Phenylphosphinacalix[3]trifuran: Synthesis, Coordination and Application in Suzuki-Miyaura cross-coupling reaction in water

Yue Sun,[a] Meng-Qi Yan,[c] Yan Liu,[c] Ze-Yu Lian,[b] Tong Meng,[a] Sheng-Hua Liu,[a] Jian Chen,[a] Guang-Ao Yu*[a]

[a]*Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, Central China Normal University, Wuhan 430079, China. E-Mail: yuguang@mail.ccnu.edu.cn, chshliu@mail.ccnu.edu.cn*
[b]*State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*
[c]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

E-Mail: yuguang@mail.ccnu.edu.cn

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1. Experimental Section

General methods and experimental details

Schlenk- and vacuum-line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon before use. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Mercury-Plus spectrometer (400 MHz). Mass spectra (EI-MS) were recorded on a HP 5989B Mass Spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 C analyzer.

Phenylphosphinacalix[3]trifuran (1).
In a 100 mL flask, furan (5.0 mL, 69 mmol) was dissolved in THF (40 mL) under an argon atmosphere. The mixture was cooled to -78 ℃, and ^{n}BuLi (30 mL, 2.5 mol/L solution in hexane, 75 mmol) was added. The solution was stirred for 30 min at -78 ℃ and then for 2 h at ambient temperature. Then the mixture was cooled to -60 ℃ and $PhPCl_2$ (4.7 mL, 34.5 mmol) was added. The mixture was warmed to room temperature and stirred for additional 2 h. The mixture was cooled to -60 ℃ and ^{n}BuLi (30 mL, 2.5 mol/L solution in hexane, 75 mmol) was added. The solution was stirred for 30 min at -78 ℃ and then for 4 h at ambient temperature. Then the mixture was cooled to -60 ℃ and $PhPCl_2$ (4.7 mL, 34.5 mmol) was added. The mixture was warmed to room temperature and refluxed for 24 h. The LiCl that formed was removed by filtration over a pad of Celite. 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 solvent in vacuo, the residue was subject to column chromatography (silica, CH_2Cl_2/Hexane 3:1) to give a white solid (523 mg, 4% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.62 (m, 6H, Ph-H), 7.28-7.30 (m, 3H, Ph-H), 6.15-7.17 (m, 6H, Ph-H), 6.80 (s, 6H, 2-furyl-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 156.60, 134.34, 133.52, 133.32, 128.65, 128.08, 128.00, 121.76 ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ -61.95 (s) ppm. EI-MS (m/z): 522 $[M]^+$, Anal. Calcd for $C_{30}H_{21}O_3P_3$: C, 68.97, H, 4.05; found: C, 68.80, H, 4.25.

Phenylphosphinacalix[3]trifuran trioxide (2).
In a 50 mL flask, compound **1** (42 mg, 0.08 mmol) was dissolved in CH_2Cl_2 (20 mL). The mixture was cooled to 0 ℃, and H_2O_2 (1.0 mL, 30%, 8.8 mmol) was added slowly. The solution was stirred for 24 h at ambient temperature. The organic layer was then separated from the aqueous layer, dried over $MgSO_4$, and filtered. After evaporation of solvent in vacuo, the residue was subject to column chromatography (silica, THF/hexane 3:1) to give a white solid (28 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.85 (m, 6H, Ph-H), 7.60-7.62 (m, 3H, Ph-H), 7.40-7.43(m, 6H, Ph-H), 7.33 (s, 6H, 2-furyl-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 153.18, 133.08, 130.93, 130.82, 128.71, 128.58, 121.71 ppm. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 2.62 (s) ppm. EI-MS (m/z): 570 $[M]^+$, Anal. Calcd for $C_{30}H_{21}O_6P_3$: C, 63.17, H, 3.71; found: C, 62.95, H, 3.78.

Phenylphosphinacalix[3]trifuran trisulfide (3).

In a 50 mL flask, compound **1** (42 mg, 0.08 mmol) was dissolved in THF (10 mL) under an argon atmosphere. Element sulfur (16 mg, 0.5 mmol) was added. The mixture was refluxed for 24 h. After evaporation of solvent in vacuo, the residue was subject to column chromatography (silica, THF/hexane 5:1) to give a yellow solid (44 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.94 (m, 6H, Ph-H), 7.55-7.57 (m, 3H, Ph-H), 7.33-7.38(m, 12H, Ph-H, 2-furyl-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 154.58, 132.39, 131.14, 131.02, 128.60, 122.74, 122.60 ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 9.01 (s) ppm. EI-MS (m/z): 618 $[M]^+$, Anal. Calcd for $C_{30}H_{21}O_3P_3S_3$: C, 58.25, H, 3.42; found: C, 57.98, H, 3.64.

Phenylphosphinacalix[3]trifuran triselenide (4).

In a 50 mL flask, compound **1** (42 mg, 0.08 mmol) was dissolved in $CHCl_3$ (10 mL) under an argon atmosphere. Element selenium (39.5 mg, 0.5 mmol) was added. The mixture was refluxed for 24 h. After evaporation of solvent in vacuo, the residue was subject to column chromatography (silica, THF/hexane 5:1) to give a red solid (55 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.91 (m, 6H, Ph-H), 7.55-7.60 (m, 3H, Ph-H), 7.33-7.53(m, 12H, Ph-H, 2-furyl-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 153.52, 132.04, 131.34, 131.21, 131.13, 128.38, 128.25, 123.56 ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -5.17 (s, $^{1}J_{P\text{-}Se}$ = 821 Hz) ppm. EI-MS (m/z): 762 $[M]^+$, Anal. Calcd for $C_{30}H_{21}O_3P_3Se_3$: C, 47.46, H, 2.79; found: C, 47.40, H, 2.88.

2, 4-bis(2-furylphenylphosphino)furan C.

In a 100 mL flask, furan (5.0 mL, 69 mmol) was dissolved in THF (40 mL) under an argon atmosphere. The mixture was cooled to -78 ℃, and ^{n}BuLi (30 mL, 2.5 mol/L solution in hexane, 75 mmol) was added. The solution was stirred for 30 min at -78 ℃ and then for 2 h at ambient temperature. Then the mixture was cooled to -60 ℃ and $PhPCl_2$ (4.7 mL, 34.5 mmol) was added. The mixture was warmed to room temperature and stirred for additional 2 h. The mixture was cooled to -60 ℃ and ^{n}BuLi (30 mL, 2.5 mol/L solution in hexane, 75 mmol) was added. The solution was stirred for 30 min at -78 ℃ and then for 4 h at ambient temperature. The LiCl that formed was removed by filtration over a pad of Celite. 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 solvent in vacuo, the residue was subject to column chromatography (silica, CH_2Cl_2/Hexane 3:1) to give a white solid (1531 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (br, 2H, furyl-H), 7.40-7.43 (m, 4H, Ph-H), 7.24-7.30 (m, 6H, Ph-H), 6.65-6.72 (m, 4H, furyl-H), 6.37-6.39 (m, 2H, furyl-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 156.08, 155.95, 150.27, 147.30, 134.46, 134.38, 132.86, 132.66, 128.90, 128.34, 128.26, 121.91, 121.66, 121.52, 121.42, 121.30, 121.21, 110.70, 110.66 ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ -53.05 (s) ppm. EI-MS (m/z): 416 $[M]^+$, Anal. Calcd for $C_{24}H_{18}O_3P_2$: C, 69.24, H, 4.36; found: C, 69.20, H, 4.32.

[$PdCl_2$]{Phenylphosphinacalix[3]trifuran}$_2$ (5)

In a 50 mL flask, Phenylphosphinacalix[3]trifuran (1) (26 mg, 0.05 mmol) was dissolved in CH_2Cl_2 (15 mL) under an argon atmosphere. A solution of $PdCl_2(CH_3CN)_2$ (13 mg, 0.05 mmol) in CH_2Cl_2 (6 mL) was added slowly. After addition, the reaction mixture was stirred for 2 h at room temperature to give a green solution. The solution was carefully layered with 3 mL of methanol. After the mixture stood for 1 day, a red precipitate formed, which was filtered, washed with methanol, and dried in vacuo, a 28 mg amount (80%) of **5** as a red crystal was obtained. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17 (br, 4H), 7.75 (br, 4H), 7.51-7.38 (m, 30H), 6.48 (br, 4H) ppm. ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ -5.19 (s, 4P), -53.46 (s, 2P) ppm. Anal. Calcd for $C_{60}H_{42}Cl_4O_6P_6Pd_2$: C, 51.49, H, 3.02; found: C, 51.42, H, 3.20.

General Procedures for Reaction Condition Screenings.

Pd source (0.05 mmol), phosphine ligand **1** (0.05 mmol) and phase transfer reagent (10 mmol) were dissolved in water (10 mL). The resulting solution was stirred at room temperature for 5 minutes before immediate use. The aqueous solution of the catalyst (1.0 mL) containing Pd scource (0.005 mmol), phosphine ligand **1** (0.005 mmol) and phase transfer reagent (1.0 mmol) was loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. Bromobenzene (112 mg, 1.0 mmol), 4-methoxyphenylboronic acid (182 mg, 1.2 mmol), base (3.0 mmol) and water (1.0 mL) were added. The tube was evacuated and flushed with nitrogen for three times, placed into a preheated oil bath (100 ℃) and stirred for 8 h. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (10 ml) and dodecane (22.6 mg, 0.1 mmol, internal standard) were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve. The product was purified by column chromatography (hexane/ethyl acetate as eluent).

General Procedure for Suzuki-Miyaura Cross-Coupling Reaction in Water.

$Pd(OAc)_2$ (11 mg, 0.05 mmol) and ligand **1** (0.05 mmol) were dissolved in water

(10 mL). The resulting solution was stirred at room temperature for 5 minutes before immediate use. The aqueous solution of the catalyst (1.0 mL) containing $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and ligand **1** (6.5 mg, 0.005 mmol) was loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. Aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), base (3.0 mmol) and water (1.0 mL) were added. The tube was evacuated and flushed with nitrogen for three times, and then placed into a preheated oil bath (100 ℃) for 8 h. After completion of reaction, the reaction tube was allowed to cool to room temperature, water was draw with dropper and the reaction mixture was adsorbed onto silica gel, and then purified by column chromatography (hexane/ethyl acetate as eluent) to afford the desired product.

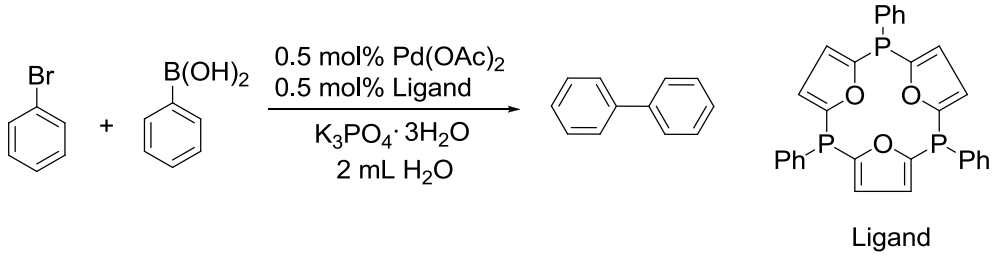
Crystallographic Studies

Crystals of **2**-**4** for X-ray diffraction were obtained by recrystallization of the pure product from $CHCl_3$/hexane layers, crystals of **5** were obtained by recrystallization of the pure product from $CHCl_3$/methanol layers. Crystallographic data was collected on a Bruker SMART CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction measurements were made at room temperature. An absorption correction by SADABS was applied to the intensity data. The structures were solved by Patterson method. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package. The crystal data and structural refinements details are listed in Table S1.

Table S1 Crystal data and structure refinement for **2-5**

	2	**3**	4	5
Empirical formula	$C_{15}H_{10.5}O_3P_{1.5}$	$C_{31}H_{22}Cl_3O_3P_3S_3$	$C_{60.5}H_{42.5}Cl_{11.5}O_6P_6Se_6$	$C_{62}H_{44}Cl_{10}O_6P_6Pd_2$
Formula weight	285.19	737.93	1578.2	1638.09
Temperature (K)	200(2)	200(2)	200(2)	298(2)
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	P-1	Pnma	P-1	P2(1)/m
a (Å)	8.664(3)	11.0433(12)	11.165(2)	9.319(2)
b (Å)	12.433(5)	16.6075(19)	12.927(3)	19.982(4)
c (Å)	13.034(5)	18.186(2)	21.775(4)	18.209(4)
α (º)	90.964(6)	90	83.949(3)	90
β (º)	90.323(6)	90	84.534(3)	92.581(4)
γ (º)	106.542(6)	90	77.702(3)	90
Volume ($Å^3$)	1345.7(9)	3335.3(6)	3044.9(10)	3387.4(13)
Z, D_{calc} (mg m^{-3})	4, 1.408	4, 1.470	2, 1.721	2, 1.606
Abs coefficient (mm^{-1})	0.265	0.639	3.879	1.116
F(000)	588	1504	1546	1632
Crystal size (mm^3)	0.23×0.20×0.20	0.16×0.12×0.10	0.16×0.15×0.12	0.12×0.10×0.10
θ range (º)	1.56-25.00	2.48-25.02	1.62-25.00	1.02- 23.71
Reflections collected	8170	19984	20584	20365
Independent reflections	4637	3040	10542	5188
Completeness to θ (%)	97.5	99.5	98.3	97.6
Max. and min. transmission	0.9489, 0.9416	0.9389, 0.9047	0.6532, 0.5757	0.8966, 0.8778
Data/restraints/params	4637/0/354	3040/6/220	10542/30/733	5188/1/383
Goodness-of-fit on F^2	1.062	1.108	1.075	1.113
R_1 and wR_2 [$I>2\sigma(I)$]	0.0672, 0.2008	0.0657, 0.2091	0.0810, 0.2066	0.1030, 0.2645
R_1 and wR_2 (all data)	0.0909, 0.2280	0.0825, 0.2237	0.1081, 0.2184	0.1176, 0.2747

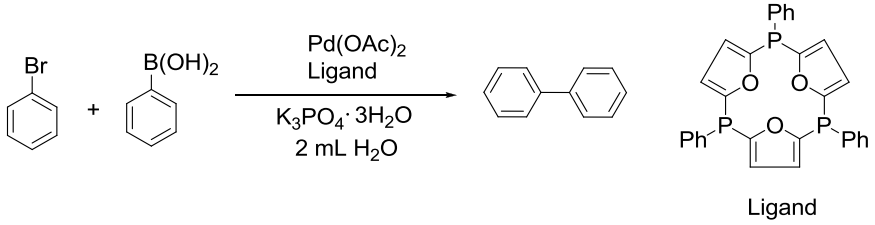
Table S2 Optimization of the reaction conditions[a]



Entry	Pd source	Phase Transfer Reagent	Temperature (℃)	Yield (%)[b]
1	$Pd(OAc)_2$	-	100	98
2	$Pd(OAc)_2$	TBAB	100	89
3	$Pd(OAc)_2$	$Me(octyl)_3N^+Cl^-$	100	97
4	$PdCl_2(CN)_2$	-	100	18
5	$PdCl_2$	-	100	53
6	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	-	100	56
7	**5**	-	100	89
8	$Pd(OAc)_2$	-	25	5
9	$Pd(OAc)_2$	-	60	58
10	$Pd(OAc)_2$	-	80	74

[a]Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol of phenylboronic acid, 1.0 mmol phase transfer reagent, 0.5 mol% $Pd(OAc)_2$, 0.5 mol% ligand, 3.0 mmol of K_3PO_4 $3H_2O$, 2.0 mL H_2O, reaction time 8 h. [b]GC yield.

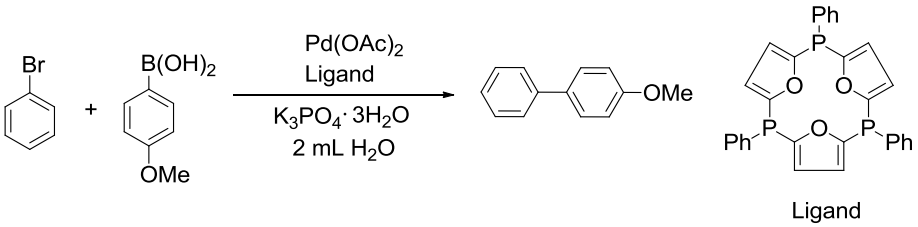
Table S3 Suzuki-Miyaura coupling reaction using ultra-low loading of catalyst[a]



Entry	Time (h)	Yield (%)[b]	TON
1	16	9	4 500 000
2	24	16	8 000 000
3	48	28	14 000 000
4	72	61	30 500 000

[a]Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol of phenylboronic acid, 2×10^{-8} mmol $Pd(OAc)_2$, 1.33×10^{-8} mmol ligand, 3.0 mmol of K_3PO_4 $3H_2O$, 2.0 mL H_2O. [b]GC yield.

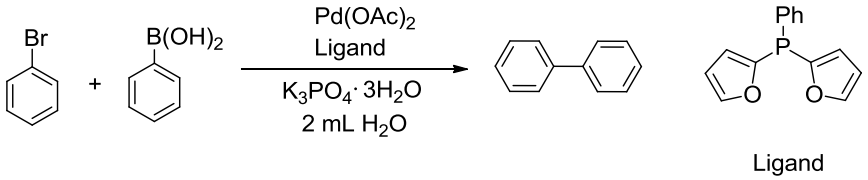
Table S4 Suzuki-Miyaura coupling reaction using ultra-low loading of catalyst[a]



Entry	Time (h)	Yield (%)[b]	TON
1	16	5	2 500 000
2	24	9	4 500 000
3	48	17	8 500 000
4	72	51	25 500 000

[a]Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol of 2-methoxy phenylboronic acid, 2×10^{-8} mmol $Pd(OAc)_2$, 1.33×10^{-8} mmol ligand, 3.0 mmol of K_3PO_4 $3H_2O$, 2.0 mL H_2O. [b]GC yield.

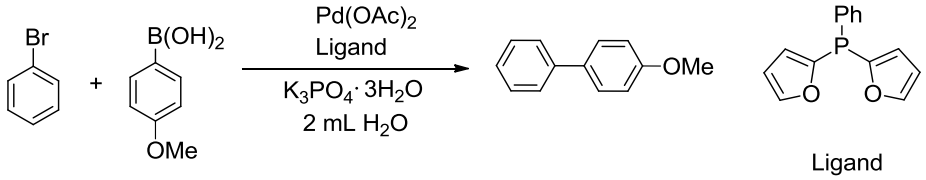
Table S5 Suzuki-Miyaura coupling reaction using ultra-low loading of catalyst[a]



Entry	Time (h)	Yield (%)[b]	TON
1	16	15	7 500 000
2	24	20	10 000 000
3	48	26	13 000 000
4	72	30	15 000 000

[a]Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol of phenylboronic acid, 2×10^{-8} mmol $Pd(OAc)_2$, 4×10^{-8} mmol ligand, 3.0 mmol of K_3PO_4 $3H_2O$, 2.0 mL H_2O. [b]GC yield.

Table S6 Suzuki-Miyaura coupling reaction using ultra-low loading of catalyst[a]



Entry	Time (h)	Yield (%)[b]	TON
1	16	8	4 000 000
2	24	14	7 000 000
3	48	21	11 500 000
4	72	32	16 000 000

[a]Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol of phenylboronic acid, 2×10^{-8} mmol $Pd(OAc)_2$, 1.33×10^{-8} mmol ligand, 3.0 mmol of K_3PO_4 $3H_2O$, 2.0 mL H_2O.
[b]GC yield.

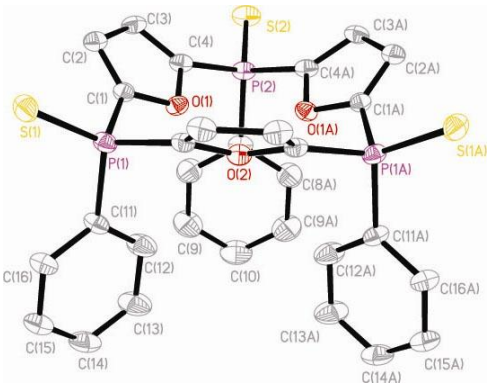


Figure S1 Molecular structure of **3** with 30% probability level ellipsoids.

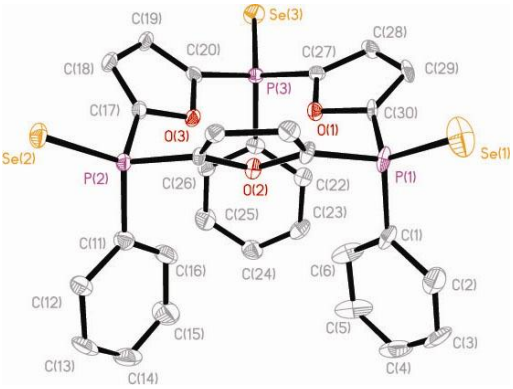


Figure S2 Molecular structure of **4** with 30% probability level ellipsoids.

Figure S3 A Chinese Bronze Tripod. The molecular structures of **2-4** look like an ancient cauldron with three legs

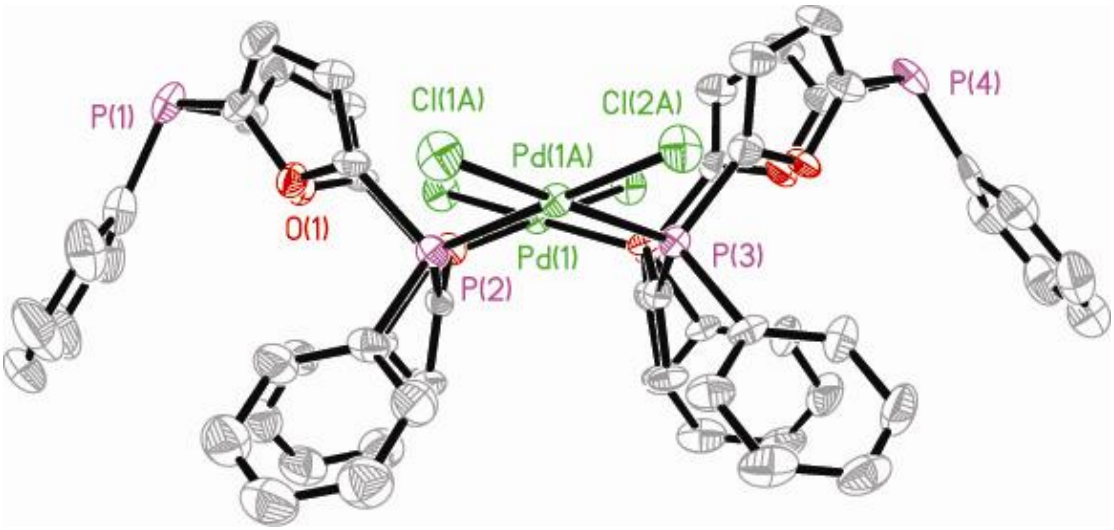
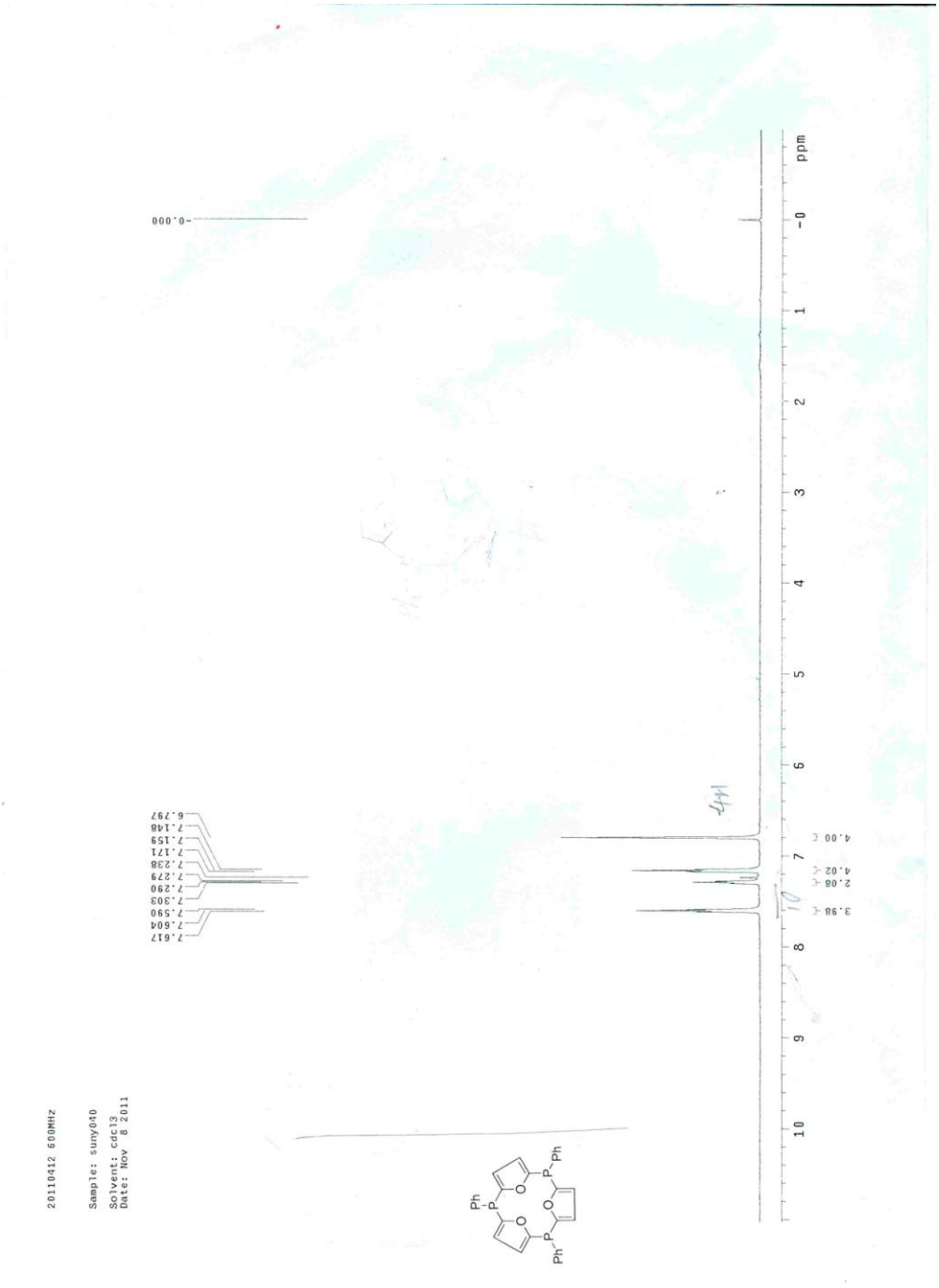
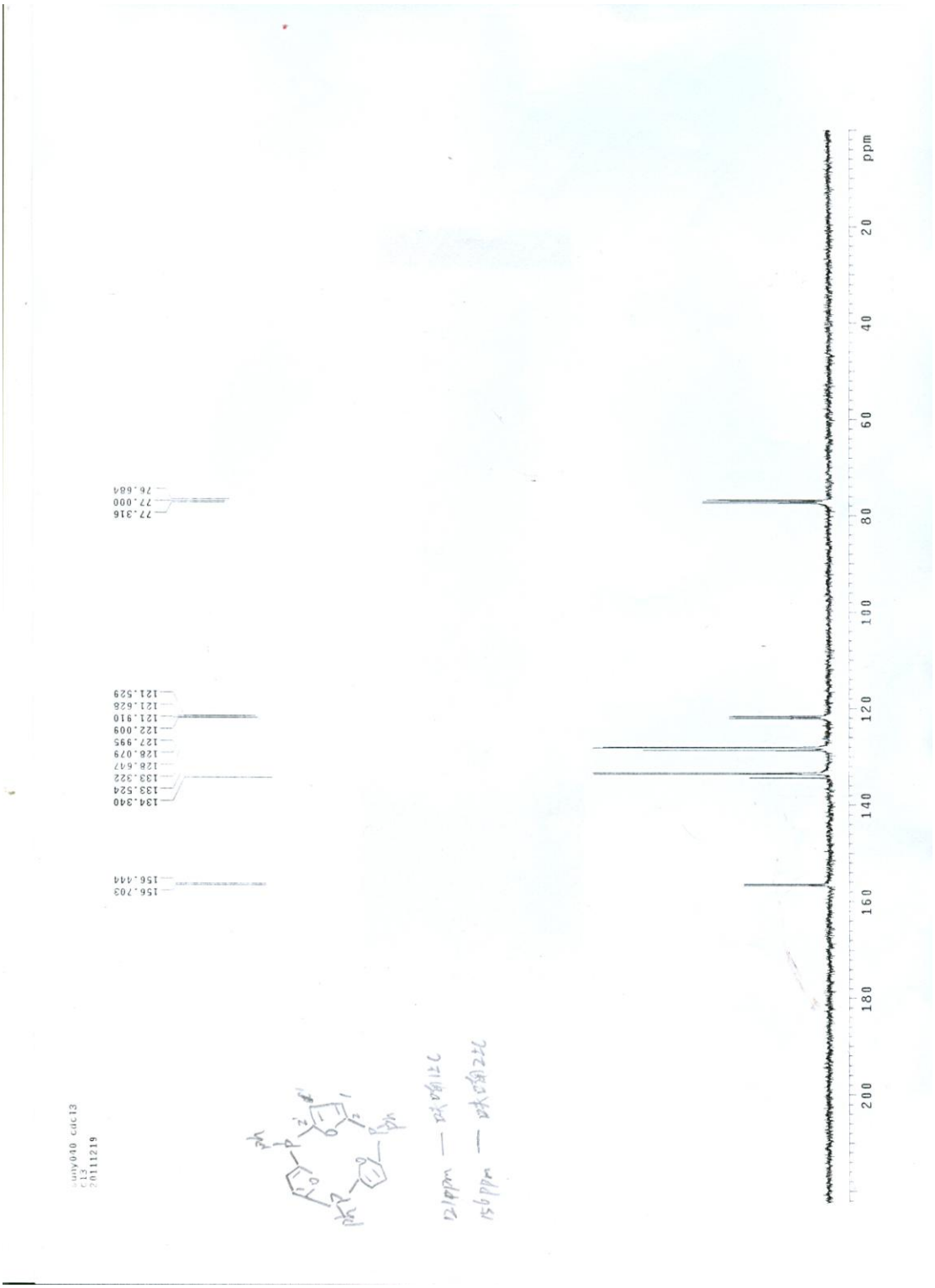


Figure S4 Molecular structure of **5** with 30% probability level ellipsoids.

Figure S5 Si Muwu square vessel (an ancient cauldron with four legs). The molecular structure of **5** looks like an ancient cauldron with four legs

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of compounds 1-5 and C

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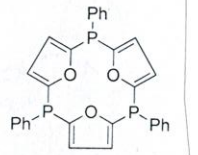

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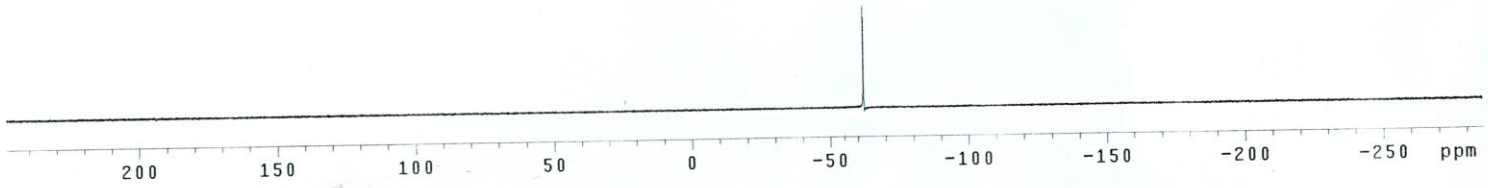

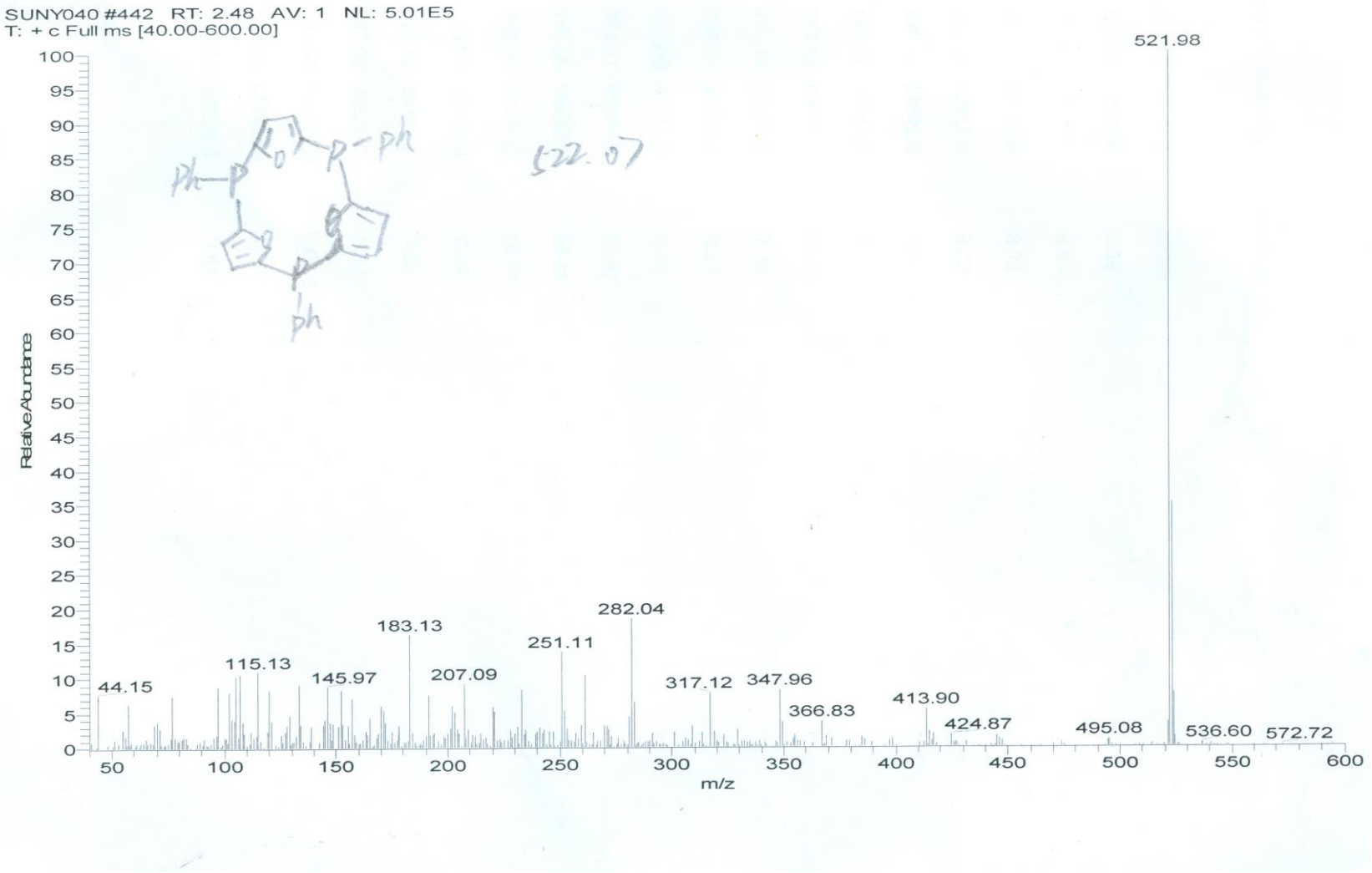
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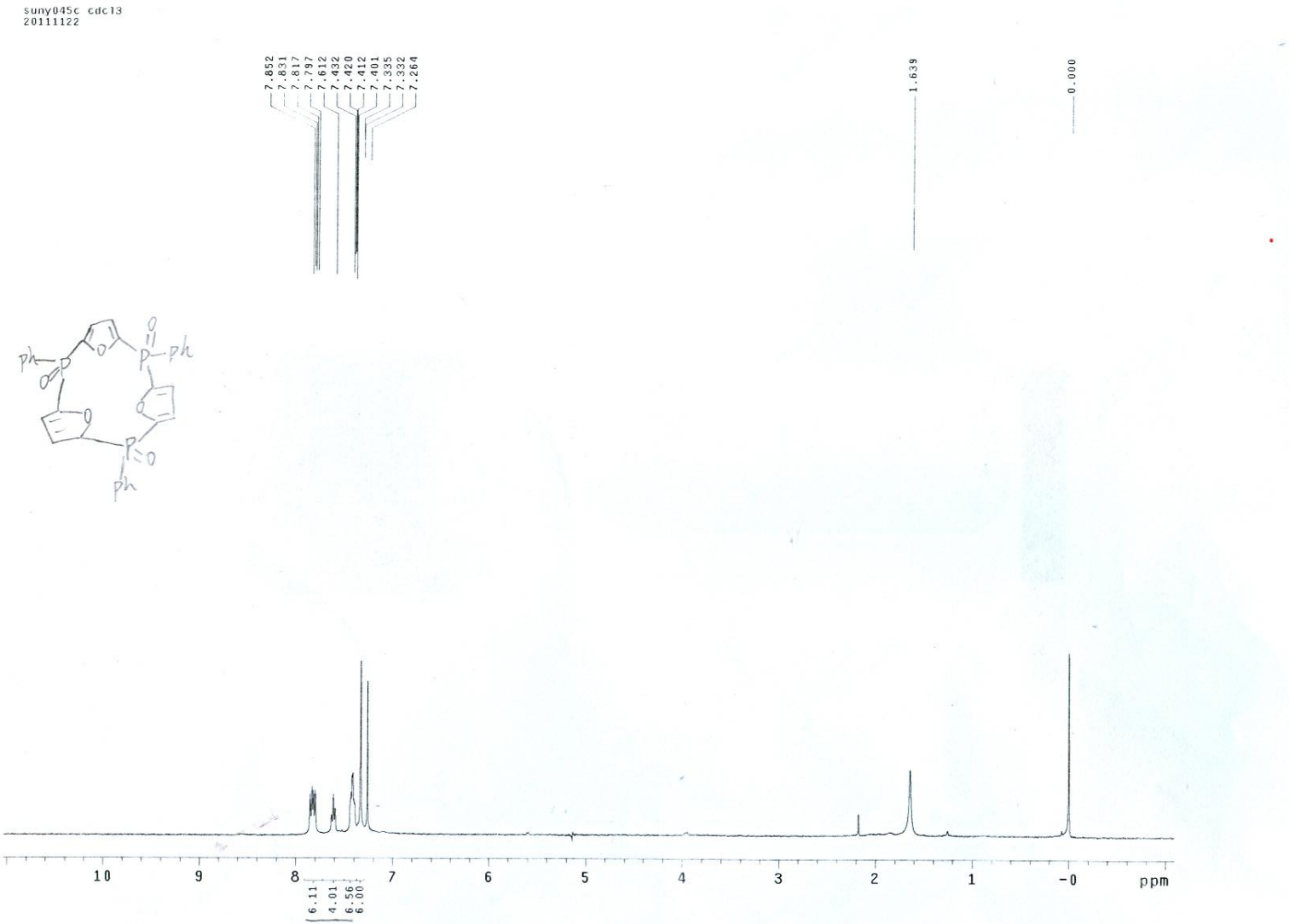
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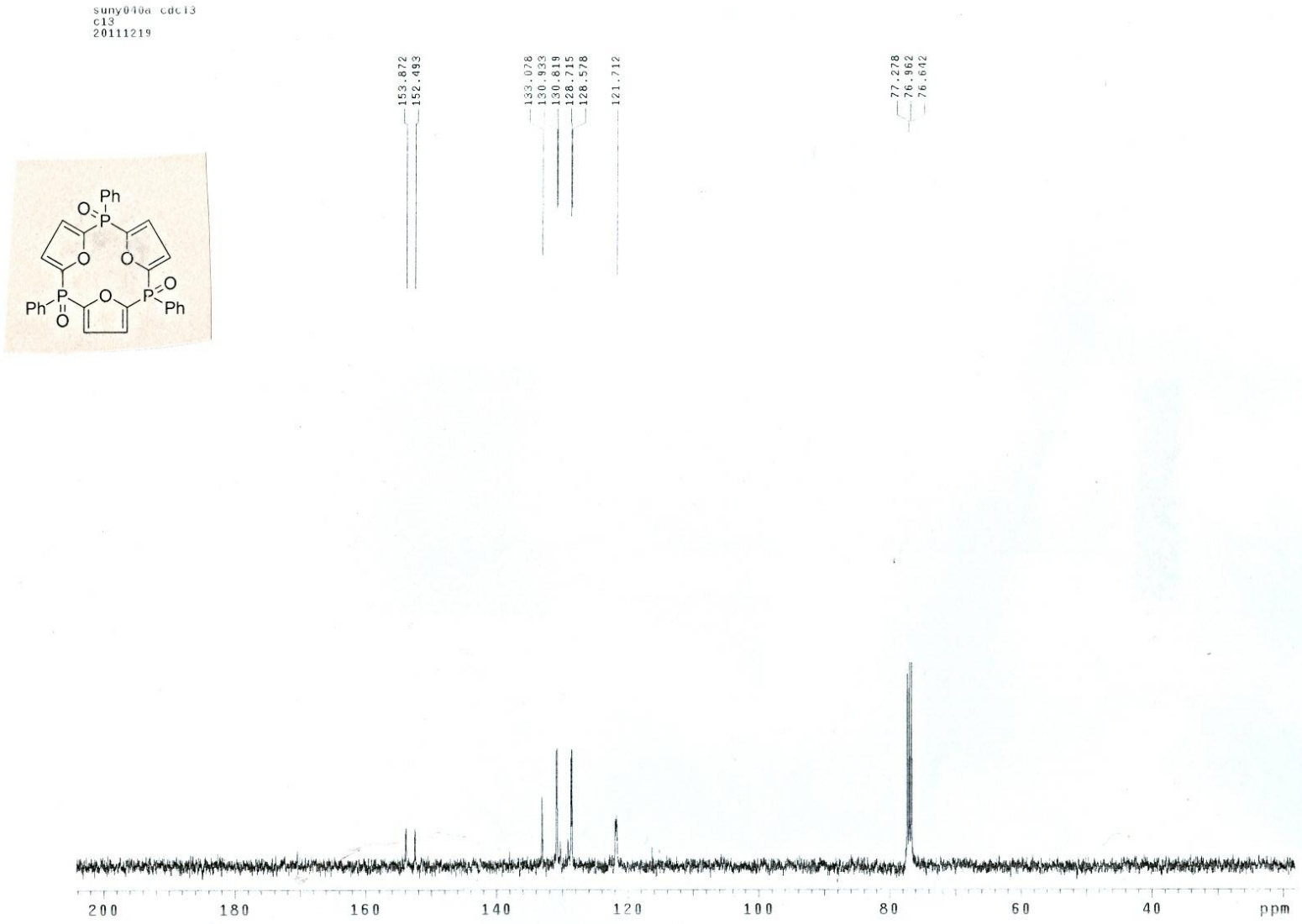
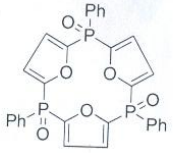
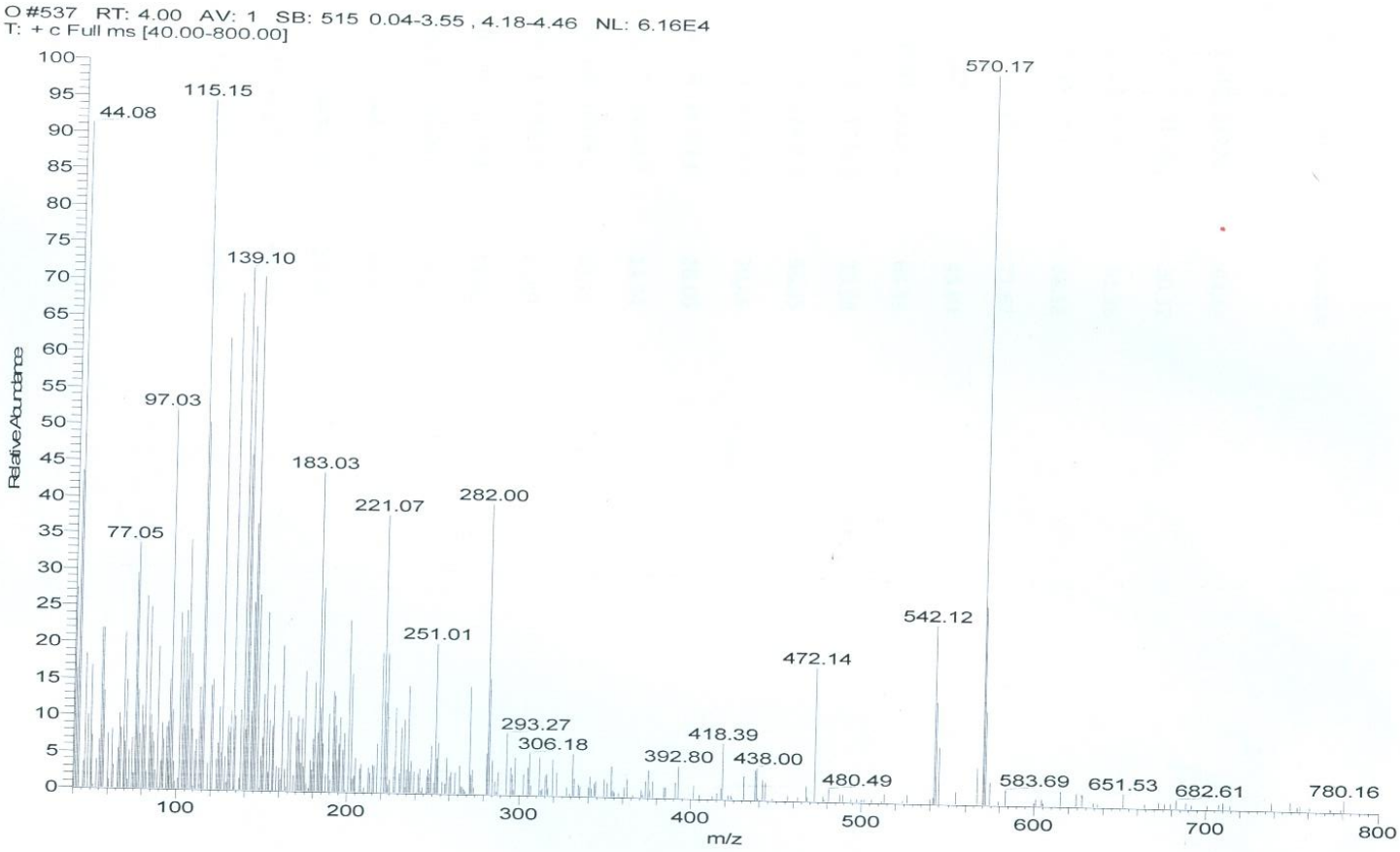
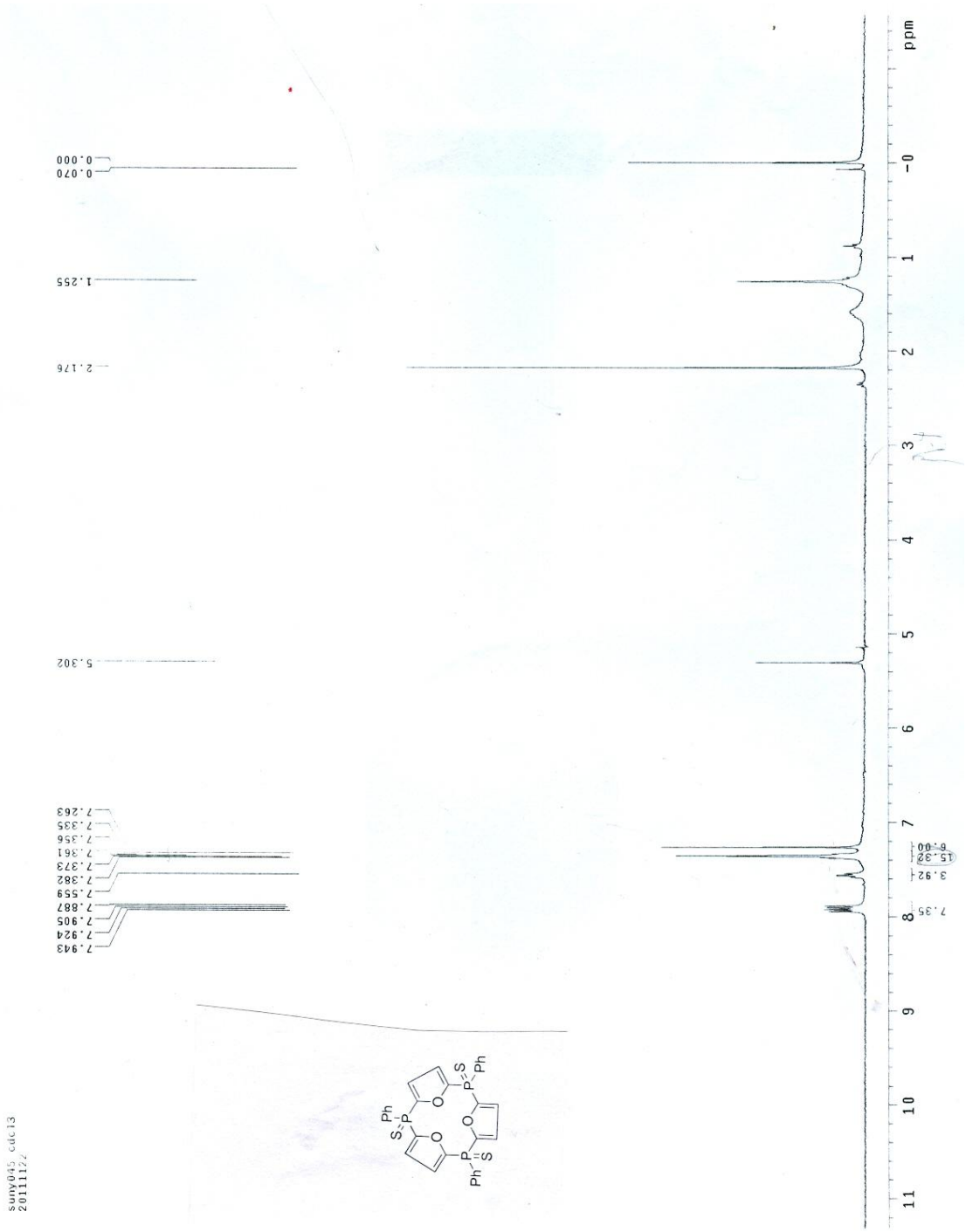
1
-0
ppm
6.11
4.01
6.56
6.00


suny040a cdcl3
c13
20111219
153.872
152.493
133.078
130.933
130.819
128.715
128.578
121.712
77.278
76.962
76.642
Ph
O
P
O
O
O
P
O
P
Ph
Ph
P
O
200
180
160
140
120
100
80
60
40
ppm

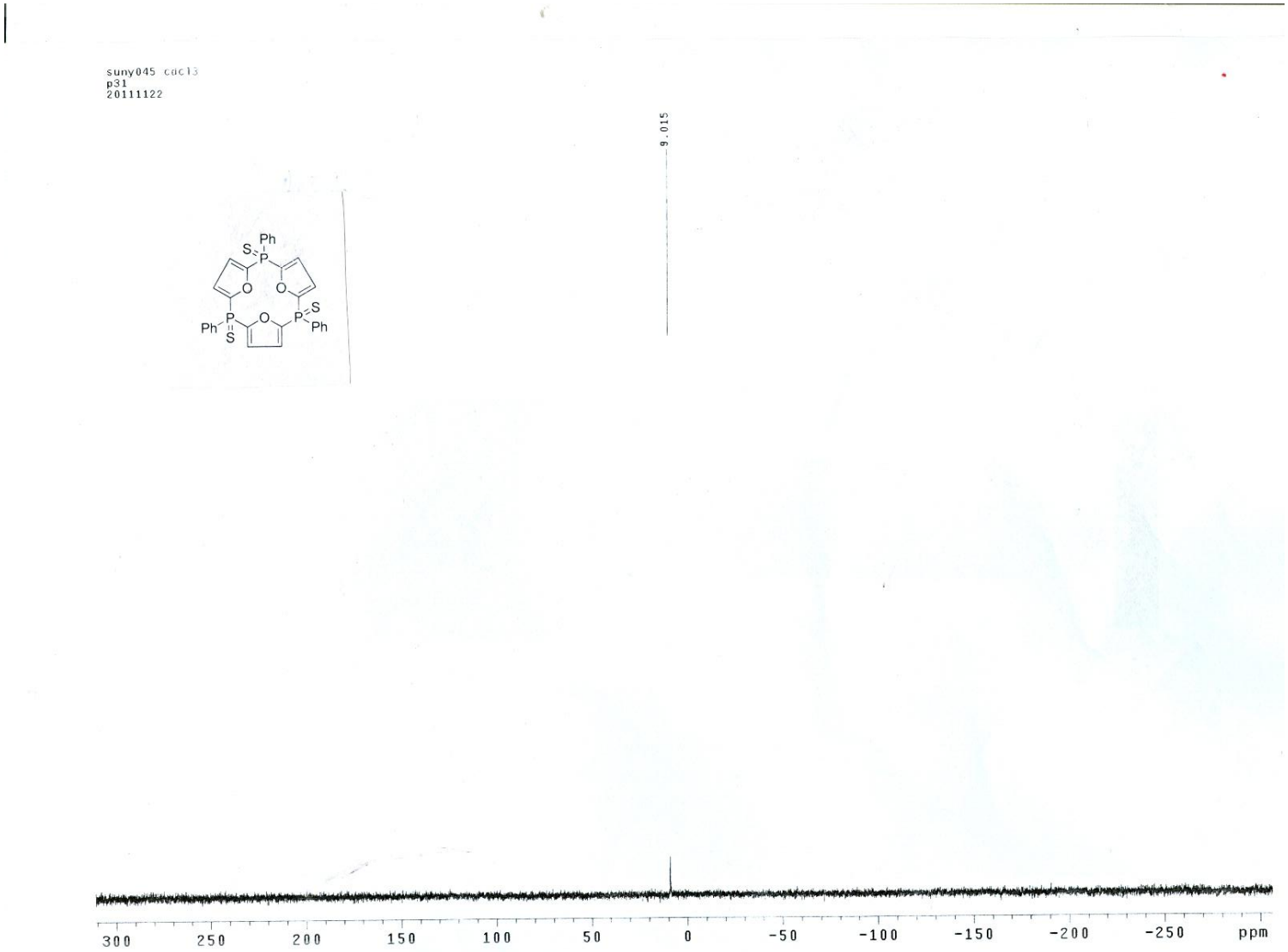
sunyu45c p31
20111122
2.619
Ph
O
P
O
Ph
O
O
P
O
Ph
O
P
O
Ph
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
ppm

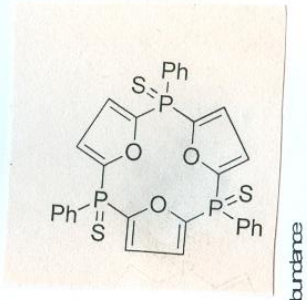

Ph
O
P
O
O
O
P
O
Ph
Ph
P
O
O
P
O
Ph

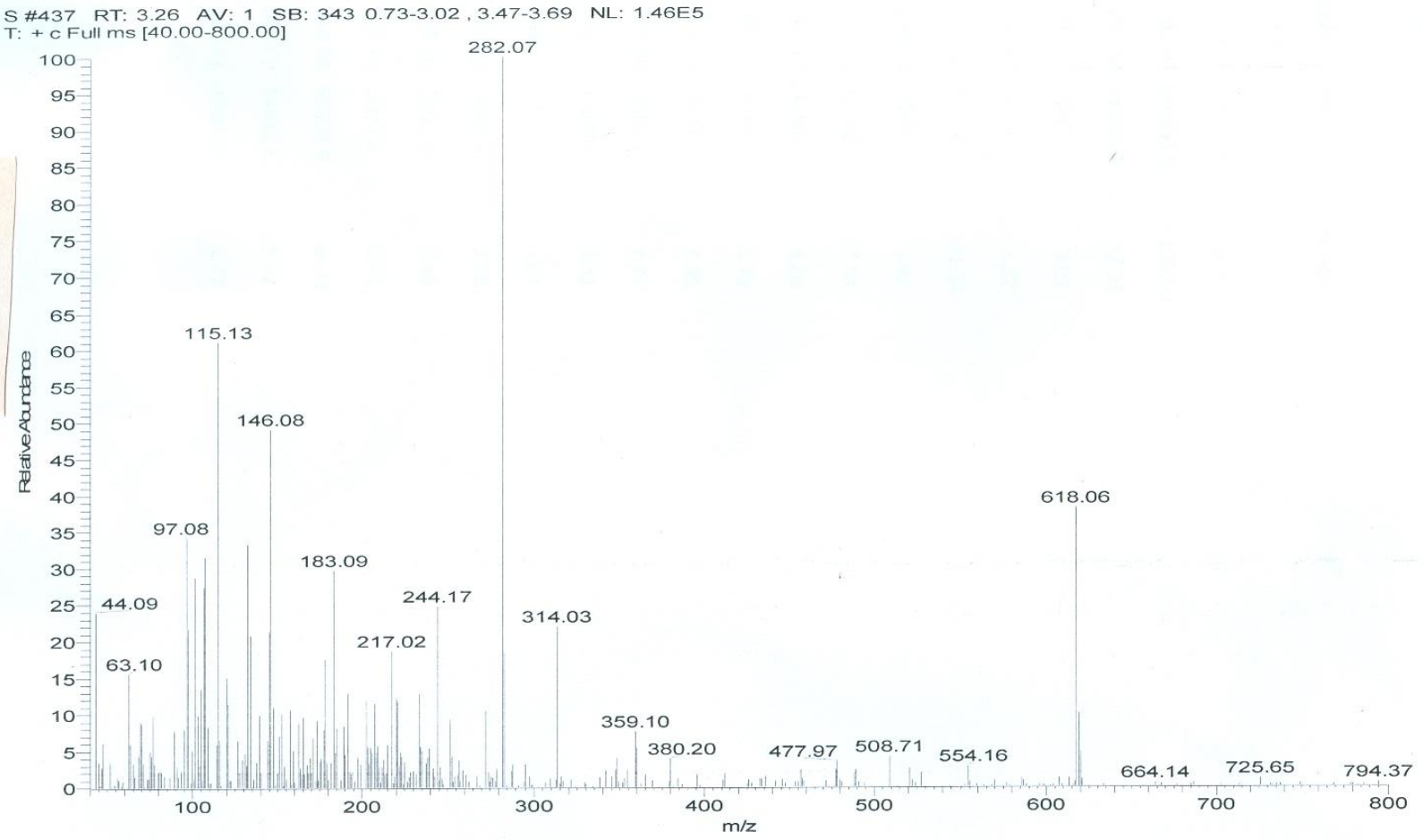

O #537 RT: 4.00 AV: 1 SB: 515 0.04-3.55 , 4.18-4.46 NL: 6.16E4
T: + c Full ms [40.00-800.00]
Relative Abundance
m/z
44.08
115.15
139.10
97.03
183.03
221.07
282.00
77.05
251.01
293.27
306.18
392.80
418.39
438.00
472.14
480.49
542.12
570.17
583.69
651.53
682.61
780.16


suny045 cdcl3
20111122
0.000
0.070
1.255
2.176
5.302
7.263
7.335
7.356
7.361
7.373
7.382
7.559
7.887
7.905
7.924
7.943
15.32
6.00
3.92
7.35
ppm
Ph
S
P
O
P
S
Ph

suny040b cdcl3
c13
20111220
155.141
154.024
153.982
132.389
131.139
131.021
130.895
128.647
128.510
122.782
122.695
122.569
122.478
77.320
77.000
76.684
Ph
S
P
O
Ph
S
P
O
O
P
S
Ph
ppm
200
180
160
140
120
100
80
60
40
20


suny045 cdcl3
p31
20111122
9.015
Ph
S
P
O
O
P
S
Ph
Ph
S
P
O
O
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
ppm


Ph
S
P
O
O
Ph
P
S
O
P
S
Ph


S #437 RT: 3.26 AV: 1 SB: 343 0.73-3.02 , 3.47-3.69 NL: 1.46E5
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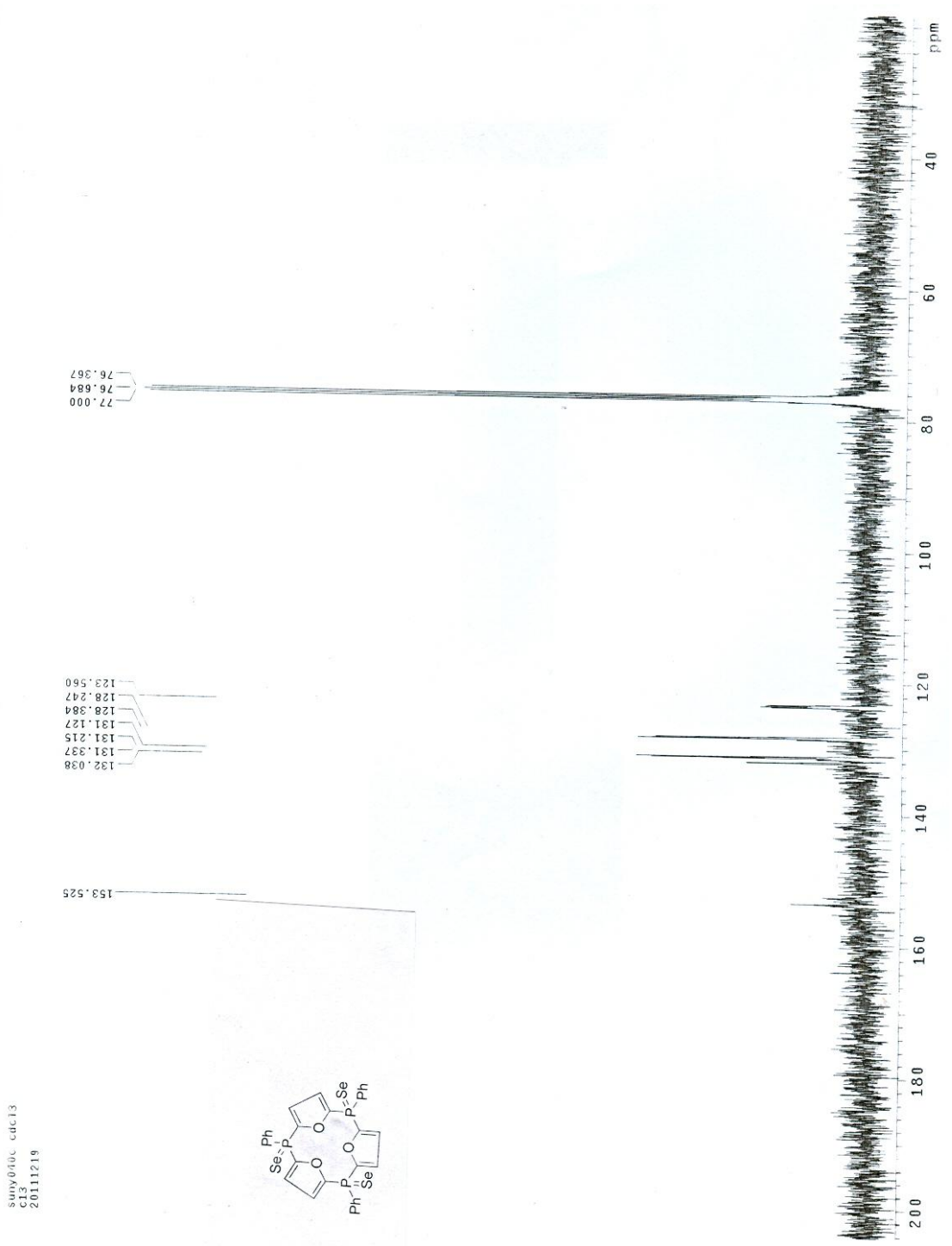
Relative Abundance
m/z
282.07
115.13
146.08
618.06
97.08
183.09
244.17
314.03
44.09
217.02
63.10
359.10
380.20
477.97
508.71
554.16
664.14
725.65
794.37


sunyc40c cdcl3
20111219
-0.084
-0.000
1.615
2.180
5.305
7.182
7.265
7.329
7.336
7.348
7.414
7.419
7.424
7.432
7.520
7.537
7.554
7.604
7.819
7.832
7.850
7.869
7.888
7.907
Se
Ph
P
O
ppm
3.54
6.00
2.54
6.02


sunyd4dc cdcl3
c13
20111219
153.525
132.038
131.337
131.215
131.127
128.384
128.247
123.560
77.000
76.684
76.367
Ph
Se
P
O
Se
Ph
ppm
200
180
160
140
120
100
80
60
40

suny beisan cc14//20120602
31P NMR
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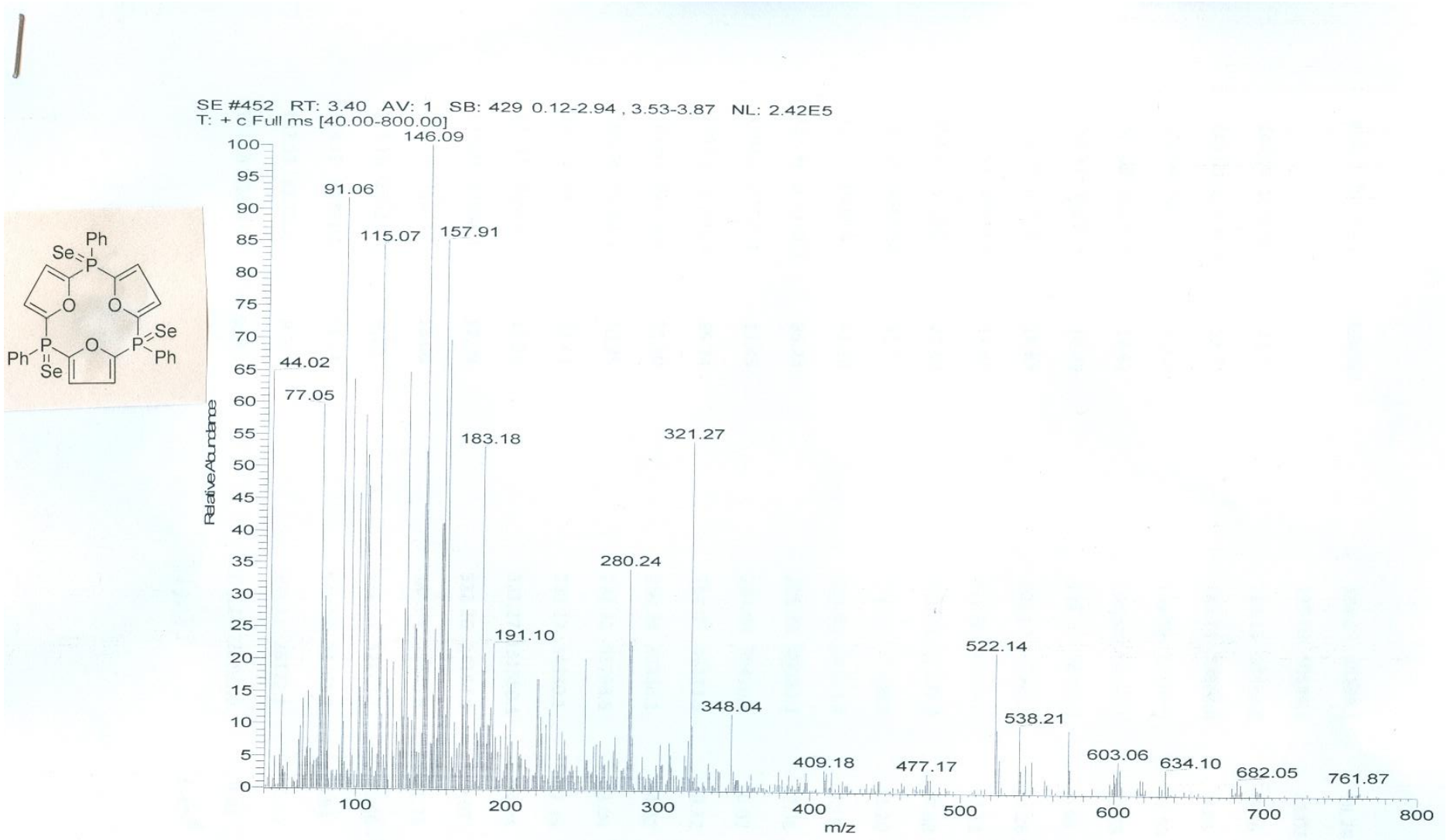
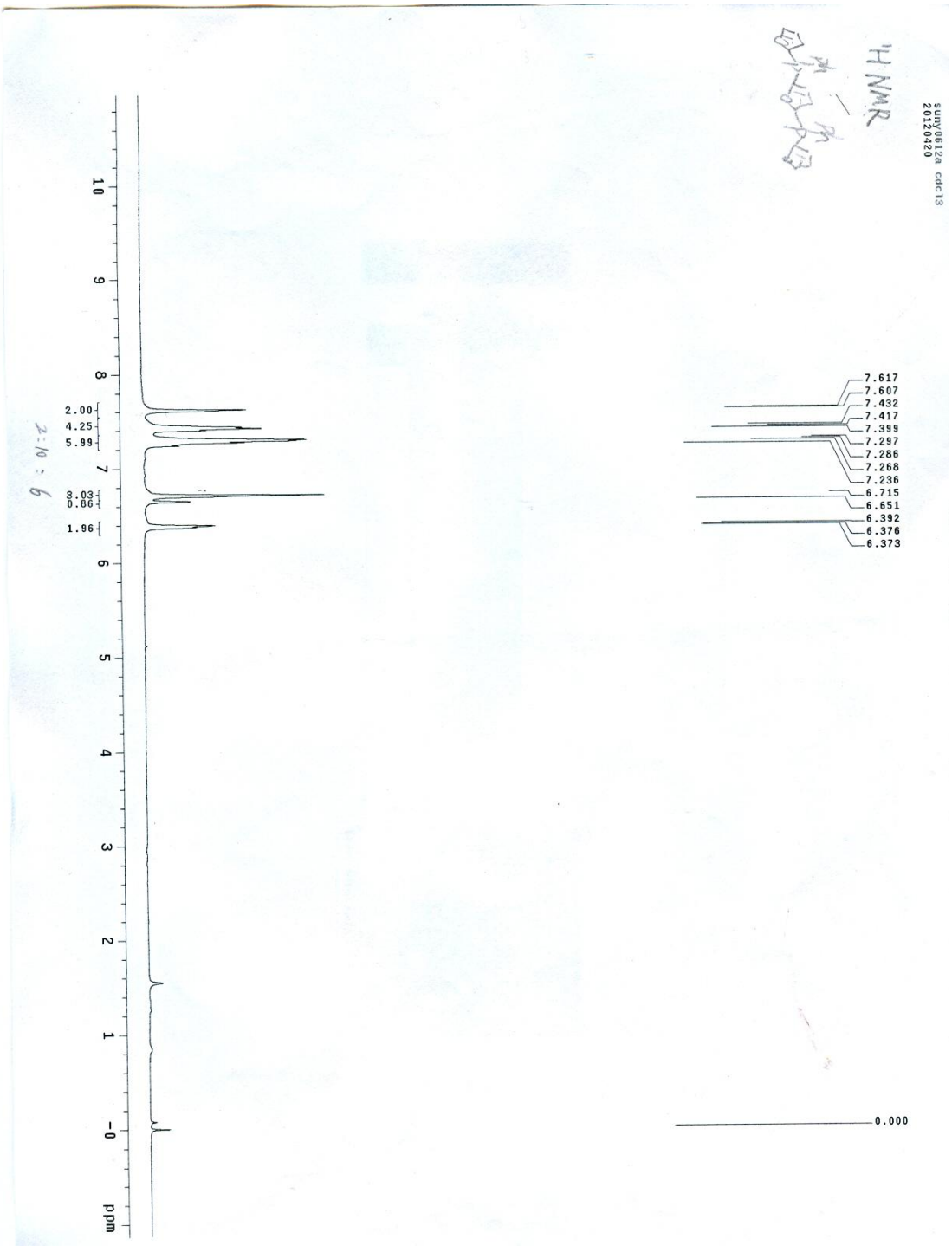
-2.638
ppm


SE #452 RT: 3.40 AV: 1 SB: 429 0.12-2.94 , 3.53-3.87 NL: 2.42E5
T: + c Full ms [40.00-800.00]
Relative Abundance
m/z
146.09
91.06
115.07
157.91
44.02
77.05
183.18
321.27
280.24
191.10
522.14
348.04
538.21
409.18
477.17
603.06
634.10
682.05
761.87
Ph
Se
P
O
Se
Ph
P
Se
Ph
P
O
Se
Ph


sunv0612a cdcl3
20120420
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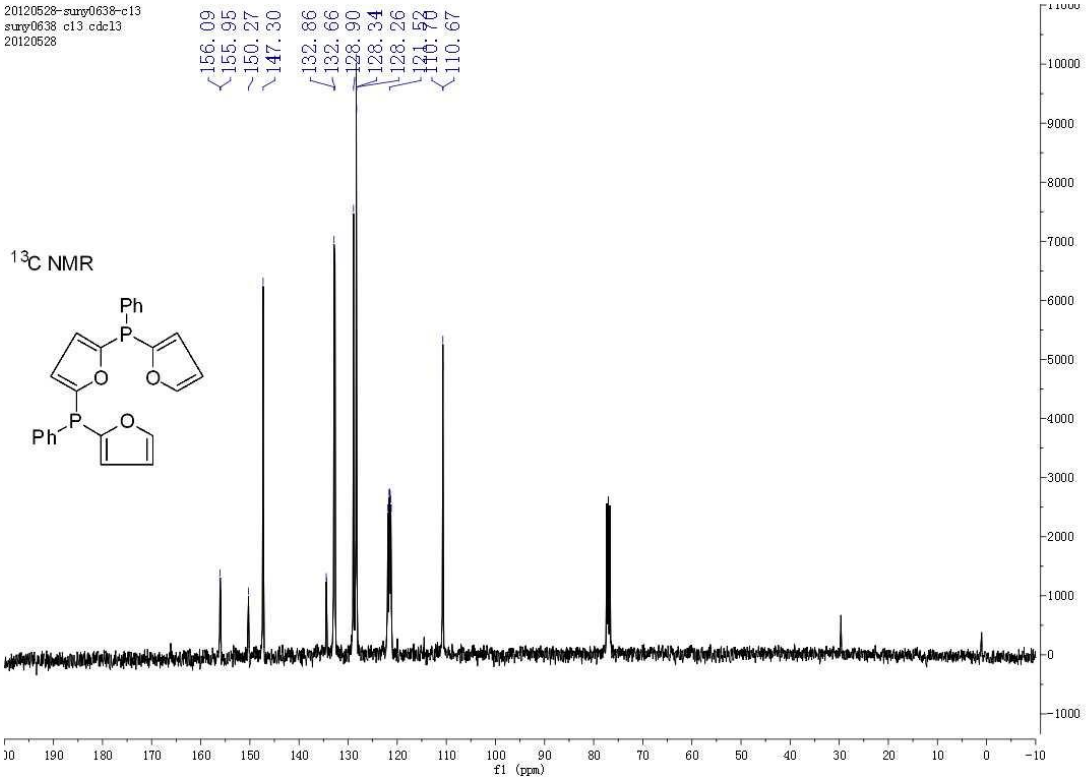
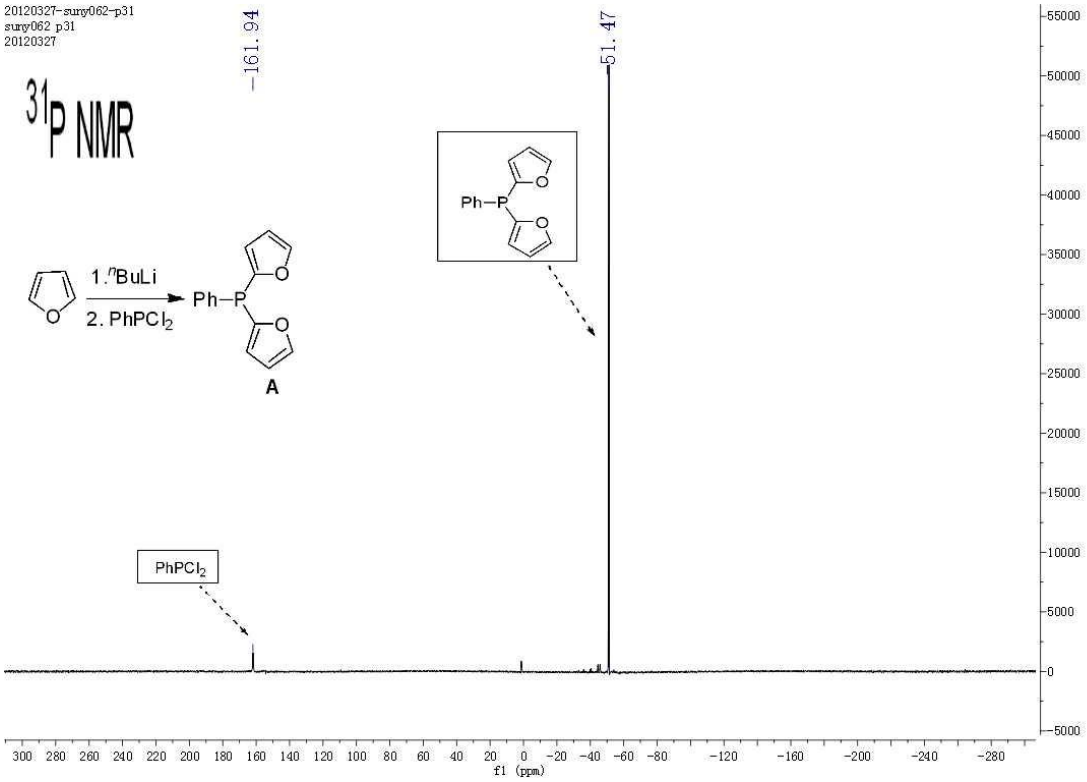
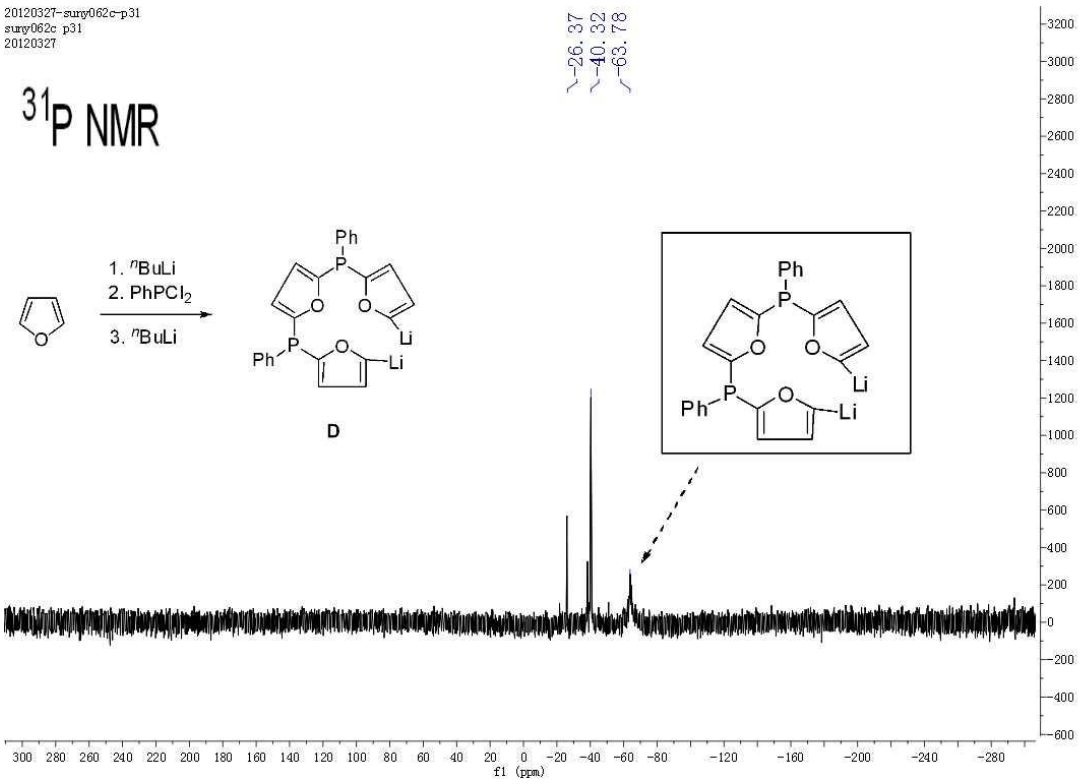
7.607
7.432
7.417
7.399
7.297
7.286
7.268
7.236
6.715
6.651
6.392
6.376
6.373
0.000
2.00
4.25
5.99
3.03
0.86
1.96
ppm

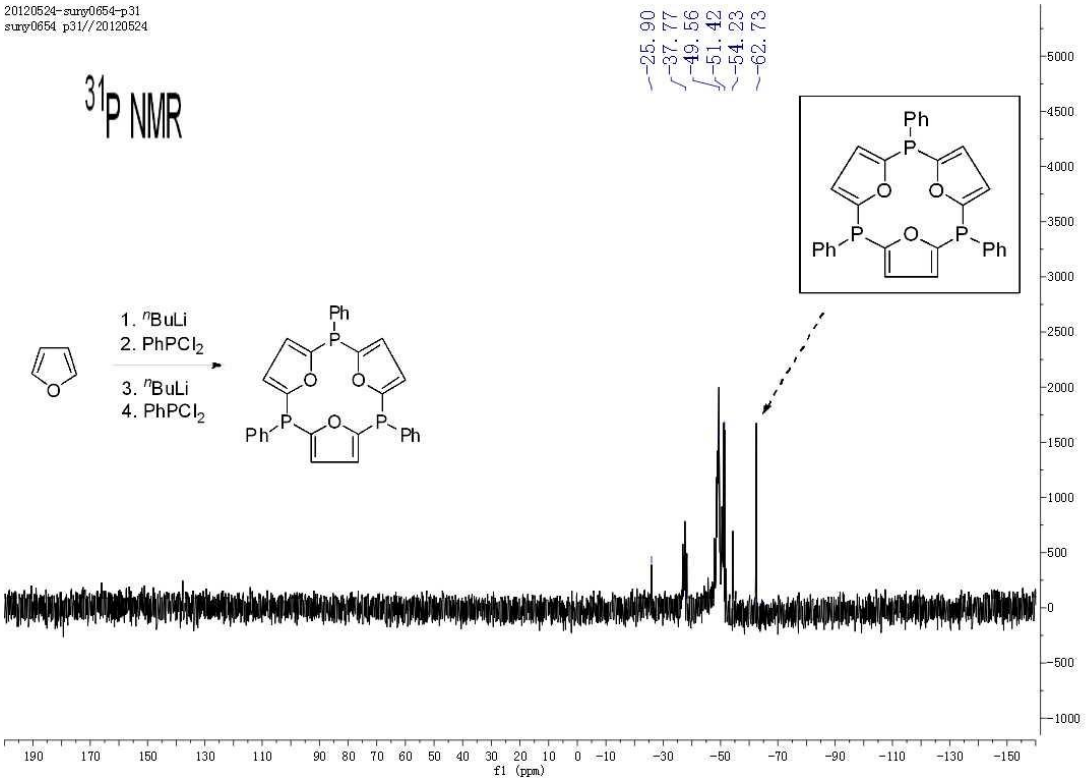

20120528-sunv0638-c13
sunv0638 c13 cdcl3
20120528
156.09
155.95
150.27
147.30
132.86
132.66
128.90
128.34
128.26
121.52
110.67
13C NMR
Ph
P
O
O
P
Ph
O
f1 (ppm)

sunv065c cdcl3
p31
20120329
31 P NMR
-53.045
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
ppm

^{31}P NMR spectra of the reaction mixture about possible mechanism for the formation of 1.

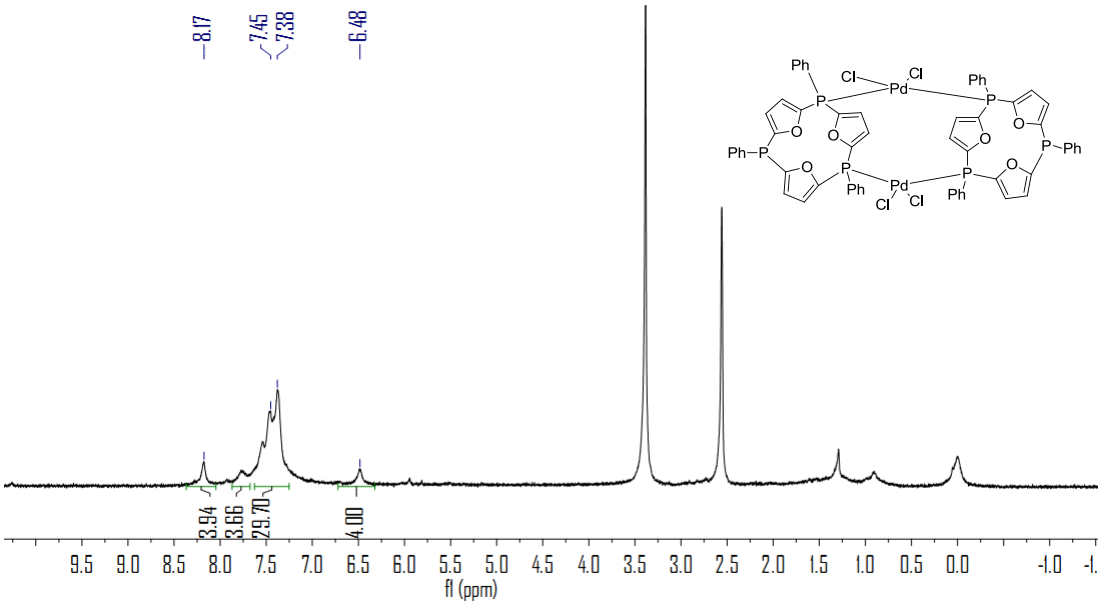




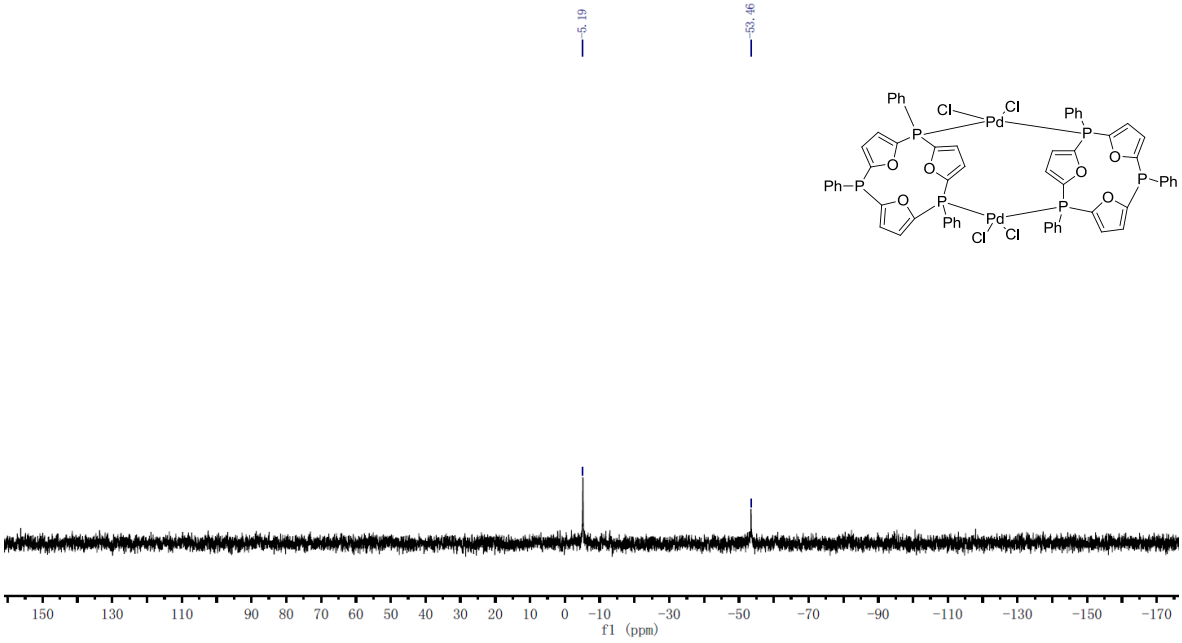


^{1}H NMR and ^{13}P NMR spectra of 5

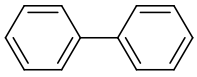
^{1}H NMR of 5 (400 MHz, DMSO-d_6)



^{13}P NMR of 5 (162 MHz, DMSO-d_6)

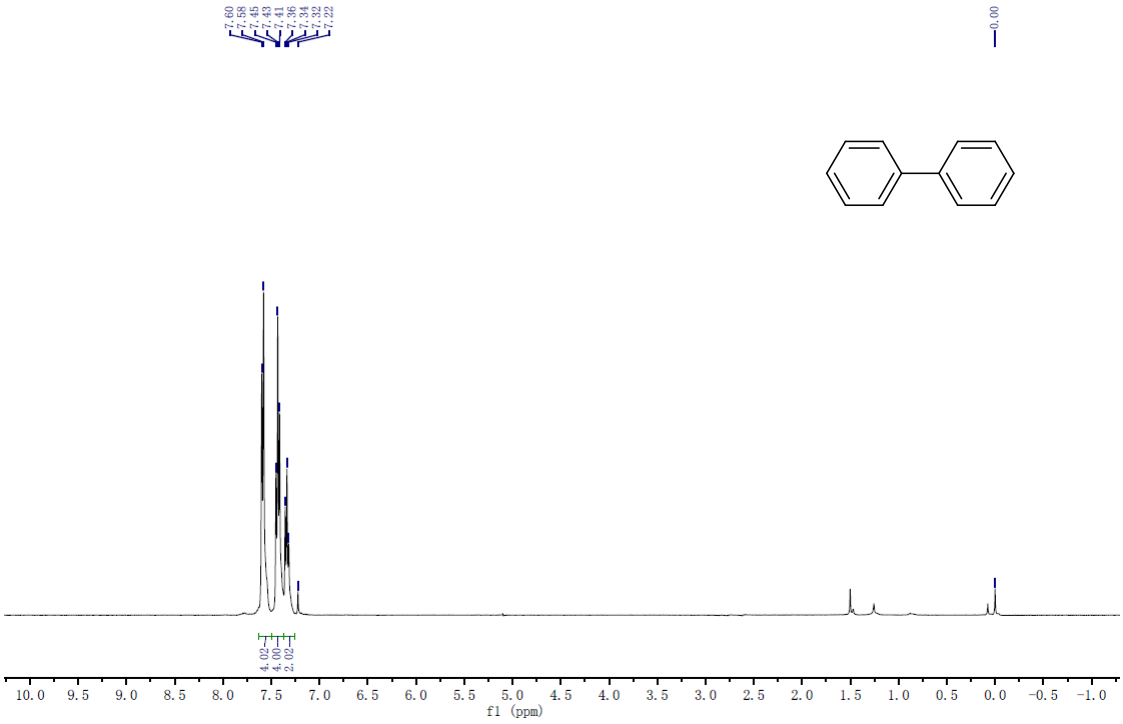


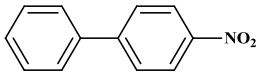
^{1}H NMR spectra of Suzuki-Miyaura coupling Products



1,1'-biphenyl,

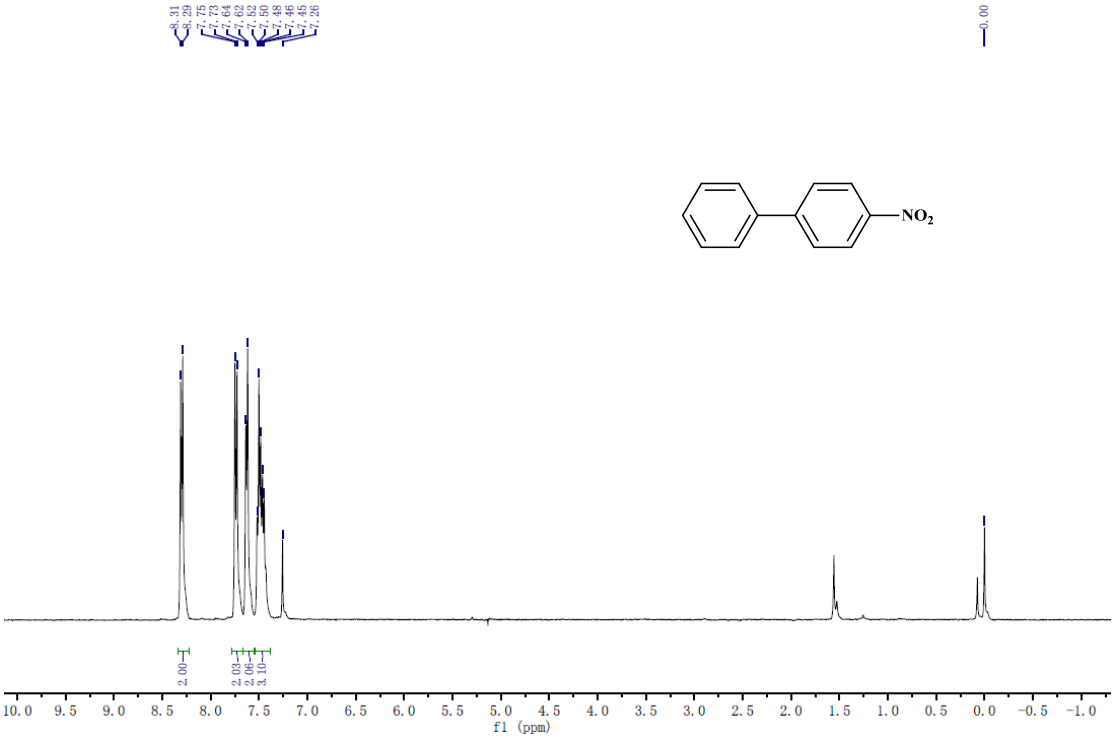
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 4H), 7.43 (t, J = 8.0 Hz, 4H), 7.34 (t, J = 8.0 Hz, 2H) ppm. Data is consistent with that reported in the literature.[1]

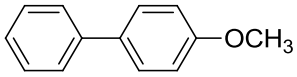




4-nitro-1,1'-biphenyl,

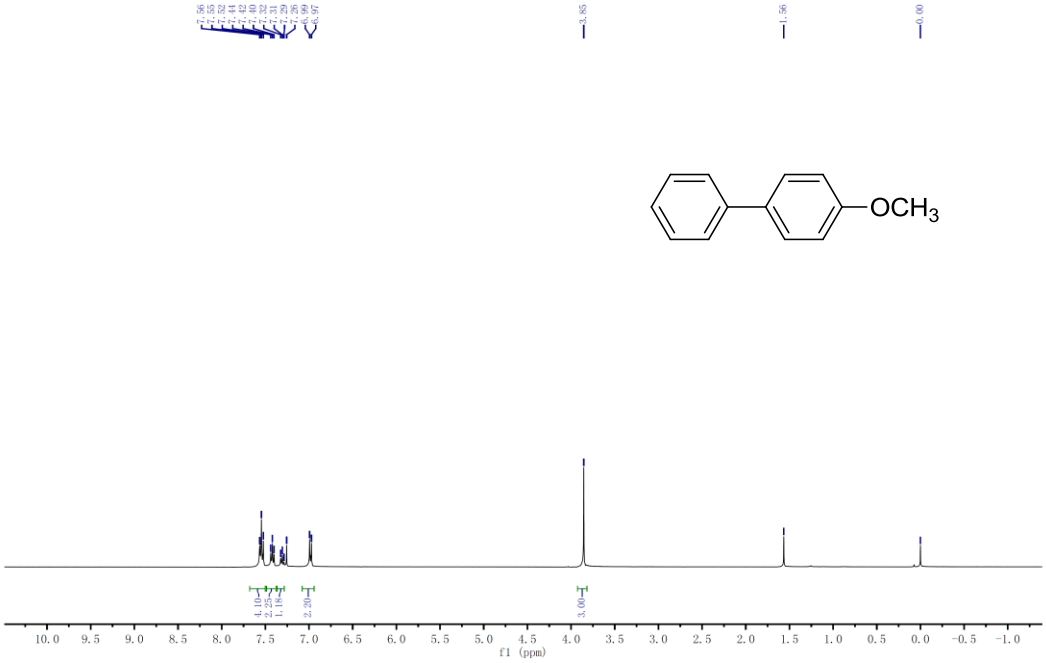
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.50-7.45 (m ,3H) ppm. Data is consistent with that reported in the literature.[2]

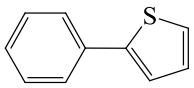




4-Methoxybiphenyl,

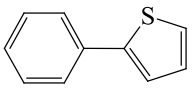
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 4H), 7.40 (t, J = 6.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H) ppm. Data is consistent with that reported in the literature.[3]

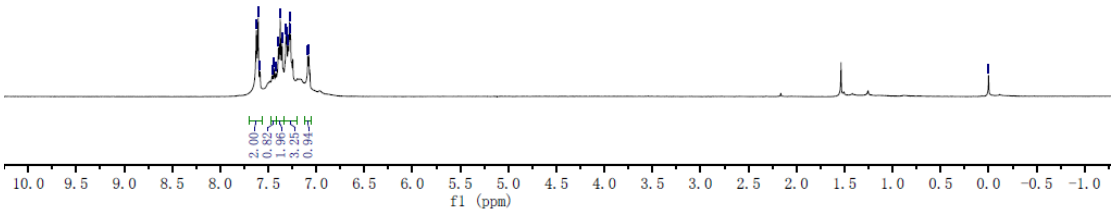


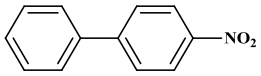


2-phenylthiophene,

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 2H), 7.39-7.27 (m, 5H), 7.09 (d, J = 4.0 Hz, 1H) ppm. Data is consistent with that reported in the literature.[4]

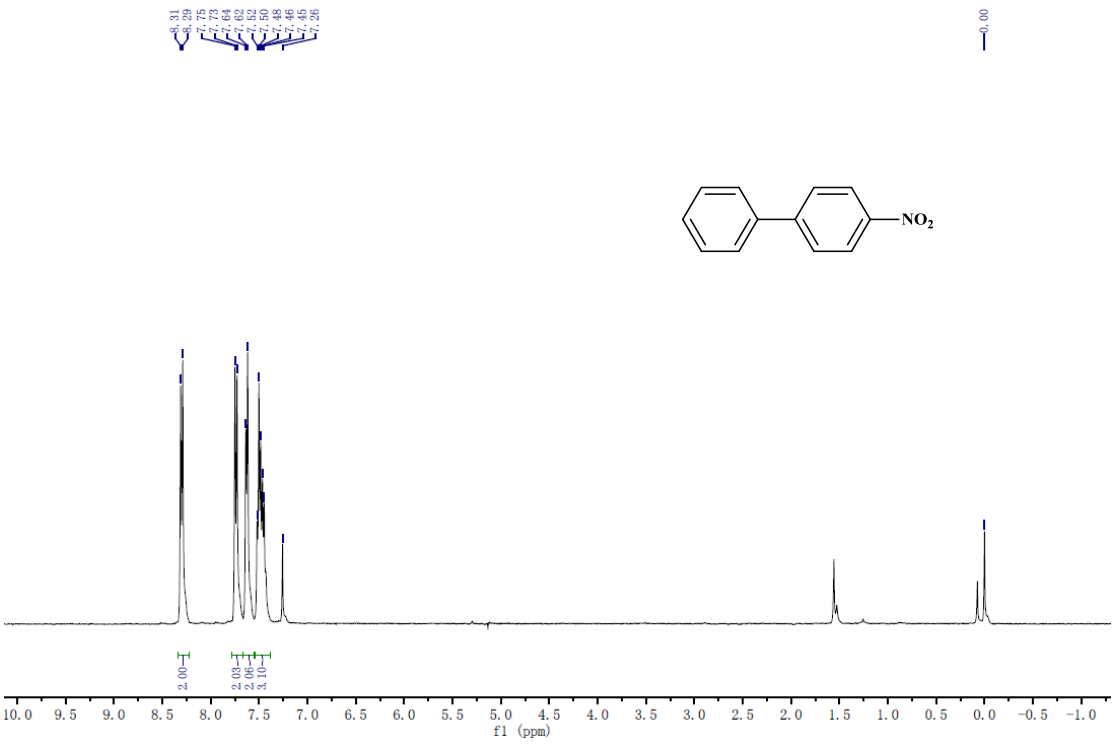


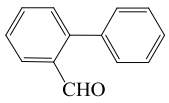




4-nitro-1,1'-biphenyl,

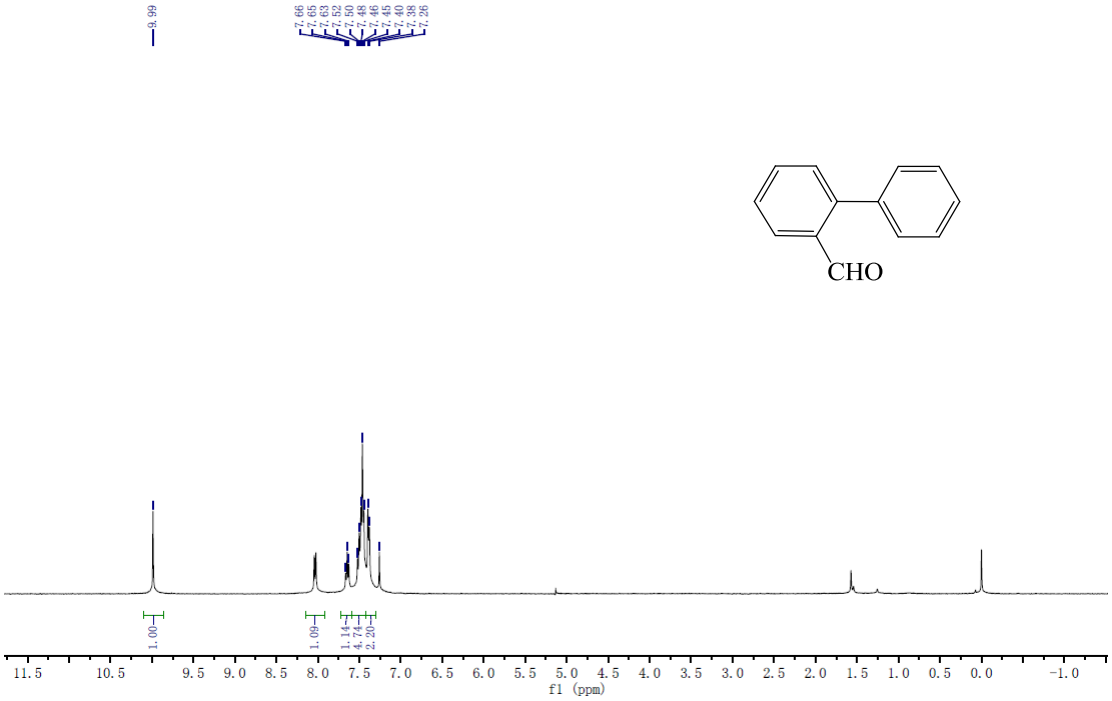
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.50-7.45 (m ,3H) ppm. Data is consistent with that reported in the literature.[2]



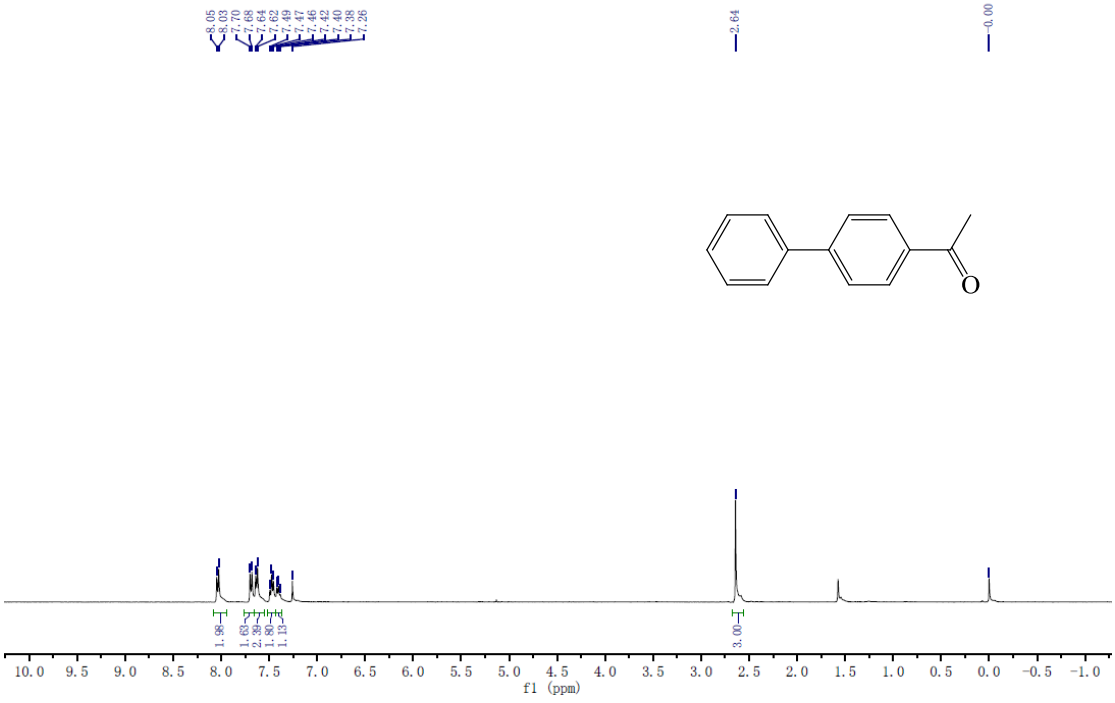


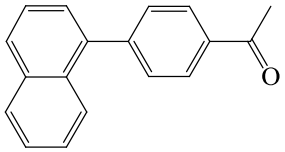
[1,1'-biphenyl]-2-carbaldehyde,

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 6.0 Hz, 1H), 7.52-7.45 (m, 5H), 7.39 (d, J = 8.0 Hz, 2H). Data is consistent with that reported in the literature.[5]



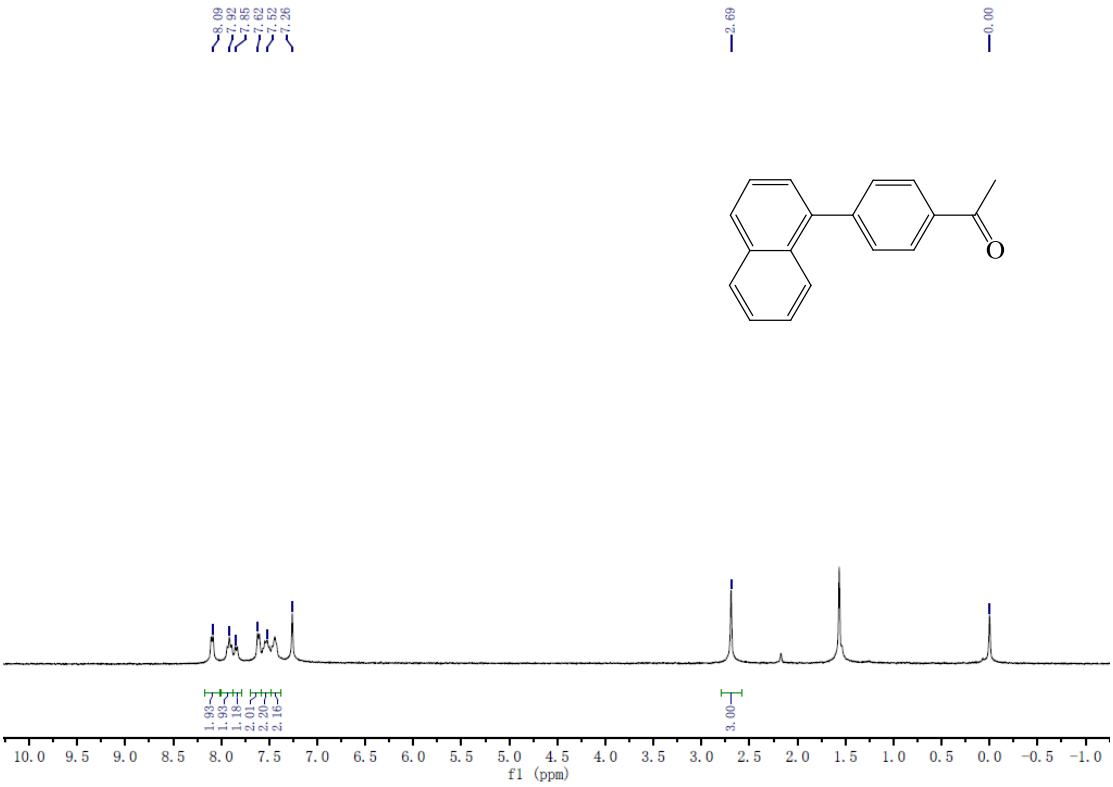
1-([1,1'-biphenyl]-4-yl)ethanone,
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 6.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 2.64 (s, 3H). Data is consistent with that reported in the literature.[6]

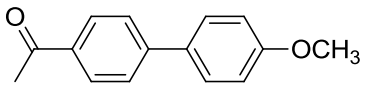




1-(4-(naphthalen-1-yl)phenyl)ethanone,

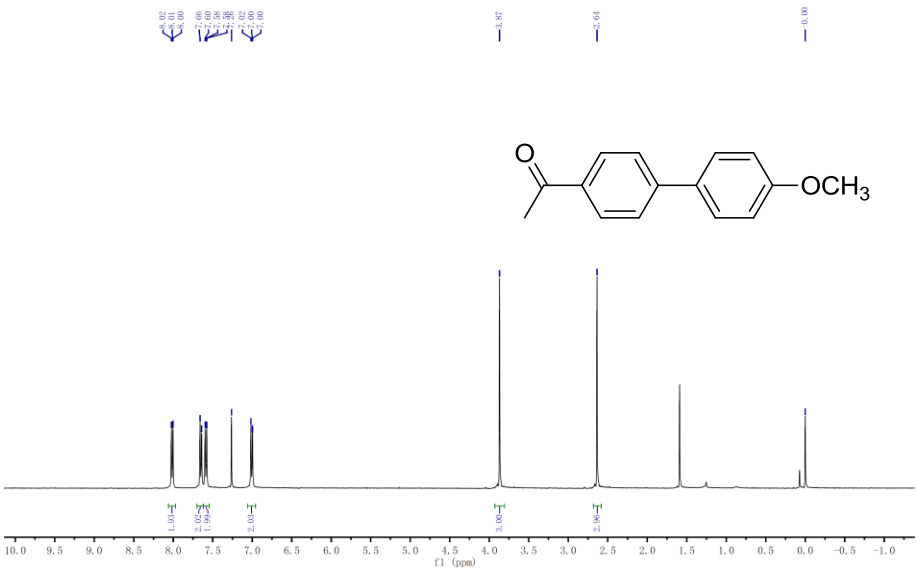
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (br, 2H), 7.92 (br, 2H), 7.85 (br, 1H), 7.62 (br, 2H), 7.52 (br, 2H), 2.69 (s, 3H). Data is consistent with that reported in the literature.[7]

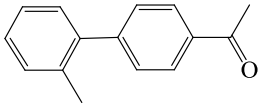




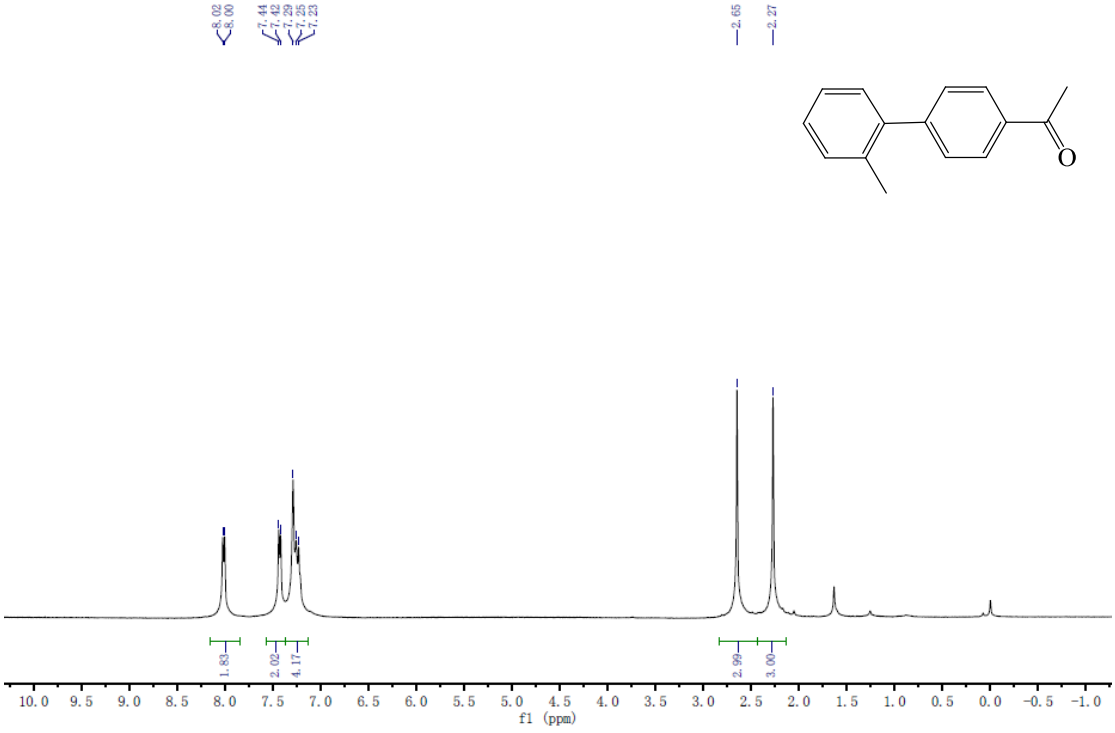
1-(4’-Methoxy-[1, 1’-biphenyl]-4-yl) ethanone,

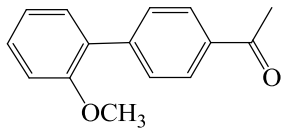
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 7.2 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H) ppm. Data is consistent with that reported in the literature.[8]



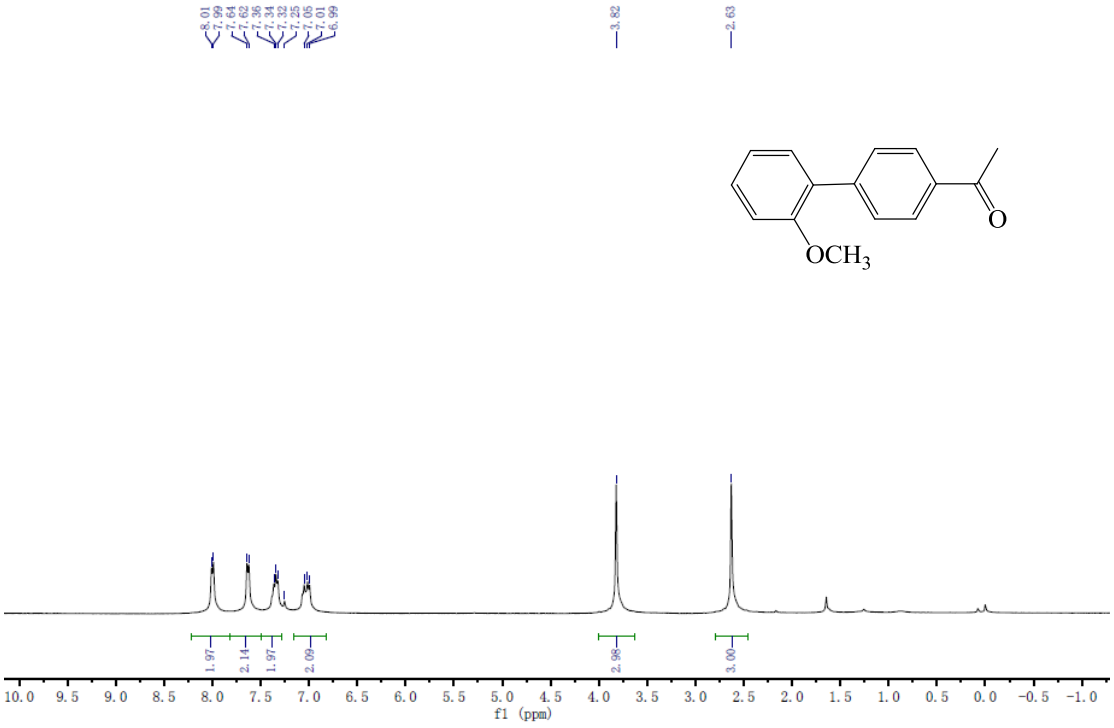


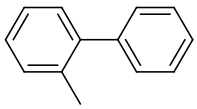
1-(2'-methyl-[1,1'-biphenyl]-4-yl)ethanone,
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.29-7.23 (m, 4H), 2.65 (s, 3H), 2.27 (s, 3H). Data is consistent with that reported in the literature.[9]





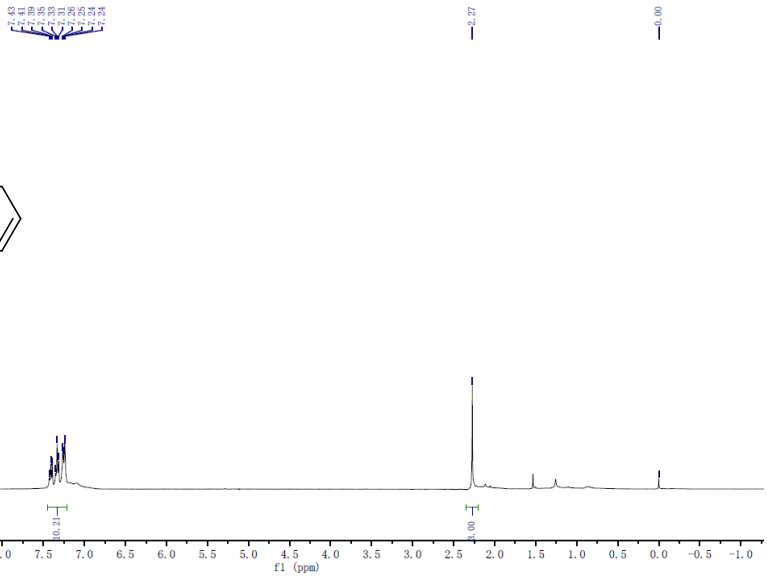
1-(2'-methoxy-[1,1'-biphenyl]-4-yl)ethanone,
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.05-6.99 (m, 2H), 3.82 (s, 3H), 2.63 (s, 3H). Data is consistent with that reported in the literature.[6]

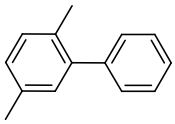




2-methyl-1,1'-biphenyl

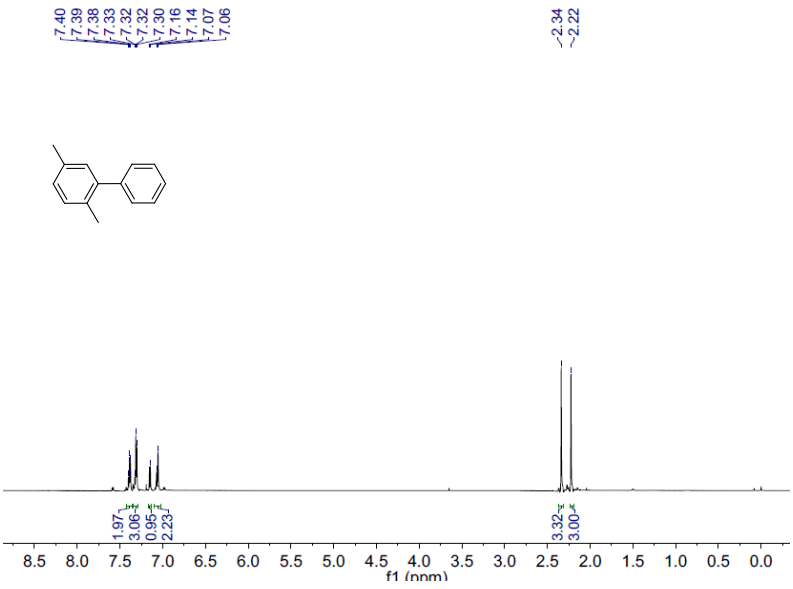
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.24 (m, 9H), 2.27 (s, 3H) ppm. Data is consistent with that reported in the literature.[10]

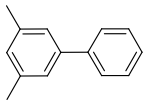




2,5-dimethyl-1,1'-biphenyl

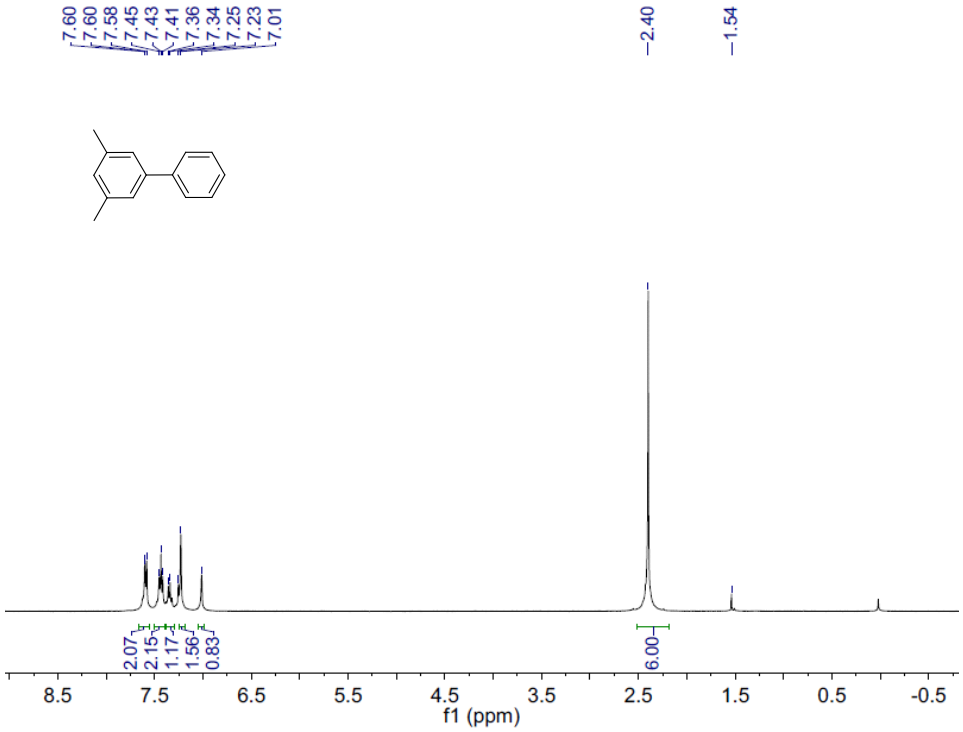
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.33-7.30 (m, 3H), 7.16 (d, *J* = 12.0 Hz, 1H), 7.07-7.06 (d, 2H), 2.34 (s, 3H), 2.22 (s, 3H) ppm. Data is consistent with that reported in the literature.[11]

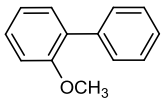




3,5-dimethyl-1,1'-biphenyl

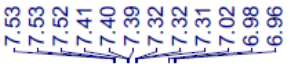
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.36-7.34 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 2H), 7.01 (s, 1H), 2.40 (s, 6H). Data is consistent with that reported in the literature.[12]

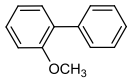


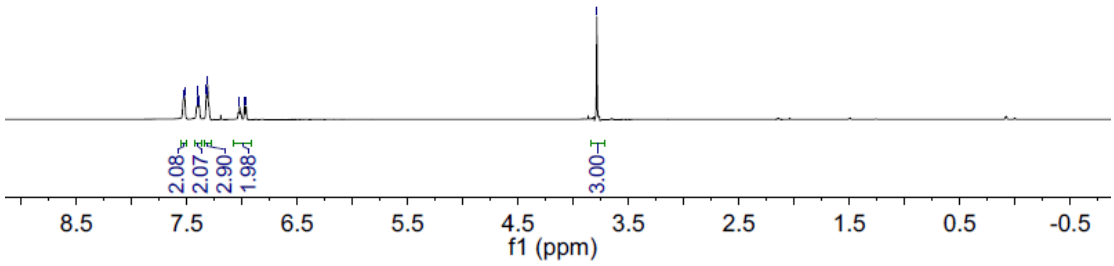


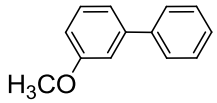
2-methoxy-1,1'-biphenyl

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53-7.52 (t, 2H), 7.41-7.39 (m, 2H), 7.32-7.31 (m, 3H), 7.02 (s, 1H), 6.98-6.96 (d, *J* = 12.0 Hz, 1H), 3.79 (s, 3H). Data is consistent with that reported in the literature.[13]



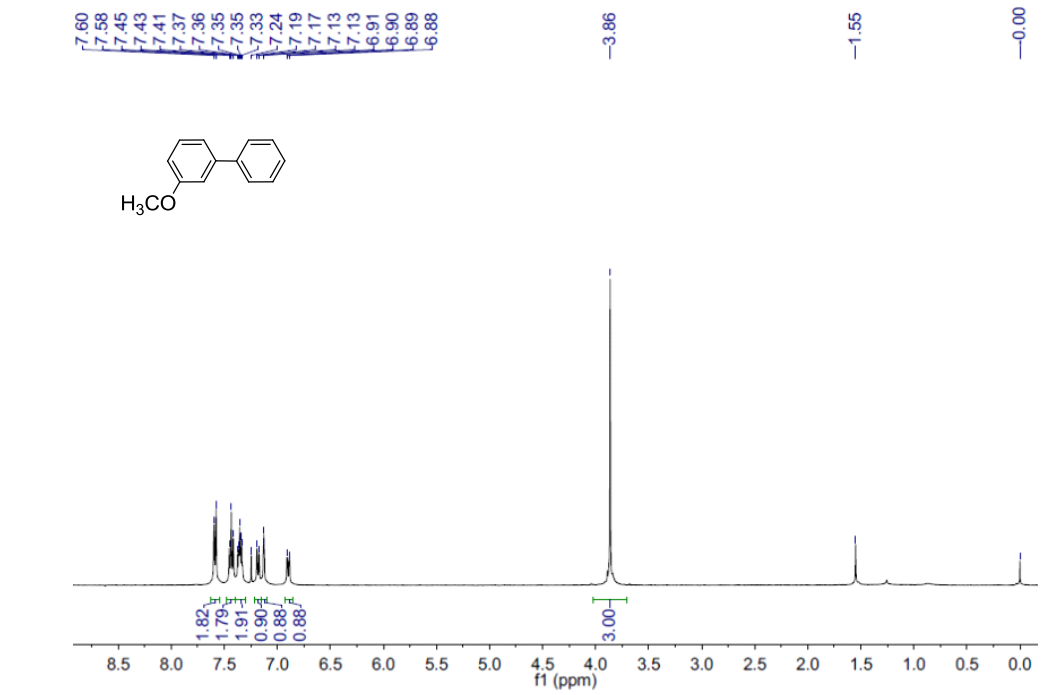


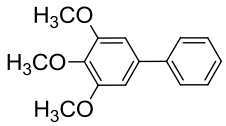




3-methoxy-1,1'-biphenyl

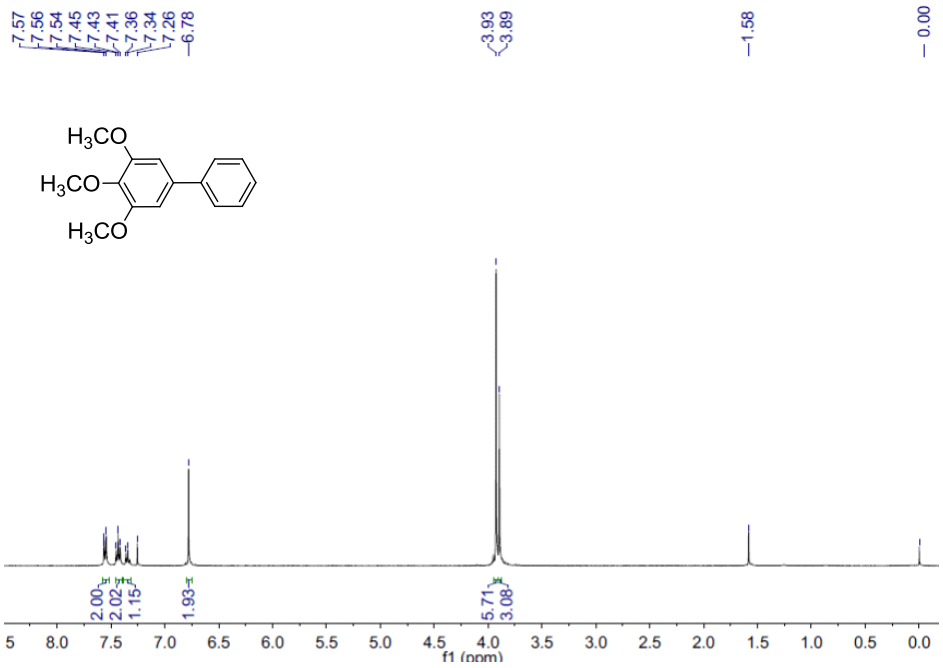
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (d, 2H), 7.45-7.41 (m, 2H), 7.35-7.33 (m, 2H), 7.19-7.17 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 6.91-6.88 (m, 1H), 3.86 (s, 3H). Data is consistent with that reported in the literature.[9]

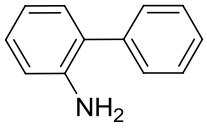




3,4,5-trimethoxy-1,1'-biphenyl

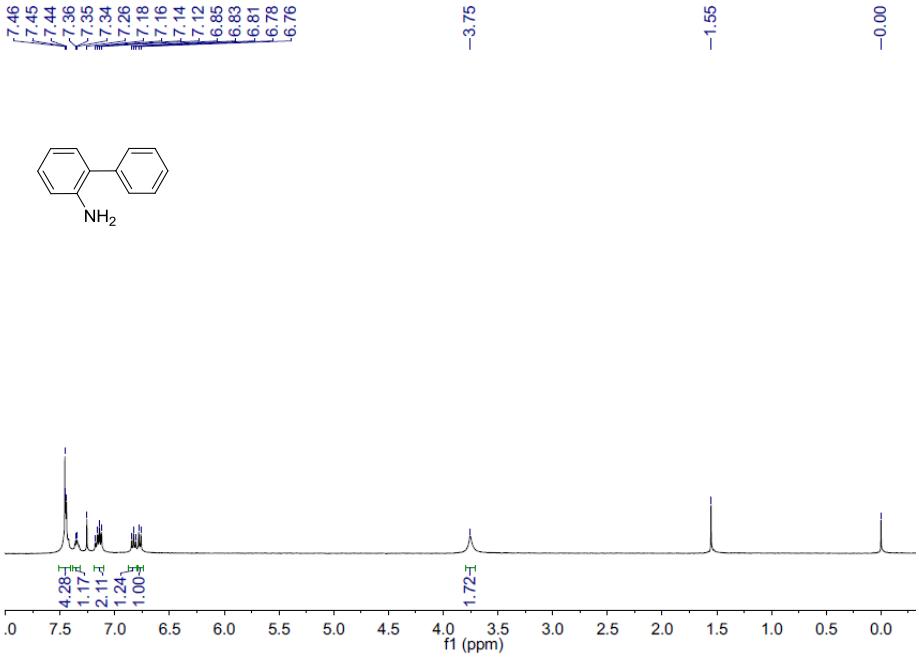
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.45-7.41 (m, 2H), 7.36-7.34 (d, *J* = 8.0 Hz, 1H), 6.78 (s, 2H), 3.93 (s, 6H), 3.89 (s, 3H). Data is consistent with that reported in the literature.[14]

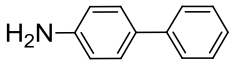




[1,1'-biphenyl]-2-amine

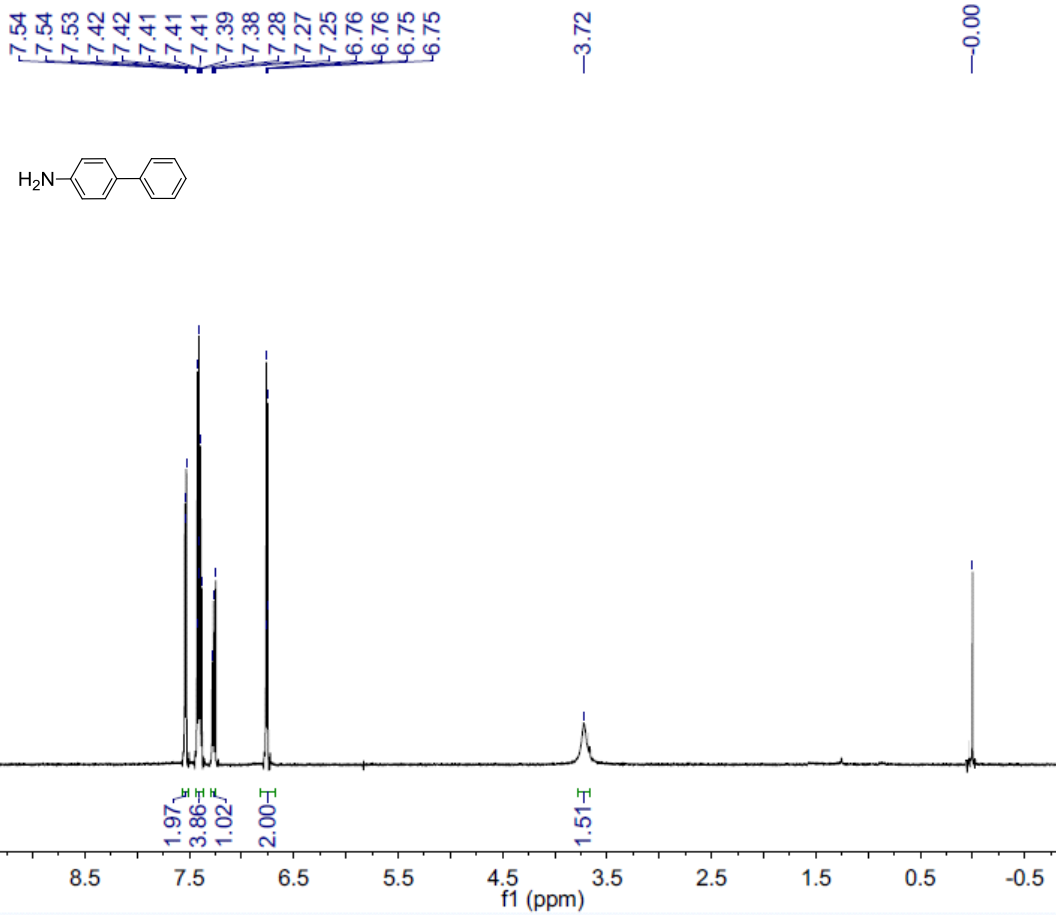
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.44 (m, 4H), 7.36-7.34 (m, 1H), 7.18-7.12 (m, 2H), 6.85-6.81 (m, 1H), 6.78-6.76 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 2H). Data is consistent with that reported in the literature.[9]





[1,1'-biphenyl]-4-amine

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54-7.53 (d, *J* = 6.0 Hz, 2H), 7.42-7.41 (m, 4H), 7.28-7.27 (d, *J* = 6.0 Hz, 1H), 6.77-6.75 (m, 2H), 3.72 (s, 2H). Data is consistent with that reported in the literature.[15]



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