Electronic Supplementary Material (ESI) for ChemComm.

Copper-Catalyzed propargylic [3+3] Cycloaddition with 1*H*-pyrazol-5(4*H*)-ones: enantioselective access to optically active dihydropyrano [2, 3-*c*] pyrazoles

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Supporting Information

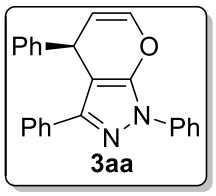
General Information

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 protium in the NMR solvent ($CHCl_3$ = δ 7.28). 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 77.07). 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 hexane and *i*-PrOH as solvents. 1*H*-pyrazol-5(4*H*)-ones **1**[1] and propargylic esters **2**[2] were prepared following the method from the literature.

General Procedure for Copper-Catalyzed Asymmetric Formal [3+3] Cycloaddition of 3-Trimethylsilylpropargylic Esters with 1*H*-pyrazol-5(4*H*)-ones

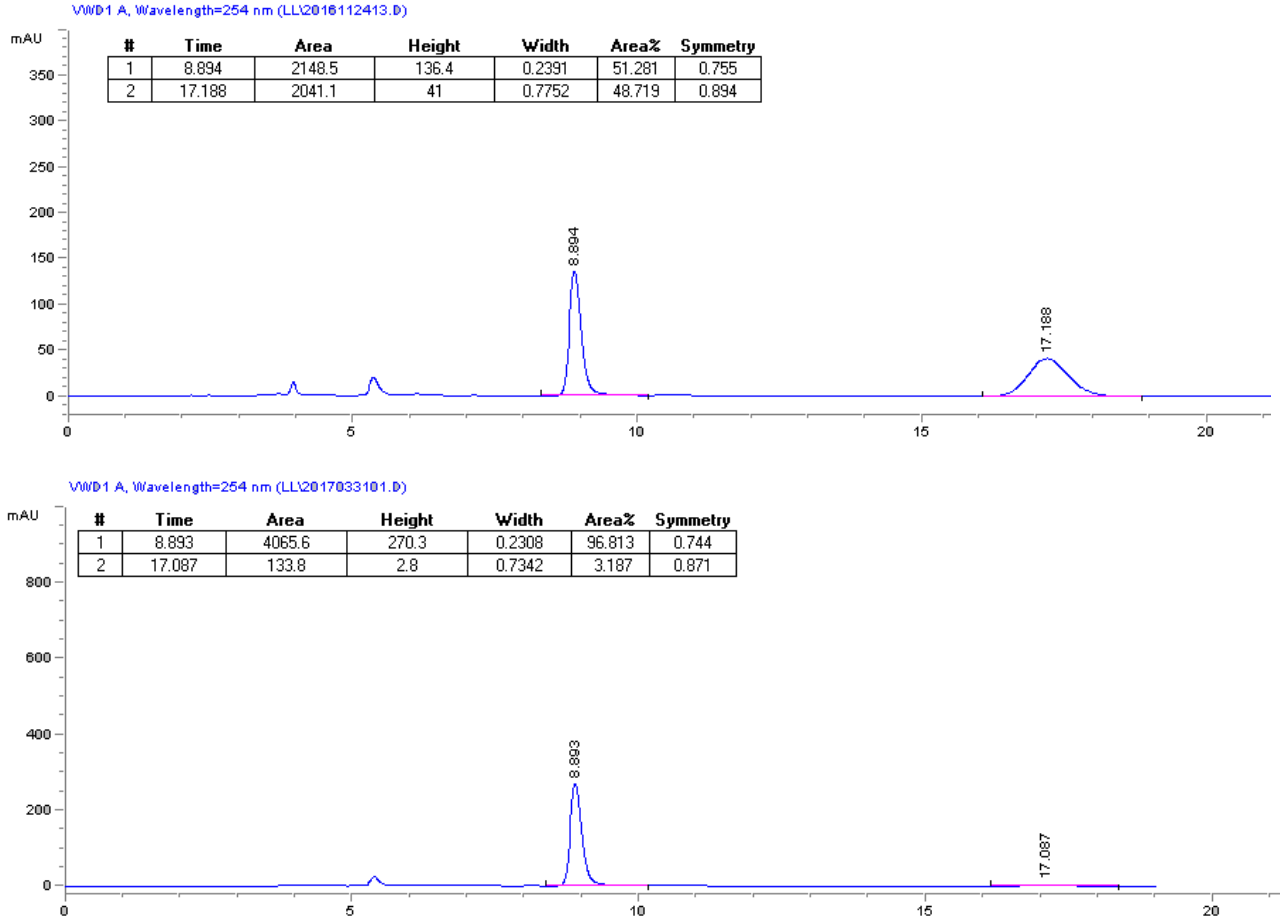
A solution of $Cu(OAc)_2{\cdot}H_2O$ (2.0 mg, 0.01 mmol) and (*S*)-**L$_1$** (5.5 mg, 0.011 mmol) in 1 mL of anhydrous methanol placed in an oven-dried Schlenk flask was stirred at room temperature under a nitrogen atmosphere for 1 h. After lowering the reaction temperature to 10 °C, a solution of 1*H*-pyrazol-5(4*H*)-ones **1** (0.2 mmol), 3-trimethylsilylpropargylic esters **2** (0.24 mmol) and Cs_2CO_3 (78.2 mg, 0.24 mmol) in 2 mL of anhydrous methanol was added. The mixture was stirred at 10 °C for 24 h. The reaction mixture was then concentrated under vaccum, and the residue was purified by silica gel chromatography to afford 1,4-dihydropyran[2,3-*c*] pyrazoles **3**.

(*R*)-1,3,4-triphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3aa). Colorless oil was obtained in 87% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 94 % ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.0 min, t_R (minor) = 17.4 min. ^{1}H NMR (400 MHz,



3aa

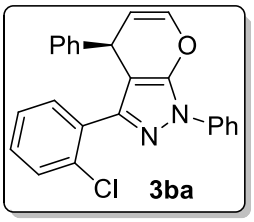
DMSO-d_6) δ 7.87–7.84 (m, 2H), 7.62–7.55 (m, 4H), 7.41–7.37 (m, 1H), 7.29–7.21 (m, 7H), 7.16–7.10 (m, 1H), 6.87 (dd, J = 6.0, 1.5 Hz, 1H), 5.26 (dd, J = 6.0, 4.2 Hz, 1H), 5.12 (dd, J = 4.1, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.5, 147.5, 145.1, 138.2, 138.0, 133.1, 129.9, 129.0, 128.7, 128.4, 128.1, 127.2, 127.1, 126.9, 121.3, 108.9, 97.6, 37.1. HRMS (ESI): m/z calcd for $C_{24}H_{19}N_2O$ [M + H] 351.1497, found 351.1500.



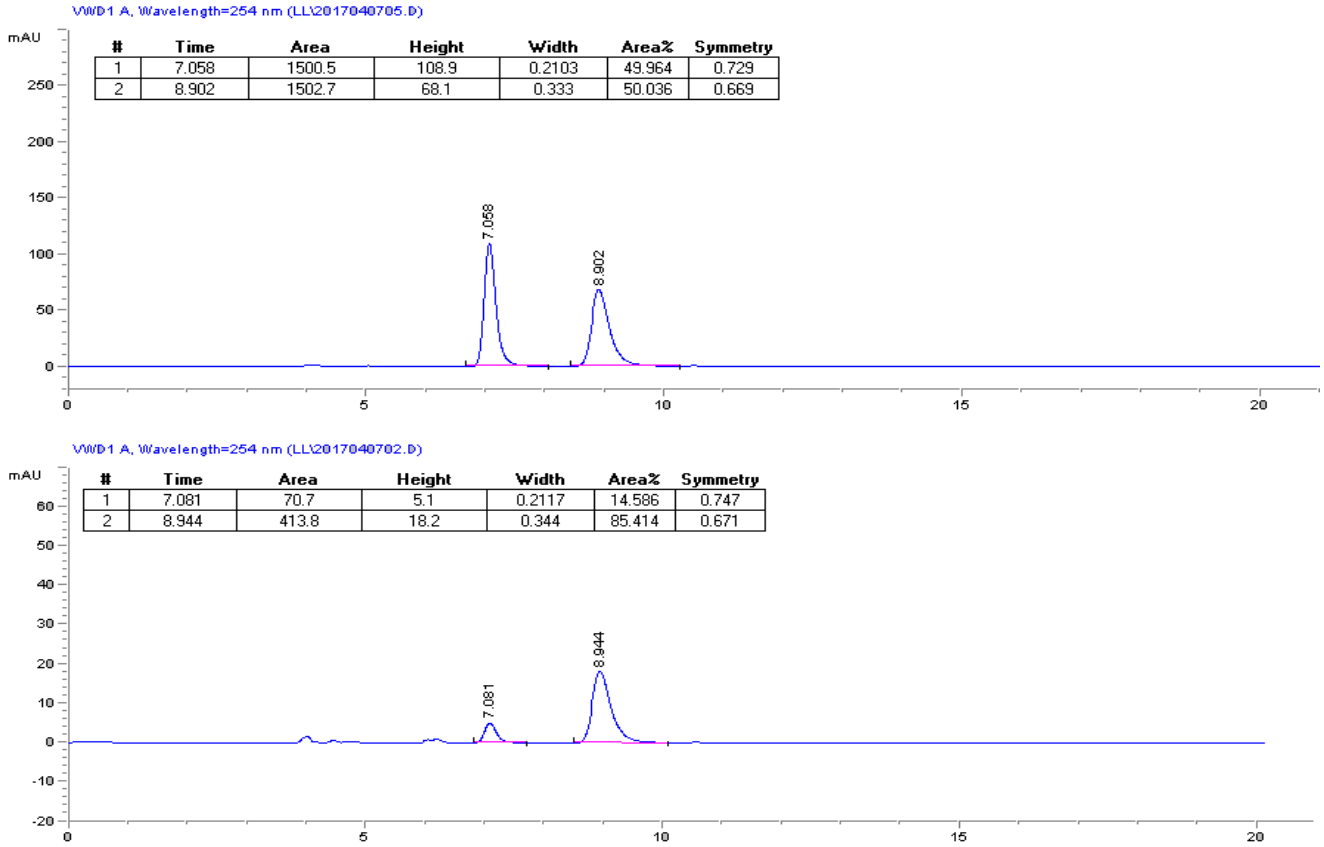
#	Time	Area	Height	Width	Area%	Symmetry
1	8.894	2148.5	136.4	0.2391	51.281	0.755
2	17.188	2041.1	41	0.7752	48.719	0.894

#	Time	Area	Height	Width	Area%	Symmetry
1	8.893	4065.6	270.3	0.2308	96.813	0.744
2	17.087	133.8	2.8	0.7342	3.187	0.871

(*R*)-3-(2-chlorophenyl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ba). Pale red solid was obtained in



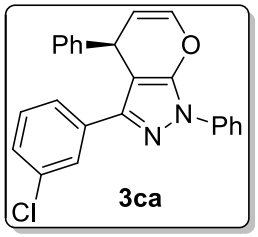
39% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 126–128 °C. 71% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 7.1 min, t_R (major) = 8.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.84 (m, 2H), 7.47–7.43 (m, 2H), 7.32–7.24 (m, 2H), 7.18–6.96 (m, 8H), 6.69 (dd, J = 6.1, 1.8 Hz, 1H), 5.10 (dd, J = 6.1, 3.6 Hz, 1H), 4.82 (dd, J = 3.5, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 145.8, 144.0, 138.6, 138.6, 133.6, 132.6, 131.6, 129.5, 129.1, 128.0, 127.8, 126.5, 126.4, 126.3, 120.9, 107.4, 100.8, 37.4. HRMS (ESI): m/z calcd for $C_{24}H_{18}ClN_2O$ [M + H] 385.1108, found 385.1113.



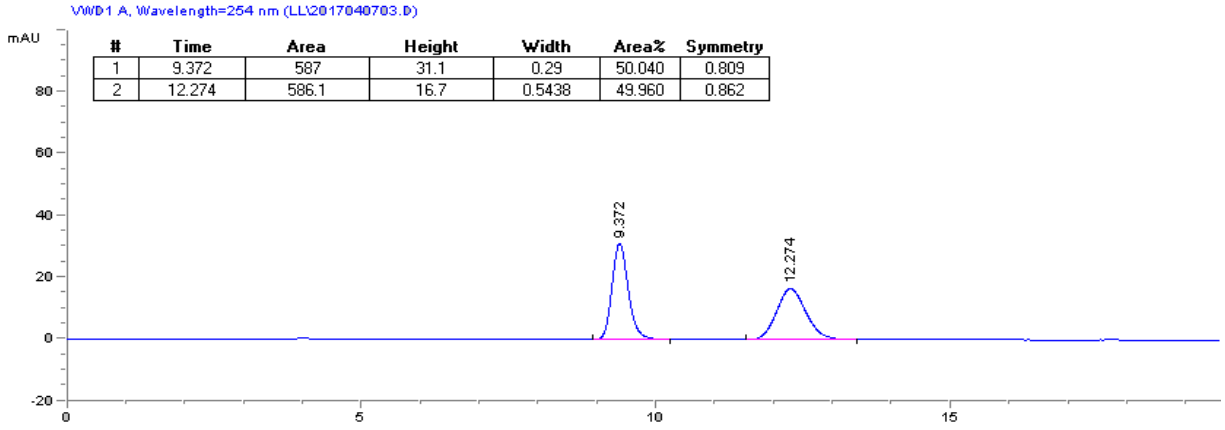
#	Time	Area	Height	Width	Area%	Symmetry
1	7.058	1500.5	108.9	0.2103	49.964	0.729
2	8.902	1502.7	68.1	0.333	50.036	0.669

#	Time	Area	Height	Width	Area%	Symmetry
1	7.081	70.7	5.1	0.2117	14.586	0.747
2	8.944	413.8	18.2	0.344	85.414	0.671

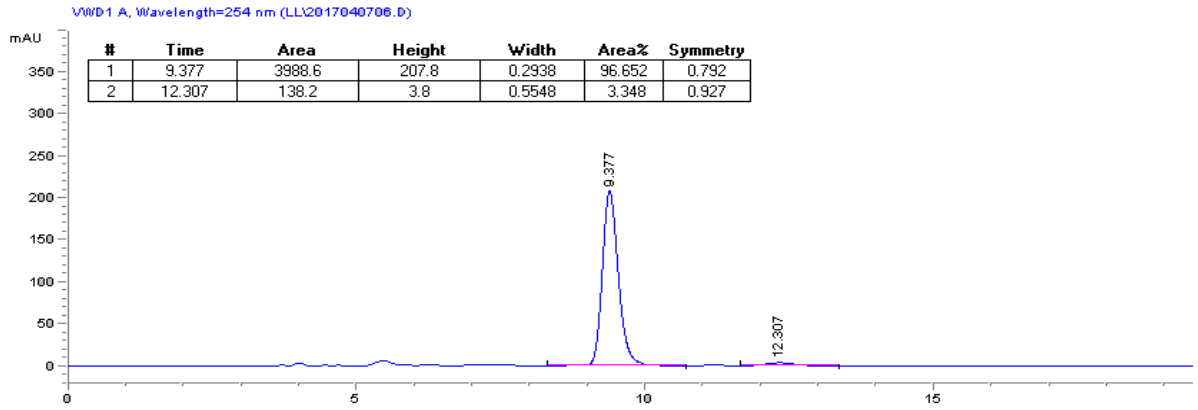
(*R*)-3-(3-chlorophenyl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ca). Colorless oil was obtained in



83% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 93% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.4 min, t_R (minor) = 12.3 min. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71–7.68 (m, 2H), 7.42–7.38 (m, 4H), 7.25–7.21 (m, 1H), 7.12–7.08 (m, 6H), 7.00–6.96 (m, 1H), 6.70 (dd, J = 6.0, 1.5 Hz, 1H), 5.08 (dd, J = 6.0, 4.1 Hz, 1H), 4.95 (dd, J = 4.0, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.6, 146.1, 144.9, 138.0, 135.0, 133.5, 130.6, 129.9, 129.0, 128.2, 127.4, 127.2, 126.5, 125.5, 121.5, 108.8, 98.0, 37.0. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}ClN_2O$ [M + H] 385.1108, found 385.1110.

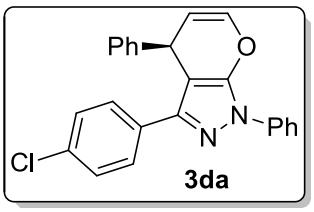


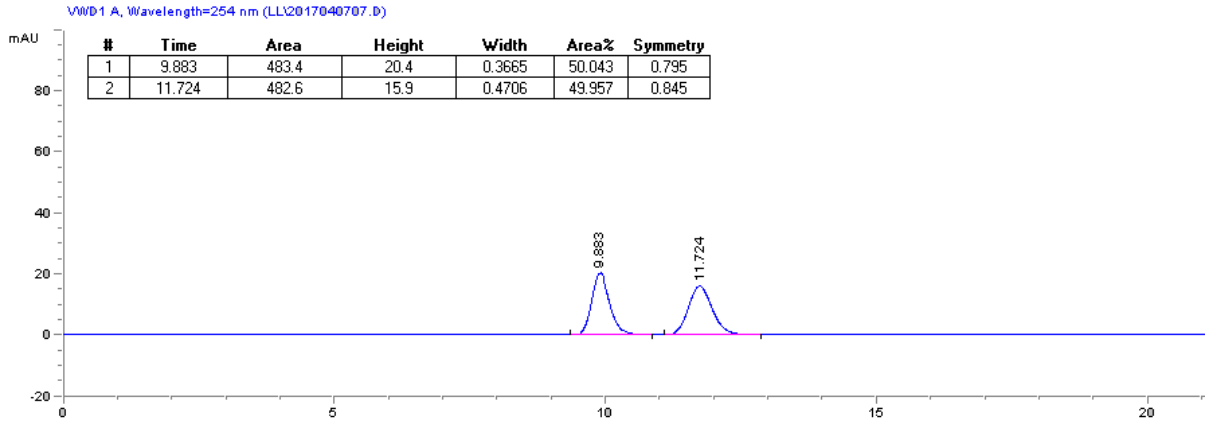
#	Time	Area	Height	Width	Area%	Symmetry
1	9.372	587	31.1	0.29	50.040	0.809
2	12.274	586.1	16.7	0.5438	49.960	0.862



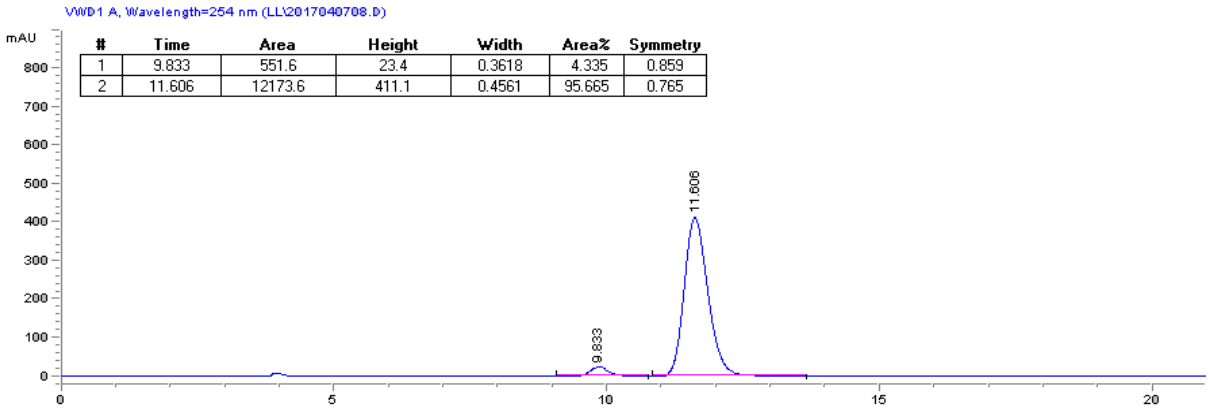
#	Time	Area	Height	Width	Area%	Symmetry
1	9.377	3988.6	207.8	0.2938	96.652	0.792
2	12.307	138.2	3.8	0.5548	3.348	0.927

(*R*)-3-(4-chlorophenyl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3da). Colorless oil was obtained in 74% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 91% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 9.8 min, t_R (major) = 11.6 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.67 (m, 2H), 7.30–7.25 (m, 4H), 7.13–6.97 (m, 8H), 6.37 (dd, *J* = 6.0, 1.5 Hz, 1H), 4.96 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.70 (dd, *J* = 4.0, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 147.0, 144.5, 138.2, 137.3, 133.7, 131.6, 129.2, 128.8, 128.4, 128.2, 127.7, 127.0, 126.6, 121.1, 108.4, 97.3, 37.9. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}ClN_2O$ [M + H] 385.1108, found 385.1108.



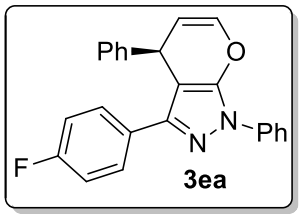


#	Time	Area	Height	Width	Area%	Symmetry
1	9.883	483.4	20.4	0.3665	50.043	0.795
2	11.724	482.6	15.9	0.4706	49.957	0.845

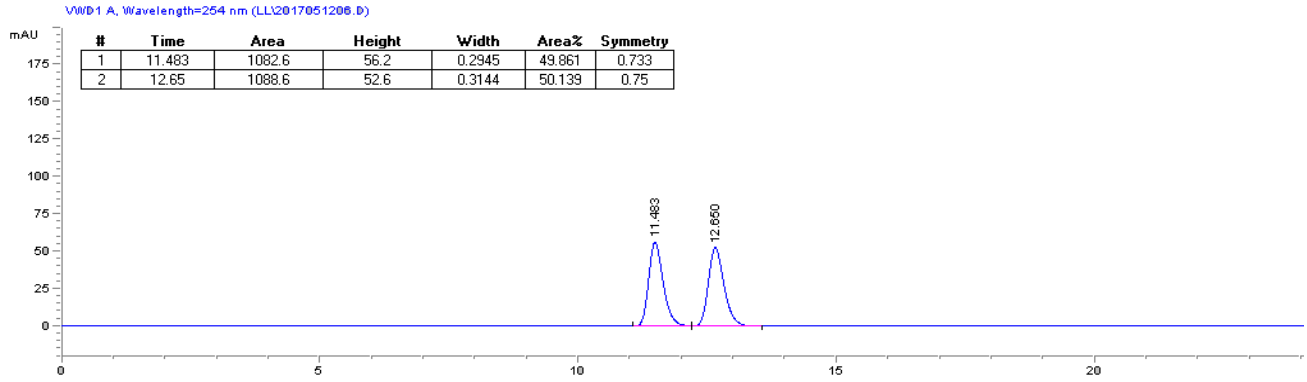


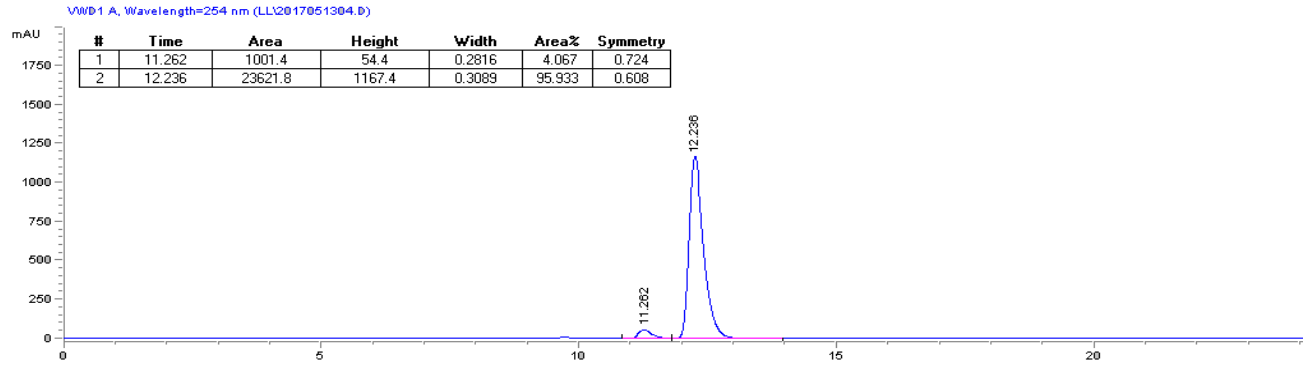
#	Time	Area	Height	Width	Area%	Symmetry
1	9.833	551.6	23.4	0.3618	4.335	0.859
2	11.606	12173.6	411.1	0.4561	95.665	0.765

(*R*)-3-(4-fluorophenyl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ea). Colorless oil was obtained in

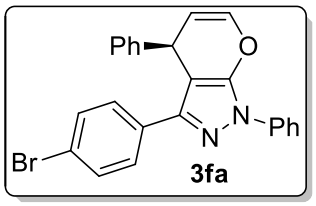


77% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 92% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 11.3 min, t_R (major) = 12.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.50–7.45 (m, 4H), 7.31–7.14 (m, 6H), 6.91–6.87 (m, 2H), 6.55 (dd, *J* = 6.0, 1.4 Hz, 1H), 5.13 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.87 (dd, *J* = 3.8, 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.5 (d, *J* = 247.1 Hz), 147.4, 147.4, 144.6, 138.3, 137.3, 129.3 (d, *J* = 3.2 Hz), 129.2, 128.8 (d, *J* = 8.1 Hz), 128.8, 127.7, 127.0, 126.5, 121.0, 115.1 (d, *J* = 21.5 Hz), 108.4, 97.3, 37.9. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}FN_2O$ [M + H] 369.1403, found 369.1404.



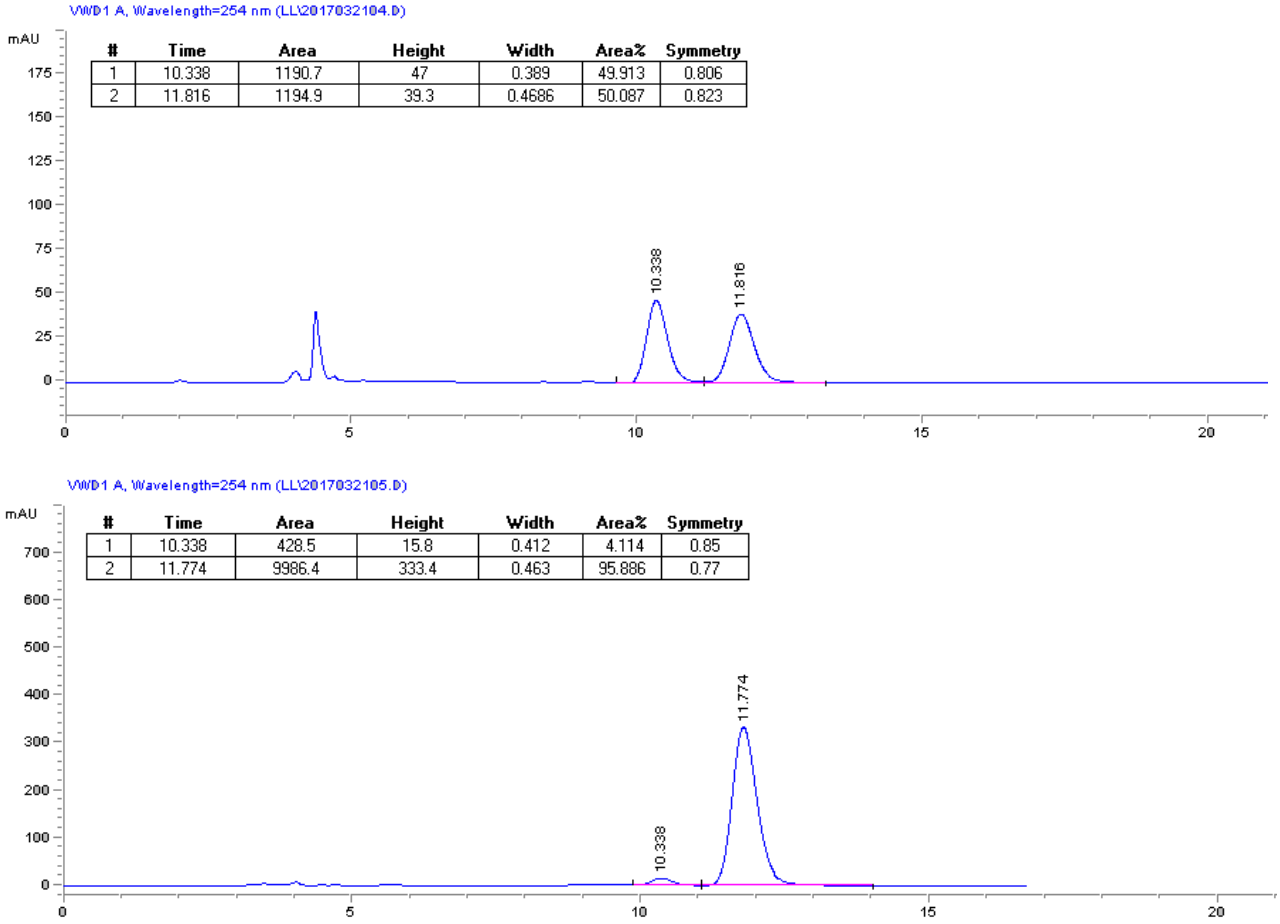


(*R*)-3-(4-bromophenyl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3fa). Colorless oil was obtained in

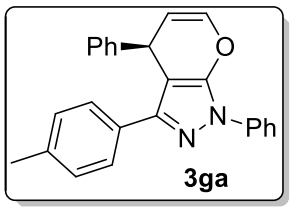


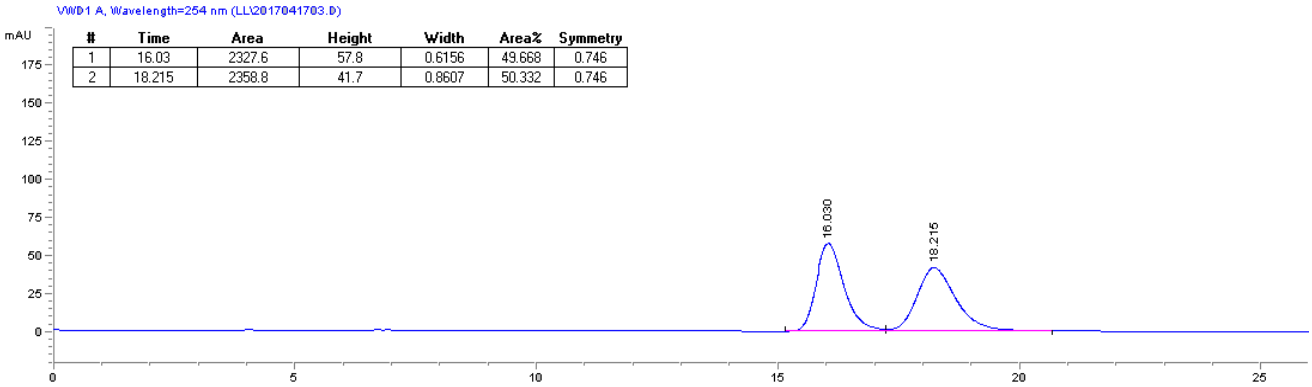
72% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 92% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 10.2 min, t_R (major) = 11.7 min. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69–7.67 (m, 2H), 7.41–7.38 (m, 4H), 7.29–7.21 (m, 3H), 7.08–7.06 (m, 4H), 6.99–6.94 (m, 1H), 6.70 (dd, *J* = 6.0,

1.2 Hz, 1H), 5.09 (dd, J = 5.9, 4.2 Hz, 1H), 4.95–4.94 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.6, 146.4, 144.8, 138.0, 132.3, 131.6, 129.9, 129.0, 128.9, 128.2, 127.3, 127.2, 121.7, 121.4, 108.8, 97.8, 37.0. HRMS (ESI): m/z calcd for $C_{24}H_{18}BrN_2O$ [M + H] 429.0603, found 429.0602.

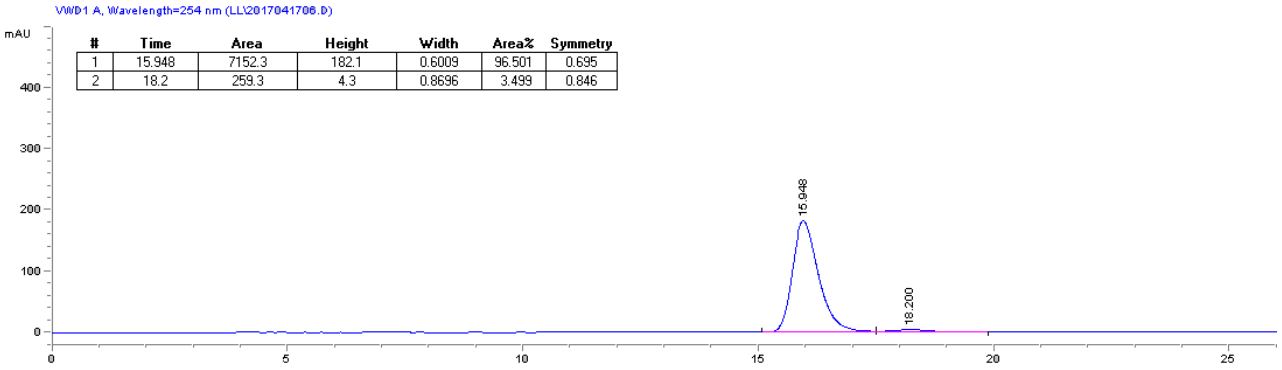


(*R*)-1,4-diphenyl-3-(p-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3ga). Colorless oil was obtained in 92% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 93% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 ml/min, 254 nm, 40 °C): t_R (major) = 16.0 min, t_R (minor) = 18.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.48–7.42 (m, 4H), 7.32–7.21 (m, 5H), 7.17–7.13 (m, 1H), 7.03–7.01 (m, 2H), 6.55 (dd, J = 6.0, 1.5 Hz, 1H), 5.14 (dd, J = 6.0, 4.1 Hz, 1H), 4.91 (dd, J = 4.1, 1.4 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 147.4, 144.9, 138.4, 137.6, 137.3, 130.3, 129.1, 128.9, 128.7, 127.7, 126.9, 126.8, 126.3, 121.1, 108.5, 97.1, 38.0, 21.3. HRMS (ESI): m/z calcd for $C_{25}H_{21}N_2O$ [M + H] 365.1654, found 365.1650.



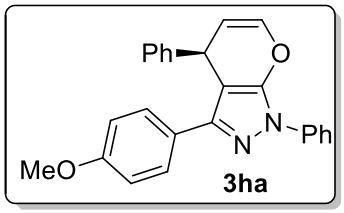


#	Time	Area	Height	Width	Area%	Symmetry
1	16.03	2327.6	57.8	0.6156	49.668	0.746
2	18.215	2358.8	41.7	0.8607	50.332	0.746

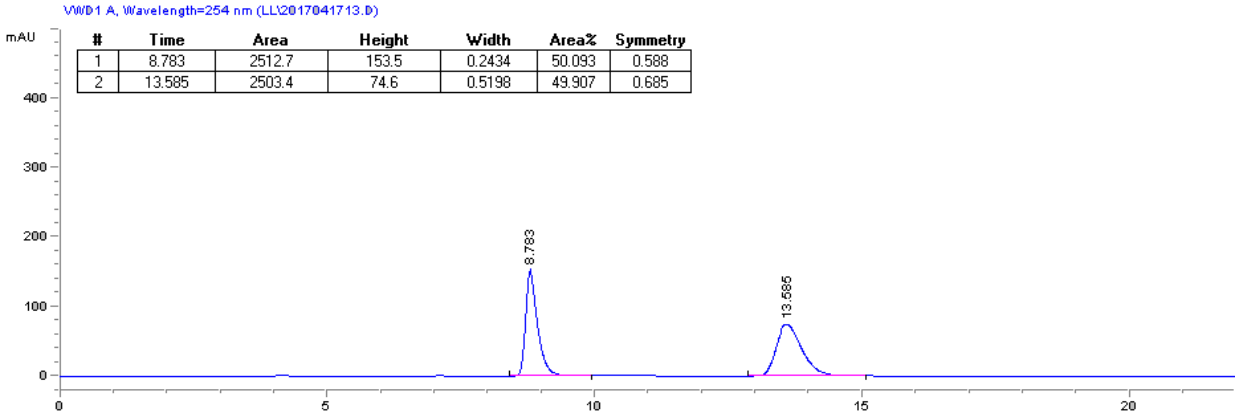


#	Time	Area	Height	Width	Area%	Symmetry
1	15.948	7152.3	182.1	0.6009	96.501	0.695
2	18.2	259.3	4.3	0.8696	3.499	0.846

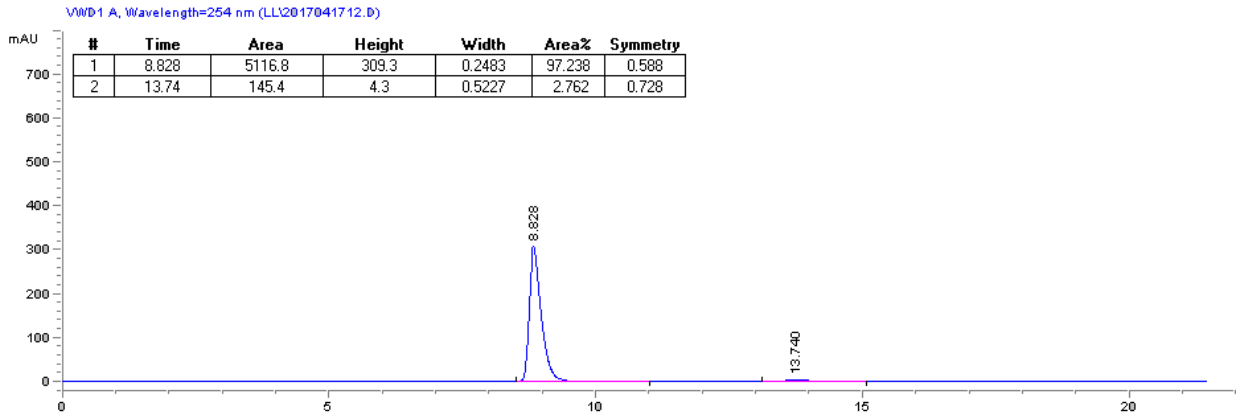
(*R*)-3-(4-methoxyphenyl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ha). Colorless oil was obtained



in 97% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 50/1). 94% ee was determined by chiral HPLC (Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 8.8 min, t_R (minor) = 13.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.48–7.44 (m, 4H), 7.30–7.21 (m, 5H), 7.19–7.14 (m, 1H), 6.75–6.72 (m, 2H), 6.56 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.15 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.89 (dd, *J* = 4.0, 1.4 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 148.0, 147.4, 144.8, 138.4, 137.3, 129.1, 128.8, 128.3, 127.7, 126.8, 126.2, 125.8, 121.0, 113.6, 108.5, 96.9, 55.2, 38.0. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{21}N_2O_2$ [M + H] 381.1603, found 381.1610.

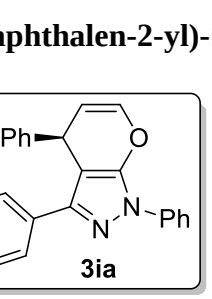


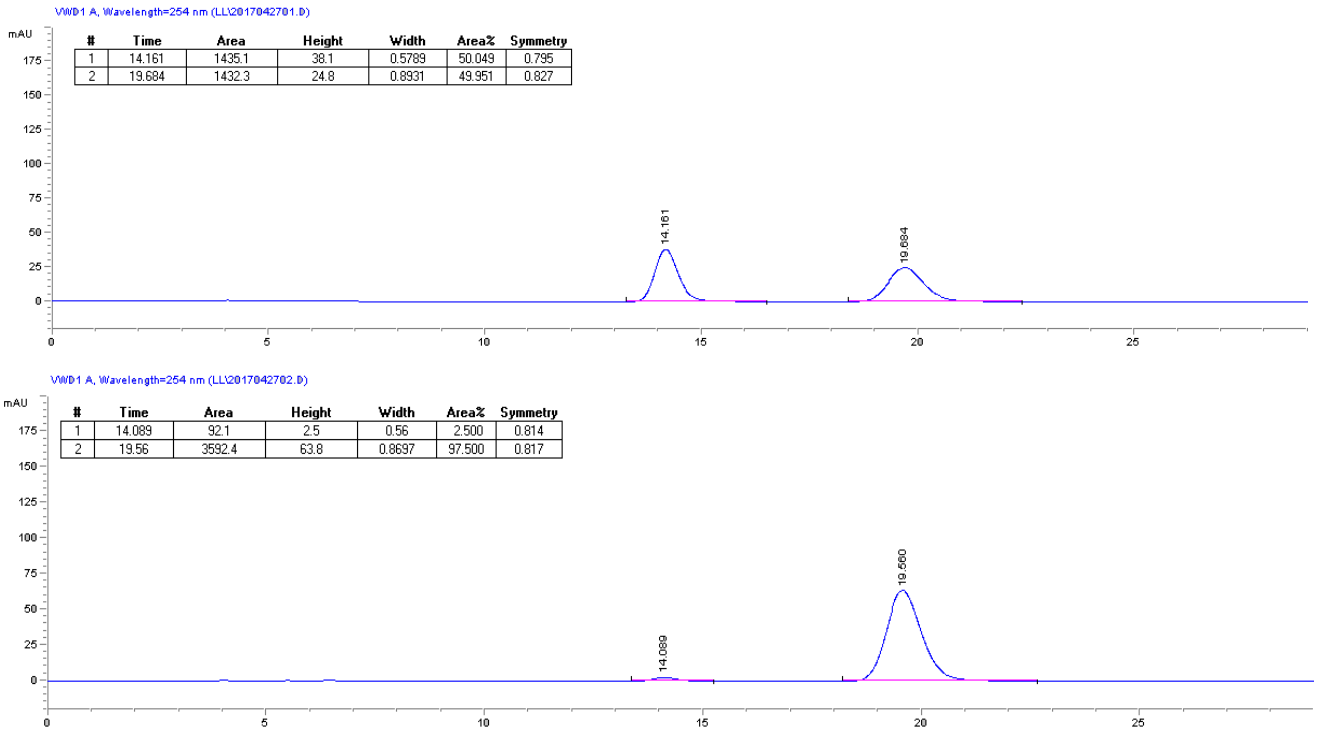
#	Time	Area	Height	Width	Area%	Symmetry
1	8.783	2512.7	153.5	0.2434	50.093	0.588
2	13.585	2503.4	74.6	0.5198	49.907	0.685



#	Time	Area	Height	Width	Area%	Symmetry
1	8.828	5116.8	309.3	0.2483	97.238	0.588
2	13.74	145.4	4.3	0.5227	2.762	0.728

(*R*)-3-(naphthalen-2-yl)-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ia). Colorless oil was obtained in 96% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 92-94 °C. 95% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 14.1 min, t_R (major) = 19.6 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.87 (m, 3H), 7.79–7.71 (m, 3H), 7.58–7.47 (m, 3H), 7.41–7.37 (m, 2H), 7.33–7.22 (m, 5H), 7.18–7.14 (m, 1H), 6.57 (dd, *J* = 6.0, 1.4 Hz, 1H), 5.18 (dd, *J* = 6.0, 4.1 Hz, 1H), 5.00 (dd, *J* = 3.9, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.6, 145.0, 138.4, 137.3, 133.1, 132.9, 130.6, 129.2, 128.9, 128.2, 127.9, 127.8, 127.6, 127.0, 126.5, 126.4, 126.0, 124.9, 121.2, 108.6, 97.6, 38.2. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{21}N_2O$ [M + H] 401.1654, found 401.1658.

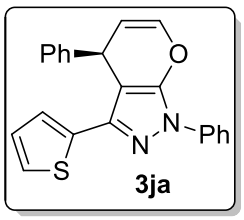


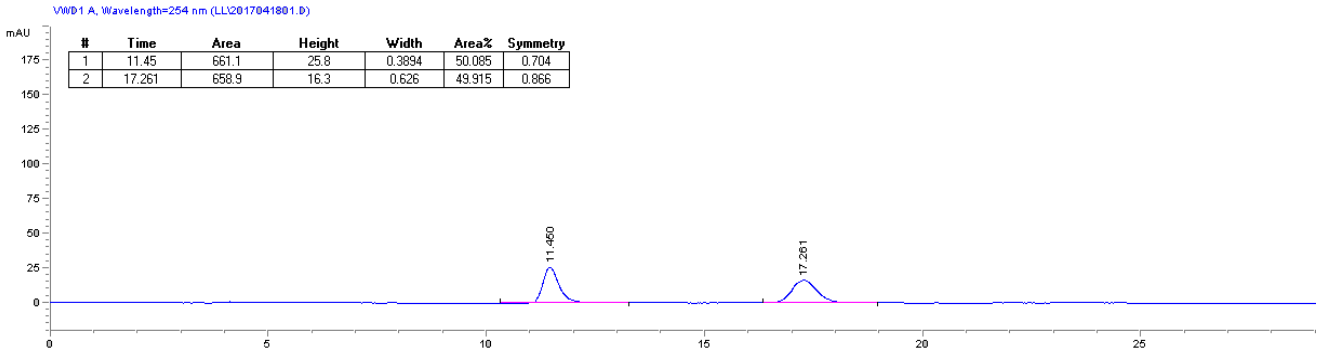


#	Time	Area	Height	Width	Area%	Symmetry
1	14.161	1435.1	38.1	0.5789	50.049	0.795
2	19.684	1432.3	24.8	0.8931	49.951	0.827

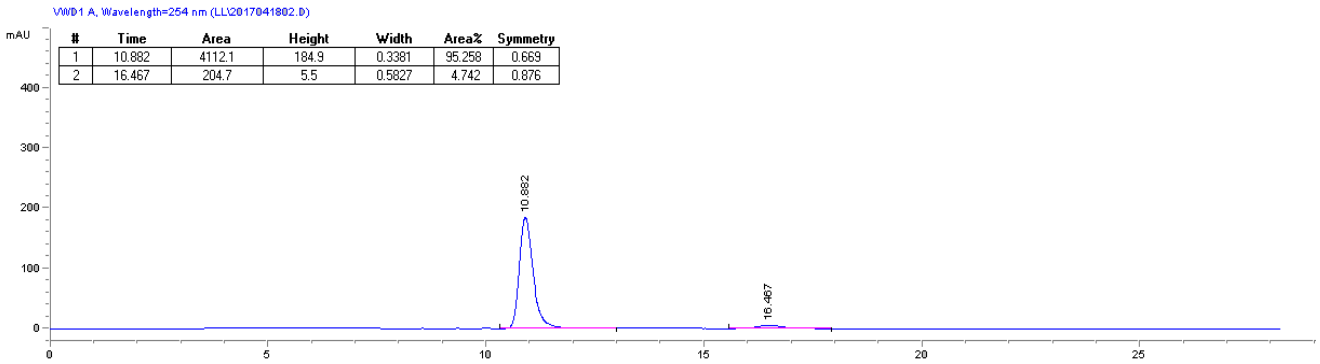
#	Time	Area	Height	Width	Area%	Symmetry
1	14.089	92.1	2.5	0.56	2.500	0.814
2	19.56	3592.4	63.8	0.8697	97.500	0.817

(*R*)-1,4-diphenyl-3-(thiophen-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3ja). Colorless oil was obtained in 72% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 91% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 10.9 min, t_R (minor) = 16.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.86 (m, 2H), 7.48–7.44 (m, 2H), 7.30–7.12 (m, 7H), 6.83–6.79 (m, 2H), 6.52 (dd, *J* = 6.1, 1.5 Hz, 1H), 5.15 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.85 (dd, *J* = 4.0, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 144.4, 143.7, 138.1, 137.2, 135. 8, 129.2, 128.9, 127.7, 127.2, 127.0, 126. 5, 125.4, 125.0, 121.1, 108.6, 96.6, 37.5. HRMS (ESI): *m*/*z* calcd for $C_{22}H_{17}N_2OS$ [M + H] 357.1062, found 357.1068.



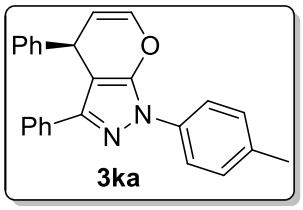


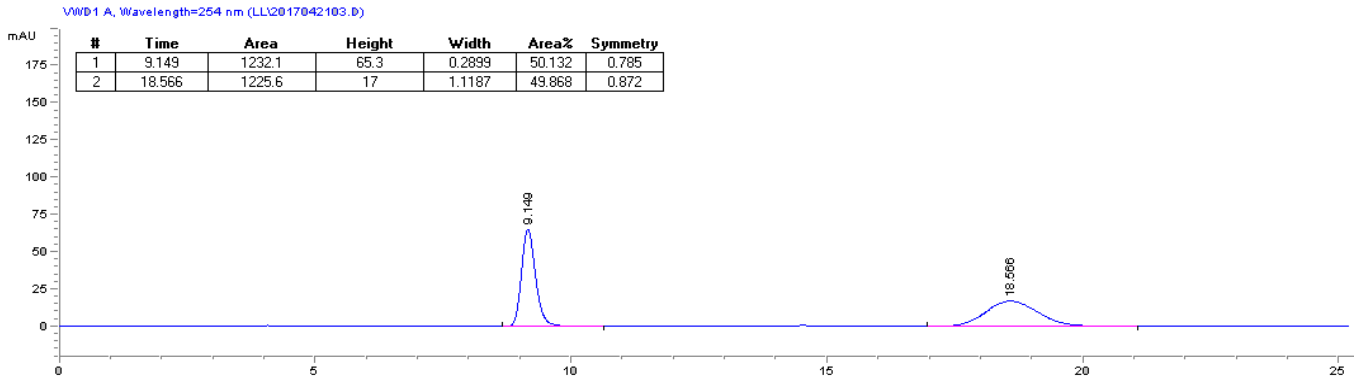
#	Time	Area	Height	Width	Area%	Symmetry
1	11.45	661.1	25.8	0.3894	50.085	0.704
2	17.261	658.9	16.3	0.626	49.915	0.866



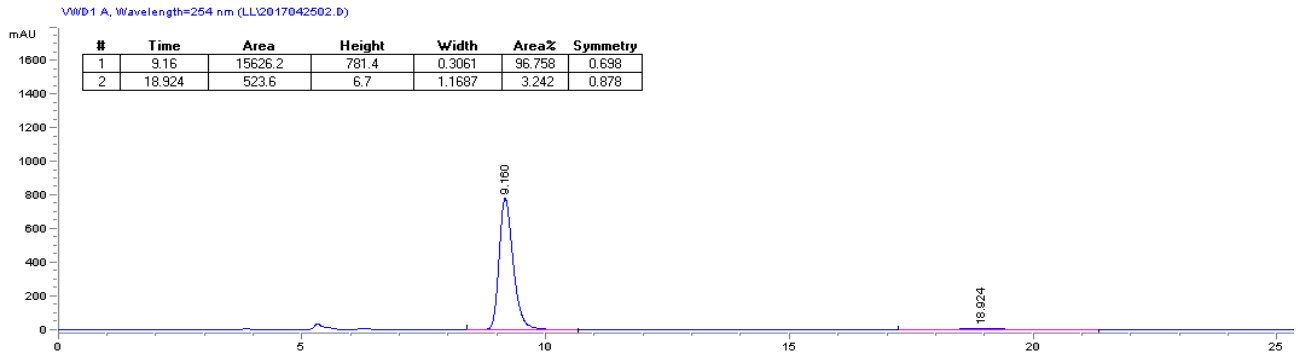
#	Time	Area	Height	Width	Area%	Symmetry
1	10.882	4112.1	184.9	0.3381	95.258	0.669
2	16.467	204.7	5.5	0.5827	4.742	0.876

(*R*)-3,4-diphenyl-1-(p-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3ka). Pale red solid was obtained in 89% yield after purification with column chromatography on silica gel (petroleum ether /ethyl acetate, 100/1). M.p.: 122-124 °C. 94% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.2 min, t_R (minor) = 18.9 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.54–7.51 (m, 2H), 7.28–7.17 (m, 9H), 7.16–7.12 (m, 1H), 6.55 (dd, *J* = 6.0, 1.4 Hz, 1H), 5.14 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.92 (dd, *J* = 4.0, 1.3 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.3, 144.8, 137.4, 136.2, 135.9, 133.2, 129.7, 128.7, 128.1, 127.8, 127.7, 127.0, 126.8, 121.2, 108.5, 97.2, 38.0, 21.1. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{21}N_2O$ [M + H] 365.1654, found 365.1656.



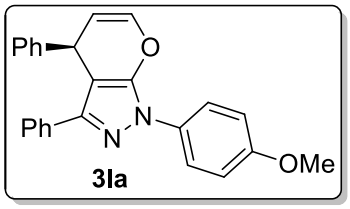


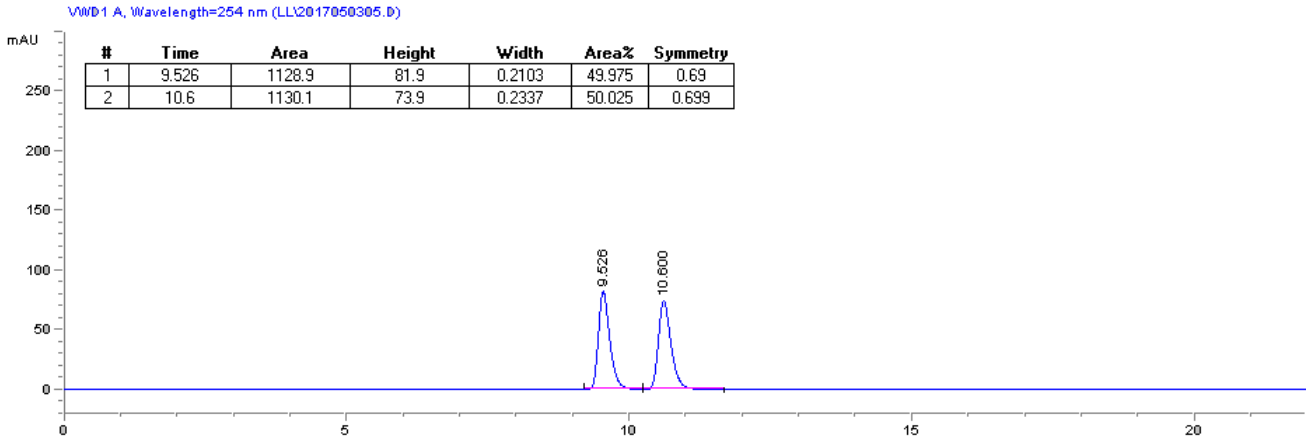
#	Time	Area	Height	Width	Area%	Symmetry
1	9.149	1232.1	65.3	0.2899	50.132	0.785
2	18.566	1225.6	17	1.1187	49.868	0.872



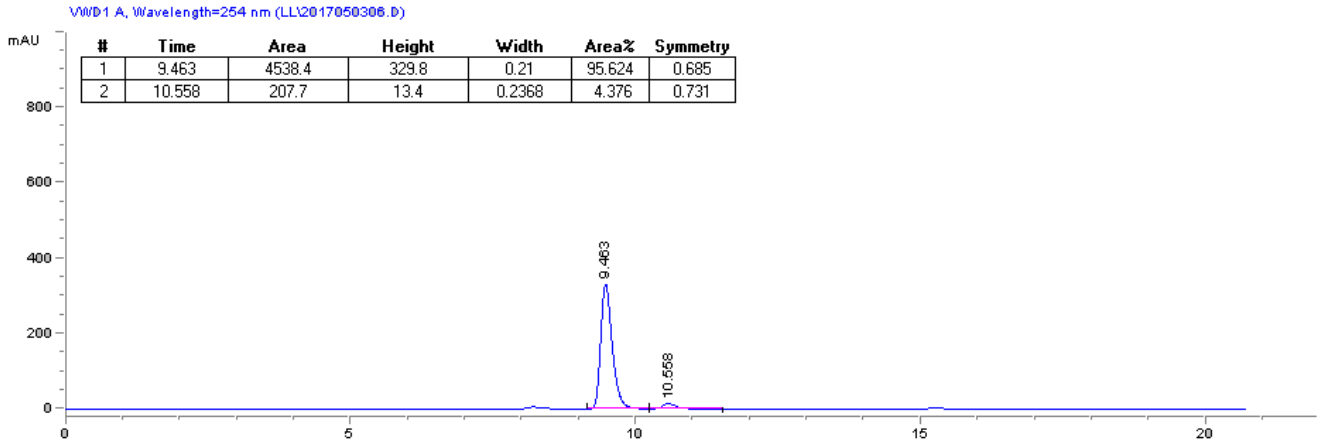
#	Time	Area	Height	Width	Area%	Symmetry
1	9.16	15626.2	781.4	0.3061	96.758	0.698
2	18.924	523.6	6.7	1.1687	3.242	0.878

(*R*)-1-(4-methoxyphenyl)-3,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3la). Colorless oil was obtained in 86% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 50/1). M.p.: 76-78 °C. 91% ee was determined by chiral HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.5 min, t_R (minor) = 10.6 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.74 (m, 2H), 7.53–7.51 (m, 2H), 7.24–7.14 (m, 8H), 7.01–6.98 (m, 2H), 6.54 (dd, *J* = 6.0, 1.4 Hz, 1H), 5.13 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.92 (dd, *J* = 4.0, 1.3 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 147.7, 147.1, 144.8, 137.4, 133.3, 131.6, 128.7, 128.1, 127.8, 127.7, 127.0, 126.8, 122.9, 114.3, 108.5, 97.0, 55.6, 38.0. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{21}N_2O_2$ [M + H] 381.1603, found 381.1605.



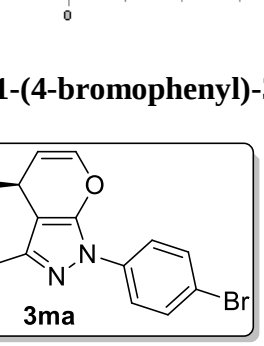


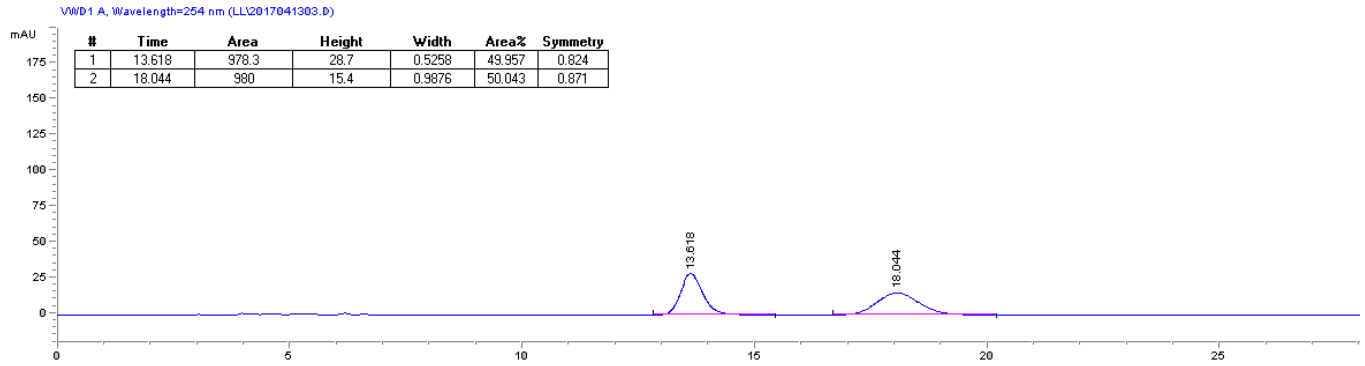
#	Time	Area	Height	Width	Area%	Symmetry
1	9.526	1128.9	81.9	0.2103	49.975	0.69
2	10.6	1130.1	73.9	0.2337	50.025	0.699



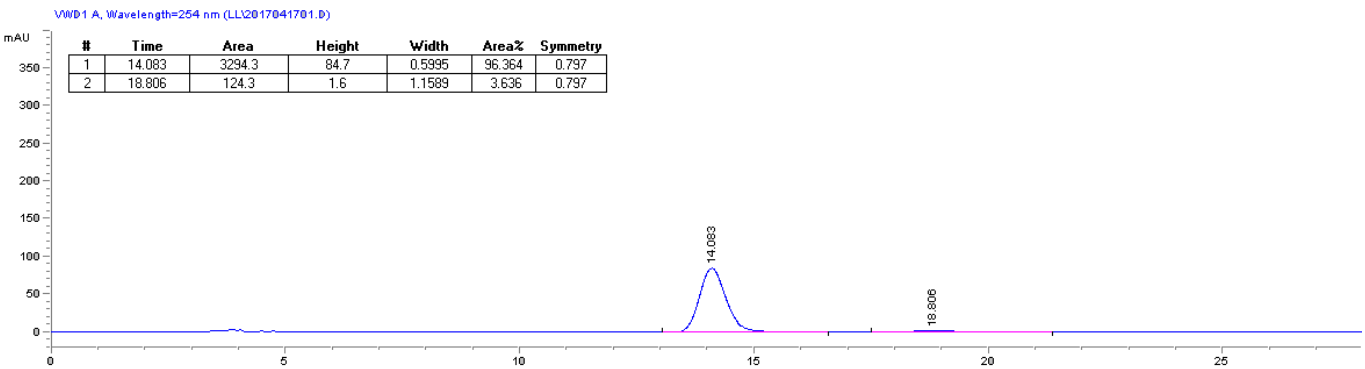
#	Time	Area	Height	Width	Area%	Symmetry
1	9.463	4538.4	329.8	0.21	95.624	0.685
2	10.558	207.7	13.4	0.2368	4.376	0.731

(*R*)-1-(4-bromophenyl)-3,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazole (3ma). Colorless oil was obtained in 81% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 102-104 °C. 93% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 14.1 min, t_R (minor) = 18.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.80 (m, 2H), 7.60–7.57 (m, 2H), 7.52–7.50 (m, 2H), 7.26–7.13 (m, 8H), 6.57 (dd, *J* = 6.0, 1.4 Hz, 1H), 5.16 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.91 (dd, *J* = 4.0, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.4, 144.5, 137.5, 137.3, 132.9, 132.2, 128.7, 128.2, 128.0, 127.7, 127.0, 126.9, 122.2, 119.5, 108.6, 97.7, 37.8. HRMS (ESI): *m/z* calcd for $C_{24}H_{18}BrN_2O$ [M + H] 429.0603, found 429.0607.



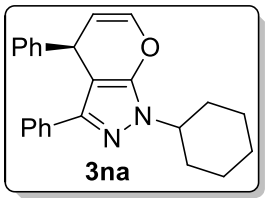


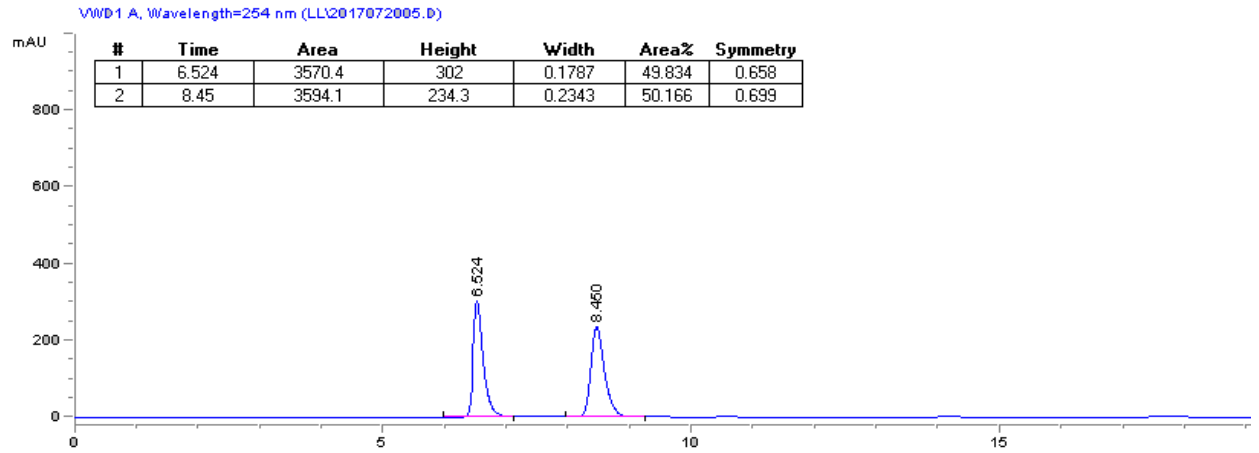
#	Time	Area	Height	Width	Area%	Symmetry
1	13.618	978.3	28.7	0.5258	49.957	0.824
2	18.044	980	15.4	0.9876	50.043	0.871



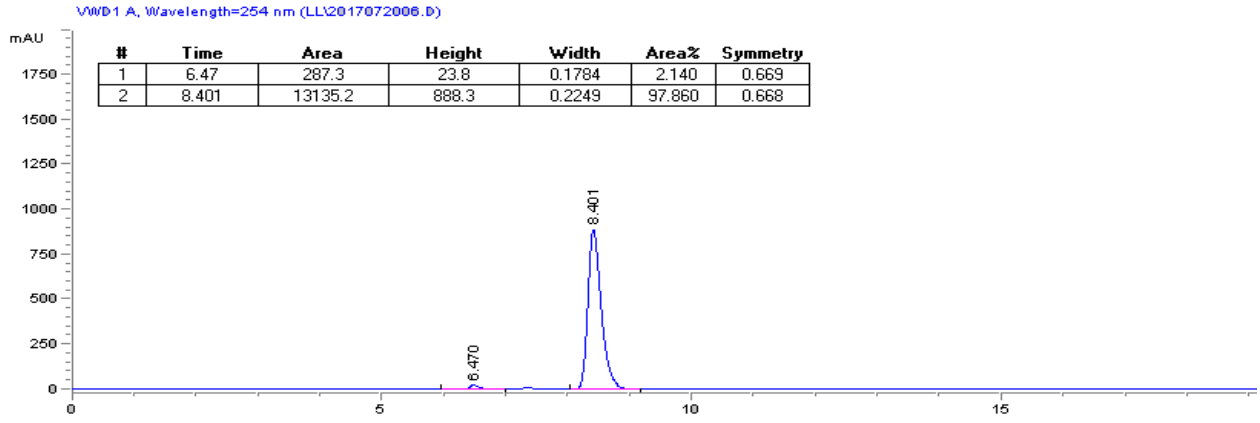
#	Time	Area	Height	Width	Area%	Symmetry
1	14.083	3294.3	84.7	0.5995	96.364	0.797
2	18.806	124.3	1.6	1.1589	3.636	0.797

(*R*)-1-cyclohexyl-3,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3na). Colorless oil was obtained in 83% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 96% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 6.5 min, t_R (major) = 8.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.41 (m, 2H), 7.23 –7.09 (m, 8H), 6.48 (dd, *J* = 6.1, 1.5 Hz, 1H), 5.06 (dd, *J* = 6.1, 4.1 Hz, 1H), 4.84 (dd, *J* = 4.0, 1.4 Hz, 1H), 4.22–4.14 (m, 1H), 2.06–1.90 (m, 6H), 1.73–1.70 (m, 1H), 1.48–1.23(m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 146.0, 145.2, 137.2, 133.9, 128.6, 128.0, 127.7, 127.1, 126.8, 126.6, 108.4, 95.4, 57.5, 38.0, 32.1, 32.1, 25.7, 25.3. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{25}N_2O$ [M + H] 357.1967, found 357.1964.



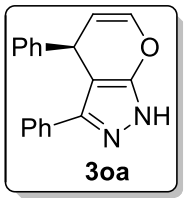


#	Time	Area	Height	Width	Area%	Symmetry
1	6.524	3570.4	302	0.1787	49.834	0.658
2	8.45	3594.1	234.3	0.2343	50.166	0.699

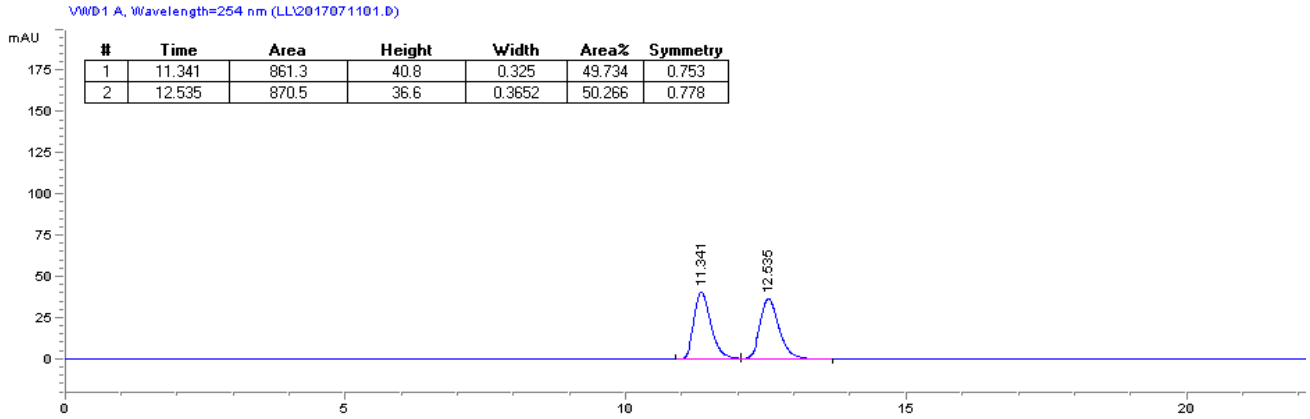


#	Time	Area	Height	Width	Area%	Symmetry
1	6.47	287.3	23.8	0.1784	2.140	0.669
2	8.401	13135.2	888.3	0.2249	97.860	0.668

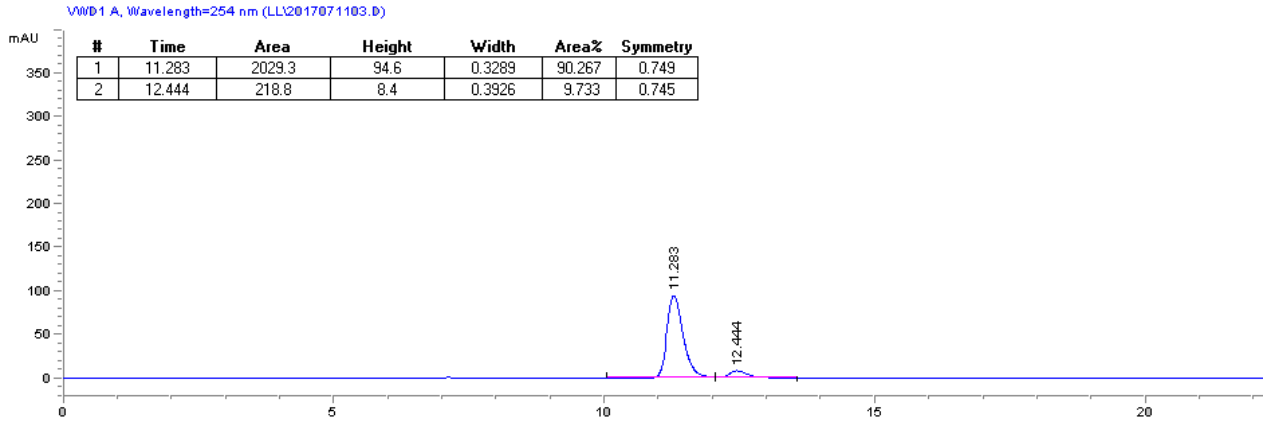
(*R*)-3,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazole (3oa). Colorless oil was obtained in 36% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 10/1). 81% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 11.3 min, t_R (minor) = 12.4 min. ^{1}H NMR (400 MHz,



DMSO-d_6) δ 12.71 (s, 1H), 7.46–7.41 (m, 2H), 7.30–7.06 (m, 8H), 6.71–6.69 (m, 1H), 5.04–4.98 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) 145.6, 139.0, 129.0, 128.8, 128.4, 127.9, 126.8, 126.5, 107.1, 101.8, 36.5. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{15}N_2O$ [M + H] 275.1184, found 275.1185.

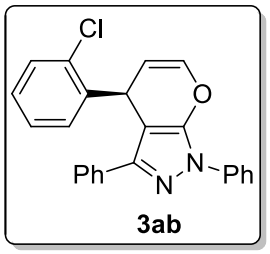


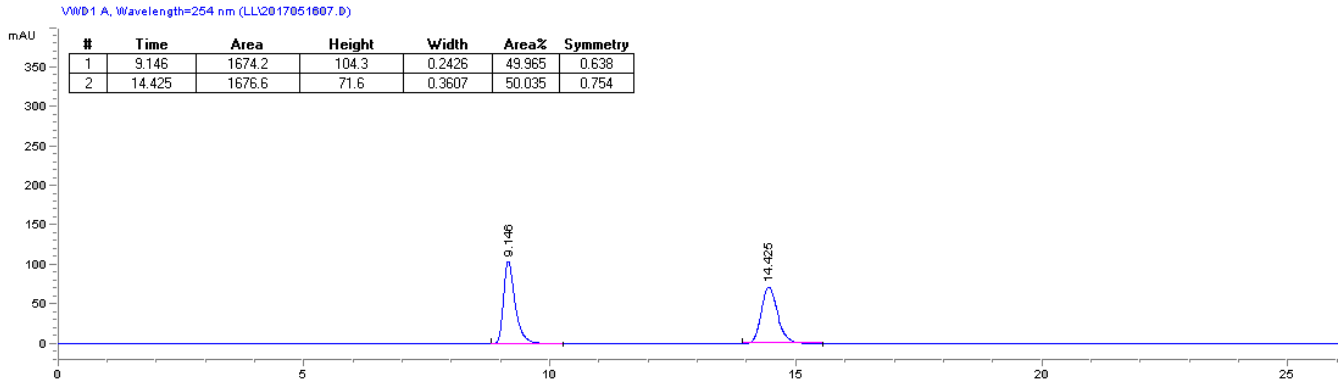
#	Time	Area	Height	Width	Area%	Symmetry
1	11.341	861.3	40.8	0.325	49.734	0.753
2	12.535	870.5	36.6	0.3652	50.266	0.778



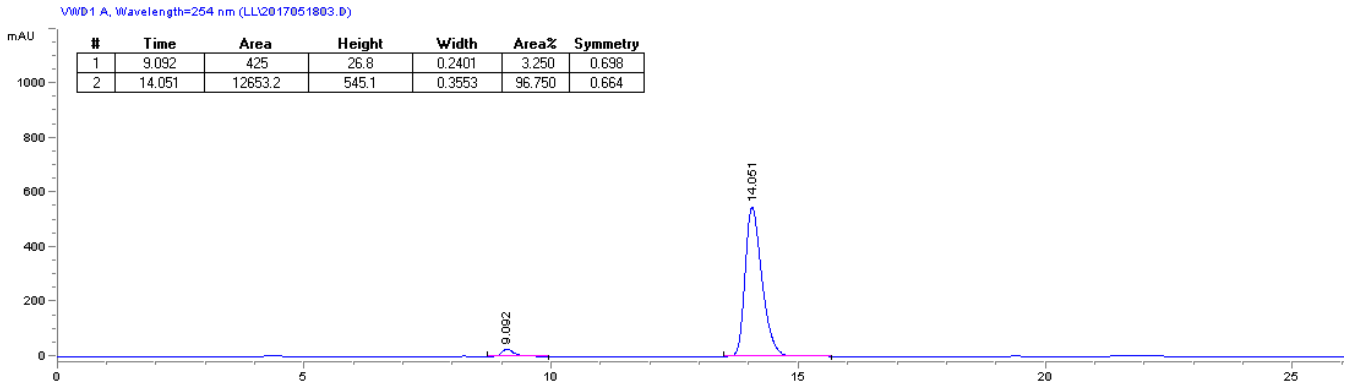
#	Time	Area	Height	Width	Area%	Symmetry
1	11.283	2029.3	94.6	0.3289	90.267	0.749
2	12.444	218.8	8.4	0.3926	9.733	0.745

(*R*)-4-(2-chlorophenyl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ab). Pale pink solid oil was obtained in 68% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 138-140 °C. 94% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 9.1 min, t_R (major) = 14.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.55–7.53 (m, 2H), 7.48–7.45 (m, 2H), 7.34–7.27 (m, 2H), 7.23–7.03 (m, 6H), 6.54 (dd, *J* = 6.1, 1.5 Hz, 1H), 5.49 (dd, *J* = 3.9, 1.5 Hz, 1H), 5.23 (dd, *J* = 6.0, 4.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.7, 141.4, 138.4, 138.0, 132.9, 132.1, 130.2, 129.4, 129.2, 128.3, 128.1, 127.9, 127.6, 126.5, 121.0, 106.3, 96.2, 34.5. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}ClN_2O$ [M + H] 385.1108, found 385.1107.



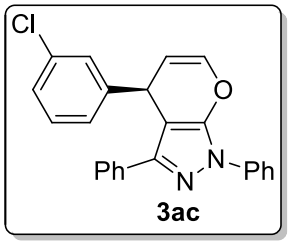


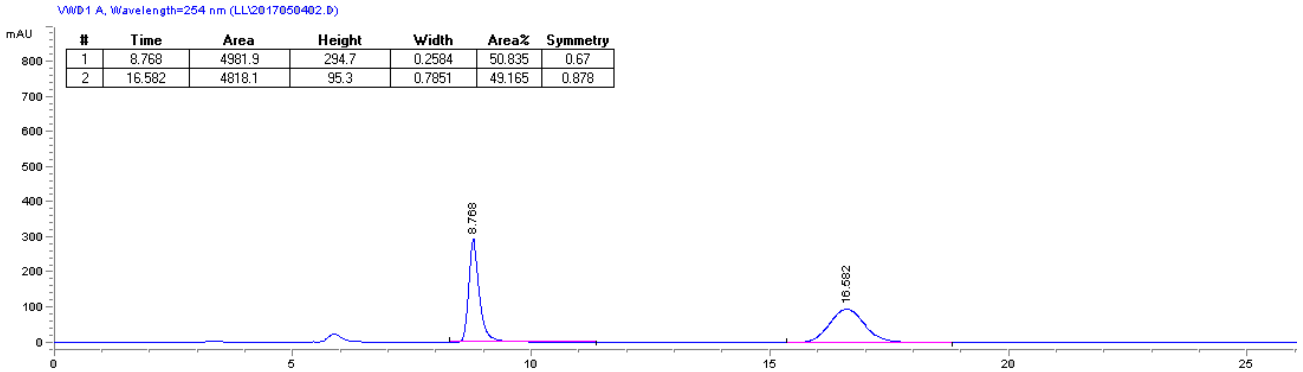
#	Time	Area	Height	Width	Area%	Symmetry
1	9.146	1674.2	104.3	0.2426	49.965	0.638
2	14.425	1676.6	71.6	0.3607	50.035	0.754



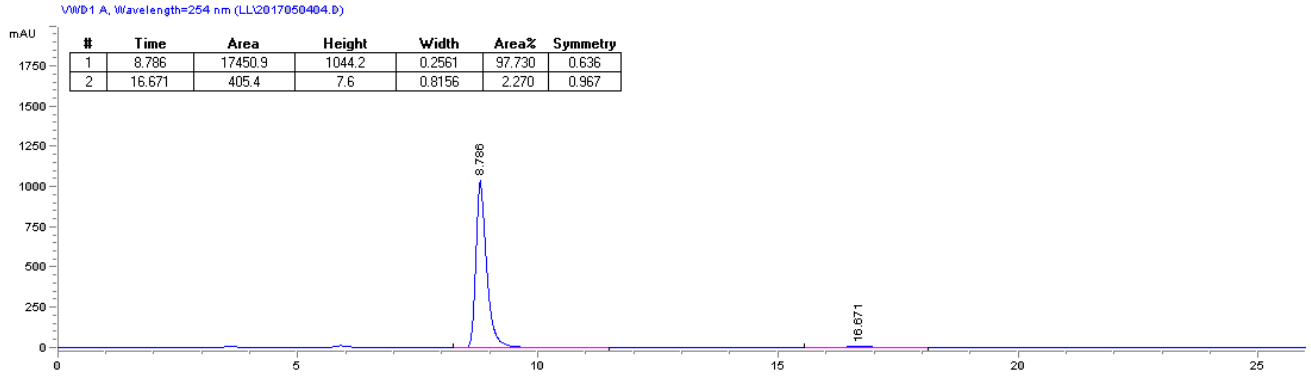
#	Time	Area	Height	Width	Area%	Symmetry
1	9.092	425	26.8	0.2401	3.250	0.698
2	14.051	12653.2	545.1	0.3553	96.750	0.664

(*R*)-4-(3-chlorophenyl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ac). Colorless oil was obtained in 91% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 95% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 8.8 min, t_R (minor) = 16.7 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.53–7.44 (m, 4H), 7.31–7.05 (m, 8H), 6.57 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.09 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.90 (dd, *J* = 4.0, 1.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 147.3, 146.7, 138.2, 137.8, 134.6, 133.0, 129.9, 129.2, 128.3, 128.0, 128.0, 127.1, 127.0, 126.5, 125.9, 121.1, 107.7, 96.9, 37.7. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}ClN_2O$ [M + H] 385.1108, found 385.1115.



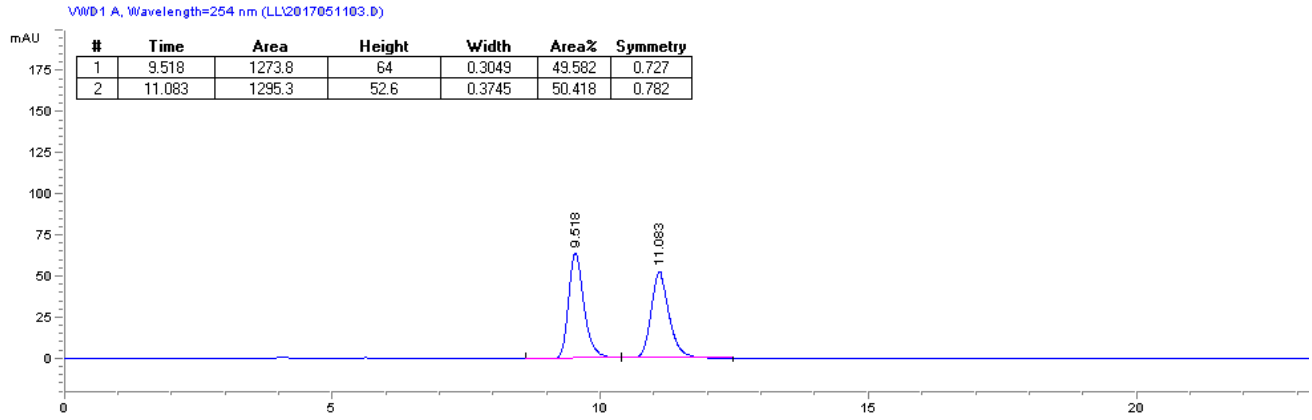


#	Time	Area	Height	Width	Area%	Symmetry
1	8.768	4981.9	294.7	0.2584	50.835	0.67
2	16.582	4818.1	95.3	0.7851	49.165	0.878

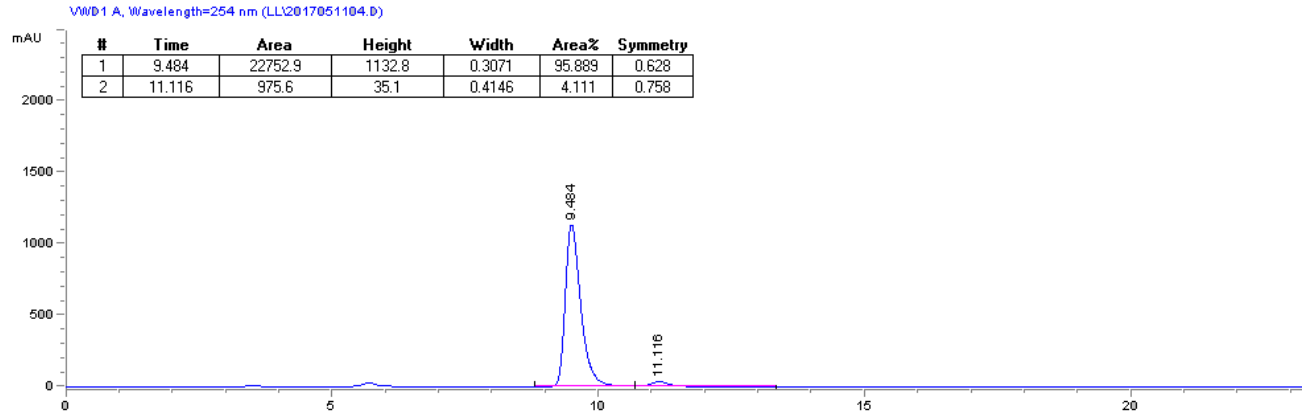


#	Time	Area	Height	Width	Area%	Symmetry
1	8.786	17450.9	1044.2	0.2561	97.730	0.636
2	16.671	405.4	7.6	0.8156	2.270	0.967

(*R*)-4-(4-chlorophenyl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ad). Colorless oil was obtained in 96% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 92% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.5 min, t_R (minor) = 11.1 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.53–7.44 (m, 4H), 7.30–7.10 (m, 8H), 6.55 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.08 (dd, *J* = 6.0, 4.1 Hz, 1H), 4.90 (dd, *J* = 4.0, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.3, 143.2, 138.3, 137.7, 133.0, 132.5, 129.2, 129.1, 128.9, 128.3, 128.0, 127.0, 126.5, 121.1, 108.0, 97.0, 37.4. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}ClN_2O$ [M + H] 385.1108, found 385.1107.

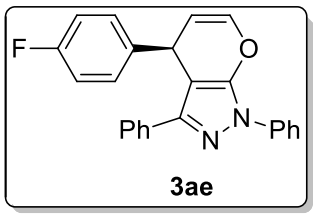


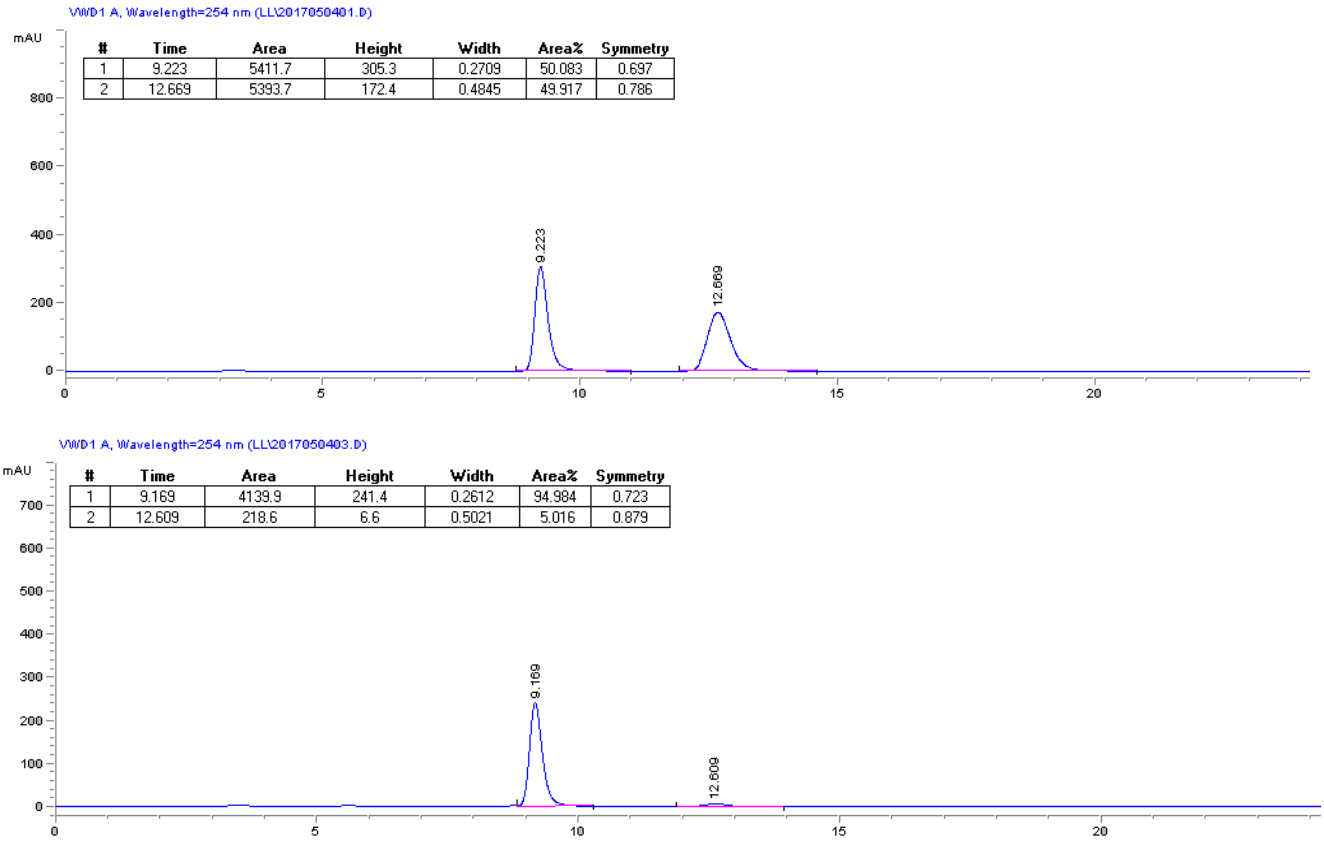
#	Time	Area	Height	Width	Area%	Symmetry
1	9.518	1273.8	64	0.3049	49.582	0.727
2	11.083	1295.3	52.6	0.3745	50.418	0.782



#	Time	Area	Height	Width	Area%	Symmetry
1	9.484	22752.9	1132.8	0.3071	95.889	0.628
2	11.116	975.6	35.1	0.4146	4.111	0.758

(*R*)-4-(4-fluorophenyl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ae). Colorless oil was obtained in 86% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 90% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.2 min, t_R (minor) = 12.6 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.55–7.50 (m, 2H), 7.47–7.41 (m, 2H), 7.29–7.25 (m, 1H), 7.24–7.18 (m, 3H), 7.17–7.11 (m, 2H), 6.92–6.86 (m, 2H), 6.53 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.07 (dd, *J* = 6.0, 4.0 Hz, 1H), 4.89 (dd, *J* = 4.0, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ161.6 (d, *J* = 245.1 Hz), 148.2, 147.3, 140.6 (d, *J* = 3.1 Hz), 138.3, 137.5, 133.1, 129.3 (d, *J* = 8.1 Hz), 129.2, 128.2, 128.0, 127.0, 126.5, 121.0, 115.5 (d, *J* = 21.4 Hz), 108.3, 97.4, 37.2. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}FN_2O$ [M + H] 369.1403, found 369.1411.

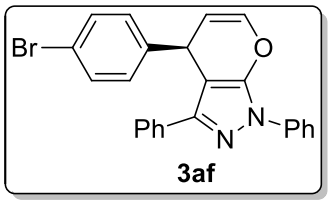




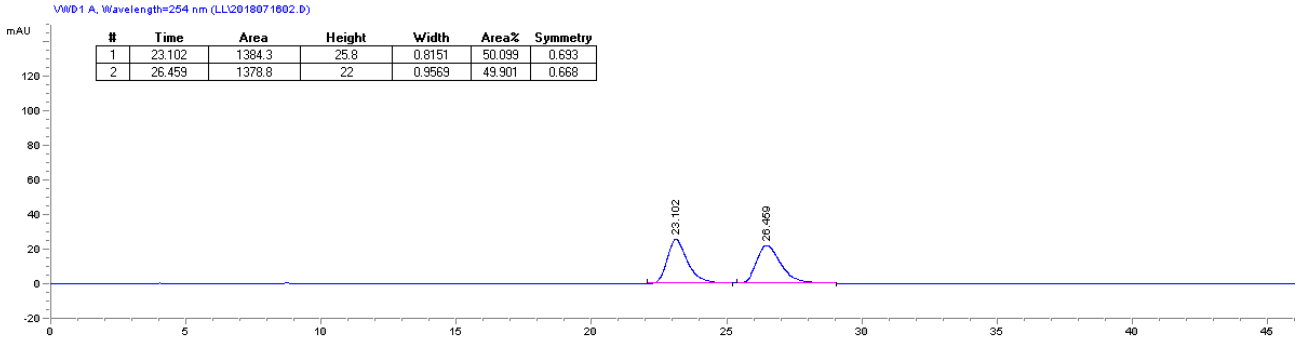
#	Time	Area	Height	Width	Area%	Symmetry
1	9.223	5411.7	305.3	0.2709	50.083	0.697
2	12.669	5393.7	172.4	0.4845	49.917	0.786

#	Time	Area	Height	Width	Area%	Symmetry
1	9.169	4139.9	241.4	0.2612	94.984	0.723
2	12.609	218.6	6.6	0.5021	5.016	0.879

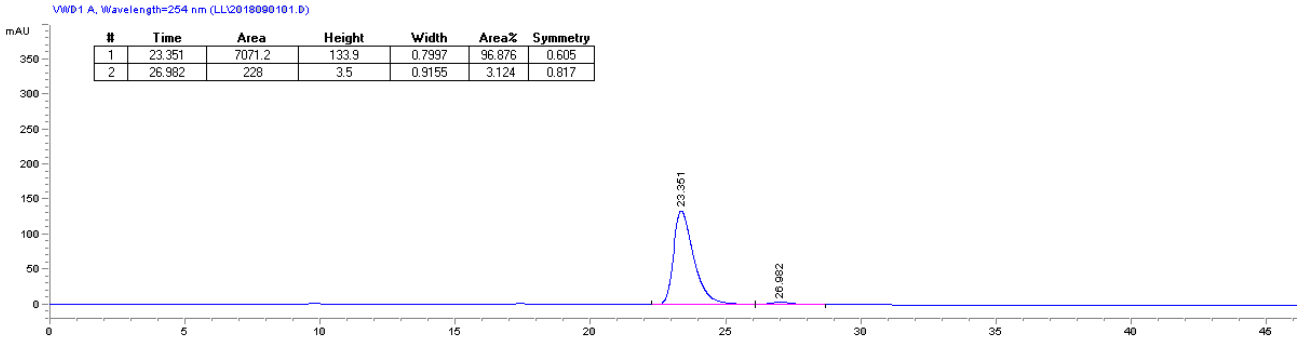
(*R*)-4-(4-bromophenyl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3af). Pale pink solid was obtained in 91% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 140-142 °C. 93% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 23.4 min, t_R (minor) = 27.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.53–7.52 (m, 2H), 7.49–7.46 (m, 2H), 7.36–7.23 (m, 6H), 7.09–7.07 (m, 2H), 6.59-6.58 (m, 1H), 5.12-5.10 (m, 1H), 4.92–4.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ



148.1, 147.3, 143.8, 138.3, 137.7, 133.0, 131.8, 129.4, 129.1, 128.2, 128.0, 127.0, 126.5, 121.1, 120.7, 107.9, 96.9, 37.4. HRMS (ESI): *m*/*z* calcd for $C_{24}H_{18}BrN_2O$ [M + H] 429.0603, found 429.0601.

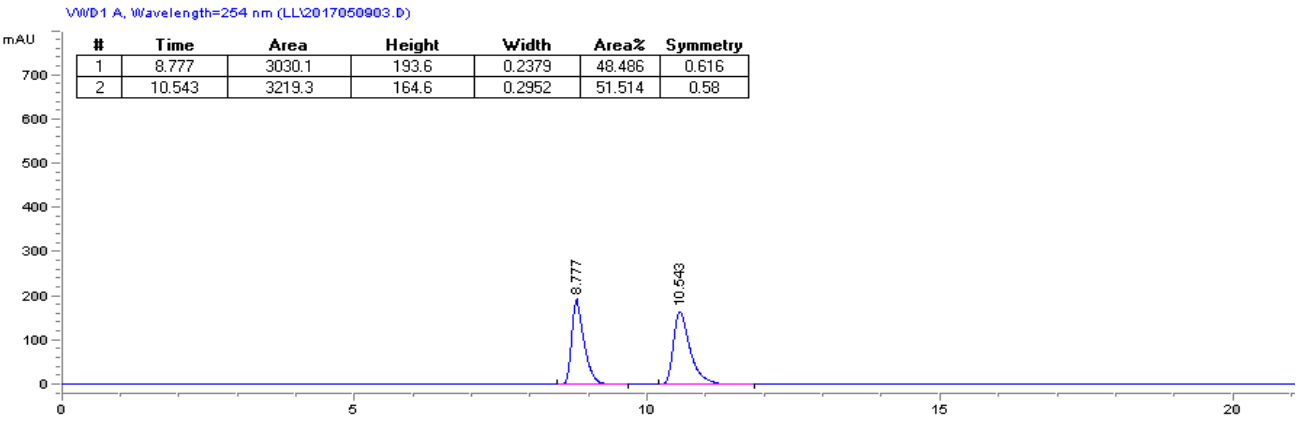


#	Time	Area	Height	Width	Area%	Symmetry
1	23.102	1384.3	25.8	0.8151	50.099	0.693
2	26.459	1378.8	22	0.9569	49.901	0.668

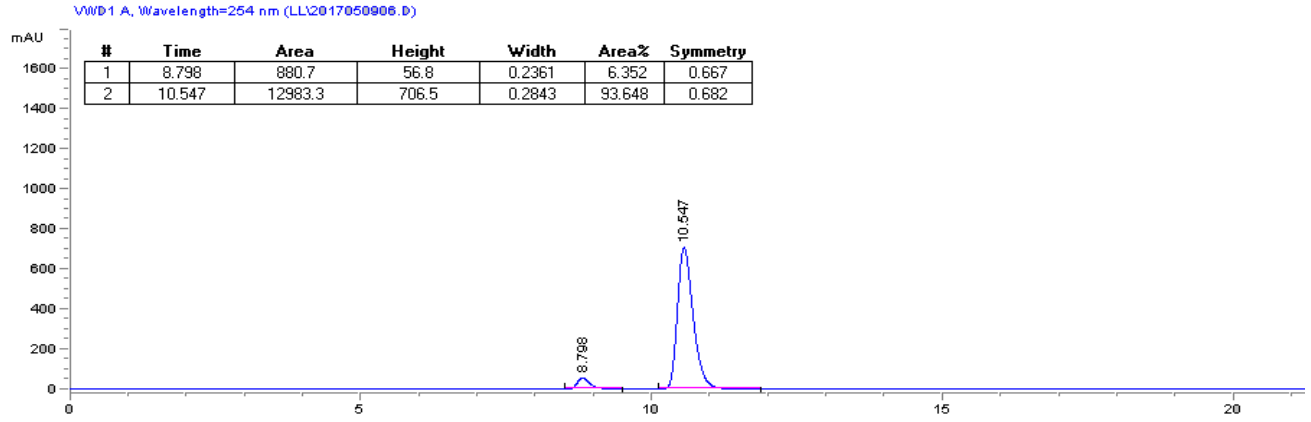


#	Time	Area	Height	Width	Area%	Symmetry
1	23.351	7071.2	133.9	0.7997	96.876	0.605
2	26.982	228	3.5	0.9155	3.124	0.817

(*R*)-1,3-diphenyl-4-(p-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3ag). Colorless oil was obtained in 95% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 87% ee was determined by chiral HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 8.8 min, t_R (major) = 10.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.57–7.56 (m, 2H), 7.49–7.45 (m, 2H), 7.30–7.17 (m, 4H), 7.11–7.04 (m, 4H), 6.55 (dd, *J* = 6.0, 0.9 Hz, 1H), 5.14 (dd, *J* = 5.9, 4.2 Hz, 1H), 4.89–4.88 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.4, 141.9, 138.4, 137.2, 136.4, 133.2, 129.4, 129.1, 128.2, 127.8, 127.6, 127.0, 126.3, 121.1, 108.8, 97.5, 37.5, 21.1. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{21}N_2O$ [M + H] 365.1654, found 365.1651.

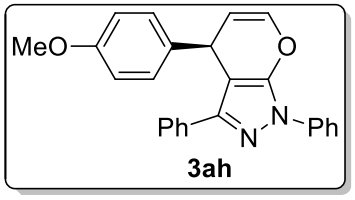


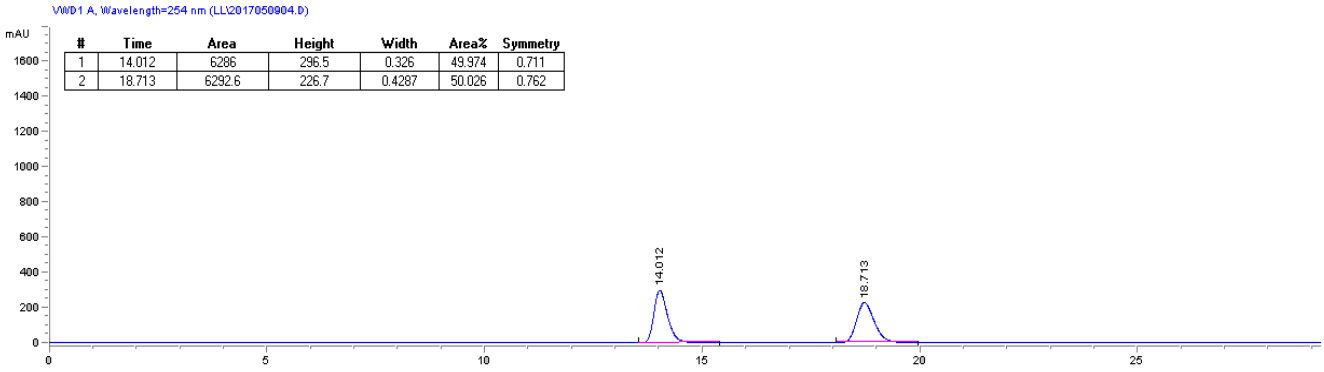
#	Time	Area	Height	Width	Area%	Symmetry
1	8.777	3030.1	193.6	0.2379	48.486	0.616
2	10.543	3219.3	164.6	0.2952	51.514	0.58



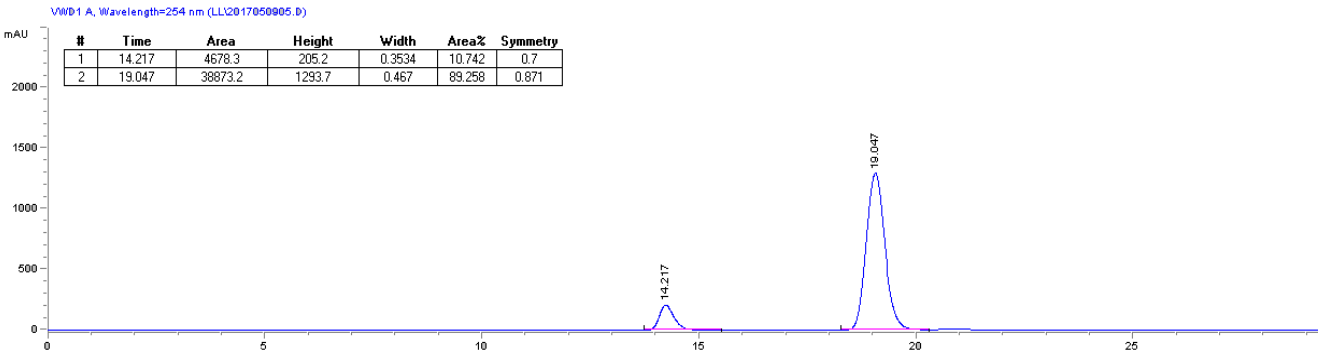
#	Time	Area	Height	Width	Area%	Symmetry
1	8.798	880.7	56.8	0.2361	6.352	0.667
2	10.547	12983.3	706.5	0.2843	93.648	0.682

(*R*)-4-(4-methoxyphenyl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ah). Colorless oil was obtained in 92% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1).79% ee was determined by chiral HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 14.2 min, t_R (major) = 19.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.57–7.55 (m, 2H), 7.50–7.44 (m, 2H), 7.30–7.17 (m, 4H), 7.13–7.11 (m, 2H), 6.78–6.76 (m, 2H), 6.53 (dd, *J* = 6.0, 0.8 Hz, 1H), 5.11 (dd, *J* = 5.9, 4.2 Hz, 1H), 4.87–4.86 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 148.2, 147.4, 138.4, 137.1, 133.2, 129.1, 128.7, 128.2, 127.8, 127.1, 126.4, 121.1, 114.1, 108.8, 97.7, 55.2, 37.1. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{21}N_2O_2$ [M + H] 381.1603, found 381.1606.



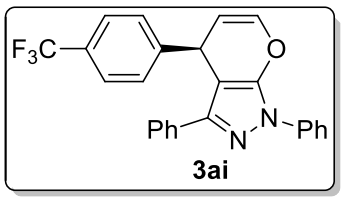


#	Time	Area	Height	Width	Area%	Symmetry
1	14.012	6286	296.5	0.326	49.974	0.711
2	18.713	6292.6	226.7	0.4287	50.026	0.762

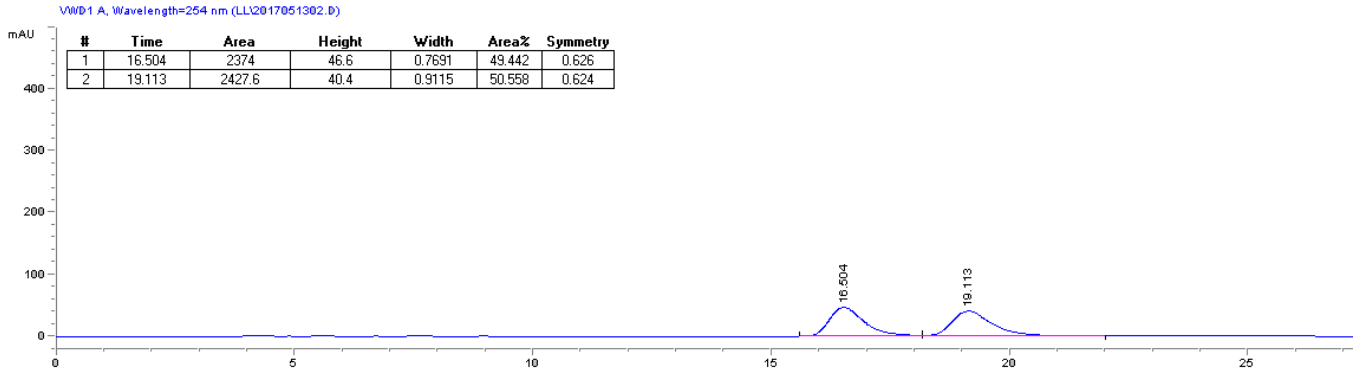


#	Time	Area	Height	Width	Area%	Symmetry
1	14.217	4678.3	205.2	0.3534	10.742	0.7
2	19.047	38873.2	1293.7	0.467	89.258	0.871

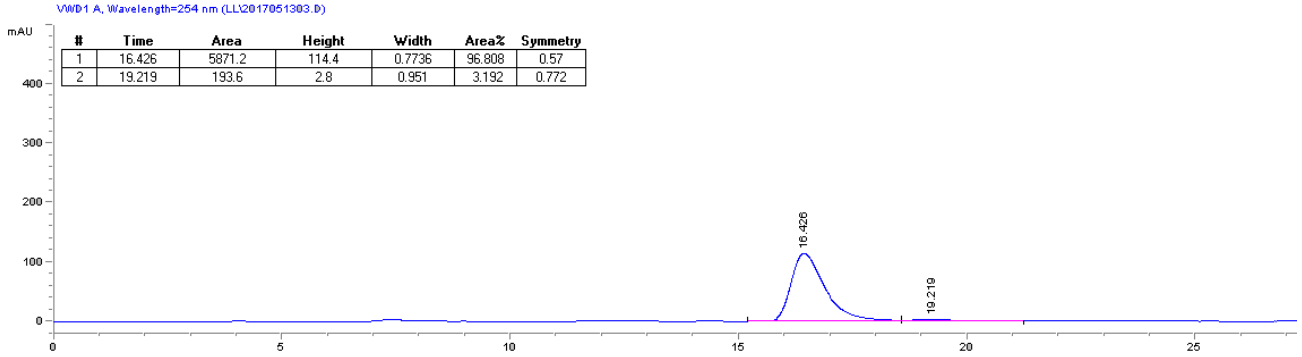
(*R*)-1,3-diphenyl-4-(4-(trifluoromethyl)phenyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3ai). Colorless oil was obtained in 85% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 94% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 16.4 min, t_R (minor) = 19.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.87 (m, 2H), 7.52–7.45 (m, 6H), 7.32–7.28 (m, 3H), 7.25–7.20 (m, 3H), 6.60 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.11 (dd, *J* = 6.0, 4.1 Hz, 1H), 5.02 (dd, *J* = 4.0, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5 (d, *J* = 1.0 Hz), 148.1, 147.3, 138.2, 138.0, 132.9, 129.2, 129.1 (q, *J* = 32.3 Hz), 128.3, 128.1, 128.1, 126.9, 126.6, 125.7 (q, *J* = 3.7 Hz), 124.1 (d, *J* = 272.0 Hz), 121.1, 107.6, 96.6, 37.8. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{18}F_3N_2O$ [M + H] 419.1371, found 419.1376.



3ai

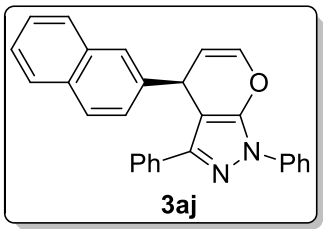


#	Time	Area	Height	Width	Area%	Symmetry
1	16.504	2374	46.6	0.7691	49.442	0.626
2	19.113	2427.6	40.4	0.9115	50.558	0.624



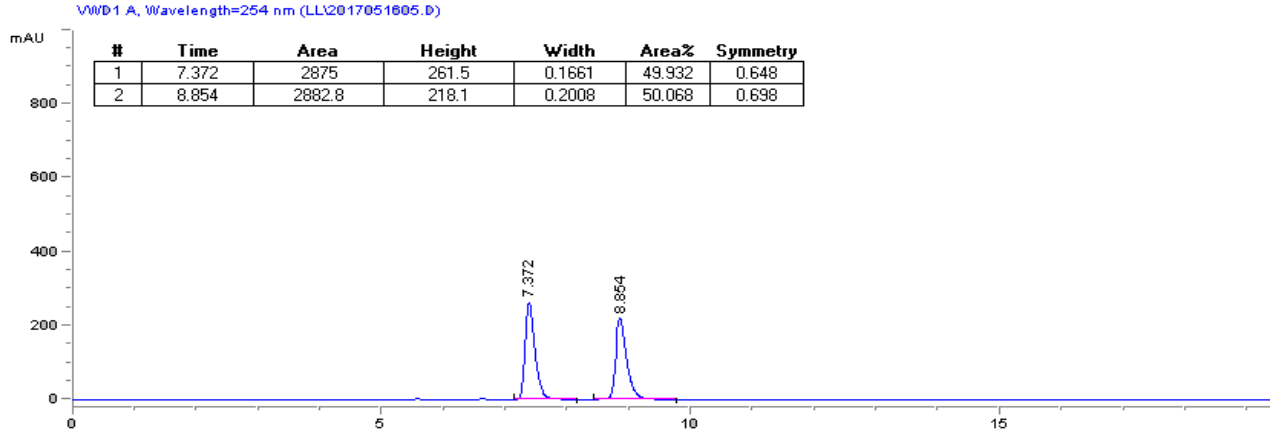
#	Time	Area	Height	Width	Area%	Symmetry
1	16.426	5871.2	114.4	0.7736	96.808	0.57
2	19.219	193.6	2.8	0.951	3.192	0.772

(*R*)-4-(naphthalen-2-yl)-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3aj). Pale pink solid was obtained in 95% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). M.p.: 138-140 °C. 91% ee was determined by chiral HPLC (Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 7.3 min, t_R (major) = 8.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.74–7.69 (m, 3H), 7.62–7.55 (m, 3H), 7.49–7.45 (m, 2H), 7.41–7.34 (m, 3H), 7.30–7.26 (m, 1H), 7.18–7.11 (m, 3H), 6.55 (dd, *J* = 6.0, 1.3 Hz, 1H), 5.16 (dd, *J* = 5.9, 4.2 Hz, 1H), 5.07–5.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 147.5, 142.1, 138.5, 137.6, 133.6, 133.1,

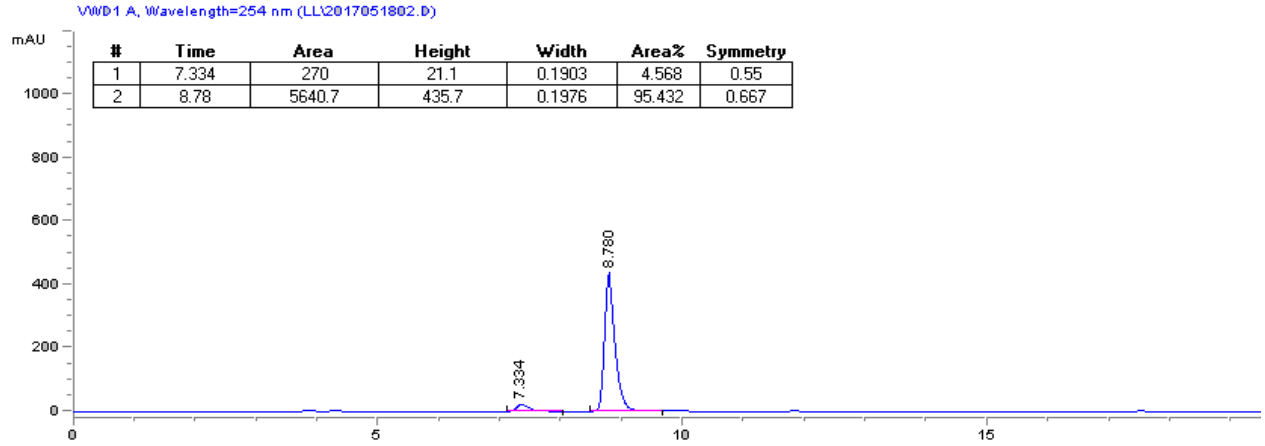


3aj

132.5, 129.2, 128.7, 128.2, 127.9, 127.9, 127.7, 127.0, 126.4, 126.3, 126.2, 126.0, 125.7, 121.1, 108.4, 97.4, 38.1. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{21}N_2O$ [M + H] 401.1654, found 401.1651.

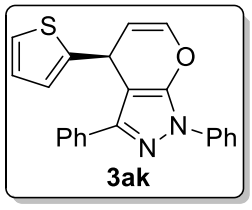


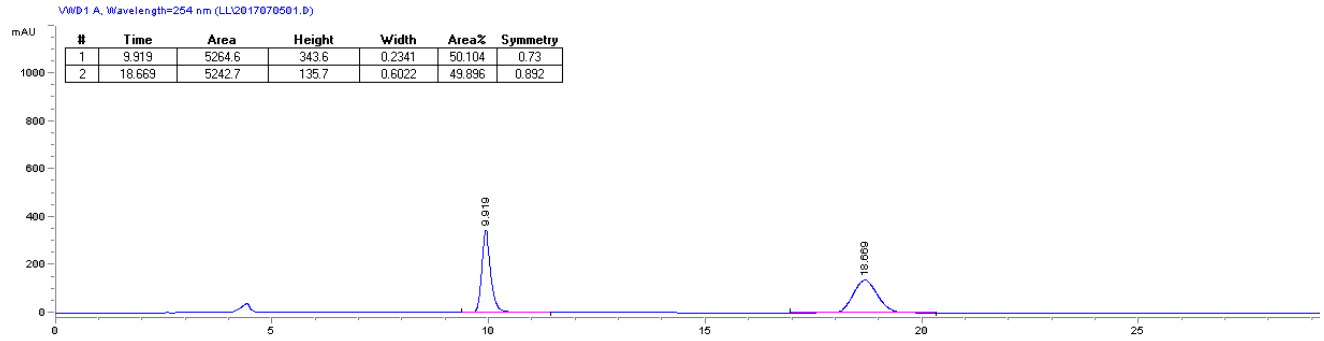
#	Time	Area	Height	Width	Area%	Symmetry
1	7.372	2875	261.5	0.1661	49.932	0.648
2	8.854	2882.8	218.1	0.2008	50.068	0.698

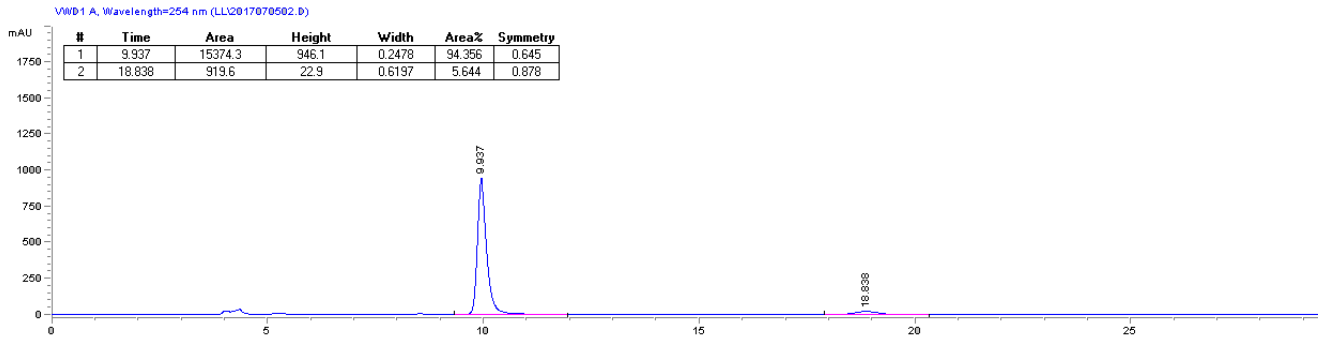


#	Time	Area	Height	Width	Area%	Symmetry
1	7.334	270	21.1	0.1903	4.568	0.55
2	8.78	5640.7	435.7	0.1976	95.432	0.667

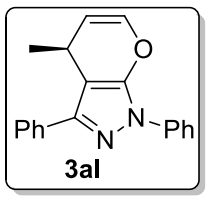
(*S*)-1,3-diphenyl-4-(thiophen-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3ak). Colorless oil was obtained in 96% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 89% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL/min, 254 nm, 40 °C): t_R (major) = 9.9 min, t_R (minor) = 18.8 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.86 (m, 2H), 7.64–7.62 (m, 2H), 7.46–7.43 (m, 2H), 7.29–7.23 (m, 4H), 7.07–7.06 (m, 1H), 6.81–6.79 (m, 2H), 6.58–6.54 (m, 1H), 5.24–5.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 148.1, 146.8, 138.3, 137.8, 133.2, 129.2, 128.3, 128.0, 127.1, 126.7, 126.5, 124.6, 124.1, 121.1, 108.0, 97.7, 32.8. HRMS (ESI): *m*/*z* calcd for $C_{22}H_{17}N_2OS$ [M + H] 357.1062, found 357.1063.

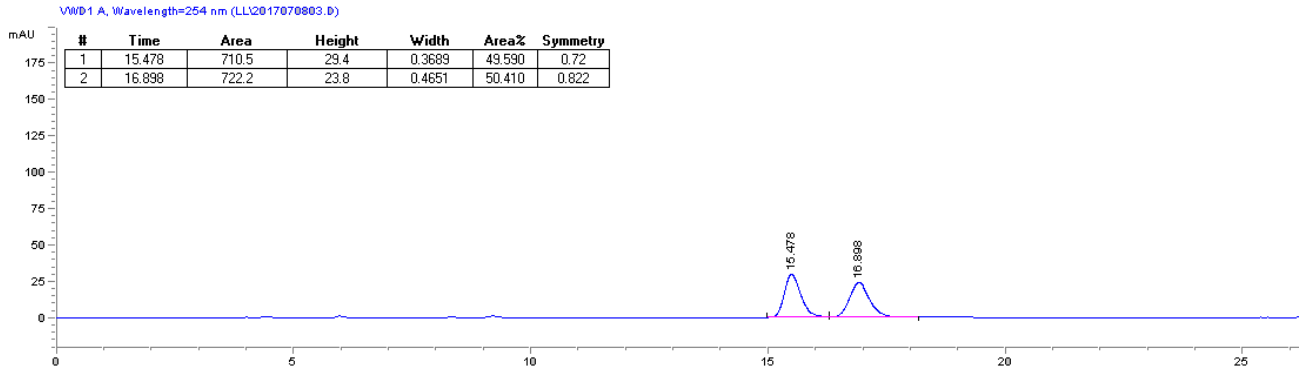


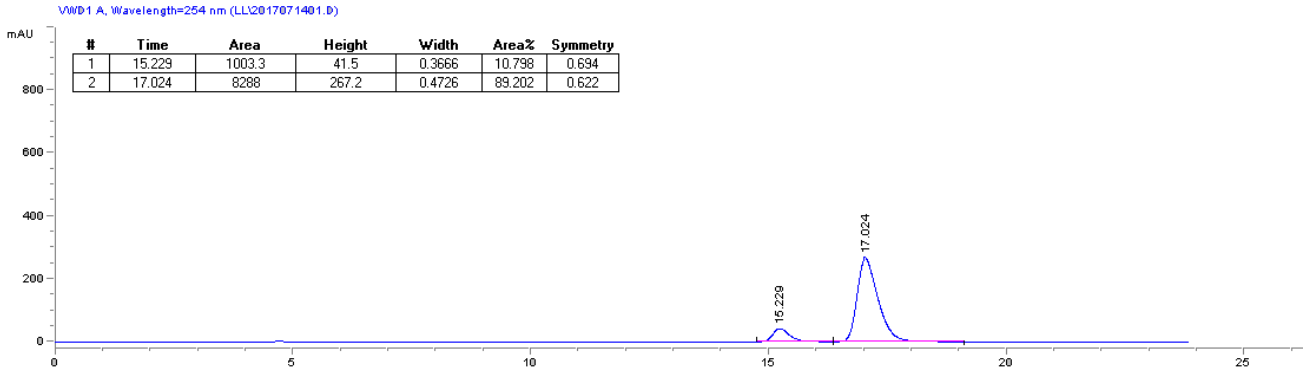




(*S*)-4-methyl-1,3-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3al). Colorless oil was obtained in 34% yield after purification with column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1). 78% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm, 40 °C): t_R (minor) = 15.2 min, t_R (major) = 17.0 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 4H), 7.46–7.41 (m, 4H), 7.36–7.25 (m, 2H), 6.54–6.53 (m, 1H), 5.05–5.03 (m, 1H), 3.94–3.90 (m, 1H), 1.22 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 146.5, 138.3, 138.1, 134.0, 129.0, 128.5, 127.9, 127.0, 126.3, 121.1, 109.2, 99.7, 26.2, 23.6. HRMS (ESI): *m*/*z* calcd for $C_{19}H_{17}N_2O$ [M + H] 289.1341, found 289.1338.





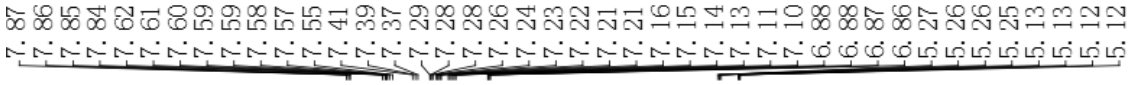


#	Time	Area	Height	Width	Area%	Symmetry
1	15.229	1003.3	41.5	0.3666	10.798	0.694
2	17.024	8288	267.2	0.4726	89.202	0.622

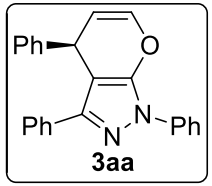
References

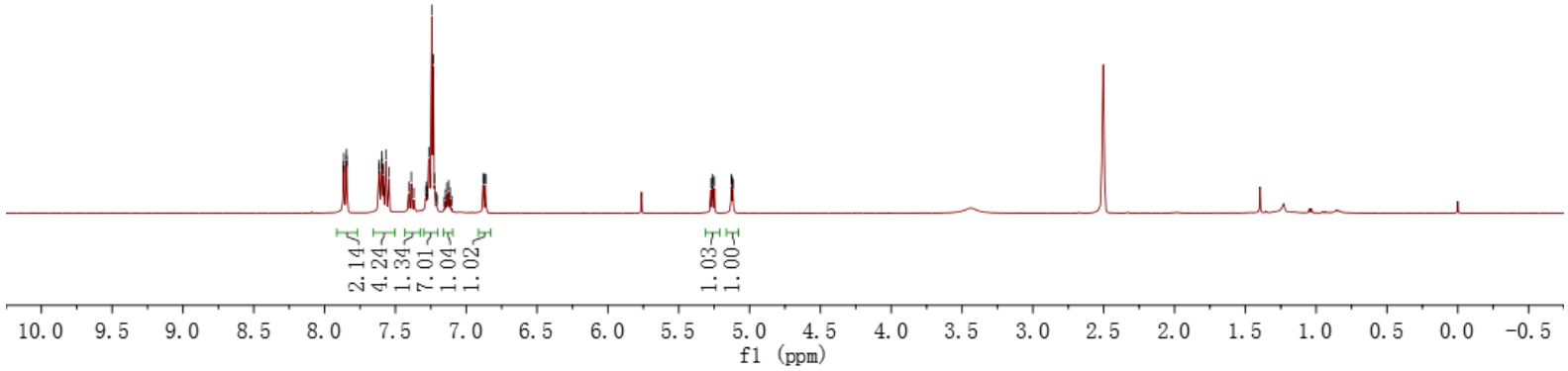
1. M. I. Marzouk, G. H. Sayed, M. S. A. ElHalim and S. Y. Mansour, *Eur. J. Chem.*, 2014, **5**, 24.

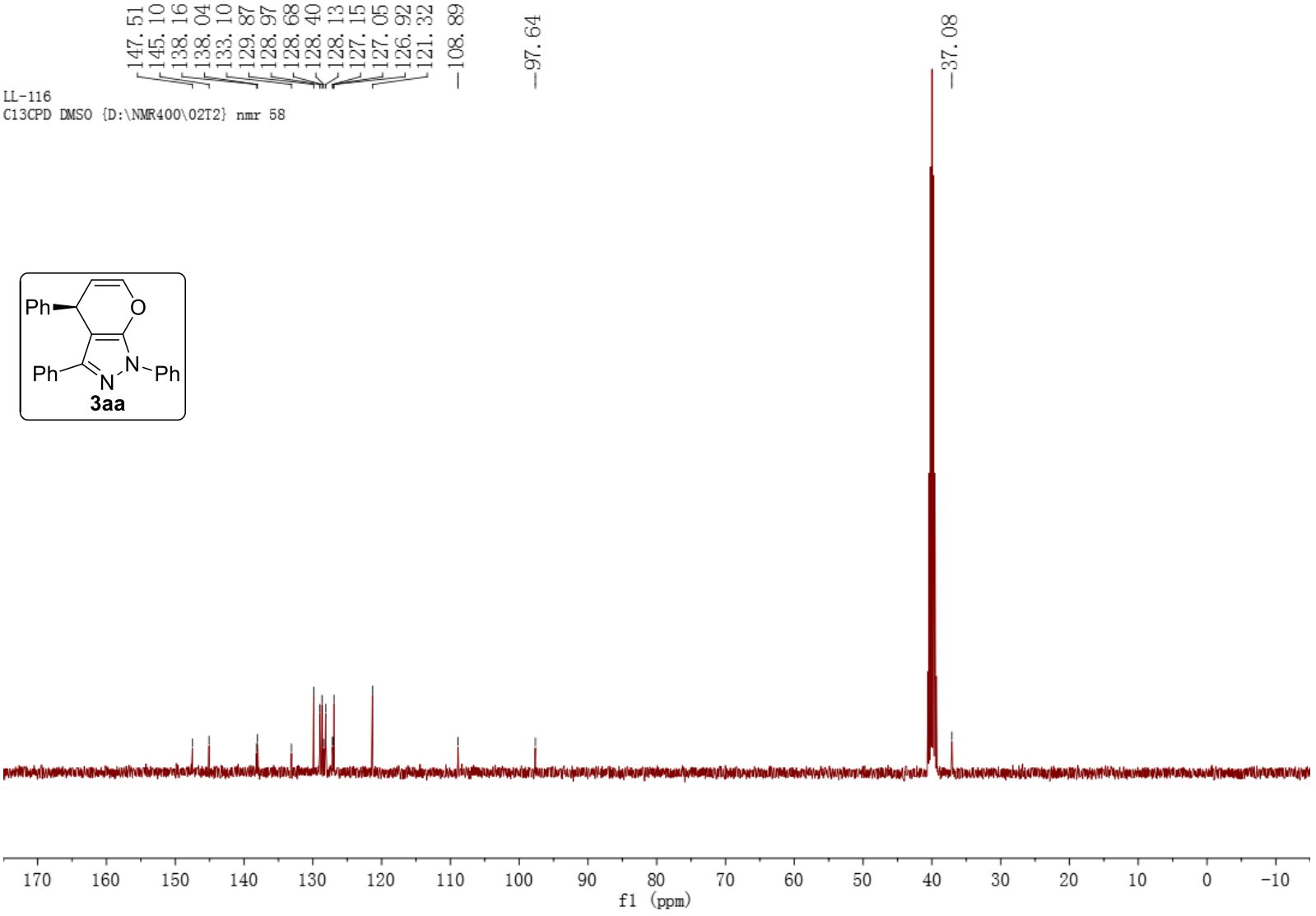
2. (a) P. Fang and X.-L. Hou, *Org. Lett.*, 2009, **11**, 4612; (b) M. Bhanuchandra, M. R. Kuram and A. K. Sahoo, *J. Org. Chem.*, 2013, **78**, 11824..

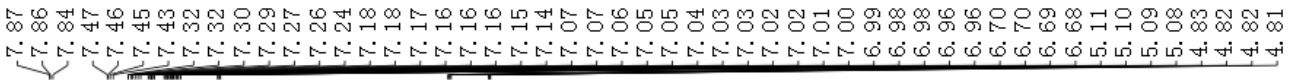


LL-116
PROTON DMSO {D:\NMR400\02T2} nmr 58

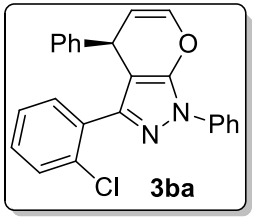


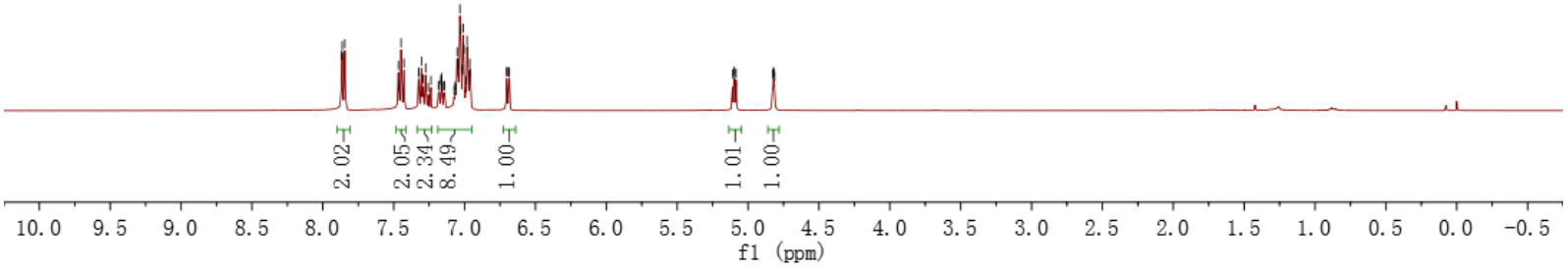



147.51
145.10
138.16
138.04
133.10
129.87
128.97
128.68
128.40
128.13
127.15
127.05
126.92
121.32
108.89
97.64
37.08
LL-116
C13CPD DMSO {D:\NMR400\02T2} nmr 58
Ph
O
Ph
N
N
Ph
3aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



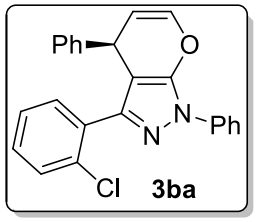
LL-181
PROTON CDC13 {D:\NMR400\02T2} nmr 9



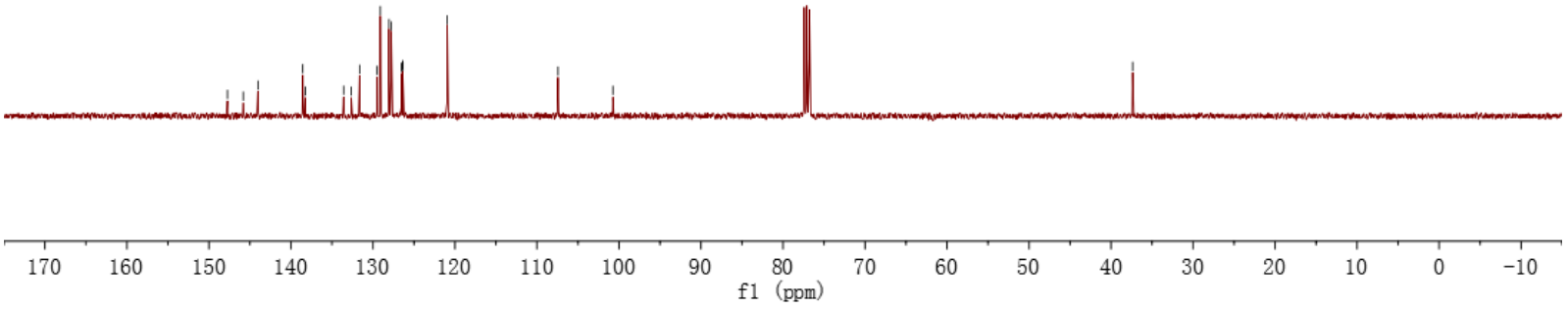


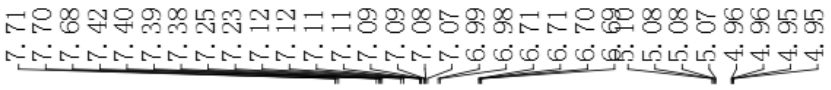
147.75
145.81
144.03
138.55
138.26
133.57
132.64
131.63
129.49
129.10
128.04
127.76
126.53
126.37
126.34
120.94
107.43
100.75
37.36

LL-181
C13CPD CDC13 {D:\NMR400\02T2} nmr 9

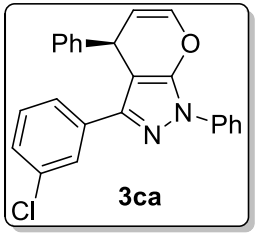


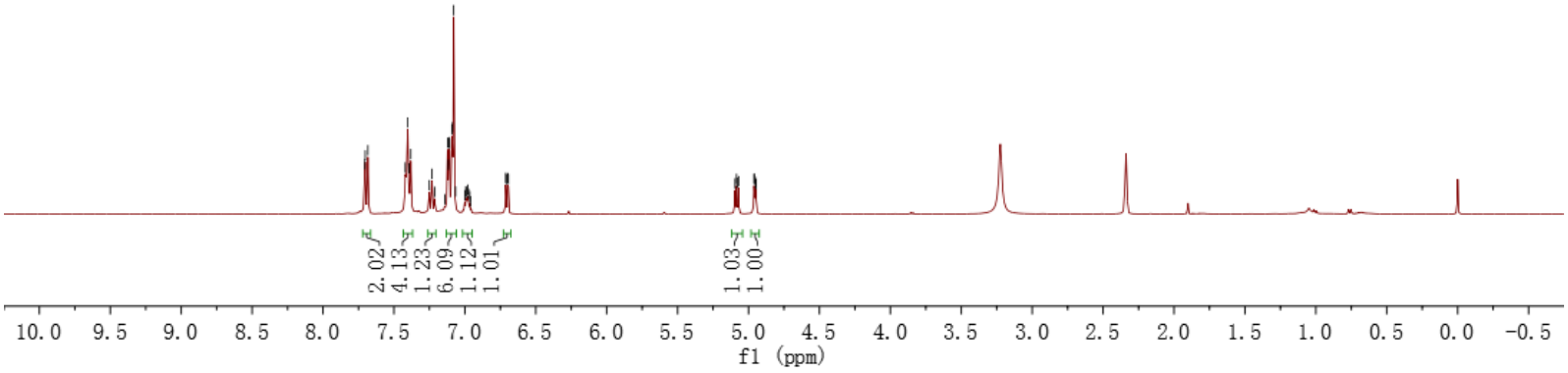
3ba

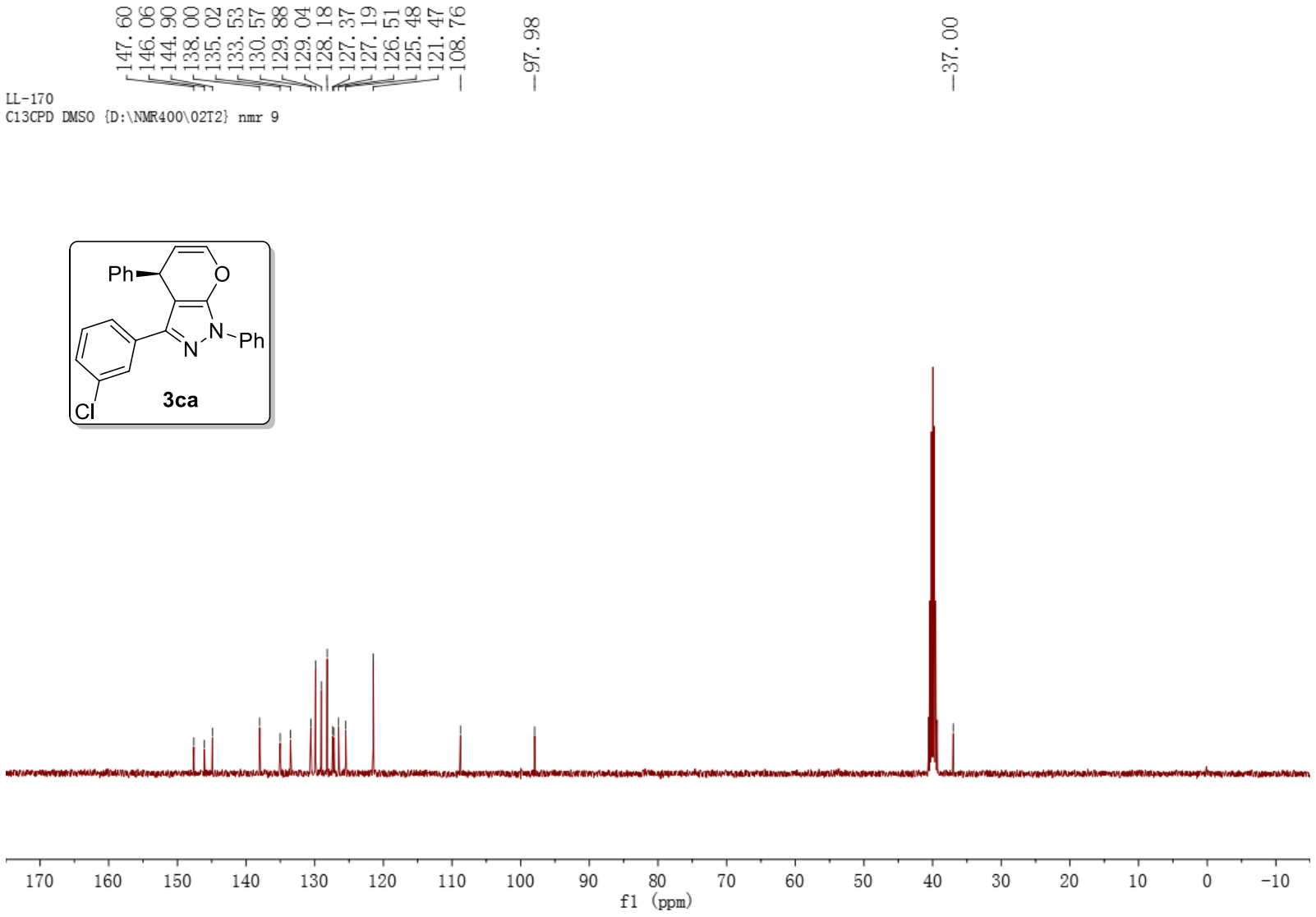


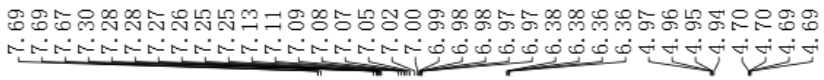


LL-170
PROTON DMSO {D:\NMR400\02T2} nmr 9

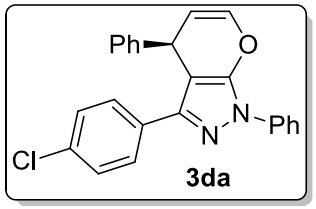


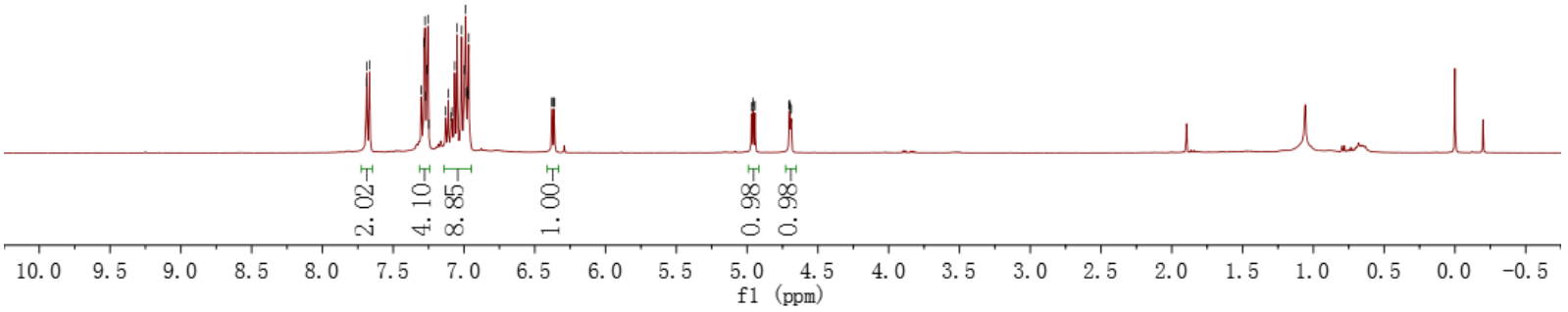



147.60
146.06
144.90
138.00
135.02
133.53
130.57
129.88
129.04
128.18
127.37
127.19
126.51
125.48
121.47
108.76
97.98
37.00
LL-170
C13CPD DMSO {D:\NMR400\02T2} nmr 9
Ph
O
N
N
Ph
Cl
3ca
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



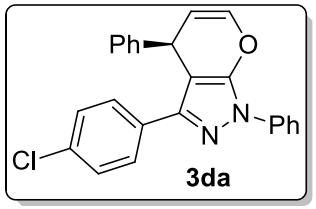
LL-182
PROTON CDC13 {D:\NMR400\02T2} nmr 54



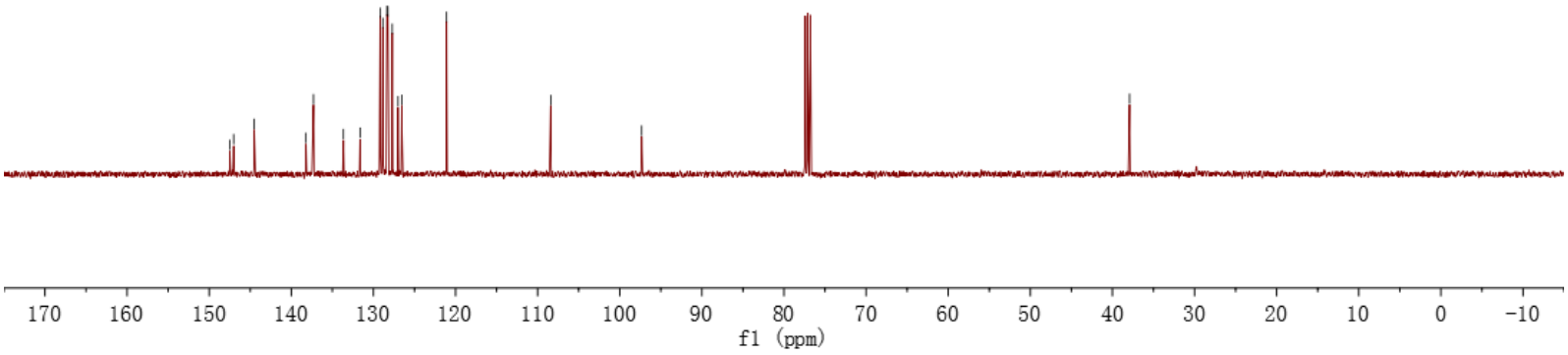


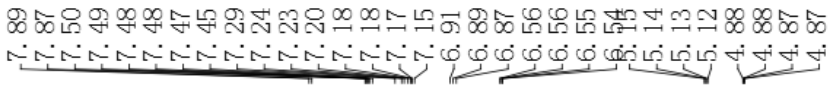
147.49
147.03
144.52
138.21
137.29
133.66
131.62
129.18
128.85
128.35
128.24
127.70
127.00
126.55
121.09
108.40
97.33
37.92

LL-182
C13CPD CDC13 {D:\NMR400\02T2} nmr 31

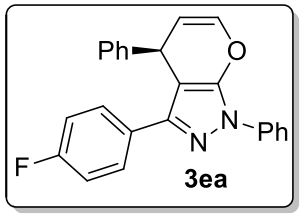


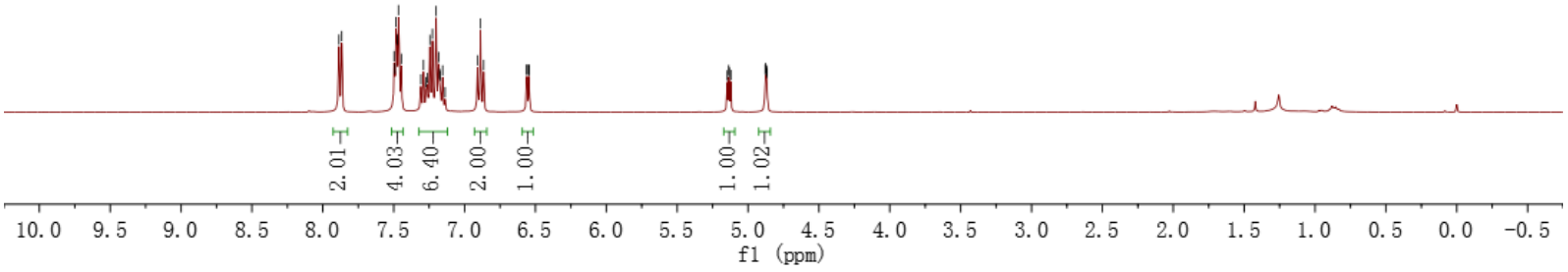
3da

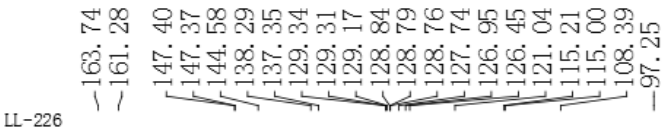




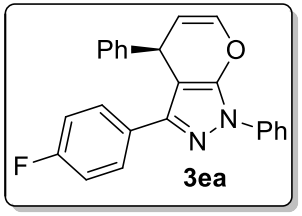
LL-226
PROTON CDC13 {D:\NMR400\02T2} nmr 8



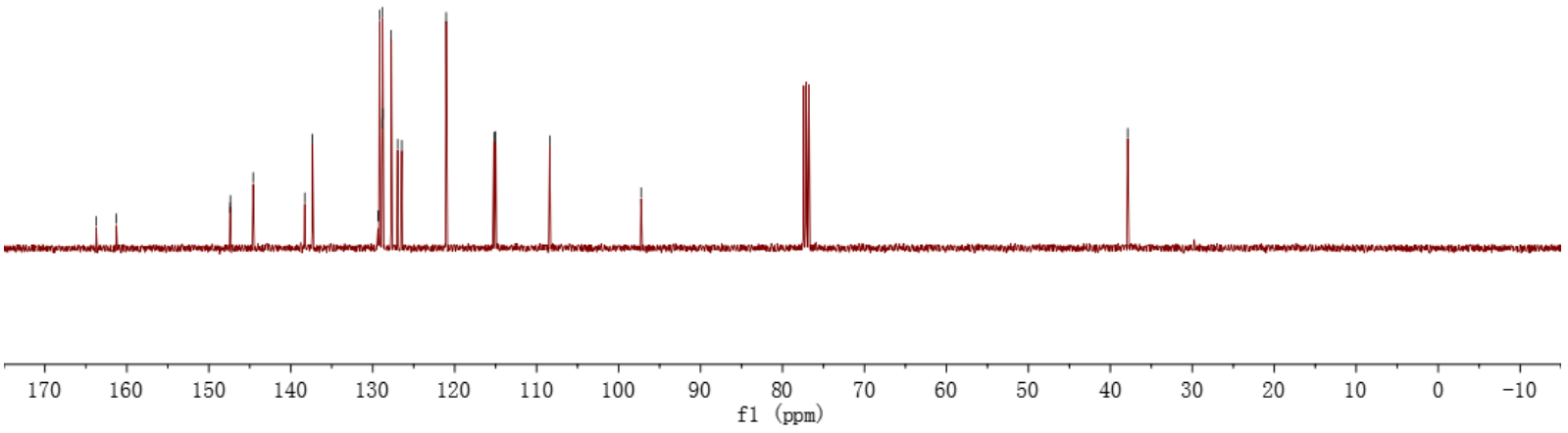


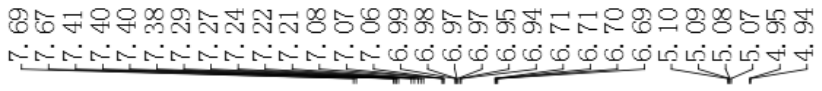


LL-226
C13CPD CDC13 {D:\NMR400\02T2} nmr 8

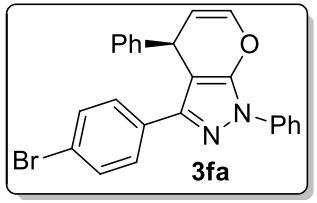


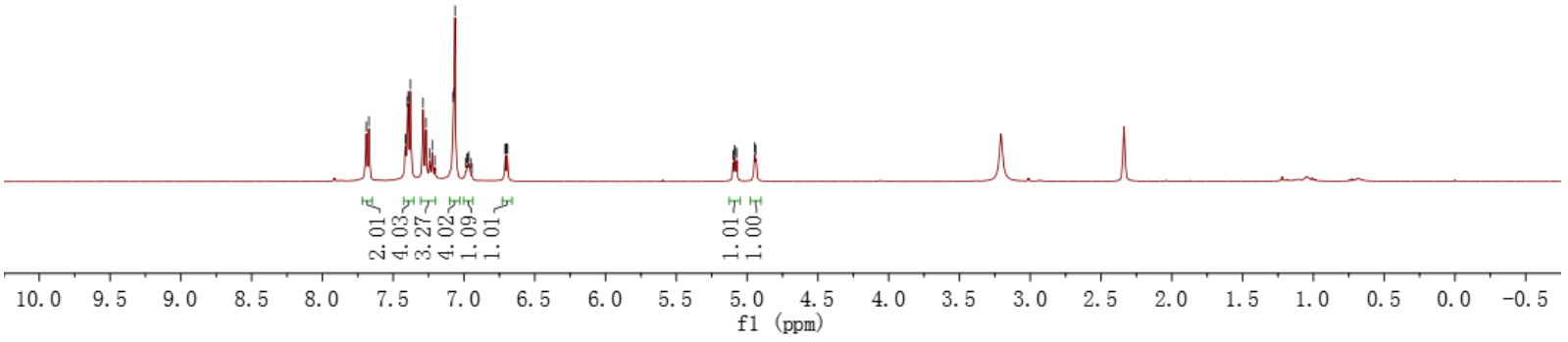
3ea

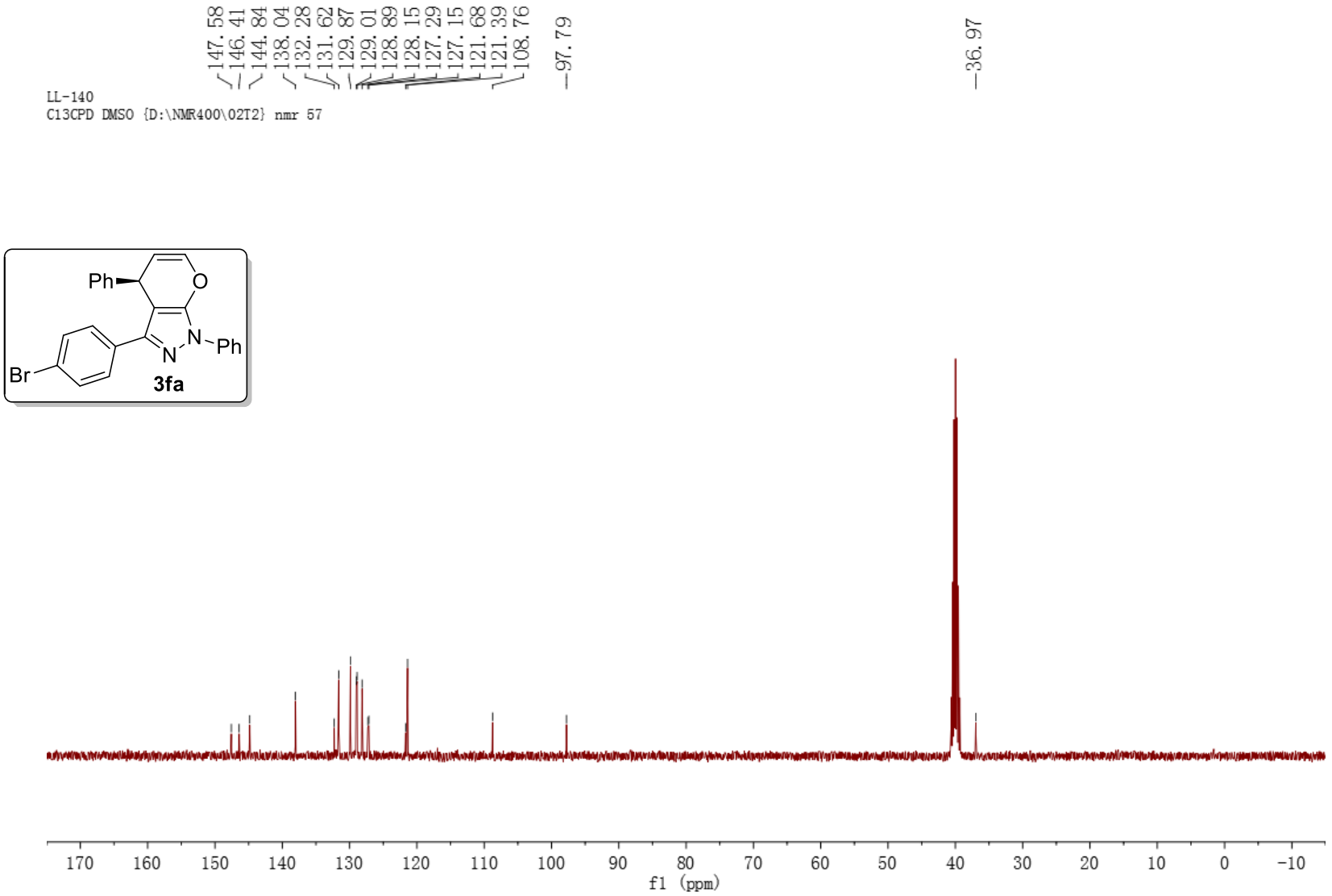


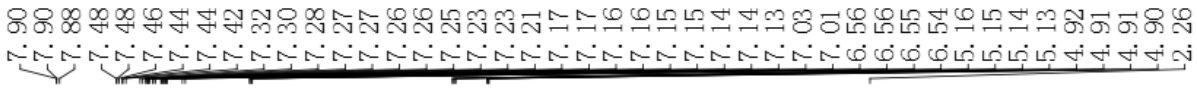


LL-140
PROTON DMSO {D:\NMR400\02T2} nmr 57

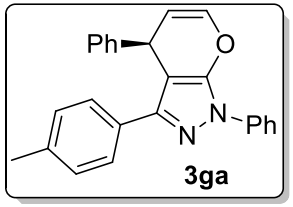


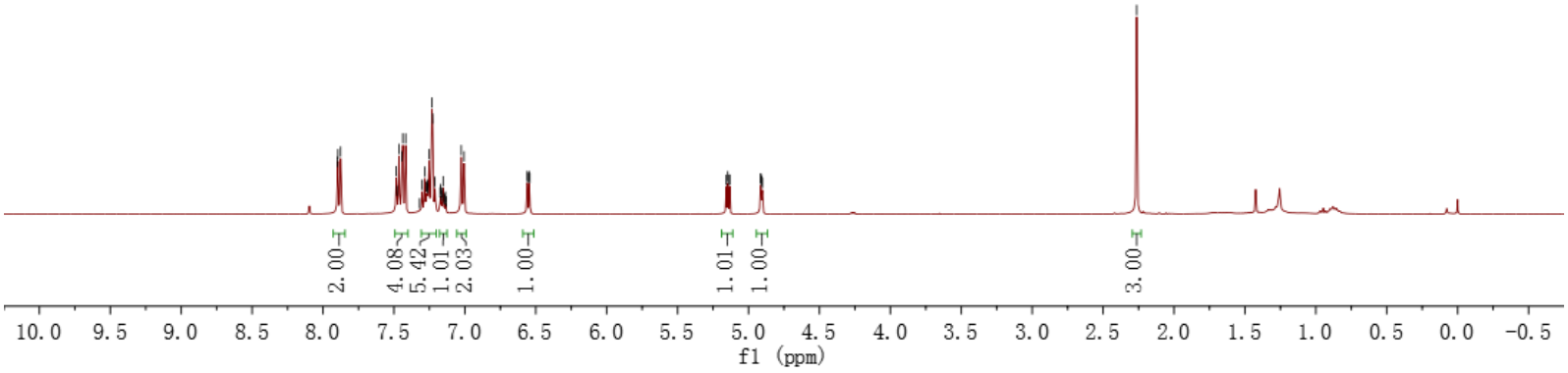



147.58
146.41
144.84
138.04
132.28
131.62
129.87
129.01
128.89
128.15
127.29
127.15
121.68
121.39
108.76
97.79
36.97
LL-140
C13CPD DMSO {D:\NMR400\02T2} nmr 57
Ph
O
N
N
Ph
Br
3fa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



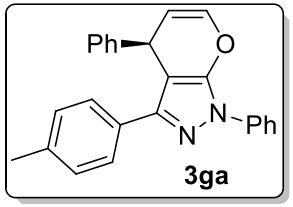
LL-172
PROTON CDC13 {D:\NMR400\02T2} nmr 39



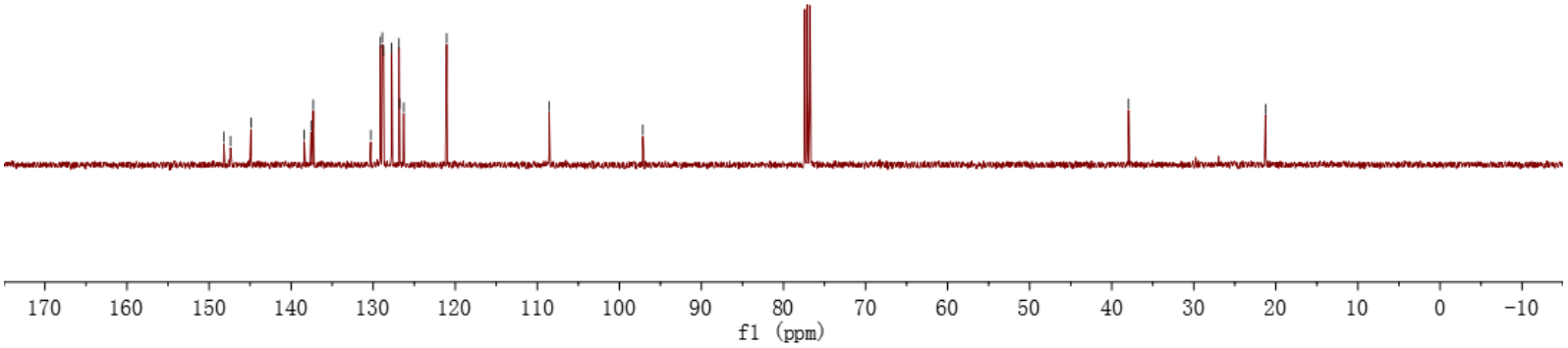


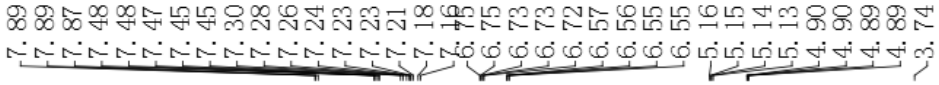
148.20
147.39
144.89
138.40
137.57
137.30
130.28
129.11
128.88
128.74
127.74
126.85
126.79
126.28
121.05
108.54
97.14
37.95
21.26

LL-172
C13CPD CDC13 {D:\NMR400\02T2} nmr 39

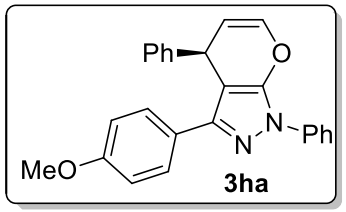


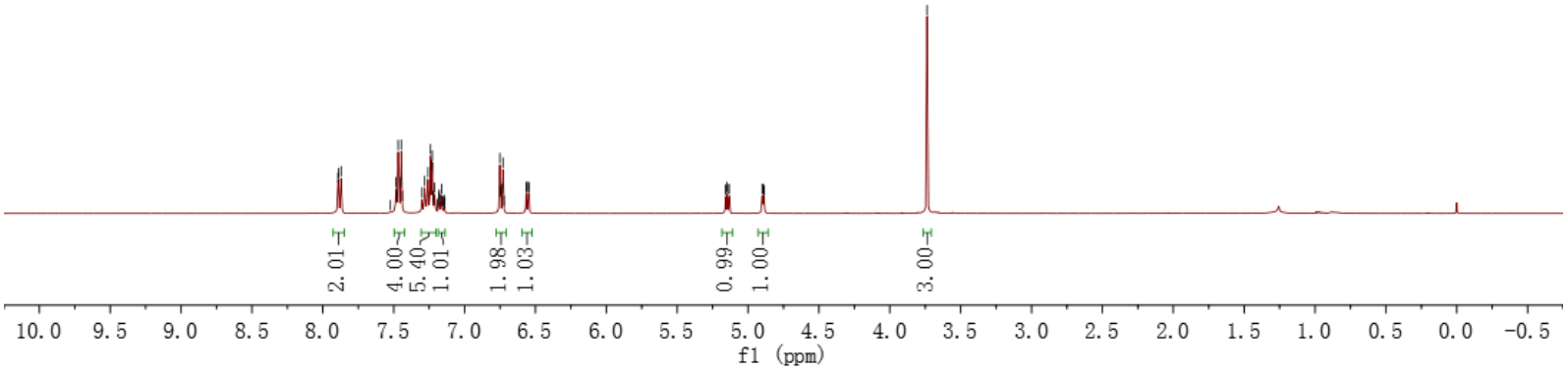
3ga

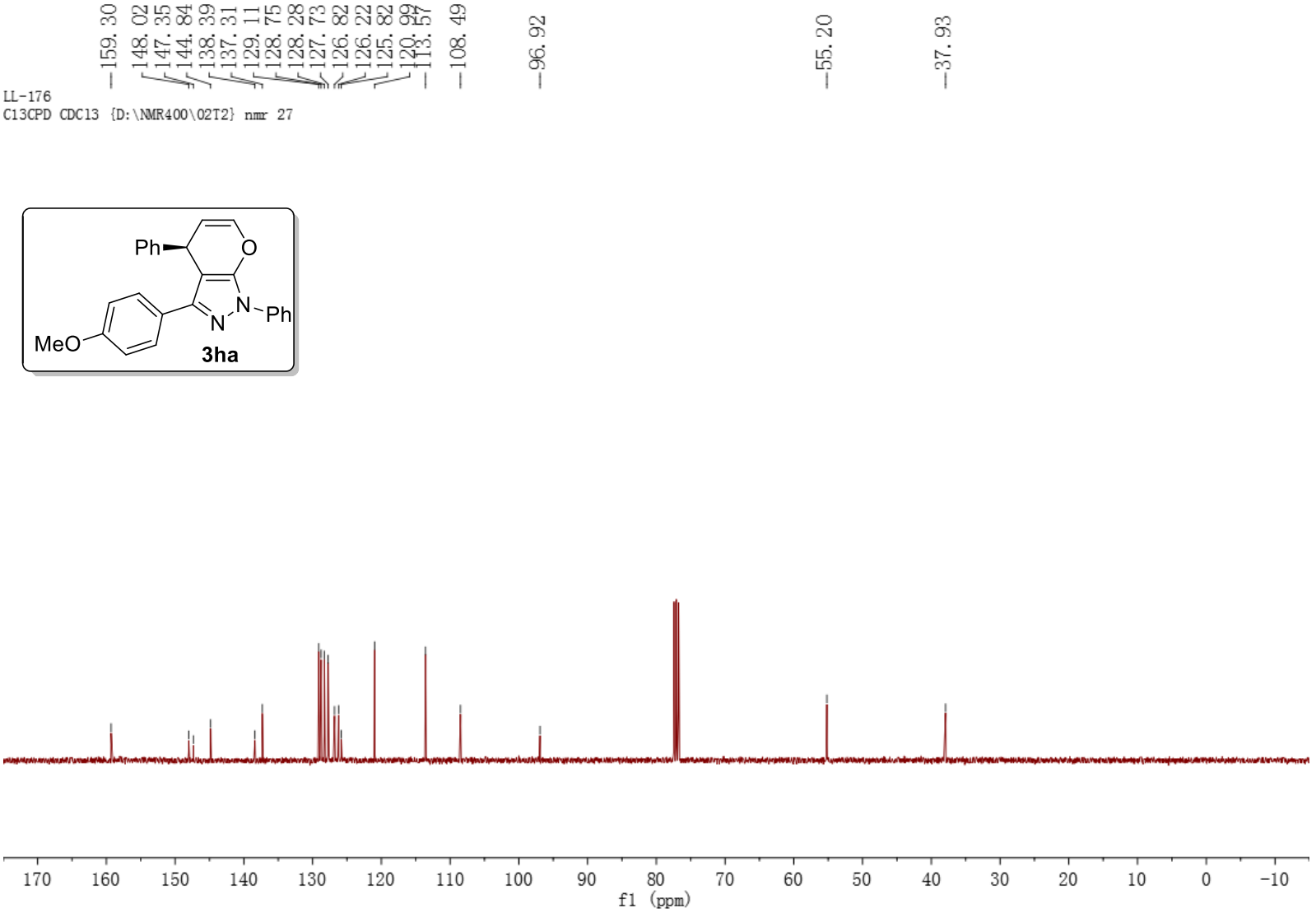


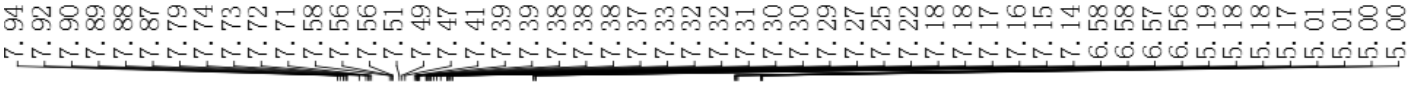


LL-176
PROTON CDC13 {D:\NMR400\02T2} nmr 27

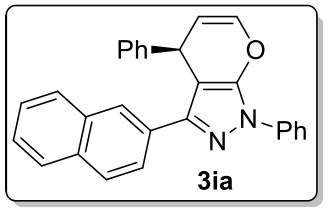




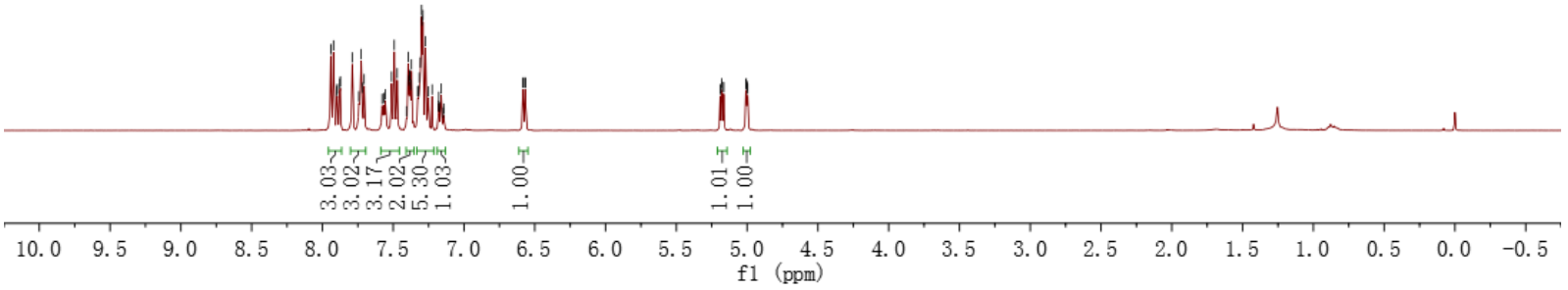

159.30
148.02
147.35
144.84
138.39
137.31
129.11
128.75
128.28
127.73
126.82
126.22
125.82
120.99
113.57
108.49
96.92
55.20
37.93
LL-176
C13CPD CDC13 {D:\NMR400\02T2} nmr 27
Ph
O
N
N
Ph
MeO
3ha
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

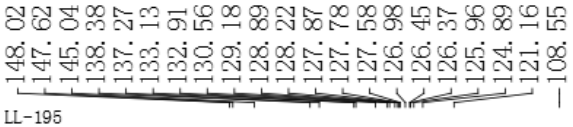


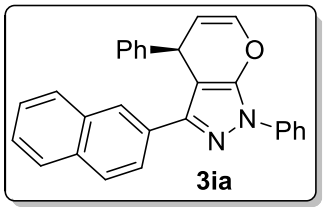
LL-195
PROTON CDC13 {D:\NMR400\02T2} nmr 37

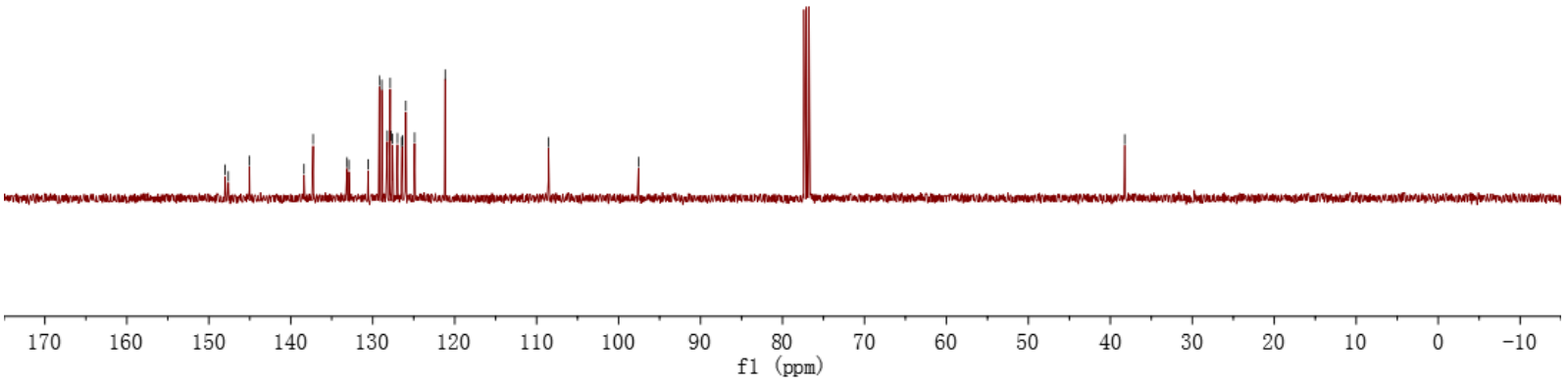


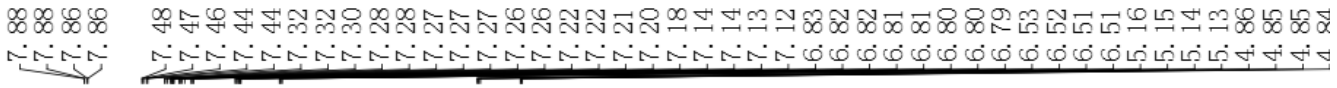
3ia



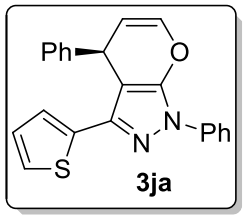

148.02
147.62
145.04
138.38
137.27
133.13
132.91
130.56
129.18
128.89
128.22
127.87
127.78
127.58
126.98
126.45
126.37
125.96
124.89
121.16
108.55
97.57
38.24
LL-195
C13CPD CDC13 {D:\NMR400\02T2} nmr 37

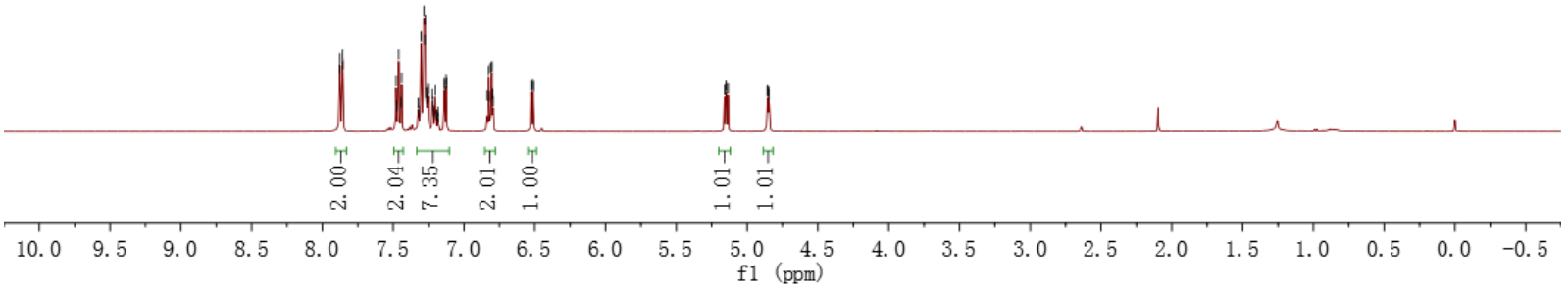

Ph
O
N
N
Ph
3ia

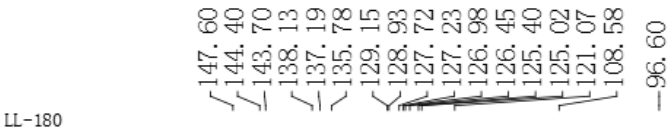

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



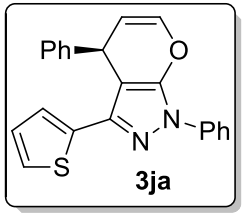
LL-180
PROTON CDC13 {D:\NMR400\02T2} nmr 30



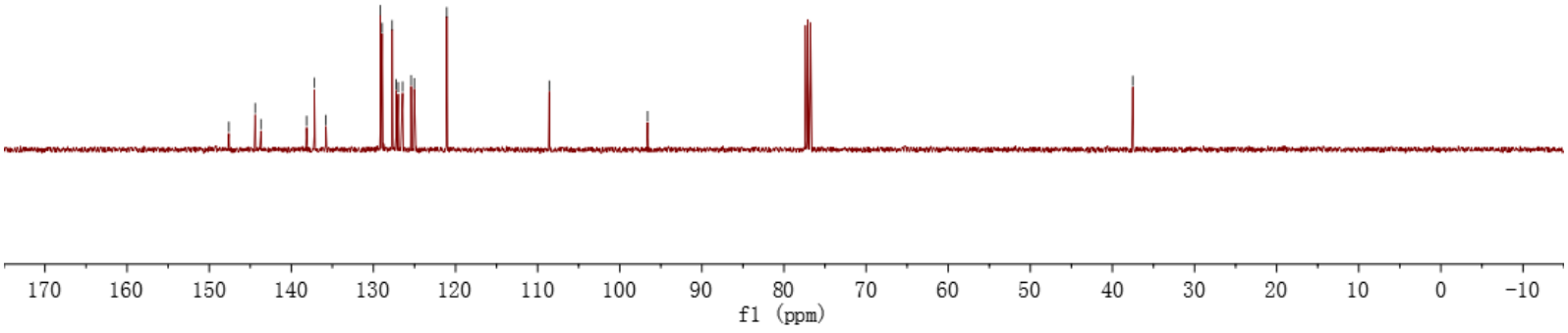


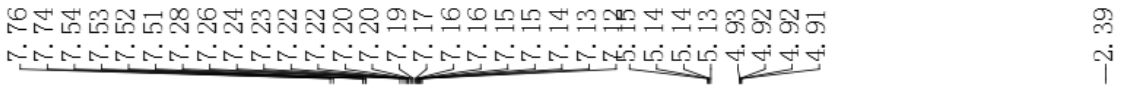


LL-180
C13CPD CDC13 {D:\NMR400\02T2} nmr 52

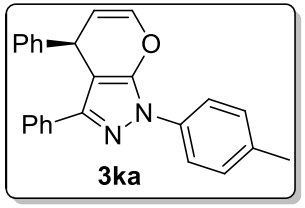


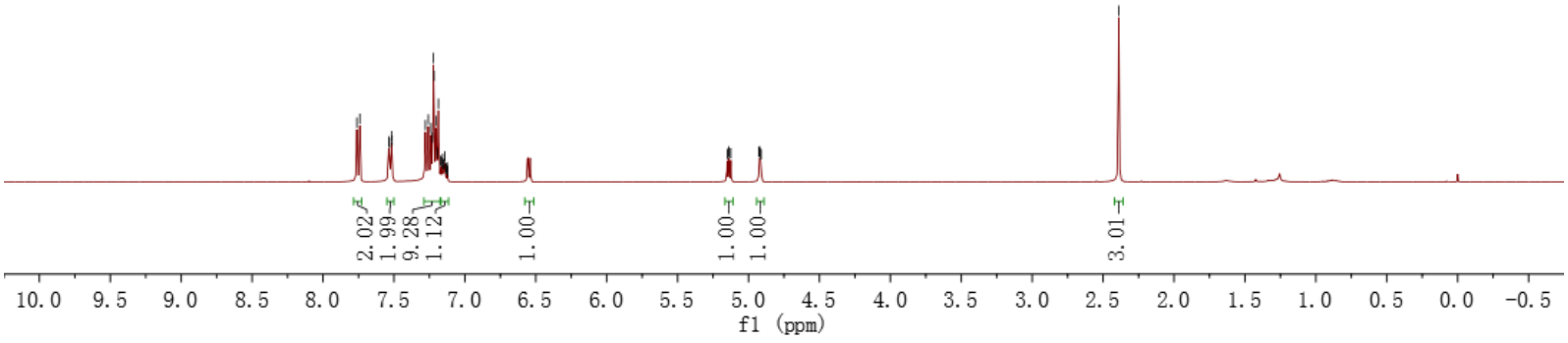
3ja

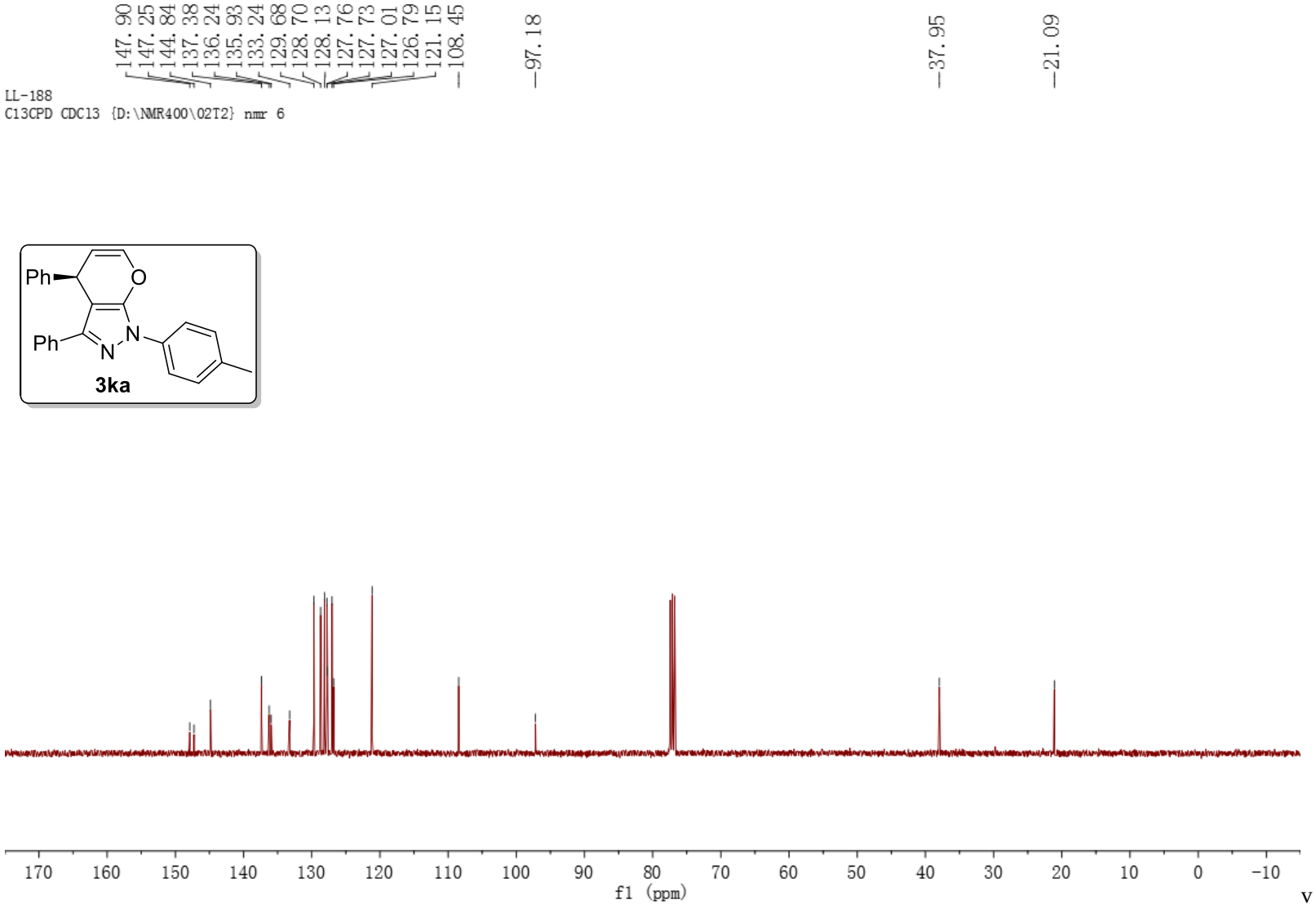


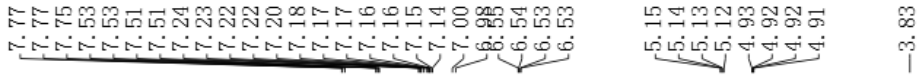


LL-188
PROTON CDC13 {D:\NMR400\02T2} nmr 10

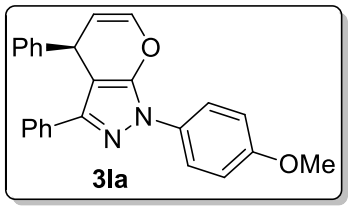




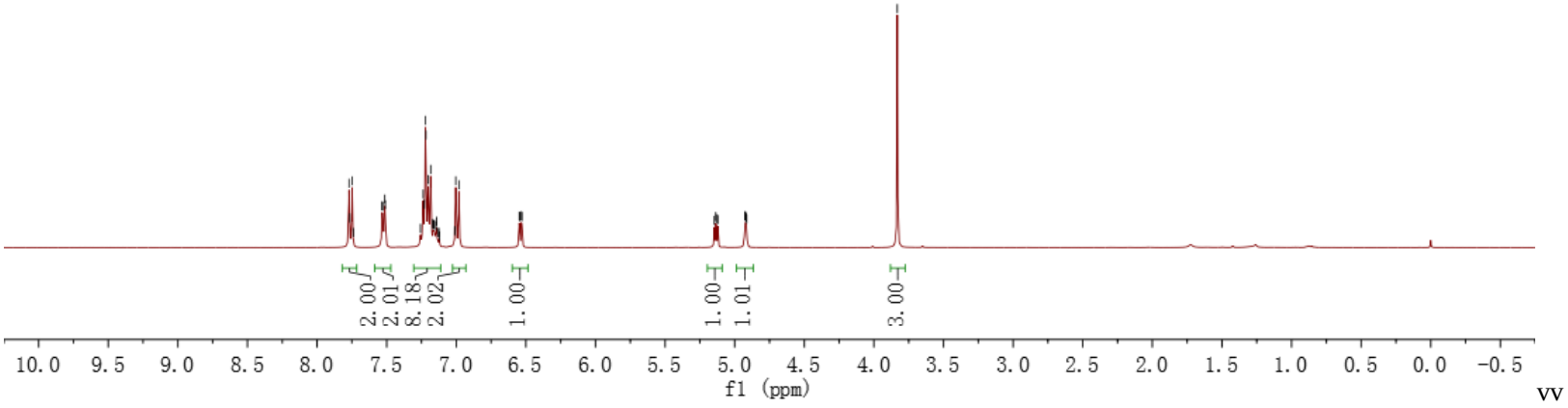

147.90
147.25
144.84
137.38
136.24
135.93
133.24
129.68
128.70
128.13
127.76
127.73
127.01
126.79
121.15
108.45
97.18
37.95
21.09
LL-188
C13CPD CDC13 {D:\NMR400\02T2} nmr 6
Ph
O
Ph
N
N
3ka
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



LL-199
PROTON CDC13 {D:\NMR400\02T2} nmr 5

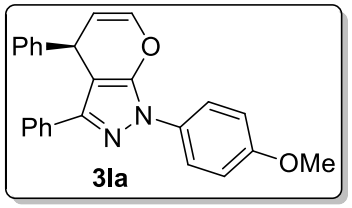


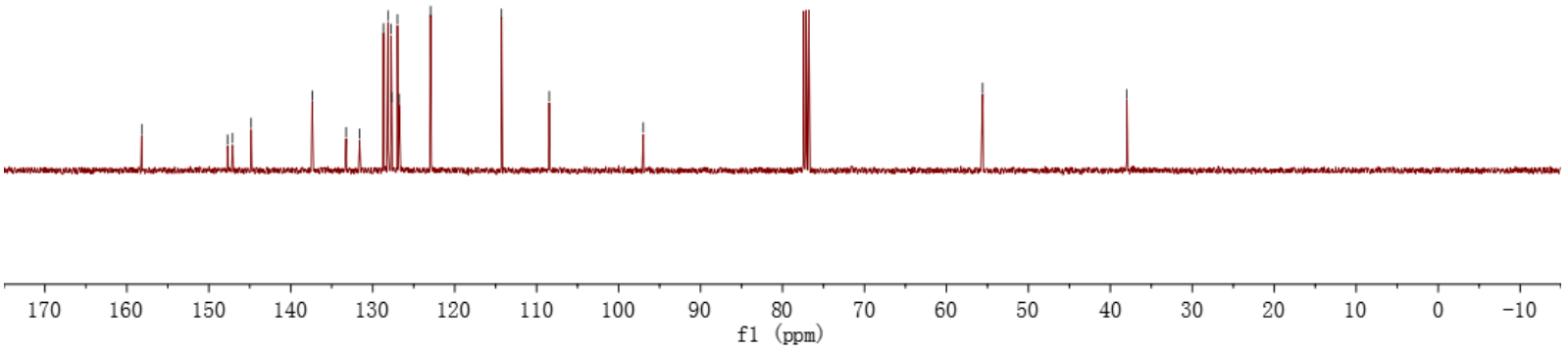
3la

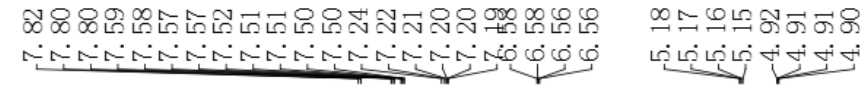


vv

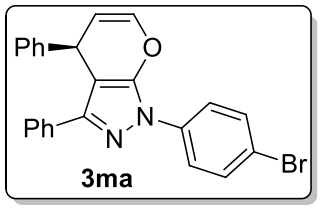

158.18
147.72
147.10
144.83
137.38
133.25
131.61
128.70
128.13
127.76
127.69
126.98
126.79
122.94
114.29
108.46
96.98
55.58
37.98
LL-199
C13CPD CDC13 {D:\NMR400\02T2} nmr 5

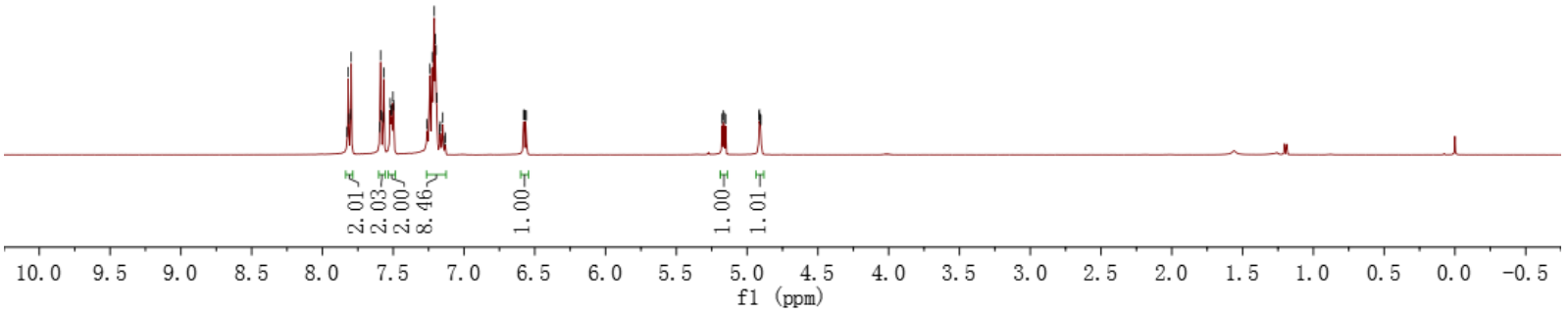

Ph
O
Ph
N
N
OMe
3la


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



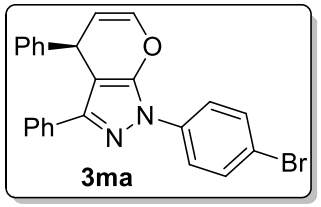
LL-183
PROTON CDC13 {D:\NMR400\02T2} nmr 8



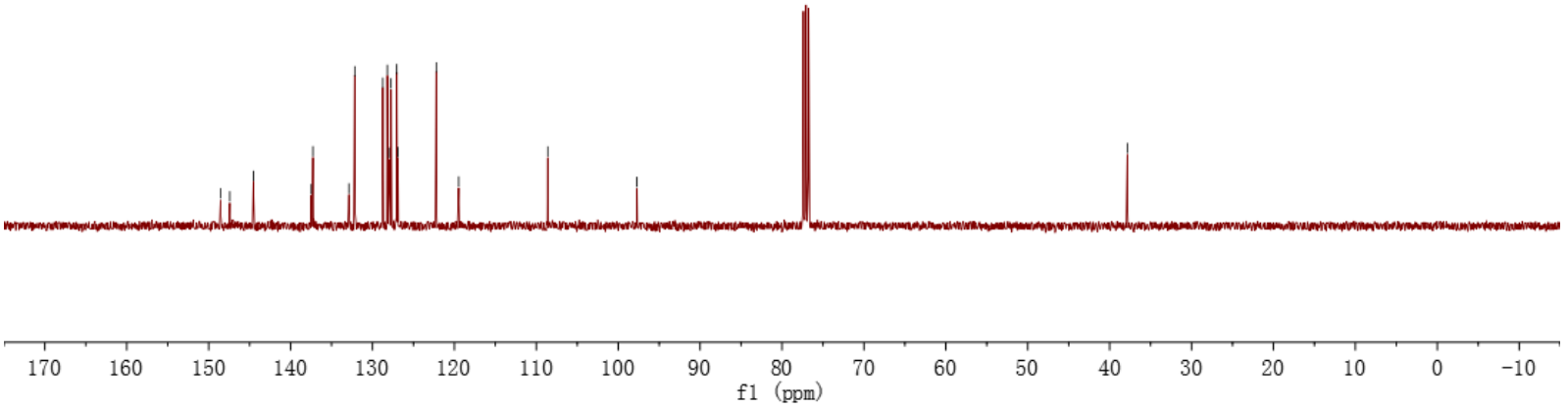


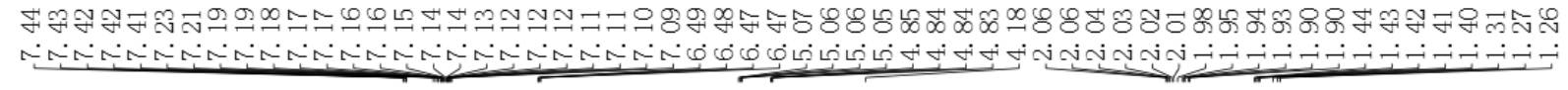
148.55
147.42
144.54
137.48
137.27
132.88
132.16
128.74
128.19
128.00
127.73
127.03
126.89
122.20
119.48
108.59
97.71
37.84

LL-183
C13CPD CDC13 {D:\NMR400\02T2} nmr 8

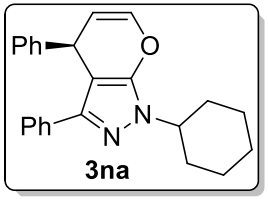


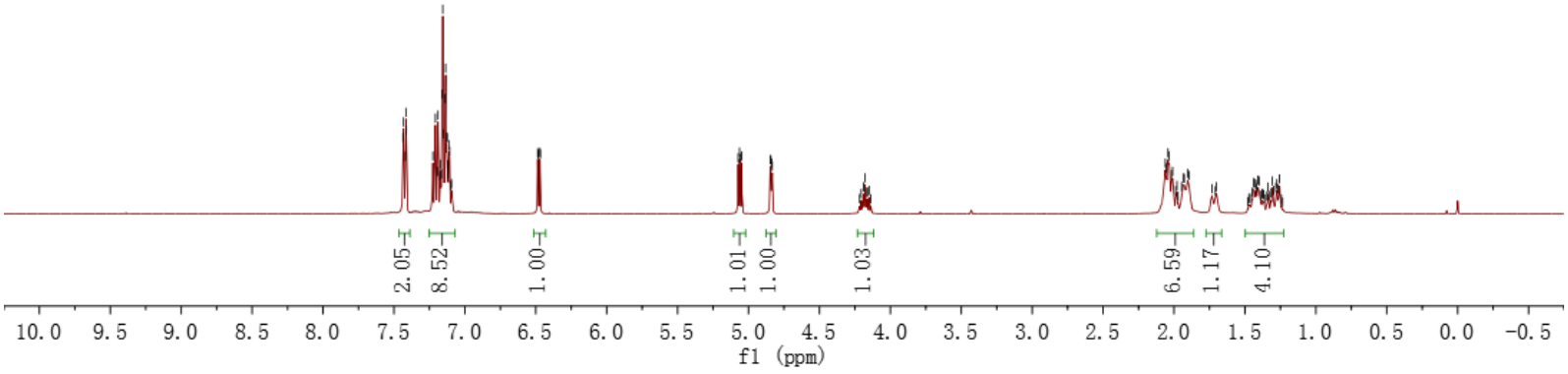
3ma

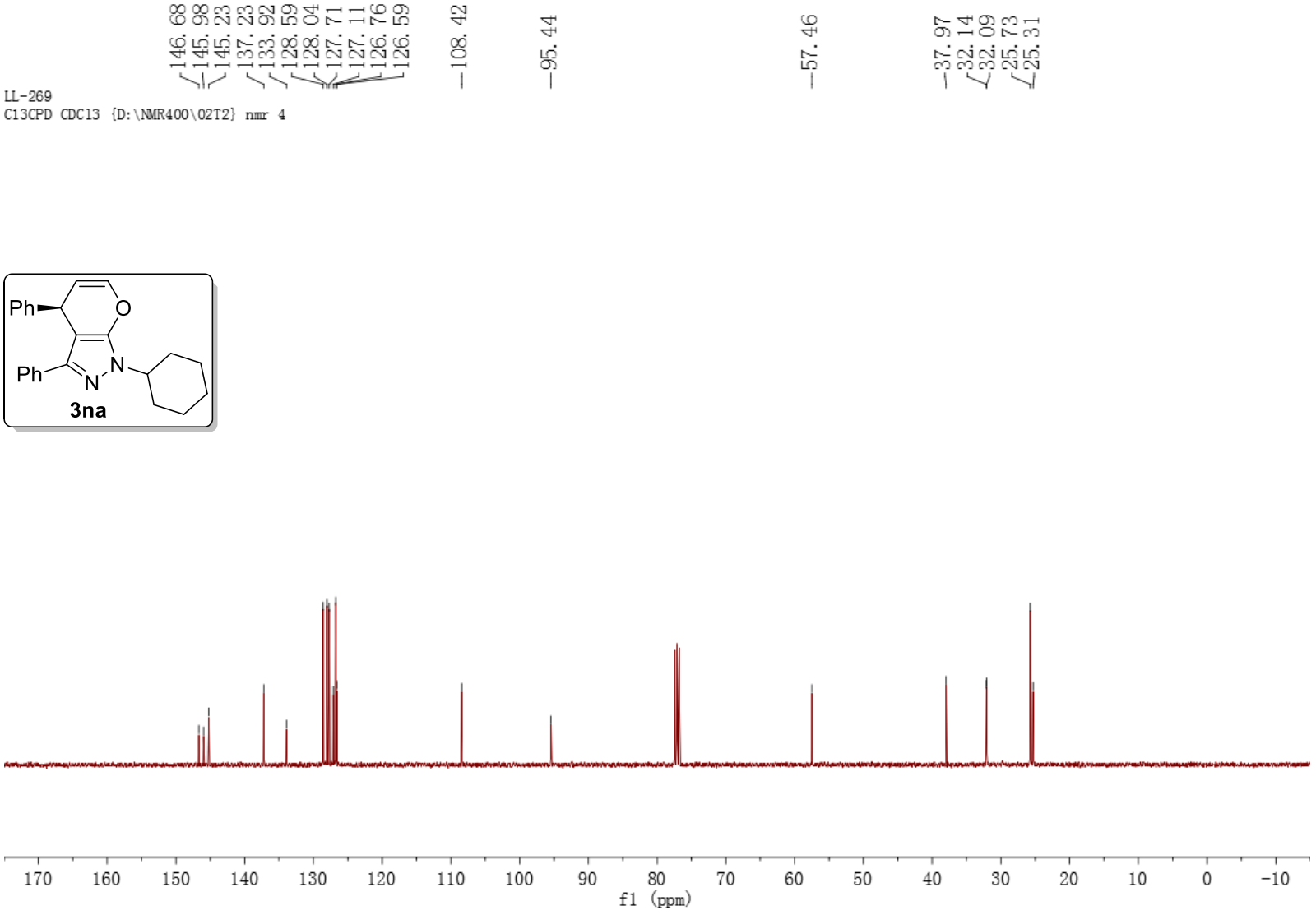


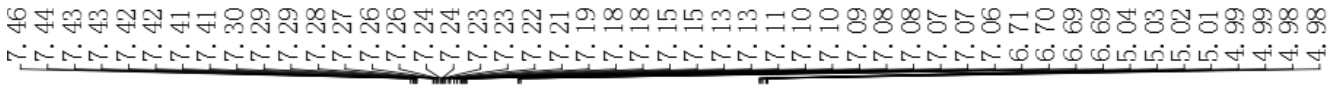


LL-269
PROTON CDC13 {D:\NMR400\02T2} nmr 4

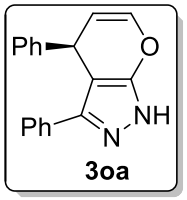




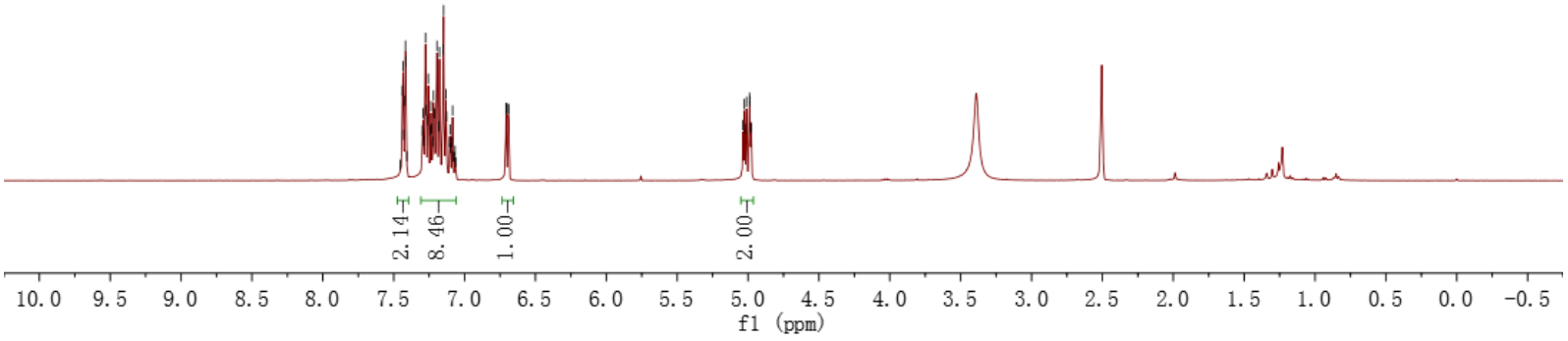

146.68
145.98
145.23
137.23
133.92
128.59
128.04
127.71
127.11
126.76
126.59
108.42
95.44
57.46
37.97
32.14
32.09
25.73
25.31
LL-269
C13CPD CDC13 {D:\NMR400\02T2} nmr 4
Ph
O
Ph
N
N
3na
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

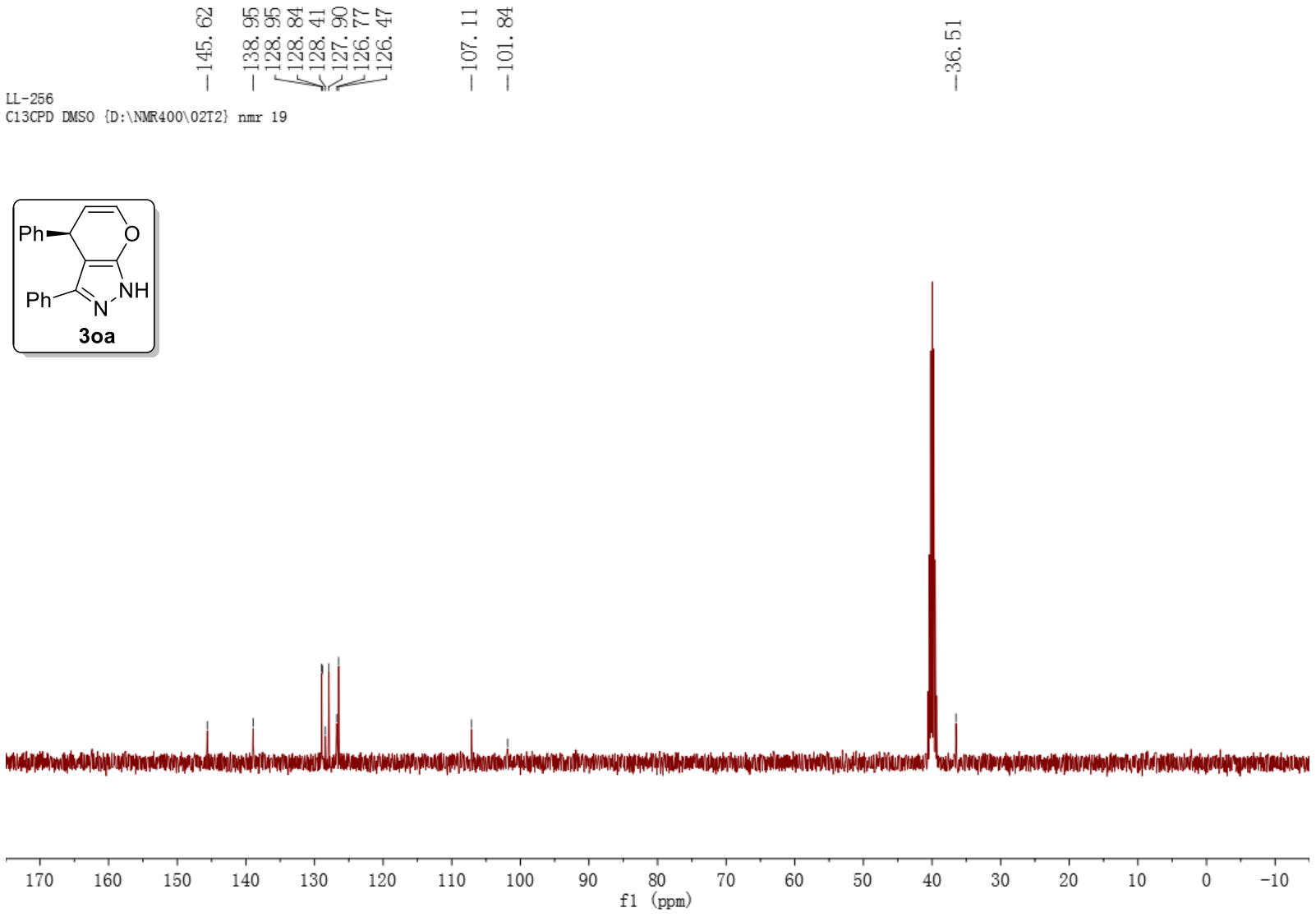


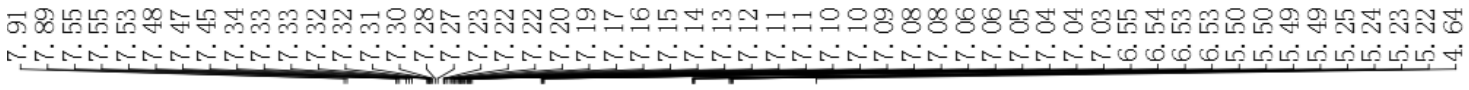
LL-256
PROTON DMSO {D:\NMR400\02T2} nmr 19



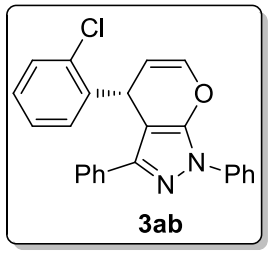
3oa



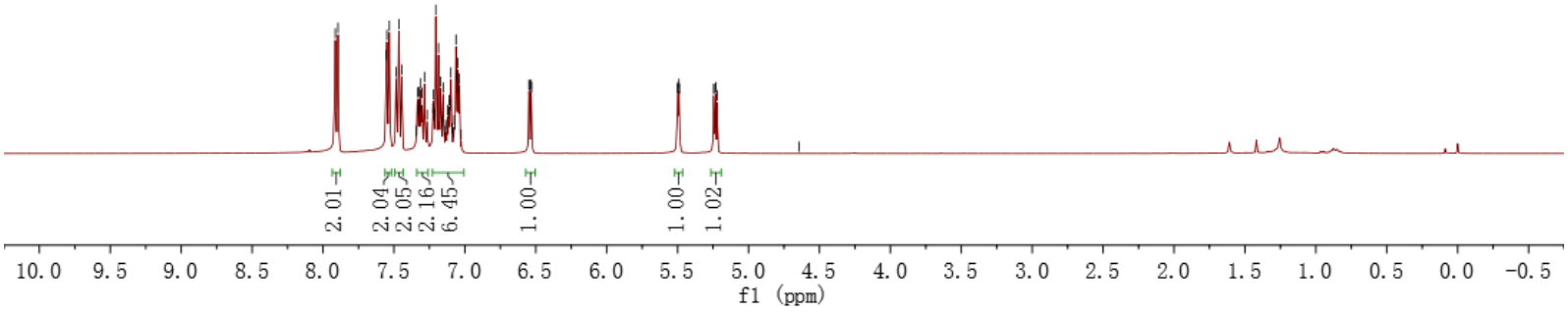

145.62
138.95
128.95
128.84
128.41
127.90
126.77
126.47
107.11
101.84
36.51
LL-256
C13CPD DMSO {D:\NMR400\02T2} nmr 19
Ph
O
Ph
N
NH
3oa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



LL-233
PROTON CDC13 {D:\NMR400\02T2} nmr 33

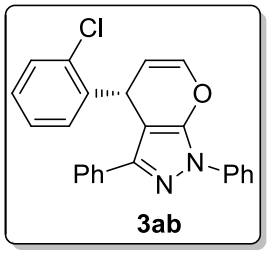


3ab

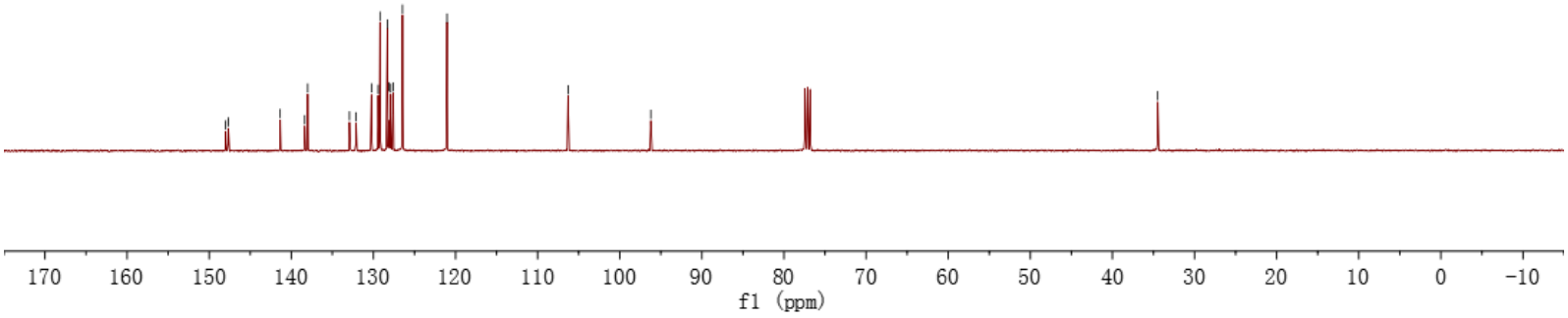


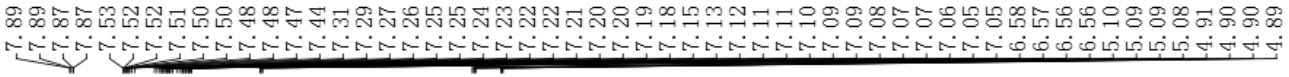
147.99
147.67
141.36
138.37
138.00
132.93
132.12
130.23
129.42
129.19
128.29
128.13
127.89
127.59
126.47
121.03
106.29
96.21
34.48

LL-233
C13CPD CDC13 {D:\NMR400\02T2} nmr 33

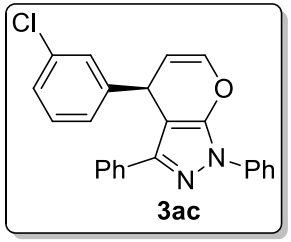


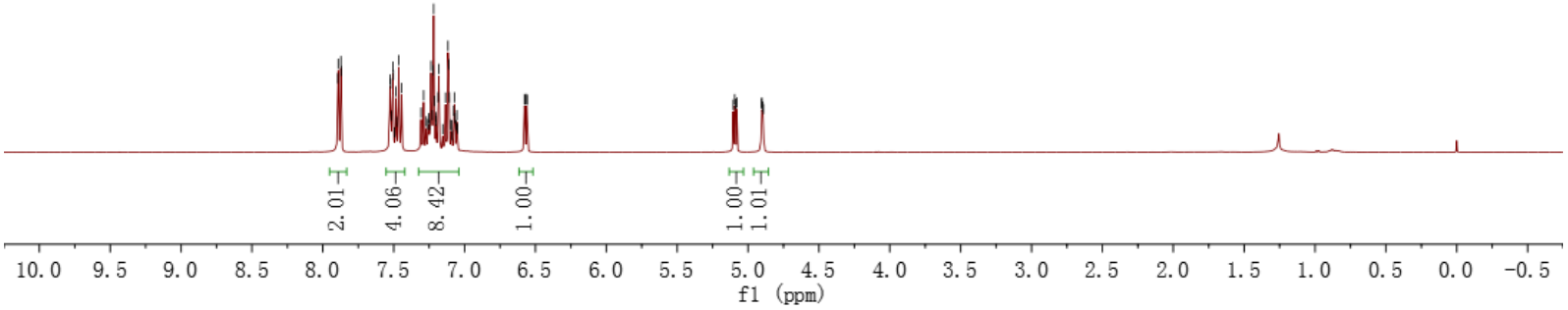
3ab

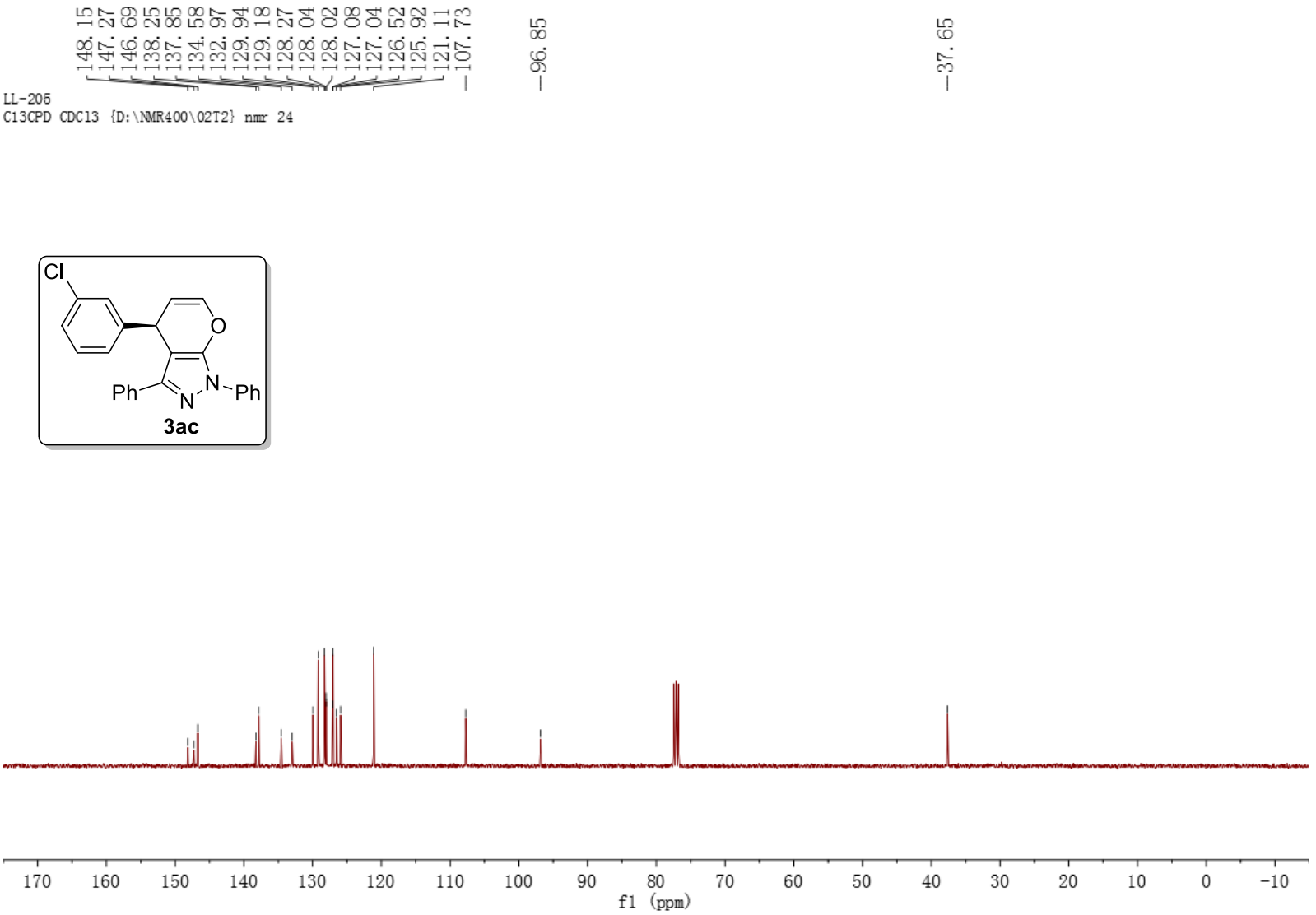


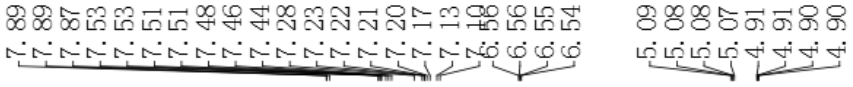


LL-205
PROTON CDC13 {D:\NMR400\02T2} nmr 24

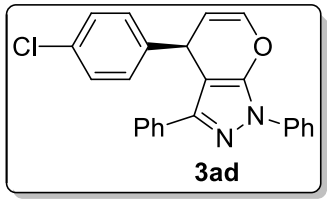


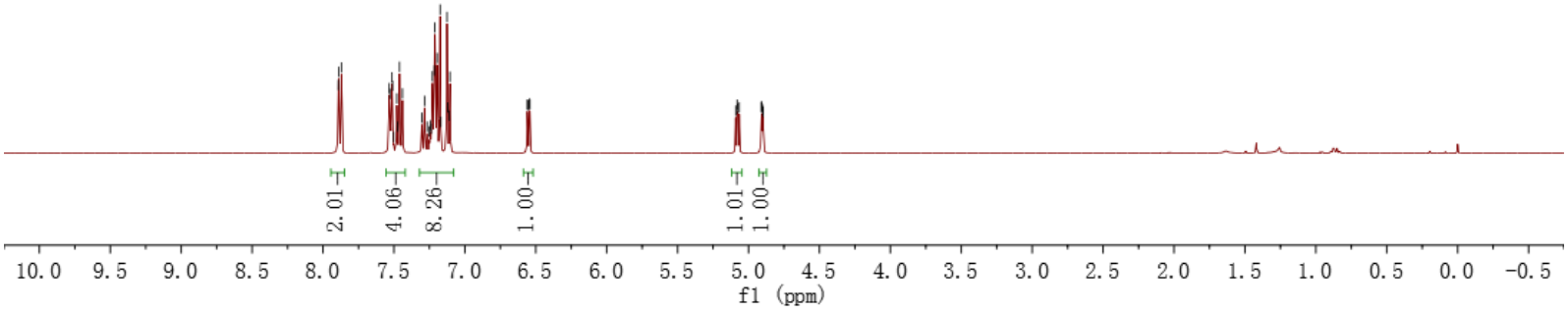



148.15
147.27
146.69
138.25
137.85
134.58
132.97
129.94
129.18
128.27
128.04
128.02
127.08
127.04
126.52
125.92
121.11
107.73
96.85
37.65
LL-205
C13CPD CDC13 {D:\NMR400\02T2} nmr 24
Cl
O
N
N
Ph
Ph
3ac
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



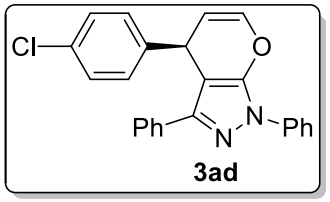
LL-220
PROTON CDC13 {D:\NMR400\02T2} nmr 31



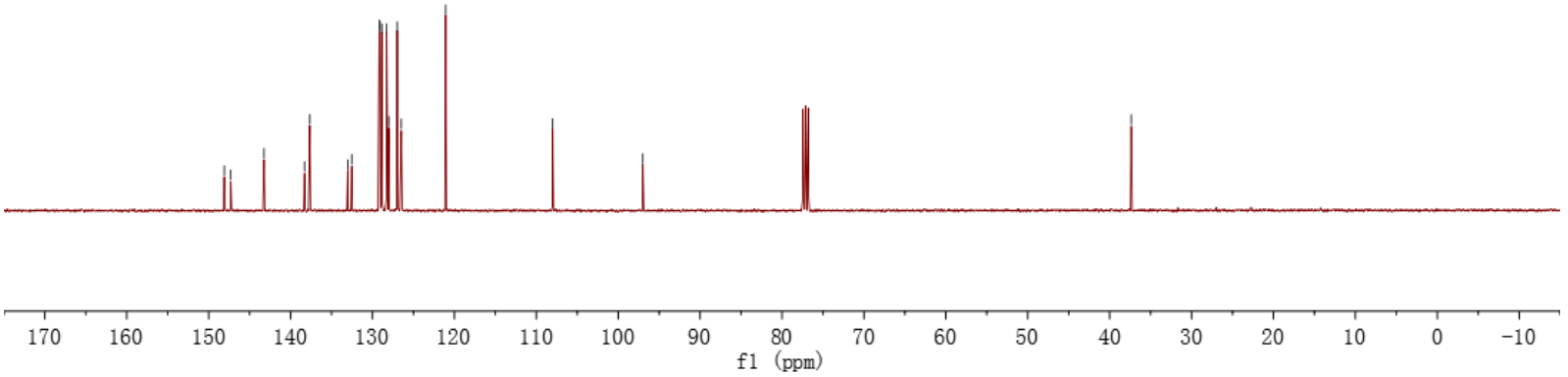


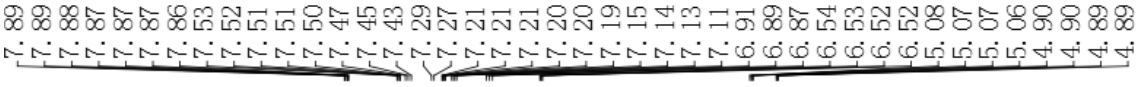
148.09
147.30
143.24
138.30
137.65
133.02
132.53
129.17
129.09
128.86
128.27
128.00
126.97
126.48
121.06
108.00
96.99
37.36

LL-220
C13CPD CDC13 {D:\NMR400\02T2} nmr 31

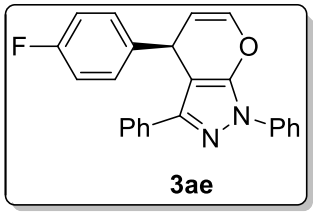


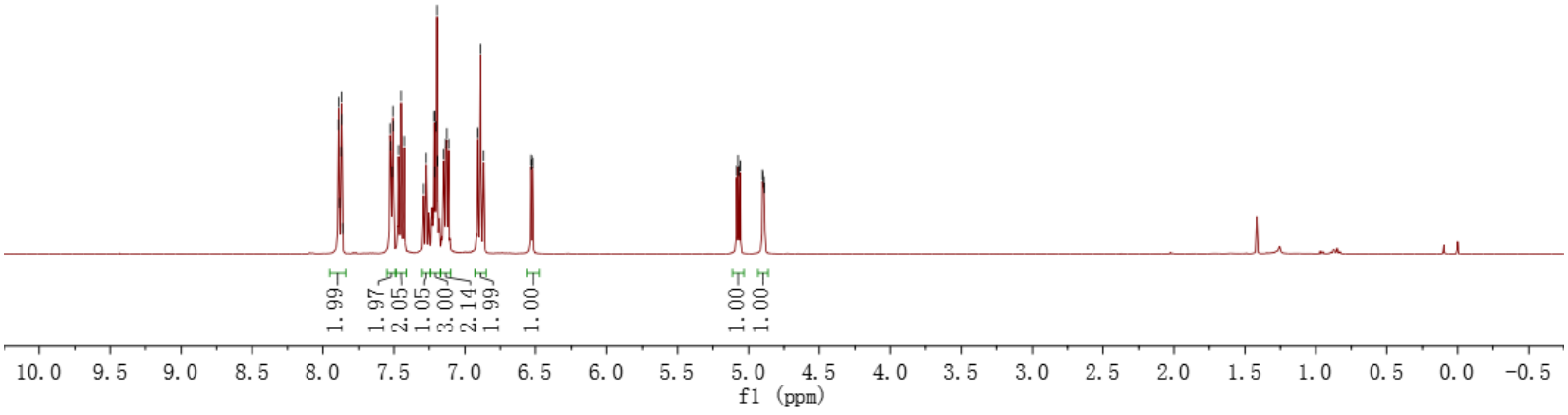
3ad

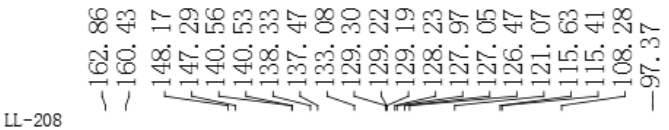


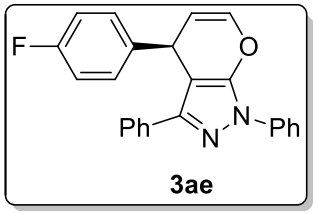


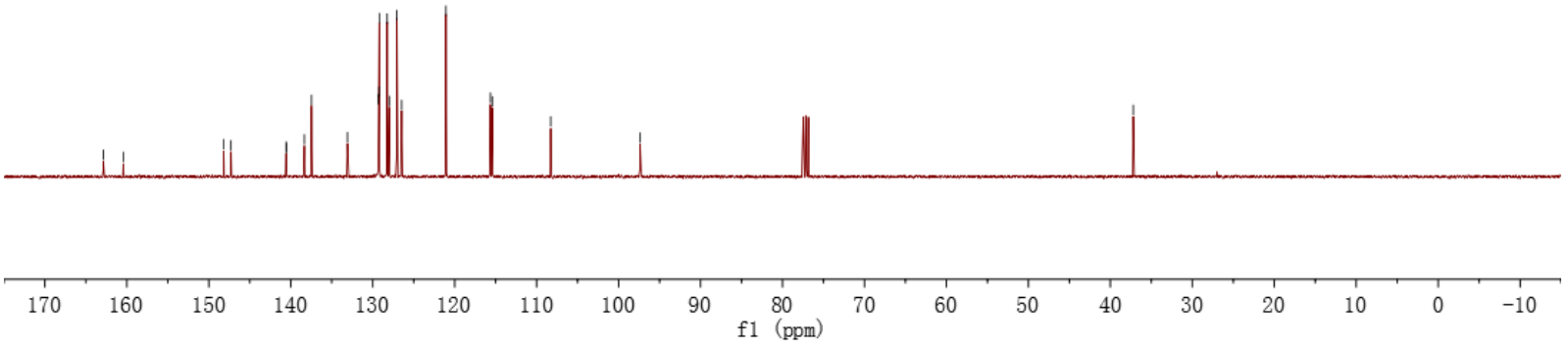
LL-208
PROTON CDC13 {D:\NMR400\02T2} nmr 36

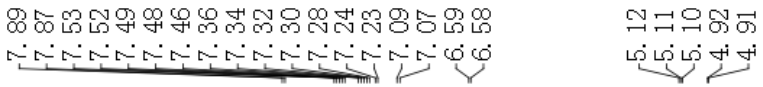




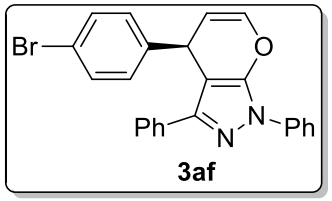

162.86
160.43
148.17
147.29
140.56
140.53
138.33
137.47
133.08
129.30
129.22
129.19
128.23
127.97
127.05
126.47
121.07
115.63
115.41
108.28
97.37
37.21
LL-208
C13CPD CDC13 {D:\NMR400\02T2} nmr 36

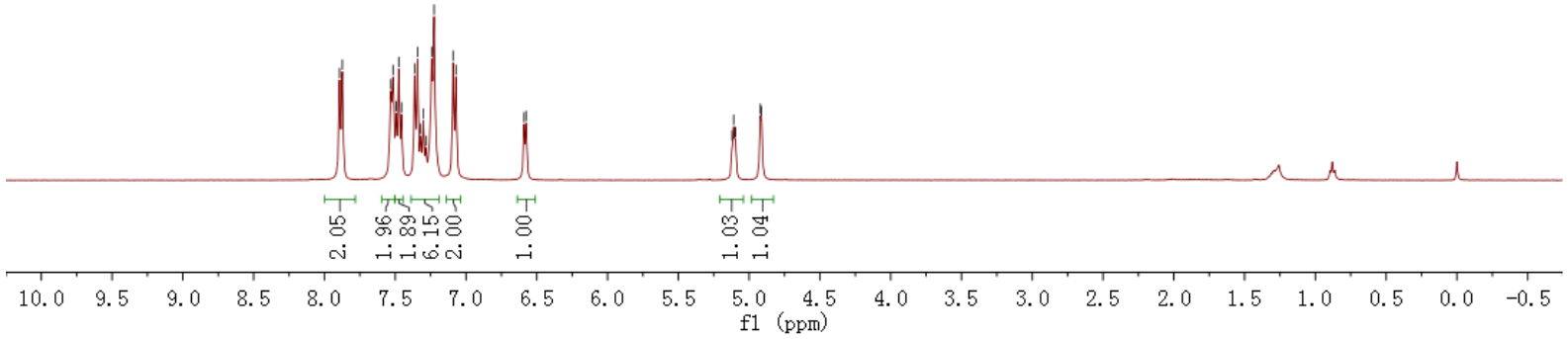

F
O
Ph
N
N
Ph
3ae

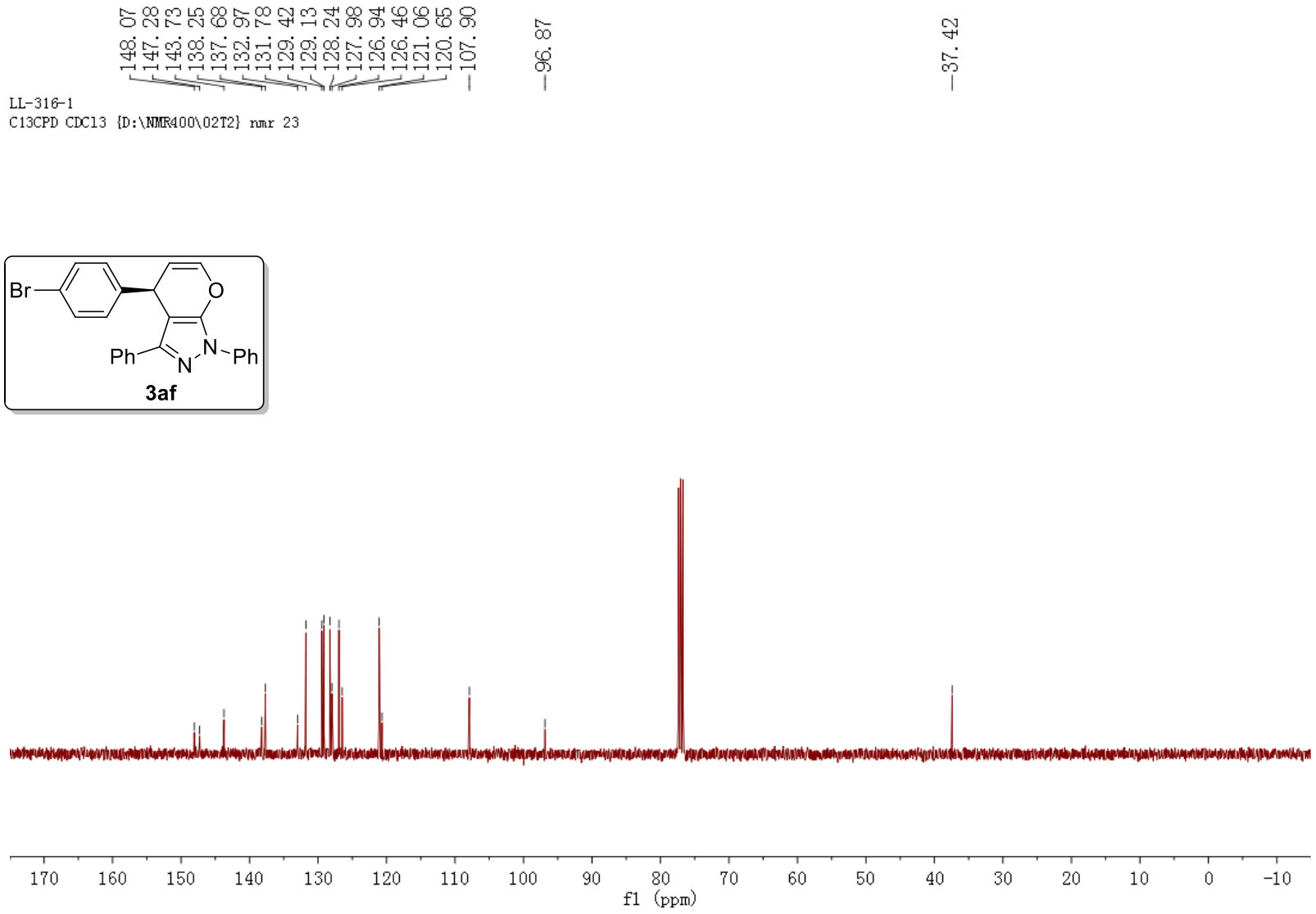

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

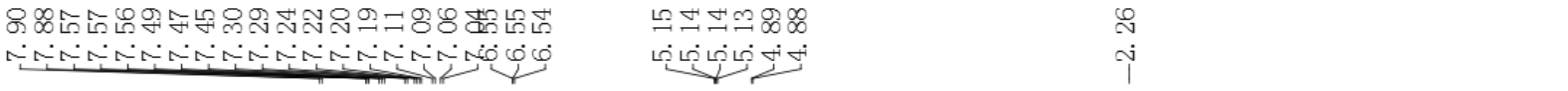


LL-316-1
PROTON CDCl3 {D:\NMR400\02T2} nmr 23

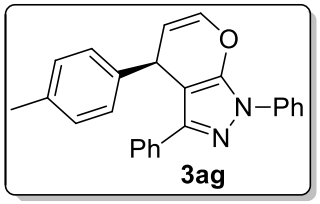




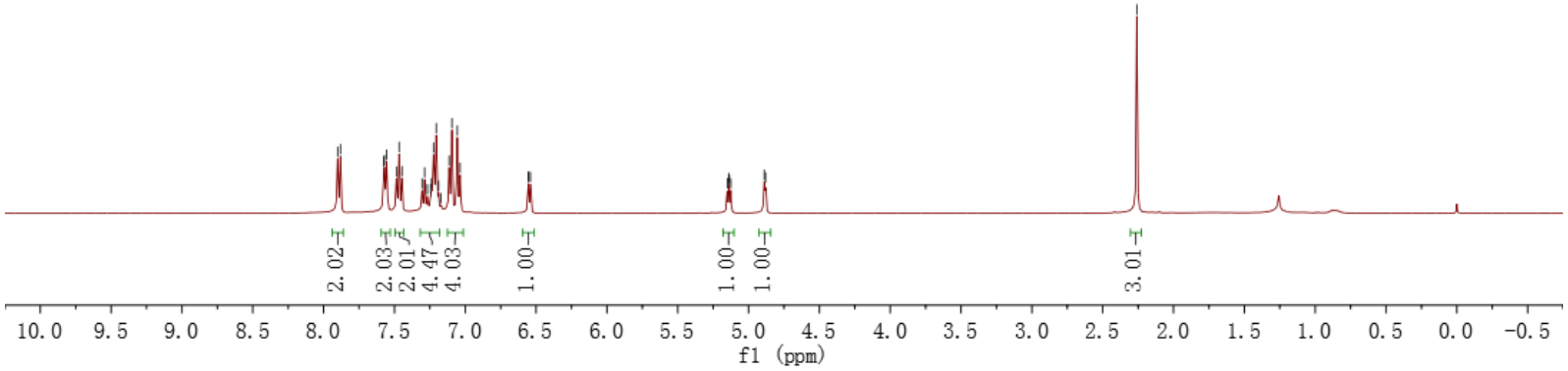

148.07
147.28
143.73
138.25
137.68
132.97
131.78
129.42
129.13
128.24
127.98
126.94
126.46
121.06
120.65
107.90
96.87
37.42
LL-316-1
C13CPD CDCl3 {D:\NMR400\02T2} nmr 23
Br
O
N
N
Ph
Ph
3af
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

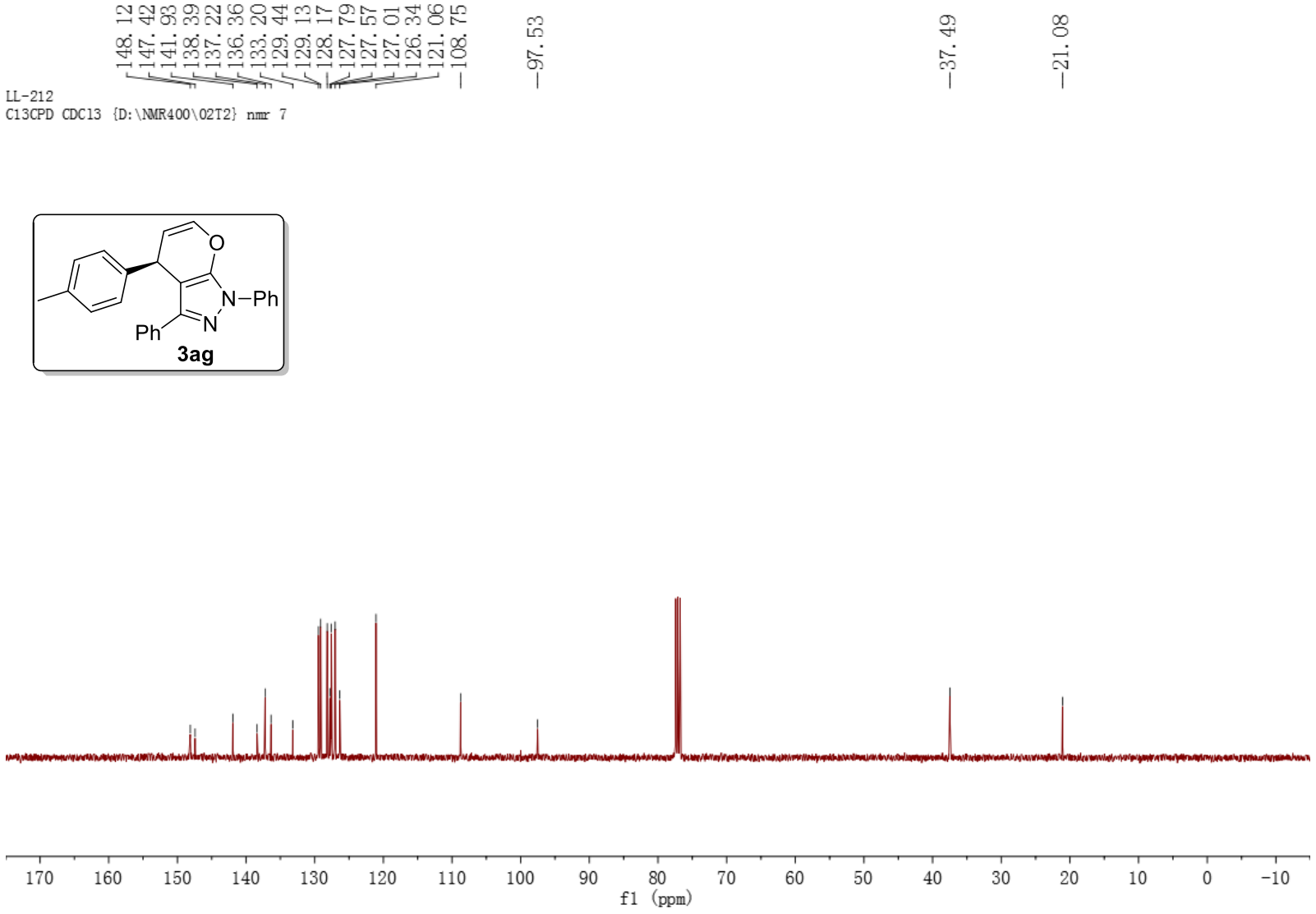


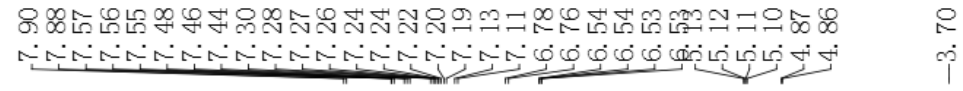
LL-212
PROTON CDC13 {D:\NMR400\02T2} nmr 7



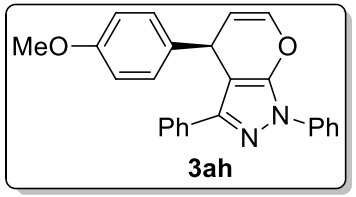
3ag

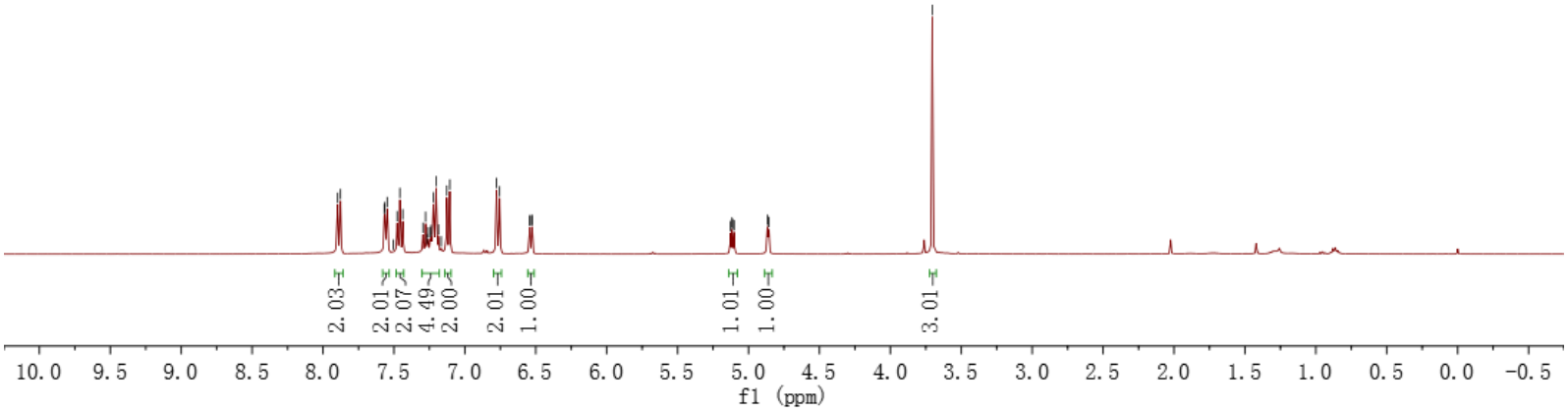



148.12
147.42
141.93
138.39
137.22
136.36
133.20
129.44
129.13
128.17
127.79
127.57
127.01
126.34
121.06
108.75
97.53
37.49
21.08
LL-212
C13CPD CDC13 {D:\NMR400\02T2} nmr 7
O
N–Ph
N
Ph
3ag
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



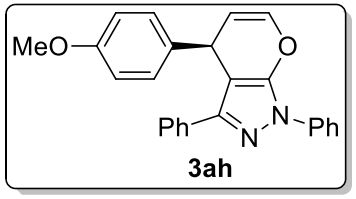
LL-214
PROTON CDC13 {D:\NMR400\02T2} nmr 10



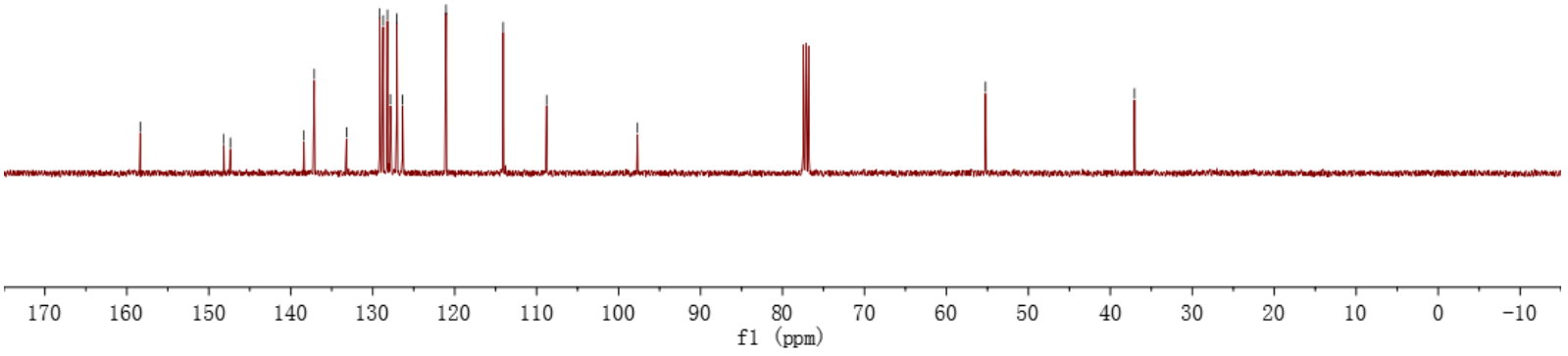


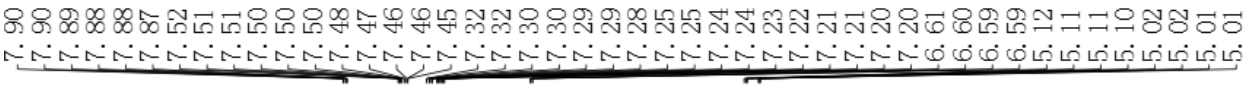
158.36
148.17
147.37
138.39
137.14
133.20
129.14
128.73
128.19
127.83
127.06
126.36
121.05
114.08
108.77
97.69
55.23
37.06

LL-214
C13CPD CDC13 {D:\NMR400\02T2} nmr 10

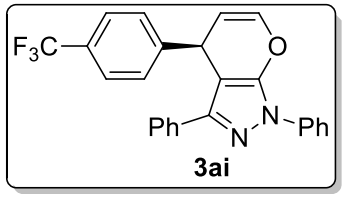


3ah

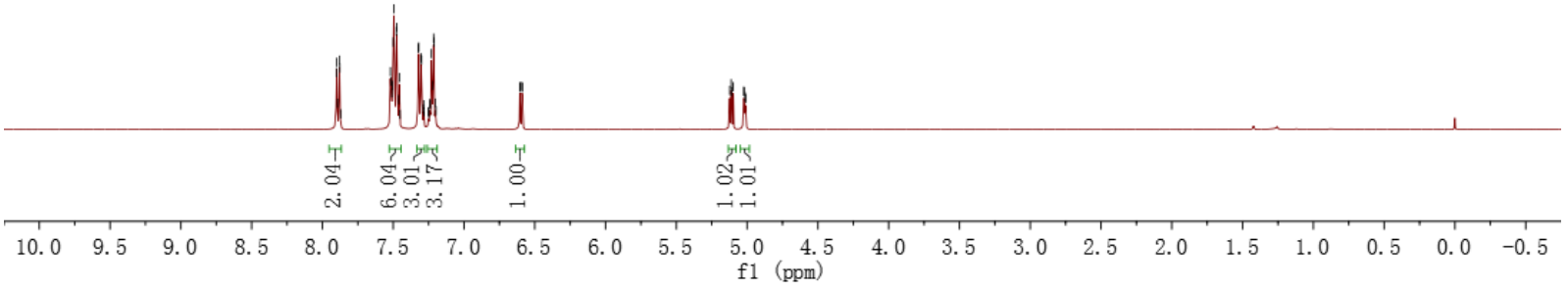


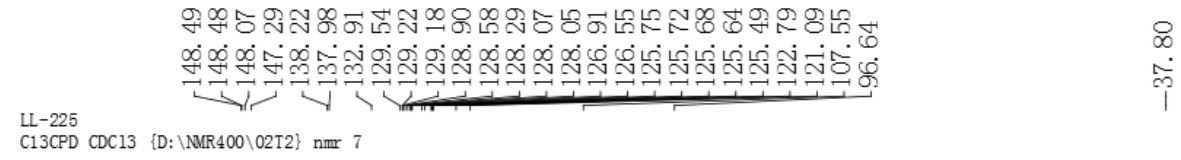


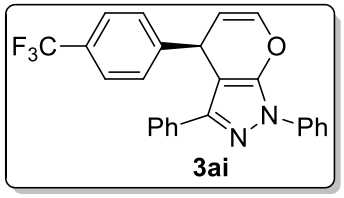
LL-225
PROTON CDC13 {D:\NMR400\02T2} nmr 7

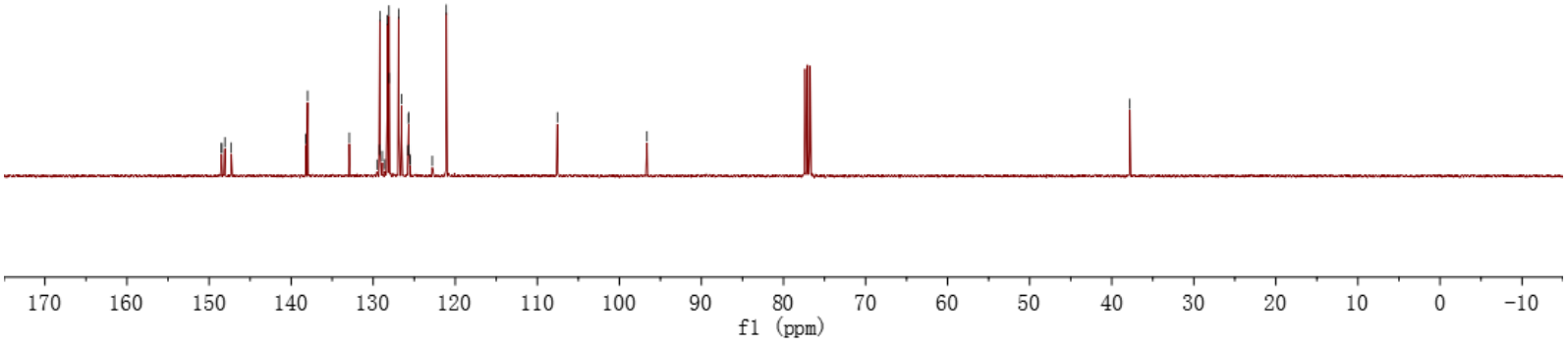


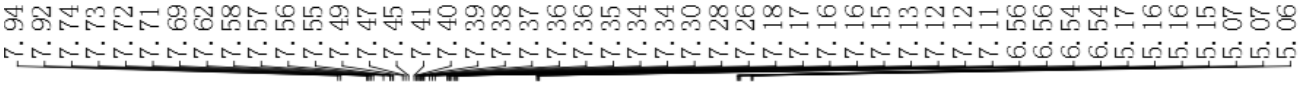
3ai



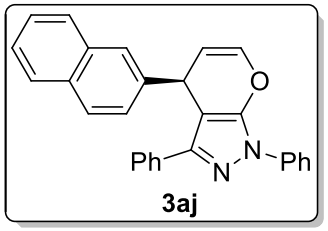

148.49
148.48
148.07
147.29
138.22
137.98
132.91
129.54
129.22
129.18
128.90
128.58
128.29
128.07
128.05
126.91
126.55
125.75
125.72
125.68
125.64
125.49
122.79
121.09
107.55
96.64
37.80
LL-225
C13CPD CDC13 {D:\NMR400\02T2} nmr 7


F3C
O
Ph
N
N
Ph
3ai

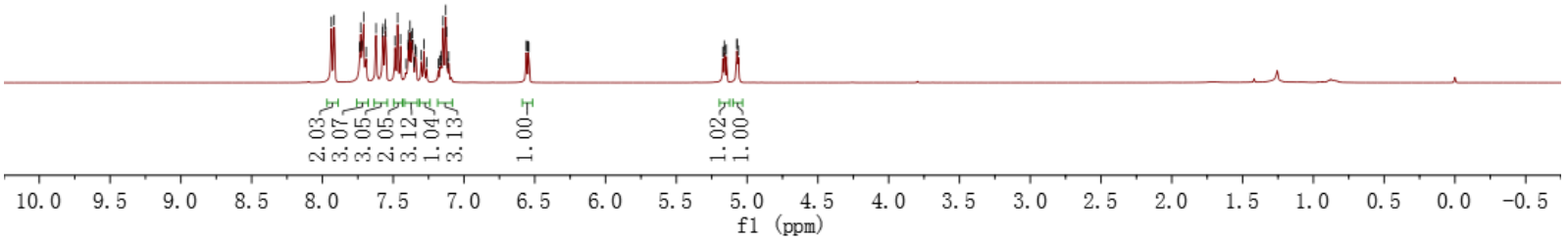

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

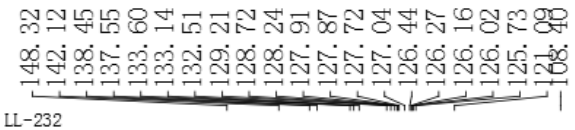


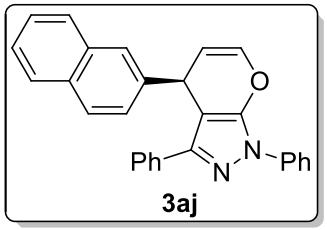
LL-232
PROTON CDC13 {D:\NMR400\02T2} nmr 26

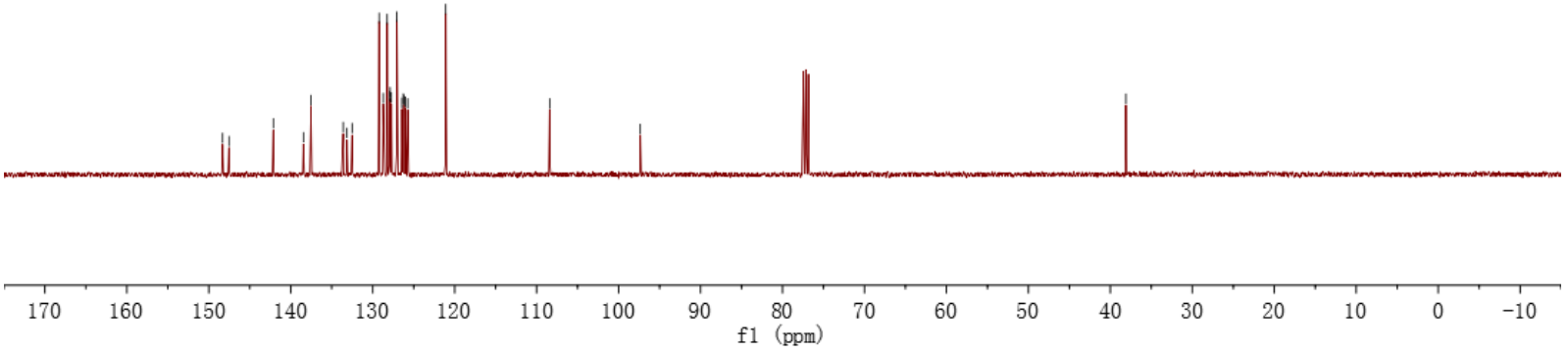


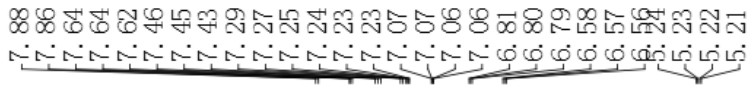
3aj



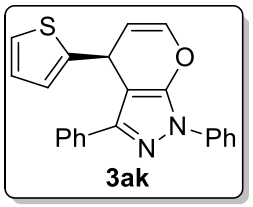

148.32
142.12
138.45
137.55
133.60
133.14
132.51
129.21
128.72
128.24
127.91
127.87
127.72
127.04
126.44
126.27
126.16
126.02
125.73
121.09
108.40
97.35
38.09
LL-232
C13CPD CDC13 {D:\NMR400\02T2} nmr 26


O
Ph
N
N
Ph
3aj

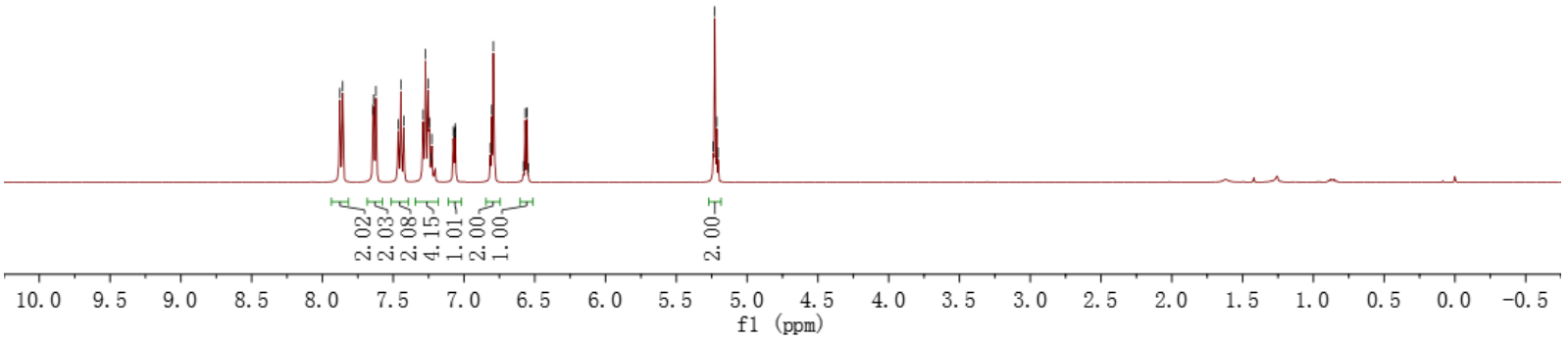

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

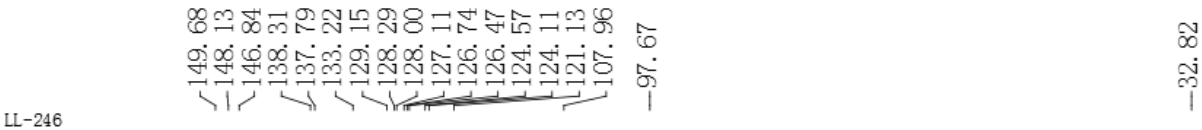


LL-246
PROTON CDC13 {D:\NMR400\02T2} nmr 7

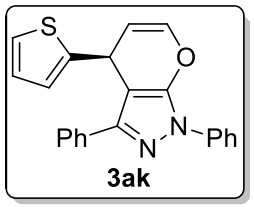


3ak

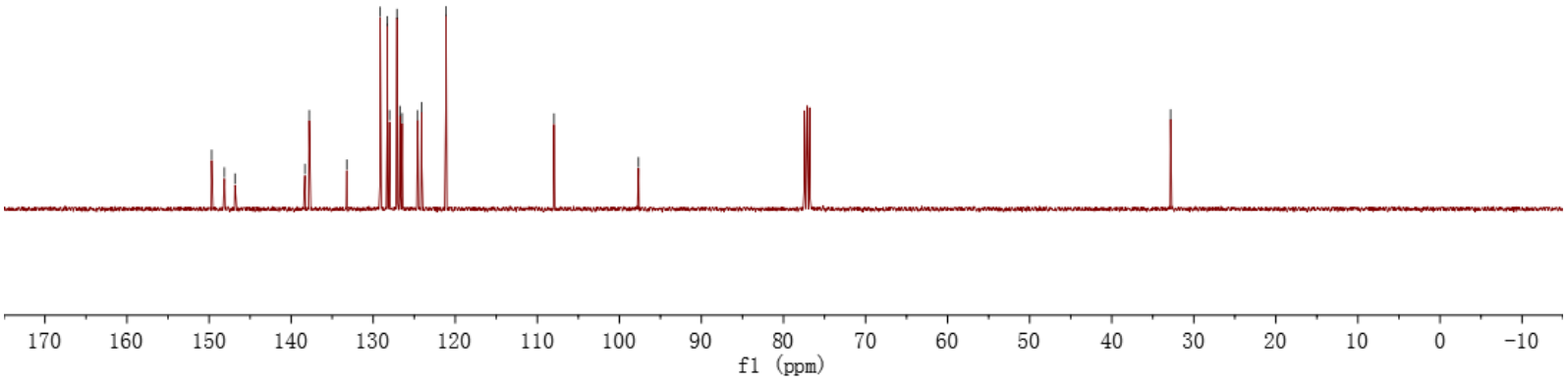


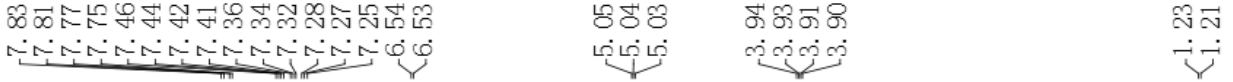


LL-246
C13CPD CDC13 {D:\NMR400\02T2} nmr 7

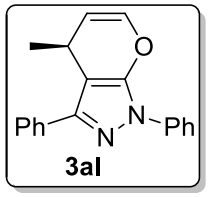


3ak

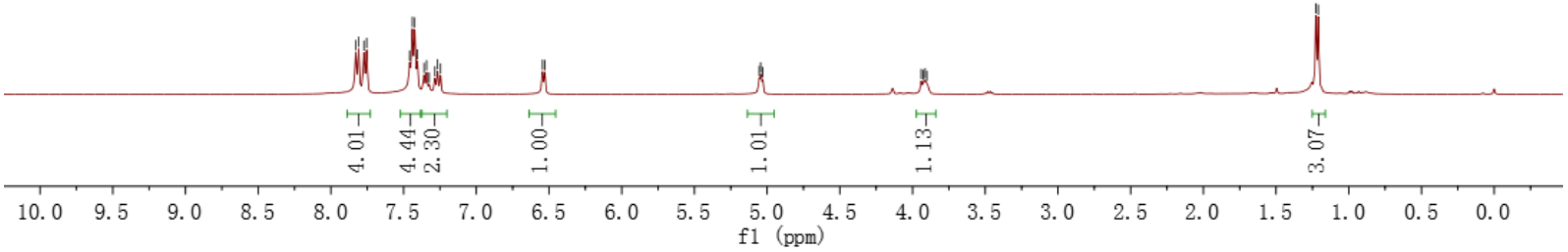


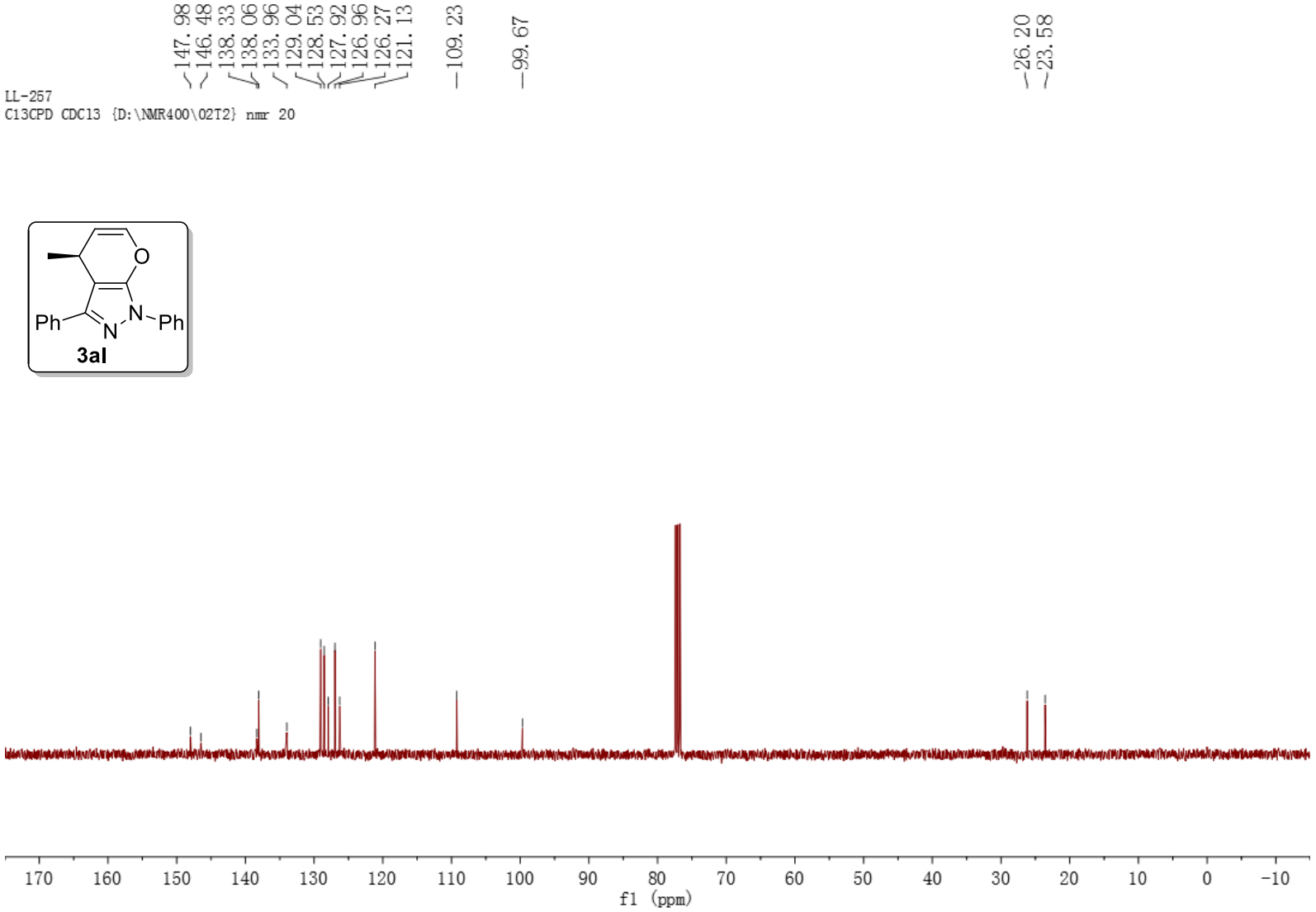


LL-251-1
PROTON CDC13 {D:\NMR400\02T2} nmr 13



3al




147.98
146.48
138.33
138.06
133.96
129.04
128.53
127.92
126.96
126.27
121.13
109.23
99.67
26.20
23.58
LL-257
C13CPD CDCl3 {D:\NMR400\02T2} nmr 20
O
N
N
Ph
Ph
3al
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)