Supporting information

Stereodivergent Synthesis of Trisubstituted Enamides: Direct Access to Both Pure Geometrical Isomers.

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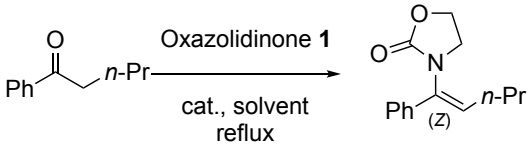
1. Conditions screening for synthesis of (*Z/E*)-enamides.

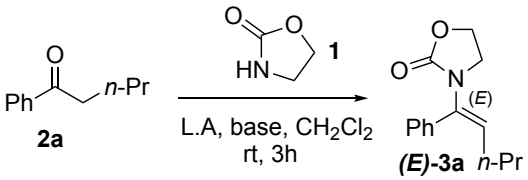
Table S1. Screening of Brønsted acid conditions for synthesis of (*Z*)-enamides



Entry	catalyst (mol%)	Oxazolidinone (eq)	solvent	d.r. [*E*:*Z*]	conv. [%]
1	$NH(Tf)_2$(10)	2	toluene	33:67	4
2	TfOH(10)	2	toluene	19:81	8
3	SI-*p*-TSA[a](10)	2	toluene	17:83	6
4	PTSA(10)	2	cyclohexane	10:90	3
5	PTSA(10)	2	DME	23:77	6
6	H_2SO_4(10)	2	toluene	22:78	4
7	CSA[b](10)	2	toluene	25:75	16
8	PTSA(10)	2	toluene	15:85	40
9	PTSA(10)	2	$PhCF_3$	21:79	35
10	PTSA(10)	2	Benzene	11:89	30
11	PTSA(10)	3	PhEt	28:72	17
12	PTSA(5)	3	toluene	14:86	31
13	PTSA(20)	3	toluene	18:82	46
14[c]	PTSA(10)	3	toluene	15:85	50
15[d]	PTSA(10)	3	toluene	-	nr
16[e]	PTSA(10)	3	toluene	-	nr

Standard condition: 3 equiv. oxazolidinone, 10 mol% *p*-TSA, Dean Stark. *[a]* SI-p-TSA= p-Toluenesulfonic acid on silica; *[b]* CAS= Camphor sulfonic acid; *[c]* Reaction time of 36 h. *[d]* Addition of molecular sieves 3Å. *[e]* Addition of 1 equiv. of Na_2SO_4.

Table S2. Screening of Lewis acid conditions for synthesis of (*E*)-enamides

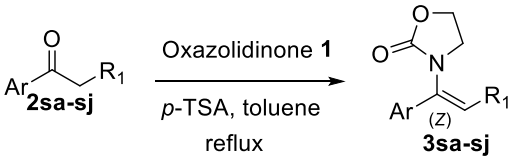


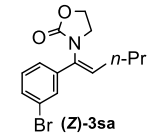
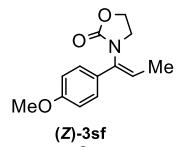
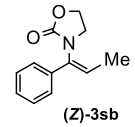
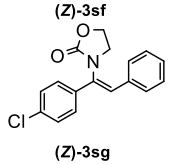
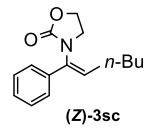
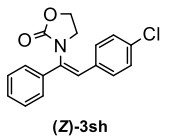
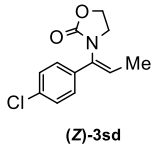
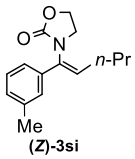
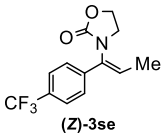
Entry	Oxazolidinone (equiv)	L.A. (equiv)	Base (equiv)	d.r. [*E*:*Z*]	conv. [%]
1	0.9	$AlCl_3$(1.2)	-	-	nr
2	0.9	$TiCl_4$(1.2)	-	-	nr
3	0.9	$TiCl_4$(1.2)	NEt_3(5)	98:2	38
4	2	$TiCl_4$(1.2)	NEt_3(5)	97:3	44
5	3	$TiCl_4$(1.2)	NEt_3(5)	97:3	55
6	3	$TiCl_4$(2.4)	NEt_3(10)	96:4	50
7[a]	3	$TiCl_4$(1.2)	NEt_3(5)	96:4	38
8	p.w.[b]	$TiCl_4$(1.2)	NEt_3(5)	98:2	31
9	5	$TiCl_4$(1.2)	NEt_3(5)	97:3	45
10	3	$TiCl_4$(5)	NEt_3(15)	96:4	49
11[c]	3	$TiCl_4$(1.2)	NEt_3(5)	97:3	30
12	6	$TiCl_4$(2.4)	NEt_3(10)	96:4	58

[a] Addition of molecular sieves 3 Å; [b] **1** added in portion of 0.2 equiv. each minutes; [c] **2a** added with syringe pump (0.3 equiv./h.).

2. Additional data for (*Z*)-enecarbamates.

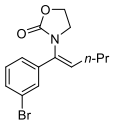
Table S3. Substrates scope for (*Z*)-enamides



Entry	Enamide	Yield[a] [%]	Recovered s.m.[b][%]	Corrected Yield[c][%]	Entry	Enamide	Yield [%]	Recovered s.m.[b][%]	Corrected Yield[%]
1	 (*Z*)-3sa	21	67	64	6	 (*Z*)-3sf	24	55	53
2	 (*Z*)-3sb	46	53	96	7	 (*Z*)-3sg	11	83	65
3	 (*Z*)-3sc	24	70	80	8	 (*Z*)-3sh	5	92	63
4	 (*Z*)-3sd	45	39	74	9	 (*Z*)-3si	19	76	79
5	 (*Z*)-3se	19	60	47					

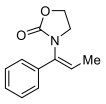
Standard condition: 3 equiv. oxazolidinone, 10 mol% *p*-TSA, Dean Stark; [a] Isolated yield; [b] Isolated amount of ketones after purification; [c] Yield corrected by recovered starting material.

Characterization NMR data of new α,β-enecarbamates not present in the manuscript (*Z*-isomer).



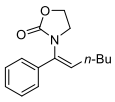
(*Z*)-3-(1-(3-bromophenyl)pent-1-en-1-yl)oxazolidin-2-one (3sa)

Colorless oil, 0.649g (21% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (t, *J* = 1.8 Hz, 1H), 7.44 (dt, *J* = 7.5, 1.9, 1.4 Hz, 1H), 7.31 – 7.20 (m, 2H), 6.04 (t, *J* = 7.2 Hz, 1H), 4.57 – 4.45 (m, 2H), 3.74 – 3.64 (m, 2H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.61 – 1.50 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.4, 138.2, 132.7, 132.1, 131.2, 130.2, 128.9, 124.4, 122.9, 62.3, 45.7, 30.4, 22.0, 14.1. HRMS (ESI-TOF) calcd for $C_{14}H_{16}BrNO_2Na$ $[M+Na]^+$:332.0257, found: 332.0265.



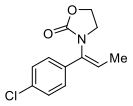
(*Z*)-3-(1-phenylprop-1-en-1-yl)oxazolidin-2-one(3sb)

Yellow oil, 0.934g (46% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 5H), 6.11 (q, *J* = 7.0 Hz, 1H), 4.54 – 4.47 (m, 2H), 3.71 – 3.65 (m, 2H), 1.86 (d, *J* = 7.0 Hz, 3H). ^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 156.3, 135.8, 134.8, 128.7, 128.2, 125.8, 124.9, 62.3, 45.4, 13.9. HRMS (ESI-TOF) calcd for $C_{12}H_{13}NO_2Na$ $[M+Na]^+$: 226.0838, found: 226.0828.



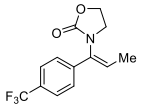
(*Z*)-3-(1-phenylhex-1-en-1-yl)oxazolidin-2-one(3sc)

White solid, mp 61.9-64.2 °C, 0.588g (24% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 5H), 6.00 (t, *J* = 7.2 Hz, 1H), 4.52 – 4.37 (m, 2H), 3.70 – 3.56 (m, 2H), 2.23 (q, *J* = 7.3 Hz, 2H), 1.58 – 1.26 (m, 5H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.6 , 136.0 , 133.8 , 130.9 , 128.8 , 128.3 , 126.0 , 62.4 , 45.8 , 31.2 , 28.1 , 22.7 , 14.1 . HRMS (ESI-TOF) calcd for $C_{15}H_{19}NO_2Na$ $[M+Na]^+$:: 268.1308, found: 268.1301.



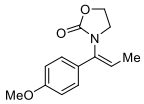
(*Z*)-3-(1-(4-chlorophenyl)prop-1-en-1-yl)oxazolidin-2-one(3sd)

White solid, mp 78.8-81.9 °C, 1.066g (45% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 2H), 6.1 (q, *J* = 7.0 Hz, 1H), 4.6 – 4.4 (m, 2H), 3.7 – 3.6 (m, 2H), 1.8 (d, *J* = 7.1 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3 , 134.5 , 134.1 , 134.1 , 129.0 , 127.2 , 125.7 , 62.4 , 45.5 , 14.1. HRMS (ESI-TOF) calcd for $C_{12}H_{12}ClNO_2Na$ $[M+Na]^+$:: 260.0449, found: 260.0448.



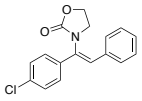
(*Z*)-3-(1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)oxazolidin-2-one(3se)

Yellow oil, 0.515g (19% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.59 (m, 2H), 7.48 – 7.41 (m, 2H), 6.20 (q, *J* = 7.0 Hz, 1H), 4.55 – 4.49 (m, 2H), 3.70 – 3.64 (m, 2H), 1.88 (d, *J* = 7.0 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3, 139.6, 134.0, 130.2 (q, *J* = 32.6 Hz), 127.5, 126.1, 125.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.0 Hz), 62.5, 45.5, 14.1. HRMS (ESI-TOF) calcd for $C_{13}H_{12}F_3NO_2Na$ $[M+Na]^+$:: 294.0712, found: 297.0725.



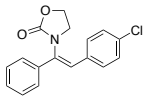
(*Z*)-3-(1-(4-methoxyphenyl)prop-1-en-1-yl)oxazolidin-2-one(3sf)

Colorless oil, 0.560g (24% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 6.4, 2.4 Hz, 3H), 6.90 – 6.85 (m, 2H), 5.96 (q, *J* = 7.0 Hz, 1H), 4.52 – 4.44 (m, 2H), 3.81 (s, 3H), 3.69 – 3.62 (m, 2H), 1.81 (d, *J* = 7.0 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 159.8 , 156.4 , 134.6 , 128.6 , 127.3 , 123.1 , 114.2 , 62.4 , 55.5 , 45.6 , 14.0 . HRMS (ESI-TOF) calcd for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$:: 256.0944, found: 256.0940.



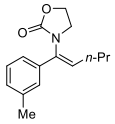
(*Z*)-3-(1-(4-chlorophenyl)-2-phenylvinyl)oxazolidin-2-one(3sg)[1]

0.329g (11% yield). The compound is in agreement with reported data.[1]



(*Z*)-3-(2-(4-chlorophenyl)-1-phenylvinyl)oxazolidin-2-one(3sh)[1]

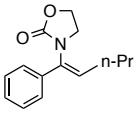
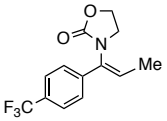
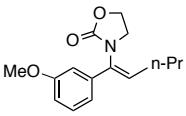
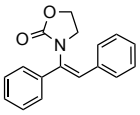
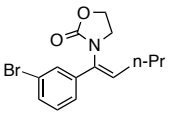
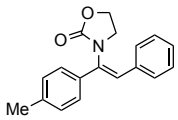
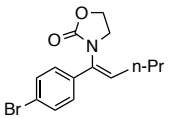
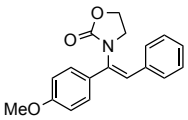
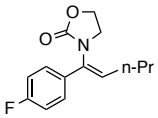
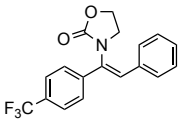
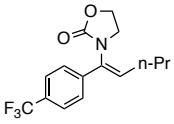
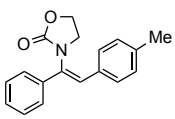
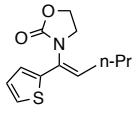
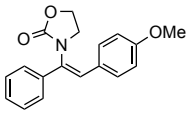
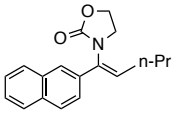
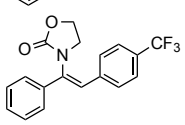
0.150g (5% yield). The compound is in agreement with reported data.[1]

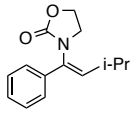
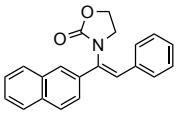
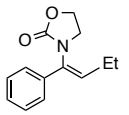
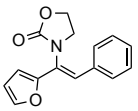
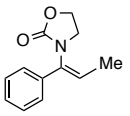
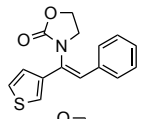
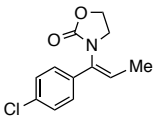
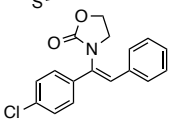
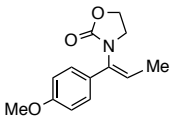
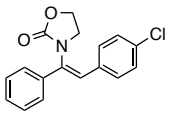


(*Z*)-3-(1-(m-tolyl)pent-1-en-1-yl)oxazolidin-2-one(3si)

Colorless oil, 0.466g (19% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.19 (m, 1H), 7.20 – 7.09 (m, 3H), 6.01 (t, J = 7.2 Hz, 1H), 4.55 – 4.40 (m, 2H), 3.73 – 3.61 (m, 2H), 2.38 (d, J = 0.7 Hz, 3H), 2.23 (q, J = 7.3 Hz, 2H), 1.66 – 1.51 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-d) δ 156.5, 138.3, 135.9, 134.0, 130.4, 129.0, 128.6, 126.5, 123.1, 62.2, 45.7, 30.3, 22.1, 21.5, 14.1. HRMS (ESI-TOF) calcd for $C_{15}H_{19}NO_2Na$ $[M+Na]^+$:: 268.1308, found: 268.1303.

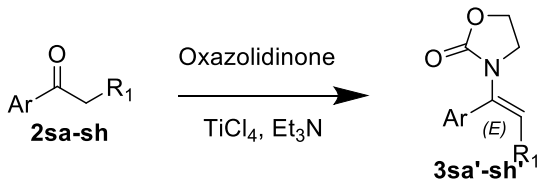
Table S4: *E* and *Z* isomers ratio of the Brønsted Acid reactions before isolation of the products

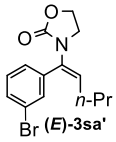
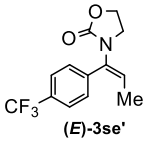
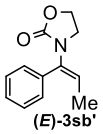
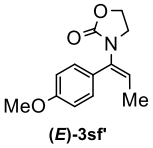
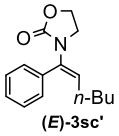
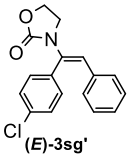
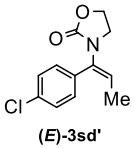
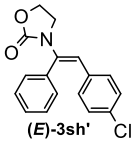
Entry	Enamide	d.r. (*E*:*Z*)	Entry	Enamide	d.r. (*E*:*Z*)
1		15:85	14		14:86
2		20:80	15		10:90
3		10:90	16		12:88
4		20:80	17		15:85
5		16:84	18		14:86
6		20:80	19		20:80
7		13:87	20		18:82
8		1:99	21		20:80

9		4:96	22		8:92
10		20:80	23		9:91
11		12:88	24		8:92
12		16:84	25		20:80
13		12:88	26		20:80

2. Additional data for (*E*)-enecarbamates.

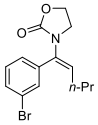
Table S5. Substrates scope for (*E*)-enamides



Entry	Enamide	Yield[a] [%]	Recovered s.m.[b][%]	Corrected Yield[c][%]	Entry	Enamide	Yield [%]	Recovered s.m.[b][%]	Corrected Yield[%]
1	 (*E*)-3sa'	23	52	48	5	 (*E*)-3se'	26	59	63
2	 (*E*)-3sb'	38	52	79	6	 (*E*)-3sf'	46	48	89
3	 (*E*)-3sc'	44	51	90	7	 (*E*)-3sg'	27	62	71
4	 (*E*)-3sd'	35	46	77	8	 (*E*)-3sh'	40	54	87

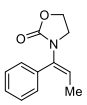
Standard condition: 3 equiv. oxazolidinone, 1.2 equiv. $TiCl_4$, 5 equiv. NEt_3, 0-r.t.; [a] Isolated yield; [b] Isolated amount of ketones after purification; [c] Yield corrected by recovered starting material.

Characterization NMR data of new α,β-enecarbamates not present in the manuscript (*E*-isomer)



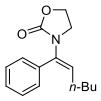
(*E*)-3-(1-(3-bromophenyl)pent-1-en-1-yl)oxazolidin-2-one(3sa′)

Yellow oil, 0.710g (23% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (ddd, *J* = 7.7, 2.0, 1.4 Hz, 1H), 7.40 (t, *J* = 1.8 Hz, 1H), 7.27 – 7.18 (m, 2H), 5.81 (t, *J* = 7.8 Hz, 1H), 4.37 – 4.29 (m, 2H), 3.61 – 3.54 (m, 2H), 2.06 (q, *J* = 7.5 Hz, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.3 , 136.8 , 133.4 , 131.7 , 131.3 , 130.0 , 127.6 , 126.3 , 61.6 , 46.1 , 29.9 , 23.0 , 13.7. HRMS (ESI-TOF) calcd for $C_{14}H_{16}BrNO_2Na$ $[M+Na]^+$: 332.0257 (^{79}Br), found: (^{79}Br) 332.0240.



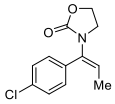
(*E*)-3-(1-phenylprop-1-en-1-yl)oxazolidin-2-one(3sb′)

Yellow oil, 0.771g (38% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.27 (m, 5H), 5.96 (q, *J* = 7.2 Hz, 1H), 4.35 – 4.28 (m, 2H), 3.57 – 3.51 (m, 2H), 1.76 (d, *J* = 7.2 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.7, 135.0, 134.3, 128.9, 128.5, 128.2, 120.6, 61.5, 46.1, 13.9. HRMS (ESI-TOF) calcd for $C_{12}H_{13}NO_2Na$ [M+Na]$^+$: 226.0838, found: 226.0841.



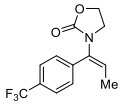
(*E*)-3-(1-phenylhex-1-en-1-yl)oxazolidin-2-one(3sc′)

Colorless oil, 1.078g (44% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 3H), 7.29 – 7.23 (m, 2H), 5.86 (t, *J* = 7.8 Hz, 1H), 4.35 – 4.25 (m, 2H), 3.60 – 3.45 (m, 2H), 2.10 (q, *J* = 7.6 Hz, 2H), 1.47 – 1.18 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.6 , 134.8 , 134.5 , 129.0 , 128.5 , 128.3 , 126.0 , 61.6 , 46.2 , 32.1 , 27.9 , 22.4 , 14.0 . HRMS (ESI-TOF) calcd for $C_{15}H_{19}NO_2Na$ [M+Na]$^+$: 268.1308, found: 268.1307.



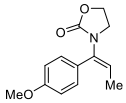
(*E*)-3-(1-(4-chlorophenyl)prop-1-en-1-yl)oxazolidin-2-one(3sd′)

White solid, mp 77.5-77.7 °C, 0.830g (35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 2H), 7.23 – 7.14 (m, 2H), 5.88 (q, *J* = 7.2 Hz, 1H), 4.35 – 4.23 (m, 2H), 3.63 – 3.49 (m, 2H), 1.72 (d, *J* = 7.5 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5 , 138.3 , 134.3 , 129.4 , 125.5 (q, *J* = 4.0, 3.5 Hz), 122.7 , 121.3 , 61.7 , 46.2 , 13.9 . HRMS (ESI-TOF) calcd for $C_{12}H_{12}ClNO_2Na$ [M+Na]$^+$: 260.0449, found: 260.0448.



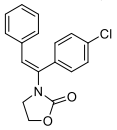
(*E*)-3-(1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)oxazolidin-2-one(3se′)

Brown solid, mp 46.7-47.6 °C, 0.705g (26% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.6 (d, *J* = 8.2 Hz, 2H), 7.4 (d, *J* = 7.6 Hz, 2H), 5.9 (q, *J* = 7.3 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.7 – 3.5 (m, 2H), 1.7 (d, *J* = 7.3 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.5, 138.3, 134.3, 130.2 (q, *J* = 33.7, 32.9 Hz), 125.5 (q, *J* = 4.3 Hz), 123.6 (q, *J* = 273.1 Hz), 121.3, 61.7, 46.2, 13.8. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.7. HRMS (ESI-TOF) calcd for $C_{13}H_{12}F_3NO_2Na$ [M+Na]$^+$: 294.0712, found: 294.0725.



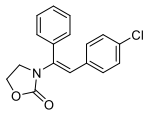
(*E*)-3-(1-(4-methoxyphenyl)prop-1-en-1-yl)oxazolidin-2-one(3sf′)

White solid, mp 54.7-55.8 °C, 1.072g (46% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.85 (q, *J* = 7.2 Hz, 1H), 4.34 – 4.22 (m, 2H), 3.80 (s, 3H), 3.57 – 3.44 (m, 2H), 1.72 (d, *J* = 7.2 Hz, 3H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 159.4 , 156.7 , 134.8 , 130.2 , 126.6 , 119.8 , 113.9 , 61.6 , 55.3 , 46.2 , 13.9 . HRMS (ESI-TOF) calcd for $C_{13}H_{15}NO_3Na$ [M+Na]$^+$: 256.0944, found: 256.0940.



(*E*)-3-(1-(4-chlorophenyl)-2-phenylvinyl)oxazolidin-2-one(3sg′)

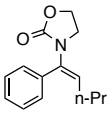
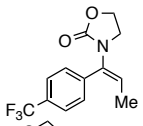
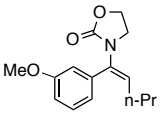
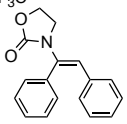
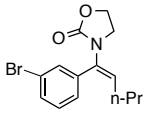
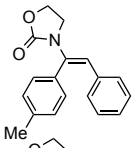
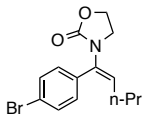
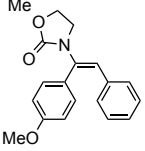
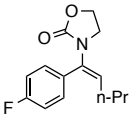
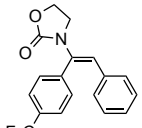
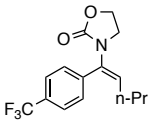
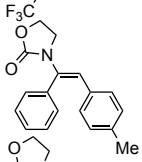
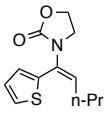
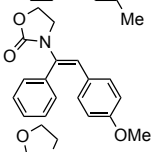
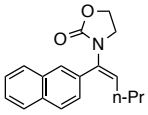
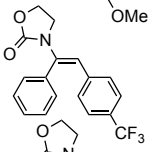
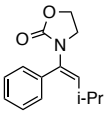
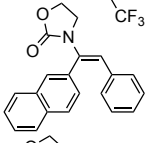
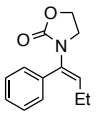
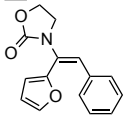
White solid, mp 98.2-99.9 °C, 0.807g (27% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.08 (m, 3H), 7.01 – 6.93 (m, 2H), 6.75 (s, 1H), 4.38 (td, *J* = 7.8, 1.0 Hz, 2H), 3.69 – 3.62 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.0 , 135.2 , 134.8 , 134.6 , 132.9 , 129.3 , 129.2 , 128.2 , 127.1 , 123.1 , 61.7 , 46.1 . HRMS (ESI-TOF) calcd for $C_{17}H_{14}ClNO_2Na$ [M+Na]$^+$: 322.0611, found: 322.0614.



(*E*)-3-(2-(4-chlorophenyl)-1-phenylvinyl)oxazolidin-2-one(3sh')

White solid, mp 133.6-136.4 °C, 1.196g (40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.32 (m, 3H), 7.30 – 7.23 (m, 2H), 7.09 – 7.02 (m, 2H), 6.89 – 6.84 (m, 2H), 6.79 (s, 1H), 4.39 – 4.31 (m, 2H), 3.63 – 3.55 (m, 2H). ^{13}C{1H} NMR (101 MHz, Chloroform-*d*) δ 156.1 , 136.2 , 134.2 , 134.1 , 132.5 , 130.5 , 129.6 , 129.2 , 129.2 , 128.3 , 121.3 , 61.7 , 46.0 . HRMS (ESI-TOF) calcd for $C_{17}H_{14}ClNO_2Na$ $[M+Na]^+$: 322.0611, found: 322.0618.

Table S6: *E* and *Z* isomers ratio of the Lewis Acid reactions before isolation of the products.

Entry	Enamide	d.r. (*E*:*Z*)	Entry	Enamide	d.r. (*E*:*Z*)
1		97:3	14		99:1
2		98:2	15		98:2
3		99:1	16		90:10
4		99:1	17		96:4
5		99:1	18		95:5
6		99:1	19		95:5
7		80:20	20		95:5
8		85:15	21		96:4
9		99:1	22		93:7
10		99:1	23		92:8

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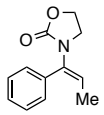
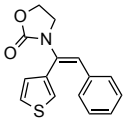
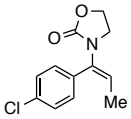
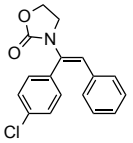
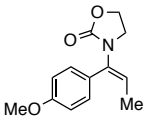
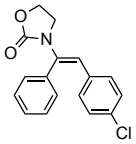
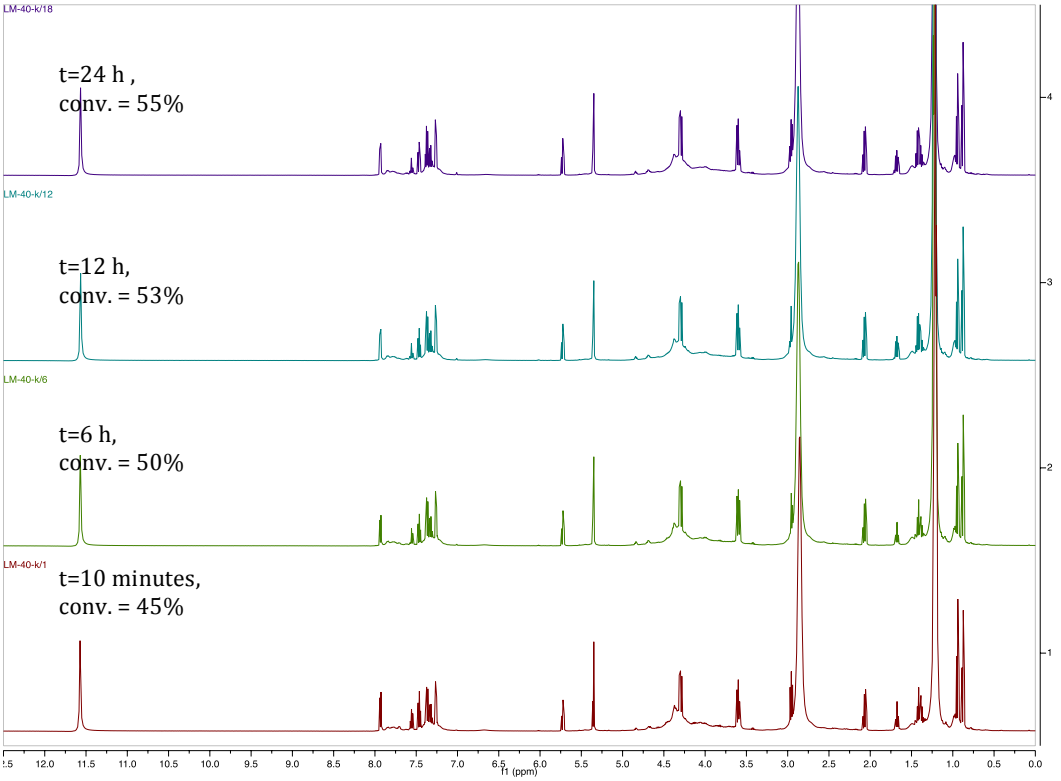
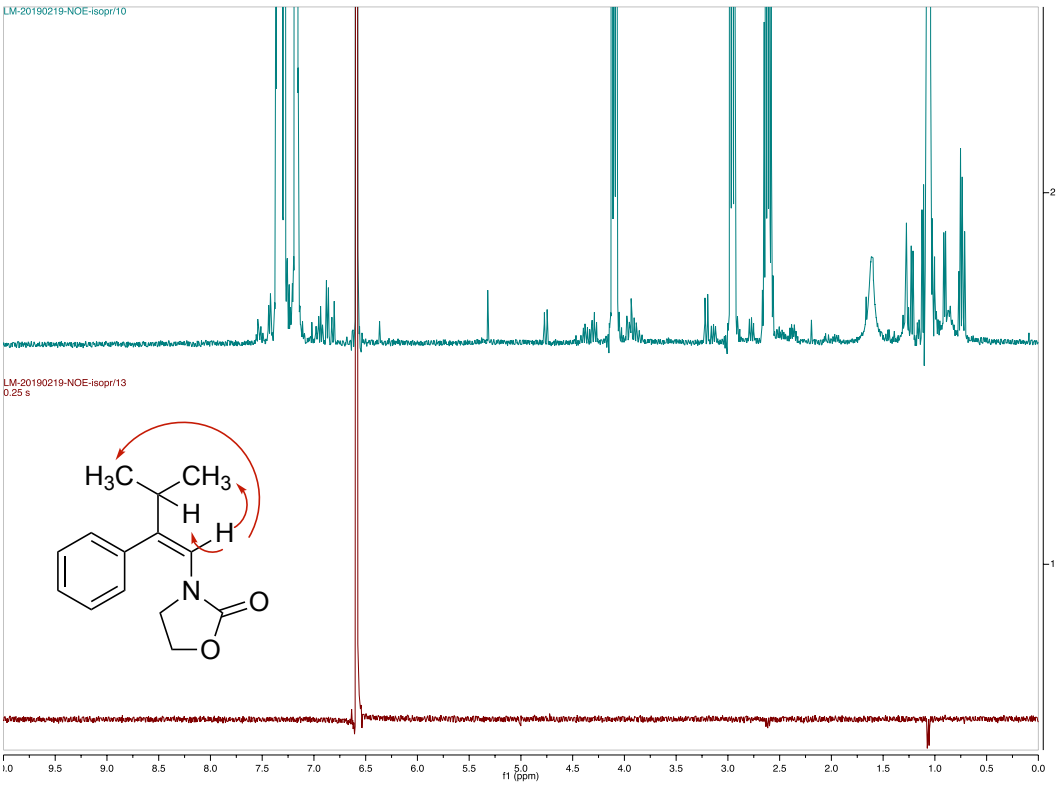
11		99:1	24		93:7
12		99:1	25		99:1
13		95:5	26		95:5



^{1}H NMR (500 MHz, CD_2Cl_2). Stacked spectra recorded over time of the Lewis Acid catalyzed reaction.

Figure S1 Kinetic study of Lewis Acid catalyzed reaction.



(Irradiated resonance 6.60-6.57, difference at *i*-pr chain.) *(Z)*-geometry of the double bond

Figure S2 NOE experiment to determine the geometry of the double bond

2. (*E*)- and *(Z)*- isomer energies.

Computational Details

The Gaussian 09[2] package was used for all calculations carried out. The two isomers were first optimized using B3LYP/6-31+g(d).[3] The optimised 6-31+g(d) structures were then further optimized at B3LYP/6-311++g(d). The relative energies that are presented were obtained from the optimized gas phase calculations. The XYZ coordinates of the calculated structures are also listed below. All computations were carried out using the computational cluster resources at the National Supercomputer Centre based at Linkoping University, Sweden and at the Center for High Performance Computing, South Africa.

Gas phase energies

Structure	**Relative energy/kcal mol^{-1}**
Z_isomer	0
E_isomer	2.21

XYZ coordinates of structures calculated

Z_isomer (Energy = -749,111839 Hartrees, 0 kcal mol^{-1})

C,-5.0864436615,0.4323134834,-1.0159199977
C,-3.7277067957,0.445139407,-0.7142416175
C,-3.2250877054,-0.2937555965,0.3675562948
C,-4.1269793923,-1.0292564074,1.1485952065
C,-5.4867562314,-1.0437193899,0.8458706003
C,-5.9720222109,-0.3126640726,-0.2370752326
H,-5.4539505413,0.9985488489,-1.8659219515
H,-3.0431603589,1.0086596599,-1.340491732
H,-6.169405319,-1.6178759561,1.464422145
H,-7.0317314603,-0.3198507162,-0.470763803
C,-1.7670889808,-0.3034936641,0.662743231
C,-1.0924948689,-1.4253406895,0.9565171855
H,-1.6549140149,-2.3553131512,0.9087978842
C,0.3609979803,-1.5506178174,1.2961747288
H,0.9143942271,-1.8303538003,0.3898861286
H,0.764700011,-0.5779027477,1.5951275173
C,0.6289924614,-2.589843109,2.3965969807
H,0.2179864897,-3.5588779579,2.0875670048
H,0.084951304,-2.3066426119,3.3058221088
C,2.1172907116,-2.7453483279,2.7144799824
H,2.5531524963,-1.8022558996,3.0593696216
H,2.2827421562,-3.4903995449,3.4978115088
H,2.6814453522,-3.062261512,1.8318512194
H,-3.7589046093,-1.5804749428,2.0078571119
N,-1.1014076951,0.9538785865,0.5709522896

C,-0.124853905,1.2469617524,-0.3632322647
C,-1.5714989484,2.1600843046,1.2469248871
C,-0.4247649213,3.1277090812,0.9247590477
H,-2.5327203989,2.4980144982,0.845105676
H,-0.7572896049,4.1349326758,0.677672179
O,0.3706033138,0.518402281,-1.1789820237
O,0.2160766773,2.5691460034,-0.234835231
H,-1.6871243223,1.9918075734,2.3196240275
H,0.3094584556,3.1764733791,1.7335080567

E_isomer (Energy = -749,108320 Hartrees, 2.21 kcal mol^{-1})
C,-5.7015673031,-0.8331938926,0.4241750141
C,-4.4196867085,-0.9649065665,0.9558363577
C,-3.3402658403,-0.2603180194,0.4078101358
C,-3.5818263018,0.5958801358,-0.6771304764
C,-4.8611399469,0.7265146642,-1.2098531931
C,-5.9263065673,0.0117530499,-0.6607906709
H,-6.5259937907,-1.3858912246,0.8635343894
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H,-5.0265700829,1.3832626857,-2.0580688079
H,-6.9241355871,0.1158360861,-1.0745706132
C,-1.966413588,-0.3912238404,0.9682581304
C,-1.2960057857,-1.5400730096,1.137556836
H,-2.7555243748,1.1465515094,-1.1161826851
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C,-0.7015520197,-3.5567769448,-0.2941093461
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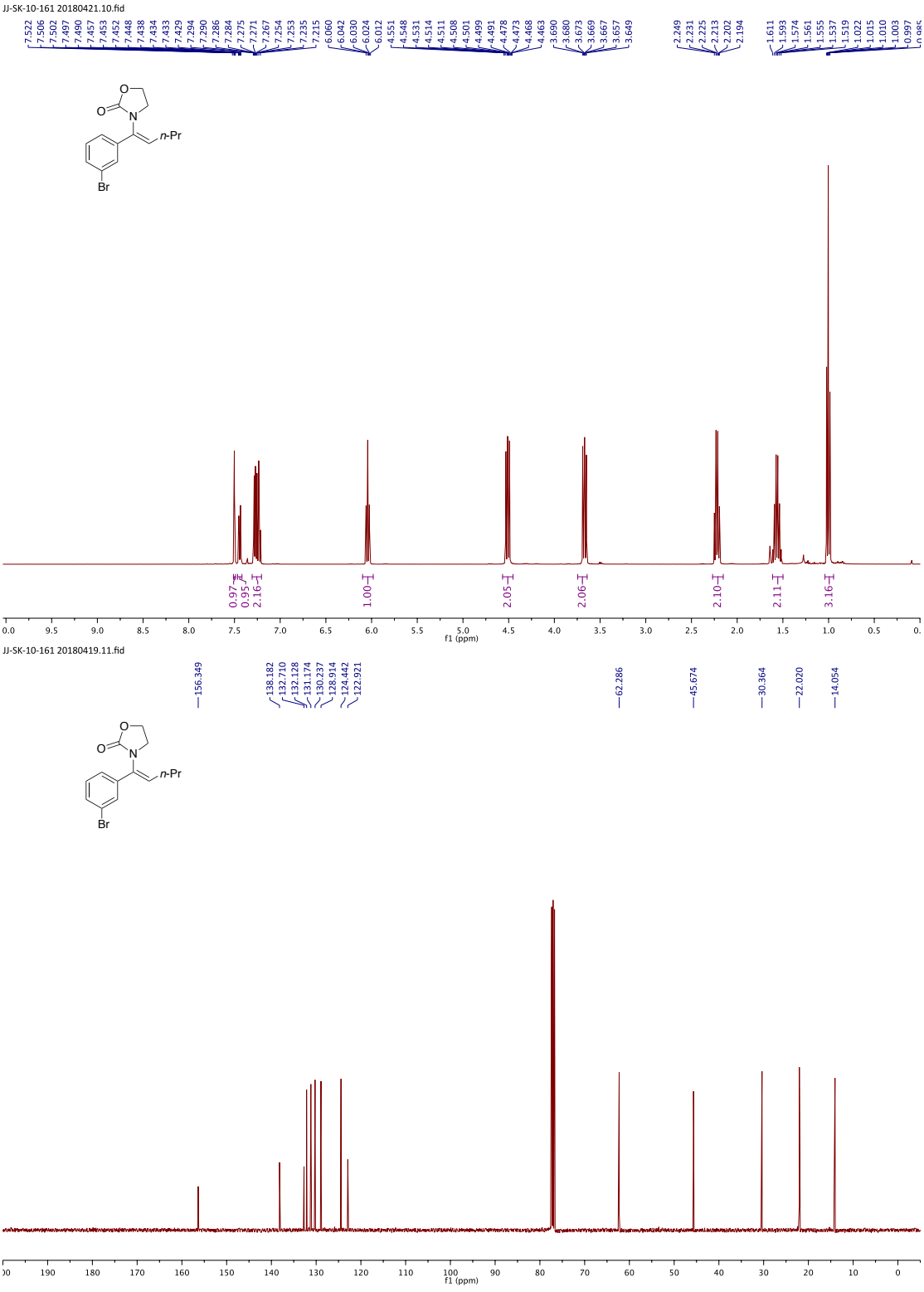
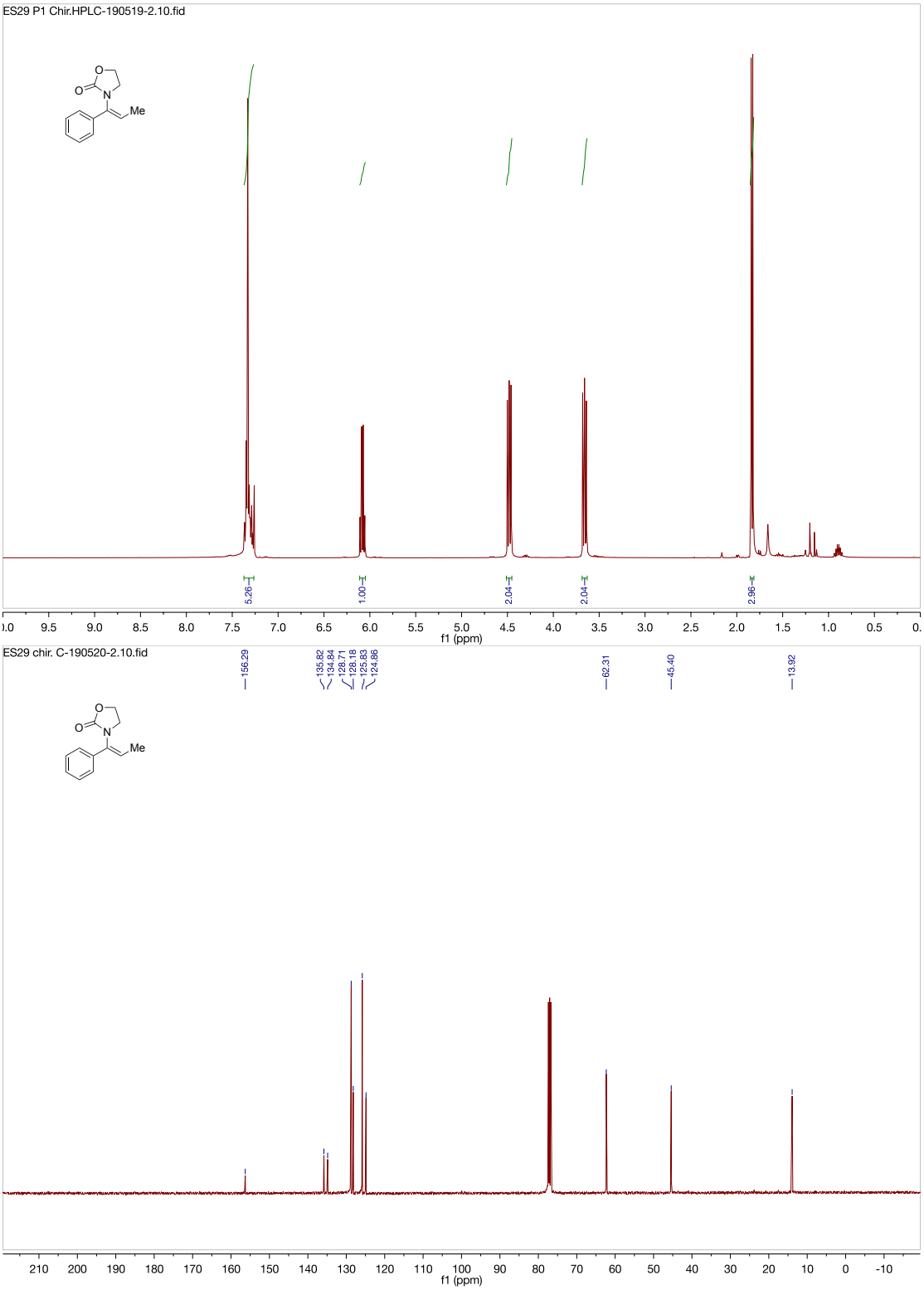
H,-0.309492361,-1.4597841204,1.5851241477

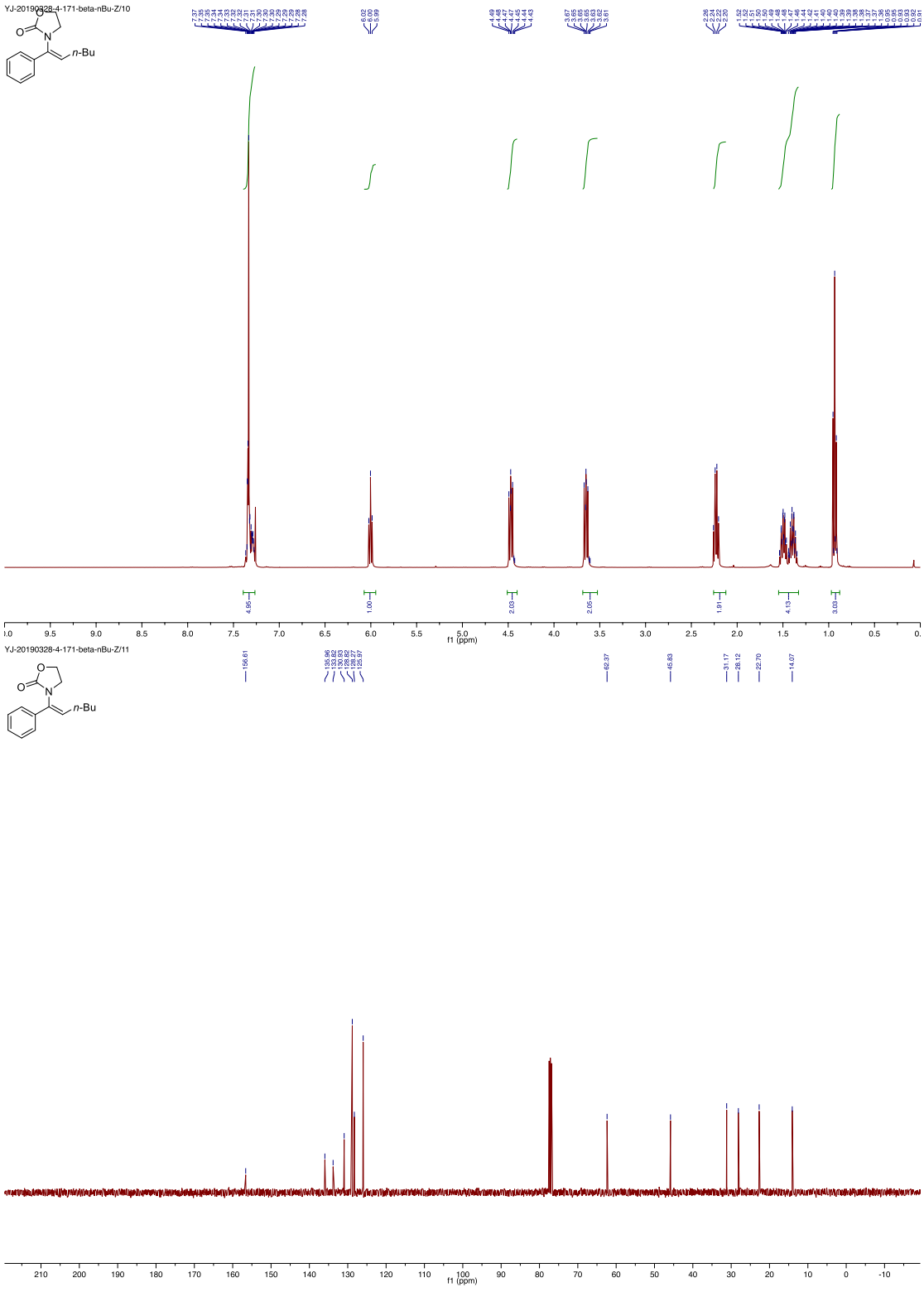
4. NMR spectra of new compounds



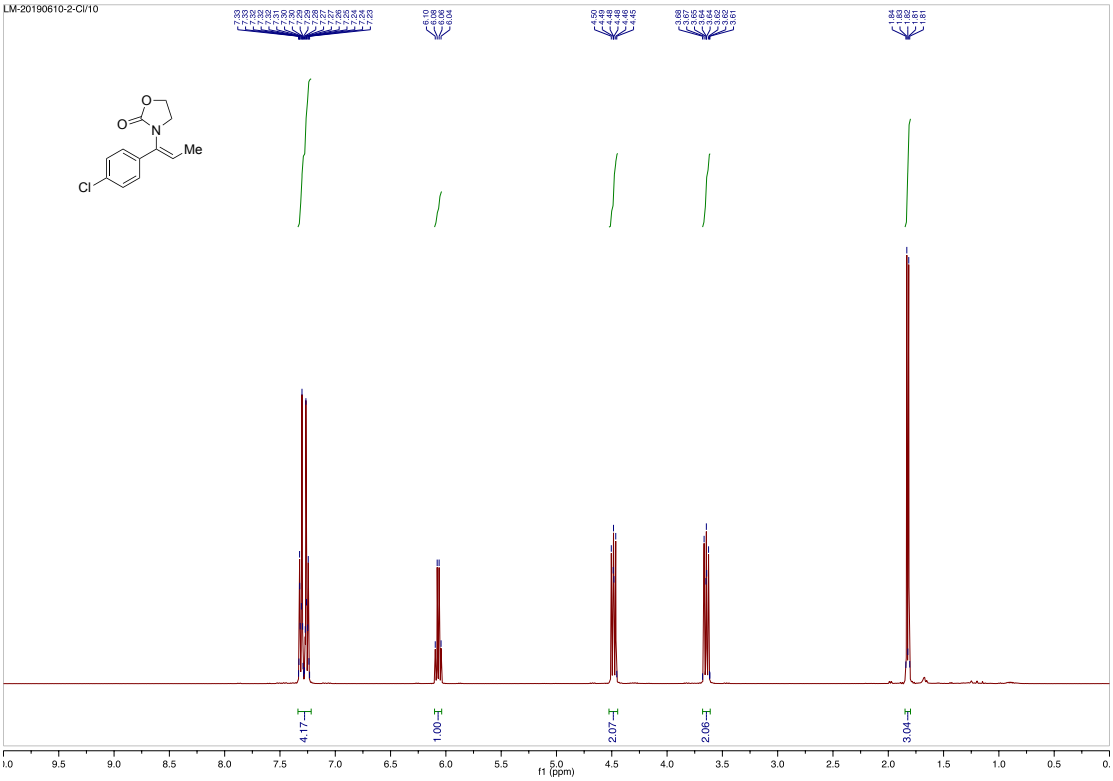
^{1}H and ^{13}C{1H} NMR spectra of **3sa**

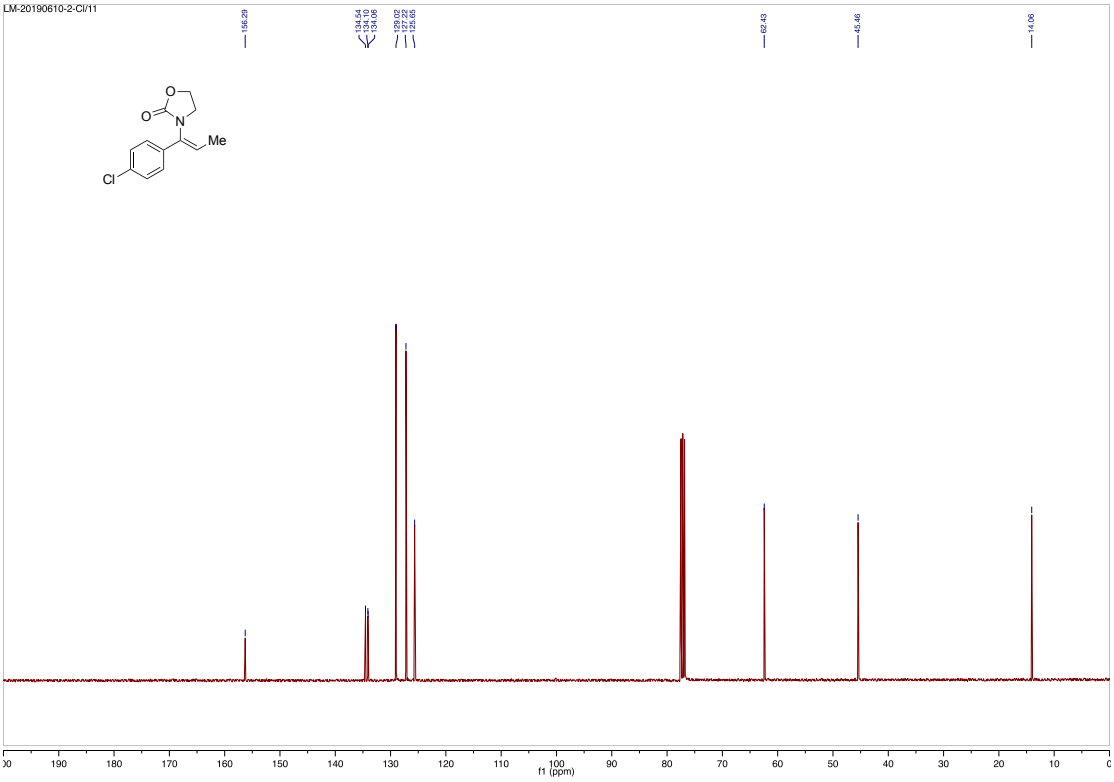


^{1}H and ^{13}C{1H} NMR spectra of **3sb**

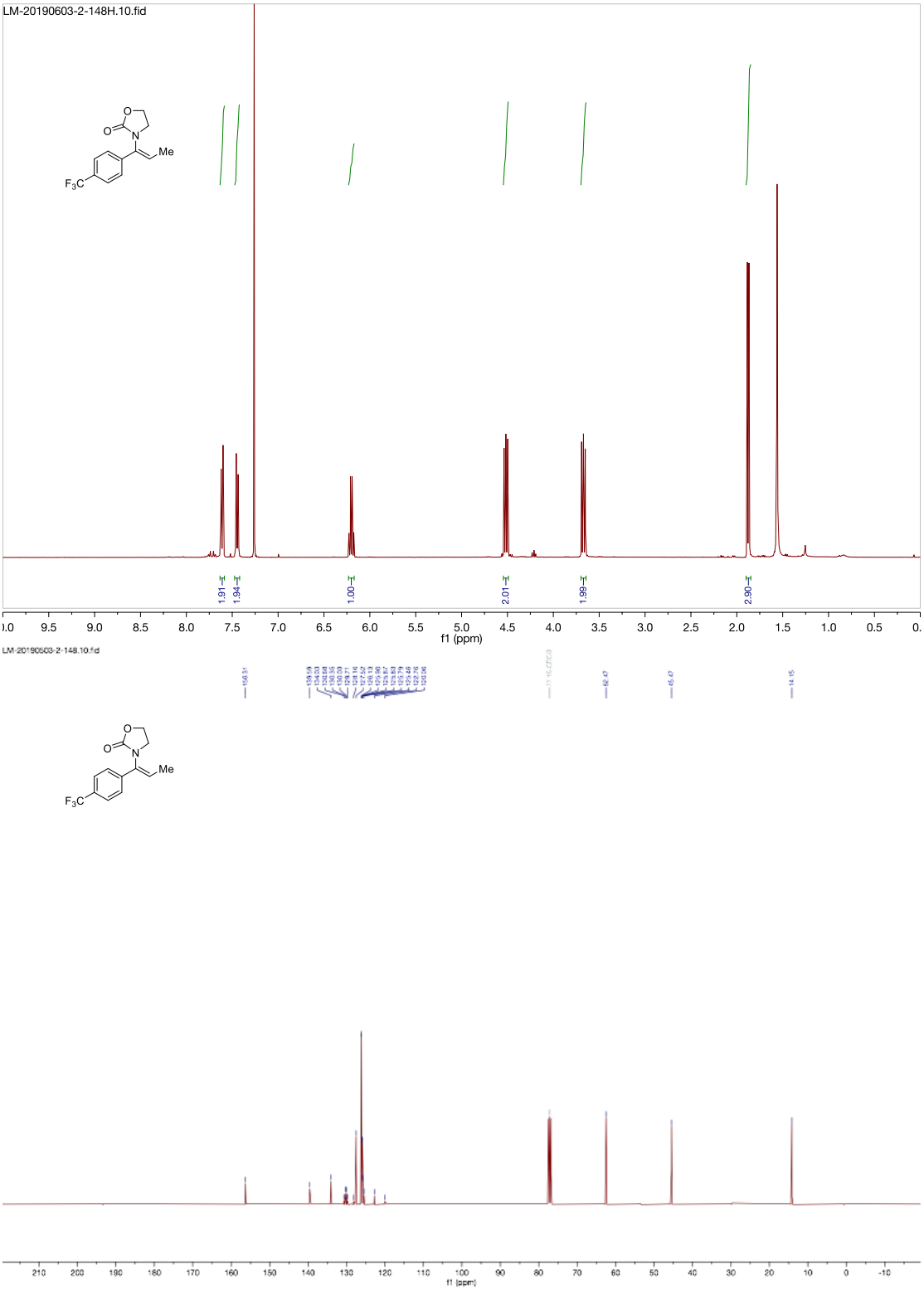


^{1}H and ^{13}C{1H} NMR spectra of **3sc**

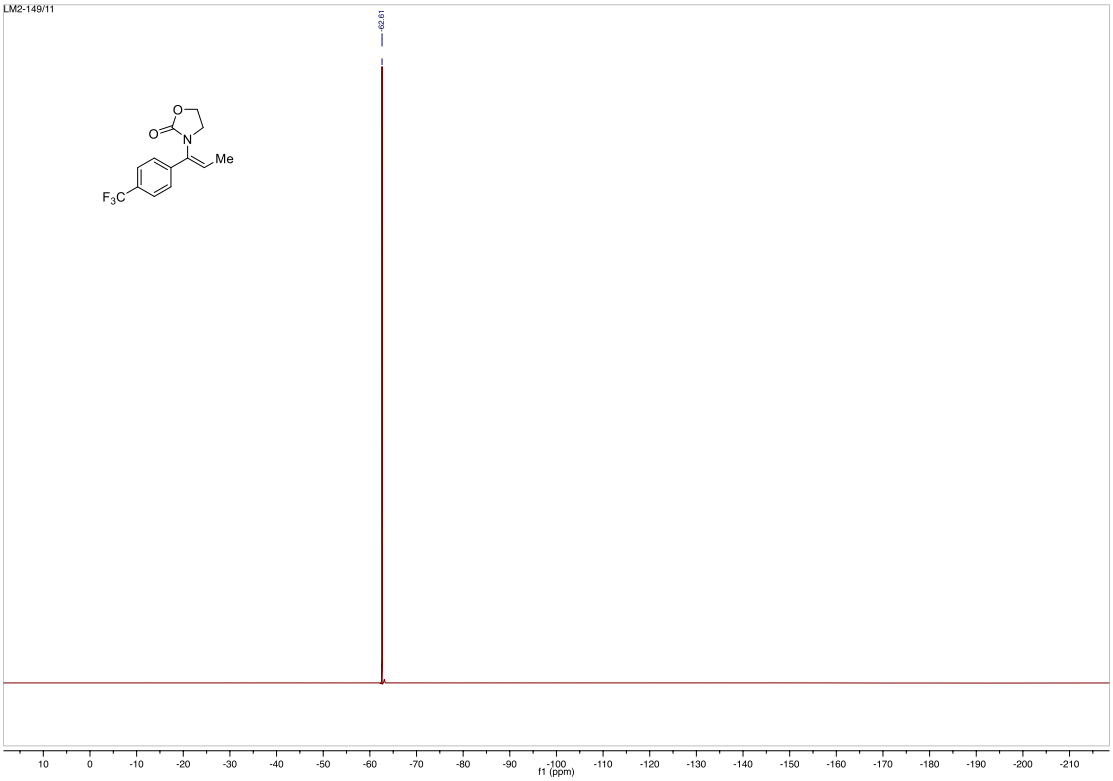




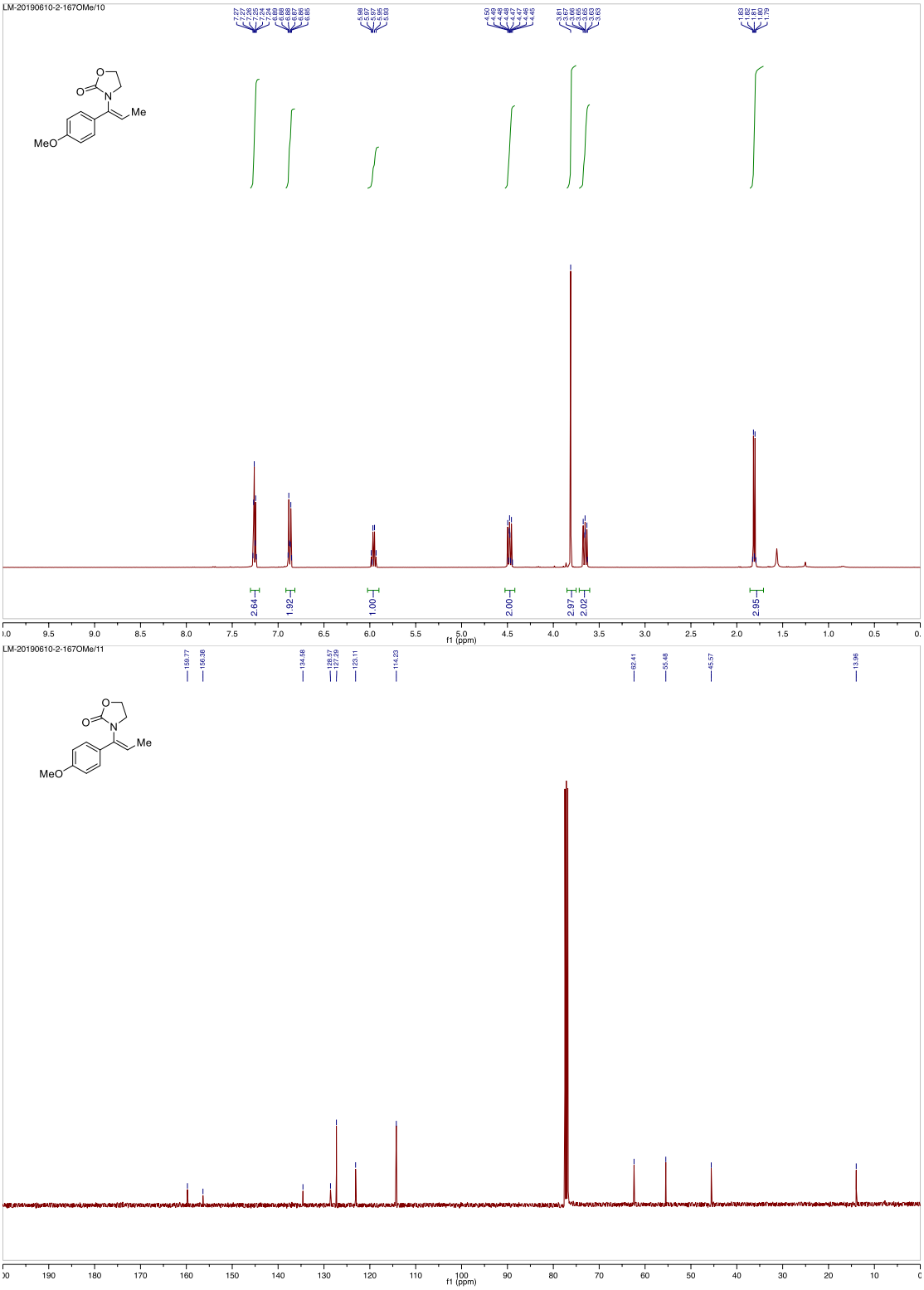
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3sd**



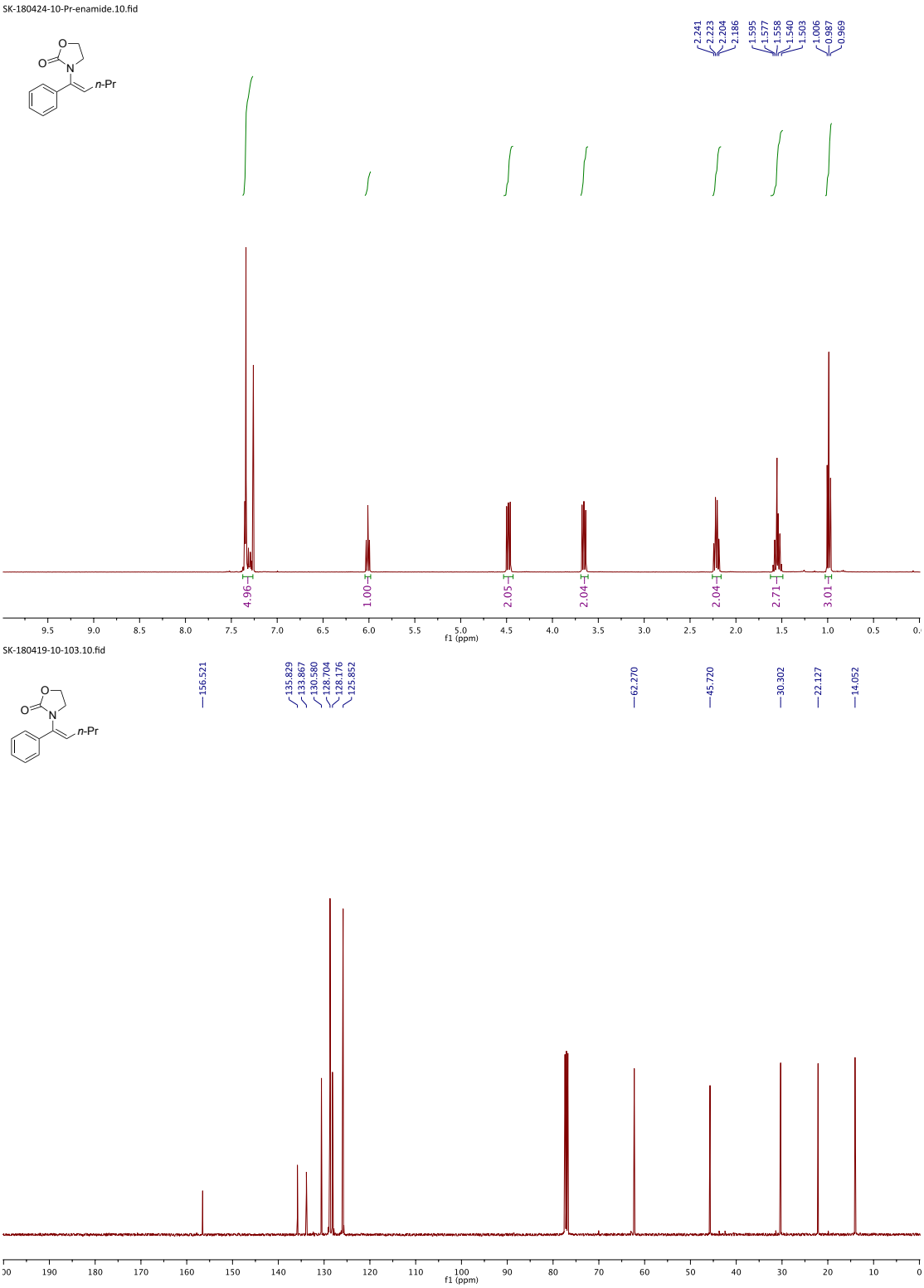
^{1}H and ^{13}C{1H} NMR spectra of **3se**



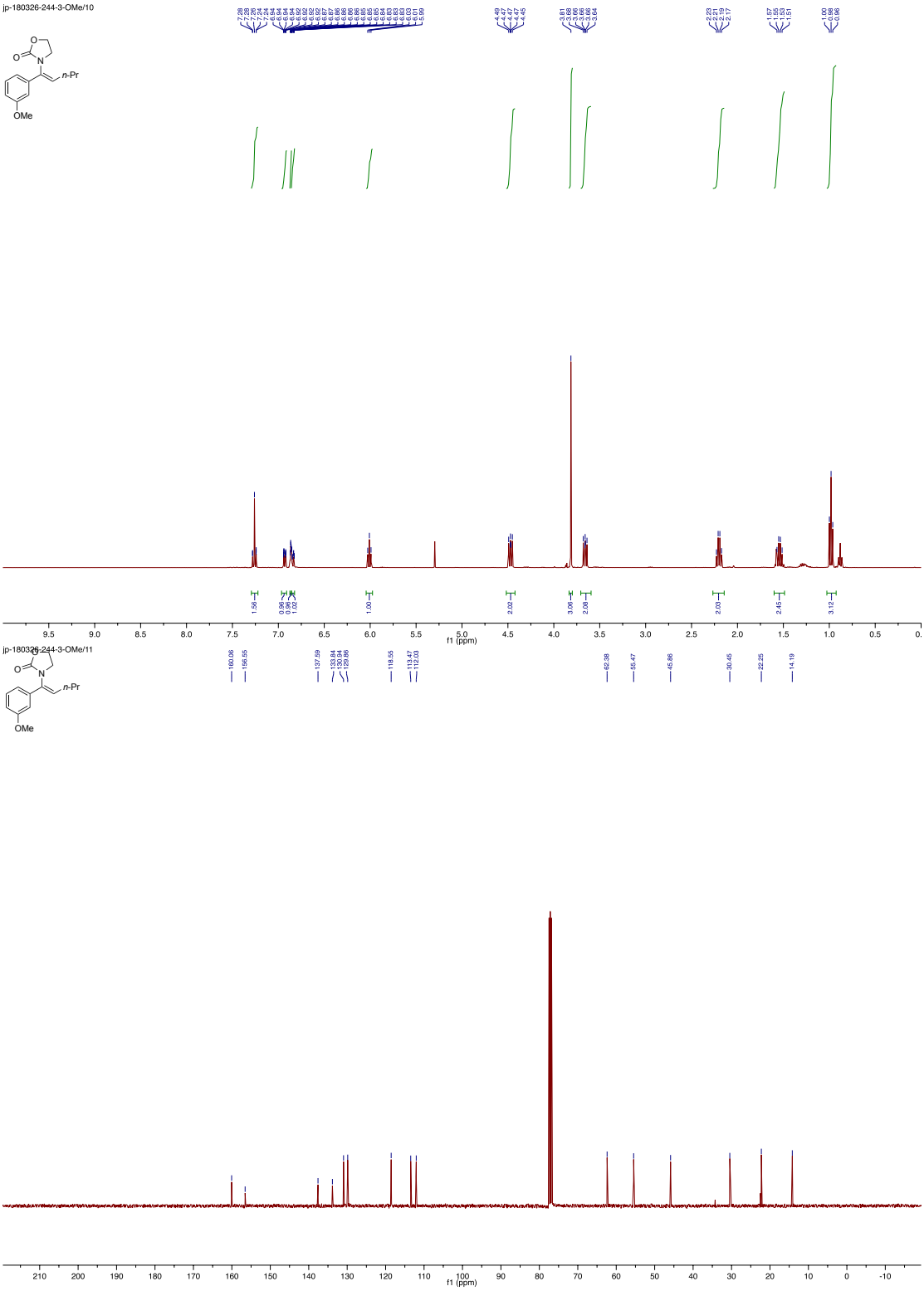
^{19}F NMR spectra of **3se**



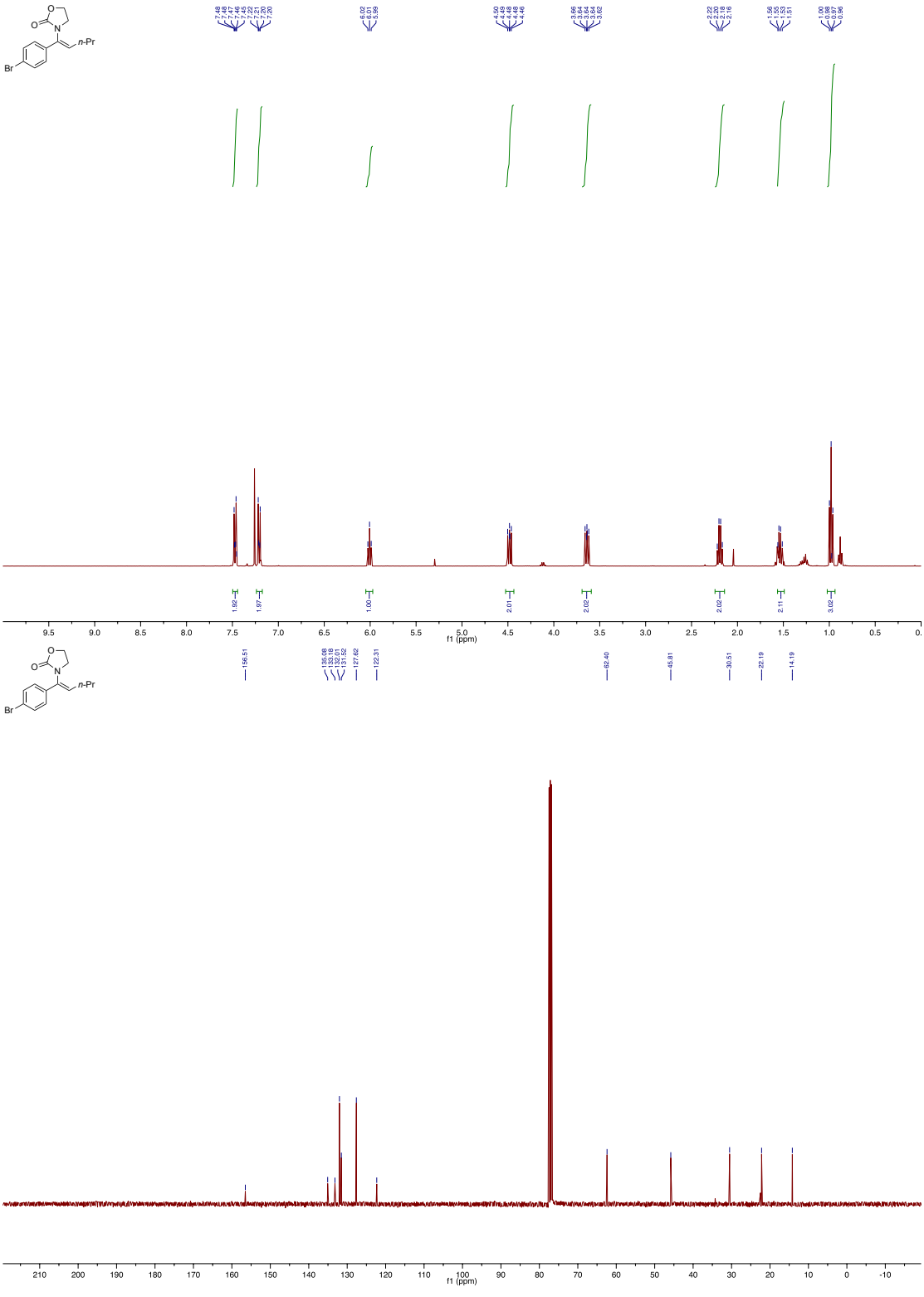
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3sf**



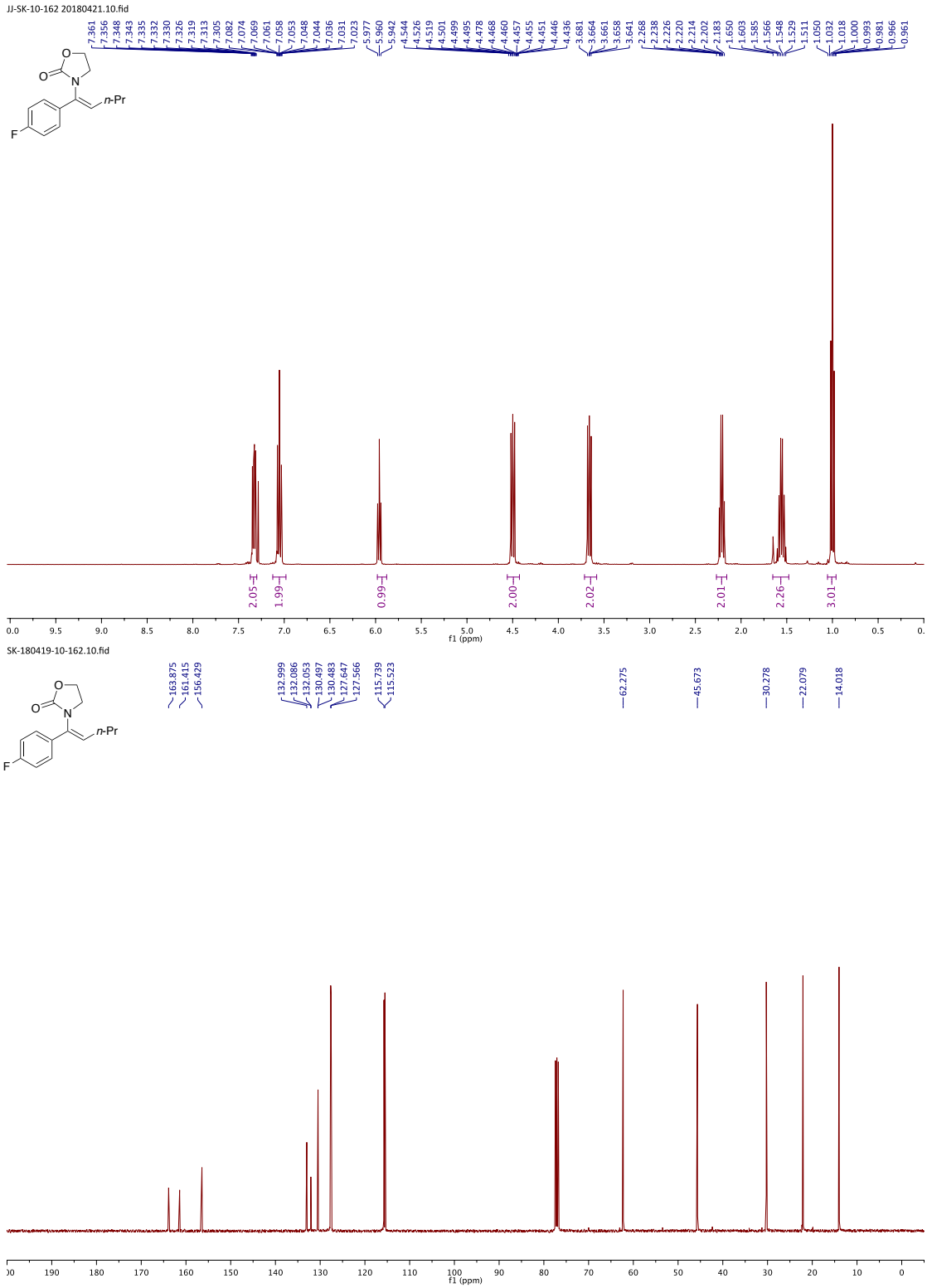
^{1}H and ^{13}C{1H} NMR spectra of **3a**



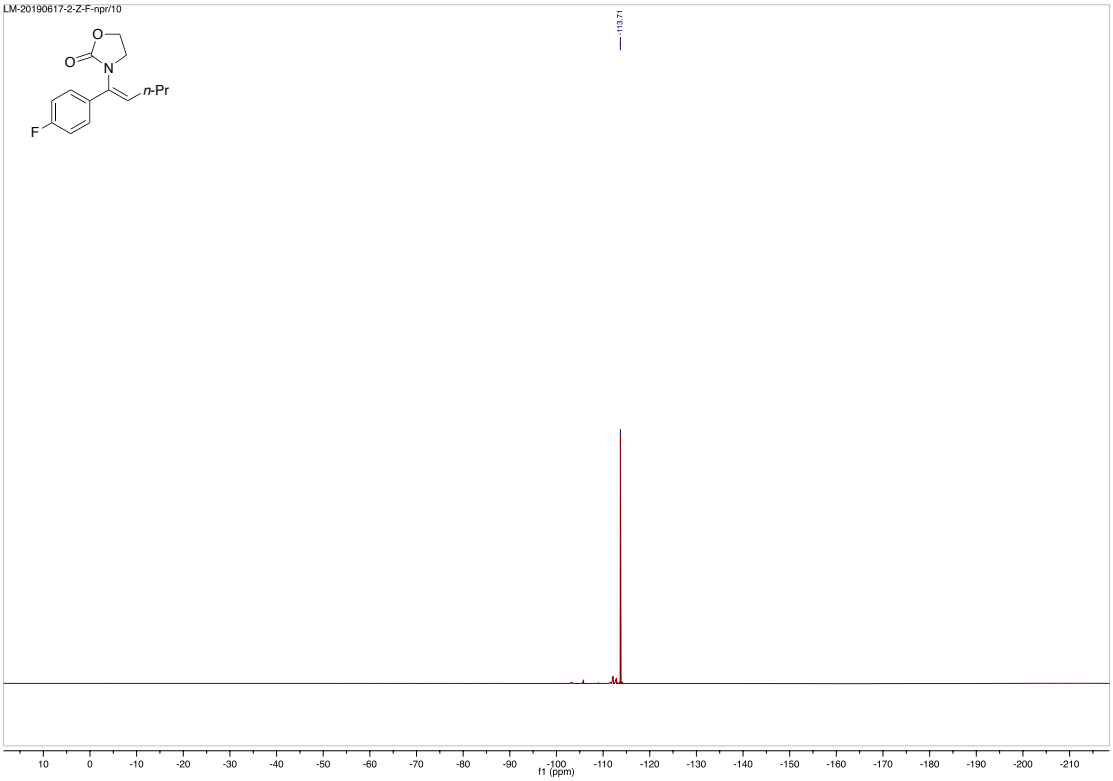
^{1}H and ^{13}C{1H} NMR spectra of **3b**



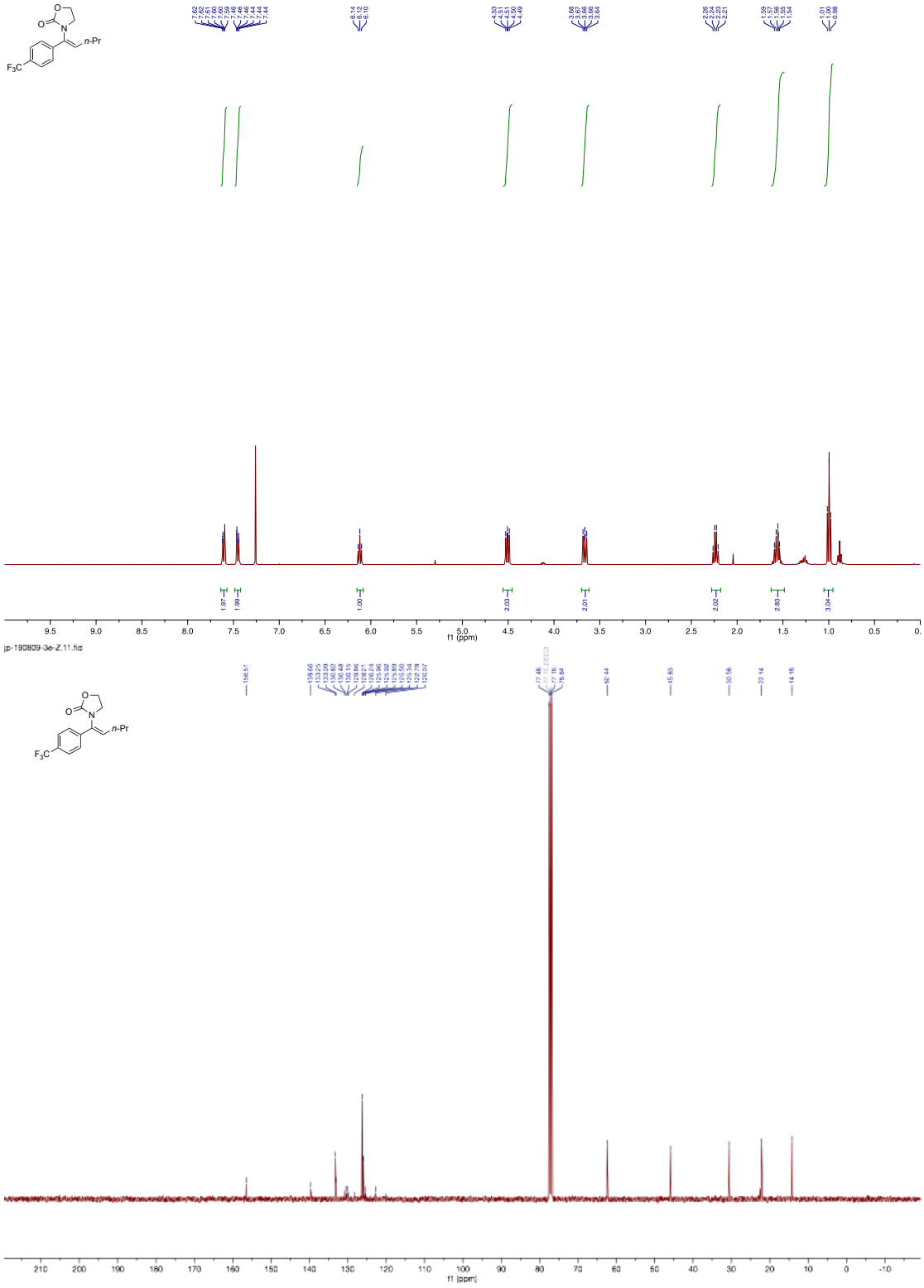
^{1}H and ^{13}C{1H} NMR spectra of **3c**



^{1}H and ^{13}C{1H} NMR spectra of **3d**



^{19}F NMR spectra of **3d**



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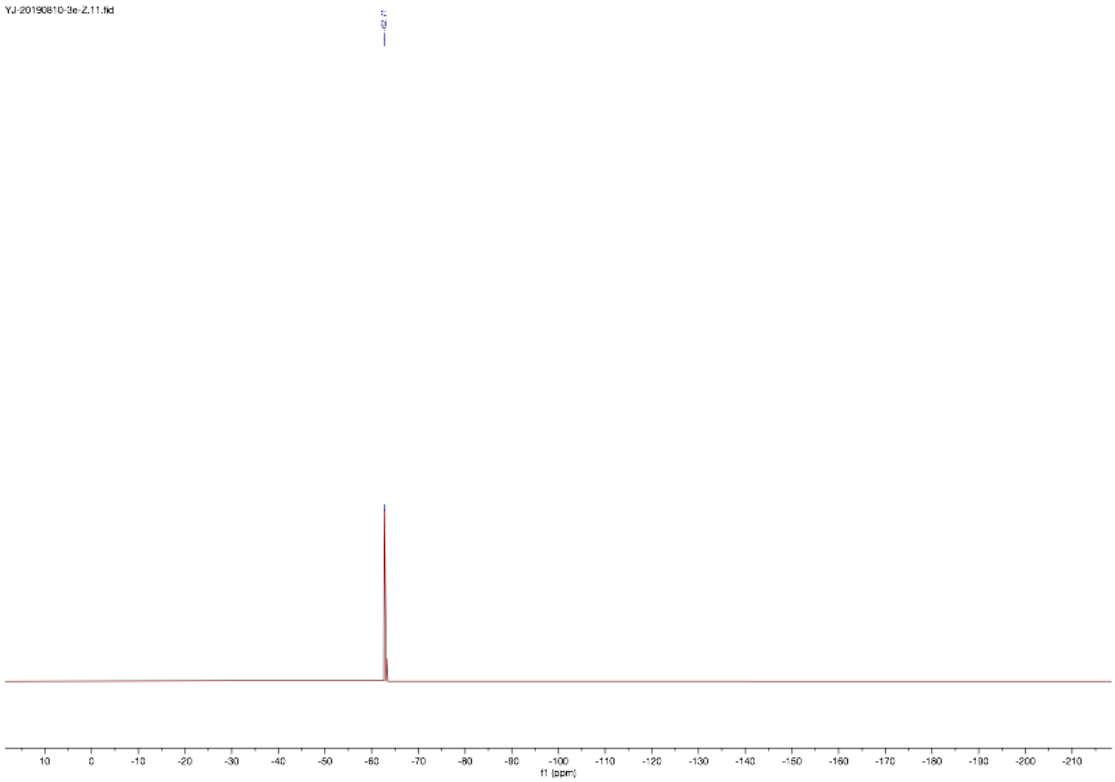
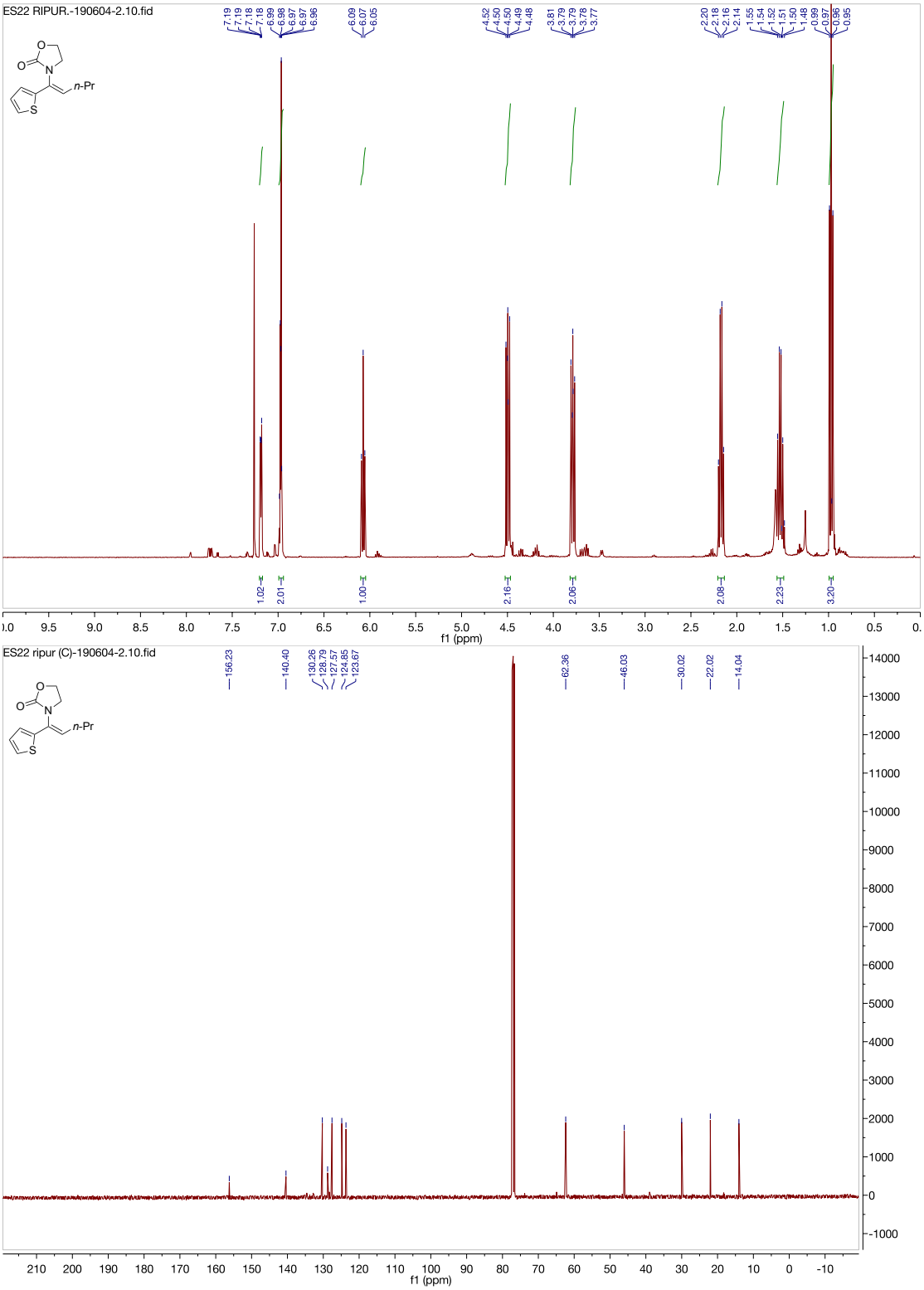
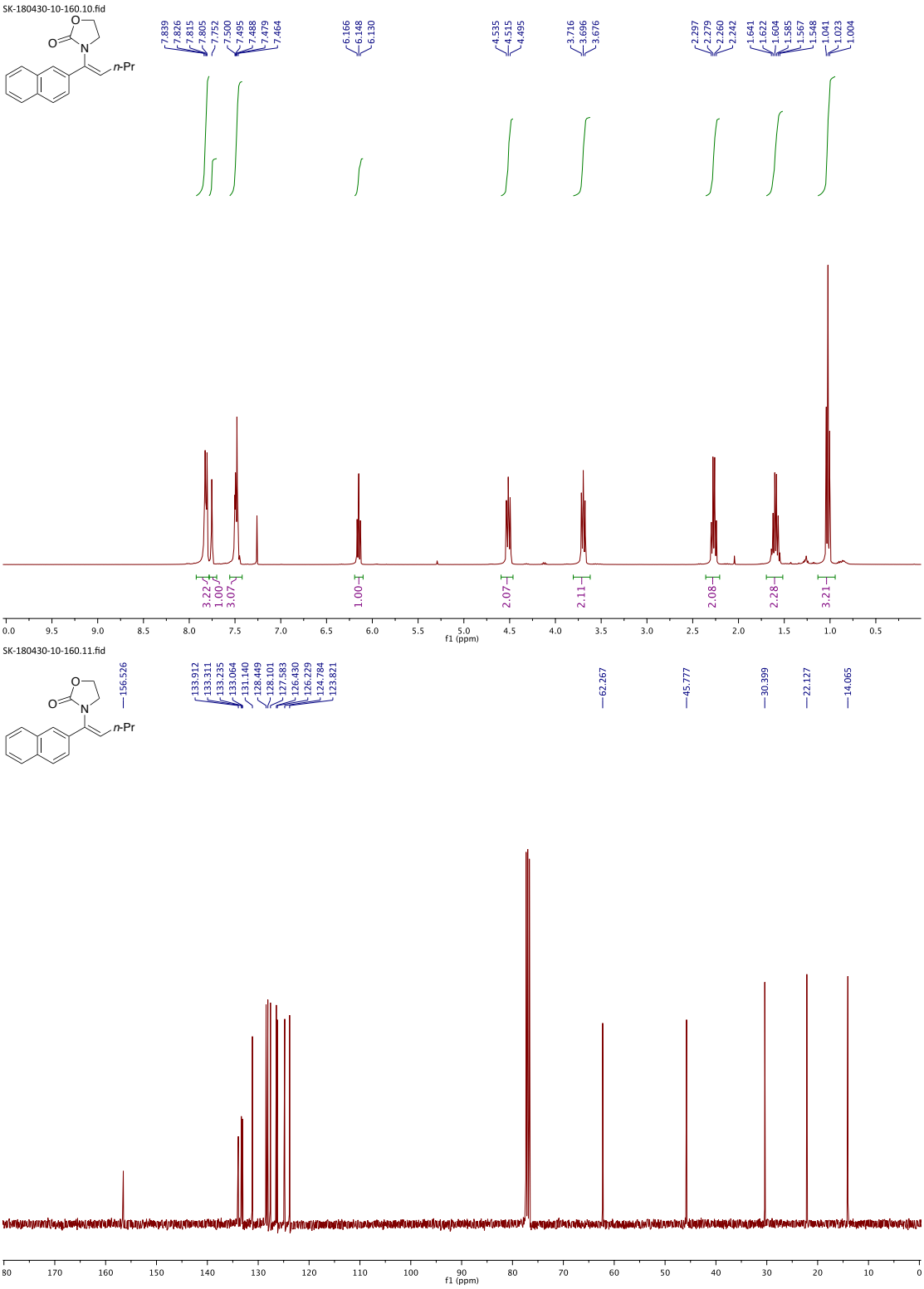


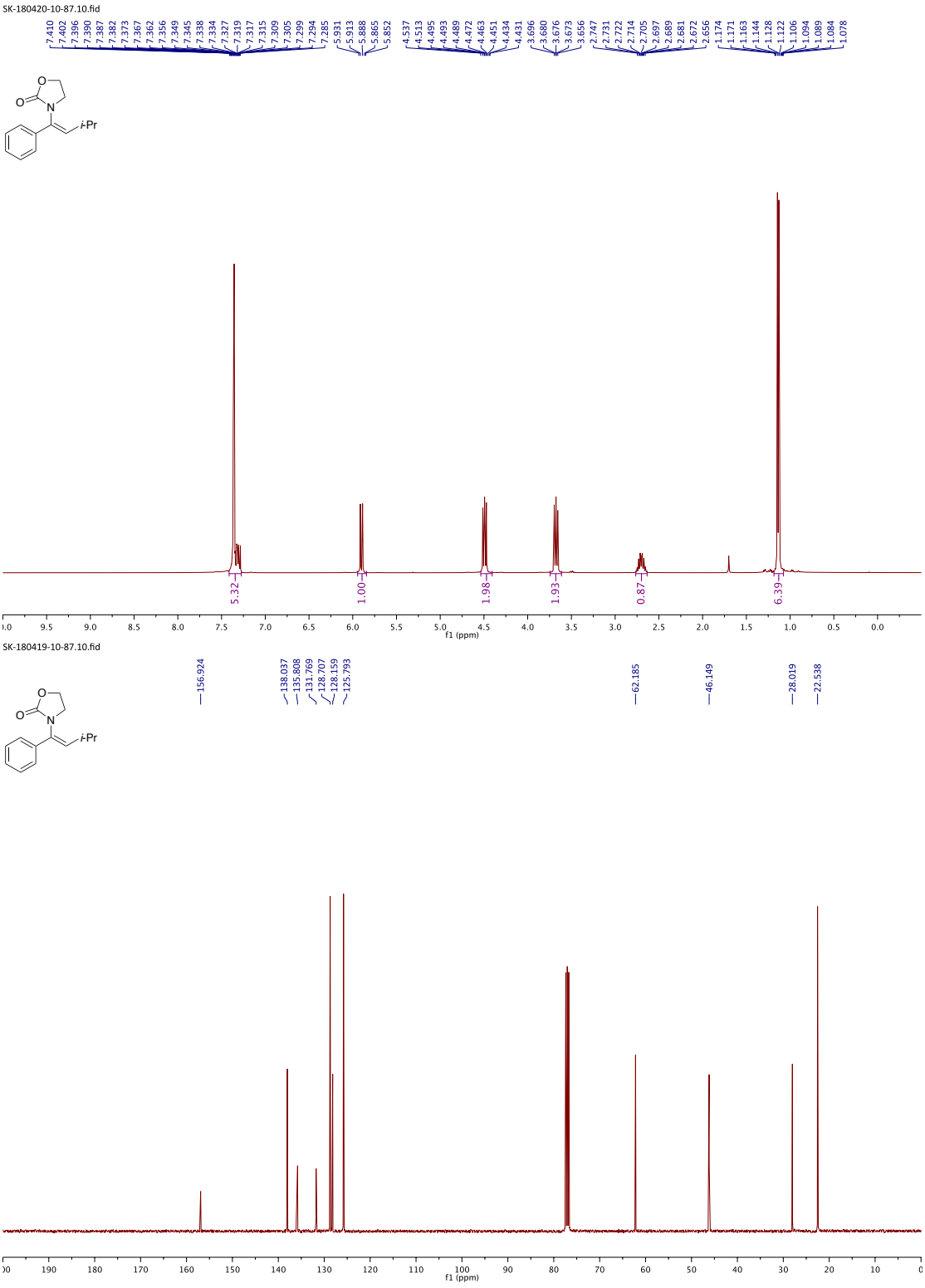
^{19}F NMR spectra of **3e**



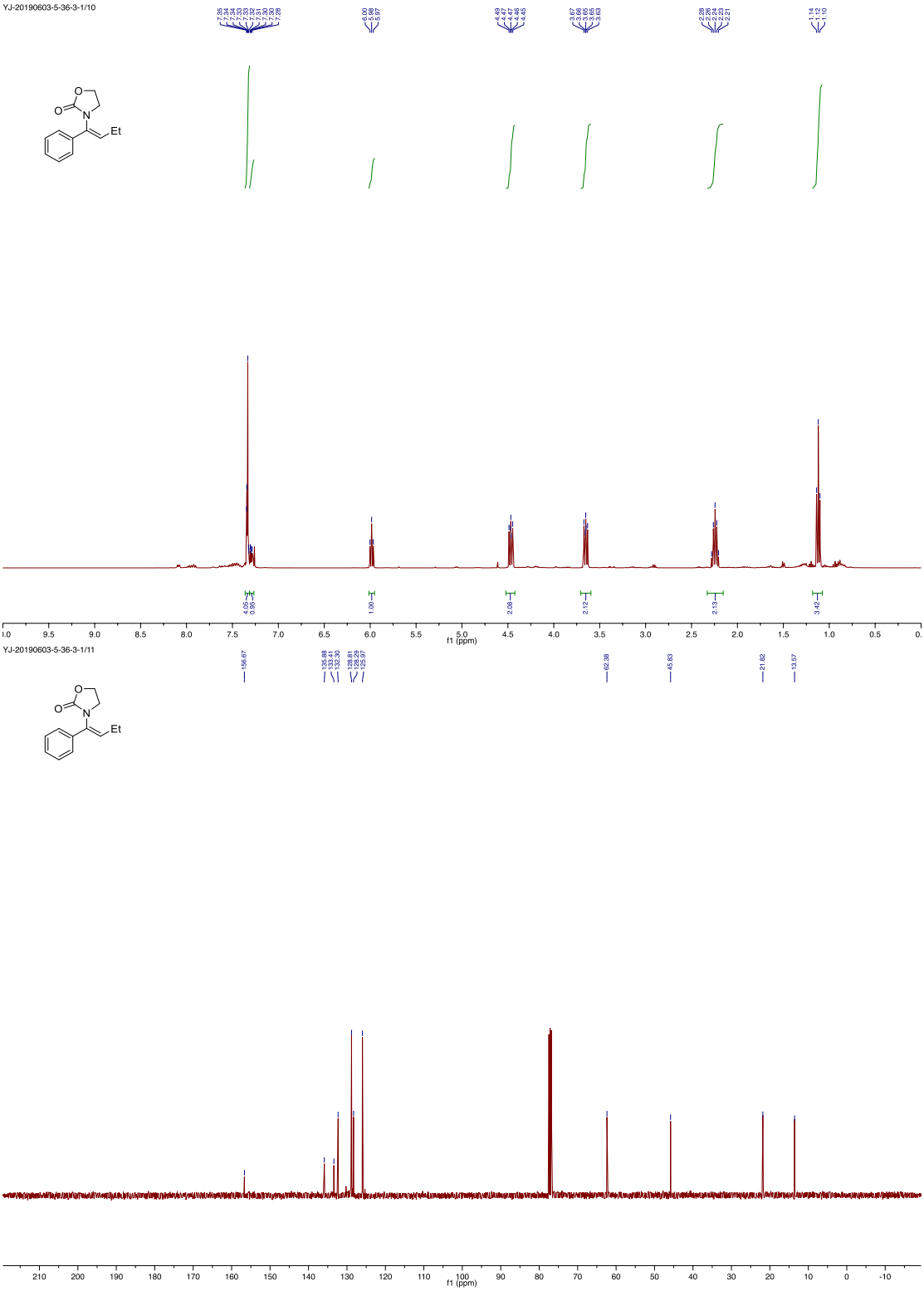
^{1}H and ^{13}C{1H} NMR spectra of **3f**



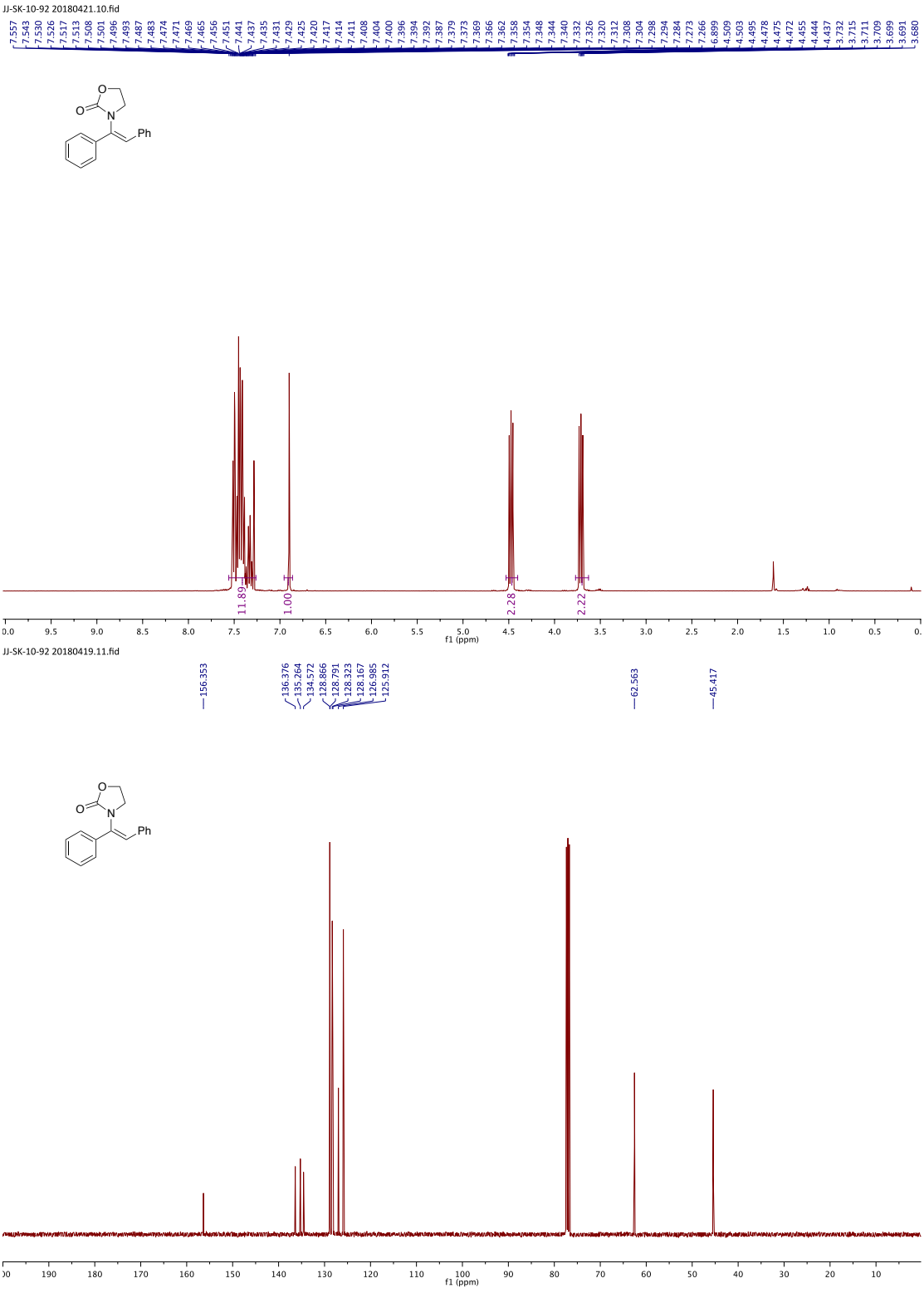
^{1}H and ^{13}C{1H} NMR spectra of **3g**



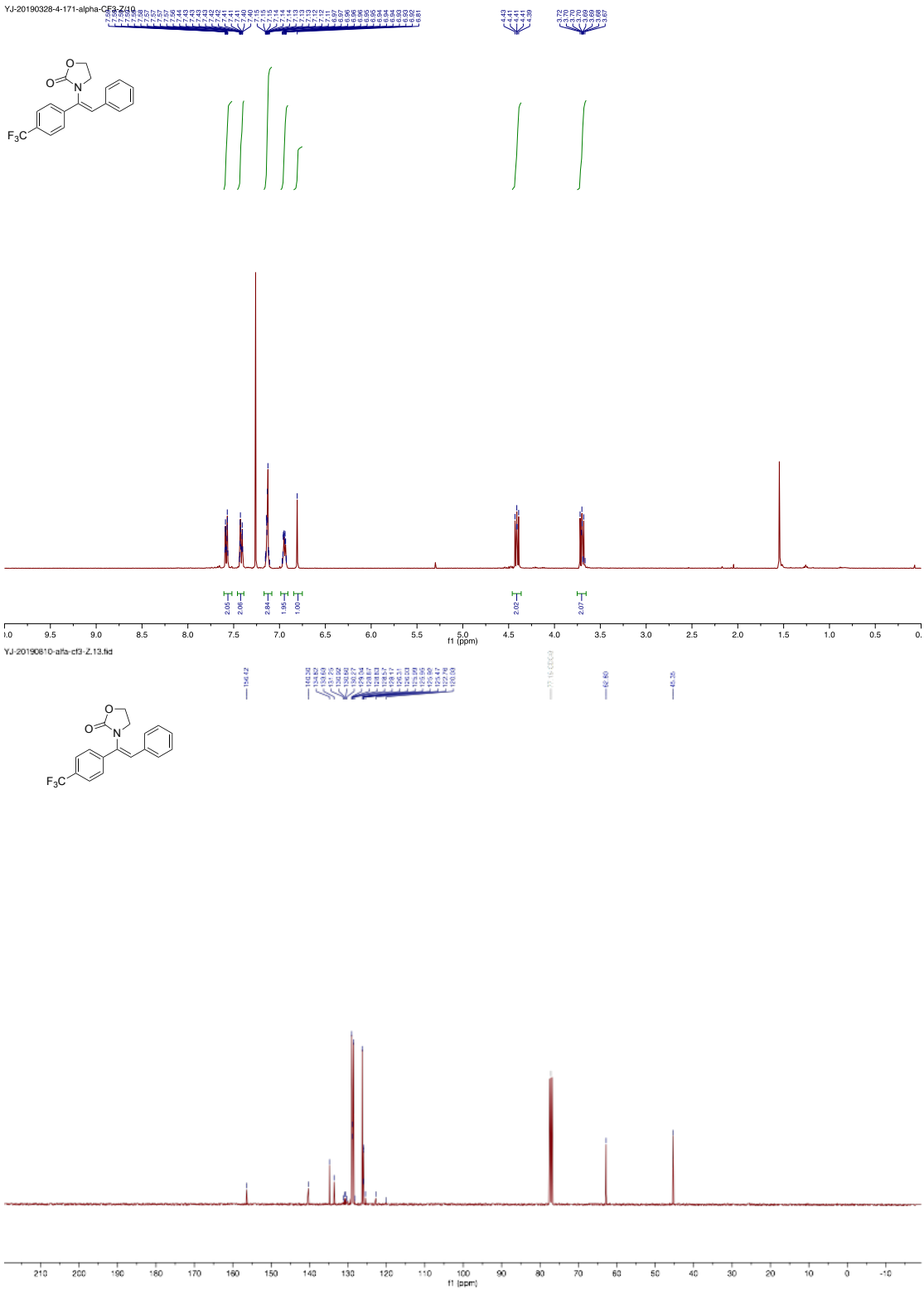
^{1}H and ^{13}C{1H} NMR spectra of **3h**



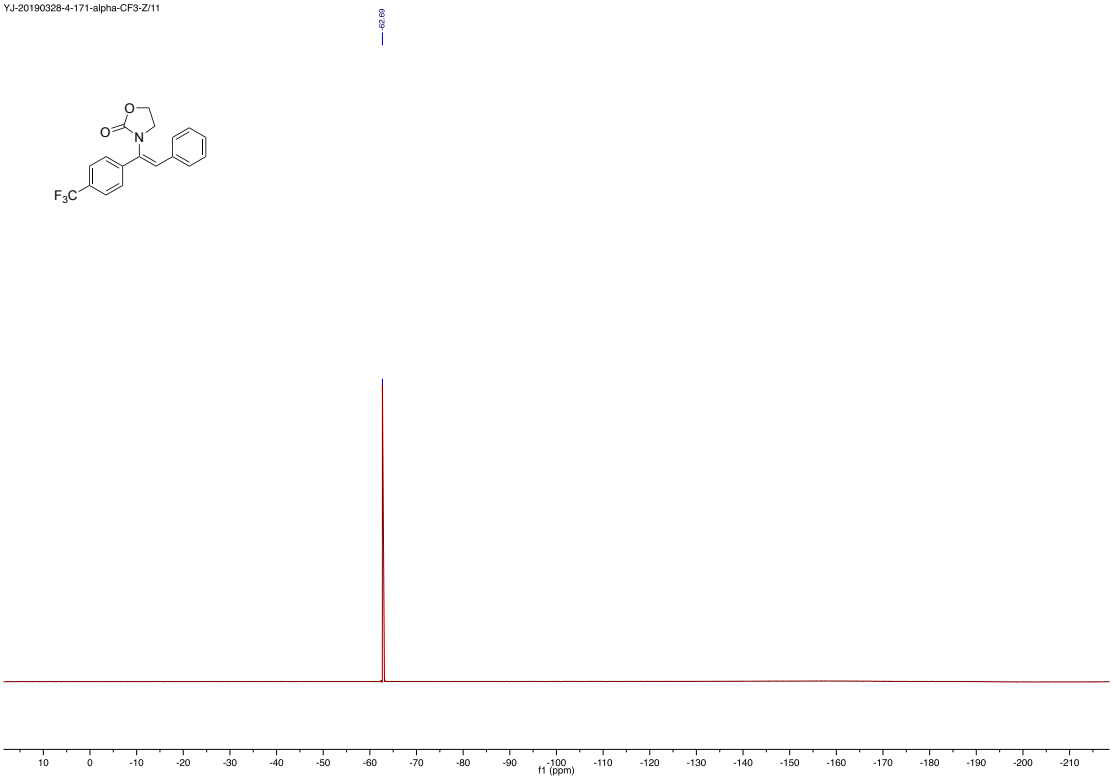
^{1}H and ^{13}C{1H} NMR spectra of **3i**



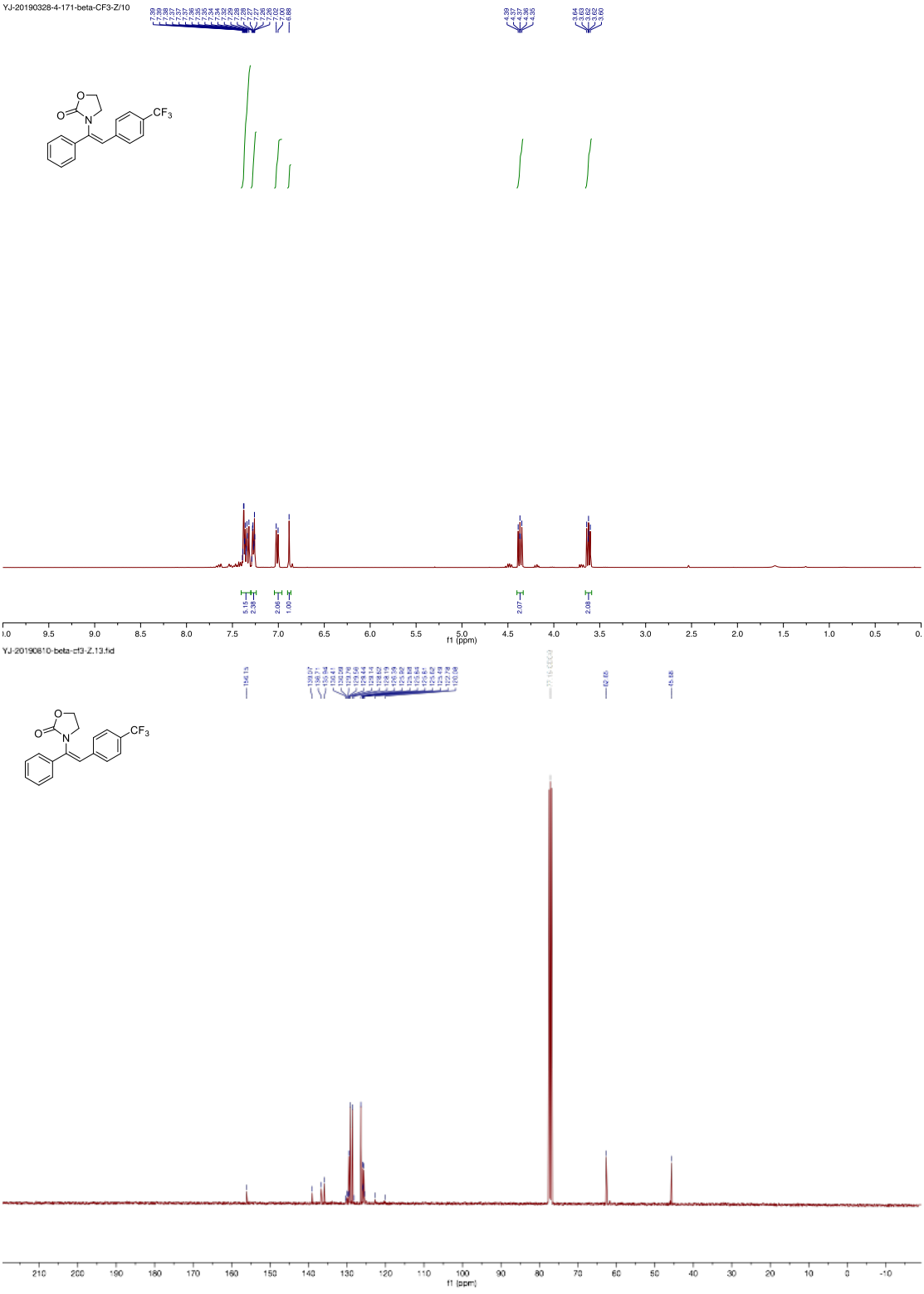
^{1}H and ^{13}C{1H} NMR spectra of **3j**



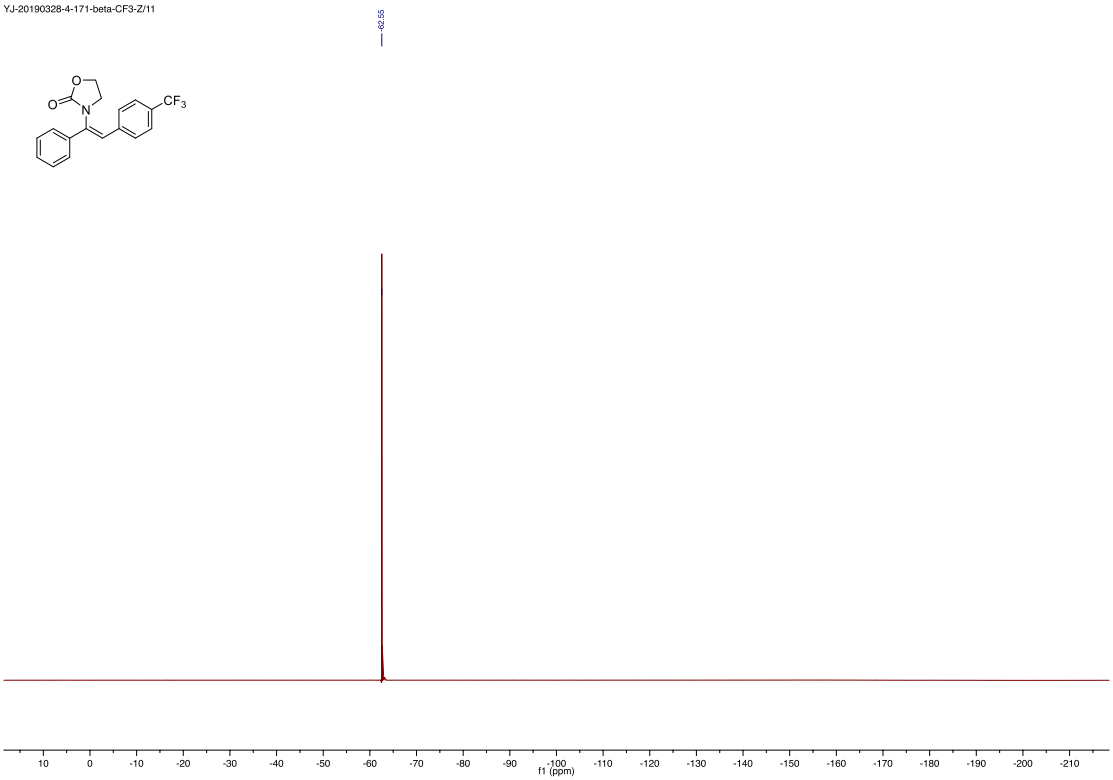
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3m**



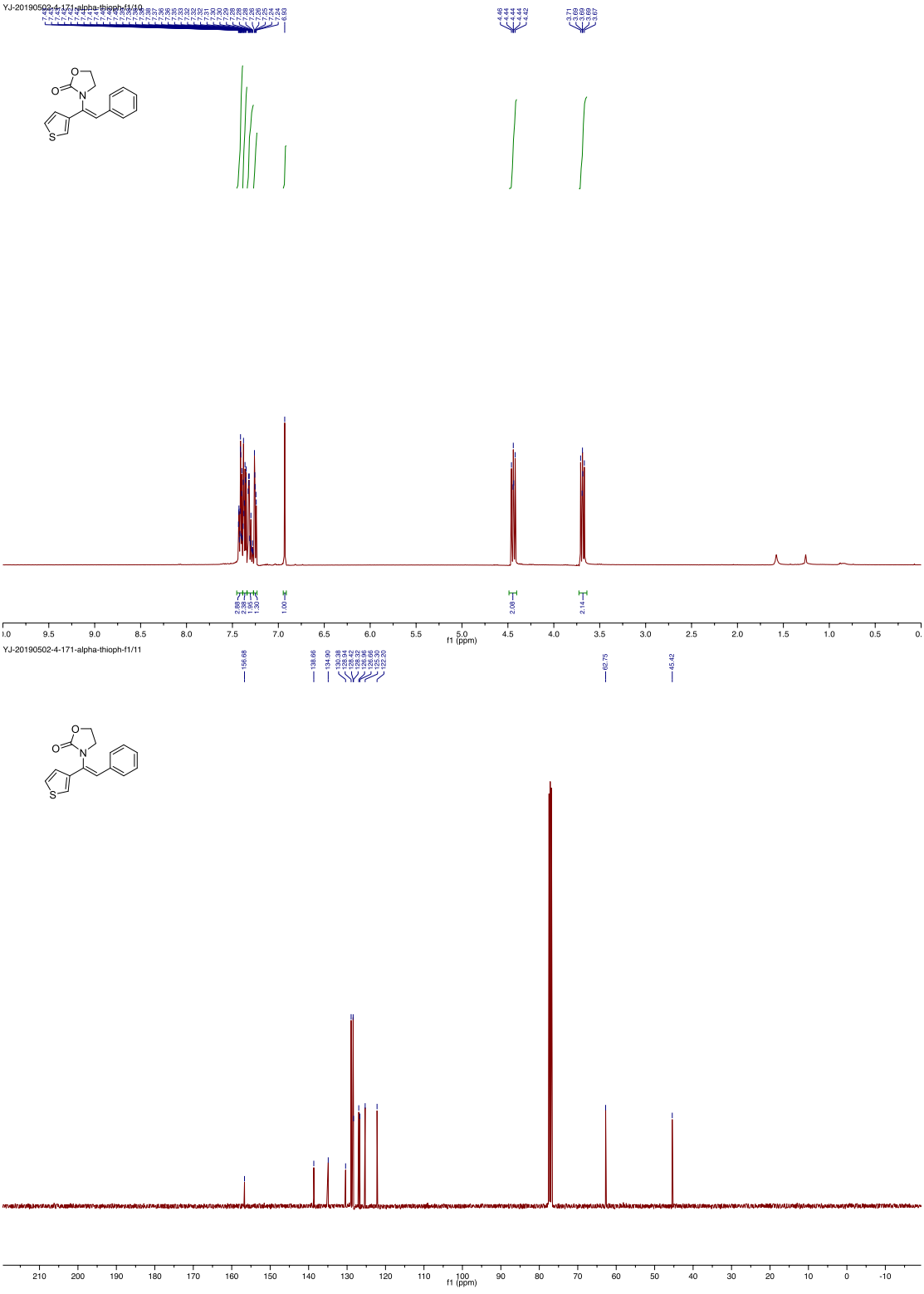
^{19}F NMR spectra of **3m**



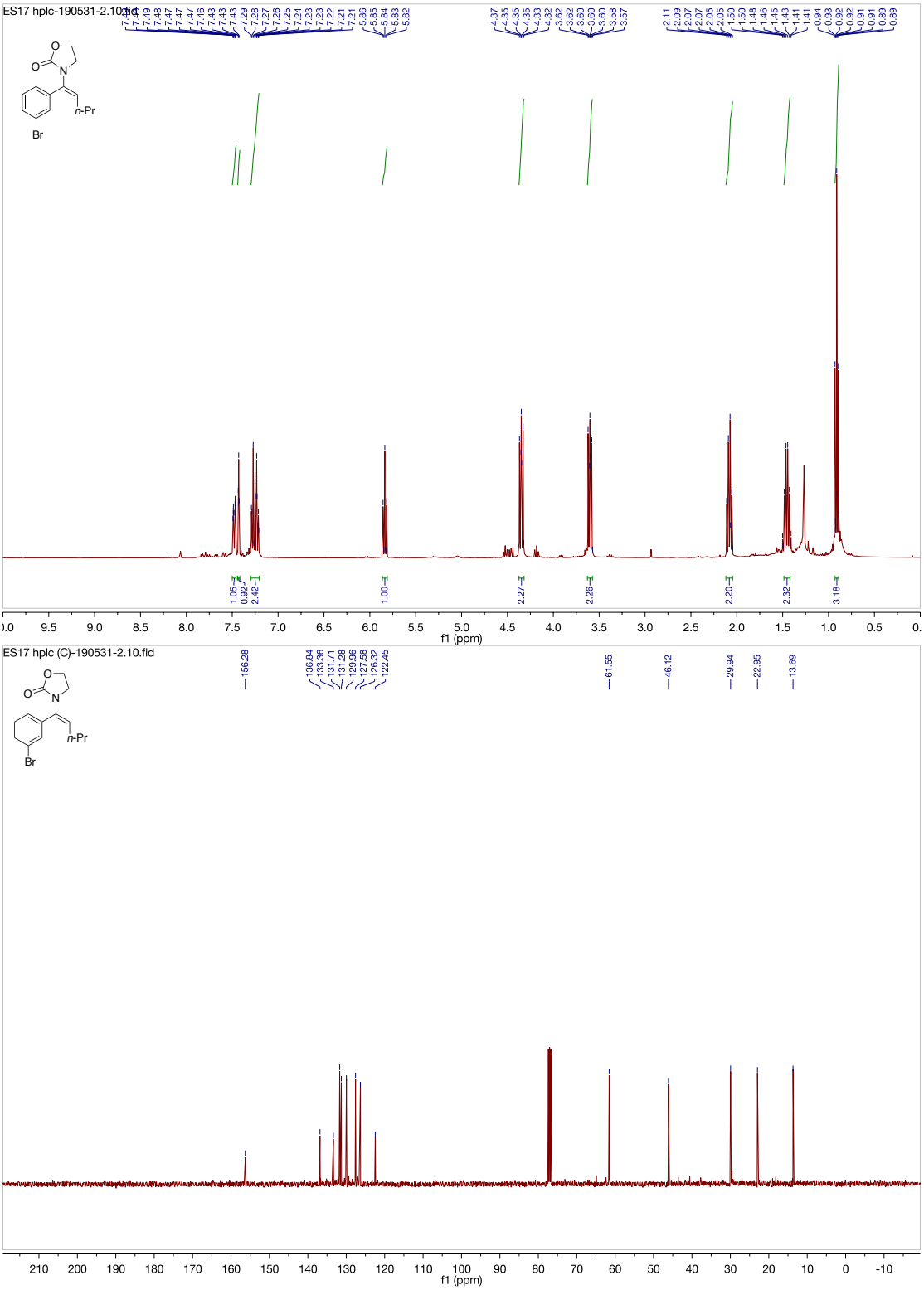
^{1}H and ^{13}C{1H} NMR spectra of **3p**



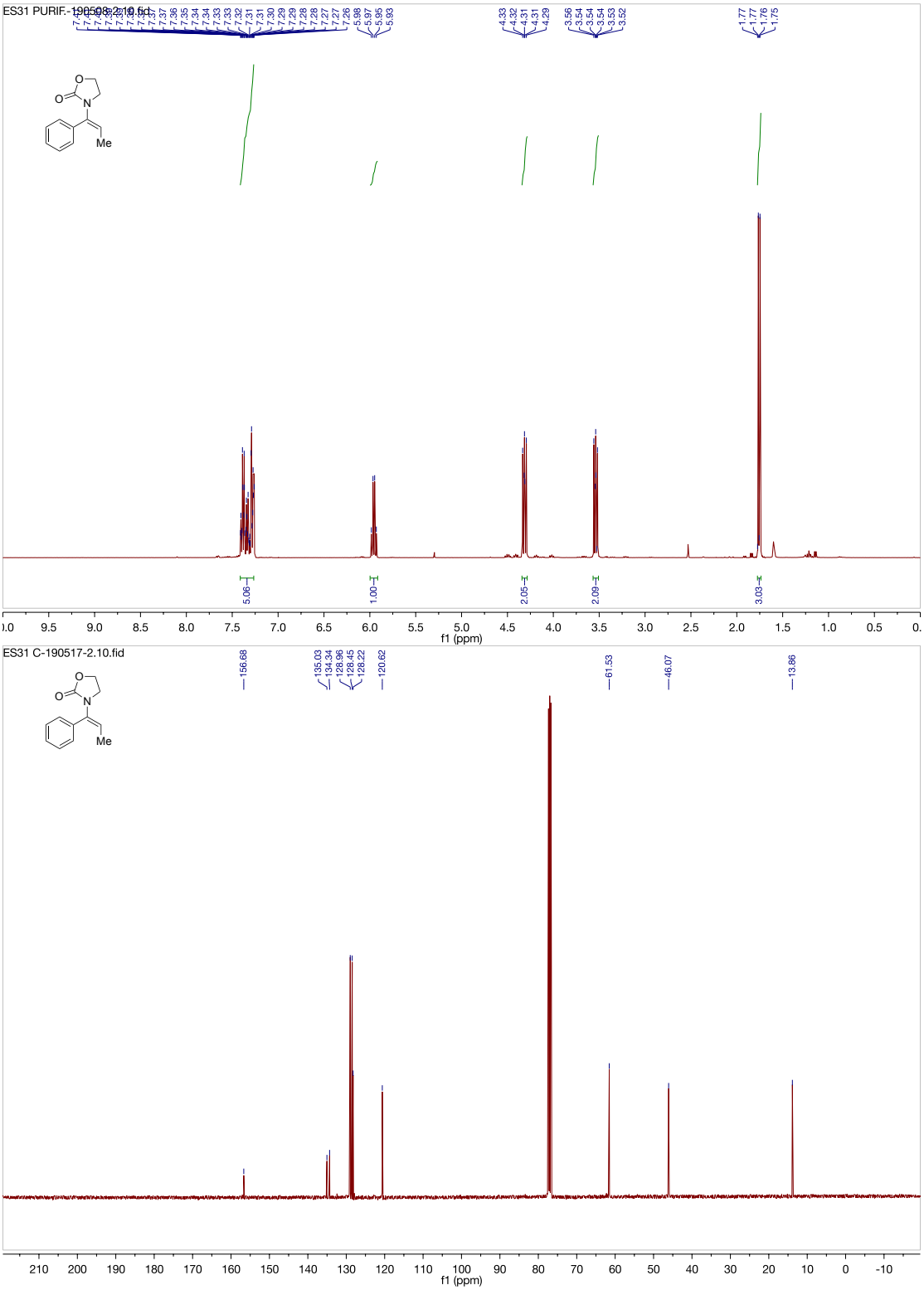
^{19}F NMR spectra of **3p**



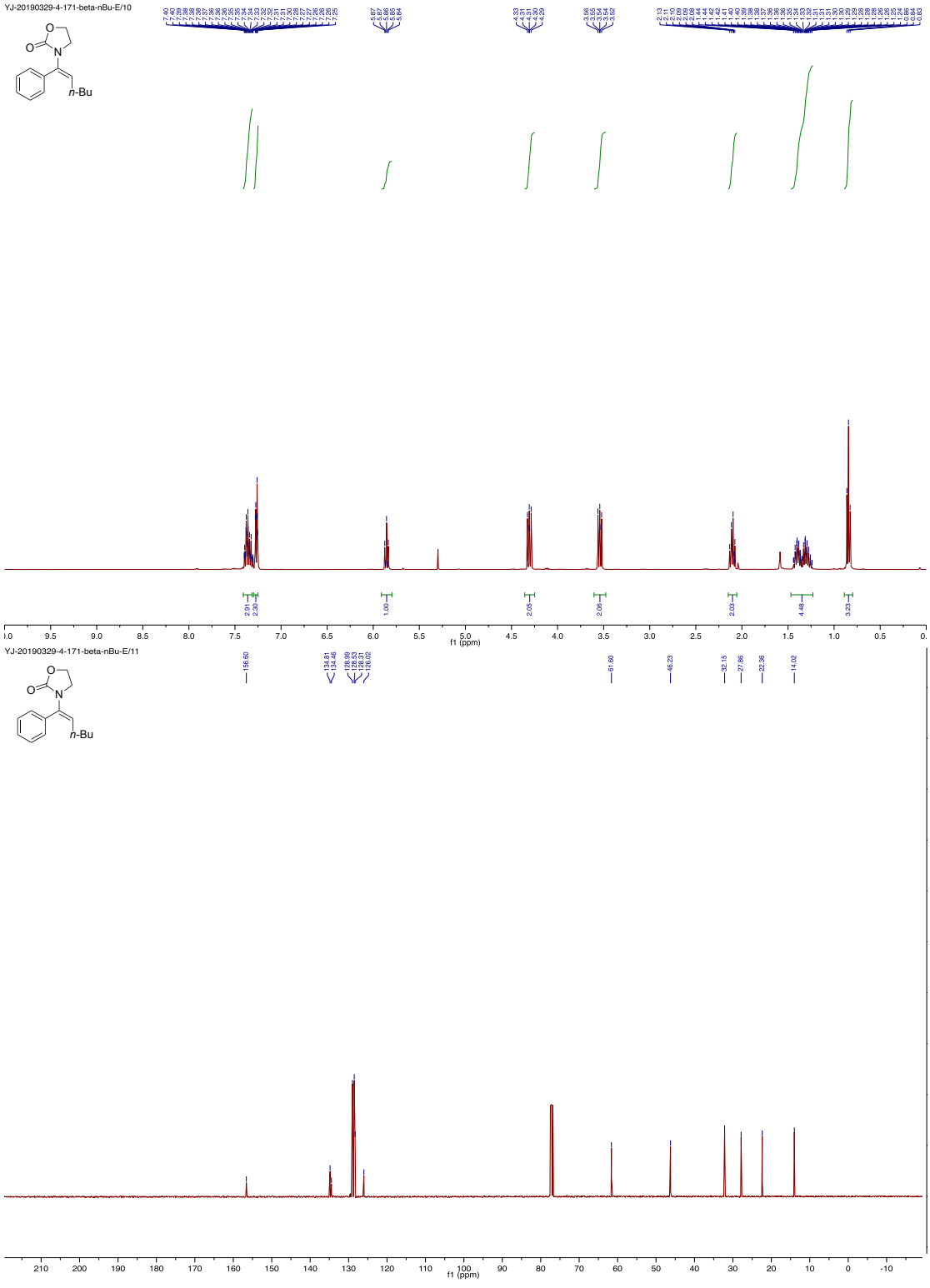
^{1}H and ^{13}C{1H} NMR spectra of **3s**



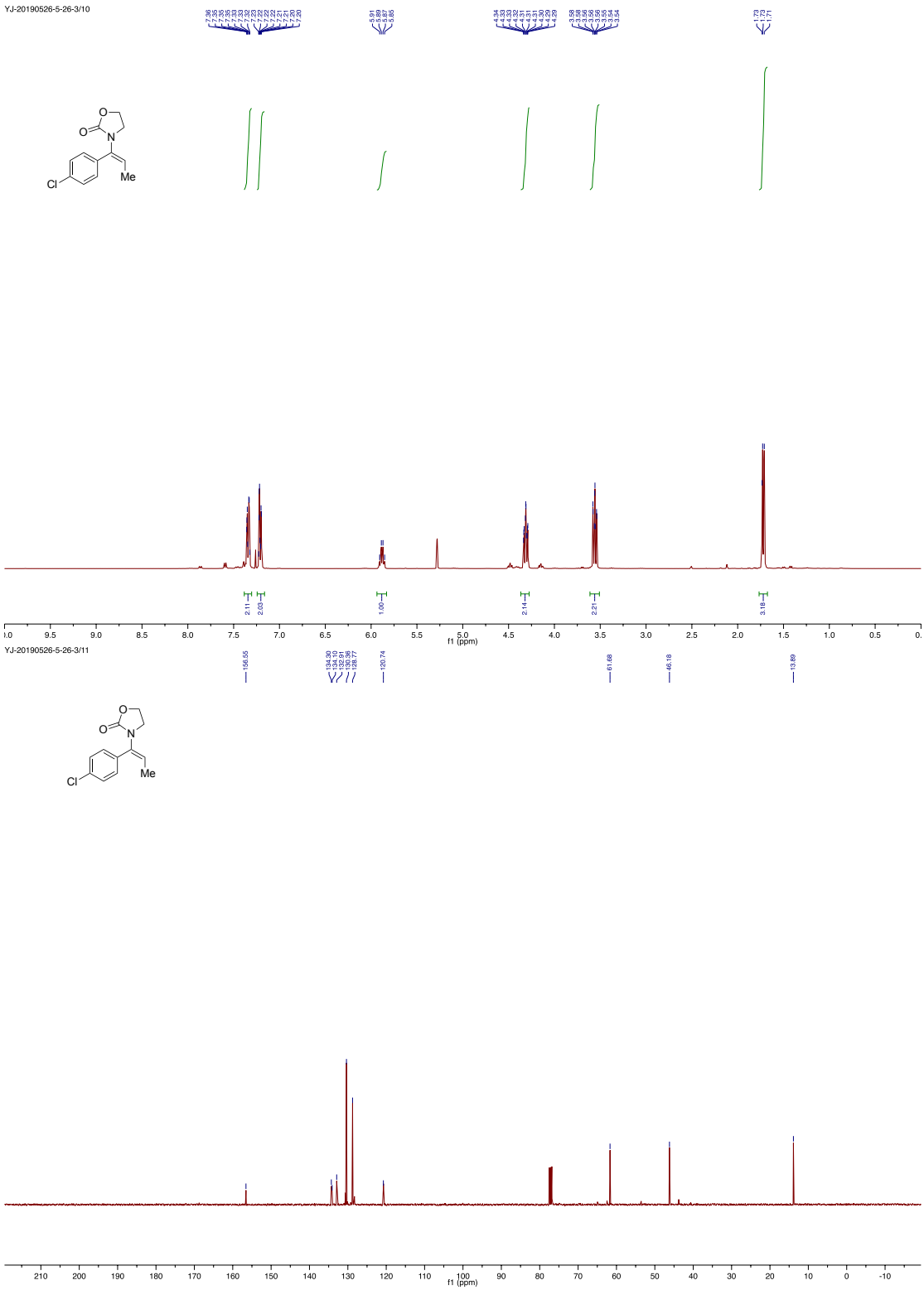
^{1}H and ^{13}C{1H} NMR spectra of **3sa'**



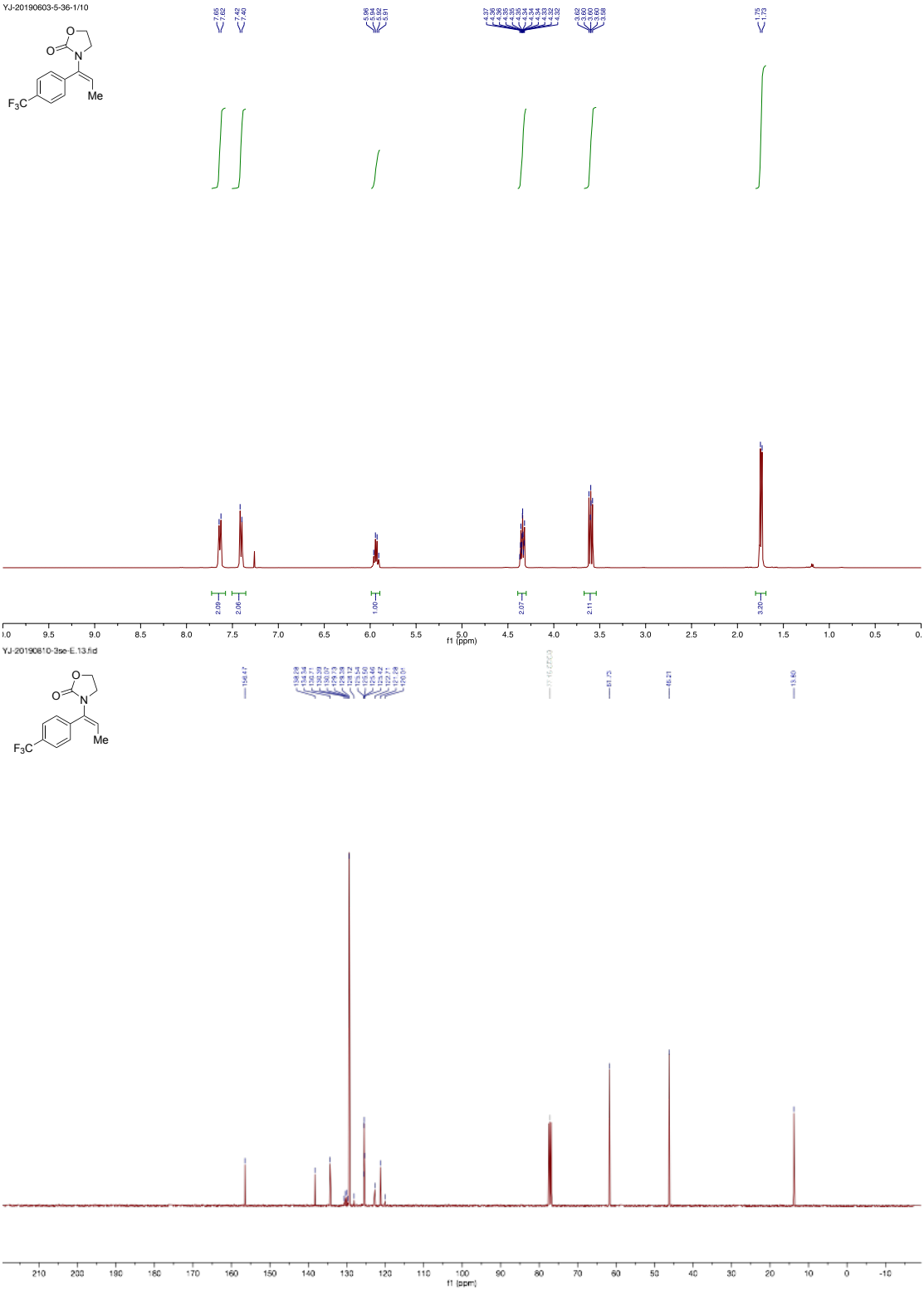
^{1}H and ^{13}C{1H} NMR spectra of **3sb'**



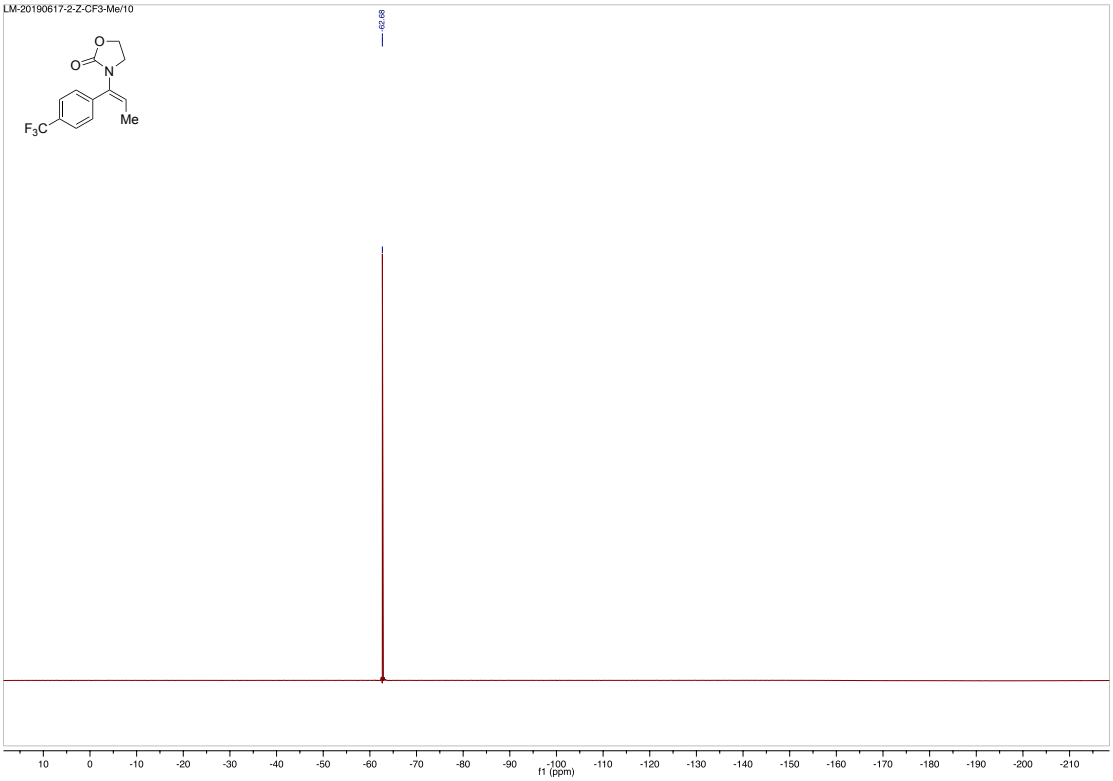
^{1}H and ^{13}C{1H} NMR spectra of **3sc'**



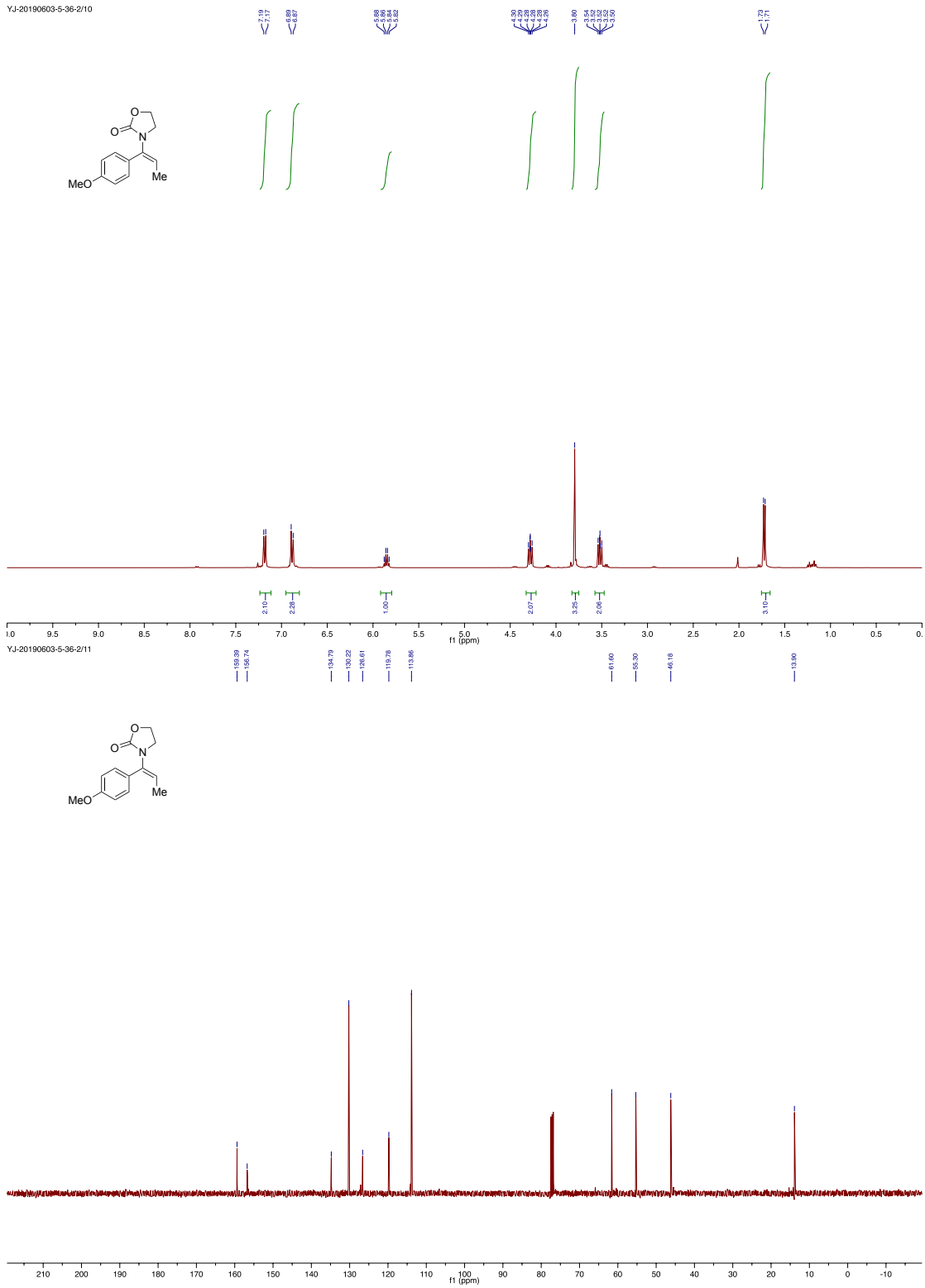
^{1}H and ^{13}C{1H} NMR spectra of **3sd'**



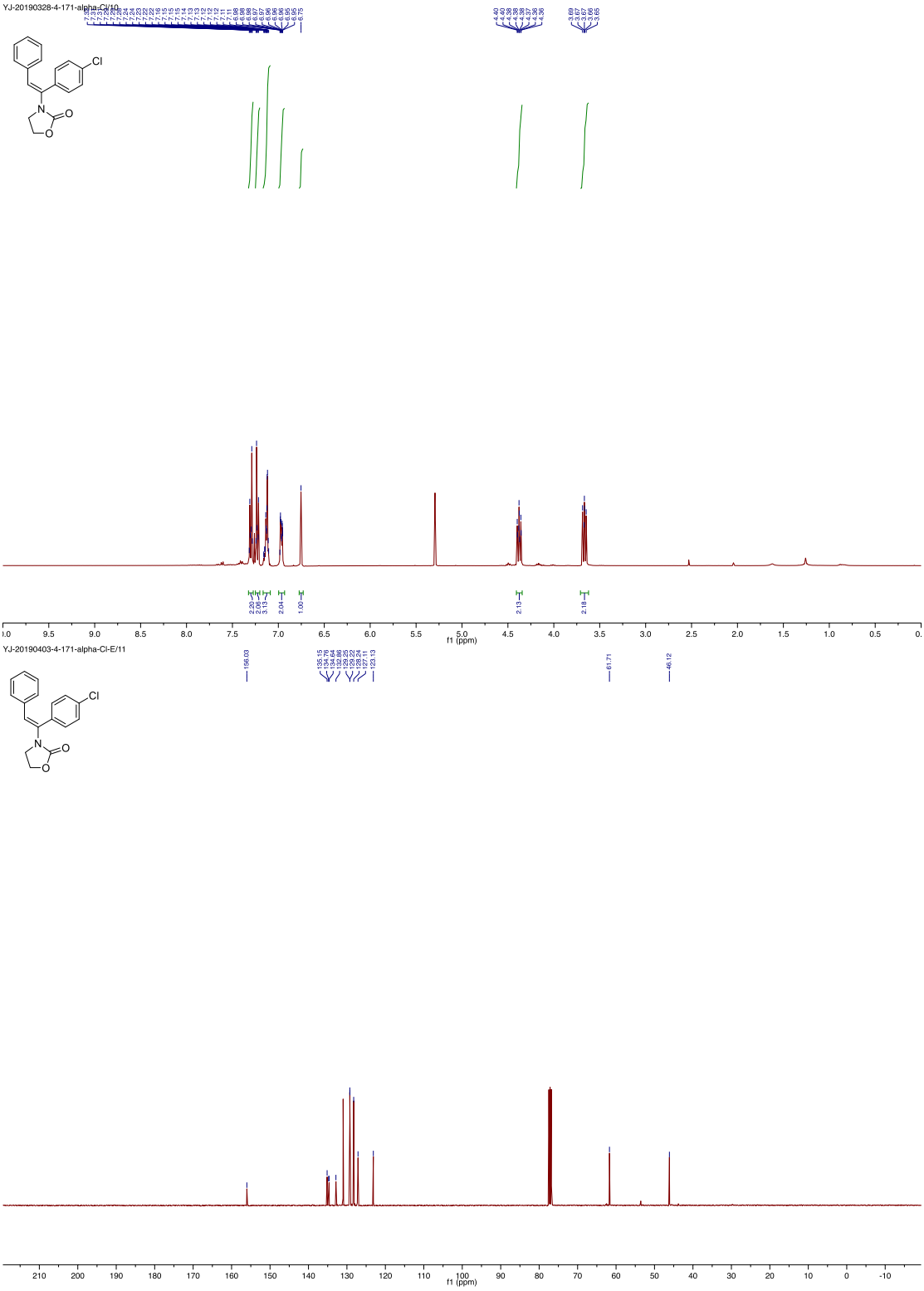
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3se'**



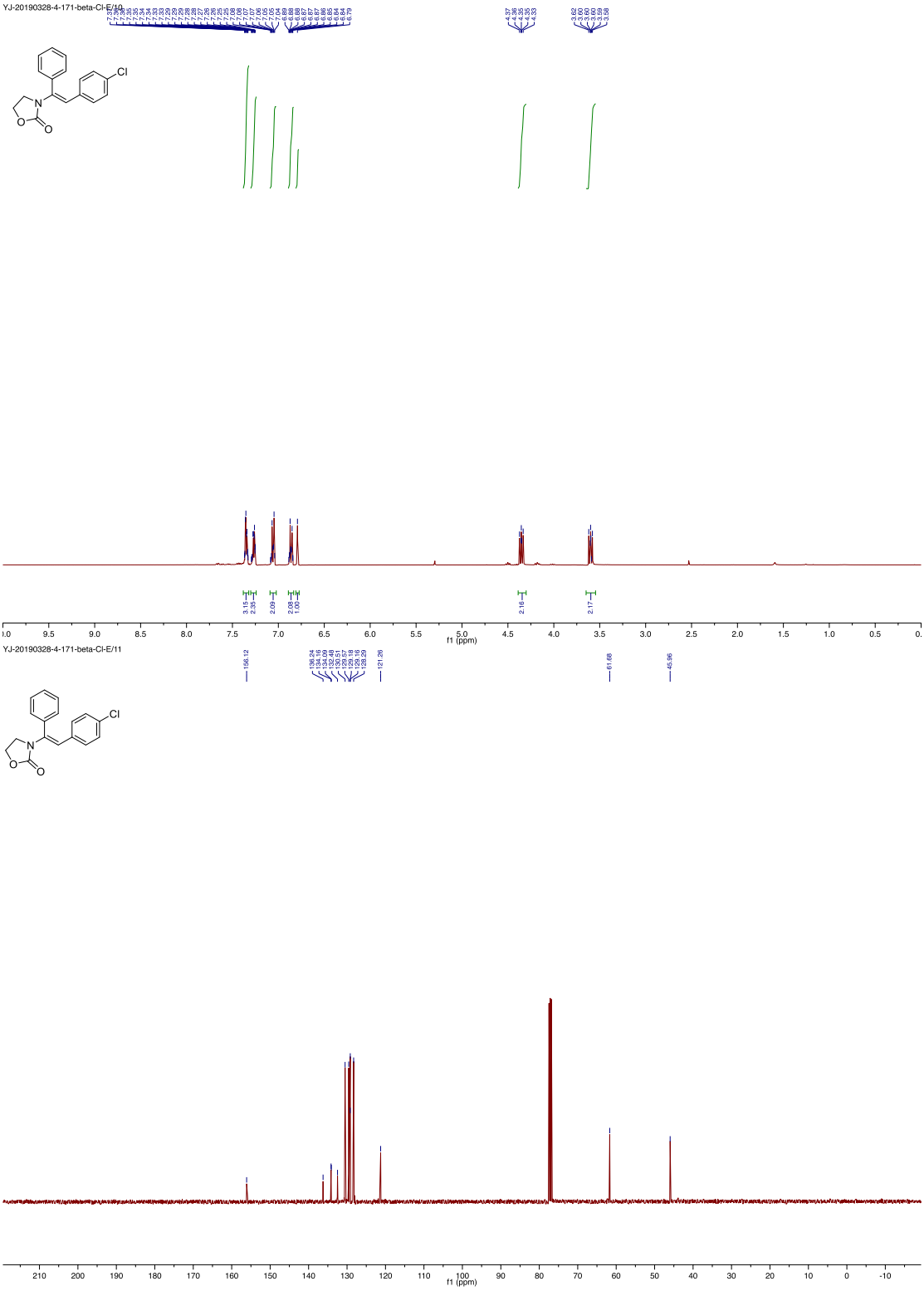
^{19}F NMR spectra of **3se'**



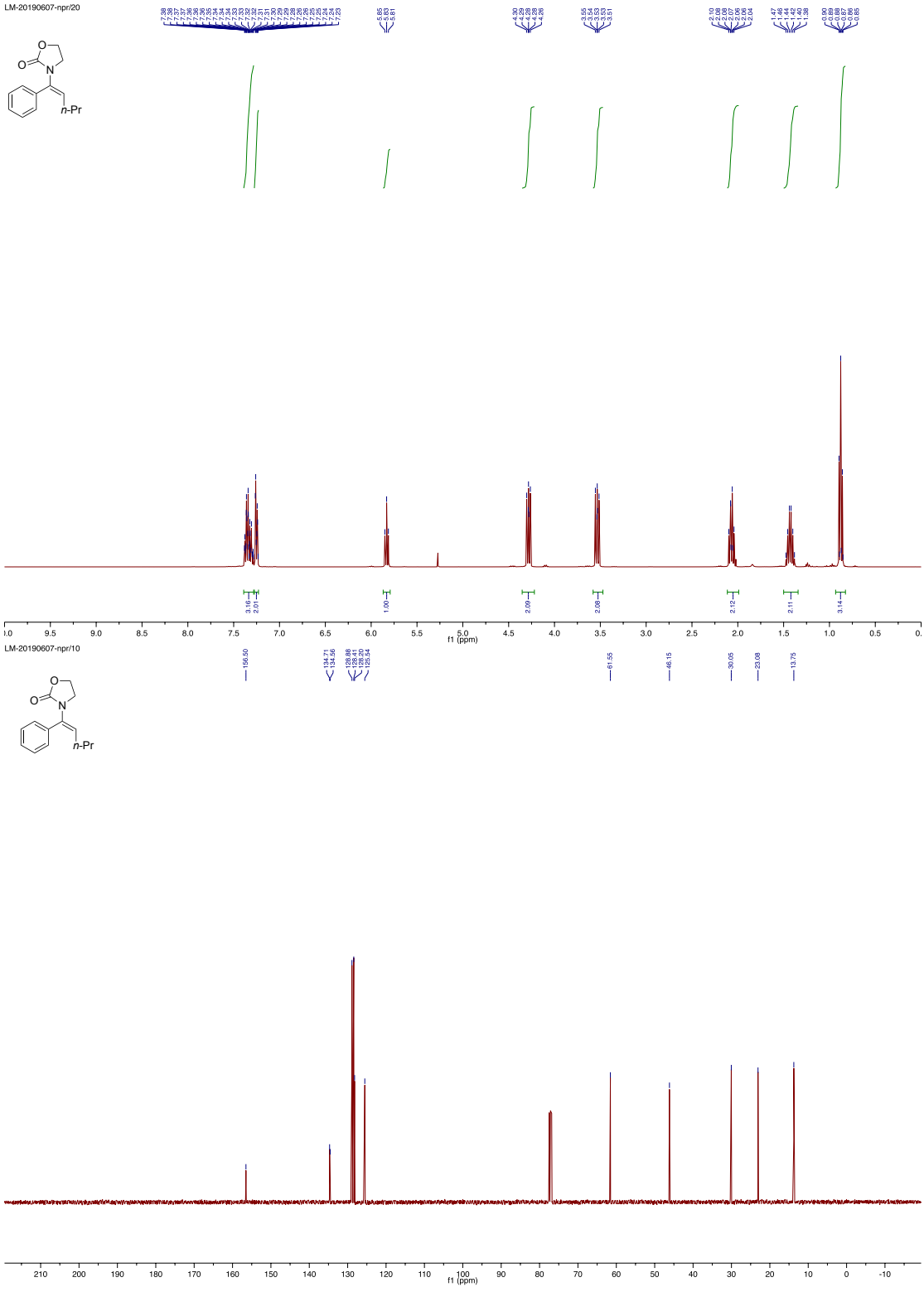
^{1}H and ^{13}C{1H} NMR spectra of **3sf'**



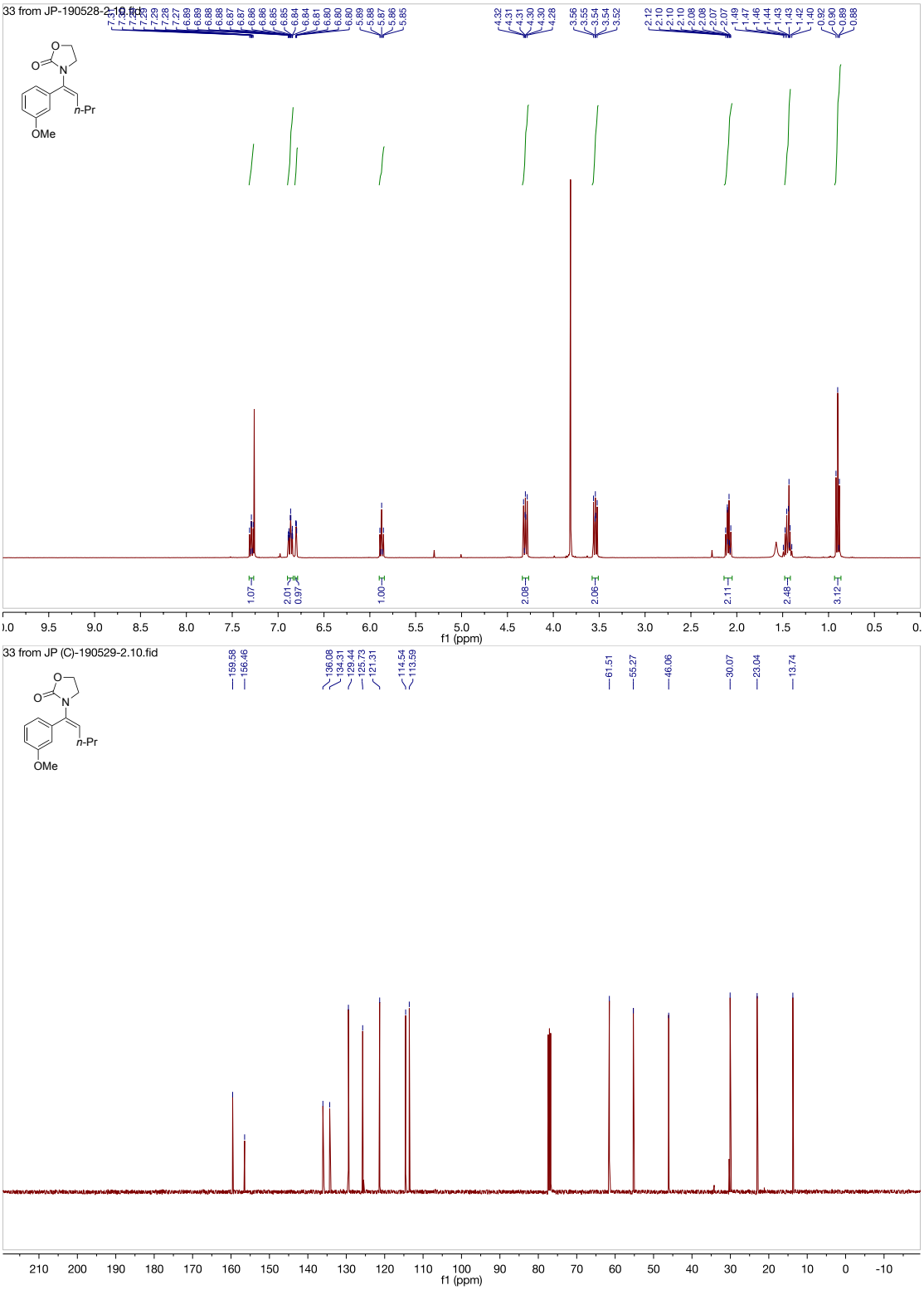
^{1}H and ^{13}C{1H} NMR spectra of **3sg'**



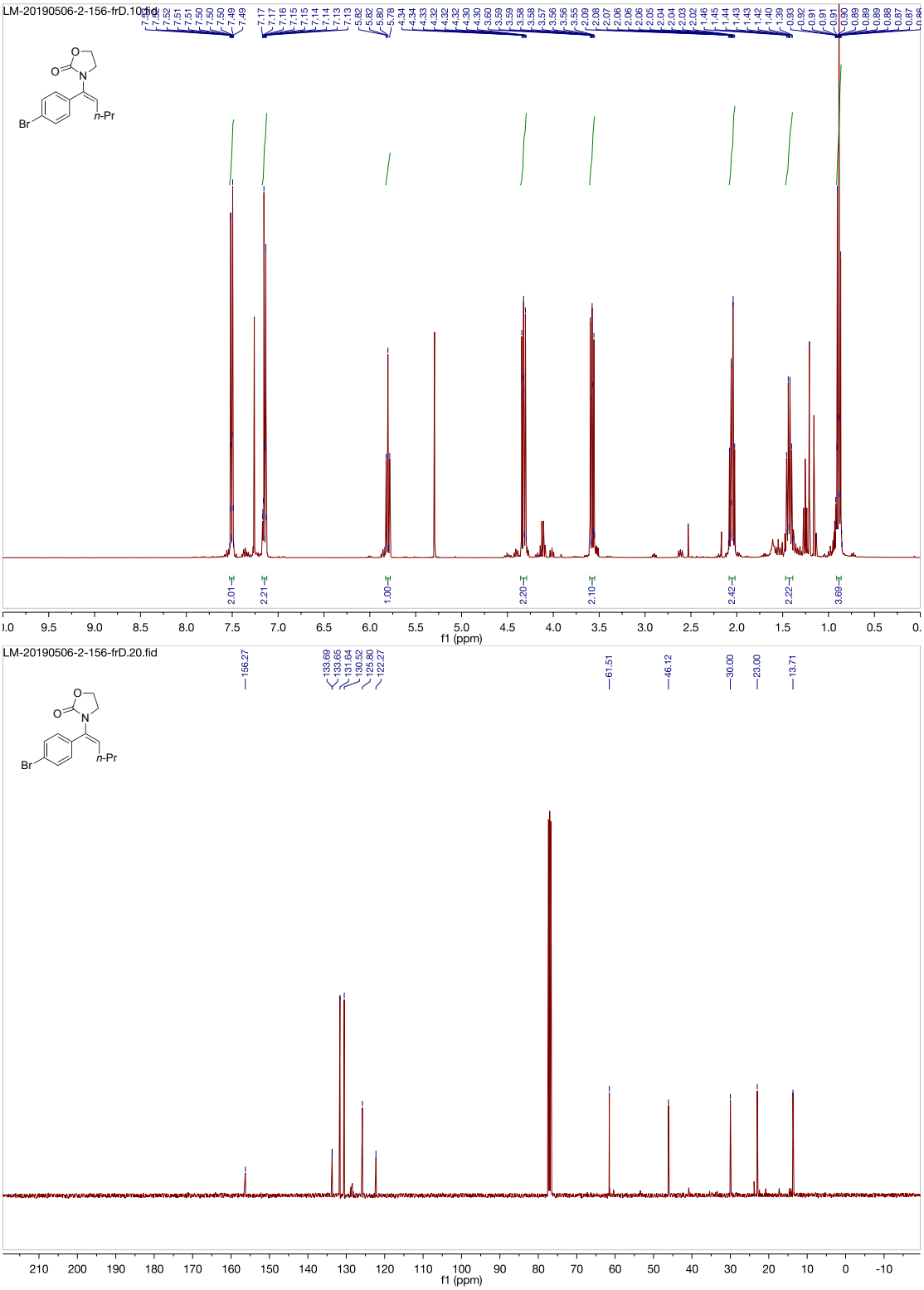
^{1}H and ^{13}C{1H} NMR spectra of **3sh'**



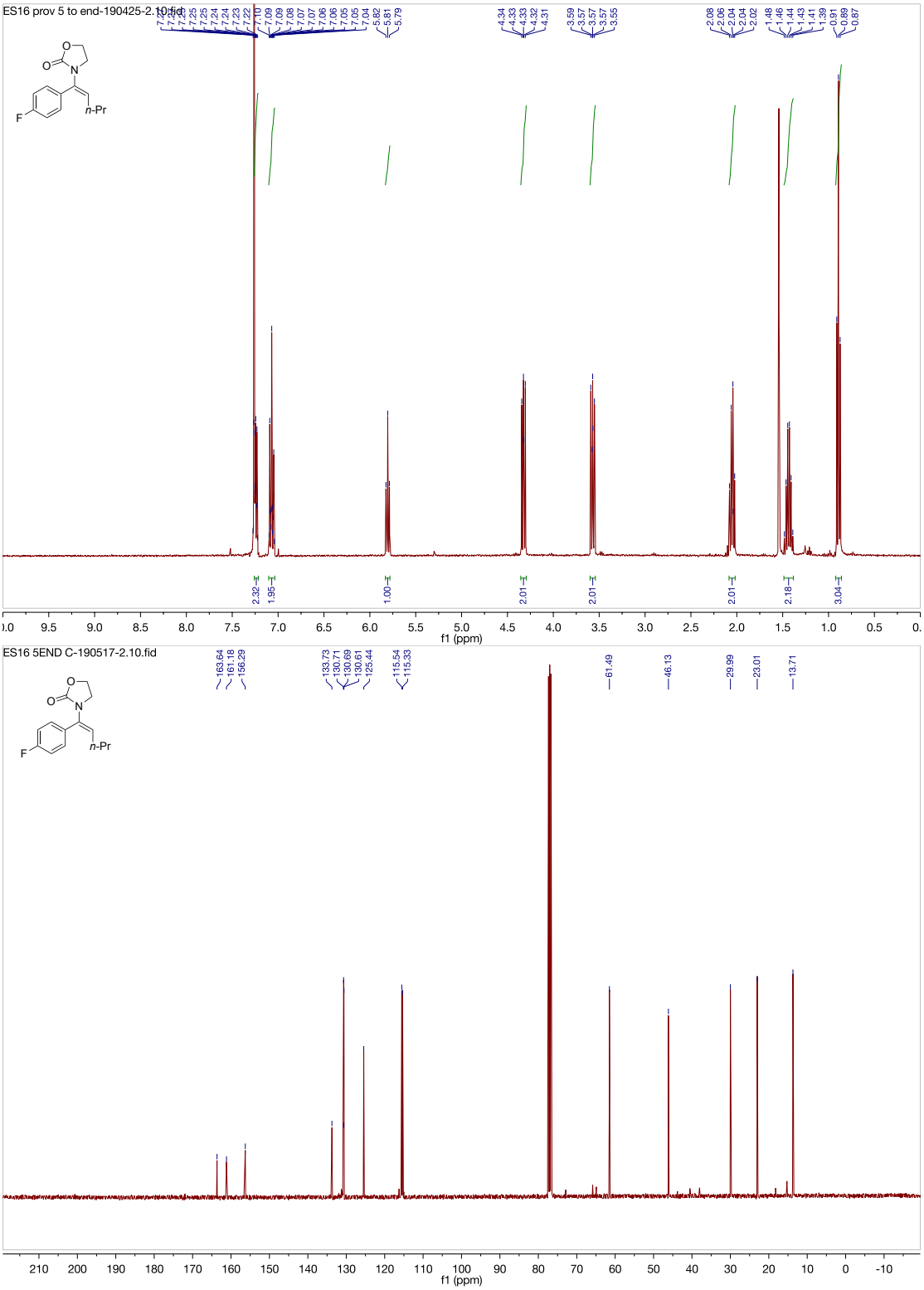
^{1}H and ^{13}C{1H} NMR spectra of **3a'**



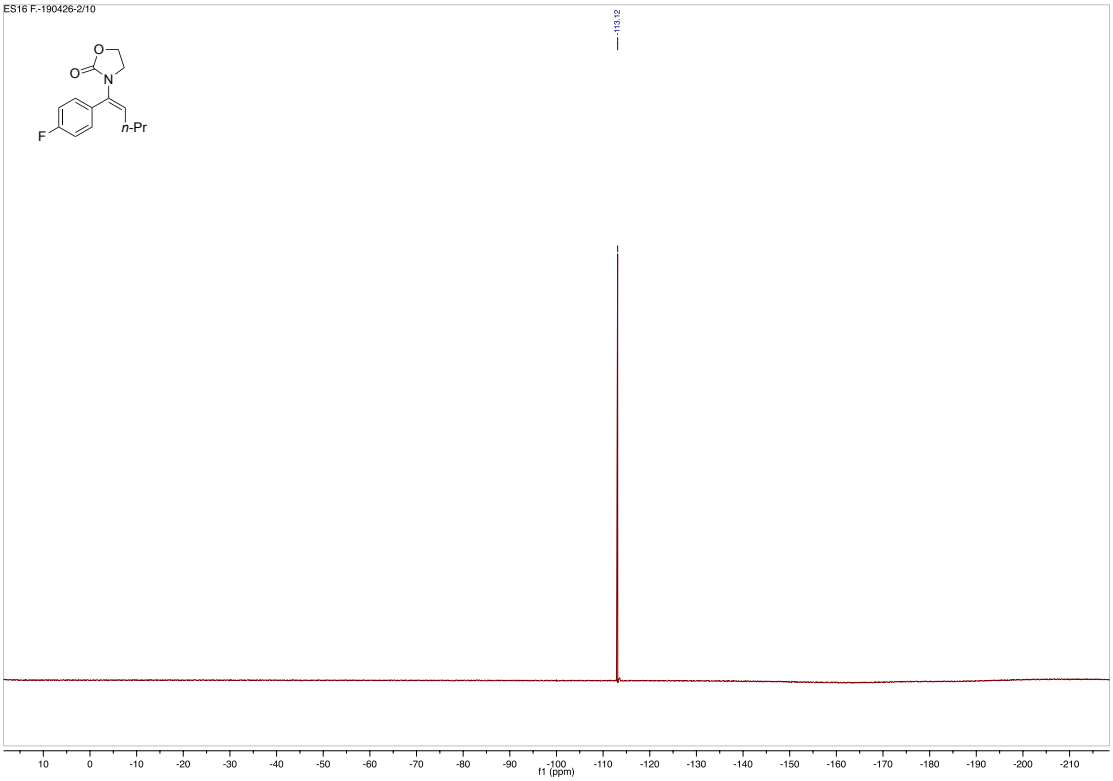
^{1}H and ^{13}C{1H} NMR spectra of **3b'**



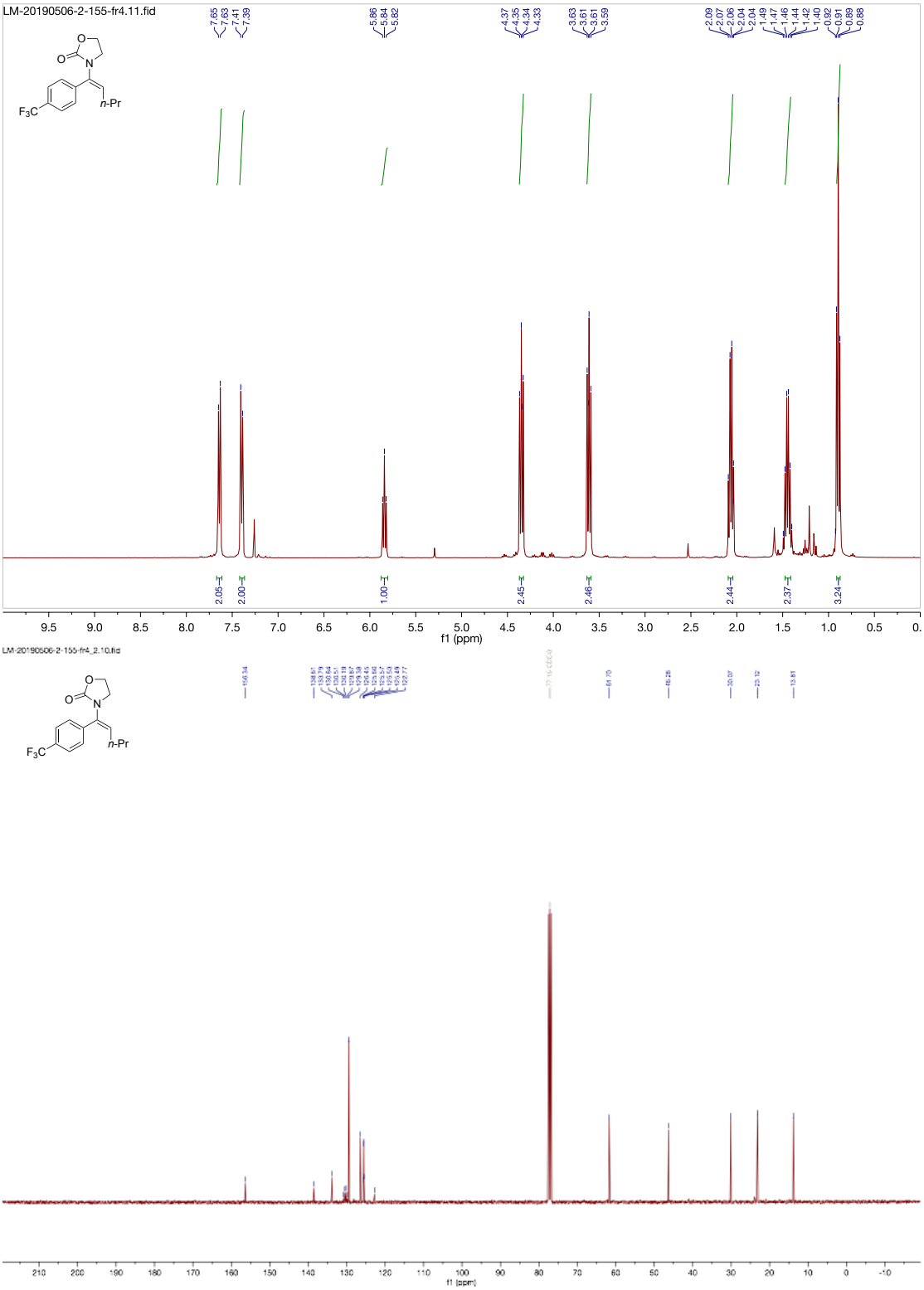
^{1}H and ^{13}C{1H} NMR spectra of **3c'**



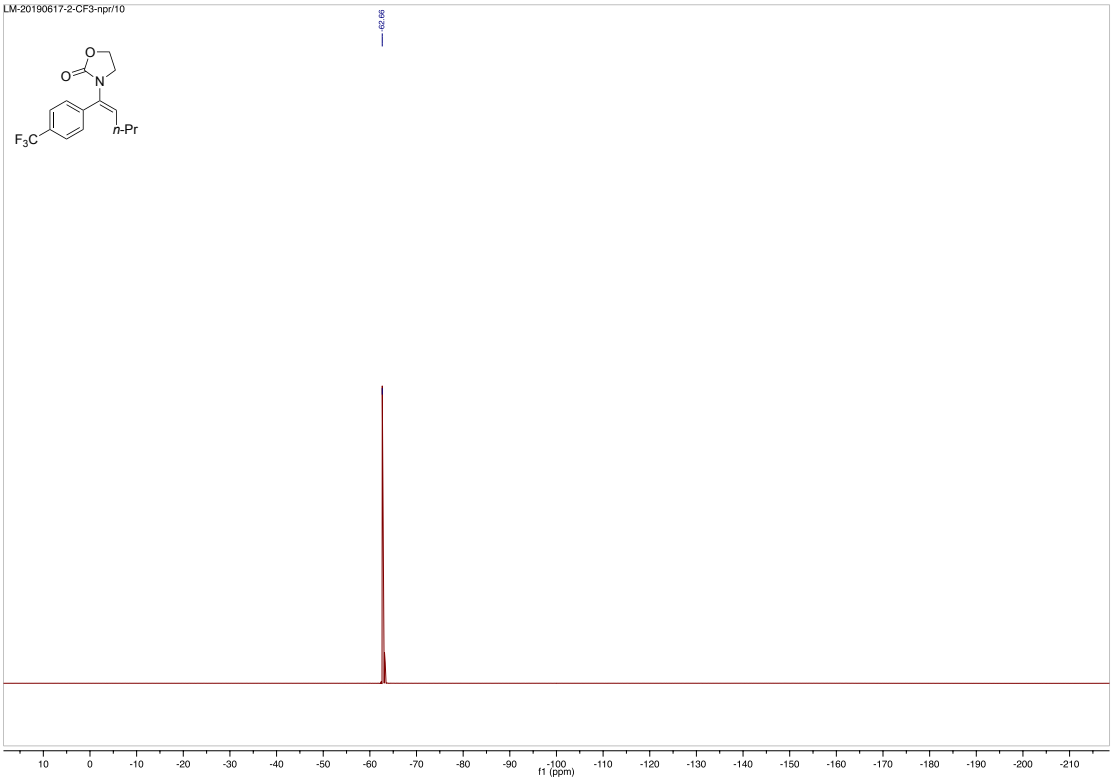
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3d'**



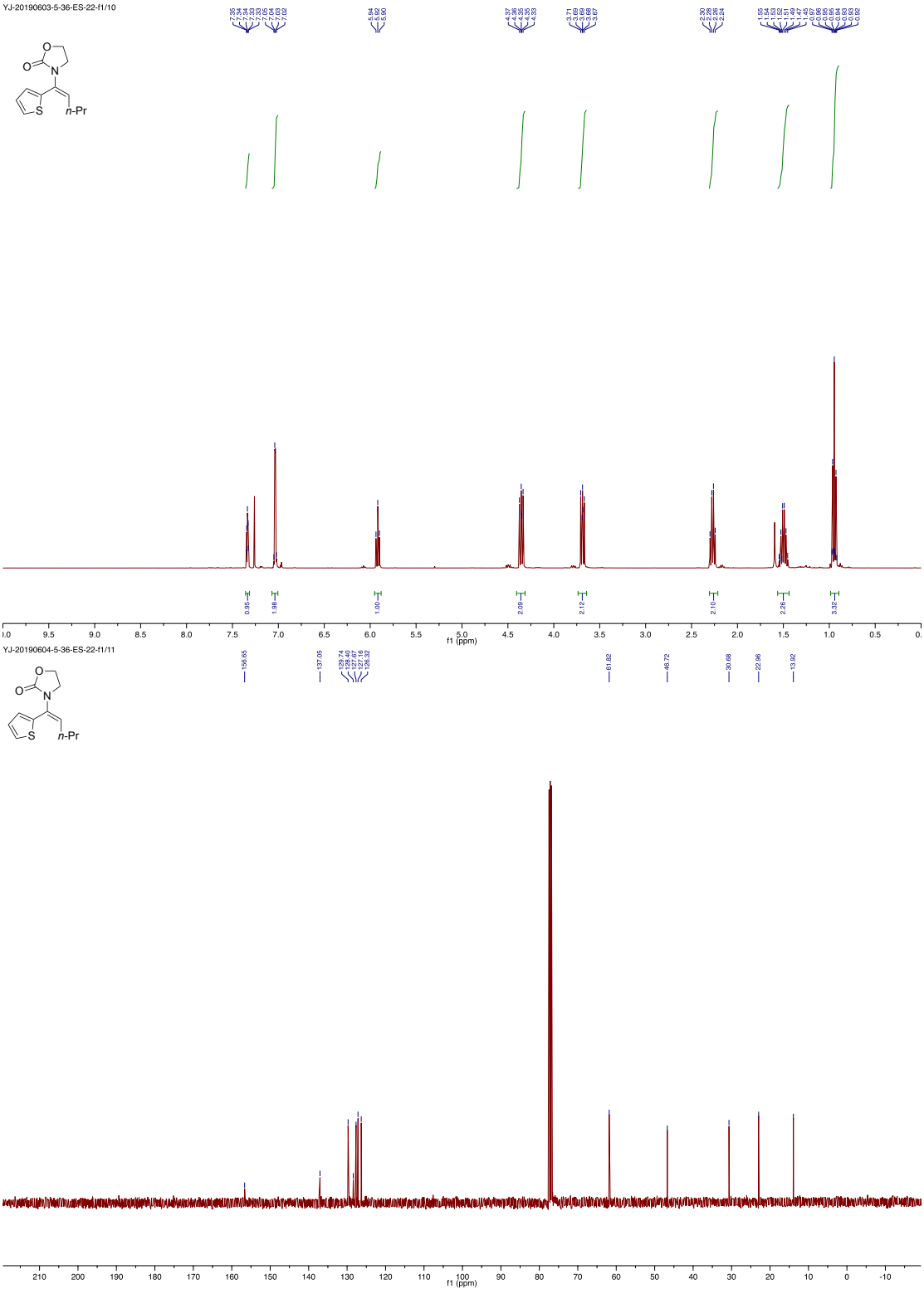
^{19}F NMR spectra of **3d'**



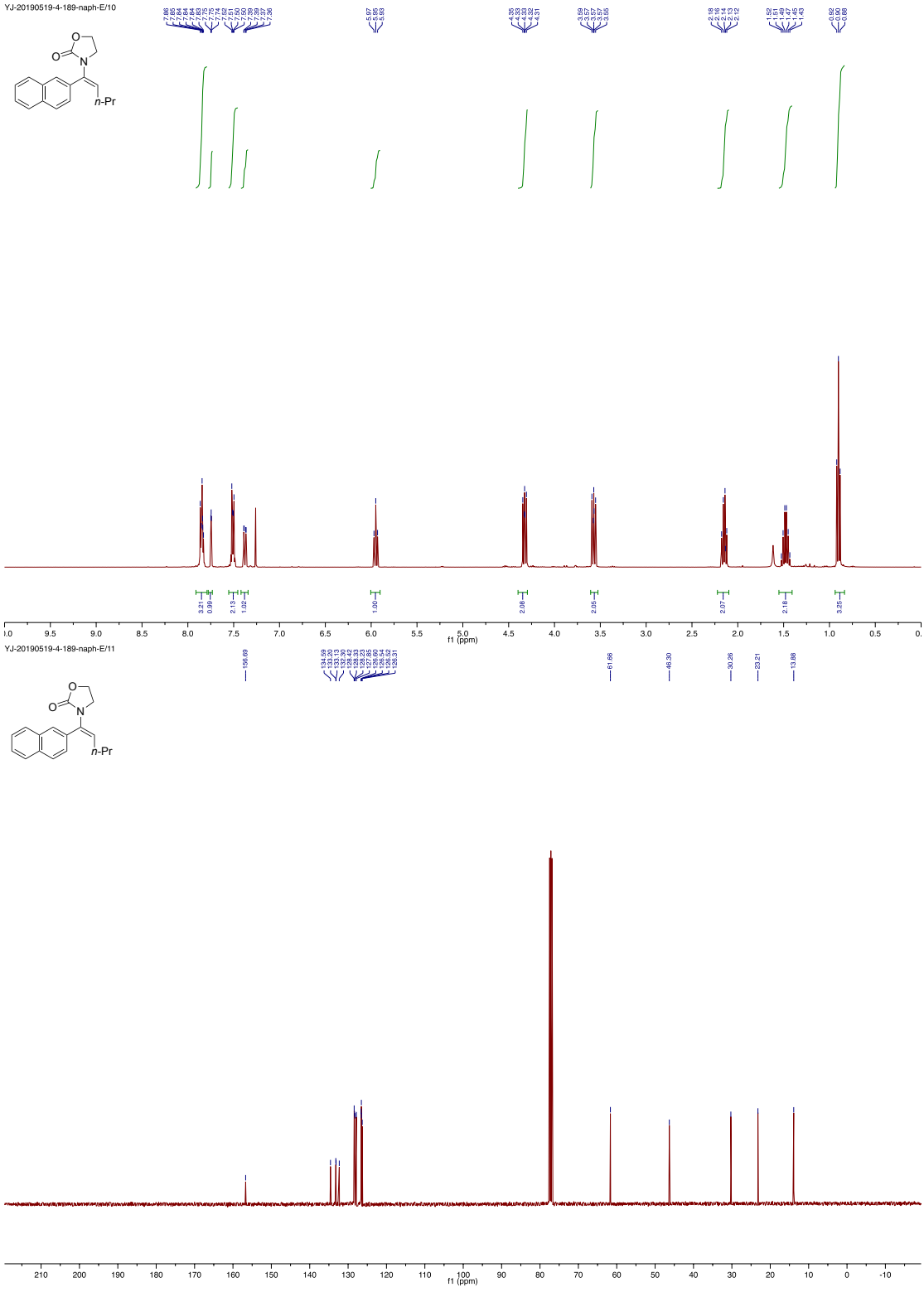
^{1}H and ^{13}C{1H} NMR spectra of **3e'**



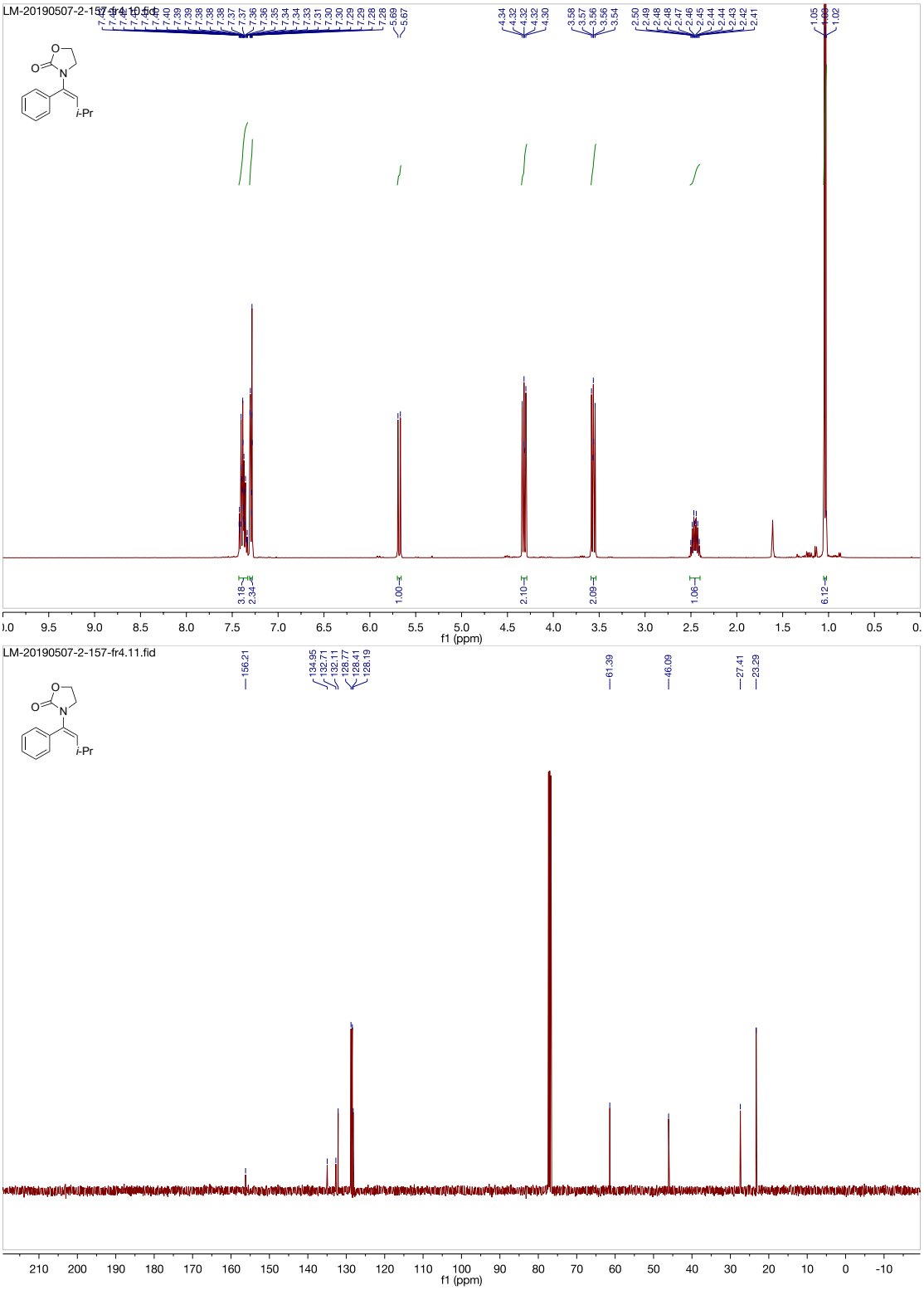
^{19}F NMR spectra of **3e'**



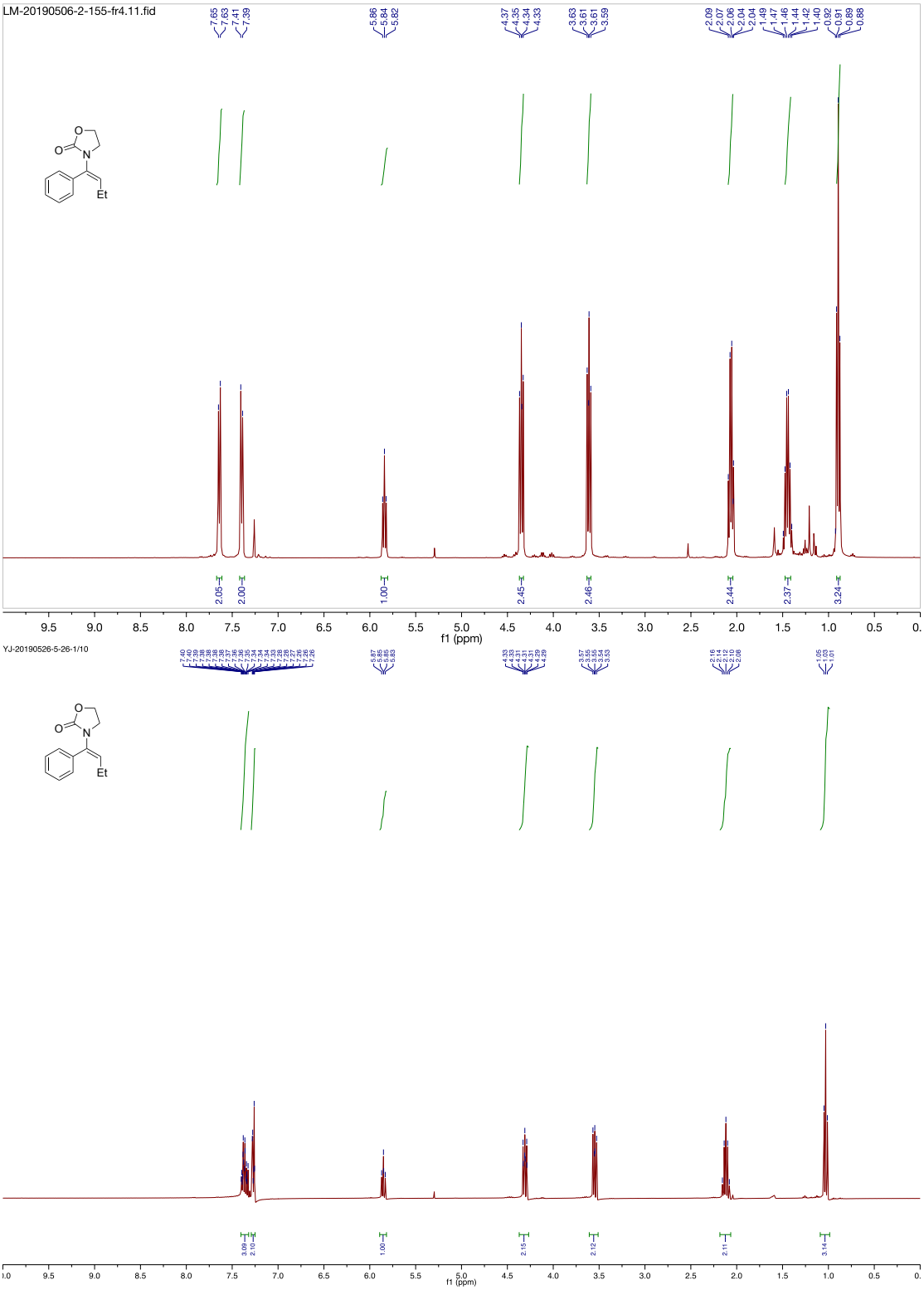
^{1}H and ^{13}C{1H} NMR spectra of **3f'**



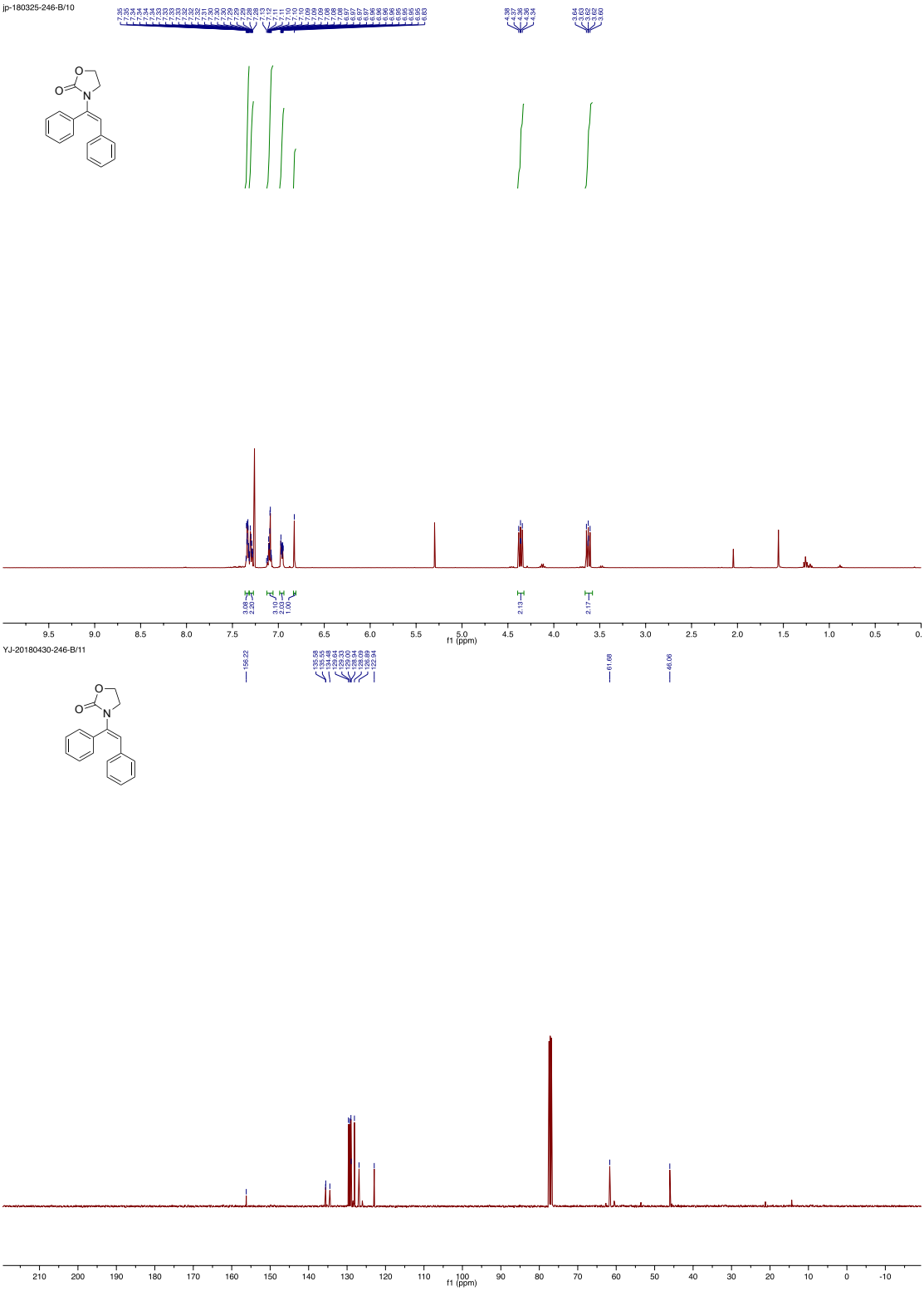
^{1}H and ^{13}C{1H} NMR spectra of **3g'**



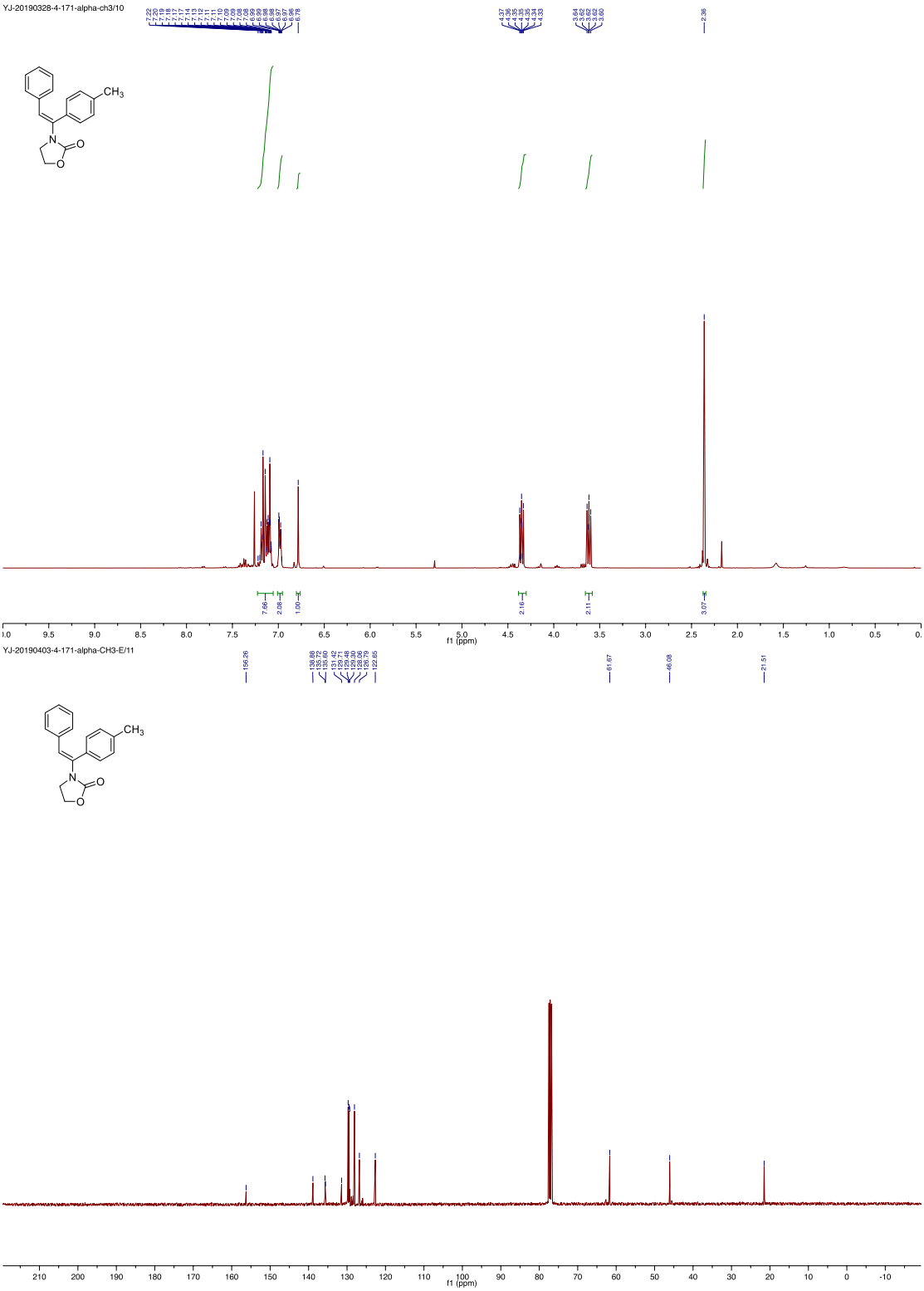
^{1}H and ^{13}C{1H} NMR spectra of **3h'**



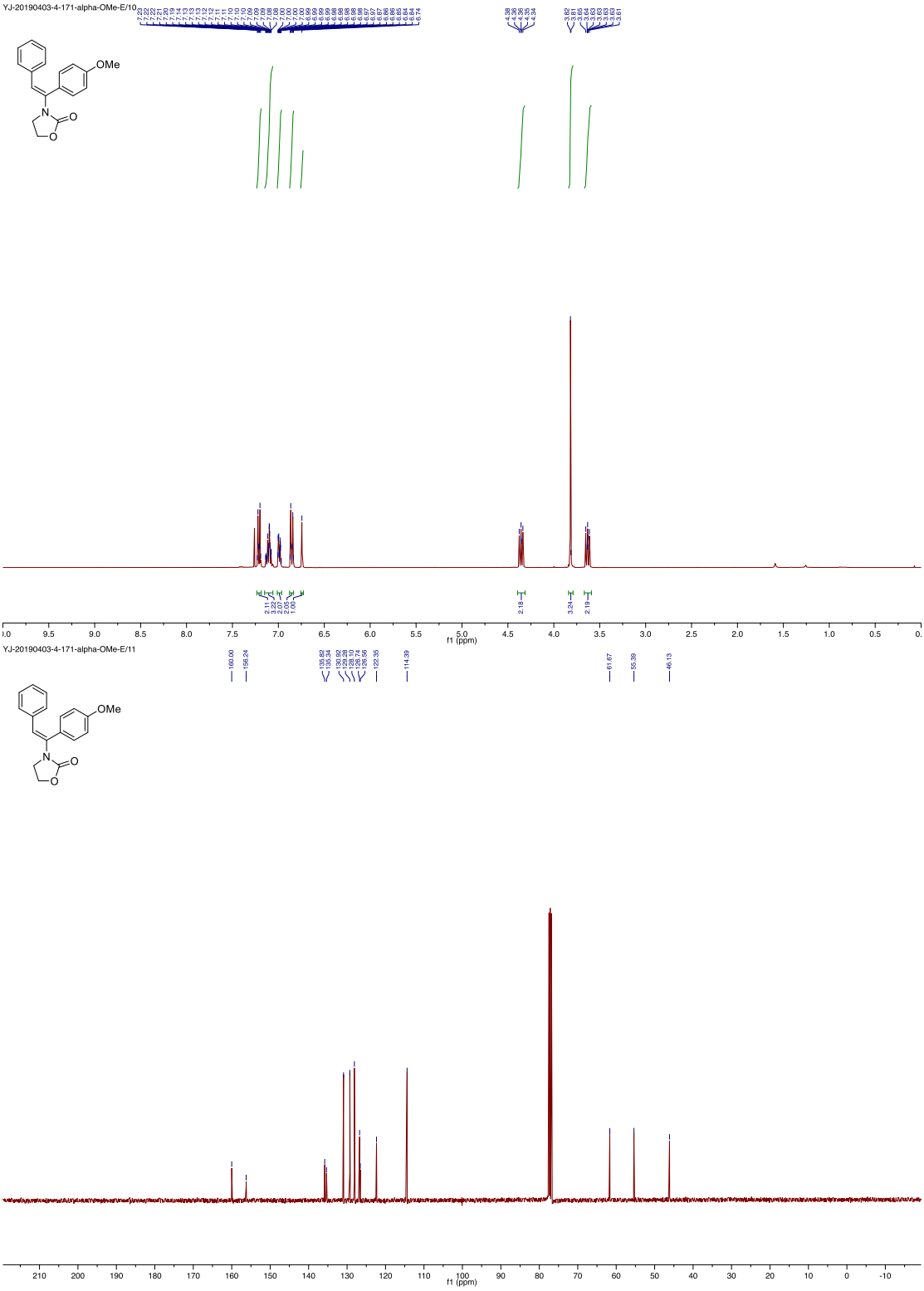
^{1}H and ^{13}C{1H} NMR spectra of **3i'**



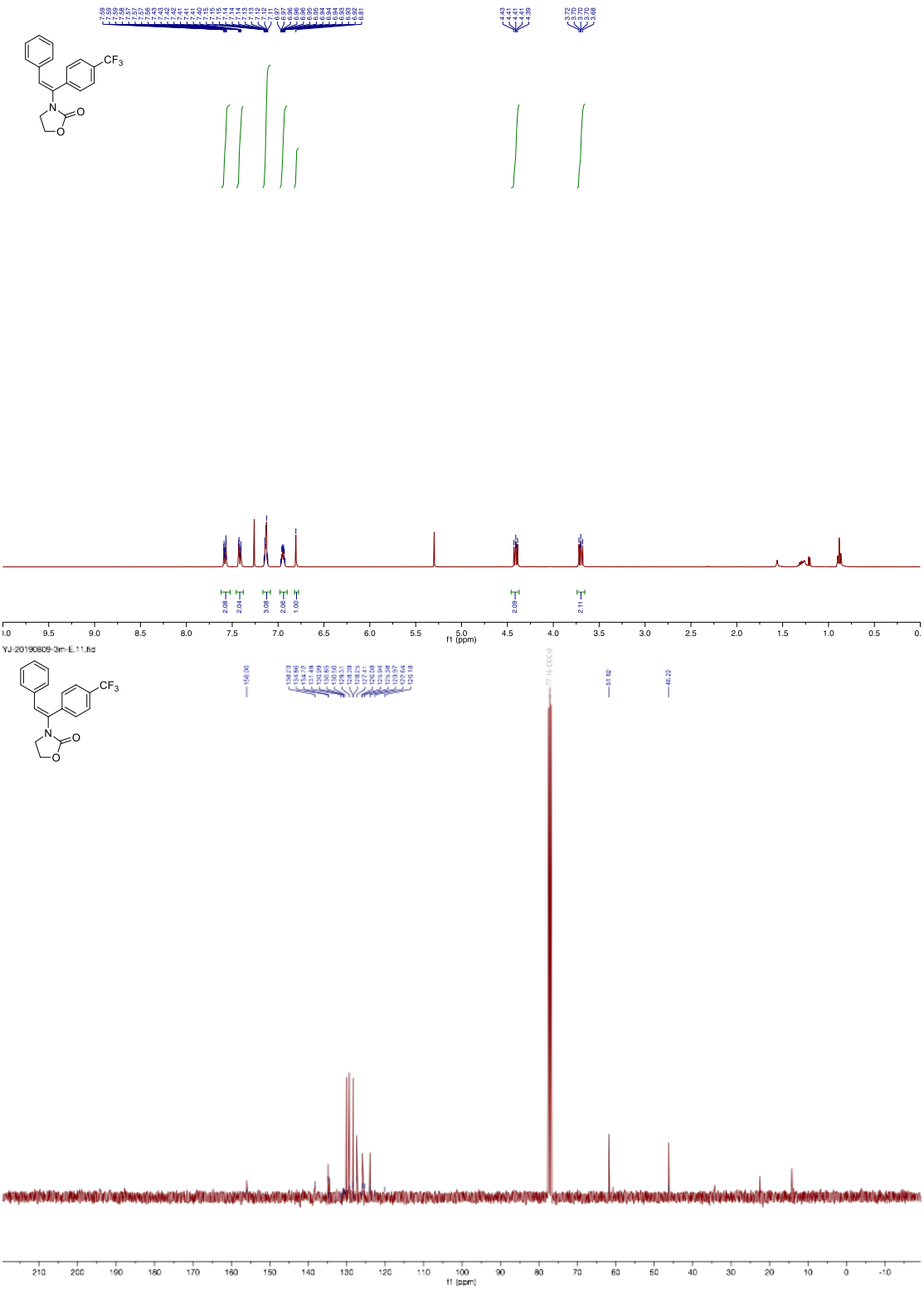
^{1}H and ^{13}C{1H} NMR spectra of **3j'**



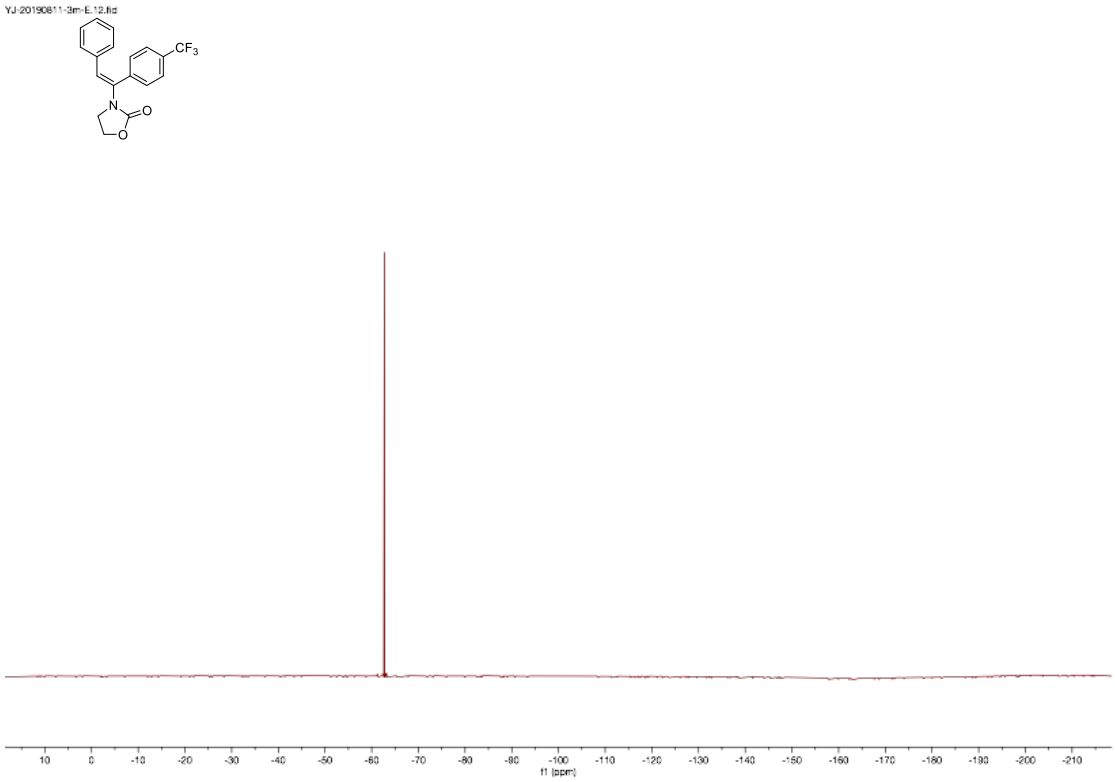
^{1}H and ^{13}C{1H} NMR spectra of **3k'**



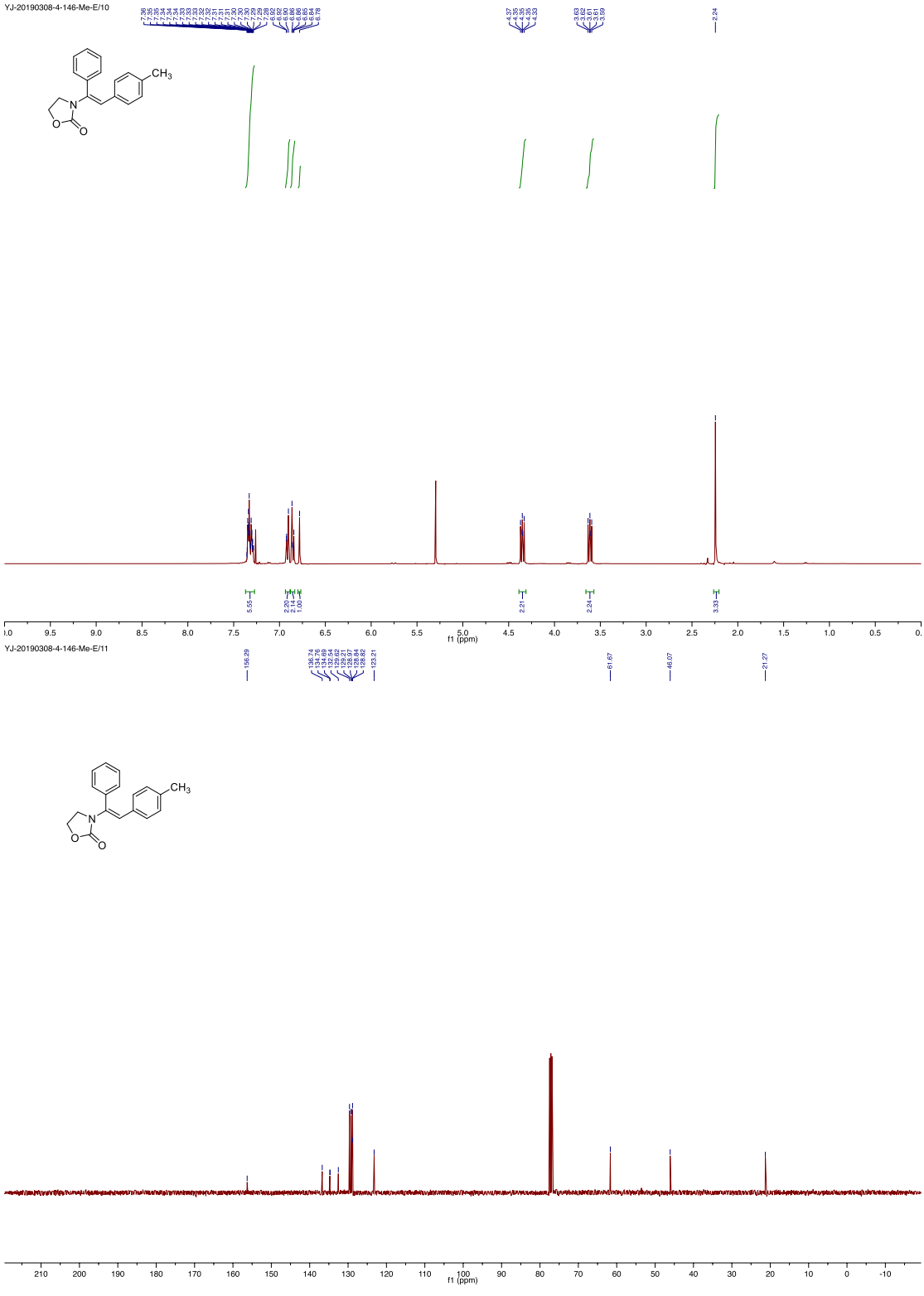
^{1}H and ^{13}C{1H} NMR spectra of **3l'**



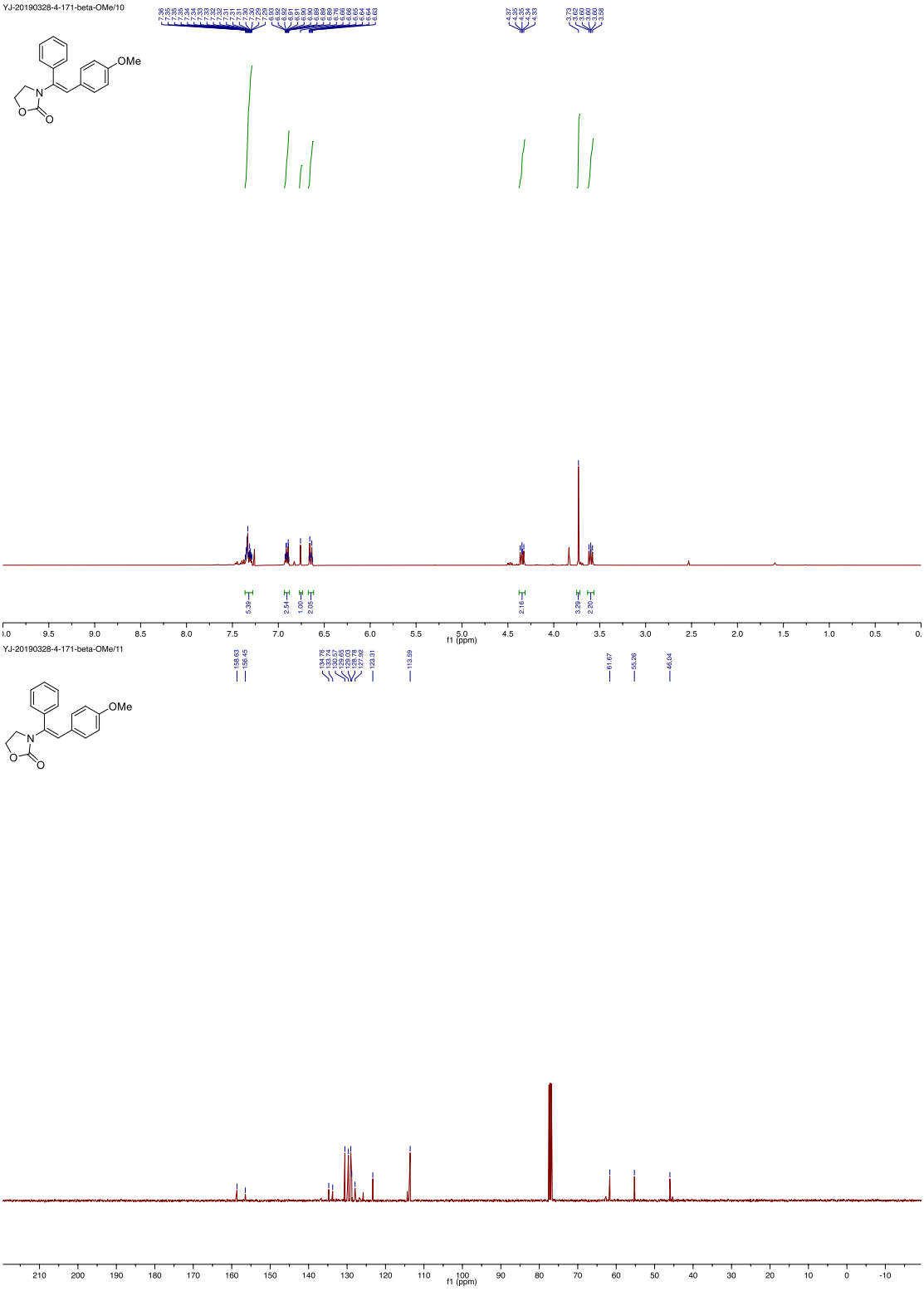
^{1}H and ^{13}C{1H} NMR spectra of **3m'**



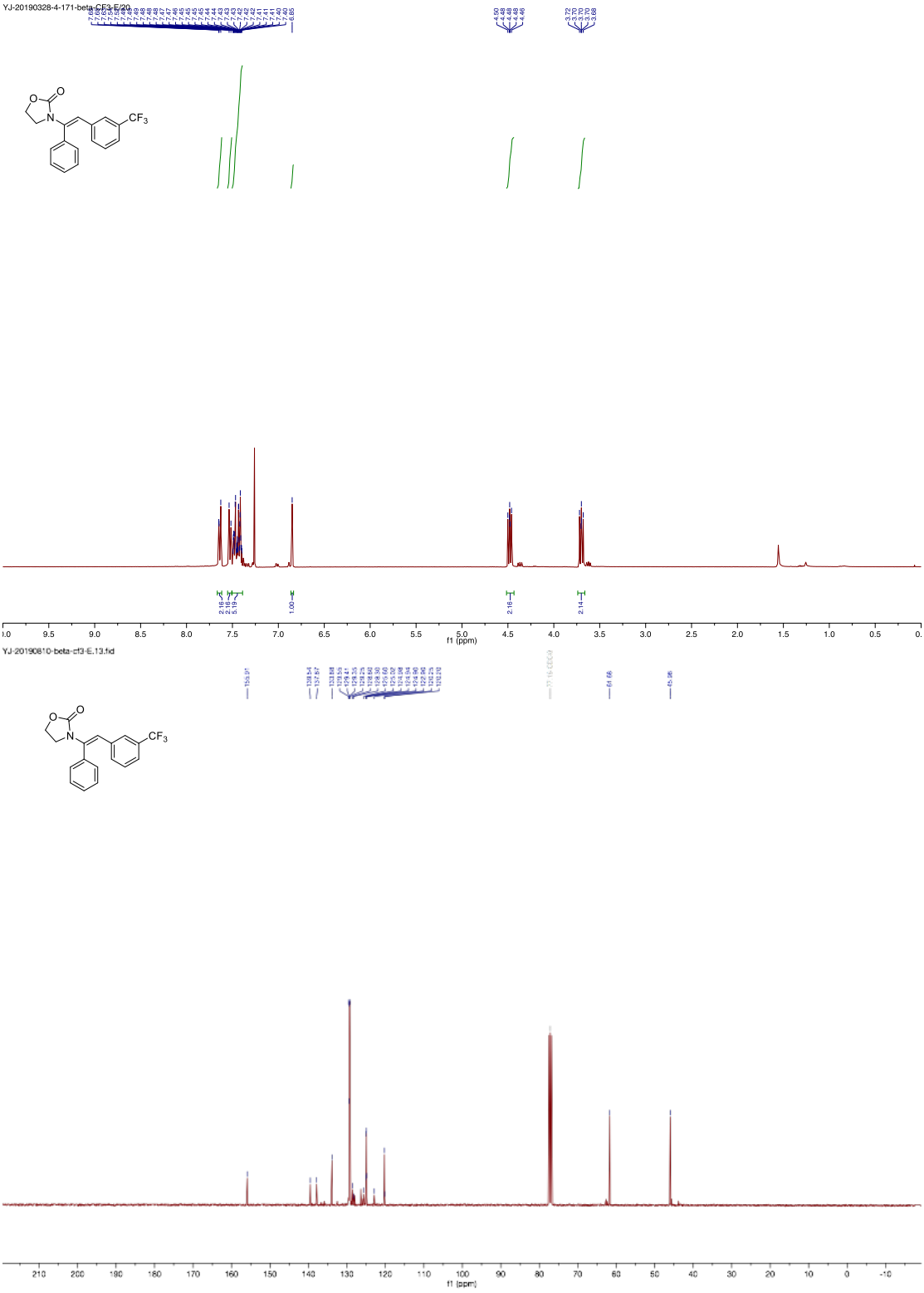
^{19}F NMR spectra of **3m'**



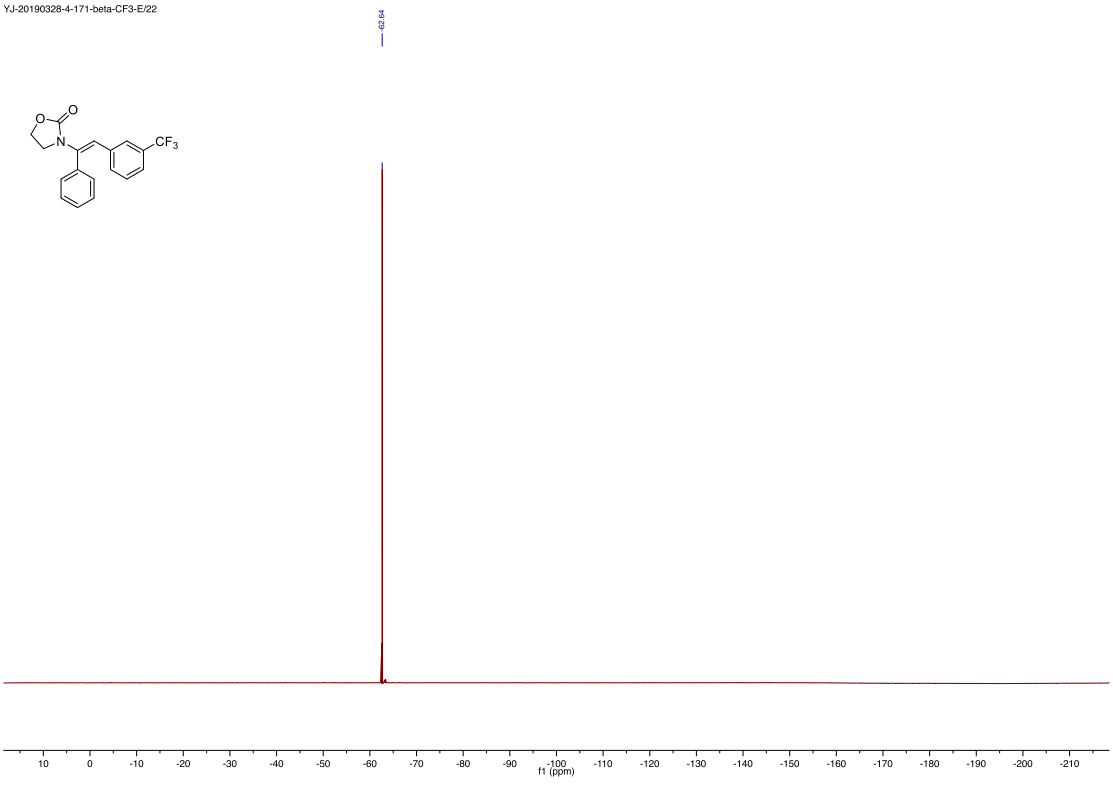
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3n'**



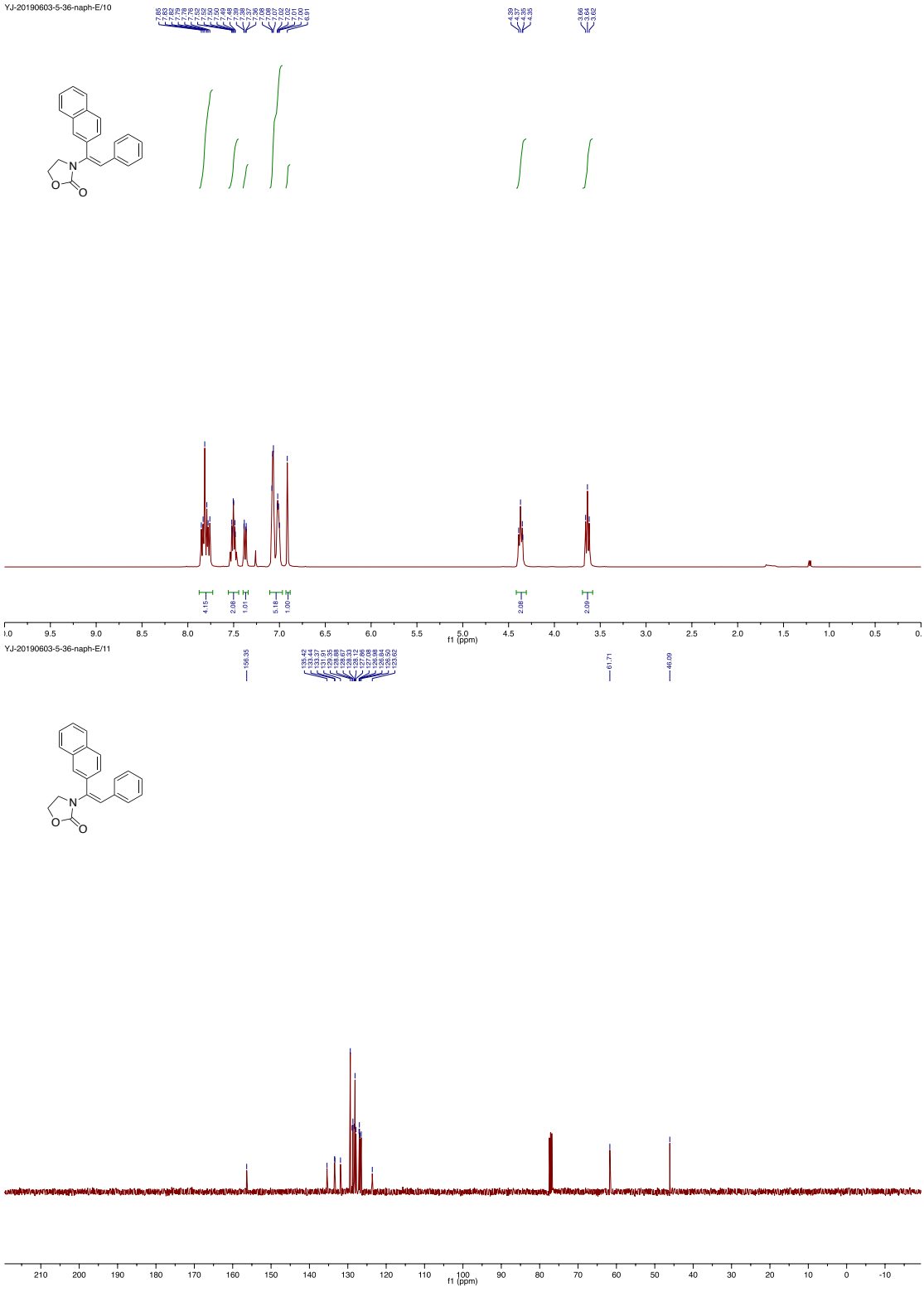
^{1}H and ^{13}C{1H} NMR spectra of **3o'**



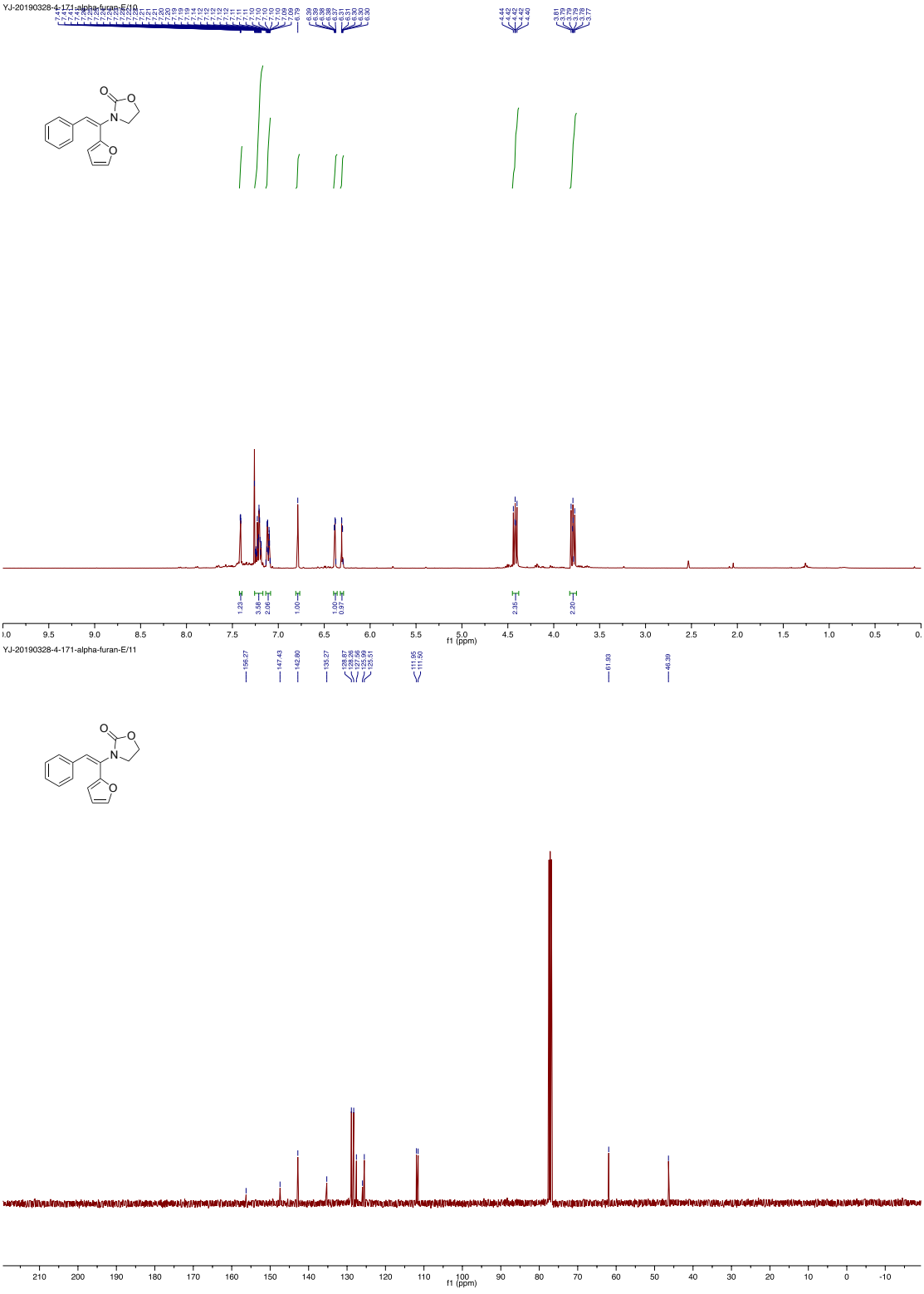
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3p'**



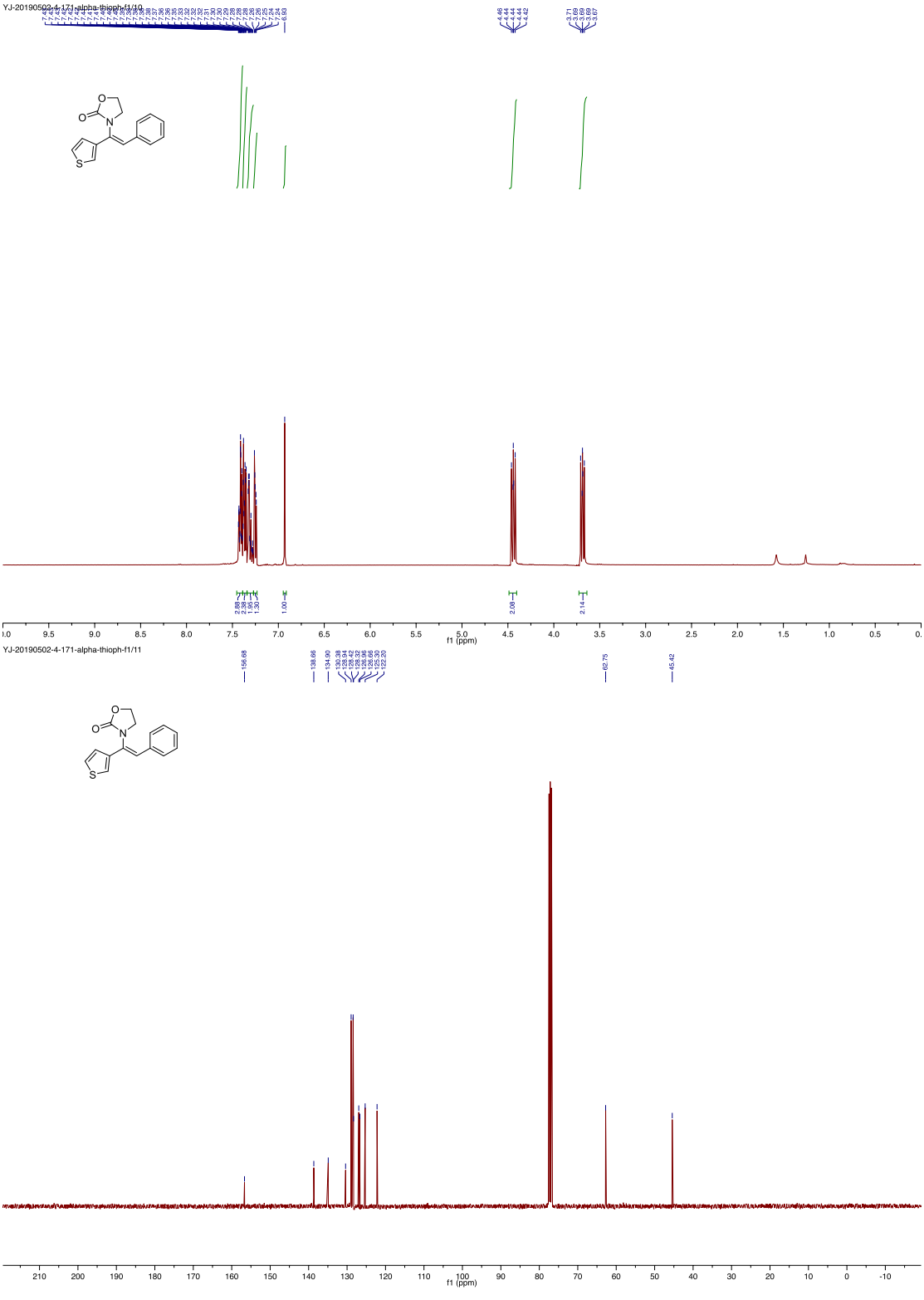
^{19}F NMR spectra of **3p'**



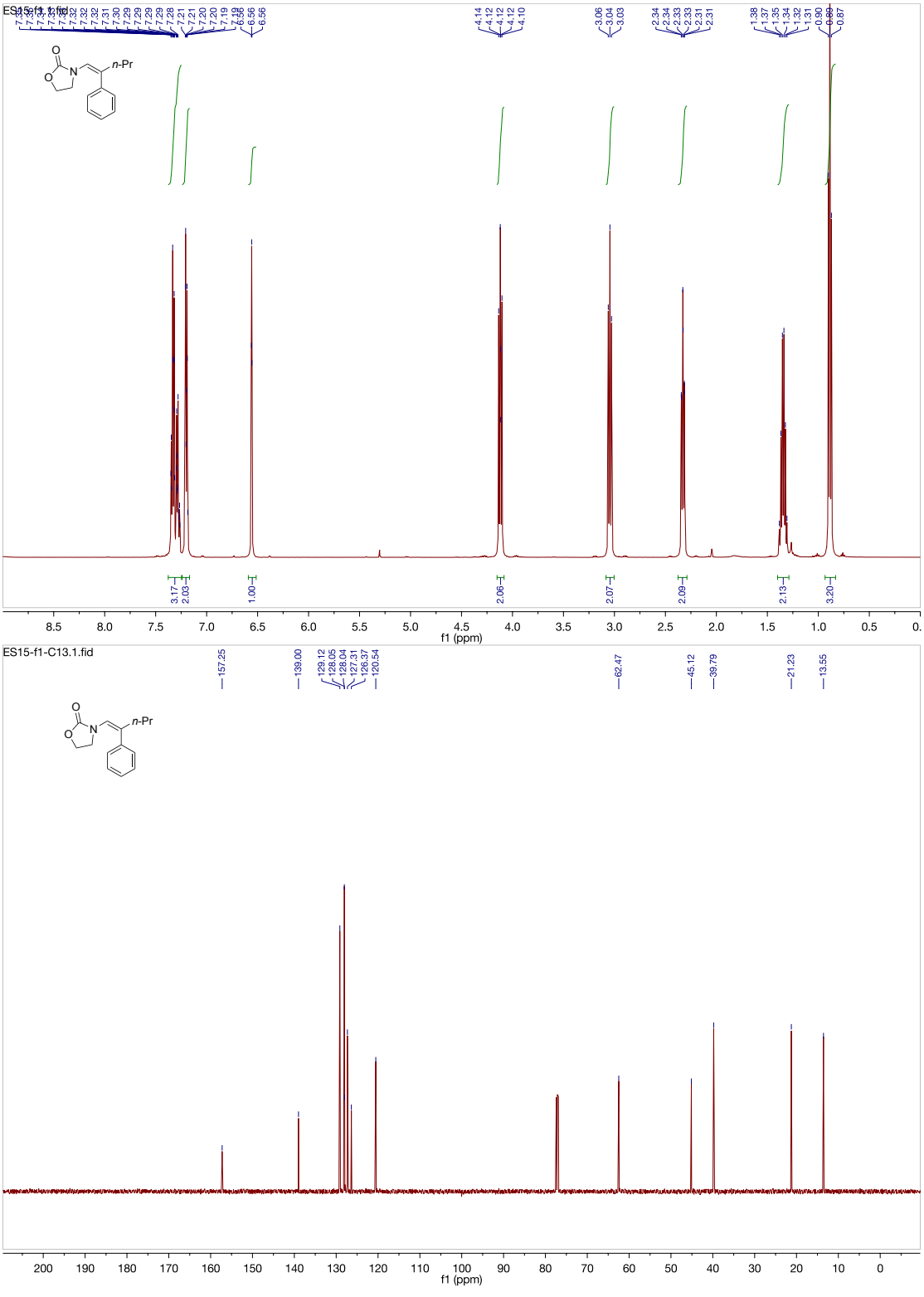
^{1}H and $^{13}C\{1H\}$ NMR spectra of **3q'**



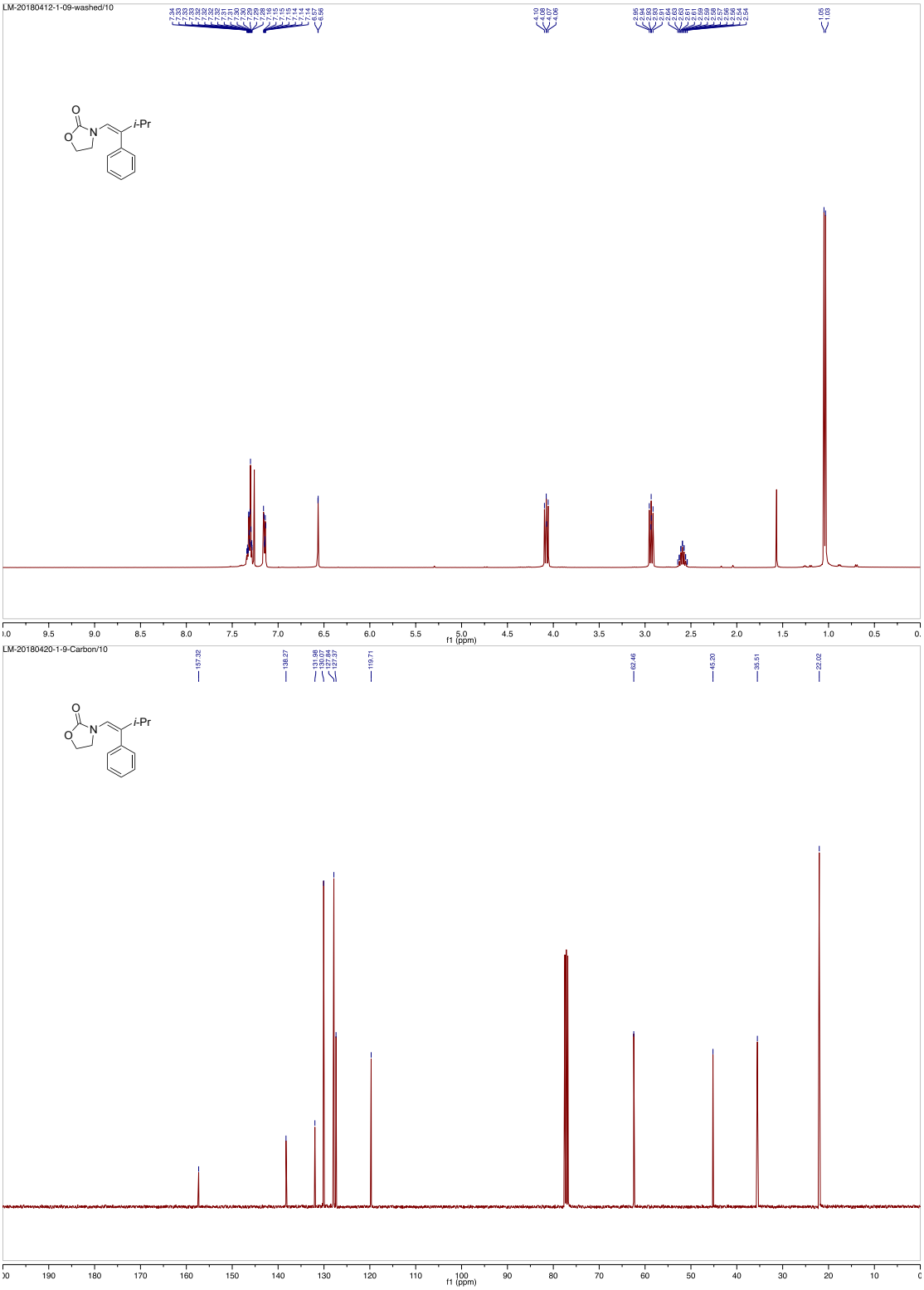
^{1}H and ^{13}C{1H} NMR spectra of **3r'**



^{1}H and ^{13}C{1H} NMR spectra of **3s'**



^{1}H and ^{13}C{1H} NMR spectra of **5a**



^{1}H and ^{13}C{1H} NMR spectra of **5c**

5. references

1. Yang, Y.; Wang, L.; Zhang, F.; Zhu, G., Preparation of (*Z*)-α,β-Disubstituted Enamides via Palladium-Catalyzed Addition of Boronic Acids to Ynamides. *J. Org. Chem.* **2014,** *79* (19), 9319-9324.

2. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

3. W. Koch, M. C. A. Holthausen, Chemist's Guide to Density Functional Theory. (2nd Ed), **2001**, Wiley-Vch Weinheim.