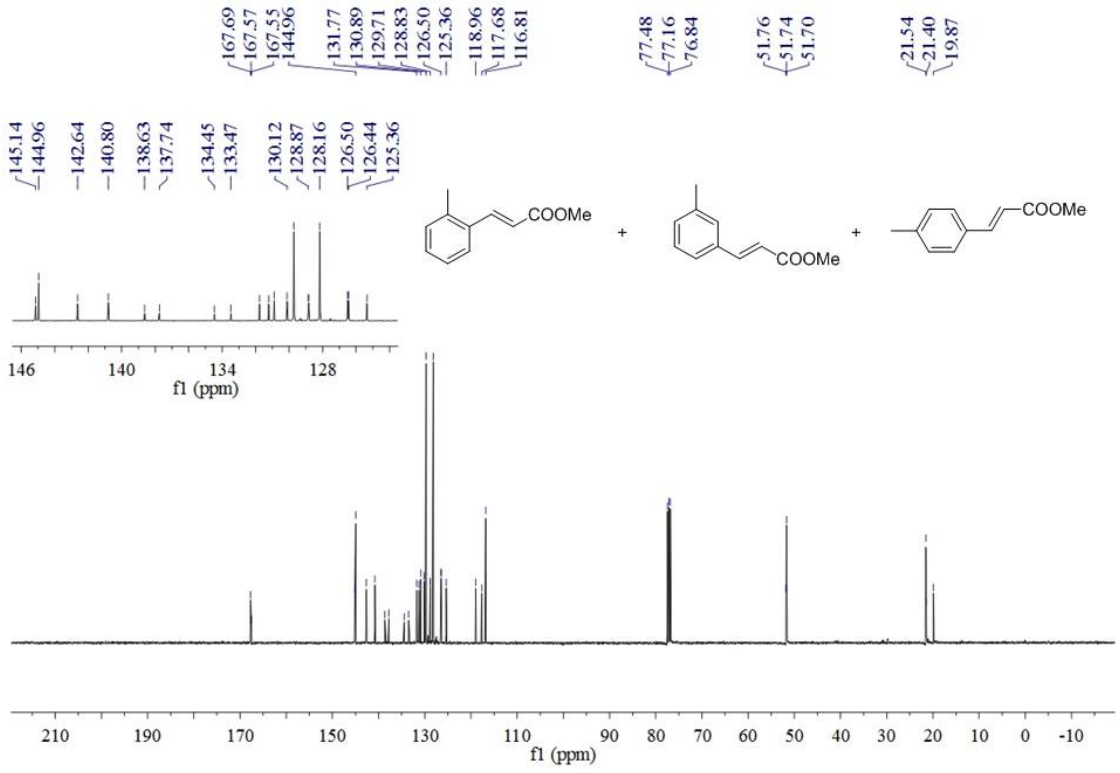
COOMe
COOMe
COOMe
f1 (ppm)
f1 (ppm)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77.16
76.84
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51.74
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21.54
21.40
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145.14
144.96
142.64
140.80
138.63
137.74
134.45
133.47
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126.50
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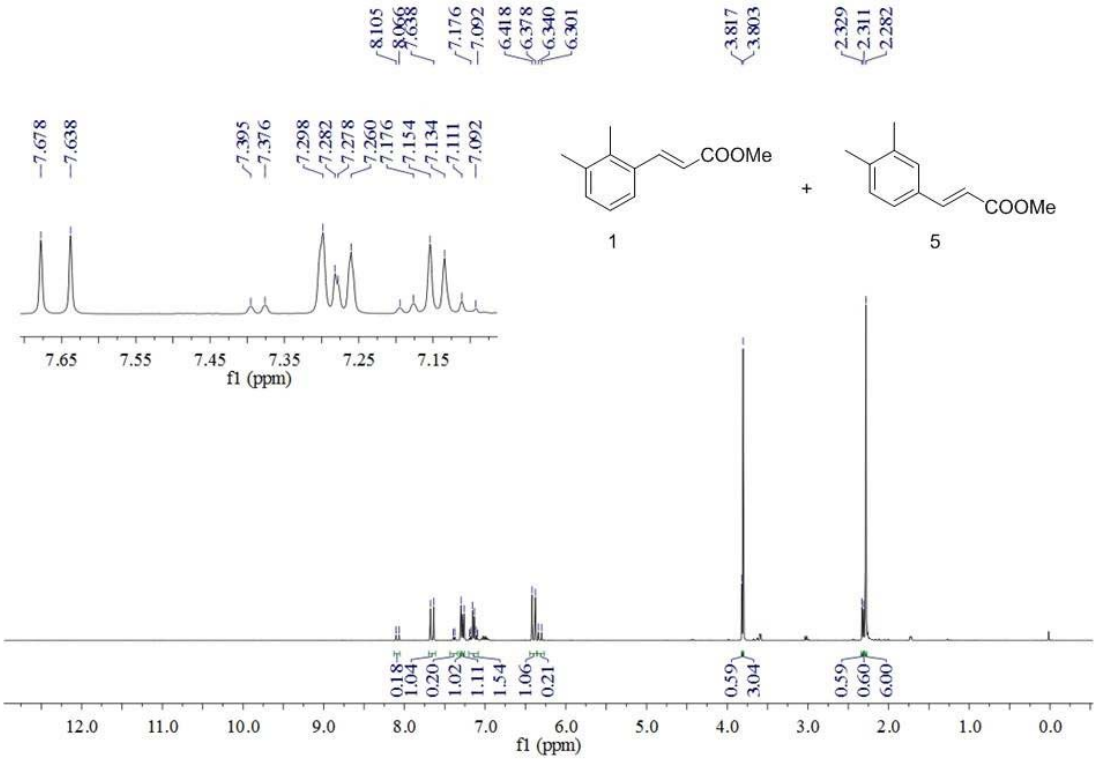
COOMe
COOMe
COOMe
f1 (ppm)
f1 (ppm)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3.803
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2.282
7.678
7.638
7.395
7.376
7.298
7.282
7.278
7.260
7.176
7.154
7.134
7.111
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COOMe
1
+
COOMe
5
7.65
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
0.18
1.04
0.20
1.02
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1.54
1.06
0.21
0.59
3.04
0.59
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6.00
12.0
11.0
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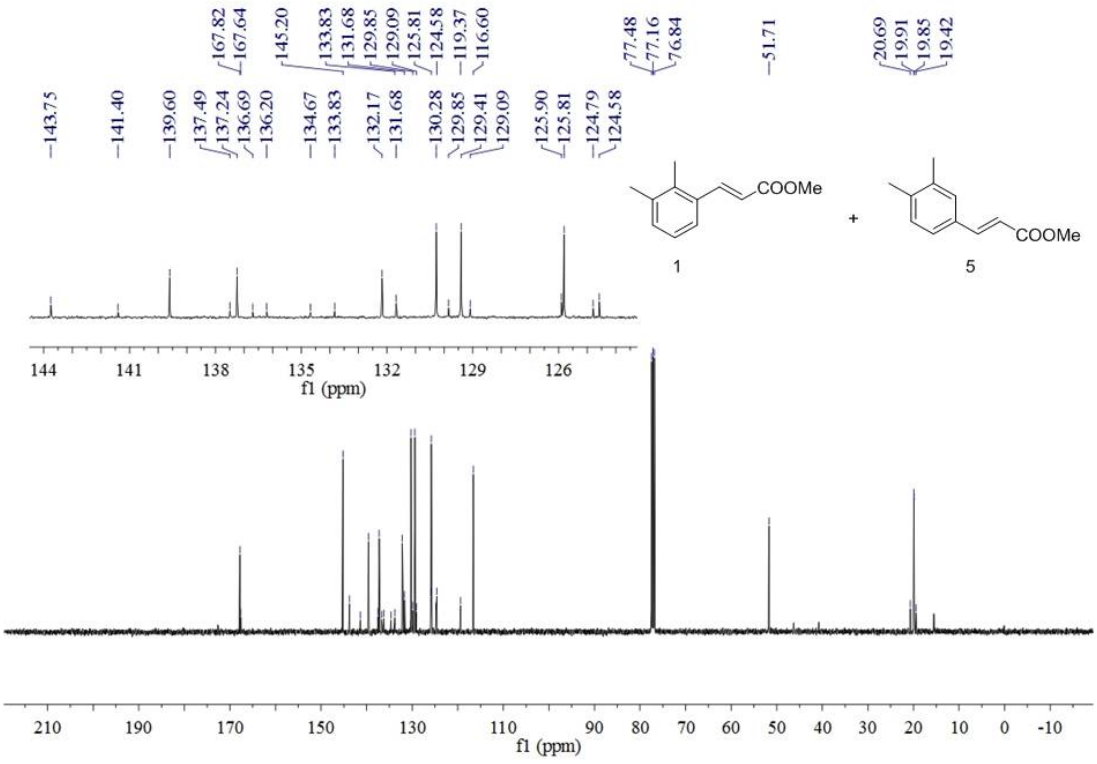
0.0
f1 (ppm)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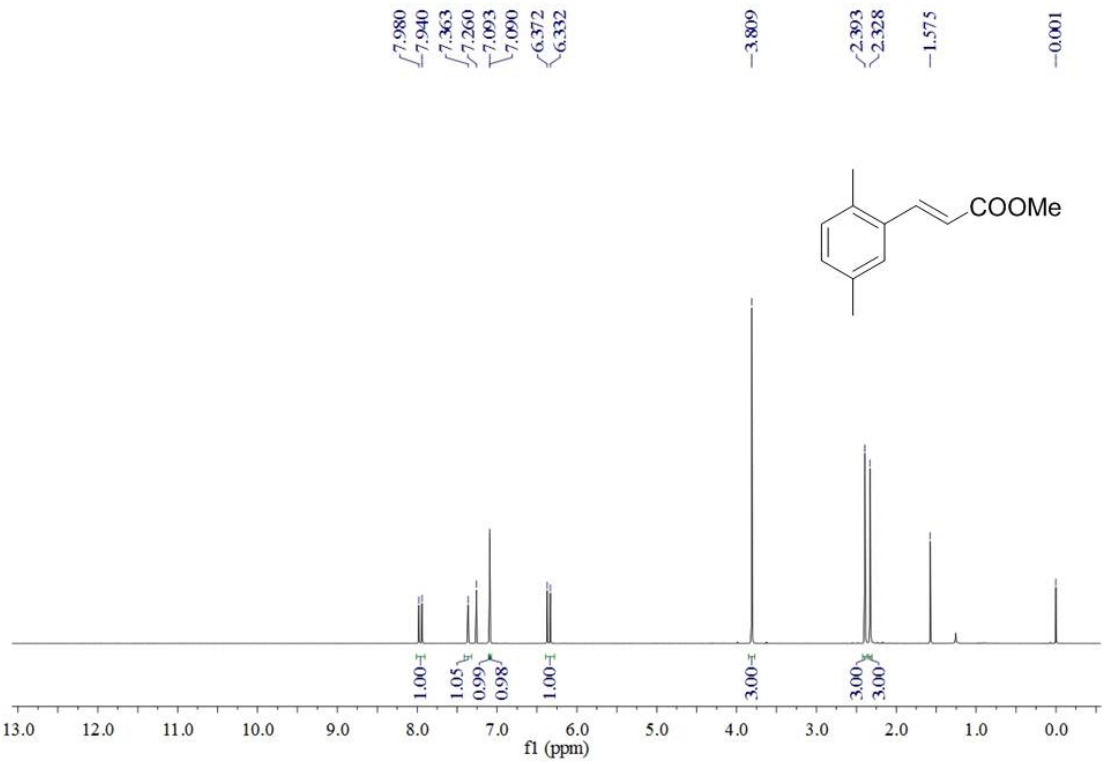
76.84
51.71
20.69
19.91
19.85
19.42
143.75
141.40
139.60
137.49
137.24
136.69
136.20
134.67
133.83
132.17
131.68
130.28
129.85
129.41
129.09
125.90
125.81
124.79
124.58
COOMe
1
+
COOMe
5
144
141
138
135
132
129
126
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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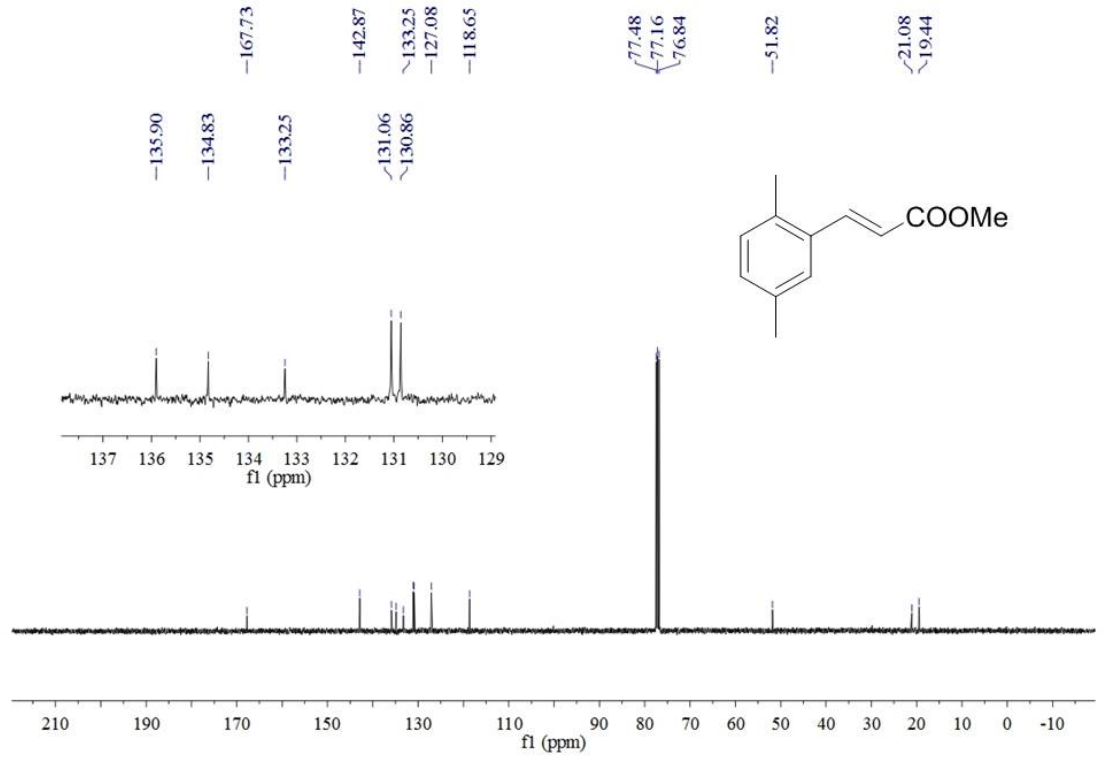
f1 (ppm)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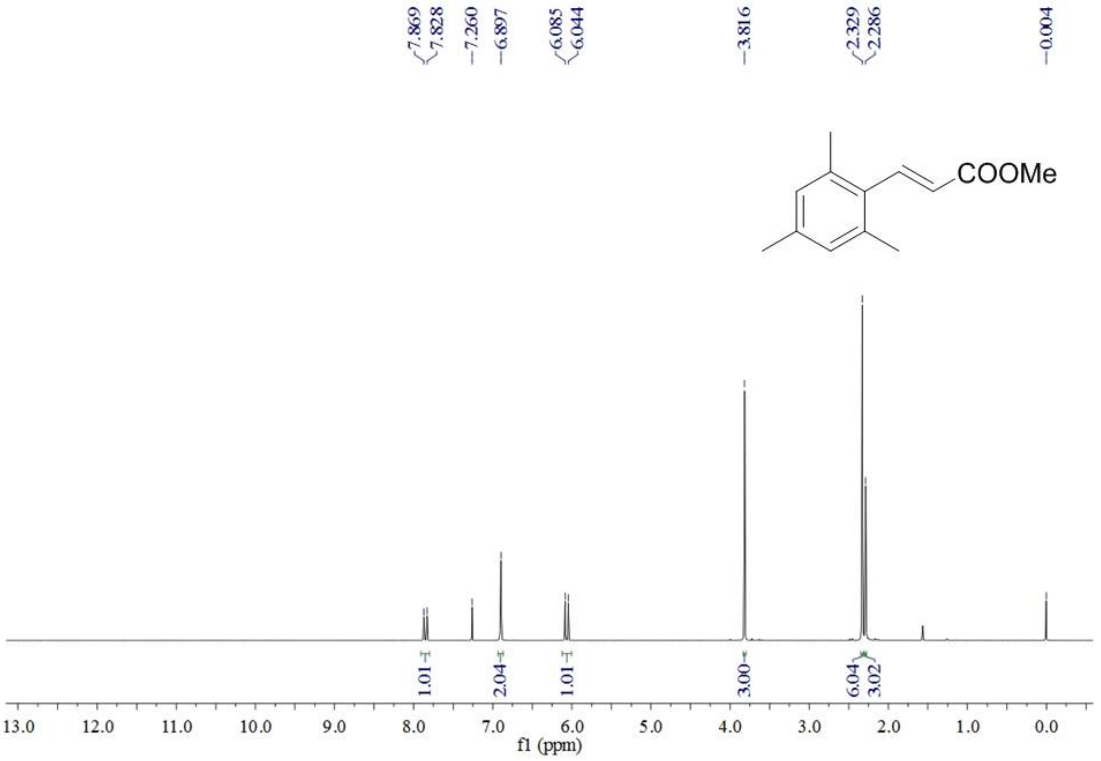
f1 (ppm)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1.01
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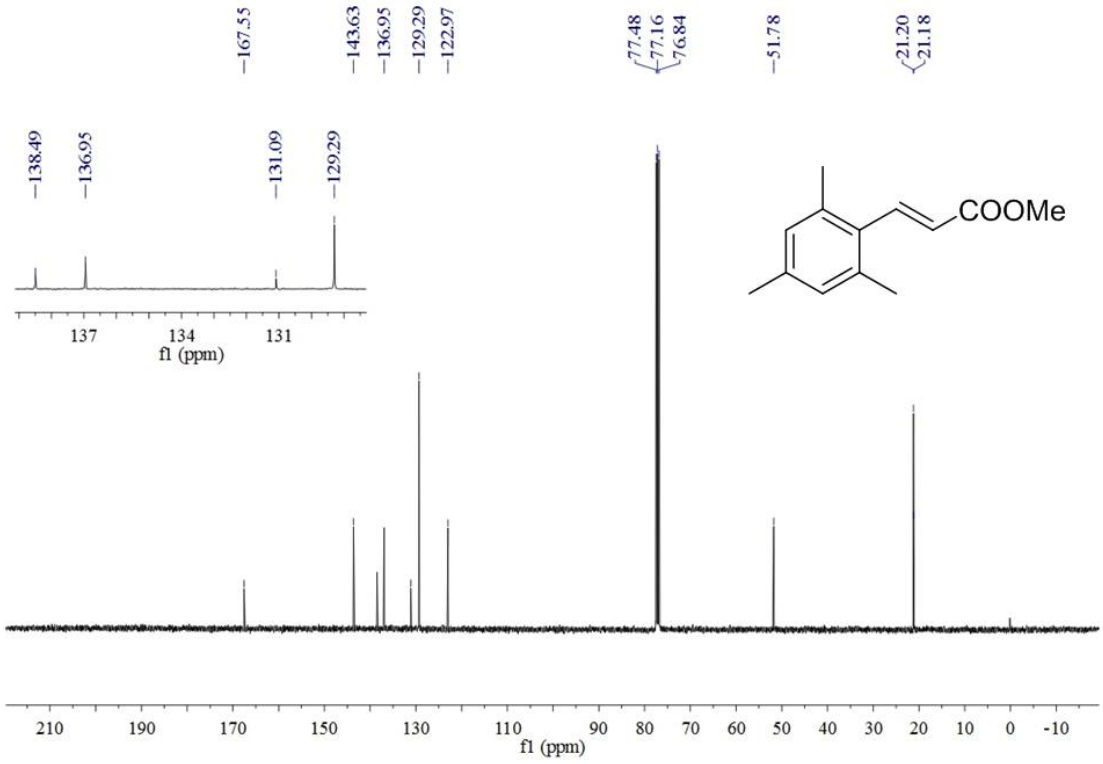
f1 (ppm)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129.29
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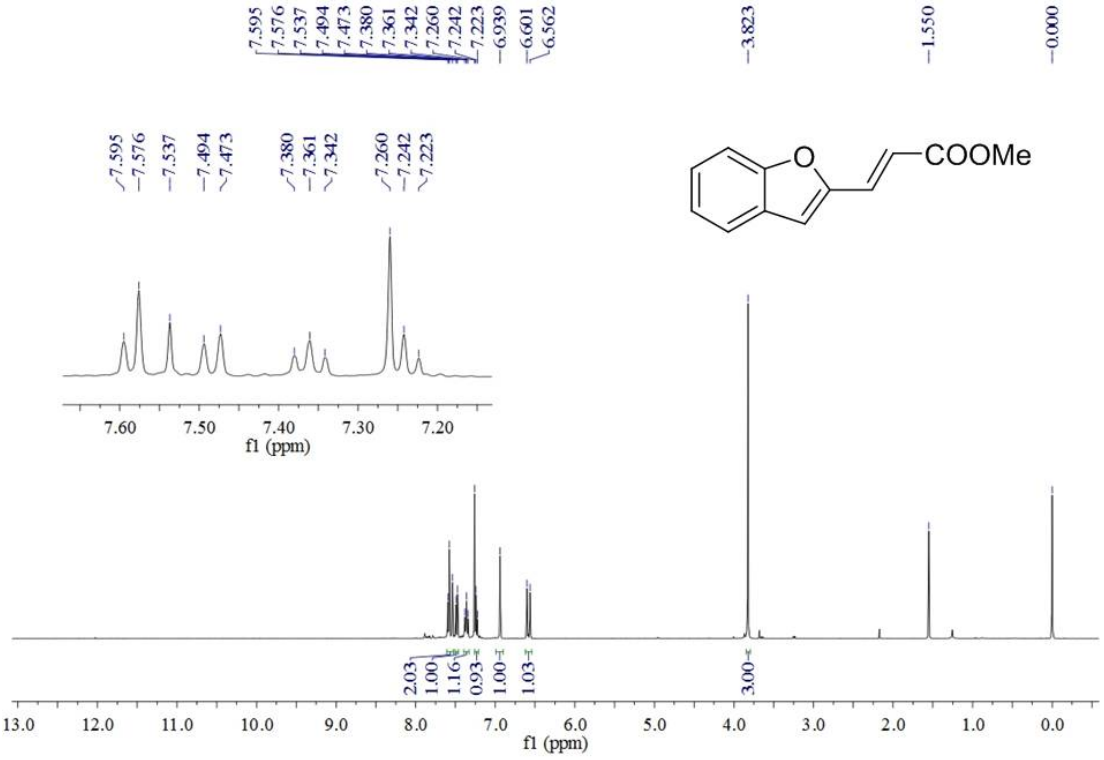
f1 (ppm)
f1 (ppm)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7.242
7.223
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6.601
6.562
3.823
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COOMe
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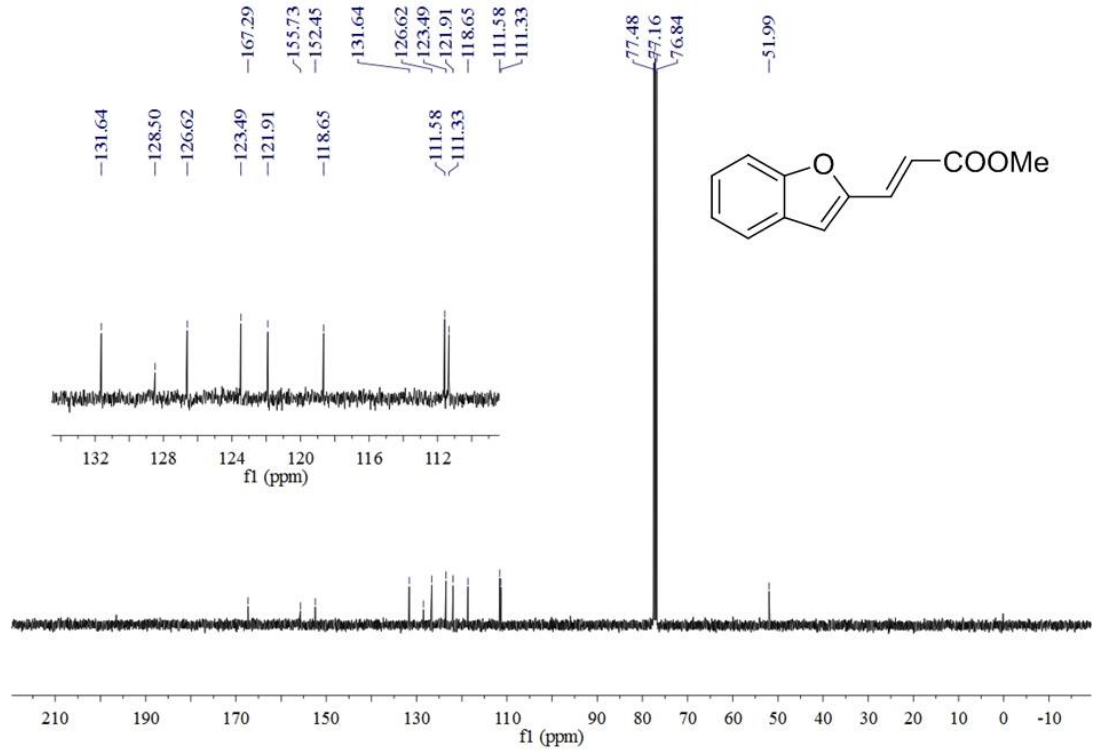
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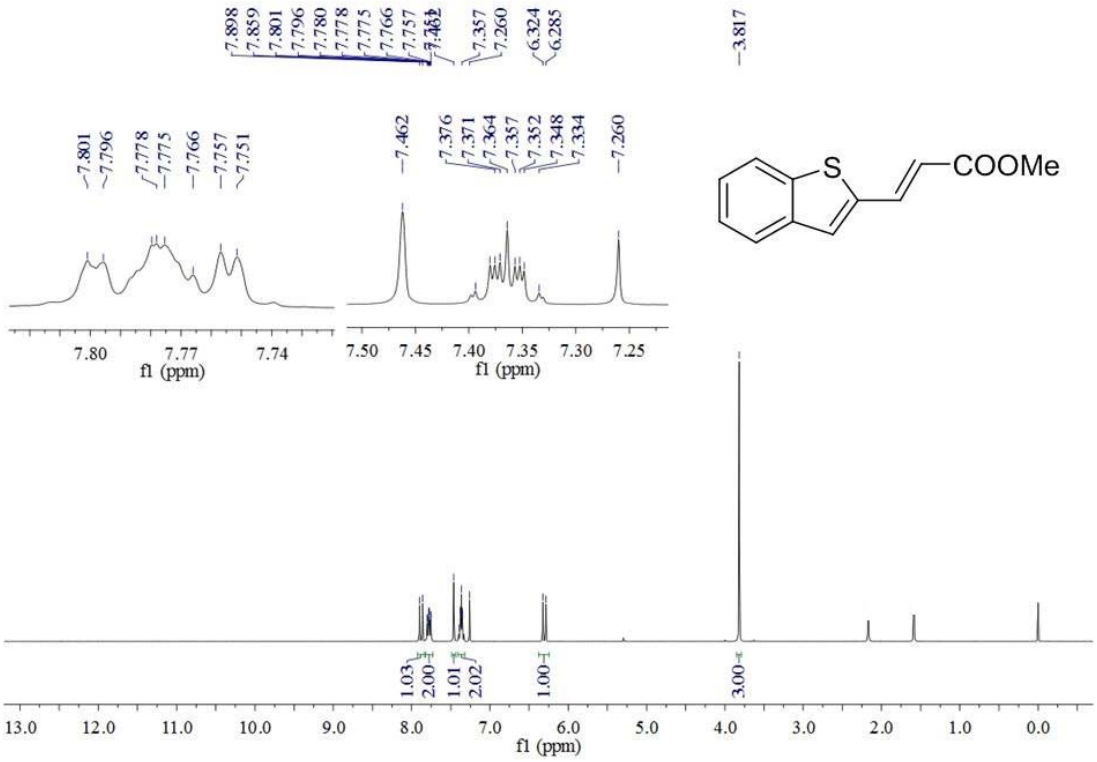
77.48
77.16
76.84
51.99
COOMe
f1 (ppm)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6.285
3.817
7.801
7.796
7.778
7.775
7.766
7.757
7.751
7.462
7.376
7.371
7.364
7.357
7.352
7.348
7.334
7.260
S
COOMe
7.80
7.77
7.74
f1 (ppm)
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)
1.03
2.00
1.01
2.02
1.00
3.00
13.0
12.0
11.0
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7.0
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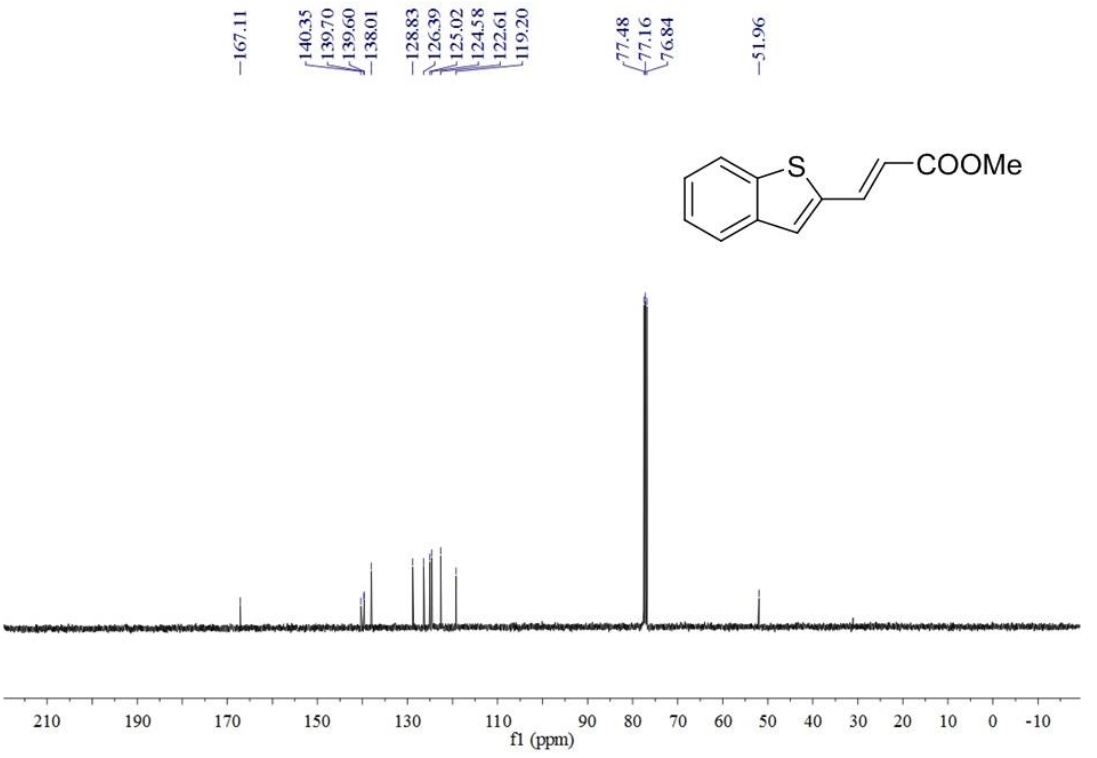
2.0
1.0
0.0
f1 (ppm)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76.84
51.96
S
COOMe
210
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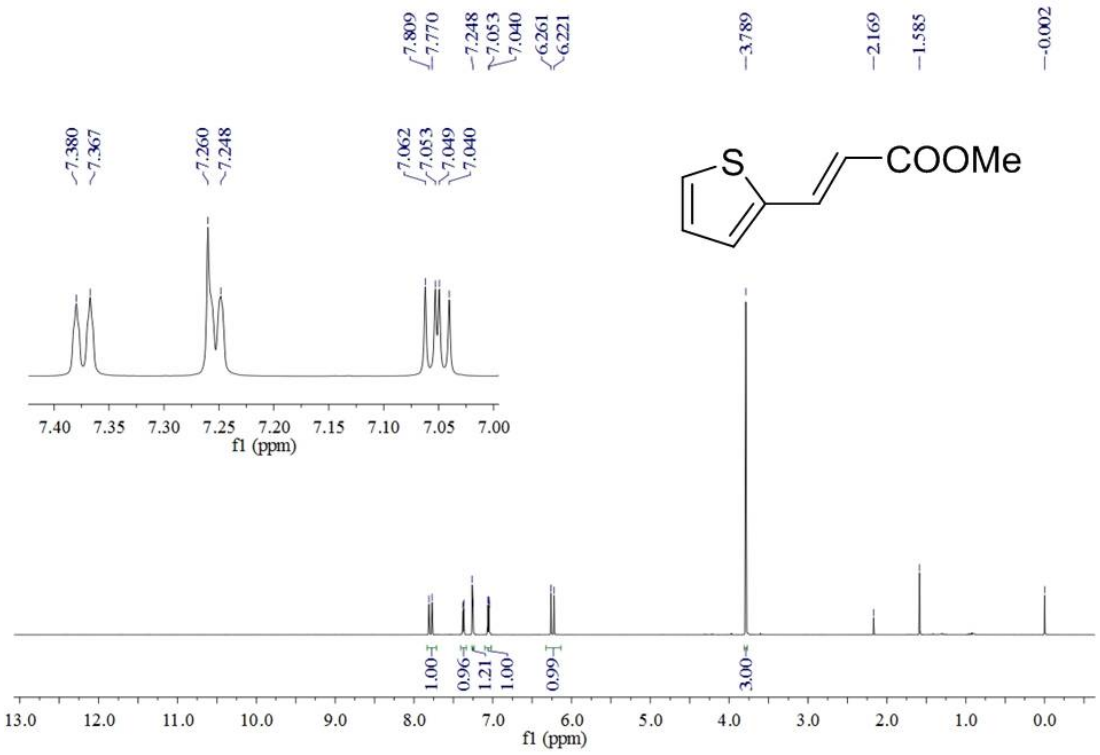
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.367
7.260
7.248
7.062
7.053
7.049
7.040
S
COOMe
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
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0.96
1.21
1.00
0.99
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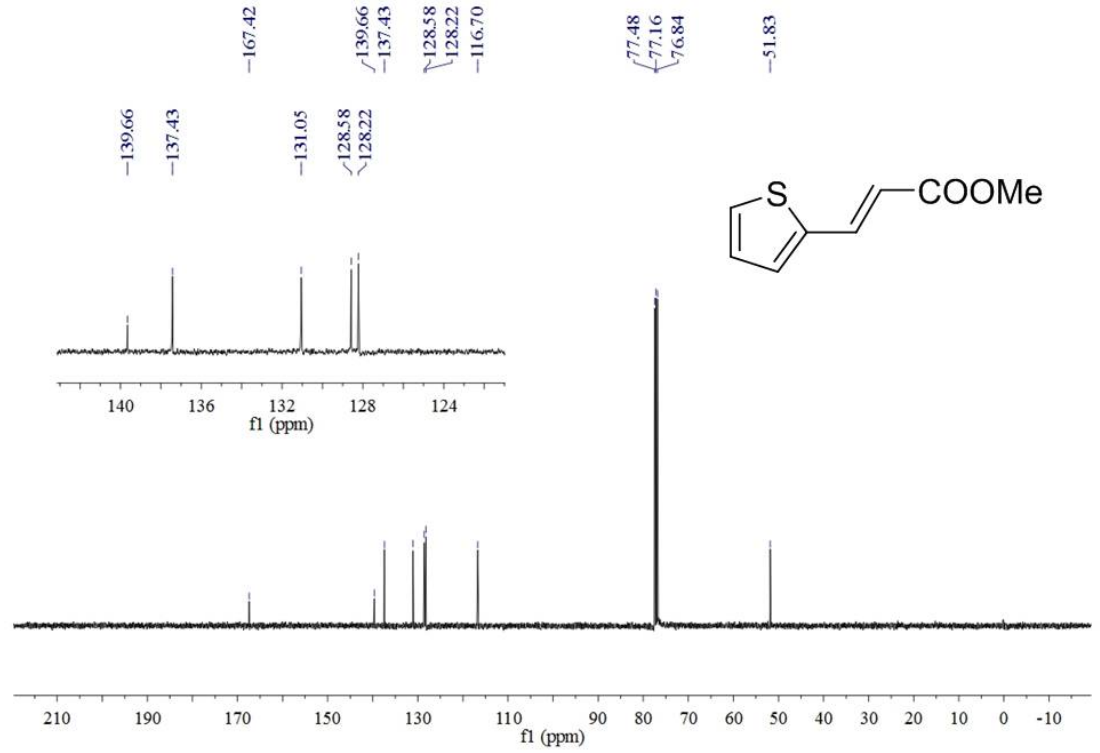
f1 (ppm)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77.16
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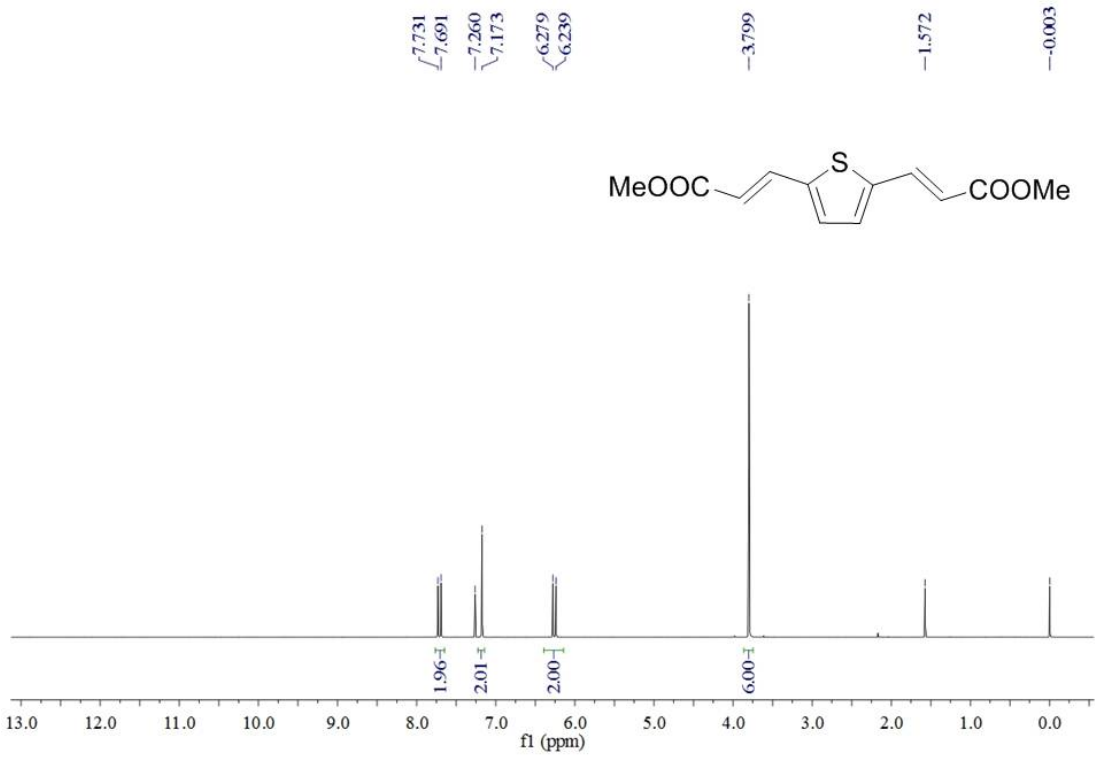
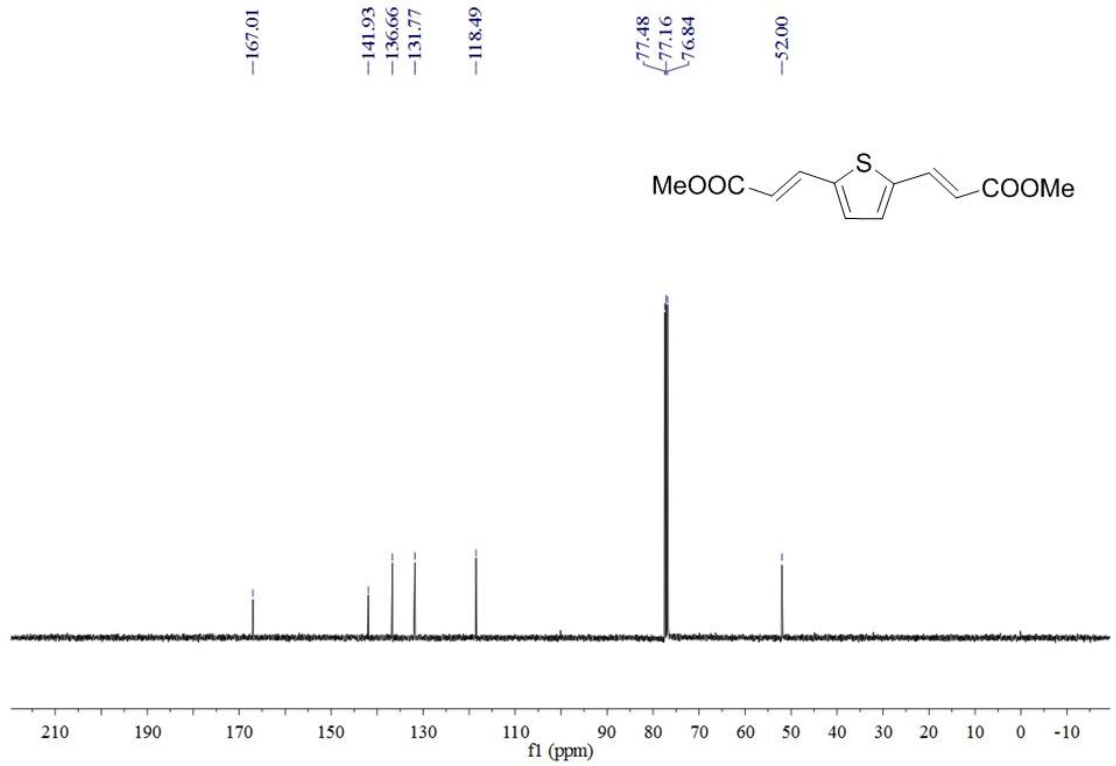
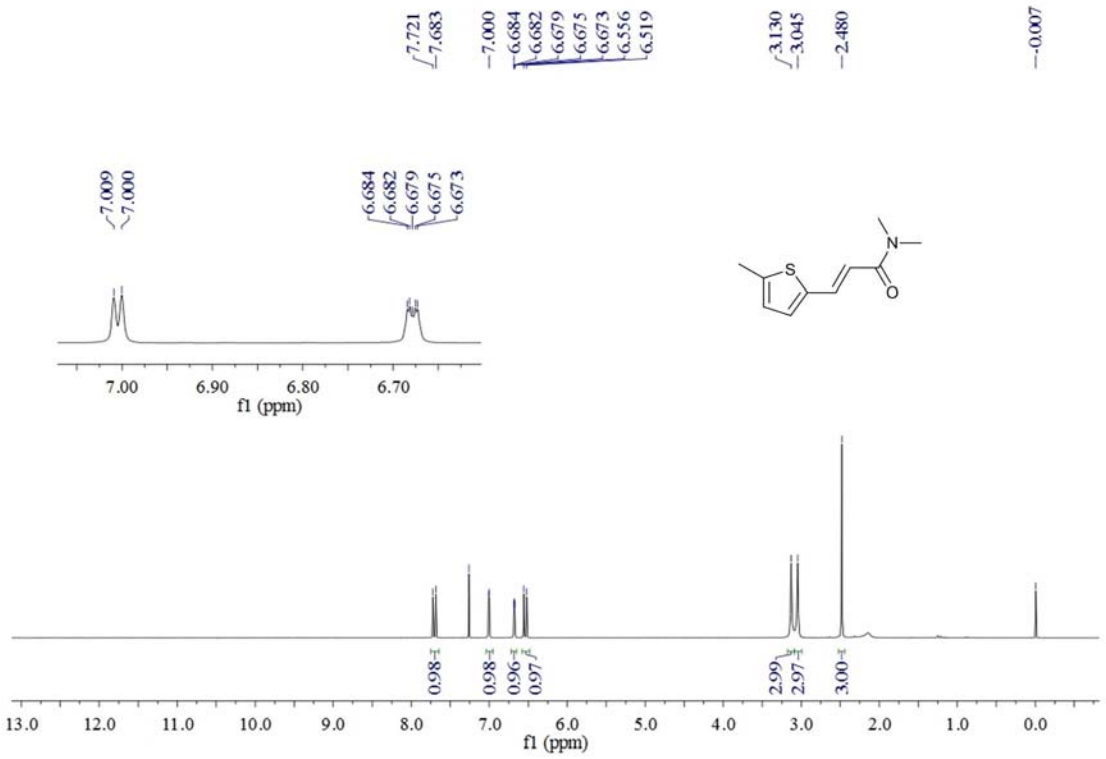
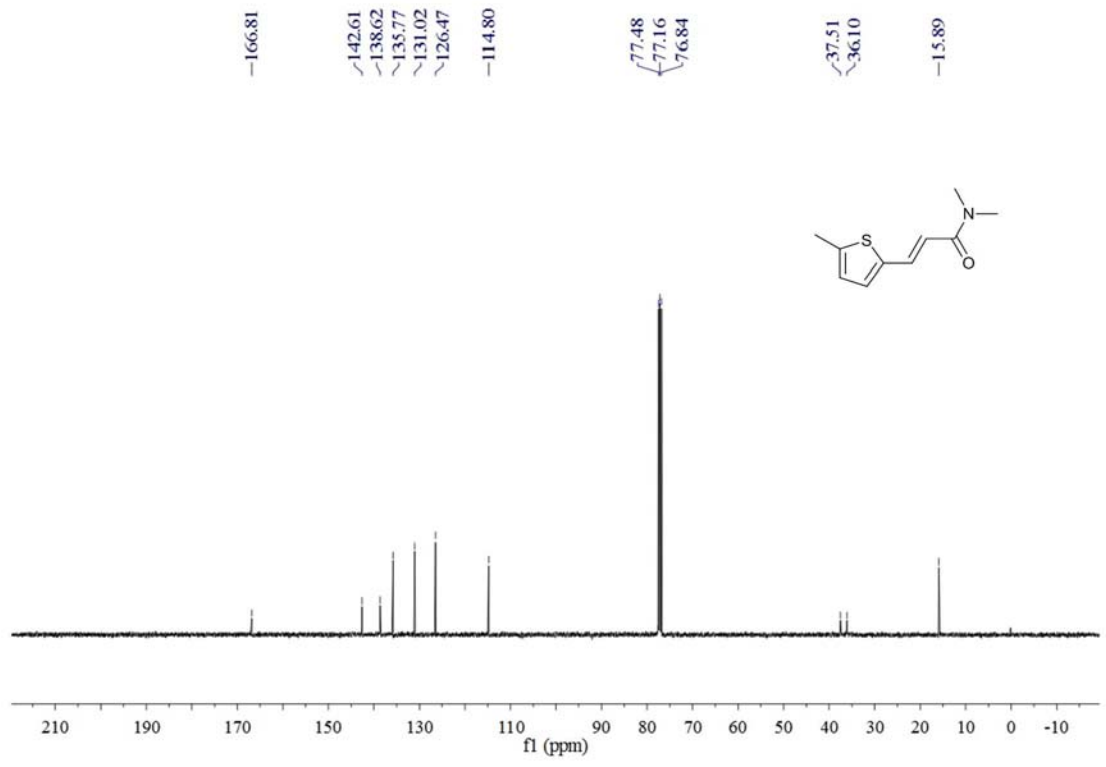
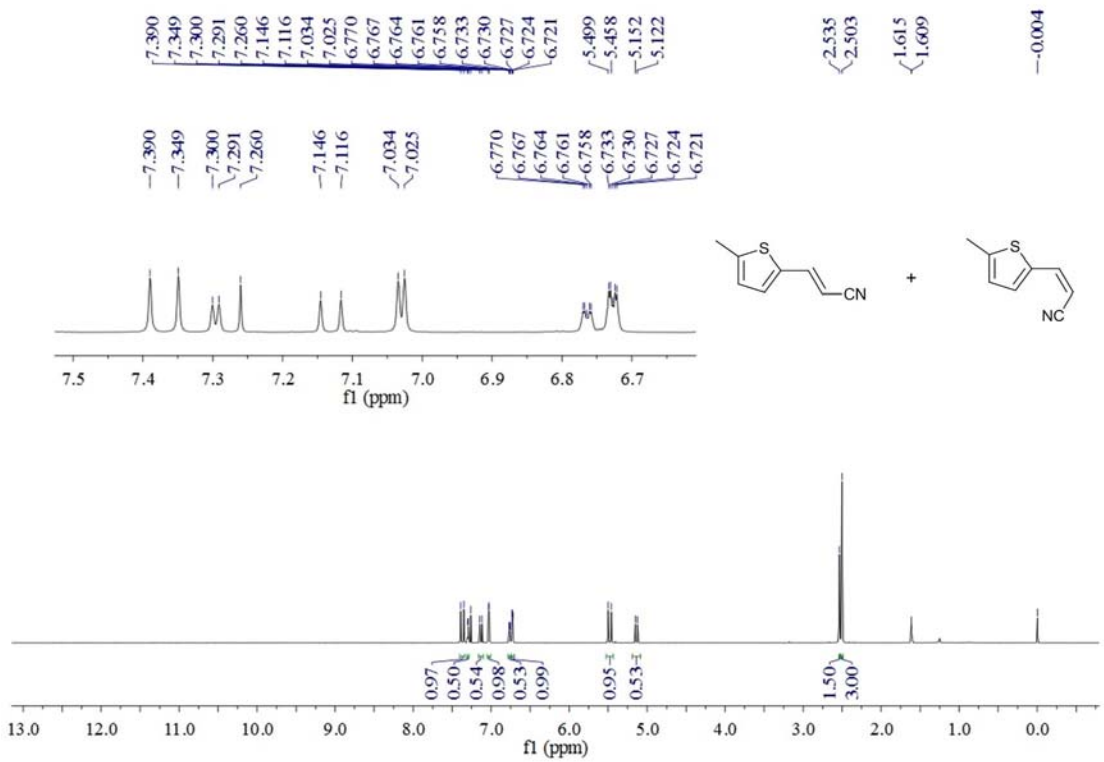
51.83
139.66
137.43
131.05
128.58
128.22
S
COOMe
140 136 132 128 124
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

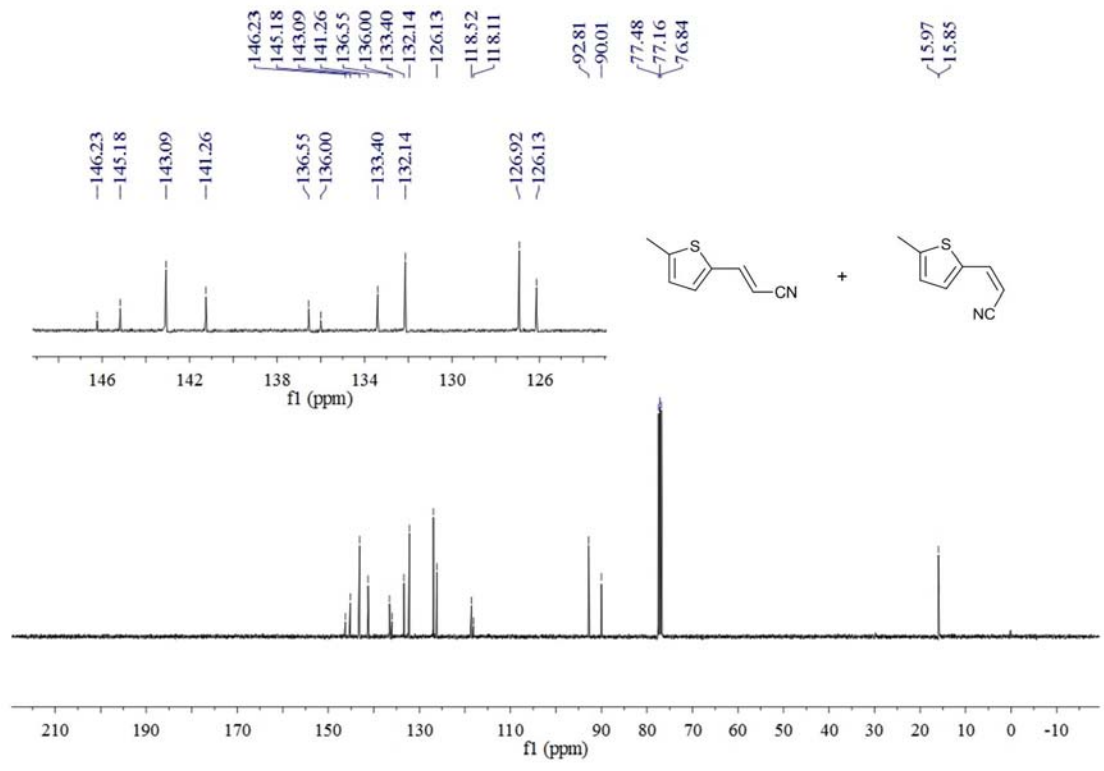

7.731
7.691
7.260
7.173
6.279
6.239
3.799
1.572
0.003
MeOOC
S
COOMe
1.96
2.01
2.00
6.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

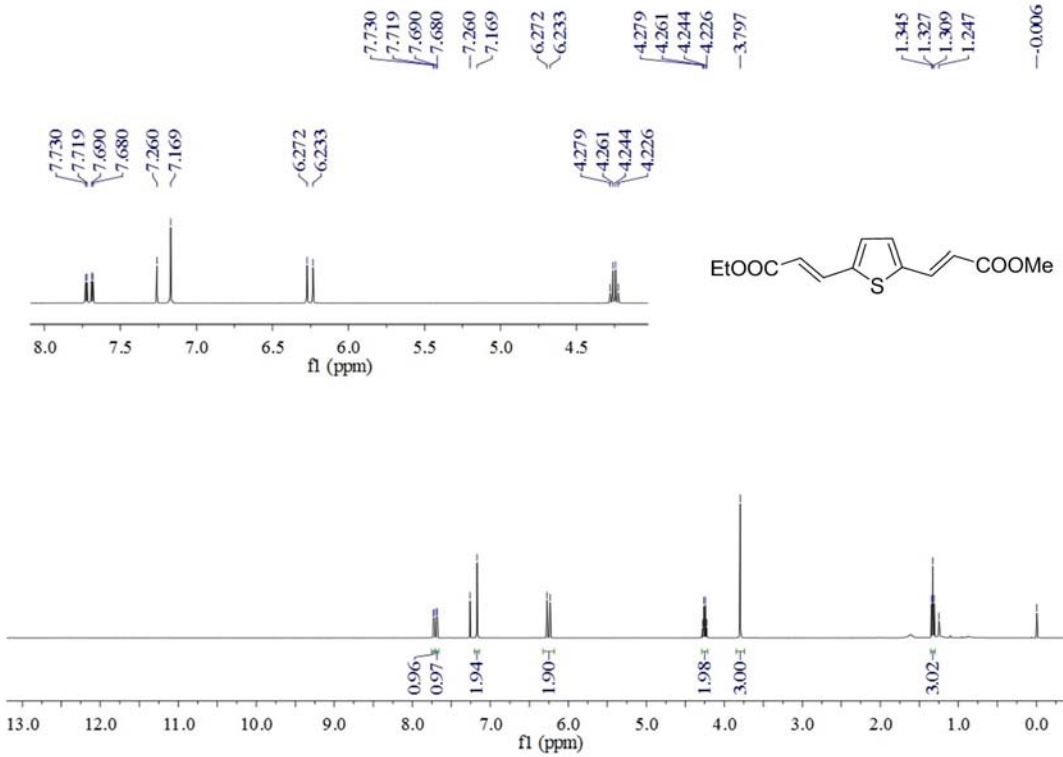

167.01
141.93
136.66
131.77
118.49
77.48
77.16
76.84
52.00
MeOOC
S
COOMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

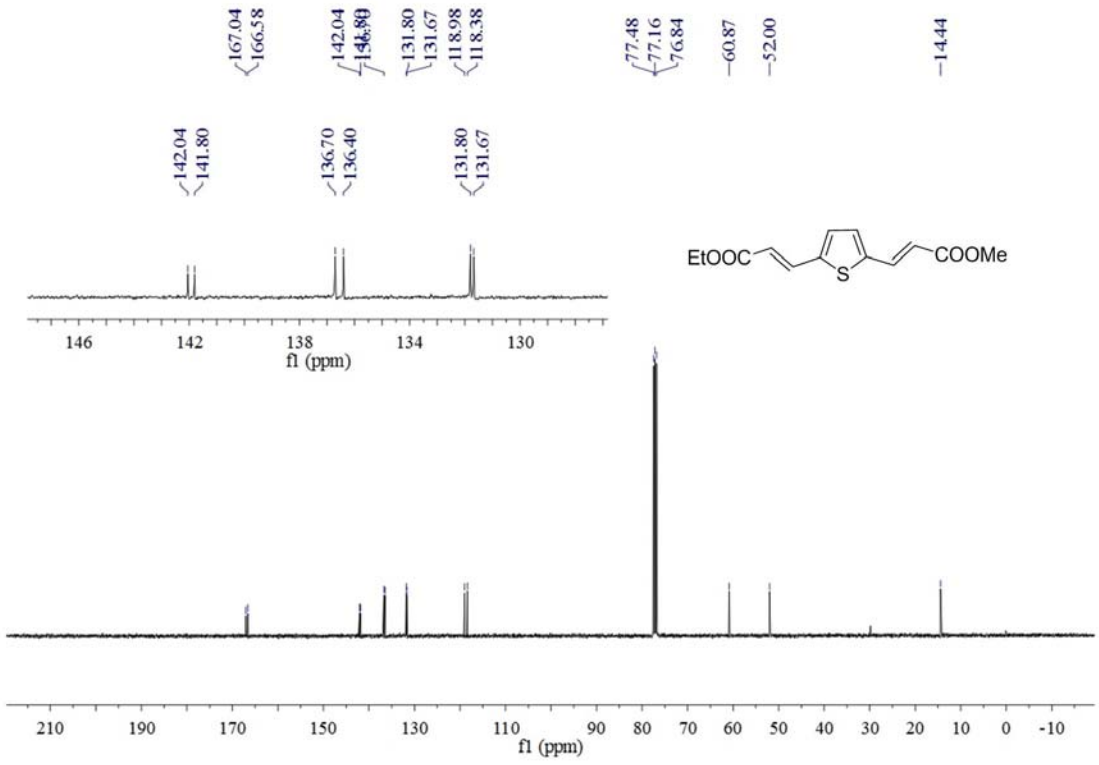

7.721
7.683
7.000
6.684
6.682
6.679
6.675
6.673
6.556
6.519
3.130
3.045
2.480
0.007
7.009
7.000
6.684
6.682
6.679
6.675
6.673
7.00
6.90
6.80
6.70
f1 (ppm)
N
S
O
0.98
0.98
0.96
0.97
2.99
2.97
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

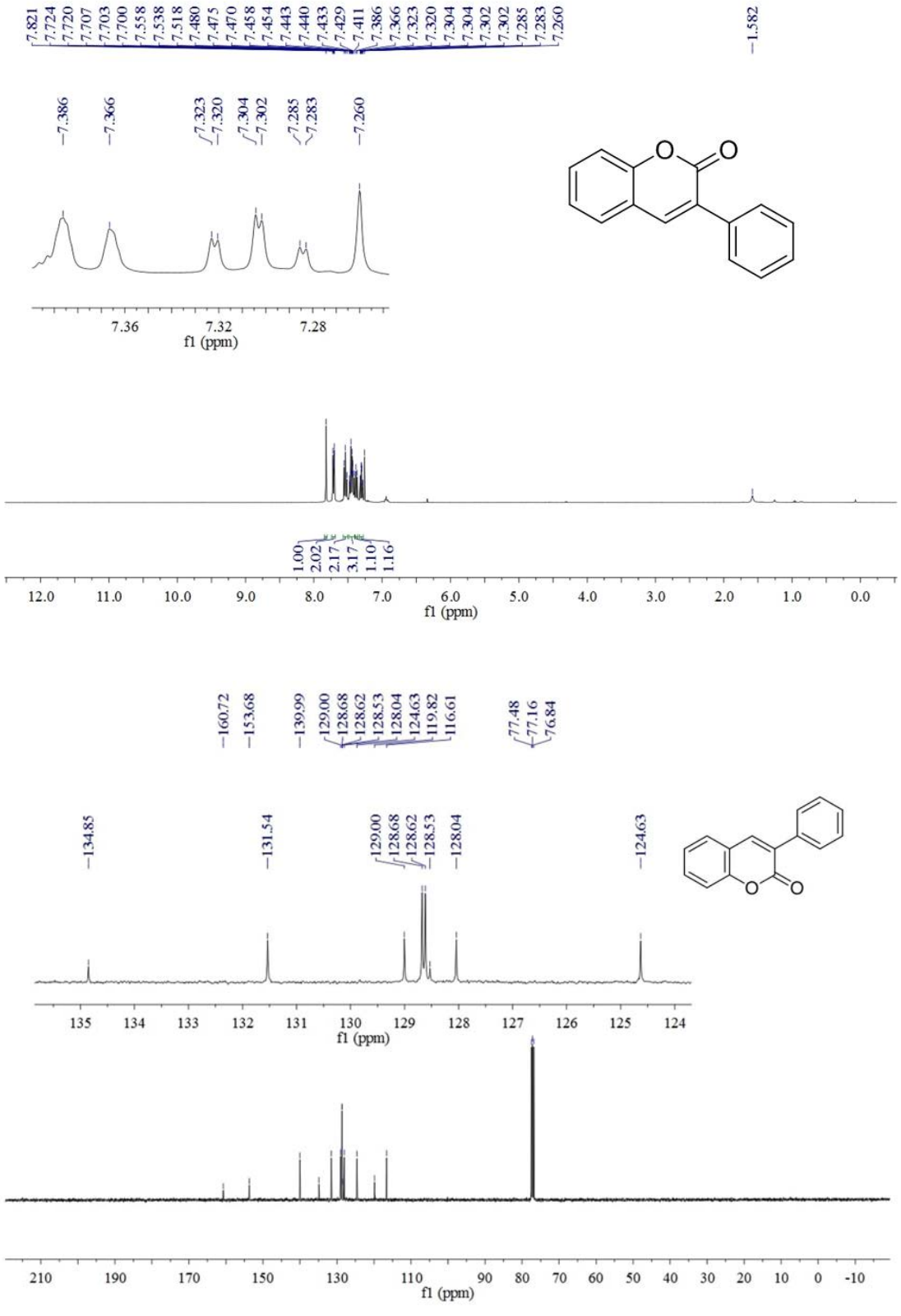

166.81
142.61
138.62
135.77
131.02
126.47
114.80
77.48
77.16
76.84
37.51
36.10
15.89
N
S
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

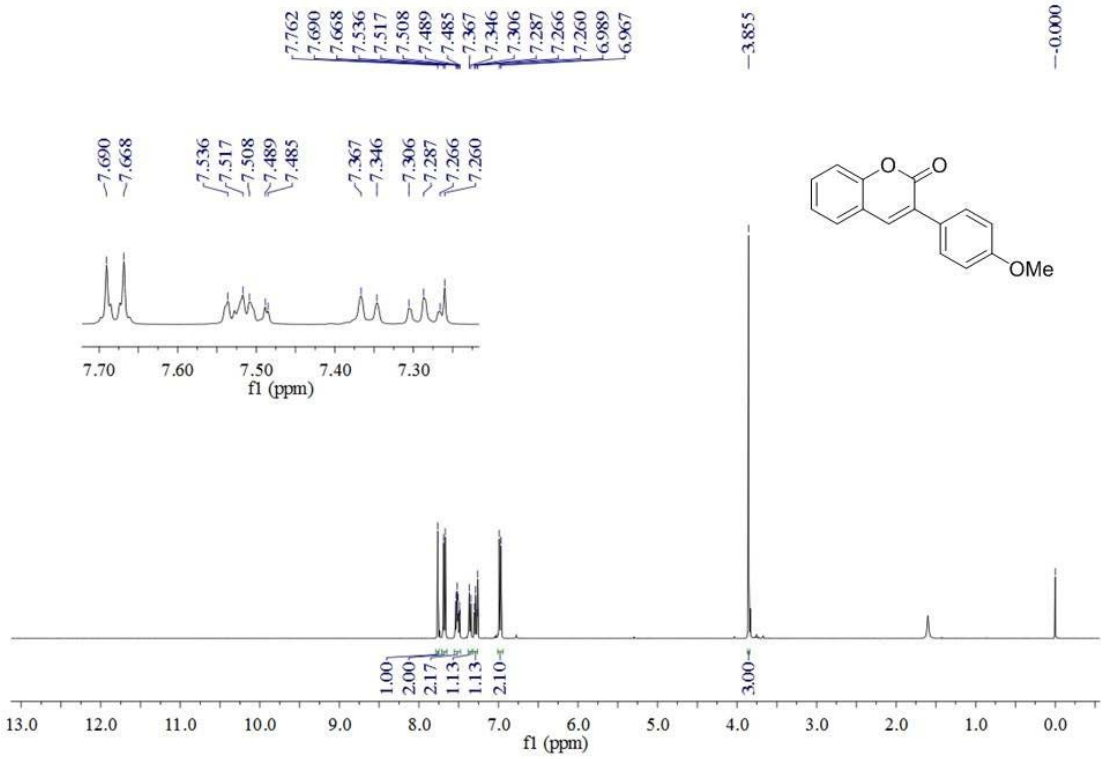

7.390
7.349
7.300
7.291
7.260
7.146
7.116
7.034
7.025
6.770
6.767
6.764
6.761
6.758
6.733
6.730
6.727
6.724
6.721
5.499
5.458
5.152
5.122
2.535
2.503
1.615
1.609
-0.004
f1 (ppm)
CN
NC
0.97
0.50
0.54
0.98
0.53
0.99
0.95
0.53
1.50
3.00

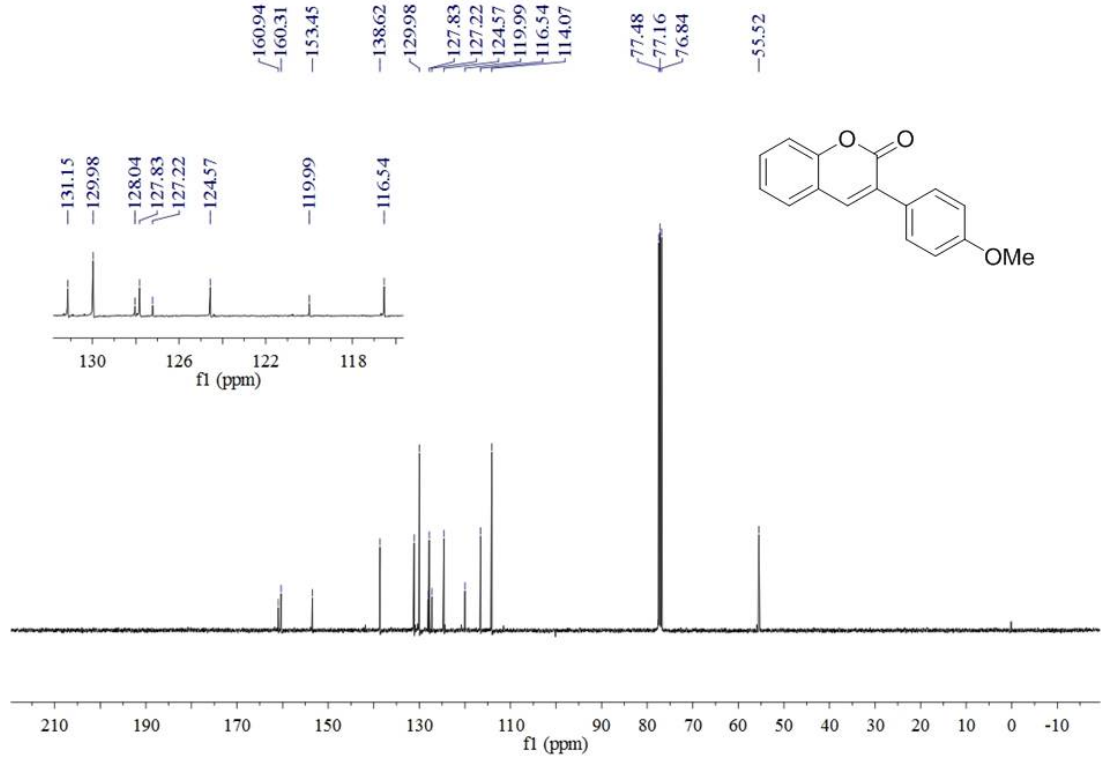

146.23
145.18
143.09
141.26
136.55
136.00
133.40
132.14
126.13
118.52
118.11
92.81
90.01
77.48
77.16
76.84
15.97
15.85
126.92
f1 (ppm)
CN
NC

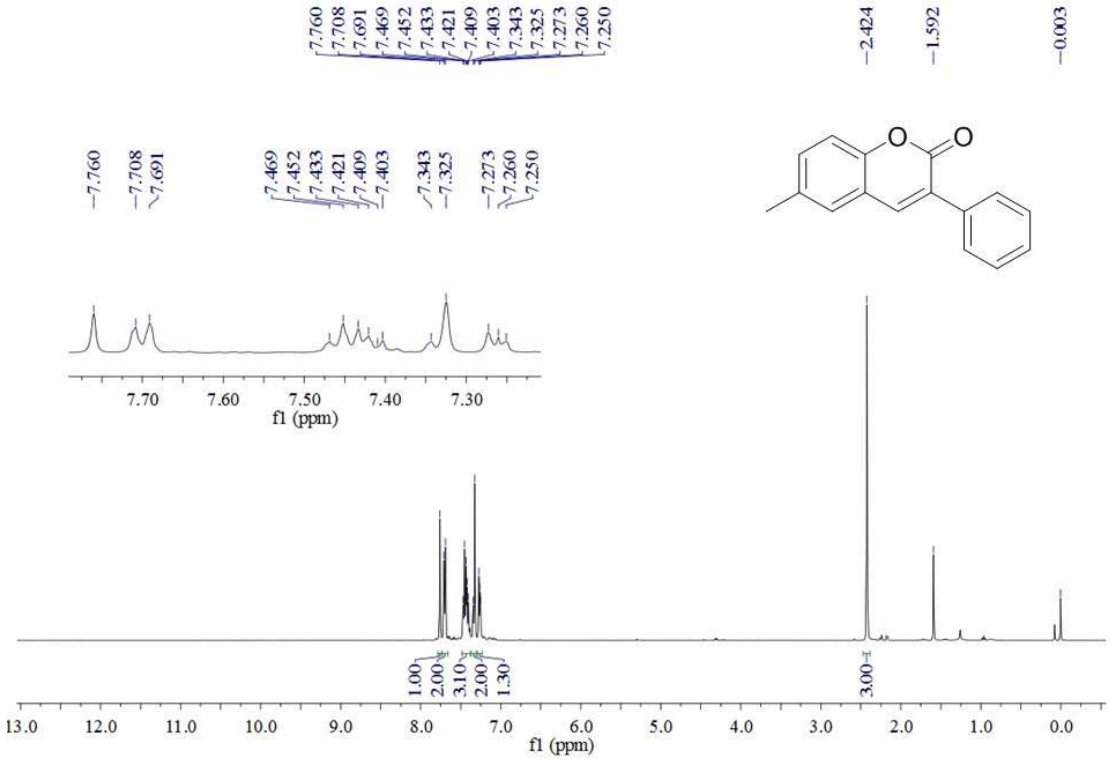

7.730
7.719
7.690
7.680
7.260
7.169
6.272
6.233
4.279
4.261
4.244
4.226
3.797
1.345
1.327
1.309
1.247
0.006
EtOOC
COOMe
S
f1 (ppm)
0.96
0.97
1.94
1.90
1.98
3.00
3.02

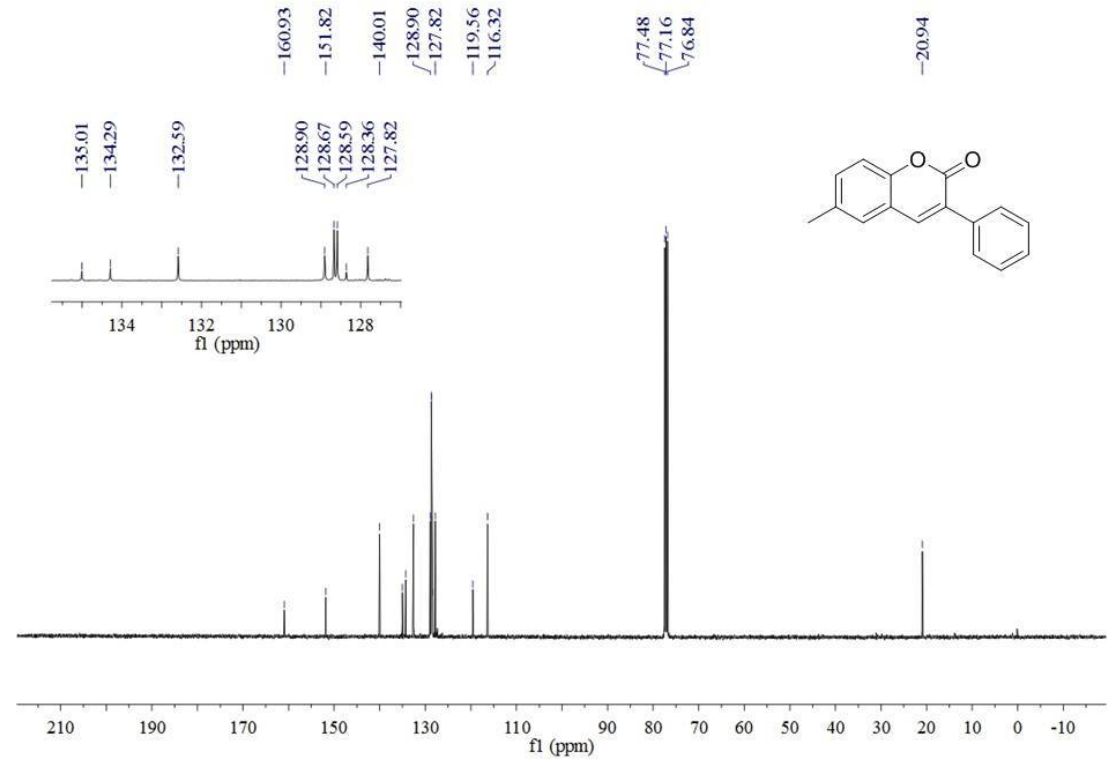

167.04
166.58
142.04
141.80
136.70
136.40
131.80
131.67
118.98
118.38
77.48
77.16
76.84
60.87
52.00
14.44
EtOOC
COOMe
S
f1 (ppm)

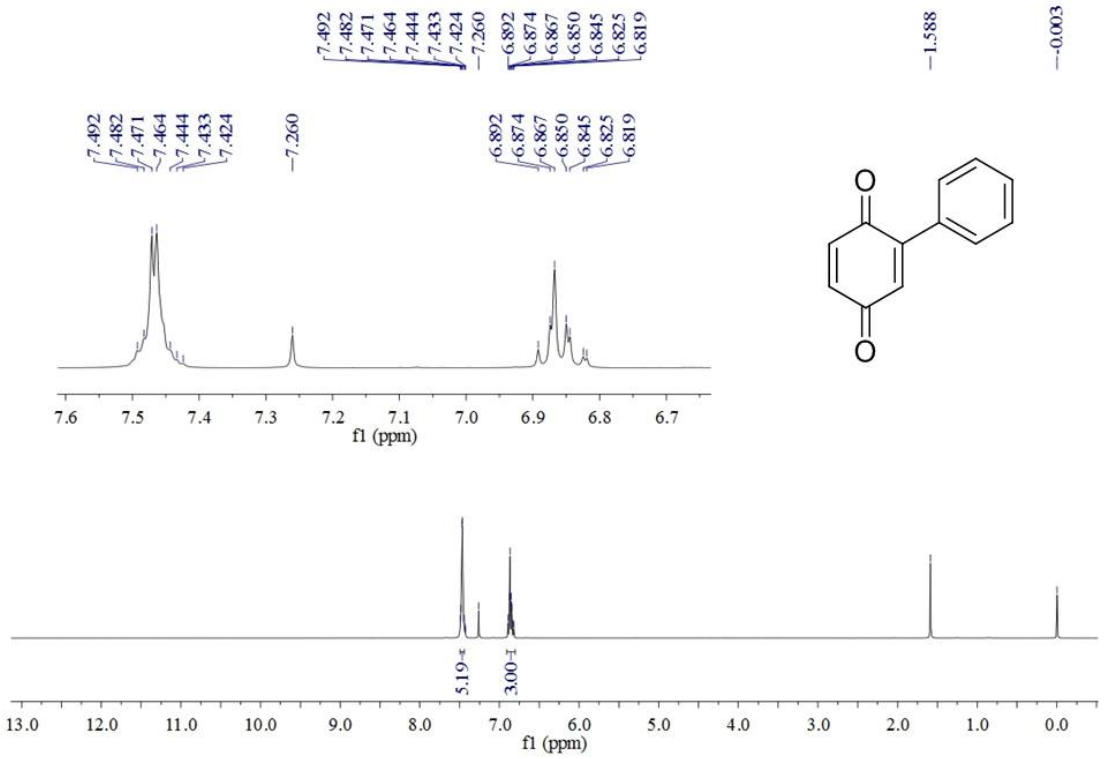

7.821
7.724
7.720
7.707
7.703
7.700
7.558
7.538
7.518
7.480
7.475
7.470
7.458
7.454
7.443
7.440
7.433
7.429
7.411
7.386
7.366
7.323
7.320
7.304
7.302
7.285
7.283
7.260
1.582
7.36
7.32
7.28
f1 (ppm)
1.00
2.02
2.17
3.17
1.10
1.16
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
160.72
153.68
139.99
129.00
128.68
128.62
128.53
128.04
124.63
119.82
116.61
77.48
77.16
76.84
134.85
131.54
129.00
128.68
128.62
128.53
128.04
124.63
135
134
133
132
131
130
129
128
127
126
125
124
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

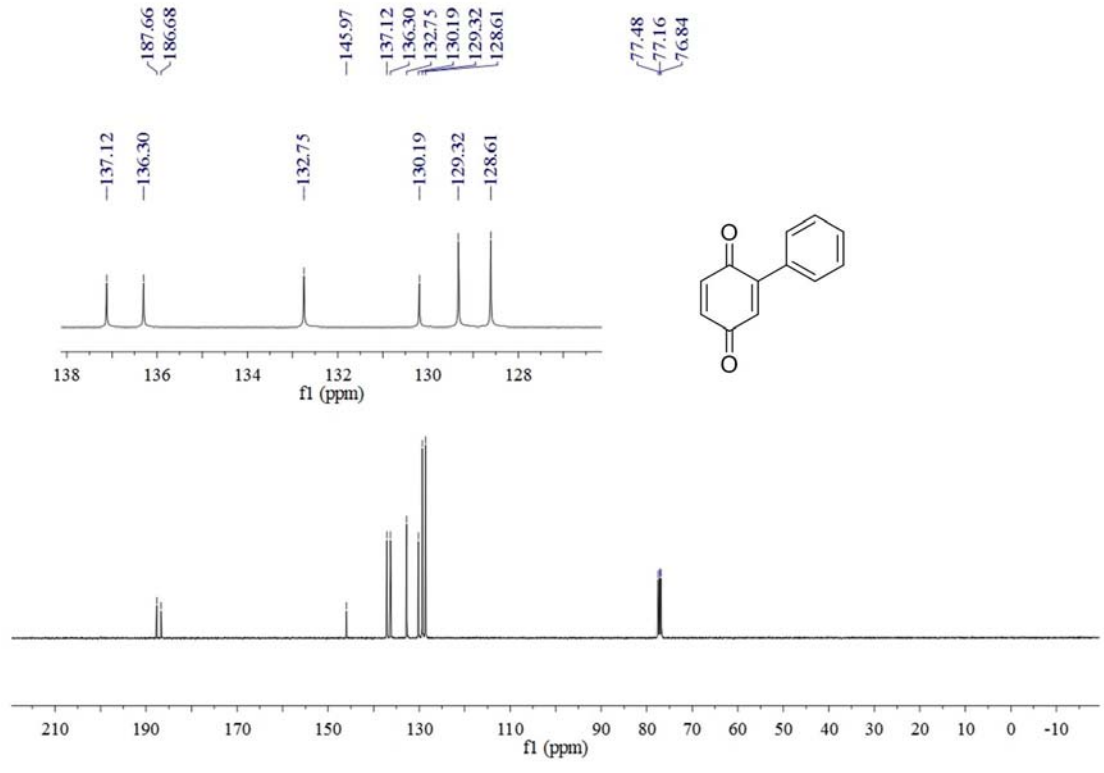

7.762
7.690
7.668
7.536
7.517
7.508
7.489
7.485
7.367
7.346
7.306
7.287
7.266
7.260
6.989
6.967
3.855
-0.000
O
O
OMe
1.00
2.00
2.17
1.13
1.13
2.10
3.00
f1 (ppm)

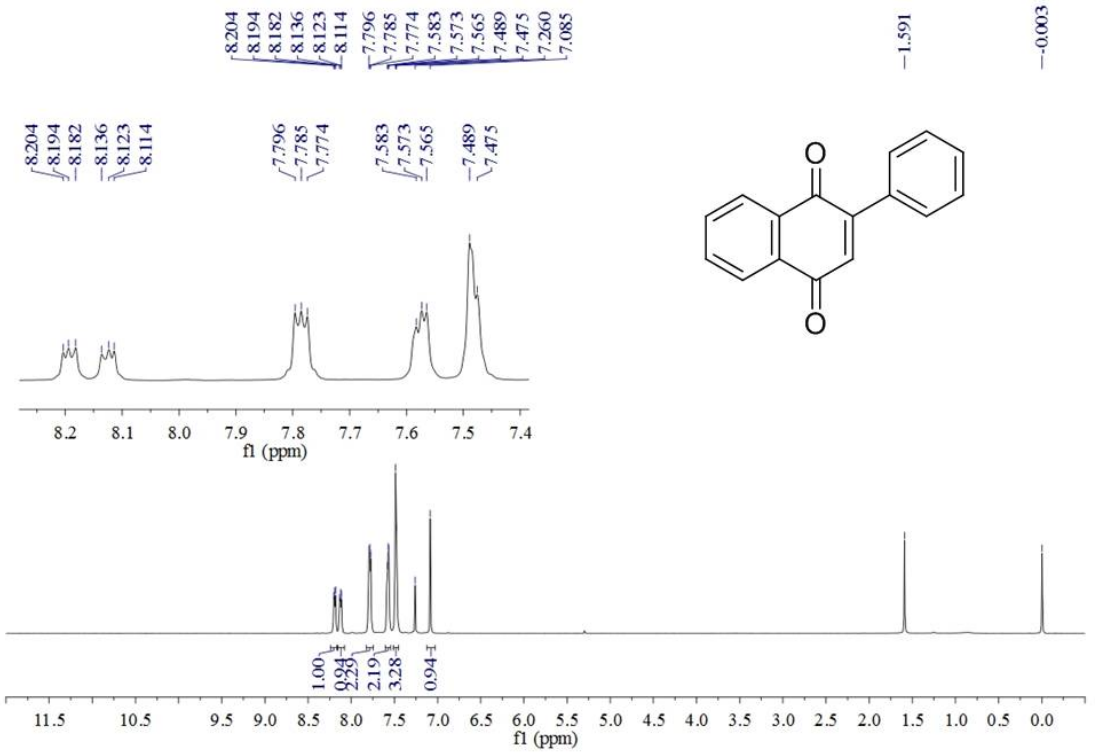

160.94
160.31
153.45
138.62
129.98
127.83
127.22
124.57
119.99
116.54
114.07
77.48
77.16
76.84
55.52
O
O
OMe
f1 (ppm)

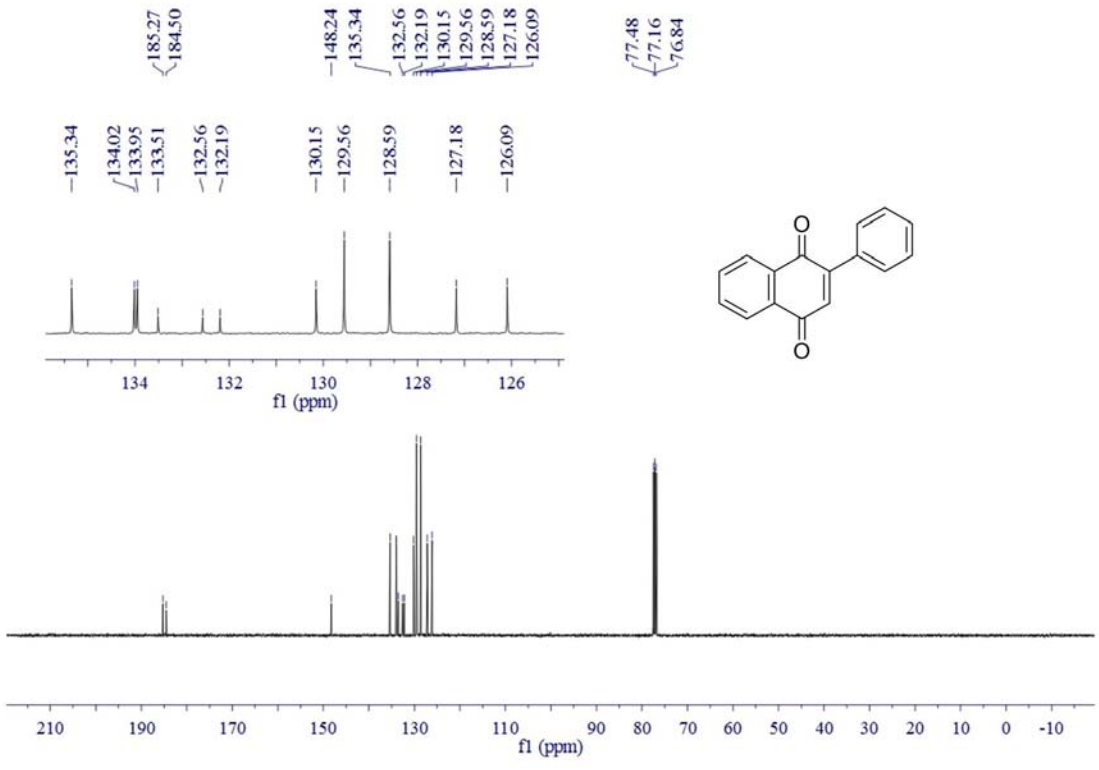

7.760
7.708
7.691
7.469
7.452
7.433
7.421
7.409
7.403
7.343
7.325
7.273
7.260
7.250
2.424
1.592
0.003
O
O
7.70
7.60
7.50
7.40
7.30
f1 (ppm)
1.00
2.00
3.10
2.00
1.30
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

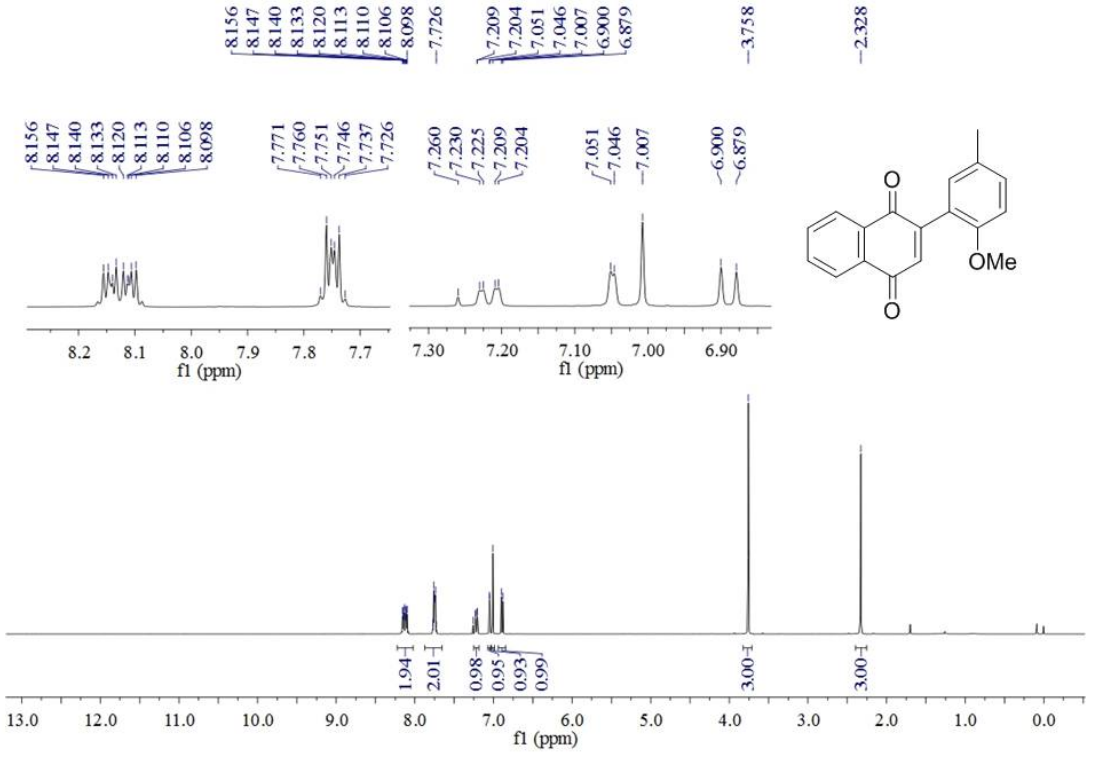

160.93
151.82
140.01
128.90
127.82
119.56
116.32
77.48
77.16
76.84
20.94
135.01
134.29
132.59
128.90
128.67
128.59
128.36
127.82
O
O
134
132
130
128
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

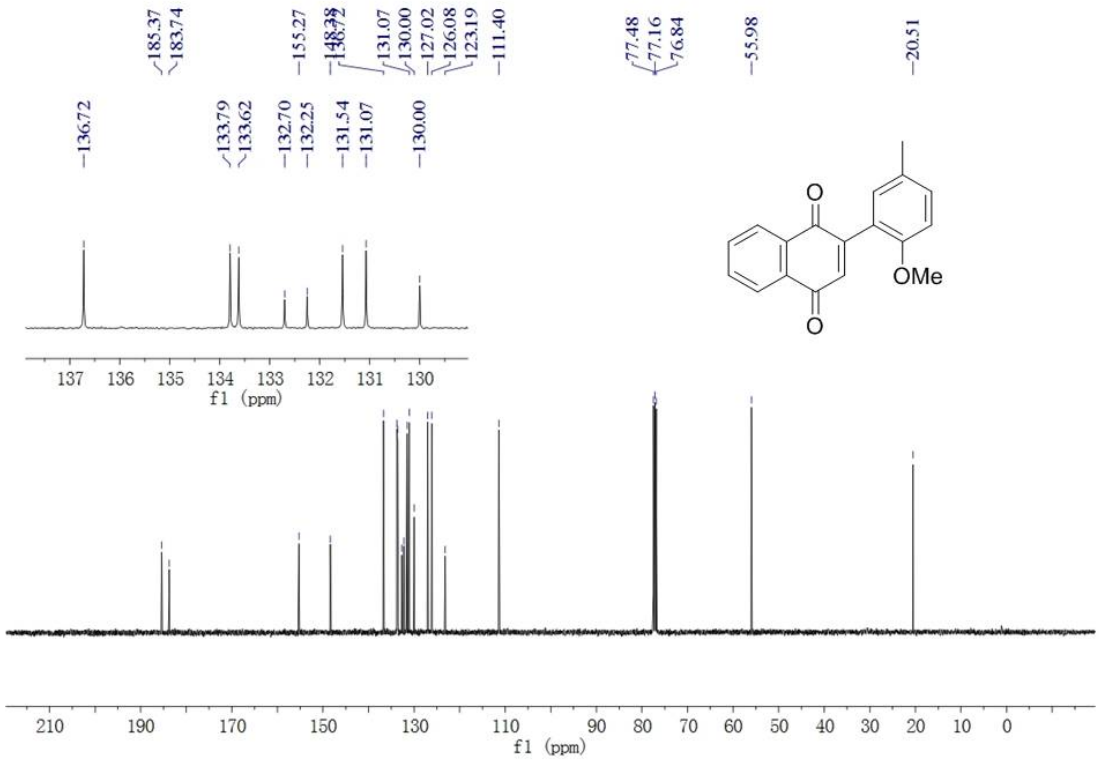

7.492
7.482
7.471
7.464
7.444
7.433
7.424
7.260
6.892
6.874
6.867
6.850
6.845
6.825
6.819
1.588
0.003
f1 (ppm)
5.19
3.00
f1 (ppm)

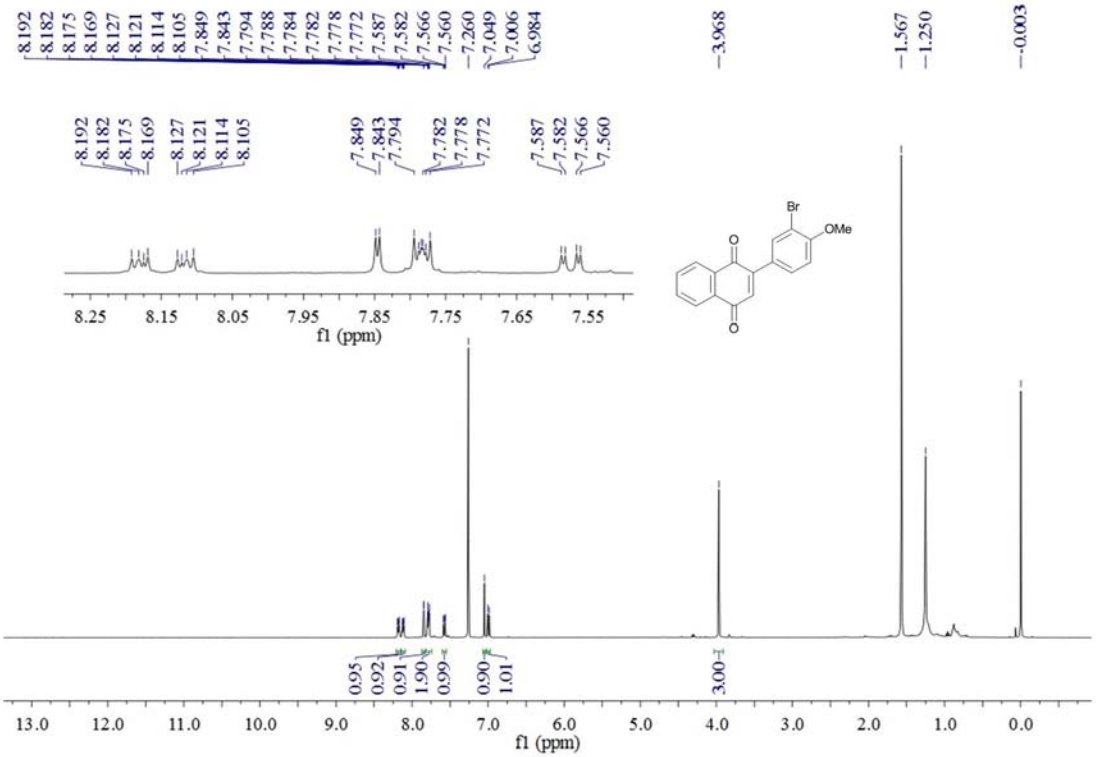

187.66
186.68
145.97
137.12
136.30
132.75
130.19
129.32
128.61
77.48
77.16
76.84
f1 (ppm)
f1 (ppm)

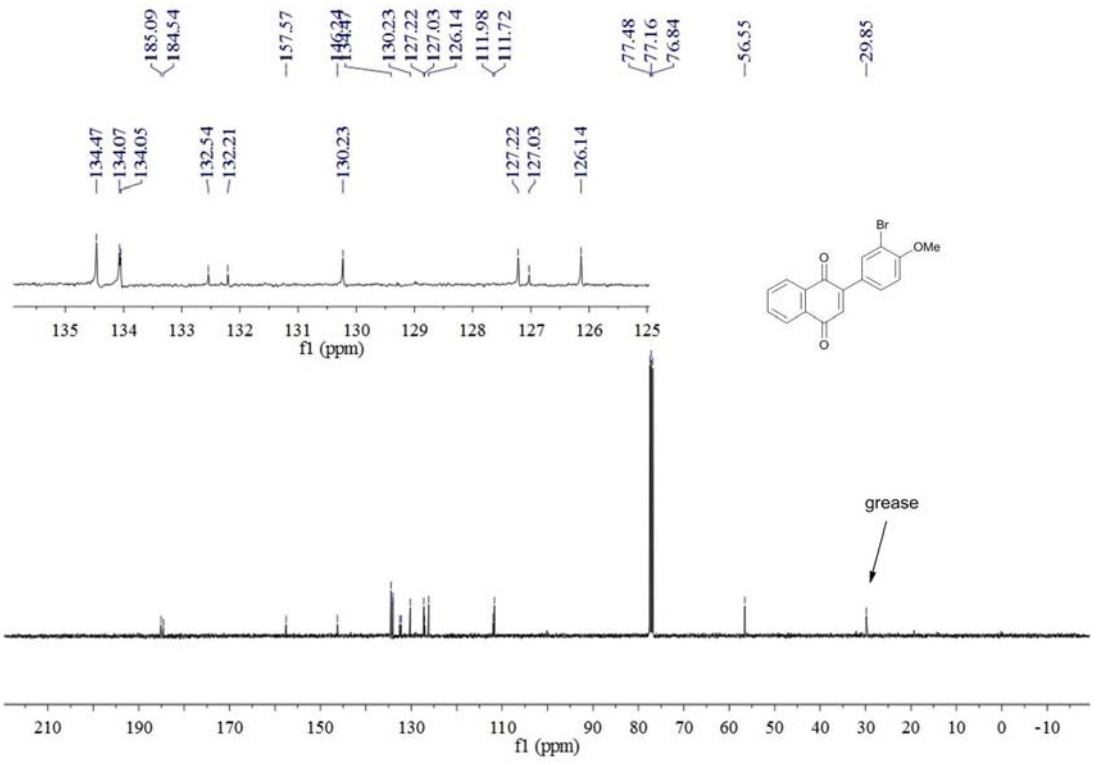

8.204
8.194
8.182
8.136
8.123
8.114
7.796
7.785
7.774
7.583
7.573
7.565
7.489
7.475
7.260
7.085
1.591
0.003
O
O
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)
1.00
0.94
2.19
3.28
0.94
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

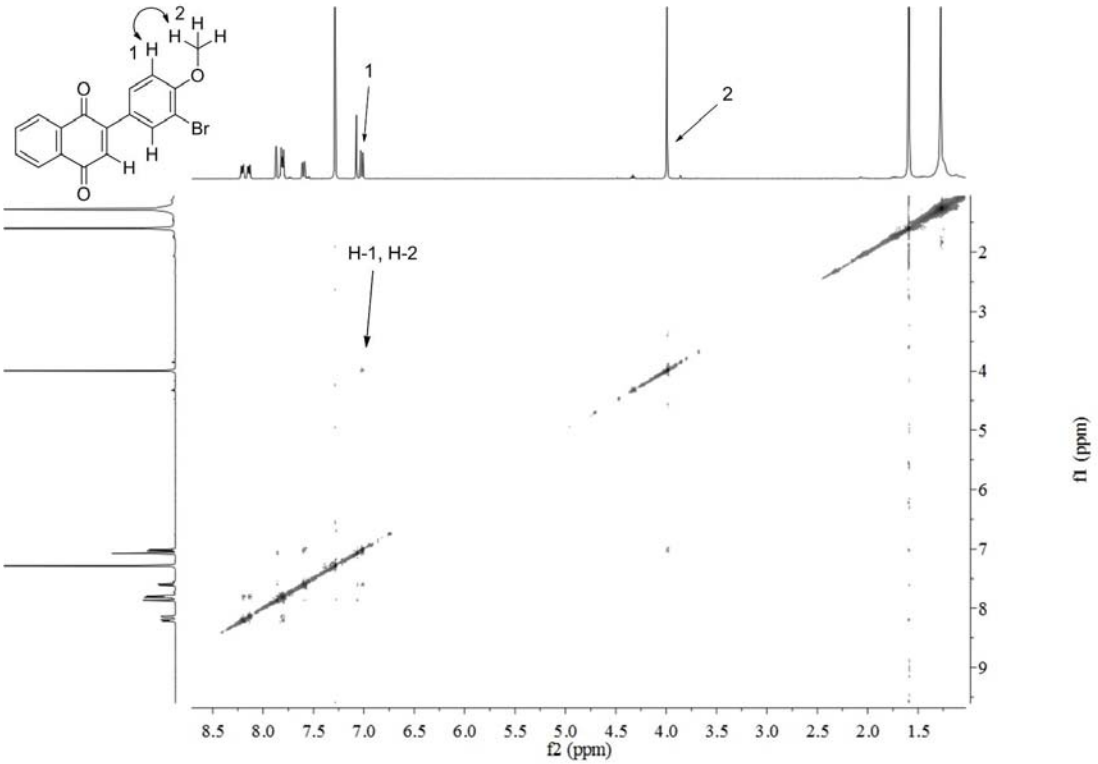

185.27
184.50
148.24
135.34
132.56
132.19
130.15
129.56
128.59
127.18
126.09
77.48
77.16
76.84
135.34
134.02
133.95
133.51
132.56
132.19
130.15
129.56
128.59
127.18
126.09
O
O
134
132
130
128
126
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

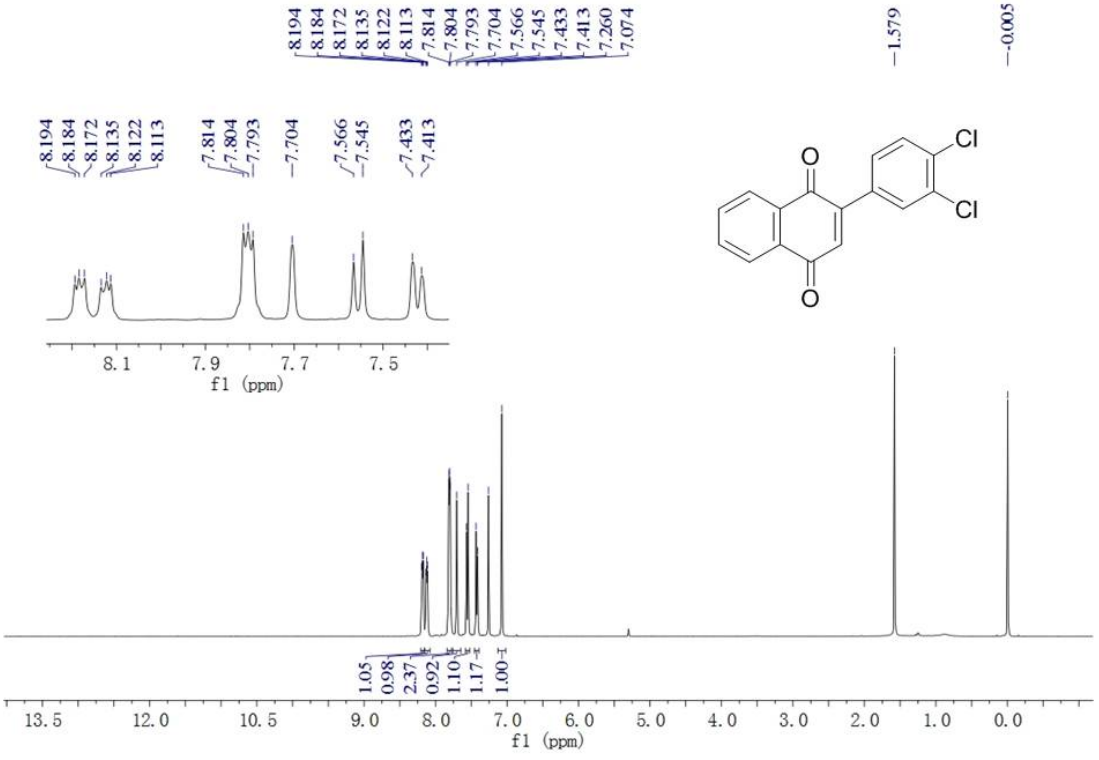

8.156
8.147
8.140
8.133
8.120
8.113
8.110
8.106
8.098
7.726
7.209
7.204
7.051
7.046
7.007
6.900
6.879
3.758
2.328
f1 (ppm)
1.94
2.01
0.98
0.95
0.93
0.99
3.00
3.00
OMe
O

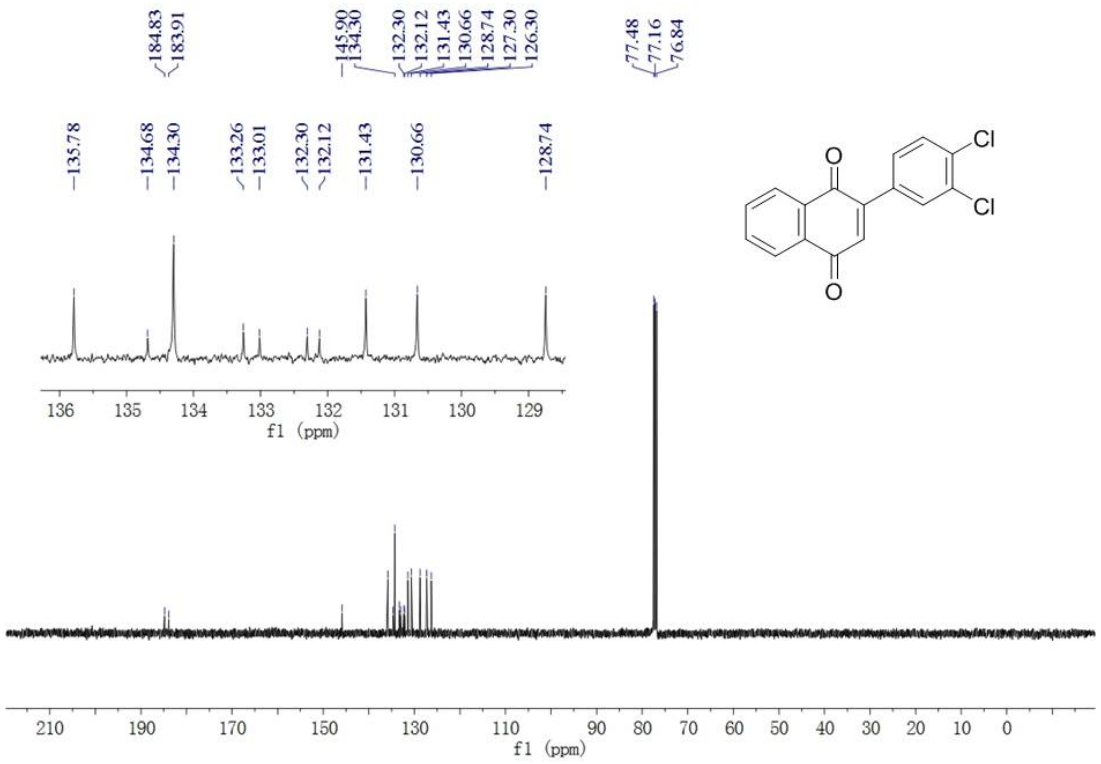

185.37
183.74
155.27
131.07
130.00
127.02
126.08
123.19
111.40
77.48
77.16
76.84
55.98
20.51
136.72
133.79
133.62
132.70
132.25
131.54
131.07
130.00
f1 (ppm)
OMe
O


8.192
8.182
8.175
8.169
8.127
8.121
8.114
8.105
7.849
7.843
7.794
7.788
7.784
7.782
7.778
7.772
7.587
7.582
7.566
7.560
7.260
7.049
7.006
6.984
3.968
1.567
1.250
0.003
Br
OMe
O
O
f1 (ppm)
0.95
0.92
0.91
1.90
0.99
0.90
1.01
3.00


185.09
184.54
157.57
146.24
134.47
130.23
127.22
127.03
126.14
111.98
111.72
77.48
77.16
76.84
56.55
29.85
134.47
134.07
134.05
132.54
132.21
130.23
127.22
127.03
126.14
Br
OMe
O
O
f1 (ppm)
grease


H-1, H-2
f2 (ppm)
f1 (ppm)


8.194
8.184
8.172
8.135
8.122
8.113
7.814
7.804
7.793
7.704
7.566
7.545
7.433
7.413
7.260
7.074
1.579
0.005
Cl
Cl
O
O
f1 (ppm)
1.05
0.98
2.37
0.92
1.10
1.17
1.00


184.83
183.91
145.90
134.30
132.30
132.12
131.43
130.66
128.74
127.30
126.30
77.48
77.16
76.84
135.78
134.68
134.30
133.26
133.01
132.30
132.12
131.43
130.66
128.74
O
O
Cl
Cl
136
135
134
133
132
131
130
129
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)