New P,N_{sp3} ligands for palladium-catalyzed asymmetric allylic substitutions

Qin Su[a], Chuan-Jin Hou[*,a], De-Quan Wei[a,b], Hao Qin[a], Ding-Hua Liang[a], Xiang-Ping Hu[*,b]

[a] *School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China*

[b] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

*Corresponding authors

E-mail: houcj@dlpu.edu.cn (C.-J. Hou); xiangping@dicp.ac.cn (X.-P. Hu)

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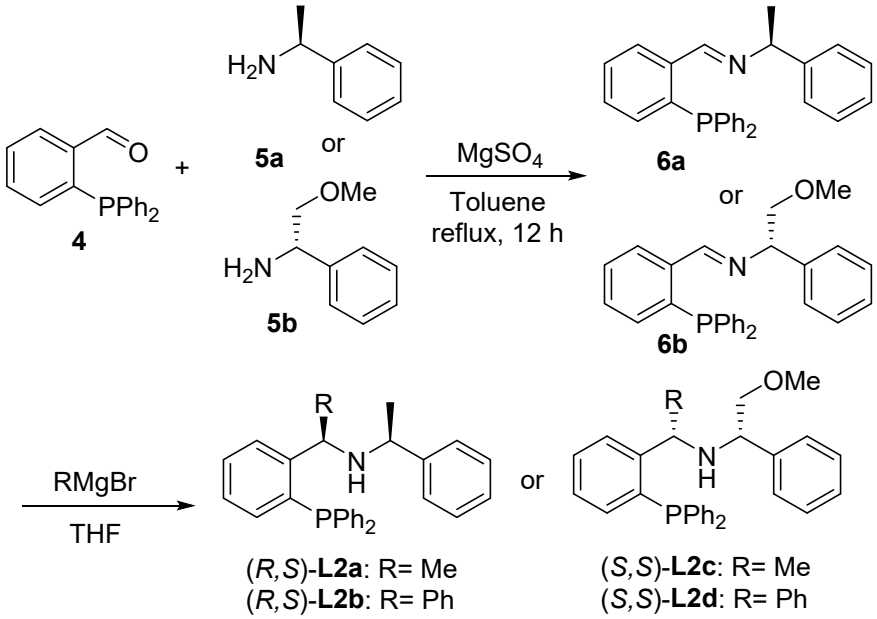
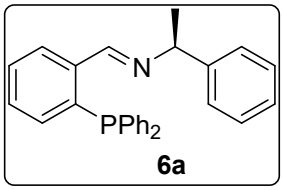
General Information

All reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash chromatography was performed on silica gel 60 (40-63μm, 60Å). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual proton in the deuterated NMR solvent ($CDCl_3$ = δ 7.26 or DMSO = δ 2.50). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 100 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.02). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Only the most important and relevant frequencies are reported. Enantiomeric ratios were determined by chiral HPLC with *n*-hexane and *i*-PrOH as solvents.

Preparation of P,N_{sp3} Ligands



To an oven-dried reaction flask equipped with a magnetic stir bar was charged with 2-(Diphenylphosphino)benzaldehyde **4** (1.45 g, 5.0 mmol), (*S*)-phenylethylamine derivatives **5** (5.0 mol), anhydrous $MgSO_4$ (1.0 g) and anhydrous toluene (10 mL) under nitrogen atmosphere. The mixture was heated and refluxed for 12 h. After cooling to room temperature, $MgSO_4$ was filtered out. The solvent was removed under reduced pressure to give the Schiff base product **6**, which was dissolved in anhydrous THF (20 mL). Grignard reagent was added dropwise to the solution at 0 °C. The mixture was stirred for 5 hours. The unreacted Grignard reagent was quenched by the saturated NaCl aqueous solution. The aqueous phase was extracted with Et_2O and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give the desired ligands **L2a-d**.

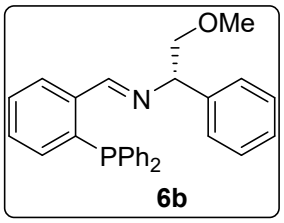


6a

(*S*)-**6a** was obtained in 90% yield as viscous liquid after purification with column chromatography on silica gel (hexane/ethyl acetate/triethylamine, 100/10/5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 4.8 Hz, 1H), 8.05-7.95 (m, 1H), 7.38-7.18 (m,

17H), 6.93-6.77 (m, 1H), 4.40 (q, J = 6.6 Hz, 1H), 1.34 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, J = 20.3 Hz), 141.8, 139.7, 139.5, 137.6, 137.4, 136.8, 136.7, 136.6, 136.5, 134.3, 134.2, 134.1, 134.0, 133.2, 130.2, 128.9, 128.8, 128.7, 128.5, 128.5, 128.4, 128.2, 128.1, 126.7, 69.8, 24.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ -13.08. HRMS $[M+H]^+$ calcd. for $C_{27}H_{25}NP^+$: 394.1719, found: 394.1724.

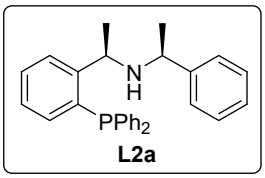
(*S*)-**6b** was obtained in 85% yield as viscous liquid after purification with column



6b

chromatography on silica gel (hexane/ethyl acetate/triethylamine, 100/50/3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 4.5 Hz, 1H), 8.00-7.89 (m, 1H), 7.34-7.12 (m, 17H), 6.85-6.72 (m, 1H), 4.38 (dd, J = 7.8, 4.7 Hz, 1H), 3.46 (dd, J = 9.7, 4.6 Hz, 1H), 3.37 (t, J = 9.0 Hz, 1H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 159. 9 (d, J = 15.9 Hz), 141.2, 139.3, 139.2, 137.6, 137.4, 137.3, 137.2, 134.2, 134.0, 133.9, 133.7, 133.6, 130.9, 129.4, 129.3, 129.2, 129.1, 128.6, 127.8, 127.5, 77.0, 740, 58.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ -12.73. HRMS $[M+H]^+$ calcd. for $C_{28}H_{27}NOP^+$: 424.1825, found: 424.1824.

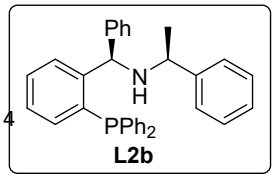
(*R,S*)-**L2a** was obtained in 75% yield as viscous liquid after purification with column



L2a

chromatography on silica gel (hexane/ethyl acetate, 10/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.6, 4.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.32- 7.28 (m, 3H), 7.27-7.21 (m, 4H), 7.21-7.12 (m, 7H), 7.11-7.08 (m, 2H), 6.94 (dd, J = 7.6, 4.2 Hz, 1H), 4.53 (p, J = 6.7 Hz, 1H), 3.48 (q, J = 6.6 Hz, 1H), 1.16 (d, J = 6.7 Hz, 3H), 1.12 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 151.1, 146.2, 137.7, 137.6, 137.4, 137.3, 135.0, 134.9, 134.5, 134.0, 133.9, 133.8, 133.7, 129.6, 128.6, 128.5, 128.4, 126.9, 126.7, 126.6, 126.5, 126.4, 55.8, 53.25 (d, J = 24.4 Hz), 24.8 (d, J = 1.8 Hz), 24.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ -19.19. HRMS $[M+H]^+$ calcd. for $C_{28}H_{29}NP^+$: 410.2032, found: 410.2034.

(*R,S*)-**L2b** was obtained in 70% yield as viscous liquid after purification with column

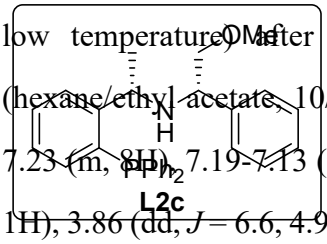


L2b

chromatography on silica gel (hexane/ethyl acetate, 10/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.7, 4.4 Hz, 1H), 7.37

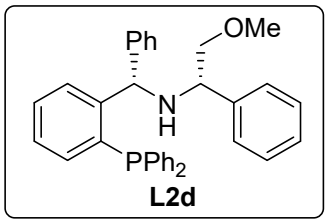
(t, J = 7.5 Hz, 1H), 7.33-7.28 (m, 3H), 7.27-7.18 (m, 6H), 7.18-7.10 (m, 8H), 7.10-7.02 (m, 3H), 7.026.93 (m, 3H), 5.70 (d, J = 7.3 Hz, 1H), 3.64 (q, J = 6.6 Hz, 1H), 1.22 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 143.6, 137.6, 137.0, 135.7, 135.1, 133.8, 133.7, 133.6, 133.5, 129.3, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.1, 126.7, 126.6, 126.5, 61.4 (d, J = 23.1 Hz), 55.5, 23.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ -18.79. HRMS $[M+H]^+$ calcd. for $C_{33}H_{31}NP^+$: 472.2189, found: 472.2187.

(*S,S*)-**L2c** was obtained in 68% yield as viscous liquid (converted into white solid at low temperature) after purification with column chromatography on silica gel (hexane/ethyl acetate, 10/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 1H), 7.34-7.23 (m, 8H), 7.19-7.13 (m, 8H), 7.06-7.01 (m, 1H), 6.82-6.76 (m, 1H), 4.78-4.65 (m, 1H), 3.86 (dd, J = 6.6, 4.9 Hz, 1H), 3.45-3.36 (m, 2H), 3.28 (s, 3H), 1.16 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.7, 141.6, 141.6, 137.6, 137.5, 137.2, 137.1, 134.6, 134.5, 134.3, 134.1, 133.9, 133.7, 133.5, 129.3, 128.7, 128.6, 128.5, 128.4, 128.1, 127.8, 127.0, 126.8, 126.6, 126.5, 76.6, 60.2, 59.0, 52.7(d, J = 26.0 Hz), 23.5.^{31}P NMR (162 MHz, $CDCl_3$): δ -17.48. HRMS $[M+Na]^+$ calcd. for $C_{29}H_{31}NOP^+$: 440.2138, found:440.2135.



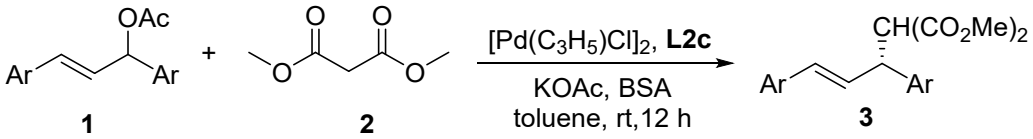
L2c

(*S,S*)-**L2d** was obtained in 65% yield as white solid after purification with column chromatography on silica gel (hexane/ethyl acetate, 10/1). Mp:63-65 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 7.6, 4.4 Hz, 1H), 7.26-7.22 (m, 3H), 7.19-7.10 (m, 8H), 7.10-7.04 (m, 7H), 7.03-6.90 (m, 4H), 6.78 (dd, J = 7.5, 3.9 Hz, 1H), 5.63 (d, J = 7.6 Hz, 1H), 5.19 (s, 1H), 3.76 (t, J = 6.0 Hz, 1H), 3.36 (d, J = 6.1 Hz, 2H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 149.0, 143.0, 140.7, 137.7, 137.6, 137.3, 137.2, 135.1, 135.0, 134.4, 134.1, 133.9, 133.8, 133.6, 123.3，133.8, 133.7, 133.5, 129.4, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.2, 127.0, 126.6, 77.0, 60.6 (d, J = 24.4 Hz), 59.7, 58.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ -17.33. HRMS $[M+H]^+$ calcd. for $C_{34}H_{33}NOP^+$: 502.2294, found: 502.2277.



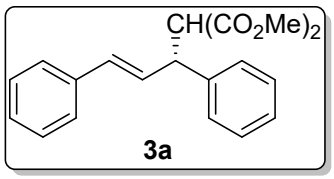
L2d

General Procedure for Pd-Catalyzed Asymmetric Allylic Alkylation

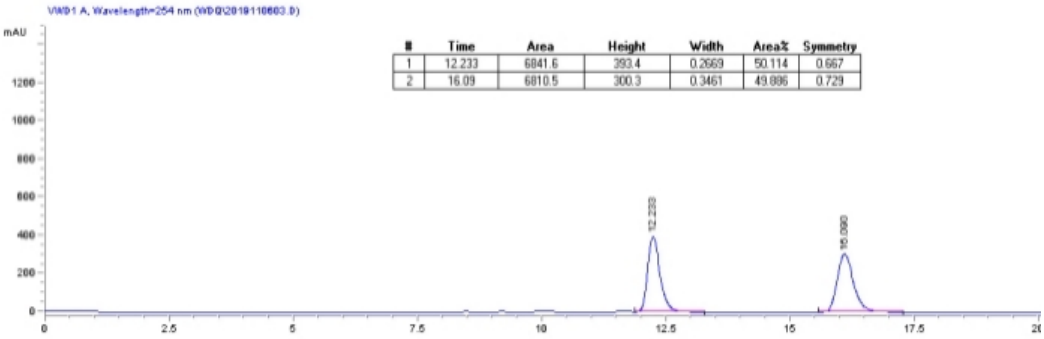


A solution of ligand (*S*,*S*)-**L2c** (2 mol%) and $[Pd(C_3H_5)Cl]_2$ (5 mol%) were dissolved in toluene (1.0 mL) in a Schlenk tube under an N_2 atmosphere. After 1 h of stirring at room temperature, allylic acetate **1** (0.5 mmol), *N*,*O*-bis(trimethylsilyl)-acetamide (1.5 mmol), KOAc (catalytic amount) and toluene (2 mL) were added. The mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography.

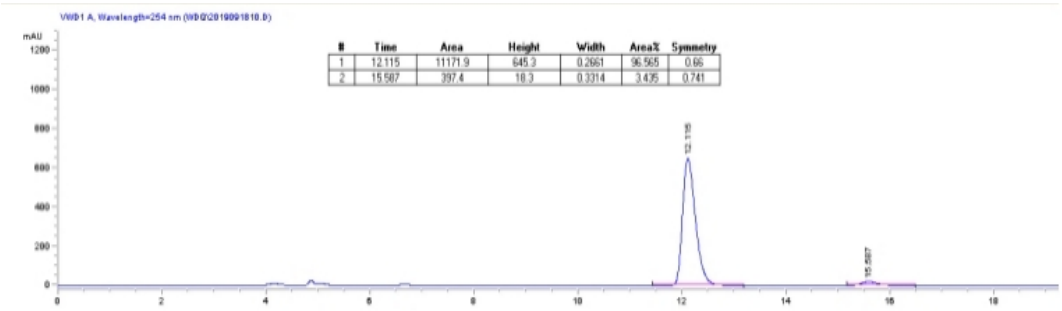
Dimethyl 2-((*R*,*E*)-1,3-diphenylallyl)malonate (3a).[1] Colorless oil was obtained in



98% yield. 93% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 12.1 min, t_R (minor) = 15.6 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 6H), 7.28-7.24 (m, 2H), 7.23-7.16 (m, 2H), 6.48 (d, J = 15.8 Hz, 1H), 6.33 (dd, J = 15.8, 8.7 Hz, 1H), 4.27 (dd, J = 10.9, 8.7 Hz, 1H), 3.96 (d, J = 10.9 Hz, 1H), 3.69 (s, 3H), 3.51 (s, 3H).

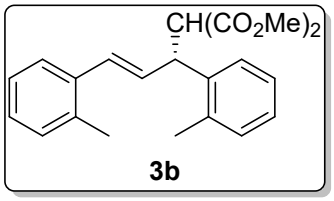


#	Time	Area	Height	Width	Area%	Symmetry
1	12.233	6841.6	393.4	0.2669	50.114	0.667
2	16.09	6810.5	300.3	0.3461	49.886	0.729

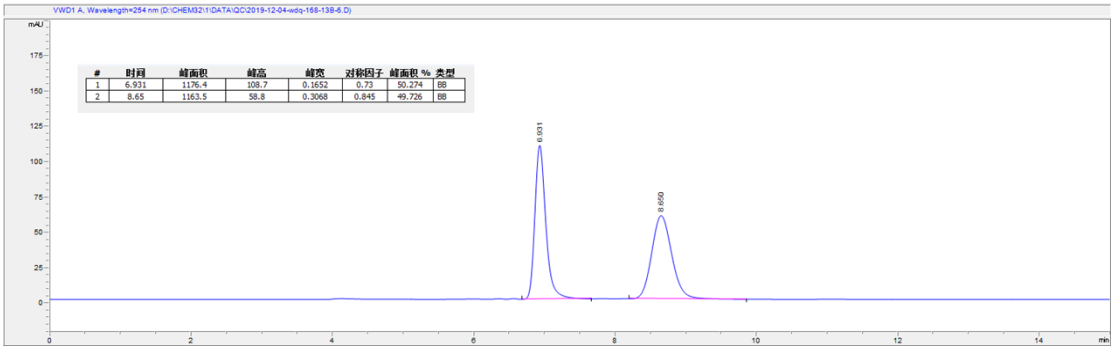


#	Time	Area	Height	Width	Area%	Symmetry
1	12.115	11171.9	645.3	0.2661	96.565	0.66
2	15.587	397.4	18.3	0.3314	3.435	0.741

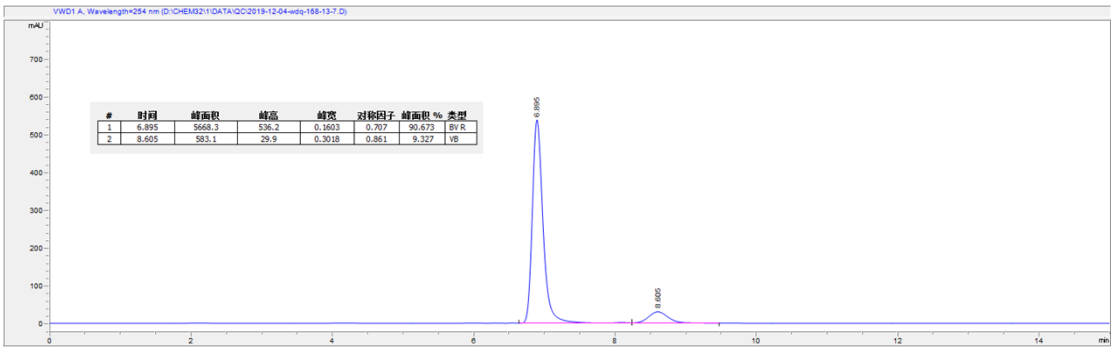
Dimethyl 2-((*R*,*E*)-1,3-di-o-tolylallyl)malonate (3b).[2] Colorless oil was obtained in



96% yield. 81% ee was determined by chiral HPLC (Chiralcel OD-H *n*-hexane/*i*-PrOH = 95/5,0.8 mL/min , 254 nm, 40 °C) : t_R(major) = 6.9 min , t_R(minor) = 8.6 min. ^{1}H NMR ($CDCl_3$) δ 7.32-7.27 (m, 1H), 7.25-7.21 (m, 1H), 7.20-7.14 (m, 2H), 7.14-7.06 (m, 4H), 6.65 (d, *J* = 15.5 Hz, 1H), 6.01 (dd, *J* = 15.5, 8.7 Hz, 1H), 4.56 (dd, *J* = 11.3, 8.7 Hz, 1H), 4.06 (d, *J* = 11.3 Hz, 1H), 3.73 (s, 3H), 3.51 (s, 3H), 2.47 (s, 3H), 2.27 (s, 3H).

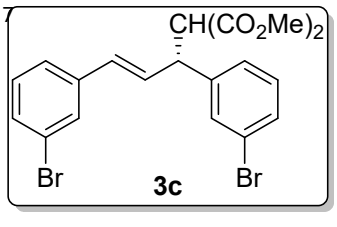


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.931	1176.4	108.7	0.1652	0.73	50.274	BB
2	8.65	1163.5	58.8	0.3068	0.845	49.726	BB

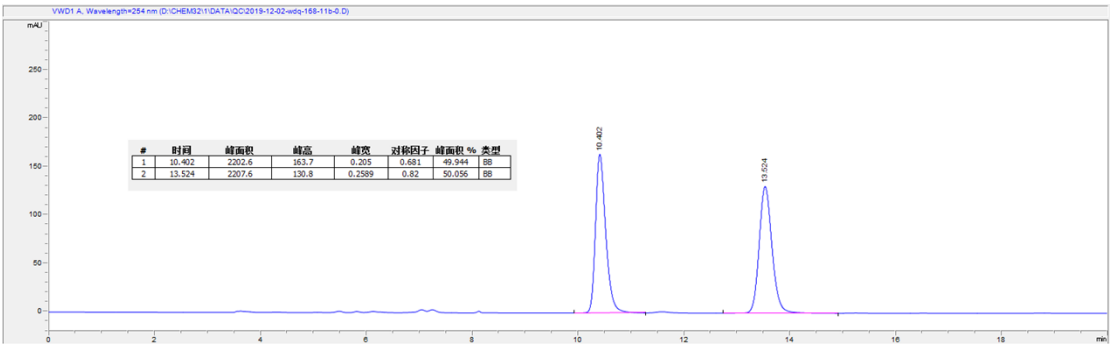


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.895	5668.3	536.2	0.1603	0.707	90.673	BV R
2	8.605	583.1	29.9	0.3018	0.861	9.327	VB

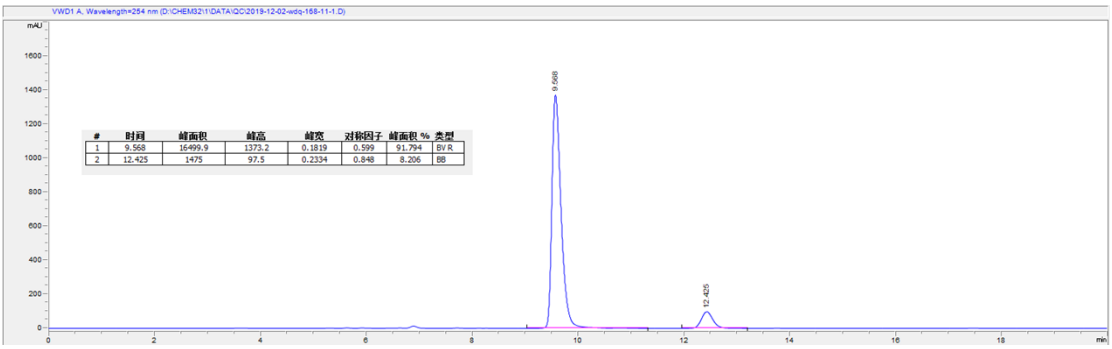
Dimethyl 2-((*R*,*E*)-1,3-bis(3-bromophenyl)allyl)malonate (3c).[3] Colorless oil was



obtained in 94% yield. 84% ee was determined by chiral HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.6 min, t_R (minor) = 12.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 12.7 Hz, 2H), 7.40-7.32 (m, 2H), 7.28-7.18 (m, 3H), 7.18-7.12 (m, 1H), 6.41 (d, J = 15.8 Hz, 1H), 6.29 (dd, J = 15.8, 8.4 Hz, 1H), 4.23 (t, J = 9.6 Hz, 2H), 3.91 (d, J = 10.8 Hz, 1H), 3.71 (s, 3H), 3.57 (s, 3H).

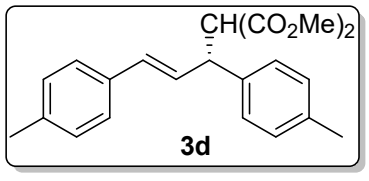


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.402	2202.6	163.7	0.205	0.681	49.944	BB
2	13.524	2207.6	130.8	0.2589	0.82	50.056	BB

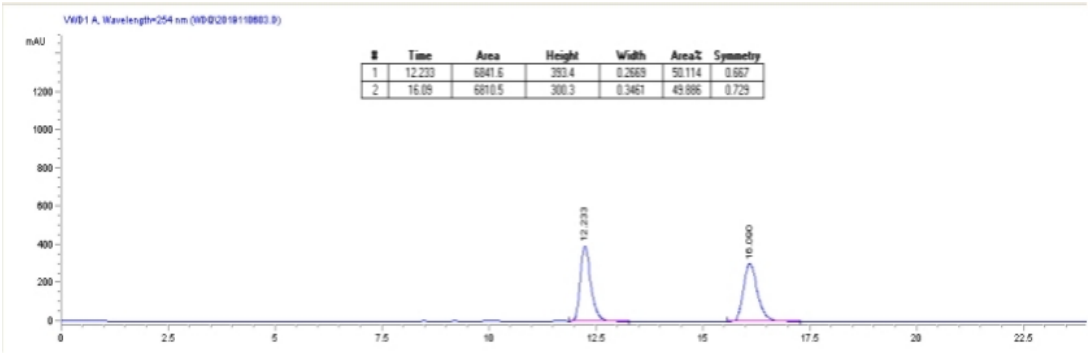


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.568	16499.9	1373.2	0.1819	0.599	91.794	BV R
2	12.425	1475	97.5	0.2334	0.848	8.206	BB

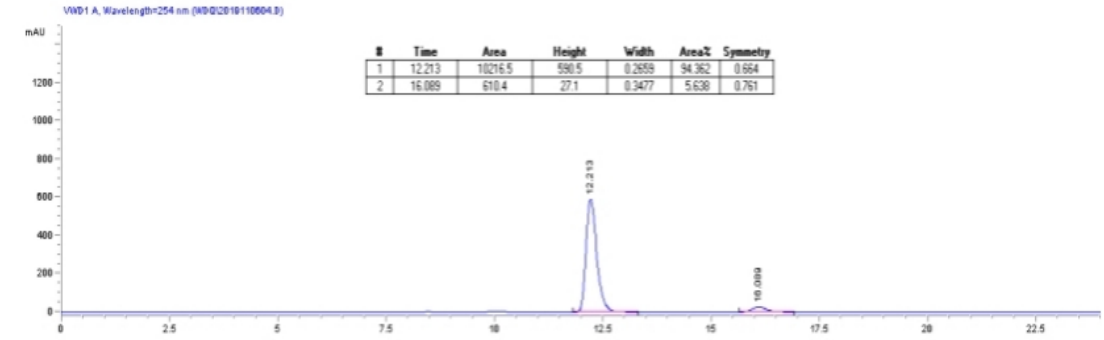
Dimethyl 2-((*R*,*E*)-1,3-dip-tolylallyl)malonate (3d).[1] Colorless oil was obtained in



96% yield. 89% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 254 nm, 40 °C): t_R (major) =12.2 min, t_R (minor) = 16.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.07 (m, 4H), 7.03 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H), 6.35 (d, J = 15.7 Hz, 1H), 6.18 (dd, J = 15.7, 8.6 Hz, 1H), 4.14 (dd, J = 10.9, 8.6 Hz, 1H), 3.85 (d, J = 10.9 Hz, 1H), 3.61 (s, 3H), 3.45 (s, 3H), 2.23 (s, 6H).

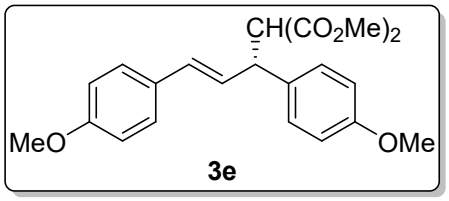


#	Time	Area	Height	Width	Area%	Symmetry
1	12.233	6841.6	393.4	0.2669	50.114	0.667
2	16.09	6810.5	300.3	0.3461	49.886	0.729

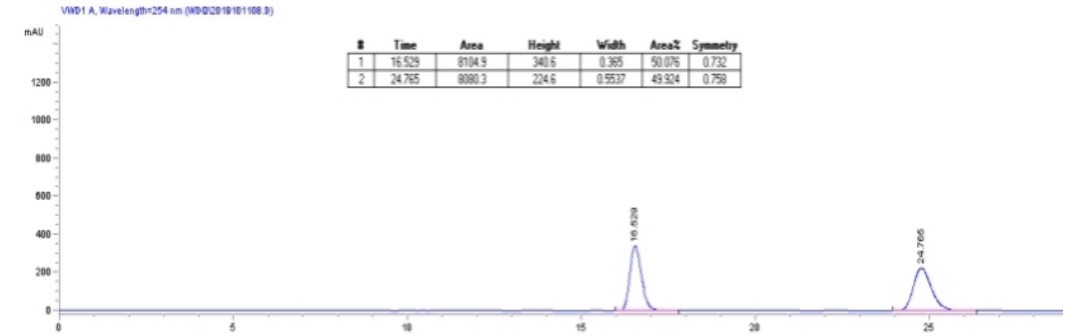


#	Time	Area	Height	Width	Area%	Symmetry
1	12.213	10216.5	590.5	0.2659	94.362	0.664
2	16.089	610.4	27.1	0.3477	5.638	0.761

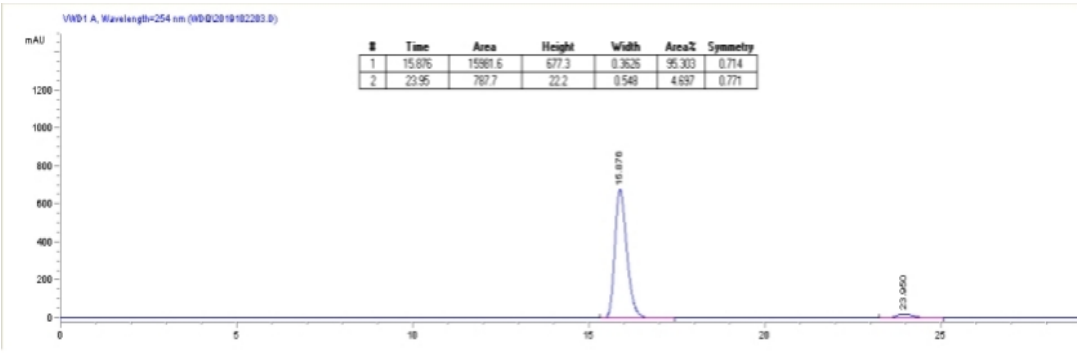
Dimethyl 2-((*R,E*)-1,3-bis(4-methoxyphenyl)allyl)malonate (3e).[1] Colorless oil was



obtained in 88% yield. 91% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 15.9 min, t_R (minor) = 24.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 6.39 (d, J = 15.7 Hz, 1H), 6.16 (dd, J = 15.7, 8.5 Hz, 1H), 4.19 (dd, J = 10.9, 8.5 Hz, 1H), 3.89 (d, J = 10.9 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.52 (s, 3H).

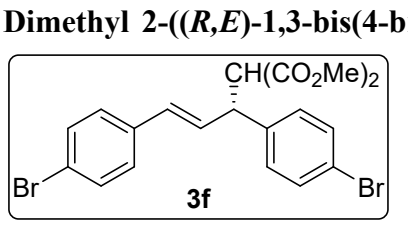


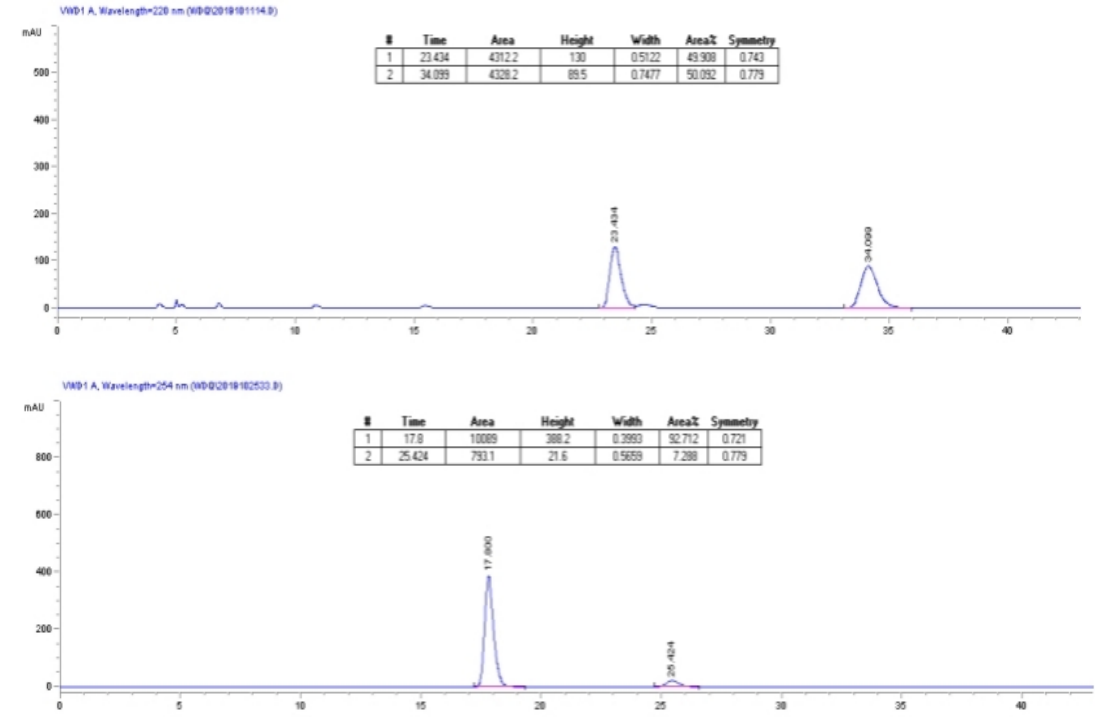
#	Time	Area	Height	Width	Area%	Symmetry
1	15.529	8104.9	340.6	0.365	50.076	0.732
2	24.765	8080.3	224.6	0.5537	49.924	0.758



#	Time	Area	Height	Width	Area%	Symmetry
1	15.876	15981.6	677.3	0.3625	95.303	0.714
2	23.95	787.7	22.2	0.548	4.697	0.771

Dimethyl 2-((*R*,*E*)-1,3-bis(4-bromophenyl)allyl)malonate (3f).[1] Colorless oil was obtained in 81% yield. 85% ee was determined by chiral HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 17.8 min, t_R (minor) = 25.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.1 Hz, 4H), 6.31 (d, J = 15.7 Hz, 1H), 6.20 (dd, J = 15.7, 8.3 Hz, 1H), 4.15 (dd, J = 10.8, 8.3 Hz, 1H), 3.82 (d, J = 10.8 Hz, 1H), 3.62 (s, 3H), 3.47 (s, 3H).

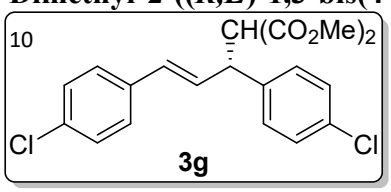




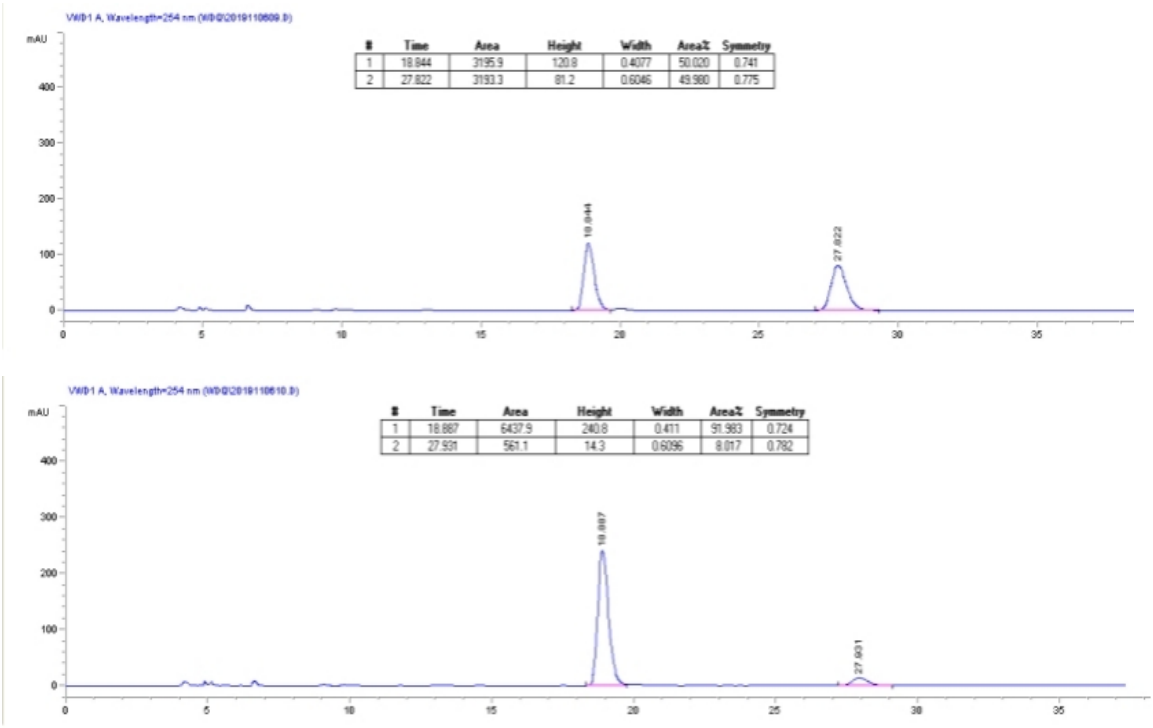
#	Time	Area	Height	Width	Area%	Symmetry
1	23.434	4312.2	130	0.5122	49.908	0.743
2	34.099	4328.2	89.5	0.7477	50.092	0.779

#	Time	Area	Height	Width	Area%	Symmetry
1	17.8	10089	388.2	0.3993	92.712	0.721
2	25.424	793.1	21.6	0.5659	7.288	0.779

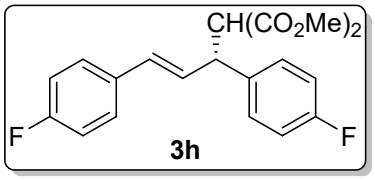
Dimethyl 2-((*R*,*E*)-1,3-bis(4-chlorophenyl)allyl)malonate (3g).[1] Colorless oil was



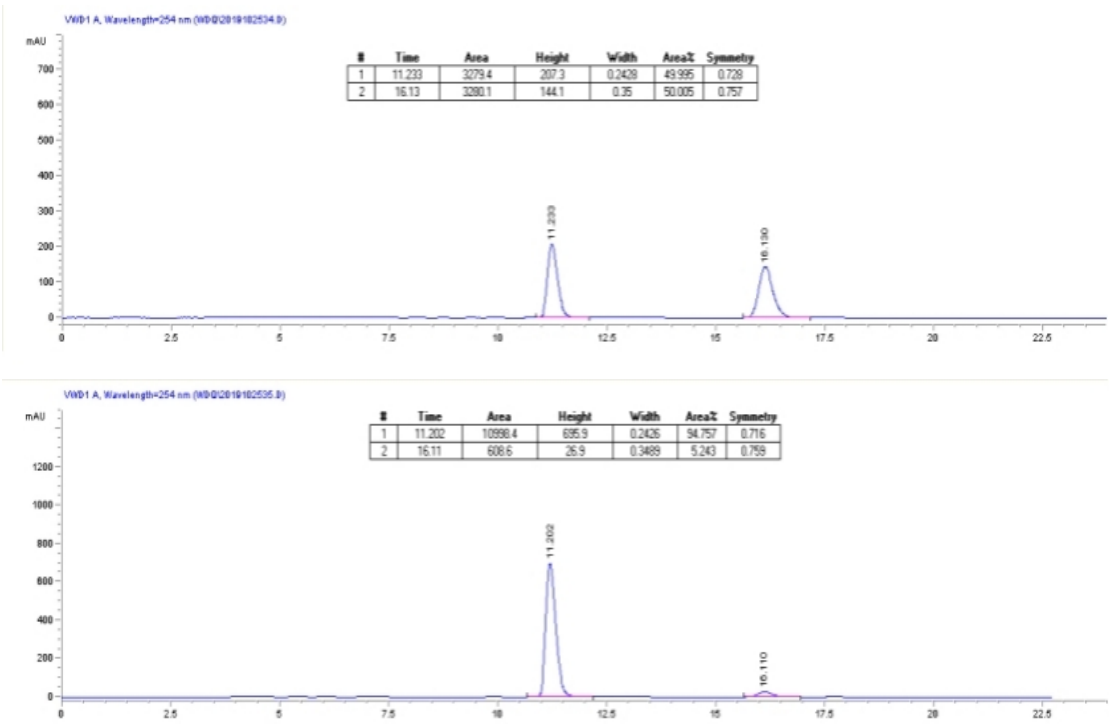
obtained in 92% yield. 84% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C): t_R (major) =18.9 min, t_R (minor) = 27.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.26-7.19 (m, 6H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.27 (dd, *J* = 15.7, 8.4 Hz, 1H), 4.24 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.90 (d, *J* = 10.7 Hz, 1H), 3.70 (s, 3H), 3.55 (s, 3H).



Dimethyl 2-((*R*,*E*)-1,3-bis(4-fluorophenyl)allyl)malonate (3h).[1] Colorless oil was



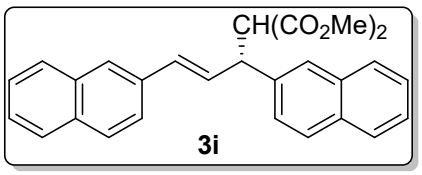
obtained in 98% yield. 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 254 nm, 40 °C): t_R (major) =11.2 min, t_R (minor) = 16.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.23 (m, 4H), 7.05-6.92 (m, 4H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.7, 8.5 Hz, 1H), 4.25 (dd, *J* = 10.8, 8.5 Hz, 1H), 3.89 (d, *J* = 10.8 Hz, 1H), 3.71 (s, 3H), 3.53 (s, 3H).



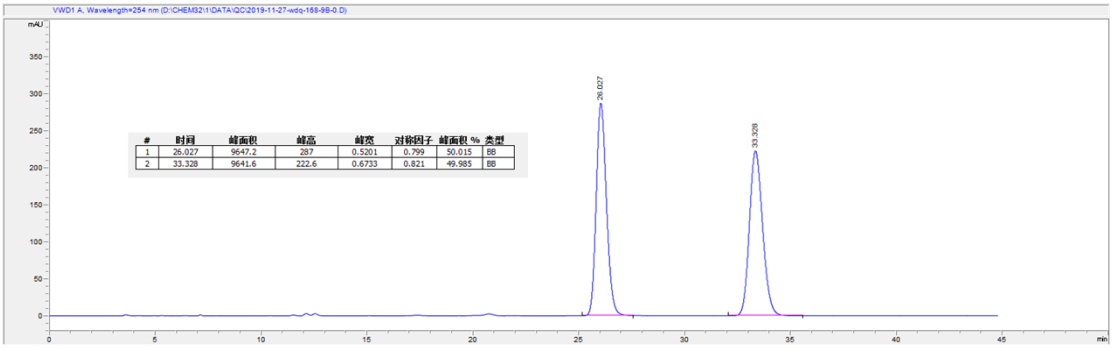
#	Time	Area	Height	Width	Area%	Symmetry
1	11.233	3279.4	207.3	0.2428	49.995	0.728
2	16.13	3280.1	144.1	0.35	50.005	0.757

#	Time	Area	Height	Width	Area%	Symmetry
1	11.202	10998.4	695.9	0.2426	94.757	0.716
2	16.11	608.6	26.9	0.3489	5.243	0.759

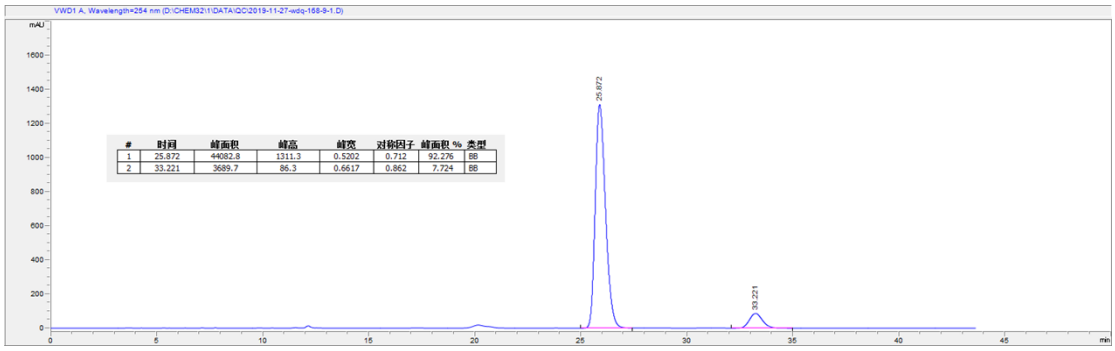
Dimethyl 2-((*R*,*E*)-1,3-di(naphthalen-2-yl)allyl)malonate (3i).[4] Colorless oil was



obtained in 76% yield. 85% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C); t_R (major)=25.9 min, t_R (minor) =33.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (m, 3H), 7.71-7.68 (m, 2H), 7.67-7.62 (m, 2H), 7.59 (s, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.41-7.36 (m, 3H), 7.36-7.29 (m, 2H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.46 (dd, *J* = 15.7, 8.4 Hz, 1H), 4.43 (dd, *J* = 10.9, 8.4 Hz, 1H), 4.05 (d, *J* = 10.9 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 3H).

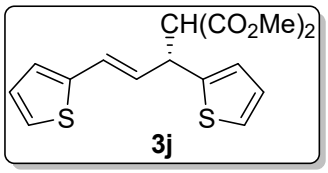


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	26.027	9647.2	287	0.5201	0.799	50.015	BB
2	33.328	9641.6	222.6	0.6733	0.821	49.985	BB

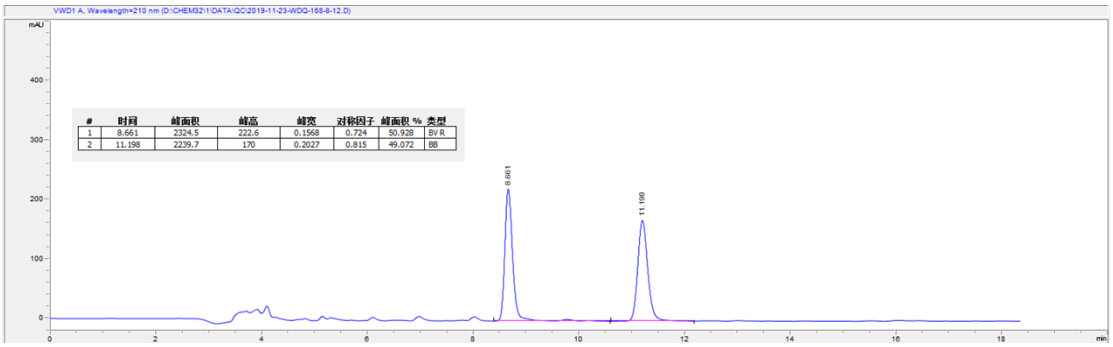


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	25.872	44082.8	1311.3	0.5202	0.712	92.276	BB
2	33.221	3689.7	86.3	0.6617	0.862	7.724	BB

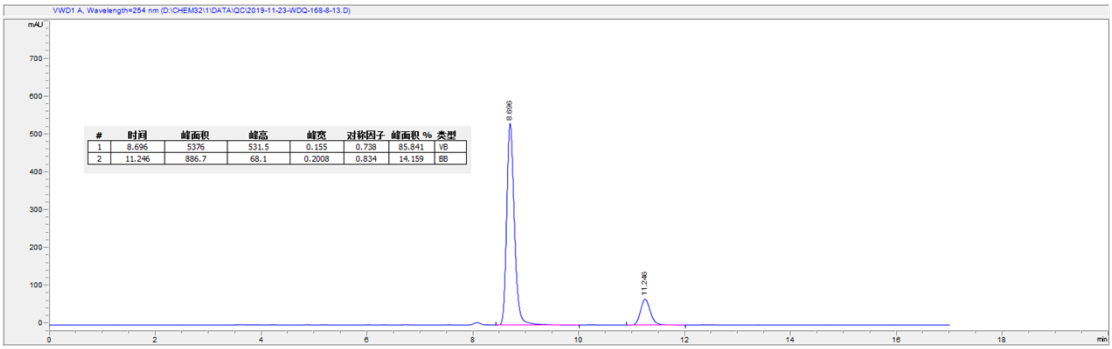
Dimethyl 2-((*R*,*E*)-1,3-di(thiophen-2-yl)allyl)malonate (3j). Colorless oil was



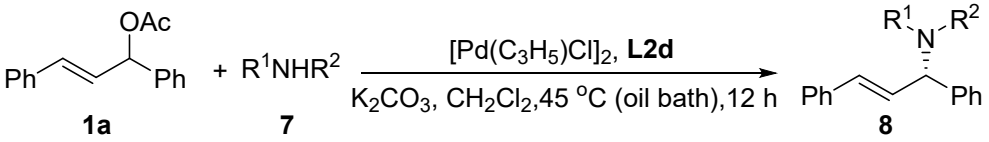
obtained in 90% yield. 72% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 85/15, 0.8 mL/min, 254 nm, 40 °C): t_R (major) =8.7 min, t_R (minor) = 11.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 4.9 Hz, 1H), 7.15-7.11 (m, 1H), 6.98-6.87 (m, 4H), 6.63 (d, J = 15.5 Hz, 1H), 6.17 (dd, J = 15.5, 8.8 Hz, 1H), 4.53 (t, J = 9.4 Hz, 1H), 3.89 (d, J = 10.1 Hz, 1H), 3.71 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.6, 143.2, 141.5, 127.8, 127.4, 126.9, 126.1, 125.5, 124.9, 124.6, 124.5, 58.5, 52.8, 52.7, 44.1. HRMS $[M+Na]^+$ calcd. for $C_{16}H_{16}NaO_4S_2^+$: 359.0382, found: 359.0378.



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.661	2324.5	222.6	0.1568	0.724	50.928	BV R
2	11.198	2239.7	170	0.2027	0.815	49.072	BB

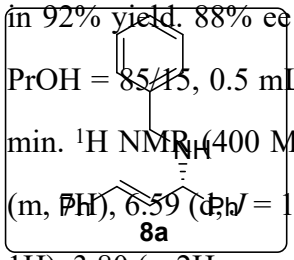


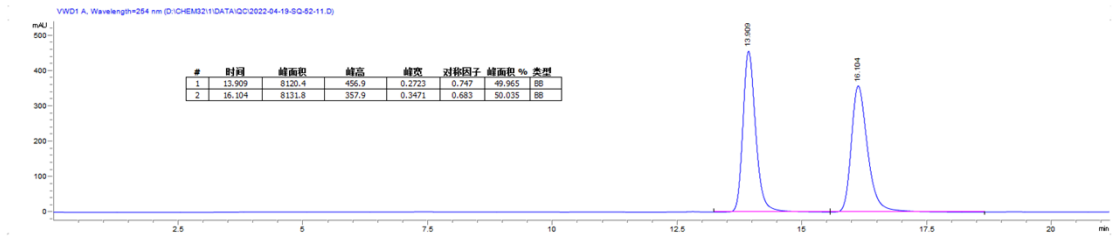
General Procedure for Pd-Catalyzed Asymmetric Allylic Amination



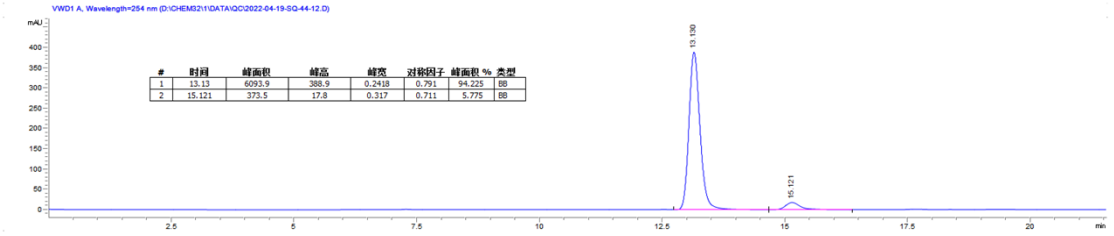
Ligand (*S,S*)-**L2d** (0.012 mmol) and $[Pd(C_3H_5)Cl]_2$ (0.006 mmol) was dissolved in CH_2Cl_2 (1.0 mL) in a Schlenk tube under an N_2 atmosphere. After 1 h of stirring at room temperature, 1,3-phenyl-2-propenyl acetate **1a** (0.2 mmol), amines **7** (0.6 mmol), K_2CO_3 (1.0 mmol) and CH_2Cl_2 (2.0 mL) was added. The mixture was heated to 45 °C (oil bath) for 12 or 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the desired product **8**.

(*S*, *E*)-N-benzyl-1,3-diphenylprop-2-en-1-amine (8a).[1] Colorless oil was obtained in 92% yield. 88% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 85/15, 0.5 mL/min, 254 nm, 25 °C): t_R (major) = 13.1 min, t_R (minor) = 15.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2H), 7.38-7.33 (m, 6H), 7.30-7.25 (m, 2H), 6.59 (d, J = 15.9 Hz, 1H), 6.35 (dd, J = 15.9, 7.5 Hz, 1H), 4.42 (d, J = 7.5 Hz, 1H), 3.80 (s, 2H).



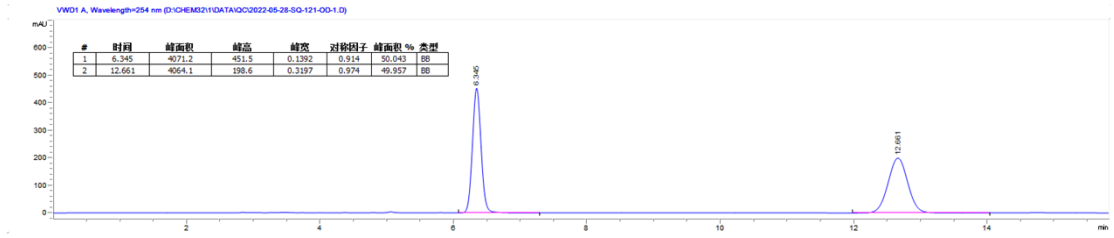


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.909	8120.4	456.9	0.2723	0.747	49.965	BB
2	16.104	8131.8	357.9	0.3471	0.683	50.035	BB

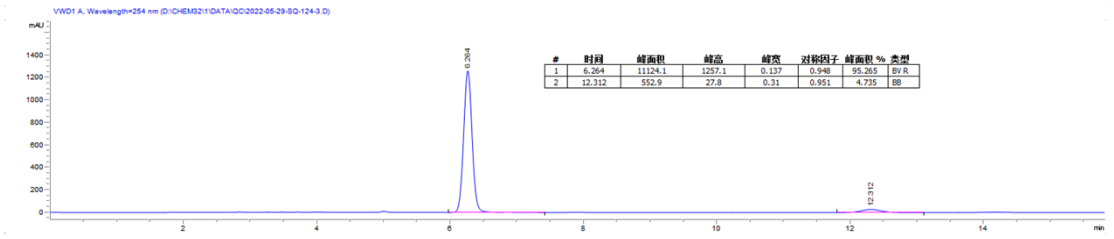


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.13	6093.9	388.9	0.2418	0.791	94.225	BB
2	15.121	373.5	17.8	0.317	0.711	5.775	BB

(*S*,*E*)-4-(1,3-Diphenylallyl)morpholine (8b).[1] Colorless oil was obtained in 93% yield. 91% ee was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm, 25 °C): t_R (major) = 6.3 min, t_R (minor) = 12.3 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 7.40-7.33 (m, 4H), 7.33-7.27 (m, 3H), 7.25-7.21 (m, 1H), 6.60 (d, J = 15.8 Hz, 1H), 6.31 (dd, J = 15.8, 8.9 Hz, 1H), 3.82 (d, J = 8.9 Hz, 1H), 3.78-3.64 (m, 4H), 2.65-2.51 (m, 2H), 2.48-2.36 (m, 2H).

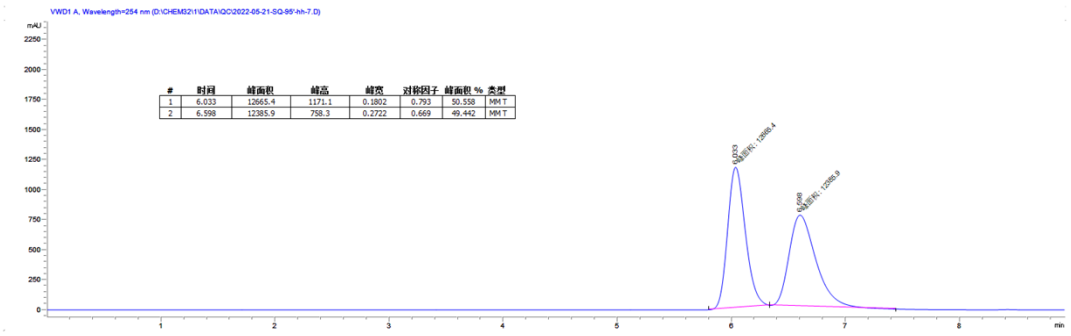


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.345	4071.2	451.5	0.1392	0.914	50.043	BB
2	12.661	4064.1	198.6	0.3197	0.974	49.957	BB

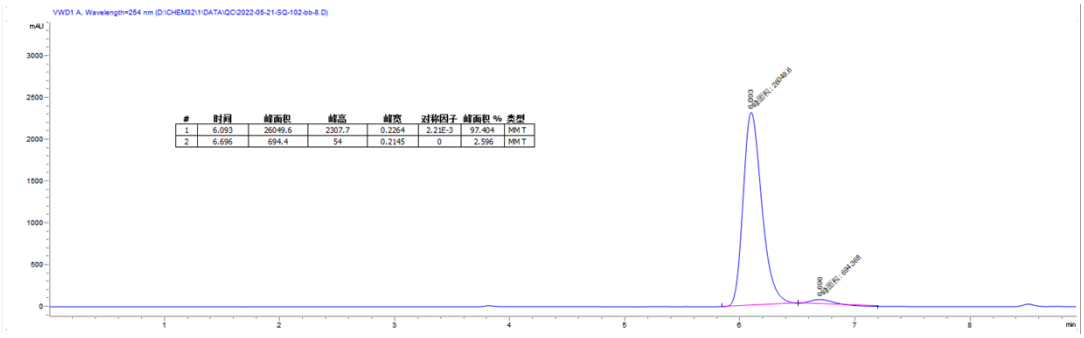


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.264	11124.1	1257.1	0.137	0.948	95.265	BV R
2	12.312	552.9	27.8	0.31	0.951	4.735	BB

(*S*,*E*)-1-(1,3-Diphenylallyl)Piperidine (8c).[5] Colorless oil was obtained in 96% yield. 95% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 97/3, 0.8 mL/min, 254 nm, 25 °C): t_R (major) = 6.1 min, t_R (minor) = 6.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.41 (m, 2H), 7.40-7.33 (m, 4H), 7.32-7.18 (m, 4H), 6.55 (d, J = 15.9 Hz, 1H), 6.38 (dd, J = 15.9, 8.6 Hz, 1H), 3.85 (d, J = 8.6 Hz, 1H), 2.65-2.30 (m, 4H), 1.69-1.55 (m, 4H), 1.51-1.40 (m, 2H).

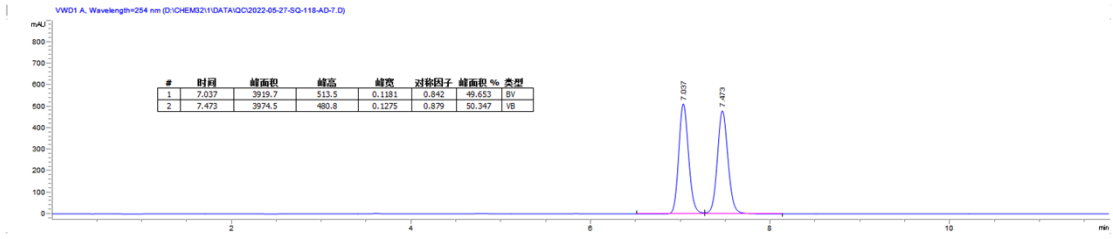


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.033	12665.4	1171.1	0.1802	0.793	50.558	MM T
2	6.598	12385.9	758.3	0.2722	0.669	49.442	MM T

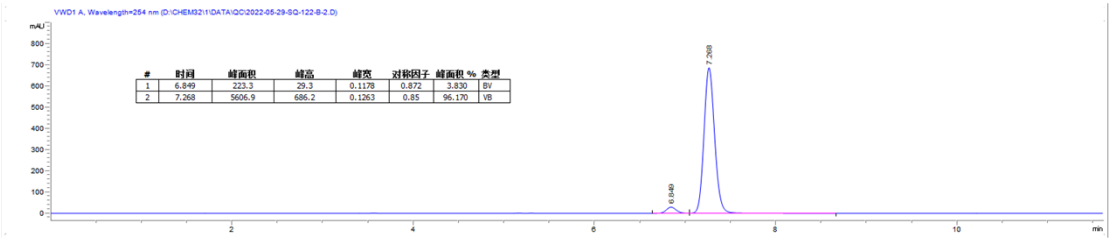


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.093	26049.6	2307.7	0.2264	2.21E-3	97.404	MM T
2	6.696	694.4	54	0.2145	0	2.596	MM T

(*S*,*E*)-1-(1,3-Diphenylallyl)pyrrolidine (8d).[1] Colorless oil was obtained in 98% yield. 92% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 25 °C): t_R (minor) = 6.8 min, t_R (major) = 7.3 min. ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.49-7.42 (m, 2H), 7.41-7.32 (m, 4H), 7.32-7.24 (m, 3H), 7.23-7.18 (m, 1H), 6.59 (d, J = 15.8 Hz, 1H), 6.45 (dd, J = 15.8, 8.6 Hz, 1H), 3.79 (d, J = 8.6 Hz, 1H), 2.65-2.53 (m, 2H), 2.52-2.39 (m, 2H), 1.88-1.74 (m, 4H).

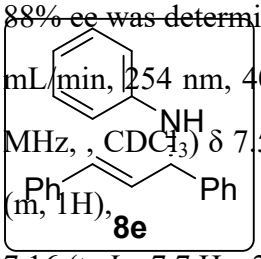


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.037	3919.7	513.5	0.1181	0.842	49.653	BV
2	7.473	3974.5	480.8	0.1275	0.879	50.347	VB



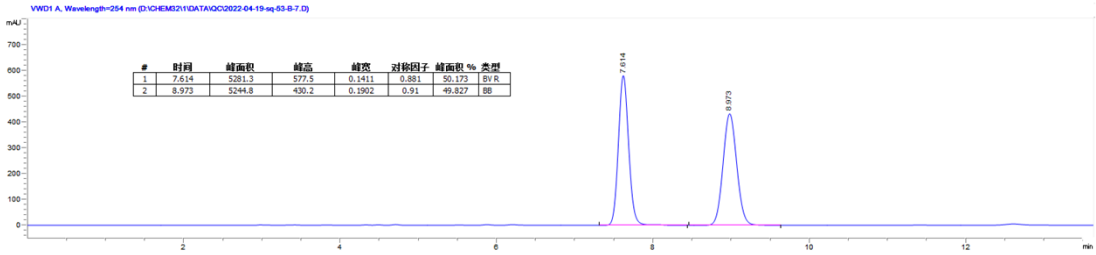
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.849	223.3	29.3	0.1178	0.872	3.830	BV
2	7.268	5606.9	686.2	0.1263	0.85	96.170	VB

(*S*,*E*)-*N*-(1,3-diphenylallyl)aniline (8e).[1] Colorless oil was obtained in 77% yield. 88% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm, 40 °C): t_R (minor) = 7.5 min, t_R (major) = 8.8 min. ^{1}H NMR (400 MHz, , $CDCl_3$) δ 7.50-7.42 (m, 2H), 7.42-7.35 (m, 4H), 7.34-7.28 (m, 3H), 7.26-7.23 (m, 1H),

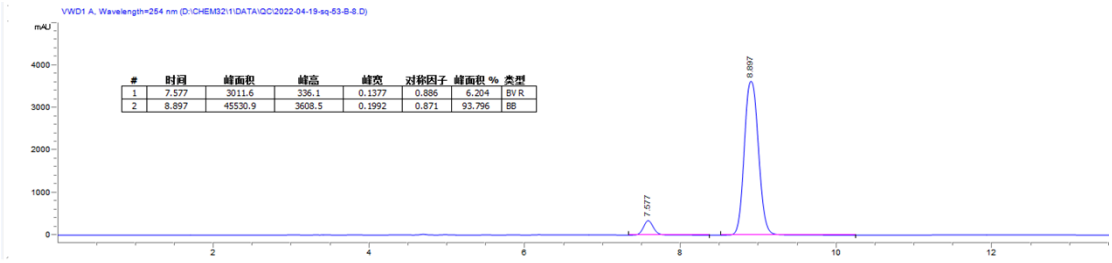


8e

7.16 (t, *J* = 7.7 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.70-6.59 (m, 3H), 6.42 (dd, *J* = 15.8, 6.1 Hz, 1H), 5.11 (d, *J* = 6.1 Hz, 1H), 4.18 (br, 1H).

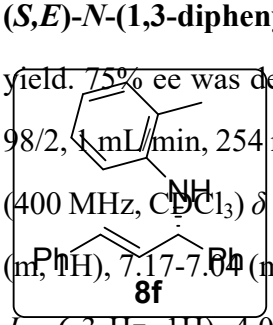


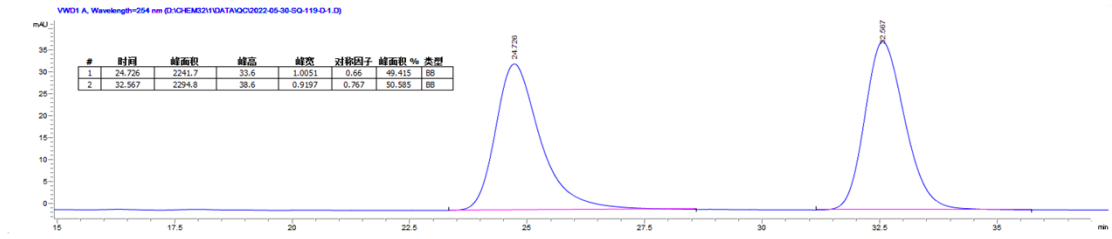
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.614	5281.3	577.5	0.1411	0.881	50.173	BV R
2	8.973	5244.8	430.2	0.1902	0.91	49.827	BB



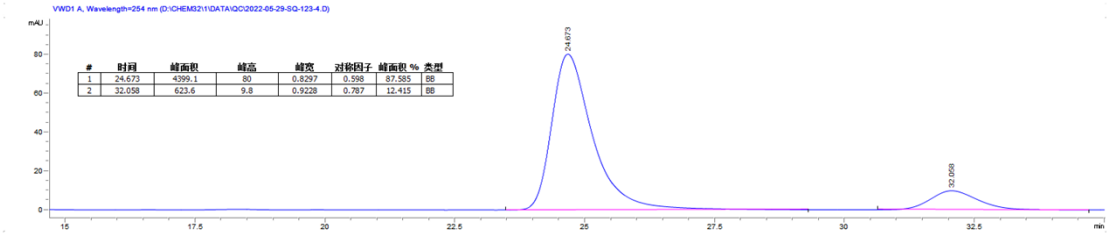
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.577	3011.6	336.1	0.1377	0.886	6.204	BV R
2	8.897	45530.9	3608.5	0.1992	0.871	93.796	BB

(*S*,*E*)-*N*-(1,3-diphenylallyl)-2-methylaniline (8f). Colorless oil was obtained in 83% yield. 75% ee was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm, 25 °C): t_R (major) = 24.7 min, t_R (minor) = 32.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.537.47(m, 2H), 7.45-7.39 (m, 4H), 7.37-7.32 (m, 3H), 7.30-7.27 (m, 1H), 7.17-7.04 (m, 2H), 6.76-6.60 (m, 3H), 6.49 (dd, J = 15.8, 6.3 Hz, 1H), 5.19 (d, J = 6.3 Hz, 1H), 4.01 (br, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.2, 136.7, 131.2, 131.0, 130.1, 128.9, 128.6, 127.8, 127.6, 127.2, 127.1, 126.6, 122.2, 117.4, 111.4, 60.6, 17.8. HRMS $[M+H]^+$ calcd. for $C_{22}H_{22}N^+$: 300.1747, found: 300.1748.



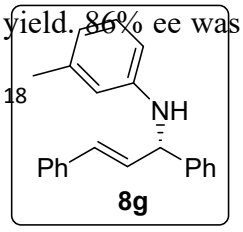


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	24.726	2241.7	33.6	1.0051	0.66	49.415	BB
2	32.567	2294.8	38.6	0.9197	0.767	50.585	BB

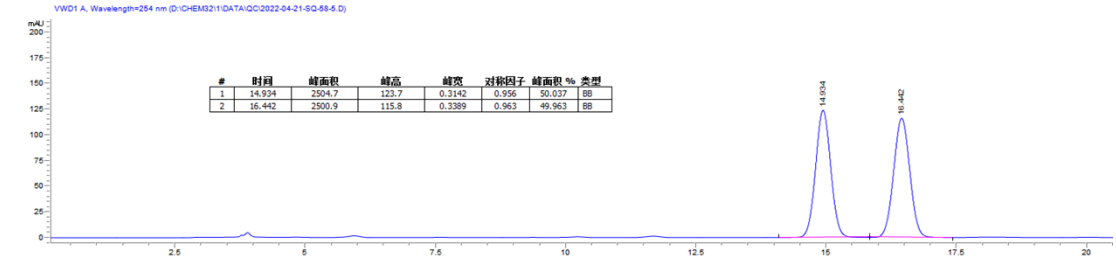


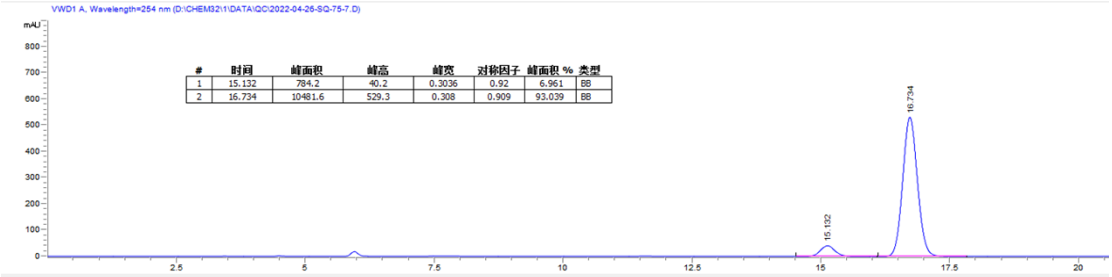
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	24.673	4399.1	80	0.8297	0.598	87.585	BB
2	32.058	623.6	9.8	0.9228	0.787	12.415	BB

(*S*,*E*)-*N*-(1,3-diphenylallyl)-3-methylaniline (8g). Colorless oil was obtained in 83% yield. 86% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH =

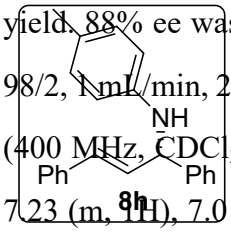


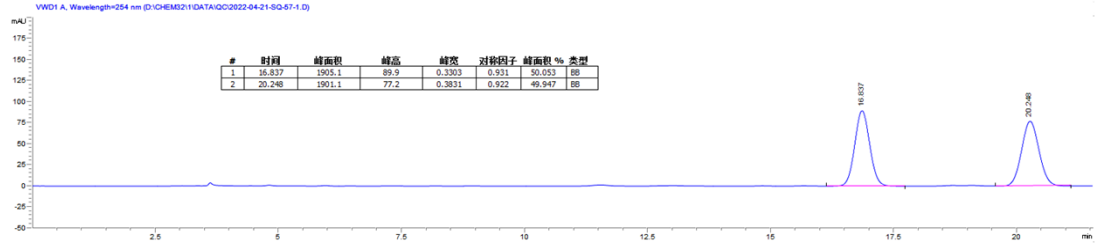
98/2, 1 mL/min, 254 nm, 40 °C): t_R (minor) = 15.1 min, t_R (major) = 16.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.45-7.38 (m, 4H), 7.37-7.31 (m, 3H), 7.30-7.26 (m, 1H), 7.08 (t, J = 7.7 Hz, 1H), 6.68 (d, J = 15.9 Hz, 1H), 6.59 (d, J = 7.5 Hz, 1H), 6.56-6.41 (m, 3H), 5.13 (d, J = 6.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 142.3, 139.0, 136.8, 131.1, 130.9, 129.1, 128.9, 128.6, 127.7, 127.6, 127.3, 126.6, 118.8, 114.5, 110.7, 60.7, 21.7. HRMS $[M+H]^+$ calcd. for $C_{22}H_{22}N^+$: 300.1747, found: 300.1746.



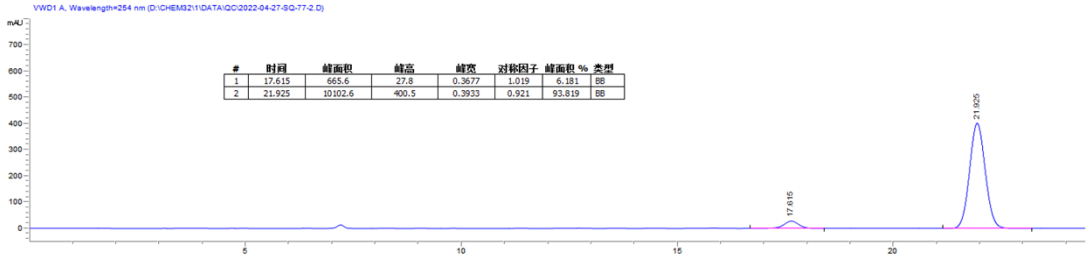


(*S*,*E*)-*N*-(1,3-diphenylallyl)-4-methylaniline (8h).[6] Colorless oil was obtained in 89% yield. 88% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm, 40 °C): t_R (minor) = 17.6 min, t_R (major) = 21.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 2H), 7.45-7.37 (m, 4H), 7.37-7.30 (m, 3H), 7.29-7.23 (m, 1H), 7.01 (d, J = 7.9 Hz, 2H), 6.73-6.56 (m, 3H), 6.44 (dd, J = 15.9, 6.2 Hz, 1H), 5.10 (d, J = 6.2 Hz, 1H), 4.05 (br, 1H), 2.27 (s, 3H).



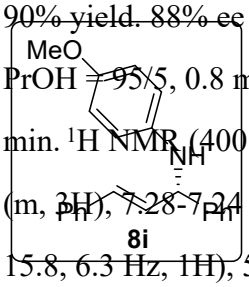


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	16.837	1905.1	89.9	0.3303	0.931	50.053	BB
2	20.248	1901.1	77.2	0.3831	0.922	49.947	BB

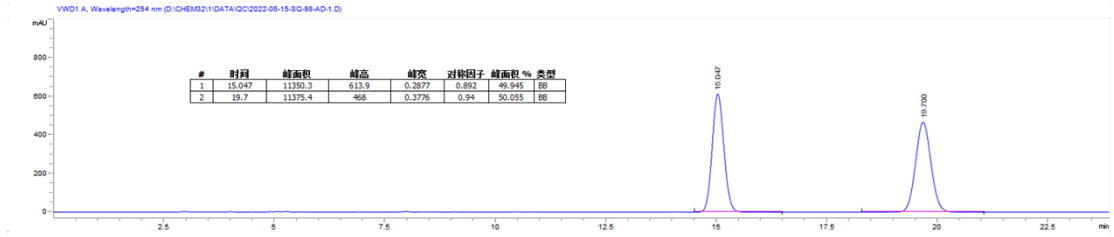


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.615	665.6	27.8	0.3677	1.019	6.181	BB
2	21.925	10102.6	400.5	0.3933	0.921	93.819	BB

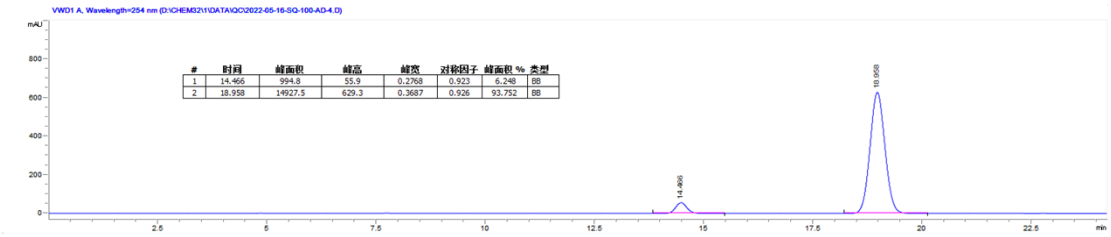
(*S*,*E*)-*N*-(1,3-diphenylallyl)-4-methoxyaniline (8i).[7] Colorless oil was obtained in 90% yield. 88% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm, 25 °C): t_R (minor) = 14.5 min, t_R (major) = 19.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.44 (m, 2H), 7.44-7.37 (m, 4H), 7.36-7.30 (m, 2H), 7.28-7.24 (m, 1H), 6.78 (d, J = 8.4 Hz, 2H), 6.71-6.60 (m, 3H), 6.44 (dd, J = 15.8, 6.3 Hz, 1H), 5.05 (d, J = 6.3 Hz, 1H), 3.76 (s, 3H).



8i

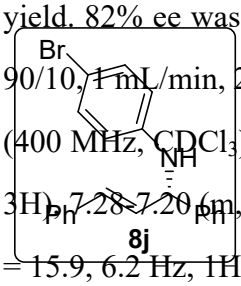


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.047	11350.3	613.9	0.2877	0.892	49.945	BB
2	19.7	11375.4	468	0.3776	0.94	50.055	BB

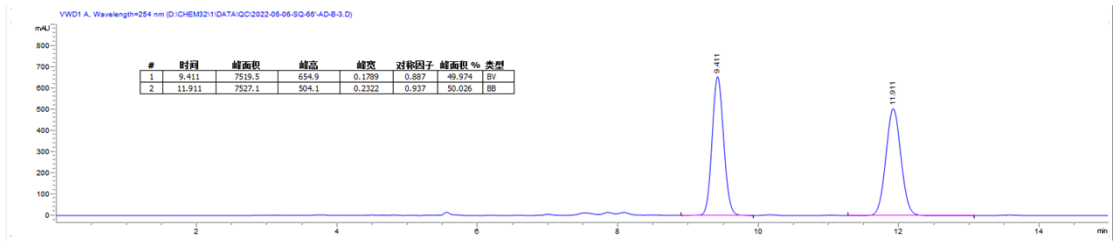


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.466	994.8	55.9	0.2768	0.923	6.248	BB
2	18.958	14927.5	629.3	0.3687	0.926	93.752	BB

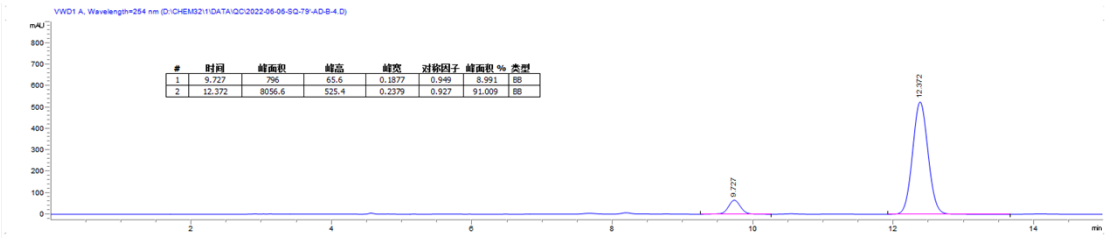
(*S*,*E*)-4-bromo-*N*-(1,3-diphenylallyl)aniline (8j).[8] Colorless oil was obtained in 87% yield. 82% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm, 25 °C): t_R (minor) = 9.7 min, t_R (major) = 12.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.36 (m, 6H), 7.35-7.29 (m, 3H), 7.28-7.20 (m, 3H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 2H), 6.39 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.06 (d, *J* = 6.2 Hz, 1H).



8j

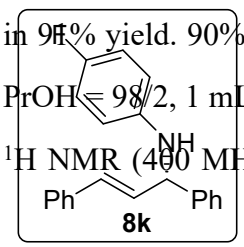


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.411	7519.5	654.9	0.1789	0.887	49.974	BV
2	11.911	7527.1	504.1	0.2322	0.937	50.026	BB



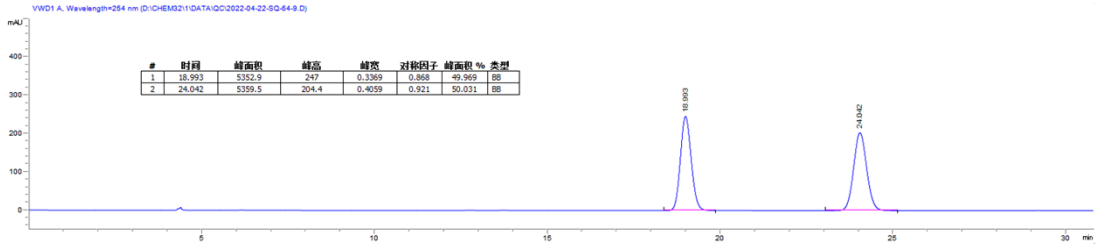
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.727	796	65.6	0.1877	0.949	8.991	BB
2	12.372	8056.6	525.4	0.2379	0.927	91.009	BB

(*S*,*E*)-4-fluorophenyl-*N*-(1,3-diphenylallyl)aniline (8k).[9] Colorless oil was obtained in 91% yield. 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm, 40 °C): t_R (minor) = 18.6 min, t_R (major) = 23.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.43 (m, 2H), 7.43-7.36 (m, 4H), 7.36-7.29 (m,

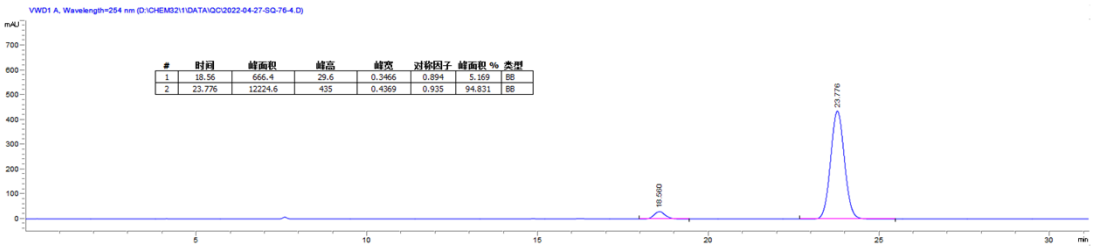


8k

3H), 7.29-7.25 (m, 1H), 6.88 (t, J = 8.5 Hz, 2H), 6.71-6.52 (m, 3H), 6.42 (dd, J = 15.8, 6.3 Hz, 1H), 5.05 (d, J = 6.3 Hz, 1H).

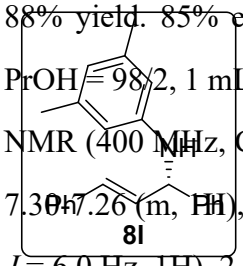


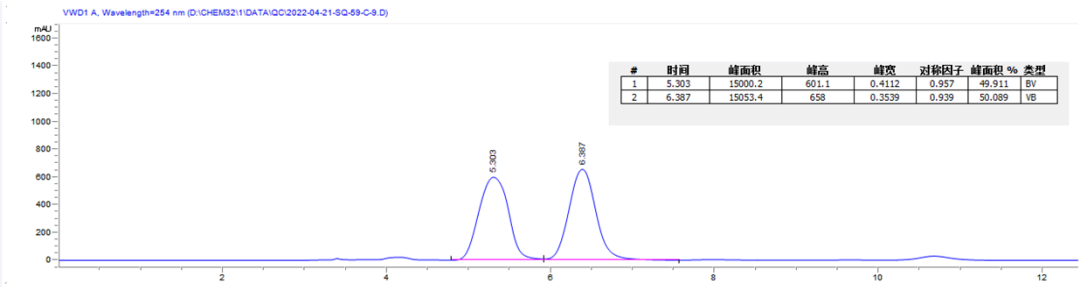
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	18.993	5352.9	247	0.3369	0.868	49.969	BB
2	24.042	5359.5	204.4	0.4059	0.921	50.031	BB



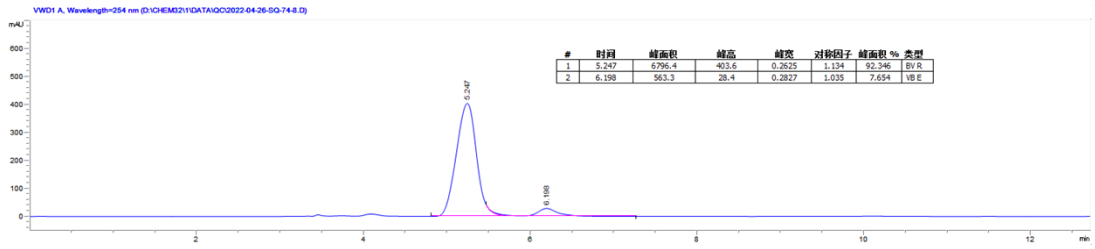
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	18.56	666.4	29.6	0.3466	0.894	5.169	BB
2	23.776	12224.6	435	0.4369	0.935	94.831	BB

(*S*,*E*)-*N*-(1,3-diphenylallyl)-3,5-dimethylaniline (8l).[10] Colorless oil was obtained in 88% yield. 85% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm, 40 °C): t_R (major) = 5.2 min, t_R (minor) = 6.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51--7.46 (m, 2H), 7.45-7.39 (m, 4H), 7.37-7.31 (m, 3H), 7.30-7.26 (m, 1H), 6.69 (d, J = 15.8 Hz, 1H), 6.50-6.40 (m, 2H), 6.35 (s, 2H), 5.13 (d, J = 6.0 Hz, 1H), 2.27 (s, 6H).



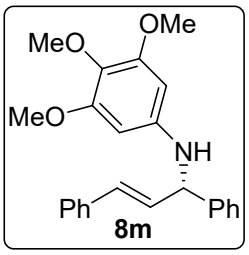


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	5.303	15000.2	601.1	0.4112	0.957	49.911	BV
2	6.387	15053.4	658	0.3539	0.939	50.089	VB

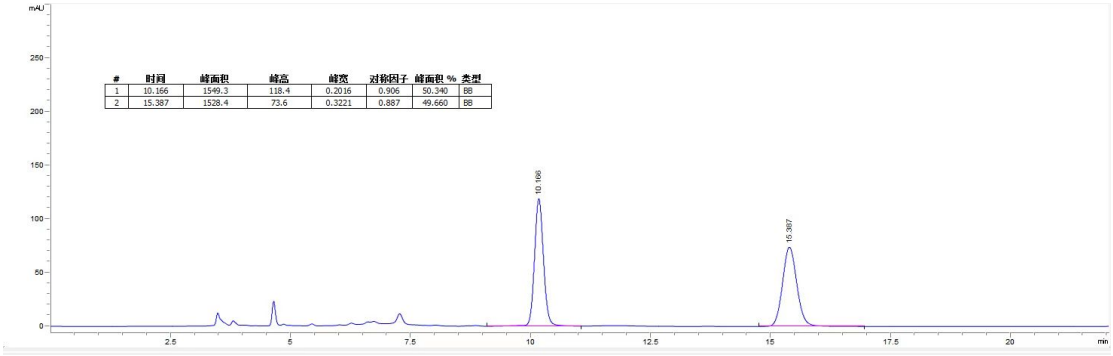


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	5.247	6796.4	403.6	0.2625	1.134	92.346	BV R
2	6.198	563.3	28.4	0.2827	1.035	7.654	VB E

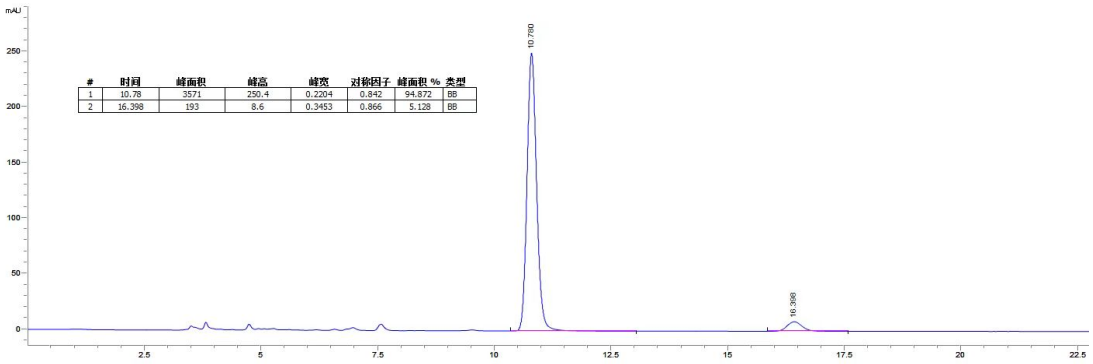
(*S*,*E*)-*N*-(1,3-diphenylallyl)-3,4,5-trimethoxyaniline (8m). Colorless oil was



obtained in 99% yield. 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 10.8 min, t_R (minor) = 16.4 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.46 (m, 2H), 7.43-7.38 (m, 4H), 7.36-7.31 (m, 3H), 7.28-7.24 (m, 1H), 6.68 (d, J = 15.8 Hz, 1H), 6.43 (dd, J = 15.8, 6.4 Hz, 1H), 5.93 (s, 2H), 5.07 (d, J = 6.4 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 144.1, 142.3, 136.7, 131.3, 130.9, 129.0, 128.6, 127.8, 127.7, 127.2, 126.5, 91.4, 61.5, 61.1, 55.9. HRMS $[M+H]^+$ calcd. for $C_{24}H_{26}NO_3^+$: 376.1907, found: 376.1905.

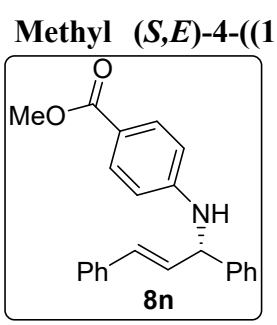


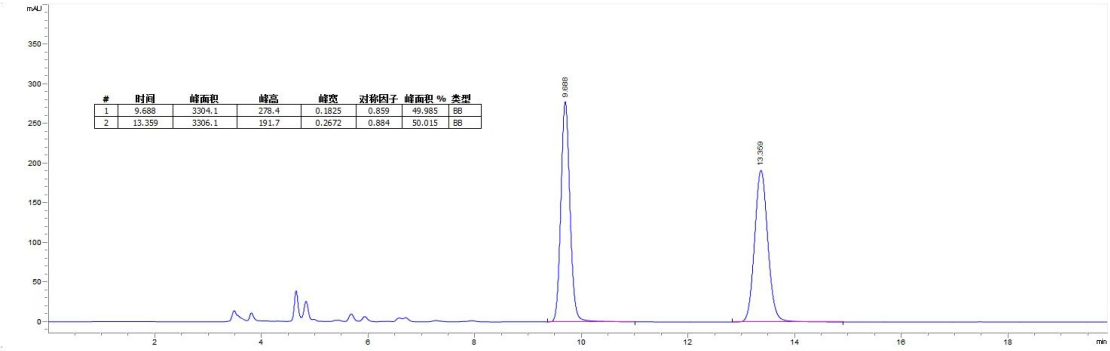
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.166	1549.3	118.4	0.2016	0.906	50.340	BB
2	15.387	1528.4	73.6	0.3221	0.887	49.660	BB



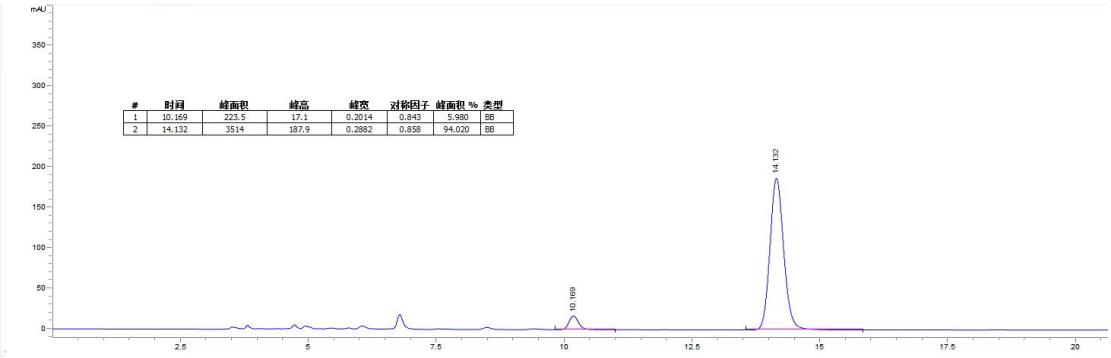
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.78	3571	250.4	0.2204	0.842	94.872	BB
2	16.398	193	8.6	0.3453	0.866	5.128	BB

Methyl (*S*,*E*)-4-((1,3-diphenylallyl)amino)benzoate (8n).[11] Colorless oil was obtained in 99% yield. 88% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 10.2 min, t_R (major) = 14.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.45-7.42 (m, 2H), 7.41-7.38 (m, 3H), 7.37-7.34 (m, 1H), 7.34-7.30 (m, 2H), 7.29-7.25 (m, 1H), 6.67-6.59 (m, 3H), 6.41 (dd, J = 15.8, 6.0 Hz, 1H), 5.21 (d, J = 6.0 Hz, 1H), 4.60 (s, 1H), 3.86 (s, 3H).



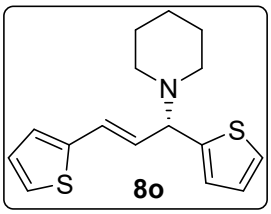


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.688	3304.1	278.4	0.1825	0.859	49.985	BB
2	13.359	3306.1	191.7	0.2672	0.884	50.015	BB

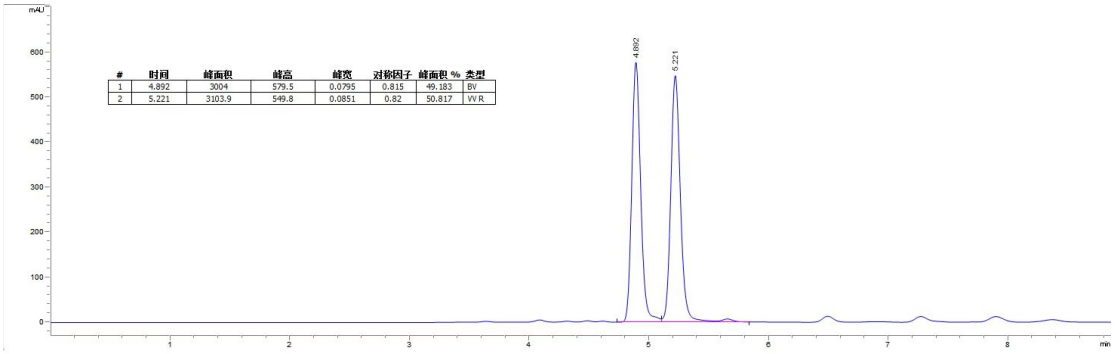


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.169	223.5	17.1	0.2014	0.843	5.980	BB
2	14.132	3514	187.9	0.2882	0.858	94.020	BB

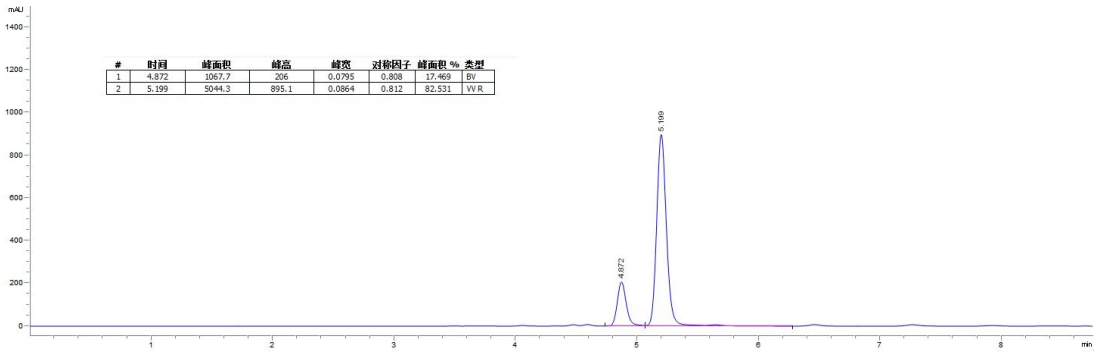
(*S*,*E*)-1-(1,3-di(thiophen-2-yl)allyl)piperidine (8o). Colorless oil was obtained in



99% yield. 65% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 4.9 min, t_R (major) = 5.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 1H), 7.19-7.16 (m, 1H), 7.00-6.97 (m, 3H), 6.96-6.93 (m, 1H), 6.71 (d, J = 15.6 Hz, 1H), 6.26 (dd, J = 15.6, 8.4 Hz, 1H), 4.27 (d, J = 8.4 Hz, 1H), 2.63-2.53 (m, 2H), 2.52-2.42 (m, 2H), 1.67-1.57 (m, 4H), 1.51-1.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 129.5, 127.4, 126.5, 125.6, 125.5, 124.8, 124.7, 124.2, 68.6, 51.8, 26.2, 24.6. HRMS $[M+H]^+$ calcd. for $C_{16}H_{20}NS_2^+$: 290.1032, found: 290.1032.

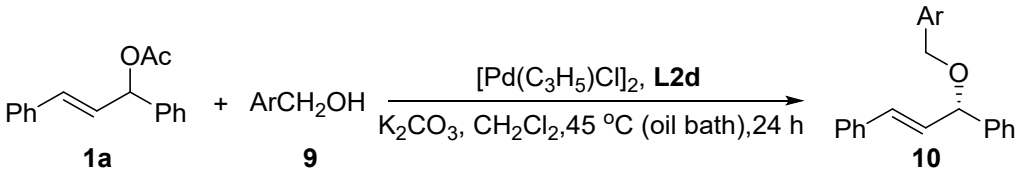


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	4.892	3004	579.5	0.0795	0.815	49.183	BV
2	5.221	3103.9	549.8	0.0851	0.82	50.817	VV R



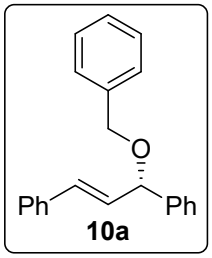
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	4.872	1067.7	206	0.0795	0.808	17.469	BV
2	5.199	5044.3	895.1	0.0864	0.812	82.531	VV R

General Procedure for Pd-Catalyzed Asymmetric Allylic Etherification

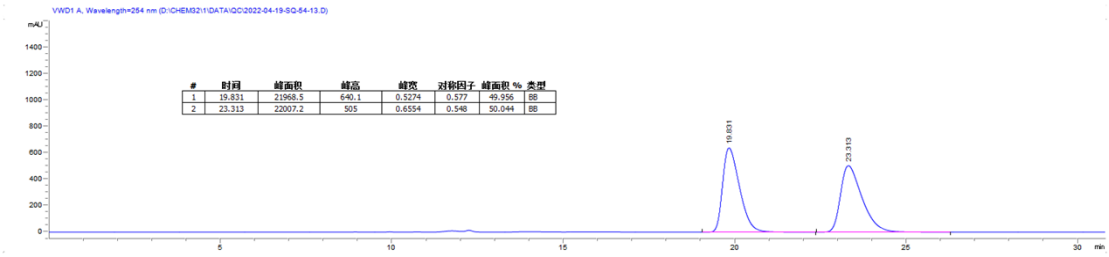


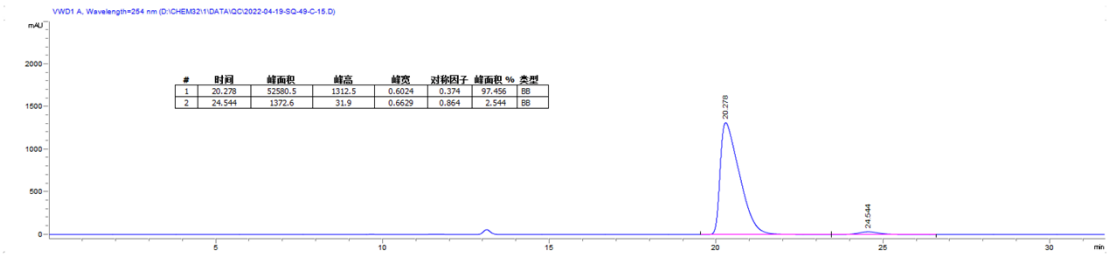
Ligand (*S,S*)-**L2d** (0.012 mmol) and $[Pd(C_3H_5)Cl]_2$ (0.006 mmol) were dissolved in CH_2Cl_2 (1.0 mL) in a Schlenk tube under an N_2 atmosphere. After 1 h of stirring at room temperature, 1,3-phenyl-2-propenyl acetate **1a** (0.2 mmol), alcohol **9** (0.6 mmol), K_2CO_3 (1.0 mmol) and CH_2Cl_2 (2.0 mL) was added. The mixture was heated to 45 °C (oil bath) for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate to afford the corresponding product.

(*S*, *E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (10a).[1] Colorless oil was



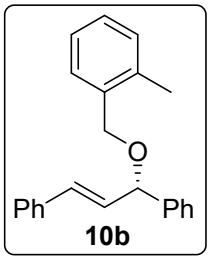
obtained in 84% yield. 95% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 20.3 min, t_R (minor) = 24.5 min. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47-7.42 (m, 2H), 7.42-7.34 (m, 8H), 7.33-7.28 (m, 4H), 7.26-7.23 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.35 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.03 (d, *J* = 7.0 Hz, 1H), 4.59 (s, 2H).



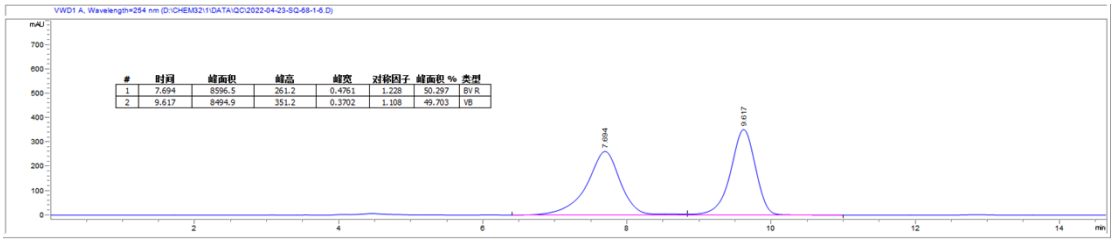


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	20.278	52580.5	1312.5	0.6024	0.374	97.456	BB
2	24.544	1372.6	31.9	0.6629	0.864	2.544	BB

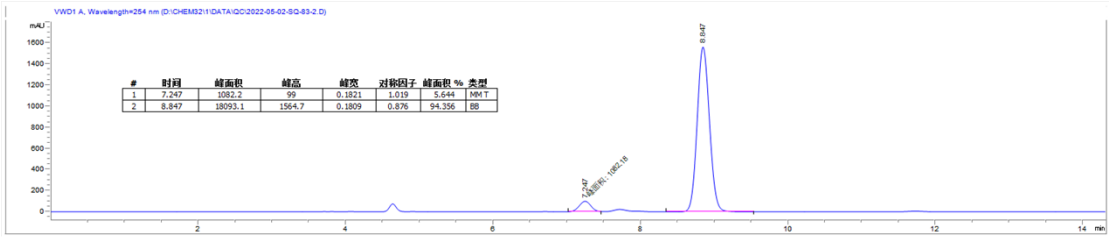
(*S*, *E*)-(3-((2-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10b).[12] Colorless oil was obtained in 80% yield. 89% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 98/2, 1 mL/min, 254 nm, 40 °C): t_R (minor) = 7.2 min, t_R (major) = 8.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.46-7.40 (m, 5H), 7.38-7.32 (m, 3H), 7.29-7.21 (m, 4H), 6.70 (d, J = 15.9 Hz, 1H), 6.40 (dd, J = 15.9, 7.0 Hz, 1H), 5.07 (d, J = 7.0 Hz, 1H), 4.61 (q, J = 11.8 Hz, 2H), 2.38 (s, 3H).



10b

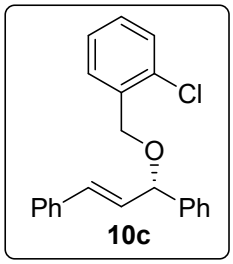


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.694	8596.5	261.2	0.4761	1.228	50.297	BV R
2	9.617	8494.9	351.2	0.3702	1.108	49.703	VB



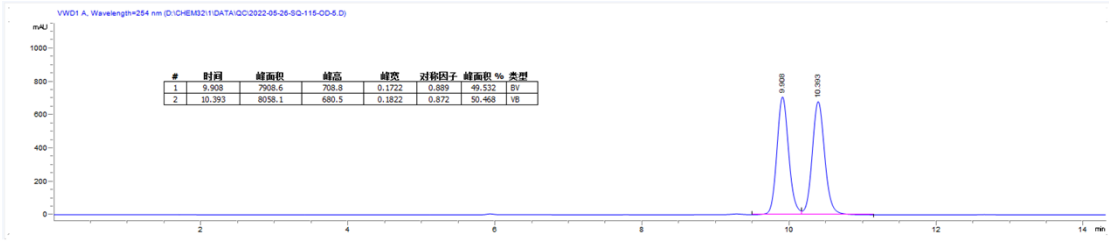
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.247	1082.2	99	0.1821	1.019	5.644	MM T
2	8.847	18093.1	1564.7	0.1809	0.876	94.356	BB

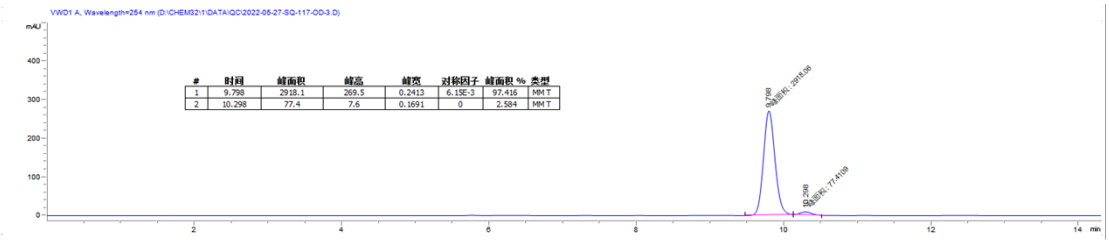
(*S*, *E*)-(3-((2-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10c).[13] Colorless oil was obtained in 80% yield. 95% ee was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm, 25 °C): t_R (major) = 9.8 min, t_R (minor) = 10.3 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.54-7.47 (m,



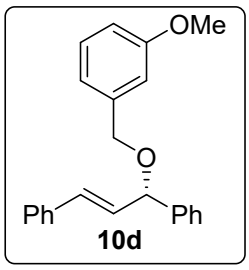
10c

2H), 7.46- 7.39 (m, 4H), 7.39-7.29 (m, 5H), 7.28-7.23 (m, 2H), 6.71 (d, J = 15.9 Hz, 1H), 6.39 (dd, J = 15.9, 7.0 Hz, 1H), 5.10 (d, J = 7.0 Hz, 1H), 4.71 (q, J = 13.1 Hz, 2H).

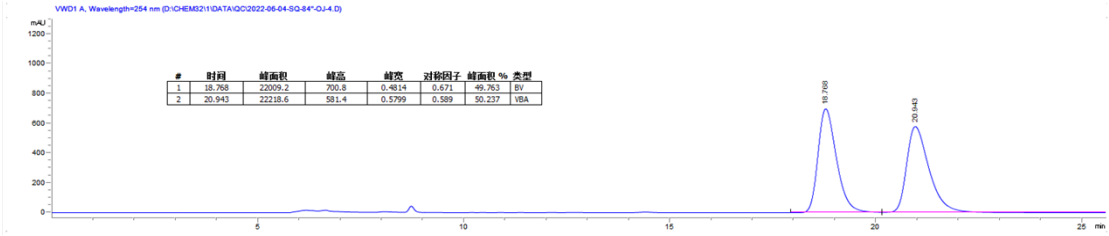


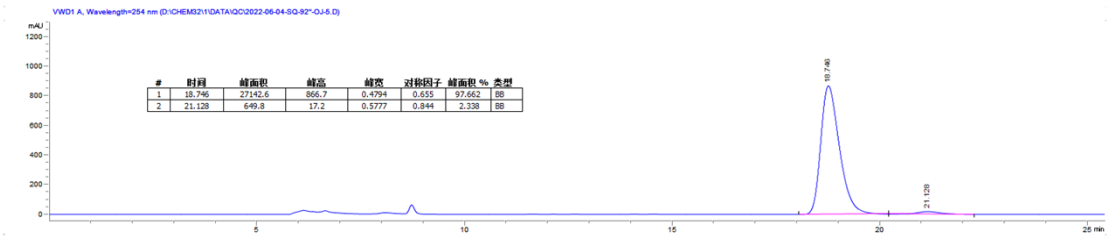


(*S*, *E*)-(3-((3-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10d).[12] Colorless



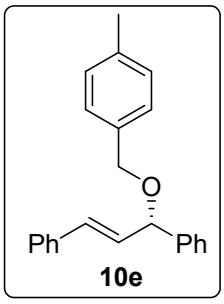
oil was obtained in 70% yield. 95% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.5 mL/min, 254 nm, 25 °C): t_R (major) = 18.7 min, t_R (minor) = 21.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.44-7.38 (m, 4H), 7.37-7.30 (m, 4H), 7.28-7.24 (m, 1H), 7.02-6.94 (m, 2H), 6.87 (d, J = 8.2 Hz, 1H), 6.67 (d, J = 15.9 Hz, 1H), 6.38 (dd, J = 15.9, 7.0 Hz, 1H), 5.05 (d, J = 7.0 Hz, 1H), 4.60 (s, 2H), 3.83 (s, 3H).





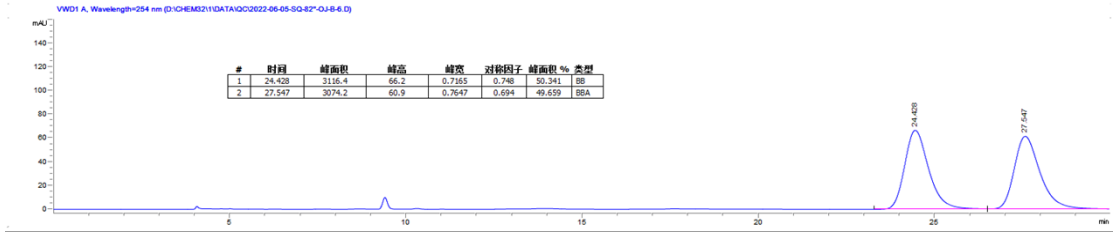
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	18.746	27142.6	866.7	0.4794	0.655	97.662	BB
2	21.128	649.8	17.2	0.5777	0.844	2.338	BB

(*S*, *E*)-(3-((4-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10e).[12] Colorless

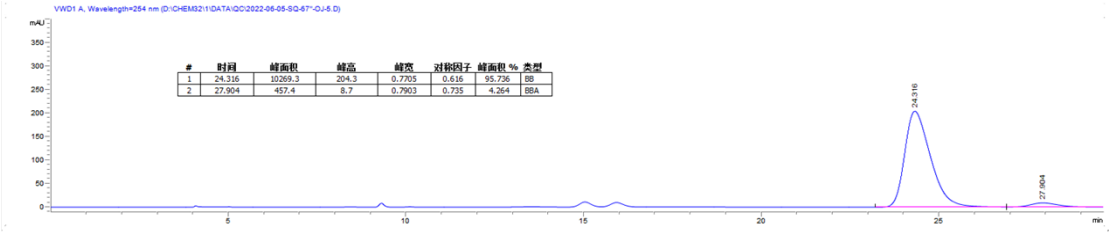


10e

oil was obtained in 90% yield. 91% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.75 mL/min, 254 nm, 40 °C): t_R (major) = 24.3 min, t_R (minor) = 27.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.42-7.35 (m, 5H), 7.34-7.27 (m, 5H), 7.21-7.16 (m, 2H), 6.64 (d, J = 15.9 Hz, 1H), 6.35 (dd, J = 15.9, 7.0 Hz, 1H), 5.02 (d, J = 7.0 Hz, 1H), 4.56 (s, 2H), 2.37 (s, 3H).

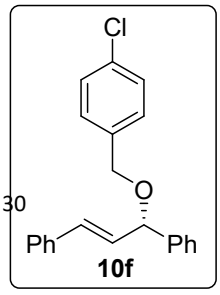


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	24.428	3116.4	66.2	0.7165	0.748	50.341	BB
2	27.547	3074.2	60.9	0.7647	0.694	49.659	BBA



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	24.316	10269.3	204.3	0.7705	0.616	95.736	BB
2	27.904	457.4	8.7	0.7903	0.735	4.264	BBA

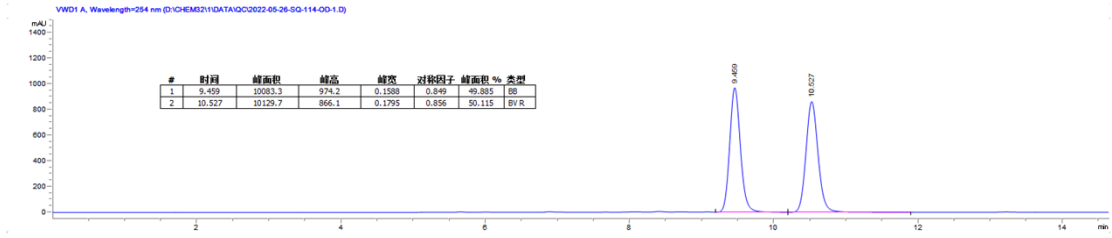
(*S*, *E*)-(3-((4-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10f).[1] Colorless oil



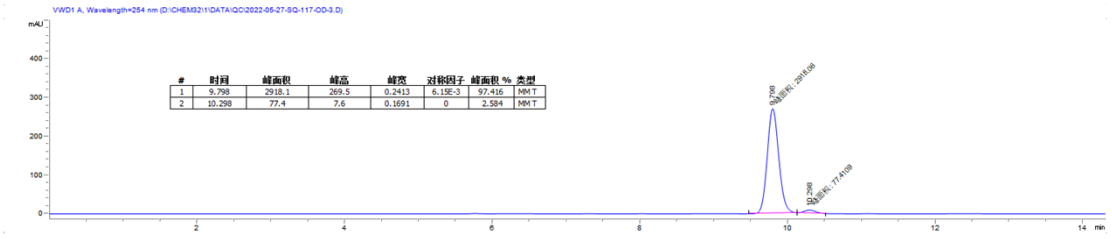
10f

was obtained in 91% yield. 95% ee was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm, 25 °C): t_R (major) = 9.8 min, t_R (minor) = 10.3 min. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.47-7.38 (m, 6H), 7.36-7.29 (m, 7H), 7.27-7.22 (m, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.35 (dd, J = 15.9, 7.0 Hz, 1H), 5.01 (d, J = 7.0 Hz, 1H), 4.56 (q, J = 12.0 Hz, 2H).

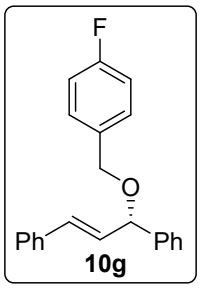


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.459	10083.3	974.2	0.1588	0.849	49.885	BB
2	10.527	10129.7	866.1	0.1795	0.856	50.115	BV R

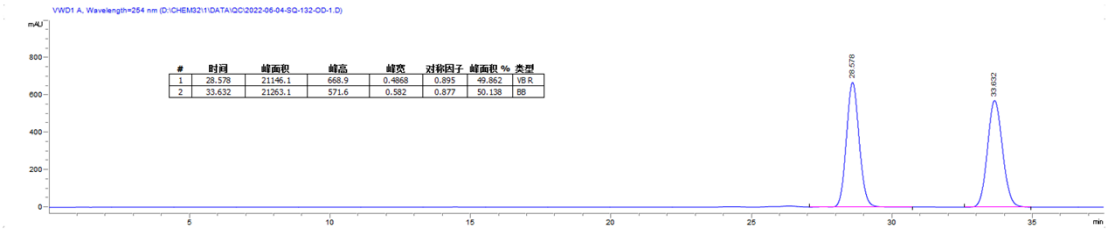


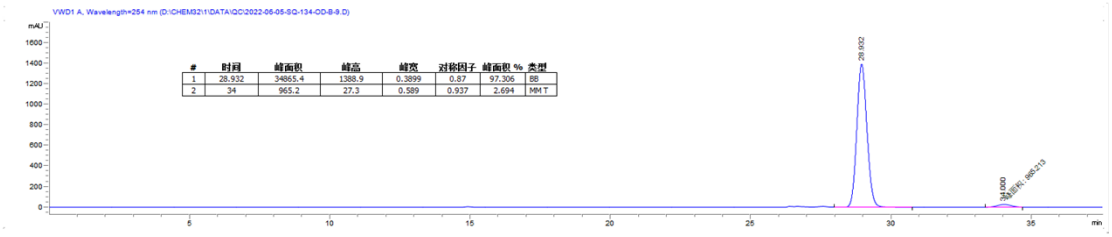
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.798	2918.1	269.5	0.2413	6.15E-3	97.416	MM T
2	10.298	77.4	7.6	0.1691	0	2.584	MM T

(*S*,*E*)-(3-((4-Fluorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10g).[12] Colorless

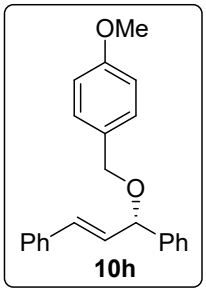


oil was obtained in 86% yield. 95% ee was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99/1, 0.2mL/min, 254 nm, 25 °C): t_R (major) = 28.9 min, t_R (minor) = 34.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.43-7.38 (m, 4H), 7.38-7.29 (m, 5H), 7.28-7.22 (m, 1H), 7.06 (t, J = 8.5 Hz, 2H), 6.65 (d, J = 15.8 Hz, 1H), 6.36 (dd, J = 15.8, 7.0 Hz, 1H), 5.03 (d, J = 7.0 Hz, 1H), 4.57 (q, J = 11.8 Hz, 2H).

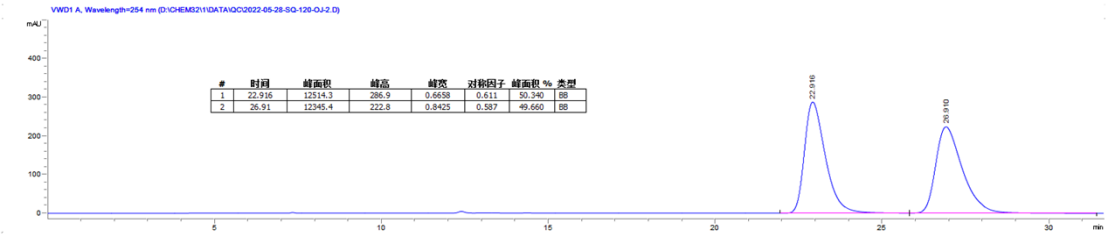


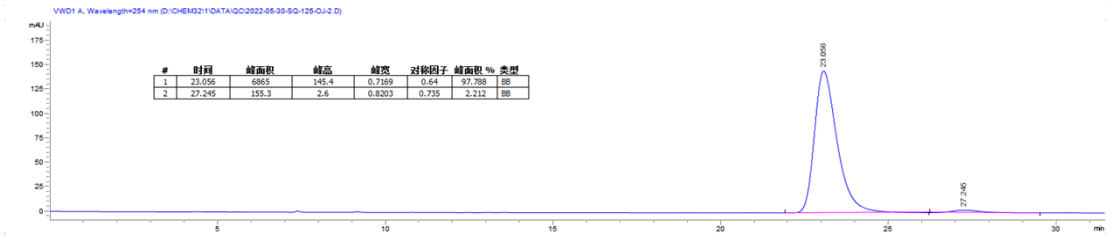


(*S*, *E*)-(3-((4-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10h).[1] Colorless



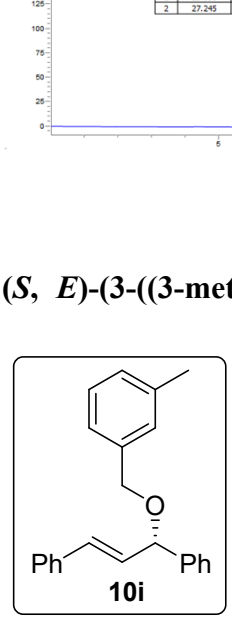
oil was obtained in 94% yield. 96% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 86/14, 0.7 mL/min, 254 nm, 25 °C): t_R (major) = 23.1 min, t_R (minor) = 27.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.43-7.38 (m, 4H), 7.36-7.29 (m, 5H), 7.27-7.23 (m, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.03 (d, *J* = 7.0 Hz, 1H), 4.54 (s, 2H), 3.84 (s, 3H).



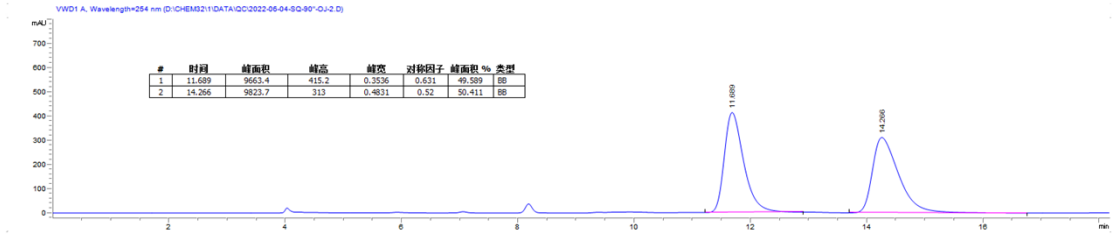


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	23.056	6865	145.4	0.7169	0.64	97.788	BB
2	27.245	155.3	2.6	0.8203	0.735	2.212	BB

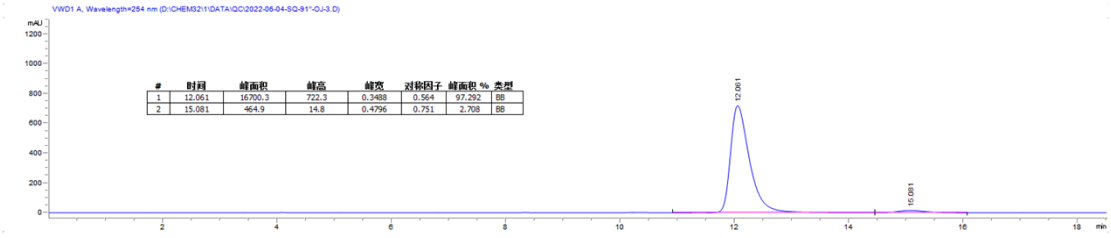
(*S*, *E*)-(3-((3-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (10i).[12] Colorless oil was obtained in 90% yield. 95% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 96/4, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 12.1 min, t_R (minor) = 15.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.43-7.37 (m, 4H), 7.35-7.30 (m, 3H), 7.28-7.24 (m, 2H), 7.23-7.18 (m, 2H), 7.15-7.10 (m, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.37 (dd, J = 15.9, 7.0 Hz, 1H), 5.04 (d, J = 7.0 Hz, 1H), 4.57 (s, 2H), 2.38 (s, 3H).



10i

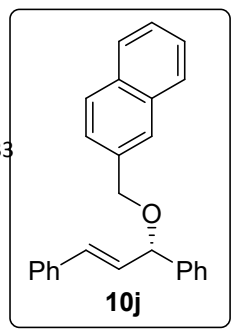


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.689	9663.4	415.2	0.3536	0.631	49.589	BB
2	14.266	9823.7	313	0.4831	0.52	50.411	BB



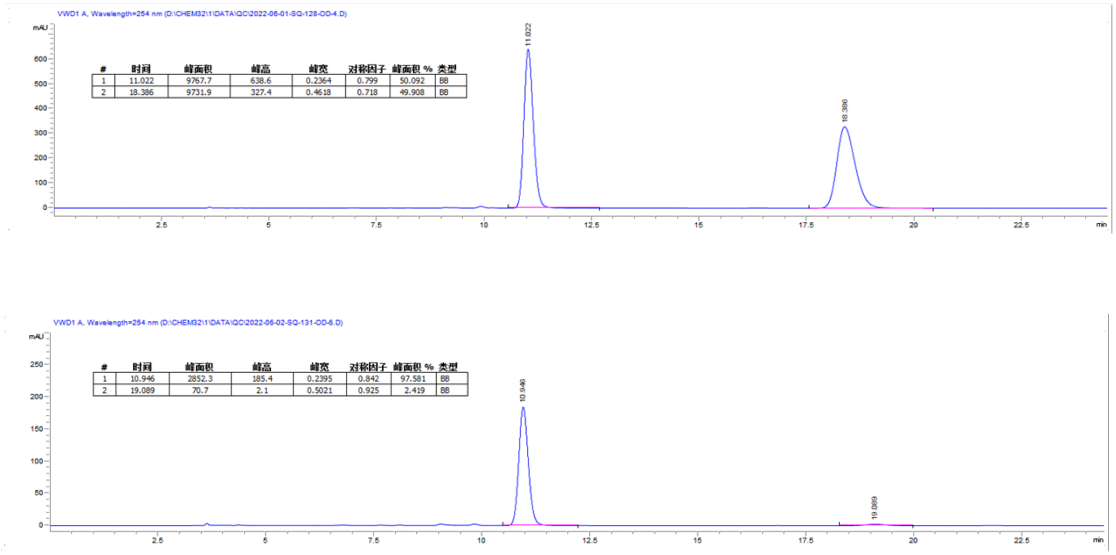
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.061	16700.3	722.3	0.3488	0.564	97.292	BB
2	15.081	464.9	14.8	0.4796	0.751	2.708	BB

(*S*,*E*)-2-(((1,3-diphenylallyl)oxy)methyl)naphthalene (10j).[14] Colorless oil was obtained in 93% yield. 95% ee was determined by chiral HPLC (Chiralpak OD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm,

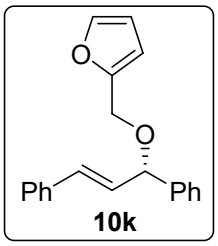


10j

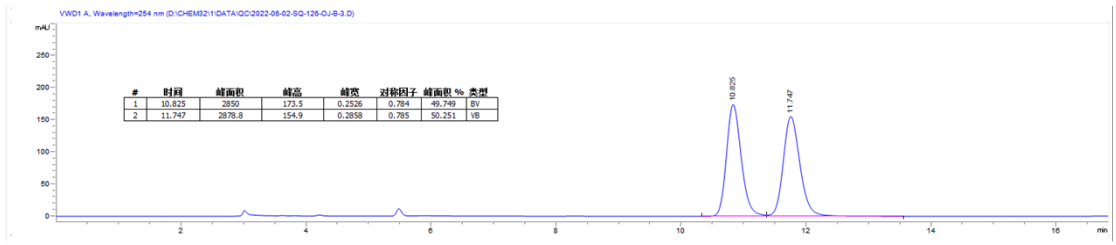
25 °C): t_R (major) = 10.9 min, t_R (minor) = 19.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.82 (m, 4H), 7.57-7.47 (m, 5H), 7.46-7.39 (m, 4H), 7.38-7.31 (m, 3H), 7.29-7.24 (m, 1H),6.69 (d, J = 15.9 Hz, 1H), 6.42 (dd, J = 15.8, 7.0 Hz, 1H), 5.10 (d, J = 7.0 Hz, 1H), 4.78 (s, 2H).

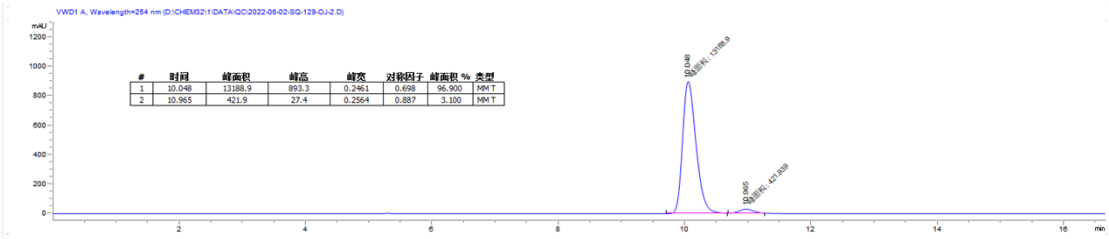


(S,*E*)-2-(((1,3-Diphenylallyl)oxy)methyl)furan (10k).[1] Colorless oil was obtained in



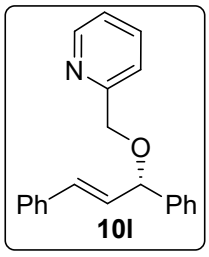
92% yield. 94% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 90/10, 1 mL/min, 254 nm, 25 °C): t_R (major) = 10.0min, t_R (minor) = 11.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.43 (m, 3H), 7.43-7.36 (m, 4H), 7.36-7.29 (m, 3H), 7.28-7.24 (m, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.47-6.26 (m, 3H), 5.06 (d, J = 7.0 Hz, 1H), 4.54 (s, 2H).



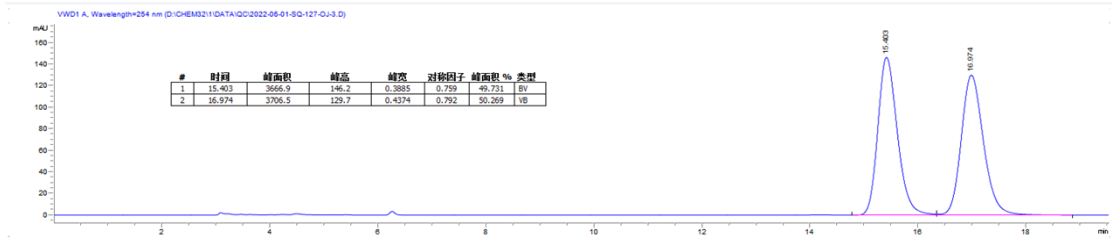


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.048	13188.9	893.3	0.2461	0.698	96.900	MM T
2	10.965	421.9	27.4	0.2564	0.887	3.100	MM T

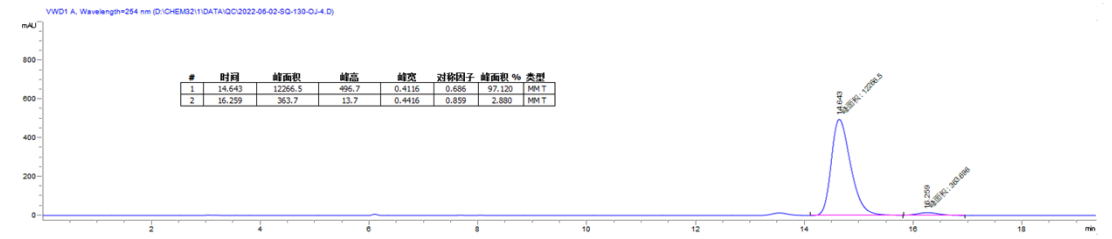
(*S*, *E*)-2-(((1,3-diphenylallyl)oxy)methyl)pyridine (10l).[1] Colorless oil was obtained



in 66% yield. 94% ee was determined by chiral HPLC (Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 95/5, 1 mL/min, 254 nm, 40 °C): t_R (major) = 14.6 min, t_R (minor) = 16.3 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 4.9 Hz, 1H), 7.74 (t, J = 7.7 Hz, 1H), 7.67 – 7.54 (m, 1H), 7.53–7.44 (m, 2H), 7.43–7.35 (m, 4H), 7.35–7.27 (m, 3H), 7.26–7.17 (m, 2H), 6.70 (d, J = 15.9 Hz, 1H), 6.37 (dd, J = 15.9, 7.1 Hz, 1H), 5.11 (d, J = 7.1 Hz, 1H), 4.75 (q, J = 13.6 Hz, 2H).

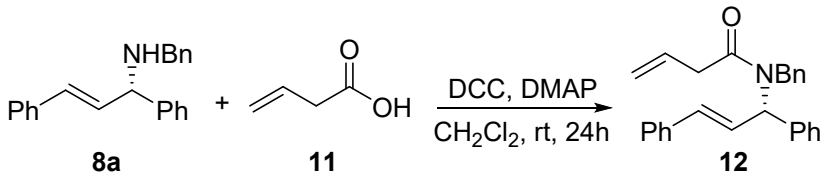


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.403	3666.9	146.2	0.3885	0.759	49.731	BV
2	16.974	3706.5	129.7	0.4374	0.792	50.269	VB

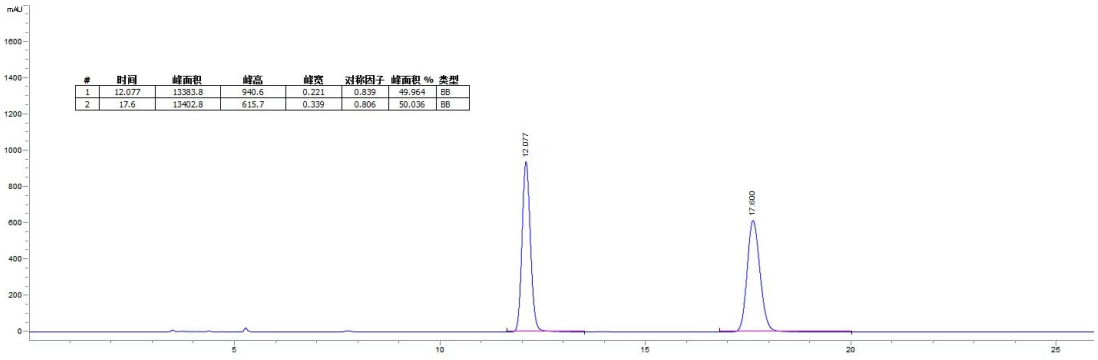


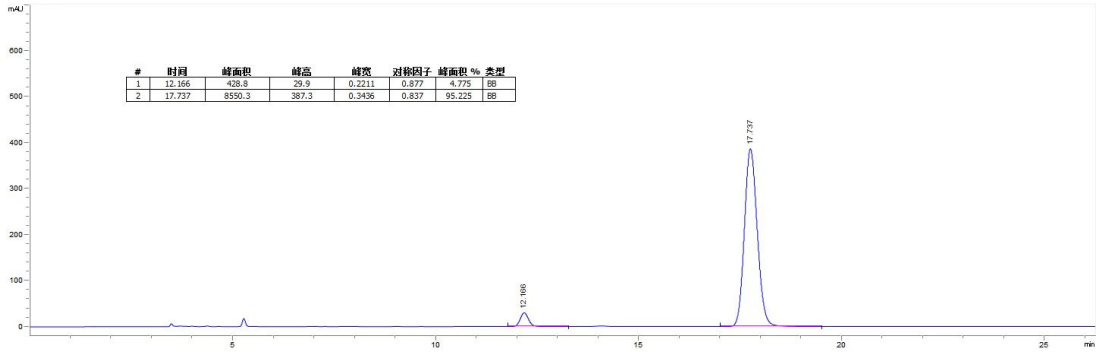
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.643	12266.5	496.7	0.4116	0.686	97.120	MM T
2	16.259	363.7	13.7	0.4416	0.859	2.880	MM T

Synthetic Application of Asymmetric Allylic Amination Product 8a [15]



To an oven-dried reaction flash was added asymmetric allylic amination product **8a** (134 mg, 0.44 mmol), 3-butenoic **11** (38.5 mg, 0.44 mmol), DCC (90.8 mg, 0.44 mmol), DMAP (10.8 mg, 0.088 mmol) and CH_2Cl_2 (5 mL). The reaction mixture was stirred for 24h at room temperature. The reaction mixture was filtered and the filtration was concentrated under vacuum to give the crude product, which was further purified by column chromatography to afford the desired product **12** as colorless oil in 88% yield. 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 12.2 min, t_R (major) = 17.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 4H), 7.32-7.24 (m, 6H), 7.24-7.18 (m, 3H), 7.17-7.10 (m, 2H), 6.76-6.66 (m, 1H), 6.65-6.33 (m, 1H), 6.33-6.10 (m, 1H), 6.10-5.77 (m, 1H), 5.32-5.03 (m, 2H), 5.00-4.64 (m, 1H), 4.61-4.27 (m, 1H), 3.51-2.99 (m, 2H).





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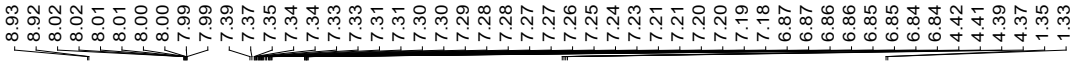
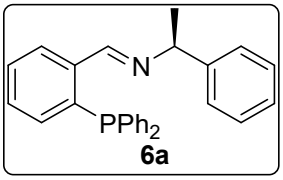
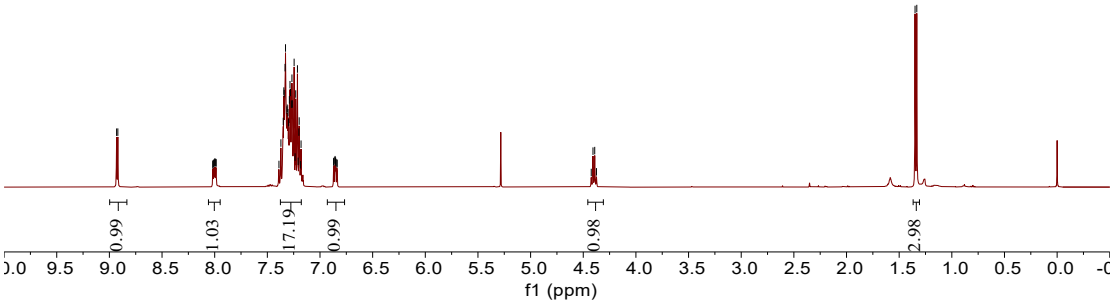
Copies of ^{1}H, ^{13}C and ^{31}P NMR Spectra



WDQ-61

PROTON CDC13 {D:\NMR400\02T2} nmr 59

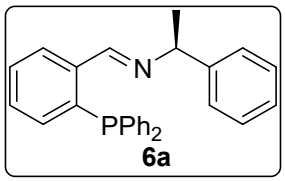


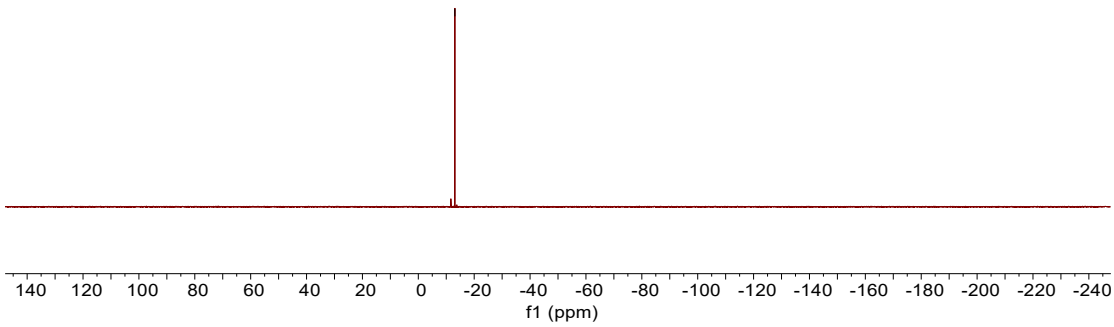


^{1}H NMR of **6a**

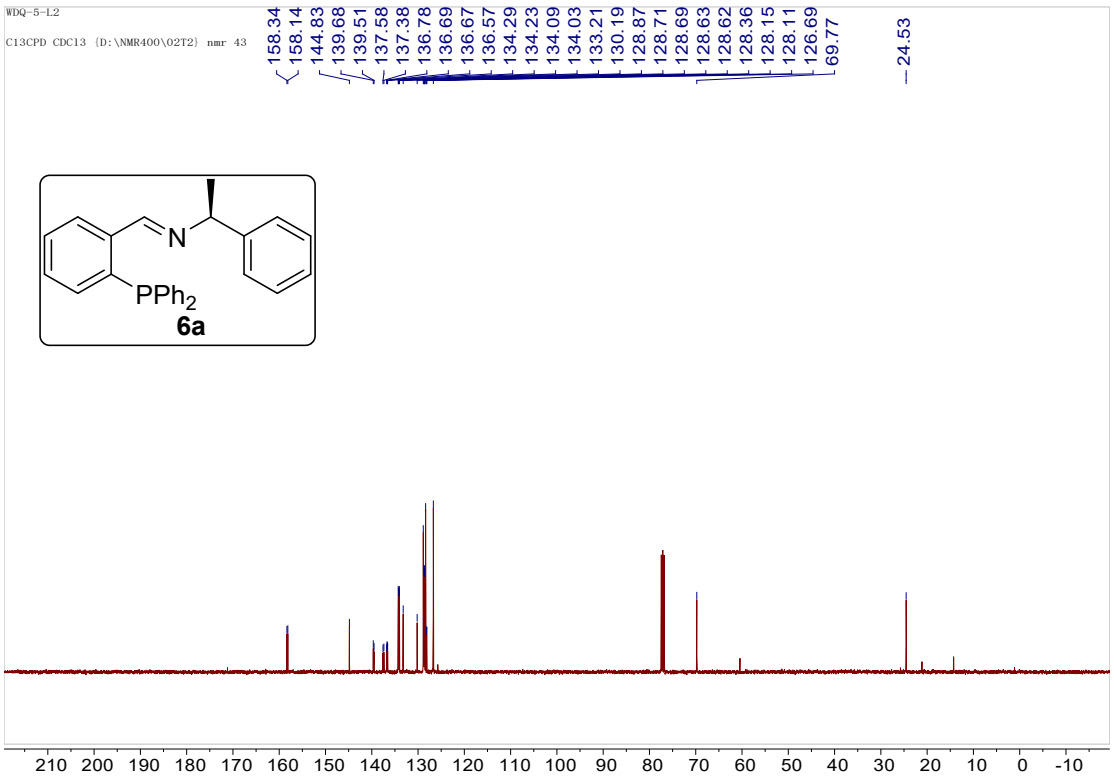
WDQ-61

P31CPD CDC13 {D:\NMR400\02T2} nmr 59

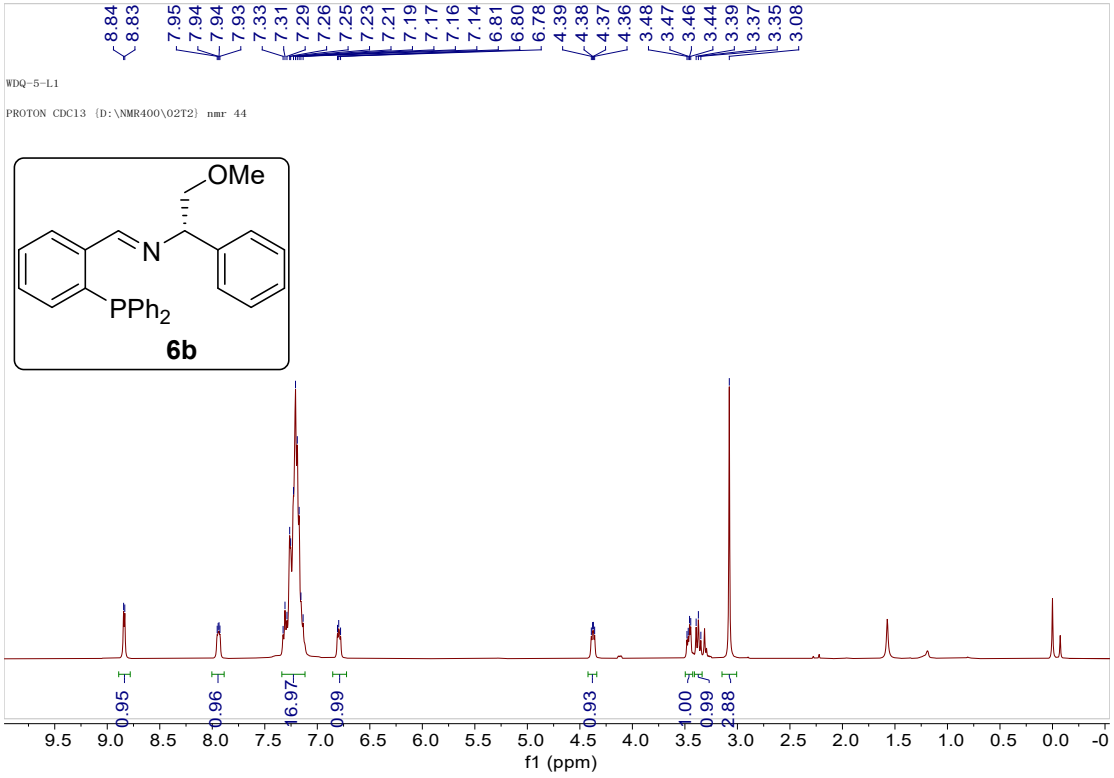




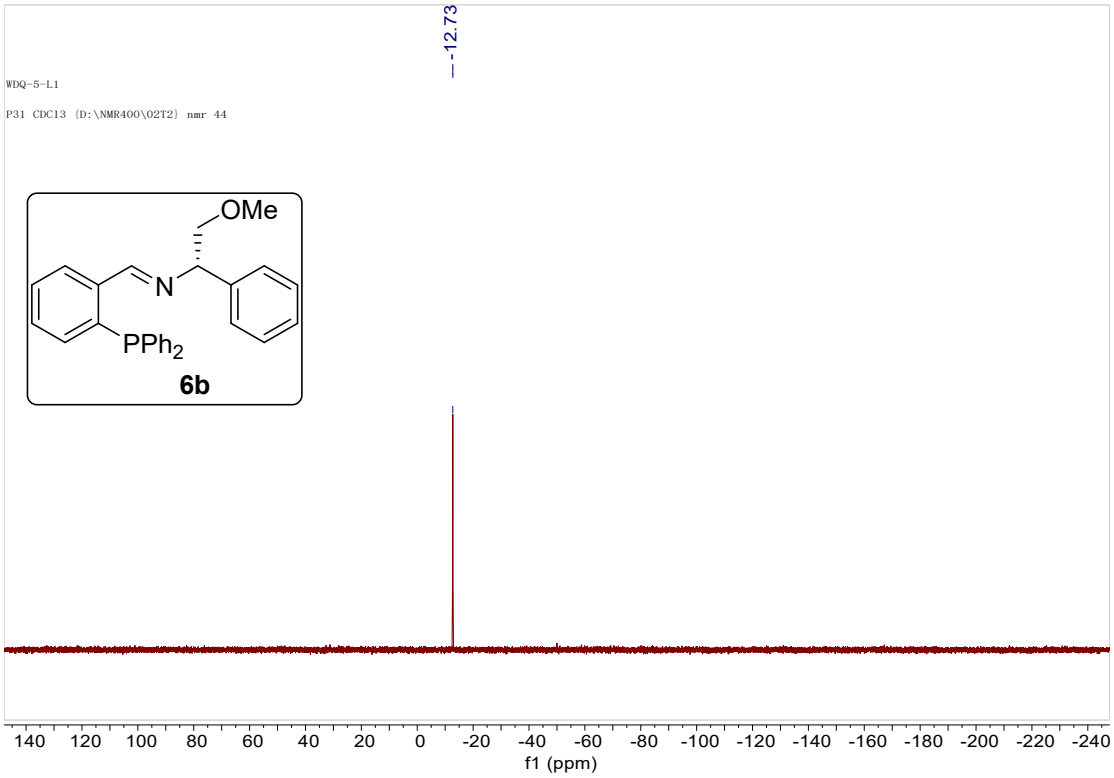
^{31}P NMR of **6a**



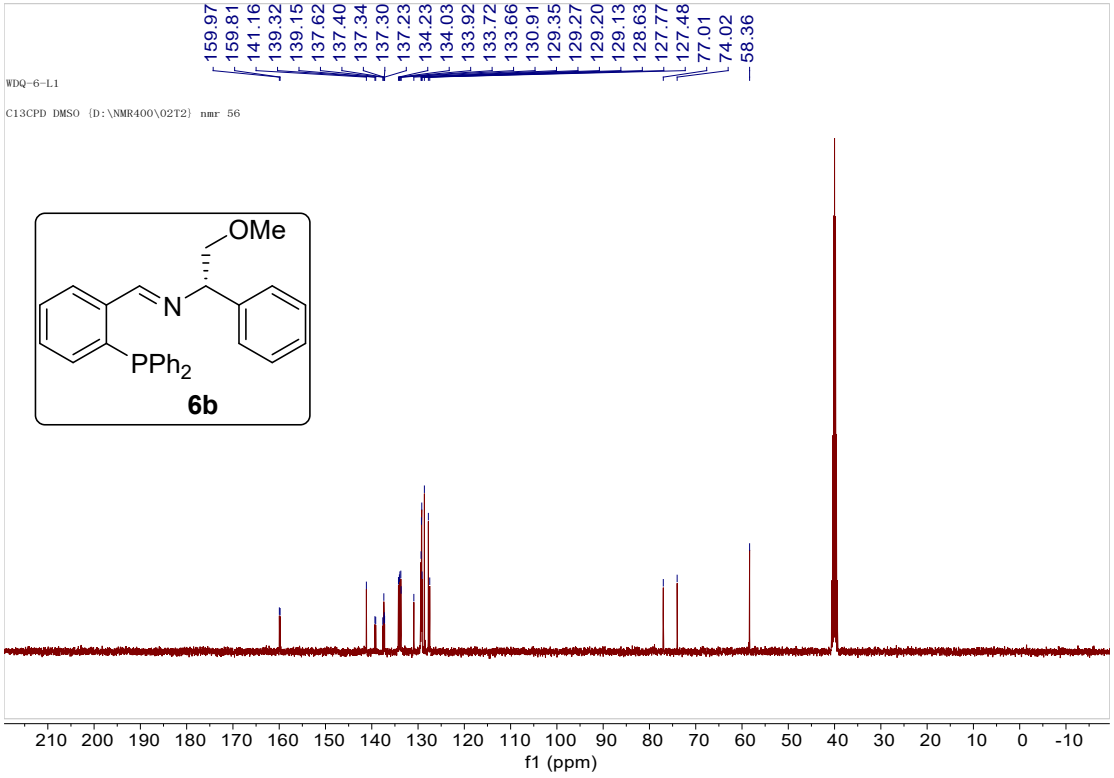
^{13}C NMR of **6a**



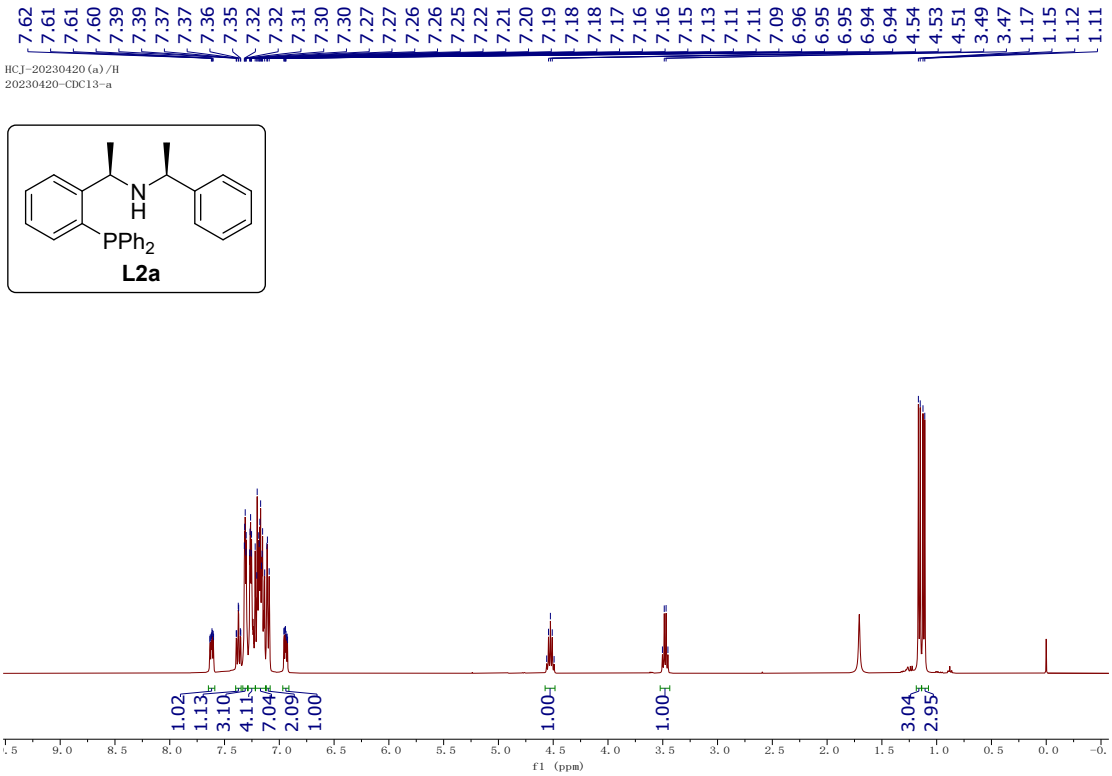
^{1}H NMR of **6b**



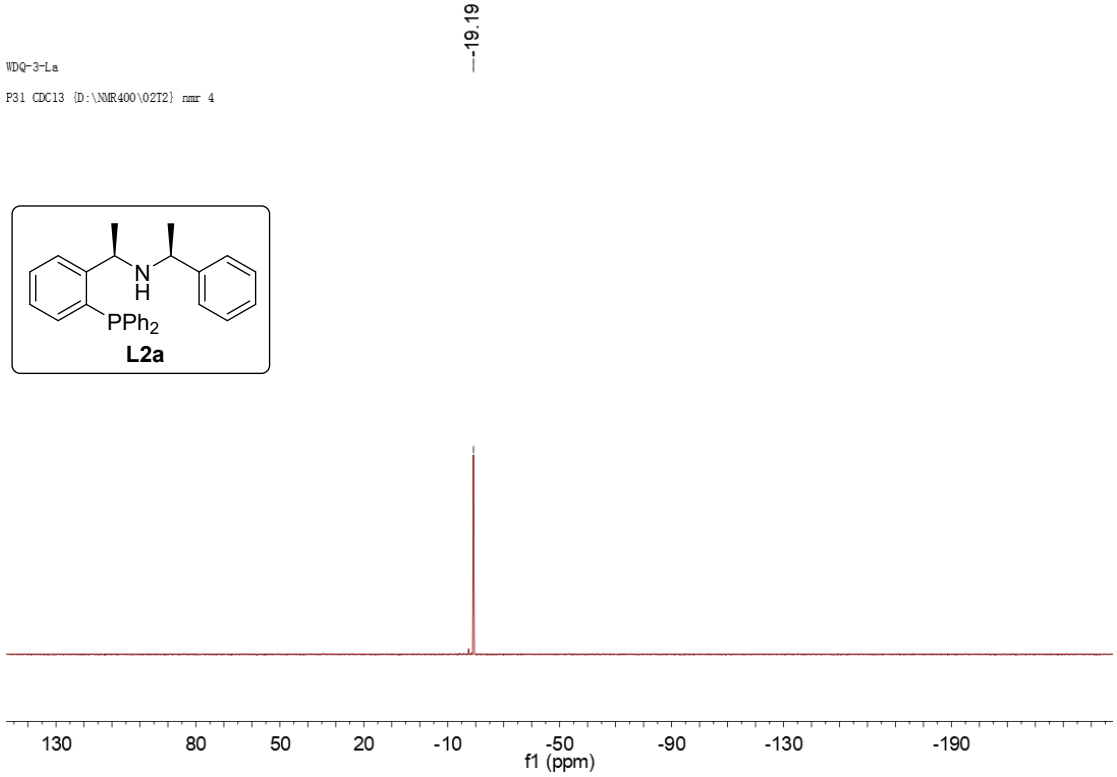
^{31}P NMR of **6b**



^{13}C NMR of **6b**



^{1}H NMR of **L2a**



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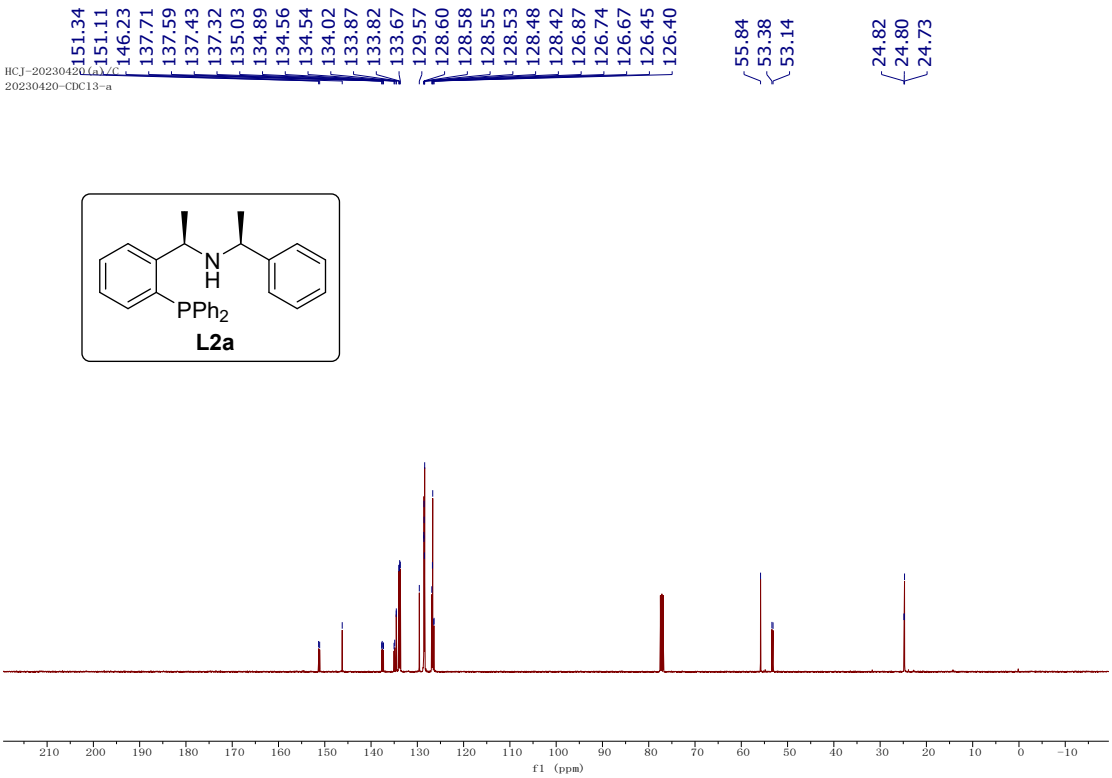
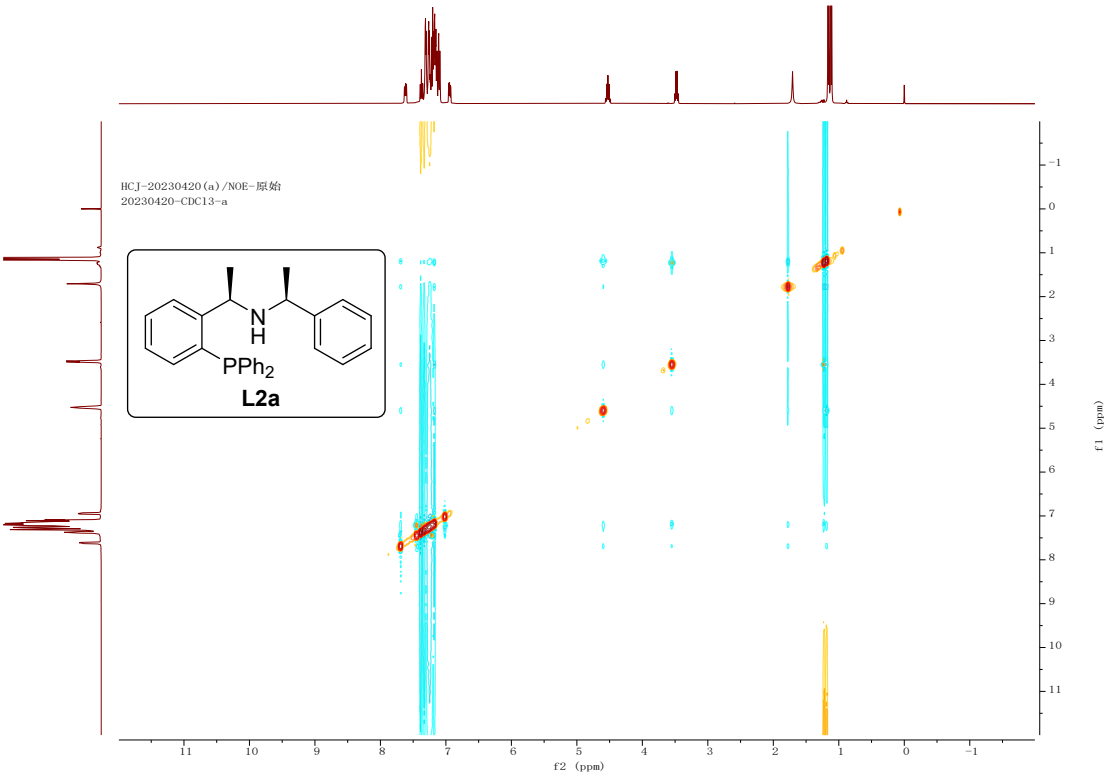
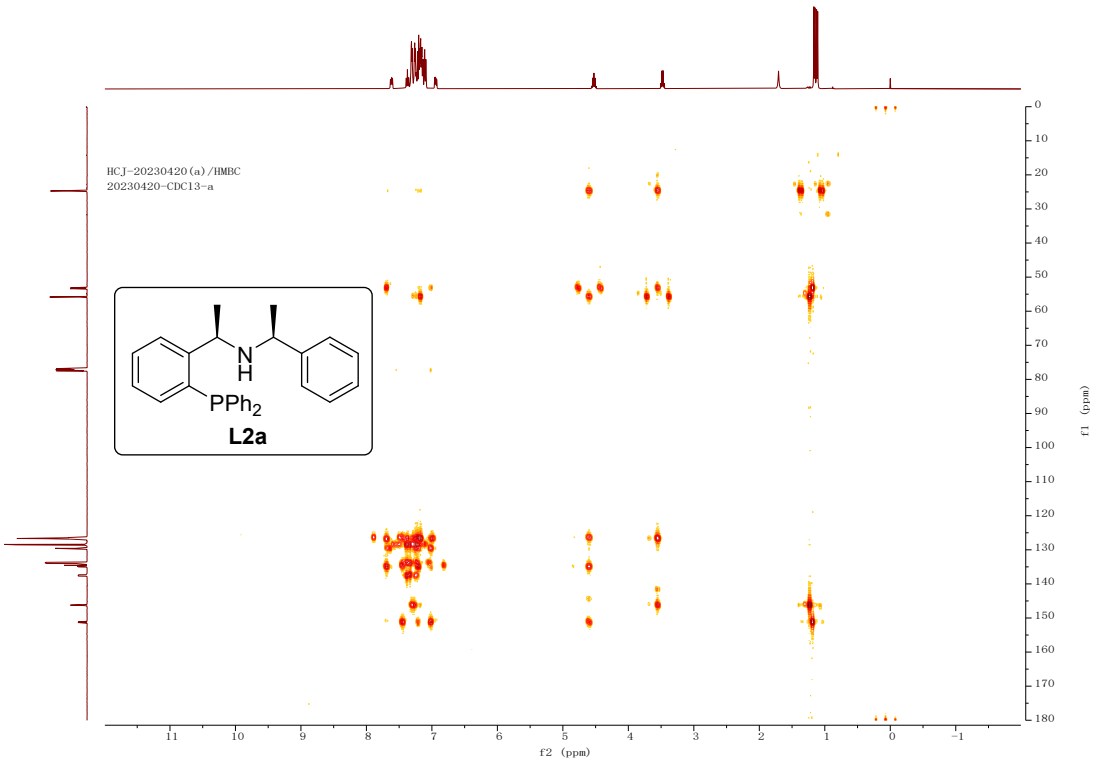


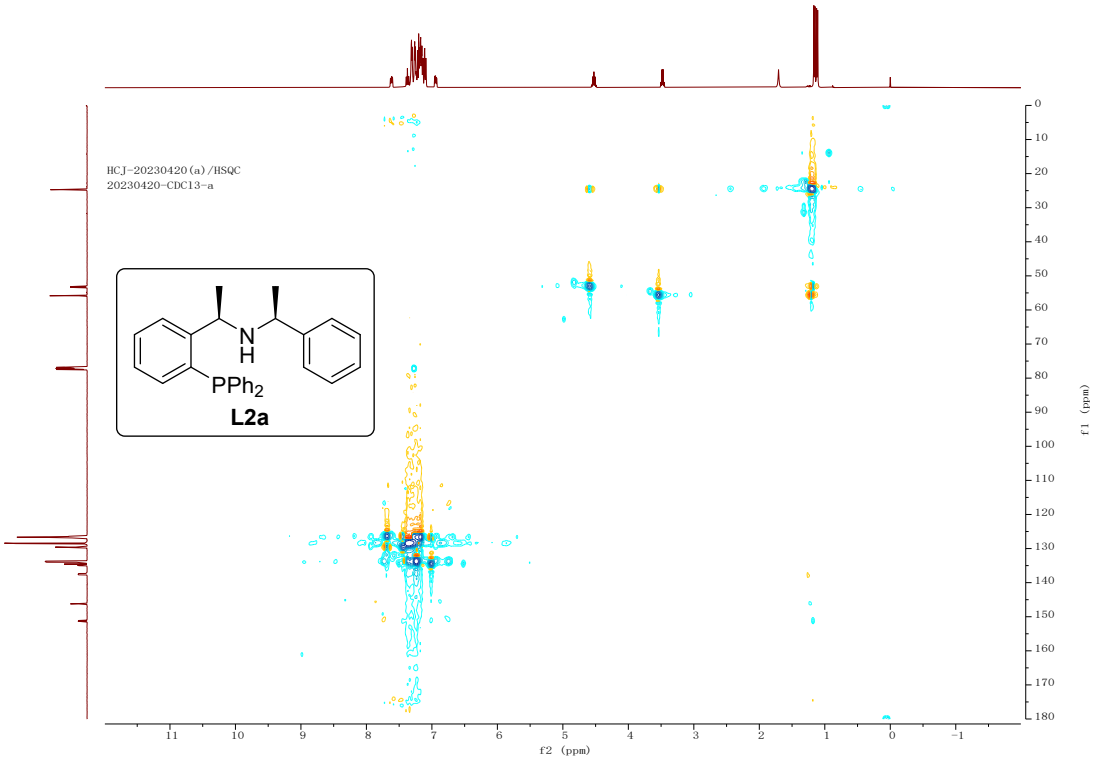
^{13}C NMR of **L2a**



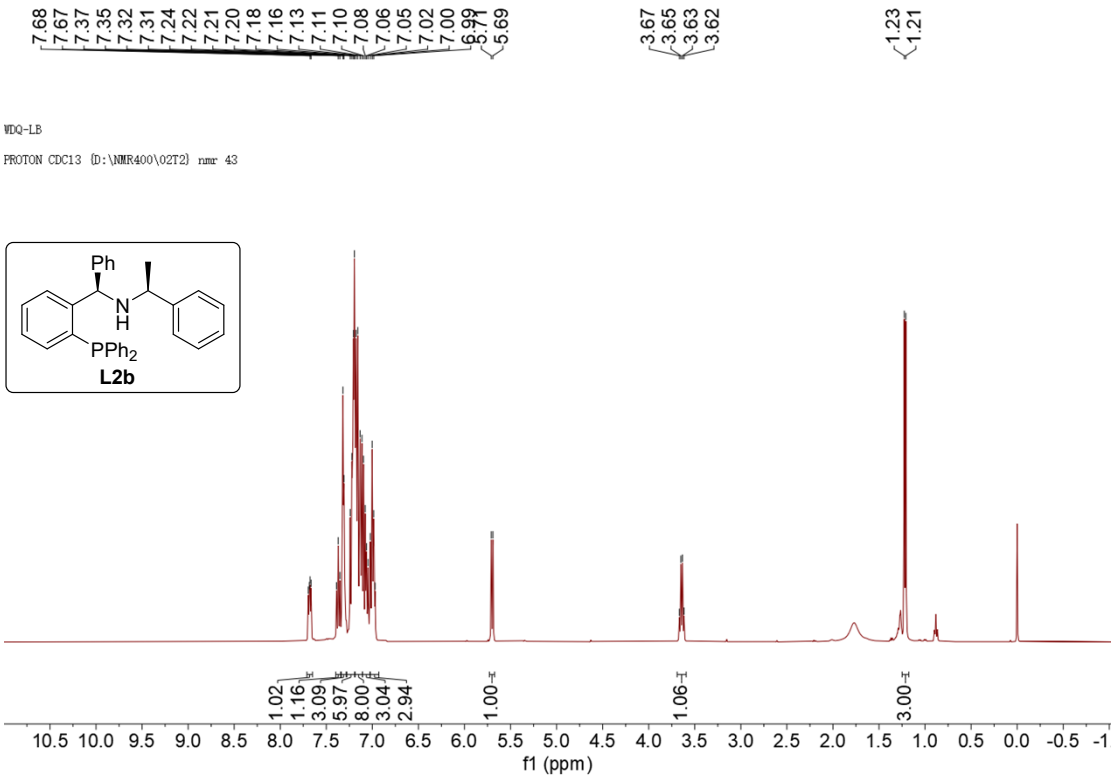
NOESY of **L2a**



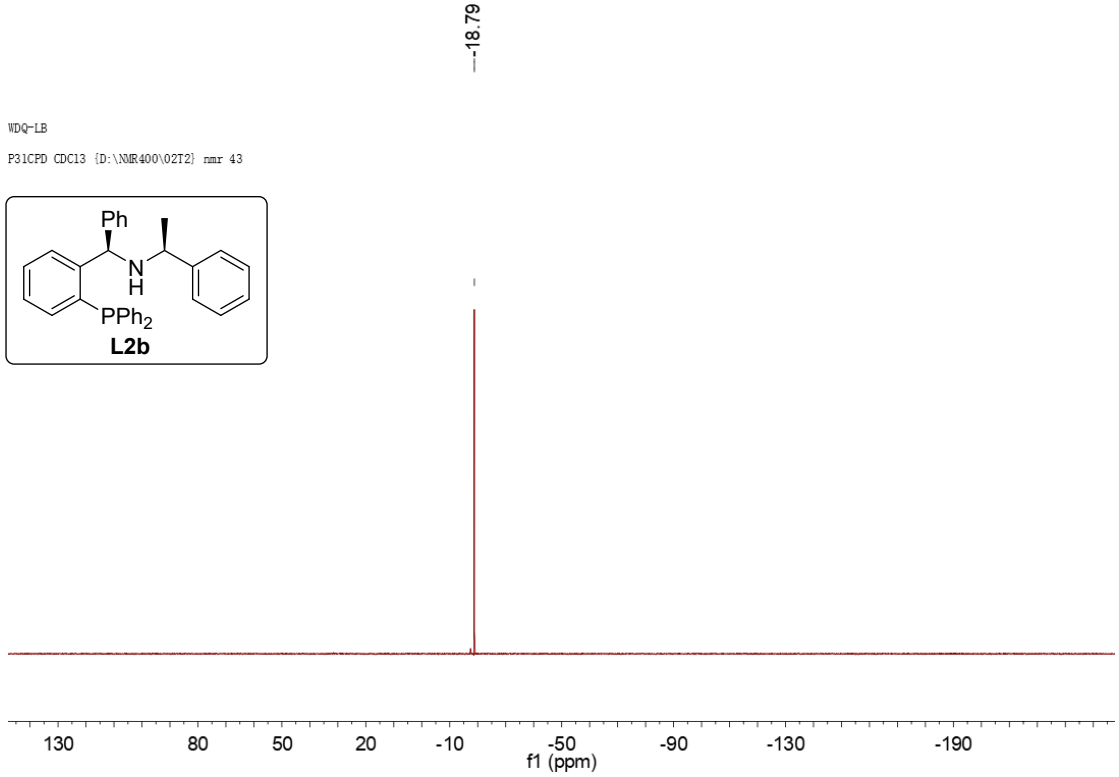
HMBC of **L2a**



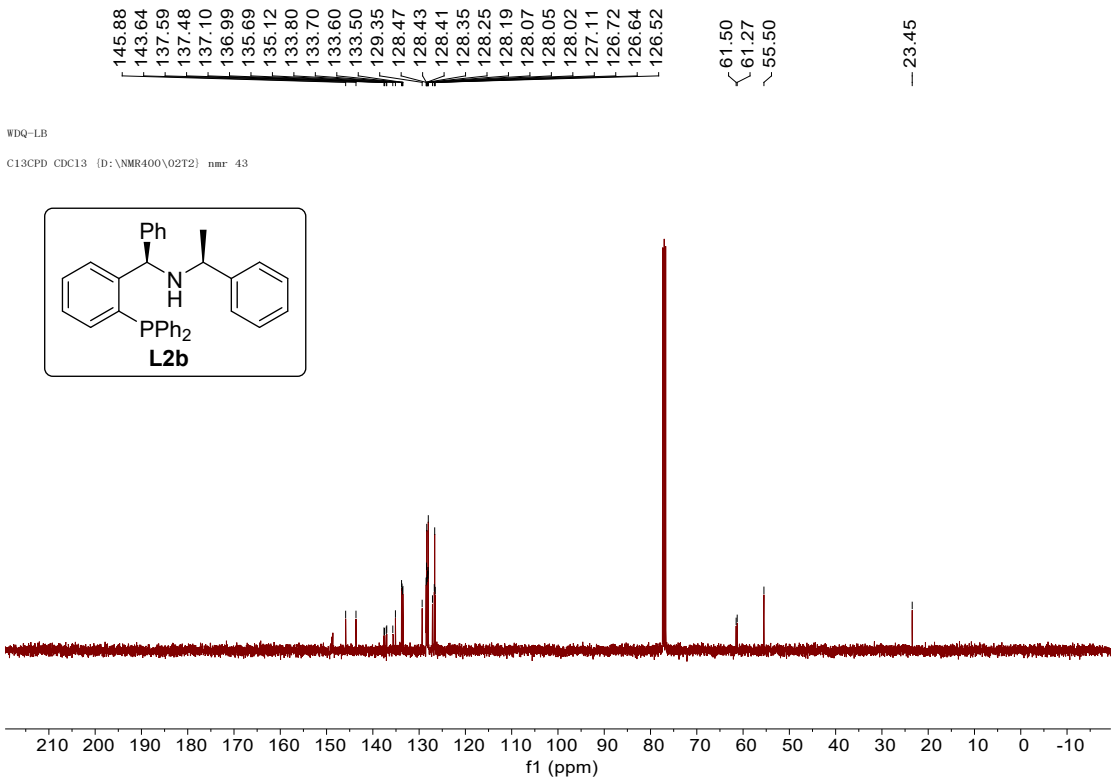
HSQC of **L2a**



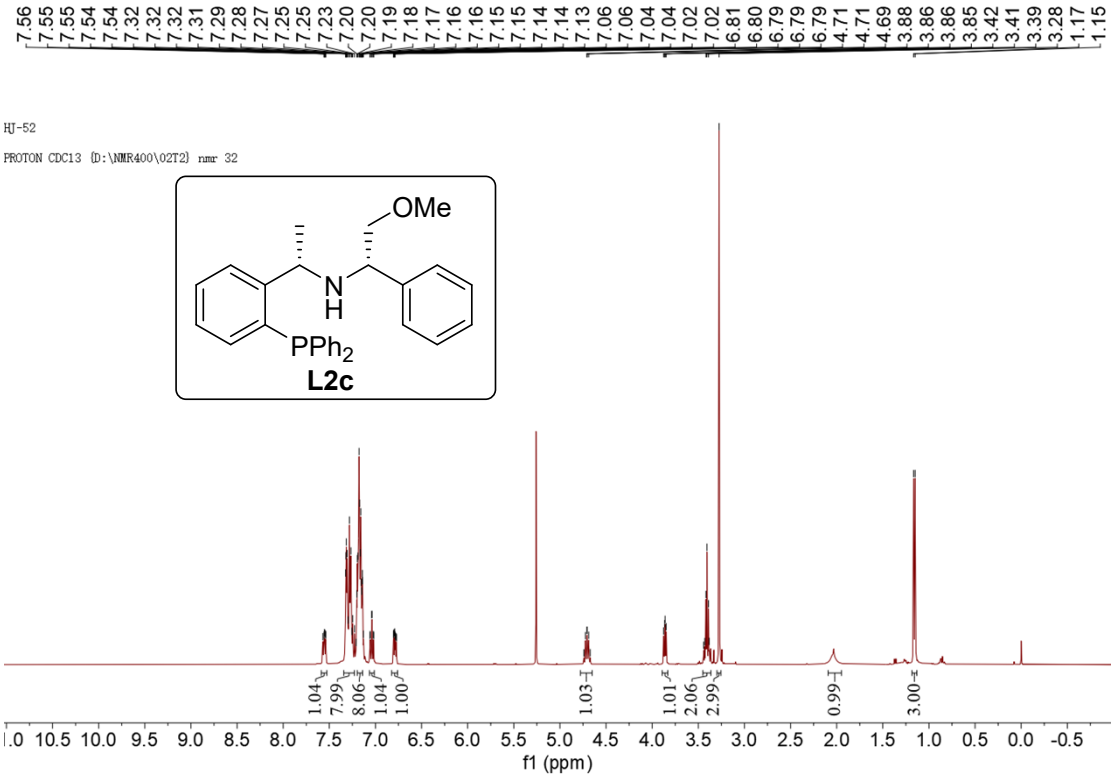
^{1}H NMR of **L2b**



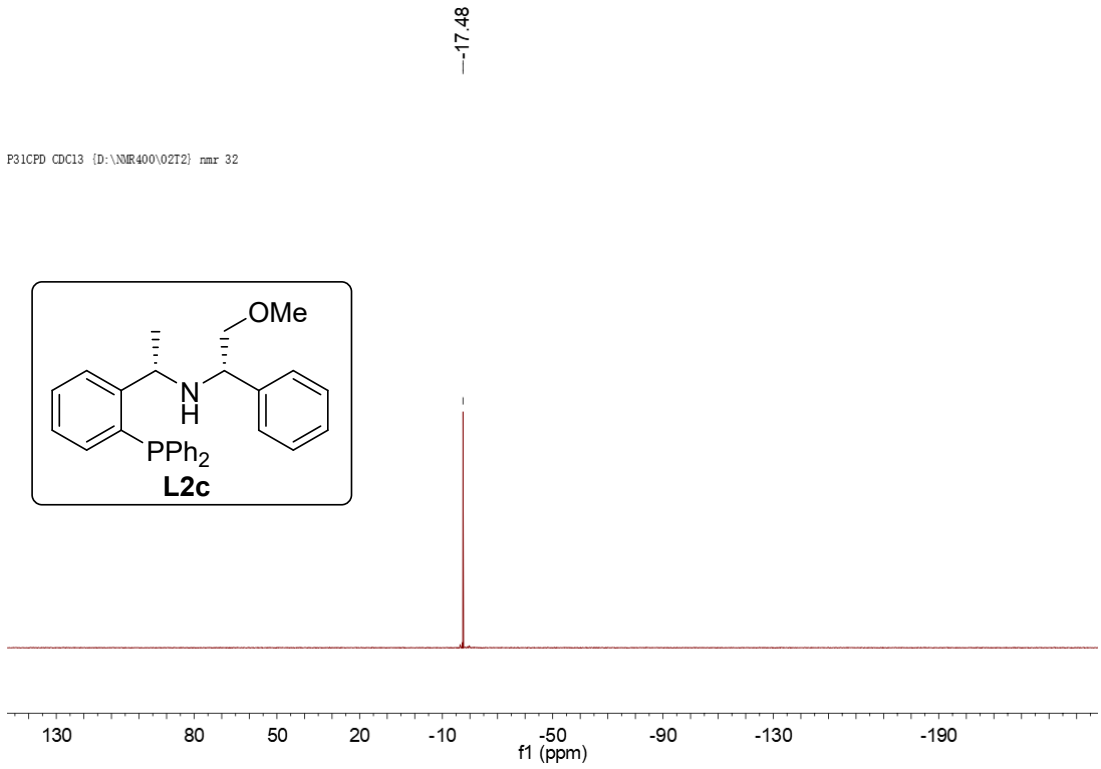
^{31}P NMR of **L2b**



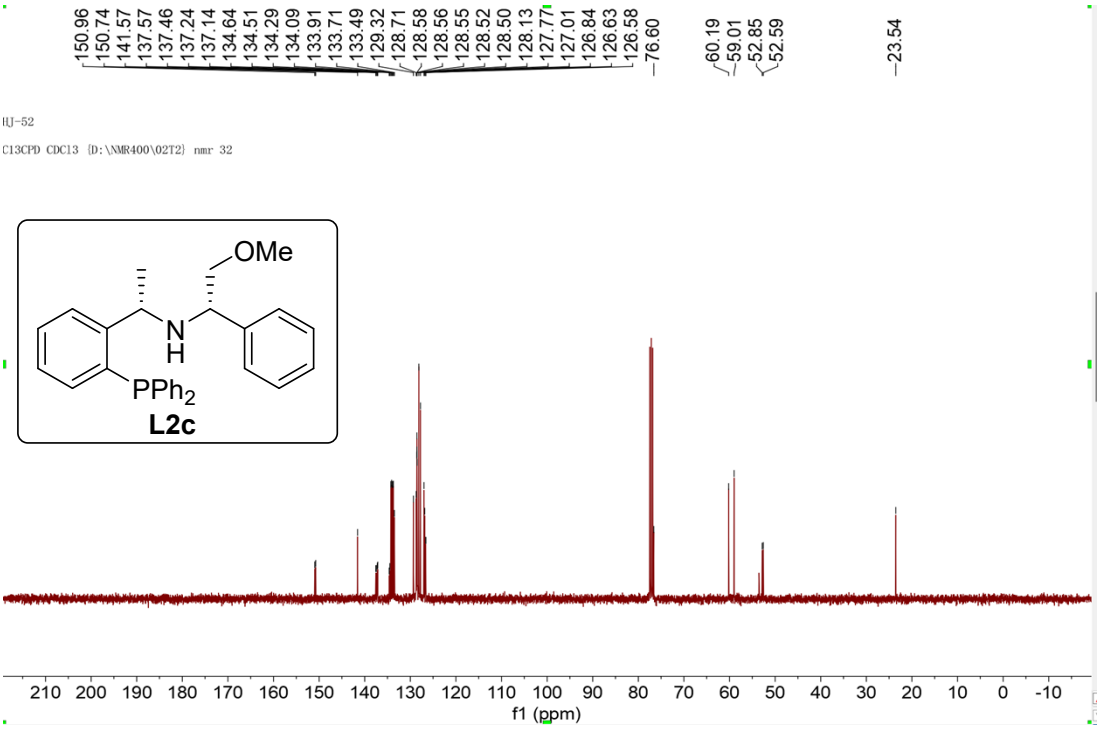
^{13}C NMR of **L2b**



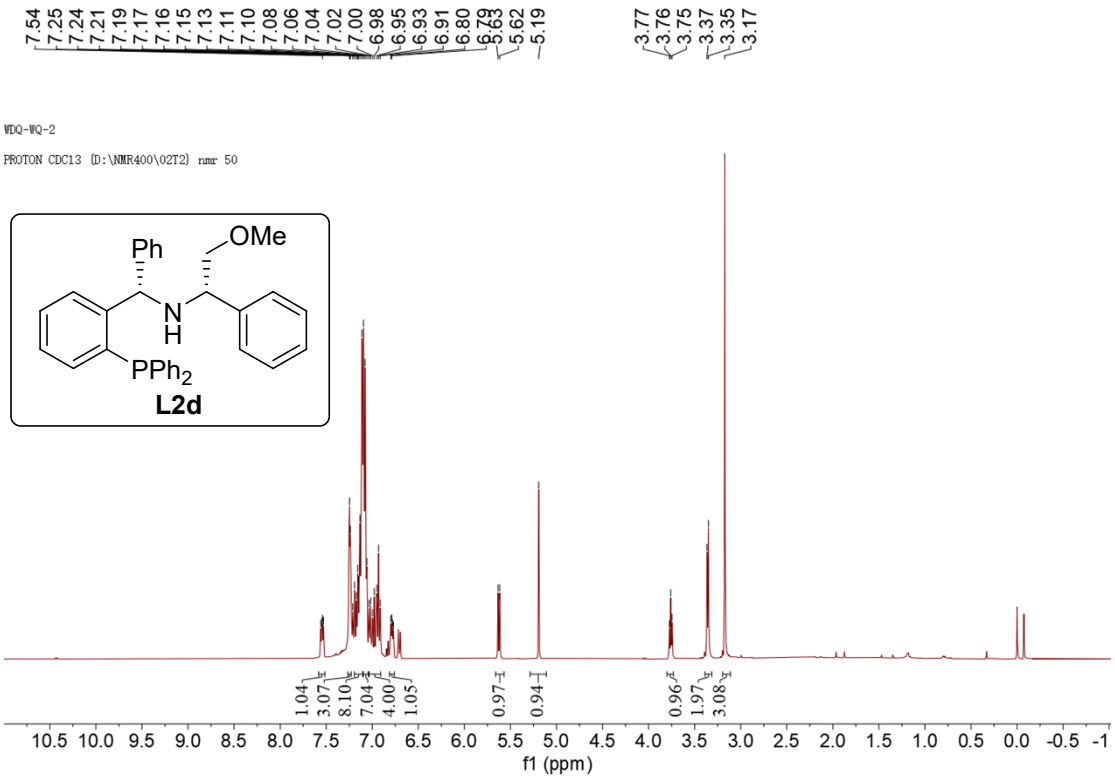
^{1}H NMR of **L2c**



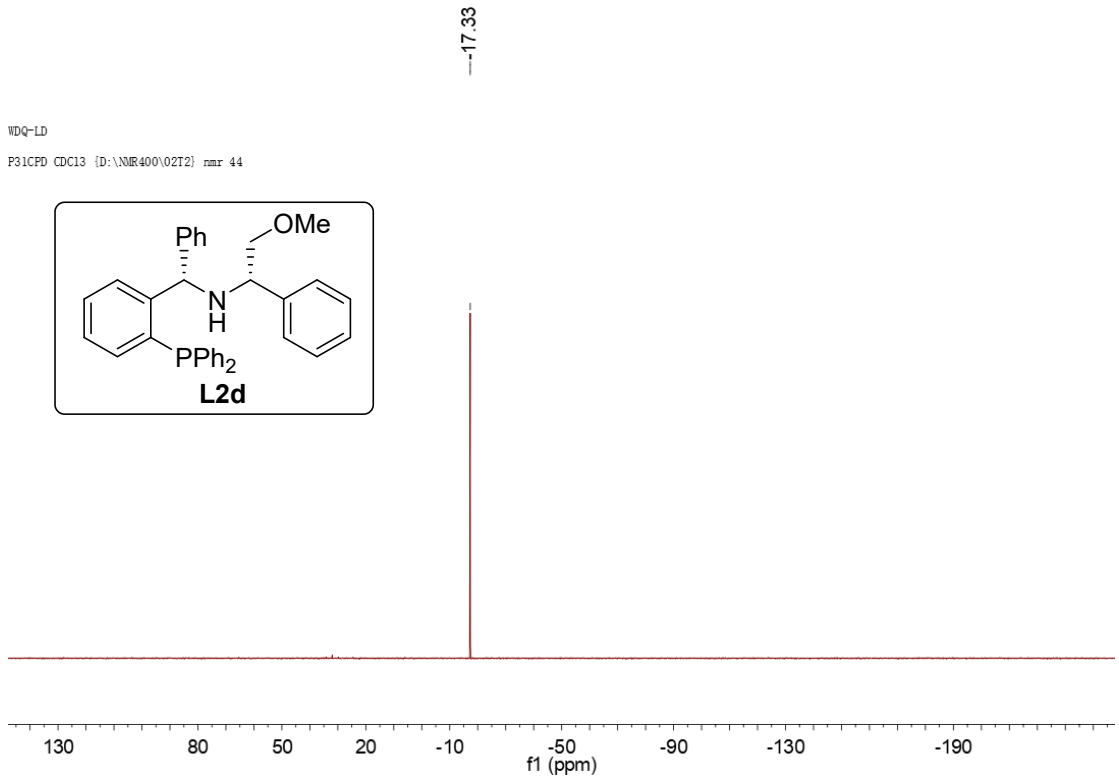
^{31}P NMR of **L2c**



^{13}C NMR of **L2c**



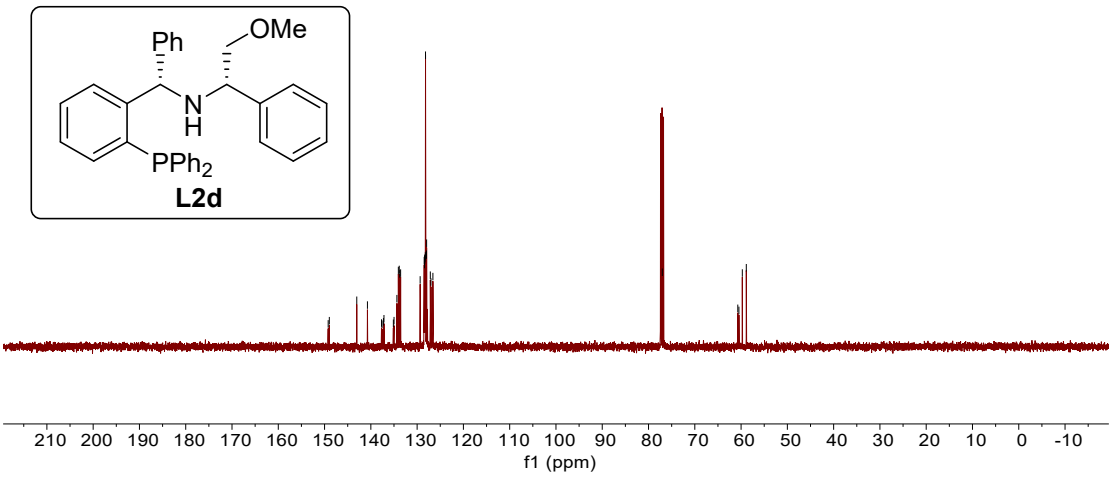
^{1}H NMR of **L2d**



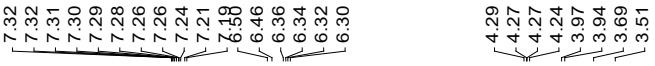
^{31}P NMR of **L2d**

WDQ-110

C13CPD CDC13 {D:\NMR400\02T2} nmr 34

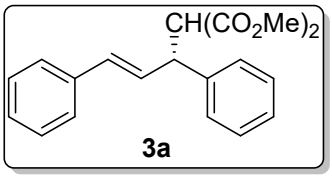


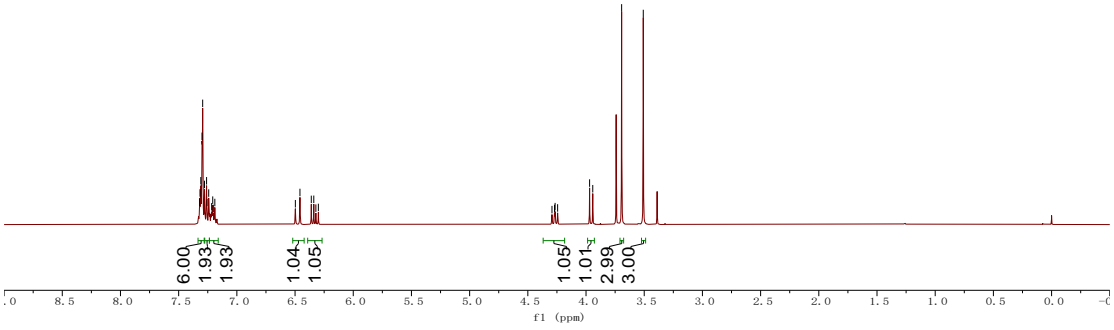
^{13}C NMR of **L2d**



WDQ-2-161

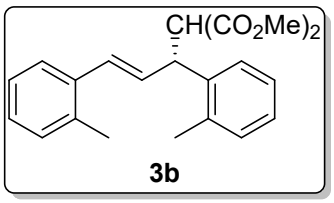
PROTON CDC13 {D:\NMR400\02T2} nmr 56

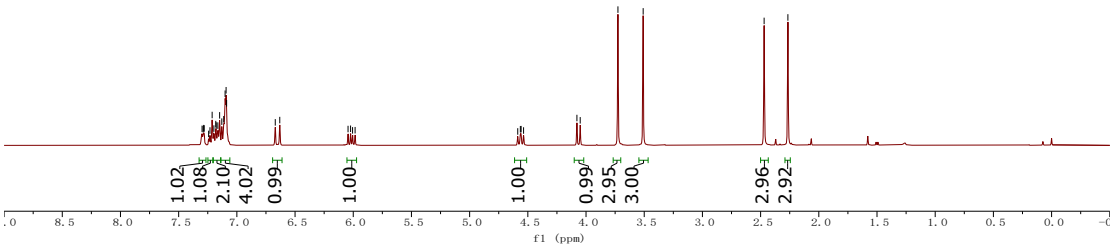




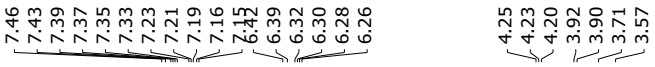
^{1}H NMR of **3a**

168-13.10.fid
PROTON CDC13 {D:\NMR400\02T2} nmr 50

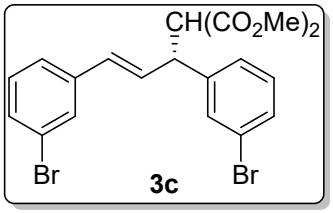


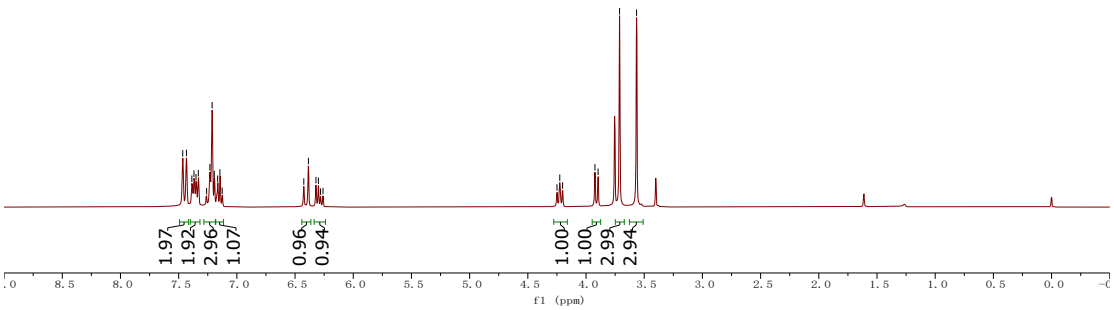


^{1}H NMR of **3b**

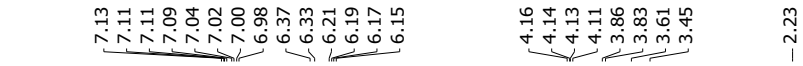


168-11.10.fid
PROTON CDC13 {D:\NMR400\02T2} nmr 34

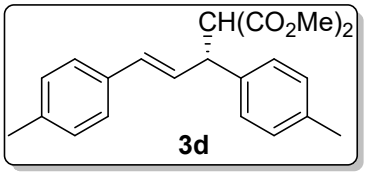


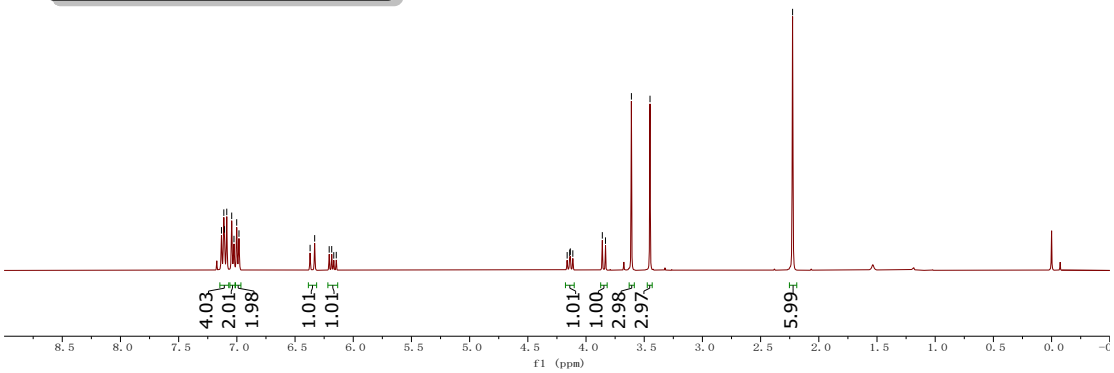


^{1}H NMR of **3c**

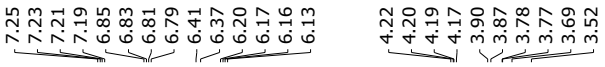


WDQ-3-168-5.10.fid
PROTON CDC13 (D:\NMR400\506) nmr 32

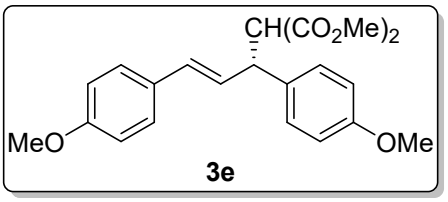


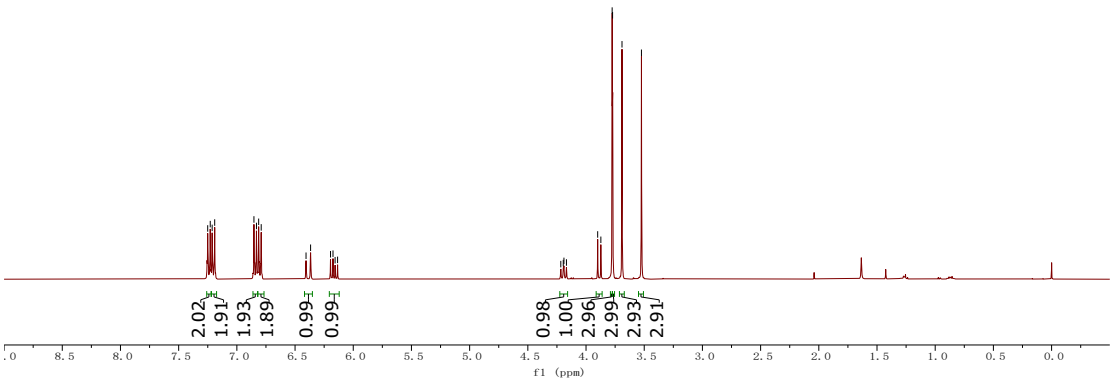


^{1}H NMR of **3d**

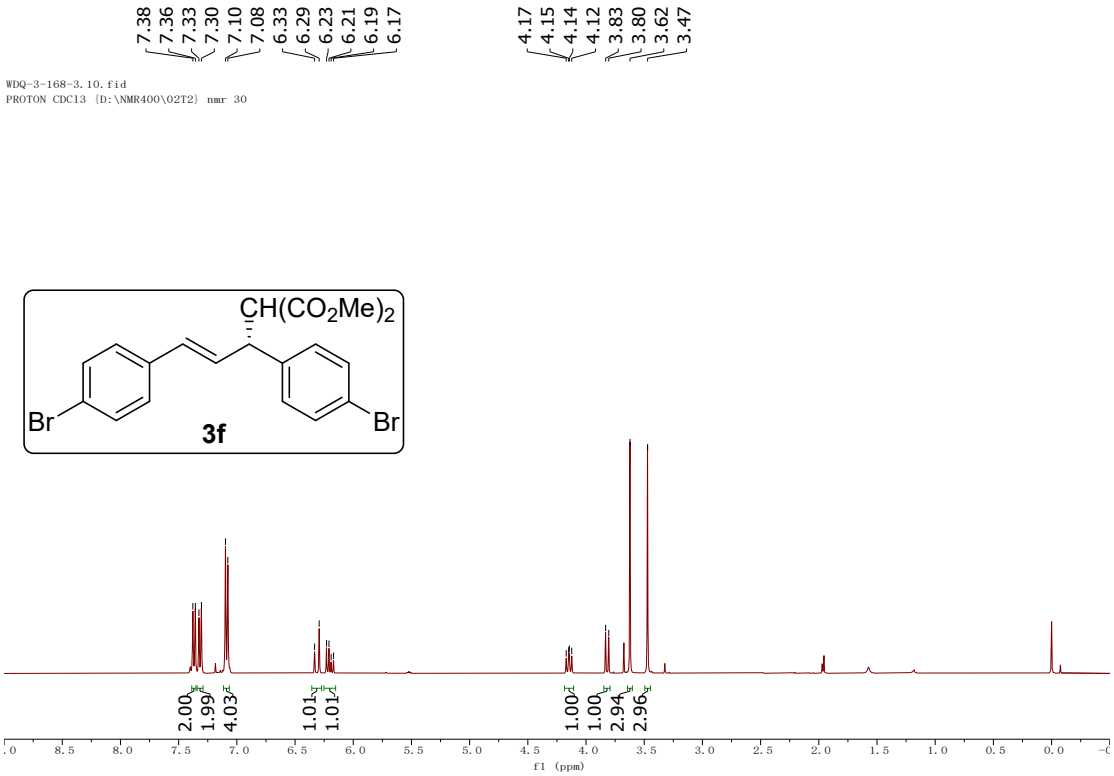


WDQ-168-2.10.fid
PROTON CDC13 (D:\NMR400\02T2) nmr 57

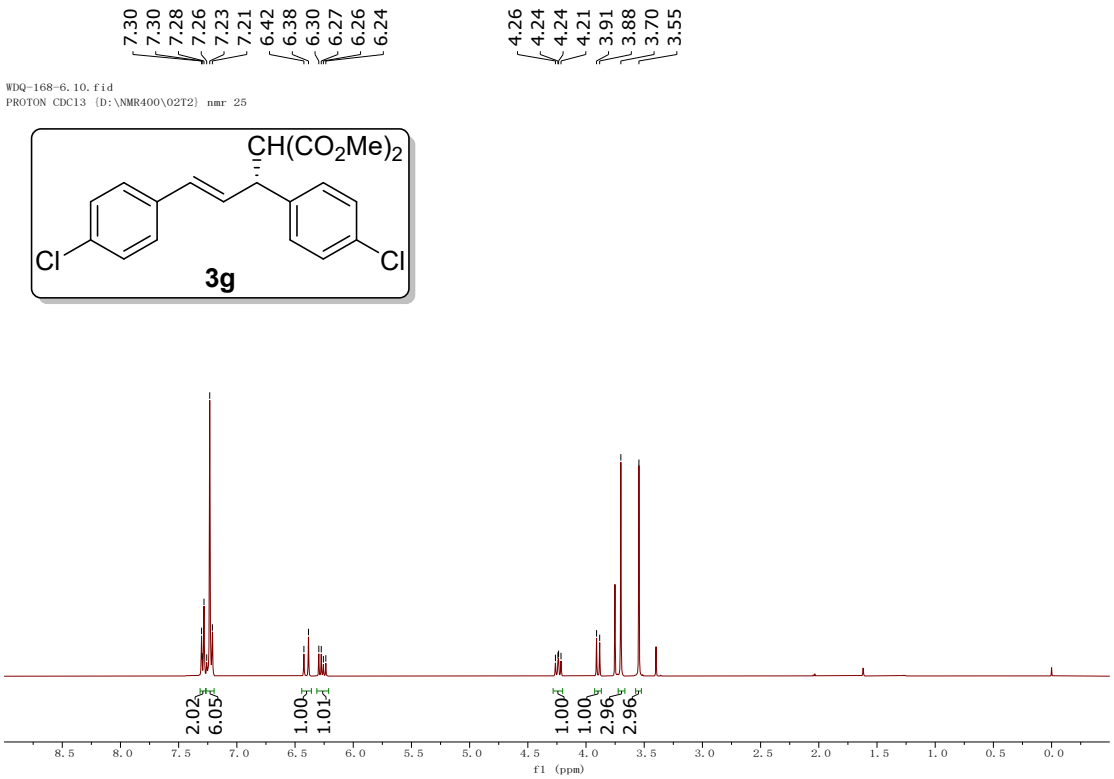




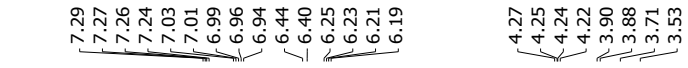
^{1}H NMR of **3e**



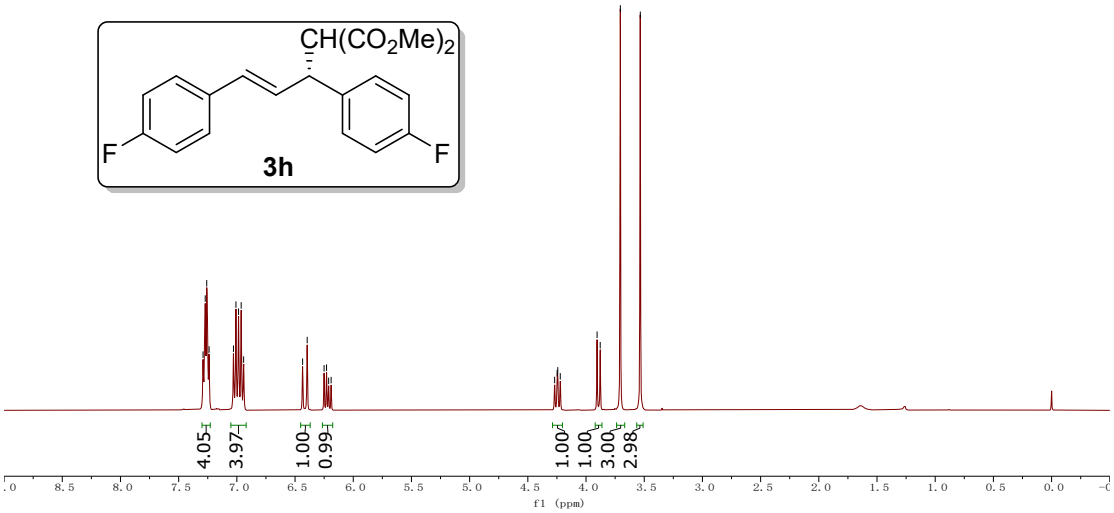
^{1}H NMR of **3f**



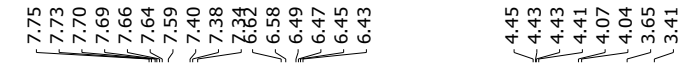
^{1}H NMR of **3g**



WDQ-3-168-4.10.fid
PROTON CDC13 (D:\NMR400\02T2) nmr 31



^{1}H NMR of **3h**



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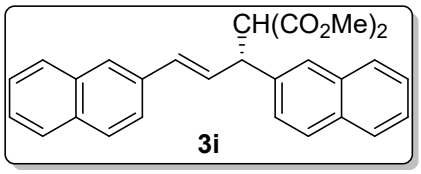
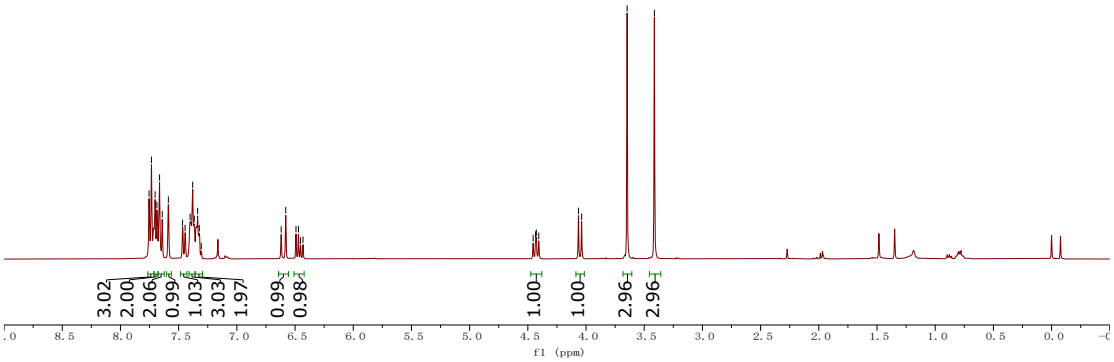
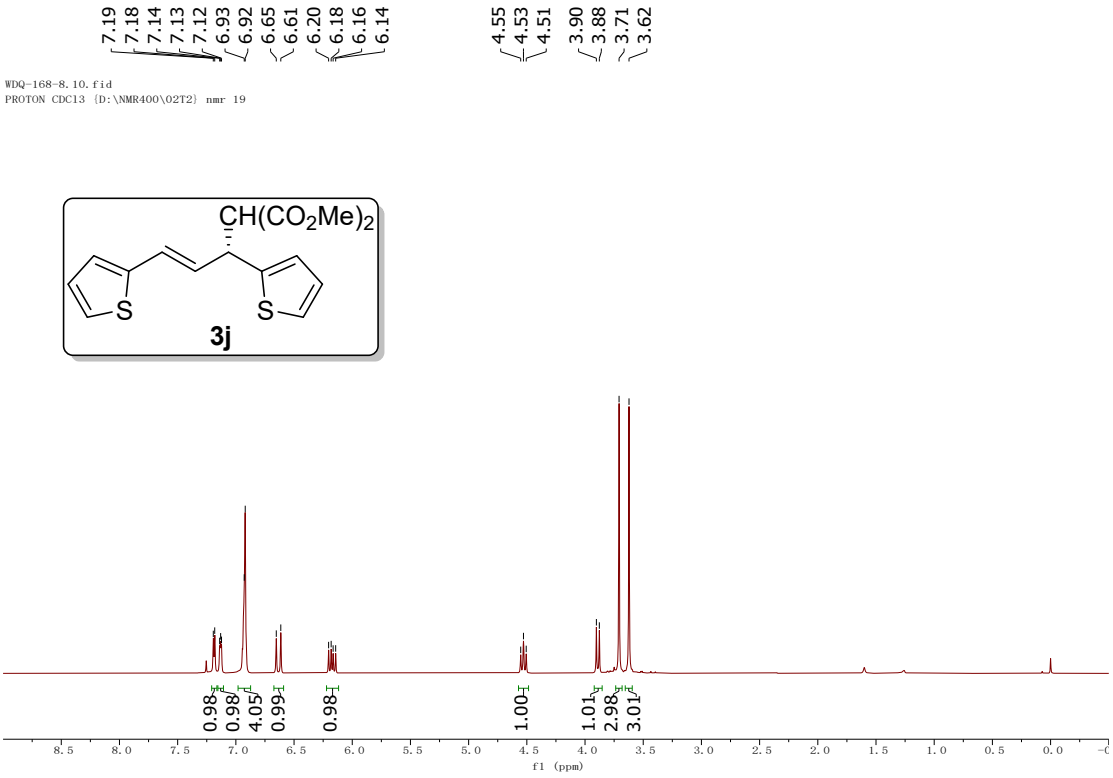
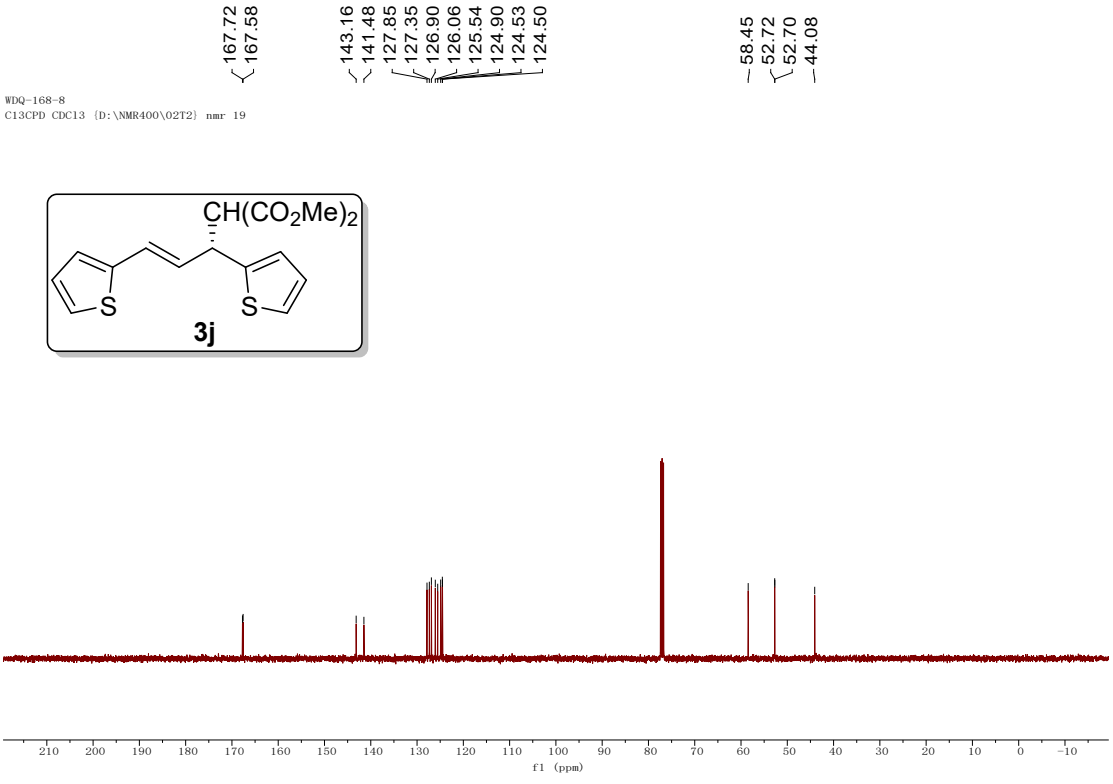




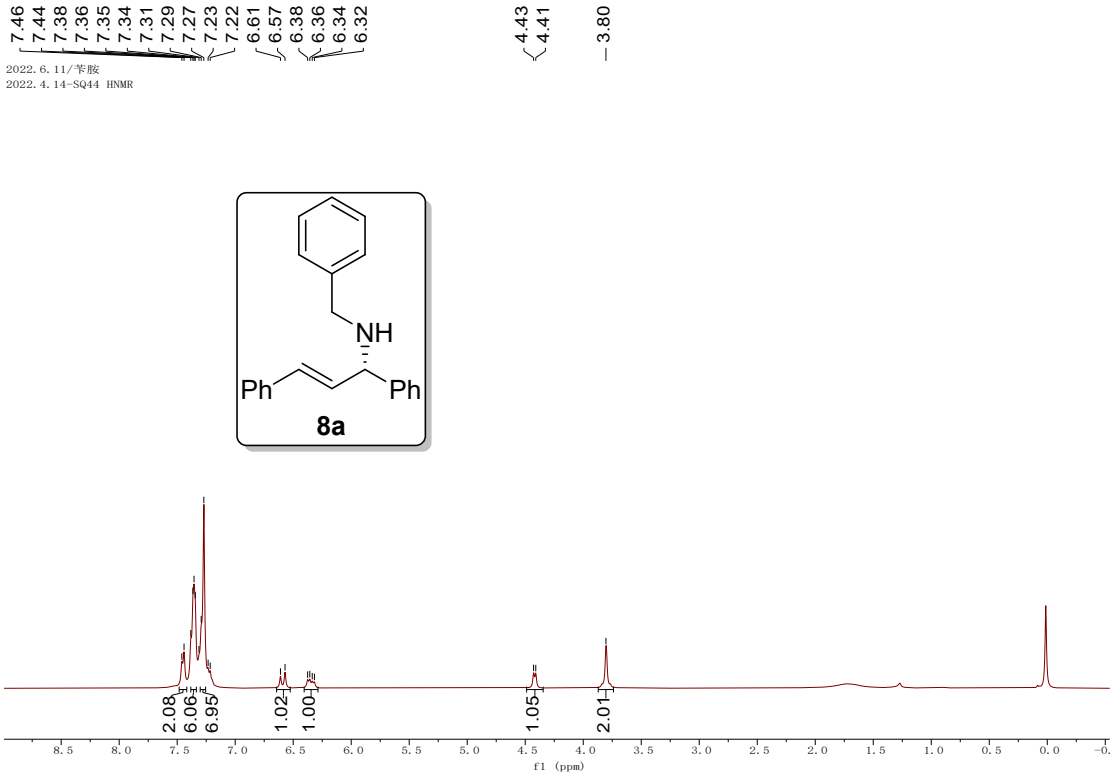
^{1}H NMR of **3i**



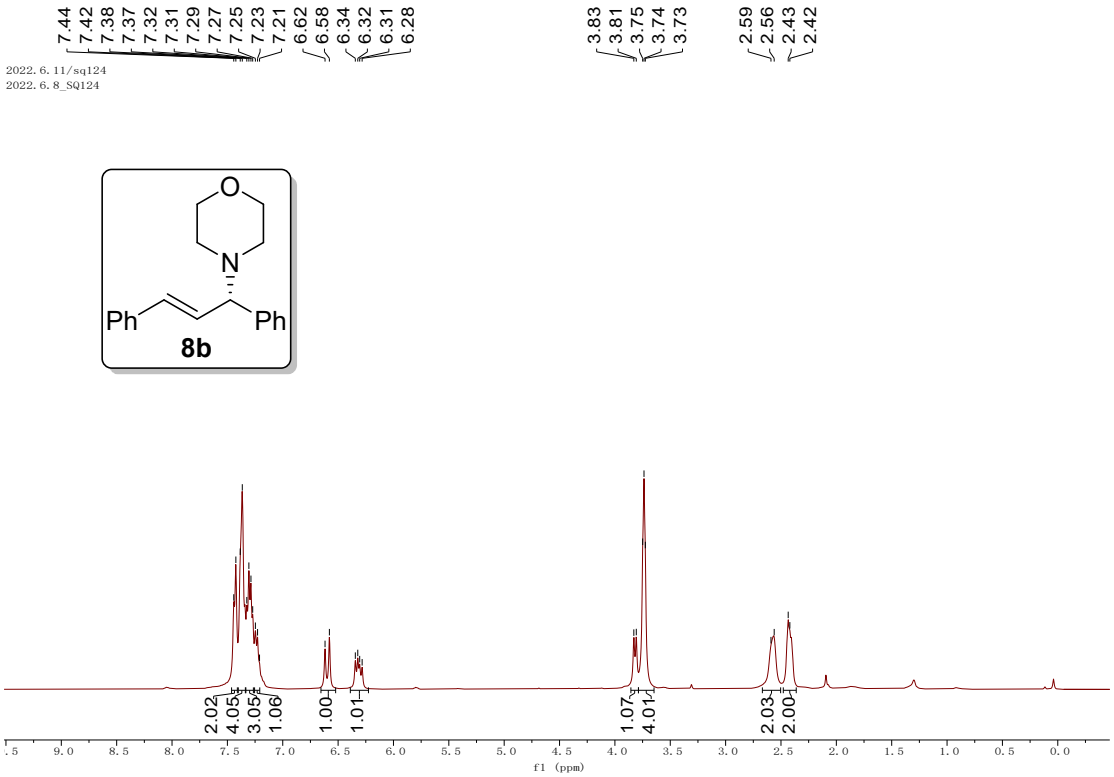
^{1}H NMR of **3j**



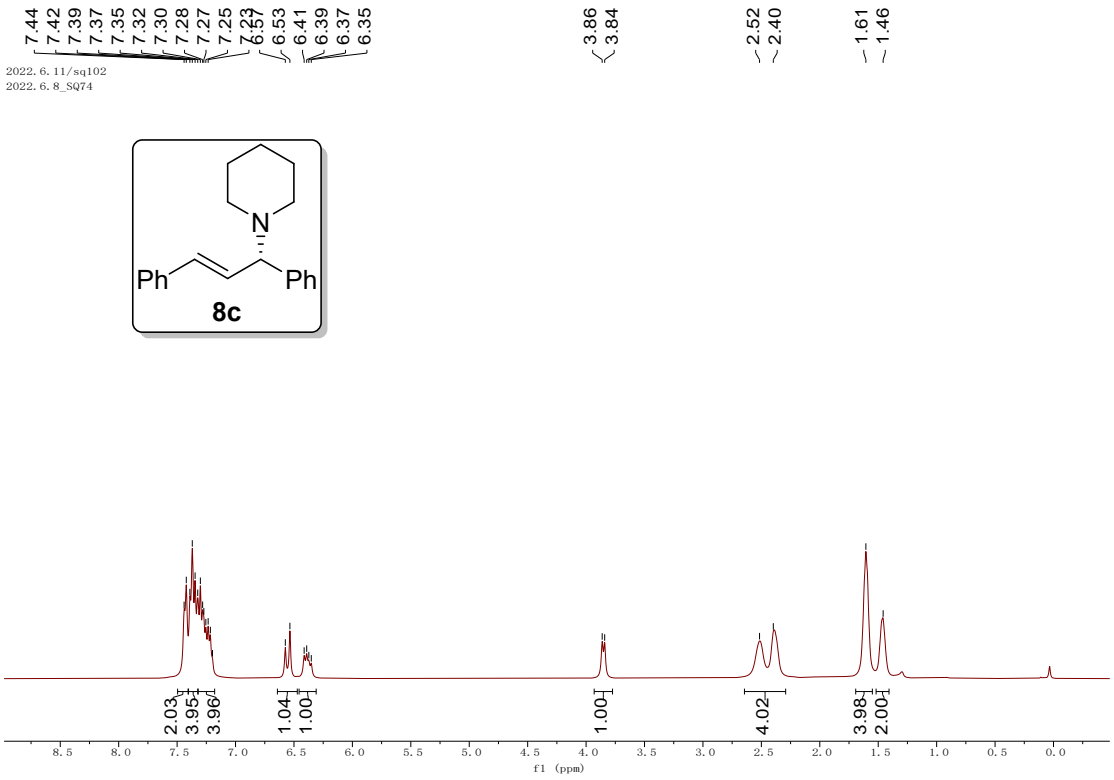
^{13}C NMR of **3j**



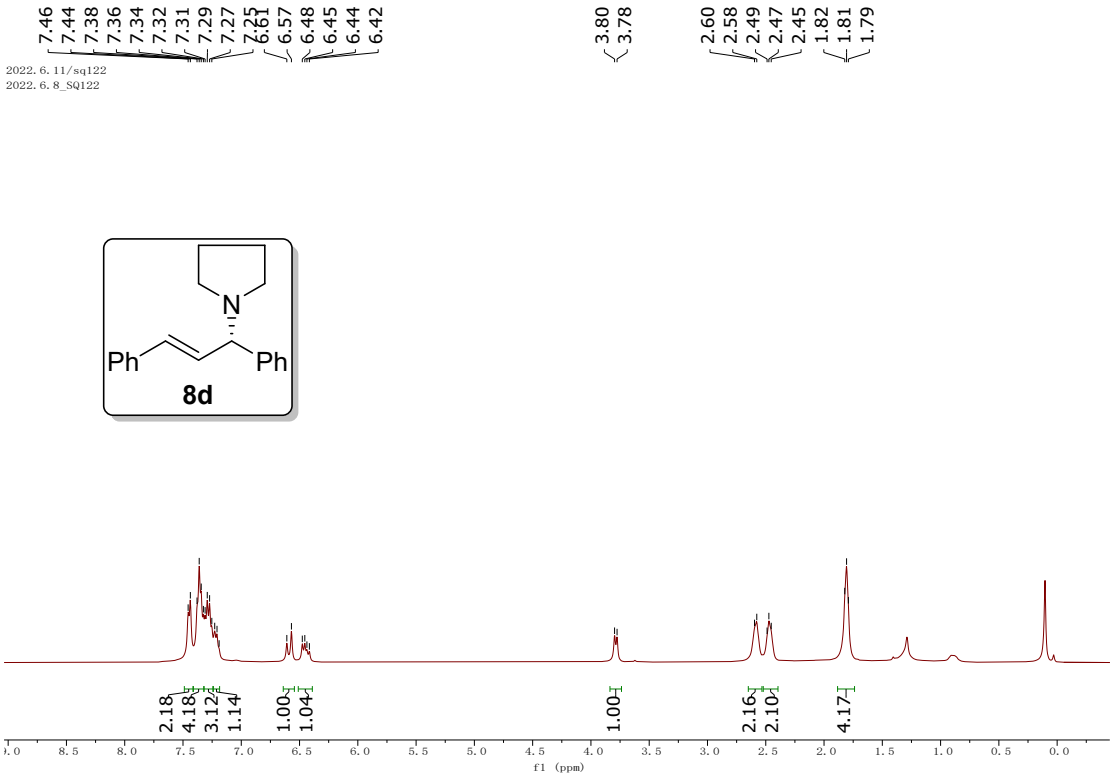
^{1}H NMR of **8a**



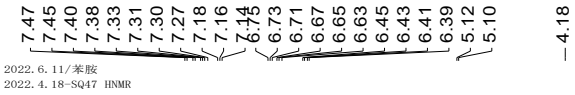
^{1}H NMR of **8b**

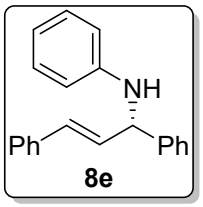


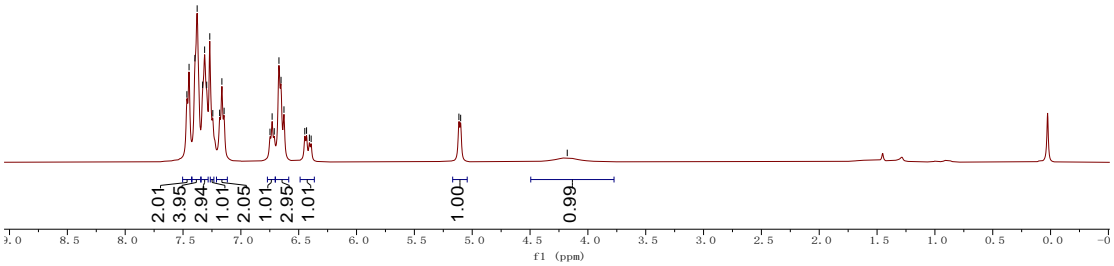
^{1}H NMR of **8c**



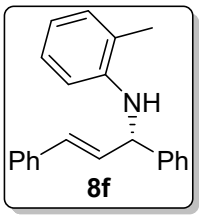
^{1}H NMR of **8d**

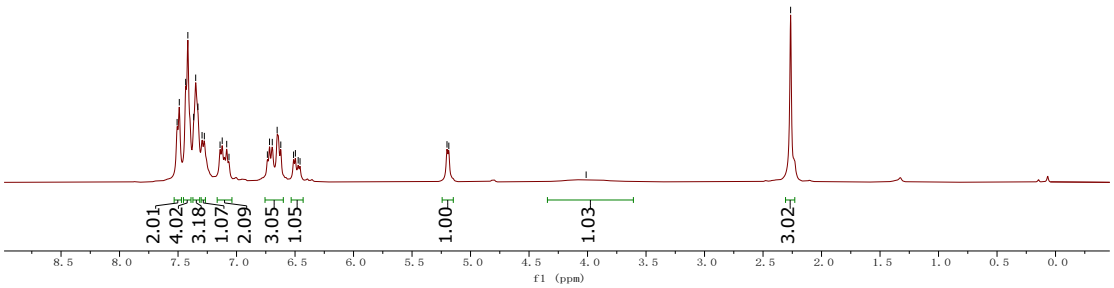




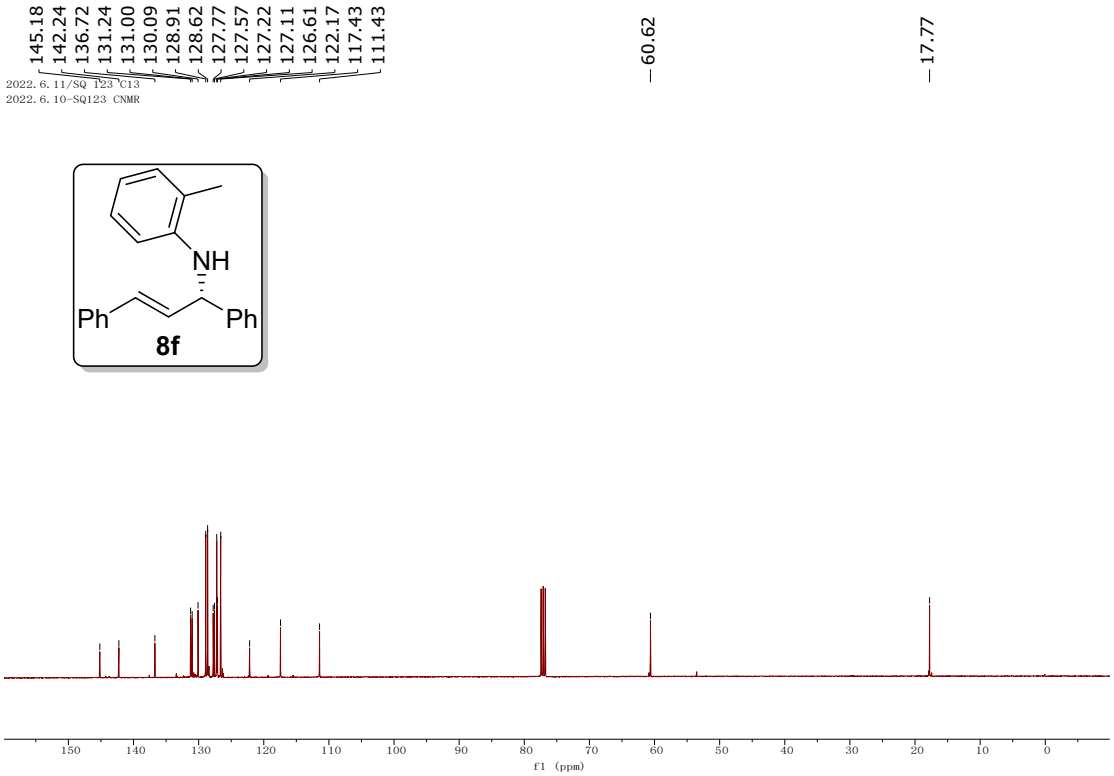


^{1}H NMR of **8e**

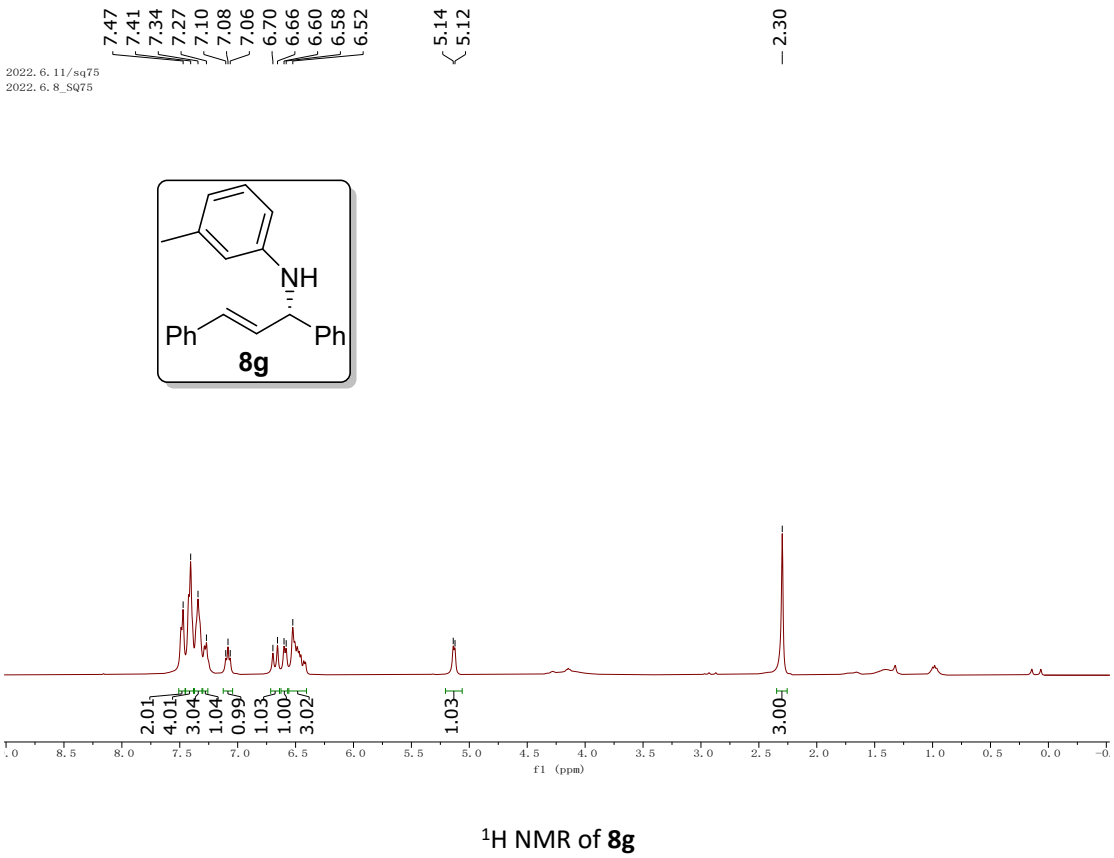




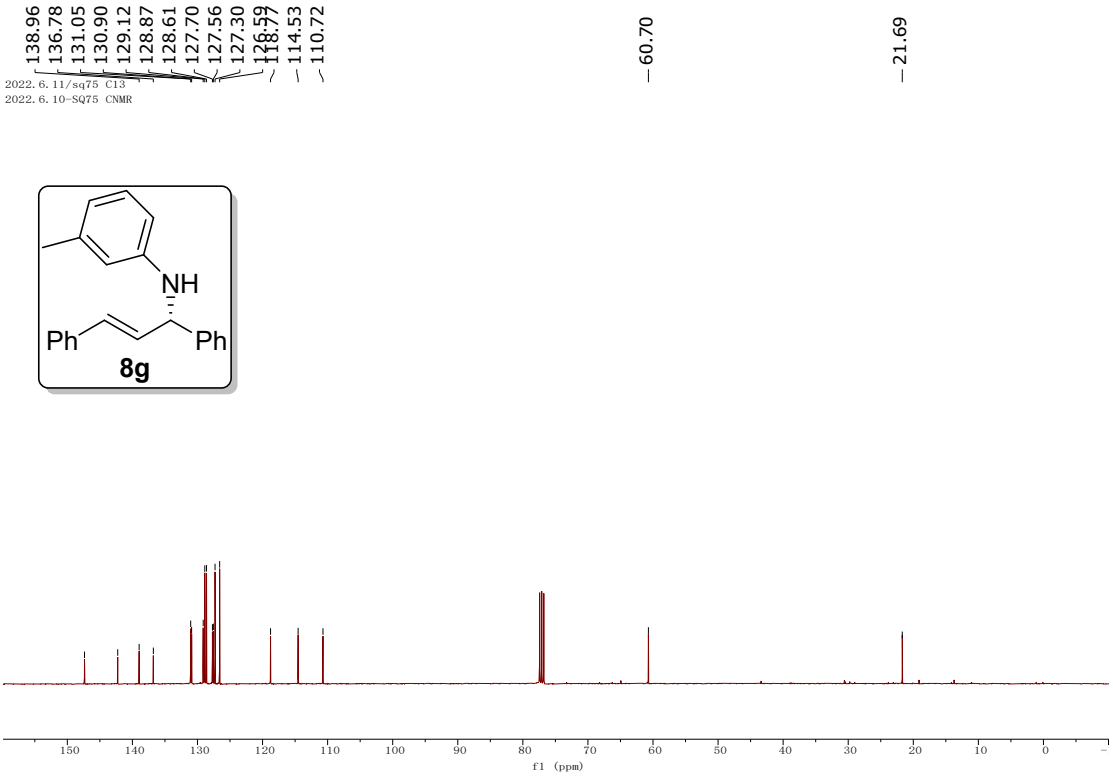
^{1}H NMR of **8f**



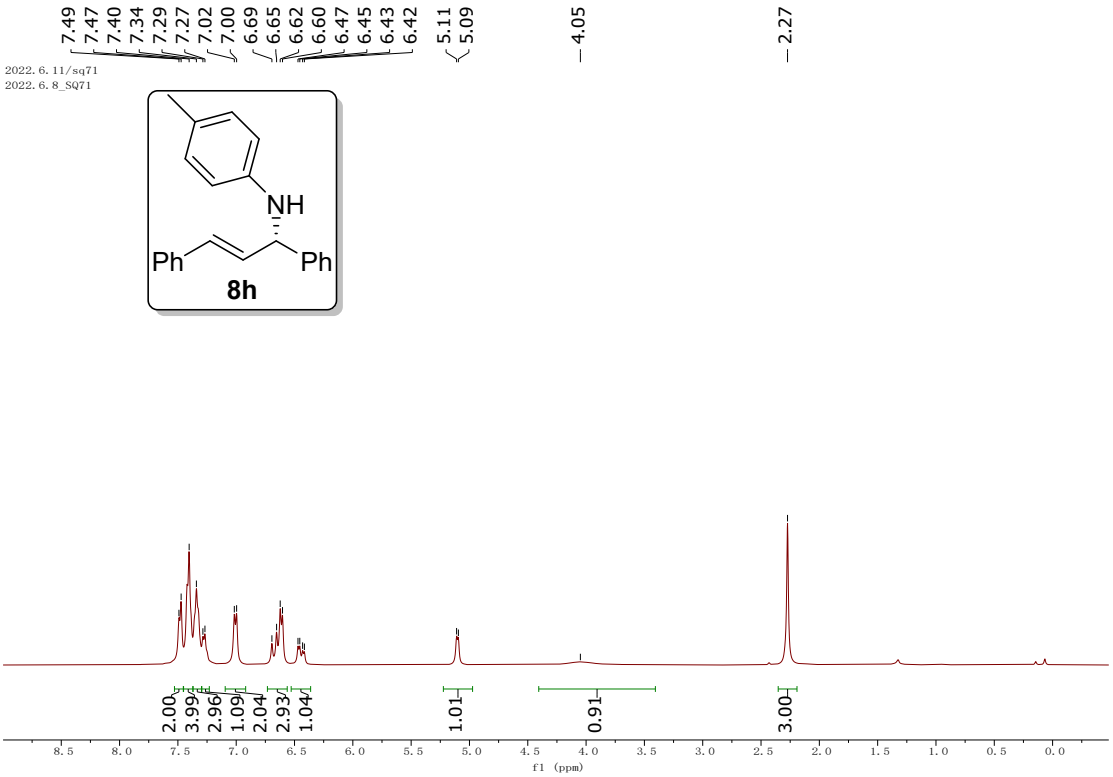
^{13}C NMR of **8f**



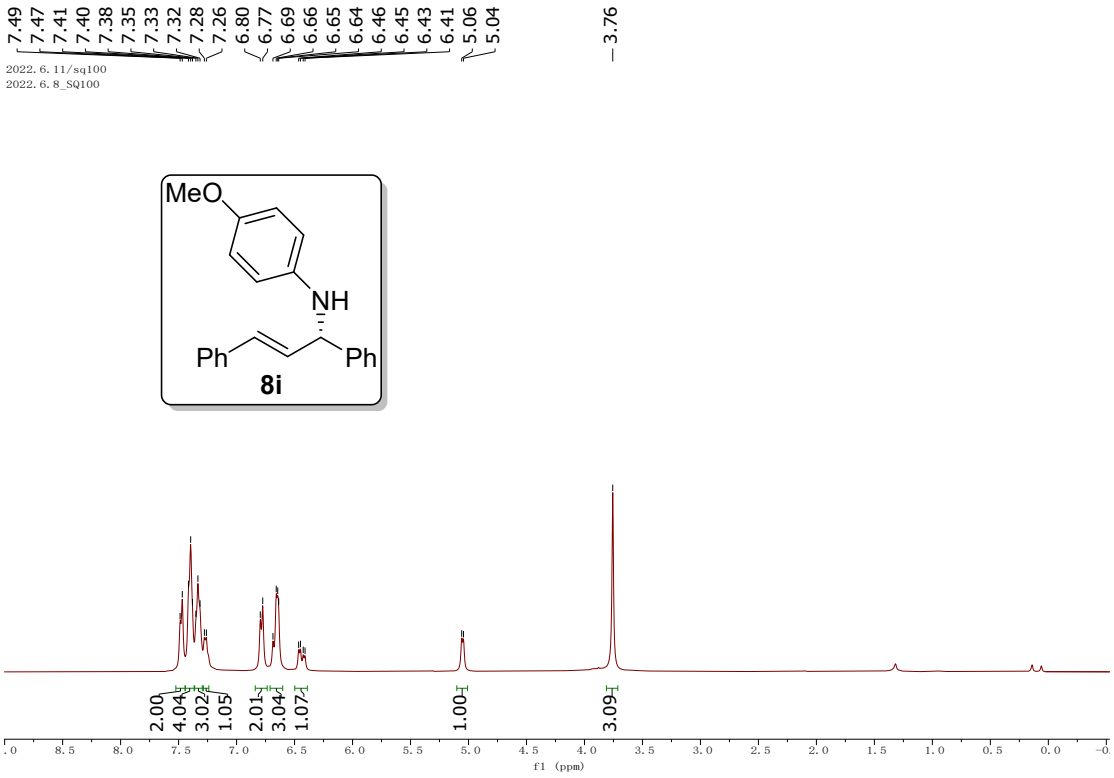
^{1}H NMR of **8g**



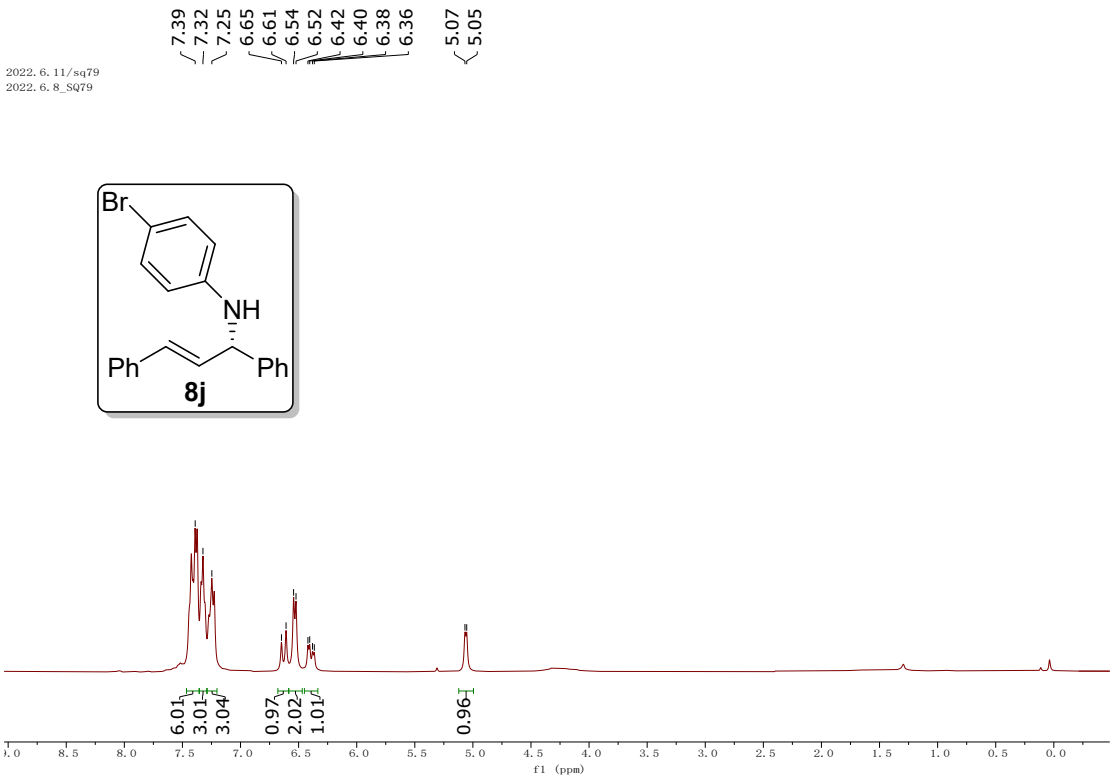
^{13}C NMR of **8g**



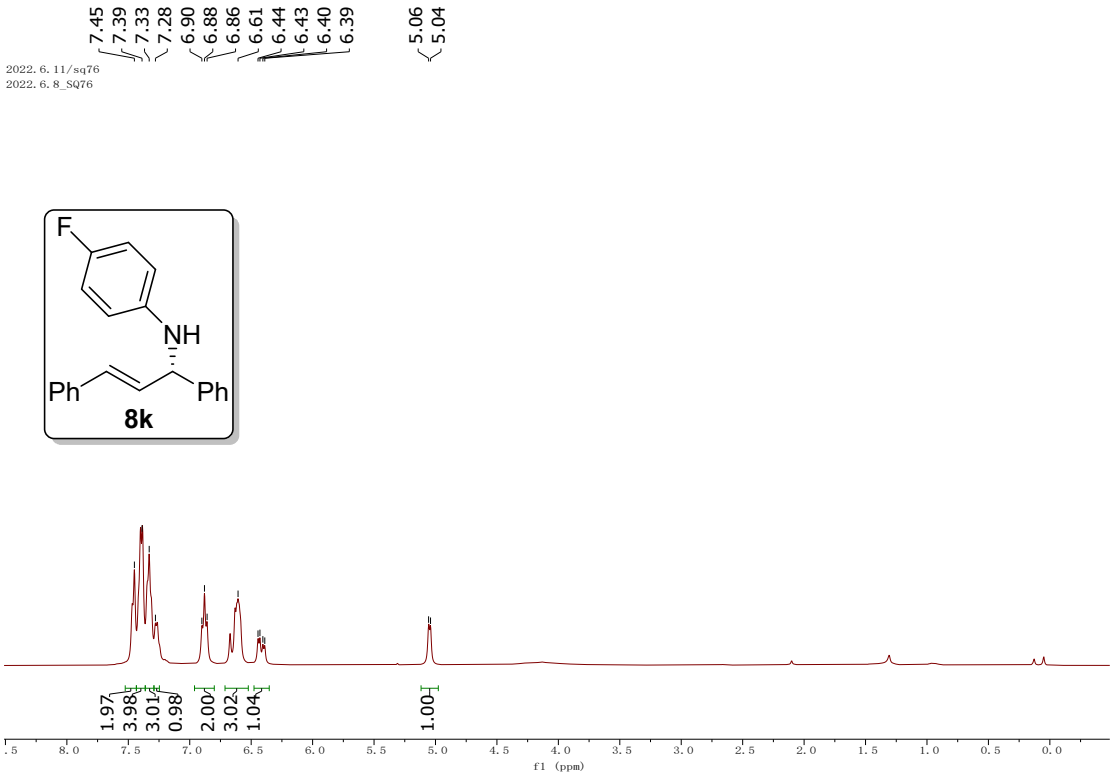
^{1}H NMR of **8h**



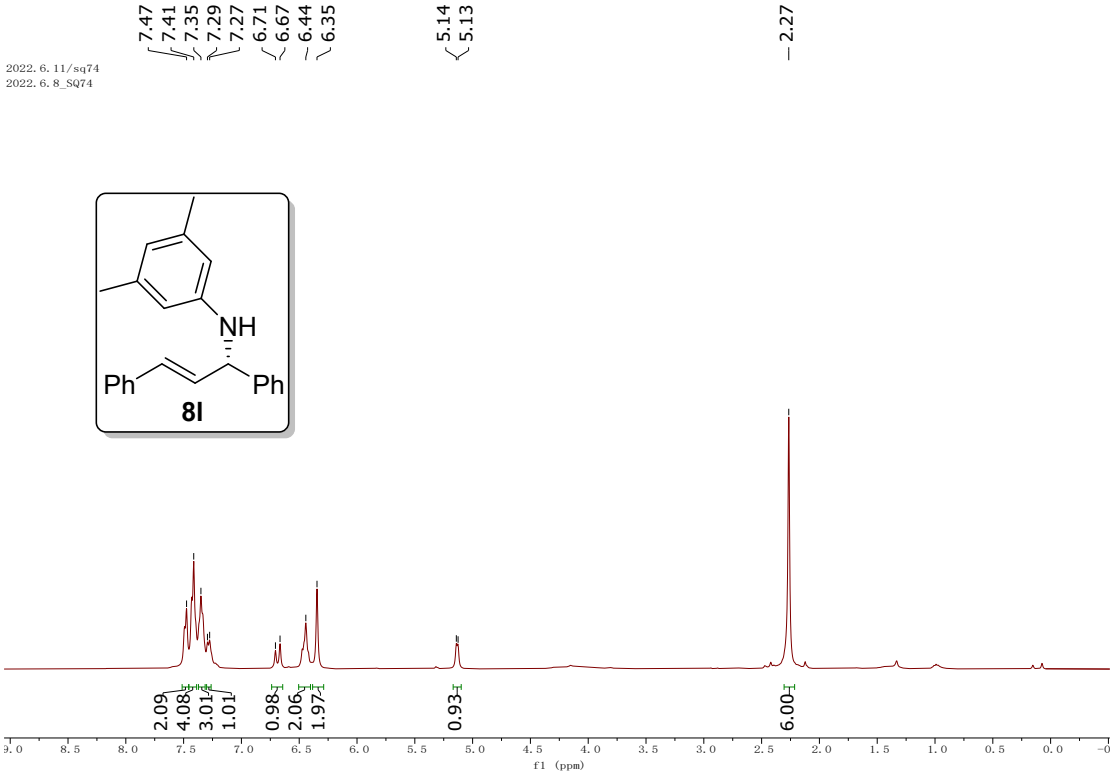
^{1}H NMR of **8i**



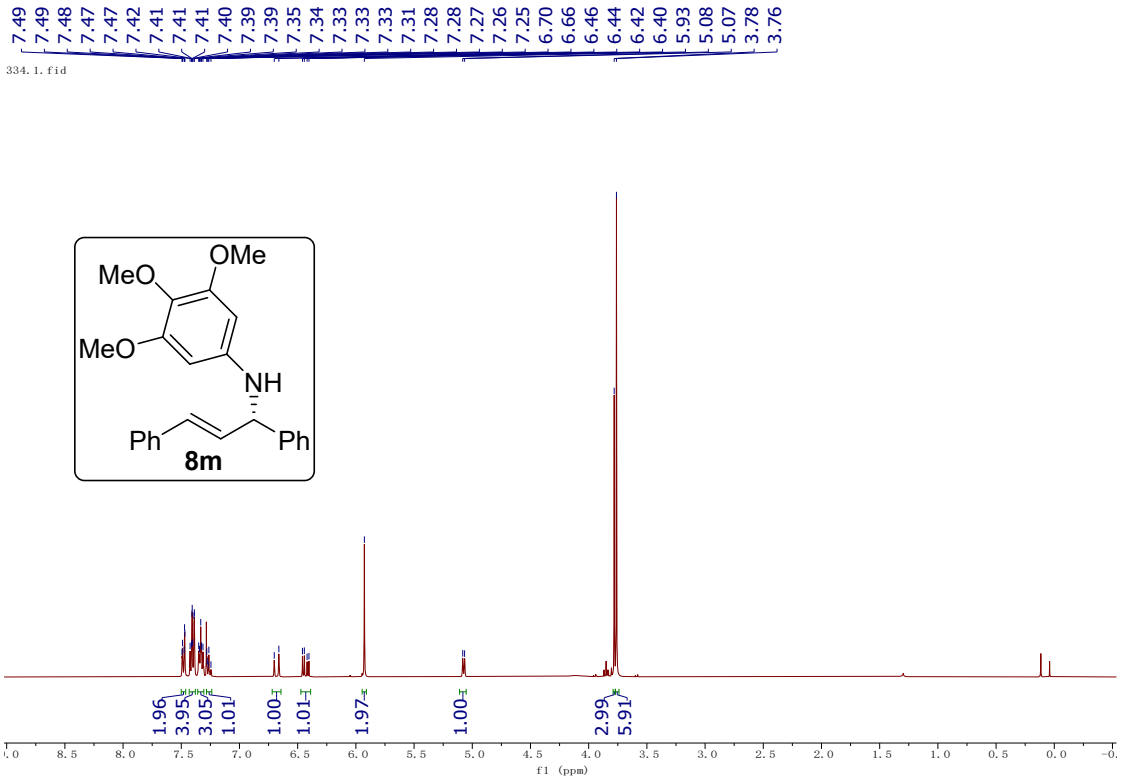
^{1}H NMR of **8j**



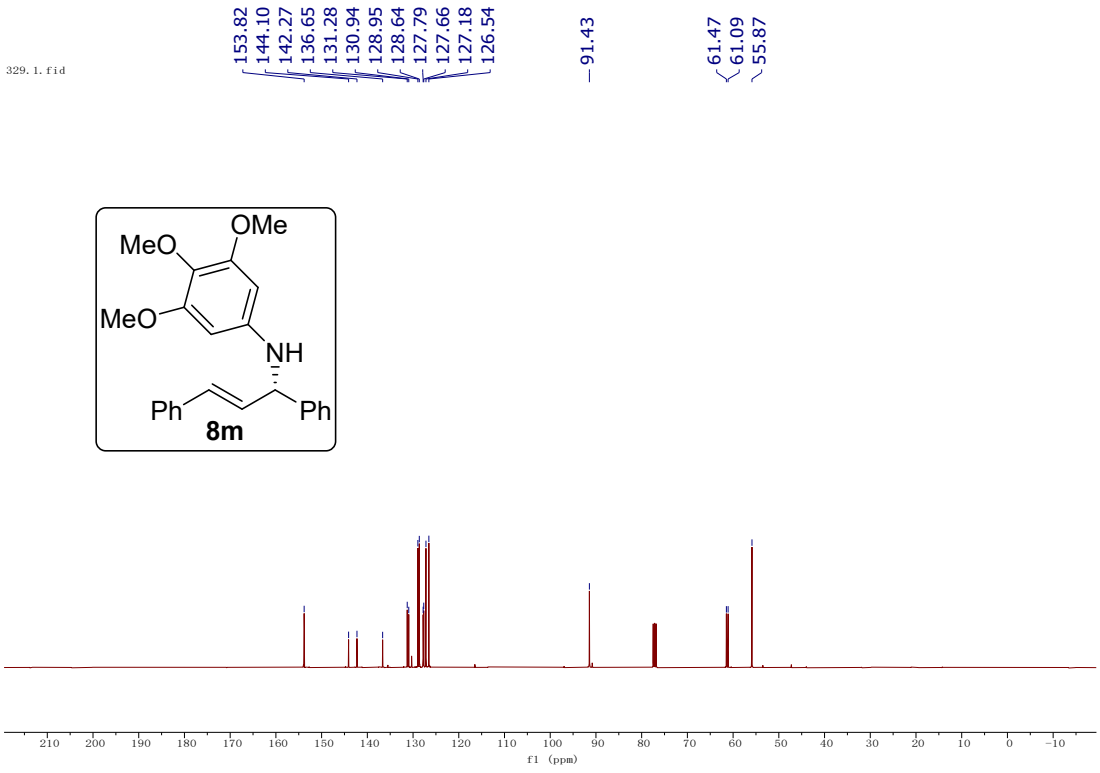
^{1}H NMR of **8k**



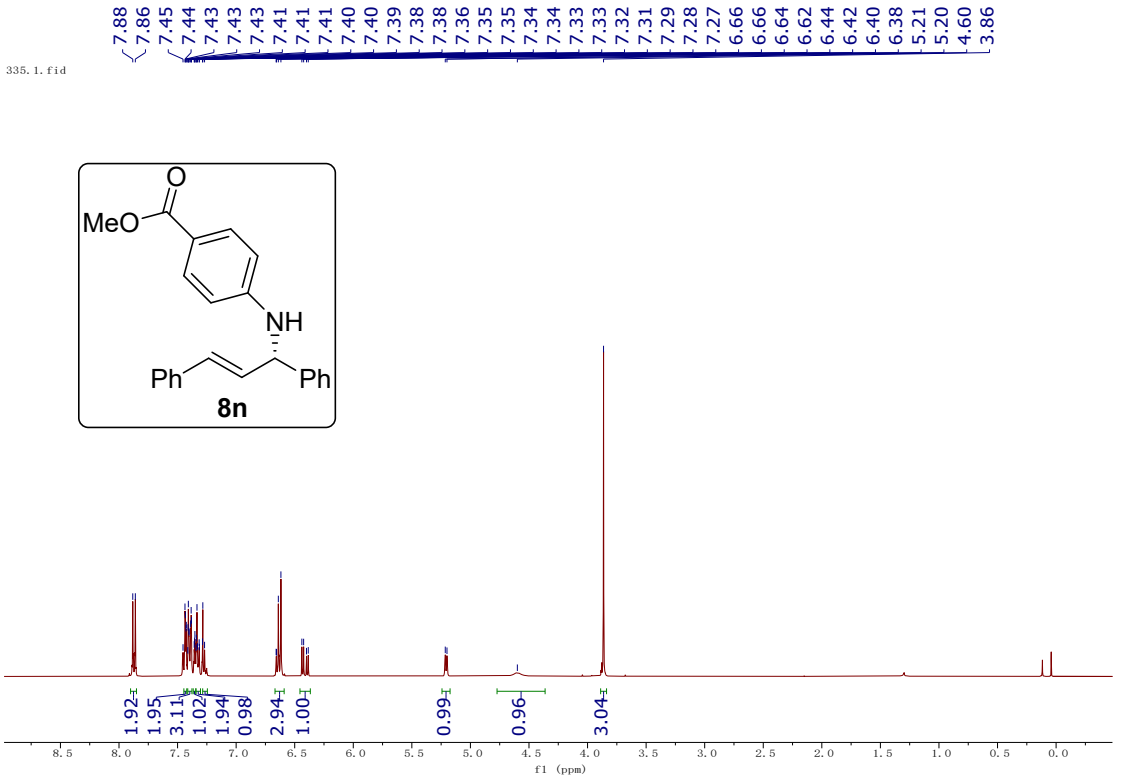
^{1}H NMR of **8l**



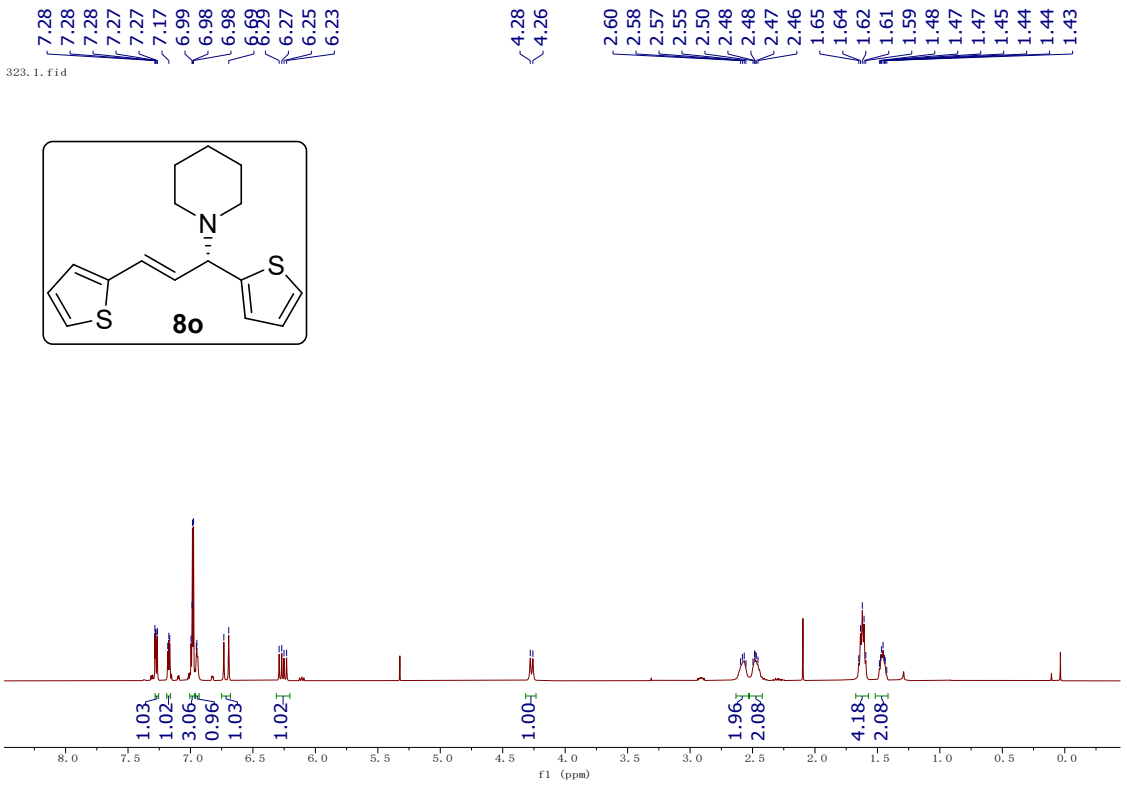
^{1}H NMR of **8m**



^{13}C NMR of **8m**


335.1.fid
7.88 7.86 7.45 7.44 7.43 7.43 7.43 7.41 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.29 7.28 7.27 6.66 6.66 6.64 6.62 6.44 6.42 6.40 6.38 5.21 5.20 4.60 3.86
MeO
O
NH
Ph
Ph
8n
1.92 1.95 3.11 1.02 1.94 0.98 2.94 1.00 0.99 0.96 3.04
f1 (ppm)

^{1}H NMR of **8n**


323.1.fid
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4.28 4.26
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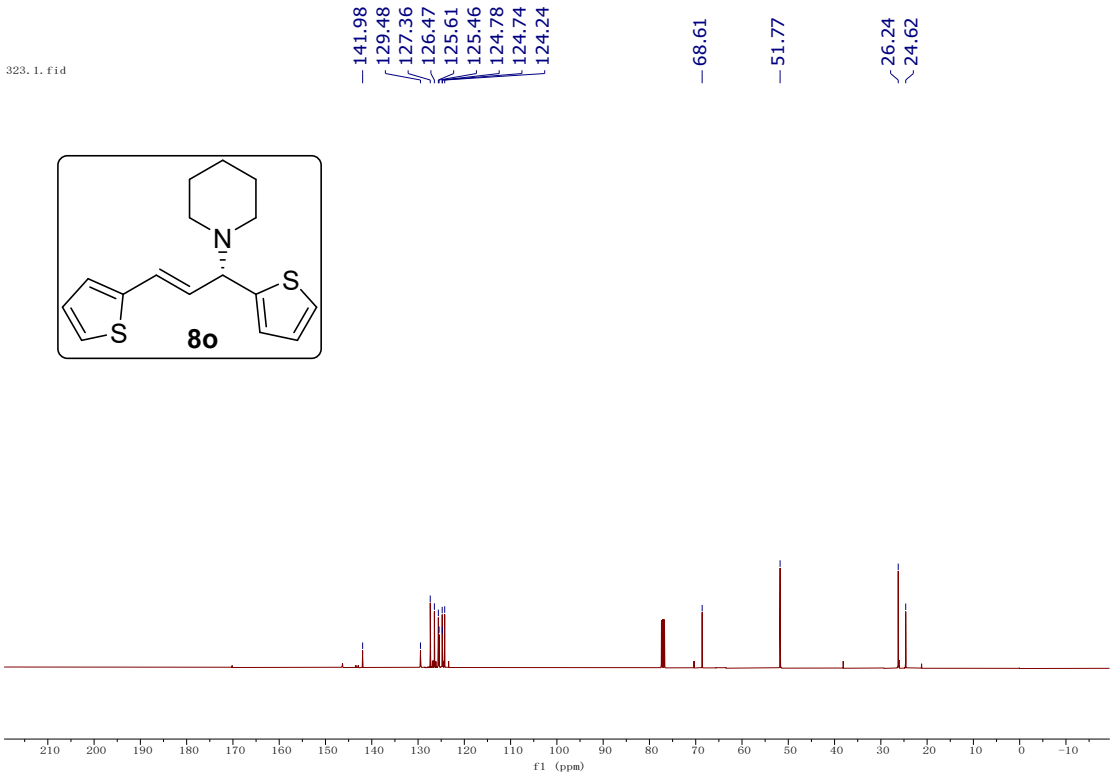
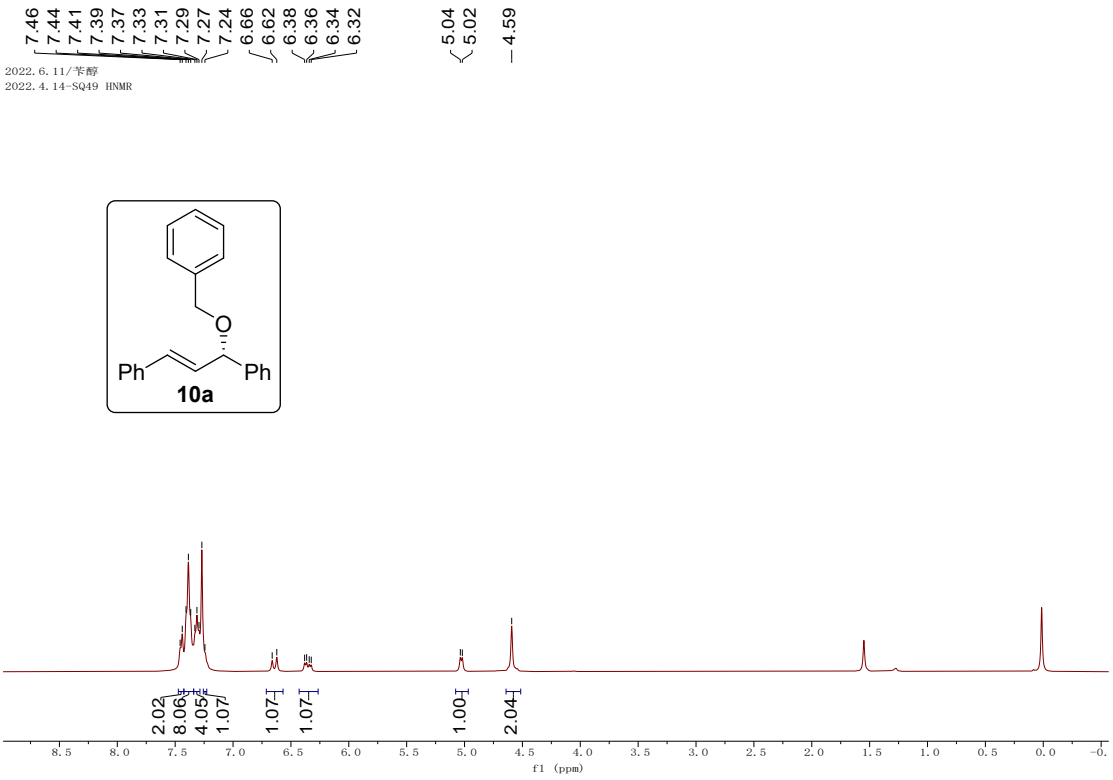
N
S
S
8o
1.03 1.02 3.06 0.96 1.03 1.02 1.00 1.96 2.08 4.18 2.08
f1 (ppm)

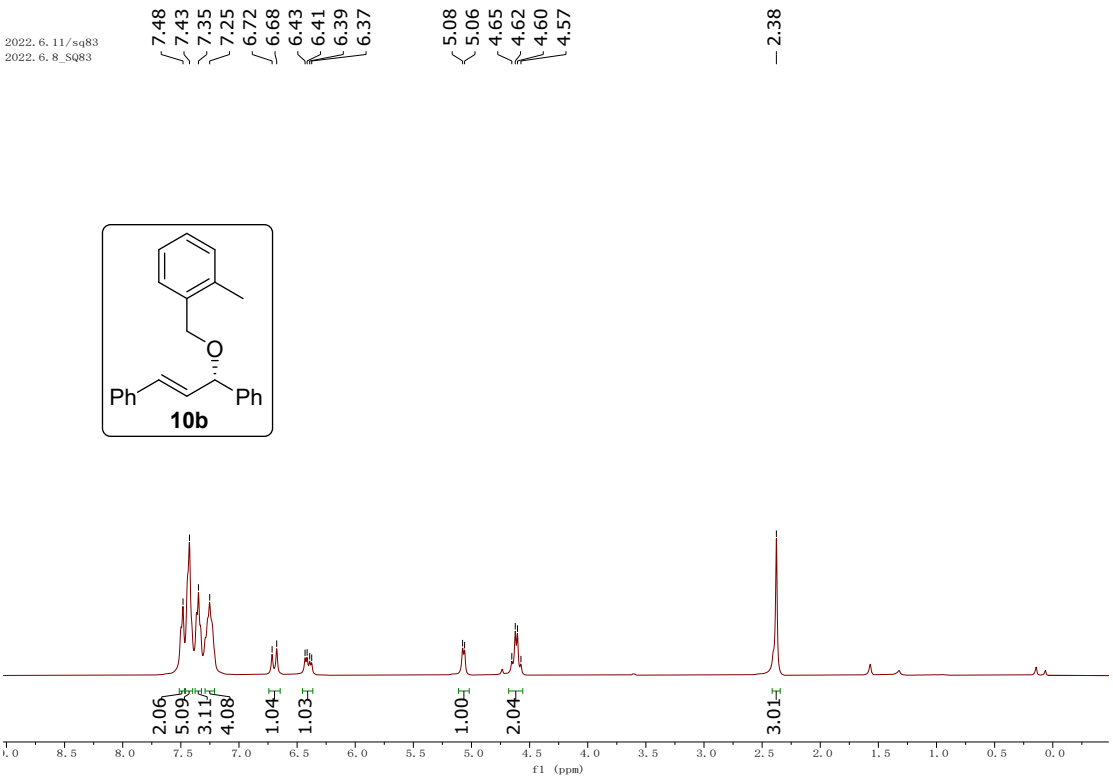
^{1}H NMR of **8o**



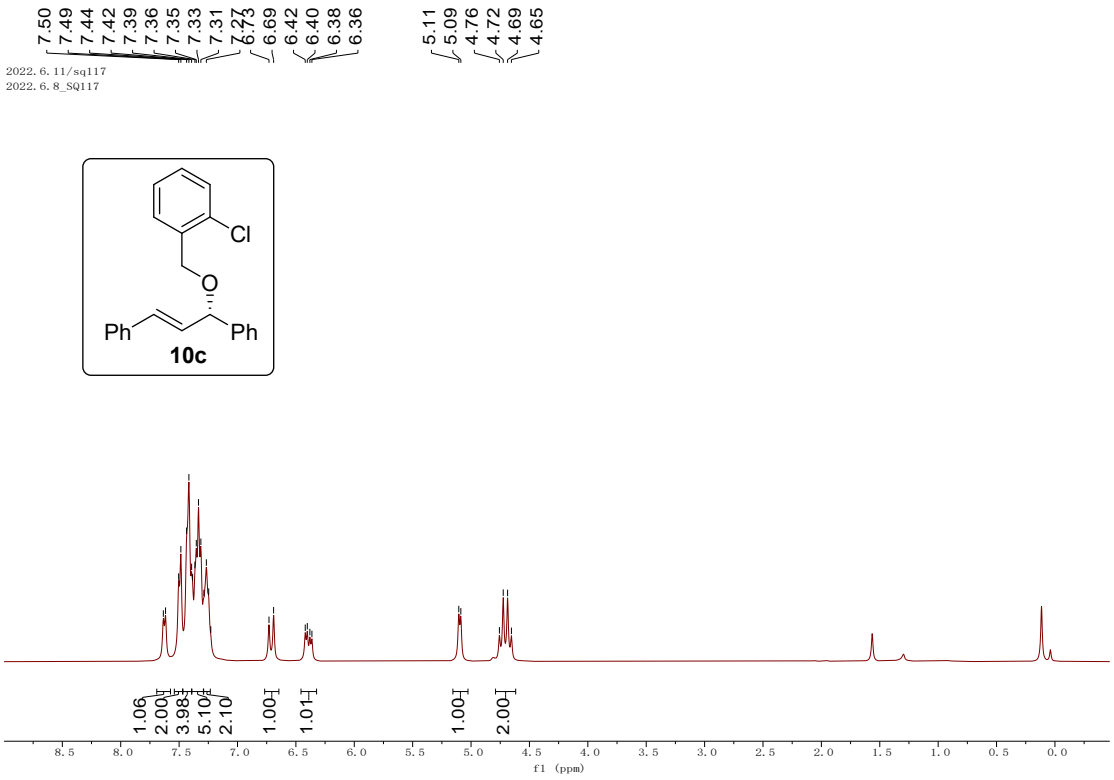
^{13}C NMR of **8o**



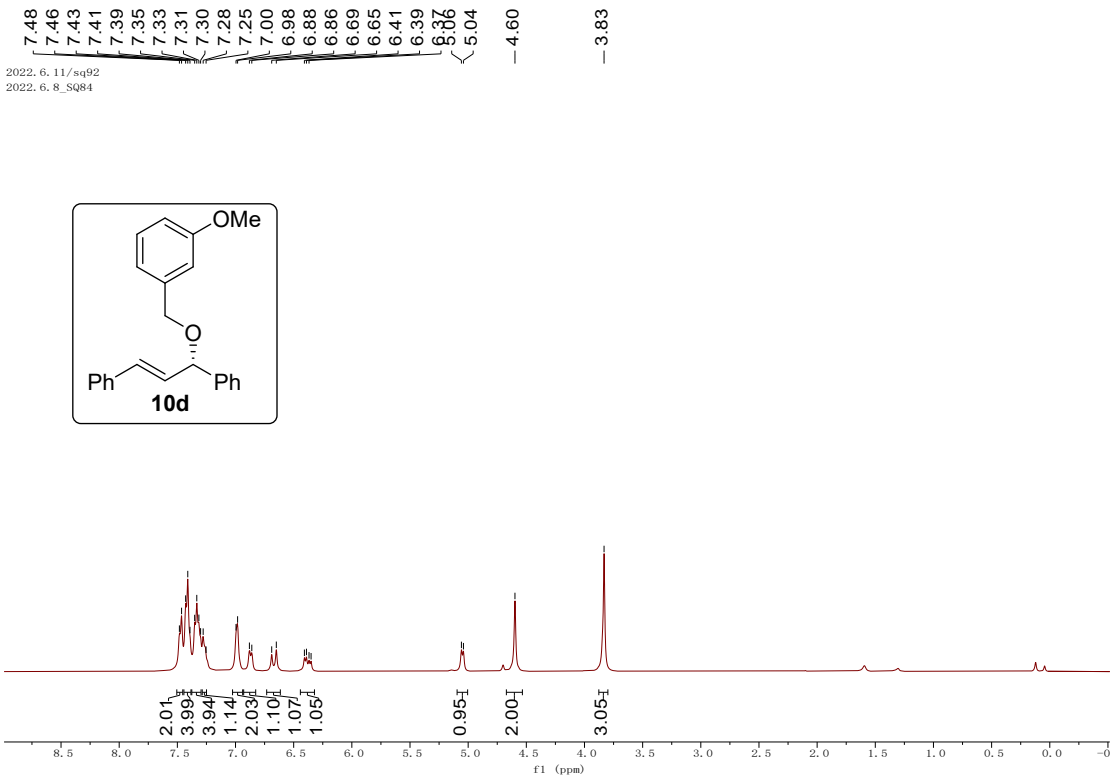
^{1}H NMR of **10a**



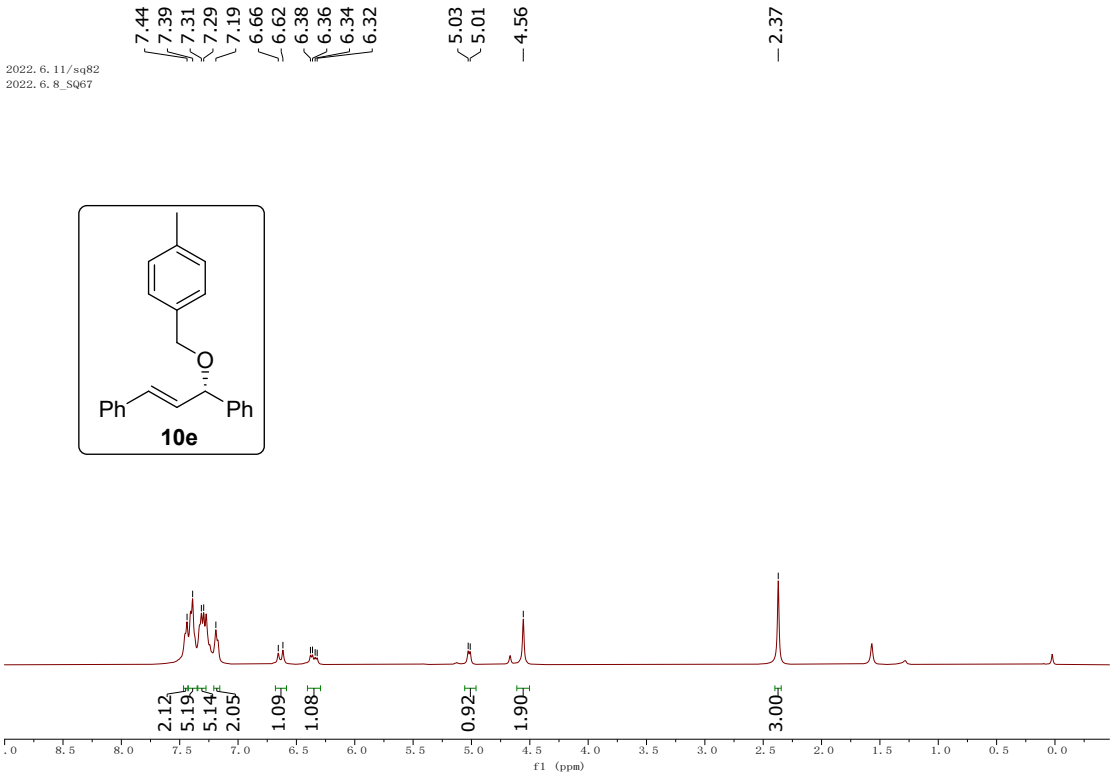
^{1}H NMR of **10b**



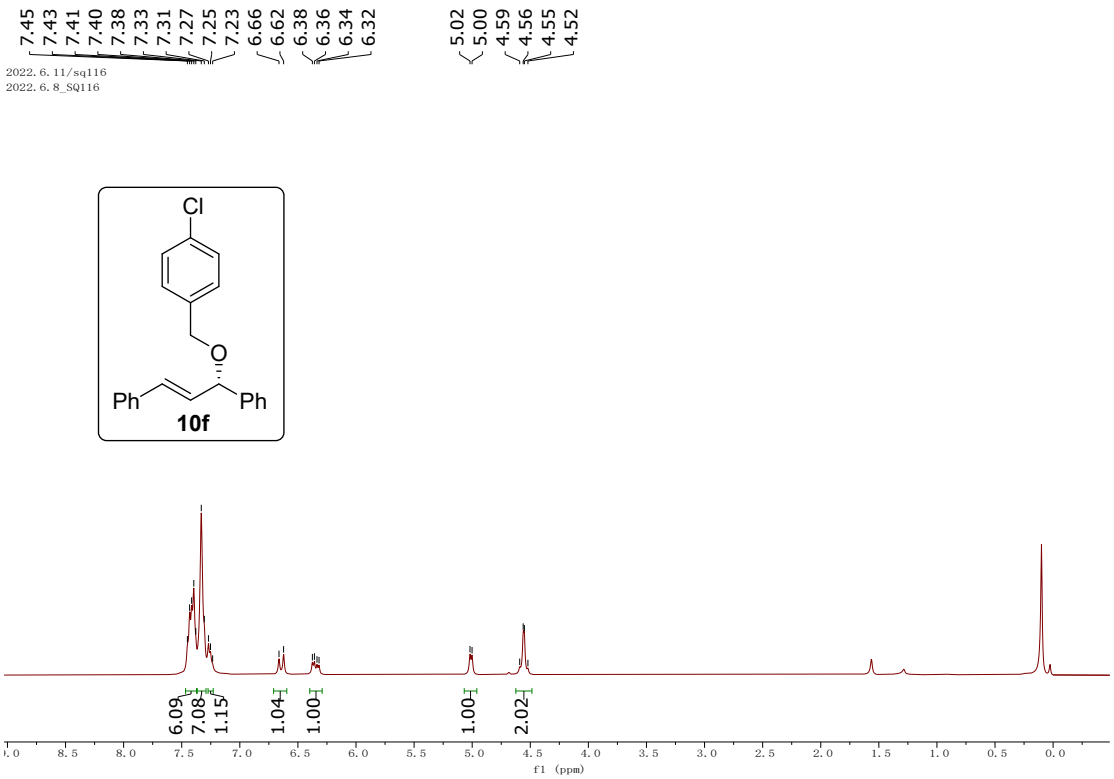
^{1}H NMR of **10c**



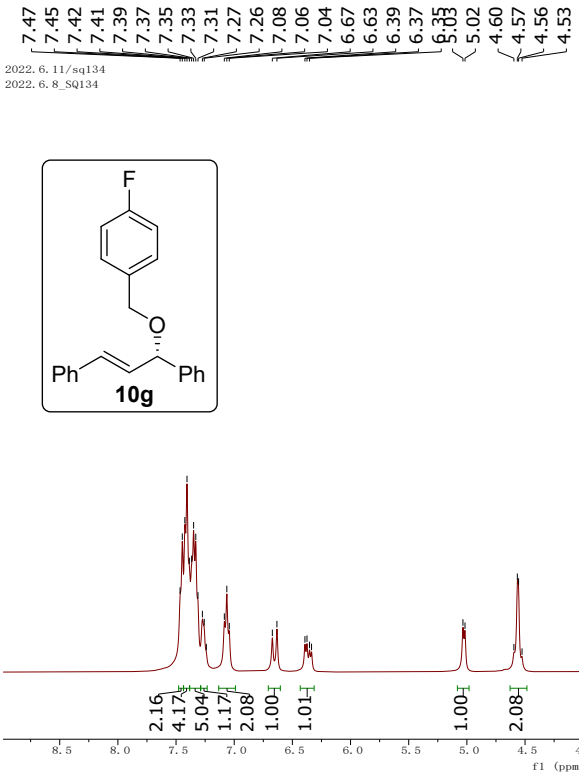
^{1}H NMR of **10d**



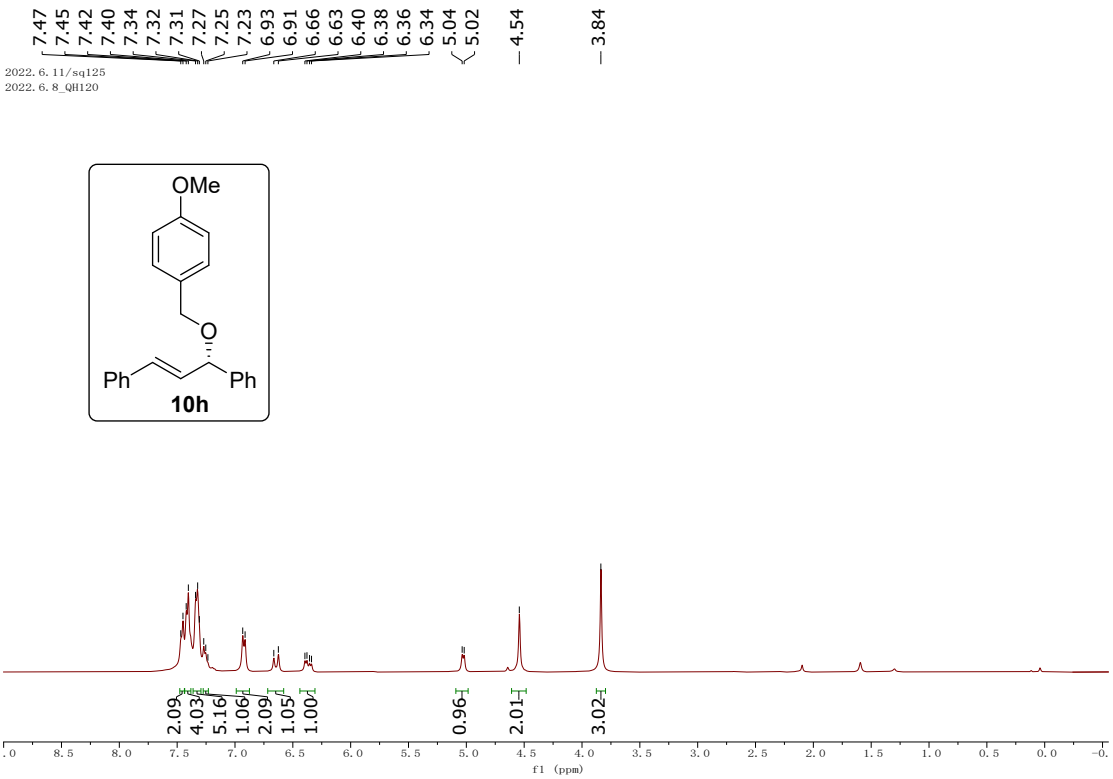
^{1}H NMR of **10e**



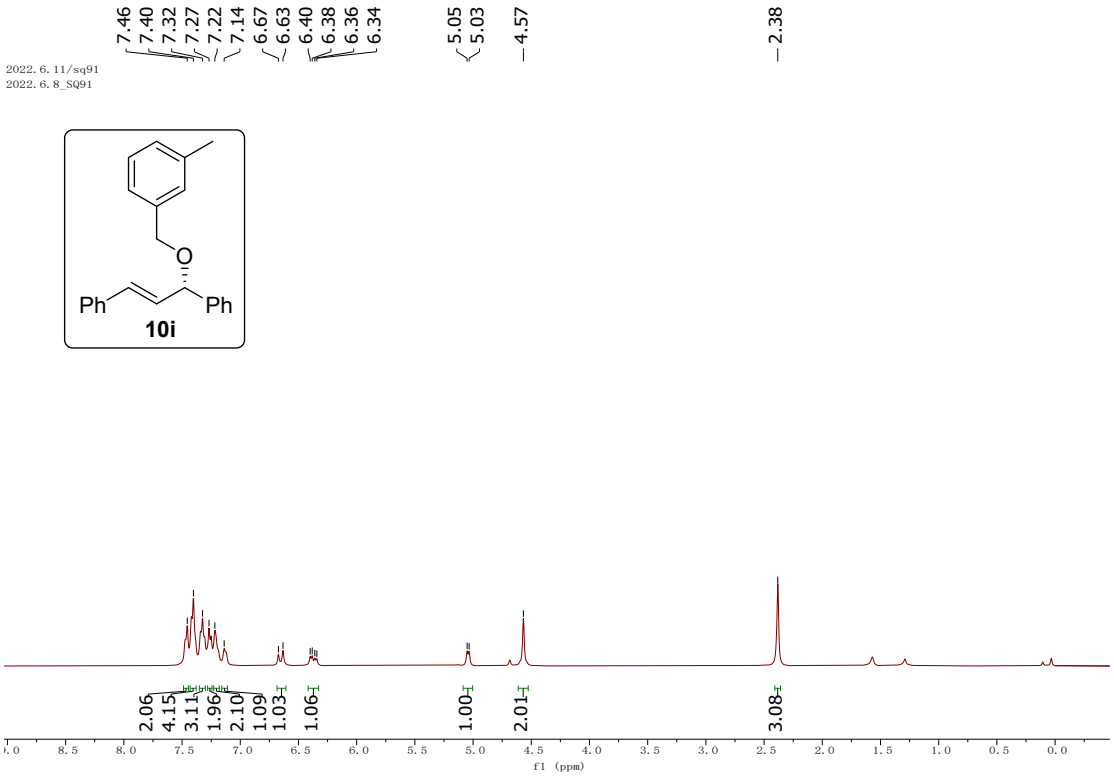
^{1}H NMR of **10f**



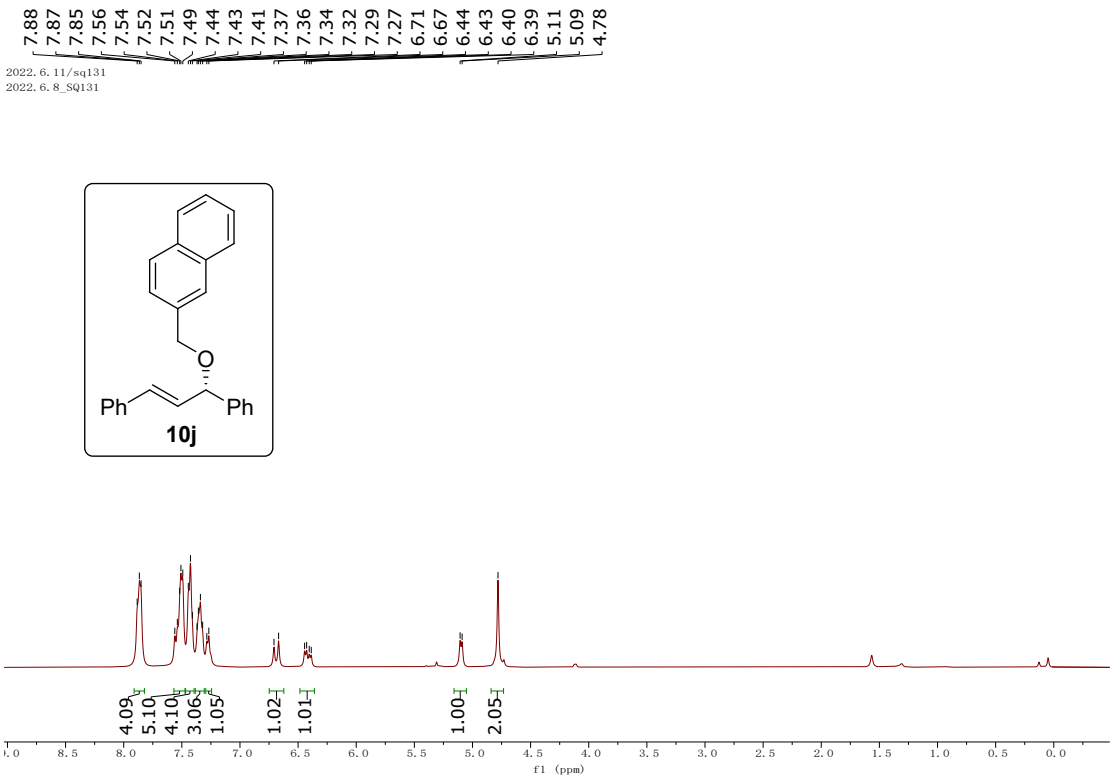
^{1}H NMR of **10g**



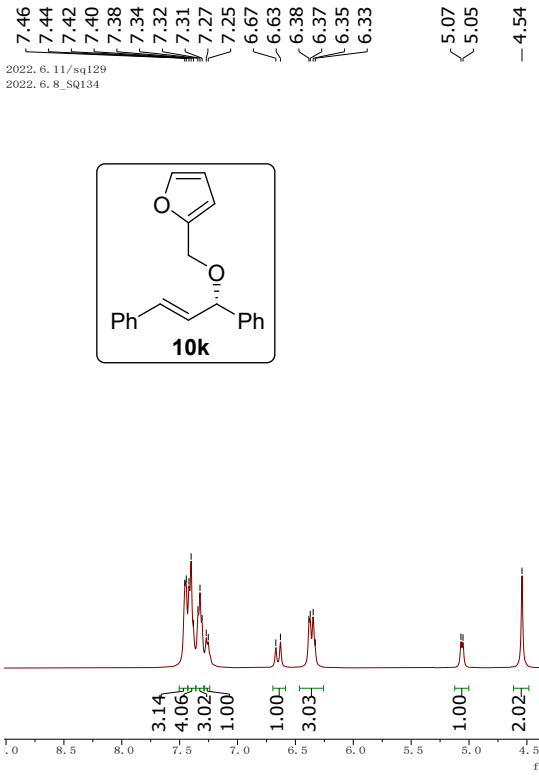
^{1}H NMR of **10h**



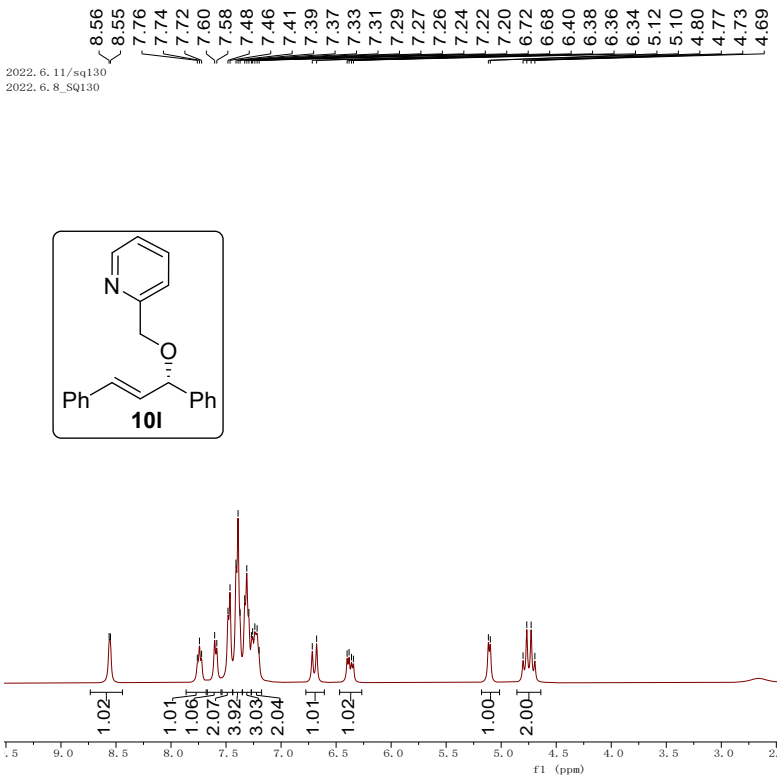
^{1}H NMR of **10i**



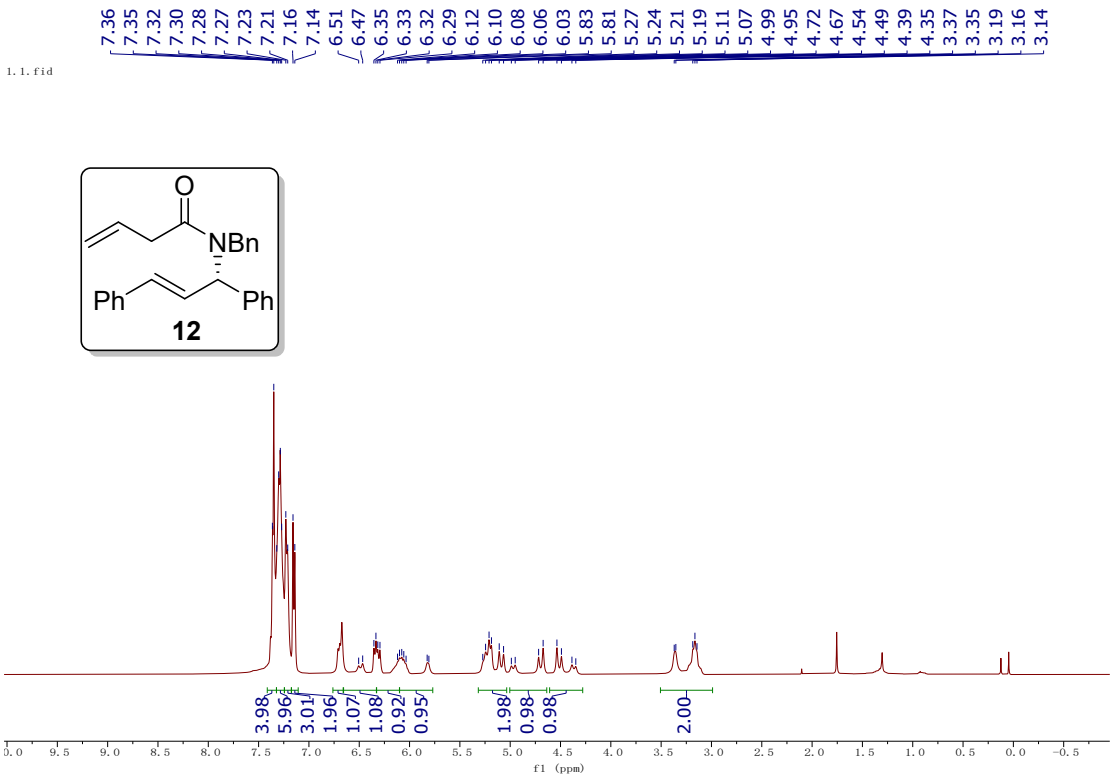
^{1}H NMR of **10j**



^{1}H NMR of **10k**



^{1}H NMR of **10l**


7.36
7.35
7.32
7.30
7.28
7.27
7.23
7.21
7.16
7.14
6.51
6.47
6.35
6.33
6.32
6.29
6.12
6.10
6.08
6.06
6.03
5.83
5.81
5.27
5.24
5.21
5.19
5.11
5.07
4.99
4.95
4.72
4.67
4.54
4.49
4.39
4.35
3.37
3.35
3.19
3.16
3.14
1. 1. fid
O
NBn
Ph
Ph
12
3.98
5.96
3.01
1.96
1.07
1.08
0.92
0.95
1.98
0.98
0.98
2.00
f1 (ppm)

^{1}H NMR of **12**