Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Gold(I)-Catalyzed Asymmetric [3+2]-Cycloadditons of -1-Ethoxyethoxy-propiolates and Aldehydes

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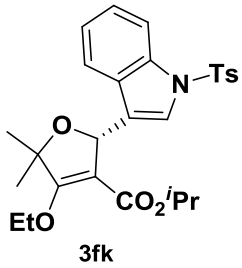
General Methods:

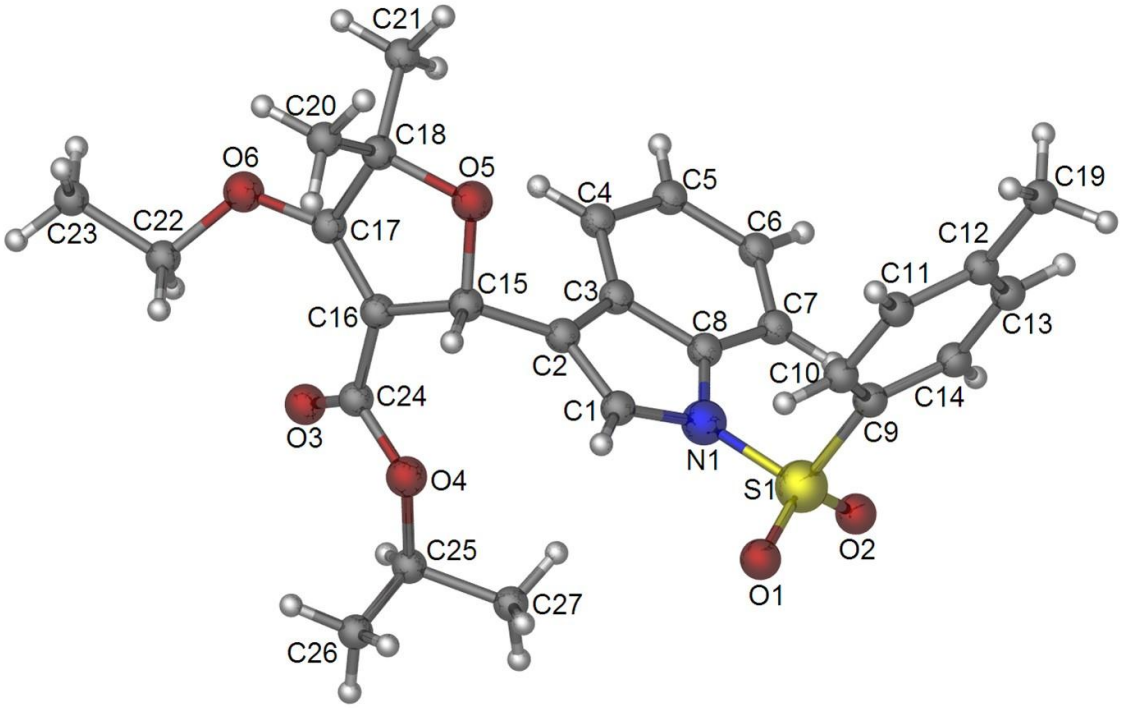
All reactions were carried out in oven-dried standard Schlenk techniques with magnetic stirring. Dichloromethane (DCM) and dichloroethane (DCE) was distilled from CaH_2 under an atmosphere of argon. Toluene was as distilled from Sodium under an atmosphere of argon. 1H NMR spectra were recorded on a BRUKER 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane(TMS: 0 ppm) with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). 13C NMR spectra were recorded on a BRUKER 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, acetone-d_6: 205.87)

Aldehydes were purchased from commercial company and **2a-2f** were synthesized according to the literature procedure[11].

Figure S1. X-ray of 3fk

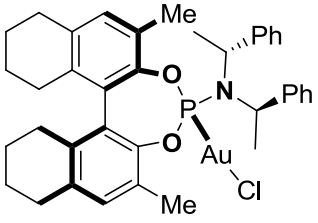


3fk



(1) Zhang, G.; Zhang, L. *J. Am. Chem. Soc*. **2008**, *130*, 12598.

Figure S2. X-ray of (*R,R,R*)-5bAuCl



(*R,R,R*)-**5b**AuCl

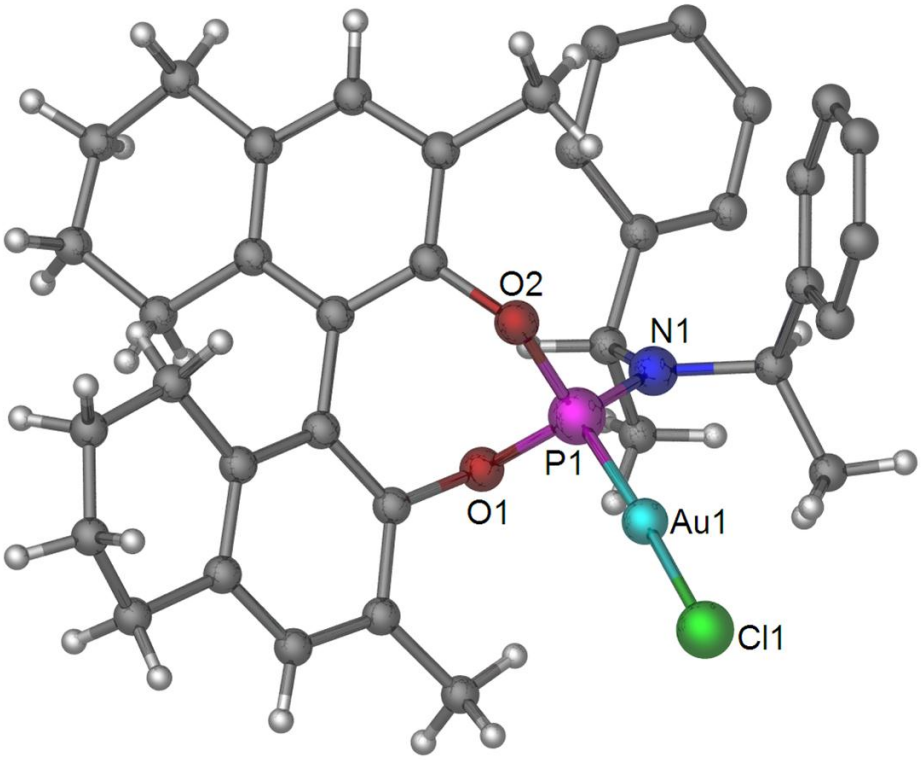
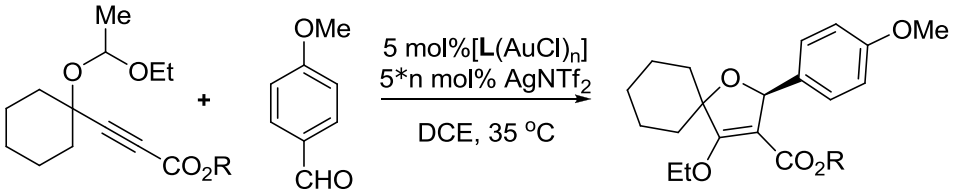


Table S1. Additionally Screened Reaction Conditions[a]:



Entry	Ligand(5% mol)	$AgNTf_2$(mol%)	Yield (%)	Ee %
1	(*R*)–MeO-BIPHEP	10	61	14.1
2	(*S*)-SEGPHOS	10	49	13.1
3	(*R*)-MeO-XylBIPHEP	10	65	47
4	(*R*)-MeO-XylBIPHEP	AgOTf (10)	16	48
5	(*R*)-MeO-XylBIPHEP	$AgSbF_6$ (10)	45	46
6	(*R*)-MeO-DTF-BIPHEP	10	52	39
7	(*R*)-MeO-TF-BIPHEP	10	53	42
8	(*R*)-MeO-DTBM-BIPHEP	10	31	65
9	(S)-MOP	10	50	40
10	(*S*)-Bn-MOP	10	53	34
11	(*R*)-DTBM-SEGPHOS	10	20	31
12	(*S, R, R*)-**4a**	5	48	68
13	(*R*)-MeO-DTF-O-BIPHEP	10	56	45
14[b]	(*S,R,R*)-**5a**	AgOTf	39	81
15[b]	(*S,R,R*)-**5a**	$AgSbF_6$	50	88
16[b]	(*S,R,R*)-**5a**	$AgOC_4F_7$	--	--
17[b]	(*S,R,R*)-**5a**	$AgBF_4$	46	88
18[b]	(*S,R,R*)-**5a**	$AgBAr_4$[c]	17	91

[a] General conditions: substrate **1a** (0.4 mmol, 1 equiv), anisaldehyde **2a** (2 equiv) and $LAu_n(NTf_2)_n$, (5*n mol% $AgNTf_2$, n= 1 or 2) in 8 mL solvent at 25 °C for 1h. Isolated yields are shown, unless otherwise noted. [b] Reaction performed at 0 °C. [c] Ar = 3,5-$CF_3C_6H_3$.

General Procedure for asymmetric gold-catalyzed cycloaddition

After the solution of ligand (5.0 mol %) and Me_2SAuCl (5 mol %) in $CH_2Cl_2$was stirred at rt for 2 h, the solvent was removed in vacuum. Then a solution of $AgNTf_2$ (5 mol %) in DCM (1 mL) was added to the residue and the mixture was stirred at 0 °C for 15 min. The above catalyst solution then was added to the solution of alkyne **1** (0.4 mmol) and aldehyde **2** (0.8 mmol) with 150 mg 3Å MS in DCM (7 mL) at 0 °C. The reaction was determined by TLC, after the less component was consumed, the solution was removed under reduced pressure. The diastereomeric ratio was determined by crude ^1H NMR, the resulting crude mixture was purified by flash column chromatography on silica gel to afford product. The enantiomeric excesses of the products were determined by chiral stationary phase HPLC using a Chiralpak IC, AD-H, AD-3 and Chiralcel OZ-3.

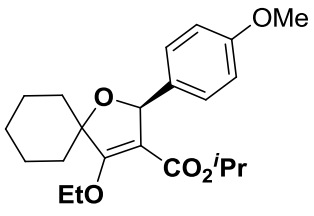
General Procedure **A**: (*S*,*R*,*R*)-**5a** used as the ligand.

General Procedure **B**: (*R*,*R*,*R*)-**5b** used as the ligand.

General Procedure **C** :(***R***)-MeO-DTBM-BIPHEP as the ligand, Me_2SAuCl (10 mol %).

General Procedure **D** :(***S***)-MeO-DTBM-BIPHEP as the ligand, Me_2SAuCl (10 mol %).

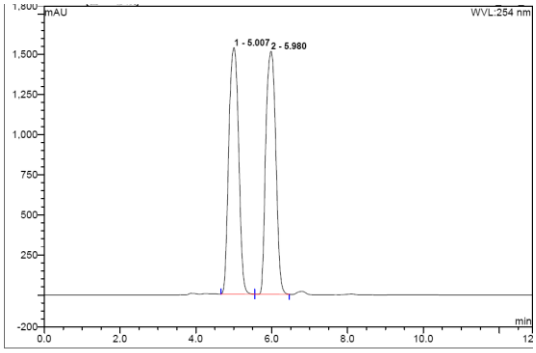
Characterization Data for New Compounds:



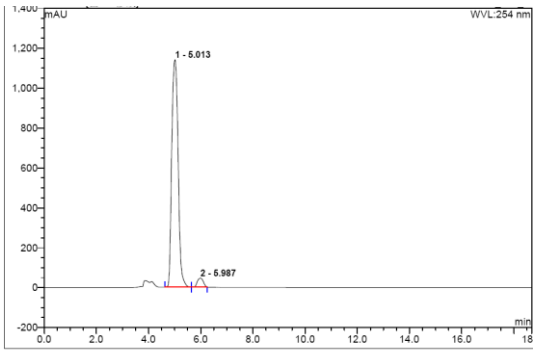
3aa

1. (*S*)-isopropyl 4-ethoxy-2-(4-methoxyphenyl)-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 73% yield; 93% ee; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.74(s, 1H), 4.81 -4.73 (m, 1H), 4.68-4.59 (m, 1H), 4.25-4.16 (m, 1H), 3.77 (s, 3H), 1.75-1.57 (m, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.29-1.20 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H), 0.76 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.47, 163.30, 159.29, 134.63, 129.19, 113.30, 102.76, 85.71, 83.59, 69.65, 67.20, 55.19, 34.86, 33.48, 24.99, 21.88, 21.70, 21.45, 21.01, 15.19; **MS** (EI): m/z (%): 374 (M^+, 36.12); 285 (100), **HRMS** calcd for $C_{22}H_{30}O_5$: 374.2093, found: 374.2094. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 5.01 min, minor enantiomer tr = 5.99 min.

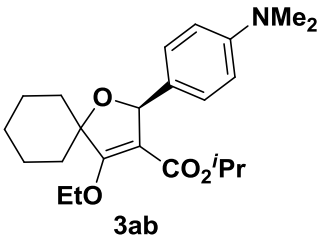


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.01	n.a.	1536.548	462.394	50.14	n.a.	BM *
2	5.98	n.a.	1515.082	459.745	49.86	n.a.	MB*
总和:			3051.630	922.139	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.01	n.a.	1139.478	321.807	96.48	n.a.	BM *
2	5.99	n.a.	44.474	11.724	3.52	n.a.	MB*
总和:			1183.952	333.531	100.00	0.000	

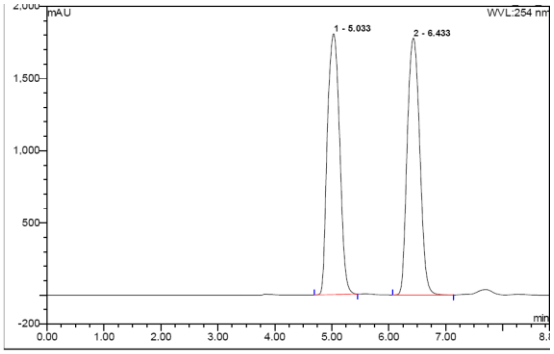
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.01	462.394	50.14	1	5.01	321.807	96.48
2	5.98	459.745	49.86	2	5.99	11.724	3.52



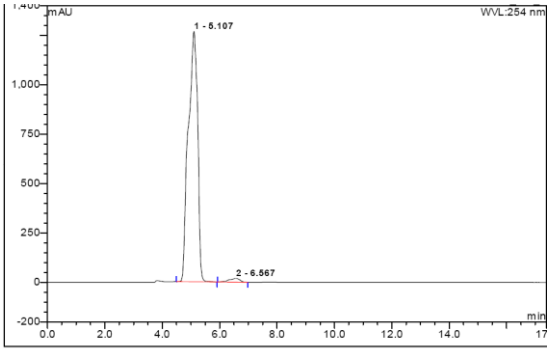
3ab

2. (*S*)-isopropyl 2-(4-(dimethylamino)phenyl)-4-ethoxy-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 65% yield; 97% ee; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 5.71 (s, 1H), 4.81-4.74 (m, 1H), 4.66-4.58 (m, 1H), 4.23-4.14 (m, 1H), 2.90 (s, 6H), 1.75-1.58 (m, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.26-1.17 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H), 0,79 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.19, 163.58, 150.56, 130.52, 128.82, 112.33, 103.09, 85.46, 83.83, 69.54, 67.17, 40.76, 34.94, 33.58, 25.09, 21.95, 21.77, 21.52, 21.10, 15.23; **MS** (EI): m/z (%): 387 (M^+, 63.19); 148 (100), **HRMS** calcd for $C_{23}H_{33}NO_4$: 387.2410, found: 387.2412. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 5.11 min, minor enantiomer tr = 6.57 min.

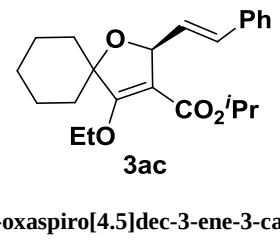


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.03	n.a.	1806.649	448.955	49.94	n.a.	BMB
2	6.43	n.a.	1778.375	450.046	50.06	n.a.	BMB
总和:			3585.024	899.001	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.11	n.a.	1268.016	480.124	98.38	n.a.	BMB
2	6.57	n.a.	18.627	7.886	1.62	n.a.	BMB
总和:			1286.642	488.010	100.00	0.000	

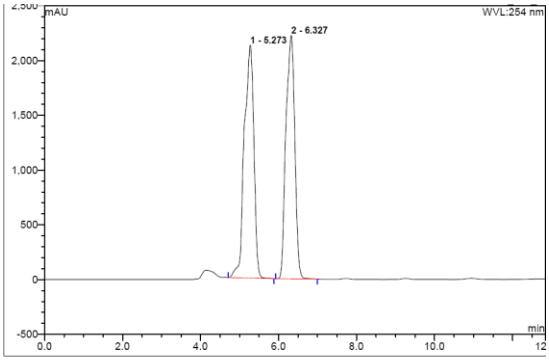
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.03	448.955	49.94	1	5.11	480.124	98.38
2	6.43	450.046	50.06	2	6.57	7.886	1.62

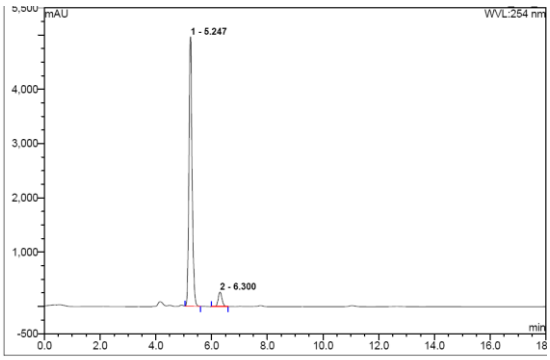


3ac

3. (*S*,*E*)-isopropyl 4-ethoxy-2-styryl-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 73% yield; 88% ee; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.31-7.23 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.18 (dd, *J* = 15.6 Hz, 7.2 Hz, 1H), 5.43 (d, *J* = 7.2 Hz, 1H), 5.10-4.95 (m, 1H), 4.60-4.48 (m, 1H), 4.40-4.29 (m, 1H), 1.70-1.59 (m, 10H), 1.31 (t, *J* = 7.2 Hz, 3H), 2.24 (d, *J* = 6.0 Hz, 3H), 1.15 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ 167.78, 163.12, 136.98, 131.45, 130.86, 128.42, 127.43, 126.57, 101.28, 86.22, 82.86, 70.08, 67.45, 35.30, 34.19, 25.00, 21.95, 21.80, 21.72, 21.66, 15.31; **MS** (EI): m/z (%): 370 (M^+, 4.40); 128 (100), **HRMS** calcd for $C_{23}H_{30}O_4$: 370.2144, found: 370.2142. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 5.25 min, minor enantiomer tr = 6.30 min.

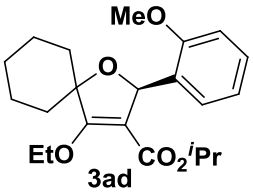




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.27	n.a.	2127.484	604.919	50.82	n.a.	BMB
2	6.33	n.a.	2221.742	585.406	49.18	n.a.	BMB
总和:			4349.226	1190.325	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.25	n.a.	4962.726	650.177	93.90	n.a.	BMB
2	6.30	n.a.	267.614	42.266	6.10	n.a.	BMB
总和:			5230.340	692.442	100.00	0.000	

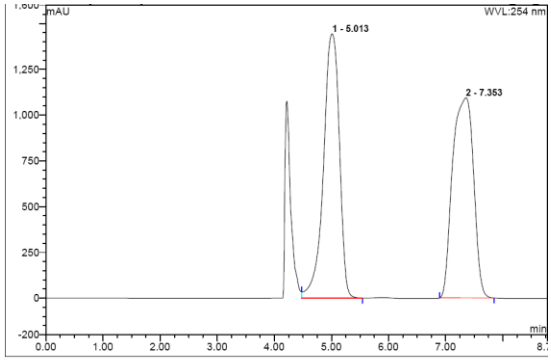
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.27	604.919	50.82	1	5.25	650.177	93.90
2	6.33	585.325	49.18	2	6.30	42.266	6.10

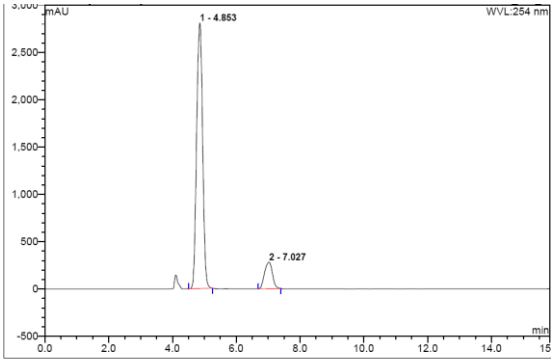


3ad

4. (*S*)-isopropyl 4-ethoxy-2-(2-methoxyphenyl)-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 71% yield; 77% ee; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 1H), 7.23-7.18 (m, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.35 (s, 1H), 4.80-4.60 (m, 2H), 4.28-4.19 (s, 1H), 3.84 (s, 3H), 1.80-1.55 (m, 10H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.64 (d, *J* = 6.0 Hz, 3H)； **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.90, 163.23, 157.57, 128.77, 128.73, 120.56, 110.45, 102.64, 96.40, 85.65, 75.99, 69.73, 66.93, 55.37, 34.70, 33.43 25.04, 25.01, 21.91, 21.59, 21.43, 20.71； **MS** (EI): m/z (%): 374 (M^+, 33.22); 285 (100), **HRMS** calcd for $C_{22}H_{30}O_5$: 374.2093, found: 374.2094. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 4.85 min, minor enantiomer tr = 7.03 min.

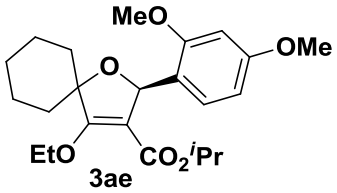




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.01	n.a.	1443.702	466.764	50.02	n.a.	MB*
2	7.35	n.a.	1093.314	466.454	49.98	n.a.	BMB*
总和:			2537.016	933.219	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	4.85	n.a.	2807.758	611.826	88.45	n.a.	BMB*
2	7.03	n.a.	280.354	79.895	11.55	n.a.	BMB*
总和:			3088.113	691.721	100.00	0.000	

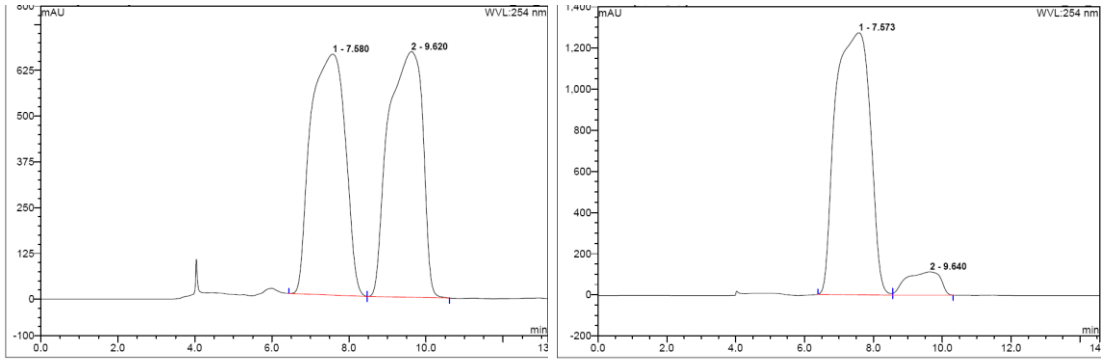
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.01	466.764	50.02	1	4.85	611.826	88.45
2	7.35	466.016	49.98	2	7.03	79.895	11.55



3ae

5. (*S*)-isopropyl 2-(2,4-dimethoxyphenyl)-4-ethoxy-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

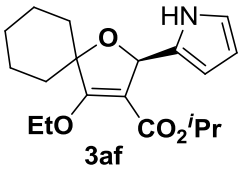
Prepared according to the general procedure **A**: 78% yield; 84% ee; white solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 6.40 (s, 1H), 6.25 (s, 1H), 4.79-4.72 (m, 1H), 4.68-4.60 (m, 1H), 4.25-4.17 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 1.74-1.57 (m, 9H), 1.32 (t, *J* = 6.4 Hz, 3H), 1.60-1.90 (m, 1H), 1.09 (d, *J* = 5.6 Hz, 3H), 0.71 (d, *J* = 5.6 Hz, 3H)； **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.53, 163.36, 160.33, 158.55, 129.50, 123.40, 104.44, 102.70, 98.01, 85.34, 75.85, 69.58, 66.90, 55.28, 55.24, 34.72, 33.38, 25.02, 21.89, 21.61, 21.42, 20.86, 15.19； **MS** (EI): m/z (%): 404 (M^+, 14.87; 165 (100), **HRMS** calcd for $C_{23}H_{32}O_6$: 404.2199, found: 404.2200. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 7.57 min, minor enantiomer tr = 9.64 min.



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.58	n.a.	658.031	682.750	49.76	n.a.	BMb*
2	9.62	n.a.	670.782	689.300	50.24	n.a.	bMB*
总和:			1328.813	1372.050	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.57	n.a.	1273.759	1485.704	92.02	n.a.	BM *
2	9.64	n.a.	113.257	128.760	7.98	n.a.	MB*
总和:			1387.016	1614.464	100.00	0.000	

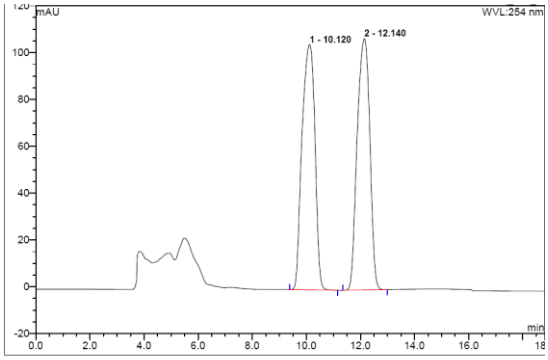
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	7.58	82.750	49.76	1	7.57	1485.704	92.02
2	9.62	689.300	50.24	2	9.64	128.760	7.98

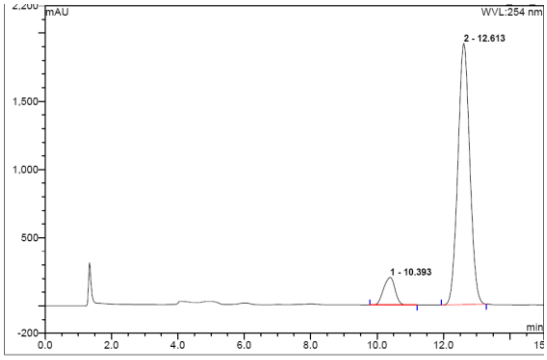


3af

6. (*R*)-isopropyl 4-ethoxy-2-(1H-pyrrol-2-yl)-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 71% yield; 82% ee; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 6.70-6.68 (m, 1H), 6.15-6.13 (m, 1H), 6.11-6.08 (m, 1H), 5.88 (s, 1H), 4.95-4.87 (m, 1H), 4.57-4.49 (m, 1H), 4.31-4.22 (m, 1H), 1.69-1.59 (m, 10H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.18(d, *J* = 6.0 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.75, 163.54, 132.87, 117.27, 108.12, 106.89, 101.45, 85.79, 77.44, 70.06, 67.72, 34.97, 33.70, 25.00, 21.80, 21.63, 21.28, 15.29; **MS** (EI): m/z (%): 333 (M^+, 54.27); 244 (100), **HRMS** calcd for $C_{19}H_{27}NO_4$: 333.1940, found: 333.1938. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); minor enantiomer tr = 10.39 min, major enantiomer tr = 12.61 min.

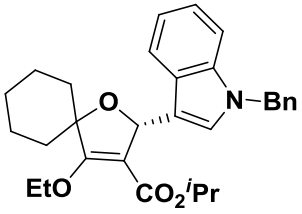




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	10.12	n.a.	104.835	57.915	49.93	n.a.	BMB
2	12.14	n.a.	107.390	58.085	50.07	n.a.	BMB
总和:			212.225	116.000	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	10.39	n.a.	201.909	80.923	9.24	n.a.	BMB
2	12.61	n.a.	1914.442	794.523	90.76	n.a.	BMB
总和:			2116.351	875.446	100.00	0.000	

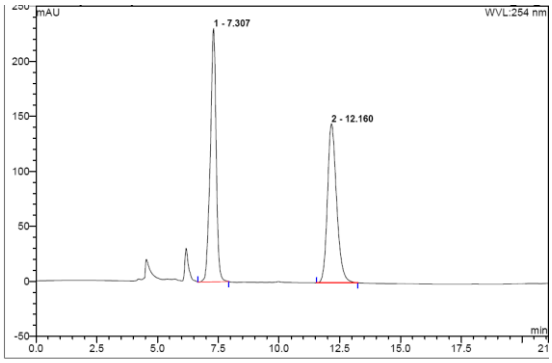
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	10.12	57.915	49.93	1	10.39	80.923	9.24
2	12.14	58.085	50.07	2	12.61	794.446	90.76

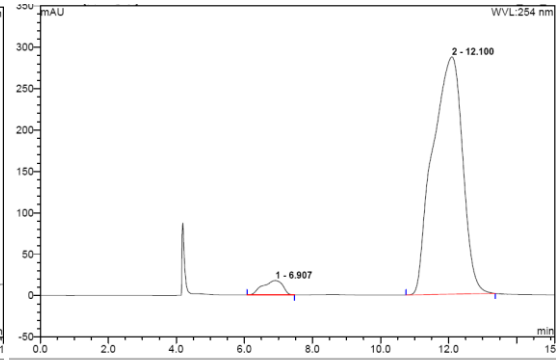


3ag

7. (*R*)-isopropyl 2-(1-benzyl-1H-indol-3-yl)-4-ethoxy-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **B**: 62% yield; 92% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.28-7.19 (m, 4H), 7.14-7.05 (m, 5H), 6.13 (s, 1H), 5.23 (s, 2H), 4.75-4.64 (m, 2H), 4.22-4.17 (m, 1H), 1.84-1.51 (m, 9H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.22-1.18 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.53 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 163.77, 137.42, 136.89, 128.59, 127.63, 127.50, 127.28, 126.90, 121.57, 120.32, 119.21, 116.72, 109.46, 102.54, 85.25, 76.79, 69.51, 67.01, 49.96, 34.25, 33.19, 25.05, 21.97, 21.57, 20.85, 15.26; **MS** (EI): m/z (%): 473 (M^+, 27.93); 91 (100), **HRMS** calcd for $C_{30}H_{35}NO_4$: 473.2566, found: 473.2568. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (98:2 hexane: 2-propanol, 0.8 mL/min, 254 nm); minor enantiomer tr = 6.91 min, major enantiomer tr = 12.10 min.

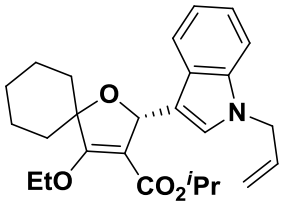




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.31	n.a.	230.234	63.927	50.33	n.a.	BMB*
2	12.16	n.a.	144.547	63.086	49.67	n.a.	BMB*
总和:			374.781	127.013	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	6.91	n.a.	17.190	11.685	3.85	n.a.	BMB*
2	12.10	n.a.	286.610	291.995	96.15	n.a.	BMB*
总和:			303.800	303.680	100.00	0.000	

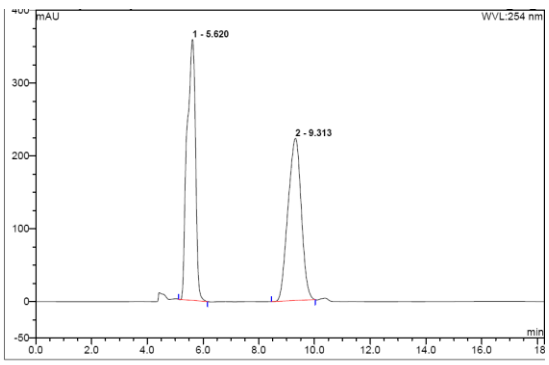
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	7.31	63.927	50.33	1	6.91	11.685	3.85
2	12.16	63.0086	49.67	2	12.10	291.995	96.15

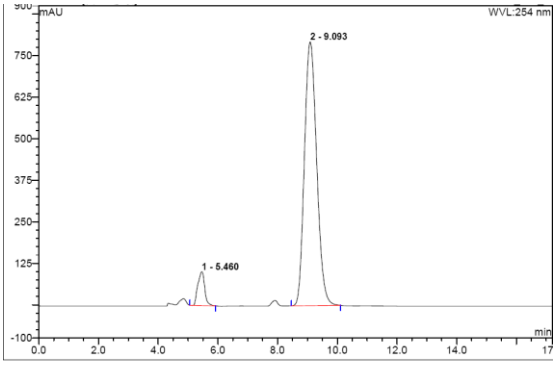


3ah

8. (*R*)-isopropyl 2-(1-allyl-1H-indol-3-yl)-4-ethoxy-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **B**: 70% yield; 87% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 1H), 7.17-7.12 (m, 1H), 7.08-7.04 (m, 2H), 6.13 (s, 1H), 5.98-5.89 (m, 1H), 5.16 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.10 (dd, *J* = 16.8, 1.2 Hz, 1H), 4.76-4.63 (m, 4H), 4.23-4.16 (m, 1H), 1.84-1.52 (m, 9H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.26-1.17 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.57 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.87, 163.78, 136.65, 133.40, 127.28, 127.21, 121.34, 120.24, 119.07, 117.22, 116.30, 109.33, 102.57, 85.20, 76.77, 69.47, 66.96, 48.73, 34.21, 33.10, 25.03, 21.95, 21.57, 21.55, 20.82, 15.23; **MS** (EI): m/z (%): 423 (M^+, 100.00); 423 (100), **HRMS** calcd for $C_{26}H_{33}NO_4$: 423.2410, found: 423.2411. Enantiomeric excess was determined by HPLC with a Chiralcel OZ-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); minor enantiomer tr = 5.46 min, major enantiomer tr = 9.09 min.

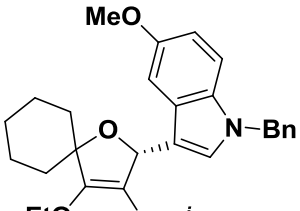




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.62	n.a.	358.380	125.706	50.63	n.a.	BMB*
2	9.31	n.a.	222.790	122.579	49.37	n.a.	BMB*
总和:			581.170	248.284	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.46	n.a.	101.991	27.007	6.68	n.a.	BMB*
2	9.09	n.a.	793.902	377.244	93.32	n.a.	BMB*
总和:			895.893	404.250	100.00	0.000	

#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.62	1256.7	50.63	1	5.46	27.007	6.68
2	9.31	125.579	49.37	2	9.09	377.244	93.32

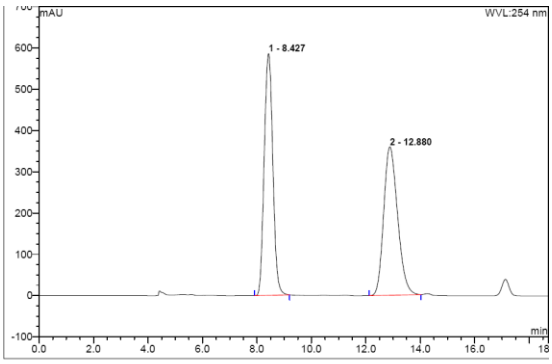


3ai

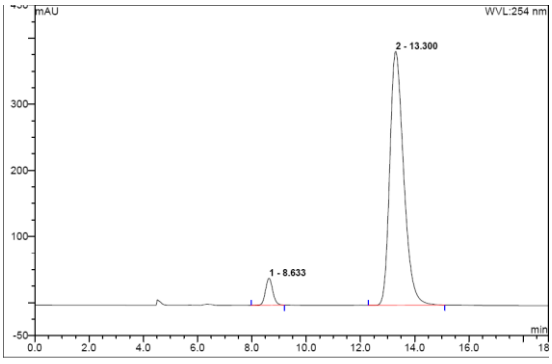
9. (*R*)-isopropyl 2-(1-benzyl-5-methoxy-1H-indol-3-yl)-4-ethoxy-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **B**: 63% yield; 90% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 4H), 7.10-7.06 (m, 4H), 6.78 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.11 (s, 1H), 5.19 (s, 2H), 4.77-4.61 (m, 2H), 4.25-4.18 (m, 1H), 3.82 (s, 3H), 1.85-1.54 (m, 9H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.26-1.17 (m, 1H), 1.01 (d, *J* = 6.0 Hz, 3H), 0.57 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.85, 163.71, 153.61, 137.44, 132.08, 128.53, 128.17, 127.63, 127.44, 126.76, 116.06, 111.69, 110.20, 102.39, 102.02, 85.15, 76.76, 69.50, 67.00, 55.66, 50.10,

34.27, 33.11, 25.00, 21.92, 21.58, 21.53, 20.87, 15.24; **MS** (EI): m/z (%): 503 (M^+, 45.85); 91 (100), **HRMS** calcd for $C_{31}H_{37}NO_5$: 503.2672, found: 503.2670. Enantiomeric excess was determined by HPLC with a Chiralecl OZ-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); minor enantiomer tr = 8.63 min, major enantiomer tr = 13.30 min.

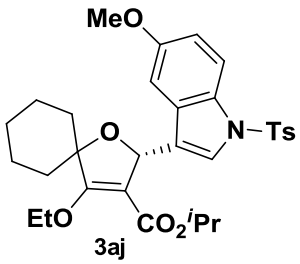


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	8.43	n.a.	585.861	214.797	50.28	n.a.	BMB
2	12.88	n.a.	359.585	212.417	49.72	n.a.	BMB*
总和:			945.446	427.214	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	8.63	n.a.	40.747	12.625	5.26	n.a.	BMB
2	13.30	n.a.	384.062	227.588	94.74	n.a.	BMB*
总和:			424.809	240.213	100.00	0.000	

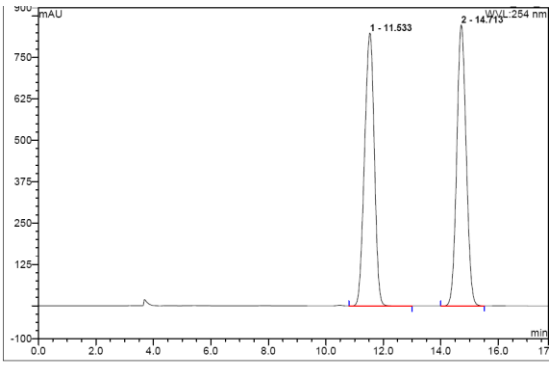
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	8.43	214.797	50.28	1	8.63	12.625	5.26
2	12.88	212.417	49.72	2	13.30	227.588	94.74

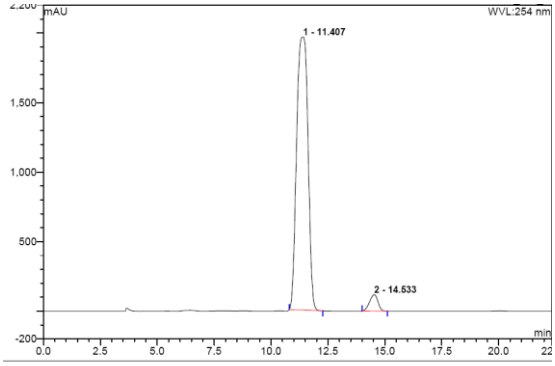


3aj

10. (*R*)-isopropyl 4-ethoxy-2-(5-methoxy-1-tosyl-1H-indol-3-yl)-1-oxaspiro[4.5]dec-3-ene-3-carboxylate.

Prepared according to the general procedure **B**: 62% yield; 92% ee; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H),7.45 (s, 1H), 7.21-7.15 (m, 3H), 6.89 (dd, *J* = 9.2, 2.4 Hz, 1H), 5.99 (s, 1H), 4.75-4.63 (m, 2H), 4.33-4.28 (m, 1H), 3.80 (s, 3H), 2.33 (s, 3H), 1.74-1.44 (m, 9H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.21-1.17 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.51 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.23, 162.95, 155.99, 144.71, 135.30, 130.68, 129.97, 129.74, 126.77, 125.59, 124.09, 114.24, 113.56, 103.09, 100.97, 86.07, 76.05, 70.12, 67.24, 55.56, 34.23, 33.23, 24.91, 21.81, 21.62, 21.52, 20.83, 15.30;**MS** (EI): m/z (%): 567 (M^+, 48.82); 91 (100), **HRMS** calcd for $C_{31}H_{37}NO_7S$: 567.2291, found: 567.2294. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 11.41 min, minor enantiomer tr = 14.53 min.

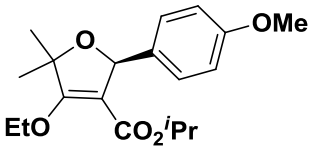




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	11.53	n.a.	824.586	324.602	50.11	n.a.	BMB
2	14.71	n.a.	848.948	323.181	49.89	n.a.	BMB
总和:			1673.534	647.783	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	11.41	n.a.	1964.851	1137.756	95.83	n.a.	BMB
2	14.53	n.a.	117.359	49.506	4.17	n.a.	BMB
总和:			2082.210	1187.263	100.00	0.000	

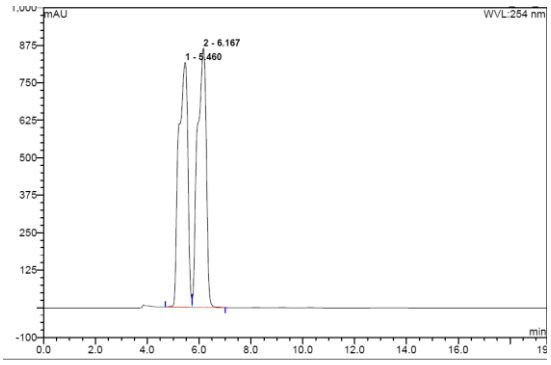
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	11.53	324.602	50.11	1	11.41	1137.756	95.83
2	14.71	323.181	49.89	2	14.53	49.506	4.17

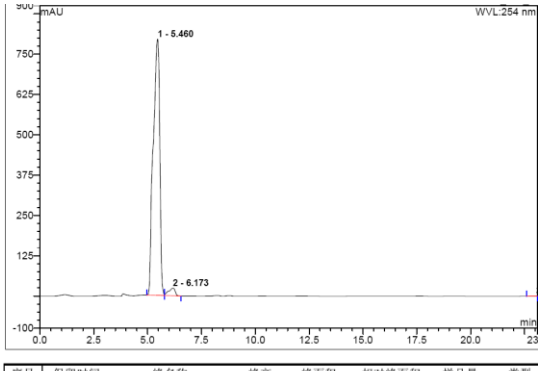


3fa

11. (*S*)-isopropyl 4-ethoxy-2-(4-methoxyphenyl)-5,5-dimethyl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **A**: 68% yield; 94% ee; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.76 (s, 1H), 4.83-4.72 (m,1H), 4.71-4.63 (m, 1H), 4.29-4.20 (m, 1H), 3.77 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H), 7.40 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.30, 163.14, 159.37, 134.23, 129.00, 113.42, 102.05, 84.56, 83.63, 69.66, 67.24, 55.17, 26.67, 25.63, 21.66, 20.95, 15.12; **MS** (EI): m/z (%): 334 (M^+, 15.26); 245 (100), **HRMS** calcd for $C_{19}H_{26}O_5$: 334.1780, found: 334.1777. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column 95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 5.46 min, minor enantiomer tr = 6.17 min.

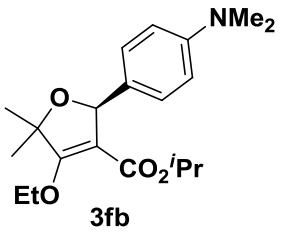




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.46	n.a.	816.402	330.941	49.45	n.a.	BM
2	6.17	n.a.	864.358	338.316	50.55	n.a.	MB
总和:			1680.761	669.257	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.46	n.a.	794.876	280.132	97.13	n.a.	BM
2	6.17	n.a.	23.817	8.255	2.86	n.a.	MB
3	23.03	n.a.	0.053	0.030	0.01	n.a.	BMB
总和:			818.745	288.416	100.00	0.000	

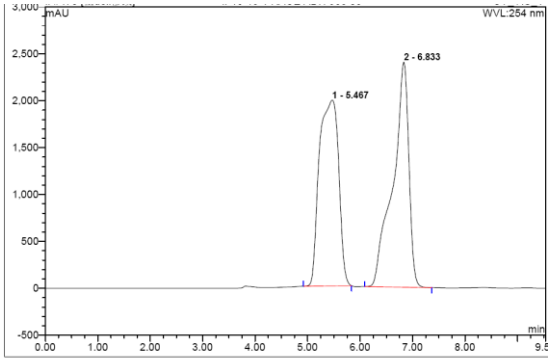
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.46	330.941	49.45	1	5.46	280.132	97.13
2	6.17	338.316	50.55	2	6.17	8.255	2.86

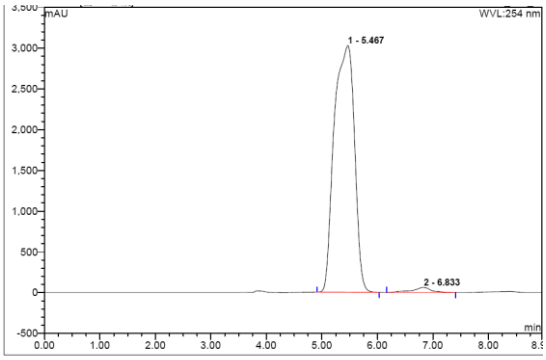


3fb

12. (*S*)-isopropyl 2-(4-(dimethylamino)phenyl)-4-ethoxy-5,5-dimethyl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **A**: 82% yield; 96% ee; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.8, 1.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.73 (s, 1H), 4.83-4.73 (m, 1H), 4.71-4.62 (m, 1H), 4.27-4.18 (m, 1H), 2.90 (s, 6H), 1.41 (s, 3H), 1.38 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 3H), 0.76 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.93, 163.36, 150.55, 130.02, 128.56, 112.34, 102.29, 84.25, 83.84, 69.49, 67.15, 40.66, 26.72, 25.68, 21.69, 21.00, 15.12; **MS** (EI): m/z (%): 347 (M^+, 47.04); 258 (100), **HRMS** calcd for $C_{20}H_{29}NO_4$: 347.2097, found: 347.2094. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 5.47 min, minor enantiomer tr = 6.83 min.

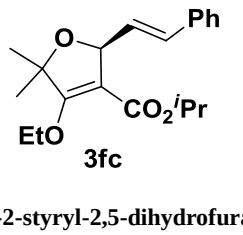




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.47	n.a.	1981.971	847.307	49.96	n.a.	BMB*
2	6.83	n.a.	2401.066	848.678	50.04	n.a.	BMB*
总和:			4383.036	1695.986	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.47	n.a.	3026.156	1282.553	98.13	n.a.	BMB*
2	6.83	n.a.	63.036	24.404	1.87	n.a.	BMB
总和:			3089.192	1306.957	100.00	0.000	

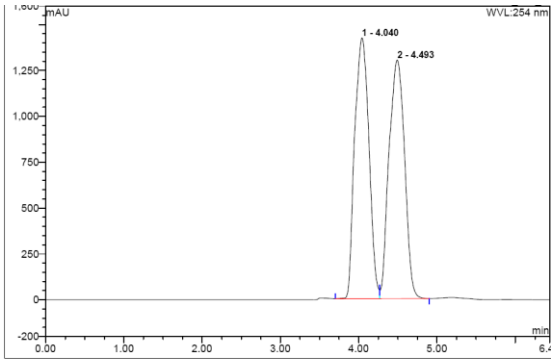
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.47	847.307	59.96	1	5.47	1282.553	98.13
2	6.83	848.678	50.04	2	6.83	24.404	1.87

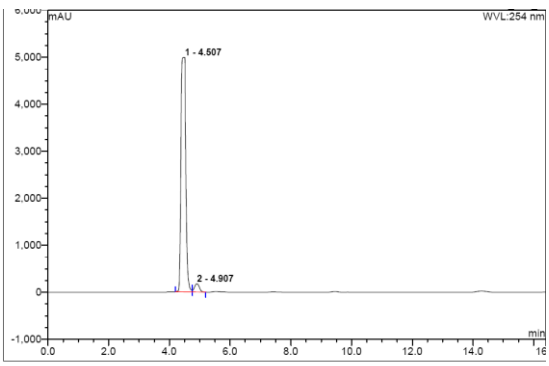


3fc

13. (*S*,*E*)-isopropyl 4-ethoxy-5,5-dimethyl-2-styryl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **A**: 66% yield; 93% ee; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.32-7.26 (m, 2H), 7.24-7.19 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H) 6.19 (dd, *J* = 16.0, 7.6 Hz, 1H), 5.44 (d, *J* = 7.6 Hz, 1 H), 5.03-4.90 (m, 1H), 4.60-4.50 (m, 1H), 4.39-4.30 (m, 1H), 1.42 (s, 3H), 1.37 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.15 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.48, 163.05, 136.90, 131.88, 130.40, 128.45, 127.52, 126.59, 101.01, 85.01, 82.83, 70.05, 67.54, 27.23, 26.19, 21.96, 21.80, 15.27; **MS** (EI): m/z (%): 330 (M^+, 6.49); 128 (100), **HRMS** calcd for $C_{20}H_{26}O_4$: 330.1830, found: 330.1831. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 4.51 min, minor enantiomer tr = 4.91 min.

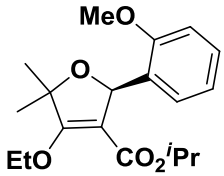




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	4.04	n.a.	1421.543	300.042	49.95	n.a.	BM
2	4.49	n.a.	1300.796	300.588	50.05	n.a.	MB
总和:			2722.339	600.629	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	4.51	n.a.	4992.306	916.162	96.51	n.a.	BM
2	4.91	n.a.	175.166	33.110	3.49	n.a.	MB
总和:			5167.472	949.272	100.00	0.000	

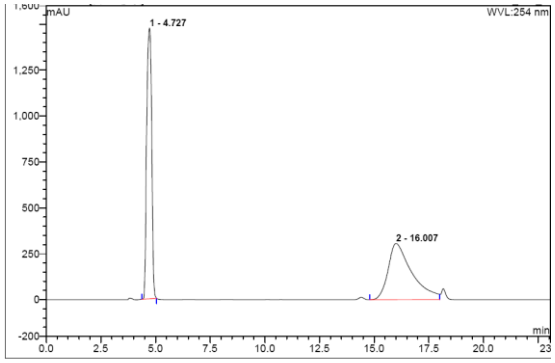
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	4.04	300.042	49.95	1	4.51	916.162	96.51
2	4.49	300.588	50.05	2	4.91	33.110	3.49

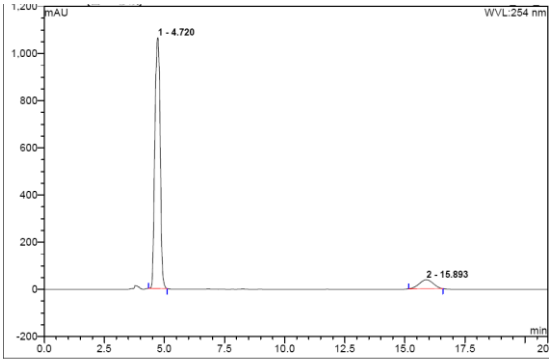


3fd

14. (*S*)-isopropyl 4-ethoxy-2-(2-methoxyphenyl)-5,5-dimethyl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **A**: 65% yield; 83% ee; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.19 (m, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H). 6.36 (s, 1H), 4.81-4.65 (m, 2H), 4.35-4.26 (m, 1H), 3.84 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 6.4 Hz, 3H), 0.65 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.71, 163.12, 157.67, 130.27, 128.95, 128.38, 120.58, 110.55, 101.68, 84.74, 76.50, 69.86, 67.08, 55.47, 26.60, 25.82, 21.66, 20.77, 15.24; **MS** (EI): m/z (%): 334 (M^+, 13.32); 245 (100), **HRMS** calcd for $C_{19}H_{26}O_5$: 334.1780, found: 334.1777. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 4.72 min, minor enantiomer tr = 15.89 min.

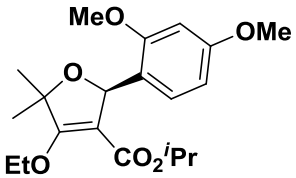




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	4.73	n.a.	1474.556	391.860	50.54	n.a.	BMB*
2	16.01	n.a.	306.082	383.528	49.46	n.a.	BM *
总和:			1780.638	775.388	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	4.72	n.a.	1063.940	275.350	91.44	n.a.	BMB*
2	15.89	n.a.	38.257	25.768	8.56	n.a.	BMB*
总和:			1102.197	301.118	100.00	0.000	

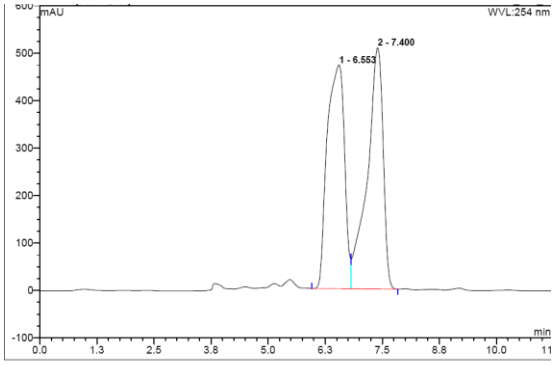
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	4.73	391.860	50.54	1	4.72	275.350	91.44
2	16.01	383.528	49.46	2	15.89	25.768	8.56

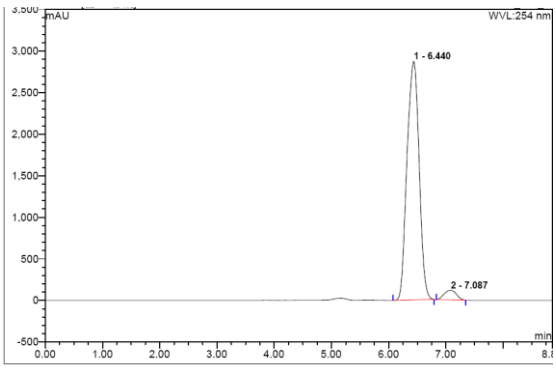


3fe

15. (*S*)-isopropyl 2-(2,4-dimethoxyphenyl)-4-ethoxy-5,5-dimethyl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **A**: 78% yield; 92% ee; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.46-6.40 (m, 2H), 6.27 (s, 1H), 4.81-4.63 (m, 2H), 4.32-4.23 (m, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 1.38 (s, 6H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.72 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.34, 163.26, 160.51, 158.69, 129.12, 123.03, 104.42, 101.75, 98.18, 84.43, 76.35, 69.72, 67.07, 55.42, 55.31, 26.62, 25.78, 21.68, 20.94, 15.21; **MS** (EI): m/z (%): 364 (M^+, 7.22); 165 (100), **HRMS** calcd for $C_{20}H_{28}O_6$: 364.1886, found: 364.1885. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 6.44 min, minor enantiomer tr = 7.09 min.

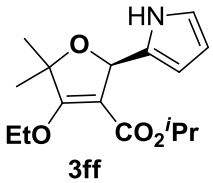




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	6.55	n.a.	472.046	207.182	50.30	n.a.	BM
2	7.40	n.a.	508.606	204.716	49.70	n.a.	MB*
总和:			980.652	411.898	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	6.44	n.a.	2869.144	701.798	96.14	n.a.	BMB*
2	7.09	n.a.	113.166	28.172	3.86	n.a.	BMB*
总和:			2982.310	729.969	100.00	0.000	

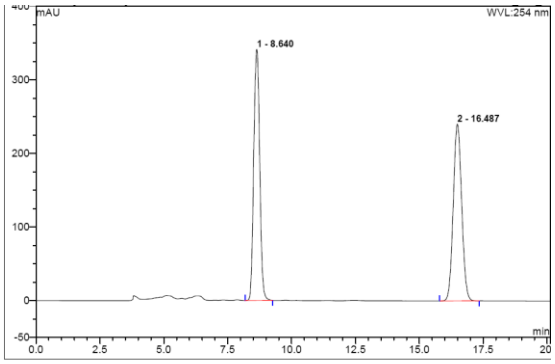
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	6.55	207.182	50.30	1	6.44	701.798	96.14
2	7.40	204.898	49.70	2	7.09	28.172	3.86

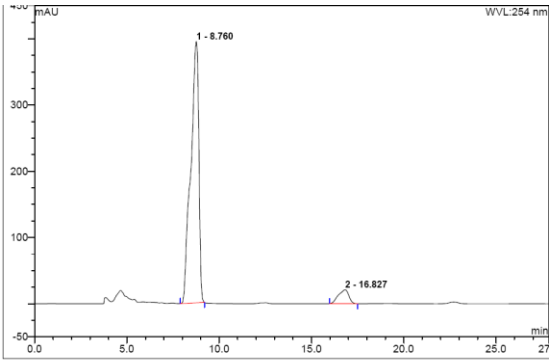


3ff

16. (*R*)-isopropyl 4-ethoxy-5,5-dimethyl-2-(1H-pyrrol-2-yl)-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **A**: 70% yield; 87% ee; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 6.69-6.66 (m, 1H), 6.15-6.12 (m, 1H), 6.11-6.07 (m, 1H), 5.89 (s, 1H), 4.93-4.86 (m, 1H), 4.63-4.54 (m, 1H), 4.32-4.24 (m, 1H), 1.39 (s, 3H), 1.37 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.44, 163.36, 132.34, 117.41, 108.15, 107.01, 100.73, 84.57, 77.28, 69.92, 67.68, 26.83, 25.75, 21.72, 21.14, 15.16; **MS** (EI): m/z (%): 293 (M^+, 21.83); 204 (100), **HRMS** calcd for $C_{16}H_{23}O_4$: 293.1627, found: 293.1626. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 8.76 min, minor enantiomer tr = 16.83 min.

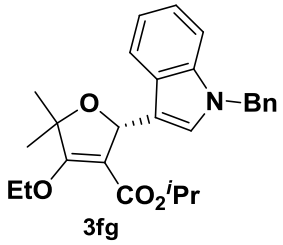




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	8.64	n.a.	341.149	92.220	50.06	n.a.	BMB*
2	16.49	n.a.	240.353	92.005	49.94	n.a.	BMB*
总和:			581.502	184.225	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	8.76	n.a.	394.527	199.618	93.59	n.a.	BMB
2	16.83	n.a.	21.012	13.661	6.41	n.a.	BMB*
总和:			415.539	213.279	100.00	0.000	

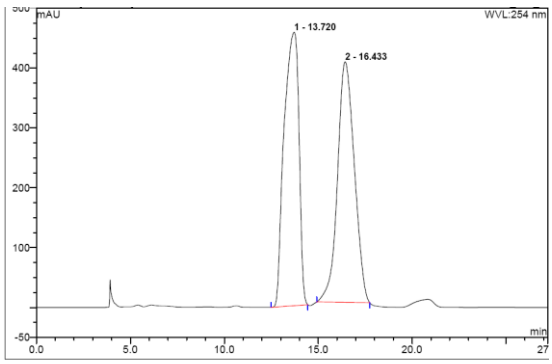
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	8.64	92.220	50.06	1	8.76	199.618	93.59
2	16.94	92.005	49.94	2	16.83	13.661	6.41

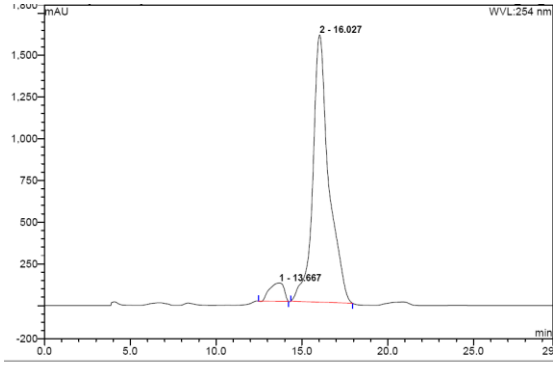


3fg

17. (*R*)-isopropyl 2-(1-benzyl-1H-indol-3-yl)-4-ethoxy-5,5-dimethyl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **B**: 84% yield; 88% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.28-7.19 (m, 4H), 7.16-7.05 (m, 5H), 6.16 (s, 1H), 5.24 (s, 2H), 4.77-4.66 (m, 2H), 4.27-4.18 (m, 1H), 1.44 (s, 3H), 1.42 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.0 Hz, 3H), 0.55 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.66, 163.62, 137.38, 136.93, 128.60, 127.58, 127.50, 127.11, 126.82, 121.67, 120.04, 119.36, 116.34, 109.52, 101.92, 84.10, 76.83, 69.53, 67.12, 49.94, 26.28, 25.48, 21.58, 20.85, 15.21; **MS** (EI): m/z (%): 433 (M^+, 27.23); 91 (100), **HRMS** calcd for $C_{27}H_{31}NO_4$: 433.2253, found: 433.2253. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane: 2-propanol, 0.8 mL/min, 254 nm); minor enantiomer tr = 13.67 min, major enantiomer tr = 16.03 min.

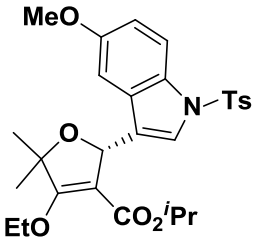




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	13.72	n.a.	456.835	417.436	49.97	n.a.	BMB*
2	16.43	n.a.	401.853	417.894	50.03	n.a.	BMB*
总和:			858.688	835.330	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	13.67	n.a.	108.645	106.770	5.80	n.a.	BMB*
2	16.03	n.a.	1602.239	1734.863	94.20	n.a.	BMB*
总和:			1710.884	1841.633	100.00	0.000	

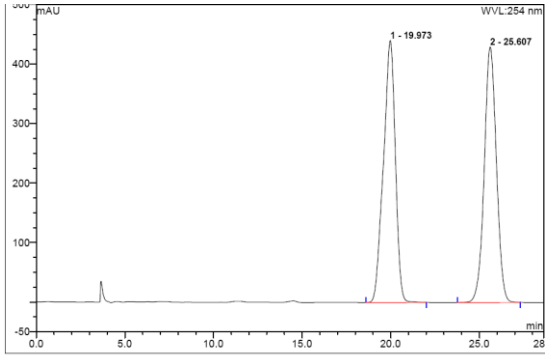
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	13.72	417.436	49.97	1	13.67	106.770	5.80
2	16.43	417.894	50.03	2	16.03	1734.863	94.20

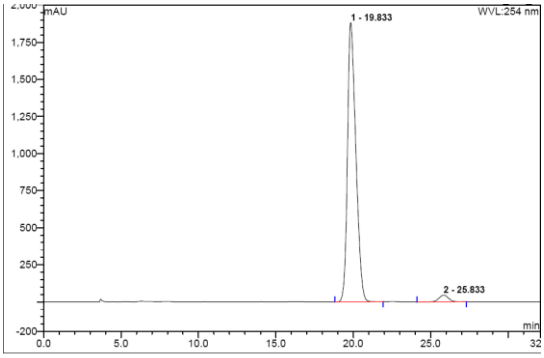


3fj

18. (*R*)-isopropyl 4-ethoxy-2-(5-methoxy-1-tosyl-1H-indol-3-yl)-5,5-dimethyl-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **B**: 82% yield; 95% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.01 (s, 1H), 4.77-4.66 (m, 2H), 4.36-4.27 (m, 1H), 3.79 (s, 3H), 2.32 (s, 3H), 1.40 (s, 6H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.51 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.66, 162.79, 156.07, 144.74, 135.26, 130.34, 130.01, 129.75, 126.75, 125.68, 123.31, 114.26, 113.67, 102.81, 100.43, 84.84, 76.14, 70.05, 67.32, 55.53, 26.10, 25.42, 21.59, 21.44, 20.80, 15.22; **MS** (EI): m/z (%): 527 (M^+, 47.77); 284 (100), **HRMS** calcd for $C_{28}H_{33}NO_7S$: 527.1978, found: 527.1979. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 19.83 min, minor enantiomer tr = 25.83 min.

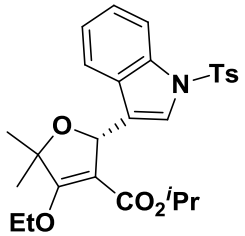




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	19.97	n.a.	440.307	343.161	50.18	n.a.	BMB
2	25.61	n.a.	429.487	340.647	49.82	n.a.	BMB
总和:			869.794	683.808	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	19.83	n.a.	1883.516	1177.645	97.30	n.a.	BMB
2	25.83	n.a.	45.487	32.677	2.70	n.a.	BMB
总和:			1929.003	1210.322	100.00	0.000	

#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	19.97	343.161	50.18	1	19.83	1177.645	97.30
2	25.61	340.647	49.82	2	25.83	32.677	2.70

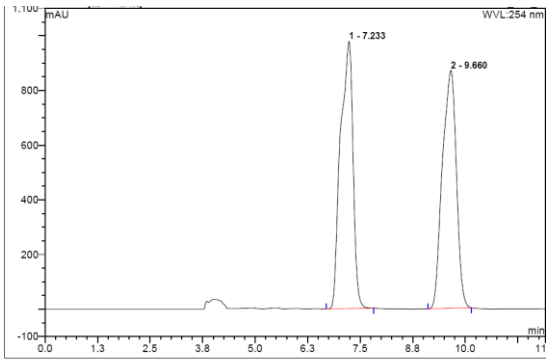


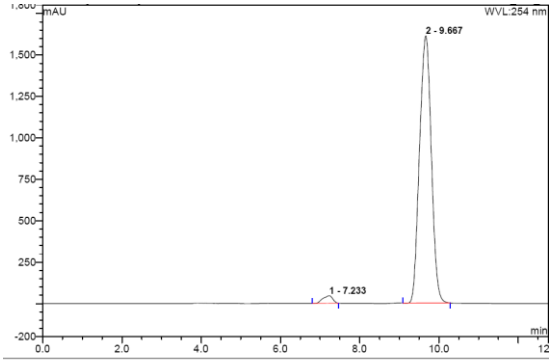
3fk

19. (*R*)-isopropyl 4-ethoxy-5,5-dimethyl-2-(1-tosyl-1H-indol-3-yl)-2,5-dihydrofuran-3-carboxylate.

Prepared according to the general procedure **B**: 79% yield; 95% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.23-7.18 (m, 3H), 6.04 (s, 1H), 4.76-4.66 (m, 2H), 4.34-4.25 (m, 1H), 2.33 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H), 1.36

(t, *J* = 7.6 Hz, 3H), 1.01 (d, *J* = 6.0 Hz, 3H), 0.46 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.60, 162.71, 144.74, 135.24, 135.17, 129.64, 129.26, 126.67, 124.98, 124.42, 123.21, 122.95, 120.40, 113.29, 100.53, 84.73, 76.08, 69.88, 67.14, 53.33, 25.89, 25.26, 21.41, 21.26, 20.59, 15.07; **MS** (EI): m/z (%): 497 (M^+, 31.87); 91 (100), **HRMS** calcd for $C_{27}H_{31}NO_6S$: 497.1872, found: 497.1874. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 hexane: 2-propanol, 0.8 mL/min, 254 nm); minor enantiomer tr = 7.23 min, major enantiomer tr = 9.67 min.

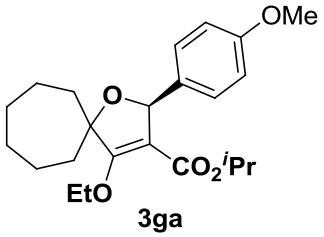




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.23	n.a.	977.738	338.044	50.18	n.a.	BMB*
2	9.66	n.a.	870.171	335.620	49.82	n.a.	BMB*
总和:			1847.909	673.663	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.23	n.a.	45.164	13.033	2.29	n.a.	BMB*
2	9.67	n.a.	1611.730	555.578	97.71	n.a.	BMB*
总和:			1656.894	568.610	100.00	0.000	

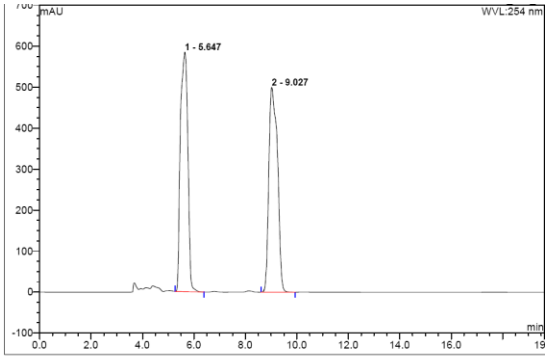
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	7.23	338.044	50.18	1	7.23	12.033	2.29
2	9.66	335.620	49.82	2	9.67	555.578	97.71



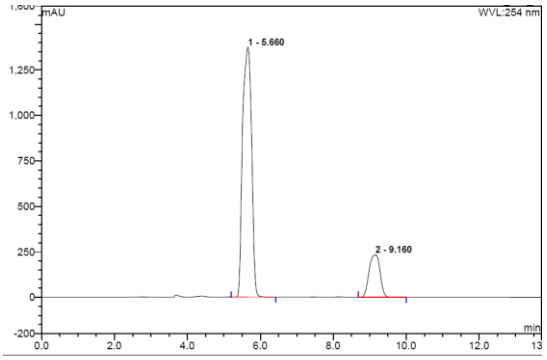
3ga

20. (*S*)-isopropyl 4-ethoxy-2-(4-methoxyphenyl)-1-oxaspiro[4.6]undec-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 56% yield; 66% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.68 (s, 1H), 4.79-4.72 (m, 1H), 4.68-4.61 (m, 1H), 4.25-4.18 (m, 1H), 3.79 (s, 3H), 2.15-2.10 (m, 1H), 2.09-1.81 (m, 3H), 1.68-1.43 (m, 8H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.74 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.15, 163.37, 159.33, 134.52, 129.22, 113.37, 101.82, 89.04, 83.38, 69.82, 67.21, 55.25, 39.55, 37.66, 30.46, 30.15, 22.97, 21.73, 21.01, 15.23; **MS** (EI): m/z (%): 388 (M^+, 51.42); 301 (100), **HRMS** calcd for $C_{23}H_{32}O_5$: 388.2250, found: 388.2249. Enantiomeric excess was determined by HPLC with a Chiralpak AD-3 column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 5.65 min, minor enantiomer tr = 9.16 min.

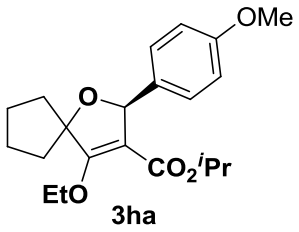


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.65	n.a.	584.651	195.681	50.22	n.a.	BMB
2	9.03	n.a.	499.678	193.999	49.78	n.a.	BMB
总和:			1084.329	389.680	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	5.66	n.a.	1373.234	393.990	82.84	n.a.	BMB
2	9.16	n.a.	234.713	81.586	17.16	n.a.	BMB
总和:			1607.948	475.576	100.00	0.000	

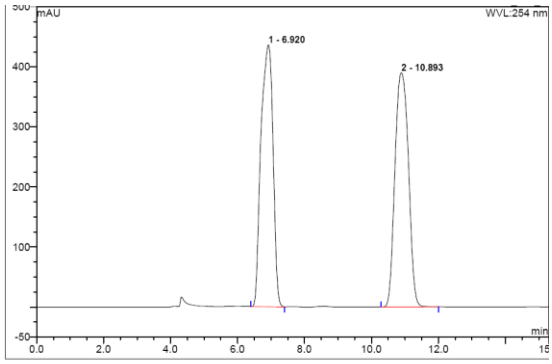
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	5.05	195.681	50.22	1	5.65	393.990	82.84
2	9.03	193.999	49.78	2	9.16	81.586	17.16



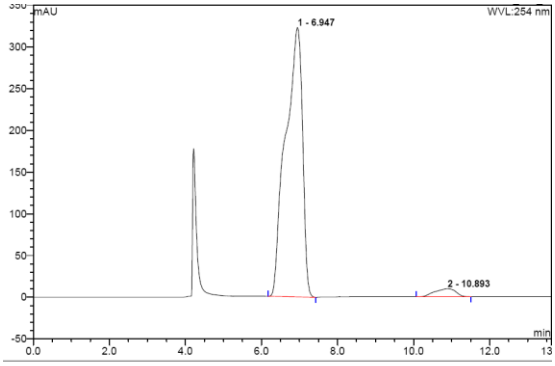
3ha

21. (*S*)-isopropyl 4-ethoxy-2-(4-methoxyphenyl)-1-oxaspiro[4.4]non-3-ene-3-carboxylate.

Prepared according to the general procedure **A**: 77% yield; 93% ee; white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.71 (s, 1H), 4.81-4.74 (m, 1H), 4.70-4.63 (m, 1H), 4.30-4.23 (m, 1H), 3.78 (s, 3H), 2.13-2.08 (m, 1H), 1.87-1.59 (m, 7H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 6.4 Hz, 3H), 0.76 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.11, 162.97, 159.39, 134.46, 129.06, 113.44, 103.27, 94.80, 84.07, 69.75, 67.27, 55.26, 38.23, 37.50, 25.22, 25.17, 21.75, 21.05, 15.22；**MS** (EI): m/z (%): 360 (M^+, 13.82);135 (100), **HRMS** calcd for $C_{21}H_{28}O_5$: 360.1937, found: 360.1938. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (98:2 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 6.95 min, minor enantiomer tr = 10.89 min.

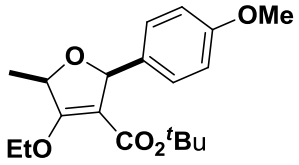


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	6.92	n.a.	435.892	181.578	49.91	n.a.	BMB
2	10.89	n.a.	390.133	182.220	50.09	n.a.	BMB
总和:			826.024	363.798	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	6.95	n.a.	322.919	166.394	96.49	n.a.	BMB
2	10.89	n.a.	9.332	6.055	3.51	n.a.	BMB
总和:			332.251	172.449	100.00	0.000	

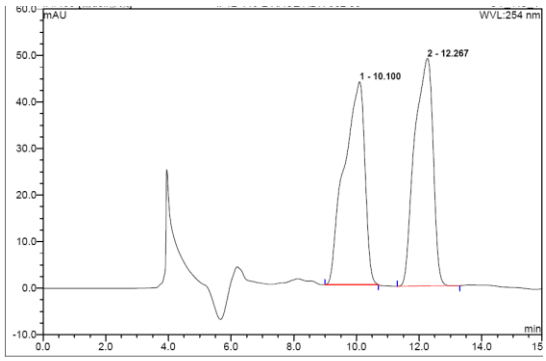
#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	6.92	181.578	49.91	1	6.95	166.394	96.49
2	10.89	182.220	50.09	2	10.89	6.055	3.51

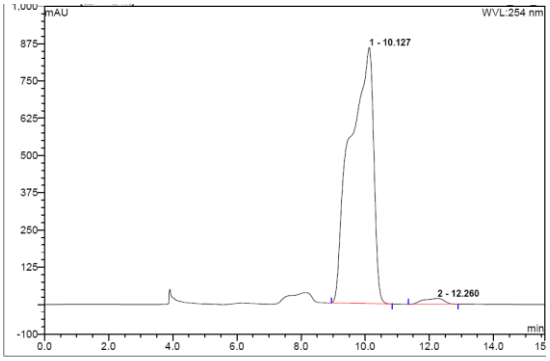


3ia

22. (2*S,5*R**)-tert-butyl 4-ethoxy-2-(4-methoxyphenyl)-5-methyl-2,5-dihydrofuran-3-carboxylate.**

Prepared according to the general procedure **D**: 55% yield; 11.4:1 dr; 96% ee; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.71 (d, *J* = 3.6 Hz, 1H), 4.78-4.71 (m, 1H), 4.60-4.51 (m, 1H), 4.23-4.14 (m, 1H), 3.79 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.34 (d, *J* = 7.2 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.08, 162.78, 159.44, 134.29, 129.08, 113.42, 104.88, 85.79, 80.23, 78.75, 68.75, 55.20, 27.67, 20.31, 15.15; **MS** (EI): m/z (%): 334 (M^+, 5.51); 231 (100), **HRMS** calcd for $C_{19}H_{26}O_5$: 334.1780, found: 334.1782. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 10.13 min, minor enantiomer tr = 12.26 min.

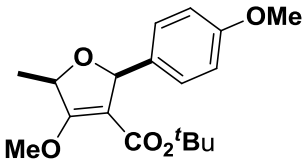




序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	10.10	n.a.	43.610	33.077	49.88	n.a.	BMB*
2	12.27	n.a.	48.936	33.238	50.12	n.a.	BMB*
总和:			92.547	66.314	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	10.13	n.a.	859.346	717.005	98.04	n.a.	BMB*
2	12.26	n.a.	18.747	14.301	1.96	n.a.	BMB*
总和:			878.093	731.306	100.00	0.000	

#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	10.10	33.077	49.88	1	10.13	717.005	98.04
2	12.27	33.238	50.12	2	12.26	14.301	1.96

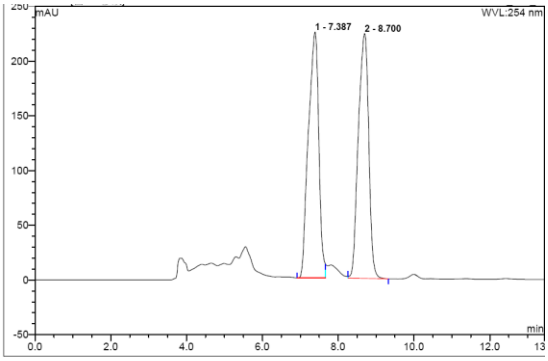


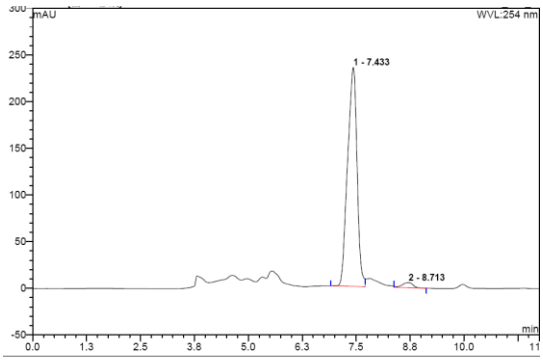
3ja

23. (2*S,5*R**)-tert-butyl 4-methoxy-2-(4-methoxyphenyl)-5-methyl-2,5-dihydrofuran-3-carboxylate.**

Prepared according to the general procedure **D**: 52% yield; 11.6:1 dr; 95% ee; colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 6.88-6.84 (m, 2H), 5.70 (d, *J* = 3.6 Hz, 1H), 4.79-4.73 (m, 1H), 4.04 (s, 3H), 3.79 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.99, 162.74, 159.52, 134.13, 129.12, 113.47, 105.01, 85.78, 80.41, 78.45, 60.49, 55.24, 27.68, 20.30; **MS** (EI): m/z (%): 320 (M^+, 7.09); 263 (100), **HRMS** calcd for $C_{18}H_{24}O_5$: 320.1624, found: 320.1626. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 hexane: 2-propanol, 0.8 mL/min, 254 nm); major enantiomer tr = 6.44 min, minor enantiomer tr = 7.09 min. The reaction under procedure C using *R*-6 as chiral ligand afford the same product in 54%

yield, 11.5:1 dr with 95% ee.





序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.39	n.a.	224.851	71.358	50.18	n.a.	BM *
2	8.70	n.a.	223.765	70.859	49.82	n.a.	MB*
总和:			448.617	142.216	100.00	0.000	

序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.43	n.a.	234.876	59.626	97.38	n.a.	BM *
2	8.71	n.a.	5.622	1.605	2.62	n.a.	MB*
总和:			240.498	61.231	100.00	0.000	

#	Time (min)	Area	Area %	#	Time (min)	Area	Area %
1	7.39	71.358	50.18	1	7.43	59.626	97.38
2	8.70	70.859	49.82	2	8.71	1.605	2.62

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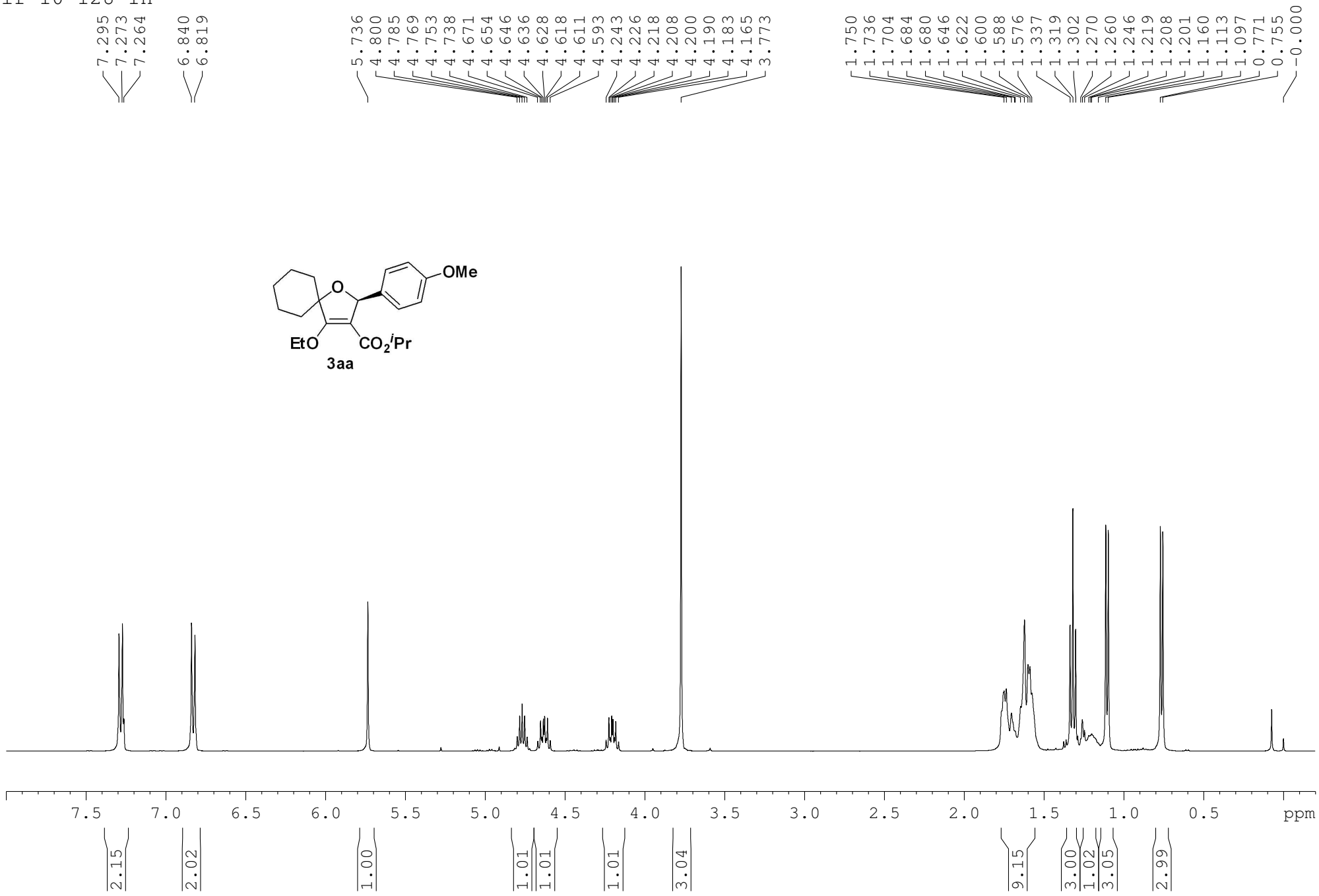
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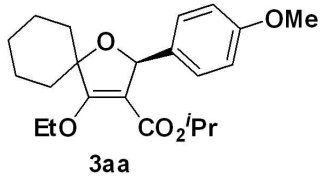
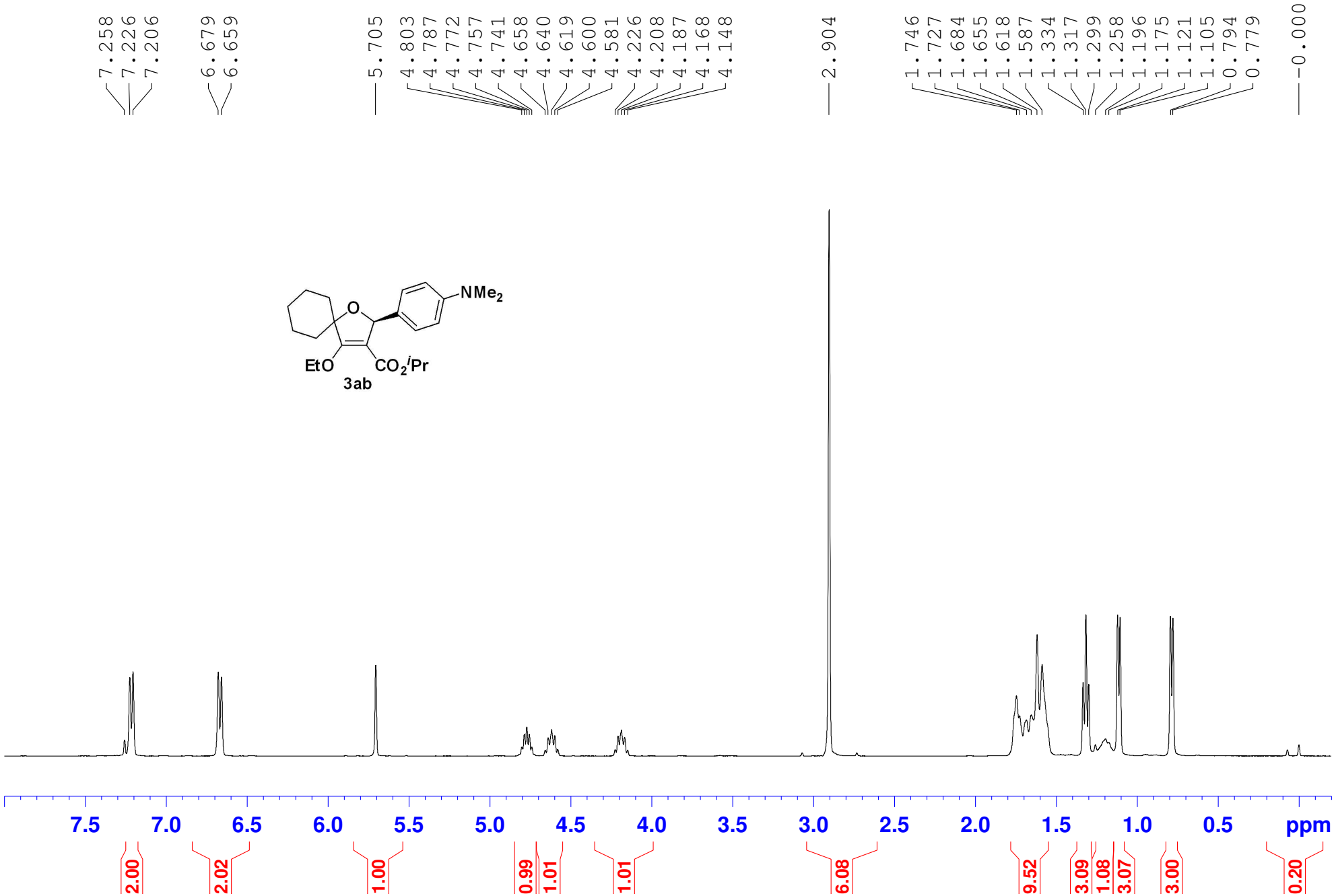


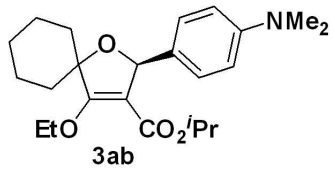
3aa

1f-10-97-2H

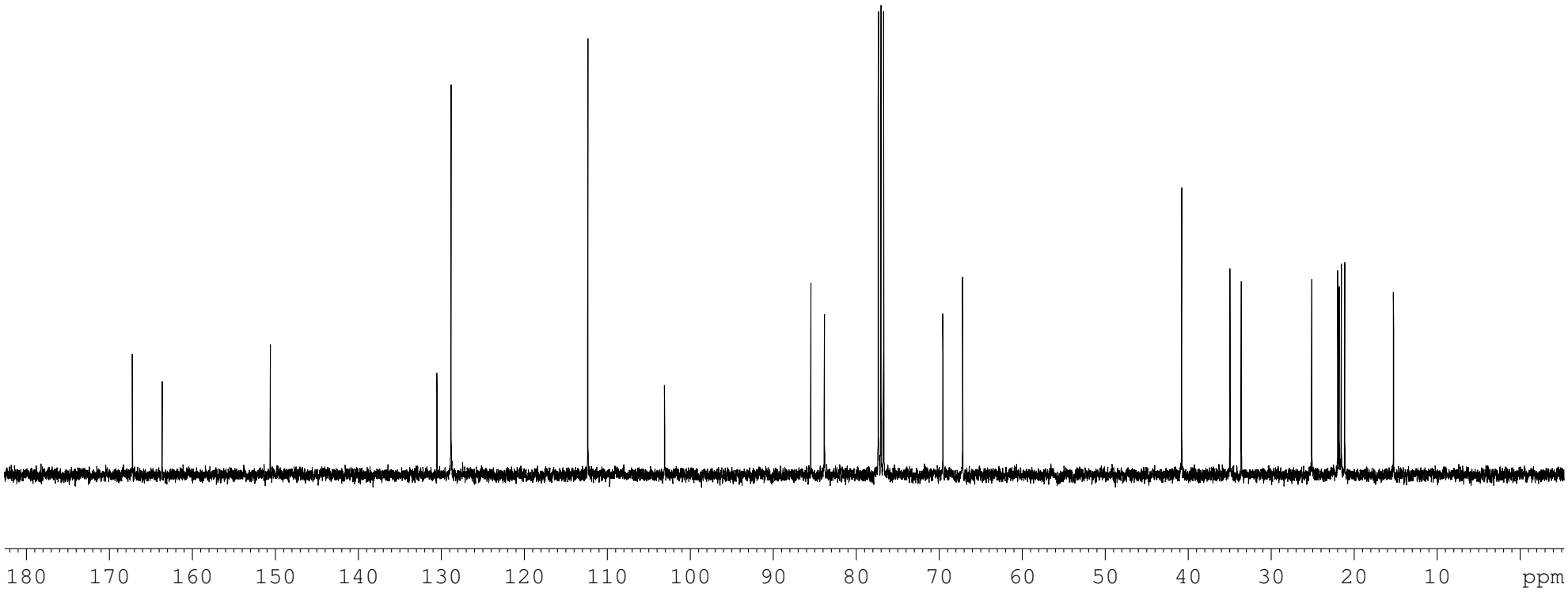

7.258
7.226
7.206
6.679
6.659
5.705
4.803
4.787
4.772
4.757
4.741
4.658
4.640
4.619
4.600
4.581
4.226
4.208
4.187
4.168
4.148
2.904
1.746
1.727
1.684
1.655
1.618
1.587
1.334
1.317
1.299
1.258
1.196
1.175
1.121
1.105
0.794
0.779
-0.000
NMe2
O
EtO
CO2iPr
3ab
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.02
1.00
0.99
1.01
1.01
6.08
9.52
3.09
1.08
3.07
3.00
0.20

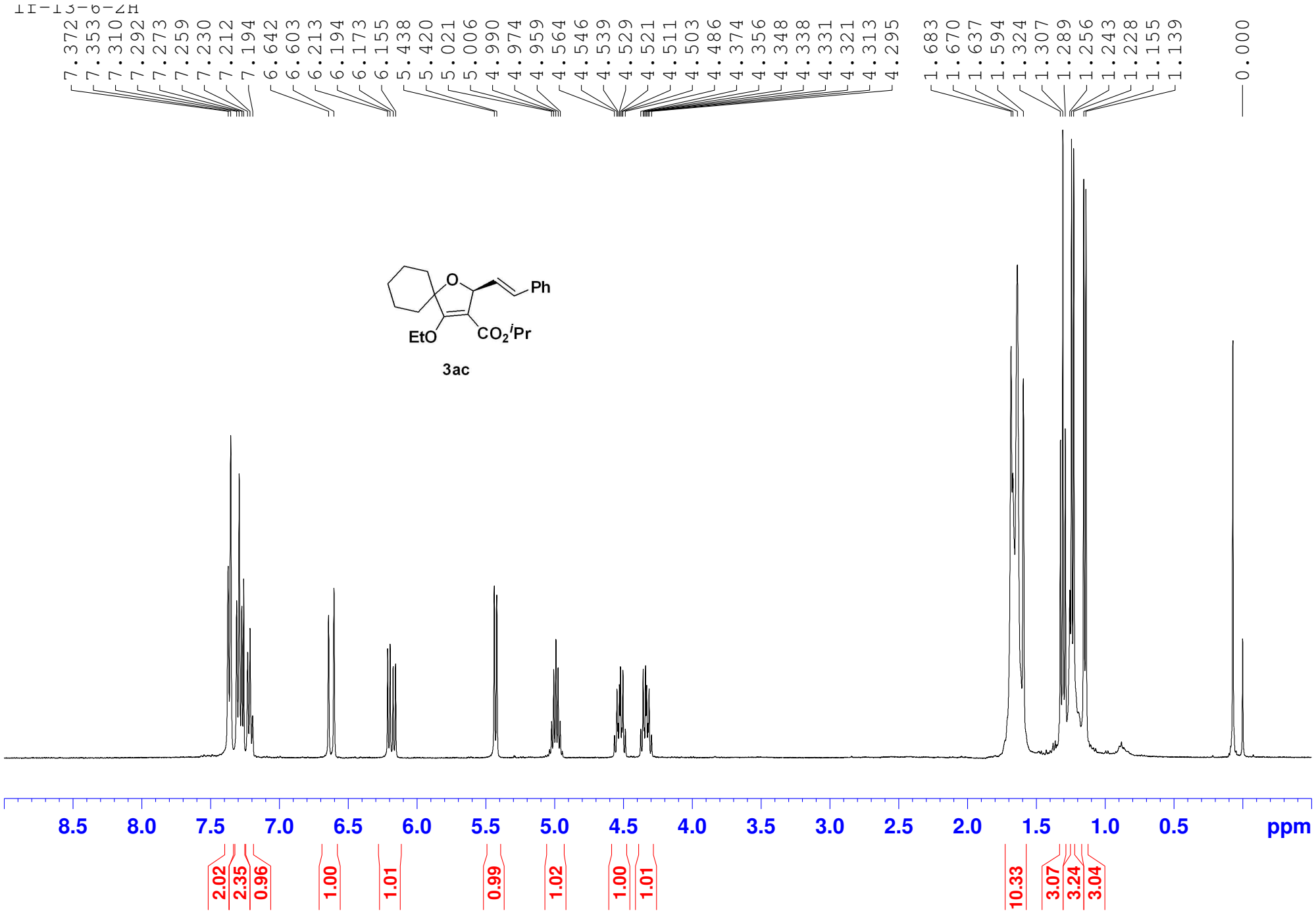
lf-10-97-2C

167.19
163.58
150.56
130.52
128.82
112.33
103.09
85.46
83.83
77.32
77.00
76.68
69.54
67.17
40.76
34.94
33.58
25.09
21.95
21.77
21.52
21.10
15.23

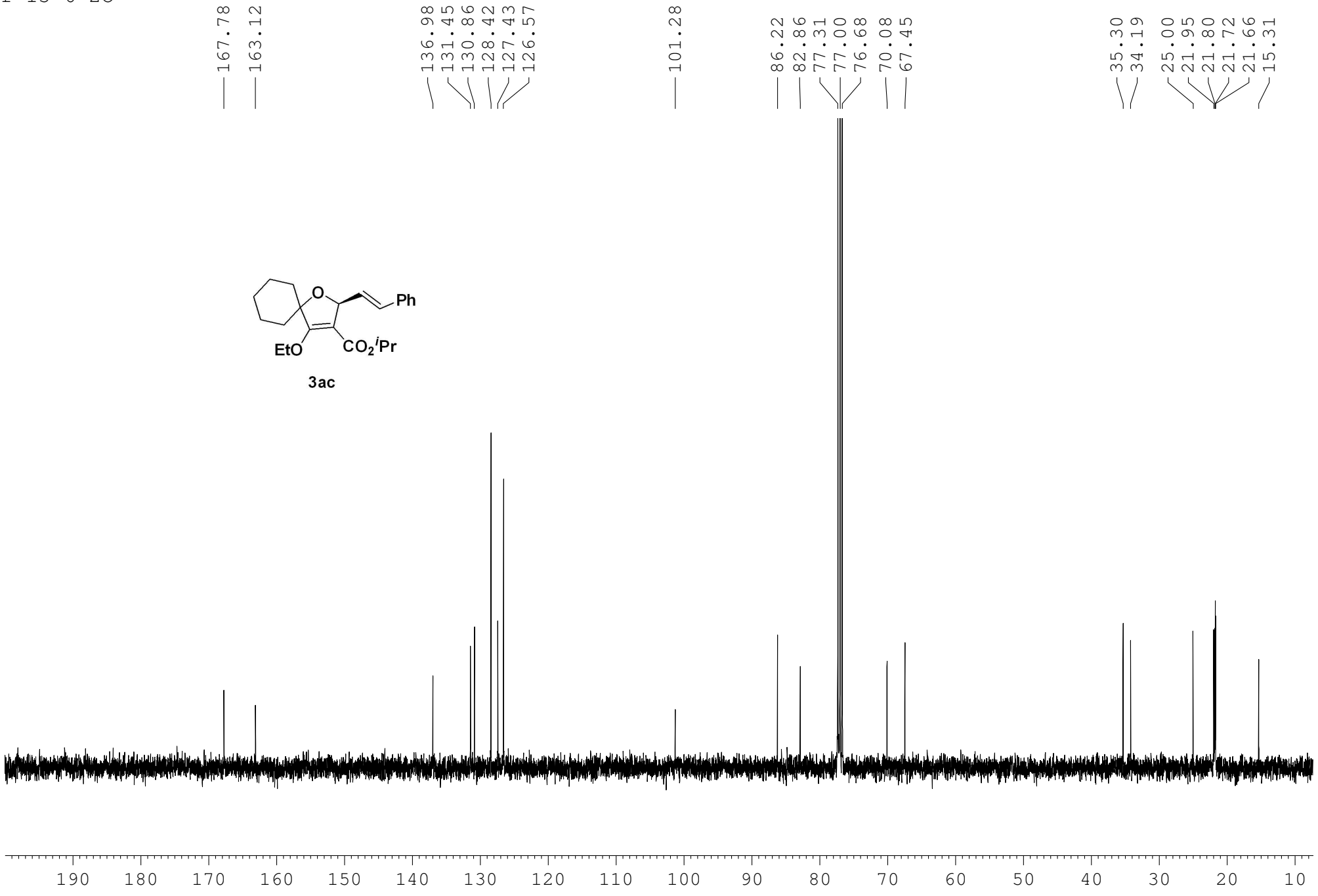


3ab




H7-9-C1-1T
7.372
7.353
7.310
7.292
7.273
7.259
7.230
7.212
7.194
6.642
6.603
6.213
6.194
6.173
6.155
5.438
5.420
5.021
5.006
4.990
4.974
4.959
4.564
4.546
4.539
4.529
4.521
4.511
4.503
4.486
4.374
4.356
4.348
4.338
4.331
4.321
4.313
4.295
1.683
1.670
1.637
1.594
1.324
1.307
1.289
1.256
1.243
1.228
1.155
1.139
0.000
O
Ph
EtO
CO2iPr
3ac
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
2.35
0.96
1.00
1.01
0.99
1.02
1.00
1.01
10.33
3.07
3.24
3.04

lf-13-6-2C

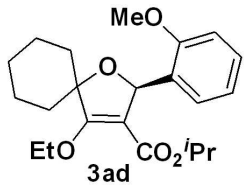

167.78
163.12
136.98
131.45
130.86
128.42
127.43
126.57
101.28
86.22
82.86
77.31
77.00
76.68
70.08
67.45
35.30
34.19
25.00
21.95
21.80
21.72
21.66
15.31
O
Ph
EtO
CO2iPr
3ac
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

lf-13-6-1

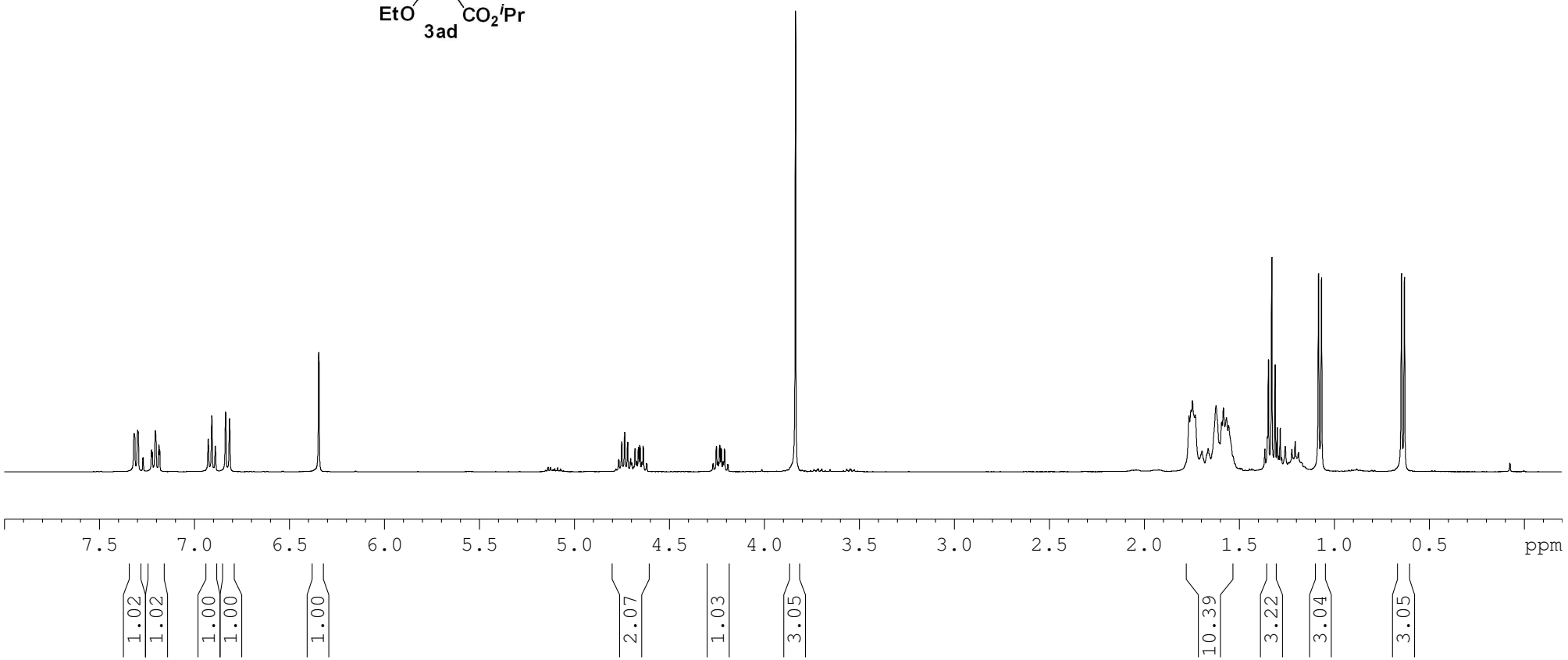
7.295 7.269 7.268 7.267 7.223 7.219 7.205 7.203 7.200 7.184 7.180 6.927 6.909 6.890 6.836 6.815 6.346

4.766 4.750 4.734 4.719 4.703 4.699 4.681 4.679 4.673 4.663 4.661 4.655 4.644 4.638 4.620 4.270 4.253 4.245 4.236 4.233 4.228 4.218 4.210 4.192 3.835

1.764 1.753 1.746 1.731 1.695 1.663 1.622 1.592 1.583 1.567 1.556 1.345 1.328 1.310 1.082 1.066 0.645 0.630

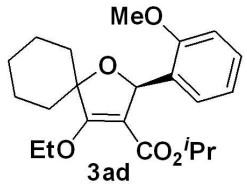


3ad

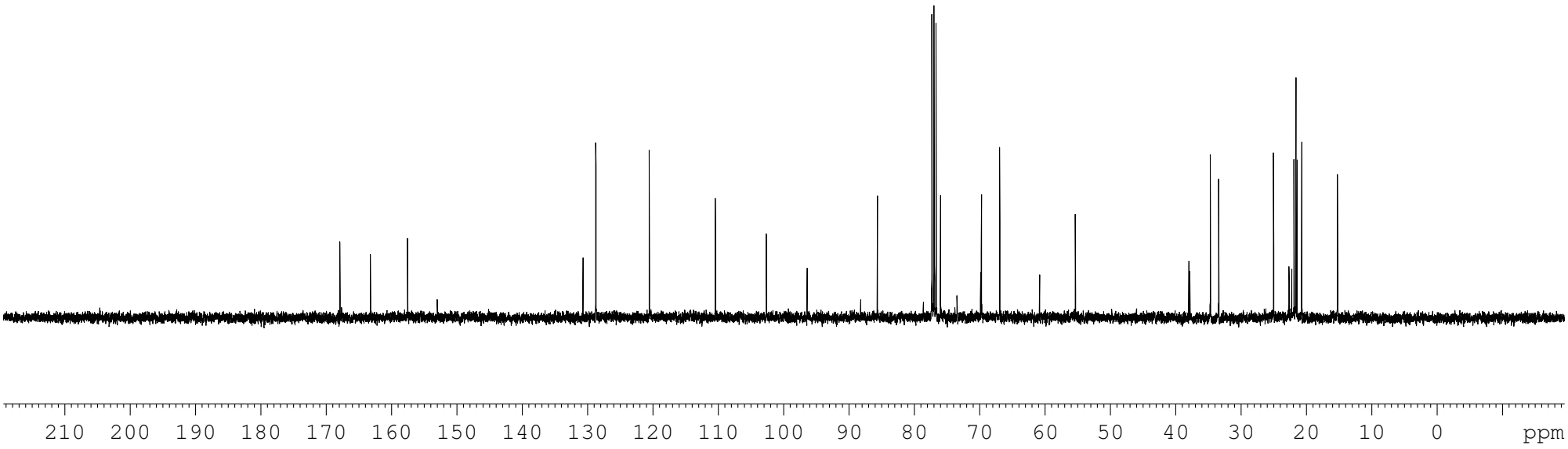


1f-13-6-1C

167.90
163.23
157.57
130.70
128.77
128.73
120.56
110.45
102.64
96.40
85.65
77.32
77.00
76.68
75.99
69.73
66.93
55.37
34.70
33.43
25.04
25.01
21.91
21.59
21.43
20.71

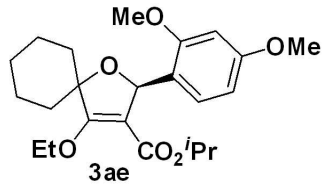


3ad

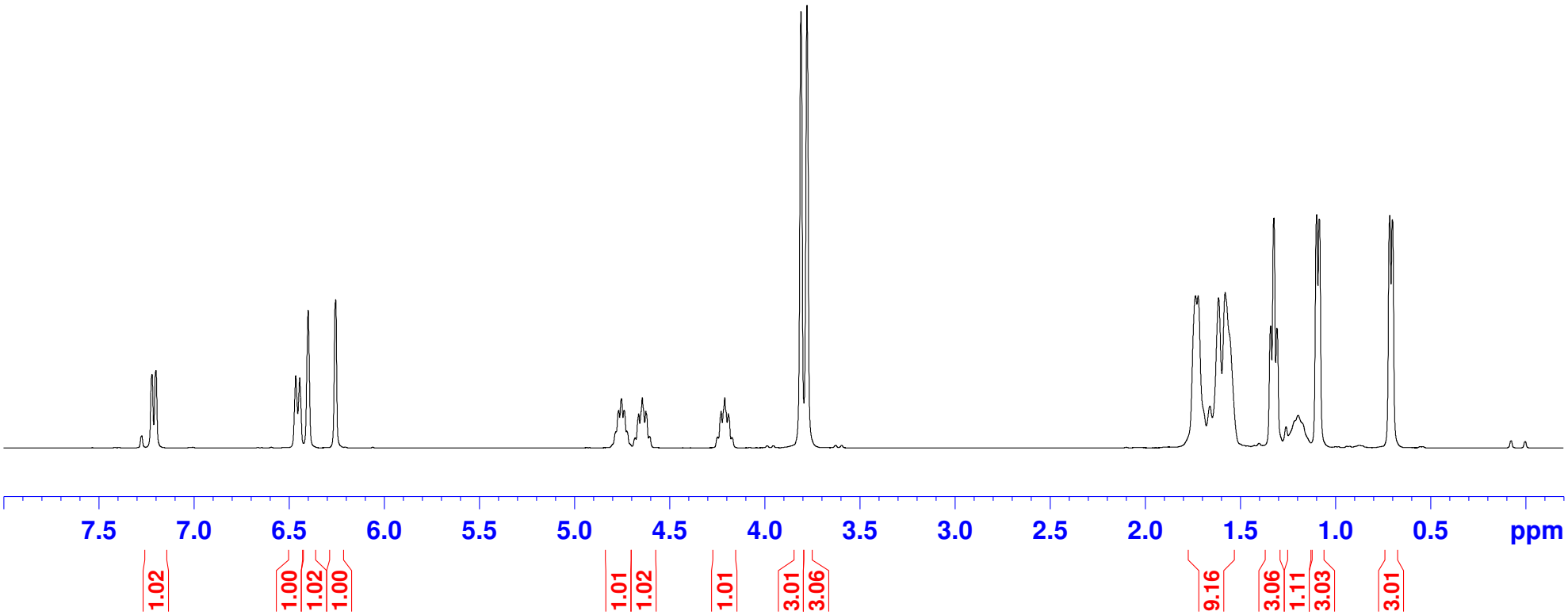


1f-10-138-2H

7.272
7.219
7.198
6.463
6.442
6.398
6.253
4.782
4.768
4.753
4.738
4.725
4.680
4.662
4.643
4.625
4.607
4.246
4.229
4.210
4.191
4.173
3.809
3.778
1.735
1.721
1.660
1.614
1.579
1.340
1.323
1.308
1.259
1.195
1.098
1.084
0.714
0.700
0.001

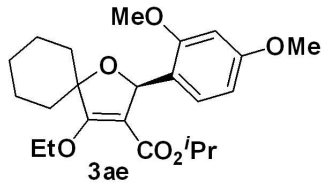


3ae

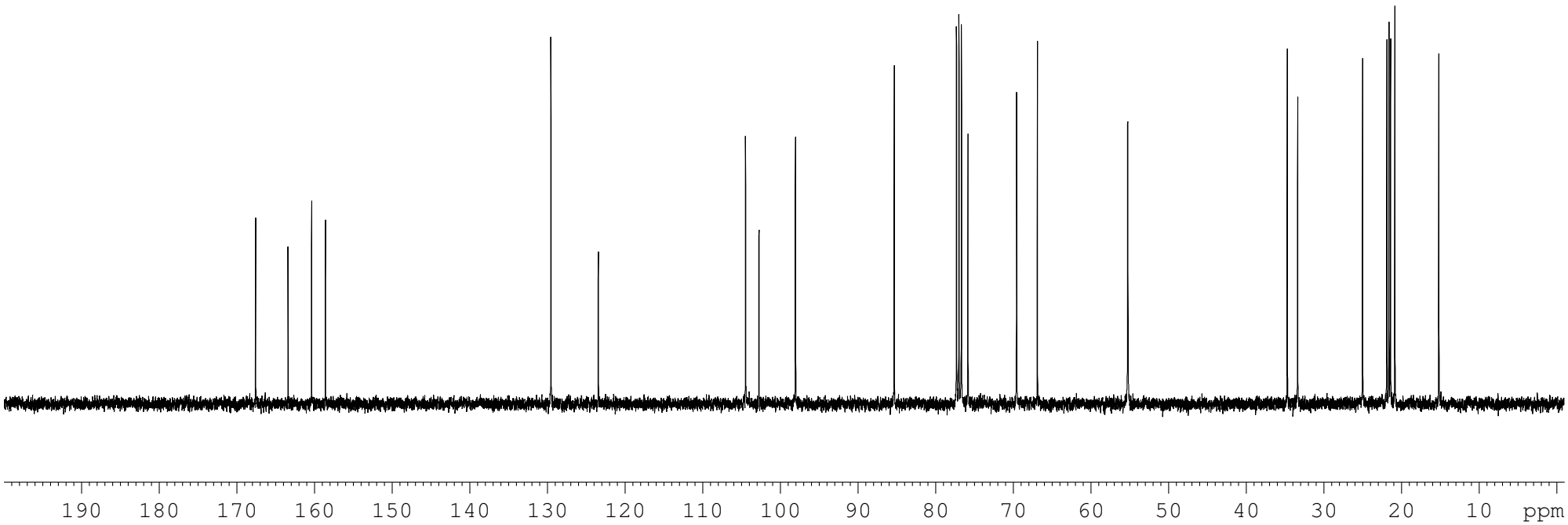


lf-10-138-2C

167.53
163.36
160.33
158.55
129.50
123.40
104.44
102.70
98.01
85.34
77.32
77.00
76.68
75.85
69.58
66.90
55.28
55.24
34.72
33.38
25.02
21.89
21.61
21.42
20.86
15.19

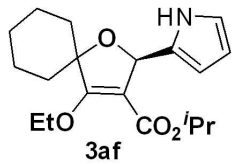


3ae

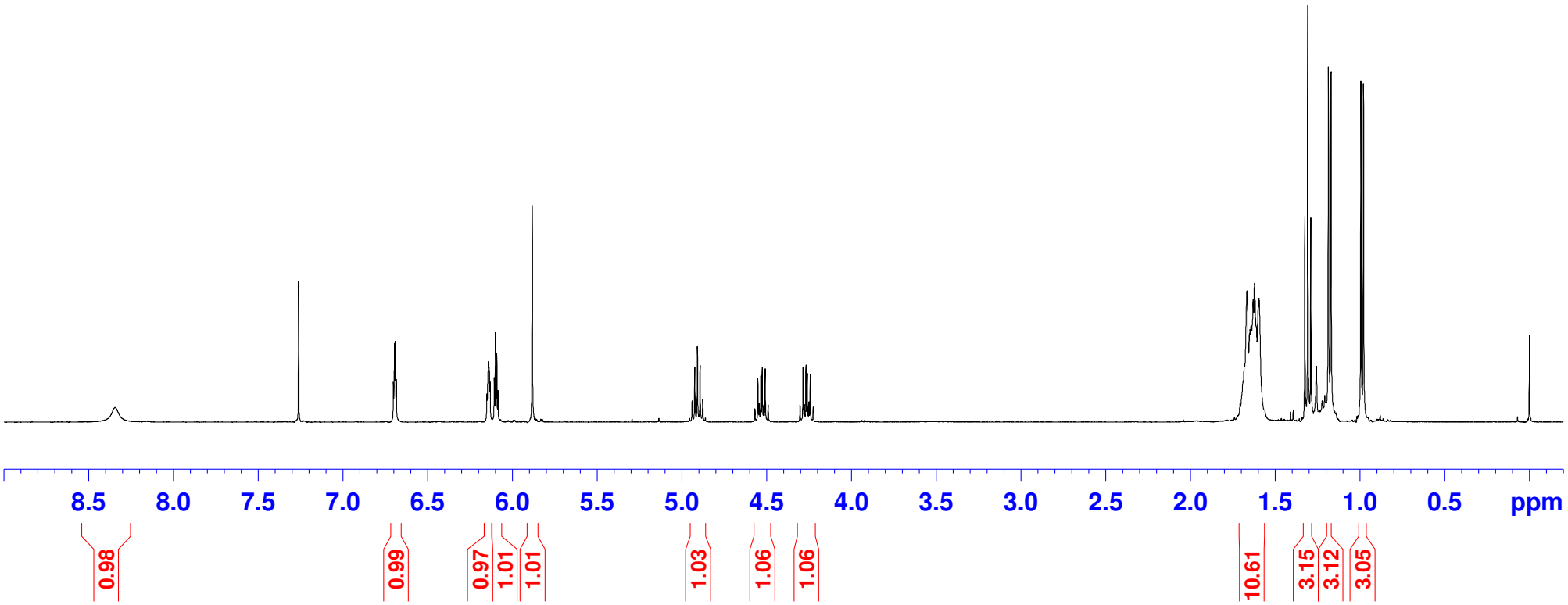


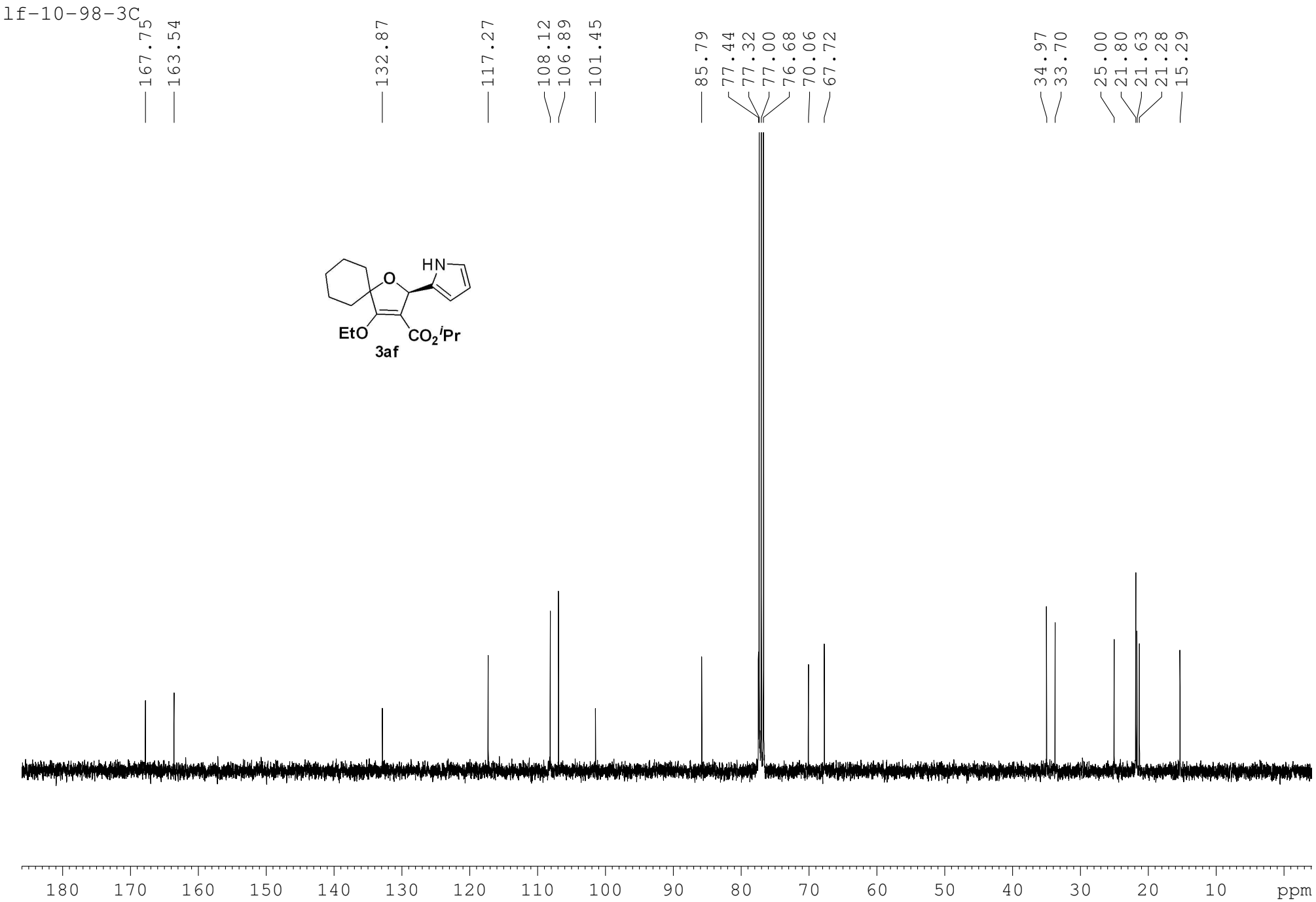
lf-10-98-3H

8.341
7.259
6.700
6.696
6.693
6.689
6.687
6.683
6.150
6.141
6.139
6.132
6.107
6.100
6.092
6.085
5.883
4.940
4.924
4.909
4.893
4.877
4.569
4.552
4.544
4.534
4.526
4.516
4.509
4.491
4.303
4.286
4.278
4.268
4.260
4.251
4.243
4.225
1.682
1.666
1.649
1.642
1.630
1.621
1.595
1.325
1.307
1.290
1.256
1.207
1.186
1.171
0.995
0.979
0.000



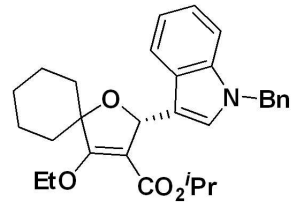
3af



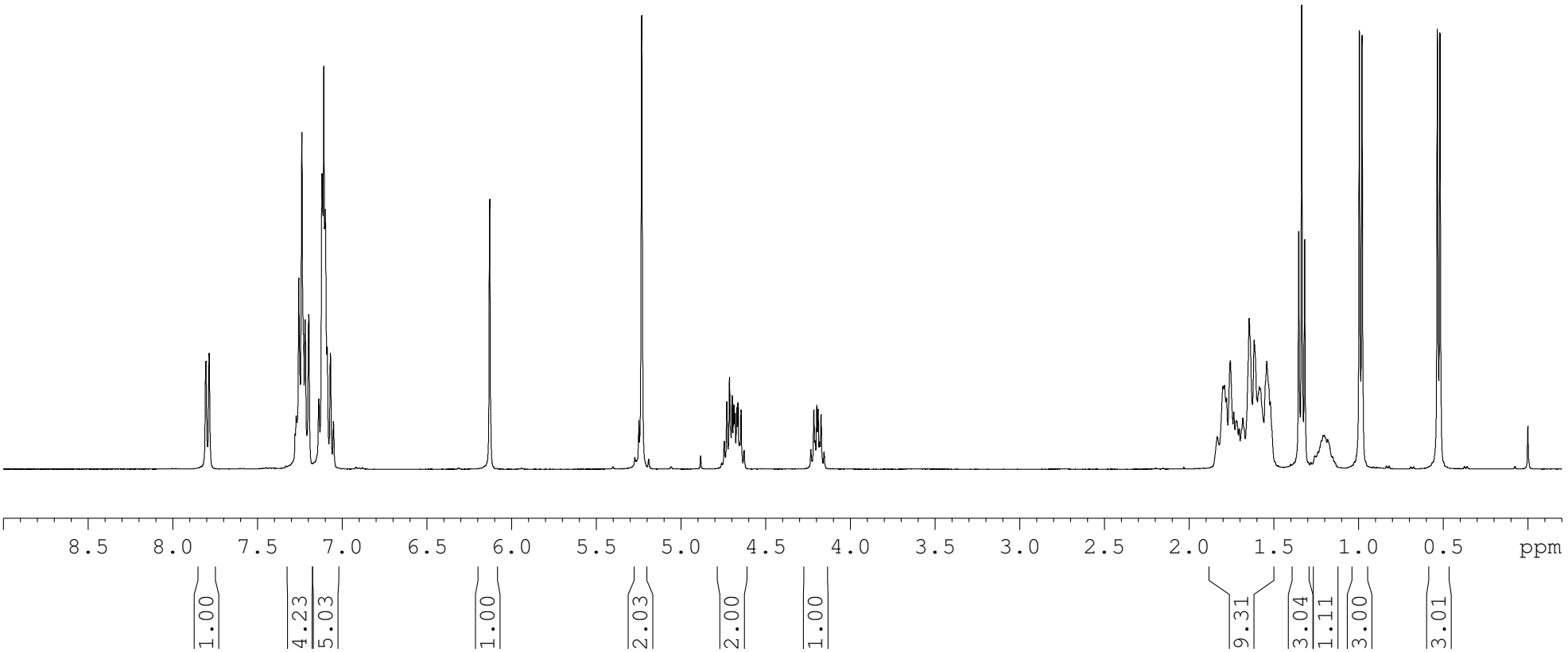

1f-10-98-3C
167.75
163.54
132.87
117.27
108.12
106.89
101.45
85.79
77.44
77.32
77.00
76.68
70.06
67.72
34.97
33.70
25.00
21.80
21.63
21.28
15.29
HN
O
EtO
CO2iPr
3af
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

lf-11-51-1H

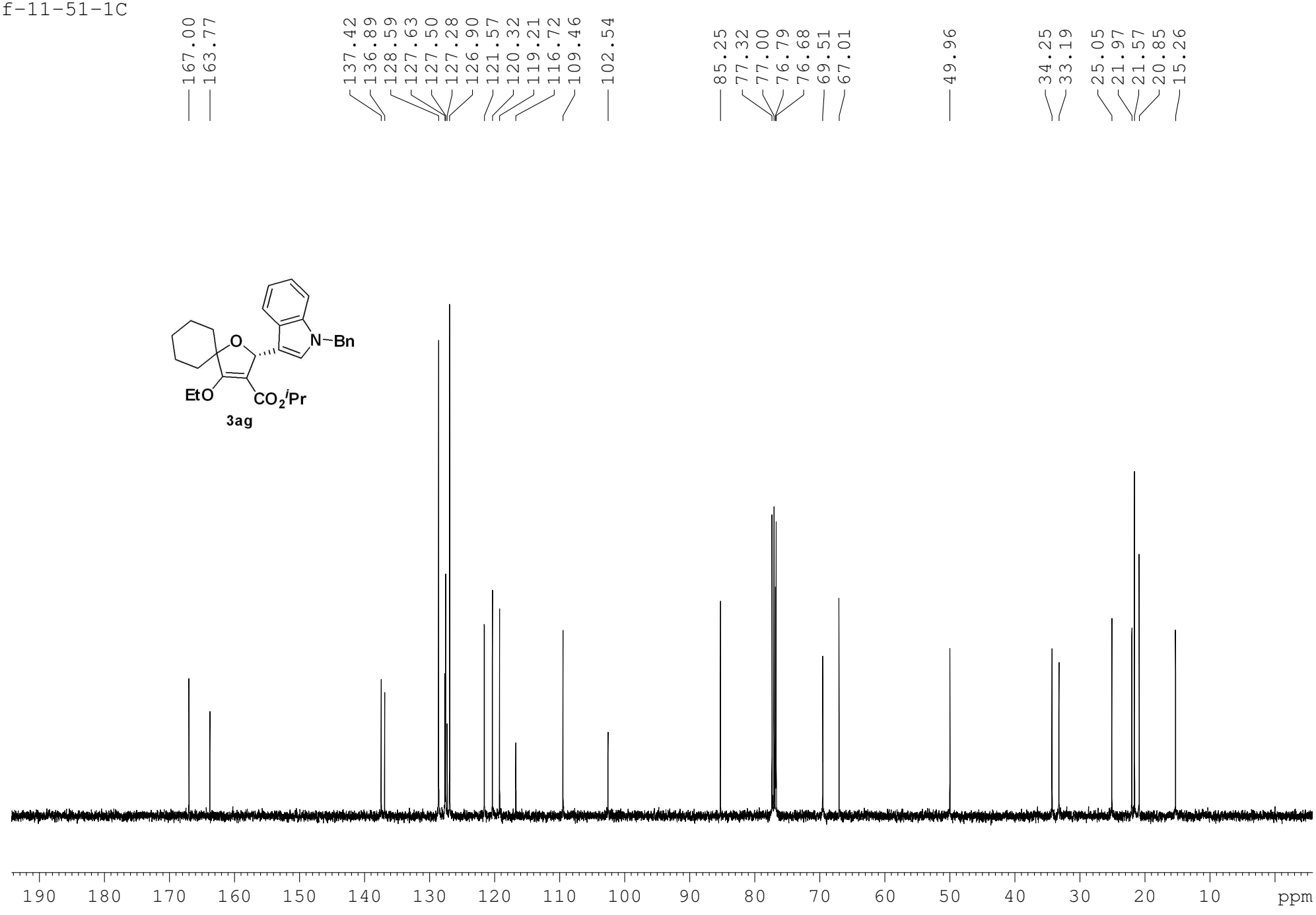
7.805 7.786 7.278 7.272 7.257 7.238 7.229 7.219 7.197 7.138 7.119 7.109 7.101 7.089 7.070 7.052 6.129 5.232 4.744 4.729 4.713 4.698 4.688 4.682 4.670 4.663 4.653 4.645 4.215 4.209 4.198 4.190 4.180 4.173 1.834 1.800 1.792 1.780 1.757 1.736 1.721 1.705 1.683 1.645 1.616 1.592 1.585 1.579 1.542 1.520 1.353 1.335 1.318 1.219 1.209 1.202 1.194 1.182 0.995 0.979 0.534 0.519 -0.000



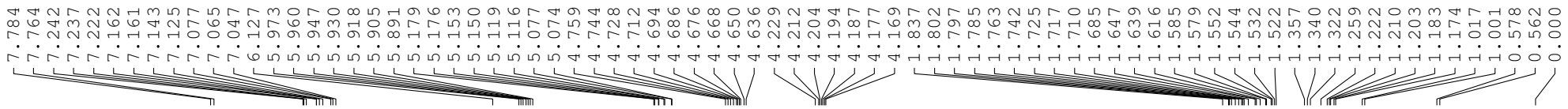
3ag

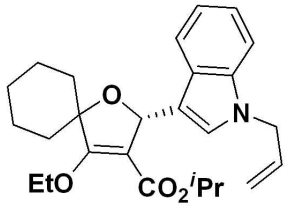


lf-11-51-1C

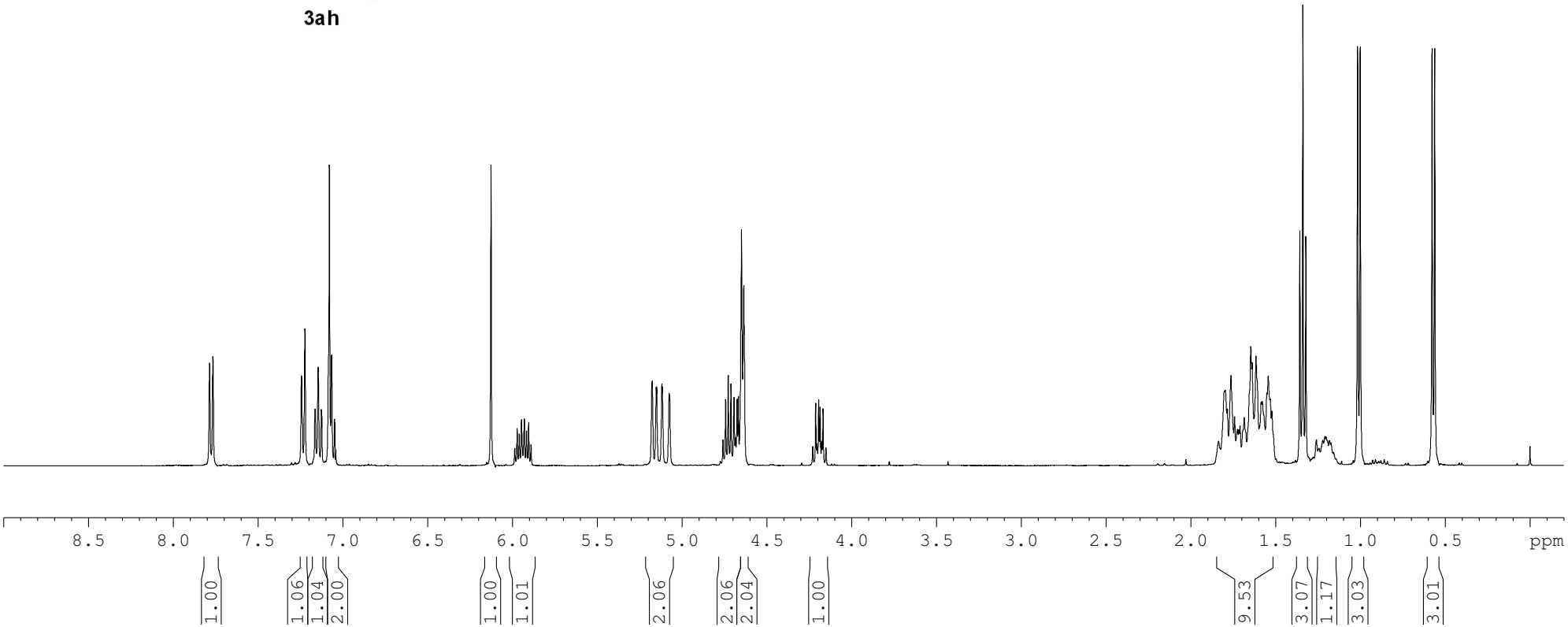

167.00
163.77
137.42
136.89
128.59
127.63
127.50
127.28
126.90
121.57
120.32
119.21
116.72
109.46
102.54
85.25
77.32
77.00
76.79
76.68
69.51
67.01
49.96
34.25
33.19
25.05
21.97
21.57
20.85
15.26
O
N–Bn
EtO
CO2iPr
3ag
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

lf-11-21-3H



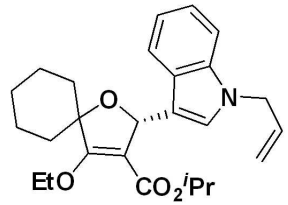


3ah

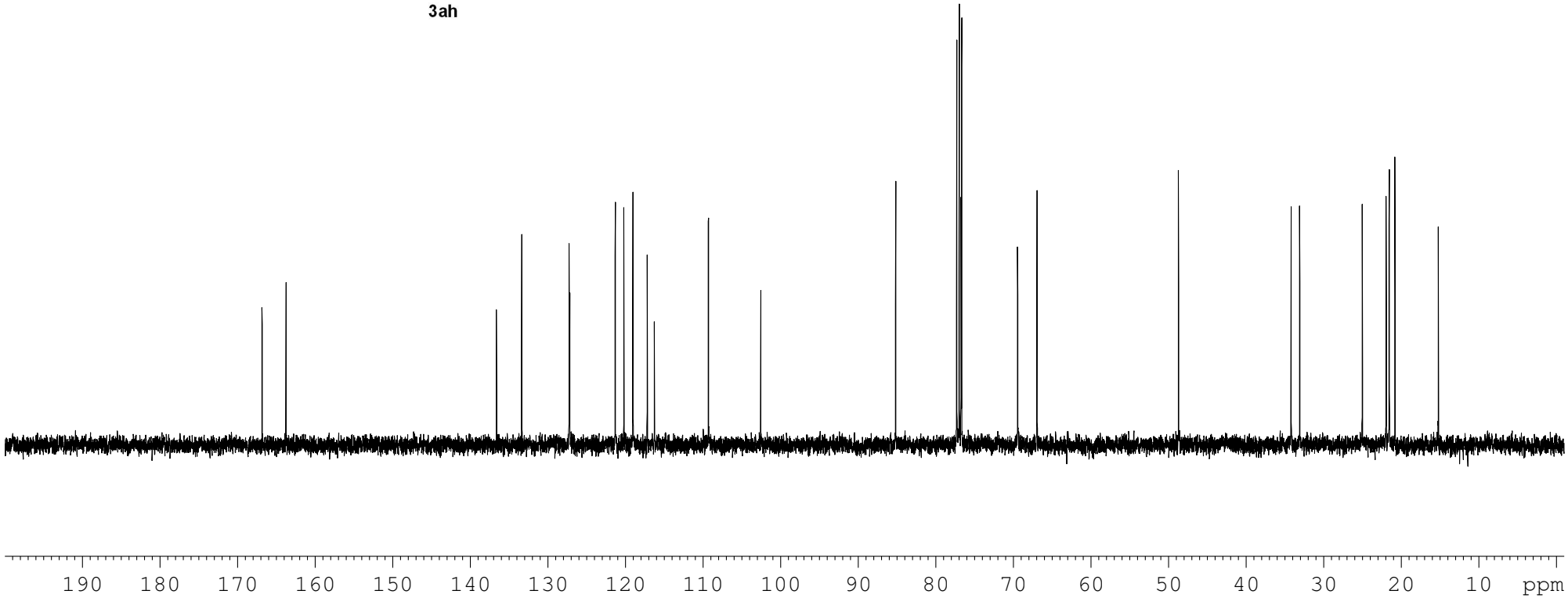


lf-11-21-3C

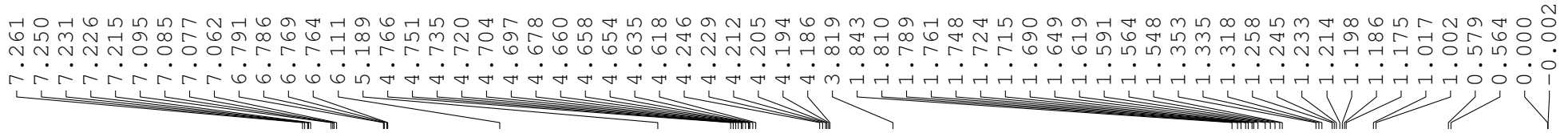
166.87
163.78
136.65
133.40
127.28
127.21
121.34
120.24
119.07
117.22
116.30
109.33
102.57
85.20
77.32
77.00
76.77
76.68
69.47
66.96
48.73
34.21
33.10
25.03
21.95
21.57
21.55
20.82
15.23

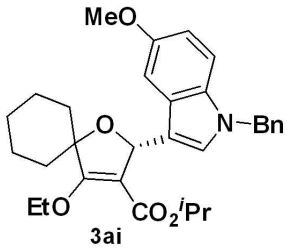


3ah

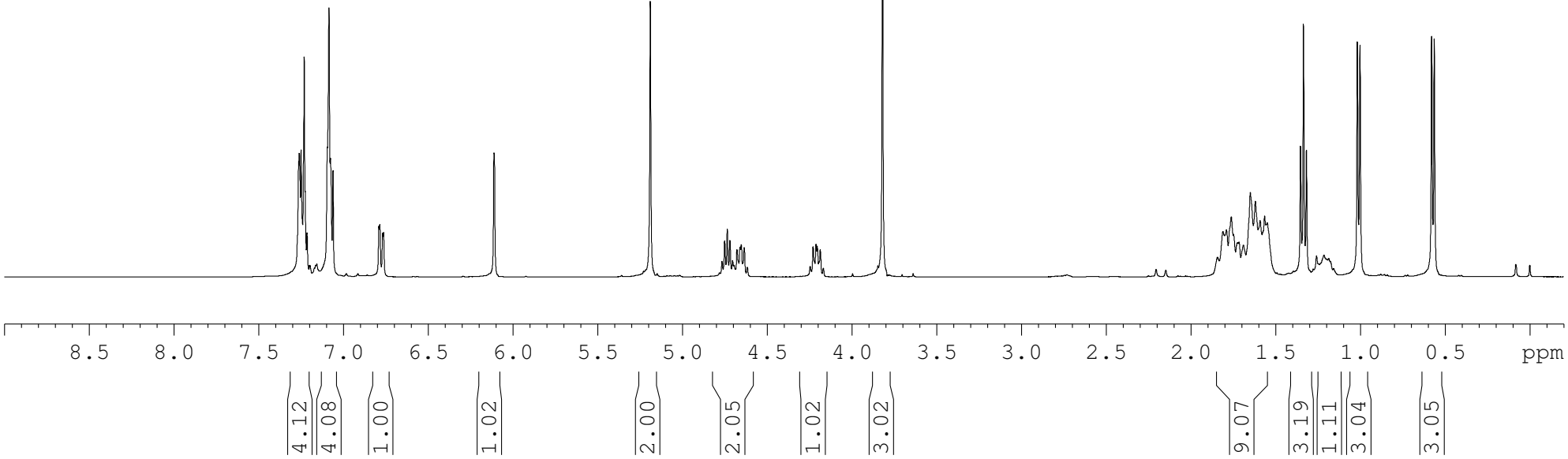


lf-11-21-21H



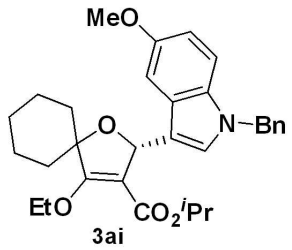


3ai

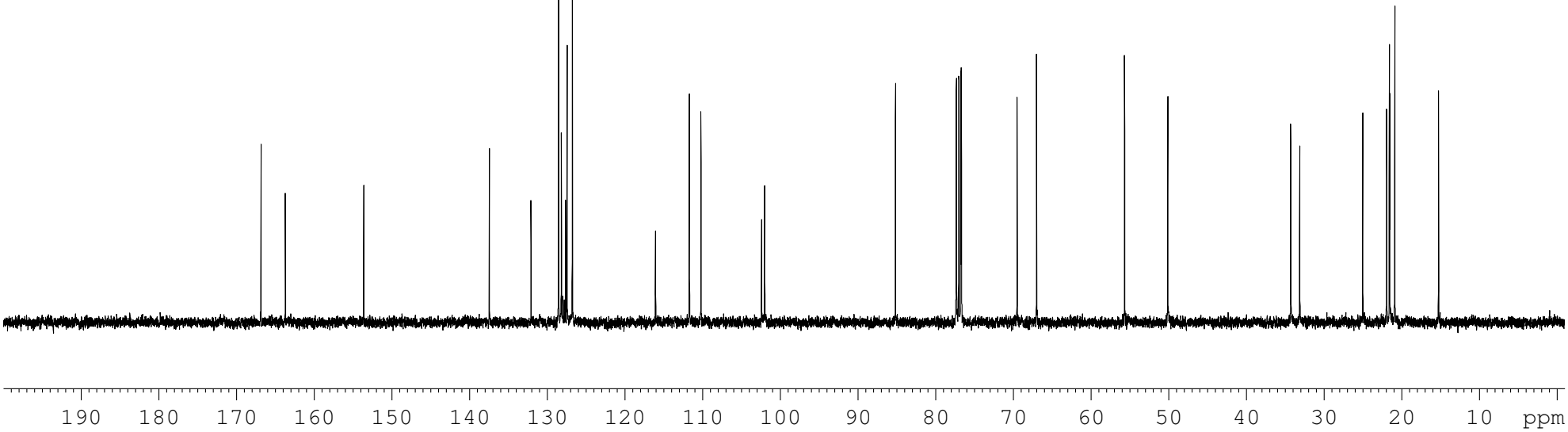


lf-11-21-21C

166.85
163.71
153.61
137.44
132.08
128.53
128.17
127.63
127.44
126.76
116.06
111.69
110.20
102.39
102.02
85.15
77.32
77.00
76.76
76.68
69.50
67.00
55.66
50.10
34.27
33.11
25.00
21.92
21.58
21.53
20.87
15.24



3ai



lf-11-84-2H

7.847
7.824
7.740
7.719
7.450
7.264
7.201
7.181
7.160
7.154
6.908
6.902
6.885
6.879
5.990
4.748
4.732
4.717
4.701
4.685
4.679
4.671
4.661
4.654
4.636
4.325
4.308
4.300
4.290
4.282
3.798
2.327
1.739
1.726
1.710
1.699
1.687
1.677
1.659
1.631
1.617
1.592
1.581
1.512
1.500
1.492
1.449
1.365
1.348
1.330
1.202
1.190
1.180
1.023
1.007
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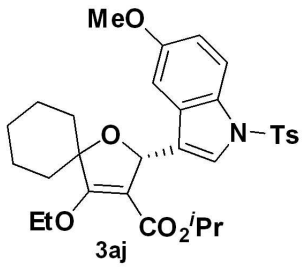
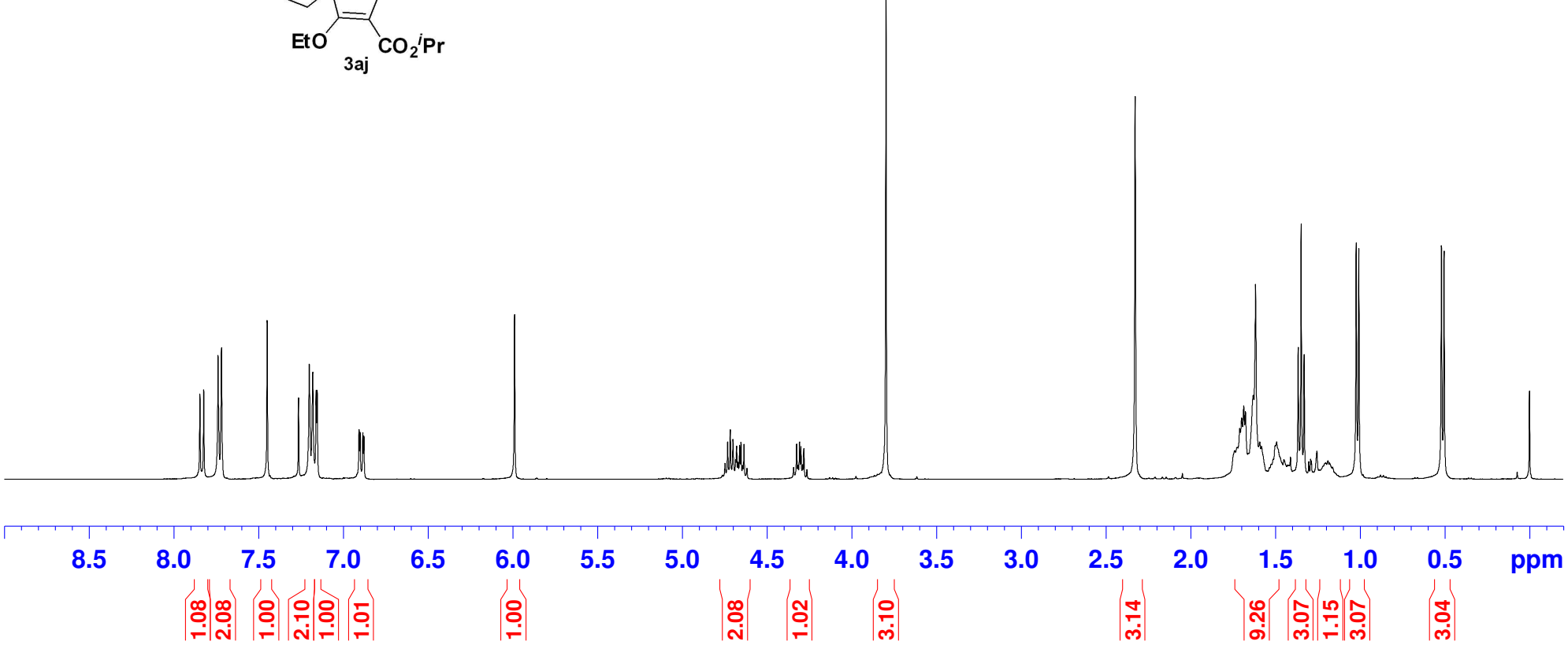
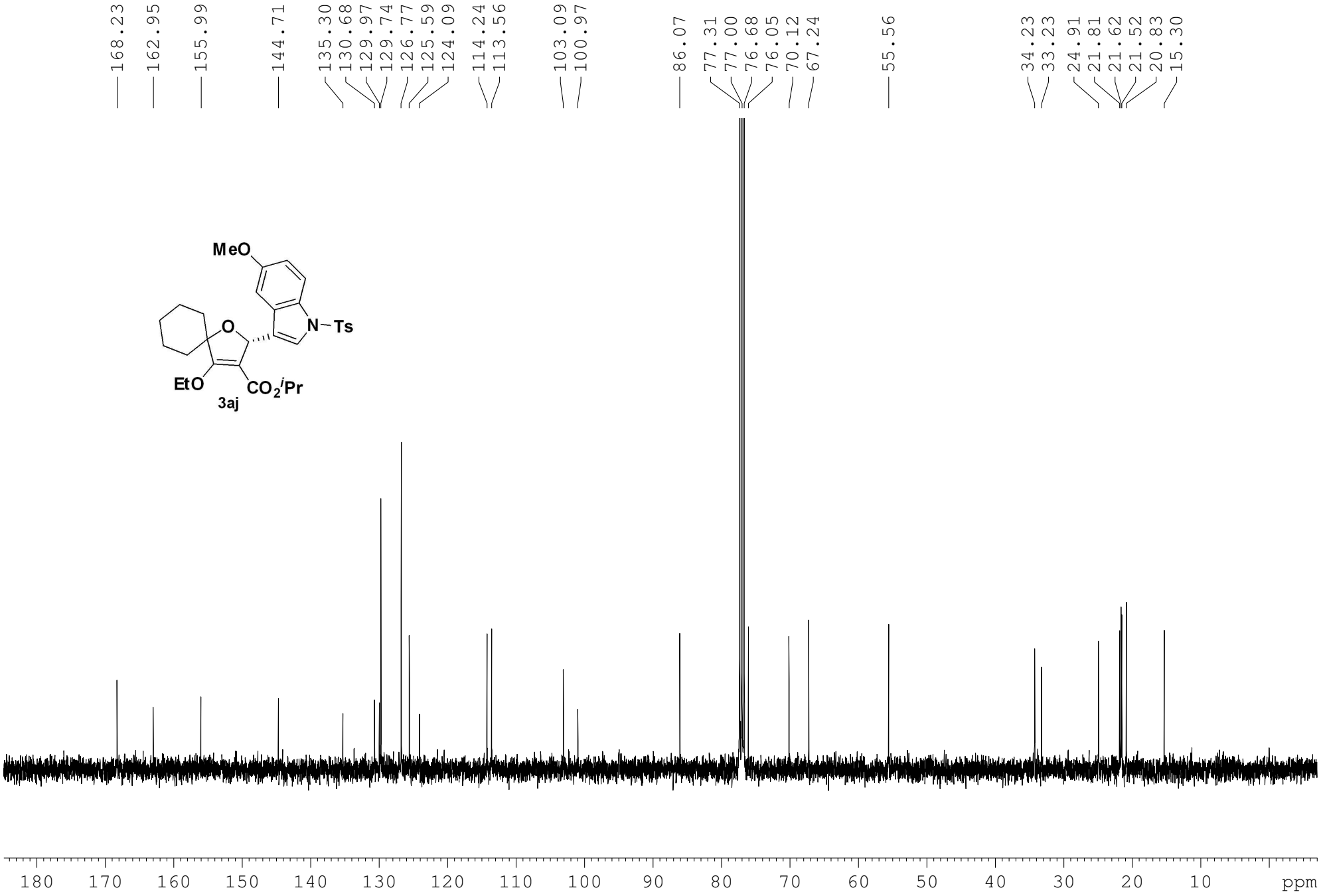
0.504
-0.000



3aj

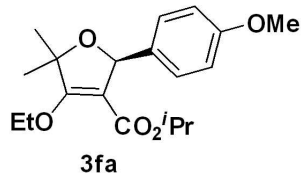


lf-11-84-2C


168.23
162.95
155.99
144.71
135.30
130.68
129.97
129.74
126.77
125.59
124.09
114.24
113.56
103.09
100.97
86.07
77.31
77.00
76.68
76.05
70.12
67.24
55.56
34.23
33.23
24.91
21.81
21.62
21.52
20.83
15.30
MeO
N–Ts
O
EtO
CO2iPr
3aj
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

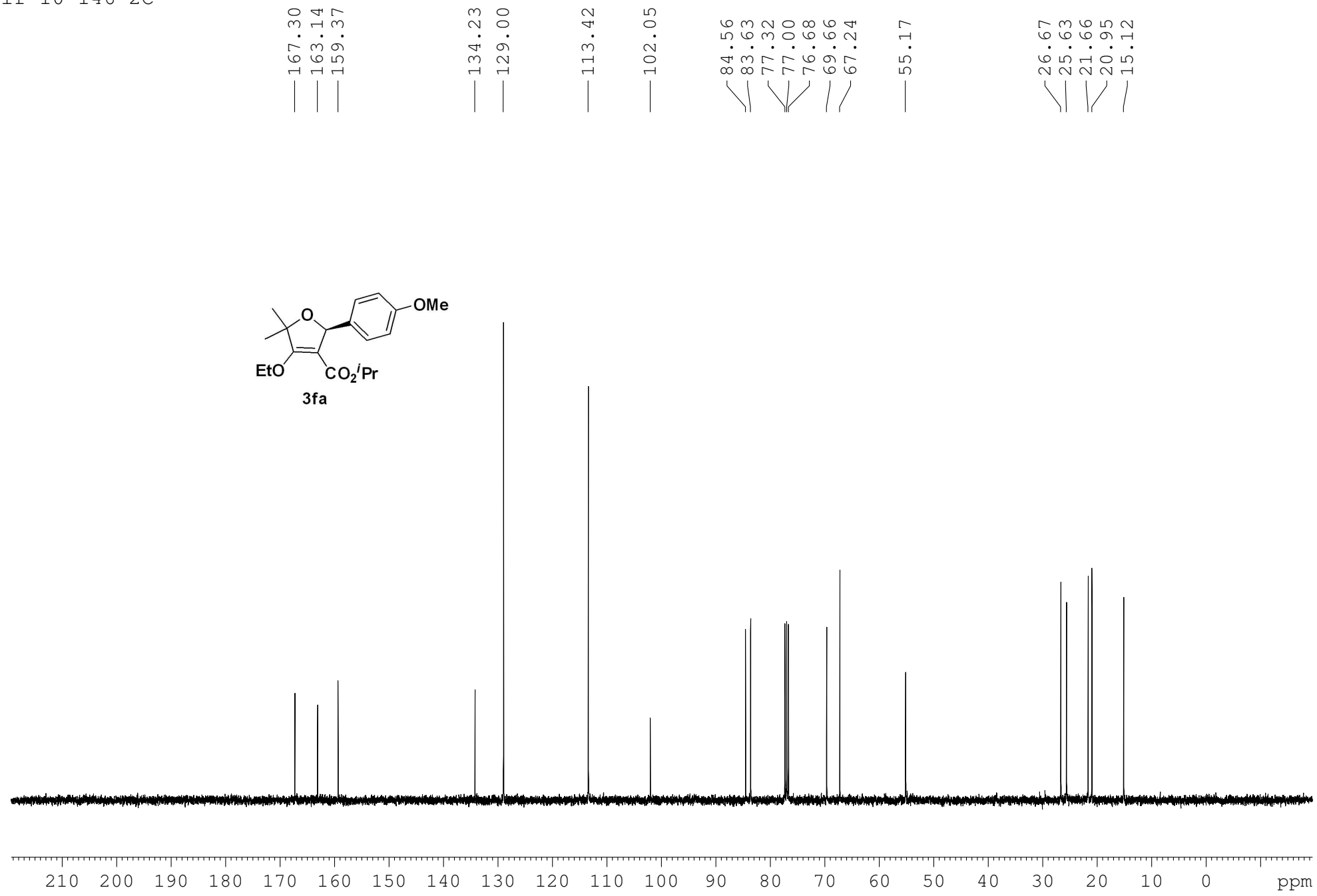
1f-10-146-2H

7.285
7.263
6.846
6.824
5.756
4.822
4.807
4.791
4.775
4.760
4.744
4.729
4.710
4.692
4.685
4.675
4.667
4.657
4.649
4.632
4.285
4.268
4.260
4.250
4.242
4.233
4.225
4.207
3.771
1.422
1.385
1.348
1.331
1.313
1.112
1.096
0.748
0.733
0.000

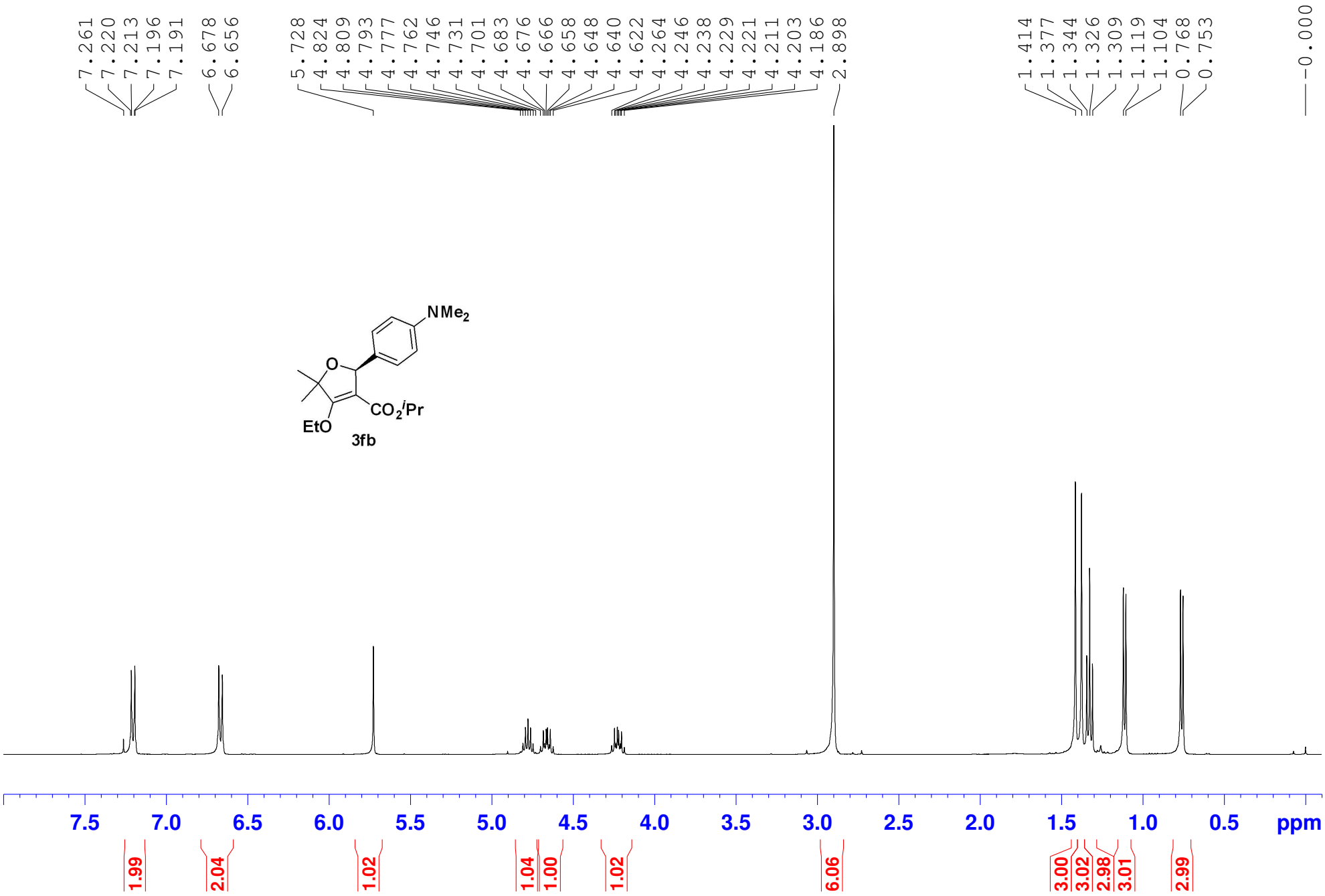


3fa

lf-10-146-2C

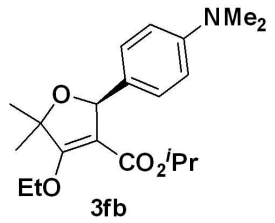

167.30
163.14
159.37
134.23
129.00
113.42
102.05
84.56
83.63
77.32
77.00
76.68
69.66
67.24
55.17
26.67
25.63
21.66
20.95
15.12
OMe
O
EtO
CO2iPr
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

1f-10-102-1H

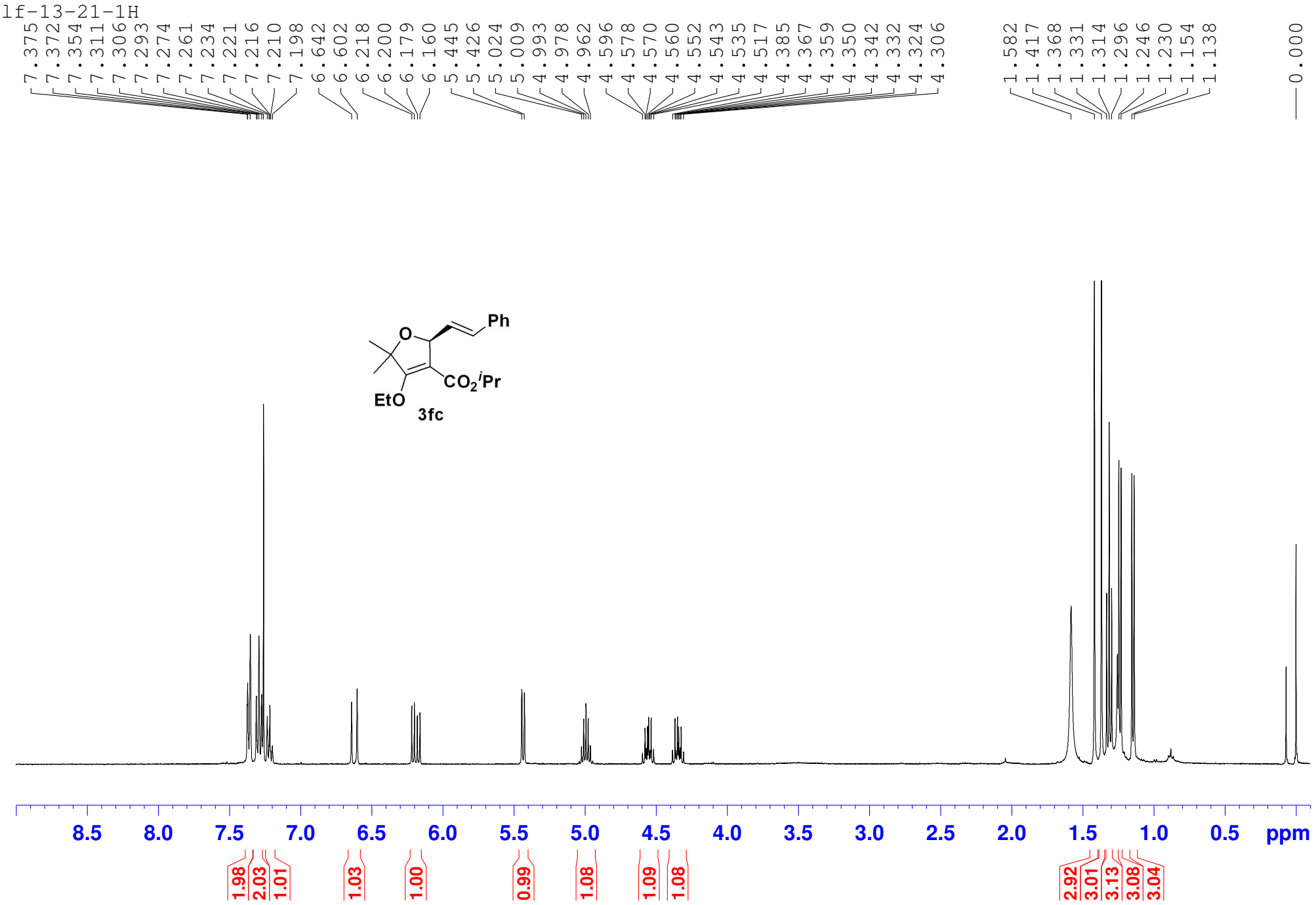

7.261
7.220
7.213
7.196
7.191
6.678
6.656
5.728
4.824
4.809
4.793
4.777
4.762
4.746
4.731
4.701
4.683
4.676
4.666
4.658
4.648
4.640
4.622
4.264
4.246
4.238
4.229
4.221
4.211
4.203
4.186
2.898
1.414
1.377
1.344
1.326
1.309
1.119
1.104
0.768
0.753
-0.000
NMe2
O
CO2iPr
EtO
3fb
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
2.04
1.02
1.04
1.00
1.02
6.06
3.00
3.02
2.98
3.01
2.99

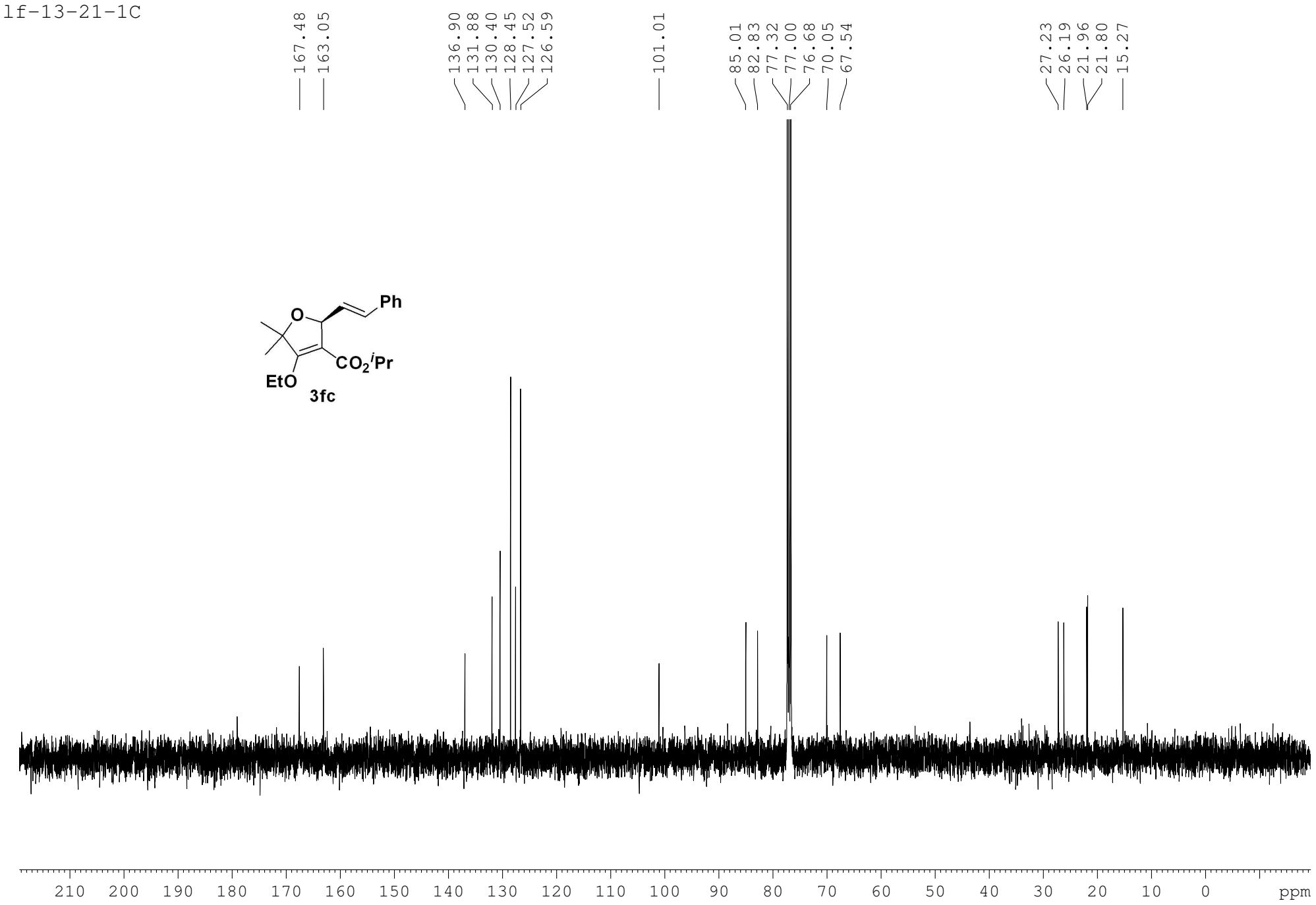
1f-10-102-1C

166.93
163.36
150.55
130.02
128.56
112.34
102.29
84.25
83.84
77.32
77.00
76.68
69.49
67.15
40.66
26.72
25.68
21.69
21.00
15.12

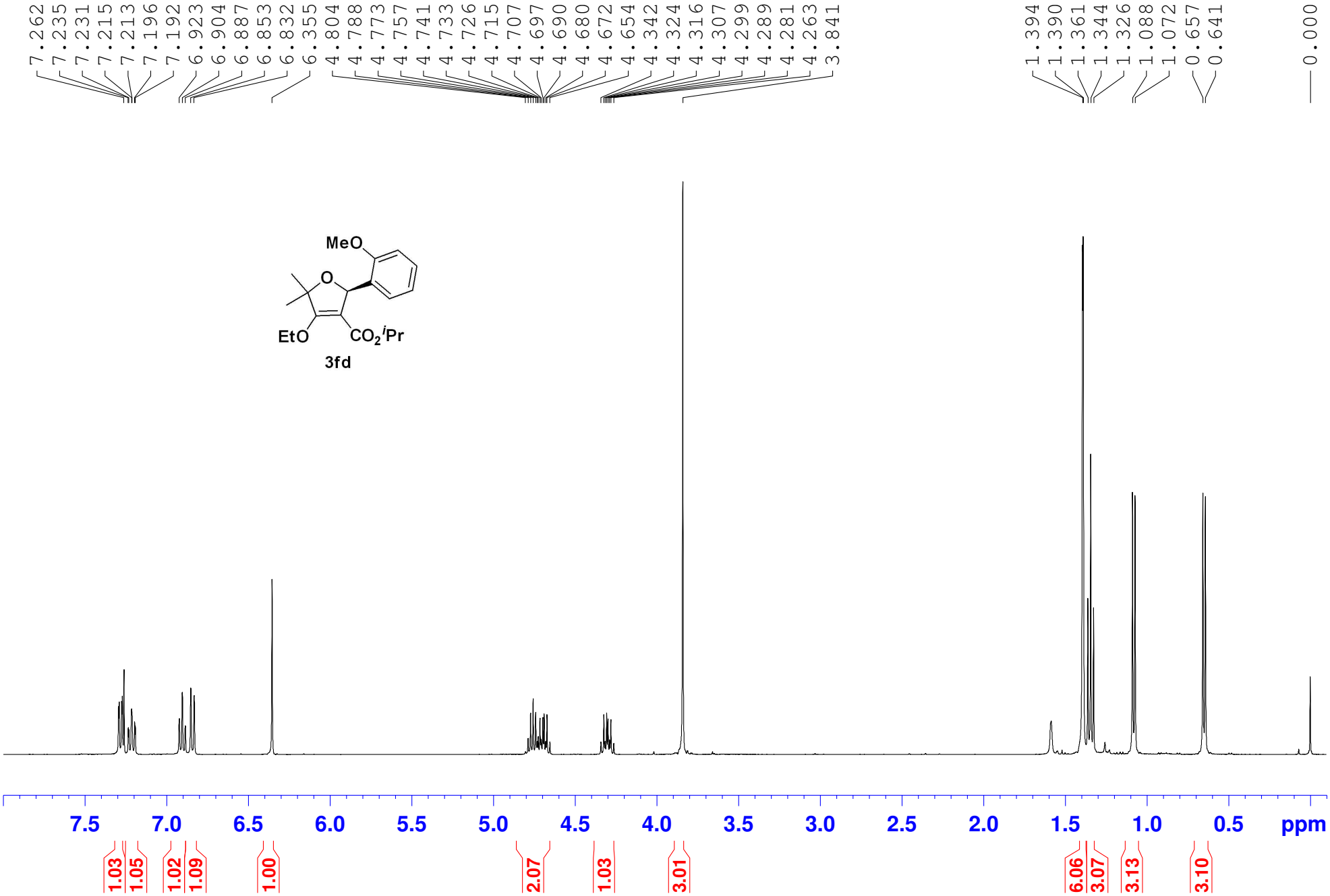


3fb

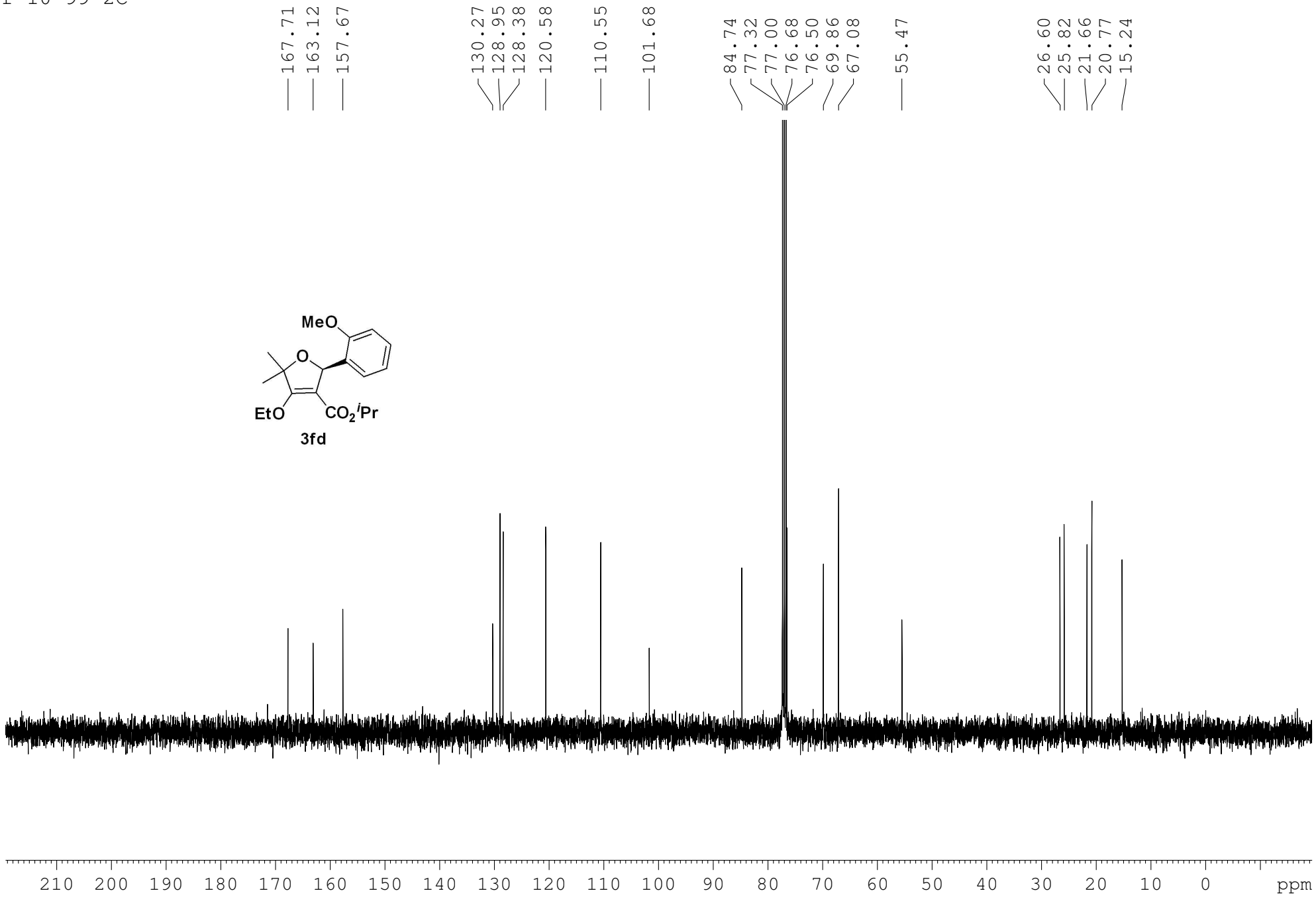

lf-13-21-1H
7.375
7.372
7.354
7.311
7.306
7.293
7.274
7.261
7.234
7.221
7.216
7.210
7.198
6.642
6.602
6.218
6.200
6.179
6.160
5.445
5.426
5.024
5.009
4.993
4.978
4.962
4.596
4.578
4.570
4.560
4.552
4.543
4.535
4.517
4.385
4.367
4.359
4.350
4.342
4.332
4.324
4.306
1.582
1.417
1.368
1.331
1.314
1.296
1.246
1.230
1.154
1.138
0.000
Ph
O
CO2iPr
EtO
3fc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.98
2.03
1.01
1.03
1.00
0.99
1.08
1.09
1.08
2.92
3.01
3.13
3.08
3.04


lf-13-21-1C
167.48
163.05
136.90
131.88
130.40
128.45
127.52
126.59
101.01
85.01
82.83
77.32
77.00
76.68
70.05
67.54
27.23
26.19
21.96
21.80
15.27
Ph
O
CO2iPr
EtO
3fc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

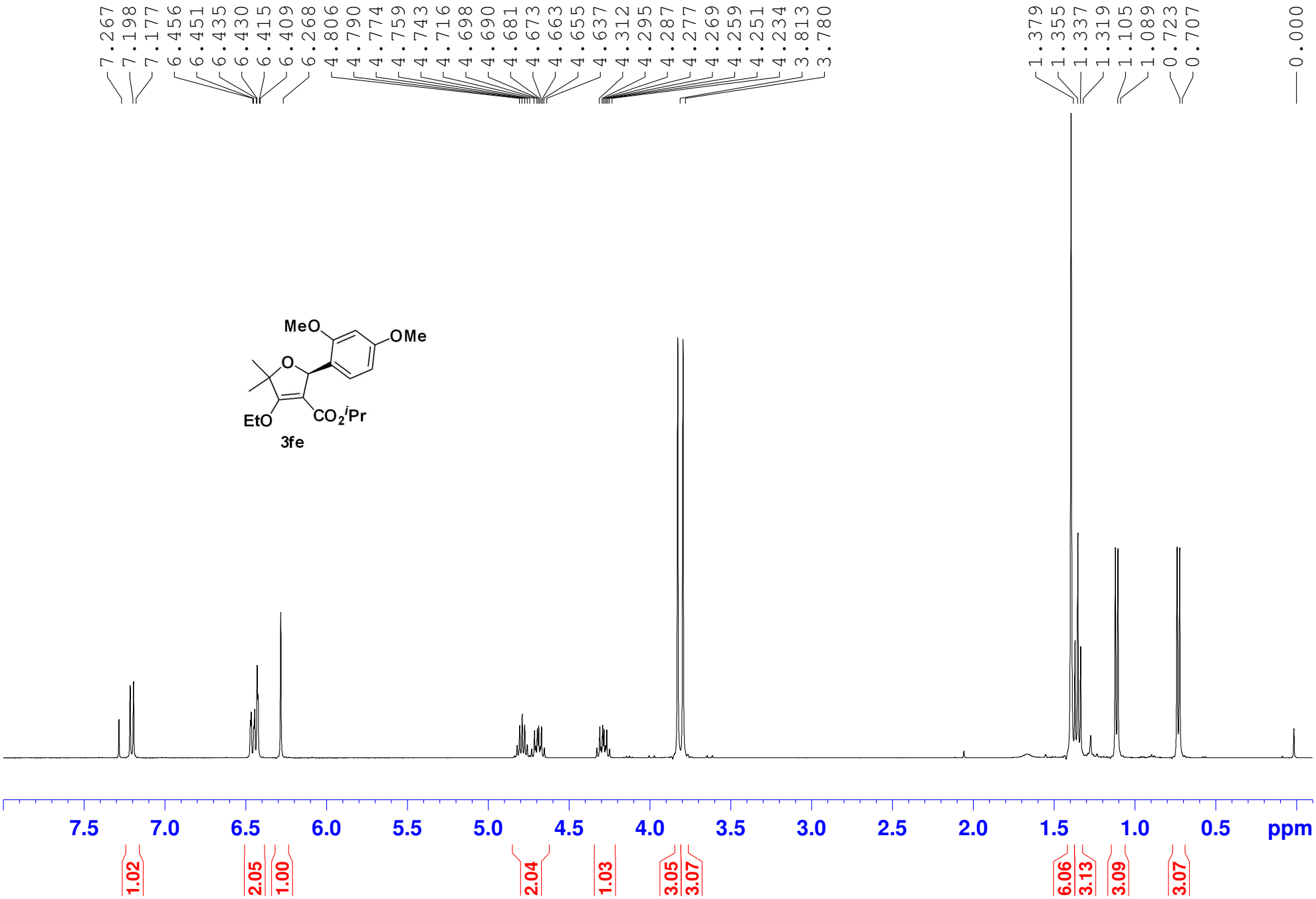
lf-10-99-2H


7.262
7.235
7.231
7.215
7.213
7.196
7.192
6.923
6.904
6.887
6.853
6.832
6.355
4.804
4.788
4.773
4.757
4.741
4.733
4.726
4.715
4.707
4.697
4.690
4.680
4.672
4.654
4.342
4.324
4.316
4.307
4.299
4.289
4.281
4.263
3.841
1.394
1.390
1.361
1.344
1.326
1.088
1.072
0.657
0.641
0.000
MeO
O
EtO
CO2iPr
3fd
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.03
1.05
1.02
1.09
1.00
2.07
1.03
3.01
6.06
3.07
3.13
3.10

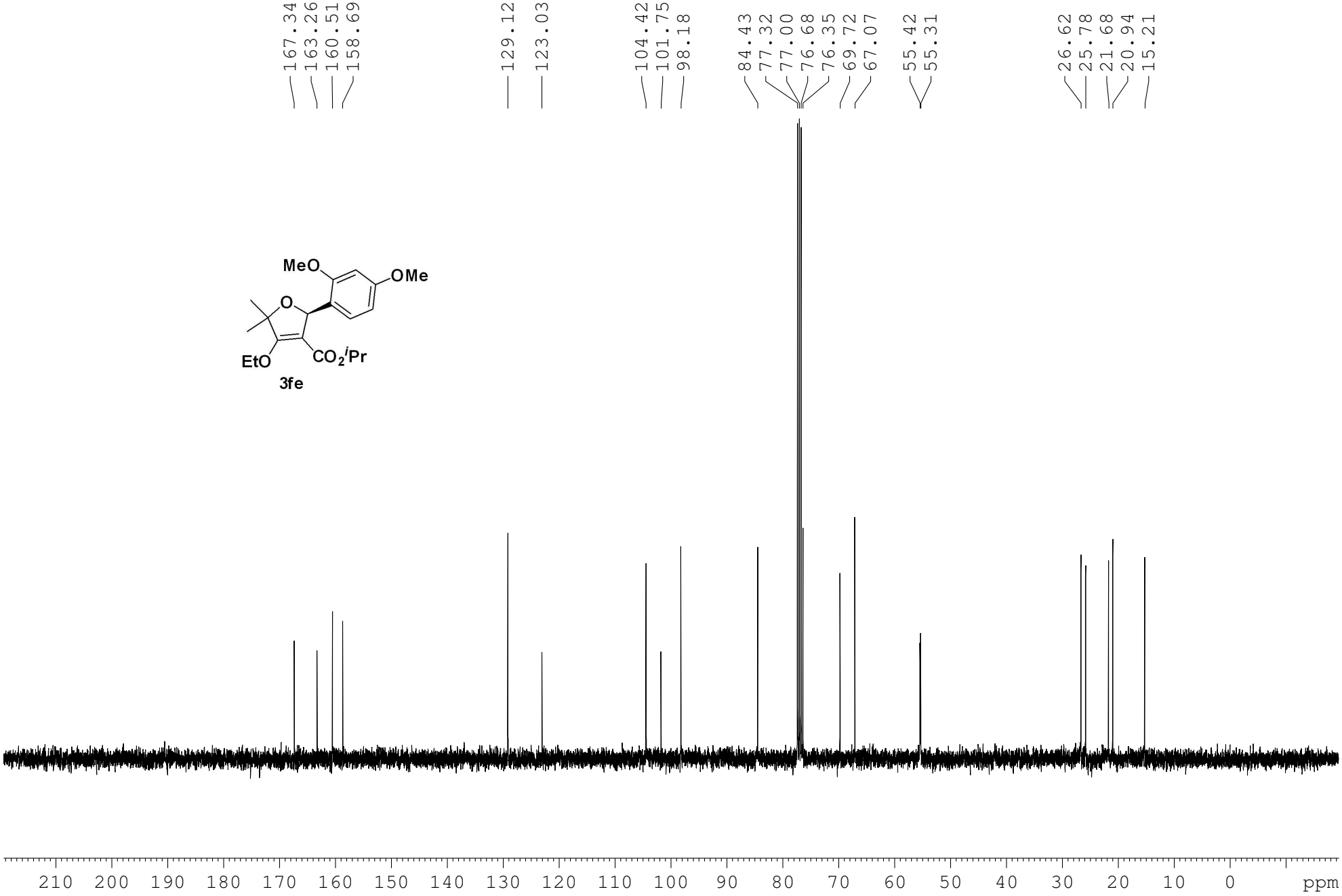
lf-10-99-2C


167.71
163.12
157.67
130.27
128.95
128.38
120.58
110.55
101.68
84.74
77.32
77.00
76.68
76.50
69.86
67.08
55.47
26.60
25.82
21.66
20.77
15.24
MeO
O
EtO
CO2iPr
3fd
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

10-95-4H

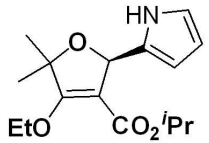

7.267
7.198
7.177
6.456
6.451
6.435
6.430
6.415
6.409
6.268
4.806
4.790
4.774
4.759
4.743
4.716
4.698
4.690
4.681
4.673
4.663
4.655
4.637
4.312
4.295
4.287
4.277
4.269
4.259
4.251
4.234
3.813
3.780
1.379
1.355
1.337
1.319
1.105
1.089
0.723
0.707
0.000
MeO
OMe
O
EtO
CO2iPr
3fe
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.02
2.05
1.00
2.04
1.03
3.05
3.07
6.06
3.13
3.09
3.07

10-95-4C


167.34
163.26
160.51
158.69
129.12
123.03
104.42
101.75
98.18
84.43
77.32
77.00
76.68
76.35
69.72
67.07
55.42
55.31
26.62
25.78
21.68
20.94
15.21
MeO
OMe
O
EtO
CO2iPr
3fe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

lf-13-21-5H

8.394 7.259 6.681 6.677 6.675 6.671 6.668 6.664 6.147 6.138 6.136 6.129 6.100 6.093 6.085 6.079 5.890 4.930 4.915 4.899 4.883 4.868 4.628 4.611 4.603 4.593 4.585 4.575 4.567 4.550 4.319 4.302 4.294 4.284 4.276 4.267 4.259 4.241 1.391 1.372 1.335 1.318 1.300 1.177 1.161 0.948 0.932 0.000

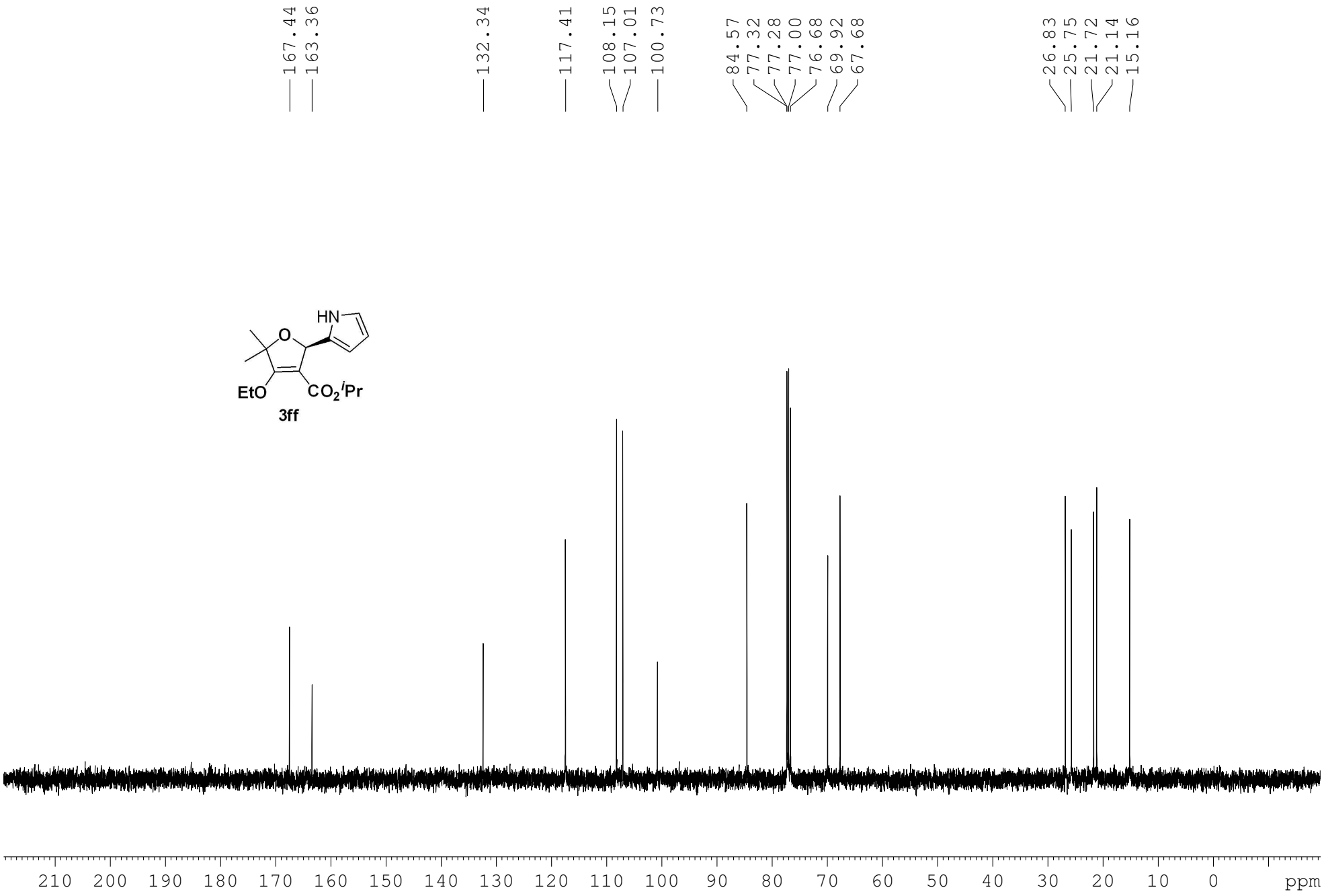


3ff

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

0.98 1.00 1.02 1.01 1.00 1.03 1.05 1.05 3.03 3.00 3.12 3.15 3.09

lf-13-21-5C


167.44
163.36
132.34
117.41
108.15
107.01
100.73
84.57
77.32
77.28
77.00
76.68
69.92
67.68
26.83
25.75
21.72
21.14
15.16
HN
O
EtO
CO2iPr
3ff
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

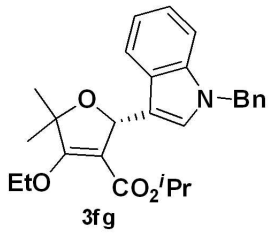
11-28-1H

7.786 7.767 7.273 7.265 7.251 7.233 7.218 7.198 7.156 7.138 7.124 7.109 7.104 7.090 7.072 7.054 6.159

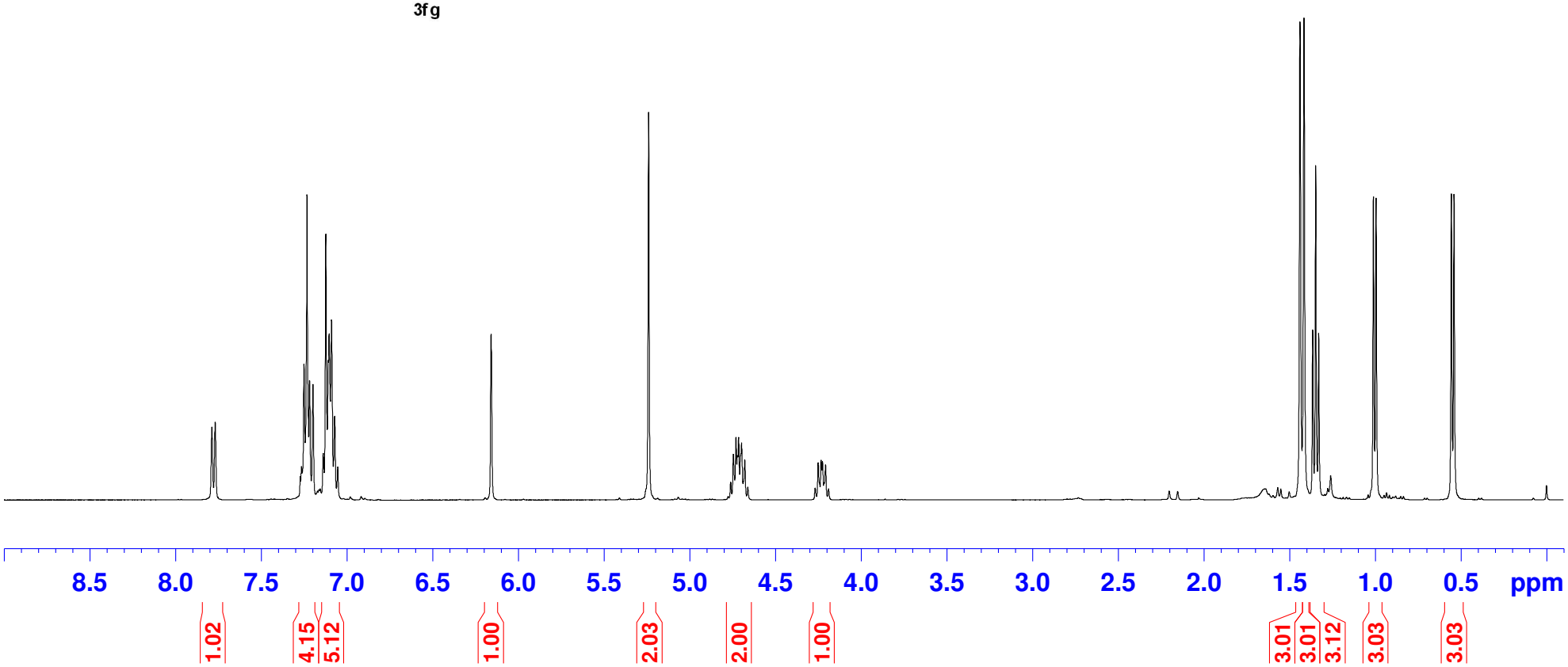
5.240 4.761 4.745 4.730 4.722 4.715 4.697 4.679 4.661 4.268 4.250 4.233 4.226 4.208 4.190

1.439 1.416 1.365 1.347 1.329 1.010 0.995 0.555 0.540

0.000

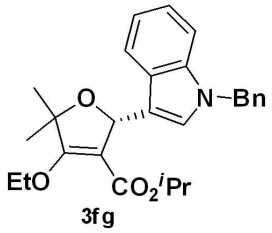


3fg



11-28-1C

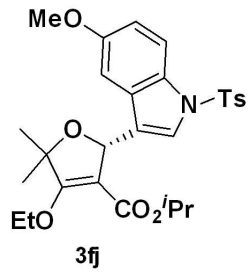
166.66
163.62
137.38
136.93
128.60
127.58
127.50
127.11
126.82
121.67
120.04
119.36
116.34
109.52
101.92
84.10
77.32
77.00
76.83
76.68
69.53
67.12
49.94
26.28
25.48
21.58
20.85
15.21



3fg

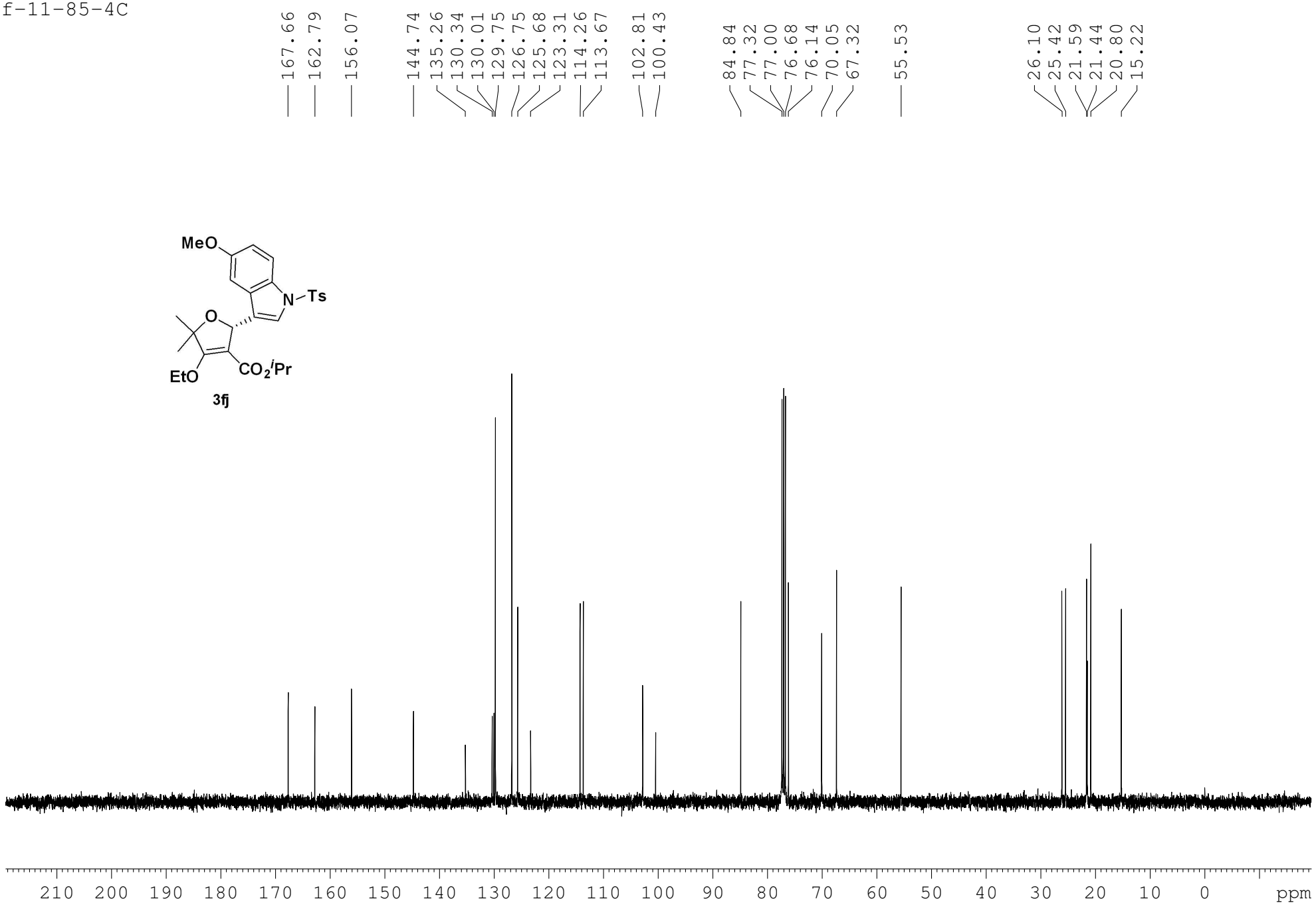
lf-11-85-4H

7.853
7.830
7.742
7.721
7.485
7.267
7.187
7.167
7.121
7.115
6.910
6.904
6.887
6.881
6.013
4.760
4.744
4.729
4.726
4.714
4.708
4.699
4.690
4.682
4.665
4.350
4.332
4.324
4.315
4.307
4.297
4.289
4.272
3.792
2.316
1.398
1.374
1.357
1.339
1.032
1.016
0.517
0.502
-0.000

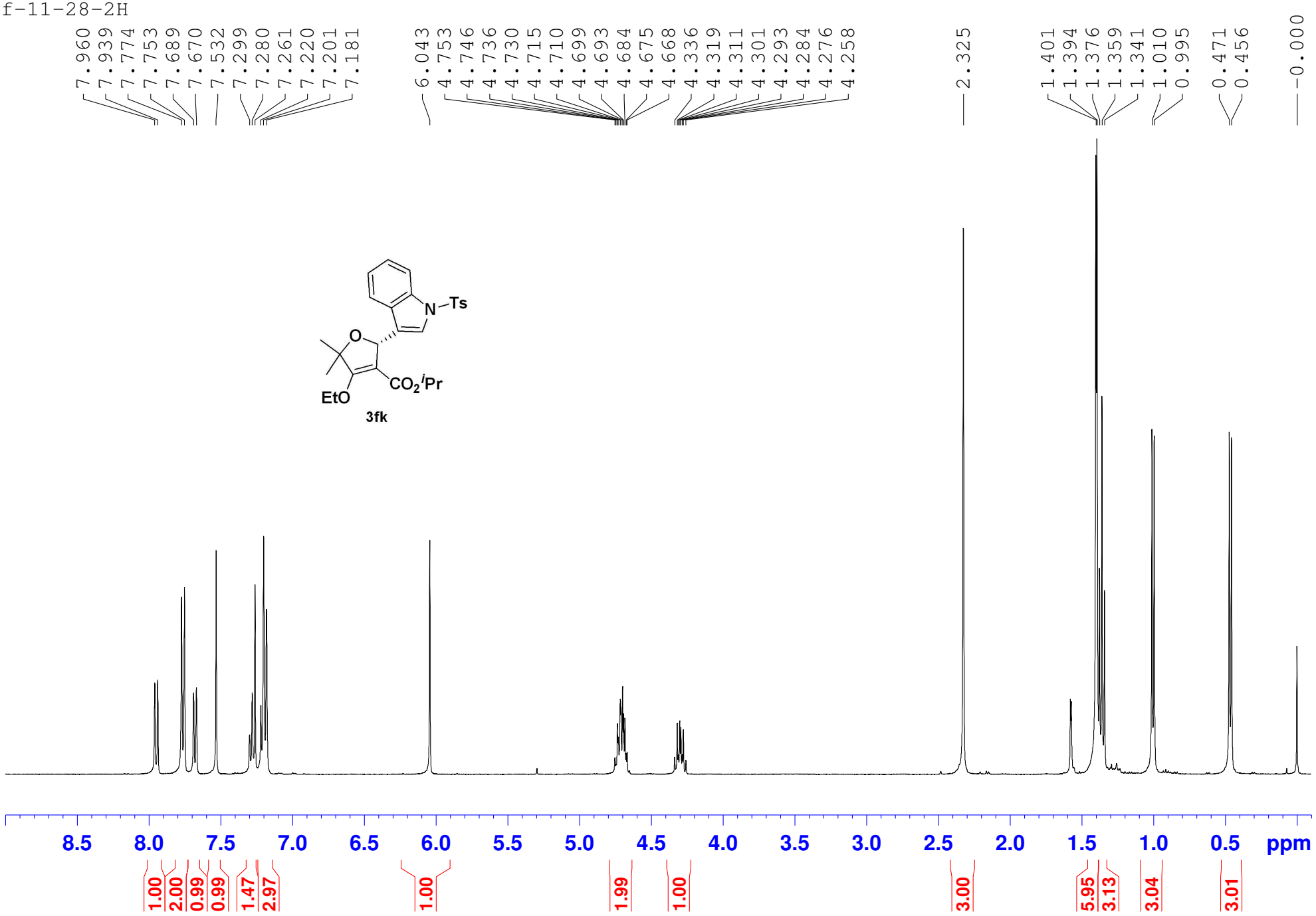


3fj

lf-11-85-4C


167.66
162.79
156.07
144.74
135.26
130.34
130.01
129.75
126.75
125.68
123.31
114.26
113.67
102.81
100.43
84.84
77.32
77.00
76.68
76.14
70.05
67.32
55.53
26.10
25.42
21.59
21.44
20.80
15.22
MeO
N–Ts
O
EtO
CO2iPr
3fj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

lf-11-28-2H


7.960
7.939
7.774
7.753
7.689
7.670
7.532
7.299
7.280
7.261
7.220
7.201
7.181
6.043
4.753
4.746
4.736
4.730
4.715
4.710
4.699
4.693
4.684
4.675
4.668
4.336
4.319
4.311
4.301
4.293
4.284
4.276
4.258
2.325
1.401
1.394
1.376
1.359
1.341
1.010
0.995
0.471
0.456
-0.000
N
Ts
O
EtO
CO2iPr
3fk
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.00
0.99
0.99
1.47
2.97
1.00
1.99
1.00
3.00
5.95
3.13
3.04
3.01

lf-11-28-2C

167.60
162.71
144.74
135.24
135.17
129.64
129.26
126.67
124.98
124.42
123.21
122.95
120.40
113.29
100.53
84.73
77.32
77.00
76.68
76.08
69.88
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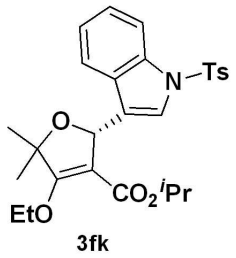
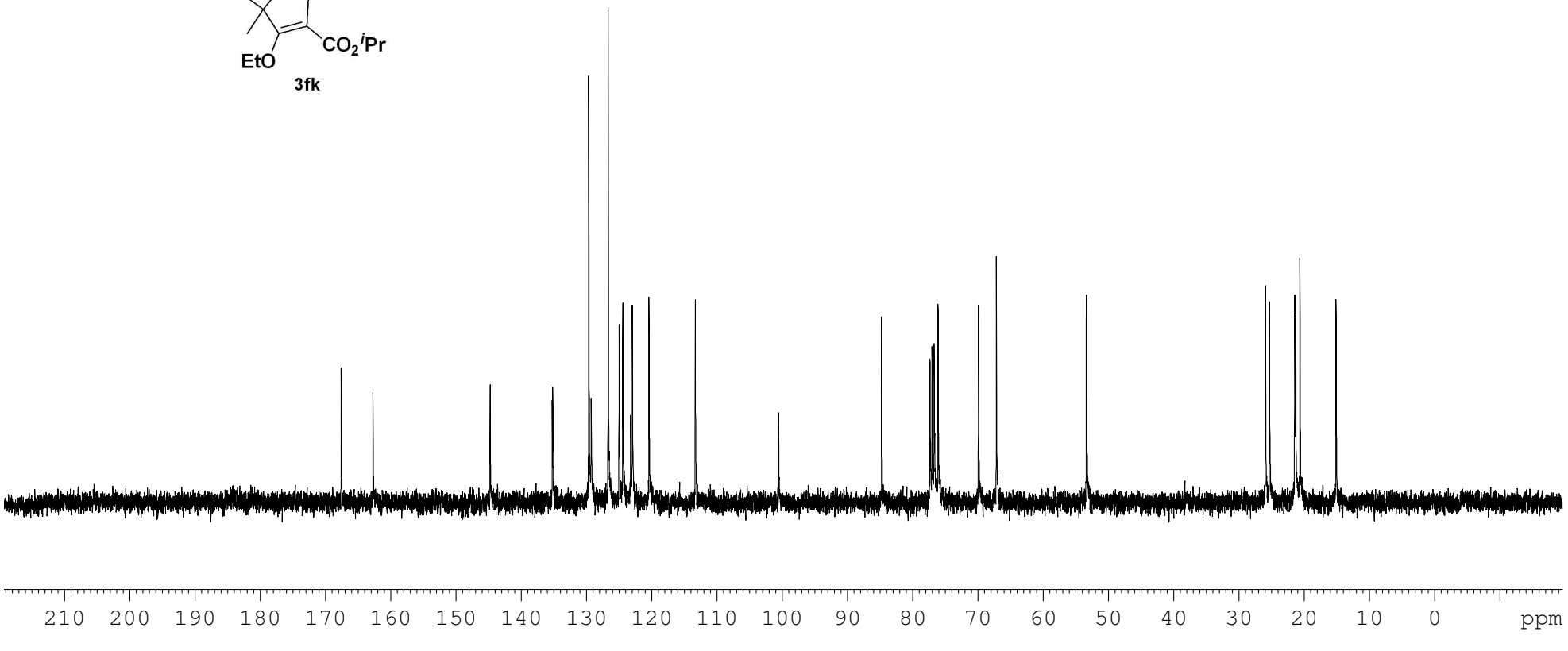
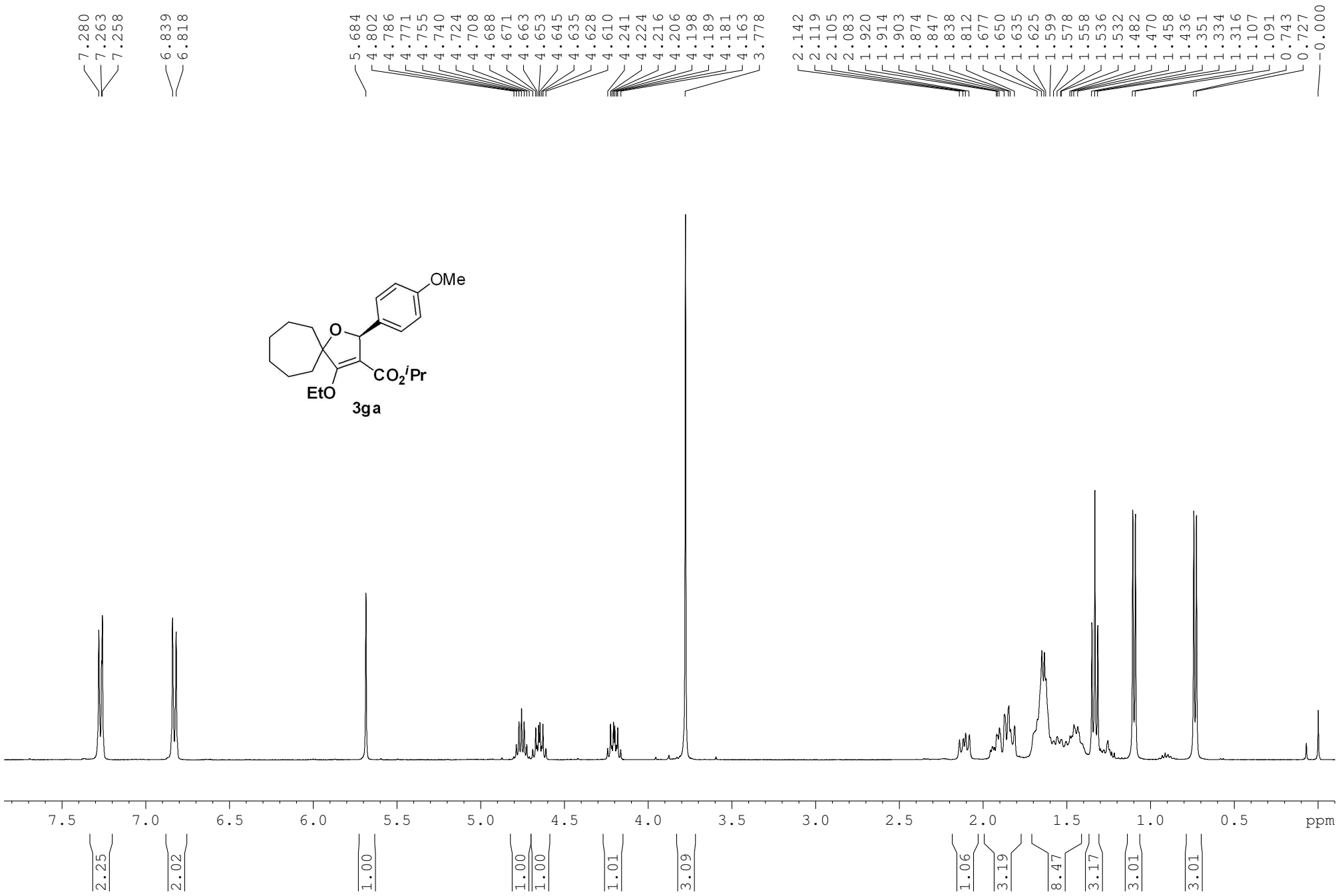
25.89
25.26
21.41
21.26
20.59
15.07



3fk

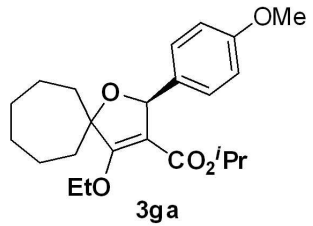


lf-11-79-1H


7.280
7.263
7.258
6.839
6.818
5.684
4.802
4.786
4.771
4.755
4.740
4.724
4.708
4.688
4.671
4.663
4.653
4.645
4.635
4.628
4.610
4.241
4.224
4.216
4.206
4.198
4.189
4.181
4.163
3.778
2.142
2.119
2.105
2.083
1.920
1.914
1.903
1.874
1.847
1.838
1.812
1.677
1.650
1.635
1.625
1.599
1.578
1.558
1.536
1.532
1.482
1.470
1.458
1.436
1.351
1.334
1.316
1.107
1.091
0.743
0.727
-0.000
OMe
O
CO2iPr
EtO
3ga
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.25
2.02
1.00
1.00
1.00
1.01
3.09
1.06
3.19
8.47
3.17
3.01
3.01

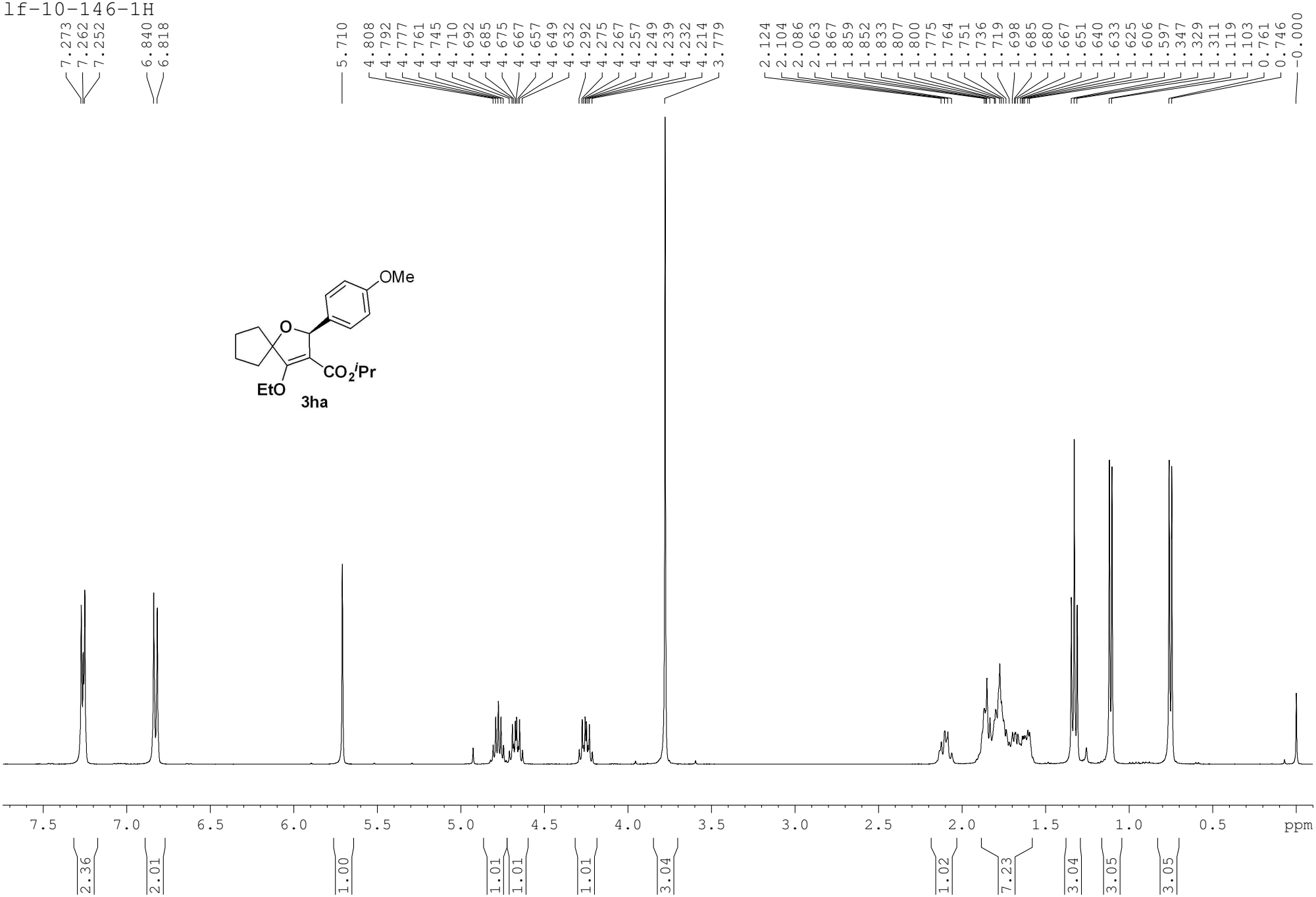
lf-11-79-1C

169.15
163.37
159.33
134.52
129.22
113.37
101.82
89.04
83.38
77.32
77.00
76.69
69.82
67.21
55.25
39.55
37.66
30.46
30.15
22.97
21.73
21.01
15.23



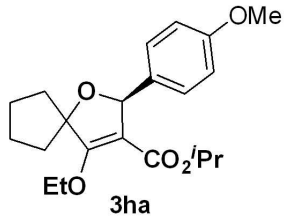
3ga

lf-10-146-1H


7.273
7.262
7.252
6.840
6.818
5.710
4.808
4.792
4.777
4.761
4.745
4.710
4.692
4.685
4.675
4.667
4.657
4.649
4.632
4.292
4.275
4.267
4.257
4.249
4.239
4.232
4.214
3.779
2.124
2.104
2.086
2.063
1.867
1.859
1.852
1.833
1.807
1.800
1.775
1.764
1.751
1.736
1.719
1.698
1.685
1.680
1.667
1.651
1.640
1.633
1.625
1.606
1.597
1.347
1.329
1.311
1.119
1.103
0.761
0.746
-0.000
OMe
O
CO2iPr
EtO
3ha
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.36
2.01
1.00
1.01
1.01
1.01
3.04
1.02
7.23
3.04
3.05
3.05

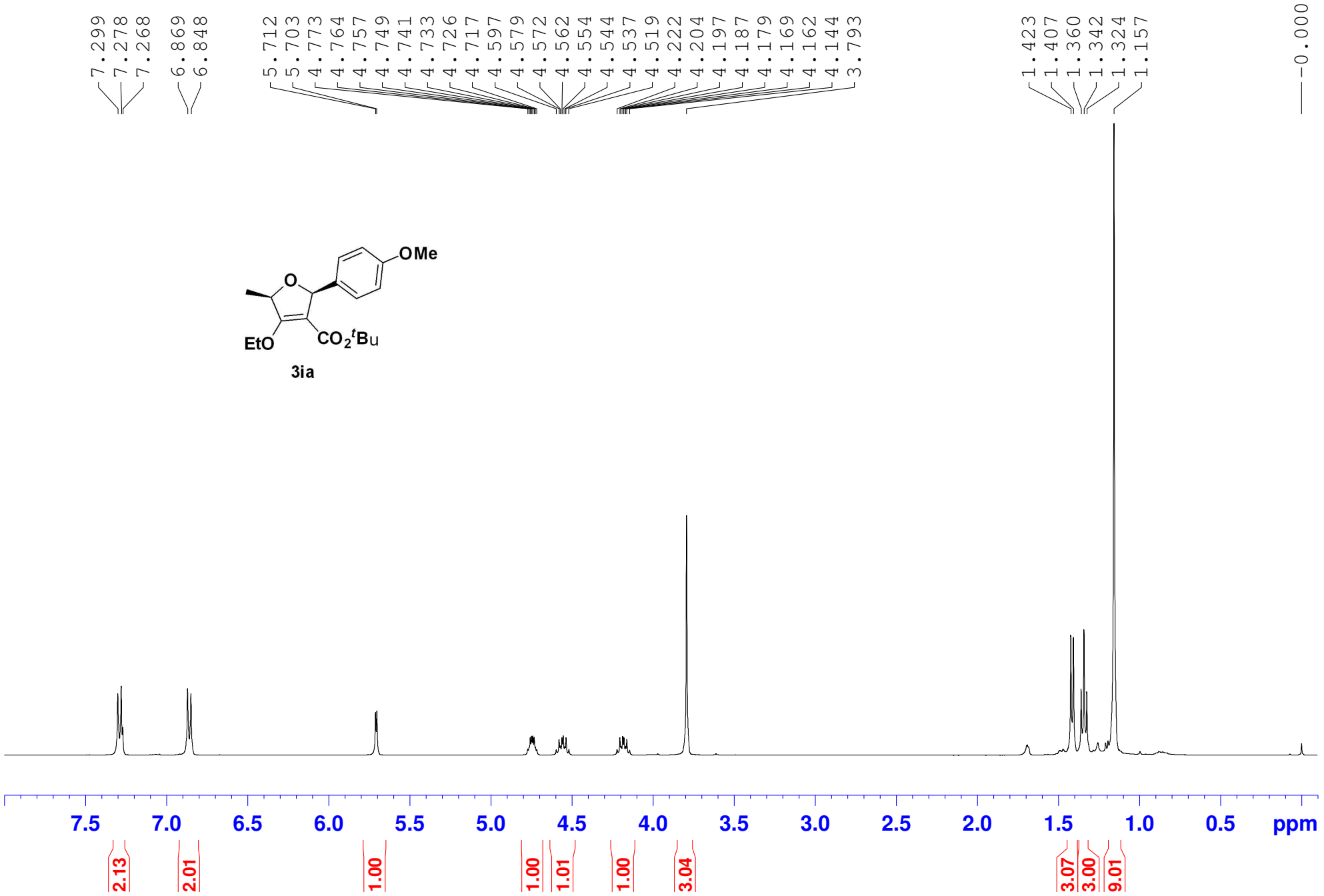
lf-10-146-1C

166.11
162.97
159.39
134.46
129.06
113.44
103.27
94.80
84.07
77.31
77.00
76.68
69.75
67.27
55.26
38.23
37.50
25.22
25.17
21.75
21.05
15.22



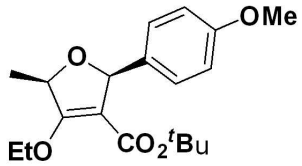
3ha

1f-12-120-1

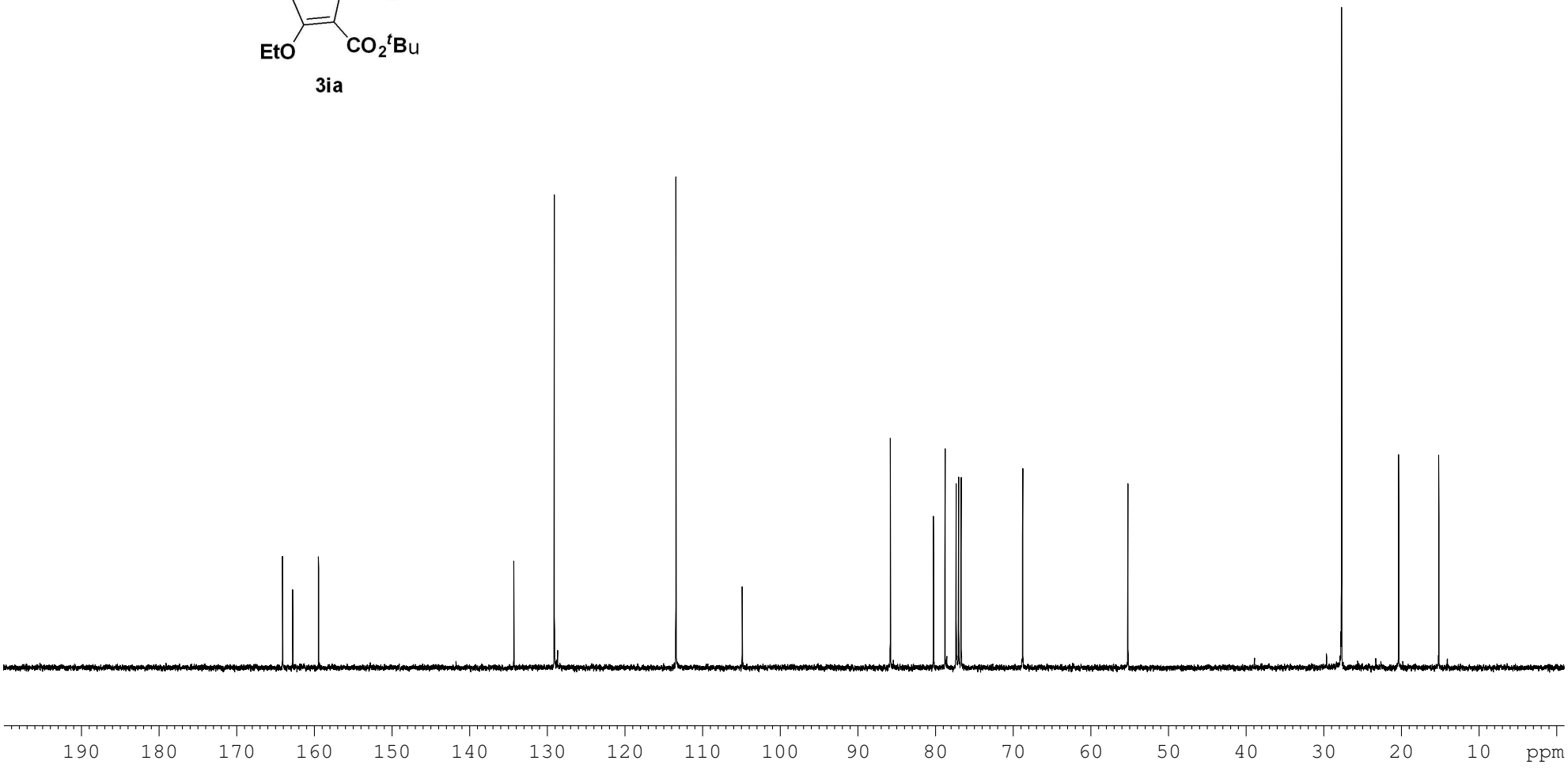

7.299
7.278
7.268
6.869
6.848
5.712
5.703
4.773
4.764
4.757
4.749
4.741
4.733
4.726
4.717
4.597
4.579
4.572
4.562
4.554
4.544
4.537
4.519
4.222
4.204
4.197
4.187
4.179
4.169
4.162
4.144
3.793
1.423
1.407
1.360
1.342
1.324
1.157
0.000
OMe
O
EtO
CO2tBu
3ia
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.13
2.01
1.00
1.00
1.01
1.00
3.04
3.07
3.00
9.01

lf-12-121-1C

164.08
162.78
159.44
134.29
129.08
113.42
104.88
85.79
80.23
78.75
77.32
77.00
76.68
68.75
55.20
27.67
20.31
15.15

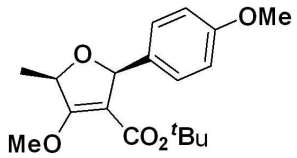


3ia



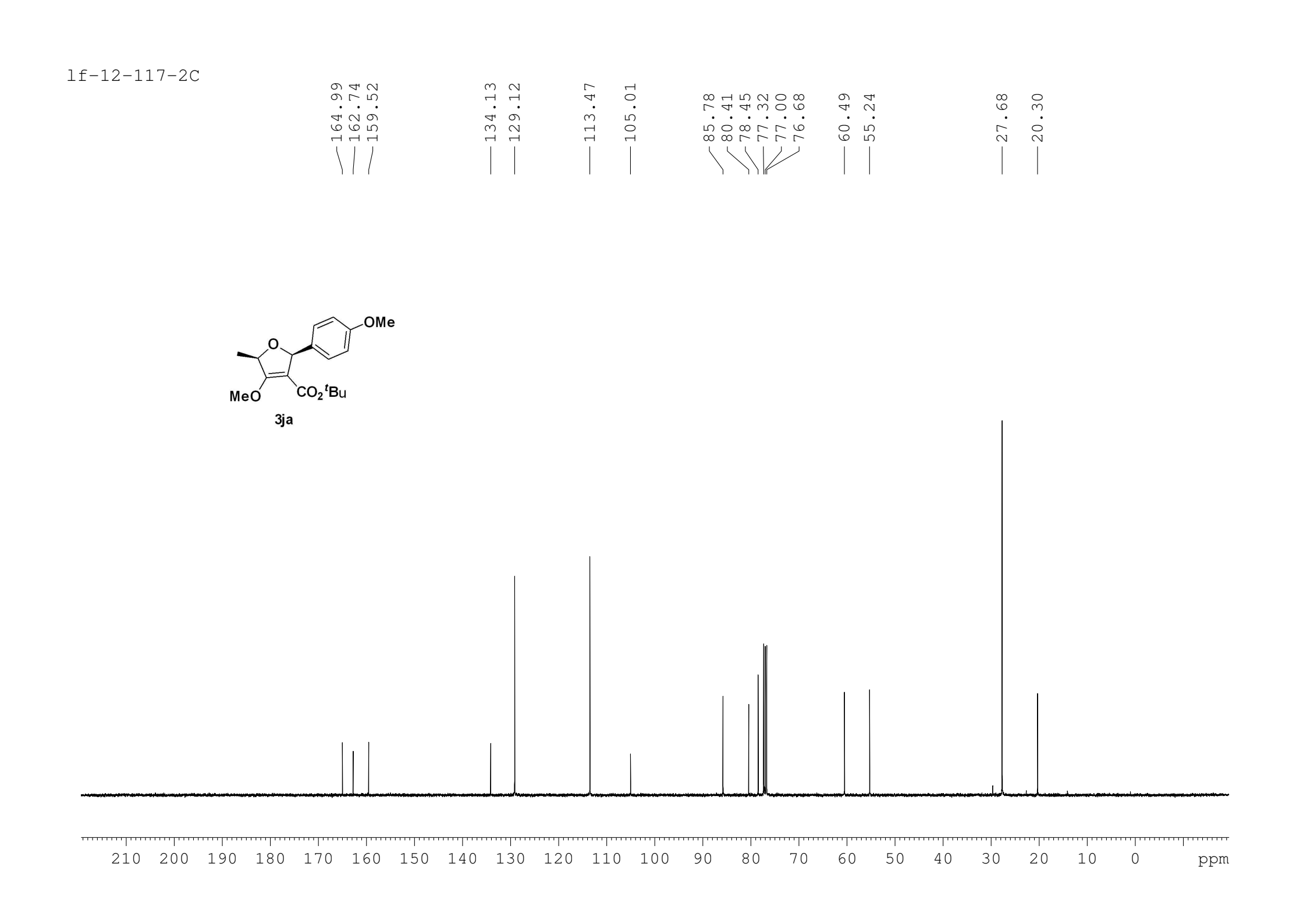
lf-12-117-2H

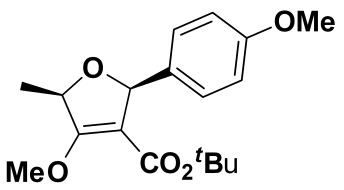
7.307
7.300
7.295
7.284
7.279
7.270
6.879
6.872
6.867
6.856
6.851
6.843
5.707
5.698
4.788
4.779
4.772
4.763
4.756
4.747
4.740
4.732
4.042
3.793
1.424
1.408
1.157
0.000



3ja

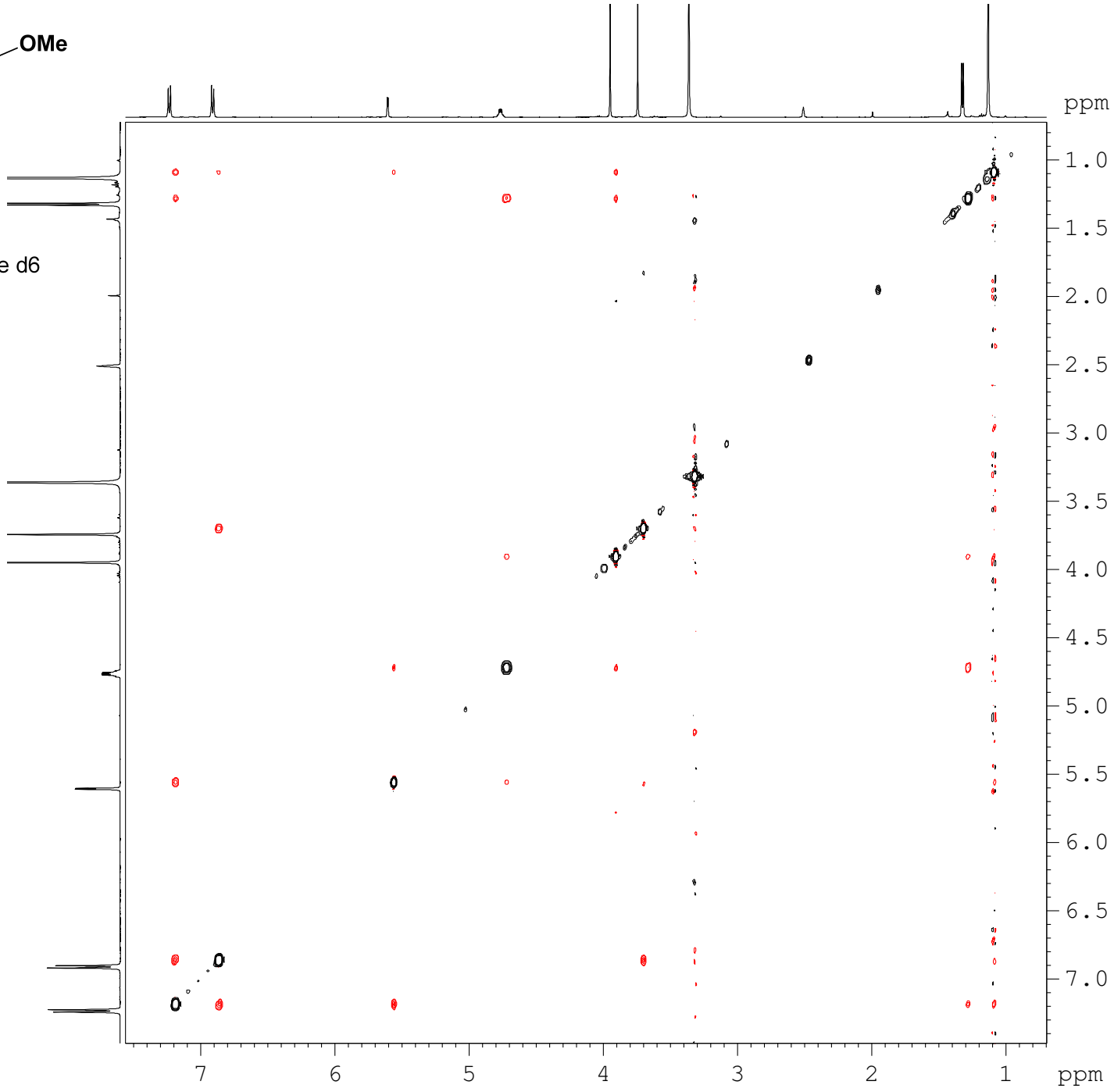
lf-12-117-2C

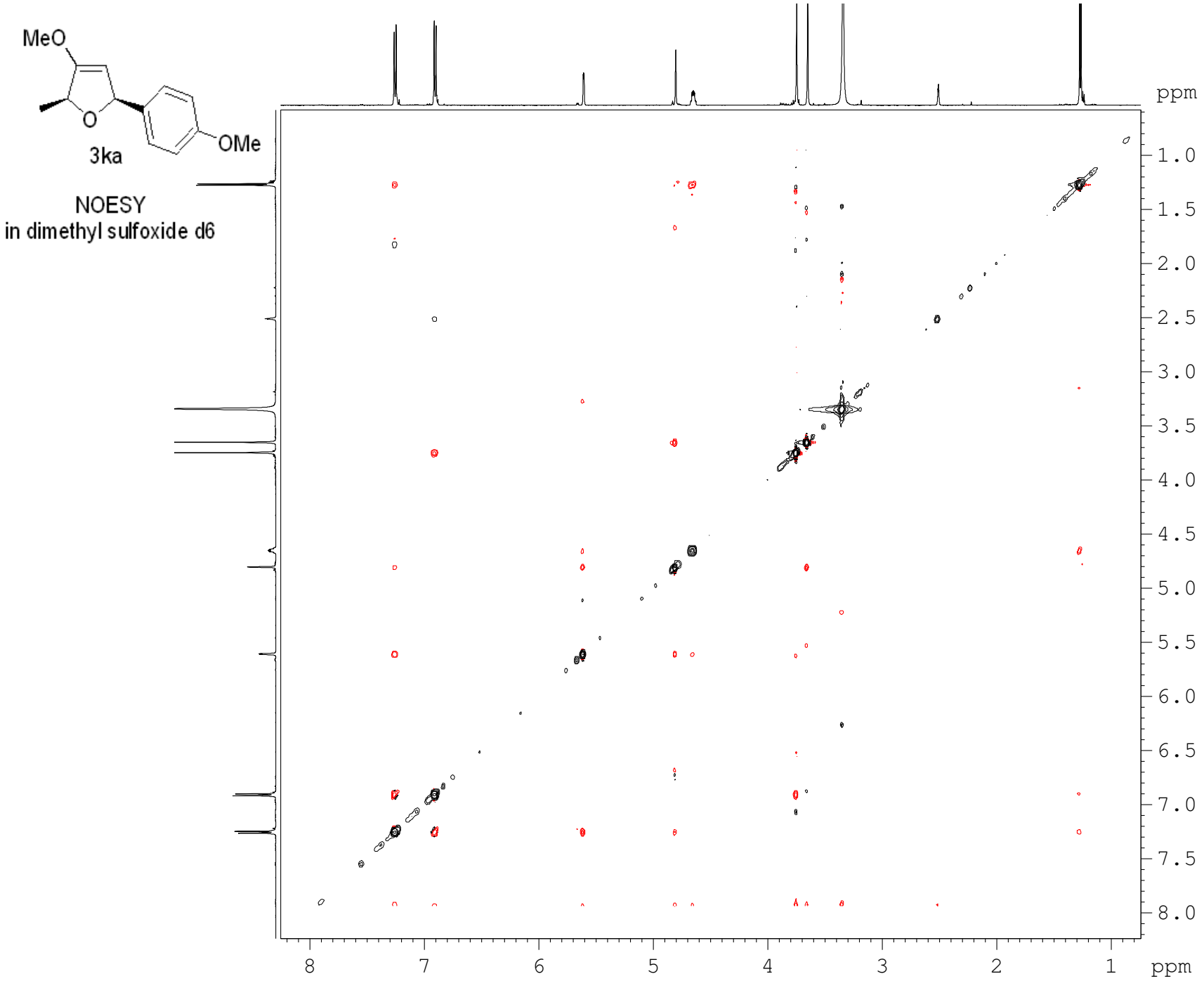

164.99
162.74
159.52
134.13
129.12
113.47
105.01
85.78
80.41
78.45
77.32
77.00
76.68
60.49
55.24
27.68
20.30
OMe
O
MeO
CO2tBu
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



3ja

NOESY
in dimethyl sulfoxide d6




MeO
O
OMe
3ka
NOESY
in dimethyl sulfoxide d6
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8
7
6
5
4
3
2
1
ppm