Supporting Information

Intramolecular hydroamination reactions catalyzed by zirconium complexes bearing bridged bis(phenolato) ligands

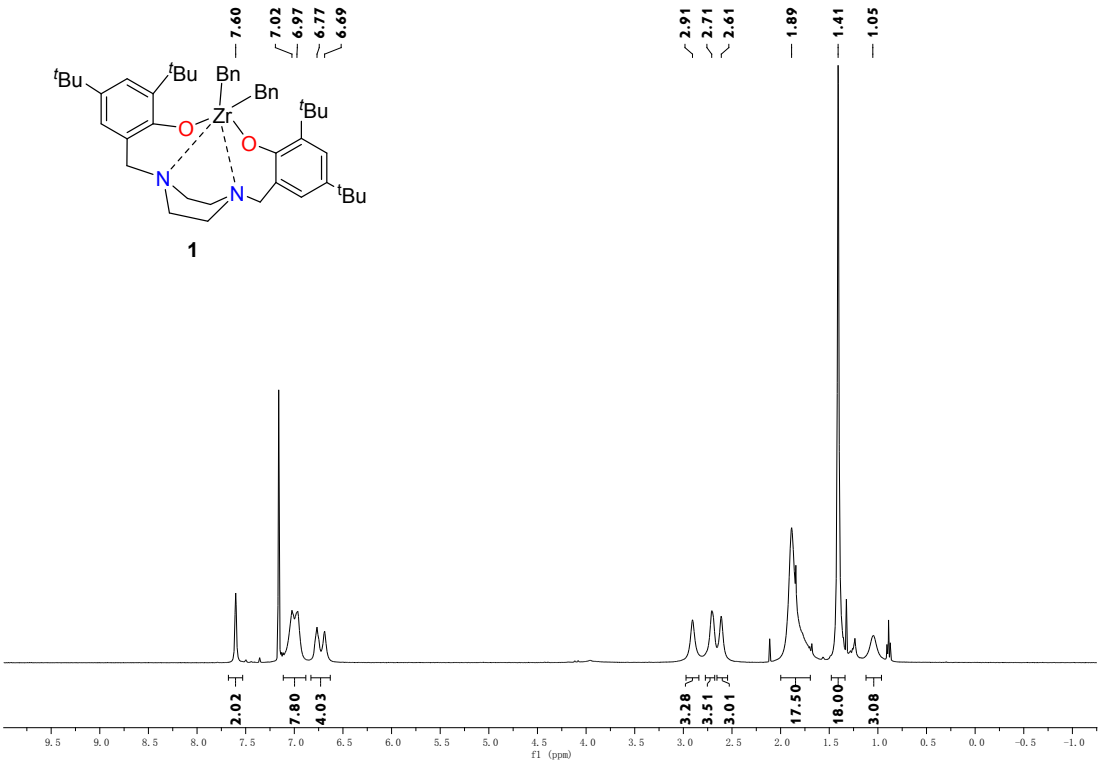
Yu Zhang, Qiu Sun, Yaorong Wang, Dan Yuan*, Yingming Yao* and Qi Shen

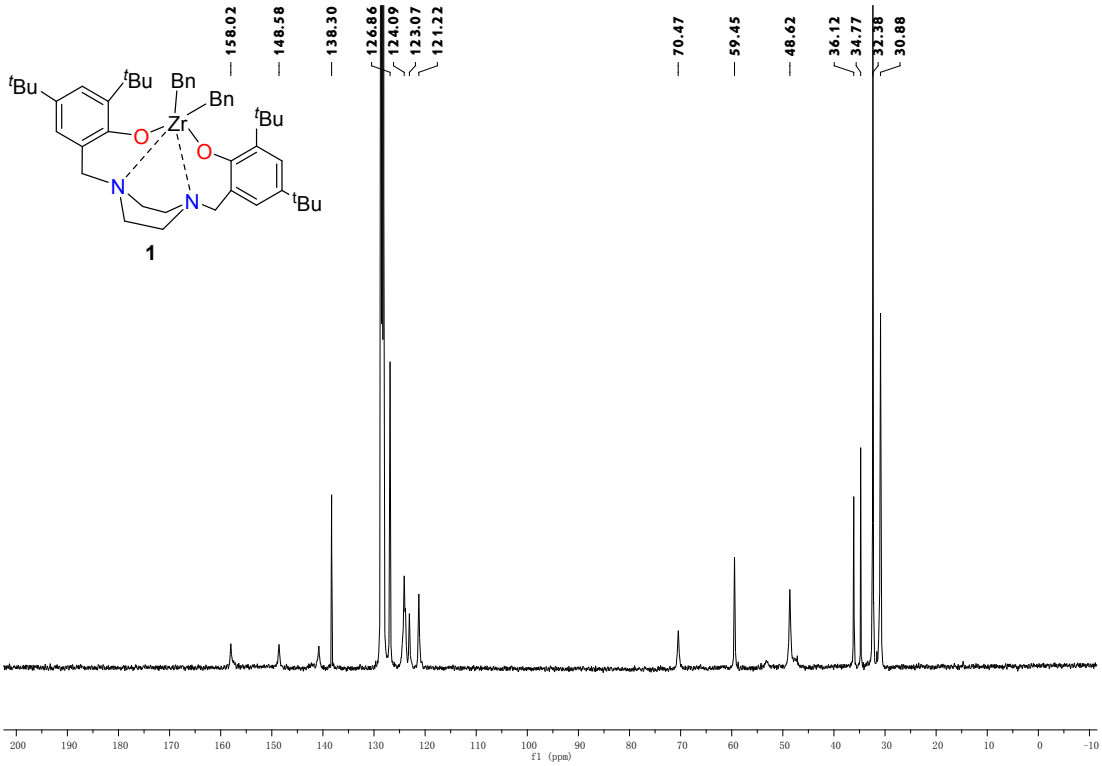
†Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China

*To whom correspondence should be addressed. Email: yuandan@suda.edu.cn; yaoym@suda.edu.cn

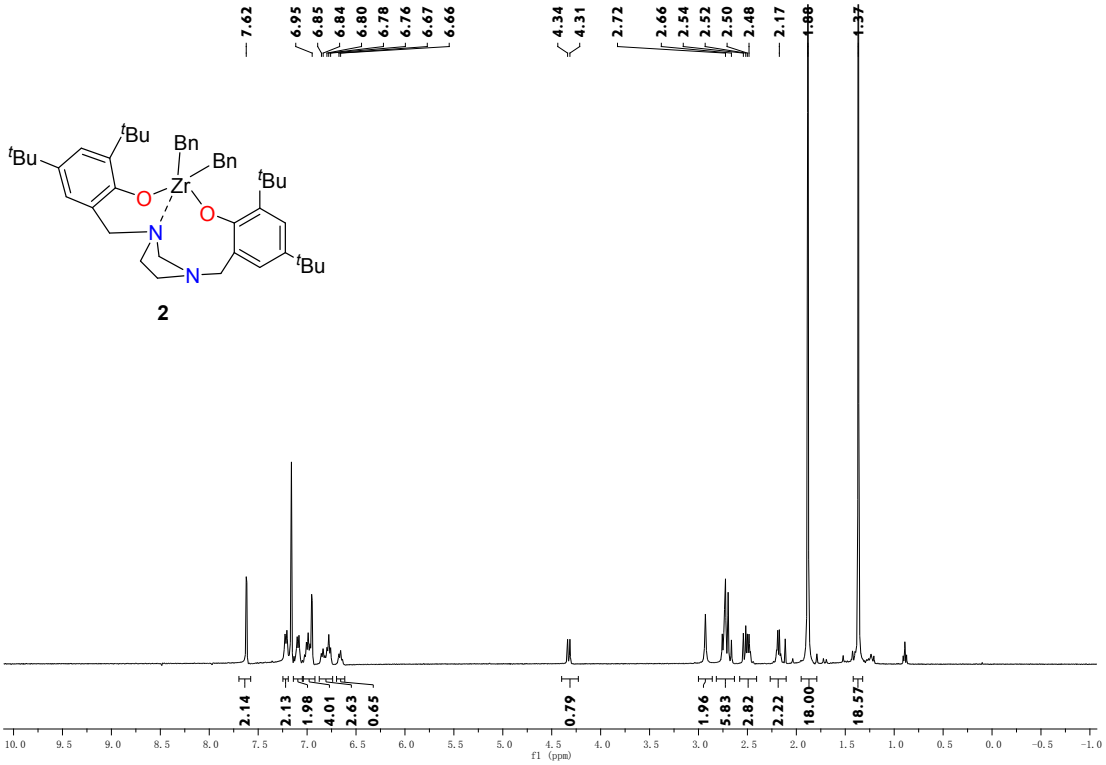
Content

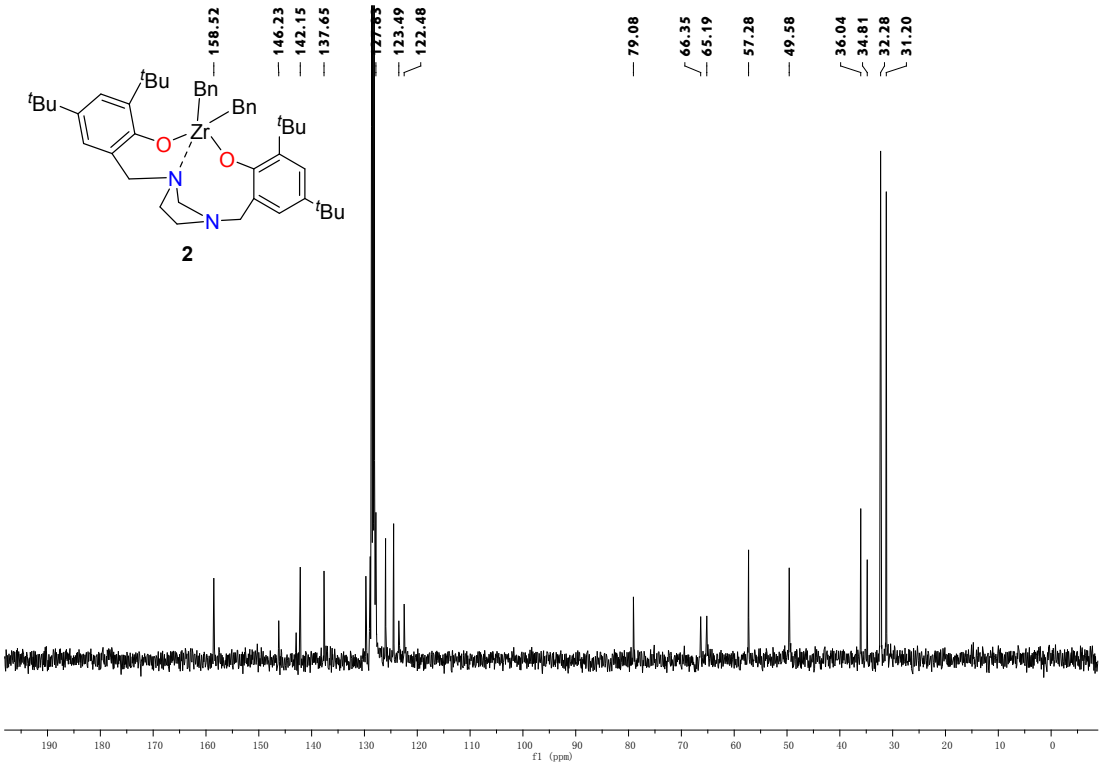
^{1}H and ^{13}C NMR spectra of complex 1



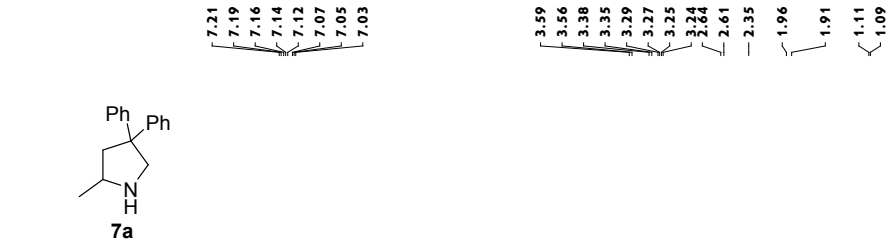


^{1}H and ^{13}C NMR spectra of complex 2

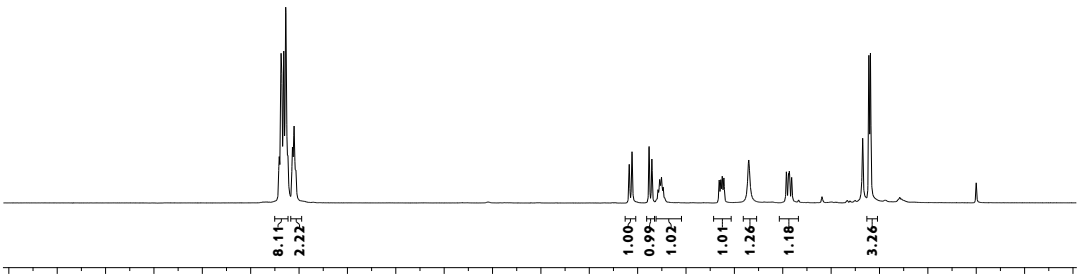


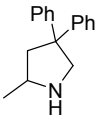


^{1}H and ^{13}C NMR spectra of cyclization products

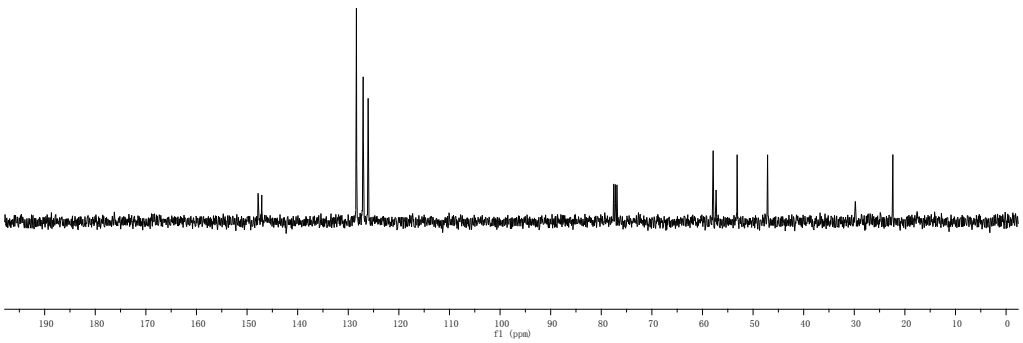


7a

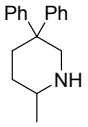




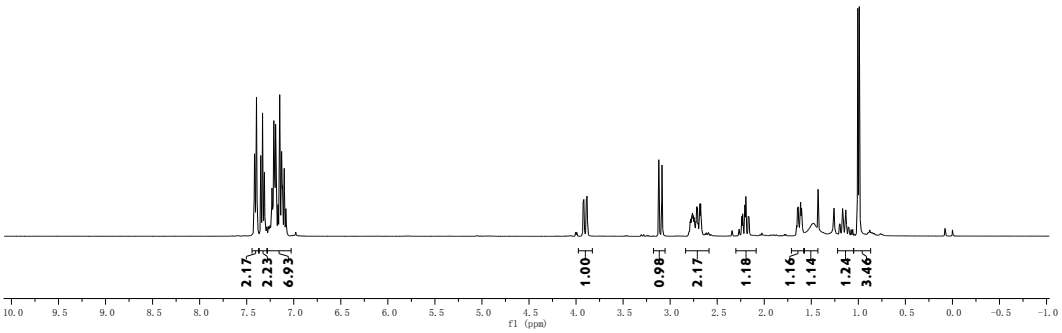
7a

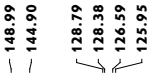


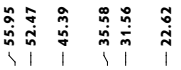

7.42
7.40
7.35
7.33
7.31
7.23
7.21
7.19
7.19
7.17
7.15
7.13
7.10
7.08
3.12
3.09
2.68
2.20
2.16
1.61
1.48
1.20
1.19
1.17
1.14
1.13
1.11
1.10
1.01
0.99

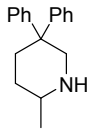

Ph
Ph
NH

7b

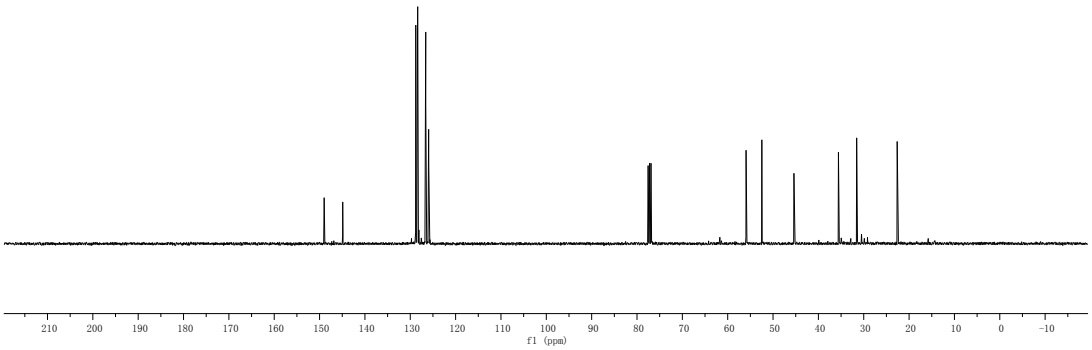

2.17
2.23
6.93
1.00
0.98
2.17
1.18
1.16
1.14
1.24
3.46
f1 (ppm)

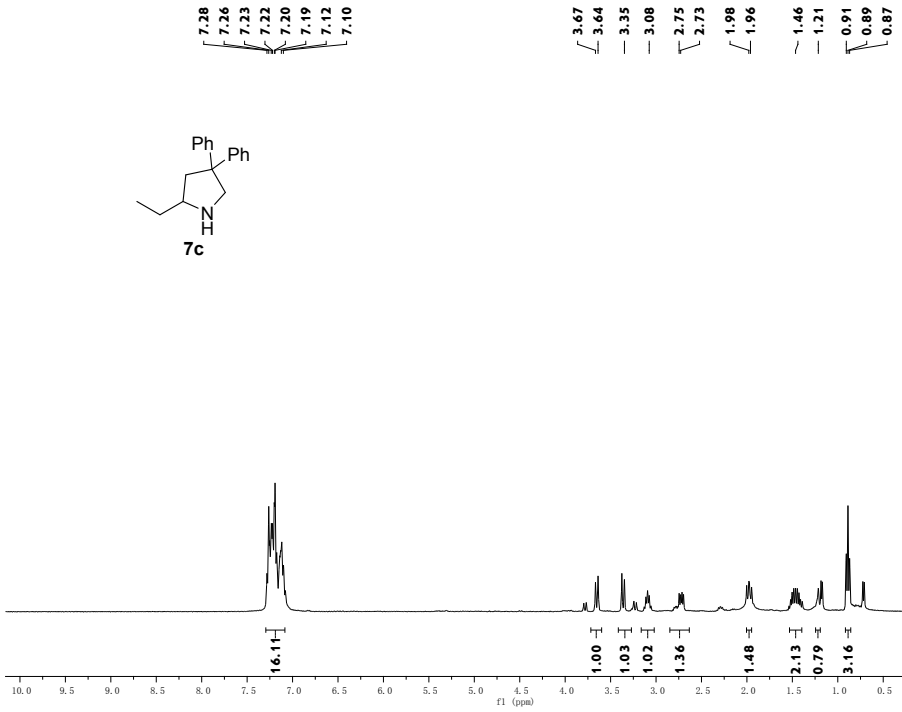

148.99
144.90
128.79
128.38
126.59
125.95

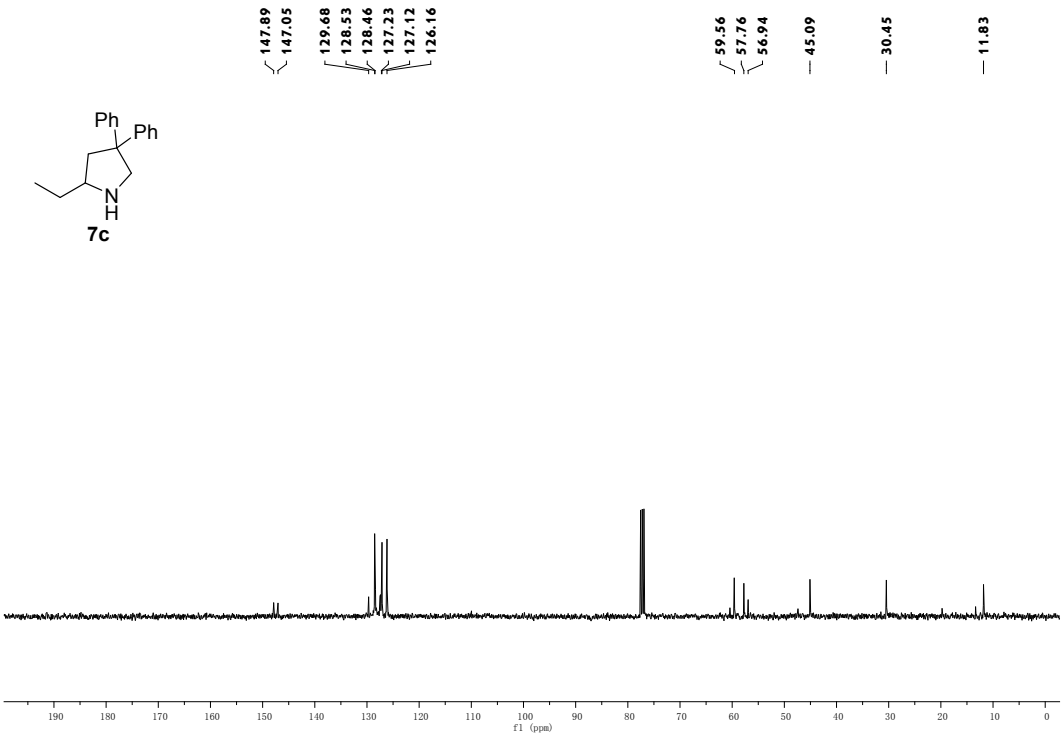

55.95
52.47
45.39
35.58
31.56
22.62

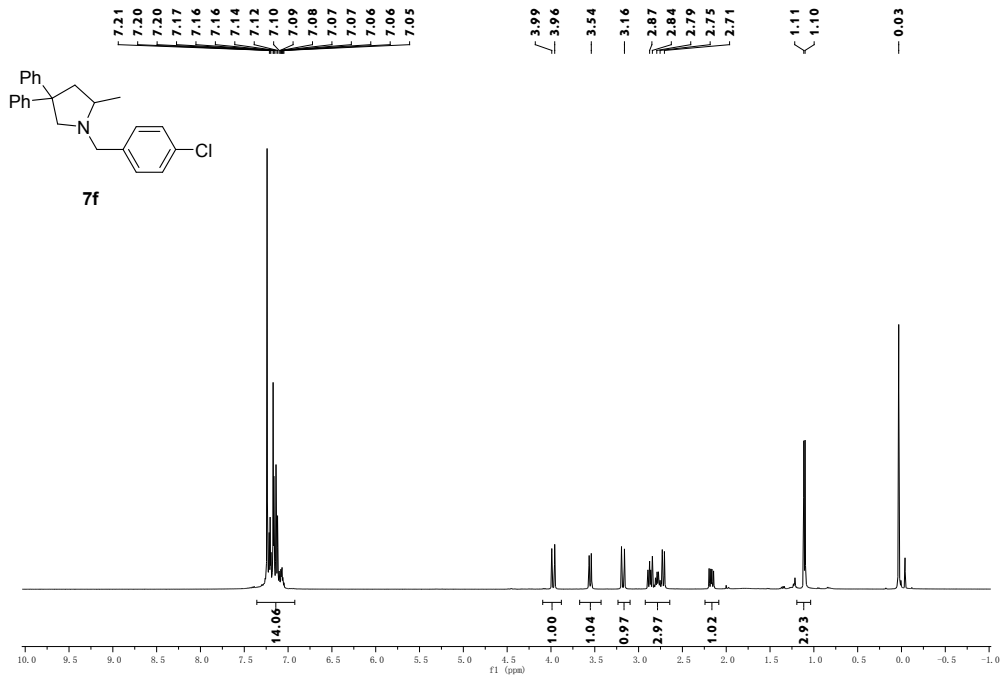

Ph
Ph
NH

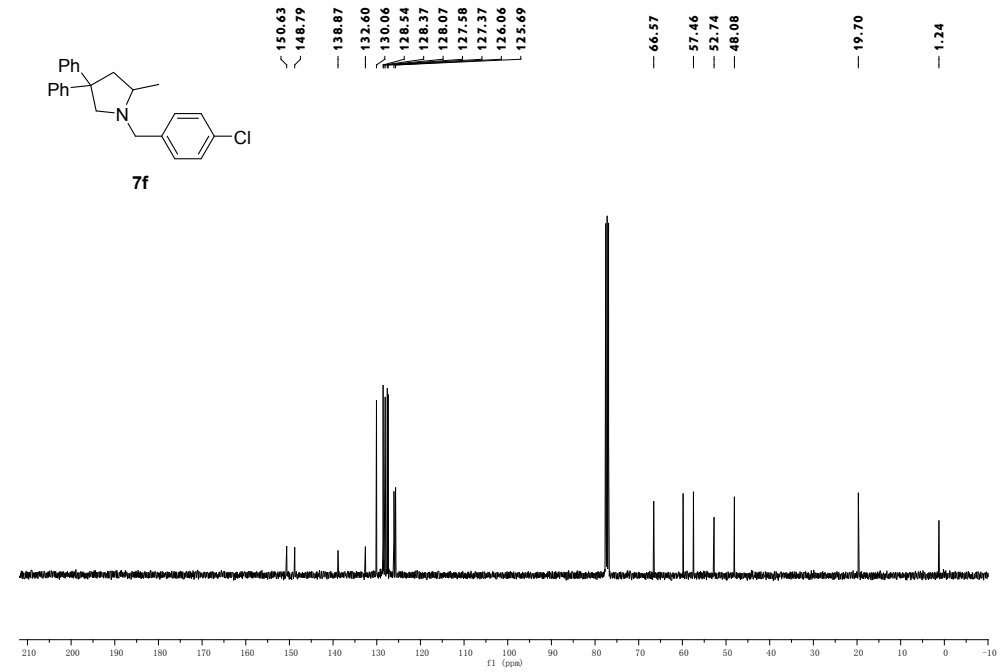
7b


f1 (ppm)

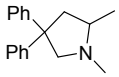

7.28
7.26
7.23
7.22
7.20
7.19
7.12
7.10
3.67
3.64
3.35
3.08
2.75
2.73
1.98
1.96
1.46
1.21
0.91
0.89
0.87
Ph
Ph
N
H
7c
16.11
1.00
1.03
1.02
1.36
1.48
2.13
0.79
3.16
f1 (ppm)


147.89
147.05
129.68
128.53
128.46
127.23
127.12
126.16
59.56
57.76
56.94
45.09
30.45
11.83
Ph
Ph
N
H
7c
f1 (ppm)

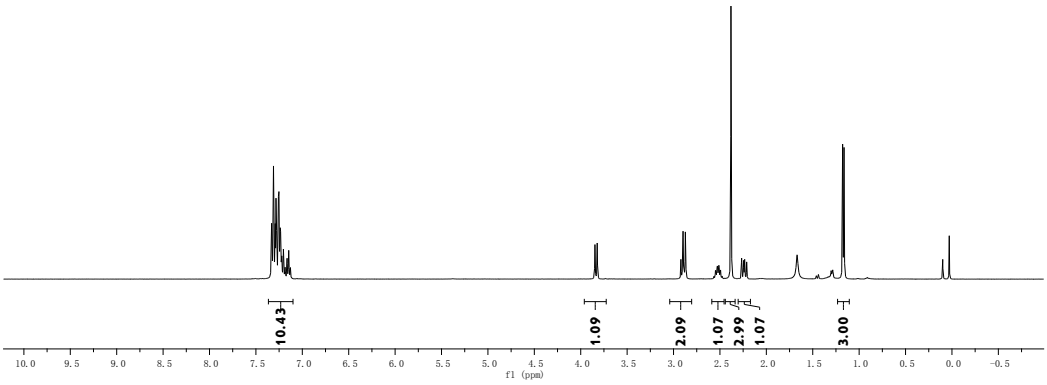

7.21
7.20
7.20
7.17
7.16
7.16
7.14
7.12
7.10
7.09
7.08
7.07
7.07
7.06
7.06
7.05
3.99
3.96
3.54
3.16
2.87
2.84
2.79
2.75
2.71
1.11
1.10
0.03
Ph
Ph
N
Cl
7f
14.06
1.00
1.04
0.97
2.97
1.02
2.93
f1 (ppm)

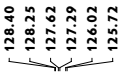

150.63
148.79
138.87
132.60
130.06
128.54
128.37
128.07
127.58
127.37
126.06
125.69
66.57
57.46
52.74
48.08
19.70
1.24
Ph
Ph
N
Cl
7f
f1 (ppm)

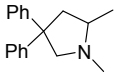

7.33
7.31
7.29
7.28
7.28
7.25
7.23
7.22
7.20
7.19
7.16
7.15
7.13
3.85
3.82
2.90
2.89
2.87
2.51
2.48
2.24
2.21
1.18
1.16


Ph
Ph
N

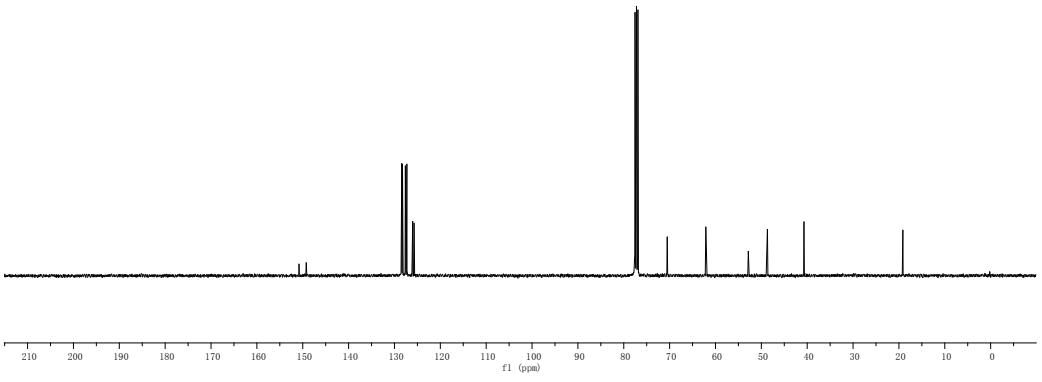
7g

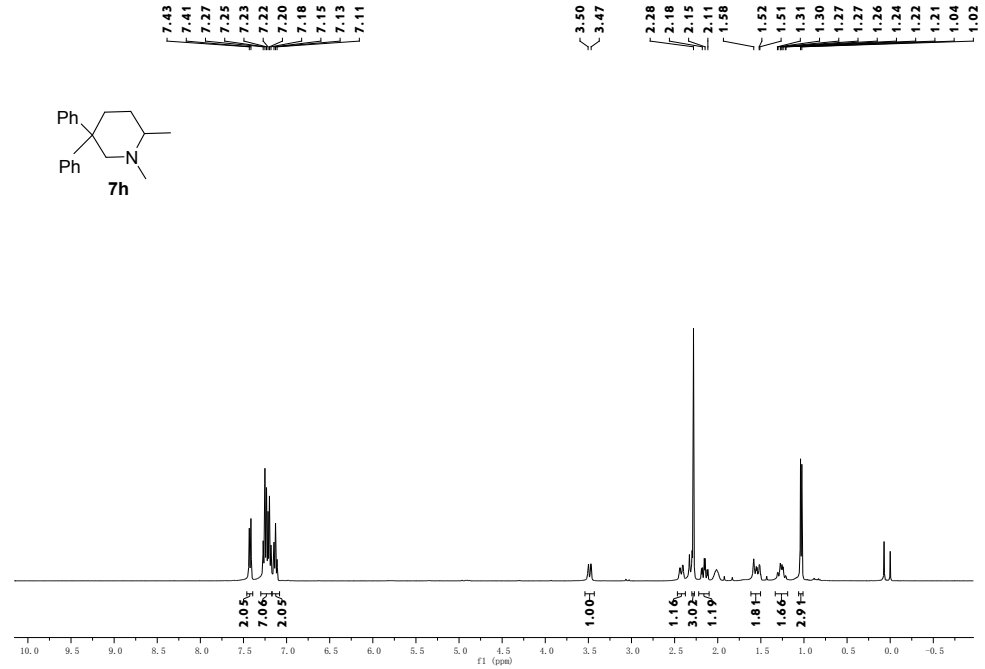

10.43
1.09
2.09
1.07
2.99
1.07
3.00
f1 (ppm)

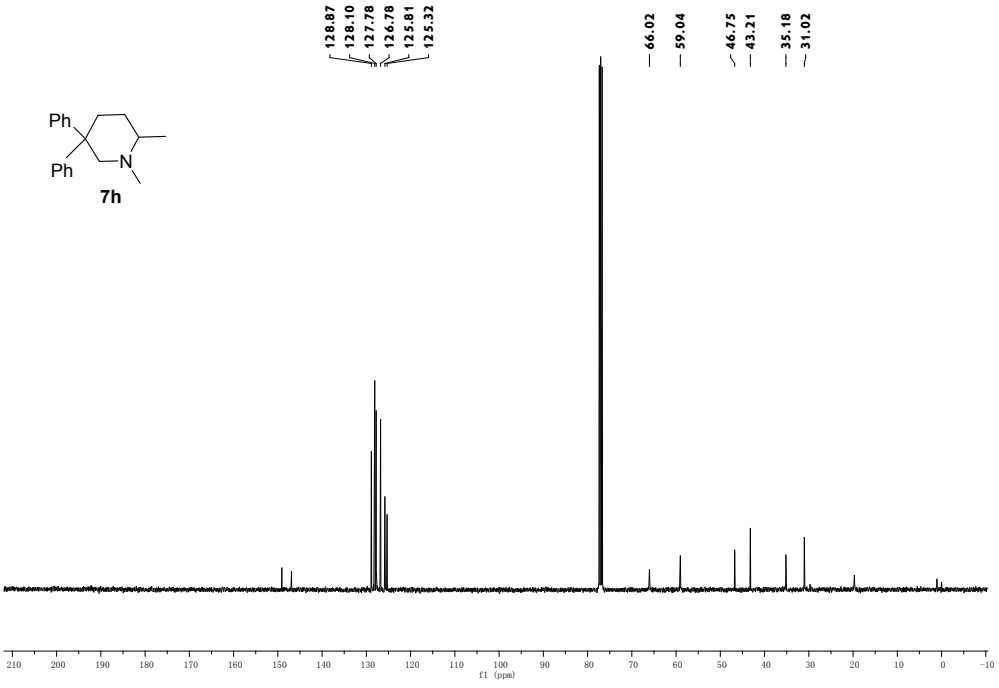

128.40
128.25
127.62
127.29
126.02
125.72
70.52
62.11
52.84
48.67
40.71
19.14


Ph
Ph
N

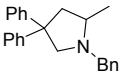
7g


f1 (ppm)

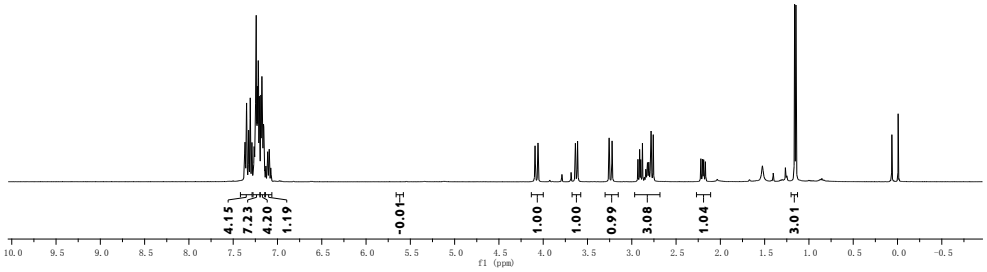

7.43
7.41
7.27
7.25
7.23
7.22
7.20
7.18
7.15
7.13
7.11
3.50
3.47
2.28
2.18
2.15
2.11
1.58
1.52
1.51
1.31
1.30
1.27
1.27
1.26
1.24
1.22
1.21
1.04
1.02
Ph
Ph
N
7h
2.05
7.06
2.05
1.00
1.16
3.02
1.19
1.81
1.66
2.91
f1 (ppm)

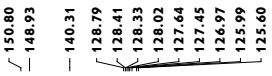

128.87
128.10
127.78
126.78
125.81
125.32
66.02
59.04
46.75
43.21
35.18
31.02
Ph
Ph
N
7h
f1 (ppm)

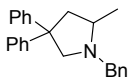

7.37
7.35
7.33
7.31
7.29
7.26
7.24
7.23
7.23
7.21
7.19
7.18
7.17
7.16
7.15
7.13
7.11
7.09
7.08
4.09
4.06
3.61
3.22
2.78
2.22
2.20
2.19
2.17
1.16
1.15


Ph
Ph
N
Bn

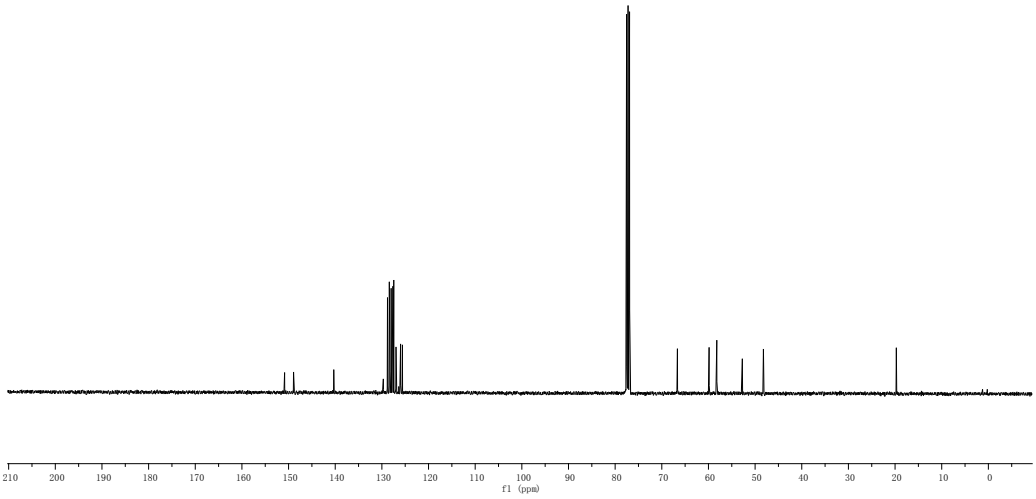
7i

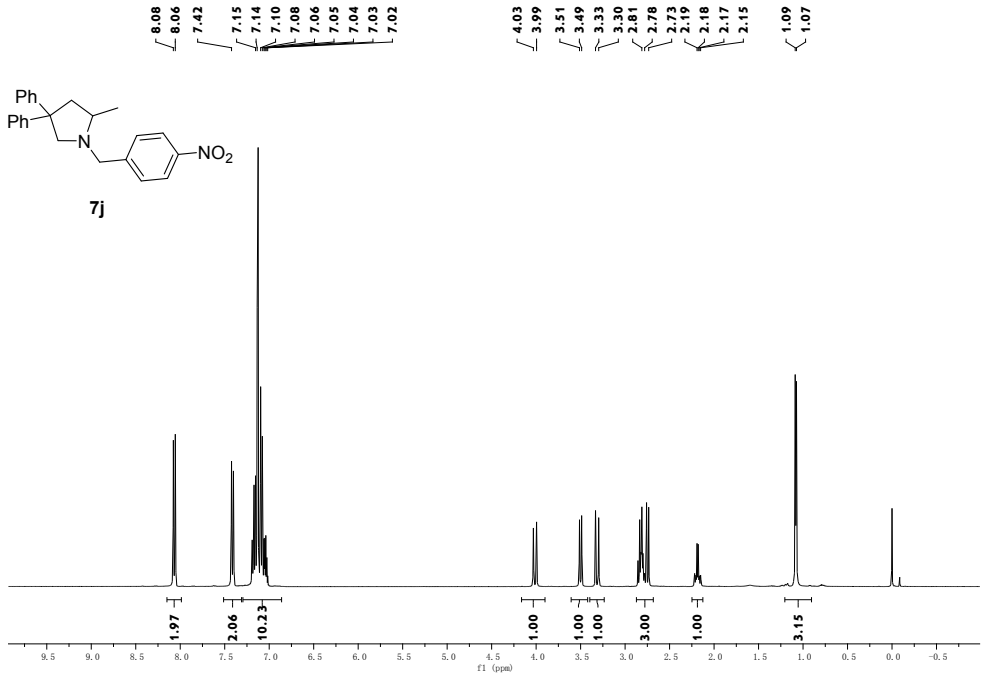

4.15
7.23
4.20
1.19
-0.01
1.00
1.00
0.99
3.08
1.04
3.01
f1 (ppm)


150.80
148.93
140.31
128.79
128.41
128.33
128.02
127.64
127.45
126.97
125.99
125.60
66.65
58.21
52.74
48.21
19.73

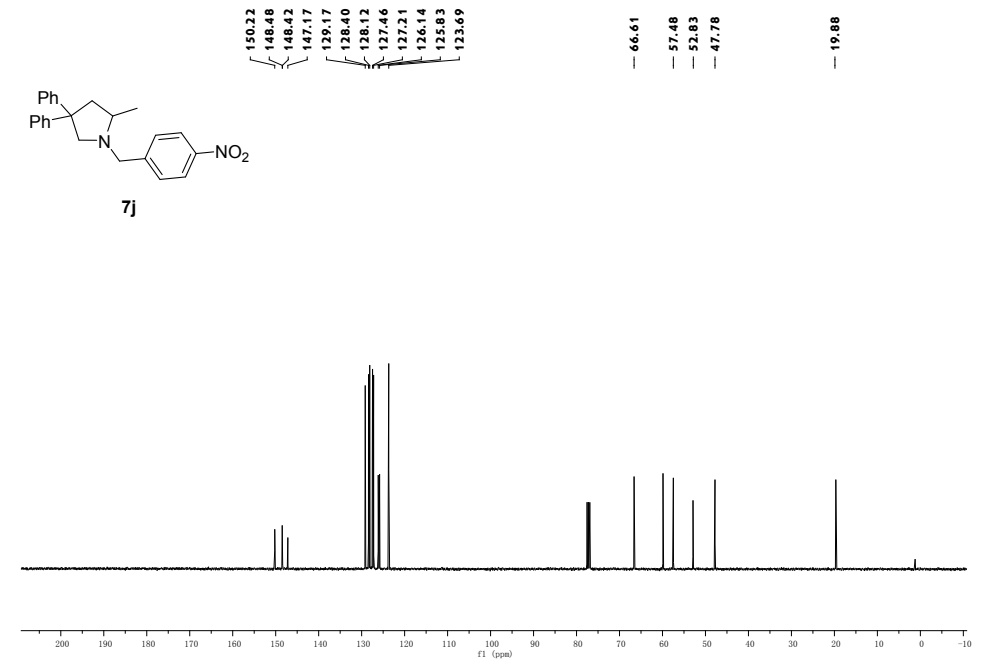

Ph
Ph
N
Bn

7i

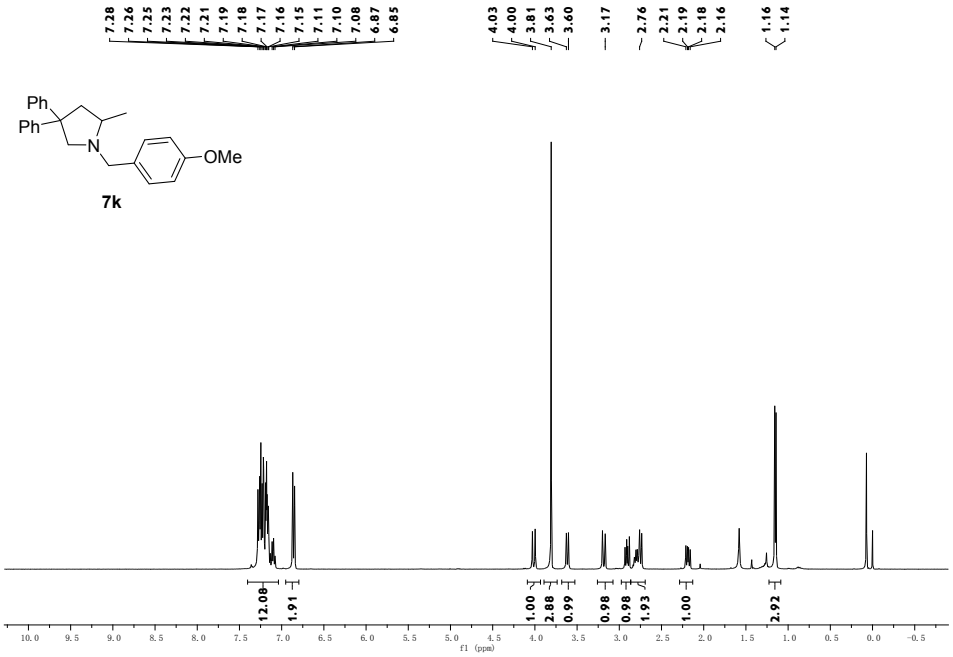

f1 (ppm)

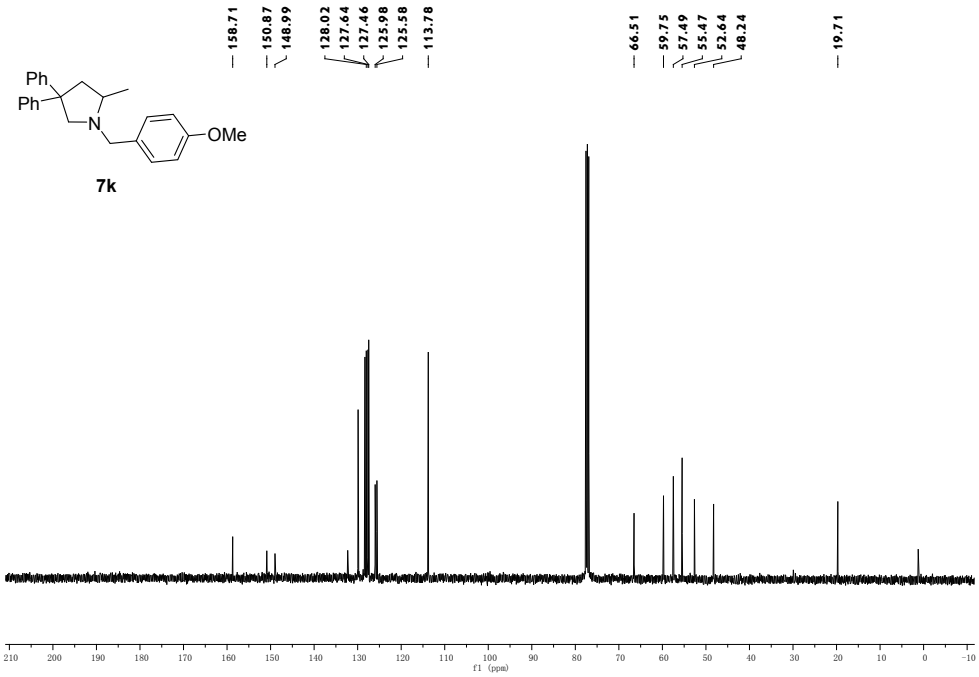

8.08
8.06
7.42
7.15
7.14
7.10
7.08
7.06
7.05
7.04
7.03
7.02
4.03
3.99
3.51
3.49
3.33
3.30
2.81
2.78
2.73
2.19
2.18
2.17
2.15
1.09
1.07
Ph
Ph
N
NO2
1.97
2.06
10.23
1.00
1.00
1.00
3.00
1.00
3.15
f1 (ppm)

7j


150.22
148.48
148.42
147.17
129.17
128.40
128.12
127.46
127.21
126.14
125.83
123.69
66.61
57.48
52.83
47.78
19.88
Ph
Ph
N
NO2
f1 (ppm)

7j

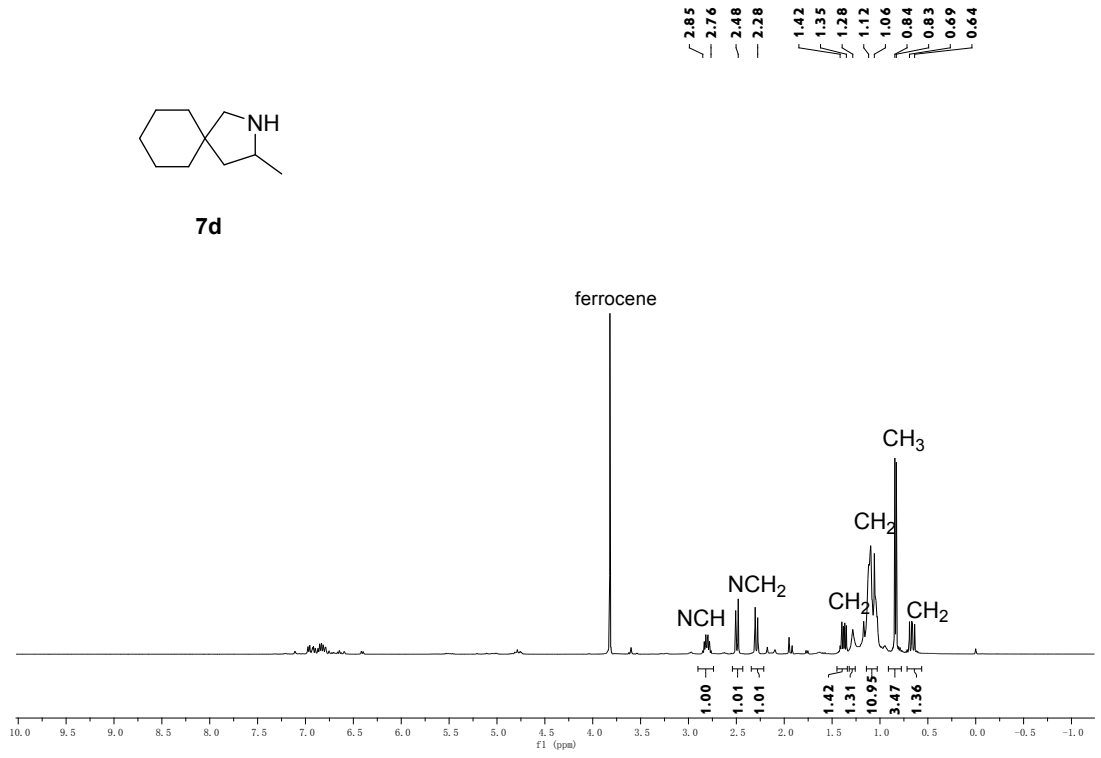

7.28
7.26
7.25
7.23
7.22
7.21
7.19
7.18
7.17
7.16
7.15
7.11
7.10
7.08
6.87
6.85
4.03
4.00
3.81
3.63
3.60
3.17
2.76
2.21
2.19
2.18
2.16
1.16
1.14
Ph
Ph
N
OMe
7k
12.08
1.91
1.00
2.88
0.99
0.98
0.98
1.93
1.00
2.92
f1 (ppm)


158.71
150.87
148.99
128.02
127.64
127.46
125.98
125.58
113.78
66.51
59.75
57.49
55.47
52.64
48.24
19.71
Ph
Ph
N
OMe
7k
f1 (ppm)

[1]H NMR monitoring of reactions

[1]H NMR (400MHz, PhBr-d_5), ferrocene as internal standard

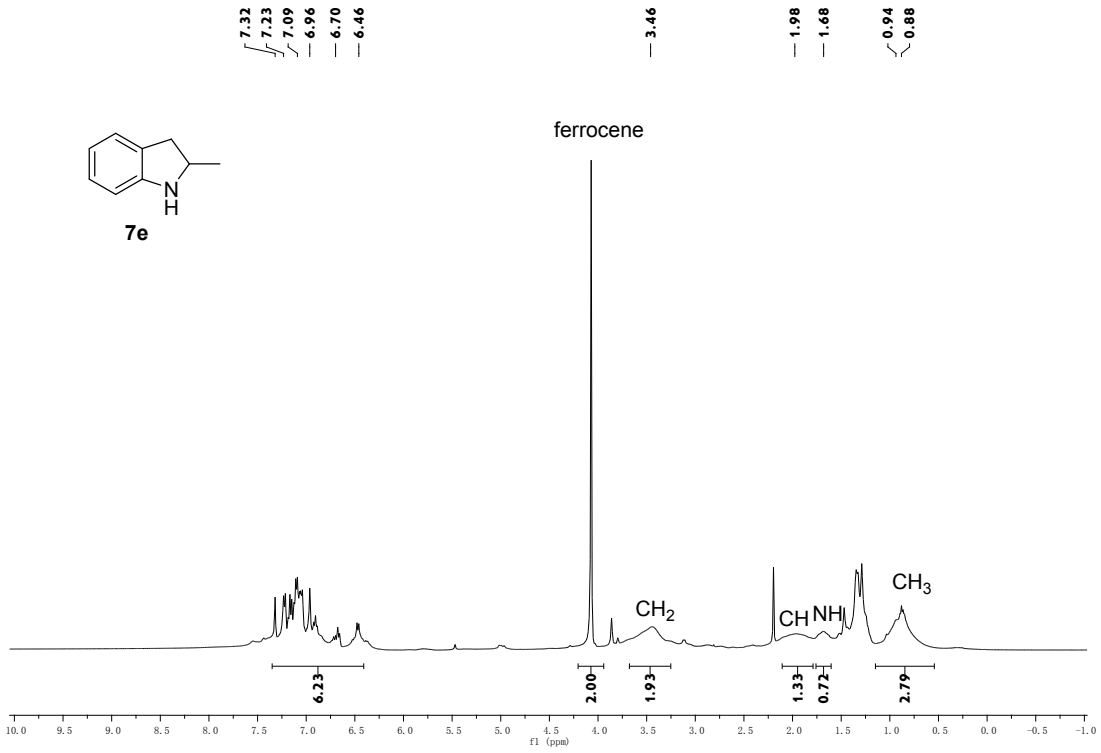
Substrate **6d**: 0.3 mmol; catalyst: 5 mol% of complex **1** and $[Ph_3C][B(C_6F_5)_4]$ (TB); condition: 140 °C, 8 h



^{1}H NMR (400MHz, PhBr-d_5), ferrocene as internal standard

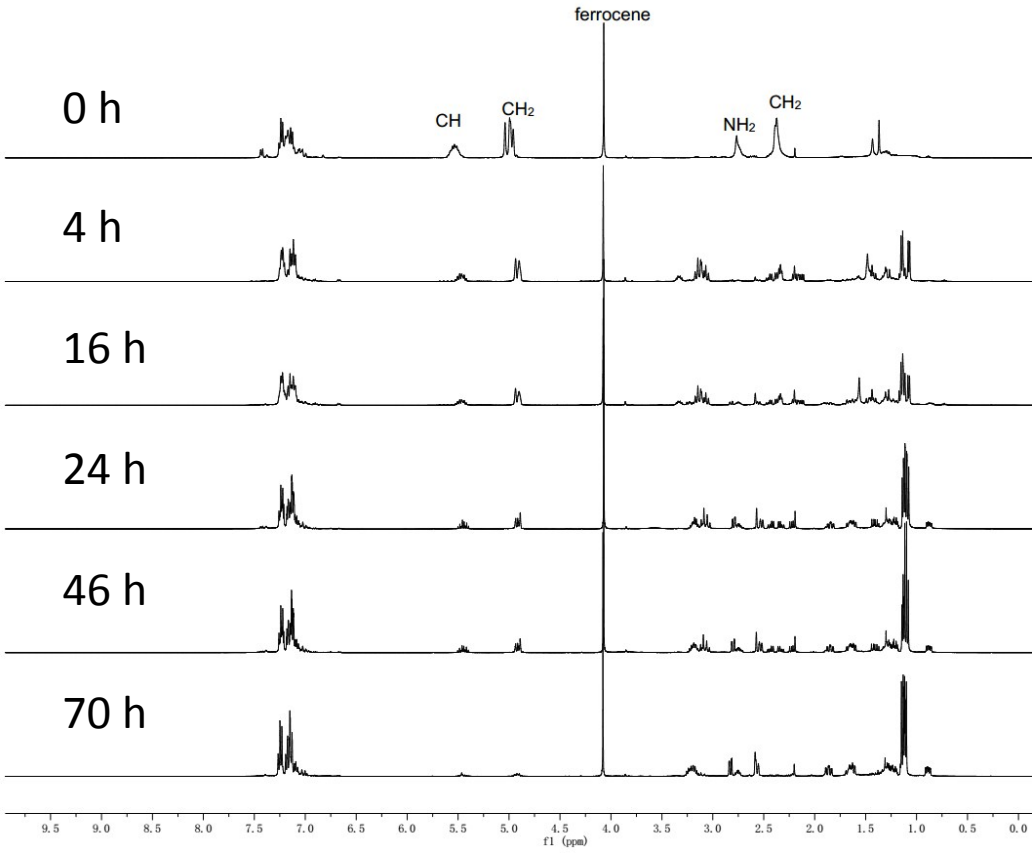
Substrate **6e**: 0.3 mmol, catalyst: 10 mol% of complex **1** and $[Ph_3C][B(C_6F_5)_4]$ (TB),

Temperature: 140 °C



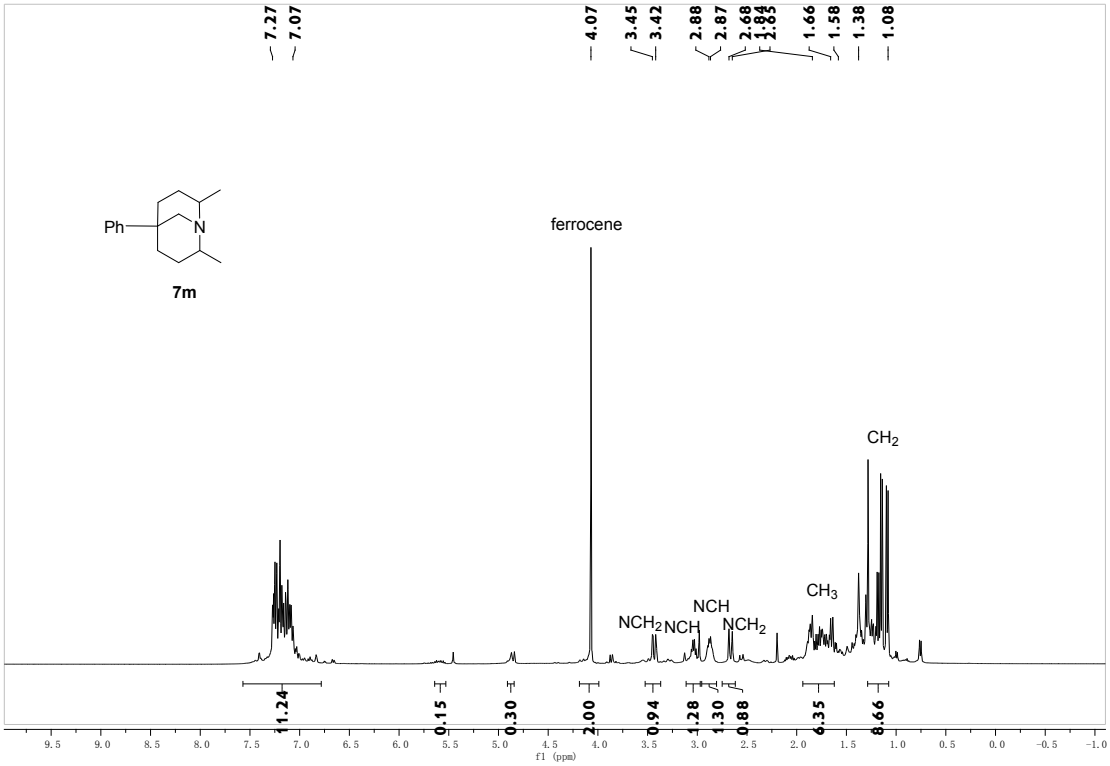
^{1}H NMR (400MHz, PhCl-d_5), ferrocene as internal standard

Substrate **6i**: 0.3 mmol; catalyst: 5 mol% of complex **1** and $[Ph_3C][B(C_6F_5)_4]$ (TB); condition: 140 °C, 48 h

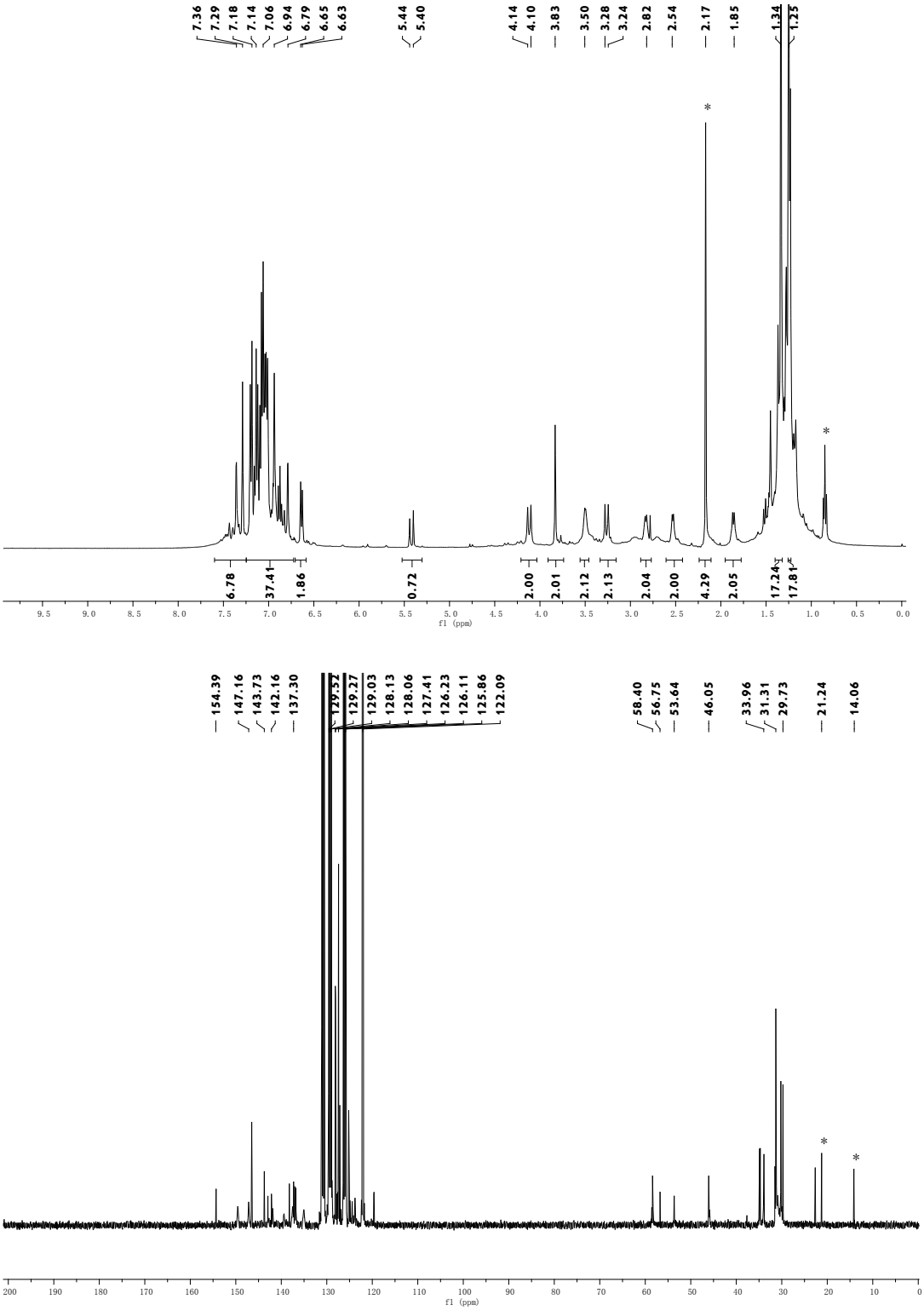


^{1}H NMR (400MHz, PhCl-d_5), ferrocene as internal standard

Substrate **6m**: 0.3 mmol; catalyst: 10 mol% of complex **1** and $[Ph_3C][B(C_6F_5)_4]$ (TB); condition: 140 °C, 96 h



^{1}H and ^{13}C NMR spectra of complex **1** + TB



Signals marked with asterisks correspond to solvent (toluene and hexane, respectively).

Table S1. Crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{48}H_{66}N_2O_2Zr$	$C_{47}H6_2N_2O_2Zr$
Fw	794.25	778.21
Temperature (K)	293(2)	223(2)
λ (Mo Kα) (Å)	0.71073	0.71073
Cryst. Syst.	orthorhombic	orthorhombic
color	colourless	yellow
Cryst size (mm)	0.40 × 0.40 × 0.40 mm	0.40 × 0.20 × 0.20 mm
Space group	Pnna	P 2_1 2_1 2_1
a (Å)	12.6905(4)	11.480(2)
b (Å)	29.8425(13)	14.798(3)
c (Å)	12.0229(5)	25.295(5)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	4553.3(3)	4297.1(15)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.159	1.203
μ (mm^{-1})	0.278	0.294
F(000)	1696	1656
θ Range (^{o})	3.11 to 25	1.59 to 26.23
No. of reflns collected	13016	12546
No. of reflns unique, R_{int}	4014, 0.0631	7290, 0.0360
Max, min transm	1.00000, 0.61724	0.9436, 0.8916
No. of variables	246	497
R_1, wR_2 [I > 2σ(I)]	0.0960, 0.1831	0.0475, 0.1213
R_1, wR_2 (all data)	0.1392,0.1934	0.0523, 0.1262
Goodness-of-fit on F^2	1.102	1.028
Largest diff. peak, hole/e Å^{-3}	0.906, -1.867	1.073, - 0.485