Supporting Information

2-Pyridylmethyl ether: a readily removable and efficient directing group for amino acid ligand accelerated *ortho*-C–H olefination of phenols

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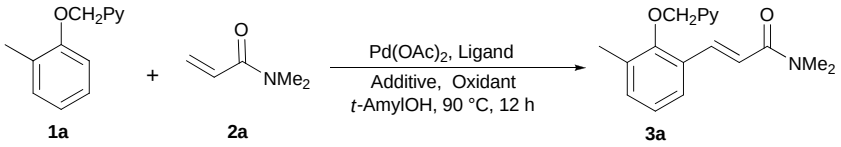
I. General remarks

The ^{1}H NMR (400 MHz or 600 MHz) chemical shifts were measured relative to TMS, $CDCl_3$ or DMSO-d_6 as the internal reference. The ^{13}C NMR (100 MHz) chemical shifts are given using $CDCl_3$ or DMSO-d_6 as the internal standard. High resolution mass spectra (HR-MS) were recorded by ESI-TOF. Melting points were determined with XRC-1 and are uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. L-Val-OH, L-Leu-OH and L-Ile-OH were used to synthesize the *N*-protected amino acid ligands according to known procedures.[1,2,3] Solvents were dried by refluxing for at least 24 h over CaH_2 (DMF, DCE, DCM) and freshly distilled prior to use. *t*-AmylOH was obtained from commercial suppliers and used directly without further purification. Py = 2-pyridyl, ^{4}Py = 4-pyridyl.

II. Optimization of the reaction condition



1a + **2a** → **3a**

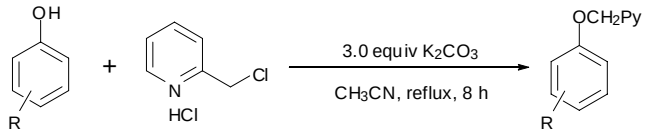
Table 1 Optimization of the reaction conditions.[a]

Entry	Ligand	Oxidant	Additive	Yield (%)[b]
1[c]	Boc-Val-OH	O_2	$KHCO_3$	17
2	Boc-Val-OH	O_2	$KHCO_3$	90
3	Ac-Val-OH	O_2	$KHCO_3$	77
4	Ac-Leu-OH	O_2	$KHCO_3$	82
5	Ac-Ile-OH	O_2	$KHCO_3$	80
6	-	O_2	$KHCO_3$	9
7	Boc-Val-OH	Air	$KHCO_3$	63

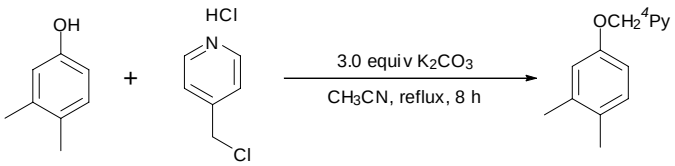
8[d]	Boc-Val-OH	O_2	$KHCO_3$	29
9	Boc-Val-OH	O_2	-	-
10[e]	-	AgOAc	$KHCO_3$	67
11[e]	-	AgOAc	Li_2CO_3	71
12[e]	-	AgOAc	-	50
13[e]	-	$Cu(OAc)_2$	-	-
14[e]	-	$PhI(OAc)_2$	-	Trace
15[e]	-	$K_2S_2O_8$	-	Trace

[a] Reactions were carried out using **1a** (0.5 mmol) and **2a** (0.75 mmol), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%) and additive (2.0 equiv) in *t*-AmylOH (2 mL) for 12 hours under 1 atm O_2. [b] Yield of isolated product. [c] 10 mol% BQ used. [d] At 60 °C. [e] Reaction was carried out using **1a** (0.5 mmol) and **2a** (0.75 mmol), $Pd(OAc)_2$ (10 mol%), additive (2.0 equiv) and oxidant (1.0 mmol) in DCE (2 mL) at 110 °C for 24 hours under N_2. DCE = 1,2-dichloroethane, *t*-AmylOH = tert-amyl alcohol, Py = 2-pyridyl.

III. Preparation of starting materials and characterization

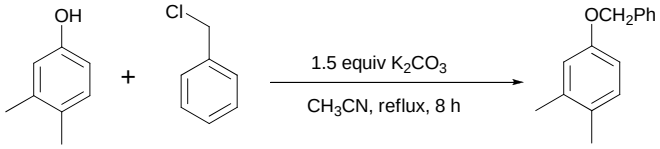


A mixture of phenols (10.0 mmol), 2-(chloromethyl)pyridine hydrochloride (10.0 mmol), and K_2CO_3 (4.14 g, 30.0 mmol) was dissolved in CH_3CN (20 mL) and heated to reflux under nitrogen for 8 hours. After being cooled to room temperature, the reaction mixture was filtered and washed with CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

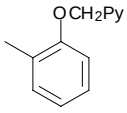


A mixture of 3,4-dimethylphenol (10.0 mmol), 4-(chloromethyl)pyridine hydrochloride (10.0 mmol), and K_2CO_3 (4.14 g, 30.0 mmol) was dissolved in CH_3CN

(20 mL) and heated to reflux under nitrogen for 8 hours. After being cooled to room temperature, the reaction mixture was filtered and washed with CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product 1,2-dimethyl-4-(pyridin-4-ylmethoxy)benzene.

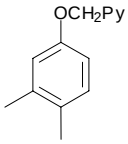


A mixture of 3,4-dimethylphenol (10.0 mmol), Benzyl chloride (10.0 mmol), and K_2CO_3 (2.07 g, 15.0 mmol) was dissolved in CH_3CN (20 mL) and heated to reflux under nitrogen for 8 hours. After being cooled to room temperature, the reaction mixture was filtered and washed with CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide the desired product.



2-(Pyridin-2-ylmethoxy)toluene

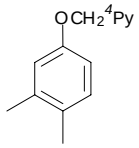
The title compound was obtained as colorless oil (1.8 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.34 (s, 3H), 5.22 (s, 2H), 6.85-6.90 (m, 2H), 7.12-7.22 (m, 3H), 7.55 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 8.58 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5, 70.5, 111.5, 120.9, 121.0, 122.6, 126.9, 127.0, 130.9, 136.9, 149.2, 156.5, 157.9 ppm.



1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene

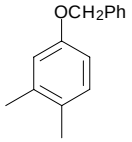
The title compound was obtained as colorless oil (1.9 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.18 (s, 3H), 2.22 (s, 3H), 5.17 (s, 2H), 6.70 (d, J = 8.0 Hz, 1H), 6.81 (s,

1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 6.4 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 8.57 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 20.1, 70.7, 111.8, 116.5, 121.3, 122.6, 129.2, 130.5, 136.9, 137.9, 149.2, 156.6, 157.8 ppm.



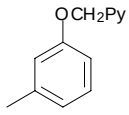
1,2-Dimethyl-4-(pyridin-4-ylmethoxy)benzene

The title compound was obtained as a white solid (1.77 g, 83%). M.p.: 44-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.20 (s, 3H), 2.24 (s, 3H), 5.05 (s, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.78 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 7.34(d, *J* = 5.6 Hz, 2H), 8.59 (d, *J* = 6.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 20.2, 68.3, 111.7, 116.5, 121.6, 129.6, 130.5, 138.1, 146.8, 150.1, 156.5 ppm.



4-(Benzyloxy)-1,2-dimethylbenzene

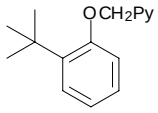
The title compound was obtained as colorless oil (1.8 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.22 (s, 3H), 2.26 (s, 3H), 5.05 (s, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.32-7.46 (m, 5H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 20.2, 70.2, 111.9, 116.6, 127.6, 127.9, 128.7, 129.0, 130.4, 137.5, 137.9, 157.1 ppm.



3-(Pyridin-2-ylmethoxy)toluene

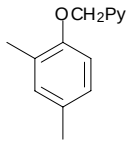
The title compound was obtained as colorless oil (1.75 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.32 (s, 3H), 5.19 (s, 2H), 6.78-6.82 (m, 3H), 7.14-7.22 (m, 2H), 7.51 (d,

J = 7.6 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 8.58 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 70.6, 111.7, 115.8, 121.3, 122.1, 122.6, 129.4, 136.9, 139.7, 149.3, 157.6, 158.5 ppm.



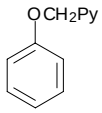
tert-Butyl-2-(pyridin-2-ylmethoxy)benzene

The title compound was obtained as colorless oil (2.2 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.50 (s, 9H), 5.32 (s, 2H), 6.94-6.99 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 6.0 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 8.64 (d, *J* = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.0, 35.0, 71.0, 112.9, 121.0, 121.3, 122.6, 126.9, 127.3, 137.0, 138.4, 149.3, 157.2, 157.9 ppm.



1,3-Dimethyl-4-(pyridin-2-ylmethoxy)benzene

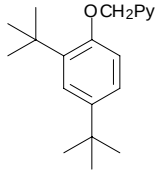
The title compound was obtained as a slight yellow solid (2.0 g, 94%). M.p.: 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.26 (s, 3H), 2.31 (s, 3H), 5.20 (s, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 7.20 (t, *J* = 6.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 8.58 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5, 20.6, 70.8, 111.6, 121.1, 122.6, 126.7, 127.2, 130.2, 131.8, 137.0, 149.1, 154.5, 158.1 ppm.



Pyridin-2-ylmethoxybenzene

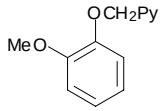
The title compound was obtained as colorless oil (1.7 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.21 (s, 2H), 6.95-7.00 (m, 3H), 7.20 (t, *J* = 6.0 Hz, 1H), 7.27-7.31 (m,

2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 8.59 (d, *J* = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.6, 115.0, 121.3, 121.4, 122.7, 129.7, 137.0, 149.3, 157.5, 158.5 ppm.



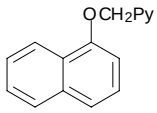
1,3-Di-*tert*-butyl-4-(pyridin-2-ylmethoxy)benzene

The title compound was obtained as a white solid (2.6 g, 88%). M.p.: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.31 (s, 9H), 1.47 (s, 9H), 5.25 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 6.0 Hz, 1H), 7.37 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 8.59 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1, 31.7, 34.4, 35.2, 71.1, 112.2, 121.3, 122.5, 123.6, 124.2, 137.0, 137.5, 143.2, 149.2, 155.0, 158.2 ppm.



2-(Pyridin-2-ylmethoxy)anisole

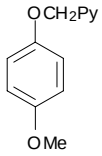
The title compound was obtained as a white solid (1.8 g, 84%). M.p.: 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3H), 5.29 (s, 2H), 6.85-6.93 (m, 4H), 7.19 (t, *J* = 6.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.1, 71.6, 112.1, 114.0, 121.0, 121.4, 121.7, 122.7, 137.0, 148.0, 149.2, 149.7, 157.6 ppm.



1-(Pyridin-2-ylmethoxy)naphthalene

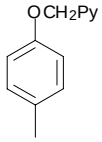
The title compound was obtained as a white solid (1.9 g, 81%). M.p.: 46-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40 (s, 2H), 6.85 (d, *J* =7.6 Hz, 1H), 7.21 (t, *J* = 6.0 Hz,

1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.49-7.52 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.80-7.82 (m, 1H), 8.39 (t, *J* = 6.0 Hz, 1H), 8.61 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.9, 105.5, 120.9, 121.2, 122.1, 122.7, 125.4, 125.8, 126.0, 126.6, 127.7, 134.7, 137.0, 149.3, 154.1, 157.5 ppm.



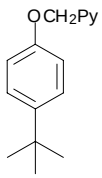
4-(Pyridin-2-ylmethoxy)anisole

The title compound was obtained as a white solid (1.75 g, 81%). M.p.: 39-41 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.76 (s, 3H), 5.16 (s, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 7.20 (t, *J* = 6.4 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 8.58 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 71.4, 114.8, 115.9, 121.4, 122.7, 136.9, 149.3, 152.7, 154.2, 157.7 ppm.



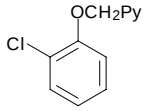
4-(Pyridin-2-ylmethoxy)toluene

The title compound was obtained as colorless oil (1.7 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 5.18 (s, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 6.4 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 8.58 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 70.8, 114.8, 121.4, 122.6, 130.1, 130.5, 136.9, 149.3, 156.4, 157.7 ppm.



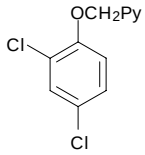
***tert*-Butyl-4-(pyridin-2-ylmethoxy)benzene**

The title compound was obtained as colorless oil (2.0 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9H), 5.20 (s, 2H), 6.92 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 6.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 8.59 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.6, 34.2, 70.8, 114.4, 121.4, 122.7, 126.4, 136.9, 144.0, 149.3, 156.3, 157.8 ppm.



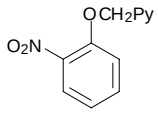
4-(Pyridin-2-ylmethoxy)chlorobenzene

The title compound was obtained as a white solid (1.9 g, 88%). M.p.: 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (s, 2H), 6.90 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.17-7.24 (m, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 8.58 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.3, 113.9, 121.3, 122.0, 122.8, 123.2, 127.9, 130.5, 137.1, 149.2, 154.0, 157.0 ppm.



1,3-Dichloro-4-(pyridin-2-ylmethoxy)benzene

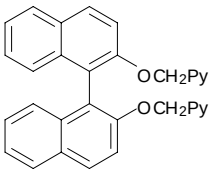
The title compound was obtained as a white solid (2.3 g, 91%). M.p.: 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (s, 2H), 6.89 (d, J = 8.8 Hz, 1H), 7.14 (d, J = 10.0 Hz, 1H), 7.22 (t, J = 6.0 Hz, 1H), 7.39 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 8.58 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.7, 114.7, 121.3, 123.0, 124.0, 126.4, 127.8, 130.2, 137.2, 149.3, 152.8, 156.5 ppm.



2-(Pyridin-2-ylmethoxy)nitrobenzene

The title compound was obtained as a slight yellow solid (2.0 g, 87%). M.p.: 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.34 (s, 2H), 7.05 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 8.4

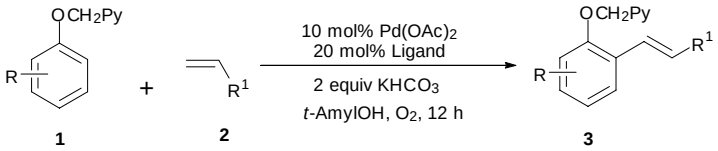
Hz, 1H), 7.23 (t, *J* = 6.4 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.6, 115.0, 121.0, 121.4, 123.1, 126.0, 134.5, 137.3, 140.1, 149.2, 151.8, 156.0 ppm.



2,2'-Bis(pyridin-2-ylmethoxy)-1,1'-binaphthyl

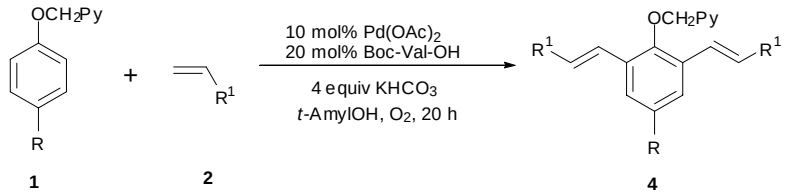
The title compound was obtained as a white solid (3.2 g, 71%). M.p.: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.20 (s, 4H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 6.4 Hz, 2H), 7.22-7.24 (m, 6H), 7.31-7.34 (m, 2H), 7.44 (d, *J* = 9.2 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 8.42 (d, *J* = 4.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.6, 115.2, 120.3, 120.9, 122.3, 124.0, 125.6, 126.6, 128.1, 129.5, 129.7, 134.3, 136.6, 148.7, 153.8, 157.8 ppm.

IV. General procedure for 2-pyridylmethyl ether directed C–H *ortho*-olefination of phenols

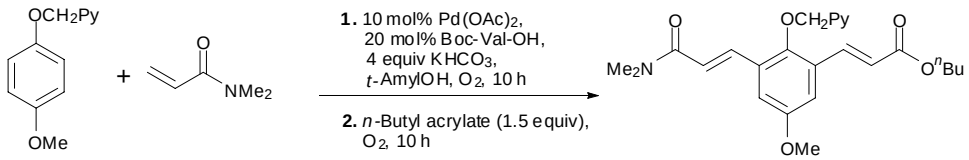


A mixture of phenol ethers **1** (0.5 mmol), alkenes **2** (0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 10 mol%), $KHCO_3$ (100 mg, 1.0 mmol) and ligand (20 mol%) was dissolved in *t*-AmylOH (2 mL) in a 50 mL Schlenk-type sealed tube. The reaction tube was filled with O_2. Subsequently, the reaction mixture was stirred for 10 min at room temperature, and then heated at 90 ºC for 12 h. After being cooled to room temperature, the reaction mixture was diluted with 5 mL of CH_2Cl_2, filtered through a plug of celite, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts

were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product **3**.



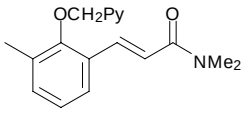
A mixture of phenol ethers **1** (0.5 mmol), alkenes **2** (2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 10 mol%), $KHCO_3$ (200 mg, 2.0 mmol) and Boc-Val-OH (21.7 mg, 20 mol%) was dissolved in *t*-AmylOH (2 mL) in a 50 mL Schlenk-type sealed tube. The reaction tube was filled with O_2. Subsequently, the reaction mixture was stirred for 10 min at room temperature, and then heated at 90 ºC for 20 h. After being cooled to room temperature, the reaction mixture was diluted with 5 mL of CH_2Cl_2, filtered through a plug of celite, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product **4**.



A mixture of 4-(pyridin-2-ylmethoxy)anisole (0.5 mmol), *N,N*-dimethylacryl-amide (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 10 mol%), $KHCO_3$ (200 mg, 2.0 mmol) and Boc-Val-OH (21.7 mg, 20 mol%) was dissolved in *t*-AmylOH (2 mL) in a 50 mL Schlenk-type sealed tube. The reaction tube was filled with O_2. Subsequently, the reaction mixture was stirred for 10 min at room temperature, and then heated at 90 ºC for 10 h. After being cooled to room temperature, *n*-butyl acrylate was added into the mixture under the oxygen environment, and then the mixture was heated at 90 ºC for another 10 h. After being cooled to room temperature, the reaction mixture was diluted with 5 mL of CH_2Cl_2, filtered through a plug of celite, and washed with 10-20 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired

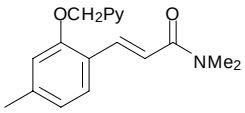
product.

V. Experimental data for the described substances



(*E*)-*N*,*N*-Dimethyl-3-(3-methyl-2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3a)

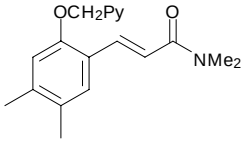
2-(Pyridin-2-ylmethoxy)toluene (100 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (134 mg, 90% yield). M.p.: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 3.02 (s, 3H), 3.06 (s, 3H), 4.96 (s, 2H), 6.97 (d, J = 15.6 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 6.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.90 (d, J = 15.6 Hz, 1H), 8.57 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3, 36.0, 37.4, 75.7, 119.4, 121.8, 122.9, 124.6, 126.5, 129.2, 132.2, 132.6, 137.0, 137.7, 149.3, 156.1, 157.2, 167.0 ppm. HRMS (ESI^+): calcd for $C_{18}H_{20}N_2O_2$ $[M+H]^+$ 297.1603, found 297.1609.



(*E*)-*N*,*N*-Dimethyl-3-(4-methyl-2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3b)

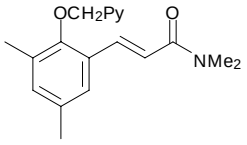
3-(Pyridin-2-ylmethoxy)toluene (100 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (126 mg, 85% yield). M.p.: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.05 (s, 3H), 3.08 (s, 3H), 5.28 (s, 2H), 6.79-6.80 (m,

2H), 6.98 (d, *J* = 15.6 Hz, 1H), 7.26-7.27 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.77 (t, *J* = 4.0 Hz, 1H), 7.98 (d, *J* = 15.6 Hz, 1H), 8.59 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 36.0, 37.4, 70.8, 113.4, 117.6, 121.7, 122.0, 122.1, 122.9, 129.1, 137.4, 137.8, 141.4, 149.0, 156.9, 167.5 ppm. HRMS (ESI^+): calcd for $C_{18}H_{20}N_2O_2$ $[M+H]^+$ 297.1603, found 297.1615.



(*E*)-3-(4,5-Dimethyl-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3c)

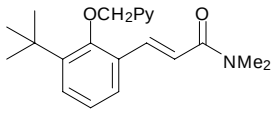
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (143 mg, 92% yield). M.p.: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 2.23 (s, 3H), 3.05 (s, 3H), 3.09 (s, 3H), 5.24 (s, 2H), 6.76 (s, 1H), 6.98 (d, *J* = 15.6 Hz, 1H), 7.22-7.28 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 15.6 Hz, 1H), 8.58 (d, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 20.4, 36.0, 37.5, 71.2, 114.3, 117.5, 121.6, 122.1, 122.8, 129.2, 130.3, 137.1, 138.0, 139.8, 149.2, 155.2, 157.3, 167.7 ppm. HRMS (ESI^+): calcd for $C_{19}H_{22}N_2O_2$ $[M+H]^+$ 311.1760, found 311.1756.



(*E*)-3-(3,5-Dimethyl-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3d)

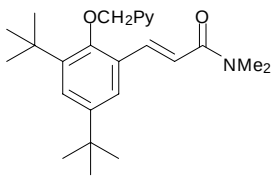
1,3-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (107 mg, 0.5 mmol),

N,N-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (141 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.28 (s, 3H), 3.00 (s, 3H), 3.05 (s, 3H), 4.90 (s, 2H), 6.94 (d, J = 15.6 Hz, 1H), 7.00 (s, 1H), 7.18 (s, 1H), 7.20 (t, J = 6.0 Hz, 1H), 7.70-7.78 (m, 2H), 7.86 (d, J = 15.6 Hz, 1H), 8.54 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1, 20.8, 35.9, 37.3, 75.6, 118.9, 121.8, 122.8, 126.5, 128.5, 131.6, 133.4, 133.9, 137.1, 137.7, 149.0, 153.8, 157.0, 166.9 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{22}N_2O_2$ $[M+H]^+$ 311.1760, found 311.1764.



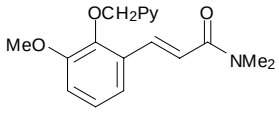
(*E*)-3-(3-*tert*-Butyl-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3e)

tert-Butyl-2-(pyridin-2-ylmethoxy)benzene (121 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (159 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (s, 9H), 2.98 (s, 3H), 3.05 (s, 3H), 5.03 (s, 2H), 6.88 (d, J = 15.6 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 5.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.78-7.84 (m, 2H), 7.89 (d, J = 15.6 Hz, 1H), 8.54 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 35.2, 35.9, 37.4, 76.7, 119.0, 121.3, 122.7, 124.1, 126.8, 128.7, 130.0, 137.2, 138.5, 143.5, 148.9, 157.0, 157.3, 166.7 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{26}N_2O_2$ $[M+H]^+$ 339.2073, found 339.2069.



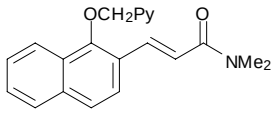
(*E*)-3-(3,5-Di-*tert*-butyl-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3f)

1,3-Di-*tert*-butyl-4-(pyridin-2-ylmethoxy)benzene (149 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (188 mg, 95% yield). M.p.: 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9H), 1.40 (s, 9H), 2.99 (s, 3H), 3.05 (s, 3H), 5.05 (s, 2H), 6.87 (d, J = 15.6 Hz, 1H), 7.26 (m, 1H), 7.37(s, 1H), 7.40 (s, 1H), 7.85-7.89 (m, 3H), 8.55 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.1, 31.6, 34.7, 35.4, 35.9, 37.4, 76.2, 118.8, 121.4, 122.7, 123.9, 126.1, 129.1, 137.5, 139.3, 142.5, 146.4, 148.6, 154.6, 157.4, 166.9 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{34}N_2O_2$ $[M+H]^+$ 395.2699, found 395.2690.



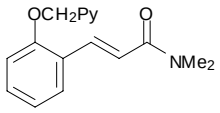
(*E*)-3-(3-Methoxy-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3g)

2-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (125 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 3H), 3.01 (s, 3H), 3.80 (s, 3H), 5.12 (s, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 15.6 Hz, 1H), 7.02 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.18-7.19 (m, 1H), 7.70-7.75 (m, 2H), 7.87 (d, J = 15.6 Hz, 1H), 8.50 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.7, 37.2, 55.7, 75.2, 113.1, 119.4, 119.8, 121.9, 122.5, 124.3, 129.5, 136.8, 137.0, 146.5, 148.7, 153.0, 157.3, 166.7 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{20}N_2O_3$ $[M+H]^+$ 313.1552, found 313.1553.



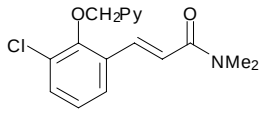
(*E*)-*N*,*N*-Dimethyl-3-(1-(pyridin-2-ylmethoxy)naphthalen-2-yl)acrylamide (3h)

1-(Pyridin-2-ylmethoxy)naphthalene (118 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (146 mg, 88% yield). M.p.: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.06 (s, 3H), 3.14 (s, 3H), 5.17 (s, 2H), 7.05 (d, J = 15.6 Hz, 1H), 7.29 (t, J = 5.2 Hz, 1H), 7.48-7.51 (m, 2H), 7.63-7.67 (m, 2H), 7.82-7.89 (m, 3H), 8.15-8.19 (m, 2H), 8.63 (d, J = 3.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 37.5, 77.4, 119.1, 122.2, 122.9, 123.2, 124.3, 124.4, 124.9, 126.8, 127.3, 128.1, 128.3, 135.5, 136.8, 137.5, 149.1, 154.1, 156.7, 166.9 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{20}N_2O_2$ $[M+H]^+$ 333.1603, found 333.1601.



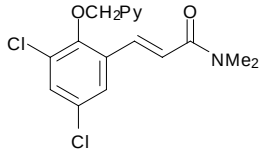
(*E*)-*N*,*N*-Dimethyl-3-(2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3i)

Pyridin-2-ylmethoxybenzene (93 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (88 mg, 62% yield). M.p.: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.06 (s, 3H), 3.10 (s, 3H), 5.31 (s, 2H), 6.96-7.00 (m, 2H), 7.02 (d, J = 15.6 Hz, 1H), 7.26-7.31 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.61 (t, J = 6.4 Hz, 1H), 7.76-7.81 (m, 1H), 8.02 (d, J = 15.6 Hz, 1H), 8.59 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 37.5, 70.9, 112.6, 118.8, 121.3, 121.7, 123.0, 124.8, 129.2, 130.8, 137.4, 137.8, 149.1, 156.86, 156.93, 167.3 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{18}N_2O_2$ $[M+H]^+$ 283.1447, found 283.1443.



(*E*)-3-(3-Chloro-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3j)

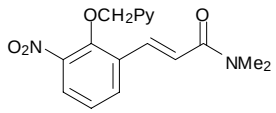
2-(Pyridin-2-ylmethoxy)chlorobenzene (110 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Ac-Ile-OH (17.3 mg, 0.1 mmol) or Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded colorless oil (124 mg, 78% yield) or (81 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (s, 3H), 3.05 (s, 3H), 5.10 (s, 2H), 7.03 (d, J = 15.6 Hz, 1H), 7.08 (t, J = 8.0 Hz, 1H), 7.25-7.27 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.77-7.79 (m, 2H), 7.81 (d, J = 15.6 Hz, 1H), 8.56 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.9, 37.3, 75.6, 120.8, 122.2, 123.0, 125.4, 127.4, 129.0, 131.25, 131.29, 136.5, 137.1, 149.0, 153.3, 156.4, 166.5 ppm. HRMS (ESI^+): calcd for $C_{17}H_{17}ClN_2O_2$ $[M+H]^+$ 317.1057, found 317.1054.



(*E*)-3-(3,5-Dichloro-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-dimethylacrylamide (3k)

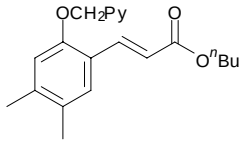
1,3-Dichloro-4-(pyridin-2-ylmethoxy)benzene (127 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Ac-Ile-OH (17.3 mg, 0.1 mmol) or Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (126 mg, 72% yield) or (47 mg, 27% yield). M.p.: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.03 (s, 3H), 3.09 (s, 3H), 5.09 (s, 2H), 6.98 (d, J = 15.6 Hz, 1H), 7.26 (t, J = 6.0 Hz, 1H), 7.40-7.42 (m, 2H), 7.74-7.83 (m,

3H), 8.56 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 37.5, 75.9, 121.9, 122.3, 123.2, 126.8, 129.9, 130.2, 130.8, 132.4, 135.3, 137.3, 149.0, 152.1, 156.1, 166.1 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{16}Cl_2N_2O_2$ $[M+H]^+$ 351.0667, found 351.0669.



(*E*)-*N*,*N*-Dimethyl-3-(3-nitro-2-(pyridin-2-ylmethoxy)phenyl)acrylamide (3l)

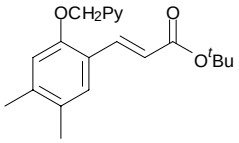
2-(Pyridin-2-ylmethoxy)nitrobenzene (115 mg, 0.5 mmol), *N,N*-dimethylacrylamide (75 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Ac-Ile-OH (17.3 mg, 0.1 mmol) or Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (98 mg, 60% yield) or (50 mg, 31% yield). M.p.: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.04 (s, 3H), 3.08 (s, 3H), 5.18 (s, 2H), 7.10 (d, J = 15.6 Hz, 1H), 7.25-7.31 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.76-7.86 (m, 4H), 8.56 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.1, 37.4, 77.5, 122.5, 123.4, 124.9, 125.9, 132.6, 133.4, 135.3, 137.5, 145.2, 148.88, 148.93, 150.3, 155.6, 166.1 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{17}N_3O_4$ $[M+H]^+$ 328.1297, found 328.1296.



(*E*)-Butyl 3-(4,5-dimethyl-2-(pyridin-2-ylmethoxy)phenyl)acrylate (3m)

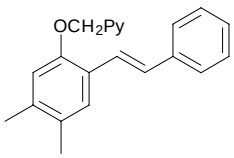
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106.0 mg, 0.5 mmol), butyl acrylate (96.0 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded colorless oil (146 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.6 Hz, 3H), 1.39-1.49 (m, 2H), 1.65-1.72 (m, 2H), 2.19 (s,

3H), 2.22 (s, 3H), 4.18 (t, *J* = 6.4 Hz, 2H), 5.26 (s, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.73 (s, 1H), 7.24-7.26 (m, 1H), 7.31 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.71-7.73 (m, 1H), 8.06 (d, *J* = 16.4 Hz, 1H), 8.59 (d, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 18.9, 19.4, 20.5, 30.9, 64.3, 71.0, 114.3, 117.7, 121.2, 121.3, 122.8, 129.4, 129.6, 137.3, 139.8, 140.9, 149.1, 155.2, 157.2, 167.9 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{25}NO_3$ $[M+H]^+$ 340.1913, found 340.1914.



(*E*)-*tert*-Butyl 3-(4,5-dimethyl-2-(pyridin-2-ylmethoxy)phenyl)acrylate (3n)

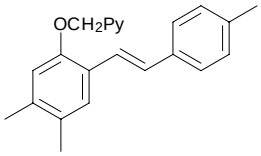
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), *tert*-butyl acrylate (96 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (128 mg, 75% yield). M.p.: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 9H), 2.19 (s, 3H), 2.22 (s, 3H), 5.26 (s, 2H), 6.41 (d, J = 16.4 Hz, 1H), 6.73 (s, 1H), 7.24-7.26 (m, 1H), 7.31 (s, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.72-7.74 (m, 1H), 8.00 (d, J = 16.4 Hz, 1H), 8.58 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 20.5, 28.4, 71.0, 80.2, 114.3, 119.5, 121.3, 122.8, 129.4, 137.3, 138.7, 140.6, 149.0, 155.1, 157.3, 167.1 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{25}NO_3$ $[M+H]^+$ 340.1913, found 340.1909.



(*E*)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-styrylbenzene (3o)

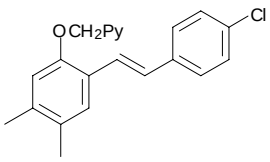
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), styrene (78 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2.

Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (131 mg, 83% yield). M.p.: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 6H), 5.29 (s, 2H), 6.74 (s, 1H), 7.11 (d, J = 16.4 Hz, 1H), 7.22-7.26 (m, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.40 (s, 1H), 7.52-7.60 (m, 4H), 7.73 (t, J = 7.6 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 20.2, 71.2, 114.5, 121.3, 122.7, 123.5, 124.2, 126.5, 127.3, 127.8, 128.3, 128.7, 129.3, 137.2, 137.5, 138.3, 149.0, 153.9, 157.7 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{21}NO$ $[M+H]^+$ 316.1701, found 316.1704.



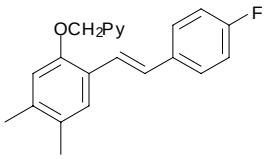
(*E*)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(4-methylstyryl)benzene (3p)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 4-methylstyrene (89 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (147 mg, 89% yield). M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.24 (s, 3H), 2.36 (s, 3H), 5.28 (s, 2H), 6.74 (s, 1H), 7.09 (d, J = 16.4 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H), 7.23 (t, J = 6.4 Hz, 1H), 7.39-7.44 (m, 3H), 7.48 (d, J = 16.4 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 20.2, 21.3, 71.2, 114.5, 121.3, 122.5, 122.7, 124.4, 126.5, 127.7, 128.3, 129.3, 129.4, 135.5, 137.1, 137.2, 149.0, 153.8, 157.8 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{23}NO$ $[M+H]^+$ 330.1858, found 330.1856.



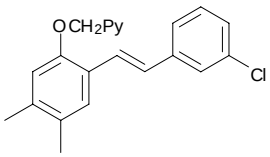
(*E*)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(4-chlorostyryl)benzene (3q)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 4-chlorostyrene (104 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (152 mg, 87% yield). M.p.: 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 6H), 5.28 (s, 2H), 6.73 (s, 1H), 7.05 (d, J = 16.4 Hz, 1H), 7.23 (t, J = 6.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.37(s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.48-7.56 (m, 2H), 7.72 (t, J = 7.6 Hz, 1H), 8.62 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 20.2, 71.3, 114.5, 121.3, 122.8, 123.8, 124.2, 127.0, 127.7, 127.8, 128.9, 129.4, 132.8, 136.8, 137.2, 137.8, 149.2, 154.0, 157.7 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{20}ClNO$ $[M+H]^+$ 350.1312, found 350.1312.



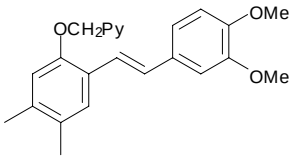
(*E*)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(4-fluorostyryl)benzene (3r)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 4-fluorostyrene (92 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (130 mg, 78% yield). M.p.: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 6H), 5.28 (s, 2H), 6.73 (s, 1H), 7.02-7.11 (m, 3H), 7.23 (t, J = 6.0 Hz, 1H), 7.37(s, 1H), 7.43-7.50 (m, 3H), 7.55 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 20.2, 71.3, 114.5, 115.5, 115.7, 121.3, 122.7, 123.32, 123.34, 124.0, 127.1, 127.7, 127.9, 128.0, 129.4, 134.45, 134.49, 137.1, 137.5, 149.1, 153.9, 157.7, 161.0, 163.5 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{20}FNO$ $[M+H]^+$ 334.1607, found 334.1606.



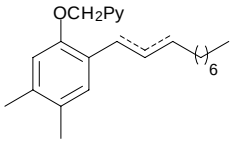
(*E*)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(3-chlorostyryl)benzene (3s)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 3-chlorostyrene (276 mg, 2.0 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (126 mg, 72% yield). M.p.: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 6H), 5.28 (s, 2H), 6.73 (s, 1H), 7.04 (d, J = 16.4 Hz, 1H), 7.18-7.26 (m, 3H), 7.36-7.38 (m, 2H), 7.51-7.55 (m, 3H), 7.72 (t, J = 7.6 Hz, 1H), 8.61 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 20.3, 71.4, 114.6, 121.3, 122.8, 123.7, 124.8, 125.1, 126.3, 126.8, 127.1, 127.9, 129.4, 129.9, 134.7, 137.2, 138.0, 140.2, 149.2, 154.1, 157.6 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{20}ClNO$ $[M+H]^+$ 350.1312, found 350.1307.



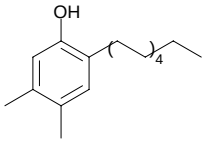
(*E*)-4,5-Dimethyl-1-(pyridin-2-ylmethoxy)-2-(3,4-dimethoxystyryl)benzene (3t)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), 3,4-dimethoxystyrene (123 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a white solid (141 mg, 75% yield). M.p.: 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 6H), 3.90 (s, 3H) 3.93 (s, 3H), 5.28 (s, 2H), 6.72 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 7.05-7.09 (m, 3H), 7.22 (t, *J* = 6.0 Hz, 1H), 7.38-7.42 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 8.60 (d, *J* = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 20.2, 55.9, 56.1, 71.3, 108.9, 111.4, 114.5, 119.7, 121.3, 121.7, 122.7, 124.4, 127.6, 128.1, 129.4, 131.5, 137.1, 148.7, 149.1, 149.2, 153.8, 157.8 ppm. HRMS (ESI$^+$): calcd for $C_{24}H_{25}NO_3$ $[M+H]^+$ 376.1913, found 376.1914.



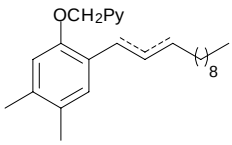
(3u+3u′)

1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), *n*-decene (105 mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a mixture as colorless oil (132 mg, 75% yield). The two products could not be isolated by silica gel column chromatography, but a single *ortho*-alkyl phenol **3ua** could be obtained by catalytic hydrogenation of the mixture (**3u+3u′**, 1:1.5).



2-Decyl-4,5-dimethylphenol (3ua)

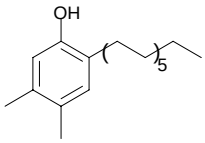
To a stirred solution of the mixture (**3u**+**3u′**, 0.3 mmol) and absolute EtOH (6.0 mL) was added Pd/C (100 mg, 10% Pd). After being stirred under an atmosphere of H_2 (balloon) for overnight, the mixture was filtered over a pad of celite with EtOAc (20 mL) and concentrated under reduce pressure. The residue was purified by flash chromatography over silica gel to give desired product **3ua** as colorless oil (71 mg, 90% Yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.2 Hz, 3H), 1.20-1.32 (m, 14H), 1.56-1.61 (m, 2H), 2.16 (s, 3H), 2.17 (s, 3H), 2.50 (t, J = 7.6 Hz, 2H), 4.47 (br. s., 1H), 6.56 (s, 1H), 6.86 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 18.9, 19.45, 19.48, 22.8, 29.5, 29.7, 29.8, 29.9, 30.0, 30.3, 32.1, 116.8, 125.7, 128.6, 131.4, 135.2, 151.4 ppm. HRMS (ESI^+): calcd for $C_{18}H_{30}O$ $[M+Na]^+$ 285.2194, found 285.2196.



(3v+3v′)

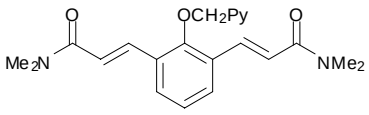
1,2-Dimethyl-4-(pyridin-2-ylmethoxy)benzene (106 mg, 0.5 mmol), *n*-dodecene (126

mg, 0.75 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (100 mg, 1.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a mixture as colorless oil (125 mg, 66% yield). The two products could not be isolated by silica gel column chromatography, but a single *ortho*-alkyl phenol **3va** could be obtained by catalytic hydrogenation of the mixture (**3v**+**3v′**, 1:2.5).



2-Dodecyl-4,5-dimethylphenol (3va)

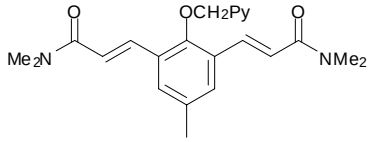
To a stirred solution of the mixture (**3v**+**3v′**, 0.3 mmol) and absolute EtOH (6.0 mL) was added Pd/C (100 mg, 10% Pd). After being stirred under an atmosphere of H_2 (balloon) for overnight, the mixture was filtered over a pad of celite with EtOAc (20 mL) and concentrated under reduce pressure. The residue was purified by flash chromatography over silica gel to give desired product **3va** as colorless oil (75 mg, 86% Yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.8 Hz, 3H), 1.20-1.32 (m, 18H), 1.54-1.59 (m, 2H), 2.16 (s, 3H), 2.17 (s, 3H), 2.50 (t, J = 8.0 Hz, 2H), 4.48 (br. s., 1H), 6.56 (s, 1H), 6.86 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 18.9, 19.45, 19.48, 22.8, 27.9, 29.5, 29.71, 29.77, 29.80, 29.83, 30.0, 30.3, 32.1, 116.7, 125.7, 128.6, 131.4, 135.2, 151.4 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{34}O$ $[M+Na]^+$ 313.2507, found 313.2510.



(*2E,2′E*)-3,3'-(2-(Pyridin-2-ylmethoxy)-1,3-phenylene)bis(*N*,*N*-dimethylacrylamide) (4a)

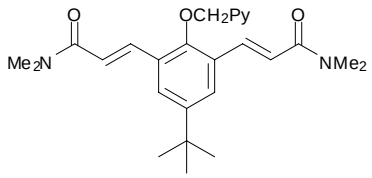
Pyridin-2-ylmethoxybenzene (93 mg, 0.5 mmol), *N,N*-dimethylacrylamide (248 mg, 2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2.

Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a slight yellow solid (139 mg, 73% yield). M.p.: 38-40 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.01(s, 6H), 3.05 (s, 6H), 4.95 (s, 2H), 7.02 (d, *J* = 15.6 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.73-7.79 (m, 2H), 7.86 (d, *J* = 15.6 Hz, 2H), 8.54 (d, *J* = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 37.4, 76.8, 120.3, 122.2, 123.1, 125.1, 130.0, 130.1, 137.0, 137.2, 149.2, 156.3, 156.4, 166.7 ppm. HRMS (ESI^+): calcd for $C_{22}H_{25}N_3O_3$ $[M+H]^+$ 380.1974, found 380.1967.



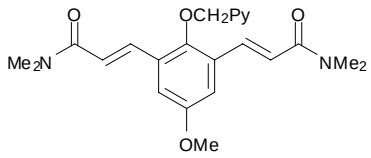
(*2E*,*2'E*)-3,3'-(5-Methyl-2-(pyridin-2-ylmethoxy)-1,3-phenylene)bis(*N*,*N*-dimethyl acrylamide) (4b)

4-(Pyridin-2-ylmethoxy)toluene (100 mg, 0.5 mmol), *N,N*-dimethylacrylamide (248 mg, 2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a white solid (142 mg, 72% yield). M.p.: 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 3.02 (s, 6H), 3.08 (s, 6H), 4.98 (s, 2H), 6.99 (d, J = 15.6 Hz, 2H), 7.30-7.31 (m, 1H), 7.35 (s, 2H), 7.83-7.87 (m, 4H), 8.53 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 36.0, 37.4, 76.5, 120.0, 122.4, 123.2, 129.6, 130.4, 134.5, 137.0, 137.7, 148.7, 154.2, 156.2, 166.8 ppm. HRMS (ESI^+): calcd for $C_{23}H_{27}N_3O_3$ $[M+H]^+$ 394.2131, found 394.2130.



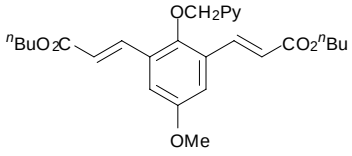
(*2E*,*2'E*)-3,3'-(5-*tert*-Butyl-2-(pyridin-2-ylmethoxy)-1,3-phenylene)bis(*N*,*N*-dimethylacrylamide) (4c)

tert-Butyl-4-(pyridin-2-ylmethoxy)benzene (121 mg, 0.5 mmol), *N,N*-dimethylacrylamide (248 mg, 2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a white solid (164 mg, 75% yield). M.p.: 162-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9H), 3.02 (s, 6H), 3.06 (s, 6H), 4.97 (s, 2H), 7.03 (d, J = 15.6 Hz, 2H), 7.28 (t, J = 6.0 Hz, 1H), 7.53 (s, 2H), 7.80-7.87 (m, 4H), 8.56 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 34.6, 36.0, 37.4, 76.0, 120.0, 122.2, 123.1, 127.5, 129.2, 137.6, 137.7, 147.7, 148.8, 154.1, 156.4, 166.9 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{33}N_3O_3$ $[M+H]^+$ 436.2600, found 436.2603.



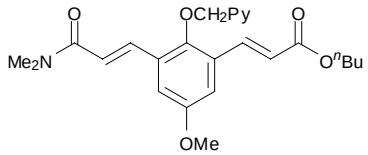
(*2E*,*2'E*)-3,3'-(5-Methoxy-2-(pyridin-2-ylmethoxy)-1,3-phenylene)bis(*N*,*N*-dimethylacrylamide) (4d)

4-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), *N,N*-dimethylacrylamide (248 mg, 2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 20 h under 1 atm O_2. Purification via silica gel column chromatography using 50% acetone in petroleum ether afforded a slight yellow solid (143 mg, 70% yield). M.p.: 167-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (s, 3H), 3.07 (s, 6H), 3.85 (s, 6H), 4.97 (s, 2H), 6.99 (d, J = 15.2 Hz, 2H), 7.06 (s, 2H), 7.30 (t, J = 5.6 Hz, 1H), 7.81-7.89 (m, 4H), 8.55 (d, J = 4.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0, 37.4, 55.9, 76.5, 114.7, 120.5, 122.5, 123.2, 130.7, 136.9, 137.9, 148.5, 150.2, 156.2, 166.7 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{27}N_3O_4$ $[M+H]^+$ 410.2080, found 410.2075.



(*2E*,*2'E*)-Di-Butyl 3,3'-(5-methoxy-2-(pyridin-2-ylmethoxy)-1,3-phenylene) diacrylate (4e)

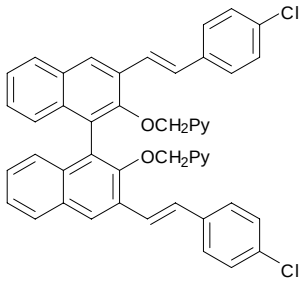
4-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), *n*-butyl acrylate (320 mg, 2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 10% EtOAc in petroleum ether afforded a slight yellow solid (187 mg, 80% yield). M.p.: 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.2 Hz, 6H), 1.33-1.43 (m, 4H), 1.60-1.67 (m, 4H), 3.83 (s, 3H), 4.14 (t, *J* = 6.4 Hz, 4H), 4.94 (s, 2H), 6.41 (d, *J* = 16.0 Hz, 2H), 7.12 (s, 2H), 7.26-7.27 (m, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.78 (m, 1H), 7.90 (d, *J* = 16.0 Hz, 2H), 8.57 (d, *J* = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.3, 30.8, 55.8, 64.6, 78.2, 114.4, 120.7, 122.2, 123.2, 130.0, 137.4, 138.5, 149.1, 150.7, 156.1, 156.3, 166.8 ppm. HRMS (ESI^+): calcd for $C_{27}H_{35}NO_6$ $[M+H]^+$ 468.2386, found 468.2384.



(*E*)-Butyl 3-(3-((*E*)-3-(dimethylamino)-3-oxoprop-1-enyl)-5-methoxy-2-(pyridin-2-ylmethoxy)phenyl)acrylate (4f)

4-(Pyridin-2-ylmethoxy)anisole (108 mg, 0.5 mmol), *N,N*-dimethylacrylamide (50 mg, 0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 10 h under 1 atm O_2. Subsequently, butyl acrylate (96.0 mg, 0.75 mmol) was added for another 10 h under 1 atm O_2. Purification via silica gel column chromatography using 50% EtOAc in petroleum ether afforded a white solid (105 mg, 48% yield). M.p.: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.6 Hz, 3H), 1.31-1.40 (m, 2H), 1.57-1.64 (m, 2H), 3.00 (s, 3H), 3.05 (s, 3H), 3.81 (s, 3H), 4.12 (t, J = 6.4 Hz, 2H), 4.89 (s, 2H), 6.38 (d, J = 16.0 Hz, 1H), 7.00-7.08 (m, 3H), 7.21 (t, J = 6.0 Hz, 1H), 7.66-7.83 (m, 3H), 7.90 (d, J = 16.0 Hz, 1H), 8.54 (d, J = 4.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

13.9, 19.3, 29.8, 36.1, 37.5, 55.9, 64.6, 77.8, 112.9, 116.4, 120.5, 120.7, 122.2, 123.1, 129.9, 130.9, 136.9, 137.1, 138.8, 149.4, 150.6, 156.2, 156.4, 166.7, 166.9 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{30}N_2O_5$ $[M+H]^+$ 439.2233, found 439.2232.

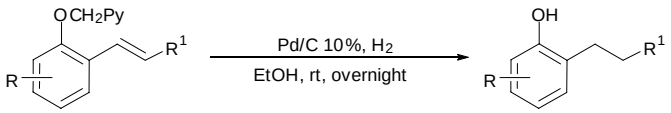


(*E*)-3,3'-Bis(4-chlorostyryl)-2,2'-bis(pyridin-2-ylmethoxy)-1,1'-binaphthyl (4g)

2,2'-Bis(pyridin-2-ylmethoxy)-1,1'-binaphthyl (234 mg, 0.5 mmol), 4-chlorostyrene (345 mg, 2.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), Boc-Val-OH (21.7 mg, 0.1 mmol), and $KHCO_3$ (200 mg, 2.0 mmol) in *t*-AmylOH (2 mL) at 90 ºC for 12 h under 1 atm O_2. Purification via silica gel column chromatography using 15% EtOAc in petroleum ether afforded a white solid (204 mg, 55% yield). M.p.: 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.70 (d, J = 13.2 Hz, 2H), 4.99 (d, J = 13.2 Hz, 2H), 6.79 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 6.4 Hz, 2H), 7.19-7.30 (m, 10H), 7.38-7.41 (m, 8H), 7.49 (d, J = 16.4 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 8.18 (s, 2H), 8.30 (d, J = 4.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.3, 121.4, 122.4, 124.6, 125.6, 125.8, 125.9, 126.4, 126.9, 128.0, 128.2, 129.0, 129.7, 131.1, 133.5, 133.8, 136.1, 136.7, 136.8, 148.3, 153.8, 157.2 ppm. HRMS (ESI$^+$): calcd for $C_{48}H_{34}Cl_2N_2O_2$ $[M+H]^+$ 741.2076, found 741,2071.

VI. Deprotection of *ortho*-alkenylated phenols and characterization

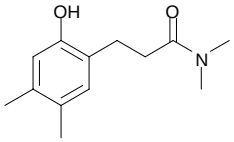
General procedure for deprotection by catalytic hydrogenation



Method A (H_2, 1 atm): To a stirred solution of *ortho*-alkenyl phenol ethers (0.3 mmol) in absolute EtOH (6.0 mL) was added Pd/C (100 mg, 10% Pd). After being stirred under an atmosphere of H_2 (balloon) for overnight, the mixture was filtered over a pad

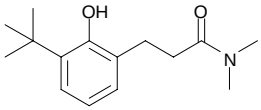
of celite with EtOAc (20 mL) and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel to give corresponding phenols.

Method B (H_2, 15 atm): To a stirred solution of *ortho*-alkenyl phenol ethers (0.3 mmol) in absolute EtOH (6.0 mL) was added Pd/C (10 mg, 10% Pd). After being stirred under 15 atm H_2 for overnight, the mixture was filtered over a pad of celite with EtOAc (20 mL) and concentrated under reduce pressure. The residue was purified by flash chromatography over silica gel to give the corresponding phenols.



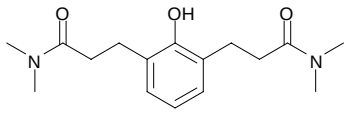
3-(2-Hydroxy-4,5-dimethylphenyl)-*N*,*N*-dimethylpropanamide (3ca)

The product **3ca** was synthesized according to **Method A** (60 mg, 90% yield) or **Method B** (61 mg, 92% yield) as a white solid. M.p.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3H), 2.17 (s, 3H), 2.66-2.69 (m, 2H), 2.86-2.89 (m, 2H), 2.93 (s, 3H), 2.95 (s, 3H), 6.73 (s, 1H), 6.80 (s, 1H), 9.40 (br. s., 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 19.6, 24.3, 35.7, 36.0, 37.2, 119.3, 125.6, 127.9, 131.7, 136.3, 153.4, 174.0 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{19}NO_2$ $[M+Na]^+$ 244.1313, found 244.1317.



3-(3-*tert*-Butyl-2-hydroxyphenyl)-*N*,*N*-dimethylpropanamide (3ea)

The product **3ea** was synthesized according to **Method A** as colorless oil (63 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (s, 9H), 2.70 (t, J = 4.2 Hz, 2H), 2.92-2.95 (m, 8H), 6.75 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 9.79 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7, 29.9, 35.1, 35.8, 36.1, 37.2, 119.4, 125.2, 128.6, 129.5, 138.6, 154.6, 174.2 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{23}NO_2$ $[M+Na]^+$ 272.1626, found 272.1625.



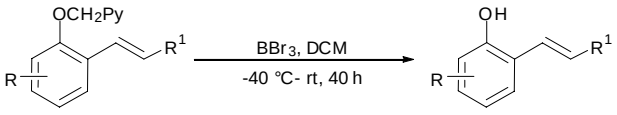
3,3'-(2-Hydroxy-1,3-phenylene)bis(*N*,*N*-dimethylpropanamide) (4aa)

The product **4aa** was synthesized according to **Method A** as a white solid (75 mg, 85% yield). M.p.: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (t, J = 6.8 Hz, 4H), 2.93-2.99 (m, 16H), 6.73 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 7.6 Hz, 2H), 9.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 34.9, 35.8, 37.4, 119.9, 128.9, 129.2, 153.8, 173.8 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{24}N_2O_3$ $[M+Na]^+$ 315.1685, found 315.1683.

General procedure for deprotection by Mg in methanol

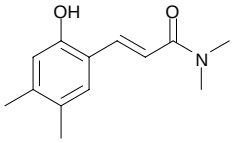
To a stirred solution of (*E*)-3-(4,5-dimethyl-2-(pyridin-2-ylmethoxy)phenyl)-*N*,*N*-di methylacrylamide (**3c**, 0.3 mmol) in MeOH (10 mL) was added Mg turnings (50.4 mg, 2.1 mmol) at 0 °C. The suspension then warmed to room temperature and stirred for 24 h. The mixture was filtered over a pad of celite with EtOAc (20 mL). The filtrate was successively washed with aqueous saturated solution of $NaHCO_3$ (10 mL) and brine (10 mL), dried (Na_2SO4) and then concentrated under reduced pressure. The residue was purified by flash chromatography to give the corresponding product **3ca** as a white solid (47 mg, 70%). M.p.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3H), 2.17 (s, 3H), 2.66-2.69 (m, 2H), 2.86-2.89 (m, 2H), 2.93 (s, 3H), 2.95 (s, 3H), 6.73 (s, 1H), 6.80 (s, 1H), 9.40 (br. s., 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 19.6, 24.3, 35.7, 36.0, 37.2, 119.3, 125.6, 127.9, 131.7, 136.3, 153.4, 174.0 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{19}NO_2$ $[M+Na]^+$ 244.1313, found 244.1317.

General procedure for deprotection by BBr_3



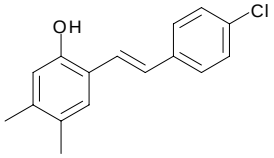
To a solution of *ortho*-alkenyl phenol ethers (2 mmol) in dry CH_2Cl_2 (40 mL) at -40 °C was slowly added BBr_3 (3 mL, 4.0 M solution in CH_2Cl_2; 12 mmol) under a

nitrogen atmosphere. The solution was stirred for 15 min at the same temperature and then allowed to worm to room temperature and further stirred 40 h. The reaction was quenched with excess amount of H_2O. Then the mixture was neutralized by $NaHCO_3$. Subsequently, the mixture was worked up by an appropriate method to give the desired products.



(*E*)-3-(2-Hydroxy-4,5-dimethylphenyl)-*N*,*N*-dimethylacrylamide (3cb)

The crude product was precipitated after neutralization by $NaHCO_3$, and was purified by flash chromatography to give the corresponding product **3cb** as a white solid (341 mg, 78% yield). M.p.: > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.13 (s, 3H), 2.14 (s, 3H), 2.92 (s, 3H), 3.13 (s, 3H), 6.67 (s, 1H), 7.03 (d, J = 15.6 Hz, 1H), 7.40 (s, 1H), 7.67 (d, J = 15.6 Hz, 1H), 9.62 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.3, 19.5, 35.3, 36.8, 115.8, 117.1, 119.2, 126.7, 128.7, 136.6, 139.1, 154.2, 166.2 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{17}NO_2$ $[M+Na]^+$ 242.1157, found 242.1153.



(*E*)-2-(4-Chlorostyryl)-4,5-dimethylphenol (3qb)

After the neutralization, the mixture was extracted with CH_2Cl_2, and the organic layers were dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by column chromatography to give the desired products as a white solid (319 mg, 62% Yield). M.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.32 (s, 3H), 4.70 (br. s, 1H), 7.04 (s, 1H), 7.22 (d, J = 15.6 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.73 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 20.2, 118.9, 122.3, 128.85, 128.89, 129.00, 129.5, 131.07, 131.10, 133.0, 139.1, 144.4, 150.2 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{15}ClO$ $[M+Na]^+$ 281.0709,

found 281.0714.

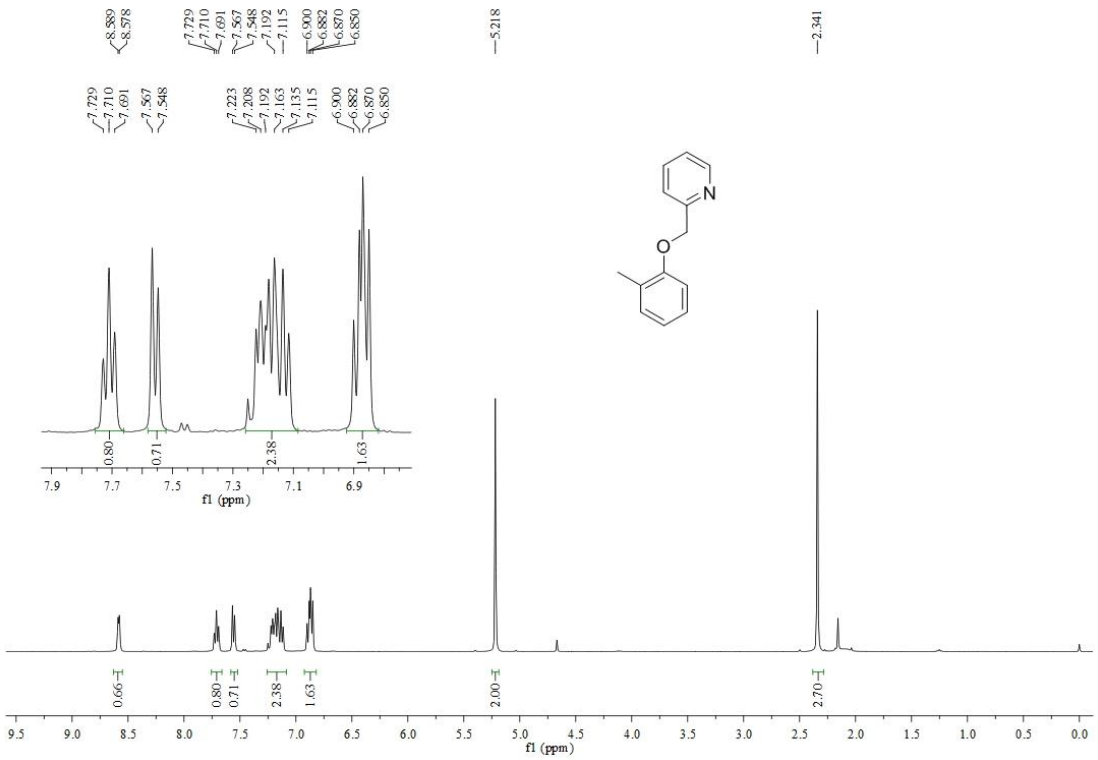
References:

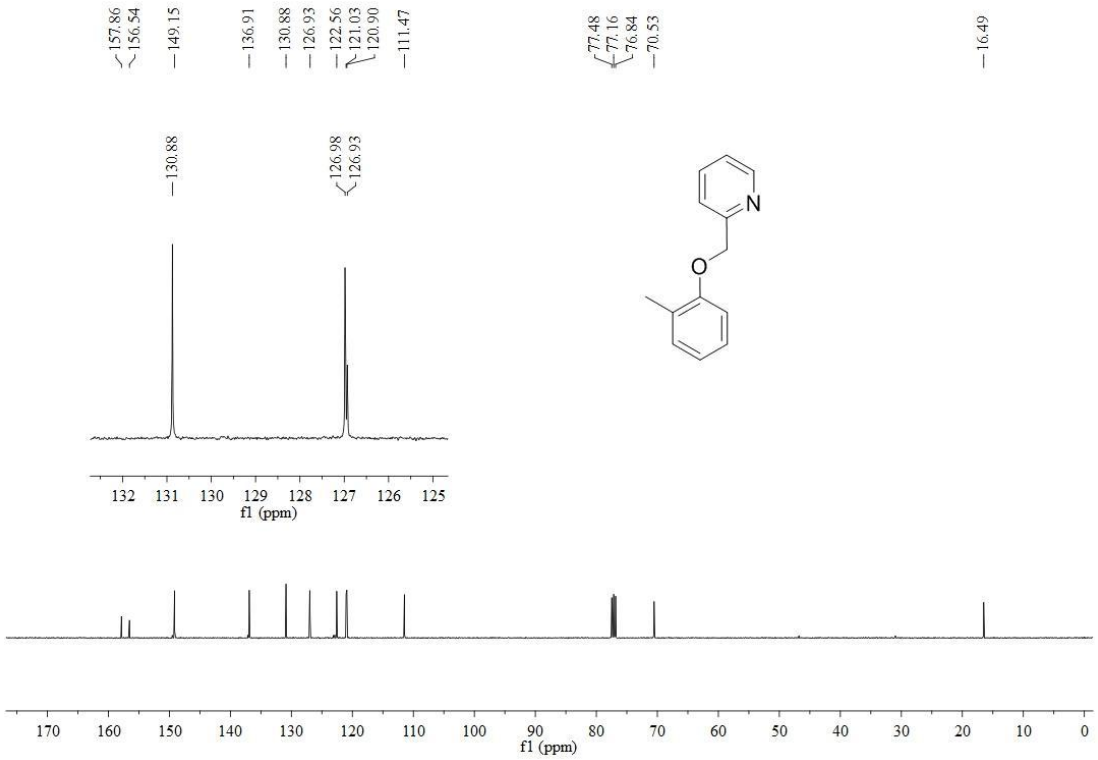
1 I. M. Pastor, P. Västilä and H. Adolfsson, *Chem. Eur. J*., **2003**, *9*, 4031.

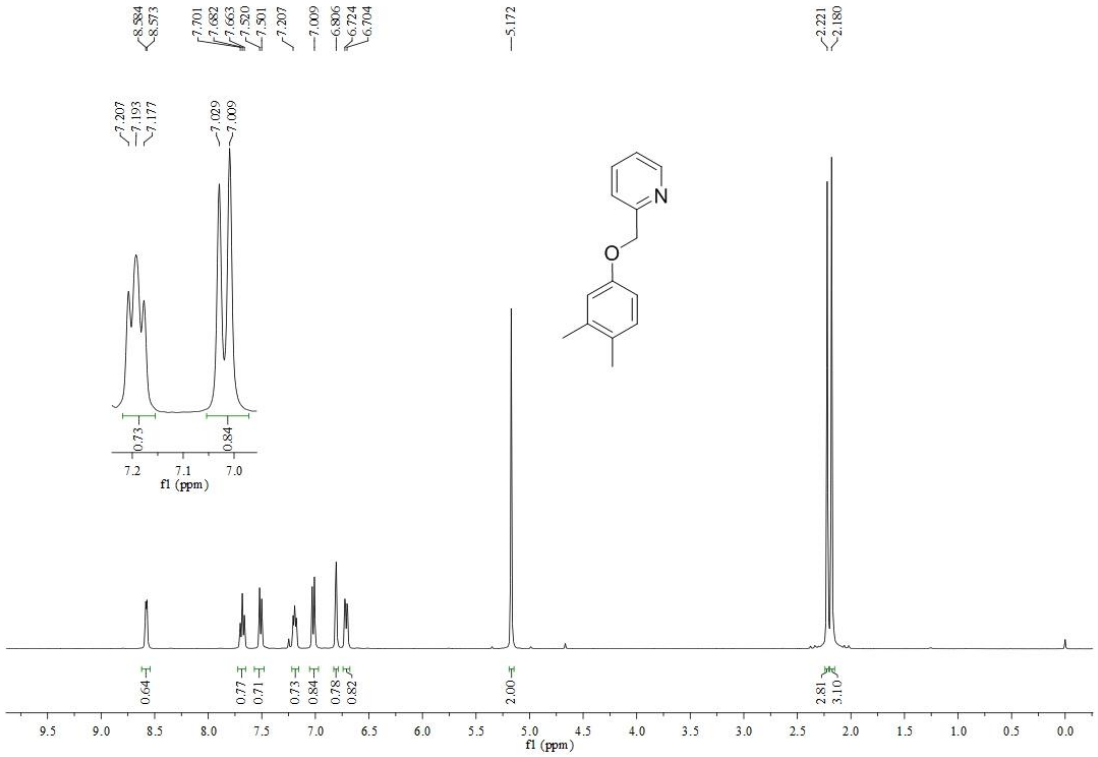
2 B.-F. Shi, N. Maugel, Y.-H. Zhang and J.-Q. Yu, *Angew. Chem. Int. Ed*., **2008**, *47*, 4882.

3 H. K. Chenault, J. Dahmer, and G. M. Whitesides, *J. Am. Chem. Soc*., **1989**, *111*, 6354.

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



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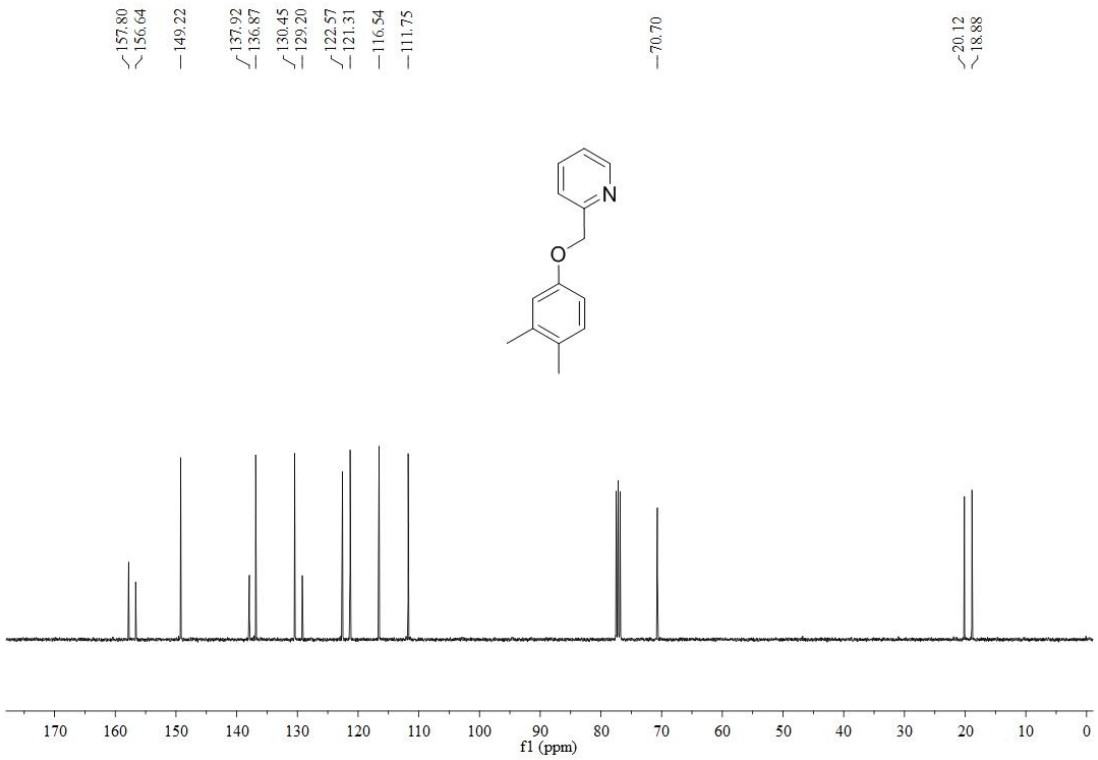
7.701
7.682
7.663
7.520
7.501
7.207
7.009
6.806
6.724
6.704
5.172
2.221
2.180
7.207
7.193
7.177
7.029
7.009
0.73
0.84
7.2
7.1
7.0
f1 (ppm)
N
O
0.64
0.77
0.71
0.73
0.84
0.78
0.82
2.00
2.81
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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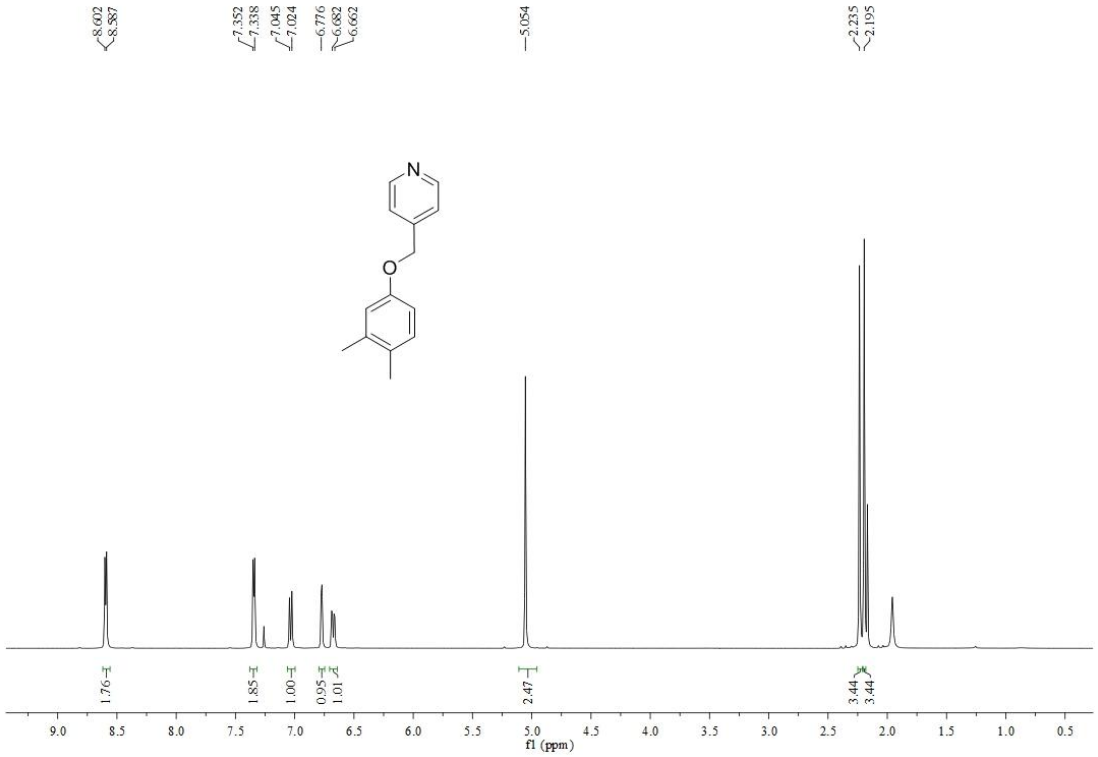
156.64
149.22
137.92
136.87
130.45
129.20
122.57
121.31
116.54
111.75
70.70
20.12
18.88
N
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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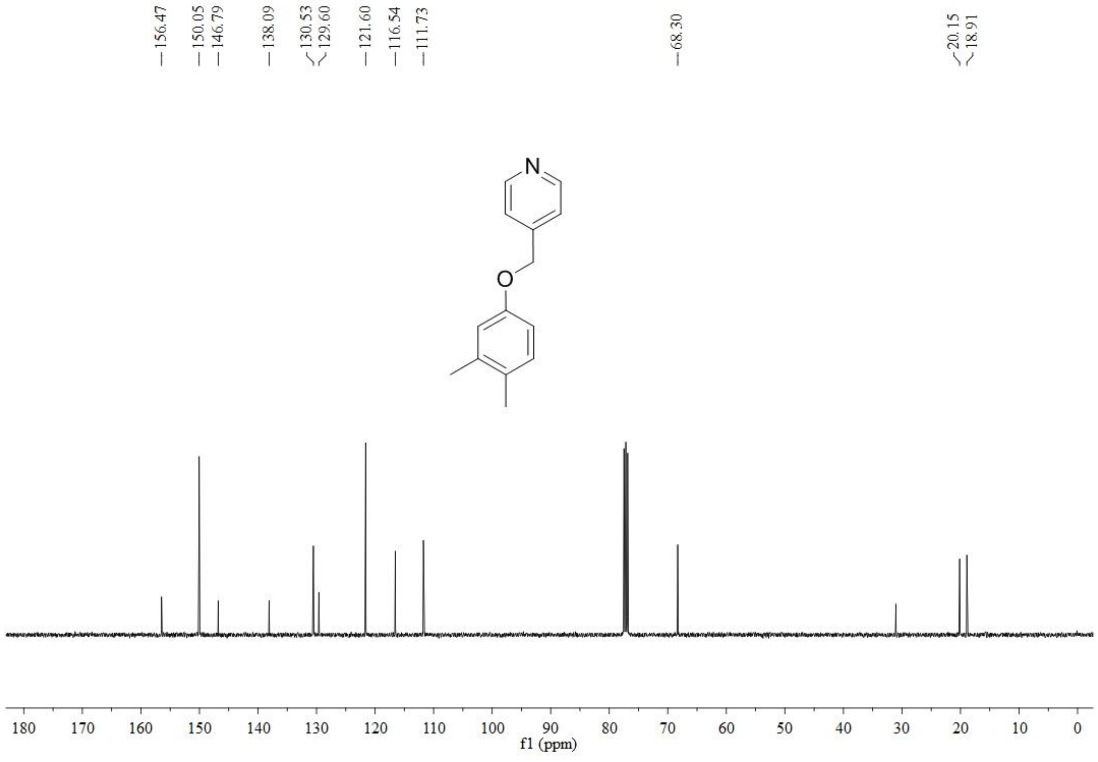
8.587
7.352
7.338
7.045
7.024
6.776
6.682
6.662
5.054
2.235
2.195
N
O
1.76
1.85
1.00
0.95
1.01
2.47
3.44
3.44
f1 (ppm)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150.05
146.79
138.09
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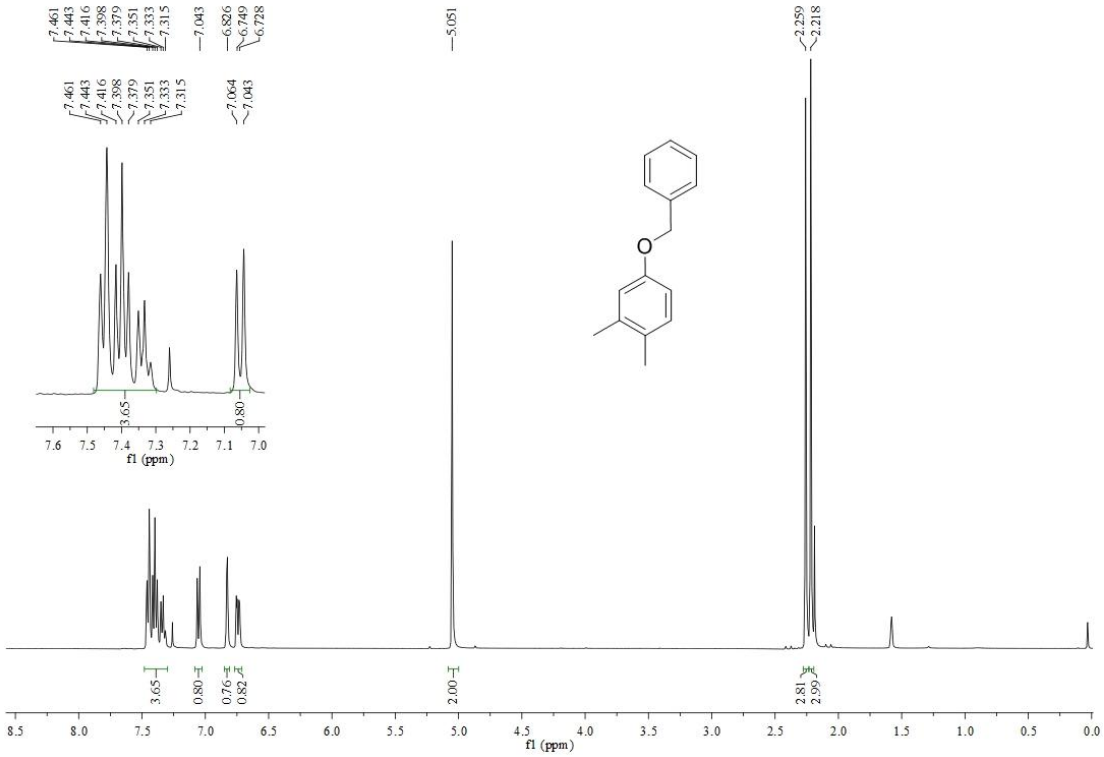
116.54
111.73
68.30
20.15
18.91
N
O
f1 (ppm)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7.416
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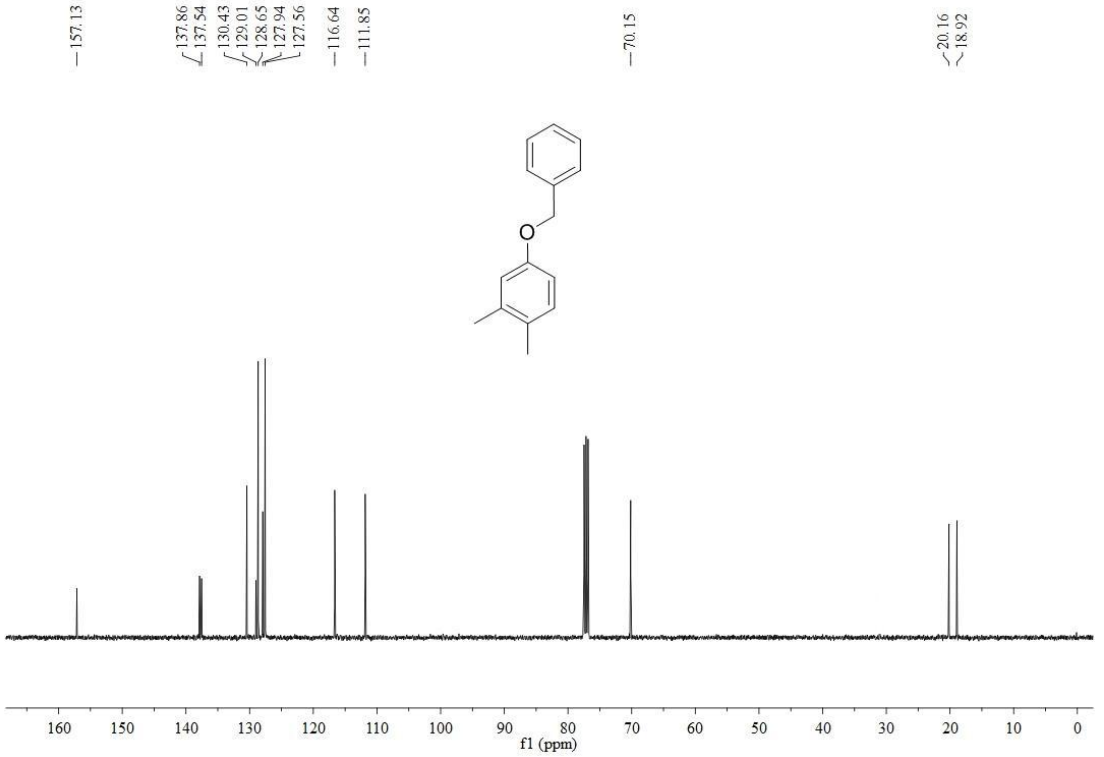
7.379
7.351
7.333
7.315
7.043
6.826
6.749
6.728
5.051
2.259
2.218
7.064
7.043
3.65
0.80
f1 (ppm)
O
3.65
0.80
0.76
0.82
2.00
2.81
2.99
f1 (ppm)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137.86
137.54
130.43
129.01
128.65
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127.56
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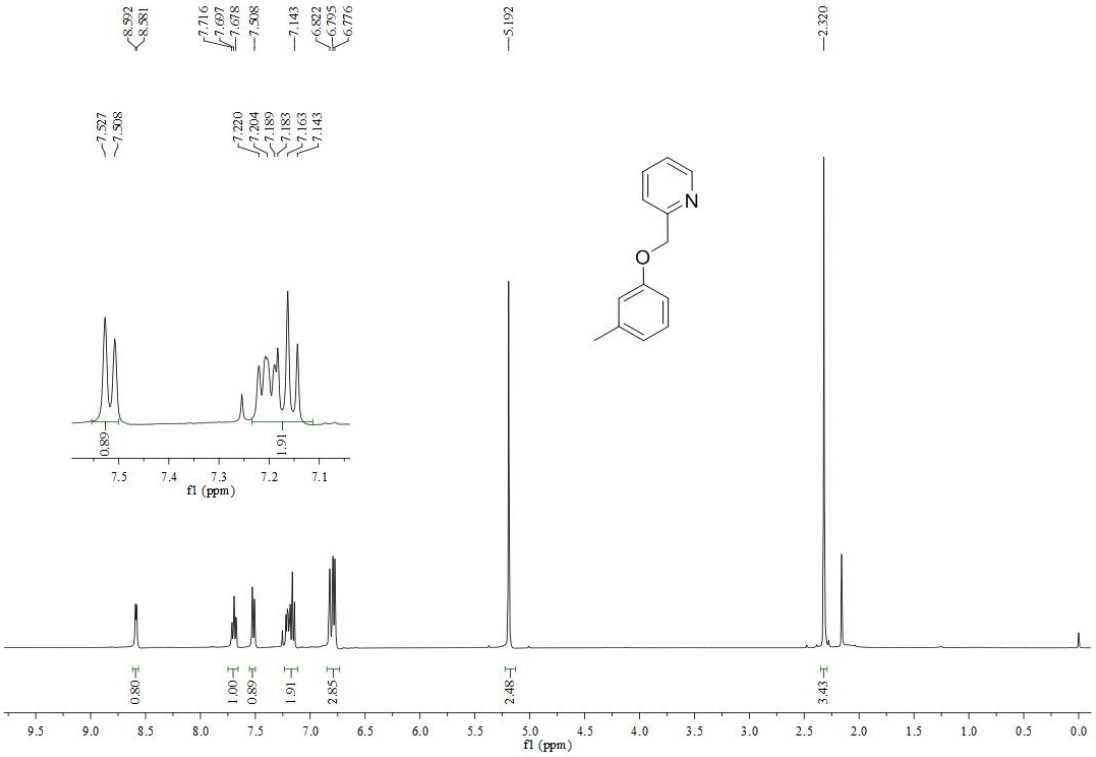
70.15
20.16
18.92
O
f1 (ppm)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7.716
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7.143
6.822
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6.776
5.192
2.320
7.527
7.508
7.220
7.204
7.189
7.183
7.163
7.143
N
O
0.89
1.91
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
0.80
1.00
0.89
1.91
2.85
2.48
3.43
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
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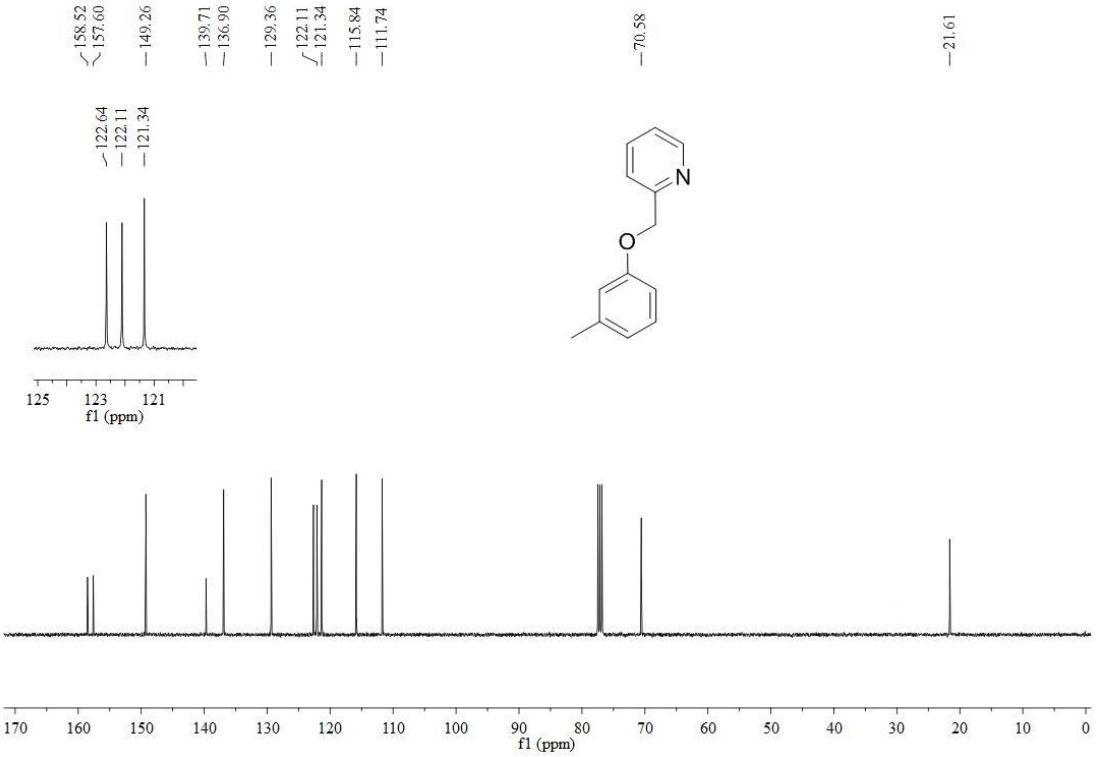
0.0
f1 (ppm)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121.34
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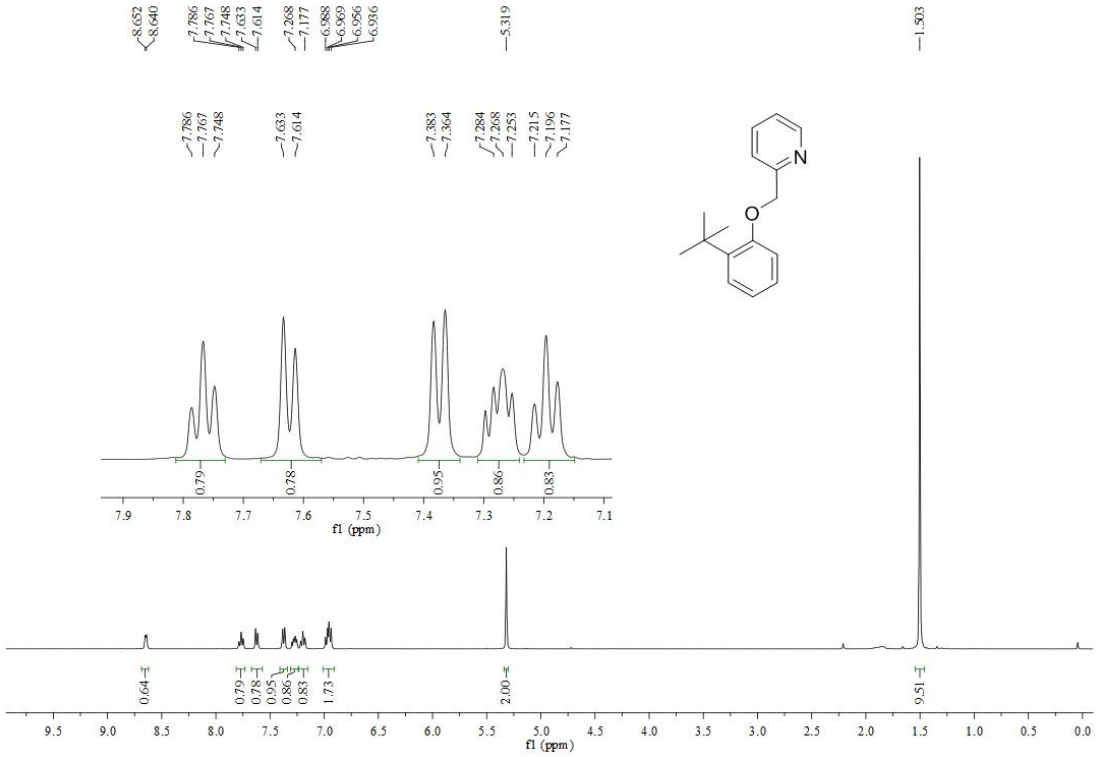
111.74
70.58
21.61
122.64
122.11
121.34
N
O
125
123
121
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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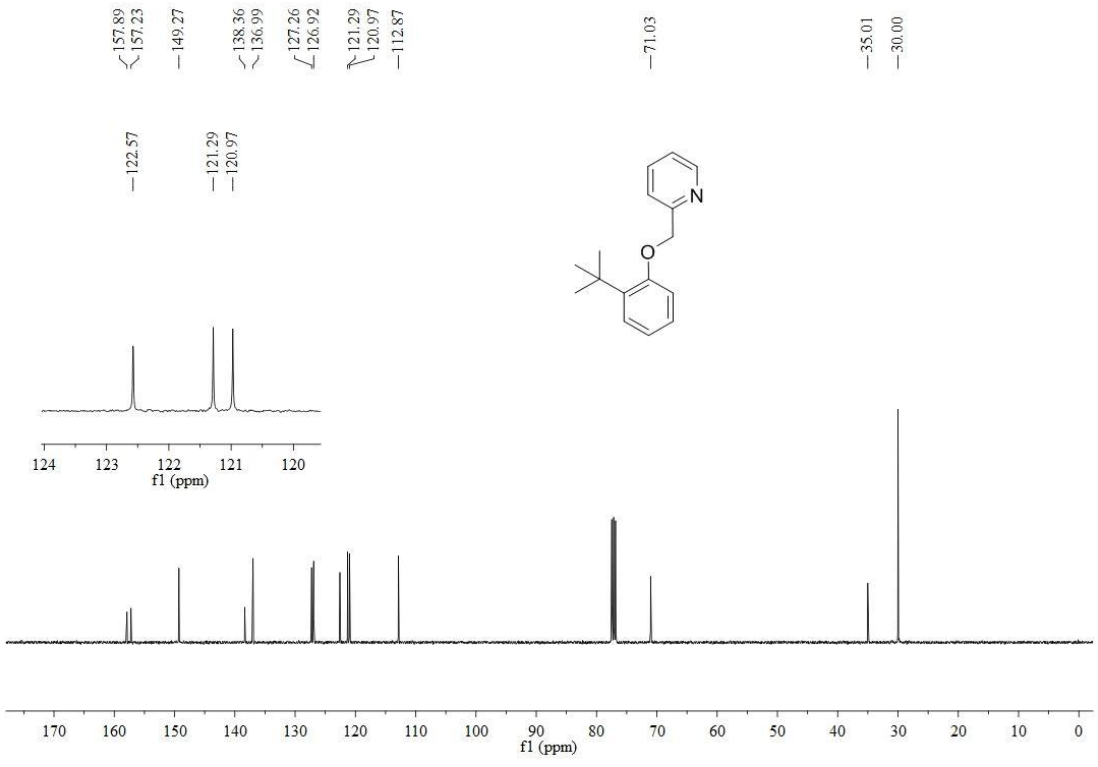
1.503
f1 (ppm)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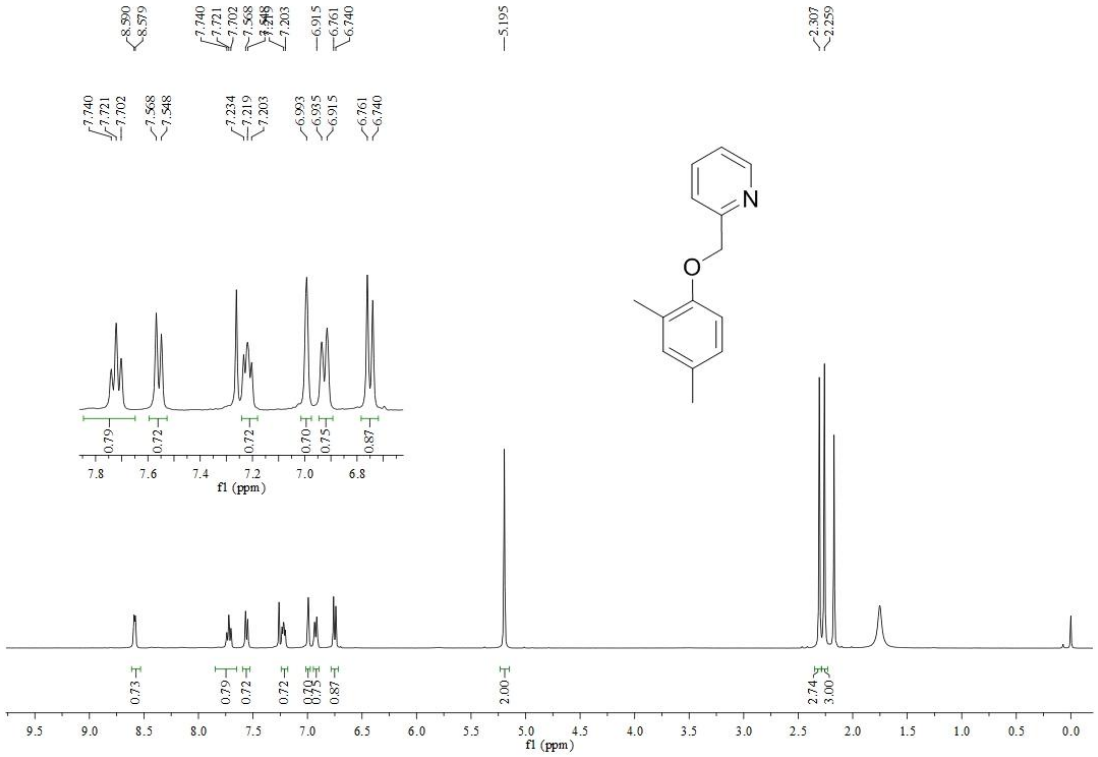
121.29
120.97
f1 (ppm)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6.740
5.195
2.307
2.259
6.993
6.935
6.915
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0.72
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0.75
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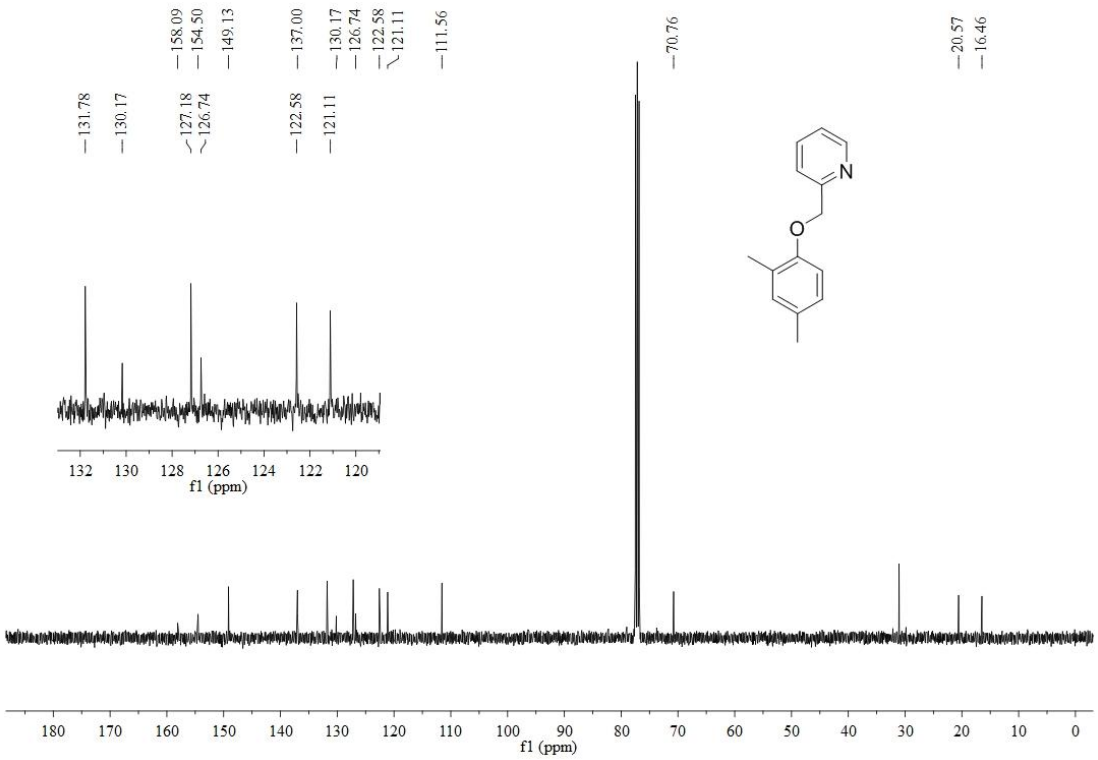
2.00
2.74
3.00
f1 (ppm)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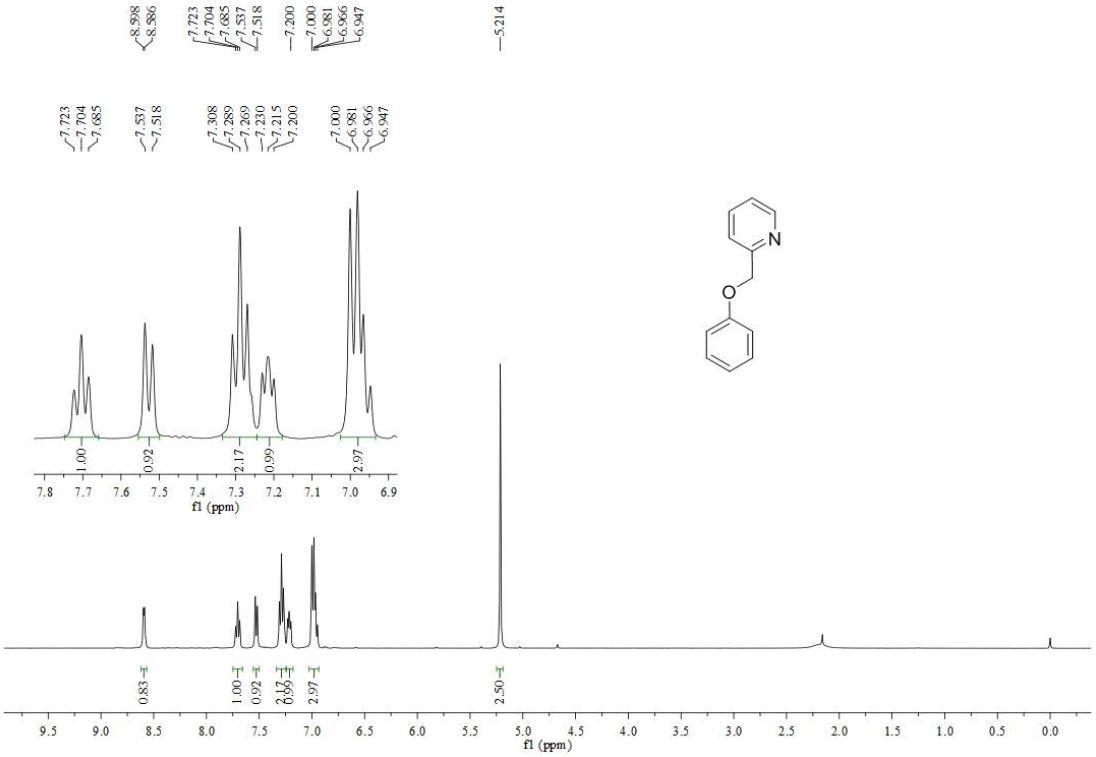
122.58
121.11
f1 (ppm)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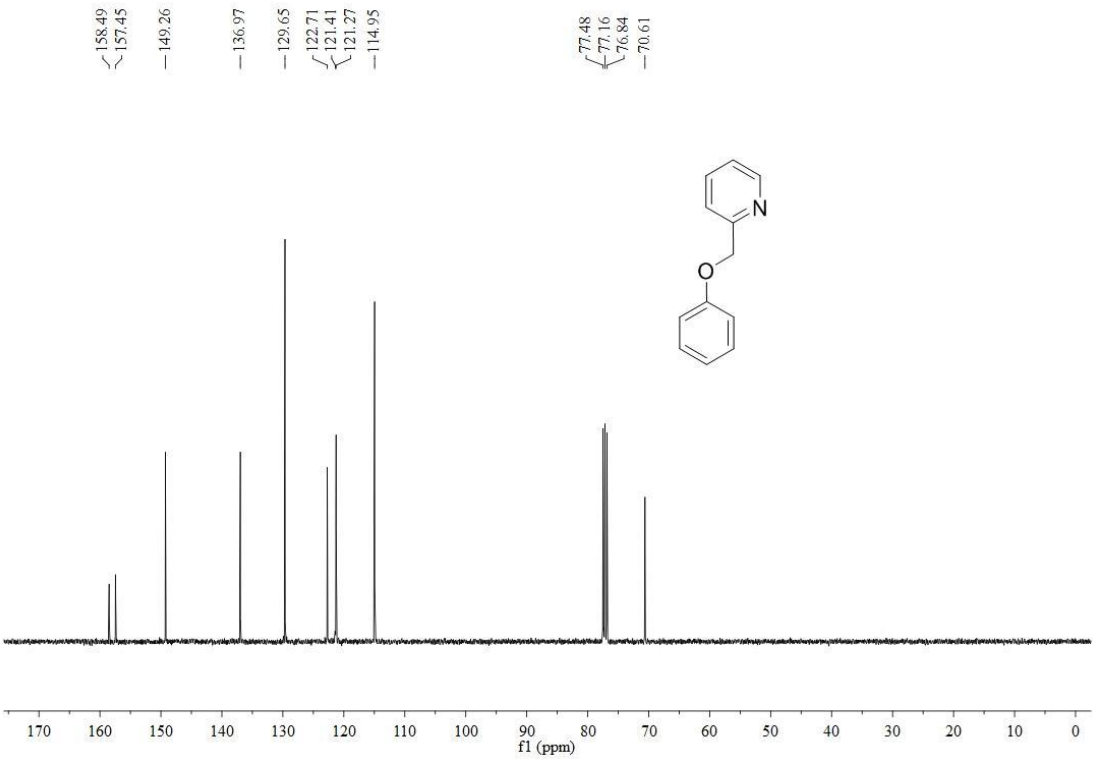
f1 (ppm)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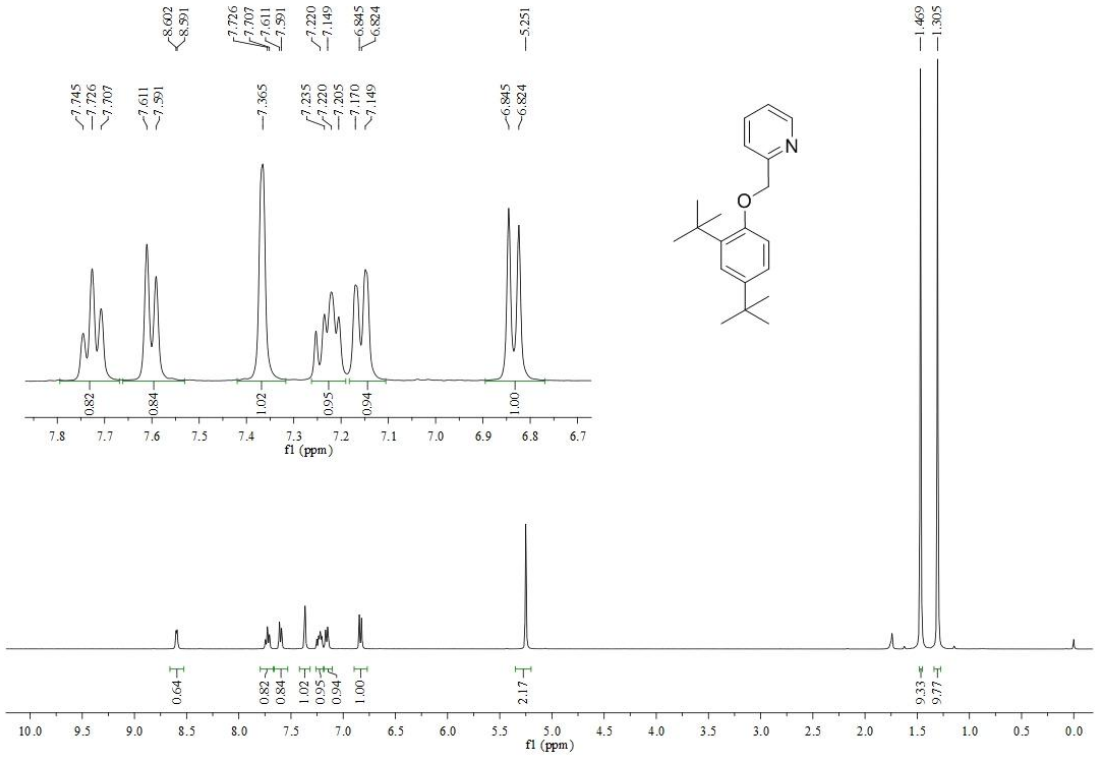
O
f1 (ppm)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7.707
7.611
7.591
7.365
7.235
7.220
7.205
7.170
7.149
6.845
6.824
N
O
0.82
0.84
1.02
0.95
0.94
1.00
f1 (ppm)
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0.84
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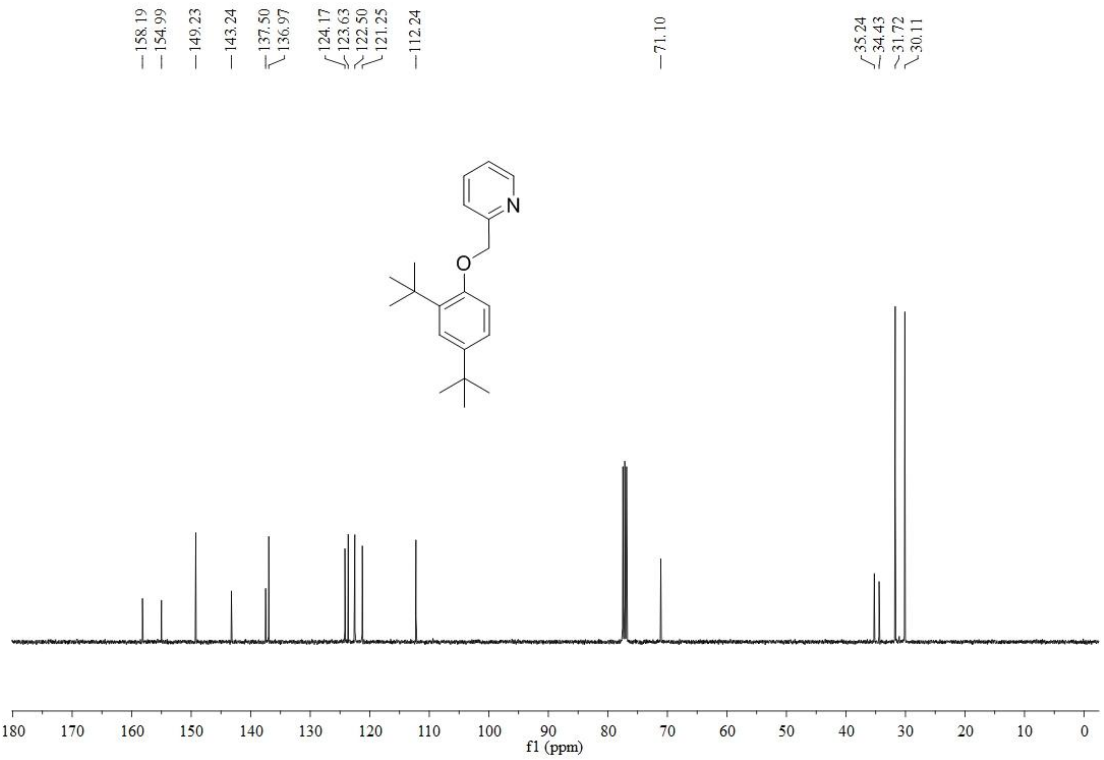
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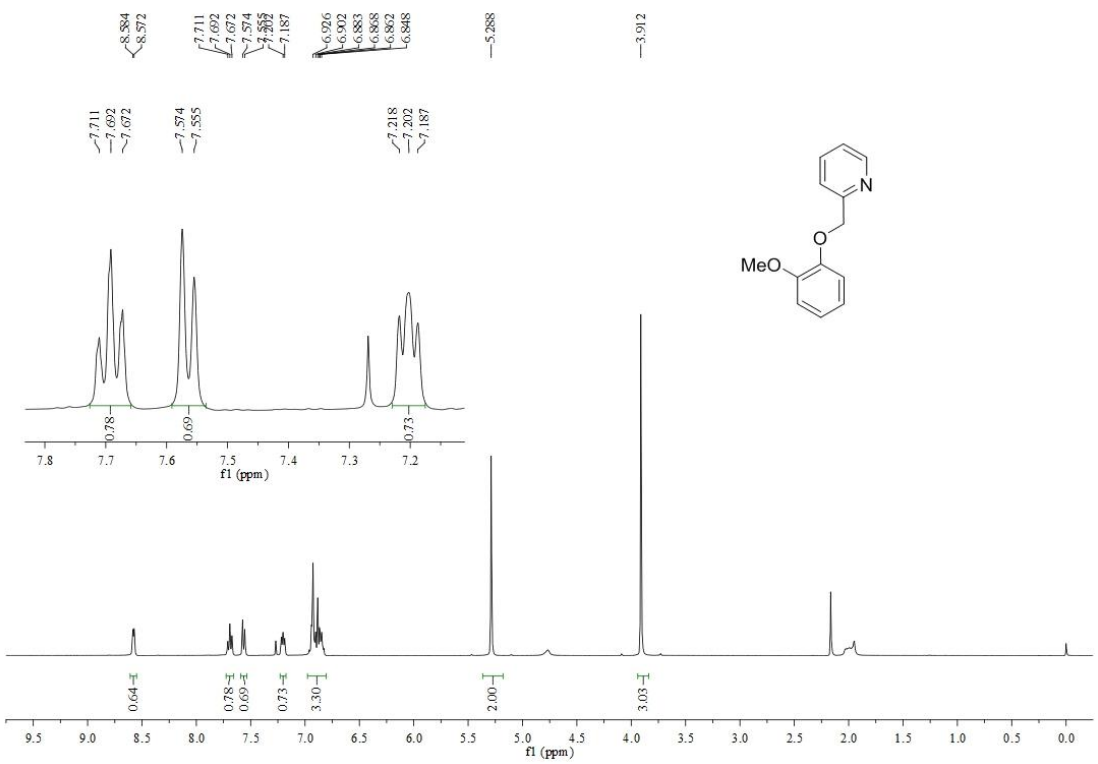
O
f1 (ppm)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6.883
6.868
6.862
6.848
5.288
3.912
N
O
MeO
0.78
0.69
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f1 (ppm)
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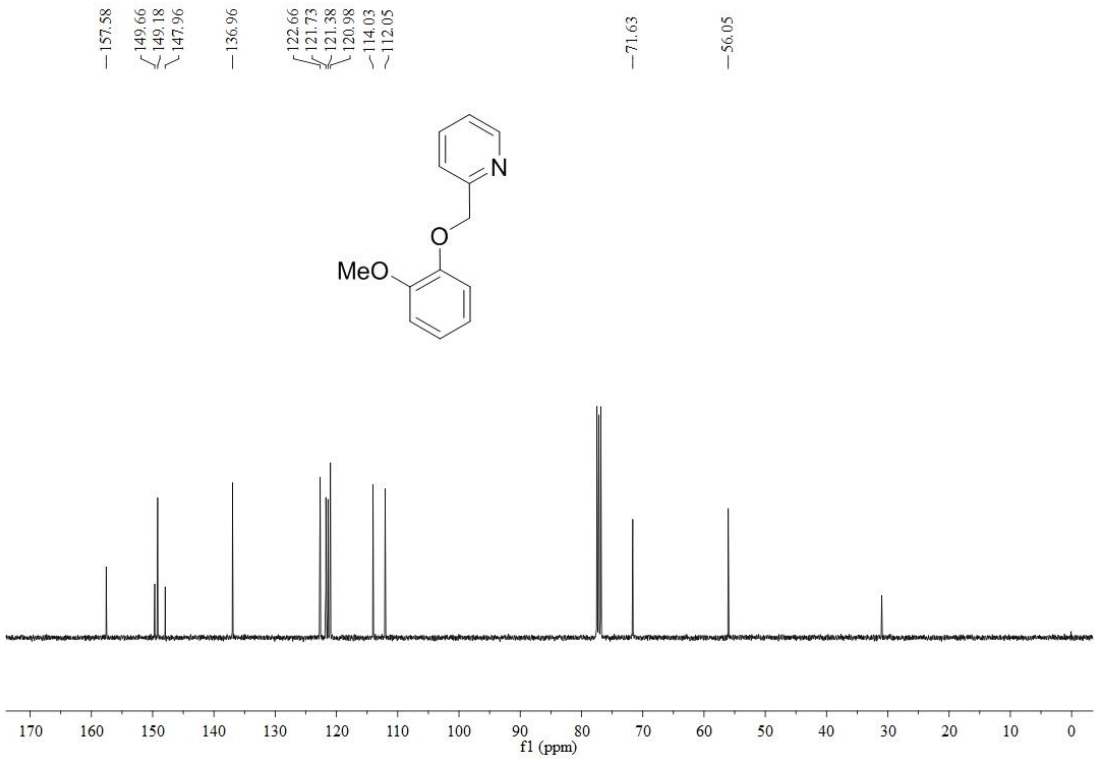
0.78
0.69
0.73
3.30
2.00
3.03
f1 (ppm)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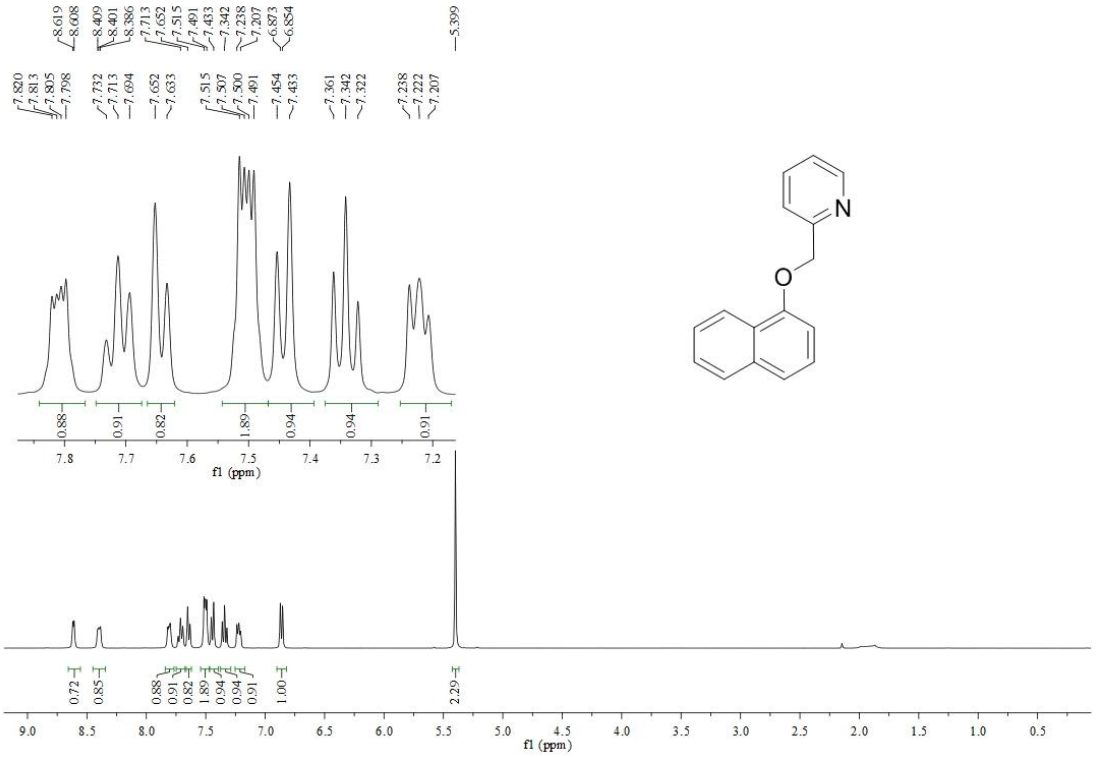
MeO
f1 (ppm)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0.91
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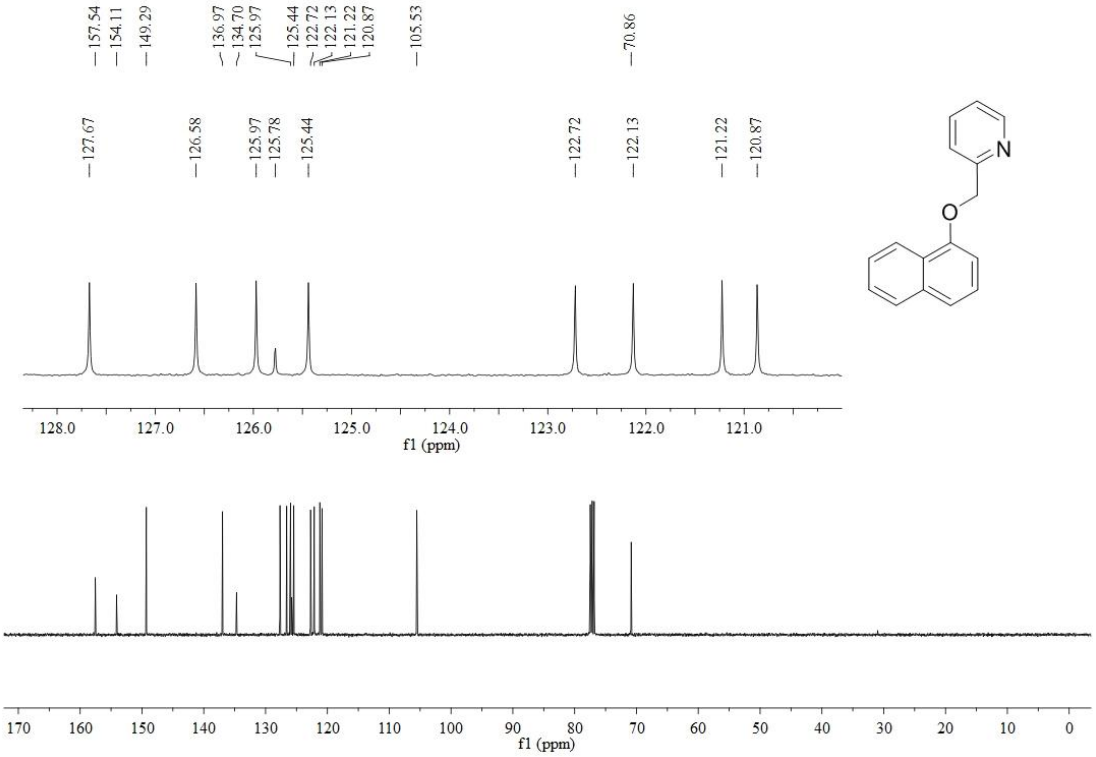
O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127.67
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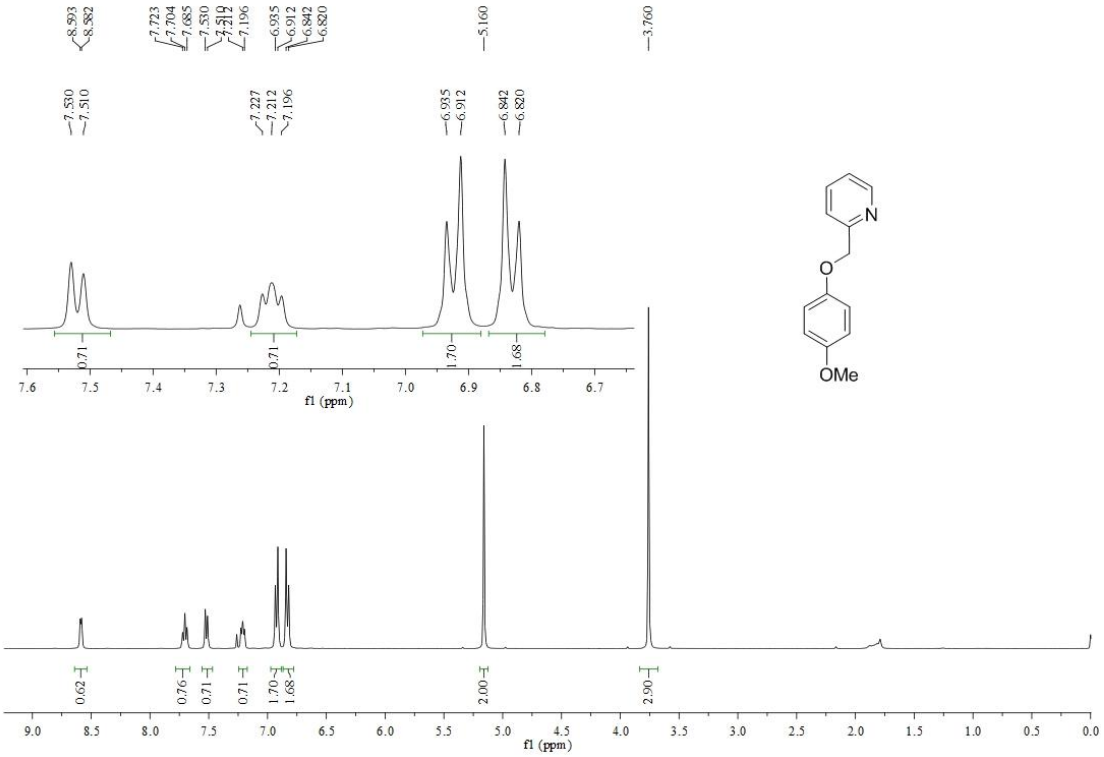
121.22
120.87
f1 (ppm)
f1 (ppm)
N
O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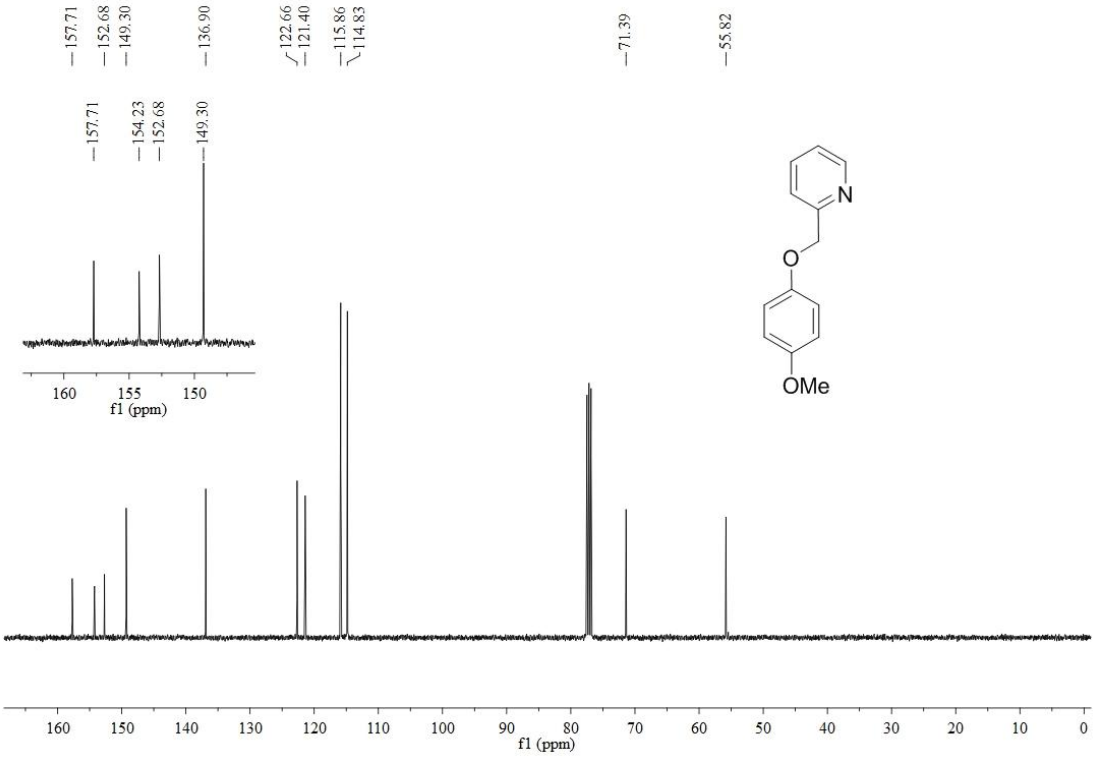
N
O
OMe
f1 (ppm)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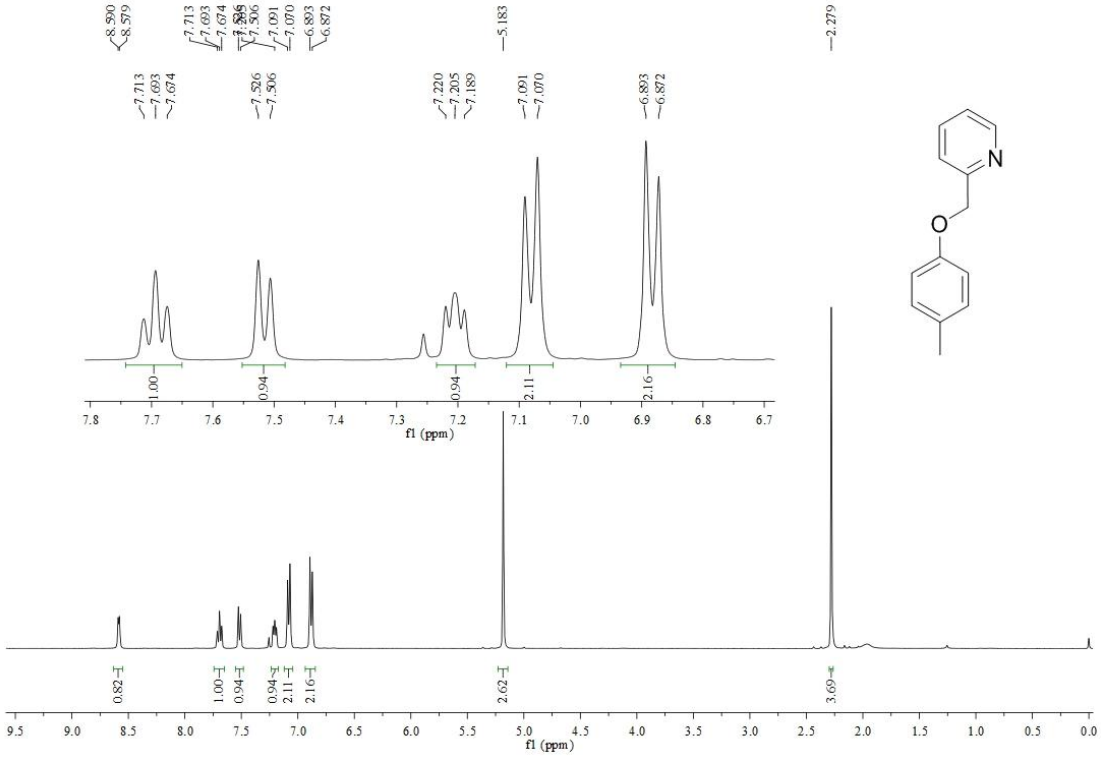
OMe
f1 (ppm)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6.893
6.872
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2.279
N
O
1.00
0.94
0.94
2.11
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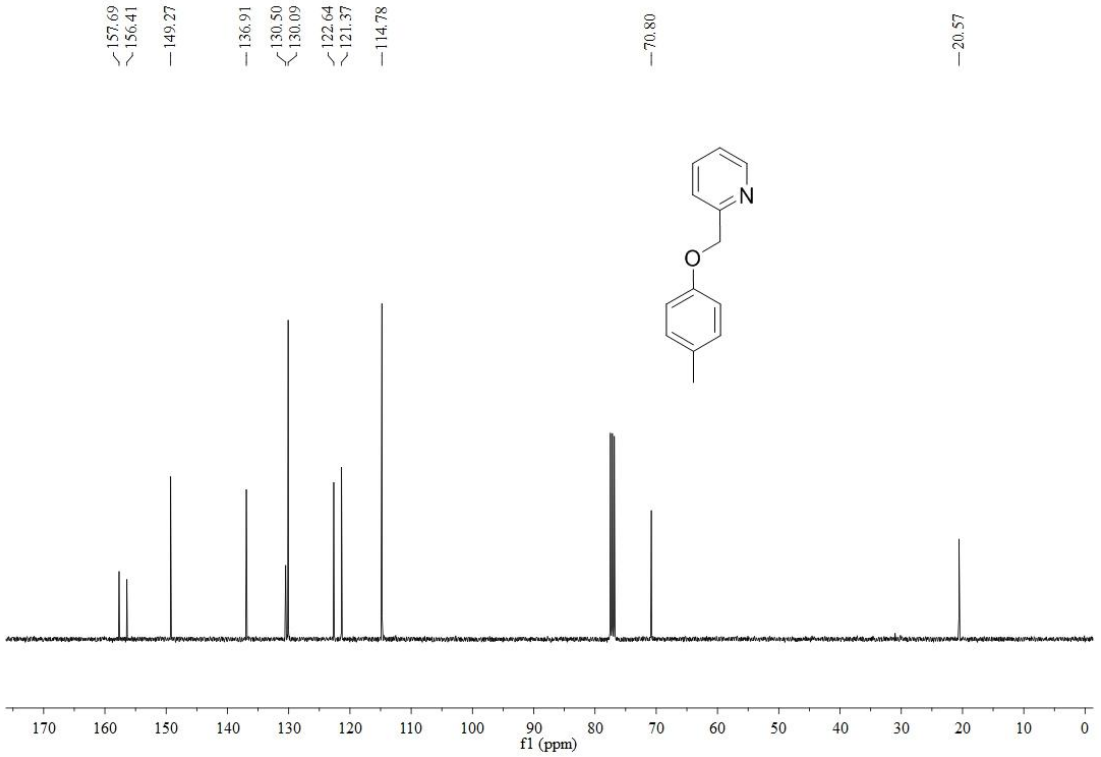
3.69
f1 (ppm)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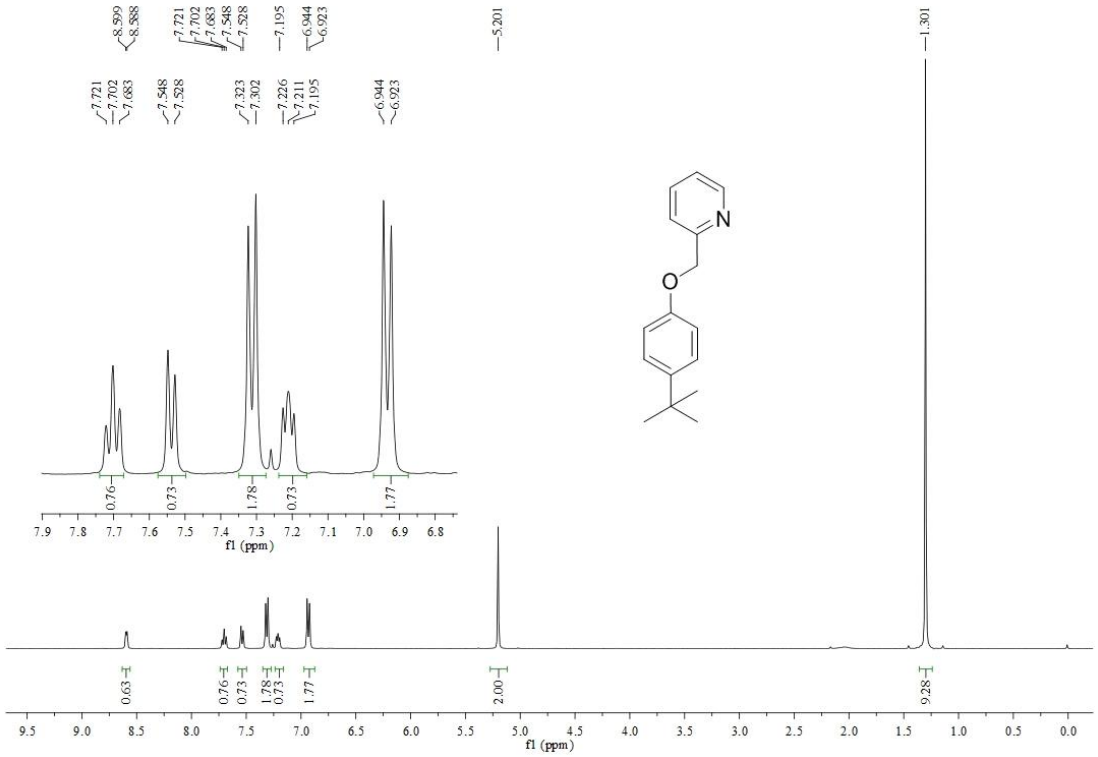
O
f1 (ppm)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N
O
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0.73
1.78
0.73
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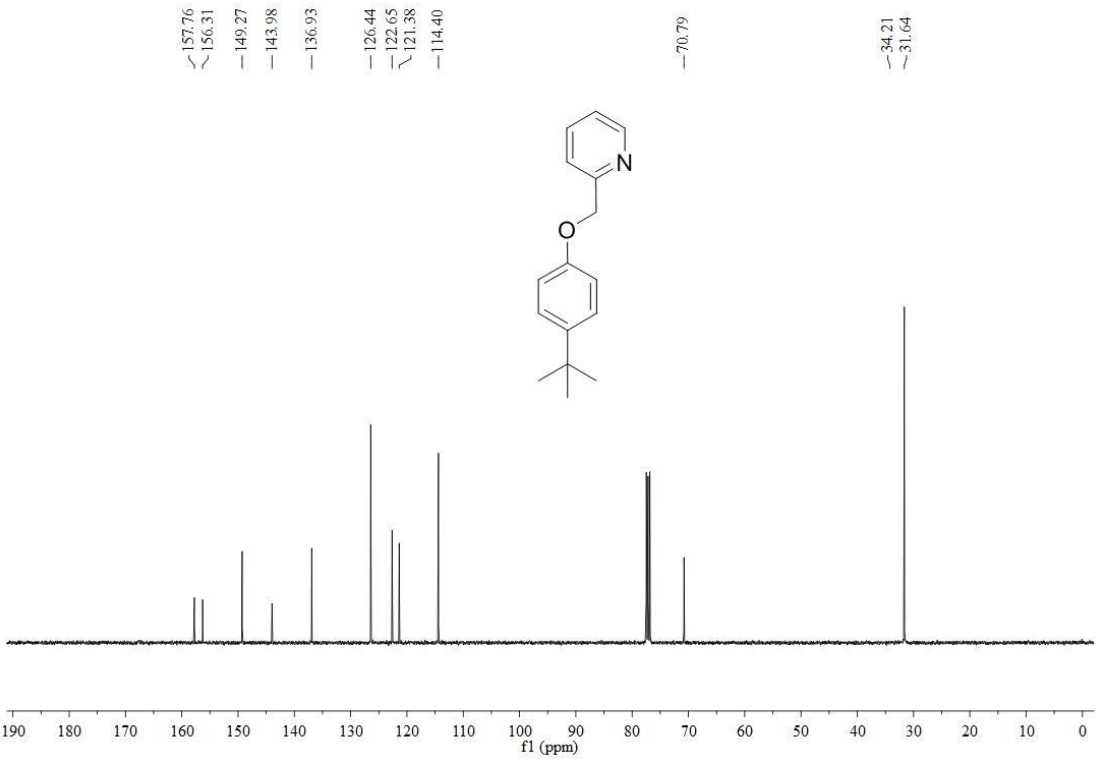
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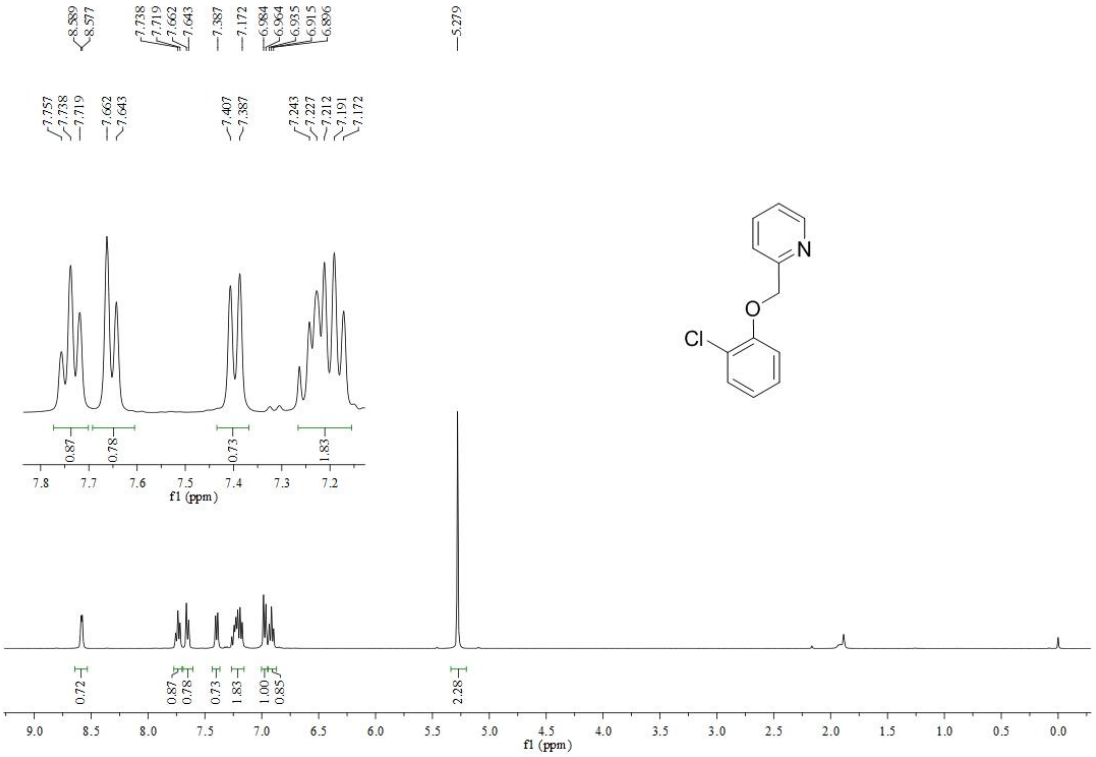
f1 (ppm)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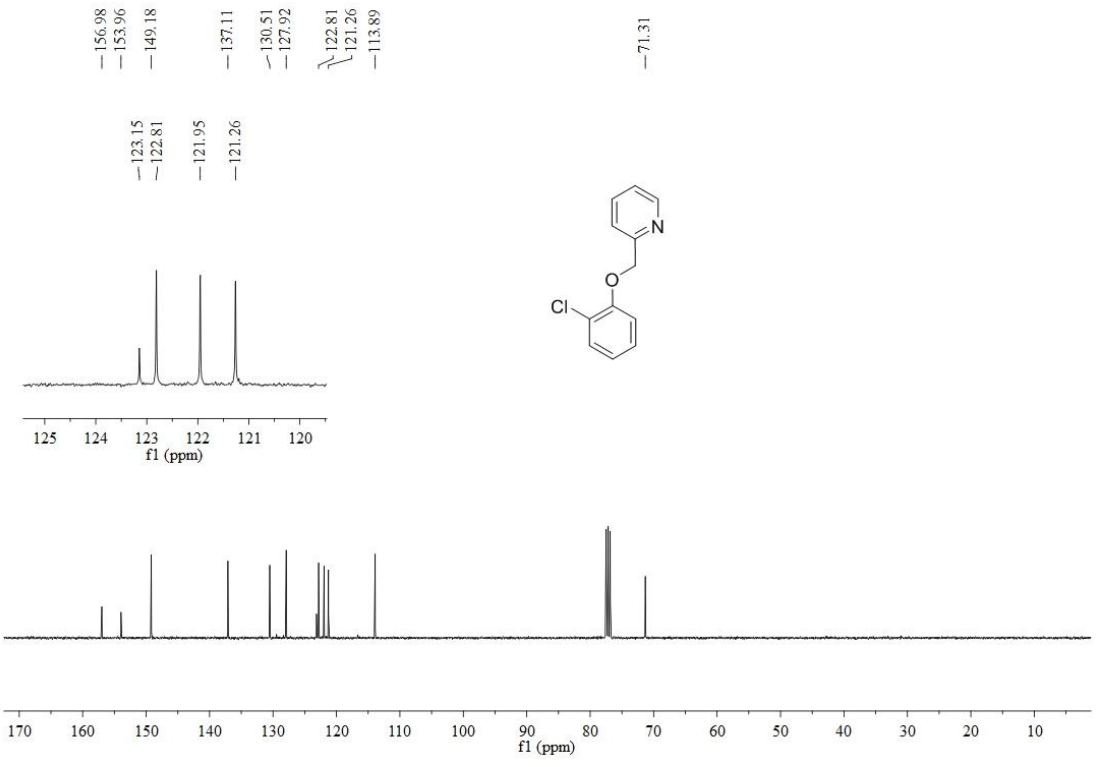
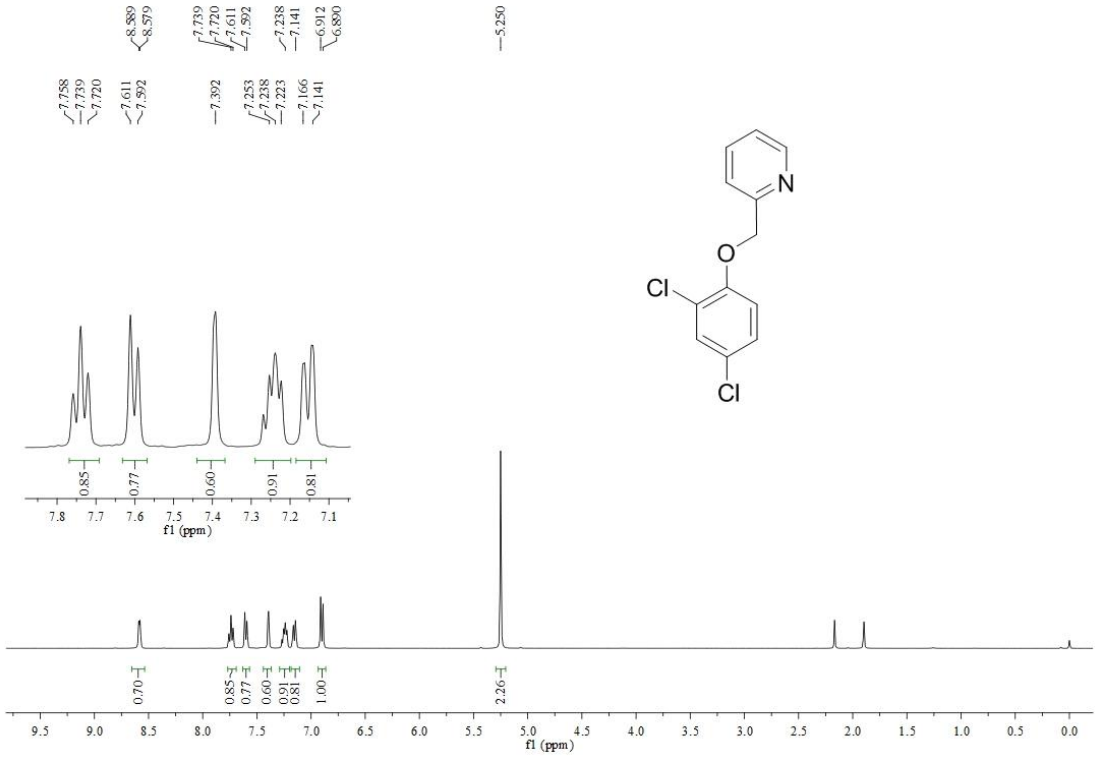
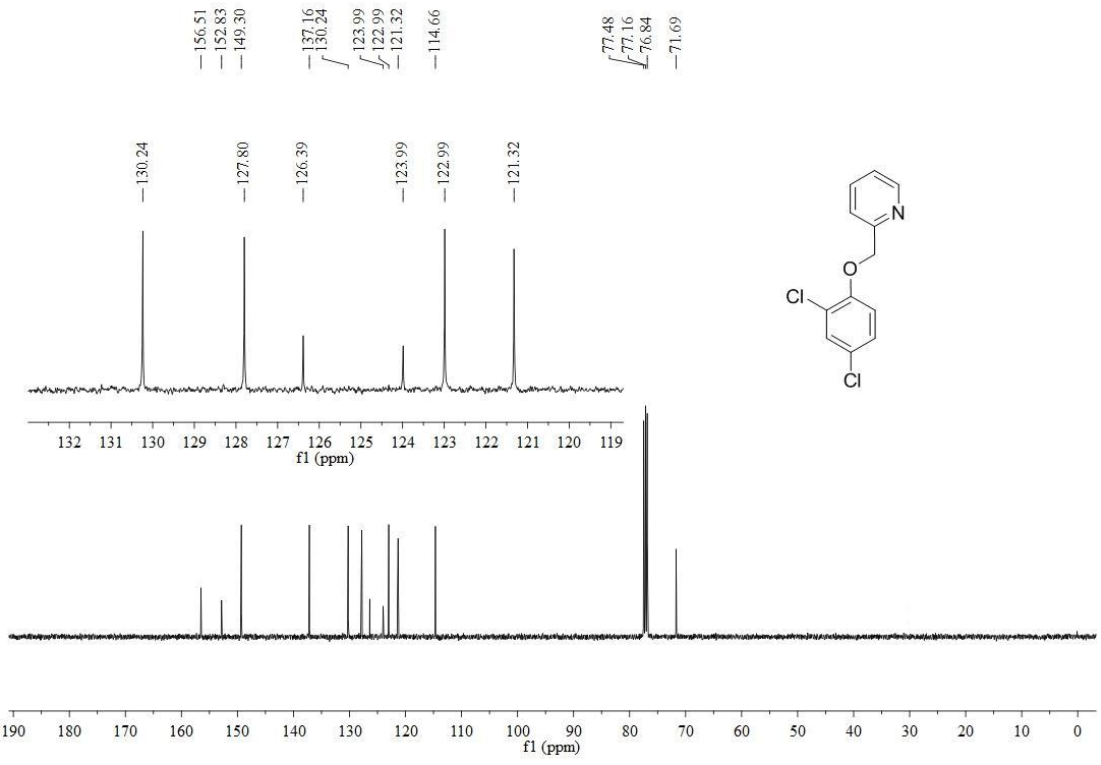
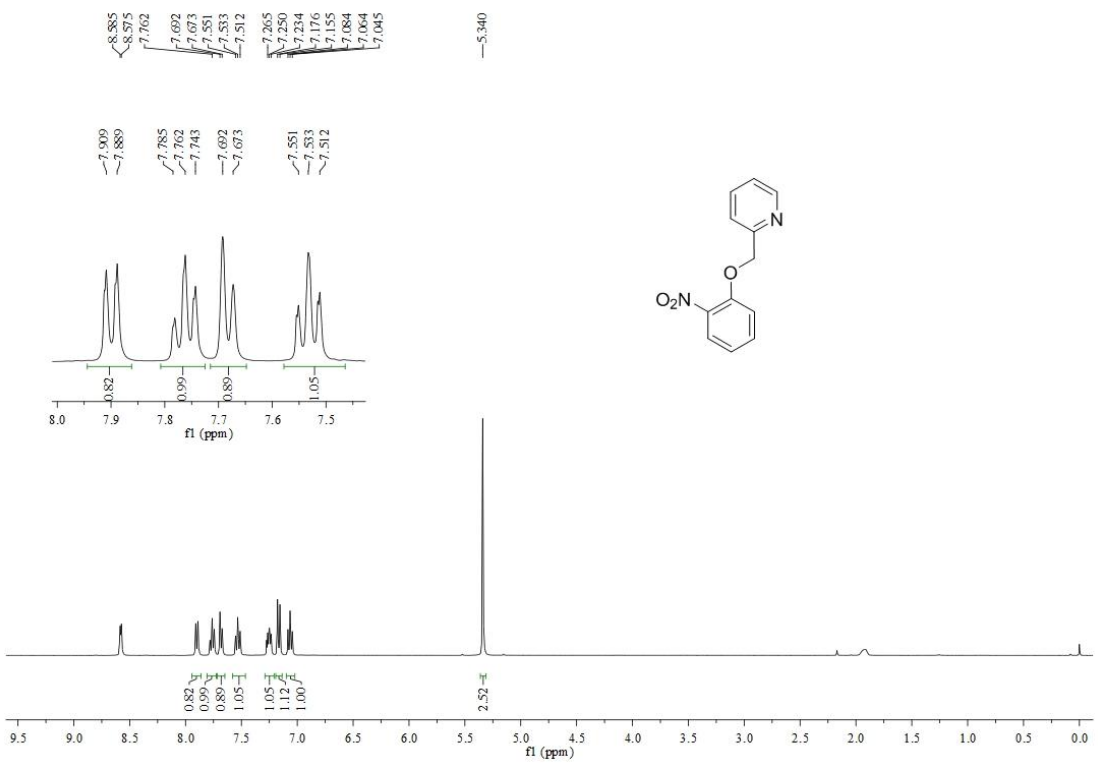
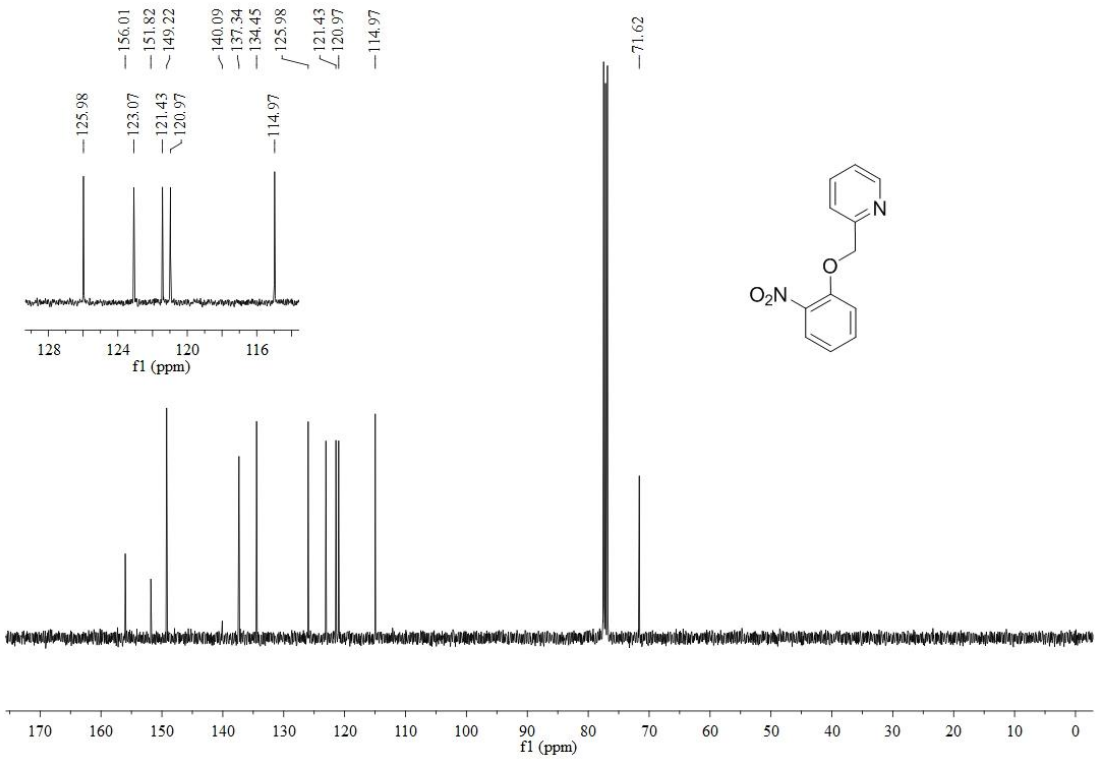
7.662
7.643
7.387
7.172
6.984
6.964
6.935
6.915
6.896
5.279
7.757
7.738
7.719
7.662
7.643
7.407
7.387
7.243
7.227
7.212
7.191
7.172
N
O
Cl
0.87
0.78
0.73
1.83
f1 (ppm)
0.72
0.87
0.78
0.73
1.83
1.00
0.85
2.28
f1 (ppm)

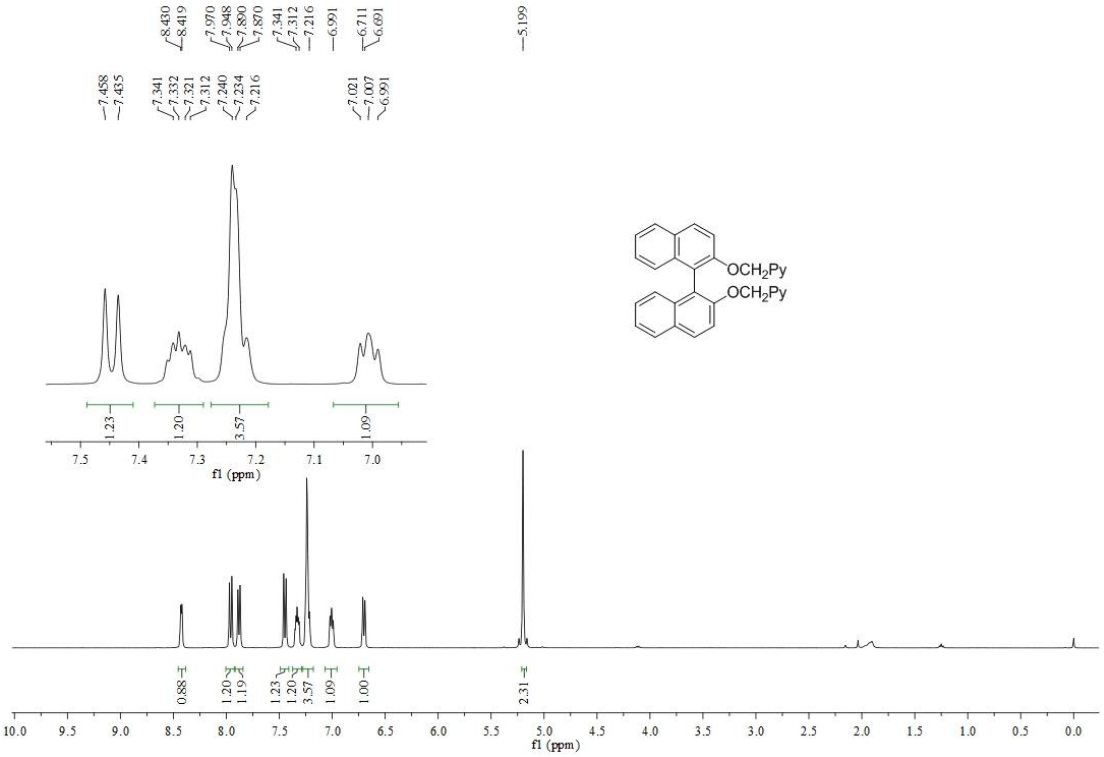

156.98
153.96
149.18
137.11
130.51
127.92
122.81
121.26
113.89
71.31
123.15
122.81
121.95
121.26
N
O
Cl
f1 (ppm)
f1 (ppm)

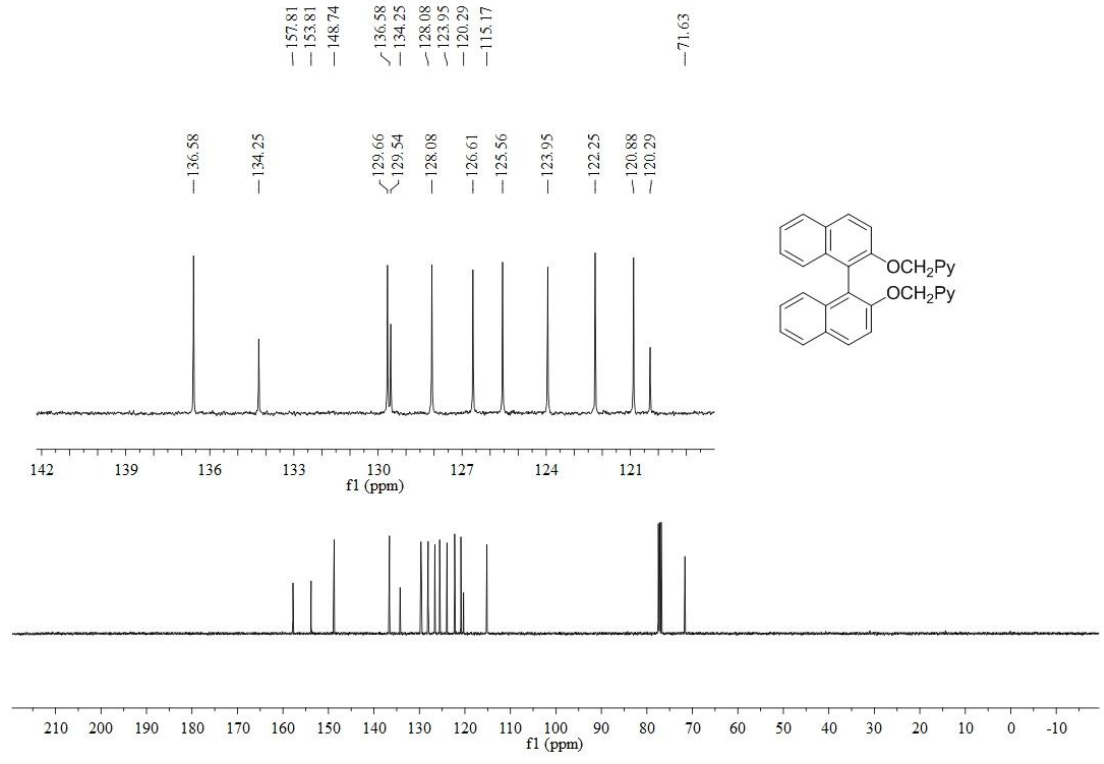

8.589
8.579
7.739
7.720
7.611
7.592
7.238
7.141
6.912
6.890
5.250
7.758
7.739
7.720
7.611
7.592
7.392
7.253
7.238
7.223
7.166
7.141
N
O
Cl
Cl
0.85
0.77
0.60
0.91
0.81
f1 (ppm)
0.70
0.85
0.77
0.60
0.91
0.81
1.00
2.26
f1 (ppm)

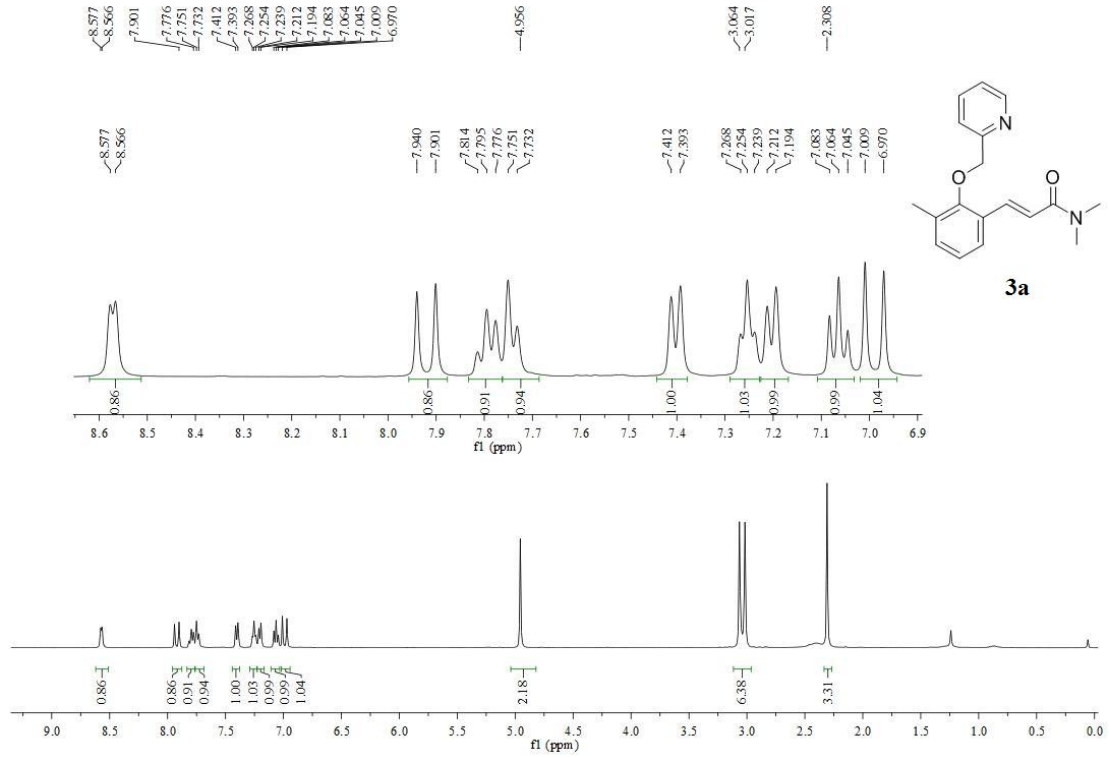

156.51
152.83
149.30
137.16
130.24
123.99
122.99
121.32
114.66
77.48
77.16
76.84
71.69
130.24
127.80
126.39
123.99
122.99
121.32
N
O
Cl
Cl
f1 (ppm)
f1 (ppm)

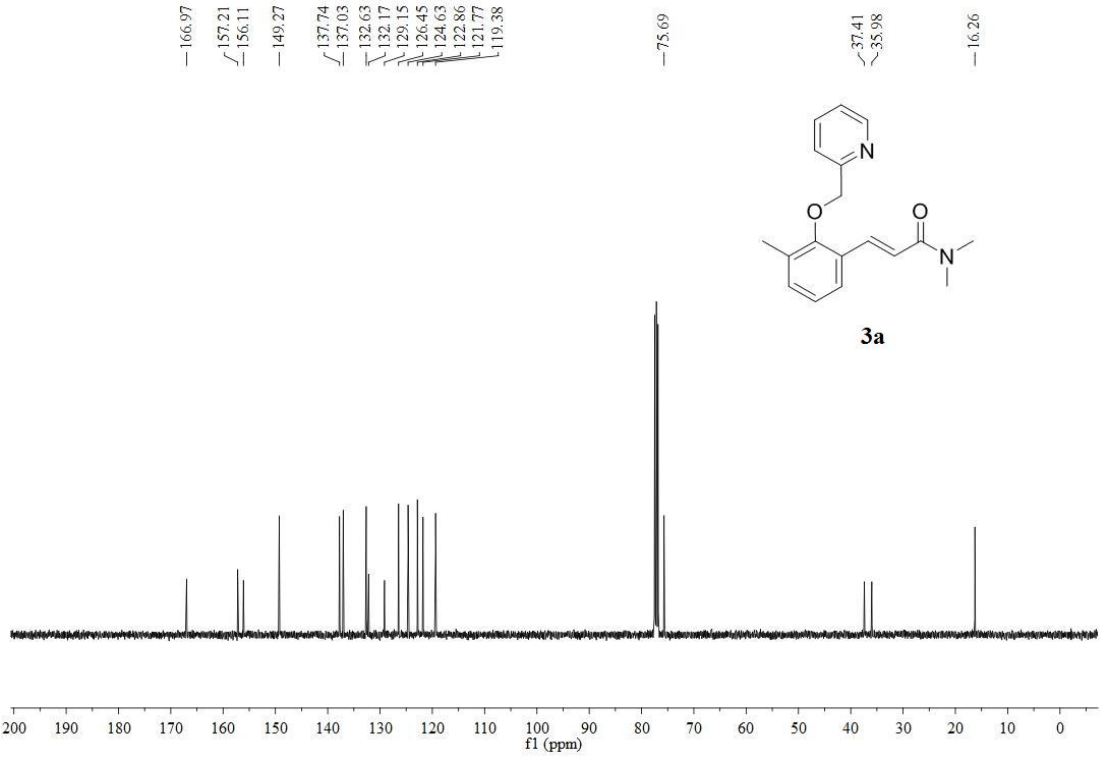

8.585
8.575
7.762
7.692
7.673
7.551
7.533
7.512
7.265
7.250
7.234
7.176
7.155
7.084
7.064
7.045
5.340
7.909
7.889
7.785
7.762
7.743
7.692
7.673
7.551
7.533
7.512
0.82
0.99
0.89
1.05
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
N
O
O2N
0.82
0.99
0.89
1.05
1.05
1.12
1.00
2.52
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

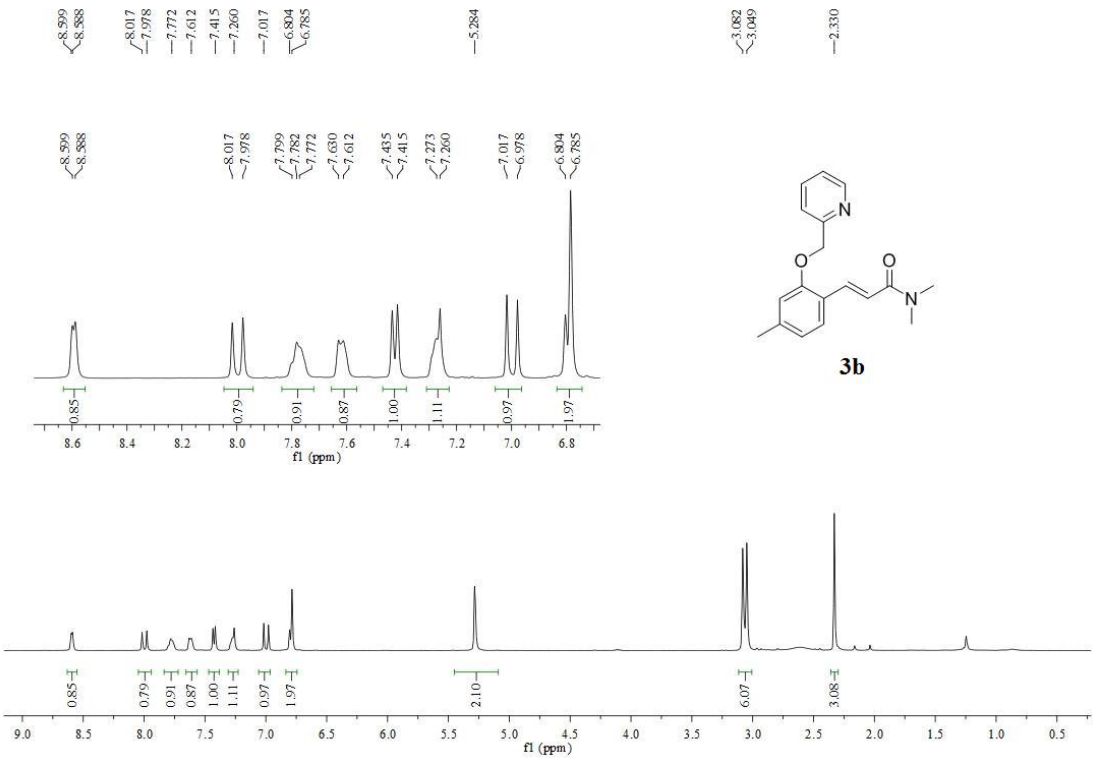

156.01
151.82
149.22
140.09
137.34
134.45
125.98
121.43
120.97
114.97
71.62
125.98
123.07
121.43
120.97
114.97
128
124
120
116
f1 (ppm)
N
O
O2N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

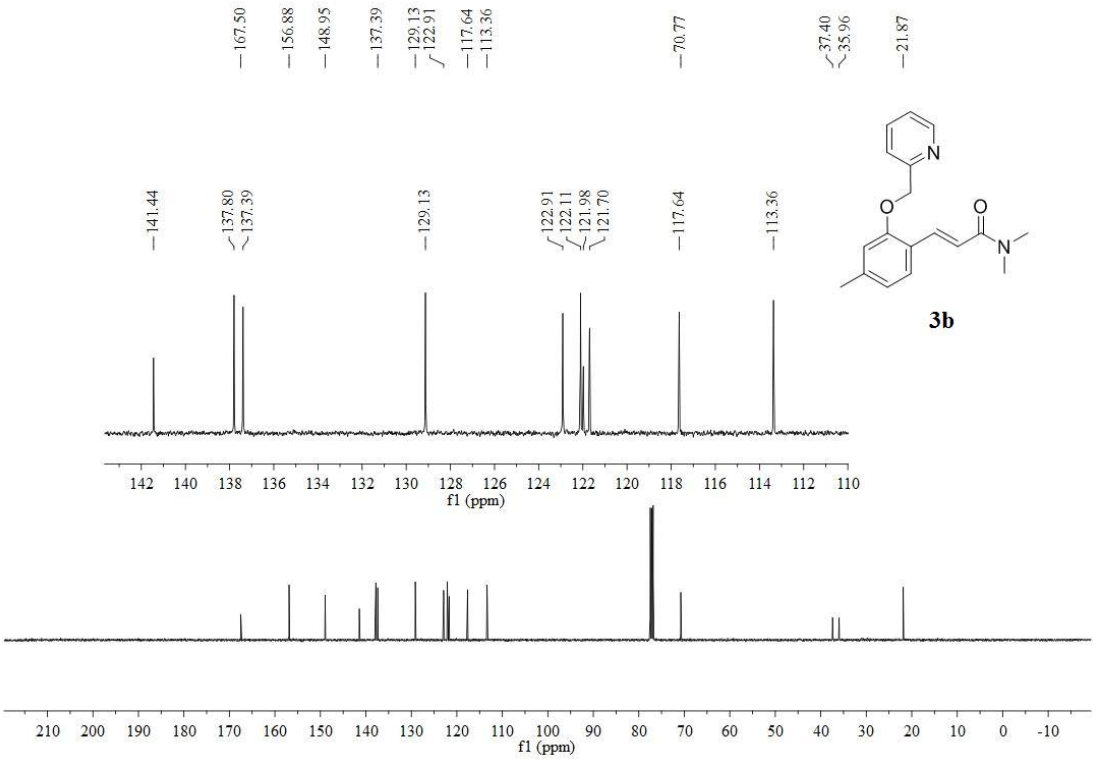

8.430
8.419
7.970
7.948
7.890
7.870
7.341
7.312
7.216
6.991
6.711
6.691
5.199
7.458
7.435
7.341
7.332
7.321
7.312
7.240
7.234
7.216
7.021
7.007
6.991
OCH2Py
OCH2Py
1.23
1.20
3.57
1.09
f1 (ppm)
0.88
1.20
1.19
1.23
1.20
3.57
1.09
1.00
2.31
f1 (ppm)

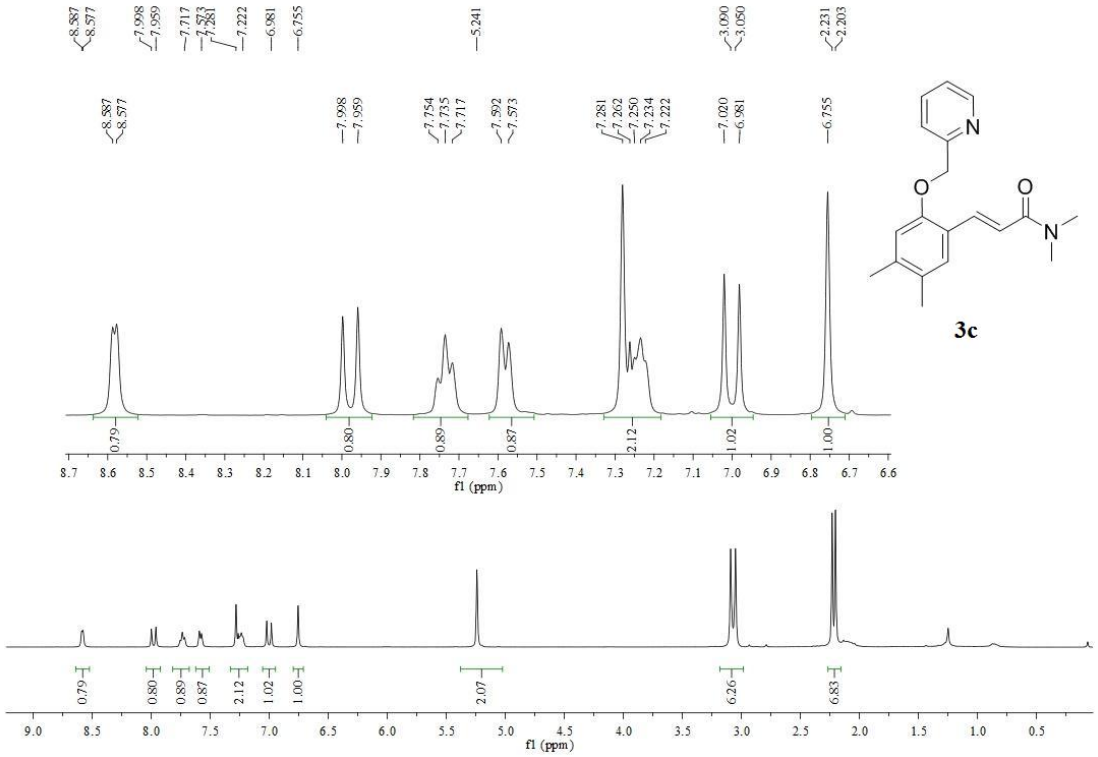

157.81
153.81
148.74
136.58
134.25
128.08
123.95
120.29
115.17
71.63
136.58
134.25
129.66
129.54
128.08
126.61
125.56
123.95
122.25
120.88
120.29
OCH2Py
OCH2Py
f1 (ppm)
f1 (ppm)

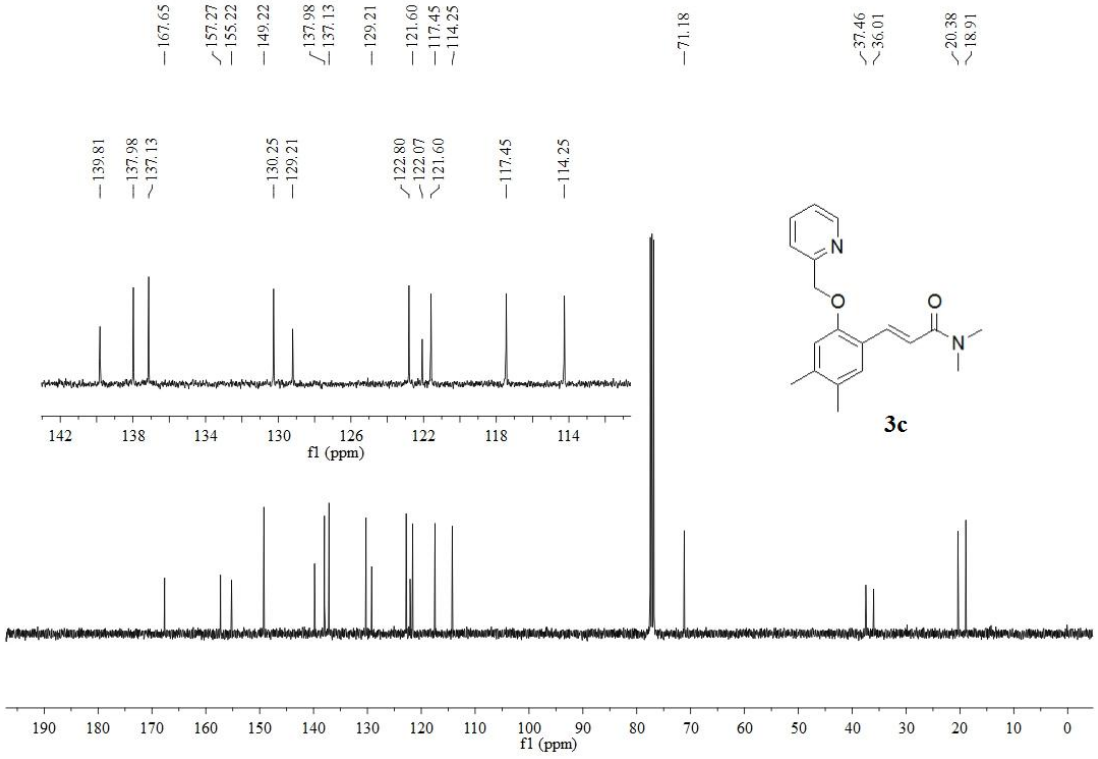

8.577
8.566
7.901
7.776
7.751
7.732
7.412
7.393
7.268
7.254
7.239
7.212
7.194
7.083
7.064
7.045
7.009
6.970
4.956
3.064
3.017
2.308
7.940
7.901
7.814
7.795
7.776
7.751
7.732
7.412
7.393
7.268
7.254
7.239
7.212
7.194
7.083
7.064
7.045
7.009
6.970
0.86
0.86
0.91
0.94
1.00
1.03
0.99
0.99
1.04
f1 (ppm)
0.86
0.86
0.91
0.94
1.00
1.03
0.99
0.99
1.04
2.18
6.38
3.31
f1 (ppm)
N
O
O
N
3a

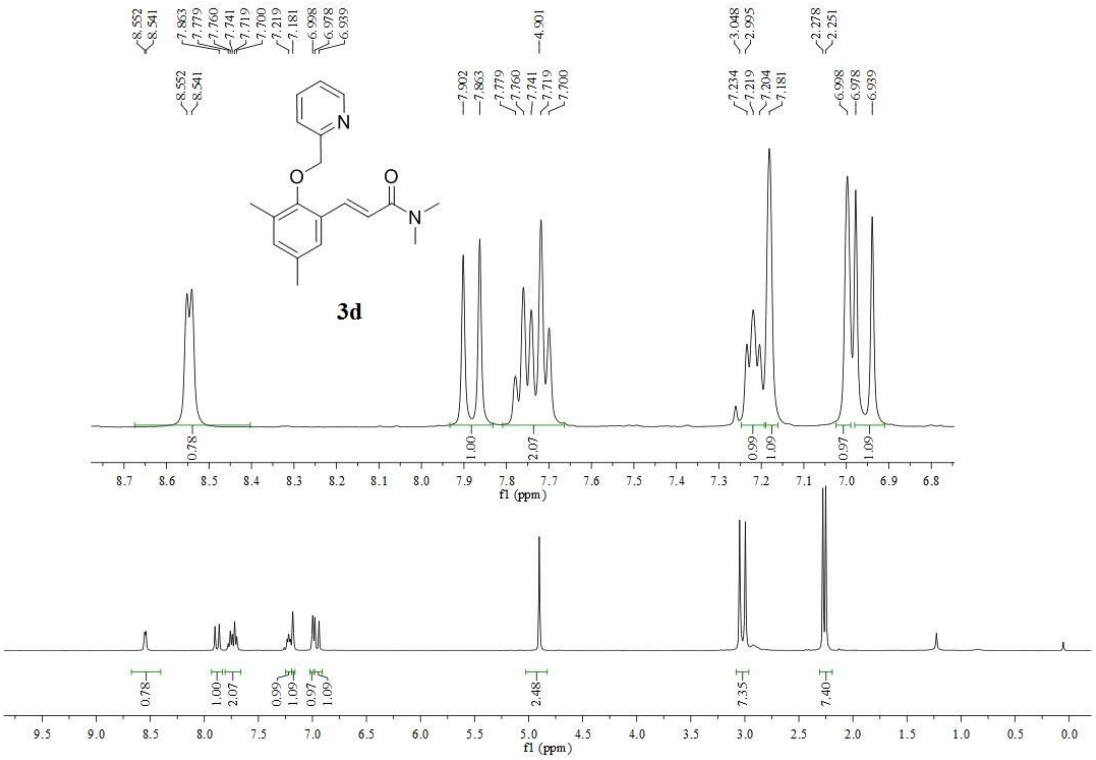

166.97
157.21
156.11
149.27
137.74
137.03
132.63
132.17
129.15
126.45
124.63
122.86
121.77
119.38
75.69
37.41
35.98
16.26
f1 (ppm)
N
O
O
N
3a

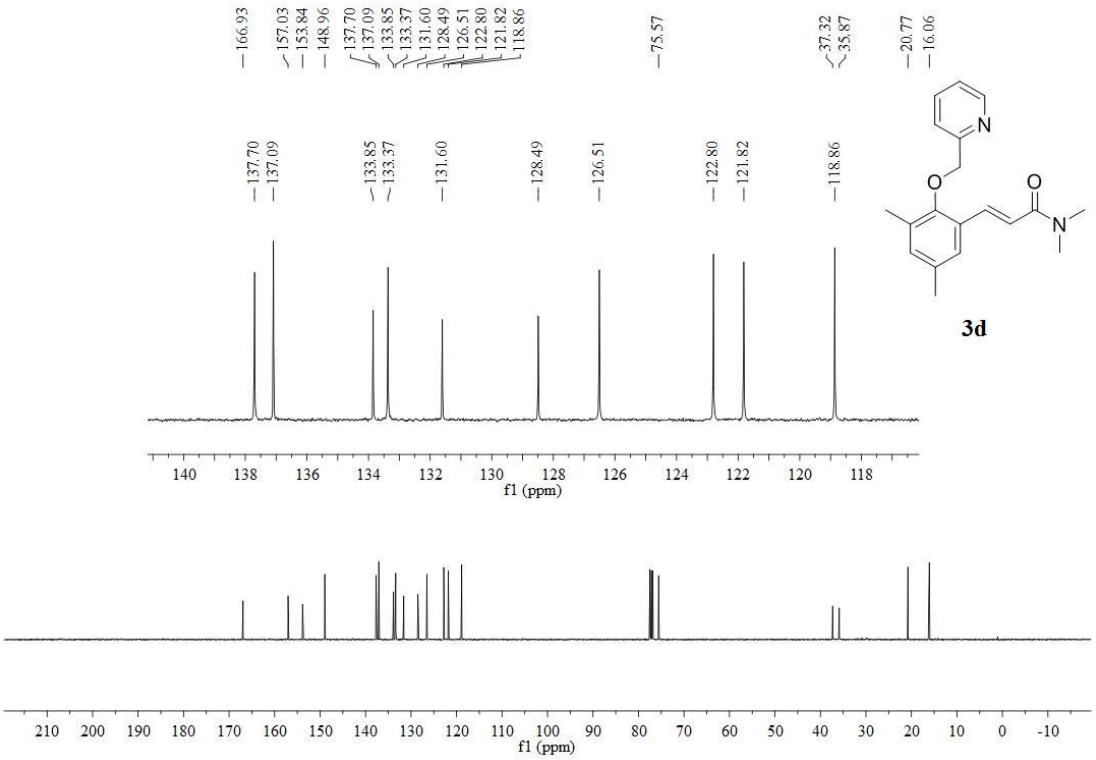

8.999
8.988
8.017
7.978
7.772
7.612
7.415
7.260
7.017
6.804
6.785
5.284
3.082
3.049
2.330
7.799
7.782
7.772
7.630
7.612
7.435
7.415
7.273
7.260
6.978
f1 (ppm)
0.85
0.79
0.91
0.87
1.00
1.11
0.97
1.97
2.10
6.07
3.08
3b

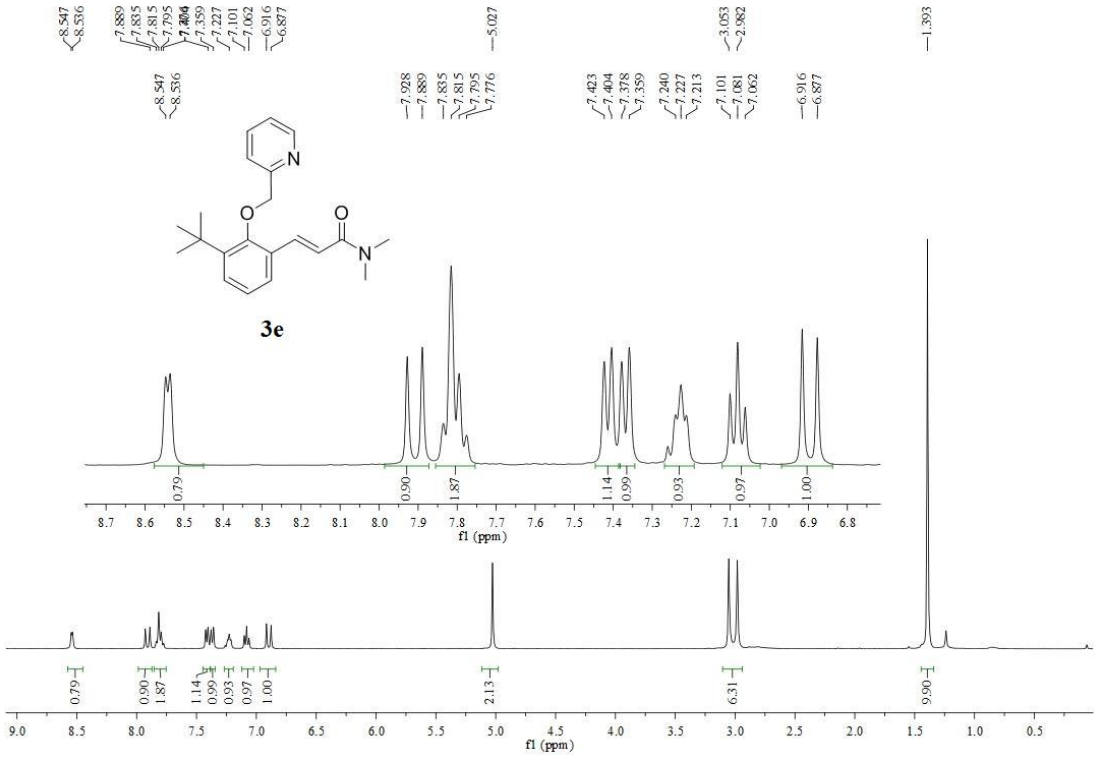

167.50
156.88
148.95
137.39
129.13
122.91
117.64
113.36
70.77
37.40
35.96
21.87
141.44
137.80
137.39
122.11
121.98
121.70
f1 (ppm)
3b

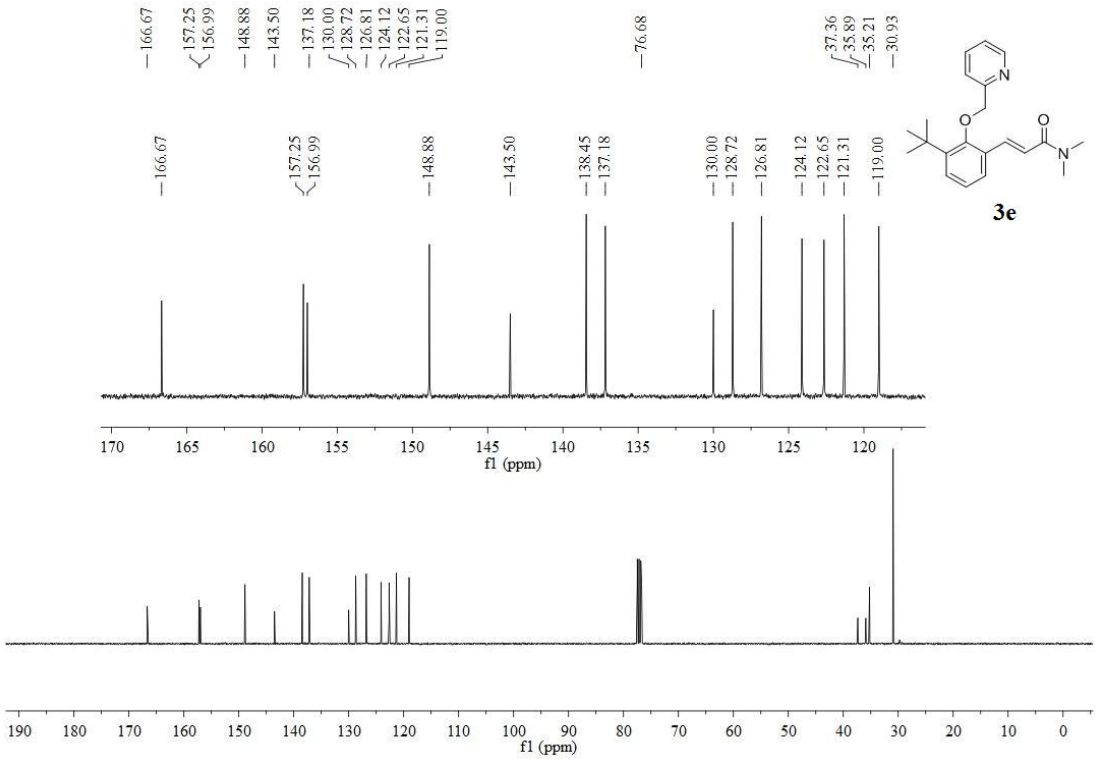

8.887
8.577
7.998
7.959
7.717
7.573
7.281
7.222
6.981
6.755
5.241
3.090
3.050
2.231
2.203
7.754
7.735
7.717
7.592
7.573
7.262
7.250
7.234
7.020
0.79
0.80
0.89
0.87
2.12
1.02
1.00
2.07
6.26
6.83
f1 (ppm)
3c

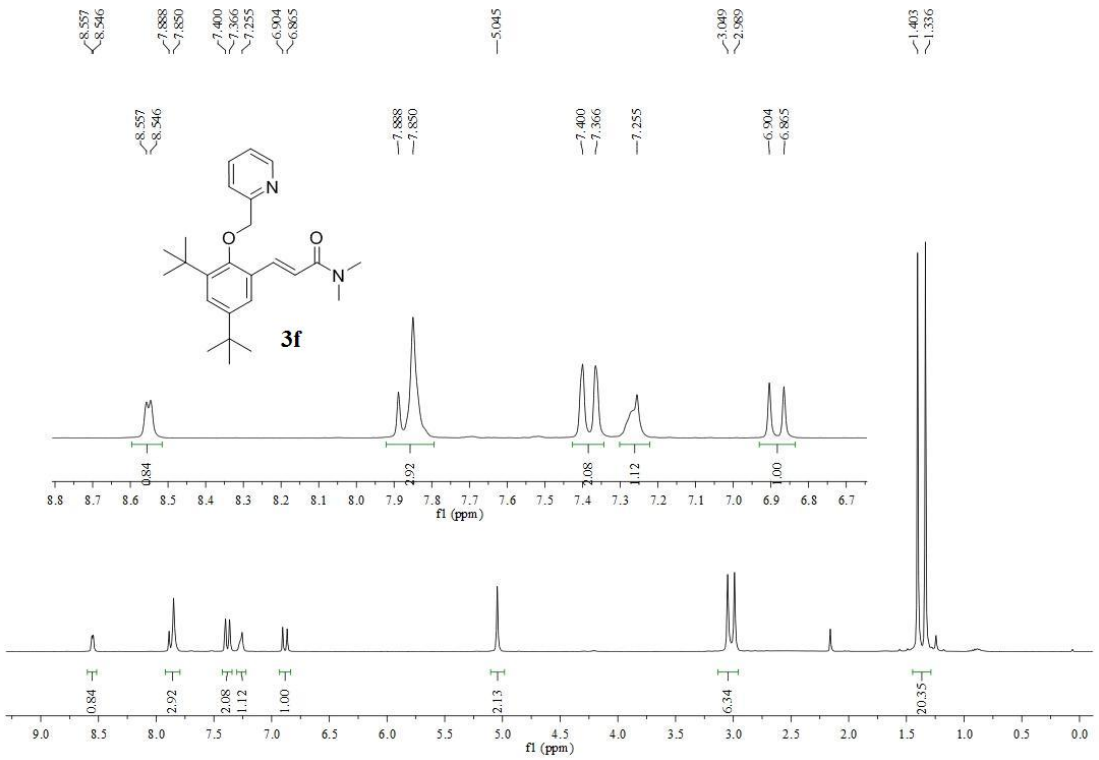

167.65
157.27
155.22
149.22
137.98
137.13
129.21
121.60
117.45
114.25
71.18
37.46
36.01
20.38
18.91
139.81
130.25
122.80
122.07
f1 (ppm)
3c

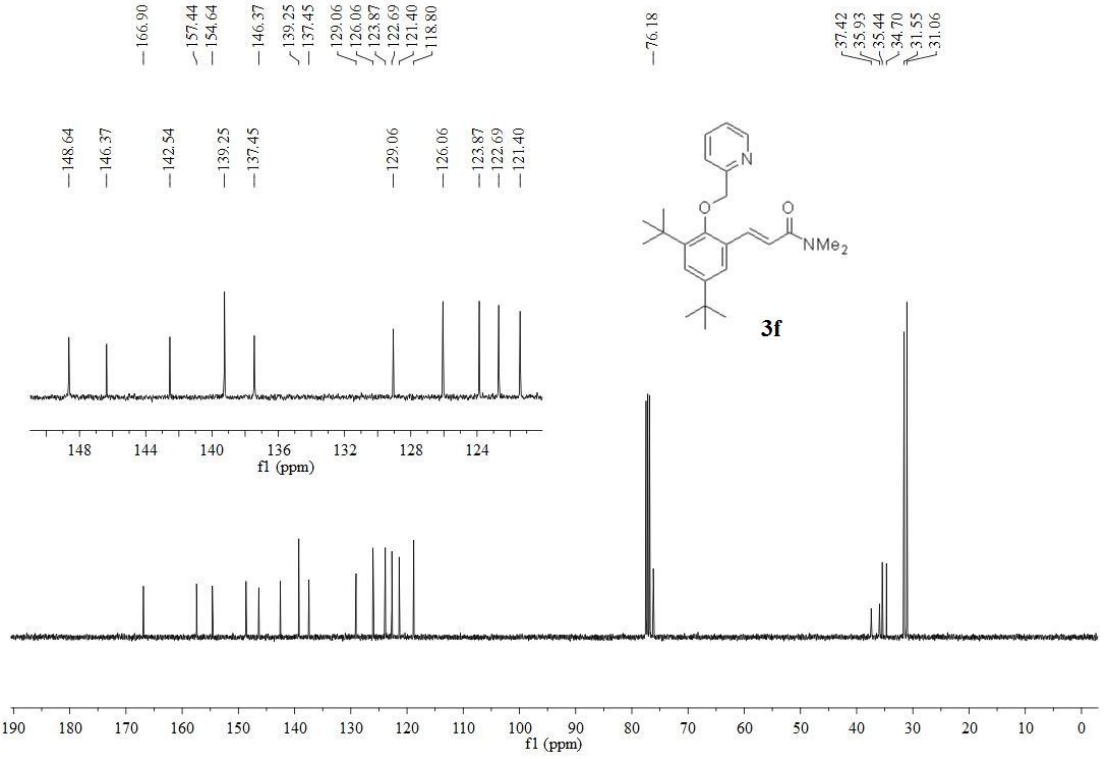

8.552
8.541
7.863
7.779
7.760
7.741
7.719
7.700
7.219
7.181
6.998
6.978
6.939
4.901
3.048
2.995
2.278
2.251
3d
f1 (ppm)

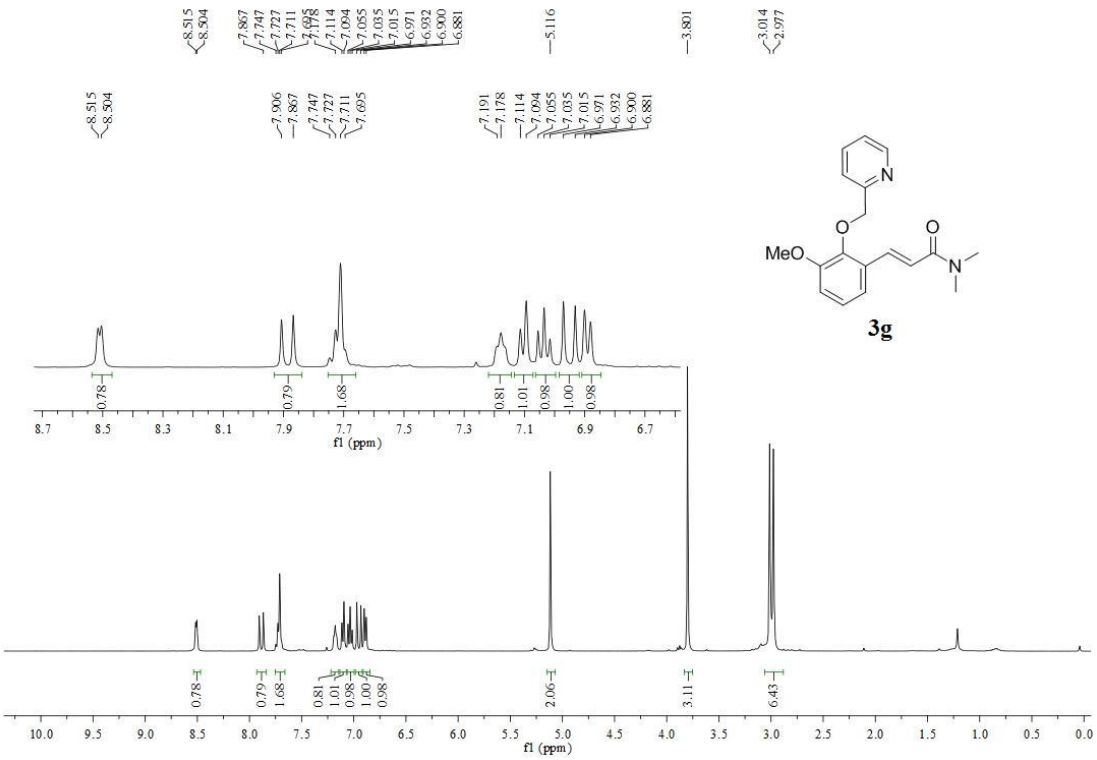

166.93
157.03
153.84
148.96
137.70
137.09
133.85
133.37
131.60
128.49
126.51
122.80
121.82
118.86
75.57
37.32
35.87
20.77
16.06
3d
f1 (ppm)

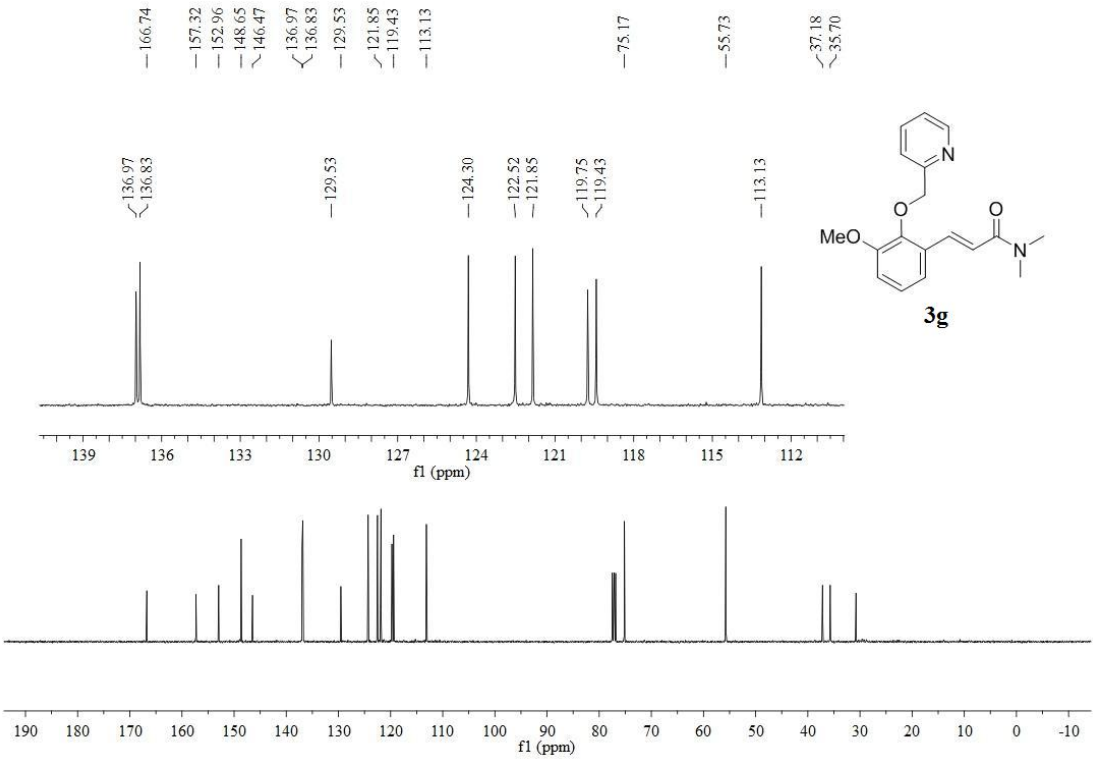

8.547
8.536
7.889
7.835
7.815
7.795
7.404
7.359
7.227
7.101
7.062
6.916
6.877
5.027
3.053
2.982
1.393
3e
f1 (ppm)

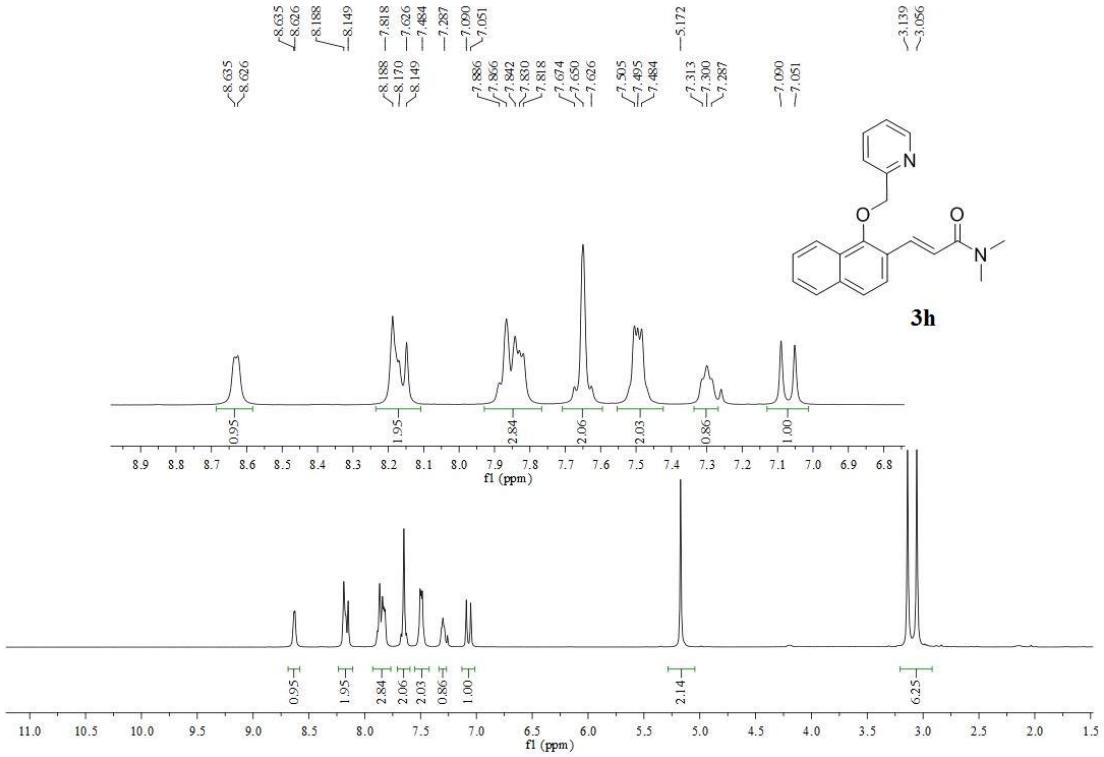

166.67
157.25
156.99
148.88
143.50
137.18
130.00
128.72
126.81
124.12
122.65
121.31
119.00
76.68
37.36
35.89
35.21
30.93
138.45
3e
f1 (ppm)

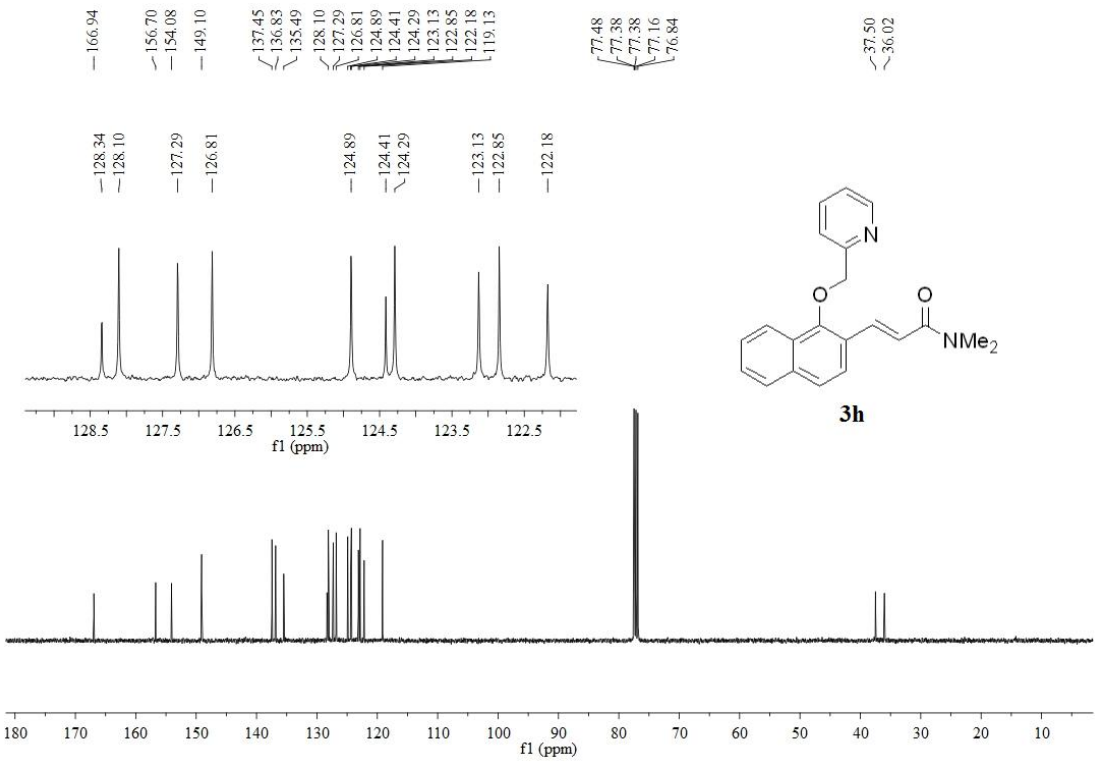

8.557
8.546
7.888
7.850
7.400
7.366
7.255
6.904
6.865
5.045
3.049
2.989
1.403
1.336
3f
f1 (ppm)

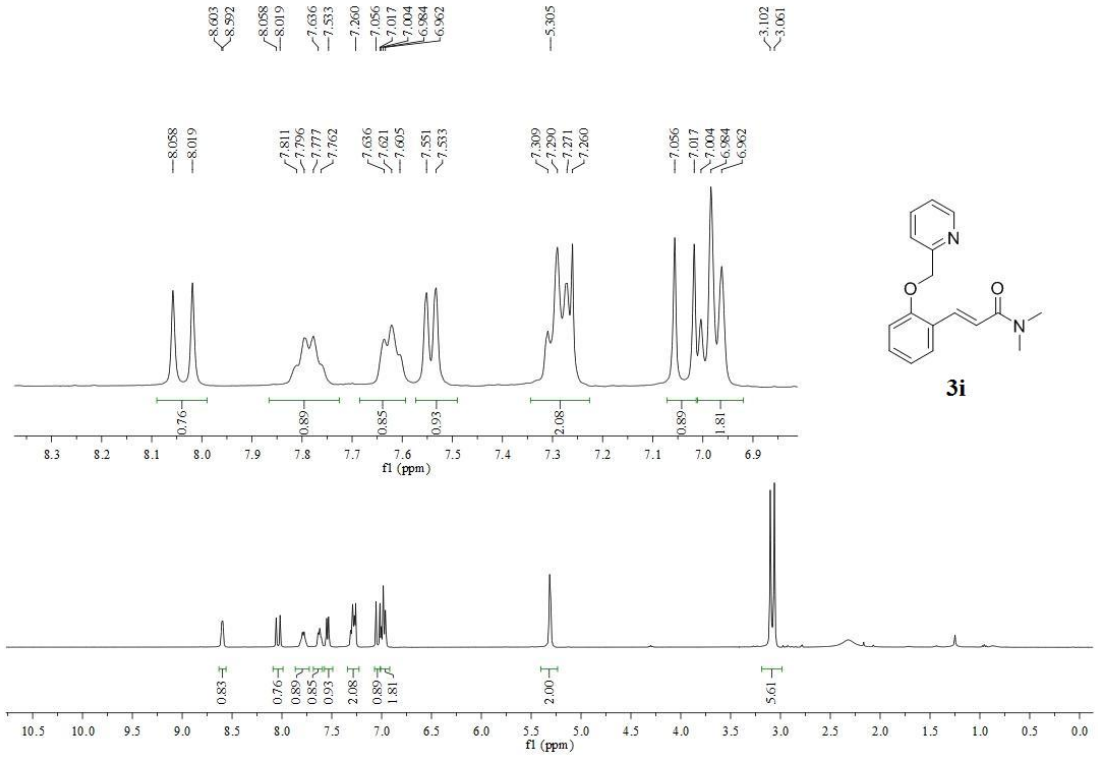

166.90
157.44
154.64
146.37
139.25
137.45
129.06
126.06
123.87
122.69
121.40
118.80
76.18
37.42
35.93
35.44
34.70
31.55
31.06
3f
NMe2
f1 (ppm)

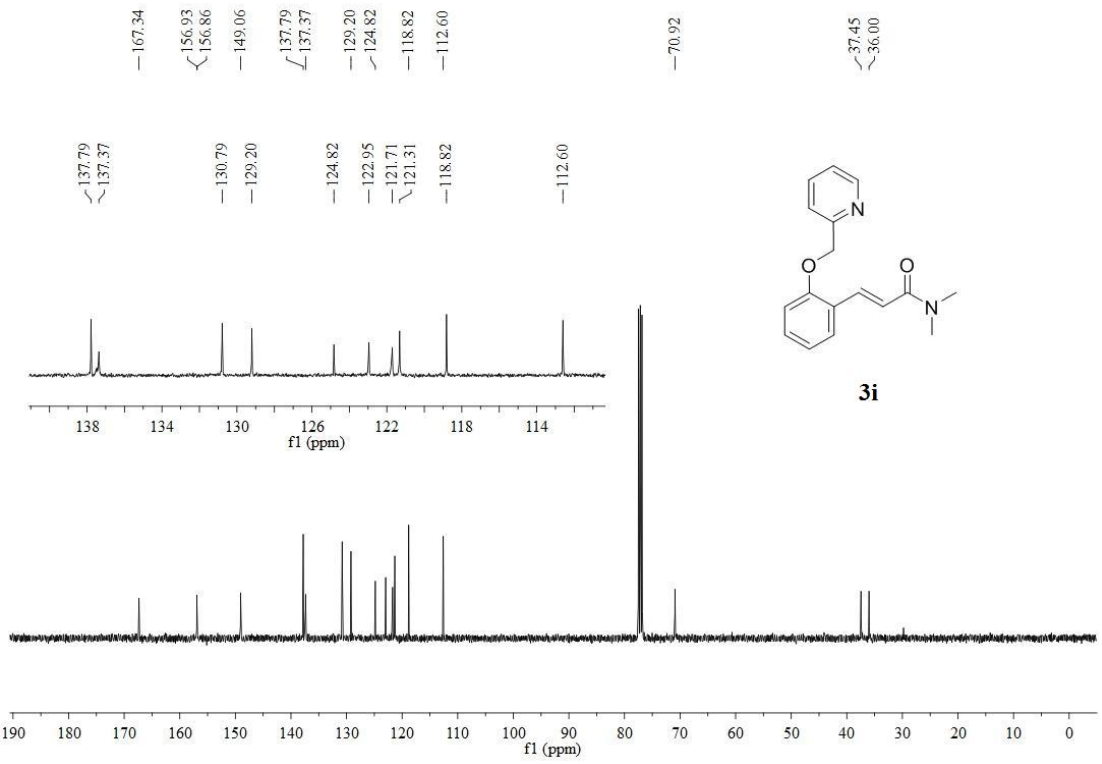

8.515
8.504
7.867
7.747
7.727
7.711
7.695
7.191
7.178
7.114
7.094
7.055
7.035
7.015
6.971
6.932
6.900
6.881
5.116
3.801
3.014
2.977
MeO
N
O
3g
f1 (ppm)

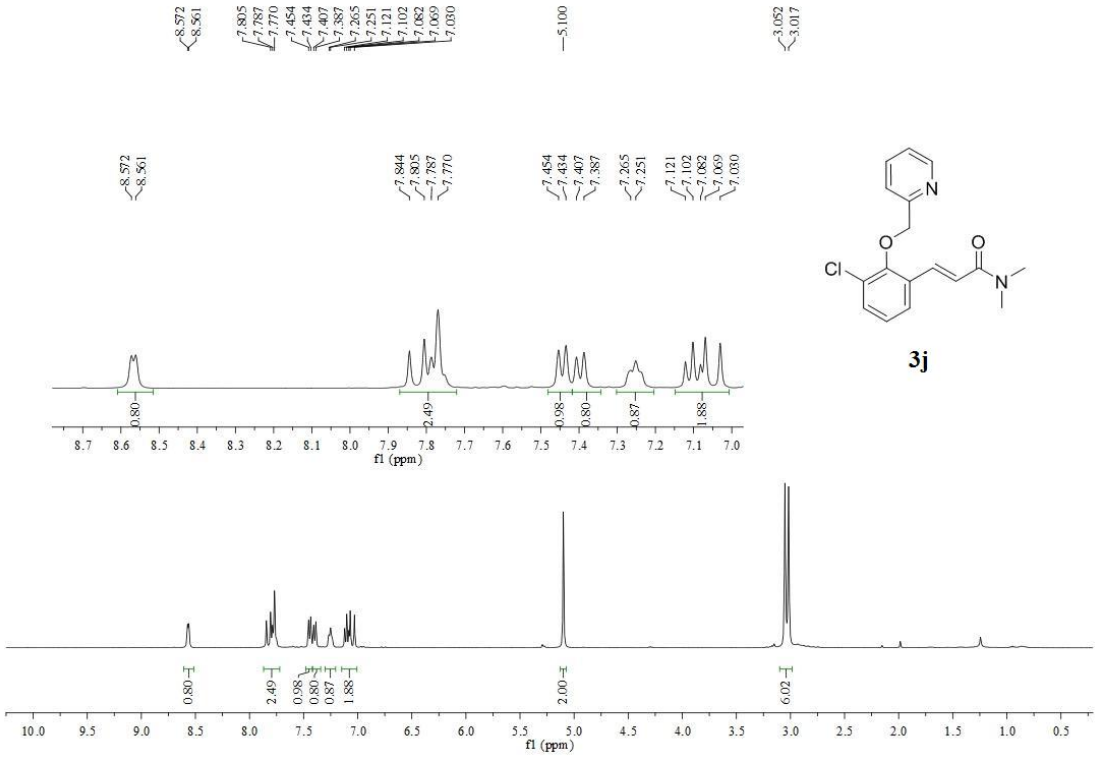

166.74
157.32
152.96
148.65
146.47
136.97
136.83
129.53
121.85
119.43
113.13
75.17
55.73
37.18
35.70
124.30
122.52
119.75
MeO
N
O
3g
f1 (ppm)


8.635
8.626
8.188
8.149
7.818
7.626
7.484
7.287
7.090
7.051
5.172
3.139
3.056
3h
f1 (ppm)

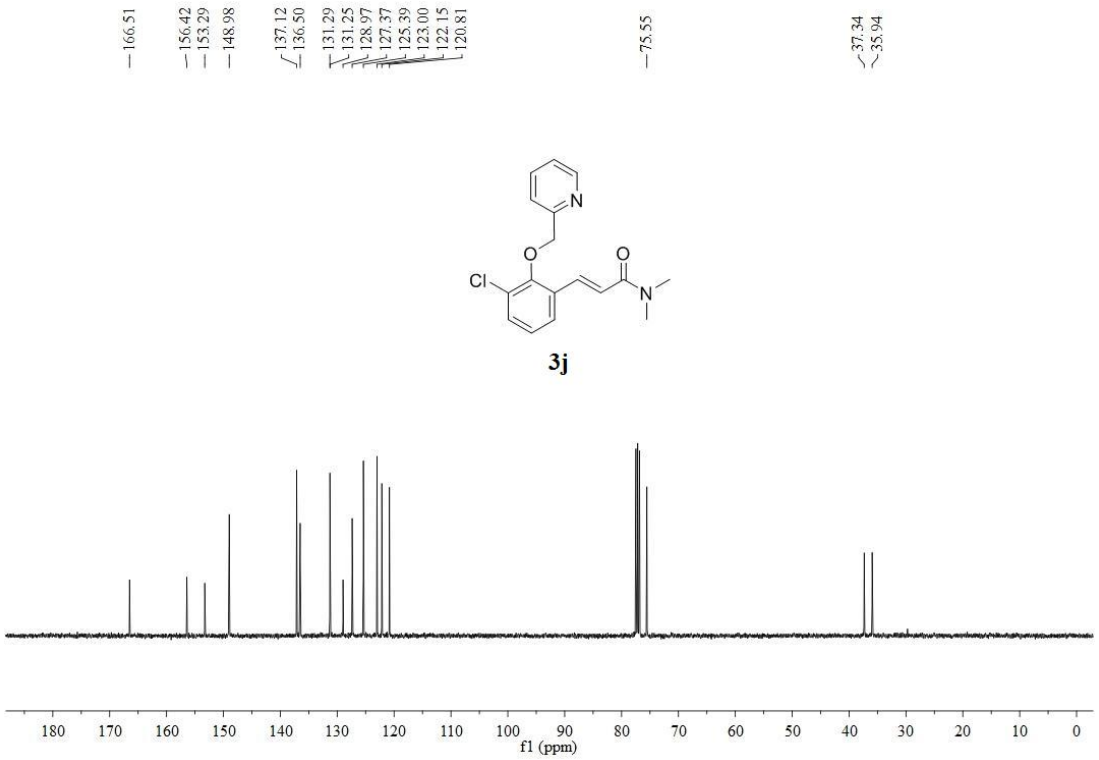

166.94
156.70
154.08
149.10
137.45
136.83
135.49
128.10
127.29
126.81
124.89
124.41
124.29
123.13
122.85
122.18
119.13
77.48
77.38
77.38
77.16
76.84
37.50
36.02
3h
NMe2
f1 (ppm)


8.603
8.592
8.058
8.019
7.636
7.533
7.260
7.056
7.017
7.004
6.984
6.962
5.305
3.102
3.061
f1 (ppm)
3i

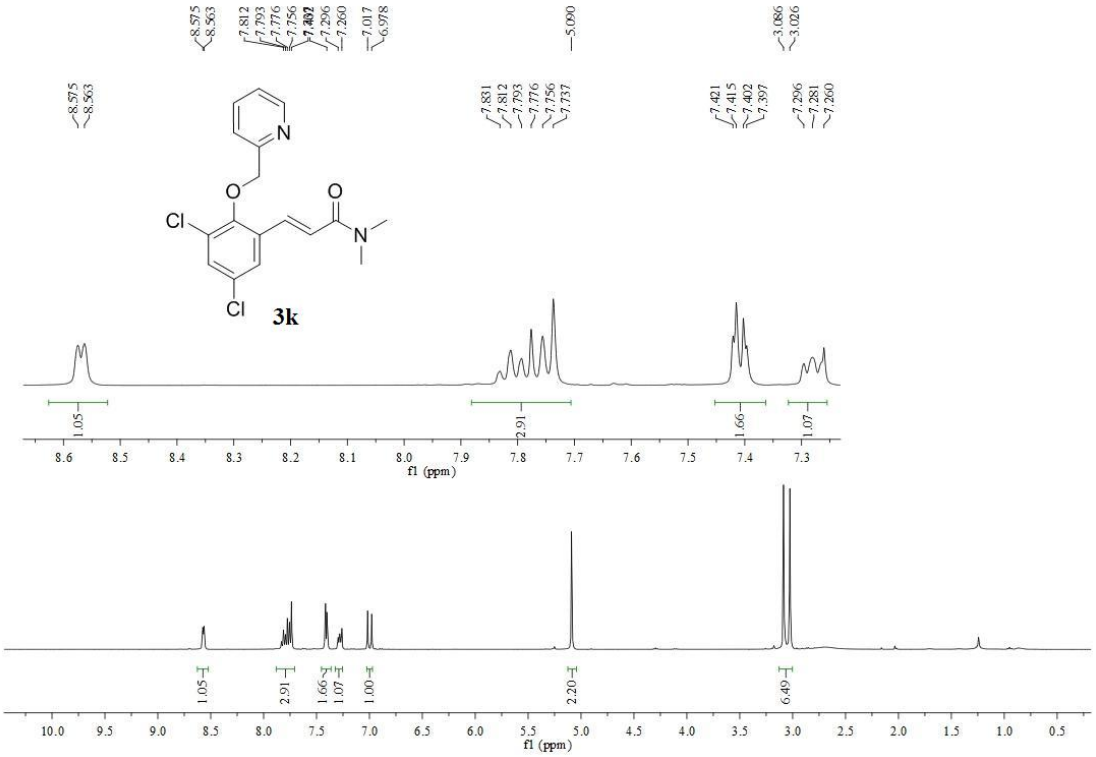

167.34
156.93
156.86
149.06
137.79
137.37
129.20
124.82
118.82
112.60
70.92
37.45
36.00
130.79
122.95
121.71
121.31
f1 (ppm)
3i

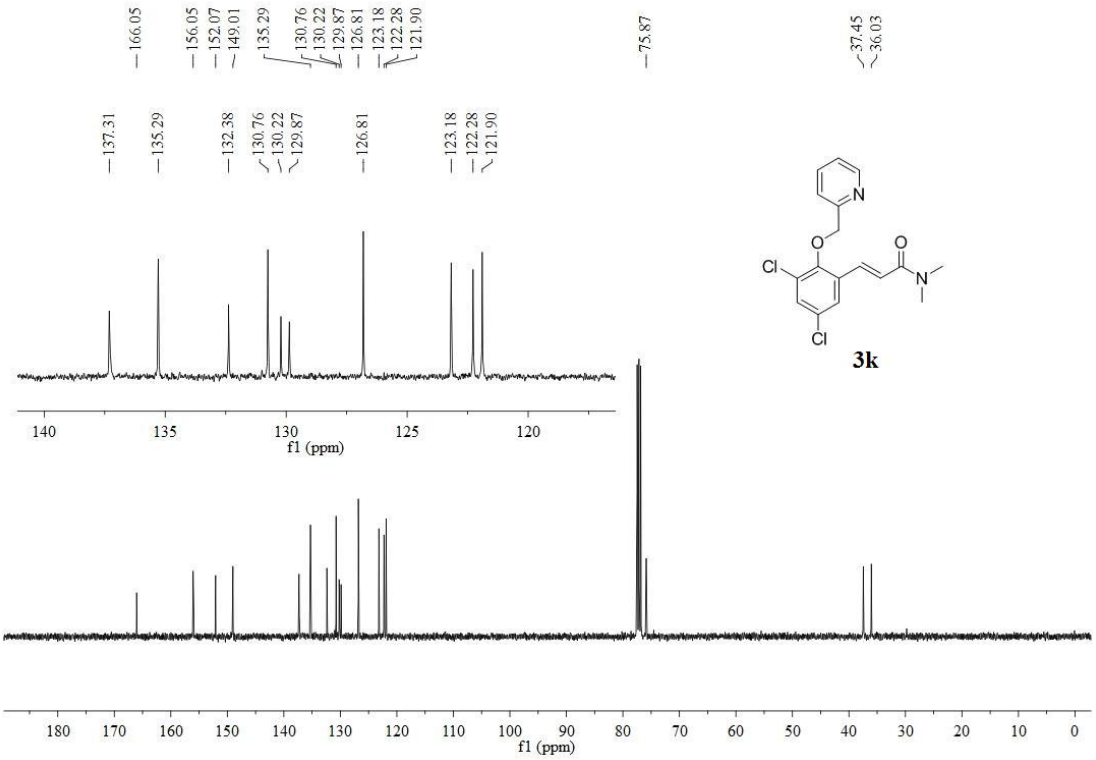

8.572
8.561
7.805
7.787
7.770
7.454
7.434
7.407
7.387
7.265
7.251
7.121
7.102
7.082
7.069
7.030
5.100
3.052
3.017
0.80
2.49
0.98
0.80
0.87
1.88
2.00
6.02
f1 (ppm)

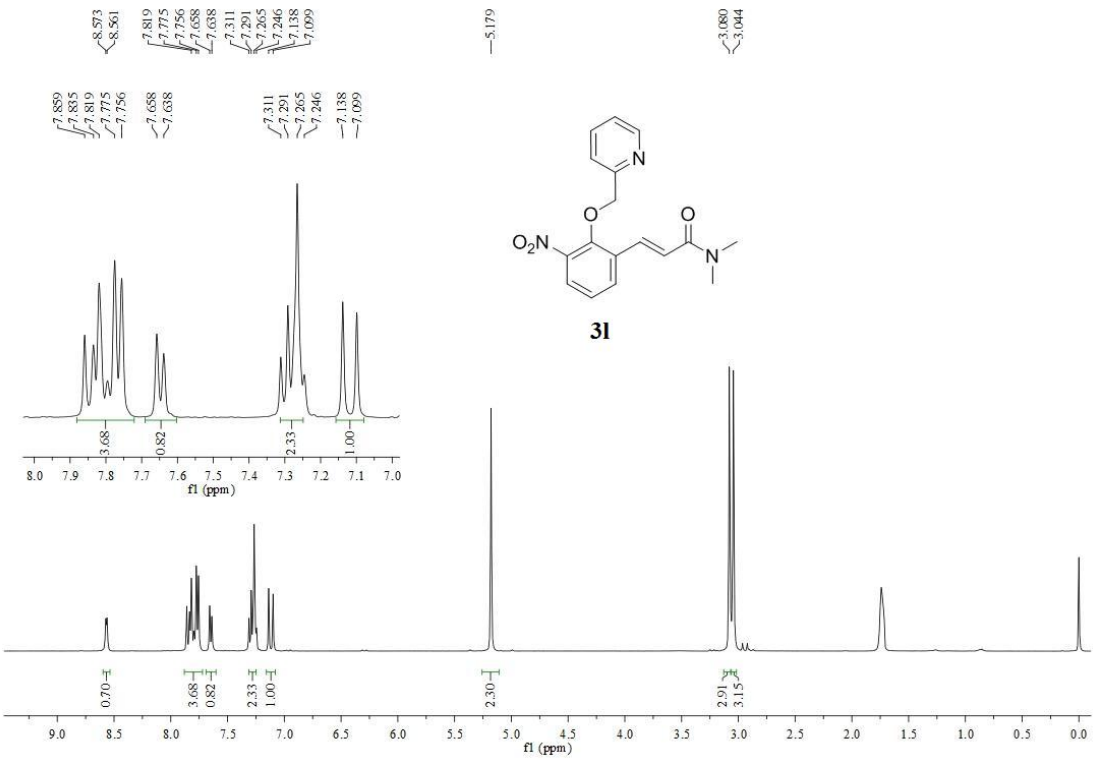
3j

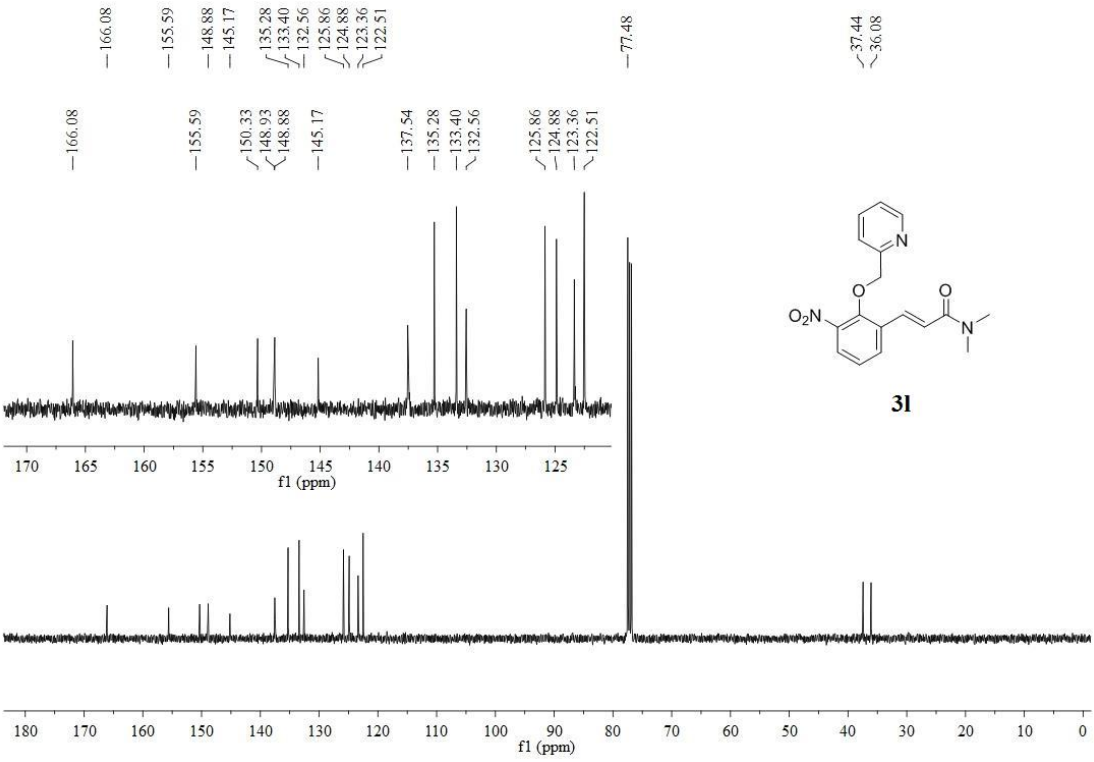

166.51
156.42
153.29
148.98
137.12
136.50
131.29
131.25
128.97
127.37
125.39
123.00
122.15
120.81
75.55
37.34
35.94
f1 (ppm)

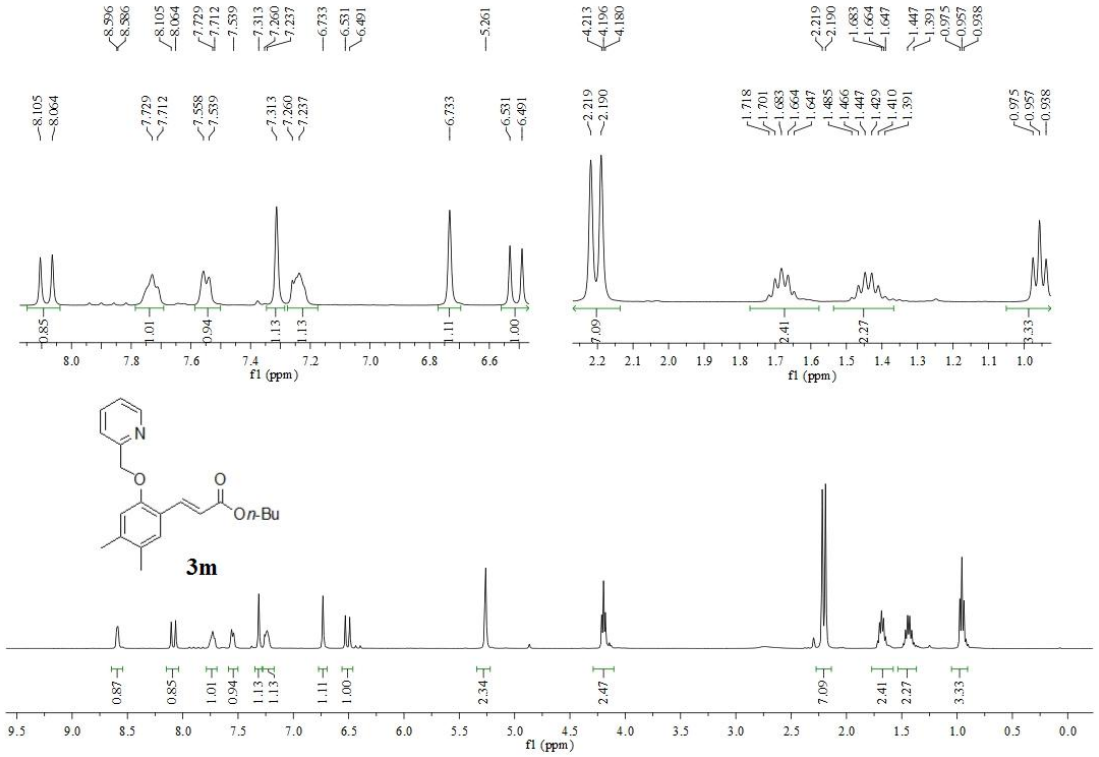
3j

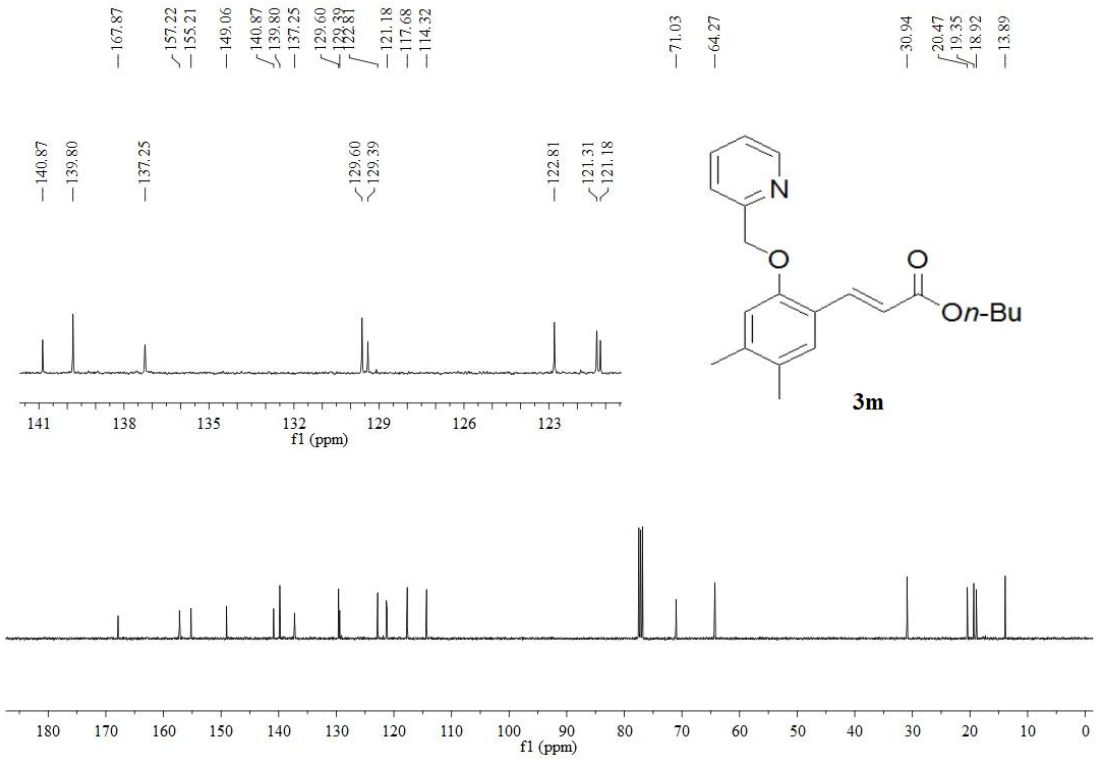

8.575
8.563
7.812
7.793
7.776
7.756
7.737
7.421
7.415
7.402
7.397
7.296
7.281
7.260
7.017
6.978
5.090
3.086
3.026
N
O
O
Cl
N
Cl
3k
1.05
2.91
1.66
1.07
1.00
2.20
6.49
f1 (ppm)

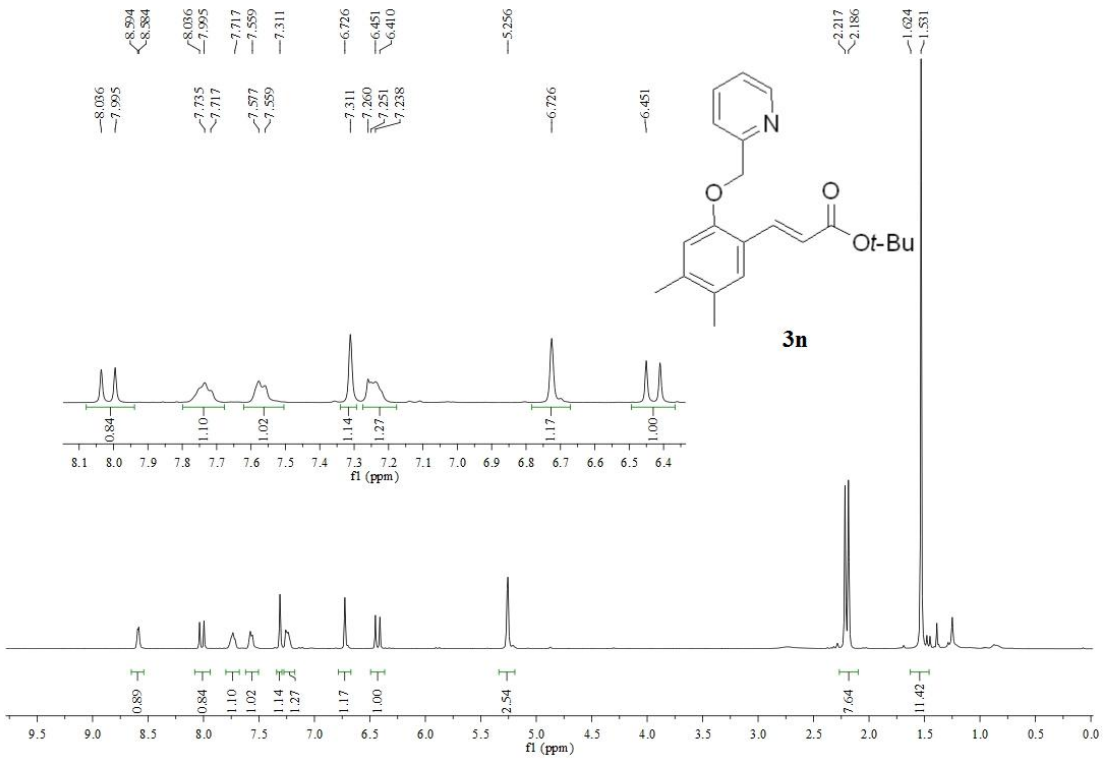

166.05
156.05
152.07
149.01
135.29
130.76
130.22
129.87
126.81
123.18
122.28
121.90
75.87
37.45
36.03
137.31
132.38
N
O
O
Cl
N
Cl
3k
f1 (ppm)

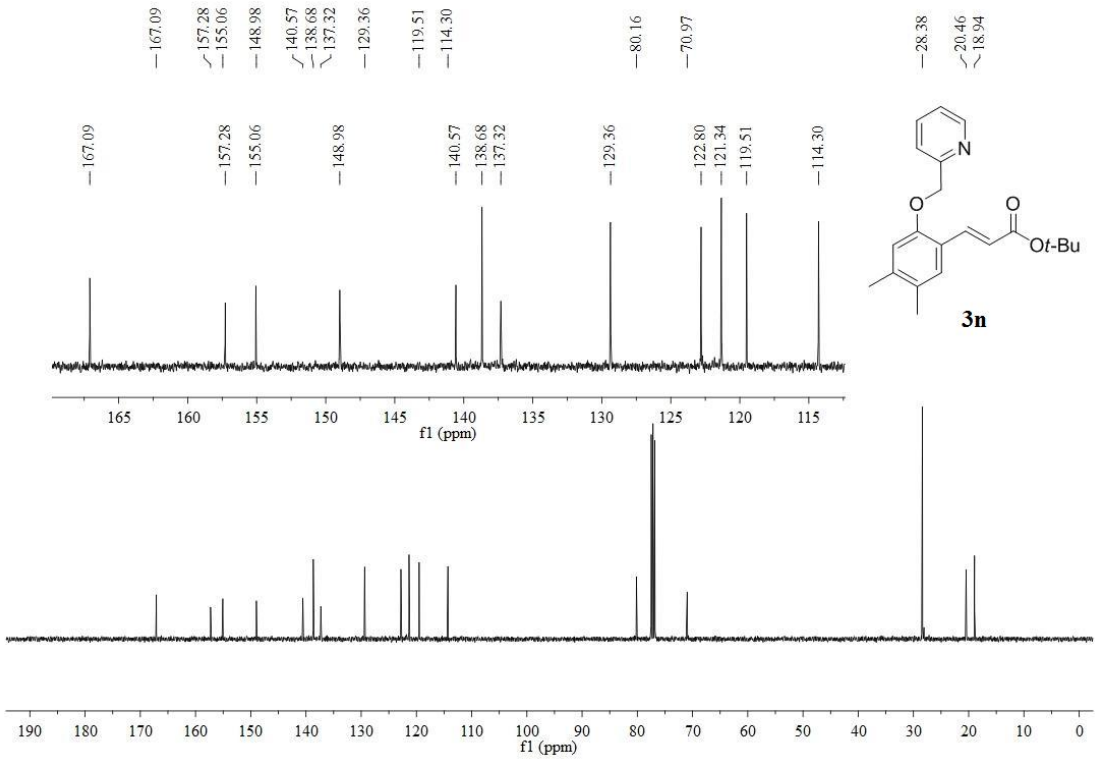

8.573
8.561
7.819
7.775
7.756
7.658
7.638
7.311
7.291
7.265
7.246
7.138
7.099
5.179
3.080
3.044
7.859
7.835
7.819
7.775
7.756
7.658
7.638
7.311
7.291
7.265
7.246
7.138
7.099
3.68
0.82
2.33
1.00
f1 (ppm)
0.70
3.68
0.82
2.33
1.00
2.30
2.91
3.15
f1 (ppm)
O2N
N
O
O
N
3l

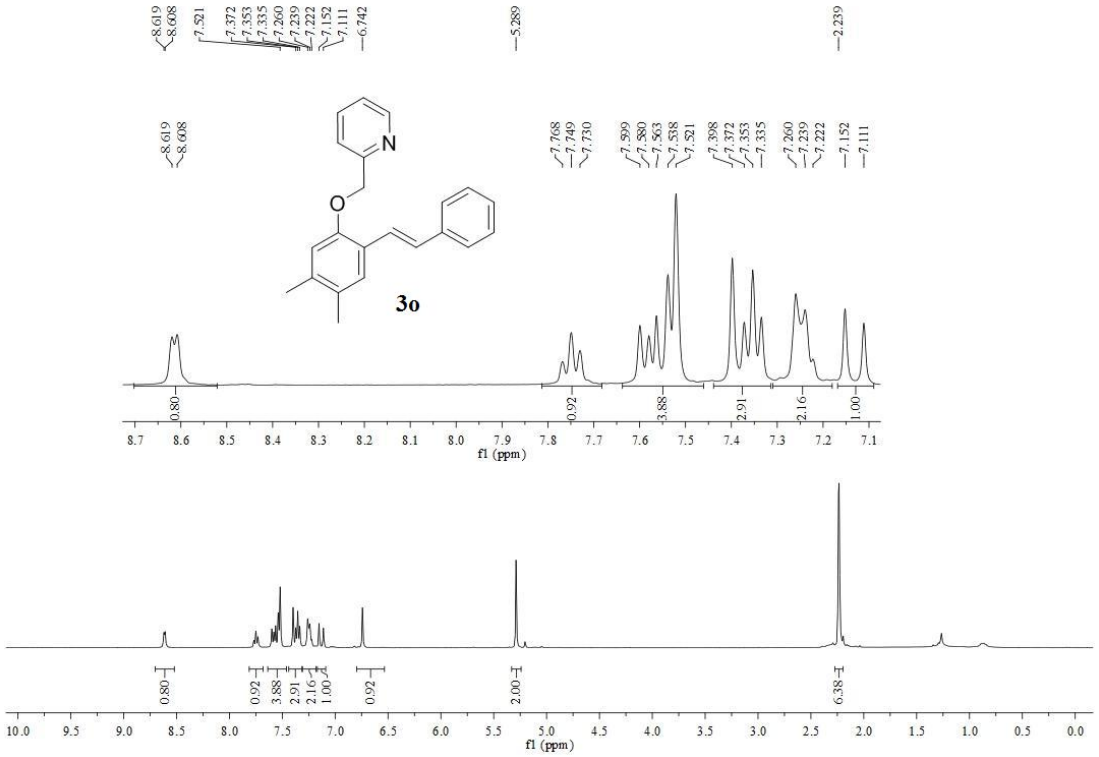

166.08
155.59
148.88
145.17
135.28
133.40
132.56
125.86
124.88
123.36
122.51
77.48
37.44
36.08
166.08
155.59
150.33
148.93
148.88
145.17
137.54
135.28
133.40
132.56
125.86
124.88
123.36
122.51
f1 (ppm)
f1 (ppm)
O2N
N
O
O
N
3l

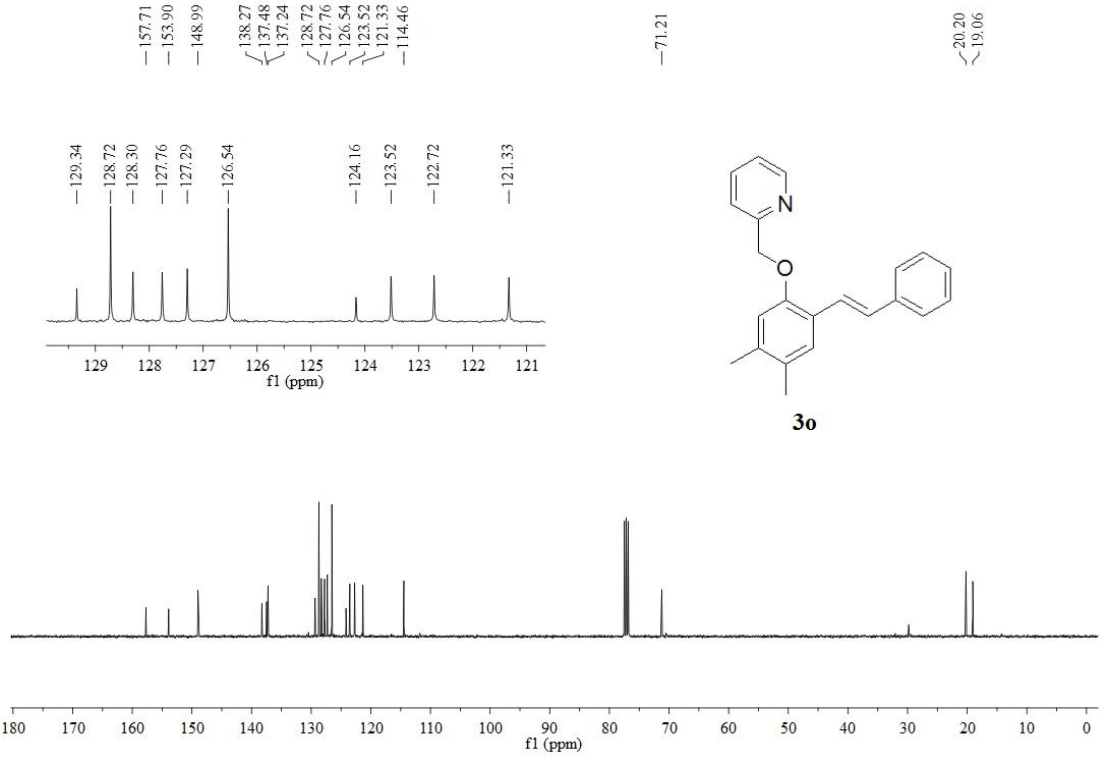

8.596
8.586
8.105
8.064
7.729
7.712
7.558
7.539
7.313
7.260
7.237
6.733
6.531
6.491
5.261
4.213
4.196
4.180
2.219
2.190
1.718
1.701
1.683
1.664
1.647
1.485
1.466
1.447
1.429
1.410
1.391
0.975
0.957
0.938
f1 (ppm)
On-Bu
3m

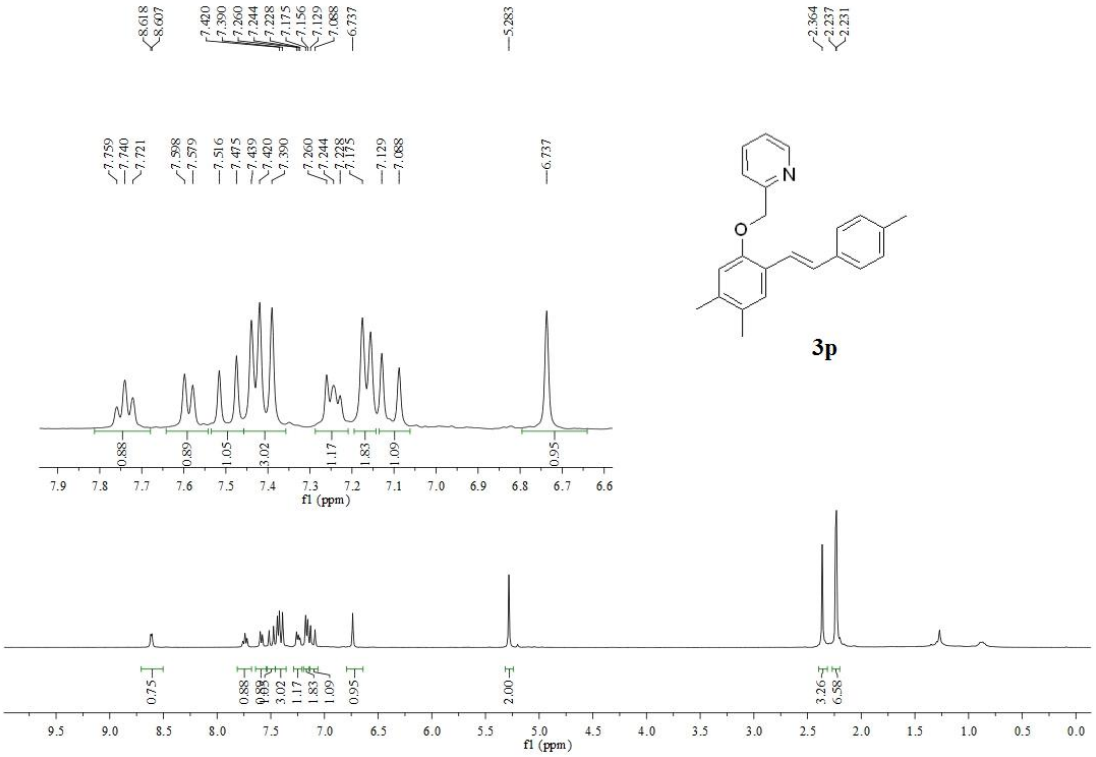

167.87
157.22
155.21
149.06
140.87
139.80
137.25
129.60
129.39
122.81
121.18
117.68
114.32
71.03
64.27
30.94
20.47
19.35
18.92
13.89
f1 (ppm)
On-Bu
3m

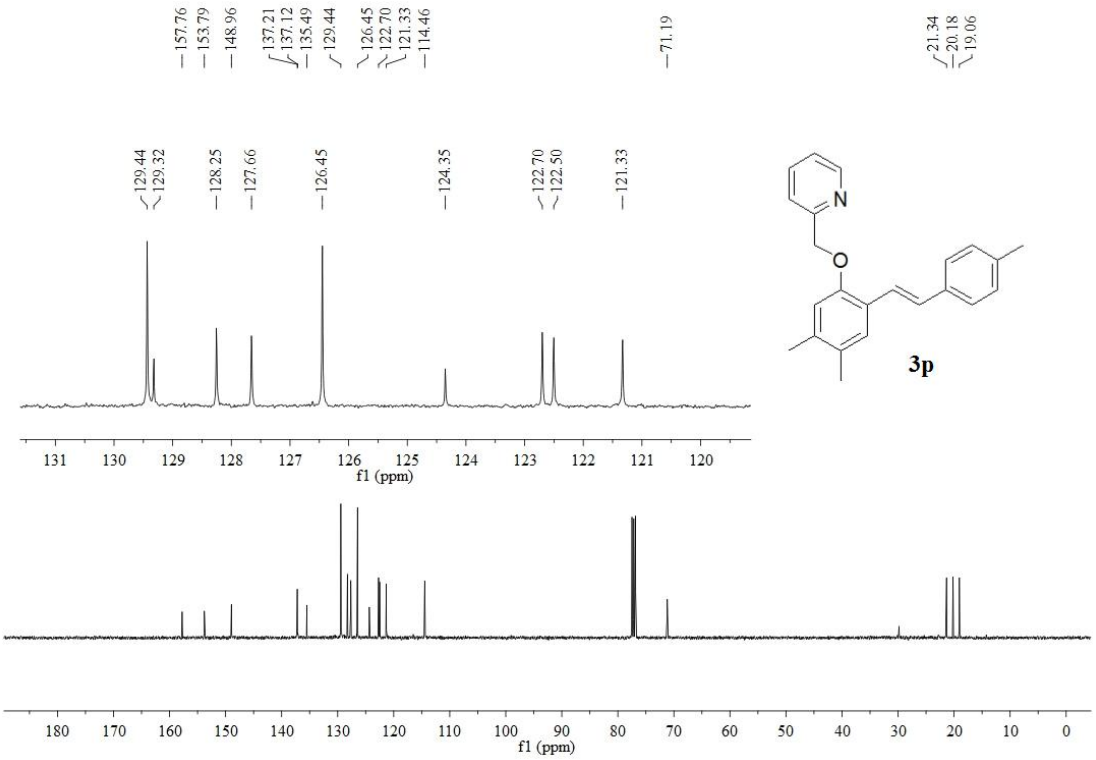

8.594
8.584
8.036
7.995
7.717
7.559
7.311
6.726
6.451
6.410
5.256
2.217
2.186
1.624
1.531
O
N
O
Ot-Bu
3n
0.84
1.10
1.02
1.14
1.27
1.17
1.00
0.89
2.54
7.64
11.42
f1 (ppm)


167.09
157.28
155.06
148.98
140.57
138.68
137.32
129.36
119.51
114.30
80.16
70.97
28.38
20.46
18.94
122.80
121.34
O
N
O
Ot-Bu
3n
f1 (ppm)


8.619
8.608
7.521
7.372
7.353
7.335
7.260
7.239
7.222
7.152
7.111
6.742
5.289
2.239
7.768
7.749
7.730
7.599
7.580
7.563
7.538
7.521
7.398
7.372
7.353
7.335
7.260
7.239
7.222
7.152
7.111
N
O
3o
0.80
0.92
3.88
2.91
2.16
1.00
f1 (ppm)
0.80
0.92
3.88
2.91
2.16
1.00
0.92
2.00
6.38
f1 (ppm)


157.71
153.90
148.99
138.27
137.48
137.24
128.72
127.76
126.54
123.52
121.33
114.46
71.21
20.20
19.06
129.34
128.72
128.30
127.76
127.29
126.54
124.16
123.52
122.72
121.33
f1 (ppm)
N
O
3o
f1 (ppm)


8.618
8.607
7.420
7.390
7.260
7.244
7.228
7.175
7.156
7.129
7.088
6.737
5.283
2.364
2.237
2.231
7.759
7.740
7.721
7.598
7.579
7.516
7.475
7.439
7.420
7.390
7.260
7.244
7.228
7.175
7.129
7.088
6.737
N
O
3p
0.88
0.89
1.05
3.02
1.17
1.83
1.09
0.95
f1 (ppm)
0.75
0.88
0.89
3.02
1.17
1.83
1.09
0.95
2.00
3.26
6.58
f1 (ppm)


157.76
153.79
148.96
137.21
137.12
135.49
129.44
126.45
122.70
121.33
114.46
71.19
21.34
20.18
19.06
129.44
129.32
128.25
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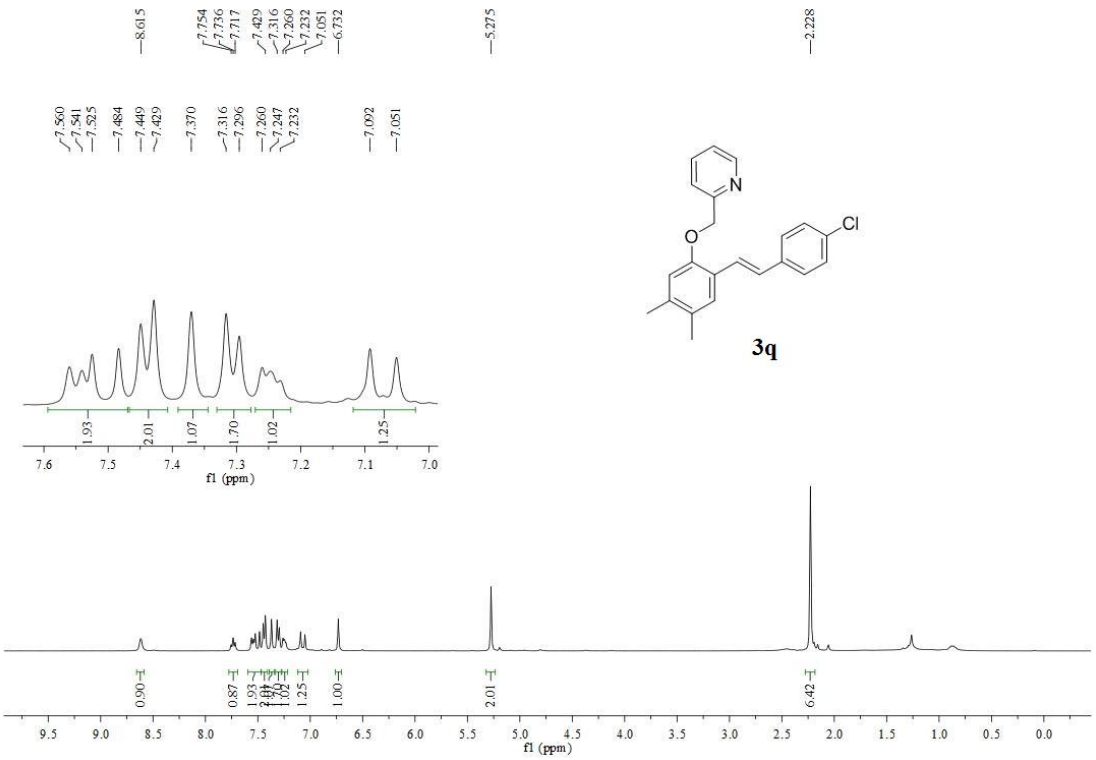
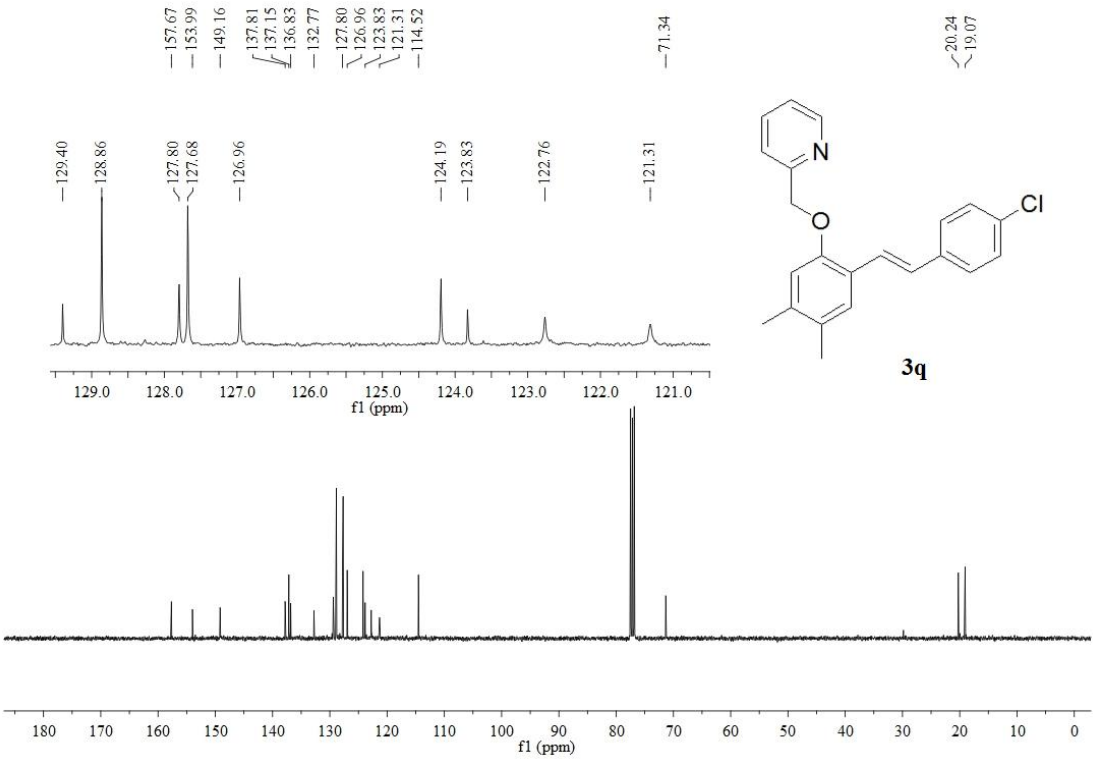
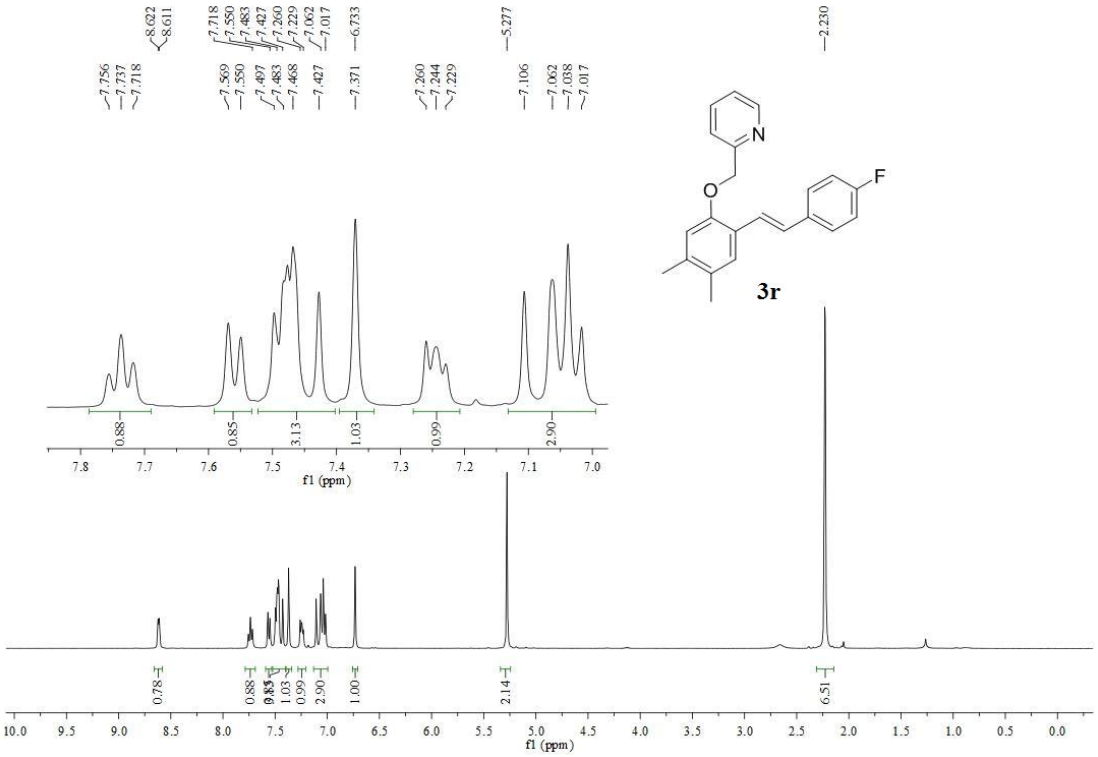
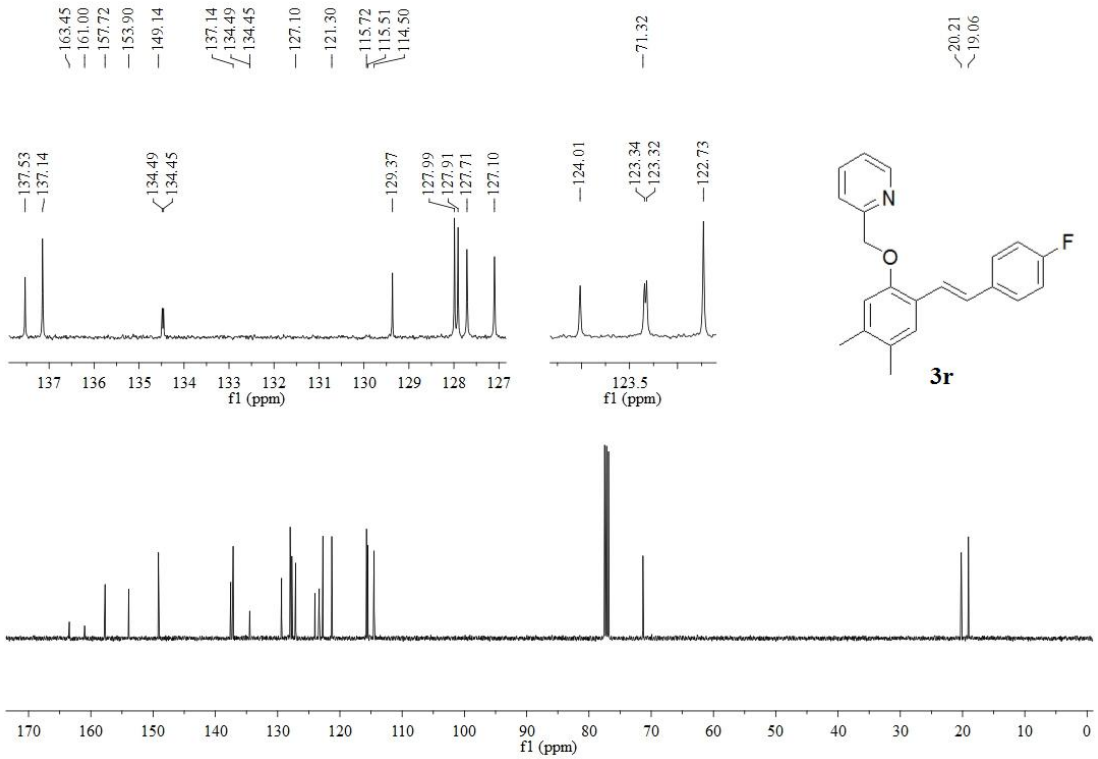
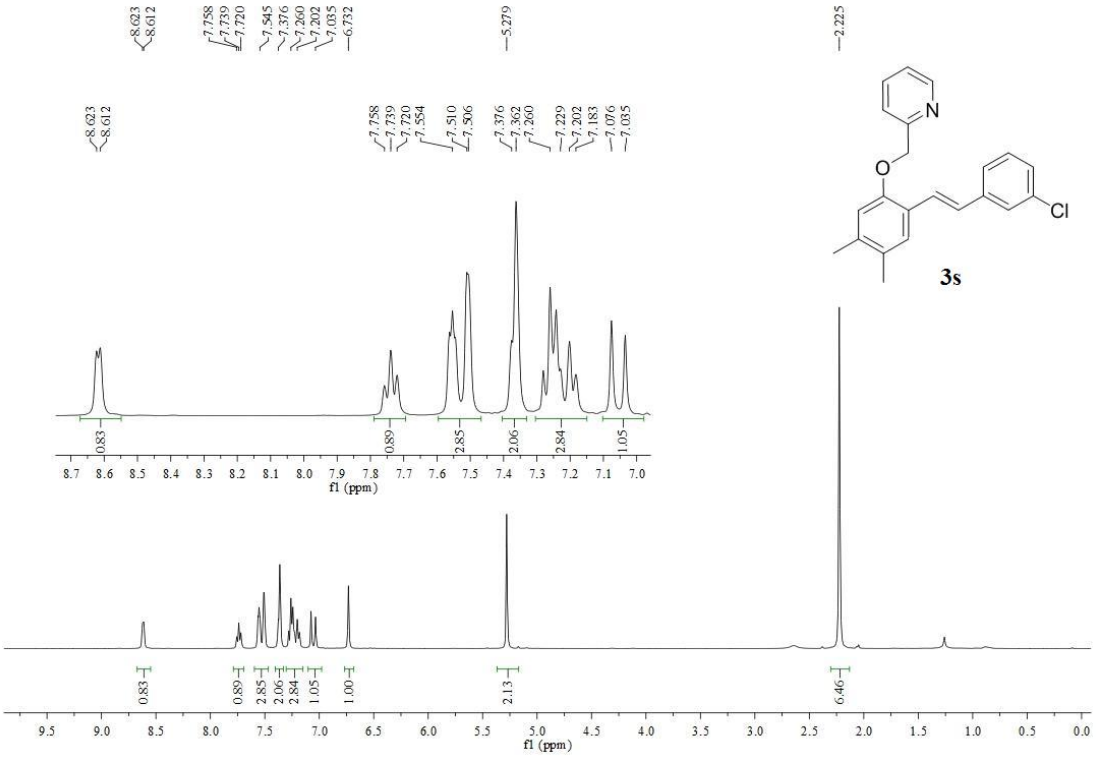
124.35
122.70
122.50
121.33
N
O
3p
f1 (ppm)
f1 (ppm)

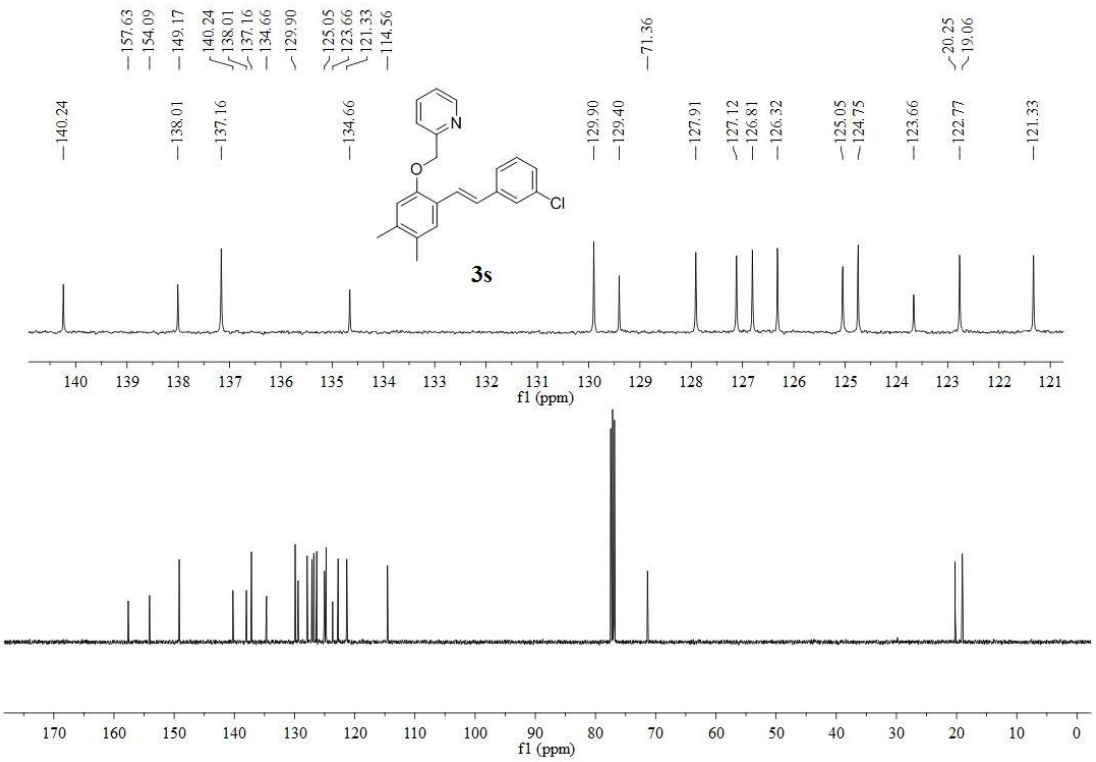

8.615
7.754
7.736
7.717
7.429
7.316
7.260
7.232
7.051
6.732
5.275
2.228
7.560
7.541
7.525
7.484
7.449
7.429
7.370
7.316
7.296
7.260
7.247
7.232
7.092
7.051
N
O
Cl
3q
1.93
2.01
1.07
1.70
1.02
1.25
f1 (ppm)
0.90
0.87
1.00
2.01
6.42
f1 (ppm)

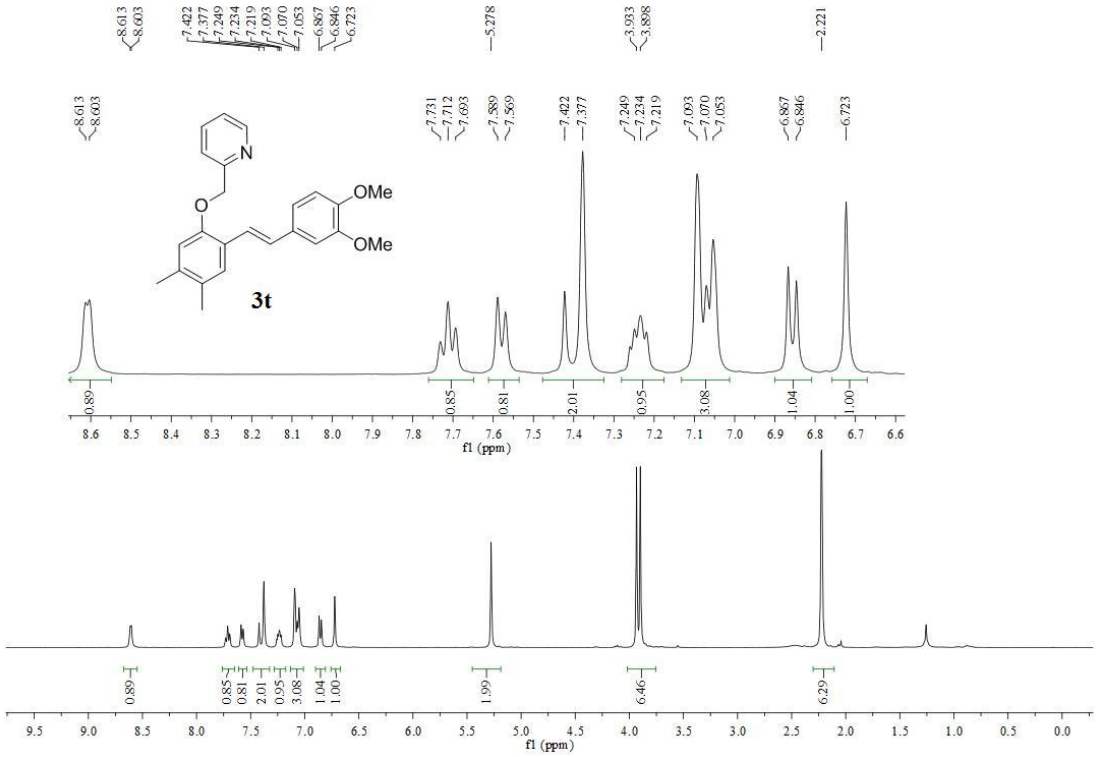

157.67
153.99
149.16
137.81
137.15
136.83
132.77
127.80
126.96
123.83
121.31
114.52
71.34
20.24
19.07
129.40
128.86
127.80
127.68
126.96
124.19
123.83
122.76
121.31
N
O
Cl
3q
f1 (ppm)
f1 (ppm)

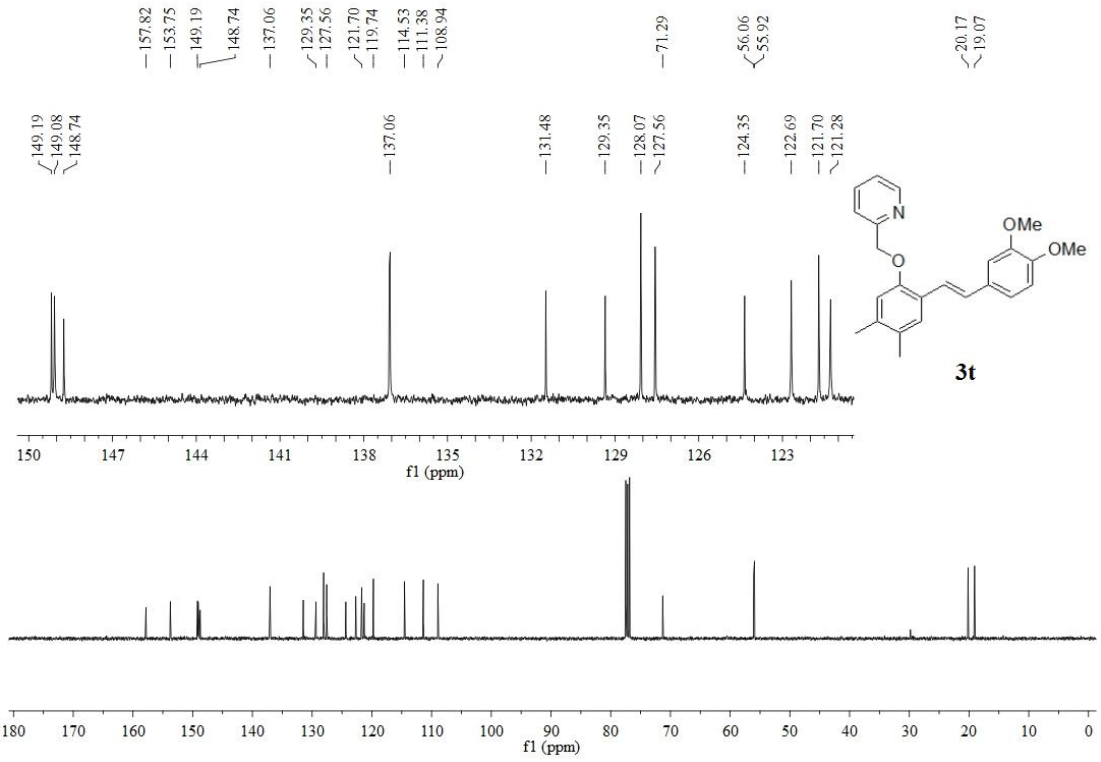

8.622
8.611
7.756
7.737
7.718
7.718
7.569
7.550
7.497
7.483
7.468
7.427
7.427
7.371
7.733
7.260
7.244
7.229
5.277
7.106
7.062
7.038
7.017
7.017
2.230
N
O
F
3r
0.88
0.85
3.13
1.03
0.99
2.90
f1 (ppm)
0.78
0.88
1.03
0.99
2.90
1.00
2.14
6.51
f1 (ppm)

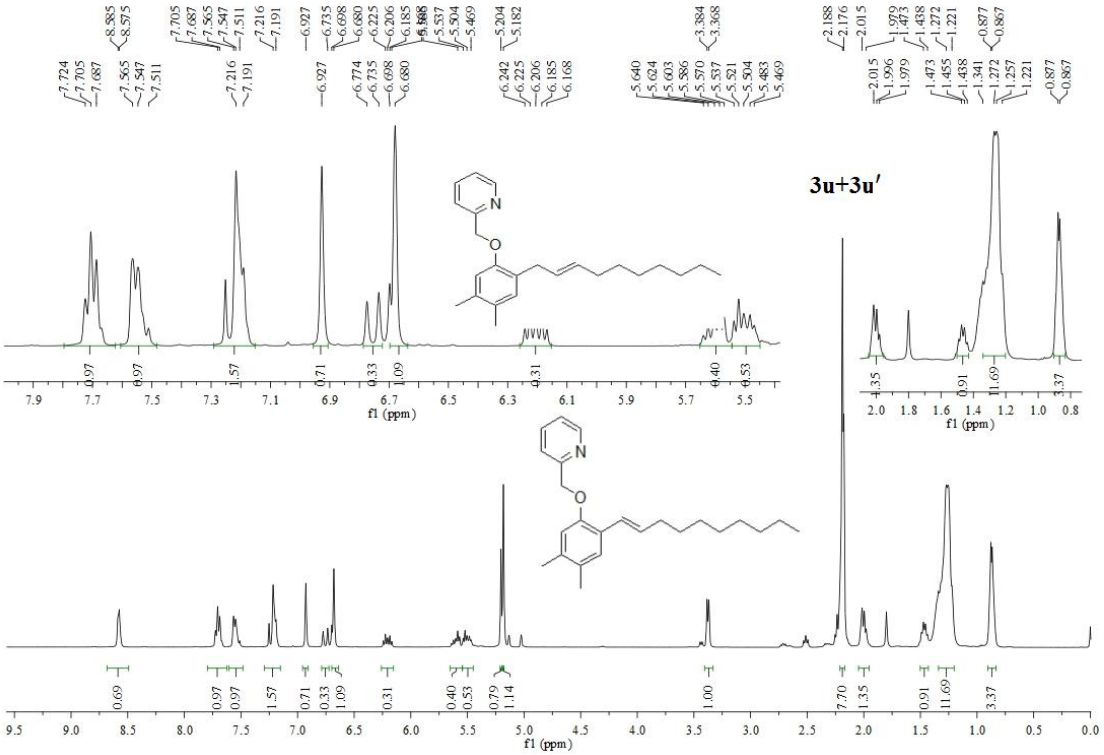

163.45
161.00
157.72
153.90
149.14
137.14
134.49
134.45
127.10
121.30
115.72
115.51
114.50
71.32
20.21
19.06
137.53
137.14
134.49
134.45
129.37
127.99
127.91
127.71
127.10
124.01
123.34
123.32
122.73
N
O
F
3r
f1 (ppm)
123.5
f1 (ppm)
f1 (ppm)

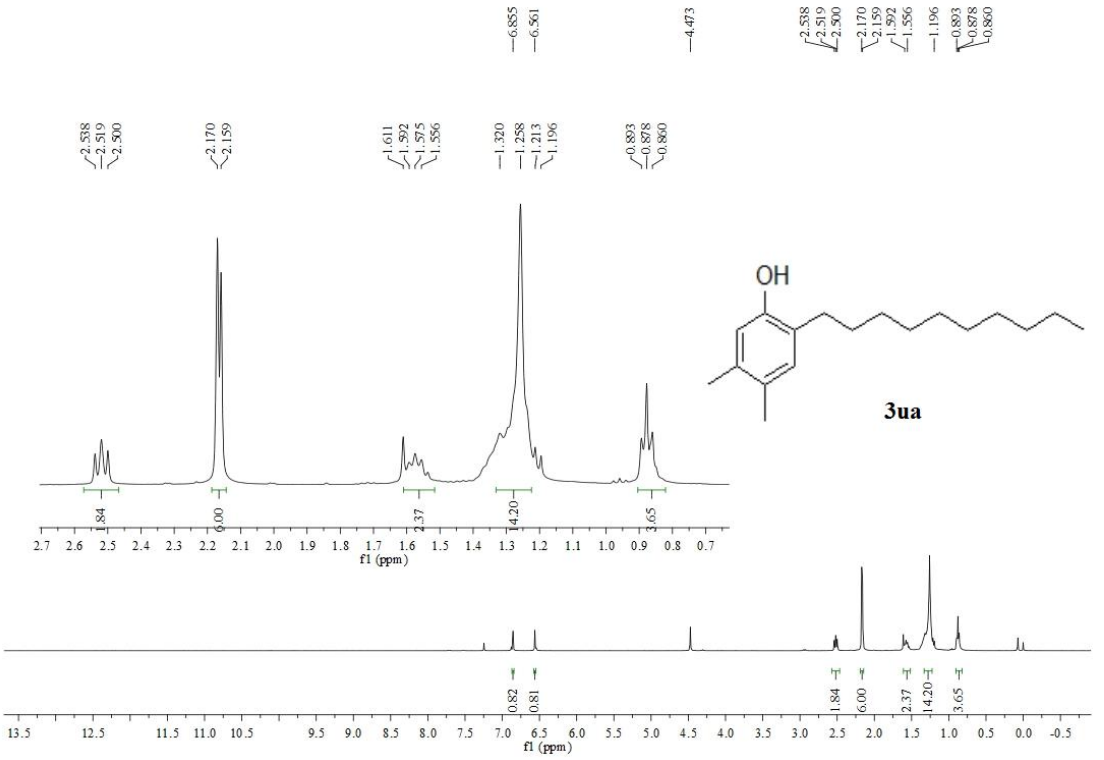

8.623
8.612
7.758
7.739
7.720
7.545
7.376
7.260
7.202
7.035
6.732
5.279
2.225
N
O
Cl
3s
f1 (ppm)

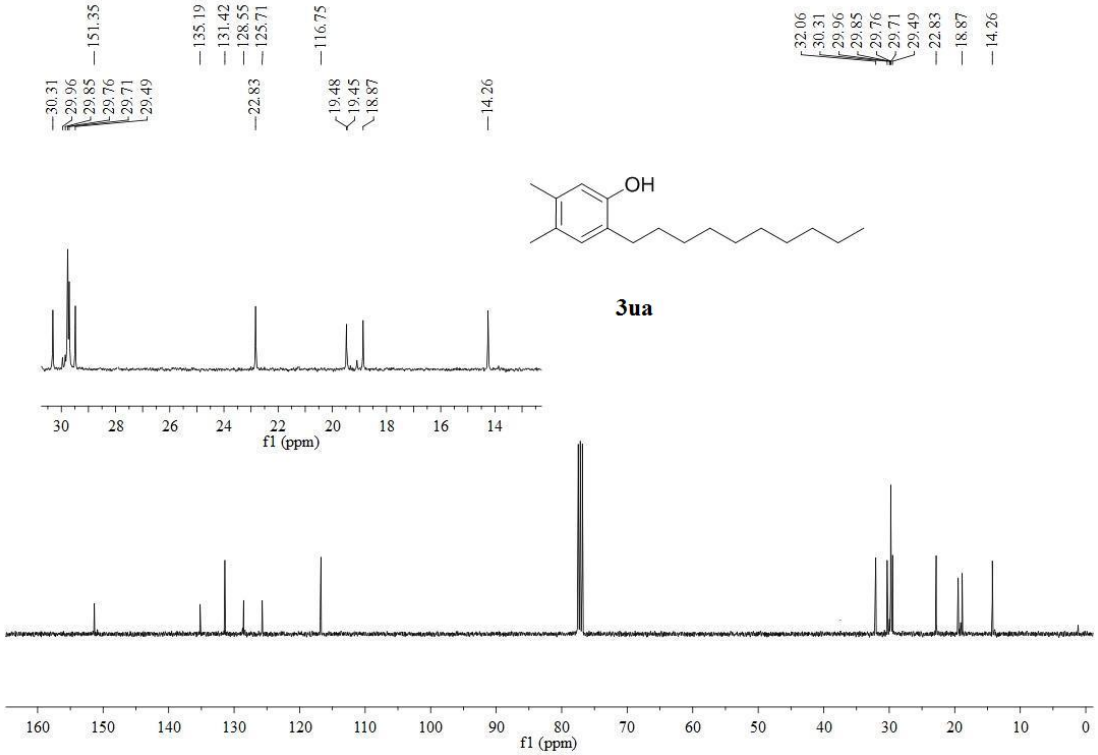

157.63
154.09
149.17
140.24
138.01
137.16
134.66
129.90
125.05
123.66
121.33
114.56
71.36
20.25
19.06
N
O
Cl
3s
f1 (ppm)

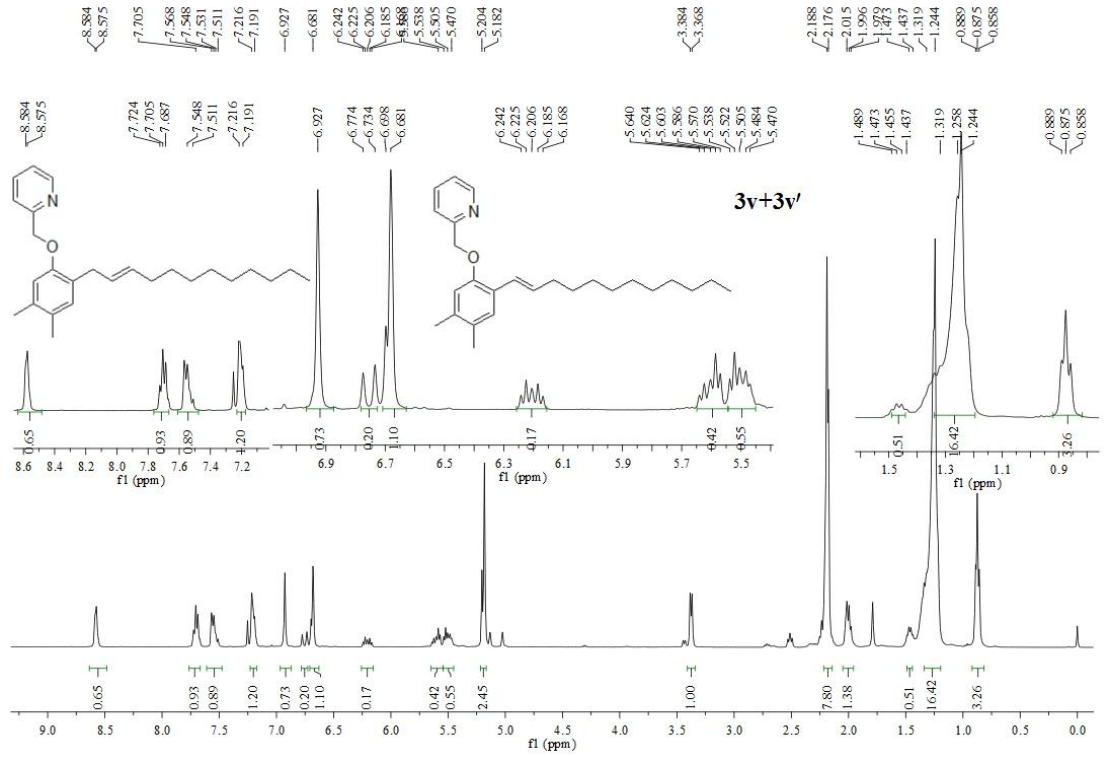

8.613
8.603
7.422
7.377
7.249
7.234
7.219
7.093
7.070
7.053
6.867
6.846
6.723
5.278
3.933
3.898
2.221
OMe
OMe
3t
f1 (ppm)

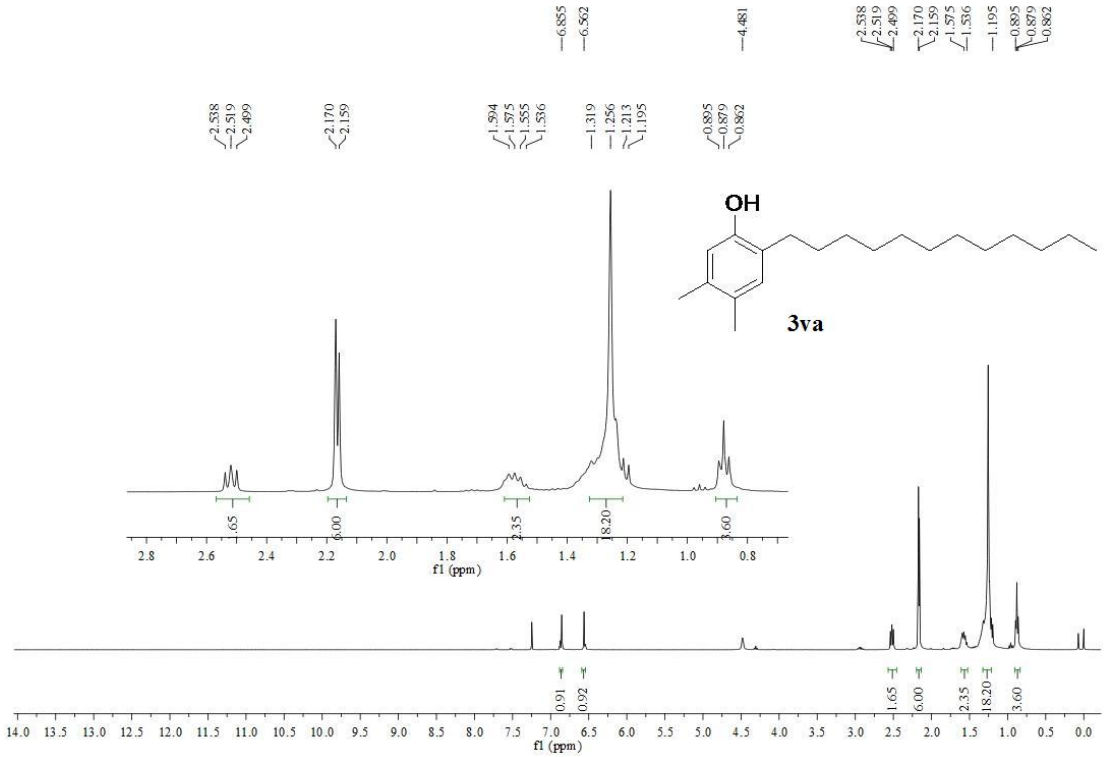

157.82
153.75
149.19
148.74
137.06
129.35
127.56
121.70
119.74
114.53
111.38
108.94
71.29
56.06
55.92
20.17
19.07
OMe
OMe
3t
f1 (ppm)

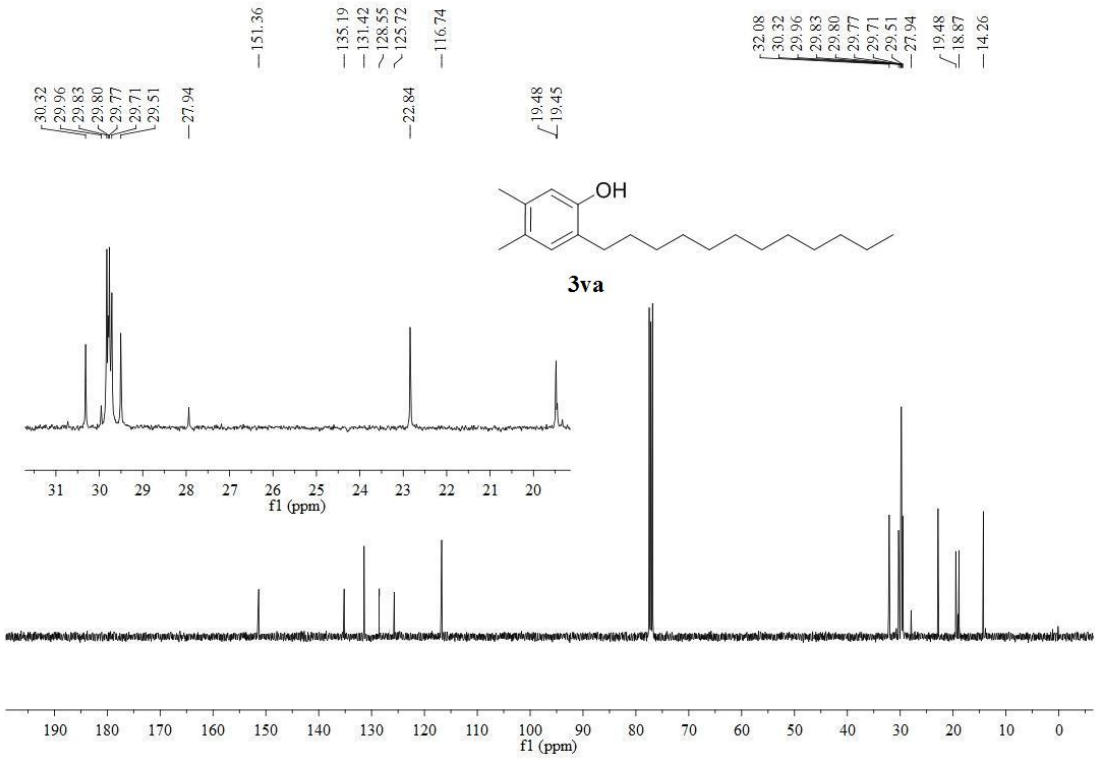

3u+3u′
f1 (ppm)

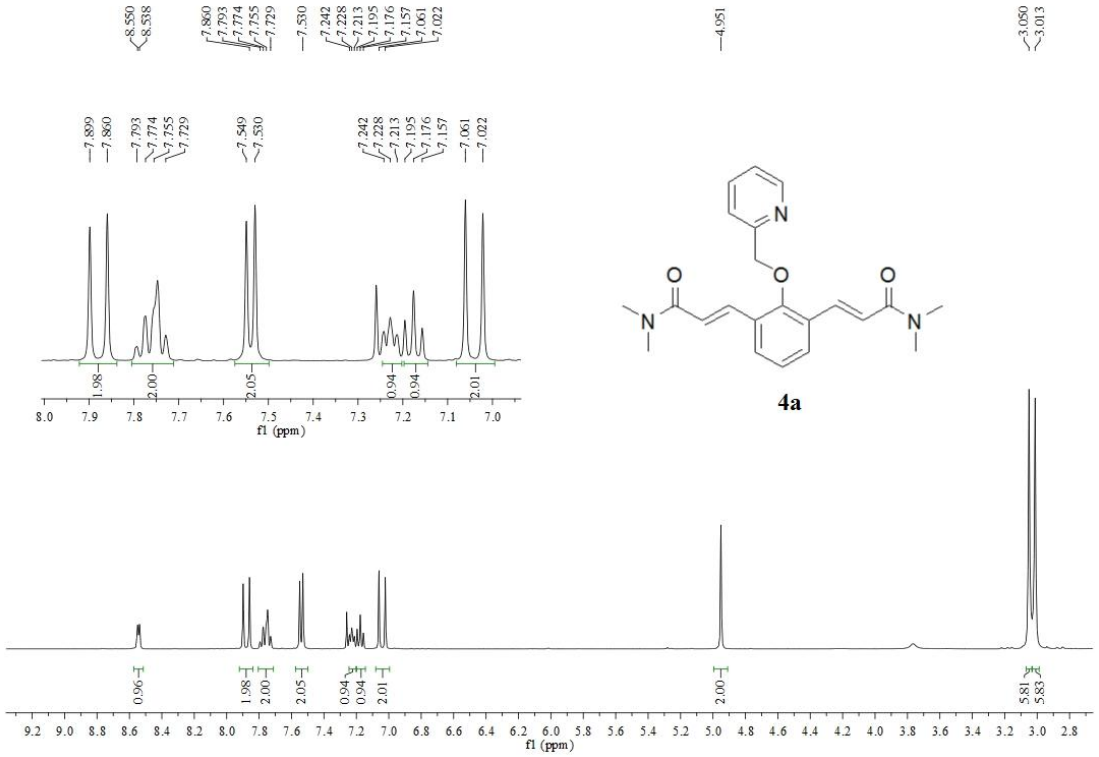

OH
3ua
f1 (ppm)

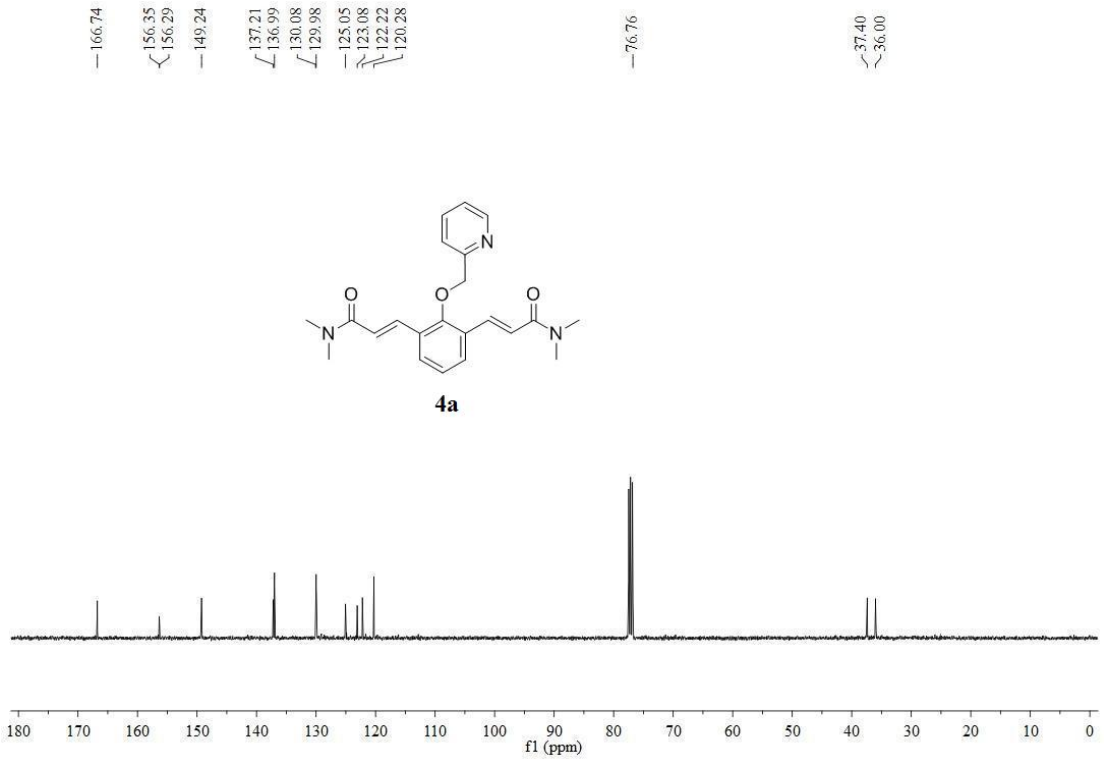

151.35
135.19
131.42
128.55
125.71
116.75
32.06
30.31
29.96
29.85
29.76
29.71
29.49
22.83
18.87
14.26
OH
3ua
f1 (ppm)
f1 (ppm)

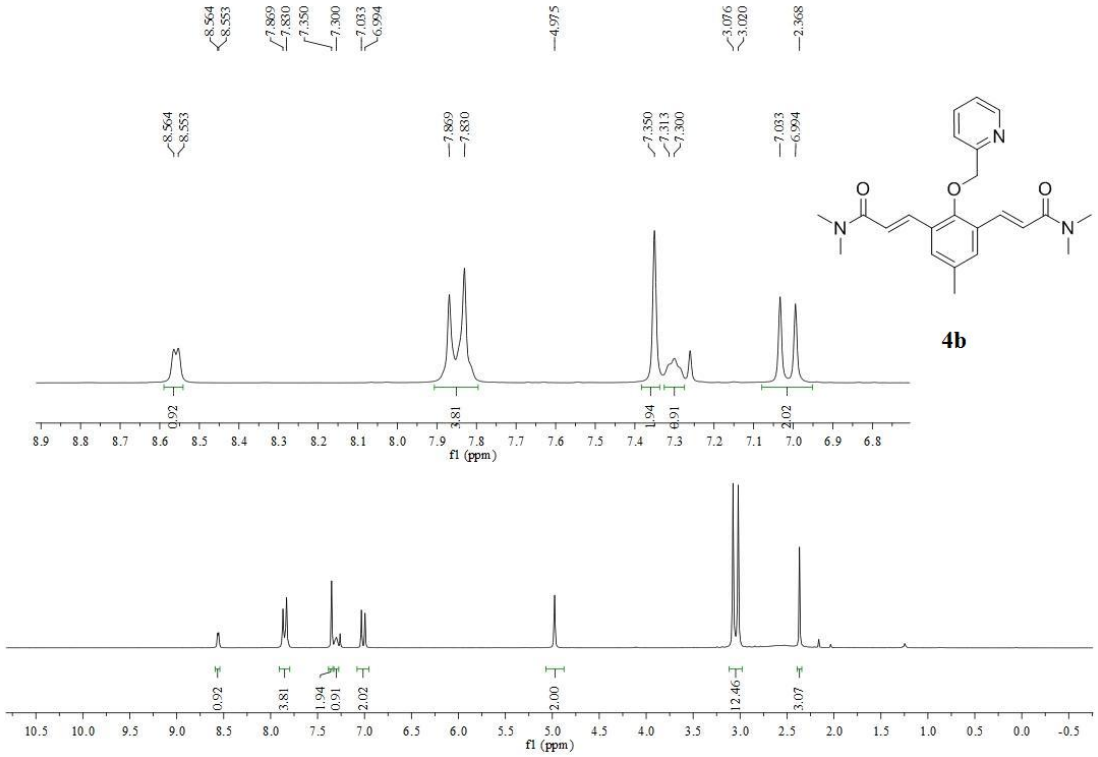

3v+3v′
f1 (ppm)


OH
3va
f1 (ppm)

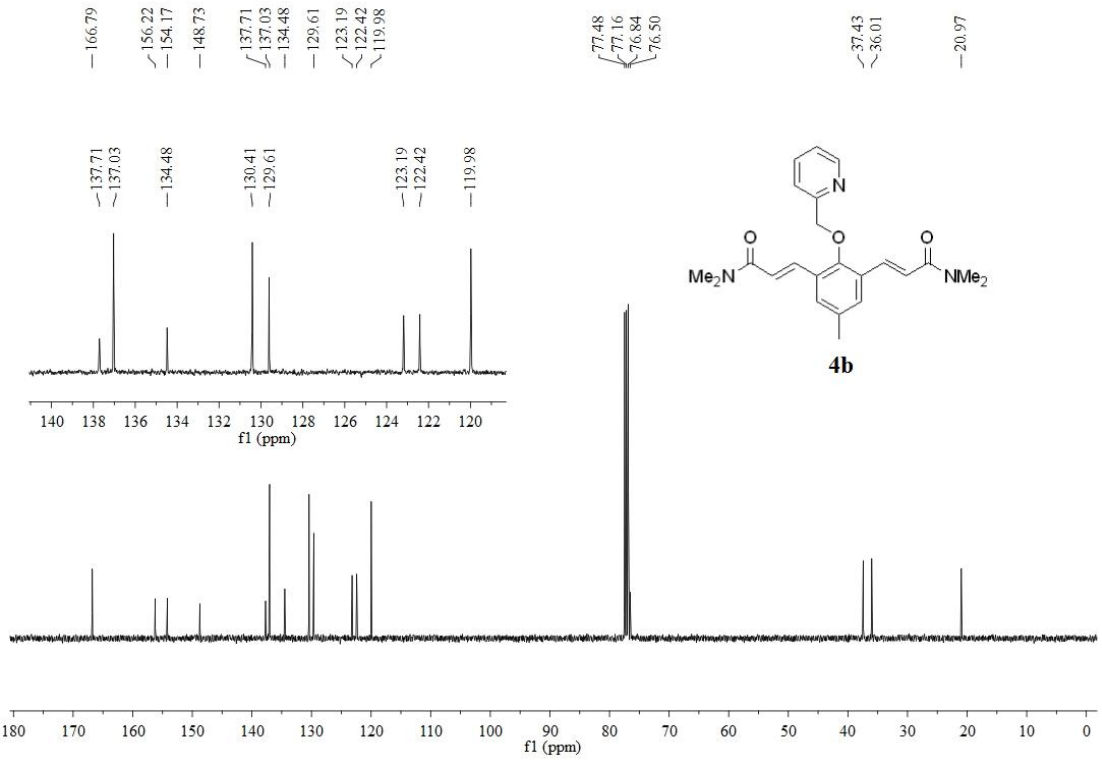

151.36
135.19
131.42
128.55
125.72
116.74
32.08
30.32
29.96
29.83
29.80
29.77
29.71
29.51
27.94
19.48
18.87
14.26
30.32
29.96
29.83
29.80
29.77
29.71
29.51
27.94
22.84
19.48
19.45
OH
3va
31 30 29 28 27 26 25 24 23 22 21 20
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.550
8.538
7.860
7.793
7.774
7.755
7.729
7.530
7.242
7.228
7.213
7.195
7.176
7.157
7.061
7.022
4.951
3.050
3.013
1.98
2.00
2.05
0.94
0.94
2.01
f1 (ppm)
4a
0.96
1.98
2.00
2.05
0.94
0.94
2.01
2.00
5.81
5.83
f1 (ppm)

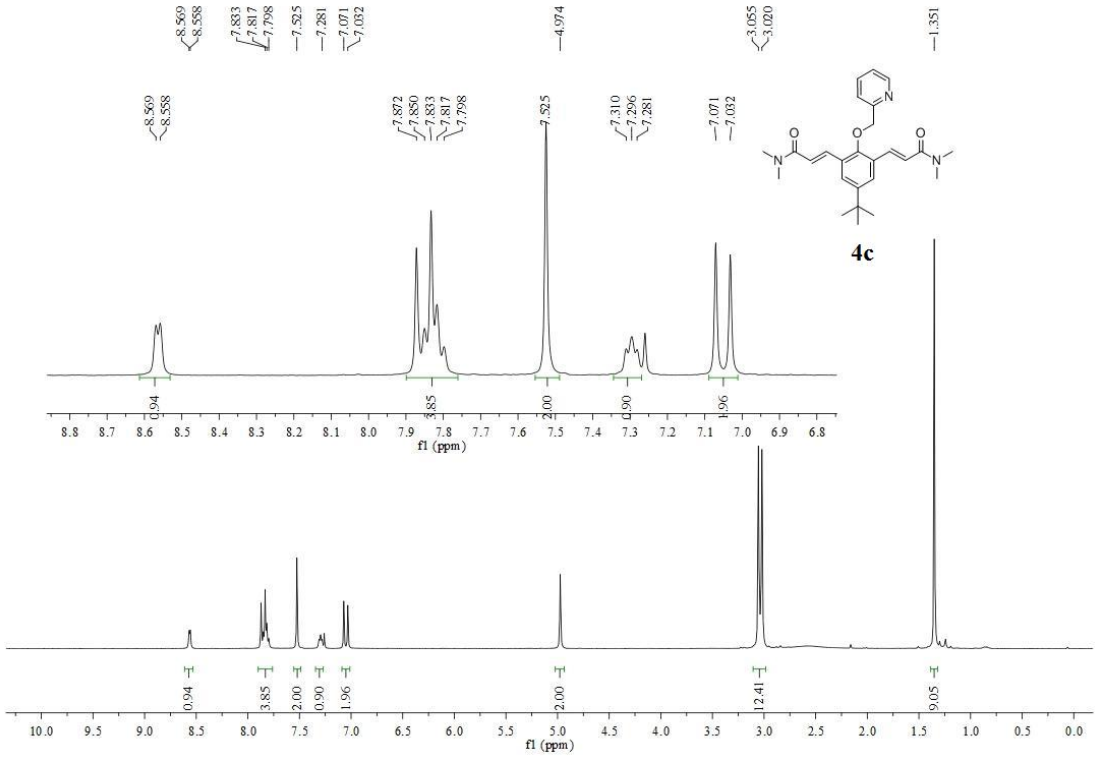

166.74
156.35
156.29
149.24
137.21
136.99
130.08
129.98
125.05
123.08
122.22
120.28
76.76
37.40
36.00
4a
f1 (ppm)

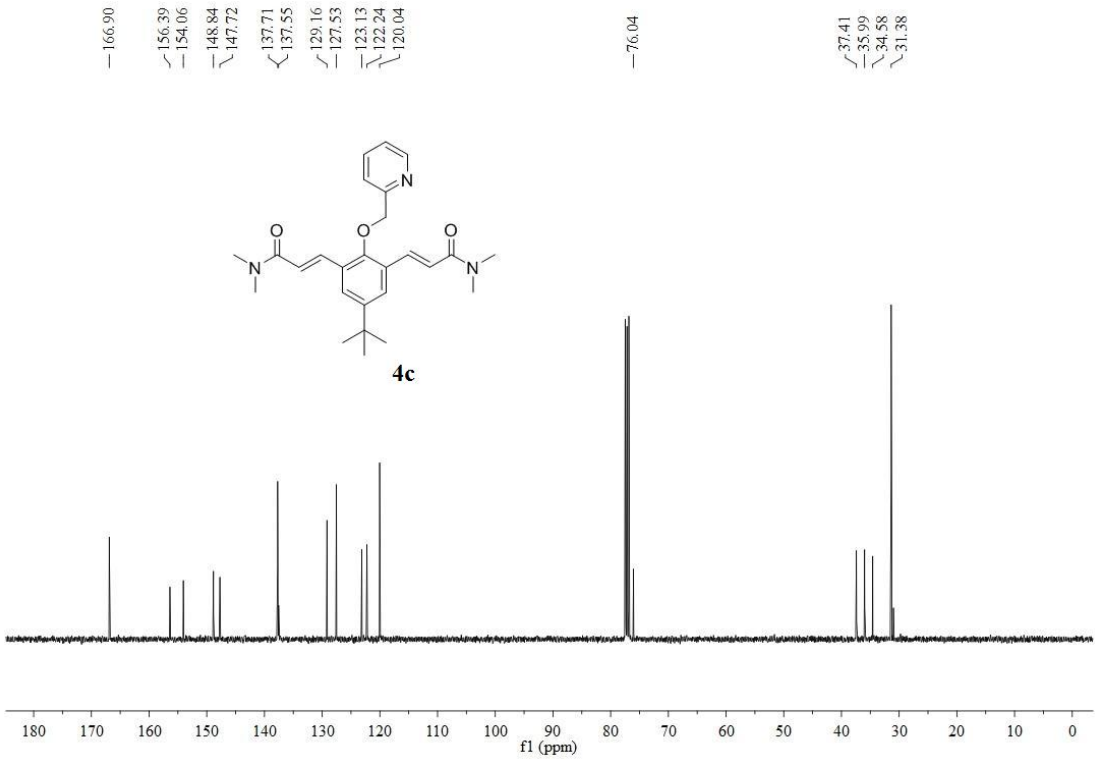

8.564
8.553
7.869
7.830
7.350
7.313
7.300
7.033
6.994
4.975
3.076
3.020
2.368
0.92
3.81
1.94
0.91
2.02
2.00
12.46
3.07
f1 (ppm)

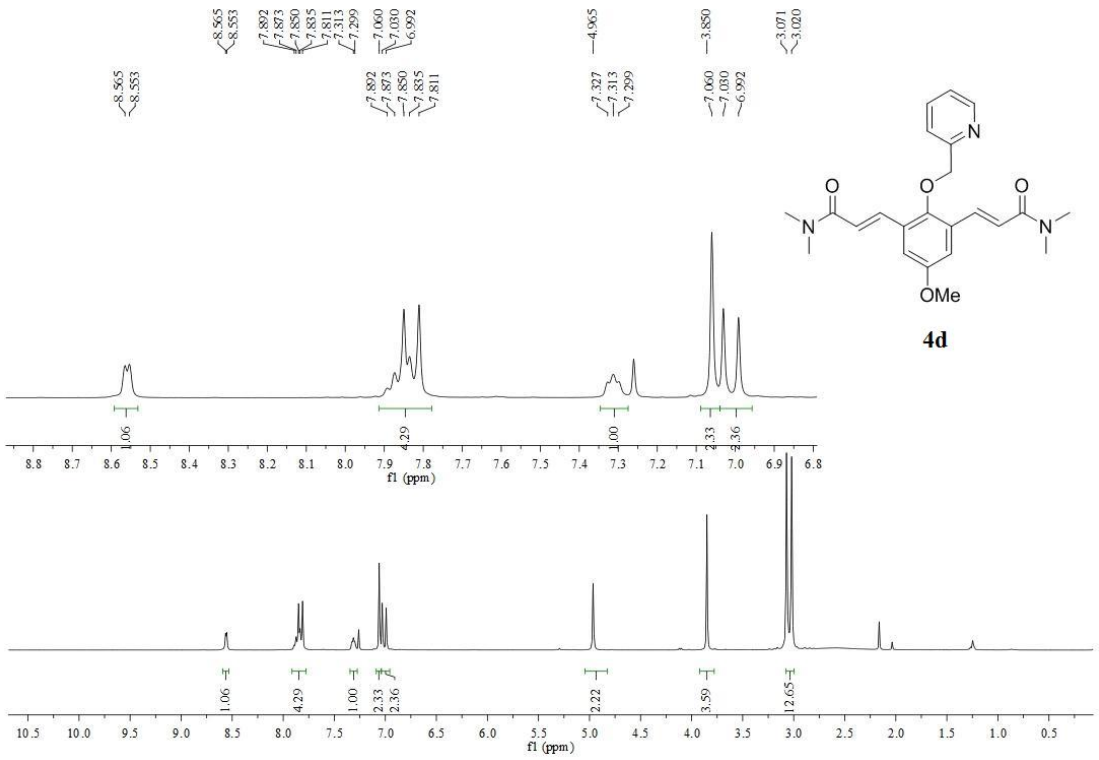
4b

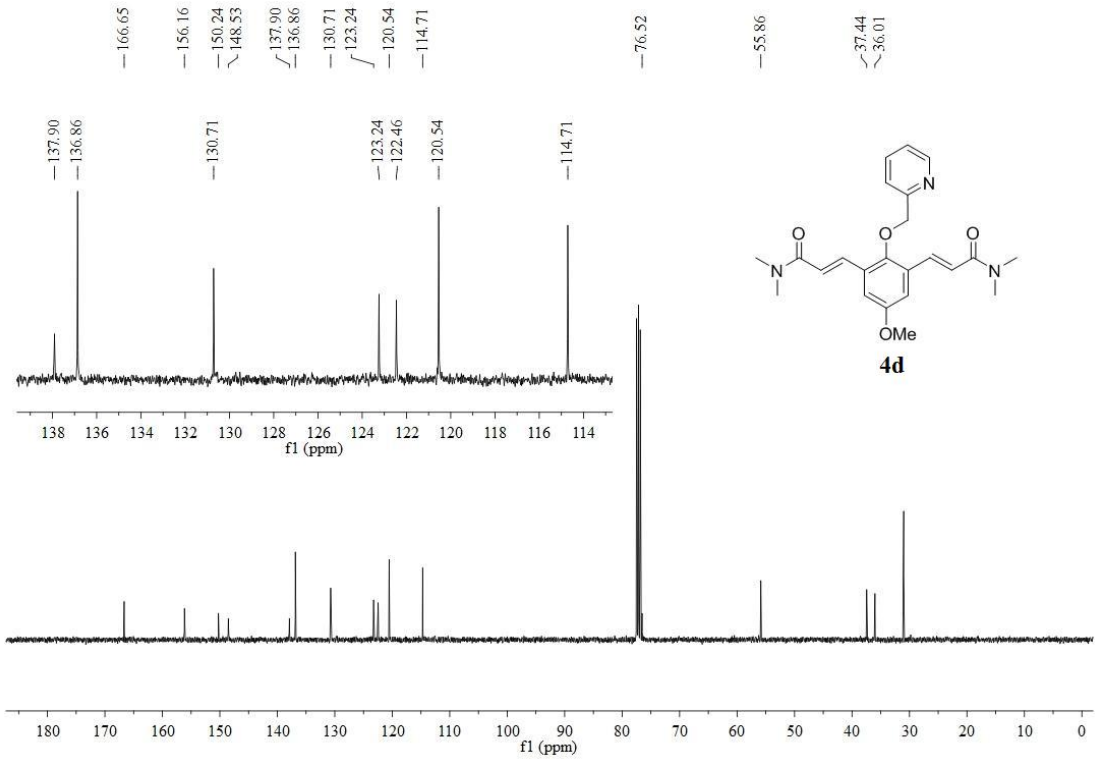

166.79
156.22
154.17
148.73
137.71
137.03
134.48
129.61
123.19
122.42
119.98
77.48
77.16
76.84
76.50
37.43
36.01
20.97
130.41
f1 (ppm)

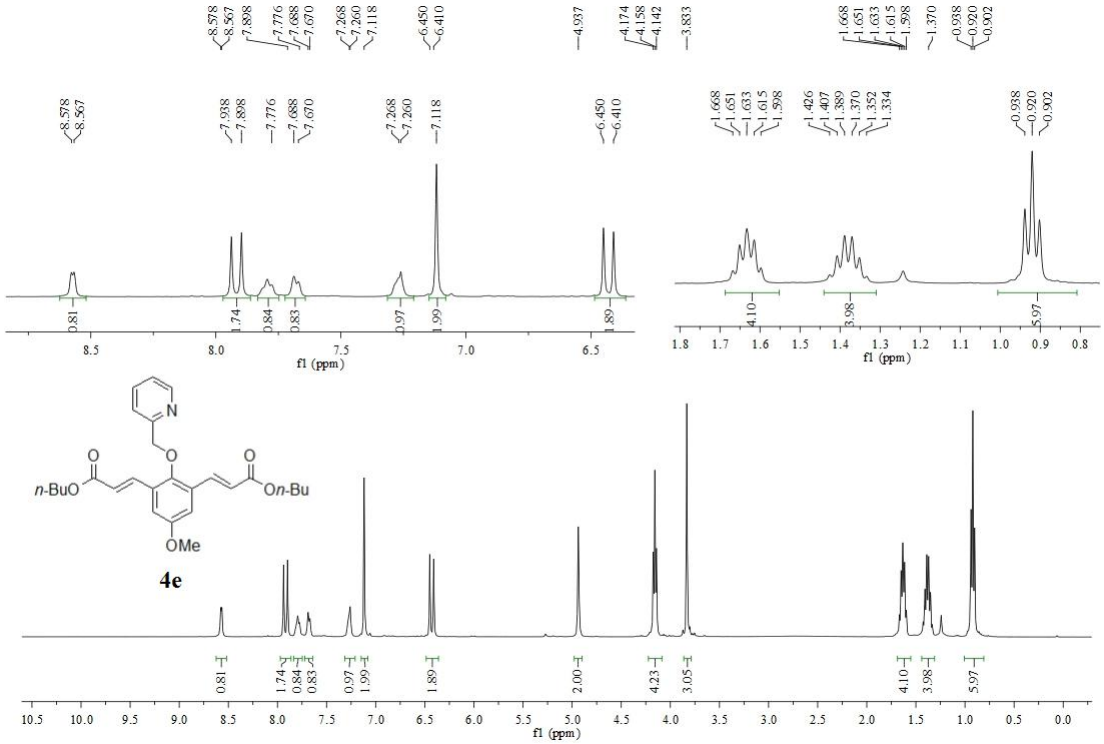
4b

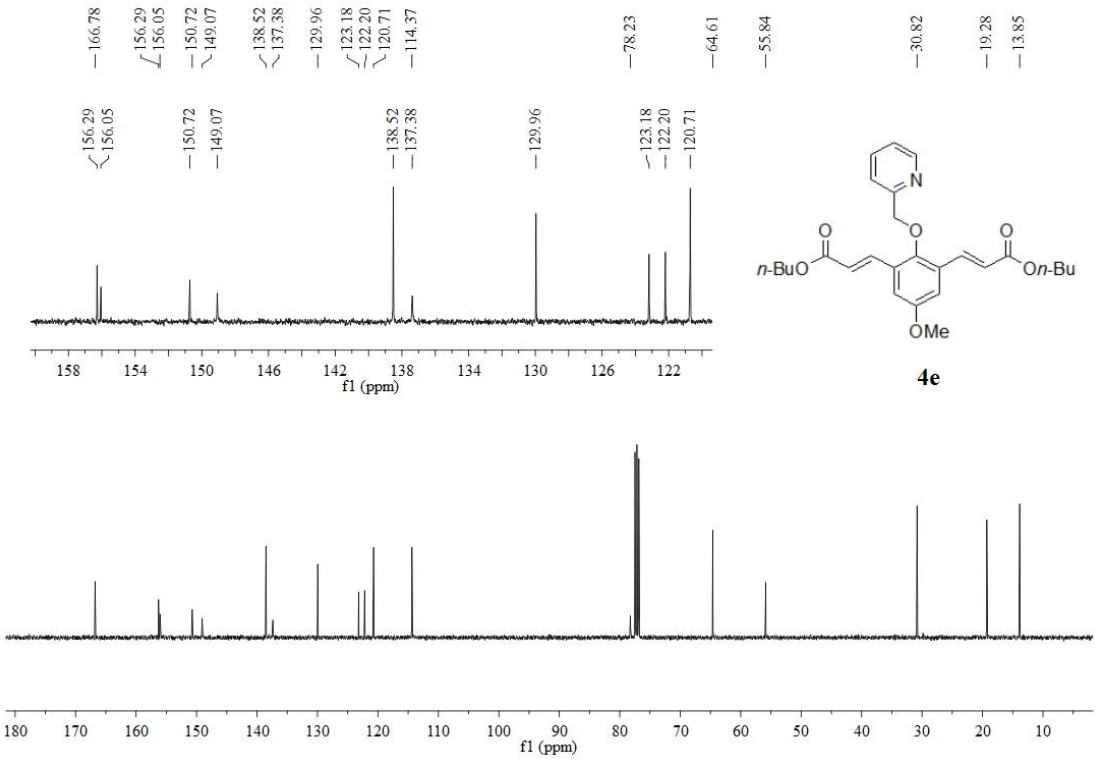

8.569
8.558
7.883
7.817
7.798
7.525
7.281
7.071
7.032
4.974
3.055
3.020
1.351
4c
f1 (ppm)

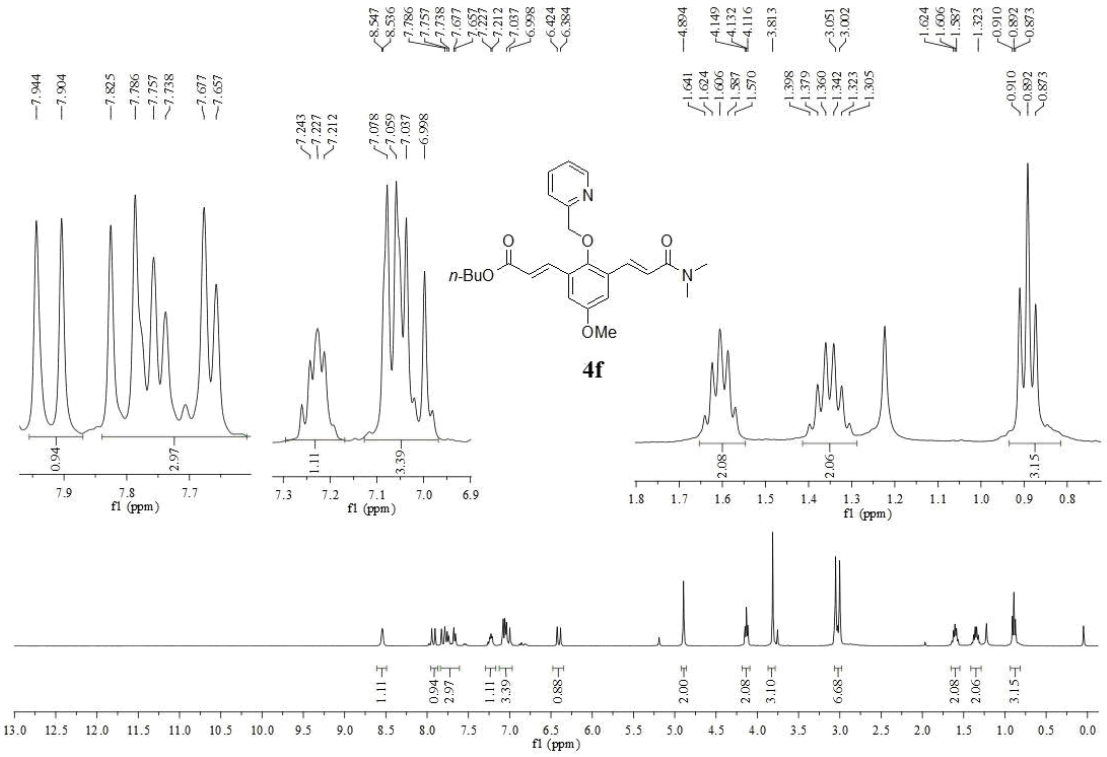

166.90
156.39
154.06
148.84
147.72
137.71
137.55
129.16
127.53
123.13
122.24
120.04
76.04
37.41
35.99
34.58
31.38
4c
f1 (ppm)

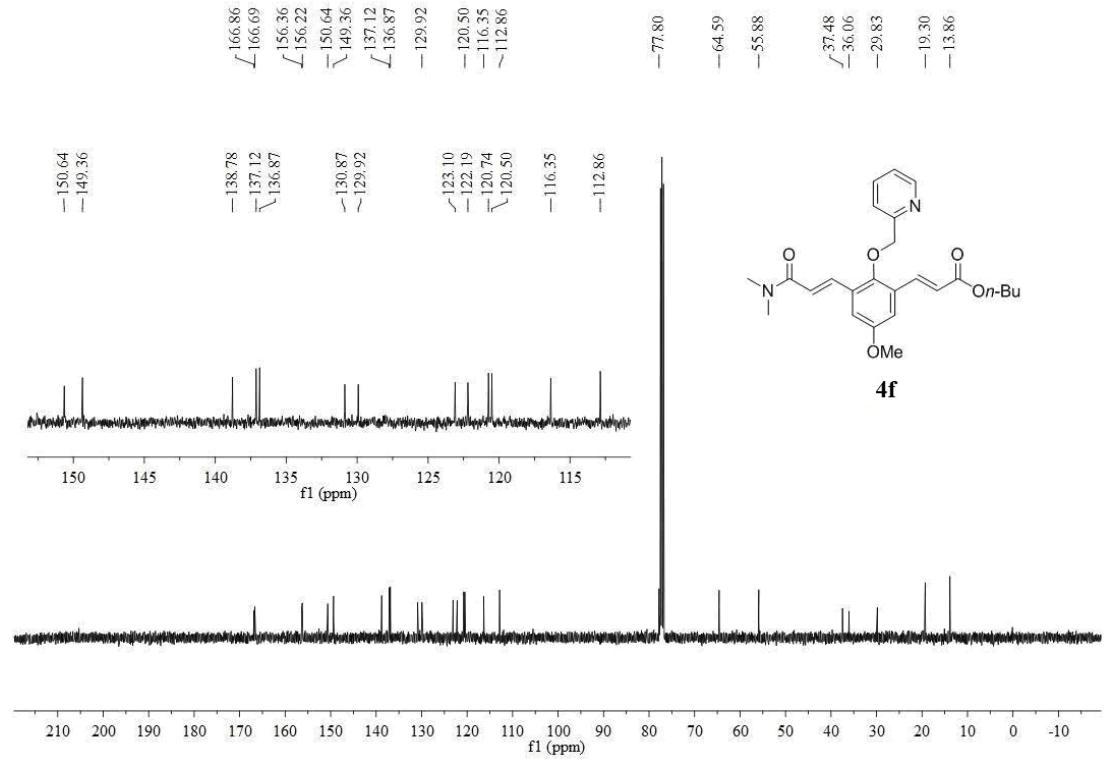

8.565
8.553
7.892
7.873
7.850
7.835
7.811
7.313
7.299
7.060
7.030
6.992
4.965
3.850
3.071
3.020
f1 (ppm)
4d

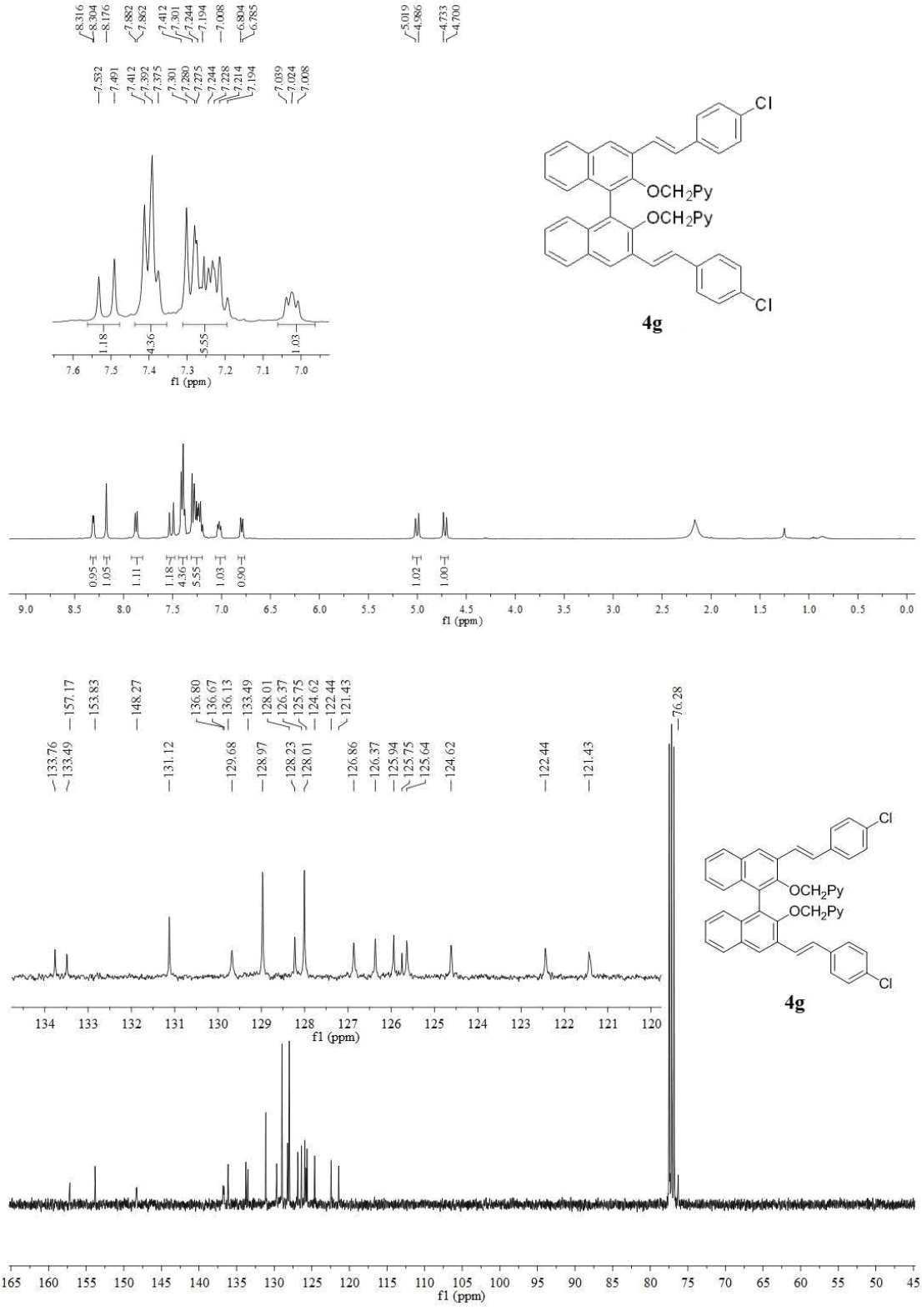

166.65
156.16
150.24
148.53
137.90
136.86
130.71
123.24
122.46
120.54
114.71
76.52
55.86
37.44
36.01
f1 (ppm)
4d

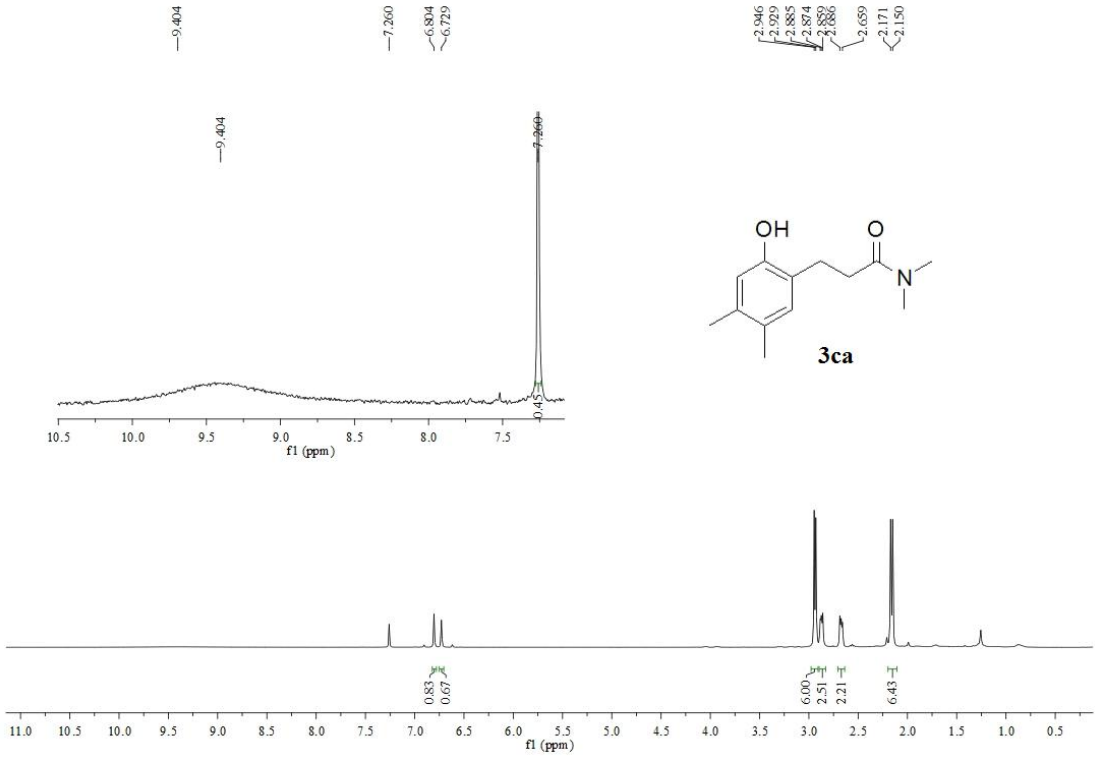

8.578
8.567
7.938
7.898
7.776
7.688
7.670
7.268
7.260
7.118
6.450
6.410
4.937
4.174
4.158
4.142
3.833
1.668
1.651
1.633
1.615
1.598
1.426
1.407
1.389
1.370
1.352
1.334
0.938
0.920
0.902
f1 (ppm)
n-BuO
On-Bu
OMe
4e

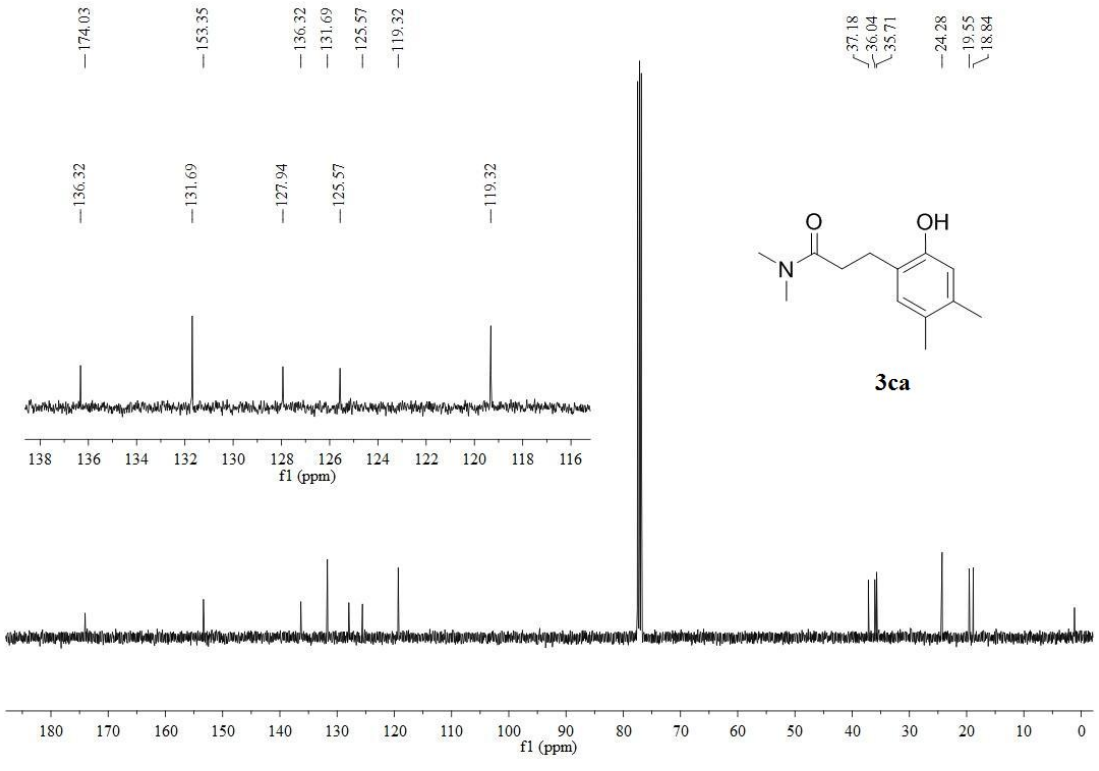

166.78
156.29
156.05
150.72
149.07
138.52
137.38
129.96
123.18
122.20
120.71
114.37
78.23
64.61
55.84
30.82
19.28
13.85
f1 (ppm)
n-BuO
On-Bu
OMe
4e

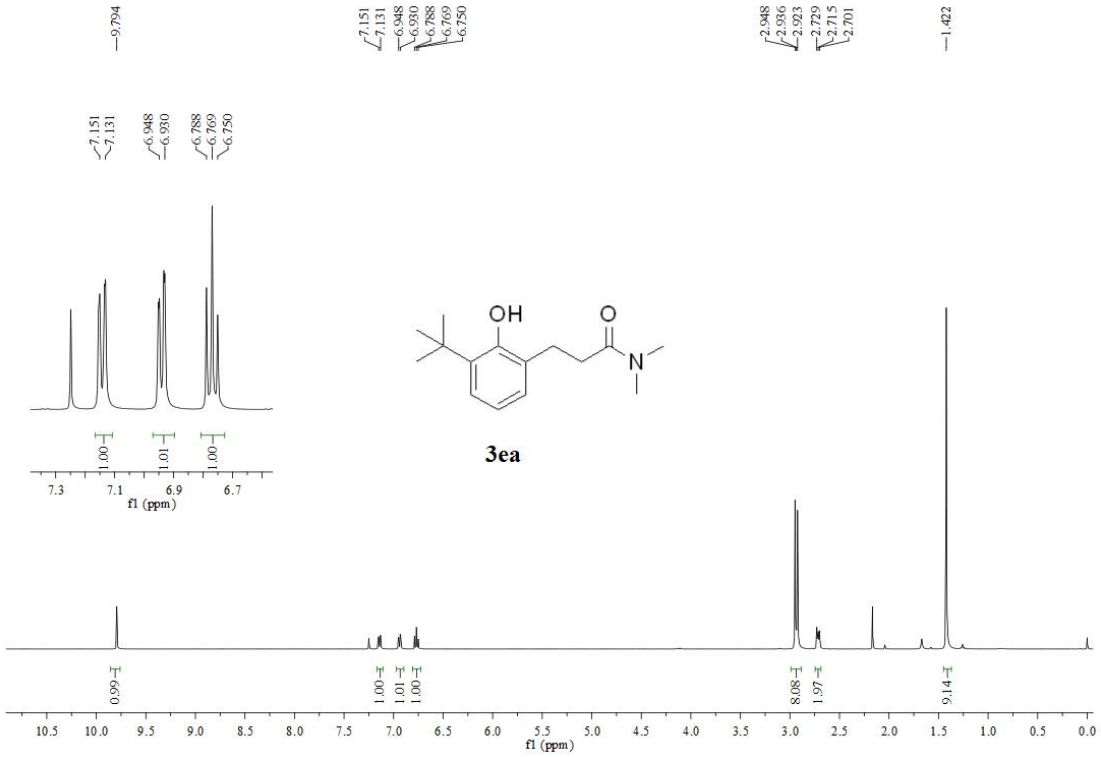

n-BuO
OMe
4f
f1 (ppm)

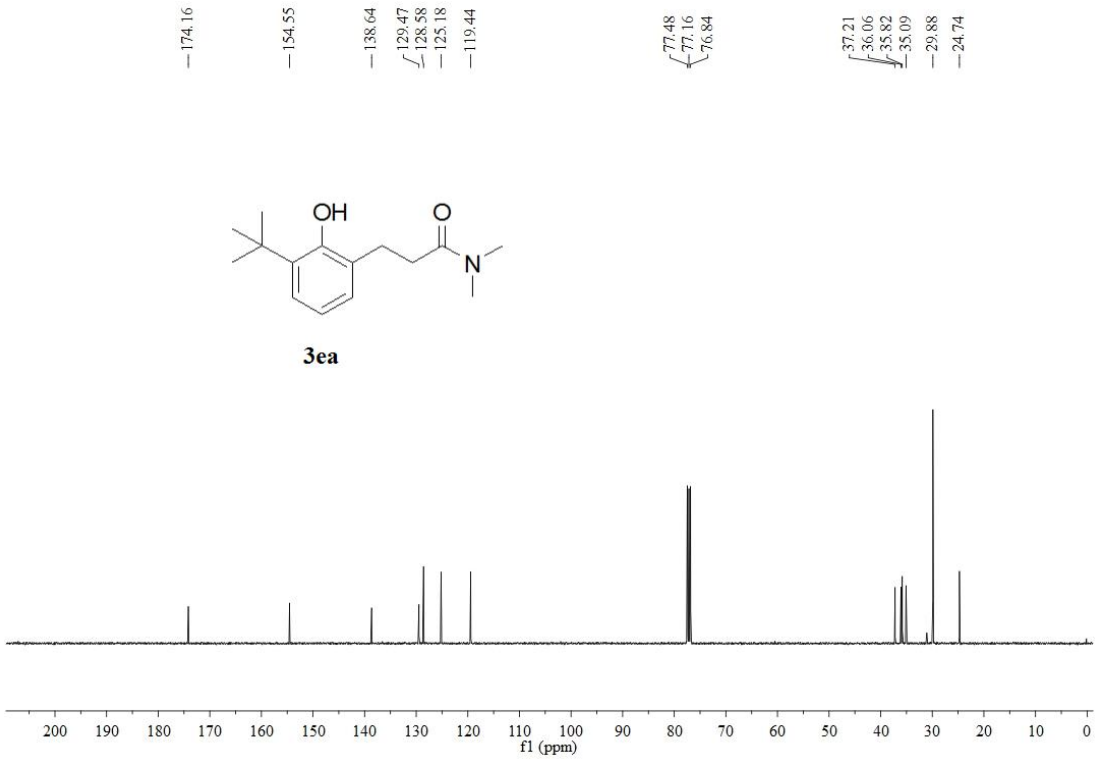

On-Bu
OMe
4f
f1 (ppm)

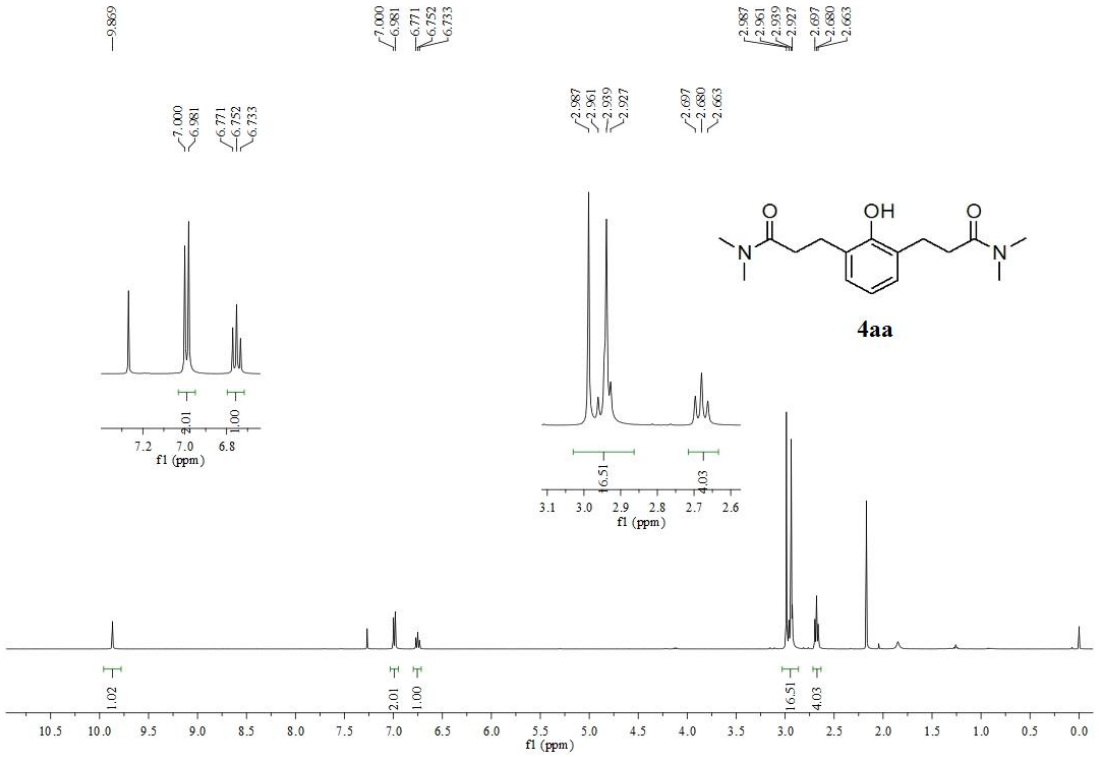

8.316
8.304
8.176
7.882
7.862
7.412
7.301
7.244
7.194
7.008
6.804
6.785
5.019
4.986
4.733
4.700
7.532
7.491
7.412
7.392
7.375
7.301
7.280
7.275
7.244
7.228
7.214
7.194
7.039
7.024
7.008
1.18
4.36
5.55
1.03
f1 (ppm)
Cl
OCH2Py
OCH2Py
Cl
4g
0.95
1.05
1.11
1.18
4.36
5.55
1.03
0.90
1.02
1.00
f1 (ppm)
157.17
153.83
148.27
136.80
136.67
136.13
133.49
128.01
126.37
125.75
124.62
122.44
121.43
76.28
133.76
133.49
131.12
129.68
128.97
128.23
128.01
126.86
126.37
125.94
125.75
125.64
124.62
122.44
121.43
f1 (ppm)
f1 (ppm)
Cl
OCH2Py
OCH2Py
Cl
4g

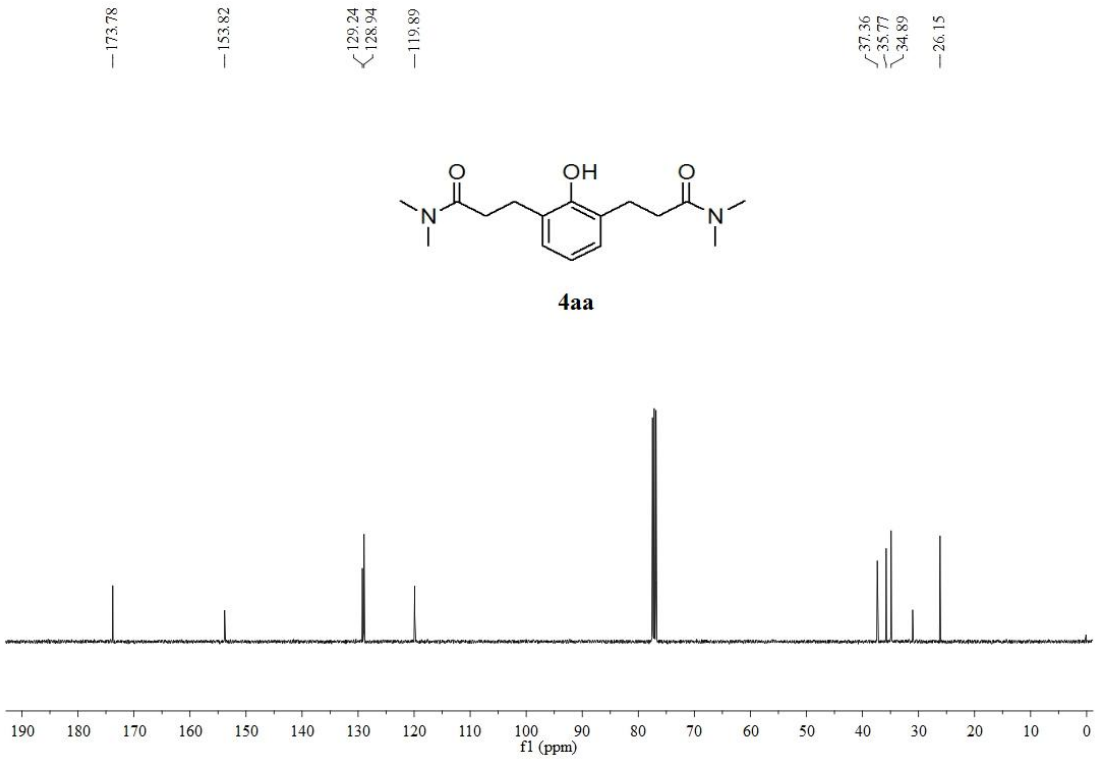

9.404
7.260
6.804
6.729
2.946
2.929
2.885
2.874
2.659
2.171
2.150
OH
O
N
3ca
f1 (ppm)
0.83
0.67
6.00
2.51
2.21
6.43

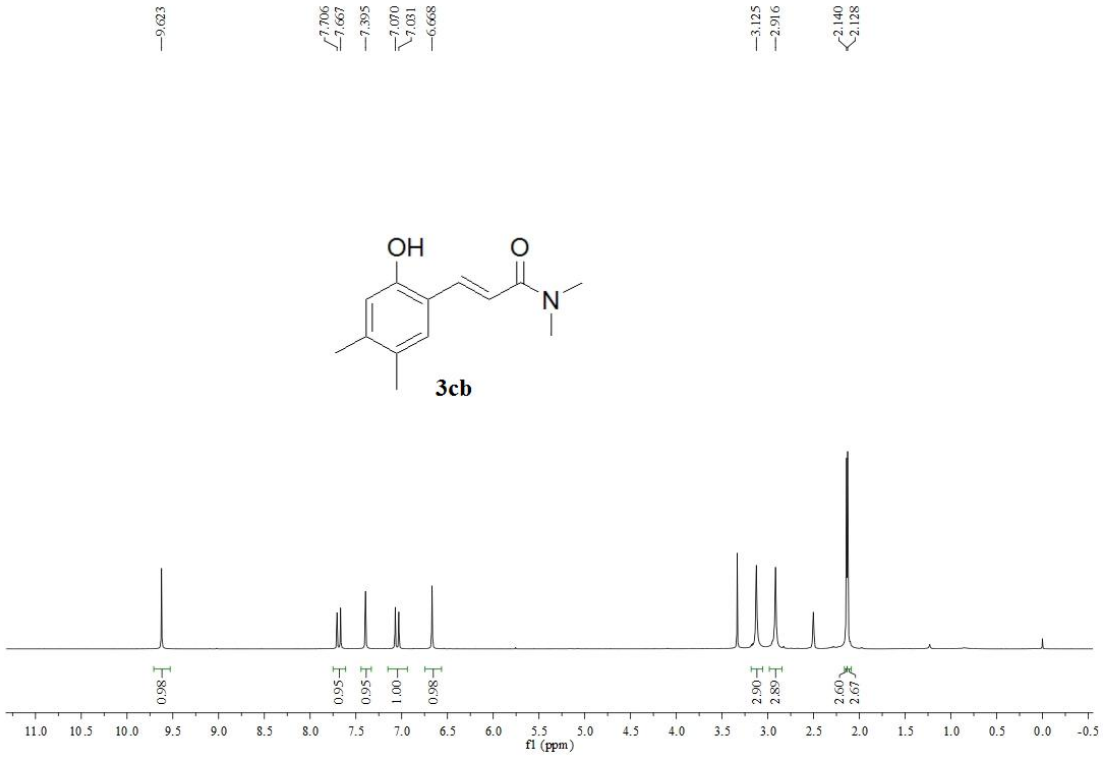

174.03
153.35
136.32
131.69
125.57
119.32
37.18
36.04
35.71
24.28
19.55
18.84
127.94
O
OH
N
3ca
f1 (ppm)

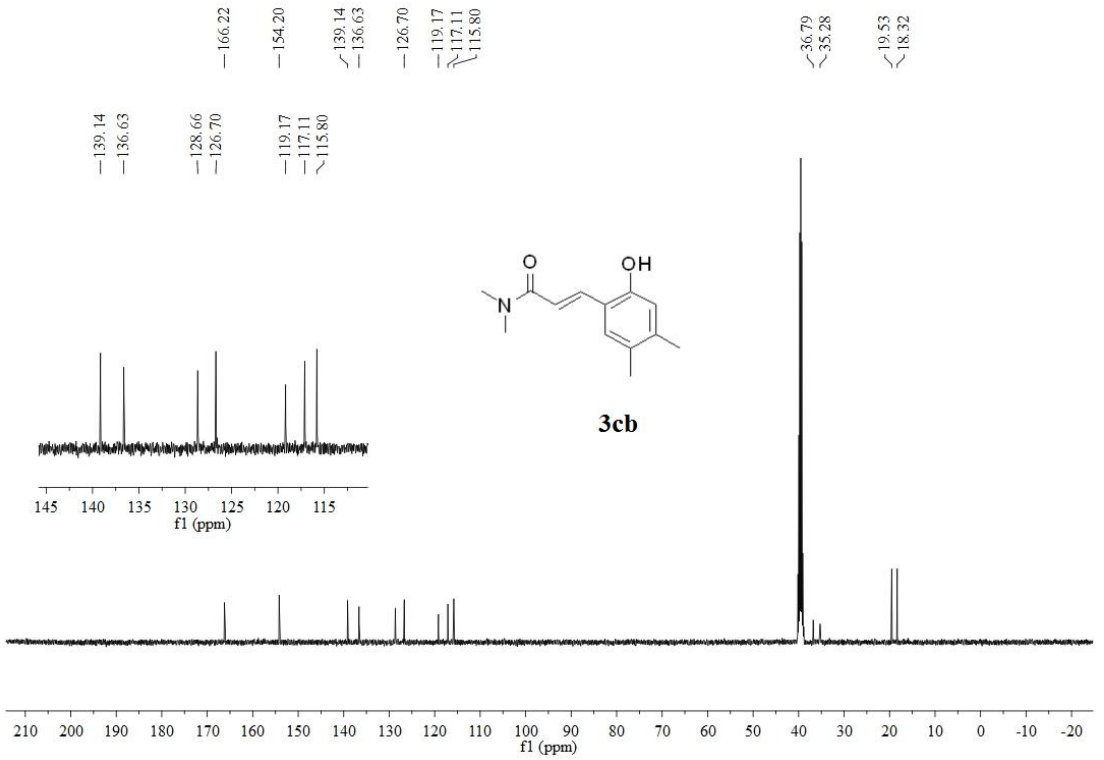

9.794
7.151
7.131
6.948
6.930
6.788
6.769
6.750
2.948
2.936
2.923
2.729
2.715
2.701
1.422
OH
O
N
3ea
1.00
1.01
1.00
0.99
1.00
1.01
1.00
8.08
1.97
9.14
f1 (ppm)

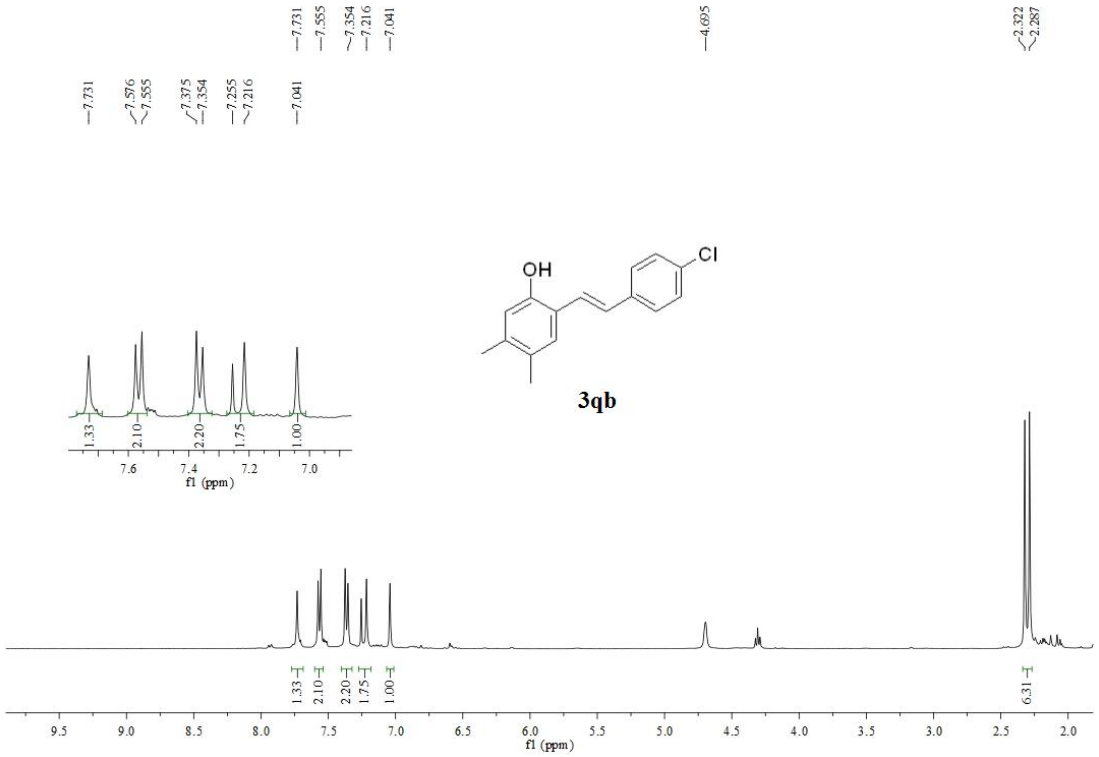

174.16
154.55
138.64
129.47
128.58
125.18
119.44
77.48
77.16
76.84
37.21
36.06
35.82
35.09
29.88
24.74
OH
O
N
3ea
f1 (ppm)

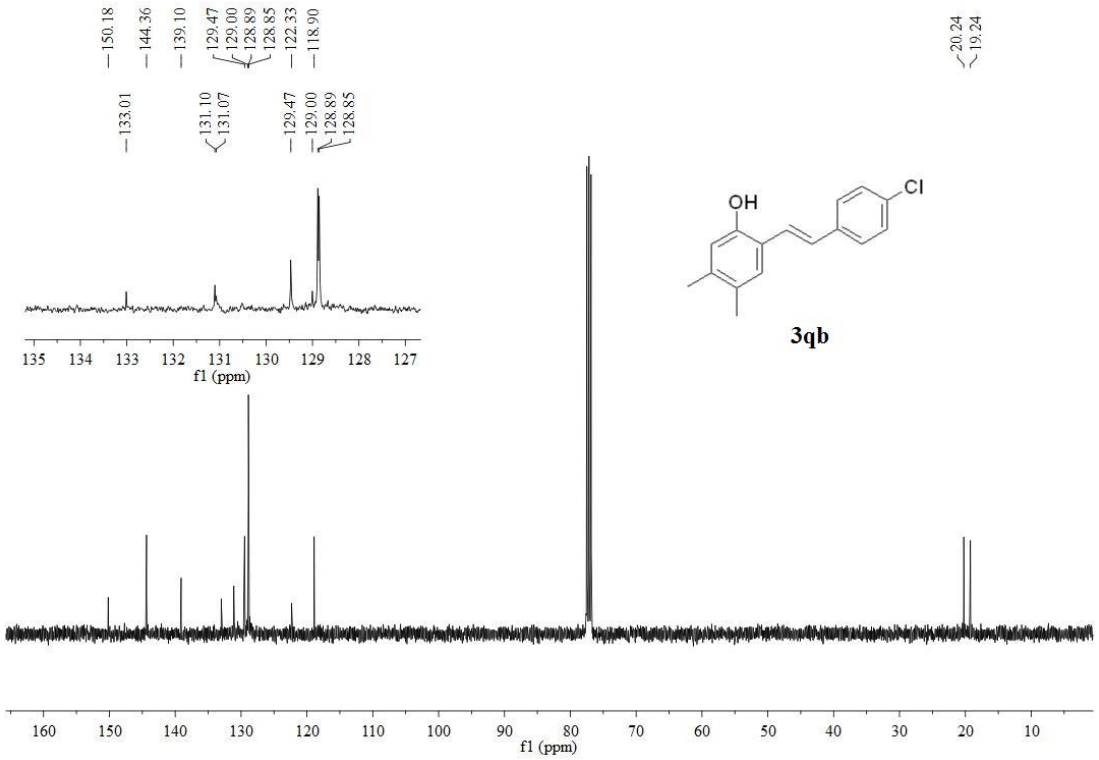

9.869
7.000
6.981
6.771
6.752
6.733
2.987
2.961
2.939
2.927
2.697
2.680
2.663
OH
O
N
4aa
1.02
2.01
1.00
16.51
4.03
f1 (ppm)


173.78
153.82
129.24
128.94
119.89
37.36
35.77
34.89
26.15
OH
O
N
4aa
f1 (ppm)


9.623
7.706
7.667
7.395
7.070
7.031
6.668
3.125
2.916
2.140
2.128
OH
O
N
3cb
0.98
0.95
0.95
1.00
0.98
2.90
2.89
2.60
2.67
f1 (ppm)


166.22
154.20
139.14
136.63
126.70
119.17
117.11
115.80
36.79
35.28
19.53
18.32
128.66
O
OH
N
3cb
f1 (ppm)


7.731
7.555
7.354
7.216
7.041
4.695
2.322
2.287
OH
Cl
3qb
1.33
2.10
2.20
1.75
1.00
6.31
f1 (ppm)


150.18
144.36
139.10
129.47
129.00
128.89
128.85
122.33
118.90
133.01
131.10
131.07
20.24
19.24
OH
Cl
3qb
f1 (ppm)