Supporting Information

Nickel-Catalyzed Synthesis of (*E*)-Olefins from Benzylic Alcohol Derivatives and Arylacetonitriles via C-O Activation

Jing Xiao,[1] Jia Yang,[1] Tieqiao Chen,*[1] Li-Biao Han*[2]

E-mail: chentieqiao@hnu.edu.cn; libiao-han@aist.go.jp

[1]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. [2]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan.

Table of Contents

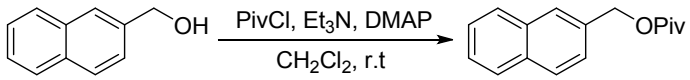
1. General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All solvents were dried by standard methods. $Ni(COD)_2$ and phosphine ligands are stored under nitrogen in the glove box. Unless otherwise noted, all coupling reactions were performed in 10-mL glass vessel tubes and carried out under N_2 atmosphere.

Flash column chromatography was performed using 200-300 mesh silica gel. Visualization on TLC was achieved by the use of UV light (254 nm). All reactions were monitored by GC, GC-MS. ^1H NMR, ^{13}C NMR spectra were measured on a Bruker Avance III-400 spectrometer. (^1H 400 MHz, ^{13}C 101 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.0 ppm for ^{13}C). The coupling constants *J* are given in Hz. Mass spectra were recorded by GCMS-QP2010 ultra spectrometer. The GC yields were accorded to the authentic samples/tridecane calibration standard from Shimadzu GC-2010 plus equipped with FID system.

2. Synthesis of starting materials

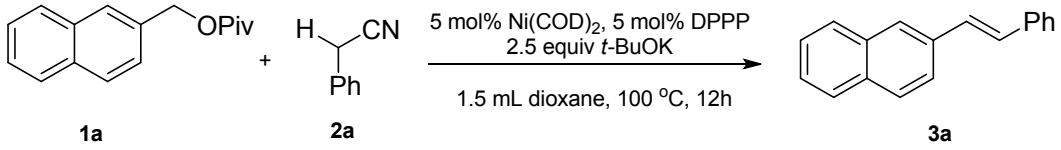
Substrates **1** were prepared according to the literature procedure.[1,2]



1a

Typical procedure: To a solution of naphthalen-2-ylmethanol (3.16 g, 20 mmol) and 4,4-dimethylaminopyridine (DMAP, 10 mol%) in CH_2Cl_2 (30 mL) was added triethylamine (3.35 mL, 24 mmol, 1.2 equiv) at room temperature. Then pivaloyl chloride (2.95 mL, 24 mmol, 1.2 equiv) was added dropwise over 3 min at 0 °C. After stirring for 15 min, the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL), then the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (25 mL × 3) and the combined organic layer was dried over Na_2SO_4 and then filtrated. After evaporation of the solvent under reduced pressure, the crude residue was purified by flash column chromatography (Petroleum ether/EtOAc = 10:1) to afford the product **1a** in 90% yield.

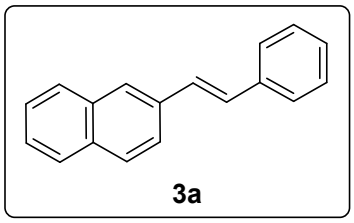
3. Typical procedure for the Nickel-catalyzed Synthesis of (E)-Olefins from Benzylic Alcohol Derivatives and Arylacetonitriles via C-O Activation



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

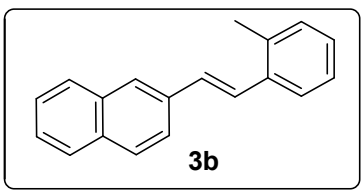
In a nitrogen-filled glove box, a 10 mL sealed schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol), $Ni(COD)_2$ (0.005 mmol), DPPP (0.005 mmol), *t*-BuOK (0.25 mmol) and **2a** (0.15 mmol) and dioxane (1.5 mL). The reaction mixture was stirred at 100 °C for 12 hours. After cooling the reaction mixture to room temperature, the mixture was passed through a short silica gel column with EtOAc as eluent. The filtrate was concentrated and the residue was further purified by column chromatography on silica gel to give the product **3a** in 81 % isolated yield (86% GC yield).

4. Characterization and analytical data of products (*average yields based on two parallel reactions*)



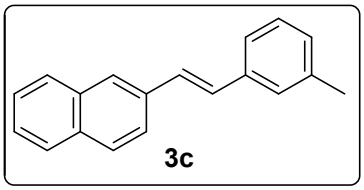
3a

(*E*)-2-styrylnaphthalene 3a, yield for pivalate 81%, 37.3 mg; yield for carbamate 65%, 29.9 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.86–7.80 (m, 4H), 7.76–7.74 (m, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.50–7.43 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H)， 7.31–7.25 (m, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.38, 134.84, 133.73, 133.06, 129.05, 128.79, 128.75, 128.32, 128.01, 127.71, 126.64, 126.56, 126.35, 125.92, 123.53. This compound is known.[1]

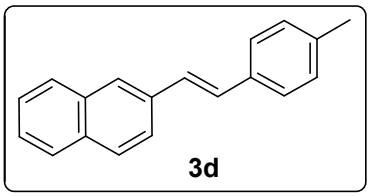


3b

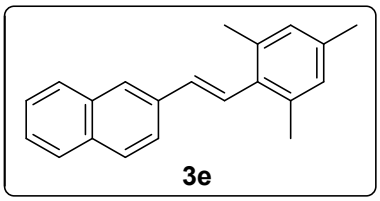
(*E*)-2-(2-methylstyryl)naphthalene 3b, yield 71%, 34.6 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.85–7.74 (m, 5H), 7.65 (d, J = 7.2 Hz, 1H), 7.49–7.42 (m, 3H), 7.24–7.14 (m, 4H), 2.47 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 136.44, 135.88, 135.20, 133.75, 133.06, 130.48, 130.10, 128.32, 128.02, 127.72, 127.63, 126.86, 126.62, 126.36, 126.27, 125.91, 125.37, 123.64, 20.00. This compound is known.[2]



(*E*)-2-(3-methylstyryl)naphthalene 3c, yield 70%, 34.2 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.82–7.78 (m, 4H), 7.73–7.70 (m, 1H), 7.47–7.40 (m, 2H), 7.36–7.34 (m, 2H), 7.27–7.20 (m, 3H), 7.08 (d, J = 19.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 138.31, 137.35, 134.98, 133.78, 133.07, 129.19, 128.68, 128.62, 128.58, 128.34, 128.05, 127.76, 127.32, 126.62, 126.37, 125.91, 123.81, 123.58, 21.53. This compound is known.[3]

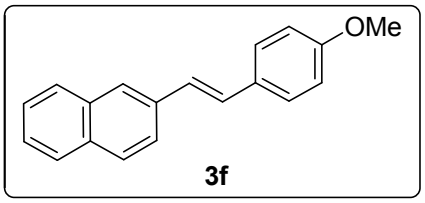


(*E*)-2-(4-methylstyryl)naphthalene 3d, yield 79%, 38.6 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.82–7.70 (m, 5H), 7.45–7.40 (m, 4H), 7.20–7.16 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.63, 135.07, 134.63, 133.79, 132.99, 129.48, 129.02, 128.29, 127.99, 127.82, 127.72, 126.51, 126.41, 126.32, 125.81, 123.56, 21.31. This compound is known.[4]



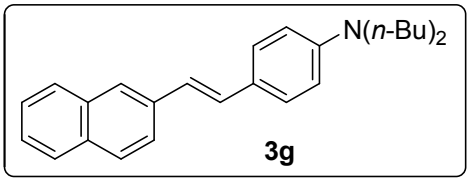
3e

(*E*)-2-(2,4,6-trimethylstyryl)naphthalene 3e, yield 91%, 49.5 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.80–7.72 (m, 5H), 7.46–7.42 (m, 2H), 7.25–7.17 (m, 1H), 6.92–6.91 (m, 2H), 6.77–6.72 (m, 1H), 2.39–2.37 (m, 6H), 2.31–2.69 (m, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 136.44, 136.28, 135.29, 134.11, 133.83, 133.07, 128.89, 128.35, 128.04, 127.79, 127.41, 126.41, 126.22, 125.88, 123.46, 21.18, 21.09. This compound is known.[5]



3f

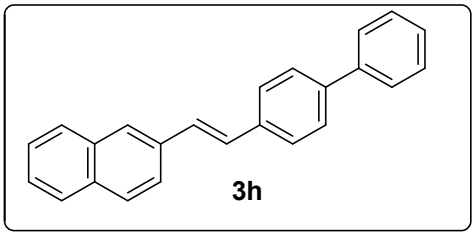
(*E*)-2-(4-methoxystyryl)naphthalene 3f, yield 85%, 44.2 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.80–7.69 (m, 5H), 7.49–7.41 (m, 4H), 7.22–7.09 (m, 2H), 6.90 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 159.41, 135.20, 133.81, 132.89, 130.21, 128.61, 128.26, 127.93, 127.79, 127.70, 126.72, 126.29, 126.13, 125.70, 123.51, 114.22, 55.35. This compound is known.[4]



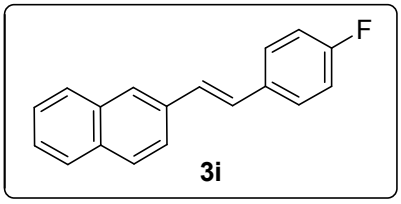
3g

(*E*)-N,N-dibutyl-4-(2-(naphthalen-2-yl)vinyl)aniline 3g, yield 58%, 41.5 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.80–7.70 (m, 5H), 7.45–7.37 (m, 4H), 7.16 (d, J = 16.0

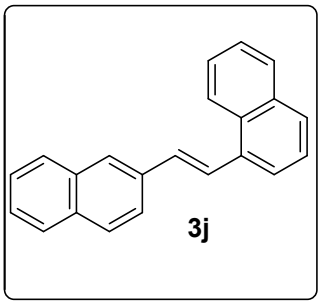
Hz, 1H), 7.03 (d, J = 16.4 Hz, 1H), 6.64 (d, J = 8.4 Hz, 2H), 3.29 (t, J = 7.6 Hz, 4H), 1.59–1.55 (m, 4H), 1.39–1.32 (m, 4H), 0.96 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ 147.92, 135.93, 133.92, 132.59, 129.35, 128.11, 127.85, 127.80, 127.67, 126.17, 125.36, 125.31, 124.51, 123.69, 123.58, 111.69, 50.83, 29.53, 20.39, 14.05.



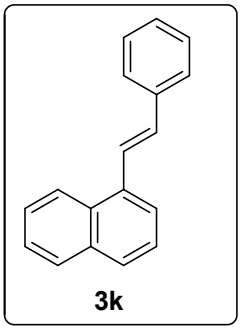
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)naphthalene 3h, yield 61%, 37.4 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.81–7.69 (m, 6H), 7.58–7.56 (m, 6H), 7.33–7.27 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.19 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 139.68, 139.40, 135.43, 133.85, 132.74, 132.07, 127.84, 127.80, 127.55, 127.33, 127.00, 126.70, 126.39, 126.34, 125.96, 125.92, 125.64, 125.35, 124.91, 122.52. This compound is known.[6]



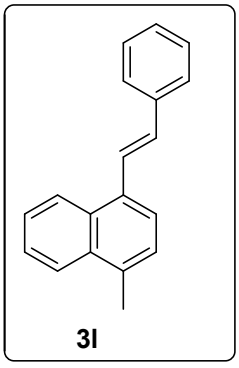
(*E*)-2-(4-fluorostyryl)naphthalene 3i, yield 70%, 34.7 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.83–7.81 (m, 4H), 7.71 (d, J = 8.8 Hz, 1H), 7.53–7.44 (m, 4H), 7.18 (s, 2H), 7.07 (t, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 162.40 (d, $J_{C\text{-}F}$ = 245.9 Hz). 134.68, 133.72, 133.57 (d, $J_{C\text{-}F}$ = 3.4 Hz), 133.07, 128.59 (d, $J_{C\text{-}F}$ = 2.3 Hz), 128.37, 128.07, 127.99, 127.82, 127.73, 126.59, 126.40, 125.96, 123.43, 115.69 (d, $J_{C\text{-}F}$ = 21.5 Hz). This compound is known.[7]



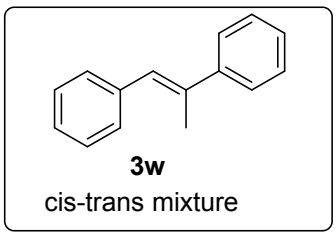
(*E*)-1-(2-(naphthalen-2-yl)vinyl)naphthalene 3j, yield 76%, 42.6 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 8.27 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 16.0 Hz, 1H), 7.91–7.78 (m, 8H), 7.57–7.43 (m, 5H), 7.31 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 135.15, 135.06, 133.82, 133.78, 133.16, 131.85, 131.46, 128.69, 128.42, 128.13, 128.09, 127.77, 126.82, 126.42, 126.16, 126.11, 126.02, 125.89, 125.76, 123.83, 123.73, 123.65. This compound is known.[8]



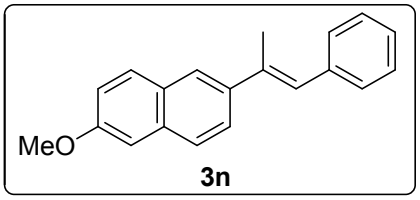
(*E*)-1-styrylnaphthalene 3k, yield 75%, 34.5 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 8.21 (d, J = 8.0 Hz, 1H), 7.90–7.85 (m, 2H), 7.79 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 6.8 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.53-7.38 (m, 3H), 7.40 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.16–7.07 (m, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.67, 135.07, 133.78, 131.82, 131.45, 128.80, 128.66, 128.08, 127.82, 126.73, 126.13, 125.87, 125.86, 125.74, 123.82, 123.67. This compound is known.[9]



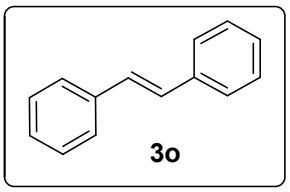
(*E*)-1-methyl-4-styrylnaphthalene 3l, yield 63%, 30.7 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 8.22–8.20 (m, 1H), 8.02–7.99 (m, 1H), 7.88–7.81 (m, 1H), 7.63–7.50 (m, 5H), 7.39–7.24 (m, 4H), 7.11–7.04 (m, 1H), 2.69 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): 137.84, 134.43, 133.48, 132.81, 131.54, 131.12, 128.80, 127.68, 126.68, 126.13, 125.80, 125.74, 124.77, 124.41, 123.47, 19.72. This compound is known.[10]



(*E*)-prop-1-ene-1,2-diyldibenzene 3m (cis-trans mixture) , yield 46%, 22.5 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.85–7.82 (m, 2H), 7.69–7.67 (m, 0.5H), 7.62–7.56 (m, 1.5H), 7.51–7.46 (m, 2.5H), 7.41– 7.21 (m, 5H), 7.00–6.99 (m, 1H), 6.64 (s, 0.5H), 2.36–2.26 (m, 3H). This compound is known.[7]

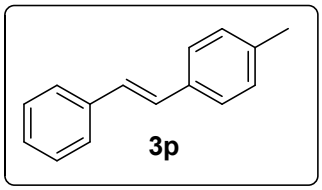


(*E*)-2-methoxy-6-(1-phenylprop-1-en-2-yl)naphthalene 3n, yield 40%, 21.9 mg. ^{1}H NMR (400 MHz $CDCl_3$): 7.86 (s, 1H), 7.76–7.69 (m, 3H), 7.40–7.36 (m, 4H), 7.26–7.25 (m, 1H), 7.16–7.13 (m, 2H), 6.97 (s, 1H), 3.92 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 157.72, 138.94, 138.53, 137.22, 133.85, 129.71, 129.24, 128.94, 128.21, 127.51, 126.70, 126.45, 124.90, 124.58, 118.98, 105.66, 55.34, 17.48. This compound is known.[11]

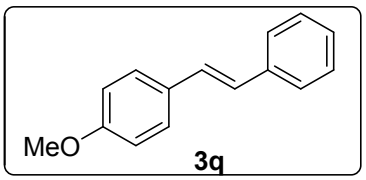


(*E*)-1,2-diphenylethene 3o, yield 73%, 26.3 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.50

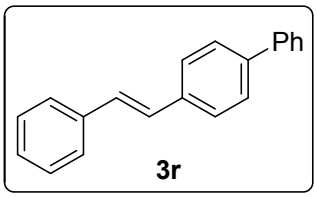
(d, J = 7.6 Hz, 4H), 7.34 (dd, J = 7.6 Hz, 7.6 Hz, 4H), 7.24 (t, J = 7.6 Hz, 2H), 7.10 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.40, 128.76, 127.69, 126.59. This compound is known.[1]



(*E*)-1-methyl-4-styrylbenzene 3p, for benzyl pivalate: yield 77%, 29.9 mg; for 4-methylbenzyl pivalate: yield 75%, 29.1 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 2.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.57, 137.55, 134.60, 129.44, 128.69, 128.67, 127.75, 127.45, 126.48, 126.44, 21.29. This compound is known.[1]

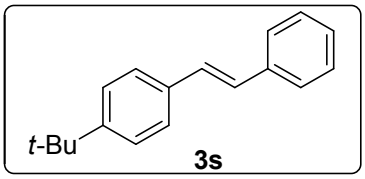


(*E*)-1-methoxy-4-styrylbenzene 3q, yield 61%, 25.6 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.49–7.44 (m, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.25–7.23 (m, 1H), 7.06 (d, J = 16.4 Hz, 1H), 6.97 (d, J = 16.4 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 159.33, 137.67, 130.17, 128.67, 128.23, 127.74, 127.23, 126.64, 126.28, 114.16, 55.35. This compound is known.[4]



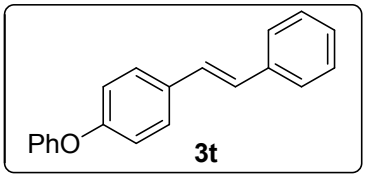
(*E*)-4-styryl-1,1'-biphenyl 3r, yield 53%, 27.1 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 7.63–7.59 (m, 6H), 7.53 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.38–7.35 (m, 3H), 7.28–7.24 (m, 1H), 7.15 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 140.70, 140.37, 137.36, 136.42, 128.83, 128.78, 128.73, 128.23, 127.68, 127.38, 127.36, 126.97,

126.95, 126.56. This compound is known.[12]



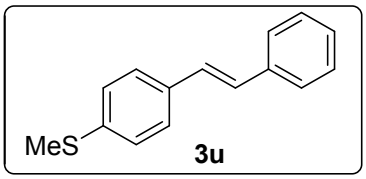
3s

(*E*)-1-(tert-butyl)-4-styrylbenzene 3s, yield 62%, 29.3 mg. ^{1}H NMR (400 MHz $CDCl_3$): 7.52–7.45 (m, 4H), 7.39–7.33 (m, 4H), 7.26–7.22 (m, 1H), 7.13–7.09 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz $CDCl_3$): δ 150.82, 137.58, 134.60, 128.67, 128.53, 127.96, 127.44, 126.44, 126.28, 125.64, 34.66, 31.33. This compound is known.[7]



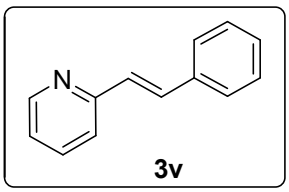
3t

(*E*)-1-phenoxy-4-styrylbenzene 3t, yield 74%, 40.3 mg. ^{1}H NMR (400 MHz $CDCl_3$): *δ* 7.48(d, *J* = 8.0 Hz, 2H), 7.36–7.23 (m, 7H), 7.17–7.03 (m, 6H), 6.90 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 157.62, 157.26, 139.32, 137.08, 129.98, 129.83, 129.50, 128.74, 128.07, 127.85, 126.63, 123.31, 121.69, 118.91, 118.17, 116.75. This compound is known.[13]



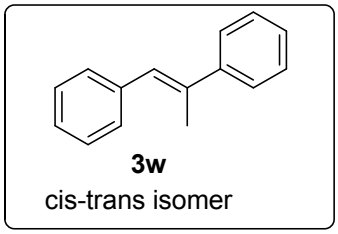
3u

(*E*)-methyl(4-styrylphenyl)sulfane 3u, yield 45%, 20.3 mg. ^{1}H NMR (400 MHz $CDCl_3$): 7.50 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25–7.23 (m, 3H), 7.06 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.85, 137.32, 134.31, 128.69, 128.09, 128.03, 127.56, 126.89, 126.73, 126.43, 15.84. This compound is known.[4]



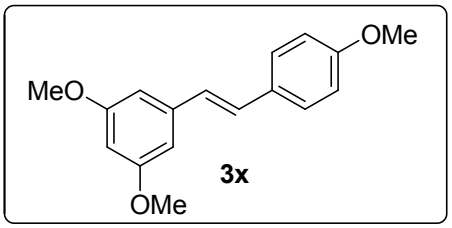
3v

(*E*)-2-styrylpyridine 3v, yield 61%, 22.1 mg; ^{1}H NMR (400 MHz $CDCl_3$): δ 8.60 (d, *J* = 4.4 Hz, 1H), 7.68–7.58 (m, 4H), 7.42–7.36 (m, 3H), 7.32–7.28 (m, 1H), 7.21–7.16 (m, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 155.49, 149.38, 136.83, 136.57, 133.10, 128.75, 128.45, 127.60, 127.17, 122.14, 122.12. This compound is known.[9]



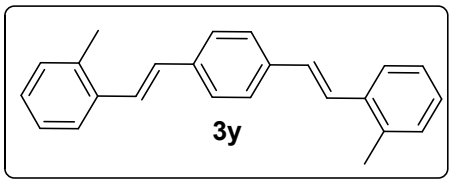
3w
cis-trans isomer

(*E*)-prop-1-ene-1,2-diyldibenzene 3w, yield 64%, 24.8 mg; ^{1}H NMR (400 MHz $CDCl_3$): *δ* 7.53–7.51 (m, 1.2H), 7.39–7.17 (m, 7H), 7.10–7.05 (m, 1H), 6.95 –6.93 (m, 0.8H), 6.84–6.47 (m, 1H), 2.28–2.20 (m, 3H). This compound is known.[1]

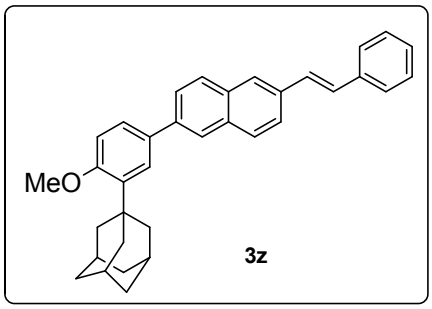


3x

(*E*)-1,3-dimethoxy-5-(4-methoxystyryl)benzene 3x, yield 92%, 49.7 mg. ^{1}H NMR (400 MHz $CDCl_3$): *δ* 7.44 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 2.0 Hz, 2H), 6.37 (t, *J* = 2.0 Hz, 1H), 3.82 (s, 9H). ^{13}C NMR (100 MHz $CDCl_3$): *δ* 160.99, 159.42, 139.72, 129.95, 128.76, 127.82, 126.59, 114.16, 104.35, 99.64, 55.37, 55.34. This compound is known.[14]



1,4-bis((E)-2-methylstyryl)benzene 3y, yield 62%, 38.4 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.61 (d, J = 7.2 Hz, 2H), 7.53 (s, 4H), 7.38 – 7.34 (m, 2H), 7.22 – 7.19 (m, 6H), 7.03 – 6.99 (m, 2H), 2.45 (s, 6H). ^{13}C NMR (100 MHz $CDCl_3$):δ 137.04, 136.36, 135.86, 130.48, 129.56, 127.61, 126.92, 126.37, 126.26, 125.29, 20.00. This compound is known.[15]



(3r,5r,7r)-1-(2-methoxy-5-(6-((E)-styryl)naphthalen-2-yl)phenyl)adamantane 3z, yield 40%, 37.6 mg. ^{1}H NMR (400 MHz $CDCl_3$): δ 7.96 (s, 1H), 7.88 – 7.86 (m, 3H), 7.77 – 7.72 (m, 2H), 7.60 – 7.52 (m, 4H), 6.39 (t, J = 7.6 Hz, 2H), 7.31 – 7.26 (m, 3H), 6.99 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (100 MHz $CDCl_3$):δ 158.62, 139.05, 138.90, 137.45, 134.51, 133.42, 133.09, 132.49, 128.87, 128.78, 128.74, 128.47, 128.35, 127.63, 126.54, 126.40, 126.14, 125.85, 125.53, 124.85, 123.85, 112.12, 61.75, 55.19, 40.65, 37.17, 29.16.

5. References

(1) S. Wu, H. Ma, X. Jia, Y. Zhong and Z. Lei, *Tetrahedron*, 2001, **67**, 250.

(2) W. H. Laarhoven, *Pure Appl. Chem.*, 1984, **56**, 1225.

(3) R. Lapouyade, A. Veyres, N. Hanafi, A. Couture and A. Lablache-Combier, *J. Org. Chem.*, 1982, **47**, 1361.

(4) S. Keesara, S. Parvathaneni and M. R. Mandapati, *Tetrahedron Lett.*, 2014, **55**, 6769.

(5) E. V. Blackburn, C. E. Loader and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163.

(6) K. Y. Amsharov, M. A. Kabdulov and M. Jansen, *Eur. J. Org. Chem.*, 2009, 6328.

(7) A. R. Ehle , Q. Zhou and M. P. Watson, *Org. Lett.*, 2012, **14**, 1202.

(8) L. Liu, B. Yang, T. J. Katz and M. K. Poindexter, *J. Org. Chem.*, 1991, **56**, 3769.

(9) Vadapalli Chandrasekhar , Ramakirushnan Suriya Narayanan, *Tetrahedron Lett.*, 2011, **52**, 3527.

(10) W. H. Laarhoven, T.H.J.H.M. Cuppen and R.J.F. Nivard, *Tetrahedron*, 1970, **26**, 1970, 4865.

(11) A. M. Seligman and A. M. Rutenburg, *J. Am. Chem. Soc.*, 1950, **72**, 3214.

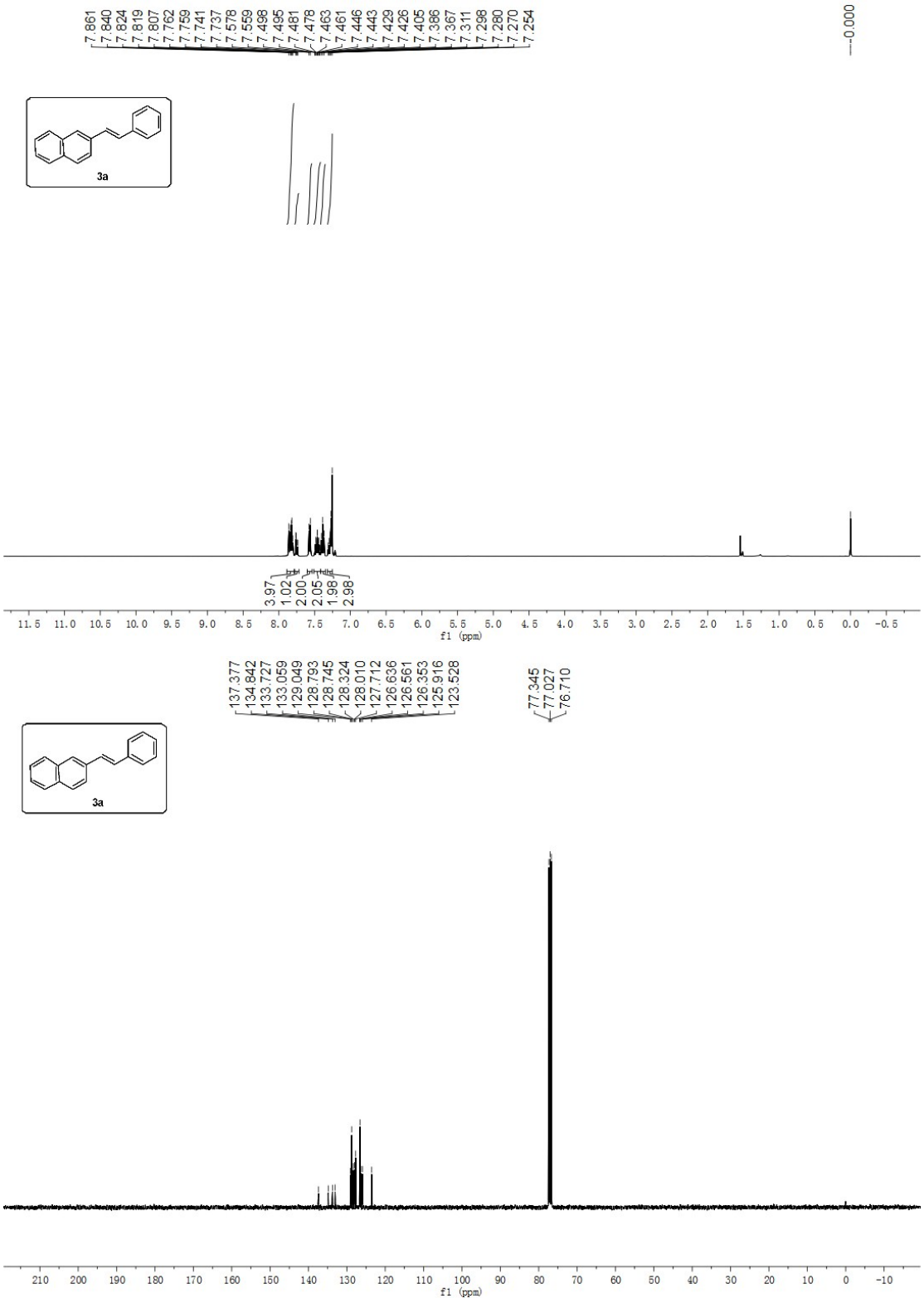
(12) X. Cui, J. Li, Z.-P. Zhang, Y. Fu, L. Liu and Q.-X. Guo, *J. Org. Chem.*, 2007, **72**, 9342.

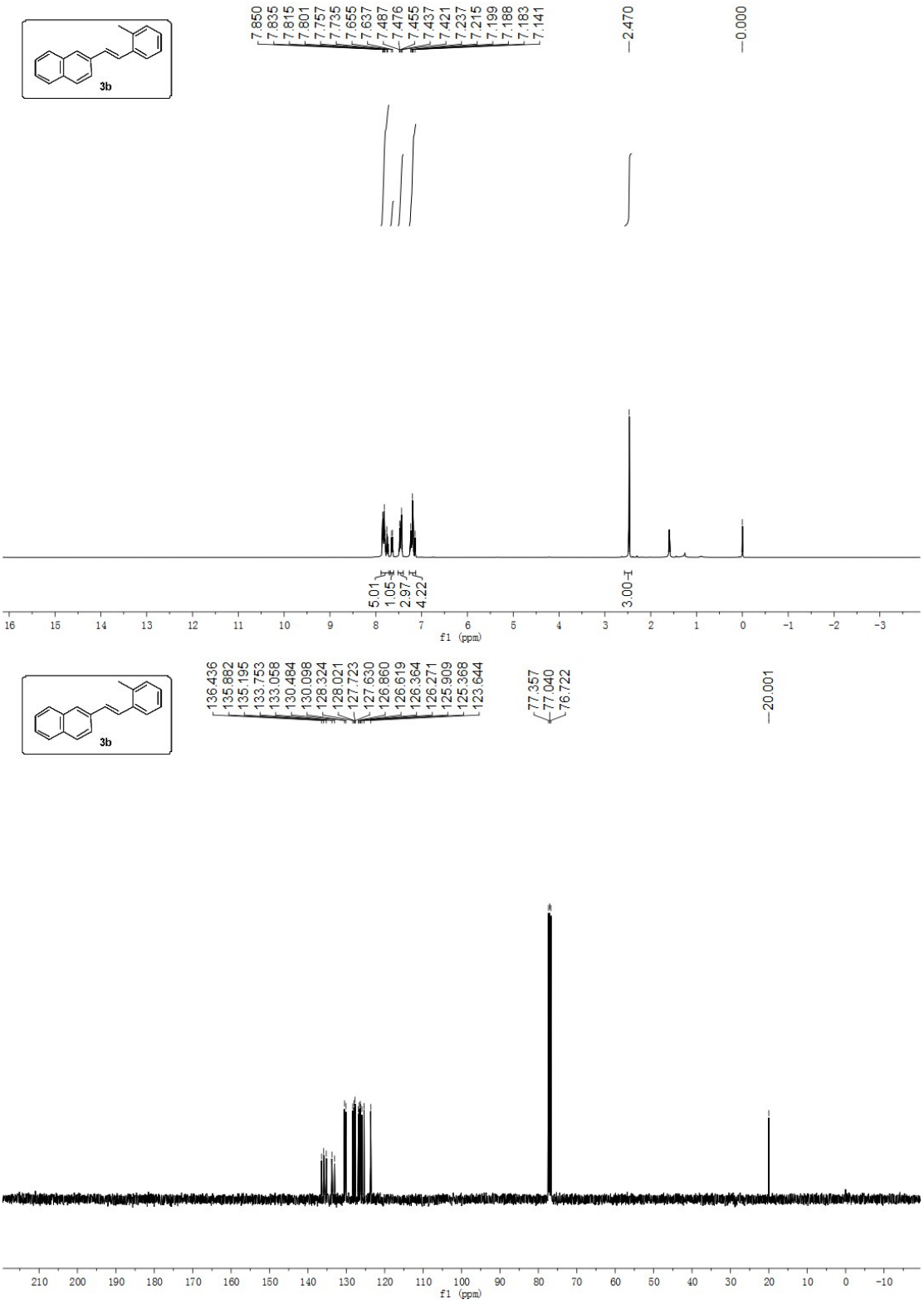
(13) M. Oberholzera and C. M. Frech, *Green Chem.*, 2013, **15**, 1678.

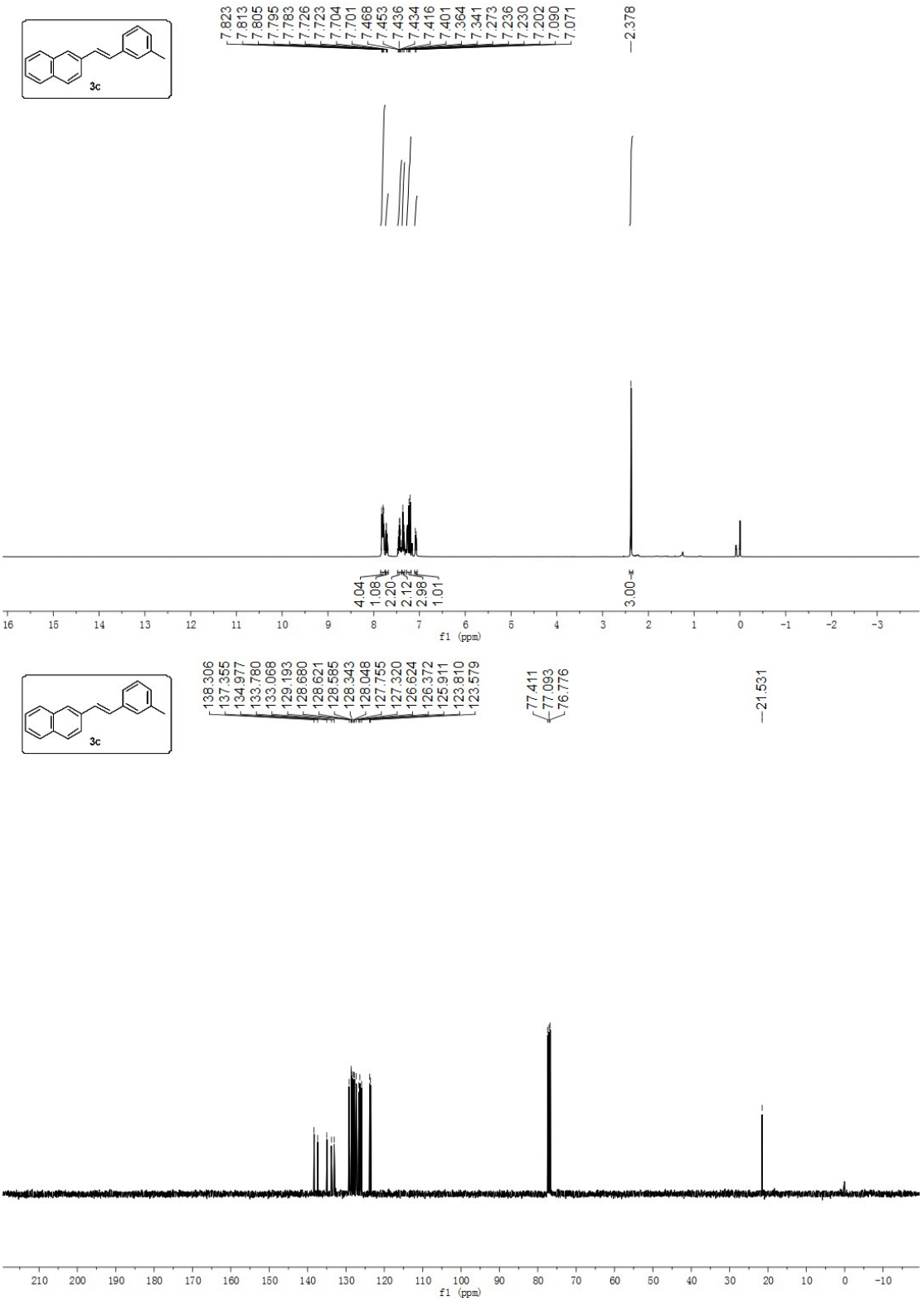
(14) K. Ferré-Filmon, L. Delaude, A. Demonceau and A. F. Noels, *Eur. J. Org. Chem.*, 2005, 3319.

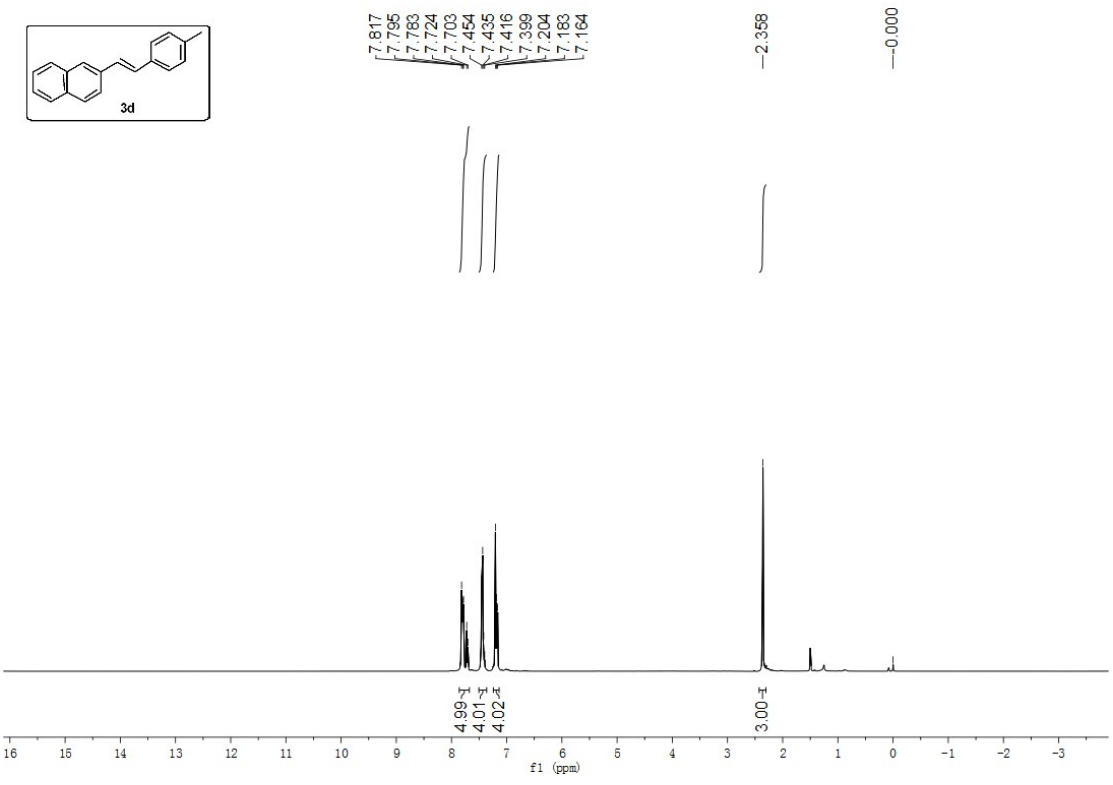
(15) V. K. Koul, and B. R. Hirani, Indian 2006MU01558, patent, Sep. 19 2008.

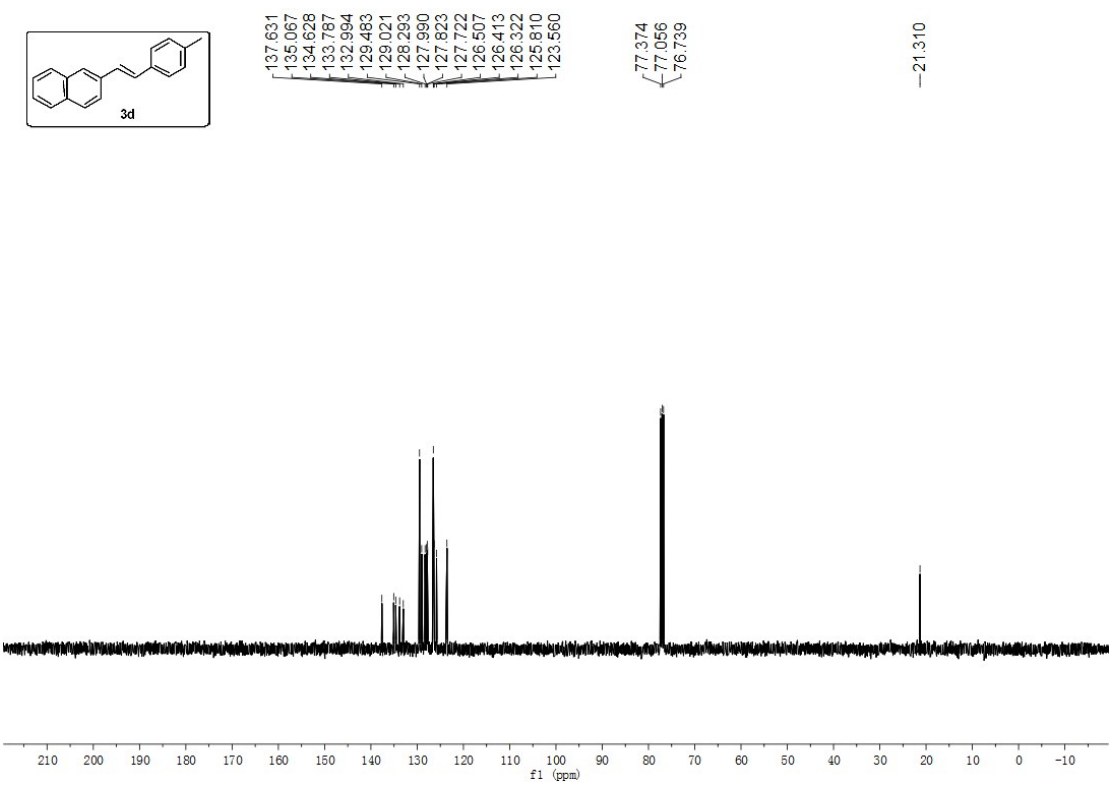
6. Copies of ^{1}H NMR and ^{13}C NMR spectra

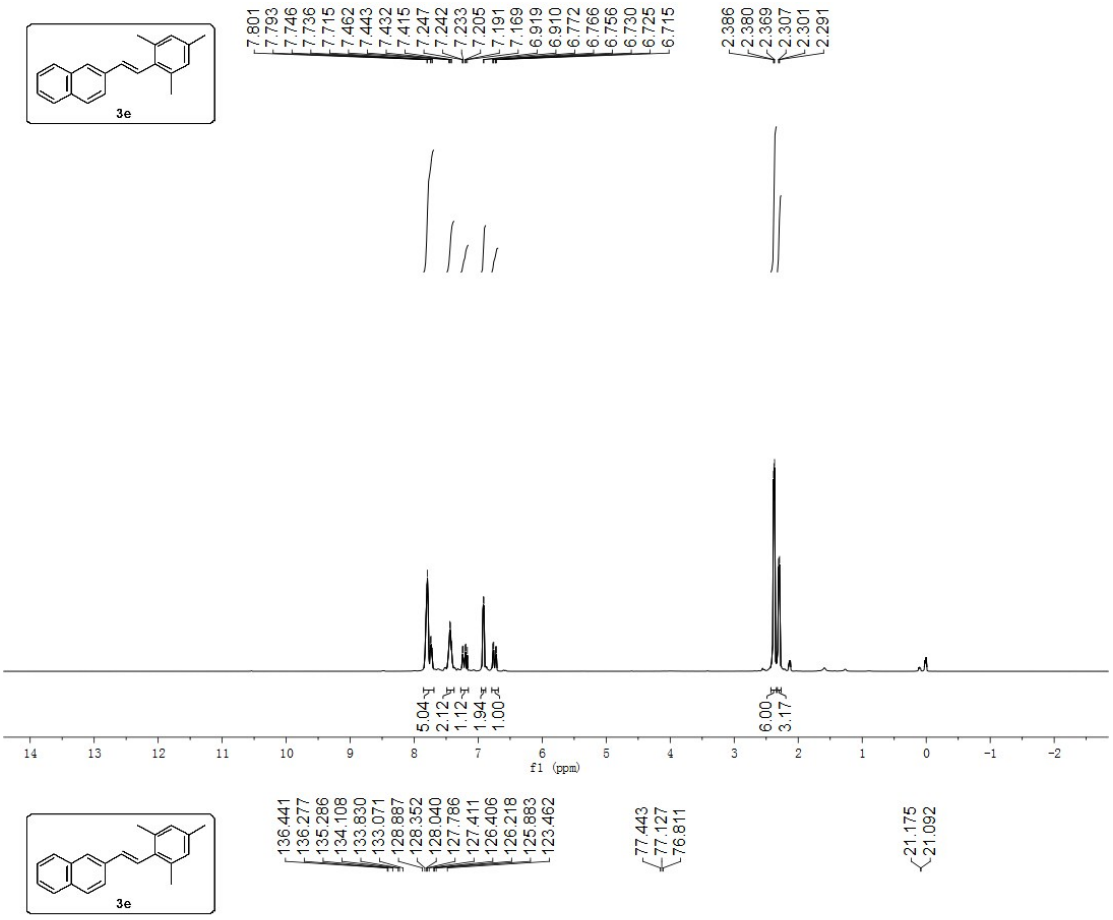


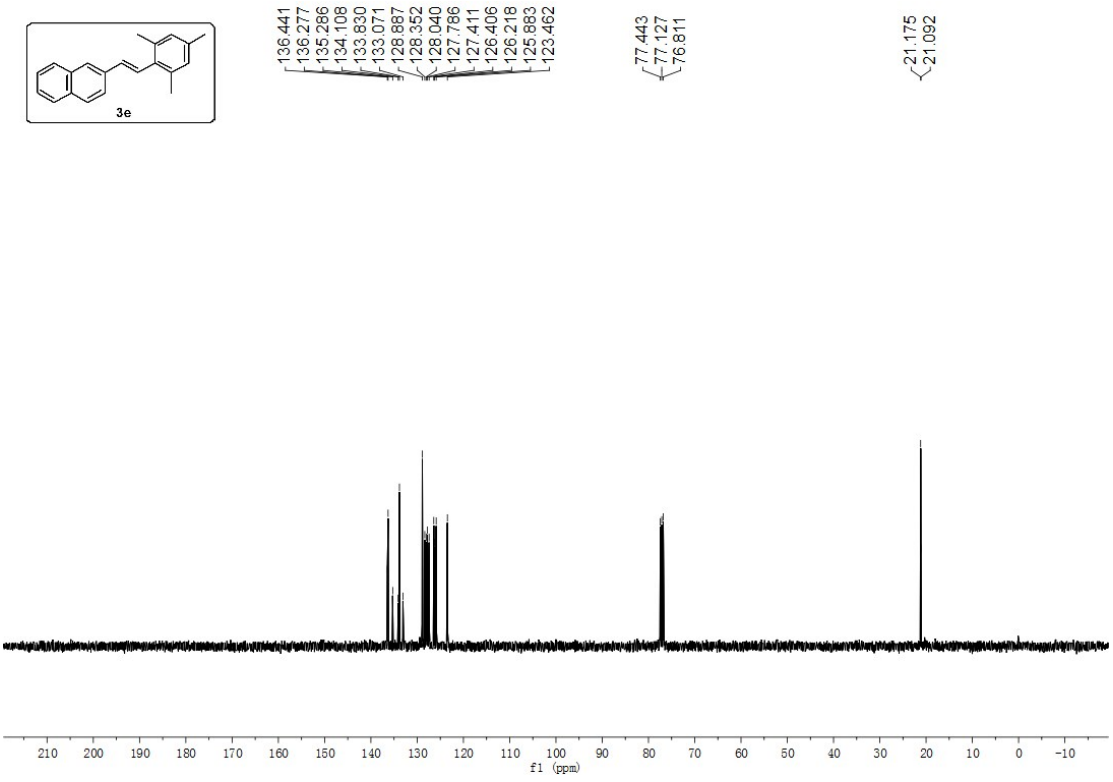

3b
7.850
7.835
7.815
7.801
7.757
7.735
7.655
7.637
7.487
7.476
7.455
7.437
7.421
7.237
7.215
7.199
7.188
7.183
7.141
2.470
0.000
5.01
1.05
2.97
4.22
3.00
f1 (ppm)
3b
136.436
135.882
135.195
133.753
133.058
130.484
130.098
128.324
128.021
127.723
127.630
126.860
126.619
126.364
126.271
125.909
125.368
123.644
77.357
77.040
76.722
20.001
f1 (ppm)

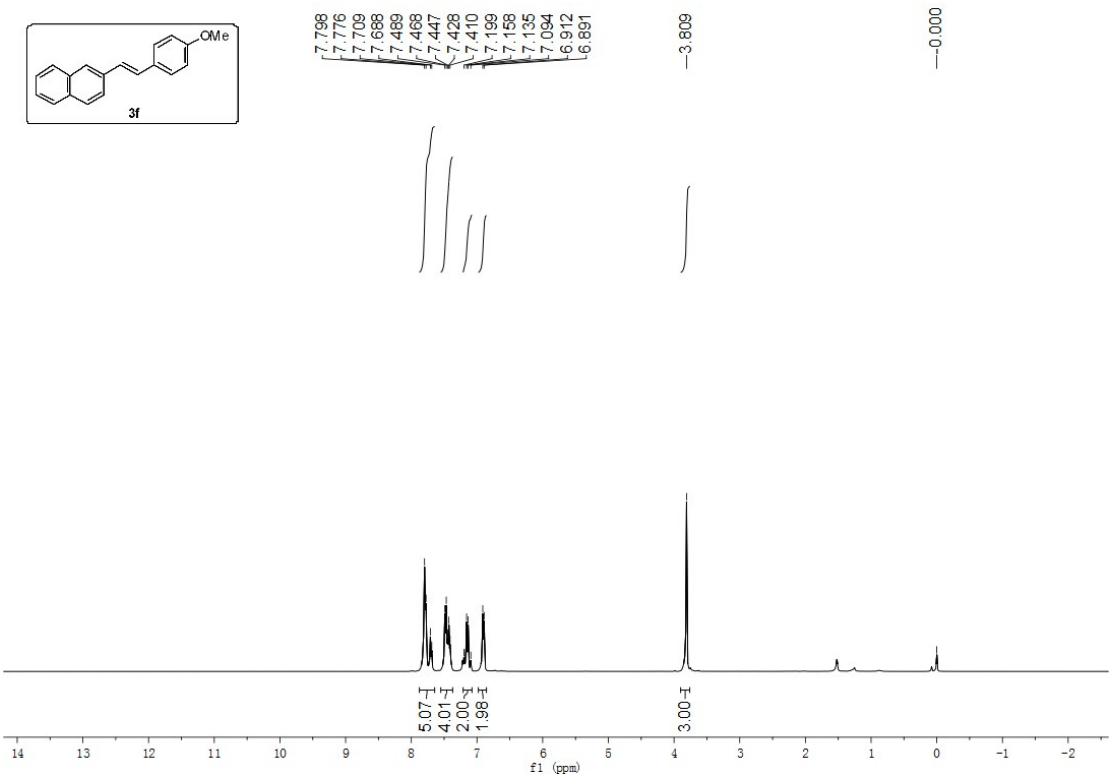

3c
7.823
7.813
7.805
7.795
7.783
7.726
7.723
7.704
7.701
7.468
7.453
7.436
7.434
7.416
7.401
7.364
7.341
7.273
7.236
7.230
7.202
7.090
7.071
2.378
4.04
1.08
2.20
2.12
2.98
1.01
3.00
f1 (ppm)
3c
138.306
137.355
134.977
133.780
133.068
129.193
128.680
128.621
128.585
128.343
128.048
127.755
127.320
126.624
126.372
125.911
123.810
123.579
77.411
77.093
76.776
21.531
f1 (ppm)

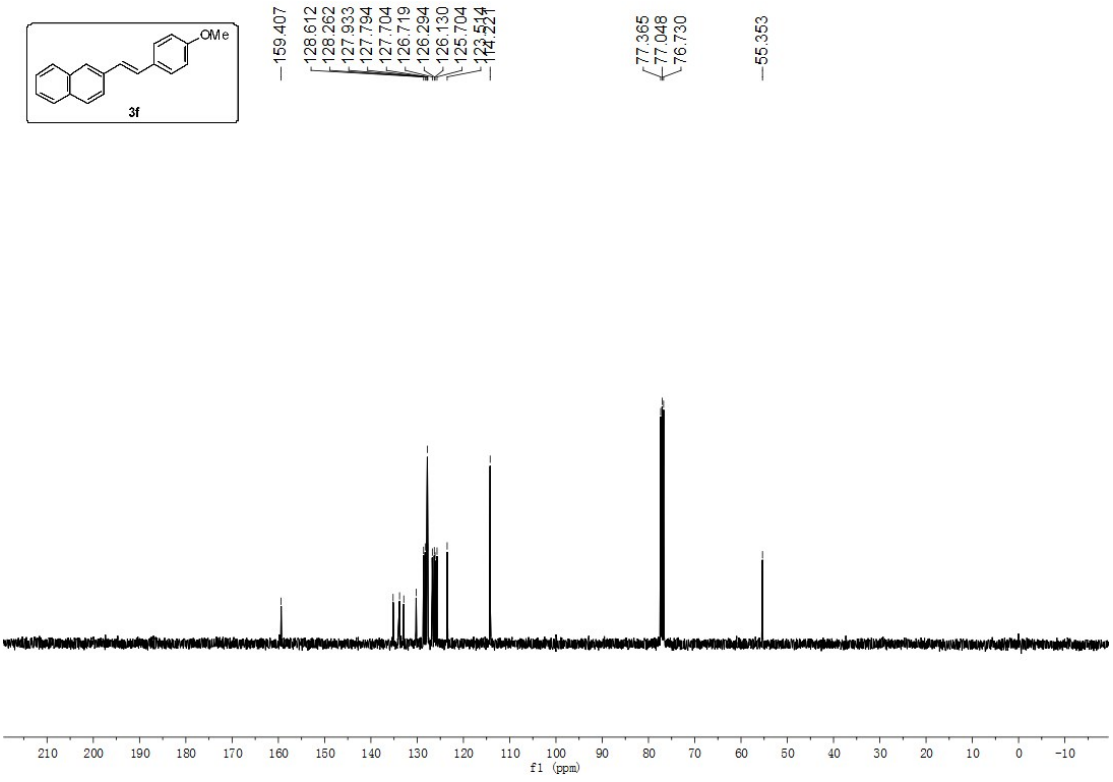

3d
7.817
7.795
7.783
7.724
7.703
7.454
7.435
7.416
7.399
7.204
7.183
7.164
2.358
0.000
4.99
4.01
4.02
3.00
f1 (ppm)

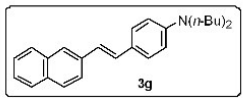

3d
137.631
135.067
134.628
133.787
132.994
129.483
129.021
128.293
127.990
127.823
127.722
126.507
126.413
126.322
125.810
123.560
77.374
77.056
76.739
21.310
f1 (ppm)

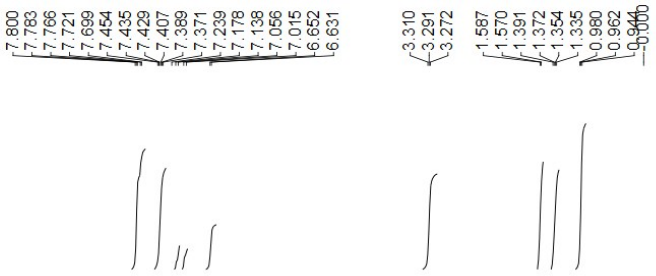

3e
7.801
7.793
7.746
7.736
7.715
7.462
7.443
7.432
7.415
7.247
7.242
7.233
7.205
7.191
7.169
6.919
6.910
6.772
6.766
6.756
6.730
6.725
6.715
2.386
2.380
2.369
2.307
2.301
2.291
5.04
2.12
1.12
1.94
1.00
6.00
3.17
f1 (ppm)

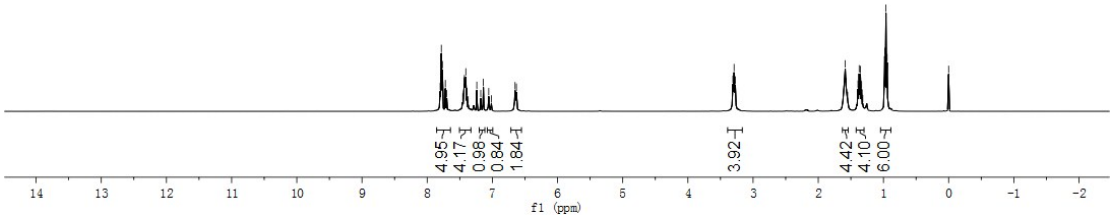

3e
136.441
136.277
135.286
134.108
133.830
133.071
128.887
128.352
128.040
127.786
127.411
126.406
126.218
125.883
123.462
77.443
77.127
76.811
21.175
21.092
f1 (ppm)

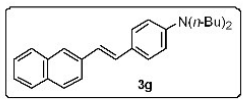

OMe
3f
7.798
7.776
7.709
7.688
7.469
7.468
7.447
7.428
7.410
7.199
7.158
7.135
7.094
6.912
6.891
3.809
0.000
5.07
4.01
2.00
1.98
3.00
f1 (ppm)

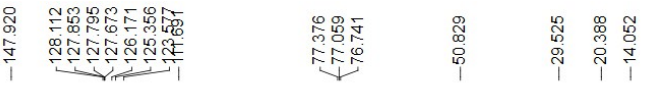

OMe
3f
159.407
128.612
128.262
127.933
127.794
127.704
126.719
126.294
126.130
125.704
123.514
114.221
77.365
77.048
76.730
55.353
f1 (ppm)

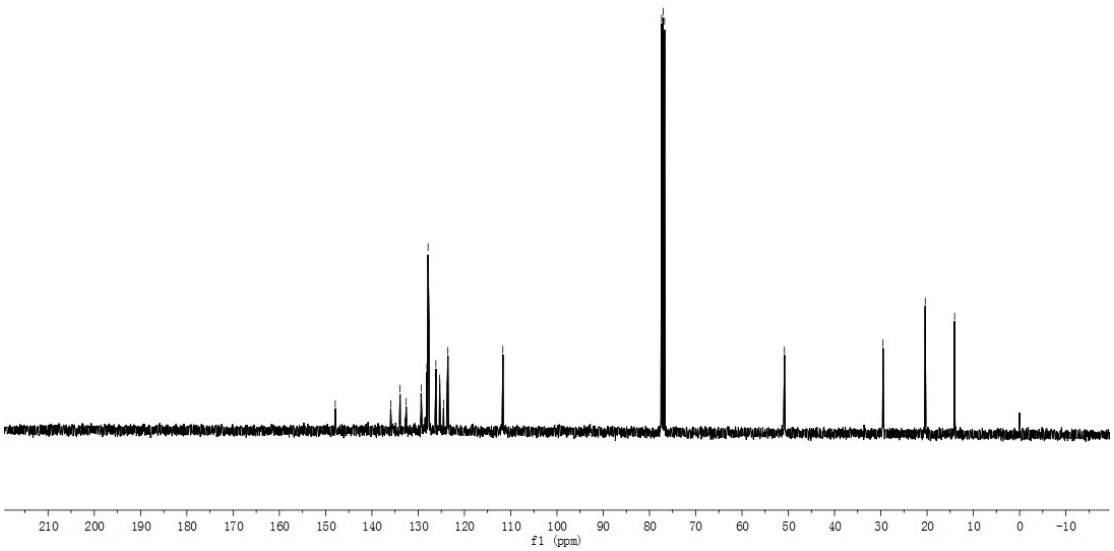

N(n-Bu)2
3g

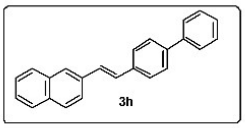

7.800
7.783
7.766
7.721
7.699
7.454
7.435
7.429
7.407
7.389
7.371
7.239
7.178
7.138
7.056
7.015
6.652
6.631
3.310
3.291
3.272
1.587
1.570
1.391
1.372
1.354
1.335
0.980
0.962
0.944
0.000

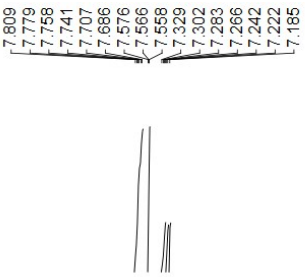

4.95
4.17
0.98
0.84
1.84
3.92
4.42
4.10
6.00
f1 (ppm)

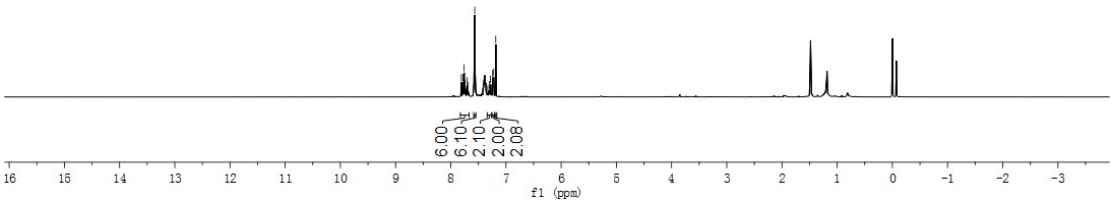

N(n-Bu)2
3g


147.920
128.112
127.853
127.795
127.673
126.171
125.356
123.577
111.691
77.376
77.059
76.741
50.829
29.525
20.388
14.052

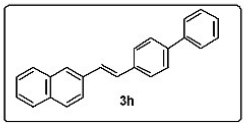

f1 (ppm)


3h

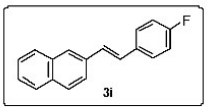

7.809
7.779
7.758
7.741
7.707
7.686
7.576
7.566
7.558
7.329
7.302
7.283
7.266
7.242
7.222
7.185

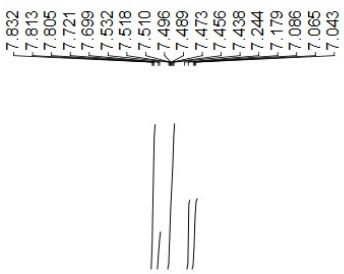

6.00
6.10
2.10
2.00
2.08
f1 (ppm)


139.675
139.403
135.430
133.848
132.735
132.073
127.841
127.803
127.550
127.326
126.998
126.698
126.388
126.335
125.965
125.918
125.640
125.347
124.913
122.518
76.312
75.994
75.677

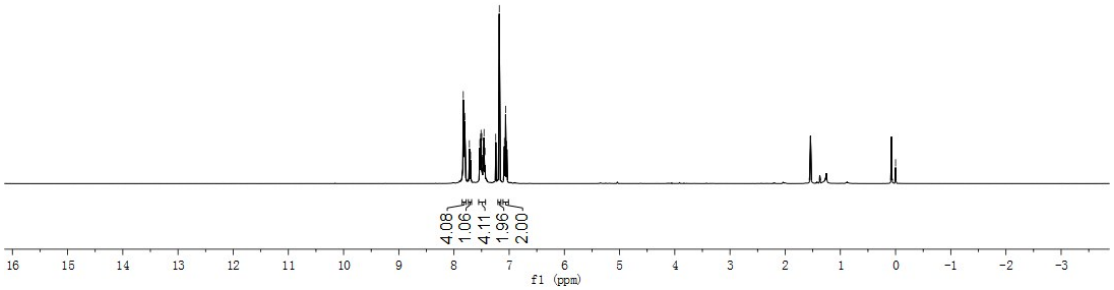

3h

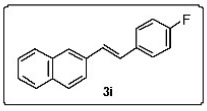
f1 (ppm)

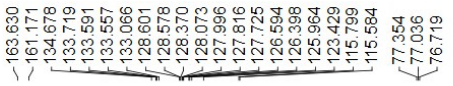

F
3i

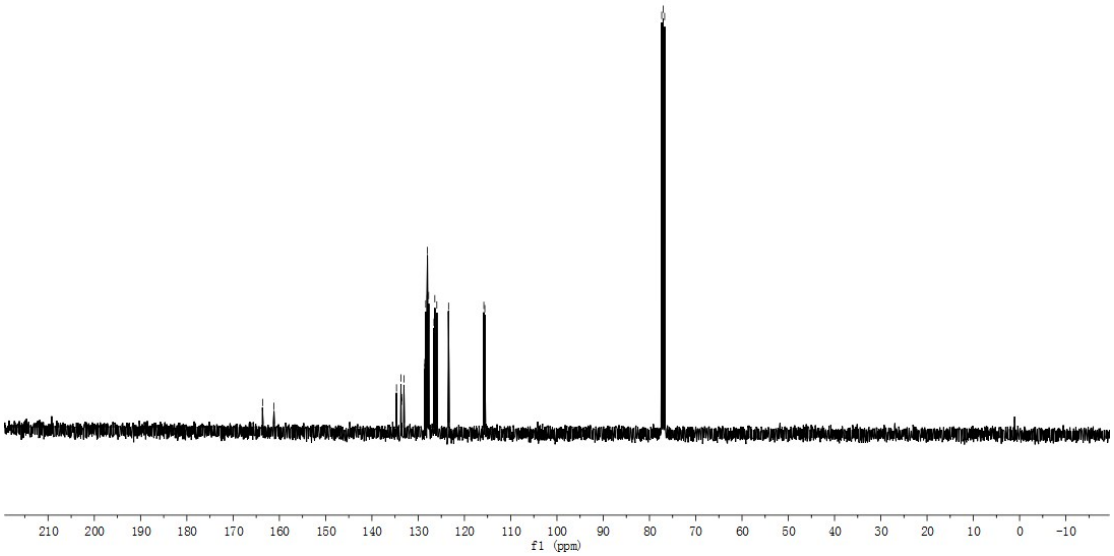

7.832
7.813
7.805
7.721
7.699
7.532
7.518
7.510
7.496
7.489
7.473
7.456
7.438
7.244
7.179
7.086
7.065
7.043

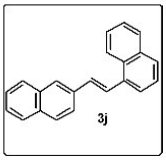

0.000

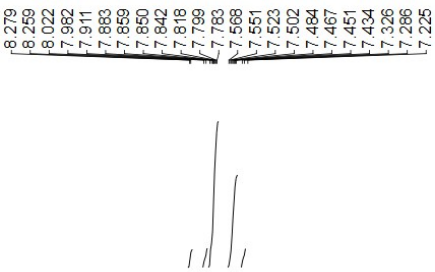

4.08
1.06
4.11
1.96
2.00
f1 (ppm)

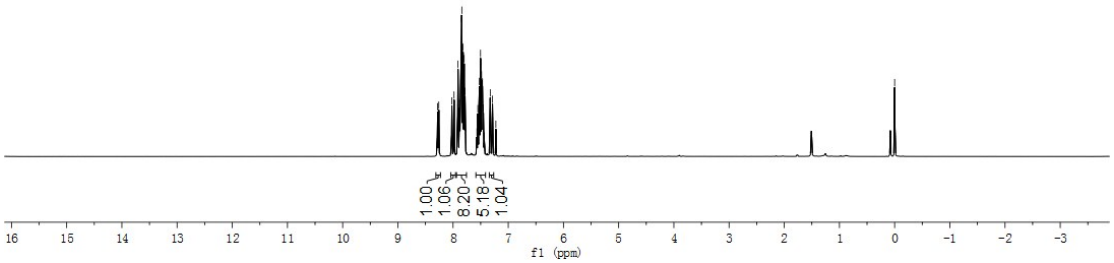

F
3i

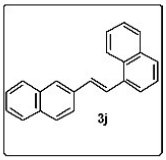

163.630
161.171
134.678
133.719
133.591
133.557
133.066
128.601
128.578
128.370
128.073
127.996
127.816
127.725
126.594
126.398
125.964
123.429
115.799
115.584
77.354
77.036
76.719


f1 (ppm)

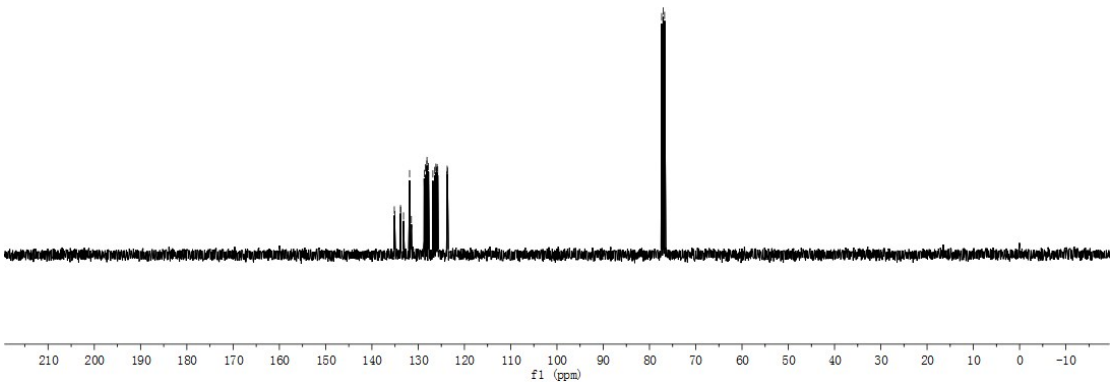

3j

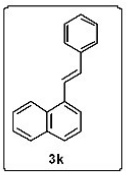

8.279
8.259
8.022
7.962
7.911
7.883
7.859
7.850
7.842
7.818
7.799
7.783
7.568
7.551
7.523
7.502
7.484
7.467
7.451
7.434
7.326
7.286
7.225
0.000

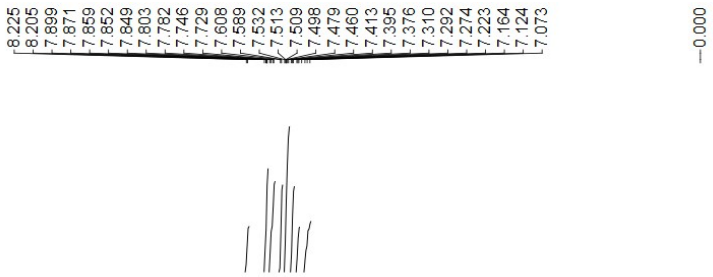

1.00
1.06
8.20
5.18
1.04
f1 (ppm)

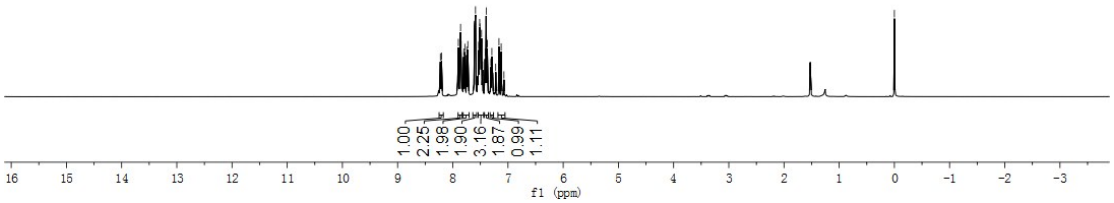

3j

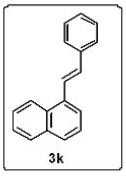

135.150
135.061
133.818
133.780
133.162
131.852
131.463
128.686
128.421
128.131
128.094
127.767
126.821
126.422
126.162
126.112
126.017
125.893
125.757
123.827
123.728
123.651
77.364
77.046
76.729

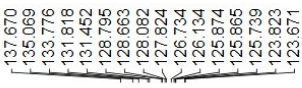

f1 (ppm)

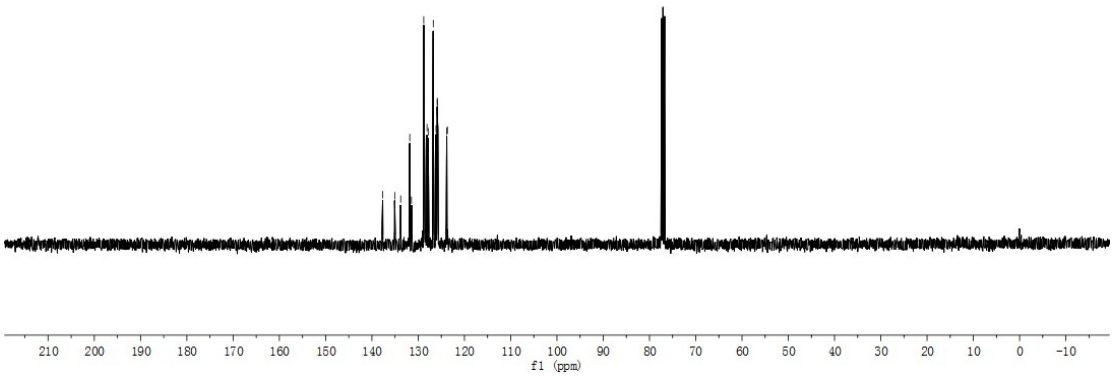

3k

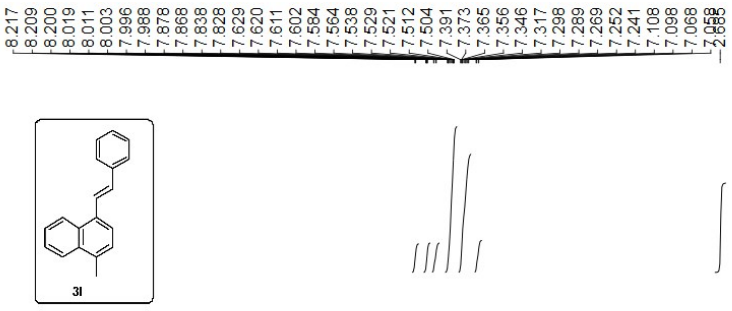

8.225
8.205
7.899
7.871
7.859
7.852
7.849
7.803
7.782
7.746
7.729
7.608
7.589
7.532
7.513
7.509
7.498
7.479
7.460
7.413
7.395
7.376
7.310
7.292
7.274
7.223
7.164
7.124
7.073
0.000

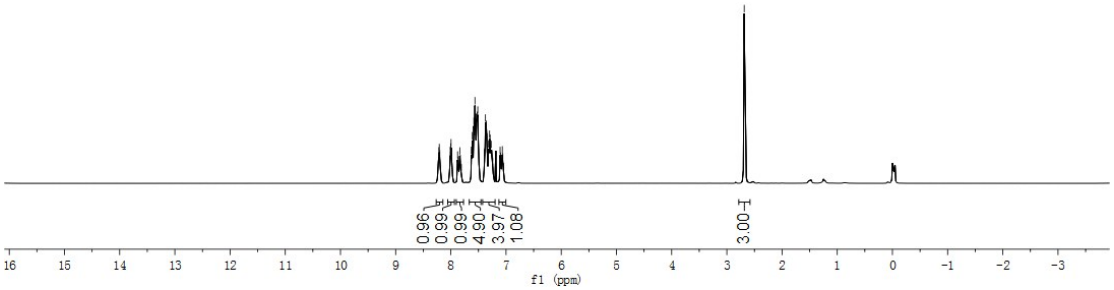

1.00
2.25
1.98
1.90
3.16
1.87
0.99
1.11
f1 (ppm)

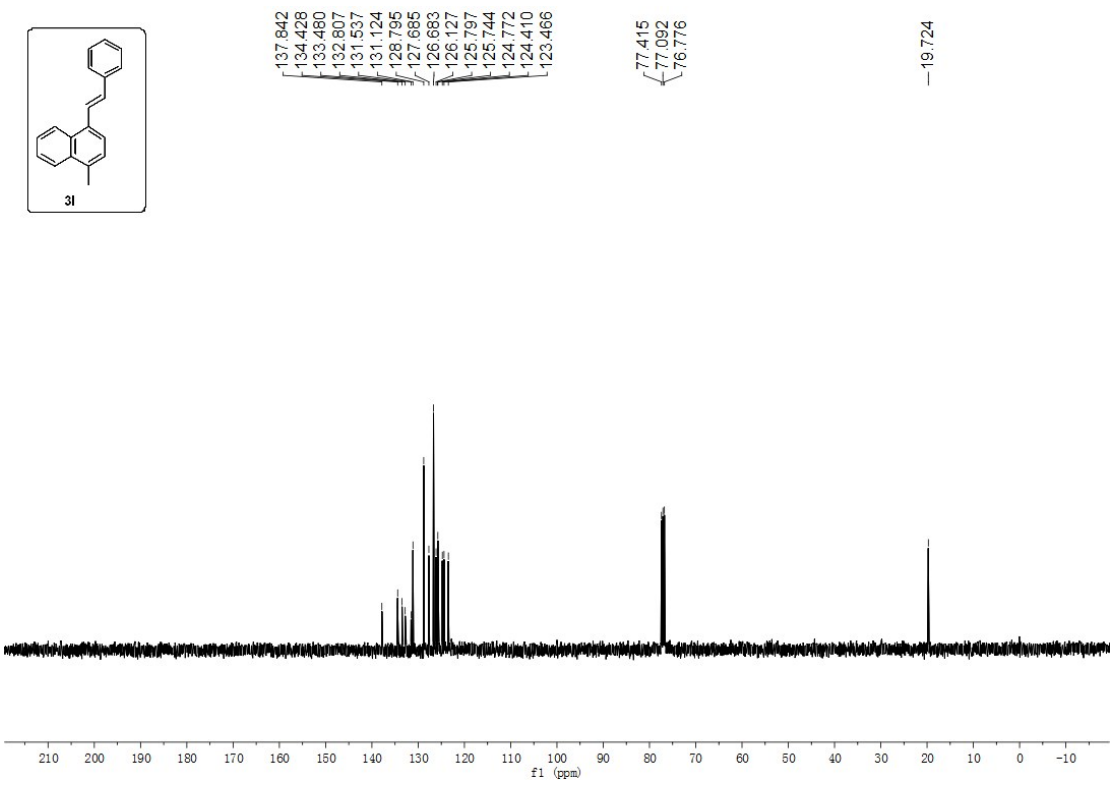

3k

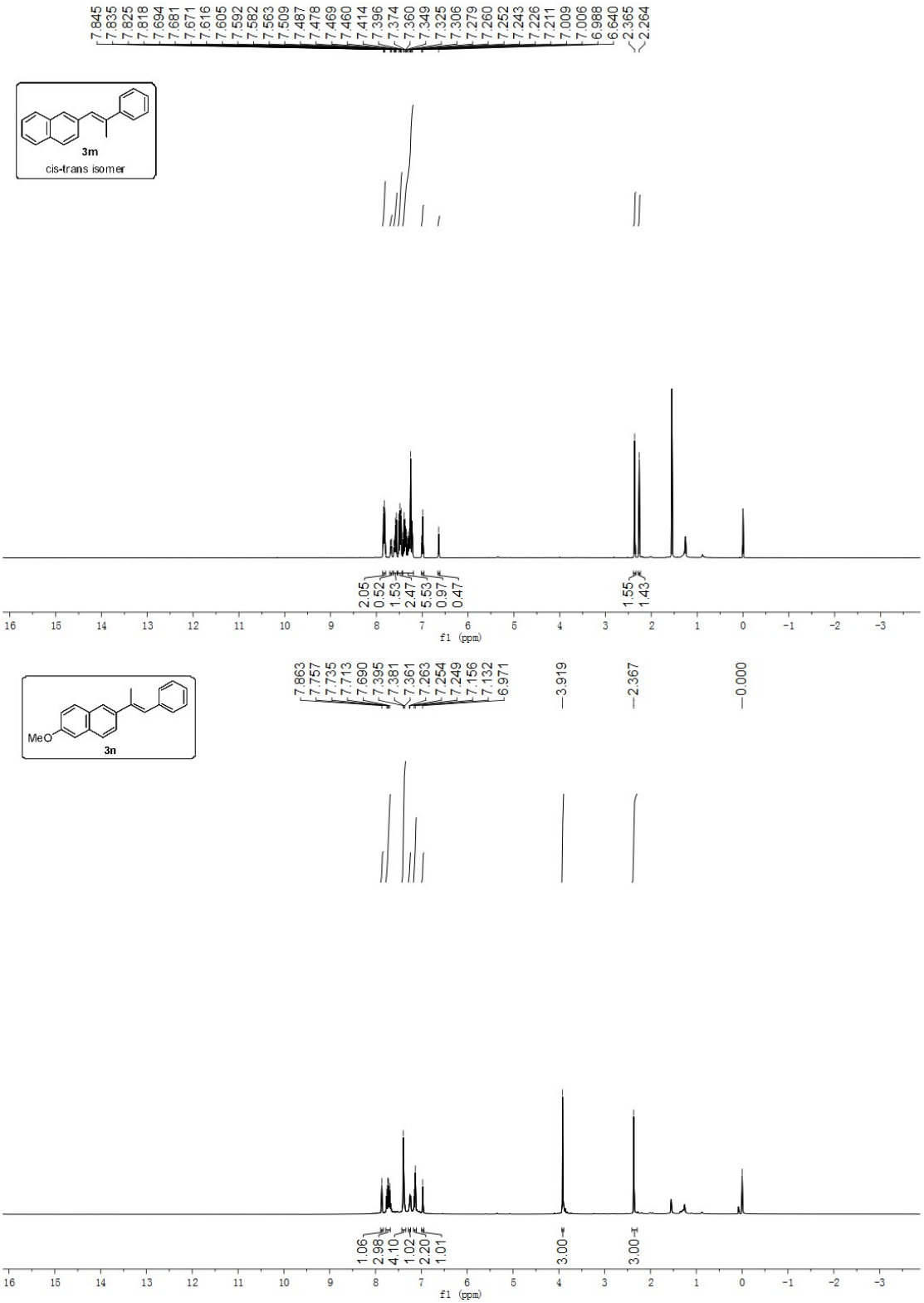

137.670
135.069
133.776
131.818
131.452
128.795
128.663
128.082
127.824
126.734
126.134
125.874
125.865
125.739
123.823
123.671

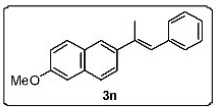

f1 (ppm)


8.217
8.209
8.200
8.019
8.011
8.003
7.996
7.988
7.878
7.868
7.838
7.828
7.629
7.620
7.611
7.602
7.584
7.564
7.538
7.529
7.521
7.512
7.504
7.391
7.373
7.365
7.356
7.346
7.317
7.298
7.289
7.269
7.252
7.241
7.108
7.098
7.068
2.685
3l


0.96
0.99
0.99
4.90
3.97
1.08
3.00
f1 (ppm)


137.842
134.428
133.480
132.807
131.537
131.124
128.795
127.685
126.683
126.127
125.797
125.744
124.772
124.410
123.466
77.415
77.092
76.776
19.724
3l
f1 (ppm)


7.845
7.835
7.825
7.818
7.694
7.681
7.671
7.616
7.605
7.592
7.582
7.563
7.509
7.487
7.478
7.469
7.460
7.414
7.396
7.374
7.360
7.349
7.325
7.306
7.279
7.260
7.252
7.243
7.226
7.211
7.009
7.006
6.988
6.640
2.365
2.264
3m
cis-trans isomer
2.05
0.52
1.53
2.47
5.53
0.97
0.47
1.55
1.43
f1 (ppm)
7.863
7.757
7.735
7.713
7.690
7.395
7.381
7.361
7.263
7.254
7.249
7.156
7.132
6.971
3.919
2.367
0.000
MeO
3n
1.06
2.98
4.10
1.02
2.20
1.01
3.00
3.00
f1 (ppm)

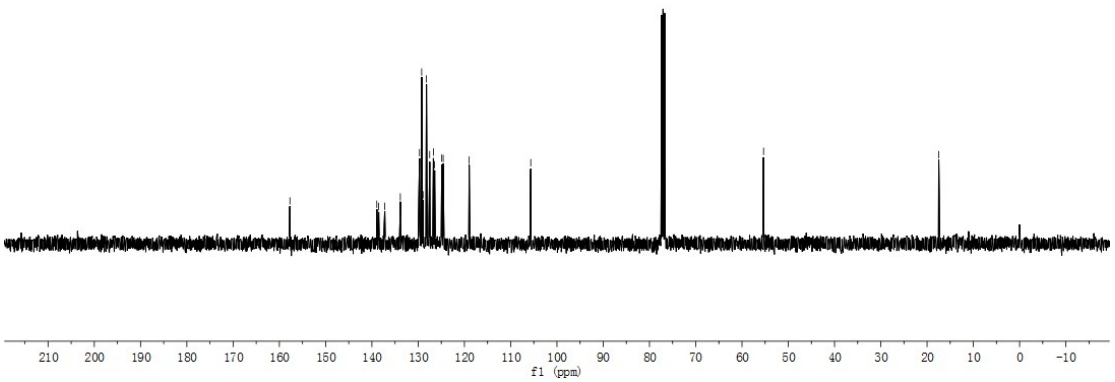

MeO

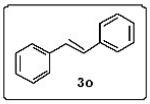
3n


157.724
133.851
129.711
129.236
128.938
128.212
127.513
126.697
126.446
124.900
124.581
118.977
105.861

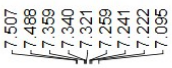

55.344


17.478

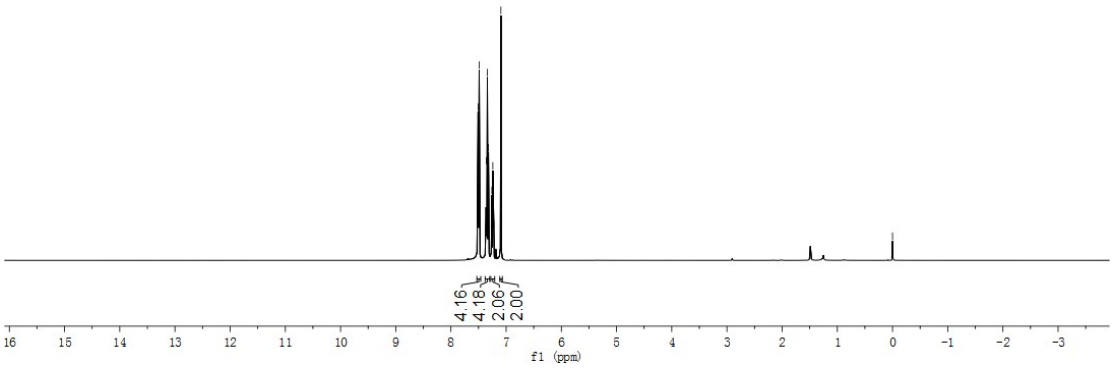

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

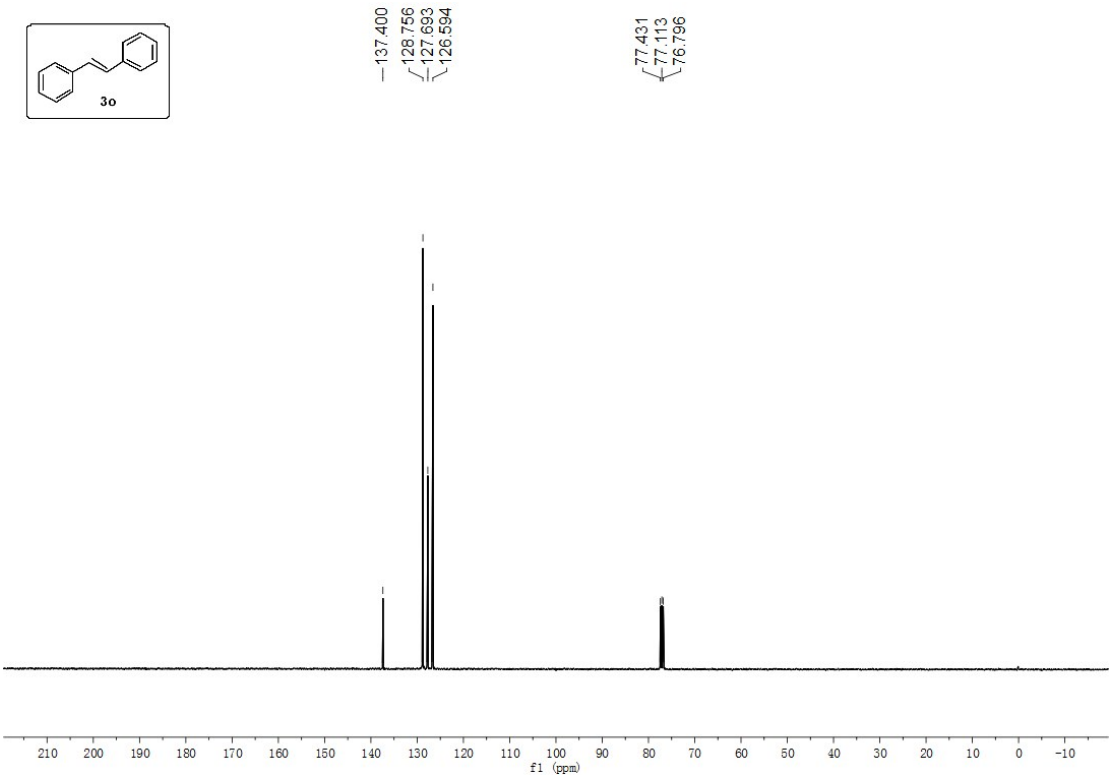


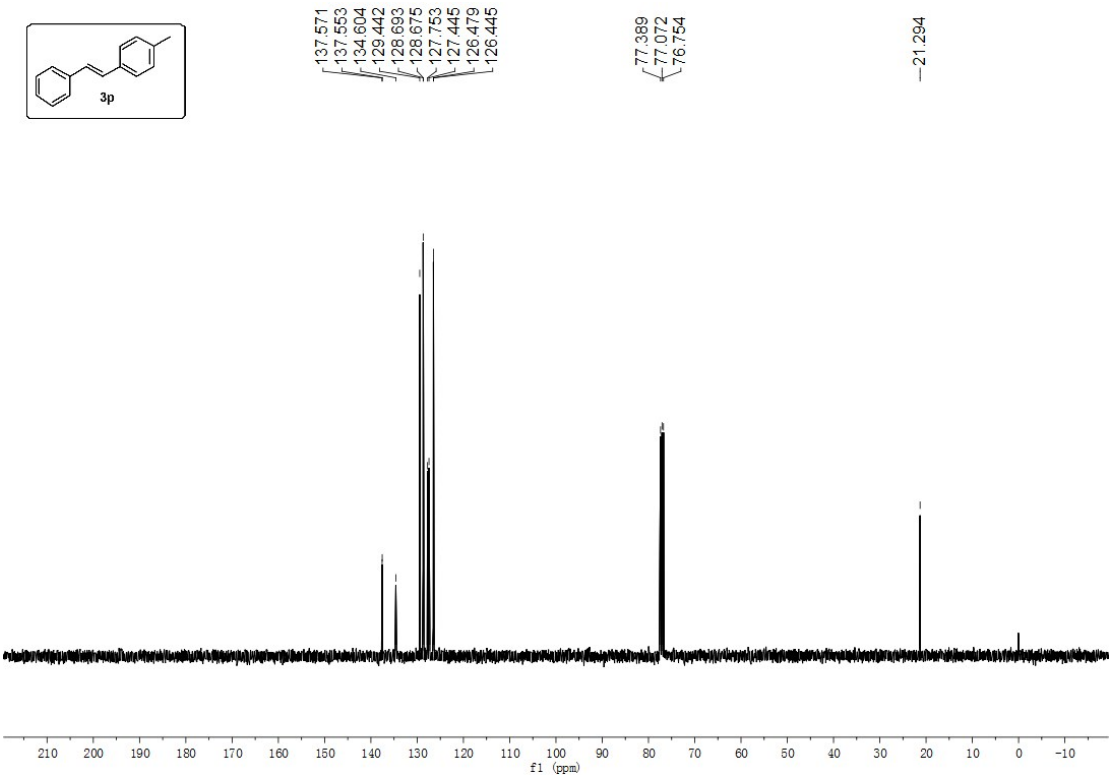
3o

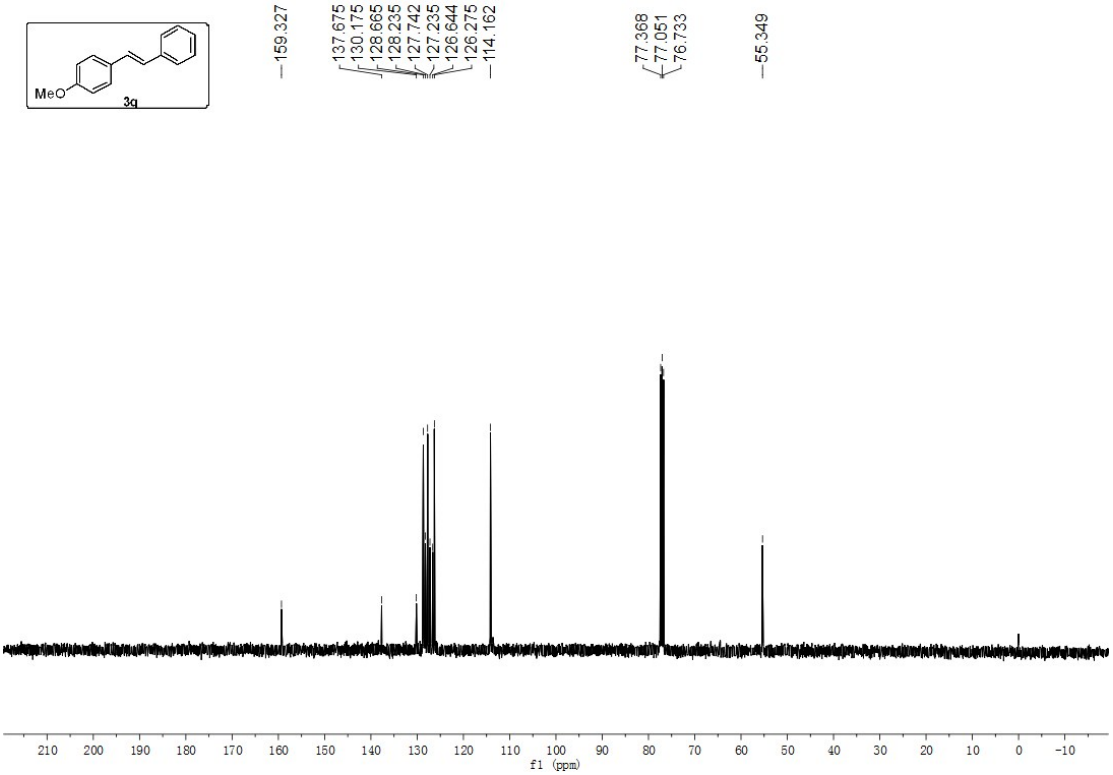

7.507
7.488
7.359
7.340
7.321
7.259
7.241
7.222
7.095

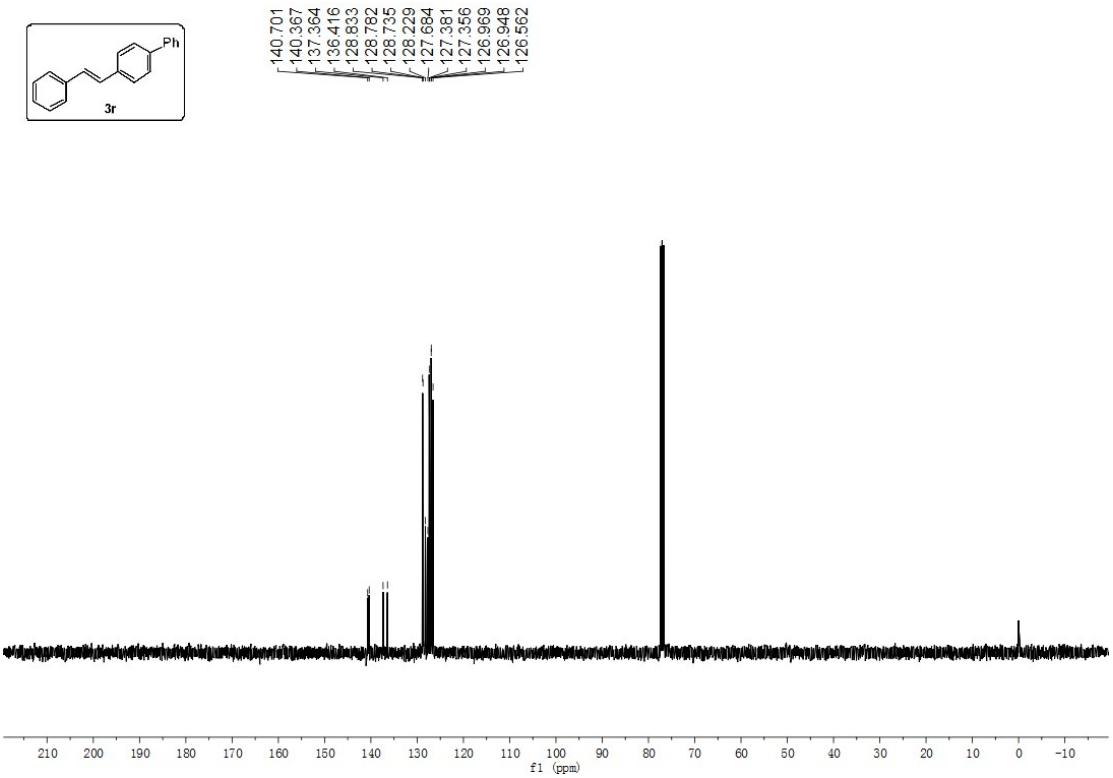

0.000

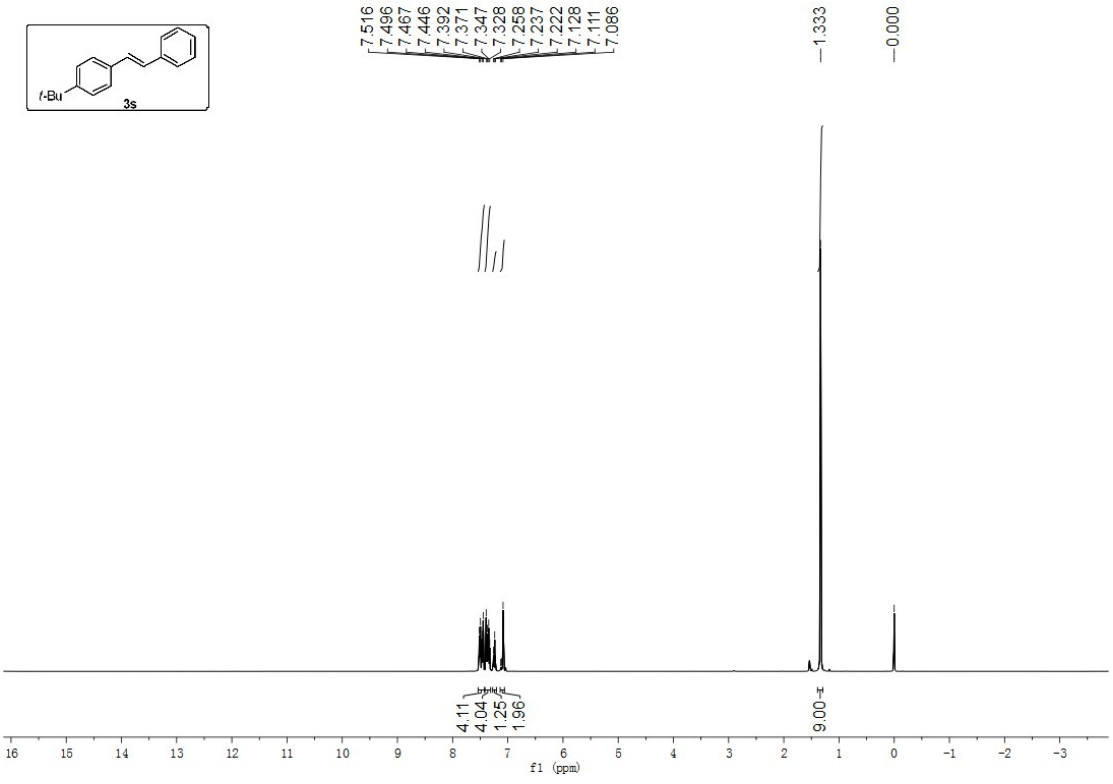

4.16
4.18
2.06
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

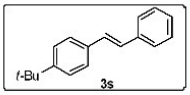

3o
137.400
128.756
127.693
126.594
77.431
77.113
76.796
f1 (ppm)
3p
7.499
7.479
7.412
7.392
7.355
7.336
7.317
7.249
7.230
7.212
7.164
7.144
7.066
7.060
2.347
0.000
2.06
2.12
2.03
1.14
2.06
1.95
3.00
f1 (ppm)

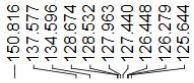

3p
137.571
137.553
134.604
129.442
128.693
128.675
127.753
127.445
126.479
126.445
77.389
77.072
76.754
21.294
f1 (ppm)
3q
MeO
7.493
7.474
7.460
7.438
7.357
7.338
7.319
7.245
7.241
7.226
7.084
7.043
6.989
6.948
6.906
6.884
3.820
0.000
4.17
2.10
1.25
1.17
1.11
1.94
3.00
f1 (ppm)


MeO
3q
159.327
137.675
130.175
128.665
128.235
127.742
127.235
126.644
126.275
114.162
77.368
77.051
76.733
55.349
f1 (ppm)
Ph
3r
7.625
7.606
7.591
7.539
7.520
7.459
7.441
7.421
7.383
7.364
7.345
7.281
7.262
7.244
7.148
0.000
5.95
2.06
2.16
2.92
1.04
2.00
f1 (ppm)


Ph
3r
140.701
140.367
137.364
136.416
128.833
128.782
128.735
128.229
127.684
127.381
127.356
126.969
126.948
126.562
f1 (ppm)

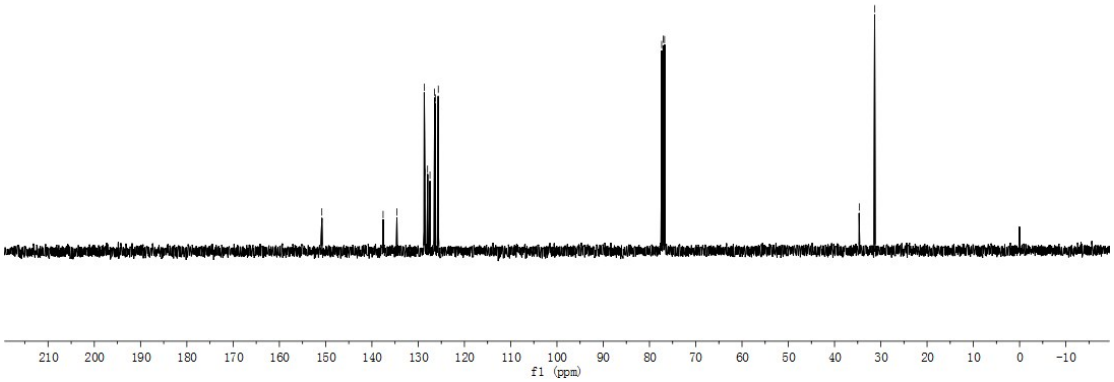

t-Bu
3s
7.516
7.496
7.467
7.446
7.392
7.371
7.347
7.328
7.258
7.237
7.222
7.128
7.111
7.086
1.333
0.000
4.11
4.04
1.25
1.96
9.00
f1 (ppm)

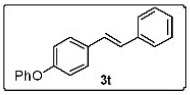

t-Bu
3s

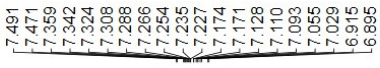

150.816
137.577
134.596
128.674
128.532
127.963
127.440
126.448
126.279
125.644


77.363
77.046
76.728

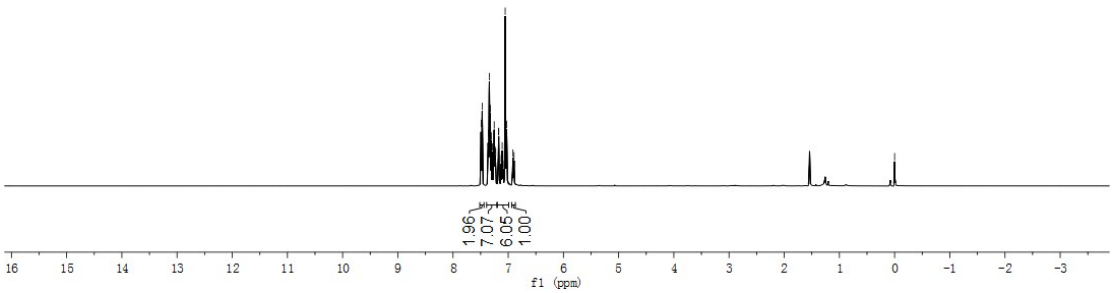

34.655
31.326

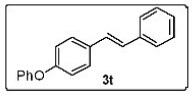

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PhO
3t

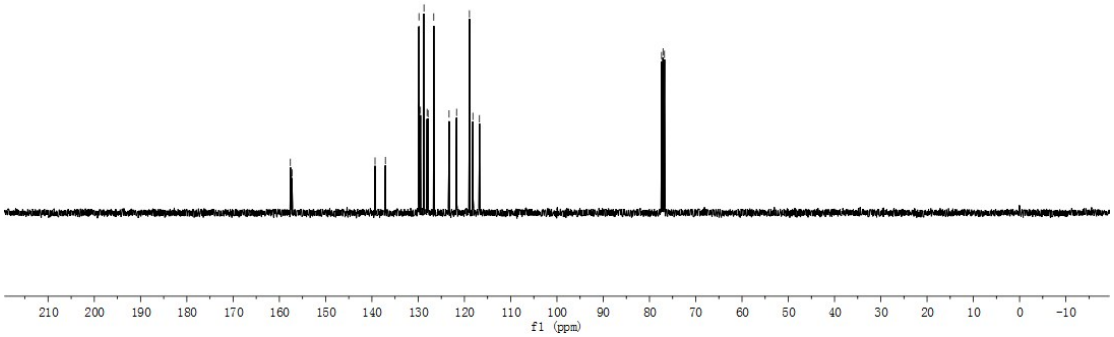

7.491
7.471
7.359
7.342
7.324
7.308
7.288
7.266
7.254
7.235
7.227
7.174
7.171
7.128
7.110
7.093
7.055
7.029
6.915
6.895

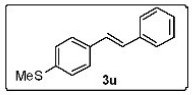

0.000


1.96
7.07
6.05
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

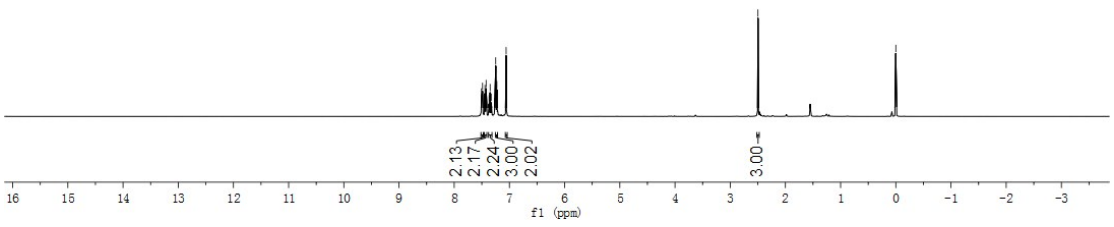


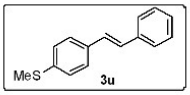
157.617
157.263
139.319
137.081
129.976
129.829
129.502
128.737
128.067
127.854
126.627
123.313
121.692
118.912
118.172
116.750
77.389
77.072
76.754





7.506
7.487
7.443
7.422
7.368
7.349
7.330
7.266
7.248
7.227
7.060
2.497
0.000

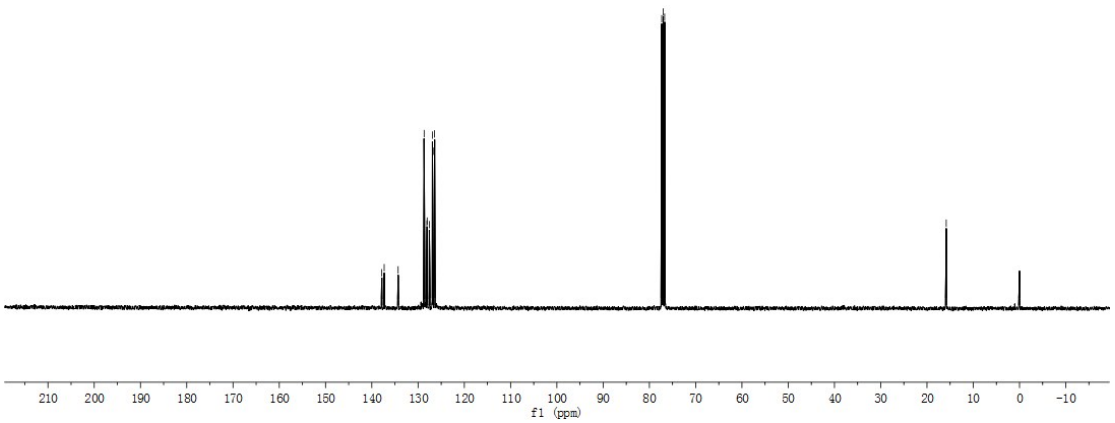


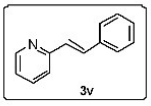

MeS
3u

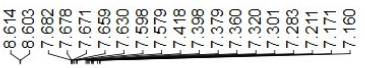

137.847
137.324
134.309
128.685
128.092
128.033
127.558
126.894
126.731
126.429


77.337
77.019
76.702

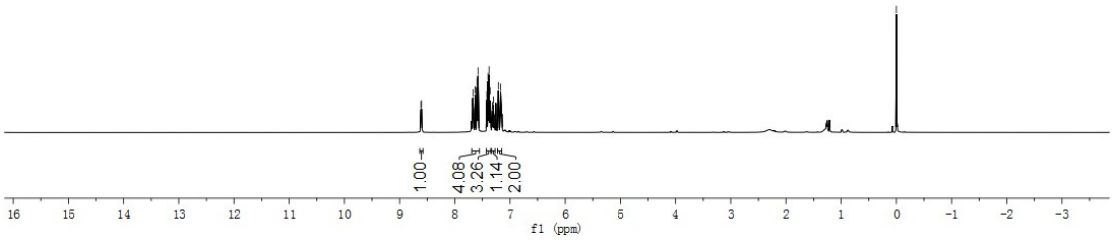

15.839

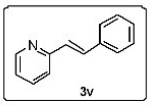

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
3v

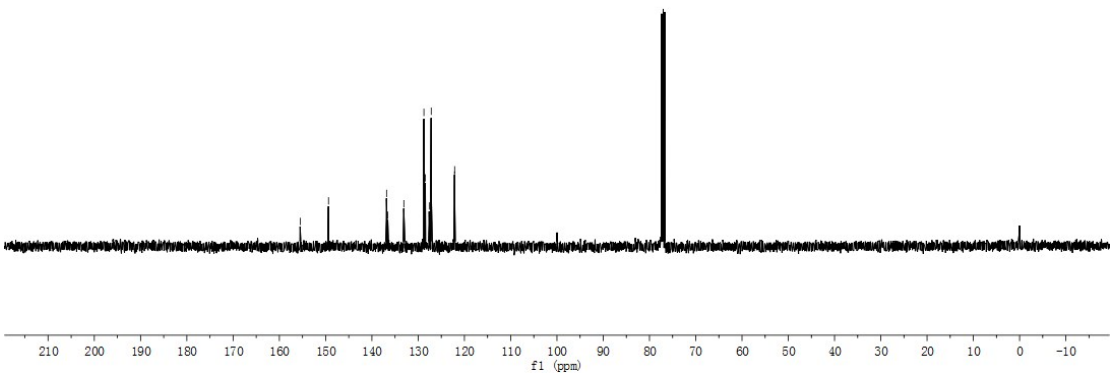

8.614
8.603
7.682
7.678
7.671
7.659
7.630
7.598
7.579
7.418
7.398
7.379
7.360
7.320
7.301
7.283
7.211
7.171
7.160

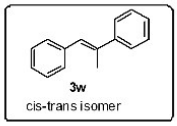

0.000


1.00
4.08
3.26
1.14
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

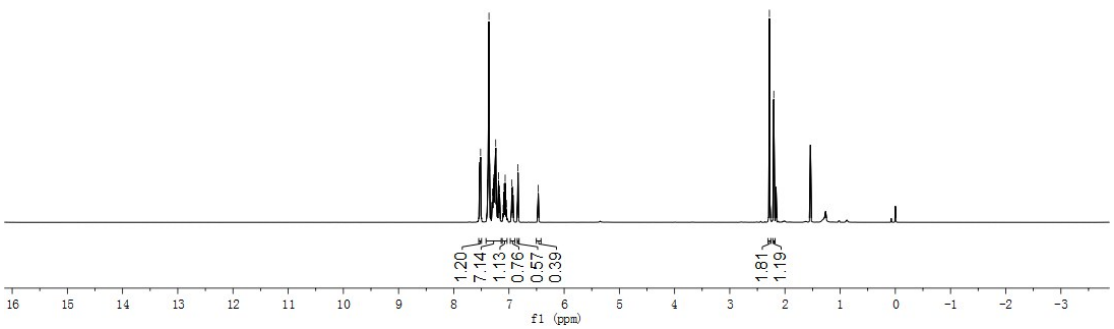


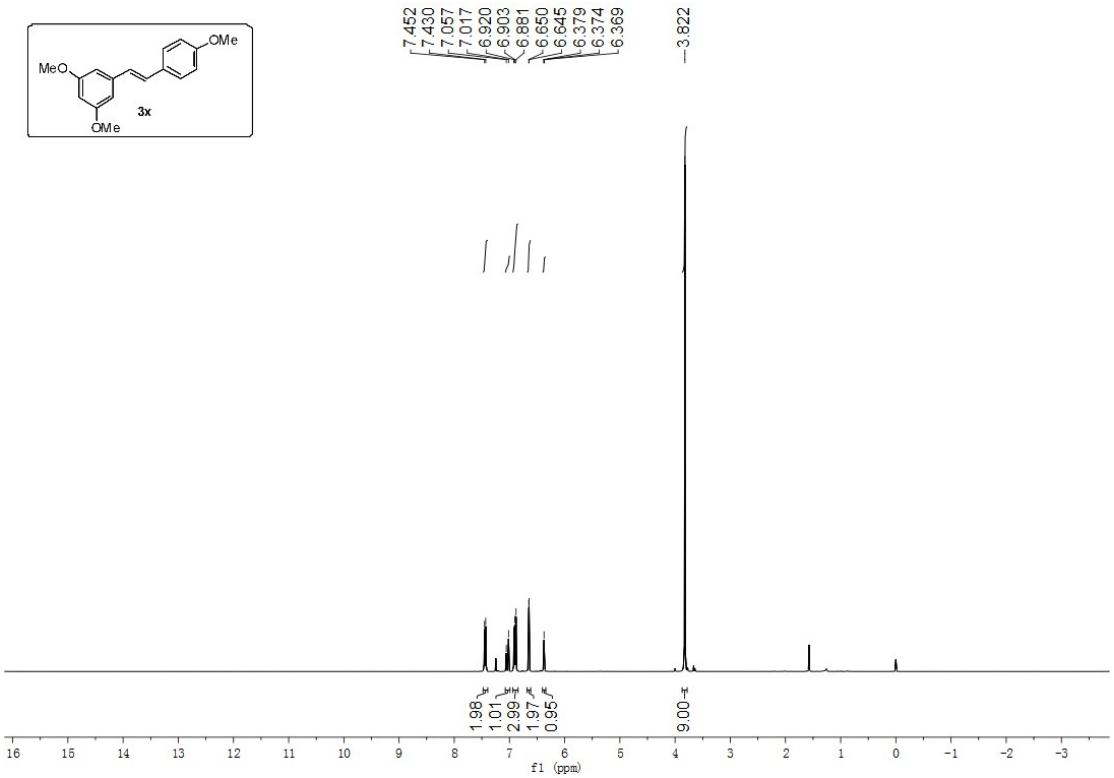
155.494
149.377
136.829
136.572
133.097
128.754
128.448
127.601
127.174
122.138
122.116

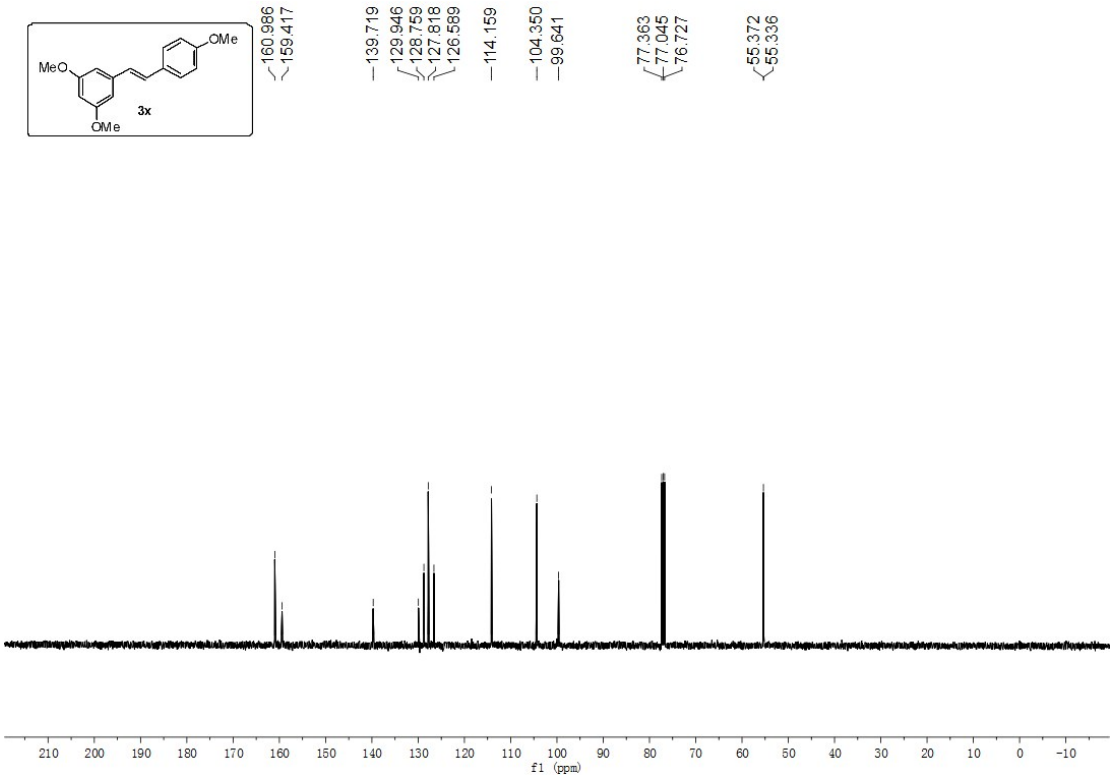


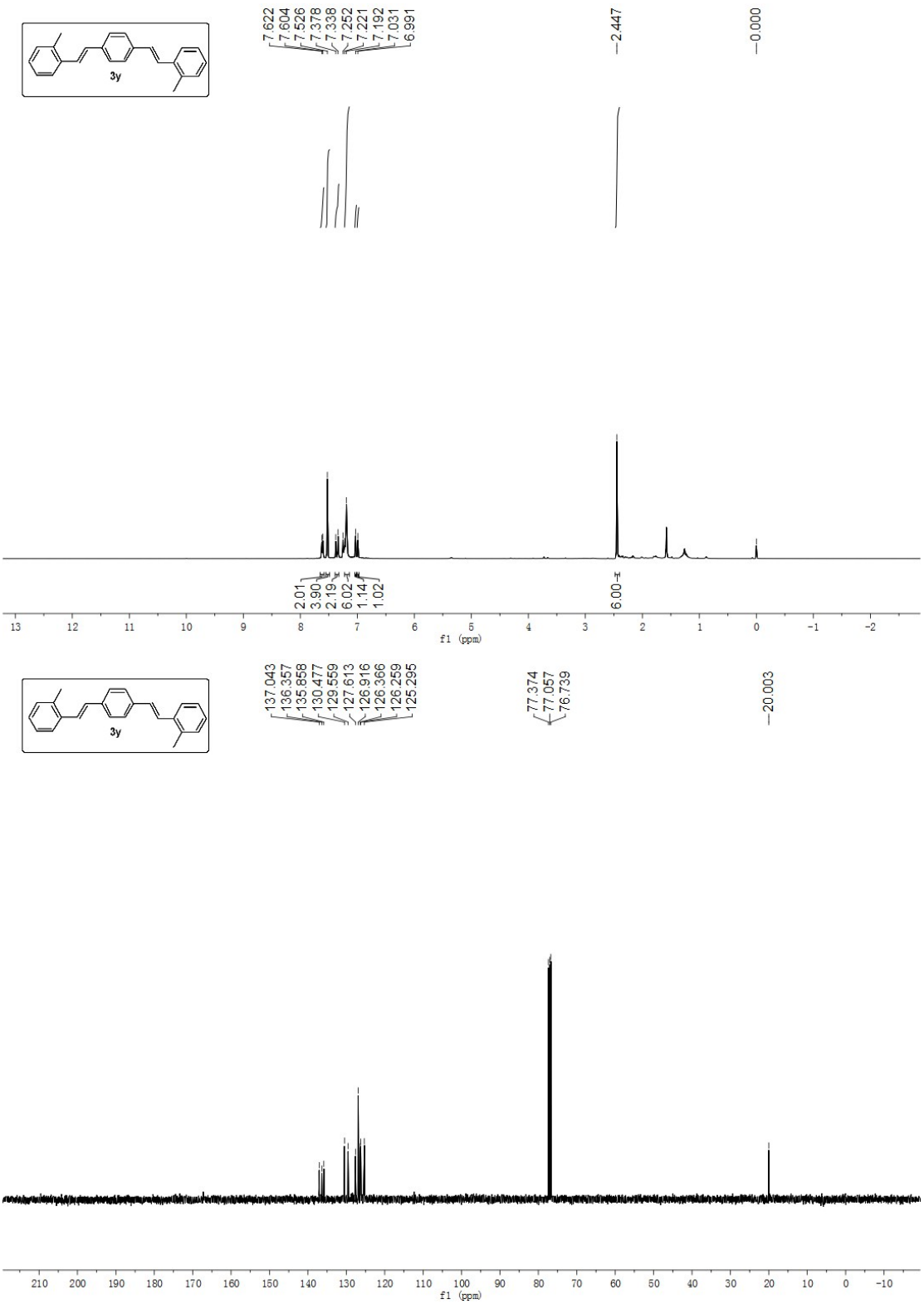


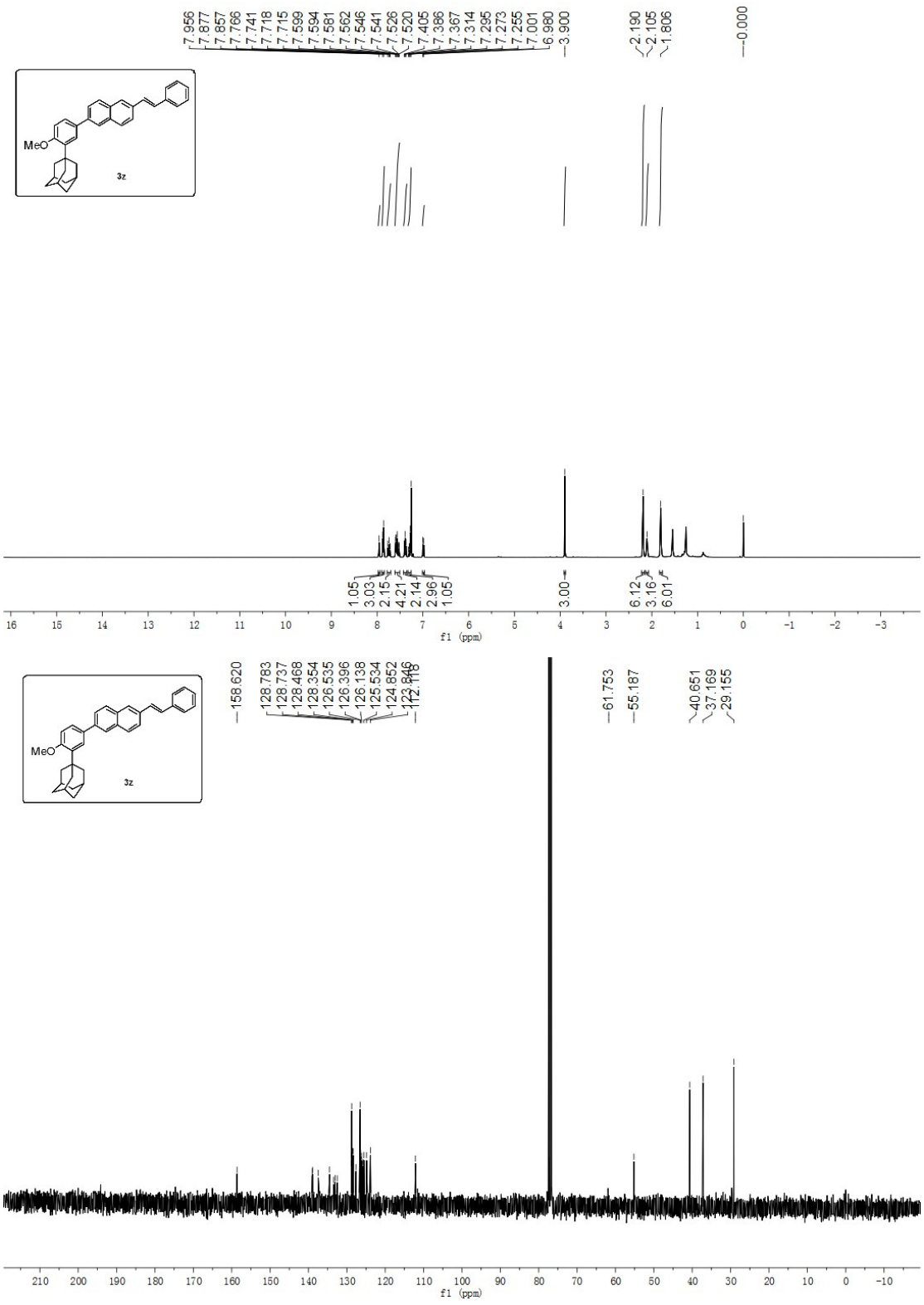
7.533
7.514
7.387
7.370
7.362
7.350
7.301
7.282
7.275
7.255
7.240
7.225
7.188
7.171
7.104
7.088
7.069
7.046
6.946
6.928
6.837
6.469
2.282
2.202




3x
7.452
7.430
7.057
7.017
6.920
6.903
6.881
6.650
6.645
6.379
6.374
6.369
3.822
1.98
1.01
2.99
1.97
0.95
9.00
f1 (ppm)


3x
160.986
159.417
139.719
129.946
128.759
127.818
126.589
114.159
104.350
99.641
77.363
77.045
76.727
55.372
55.336
f1 (ppm)


3y
7.622
7.604
7.526
7.378
7.338
7.252
7.221
7.192
7.031
6.991
2.447
0.000
2.01
3.90
2.19
6.02
1.14
1.02
6.00
f1 (ppm)
3y
137.043
136.357
135.858
130.477
129.559
127.613
126.916
126.366
126.259
125.295
77.374
77.057
76.739
20.003
f1 (ppm)


7.956
7.877
7.857
7.766
7.741
7.718
7.715
7.599
7.594
7.581
7.562
7.546
7.541
7.526
7.520
7.405
7.386
7.367
7.314
7.295
7.273
7.255
7.001
6.980
3.900
2.190
2.105
1.806
0.000
MeO
3z
1.05
3.03
2.15
4.21
2.14
2.96
1.05
3.00
6.12
3.16
6.01
f1 (ppm)
158.620
128.783
128.737
128.468
128.354
126.535
126.396
126.138
125.534
124.852
123.846
112.118
61.753
55.187
40.651
37.169
29.155
MeO
3z
f1 (ppm)