Supporting Information

A Three-component Iminolactonization Reaction *via* the Bifunctionalization of Olefins Using Molecular Iodine and Visible Light

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Contents

Figure S1. General reaction set up

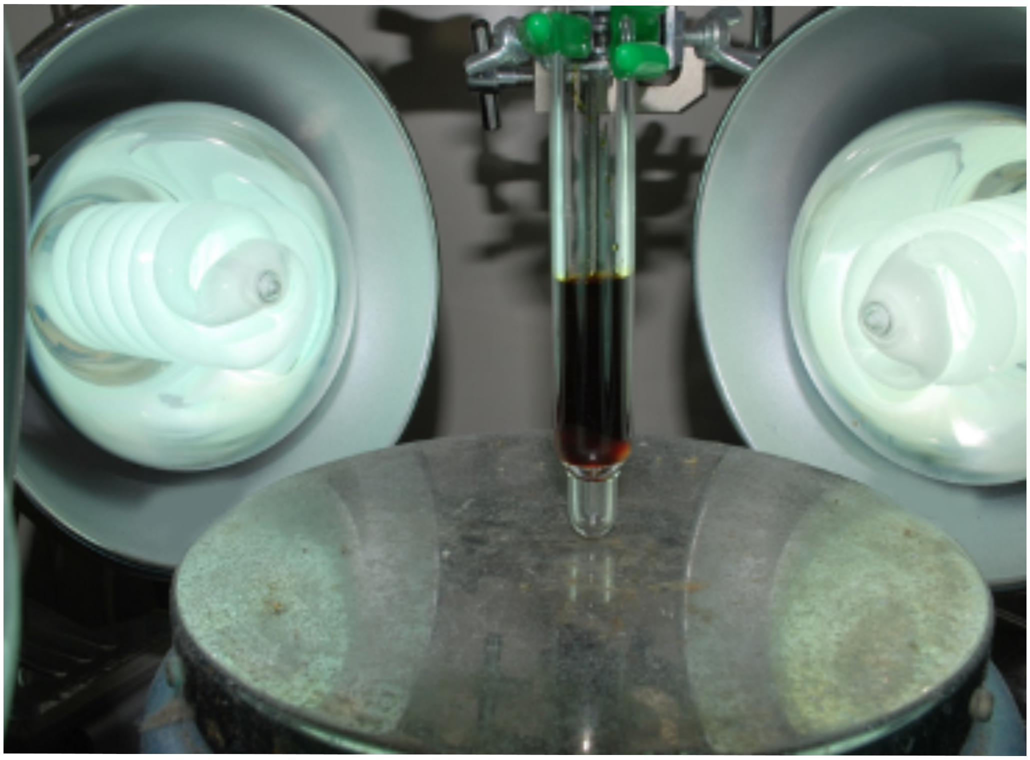


Figure S2. The wave length and spectral irradiance of fluorescent lamp (ERF25ED/22-SP-F)

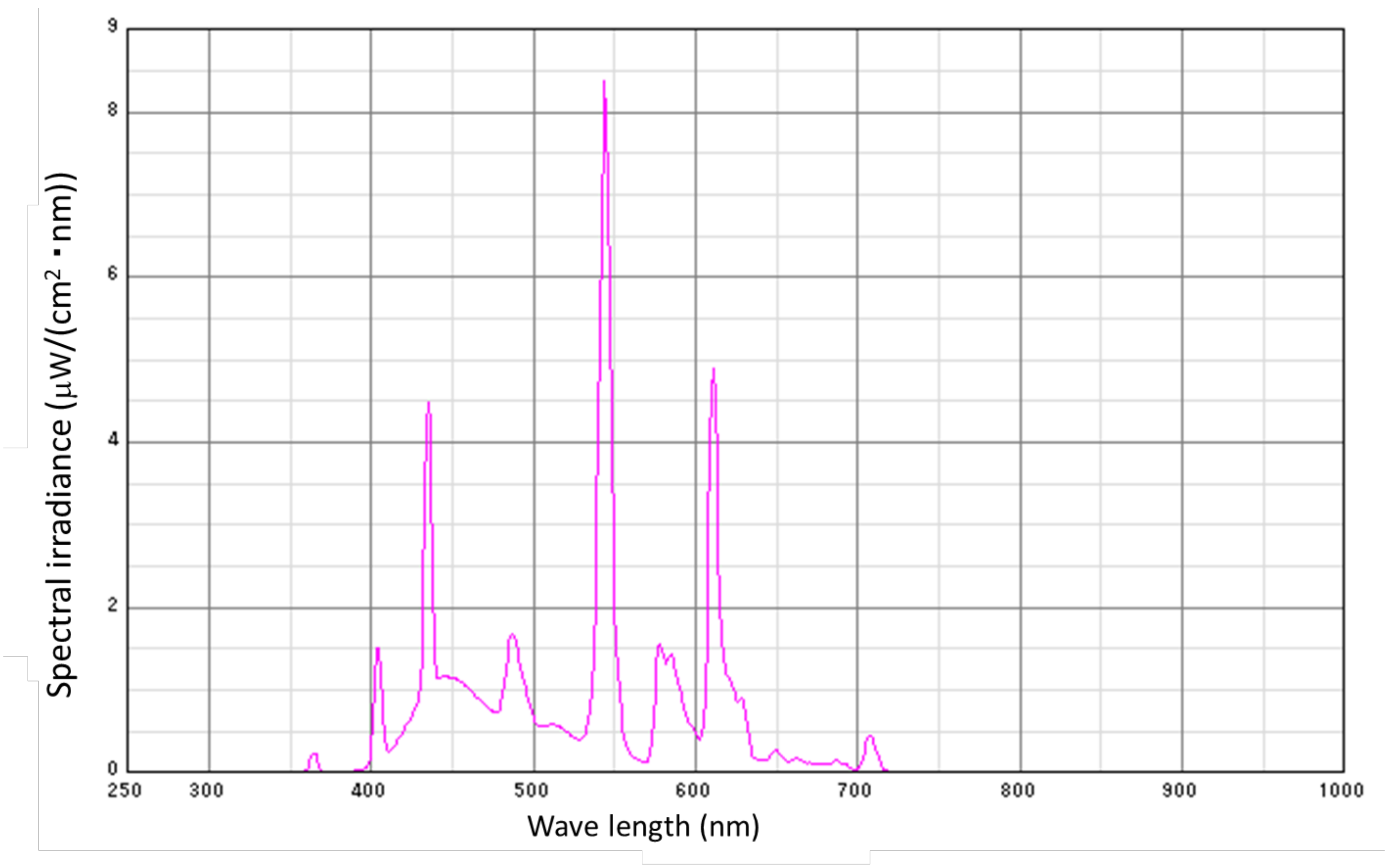
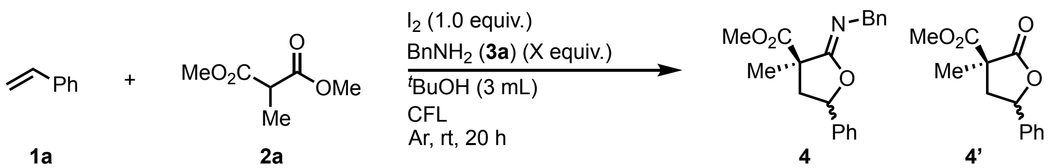


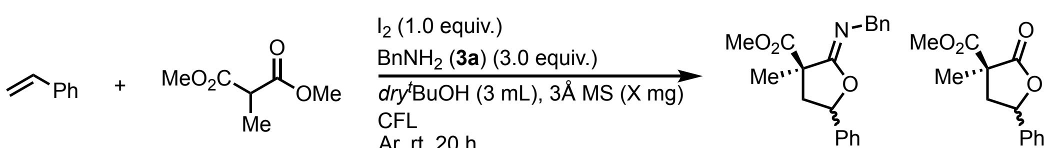
Table S1. Optimization of amount of amine



entry	$BnNH_2$ (equiv.)	**4** yield (%)[a]	*dr* (*trans* : *cis*)[b]	**4’** yield (%)[a]
1	1.0	10	80:20	12
2	1.5	30	67:33	11
3	2.0	34	80:20	6
4	2.5	37	83:17	4
5	**3.0**	**53**	**67:33**	**10**
6	3.5	50	77:23	5
7	4.0	55	68:32	7
8	4.5	41	74:26	4
9	5.0	30	60:40	2

[a] ^{1}H NMR yield. [b] Diasterememeric ratio were determined by ^{1}H NMR analysis of crude reaction mixture.

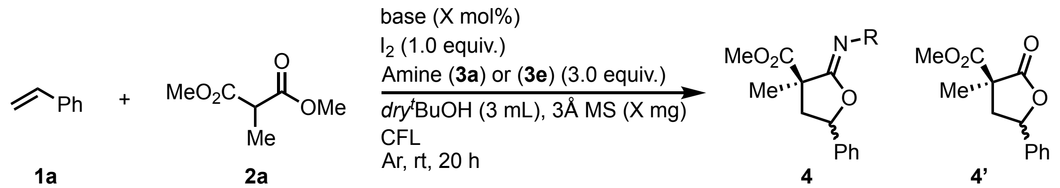
Table S2. Optimization of additives



entry	Molecular Sieves (mg)	**4** yield (%)[a]	*dr* (*trans* : *cis*)[b]	**4’** yield (%)[a]
1	3Å (30)	31	68:32	3
2	3Å (60)	55	74:26	21
3	**3Å (100)**	**70**[c]	**74:26**	**7**[c]
4	3Å (150)	67	78:22	8
5	3Å (200)	47	77:23	10

[a] 1H NMR yield. [b] Diasterememeric ratio were determined by 1H NMR analysis of crude reaction mixture. [c] Isolated yield.

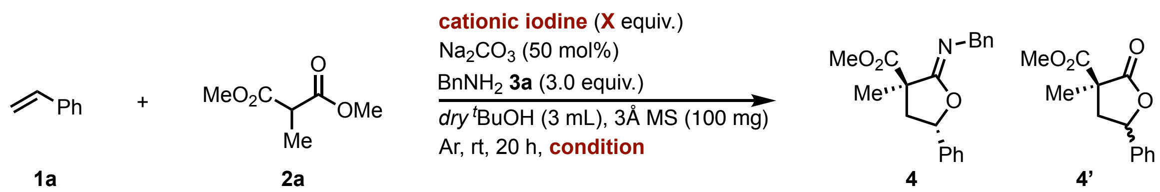
Table S3. Optimization of bases



entry	base (mol%)	**4** yield (%)[a]	*dr* (*trans* : *cis*)[b]	**4'** yield (%)[a]
1	Li_2CO_3 (100)	66	74:26	8
2	K_2CO_3 (100)	57	72:28	4
3	Na_2CO_3 (100)	75[c]	74:26	18[c]
4	Cs_2CO_3 (100)	69	78:22	8
5	none	70	74:26	5
6	Na_2CO_3 (10)	60	75:25	13
7	Na_2CO_3 (30)	76	72:28	trace
8	**Na_2CO_3 (50)**	**77**[c]	**75:25**	**6**[c]
9	Na_2CO_3 (120)	77	76:24	7
10[d]	none	78	74:26	7
10[d]	Na_2CO_3 (10)	74	73:27	4
12[d]	Na_2CO_3 (30)	72	79:21	21
13[d]	**Na_2CO_3 (50)**	**79**[c]	**73:27**	**4**
14[d]	Na_2CO_3 (100)	74	73:27	4

[a] 1H NMR yield. [b] Diasteremeric ratio were determined by 1H NMR analysis of crude reaction mixture. [c] Isolated yield. [d] Using 4-MeO Benzylamine (**3e**) instead of Benzylamine (**3a**).

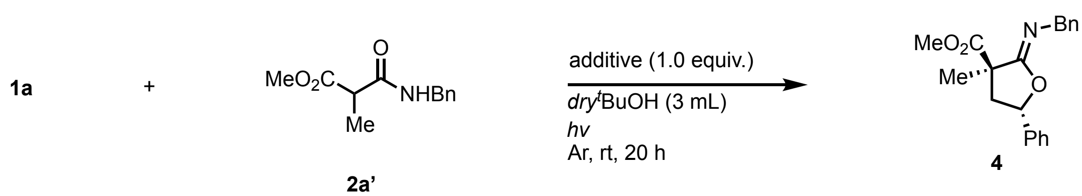
Table S4. Using cationic iodine instead of molecular iodine



entry	cationic iodine (X equiv.)	condition	**4** yield (%)[a]	*dr* (*trans* : *cis*)[b]	**4'** yield (%)[a]
1	NIS (1.0 equiv.)	h*v*	56	71:29	trace
2	NIS (1.0 equiv.)	dark	trace	-	-
3	NIS (2.0 equiv.)	h*v*	22	77:23	trace
4	NIS (2.0 equiv.)	dark	trace	-	-
5	$(DMAP)_2I^+BF_4^-$ (1.0 equiv.)	h*v*	41	75:25	7
6	$(DMAP)_2I^+BF_4^-$ (1.0 equiv.)	dark	n.r.	-	-
7	$(DMAP)_2I^+BF_4^-$ (2.0 equiv.)	h*v*	65	77:23	15
8	$(DMAP)_2I^+BF_4^-$ (2.0 equiv.)	dark	n.r.	-	-

[a] 1H NMR yield. [b] Diasteremeric ratio were determined by 1H NMR analysis of crude reaction mixture.

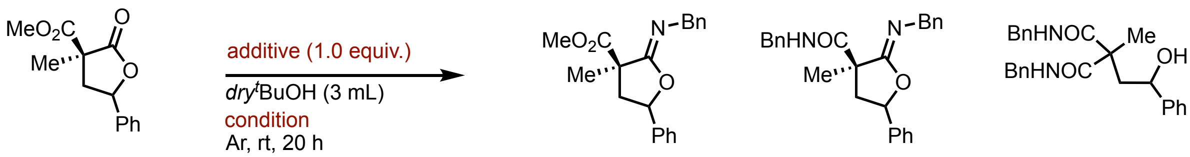
Table S5. Using amide substrate 2a' instead of malonate 2a



entry	additive (1.0 equiv.)	$BnNH_2$ (2.0 equiv.)	**4** yield (%)[a]	*dr* (*trans* : *cis*)[b]	**2a'** yield (%)[a]
1	Na_2CO_3	-	13	50:50	38
2	Na_2CO_3	added	23	50:50	-
3	$Ca(OH)_2$	-	40	60:40	6
4	NaOH	-	46	50:50	18
5	HI	-	n.d.	-	-

[a] 1H NMR yield. [b] Diasteremeric ratio were determined by 1H NMR analysis of crude reaction mixture.

Table S6. Transformation for lactone 4’ to iminolactone 4



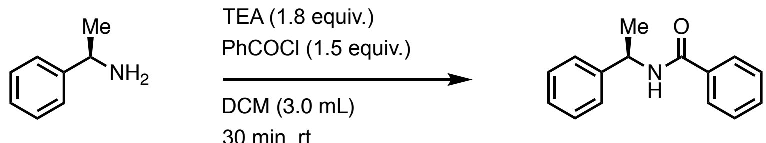
4’ **4** **4-I** **4-II**

entry	additive (1.0 equiv.)	condition	**4** yield (%)[a]	**4’** yield (%)[a]	**4-I** yield (%)[a]	**4-II** yield (%)[a]
1	I_2	hν	n.d.	61	-	-
2	-	hν	n.d.	59	-	-
3	I_2	heat, 60 ℃	n.d.	70	-	-
4	-	heat, 60 ℃	n.d.	55	-	-
5	Acetic acid	hν	n.d.	34	27	14
6	NH_4Cl	hν	n.d.	24	24	16
7	oxalic acid	hν	n.d.	44	21	9
8	H_3PO_4	hν	n.d.	44	21	9

[a] 1H NMR yield. [b] Diasteremeric ratio were determined by 1H NMR analysis of crude reaction mixture.

Scheme S1. Experiments on the isomerization of amine (D-(+)-3p)

Preparation of the sample A[16]

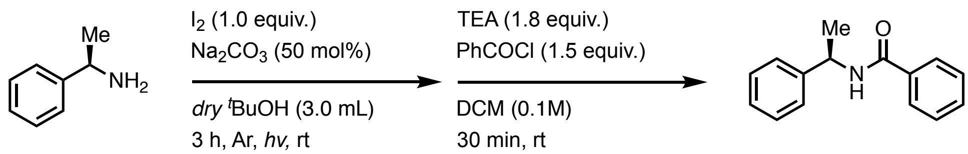


***D*-(+)-3p** **A**

The solution of *D*-(+)-1-Phenylethylamine (**3p**) (36.3 mg, 1.0 equiv., 0.3 mmol) in CH_2Cl_2 (3.0 mL) were added Et_3N (54.6 mg, 1.8 equiv., 0.54 mmol) and Benzoyl Chloride (63.2 mg, 1.5 equiv., 0.45 mmol). Upon stirring at room temperature for 30 min, the reaction mixture was purified by recrystallized in ^{n}hexane/$CHCl_3$ to give quant of **A** as white solid. The sample was subjected to determine the specific rotation in $CHCl_3$.

A: $[\alpha]^{20}_D$ = +28.7

Preparation of the sample B

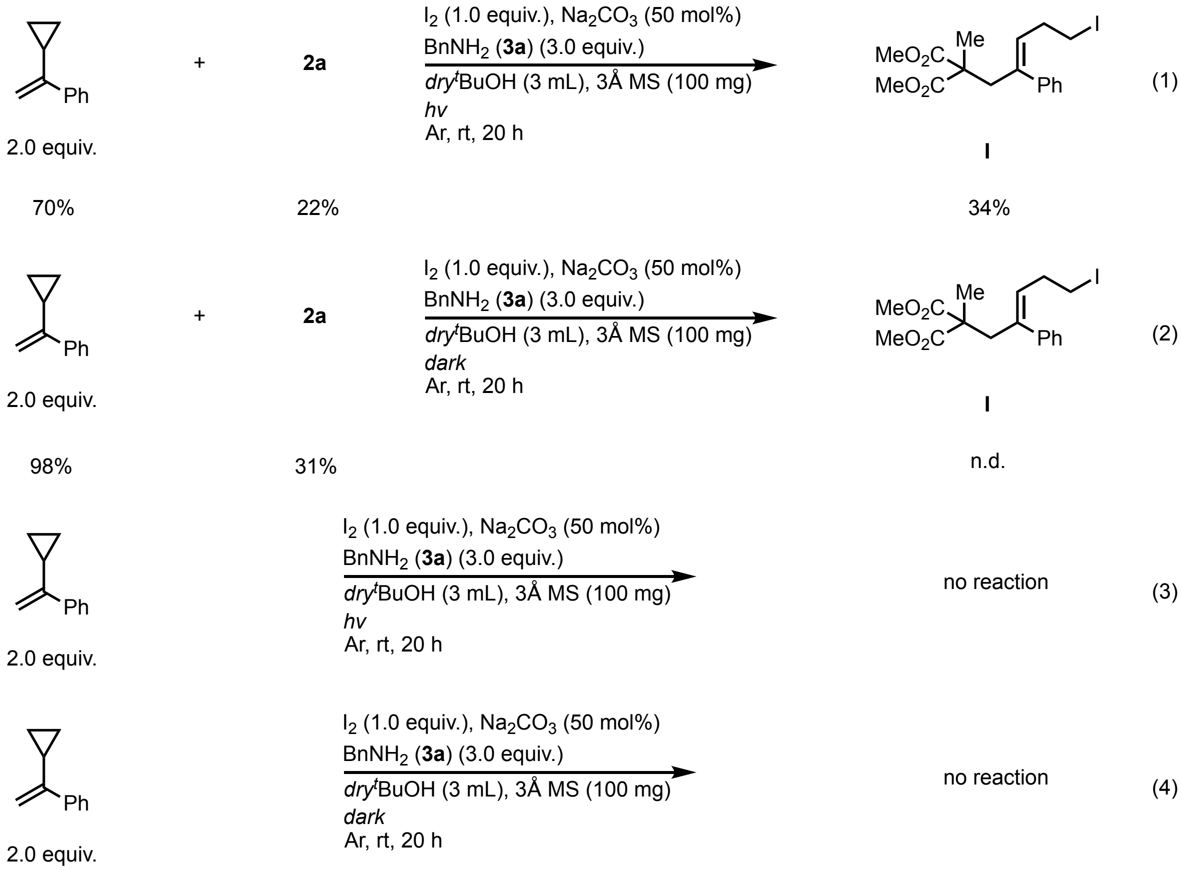


***D*-(+)-3p** **B**

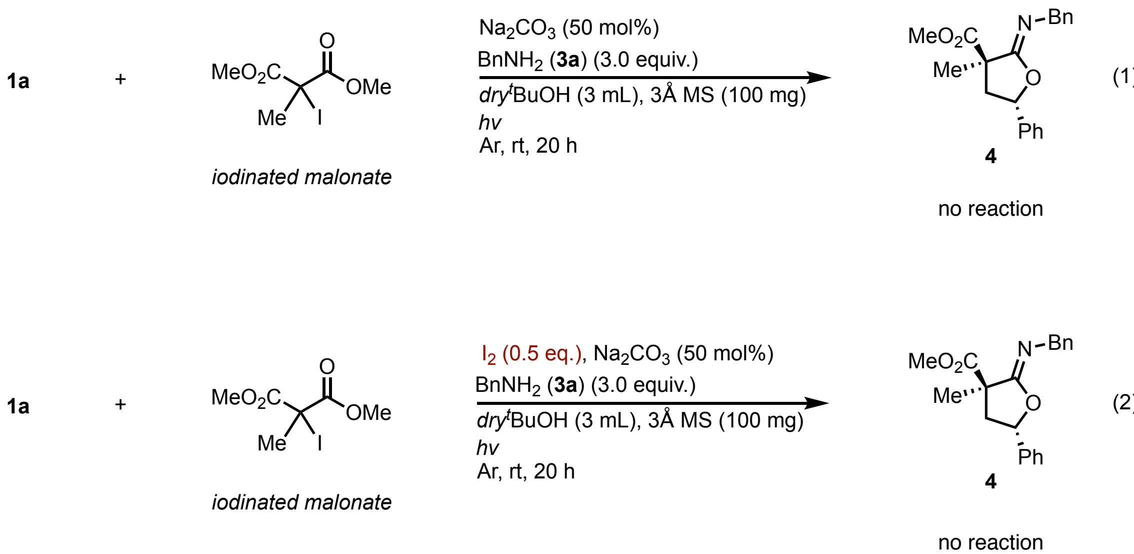
A Pyrex® test tube (16.5 cm × 1.5 cm) containing a mixture of *D*-(+)-1-Phenylethylamine (**3p**) (36.3 mg, 1.0 equiv., 0.3 mmol), I_2 (76 mg, 1.0 equiv., 0.30 mmol) and sodium carbonate (15.9 mg, 50 mol%, 0.15 mmol) in *dry*^{t}Butylalcohol (3.0 mL) was degassed *via* FPT cycling for three times and backfilled with Ar. The resulting solution was stirred at ambient temperature for 3 h, and concentrated *in vacuo*. Dissolved the reaction crude in CH_2Cl_2 (3.0 mL) were added Et_3N (54.6 mg, 1.8 equiv., 0.54 mmol) and Benzoyl Chloride (63.2 mg, 1.5 equiv., 0.45 mmol). Upon stirring at room temperature for 30 min, the reaction mixture was purified by recrystallized in ^{n}hexane/$CHCl_3$ to give quant of **A** as white solid. The sample was subjected to determine the specific rotation in $CHCl_3$.

B: $[\alpha]^{20}_D$ = +22.0

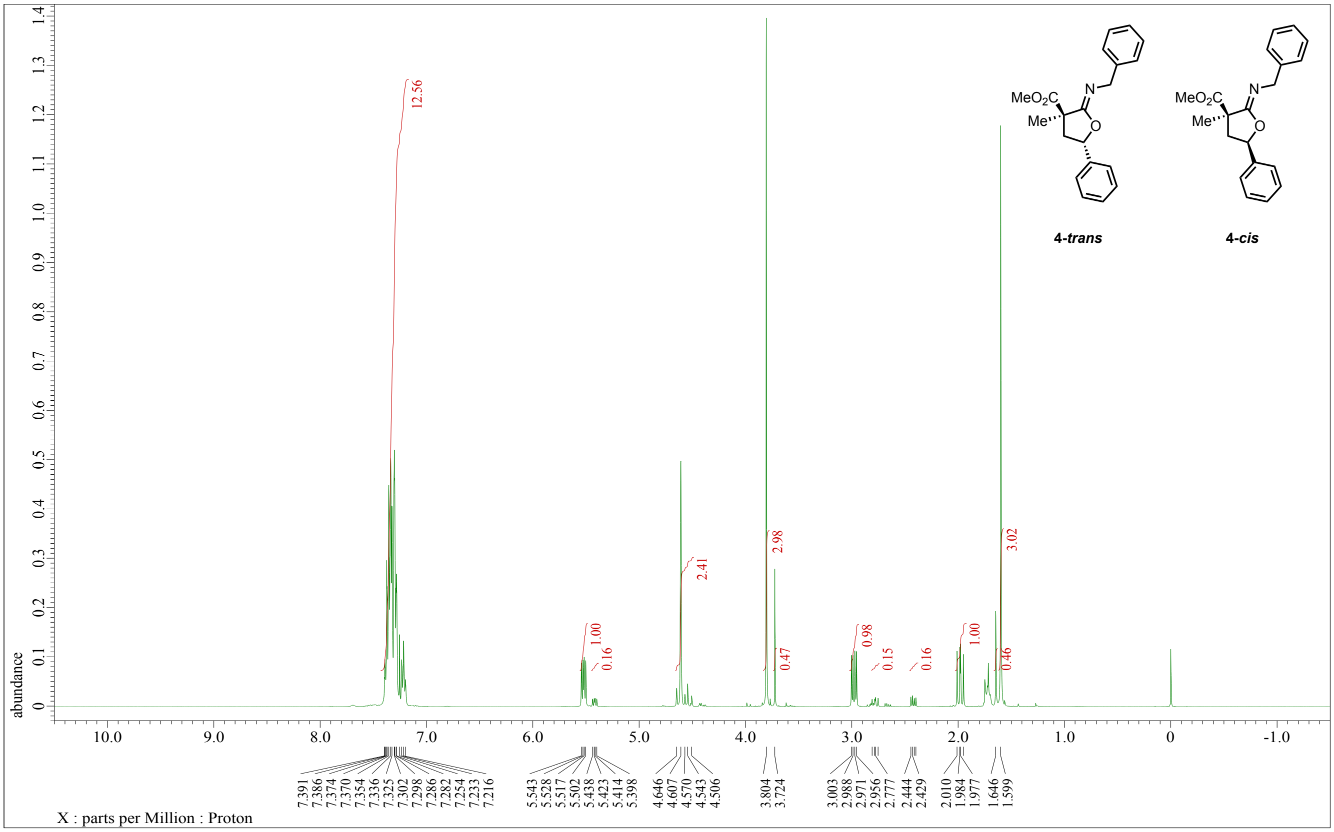
Scheme S2. Experiments of radical clock reaction

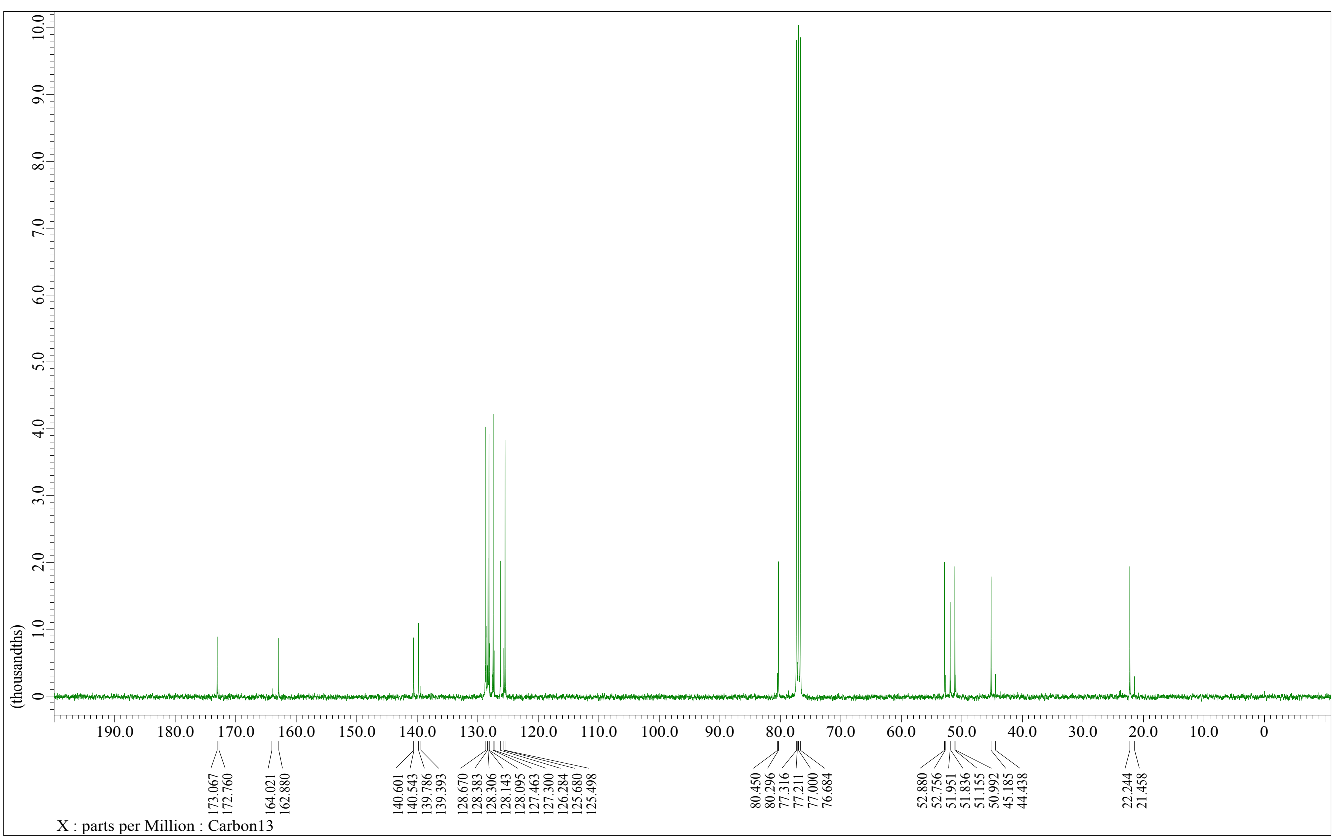


Scheme S3. Reaction of iodinated malonate to elucidate intermediate

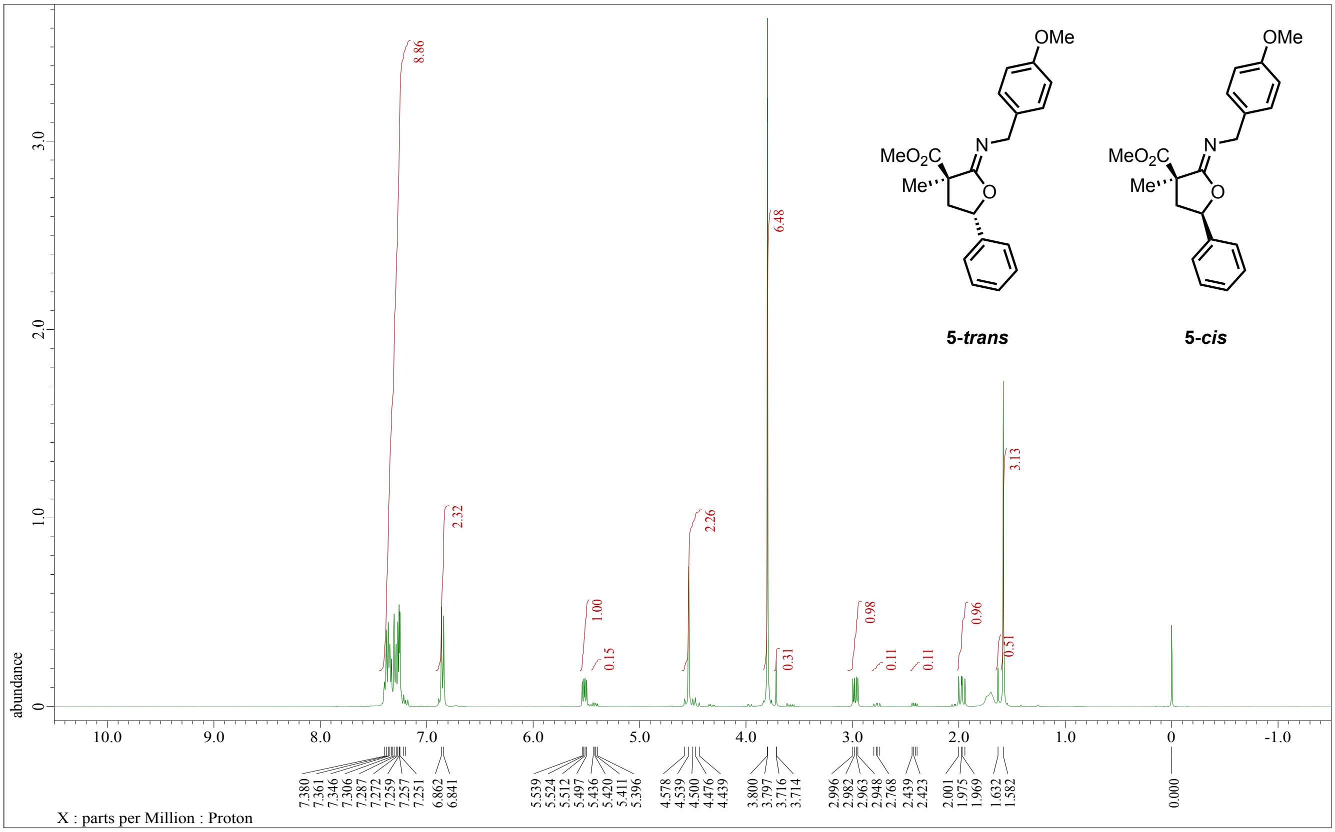


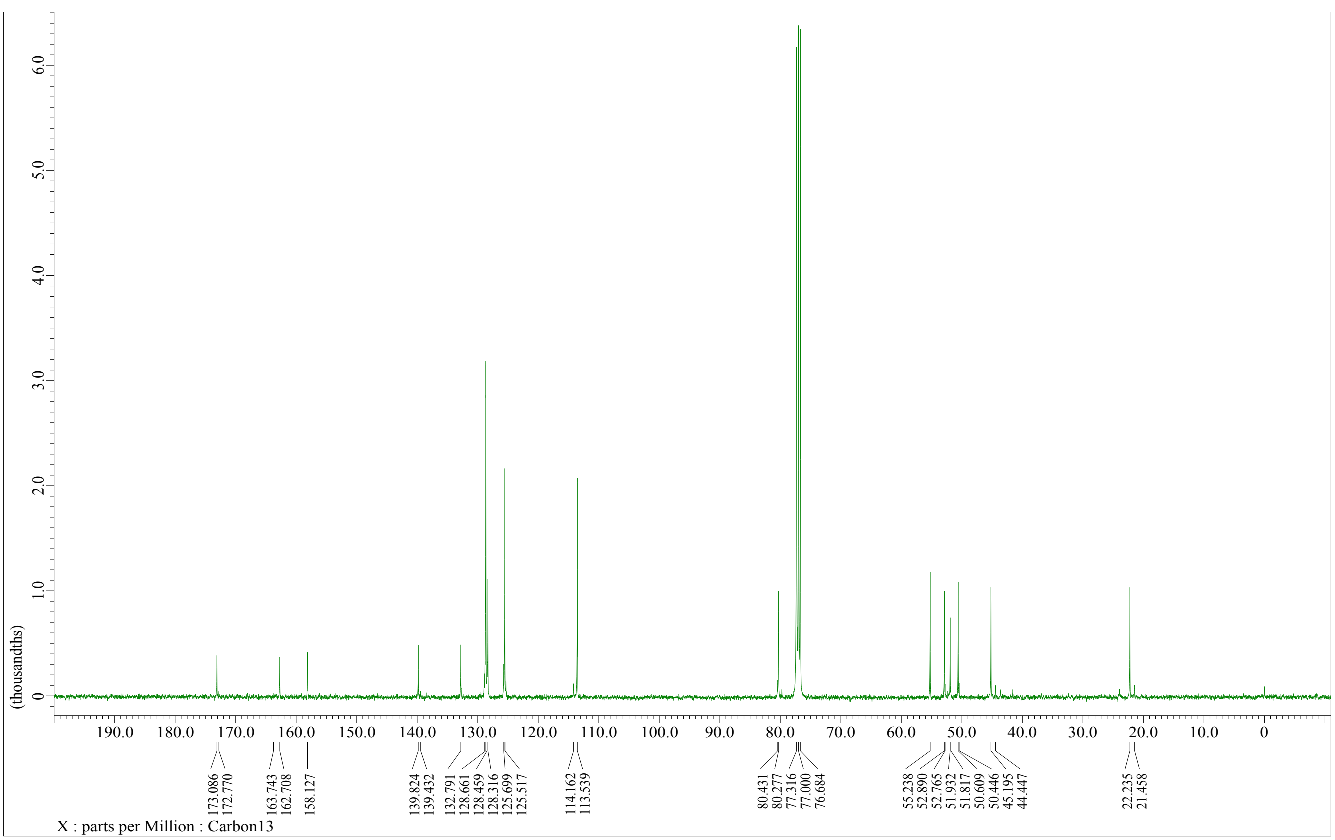
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **4**_*trans, cis*-mixture



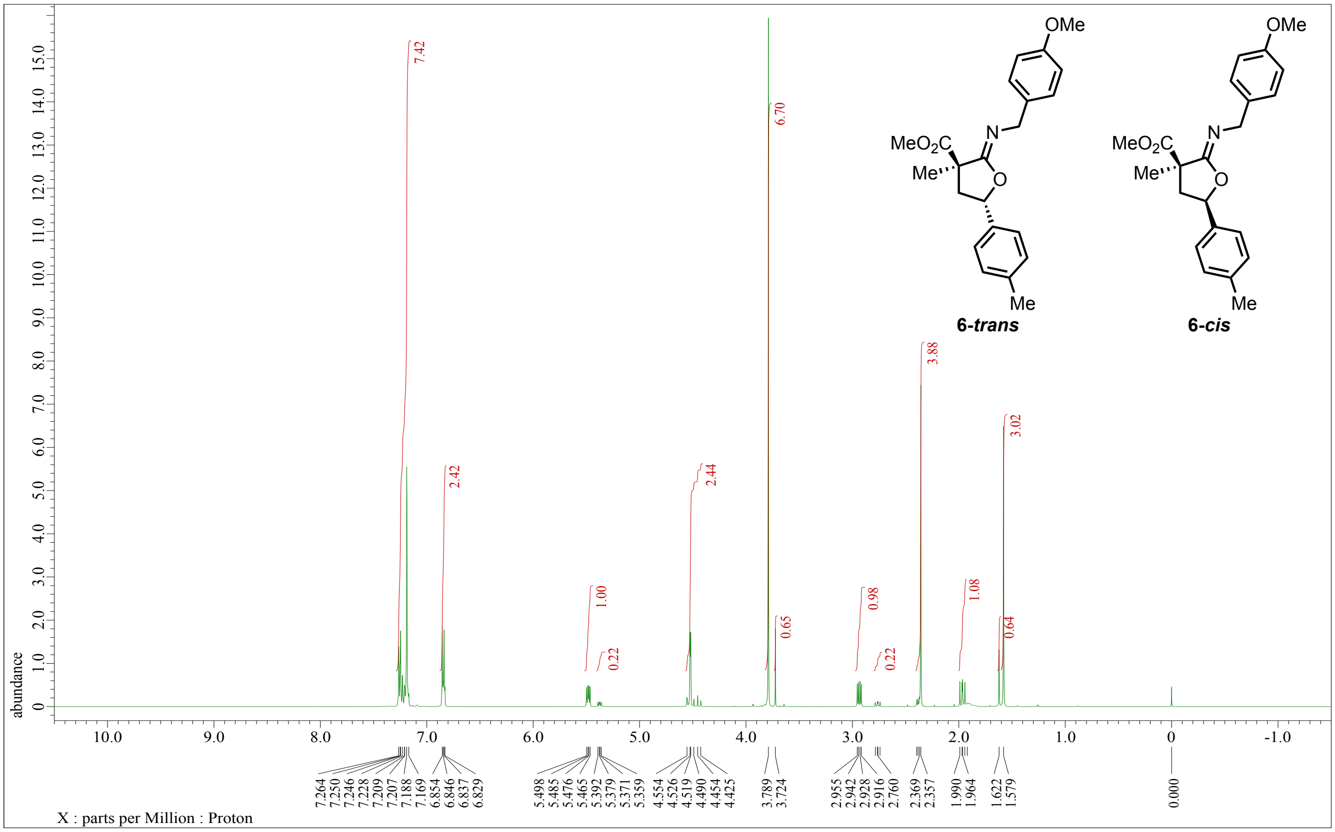


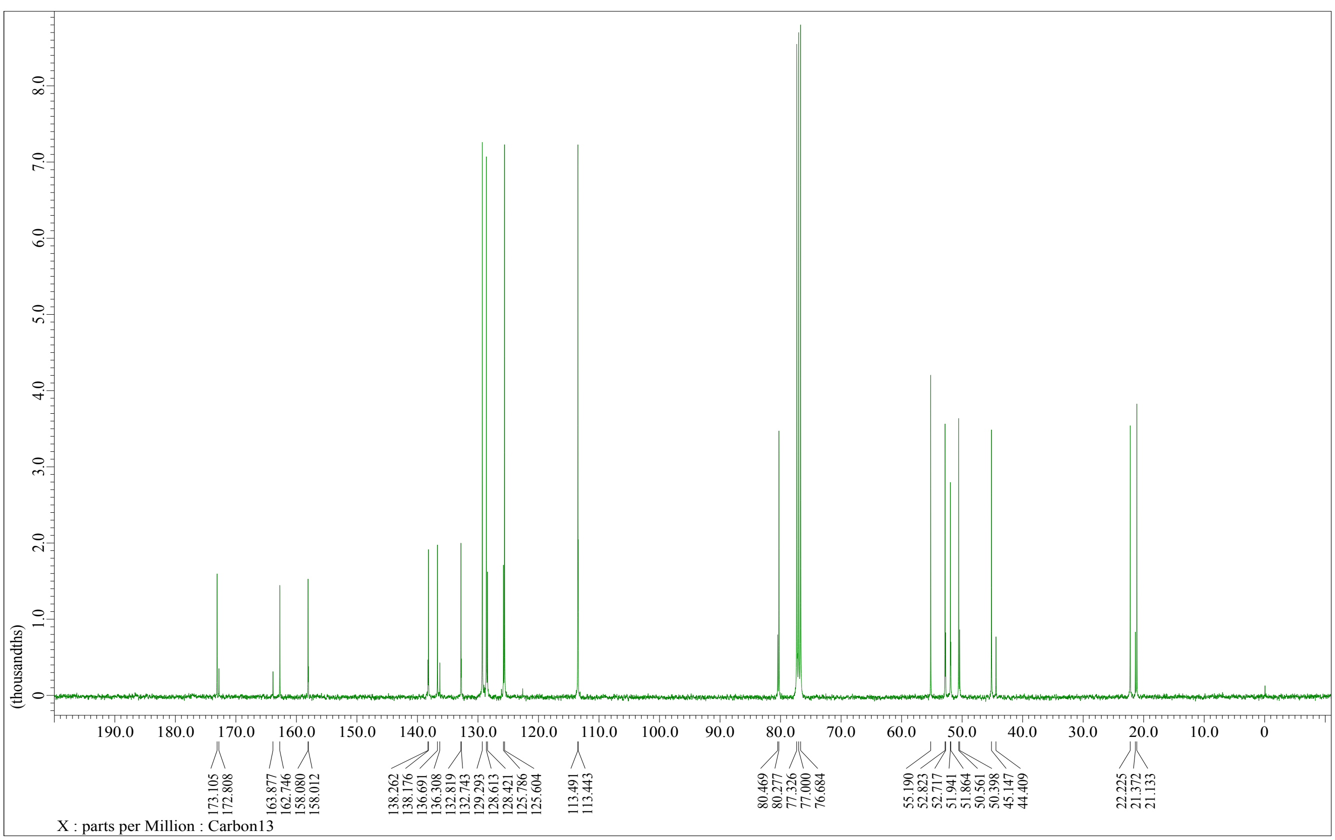
^1H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **5**_*trans, cis*-mixture



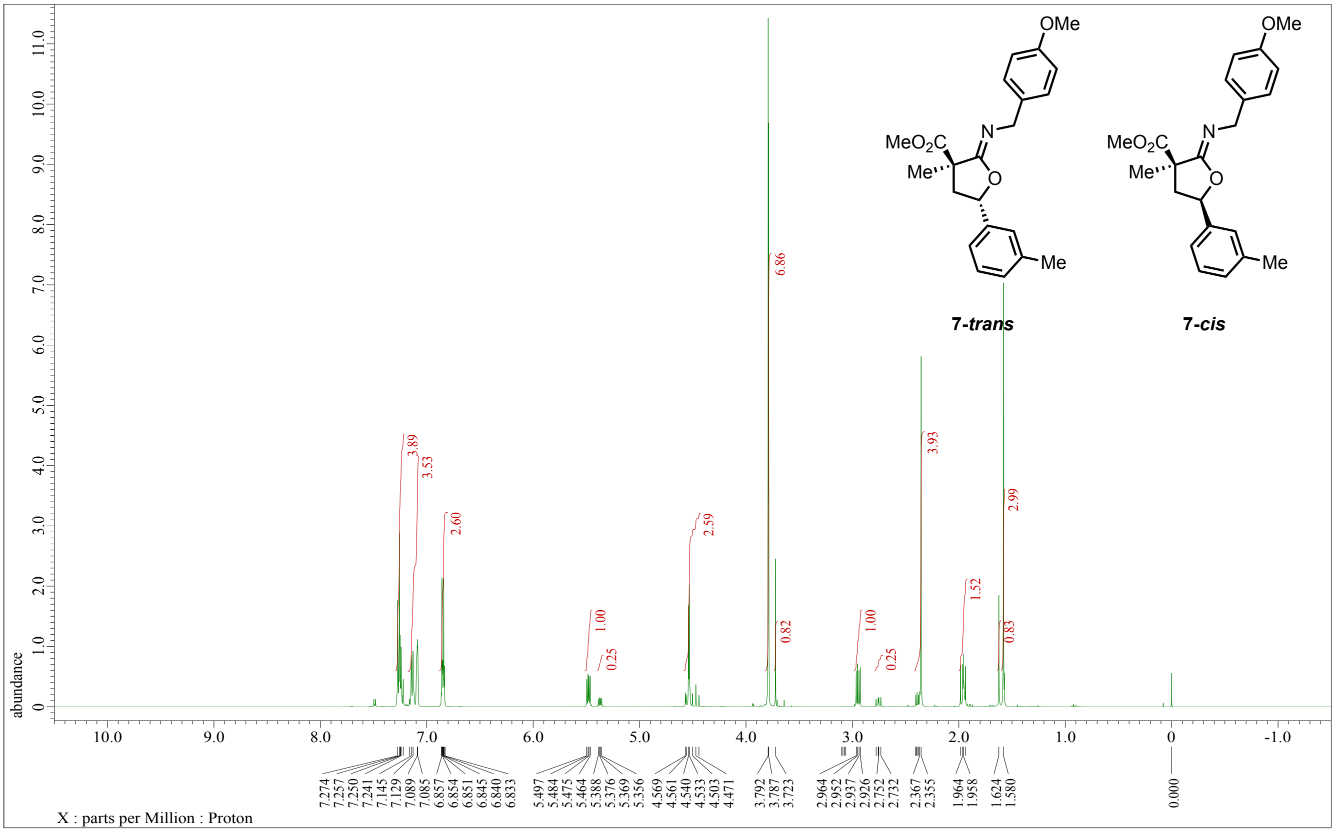


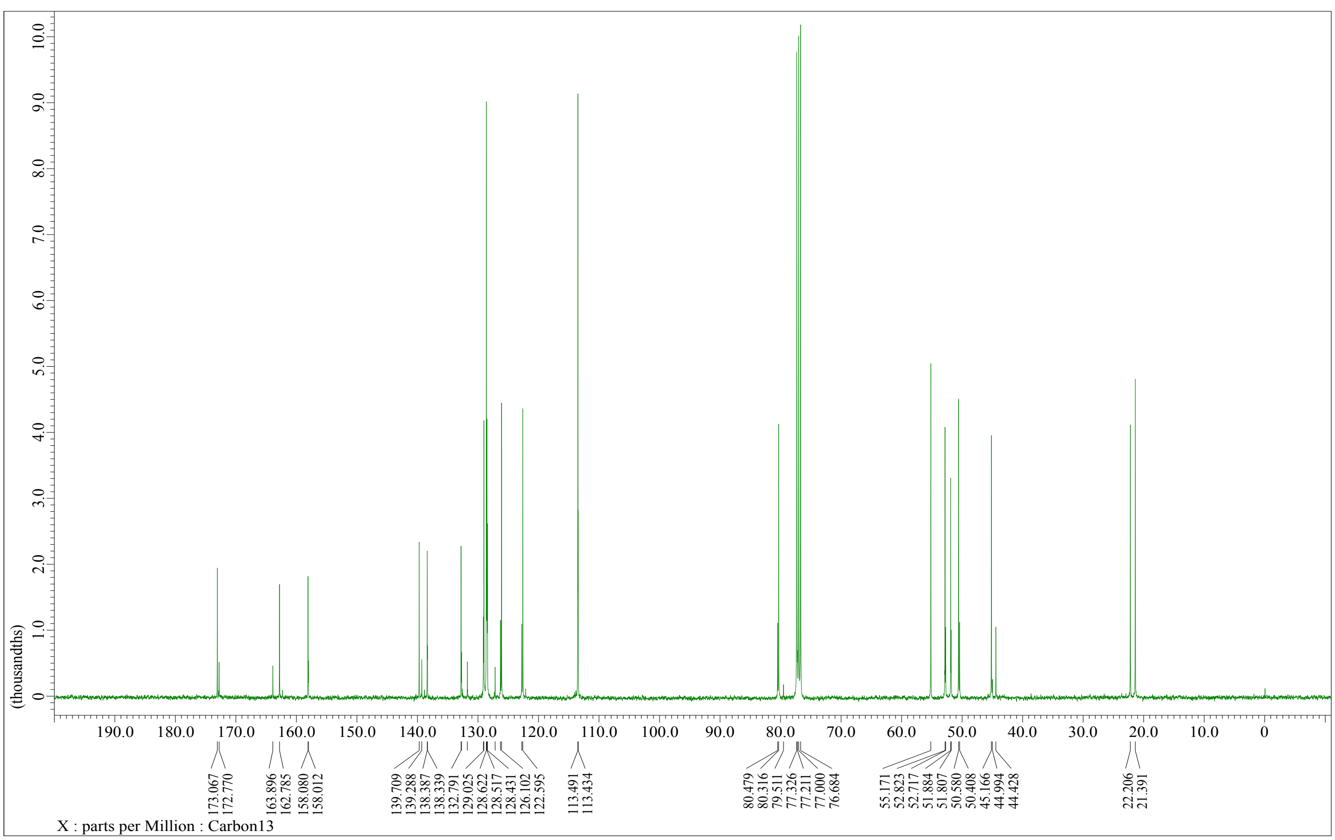
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **6**_*trans, cis*-mixture



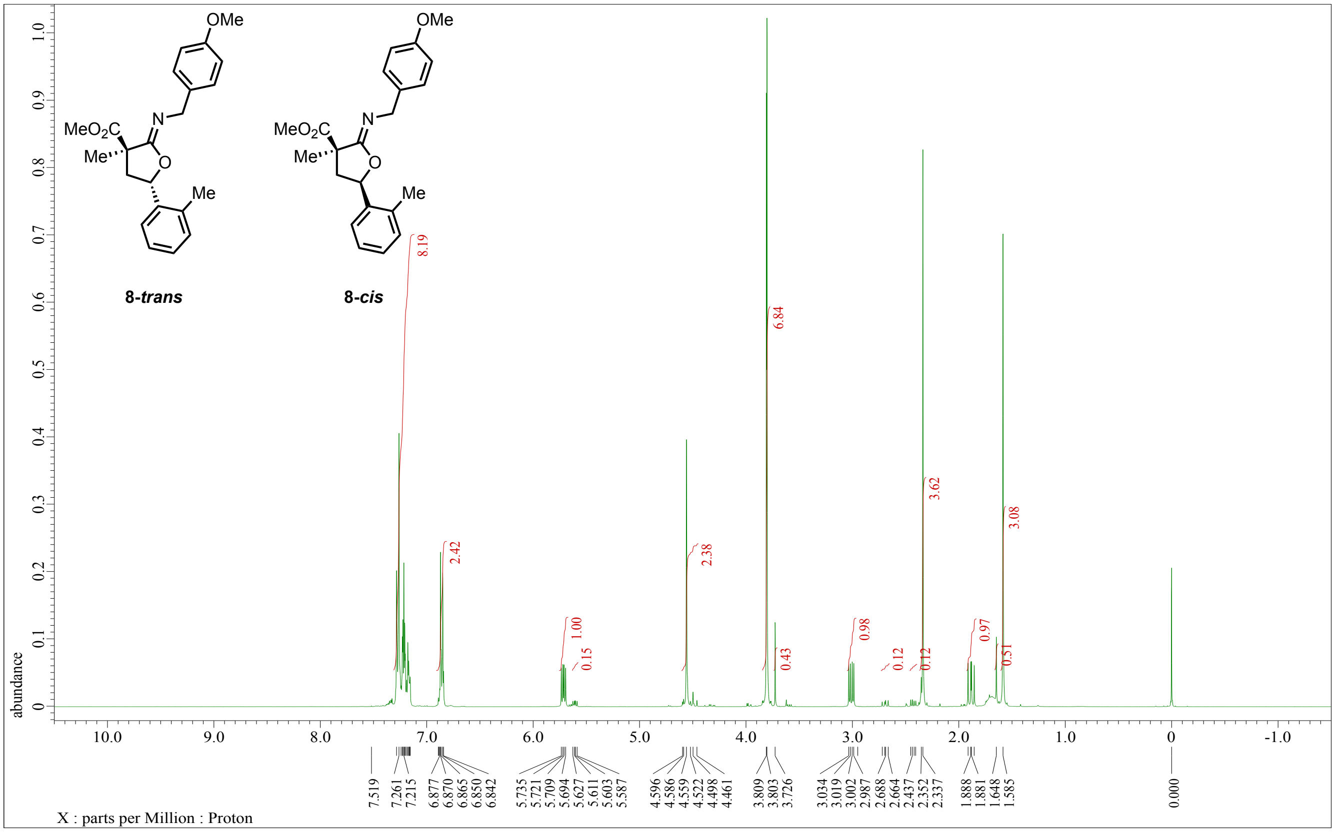


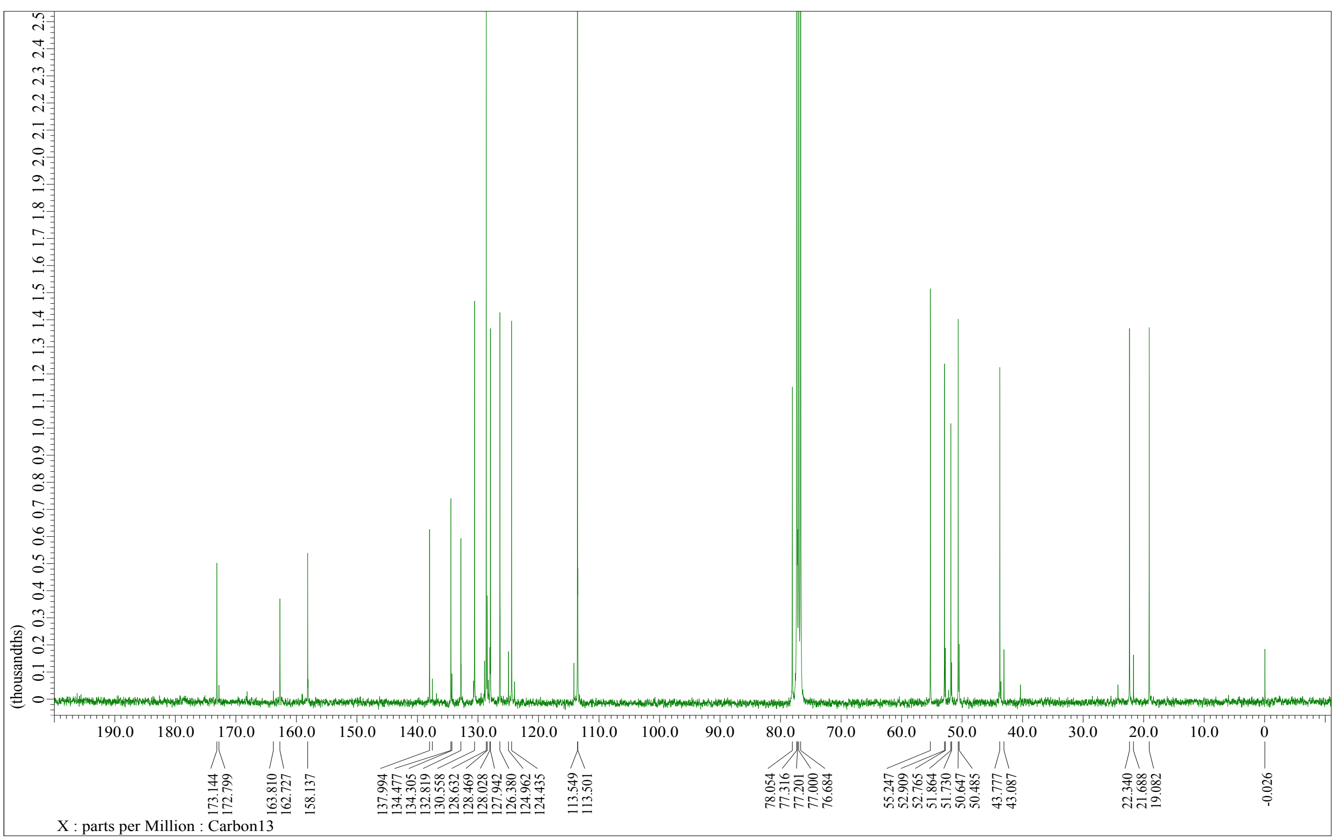
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **7**_*trans, cis*-mixture



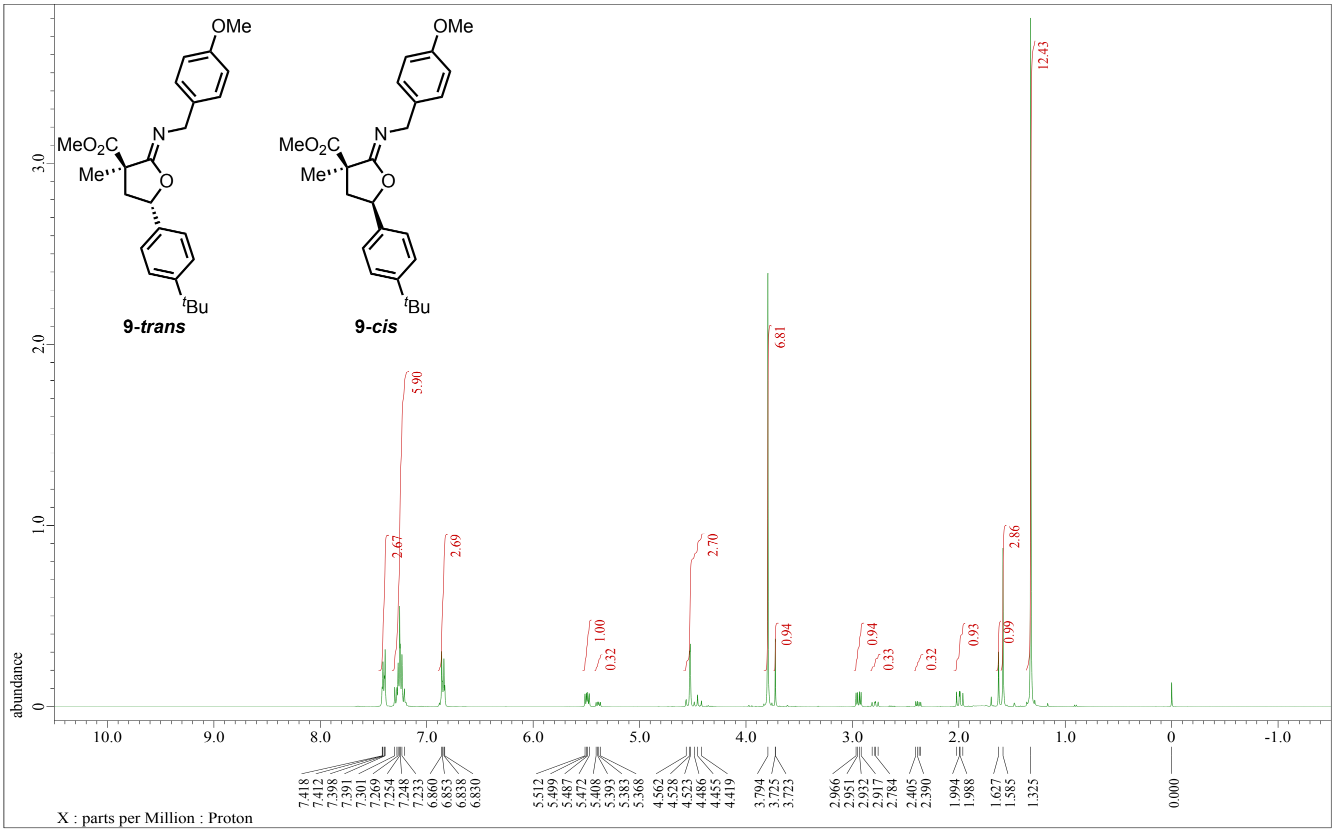


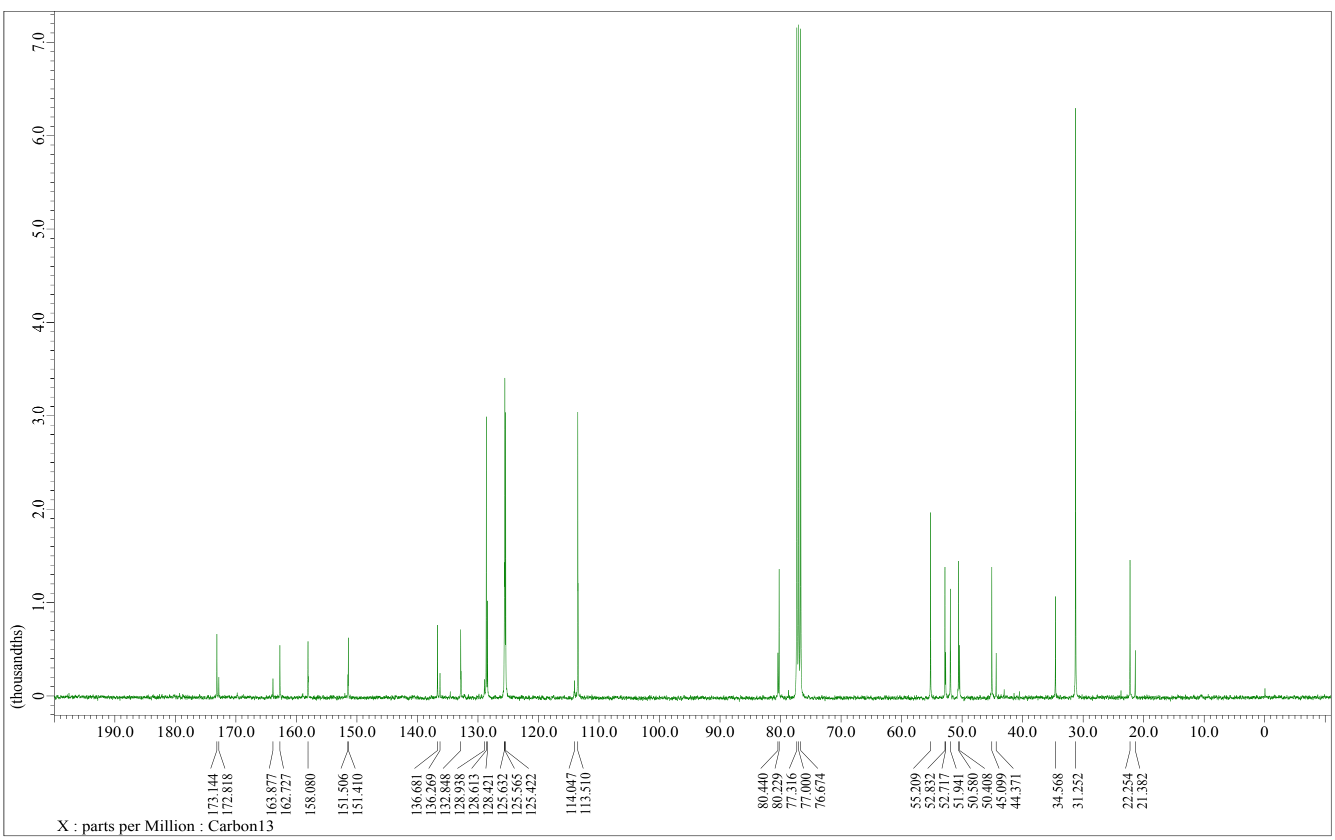
^1H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **8**_*trans, cis*-mixture



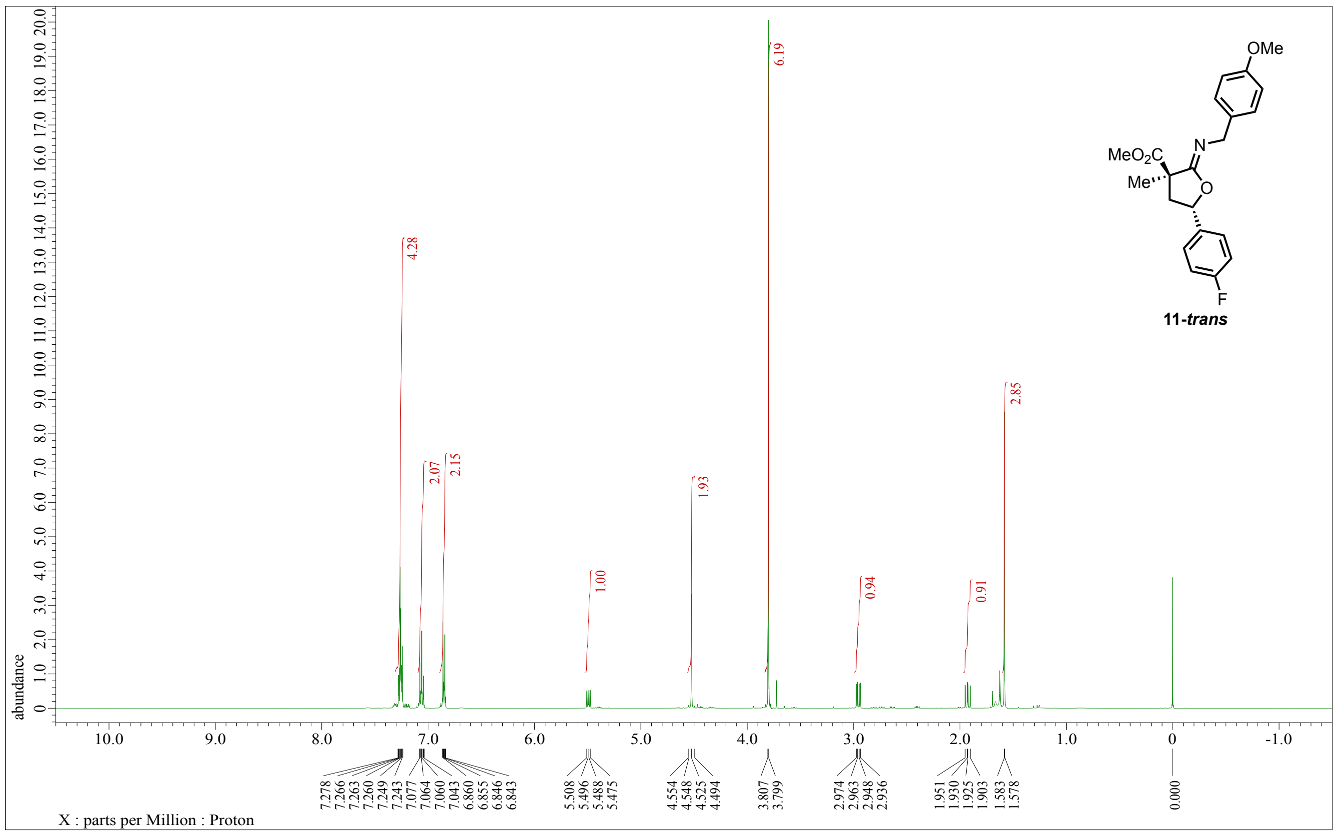


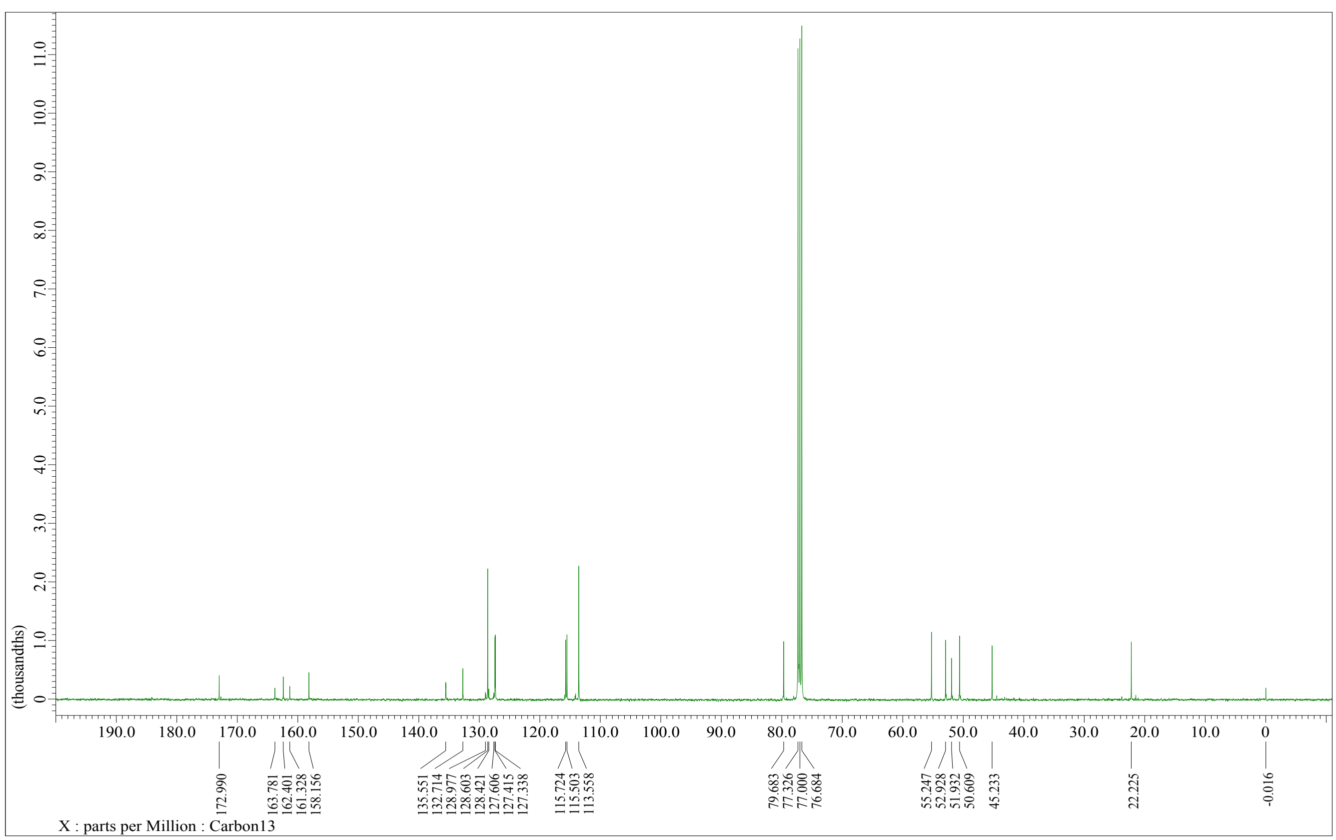
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **9**_*trans, cis*-mixture

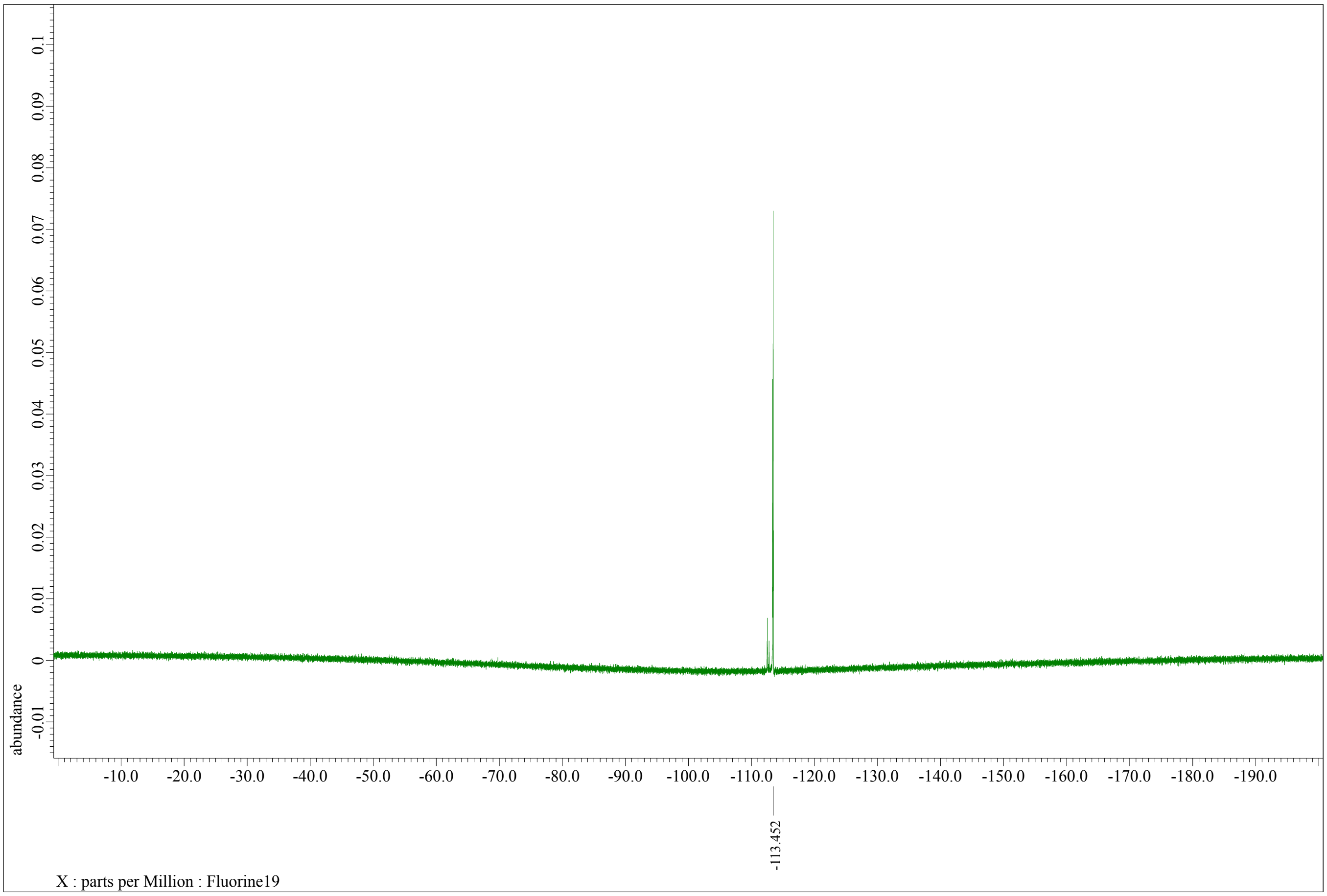




[1]H NMR ($CDCl_3$, 500 MHz), [13]C{[1]H} NMR ($CDCl_3$, 125 MHz) and [19]F NMR ($CDCl_3$, 470 MHz) spectra of **11**_*trans*







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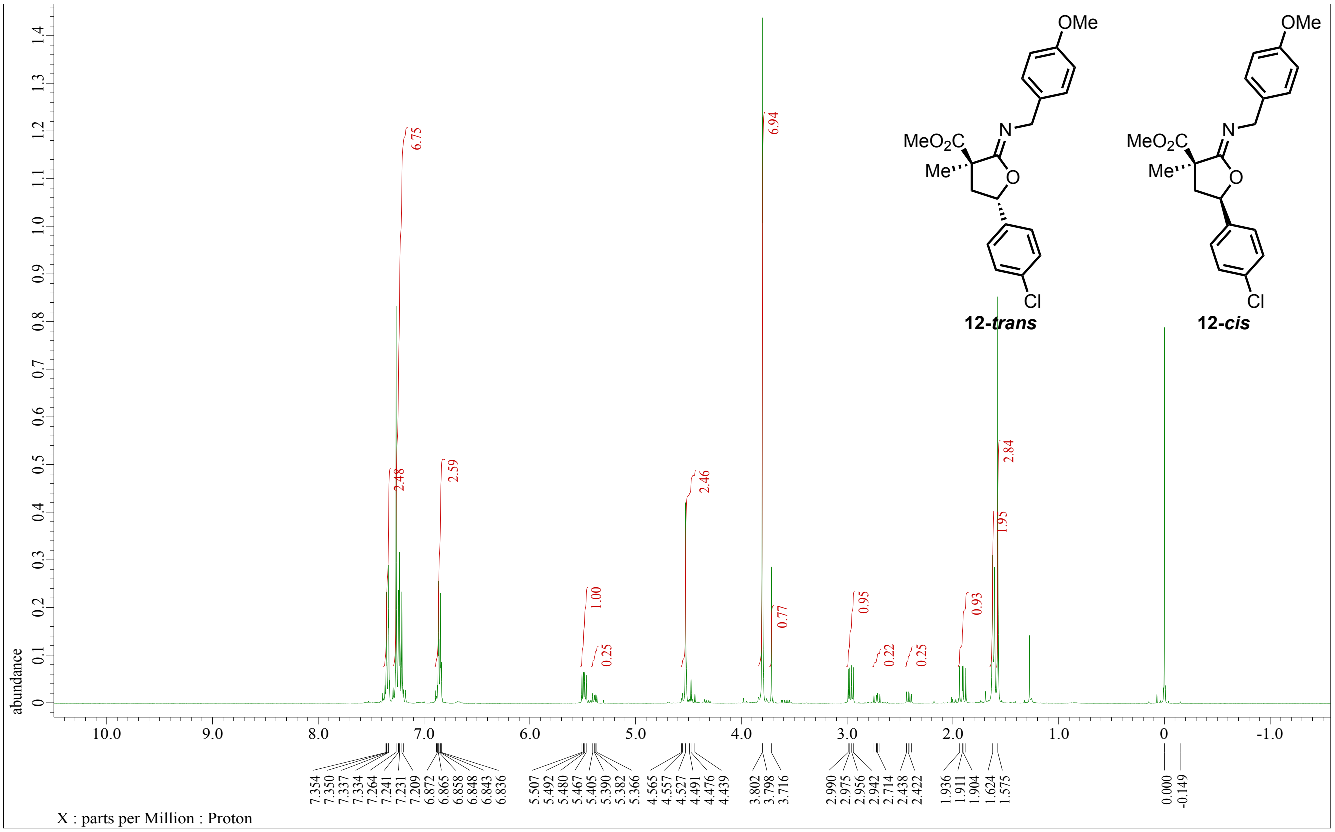
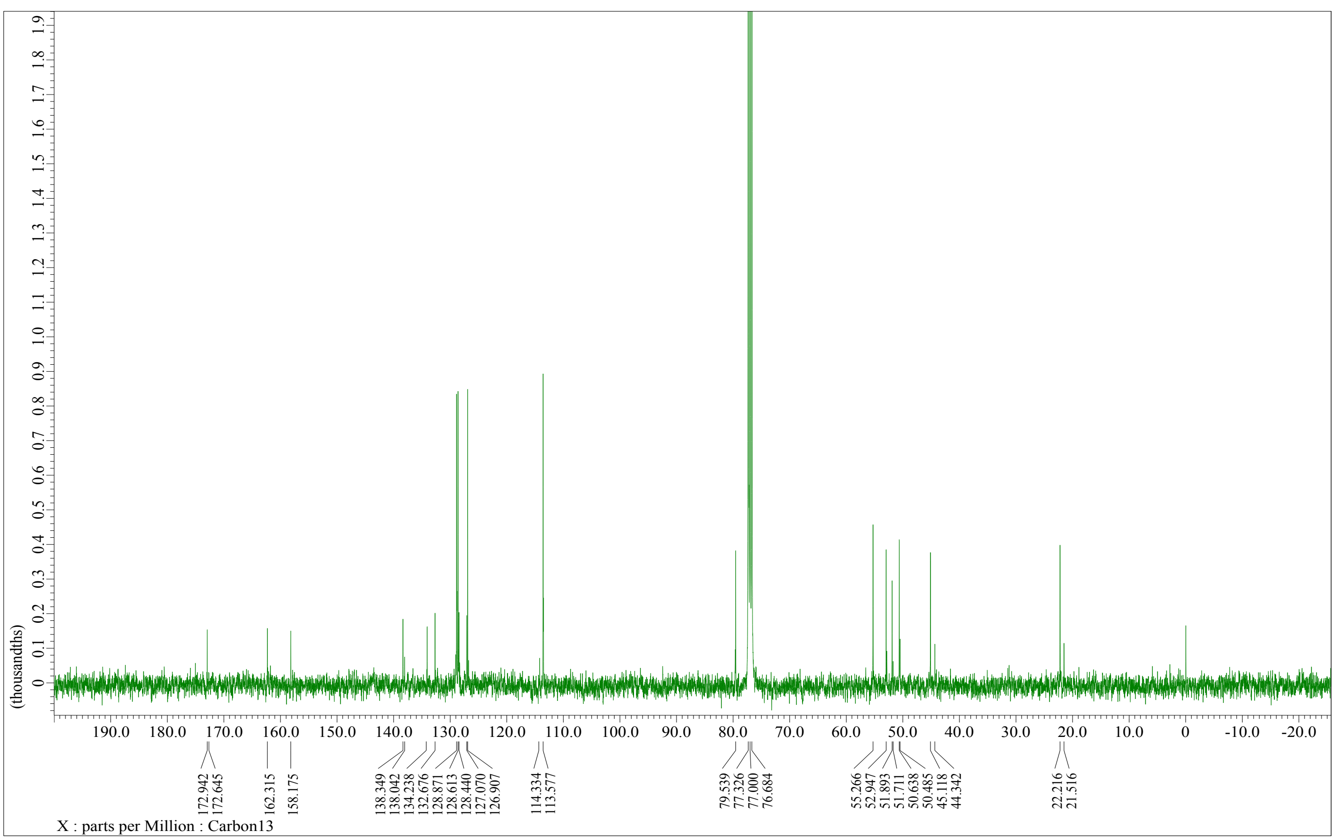
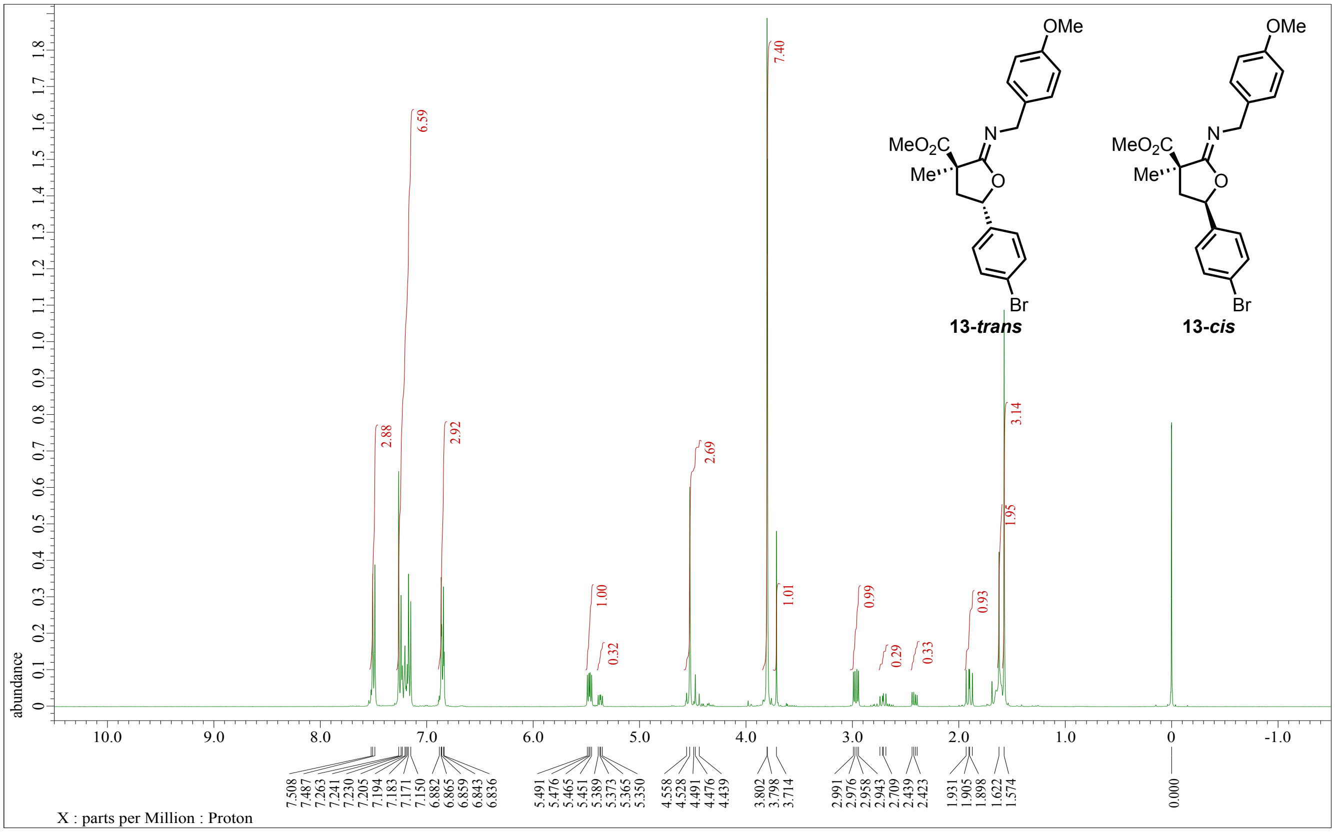
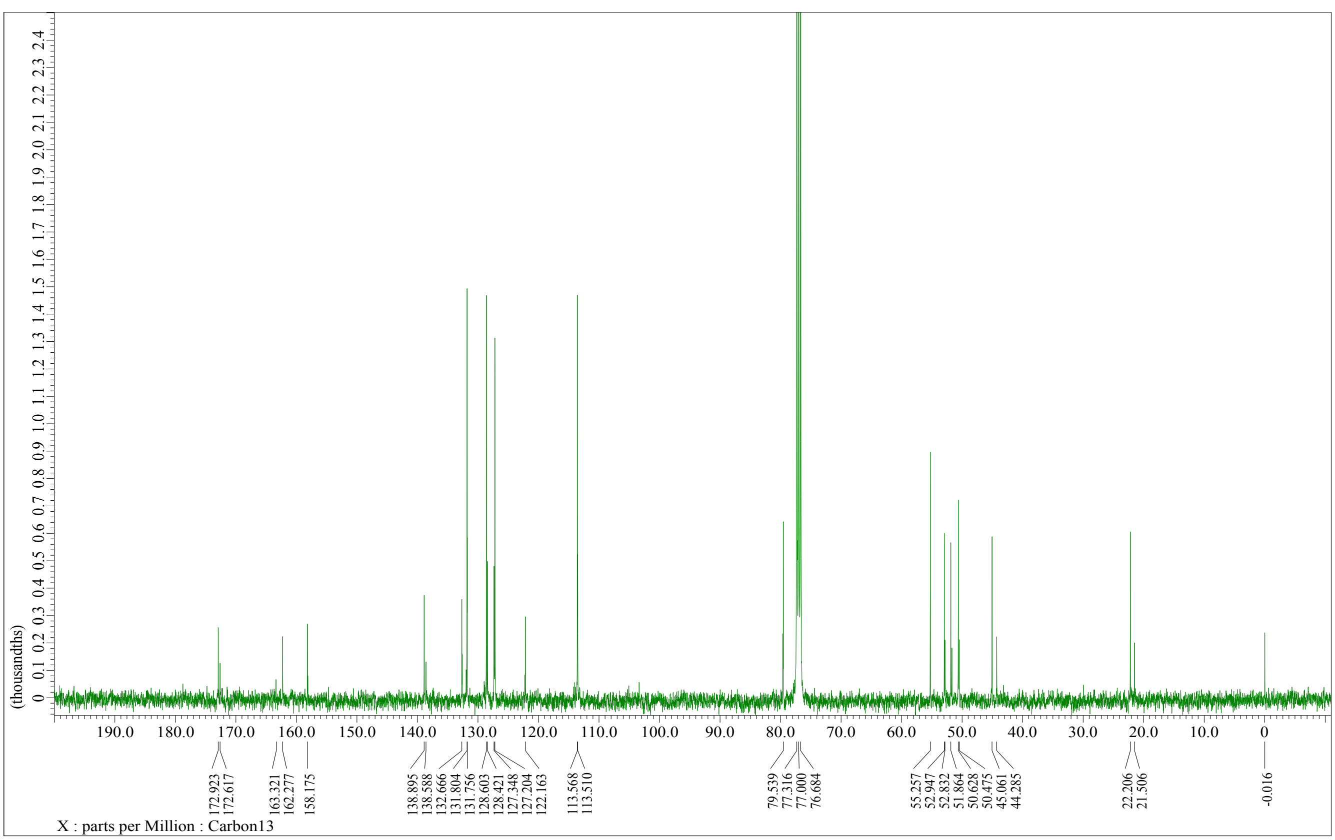
^1H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **12**_*trans, cis*-mixture



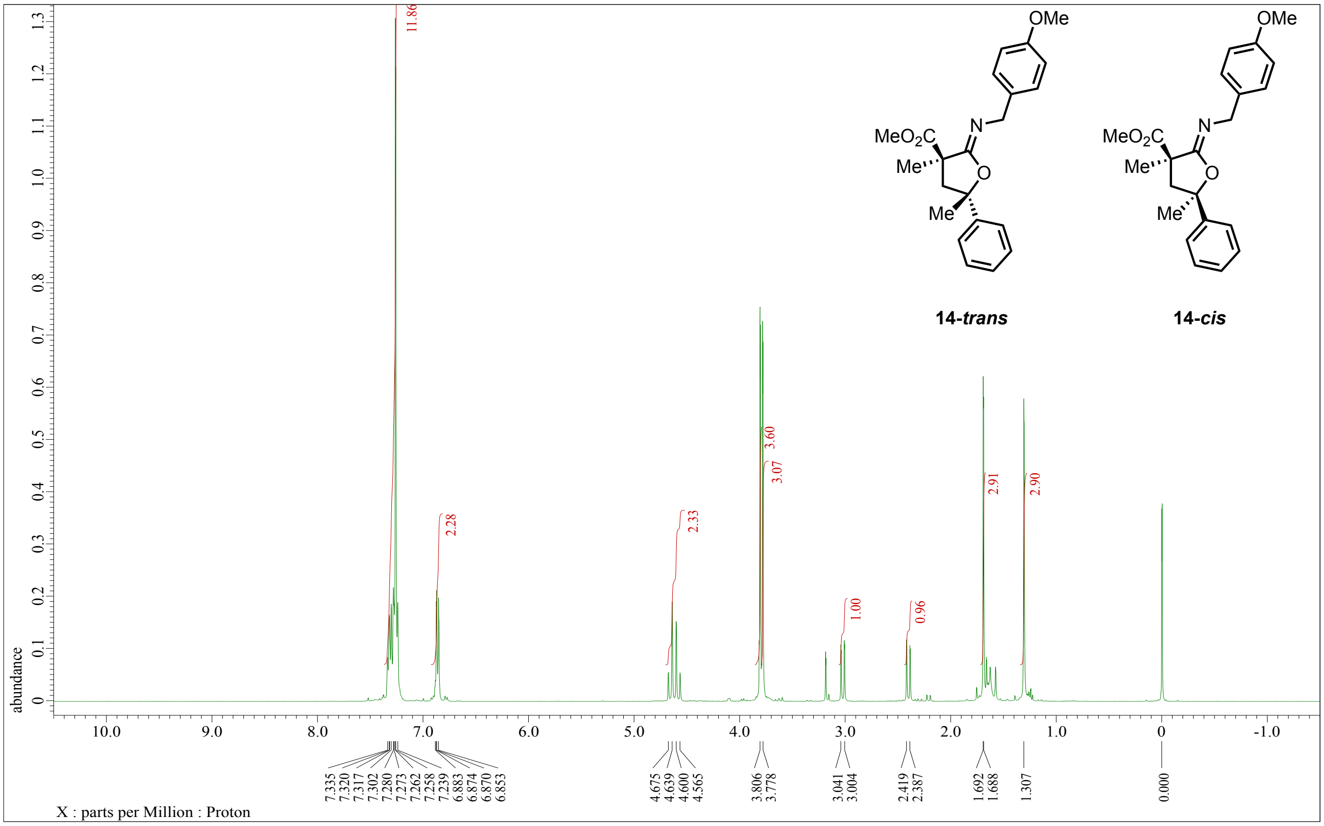


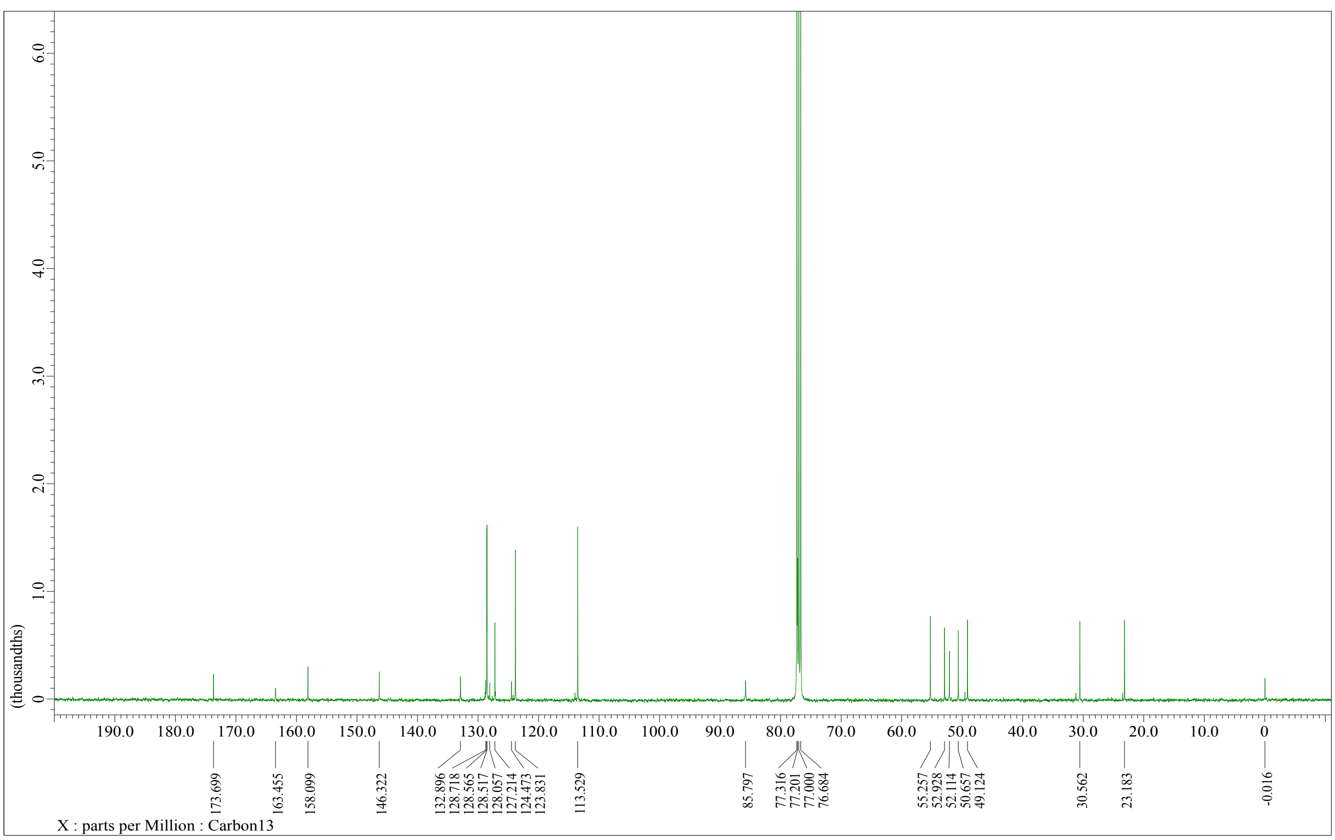
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **13**_*trans, cis*-mixture



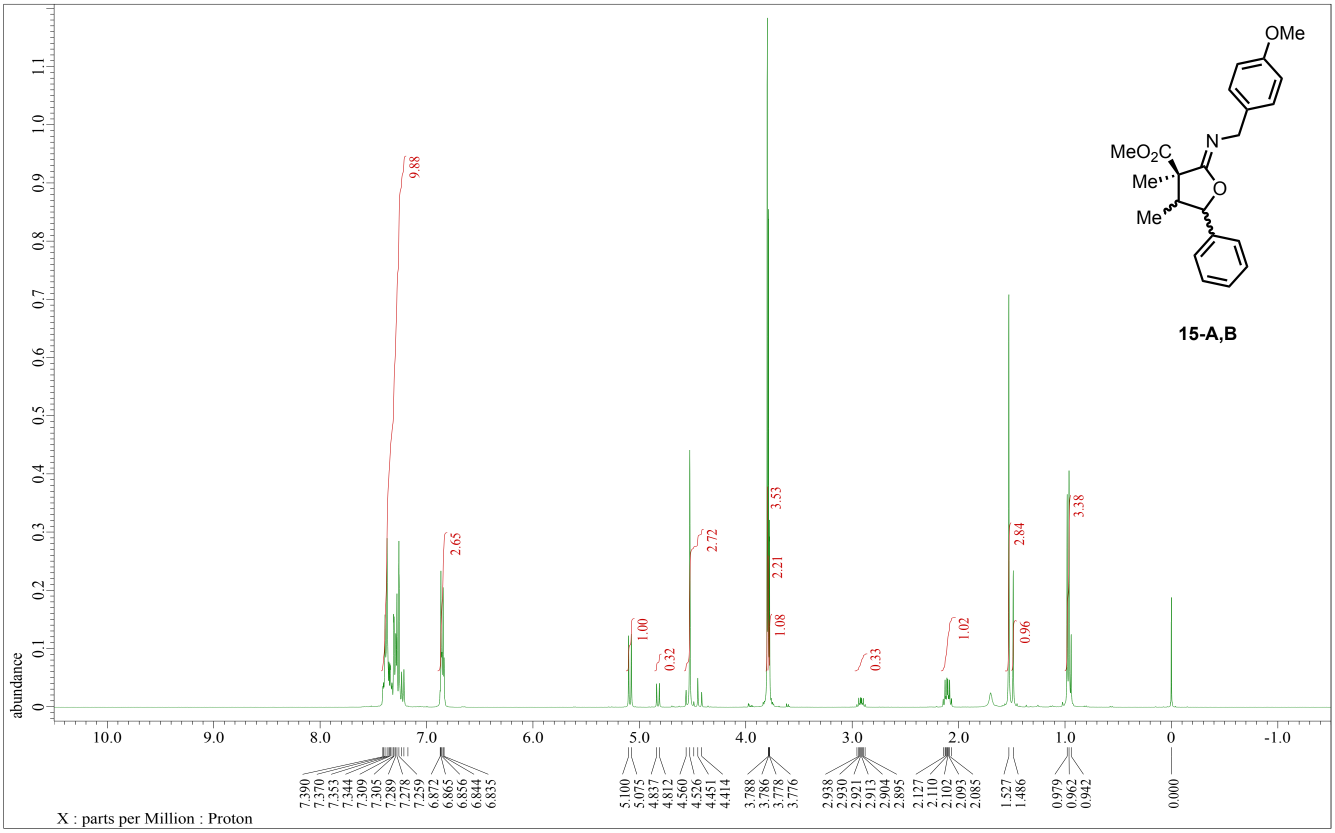


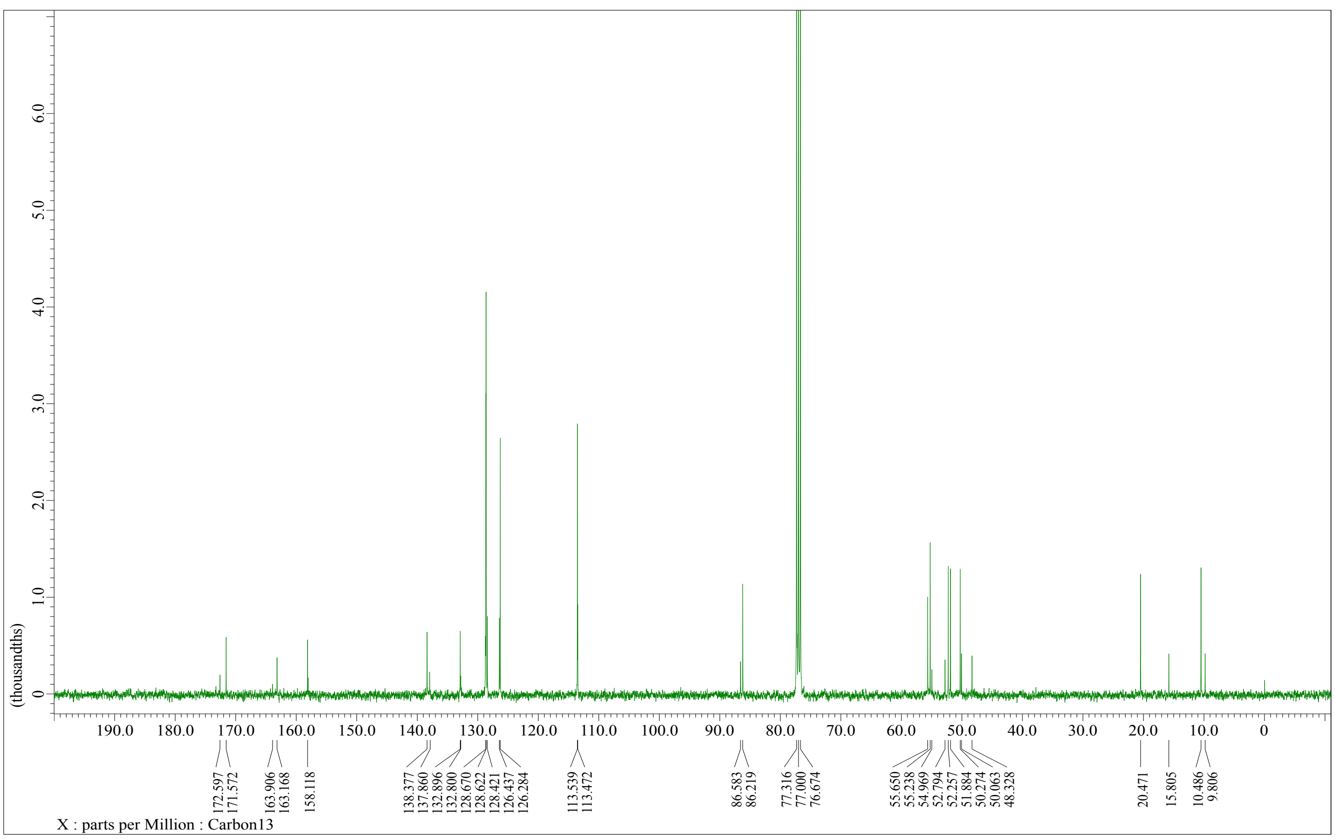
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **14**_ *trans, cis*-mixture



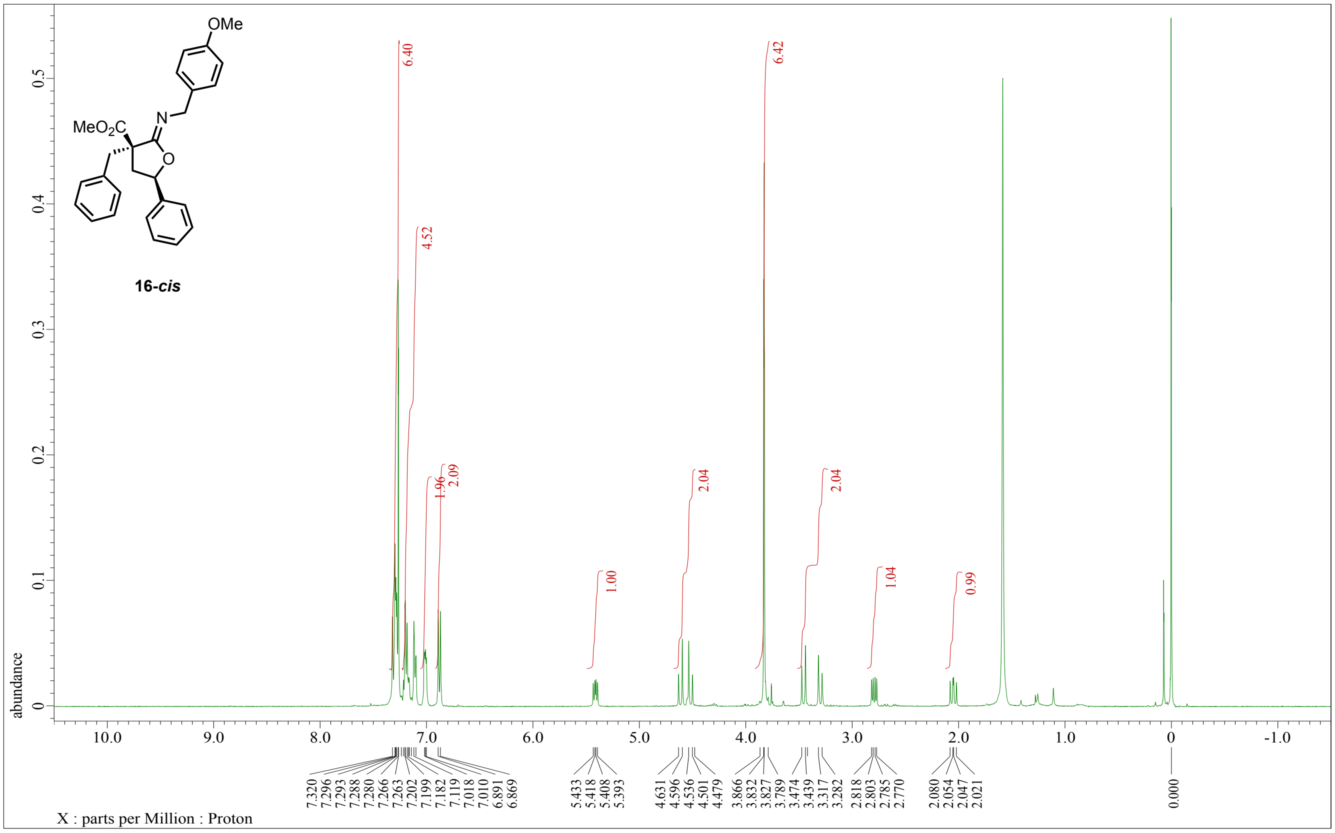


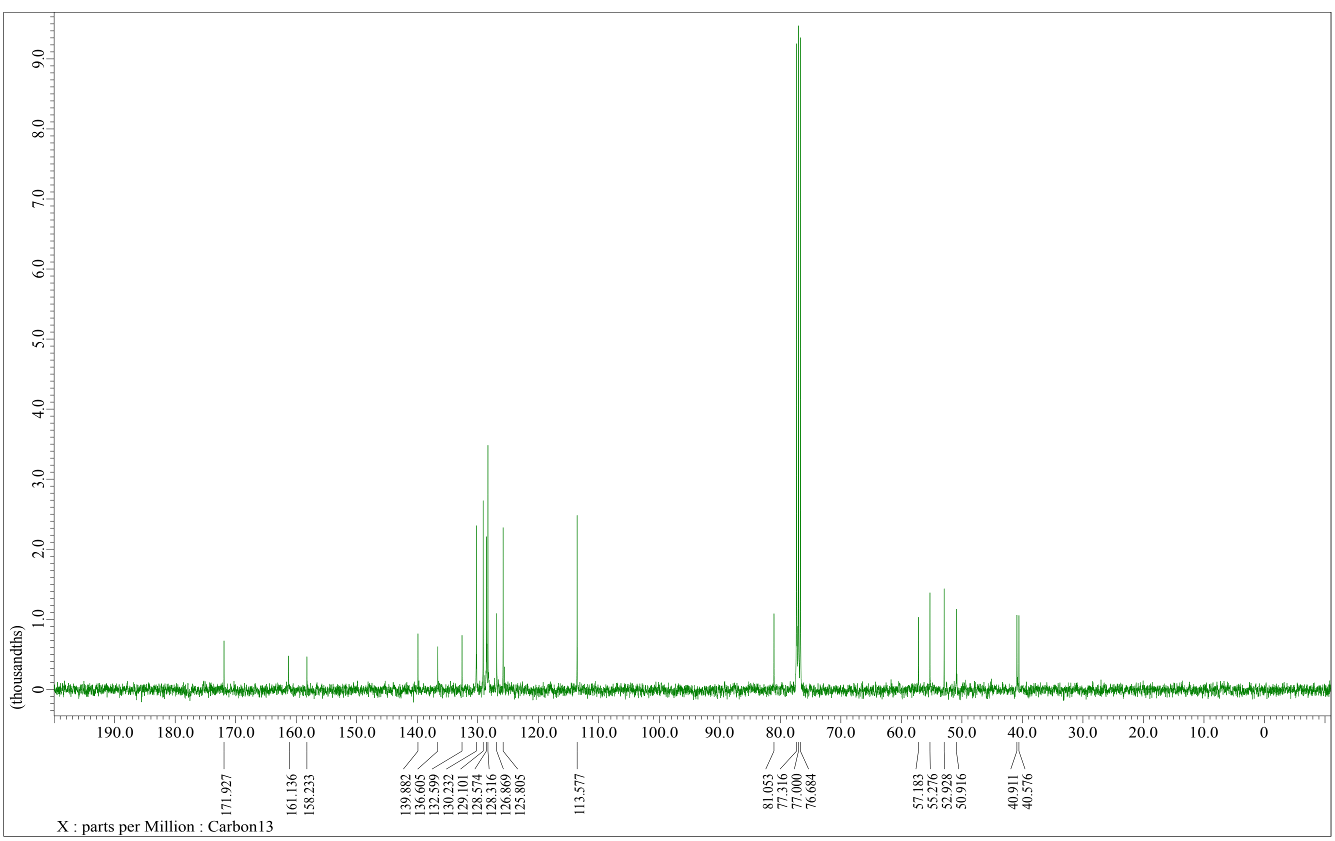
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **15_*A*, *B*-*mixture***



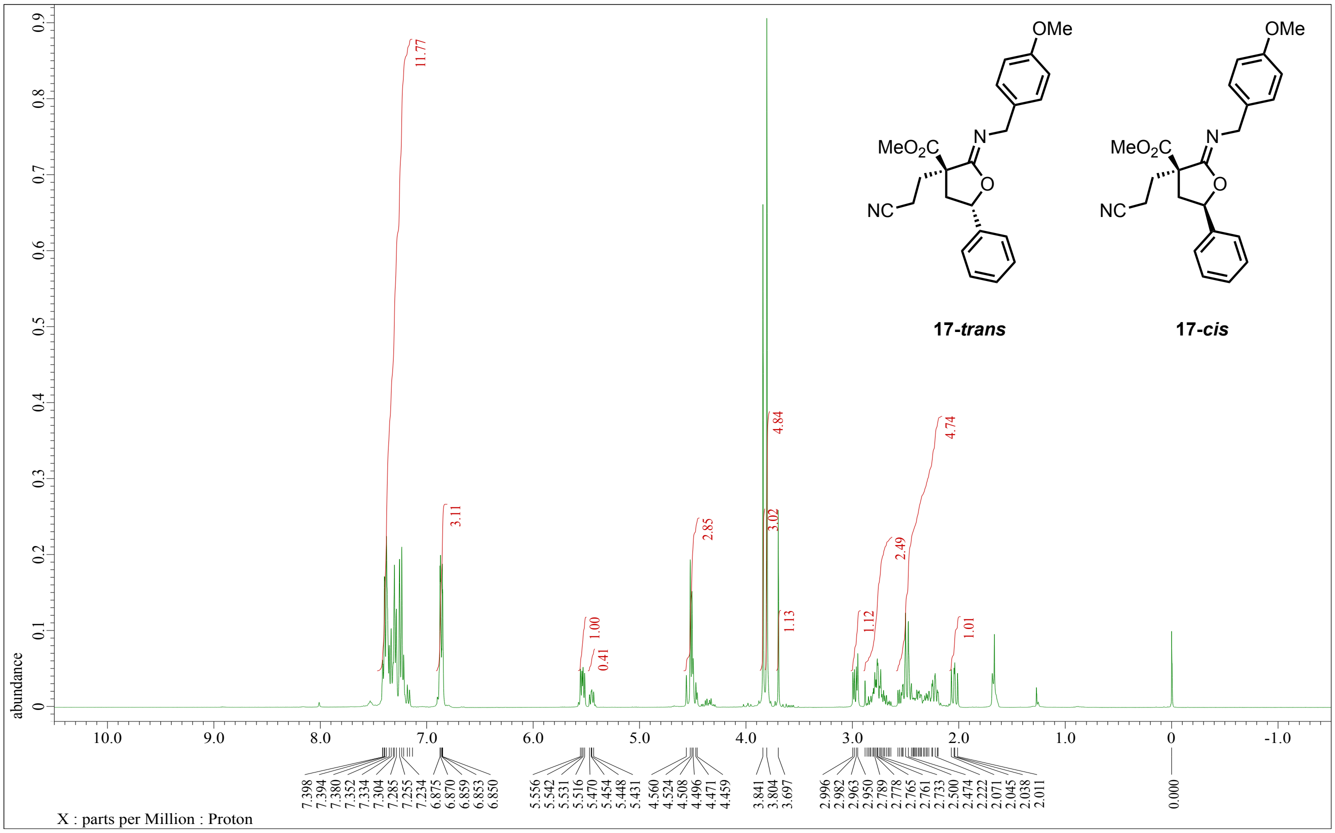


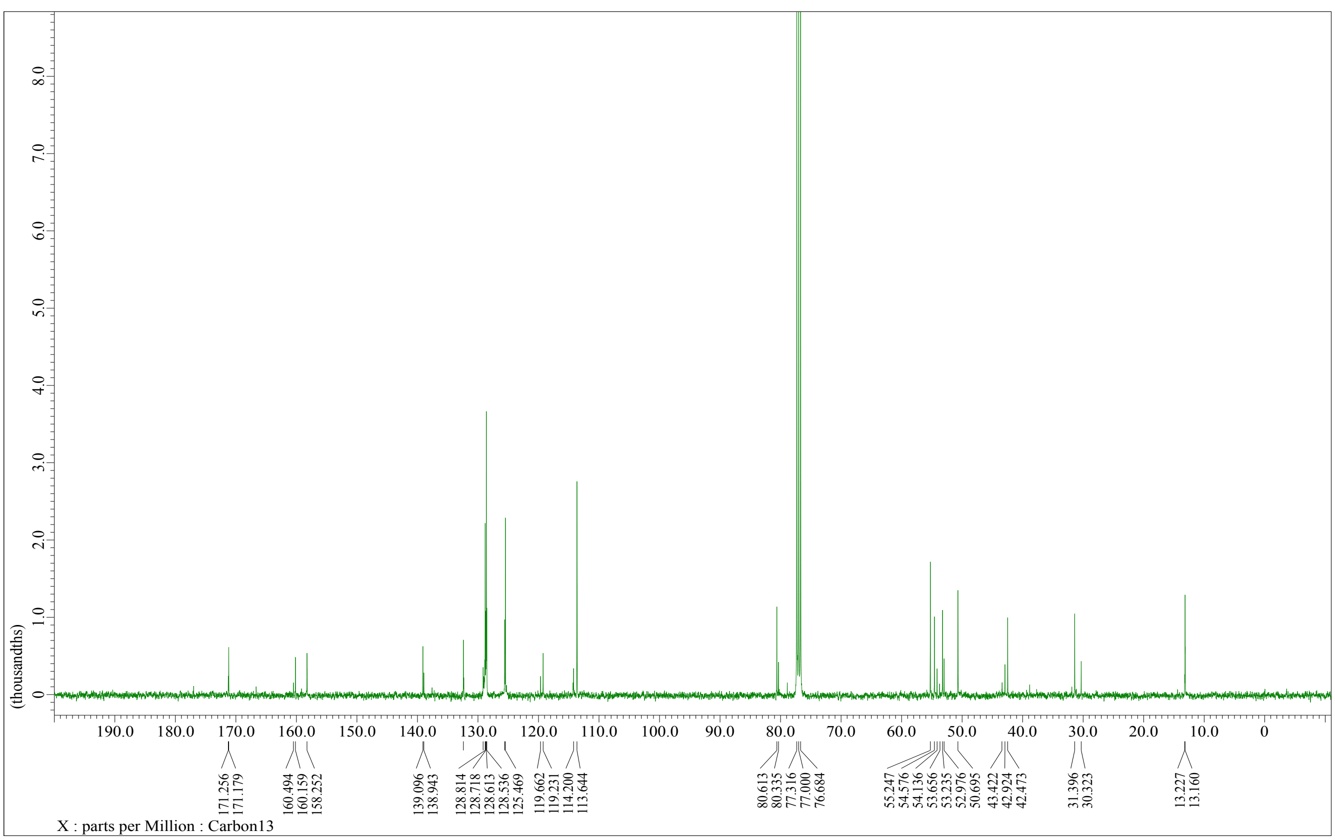
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **16**_*cis*



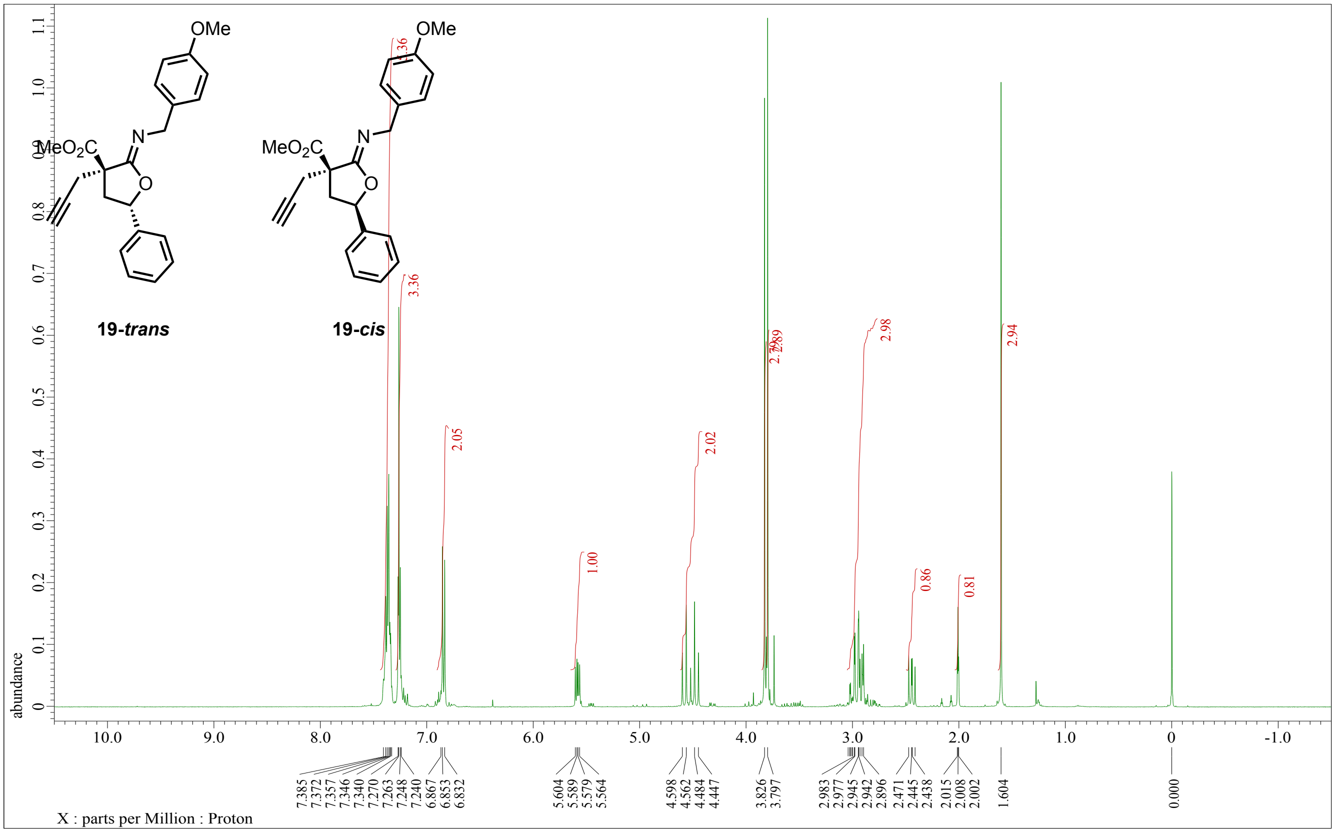


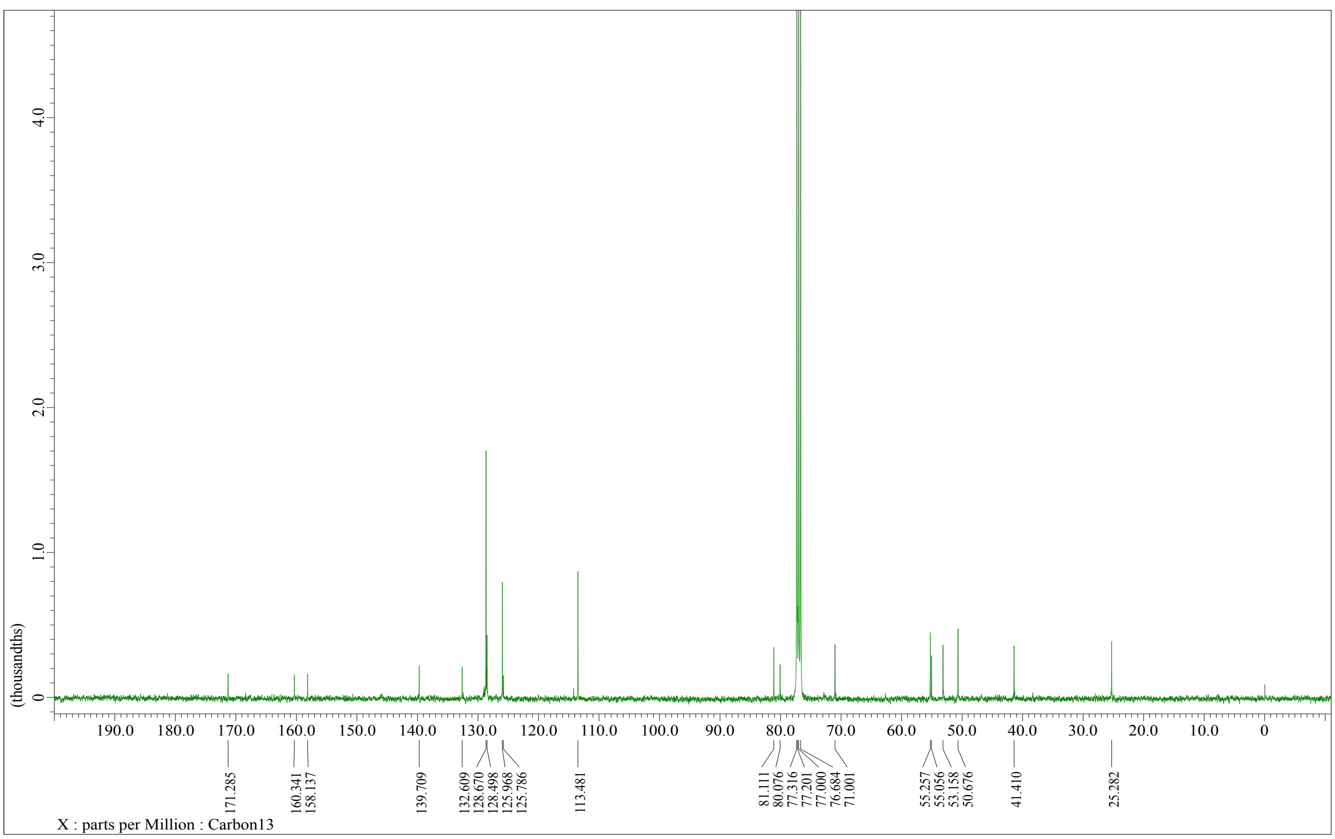
[1]H NMR ($CDCl_3$, 500 MHz) and [13]C{[1]H} NMR ($CDCl_3$, 125 MHz) spectra of **17**_*trans*, *cis*-mixture



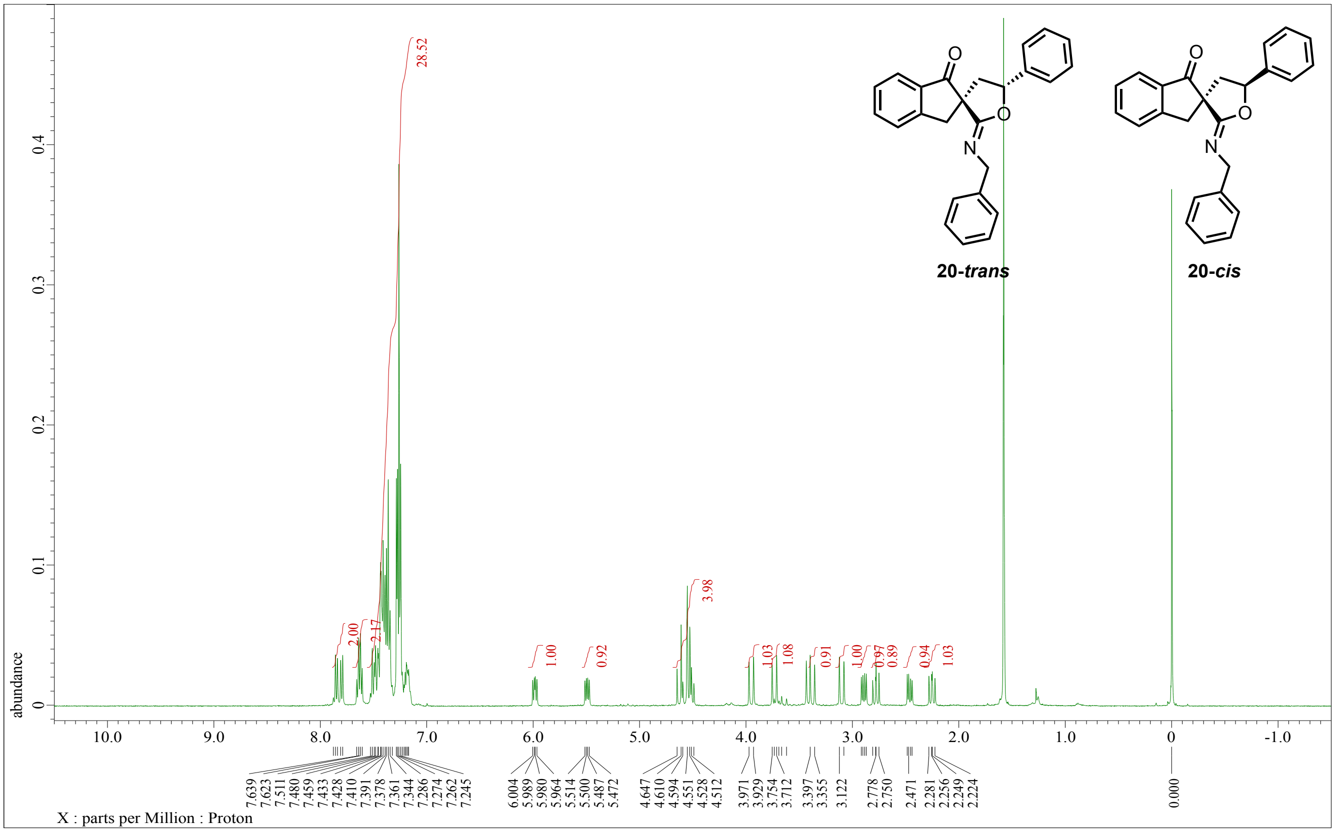


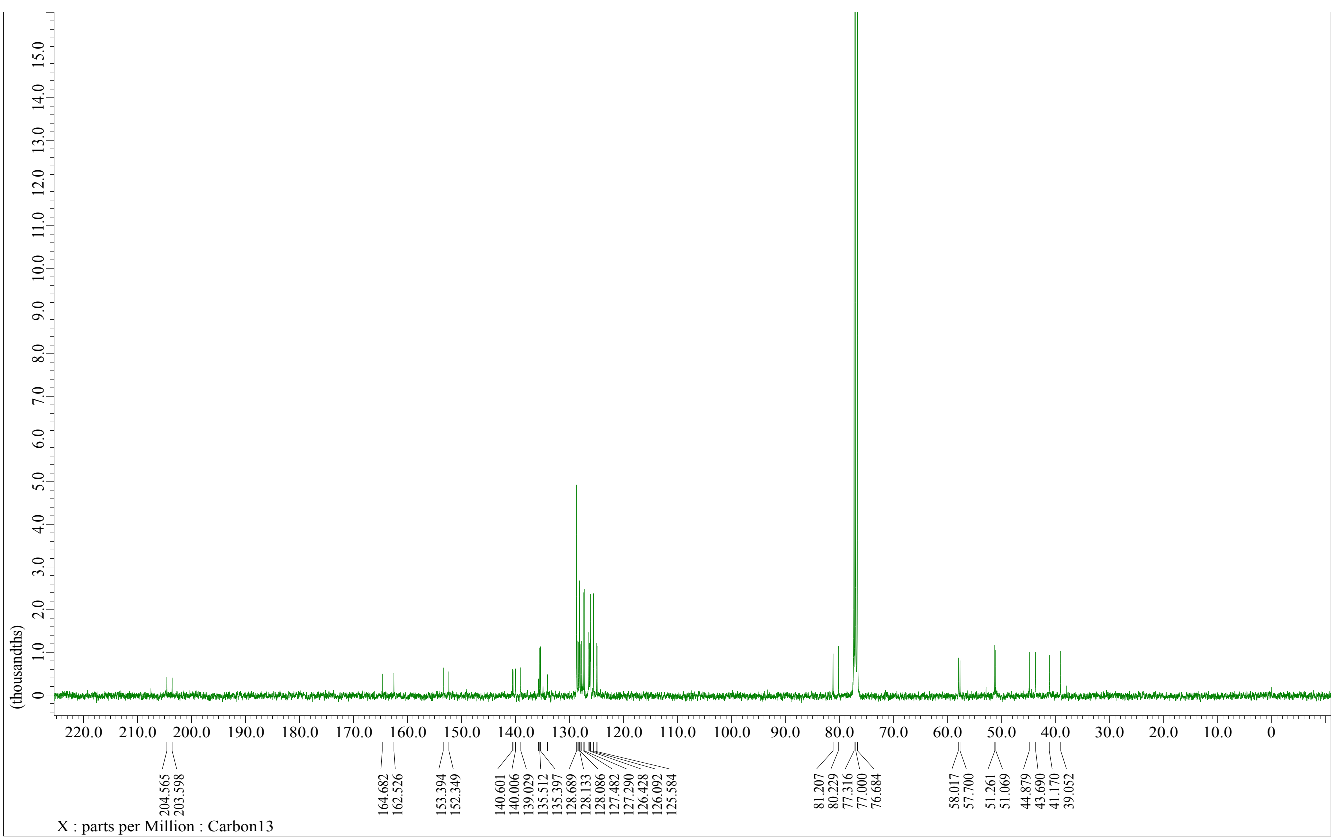
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of **19**_*trans-major*



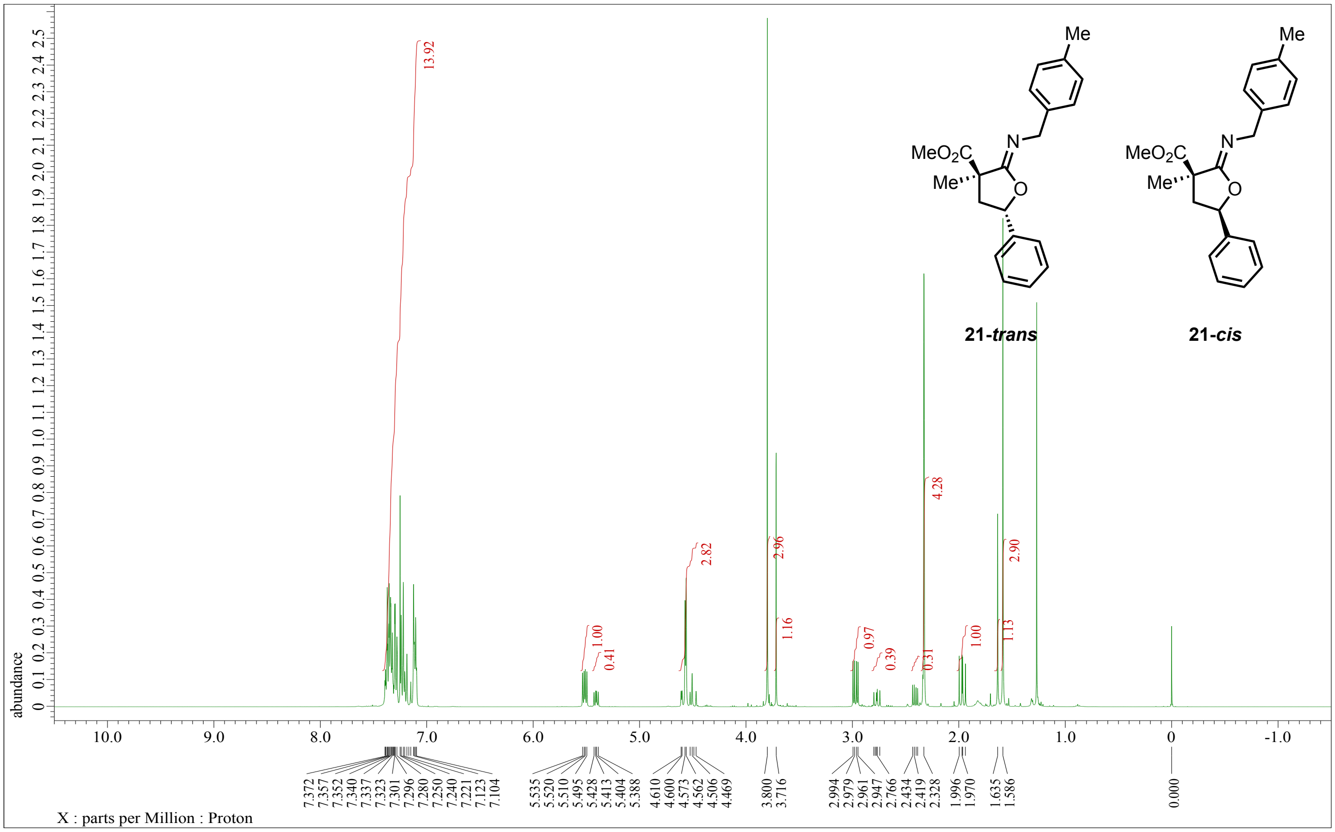


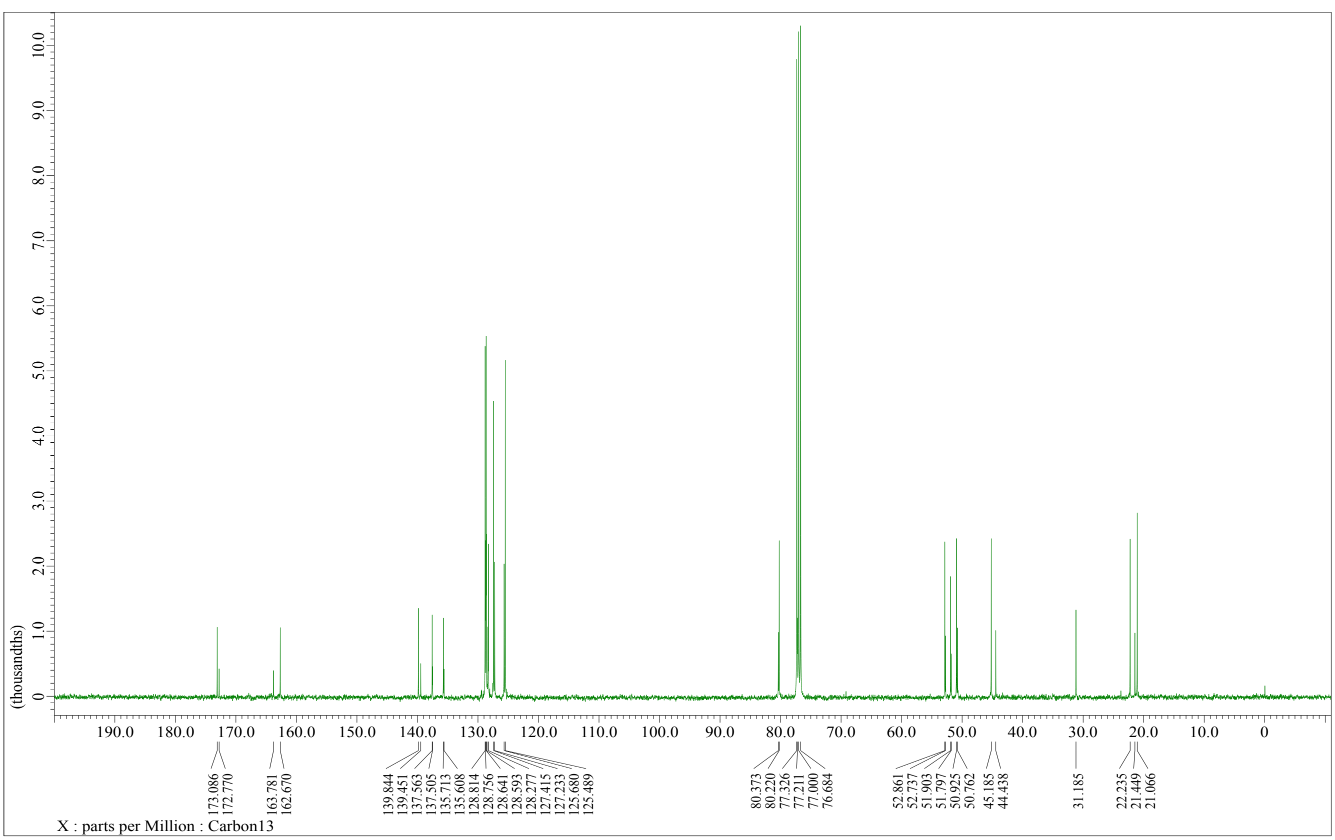
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **20**_*trans, cis*-mixture



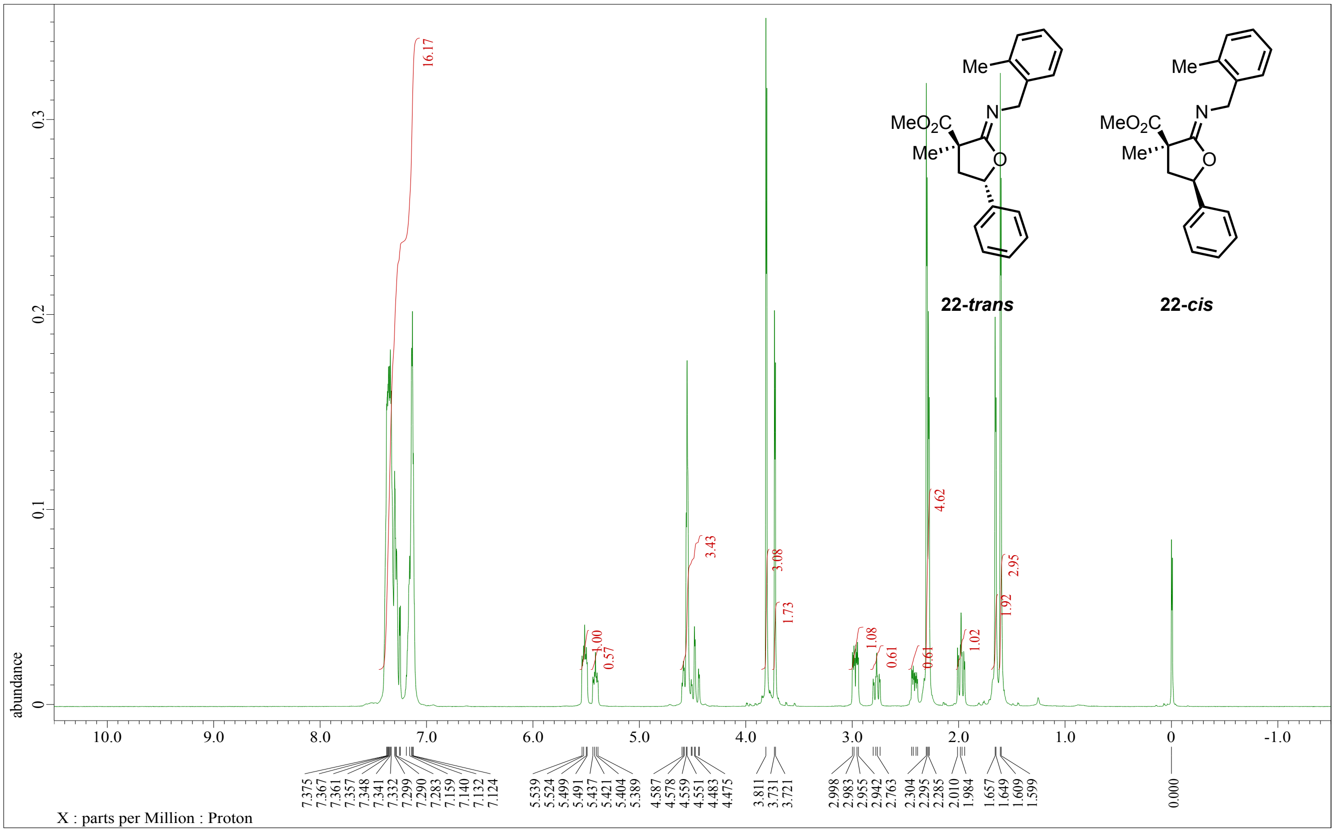


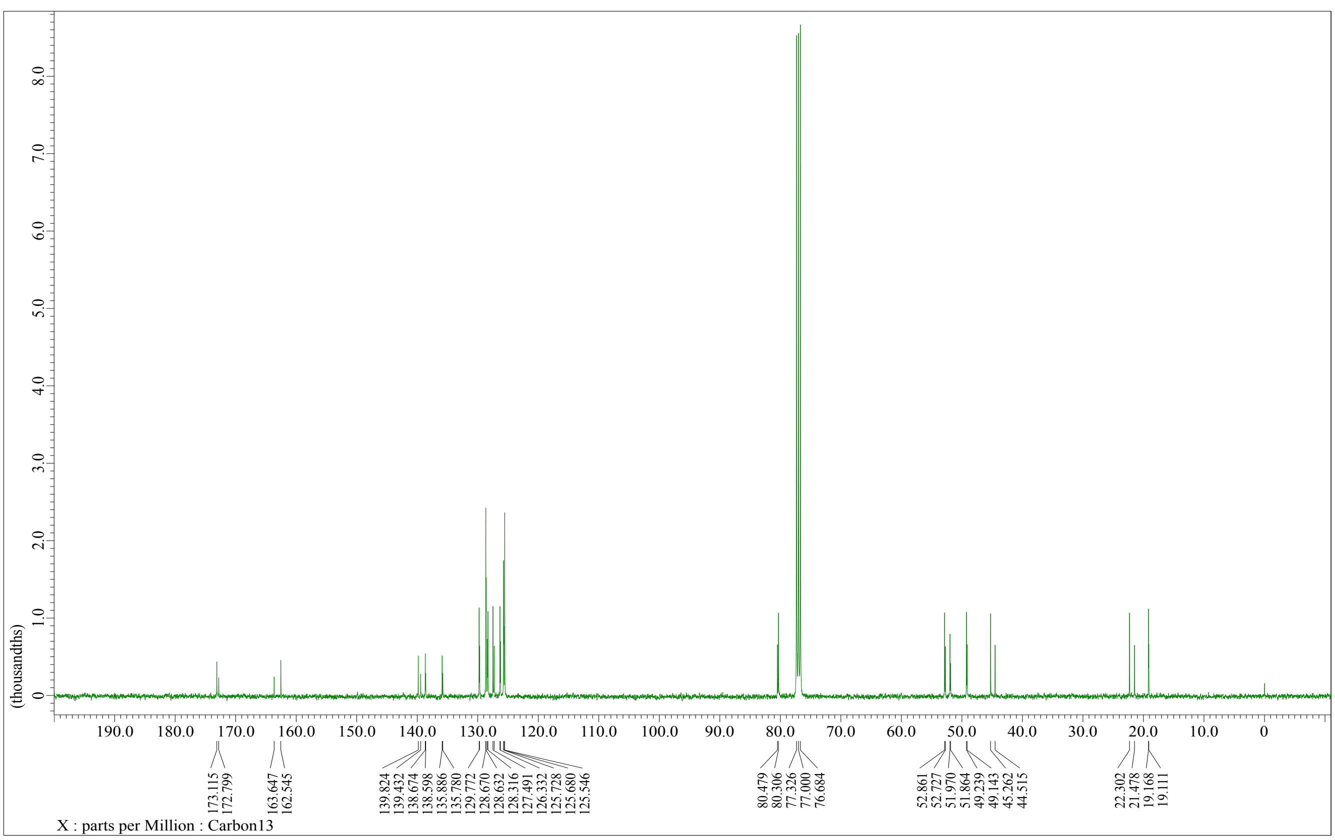
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **21**_*trans, cis*-mixture



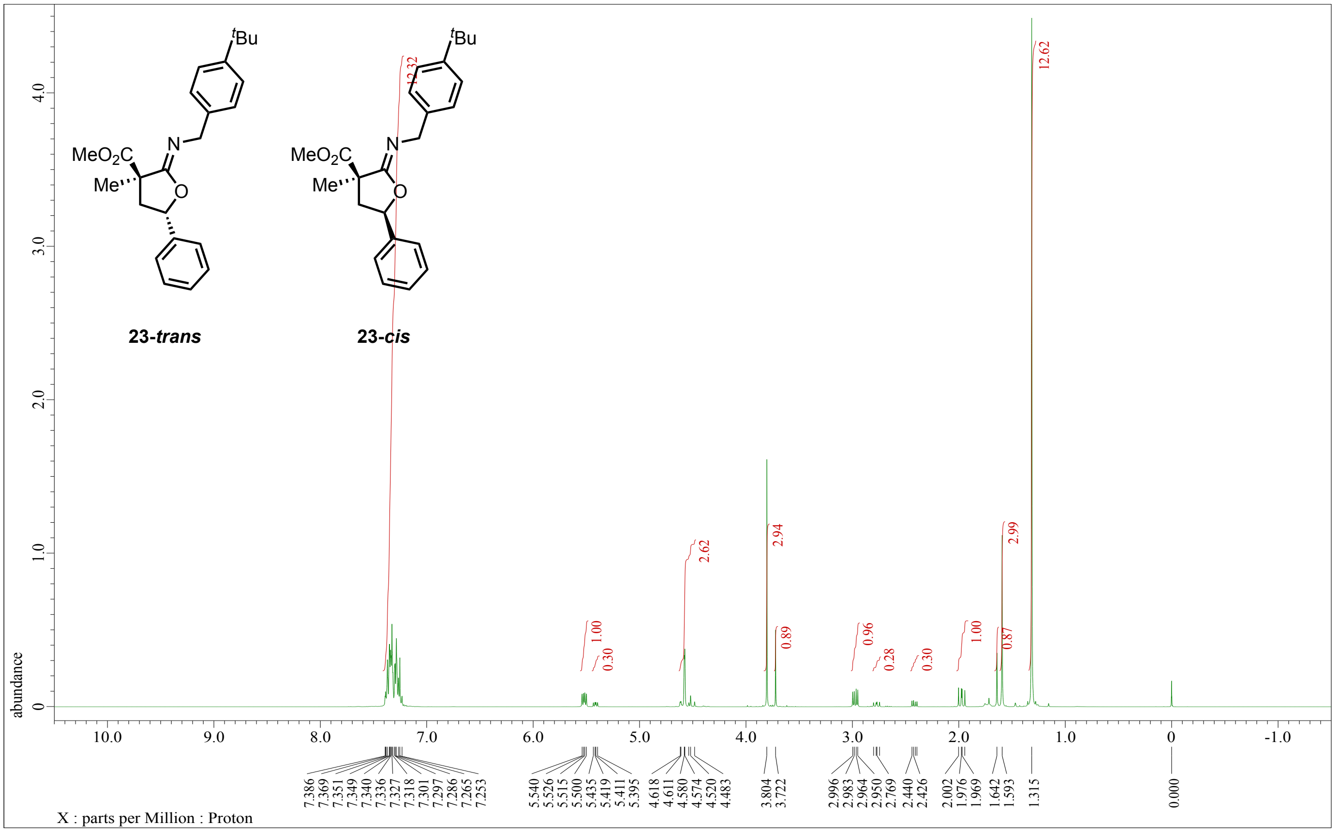


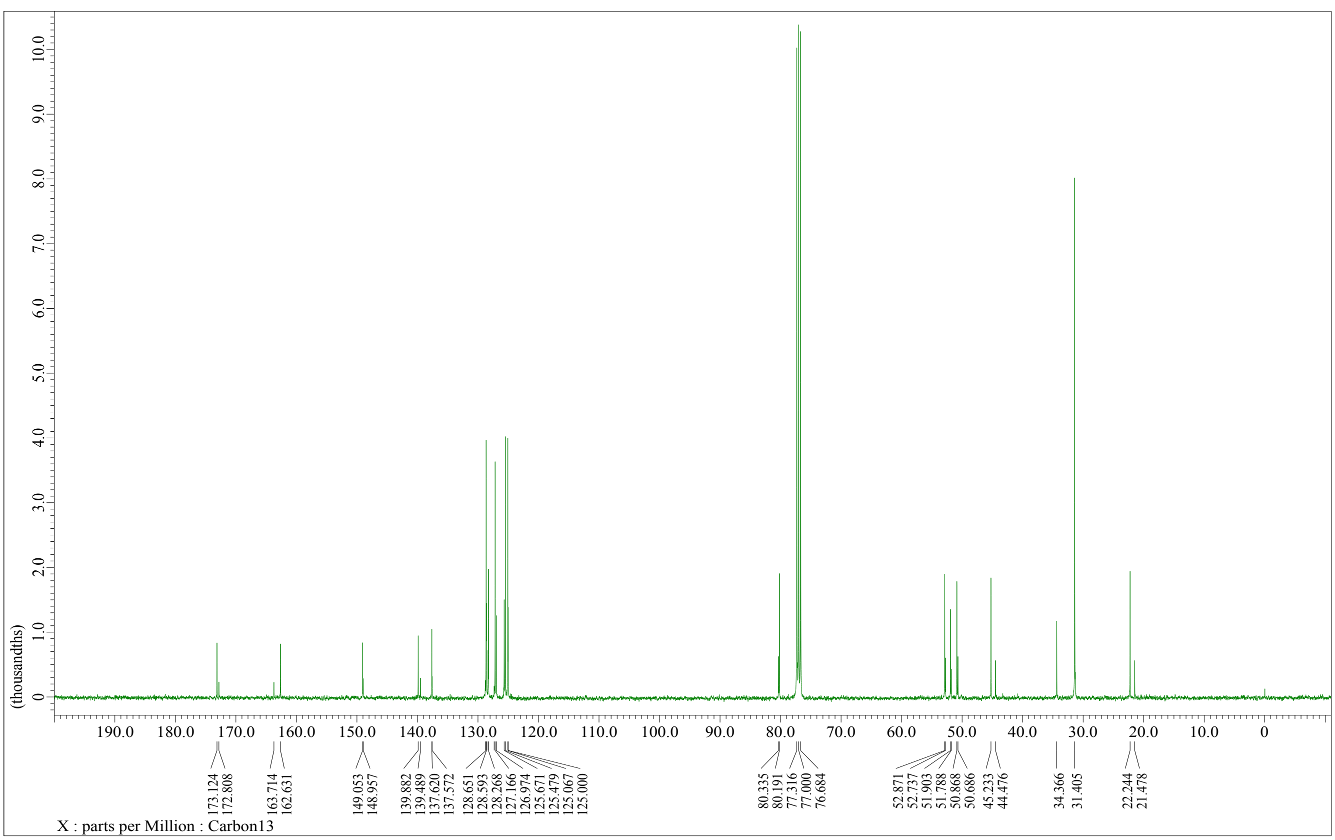
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of **22**_*trans, cis*-mixture



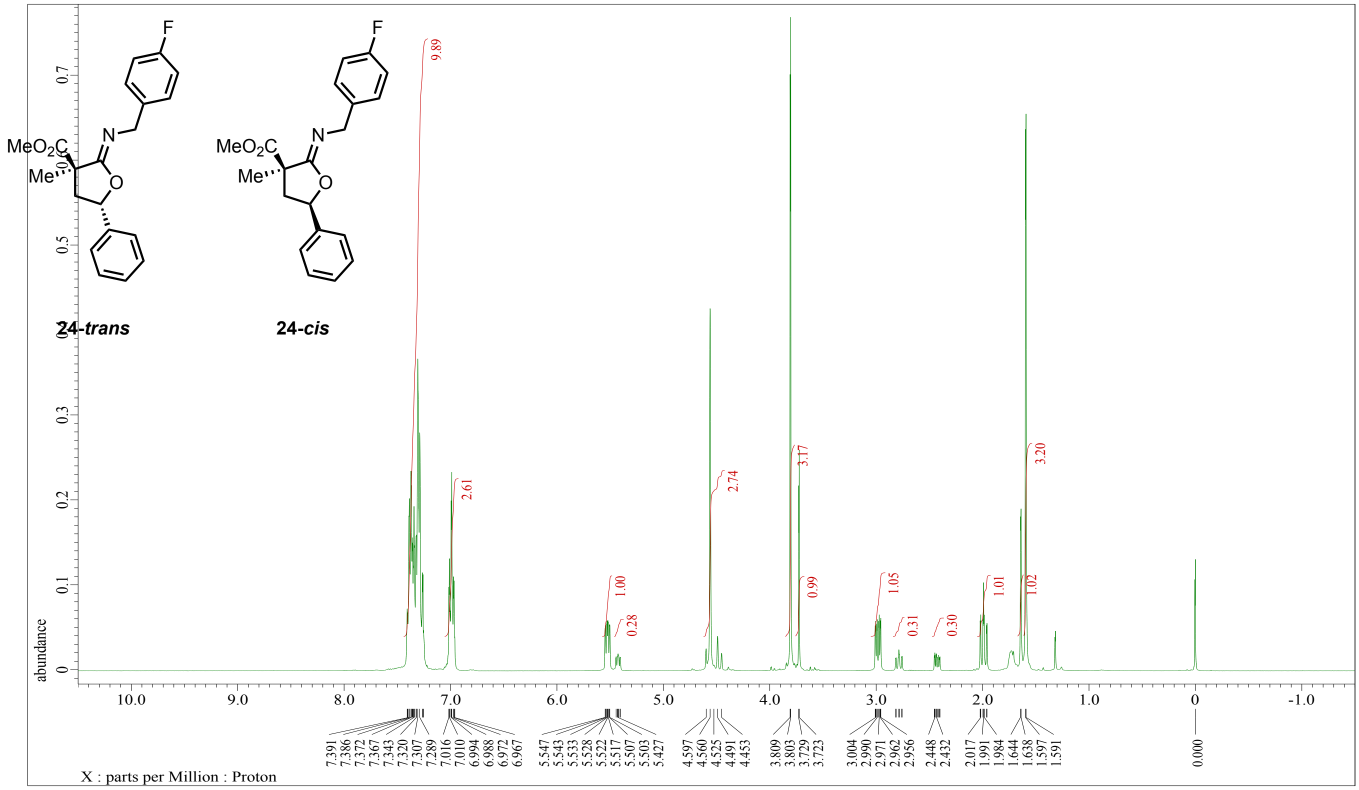


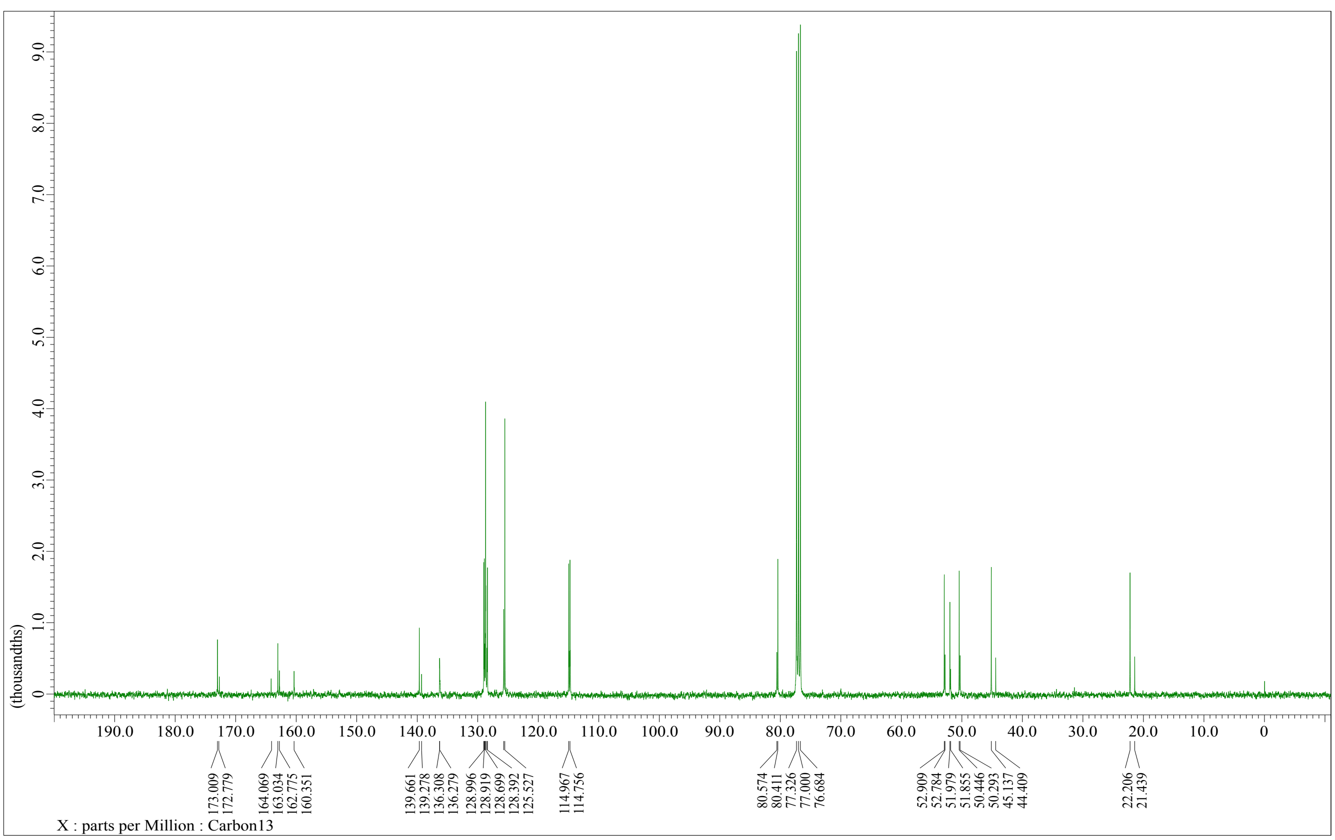
^{1}H NMR (CDCl$_3$, 500 MHz) and ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) spectra of **23**_*trans, cis*-mixture

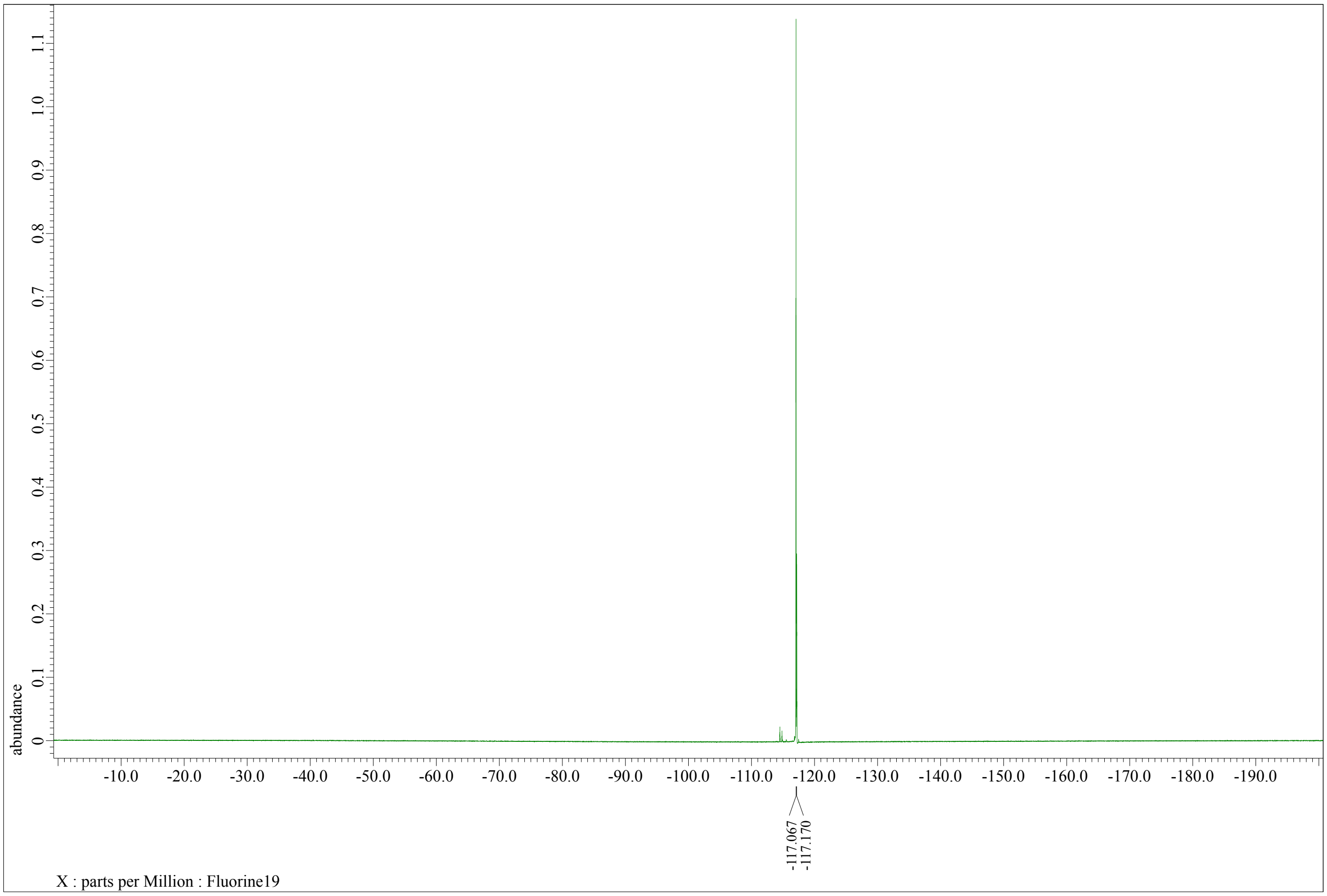




^{1}H NMR ($CDCl_3$, 500 MHz), $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) and ^{19}F NMR ($CDCl_3$, 470 MHz) spectra of **24**_*trans, cis*-mixture

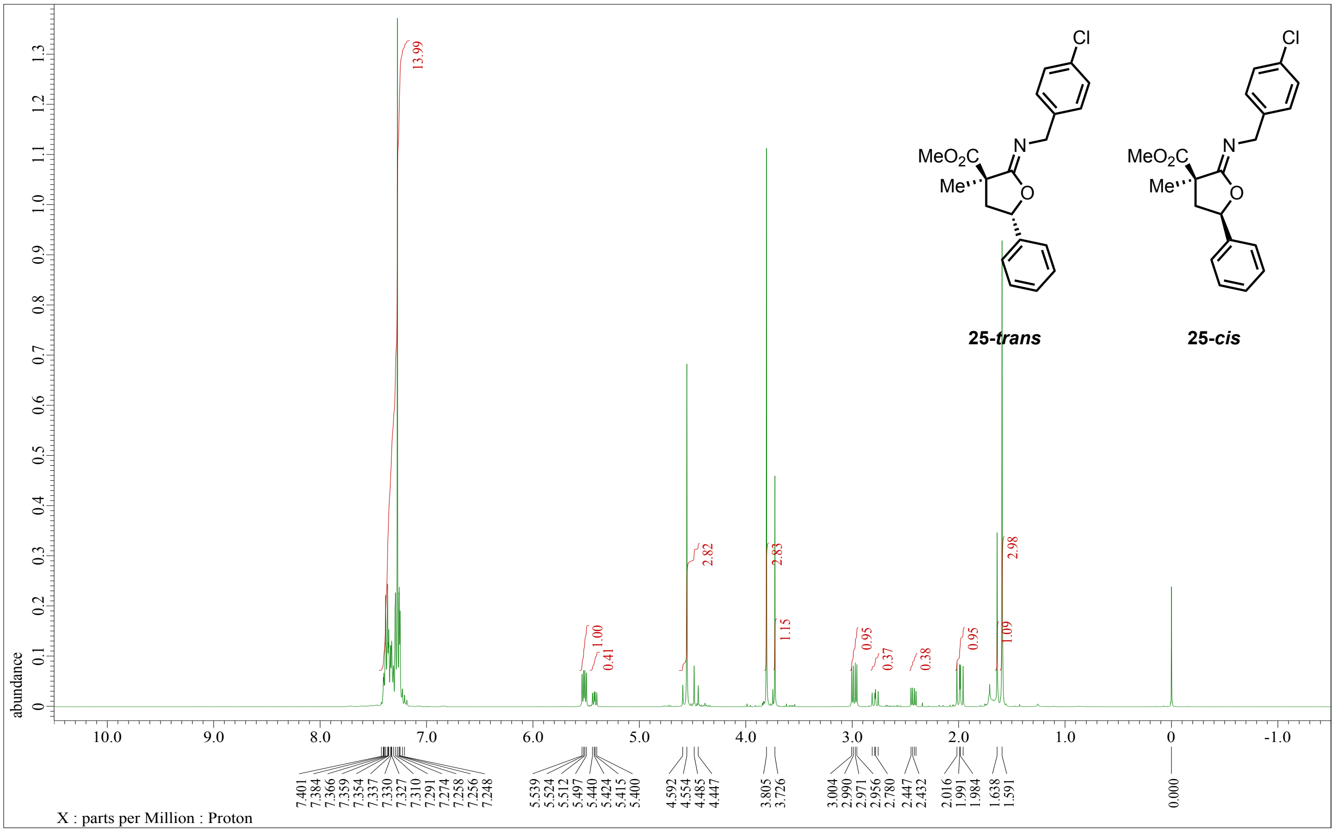


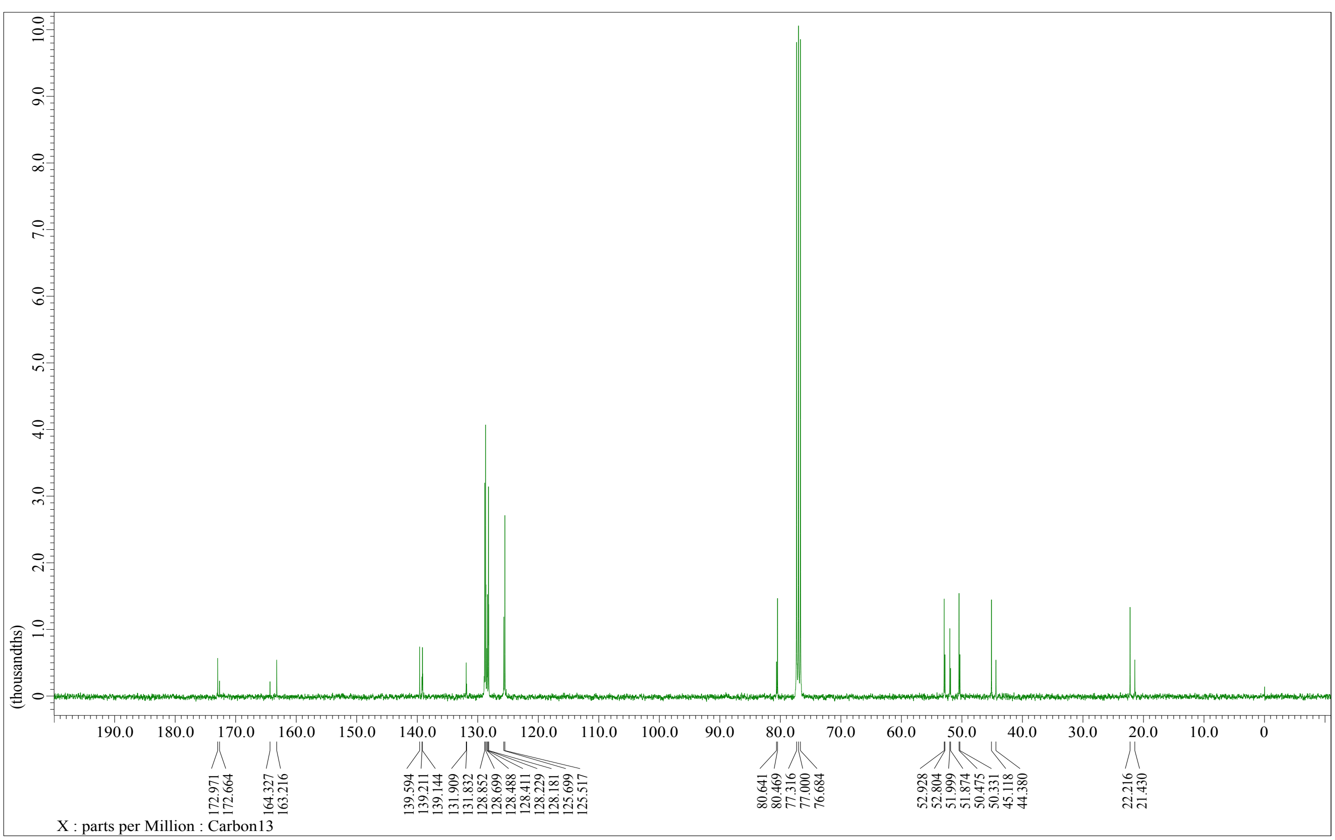




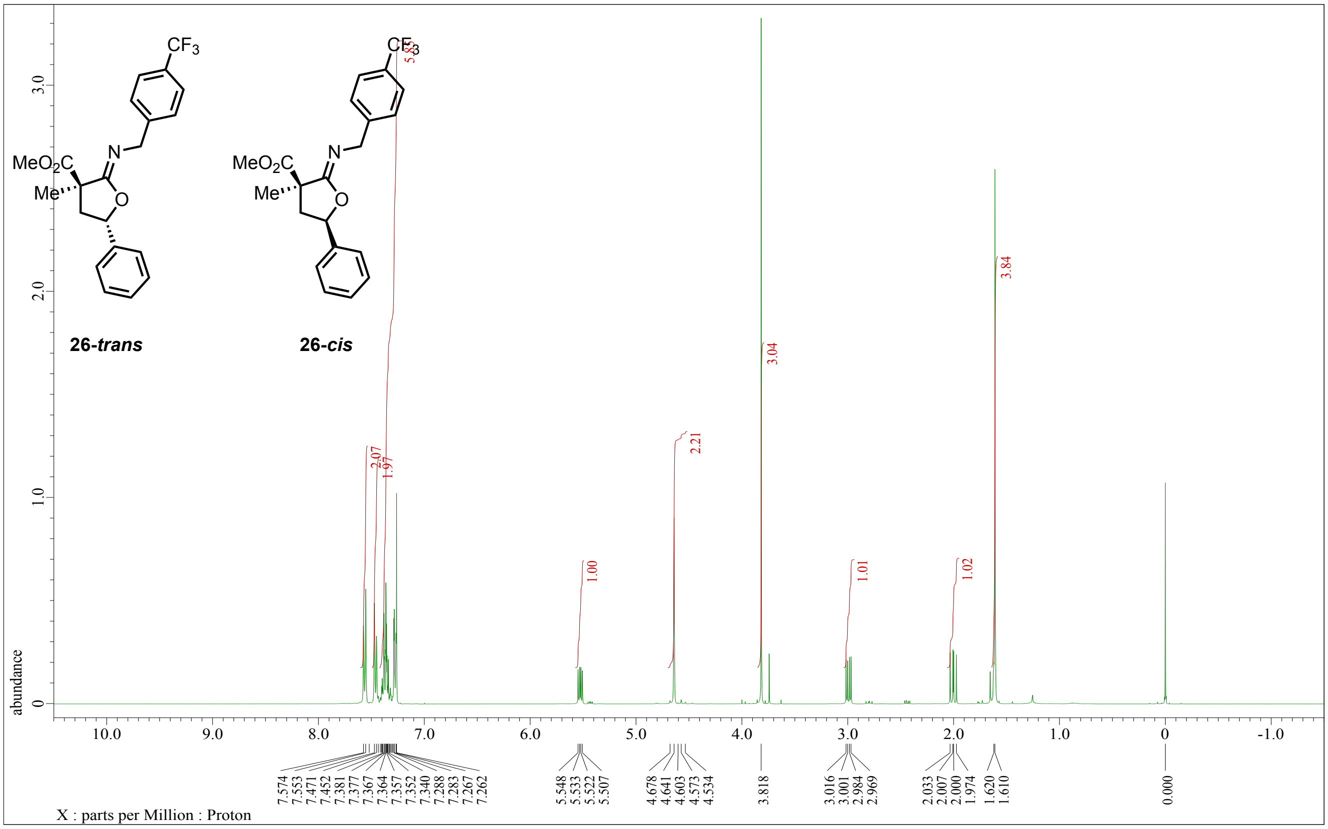
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
-10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-117.067
-117.170
X : parts per Million : Fluorine19

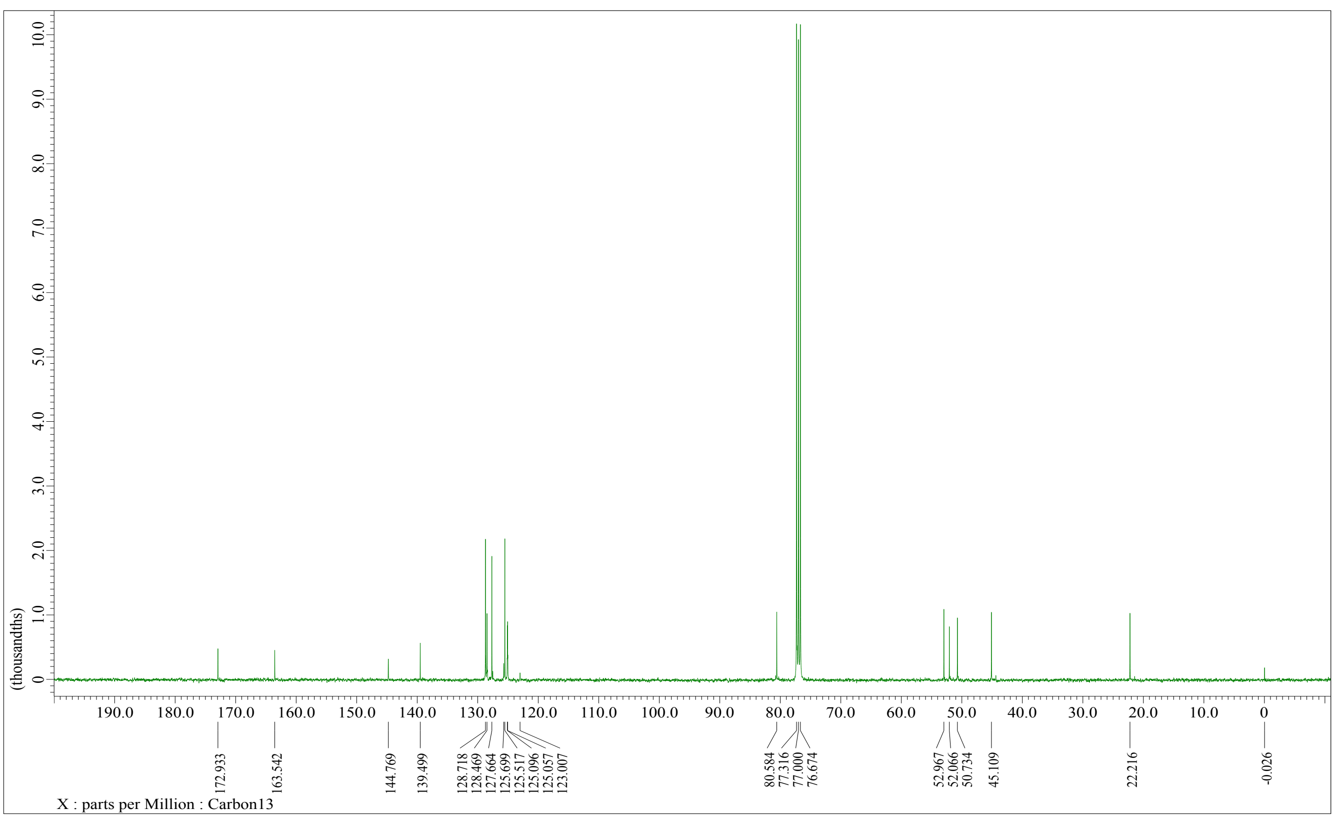
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **25**_*trans, cis*-mixture

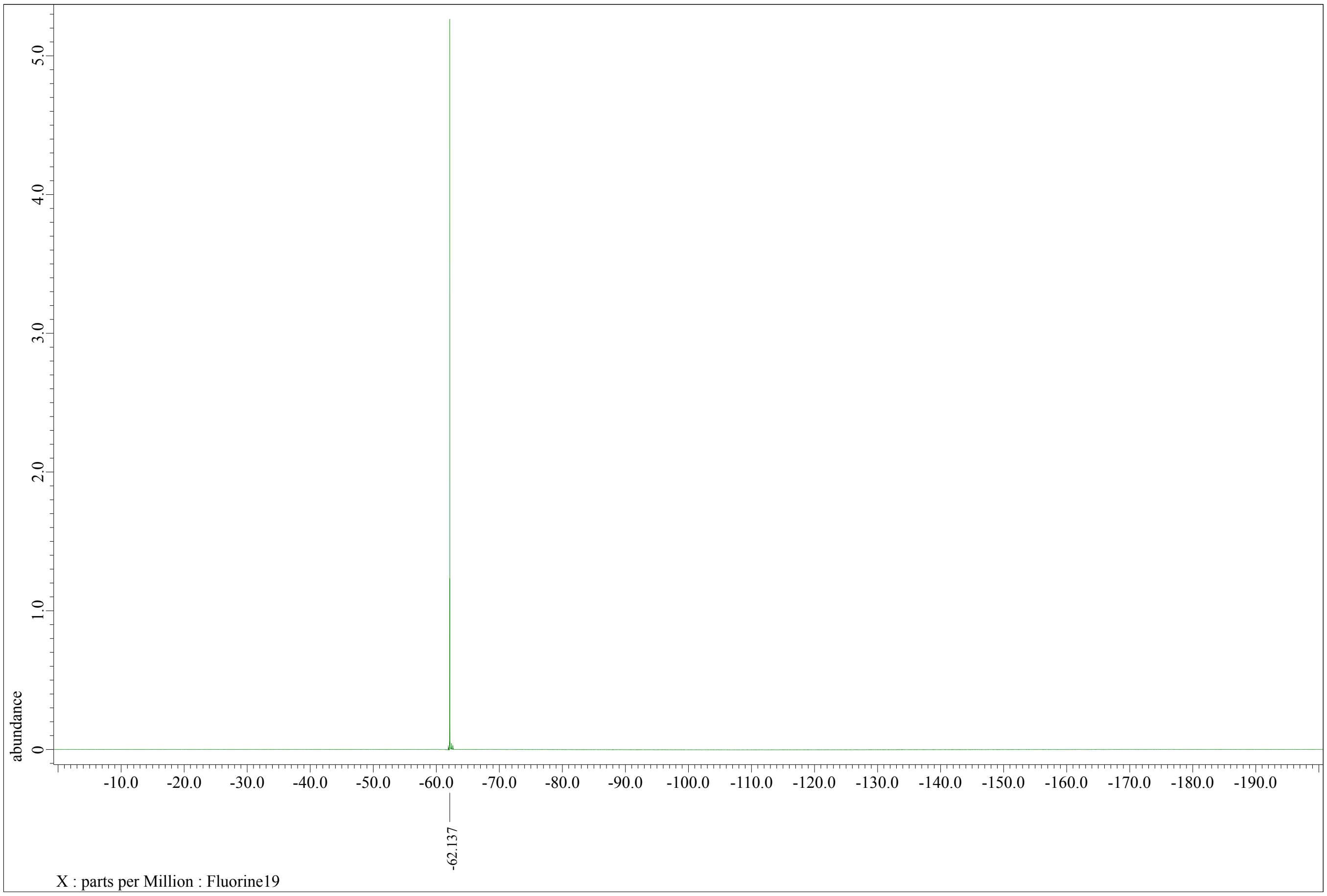




^{1}H NMR ($CDCl_3$, 500 MHz), $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) and ^{19}F NMR ($CDCl_3$, 470 MHz) spectra of **26**_*trans-major*

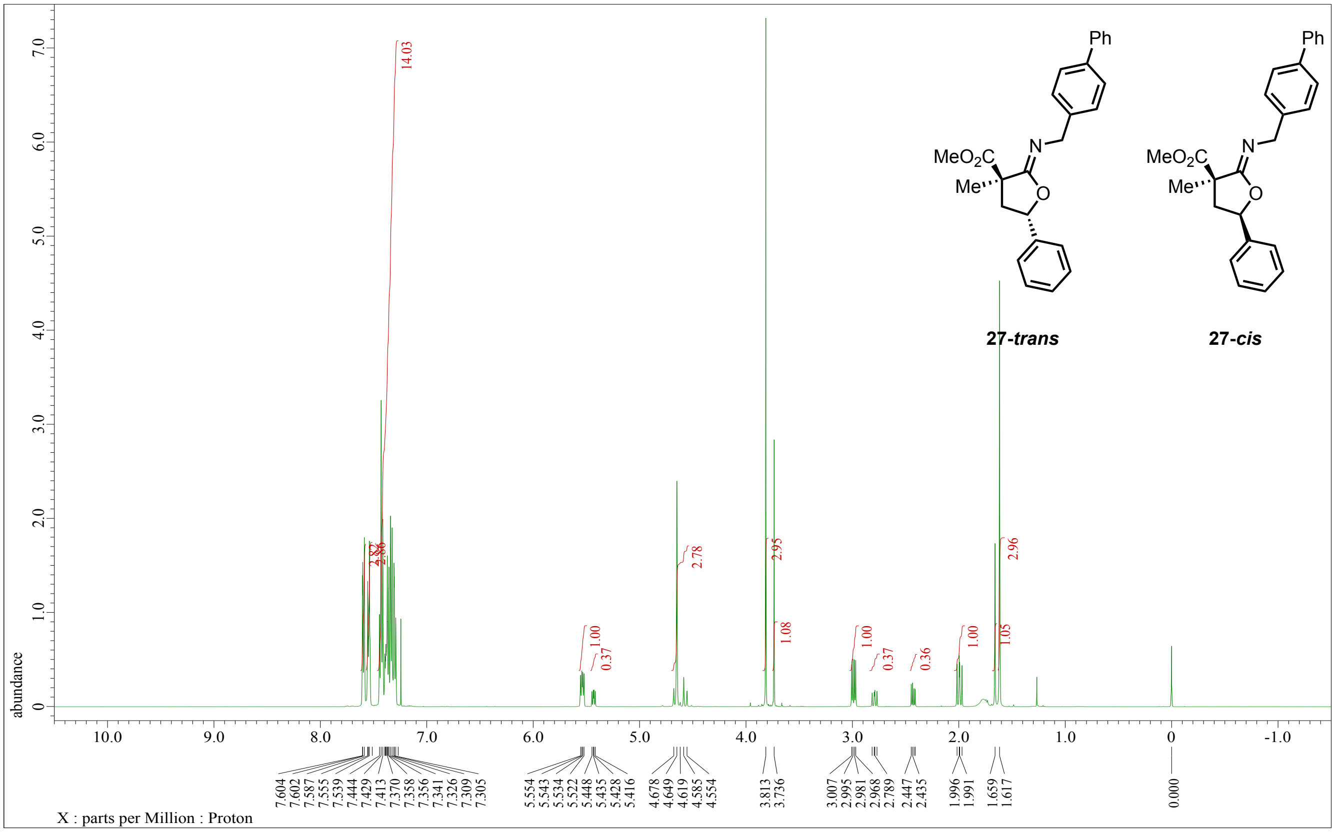


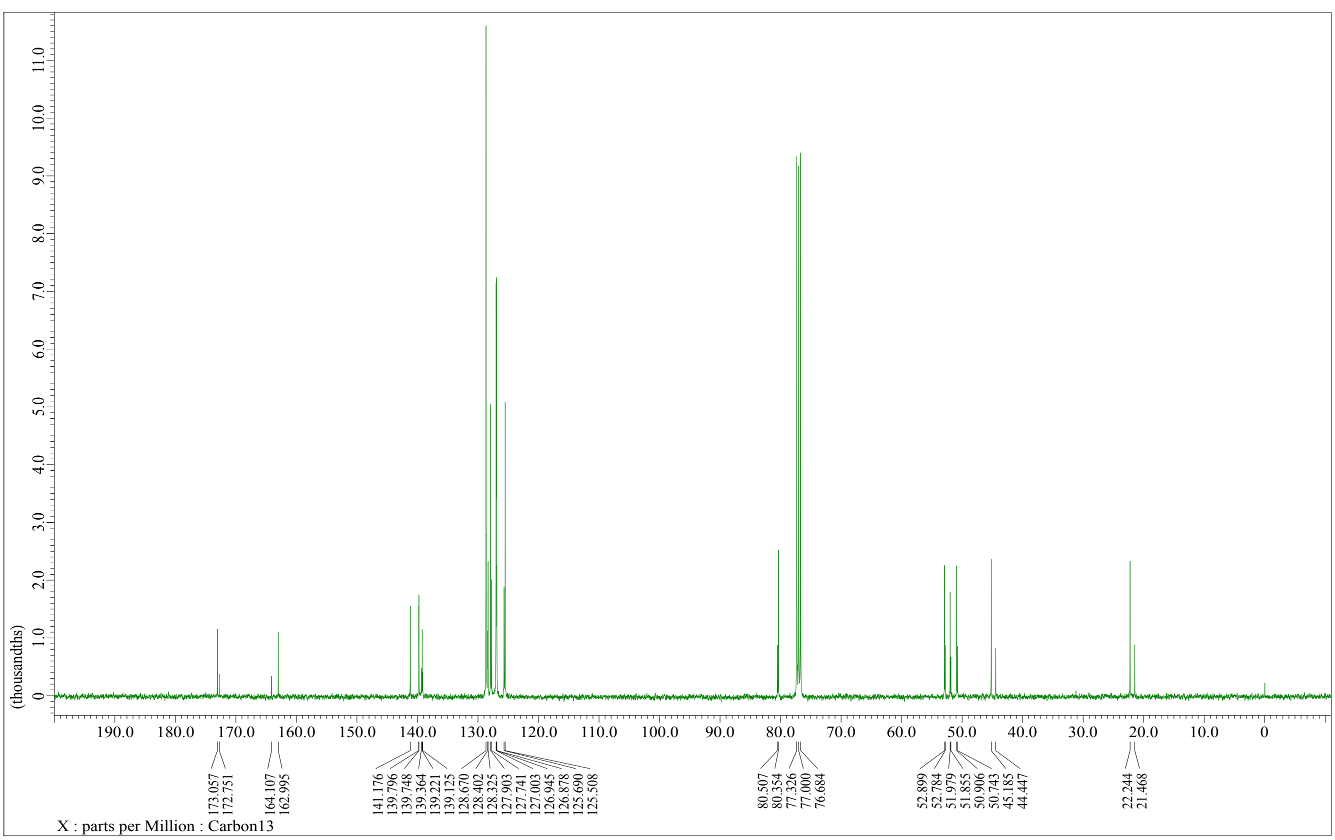




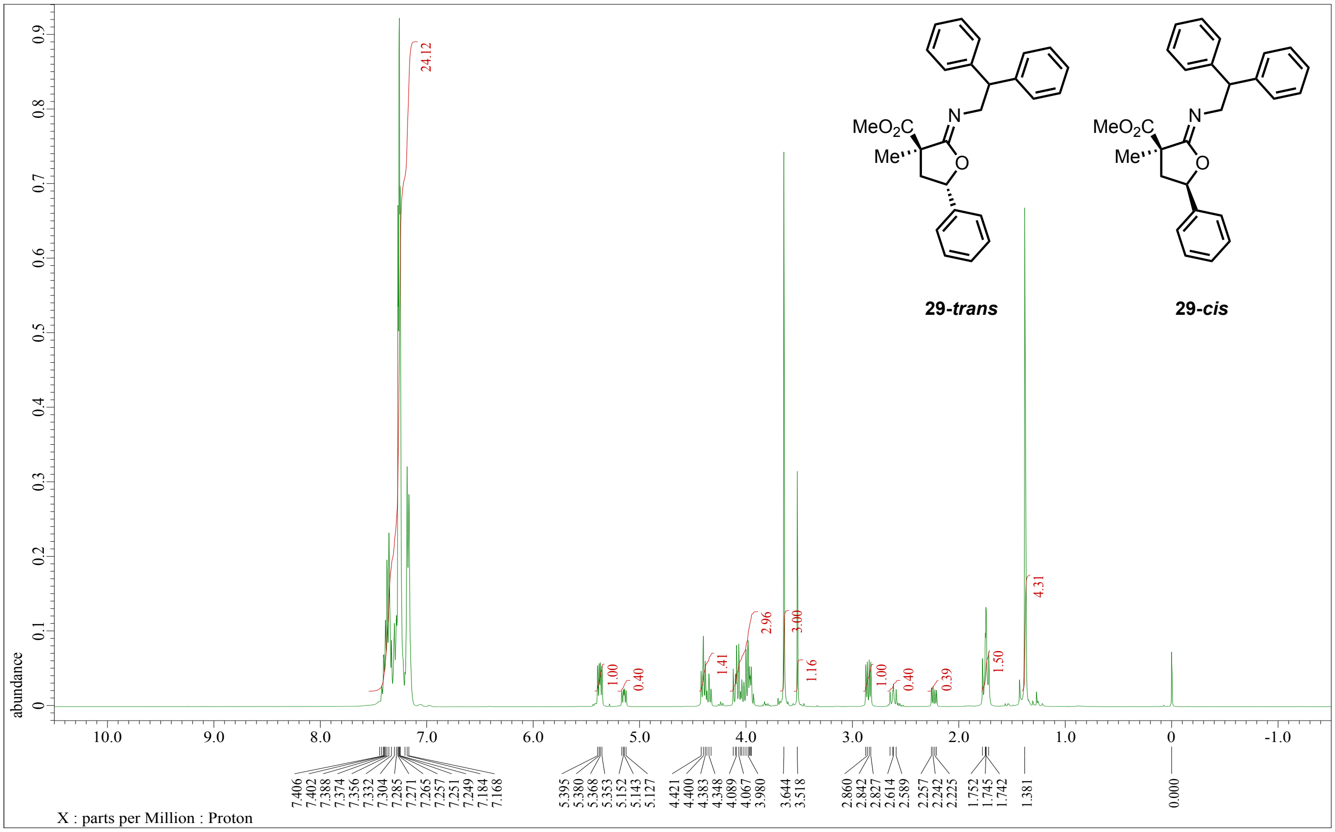
5.0
4.0
3.0
2.0
1.0
0
abundance
-10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0 -80.0 -90.0 -100.0 -110.0 -120.0 -130.0 -140.0 -150.0 -160.0 -170.0 -180.0 -190.0
-62.137
X : parts per Million : Fluorine19

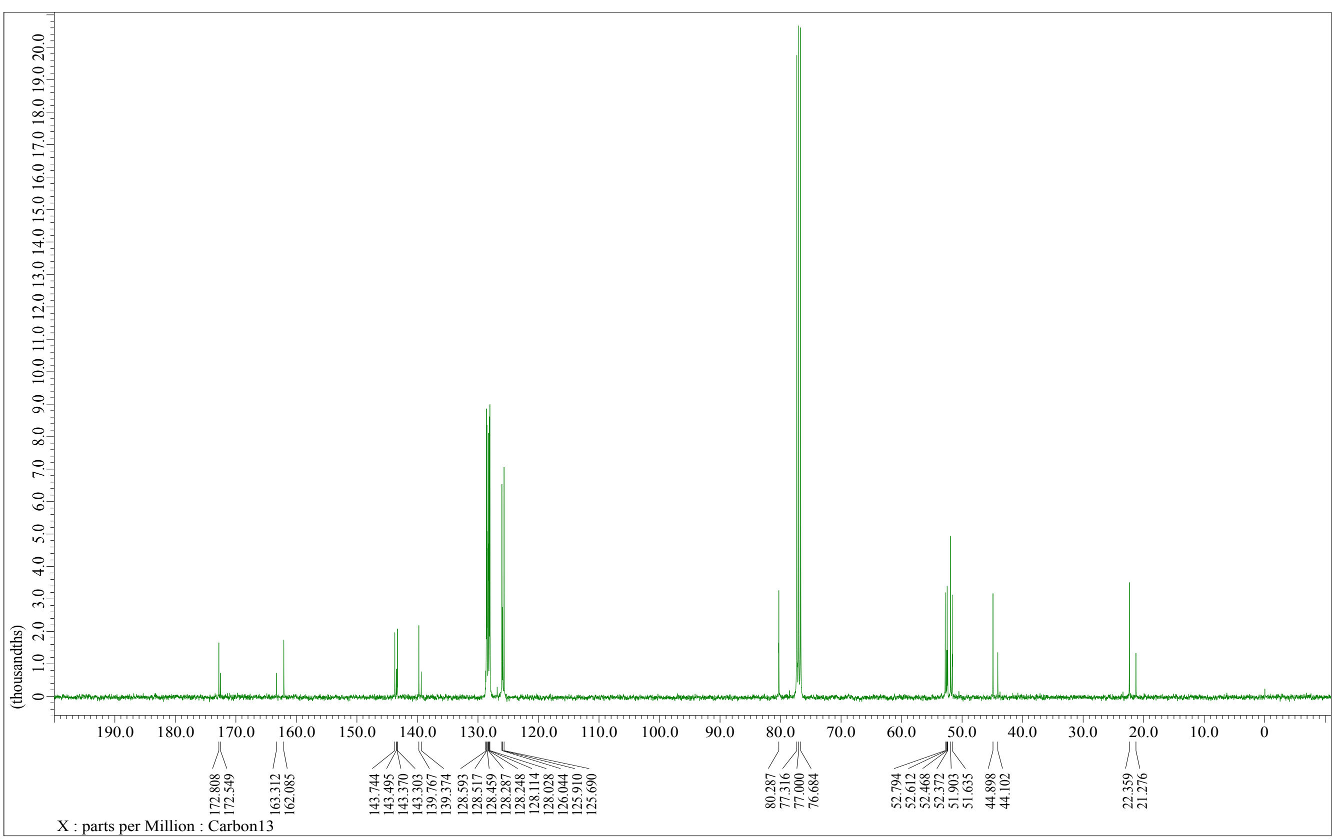
^1H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **27**_*trans, cis*-mixture



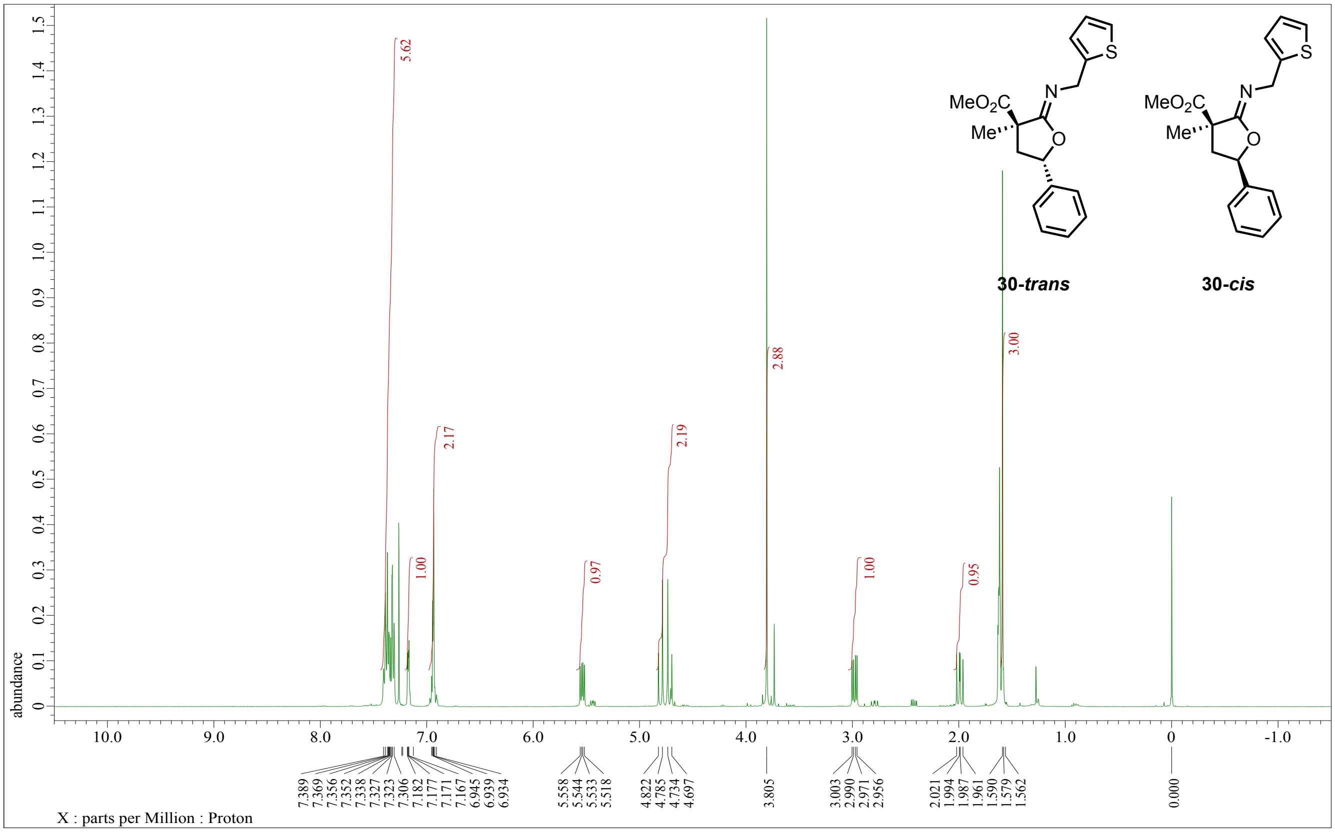


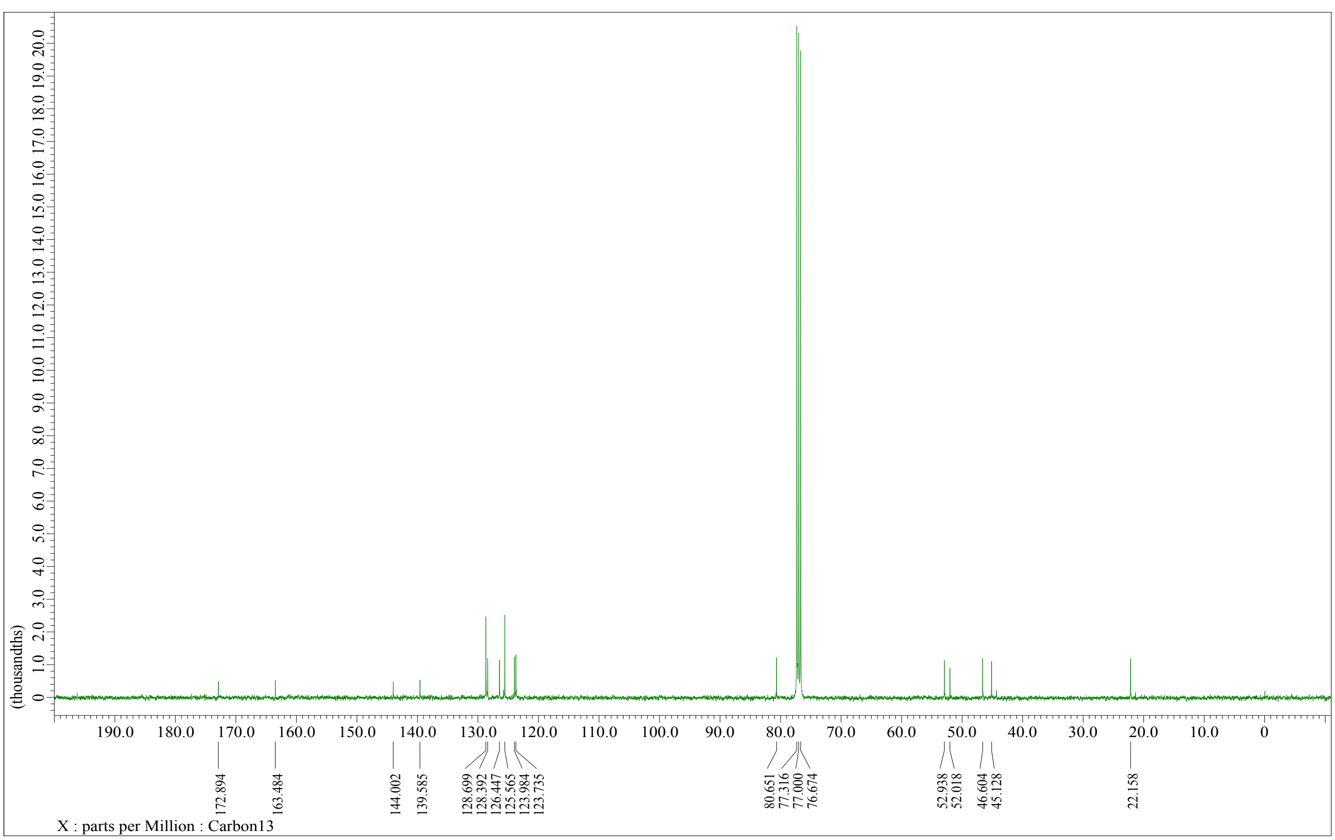
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **29**_*trans, cis*-mixture



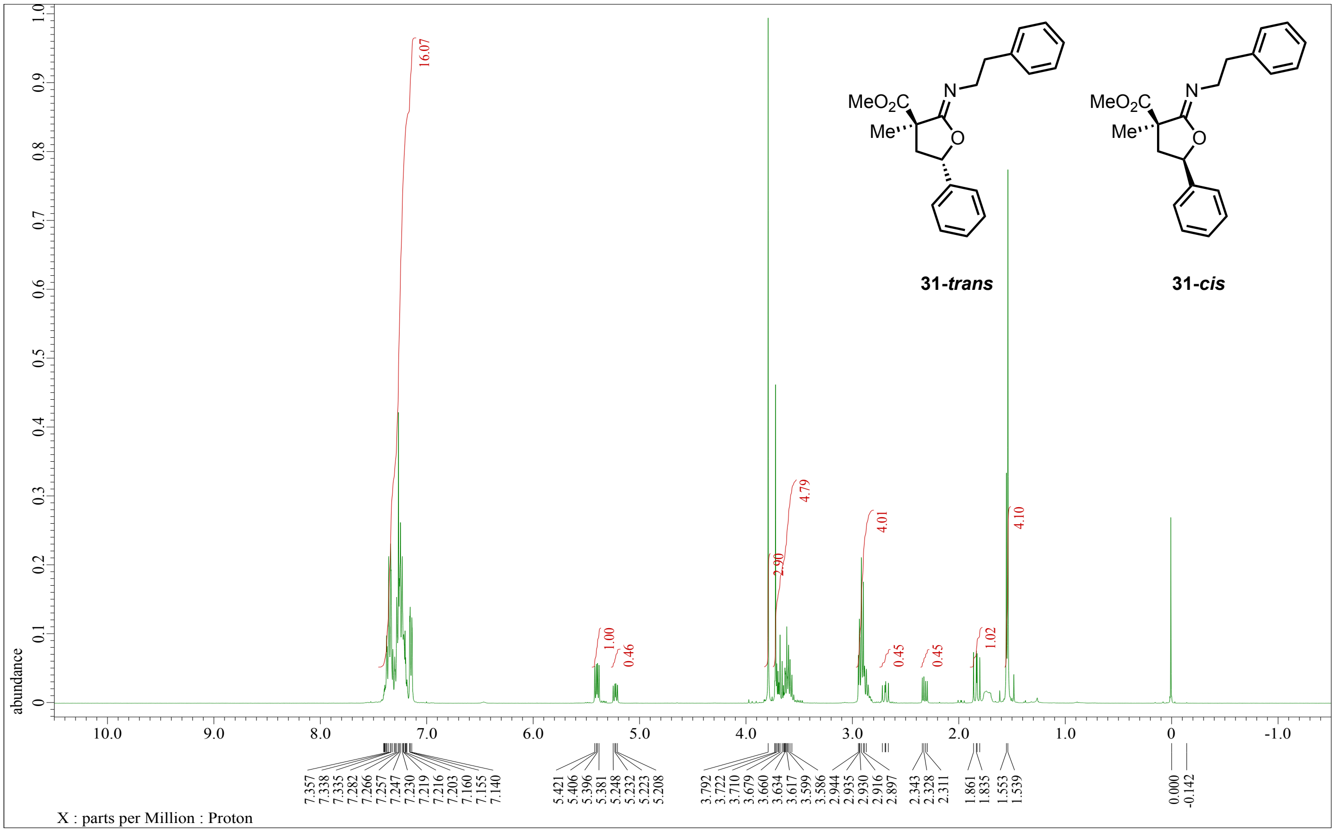


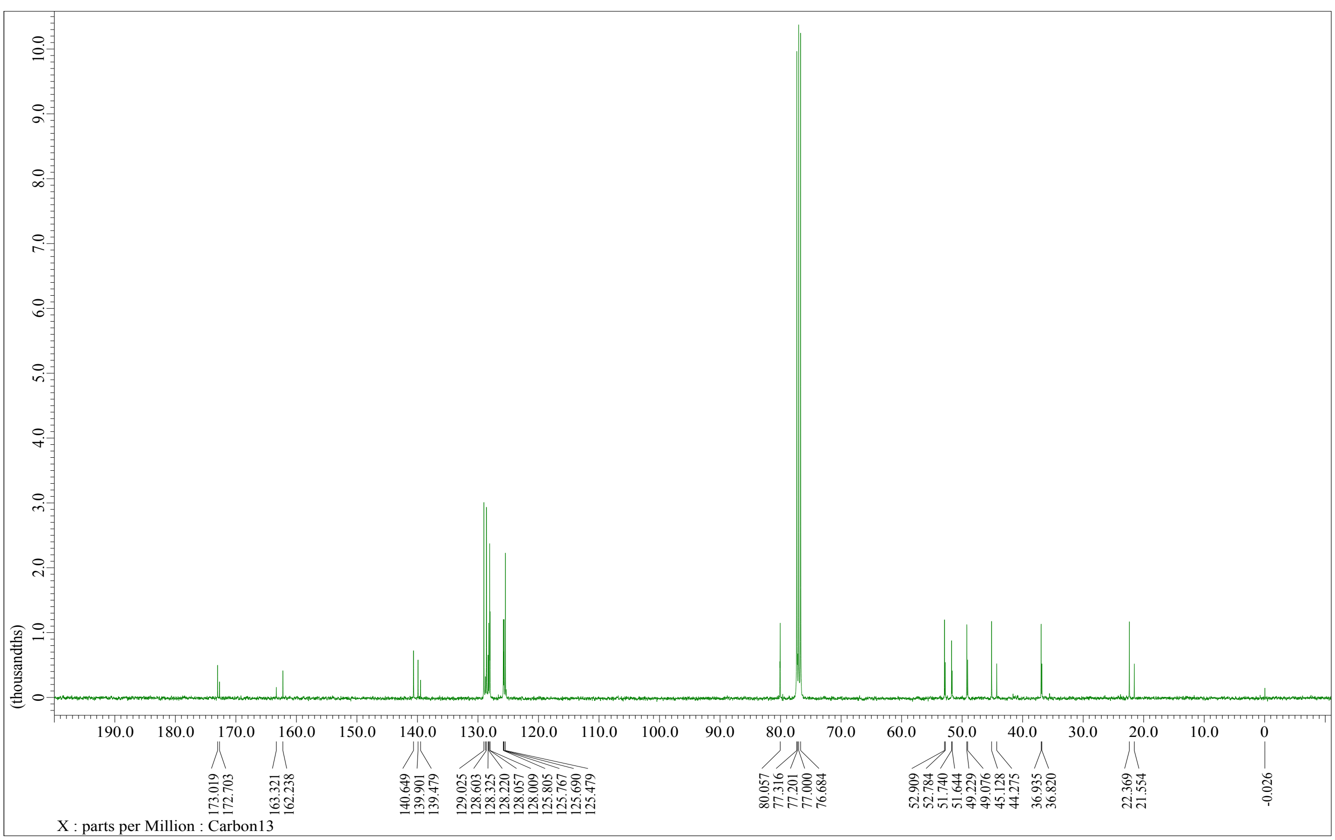
[1]H NMR ($CDCl_3$, 500 MHz) and [13]C{[1]H} NMR ($CDCl_3$, 125 MHz) spectra of **30**_*trans-major*



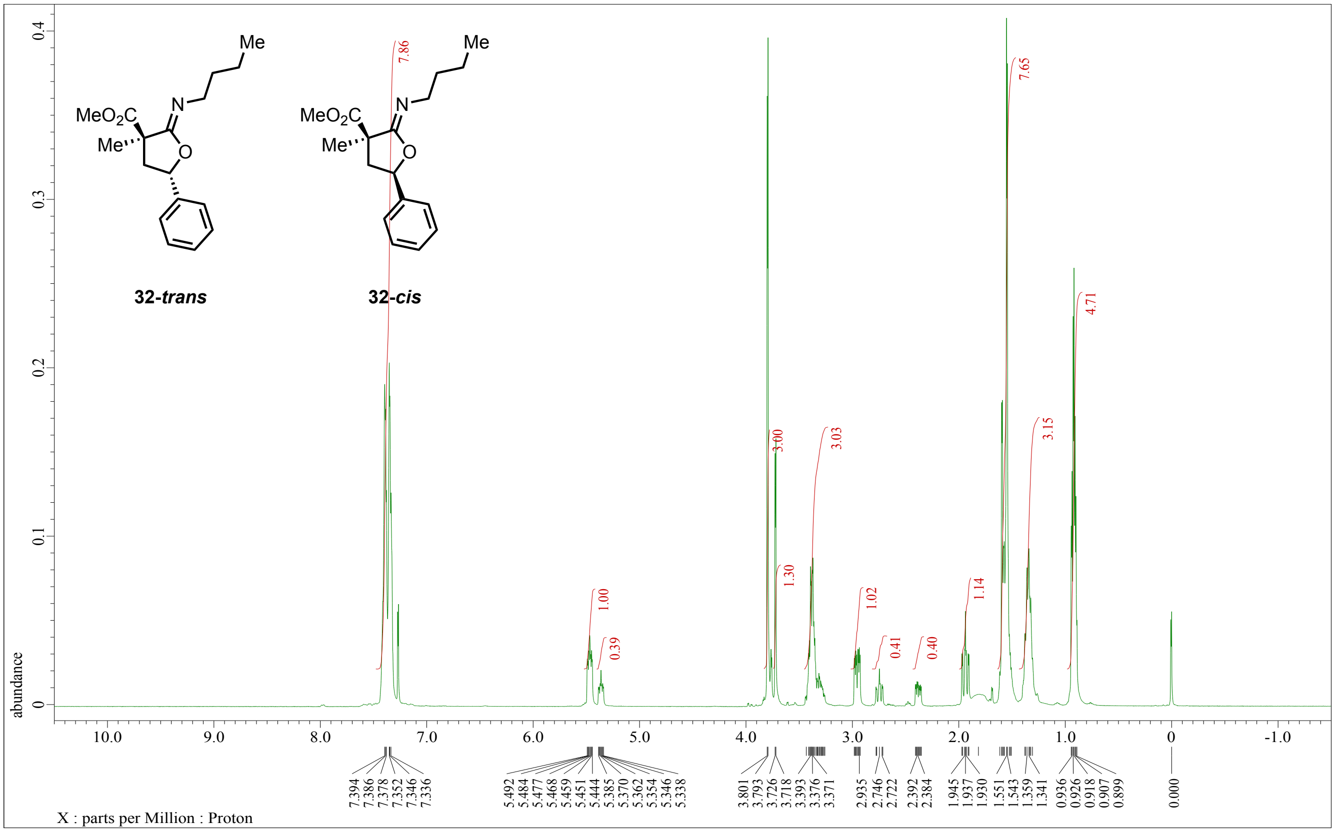


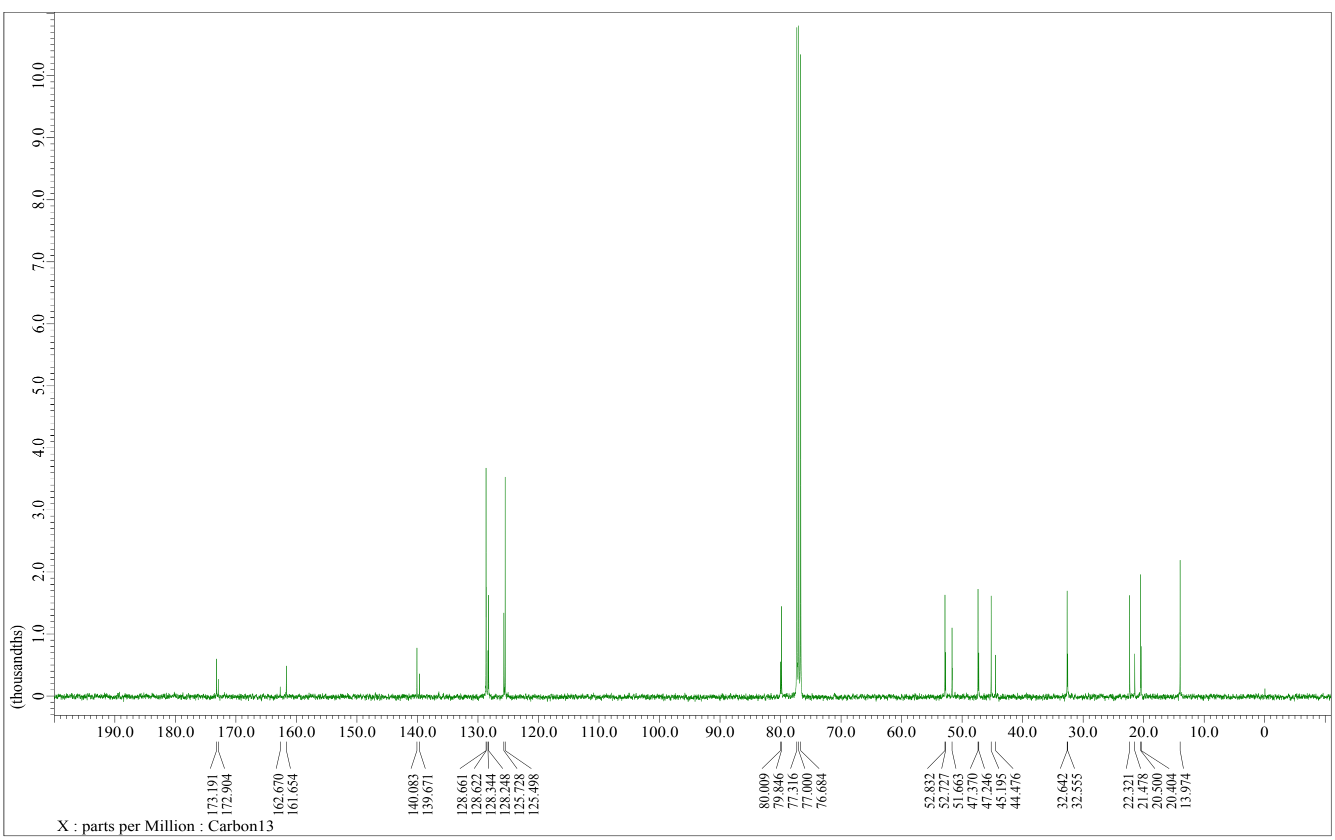
[1]H NMR ($CDCl_3$, 500 MHz) and [13]C{[1]H} NMR ($CDCl_3$, 125 MHz) spectra of **31**_*trans, cis*-mixture



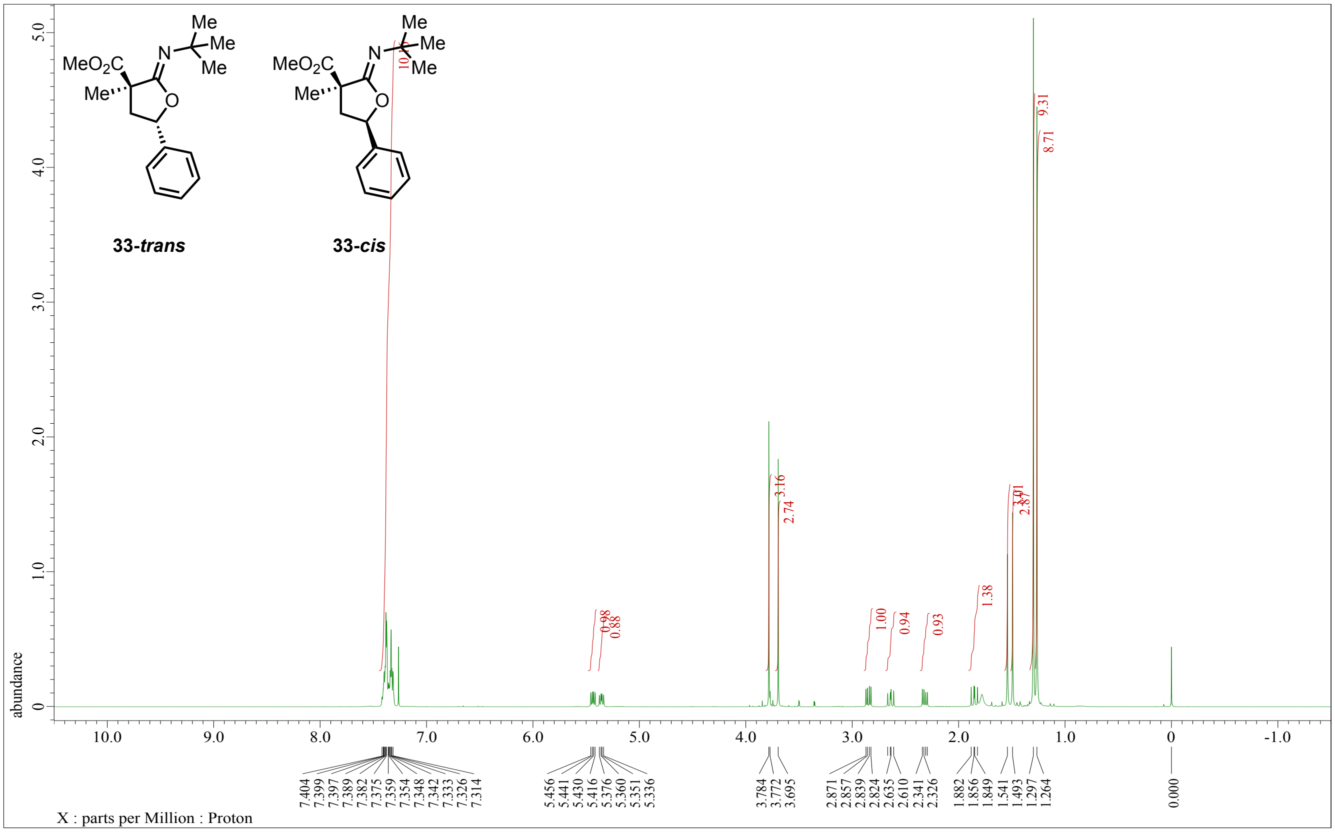


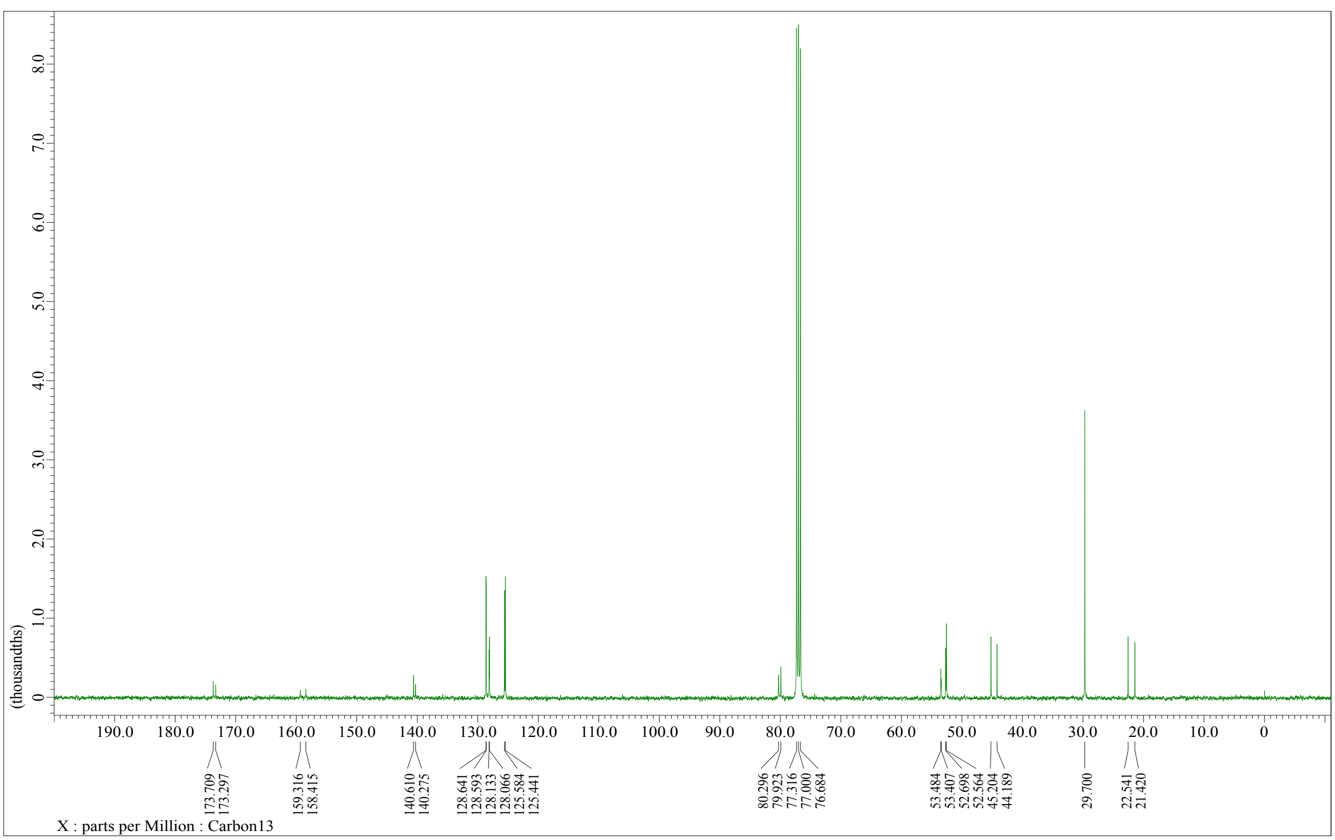
^{1}H NMR ($CDCl_3$, 500 MHz) and $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of **32**_*trans, cis*-mixture



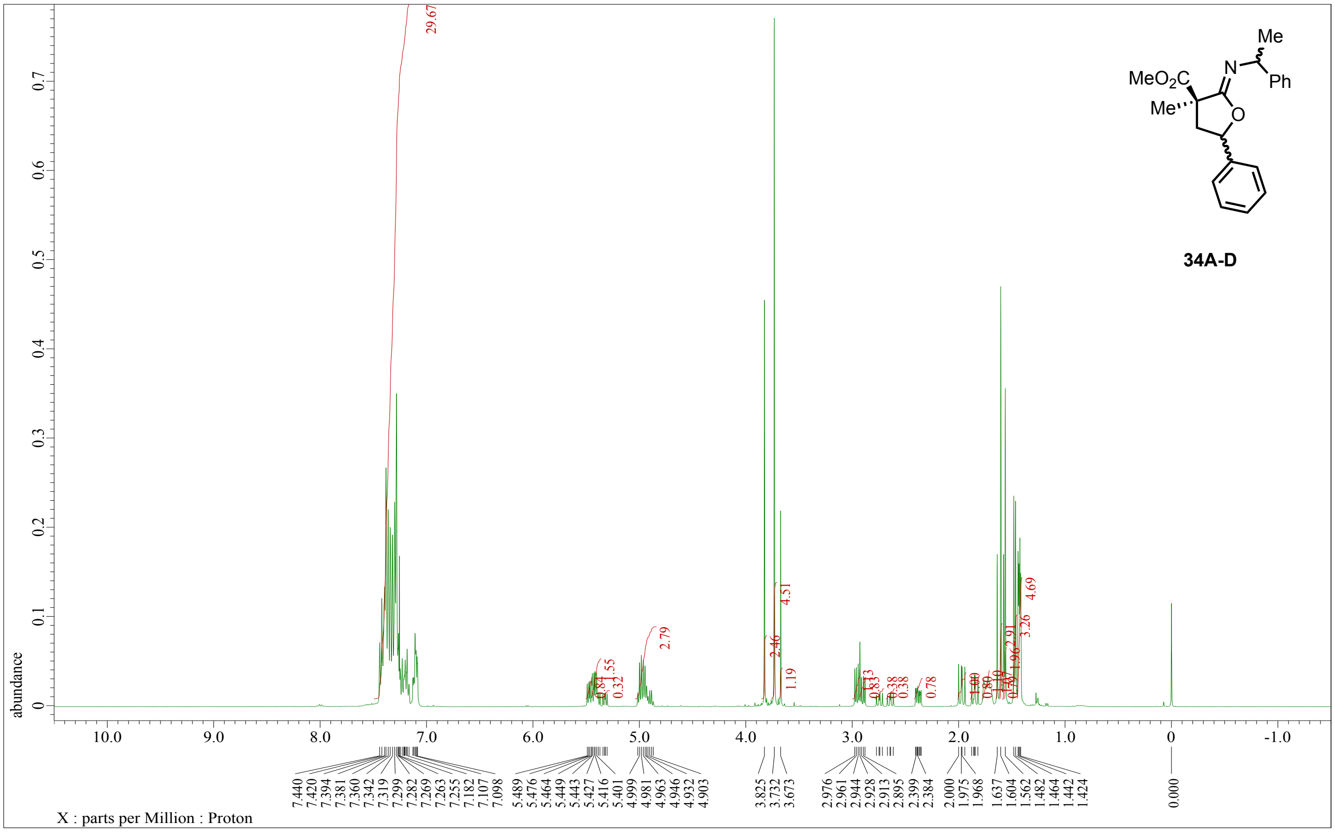


[1]H NMR ($CDCl_3$, 500 MHz) and [13]C{[1]H} NMR ($CDCl_3$, 125 MHz) spectra of **33**_*trans, cis*-mixture





^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of **34_*A, B, C, D***-mixture



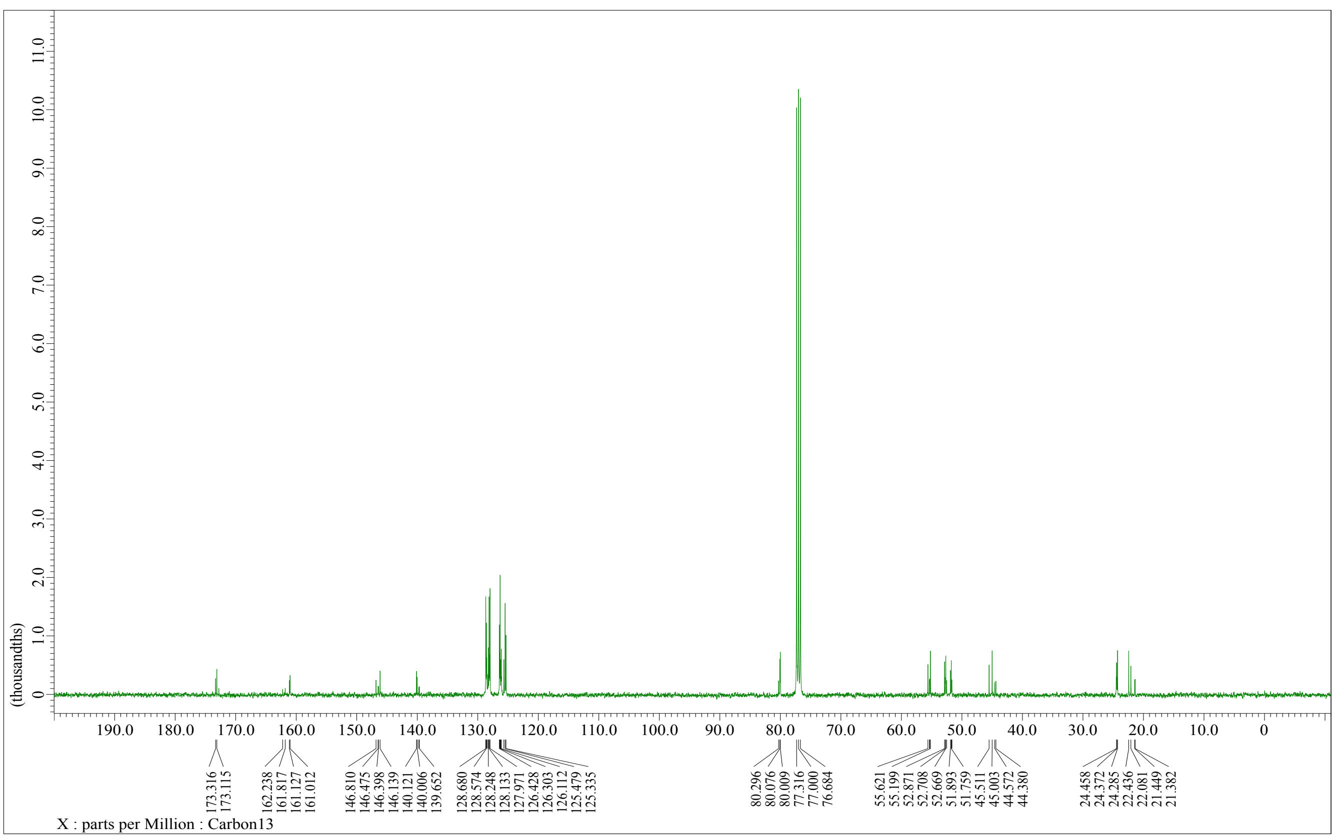
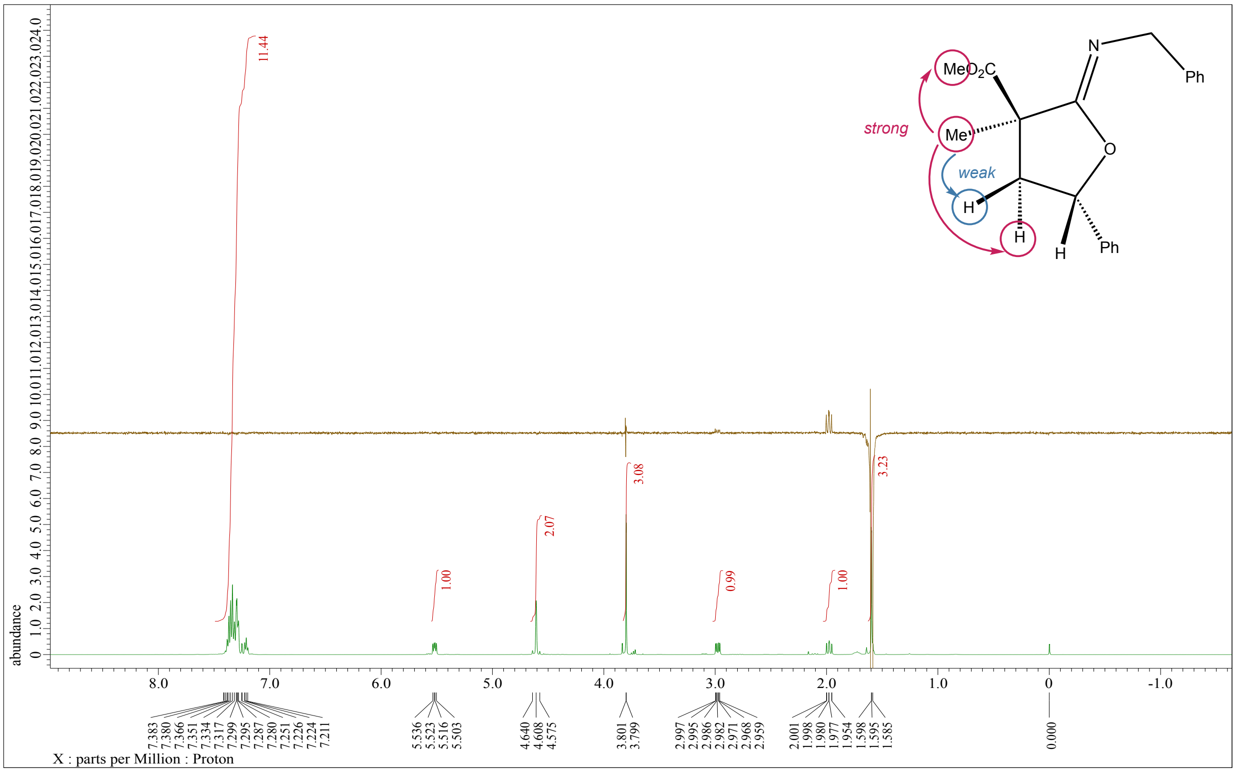
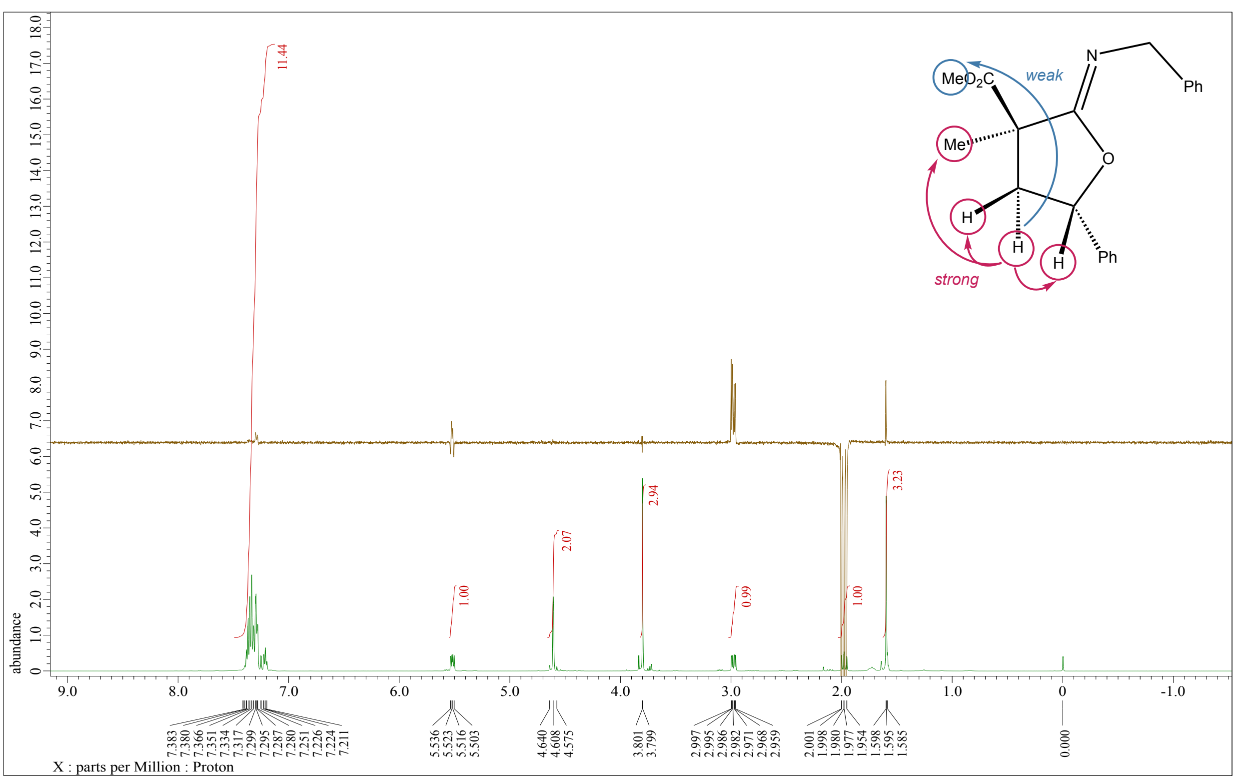


Figure S3. Key NOE of 4-trans

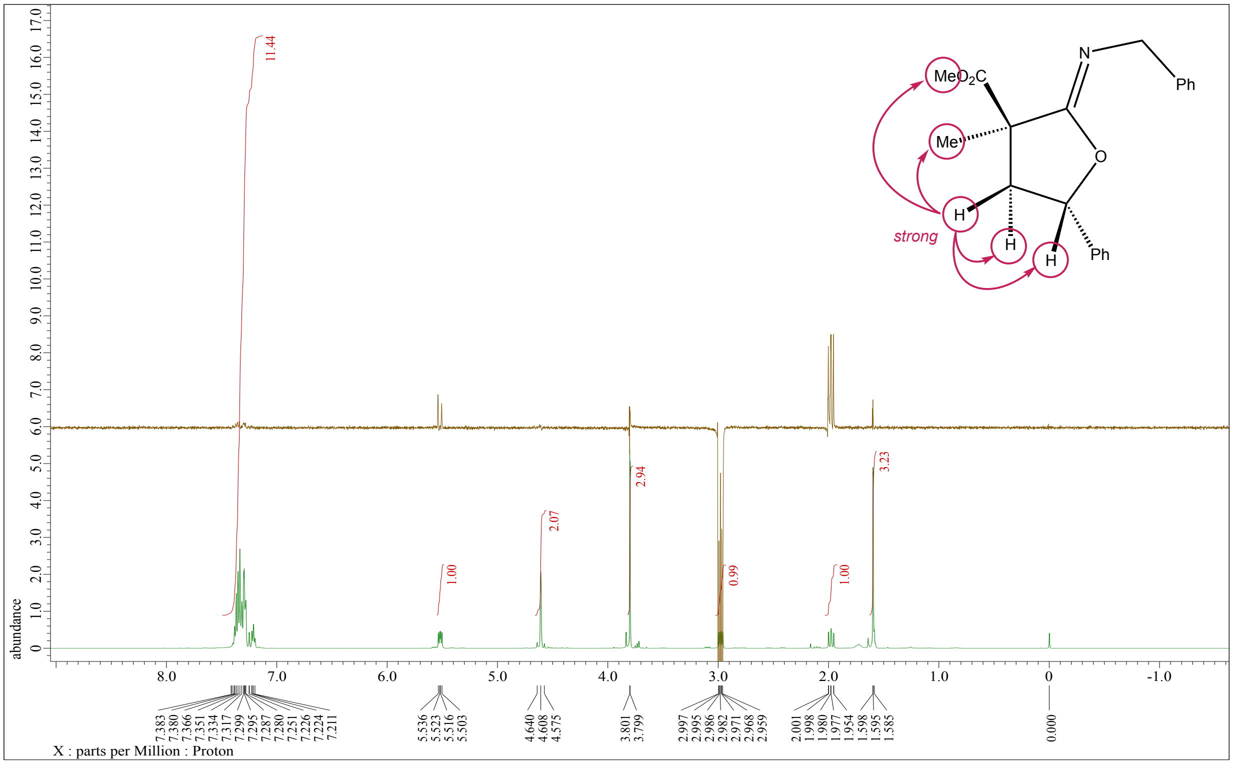
4_*trans*_NOE 1.59 ppm



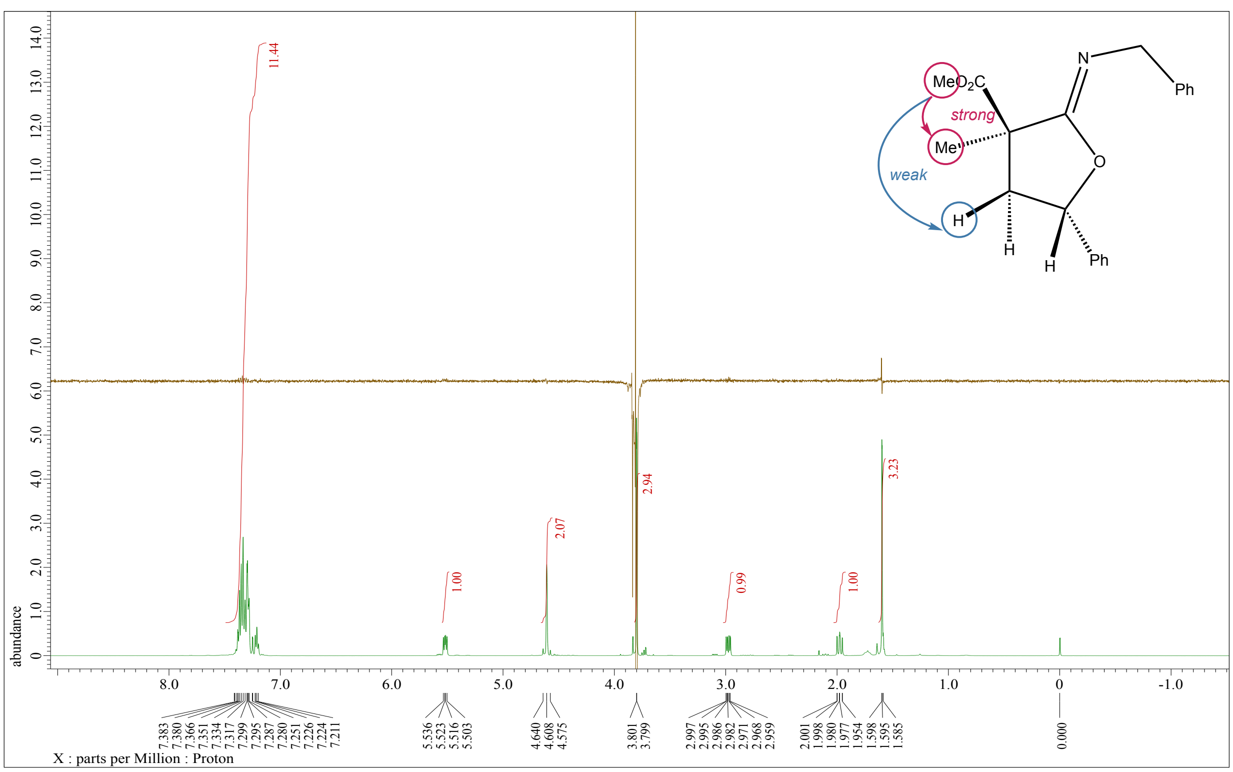
4_*trans*_NOE 1.98 ppm



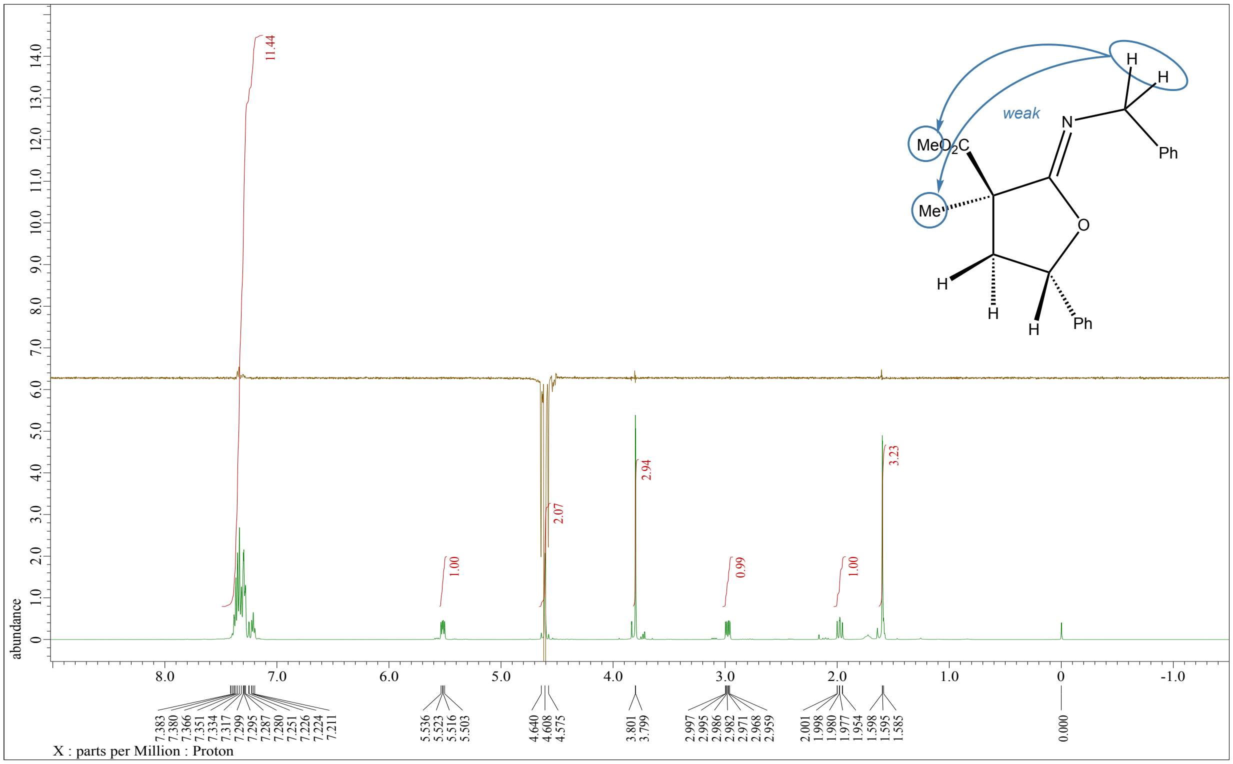
4_*trans*_NOE 2.98 ppm



4_*trans*_NOE 3.80 ppm



4_*trans*_NOE 4.60 ppm



4_*trans*_NOE 5.52 ppm

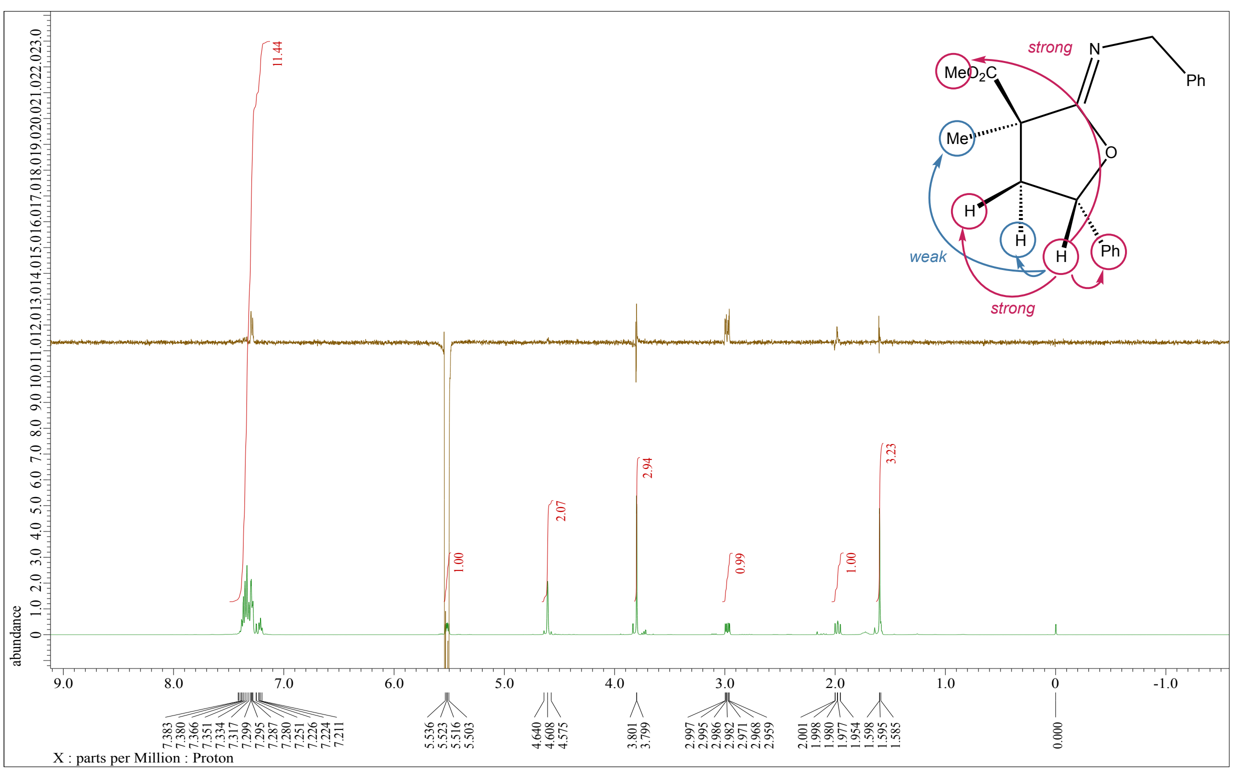
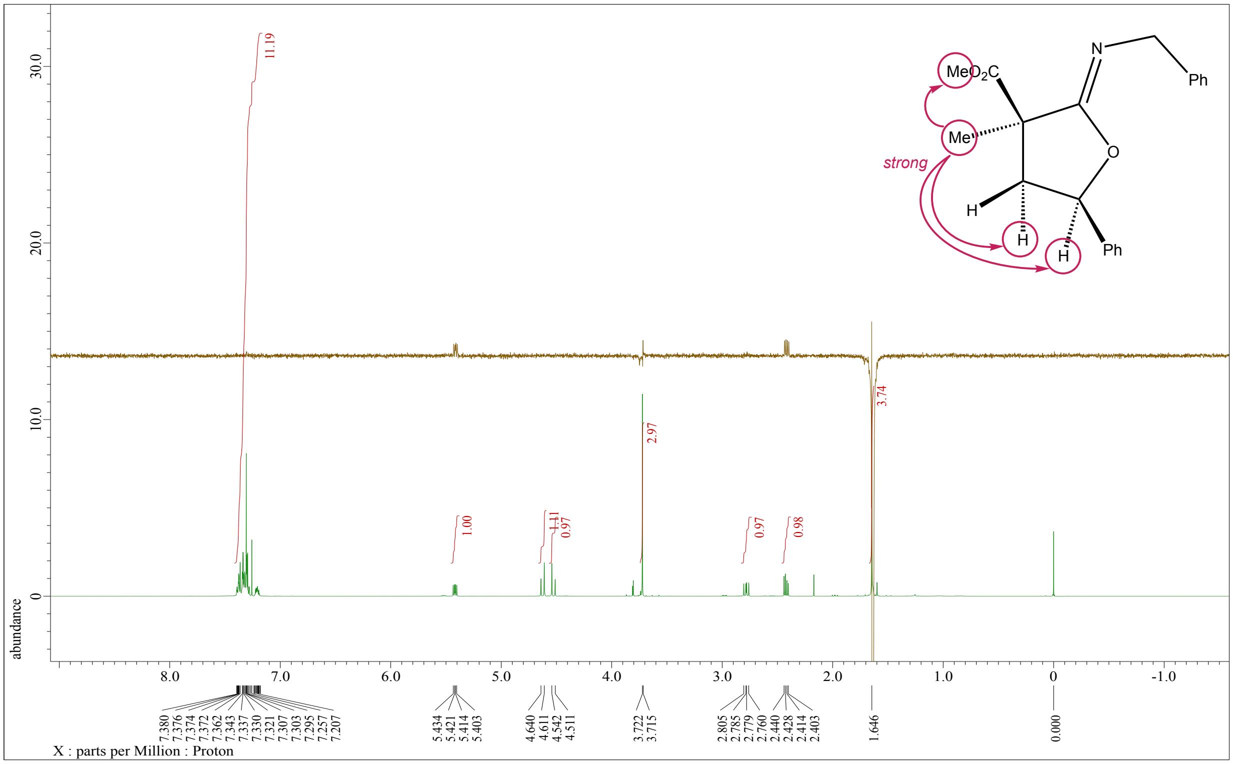
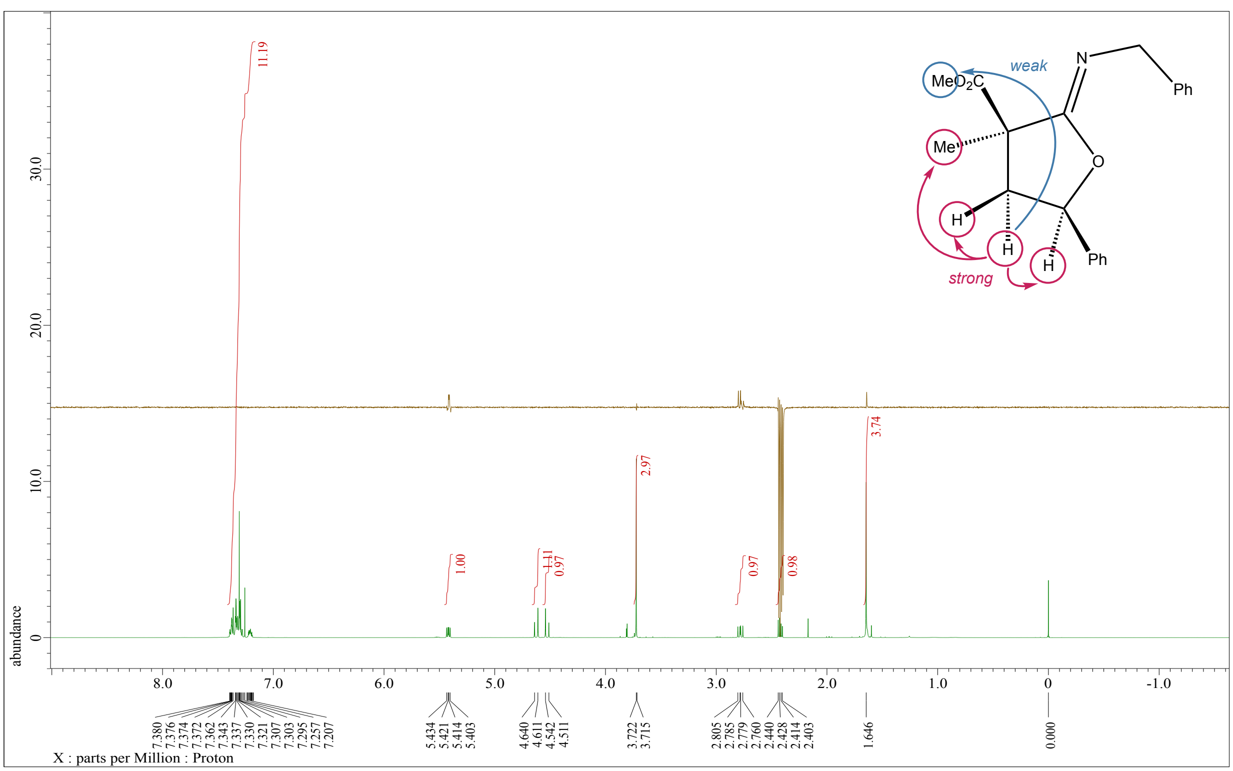


Figure S4. Key NOE of 4-cis

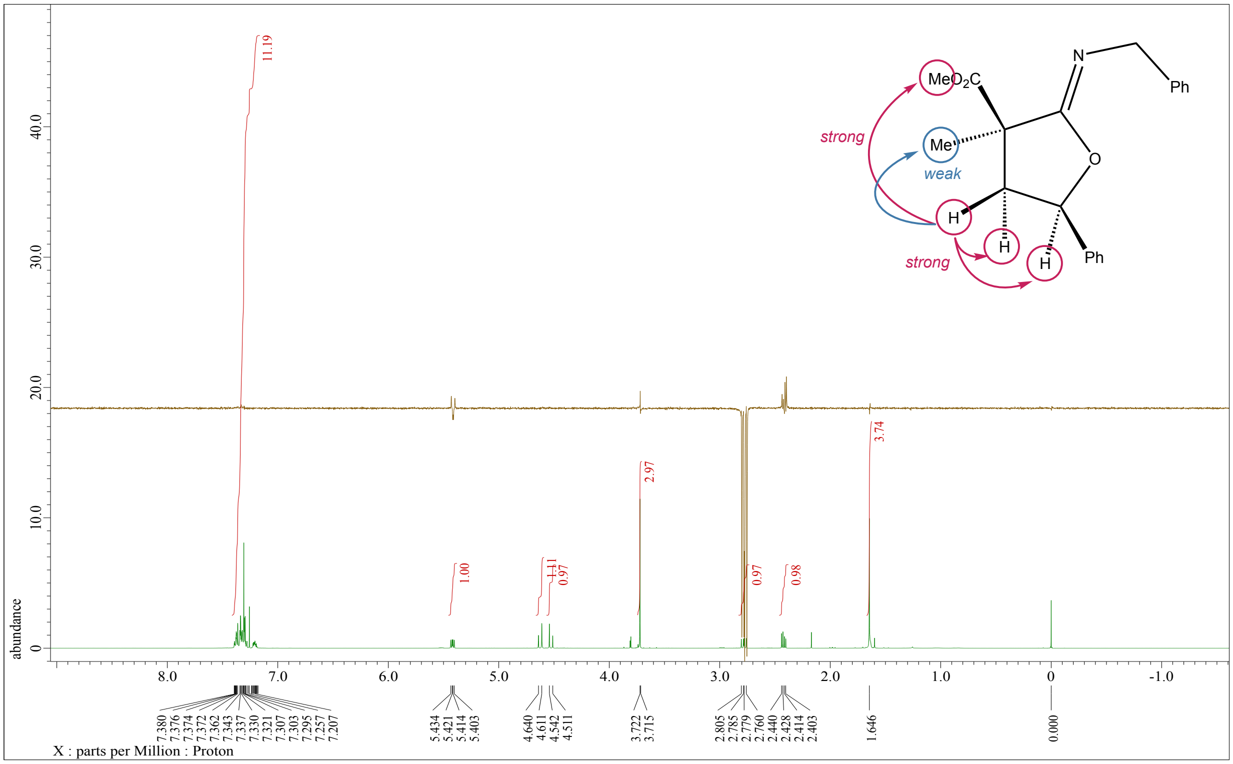
4_*cis*_NOE 1.64 ppm



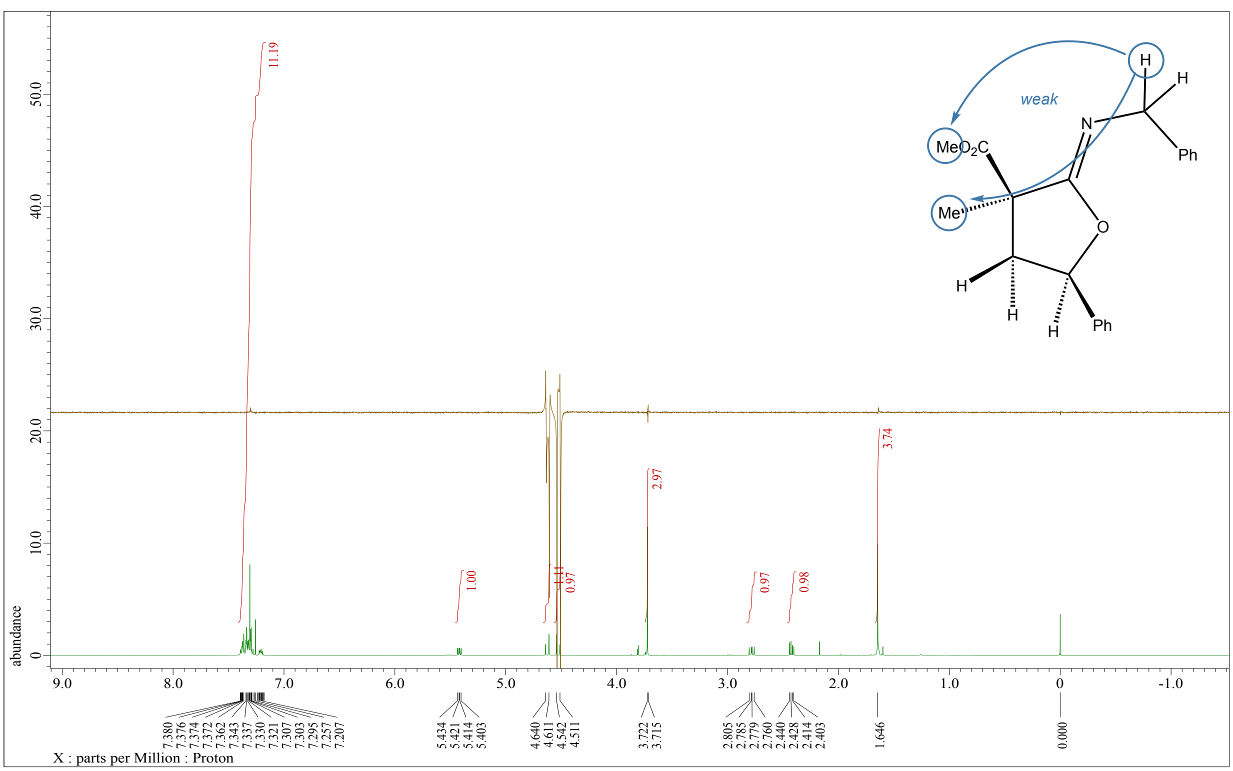
4_*cis*_NOE 2.42 ppm



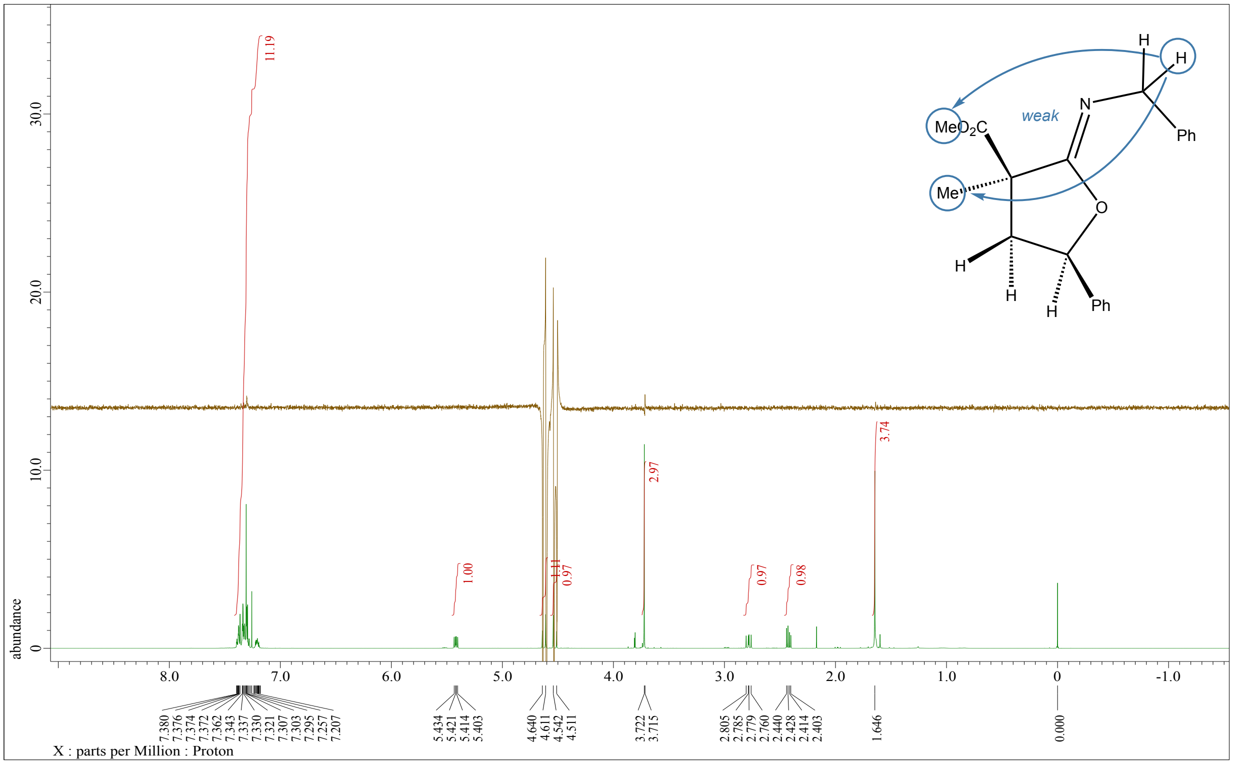
4_*cis*_NOE 2.78 ppm



4_*cis*_NOE 4.52 ppm



4_*cis*_NOE 4.62 ppm



4_*cis*_NOE 5.42 ppm