Novel chiral yttrium complex with a tridentate linked amido-indenyl ligand for intramolecular hydroamination

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Electronic Supplementary Information

Content

General Information

All reactions with air- or moisture sensitive materials were performed in oven (120 °C) or flame-dried glassware under an inert atmosphere of argon, employing standard Schlenk and glovebox techniques. All solvents were distilled over either finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. $CDCl_3$ was dried over activated 4 Å molecular sieves. C_6D_6 was distilled from sodium/benzophenone ketyl. $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$[1] and $C_9H_7CH_2SiMe_2Cl$[2] were prepared by literature methods. (1*R*, 2*R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine is commercially available or could be prepared by using literature method.[3] Elemental analysis data were obtained with a Perkin–Elmer 2400 Series II elemental analyzer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded with a Bruker AV 300 NMR spectrometer in C_6D_6 for the yttrium complex and in $CDCl_3$ for organic compounds. The aminoalkene substrates 2,2-diphenylpent-4-en-1-amine (**6a**), (*E*)-2,2,5-triphenylpent-4-en-1-amine (**6b**), 2,2-diphenylhex-5-en-1-amine (**6c**), 2,2-dimethyl-pent-4-en-1-amine (**6d**), (*E*)-2,2-dimethyl-5-phenylpent-4-en-1-amine (**6e**), 2,2-dimethylhex-5-en-1-amine (**6f**), (1-allylcyclohexyl)methanamine (**6g**), (*E*)-(1-cinnamylcyclohexyl)methane-mine (**6h**), (*E*)-(1-(4-phenylbut-3-enyl)cyclohexyl)methanamine (**6i**) were synthesized according to literature protocols.[4] Their analytical data were in agreement with those reported in literatures.

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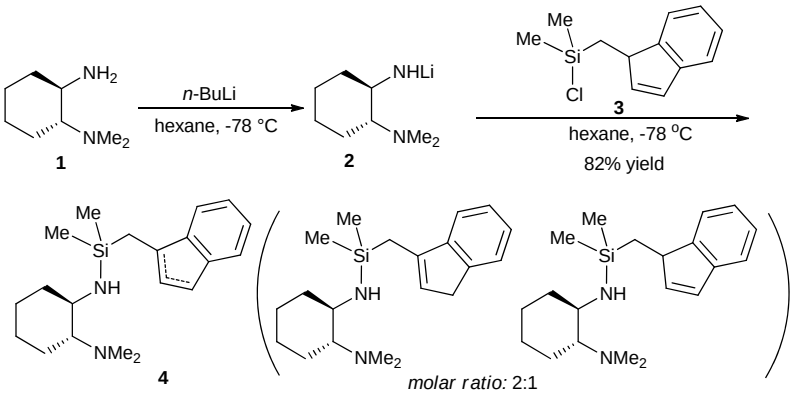
[1] (a) E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang and Z. Huang, *Organometallics,* 2003, **22**, 684; (b) S. Zhou, S. Wang, G. Yang, X. Liu, E. Sheng, K. Zhang, L. Cheng and Z. Huang, *Polyhedron,* 2003, **22**, 1019.

[2] (a) S. Wang, S, Zhou, E. Sheng, M. Xie, K. Zhang, L. Cheng, Y. Feng, L. Mao and Z. Huang, *Organometallics,* 2003, **22**, 3546; (b) S. Zhou, S. Wang, E. Sheng, L. Zhang, Z. Yu, X. Xi, G. Chen, W. Luo and Y. Li, *Eur. J. Inorg. Chem.,* 2007, 1519.

[3] (a) M. Kaik and J. Gawroński, *Tetrahedron: Asymmetry*, 2003, **14**, 1559; (b) T. Okino, Y. Hoashi and Y. Takemoto, *J. Am. Chem. Soc.,* 2003, **125**, 12672; (c) T. Okino, Y. Hoashi, T. Furukawa, X. Xu, and Y. Takemoto, *J. Am. Chem. Soc.,* 2005, **127**, 119.

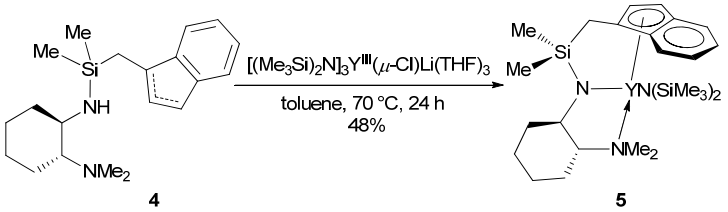
[4] (a) C. F. Bender and R. A. Widenhoefer, *J. Am. Chem. Soc.,* 2005, **127**, 1070; (b) M. R. Crimmin, A. G. M. Barrett, I. J. Casely, M. S. Hill, and P. A. Procopiou, *J. Am. Chem. Soc.,* 2009, **131**, 9670.

Preparation of ligand 4



To a solution of **1** (30.3 mmol) in hexane (50 mL) was added 26 mL of *n*-BuLi (1.17 M in hexane) at –78 °C and the resulting mixture was stirred at room temperature for 24 h to give a pale yellow suspension. This suspension was re-cooled to –78 °C and then treated with **3** (6.75 g, 30.3 mmol) in 20 mL of hexane. The resulting mixture was allowed to warm to room temperature and was stirred overnight. Then the reaction mixture was filtered and the residue was extracted with *n*-hexane (3×10 mL). The extracts were combined, and the solvent was evaporated under reduced pressure. The ligand **4** was obtained as extremely moisture-sensitive yellow oil; yield 8.16 g (82%). $[\alpha]_D^{20}$= –26.0 (c = 0.60, hexane). IR (neat): ν = 3345, 3063, 2930, 2858, 1601, 1452, 1398, 1352, 1250, 1171, 1057, 962, 906, 872, 833, 766, 719 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.56–7.08 (m, 6H), 6.30–5.90 (m, 2H), 3.48 (s, 0.5H), 3.31 (s, 2H), 2.78–2.50 (m, 1H), 2.39–1.89 (m, 15H), 1.84–1.48 (m, 5H), 1.31–0.79 (m, 6H), 0.24– 0.26 (m, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 146.3, 145.8, 144.4, 141.4, 139.0, 126.1, 125.8, 125.7, 124.5, 124.3, 124.1, 123.5, 123.4, 122.7, 119.3, 119.1, 69.6, 69.3, 69.2, 52.8, 51.5, 43.5, 40.3, 40.0, 39.8, 37.7, 36.5, 36.3, 35.7, 25.6, 25.2, 24.9, 20.7, 18.1, 15.1, 0.2, –0.1, –0.5, –3.3, –3.9. HRMS (EI–TOF) m/z M^+ calcd for $C_{20}H_{32}N_2Si$ 328.2335, found 328.2333.

Preparation of yttrium complex 5



To a solution of $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ (4.29 g, 5.18 mmol) in toluene (10.0 mL) was

added a solution of **4** (1.70 g, 5.18 mmol) in toluene (40.0 mL) at room temperature. After the reaction mixture was stirred at room temperature for 3 h, the mixture was heated at 70 °C for 24 h, during which time the solution gradually changed from pale to yellow. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2×10.0 mL). The extractions were combined and concentrated to about 5.0 mL. The yellow crystals were obtained after standing at room temperature for several days (1.43 g, 48% yield). IR (Nujol): ν = 3052, 2936, 1632, 1597, 1458, 1350, 1252, 1043, 974, 843, 762, 494, 440, 418 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.82–7.59 (m, 2H), 7.14–7.01 (m, 2H), 6.42 (brs, 1H), 5.94 (brs, 1H), 2.83–2.56 (m, 3H), 2.49–2.34 (m, 1H), 1.95–1.70 (m, 6H), 1.54–1.19 (m, 4H), 1.07–0.83 (m, 2H), 0.74–0.54 (m, 1H), 0.49 (s, 3H), 0.42–0.26 (m, 4H), 0.25–0.06 (m, 18H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 127.1, 126.1, 123.6, 121.23, 121.16, 120.8, 119.0, 116.9, 95.7, 68.2, 60.9, 44.0, 38.3, 37.0, 25.3, 25.2, 20.4, 17.2, 6.7, 5.7, 5.3, 2.4. Anal. Calcd for $C_{26}H_{48}N_3Si_3Y$: C, 54.23; H, 8.40; N, 7.30; Found: C, 54.25; H, 8.36; N, 7.23.

X-ray crystallographic analysis of complex 5 and 10

The single crystal X-ray diffraction data for complex **5** and **10** were collected on a diffractometer with graphite monchromated Mo K_α radiation (λ = 0.71073 Å) at room temperature. 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 details of the X-ray data collection, structure solution and structure refinements were given in Table S1. The Selected bond lengths and angles of complex **5** and **10** were given in Table S2. The crystal structures of **5** and **10** were given in Figure S1.

Table S1 Crystallographic data and structural refinement details for complex **5** and **10**.

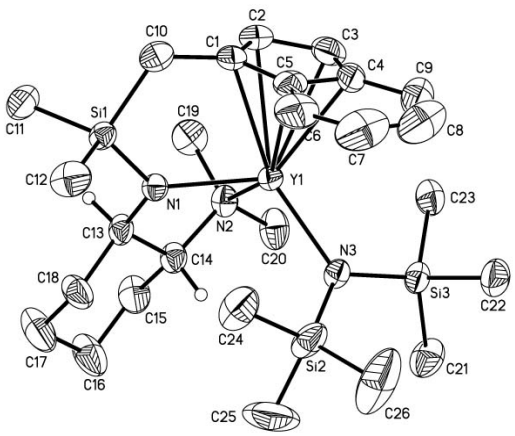
Compound	**5**	**10**
Formula	$C_{26}H_{48}N_3Si_3Y$	$C_{26}H_{48}N_3Si_3Er$
Formula weight	575.85	654.20
Temperature/K	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	11.150(2)	11.176(1)

b, Å	16.584(2)	15.744(1)
c, Å	17.122(2)	18.201(1)
V / Å ^{3}	3166.1(8)	3202.6(4)
Z	4	4
μ(Mo Ka), mm^{-1}	1.973	2.750
θ range for data collection, deg	1.7 to 27.9	1.7 to 27.8
Calculated density/(g·cm^{-3})	1.208	1.357
Reflections collected	27312	27941
Unique reflections/R_{int}	7430/R(int) = 0.068	7481/R(int) = 0.032
F (000)	1224	1340
Goodness-of-fit on F^2	0.960	0.82
Crystal dimension/mm^3	0.18×0.19×0.21	0.32 x 0.13 x 0.12
R, R_w [I > 2σ(I)]	0.0441, 0.0846	0.0253, 0.0649
Residual ρ/(e·Å $^{-3}$)	0.70, –0.35	0.56, –0.71
Flack χ	–0.009(6)	–0.016(10)
CCDC No.	960598	966418

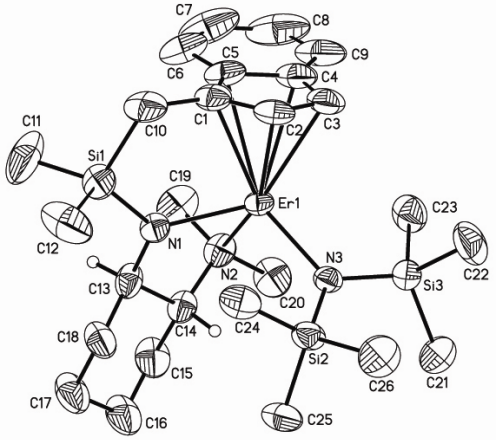
Table S2 Selected bond lengths (Å) and angles (°) of complex **5** and **10**.

	5	**10**
C1–Ln1	2.691(3)	2.644(4)
C2–Ln1	2.669(3)	2.601(4)
C3–Ln1	2.641(4)	2.615(5)
C4–Ln1	2.681(4)	2.687(5)
C5–Ln1	2.670(4)	2.706(4)
N1–Ln1	2.212(3)	2.185(3)
N2–Ln1	2.470(3)	2.455(4)
N3–Ln1	2.249(3)	2.214(3)
N1–Ln1–N2	73.7(1)	75.01(12)
N1–Ln1–N3	118.5(1)	112.76(12)
N3–Ln1–N2	104.1(1)	103.69(11)

Figure S1 X-ray structures (50 % probability ellipsoids) of complex **5** and **10**.

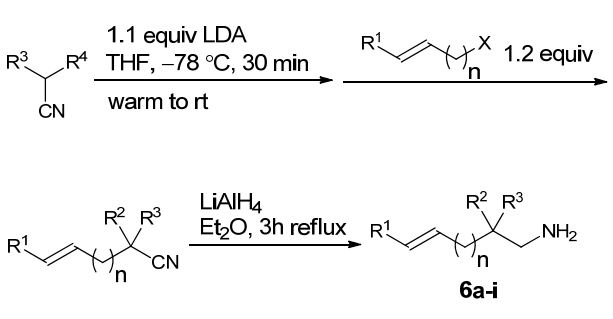


5



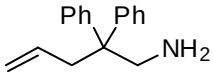
10

Preparation of aminoalkene substrates 6a–i

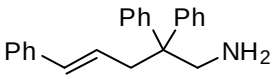


	n	R^1	R^2	R^3
6a	1	H	Ph	Ph
6b	1	Ph	Ph	Ph
6c	2	H	Ph	Ph
6d	1	H	Me	Me
6e	1	Ph	Me	Me
6f	2	H	Me	Me
6g	1	H	–$(CH_2)_5$–	
6h	1	Ph	–$(CH_2)_5$–	
6i	2	H	–$(CH_2)_5$–	

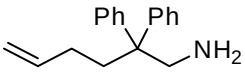
All these compounds were known compounds with references given in the General information section.



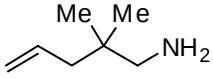
2,2-diphenylpent-4-en-1-amine (**6a**): Purified by column chromatography (petroleum ether/ethyl acetate = 2/1) to afford a viscous colorless oil in 80 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.25 (m, 4H), 7.24–7.13 (m, 6H), 5.48–5.31 (m, 1H), 5.10–4.93 (m, 2H), 3.32 (s, 2H), 2.92 (d, *J* = 7.0 Hz, 2H), 1.17–0.95 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 146.3, 134.6, 128.2, 128.1, 126.1, 117.7, 51.4, 48.6, 41.2.



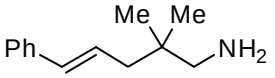
(*E*)-2,2,5-triphenylpent-4-en-1-amine (**6b**): Purified by column chromatography (petroleum ether/ethyl acetate = 2/1) to afford a white solid in 89% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.10 (m, 15H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.77 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.35 (s, 2H), 3.06 (dd, *J* = 7.3, 1.2 Hz, 2H), 1.17–0.80 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 146.3, 137.5, 132.8, 128.4, 128.3, 128.2, 127.0, 126.5, 126.2, 126.0, 52.0, 48.7, 40.3.



2,2-diphenylhex-5-en-1-amine (**6c**): Purified by column chromatography (petroleum ether/ethyl acetate = 2/1) to afford a viscous yellow oil in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.13 (m, 10H), 5.84–5.68 (m, 1H), 5.00–4.85 (m, 2H), 3.33 (s, 2H), 2.25–2.14 (m, 2H), 1.81–1.68 (m, 2H), 0.99–0.83 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 146.3, 138.8, 128.3, 128.1, 126.1, 114.4, 51.8, 49.1, 35.7, 28.6.

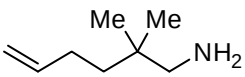


2,2-dimethylpent-4-en-1-amine (**6d**): Purified by distillation under reduced pressure (40 °C, 35 mmHg) to afford colorless oil in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91–5.73 (m, 1H), 5.09–4.95 (m, 2H), 2.45 (s, 2H), 1.97 (d, *J* = 7.5 Hz, 2H), 1.43–1.17 (brs, 2H), 0.86 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.3, 116.9, 52.7, 44.1, 34.9, 24.6.

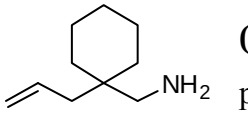


(*E*)-2,2-dimethyl-5-phenylpent-4-en-1-amine (**6e**): Purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to afford a

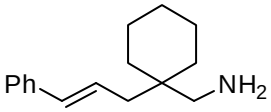
colorless oil in 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.16 (m, 5H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.24 (dt, *J* = 15.7, 7.3 Hz, 1H), 2.50 (s, 2H), 2.13 (dd, *J* = 7.3, 0.7 Hz, 2H), 1.35–1.20 (brs, 2H), 0.91 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.7, 132.2, 128.5, 127.3, 127.0, 126.0, 52.8, 43.2, 35.7, 24.8.



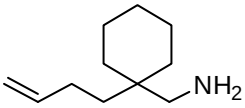
2,2-dimethylhex-5-en-1-amine (**6f**): Purified by distillation under reduced pressure (80 °C, 50 mmHg) to afford colorless oil in 50 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91–5.75 (m, 1H), 5.07–4.88 (m, 2H), 2.45 (s, 2H), 2.07–1.94 (m, 2H), 1.33–1.24 (m, 2H), 1.21–1.09 (brs, 2H), 0.85 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.6, 114.0, 52.8, 38.7, 34.5, 28.4, 24.6.



(1-allylcyclohexyl)methanamine (**6g**): Purified by distillation under reduced pressure (68 °C, 5 mmHg) to afford colorless oil in 50 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88–5.72 (m, 1H), 5.10–4.99 (m, 2H), 2.52 (s, 2H), 2.07 (d, *J* = 7.2 Hz, 2H), 1.49–1.34 (m, 6H), 1.32–1.20 (m, 4H), 1.18–1.09 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.0, 116.8, 48.8, 39.9, 37.0, 33.3, 26.4, 21.5.



(*E*)-(1-cinnamylcyclohexyl)methanamine (**6h**): Purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to afford a colorless oil in 44% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.13 (m, 5H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.21 (dt, *J* = 15.7, 7.5 Hz, 1H), 2.55 (s, 2H), 2.20 (dd, *J* = 7.5, 0.9 Hz, 2H), 1.56–1.23 (m, 10H), 1.19–1.06 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 137.7, 132.1, 128.5, 127.01, 126.96, 126.0, 48.9, 39.0, 37.8, 33.4, 26.5, 21.6.



(1-(but-3-en-1-yl)cyclohexyl)methanamine (**6i**): Purified by distillation under reduced pressure (85 °C, 5 mmHg) to afford colorless oil in 43 % yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91–5.76 (m, 1H), 5.06–4.90 (m, 2H), 2.53 (s, 2H), 2.01–1.90 (m, 2H), 1.49–1.22 (m, 12H), 1.19–1.05 (brs, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 139.7, 114.0, 48.5, 36.4, 34.2, 33.4, 27.4, 26.5, 21.5.

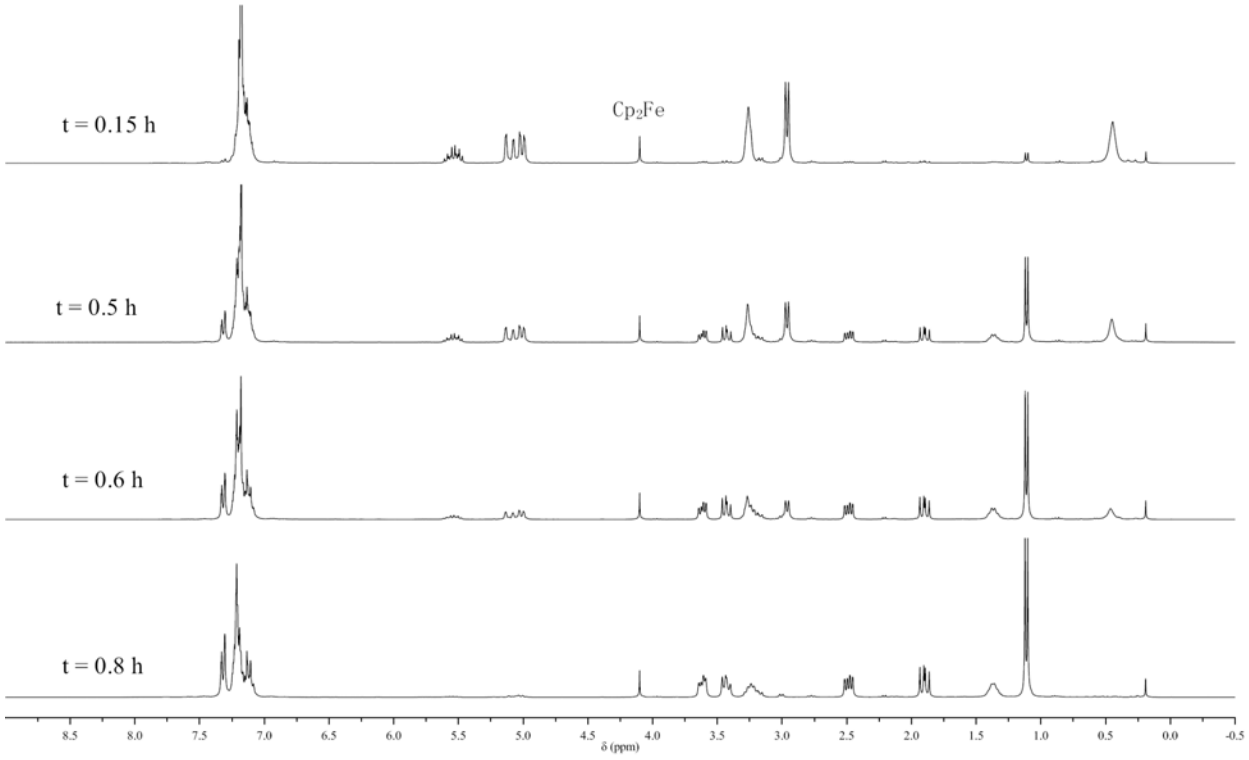
General procedure for the intramolecular hydroamination

In an argon-filled glovebox, 2 mol% of **5**, Cp_2Fe (6.0 mg, internal standard) and aminoalkene **6** (0.32 mmol) were weighed into a 5-mm NMR tube equipped with a Teflon valve (J-Young), and C_6D_6 (0.6 mL) was added. The hydroamination reaction was then monitored by ^{1}H NMR analysis for estimate of both conversion and yield.

^{1}H NMR monitoring of reactions in Table 2

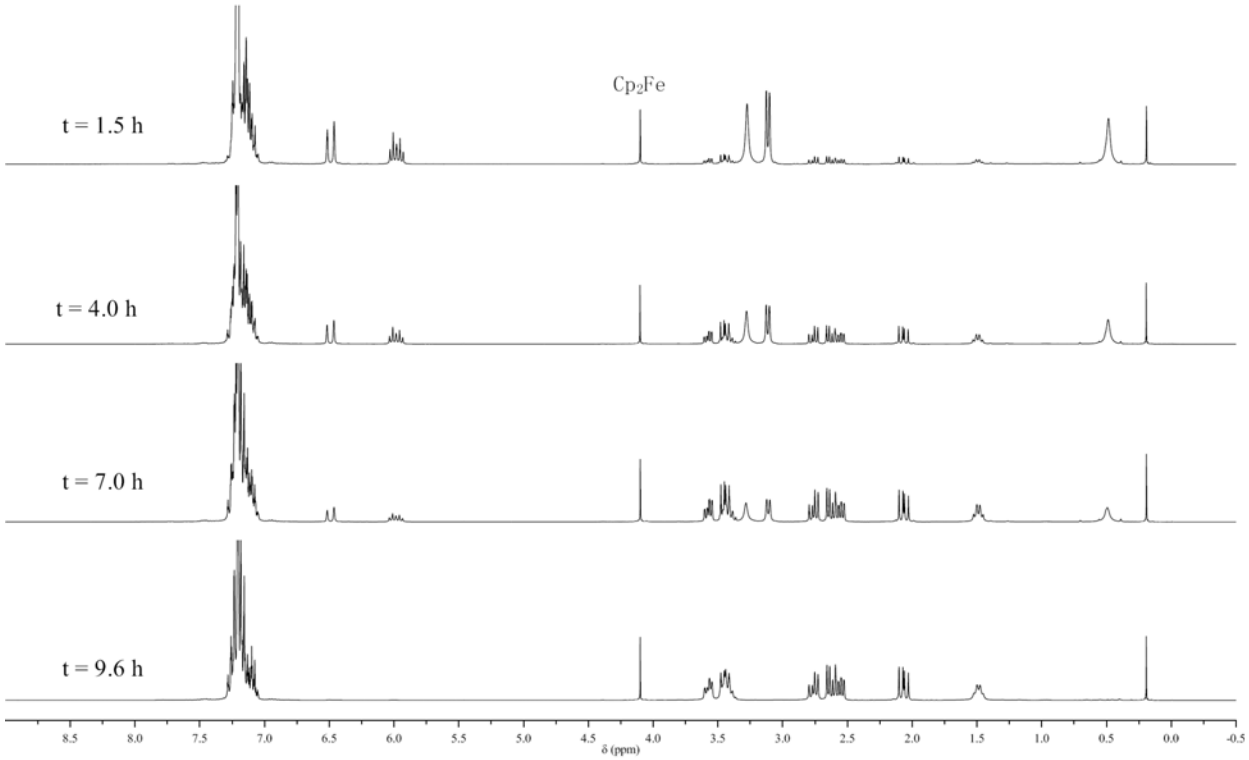
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 1 Substrate: 6**a** (0.32 mmol), Catalyst: **5** (2.0 %mol), Temperature: 25 °C



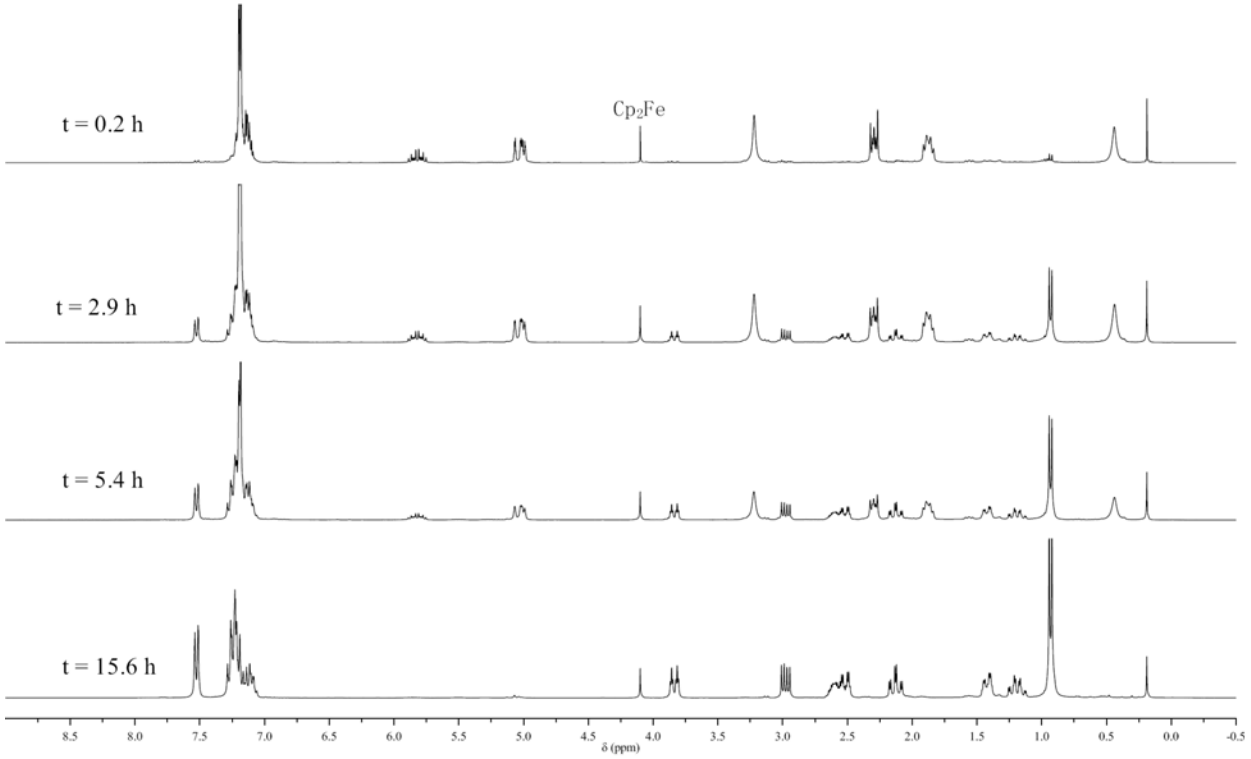
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 2 Substrate: **6b** (0.32 mmol), Catalyst: **5** (2.0 %mol), Temperature: 25 °C



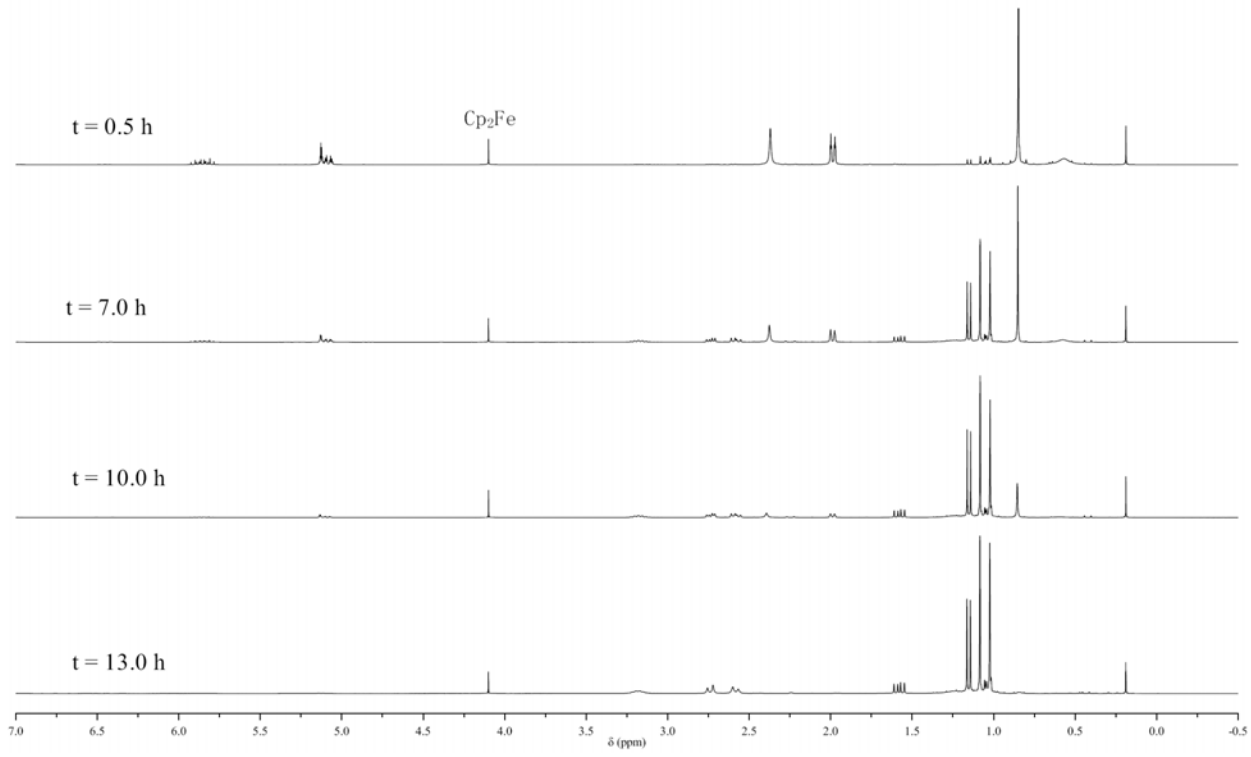
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 3 Substrate: **6c** (0.32 mmol), Catalyst: **5** (2.0 %mol), Temperature: 50 °C



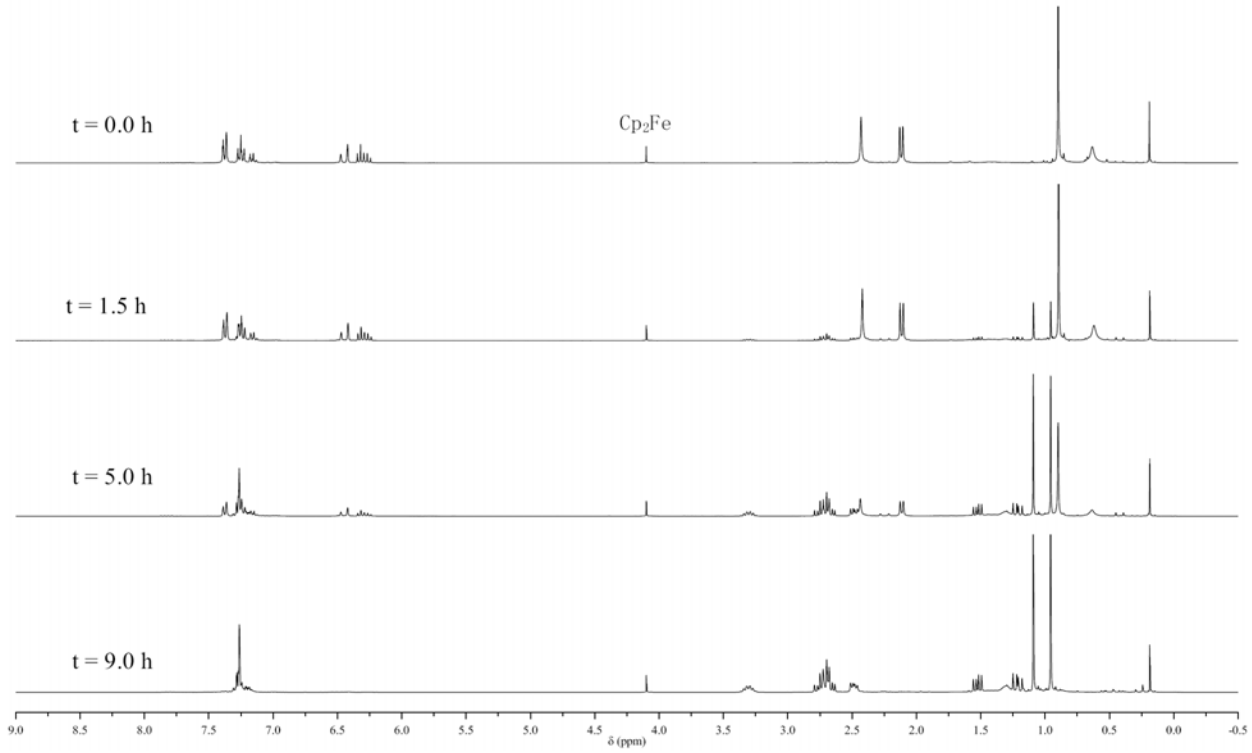
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 4 Substrate: **6d** (0.32 mmol), Catalyst: **5** (2.0 %mol), Temperature: 25 °C



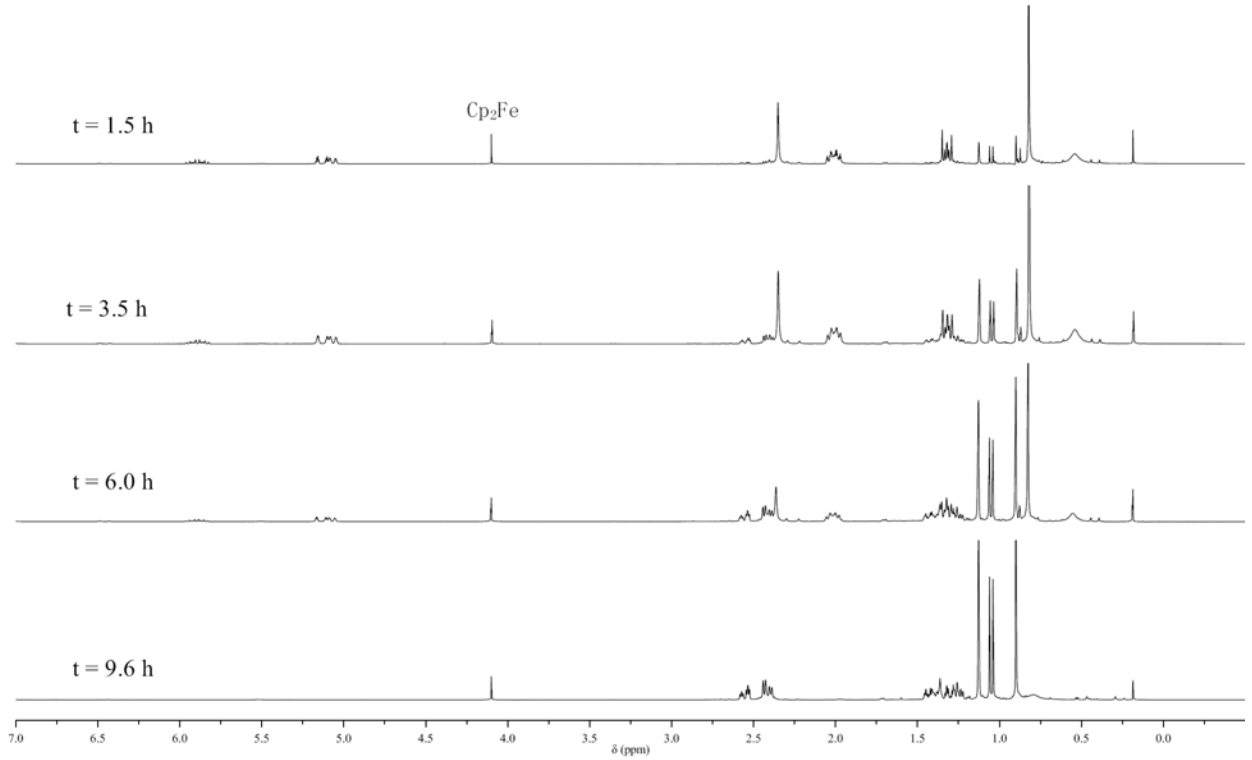
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 5 Substrate: **6e** (0.32 mmol), Catalyst: **5** (5.0 %mol), Temperature: 50 °C



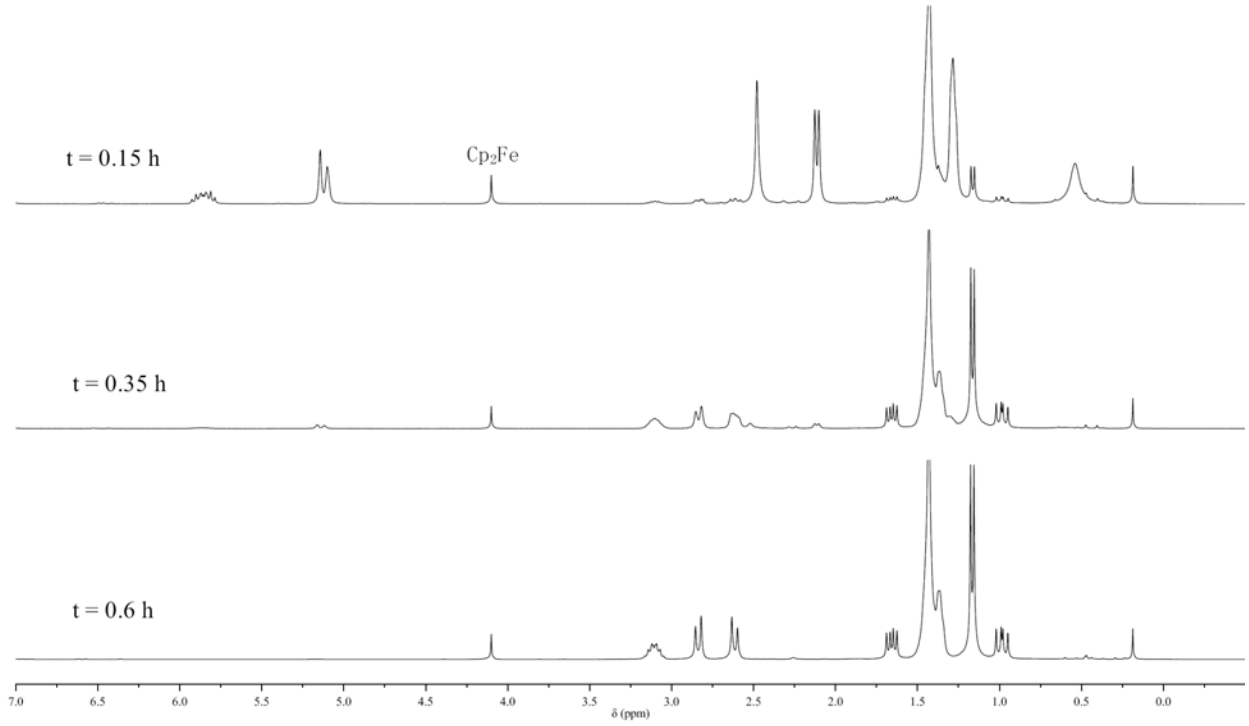
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 6 Substrate: **6f** (0.32 mmol), Catalyst: **5** (2.0 %mol), Temperature: 50 °C



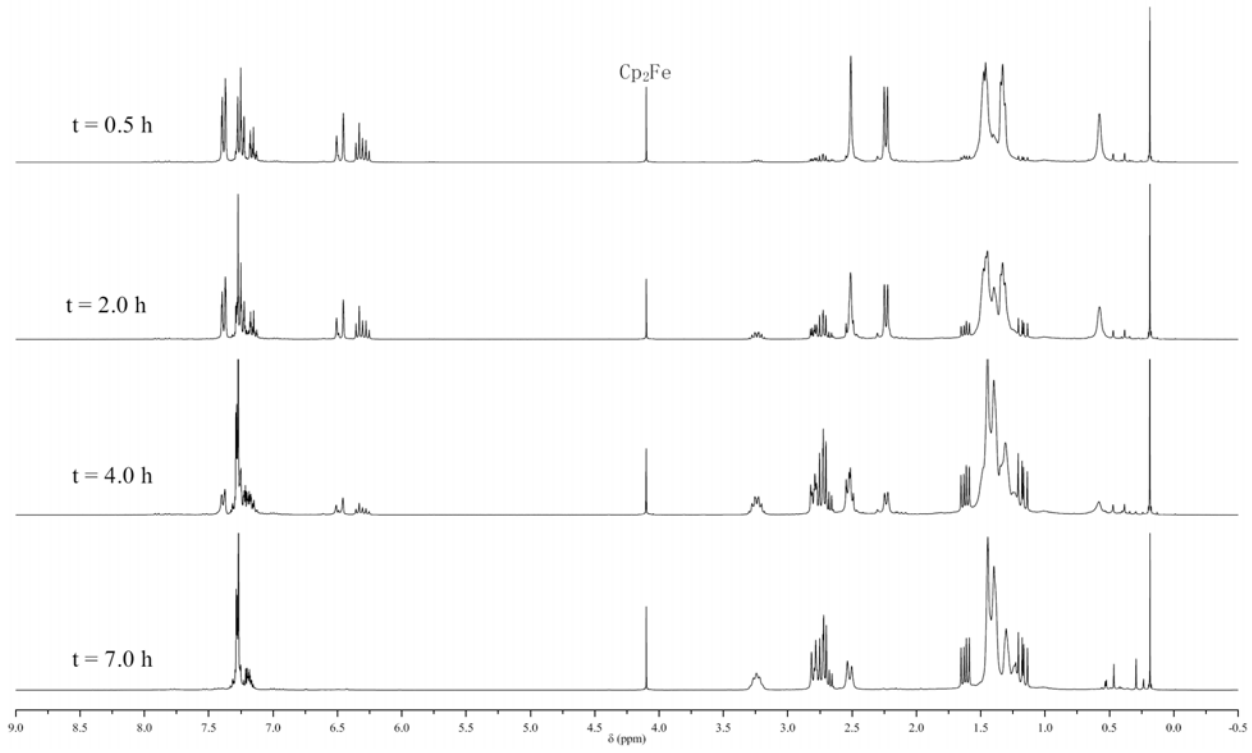
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

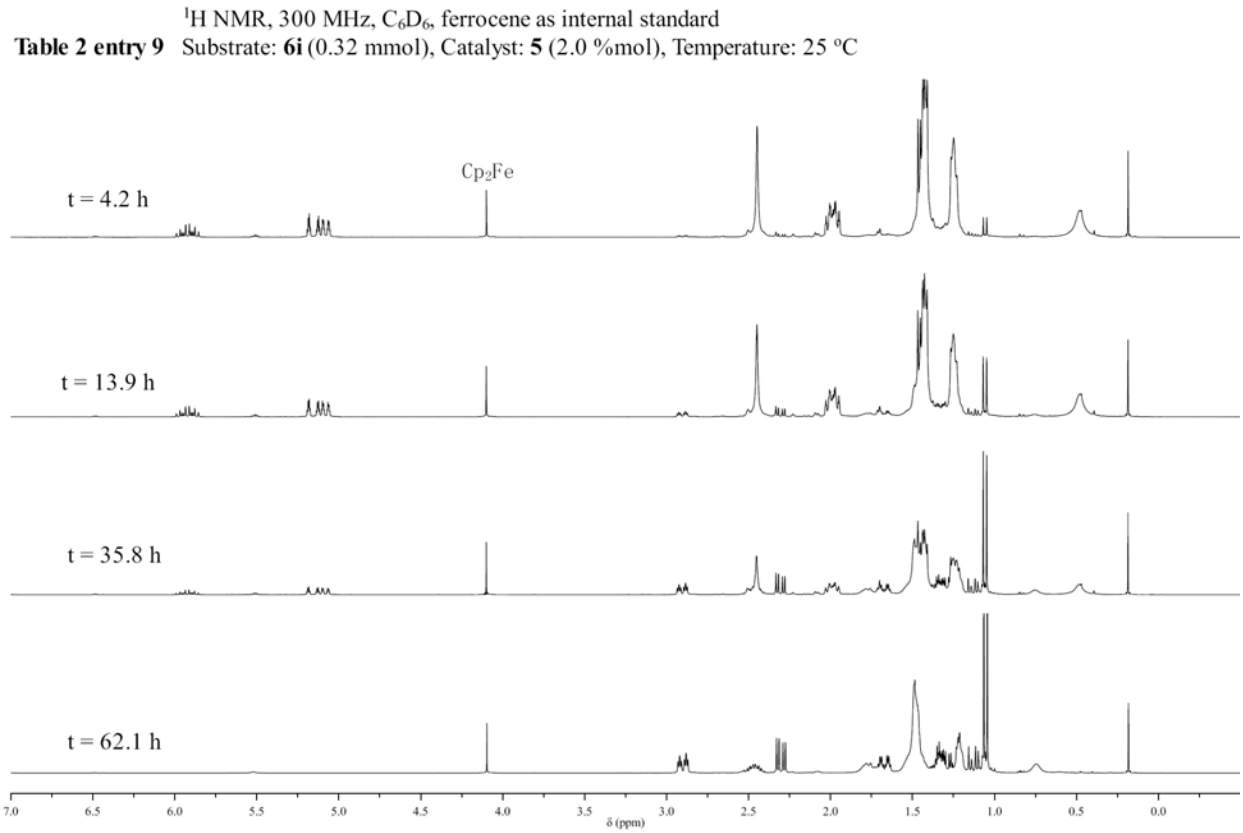
Table 2 entry 7 Substrate: **6g** (0.32 mmol), Catalyst: **5** (2.0 %mol), Temperature: 25 ºC



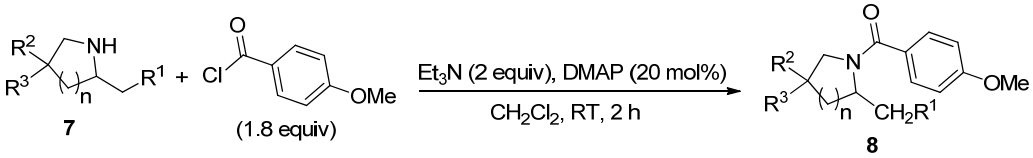
^{1}H NMR, 300 MHz, C_6D_6, ferrocene as internal standard

Table 2 entry 8 Substrate: **6h** (0.32 mmol), Catalyst: **5** (5.0 %mol), Temperature: 25 ºC

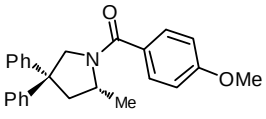




Determination of the enantiomeric excess (*ee*) values

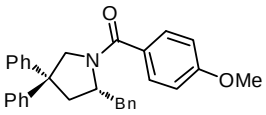


The enantiomeric excess values were determined by HPLC analysis of the **8** using AS-H, AD-H, or OJ-H column. Typical procedure of derivatization: To a solution of the corresponding cyclized product **7** (0.16 mmol) in CH_2Cl_2 (5 mL) was added 4-dimethylaminopyridine (DMAP, 4.8 mg, 0.04 mmol), triethylamine (45 μL, 0.3 mmol), and 4-methoxybenzoyl chloride (40 μL, 0.3 mmol) at ambient temperature. After stirring for 2 h, a saturated aqueous solution of ammonium chloride (5 mL) was poured into the reaction mixture and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with saturated aqueous solution of ammonium chloride (5 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC plate (silica gel).

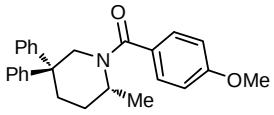


(**8a**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 85% ee. The ee was determined by HPLC analysis using a Chiralcel AS-H column (1/1 hexane/*i*-PrOH; flow rate

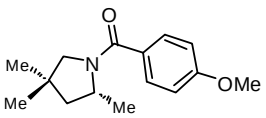
1.0 mL/min; λ = 254 nm; t_R = 30.6 (major), 10.1 (minor) min). $[\alpha]_D^{20}$= –119.2 (c = 0.53, CH_2Cl_2). IR (neat): *v* = 1624, 1607, 1572, 1512, 1491, 1458, 1447, 1420, 1398, 1254, 1171, 841, 764, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.33–7.10 (m, 8H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 4.38 (d, *J* = 11.1 Hz, 1H), 4.17–4.01 (m, 1H), 3.94–3.76 (m, 4H), 2.96–2.81 (m, 1H), 2.36 (t, *J* = 11.3 Hz, 1H), 1.45 (d, *J* = 5.8 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.8, 160.2, 144.4, 143.3, 128.5, 128.3, 127.6, 127.5, 125.7, 125.6, 125.5, 125.3, 112.6, 58.7, 54.3, 52.6, 51.5, 44.6, 18.8. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{26}NO_2$ 372.1964, found 372.1964.



(**8b**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 6/1) to afford a viscous colorless oil in 97% ee. The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 16.9 (major), 41.2 (minor) min). $[\alpha]_D^{20}$= –113.0 (c = 0.50, CH_2Cl_2). IR (neat): *v* = 1626, 1607, 1574, 1512, 1495, 1447, 1420, 1400, 1254, 1171, 1030, 841, 754, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.36–7.08 (m, 11H), 7.06–6.91 (m, 6H), 4.39–4.25 (m, 2H), 3.87 (s, 3H), 3.57 (d, *J* = 11.1 Hz, 1H), 3.31 (dd, *J* = 13.2, 3.0 Hz, 1H), 3.04 (dd, *J* = 12.9, 8.1 Hz, 1H), 2.74–2.64 (m, 1H), 2.49 (dd, *J* = 12.6, 10.5 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 169.9, 161.3, 145.2, 144.1, 138.1, 130.0, 129.5, 129.1, 128.6, 128.5, 128.4, 126.7, 126.6, 126.5, 126.4, 113.7, 60.2, 57.3, 55.4, 53.4, 42.0, 38.5. HRMS (ESI–TOF) m/z $[M + Na]^+$ calcd for $C_{31}H_{29}NO_2Na$ 470.2096, found 470.2095.

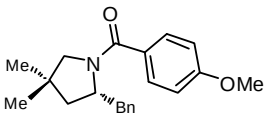


(**8c**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 4/1) to afford a white solid in 69% ee. Mp 187–188 °C. The ee was determined by HPLC analysis using a Chiralcel AD-H column (1/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 8.7 (major), 23.4 (minor) min). $[\alpha]_D^{20}$= –34.5 (c = 0.71, CH_2Cl_2). IR (neat): *v* = 1624, 1609, 1510, 1497, 1447, 1425, 1364, 1250, 1173, 1028, 839, 752, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44–7.12 (m, 12H), 6.93–6.83 (m, 2H), 5.41–5.10 (brs, 1H), 4.34–4.07 (brs, 1H), 3.81 (s, 3H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.66–2.49 (m, 2H), 1.84–1.66 (m, 1H), 1.43 (d, *J* = 13.5 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 171.0, 160.4, 147.4, 143.8, 129.3, 128.5, 128.4, 128.0, 127.7, 126.5, 126.4, 126.1, 113.8, 55.3, 48.4, 47.2, 45.9, 29.5, 26.2, 17.2. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{28}NO_2$ 386.2120, found 386.2120.

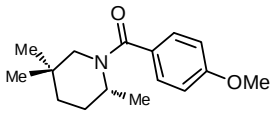


(**8d**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 4/1) to afford a viscous colorless oil in 82% ee. The ee was determined by HPLC analysis using a Chiralcel AS-H column (3/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 9.9 (major), 7.9 (minor) min). $[\alpha]_D^{20}$= –114.3 (c = 0.64,

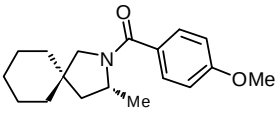
CH_2Cl_2). IR (neat): ν = 1624, 1609, 1572, 1512, 1458, 1420, 1398, 1254, 1171, 1030, 841 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, J = 8.4 Hz, 2H), 6.96–6.84 (m, 2H), 4.44–4.23 (m, 1H), 3.84 (s, 3H), 3.39–3.25 (m, 1H), 3.24–3.07 (m, 1H), 1.99–1.85 (m, 1H), 1.49–1.25 (m, 4H), 1.06 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 169.8, 161.0, 129.6, 113.4, 62.9, 55.3, 53.0, 47.6, 38.3, 25.8, 25.5, 20.3. HRMS (ESI–TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{21}NO_2Na$ 270.1470, found 270.1470.



(**8e**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 6/1) to afford a viscous colorless oil in 80% ee. The ee was determined by HPLC analysis using a Chiralcel AS-H column (2/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 13.0 (major), 7.8 (minor) min). $[\alpha]_D^{20}$= –98.9 (c = 0.39, CH_2Cl_2). IR (neat): ν = 1620, 1607, 1572, 1508, 1454, 1419, 1398, 1254, 1171, 1030, 841, 766, 702 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.56–7.48 (m, 2H), 7.34–7.18 (m, 5H), 6.95–6.87 (m, 2H), 4.65–4.50 (m, 1H), 3.84 (s, 3H), 3.27 (dd, J = 12.9, 2.6 Hz, 1H), 3.13 (d, J = 13.2 Hz, 1H), 3.05–2.88 (m, 2H), 1.70 (ddd, J = 12.6, 7.4, 1.7 Hz, 1H), 1.56 (dd, J = 12.5, 10.0 Hz, 1H), 0.95 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 169.9, 161.1, 138.4, 129.9, 129.6, 129.2, 128.2, 126.2, 113.4, 63.5, 57.9, 55.3, 43.9, 38.9, 38.0, 25.6, 25.5. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{26}NO_2$ 324.1964, found 324.1963.

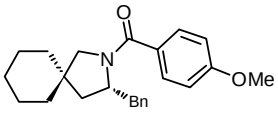


(**8f**) Purified by preparative TLC plate (petroleum ether/ethyl acetate = 5/1) to afford a viscous colorless oil in 58% ee. The ee was determined by HPLC analysis using a Chiralcel AS-H column (3/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 10.4 (major), 13.1 (minor) min). $[\alpha]_D^{20}$= –90.0 (c = 0.40, CH_2Cl_2). IR (neat): ν = 1626, 1609, 1574, 1514, 1462, 1420, 1391, 1250, 1173, 1034, 841 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 1H), 4.79–4.27 (brs, 1H), 3.83 (s, 3H), 3.76–3.36 (brs, 1H), 2.79 (d, J = 12.9 Hz, 1H), 2.00–1.83 (m, 1H), 1.65–1.50 (m, 1H), 1.42–1.24 (m, 2H), 1.20 (d, J = 6.9 Hz, 3H), 0.93 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.9, 160.2, 129.4, 128.3, 113.7, 55.3, 32.4, 31.4, 29.1, 26.1, 23.0, 16.2. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{24}NO_2$ 262.1807, found 262.1806.

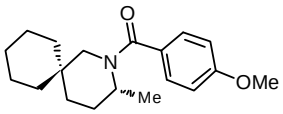


(**8g**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 4/1) to afford a viscous colorless oil in 75% ee. The ee was determined by HPLC analysis using a Chiralcel AS-H column (1/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 14.1 (major), 8.3 (minor) min). $[\alpha]_D^{20}$= –62.0 (c = 0.40, CH_2Cl_2). IR (neat): ν = 1628, 1609, 1572, 1512, 1448, 1420, 1400, 1252, 1175, 1030, 841 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, J = 8.1 Hz, 2H), 6.95–6.85 (m, 2H), 4.39–4.17 (brs, 1H), 3.84 (s, 3H), 3.36 (d, J = 10.2 Hz, 1H), 3.22 (d, J = 10.5 Hz, 1H), 2.12 (dd, J = 12.3, 7.5 Hz, 1H),

1.60–1.12 (m, 14H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 169.9, 160.9, 129.5, 113.4, 60.7, 55.3, 52.1, 44.7, 42.3, 36.3, 33.4, 26.1, 23.8, 22.5, 20.3. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{26}NO_2$ 288.1963, found 288.1961.

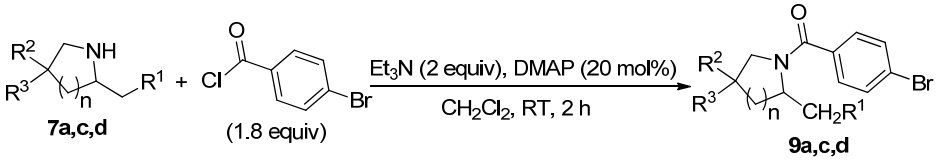


(**8h**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 9/1) to afford a viscous colorless oil in 87% ee. The ee was determined by HPLC analysis using a Chiralcel OJ-H column (20/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 20.8 (major), 13.9 (minor) min). $[\alpha]_D^{20}$= –186.0 (c = 0.60, CH_2Cl_2). IR (neat): *v* = 1624, 1607, 1512, 1452, 1420, 1398, 1252, 1173, 1030, 841, 766, 702 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.37–7.17 (m, 5H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.62–4.45 (m, 1H), 3.84 (s, 3H), 3.39–3.16 (m, 2H), 3.02–2.82 (m, 2H), 1.98–1.83 (m, 1H), 1.50–1.12 (m, 11H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.0, 161.0, 138.4, 130.0, 129.6, 129.3, 128.2, 126.2, 113.4, 61.2, 56.9, 55.3, 42.0, 40.9, 39.0, 36.0, 33.5, 26.1, 23.7, 22.4. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{30}NO_2$ 364.2276, found 364.2275.



(**8i**): Purified by preparative TLC plate (petroleum ether/ethyl acetate = 5/1) to afford a viscous colorless oil in 73% ee. The ee was determined by HPLC analysis using a Chiralcel AS-H column (3/1 hexane/*i*-PrOH; flow rate 1.0 mL/min; λ = 254 nm; t_R = 20.5 (major), 14.2 (minor) min). $[\alpha]_D^{20}$= –104.0 (c = 0.40, CH_2Cl_2). IR (neat): *v* = 1624, 1609, 1572, 1508, 1448, 1420, 1398, 1252, 1173, 1030, 841 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 731 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.73–4.31 (brs, 1H), 3.84 (s, 3H), 2.70 (d, *J* = 12.8 Hz, 1H), 2.00–1.69 (m, 2H), 1.62–1.12 (m, 16H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.9, 160.2, 129.6, 128.3, 113.7, 55.3, 38.3, 33.8, 30.9, 29.9, 26.5, 25.4, 21.6, 21.4, 16.4. HRMS (ESI–TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{28}NO_2$ 302.2120, found 302.2119.

Determination of the absolute configurations



The absolute configurations of products **7a**, **7c** and **7d** were determined by X-ray crystallographic analysis of the derivatized products **9a**, **9c** and **9d**. Typical procedure for the derivatization: to a solution of **7** (0.16 mmol) in CH_2Cl_2 (5 mL) was added dimethylaminopyridine (4.8 mg, 0.04 mmol), triethylamine (45 μL, 0.32 mmol), and 4-bromobenzoyl chloride (40 μL, 0.3 mmol) at ambient temperature. After stirring for 2 h, saturated aqueous solution of ammonium chloride (5 mL) was poured into the reaction mixture

and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were then washed with saturated aqueous solution of ammonium chloride (5 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude product was purified by preparative TLC plate (silica gel). The crystals of the **9a** and **9d** suitable for X-ray crystallographic analysis were obtained by recrystallization from a mixed solvent of CH_2Cl_2 and hexane. The crystal of the **9c** suitable for X-ray crystallographic analysis was obtained by recrystallization from ethyl acetate.

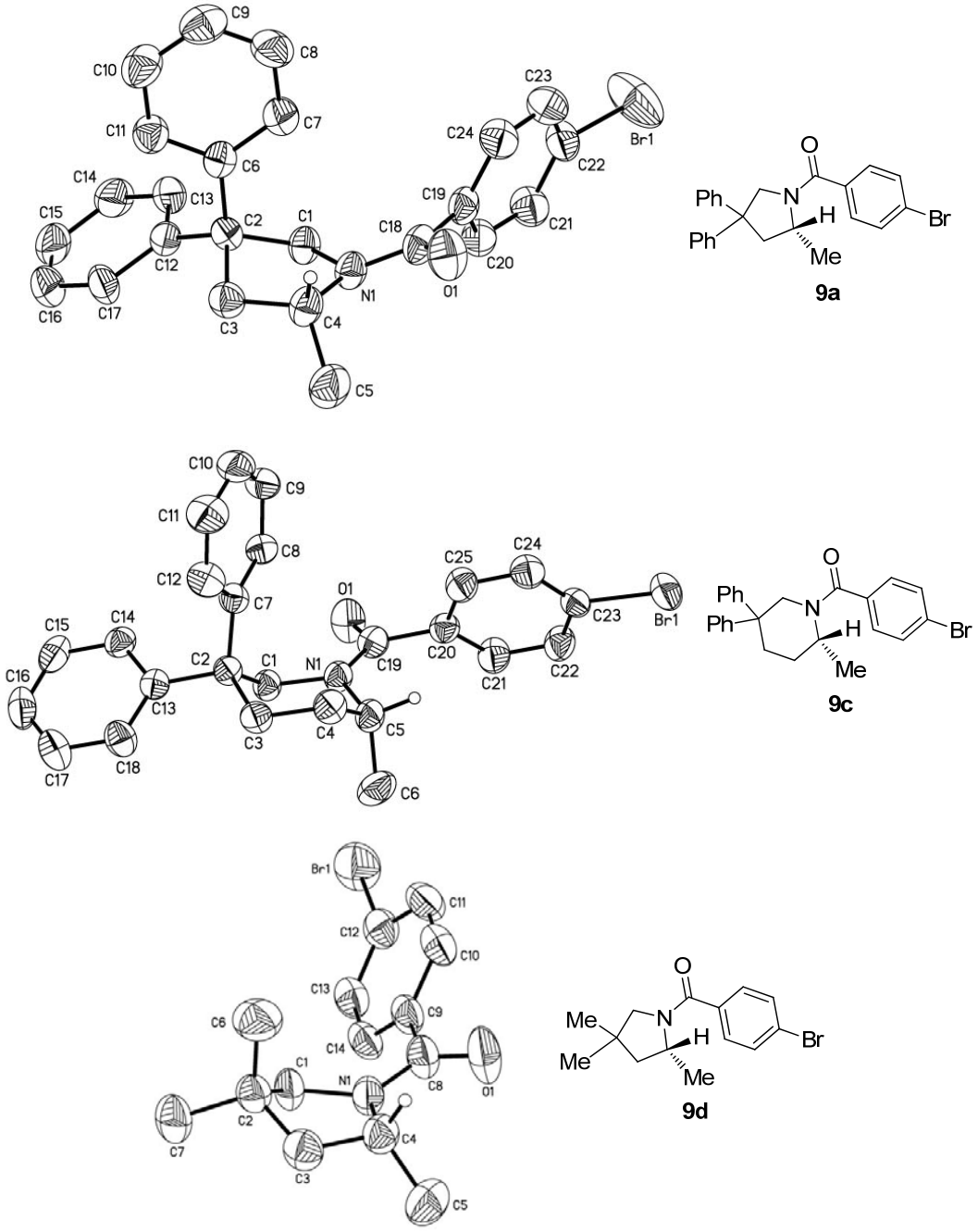
The single crystal X-ray diffraction data for compounds **9a**, **9c** and **9d** were collected on a diffractometer with graphite monchromated Mo K_α radiation (λ = 0.71073 Å) at room temperature. Saint program and SADABS program carried out the data integration. The structures were solved by a direct 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 details of the X-ray data collection, structure solution and structure refinements are given in Table S3. The crystal structures of **9a**, **9c** and **9d** are given in Figure S2.

Table S3 Crystallographic data and structural refinement details for compounds **9a**, **9c** and **9d**.

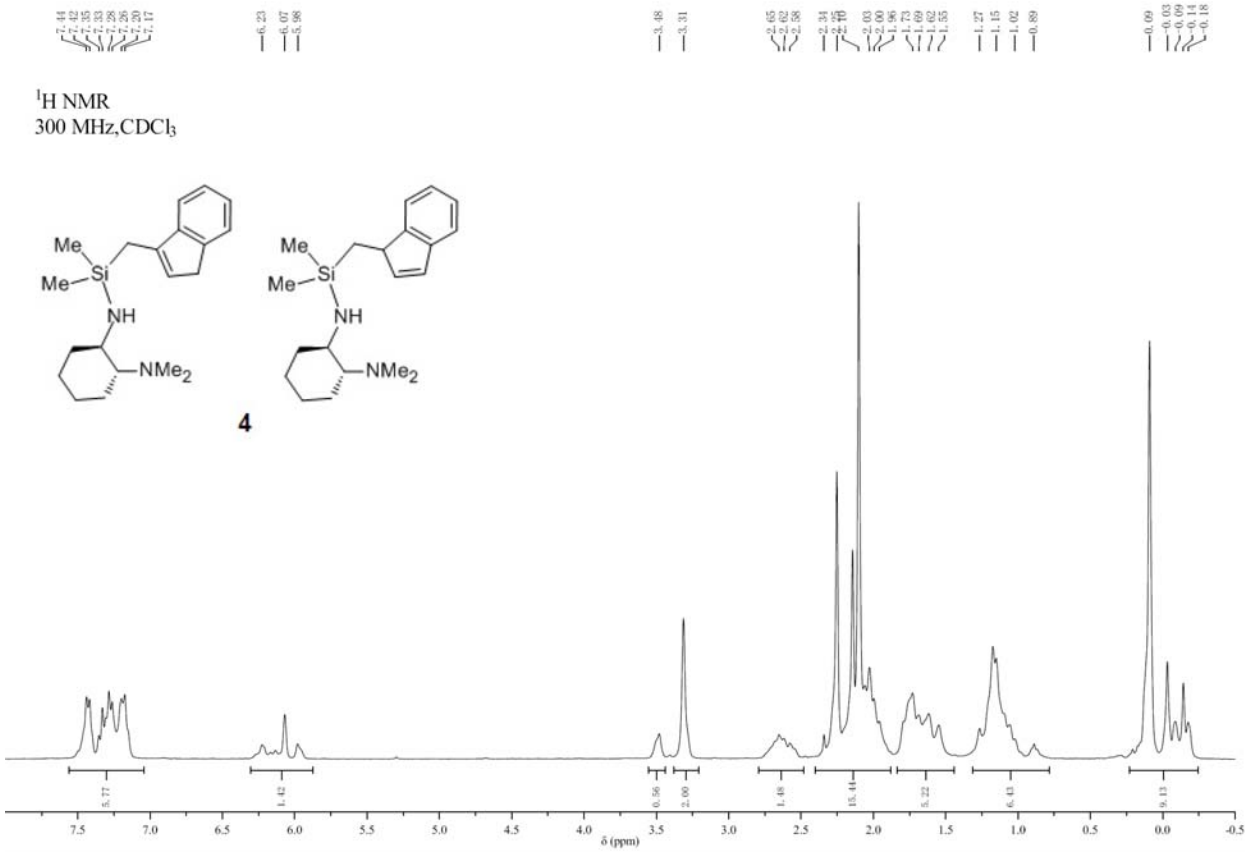
Compound	**9a**	**9c**	**9d**
Formula	$C_{24}H_{22}BrNO$	$C_{25}H_{24}BrNO$	$C_{14}H_{18}BrNO$
Formula weight	420.33	434.35	296.19
Temperature/K	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	P212121	P21	P212121
a, Å	10.329(1)	8.785(1)	7.487(1)
b, Å	11.606(1)	12.874(1)	9.521(1)
c, Å	16.666(2)	9.389(1)	19.774(3)
α, deg	90	90	90
β, deg	90	95.271(1)	90
γ, deg	90	90	90
V / Å ^{3}	1997.8(4)	1057.4(2)	1409.5(4)
Z	4	2	4
μ(Mo Ka), mm^{-1}	2.071	1.958	2.902
θ range for data collection, deg	2.1 to 29.1	2.2 to 27.4	2.1 to 27.4
Calculated density/($g \cdot cm^{-3}$)	1.398	1.364	1.396
Reflections collected	17894	8880	12032
Unique reflections/R_{int}	4936/R(int) = 0.036	4636/R(int) = 0.020	3209/R(int) = 0.029
F (000)	864	448	608
Goodness-of-fit on F^2	0.83	0.66	0.81

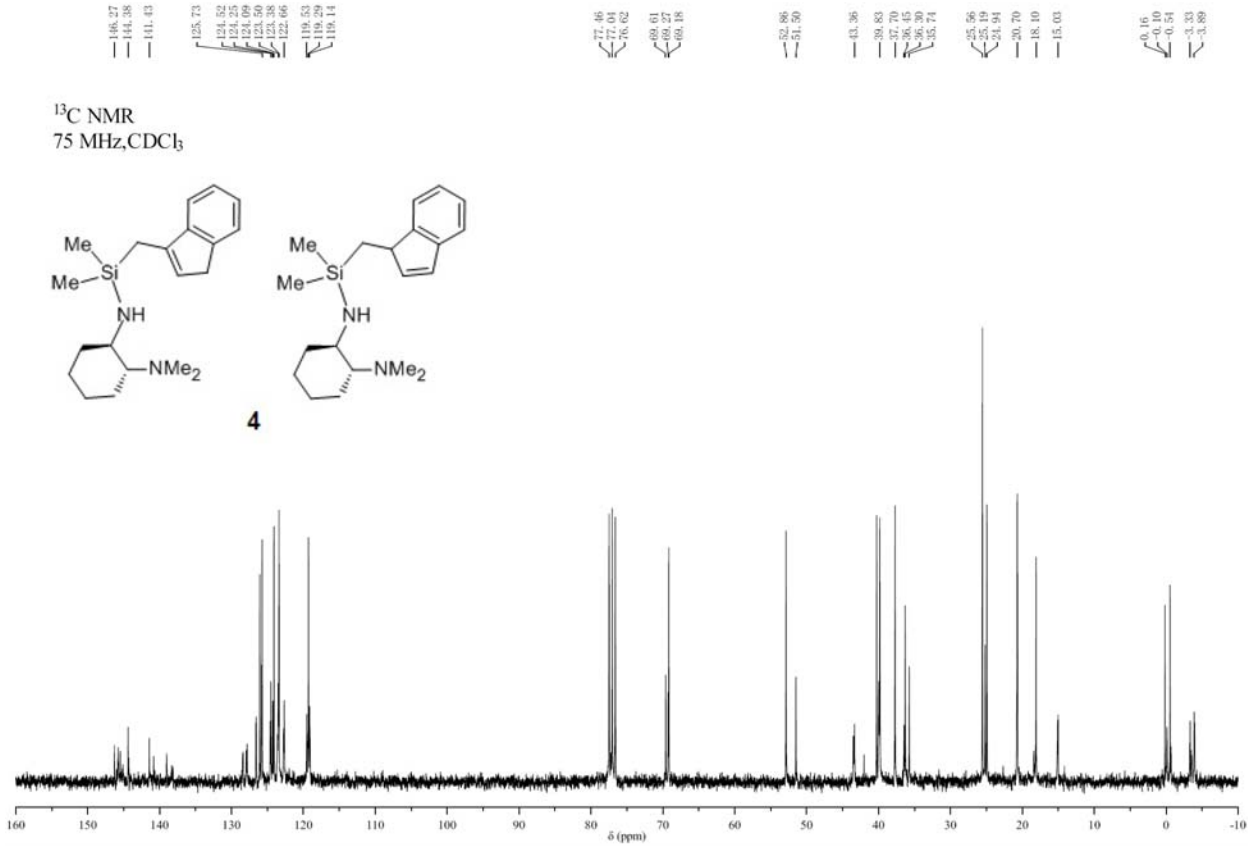
Crystal dimension/mm^3	0.20×0.22×0.25	0.15×0.19×0.20	0.23×0.25×0.28
R, R_w [$I > 2\sigma(I)$]	0.0494, 0.1775	0.0247, 0.0784	0.0345, 0.1201
Residual ρ/(e·Å^{-3})	0.97, –0.93	0.19, –0.33	0.34, –0.68
Flack χ	–0.004(13)	0.018(7)	0.012(14)
CCDC No.	960599	960600	960601

Figure S2 X-ray structures (50 % probability ellipsoids) of compounds **9a**, **9c** and **9d**.

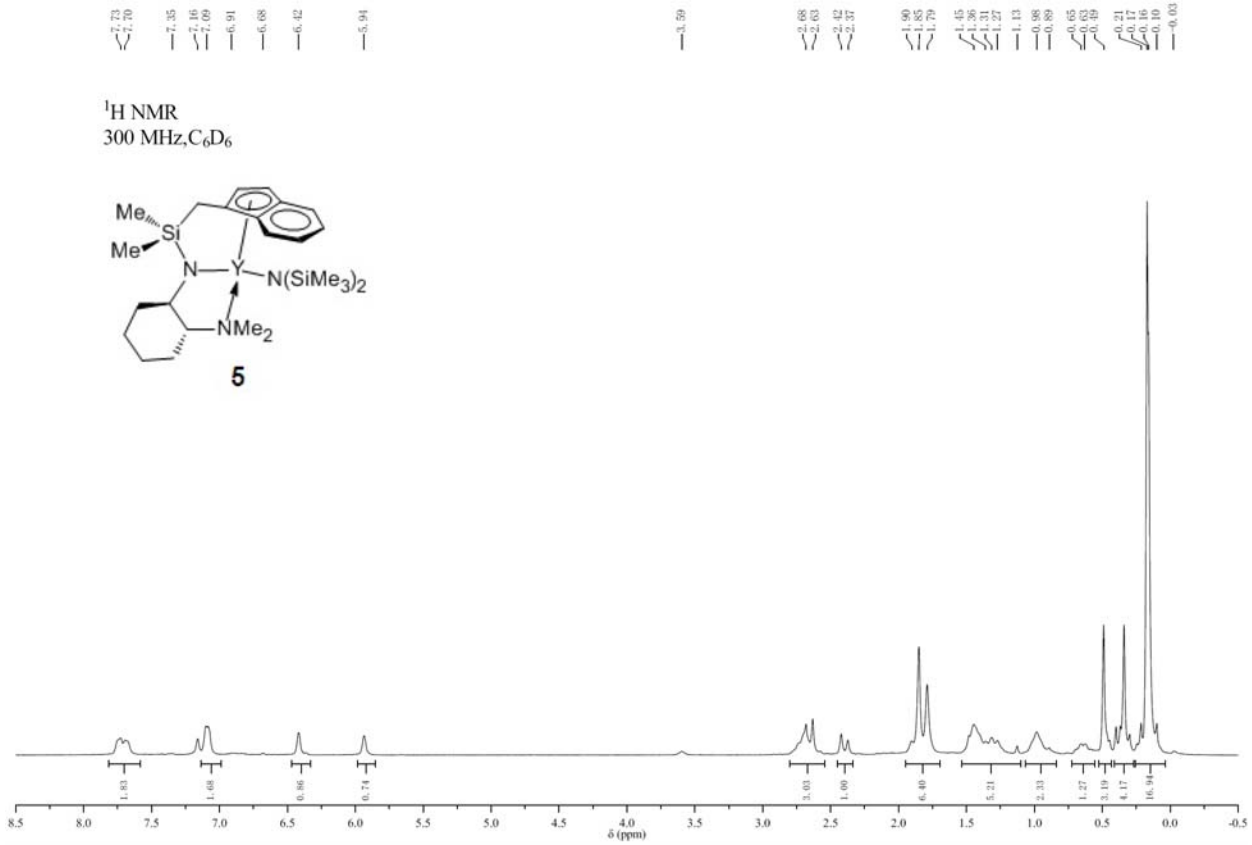


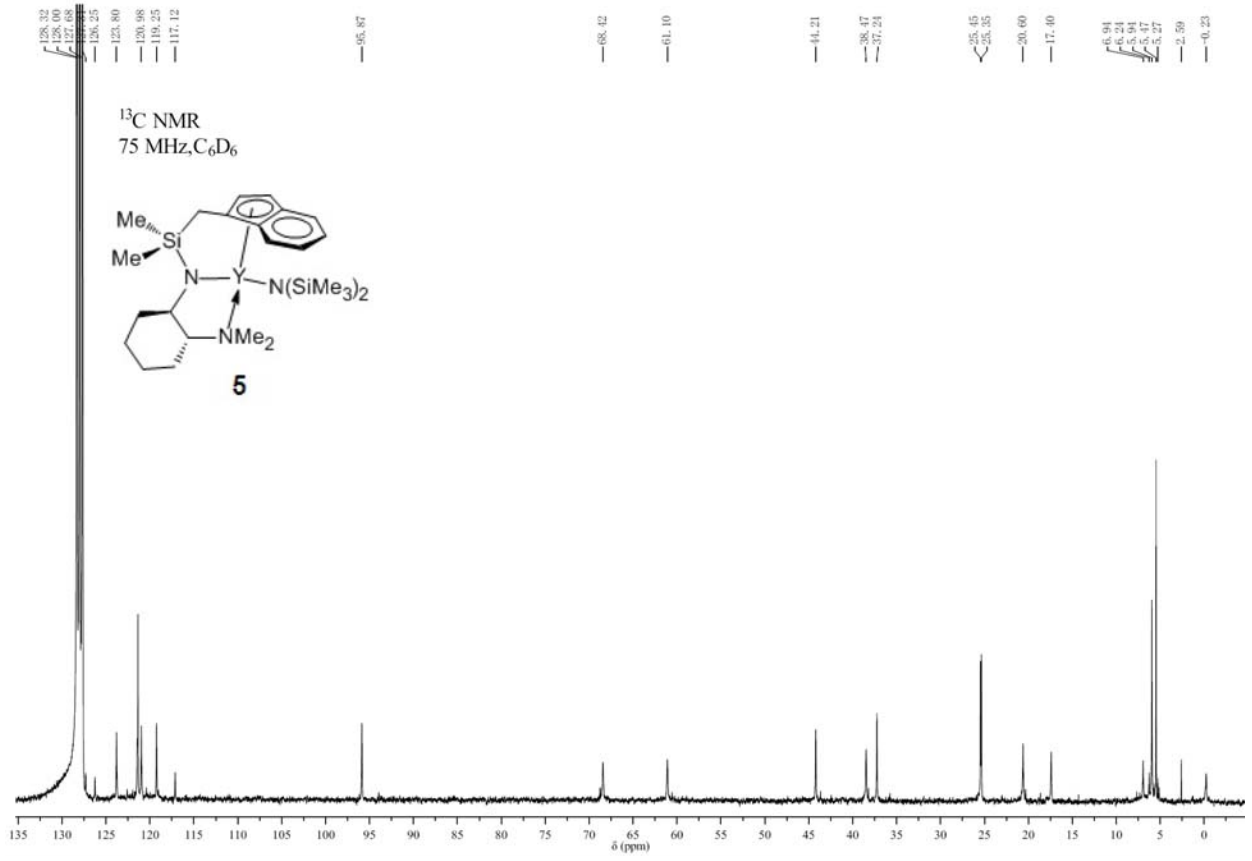
Copies of ^{1}H NMR and ^{13}C NMR for ligand 4





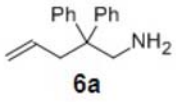
Copies of ^{1}H NMR and ^{13}C NMR for yttrium complex 5



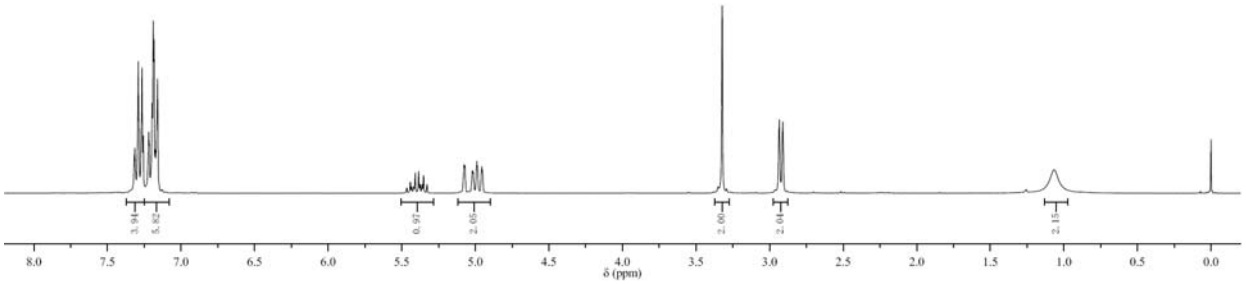


Copies of ^{1}H NMR and ^{13}C NMR for aminoalkene substrates 6a–i

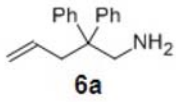
^{1}H NMR
300 MHz,$CDCl_3$



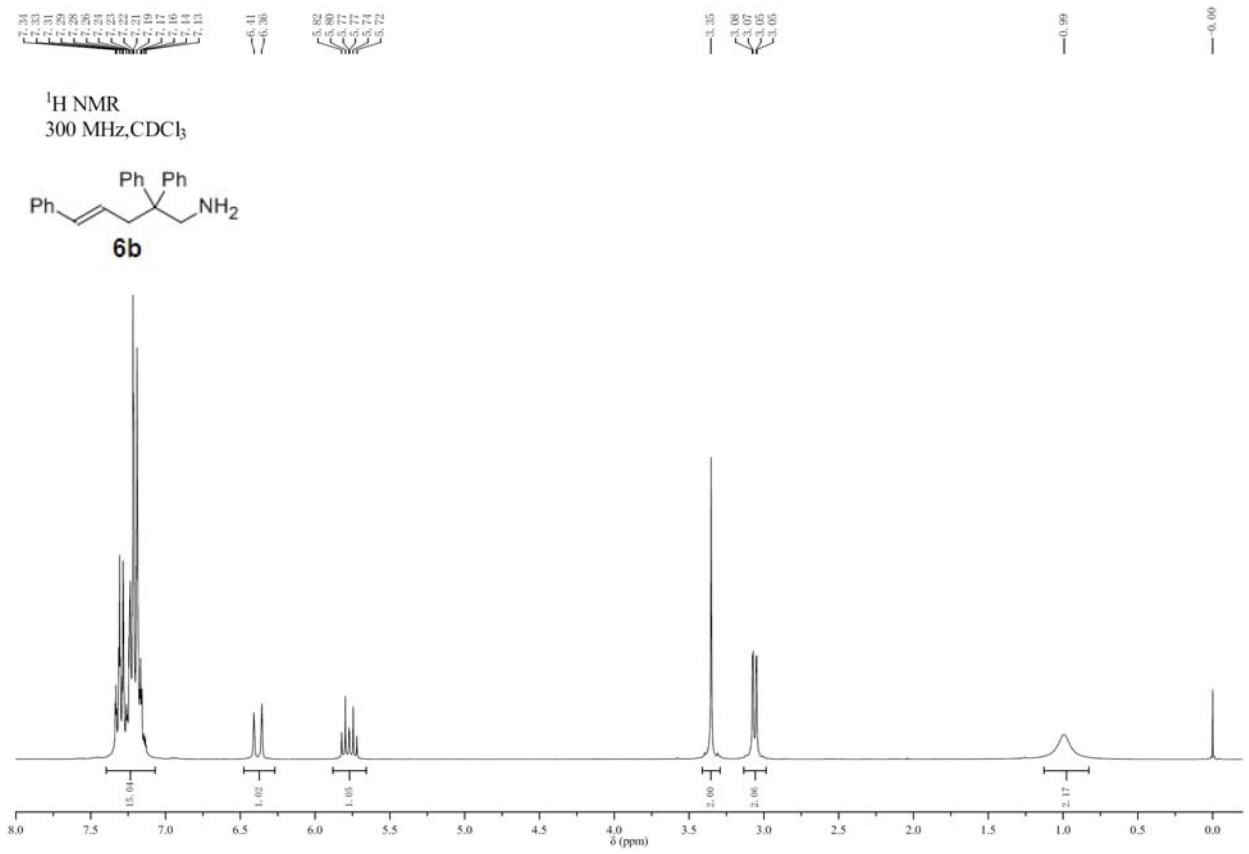
6a

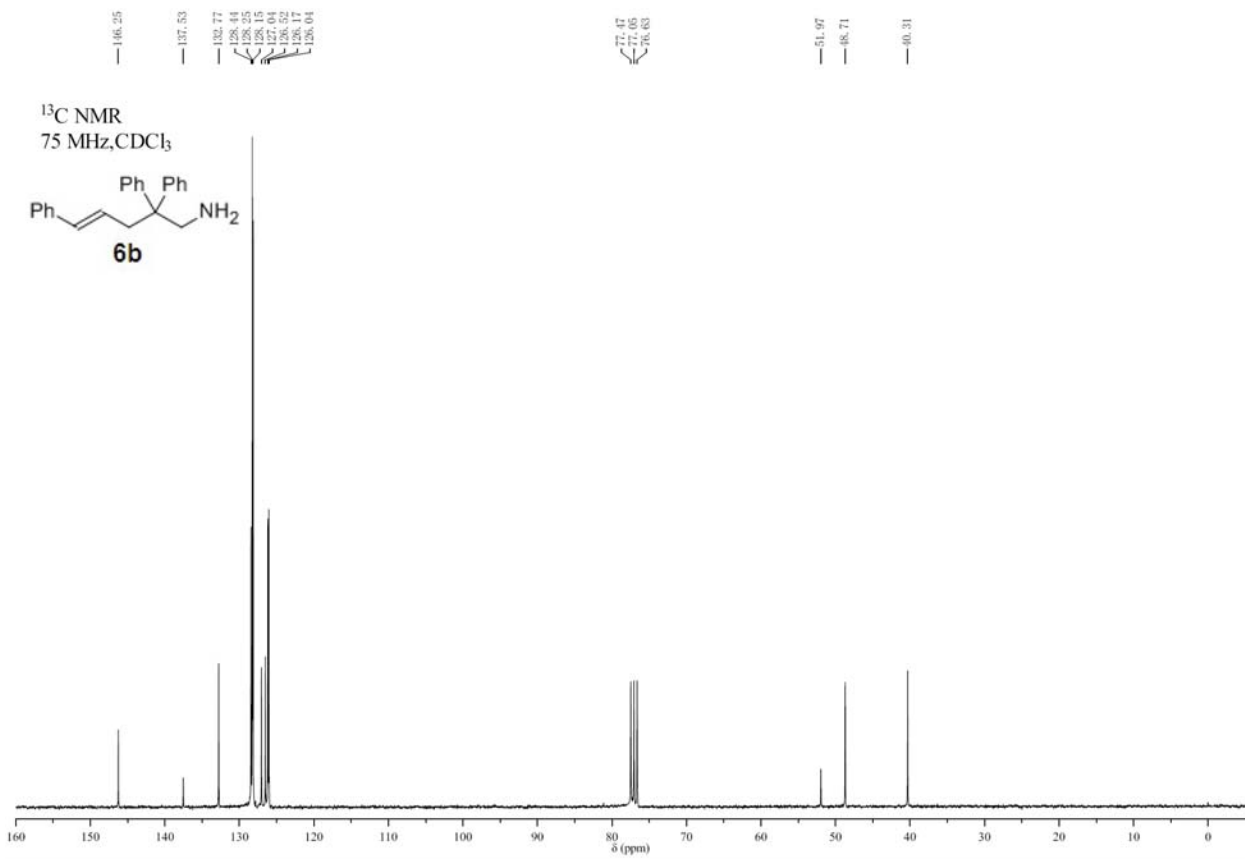


^{13}C NMR
75 MHz,$CDCl_3$

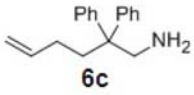


6a

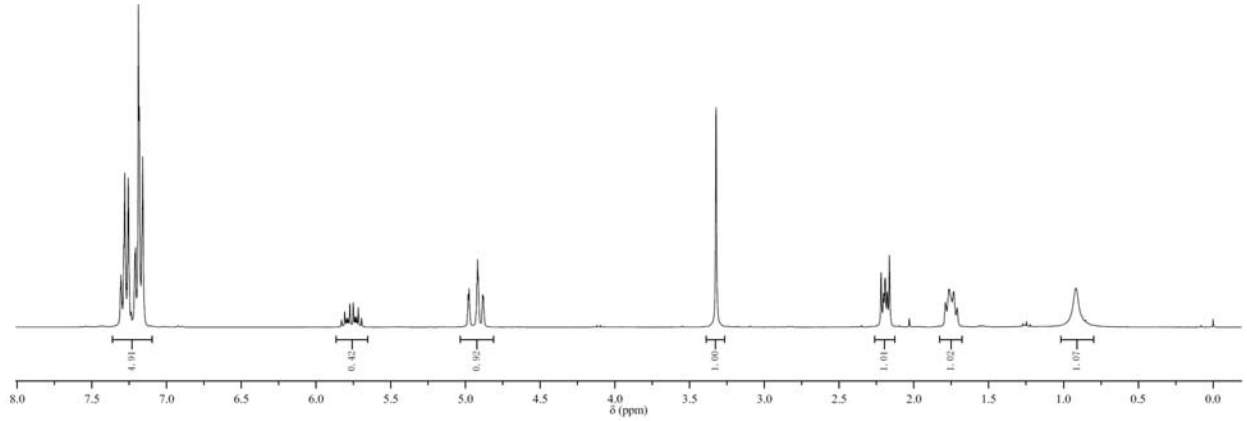

^{1}H NMR
300 MHz,CDCl$_3$
Ph
Ph
Ph
NH$_2$
6b
δ (ppm)


^{13}C NMR
75 MHz,CDCl$_3$
Ph
Ph
Ph
NH$_2$
6b
δ (ppm)

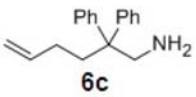
^{1}H NMR
300 MHz,$CDCl_3$



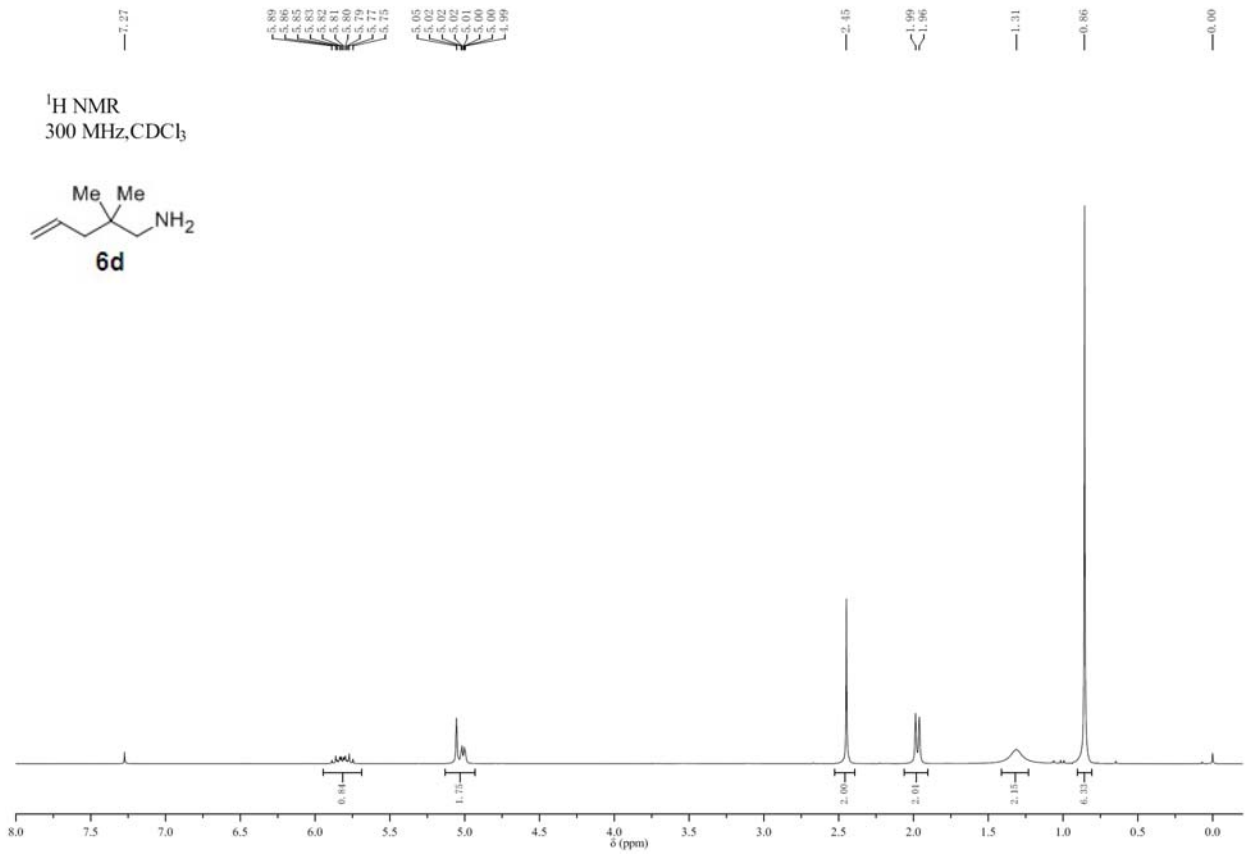
6c



^{13}C NMR
75 MHz,$CDCl_3$

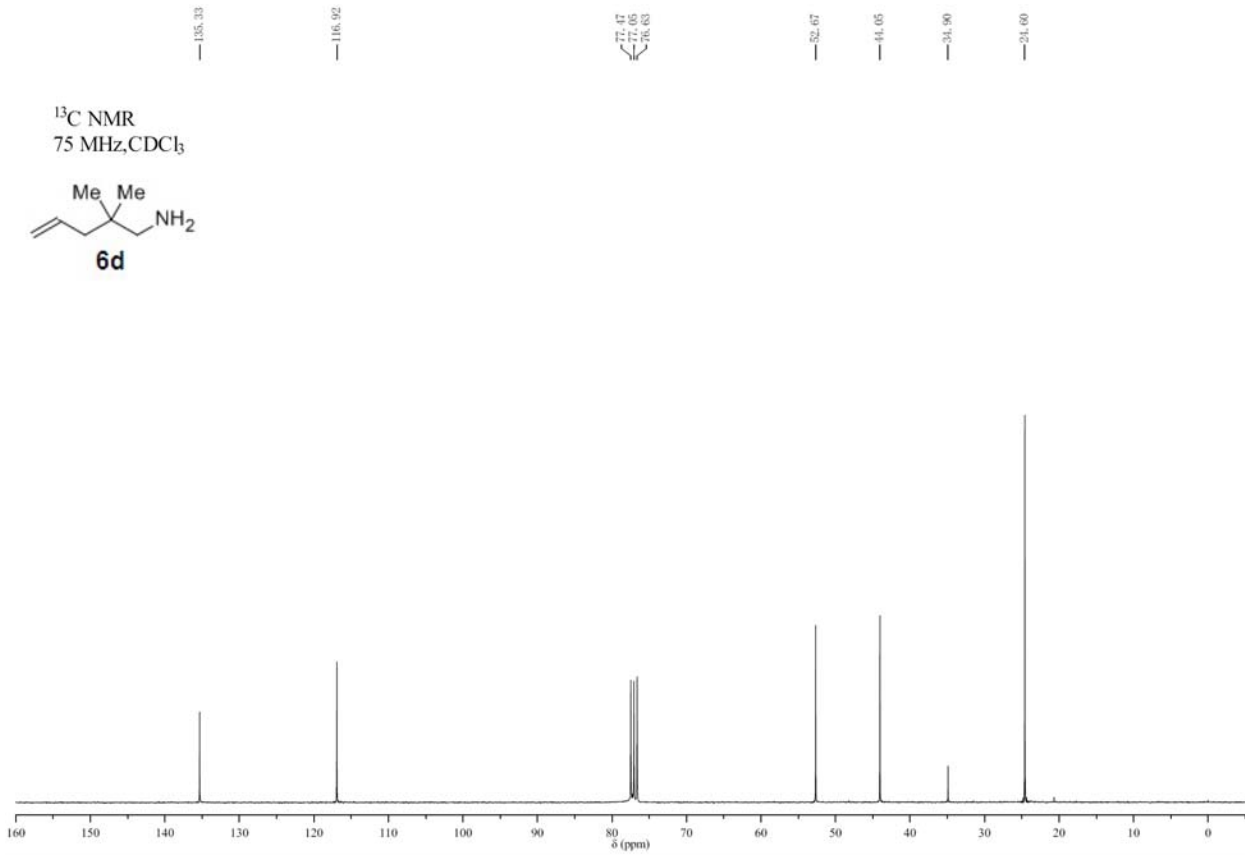


6c



^{1}H NMR
300 MHz,$CDCl_3$

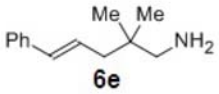
6d



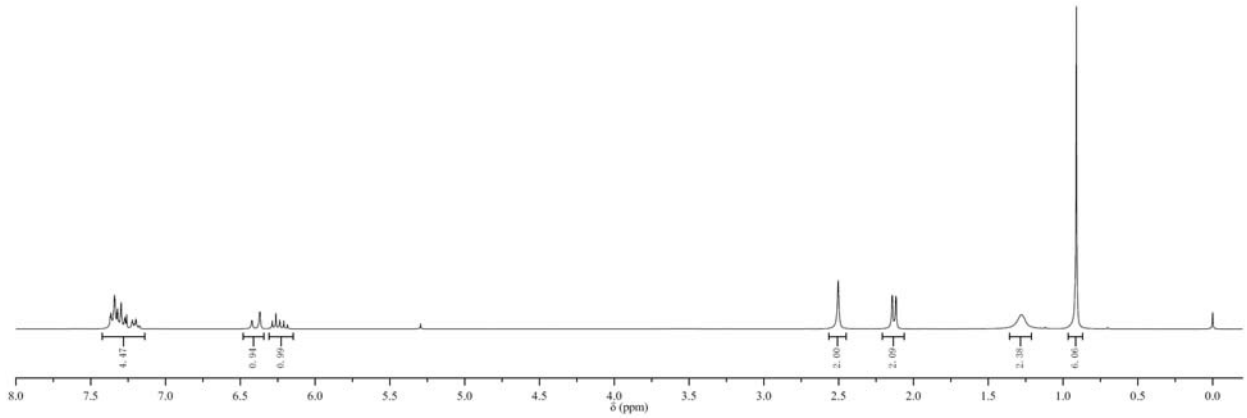
^{13}C NMR
75 MHz,$CDCl_3$

6d

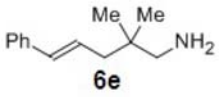
^{1}H NMR
300 MHz,$CDCl_3$



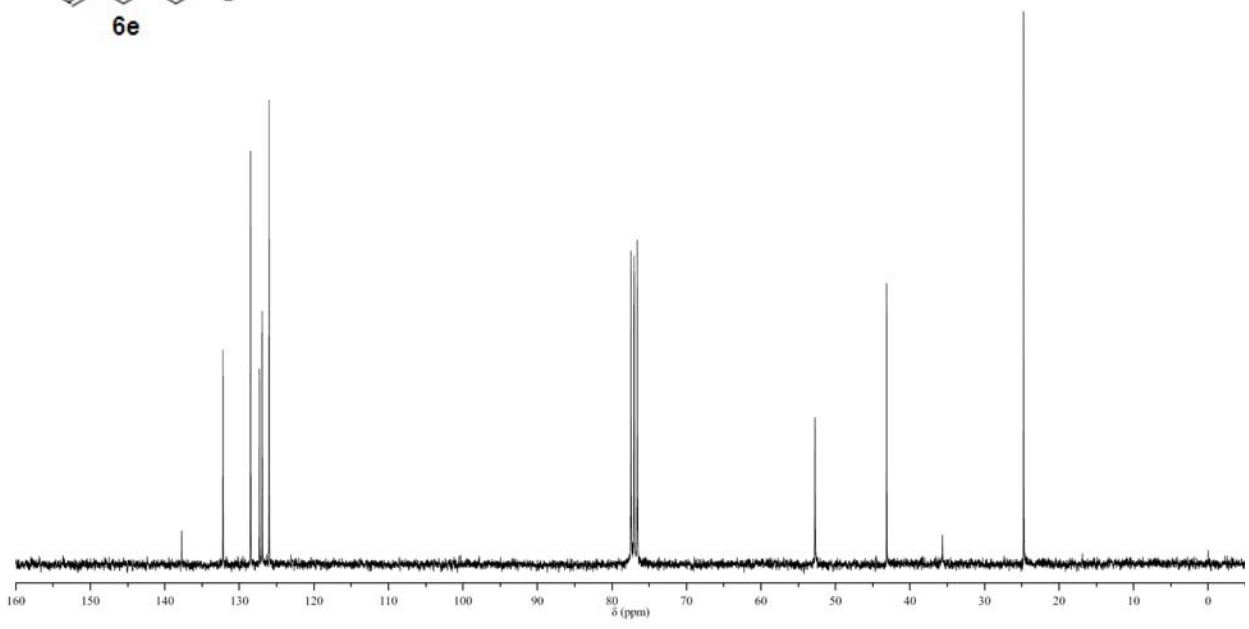
6e

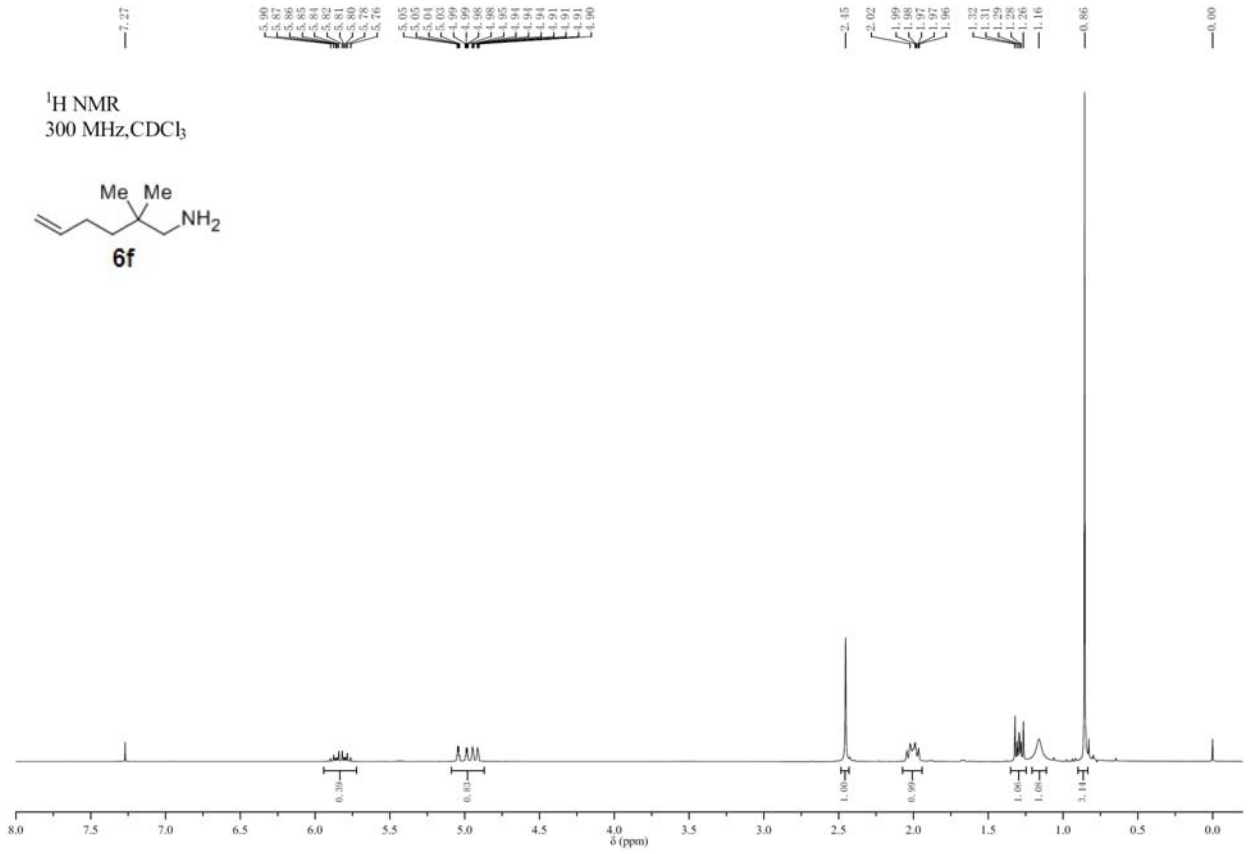


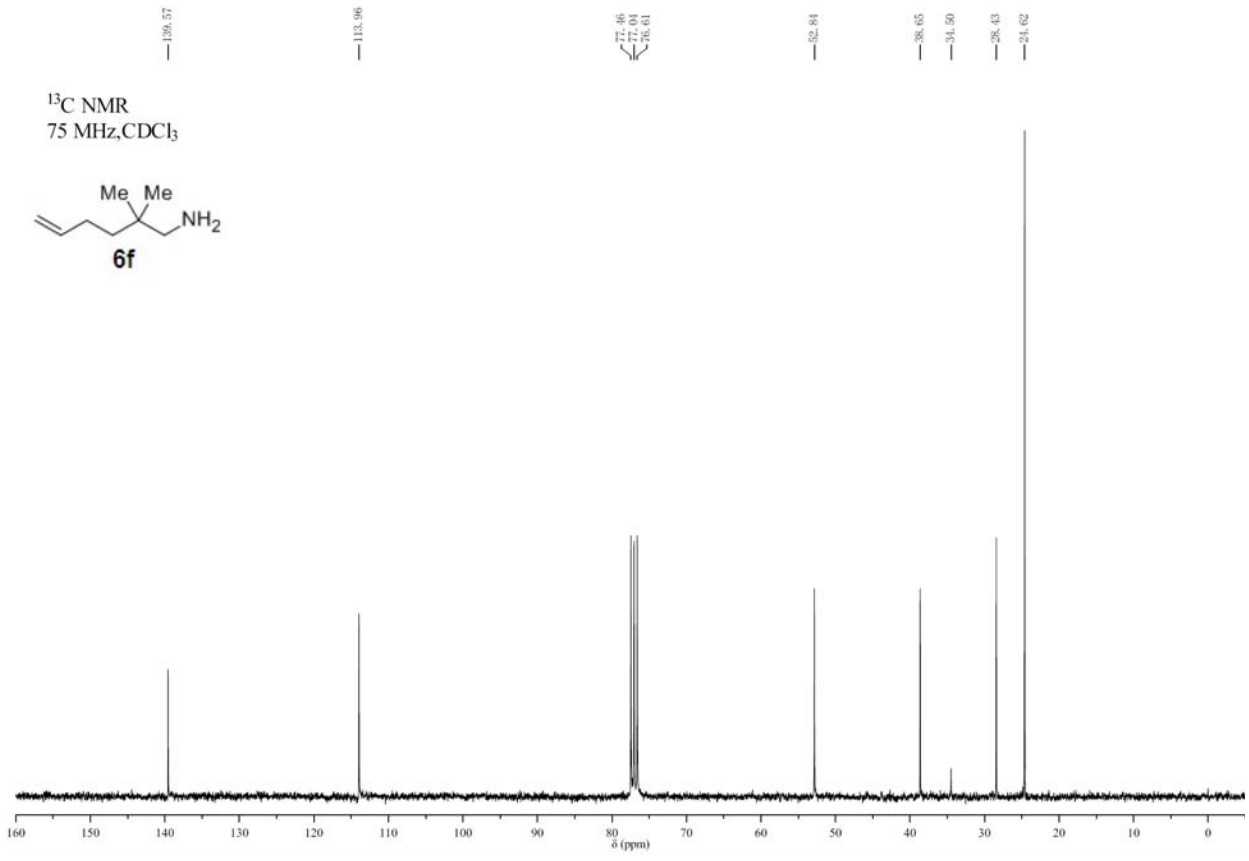
^{13}C NMR
75 MHz,$CDCl_3$



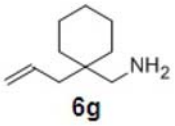
6e



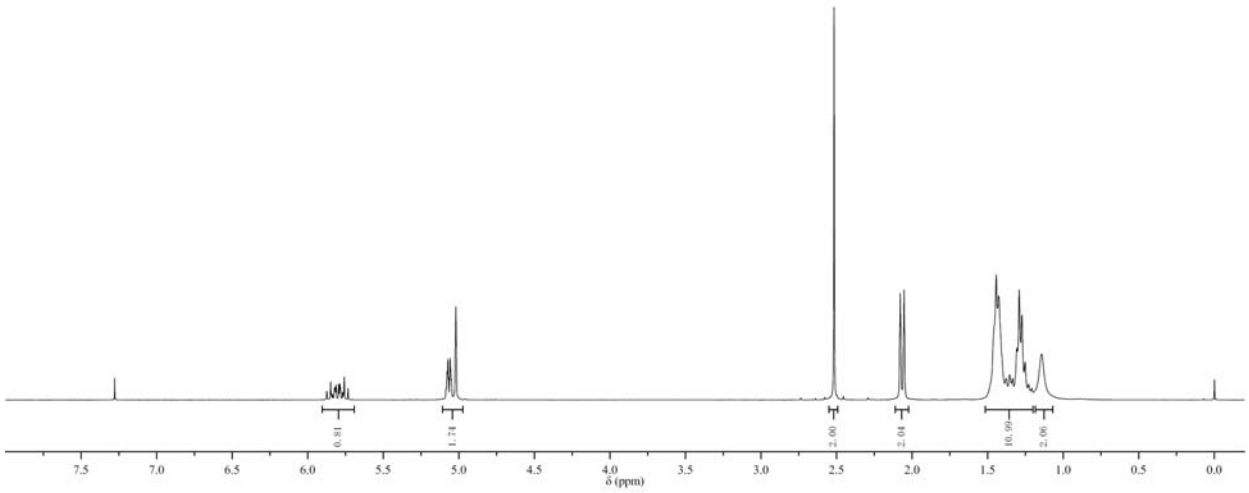

7.27
5.99
5.87
5.86
5.85
5.84
5.82
5.81
5.80
5.78
5.76
5.05
5.05
5.04
5.03
4.99
4.99
4.98
4.98
4.95
4.94
4.94
4.91
4.91
4.91
4.90
2.45
2.02
1.99
1.98
1.97
1.97
1.96
1.32
1.31
1.29
1.28
1.26
1.16
0.86
0.00
^{1}H NMR
300 MHz,CDCl$_3$
Me Me
NH$_2$
6f
6.39
6.83
1.00
0.99
1.06
1.08
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


139.57
113.96
77.46
77.04
76.61
52.84
38.65
34.50
28.43
24.62
^{13}C NMR
75 MHz,CDCl$_3$
Me Me
NH$_2$
6f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

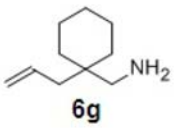
^{1}H NMR
300 MHz,$CDCl_3$



6g

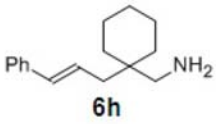


^{13}C NMR
75 MHz,$CDCl_3$

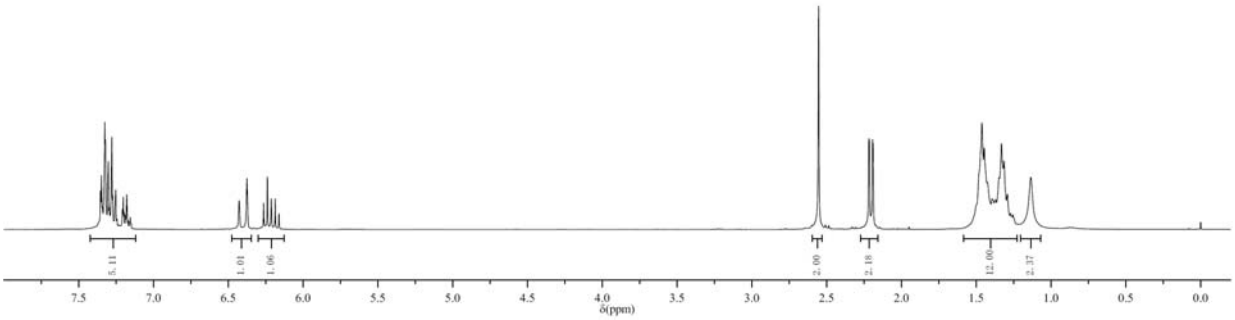


6g

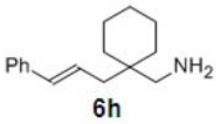
^{1}H NMR
300 MHz,$CDCl_3$



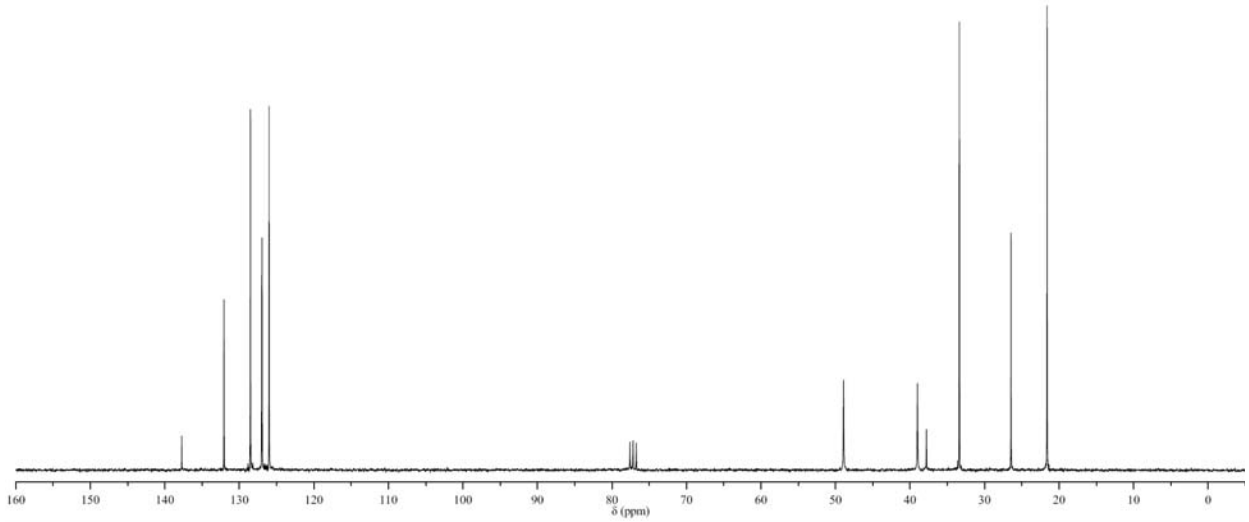
6h



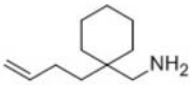
^{13}C NMR
75 MHz,$CDCl_3$



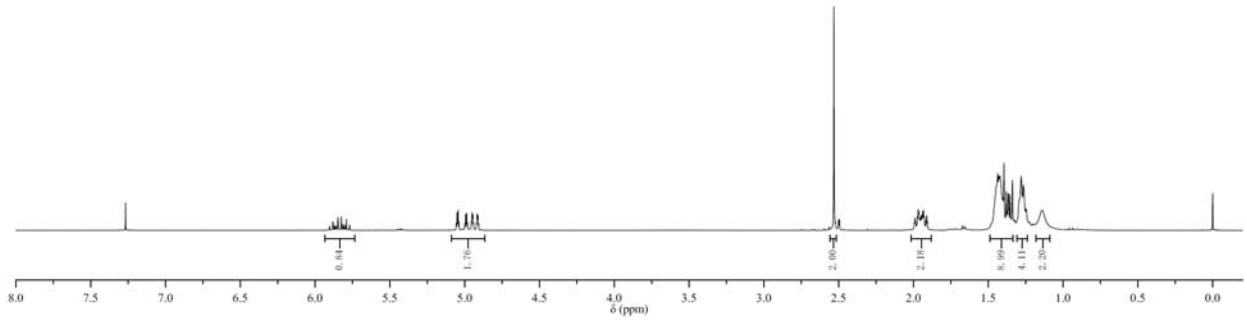
6h



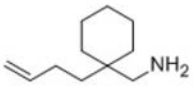
^{1}H NMR
300 MHz,$CDCl_3$



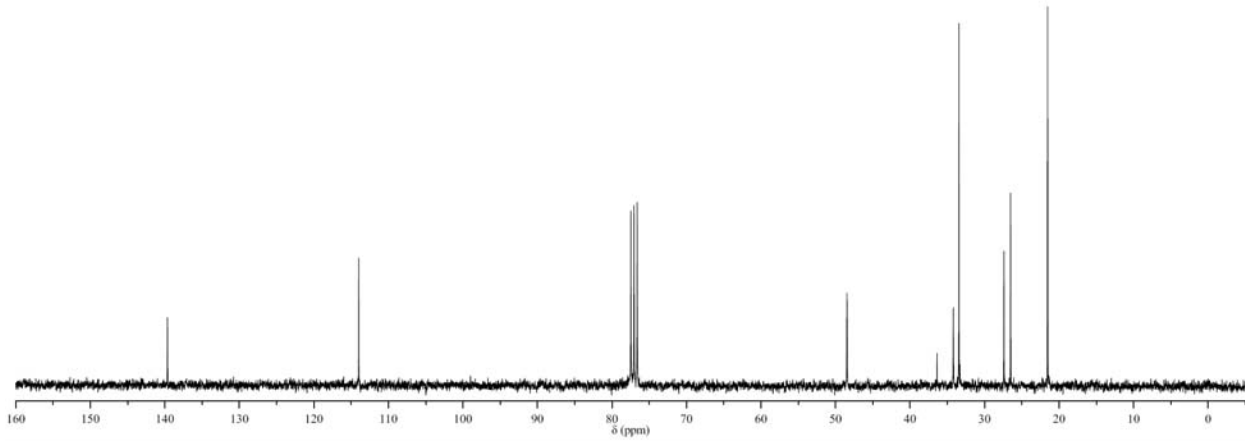
6i



^{13}C NMR
75 MHz,$CDCl_3$

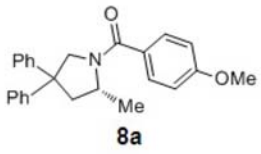


6i

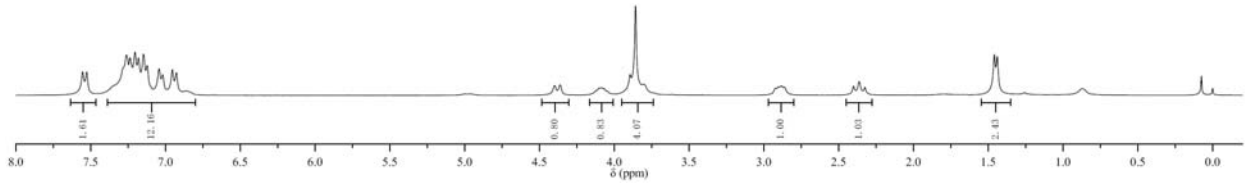


Copies of ^{1}H NMR and ^{13}C NMR for compounds 8a–i

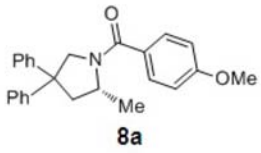
^{1}H NMR
300 MHz,$CDCl_3$



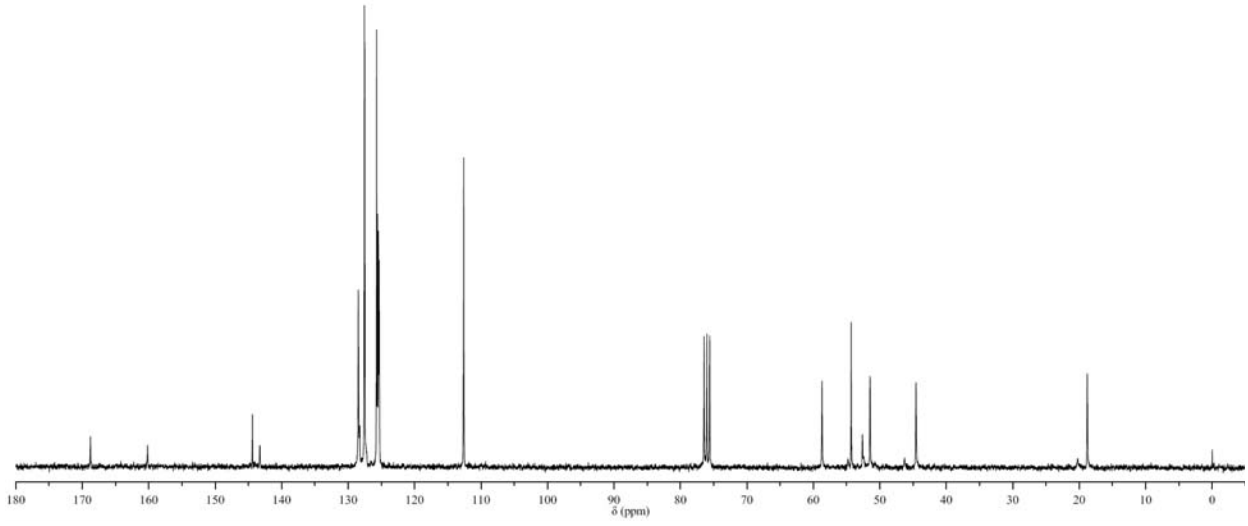
8a



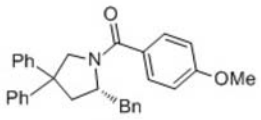
^{13}C NMR
75 MHz,$CDCl_3$



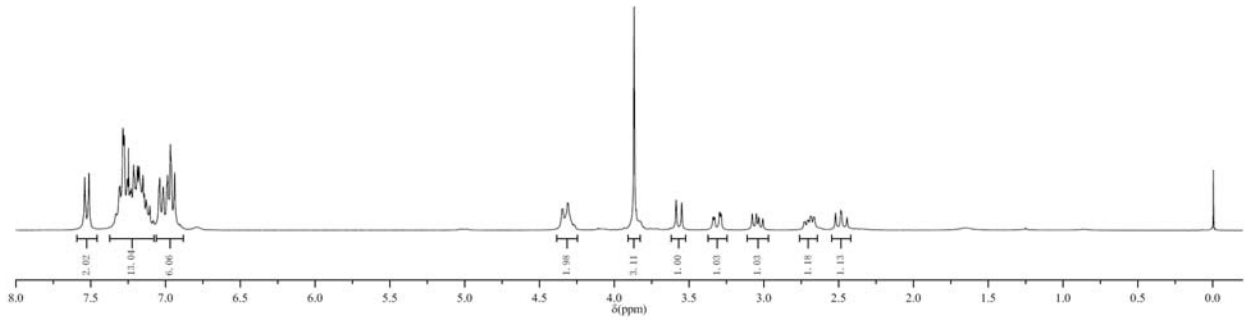
8a



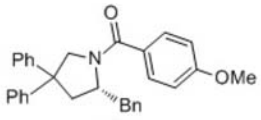
^{1}H NMR
300 MHz,$CDCl_3$



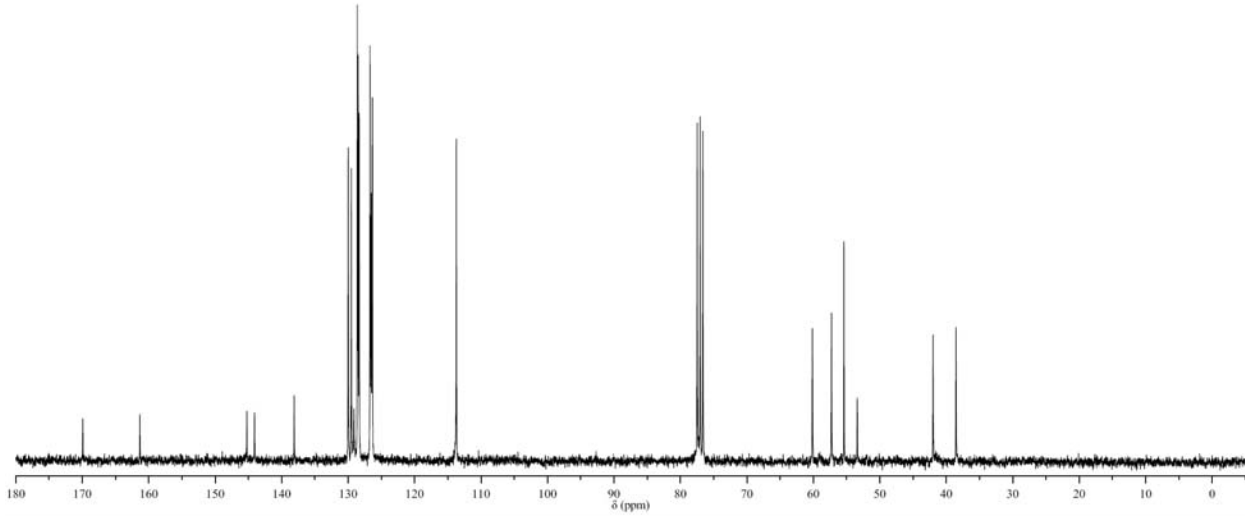
8b

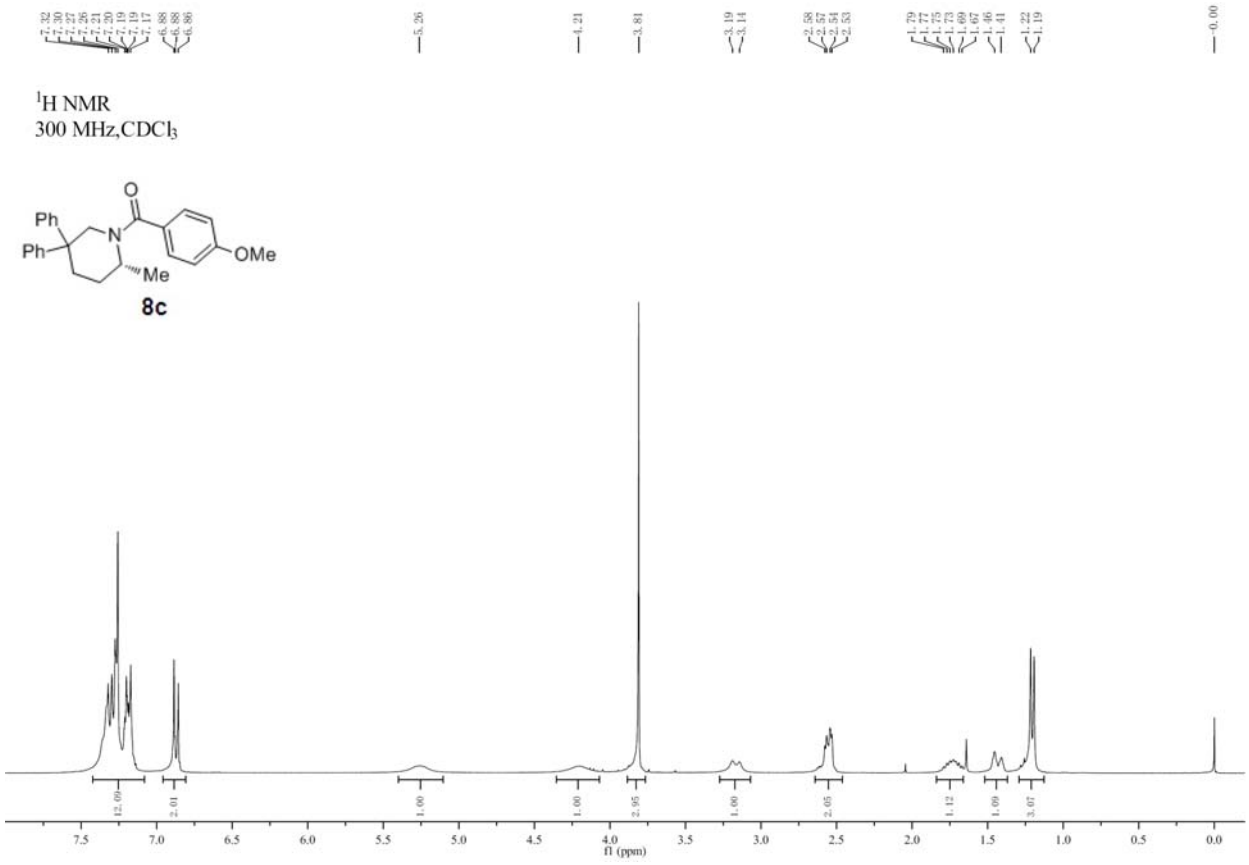


^{13}C NMR
75 MHz,$CDCl_3$



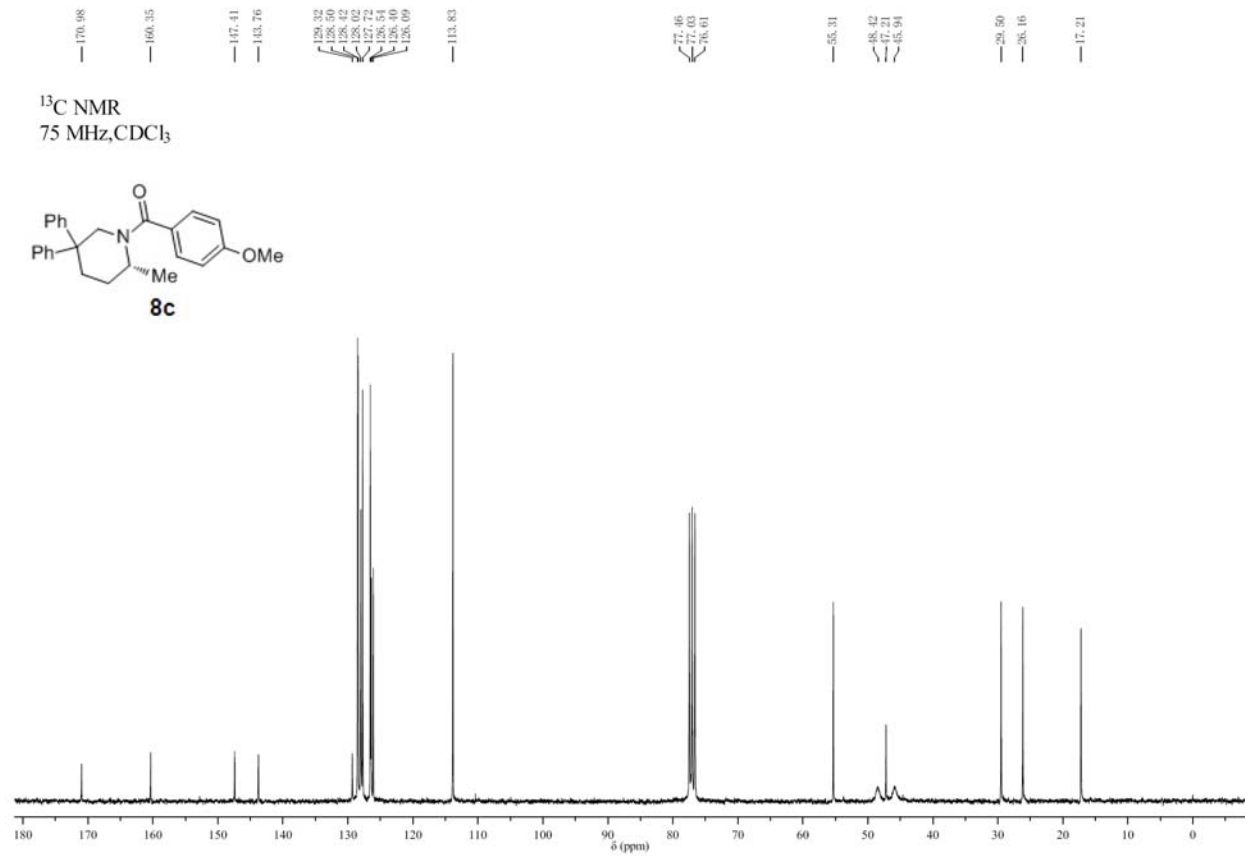
8b





^{1}H NMR
300 MHz,$CDCl_3$

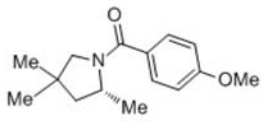
8c



^{13}C NMR
75 MHz,$CDCl_3$

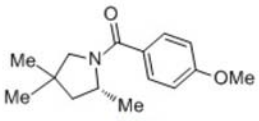
8c

^{1}H NMR
300 MHz,$CDCl_3$



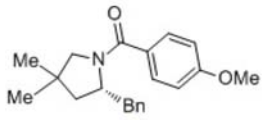
8d

^{13}C NMR
75 MHz,$CDCl_3$

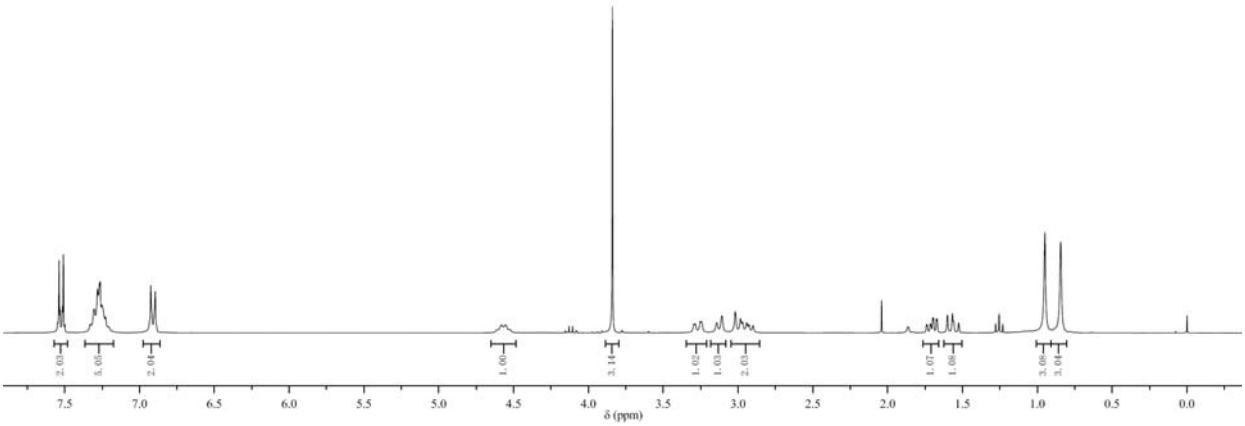


8d

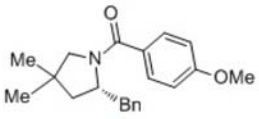
^{1}H NMR
300 MHz,$CDCl_3$



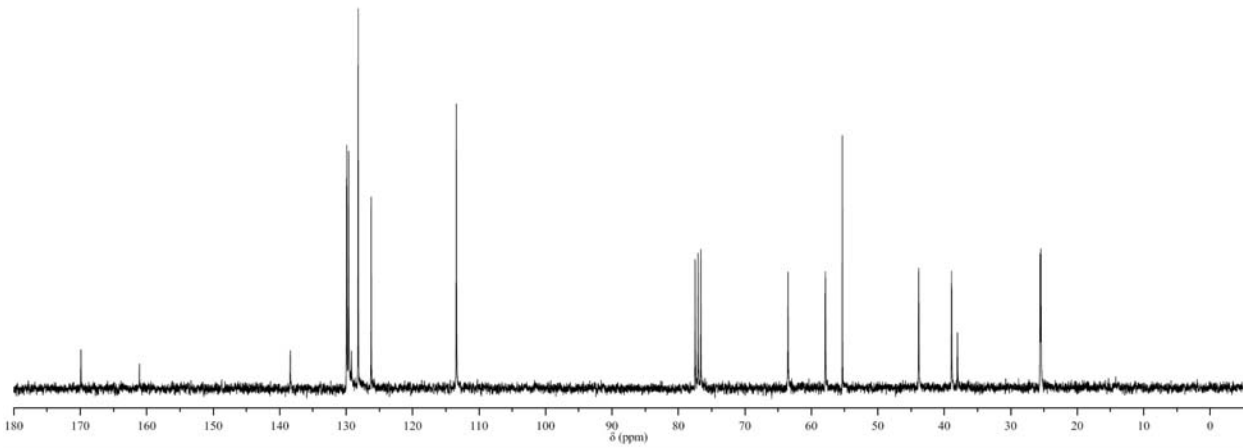
8e



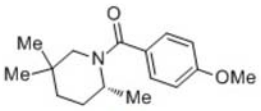
^{13}C NMR
75 MHz,$CDCl_3$



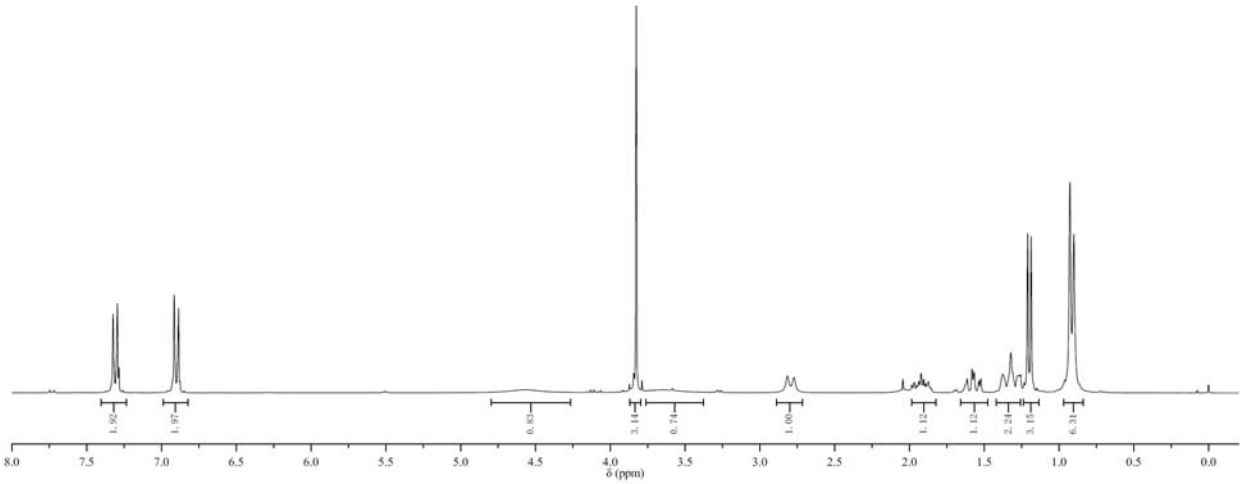
8e



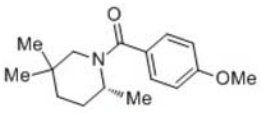
^{1}H NMR
300 MHz,$CDCl_3$



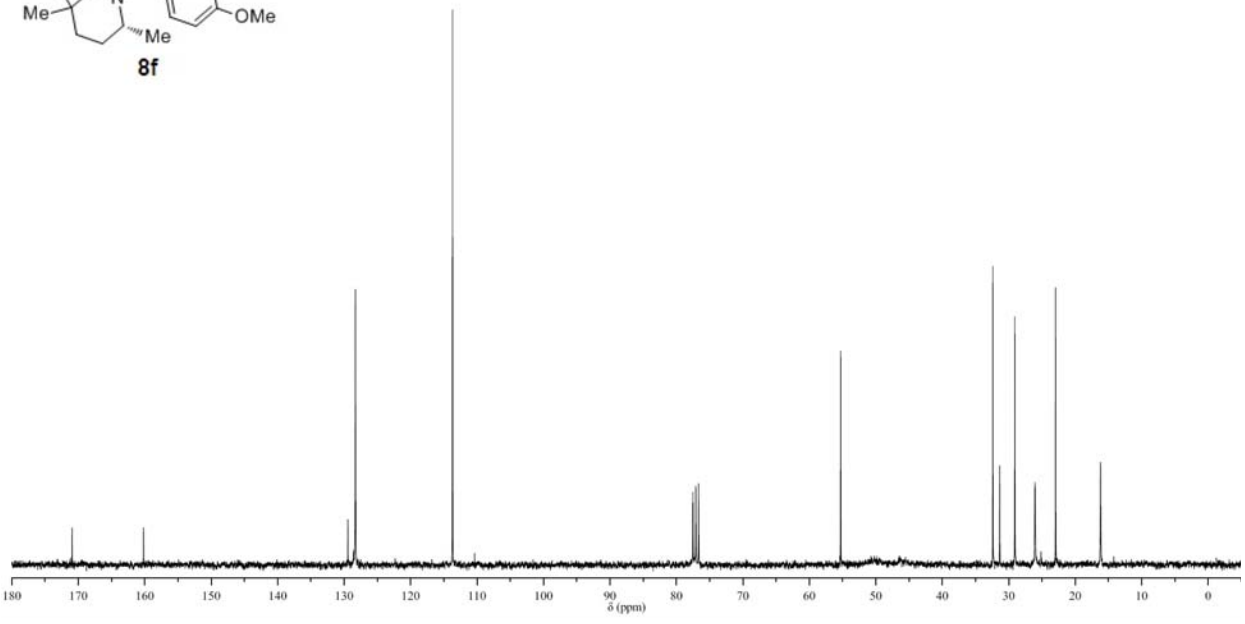
8f

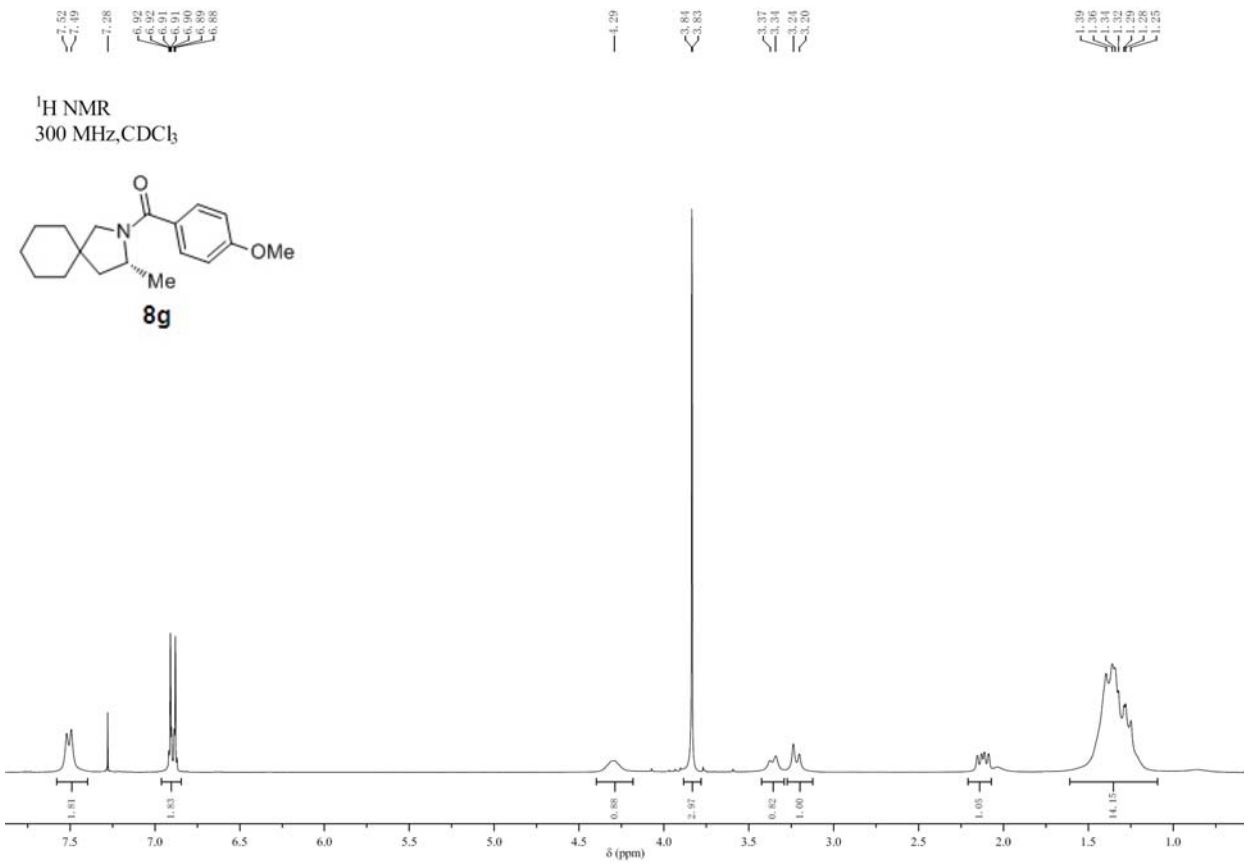


^{13}C NMR
75 MHz,$CDCl_3$



8f




7.52
7.49
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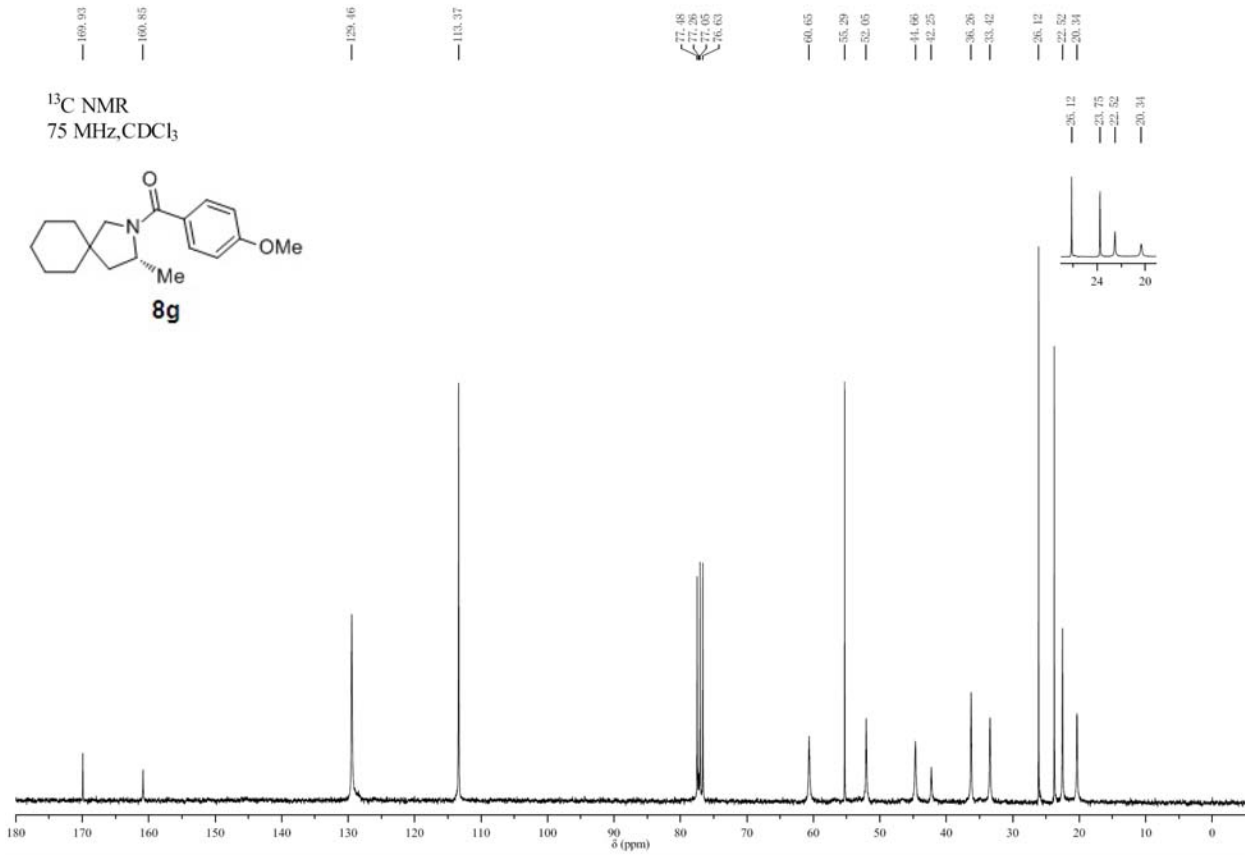
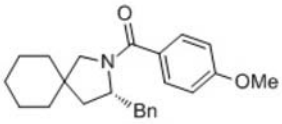
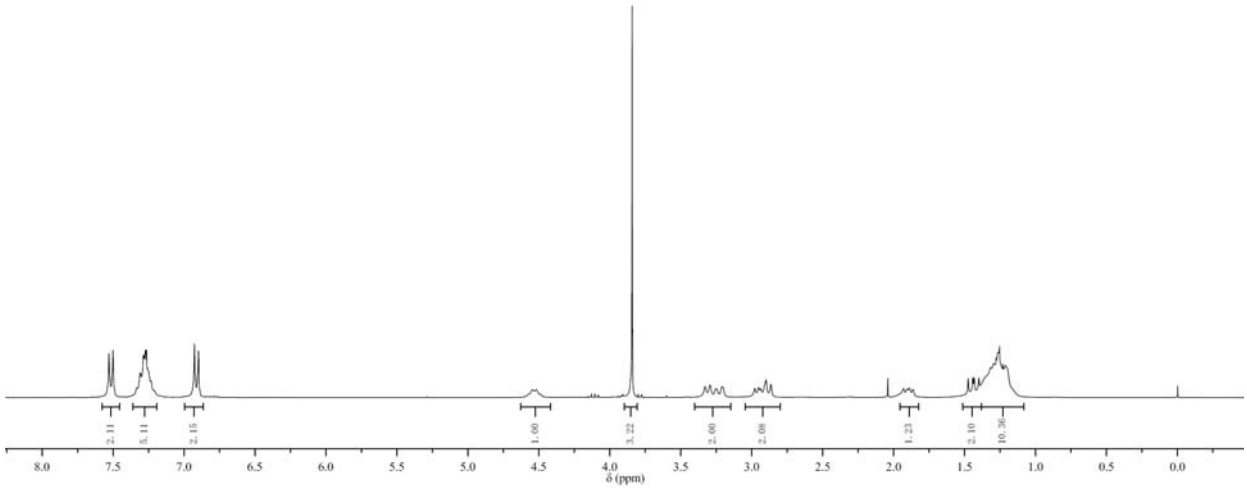
6.92
6.92
6.91
6.91
6.90
6.89
6.88
4.29
3.84
3.83
3.37
3.34
3.24
3.20
1.39
1.36
1.34
1.32
1.29
1.28
1.25
1H NMR
300 MHz,CDCl3
O
N
OMe
Me
8g
1.81
1.83
0.88
2.97
0.82
1.00
1.05
14.15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
δ (ppm)


169.93
160.85
129.46
113.37
77.48
77.26
77.05
76.63
60.65
55.29
52.05
44.66
42.25
36.26
33.42
26.12
22.52
20.34
13C NMR
75 MHz,CDCl3
O
N
OMe
Me
8g
26.12
23.75
22.52
20.34
24
20
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

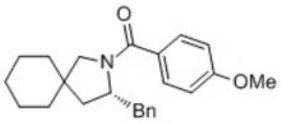
^{1}H NMR
300 MHz,$CDCl_3$



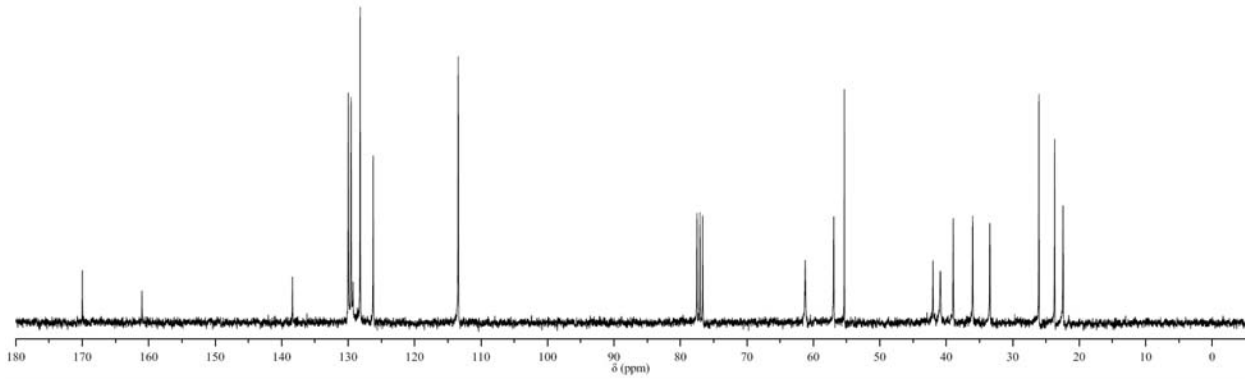
8h



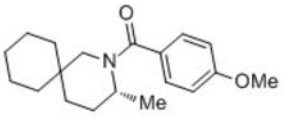
^{13}C NMR
75 MHz,$CDCl_3$



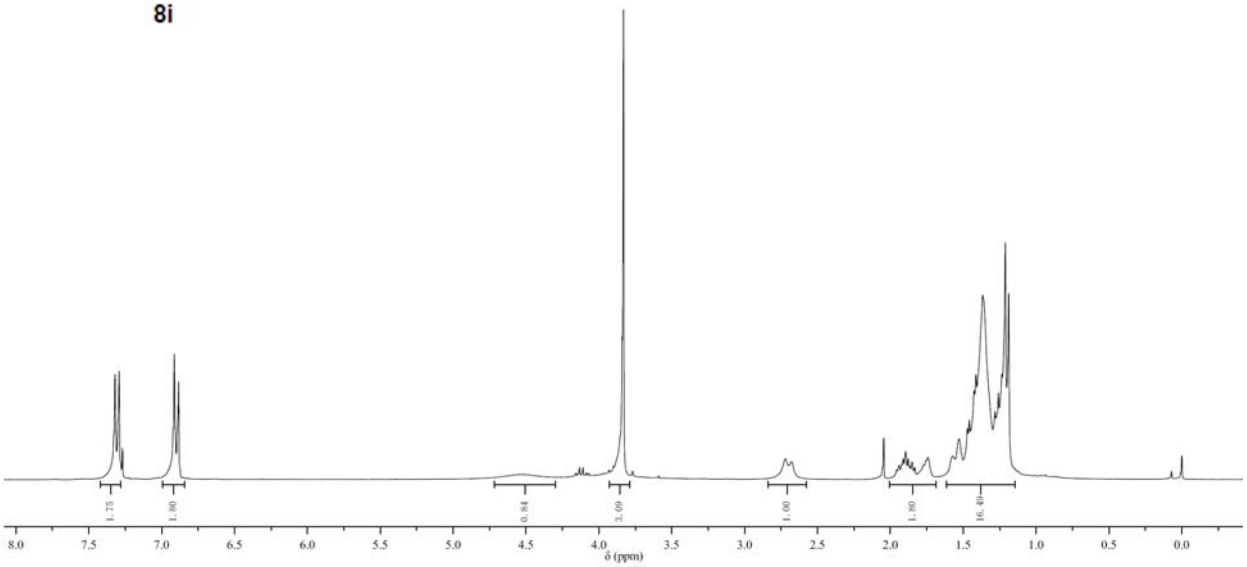
8h



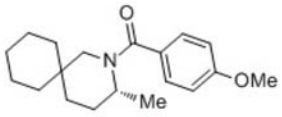
^{1}H NMR
300 MHz,$CDCl_3$



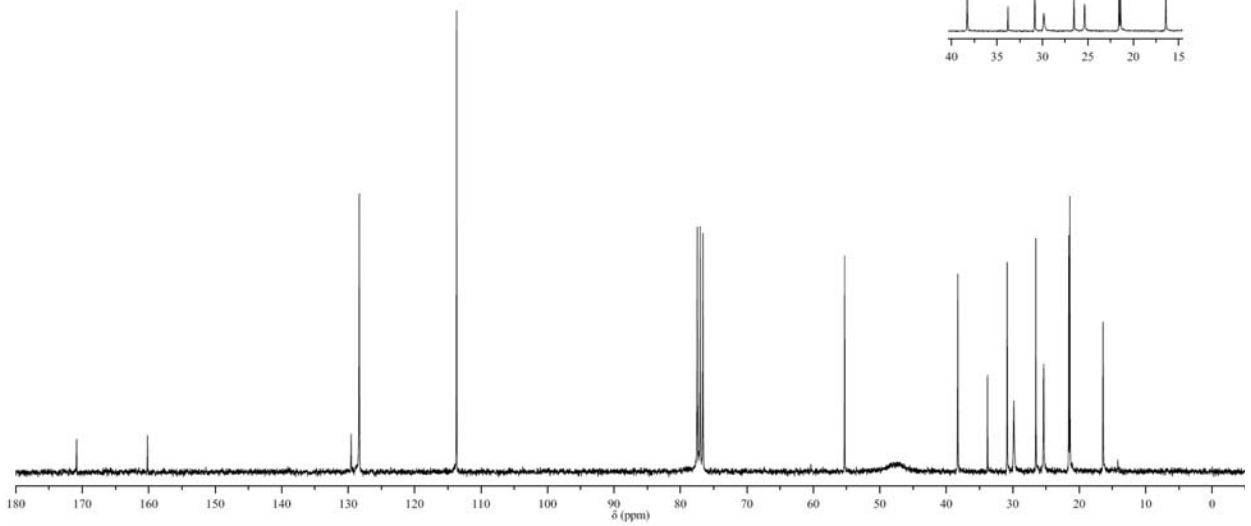
8i



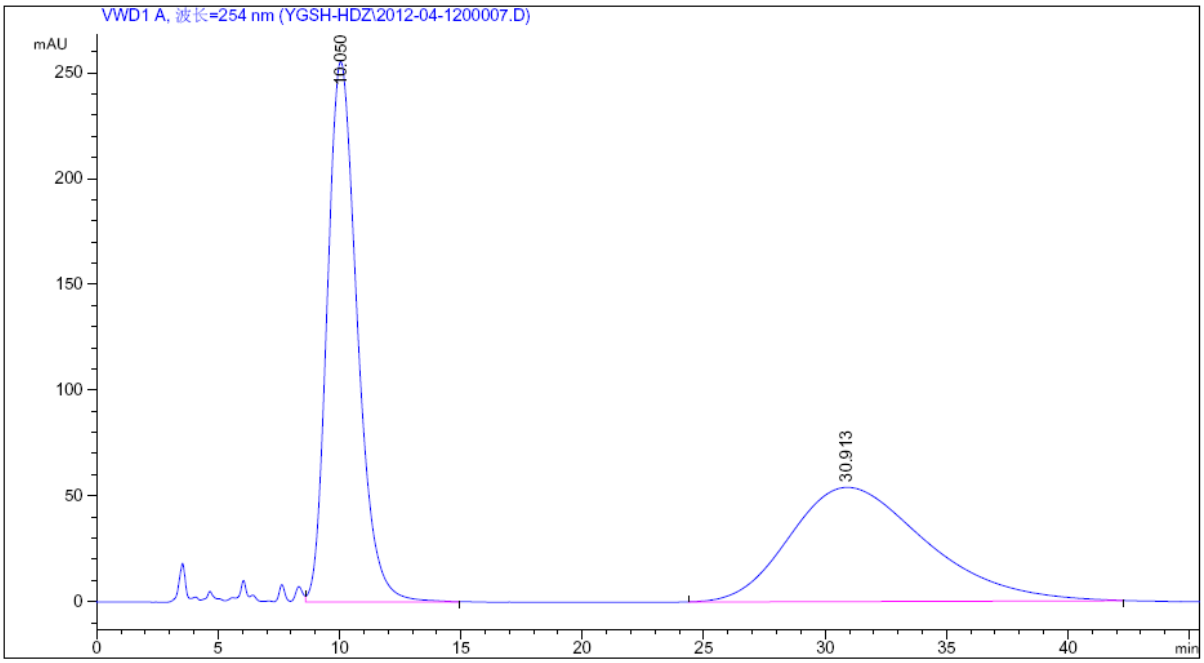
^{13}C NMR
75 MHz,$CDCl_3$



8i



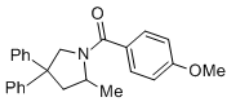
HPLC Profile of compounds 8a–i



Area Percent Report

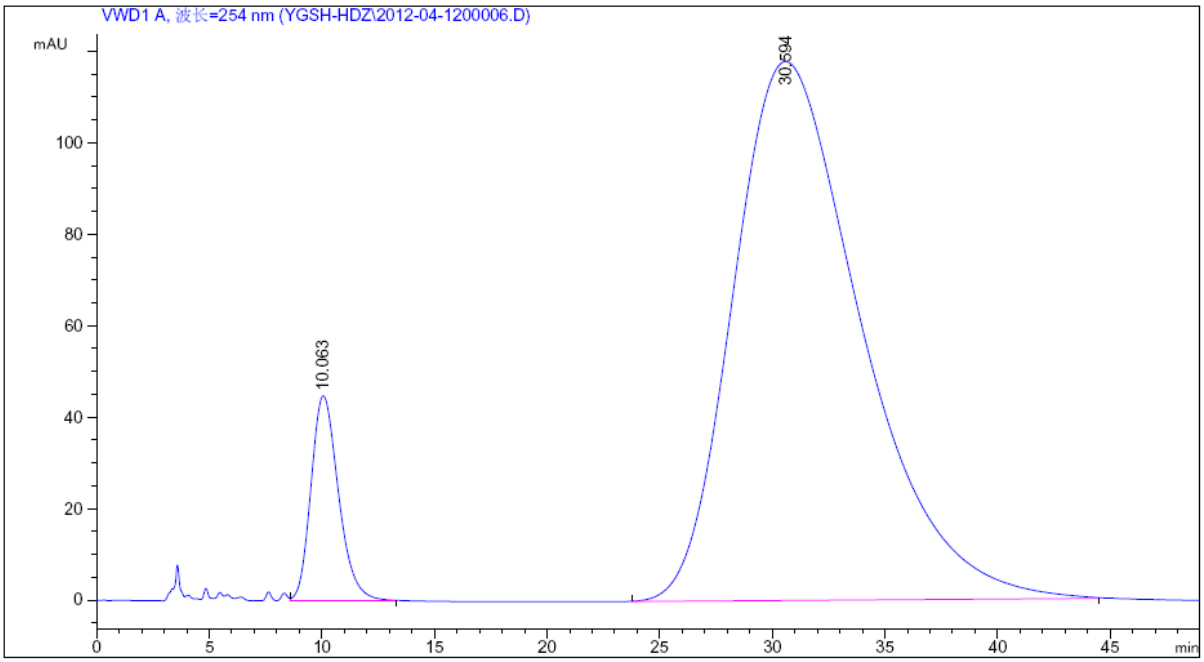
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	10.050	VB	1.3275	2.19266e4	255.46634	50.9009
2	30.913	BB	5.5342	2.11504e4	54.02491	49.0991

Racemic



8a

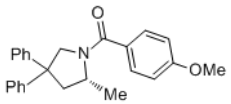
AS-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

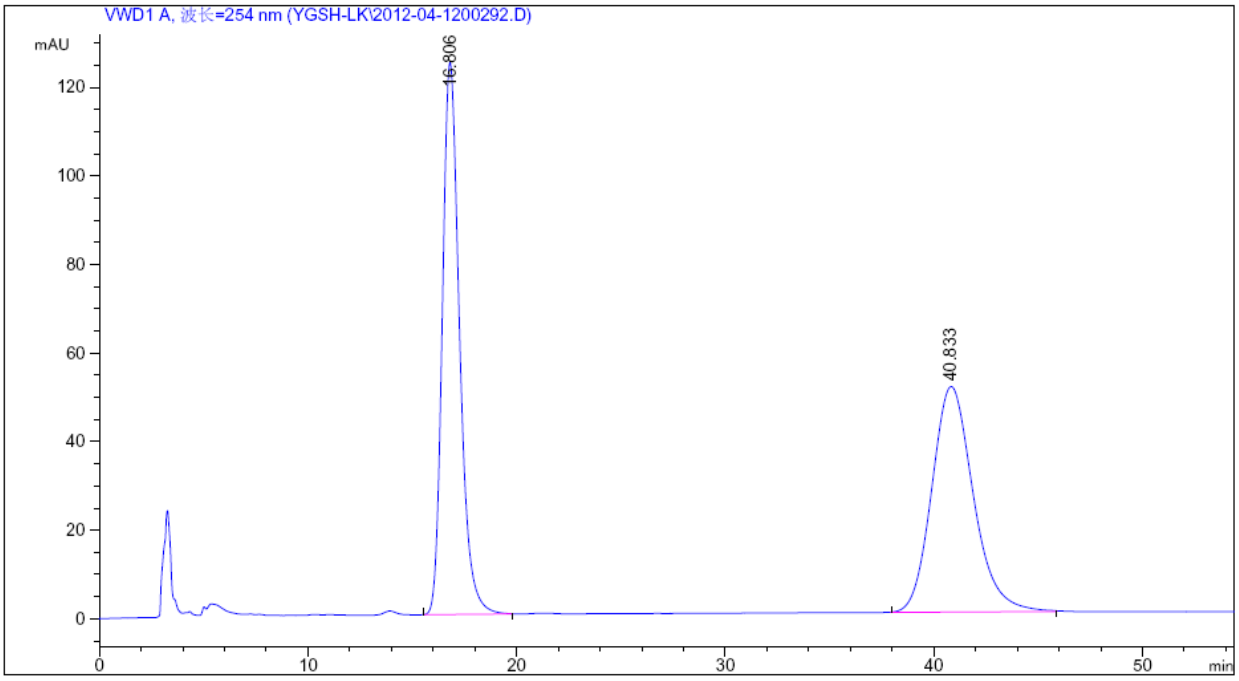
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	10.063	VB	1.3087	3817.43091	44.79712	7.6061
2	30.594	BB	5.8207	4.63714e4	117.81854	92.3939

Table 2, entry 1



8a

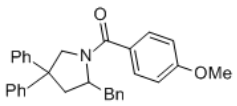
AS-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

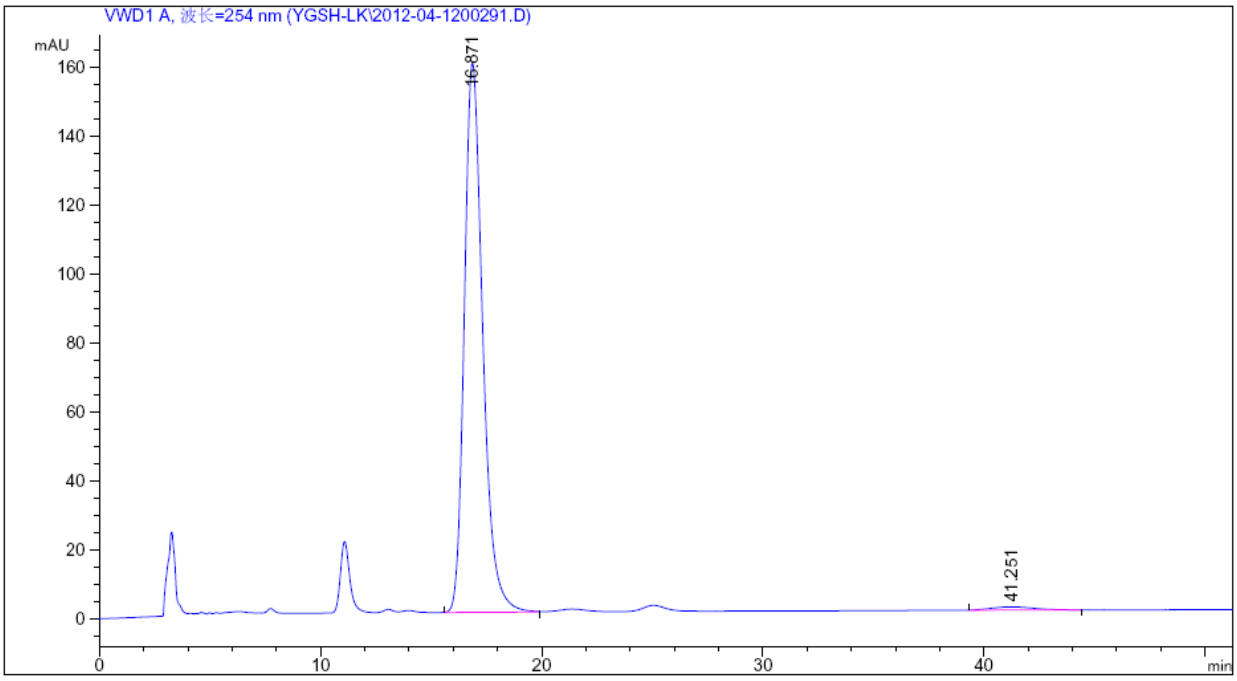
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	16.806	BB	0.8769	7130.53125	124.67223	50.2808
2	40.833	BB	2.1214	7050.88232	50.94442	49.7192

Racemic



8b

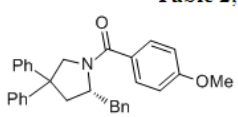
AD-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

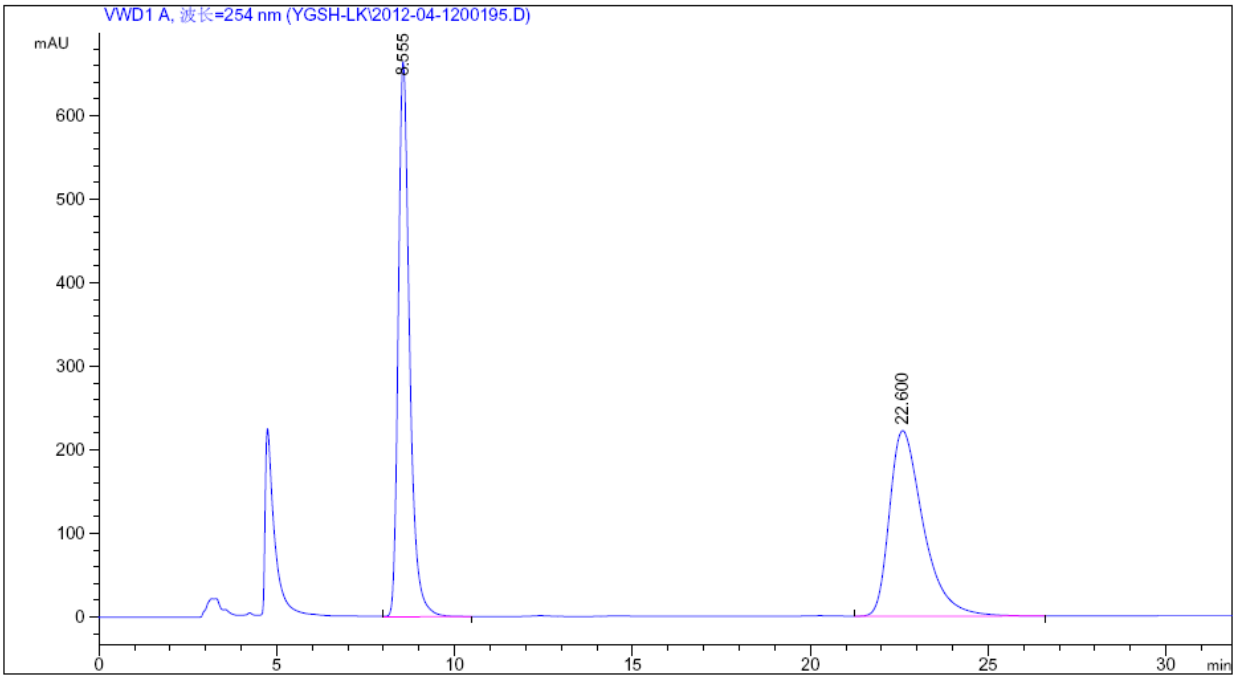
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	16.871	BB	0.8855	9238.65039	159.47234	98.6281
2	41.251	BB	1.7678	128.50723	9.55092e-1	1.3719

Table 2, entry 2



8b

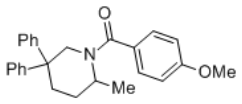
AD-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

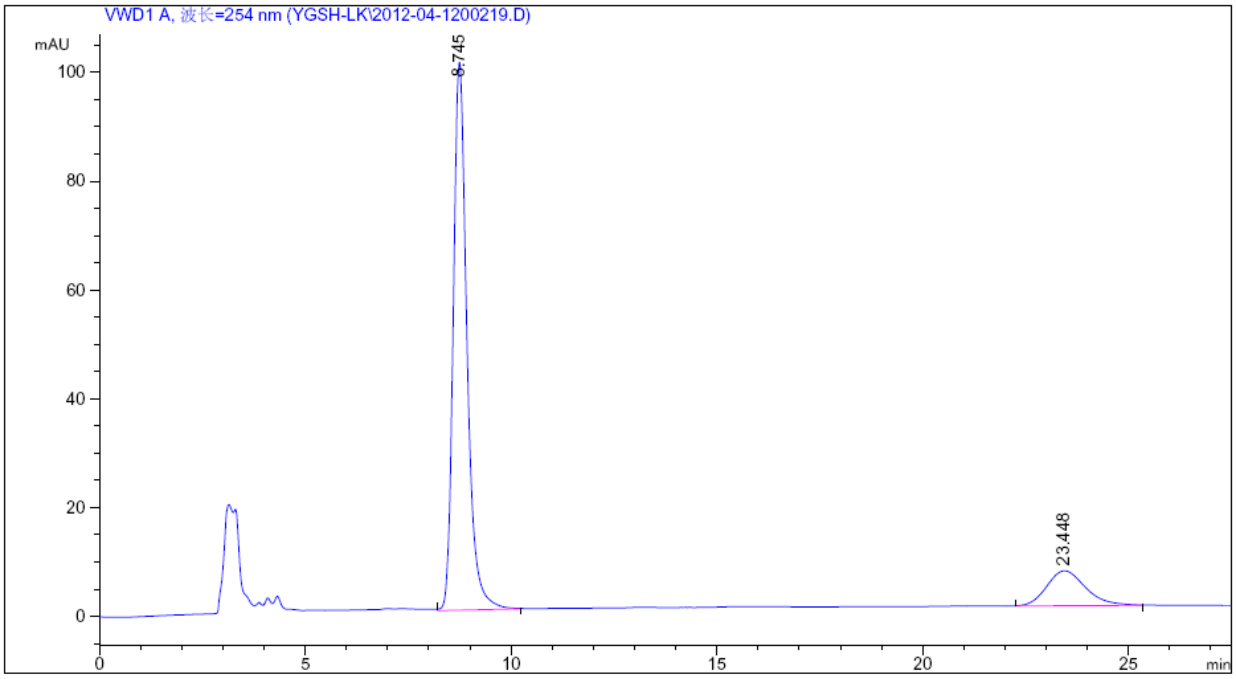
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	8.555	VB	0.3341	1.47049e4	663.85712	50.0509
2	22.600	VB	1.0038	1.46750e4	222.09303	49.9491

Racemic



8c

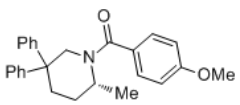
AD-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

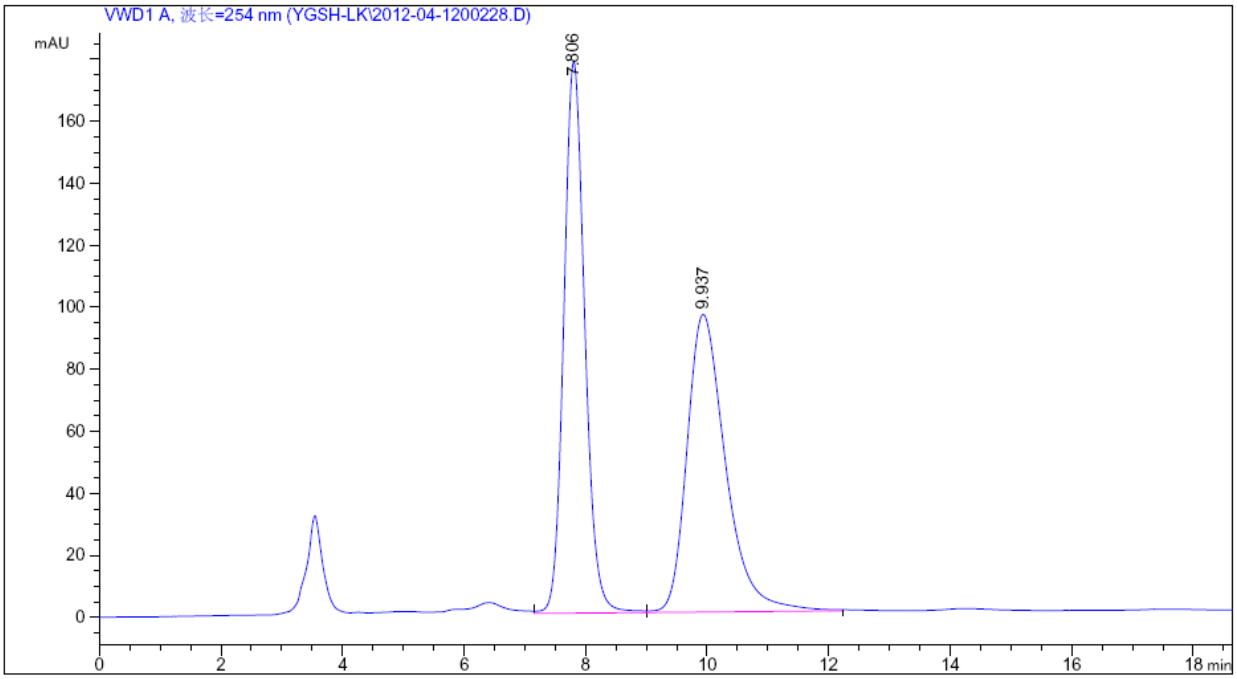
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	8.745	BB	0.3514	2327.93604	100.64504	84.6454
2	23.448	BB	1.0116	422.28522	6.42304	15.3546

Table 2, entry 3



8c

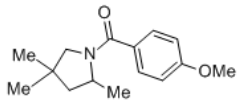
AD-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

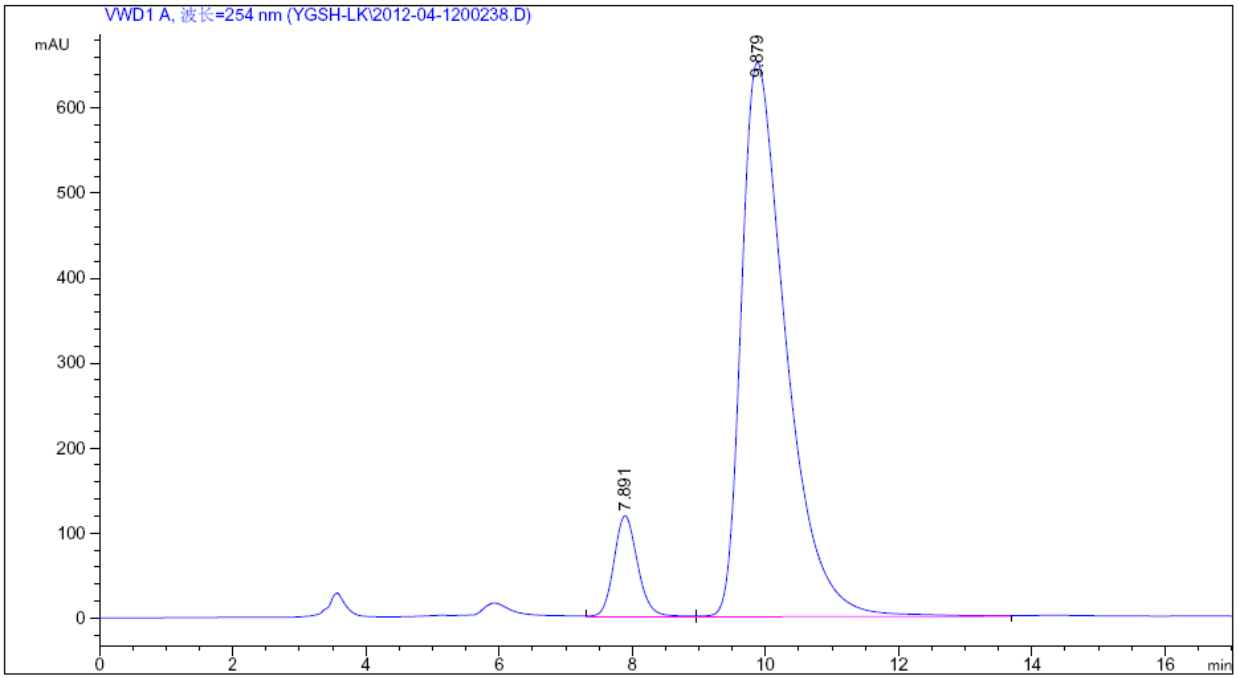
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	7.806	VV	0.3729	4259.93066	177.66173	50.1125
2	9.937	VB	0.6729	4240.79687	95.94611	49.8875

Racemic



8d

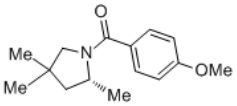
AS-H, hexane/2-propanol 3:1, 1mL/min



Area Percent Report

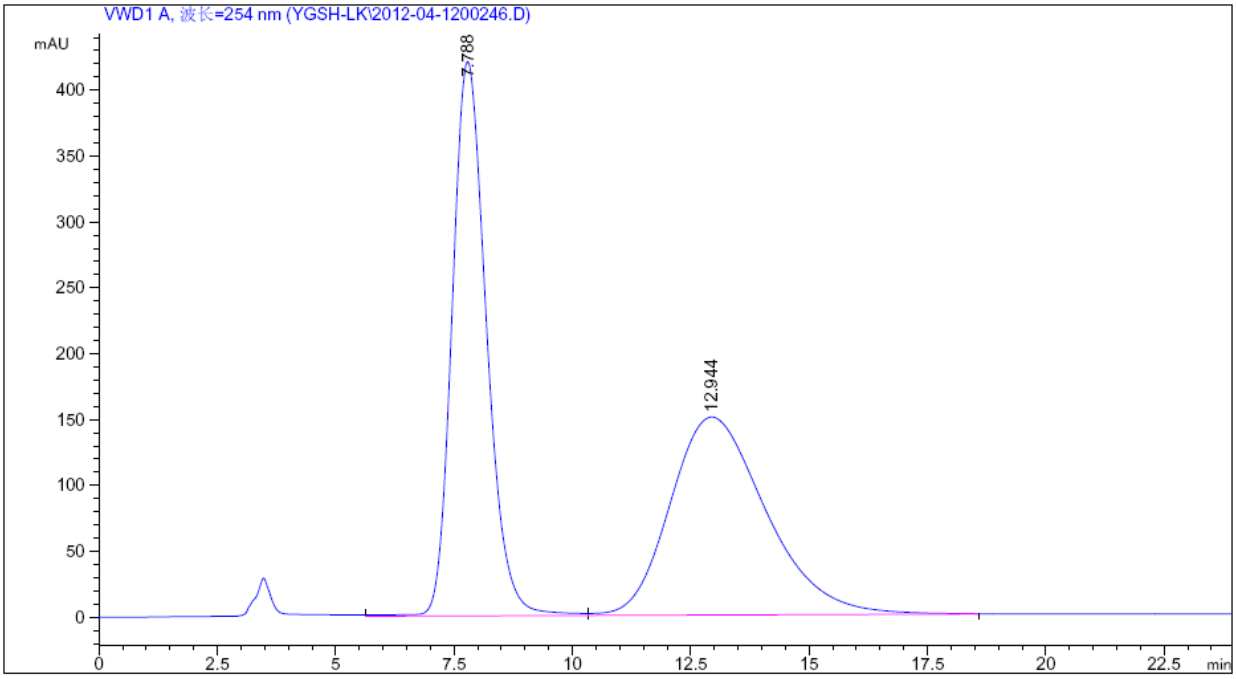
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	7.891	VV	0.3853	2980.89941	119.07238	8.9329
2	9.879	VB	0.7064	3.03889e4	652.56671	91.0671

Table 2, entry 4



8d

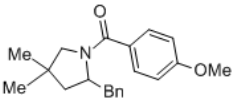
AS-H, hexane/2-propanol 3:1, 1mL/min



Area Percent Report

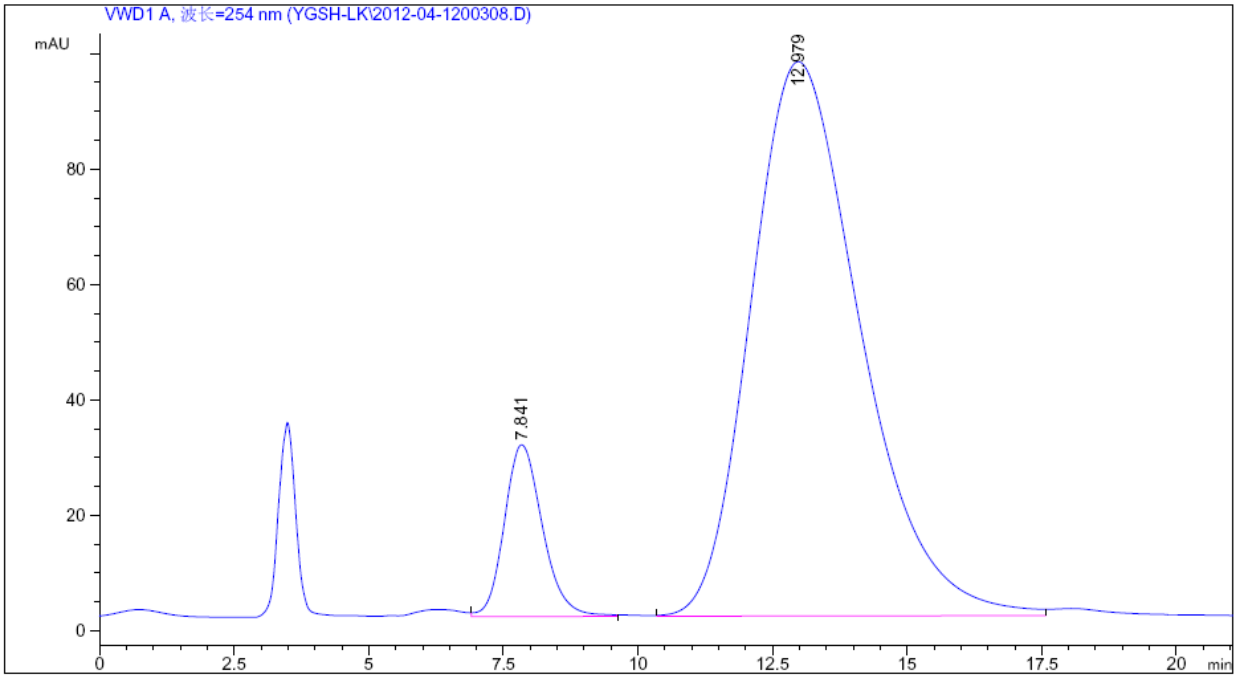
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	7.788	VV	0.7808	2.12168e4	420.53226	50.0515
2	12.944	VB	2.1862	2.11731e4	150.20801	49.9485

Racemic



8e

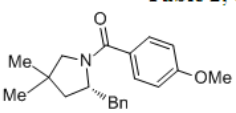
AS-H, hexane/2-propanol 2:1, 1mL/min



Area Percent Report

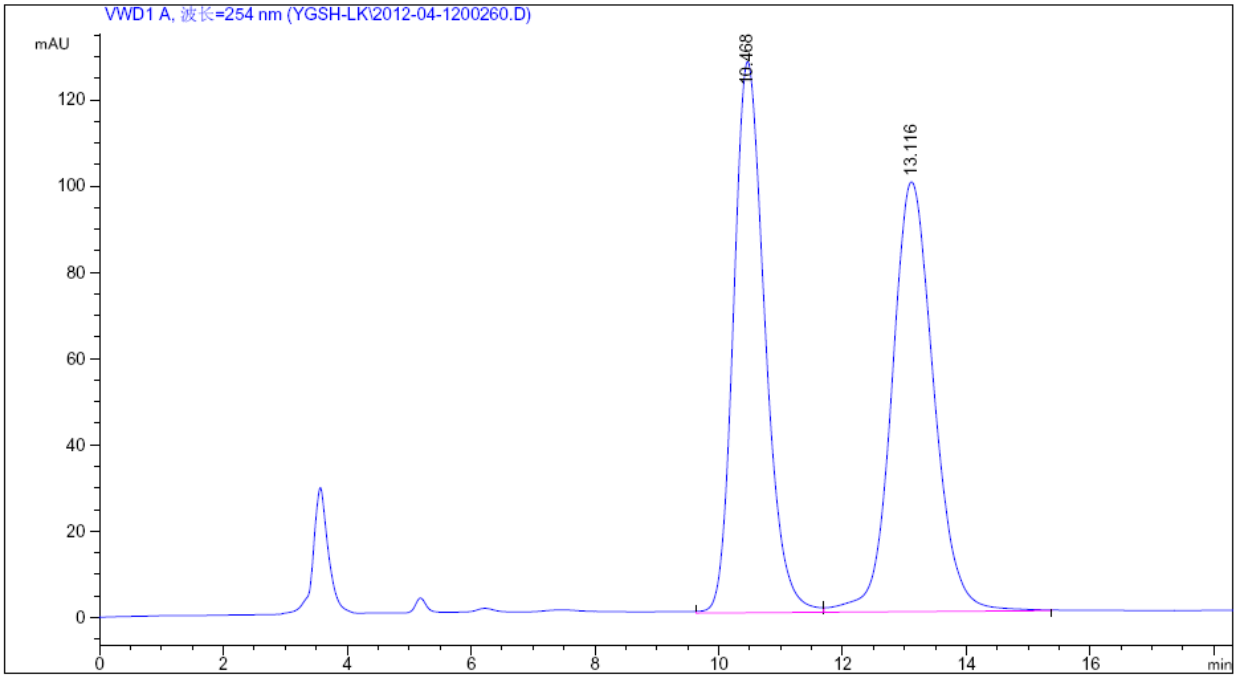
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	7.841	VB	0.7626	1469.70068	29.75681	9.7777
2	12.979	BV	2.1776	1.35614e4	96.02909	90.2223

Table 2, entry 5



8e

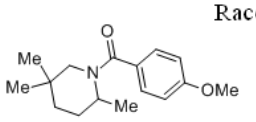
AS-H, hexane/2-propanol 2:1, 1mL/min



Area Percent Report

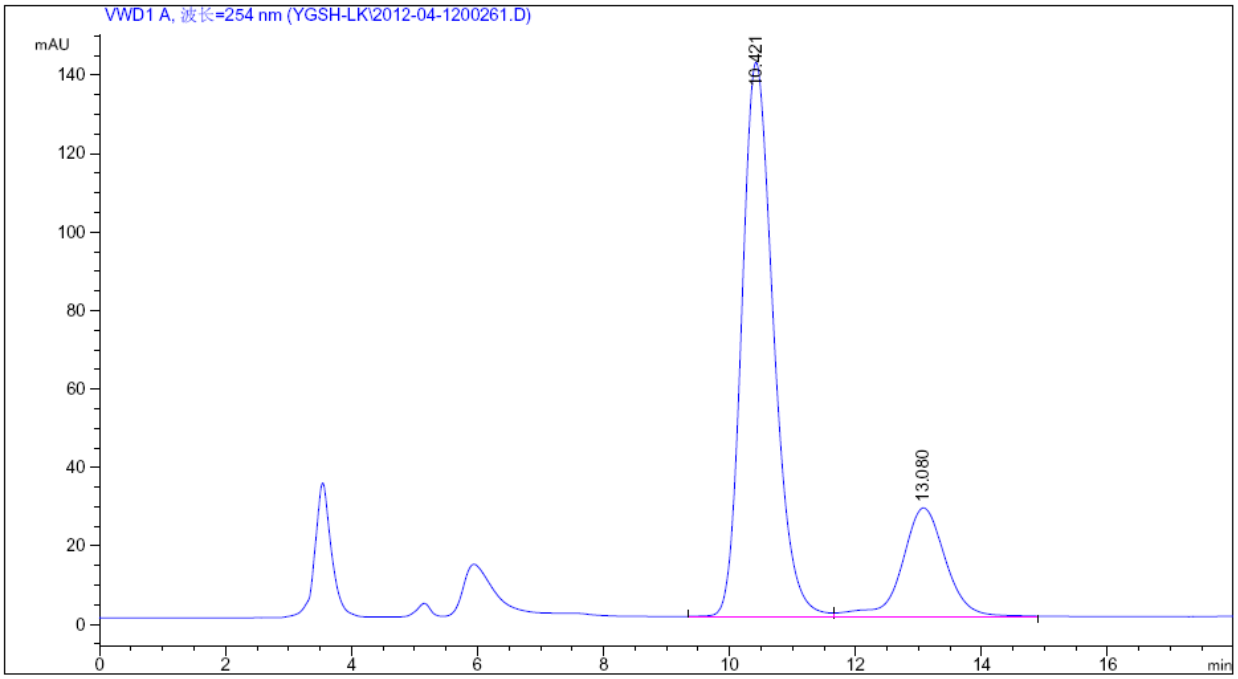
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	10.468	BV	0.5451	4500.44775	127.71635	49.0556
2	13.116	VB	0.7219	4673.73486	99.64371	50.9444

Racemic



8f

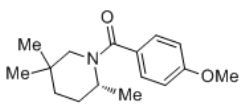
AS-H, hexane/2-propanol 3:1, 1mL/min



Area Percent Report

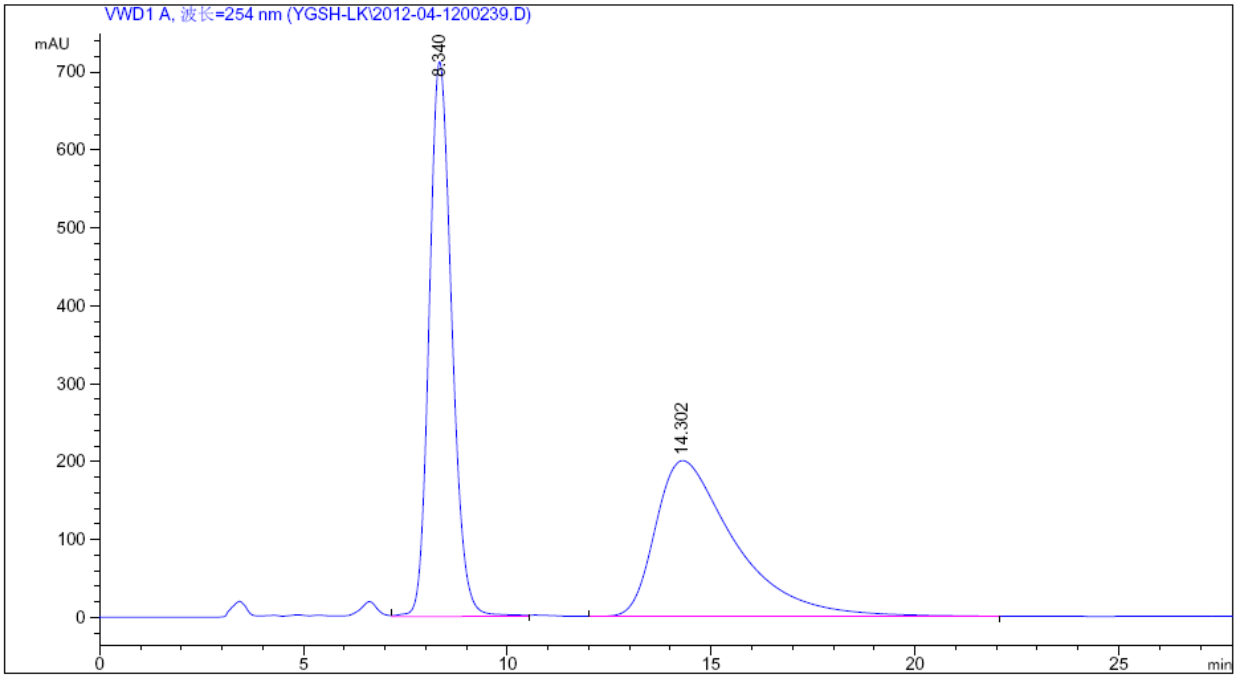
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	10.421	BV	0.5350	4922.96875	141.15567	78.7965
2	13.080	VB	0.7338	1324.72900	27.64488	21.2035

Table 2, entry 6



8f

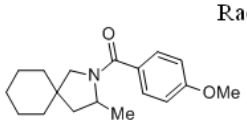
AS-H, hexane/2-propanol 3:1, 1mL/min



Area Percent Report

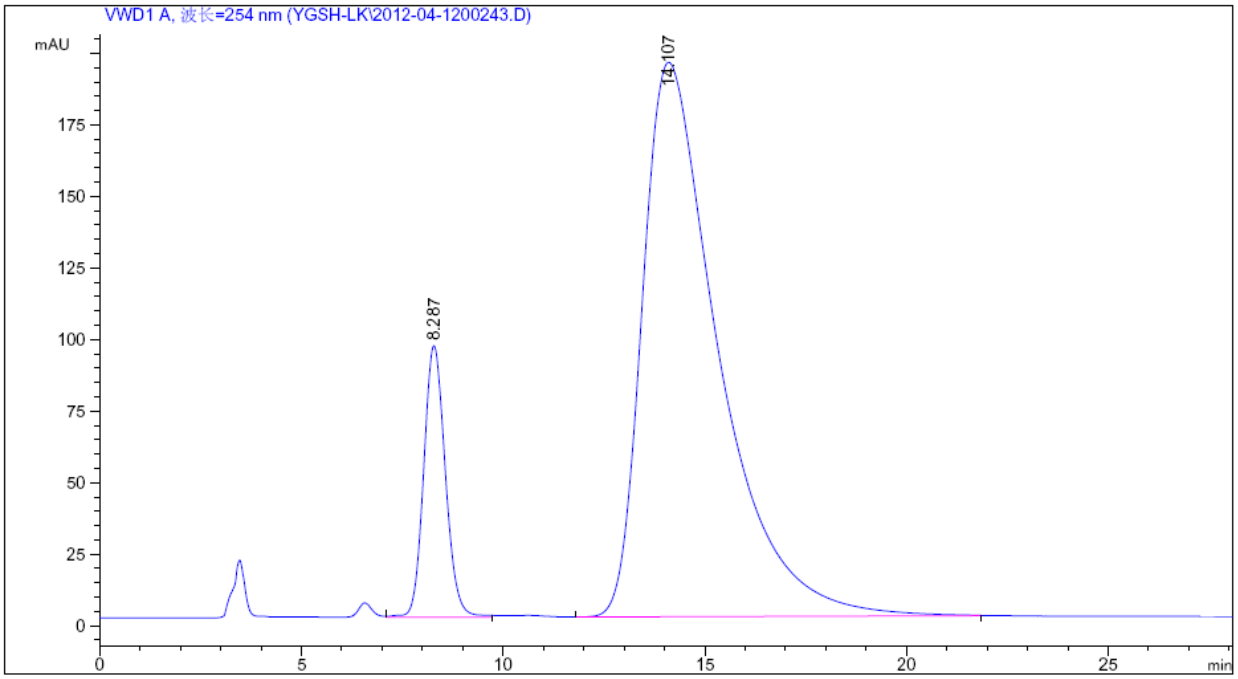
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	8.340	VB	0.6012	2.74451e4	711.83203	50.3831
2	14.302	BB	2.0091	2.70277e4	199.80716	49.6169

Racemic



8g

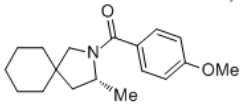
AS-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

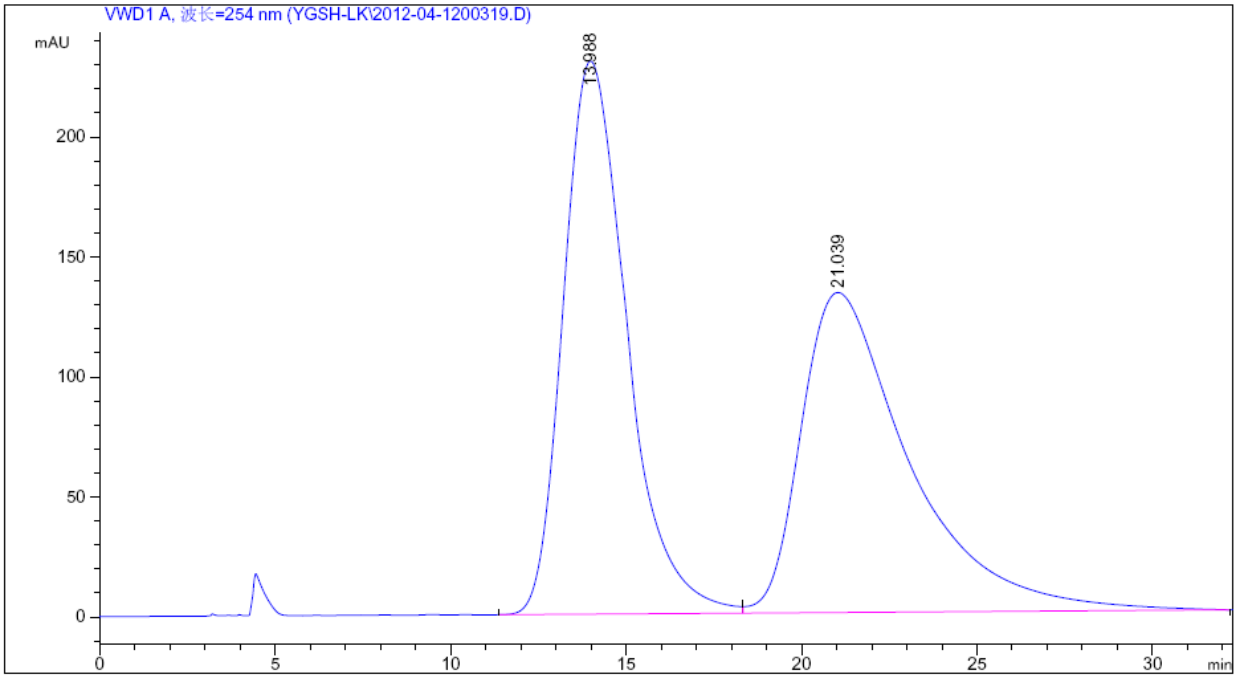
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	8.287	VB	0.5765	3551.36255	94.87296	12.2986
2	14.107	VB	1.9389	2.53247e4	193.68793	87.7014

Table 2, entry 7



8g

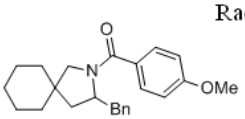
AS-H, hexane/2-propanol 1:1, 1mL/min



Area Percent Report

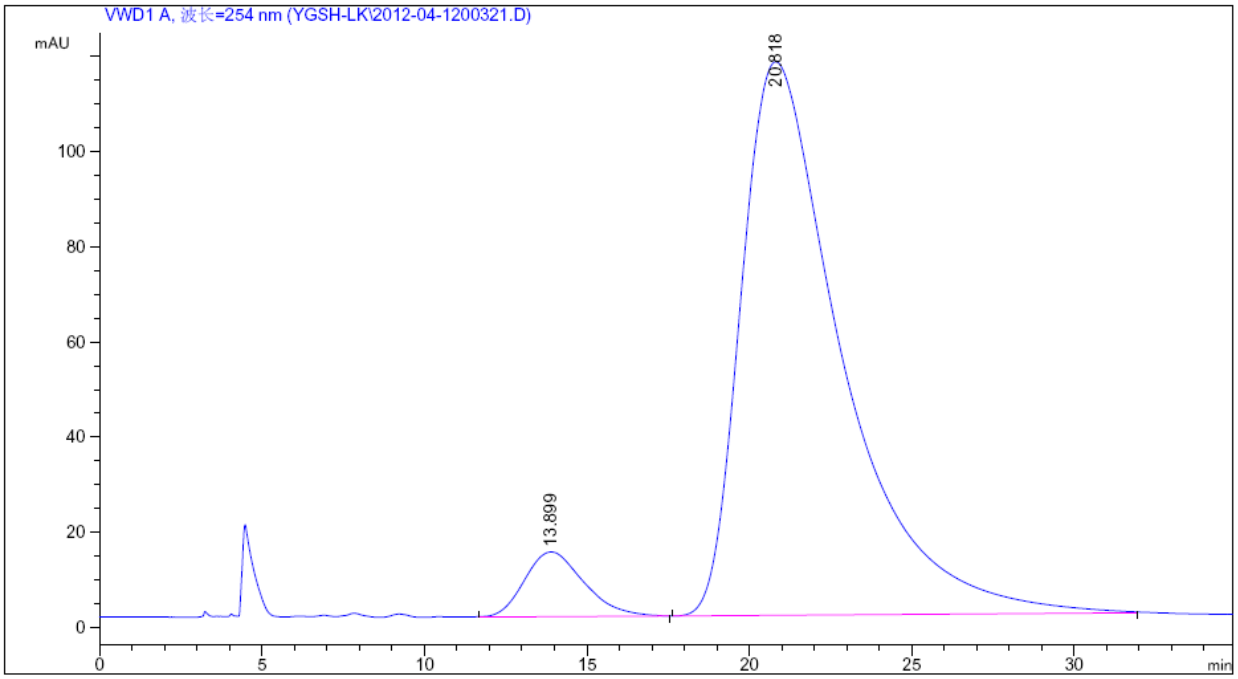
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	13.988	BV	1.9293	2.90185e4	230.42549	50.3570
2	21.039	VB	3.1559	2.86070e4	133.30702	49.6430

Racemic



8h

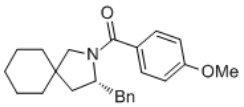
OJ-H, hexane/2-propanol 20:1, 1mL/min



Area Percent Report

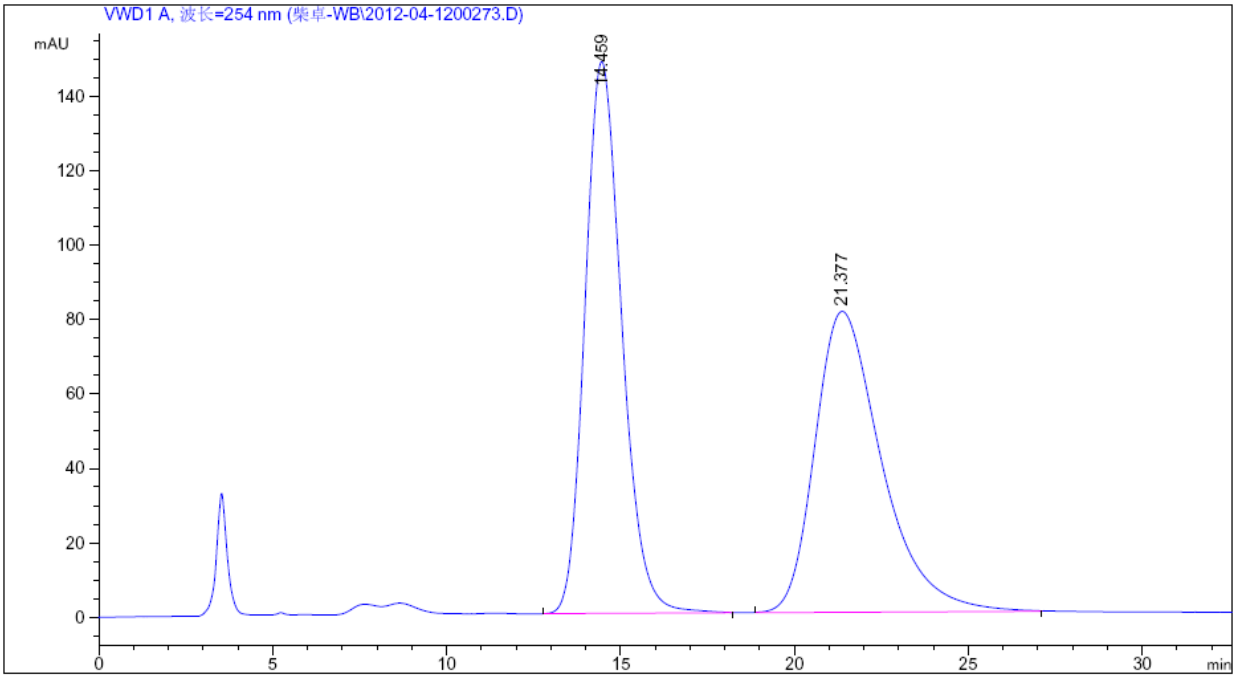
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	13.899	BB	1.9178	1725.95386	13.59606	6.4358
2	20.818	BB	3.1919	2.50922e4	116.33624	93.5642

Table 2, entry 8



8h

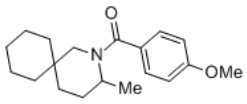
OJ-H, hexane/2-propanol 20:1, 1mL/min



Area Percent Report

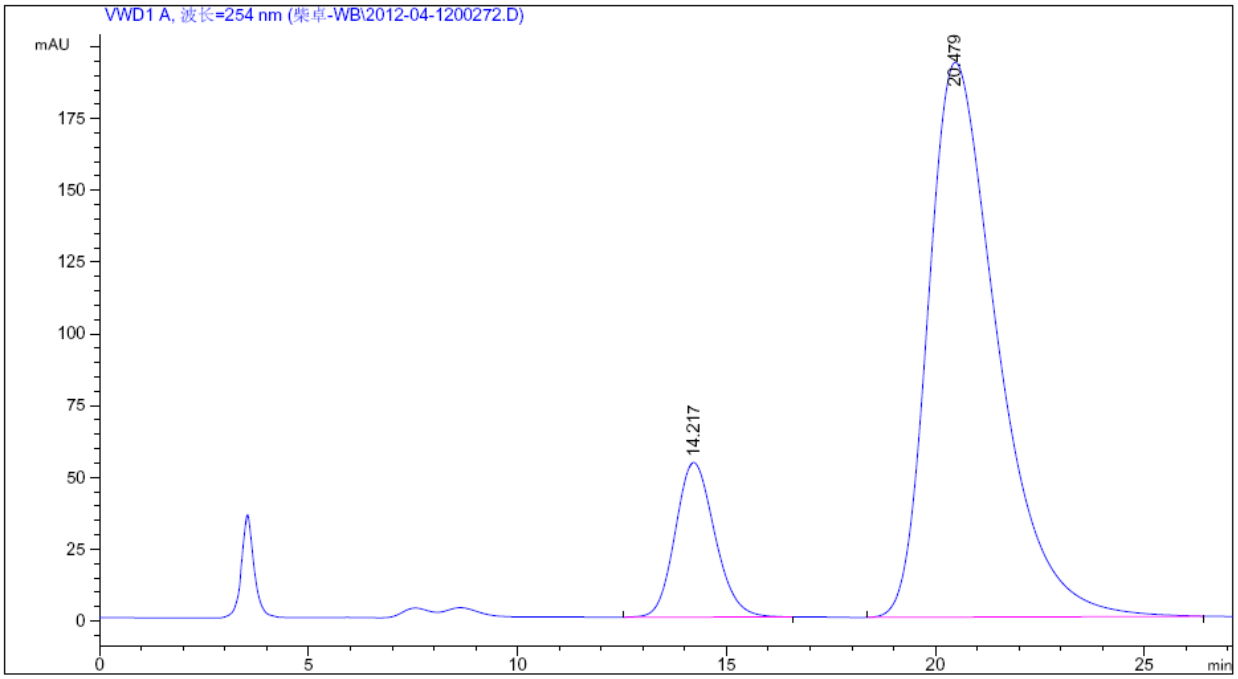
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	14.459	BB	1.1399	1.09270e4	148.16748	50.3524
2	21.377	BB	2.0271	1.07740e4	80.81483	49.6476

Racemic



8i

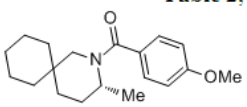
AS-H, hexane/2-propanol 3:1, 1mL/min



Area Percent Report

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	High [mAU]	Area %
1	14.217	BB	1.0178	3544.26807	53.88427	13.7388
2	20.479	BB	1.7509	2.22533e4	193.28035	86.2612

Table 2, entry 9



8i

AS-H, hexane/2-propanol 3:1, 1mL/min