Supporting Information

Regio- and Enantioselective Linear Cross-Dimerizations between Conjugated Dienes and Acrylates Catalyzed by New Ru(0) Complexes

Yuki Hiroi,[†] Nobuyuki Komine,[†‡] Sanshiro Komiya,[†‡] Masafumi Hirano[†‡*]

[†] Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-26 Nakacho, Koganei, Tokyo 184-8588, Japan.
[‡]Japan Science and Technology Agency (JST), ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

*Phone and Fax: +81 423 877 044. E-mail: hrc@cc.tuat.ac.jp.

Table of Contents

P. S2. X-ray Crystallographic data for **2d**.
P. S4-7. X-ray Crystallographic data for **4ba** and **4d**.
P. S8-10. Chiral GLC chromatogram for **10a**
P. S11-18. Chiral GLC chromatogram for **11a**
P. S19. Cross dimerization reaction between 3,4-dimethyl-2,4-hexadiene and methylmethacrylate
P. S20-21. ^{1}H, ^{13}C NMR spectra of dimethylpentadiene, dimethylhexadiene.
P. S22. ^{1}H NMR spectra of **1e**.
P. S22-27. ^{1}H, ^{13}C, ^{31}P and DEPT NMR spectra of compound **2**.
P. S28-32. ^{1}H, ^{13}C, ^{31}P and DEPT NMR spectra of compound **3**.
P. S32-35. ^{1}H and ^{13}C NMR spectra of **4**.
P. S36-39. ^{1}H and ^{13}C NMR spectra of **5**.
P. S40-47. ^{1}H, ^{13}C, ^{1}H COSY, Phase Sensitive NOESY and ^{13}C-^{1}H HETCOR NMR spectra of **6**.
P. S48-49. ^{1}H, ^{13}C, and ^{1}H COSY NMR spectra of **7**.
P. S50-51. ^{1}H and ^{13}C NMR spectra of **8**.
P. S52-58. ^{1}H, ^{13}C, ^{1}H COSY, Phase Sensitive NOESY and ^{13}C-^{1}H HETCOR NMR spectra of **9**.
P. S59-65. ^{1}H, ^{13}C and Phase Sensitive NOESY NMR spectra of **10**.
P. S66-75. ^{1}H, ^{13}C, ^{1}H COSY, Phase Sensitive NOESY and ^{13}C-^{1}H HETCOR NMR spectra of **11**.
P. S76-83. ^{1}H, ^{13}C, ^{1}H COSY, Phase Sensitive NOESY and ^{13}C-^{1}H HETCOR NMR spectra of cross-dimer between 3,4-dimethyl-2,4-hexadiene and methylmethacrylate.

•Ru(acac)$_2$(dbcot) (**2d**)

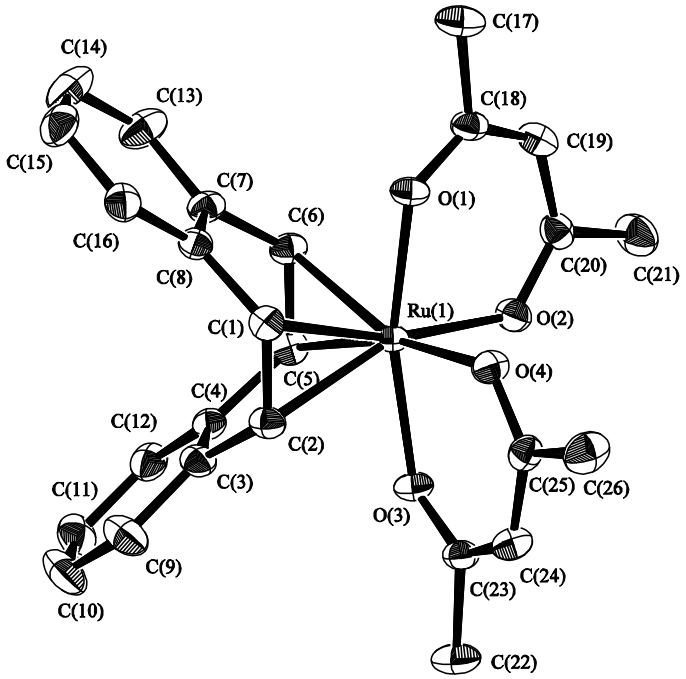


Figure S1 Molecular structure of Ru(acac)$_2$(dbcot) (**2d**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Table S1. Crystallographic and Physical Data for **2d**

chemical formula	$C_{26}H_{26}O_4Ru$
formula weight	503.56
color	yellow
crystal dimensions (mm)	0.467 X 0.319 X 0.155
crystal system	triclinic
Lattice Parameters	
a (Å)	10.4282
b (Å)	10.6707(2)
c (Å)	12.0312(7)
α(deg.)	86.53(1)
β(deg.)	82.91(1)
γ(deg.)	60.82(5)
V (Å^3)	1159.92(9)
space group	P -1(No. 2)
Z	2
D_{calcd} (g cm^{-3})	1.442
F_{000}	516
μ (mm^{-1})	0.705
radiation	Mo Ka (l = 0.71075 Å)
temp. (℃)	-73.1
Scan type	ω
diffrn reflns number	8677
reflns number total	5189
reflns number gt	4937
No. Variables	280
R1 (w*R2*)	0.0259 (0.0683)
GOF	1.085

•Ru(2,3-dimethyl-1,3-butadiene)(CO)(bod) (**4ba**)

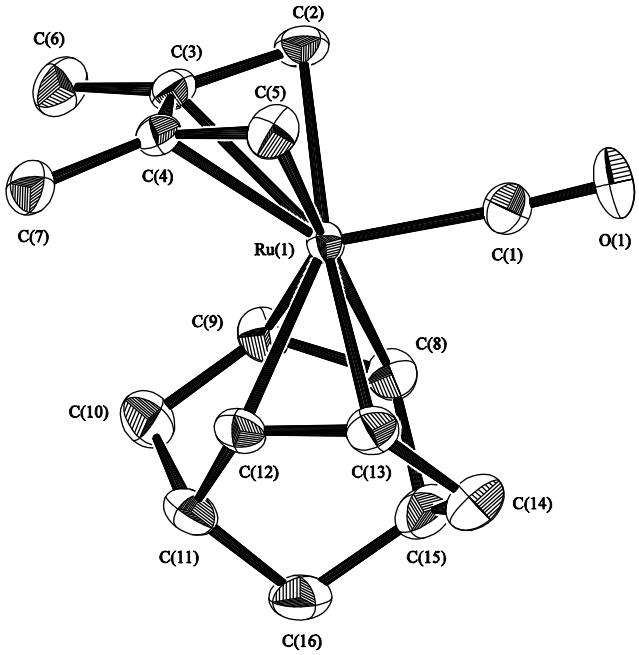


Figure S2 Molecular structure of Ru(2,3-dimethyl-1,3-butadiene)(CO)(bnd) (**4ba**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Table S2. Crystallographic and Physical Data for **4ba**

chemical formula	$C_{16}H_{22}ORu$
formula weight	331.42
color	colorless
crystal dimensions (mm)	0.260X 0.194 X 0.188
crystal system	*triclinic*
Lattice Parameters	
a (Å)	7.400(2)
b (Å)	8.555(2)
c (Å)	11.976(3)
α(deg.)	99.608(3)
β(deg.)	99.618(2)
γ(deg.)	108.609(3)
V (Å^3)	688.4(3)
space group	*P*-1 (No. 2)
Z	2
D_{calcd} (g cm^{-3})	1.599
F_{000}	340.00
μ (mm^{-1})	1.125
radiation	Mo Kα (l = 0.71075 Å)
temp. (℃)	-73.1
Scan type	ω
diffrn reflns number	5409
reflns number total	3092
reflns number gt	3010
No. Variables	163
R1 (w*R2*)	0.0288 (0.0717)
GOF	1.170

•Ru(2,3-dimethyl-1,3-butadiene)(CO)(dbcot) (**4d**)

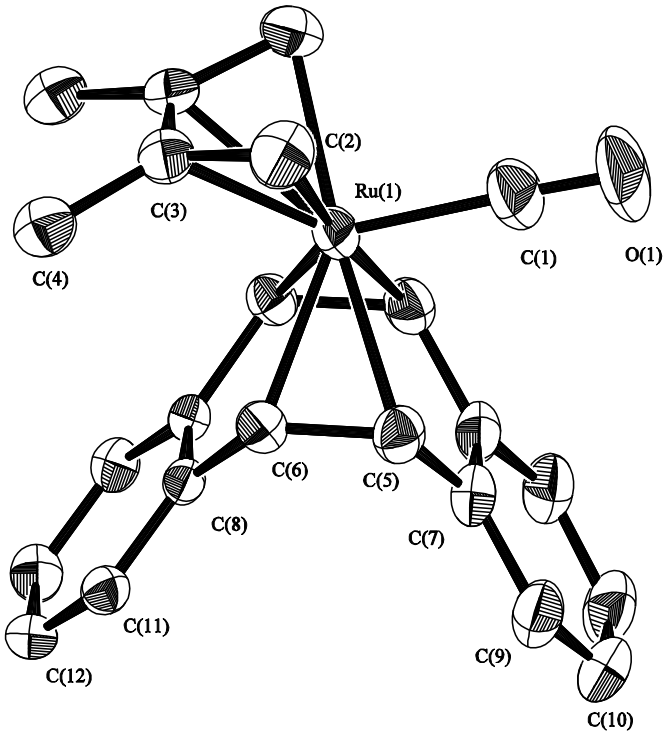


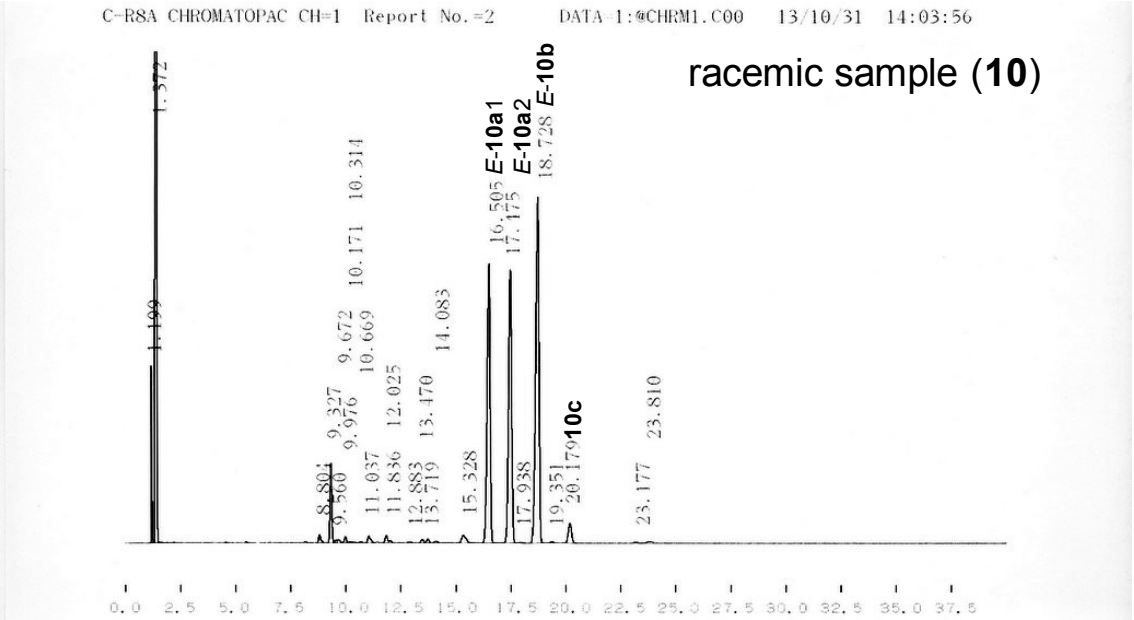
Figure S3 Molecular structure of Ru(2,3-dimethyl-1,3-butadiene)(CO)(dbcot) (**4d**), All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Table S3. Crystallographic and Physical Data for **4d**

chemical formula	$C_{23}H_{22}ORu$
formula weight	415.50
color	pale yellow
crystal dimensions (mm)	0.091X 0.089 X 0.075
crystal system	*monoclinic*
Lattice Parameters	
a (Å)	9.017(3)
b (Å)	11.509(3)
c (Å)	9.073(3)
β(deg.)	104.913(3)
V (Å^3)	909.9 (5)
space group	$P2_1/m$ (No. 11)
Z	2
D_{calcd} (g cm^{-3})	1.516
F_{000}	424.00
μ (mm^{-1})	0.869
radiation	Mo Kα (l = 0.71075 Å)
temp. (℃)	-73.1
Scan type	ω
diffrn reflns number	7319
reflns number total	2172
reflns number gt	1940
No. Variables	118
R1 (w*R2*)	0.0438 (0.0987)
GOF	1.225

Chiral GLC chromatogram for **10**

Conditions: Column Rt-γDEXsa, oven temp. = 120 ˚C, carrier gas (He) linear velocity 50 cm/sec.



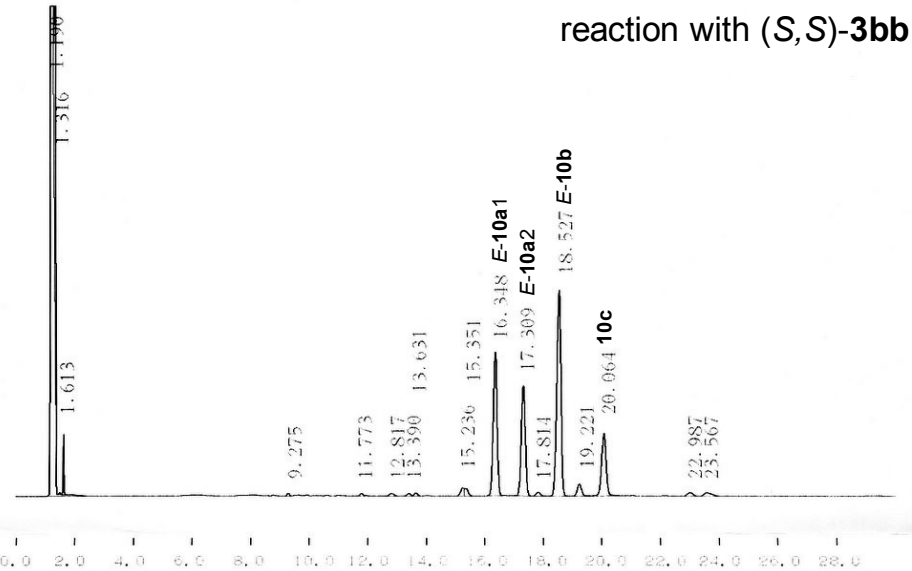
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	1.199	39799	23125	V		0.5208	
	3	1.372	6283074	2062478	SV		82.225	
	24	8.804	7368	1109			0.0964	
	25	9.327	57323	10402	V		0.7502	
	26	9.56	2348	393	V		0.0307	
	27	9.672	3454	436	V		0.0452	
	28	9.976	5482	858	V		0.0717	
	29	10.171	1050	166	V		0.0137	
	30	10.314	1653	163	V		0.0216	
	31	10.669	1597	194	V		0.0209	
	32	11.037	8600	957			0.1126	
	34	11.836	8021	1037	V		0.105	
	35	12.025	2465	331	V		0.0323	
	37	12.883	1919	171			0.0251	
	39	13.47	4100	526	V		0.0537	
	40	13.719	4265	535	V		0.0558	
	41	14.083	2615	274	V		0.0342	
	43	15.328	14248	1016			0.1865	
	44	16.505	341139	36411			4.4644	*E*-**10a**1
	46	17.475	340706	35613			4.4587	*E*-**10a**2
	47	17.938	1397	139			0.0183	
	48	18.728	471315	45144			6.168	*E*-**10b**
	49	19.351	2342	227	V		0.0306	
	50	20.179	27496	2617			0.3598	**10c**
	51	23.177	2553	185			0.0334	
	52	23.81	4991	231	V		0.0653	
		TOTAL	7641314	2224735			100	

No.	Time	Area	Area %	
1	16.51	341139	50.0	*E*-**10a1**
2	17.48	340706	50.0	*E*-**10a2**

Figure S4-1. Chiral GLC chart for the *rac*-cross dimer **10**

C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 13/11/25 16:03:48

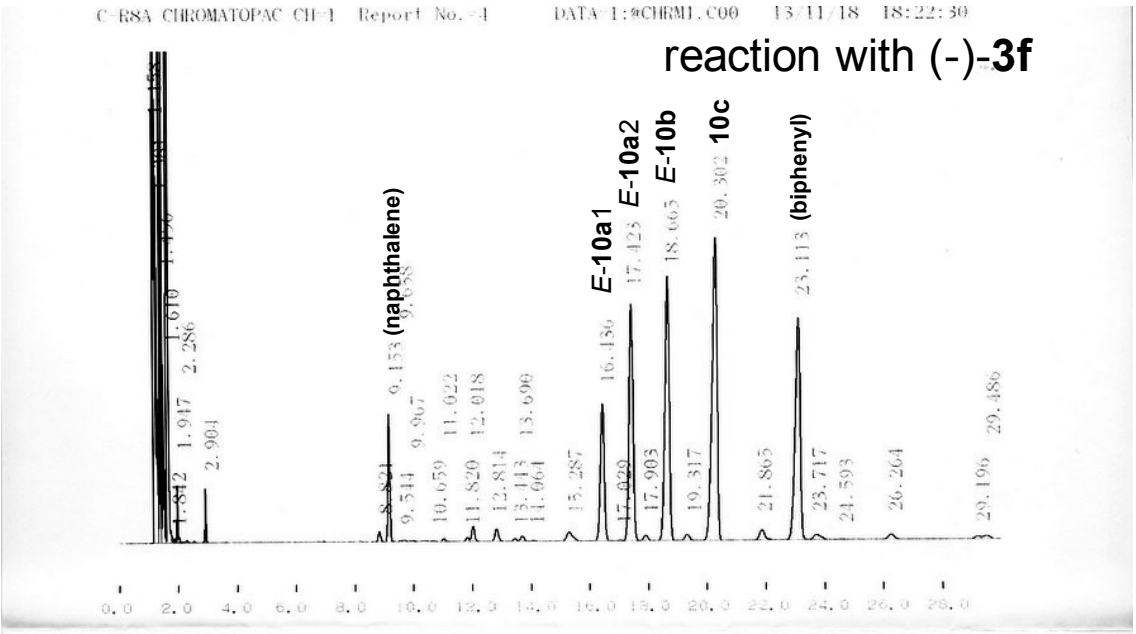


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.19	53577244	28875772	S		98.4402	
	2	1.316	477186	276314	T		0.8768	
	4	1.613	6510	3956	TV		0.012	
	26	9.275	1110	197			0.002	
	37	11.773	1239	181			0.0023	
	39	12.817	1821	173			0.0033	
	41	13.39	1350	175	V		0.0025	
	42	13.631	1674	214	V		0.0031	
	45	15.236	4680	537	V		0.0086	
	46	15.351	3829	488	V		0.007	
	47	16.348	85130	9401			0.1564	*E*-**10a**1
	49	17.309	69448	7206			0.1276	*E*-**10a**2
	50	17.814	2565	265			0.0047	
	51	18.527	132835	13473			0.2441	*E*-**10b**
	52	19.221	7887	784			0.0145	
	53	20.064	44631	4103	V		0.082	**10c**
	56	22.987	3059	240			0.0056	
	57	23.567	4010	228	V		0.0074	
		TOTAL	54426148	29193686			100	

No.	Time	Area	Area %	
1	16.35	85130	55.1	*E*-**10a1**
2	17.31	69448	44.9	*E*-**10a2**

Figure S4-2. Chiral GLC chart for the cross dimer **10** (cat. = (*S,S*)-**3bb**)



** CALCULATION REPORT **

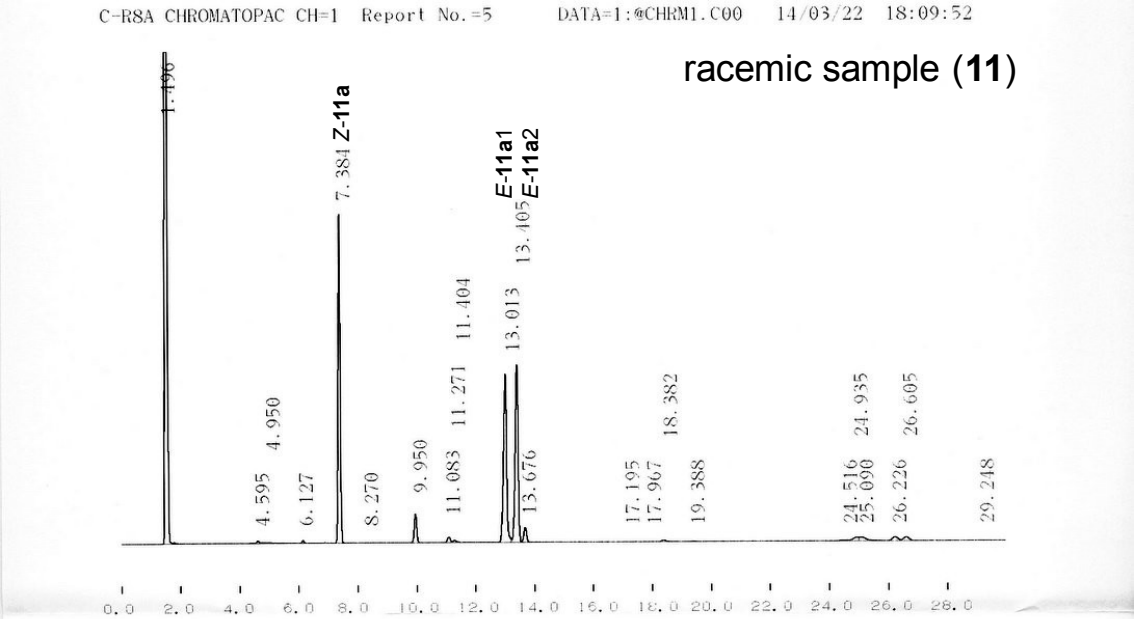
CH	PKNO	TIME	AREA	HEIGHT	MK	HDNO	CONC	NAME
1	1	1.158	887655	422994			2.4188	
	2	1.381	183276	121224	V		0.4994	
	3	1.456	134071	69855	V		0.3653	
	4	1.61	33641100	20700200	SV		91.6707	
	5	1.842	1273	434	T		0.0035	
	6	1.947	14730	7371	TV		0.0401	
	8	2.286	1416	334	TV		0.0039	
	12	2.904	14310	7027	TV		0.039	
	37	8.821	7846	1372			0.0214	
	38	9.153	74703	16626	V		0.2036	(naphthalene)
	40	9.544	1207	193	V		0.0033	
	41	9.658	1932	234	V		0.0053	
	43	9.967	1102	153	V		0.003	
	47	10.659	1207	134	V		0.0033	
	48	11.022	2416	380			0.0066	
	50	11.82	3602	531			0.0098	
	51	12.018	13513	1965	SV		0.0368	
	54	12.814	13427	1641			0.0366	
	55	13.443	3087	353	V		0.0084	
	56	13.69	5541	709	V		0.0151	
	57	14.064	1257	126	V		0.0034	
	61	15.287	16716	1193	V		0.0455	
	62	16.436	161864	17859			0.4411	*E*-10a1
	64	17.029	1004	107	V		0.0027	
	65	17.423	293336	30853	V		0.7993	*E*-10a2
	66	17.903	6935	697	V		0.0189	
	67	18.665	348765	34456			0.9504	*E*-10b
	68	19.317	8658	801			0.0236	
	70	20.302	462907	39409	V		1.2614	10c
	72	21.865	16890	1355			0.046	
	73	23.113	337954	28967			0.9209	(biphenyl)
	74	23.717	11111	645			0.0303	
	75	24.593	1166	96			0.0032	
	77	26.264	9433	681			0.0257	
	78	29.196	5293	358			0.0144	
	79	29.486	7116	450	V		0.0194	
		TOTAL	36697760	21511748			100	

No.	Time	Area	Area %	
1	16.44	161861	35.6	***E*-10a1**
2	17.42	293336	64.4	***E*-10a2**

Figure S4-3. Chiral GLC chart for the cross dimer **10** (cat. = (-)-**3f**)

Chiral GLC chromatogram for **11**

Conditions: Column Rt-γDEXsa, oven temp. = 140 ˚C, carrier gas (He) linear velocity 40 cm/sec.



** CALCULATION REPORT **

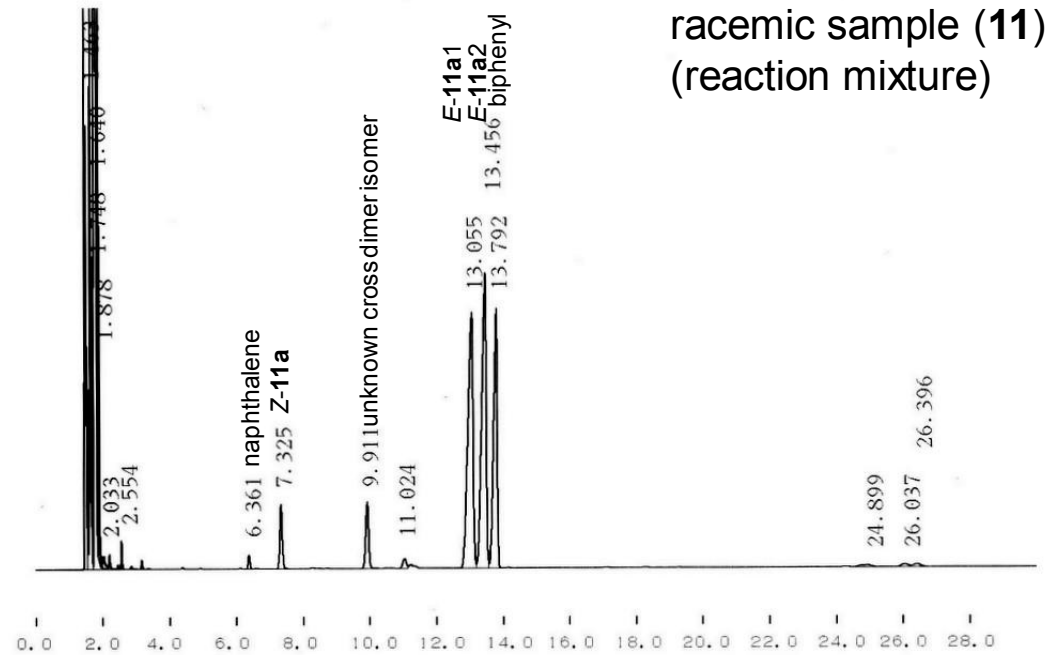
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.496	21548730	6750797	S		94.57	
	8	4.595	10262	748	V		0.045	
	9	4.95	5044	171	SV		0.0221	
	11	6.127	3039	777			0.0133	
	14	7.384	410433	85532			1.8012	– *Z*-**11a**
	17	8.27	1117	147	V		0.0049	
	21	9.95	42695	7473	S		0.1874	
	25	11.083	10654	1477			0.0468	
	26	11.271	3880	622	V		0.017	
	27	11.404	1570	260	V		0.0069	
	31	13.013	328231	43894			1.4405	*E*-**11a**1
	32	13.405	320271	46254	V		1.4056	*E*-**11a**2
	33	13.676	26414	3949	V		0.1159	— biphenyl.
	35	17.195	1402	142			0.0062	
	36	17.967	1877	144			0.0082	
	37	18.382	5717	450	V		0.0251	
	38	19.388	1777	190			0.0078	
	45	24.516	4381	244	V		0.0192	
	46	24.935	13015	919	V		0.0571	
	47	25.09	14999	906	V		0.0658	
	48	26.226	13579	1022			0.0596	
	49	26.605	13657	1025	V		0.0599	
	50	29.248	3282	77			0.0144	
		TOTAL	22786012	6947216			100	

No.	Time	Area	Area %	
1	13.01	328231	50.6	*E*-**11a1**
2	13.40	320271	49.4	*E*-**11a2**

Figure S5-1. Chiral GLC chart for the *rac*-cross dimer **11**

In some reactions, the measurement of chiral GC was carried out using the unpurified reaction mixture due to the difficulty of purification for low yield. We shown GC chart of the unpurified reaction mixture.(Fig. S5-2) Although these peaks were slightly overlapped, it was enough to estimate the such low ee value.

C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:@CHRM1.C00 14/10/08 15:32:14



** CALCULATION REPORT **

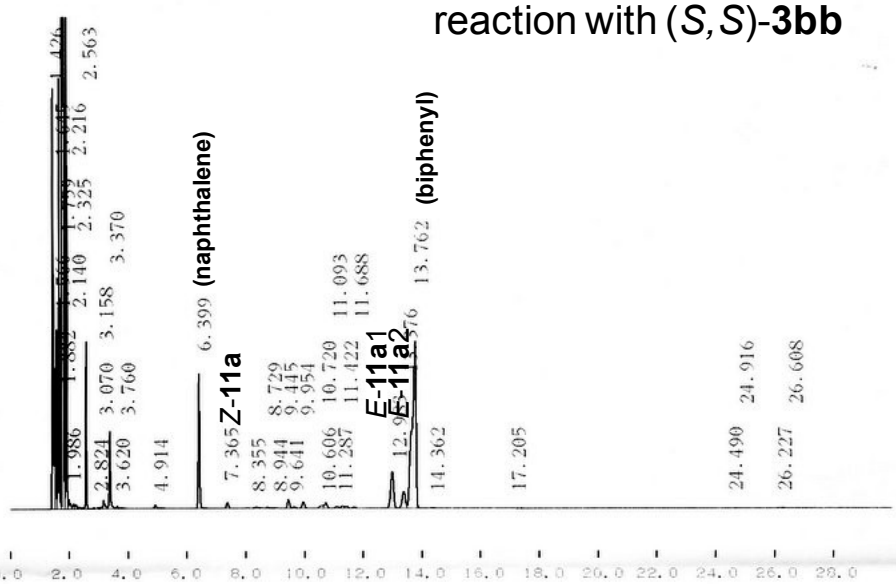
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.463	724463	296292			1.4624	
	2	1.64	845950	456927	V		1.7077	
	3	1.748	43588048	20150980	SV		87.9882	
	4	1.878	494760	315545	T		0.9987	
	6	2.033	17805	5290	TV		0.0359	
	10	2.554	25135	12976	TV		0.0507	
	20	6.361	22716	6362			0.0459	naphthalene
	23	7.325	148686	29261	S		0.3001	*Z*-**11a**
	27	9.911	187916	30319			0.3793	unknown
	29	11.024	35212	4545			0.0711	
	33	13.055	1246237	116967			2.5157	*E*-**11a**1
	34	13.456	1253345	134864	V		2.53	*E*-**11a**2
	35	13.792	887806	118646	V		1.7922	biphenyl
	42	24.899	22205	929	V		0.0448	
	43	26.037	19323	1352			0.039	
	44	26.396	18948	1375	V		0.0382	
		TOTAL	49538532	21682620			100	

No.	Time	Area	Area %	
1	13.06	1246237	49.9	*E*-**11a1**
2	13.46	1253345	51.1	*E*-**11a2**

Figure S5-2. Chiral GLC chart for the *rac*-cross dimer **11**

C-R8A CHROMATOPAC CH=1 Report No.=5 DATA=1:#CHRM1.C00 14/03/24 16:13:20

reaction with (*S*,*S*)-**3bb**

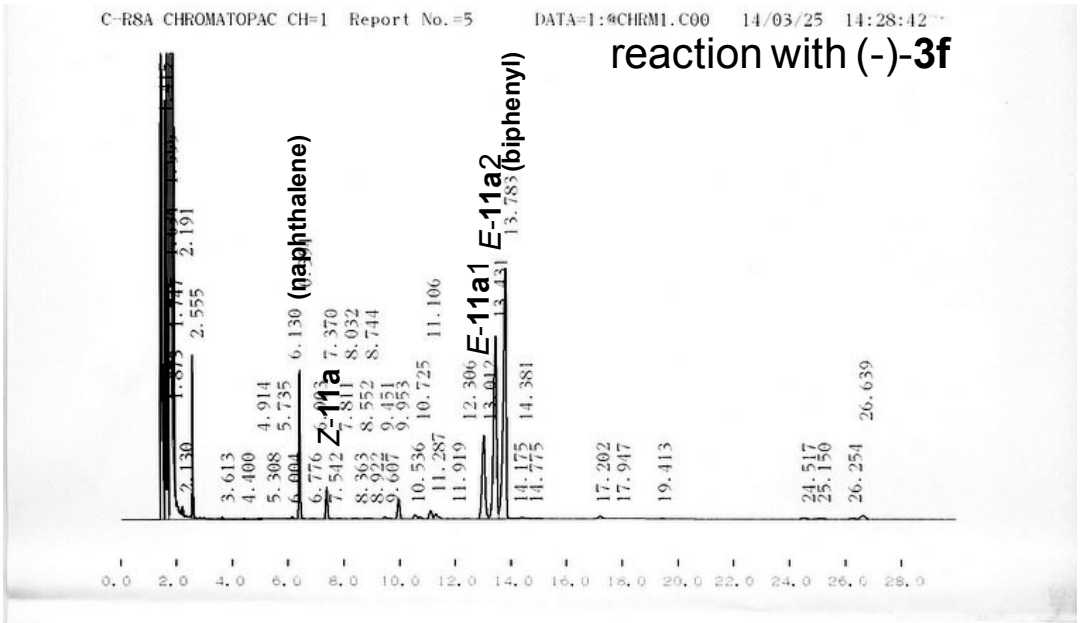


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.426	290639	109516			1.5247	
	2	1.566	80649	46708	V		0.4231	
	3	1.645	195015	112227	V		1.023	
	4	1.759	16784350	8368328	V		88.0495	
	5	1.882	839126	514608	V		4.402	
	6	1.986	10447	2436	V		0.0548	
	7	2.14	4350	1329	V		0.0228	
	8	2.216	4839	1222	V		0.0254	
	9	2.325	3188	521	V		0.0167	
	10	2.563	80144	43630	V		0.4204	
	11	2.824	1124	316	V		0.0059	
	14	3.07	1965	487	V		0.0103	
	15	3.158	9486	2207	V		0.0498	
	16	3.37	55862	20133	SV		0.293	
	17	3.62	1288	620	T		0.0068	
	18	3.76	1288	236	T		0.0068	
	23	4.914	4877	1007	T		0.0256	
	30	6.399	116866	35079	V		0.6131	(naphthalene)
	32	7.365	6532	1507			0.0343	*Z*-**11a**
	37	8.355	2838	318	V		0.0149	
	39	8.729	1651	344			0.0087	
	40	8.944	1484	183	V		0.0078	
	43	9.445	11473	2341			0.0602	
	44	9.641	2257	415	V		0.0118	
	45	9.954	9314	1666	V		0.0489	
	47	10.606	6261	748			0.0328	
	48	10.72	8842	1477	V		0.0464	
	49	11.093	3664	527			0.0192	
	50	11.287	4602	667	V		0.0241	
	51	11.422	3399	565	V		0.0178	
	52	11.688	2940	404	S		0.0154	
	57	12.983	67668	9571			0.355	*E*-**11a**1
	58	13.376	33631	4383	V		0.1764	*E*-**11a**2
	59	13.762	399965	43612	V		2.0982	(biphenyl)
	60	14.362	1679	175			0.0088	
	63	17.205	1444	149			0.0076	
	68	24.49	1602	125			0.0084	
	69	24.916	2034	111	V		0.0107	
	70	26.227	2308	175			0.0121	
	71	26.608	1360	103	V		0.0071	
		TOTAL	19062420	9330157			100.0001	

No.	Time	Area	Area %	
1	12.98	67668	66.8	*E*-**11a1**
2	13.40	33631	33.2	*E*-**11a2**

Figure S5-2. Chiral GLC chart for the cross dimer **11** (cat. = (*S*,*S*)-**3bb**)

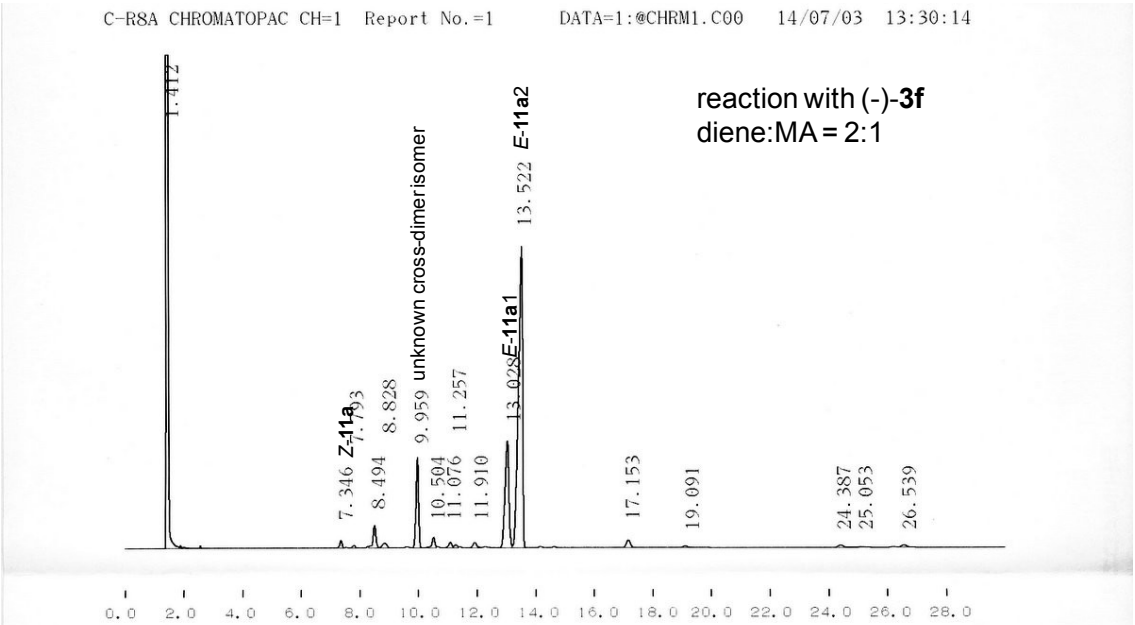


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.415	677859	325214			2.1204	
	2	1.555	173717	115149	V		0.5434	
	3	1.634	274274	152651	V		0.858	
	4	1.747	28621708	14617126	SV		89.5311	
	5	1.873	724559	480908	T		2.2665	
	6	2.13	2630	1107	T		0.0082	
	7	2.191	5221	2410	TV		0.0163	
	10	2.555	79977	44745	TV		0.2502	
	18	3.613	1696	735	TV		0.0053	
	23	4.4	1450	430	TV		0.0045	
	26	4.914	3568	264	TV		0.0112	
	27	5.308	1208	133	TV		0.0038	
	30	5.735	1521	125	TV		0.0048	
	32	6.004	1347	206	TV		0.0042	
	33	6.13	3486	804	TV		0.0109	
	34	6.394	136800	40948	TV		0.4279	(naphthalene)
	35	6.776	1231	212	TV		0.0038	
	36	6.903	2198	279	TV		0.0069	
	37	7.37	39667	8896	TV		0.1241	*Z*-11a
	38	7.542	1291	206	TV		0.004	
	39	7.811	3021	317	TV		0.0094	
	40	8.032	1013	157	TV		0.0032	
	42	8.363	3084	309	TV		0.0096	
	43	8.552	1799	226	TV		0.0056	
	44	8.744	2373	327	TV		0.0074	
	45	8.922	2379	270	TV		0.0074	
	47	9.451	4605	743	TV		0.0144	
	48	9.607	2317	334	TV		0.0072	
	49	9.953	32401	5686	TV		0.1014	
	52	10.536	10080	1235	TV		0.0315	
	53	10.725	3807	599	TV		0.0119	
	54	11.106	17165	2407	TV		0.0537	
	55	11.287	13228	1525	TV		0.0414	
	57	11.919	1414	175	TV		0.0044	
	58	12.306	1451	166	TV		0.0045	
	60	13.012	180365	22996	T		0.5642	*E*-11a1
	61	13.431	383914	50324	TV		1.2009	*E*-11a2
	62	13.783	498288	68875	TV		1.5587	(biphenyl)
	63	14.175	1073	119	TV		0.0034	
	64	14.381	5874	436	TV		0.0184	
	65	14.775	1484	117	TV		0.0046	
	70	17.202	6721	720			0.021	
	71	17.947	1195	64			0.0037	
	74	19.413	1747	181	V		0.0055	
	78	24.517	5644	432			0.0177	
	79	25.15	7628	398	V		0.0239	
	80	26.254	5174	398			0.0162	
	81	26.639	13863	1042	V		0.0434	
		TOTAL	31968438	15953108			100	

No.	Time	Area	Area %	
1	13.01	180365	32.0	***E*-11a1**
2	13.43	383914	68.0	***E*-11a2**

Figure S5-3. Chiral GLC chart for the cross dimer **11** (cat. = (-)-**3f**)

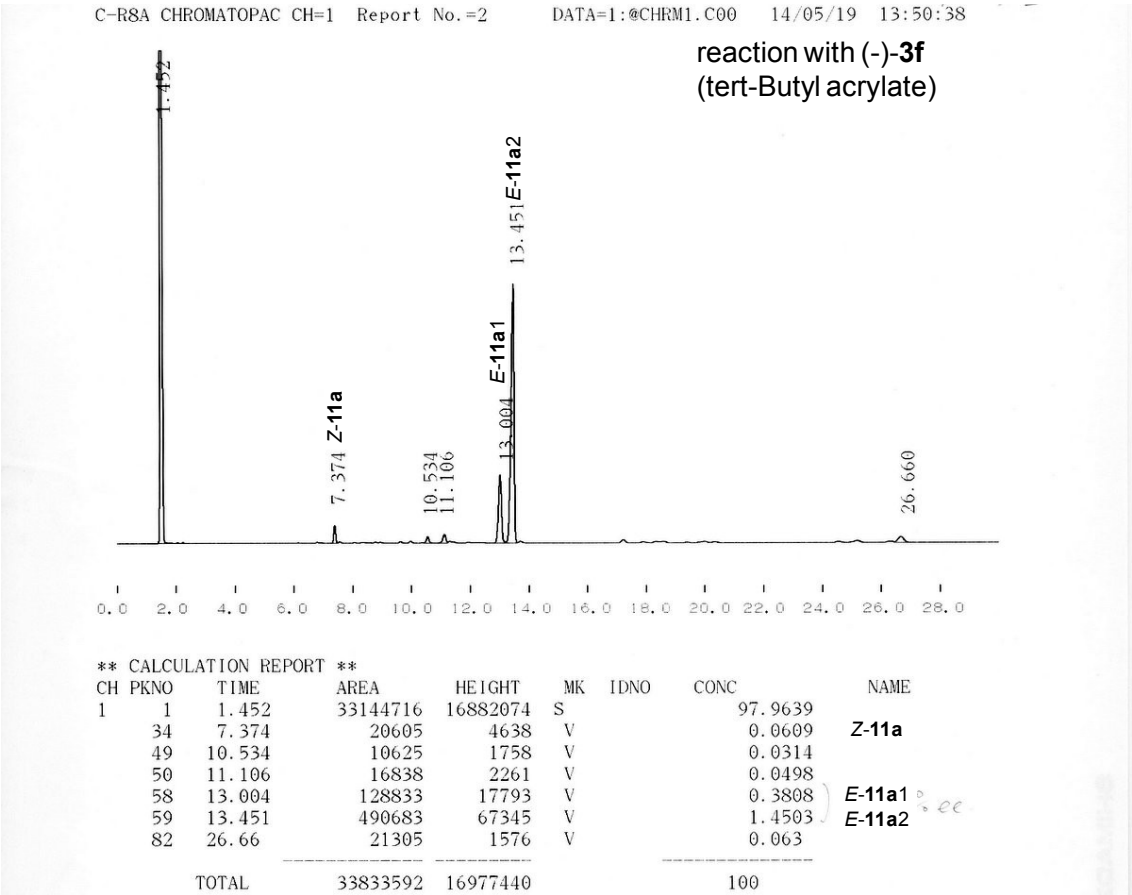


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.412	42667084	19849768	S		94.0131	
	33	7.346	23965	4198	V		0.0528	*Z*-**11a**
	35	7.793	10393	1469	V		0.0229	
	38	8.494	82142	11916	V		0.181	
	39	8.828	29243	2669	V		0.0644	
	43	9.959	287057	47101	V		0.6325	unknown cross-dimer
	44	10.504	44494	5685	V		0.098	
	46	11.076	25904	3061	V		0.0571	
	47	11.257	13674	1890	V		0.0301	
	50	11.91	29579	2937	V		0.0652	
	52	13.028	516696	55590			1.1385	*E*-**11a**1
	53	13.522	1554189	156487	V		3.4245	*E*-**11a**2
	62	17.153	40846	4209	V		0.09	
	66	19.091	11937	1090			0.0263	
	75	24.387	17180	1305			0.0379	
	76	25.053	10471	546	V		0.0231	
	78	26.539	19347	1366	V		0.0426	
		TOTAL	45384176	20151268			100	

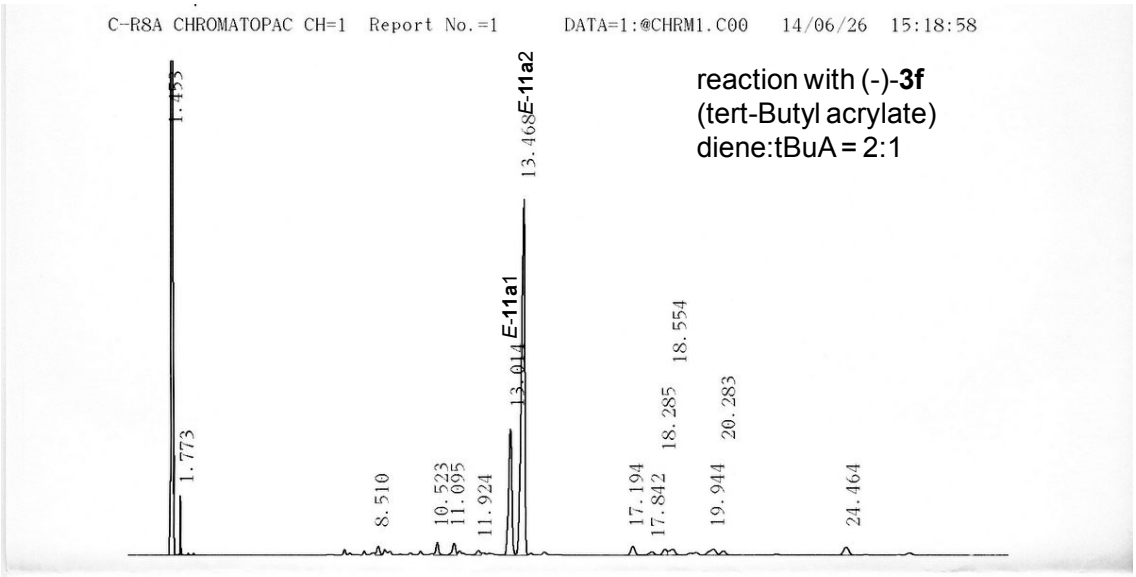
No.	Time	Area	Area %	
1	13.03	516696	25.0	***E*-11a1**
2	13.52	1554189	75.0	***E*-11a2**

Figure S5-4. Chiral GLC chart for the cross dimer **11** (cat. = (-)-**3f**, diene:MA = 2:1)



No.	Time	Area	Area %	
1	13.00	128833	20.8	***E*-11a1**
2	13.45	490683	79.2	***E*-11a2**

Figure S5-5. Chiral GLC chart for the cross dimer **11** (cat. = (-)-**3f**, tert-Butyl acrylate)

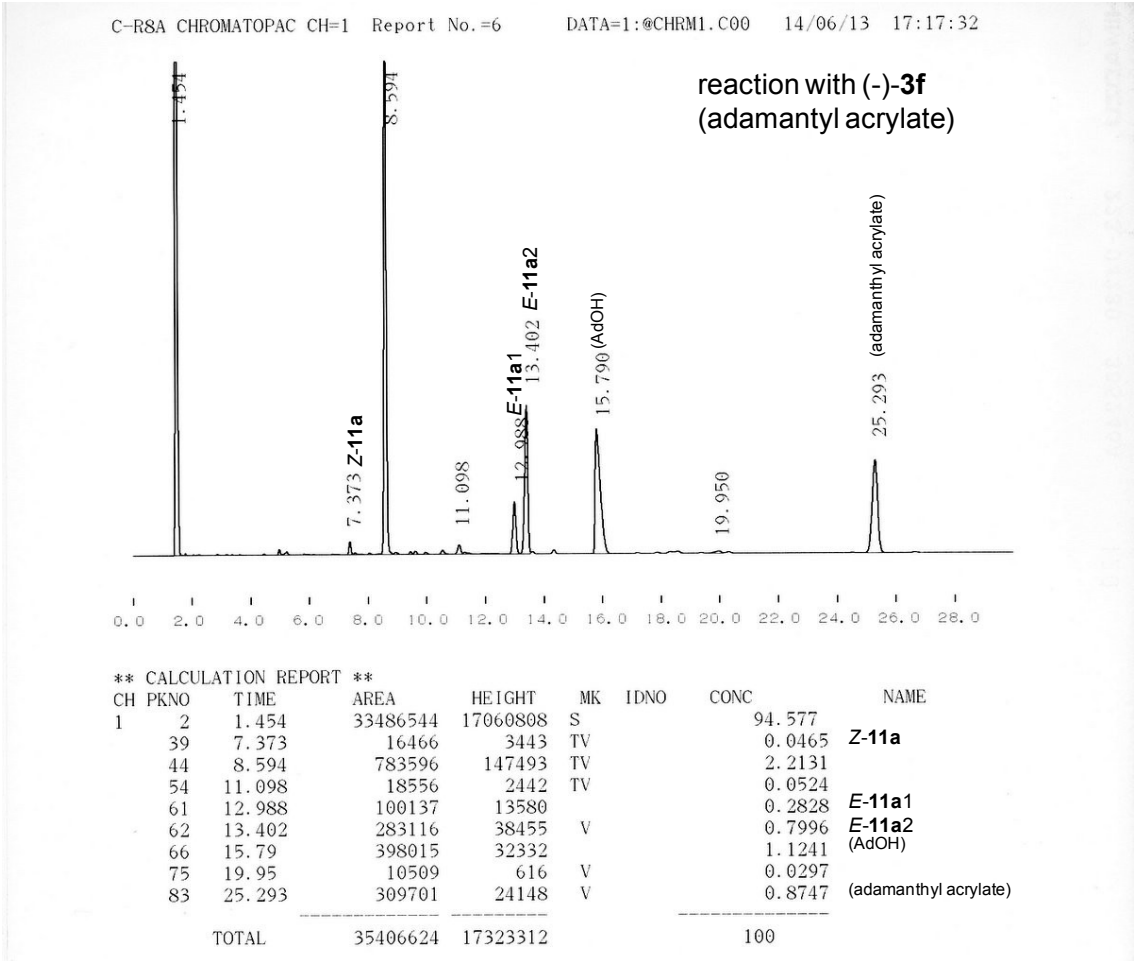


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	1.453	24550756	16096619			95.1983	
	2	1.773	23675	15496	SV		0.0918	
	34	8.51	15575	2363	V		0.0604	
	42	10.523	21534	3307	V		0.0835	
	43	11.095	25015	3113			0.097	
	47	11.924	11729	1192	V		0.0455	
	51	13.014	255863	32848	V		0.9921	*E*-**11a**1
	52	13.468	742145	92290	V		2.8778	*E*-**11a**2
	60	17.194	23138	2378	V		0.0897	
	61	17.842	11983	953	V		0.0465	
	62	18.285	17047	1562	V		0.0661	
	63	18.554	21655	1611	V		0.084	
	66	19.944	27457	1630	V		0.1065	
	67	20.283	13659	1179	V		0.053	
	73	24.464	27836	2173			0.1079	
		TOTAL	25789056	16258710			100	

No.	Time	Area	Area %	
1	13.01	255863	25.6	***E*-11a1**
2	13.47	742145	74.4	***E*-11a2**

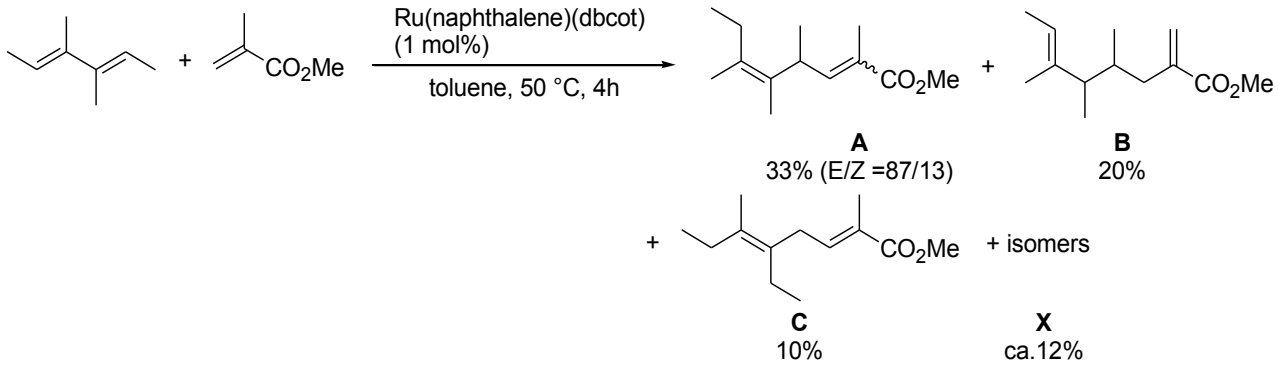
Figure S5-6. Chiral GLC chart for the cross dimer **11** (cat. = (-)-**3f**, tert-Butyl acrylate, diene:tBuA = 2:1)



No.	Time	Area	Area %	
1	12.99	100137	26.1	***E*-11a1**
2	13.40	283116	73.9	***E*-11a2**

Figure S5-7. Chiral GLC chart for the cross dimer **11** (cat. = (-)-**3f**, Adamantyl acrylate)

Cross-dimerization between 3,4-dimethyl-2,4-hexadiene and Methyl methacrylate catalyzed by Ru(naphthalene)(dbcot) (3d).



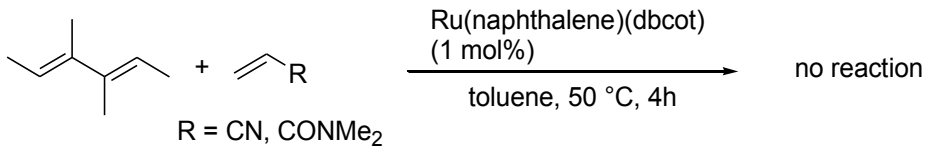
1b (18.9 mg, 0.0520 mmol, 5 mol%) in Schlenk tube was added Toluene (1 mL) 3,4-dimethyl-2,4-hexadiene 62.8 mg, 0.570 mmol and methyl methacrylate (55 μL, 0.52 mmol). The reaction mixture was stirred at 50 °C for 4 hour. Yield and product ratio were determined by GLC analysis using biphenyl as an initial standard. (**A** 33%, **B** 20%, **C** 10% and isomers(**X**) ca. 12%)And then, after quenching of the catalyst by exposure to air, all volatile matters were removed under reduced pressure, and column chromatography of the residue (silica gel: hexane/ethyl acetate = 40/1) gave (2*E,*5*Z*)-**A** and (2*E*,5*E*)-**C** (31.2 mg, **A**:**C** = 75:25) and (2*Z,*5*Z*)-**A**, (6*E*)-**B** and isomers (**X**) (21.6 mg, **A**:**B**:**X** = 13:63:24) as a colorless oil. Since **A** and **C** (similarly, **A** and **B** and **X**) could not be separated, (2*E,*5*Z*)-**A** and (2*E*,5*E*)-**C** were characterized spectroscopically as shown in Fig. S-31-1. (2*Z,*5*Z*)-**A** and (6*E*)-**B** were characterized spectroscopically as shown in Fig. S-31-6.

(2*E*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*E*, 5*Z*)-**A**). ^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ 0.92(t, *J* = 7.4 Hz, 3H, -CH_2*Me*), 1.05(d, *J* = 6.9 Hz, 3H, -*Me*), 1.56(s, 3H, -*Me*), 1.55(d(overwrapped with **C**), 3H, -*Me*), 1.82(br.s, 3H, -*Me*), 2.0-2.1(m(overwrapped with **C**), 2H, -CH_2-), 3.66(dq, *J* = 9.2, 6.9 Hz, 1H, >C*H*-), 3.69(s(overwrapped with **C**), 3H, -O*Me*), 6.73(dq, *J* = 9.2, 1.1 Hz, 1H, =C*H*-). ^{13}C{^{1}H} NMR (100.5 MHz, r.t., $CDCl_3$): δ 12.40, 13.19, 13.57, 18.31, 19.15, 27.02, 35.08. 51.68, 125.63, 128.61, 130.95, 145.89, 168.95. GC-MS(EI): *m/z* =210(M^+), 195 (M^+-Me), 179 (M^+-OMe).

(2*Z*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*Z*, 5*Z*)-**A**). ^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ 0.87(t, *J* = 7.5 Hz, 3H, -CH_2*Me*), 1.02(d, *J* = 6.9 Hz, 3H, -*Me*), 1.56(s, 3H, -*Me*), 1.85(d, *J* = 1.7 Hz, 3H, -*Me*)1.95-2.05(m(overwrapped with otherpeaks), 2H, -CH_2-), 4.40(dq, *J* = 10.3, 6.9 Hz, 1H, >C*H*-), 5.90(dq, *J* = 10.3, 1.2 Hz, 1H, =C*H*-). Other peaks were not identified. GC-MS(EI): *m/z* =210(M^+), 195 (M^+-Me), 179 (M^+-OMe).

(6*E*)-Methyl 4,5,6-trimethyl-2-methylene-oct-6-enoate ((6*E*)-**B**). ^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ 0.73(d, *J* = 6.3 Hz, 3H, -*Me*), 0.94(d, *J* = 6.9 Hz, 3H, -*Me*), 1.53(br.s, 3H, -*Me*), 1.55(d, *J* = 7.5 Hz, 3H, -*Me*), 1.55-1.65(m(partly overwrapped), 1H, >C*H*-), 1.71(dd, *J* = 13.8, 10.3 Hz, 1H, -CH_2-), 1.81(quintet, *J* = 7.5 Hz, 1H, >C*H*-), 2.45(dd, *J* = 13.8, 2.9 Hz, 1H, -CH_2-), 3.71(s, 3H, -O*Me*), 5.18(q, *J* = 6.3 Hz, 1H, =C*H*-), 5.44(s, 1H, =CH_2), 6.12(d, *J* = 1.7 Hz, 1H, =CH_2). ^{13}C{^{1}H} NMR (100.5 MHz, r.t., $CDCl_3$): δ 12.39, 13.15, 15.84, 16.38, 34.07, 38.47, 48.71, 51.66, 118.60, 125.93, 139.49, 140.06, 167.91. GC-MS(EI): *m/z* =210(M^+), 195 (M^+-Me), 181(M^+-Et).

(2*E*, 5*E*)-Methyl 5-ethyl-2,6-dimethyl-octa-2,5-dienoate((2*E*,5*E*)-**C***)*. ^{1}H NMR (400 MHz, r.t., $CDCl_3$): δ 0.93(t, *J* = 7.4 Hz, 6H, -CH_2*Me*), 1.60(s(overwrapped with **A**), 3H, -*Me*), 1.86(br.s, 3H, -*Me*), 1.95-2.05(m(overwrapped with **A**), 4H, -CH_2-), 2.85(d, *J* = 7.5 Hz, 2H, -CH_2-), 3.69(s(overwrapped with **A**), 3H, -O*Me*), 6.62(tq, *J* = 7.4, 1.1 Hz, 1H, =C*H*-). ^{13}C{^{1}H} NMR (100.5 MHz, r.t., $CDCl_3$): δ 12.40, 13.19, 13.45, 17.73, 25.18, 27.02, 31.55. 51.68, 126.80, 130.58, 132.08, 141.67, 168.79. GC-MS(EI): *m/z* =210(M^+), 195 (M^+-Me), 181(M^+-Et).



The reactions using acrylonitlile (34 μL, 0.52 mmol) and N,N-dimethylacrylamide (54 μL, 0.52 mmol) insted of MMA under the similar conditions were no reaction.

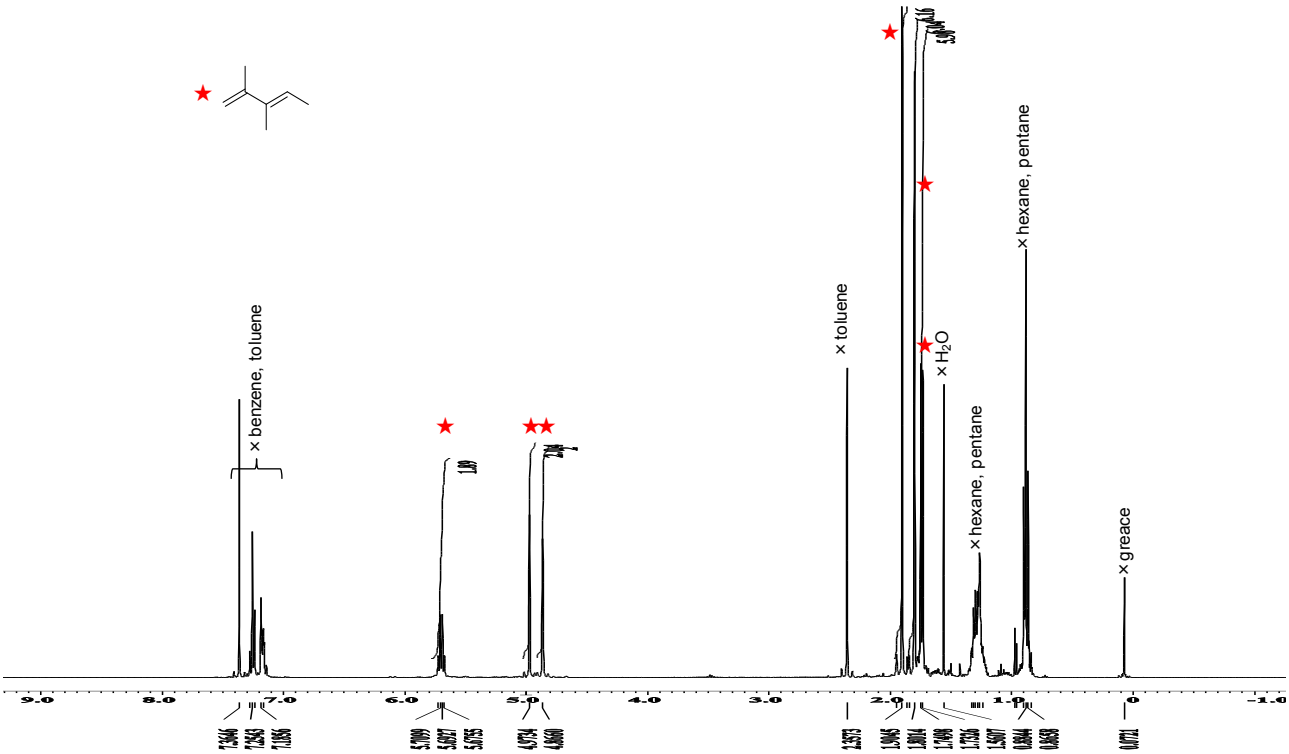


Figure S6-1. ^{1}H NMR spectrum for (*E*)-2,3-dimethyl-1,3-pentadiene (399.8 MHz, $CDCl_3$).

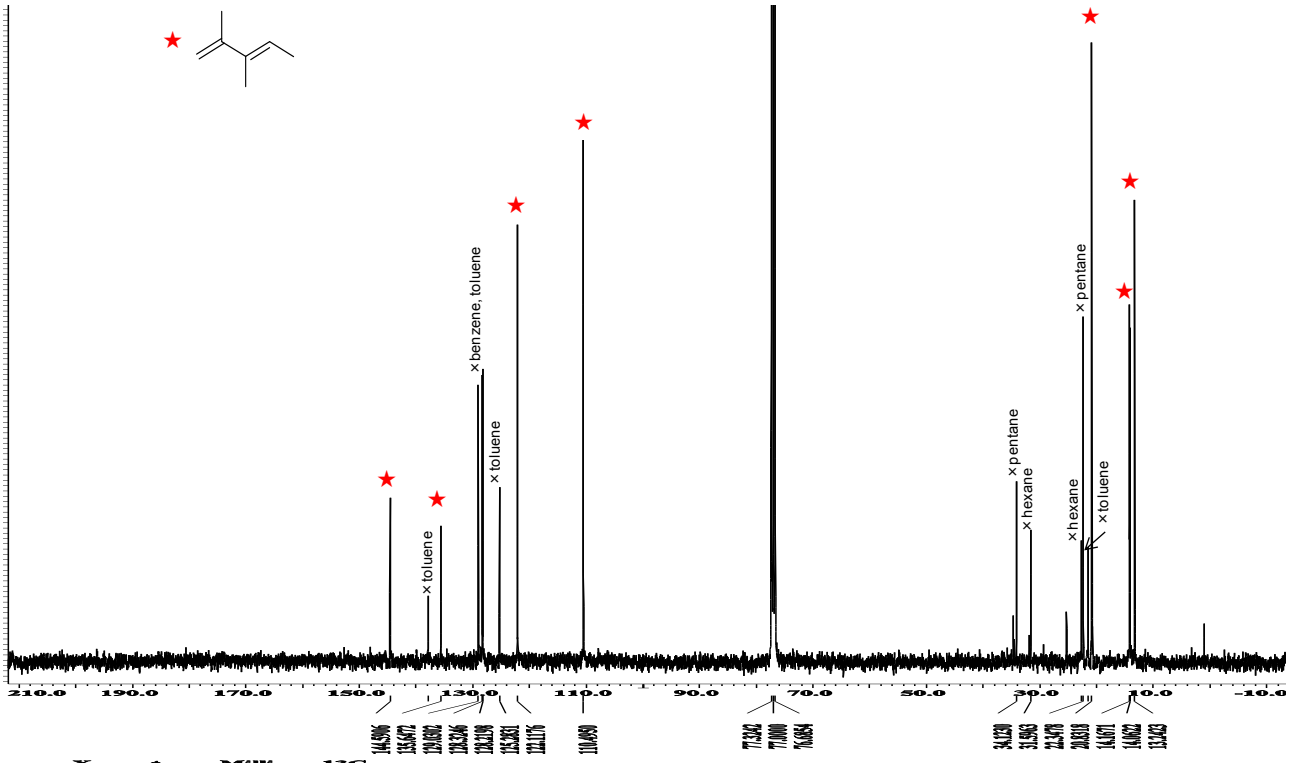


Figure S6-2. ^{13}C NMR spectrum for (*E*)-2,3-dimethyl-1,3-pentadiene (100.5 MHz, $CDCl_3$).

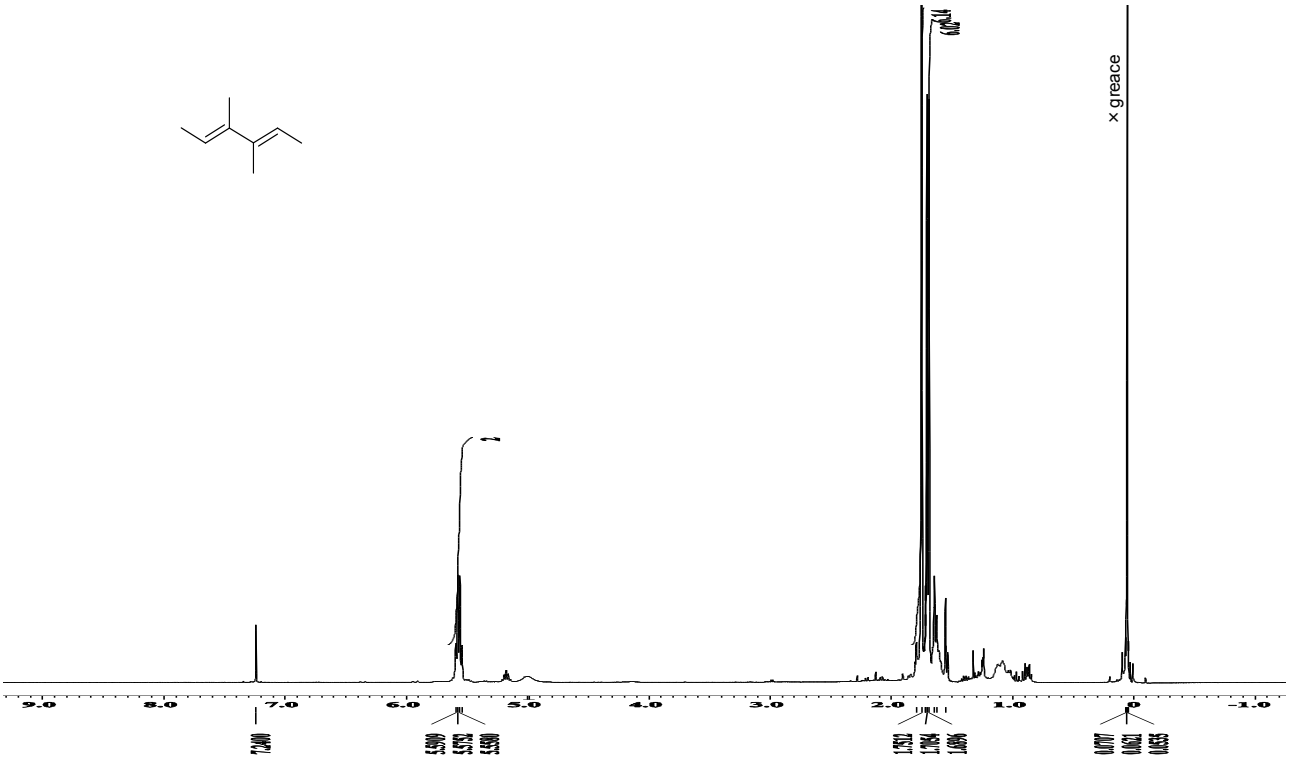


Figure S7-1. ^{1}H NMR spectrum for (*E,E*)-2,3-dimethyl-2,4-hexadiene (399.8 MHz, $CDCl_3$).

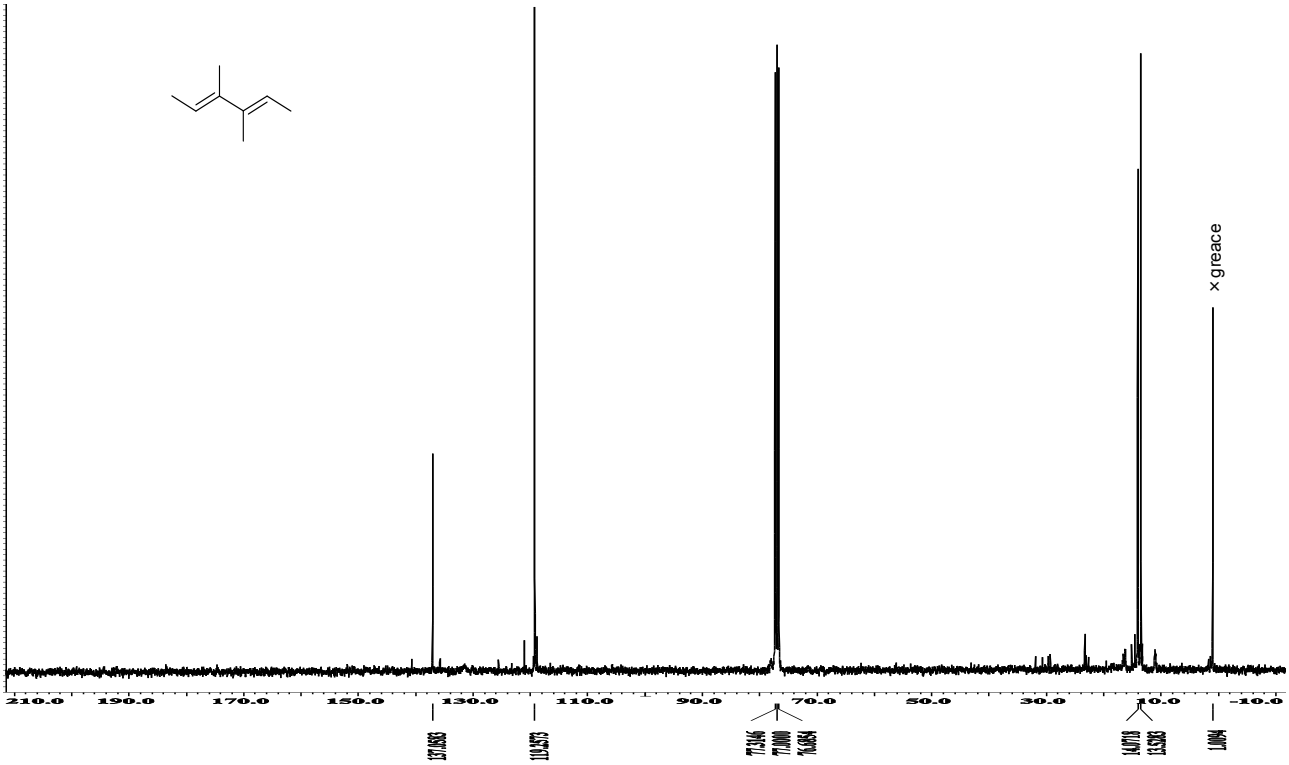


Figure S7-2. ^{13}C NMR spectrum for (*E,E*)-2,3-dimethyl-2,4-hexadiene (100.5 MHz, $CDCl_3$).

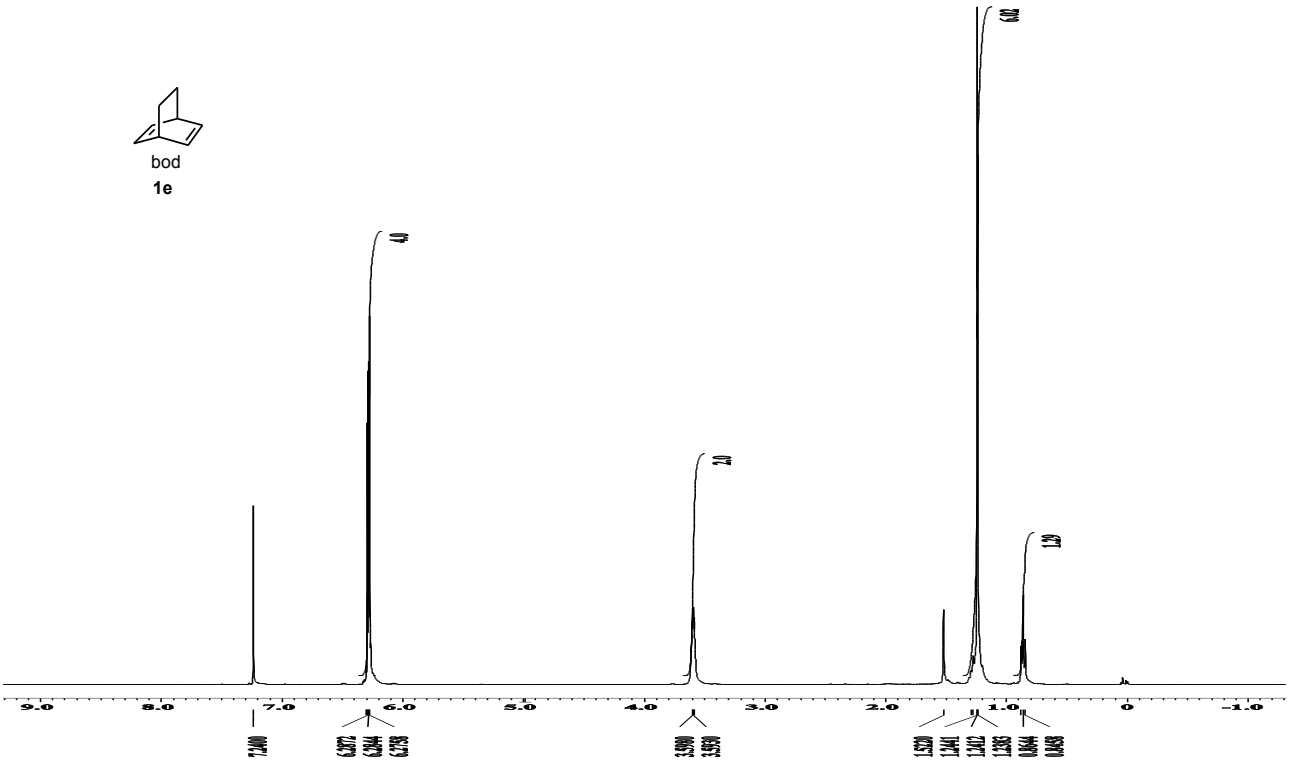


Figure S8-1. ^{1}H NMR spectrum for bicyclo[2.2.2]octa-2,5-diene (**1e**) (399.8 MHz, $CDCl_3$).

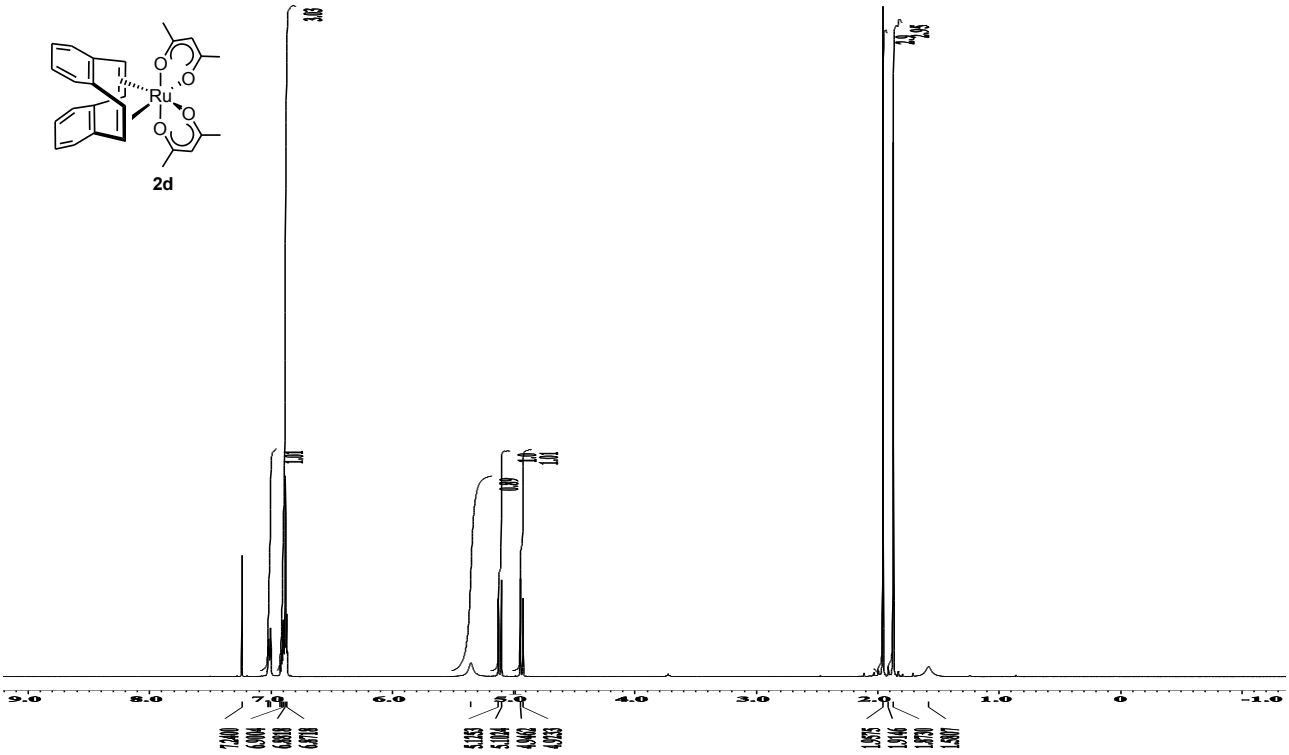


Figure S9-1. ^{1}H NMR spectrum for Ru(acac)$_2$(dibenzo[a,e]cyclooctatetraene) (**2d**) (399.8 MHz, $CDCl_3$).

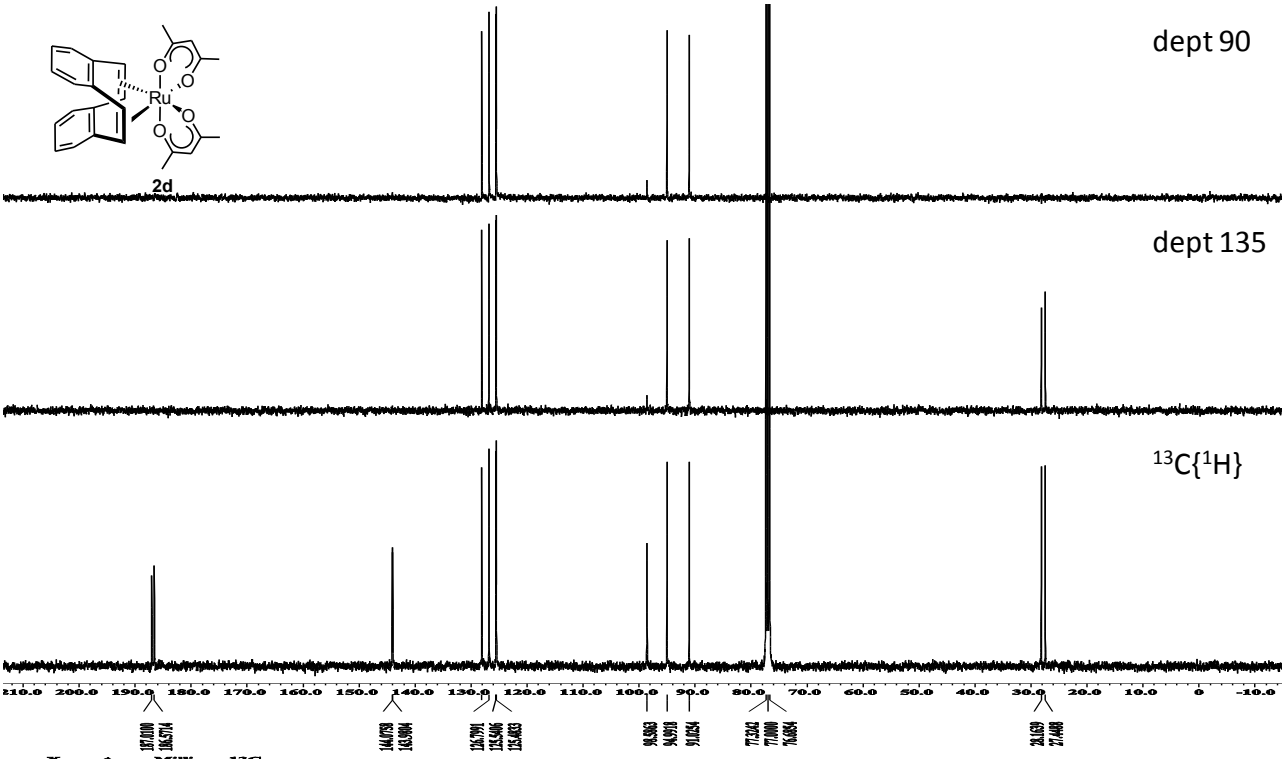


Figure S9-2. ^{13}C, dept 90, dept 135 NMR spectrum for $Ru(acac)_2$(dibenzo[a,e]cyclooctatetraene) (**2d**) (100.5 MHz, $CDCl_3$).

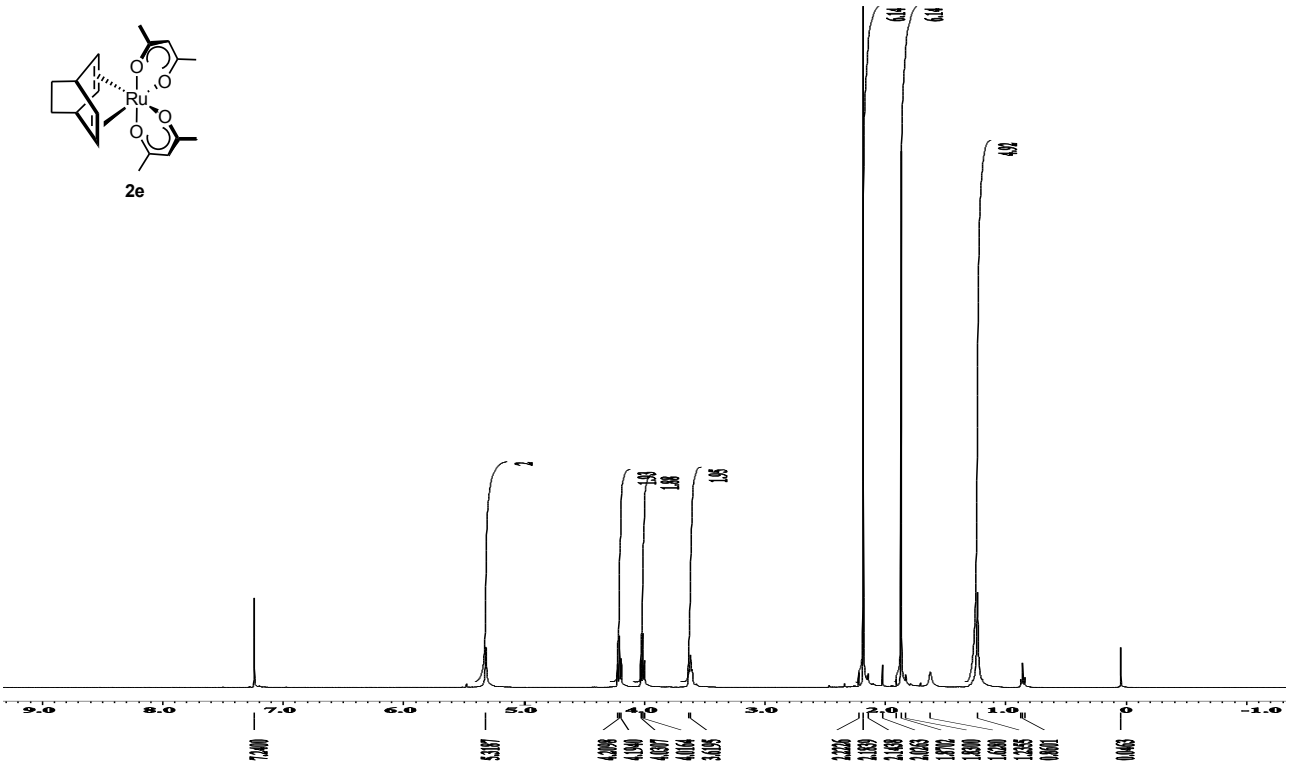


Figure S10-1. ^1H NMR spectrum for $Ru(acac)_2$(bicyclo[2.2.2]octa-2,5-diene) (**2e**) (399.8 MHz, $CDCl_3$).

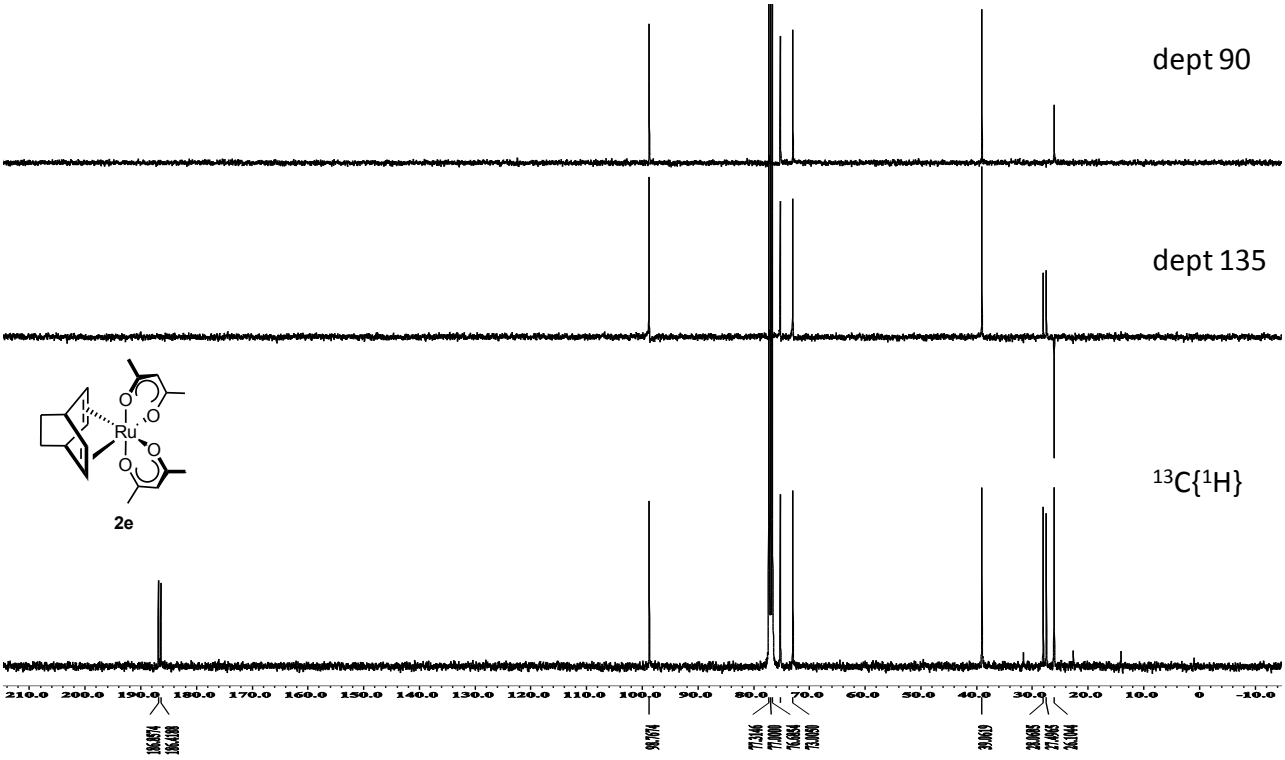


Figure S10-2. ^{13}C dept 90, dept 135 NMR spectrum for Ru(acac)$_2$(bicyclo[2.2.2]octa-2,5-diene) (**2e**) (100.5 MHz, $CDCl_3$).

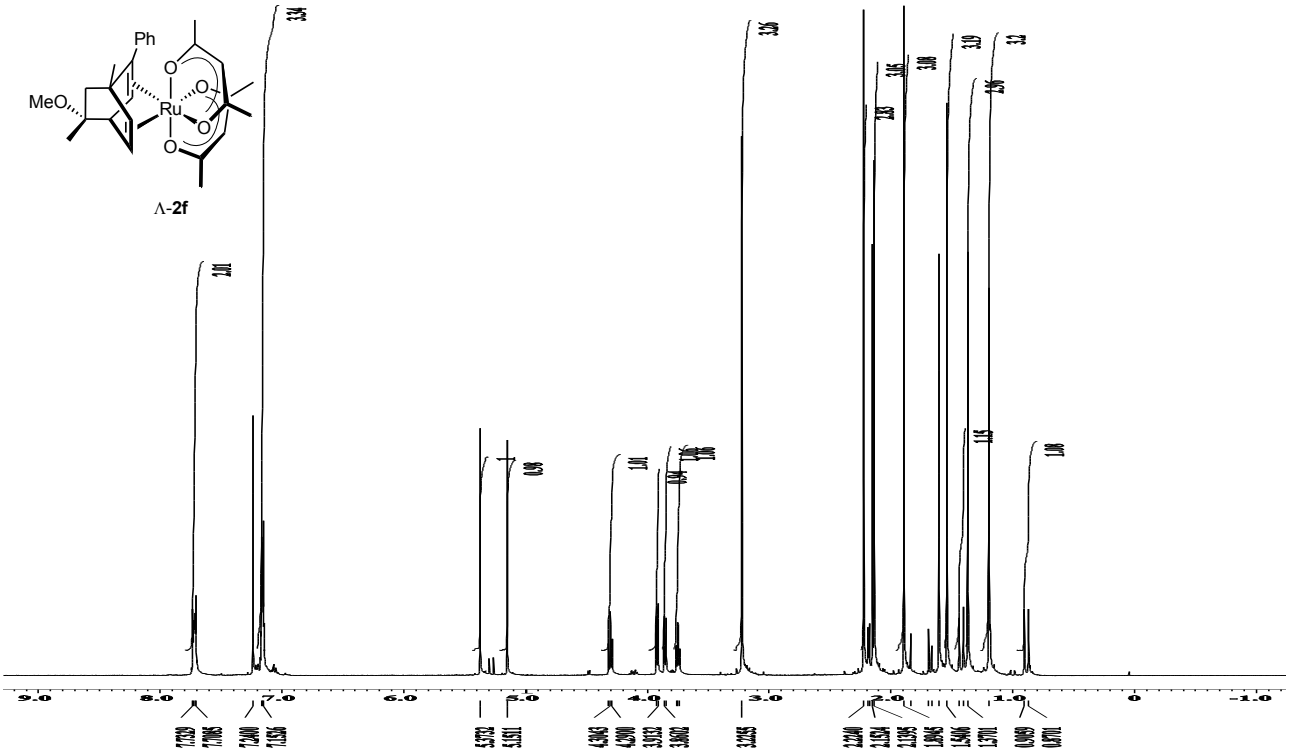


Figure S11-1. ^{1}H NMR spectrum for Λ-Ru(acac)$_2$((-)-(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-bicyclo[2.2.2]octa-2,5-diene) (**2f**) (399.8 MHz, $CDCl_3$).

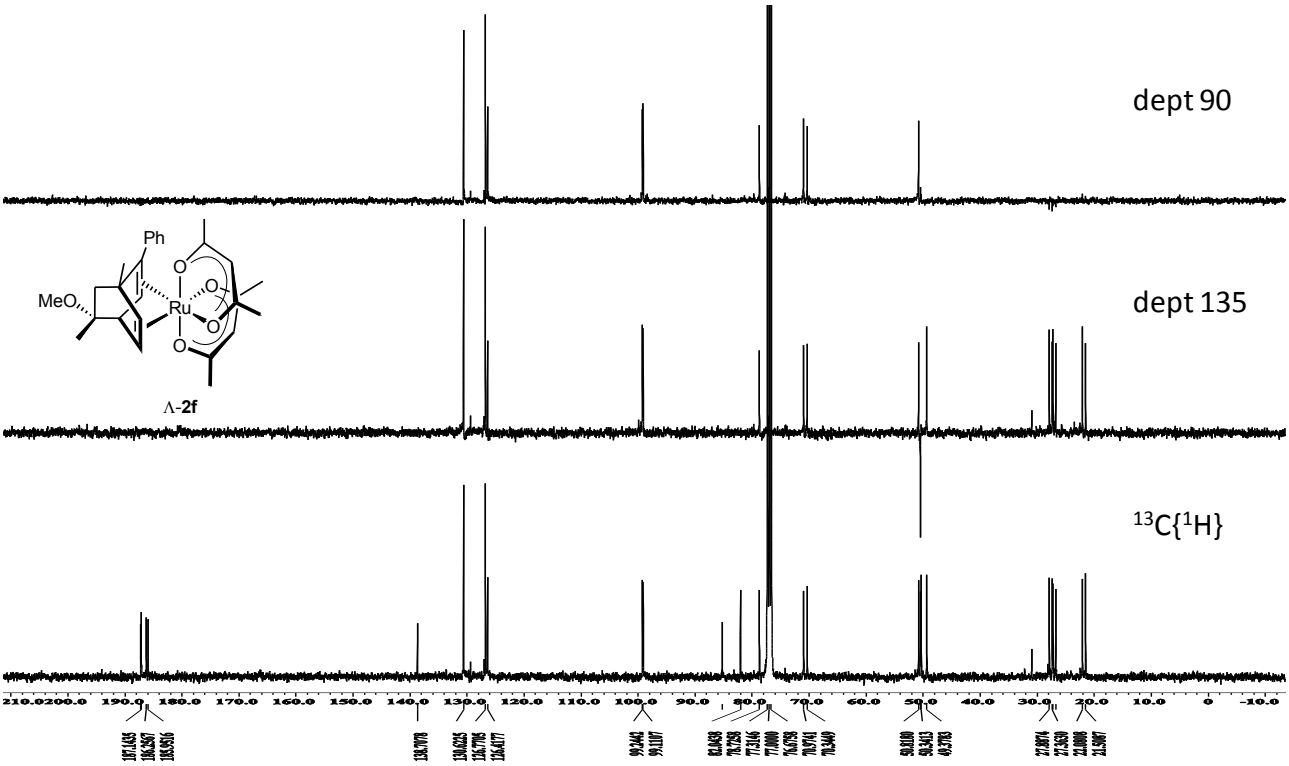


Figure S11-2. ^{13}C dept 90, dept 135 NMR spectrum for Λ-Ru(acac)$_2$((-)-(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-bicyclo[2.2.2]octa-2,5-diene) (**2f**) (100.5 MHz, $CDCl_3$).

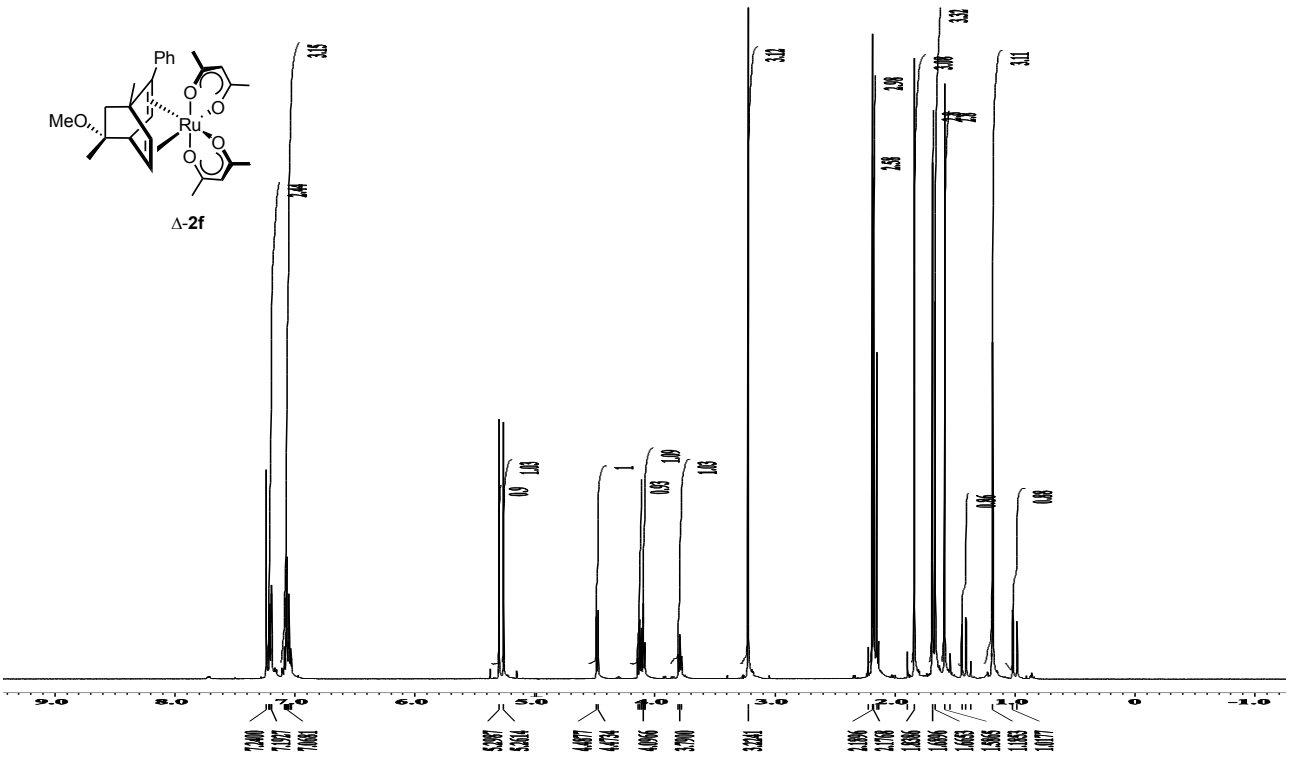


Figure S11-3. ^1H NMR spectrum for Δ-Ru(acac)$_2$((-)-(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-bicyclo[2.2.2]octa-2,5-diene) (**2f**) (399.8 MHz, $CDCl_3$).

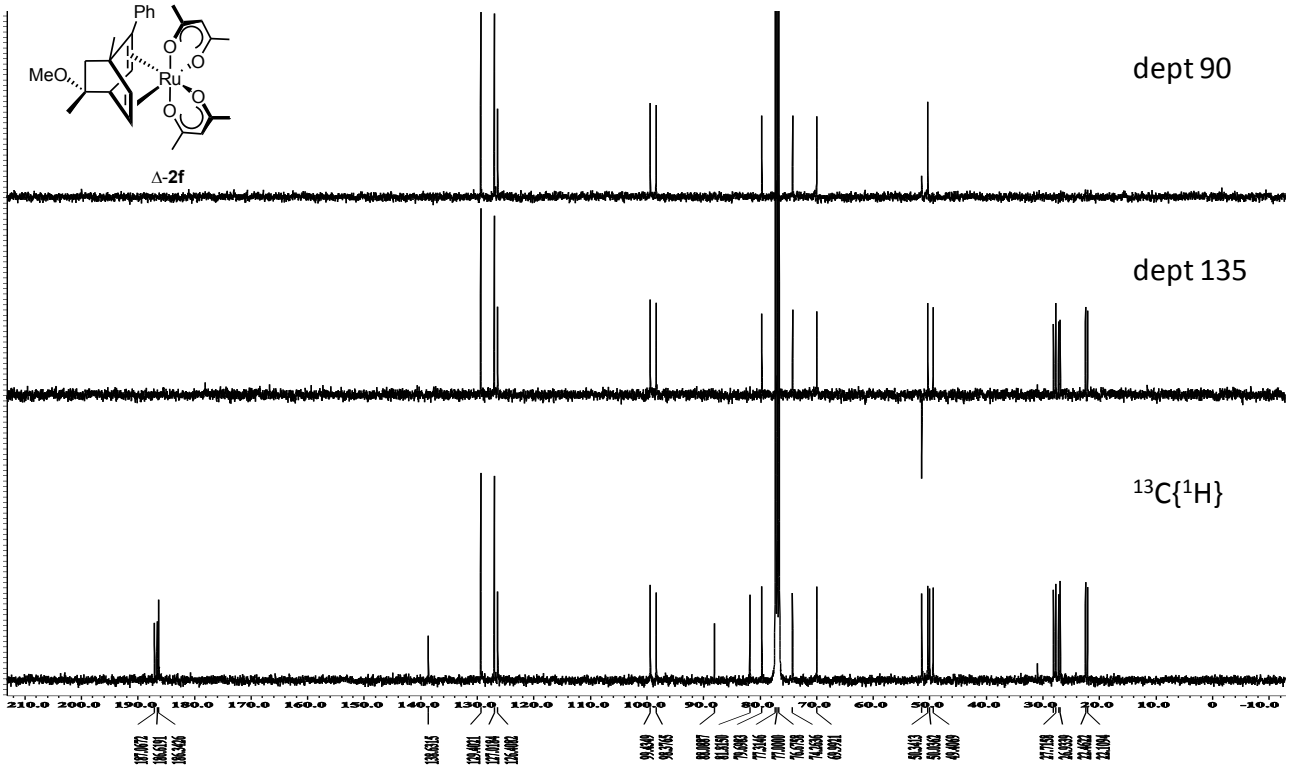


Figure S11-4. ^{13}C dept 90, dept 135 NMR spectrum for Δ-Ru(acac)$_2$((-)-(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-bicyclo[2.2.2]octa-2,5-diene) (**2f**) (100.5 MHz, $CDCl_3$).

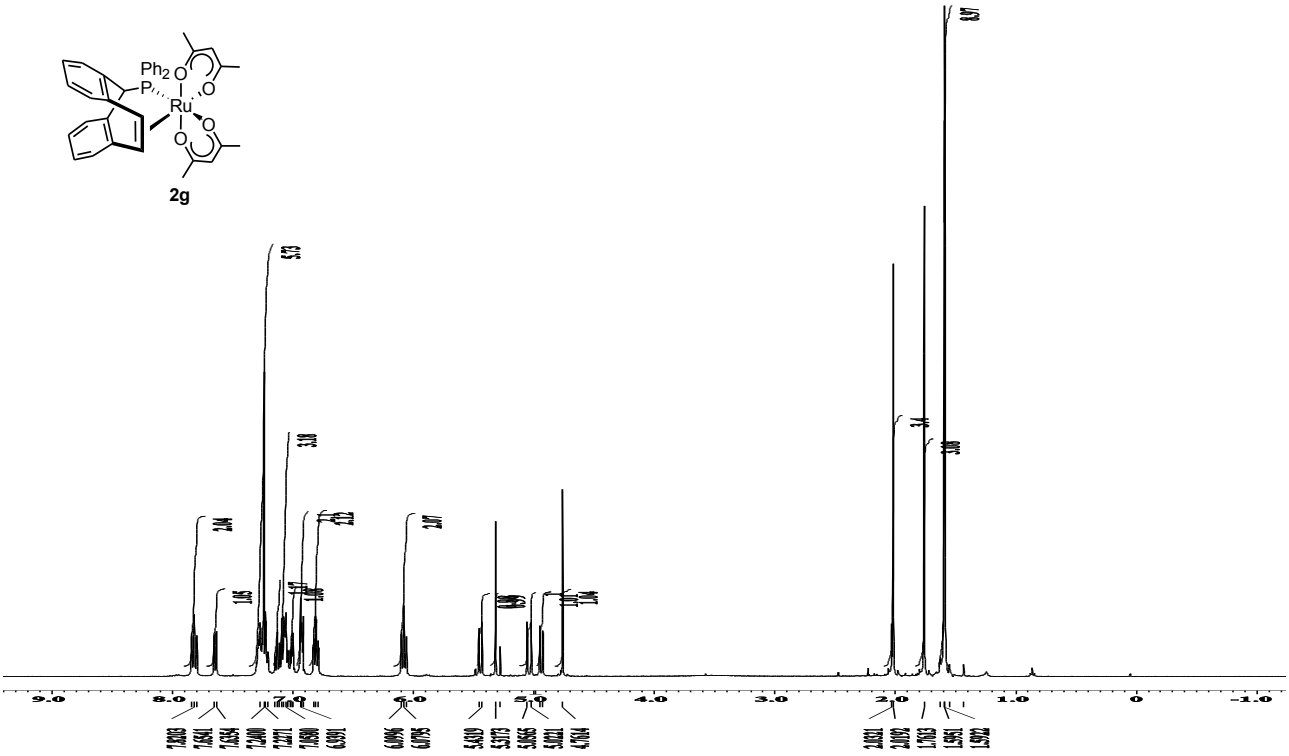


Figure S12-1. ^{1}H NMR spectrum for Ru(acac)$_2$(5-diphenylphosphonyl-5H-dibenzocycloheptene) (**2g**) (399.8 MHz, $CDCl_3$).

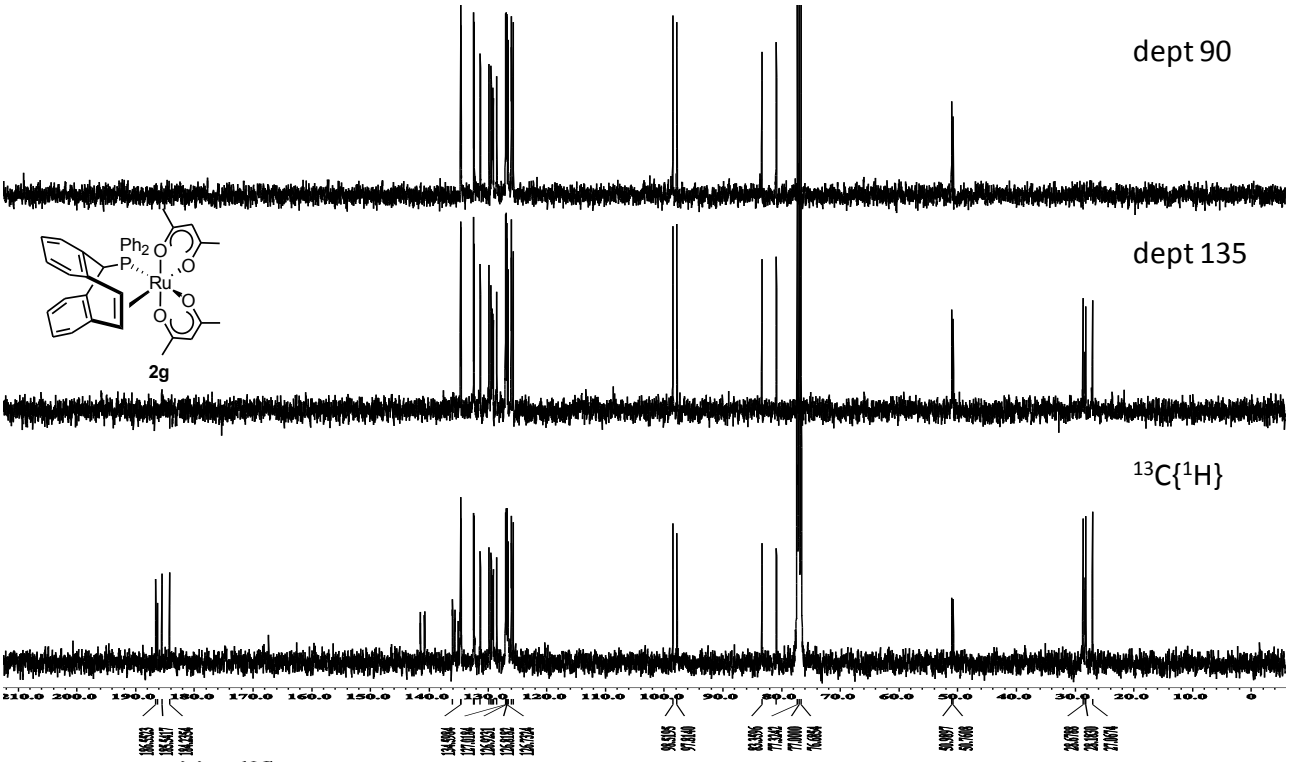


Figure S12-2. ^{13}C, dept 90, dept 135 NMR spectrum for $Ru(acac)_2$(5-diphenylphosphonyl-5H-dibenzocycloheptene) (**2g**) (100.5 MHz, $CDCl_3$).

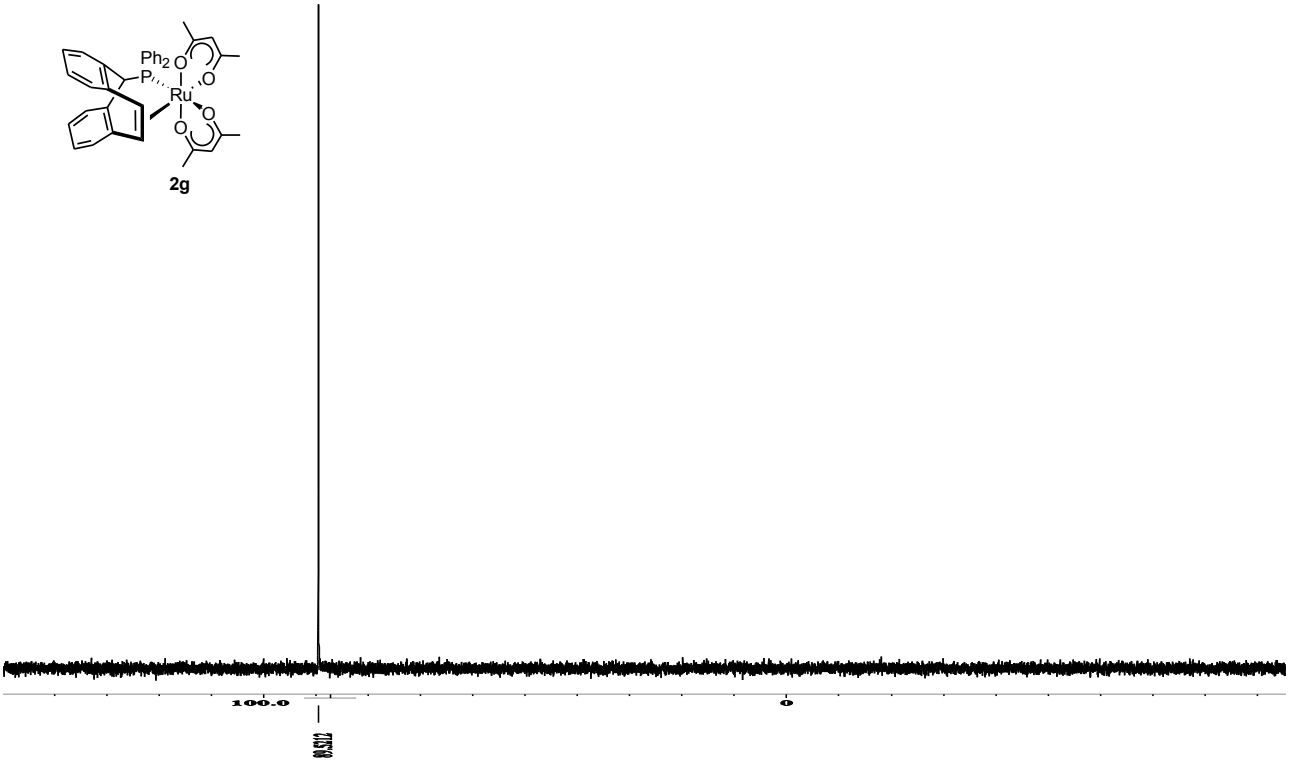


Figure S12-3. ^{31}P NMR spectrum for $Ru(acac)_2$(5-diphenylphosphonyl-5H-dibenzocycloheptene) (**2g**) (161.8 MHz, $CDCl_3$).

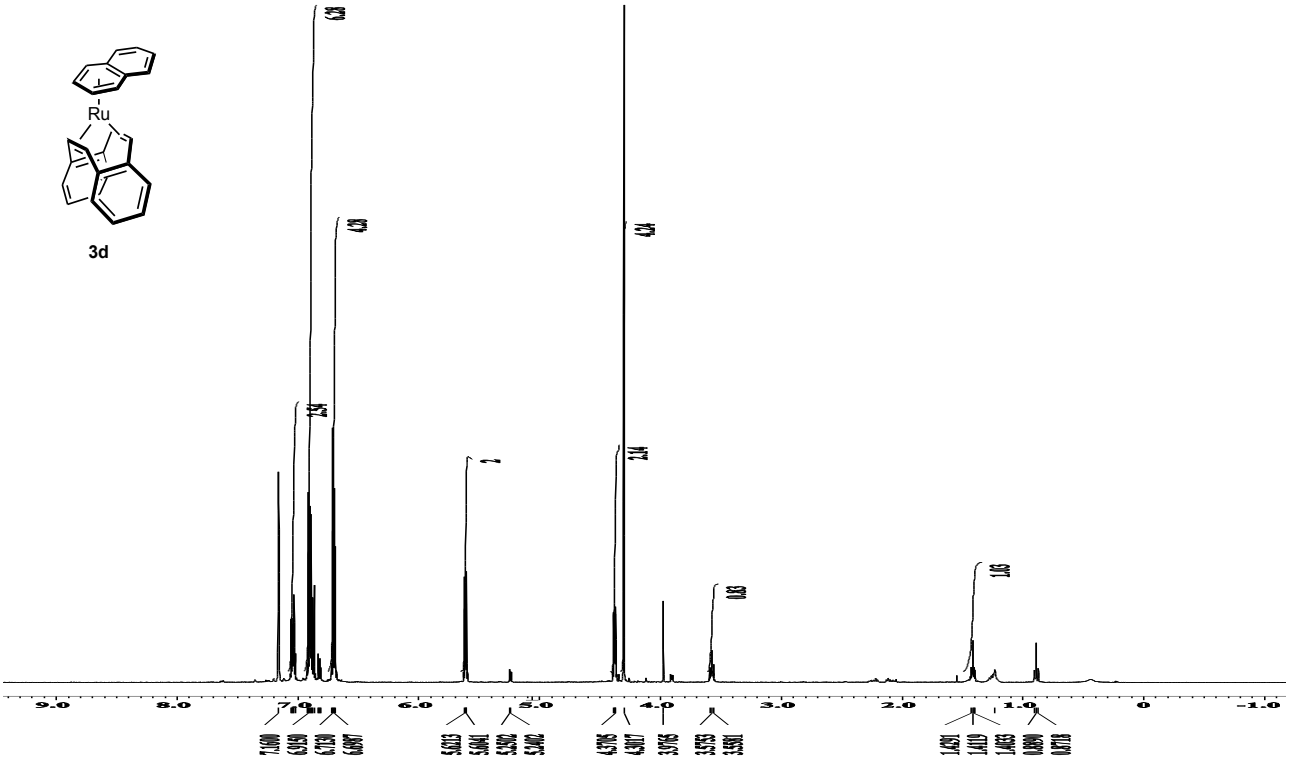


Figure S13-1. ^{1}H NMR spectrum for Ru(naphthalene)(dibenzo[a,e]cyclooctatetraene) (**3d**) (399.8 MHz, C_6D_6).

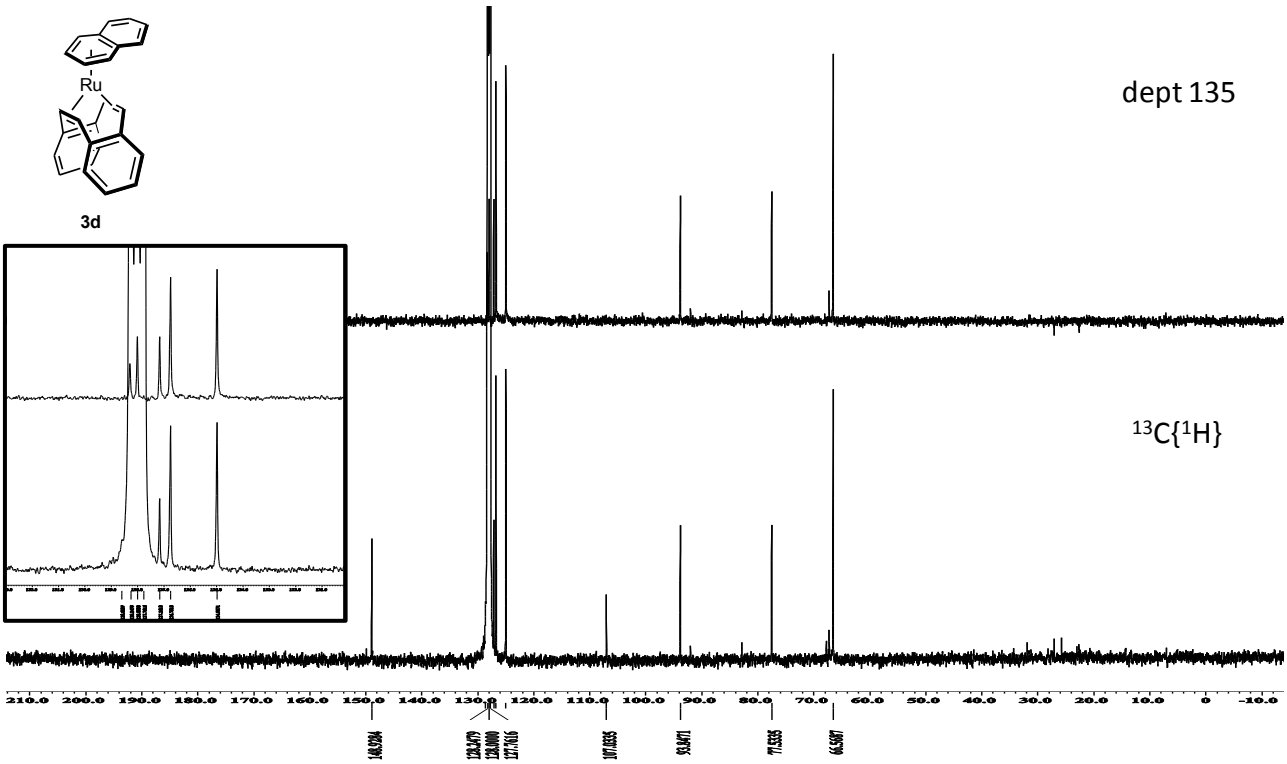


Figure S13-2. ^{13}C, dept 135 NMR spectrum for Ru(naphthalene)(dibenzo[a,e]cyclooctatetraene) (**3d**) (100.5 MHz, C_6D_6).

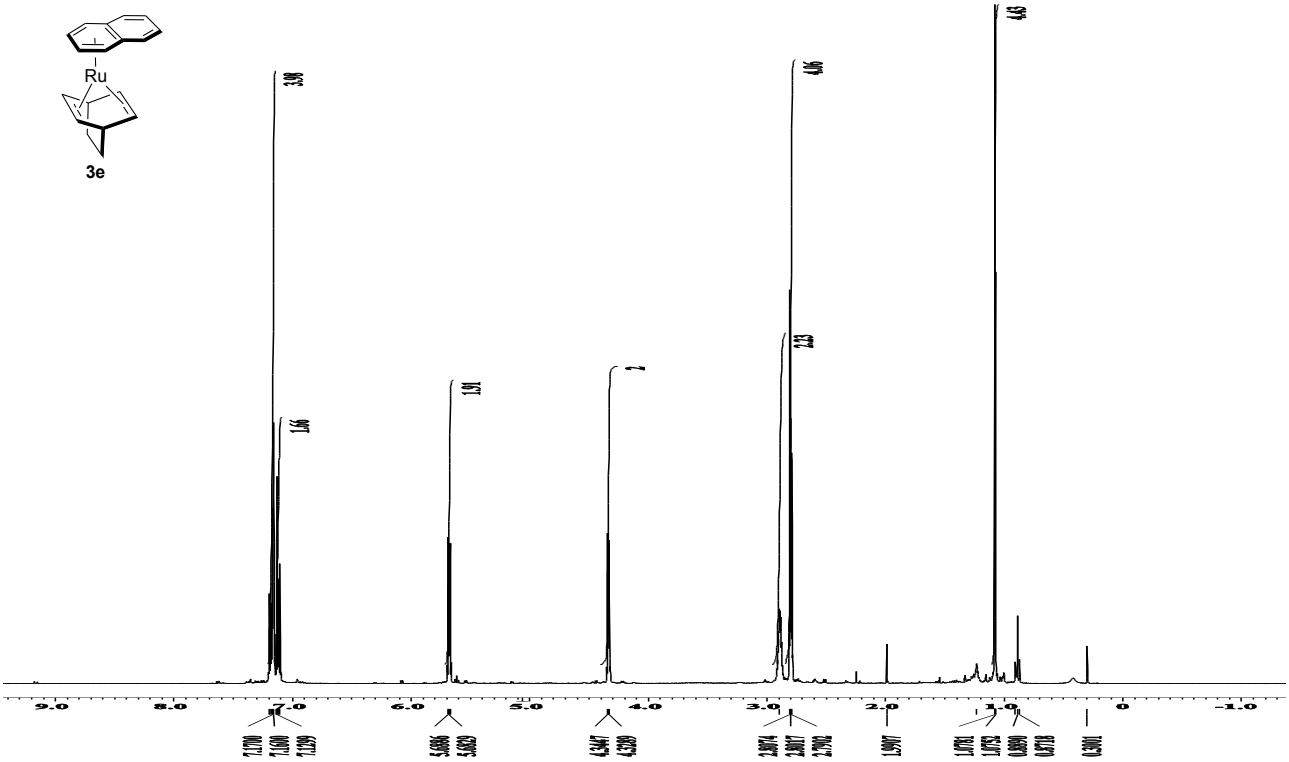


Figure S14-1. ^{1}H NMR spectrum for Ru(naphthalene)(bicyclo[2.2.2]octa-2,5-diene) (**3e**) (399.8 MHz, C_6D_6).

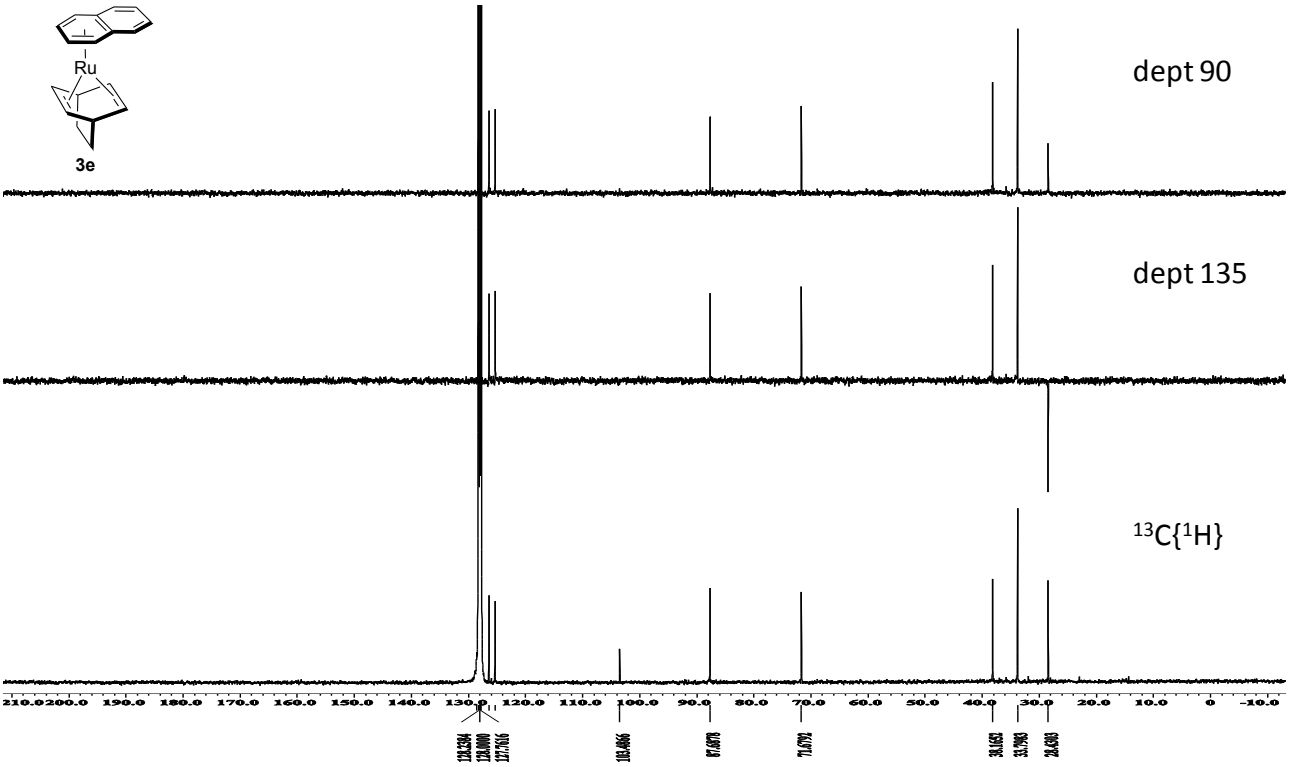


Figure S14-2. ^{13}C, dept 90, dept 135 NMR spectrum for Ru(naphthalene)(bicyclo[2.2.2]octa-2,5-diene) (**3e**) (100.5 MHz, C_6D_6).

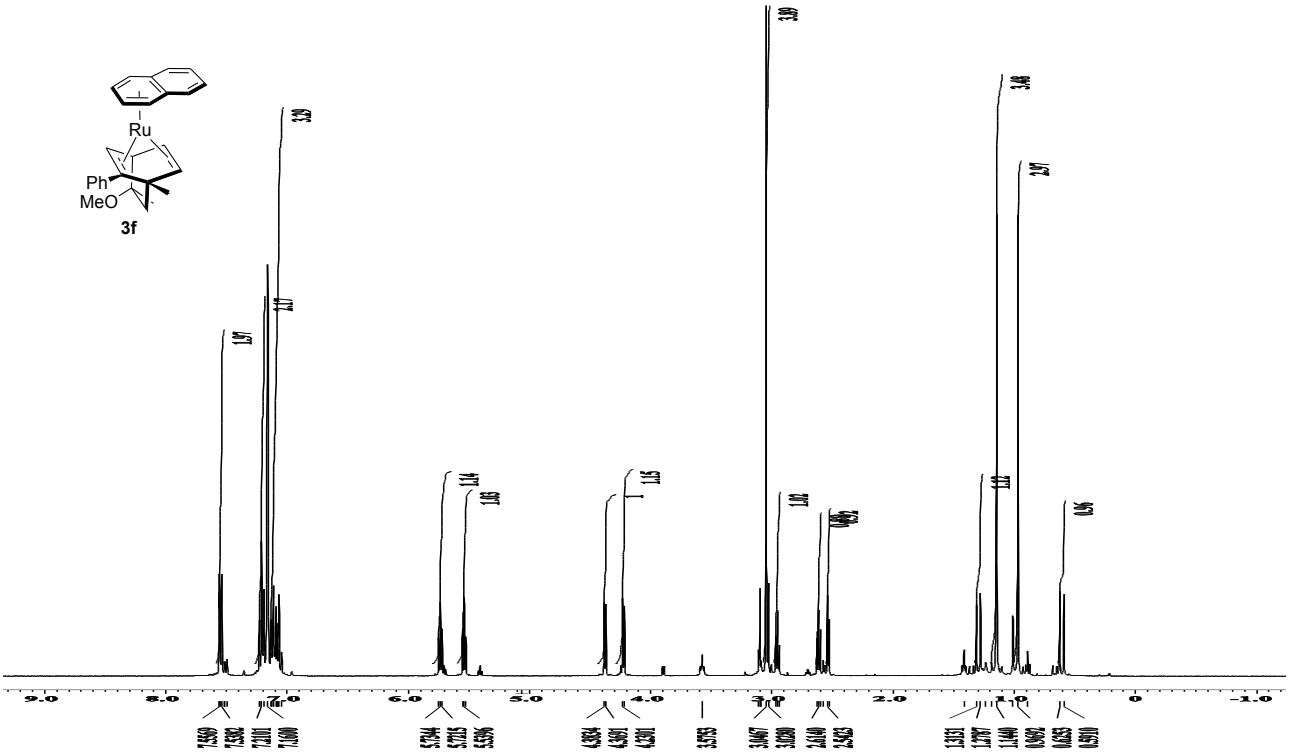


Figure S15-1. ^{1}H NMR spectrum for Ru(naphthalene)((-)-(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-bicyclo[2.2.2]octa-2,5-diene) (**3f**) (399.8 MHz, C_6D_6).

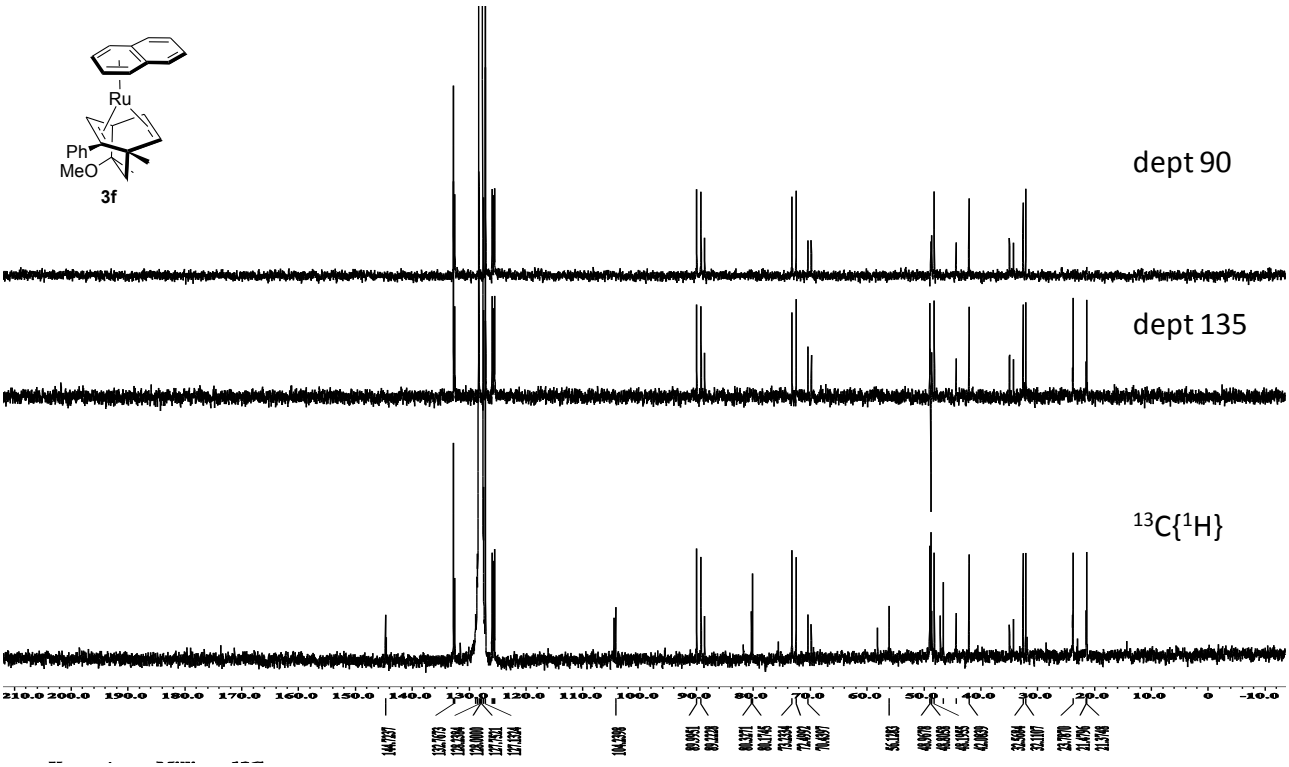


Figure S15-2. ^{13}C, dept 90, dept 135 NMR spectrum for Ru(naphthalene)((-)-(1*S*,4*R*,8*R*)-8-methoxy-1,8-dimethyl-2-phenyl-bicyclo[2.2.2]octa-2,5-diene) (**3f**) (100.5 MHz, C_6D_6).

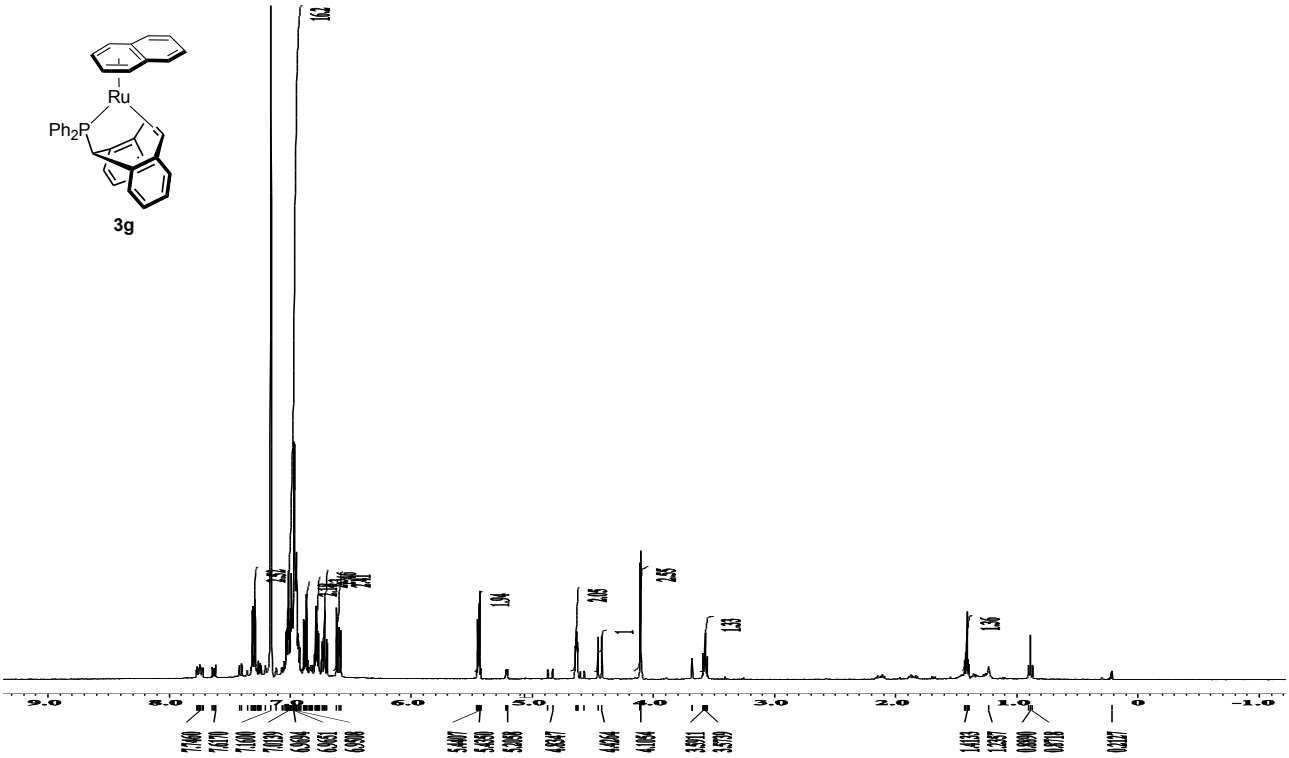


Figure S16-1. ^{1}H NMR spectrum for Ru(naphthalene)(5-diphenylphosphonyl-5H-dibenzocycloheptene) (**3g**) (399.8 MHz, C_6D_6).

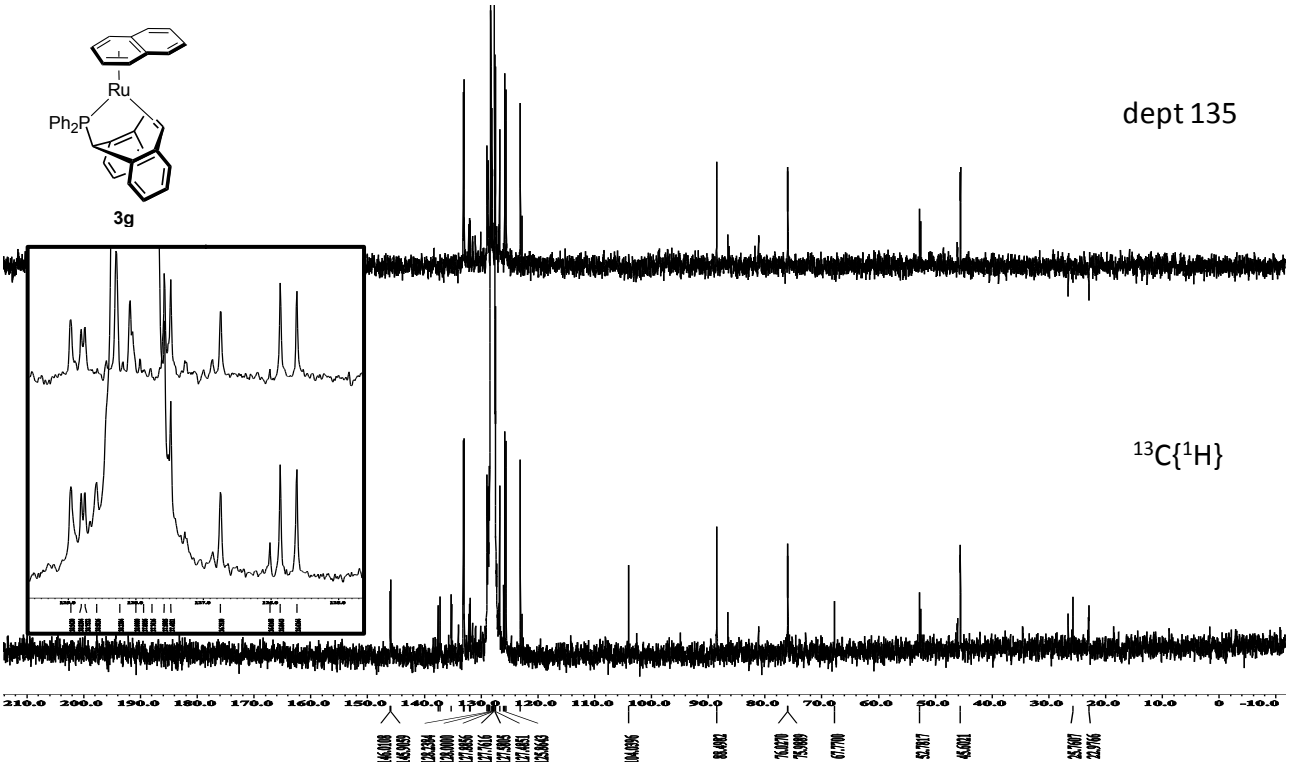


Figure S16-2. ^{13}C, dept 135 NMR spectrum for Ru(naphthalene)(5-diphenylphosphonyl-5H-dibenzocycloheptene) (**3g**) (100.5 MHz, C_6D_6).

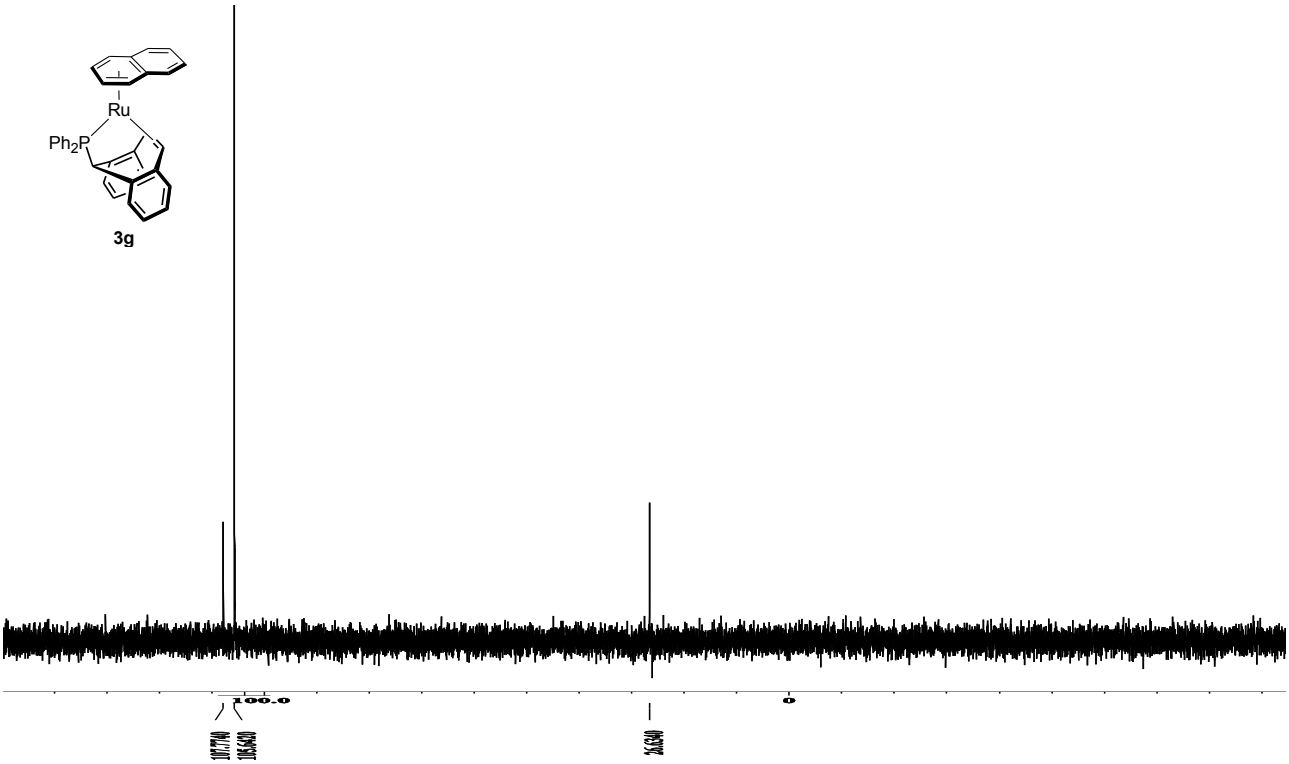


Figure S16-3. ^{31}P NMR spectrum for Ru(naphthalene)(5-diphenylphosphonyl-5H-dibenzocycloheptene) (**3g**) (161.8 MHz, $CDCl_3$).

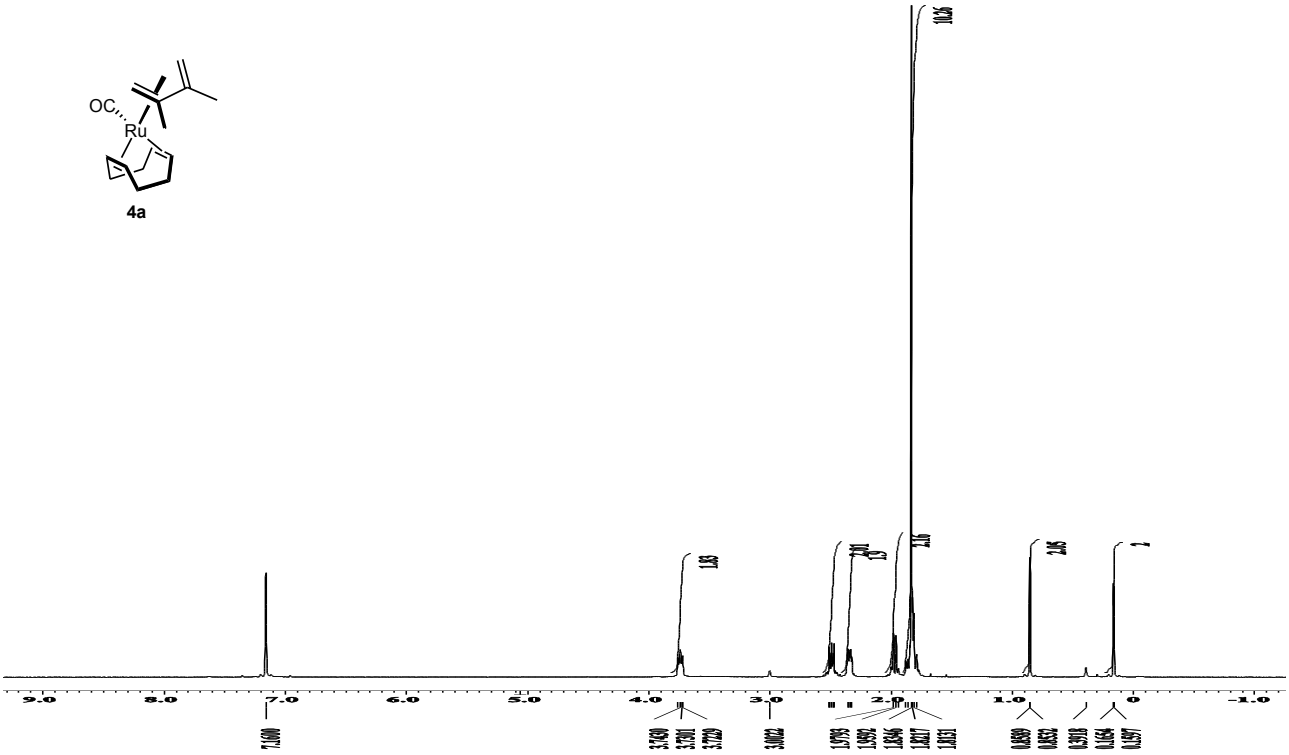


Figure S17-1. ^{1}H NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(1,5-cyclooctadiene) (**4a**) (399.8 MHz, C_6D_6).

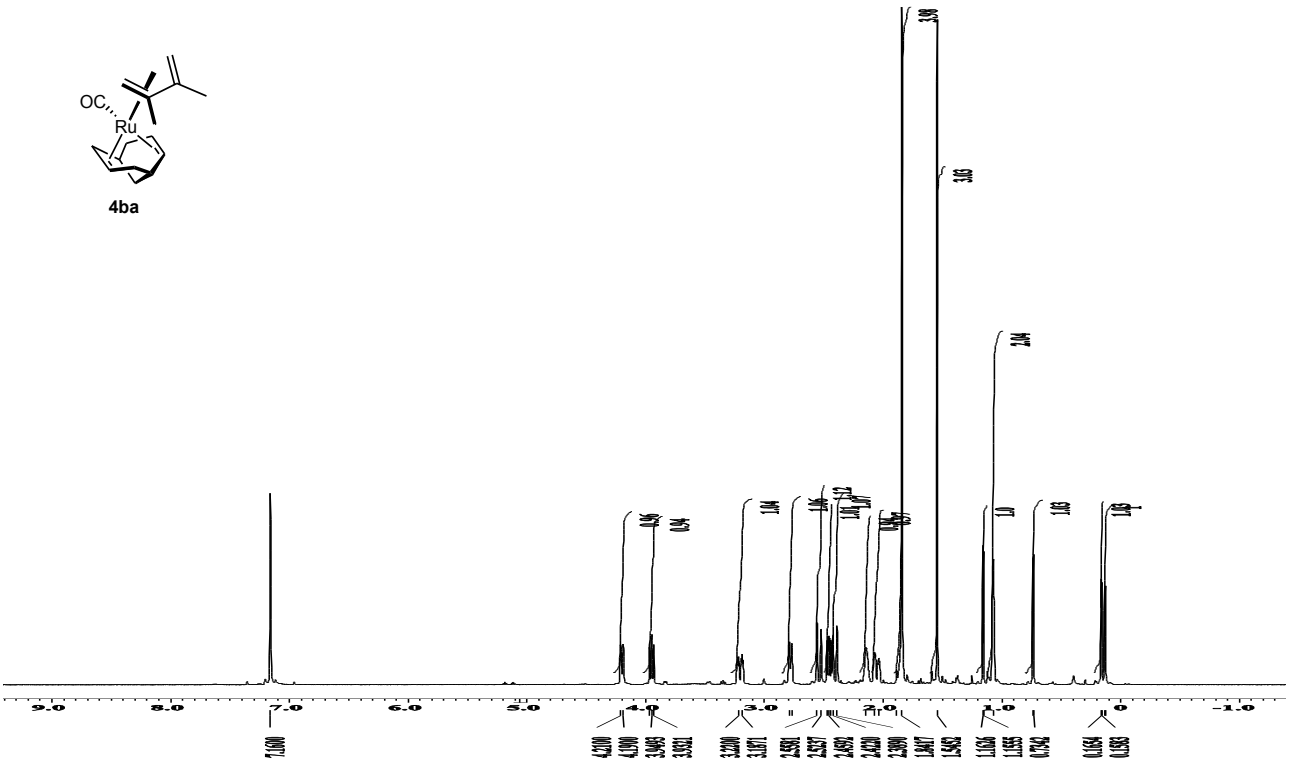


Figure S18-1. ^{1}H NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(bicyclo[3.3.1]nona-2,6-diene) (**4b**) (399.8 MHz, C_6D_6).

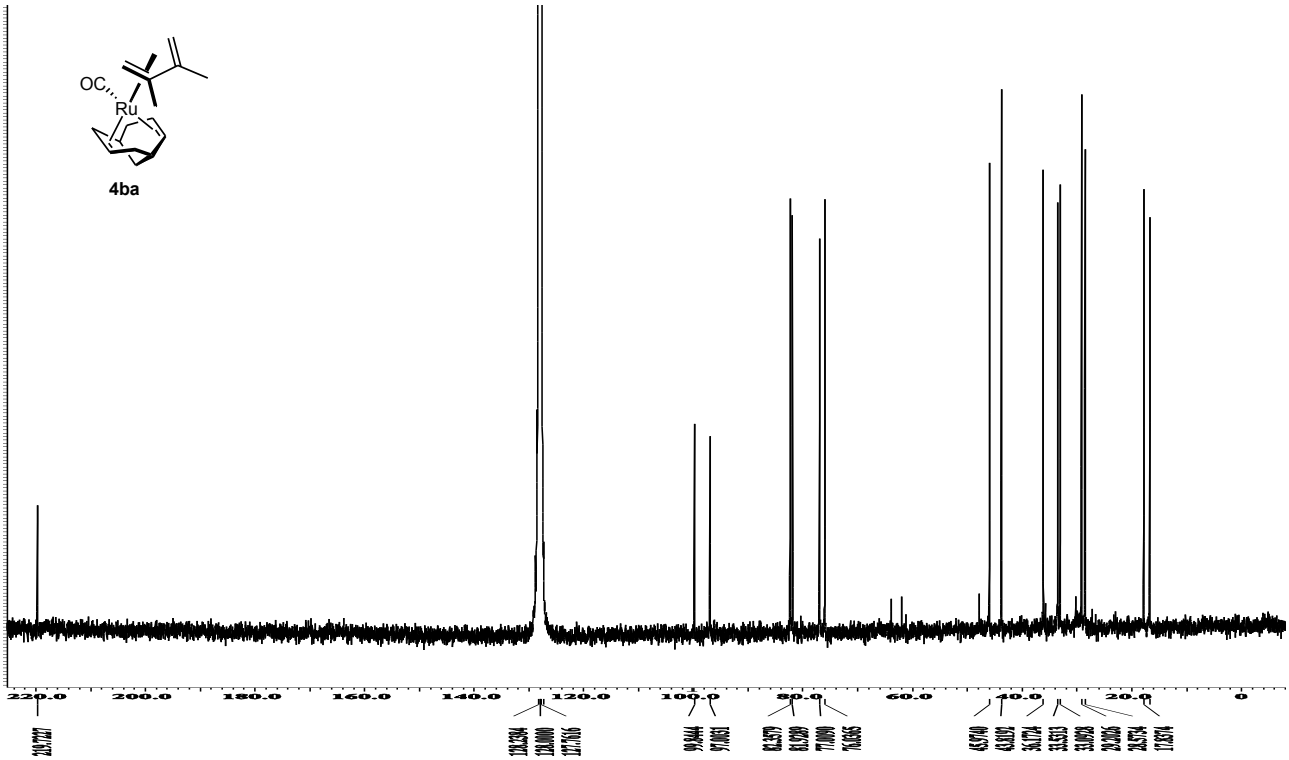


Figure S18-2. ^{13}C NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(bicyclo[3.3.1]nona-2,6-diene) (**4b**) (100.5 MHz, C_6D_6).

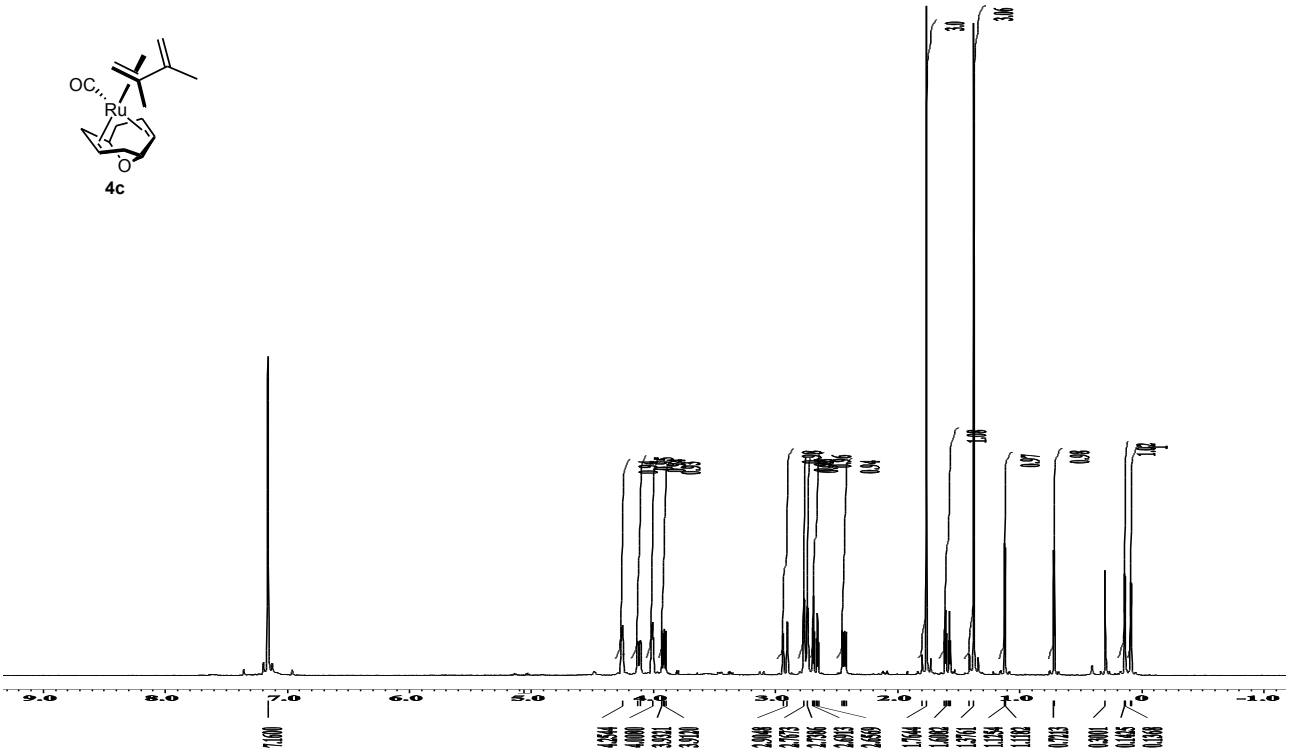


Figure S19-1. ^{1}H NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(9-oxa-bicyclo[3.3.1]nona-2,6-diene) (**4c**) (399.8 MHz, C_6D_6).

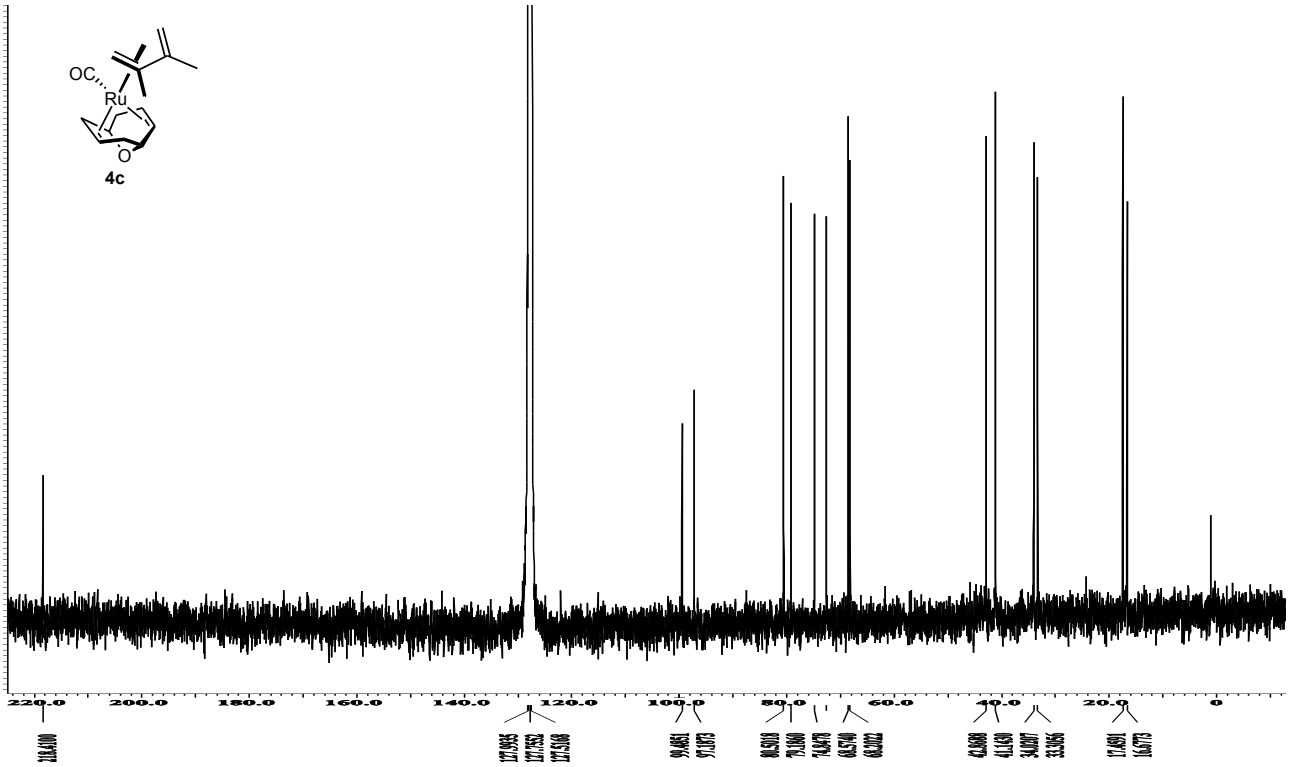


Figure S19-2. ^{13}C NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(9-oxa-bicyclo[3.3.1]nona-2,6-diene) (**4c**) (100.5 MHz, C_6D_6).

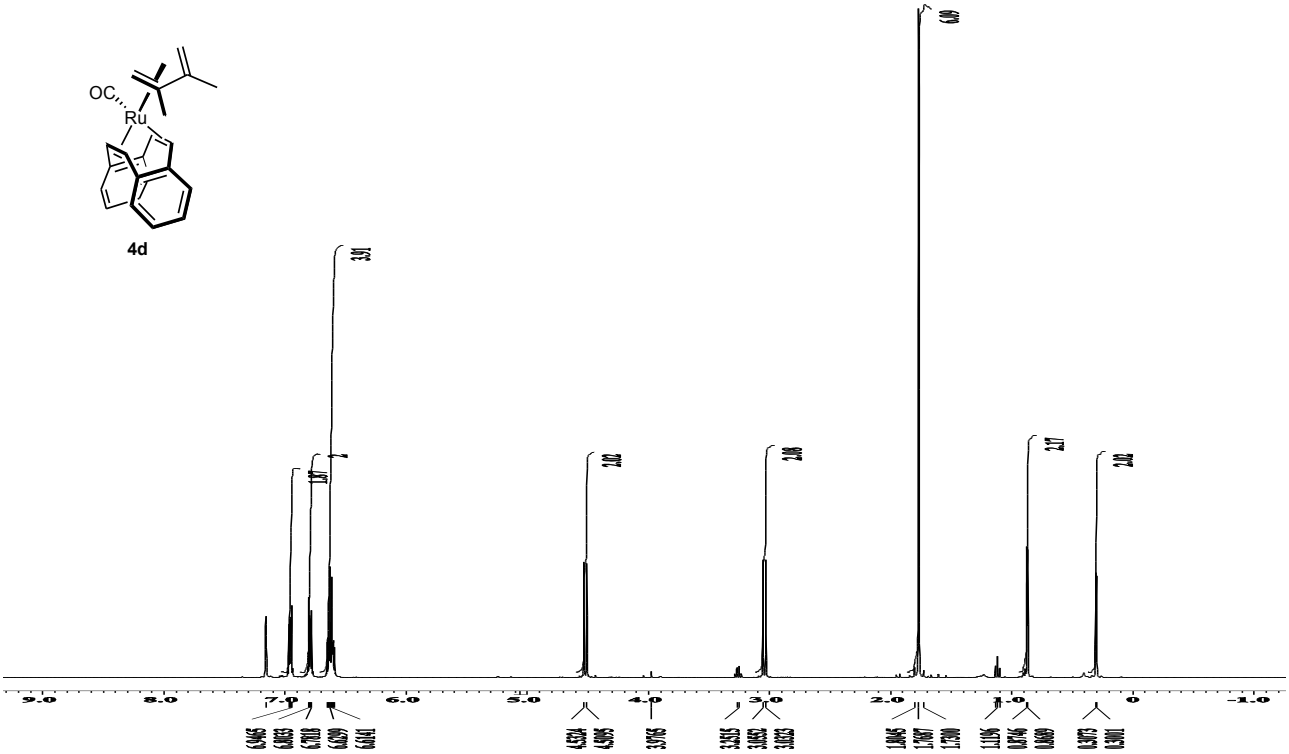


Figure S20-1. ^{1}H NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(dibenzo[a,e]cyclooctatetraene) (**4d**) (399.8 MHz, C_6D_6).

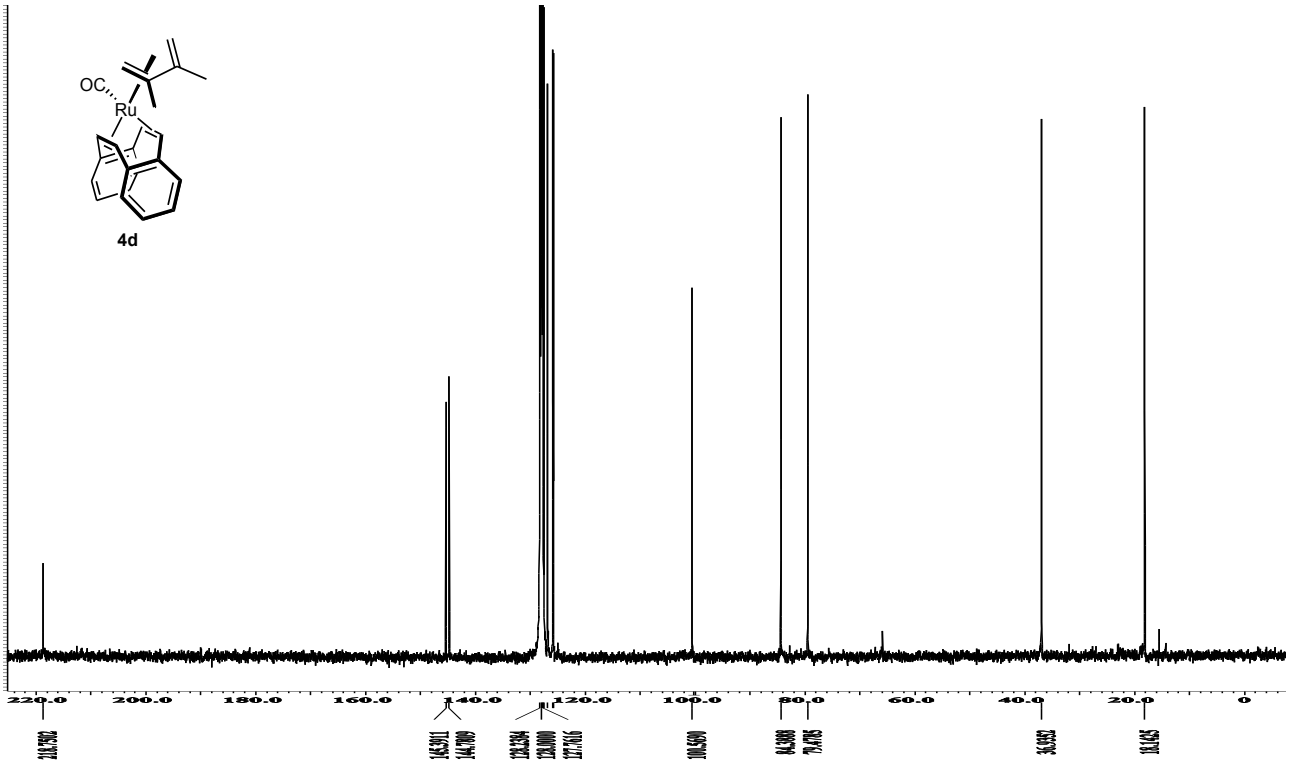


Figure S20-2. ^{13}C NMR spectrum for Ru(2,3-dimethylbutadiene)(CO)(dibenzo[a,e]cyclooctatetraene) (**4d**) (100.5 MHz, C_6D_6).

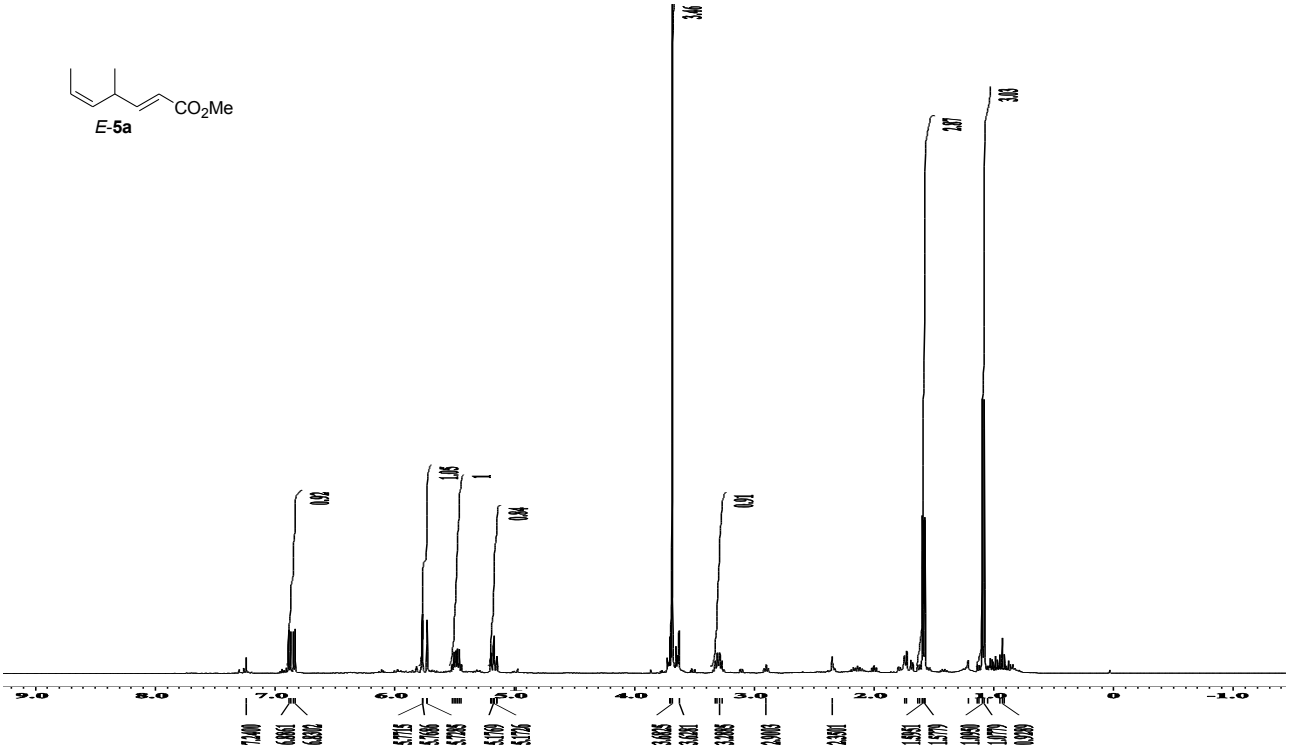


Figure S21-1. ^{1}H NMR spectrum for (2*E*,5*Z*)-methyl 4-methyl-hepta-2,5-dienoate (*E*-**5a**) (399.8 MHz, $CDCl_3$).

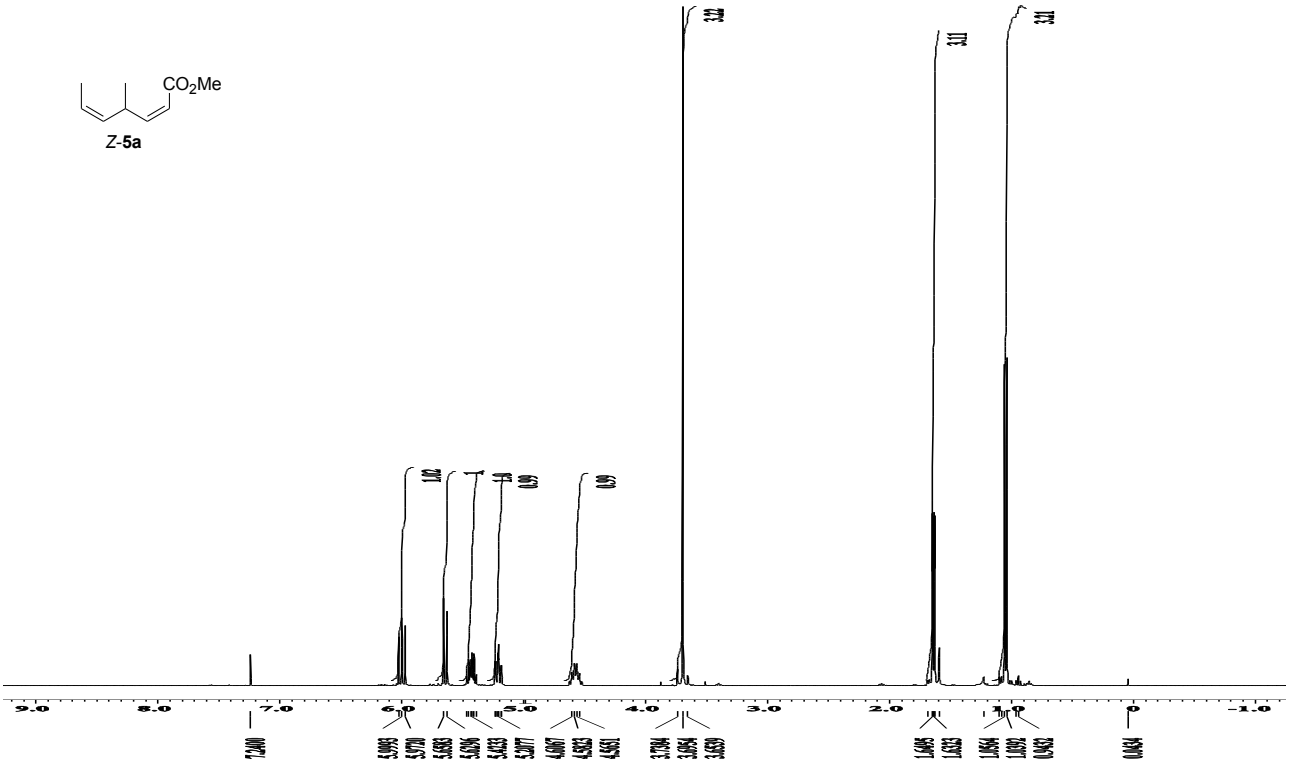


Figure S21-2. ^{1}H NMR spectrum for (2*Z*,5*Z*)-methyl 4-methyl-hepta-2,5-dienoate (*Z*-**5a**) (399.8 MHz, $CDCl_3$).

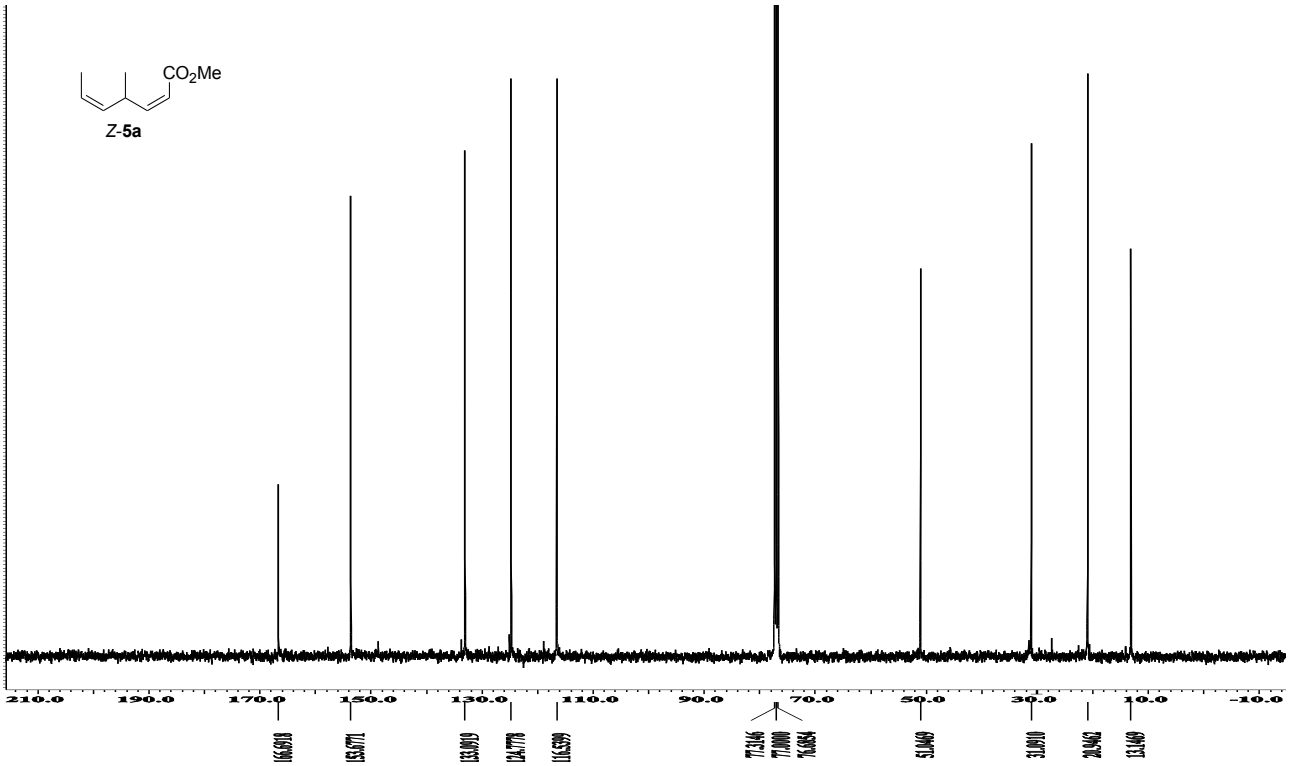


Figure S21-3. ^{13}C NMR spectrum for (2*Z*,5*Z*)-methyl 4-methyl-hepta-2,5-dienoate (*Z*-**5a**) (100.5 MHz, $CDCl_3$).

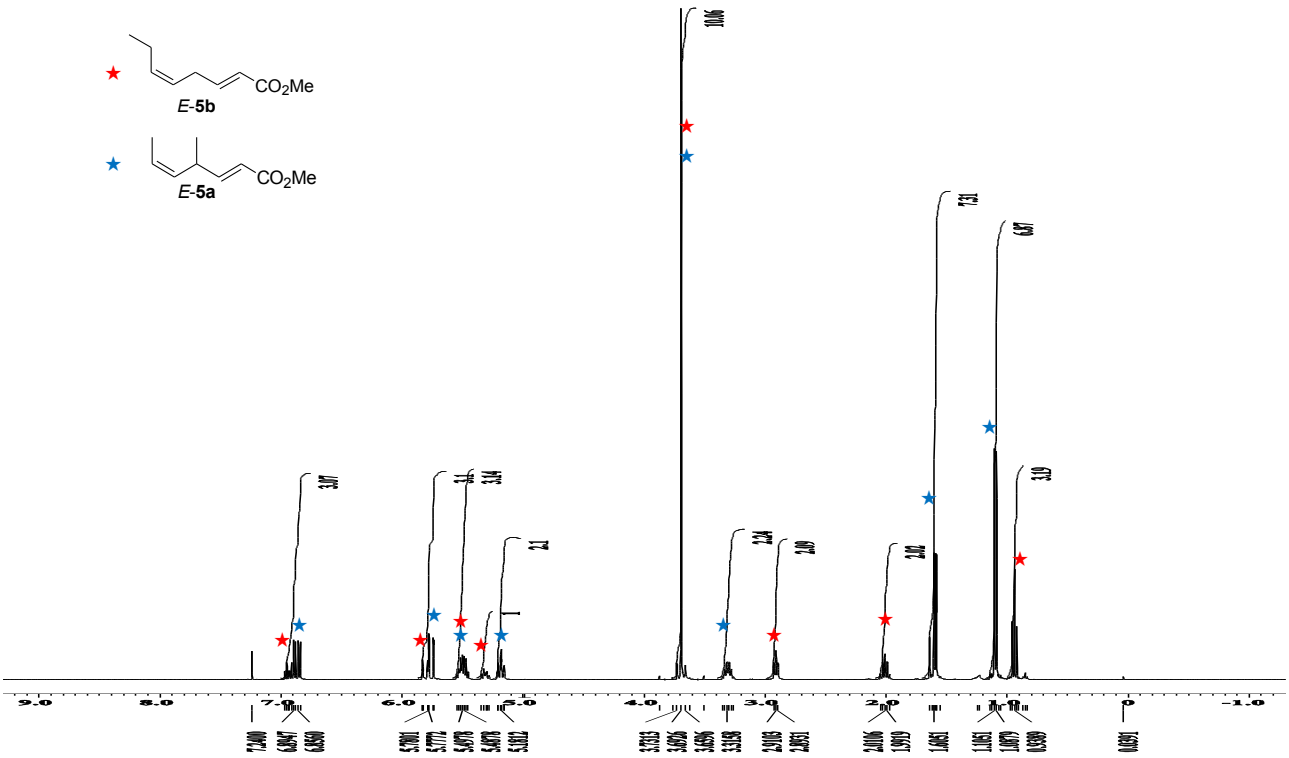


Figure S21-4. ^{1}H NMR spectrum for (2*E*,5*Z*)-Methyl octa-2,5-dienoate (*E*-**5b**) ((*E*-**5a**:*E*-**5b** = 68:32 sample), 399.8 MHz, $CDCl_3$).

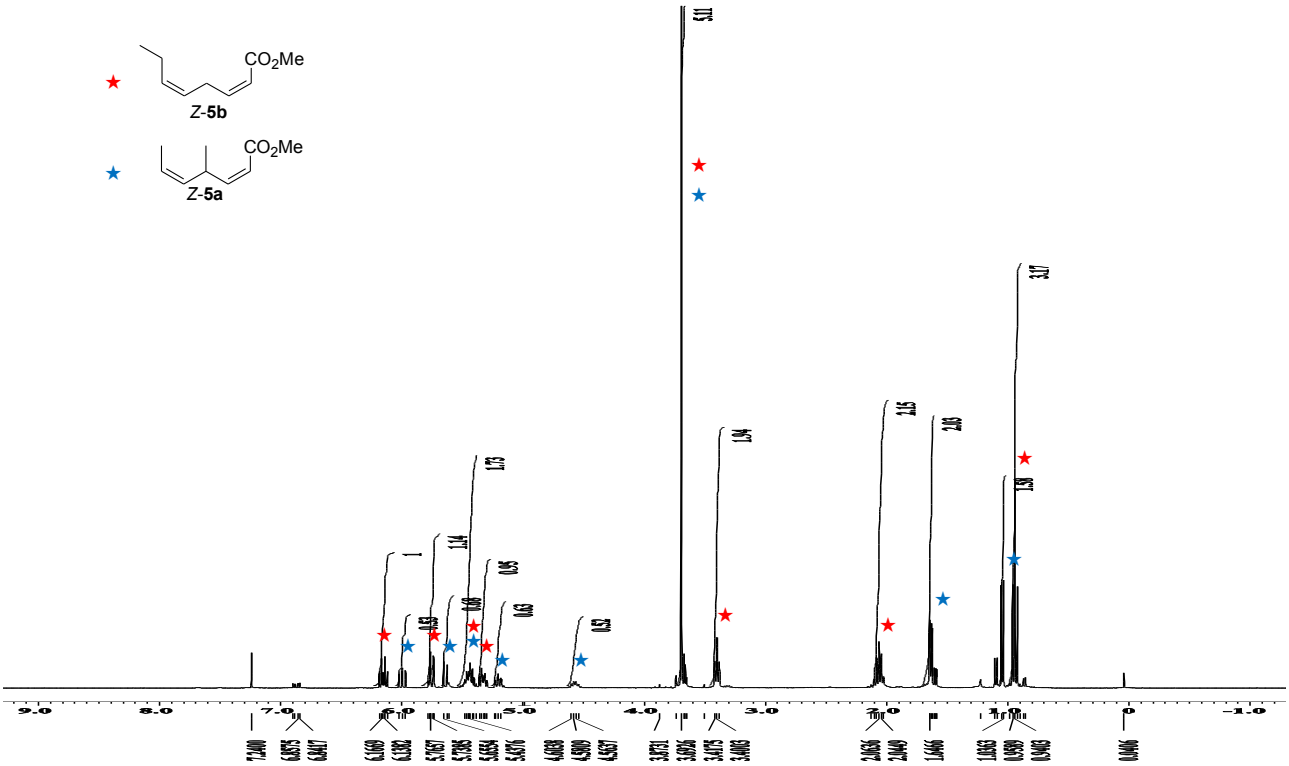


Figure S21-5. ^{1}H NMR spectrum for (2*Z*,5*Z*)-Methyl octa-2,5-dienoate (*Z*-**5b**) ((*Z*-**5a**:*Z*-**5b** = 35:65 sample), 399.8 MHz, $CDCl_3$).

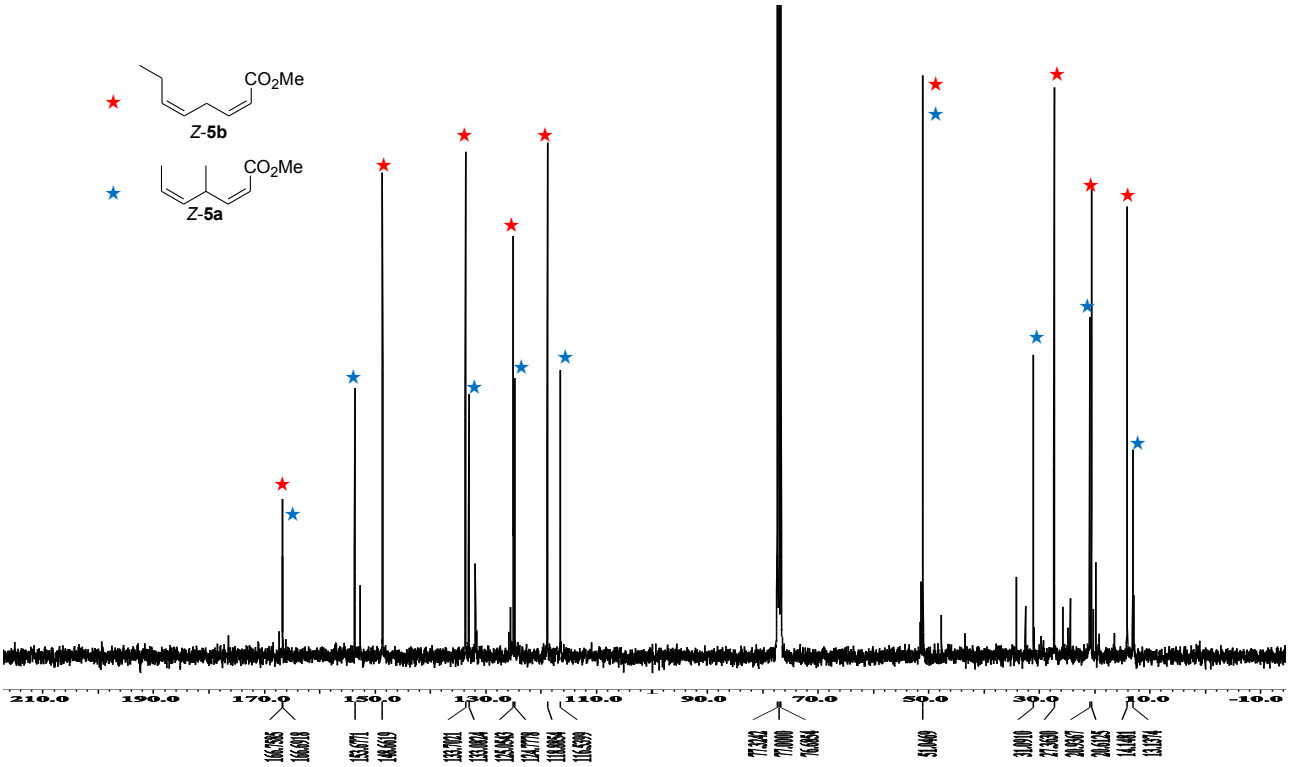


Figure S21-6. ^{13}C NMR spectrum for (2*Z*,5*Z*)-Methyl octa-2,5-dienoate (*Z*-**5b**) ((*Z*-**5a**:*Z*-**5b** = 35:65 sample), 100.5 MHz, $CDCl_3$).

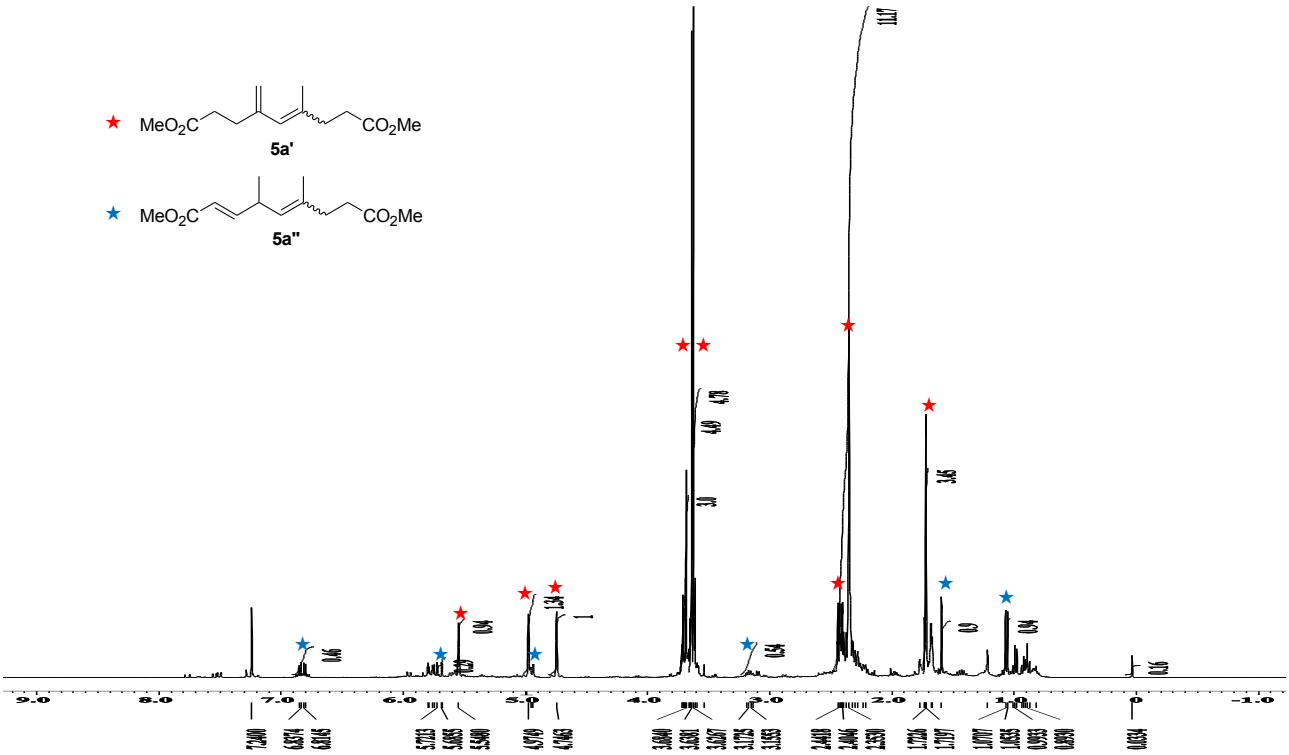


Figure S21-7. ^{1}H NMR spectrum for dimethyl 4-methyl-6-methylenenona-4-enedioate (**5a'**) and dimethyl 4,6-dimethylnona-2,5-dienedioate (**5a"**) ((cross trimer mixture sample), 399.8 MHz, $CDCl_3$).

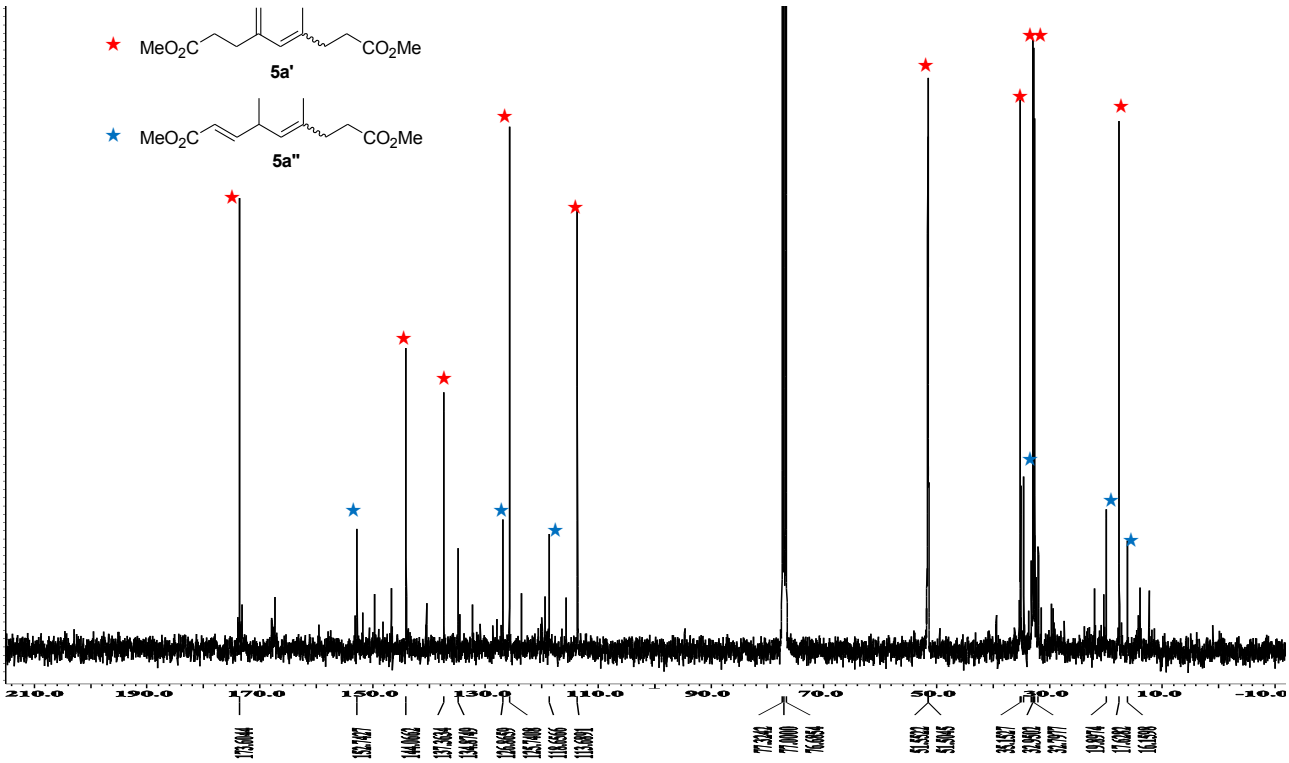


Figure S21-8. ^{13}C NMR spectrum for dimethyl 4-methyl-6-methylenenona-4-enedioate (**5a'**) and dimethyl 4,6-dimethylnona-2,5-dienedioate (**5a"**) ((cross trimer mixture sample), 100.5 MHz, $CDCl_3$).

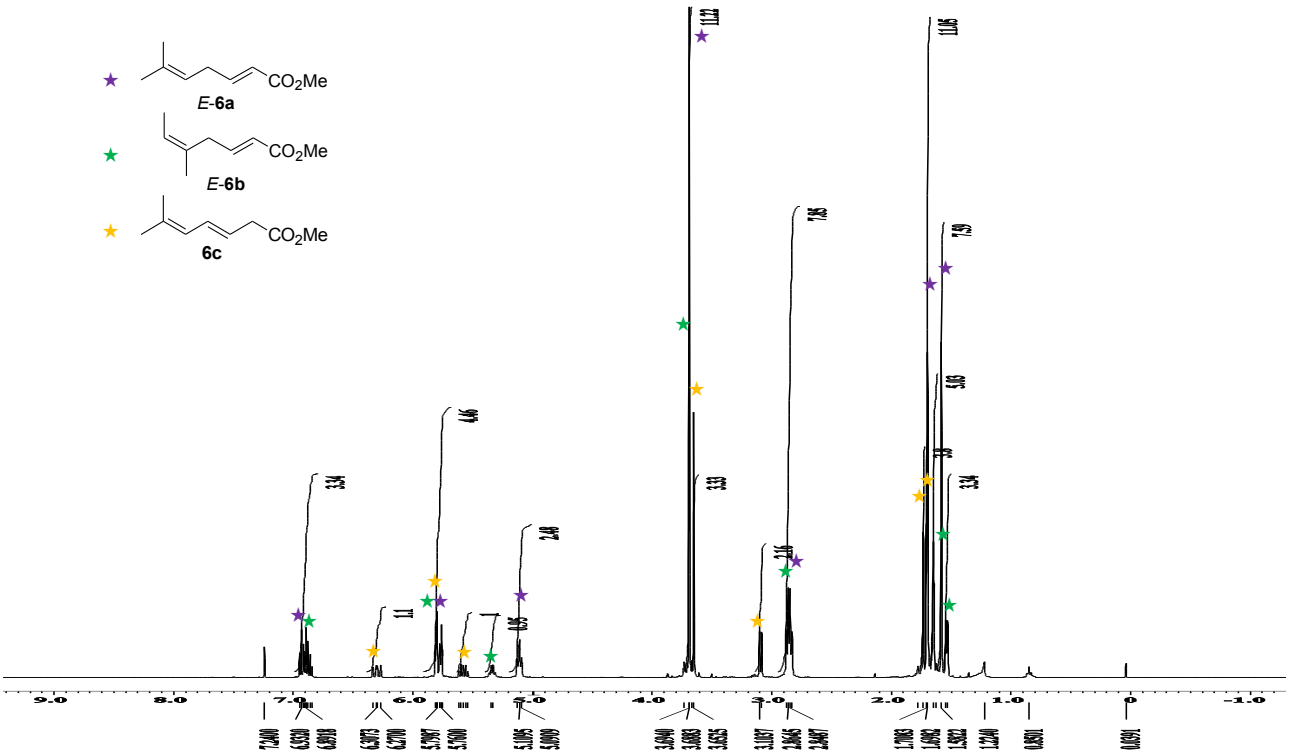


Figure S22-1. ^{1}H NMR spectrum for (2*E*)-Methyl 6-methyl-hepta-2,5-dienoate (*E*-**6a**), (2*E*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*E*-**6b**) and (3*E*)-Methyl 6-methyl-hepta-3,5-dienoate (**6c**) ((*E*-**6a**:*E*-**6b**:**6c** = 55:23:22 sample), 399.8 MHz, $CDCl_3$).

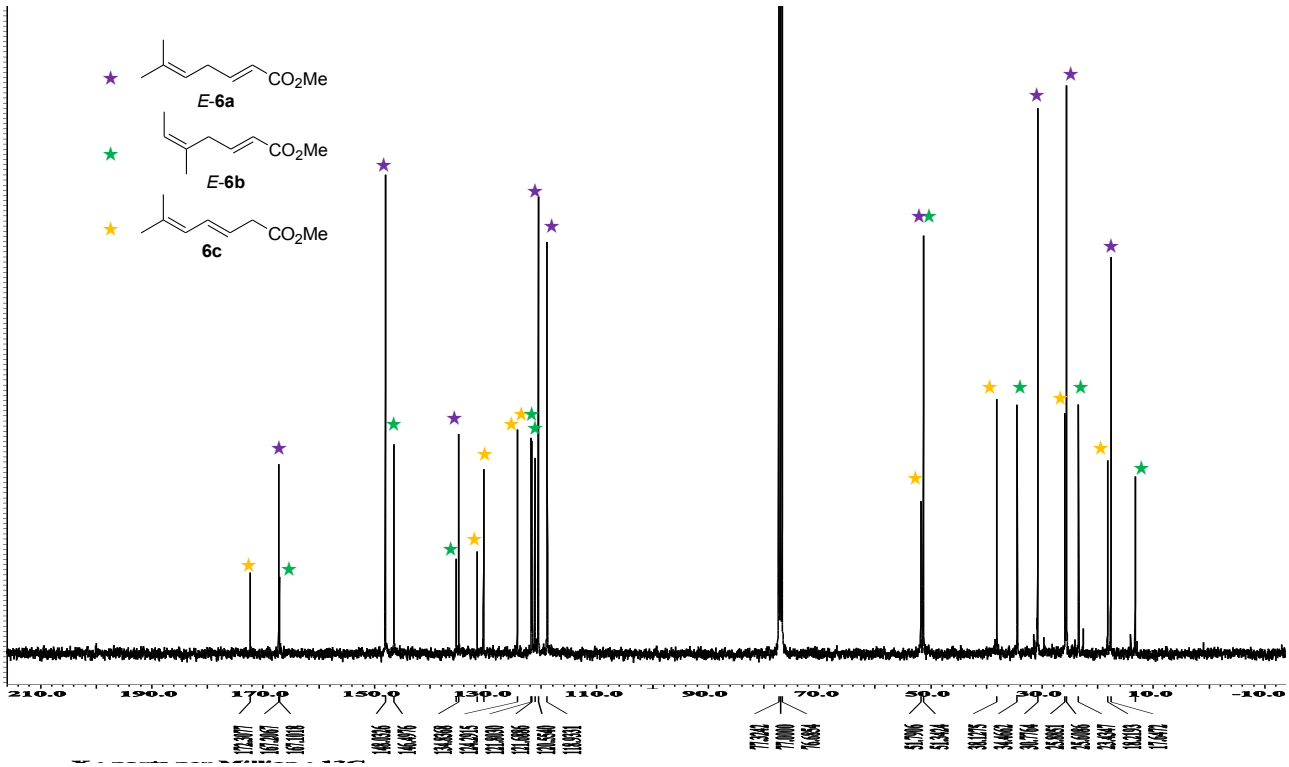


Figure S22-2. ^{13}C NMR spectrum for (2*E*)-Methyl 6-methyl-hepta-2,5-dienoate (*E*-**6a**), (2*E*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*E*-**6b**) and (3*E*)-Methyl 6-methyl-hepta-3,5-dienoate (**6c**) ((*E*-**6a**:*E*-**6b**:**6c** = 55:23:22 sample), 100.5 MHz, $CDCl_3$).

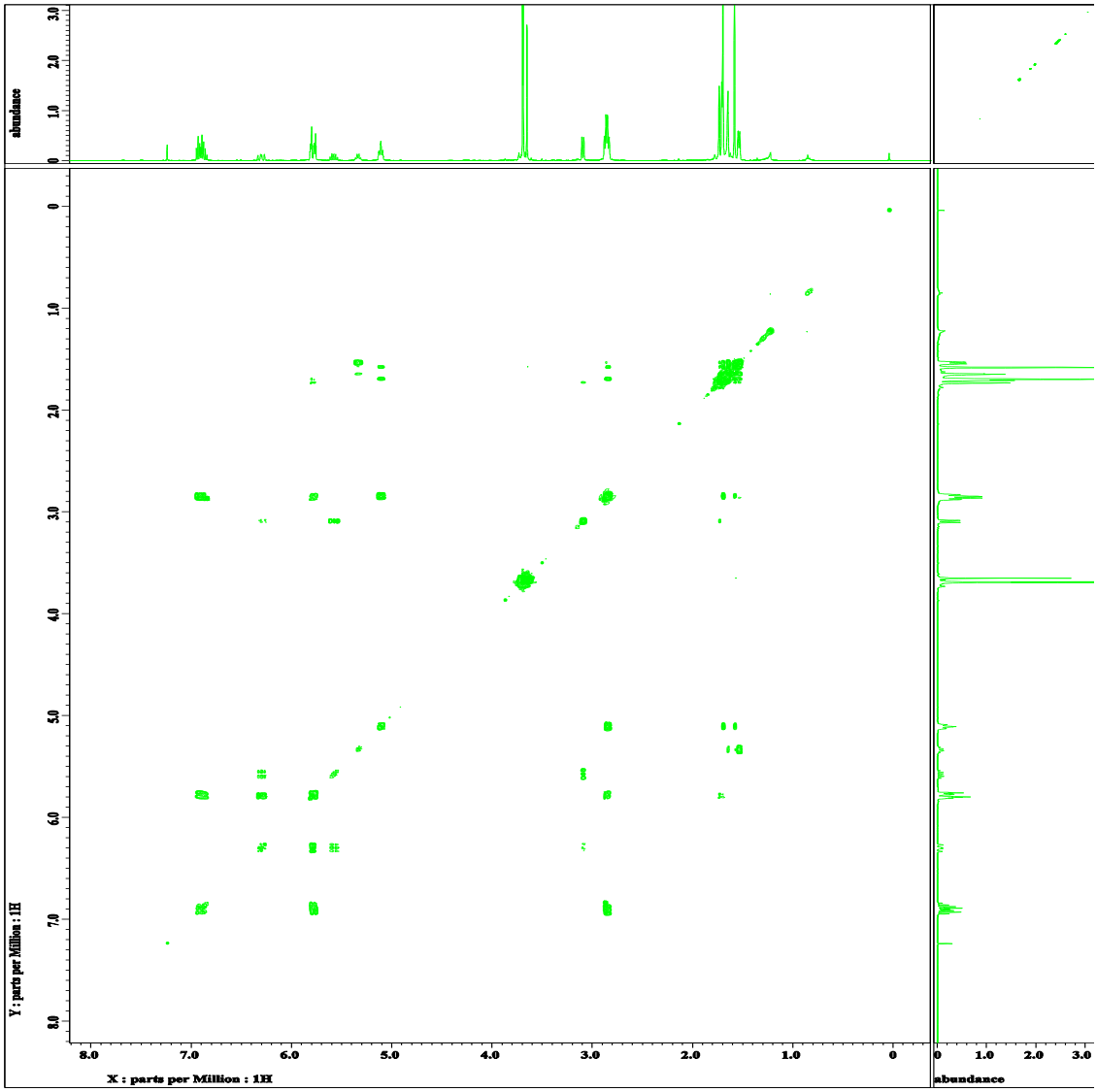


Figure S22-3. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*E*)-Methyl 6-methyl-hepta-2,5-dienoate (*E*-**6a**), (2*E*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*E*-**6b**) and (3*E*)-Methyl 6-methyl-hepta-3,5-dienoate (**6c**) ((*E*-**6a**:*E*-**6b**:**6c** = 55:23:22 sample), 399.8 MHz, $CDCl_3$).

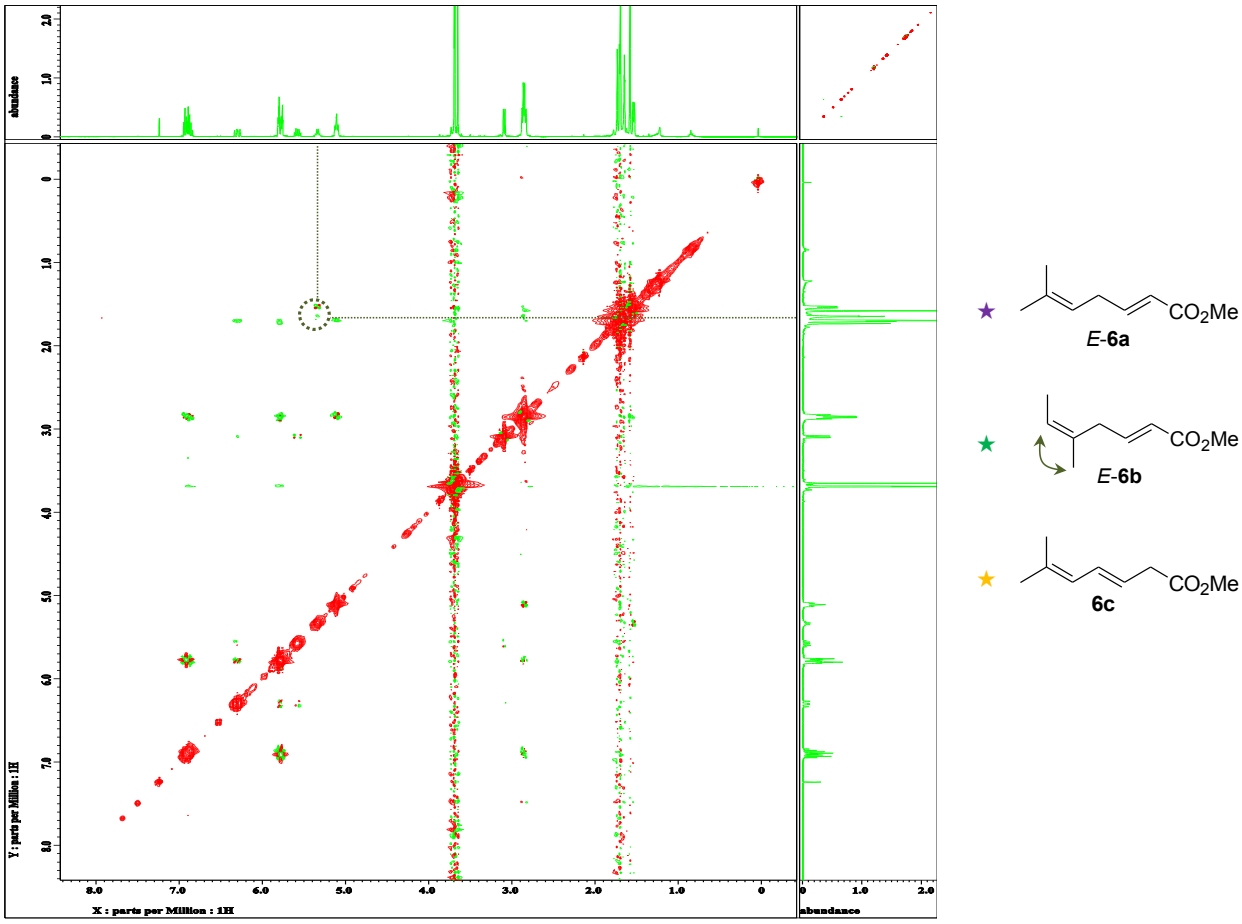


Figure S22-4. Phase sensitive NOESY 2D NMR spectrum for (2*E*)-Methyl 6-methyl-hepta-2,5-dienoate (*E*-**6a**), (2*E*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*E*-**6b**) and (3*E*)-Methyl 6-methyl-hepta-3,5-dienoate (**6c**) ((*E*-**6a**:*E*-**6b**:**6c** = 55:23:22 sample), 399.8 MHz, $CDCl_3$).

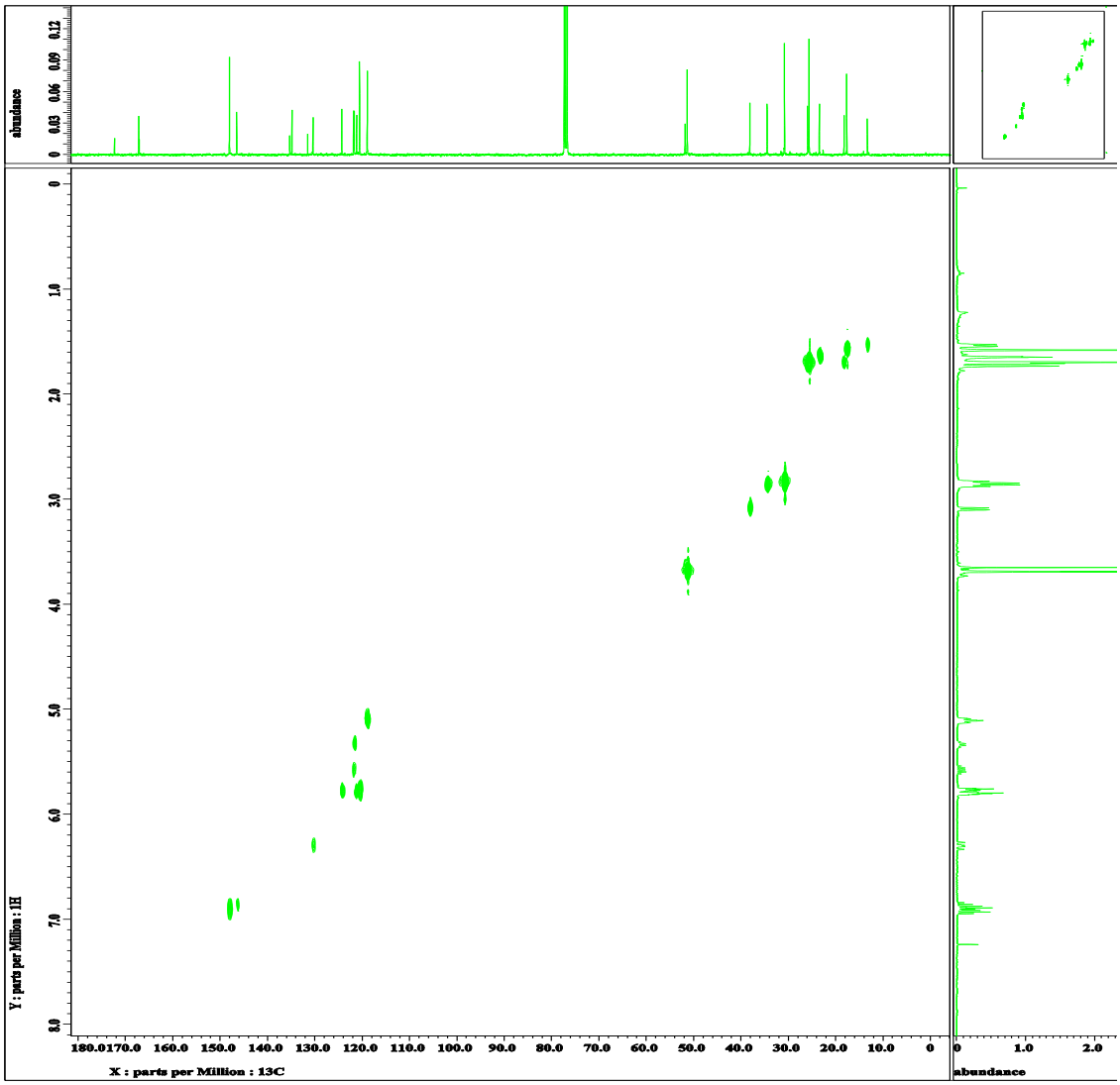


Figure S22-5. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (2*E*)-Methyl 6-methyl-hepta-2,5-dienoate (*E*-**6a**), (2*E*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*E*-**6b**) and (3*E*)-Methyl 6-methyl-hepta-3,5-dienoate (**6c**) ((*E*-**6a**:*E*-**6b**:**6c** = 55:23:22 sample), 100.5 MHz, $CDCl_3$).

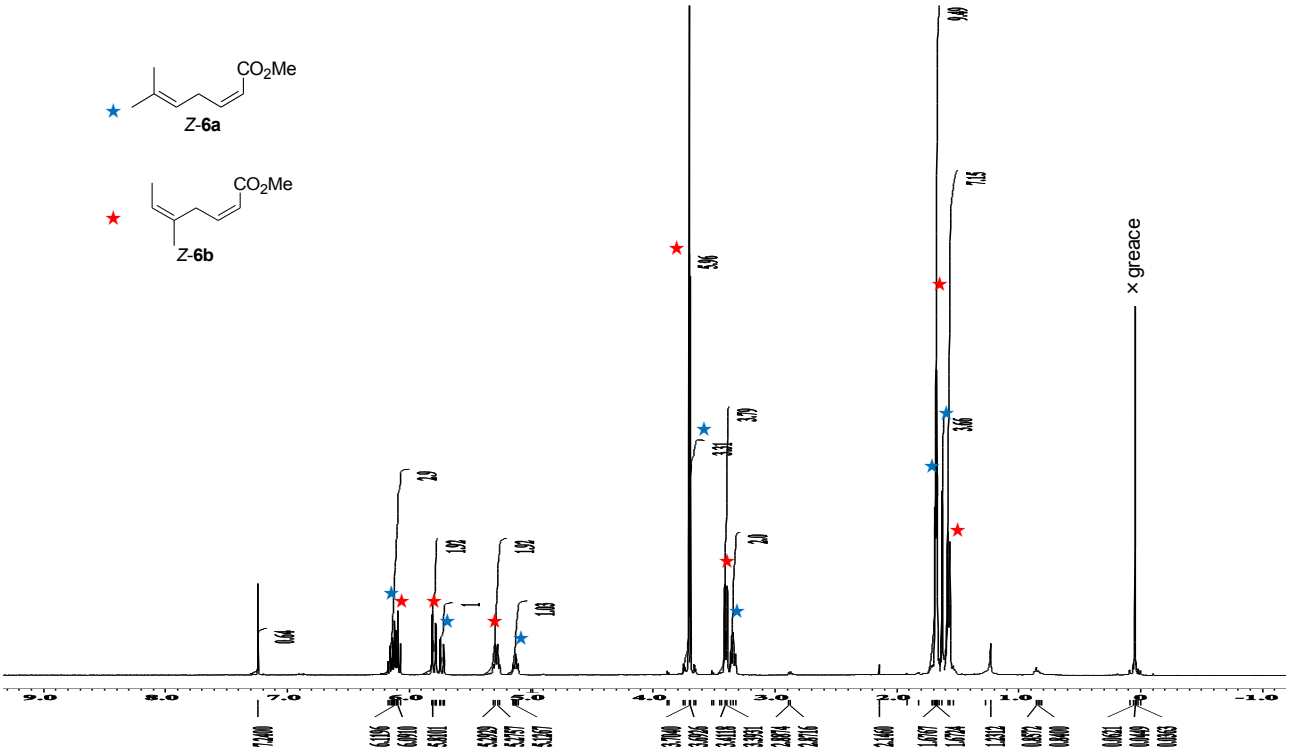


Figure S23-1. ^{1}H NMR spectrum for (2*Z*)-Methyl 6-methyl-hepta-2,5-dienoate (*Z*-**6a**) and (2*Z*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*Z*-**6b**) ((*Z*-**6a**:*Z*-**6b** = 35:65 sample), 399.8 MHz, $CDCl_3$).

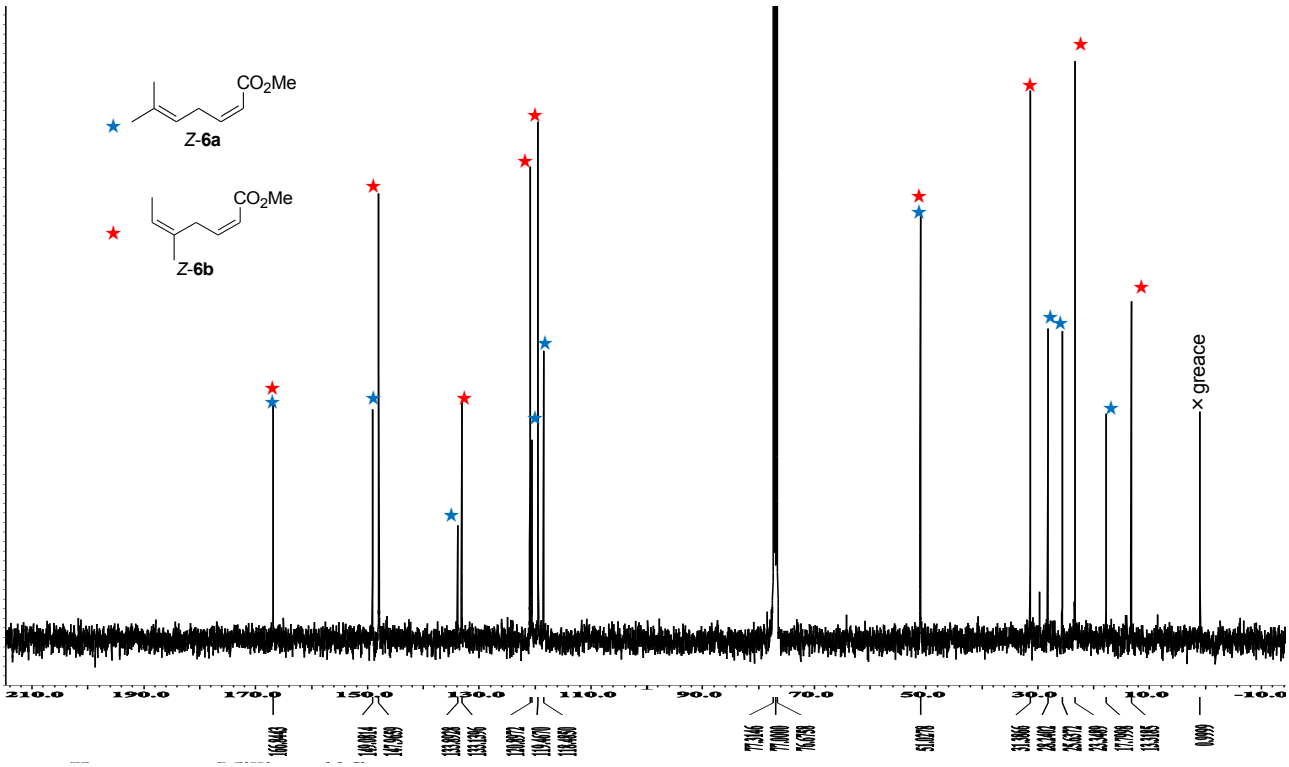


Figure S23-2. ^{13}C NMR spectrum for (2*Z*)-Methyl 6-methyl-hepta-2,5-dienoate (*Z*-**6a**) and (2*Z*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*Z*-**6b**) ((*Z*-**6a**:*Z*-**6b** = 35:65 sample), 100.5 MHz, $CDCl_3$).

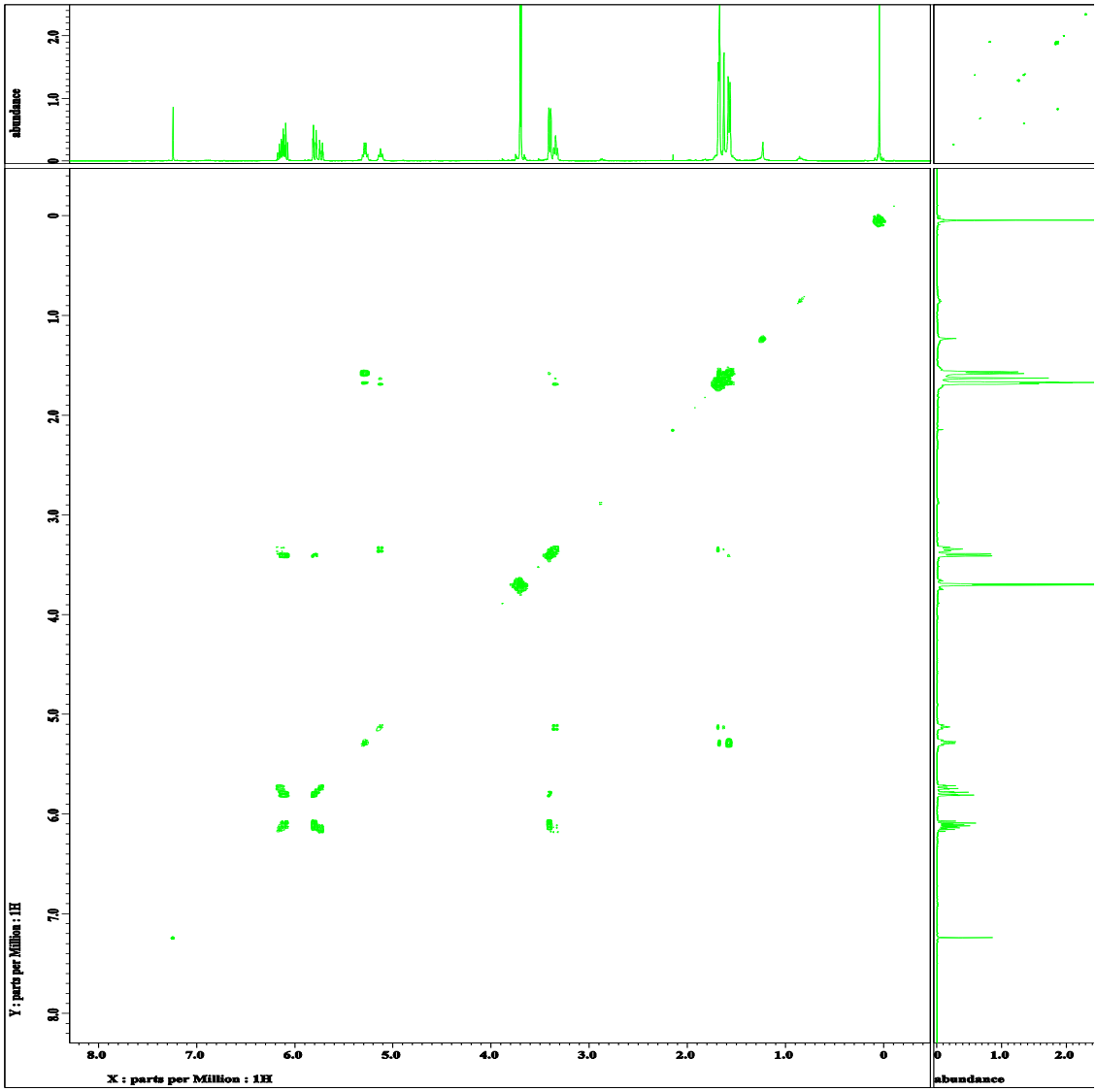


Figure S23-3. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*Z*)-Methyl 6-methyl-hepta-2,5-dienoate (*Z*-**6a**) and (2*Z*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*Z*-**6b**) ((*Z*-**6a**:*Z*-**6b** = 35:65 sample), 399.8 MHz, $CDCl_3$).

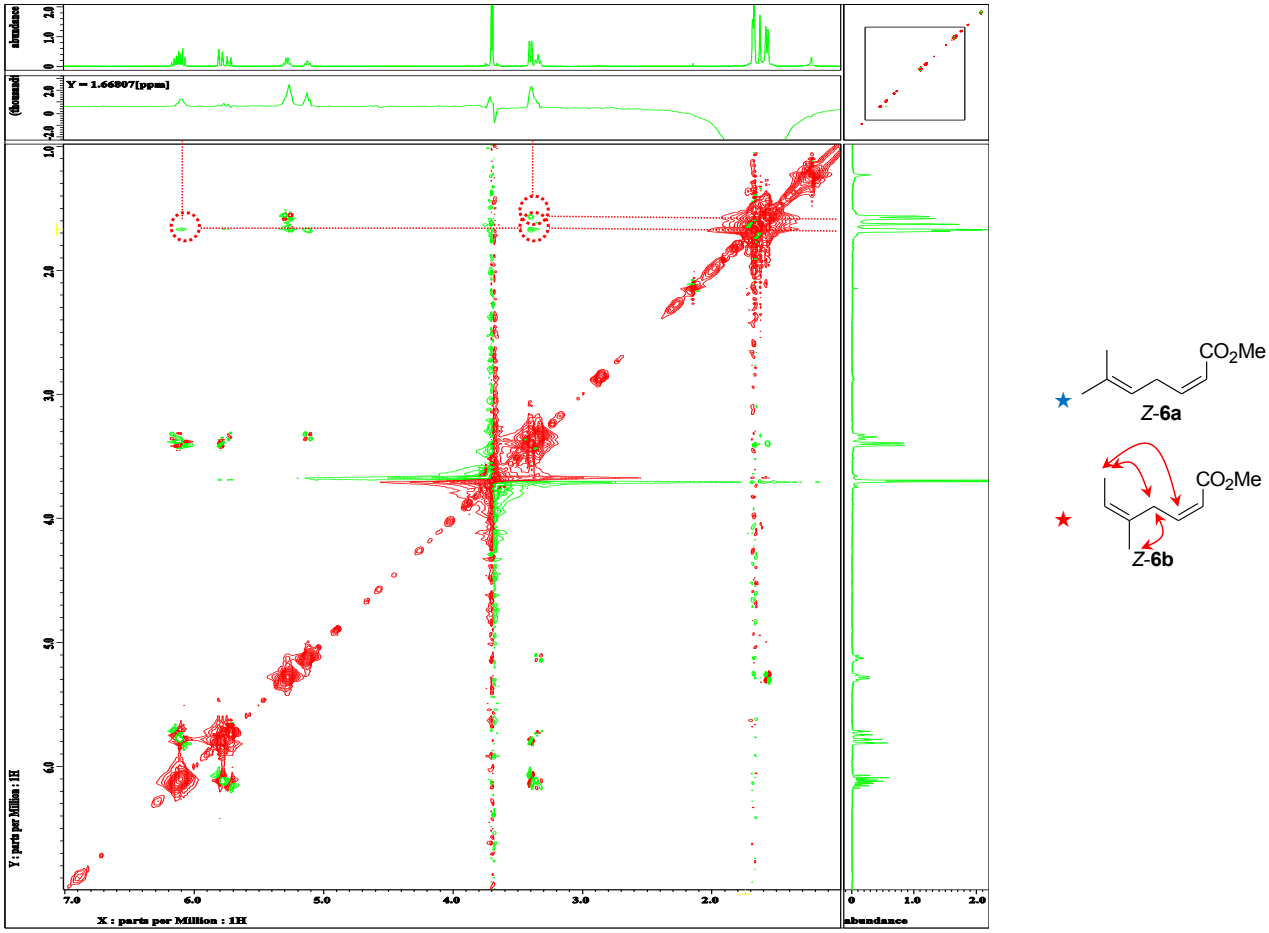


Figure S23-4. Phase sensitive NOESY 2D NMR spectrum for (2*Z*)-Methyl 6-methyl-hepta-2,5-dienoate (*Z*-**6a**) and (2*Z*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*Z*-**6b**) ((*Z*-**6a**:*Z*-**6b** = 35:65 sample), 399.8 MHz, $CDCl_3$).

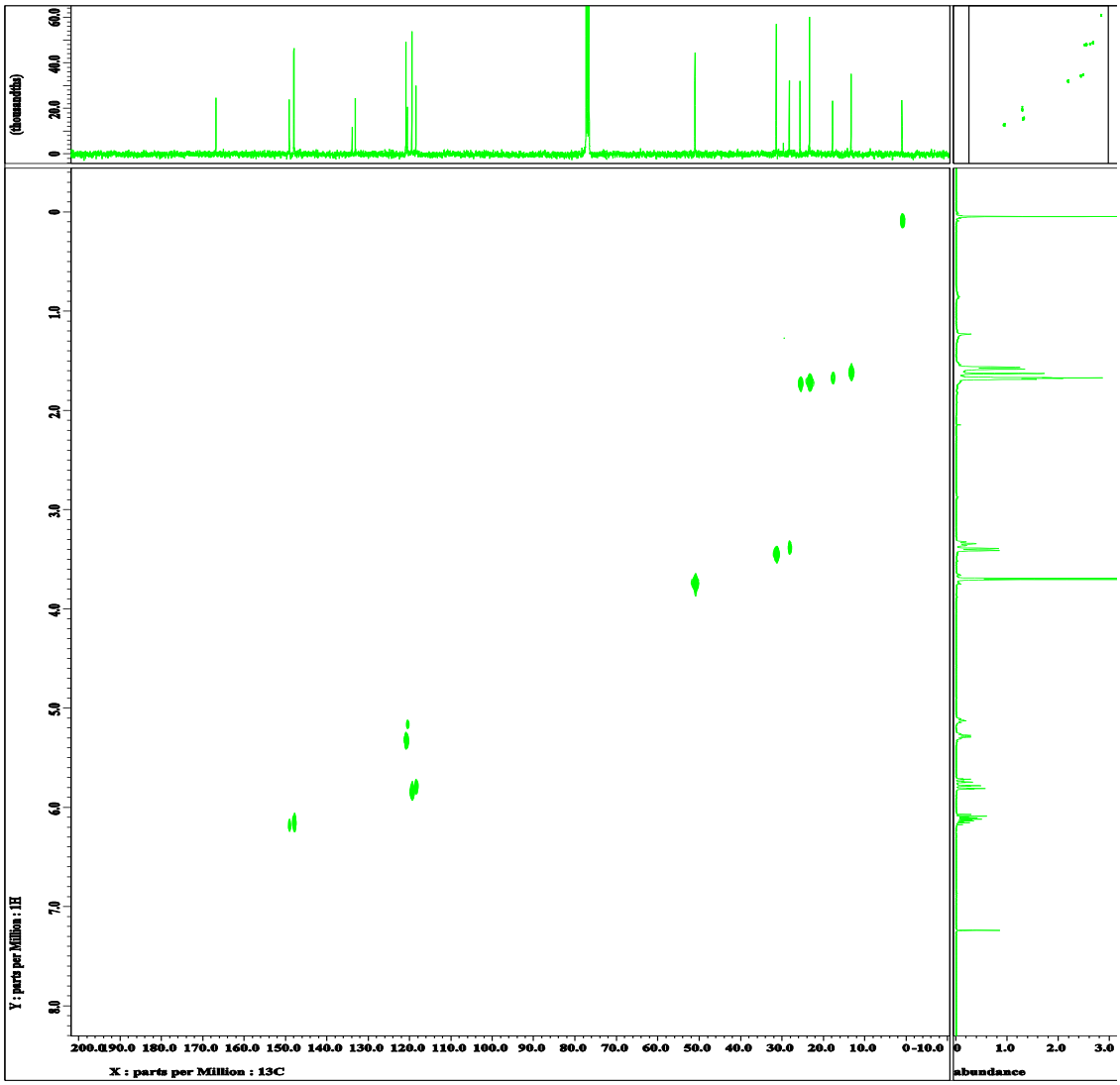


Figure S23-5. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (2*Z*)-Methyl 6-methyl-hepta-2,5-dienoate (*Z*-**6a**) and (2*Z*,5*Z*)-Methyl 5-methyl-hepta-2,5-dienoate (*Z*-**6b**) ((*Z*-**6a**:*Z*-**6b** = 35:65 sample), 100.5 MHz, $CDCl_3$).

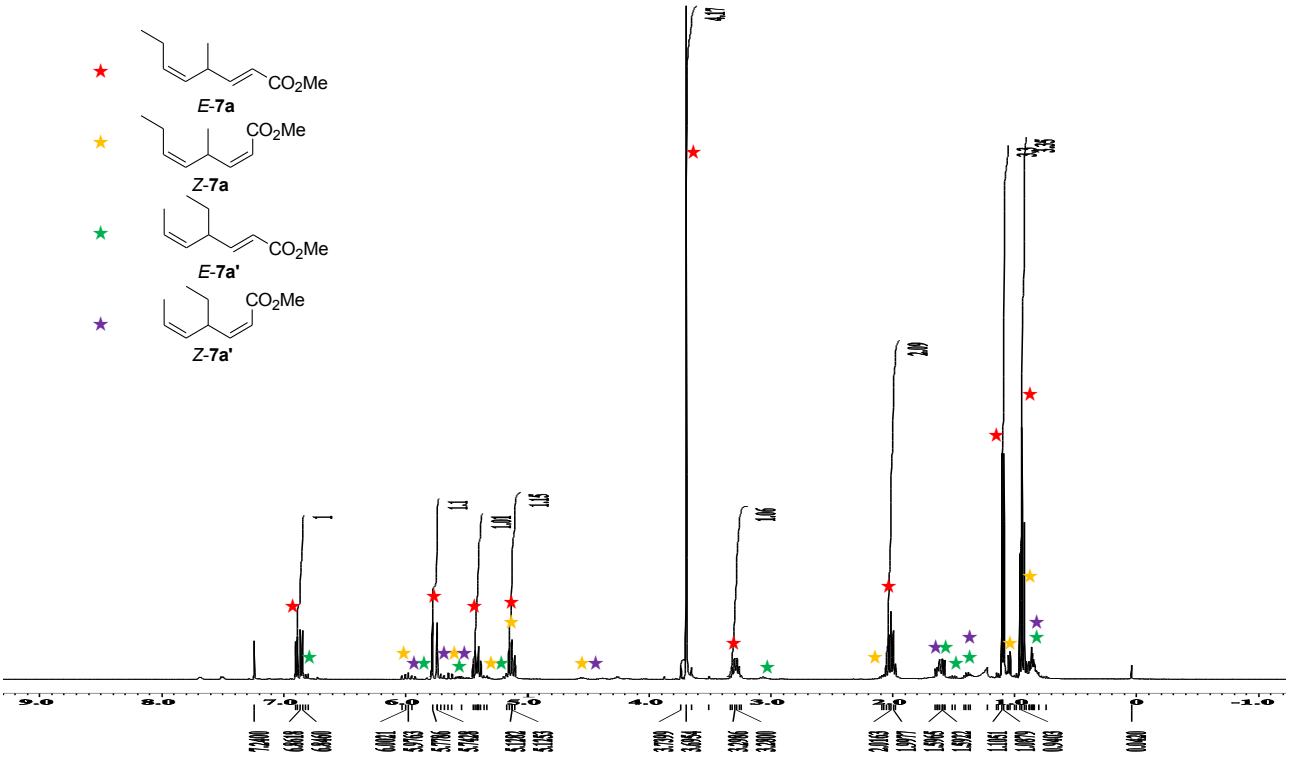


Figure S24-1. ^{1}H NMR spectrum for (2*E*,5*Z*)-Methyl 4-methyl-octa-2,5-dienoate (*E*-**7a**), (2*Z*,5*Z*)-Methyl 4-methyl-octa-2,5-dienoate (*Z*-**7a**), (2*E*,5*Z*)-Methyl 4-ethyl-hepta-2,5-dienoate (*E*-**7a**) and (2*Z*,5*Z*)-Methyl 4-ethyl-hepta-2,5-dienoate (*Z*-**7a'**) ((*E*-**7a**:*Z*-**7a**:*E*-**7a'**:*Z*-**7a'** = 79:7:9:5 sample), 399.8 MHz, $CDCl_3$).

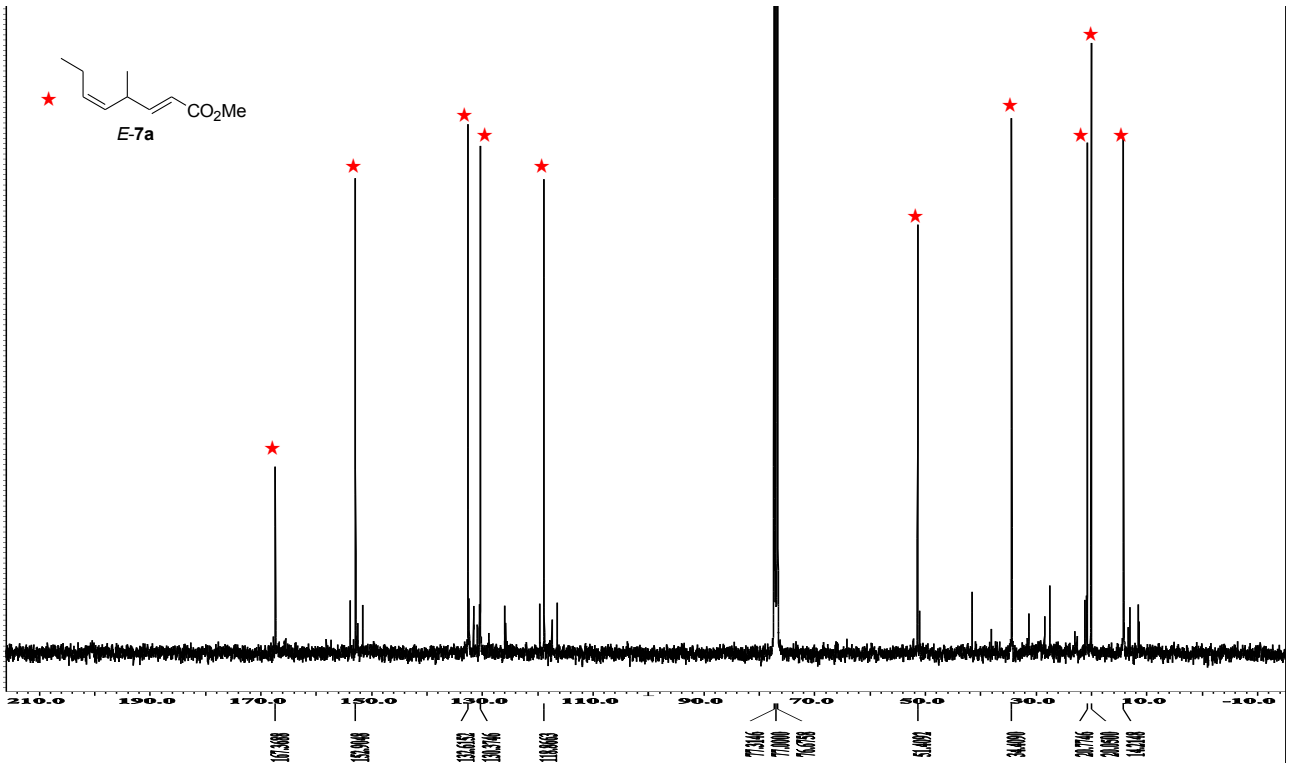


Figure S24-2. ^{13}C NMR spectrum for (2*E*,5*Z*)-Methyl 4-methyl-octa-2,5-dienoate (*E*-**7a**) ((*E*-**7a**:*Z*-**7a**:*E*-**7a'**:*Z*-**7a'** = 79:7:9:5 sample), 100.5 MHz, $CDCl_3$).

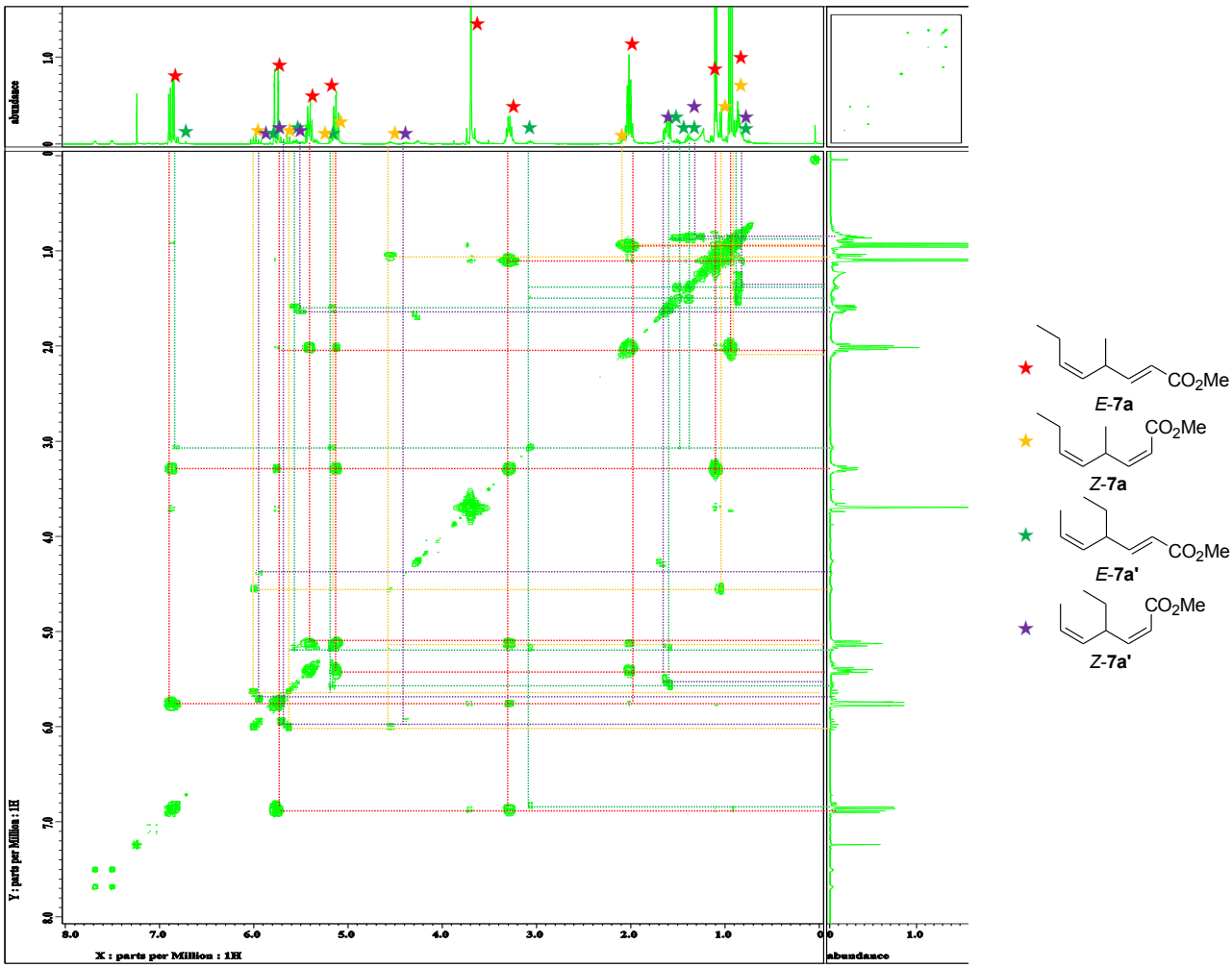


Figure S24-3. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*E*,5*Z*)-Methyl 4-methyl-octa-2,5-dienoate (*E*-**7a**), (2*Z*,5*Z*)-Methyl 4-methyl-octa-2,5-dienoate (*Z*-**7a**), (2*E*,5*Z*)-Methyl 4-ethyl-hepta-2,5-dienoate (*E*-**7a'**) and (2*Z*,5*Z*)-Methyl 4-ethyl-hepta-2,5-dienoate (*Z*-**7a'**) ((*E*-**7a**:*Z*-**7a**:*E*-**7a'**:*Z*-**7a'** = 79:7:9:5 sample), 399.8 MHz, $CDCl_3$).

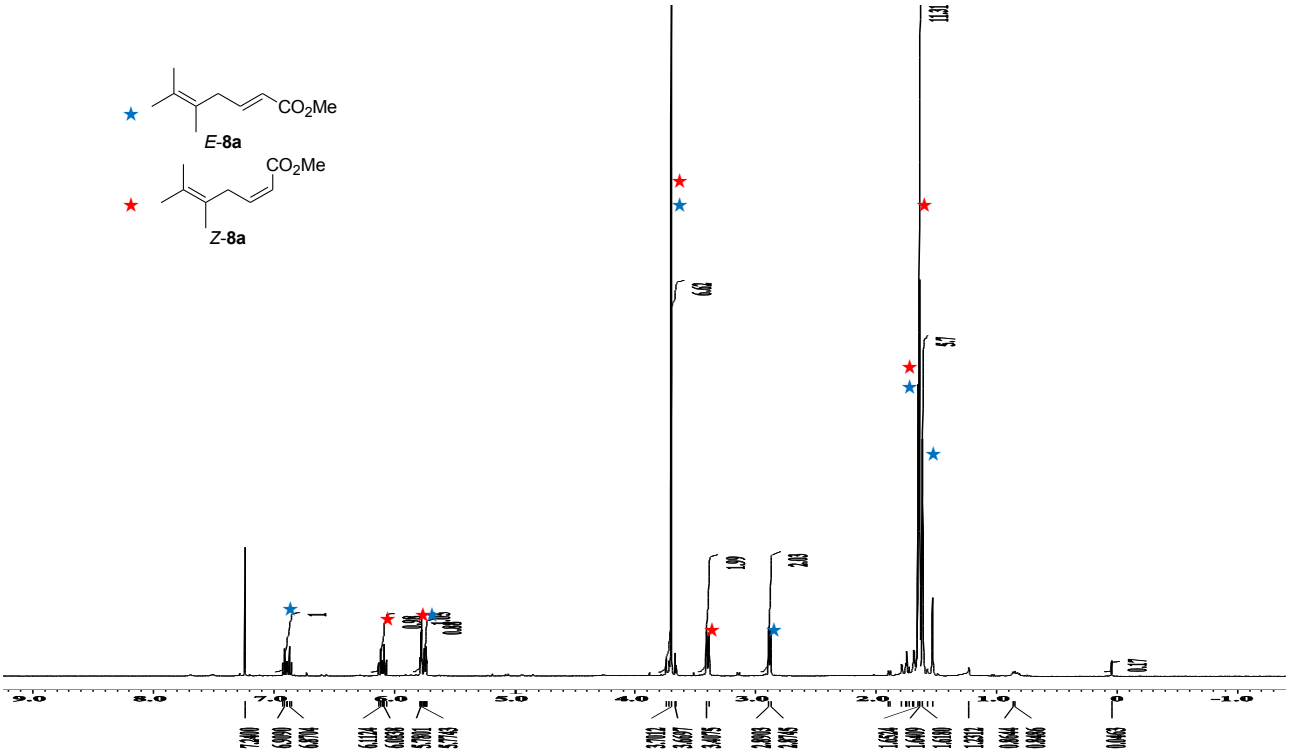


Figure S25-1. ^{1}H NMR spectrum for ((2*E*)-Methyl 5,6-dimethylhepta-2,5-dienoate (*E*-**8a**) and (2*Z*)-Methyl 5,6-dimethylhepta-2,5-dienoate (*Z*-**8a**) ((*E*-**8a**:*Z*-**8a** = 51:49 sample), 399.8 MHz, $CDCl_3$).

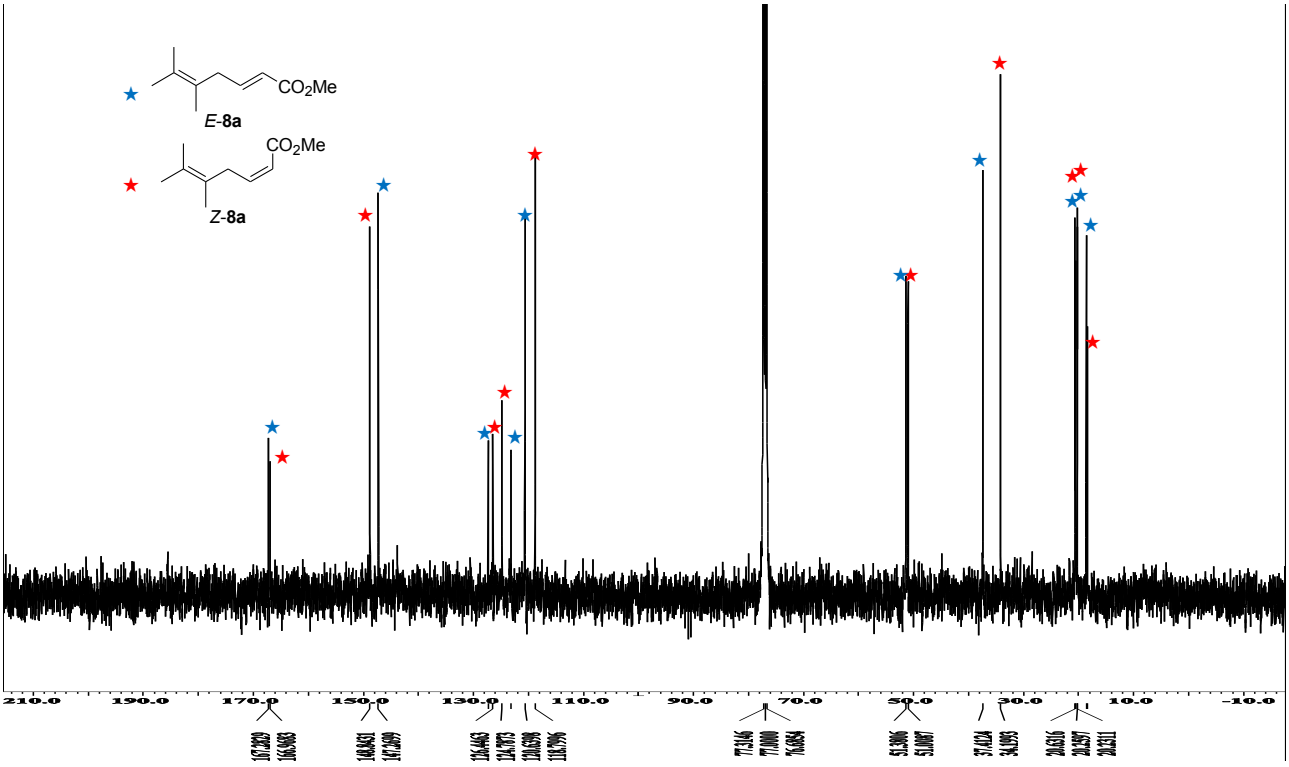


Figure S25-2. ^{13}C NMR spectrum for ((2*E*)-Methyl 5,6-dimethylhepta-2,5-dienoate (*E*-**8a**) and (2*Z*)-Methyl 5,6-dimethylhepta-2,5-dienoate (*Z*-**8a**) ((*E*-**8a**:*Z*-**8a** = 51:49 sample), 100.5 MHz, $CDCl_3$).

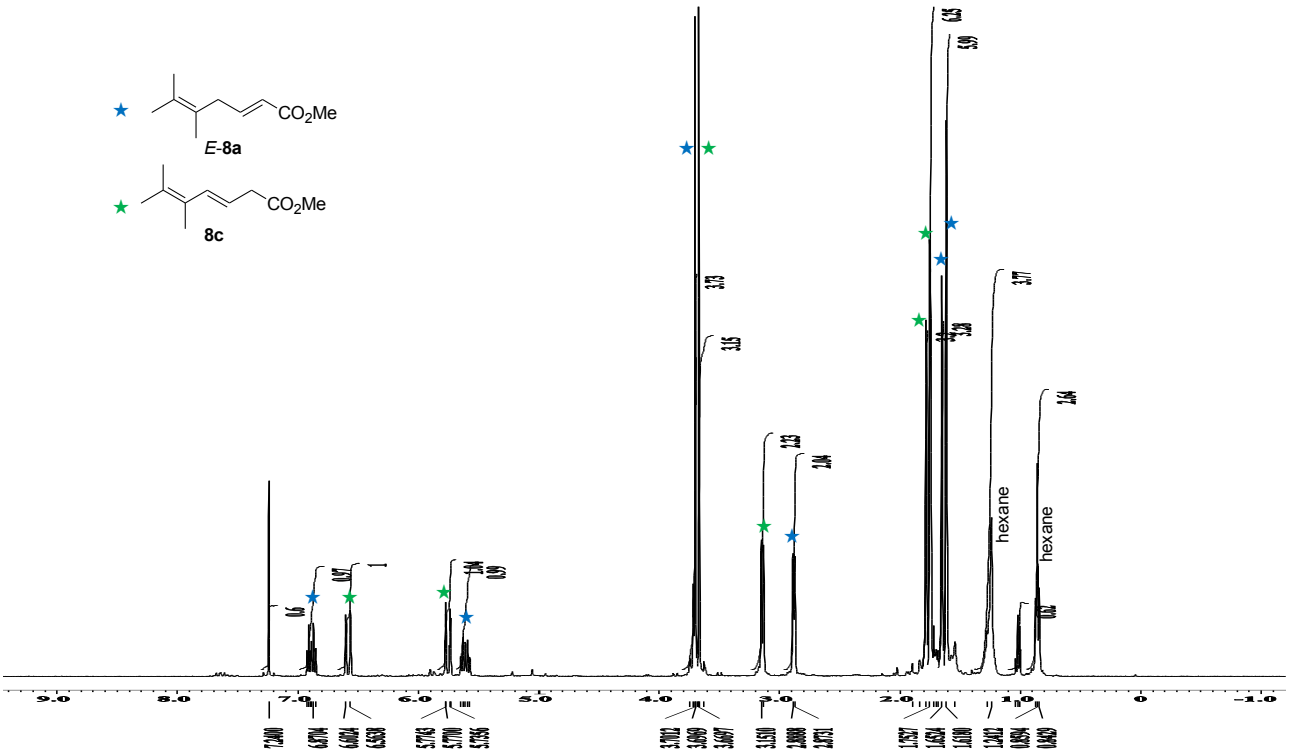


Figure S25-3. ^{1}H NMR spectrum for ((2*E*)-Methyl 5,6-dimethylhepta-2,5-dienoate (*E*-**8a**) and (3*E*)-Methyl 5,6-dimethylhepta-3,5-dienoate (**8c**) ((*E*-**8a**:**8c** = 48:52 sample), 399.8 MHz, $CDCl_3$).

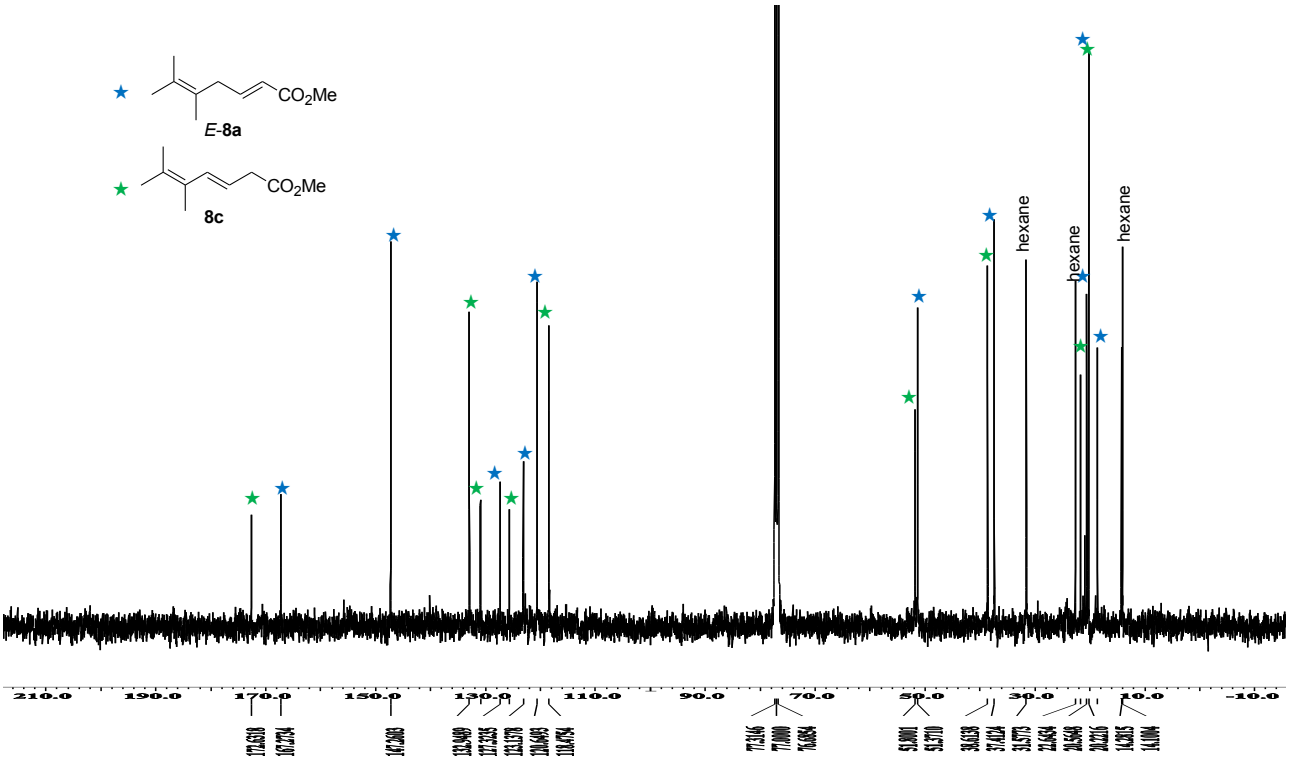


Figure S25-4. ^{13}C NMR spectrum for ((2*E*)-Methyl 5,6-dimethylhepta-2,5-dienoate (*E*-**8a**) and (3*E*)-Methyl 5,6-dimethylhepta-3,5-dienoate (**8c**) ((*E*-**8a**:**8c** = 48:52 sample), 100.5 MHz, $CDCl_3$).

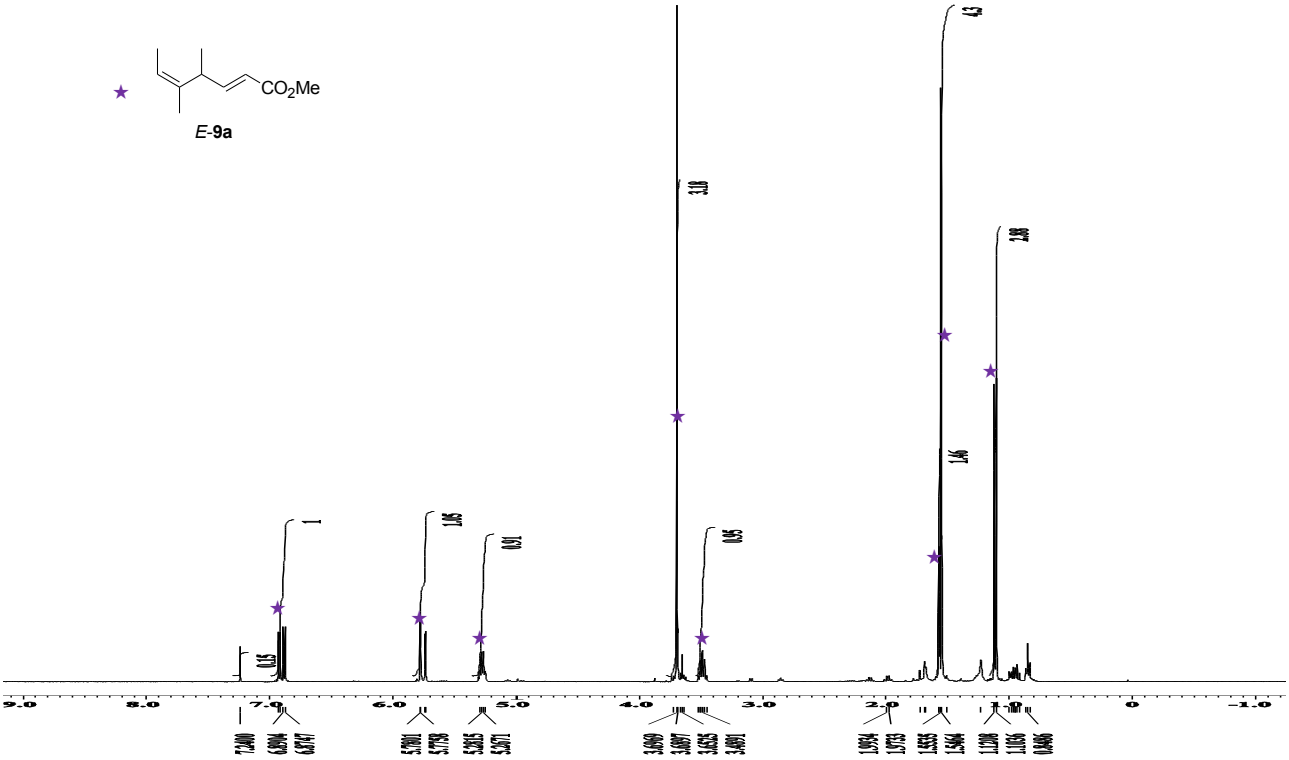


Figure S26-1. ^{1}H NMR spectrum for (2*E*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*E*-**9a**) (399.8 MHz, $CDCl_3$).

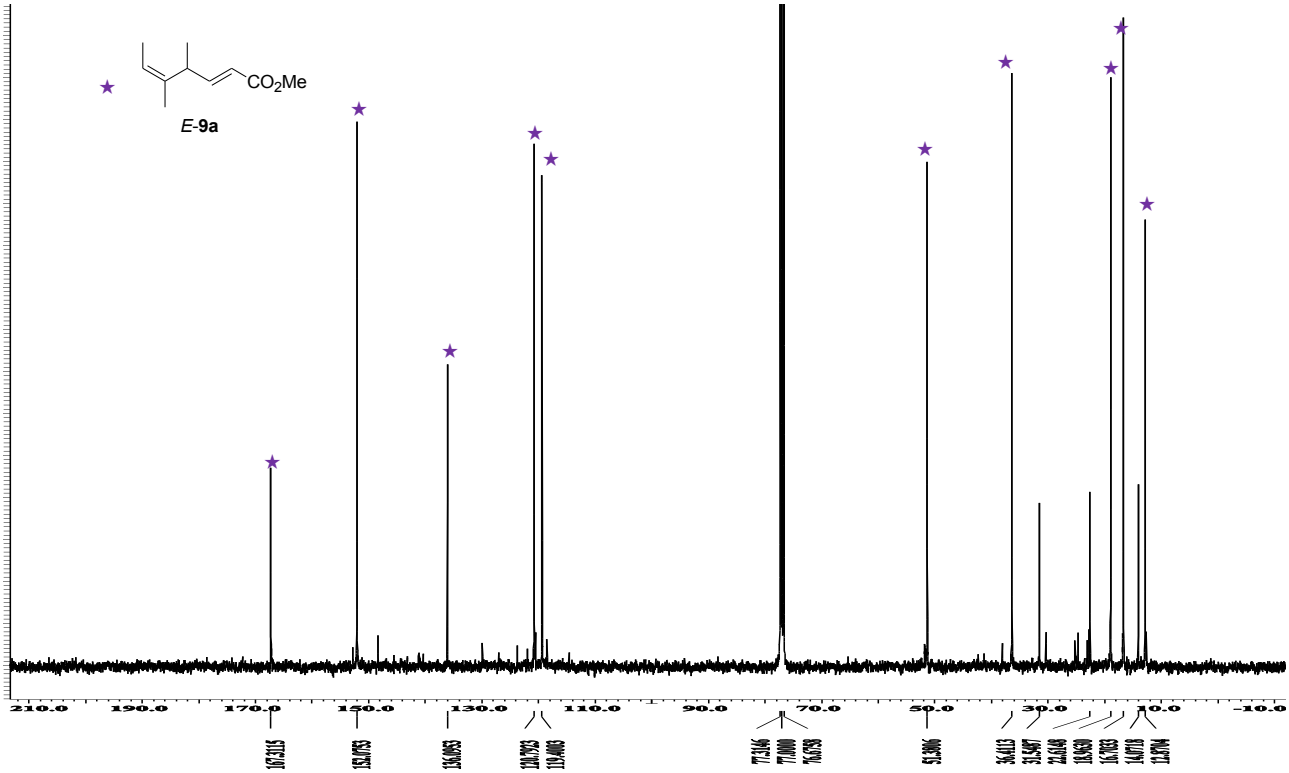


Figure S26-2. ^{13}C NMR spectrum for (2*E*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*E*-**9a**) (100.5 MHz, $CDCl_3$).

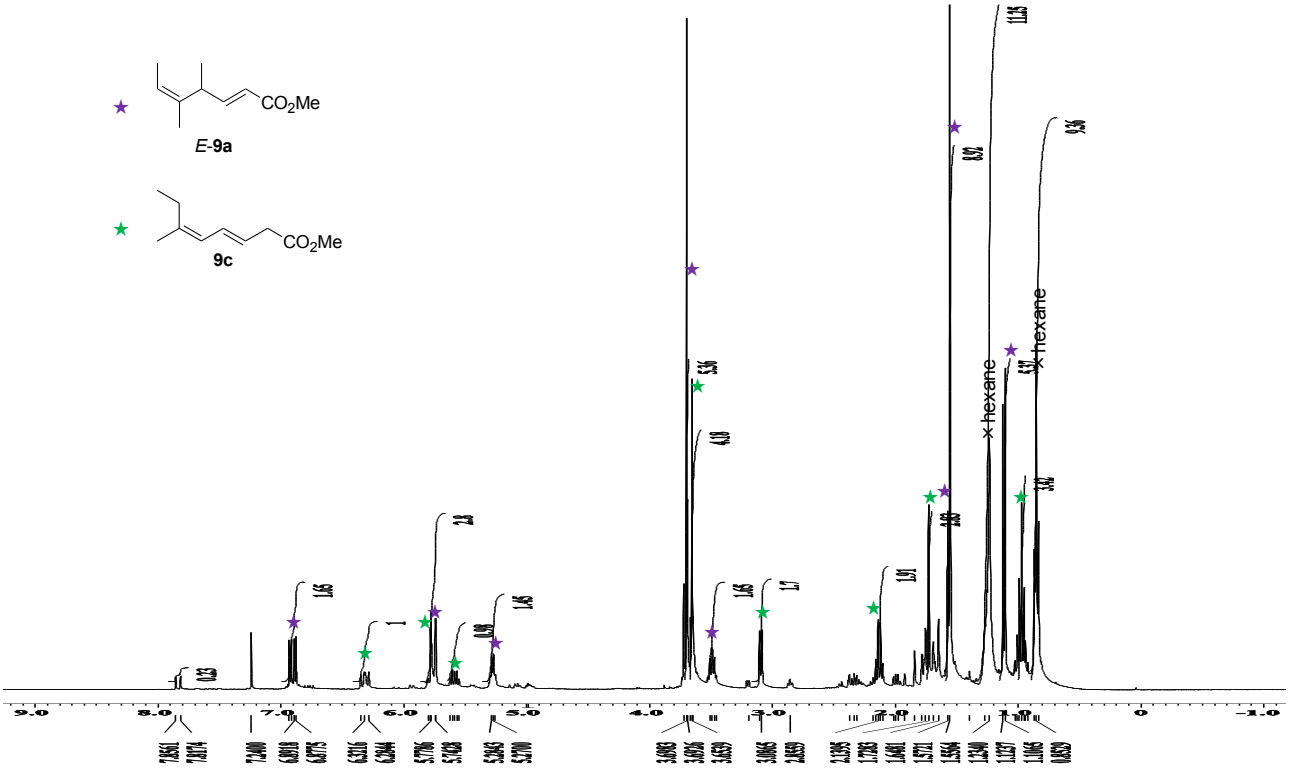


Figure S26-3. ^{1}H NMR spectrum for (3*E*)-Methyl 6-methylocta-3,5-dienoate (**9c**) ((*E*-**9a**:**9c** = 60:40 sample), 399.8 MHz, $CDCl_3$).

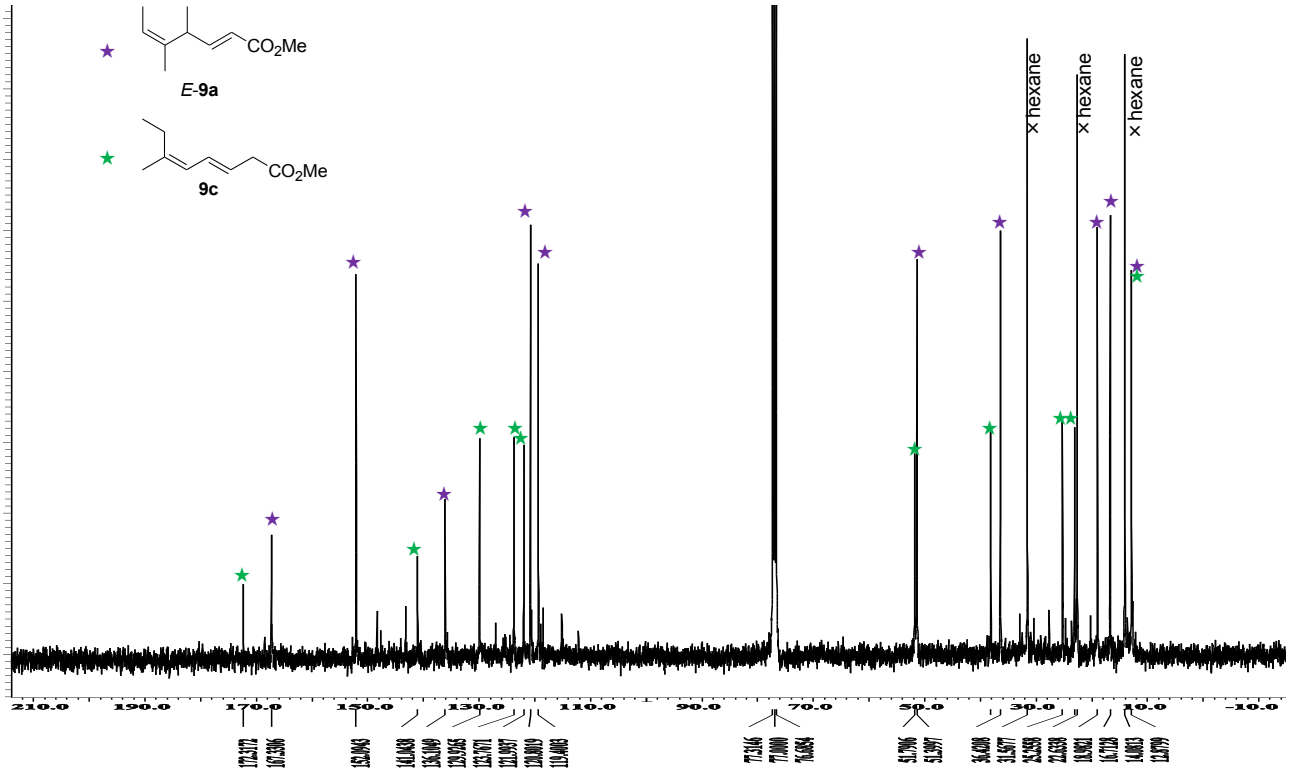


Figure S26-4. ^{13}C NMR spectrum for (3*E*)-Methyl 6-methylocta-3,5-dienoate (**9c**) ((*E*-**9a**:**9c** = 60:40 sample), 100.5 MHz, $CDCl_3$).

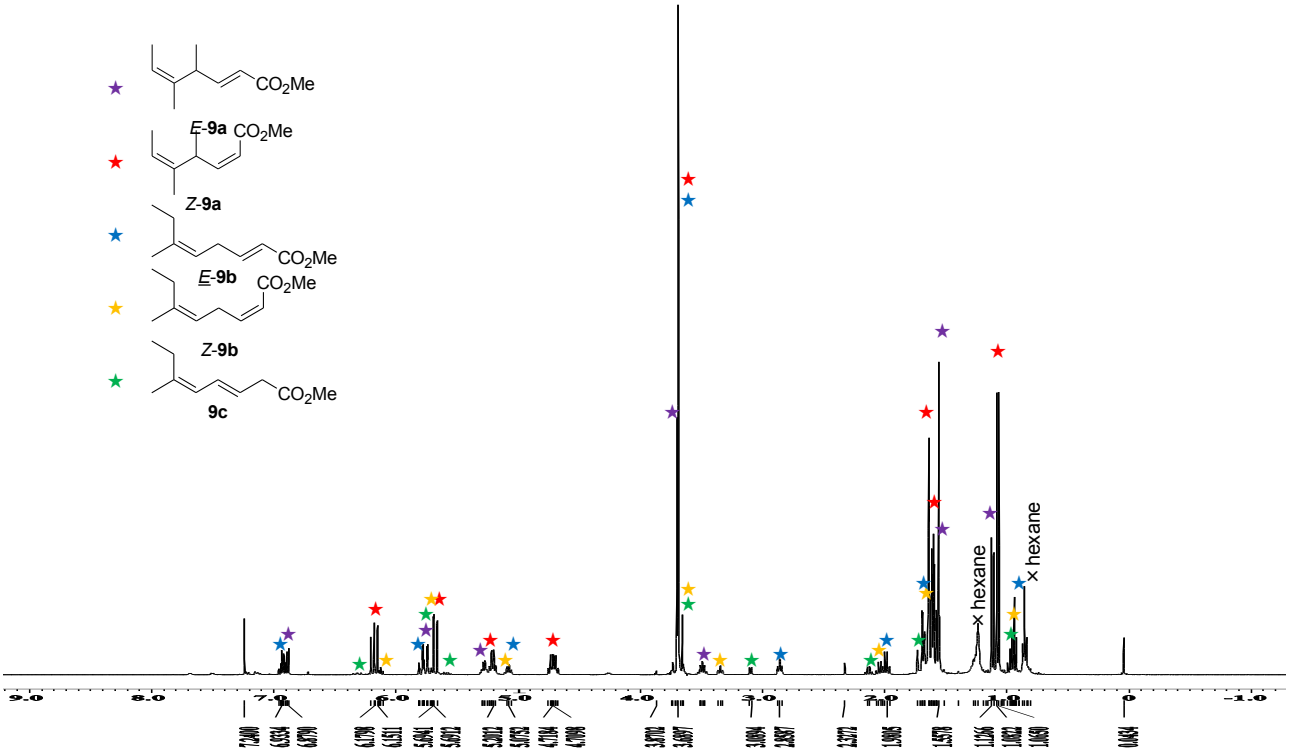


Figure S26-5. ^{1}H NMR spectrum for (2*Z*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*Z*-**9a**), (2*E*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*E*-**9b**), and (2*Z*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*Z*-**9b**) ((*E*-**9a**:*Z*-**9a**:*E*-**9b**:*Z*-**9b**:**9c** = 26:52:12:7:3 sample), 399.8 MHz, $CDCl_3$).

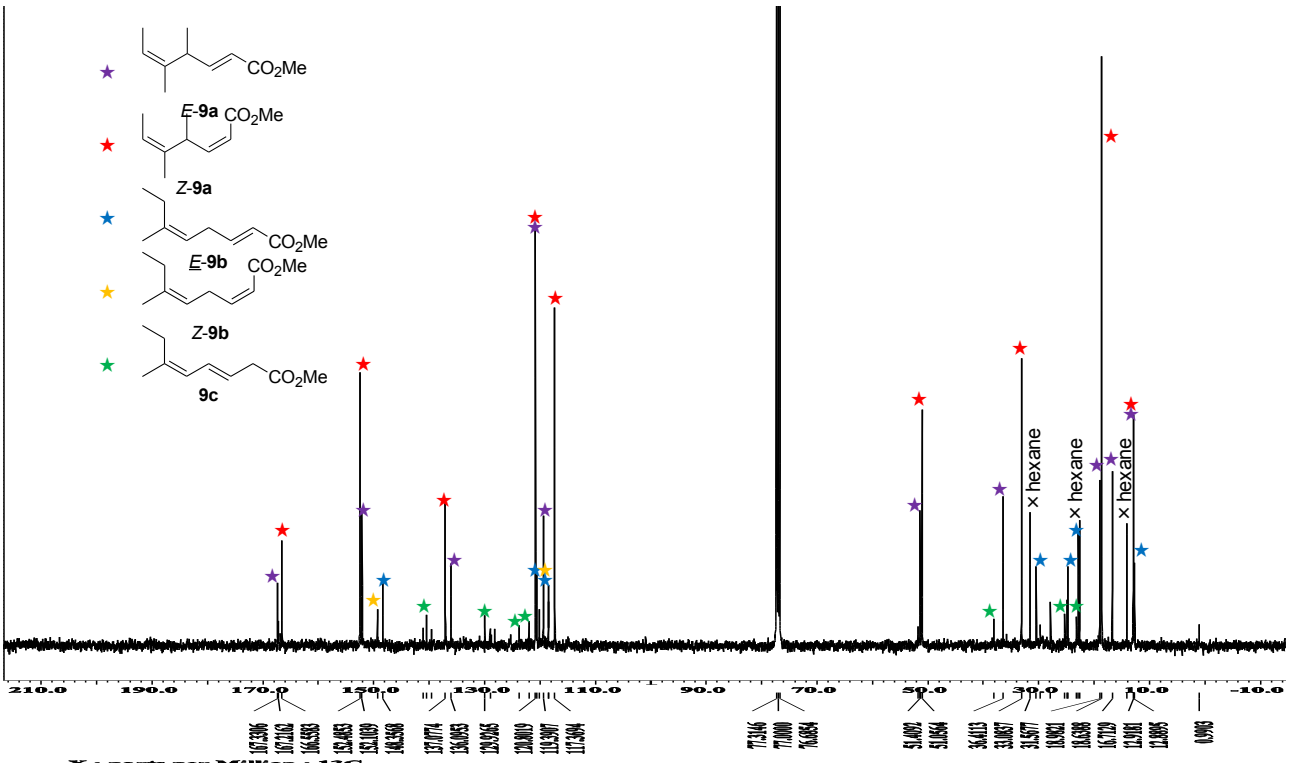


Figure S26-6. ^{13}C NMR spectrum for (2*Z*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*Z*-**9a**), (2*E*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*E*-**9b**), and (2*Z*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*Z*-**9b**) ((*E*-**9a**:*Z*-**9a**:*E*-**9b**:*Z*-**9b**:**9c** = 26:52:12:7:3 sample), 100.5 MHz, $CDCl_3$).

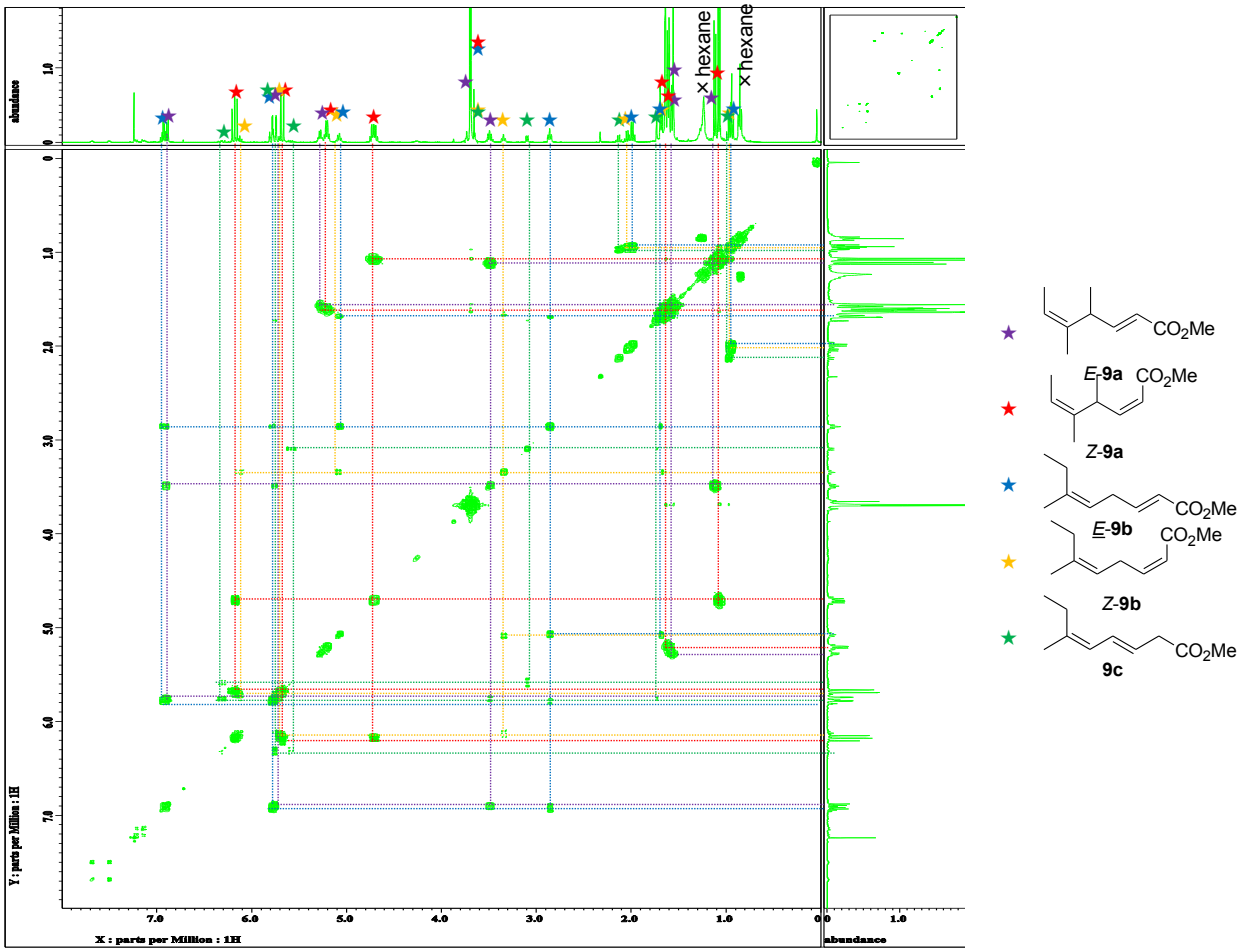


Figure S26-7. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*Z*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*Z*-**9a**), (2*E*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*E*-**9b**), and (2*Z*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*Z*-**9b**) ((*E*-**9a**:*Z*-**9a**:*E*-**9b**:*Z*-**9b**:**9c** = 26:52:12:7:3 sample), 399.8 MHz, $CDCl_3$).

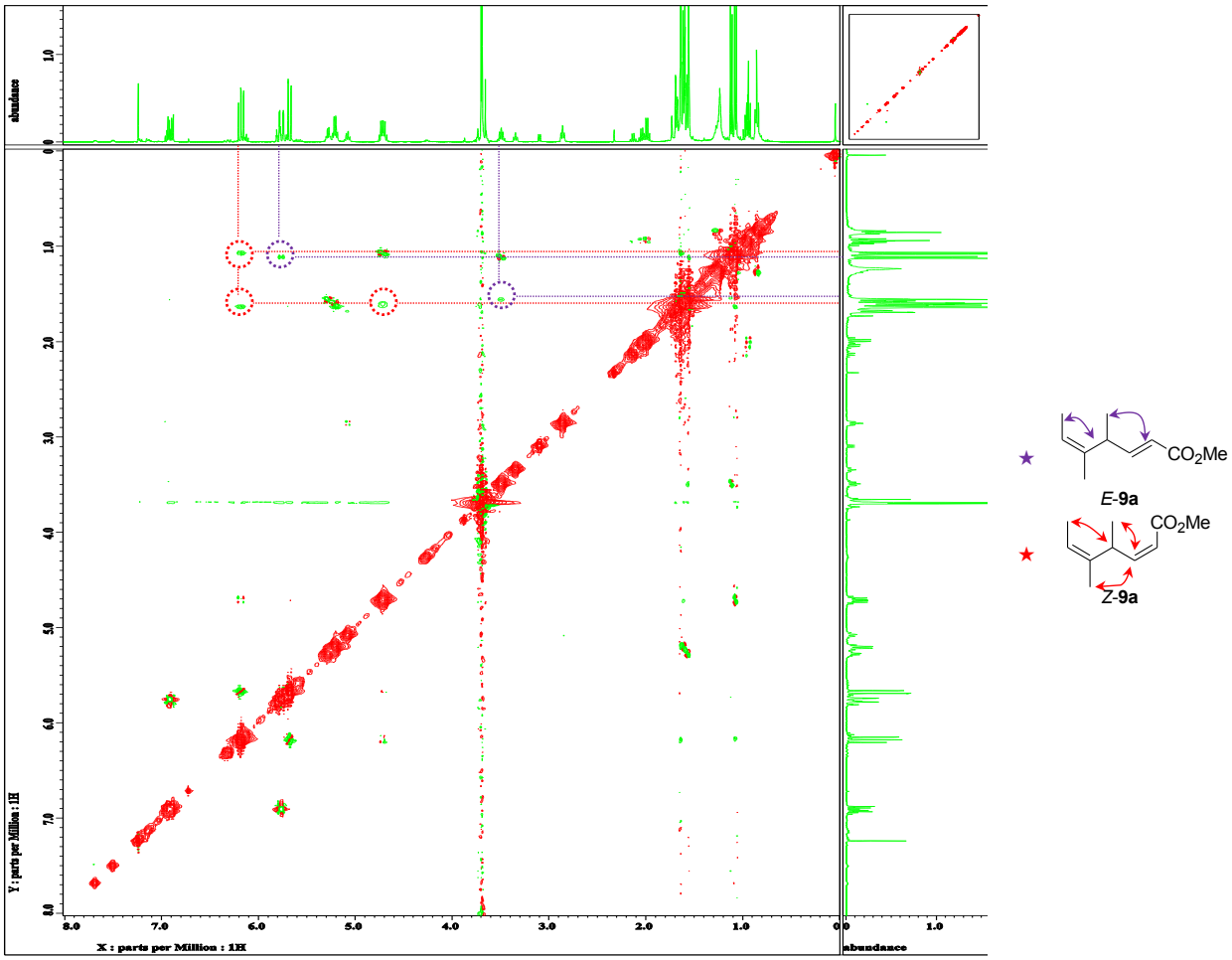


Figure S26-8-1. Phase sensitive NOESY 2D NMR spectrum for (2*E*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*E*-**9a**) and (2*Z*,5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (*Z*-**9a**) ((*E*-**9a**:*Z*-**9a**:*E*-**9b**:*Z*-**9b**:**9c** = 26:52:12:7:3 sample), 399.8 MHz, $CDCl_3$).

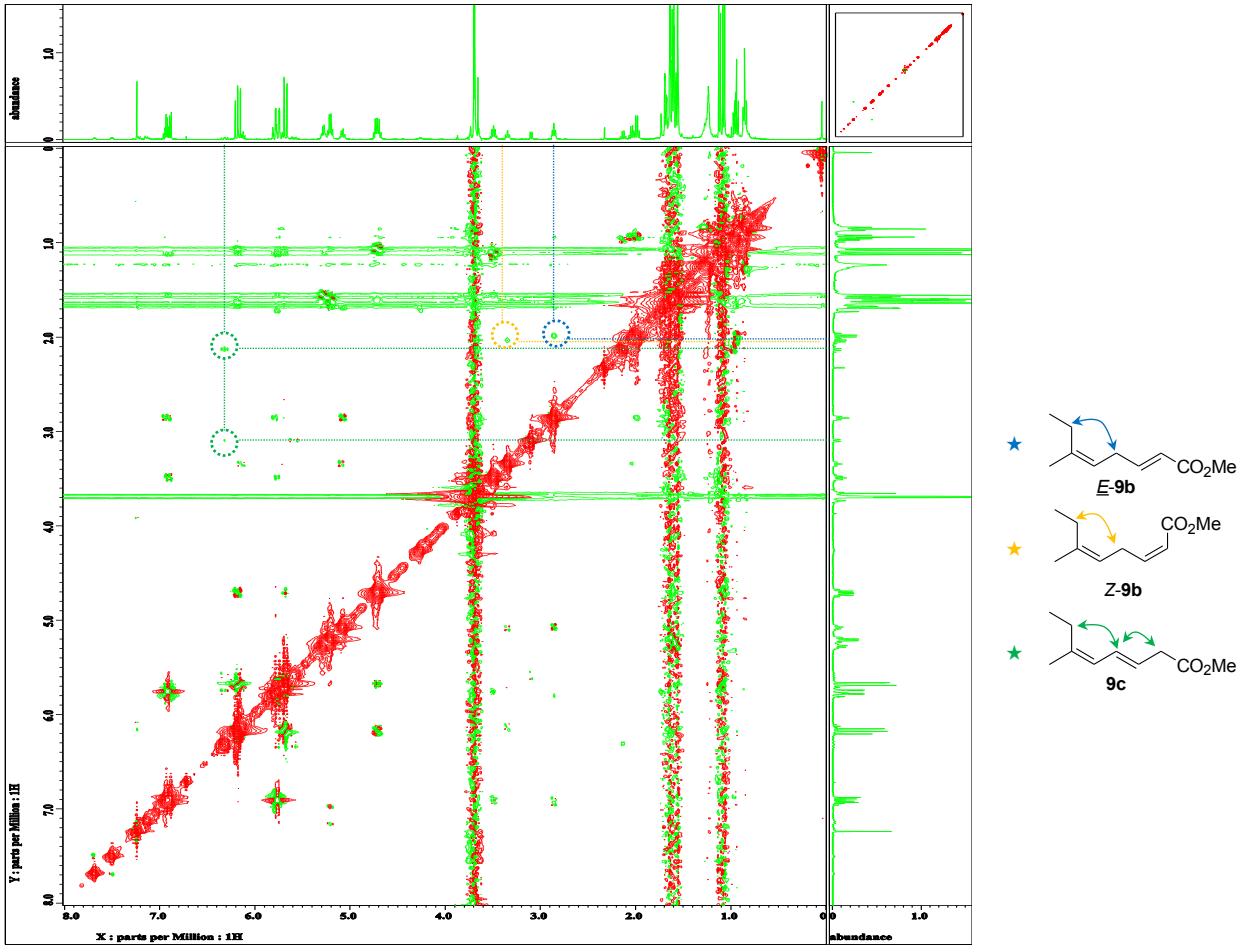


Figure S26-8-2. Phase sensitive NOESY 2D NMR spectrum for (2*E*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*E*-**9b**), (2*Z*,5*Z*)-Methyl 6-methylocta-2,5-dienoate (*Z*-**9b**) and (3*E*)-Methyl 6-methylocta-3,5-dienoate (**9c**) ((*E*-**9a**:*Z*-**9a**:*E*-**9b**:*Z*-**9b**:**9c** = 26:52:12:7:3 sample), 399.8 MHz, $CDCl_3$).

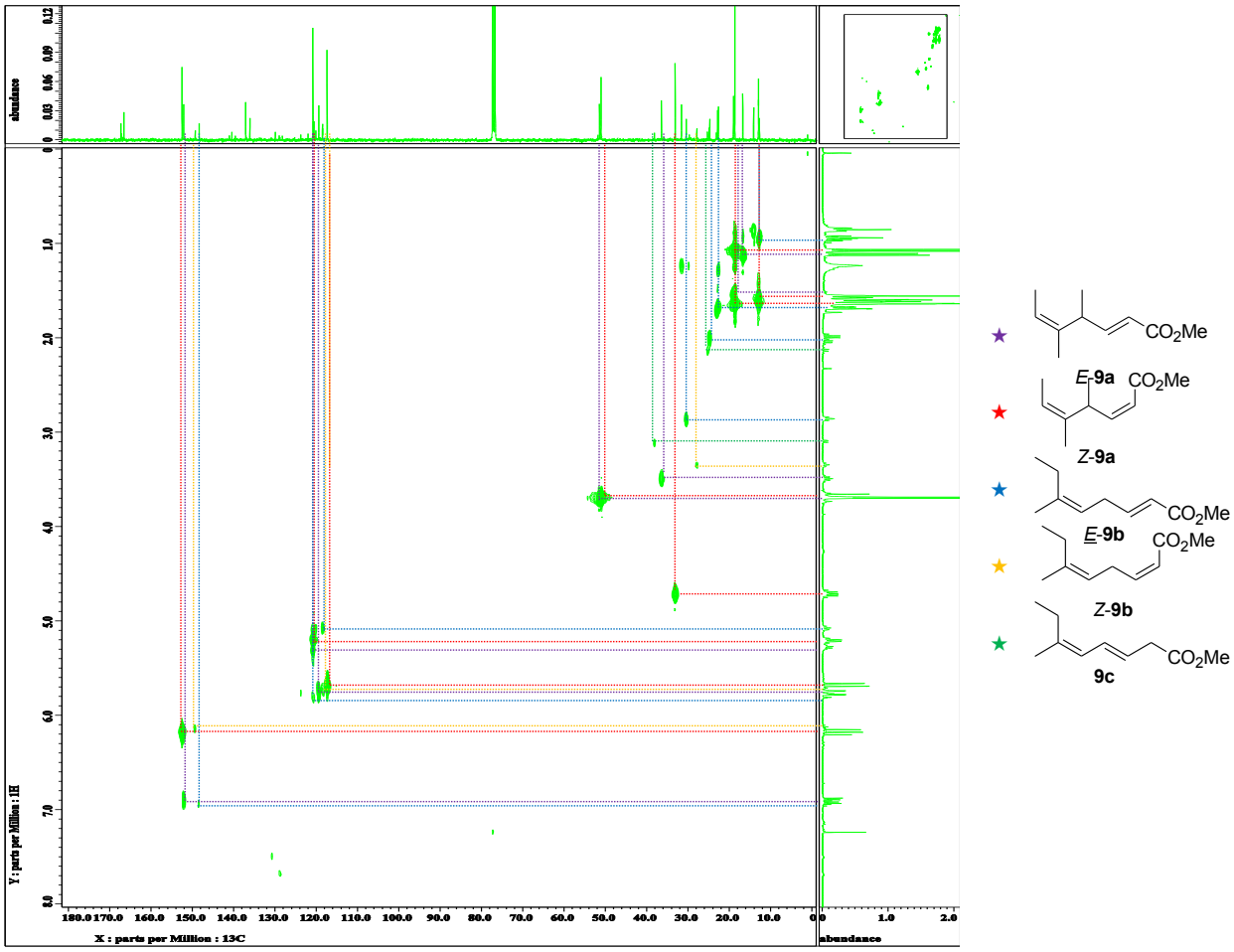


Figure S26-9. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (5*Z*)-Methyl 4,5-dimethylhepta-2,5-dienoate (**9a**), (5*Z*)-Methyl 6-methylocta-2,5-dienoate (**9b**), and (3*E*,5*Z*)-Methyl 6-methylocta-3,5-dienoate (**9c**) ((*E*-**9a**:*Z*-**9a**:*E*-**9b**:*Z*-**9b**:**9c** = 26:52:12:7:3 sample), 100.5 MHz, $CDCl_3$).

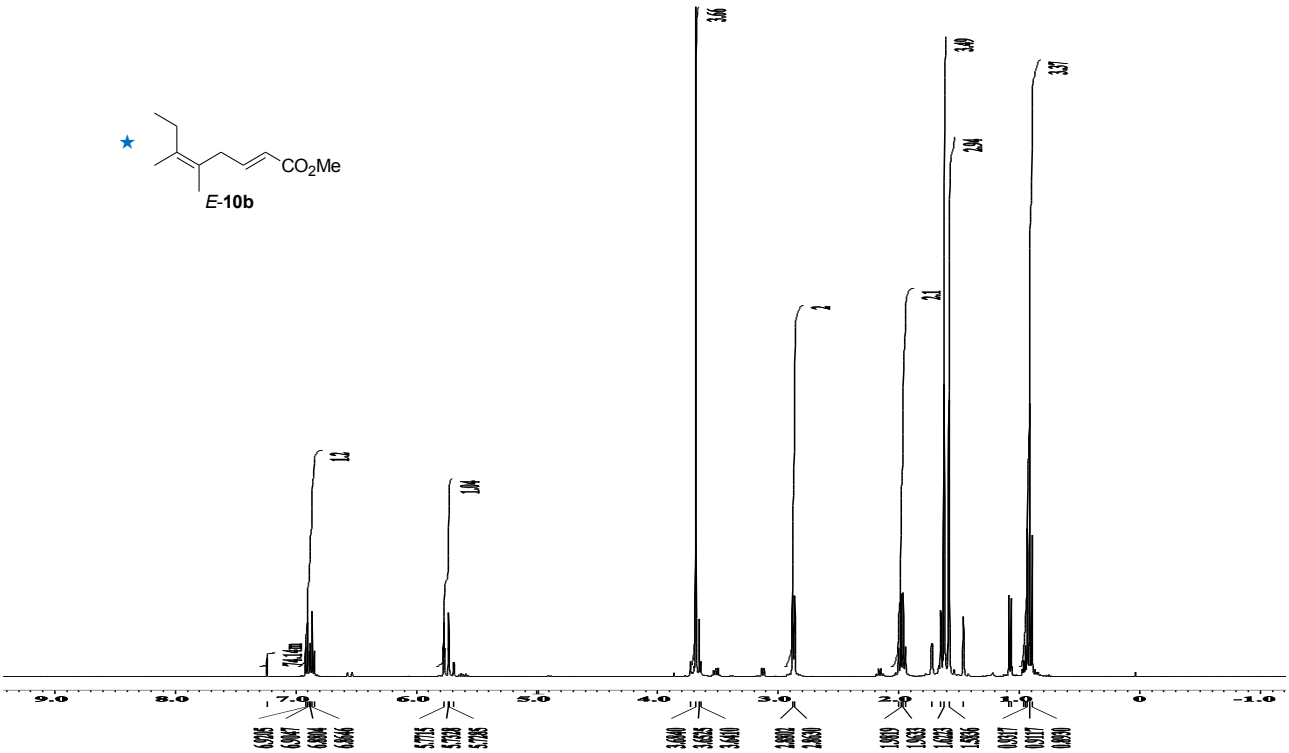


Figure S27-1. ^{1}H NMR spectrum for (2*E*,5*Z*)-Methyl 5,6-dimethylocta-2,5-dienoate (*E*-**10b**) (399.8 MHz, $CDCl_3$).

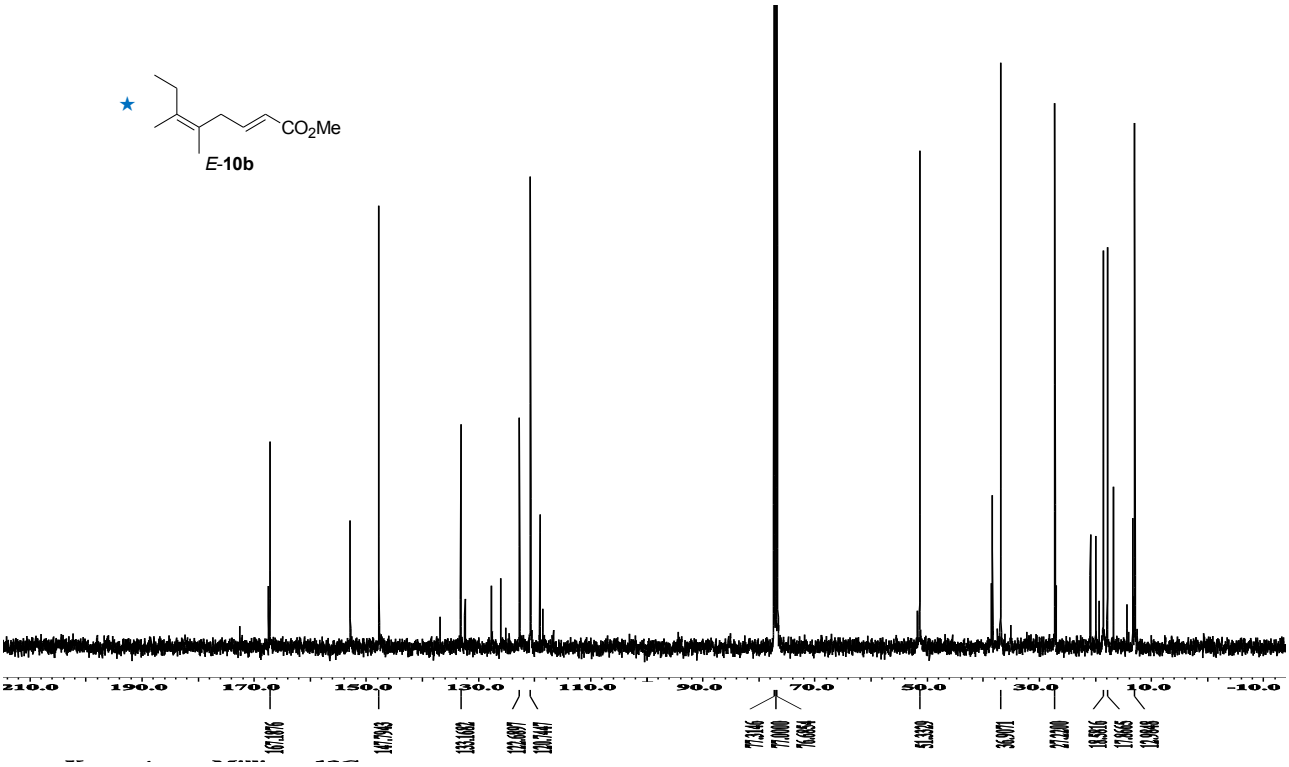


Figure S27-2. ^{13}C NMR spectrum for (2*E*,5*Z*)-Methyl 5,6-dimethylocta-2,5-dienoate (*E*-**10b**) (100.5 MHz, $CDCl_3$).

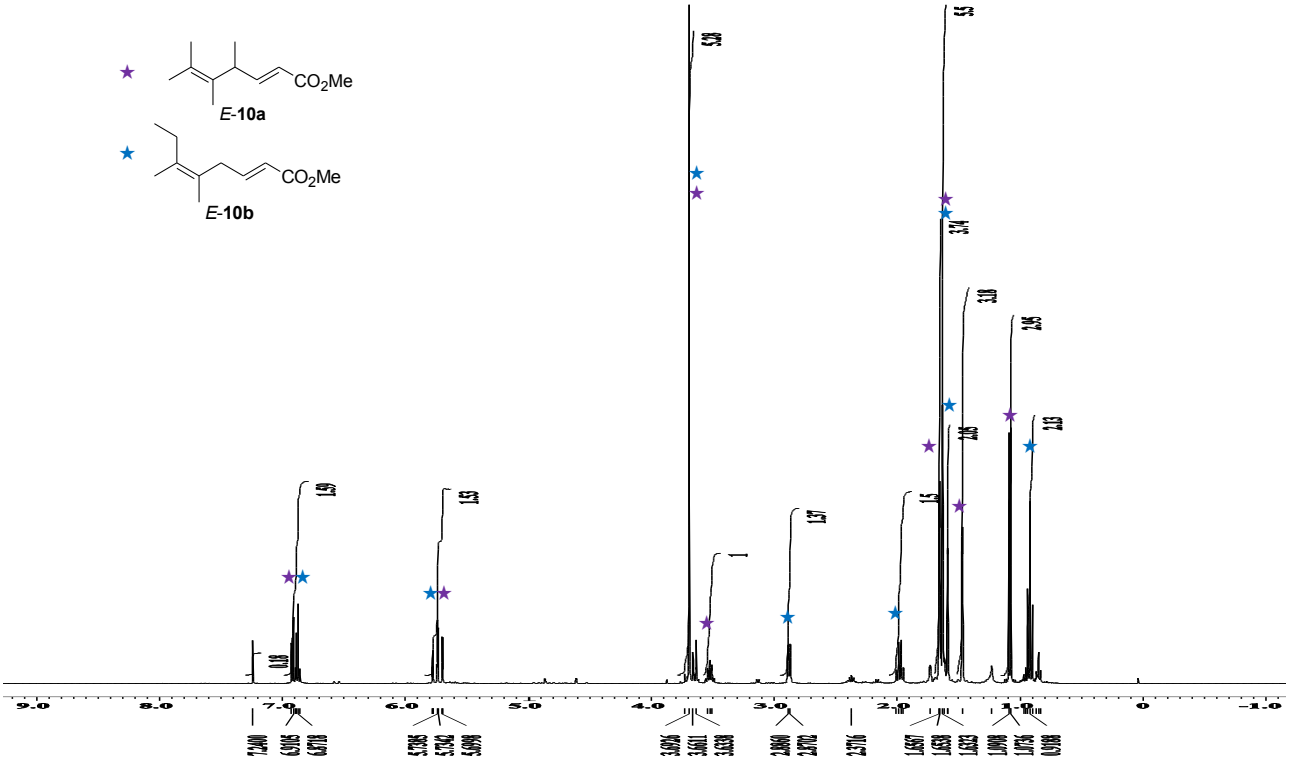


Figure S27-3. ^{1}H NMR spectrum for (2*E*,5*Z*)-Methyl 4,5,6-trimethylhepta-2,5-dienoate (*E*-**10a**) ((*E*-**10a**:*E*-**10b** = 58:42 sample), 399.8 MHz, $CDCl_3$).

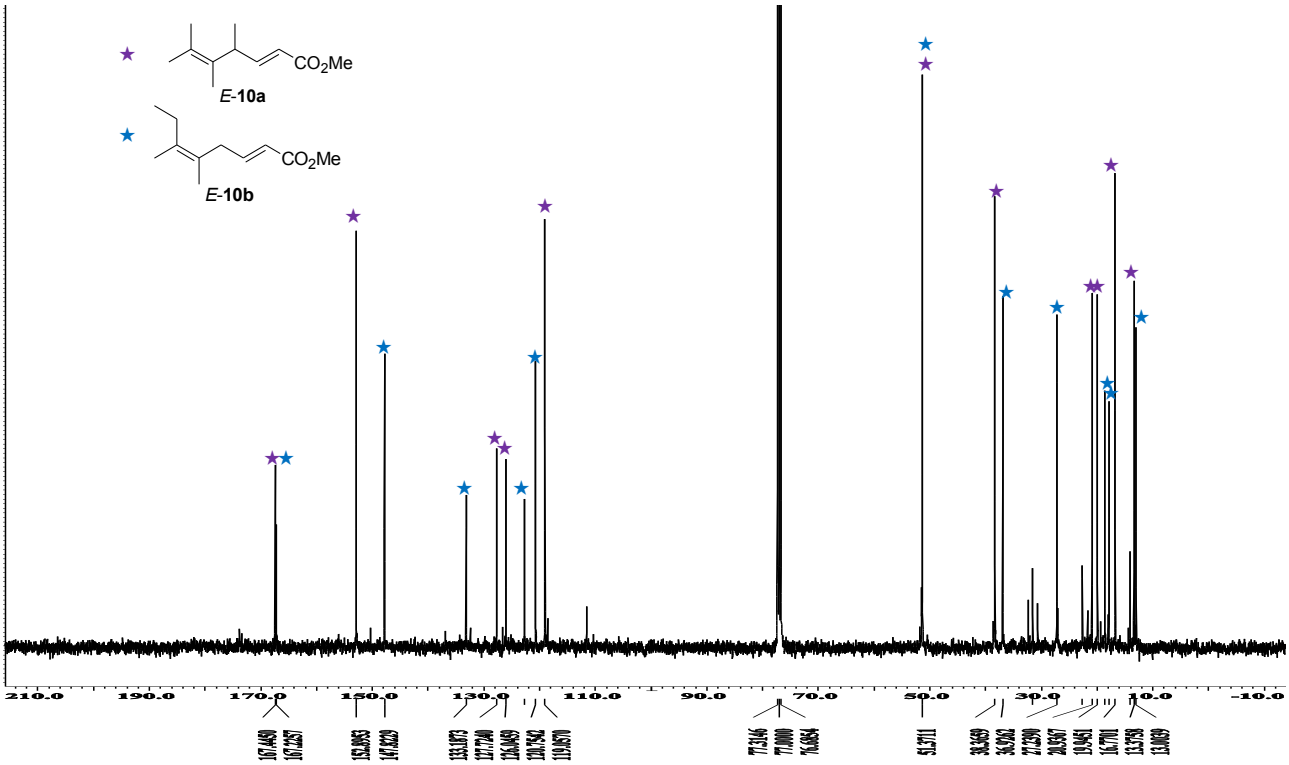


Figure S27-4. ^{13}C NMR spectrum for (2*E*,5*Z*)-Methyl 4,5,6-trimethylhepta-2,5-dienoate (*E*-**10a**) ((*E*-**10a**:*E*-**10b** = 58:42 sample), 100.5 MHz, $CDCl_3$).

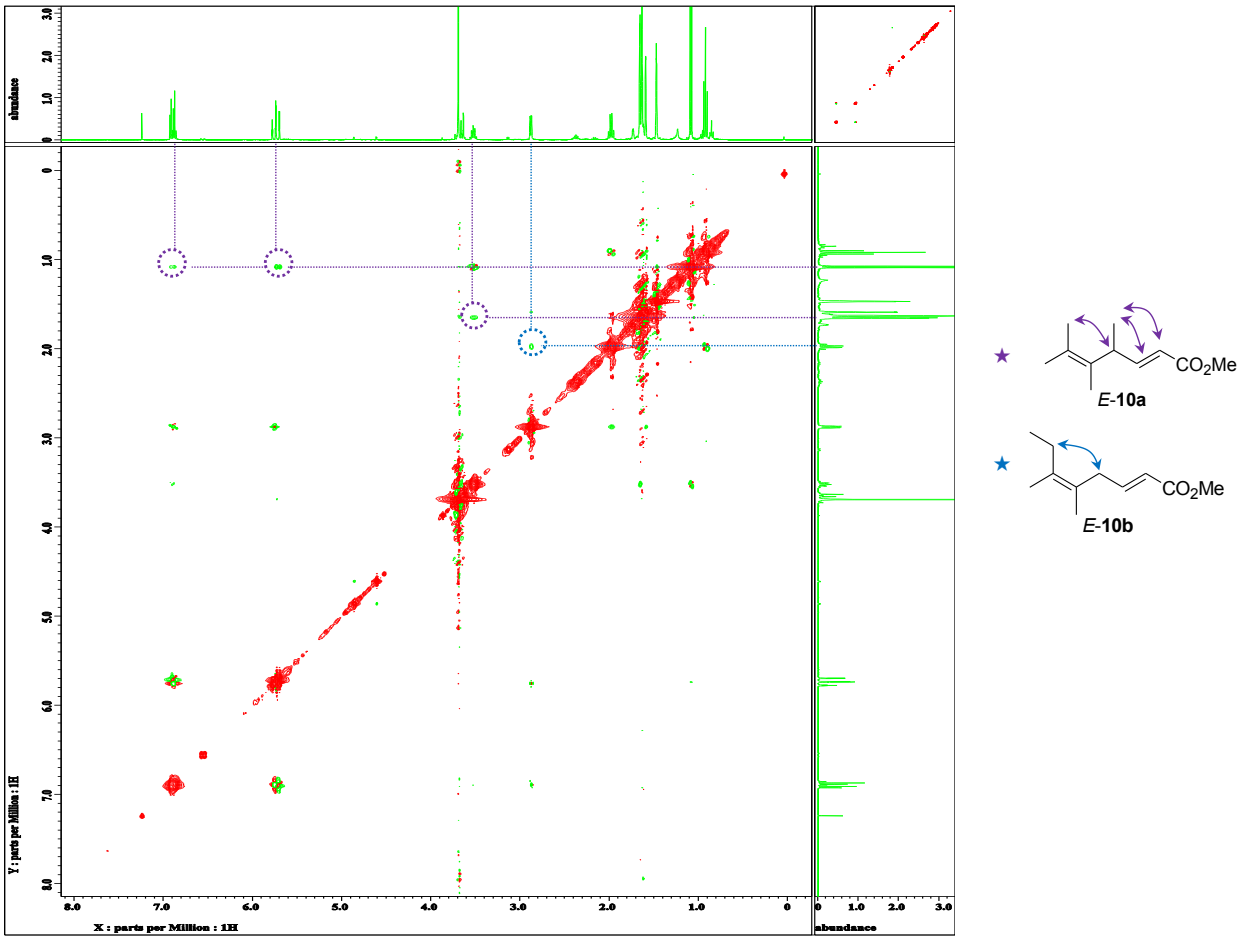


Figure S27-5. Phase sensitive NOESY 2D NMR spectrum for (2*E*,5*Z*)-Methyl 4,5,6-trimethylhepta-2,5-dienoate (*E*-**10a**) and (2*E*,5*Z*)-Methyl 5,6-dimethylocta-2,5-dienoate (*E*-**10b**) ((*E*-**10a**:*E*-**10b** = 58:42 sample), 399.8 MHz, $CDCl_3$).

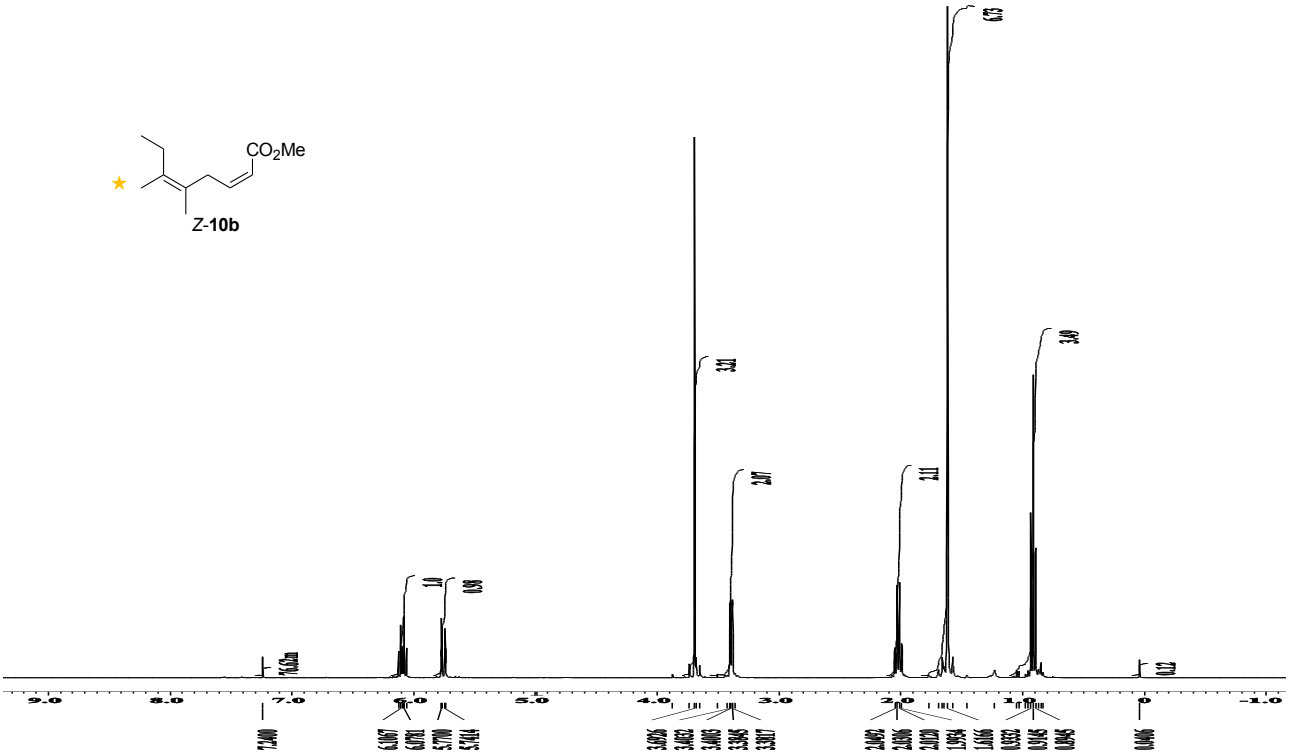


Figure S27-6. ^{1}H NMR spectrum for (2*Z*,5*Z*)-Methyl 5,6-dimethylocta-2,5-dienoate (*Z*-**10b**) (399.8 MHz, $CDCl_3$).

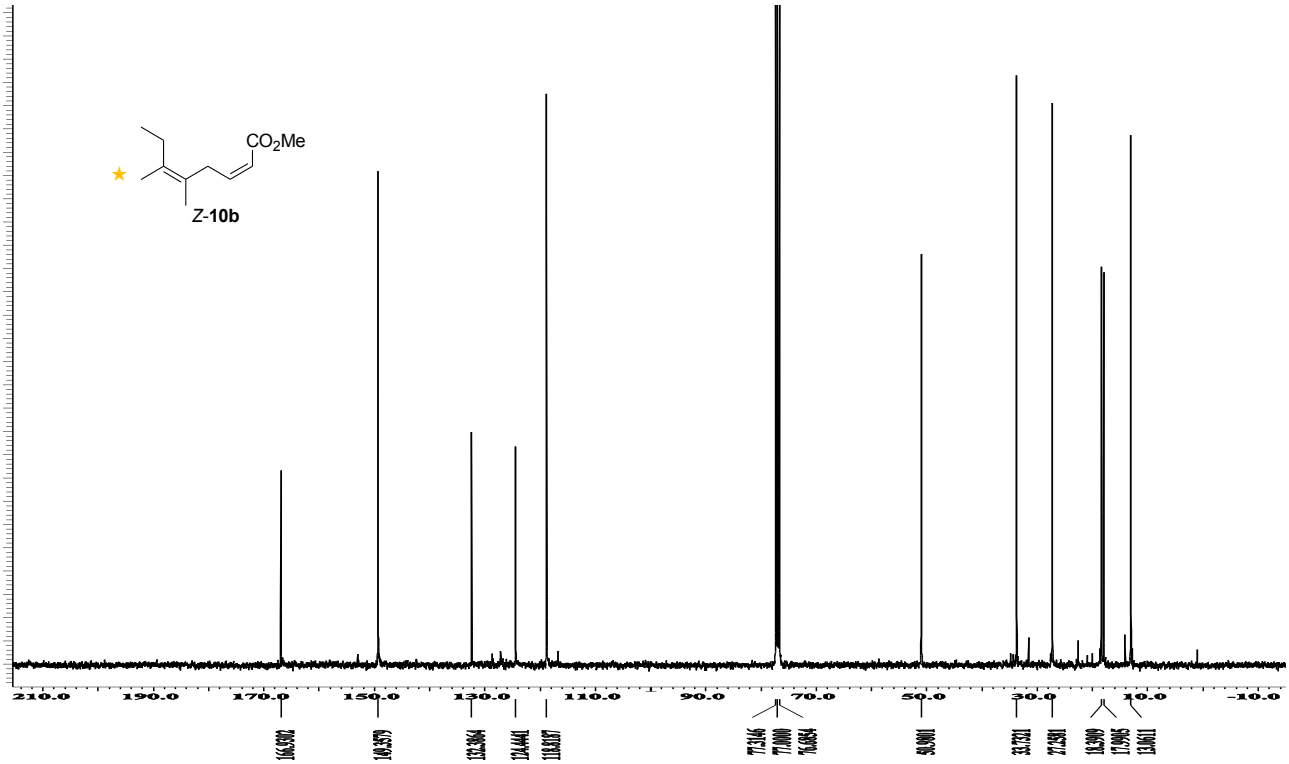


Figure S27-7. ^{13}C NMR spectrum for (2*Z*,5*Z*)-Methyl 5,6-dimethylocta-2,5-dienoate (*Z*-**10b**) (100.5 MHz, $CDCl_3$).

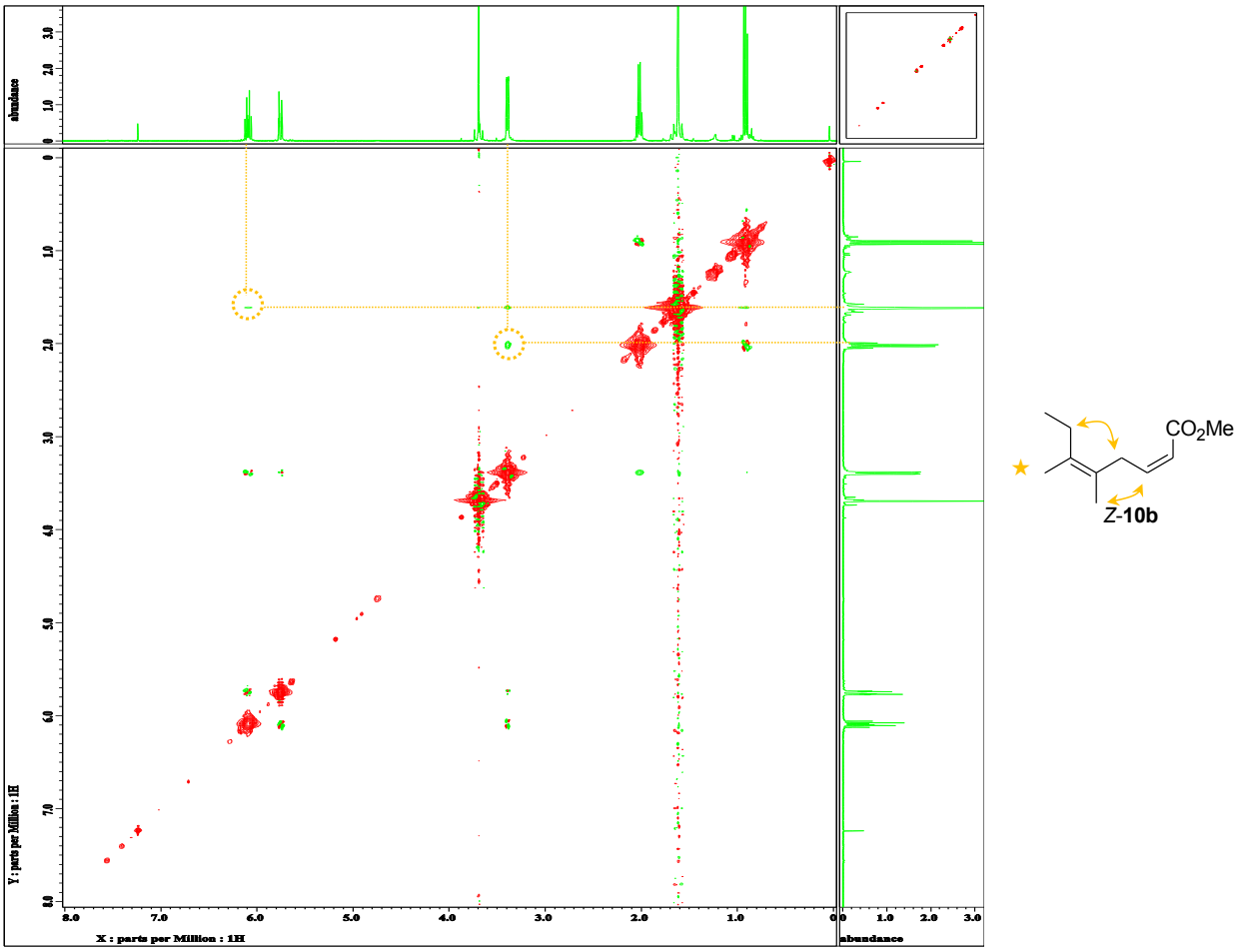


Figure S27-8. Phase sensitive NOESY 2D NMR spectrum for (2*Z*,5*Z*)-Methyl 5,6-dimethylocta-2,5-dienoate (*Z*-**10b**) (399.8 MHz, $CDCl_3$).

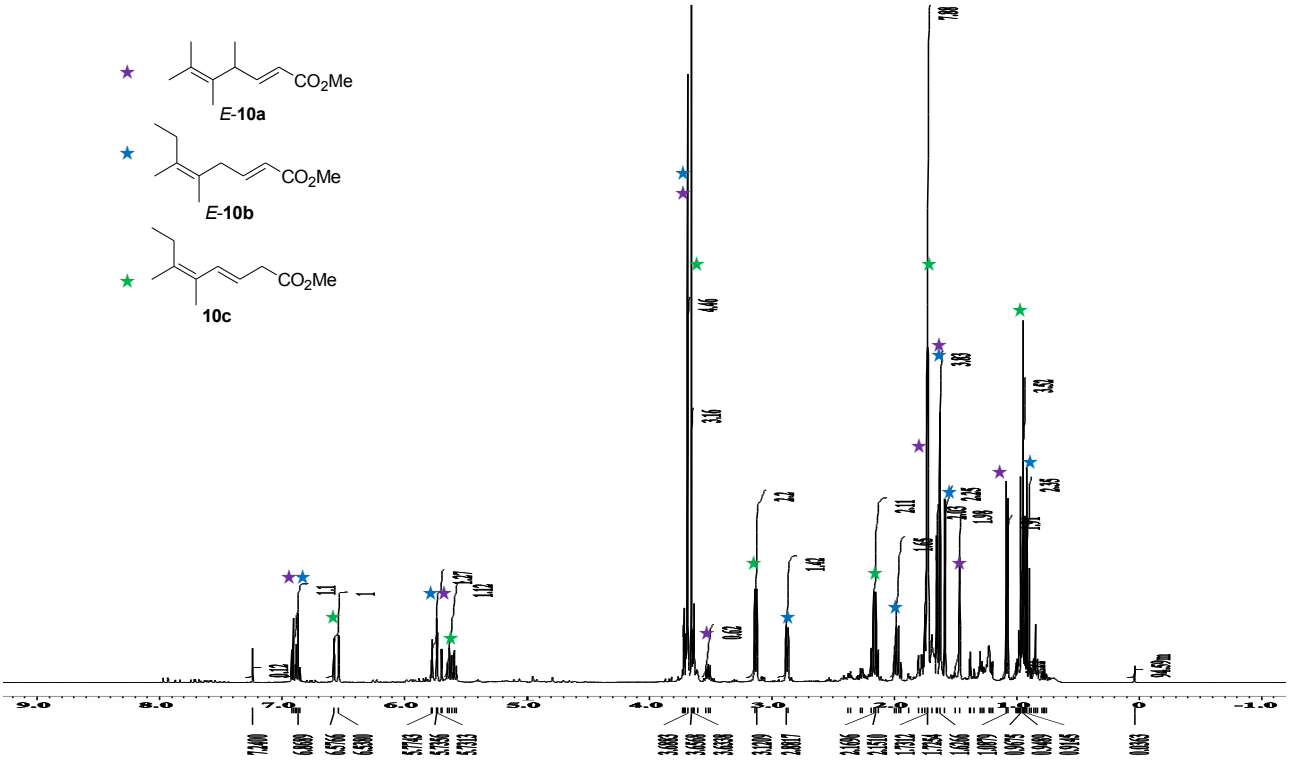


Figure S27-9. ^{1}H NMR spectrum for (3*E*,5*Z*)-Methyl 5,6-dimethylocta-3,5-dienoate (**10c**) ((*E*-**10a**:*E*-**10b**:**10c** = 26:29:45 sample), 399.8 MHz, $CDCl_3$).

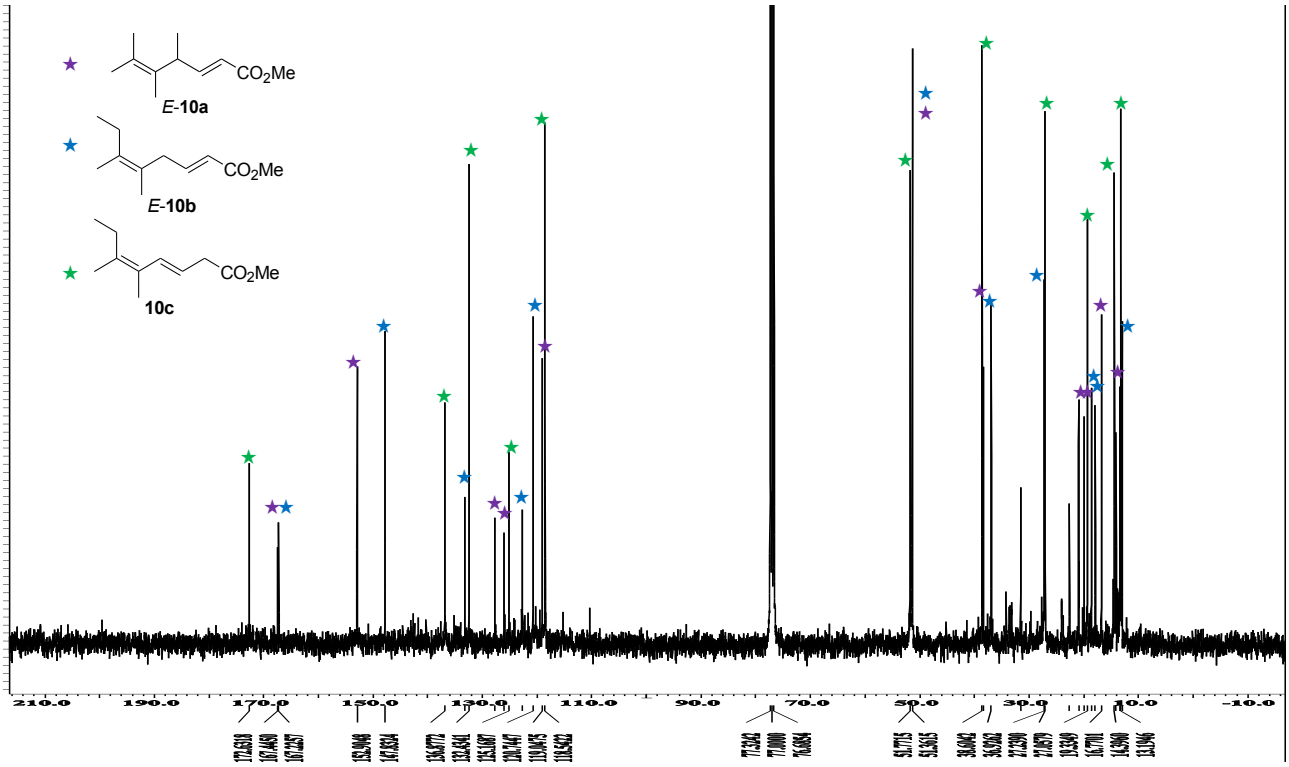


Figure S27-10. ^{13}C NMR spectrum for (3*E*,5*Z*)-Methyl 5,6-dimethylocta-3,5-dienoate (**10c**) ((*E*-**10a**:*E*-**10b**:**10c** = 26:29:45 sample), 100.5 MHz, $CDCl_3$).

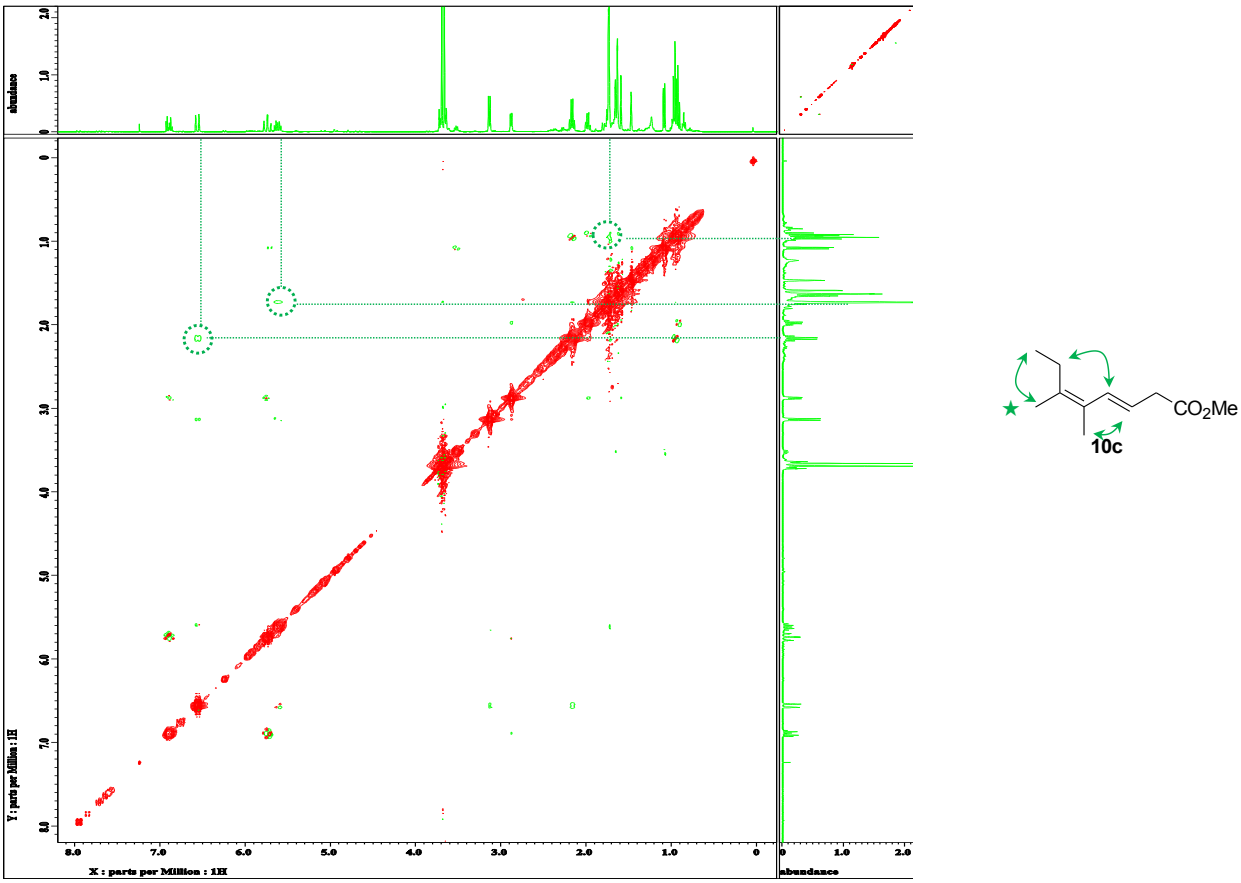


Figure S27-11. Phase sensitive NOESY 2D NMR spectrum for (3*E*,5*Z*)-Methyl 5,6-dimethylocta-3,5-dienoate (**10c**) ((*E*-**10a**:*E*-**10b**:**10c** = 26:29:45 sample), 399.8 MHz, $CDCl_3$).

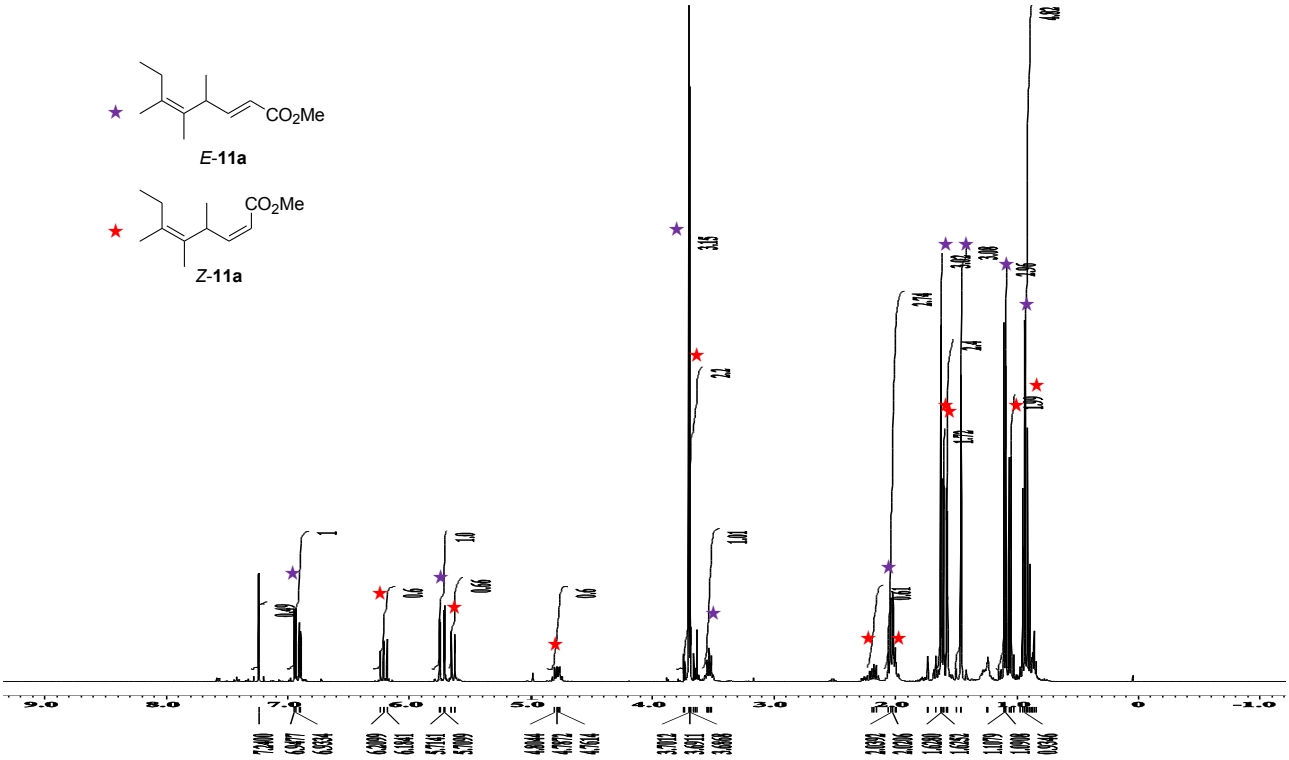


Figure S28-1. ^{1}H NMR spectrum for (2*E*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a**) ((*E*-**11a**:*Z*-**11a** = 63:37 sample), 399.8 MHz, $CDCl_3$).

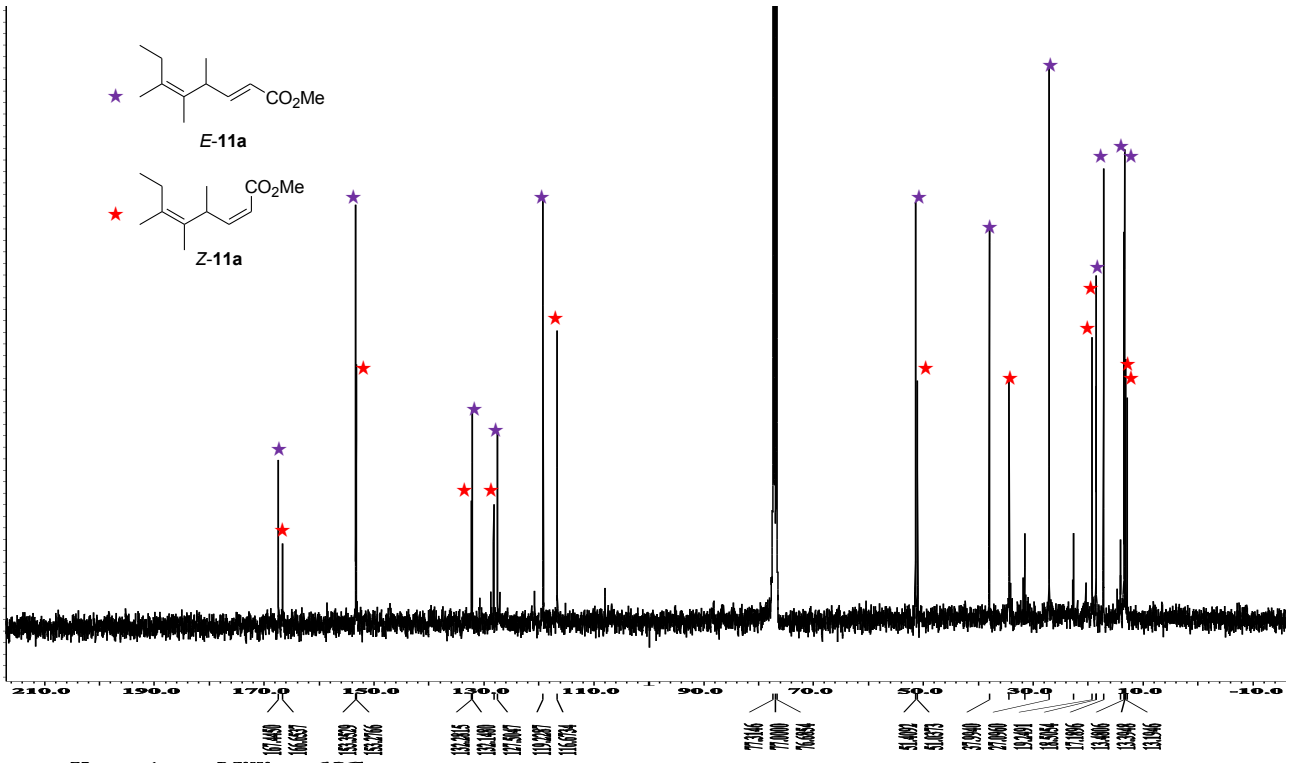


Figure S28-2. ^{13}C NMR spectrum for (2*E*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a**) ((*E*-**11a**:*Z*-**11a** = 63:37 sample), 100.5 MHz, $CDCl_3$).

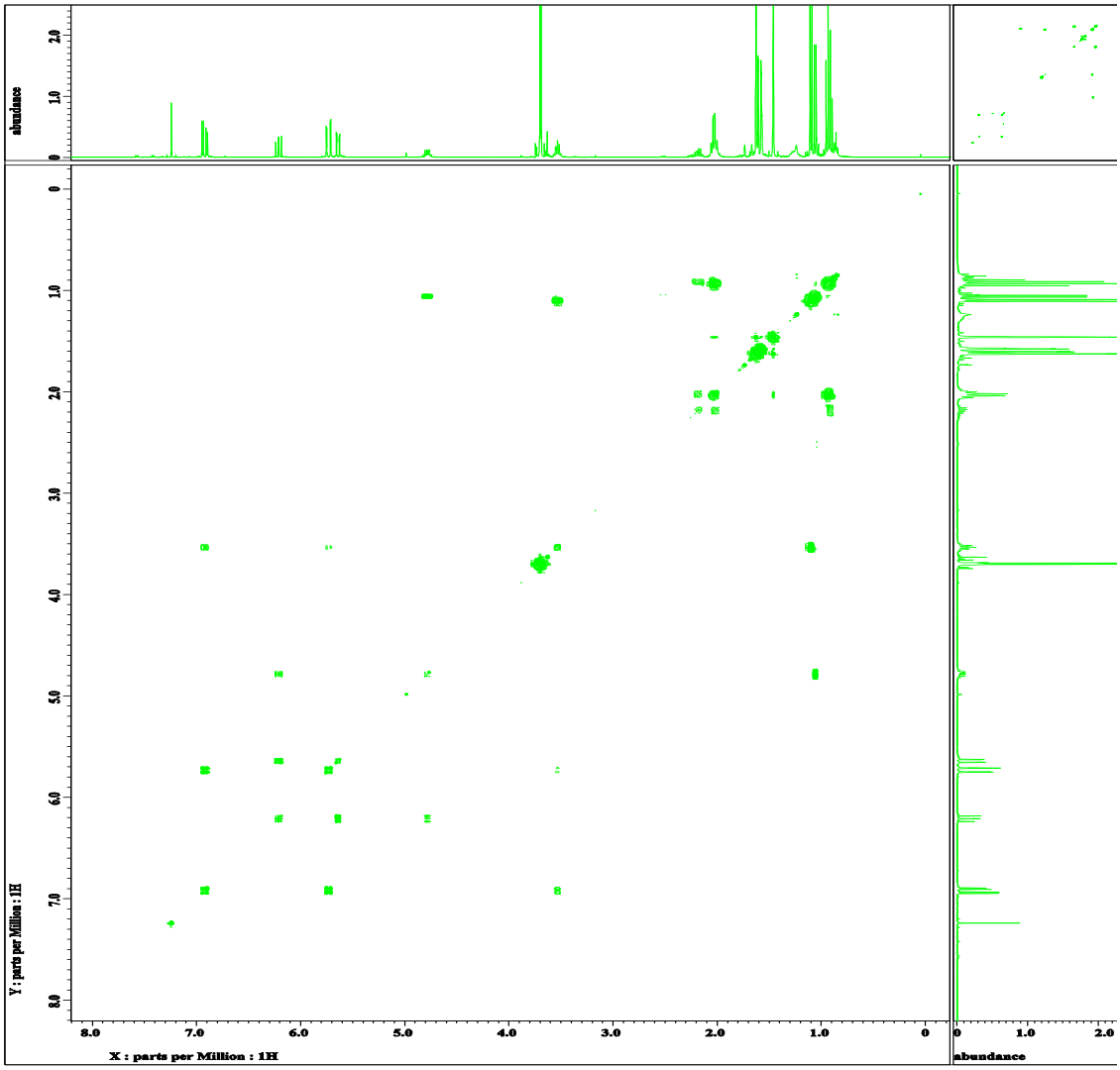


Figure S28-3. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*E*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a**) ((*E*-**11a**:*Z*-**11a** = 63:37 sample), 399.8 MHz, $CDCl_3$).

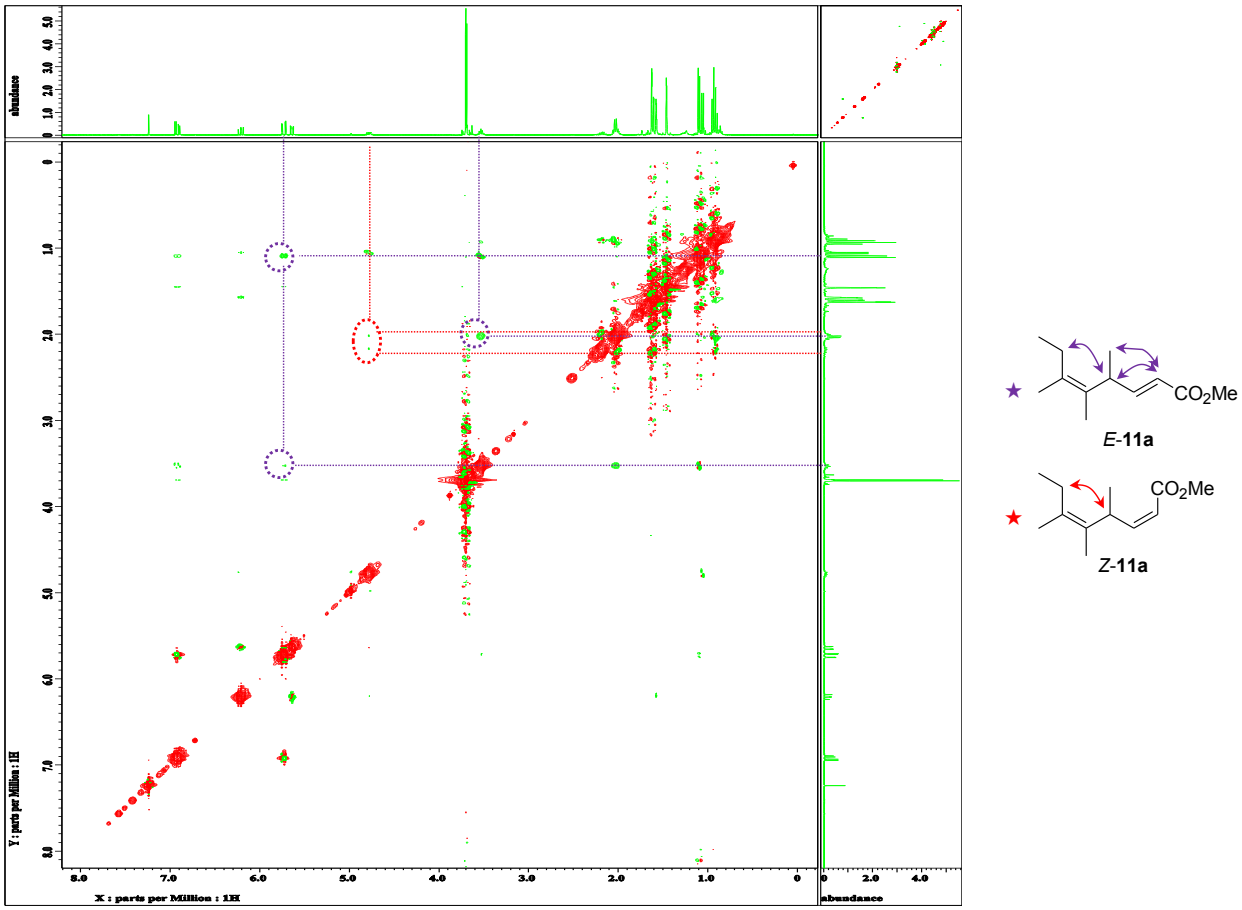


Figure S28-4. Phase sensitive NOESY 2D NMR spectrum for (2*E*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a**) ((*E*-**11a**:*Z*-**11a** = 63:37 sample), 399.8 MHz, $CDCl_3$).

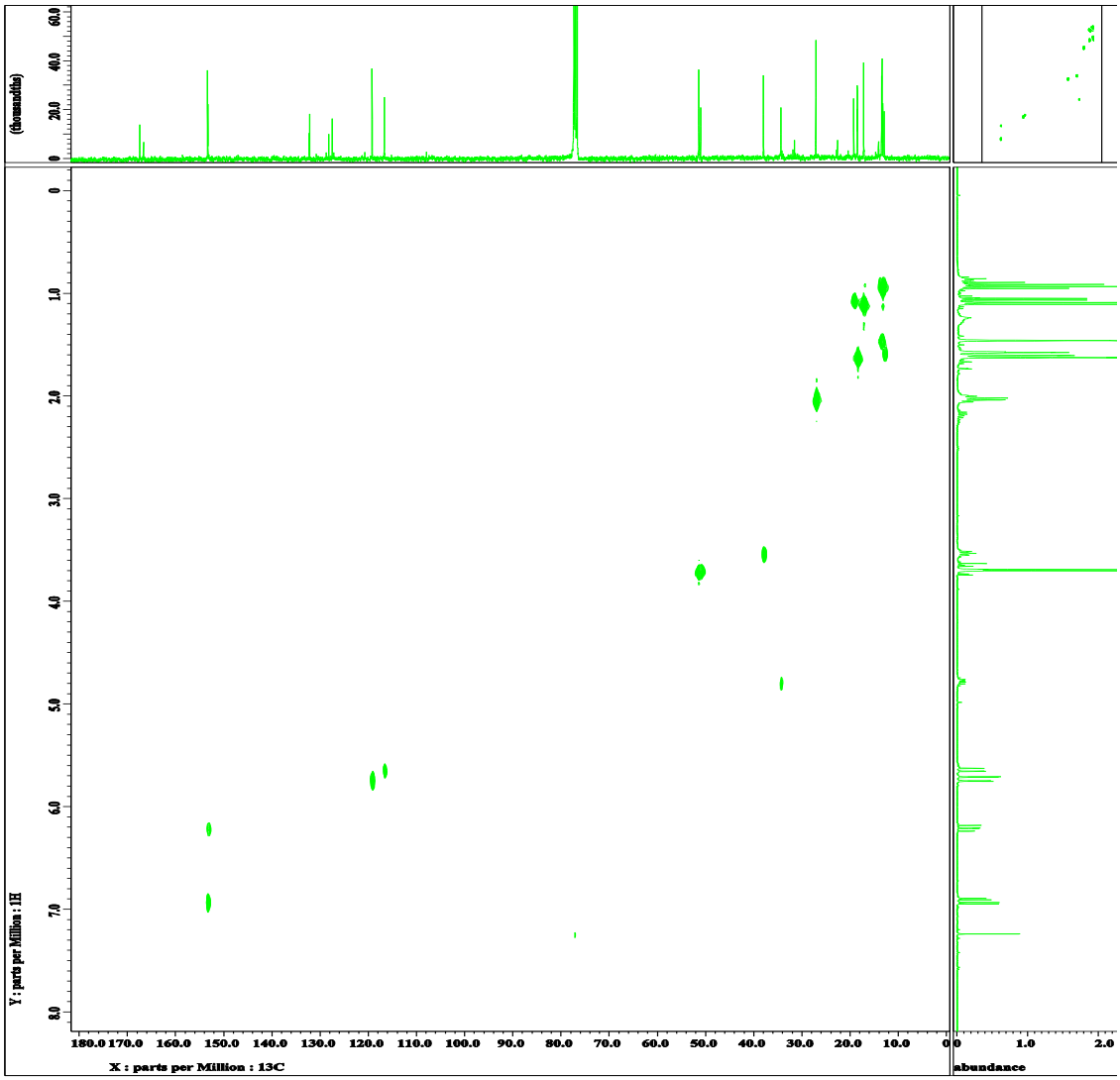


Figure S28-5. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (2*E*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a**) ((*E*-**11a**:*Z*-**11a** = 63:37 sample), 100.5 MHz, $CDCl_3$).

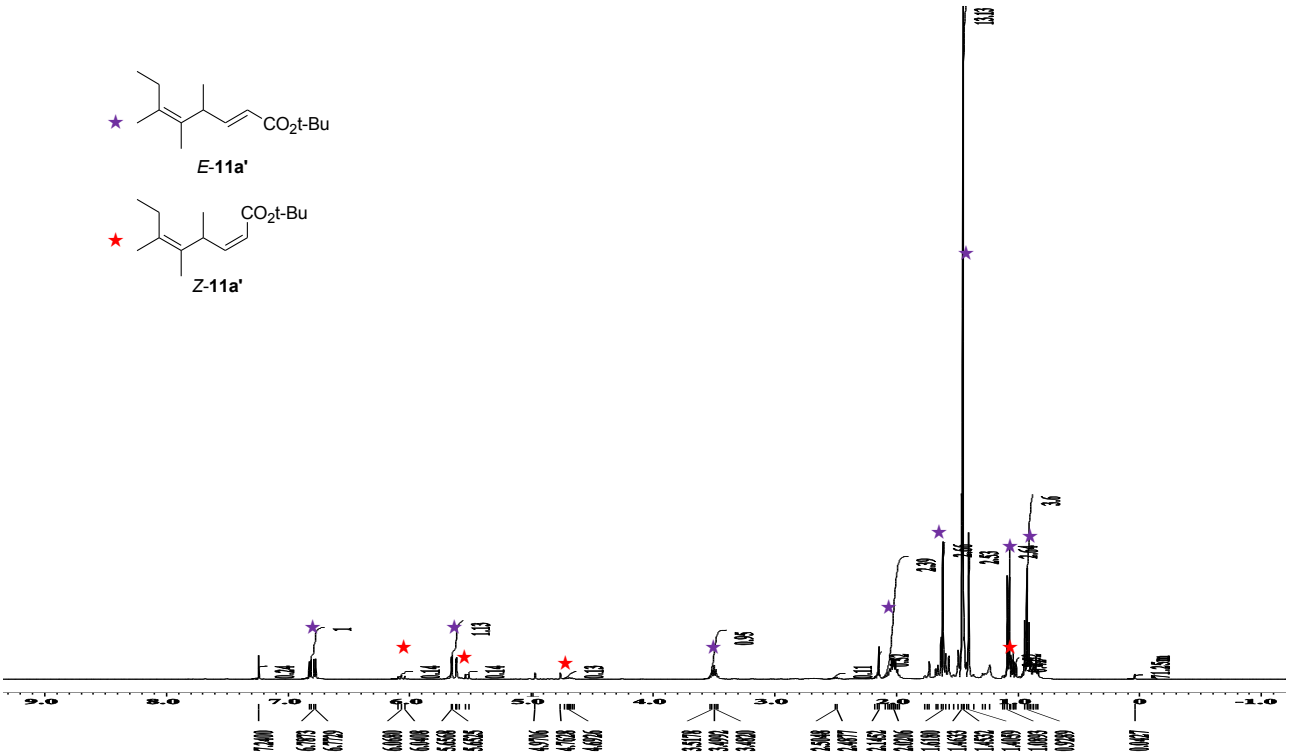


Figure S29-1. ^{1}H NMR spectrum for (2*E*, 5*Z*)-*tert*-Butyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a'**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a'**) ((*E*-**11a'**:*Z*-**11a'** = 88:12 sample), 399.8 MHz, $CDCl_3$).

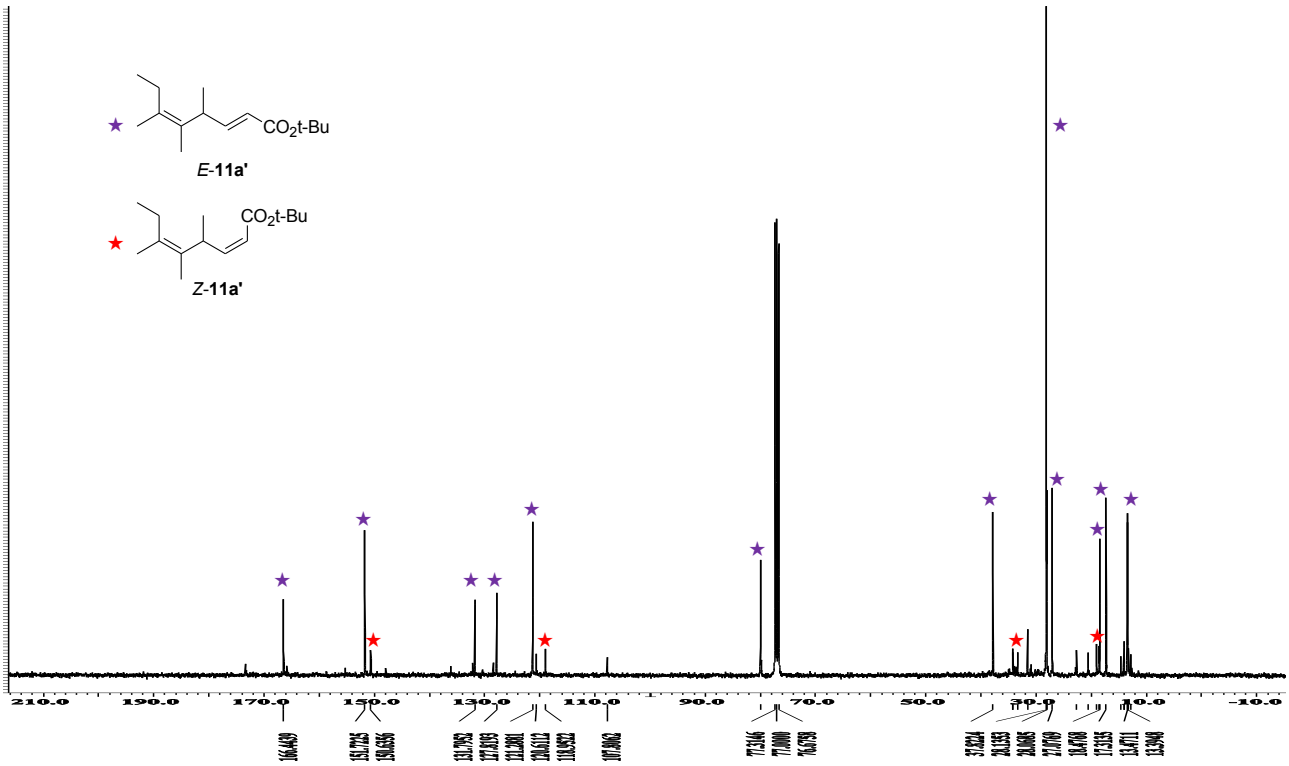


Figure S29-2. ^{13}C NMR spectrum for(2*E*, 5*Z*)-*tert*-Butyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a'**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a'**) ((*E*-**11a'**:*Z*-**11a'** = 88:12 sample), 100.5 MHz, $CDCl_3$).

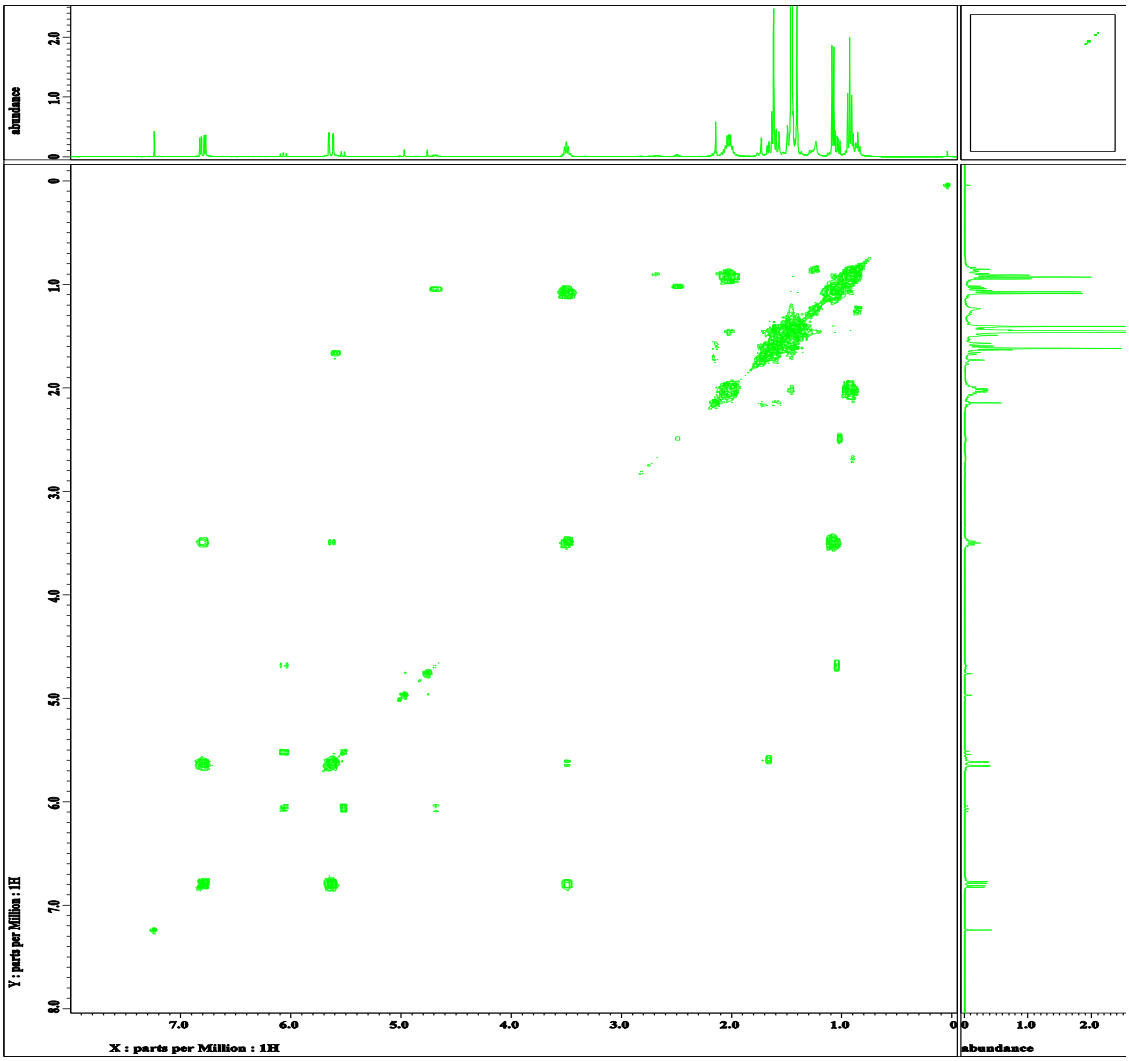


Figure S29-3. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*E*, 5*Z*)-*tert*-Butyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a'**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a'**) ((*E*-**11a'**:*Z*-**11a'** = 88:12 sample), 399.8 MHz, $CDCl_3$).

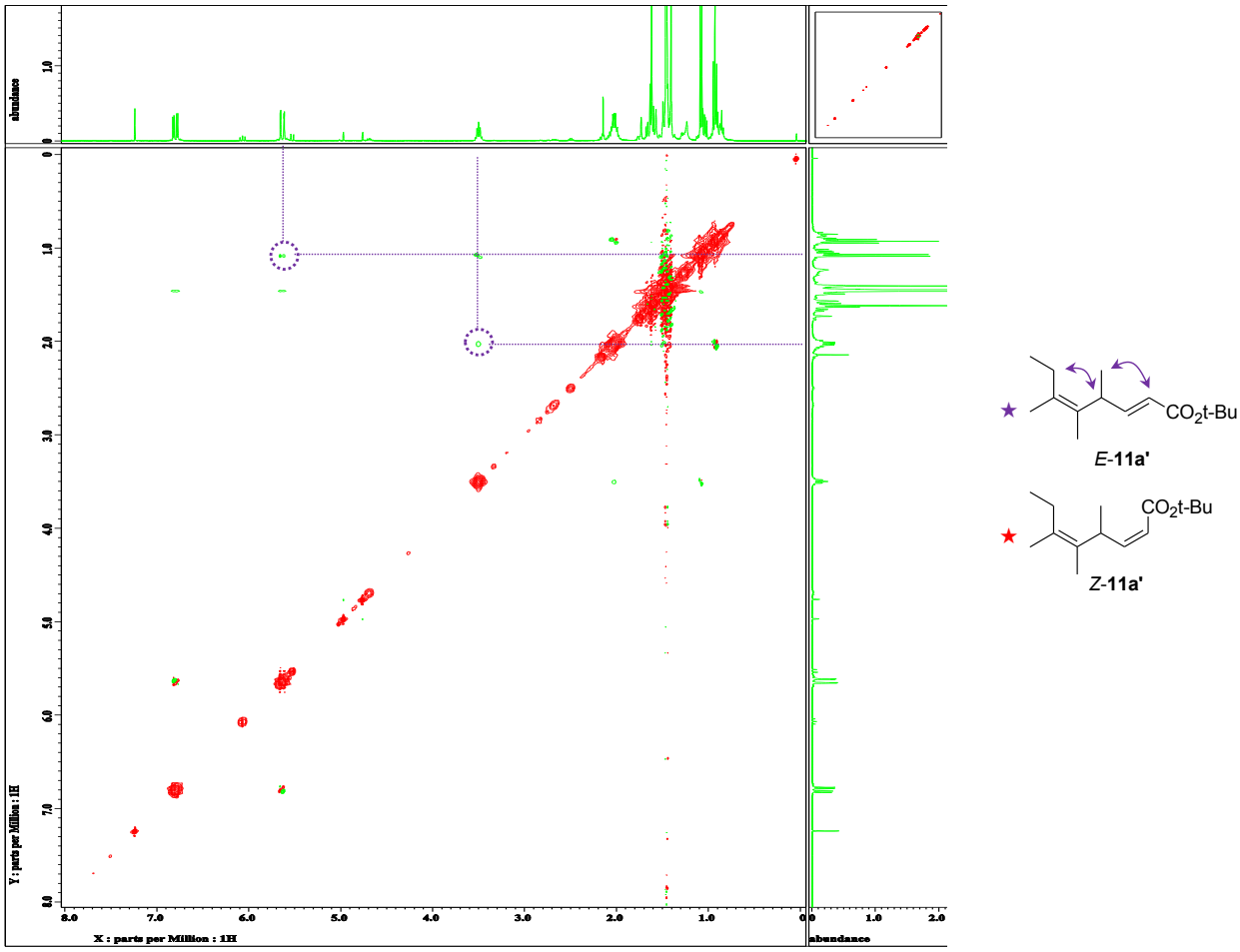


Figure S29-4. Phase sensitive NOESY 2D NMR spectrum for (2*E*, 5*Z*)-*tert*-Butyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a'**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a'**) ((*E*-**11a'**:*Z*-**11a'** = 88:12 sample), 399.8 MHz, $CDCl_3$).

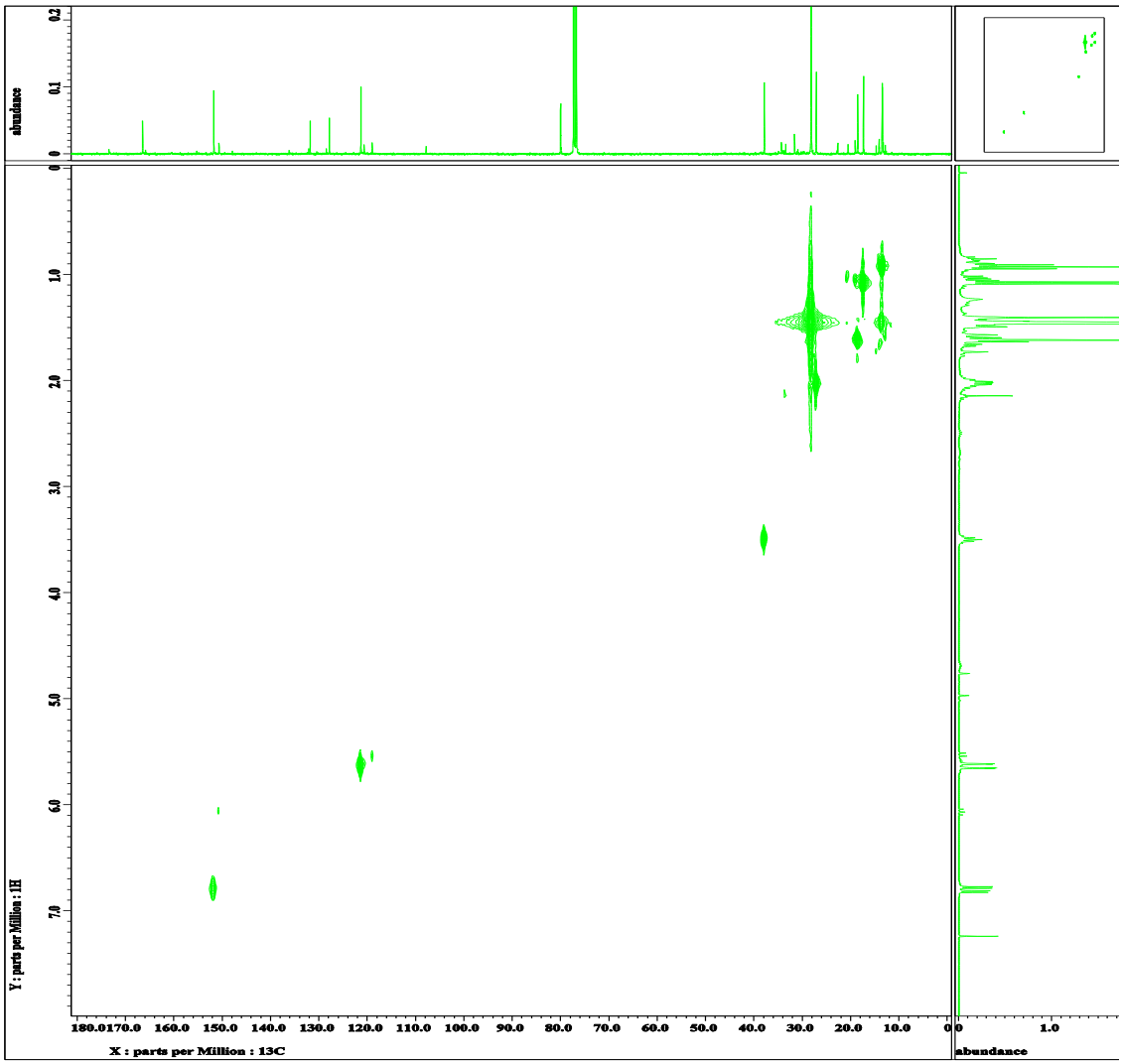


Figure S29-5. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (2*E*, 5*Z*)-*tert*-Butyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a'**) and (2*Z*, 5*Z*)-Methyl 4,5,6-trimethyl-octa-2,5-dienoate (*Z*-**11a'**) ((*E*-**11a'**:*Z*-**11a'** = 88:12 sample), 100.5 MHz, $CDCl_3$).

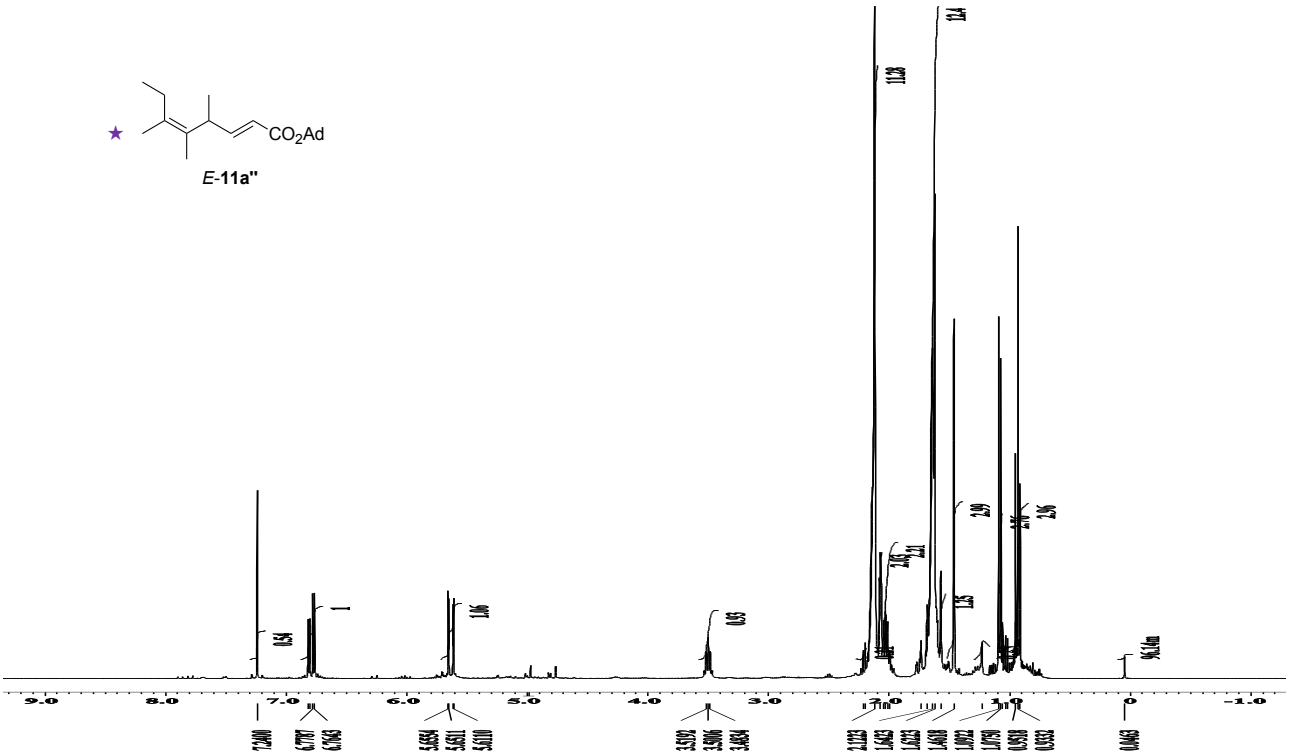


Figure S30-1. ^{1}H NMR spectrum for (2*E*, 5*Z*)-Adamantyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a"**) (399.8 MHz, $CDCl_3$).

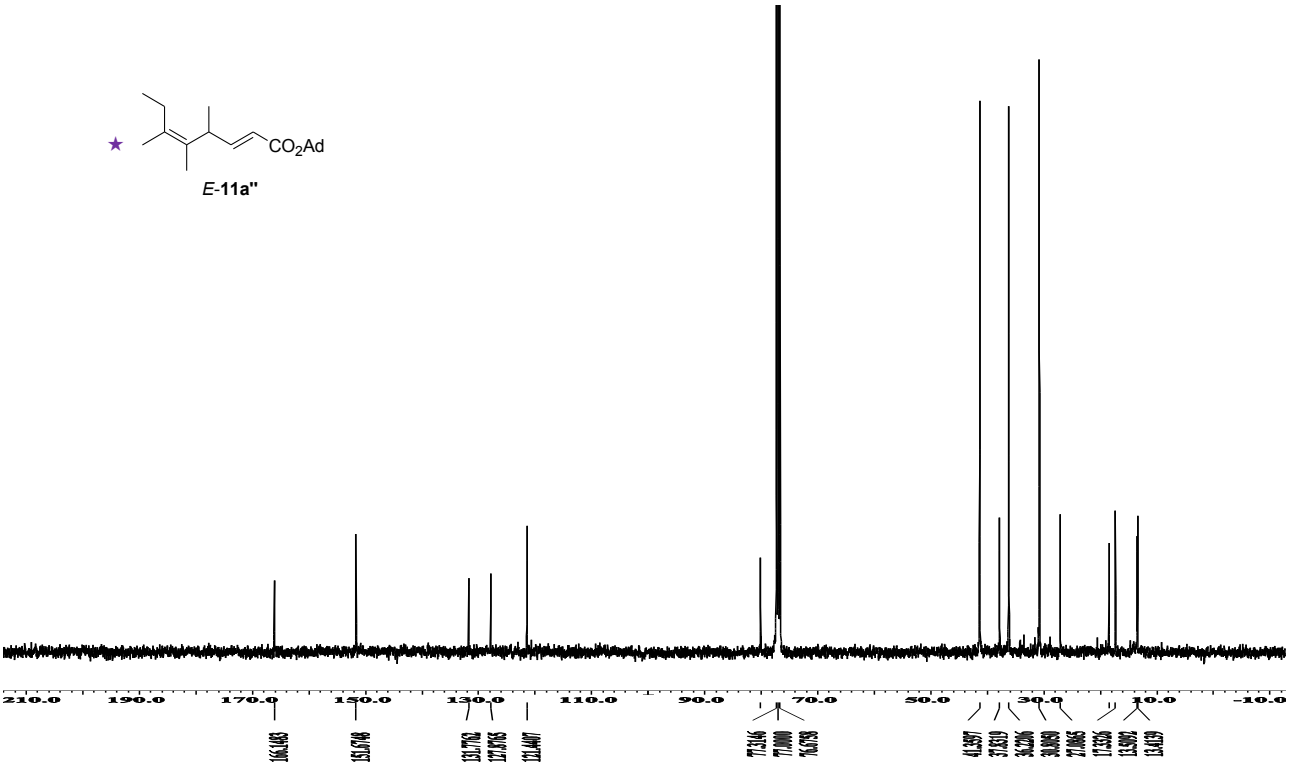


Figure S30-2. ^{13}C NMR spectrum for (2*E*, 5*Z*)-Adamantyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a"**) (100.5 MHz, $CDCl_3$).

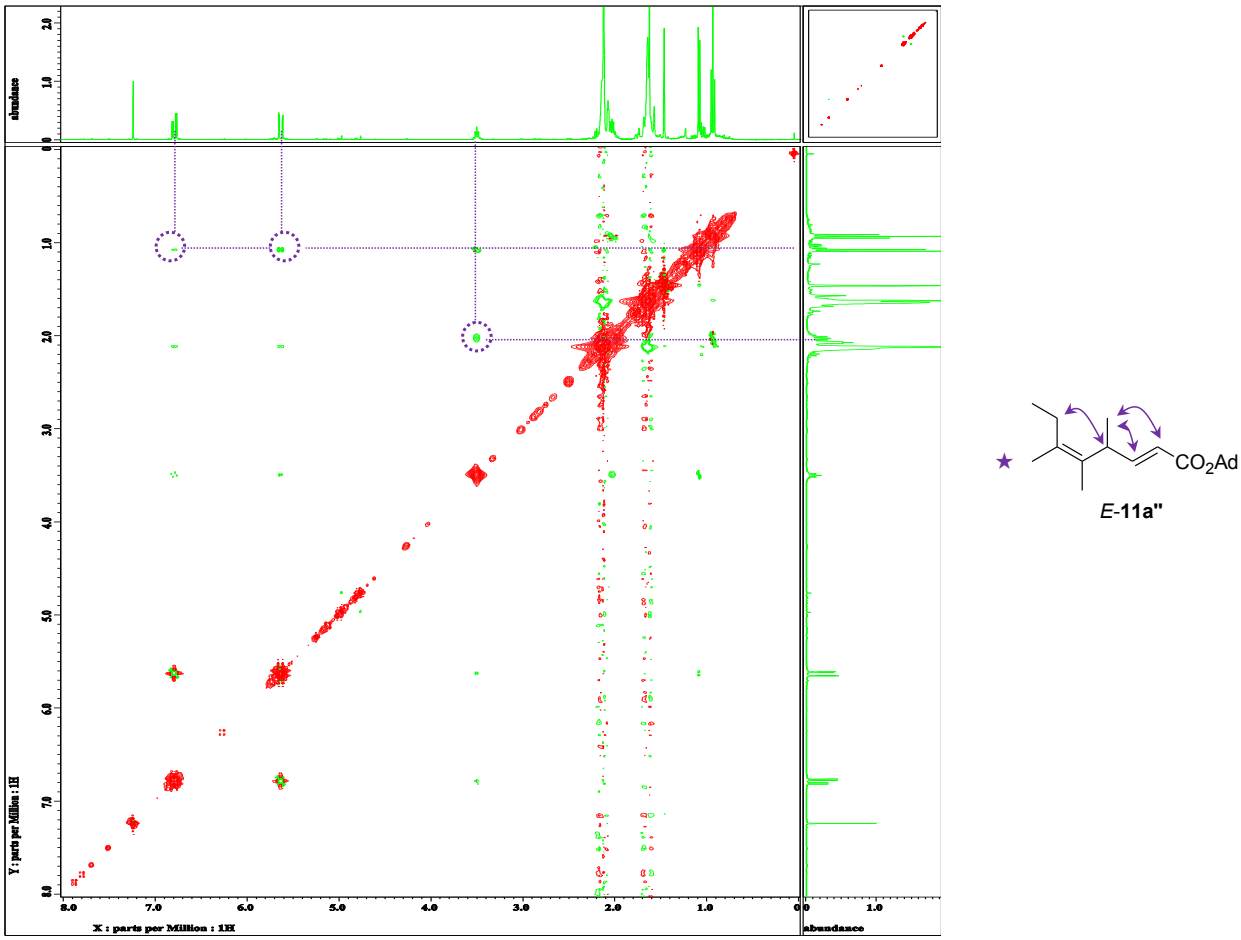


Figure S30-3. Phase sensitive NOESY 2D NMR spectrum for (2*E*, 5*Z*)-Adamantyl 4,5,6-trimethyl-octa-2,5-dienoate (*E*-**11a"**) (399.8 MHz, $CDCl_3$).

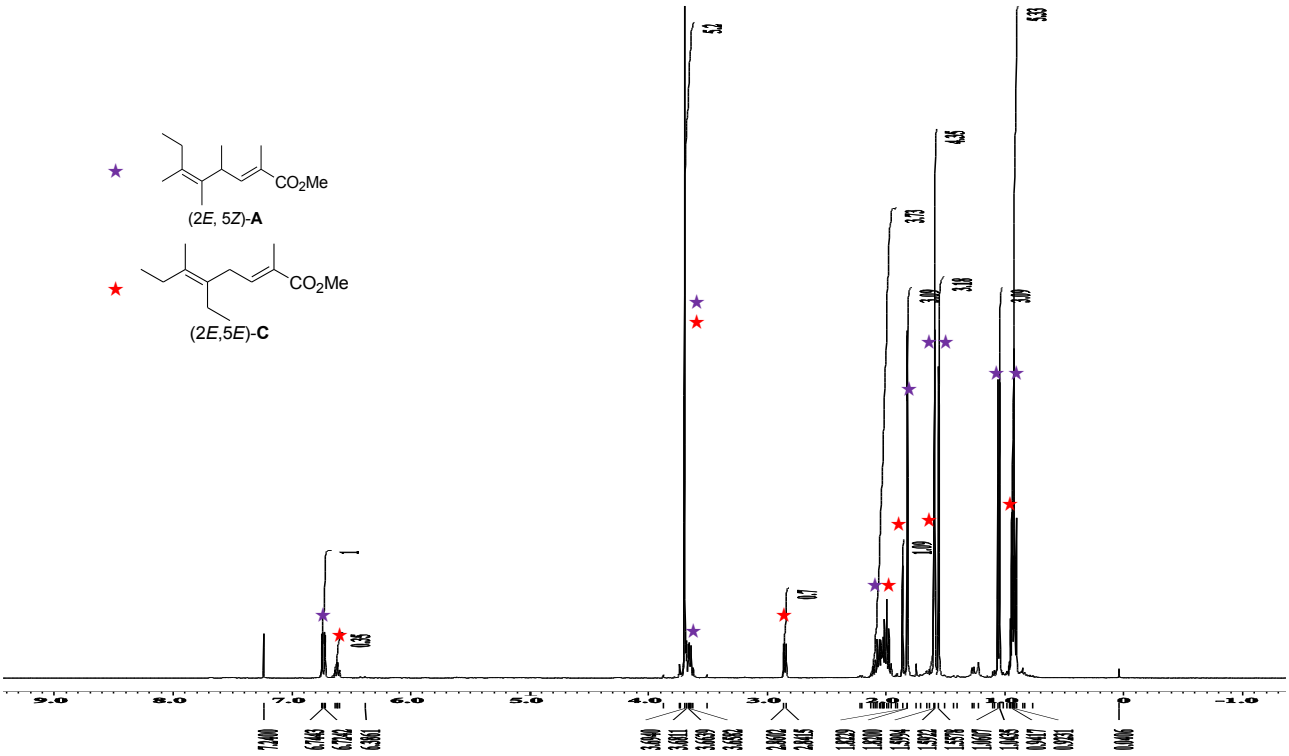


Figure S31-1. ^{1}H NMR spectrum for (2E, 5Z)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate ((2*E*, 5*Z*)-**A**) and (2E, 5E)-Methyl 5-ethyl-2,6-dimethyl-octa-2,5-dienoate ((2*E*,5*E*)-**C**) ((2*E,5Z*)-**A**:(2*E*,5*E*)-**C** = 75:25), 399.8 MHz, $CDCl_3$).

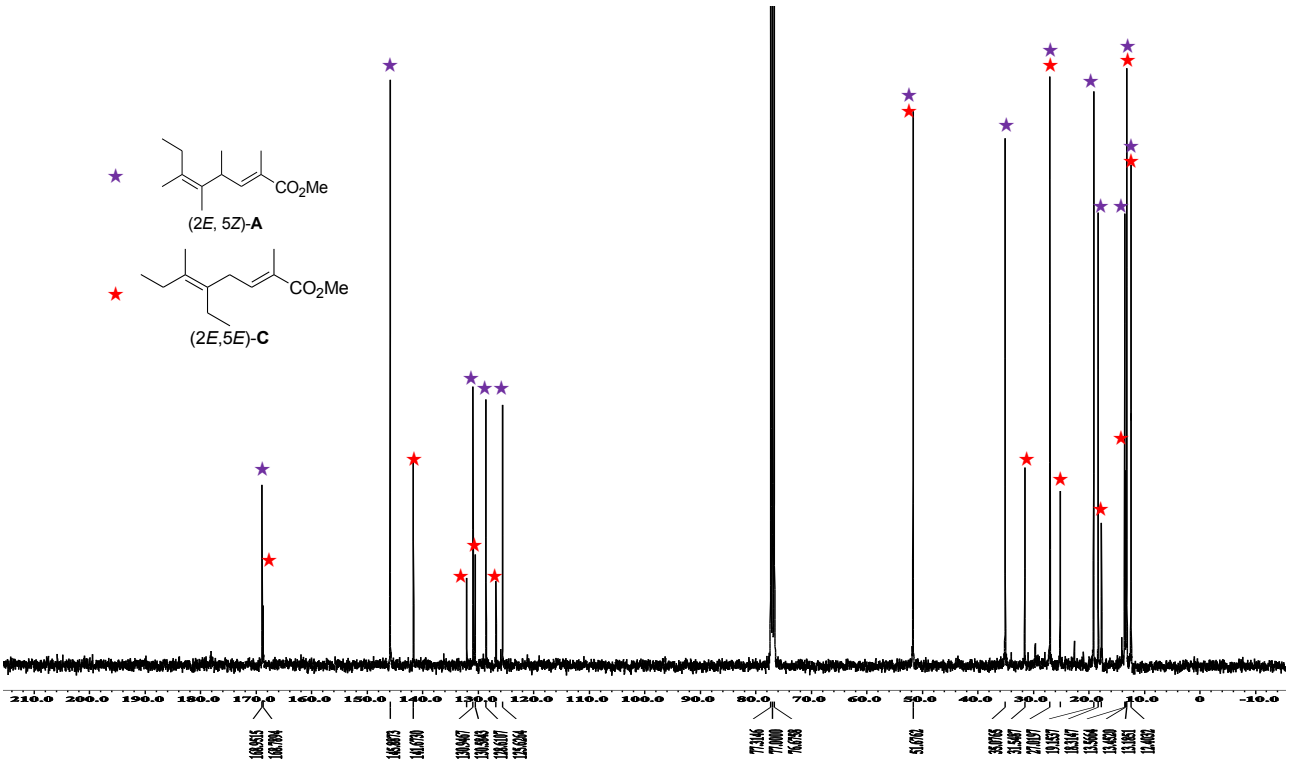


Figure S31-2. ^{13}C NMR spectrum for (2E, 5Z)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate ((2*E*, 5*Z*)-**A**) and (2E, 5E)-Methyl 5-ethyl-2,6-dimethyl-octa-2,5-dienoate ((2*E*,5*E*)-**C**) ((2*E,5Z*)-**A**:(2*E*,5*E*)-**C** = 75:25), 100.5 MHz, $CDCl_3$).

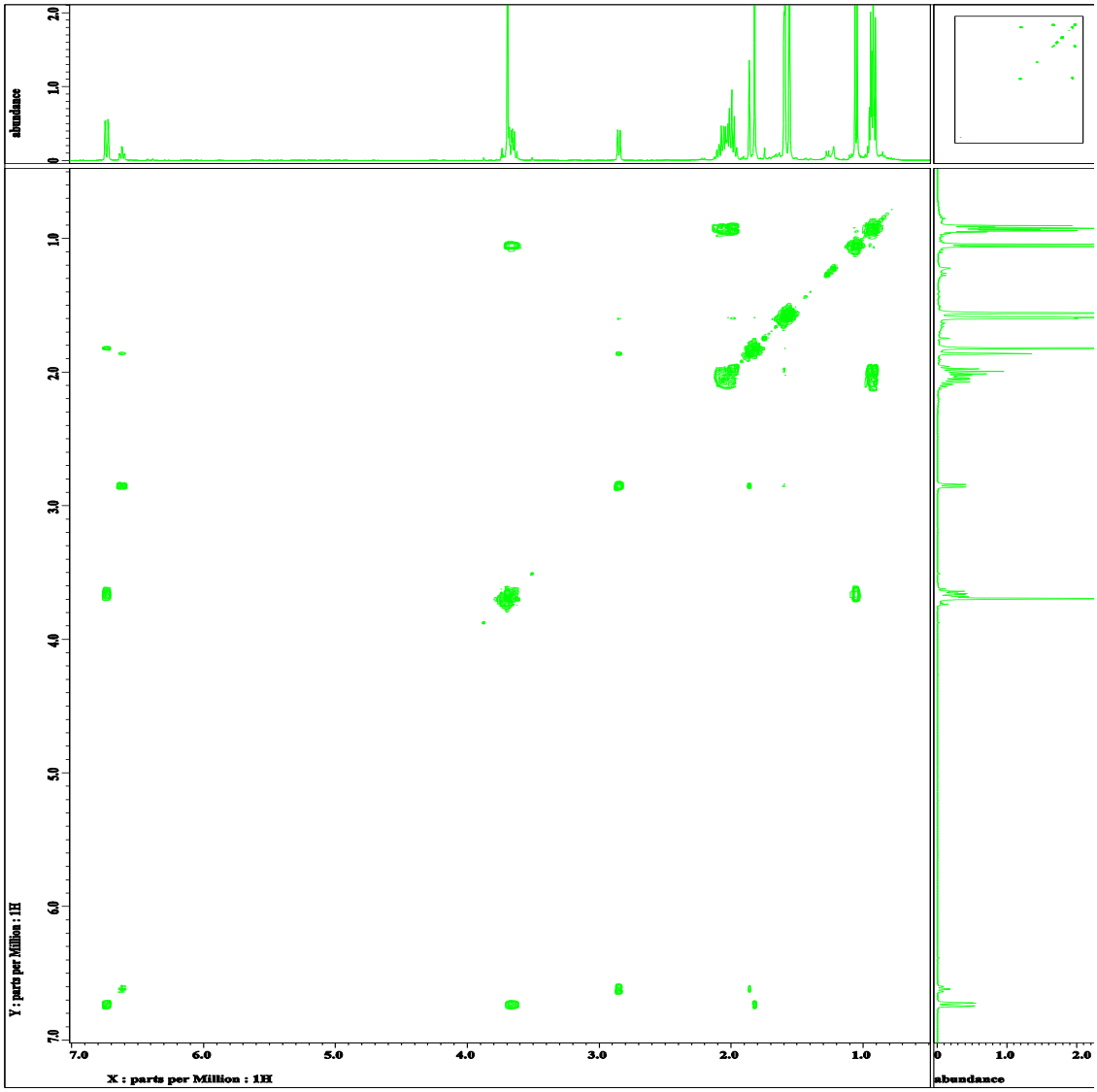


Figure S31-3. ^{1}H-^{1}H COSY 2D NMR spectrum for (2E, 5Z)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate ((2*E*, 5*Z*)-**A**) and (2E, 5E)-Methyl 5-ethyl-2,6-dimethyl-octa-2,5-dienoate ((2*E*,5*E*)-**C**) ((2*E*,5*Z*)-**A**:(2*E*,5*E*)-**C** = 75:25), 399.8 MHz, $CDCl_3$).

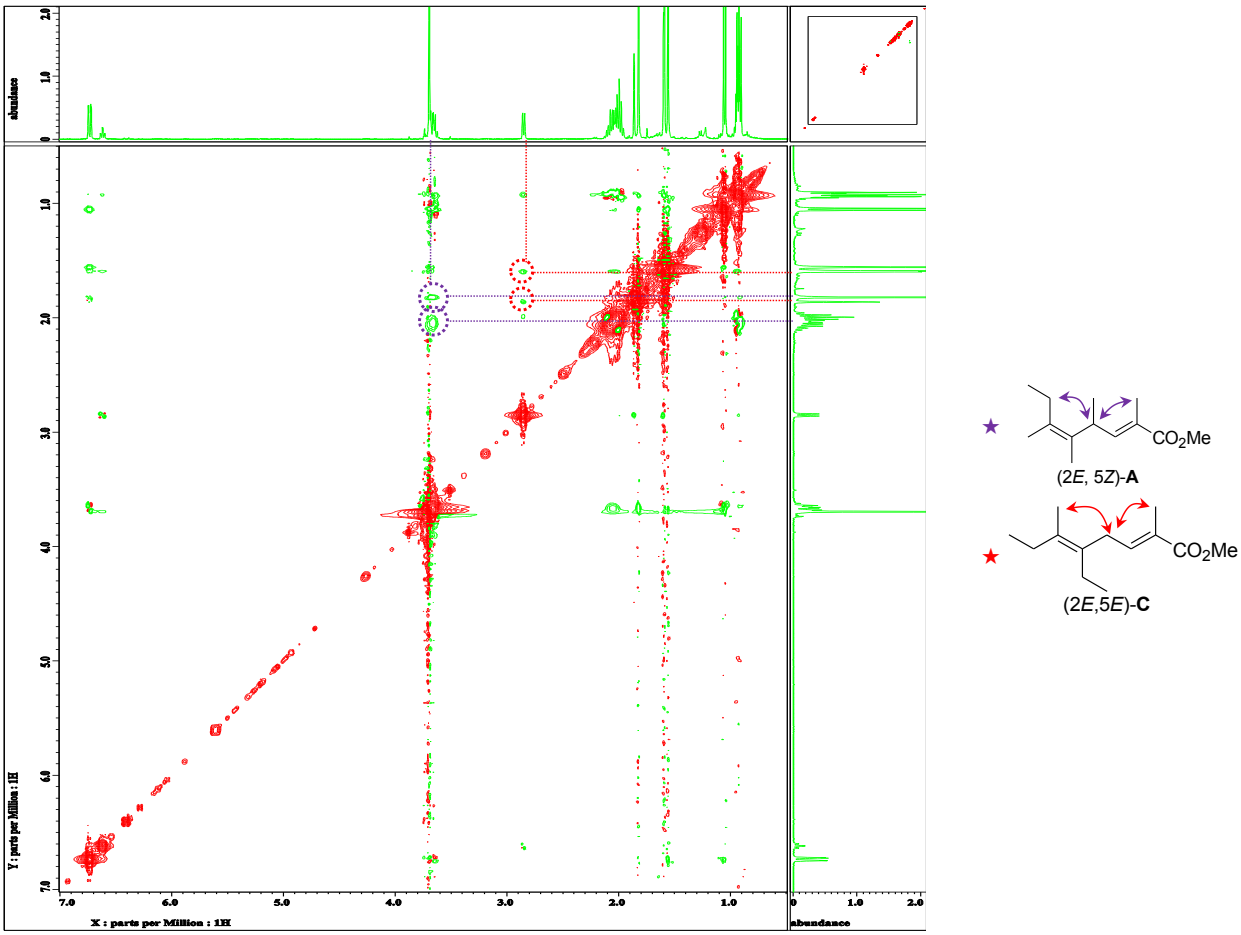


Figure S31-4. Phase sensitive NOESY 2D NMR spectrum for (2E, 5Z)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate ((2*E*, 5*Z*)-**A**) and (2E, 5E)-Methyl 5-ethyl-2,6-dimethyl-octa-2,5-dienoate ((2*E*,5*E*)-**C**) ((2*E*,5*Z*)-**A**:(2*E*,5*E*)-**C** = 75:25), 399.8 MHz, $CDCl_3$).

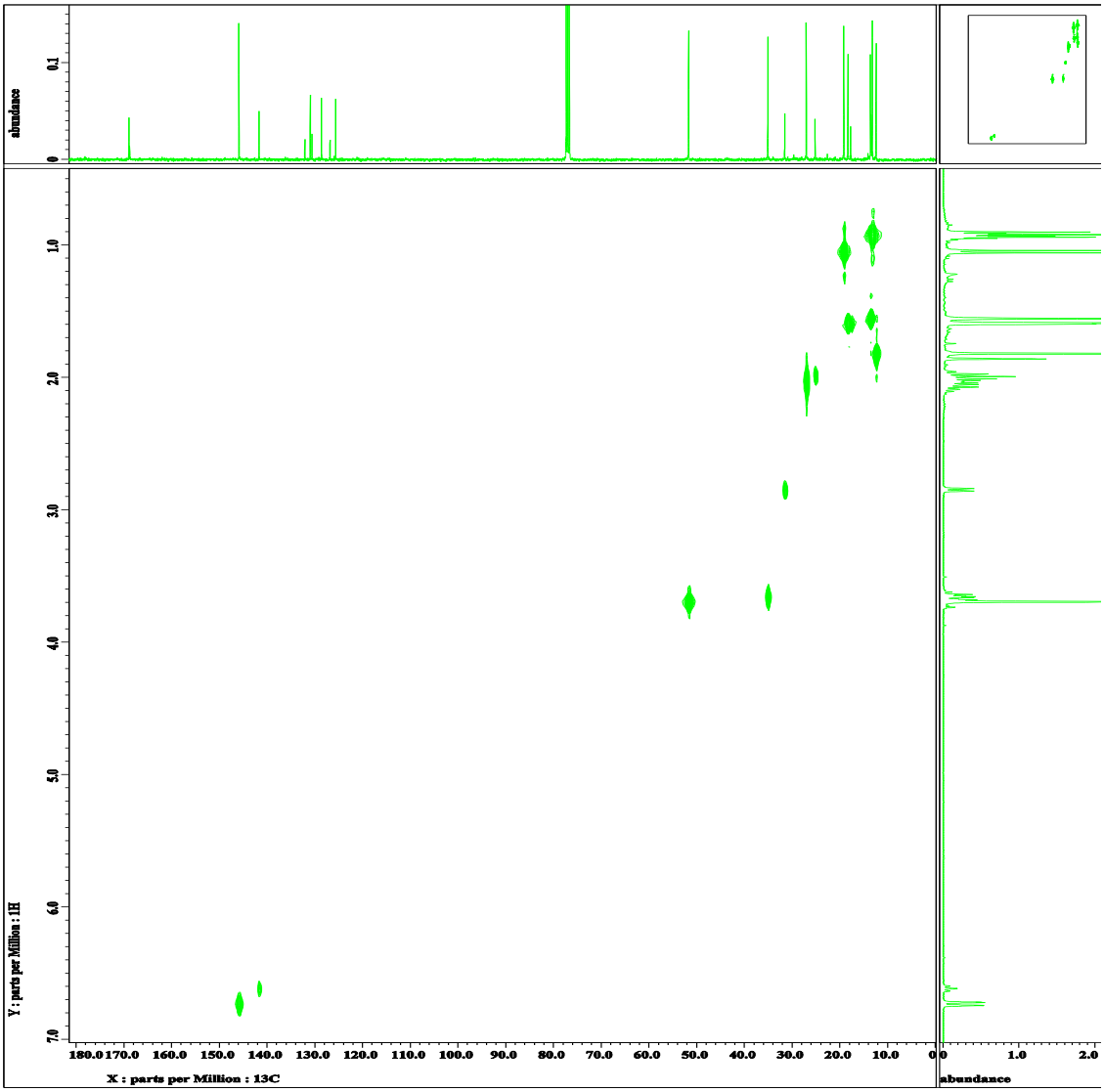


Figure S31-5. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (2E, 5Z)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate ((2*E*, 5*Z*)-**A**) and (2E, 5E)-Methyl 5-ethyl-2,6-dimethyl-octa-2,5-dienoate ((2*E*,5*E*)-**C**) ((2*E*,5*Z*)-**A**:(2*E*,5*E*)-**C** = 75:25), 100.5 MHz, $CDCl_3$).

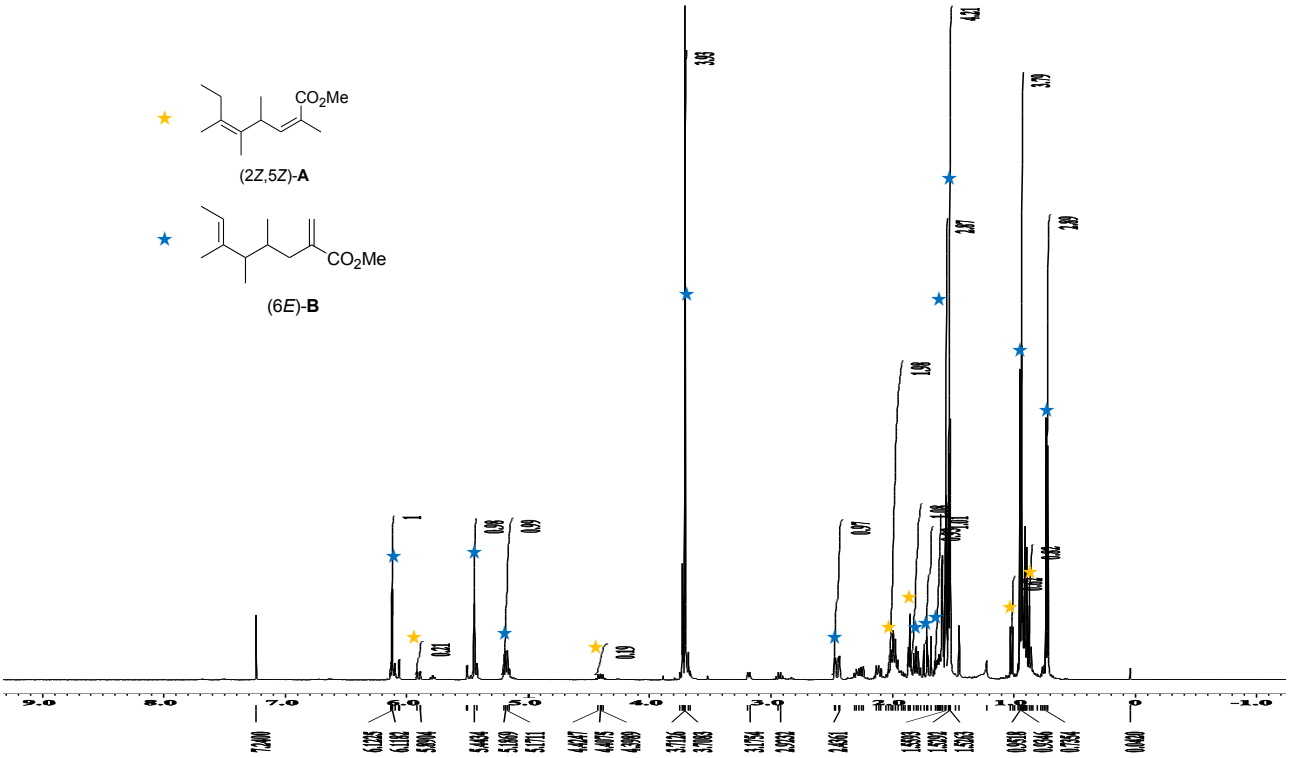


Figure S31-6. ^{1}H NMR spectrum for (2*Z*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*Z*, 5*Z*)-**A**) and (6*E*)-Methyl 4,5,6-trimethyl-2-methylene-oct-6-enoate ((6*E*)-**B**) (((2*Z*,5*Z*)-**A**:(6*E*)-**B**:**X** = 13:63:24), 399.8 MHz, $CDCl_3$).

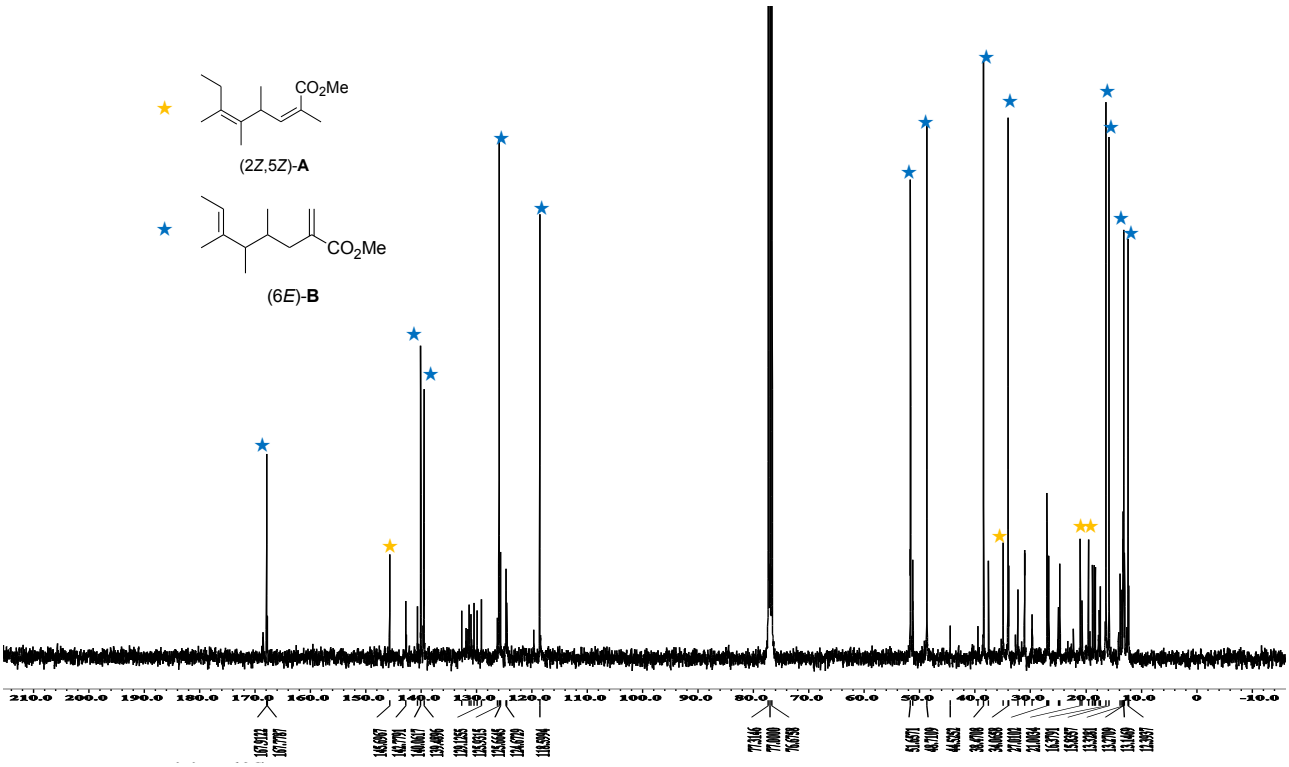


Figure S31-7. ^{13}C NMR spectrum for (2*Z*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*Z*, 5*Z*)-**A**) and (6*E*)-Methyl 4,5,6-trimethyl-2-methylene-oct-6-enoate ((6*E*)-**B**) (((2*Z*,5*Z*)-**A**:(6*E*)-**B**:**X** = 13:63:24), 100.5 MHz, $CDCl_3$).

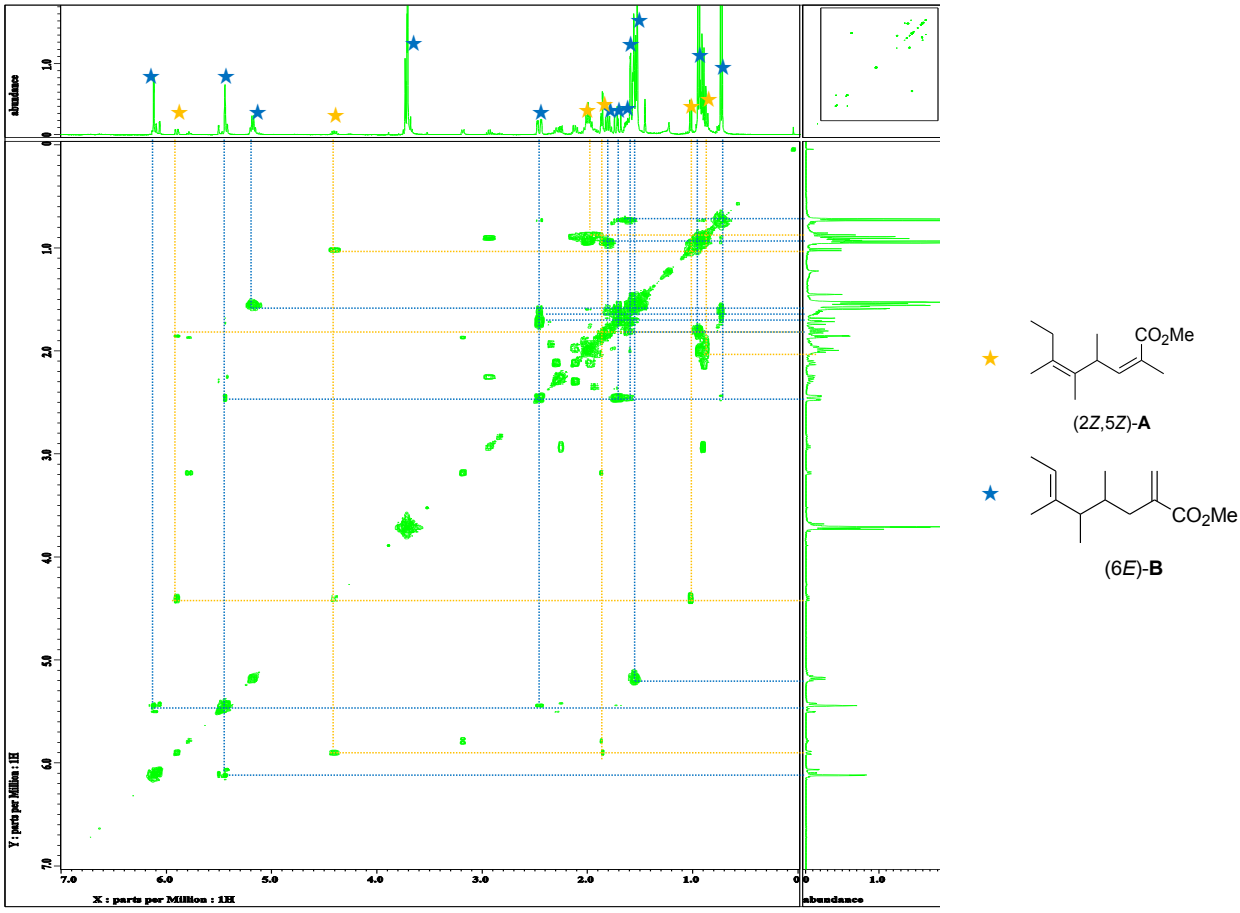


Figure S31-8. ^{1}H-^{1}H COSY 2D NMR spectrum for (2*Z*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*Z*, 5*Z*)-**A**) and (6*E*)-Methyl 4,5,6-trimethyl-2-methylene-oct-6-enoate ((6*E*)-**B**) (((2*Z*,5*Z*)-**A**:(6*E*)-**B**:**X** = 13:63:24), 399.8 MHz, $CDCl_3$).

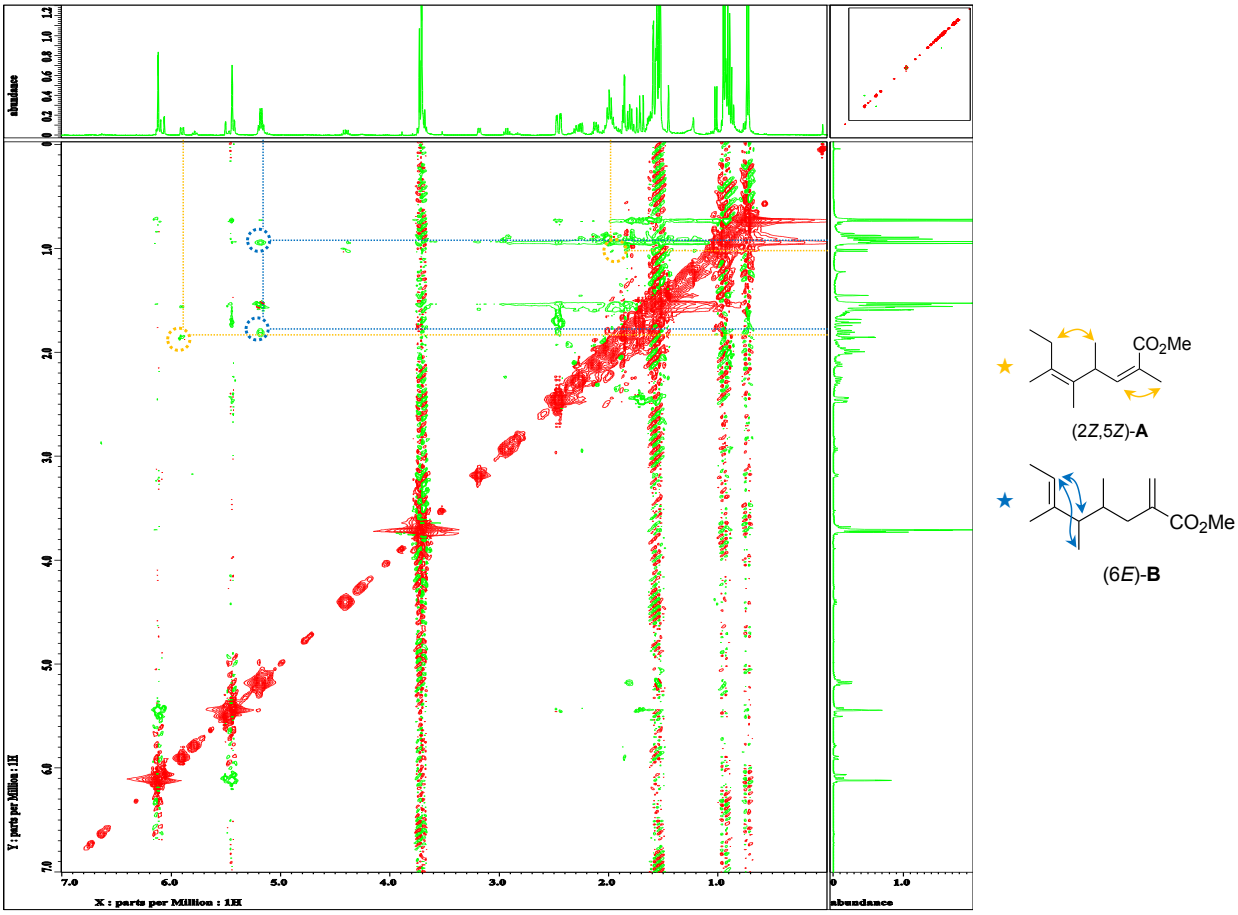


Figure S31-9. Phase sensitive NOESY 2D NMR spectrum for (2*Z*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*Z*, 5*Z*)-**A**) and (6*E*)-Methyl 4,5,6-trimethyl-2-methylene-oct-6-enoate ((6*E*)-**B**) (((2*Z*,5*Z*)-**A**:(6*E*)-**B**:**X** = 13:63:24), 399.8 MHz, $CDCl_3$).

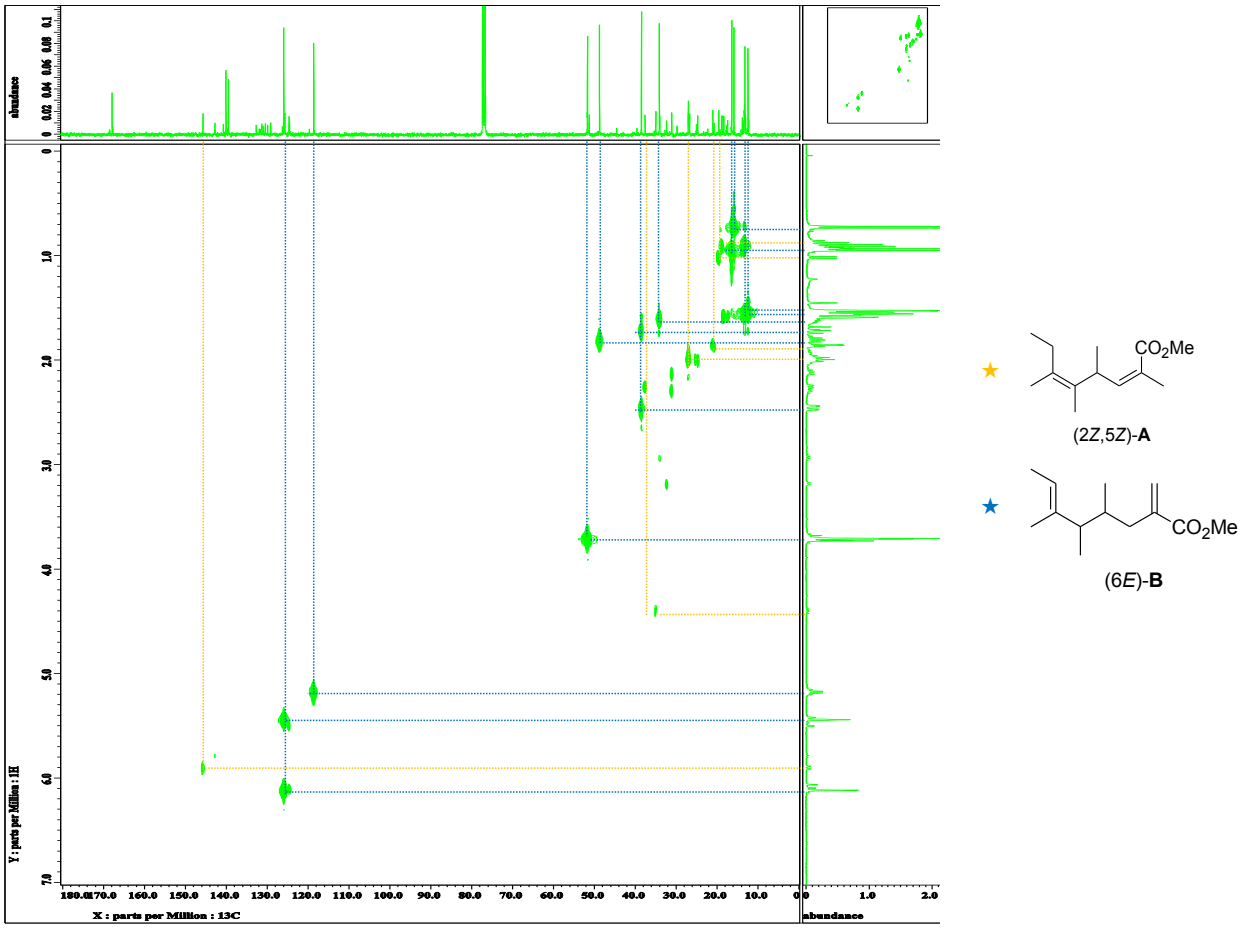


Figure S31-10. ^{13}C-^{1}H HETCOR 2D NMR spectrum for (2*Z*, 5*Z*)-Methyl 2,4,5,6-tetramethyl-octa-2,5-dienoate((2*Z*, 5*Z*)-**A**) and (6*E*)-Methyl 4,5,6-trimethyl-2-methylene-oct-6-enoate ((6*E*)-**B**) (((2*Z*,5*Z*)-**A**:(6*E*)-**B**:**X** = 13:63:24), 100.5 MHz, $CDCl_3$).