Supporting Information

Efficient and Selective Hydrogenation of C-O Bonds with a Simple Sodium Formate Catalyzed by Nickel

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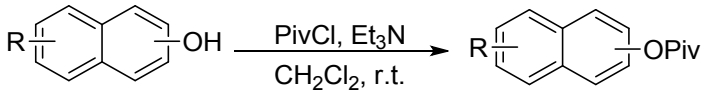
1. General information

All reactions were carried out in oven-dried Schlenk tubes under N_2 atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using silica gel 60 (particle size 37–54 μm). The pure products were obtained by means of column chromatography. ^{1}H NMR and ^{13}C NMR data were acquired on a Bruker-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C NMR spectroscopy). Chemical shifts for ^{1}H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration.

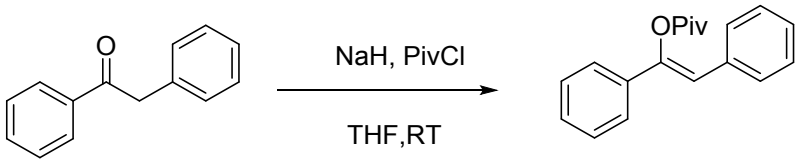
2. Synthesis of the starting materials

A、Synthesis of aryl and benzyl pivalates (**1a**–**1q**, **1v-1z**, **1ae-1af**).[1,2]



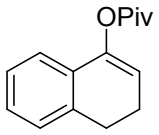
Aryl and benzyl pivalates were prepared by reactions of the alcohols with PivCl (1.20 equiv) in the presence of Et_3N (1.20 equiv) in DCM at room temperature. The products were purified by flash chromatography (petroleum ether/EtOAc as elute).

B、Synthesis of alkenyl pivalates (**1r-1u**)[3]

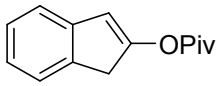


(*Z*)-1,2-diphenylvinyl pivalate (**1u**) A mineral oil suspension of NaH (60%, 0.36 g, 15 mmol) was placed in a dry 100 mL Schlenk tube under N_2 atmosphere, and THF (15 mL) was added into the flask. To this suspension, deoxybenzoin (1.96 g, 10 mmol) in THF (8 mL) was added dropwise. After stirring the mixture at room temperature for 2 h, pivaloyl chloride (3.1 g, 25 mmol) in 10 mL THF was added, then the resulting solution was stirred overnight. The reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (25 mL × 3) and the combined organic layer was dried over Na_2SO_4. After removal of the solvent, the

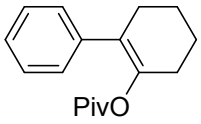
crude residue was purified by flash column chromatography (petroleum ether as elute) to afford the product as white solid in 85 % yield.



3,4-dihydronaphthalen-1-yl pivalate(**1r**). Following the procedure B with use of 3,4-dihydronaphthalen-1(2H)-one (1.33 g,10 mmol) as starting material. The product was produced as orange oil in 80 % yield (1.84 g).



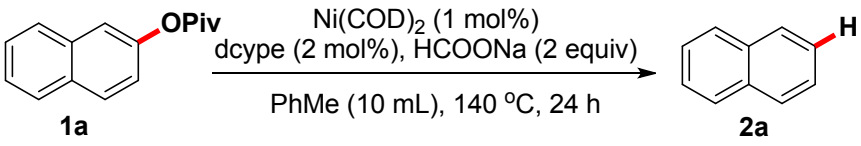
1H-inden-2-yl pivalate (**1t**). Following the procedure B with use of 1H-inden-2(3H)-one (1.19 g, 10 mmol) as starting material, the product was produced as orange oil in 75 % yield (1.62g).



3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl pivalate (**1s**). Following the procedure B with use of 1H-inden-2(3H)-one (1.74 g, 10 mmol) as starting material, the product was produced as colorless oil in 82% yield (1.62 g).

3. Experimental procedures.

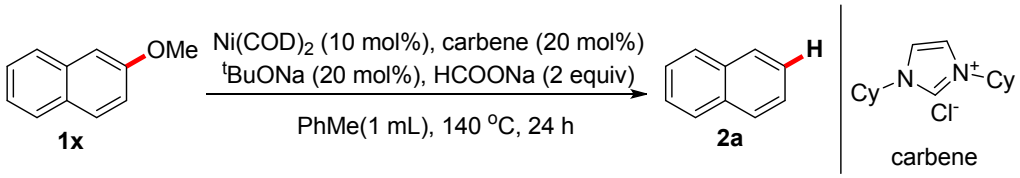
A、A typical procedure for Ni-catalyzed Hydrogenation of esters



A 10 mL Schlenk tube was charged with **1a** (114 mg, 0.5 mmol), HCOONa (68 mg, 2.0 equiv), $Ni(COD)_2$ (1.4 mg, 1 mol%), dcype (4.2 mg, 2 mol%) and 1mL anhydrous toluene. The flask was taken out of the glove box, and the mixture was stirred for 24 h

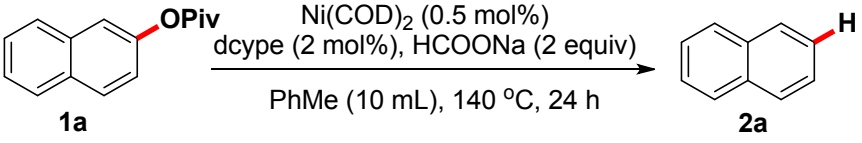
at 120 °C. The crude material was purified by silica gel column chromatography (petroleum ether as elute) to afford the product **2a** as white solid in 97 % yield (62.0 mg).

B、Ni-catalyzed Hydrogenation of 2-methoxynaphthalene (**1aa-1ad**).



A 10 mL Schlenk tube was charged with **1x** (31.6 mg, 0.2 mmol), HCOONa (27.2 mg, 2.0 equiv), $Ni(COD)_2$ (5.5 mg, 10 mol%), 1,3-dicyclohexiylimidazolium chloride (10.72 mg, 20 mol%), ^{t}BuONa (3.84 mg, 20 mol%) and 1mL anhydrous toluene. The flask was taken out of the glove box, and the mixture was stirred for 24 h at 140 °C. The crude material was purified by silica gel column chromatography (petroleum ether as elute) to afford the product **2a** as white solid in 63 % yield (16.1 mg).

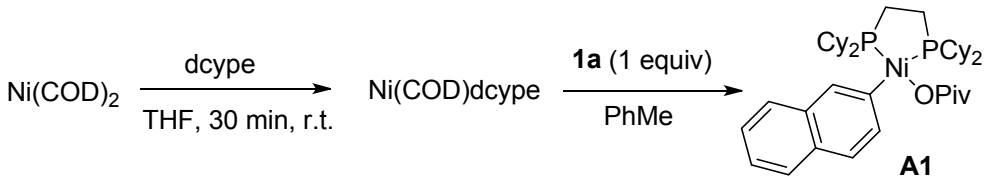
C、Ni-catalyzed Hydrogenation of **1a** at 10 mmol scale.



A 100 mL Schlenk tube was charged with **1a** (2.28 g, 10 mmol), HCOONa (1.36 g, 20 mmol), $Ni(COD)_2$ (13.7 mg, 0.5 mol%), dcype (84.4 mg, 2 mol%) and 10 mL anhydrous toluene. The flask was taken out of the glove box, and the mixture was stirred for 24 h at 140 °C. The crude material was purified by silica gel column chromatography (petroleum ether as elute) to afford the product **2a** as white solid in 97 % isolated yield (1.24 g).

4. Mechanistic considerations

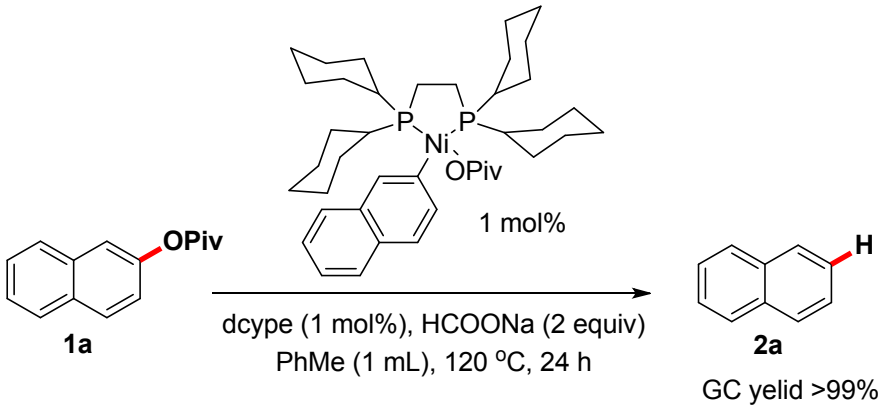
A. Synthesis of oxidative addition complex **A1**[4]



Synthesis of Ni(COD)dcype: An oven-dried 25 mL Schlenk tube containing a stirring bar was charged with $Ni(COD)_2$ (82.5 mg, 0.3 mmol) and dcype (126.6 mg, 0.3 mmol) in anhydrous THF (1 mL). After stirring the mixture at room temperature for 30 min, it was cooled down to 0 °C and the titled compound precipitated from the solution as a yellow solid. After removal the solvent, the solid was washed by anhydrous hexanes three times (3×1 mL).

Synthesis of complex **A1**: An oven-dried 25 mL Schlenk tube containing a stirring bar was charged with Ni(cod)dcype (118 mg,0.2 mmol), **1a** (45.6 mg, 0.2 mmol) and anhydrous toluene (2 mL). The tube was then taken out of the glove box and stirred at 90 °C overnight. The mixture was then cooled to room temperature, and the solvent was removed under *vacuum*. The residue was recrystallized from anhydrous hexanes at 0 °C, affording complex **A1** as orange solid in 45% yield. ^{1}H NMR (400 MHz, d^8-Tol) δ 8.02 (s, 1H), 7.98 (s, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.3 Hz, 1H), 7.05 (d, J = 7.1 Hz, 1H), 6.96 (d, J = 7.3 Hz, 1H), 2.39 (s, 2H), 2.12 (s, 2H), 1.87-0.87 (m, 53H). ^{31}P NM R (162 MHz, d^8-Tol) δ 63.22 (d, J = 13.9 Hz), 61.10 (d, J = 13.9 Hz). Spectroscopic data for Ni complex matched well with previously reported ones in the literature.[4]

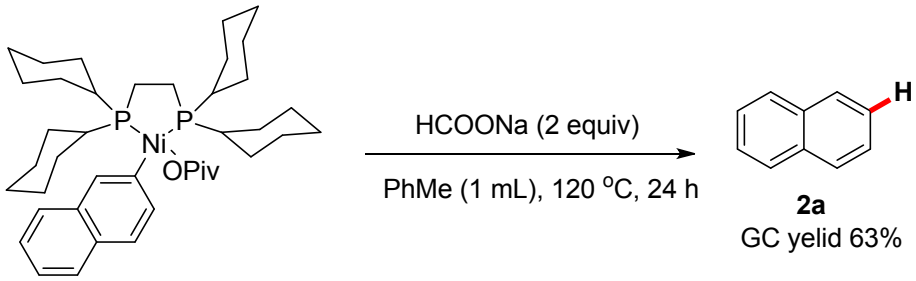
B. Catalytic hydrogenation of **1a** using complex **A1** as a catalyst.



An oven-dried 10 mL Schlenk tube containing a magnetic stirring bar was charged

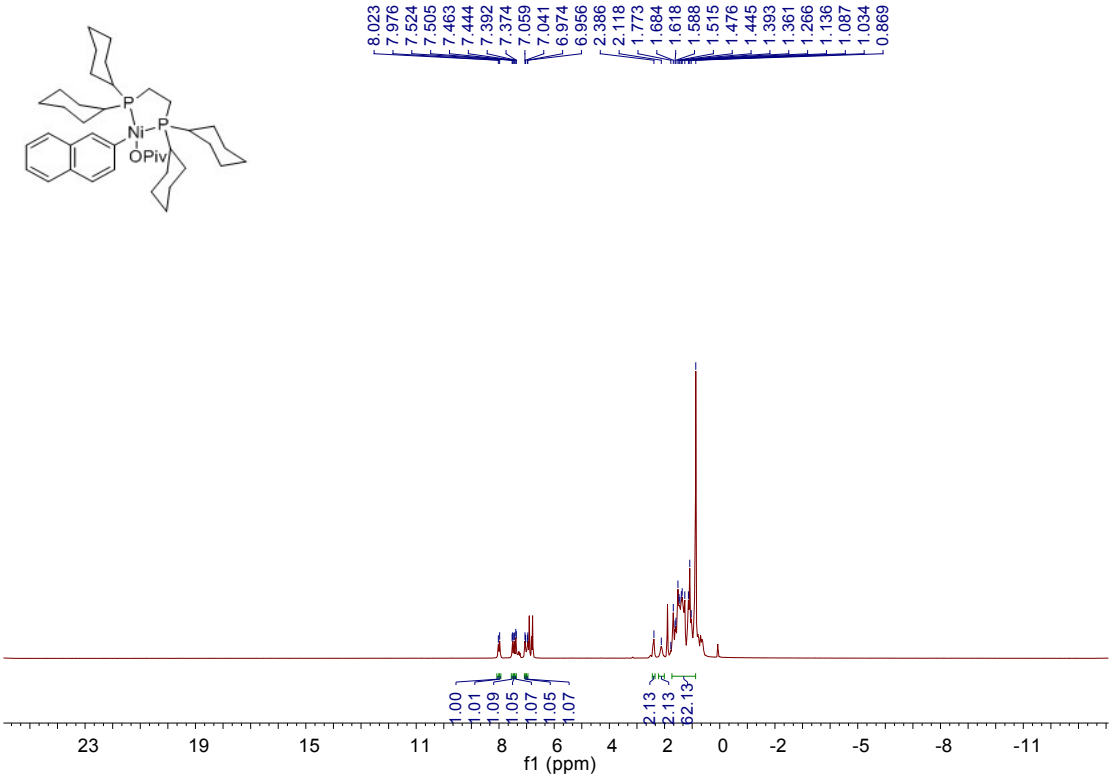
with **1a** (114 mg, 0.5 mmol), HCOONa (68 mg, 1 mmol), complex Ni **A1** (3.54 mg, 1 mol%), dcype (2.1 mg, 1 mol%) and anhydrous toluene (1 mL). The reaction tube was taken out of the glove box and stirred at 120 °C for 24 h. **2a** was produced in an almost quantitative yield as determined by GC analysis using *n*-tridecane as an internal standard.

C. Stoichiometric reaction with complex **A1**.

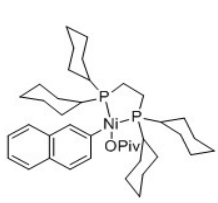


An oven-dried schlenk tube was charged with complex **A1** (35.4 mg, 0.05 mmol), HCOONa (6.8 mg, 2 equiv) and anhydrous toluene (1 mL). The reaction tube was taken out of the glove box and heated at 120 °C for 24 h. **2a** was produced in 63% yield as determined by GC analysis using *n*-tridecane as an internal standard.

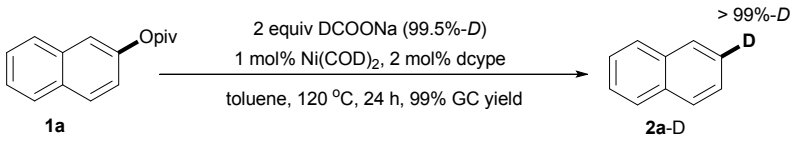
^{1}H NMR of complex A1



^{31}P NMR of complex A1



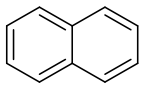
Deuturated experiment



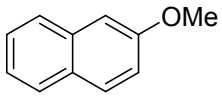
An oven-dried 10 mL Schlenk tube containing a magnetic stirring bar was charged with **1a** (114 mg, 0.5 mmol), $Ni(COD)_2$(1.4 mg, 1 mol%), dcype(4.2 mg, 2 mol%), DCOONa (69 mg, 1 mmol, 99.5%-D), dcype (2 mol%) and anhydrous toluene (1 mL). The reaction tube was taken out of the glove box and stirred at 120 °C for 24 h. **2a-D** was produced in an almost quantitative yield as determined by GC analysis using *n*-tridecane as an internal standard. The deuterium content of **2a-D** obtained under the reaction conditions was determined to be 99% by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.84 (m, 4H), 7.48-7.46 (m, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 133.47, 127.91, 127.79, 125.84, 125.75.[5] This compound is known.

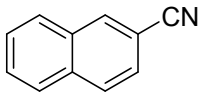
5. Characterization and analytical data of products 2.



Naphthalene (2a).[5] The compound was purified by column chromatography on silica gel using petroleum ether as elute. White solid (62.1 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (m, 4H), 7.485-7.478 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$): δ 133.47, 127.90, 125.83. This compound is known.

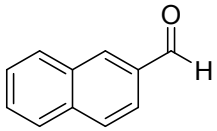


2-Methoxynaphthalene (2b).[6] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1) as elute. White solid (75.7 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 157.72, 134.60, 129.40, 128.99, 127.67, 126.75, 126.38, 123.60, 118.72, 105.79, 55.31. This compound is known.

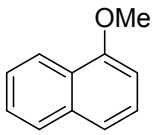


2-Naphthonitrile (2c).[7] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1) as elute. White solid (72.6 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.92-7.88 (m, 3H), 7.67-7.59 (m,

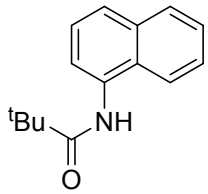
3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.67, 134.17, 132.27, 129.22, 129.06, 128.43, 128.07, 127.68, 126.35, 119.27, 109.39. This compound is known.



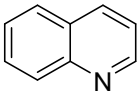
2-Naphthaldehyde (2d).[8] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1) as elute. White solid (59.3 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.35 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.95-7.90 (m, 3H), 7.67-7.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.27, 136.49, 134.54, 134.15, 132.68, 129.55, 129.12, 128.10, 127.11, 122.80. This compound is known.



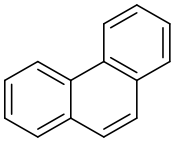
1-Methoxynaphthalene(2e).[6] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1) as elute. Colorless oil (64.7 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (b, 1H), 7.67 (d, J = 6.4 Hz, 1H), 7.36-7.23 (m, 4H), 6.66 (d, J = 7.2 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.53, 134.58, 127.55, 126.48, 125.96, 125.71, 125.27, 122.08, 120.31, 103.87, 55.54. This compound is known.



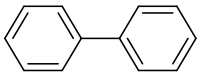
***N*-(Naphthalen-1-yl)pivalamide (2f)**.[9] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (8/1) as elute. White solid (97.6 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.55-7.46 (m, 3H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.89, 134.13, 132.63, 128.90, 127.31, 126.32, 125.91, 125.82, 125.61, 120.84, 120.21, 39.92, 27.85. This compound is known.



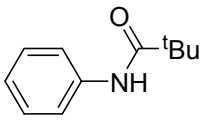
Quinoline (2g)[5]. The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1) as elute. Yellow oil (52.2 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.13-8.10 (m, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.51 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.36-7.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.36, 148.25, 136.03, 129.44, 129.41, 128.26, 127.77, 126.52, 121.05. This compound is known.



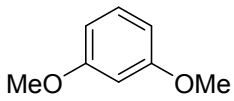
Phenanthrene (2h).[5] The compound was purified by column chromatography on silica gel using petroleum ether as elute. White solid (77.4 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 2H), 7.66 (dd, *J* = 7.2, 7.6 Hz, 4H), 7.60 (dd, *J* = 7.6, 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.07, 130.32, 128.58, 126.93, 126.58, 122.67. This compound is known.



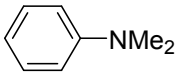
1,1'-Biphenyl (2i).[5] The compound was purified by column chromatography on silica gel using petroleum ether as elute. White solid (73.2 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 4H), 7.44 (dd, *J* = 7.2, 7.6 Hz, 4H), 7.34 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.27, 128.77, 127.27, 127.19. This compound is known.



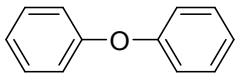
***N*-Phenylpivalamide (2j)**.[9] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (10/1) as elute. White solid (81.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.32 (b, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 1.32 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 176.56, 138.04, 128.96, 124.21, 119.96, 39.61, 27.65. This compound is known.



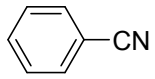
1,3-dimethoxybenzene(2k)[10]. The reaction was conducted at 0.2 mmol scale. The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (30/1) as elute. Yellow oil (19.9 mg, 72% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.0 Hz, 1H), 6.56 -6.33 (m, 3H), 3.76 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.88, 129.91, 106.18, 100.48, 55.28. This compound is known.



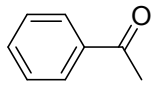
N,N-dimethylaniline(2l)[11]. The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1) as elute. Yellow oil (42.1mg, 70% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 6.74 (d, J = 5.6 Hz, 3H), 2.93 (s, 6H).^{13}C NMR (101 MHz, CDCl3) δ 150.69, 129.13, 116.67, 112.69, 40.69. This compound is known.



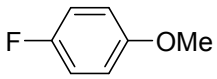
Diphenyl oxide(2m)[11]. The compound was purified by column chromatography on silica gel using petroleum ether as elute. colorless solid (74.8 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 4H), 7.09 (t, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.26, 129.75, 123.23, 118.91, 55.28. This compound is known.



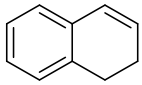
Benzonitrile (2n).[7] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (10/1) as elute. Colorless oil (33.4 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.6, 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.81, 132.14, 129.15, 118.85, 112.43. This compound is known.



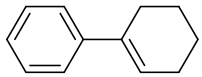
Acetophenone (2o).[12] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1) as elute. Colorless oil (57.6 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.45 (dd, *J* = 7.6, 7.2 Hz, 2H), 2.59 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.12, 137.13, 133.10, 128.57, 128.30, 26.58. This compound is known.



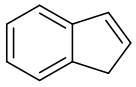
1-Fluoro-4-methoxybenzene (2p).[13] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (30/1) as elute. Colorless oil (57.2 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 8.4, 8.8 Hz, 2H), 6.82 (dd, *J* = 4.0, 8.8 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.25 (d, *J* = 236.3 Hz), 155.74 (d, *J* = 1.8 Hz), 115.76 (d, *J* = 22.9 Hz), 114.78 (d, *J* = 8.0 Hz), 55.72. This compound is known.



1,2-Dihydronaphthalene (2q).[14] The compound was purified by column chromatography on silica gel using hexane as elute. Colorless oil (57.8 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.08 (m, 3H), 7.00 (b, 1H), 6.44 (d, J = 9.6 Hz, 1H), 6.02-5.99 (m, 1H), 2.78 (t, J = 7.6 Hz, 2H), 2.29 (b, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.52, 134.20, 128.70, 127.87, 127.59, 126.91, 126.50, 125.95, 27.56, 23.26. This compound is known.

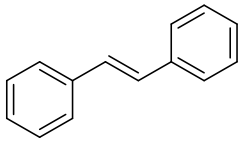


2,3,4,5-Tetrahydro-1,1'-biphenyl (2r).[15] The compound was purified by column chromatography on silica gel using hexane as elute. Colorless oil (55.3 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.2 Hz, 2H), 7.28 (dd, J = 7.2, 7.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.11 (b, 1H), 2.40 (b, 2H), 2.20 (b, 2H), 1.78-1.76 (m, 2H), 1.711.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.76, 136.66, 128.24, 126.56, 125.00, 124.81, 27.47, 25.95, 23.15, 22.25. This compound is known.

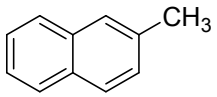


1*H*-Indene (2s).[16] The compound was purified by column chromatography on silica gel using hexane as elute. Yellow oil (36.5 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 6.8 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.27-7.24 (m, 1H), 7.19-7.16 (m, 1H), 6.86 (b, 1H), 6.53 (b, 1H), 3.37 (b, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

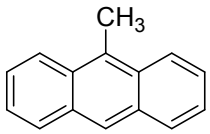
144.93, 143.75, 134.23, 132.16, 126.32, 124.63, 123.80, 121.04, 39.14. This compound is known.



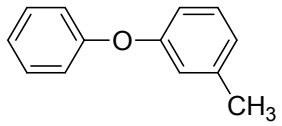
(*E*)-1,2-Diphenylethene (2t)[5] (*cis-trans* mixture, the ratio of *trans*-isomer to *cis*-isomer was ca. 70/30 by GC analysis of the reaction mixture. After purification, the ratio was ca. 58/42 by ^{1}H NMR spectra). The compound was purified by column chromatography on silica gel using petroleum ether as elute. 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 5.42H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 5.33H), 7.28-7.18 (m, 13.62H), 7.11 (s, 2.79H), 6.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.36, 137.26, 130.27, 128.88, 128.72, 128.70, 128.22, 127.63, 127.10, 126.53. This compound is known.



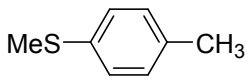
2-Methylnaphthalene (2u).[5] The compound was purified by column chromatography on silica gel using petroleum ether as elute. Colorless oil (68.9 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.71 (m, 3H), 7.58 (s, 1H), 7.42-7.36 (m 2H), 7.29-7.28 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.55, 133.83, 131.87, 128.25, 127.84, 127.75, 127.38, 126.99, 126.00, 125.09, 21.83. This compound is known.



9-Methylanthracene (2v).[5] The compound was purified by column chromatography on silica gel using petroleum ether as elute. Yellow solid (86.4 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.52-7.44 (m, 4H), 3.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.50, 130.14, 129.07, 125.30, 125.26, 124.83, 124.70, 13.95. This compound is known.

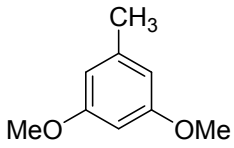


1-Methyl-4-phenoxybenzene (2w).[11] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (40/1) as elute. Colorless oil (65.3 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.6, 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 7.2, 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.82-6.79 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.45, 157.28, 139.97, 129.76, 129.52, 124.12, 123.15, 119.66, 118.92, 116.00, 21.45. This compound is known.

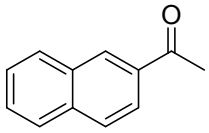


Methyl(*p*-tolyl)sulfane (2x).[17] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (30/1) as elute. Colorless oil (46.9 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.07

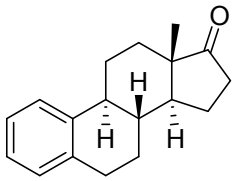
(d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.07, 134.81, 129.67, 127.36, 20.97, 16.56. This compound is known.



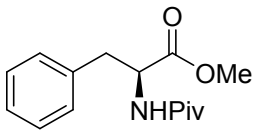
1,3-Dimethoxy-5-methylbenzene(2y).[18] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (30/1) as elute. Colorless oil (69.2 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 2H), 6.29 (s, 1H), 3.77 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.73, 140.22, 107.11, 97.54, 55.23, 21.82. This compound is known.



1-(naphthalen-2-yl)ethanone(2z)[19]. The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (30/1) as elute. White solid (22.1 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.92-7.85 (m, 2H), 7.58 (dt, *J* = 14.8, 7.1 Hz, 2H), 2.73 (s, 3H).13C NMR (101 MHz, CDCl3) δ 198.16, 135.62, 134.51, 132.54, 130.23, 129.58, 128.50, 128.45, 127.81, 126.80, 123.92, 26.73. This compound is known.



(8R,9S,13S,14S)-13-Methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one(2aa).[20] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (8/1) as elute. White solid (109 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.2 Hz, 1H), 7.17-7.09 (m, 3H), 2.93-2.91 (m, 2H), 2.54-2.41 (m, 2H), 2.34-2.29 (m, 1H), 2.19-1.93 (m, 4H), 1.87-1.40 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.91, 139.73, 136.49, 129.09, 125.85, 125.79, 125.34, 50.58, 48.02, 44.51, 38.14, 35.89, 31.65, 29.40, 26.53, 25.70, 21.62, 13.87. This compound is known.



Methyl-3-phenyl-2-pivalamidopropanoate(2ab).[21] The compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (15/1) as elute. White solid (105 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.22 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.05 (d, *J* = 6.4 Hz, 1H), 4.88-4.84 (m, 1H), 3.74 (s, 3H), 3.19-3.07 (m, 2H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.89, 172.31, 135.94, 129.31, 128.52, 127.13, 52.86, 52.30, 38.68, 37.79, 27.37. This compound is known.

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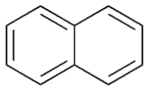
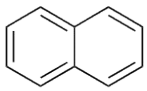
7. Copies of ^{1}H NMR and ^{13}C NMR spectra



2a



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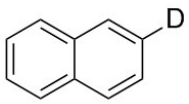
D

2a-D


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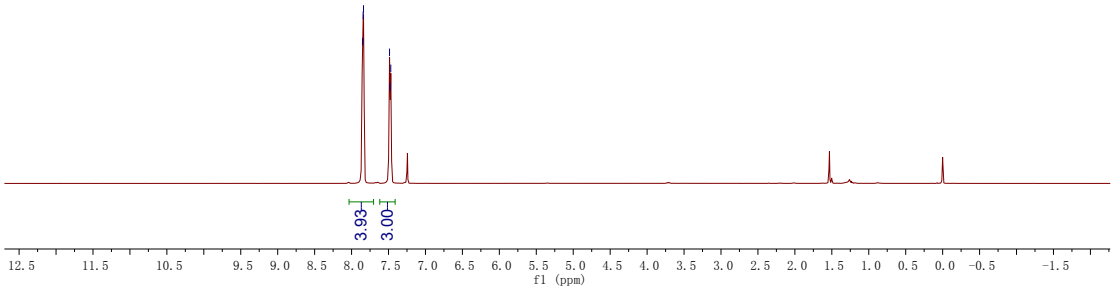
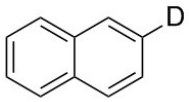

3.93
3.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)


D

2a-D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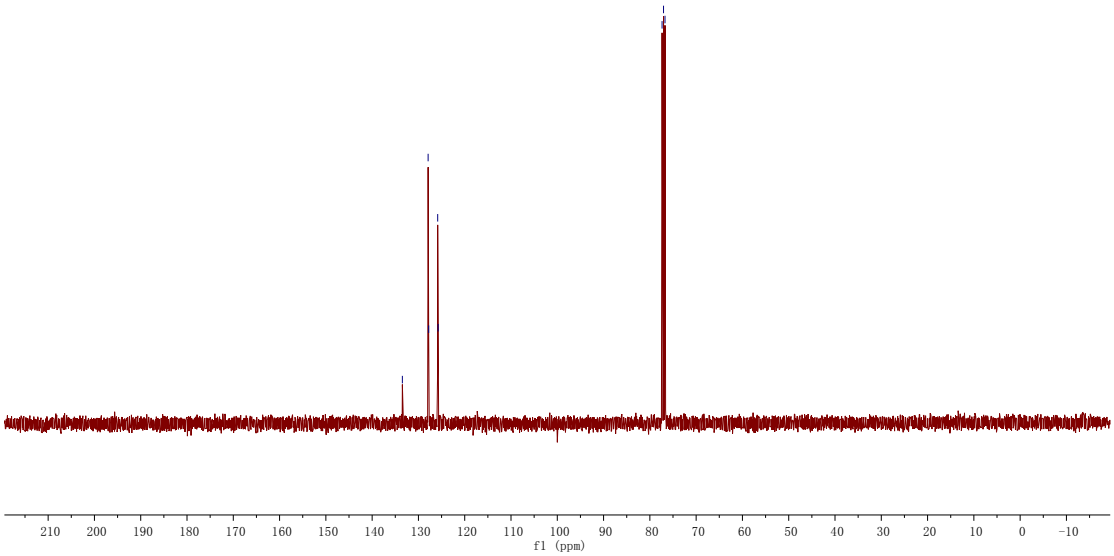
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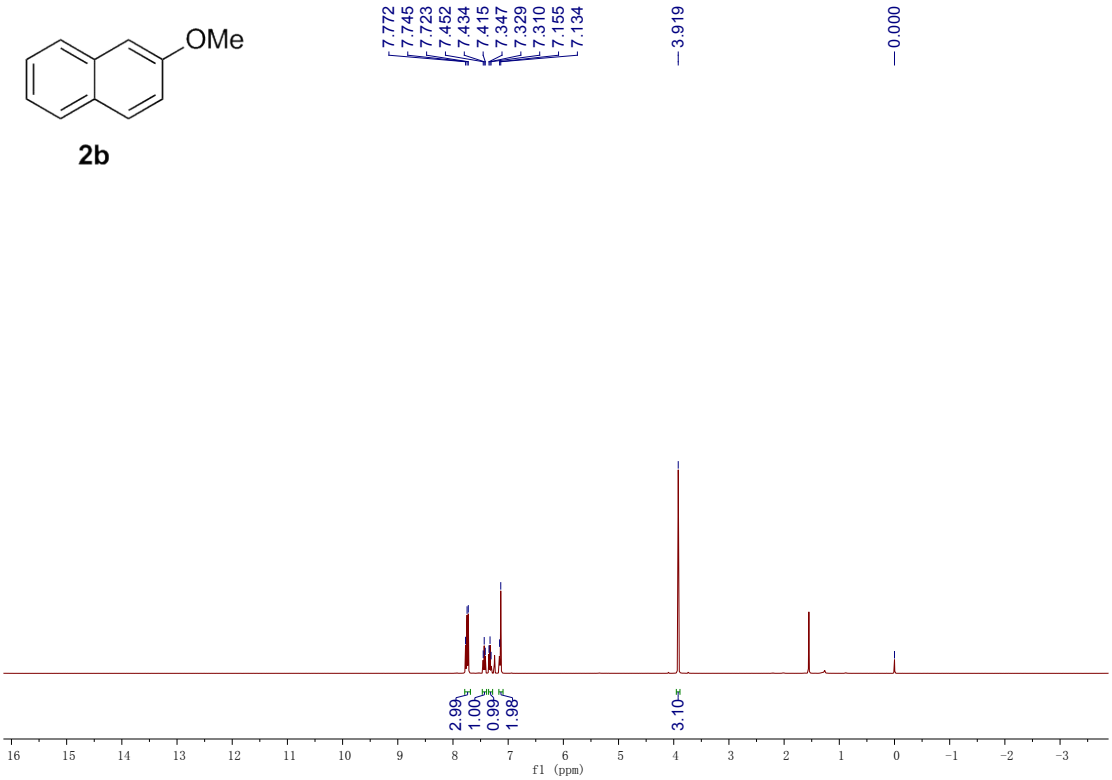
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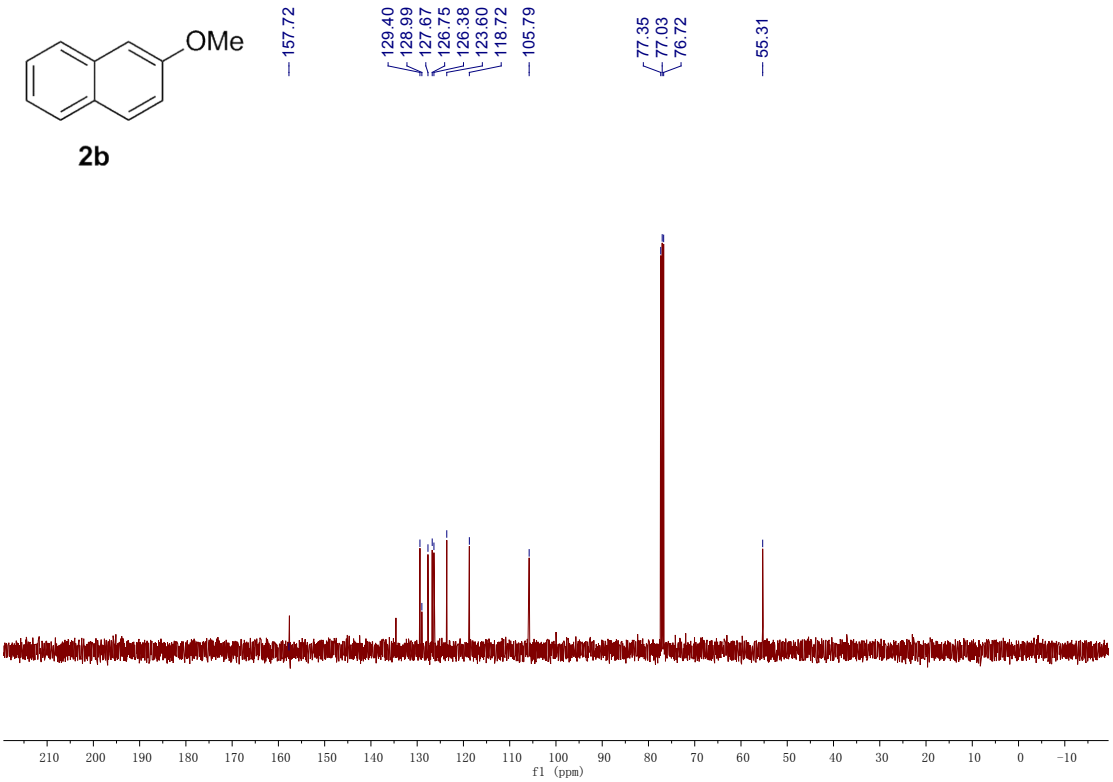
OMe
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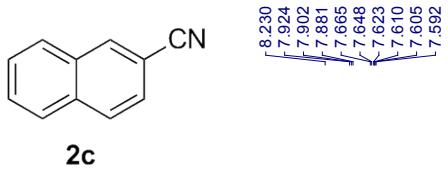
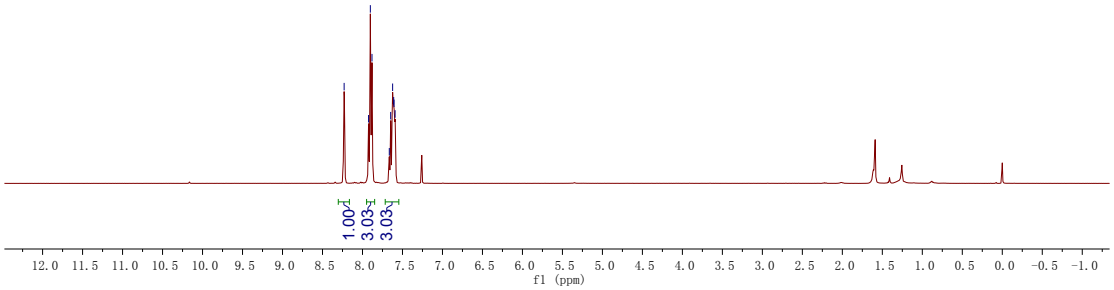
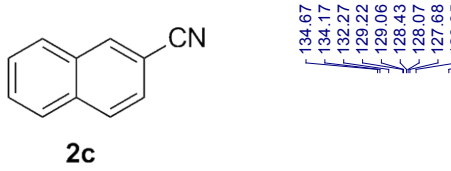
76.72
55.31
f1 (ppm)

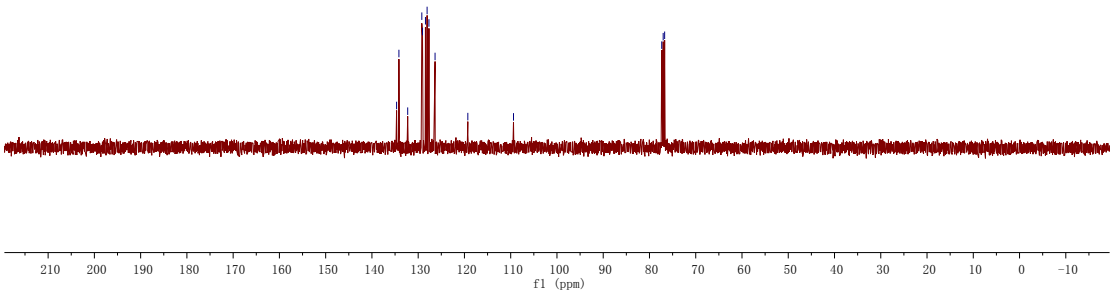

CN
8.230
7.924
7.902
7.881
7.665
7.648
7.623
7.610
7.605
7.592

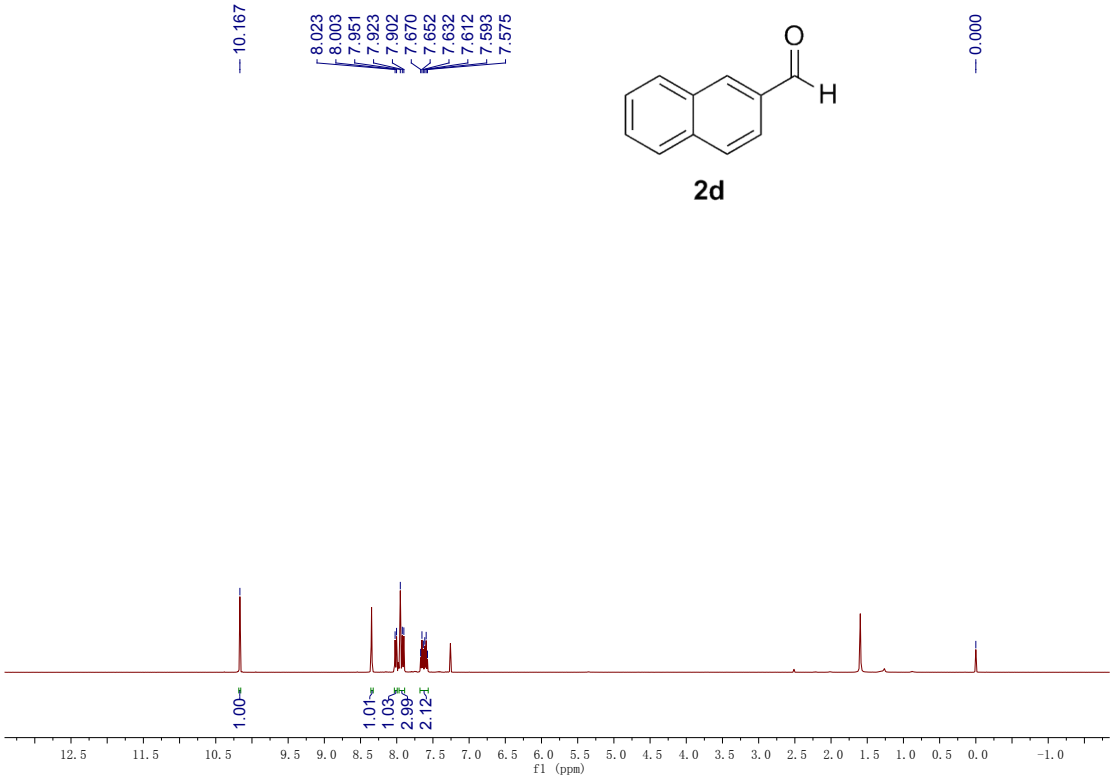
2c

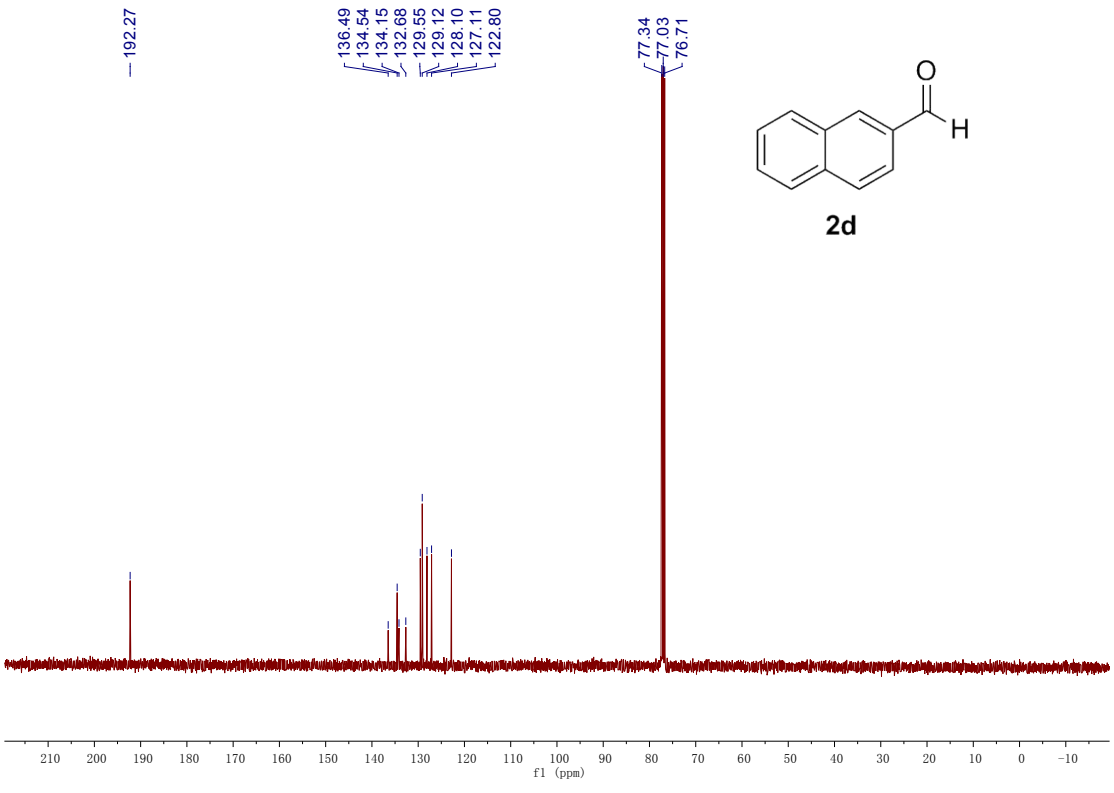

1.00
3.03
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

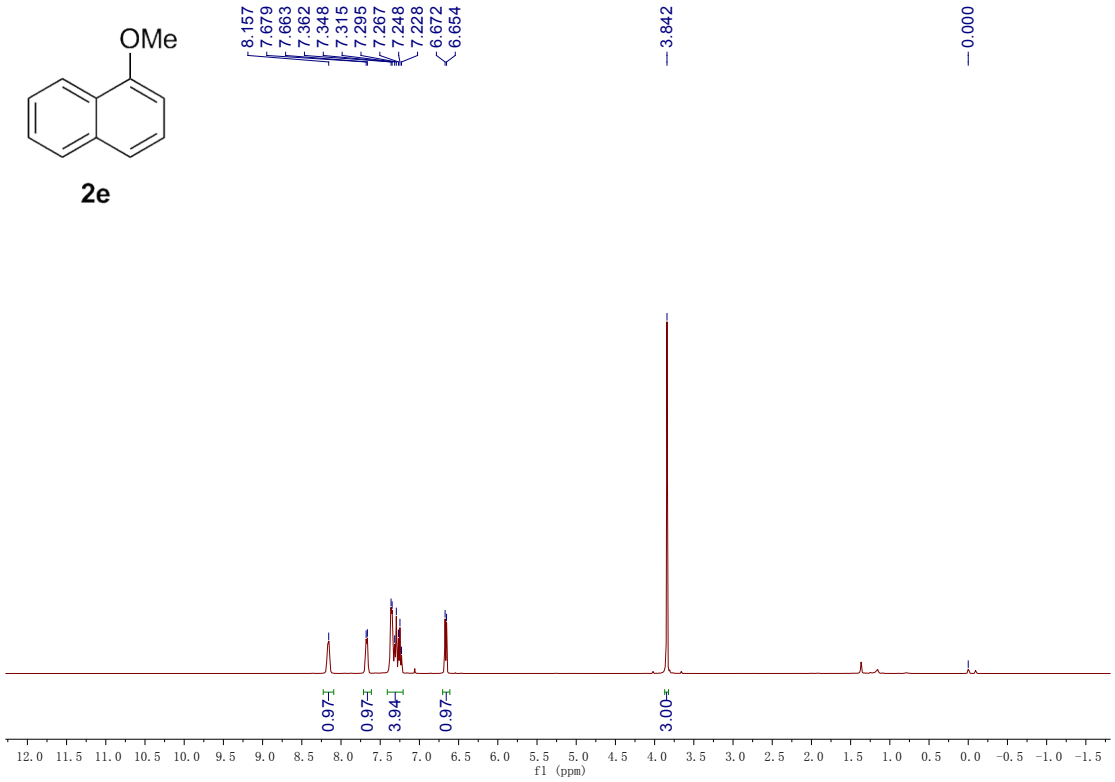

CN
134.67
134.17
132.27
129.22
129.06
128.43
128.07
127.68
126.35
119.27
109.39
77.35
77.04
76.72

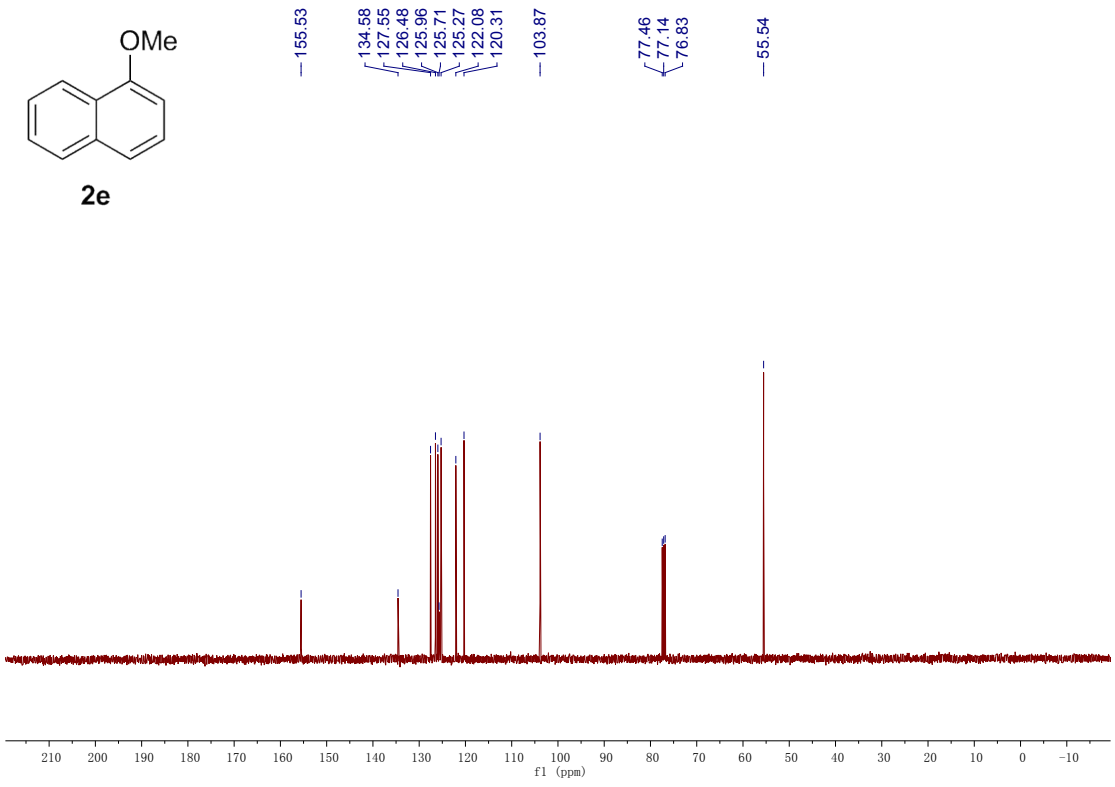
2c

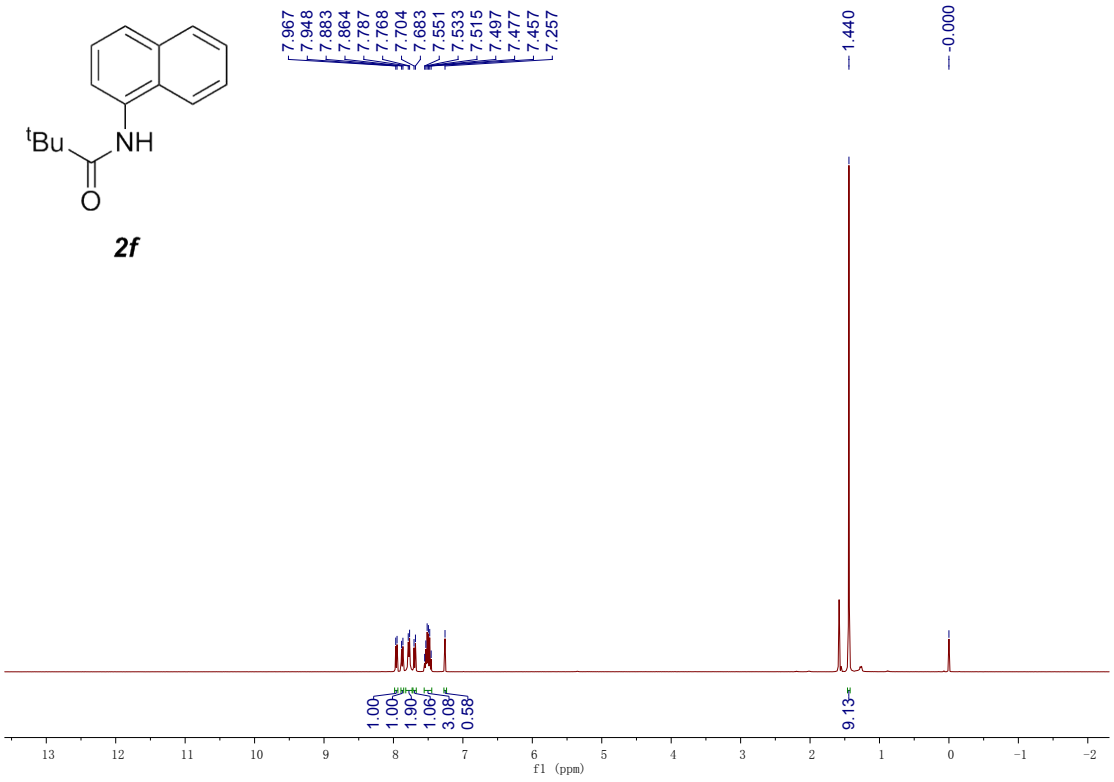

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

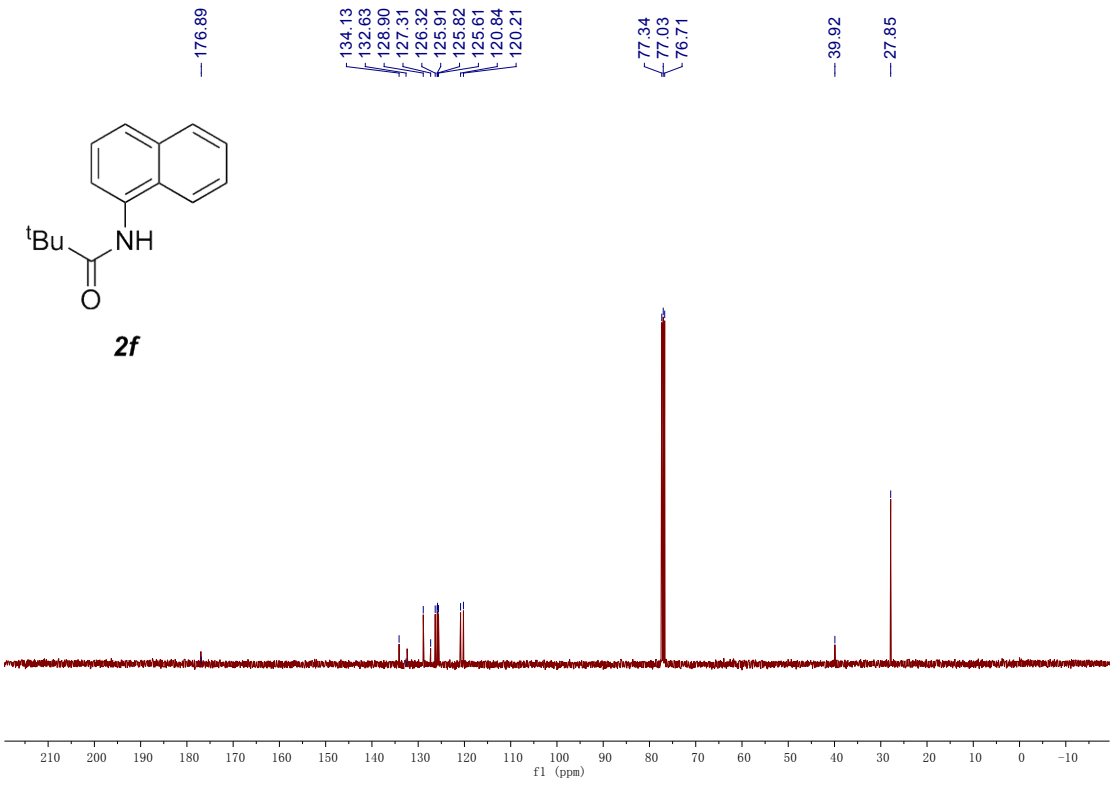

10.167
8.023
8.003
7.951
7.923
7.902
7.670
7.652
7.632
7.612
7.593
7.575
0.000
O
H
2d
1.00
1.01
1.03
2.99
2.12
f1 (ppm)

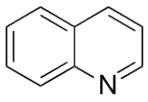

192.27
136.49
134.54
134.15
132.68
129.55
129.12
128.10
127.11
122.80
77.34
77.03
76.71
O
H
2d
f1 (ppm)


OMe
2e
8.157
7.679
7.663
7.362
7.348
7.315
7.295
7.267
7.248
7.228
6.672
6.654
3.842
0.000
0.97
0.97
3.94
0.97
3.00
f1 (ppm)


OMe
2e
155.53
134.58
127.55
126.48
125.96
125.71
125.27
122.08
120.31
103.87
77.46
77.14
76.83
55.54
f1 (ppm)

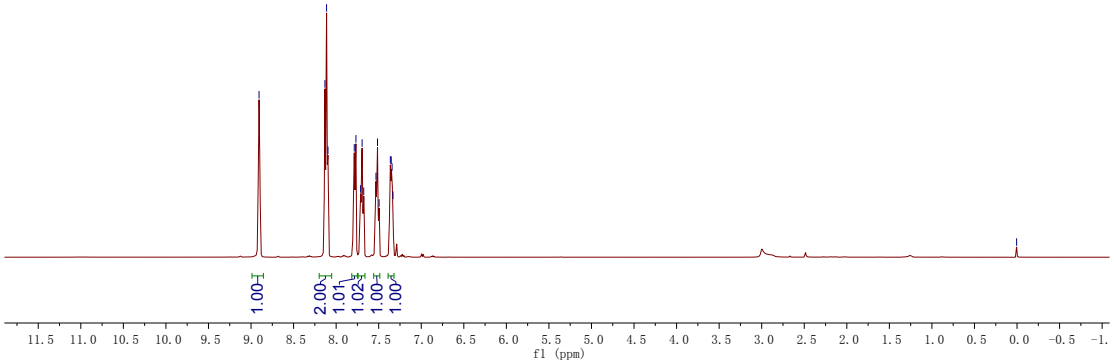

7.967
7.948
7.883
7.864
7.787
7.768
7.704
7.683
7.551
7.533
7.515
7.497
7.477
7.457
7.257
1.440
-0.000
tBu
NH
O
2f
1.00
1.00
1.90
1.06
3.08
0.58
9.13
f1 (ppm)

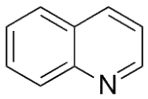

176.89
134.13
132.63
128.90
127.31
126.32
125.91
125.82
125.61
120.84
120.21
77.34
77.03
76.71
39.92
27.85
tBu
NH
O
2f
f1 (ppm)



2g

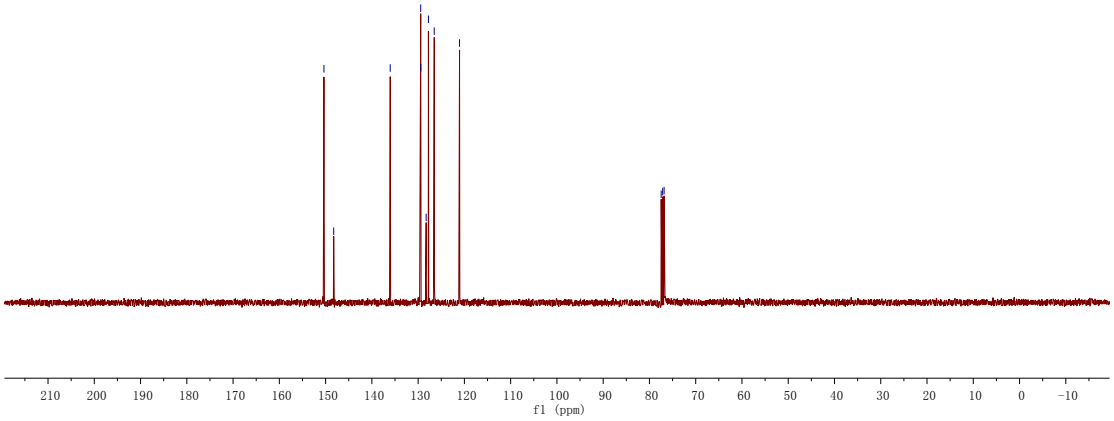

8.91
8.13
8.11
8.10
7.79
7.77
7.71
7.70
7.68
7.53
7.51
7.50
7.36
7.35
7.34
7.33
0.00

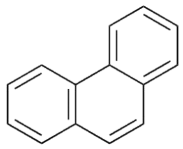

1.00
2.00
1.01
1.02
1.00
1.00
f1 (ppm)



2g


150.36
148.25
136.03
129.44
129.41
128.26
127.77
126.52
121.05
77.46
77.15
76.83

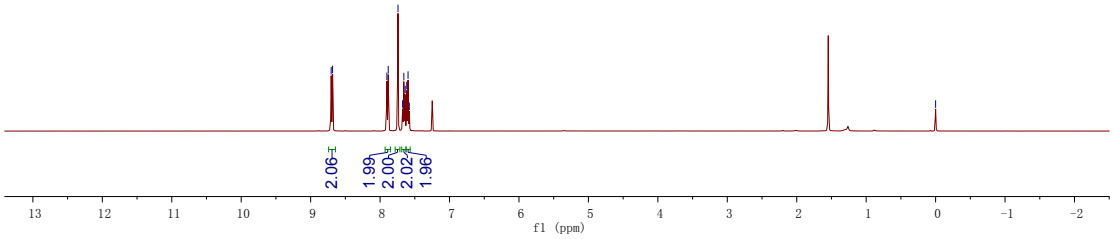

f1 (ppm)

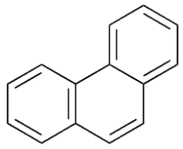


2h

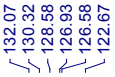

8.704
8.684
7.902
7.882
7.742
7.676
7.658
7.639
7.616
7.597
7.579

0.000

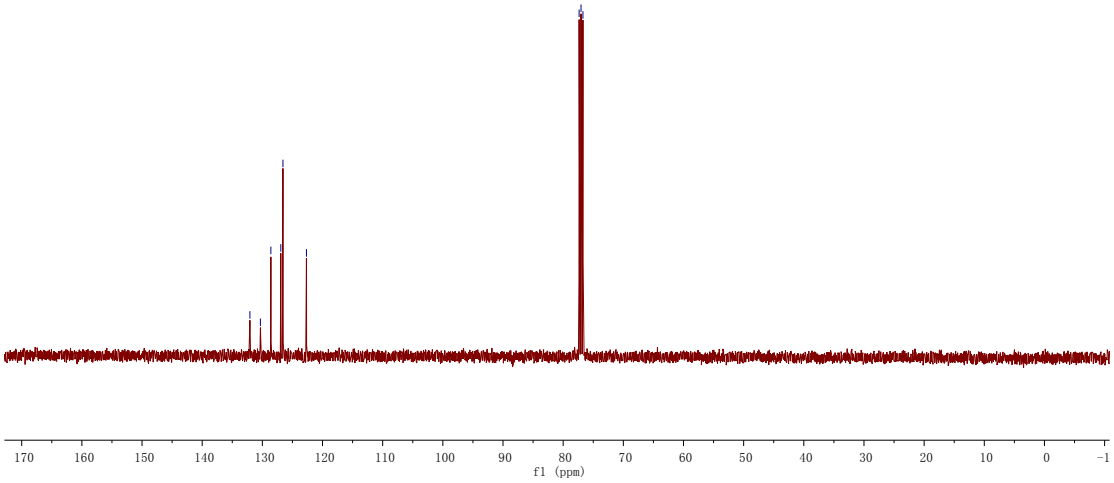

2.06
1.99
2.00
2.02
1.96
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

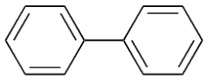


2h


132.07
130.32
128.58
126.93
126.58
122.67


77.35
77.03
76.71

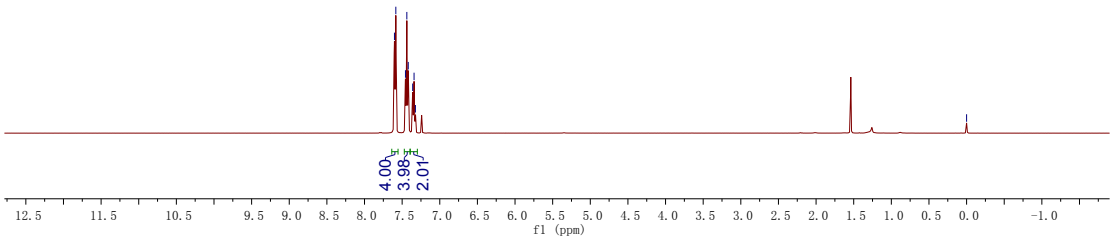

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

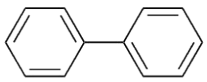


2i

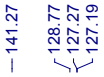

7.602
7.584
7.456
7.438
7.419
7.360
7.342
7.324


0.000

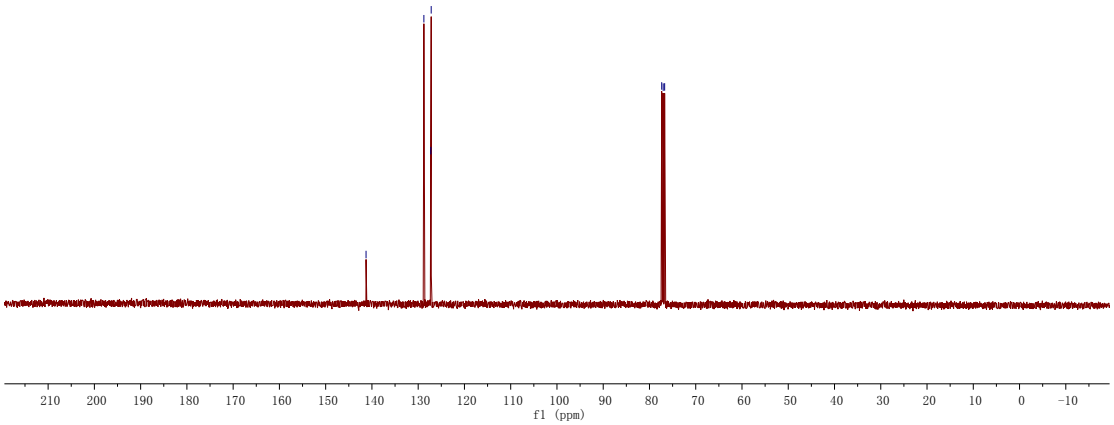

4.00
3.98
2.01
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

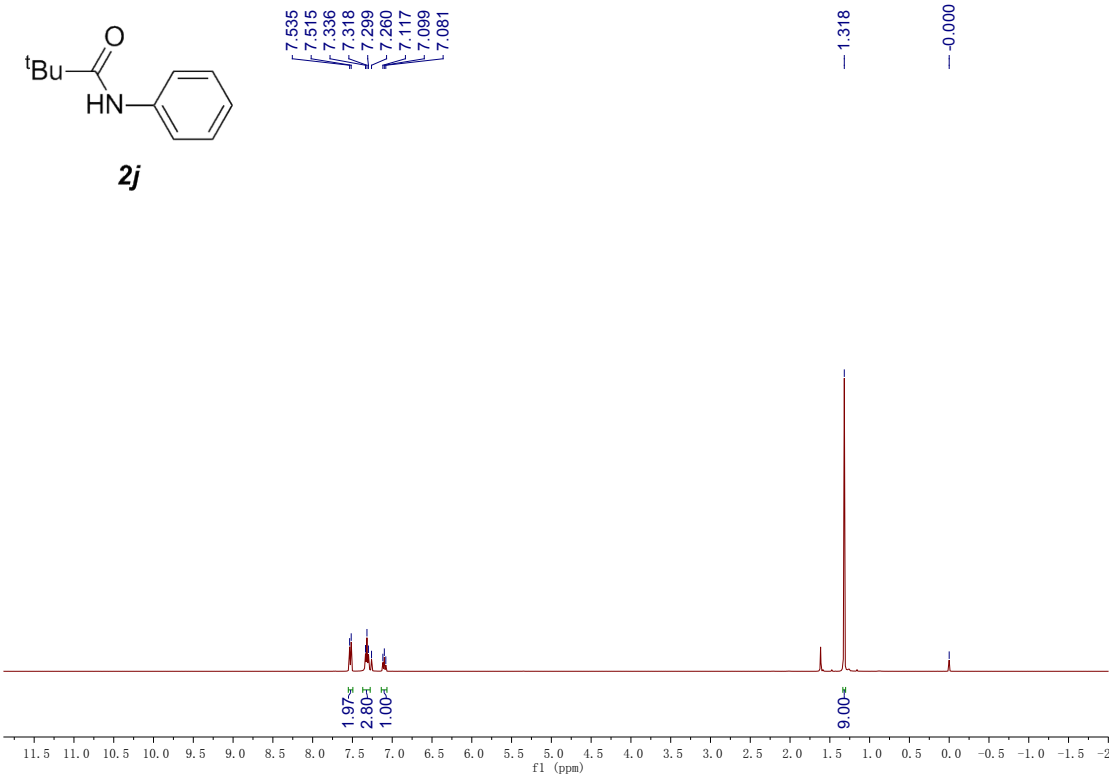


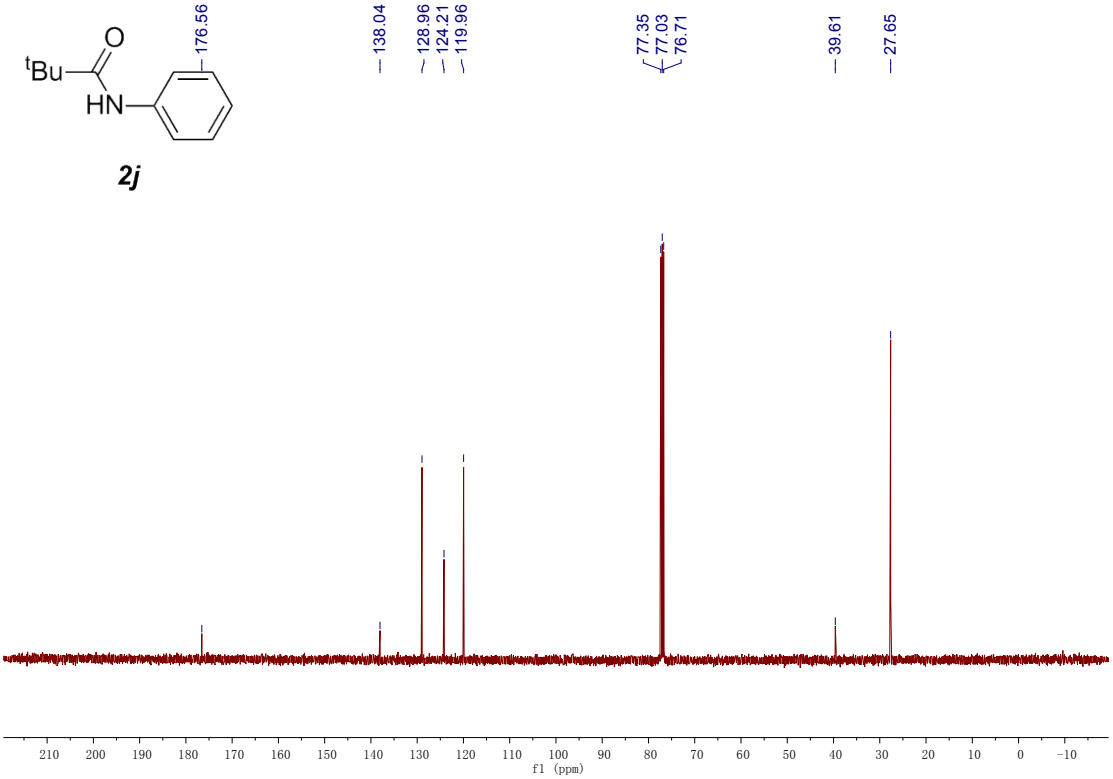
2i

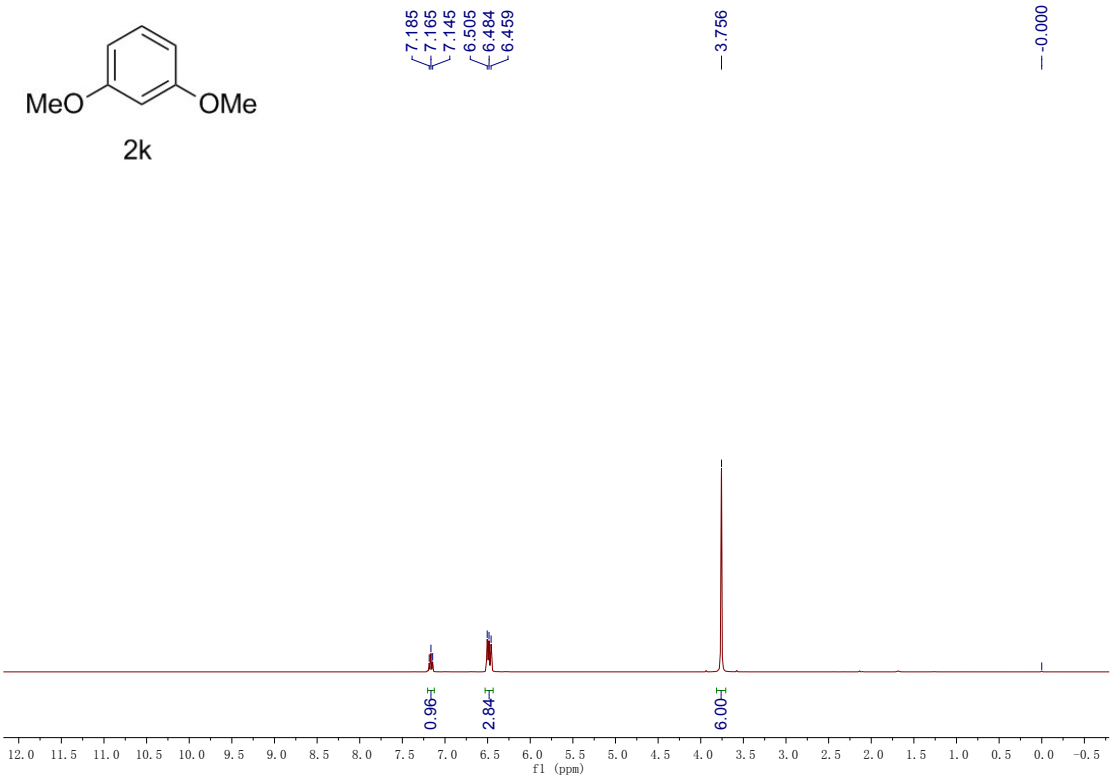

141.27
128.77
127.27
127.19

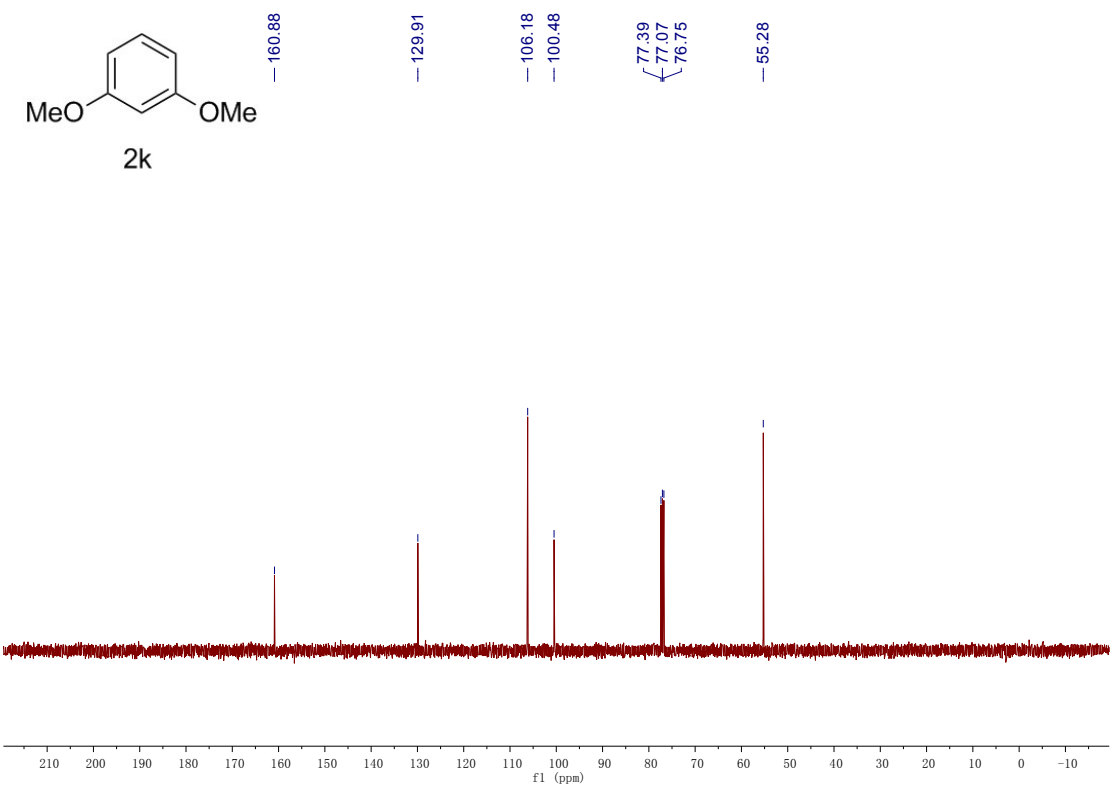

77.35
77.04
76.72

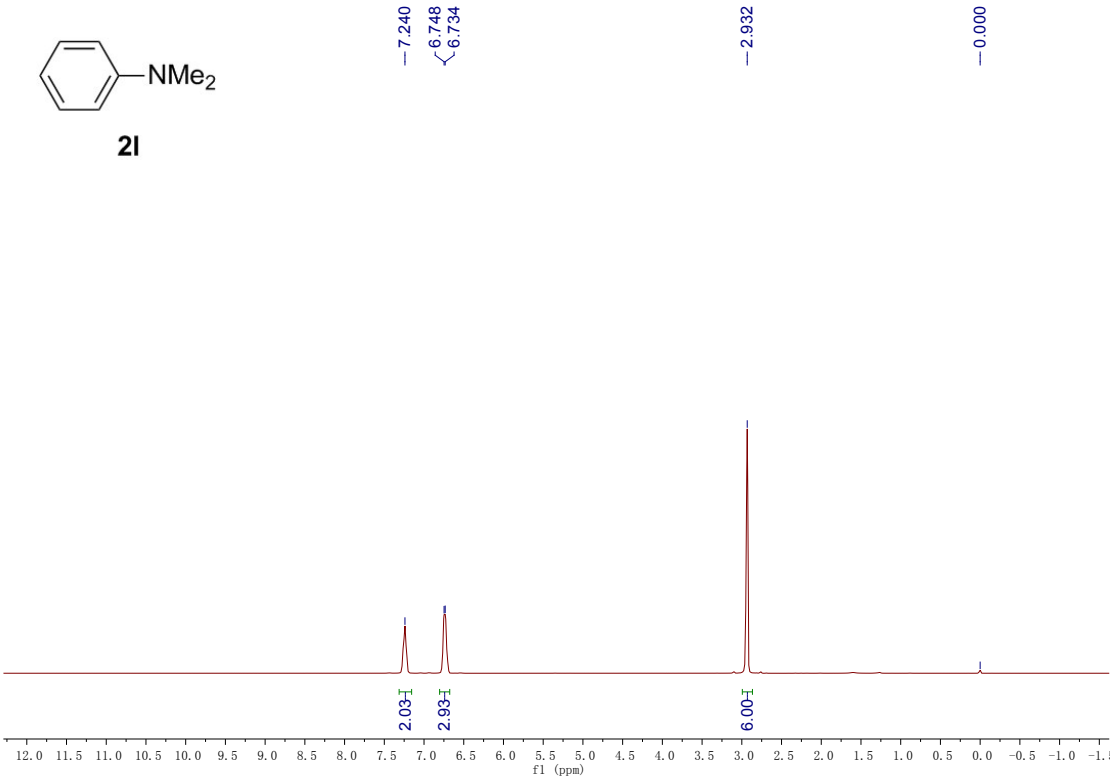

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

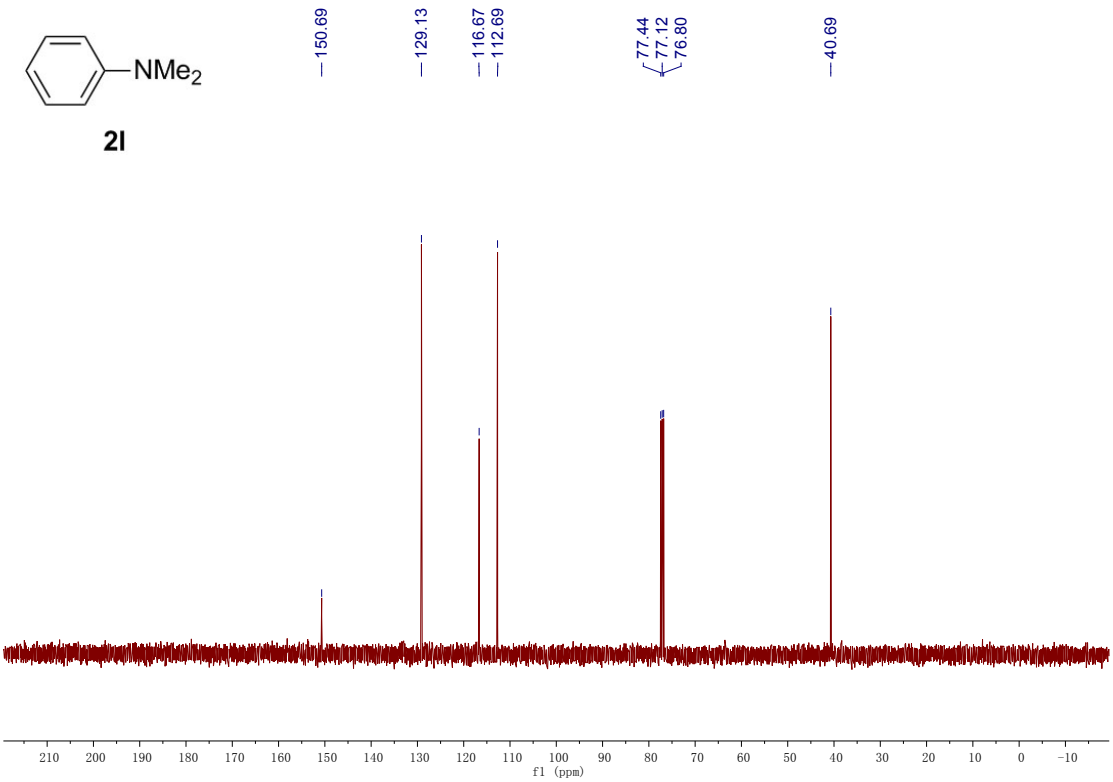

7.535
7.515
7.336
7.318
7.299
7.260
7.117
7.099
7.081
1.318
-0.000
2j
1.97
2.80
1.00
9.00
f1 (ppm)

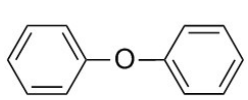

176.56
138.04
128.96
124.21
119.96
77.35
77.03
76.71
39.61
27.65
2j
f1 (ppm)


MeO
OMe
2k
7.185
7.165
7.145
6.505
6.484
6.459
3.756
0.000
0.96
2.84
6.00
f1 (ppm)

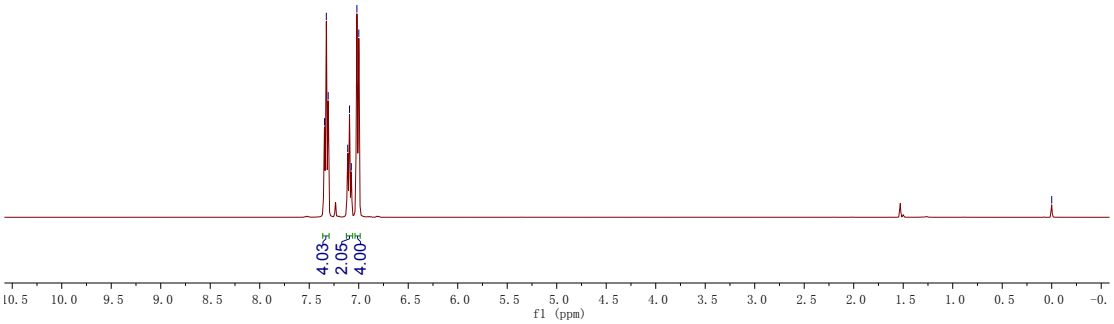

MeO
OMe
2k
160.88
129.91
106.18
100.48
77.39
77.07
76.75
55.28
f1 (ppm)

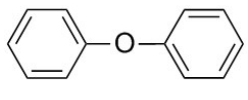

NMe2
2l
7.240
6.748
6.734
2.932
0.000
2.03
2.93
6.00
f1 (ppm)


NMe2
2l
150.69
129.13
116.67
112.69
77.44
77.12
76.80
40.69
f1 (ppm)



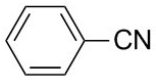
2m


7.346
7.327
7.308
7.111
7.093
7.075
7.018
6.999
0.000
4.03
2.05
4.00
f1 (ppm)

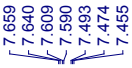


2m

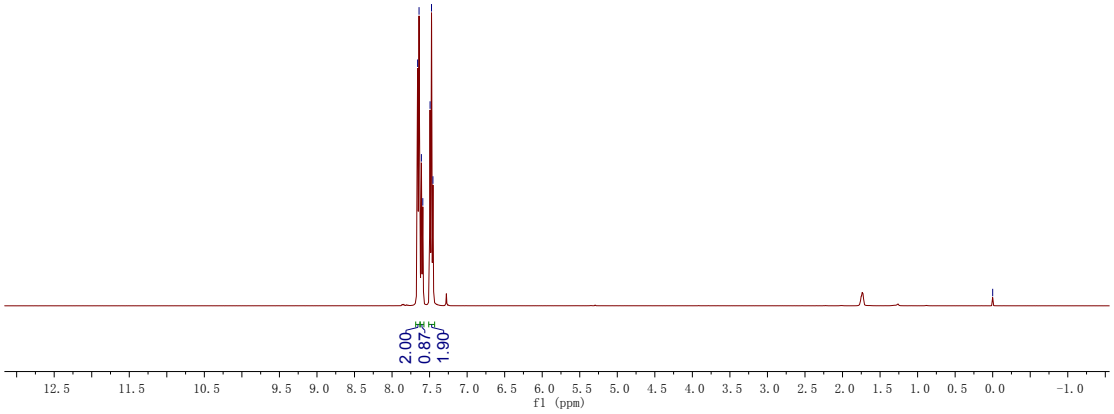
157.26
129.75
123.23
118.91
77.36
77.04
76.72
f1 (ppm)

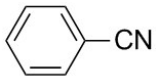

CN

2n


7.659
7.640
7.609
7.590
7.493
7.474
7.455

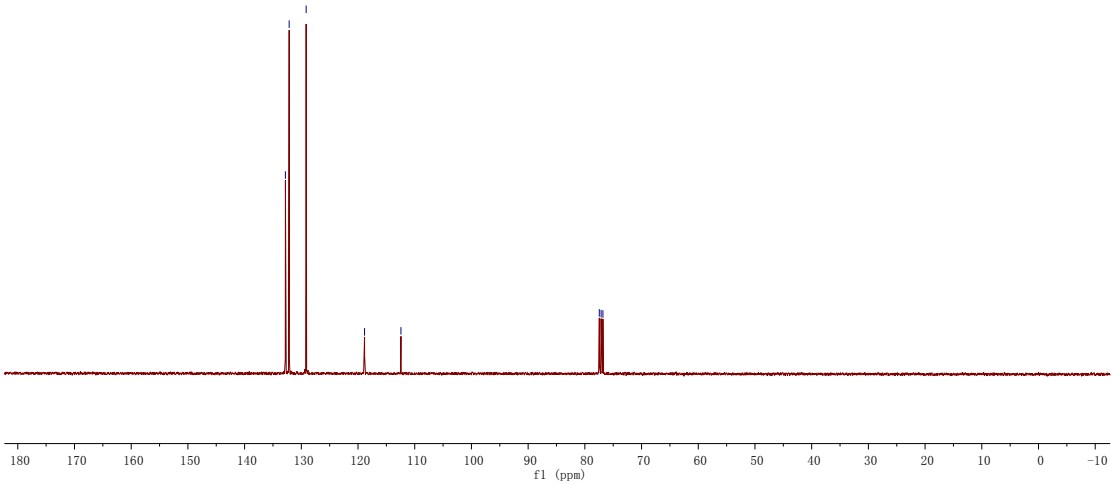

0.000

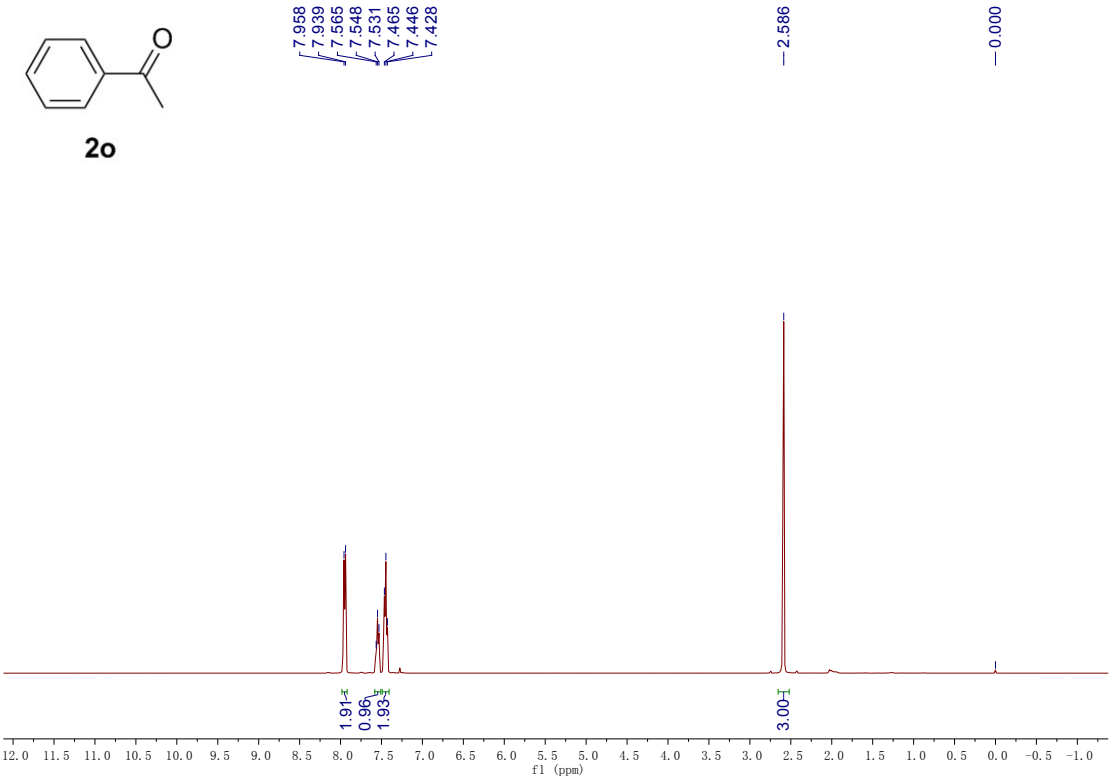

2.00
0.87
1.90
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

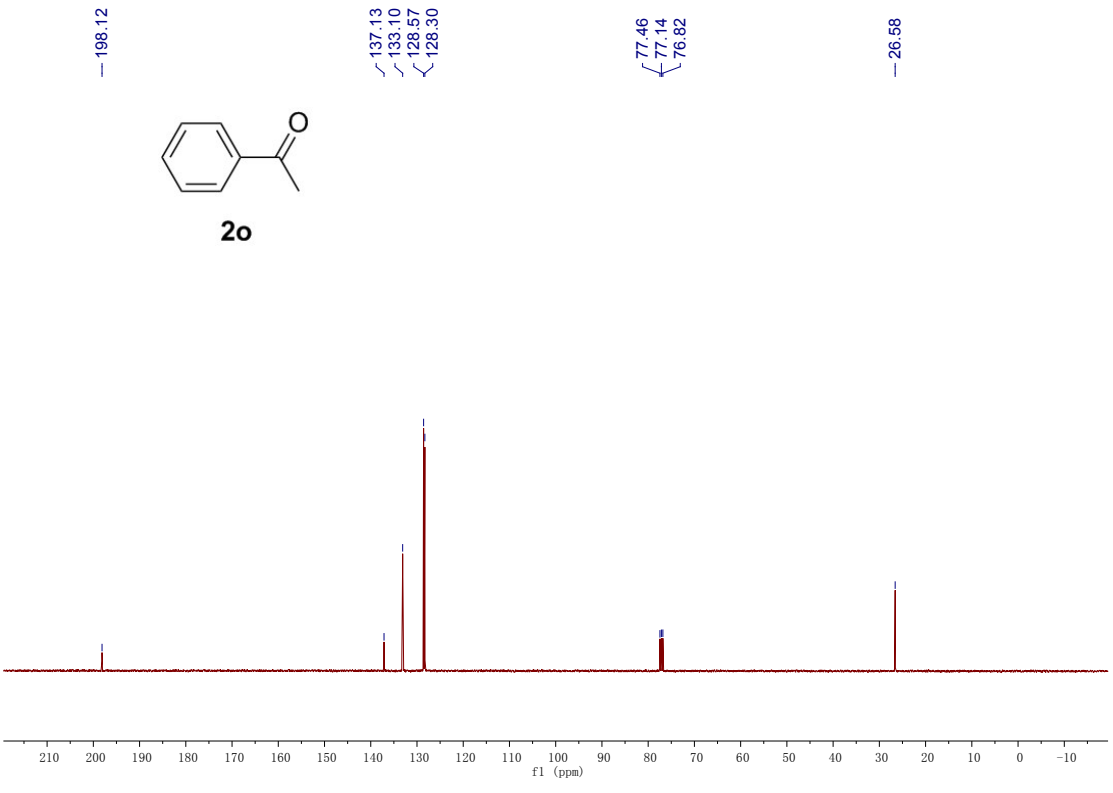

CN

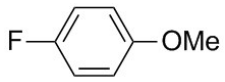
2n


132.81
132.14
129.15
118.85
112.43
77.45
77.13
76.81


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

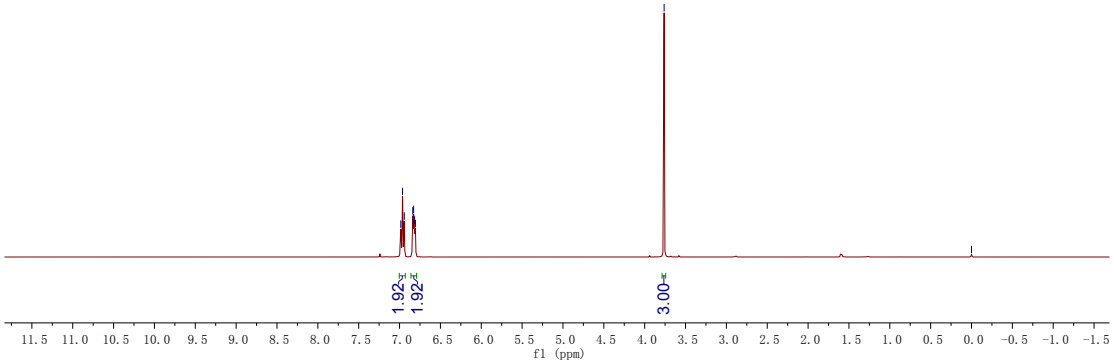

7.958
7.939
7.565
7.548
7.531
7.465
7.446
7.428
2.586
0.000
O
2o
1.91
0.96
1.93
3.00
f1 (ppm)

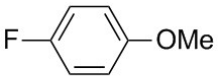

198.12
137.13
133.10
128.57
128.30
77.46
77.14
76.82
26.58
O
2o
f1 (ppm)


F
OMe

2p

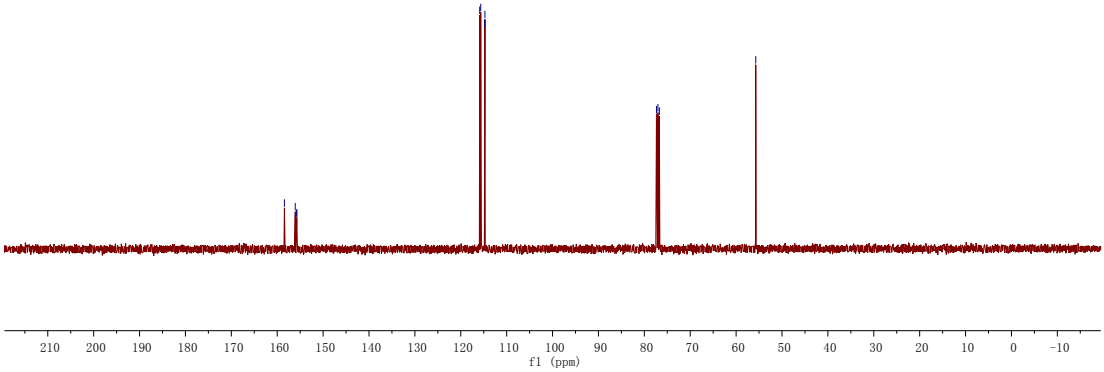

6.985
6.964
6.942
6.838
6.828
6.816
6.806
3.762
0.000

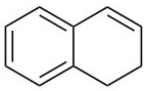

1.92
1.92
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


F
OMe

2p

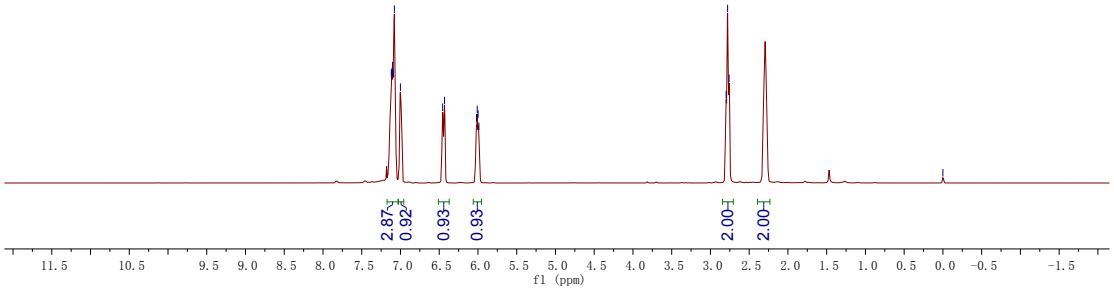

158.43
156.07
155.75
155.73
115.88
115.65
114.82
114.74
77.36
77.04
76.72
55.72

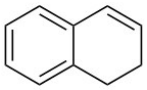

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2q

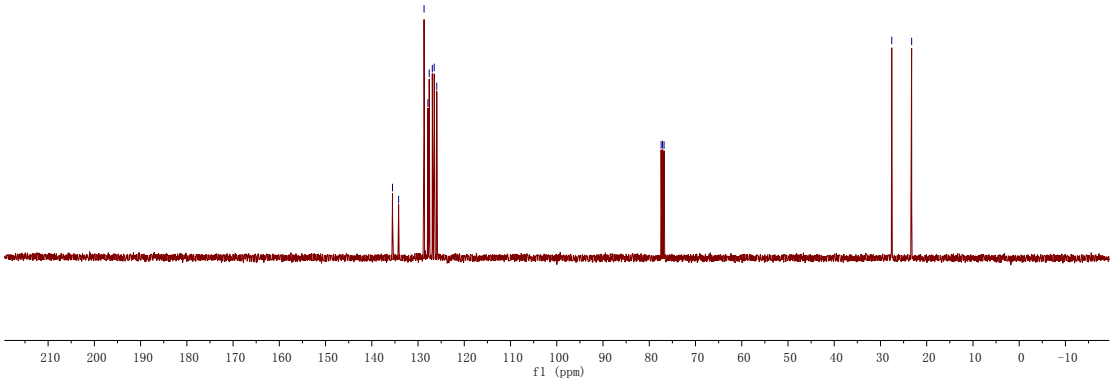

7.118
7.113
7.106
7.102
7.096
7.079
7.001
6.456
6.432
6.019
6.010
5.999
5.988
2.797
2.778
2.759
-0.000

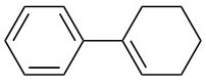

2.87
0.92
0.93
0.93
2.00
2.00
f1 (ppm)



2q


135.52
134.20
128.70
127.87
127.59
126.91
126.50
125.95
77.43
77.12
76.80
27.56
23.26

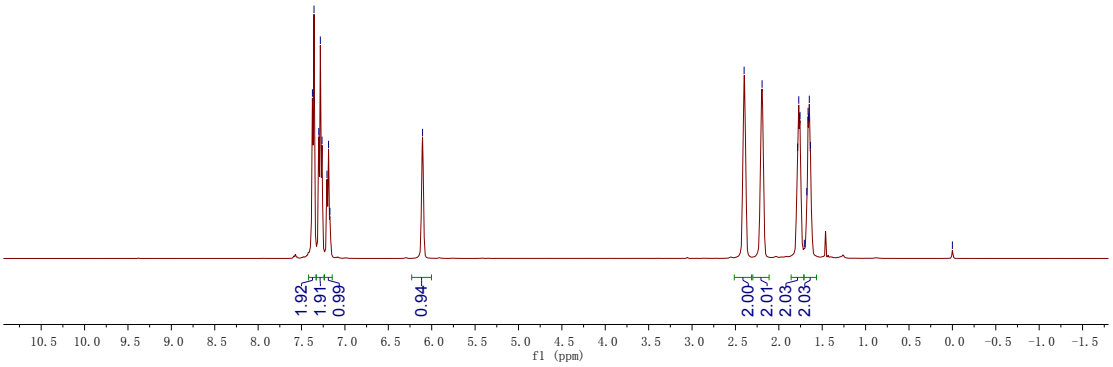

f1 (ppm)

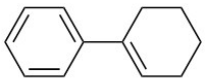


2r

7.374
7.356
7.301
7.283
7.264
7.207
7.189
7.173
6.105

2.400
2.193
1.783
1.770
1.761
1.756
1.706
1.677
1.663
1.657
1.649
1.636
-0.000



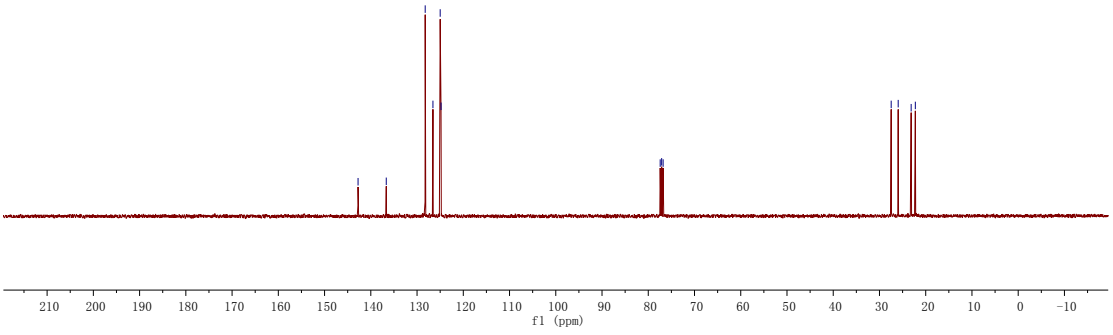


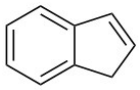
2r

142.76
136.66
128.24
126.56
125.00
124.81

77.42
77.10
76.79

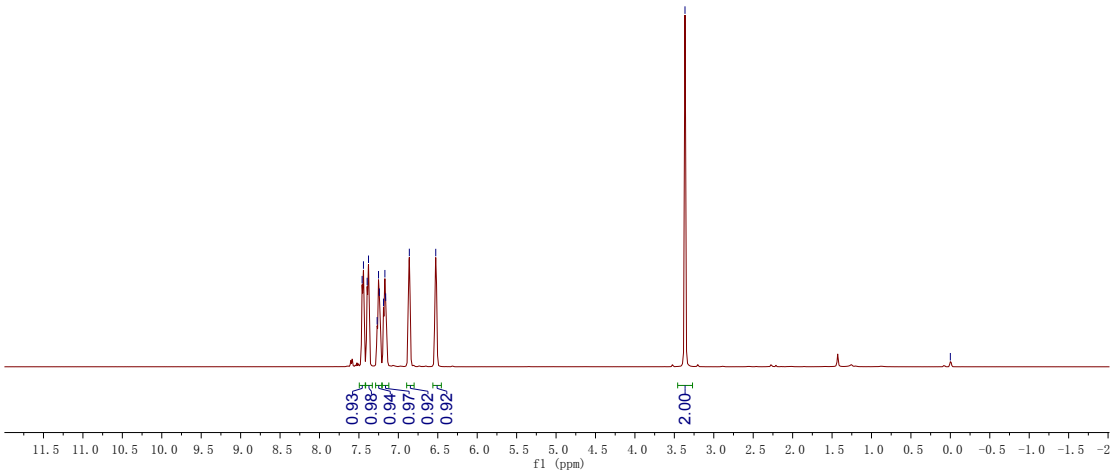
27.47
25.95
23.15
22.25

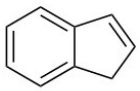




2s

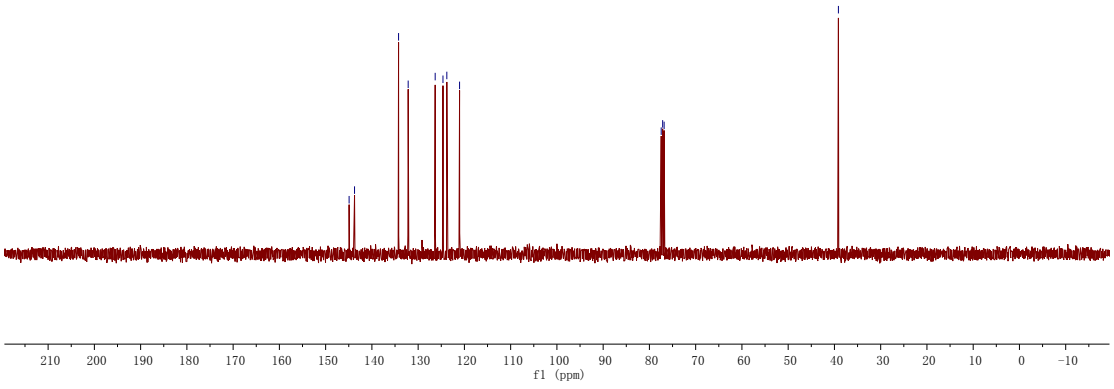

7.459
7.442
7.396
7.378
7.269
7.251
7.241
7.188
7.171
7.161
6.861
6.526
3.365
0.000

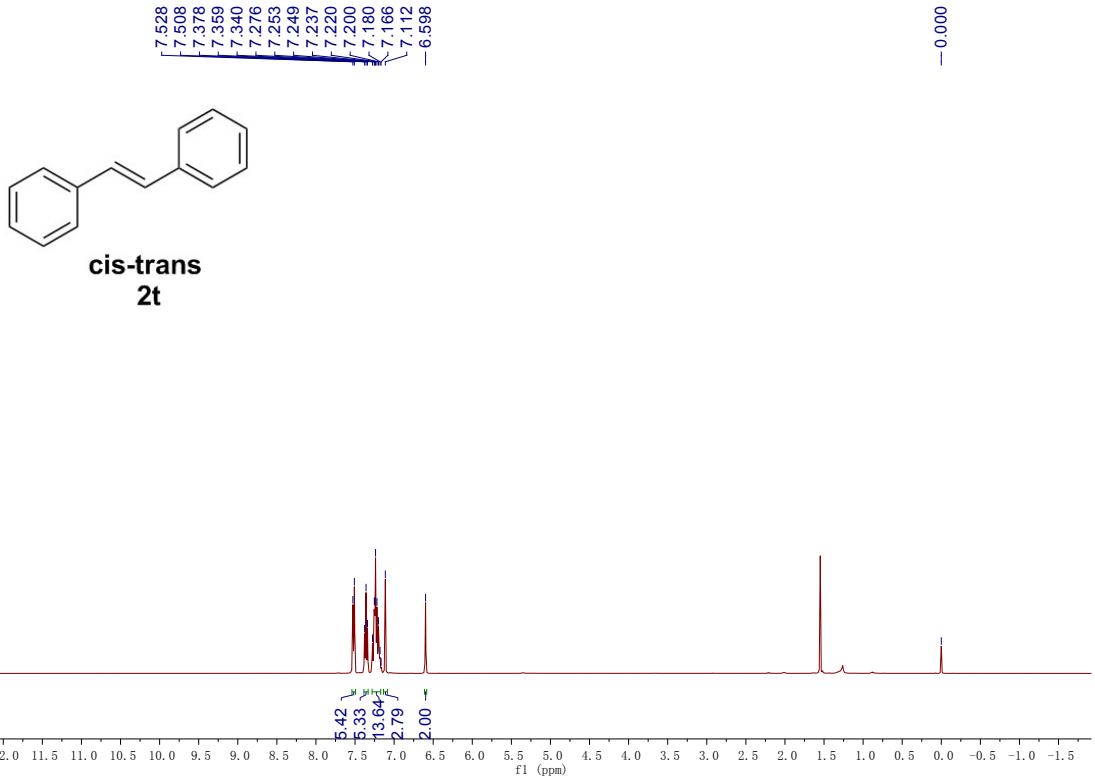

0.93
0.98
0.94
0.97
0.92
0.92
2.00
f1 (ppm)

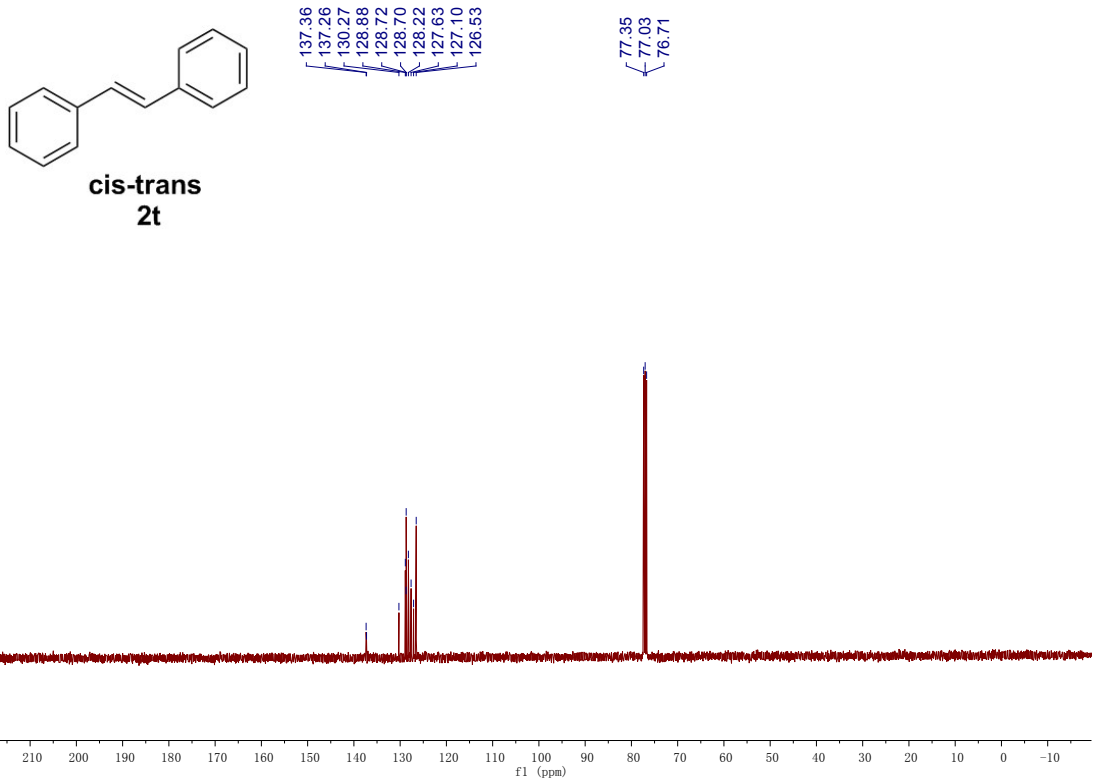


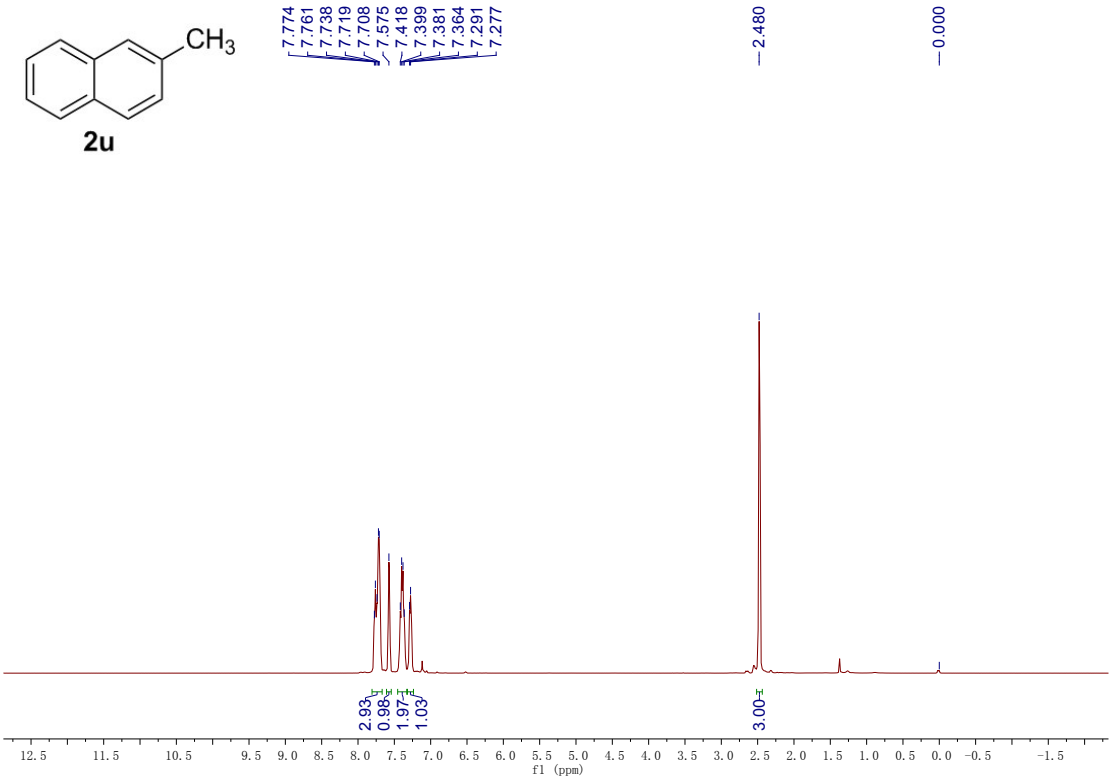
2s

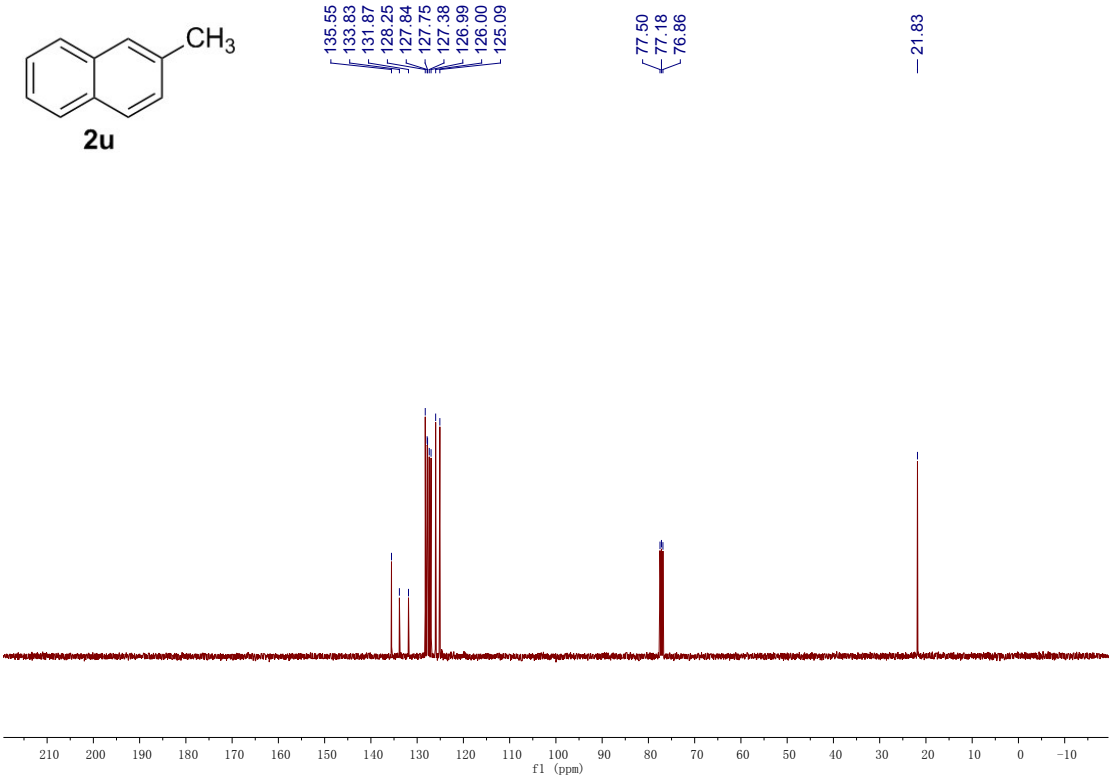

144.93
143.75
134.23
132.16
126.32
124.63
123.80
121.04
77.45
77.14
76.82
39.14

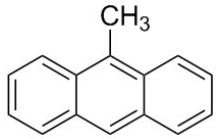

f1 (ppm)


7.528
7.508
7.378
7.359
7.340
7.276
7.253
7.249
7.237
7.220
7.200
7.180
7.166
7.112
6.598
0.000
cis-trans
2t
5.42
5.33
13.64
2.79
2.00
f1 (ppm)


137.36
137.26
130.27
128.88
128.72
128.70
128.22
127.63
127.10
126.53
77.35
77.03
76.71
cis-trans
2t
f1 (ppm)


CH3
2u
7.774
7.761
7.738
7.719
7.708
7.575
7.418
7.399
7.381
7.364
7.291
7.277
2.480
0.000
2.93
0.98
1.97
1.03
3.00
f1 (ppm)

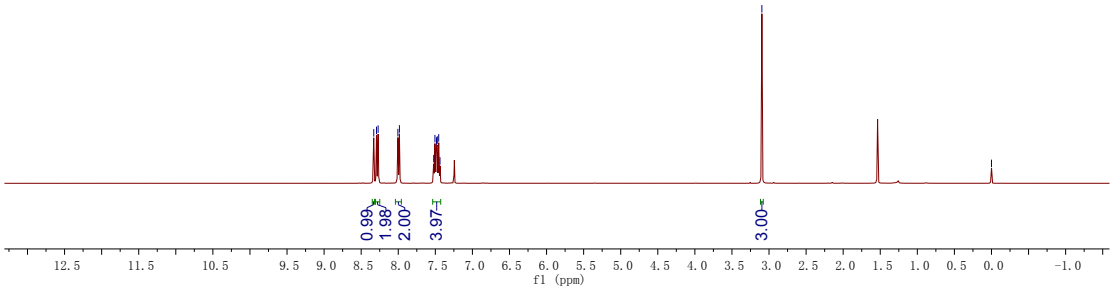

CH3
2u
135.55
133.83
131.87
128.25
127.84
127.75
127.38
126.99
126.00
125.09
77.50
77.18
76.86
21.83
f1 (ppm)

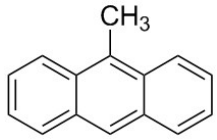

CH3

2v

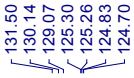

8.330
8.293
8.271
8.005
7.984
7.522
7.505
7.484
7.474
7.454
7.437


3.096
-0.000


0.99
1.98
2.00
3.97
3.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

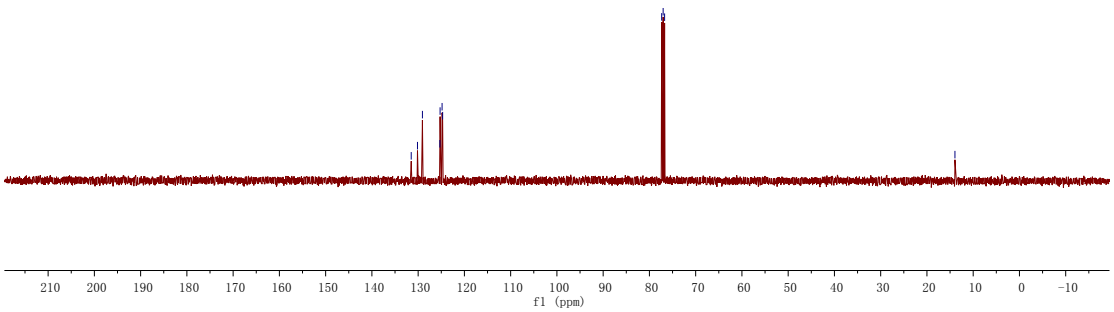

CH3

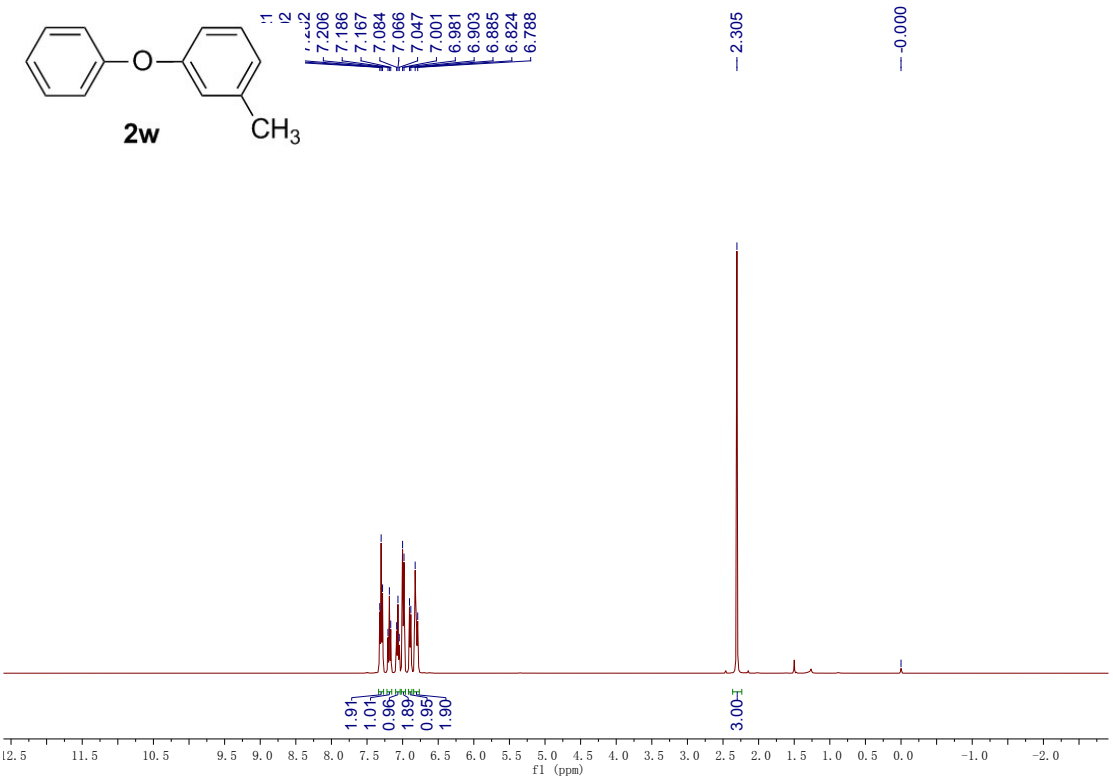
2v

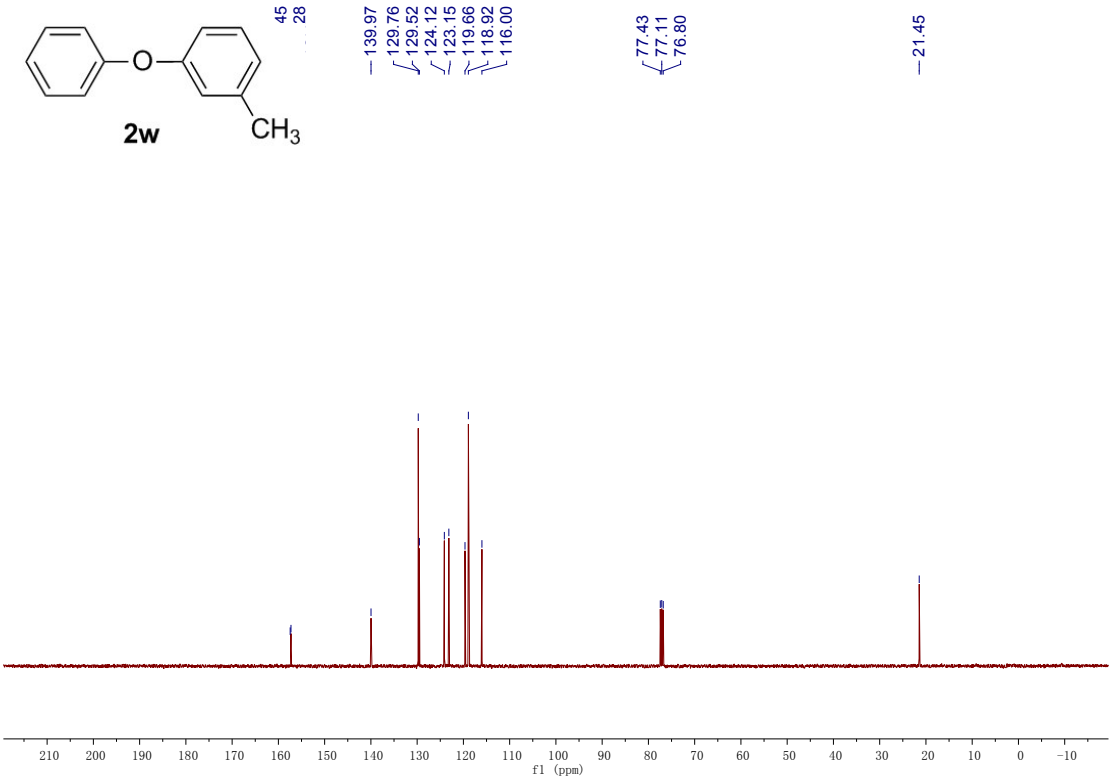

131.50
130.14
129.07
125.30
125.26
124.83
124.70

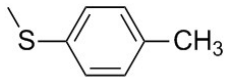

77.35
77.03
76.72


13.95


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)

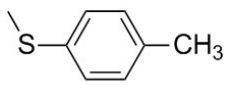

2w
CH3
7.206
7.186
7.167
7.084
7.066
7.047
7.001
6.981
6.903
6.885
6.824
6.788
2.305
0.000
1.91
1.01
0.96
1.89
0.95
1.90
3.00
f1 (ppm)


2w
CH3
139.97
129.76
129.52
124.12
123.15
119.66
118.92
116.00
77.43
77.11
76.80
21.45
f1 (ppm)


S
CH3

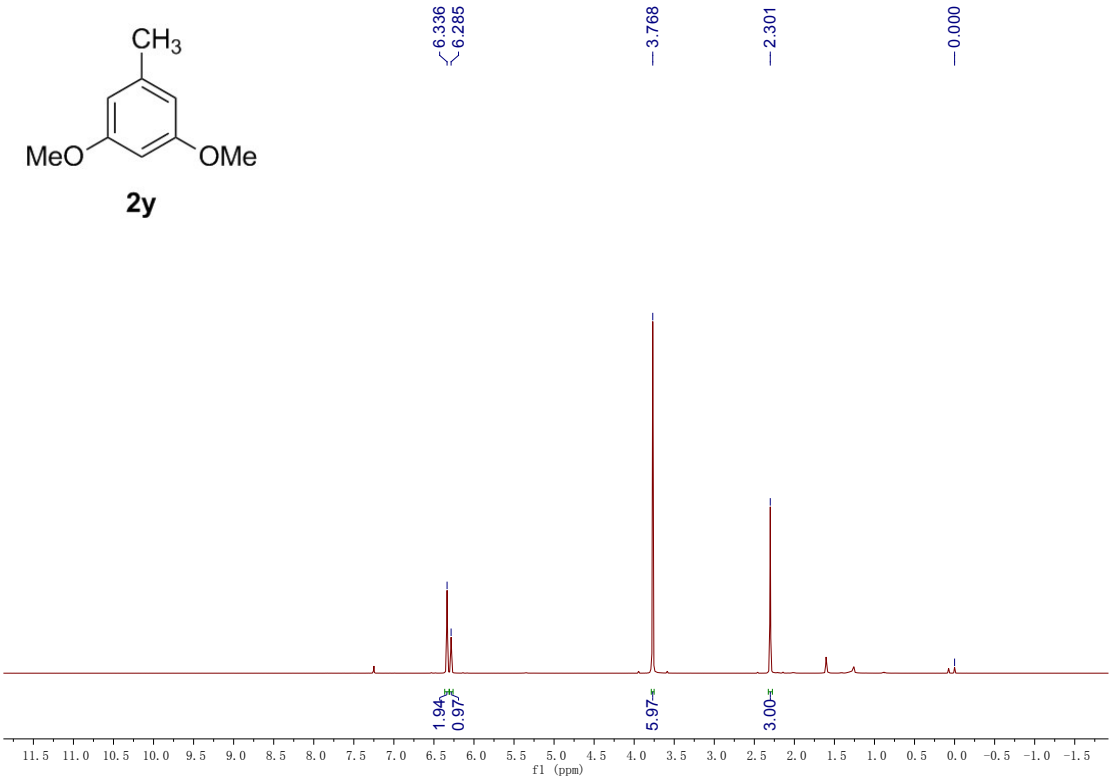
2x

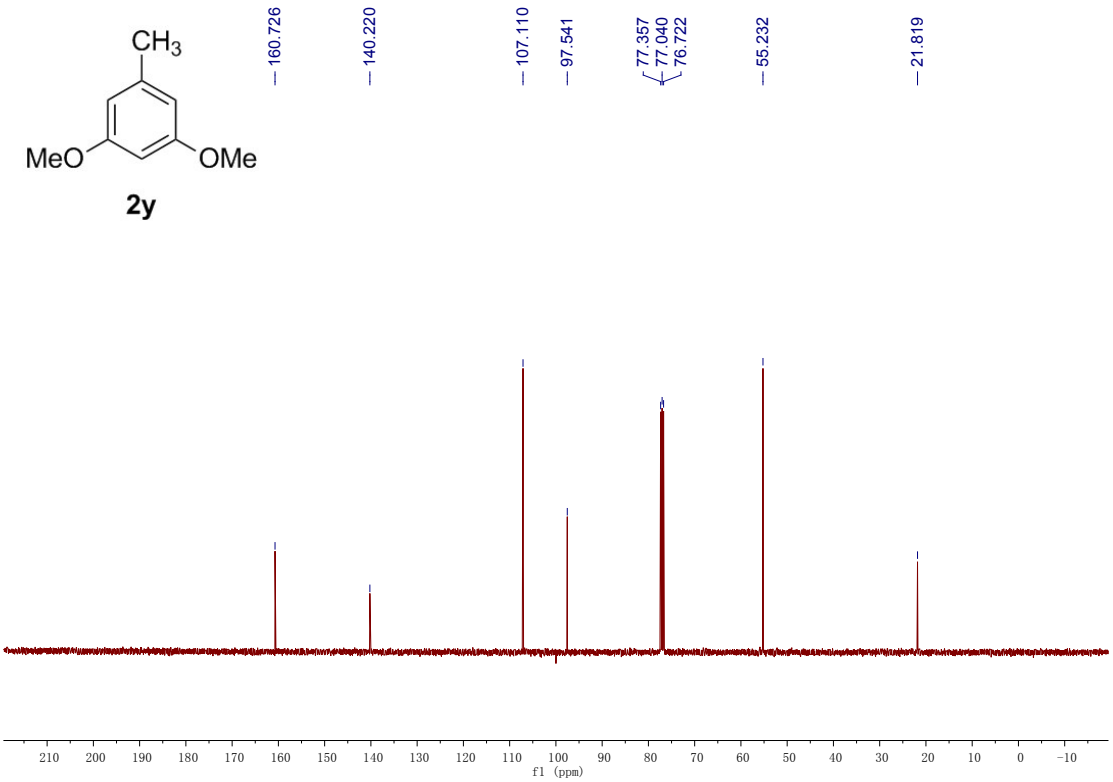
7.170
7.150
7.081
7.061
2.426
2.286
0.000
1.90
1.91
2.97
3.00
f1 (ppm)

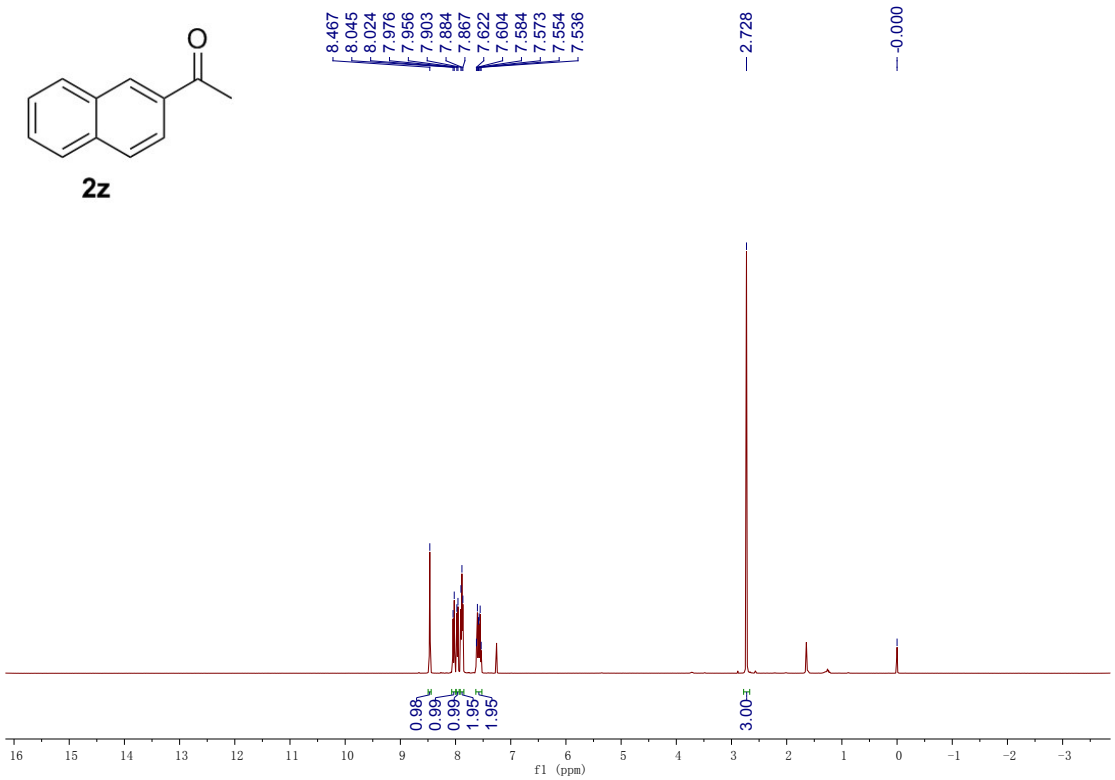

S
CH3

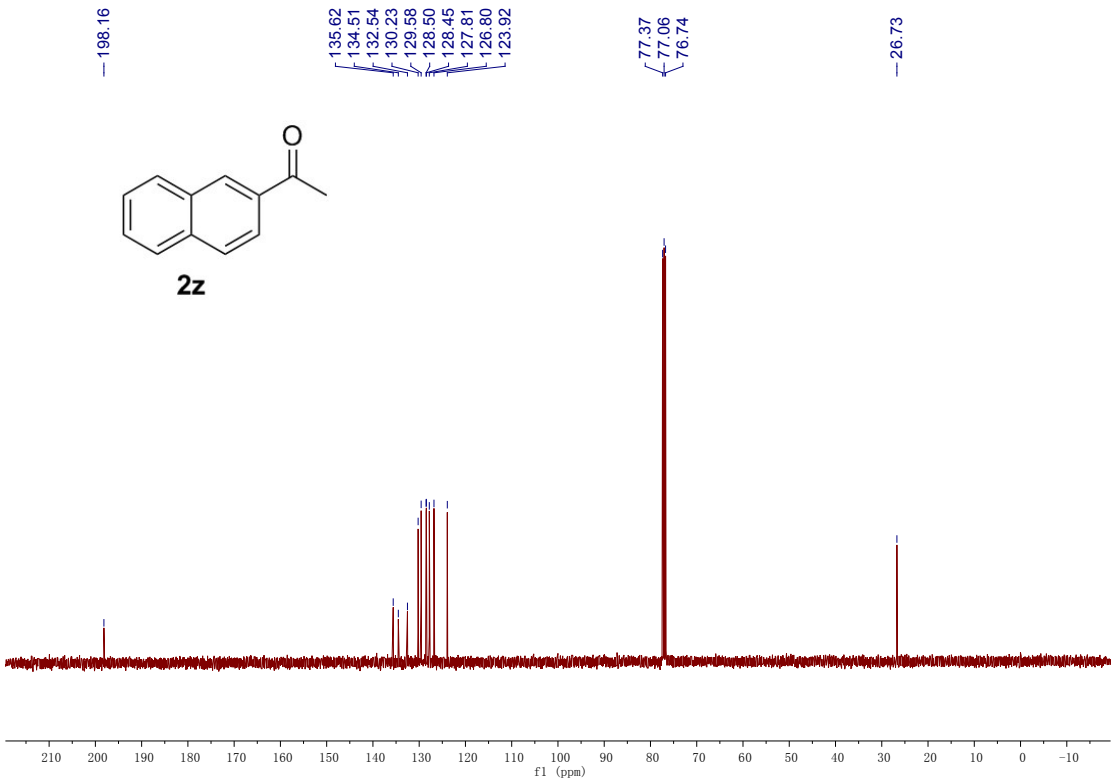
2x

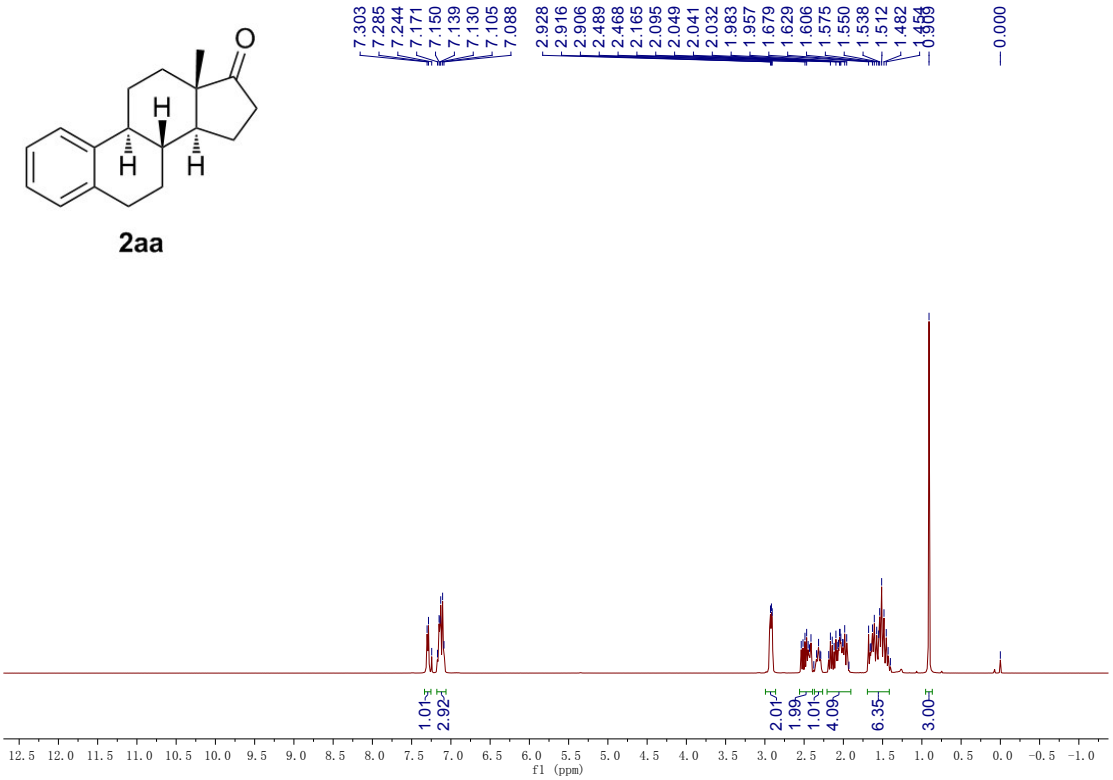
135.07
134.81
129.67
127.36
77.49
77.18
76.86
20.97
16.56
f1 (ppm)

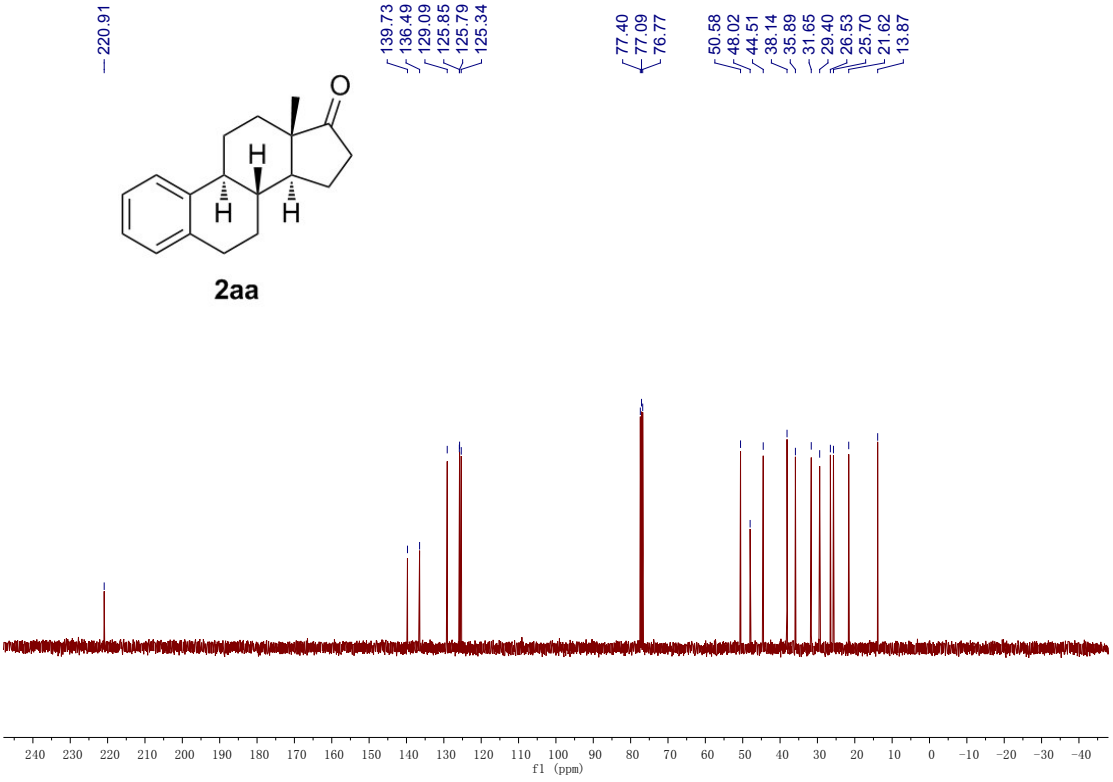

CH3
MeO
OMe
2y
6.336
6.285
3.768
2.301
0.000
1.94
0.97
5.97
3.00
f1 (ppm)

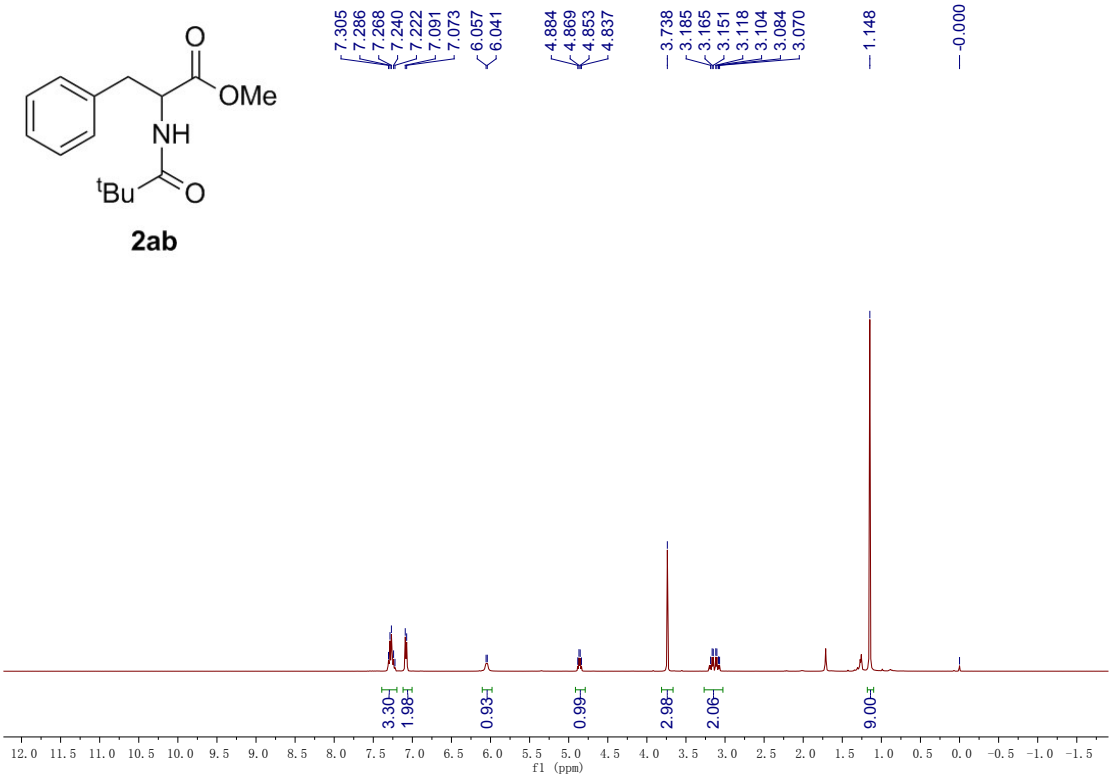

CH3
MeO
OMe
2y
160.726
140.220
107.110
97.541
77.357
77.040
76.722
55.232
21.819
f1 (ppm)

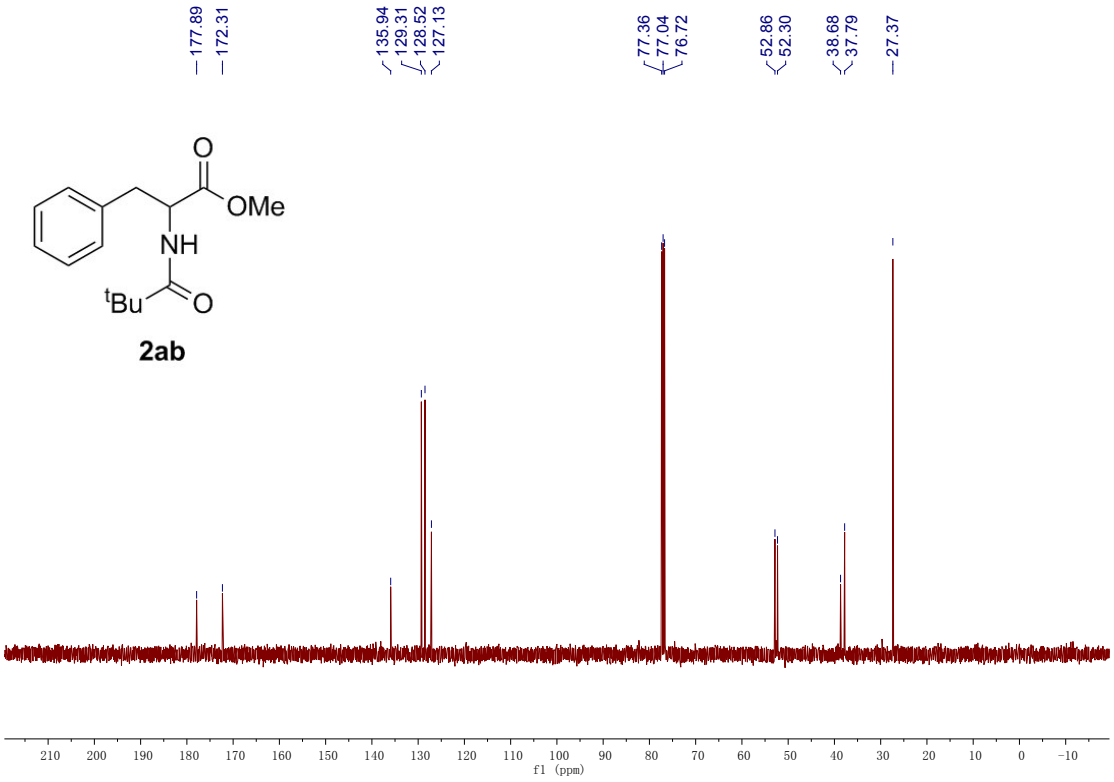

8.467
8.045
8.024
7.976
7.956
7.903
7.884
7.867
7.622
7.604
7.584
7.573
7.554
7.536
2.728
-0.000
O
2z
0.98
0.99
0.99
1.95
1.95
3.00
f1 (ppm)


198.16
135.62
134.51
132.54
130.23
129.58
128.50
128.45
127.81
126.80
123.92
77.37
77.06
76.74
26.73
O
2z
f1 (ppm)


7.303
7.285
7.244
7.171
7.150
7.139
7.130
7.105
7.088
2.928
2.916
2.906
2.489
2.468
2.165
2.095
2.049
2.041
2.032
1.983
1.957
1.679
1.629
1.606
1.575
1.550
1.538
1.512
1.482
0.909
0.000
O
H
H
H
2aa
1.01
2.92
2.01
1.99
1.01
4.09
6.35
3.00
f1 (ppm)


220.91
139.73
136.49
129.09
125.85
125.79
125.34
77.40
77.09
76.77
50.58
48.02
44.51
38.14
35.89
31.65
29.40
26.53
25.70
21.62
13.87
O
H
H
H
2aa
f1 (ppm)


7.305
7.286
7.268
7.240
7.222
7.091
7.073
6.057
6.041
4.884
4.869
4.853
4.837
3.738
3.185
3.165
3.151
3.118
3.104
3.084
3.070
1.148
-0.000
O
OMe
NH
tBu
O
2ab
3.30
1.98
0.93
0.99
2.98
2.06
9.00
f1 (ppm)


177.89
172.31
135.94
129.31
128.52
127.13
77.36
77.04
76.72
52.86
52.30
38.68
37.79
27.37
O
OMe
NH
tBu
O
2ab
f1 (ppm)