Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

An efficient indenyl-derived phosphine ligand for the Suzuki-Miyaura coupling of sterically hindered aryl halides

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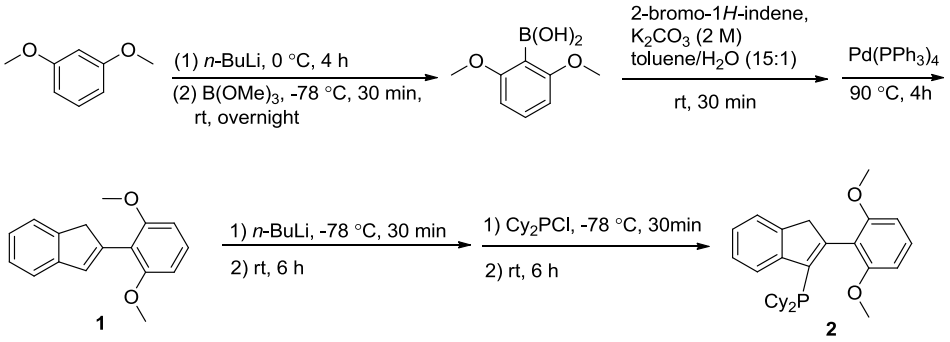
Supporting Information

1. General experimental information

1.1 General methods

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Dicyclohexyl (2-(2,6-dimethoxyphenyl)-1*H*-inden-3-yl)phosphine was prepared according to the reported procedures. Toluene was degassed by sparging with nitrogen for at least 15 min before use. All reactions were performed in a resealable screw cap Schlenk flask (approx. 10 mL volume) in the presence of a Teflon coated magnetic stirrer bar (3 mm × 50 mm). Silica gel (70–230 and 230–400 mesh) was used for column chromatography. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Mercury-Plus (400 MHz or 600 MHz) spectrometer. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. All yields reported refer to isolated yields of compounds estimated to be greater than 95% purity as determined ^{1}H NMR.

1.2 Preparation of dicyclohexyl(2-(2,6-dimethoxyphenyl)-1H-inden-3- yl)phosphine (2)



(2,6-dimethoxyphenyl)boronic acid. To an oven-dried 250 mL round bottom flask equipped with a Tefloncoated magnetic stir bar and rubber septum was added 1,3-dimethoxybenzene (3.3 mL, 30mmol) and THF (150 mL) under an argon atmosphere. The solution was cooled to 0℃ using an ice/water bath and then n-BuLi (15 mL, 2.5 M solution in hexane, 37.5 mmol) was added and stirred for 4h. Then the mixture was cooled to -78 ℃ and $B(OMe)_3$ (6 mL, 30 mmol) was added. The mixture was warmed to room temperature. And after 16 h, an aqueous solution of HCl (10%, ~30 mL) and H_2O (30 mL) was then added dropwise to the solution, stirred for additional 1 h at room temperature. The aqueous solution was extracted with Et_2O, dried over $MgSO_4$, and filtered. Removal of the solvent provided the white solid, which was dissolved in 10 mL of acetic ether. After filtration the clearfiltrate was dropped into Petroleum ether (100 mL, vigorously stirred). The white precipitate that formed wasseparated via suction filtration. Removal of the volatiles in vacuo afforded a white solid (5.04 g, 80%). ^{1}H NMR (400 MHz，d^6-DMSO): δ 7.82 (s, 2 H, Ar), 7.21 (t, *J* = 8.0 Hz, 1 H, Ar), 6.54 (d, *J* = 8.0 Hz, 2 H, Ar), 3.69 (s, 6 H, O*Me*) ppm Data is consistent with that reported in the literature.[1]

2-(2, 6-dimethoxyphenyl)-1*H*-indene (1). To an oven-dried 250 mL round bottom flask equipped with a Tefloncoated magnetic stir bar and rubber septum was added (2,6-dimethoxyphenyl)boronic acid (4.0 g, 22 mmol) and 2-bromo-1*H*-indene (3.9 g, 20 mmol). Under an argon atmosphere, K_2CO_3 (2 M, 20 mL), toluene (120 mL), and ethanol (8 mL) was added and stirred at room temperature 30 min, then a solution of $Pd(PPh_3)_4$ (680 mg, 20 mmol) in ethanol (6mL) was added. the mixture was stirred 4 h at 90 ℃. The resulting black solution was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was washed by 5% $NaHCO_3$ (aq)

(10 mL), saturated $NaHCO_3$(aq) (10 mL)，H_2O (20 mL), NaCl saturated solution (20 mL), and then the organic layer was dried over Na_2SO_4, after evaporation of the organic solvent the residue was adsorbed on silica gel and the crude product was purified by column chromatography using DCM/pentane to give a white solid (4.7 g, 93%). ^{1}H NMR (400 MHz，$CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1 H, Ar), 7.40 (d, *J* = 8.0 Hz, 1 H, Ar), 7.27-7.20 (m, 2 H, Ar), 7.16 (t, *J* = 8.0 Hz, 1 H, Ar), 7.02 (s, 1 H, Ar), 6.63 (d, *J* = 8.0 Hz, 2 H, Ar), 3.85 (s, 2 H, CH_2), 3.80 (s, 6 H, O*Me*) ppm; ^{13}C NMR (100 MHz，$CDCl_3$): δ 157.78, 145.09, 143.76, 139.82, 131.95, 128.14, 125.75, 123.83, 122.98, 120.46, 115.14, 103.96, 55.68, 42.25 ppm. HRMS (ESI/ $[M+H]^+$) Cacld. For $C_{17}H_{17}O_2$: 253.1229, found: 253.1227.

Dicyclohexyl(2-(2,6-dimethoxyphenyl)-1H-inden-3-yl)phosphine. (2) In a 100 mL flask 2-(2,6-dimethoxyphenyl)-1H-indene (2.52 g, 10 mmol) was dissolved in THF (60 mL) under an argon atmosphere. The mixture was cooled to -78 ℃, and *n*BuLi (5 mL, 2.5 M solution in hexane, 12.0 mmol) was added. The solution was stirred for 30 min at -78 ℃ and then for 12 h at ambient temperature. Then the mixture was cooled to -78 ℃ and Cy_2PCl (2,2 mL, 10 mmol) was added. The mixture was warmed to room temperature and stirred for additional 12 h .The resulting filtrate was treated dropwise with water. The organic layer was then separated from the aqueous layer, dried over $MgSO_4$, and filtered. after evaporation of the organic solvent the residue was adsorbed on silica gel and the crude product was purified by column chromatography using DCM/pentane to give a white solid (1.9 g, 47%). ^{1}H NMR (400 MHz，$CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.25-7.12 (m, 3 H), 6.55 (d, *J* = 8.0 Hz, 2 H), 3.63 (s, 6 H), 3.61 (s, 2 H), 2.25 (s, 2 H), 1.80-1.60 (m, 10 H), 1.28-1.03 (m, 10 H) ppm. ^{13}C NMR (100 MHz，$CDCl_3$): δ 157.38, 155.28, 154.96, 147.47, 147.42, 144.27, 136.34, 136.13, 128.86, 125.73, 123.69, 123.48, 121.82, 116.03, 103.15, 55.10, 43.35, 43.29, 33.53, 33.43, 33.26, 32.05, 30.22, 30.13, 27.27, 27.23, 27.10, 26.42 ppm. ^{31}P NMR(162 MHz, $CDCl_3$): δ -15.32(s) ppm. HRMS (ESI/ $[M+H]^+$) Cacld. For $C_{29}H_{37}O_2P$: 446.2609, found: 446.2609.

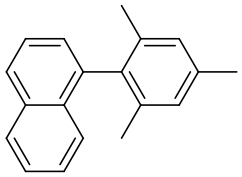
1.3 General Procedures for Reaction Condition Screenings.

2-bromomesityl (1.0 mmol), naphthenylboronic acid (1.5 mmol), potassium phosphate (3.0 mmol), $Pd(OAc)_2$ and phosphine ligand (as indicated in Table 1) was loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. The mixture was pumped and refilled with nitrogen three times, degassed toluene (1.5 mL) was added. The resulting mixture was stirred at 110 ℃ under nitrogen for 3 h, and then cooled to room temperature, partioned with water (10 mL) and dichloromethane (10 mL), the organic layer was separated, dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to provide biaryl compounds.

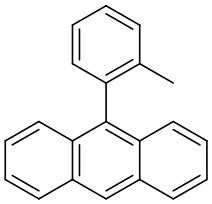
1.4 General procedure for Suzuki–Miyaura cross-coupling reaction.

A disposable tube with a screw cap, Teflon septum and stir bar was charged with $Pd(OAc)_2$ (as indicated in Tables 2-4), ligand **2** (as indicated in Tables 2-4), aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), potassium phosphate (3.0 mmol) and toluene (1.5 mL). The tube was evacuated and flushed with nitrogen three times, and then placed in a preheated oil bath (110 ℃) for the time period as indicated in Tables 2-4. After completion of the reaction, the reaction tube was allowed to cool to room temperature, partioned with water (10 mL) and dichloromethane (10 mL). The organic layer was separated, dried over sodium sulfate, concentrated, and purified by silica gel column chromatography to provide biaryl compounds.

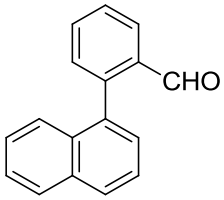
2. ^{1}H NMR and ^{13} C NMR spectrum for all isolated products



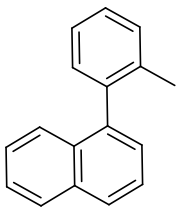
1-mesitylnaphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 1 H, Ar), 7.85 (d, *J* = 8.0 Hz, 1 H, Ar), 7.54 (t, *J* = 8.0 Hz, 1 H, Ar), 7.50 – 7.45 (m, 1 H, Ar), 7.35 (d, *J* = 8.0 Hz, 2 H, Ar), 7.27 (s, 1 H, Ar), 7.01 (s, 2 H, Ar), 2.40 (s, 3 H, *Me*), 1.88 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[2]



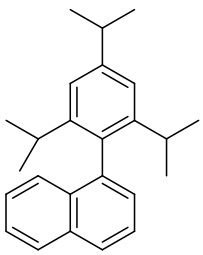
9-(o-tolyl)anthracene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1 H, Ar), 8.06 (d, *J* = 8.0 Hz, 2 H, Ar), 7.51 – 7.44 (m, 6 H, Ar), 7.38 – 7.32 (m, 4 H, Ar), 1.87 (s, 3 H, *Me*) ppm. Data is consistent with that reported in the literature.[3]



2-(naphthalen-1-yl)benzaldehyde. White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1 H, C*H*O), 8.12 (d, *J* = 8.0 Hz, 1 H, Ar), 7.95 (d, *J* = 4.0 Hz, 2 H, Ar), 7.71 (t, *J* = 8.0 Hz, 1 H, Ar), 7.61 – 7.41 (m, 7 H, Ar) ppm. Data is consistent with that reported in the literature.[4]

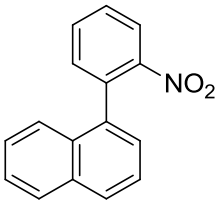


1-(o-tolyl)naphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.85 (m, 2 H, Ar), 7.52 – 7.44 (m, 3 H, Ar), 7.39 – 7.28 (m, 6 H, Ar), 2.02 (s, 3 H, *Me*) ppm. Data is consistent with that reported in the literature.[3]

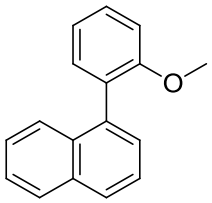


1-(2,4,6-triisopropylphenyl)naphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 4

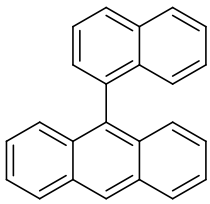
H, Ar), 7.49 (d, *J* = 8.0 Hz, 4 H, Ar), 7.13 (s, 1 H, Ar), 3.49 (t, *J* = 6.0 Hz, 1 H, C*H*Me$_2$), 3.01 (t, *J* = 6.0 Hz, 1 H, C*H*Me$_2$), 2.34 (t, *J* = 6.0 Hz, 1 H, C*H*Me$_2$), 1.37 – 1.25 (m, 10 H, CH*Me*$_2$), 1.05 – 0.95 (m, 8 H, CH*Me*$_2$) ppm. Data is consistent with that reported in the literature.[5]



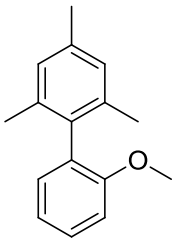
1-(2-nitrophenyl)naphthalene. Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1 H, Ar), 7.91 (d, *J* = 8.0 Hz, 2 H, Ar), 7.71 (t, *J* = 6.0 Hz, 1 H, Ar), 7.61 (t, *J* = 8.0 Hz, 1 H, Ar), 7.54 – 7.48 (m, 3 H, Ar), 7.46 – 7.39 (m, 2 H, Ar), 7.35 (d, *J* = 8.0 Hz, 1 H, Ar) ppm. Data is consistent with that reported in the literature.[6]



1-(2-methoxyphenyl)naphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (t, *J* = 8.0 Hz, 2 H, Ar), 7.59 (d, *J* = 8.0 Hz, 1 H, Ar), 7.54 (t, *J* = 6.0 Hz, 1 H, Ar), 7.48 – 7.36 (m, 4 H, Ar), 7.30 (d, *J* = 4.0 Hz, 1 H, Ar), 7.11 – 7.05 (m, 2 H, Ar), 3.70 (s, 3 H, O*Me*) ppm. Data is consistent with that reported in the literature.[7]

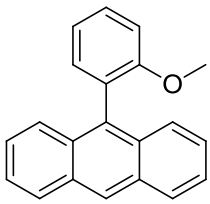


9-(naphthalen-1-yl)anthracene. White solide. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1 H, Ar), 8.11 – 8.05 (m, 3 H, Ar), 8.01 (d, *J* = 12 Hz, 1 H, Ar), 7.69 (t, *J* = 8.0 Hz, 1 H, Ar), 7.53 (d, *J* = 8.0 Hz, 1 H, Ar), 7.49 – 7.43 (m, 3 H, Ar), 7.40 (d, *J* = 8.0 Hz, 2 H, Ar), 7.25 – 7.17 (m, 3 H, Ar), 7.07 (d, *J* = 8.0 Hz, 1 H, Ar) ppm. Data is consistent with that reported in the literature.[3]

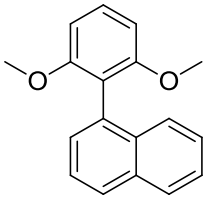


2'-methoxy-2,4,6-trimethyl-1,1'-biphenyl. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 1 H, Ar), 7.02 (t, *J* = 4.0 Hz, 1 H, Ar), 6.98 (t, *J* = 8.0 Hz, 2 H, Ar), 6.94 (s, 2 H, Ar), 3.74

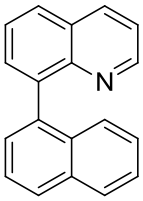
(s, 3 H, O*Me*), 2.32 (s, 3 H, *Me*), 1.98 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[8]



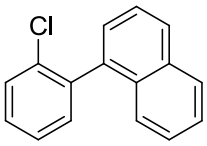
9-(2-methoxyphenyl)anthracene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1 H, Ar), 8.04 (d, *J* = 8.0 Hz, 2 H, Ar), 7.60 (d, *J* = 8.0 Hz, 2 H, Ar), 7.53 (t, *J* = 8.0 Hz, 1 H, Ar), 7.44 (t, *J* = 8.0 Hz, 2 H, Ar), 7.33 (t, *J* = 8.0 Hz, 2 H, Ar), 7.27 (s, 1 H, Ar), 7.16 (t, *J* = 8.0 Hz, 2 H, Ar), 3.61 (s, 3 H, O*Me*) ppm. Data is consistent with that reported in the literature.[3]



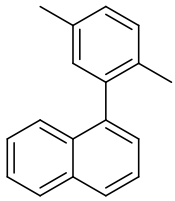
1-(2,6-dimethoxyphenyl)naphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (t, *J* = 8 Hz, 2 H, Ar), 7.54 (t, *J* = 8 Hz, 1 H, Ar), 7.48 – 7.32 (m, 5 H, Ar), 6.73 (d, *J* = 8 Hz, 2 H, Ar), 3.64 (s, 6 H, O*Me*) ppm. Data is consistent with that reported in the literature.[9]



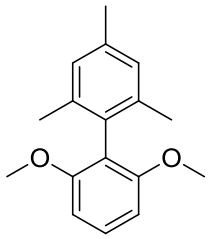
8-(naphthalen-1-yl)quinoline. Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1 H, Ar), 8.25 (d, *J* = 4 Hz, 1 H, Ar), 7.92 (t, *J* = 8 Hz, 1 H, Ar), 7.54 (d, *J* = 4 Hz, 1 H, Ar), 7.66 (t, *J* = 8 Hz, 1 H, Ar), 7.60 (t, *J* = 8 Hz, 1 H, Ar), 7.53 (d, *J* = 4 Hz, 1 H, Ar), 7.46 – 7.35 (m, 3 H, Ar), 7.28 (d, *J* = 4 Hz, 1 H, Ar) ppm. Data is consistent with that reported in the literature.[10]



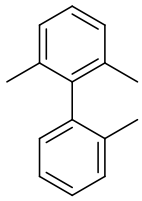
1-(2-chlorophenyl)naphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 4 Hz, 2 H, Ar), 7.55 (t, *J* = 8 Hz, 3 H, Ar), 7.48 (d, *J* = 4 Hz, 2 H, Ar), 7.43 – 7.39 (m, 4 H, Ar) ppm. Data is consistent with that reported in the literature.[11]



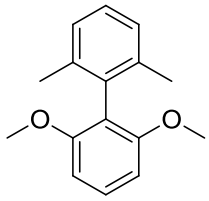
1-(2,5-dimethylphenyl)naphthalene. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.84 (m, 2 H, Ar), 7.53 – 7.47 (m, 3 H, Ar), 7.38 (t, *J* = 4 Hz, 1 H, Ar), 7.33 (d, *J* = 2 Hz, 1 H, Ar), 7.22 (d, *J* = 4 Hz, 1 H, Ar), 7.16 (d, *J*= 4 Hz, 1 H, Ar), 7.07 (s, 1 H, Ar), 2.37 (s, 3 H, *Me*), 1.97 (s, 3 H, *Me*) ppm. Data is consistent with that reported in the literature.[11]



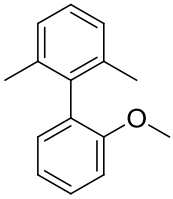
2',6'-dimethoxy-2,4,6-trimethyl-1,1'-biphenyl. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 2 Hz, 1 H, Ar)，6.93 (s, 2 H, Ar), 6.64 (d, *J* = 2 Hz, 2 H, Ar)，3.71 (s, 6 H, O*Me*), 2.31 (s, 3 H, *Me*), 1.96 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[9]



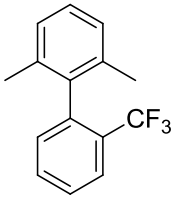
2,2',6-trimethyl-1,1'-biphenyl. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 3 H, Ar), 7.17 (t, *J* = 8 Hz, 1 H, Ar), 7.11 (d, *J* = 4 Hz, 2 H, Ar), 7.02 (d, *J* = 4 Hz, 1 H, Ar), 1.97 (s, 3 H, *Me*), 1.95 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[3]



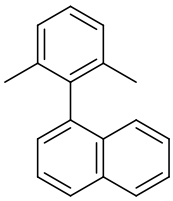
2,6-dimethoxy-2',6'-dimethyl-1,1'-biphenyl. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8 Hz, 2 H, Ar), 7.11 (t, *J* = 8 Hz, 1 H, Ar), 6.65 (d, *J* = 4 Hz, 1 H, Ar), 6.51 (d, *J* = 4 Hz, 2 H, Ar), 3.89 (s, 6 H, O*Me*), 3.70 (s, 3 H, *Me*), 1.99 (s, 3 H, *Me*) ppm. Data is consistent with that reported in the literature.[5]



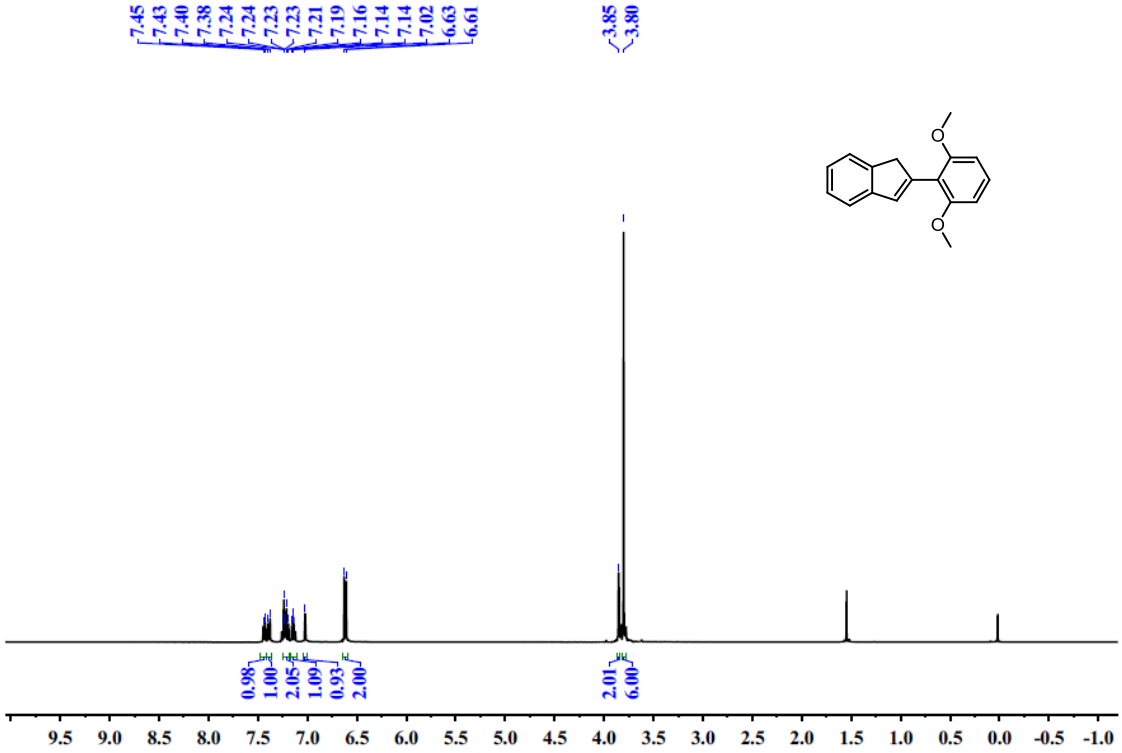
2'-methoxy-2,6-dimethyl-1,1'-biphenyl. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.32 (m, 1 H, Ar), 7.15 (t, *J* = 4 Hz, 2 H, Ar), 7.11 (d, *J* = 4 Hz, 2 H, Ar), 7.04 – 6.97 (m, 3 H, Ar), 3.74 (s, 3 H, O*Me*), 2.01 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[5]



2,6-dimethyl-2'-(trifluoromethyl)-1,1'-biphenyl. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 4 Hz, 1 H, Ar), 7.60 (t, *J* = 8 Hz, 1 H, Ar), 7.48 (t, *J* = 8 Hz, 1 H, Ar), 7.22 – 7.16 (m, 2 H, Ar), 7.09 (d, *J* = 4 Hz, 2 H, Ar), 1.94 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[12]



1-(2,6-dimethylphenyl)naphthalene. White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.86 (m, 2 H, Ar), 7.55 (t, *J* = 8 Hz, 1 H, Ar), 7.49 (t, *J* = 4 Hz, 1 H, Ar), 7.35 (d, *J* = 4 Hz, 2 H, Ar), 7.27 (t, *J* = 8 Hz, 2 H, Ar), 7.19 (d, *J* = 2 Hz, 2 H, Ar), 1.91 (s, 6 H, *Me*) ppm. Data is consistent with that reported in the literature.[7]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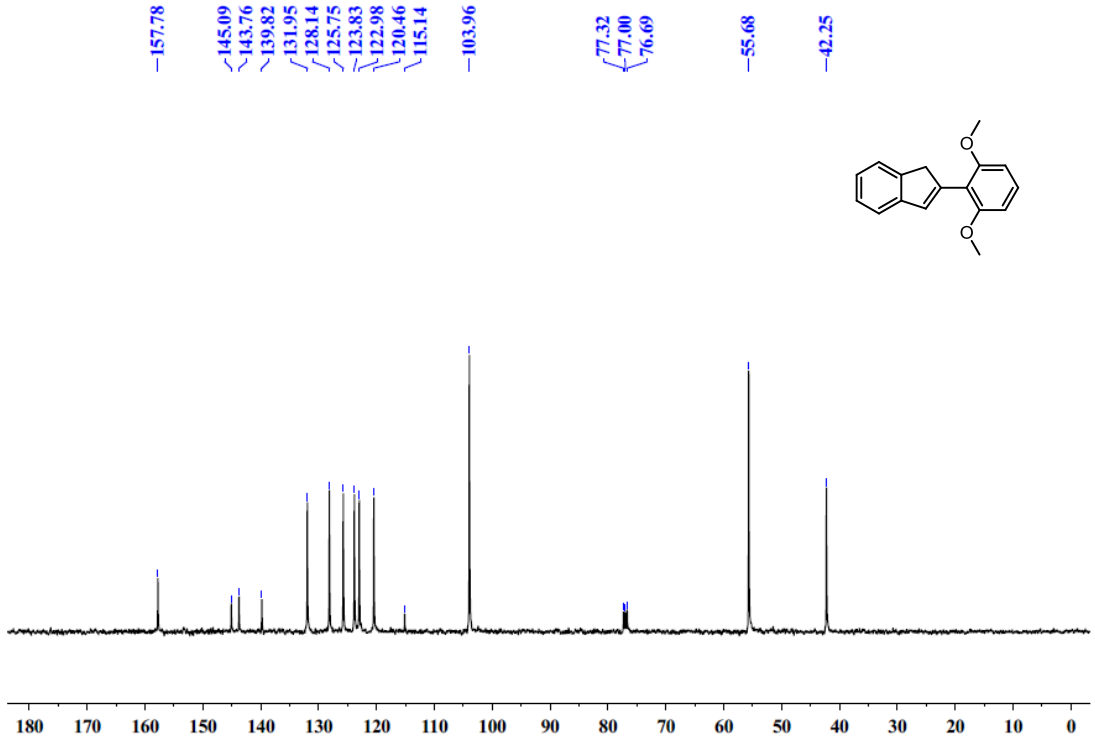
7.40
7.38
7.24
7.24
7.23
7.23
7.21
7.19
7.16
7.14
7.14
7.02
6.63
6.61
3.85
3.80
O
O
0.98
1.00
2.05
1.09
0.93
2.00
2.01
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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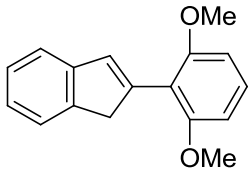
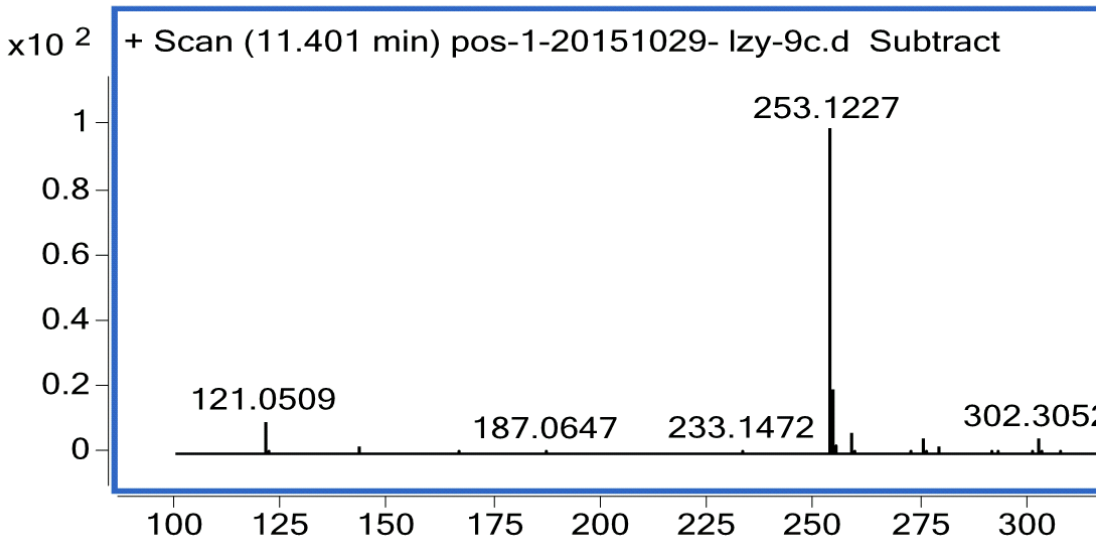
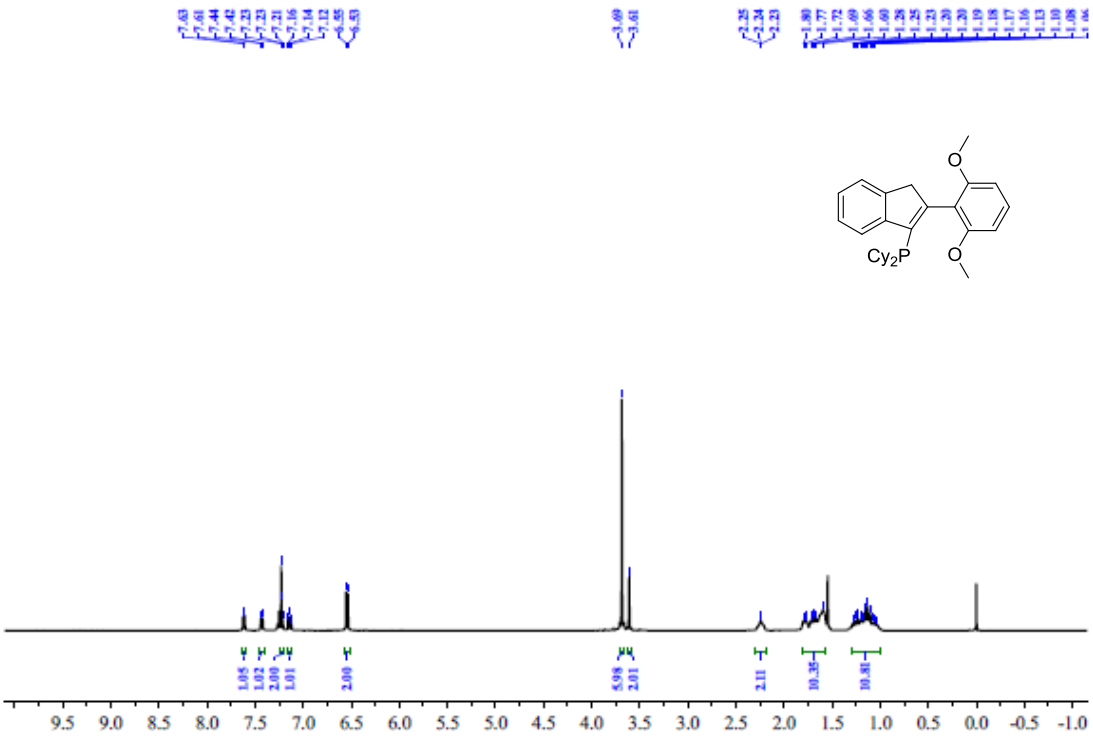
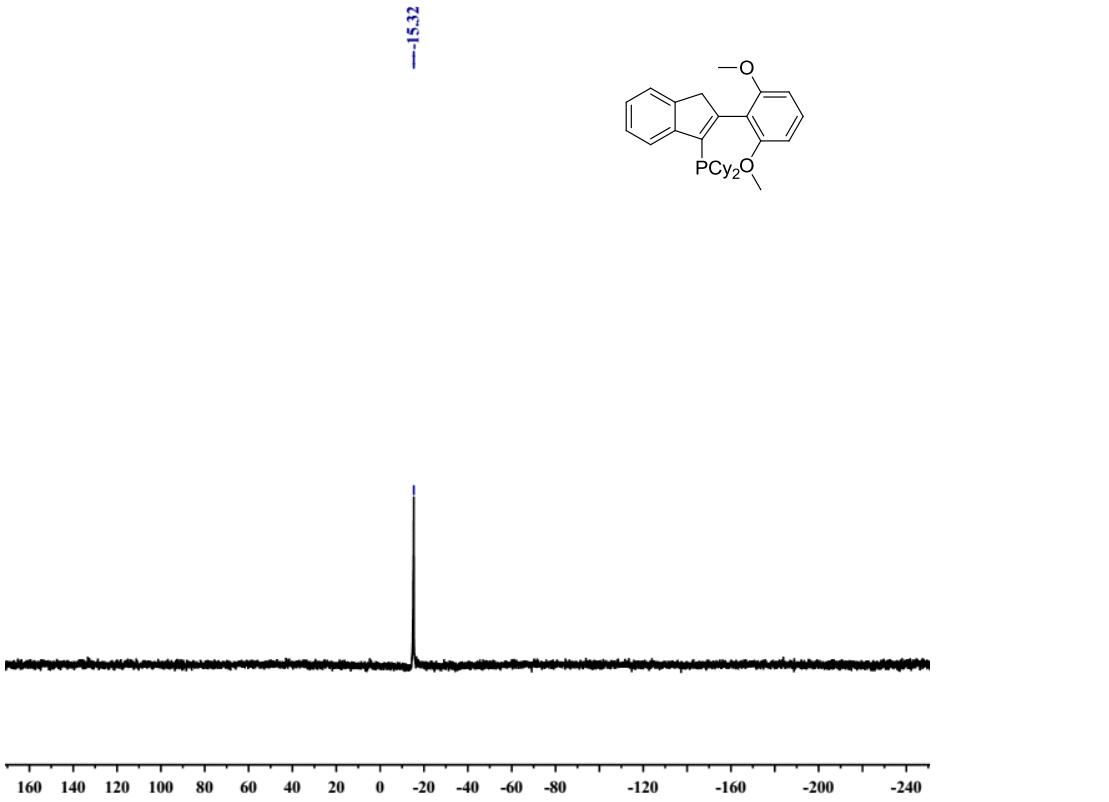
145.09
143.76
139.82
131.95
128.14
125.75
123.83
122.98
120.46
115.14
103.96
77.32
77.00
76.69
55.68
42.25
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

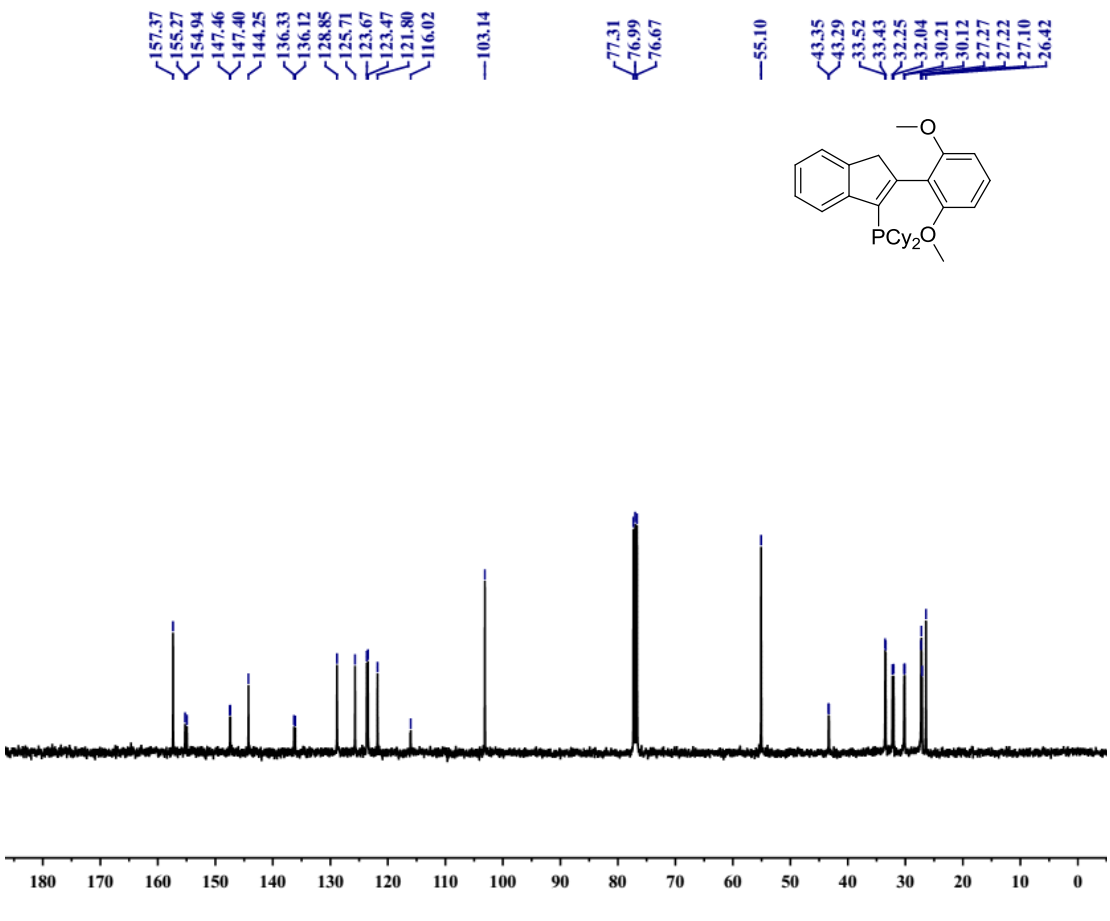

OMe
OMe

HRMS


x10 2
+ Scan (11.401 min) pos-1-20151029- lzy-9c.d Subtract
253.1227
121.0509
187.0647
233.1472
302.305
1
0.8
0.6
0.4
0.2
0
100
125
150
175
200
225
250
275
300


O
O
Cy2P
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


15.32
PCy2
O
160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240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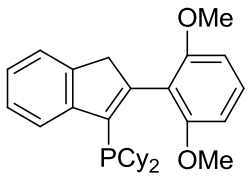
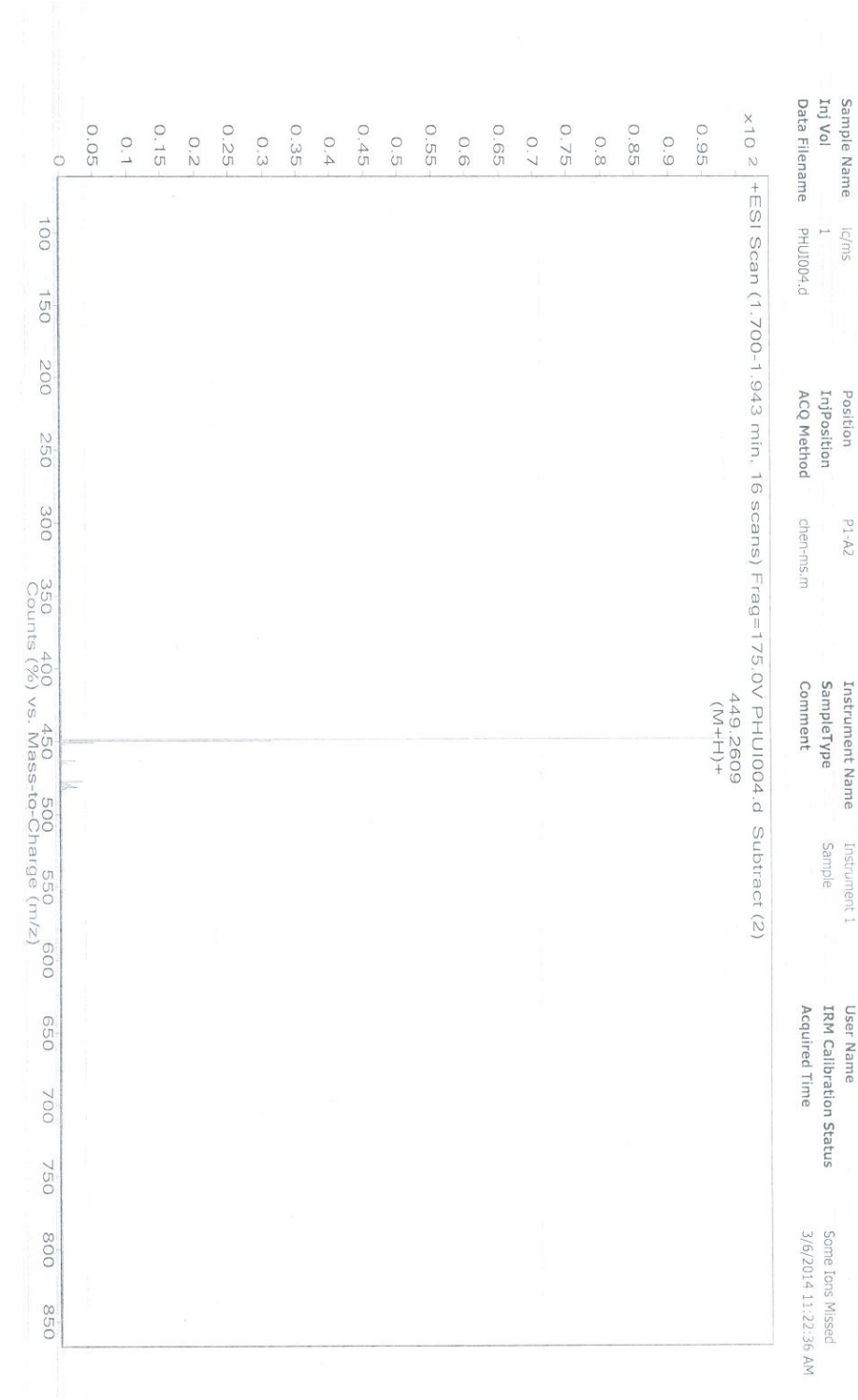
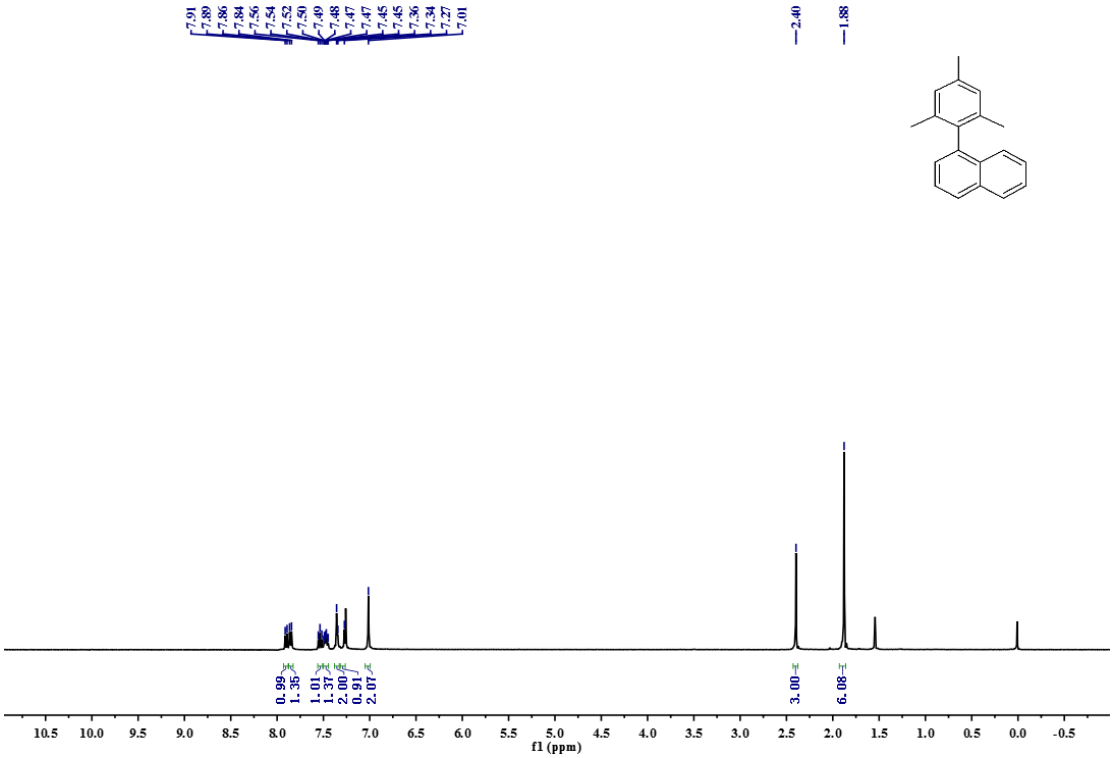
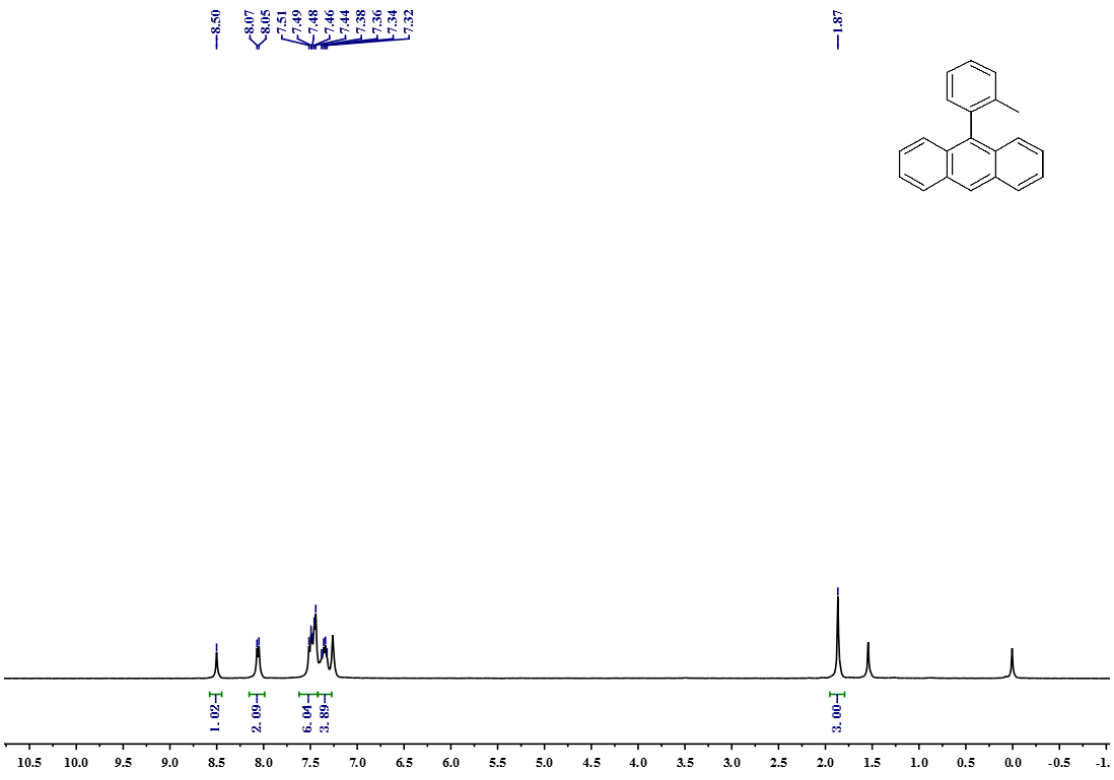
155.27
154.94
147.46
147.40
144.25
136.33
136.12
128.85
125.71
123.67
123.47
121.80
116.02
103.14
77.31
76.99
76.67
55.10
43.35
43.29
33.52
33.43
32.25
32.04
30.21
30.12
27.27
27.22
27.10
26.42
PCy2
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OMe
PCy2
OMe

HRMS


Sample Name
Inj Vol
Data Filename
lc/ms
1
PHU004.d
Position
InjPosition
ACQ Method
P1-A2
chen-ms.m
Instrument Name
SampleType
Comment
Instrument 1
Sample
User Name
IRM Calibration Status
Acquired Time
Some Ions Missed
3/6/2014 11:22:36 AM
+ESI Scan (1.700-1.943 min, 16 scans) Frag=175.0V PHU004.d Subtract (2)
449.2609
(M+H)+
×10 2
Counts (%) vs. Mass-to-Charge (m/z)


7.91
7.89
7.86
7.84
7.56
7.54
7.52
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.36
7.34
7.27
7.01
2.40
1.88
0.99
1.35
1.01
1.37
2.00
0.91
2.07
3.00
6.08
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
f1 (ppm)


8.50
8.07
8.05
7.51
7.49
7.48
7.46
7.44
7.38
7.36
7.34
7.32
1.87
1.02
2.09
6.04
3.89
3.00
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


9.63
8.13
8.11
7.95
7.94
7.73
7.71
7.69
7.61
7.59
7.58
7.56
7.54
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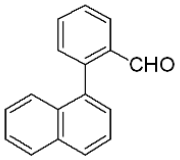
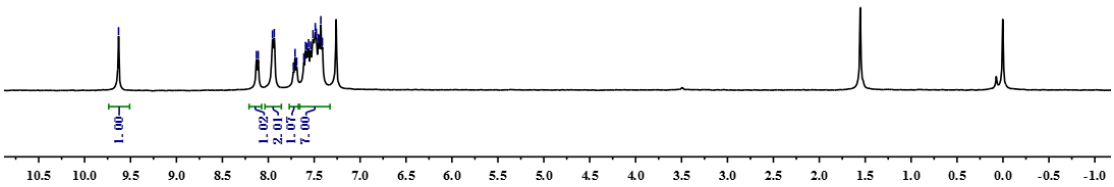
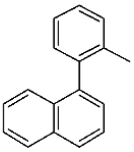
7.49
7.48
7.46
7.45
7.43
7.41

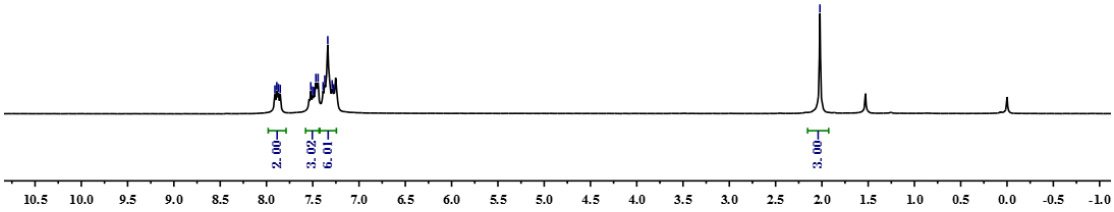

CHO

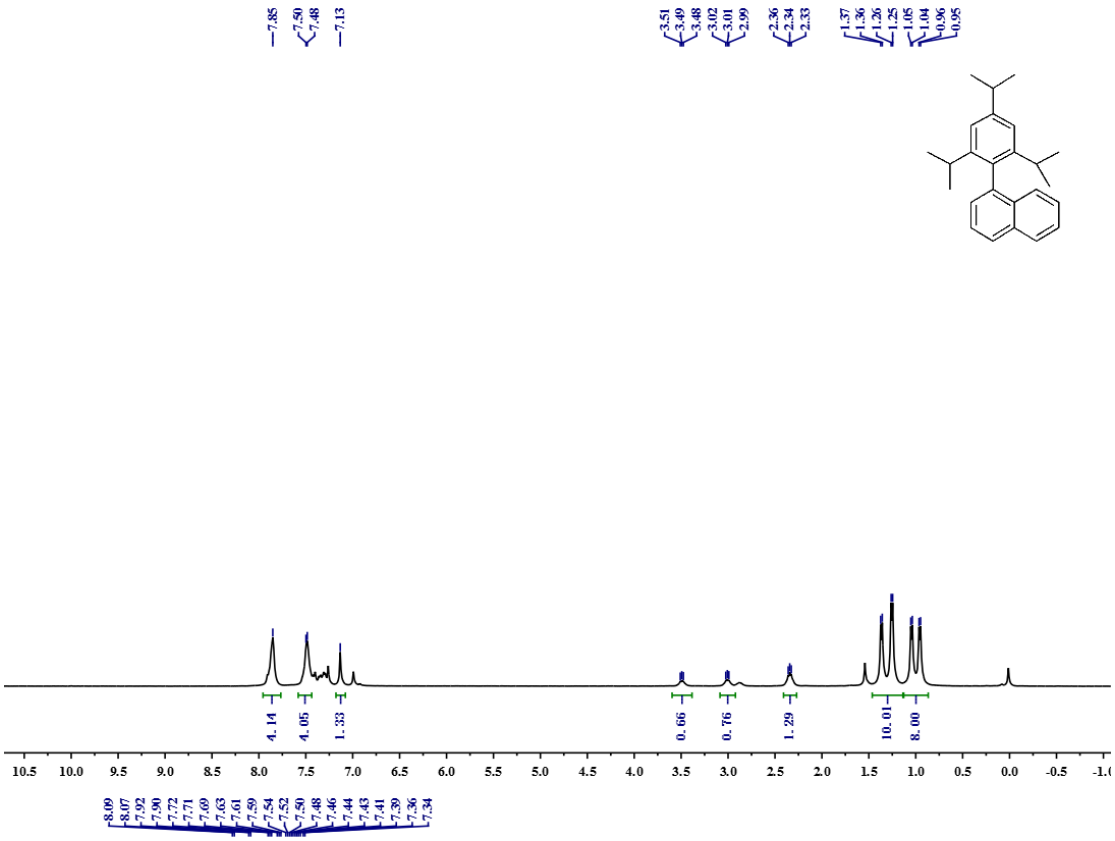

1.00
1.02
2.01
1.07
7.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

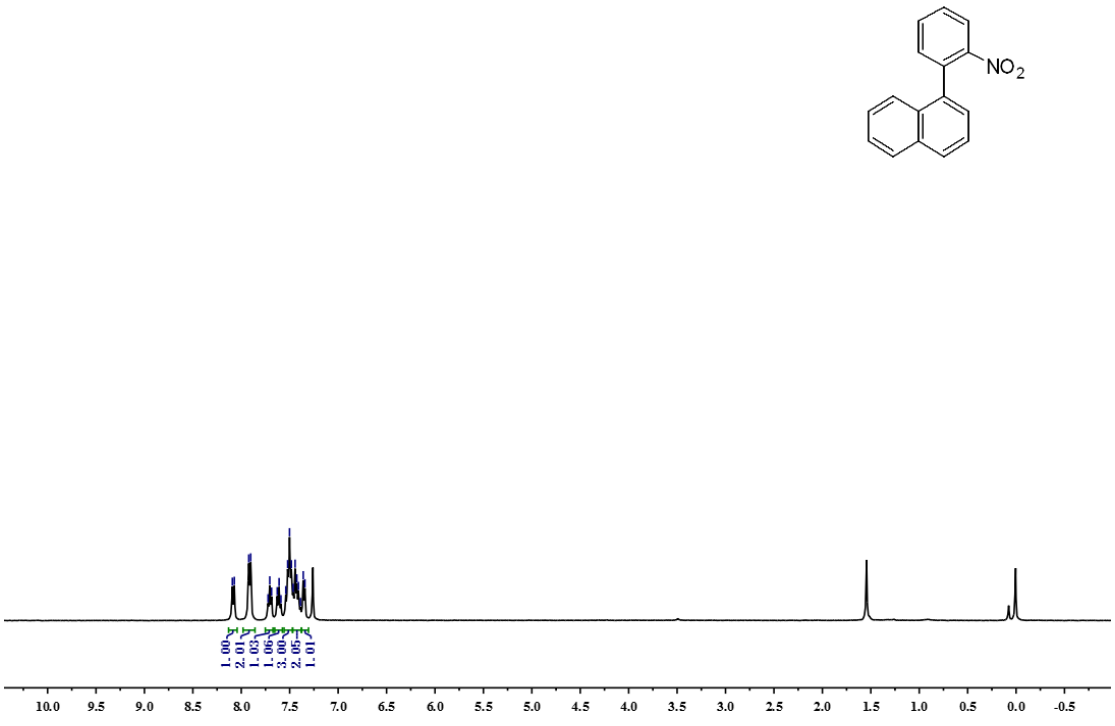

7.91
7.89
7.87
7.85
7.52
7.50
7.49
7.47
7.44
7.39
7.37
7.34
7.29
7.26

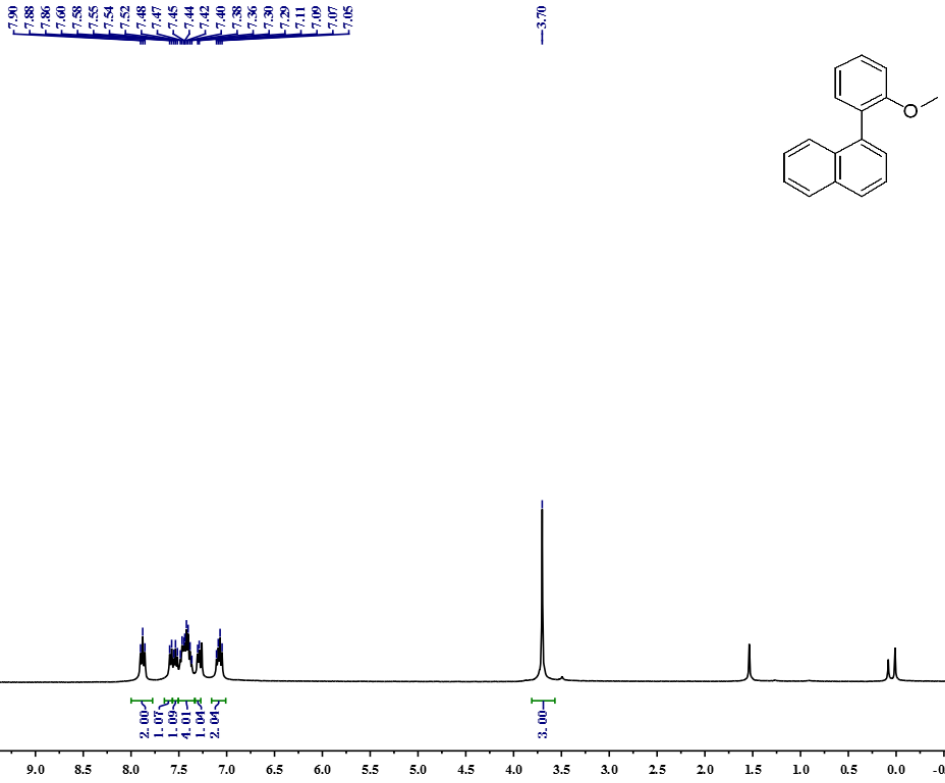

2.02




2.00
3.02
6.01
3.00
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



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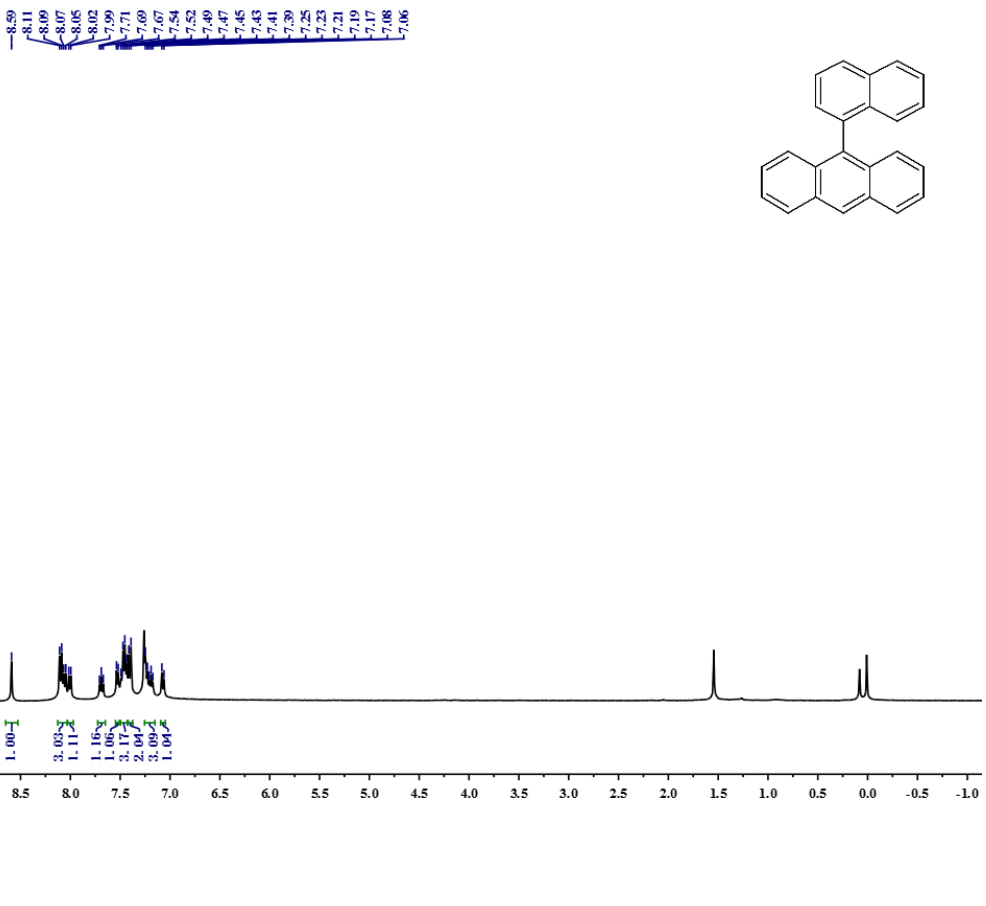
7.88
7.86
7.60
7.58
7.55
7.54
7.52
7.48
7.47
7.45
7.44
7.42
7.40
7.38
7.36
7.30
7.29
7.11
7.09
7.07
7.05
3.70
2.00
1.07
1.09
4.01
1.04
2.04
3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.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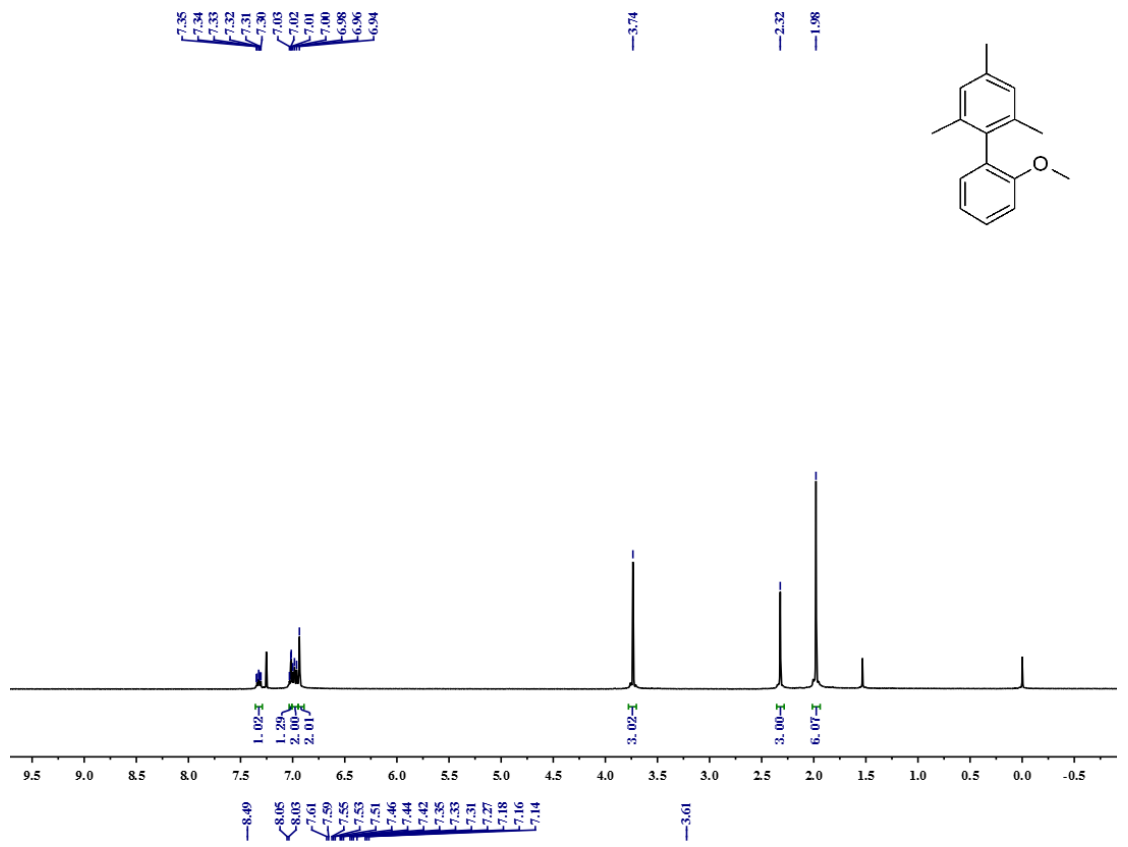
7.71
7.69
7.67
7.54
7.52
7.49
7.47
7.45
7.43
7.41
7.39
7.25
7.23
7.21
7.19
7.17
7.08
7.06
1.00
3.03
1.11
1.16
1.06
3.17
2.04
3.09
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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7.32
7.31
7.30
7.03
7.02
7.01
7.00
6.98
6.96
6.94
3.74
2.32
1.98
O
1.02
1.29
2.00
2.01
3.02
3.00
6.07
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
8.49
8.05
8.03
7.61
7.59
7.55
7.53
7.51
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7.44
7.42
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7.33
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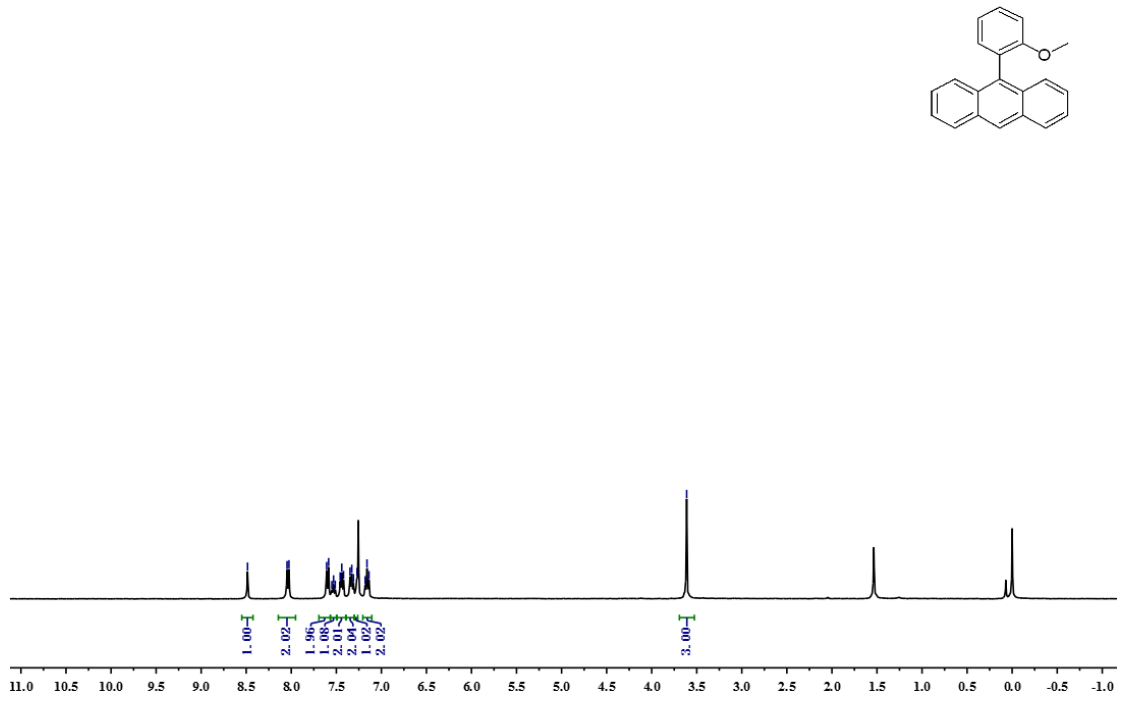
7.27
7.18
7.16
7.14
3.61


O
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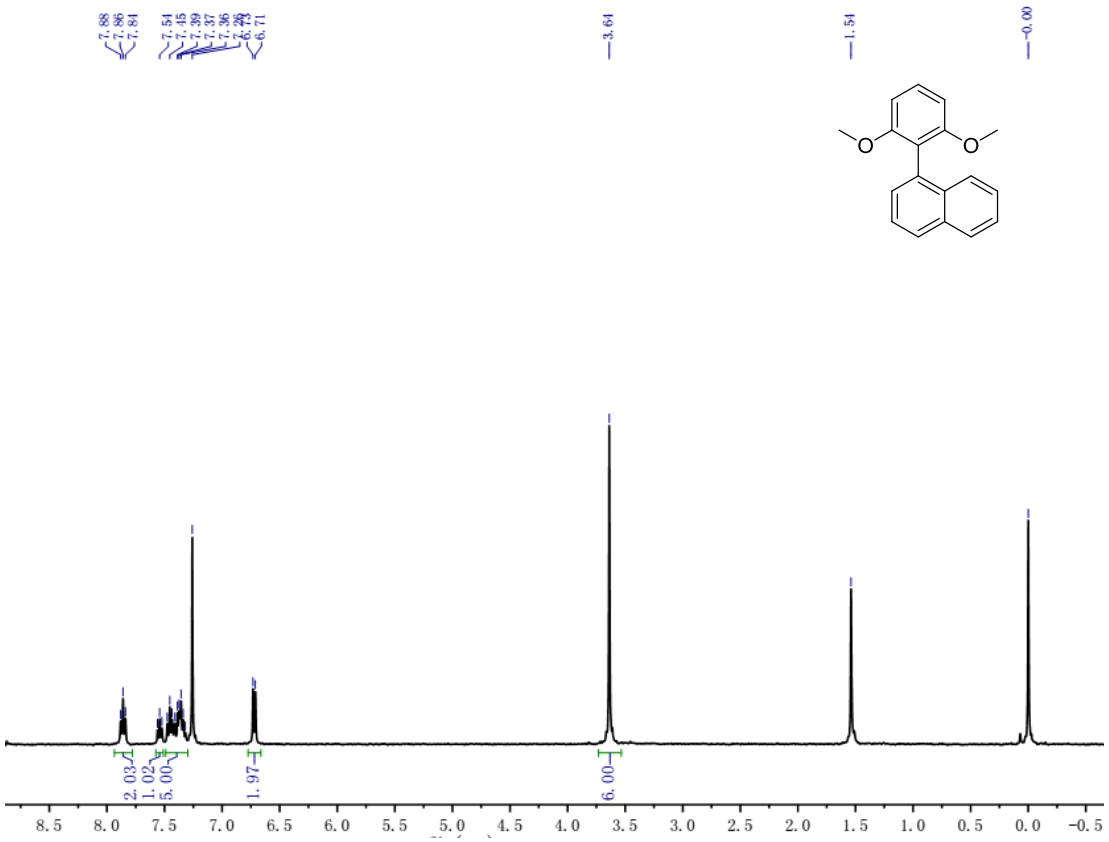
2.02
1.96
1.08
2.01
2.04
1.02
2.02
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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7.37
7.36
6.71
3.61
1.54
0.00
O
O
2.03
1.02
5.00
1.97
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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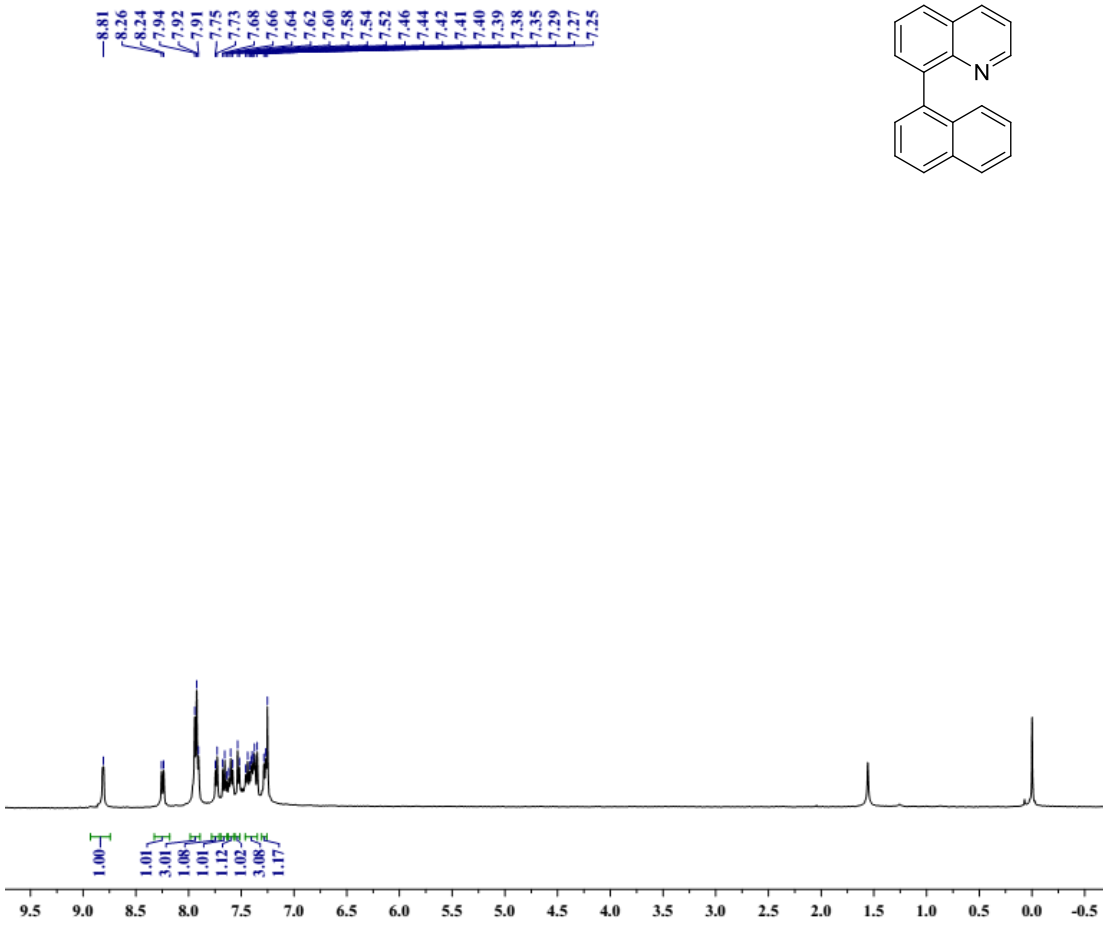
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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7.58
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7.46
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7.29
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7.25
N
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1.01
3.01
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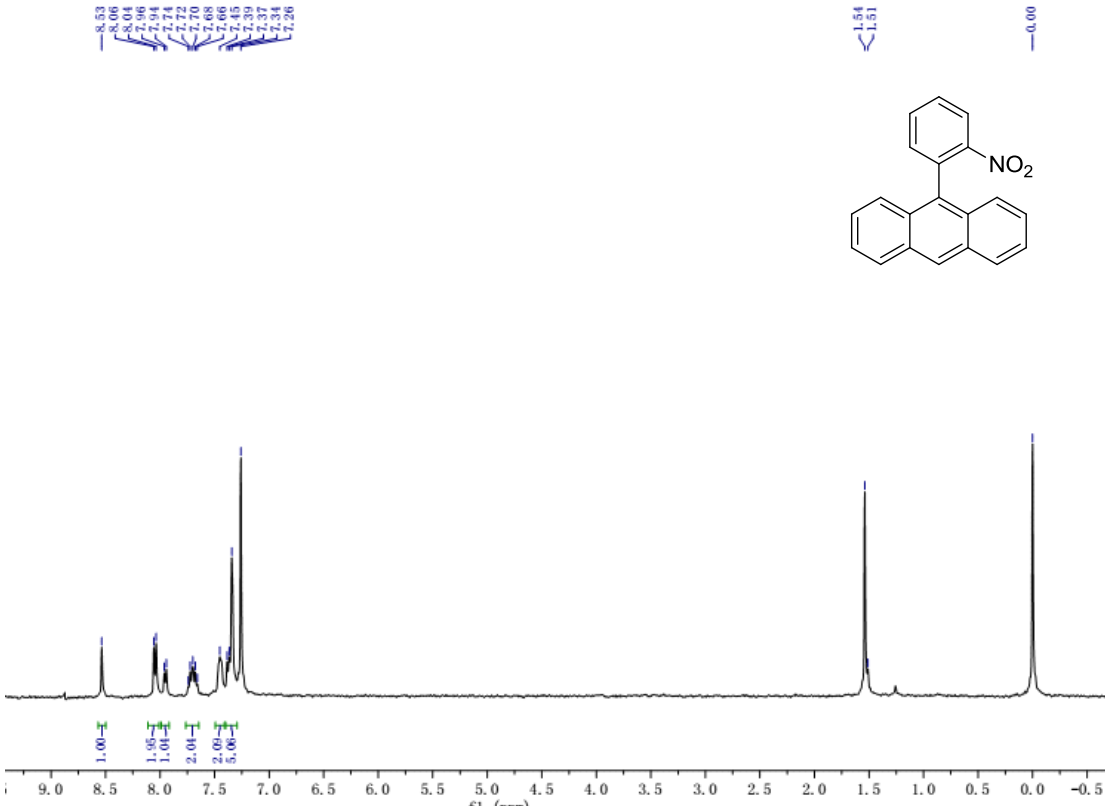
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7.37
7.34
7.26
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1.51
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NO2
1.00
1.95
1.04
2.04
2.09
5.06
9.0
8.5
8.0
7.5
7.0
6.5
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1.0
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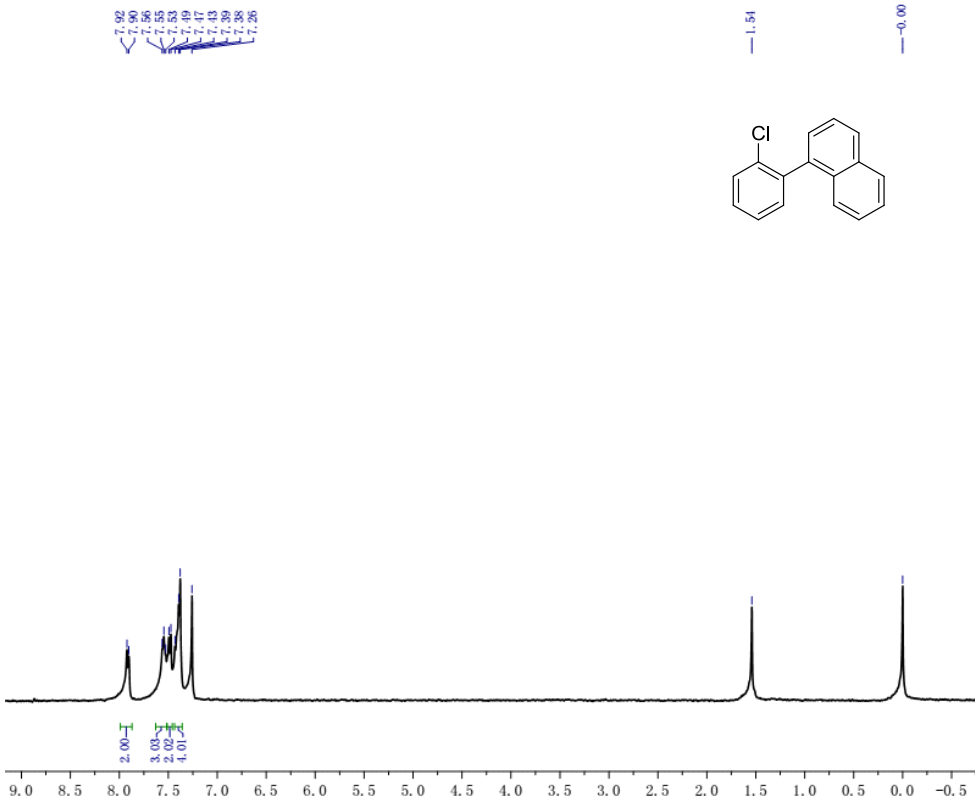
0.0
-0.5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7.39
7.38
7.26
1.54
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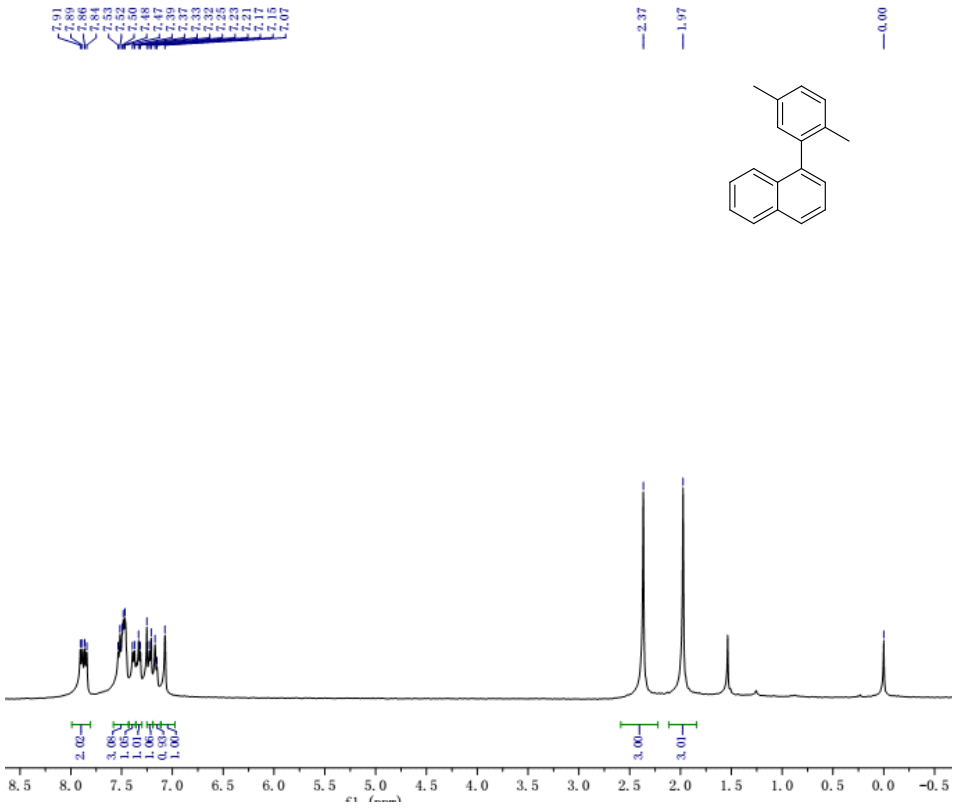
3.03
2.02
4.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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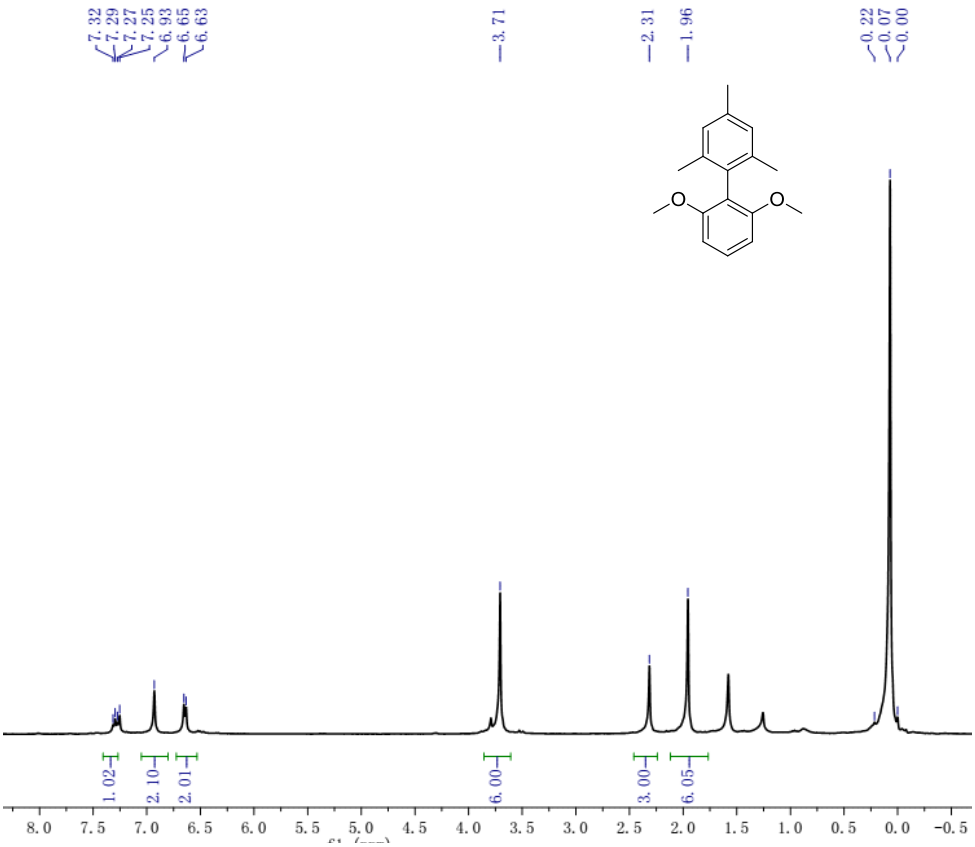
7.32
7.25
7.23
7.21
7.17
7.15
7.07
2.37
1.97
0.00
2.02
3.08
1.05
1.01
1.06
0.93
1.00
3.00
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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7.25
6.93
6.65
6.63
3.71
2.31
1.96
0.22
0.07
0.00
O
O
1.02
2.10
2.01
6.00
3.00
6.05
8.0
7.5
7.0
6.5
6.0
5.5
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1.5
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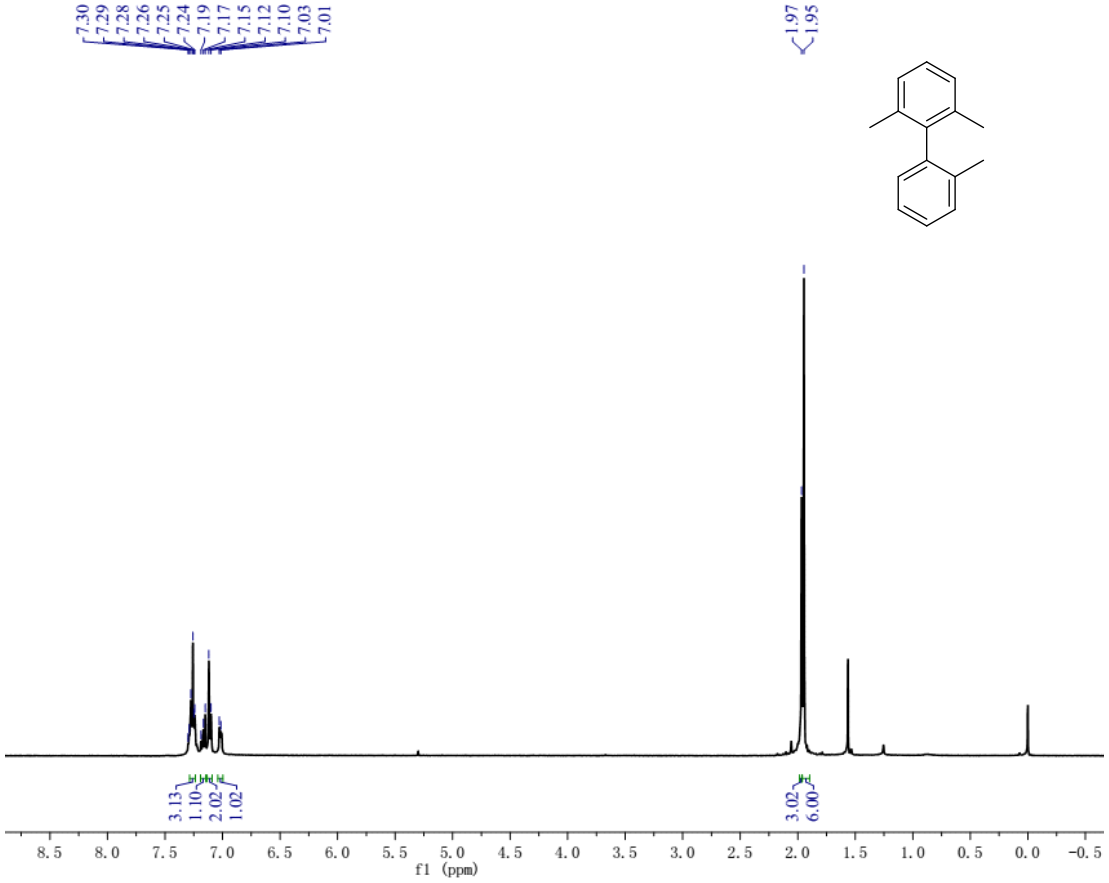
0.0
−0.5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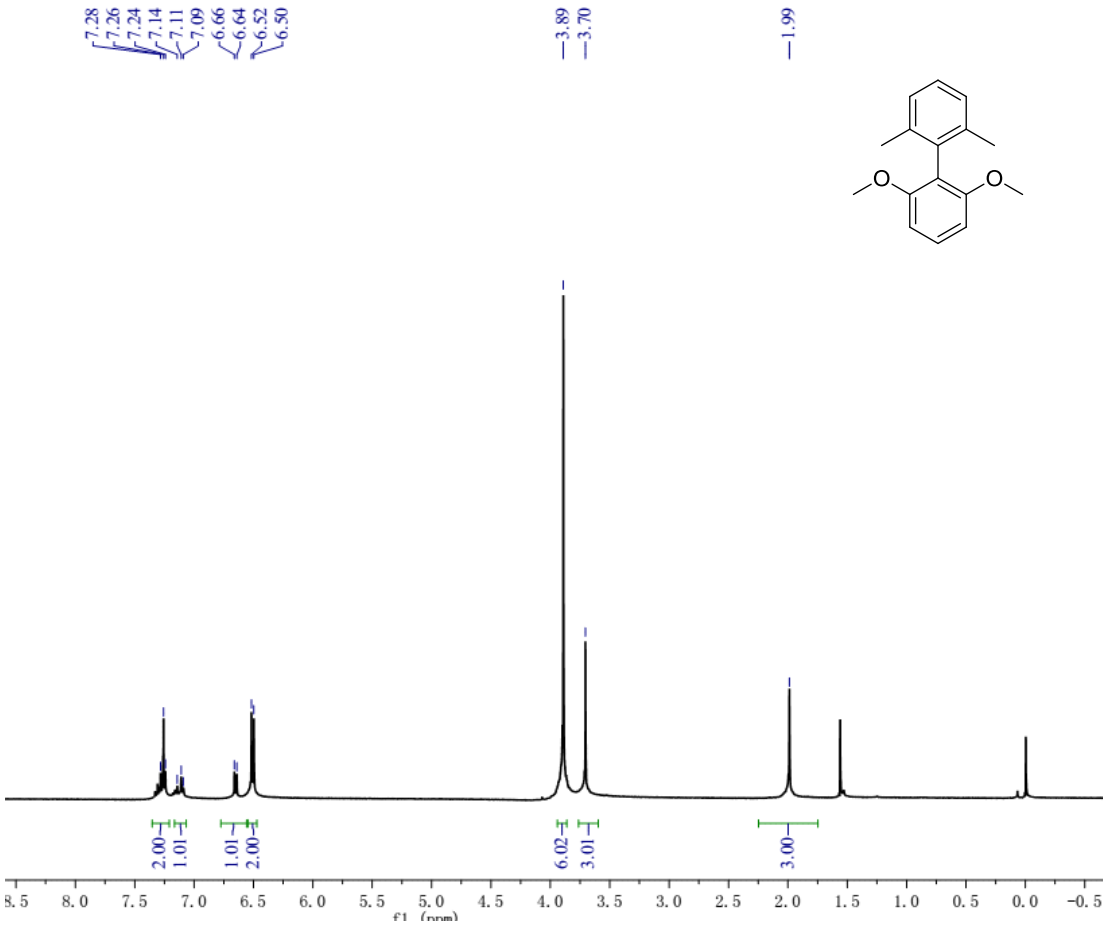
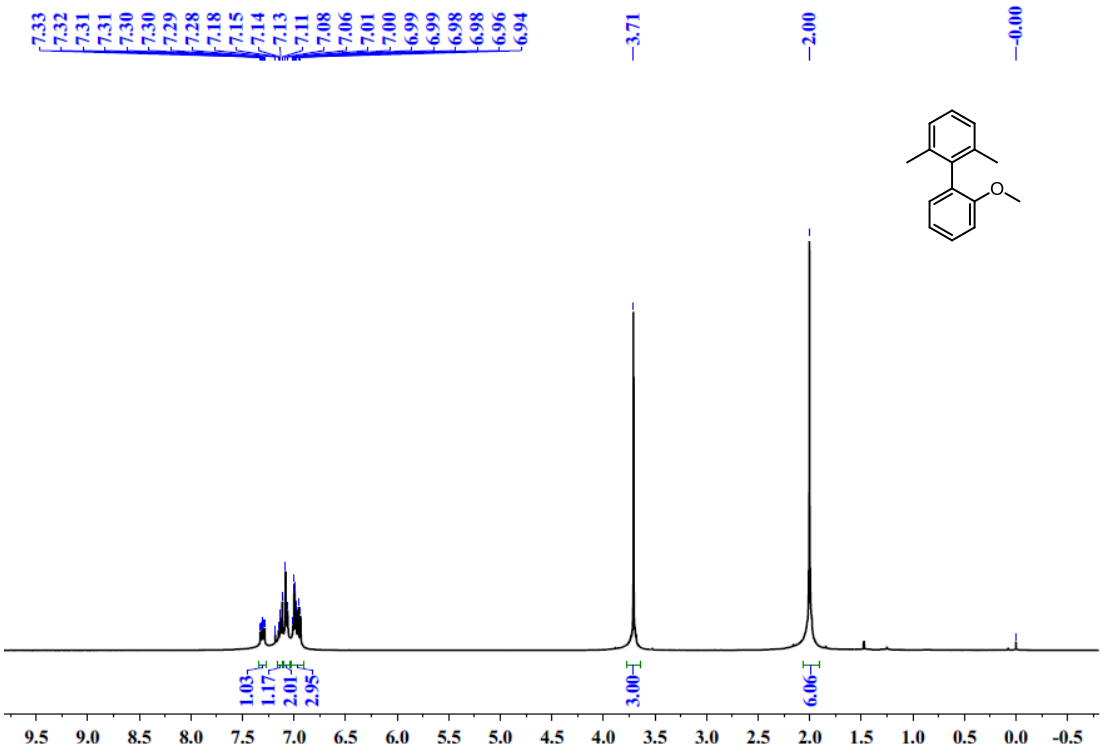
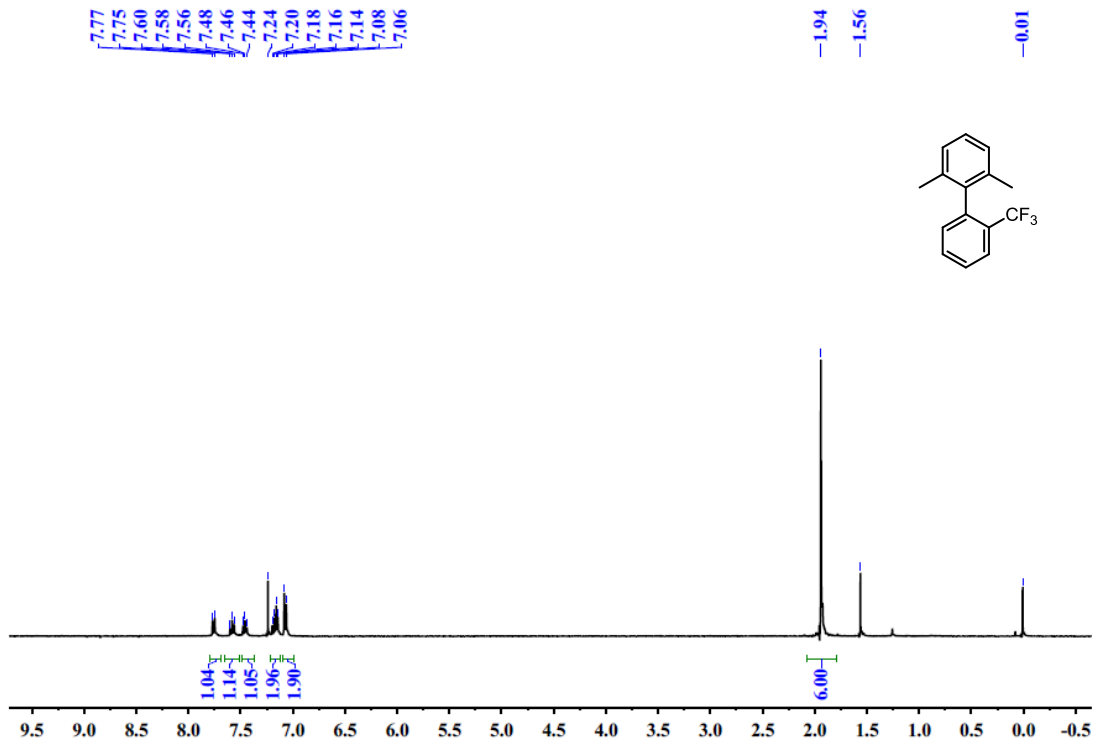
7.19
7.17
7.15
7.12
7.10
7.03
7.01
1.97
1.95
3.13
1.10
2.02
1.02
3.02
6.00
f1 (ppm)


7.28
7.26
7.24
7.14
7.11
7.09
6.66
6.64
6.52
6.50
3.89
3.70
1.99
O
O
2.00
1.01
1.01
2.00
6.02
3.01
3.00


7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.18
7.15
7.14
7.13
7.11
7.08
7.06
7.01
7.00
6.99
6.99
6.98
6.98
6.96
6.94
3.71
2.00
0.00
O
1.03
1.17
2.01
2.95
3.00
6.06
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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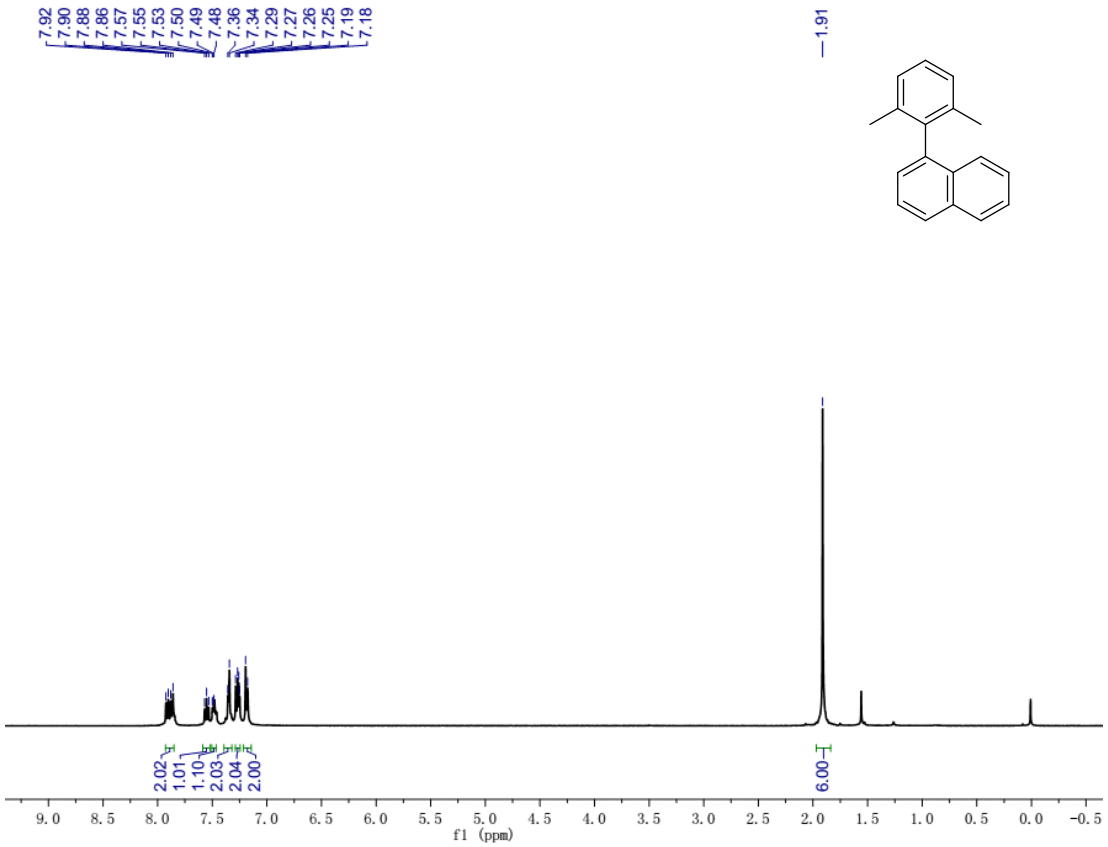
7.75
7.60
7.58
7.56
7.48
7.46
7.44
7.24
7.20
7.18
7.16
7.14
7.08
7.06
1.94
1.56
0.01
CF3
1.04
1.14
1.05
1.96
1.90
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


7.92
7.90
7.88
7.86
7.57
7.55
7.53
7.50
7.49
7.48
7.36
7.34
7.29
7.27
7.26
7.25
7.19
7.18
1.91
2.02
1.01
1.10
2.03
2.04
2.00
6.00
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
f1 (ppm)

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