Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Decarboxylation-promoted Pd-catalyzed asymmetric propargylic [3+2] annulation for enantioselective construction of quaternary stereocenter in 2,3-dihydrofurans

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Supporting Information

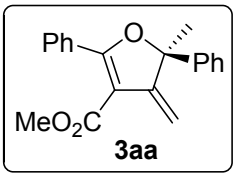
General Information

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. Carbon nuclear magnetic resonance 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. Enantiomeric ratios were determined by chiral HPLC with hexane and *i*-PrOH as solvents. Optical rotations were recorded on a JASCO P-1020 polarimeter. Tertiary propargylic esters **1**,[1] β-ketoesters **2**[2] and ligand **La-d**[3] were prepared following the method from the literature.

General Procedure for Pd-Catalyzed Asymmetric [3+2] Cycloaddition of β-Ketoesters with Tertiary Propargylic Esters

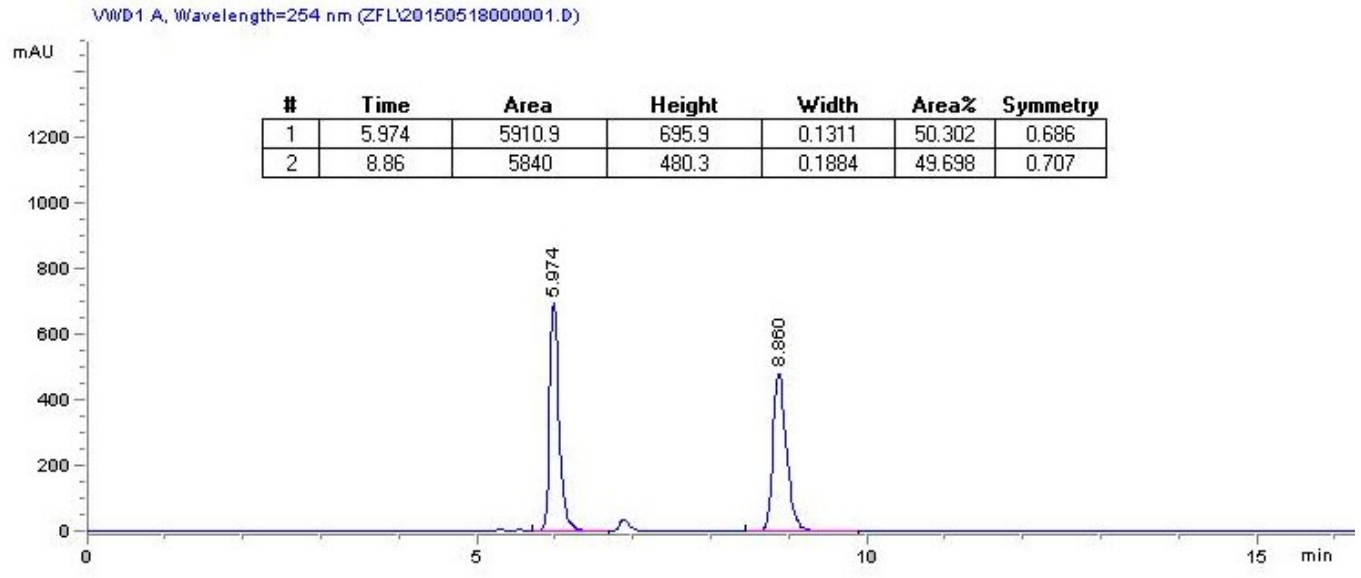
A solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (7.8 mg, 0.0075 mmol) and (R_c,S_p)-**La** (9.2 mg, 0.0165 mmol) in 1 mL of anhydrous toluene placed in an oven-dried Schlenk flask was stirred at room temperature under a nitrogen atmosphere for 1 h. A solution of β-ketoesters **2** (0.3 mmol), propargylic esters **1**(0.3 mmol) and Cs_2CO_3 (117.3 mg, 0.36 mmol) in 2 mL of anhydrous toluene was added. The mixture was stirred at 60 ^{o}C for 24 h. The reaction mixture was purified by silica gel chromatography to afford dihydrofuran products **3**.

(*S*)-Methyl 5-methyl-4-methylene-2,5-diphenyl-4,5-dihydrofuran-3-carboxylate (3aa). Pale yellow oil was obtained in 90% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 96% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 8.9 min, t_R (minor) = 6.0 min. $[\alpha]_D^{27}$ = +13.2 (*c* = 1.11, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74-7.72 (m, 2H), 7.55-7.31 (m, 8H),

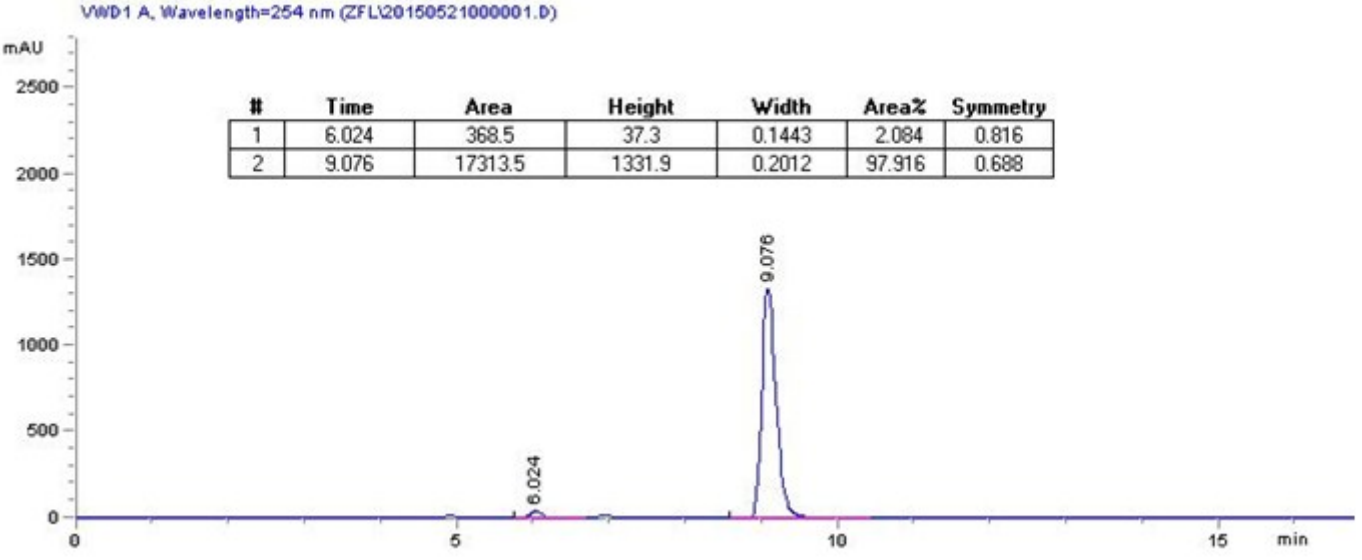


3aa

5.53 (s, 1H), 4.84 (s, 1H), 3.63 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.5, 164.5, 152.6, 143.5, 131.5, 130.2, 129.4, 129.0, 128.5, 128.4, 125.1, 105.6, 103.0, 91.4, 51.5, 27.7; HRMS (ESI): m/z calcd for $C_{20}H_{19}O_3$ [M+H] 307.1334, found 307.1332.

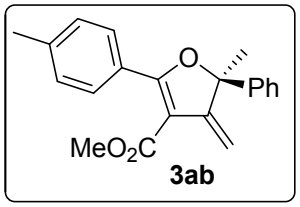


#	Time	Area	Height	Width	Area%	Symmetry
1	5.974	5910.9	695.9	0.1311	50.302	0.686
2	8.86	5840	480.3	0.1884	49.698	0.707



#	Time	Area	Height	Width	Area%	Symmetry
1	6.024	368.5	37.3	0.1443	2.084	0.816
2	9.076	17313.5	1331.9	0.2012	97.916	0.688

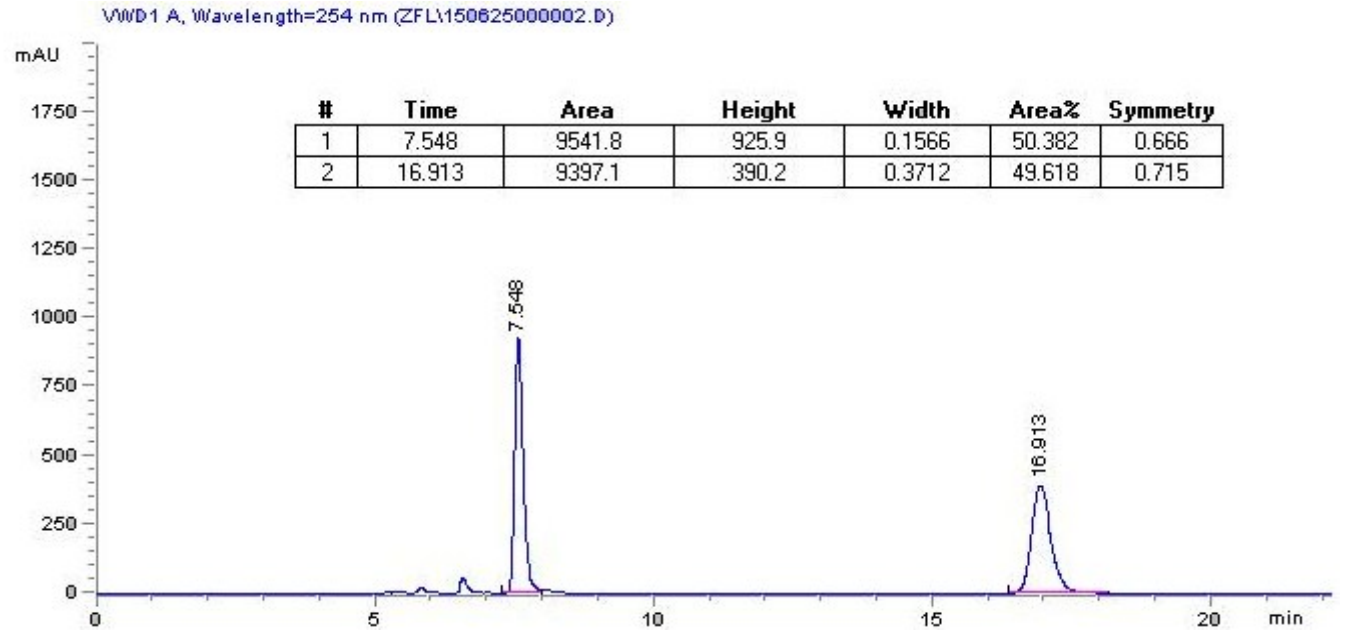
(*S*)-Methyl 5-methyl-4-methylene-5-phenyl-2-(p-tolyl)-4,5-dihydrofuran-3-carboxylate (3ab).



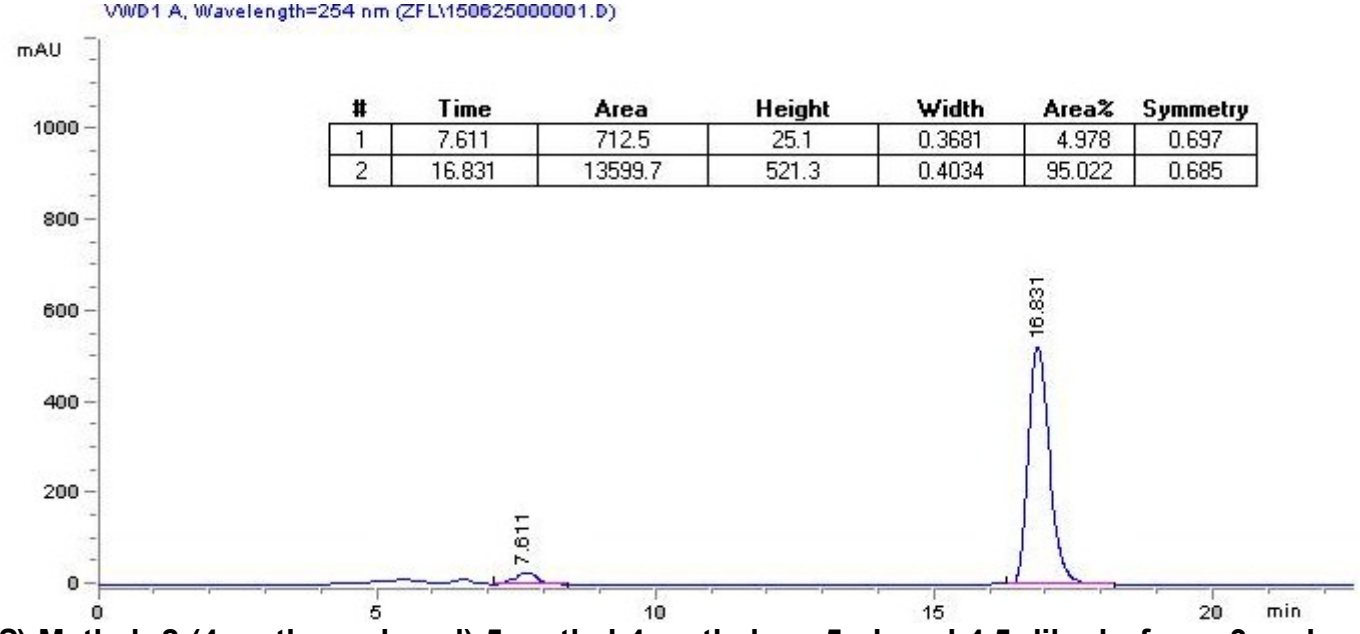
3ab

Yellow oil was obtained in 92% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 16.9 min, t_R (minor) = 7.5 min. $[\alpha]_D^{23}$ = -14.3 (*c* = 1.10, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65-7.63 (m, 2H), 7.50-7.28 (m, 7H), 5.50 (s, 1H), 4.82 (s, 1H), 3.63 (s, 3H), 2.37 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 164.6, 152.8, 143.6, 141.5, 129.4, 129.0, 129.0, 128.3, 127.3, 125.1, 105.1,

102.6, 91.1, 51.4, 27.7, 21.6; HRMS (ESI): m/z calcd for $C_{21}H_{21}O_3$ [M+H] 321.1491, found 321.1488.

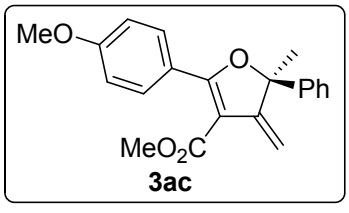


#	Time	Area	Height	Width	Area%	Symmetry
1	7.548	9541.8	925.9	0.1566	50.382	0.666
2	16.913	9397.1	390.2	0.3712	49.618	0.715



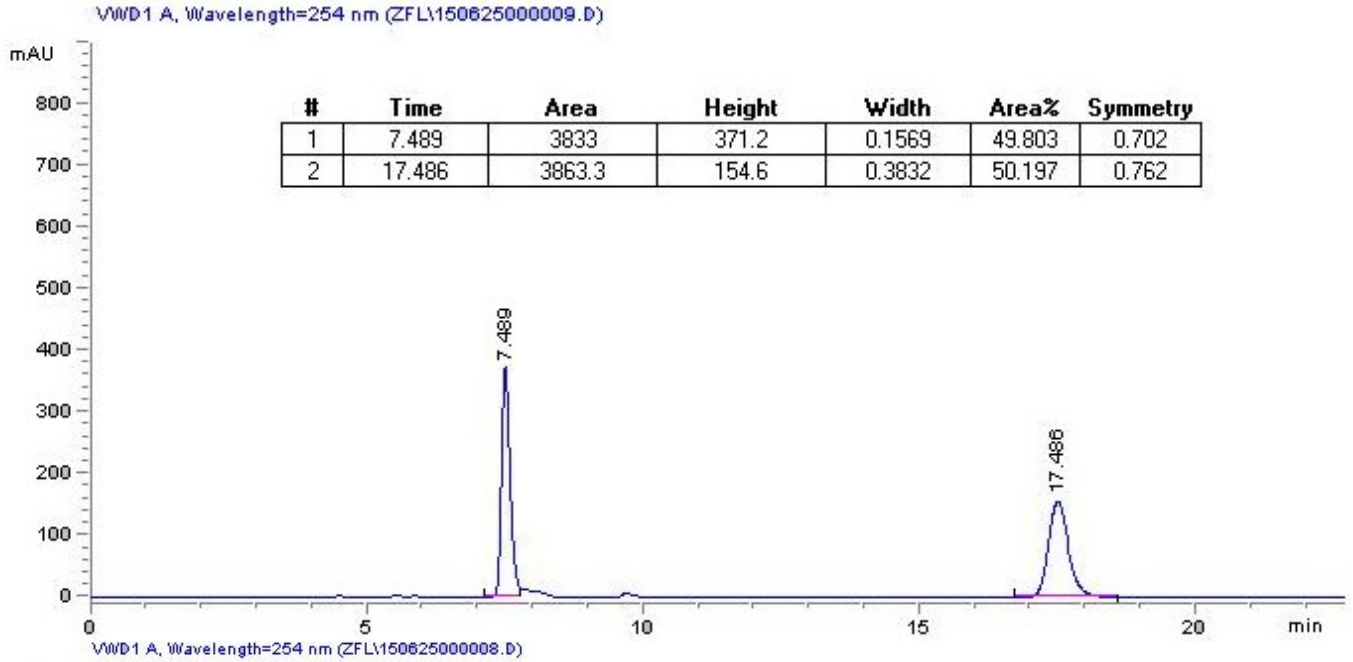
#	Time	Area	Height	Width	Area%	Symmetry
1	7.611	712.5	25.1	0.3681	4.978	0.697
2	16.831	13599.7	521.3	0.4034	95.022	0.685

(*S*)-Methyl 2-(4-methoxyphenyl)-5-methyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ac). Yellow oil was obtained in 74% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 50/1). 97% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 17.5 min, t_R (minor) = 7.5 min. $[\alpha]_D^{29}$ = +10.9 (*c* = 1.00, CH_2Cl_2). ^1H NMR (400 MHz, DMSO-d_6) δ 7.75-7.73 (m, 2H), 7.49-7.33 (m, 5H), 7.04-7.02 (m, 2H), 5.46 (s, 1H), 4.79 (s, 1H), 3.83 (s, 3H), 3.65 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 164.7, 161.9, 152.8, 143.7,

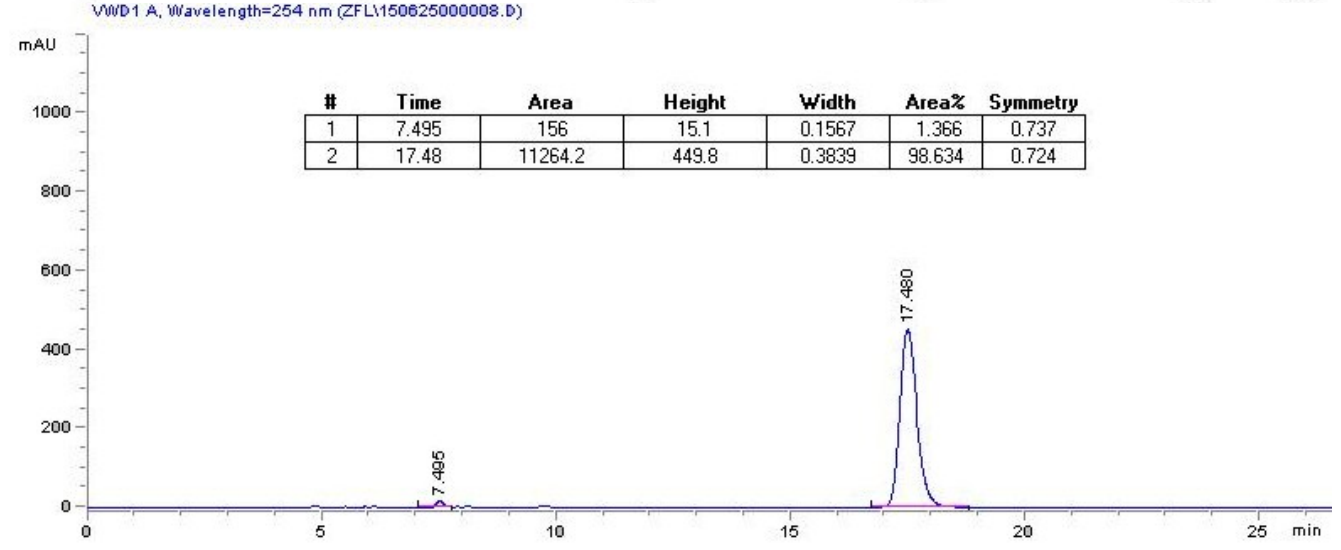


3ac

131.3, 129.0, 128.3, 125.1, 122.2, 113.9, 104.2, 102.3, 90.9, 55.8, 51.4, 27.7; HRMS (ESI): m/z calcd for $C_{21}H_{21}O_4$ [M+H] 337.1440, found 337.1438.

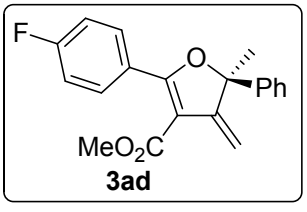


#	Time	Area	Height	Width	Area%	Symmetry
1	7.489	3833	371.2	0.1569	49.803	0.702
2	17.486	3863.3	154.6	0.3832	50.197	0.762



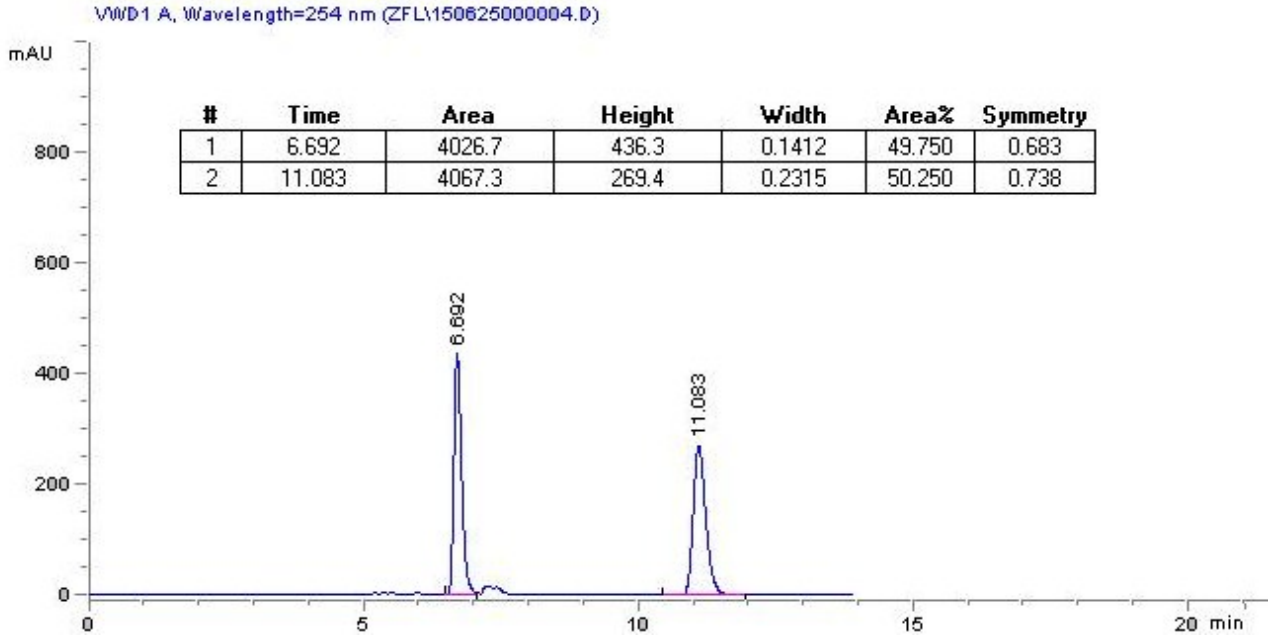
#	Time	Area	Height	Width	Area%	Symmetry
1	7.495	156	15.1	0.1567	1.366	0.737
2	17.48	11264.2	449.8	0.3839	98.634	0.724

(*S*)-Methyl 2-(4-fluorophenyl)-5-methyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ad). Yellow oil was obtained in 93% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 96% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 11.1 min, t_R (minor) = 6.7 min. $[\alpha]_D^{26}$ = -22.6 (*c* = 1.10, CH_2Cl_2). ^1H NMR (400 MHz, DMSO-d_6) δ 7.83-7.80 (m, 2H), 7.50-7.29 (m, 7H), 5.53 (s, 1H), 4.83 (s, 1H), 3.64 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.6, 164.4, 163.9 (d, *J* = 249.4 Hz) 152.5, 143.4, 132.1 (d, *J* = 8.9 Hz), 129.0, 128.4, 126.6 (d, *J* = 3.2 Hz), 125.1, 115.6 (d, *J* = 21.9 Hz), 105.6, 103.2, 91.5, 51.5, 27.7; HRMS

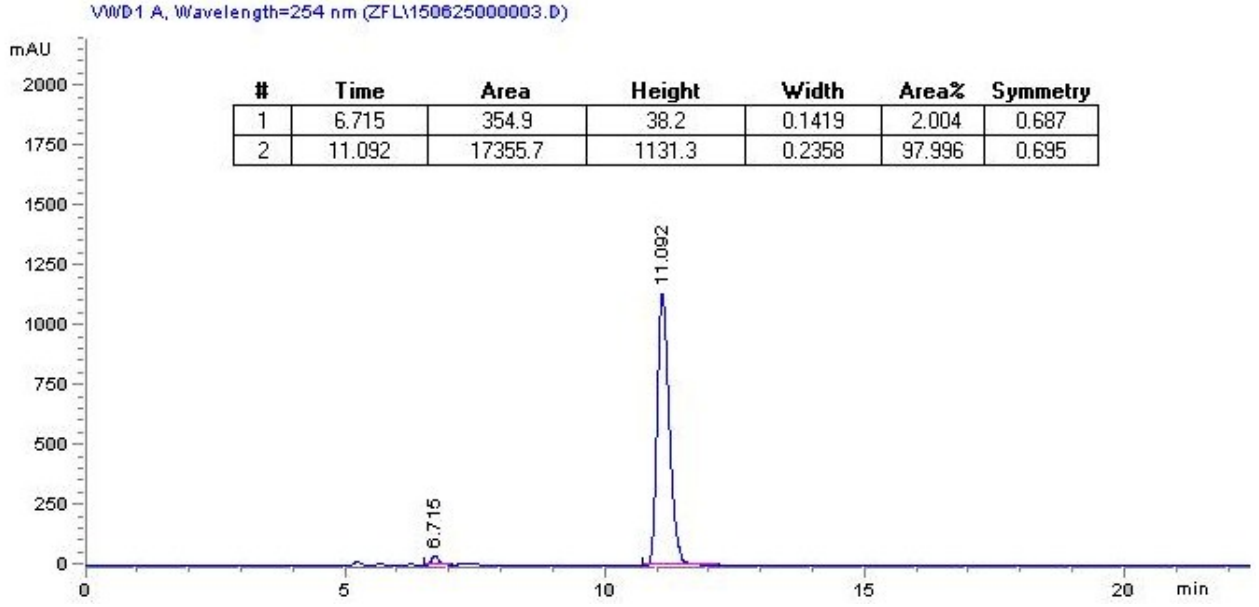


3ad

(ESI): m/z calcd for $C_{20}H_{18}FO_3$ [M+H] 325.1240, found 325.1241.

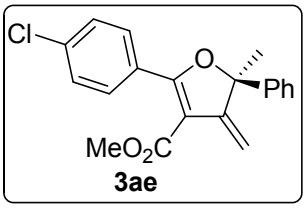


#	Time	Area	Height	Width	Area%	Symmetry
1	6.692	4026.7	436.3	0.1412	49.750	0.683
2	11.083	4067.3	269.4	0.2315	50.250	0.738

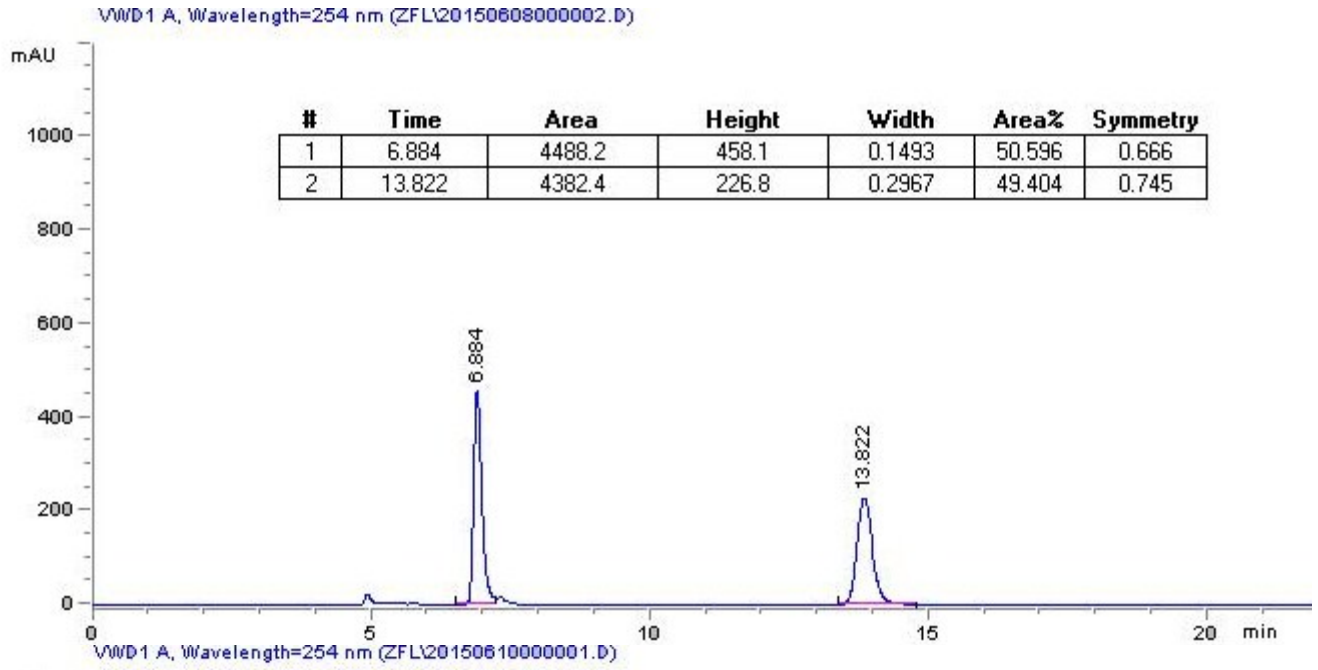


#	Time	Area	Height	Width	Area%	Symmetry
1	6.715	354.9	38.2	0.1419	2.004	0.687
2	11.092	17355.7	1131.3	0.2358	97.996	0.695

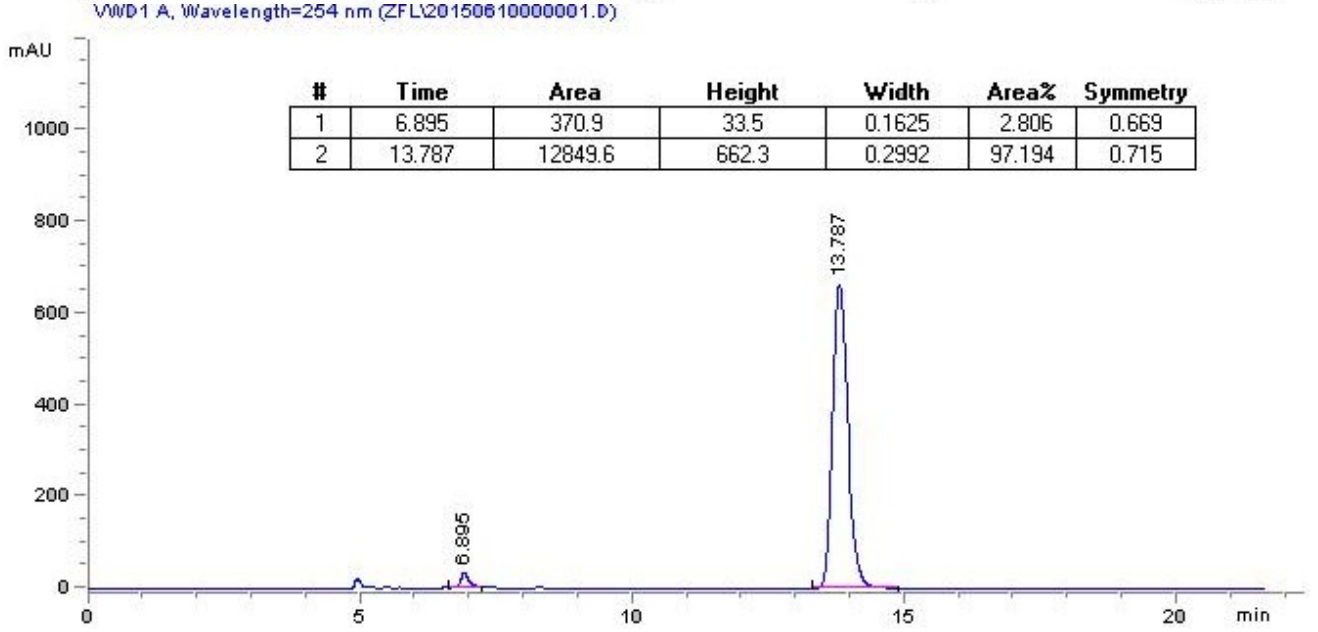
(*S*)-Methyl 2-(4-chlorophenyl)-5-methyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ae). Yellow oil was obtained in 92% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 94% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 13.8 min, t_R (minor) = 6.9 min. $[\alpha]_D^{27}$ = -23.9 (*c* = 0.77, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77-7.75 (m, 2H), 7.56-7.32 (m, 7H), 5.54 (s, 1H), 4.85 (s, 1H), 3.64 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.3, 164.3, 152.4, 143.4, 136.2, 131.3, 129.0, 128.9, 128.6, 128.4, 125.1 106.1, 103.6, 91.6, 51.5, 27.7; HRMS (ESI): m/z calcd for $C_{20}H_{18}ClO_3$ [M+H] 341.0944, found 341.0944.



3ae

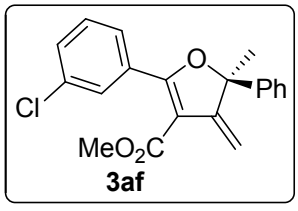


#	Time	Area	Height	Width	Area%	Symmetry
1	6.884	4488.2	458.1	0.1493	50.596	0.666
2	13.822	4382.4	226.8	0.2967	49.404	0.745

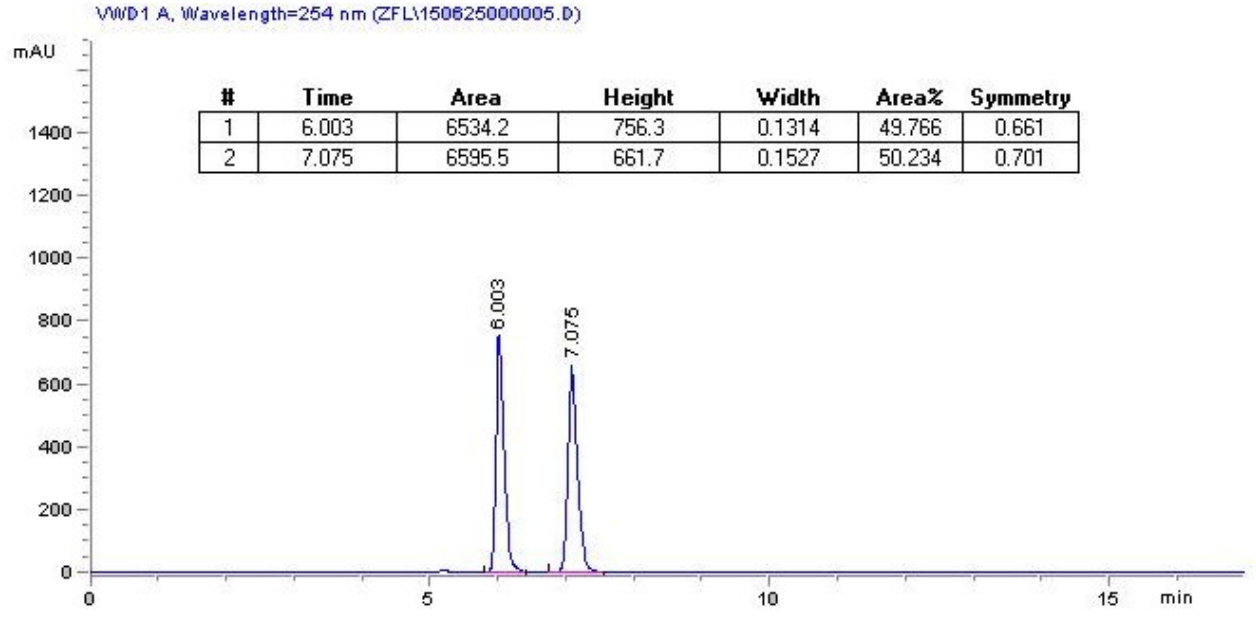


#	Time	Area	Height	Width	Area%	Symmetry
1	6.895	370.9	33.5	0.1625	2.806	0.669
2	13.787	12849.6	662.3	0.2992	97.194	0.715

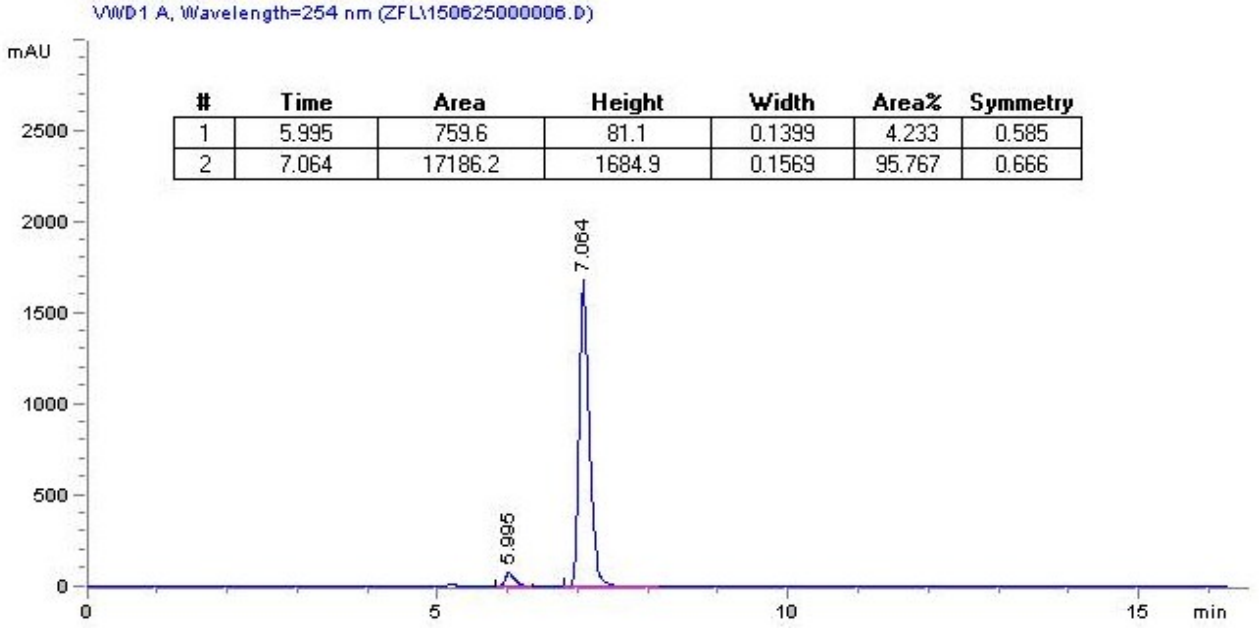
(*S*)-Methyl 2-(3-chlorophenyl)-5-methyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate (3af). Yellow oil was obtained in 90% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 92% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 7.1 min, t_R (minor) = 6.0 min. $[\alpha]_D^{26}$ = -36.7 (*c* = 1.07, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78-7.58 (m, 3H), 7.50-7.33 (m, 6H), 5.56 (s, 1H), 4.84 (s, 1H), 3.64 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.8, 164.2, 152.2, 143.3, 133.2, 132.2, 131.2, 130.4, 129.1, 129.0, 128.4, 128.1, 125.2, 106.5, 103.9, 91.8, 51.6, 27.6. HRMS (ESI): m/z calcd for $C_{20}H_{18}ClO_3$ [M+H] 341.0944, found 341.0942.



3af

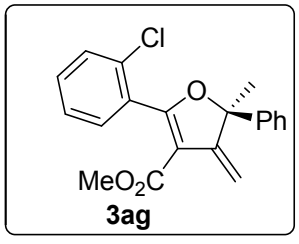


#	Time	Area	Height	Width	Area%	Symmetry
1	6.003	6534.2	756.3	0.1314	49.766	0.661
2	7.075	6595.5	661.7	0.1527	50.234	0.701

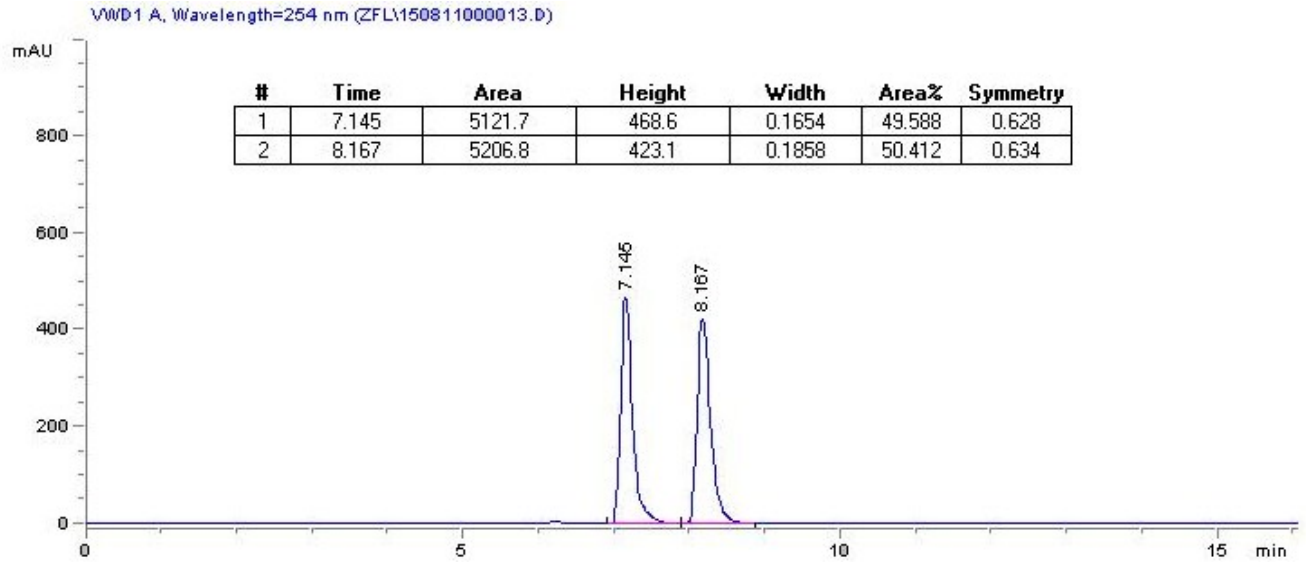


#	Time	Area	Height	Width	Area%	Symmetry
1	5.995	759.6	81.1	0.1399	4.233	0.585
2	7.064	17186.2	1684.9	0.1569	95.767	0.666

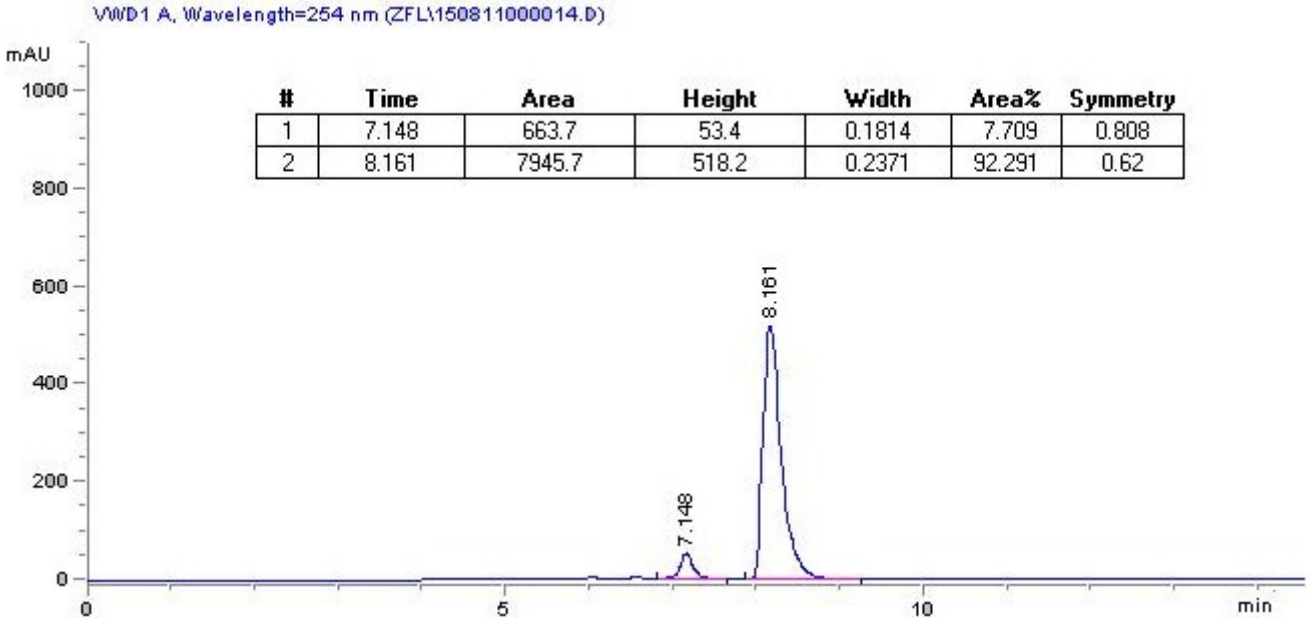
(*S*)-Methyl 2-(2-chlorophenyl)-5-methyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ag). Yellow oil was obtained in 64% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 85% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 8.2 min, t_R (minor) = 7.1 min. $[\alpha]_D^{29}$ = -17.4 (*c* = 1.04, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60-7.33 (m, 9H), 5.61 (s, 1H), 4.81 (s, 1H), 3.51 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.7, 163.7, 151.7, 142.9, 132.4, 132.1, 131.2, 130.8, 129.9, 128.9, 128.5, 127.5, 125.4, 108.2, 103.5, 92.9, 51.4, 27.6; HRMS (ESI): m/z calcd for $C_{20}H_{18}ClO_3$ [M+H] 341.0944, found 341.0941.



3ag

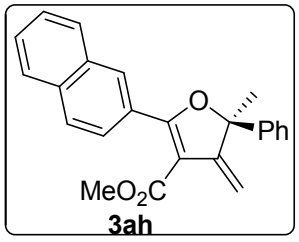


#	Time	Area	Height	Width	Area%	Symmetry
1	7.145	5121.7	468.6	0.1654	49.588	0.628
2	8.167	5206.8	423.1	0.1858	50.412	0.634

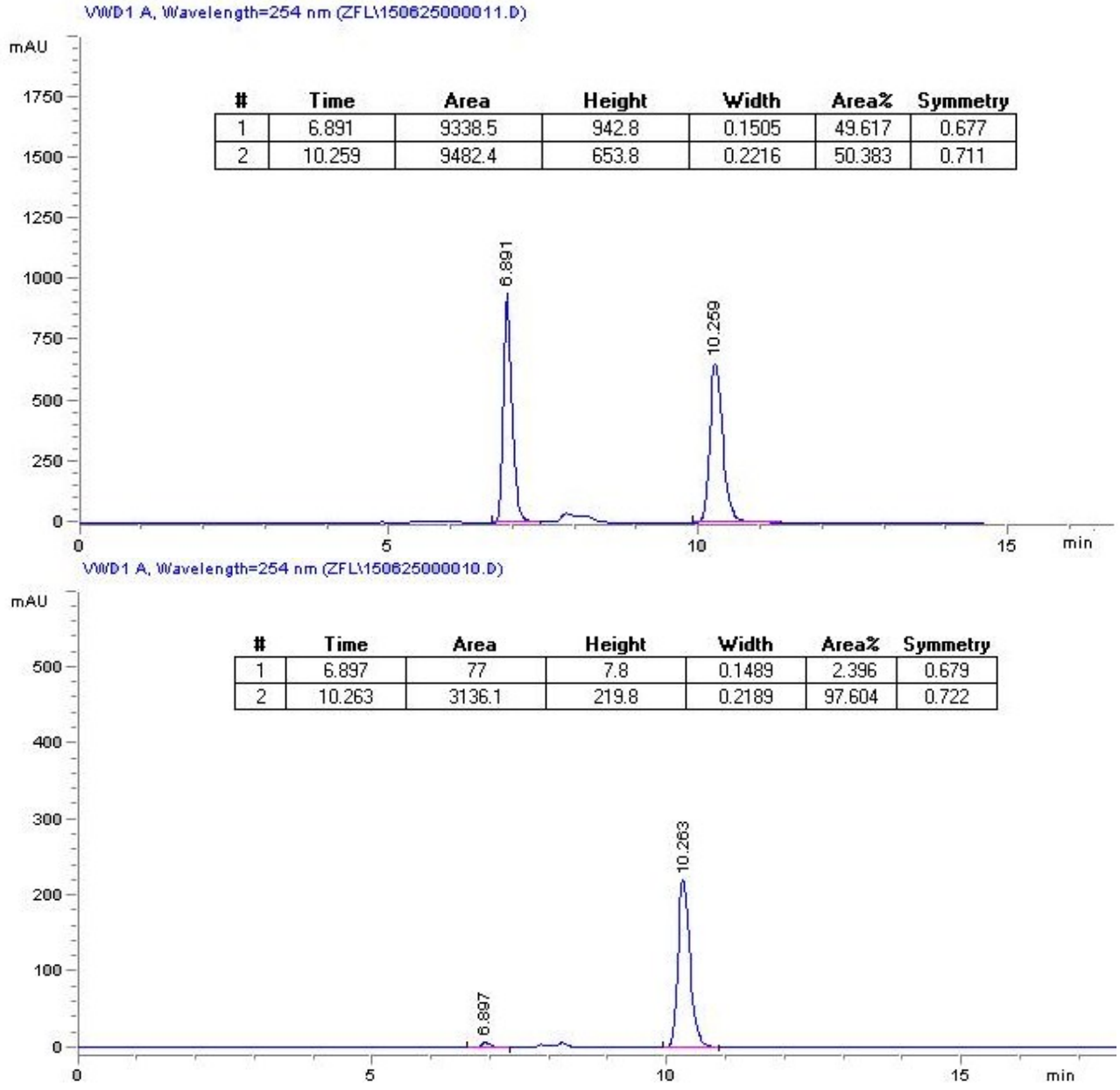


#	Time	Area	Height	Width	Area%	Symmetry
1	7.148	663.7	53.4	0.1814	7.709	0.808
2	8.161	7945.7	518.2	0.2371	92.291	0.62

(*S*)-Methyl 5-methyl-4-methylene-2-(naphthalen-2-yl)-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ah). Pale yellow solid was obtained in 92% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 50/1). M.p.: 97-98 °C. 95% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 10.3 min, t_R (minor) = 6.9 min. $[\alpha]_D^{24}$ = 35.4 (*c* 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.38 (s, 1H), 8.07-7.96 (m, 3H), 7.78 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.63-7.54 (m, 4H), 7.44-7.32 (m, 3H), 5.57 (s, 1H), 4.86 (s, 1H), 3.65 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 164.5, 152.7, 143.6, 134.3, 132.5, 129.7, 129.3, 129.0, 128.4, 128.3, 128.1, 127.8, 127.6, 127.2, 126.2, 125.2, 106.0, 103.1, 91.5, 51.5, 27.7; HRMS (ESI): m/z calcd for $C_{24}H_{21}O_3$ [M+H] 357.1491, found 357.1486.



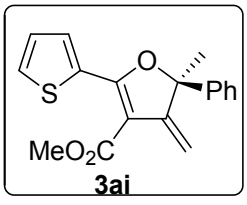
3ah



#	Time	Area	Height	Width	Area%	Symmetry
1	6.891	9338.5	942.8	0.1505	49.617	0.677
2	10.259	9482.4	653.8	0.2216	50.383	0.711

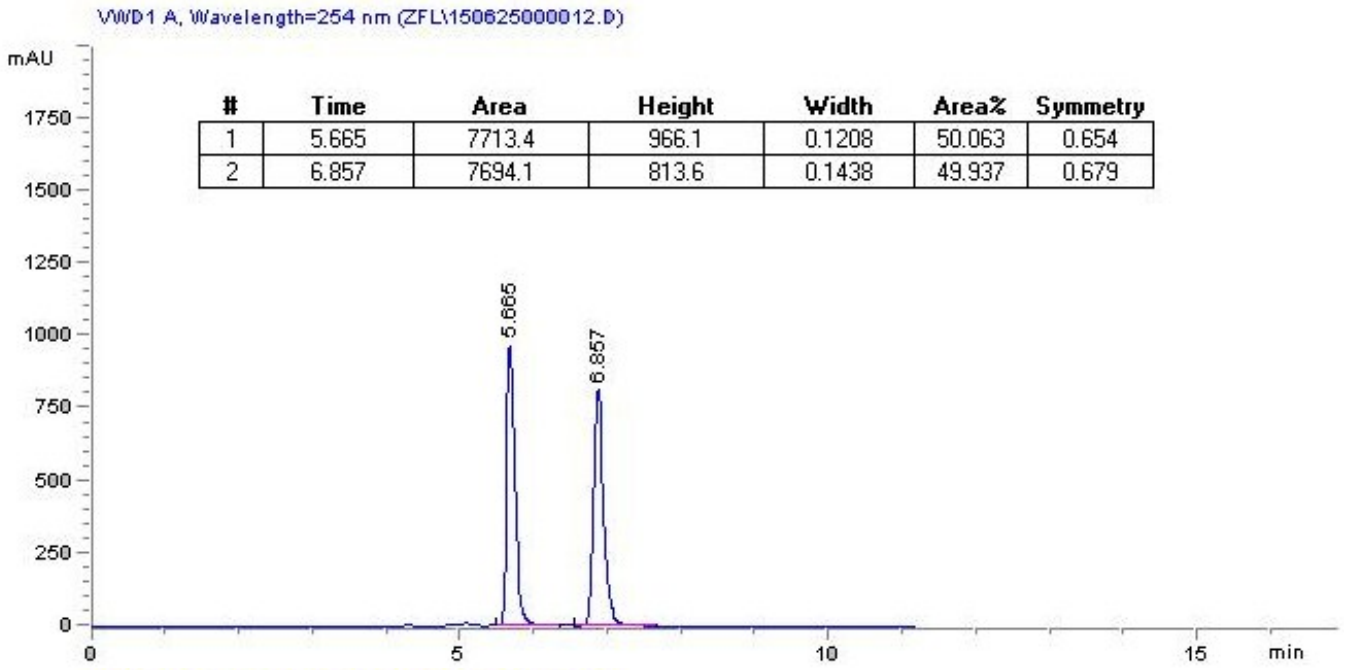
#	Time	Area	Height	Width	Area%	Symmetry
1	6.897	77	7.8	0.1489	2.396	0.679
2	10.263	3136.1	219.8	0.2189	97.604	0.722

(*S*)-Methyl 5-methyl-4-methylene-5-phenyl-2-(thiophen-2-yl)-4,5-dihydrofuran-3-carboxylat

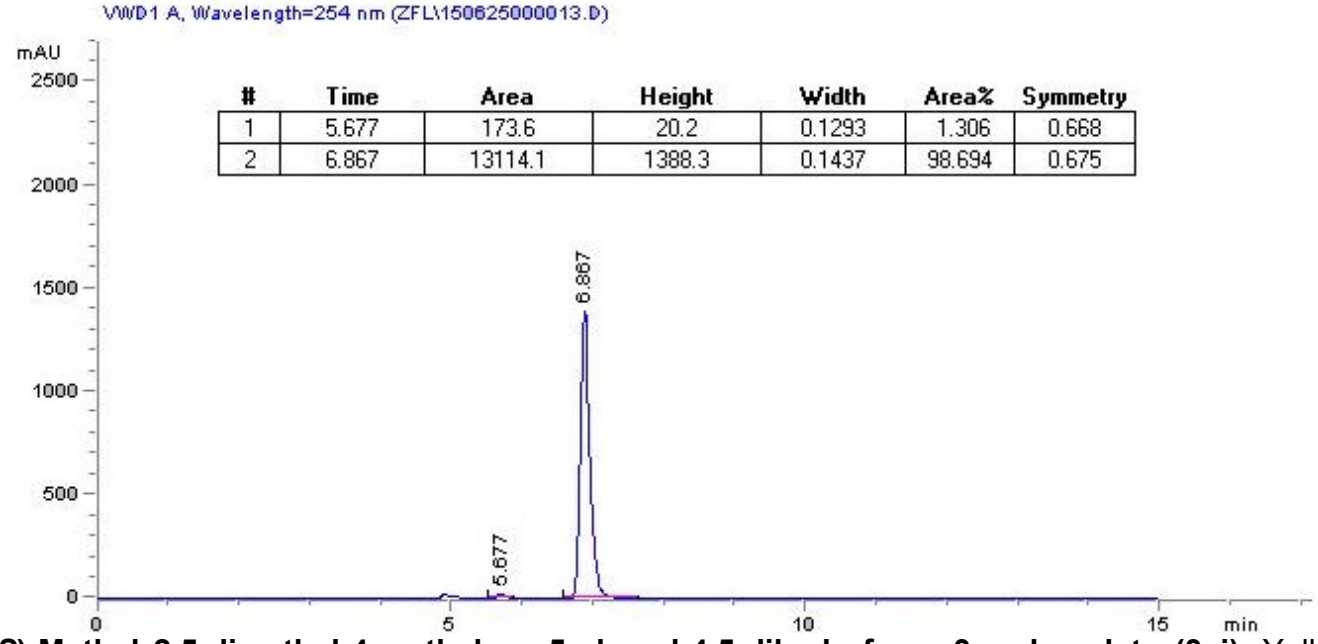


3ai

e (3ai). Yellow oil was obtained in 89% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 97% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 6.9 min, t_R (minor) = 5.7 min. $[\alpha]_D^{24}$ = +102.9 (*c* = 1.00, CH_2Cl_2). ^1H NMR (400 MHz, DMSO-d_6) δ 8.17 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.95 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.47-7.24 (m, 7H), 5.54 (s, 1H), 4.87 (s, 1H), 3.78 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.5, 162.0, 152.0, 143.7, 133.8, 133.4, 131.0, 129.0, 128.4, 128.3, 125.0, 103.8, 103.7, 90.9, 51.6, 27.7; HRMS (ESI): m/z calcd for $C_{18}H_{17}O_3S$ [M+H] 313.0898, found 313.0895.

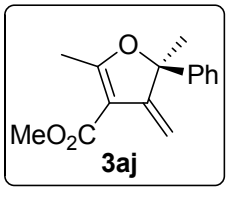


#	Time	Area	Height	Width	Area%	Symmetry
1	5.665	7713.4	966.1	0.1208	50.063	0.654
2	6.857	7694.1	813.6	0.1438	49.937	0.679

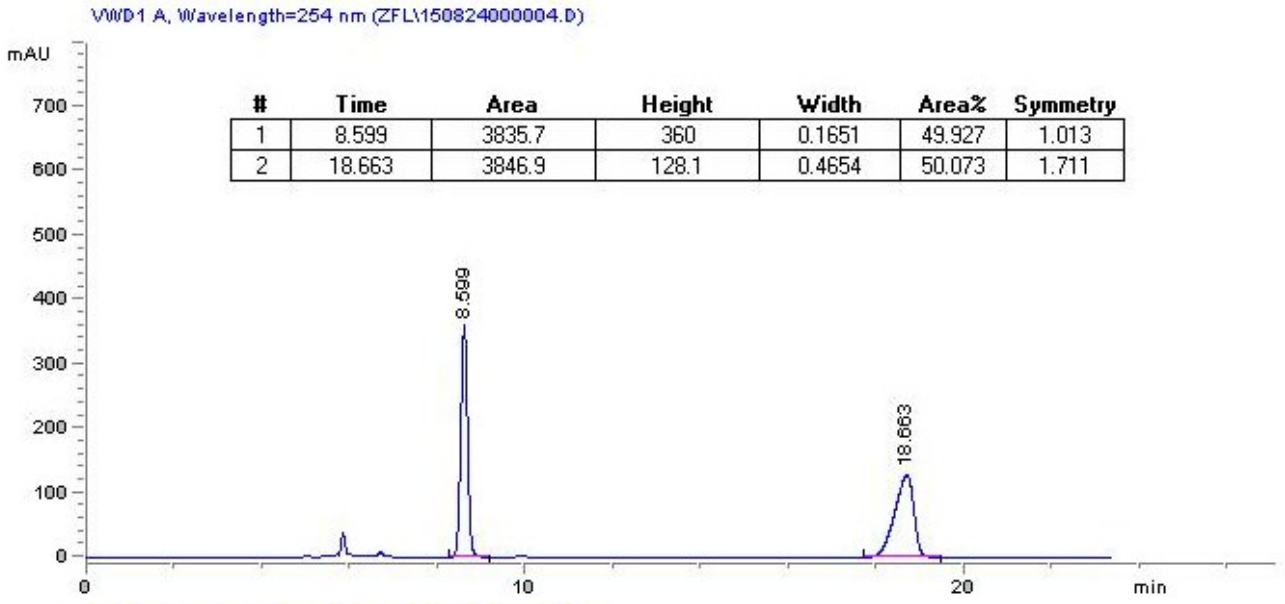


#	Time	Area	Height	Width	Area%	Symmetry
1	5.677	173.6	20.2	0.1293	1.306	0.668
2	6.867	13114.1	1388.3	0.1437	98.694	0.675

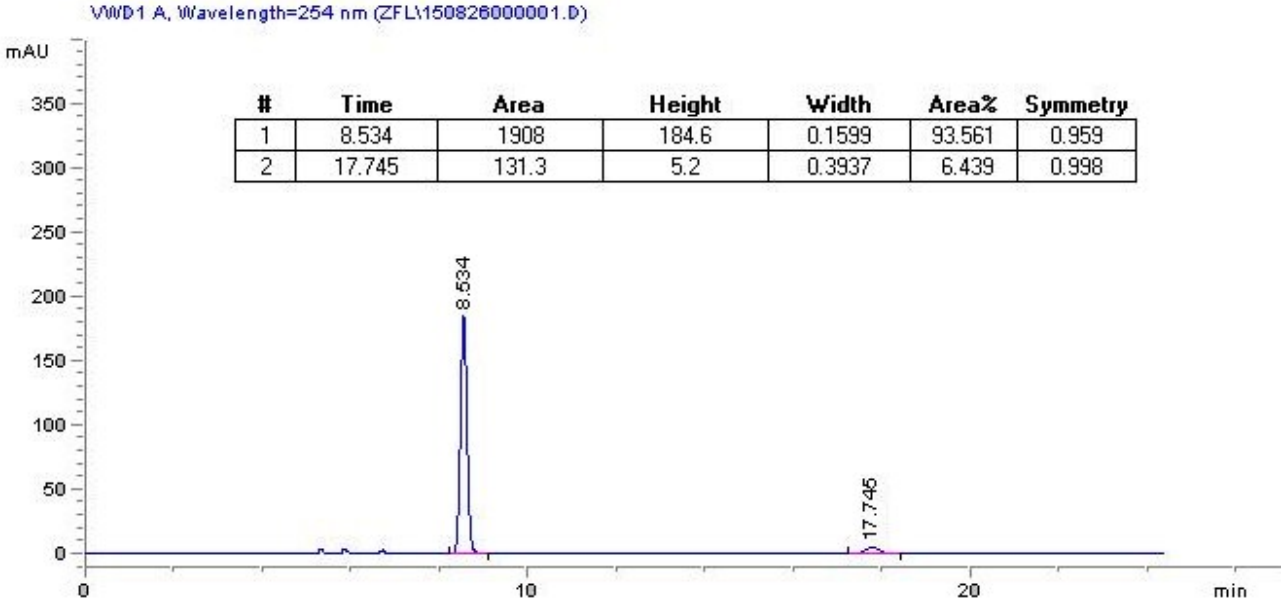
(*S*)-Methyl 2,5-dimethyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate (3aj). Yellow oil was obtained in 72% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 87% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 50/50, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 8.6 min, t_R (minor) = 18.7 min. $[\alpha]_D^{29}$ = 88.1 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41-7.32 (m, 5H), 5.39 (s, 1H), 4.63 (s, 1H), 3.71 (s, 3H), 2.40 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.3, 164.9, 151.7, 143.3, 128.9, 128.3, 125.2, 105.1, 100.9, 92.0, 51.3, 27.5, 15.9; HRMS (ESI): m/z calcd for $C_{15}H_{17}O_3$ [M+H] 245.1178, found 245.1175.



3aj

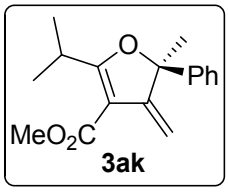


#	Time	Area	Height	Width	Area%	Symmetry
1	8.599	3835.7	360	0.1651	49.927	1.013
2	18.663	3846.9	128.1	0.4654	50.073	1.711



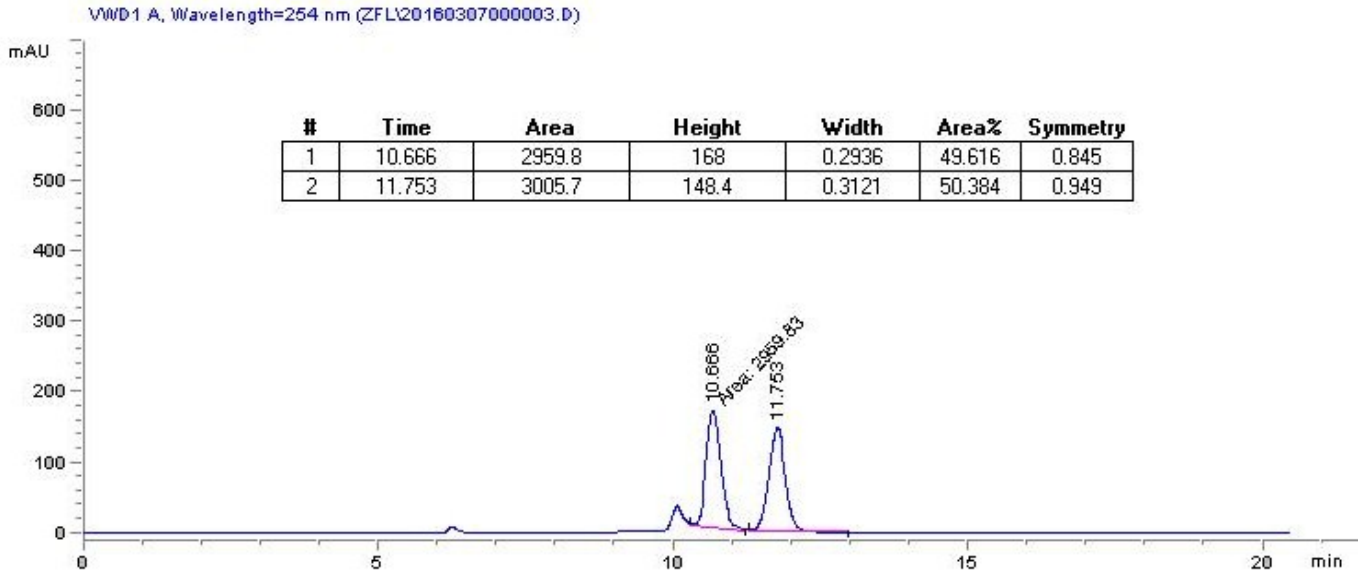
#	Time	Area	Height	Width	Area%	Symmetry
1	8.534	1908	184.6	0.1599	93.561	0.959
2	17.745	131.3	5.2	0.3937	6.439	0.998

(*S*)-Methyl 2-isopropyl-5-methyl-4-methylene-5-phenyl-4,5-dihydrofuran-3-carboxylate

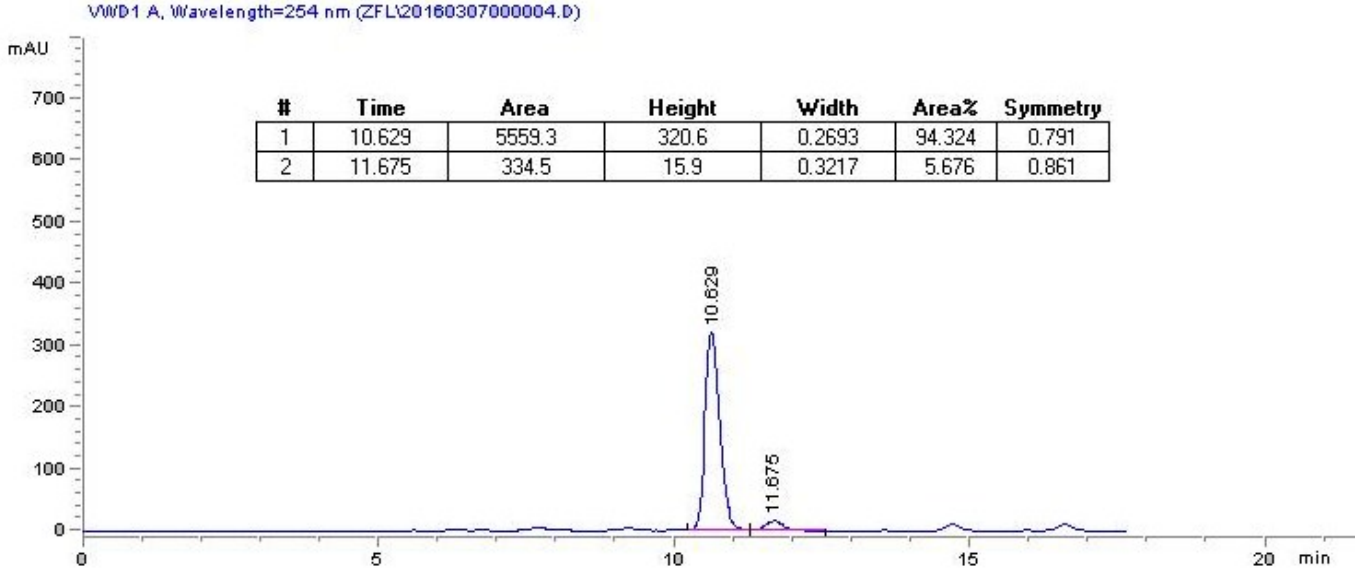


3ak

(3ak). Yellow oil was obtained in 66% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 89% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 10.6 min, t_R (minor) = 11.7 min. $[\alpha]_D^{22}$ = -77.8 (*c* = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, DMSO-d_6) δ 7.41-7.30 (m, 5H), 5.38 (s, 1H), 4.62 (s, 1H), 3.76-3.70 (m, 4H), 1.73 (s, 3H), 1.19 (dd, *J* = 12.8, 6.9 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 181.0, 164.8, 152.0, 143.5, 128.9, 128.2, 124.9, 103.3, 101.2, 91.4, 51.3, 27.8, 27.5, 19.9, 19.8; HRMS (ESI): m/z calcd for $C_{17}H_{21}O_3$ [M+H] 273.1491, found 273.1493.

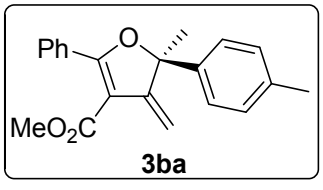


#	Time	Area	Height	Width	Area%	Symmetry
1	10.666	2959.8	168	0.2936	49.616	0.845
2	11.753	3005.7	148.4	0.3121	50.384	0.949



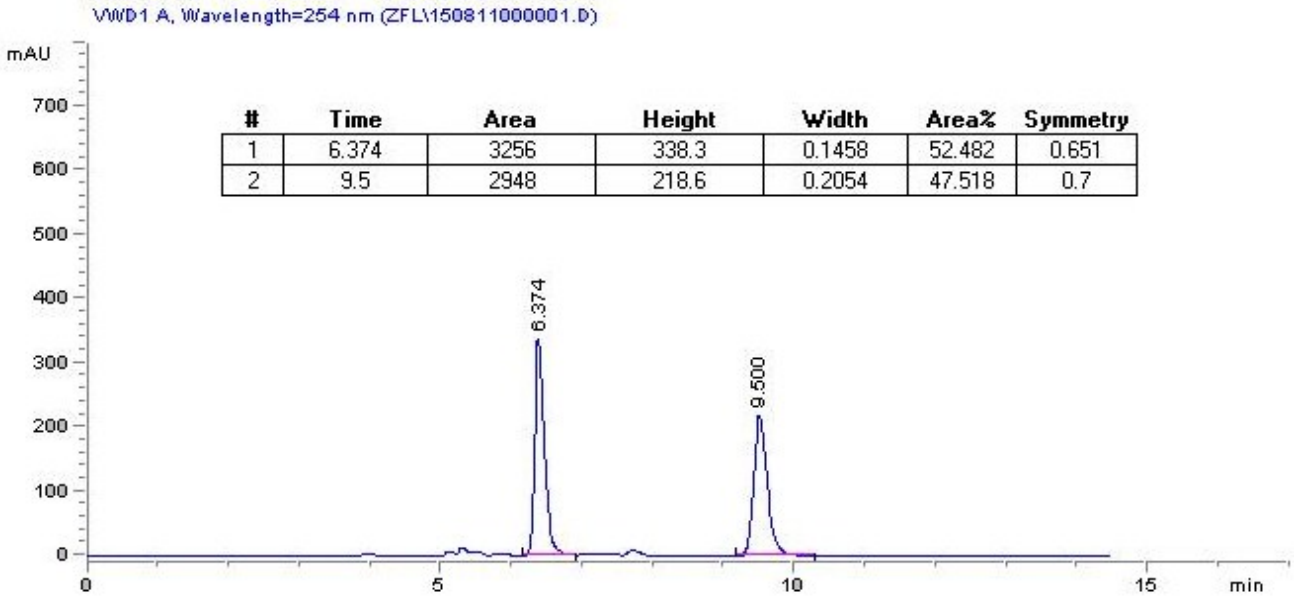
#	Time	Area	Height	Width	Area%	Symmetry
1	10.629	5559.3	320.6	0.2693	94.324	0.791
2	11.675	334.5	15.9	0.3217	5.676	0.861

(*S*)- Methyl 5-methyl-4-methylene-2-phenyl-5-(p-tolyl)-4,5-dihydrofuran-3-carboxylate (3ba).

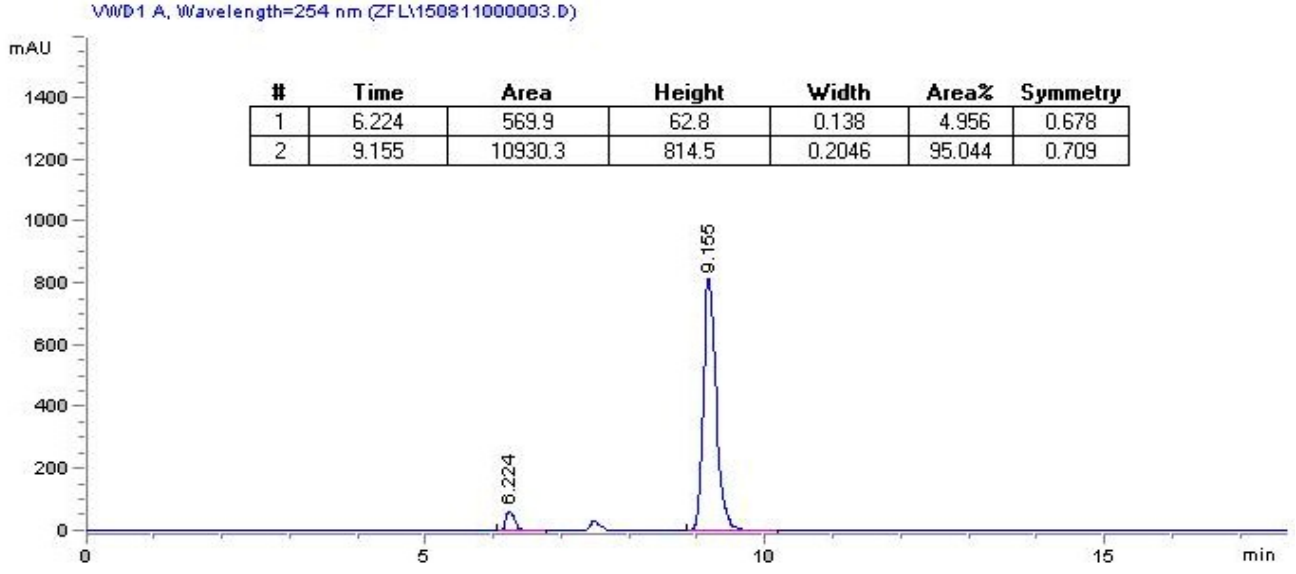


3ba

Pale yellow solid was obtained in 93% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 9.5 min, t_R (minor) = 6.4 min. $[\alpha]_D^{29}$ = -48.1 (*c* = 1.04, CH_2Cl_2). ^1H NMR (400 MHz, DMSO-d_6) δ 7.72-7.69 (m, 2H), 7.54-7.36 (m, 5H), 7.21-7.19 (m, 2H), 5.51 (s, 1H), 4.78 (s, 1H), 3.62 (s, 3H), 2.29 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 164.5, 152.8, 140.6, 137.7, 131.4, 130.3, 129.5, 129.4, 128.4, 125.2, 105.6, 102.8, 91.4, 51.4, 27.6, 21.1; HRMS (ESI): m/z calcd for $C_{21}H_{21}O_3$ [M+H] 321.1491, found 321.1487.

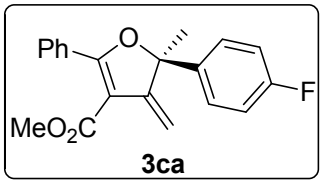


#	Time	Area	Height	Width	Area%	Symmetry
1	6.374	3256	338.3	0.1458	52.482	0.651
2	9.5	2948	218.6	0.2054	47.518	0.7

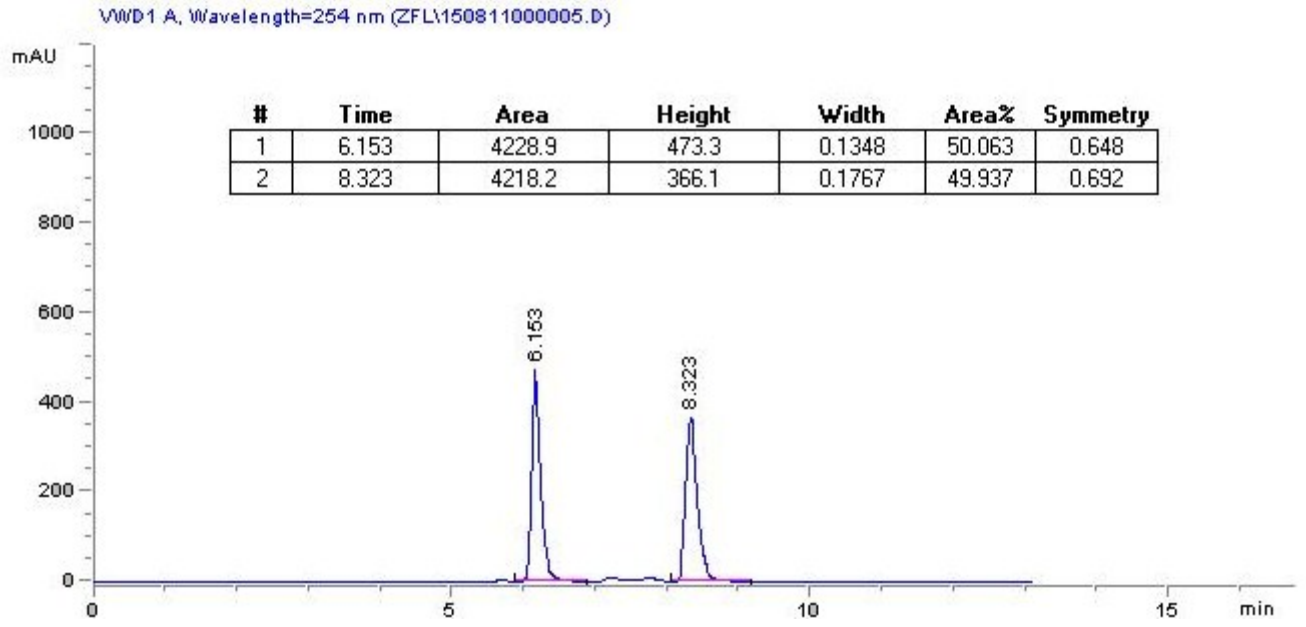


#	Time	Area	Height	Width	Area%	Symmetry
1	6.224	569.9	62.8	0.138	4.956	0.678
2	9.155	10930.3	814.5	0.2046	95.044	0.709

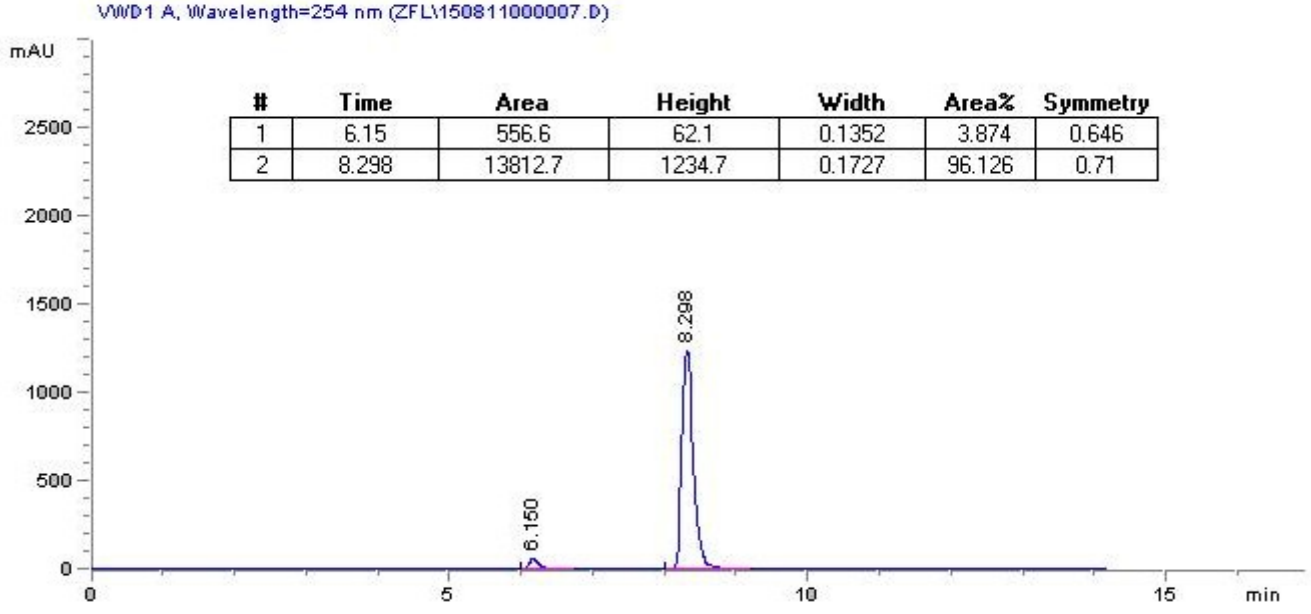
(*S*)-Methyl 5-(4-fluorophenyl)-5-methyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ca). Yellow oil was obtained in 92% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 92% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 8.3 min, t_R (minor) = 6.2 min. $[\alpha]_D^{27}$ = -52.2 (*c* = 1.07, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.72-7.70 (m, 2H), 7.54-7.47 (m, 5H), 7.25-7.20 m, 2H), 5.53 (s, 1H), 4.83 (s, 1H), 3.63 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 168.4, 164.4, 162.2 (d, *J* = 244.6 Hz), 152.5, 139.8 (d, *J* = 3.0 Hz), 131.5, 130.1, 129.4, 128.5, 127.5 (d, *J* = 8.4 Hz), 115.8 (d, *J* = 21.5 Hz), 105.6, 103.2, 90.9, 51.4, 27.7; HRMS (ESI): m/z calcd for $C_{20}H_{18}FO_3$ [M+H] 325.1240, found 325.1238.



3ca

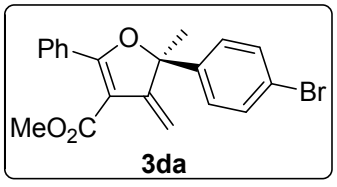


#	Time	Area	Height	Width	Area%	Symmetry
1	6.153	4228.9	473.3	0.1348	50.063	0.648
2	8.323	4218.2	366.1	0.1767	49.937	0.692

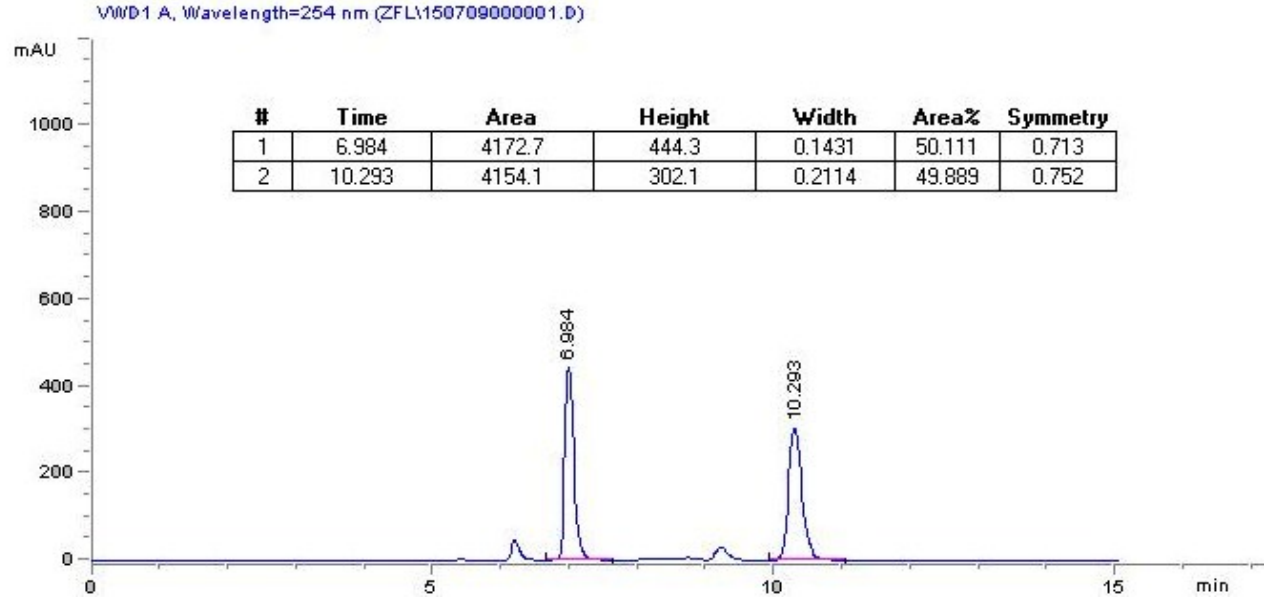


#	Time	Area	Height	Width	Area%	Symmetry
1	6.15	556.6	62.1	0.1352	3.874	0.646
2	8.298	13812.7	1234.7	0.1727	96.126	0.71

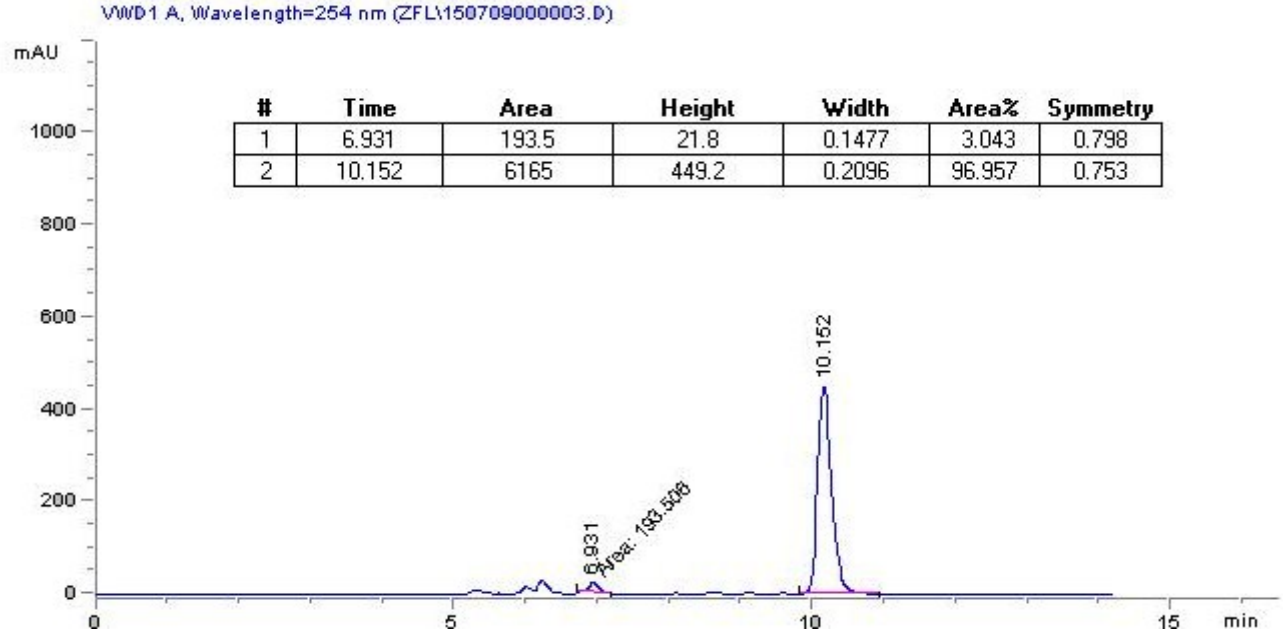
(*S*)-Methyl 5-(4-bromophenyl)-5-methyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (3da). Pale yellow solid was obtained in 76% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). M.p.: 100-101 °C. 94% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 10.3 min, t_R (minor) = 7.0 min. $[\alpha]_D^{23}$ = -32.9 (*c* = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72-7.70 (m, 2H), 7.61-7.43 (m, 7H), 5.52 (s, 1H), 4.85 (s, 1H), 3.62 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 164.4, 152.2, 142.9, 132.0, 131.5, 130.0, 129.4, 128.5, 127.5, 121.8, 105.6, 103.4, 90.8, 51.5, 27.5; HRMS (ESI): m/z calcd for $C_{20}H_{18}BrO_3$ [M+H] 385.0439, found 385.0436.



3da

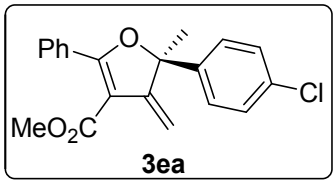


#	Time	Area	Height	Width	Area%	Symmetry
1	6.984	4172.7	444.3	0.1431	50.111	0.713
2	10.293	4154.1	302.1	0.2114	49.889	0.752

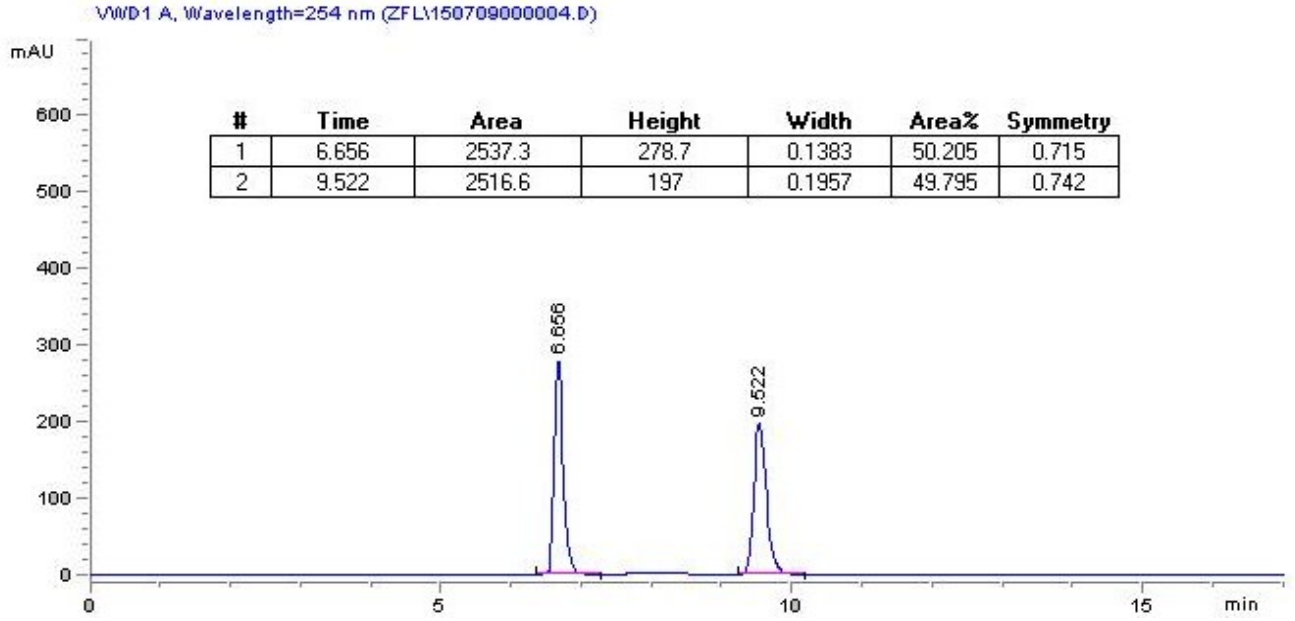


#	Time	Area	Height	Width	Area%	Symmetry
1	6.931	193.5	21.8	0.1477	3.043	0.798
2	10.152	6165	449.2	0.2096	96.957	0.753

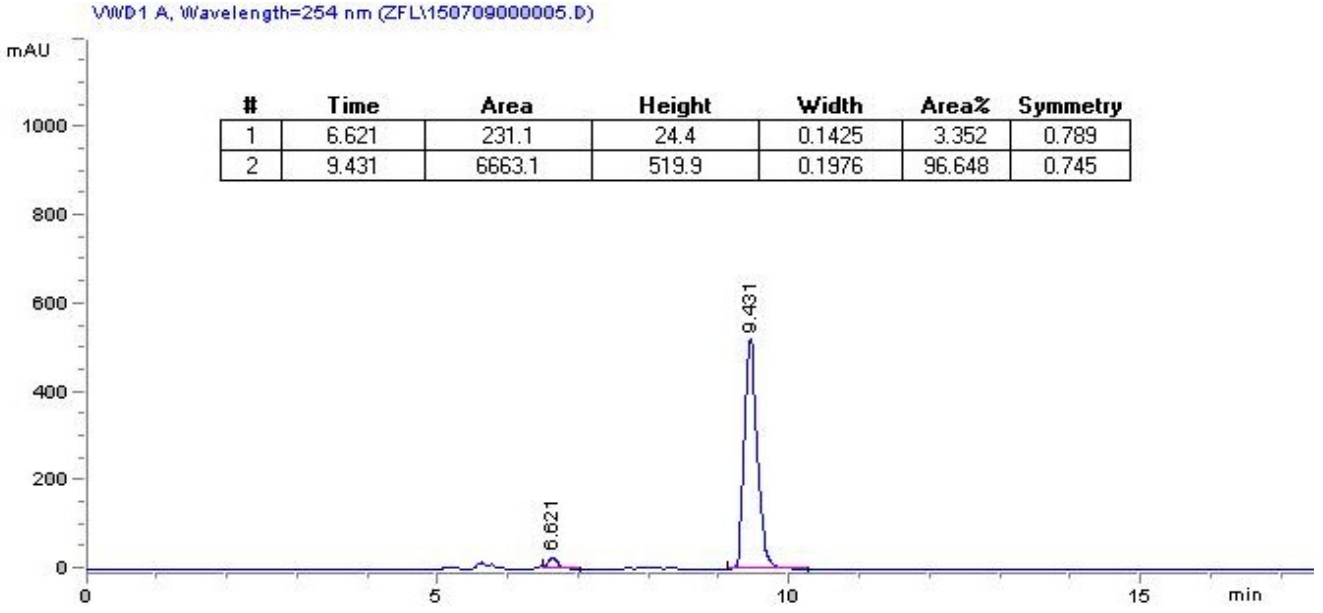
(*S*)-Methyl 5-(4-chlorophenyl)-5-methyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ea). Yellow oil was obtained in 86% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 93% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 9.5 min, t_R (minor) = 6.7 min. $[\alpha]_D^{27}$ = -56.9 (*c* = 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73-7.71 (m, 2H), 7.53-7.45 (m, 7H), 5.53 (s, 1H), 4.86 (s, 1H), 3.63 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 164.4, 152.3, 142.5, 133.2, 131.5, 130.0, 129.4, 129.0, 128.5, 127.2, 105.6, 103.3, 90.8, 51.5, 27.6; HRMS (ESI): m/z calcd for $C_{20}H_{18}ClO_3$ [M+H] 341.0944, found: 341.0944.



3ea

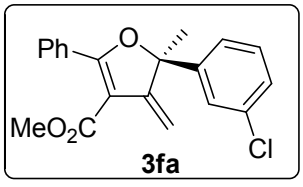


#	Time	Area	Height	Width	Area%	Symmetry
1	6.656	2537.3	278.7	0.1383	50.205	0.715
2	9.522	2516.6	197	0.1957	49.795	0.742

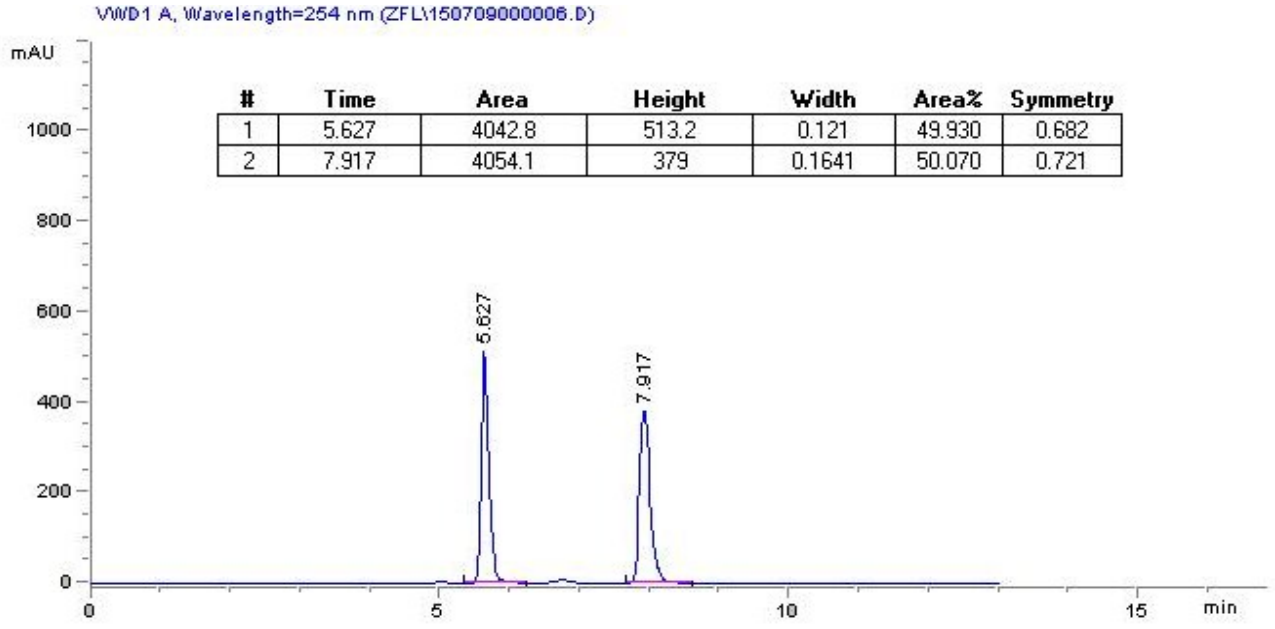


#	Time	Area	Height	Width	Area%	Symmetry
1	6.621	231.1	24.4	0.1425	3.352	0.789
2	9.431	6663.1	519.9	0.1976	96.648	0.745

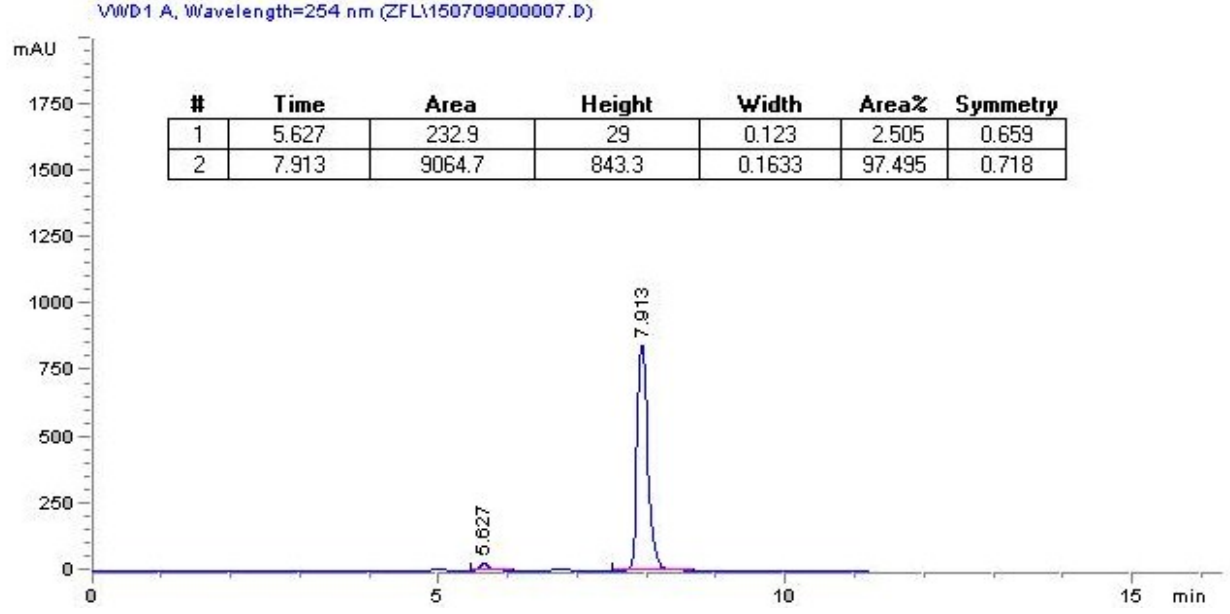
(*S*)-Methyl 5-(3-chlorophenyl)-5-methyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (3fa). Yellow oil was obtained in 85% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 95% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 7.9 min, t_R (minor) = 5.6 min. $[\alpha]_D^{27}$ = -39.1 (*c* = 0.88, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.73-7.71 (m, 2H), 7.55-7.39 (m, 7H), 5.54 (s, 1H), 4.92 (s, 1H), 3.63 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ 168.3, 164.3, 152.1, 145.9, 133.8, 131.6, 131.1, 129.9, 129.4, 128.5, 128.4, 125.0, 123.9, 105.7, 103.6, 90.7, 51.5, 27.5; HRMS (ESI): m/z calcd for $C_{20}H_{18}ClO_3$ [M+H] 341.0944, found 341.0944.



3fa

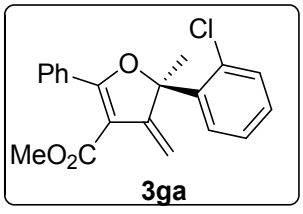


#	Time	Area	Height	Width	Area%	Symmetry
1	5.627	4042.8	513.2	0.121	49.930	0.682
2	7.917	4054.1	379	0.1641	50.070	0.721

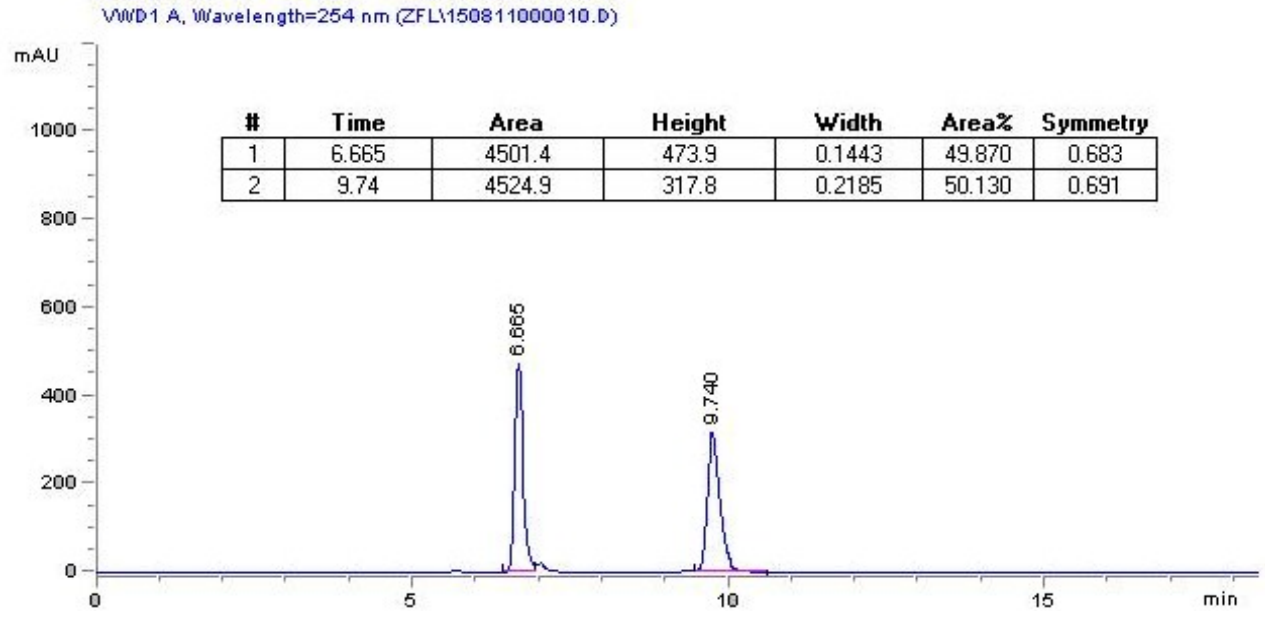


#	Time	Area	Height	Width	Area%	Symmetry
1	5.627	232.9	29	0.123	2.505	0.659
2	7.913	9064.7	843.3	0.1633	97.495	0.718

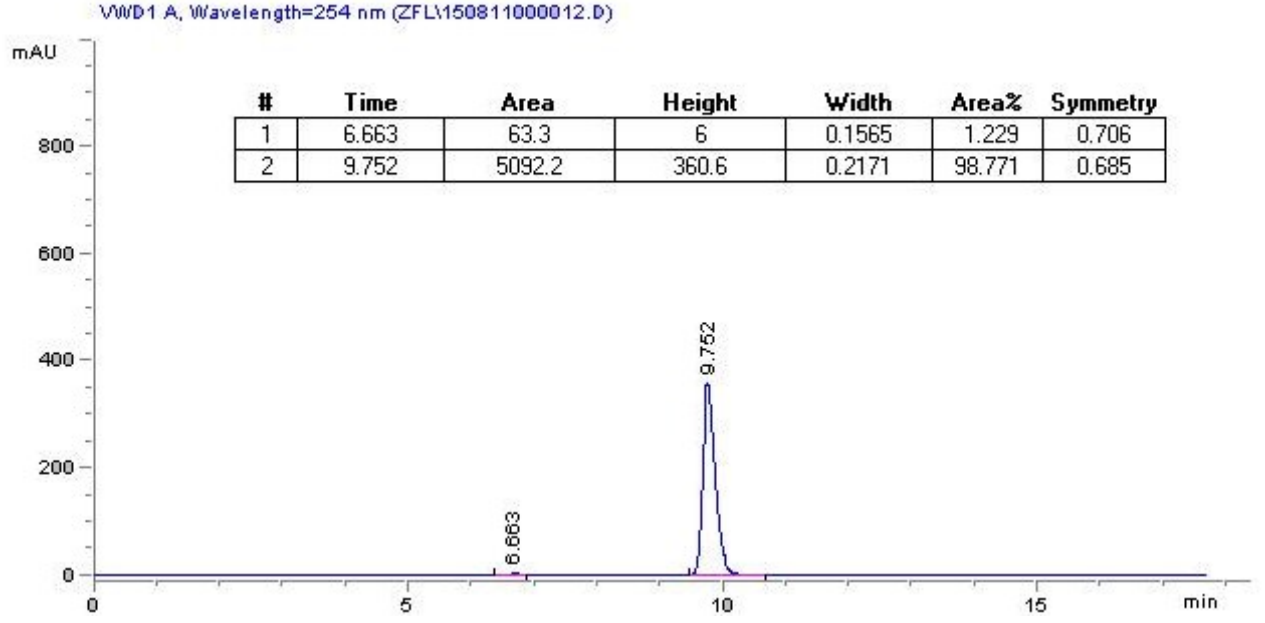
(*S*)-Methyl 5-(2-chlorophenyl)-5-methyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ga). Pale yellow solid was obtained in 62% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). M.p.: 96-97 °C. 98% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 9.7 min, t_R (minor) = 6.7 min. $[\alpha]_D^{29}$ = -28.8 (*c* = 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79-7.67 (m, 3H), 7.53-7.41 (m, 6H), 5.44 (s, 1H), 4.41 (s, 1H), 3.65 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 164.6, 152.4, 138.1, 134.2, 131.8, 131.3, 131.0, 130.6, 129.7, 129.3, 128.4, 127.4, 106.7, 102.0, 90.8, 51.4, 28.6; HRMS (ESI): m/z calcd for $C_{20}H_{18}ClO_3$ [M+H] 341.0944, found 341.0939.



3ga

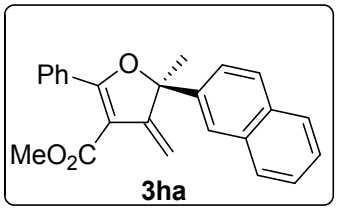


#	Time	Area	Height	Width	Area%	Symmetry
1	6.665	4501.4	473.9	0.1443	49.870	0.683
2	9.74	4524.9	317.8	0.2185	50.130	0.691

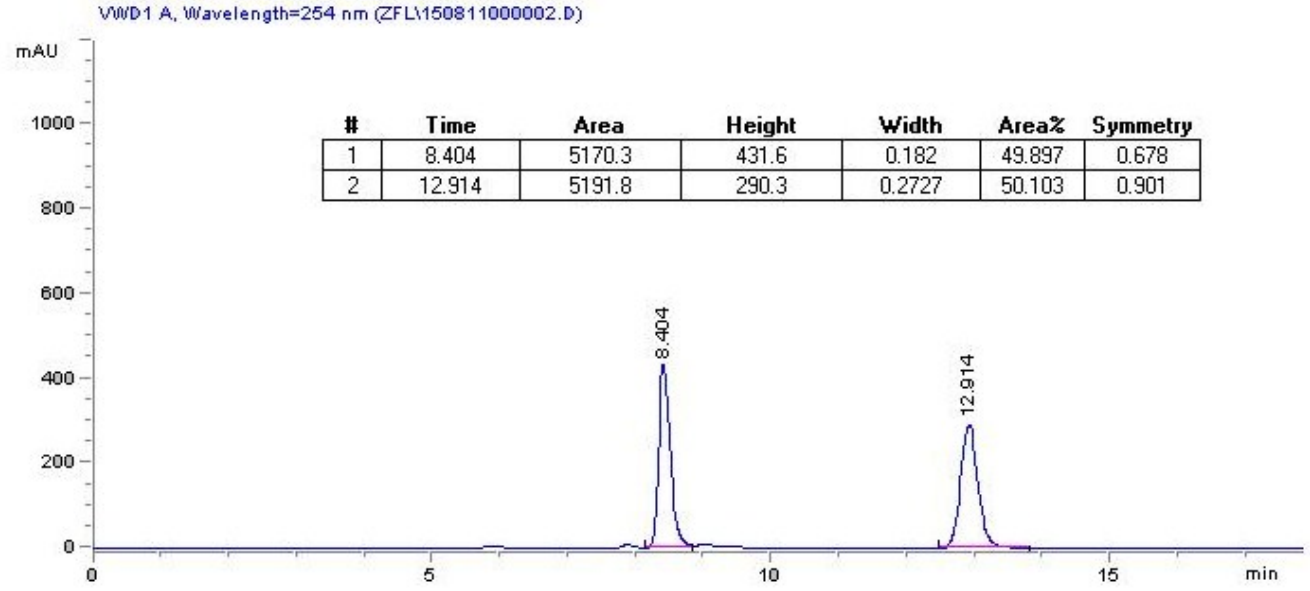


#	Time	Area	Height	Width	Area%	Symmetry
1	6.663	63.3	6	0.1565	1.229	0.706
2	9.752	5092.2	360.6	0.2171	98.771	0.685

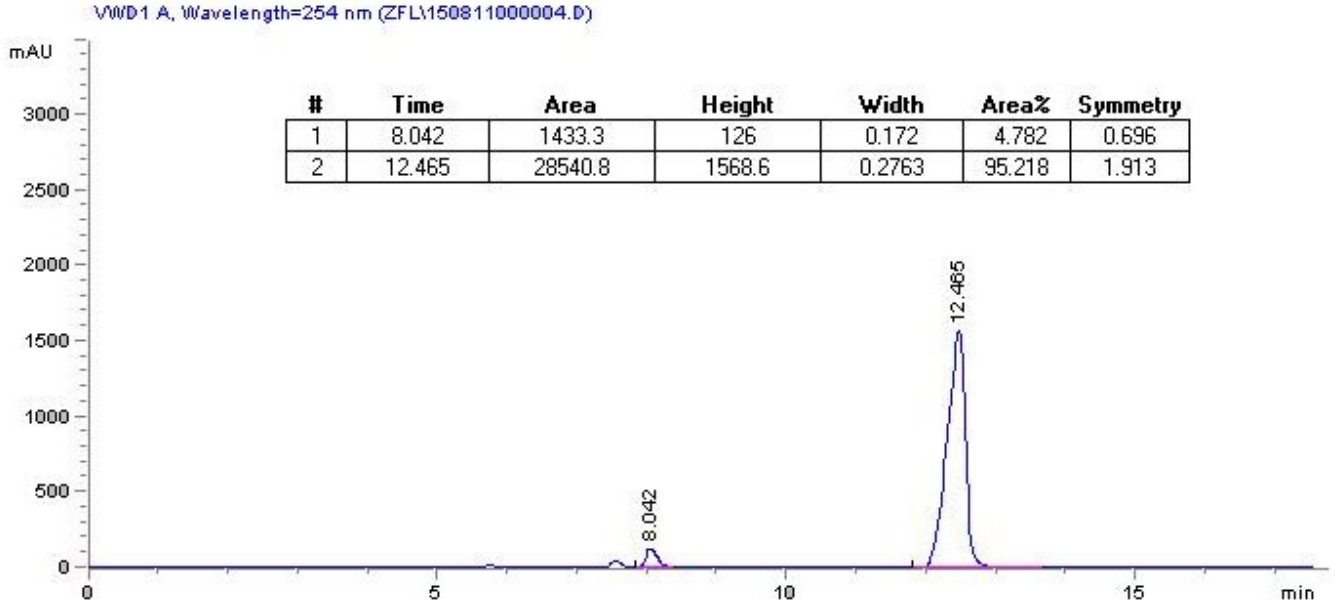
(*S*)-Methyl 5-methyl4-methylene-5-(naphthalen-2-yl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3ha). Yellow oil was obtained in 90% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 50/1). 90% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 12.9 min, t_R (minor) = 8.4 min. $[\alpha]_D^{28}$ = -37.3 (*c* = 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07-7.75 (m, 6H), 7.59-7.46 (m, 6H), 5.58 (s, 1H), 4.86 (s, 1H), 3.65 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 164.5, 152.6, 140.7, 133.0, 132.9, 131.5, 130.2, 129.5, 128.9, 128.8, 128.5, 127.9, 127.0, 126.9, 123.9, 123.7, 105.8, 103.3, 91.6, 51.5, 27.6; HRMS (ESI): m/z calcd for $C_{24}H_{21}O_3$ [M+H] 357.1491, found 357.1489.



3ha

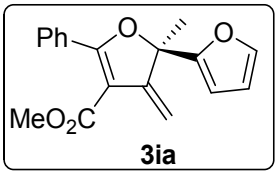


#	Time	Area	Height	Width	Area%	Symmetry
1	8.404	5170.3	431.6	0.182	49.897	0.678
2	12.914	5191.8	290.3	0.2727	50.103	0.901



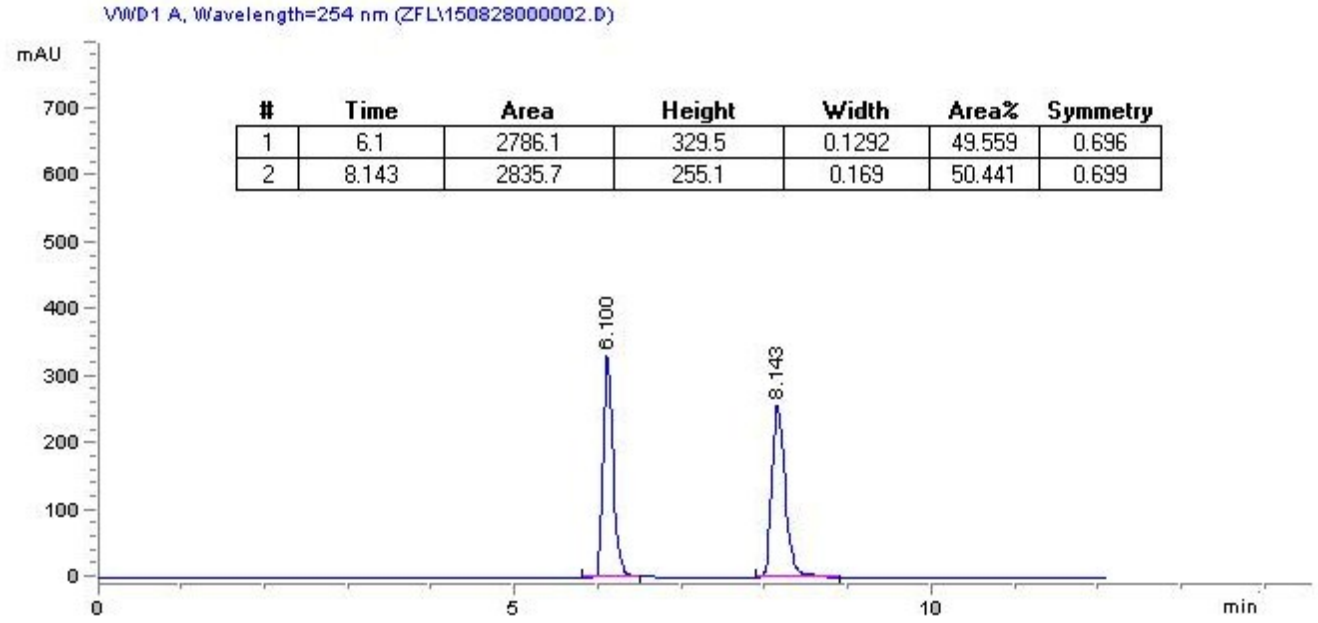
#	Time	Area	Height	Width	Area%	Symmetry
1	8.042	1433.3	126	0.172	4.782	0.696
2	12.465	28540.8	1568.6	0.2763	95.218	1.913

(*S*)-Methyl 2-methyl-3-methylene-5-phenyl-2,3-dihydro-[2,2'-bifuran]-4-carboxylate (6ia).

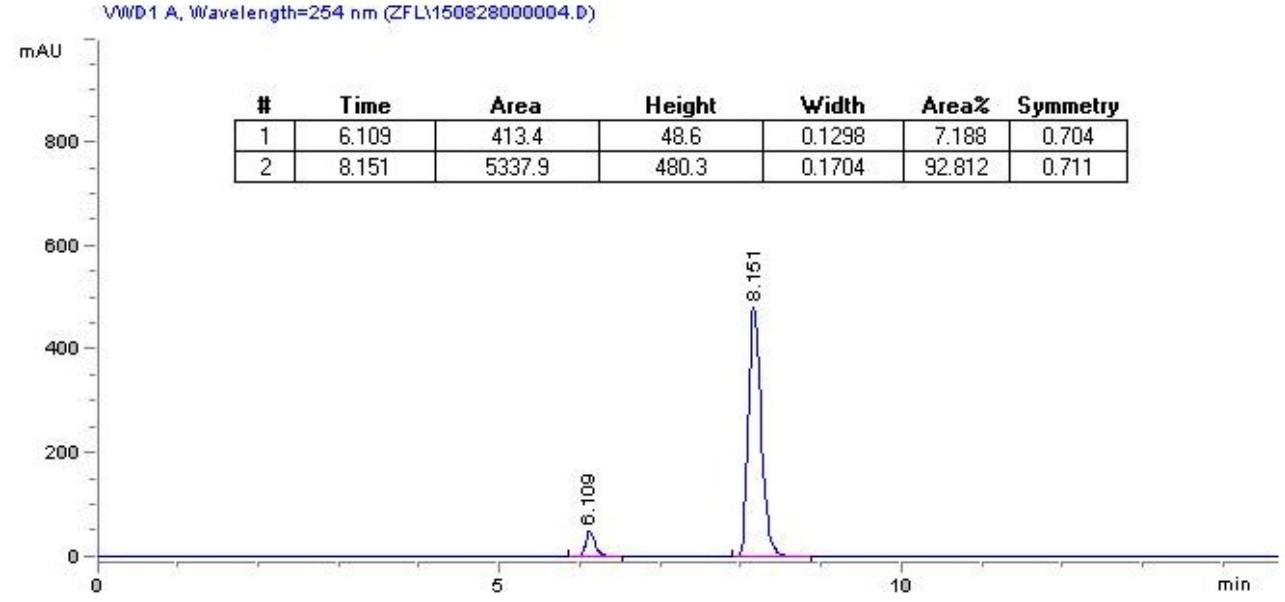


3ia

Yellow oil was obtained in 85% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 70/1). 86% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 8.1 min, t_R (minor) = 6.1 min. $[\alpha]_D^{22}$ = -59.1 (*c* = 1.13, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (d, J = 0.7 Hz, 1H), 7.64-7.62 (m, 3H), 7.53-7.43 (m, 3H), 6.56 (d, *J* = 3.3 Hz, 1H), 6.47 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.57 (s, 1H), 4.73 (s, 1H), 3.65 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.4, 164.4, 154.3, 149.9, 144.4, 131.5, 130.1, 129.4, 128.4, 110.9, 108.7, 105.5, 103.3, 86.8, 51.5, 26.0; HRMS (ESI): m/z calcd for $C_{18}H_{17}O_4$ [M+H] 297.1127, found 297.1124.

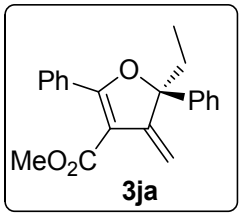


#	Time	Area	Height	Width	Area%	Symmetry
1	6.1	2786.1	329.5	0.1292	49.559	0.696
2	8.143	2835.7	255.1	0.169	50.441	0.699



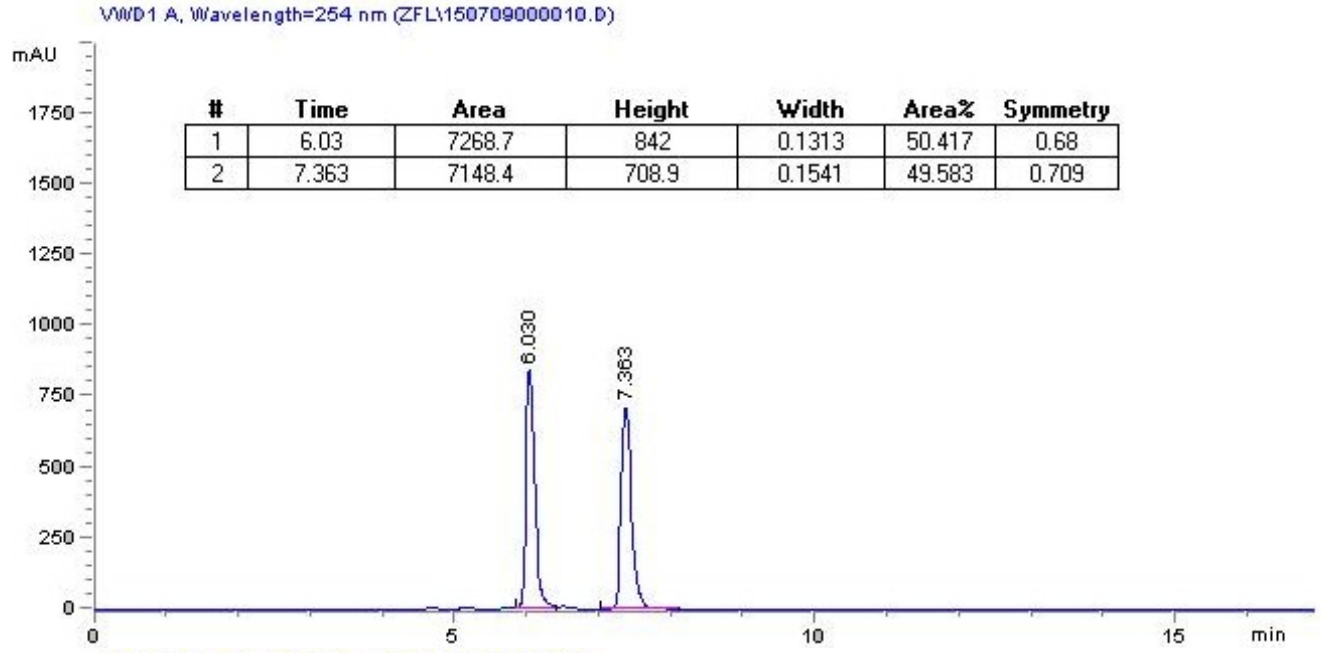
#	Time	Area	Height	Width	Area%	Symmetry
1	6.109	413.4	48.6	0.1298	7.188	0.704
2	8.151	5337.9	480.3	0.1704	92.812	0.711

(*S*)-Methyl 5-ethyl-4-methylene-2,5-diphenyl-4,5-dihydrofuran-3-carboxylate (3ja). Yellow oil

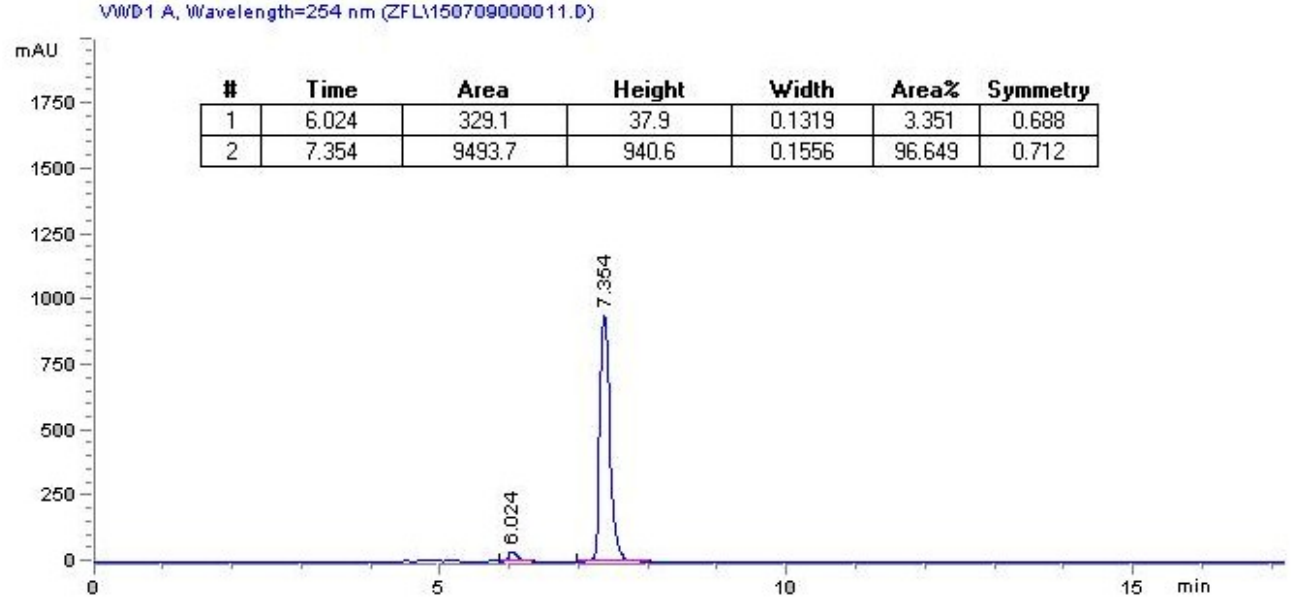


3ja

was obtained in 81% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 93% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 ^oC): t_R (major) = 7.4 min, t_R (minor) = 6.0 min. $[\alpha]_D^{18}$ = +55.3 (*c* = 0.93, CH_2Cl_2). ^1H NMR (400 MHz, DMSO-d_6) δ 7.77-7.75 (m, 2H), 7.56-7.29 (m, 8H), 5.57 (s, 1H), 4.93 (s, 1H), 3.61 (s, 3H), 2.31-2.13 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 164.4, 150.7, 143.2, 131.5, 130.1, 129.3, 129.0, 128.5, 128.1, 124.8, 106.5, 102.9, 94.0, 51.4, 33.4, 8.3; HRMS (ESI): m/z calcd for $C_{21}H_{21}O_3$ [M+H] 321.1491, found 321.1492.

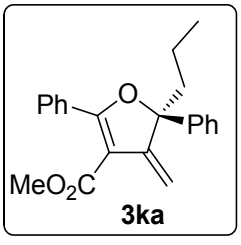


#	Time	Area	Height	Width	Area%	Symmetry
1	6.03	7268.7	842	0.1313	50.417	0.68
2	7.363	7148.4	708.9	0.1541	49.583	0.709

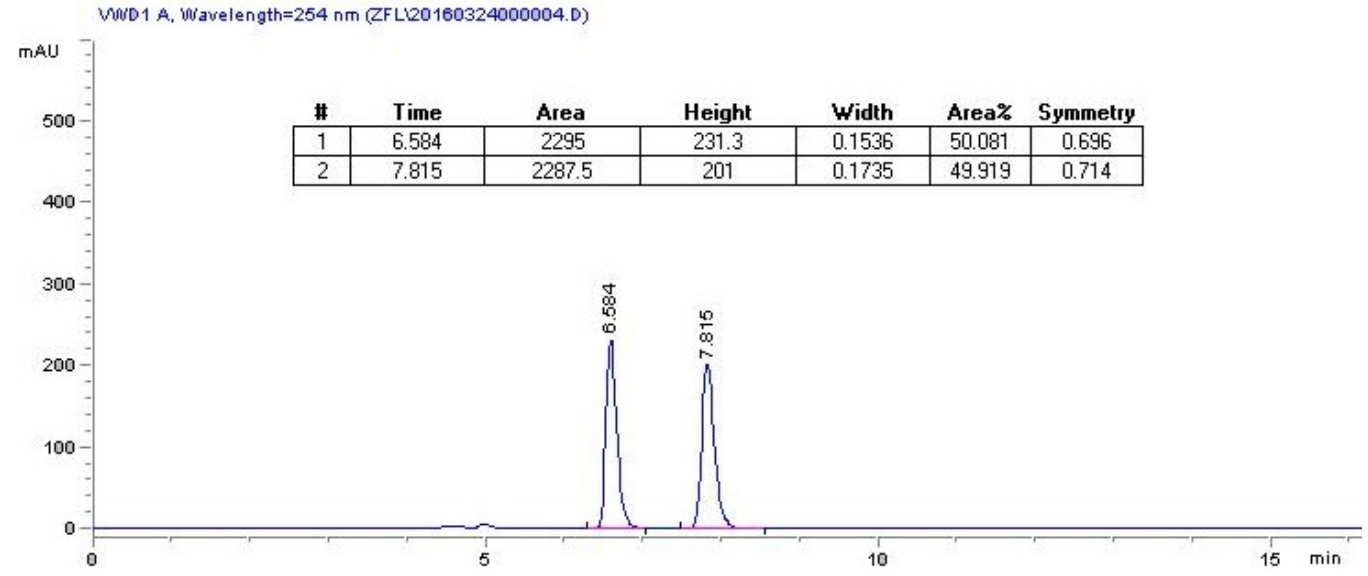


#	Time	Area	Height	Width	Area%	Symmetry
1	6.024	329.1	37.9	0.1319	3.351	0.688
2	7.354	9493.7	940.6	0.1556	96.649	0.712

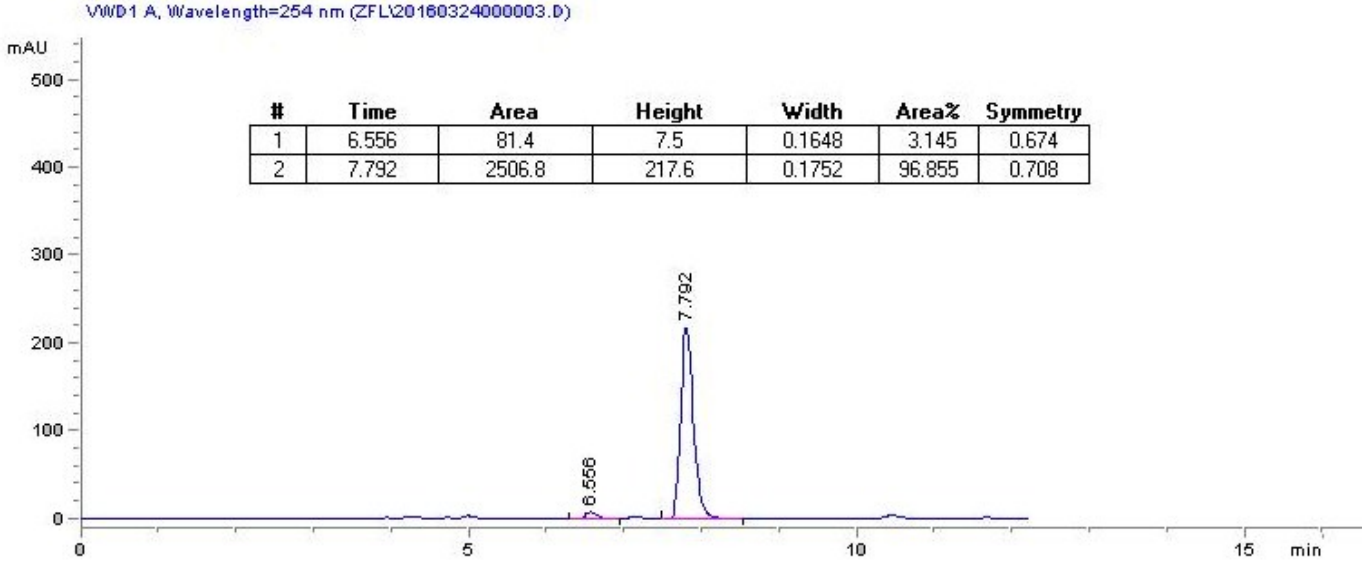
(*S*)-Methyl 4-methylene-2,5-diphenyl-5-propyl-4,5-dihydrofuran-3-carboxylate (3ka).



Yellow oil was obtained in 61% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 94% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 7.8 min, t_R (minor) = 6.6 min. $[\alpha]_D^{22}$ = +99.1 (*c* = 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75-7.73 (m, 2H), 7.57-7.30 (m, 8H), 5.51 (s, 1H), 4.94 (s, 1H), 3.61 (s, 3H), 2.26-2.08 (m, 2H), 1.43-1.21 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 164.4, 151.1, 143.3, 131.5, 130.1, 129.3, 129.0, 128.6, 128.1, 124.8, 106.3, 102.8, 93.7, 51.5, 42.7, 17.1, 14.4; HRMS (ESI): m/z calcd for $C_{22}H_{23}O_3$ [M+H] 335.1647, found 335.1648.

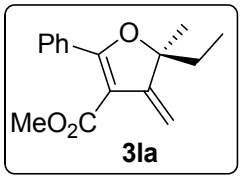


#	Time	Area	Height	Width	Area%	Symmetry
1	6.584	2295	231.3	0.1536	50.081	0.696
2	7.815	2287.5	201	0.1735	49.919	0.714



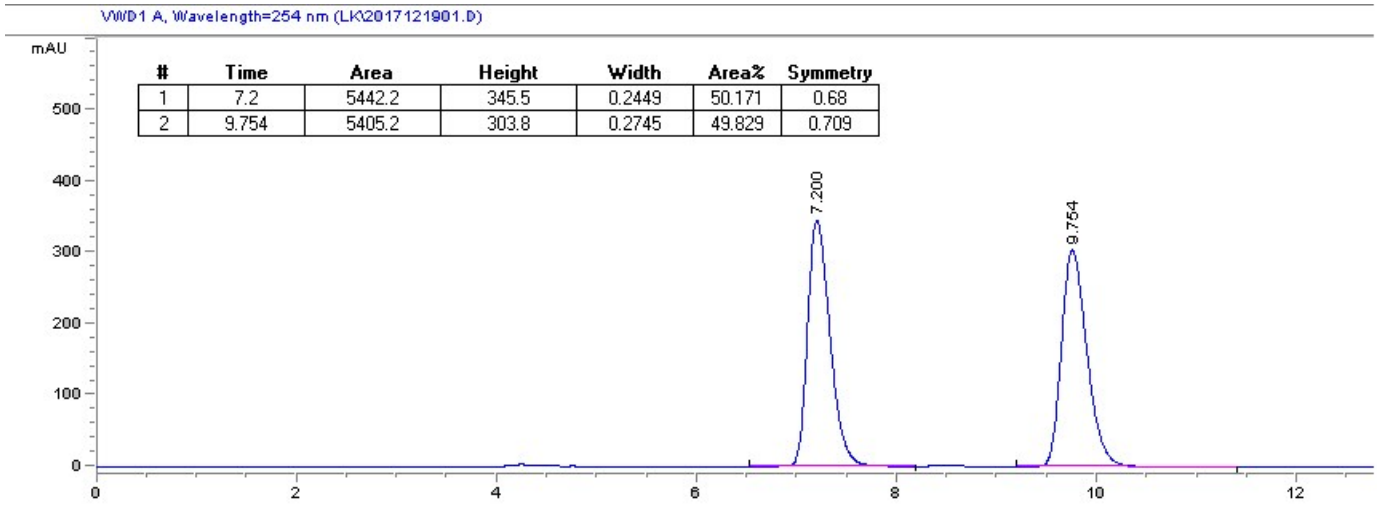
#	Time	Area	Height	Width	Area%	Symmetry
1	6.556	81.4	7.5	0.1648	3.145	0.674
2	7.792	2506.8	217.6	0.1752	96.855	0.708

(*S*)-Methyl 5-ethyl-5-methyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (3la).

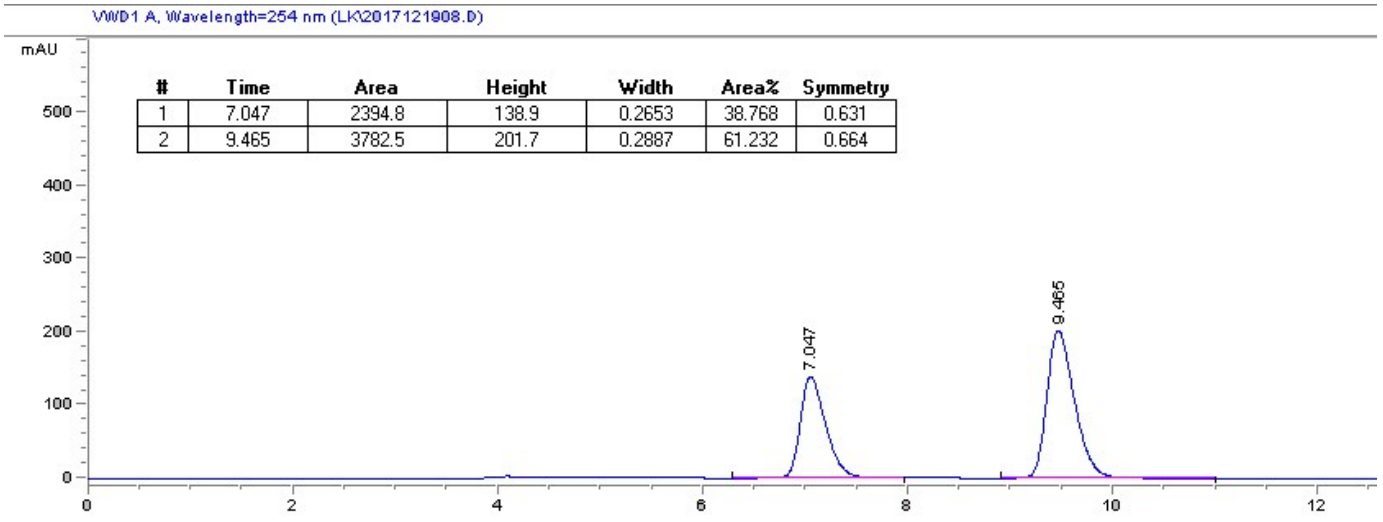


3la

Yellow oil was obtained in 75% yield after purification with column chromatography on silica gel (hexanes/ethyl acetate, 100/1). 22% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH=98/2, 0.8 mL min^{-1}, 254 nm, 40 ^{o}C): t_R (major) = 9.5 min, t_R (minor) = 7.0 min. $[\alpha]_D^{19}$ = -16.7 (*c* = 1.10, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64-7.62 (m, 2H), 7.52-7.43 (m, 3H), 5.45 (s, 1H), 4.72 (s, 1H), 3.61 (s, 3H), 1.83 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.69 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.42 (s, 3H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 164.6, 151.5, 131.2, 130.6, 129.2, 128.3, 106.3, 100.2, 92.0, 51.2, 34.2, 27.4, 7.9; HRMS (ESI): m/z calcd for $C_{16}H_{18}O_3$ [M + H] 259.1334, found 259.1326.

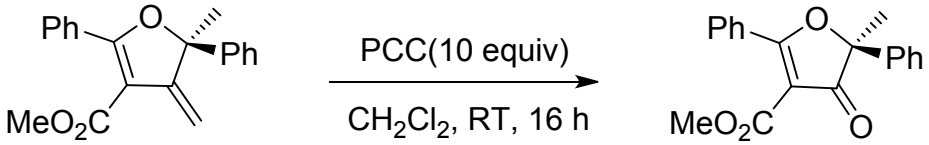


#	Time	Area	Height	Width	Area%	Symmetry
1	7.2	5442.2	345.5	0.2449	50.171	0.68
2	9.754	5405.2	303.8	0.2745	49.829	0.709



#	Time	Area	Height	Width	Area%	Symmetry
1	7.047	2394.8	138.9	0.2653	38.768	0.631
2	9.465	3782.5	201.7	0.2887	61.232	0.664

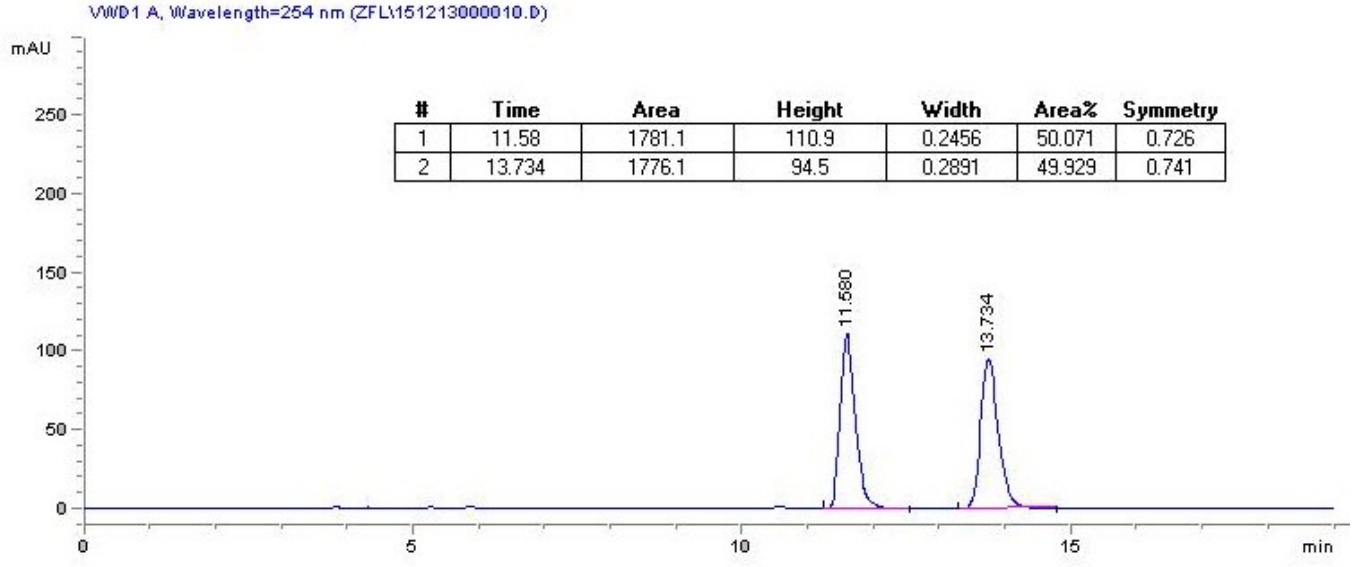
Synthetic Application of Cycloadduct 3aa



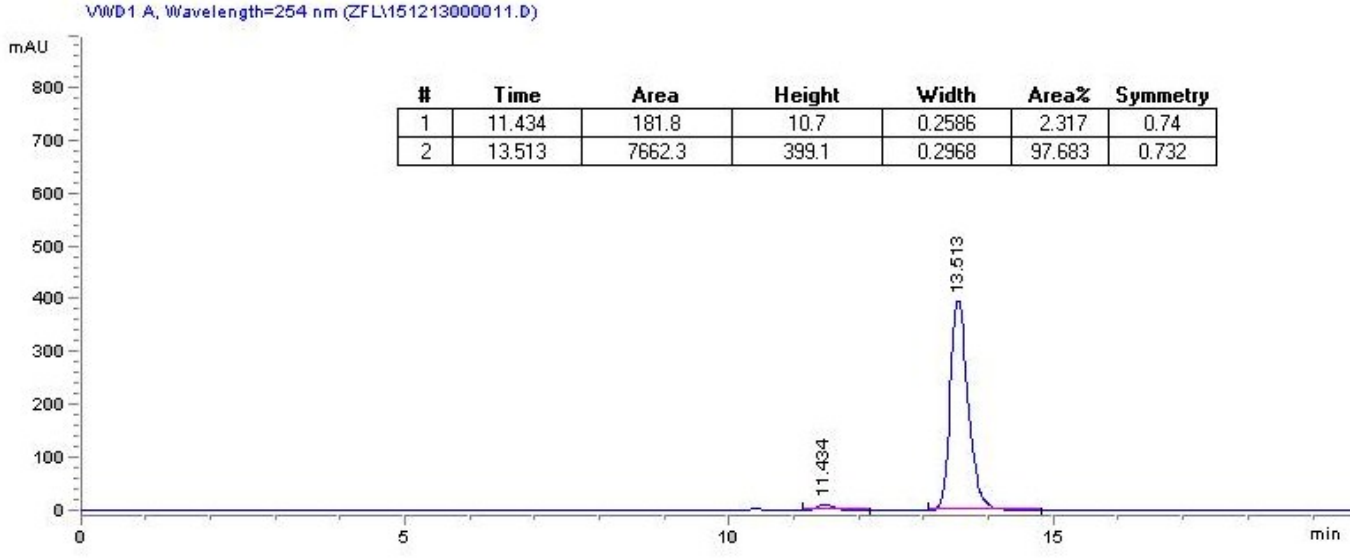
3aa **4**

A solution of **3aa** (61.3 mg, 0.20 mmol) in 4 mL of anhydrous dichloromethane was added PCC (pyridinium chlorochromate 431.1mg, 2.0 mmol), and the resulting solution was stirred at room temperature for 16 h. After the filtration of undissolved solids, the filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (hexanes/ ethyl acetate, 20/1) to afford **4** (40.1 mg, 65% yield) as a colorless oil. 95% ee was determined by chiral HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL min^{-1}, 254 nm, 40 °C): t_R (major) = 13.7 min, t_R (minor) = 11.6 min. $[\alpha]_D^{22}$ = 16.9 (*c* = 1.00, CH_2Cl_2). ^1H NMR (400 MHz,

$CDCl_3$) δ 8.03 (d, J = 7.5 Hz, 2H), 7.64-7.33 (m, 8H), 3.82 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 187.6, 163.3, 137.4, 133.5, 129.5, 128.8, 128.7, 128.5, 128.4, 124.6, 106.4, 90.7, 52.0, 24.8; HRMS (ESI): m/z calcd for $C_{19}H_{17}O_4$ [M+H] 309.1127, found 309.1127.



#	Time	Area	Height	Width	Area%	Symmetry
1	11.58	1781.1	110.9	0.2456	50.071	0.726
2	13.734	1776.1	94.5	0.2891	49.929	0.741



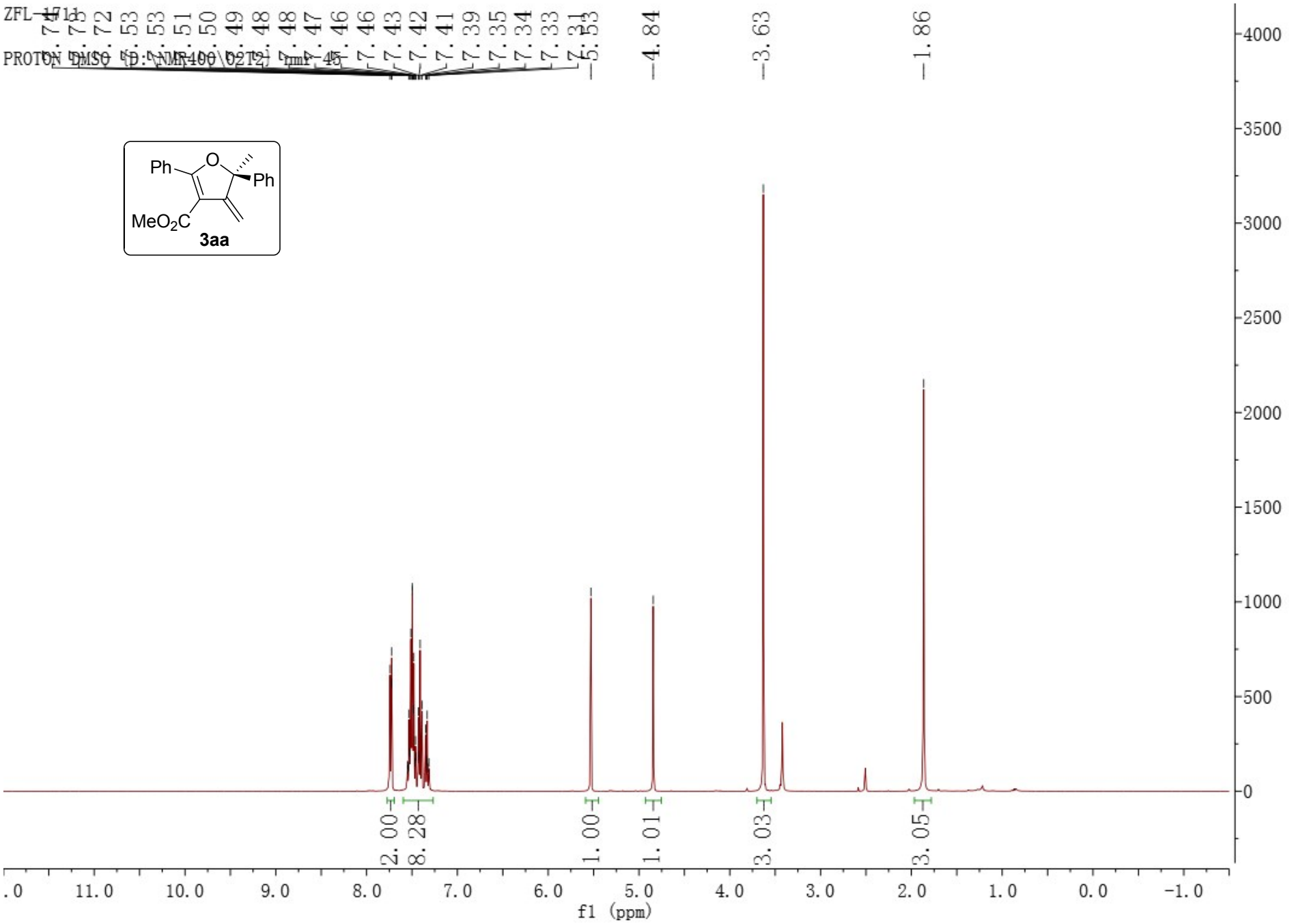
#	Time	Area	Height	Width	Area%	Symmetry
1	11.434	181.8	10.7	0.2586	2.317	0.74
2	13.513	7662.3	399.1	0.2968	97.683	0.732

References

1. J.-B. Zhao, D. A. Clark, *Org. Lett.* **2012**, *14*, 1668-1671.

2. C. N. EidJr, J. P. Konopelski, *Tetrahedron* **1991**, *47*, 975-992.

3. Y. Zhou, F.-L. Zhu, Z.-T. Liu, X.-M. Zhou, X.-P. Hu, Org. Lett. 2016, 18, 2734-2737.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7.42
7.41
7.39
7.35
7.34
7.33
7.31
5.53
4.84
3.63
1.86
Ph
O
Ph
MeO2C
3aa
2.00
8.28
1.00
1.01
3.03
3.05
4000
3500
3000
2500
2000
1500
1000
500
0
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11.0
10.0
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4.0
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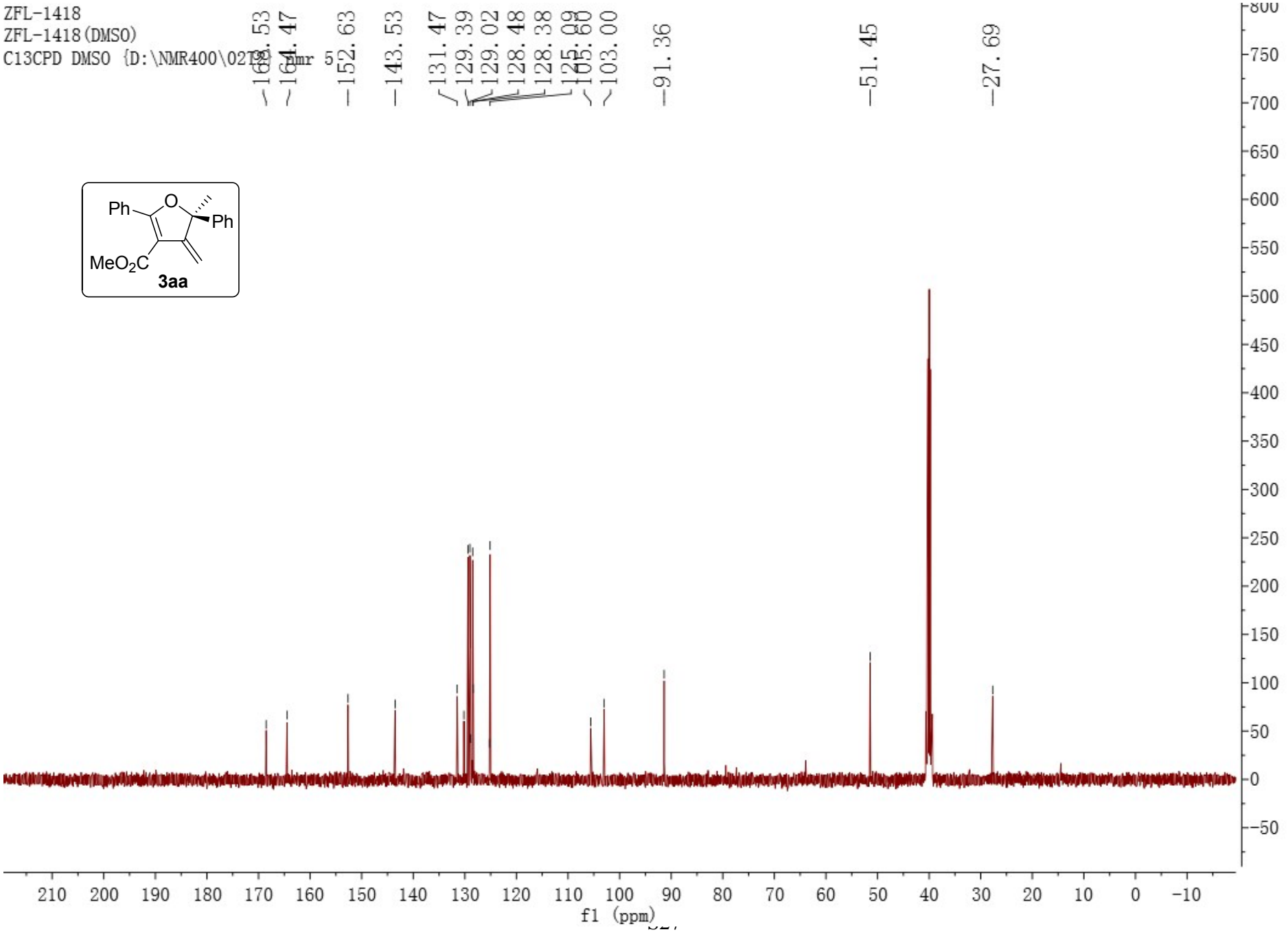
f1 (ppm)


ZFL-1418
ZFL-1418(DMSO)
C13CPD DMSO {D:\NMR400\02T8} pmr 5
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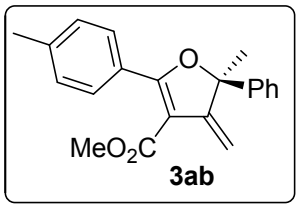
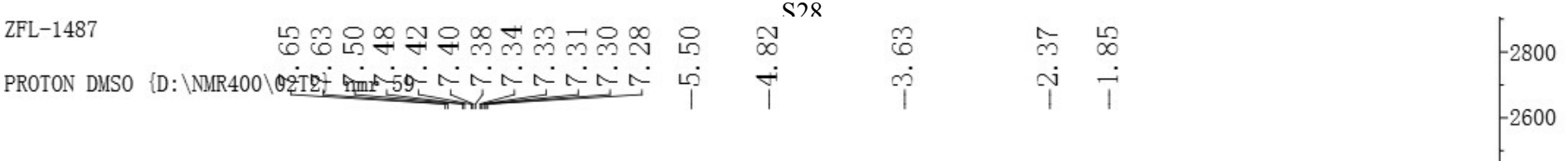
Ph
O
Ph
MeO2C
3aa
f1 (ppm)


O
Ph
MeO2C

3ab


ZFL-1487
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7.33
7.31
7.30
7.28
5.50
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2.37
1.85
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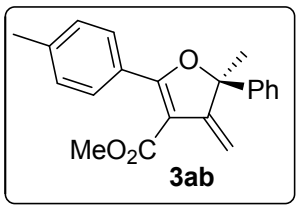
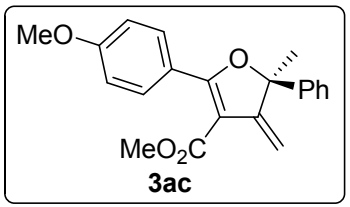
ZFL-1487

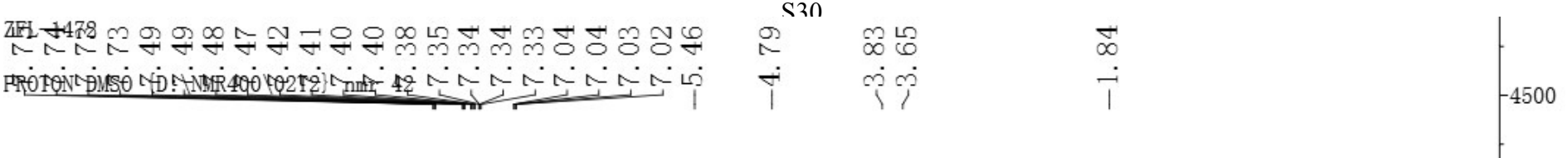
C13CPD DMSO {D:\NMR400\02\fid} pmr 59



3ab


MeO
O
Ph
MeO2C

3ac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7.33
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7.03
7.02
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3.83
3.65
1.84
4500

ZFL-1472

C13CPD DMSO {D:\NMR400\02T2...

168.42
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164.90
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143.72
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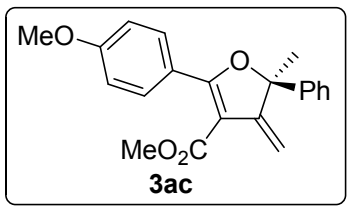
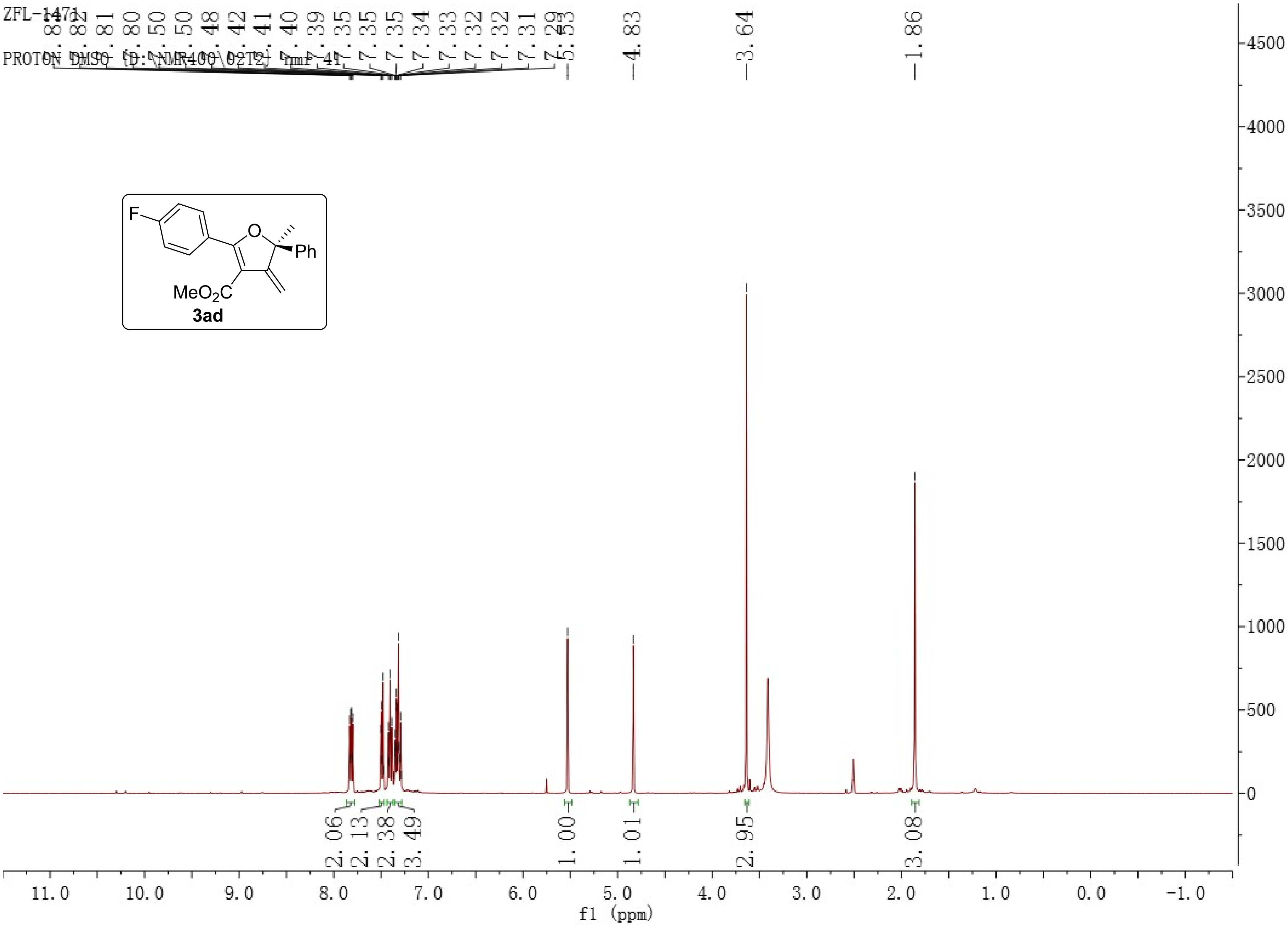
55.83
51.36
27.68

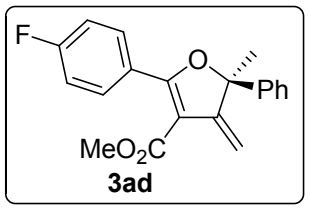


3ac

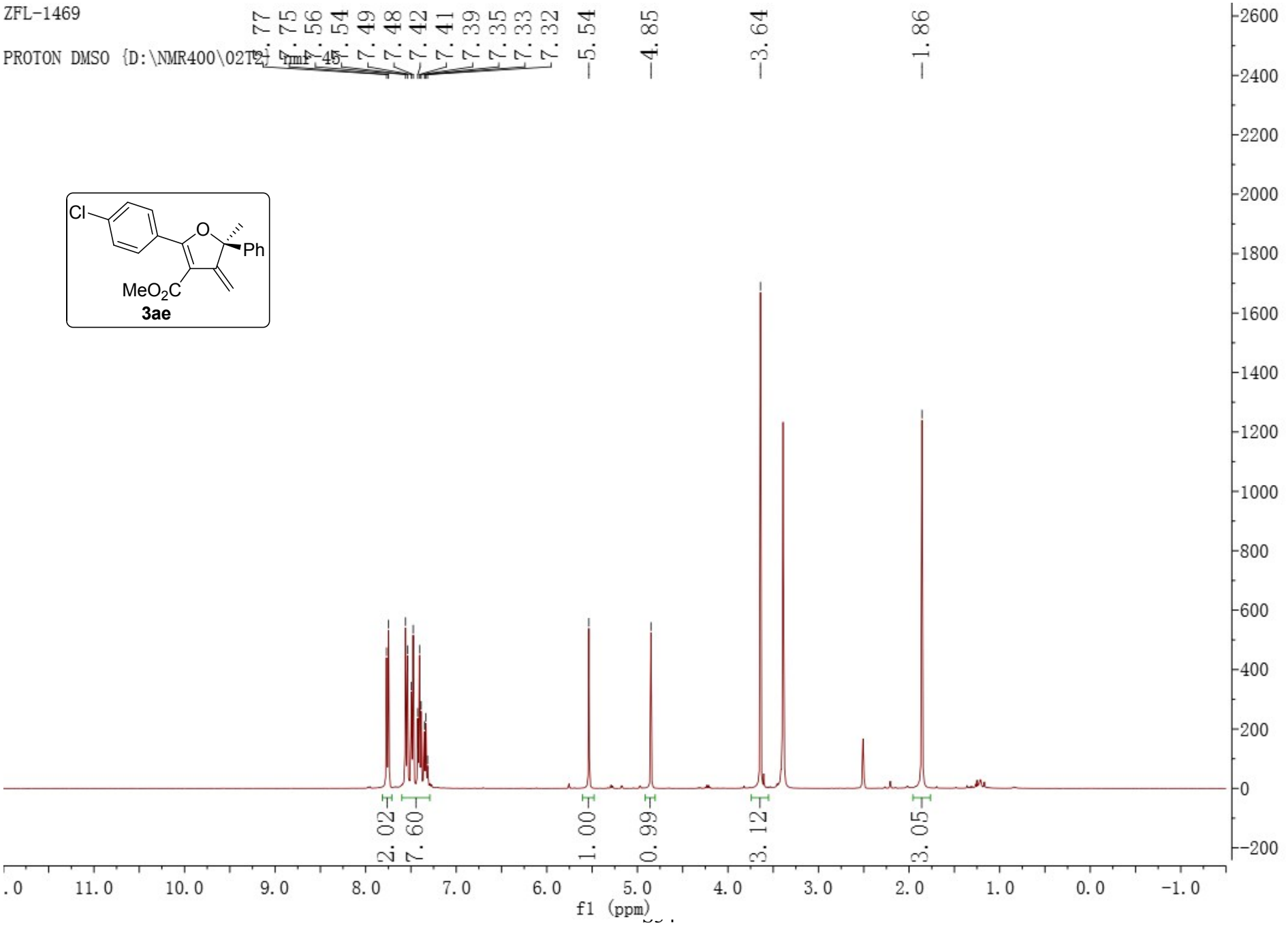

ZFL-1471
PROTON DMSO {D:\NMR400\02T2} nmr 41
7.82 7.82 7.81 7.80 7.50 7.50 7.48 7.42 7.41 7.40 7.39 7.35 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.29
5.53
4.83
3.64
1.86
F
O
Ph
MeO2C
3ad
2.06 2.13 2.38 3.49
1.00
1.01
2.95
3.08
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)
4500 4000 3500 3000 2500 2000 1500 1000 500 0

ZFL-1471

C13CPD DMSO {D:\NMR400\02T2 nmr 41

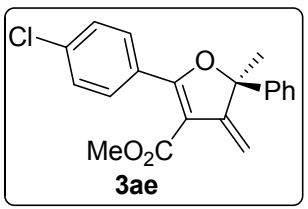


3ad

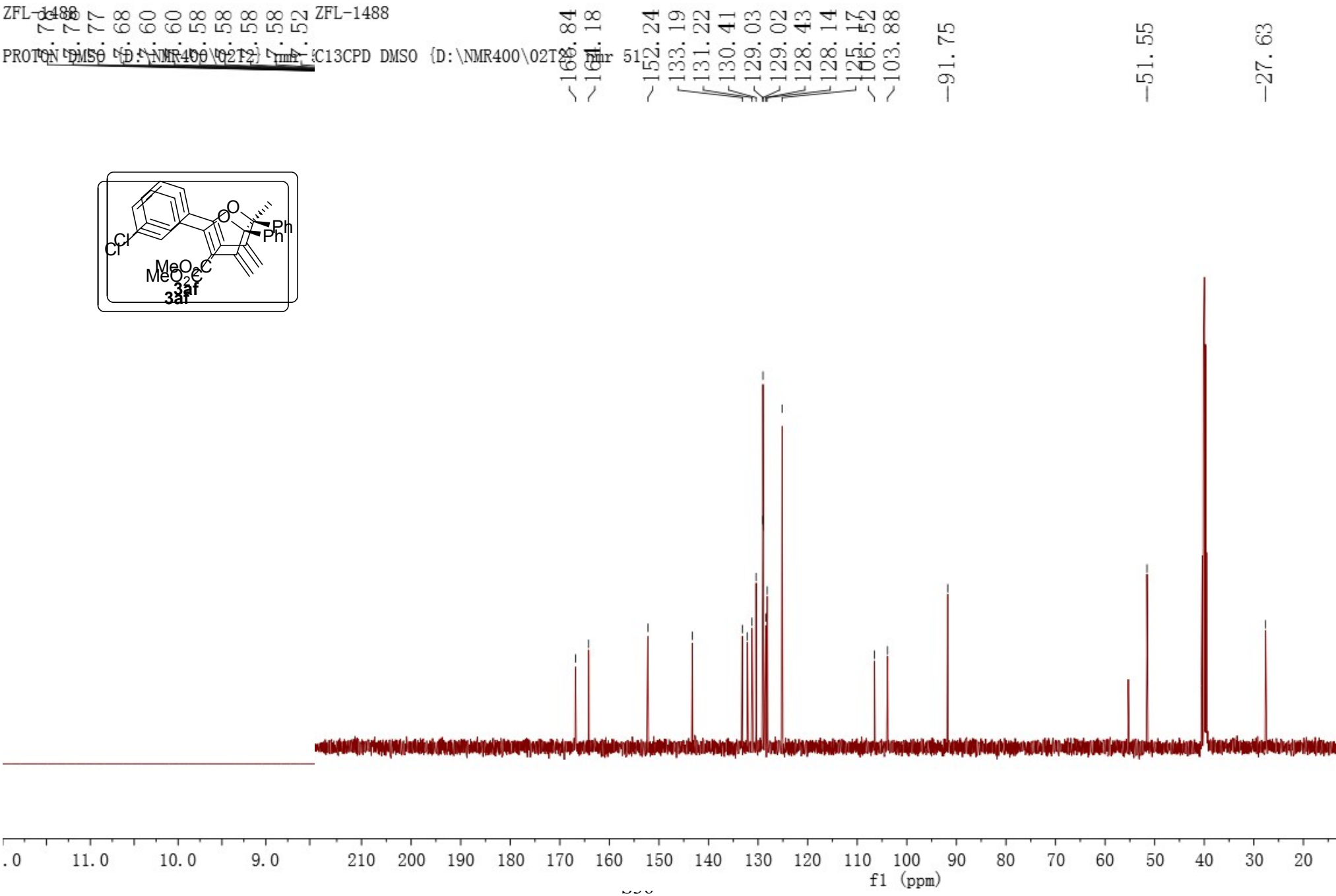

ZFL-1469
PROTON DMSO {D:\NMR400\02T2} nmr 45
7.77
7.75
7.56
7.54
7.49
7.48
7.42
7.41
7.39
7.35
7.33
7.32
5.54
4.85
3.64
1.86
Cl
O
Ph
MeO2C
3ae
2.02
7.60
1.00
0.99
3.12
3.05
f1 (ppm)

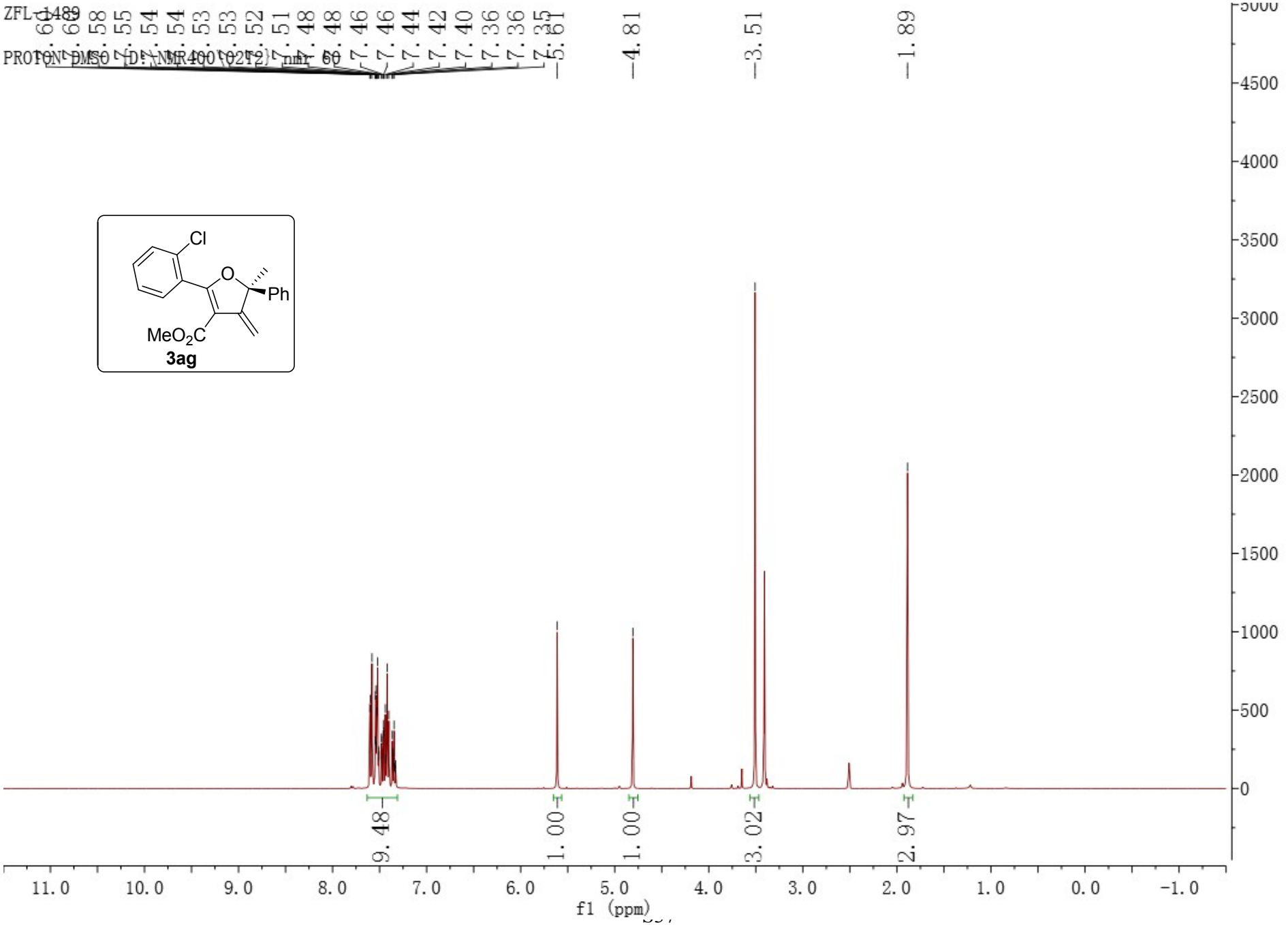
ZFL-1469

C13CPD DMSO {D:\NMR400\02T2.jnm} 45



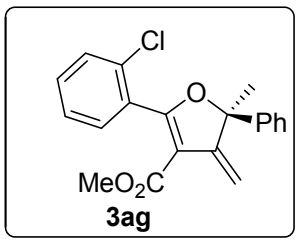
3ae


ZFL-1488
ZFL-1488
PROTON DMSO {D:\NMR400\02T2} nmr
C13CPD DMSO {D:\NMR400\02T2} nmr 51
168.84
164.18
152.24
133.19
131.22
130.41
129.03
129.02
128.43
128.14
125.17
106.52
103.88
91.75
51.55
27.63
Cl
O
Ph
Ph
MeO2C
MeO2C
3af
3af
f1 (ppm)

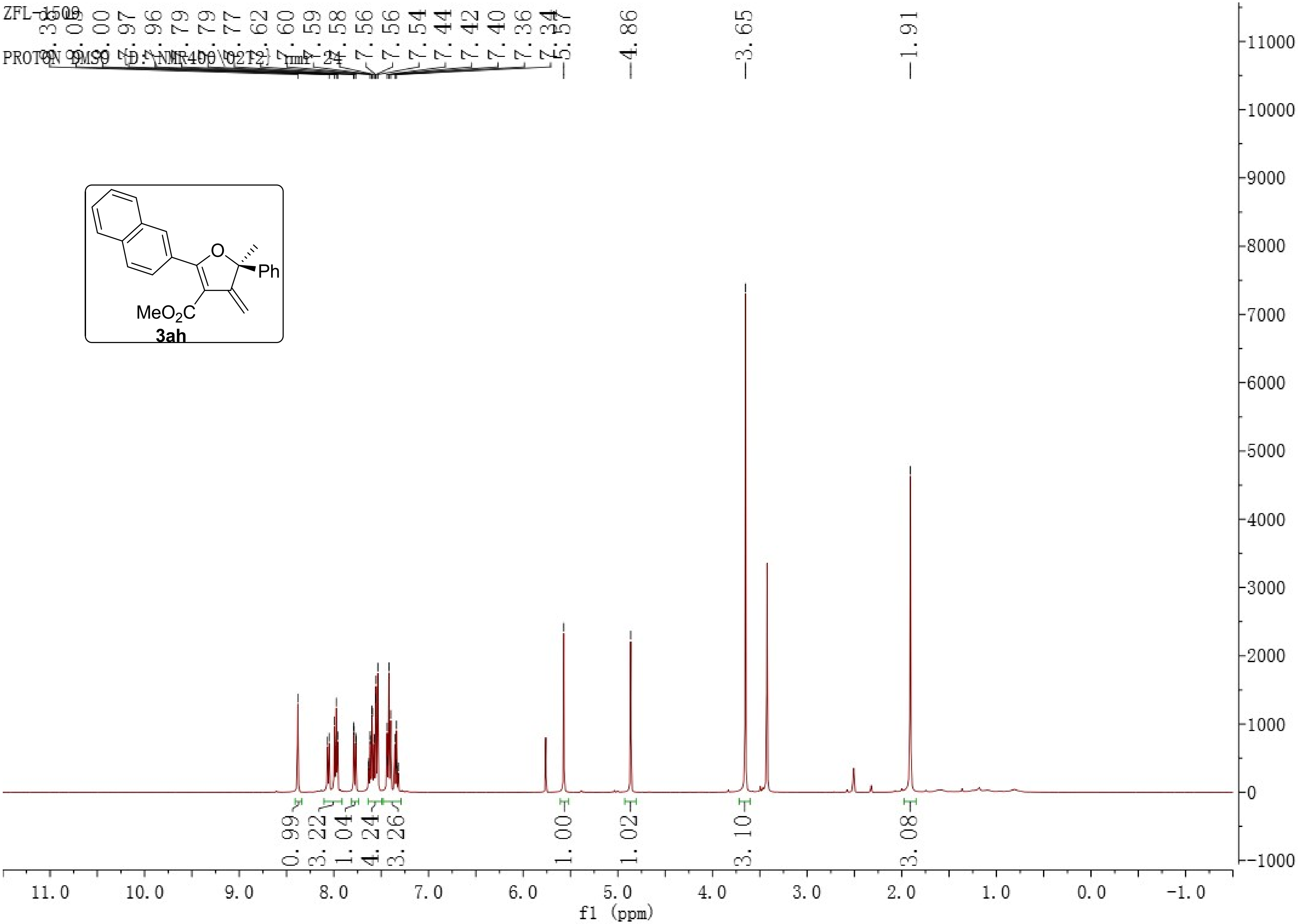

ZFL-1489
PROTON DMSO {D:\NMR400\0212} nmr 60
7.61
4.81
3.51
1.89
Cl
O
Ph
MeO2C
3ag
9.48
1.00
1.00
3.02
2.97
f1 (ppm)

ZFL-1489

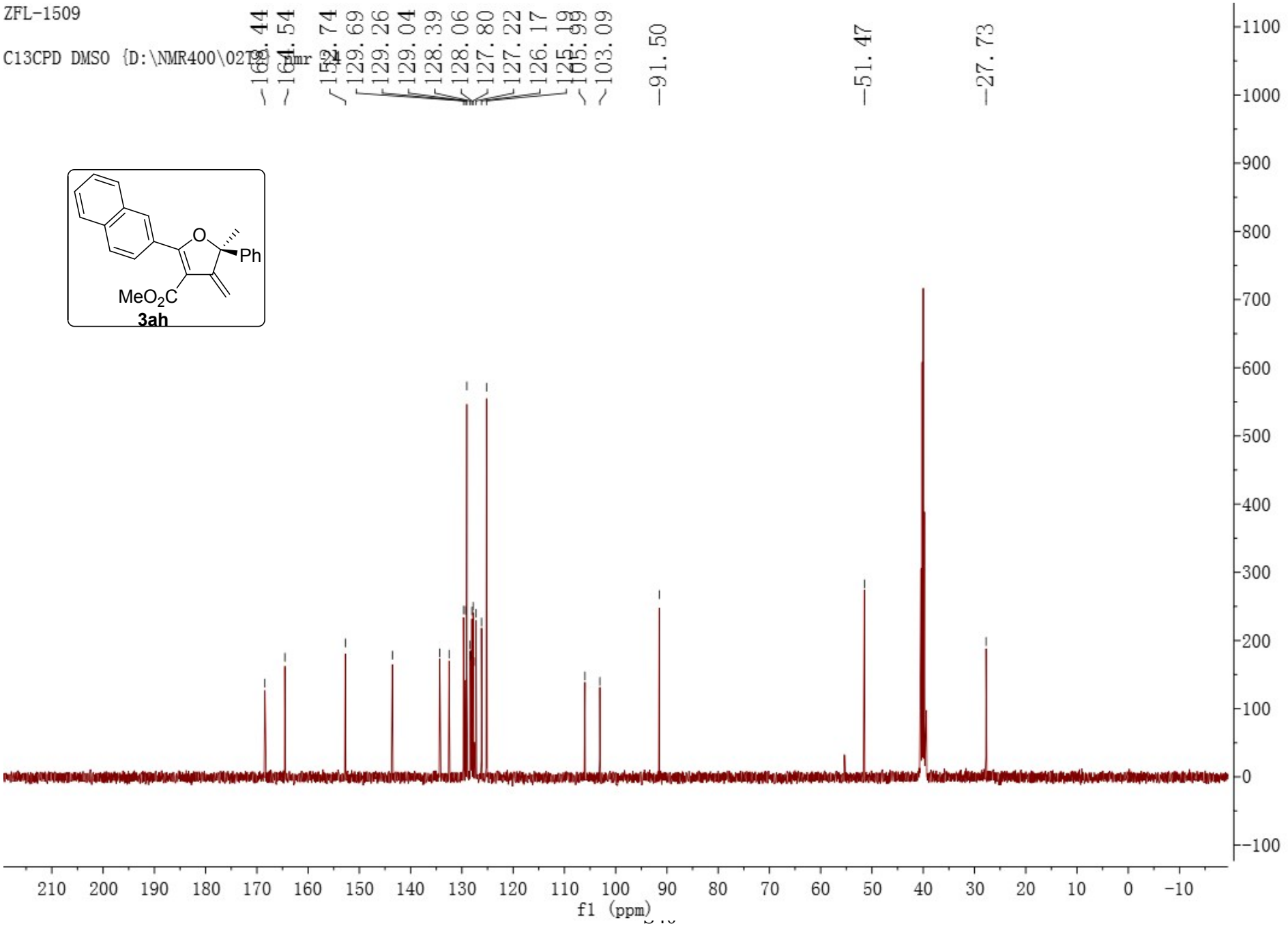
C13CPD DMSO {D:\NMR400\02TP...nmr 60}

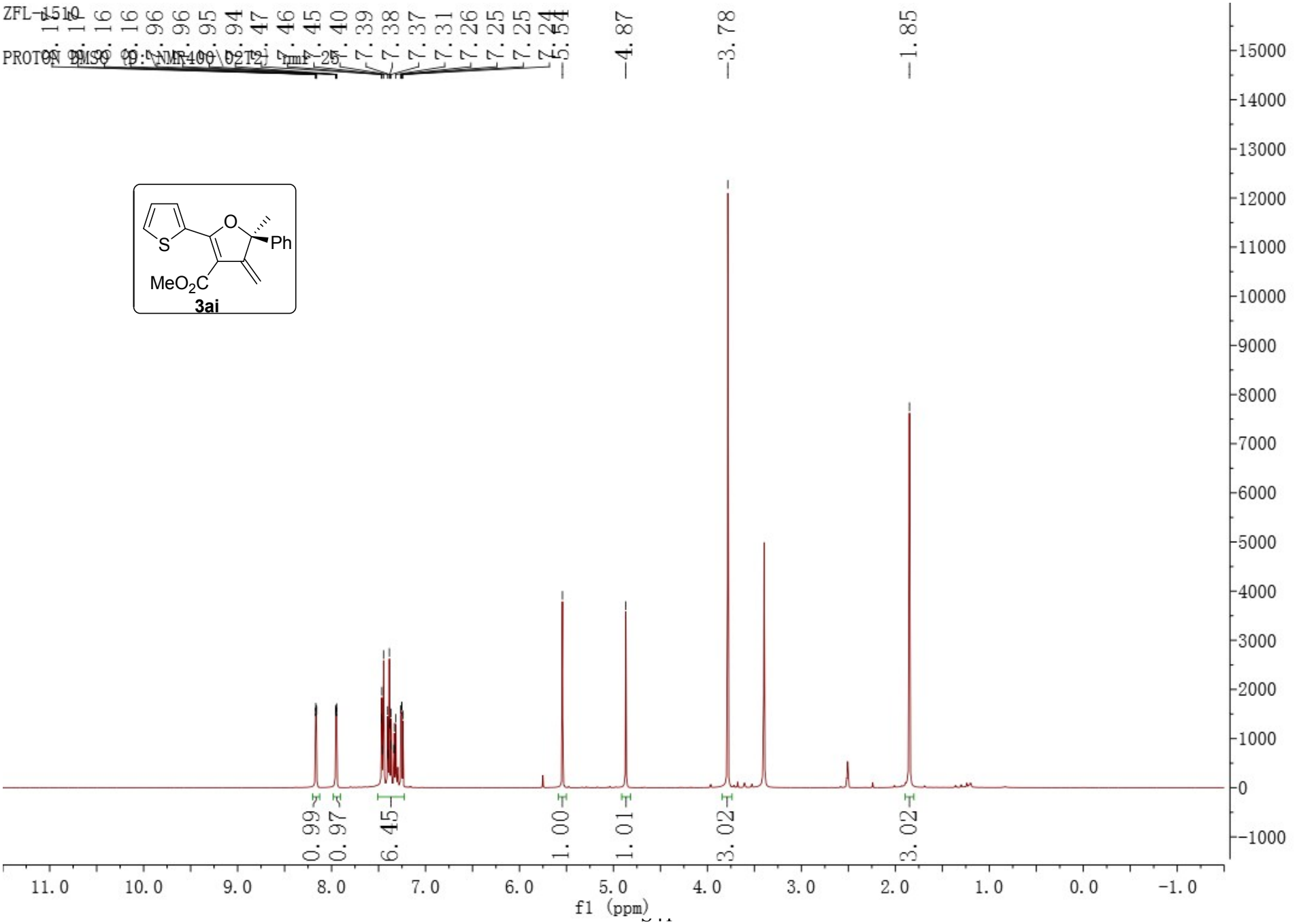


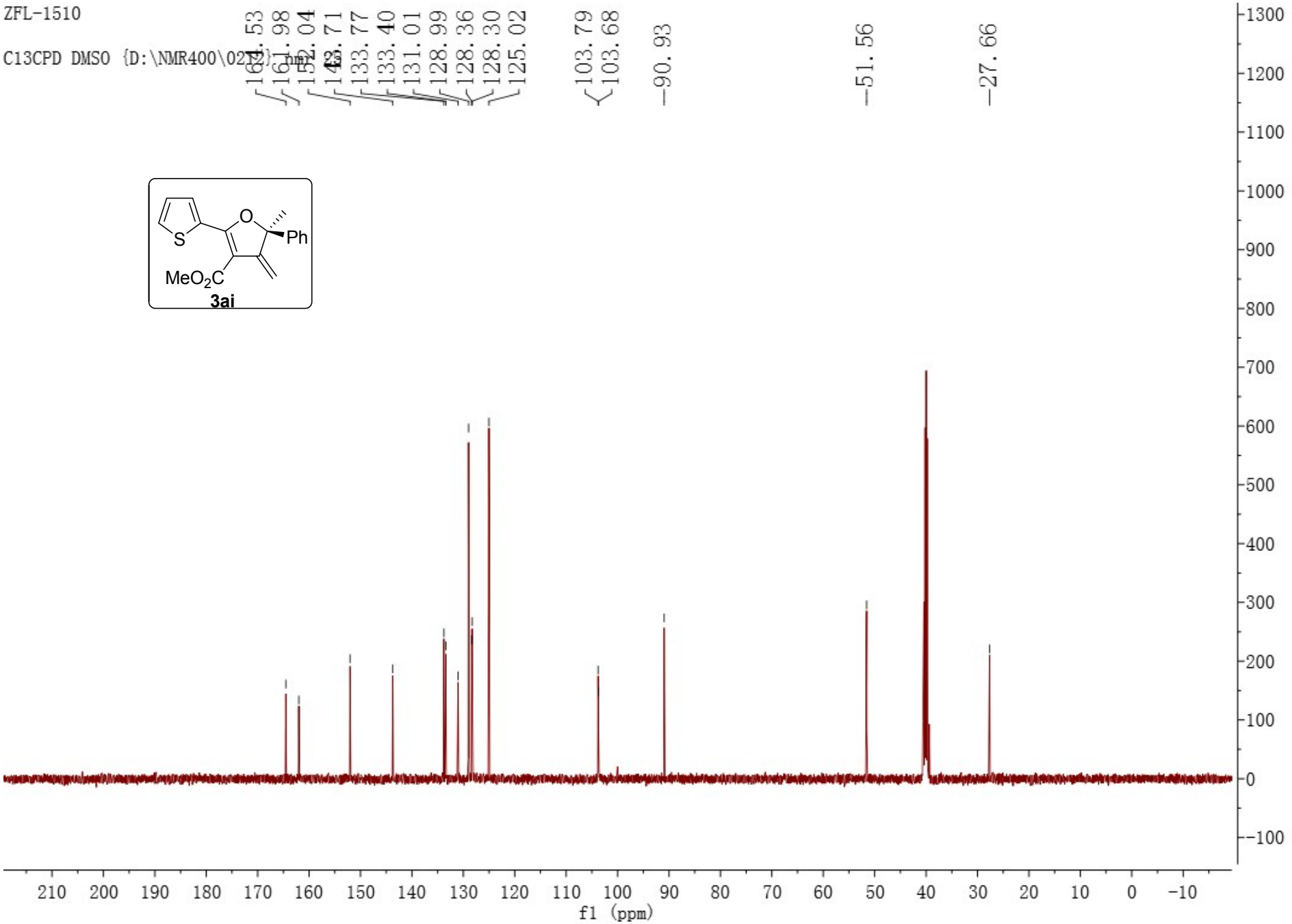
3ag



ZFL-1509
PROTON DMSO {D:\NMR400\0212} nmr 24
7.97
7.96
7.79
7.79
7.77
7.62
7.60
7.59
7.58
7.56
7.56
7.54
7.44
7.42
7.40
7.36
7.34
5.57
4.86
3.65
1.91
O
Ph
MeO2C
3ah
0.99
3.22
1.04
4.24
3.26
1.00
1.02
3.10
3.08
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

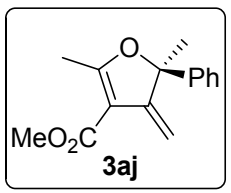

ZFL-1509
C13CPD DMSO {D:\NMR400\02ZFL.
168.44
164.54
152.74
129.69
129.26
129.04
128.39
128.06
127.80
127.22
126.17
125.19
105.99
103.09
91.50
51.47
27.73
O
Ph
MeO2C
3ah
f1 (ppm)


ZFL-1510
PROTON 2HSO (D:\NMR400\DATA)
7.96
7.95
7.94
7.47
7.46
7.45
7.40
7.39
7.38
7.37
7.31
7.26
7.25
7.25
7.24
5.54
4.87
3.78
1.85
S
O
Ph
MeO2C
3ai
0.99
0.97
6.45
1.00
1.01
3.02
3.02
f1 (ppm)

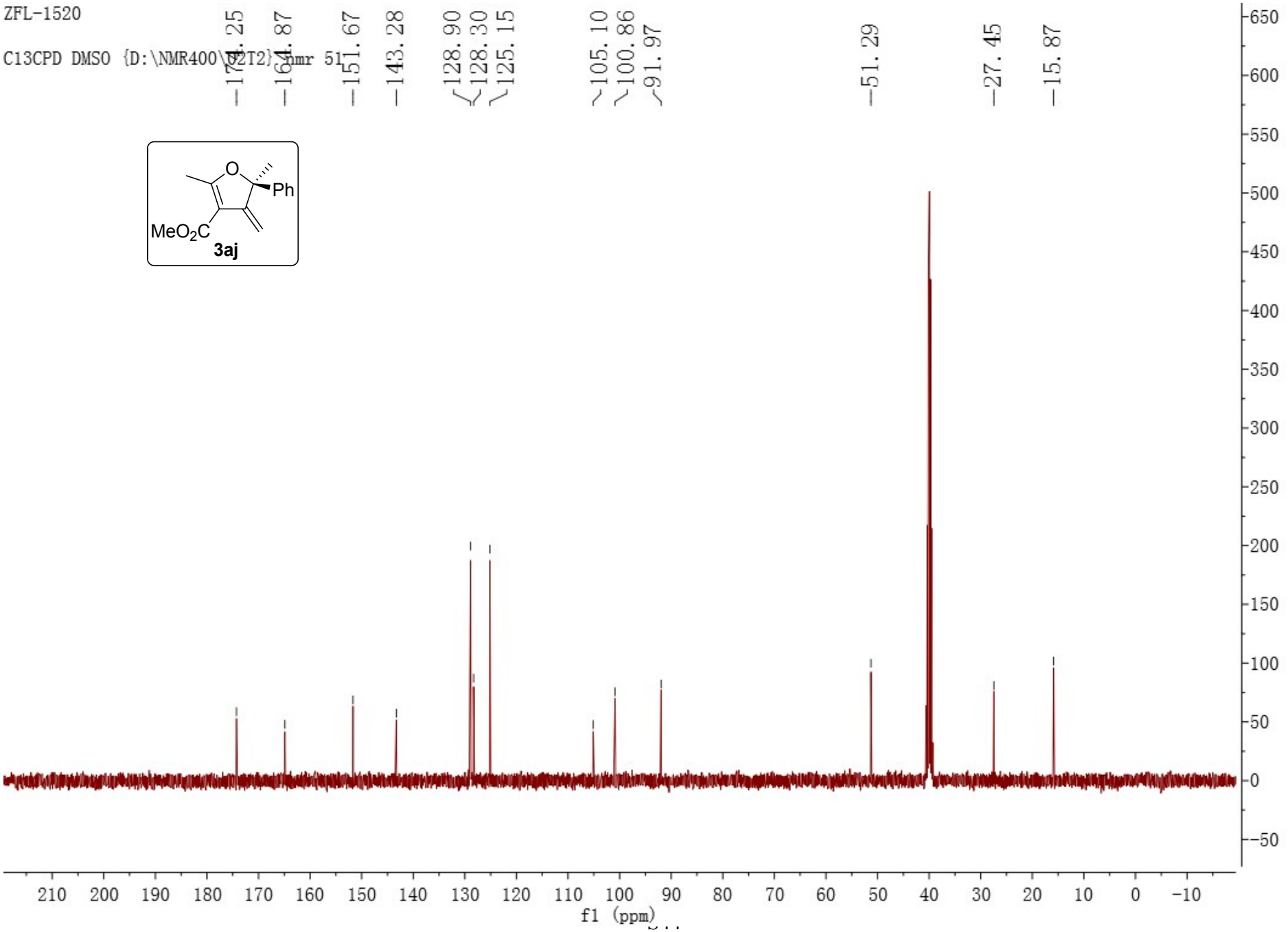

ZFL-1510
C13CPD DMSO {D:\NMR400\021}
nm
162.53
161.98
152.04
143.71
133.77
133.40
131.01
128.99
128.36
128.30
125.02
103.79
103.68
90.93
51.56
27.66
S
O
Ph
MeO2C
3ai
f1 (ppm)

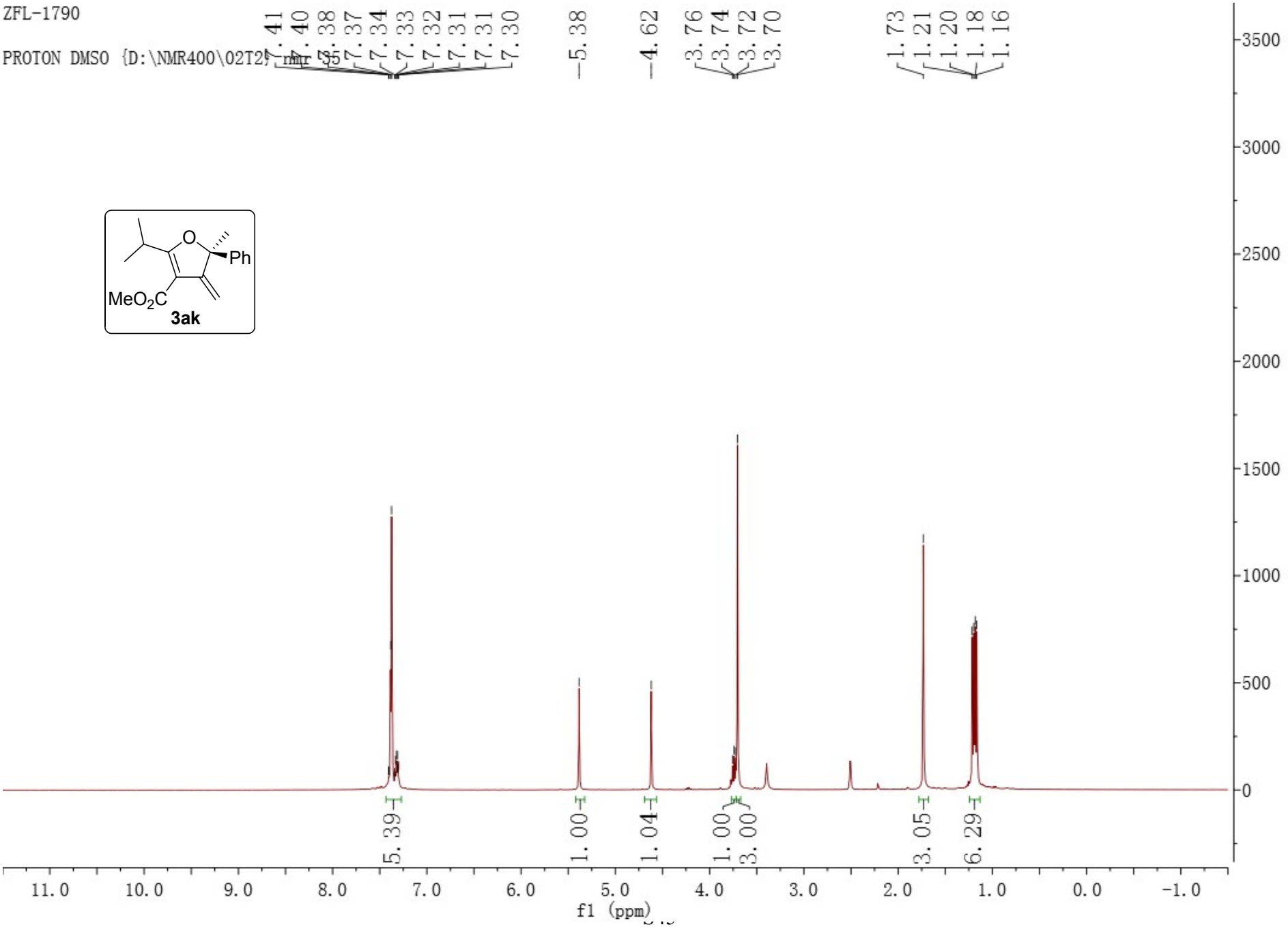
ZFL-1520

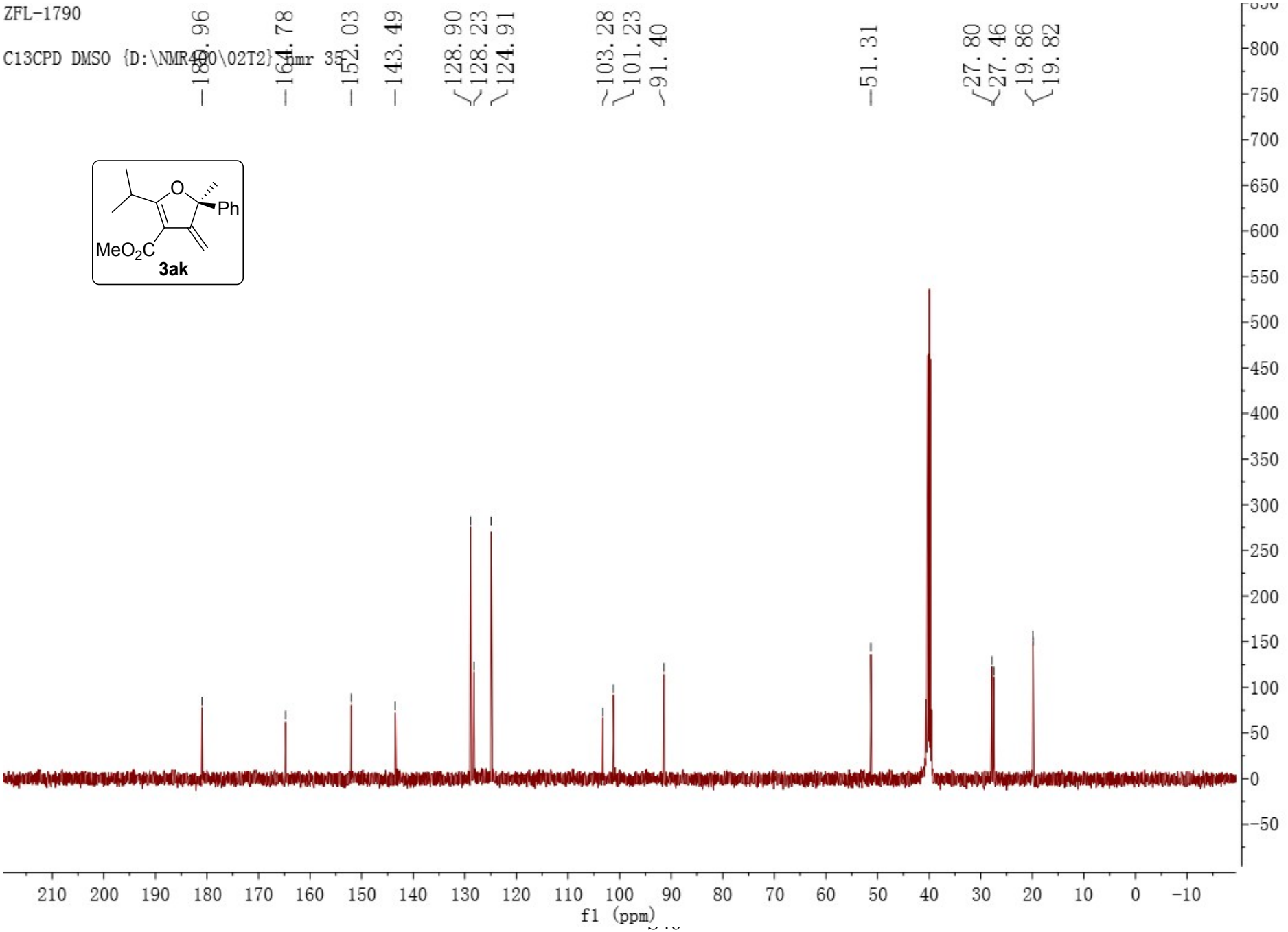
PROTON DMSO {D:\NMR400\02T2} nmr 51

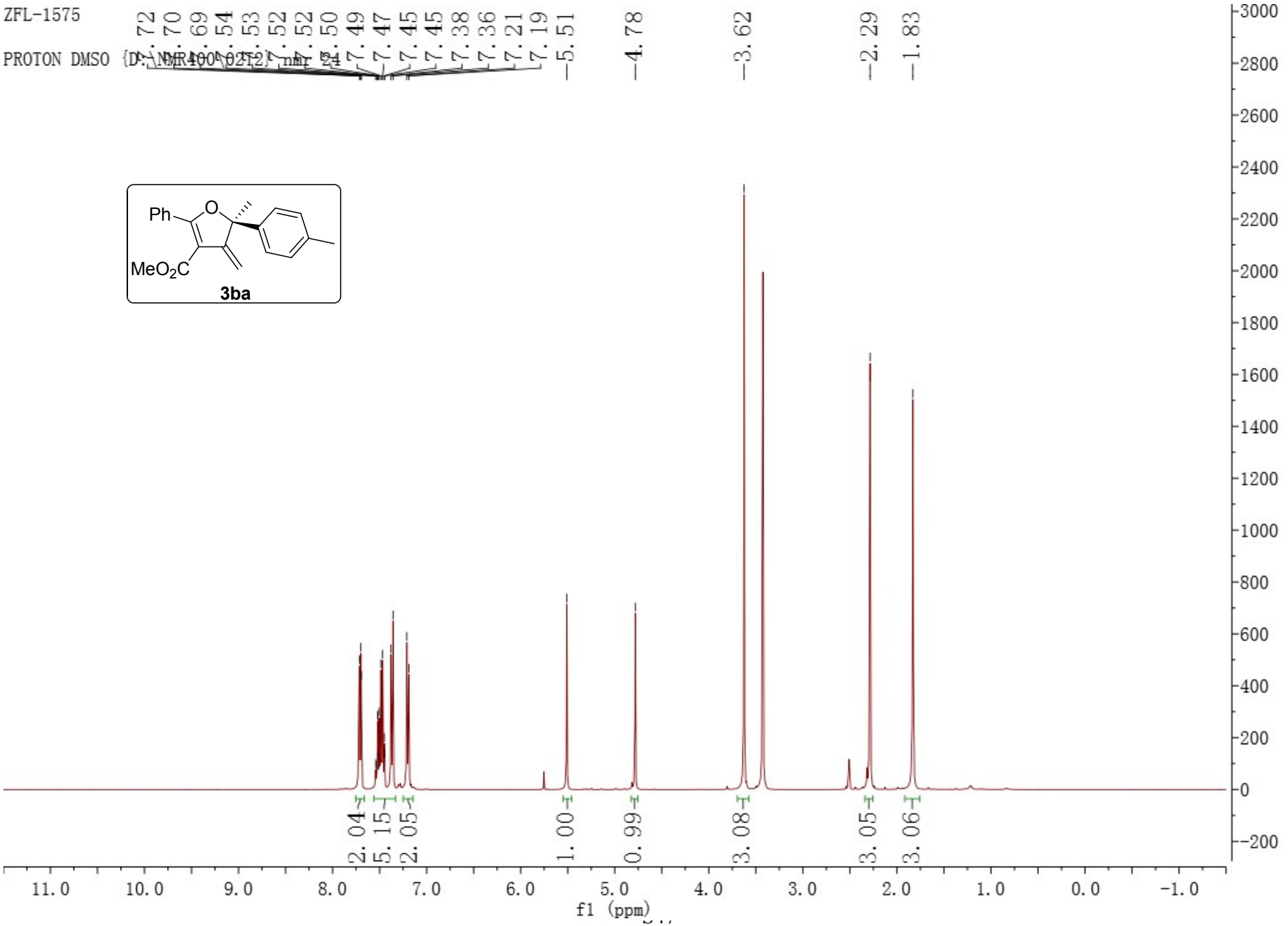


3aj


ZFL-1520
C13CPD DMSO {D:\NMR400\ZZT2} cmr 51
174.25
164.87
151.67
143.28
128.90
128.30
125.15
105.10
100.86
91.97
51.29
27.45
15.87
O
Ph
MeO2C
3aj
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

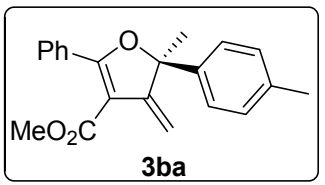

ZFL-1790
PROTON DMSO {D:\NMR400\02T2} nmr 35
7.41
7.40
7.38
7.37
7.34
7.33
7.32
7.31
7.31
7.30
5.38
4.62
3.76
3.74
3.72
3.70
1.73
1.21
1.20
1.18
1.16
Ph
MeO2C
3ak
5.39
1.00
1.04
1.00
3.00
3.05
6.29
f1 (ppm)


ZFL-1790
C13CPD DMSO {D:\NMR400\02T2} 1mr 35
180.96
164.78
152.03
143.49
128.90
128.23
124.91
103.28
101.23
91.40
51.31
27.80
27.46
19.86
19.82
O
Ph
MeO2C
3ak
f1 (ppm)

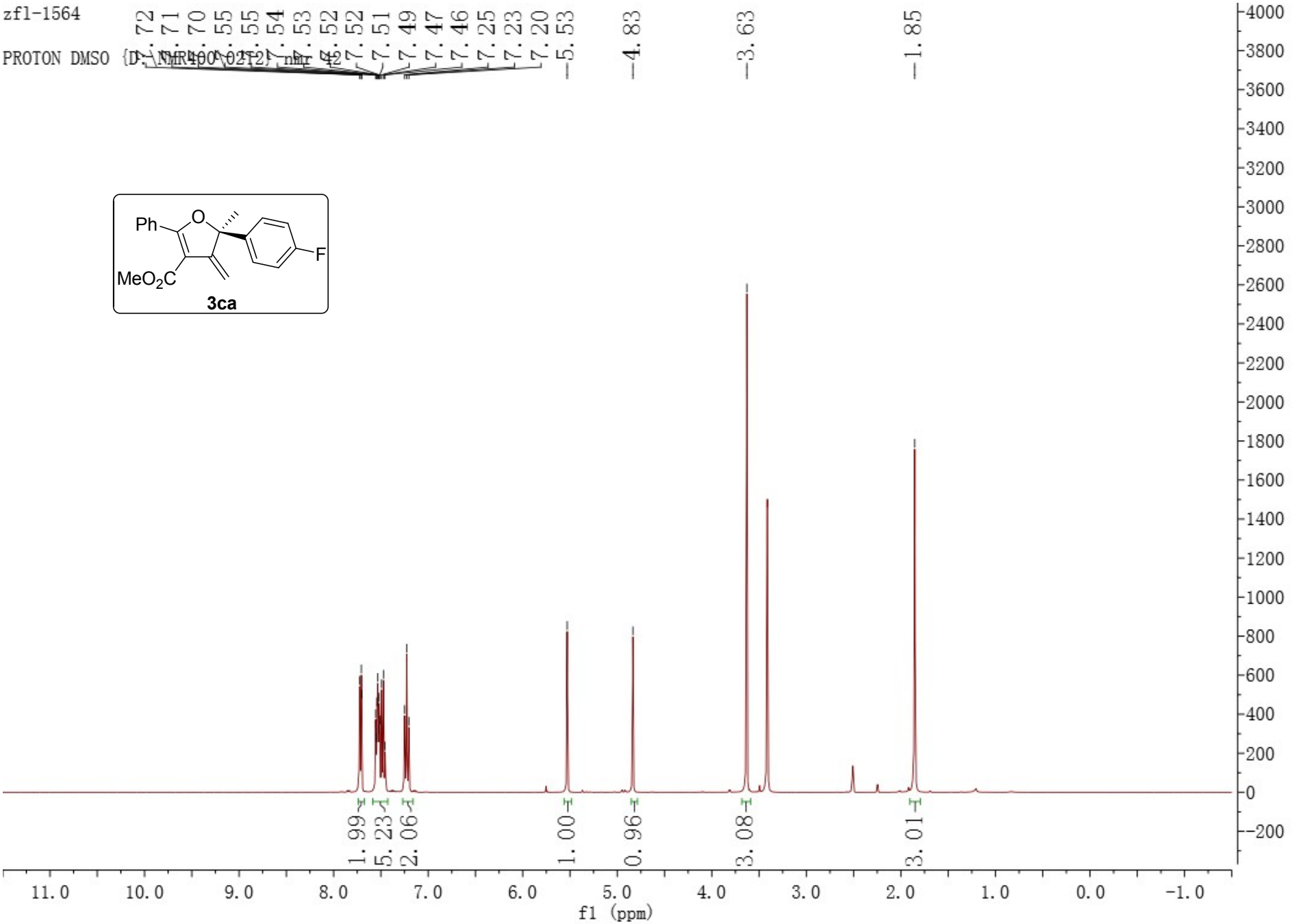

ZFL-1575
PROTON DMSO {D:\NMR400\0212} nmr 24
7.72
7.70
7.69
7.54
7.53
7.52
7.52
7.50
7.49
7.47
7.45
7.45
7.38
7.36
7.21
7.19
5.51
4.78
3.62
2.29
1.83
Ph
O
MeO2C
3ba
2.04
5.15
2.05
1.00
0.99
3.08
3.05
3.06
f1 (ppm)

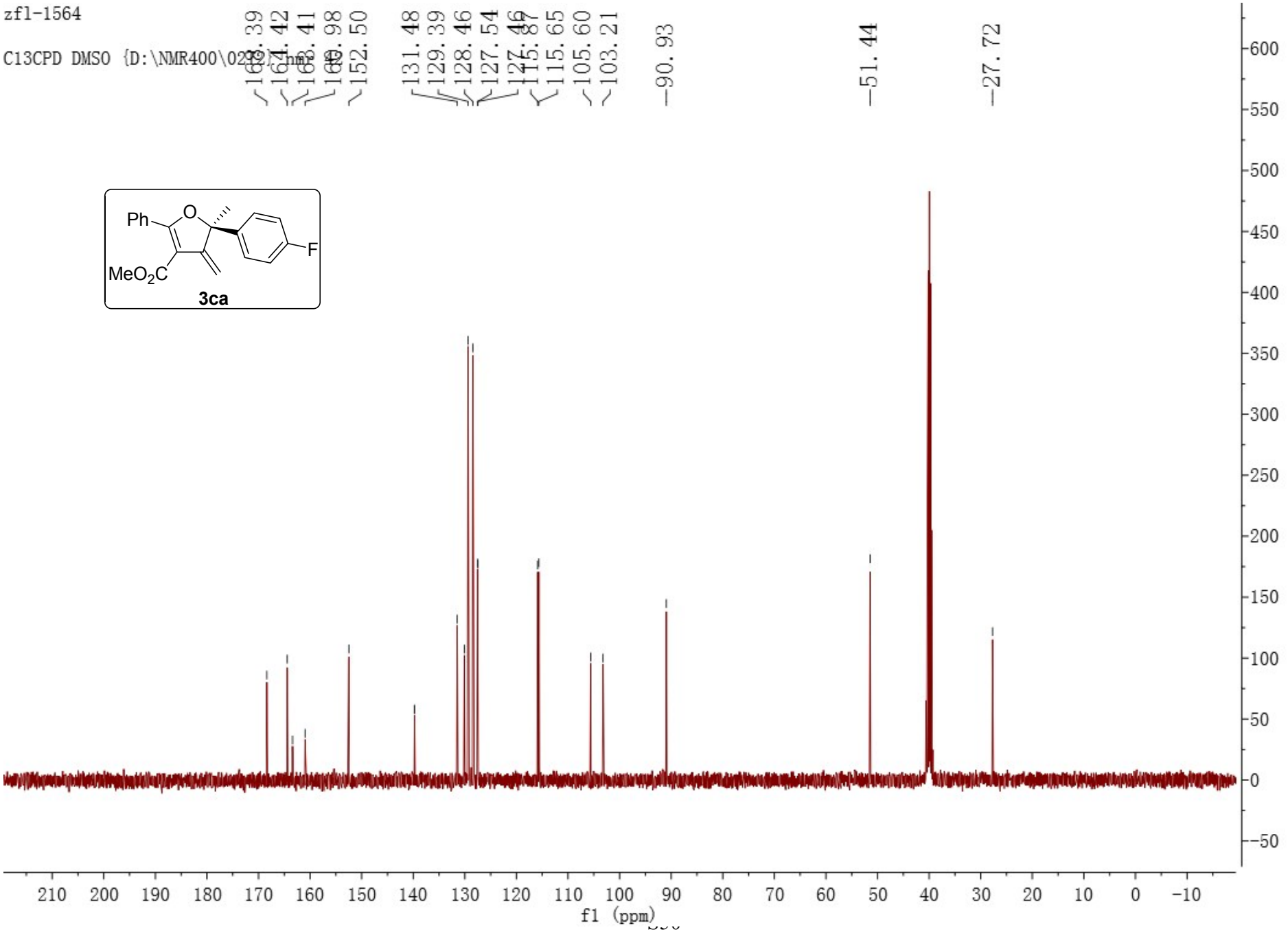
ZFL-1575

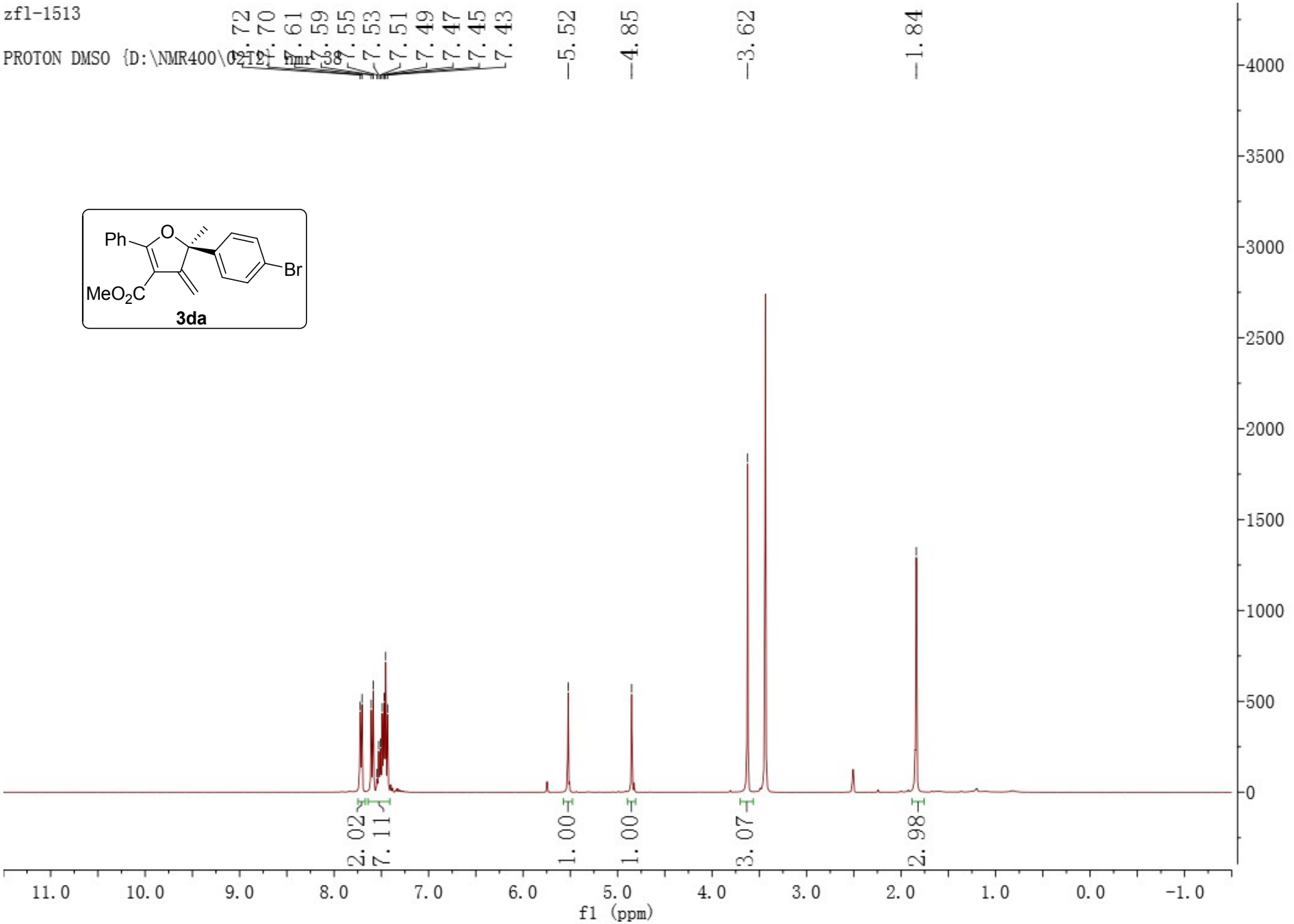
C13CPD DMSO {D:\NMR400\02\fid} pmr 24



3ba


zf1-1564
PROTON DMSO {D:\NMR400\0212} nmr 42
7.72
7.71
7.70
7.55
7.55
7.54
7.53
7.52
7.52
7.51
7.49
7.47
7.46
7.25
7.23
7.20
5.53
4.83
3.63
1.85
Ph
O
F
MeO2C
3ca
1.99
5.23
2.06
1.00
0.96
3.08
3.01
f1 (ppm)

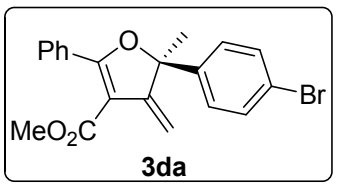

zf1-1564
C13CPD DMSO {D:\NMR400\0228}.nmr
163.39
161.42
160.41
152.50
131.48
129.39
128.46
127.54
115.65
105.60
103.21
90.93
51.44
27.72
Ph
O
F
MeO2C
3ca
f1 (ppm)


zf1-1513
PROTON DMSO {D:\NMR400\0212} nmr 38
7.72
7.70
7.61
7.59
7.55
7.53
7.51
7.49
7.47
7.45
7.43
5.52
4.85
3.62
1.84
Ph
O
Br
MeO2C
3da
2.02
7.11
1.00
1.00
3.07
2.98
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0

zf1-1513

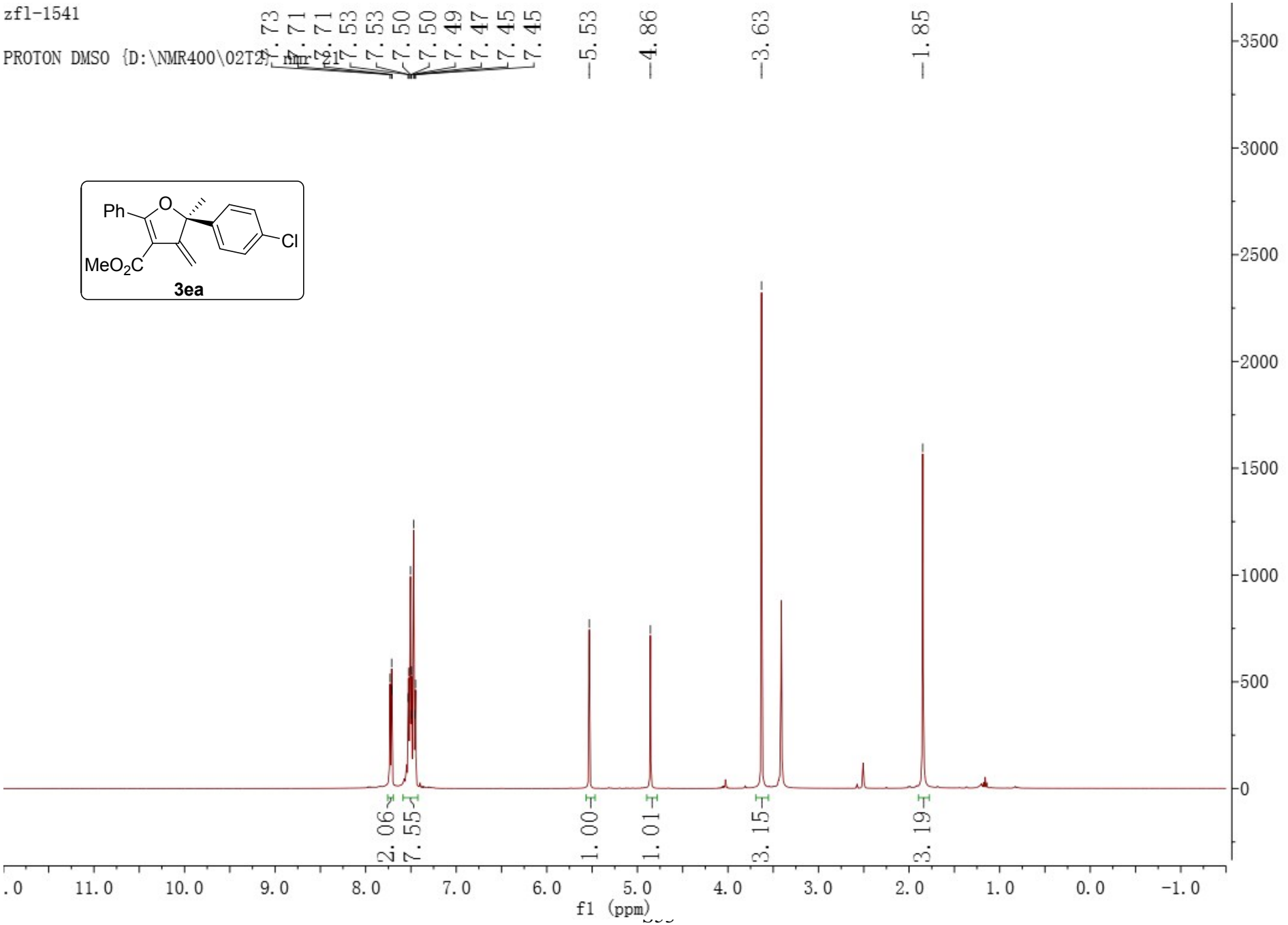
C13CPD DMSO {D:\NMR400\02T\8_nmr 38

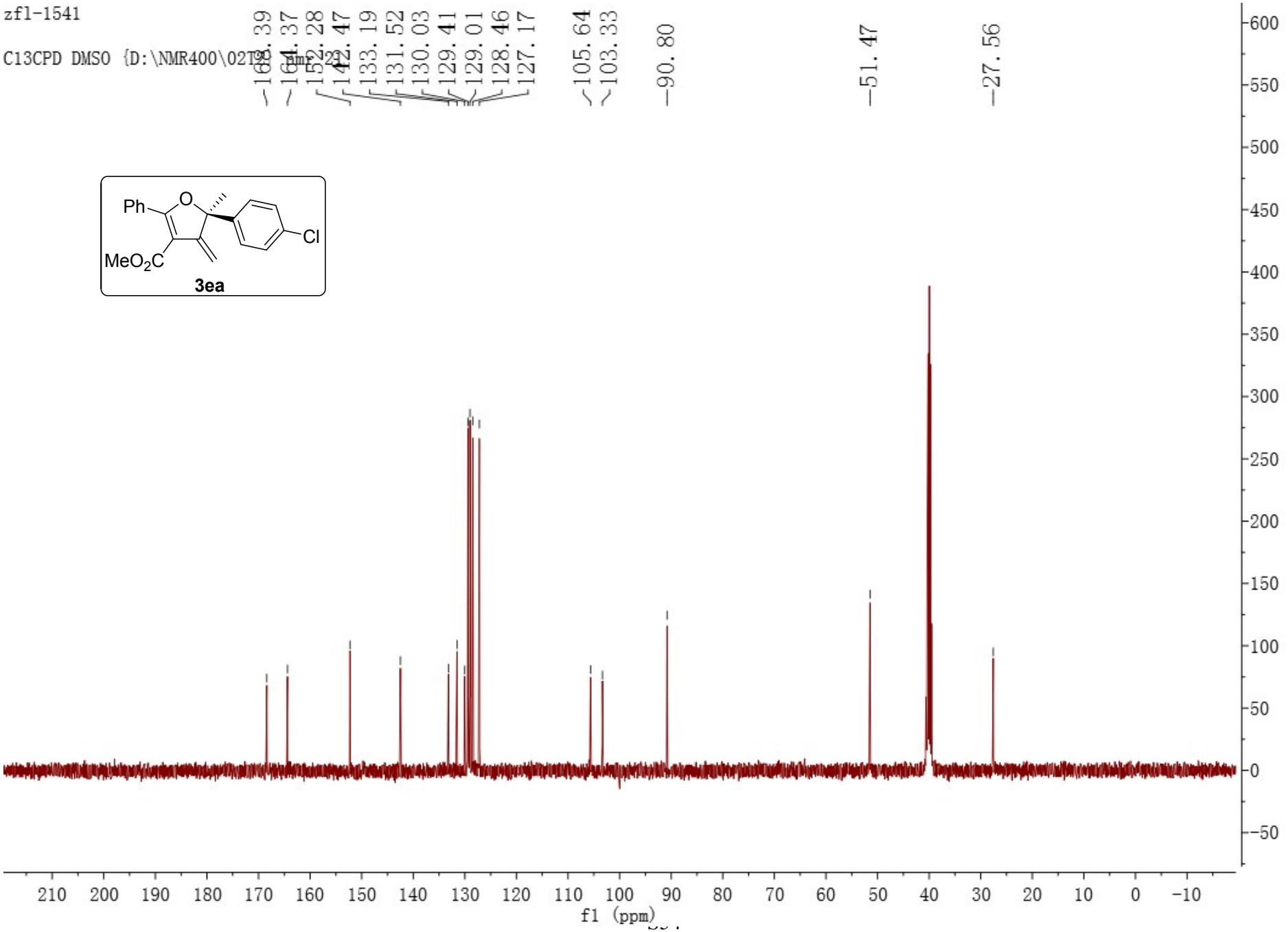
168.40
164.37
152.20
142.90
131.95
131.53
130.00
129.40
128.47
127.48
105.63
103.35
90.84
51.49
27.51

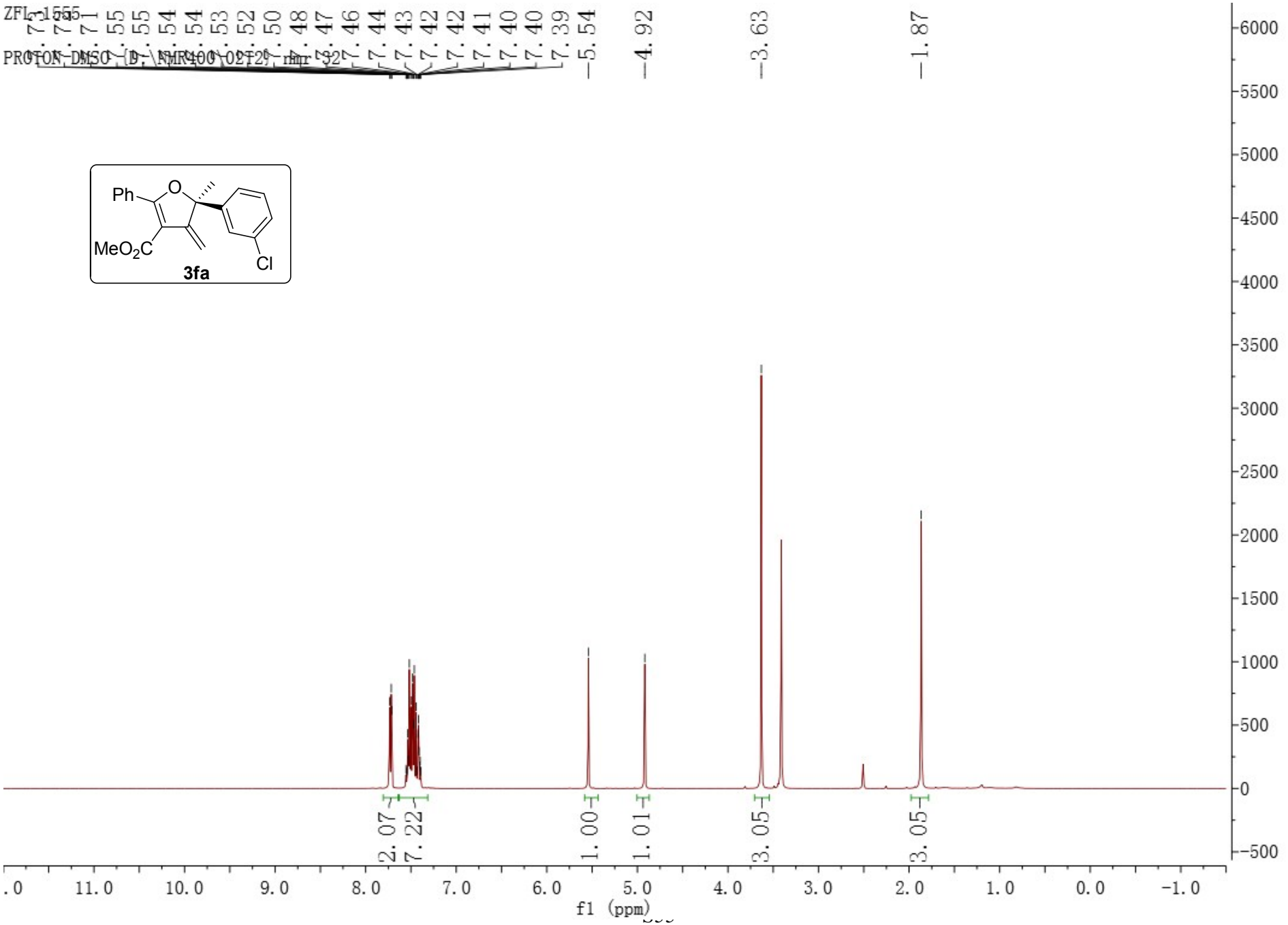


3da

f1 (ppm)

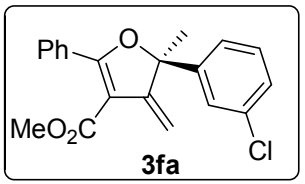

zf1-1541
PROTON DMSO {D:\NMR400\02T2} nmr 21
7.73
7.71
7.71
7.53
7.53
7.50
7.50
7.49
7.47
7.45
7.45
5.53
4.86
3.63
1.85
Ph
O
Cl
MeO2C
3ea
2.06
7.55
1.00
1.01
3.15
3.19
3500
3000
2500
2000
1500
1000
500
0
.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


zf1-1541
C13CPD DMSO {D:\NMR400\02T
168.39
164.37
152.28
142.47
133.19
131.52
130.03
129.41
129.01
128.46
127.17
105.64
103.33
90.80
51.47
27.56
Ph
O
Cl
MeO2C
3ea
f1 (ppm)

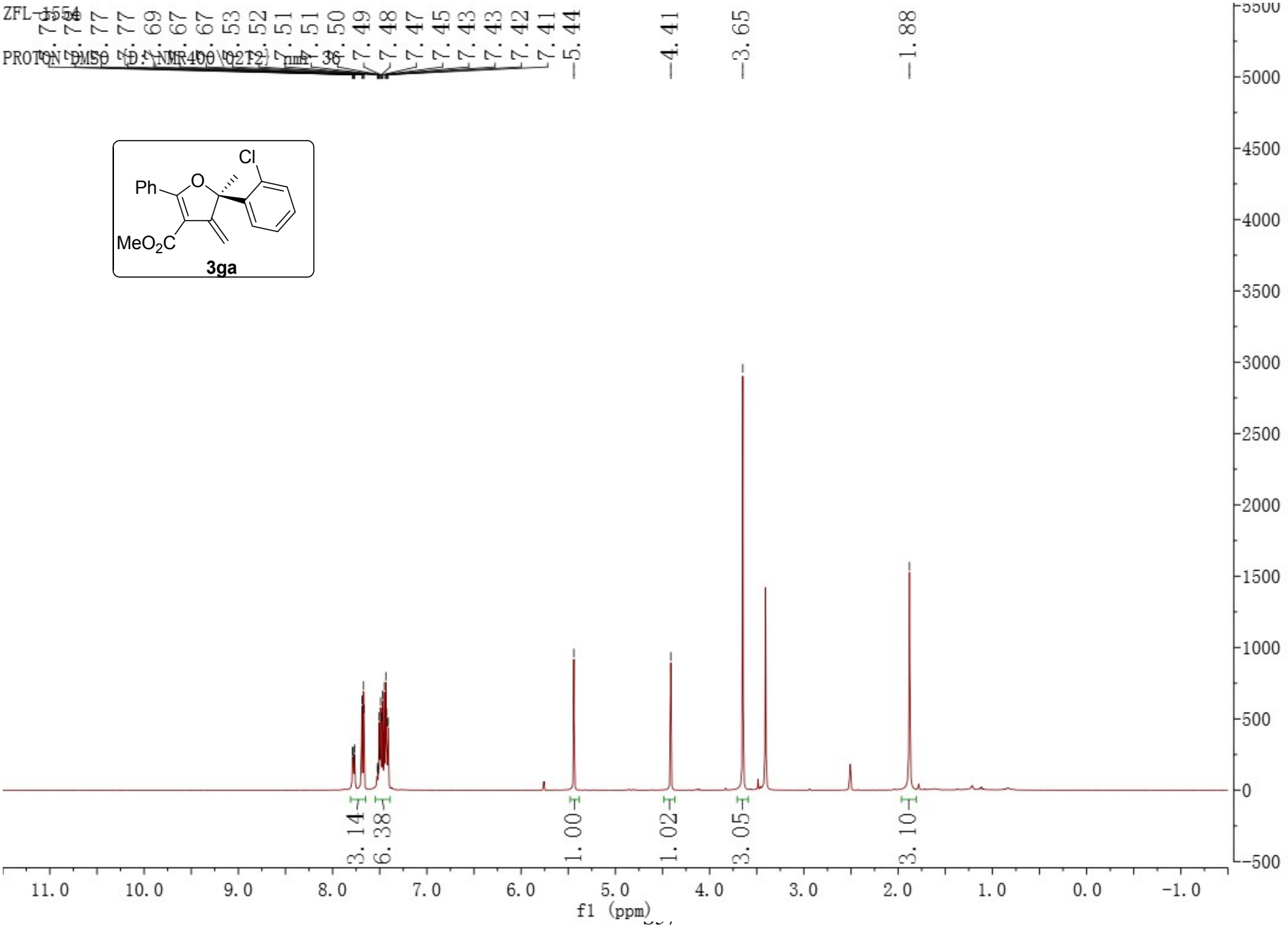

ZFL-1555
PROTON_DMSO (D:\NMR400\0212) nmr 32
7.55
7.54
7.53
7.52
7.50
7.48
7.47
7.46
7.44
7.43
7.42
7.42
7.41
7.40
7.40
7.39
5.54
4.92
3.63
1.87
Ph
O
MeO2C
Cl
3fa
2.07
7.22
1.00
1.01
3.05
3.05
f1 (ppm)

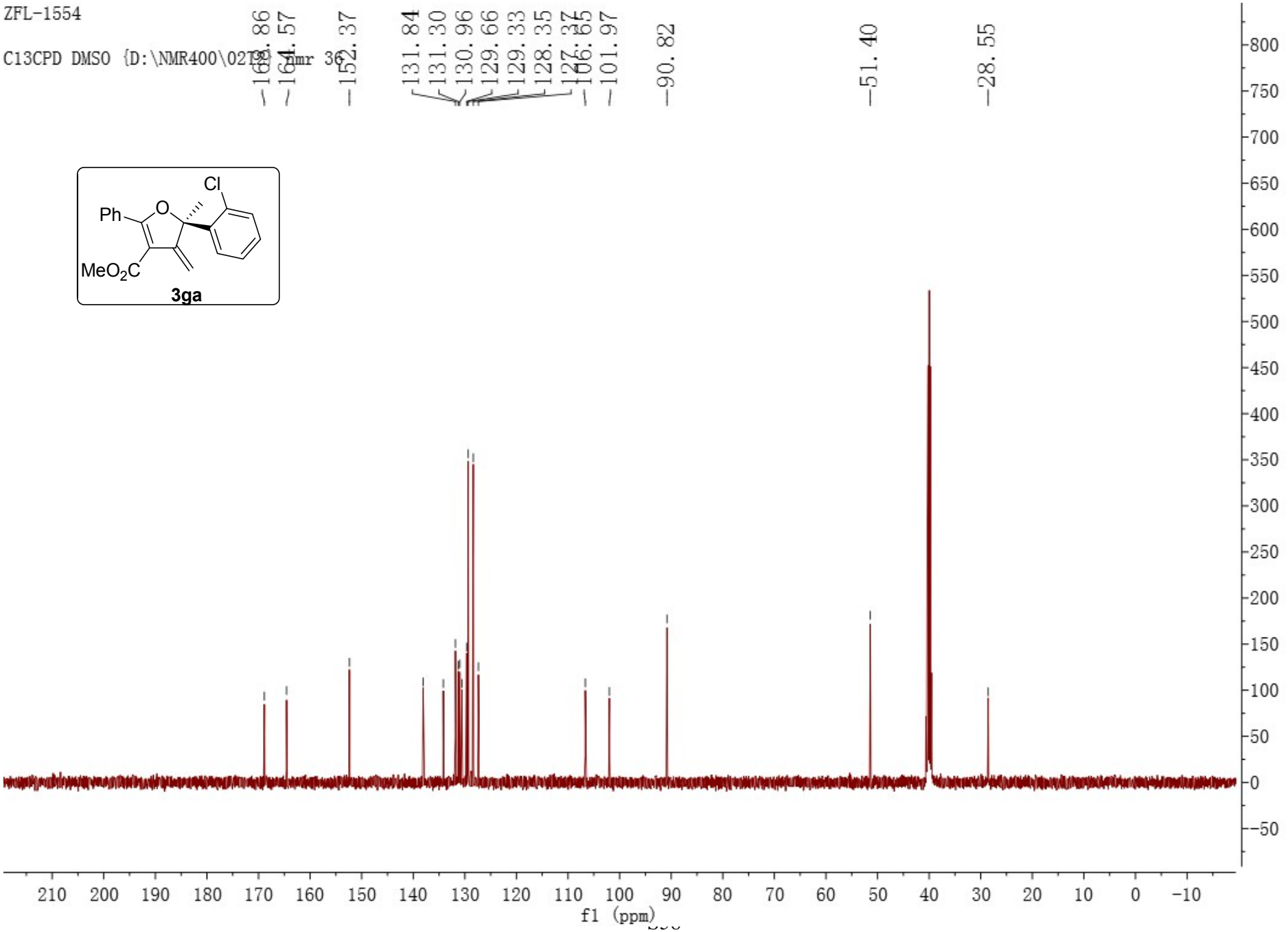
ZFL-1555

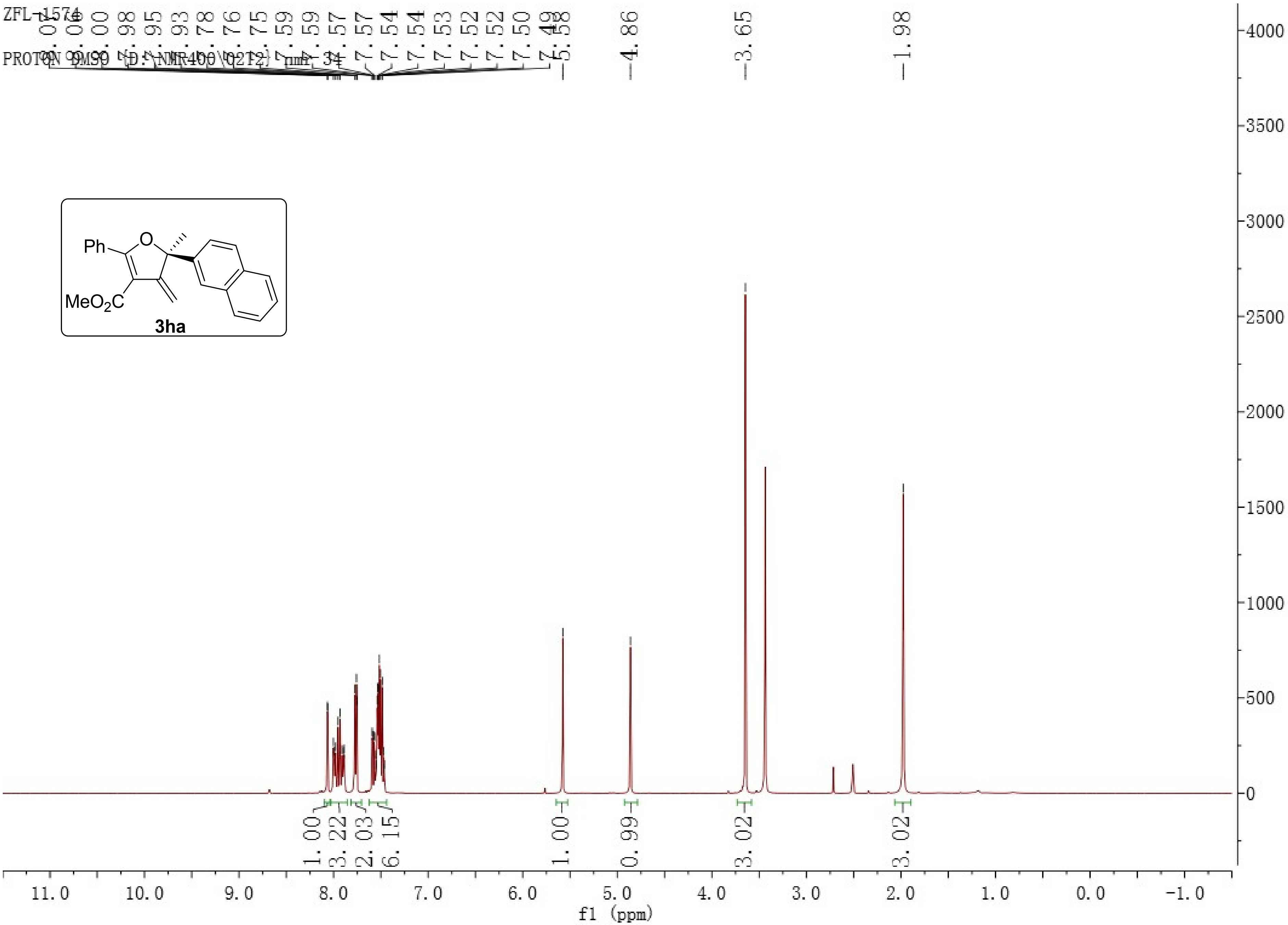
C13CPD DMSO {D:\NMR400\02T8.amr 32



3fa


ZFL-1554
PROTON DMSO (D:\NMR400\021\2) nmr 36
7.74
7.77
7.77
7.69
7.67
7.67
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.45
7.43
7.43
7.42
7.41
5.44
4.41
3.65
1.88
Cl
Ph
O
MeO2C
3ga
3.14
6.38
1.00
1.02
3.05
3.10
f1 (ppm)

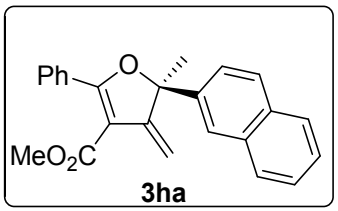

ZFL-1554
C13CPD DMSO {D:\NMR400\02ZFL-1554.esp} cmr 36
168.86
164.57
152.37
131.84
131.30
130.96
129.66
129.33
128.35
127.37
106.65
101.97
90.82
51.40
28.55
Cl
Ph
O
MeO2C
3ga
f1 (ppm)


ZFL-1574
PROTON DMSO {D:\NMR400\Q2T2} mm 34
8.05
8.00
7.98
7.95
7.93
7.78
7.76
7.75
7.59
7.59
7.57
7.57
7.54
7.54
7.53
7.52
7.52
7.50
7.49
5.58
4.86
3.65
1.98
Ph
O
MeO2C
3ha
1.00
3.22
2.03
6.15
1.00
0.99
3.02
3.02
f1 (ppm)

ZFL-1574

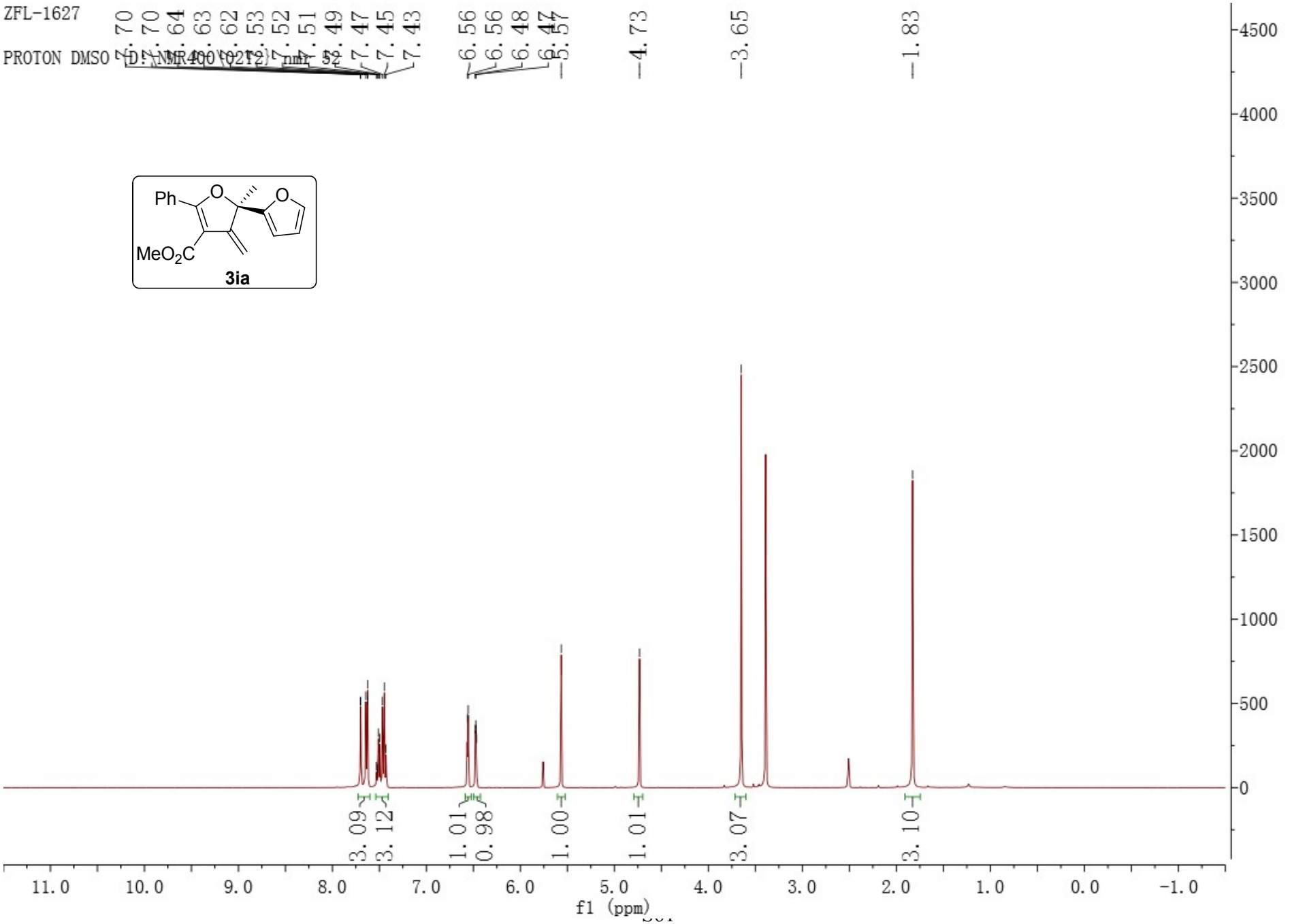
C13CPD DMSO {D:\NMR400\02T8\ pmr 34

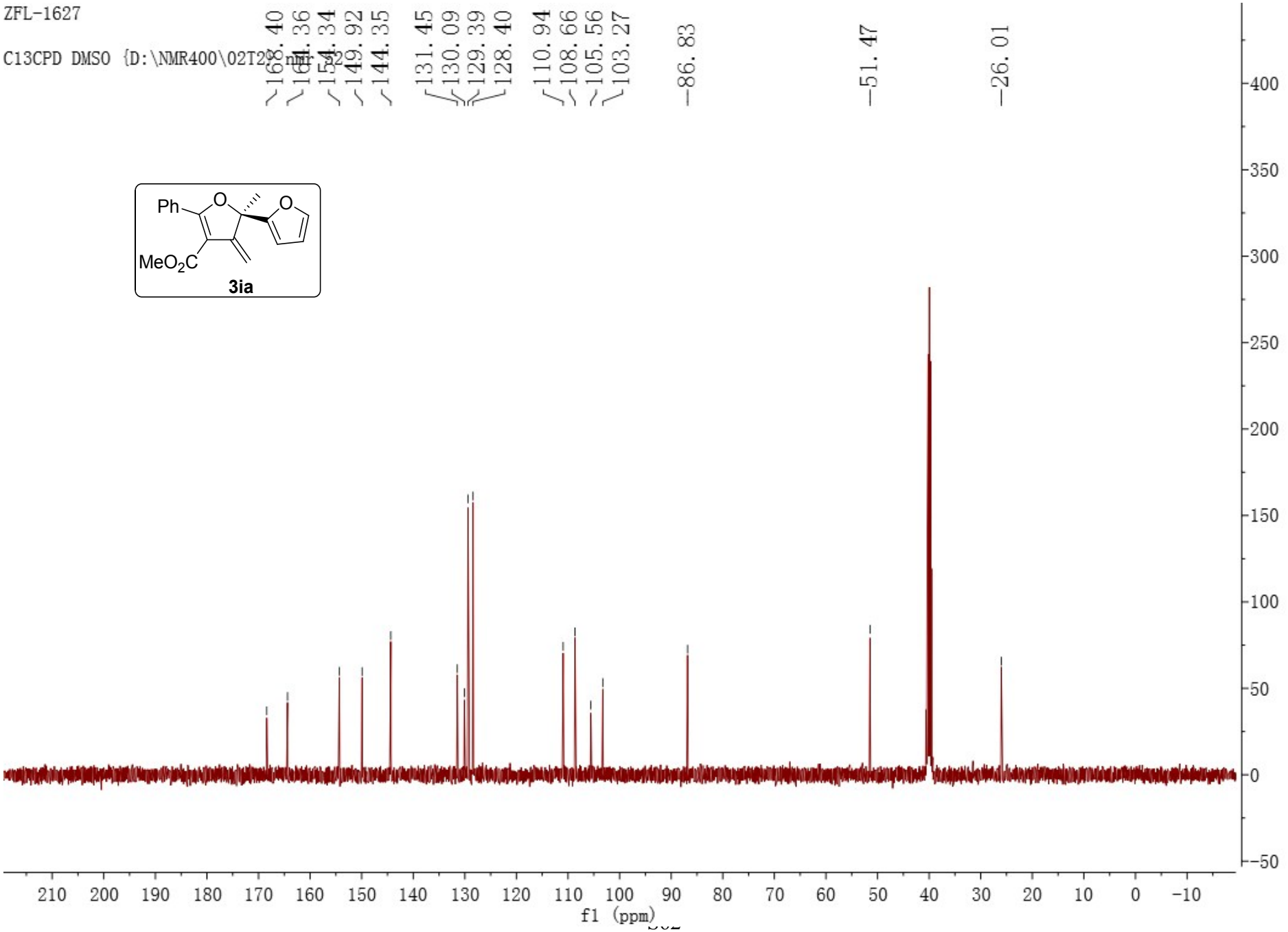
168.75
164.51
152.56
129.48
128.81
128.48
127.85
126.91
123.86
123.72
105.78
103.30
91.57
51.46
27.59

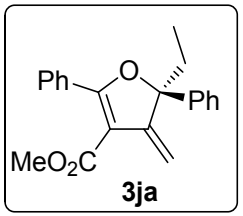


3ha

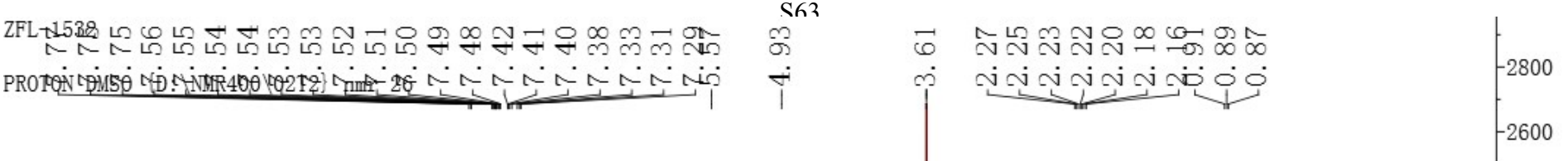
f1 (ppm)


ZFL-1627
PROTON DMSO
7.70
7.70
7.64
7.63
7.62
7.53
7.52
7.51
7.49
7.47
7.45
7.43
6.56
6.56
6.48
6.47
5.57
4.73
3.65
1.83
Ph
O
O
MeO2C
3ia
3.09
3.12
1.01
0.98
1.00
1.01
3.07
3.10
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0


ZFL-1627
C13CPD DMSO {D:\NMR400\02T28.nm} 32
168.40
164.36
154.34
149.92
144.35
131.45
130.09
129.39
128.40
110.94
108.66
105.56
103.27
86.83
51.47
26.01
Ph
O
O
MeO2C
3ia
400
350
300
250
200
150
100
50
0
-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

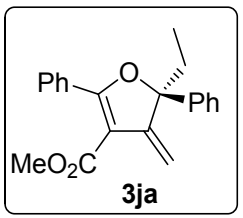

Ph
O
Ph
MeO2C

3ja

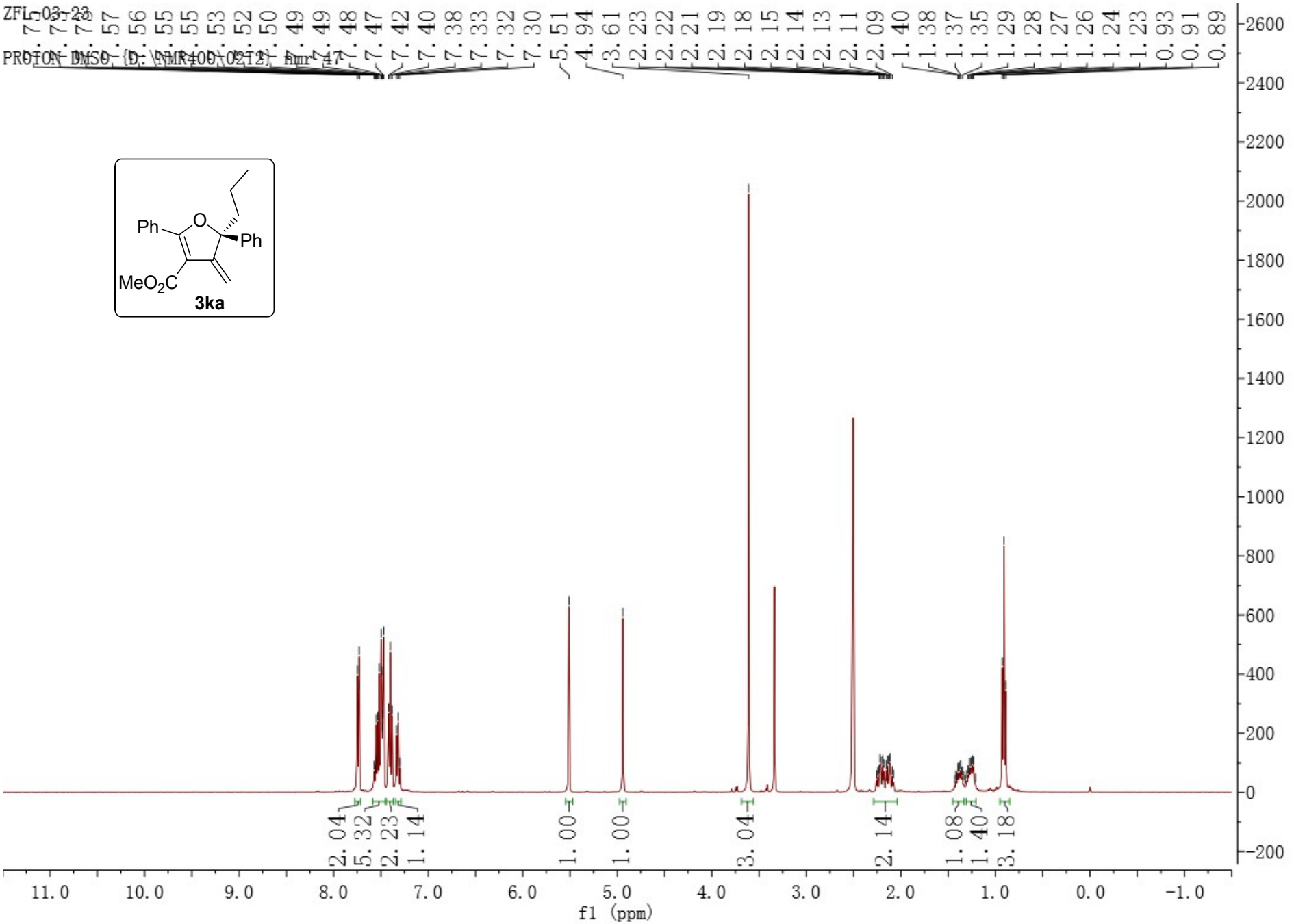

ZFL-1538
PROTON DMSO (D:\NMR400\0212) nmr 26
7.75
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.42
7.41
7.40
7.38
7.33
7.31
7.29
5.57
4.93
3.61
2.27
2.25
2.23
2.22
2.20
2.18
2.16
0.91
0.89
0.87
2800
2600

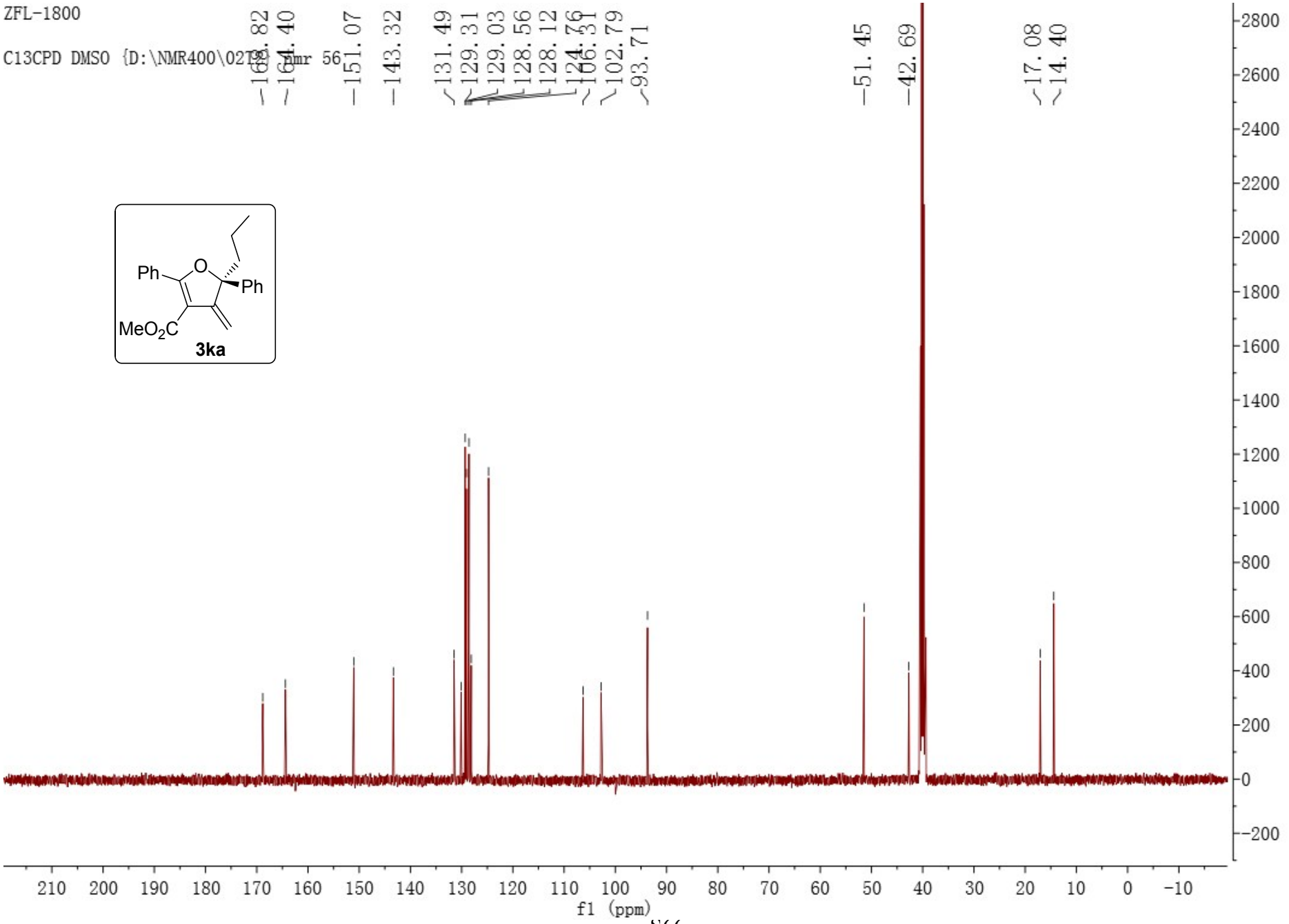
ZFL-1532

C13CPD DMSO {D:\NMR400\02TS\...mr 26

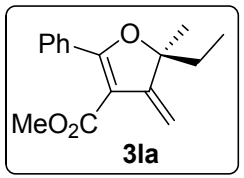


3ja

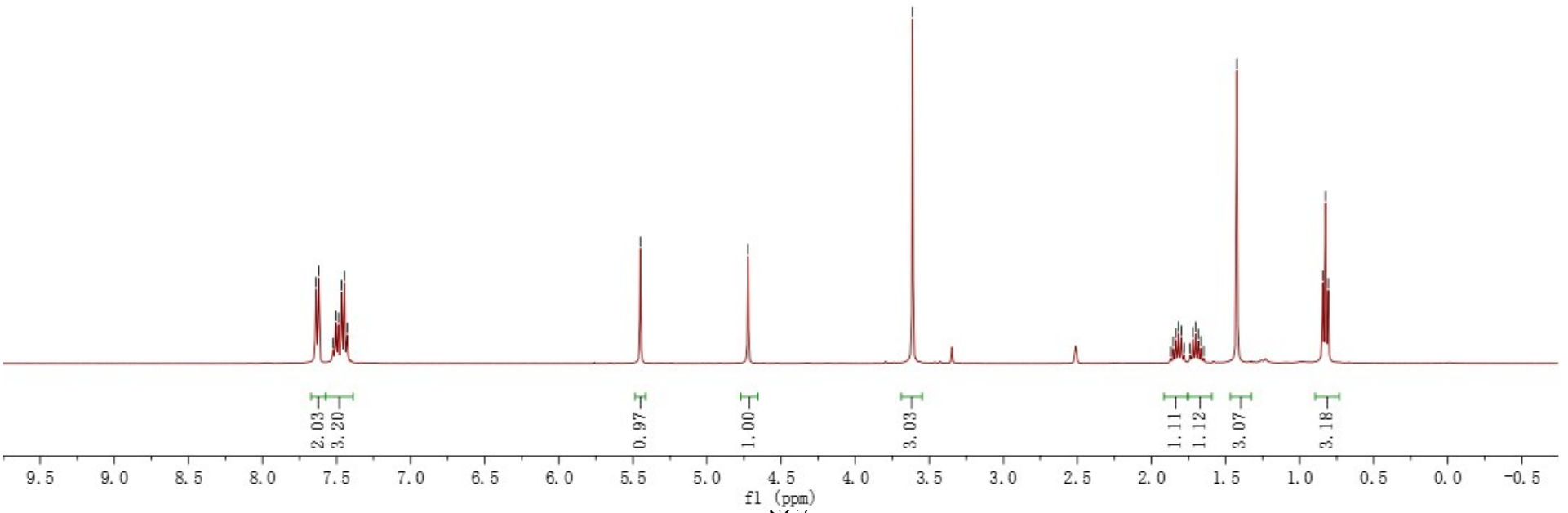

ZFL-03-23
PROTON-DMSO (D:\NMR400\0212) nmr 47
7.57 7.56 7.55 7.53 7.52 7.50 7.49 7.49 7.48 7.47 7.42 7.40 7.38 7.33 7.32 7.30 5.51 4.94 3.61 2.23 2.22 2.21 2.19 2.18 2.15 2.14 2.13 2.11 2.09 1.40 1.38 1.37 1.35 1.29 1.28 1.27 1.26 1.24 1.23 0.93 0.91 0.89
Ph
O
Ph
MeO2C
3ka
2.04 5.32 2.23 1.14 1.00 1.00 3.04 2.14 1.08 1.40 3.18
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200


ZFL-1800
C13CPD DMSO {D:\NMR400\0213\} zmr 56
168.82
164.40
151.07
143.32
131.49
129.31
129.03
128.56
128.12
124.76
106.31
102.79
93.71
51.45
42.69
17.08
14.40
Ph
O
Ph
MeO2C
3ka
f1 (ppm)

LK-823
PROTON DMSO {D:\NMR400\02T2} nmr 43

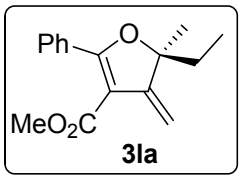


3la

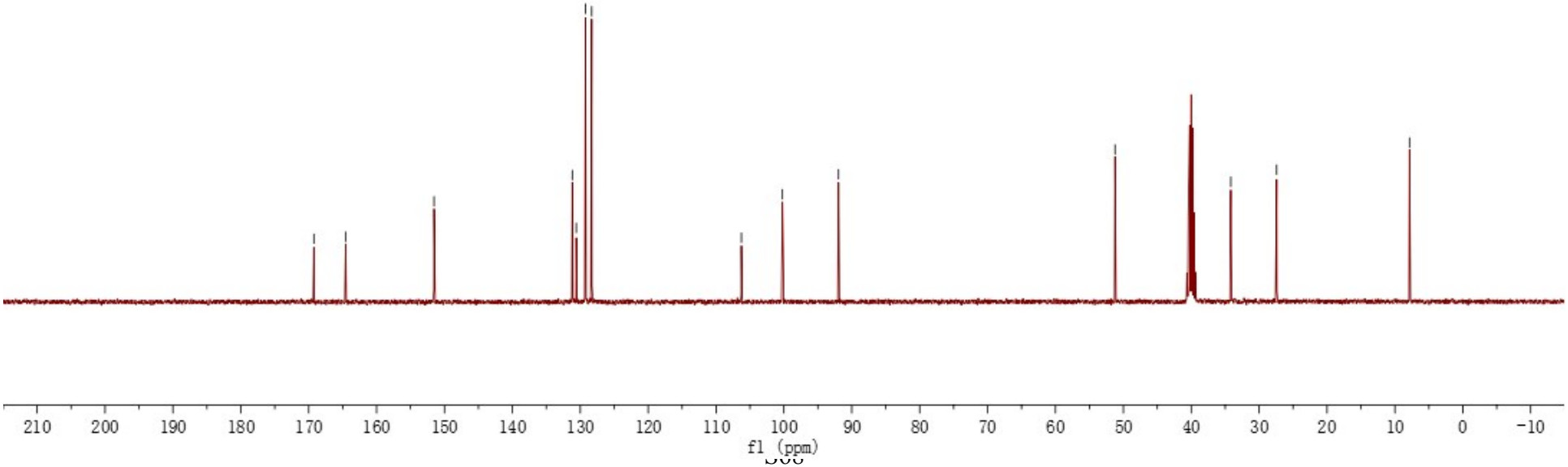


169.24
164.56
151.53
131.17
130.58
129.22
128.31
106.27
100.22
91.95
51.23
34.16
27.42
7.85

LK-823
C13CPD DMSO {D:\NMR400\02T2} nmr 43



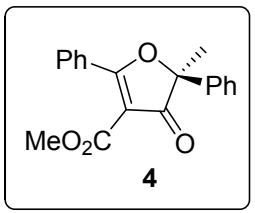
3la



ZFL-1750

PROTON CDC13 {D:\NMR400\02P2} nmr 14

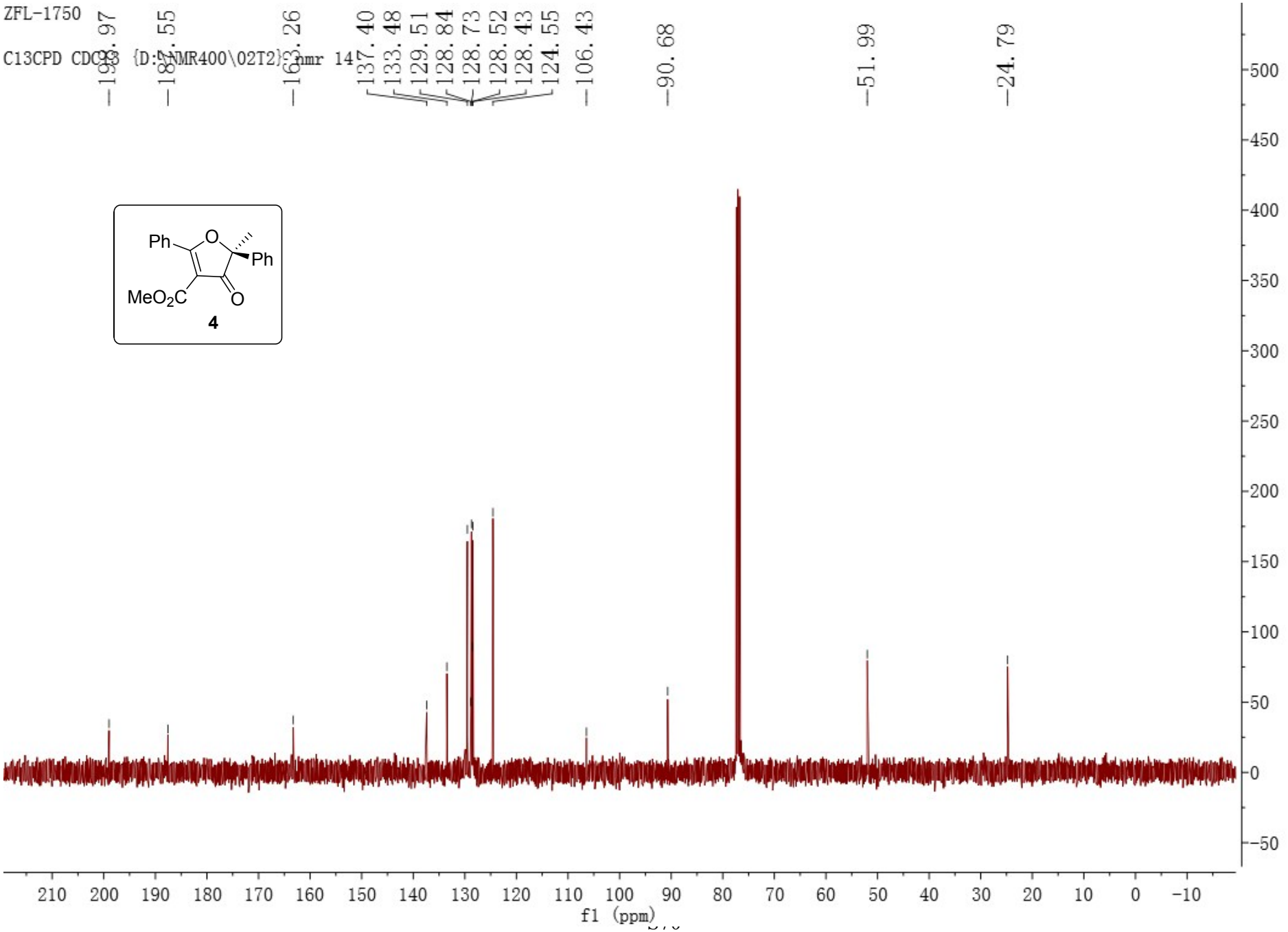
8.04
8.02
7.64
7.62
7.56
7.54
7.52
7.39
7.38
7.36
7.34
7.33
7.26
3.82
1.89



4

1.95
1.05
4.00
3.02
3.00
3.14

f1 (ppm)


ZFL-1750
C13CPD CDCl3 {D:\NMR400\02T2} nmr 14
193.97
187.55
163.26
137.40
133.48
129.51
128.84
128.73
128.52
128.43
124.55
106.43
90.68
51.99
24.79
Ph
O
Ph
MeO2C
O
4
f1 (ppm)