Electronic Supplementary Information

Synthesis, characterization and catalytic activity of rare-earth metal amides incorporating cyclohexyl bridged bis(β-diketiminato) ligands

Hui Miao,[a,b] Shaowu Wang,*[a,c] Xiancui Zhu,*[a] Shuangliu Zhou,[a] Yun Wei,[a] Qingbing Yuan[a] and Xiaolong Mu[a]

[a]*Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, P. R. China.* [b]*School of Chemistry and Materials Engineering, Fuyang Normal College, Fuyang, Anhui 236037, P. R. China.* [c]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China*

E-mail: swwang@ahnu.edu.cn; zxc0805@ahnu.edu.cn

I. X-ray crystallographic analysis of complexes 1a-c

The single crystal X-ray diffraction data for complexes **1a-1c** were collected on a CCD area diffractometer with graphite monchromated *Mo Kα* radiation (λ = 0.71073 Å) ; temperature 273(2) K. Saint program and *SADABS* program carried out the data integration. The structures were solved by a direct method and refined on F^2 using SHELXTL suite of program. All non-hydrogen atoms were anisotropically refined by full-matrix least squares methods. All hydrogen atoms were geometrically generated and isotropically refined using a riding model. The crystal structures of **1a-1c** are given in Figure S1-S3.

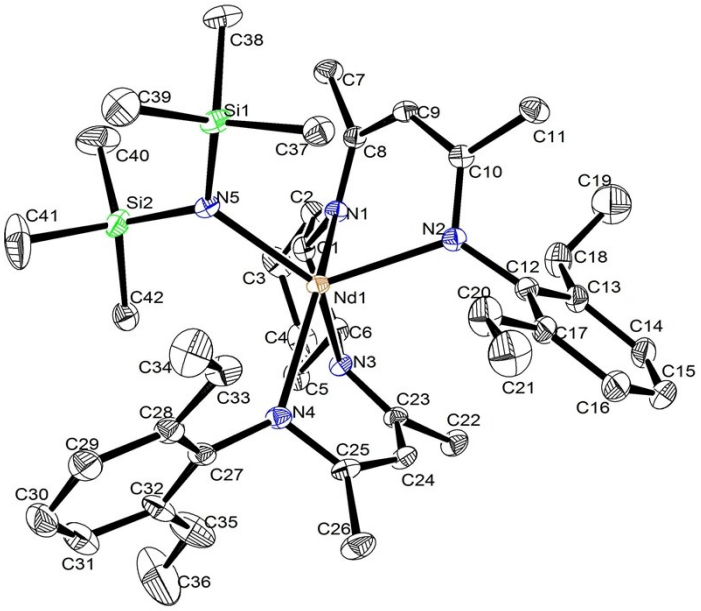


Figure S1. Molecular structure of complex **1a**. Hydrogen atoms were omitted for clarity.

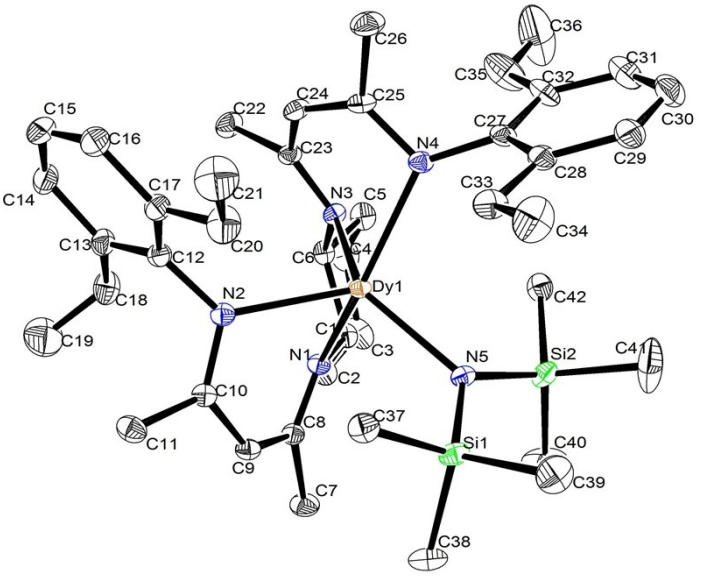


Figure S2. Molecular structure of complex **1b**. Hydrogen atoms were omitted for

clarity.

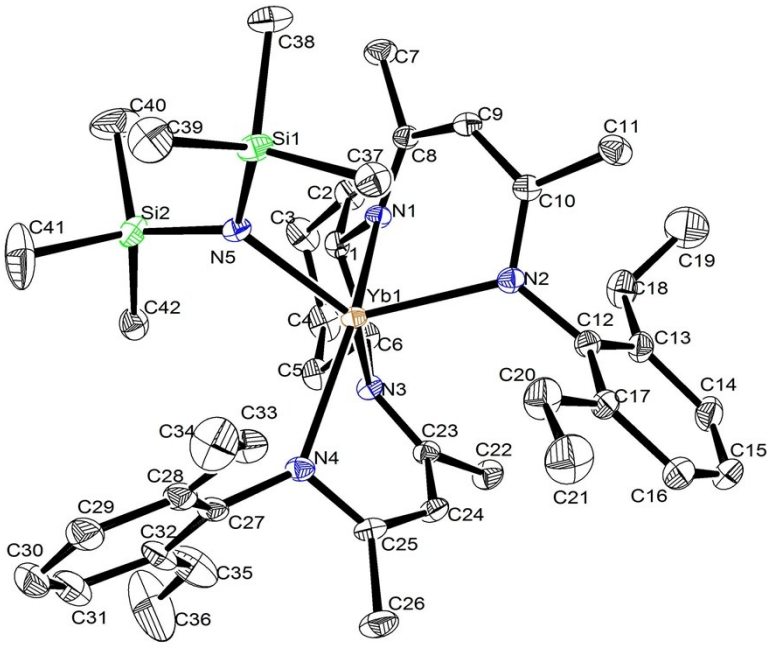


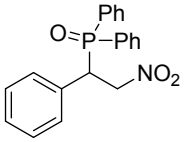
Figure S3. Molecular structure of complex **1c**. Hydrogen atoms were omitted for clarity.

II. **General procedure for hydrophosphination of β-nitroalkene and α,β-unsaturated carbonyl derivatives (4a as an example).**

A 30.0 mL Schlenk tube under dried argon was charged with complex **1d** (11.8 mg, 0.015 mmol), diphenyphosphine oxide (0.101 g, 0.5 mmol), and 5.0 mL of toluene, and then *β*-nitrostyrene (0.075 g, 0.5 mmol) was added to the mixture. The mixture was stirred at room temperature for 6 hours. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with ethyl ether, dried over anhydrous sodium sulfate, and then filtered. After the solvent was removed under reduced pressure, the final products were further purified by recrystallization from ethyl acetate or column chromatography. Compound **4a** was isolated as white solid (0.167 g, 95%).

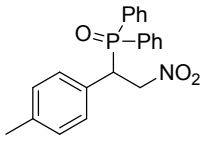
III. Data of ^{1}H NMR and ^{13}C NMR for compounds 4a-n

compound **4a**



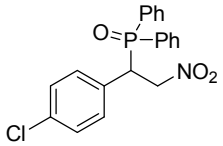
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.00-7.94 (m, 2H), 7.62-7.59 (m, 3H), 7.45-7.36 (m, 3H), 7.28-7.19 (m, 7H), 5.10-5.05 (m, 1H, CHP), 4.78-4.72 (m, 1H, CH_2CH), 4.44-4.39 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 132.8, 132.1, 131.7, 131.3, 131.1, 131.0, 130.7, 129.5, 129.3, 128.8, 128.4, 128.3, 75.8 75.7, 46.3, 45.4.

compound **4b**



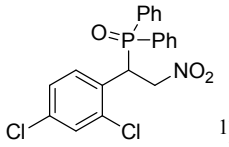
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ 8.00-7.94(m, 2H), 7.62-7.59(m, 2H), 7.50-7.38(m, 3H), 7.31-7.26(m, 3H), 7.18-7.15(m, 2H), 7.03-7.00(m, 2H), 5.12-5.02(m, 1H, CH_2), 4.76-4.70(m, 1H, CHP), 4.43-4.34(dt, 1H, CH_2), 2.25(m 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 132.8, 131.7, 131.2, 130.1, 129.8, 129.7, 129.6, 128.7, 128.2, 127.5, 127.4, 127.3, 76.0, 75.9, 45.9, 45.0, 21.1.

compound **4c**



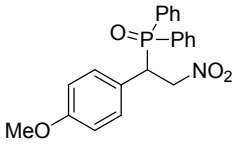
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.05-7.98 (m, 2H), 7.68-7.65 (m, 3H), 7.54-7.47 (m, 3H), 7.39-7.25 (m, 5H), 5.12-5.05 (m, 1H, CHP), 4.80-4.74 (m, 1H, CH_2CH), 4.47-4.42 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 131.9, 131.6, 131.3, 130.0, 129.9, 129.7, 129.6, 128.5, 128.0, 127.8, 127.6, 127.4, 74.6, 44.6, 43.8.

compound **4d**



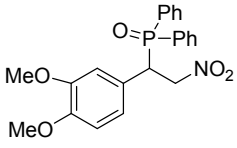
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.94-7.79 (m, 2H), 7.76-7.73 (m, 1H), 7.59-7.54 (m, 3H), 7.40-7.33 (m, 3H), 7.24-7.18 (m, 3H), 7.11-7.09 (m, 1H), 5.12-4.94(m, 2H), 4.70-4.62(m, 1H, CH_2CH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 135.6, 135.5, 134.7, 131.2, 131.1, 130.9, 130.7, 130.4, 129.9, 129.6, 129.5, 129.4, 129.0, 128.8, 128.7, 128.4, 128.3, 127.9, 75.3, 40.9, 40.1.

compound **4e**



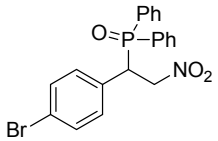
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.93-7.87 (m, 2H), 7.55-7.52(m, 2H), 7.40-7.35 (m, 3H), 7.25-7.12 (m, 5H), 6.69-6.66 (m, 2H), 5.01-4.94 (m, 1H, CHP), 4.66-4.62 (m, 1H, CH_2CH), 4.33-4.26 (m, 1H, CH_2CH), 3.67 (s, 3H, CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 159.9, 131.7, 131.1, 130.2, 130.0, 128.4, 128.2, 127.4, 127.3, 122.6, 121.0, 111.2, 110.1, 74.9, 55.6, 45.7, 45.2.

compound **4f**



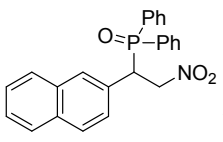
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.94-7.88 (m, 2H), 7.56-7.54(m, 2H), 7.40-7.35 (m, 3H), 7.26-7.19 (m, 3H), 6.72-6.65 (m, 3H), 5.05-4.95 (m, 1H, CHP), 4.68-4.64 (m, 1H, CH_2CH), 4.32-4.25 (m, 1H, CH_2CH), 3.74 (s, 3H, CH_3O), 3.66 (s, 3H, CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 147.9, 131.7, 131.1, 130.1, 130.0, 129.8, 128.4, 128.2, 127.4, 127.3, 122.6, 121.0, 111.2, 111.2, 110.1, 74.9, 54.8, 54.7, 44.9, 44.0.

compound **4g**



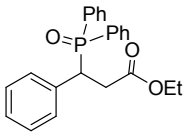
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.90-7.87 (m, 2H), 7.56-7.51 (m, 3H), 7.43-7.28 (m, 3H), 7.26-7.19 (m, 4H), 7.10-7.09 (m, 2H), 5.02-4.92 (m, 1H, CHP), 4.67-4.60 (m, 1H, CH_2CH), 4.34-4.26 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 132.9, 132.4, 132.0, 131.2, 131.1, 130.9, 130.4, 130.0, 129.4, 128.6, 128.5, 122.6, 75.6, 45.7, 44.9.

compound **4h**



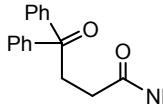
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.03-6.90 (m, 17H), 5.36 (m, 1H, CHP), 5.20 (m, 1H, CH_2CH), 4.90 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 132.9, 132.8, 131.9, 131.4, 130.7, 130.6, 129.4, 129.3, 128.9, 128.0, 127.8, 126.9, 126.5, 125.6, 125.4, 121.9, 76.3, 39.4, 38.6.

compound **4i**



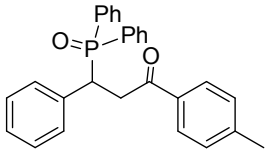
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.93-7.88 (m, 2H), 7.52-7.40 (m, 5H), 7.38-7.11 (m, 8H), 4.07-3.99 (m, 1H, CHP), 3.91-3.84 (m, 2H, CH_2CH_3), 3.09-3.00 (m, 1H, CH_2CH), 2.89-2.83 (m, 1H, CH_2CH), 0.99 (m, 3H, CH_3CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 170.2, 134.0, 131.0, 130.4, 130.1, 130.0, 129.6, 128.7, 127.9, 127.8, 127.2, 127.1, 127.0, 126.2, 59.8, 41.9 (d, $J_{C\text{-}P}$ = 67.7 Hz), 33.9, 12.9.

compound **4j**



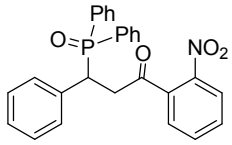
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.69-7.63 (m, 4H), 7.47-7.39 (m, 6H), 6.35 (m, 1H, NH), 3.88 (m, 1H, $CHCH_3$), 2.60-2.52 (m, 2H, CH_2CO), 2.45-2.38 (m, 2H, CH_2PO), 1.06-1.02 (m, 6H, CH_3CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 170.4, 133.0, 132.0, 131.9, 131.7, 130.7, 130.6, 128.8, 128.7, 41.4, 28.0, 25.2 (d, $J_{C\text{-}P}$ = 72.8 Hz), 22.6.

compound **4k**



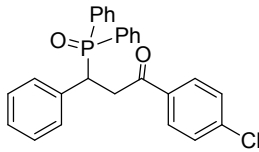
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.91 (m, 2H), 7.69-7.66 (m, 3H), 7.45-7.04 (m, 14H), 4.42-4.37 (m, 1H, CHP), 3.97-3.88 (m, 1H, CH_2CH), 3.32-3.22 (m, 1H, CH_2CH), 2.27 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 195.2 (d, $J_{C\text{-}P}$ = 10.4 Hz), 143.2, 134.9, 132.9, 131.6, 131.0, 130.4, 130.2, 130.0, 129.9, 129.6, 128.8, 128.2, 128.0, 127.8, 127.2, 127.0, 126.0, 40.0 (d, $J_{C\text{-}P}$ = 68.6 Hz), 37.8, 20.6.

compound **4l**



^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 8.56 (s, 1H), 8.27 (m, 1H), 8.07 (m, 1H), 7.91 (m, 2H), 7.54-7.19 (m, 11H), 7.12-7.07 (m, 3H), 4.37 (m, 1H, CHP), 3.94-3.87 (m, 1H, CH_2CH), 3.43-3.38 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 194.9 (d, $J_{C\text{-}P}$ = 10.5 Hz), 148.4, 135.6, 133.6, 131.6, 131.4, 131.3, 131.0, 130.9, 129.9, 129.8, 129.7, 129.1, 129.0, 128.5, 128.2, 128.1, 127.5, 127.3, 123.0, 41.3 (d, $J_{C\text{-}P}$ = 68.2 Hz), 39.4.

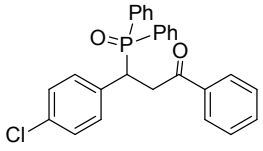
compound **4m**



^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.93-7.87 (m, 2H), 7.71-7.69 (m, 2H), 7.46-7.18 (m, 12H), 7.08-7.05 (m, 3H), 4.39-4.34 (m, 1H, CHP),

3.95-3.84 (m, 1H, CH_2CH), 3.33-3.23 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 194.6 (d, $J_{C\text{-}P}$ = 12.3 Hz), 138.8, 134.7, 134.0, 131.1, 130.5, 130.3, 130.2, 130.0, 129.9, 129.6, 128.8, 128.7, 128.5, 128.0, 127.8, 127.3, 127.1, 127.0, 40.0 (d, $J_{C\text{-}P}$ = 68.6 Hz), 37.9.

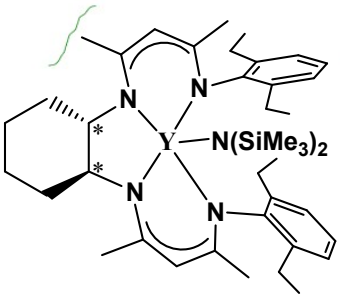
compound **4n**



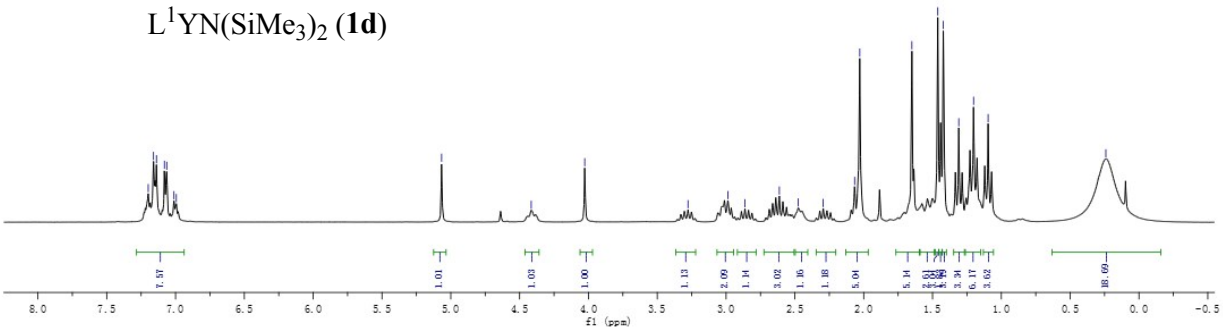
^1H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.92-7.87 (m, 2H), 7.78-7.65 (m, 2H), 7.65-7.22 (m, 12H), 7.06-7.03 (m, 3H), 4.39-4.34 (m, 1H, CHP), 3.95-3.84 (m, 1H, CH_2CH), 3.32-3.23 (m, 1H, CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, ppm): δ = 195.4 (d, $J_{C\text{-}P}$ = 13.3 Hz), 132.5, 131.1, 130.6, 130.2, 130.1, 130.0, 129.9, 129.8, 128.1, 127.9, 127.8, 127.6, 127.5, 127.3, 127.2, 127.1, 39.4 (d, $J_{C\text{-}P}$ = 68.5 Hz), 37.9.

IV. Copies of ^{1}H NMR and ^{13}C NMR for complexes 1d, 2e and compounds 4a-n

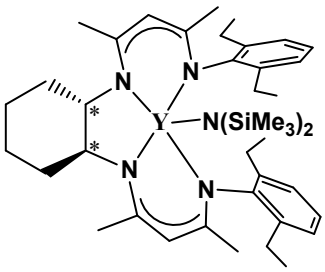
^{1}H NMR
300 MHz, C_6D_6



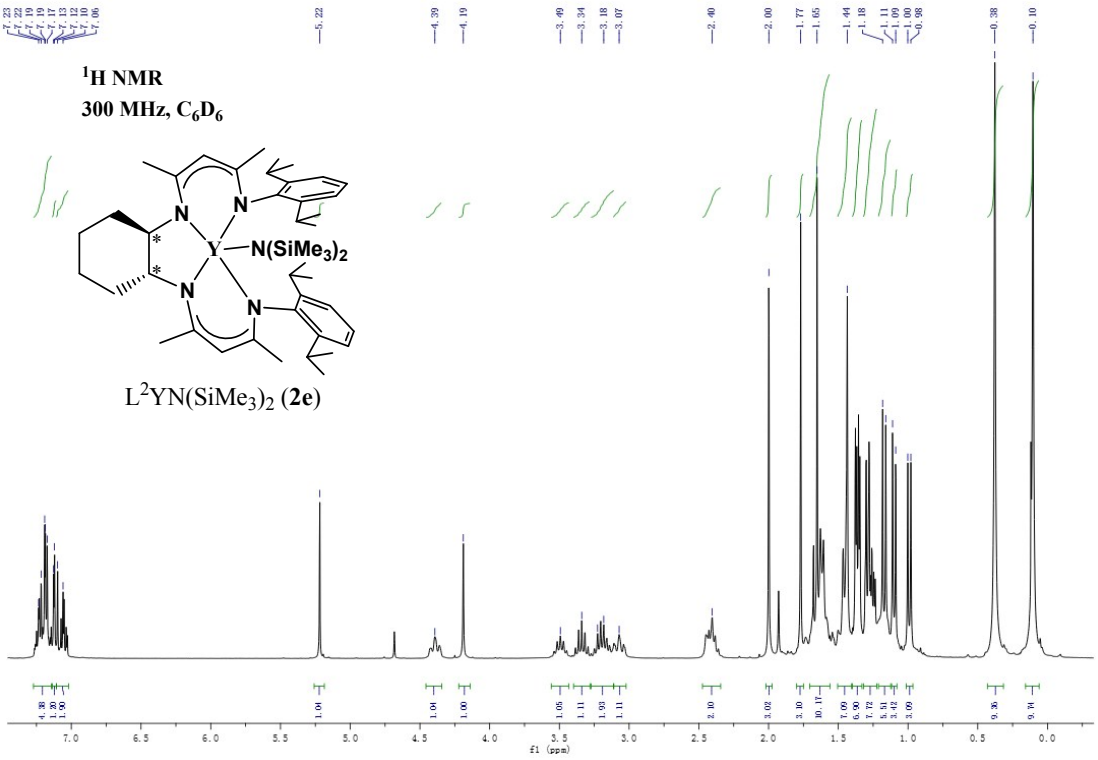
$L^1YN(SiMe_3)_2$ (**1d**)

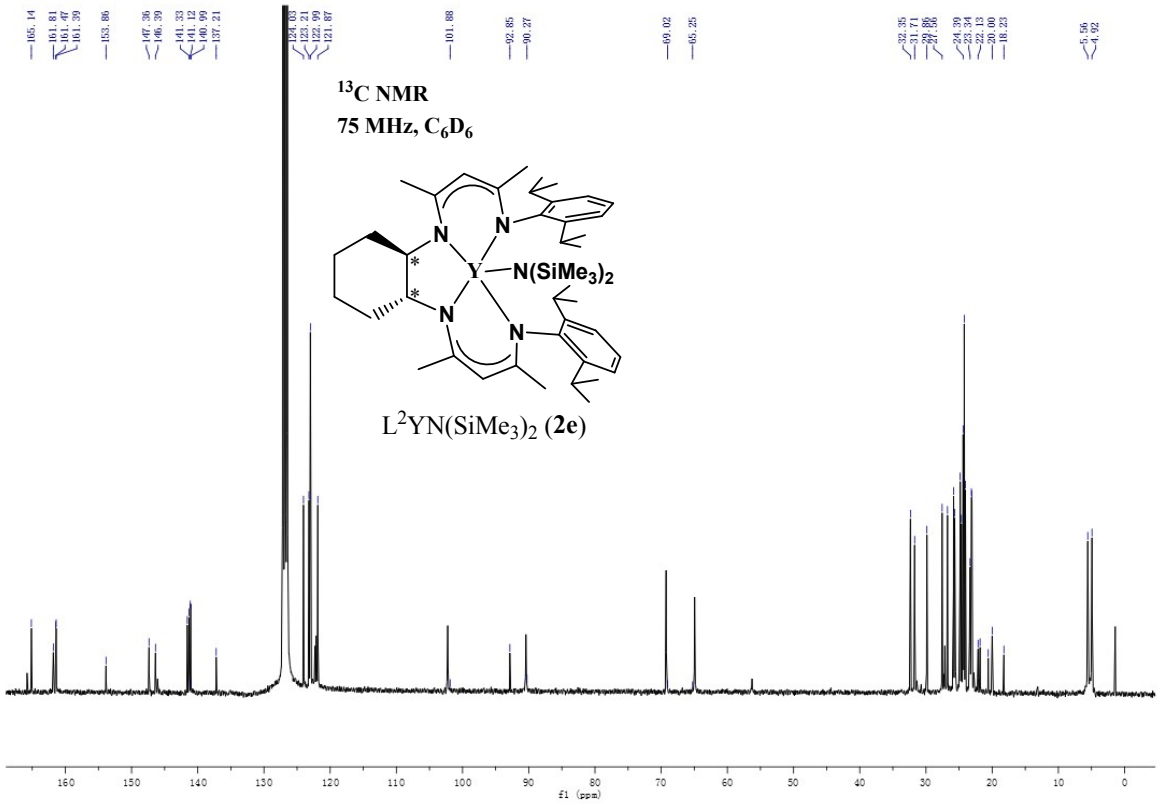


^{13}C NMR
75 MHz, C_6D_6



$L^1YN(SiMe_3)_2$ (**1d**)


7.23
7.22
7.19
7.17
7.13
7.12
7.10
7.06
5.22
4.39
4.19
3.49
3.34
3.18
3.07
2.40
2.00
1.77
1.65
1.44
1.18
1.11
1.09
1.00
0.98
0.38
0.10
1H NMR
300 MHz, C6D6
N
N
Y
N(SiMe3)2
N
N
L2YN(SiMe3)2 (2e)
4.00
1.99
1.00
1.04
1.04
1.00
1.08
1.11
1.93
1.11
2.10
3.02
3.10
10.17
7.09
6.90
7.72
5.51
3.42
3.09
9.30
9.74
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.14
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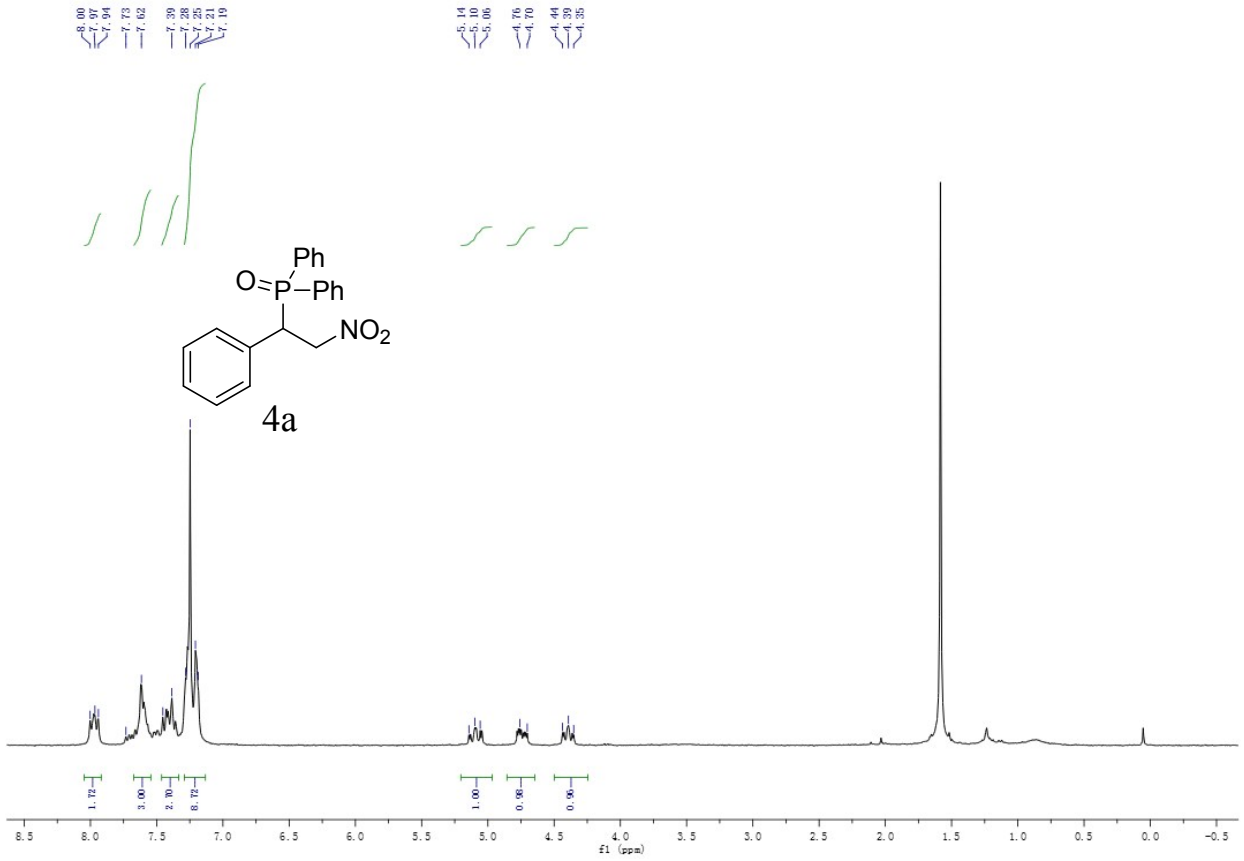
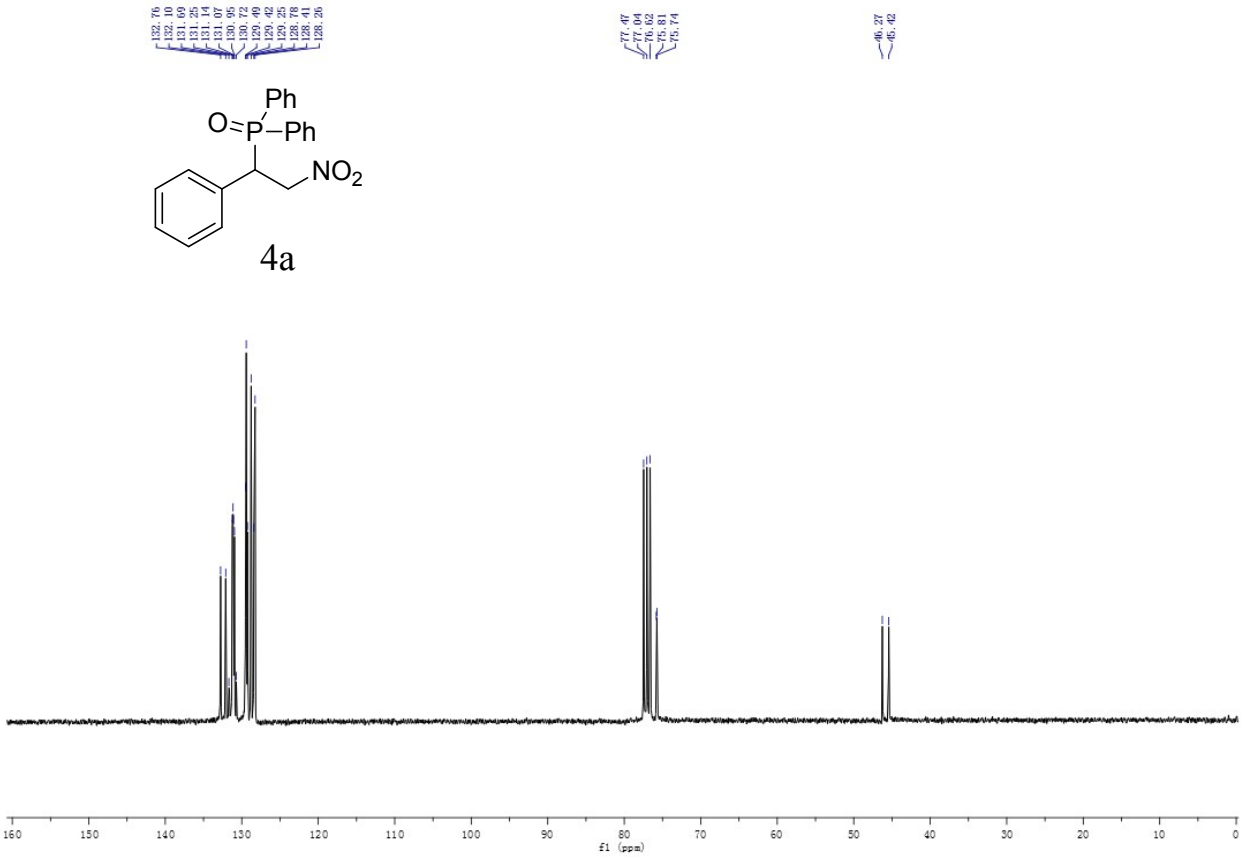
161.47
161.39
153.86
147.36
146.39
141.33
141.12
140.99
137.21
124.03
123.21
122.99
121.87
101.88
92.85
90.27
69.02
65.25
32.35
31.71
29.86
27.56
24.39
23.34
22.13
20.00
18.23
5.56
4.92
13C NMR
75 MHz, C6D6
N
N
Y
N(SiMe3)2
N
N
L2YN(SiMe3)2 (2e)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.00
7.97
7.94
7.73
7.62
7.39
7.28
7.25
7.21
7.19
5.14
5.10
5.06
4.76
4.70
4.44
4.39
4.35
Ph
O=P–Ph
NO2
4a
1.72
3.00
2.70
8.72
1.00
0.98
0.96
f1 (ppm)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131.14
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130.95
130.72
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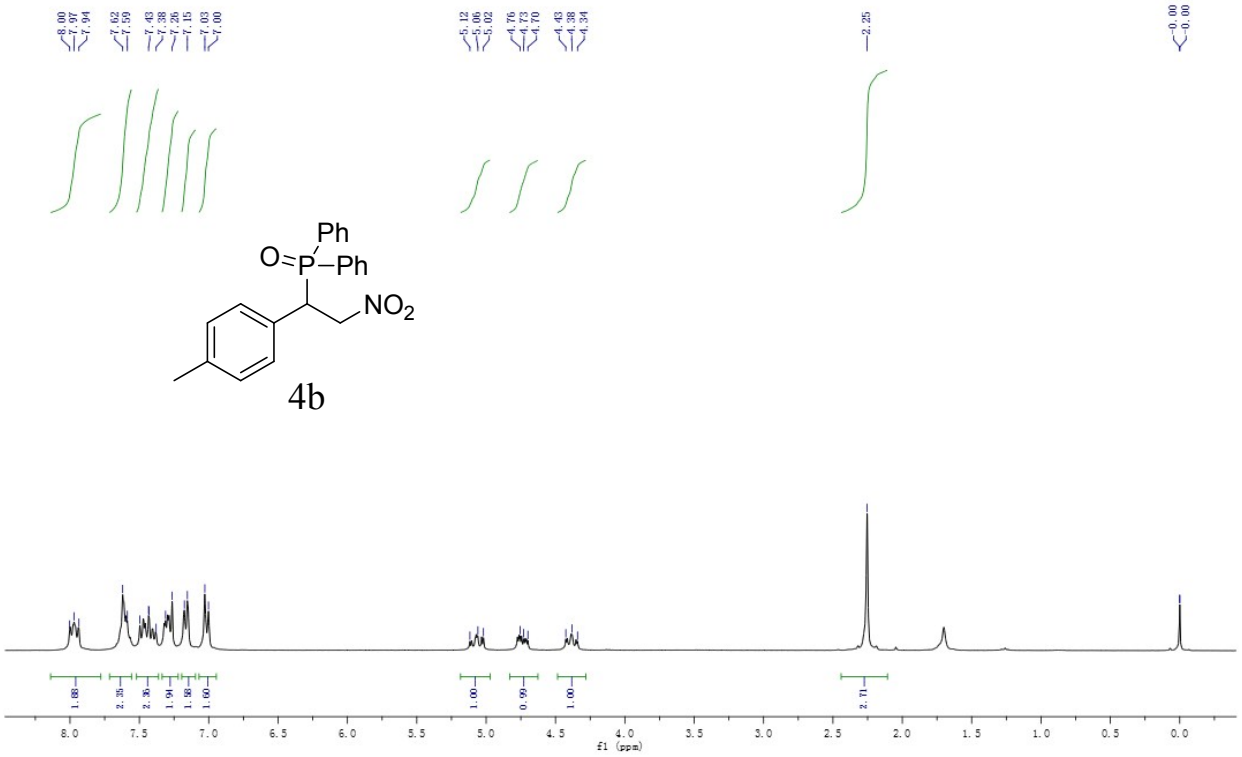
129.25
128.78
128.41
128.26
77.47
77.04
76.62
75.81
75.74
46.27
45.42
Ph
O=P–Ph
NO2
4a
f1 (ppm)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7.03
7.00
5.12
5.06
5.02
4.76
4.73
4.70
4.43
4.38
4.34
2.25
0.00
0.00
Ph
O
P
Ph
NO2
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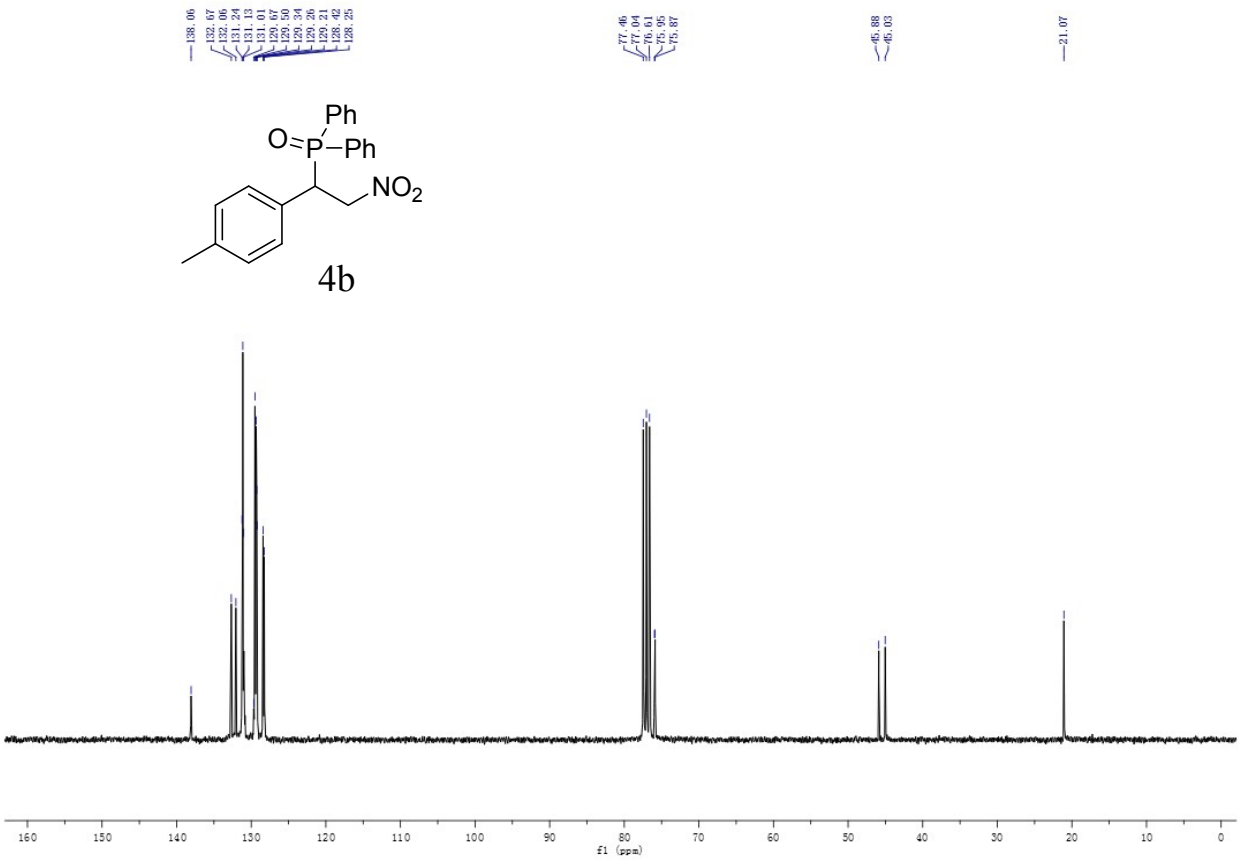
1.94
1.88
1.60
1.00
0.99
1.00
2.71
f1 (ppm)

4b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132.67
132.06
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129.26
129.21
128.42
128.25
77.46
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76.61
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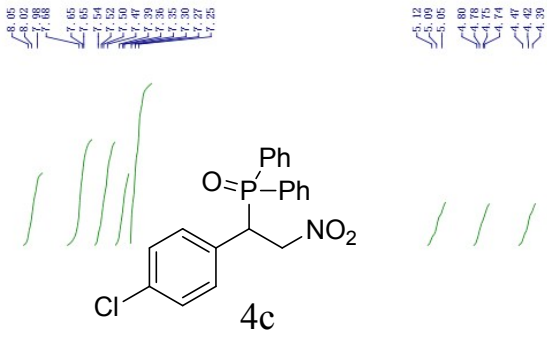
75.87
45.88
45.03
21.07
Ph
O
P
Ph
NO2
f1 (ppm)

4b



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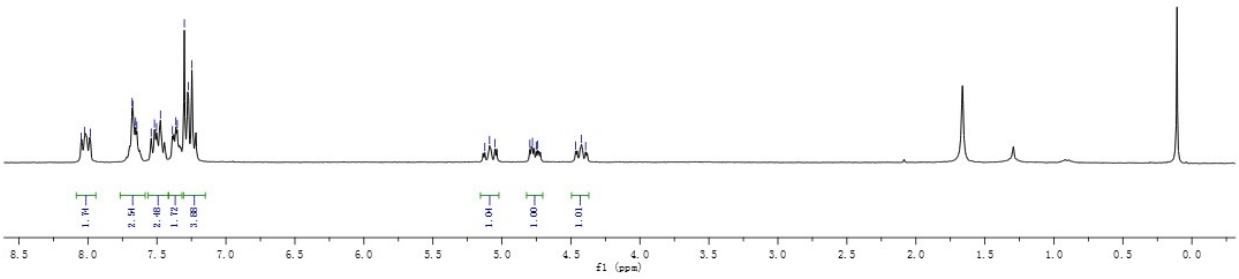

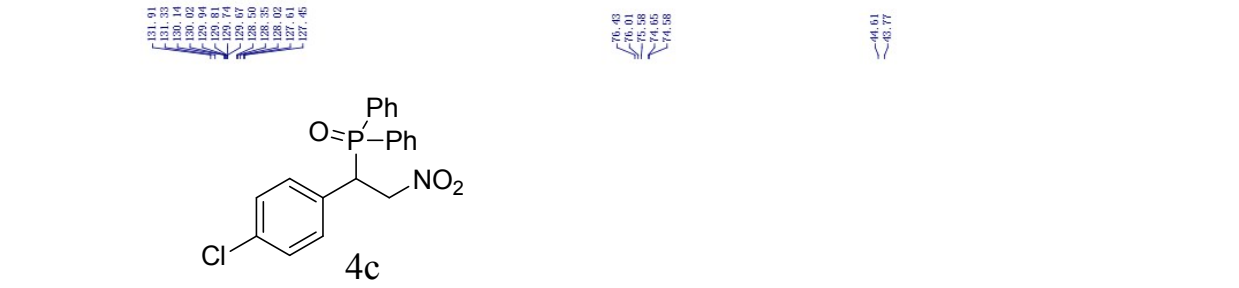

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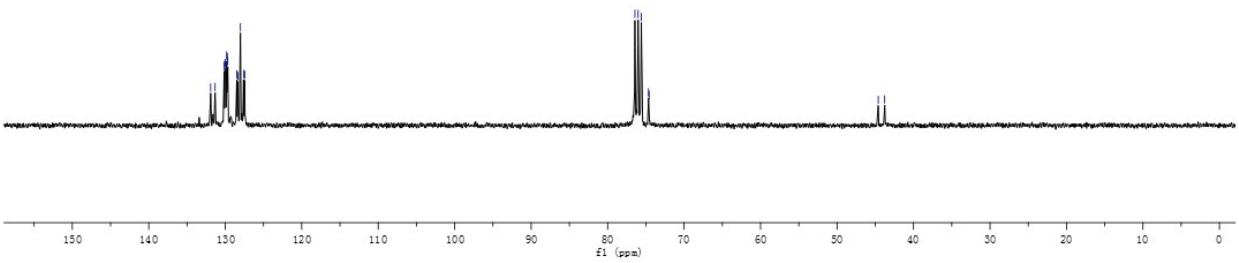
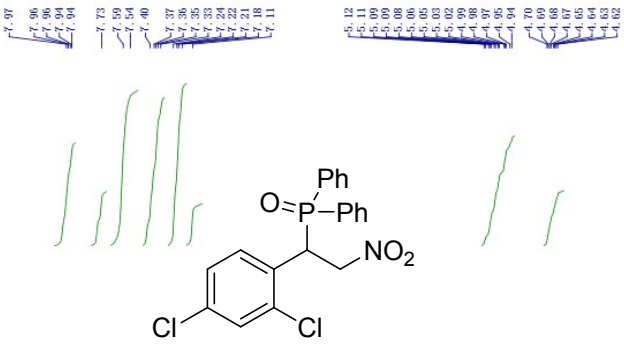
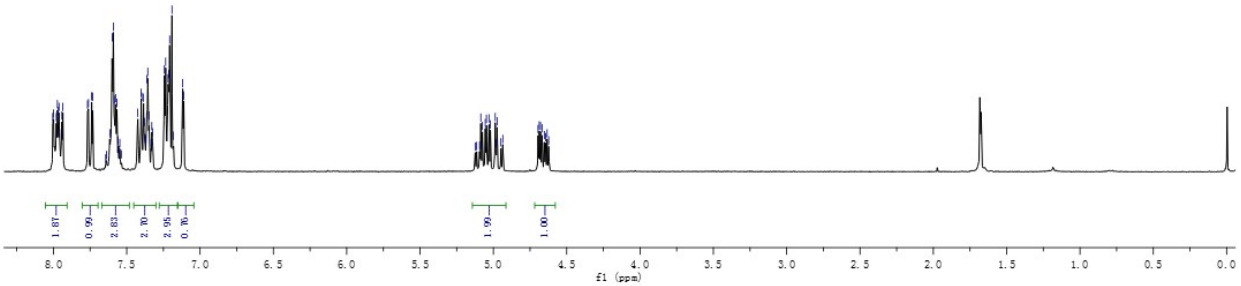
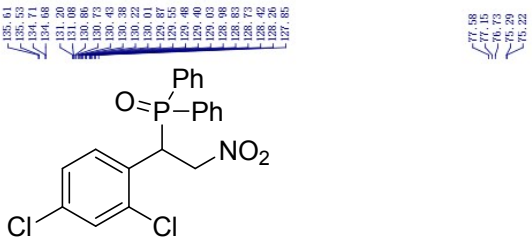




4d





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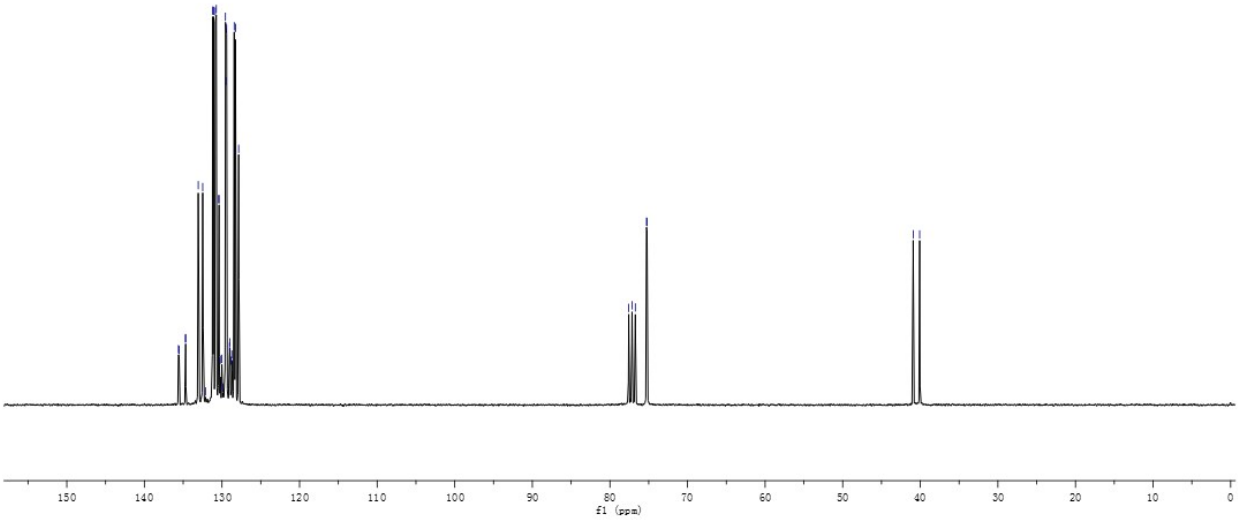

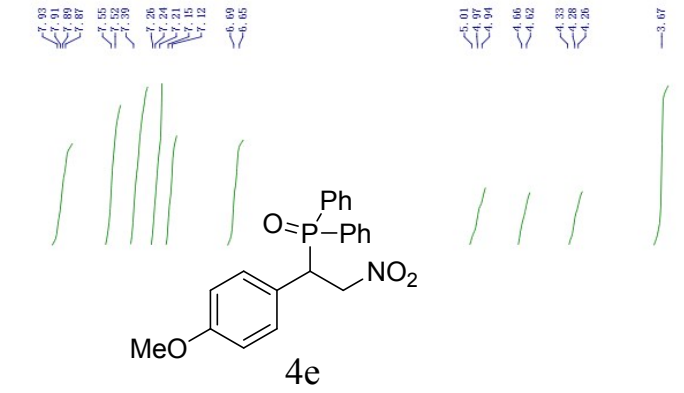

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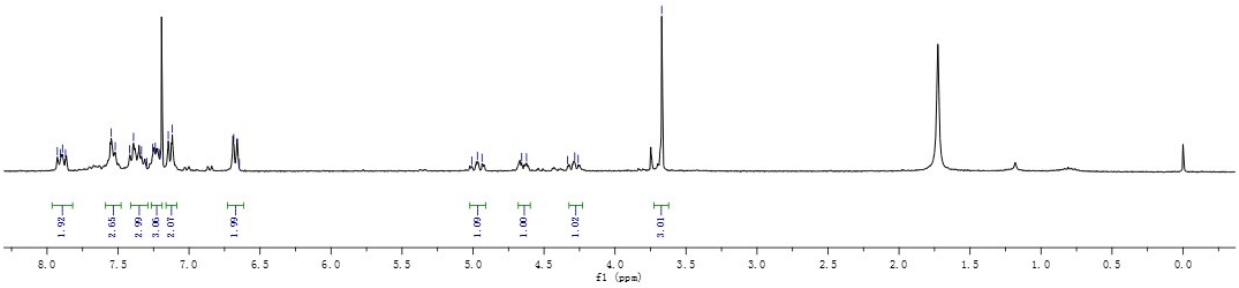
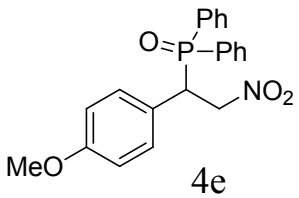
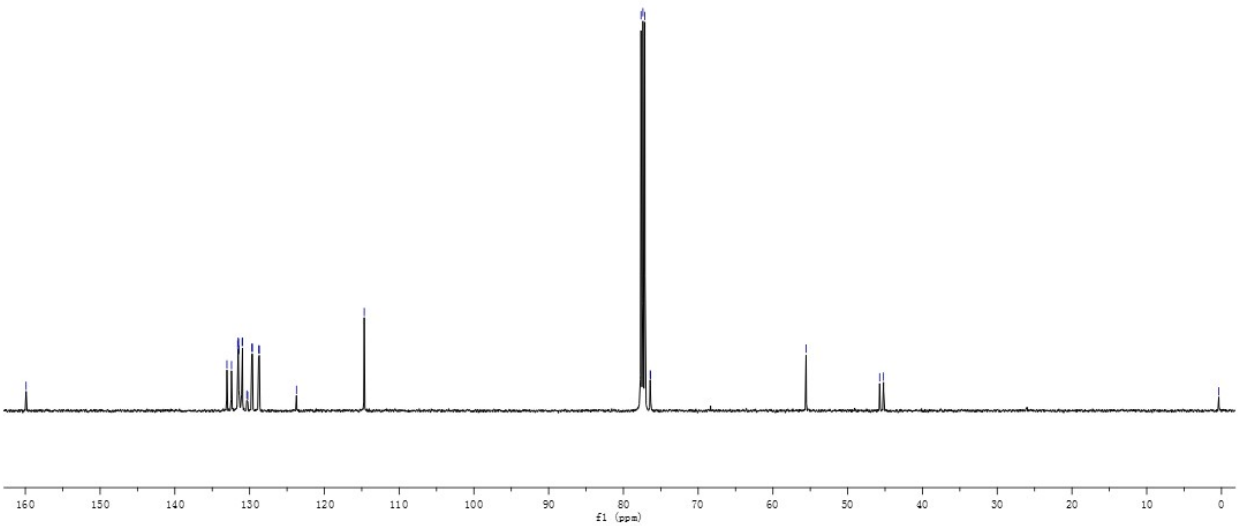
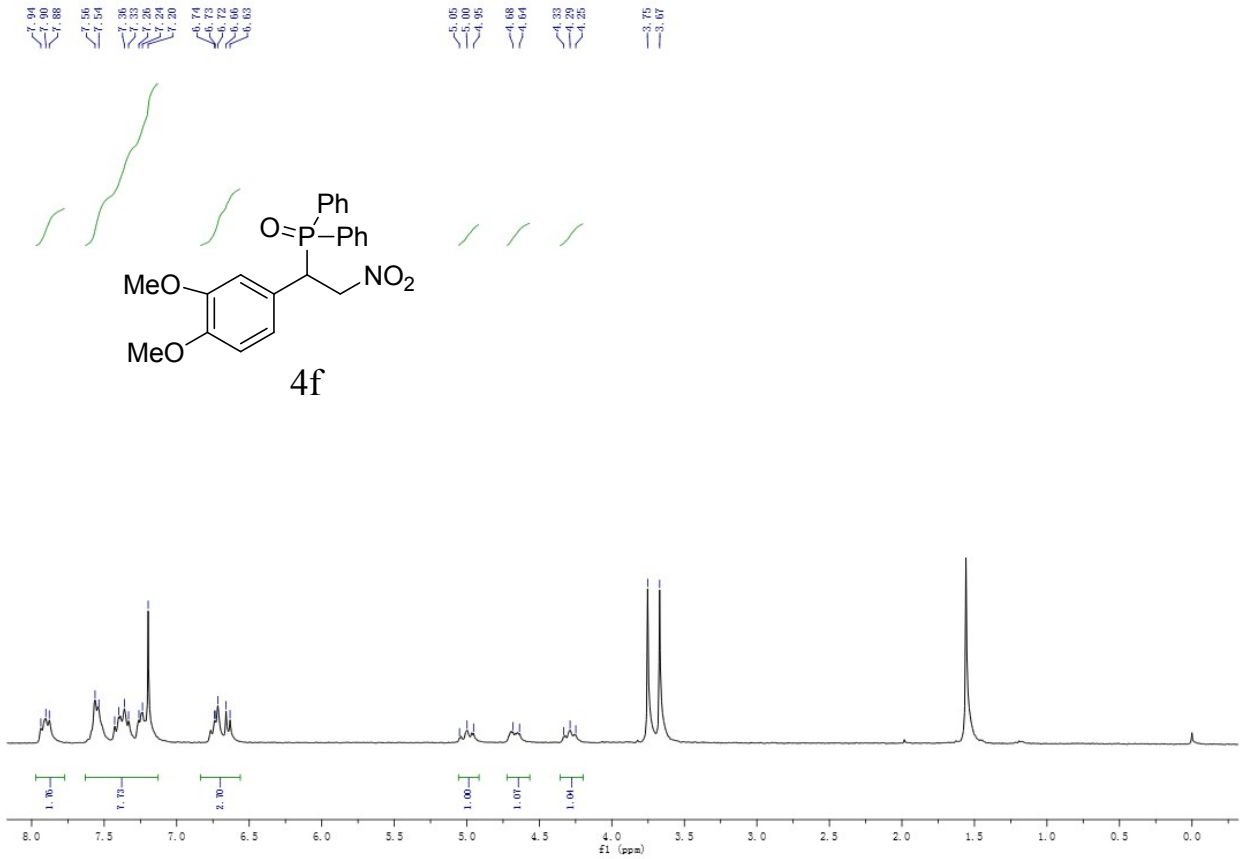




4e

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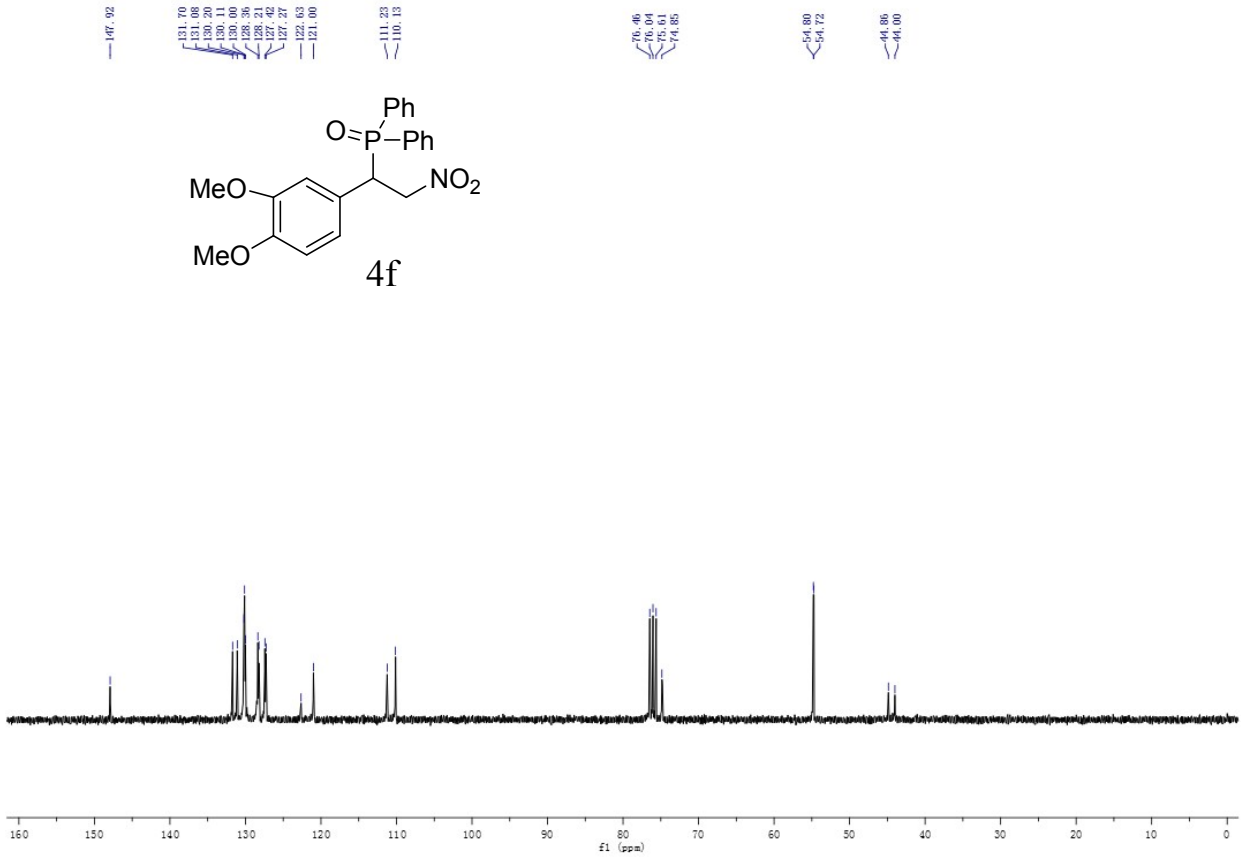
7.90
7.88
7.56
7.54
7.36
7.33
7.26
7.24
7.20
6.74
6.73
6.72
6.66
6.63
5.05
5.00
4.95
4.68
4.64
4.33
4.29
4.25
3.75
3.67
Ph
O
P
Ph
NO2
MeO
MeO
1.76
7.73
2.70
1.00
1.07
1.04
f1 (ppm)

4f


147.92
131.70
131.08
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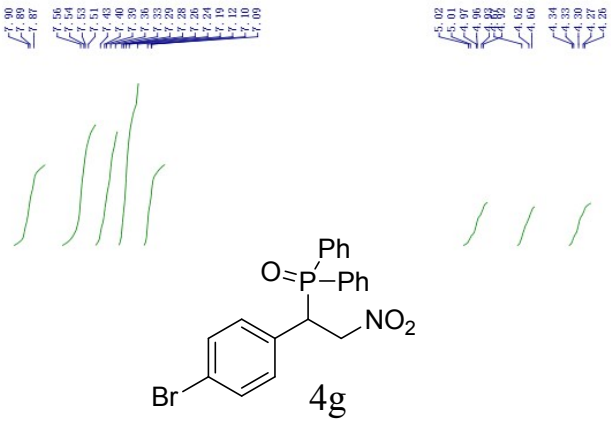
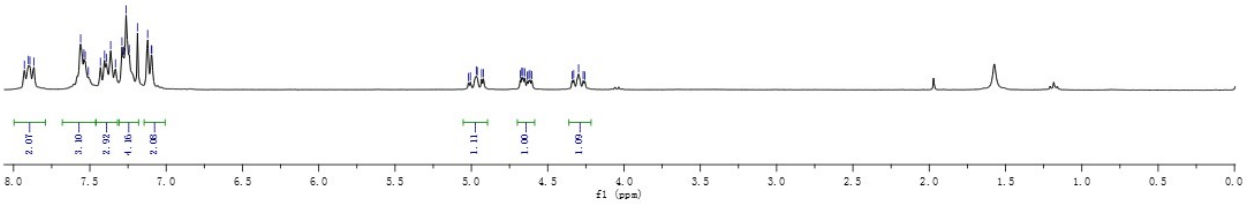
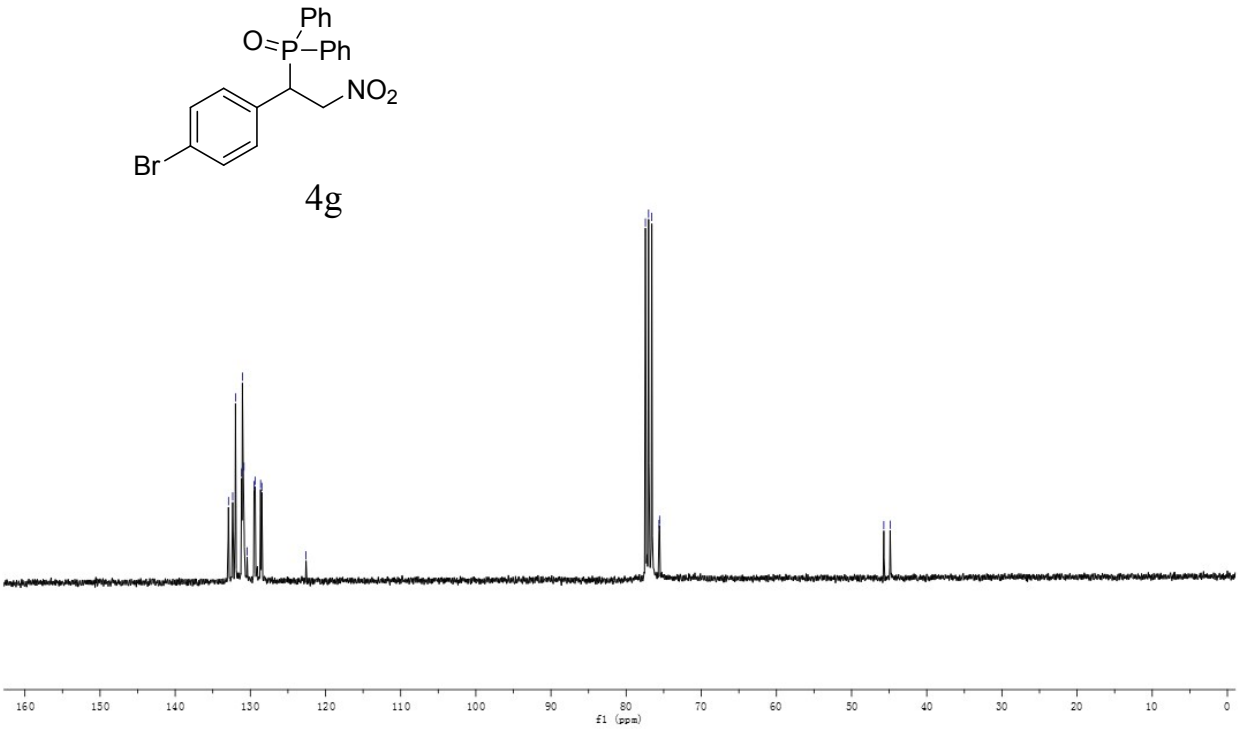
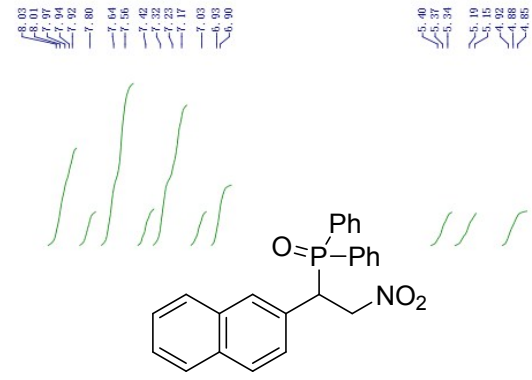
130.11
130.00
129.96
128.21
127.42
127.27
122.63
121.00
111.23
110.13
76.46
76.04
75.61
74.85
54.80
54.72
44.86
44.00
Ph
O
P
Ph
NO2
MeO
MeO
f1 (ppm)

4f

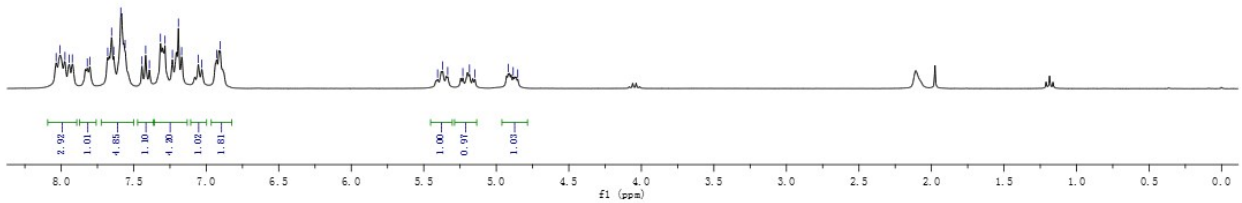

Ph
O=P–Ph
NO2
Br
4g

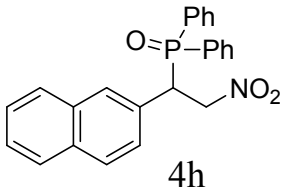

f1 (ppm)


Ph
O=P–Ph
NO2
Br
4g
f1 (ppm)

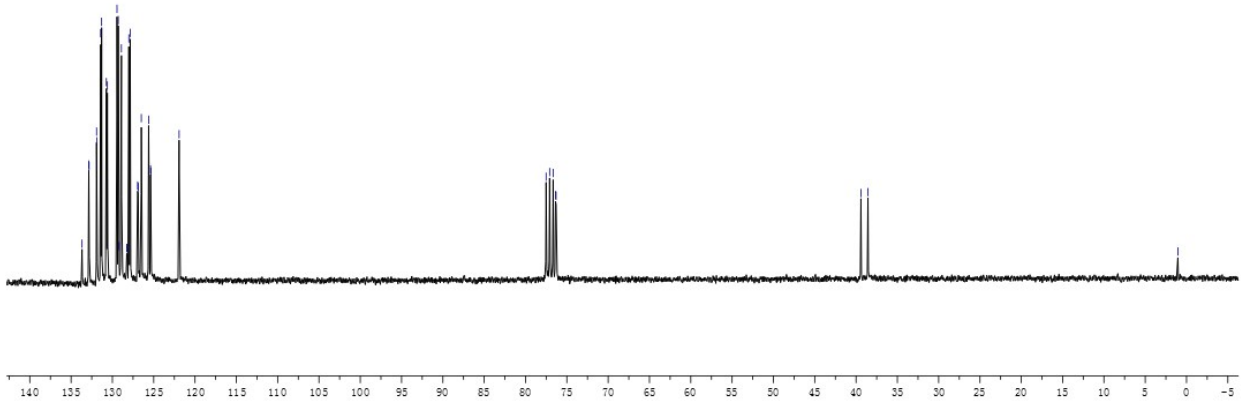


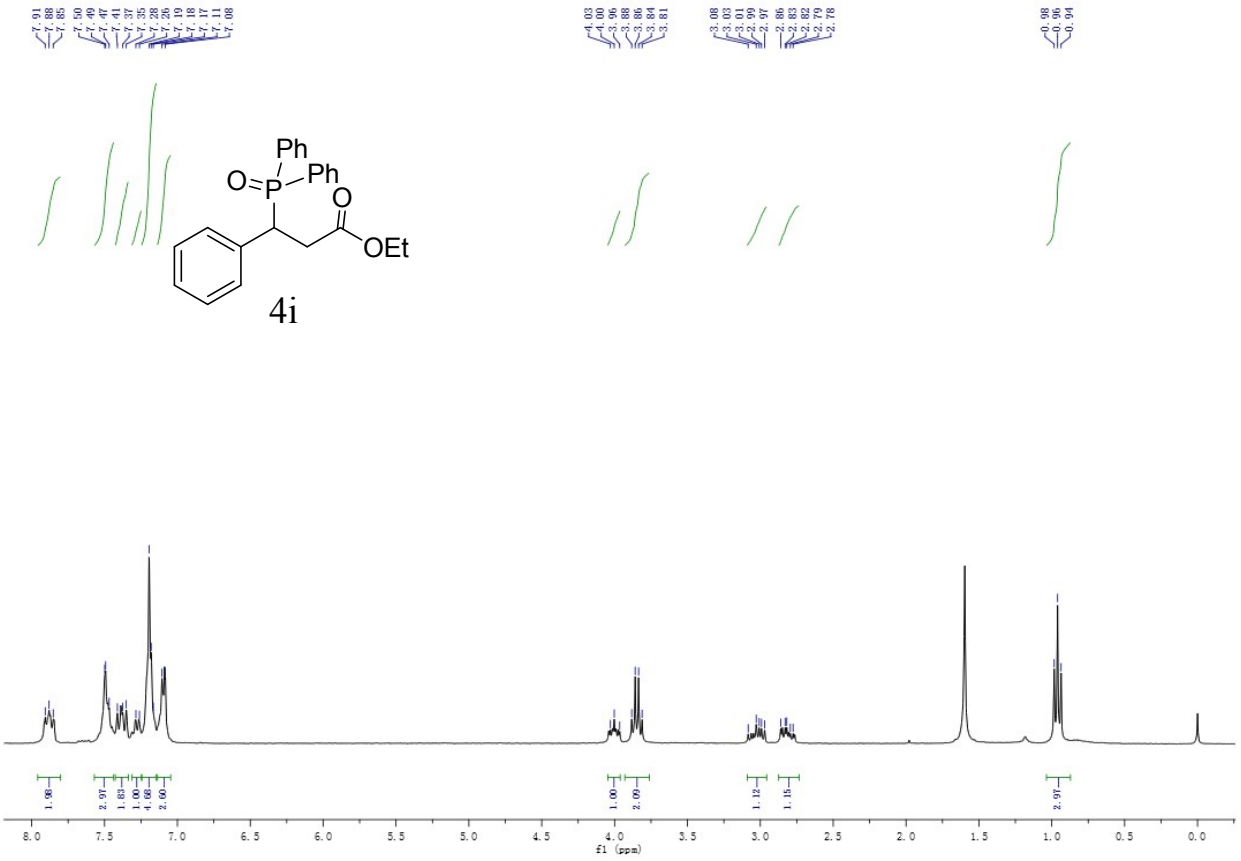
4h



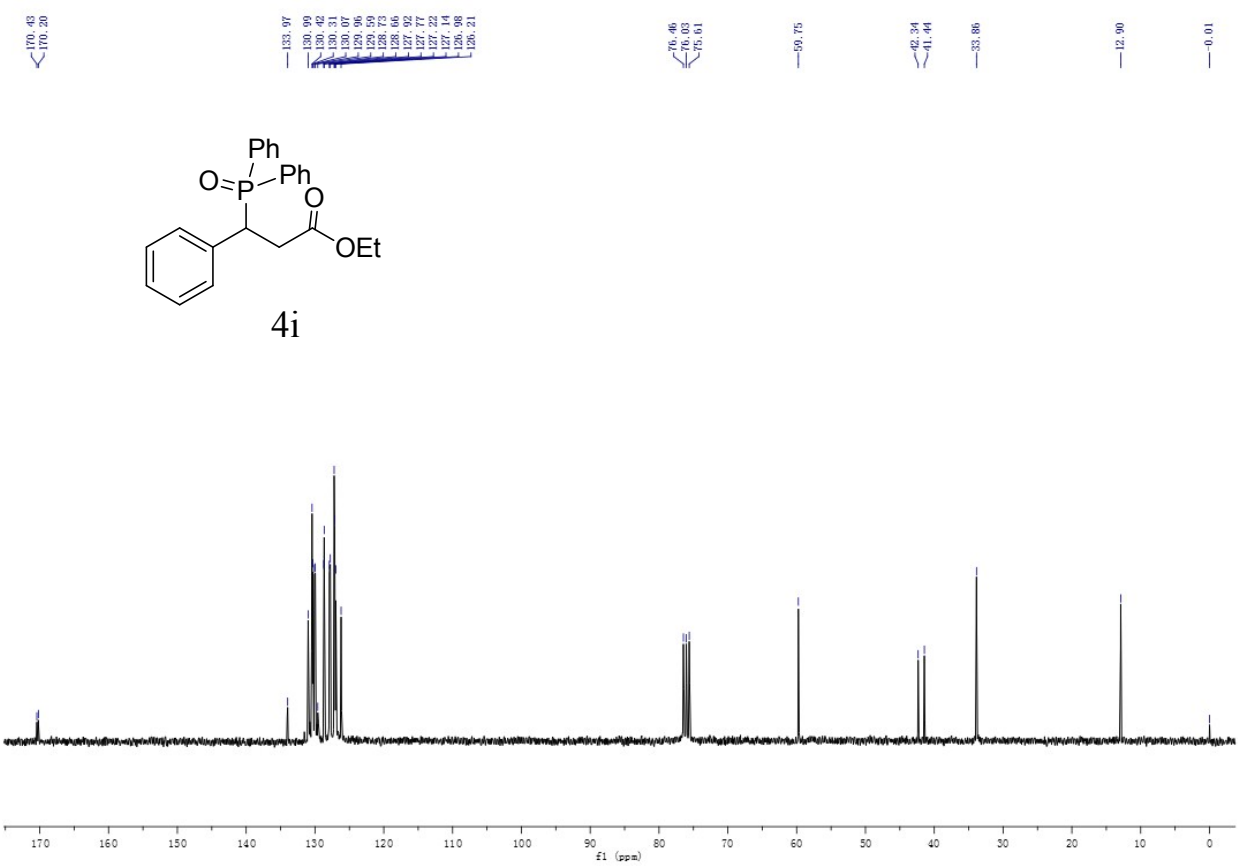


4h

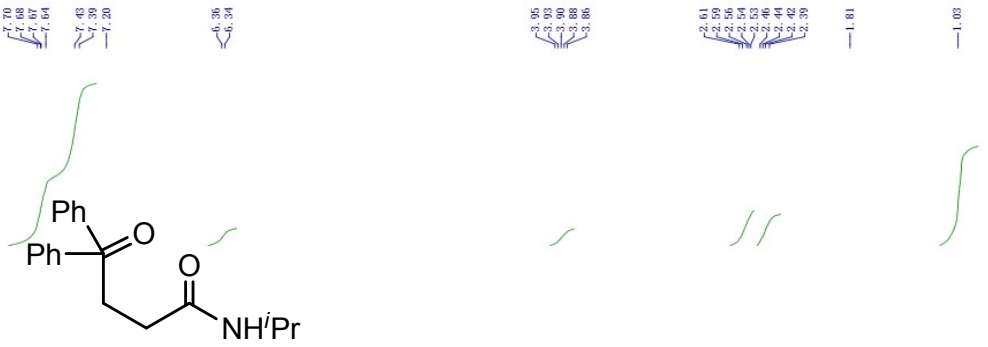




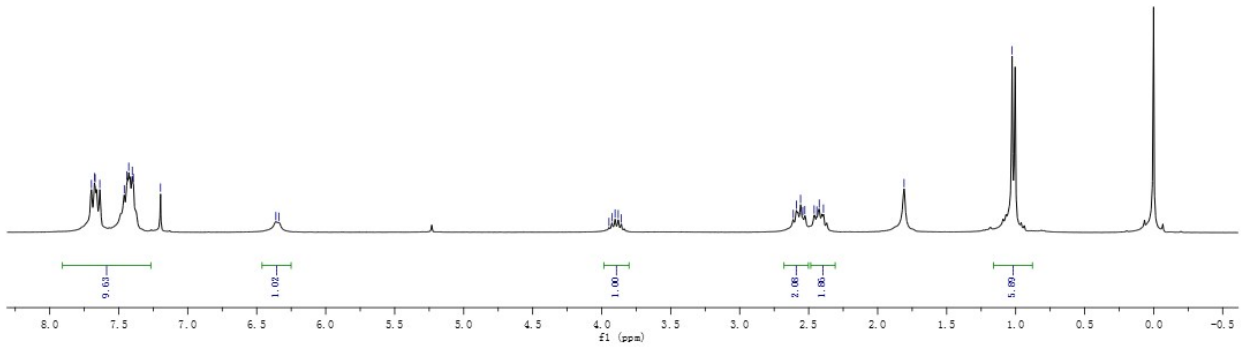
4i



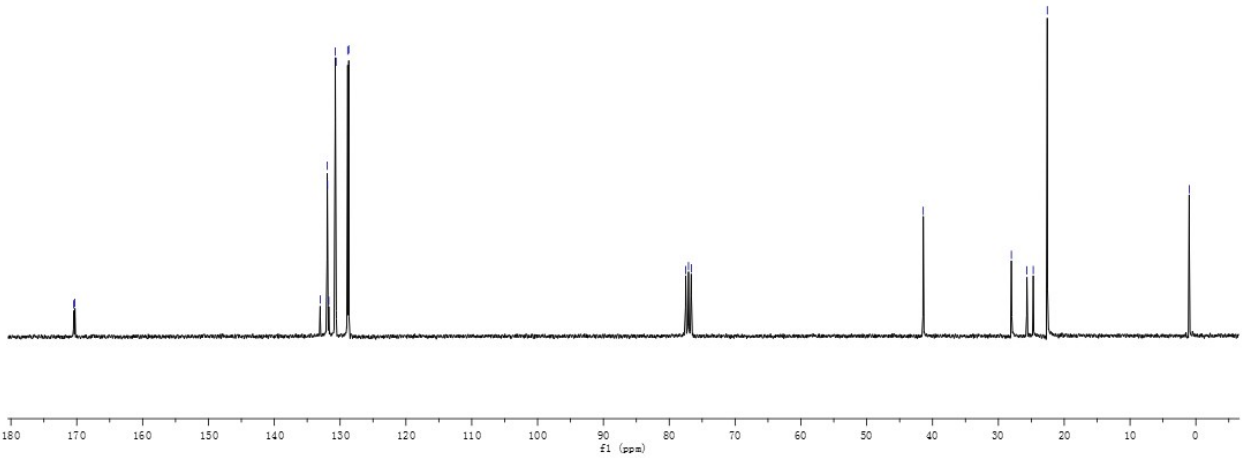
4i

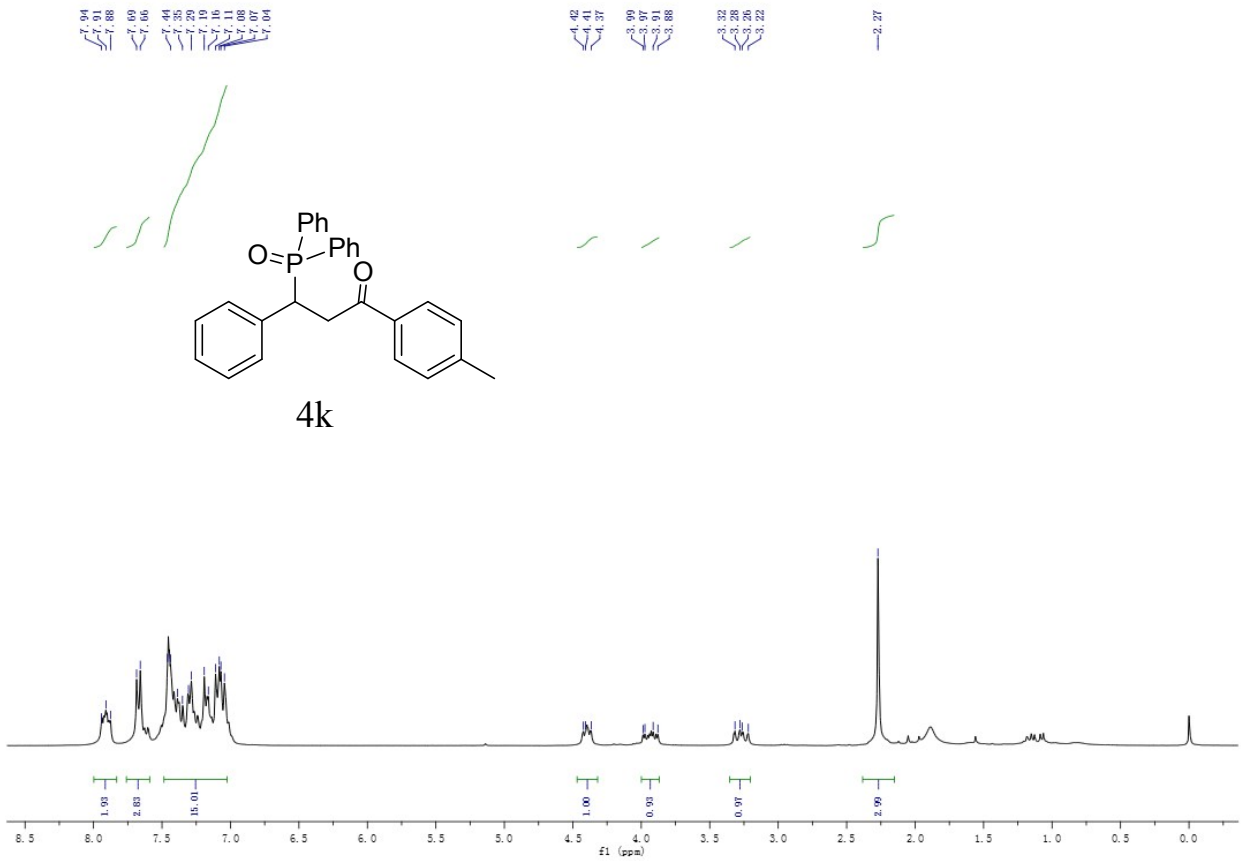


4j



4j

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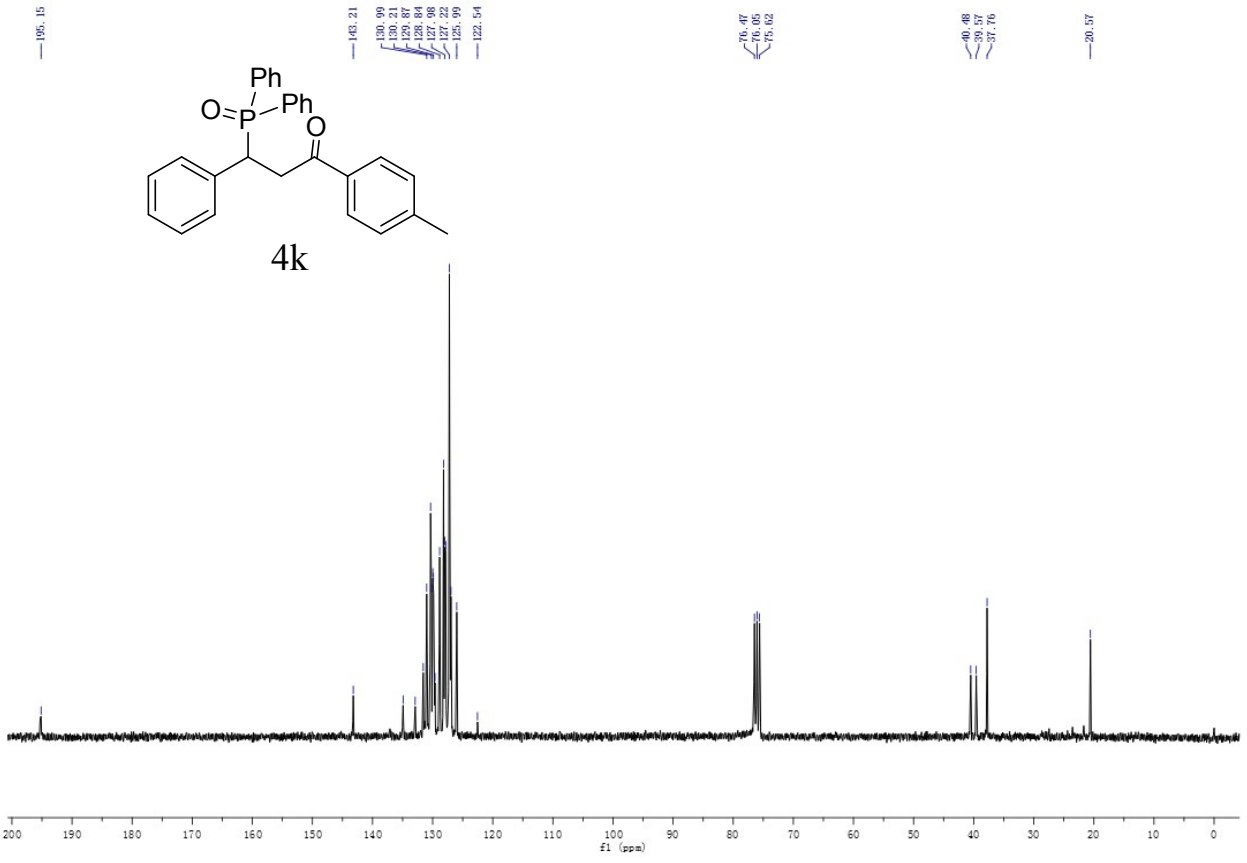
7.11
7.08
7.07
7.04
4.42
4.41
4.37
3.99
3.97
3.91
3.88
3.32
3.28
3.26
3.22
2.27
Ph
O=P
Ph
O
4k
1.93
2.83
15.01
1.00
0.93
0.97
2.99
f1 (ppm)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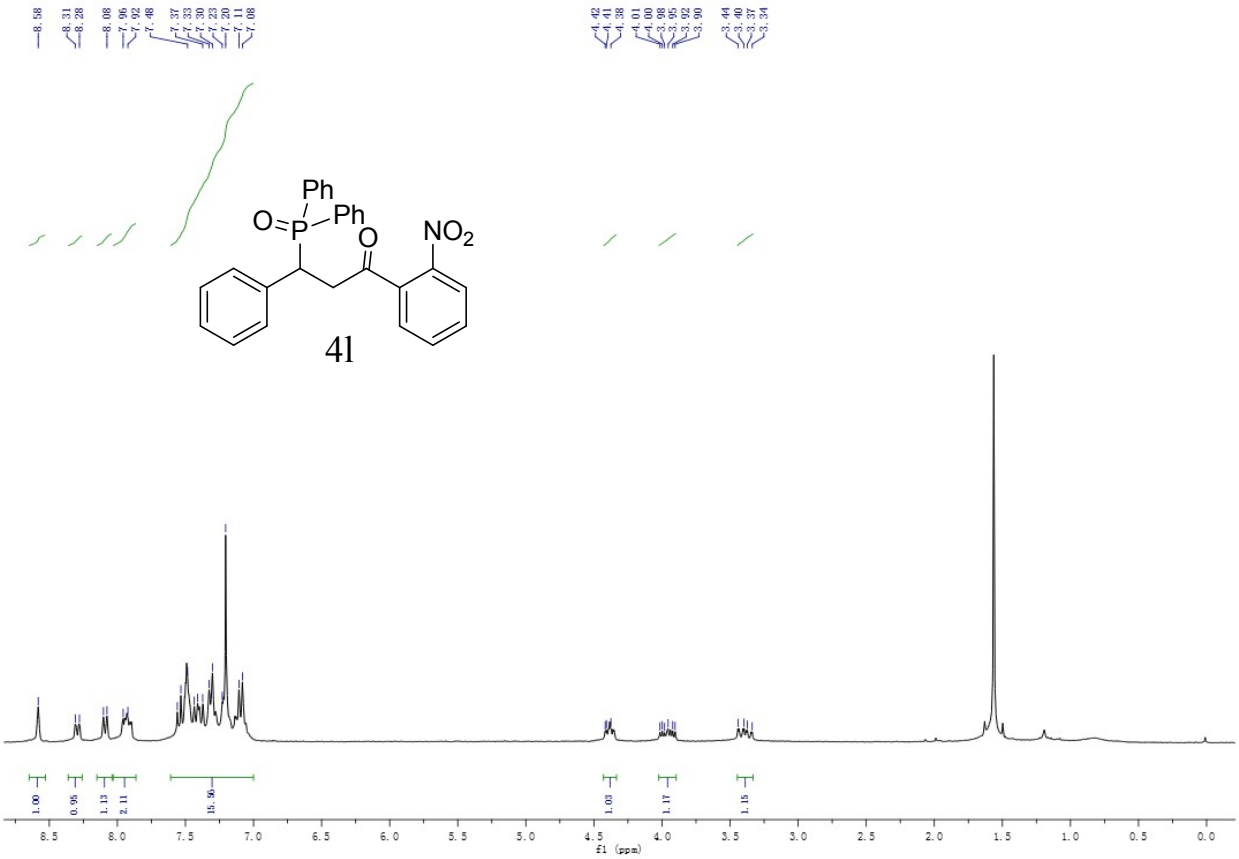
127.98
127.22
125.99
122.54
76.47
76.05
75.62
40.48
39.57
37.76
20.57
Ph
O=P
Ph
O
4k
f1 (ppm)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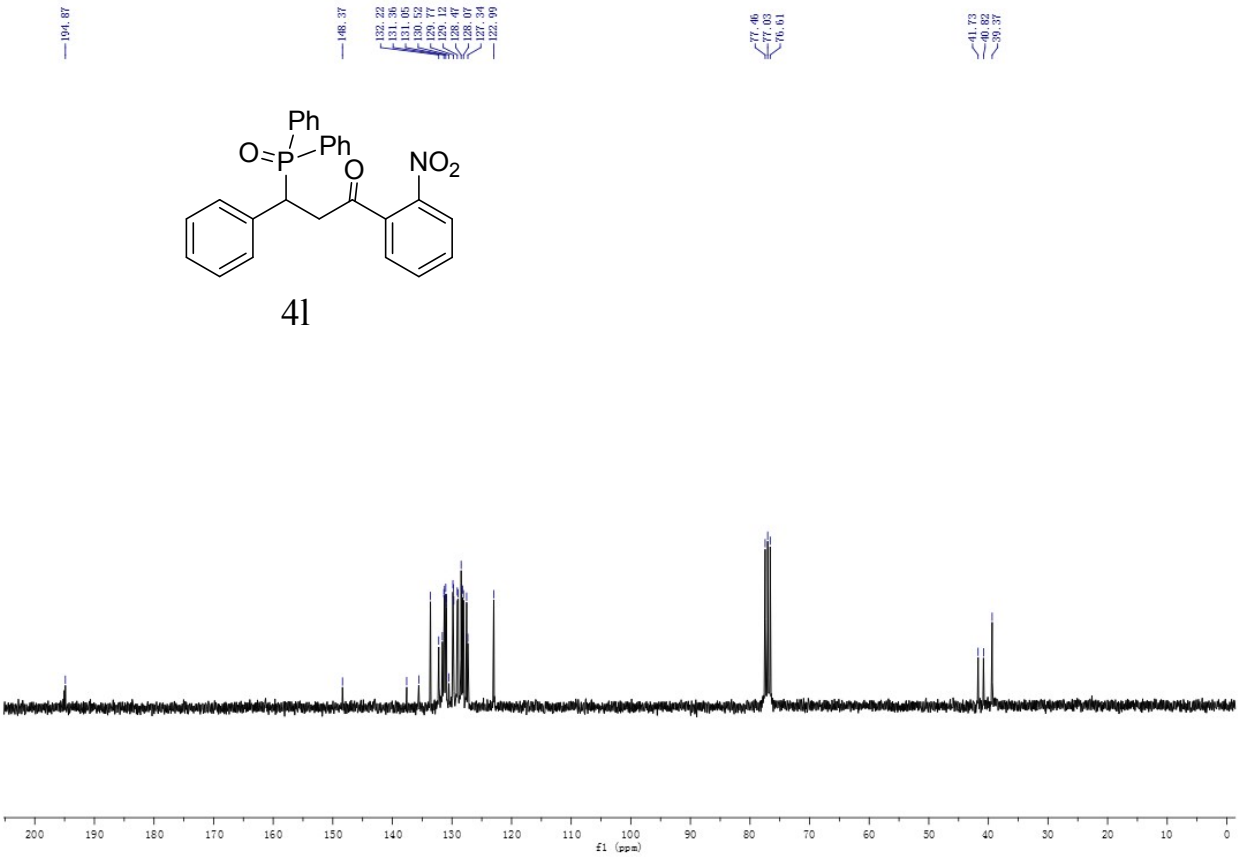
7.37
7.33
7.30
7.23
7.20
7.11
7.08
4.42
4.41
4.38
4.01
4.00
3.98
3.95
3.92
3.90
3.44
3.40
3.37
3.34
Ph
Ph
O
O
NO2
1.00
0.95
1.13
2.11
15.96
1.03
1.17
1.15
f1 (ppm)

41l


194.87
148.37
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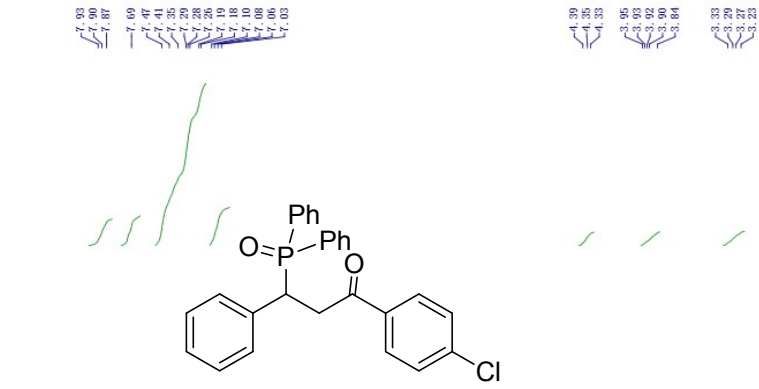
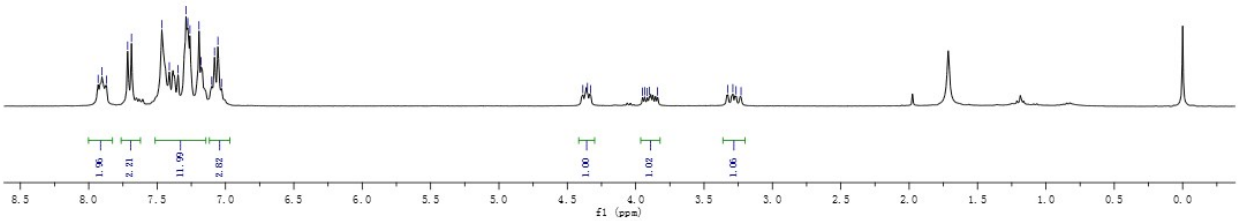
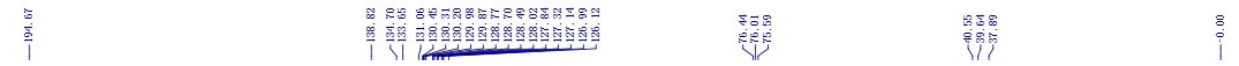
128.47
128.07
127.34
122.99
77.46
77.03
76.61
41.73
40.02
39.37
Ph
Ph
O
O
NO2
f1 (ppm)

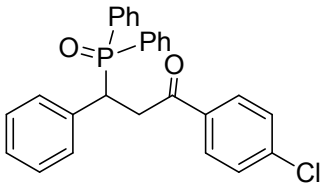
41l



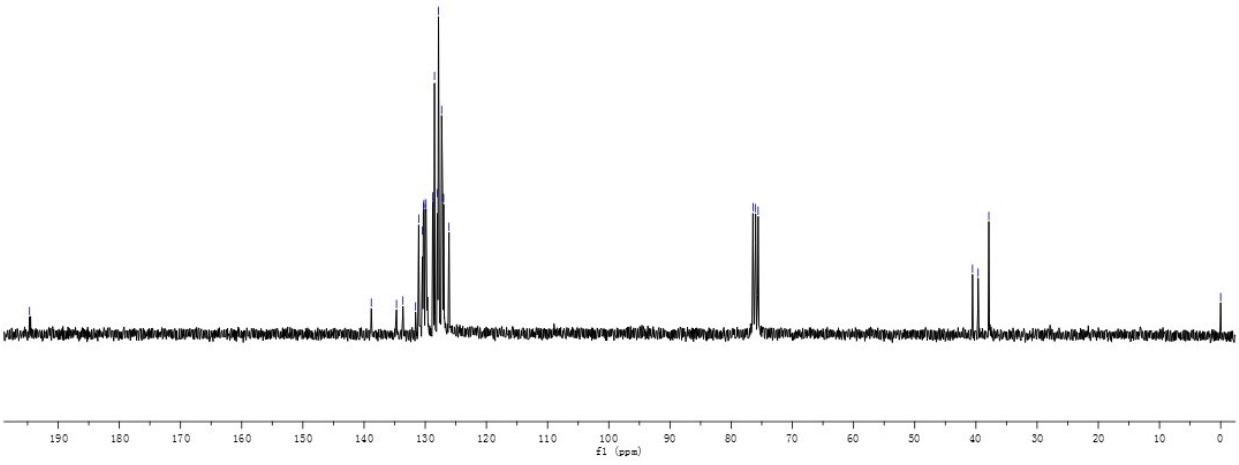
4m

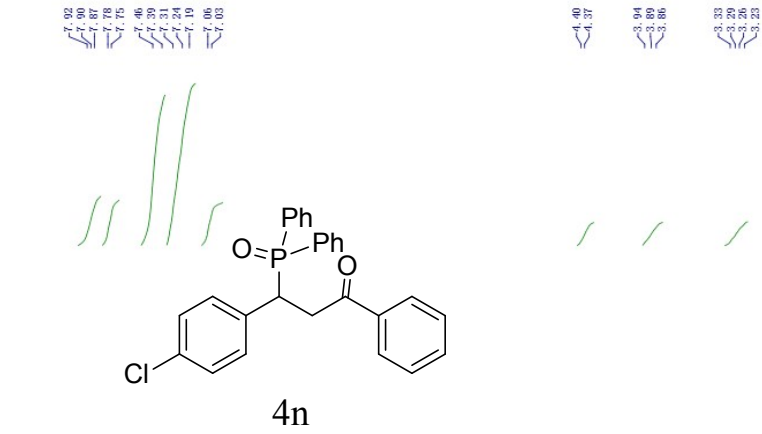




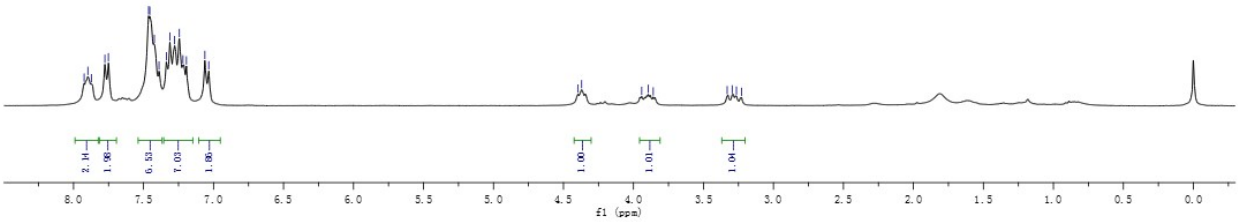


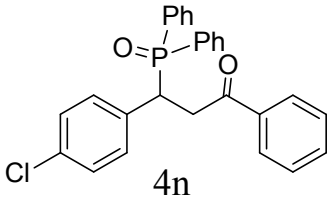
4m



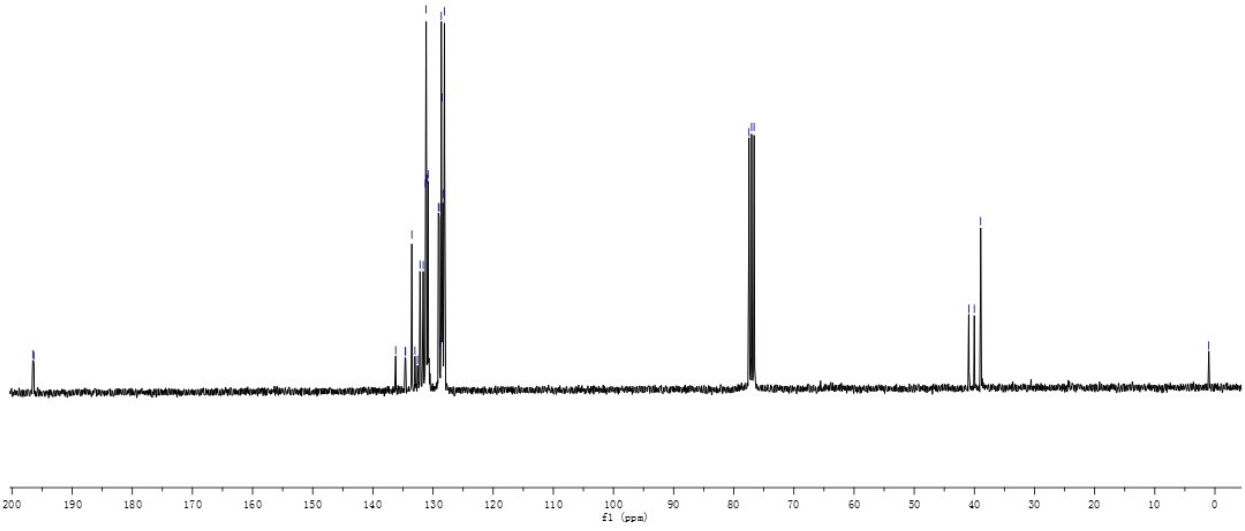


4n





4n



V. Crystallographic Data for Complexes **1a-d**

Crustal data	**1a**	**1b**	**1c**	**1d**
Empirica formula	$C_{42}H_{68}N_5NdSi_2$	$C_{42}H_{68}DyN_5Si_2$	$C_{42}H_{68}N_5Si_2Yb$	$C_{42}H_{68}N_5Si_2Y$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	12.4507(11)	12.7402(9)	12.5546(11)	12.7235(11)
b (Å)	16.3478(15)	15.6814(11)	15.7504(14)	15.6788(14)
c (Å)	22.550(2)	22.7852(16)	22.813(2)	22.7752(19)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
V ($Å^3$)	4589.9(7)	4552.1(6)	4511.1(7)	4543.4(7)
T (K)	293(2)	293(2)	293(2)	293(2)
D_{calc} (g cm^{-3})	1.221	1.257	1.284	1.152
Z	4	4	4	4
F(0 0 0)	1772	1796	1812	1688
Reflections collected	39779	39442	38677	32120
Number of unique reflections (R_{int})	10517(0.0299)	10562(0.0280)	10314(0.0331)	7947(0.0572)
Number of parameters	465	465	465	465
λ (Mo Kα radiation) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	1.215	1.726	2.159	1.368
θ Range (°)	1.54 - 27.57	1.58 - 27.65	1.57 - 27.49	1.58 - 25.00
Goodness-of-fit (GOF)	1.049	1.023	1.030	1.010
Final R indices [I> 2σ (I)]; R_1, wR_2	0.0318, 0.0748	0.0279, 0.0637	0.0445, 0.1215	0.0426, 0.0899
R indices (all data); R_1, wR_2	0.0393, 0.0791	0.0363, 0.0677	0.0516, 0.1273	0.0774, 0.1031
Largest difference in peak and hole (e $Å^{-3}$)	0.284 and -1.056	0.580 and -0.479	0.353 and -1.003	0.212 and -0.340