Electronic Supplementary Material (ESI) for Dalton Transactions.

Bis-Mixed-Carbene Ruthenium-Thiolate-Alkylidene Complexes: Synthesis and Olefin Metathesis Activity

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Supporting Information

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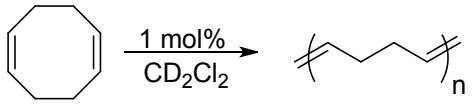
Ring Opening Metathesis Polymerization of 1,5-Cyclooctadiene:



Compound **3**			
Additive	Temperature (^oC)	Time (h)	Conversion (%)
None	25	24	0
None	45	2	5
		4	13
		6	23
		8	36
		24	100
1 mol% BCl_3	25	2	30
		4	56
		6	83
		8	100
1 mol% BCl_3	45	2	100

Compound **4**			
Additive	Temperature (^oC)	Time (h)	Conversion (%)
None	25	24	0
None	45	2	3
		4	9
		6	14
		24	58
1 mol% BCl_3	25	2	100
1 mol% BCl_3	45	2	100

Compound **5**			
Additive	Temperature (^oC)	Time (h)	Conversion (%)
None	25	24	0
None	45	2	6
		4	11
		6	16
		8	21
		24	69
1 mol % BCl_3	25	2	11
		4	16
		6	21
		8	30
		24	92
1 mol% BCl_3	45	2	26
		4	64

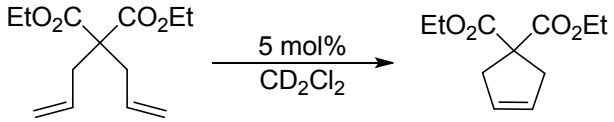
		6	90
		8	100

Compound **6**			
Additive	Temperature (^{o}C)	Time (h)	Conversion (%)
None	25	24	0
None	45	2	54
		4	100
1 mol% BCl_3	25	0.5	21
		2	61
		4	92
		6	100
1 mol% BCl_3	45	0.5	100

Compound **9**			
Additive	Temperature (^{o}C)	Time (h)	Conversion (%)
None	25	2	38
		4	58
		6	71
		8	80
		24	95
1 mol% BCl_3	25	2	100

Compound **10**			
Additive	Temperature (^{o}C)	Time (h)	Conversion (%)
None	25	2	62
		4	71
		6	84
		8	90
		24	93
1 mol% BCl_3	25	2	100

Ring Closing Metathesis of diethyl diallylmalonate:



Compound **3**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	2	6
		4	10
		6	13
		8	16
5 mol% BCl_3	25	2	0
		4	3
		6	7
		8	15
		24	33
5 mol% BCl_3	45	2	63
		4	91
		6	100

Compound **4**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
5 mol% BCl_3	25	8	3
		24	10
5 mol% BCl_3	45	2	16
		4	24
		6	28
		8	29
		24	52

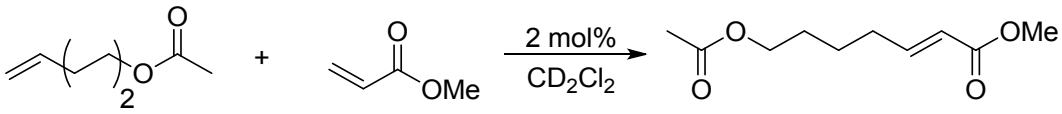
Compound **5**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
5 mol% BCl_3	25	24	0
5 mol% BCl_3	45	2	5
		4	11
		6	14
		8	21
		24	100

Compound **6**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	2	7
		4	12
5 mol% BCl_3	25	2	5
		4	13
		6	28
		8	47
		24	79
5 mol% BCl_3	45	0.5	42
		2	100

Compound **9**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	7
None	45	2	10
		4	16
		6	24
		8	30
		24	60
5 mol% BCl_3	25	2	12
		4	20
		6	32
		8	52
		24	88
5 mol% BCl_3	45	2	100

Compound **10**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	2	1
		24	15
None	45	2	9
		4	14
		6	19
		8	25
		24	56
5 mol% BCl_3	25	2	28
		4	62
		6	85
		8	90
		24	93
5 mol% BCl_3	45	2	100

Cross Metathesis of 5-hexenyl acetate and methyl acrylate:



Compound **3**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
2 mol% BCl_3	25	2	48
2 mol% BCl_3	45	2	42

Compound **4**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
2 mol% BCl_3	25	24	0
2 mol% BCl_3	45	4	21
		6	23
		8	28
		24	32

Compound **5**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
2 mol% BCl_3	25	24	0
2 mol% BCl_3	45	2	28

Compound **6**			
Additive	Temperature (°C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
2 mol% BCl_3	25	2	38
		4	46
		6	50
2 mol% BCl_3	45	2	65
		4	72

Compound **9**			
Additive	Temperature (^{o}C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
2 mol% BCl_3	25	2	15
		4	18
		6	21
2 mol% BCl_3	45	2	55
		4	60

Compound **10**			
Additive	Temperature (^{o}C)	Time (h)	Conversion (%)
None	25	24	0
None	45	24	0
2 mol% BCl_3	25	2	20
		4	50
		6	79
2 mol% BCl_3	45	2	80

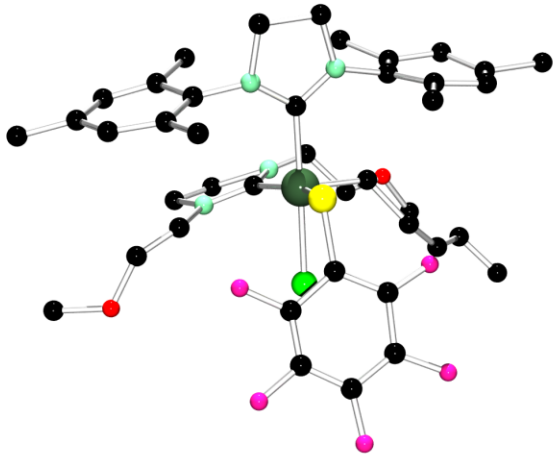


Figure S1. POV-ray depiction of the preliminary molecular structure of **9** Ru: dark green, S: yellow, O: red; Cl: green; N: aquamarine, F: deep pink, C: black. H-atoms omitted for clarity.

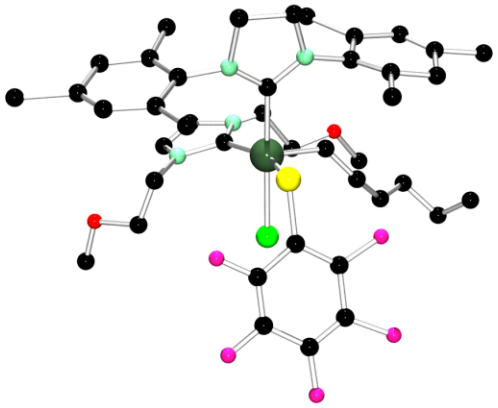


Figure S2. POV-ray depiction of the preliminary molecular structure of **10** Ru: dark green, S: yellow, O: red; Cl: green; N: aquamarine, F: deep pink, C: black. H-atoms omitted for clarity.

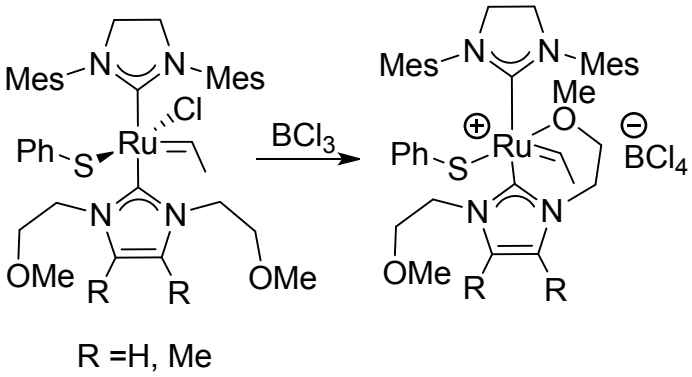


Figure S3. Proposed structure of active catalyst upon activation with BCl_3.

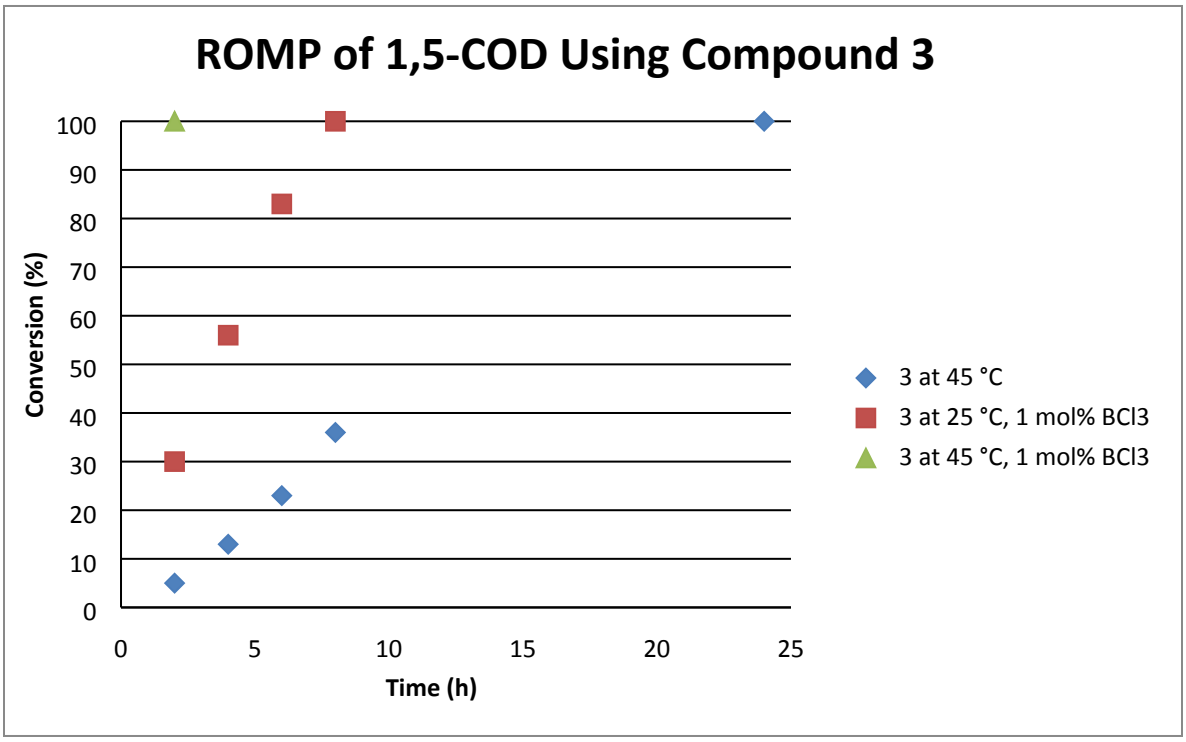


Figure S4. Plot of Catalysis for ROMP of 1,5-COD with **3**.

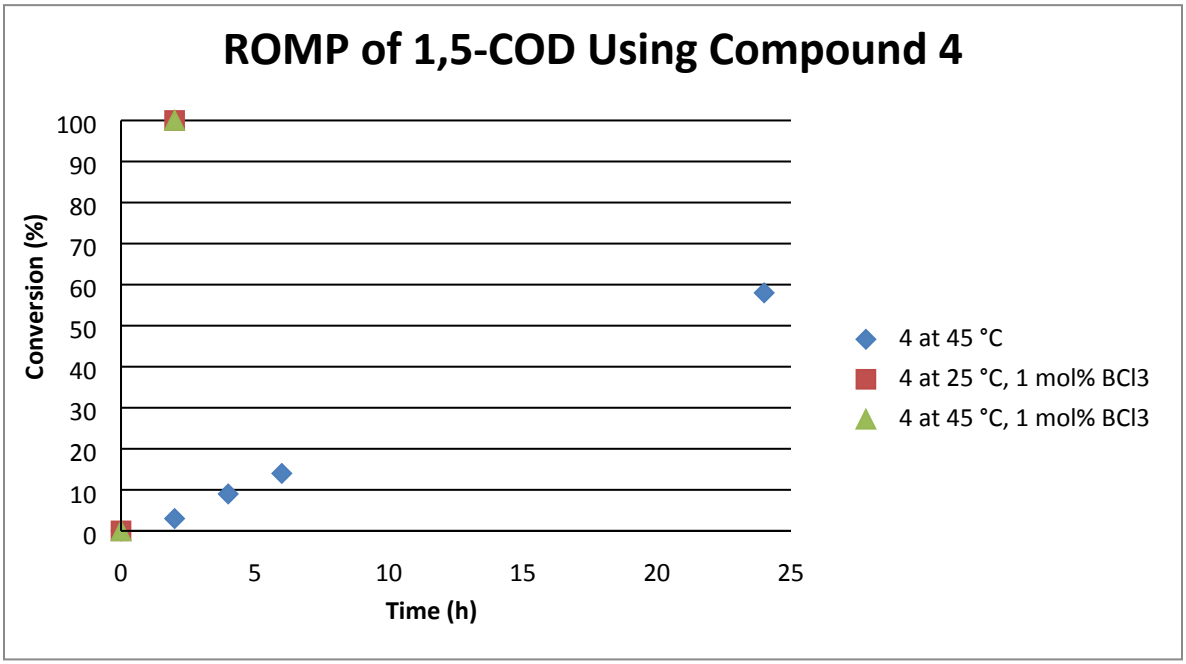


Figure S5. Plot of Catalysis for ROMP of 1,5-COD with **4**.

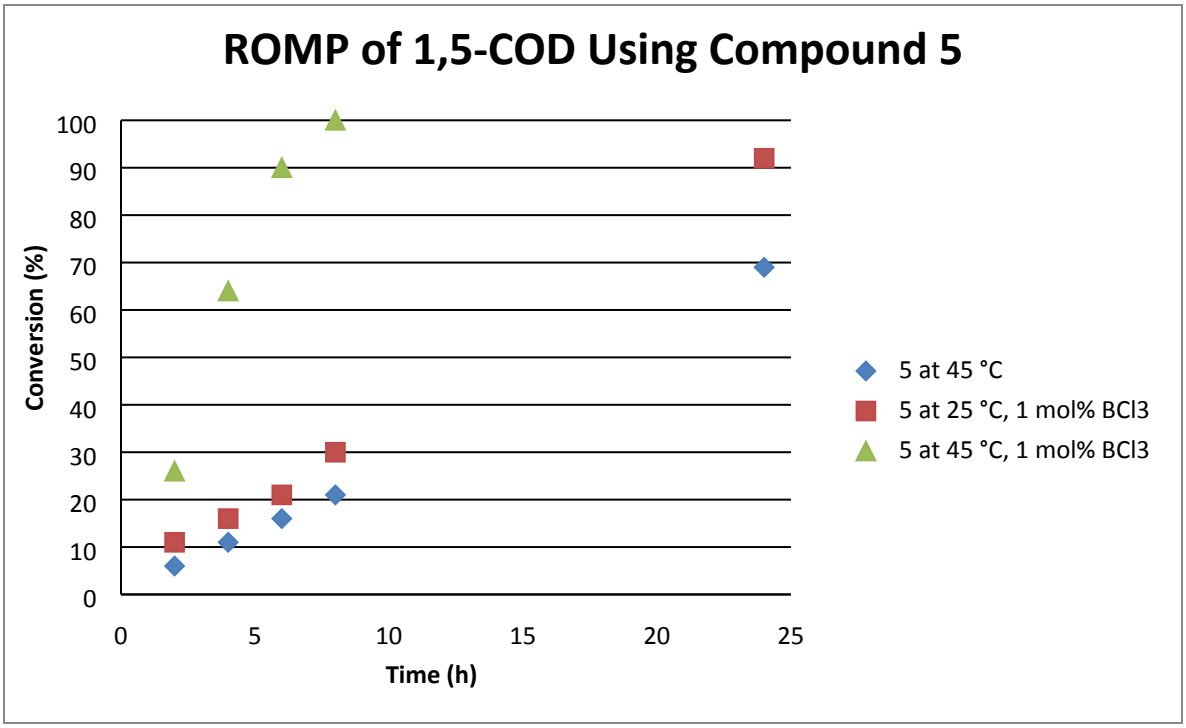


Figure S6. Plot of Catalysis for ROMP of 1,5-COD with **5**.

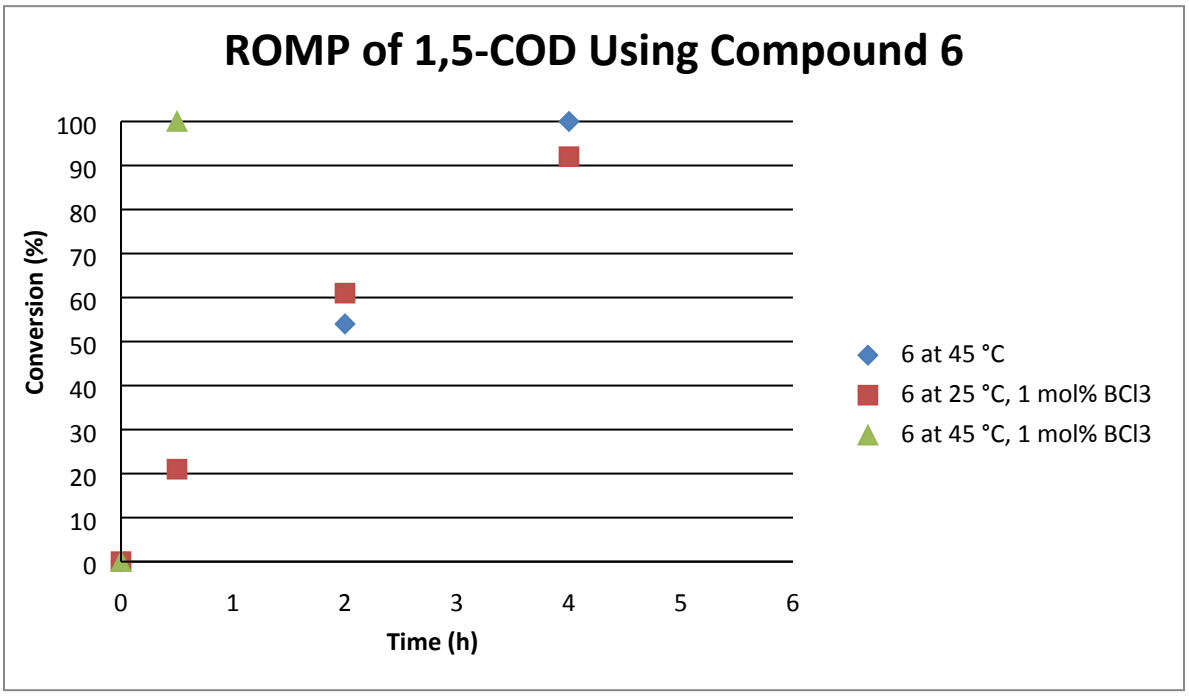


Figure S7. Plot of Catalysis for ROMP of 1,5-COD with **6**.

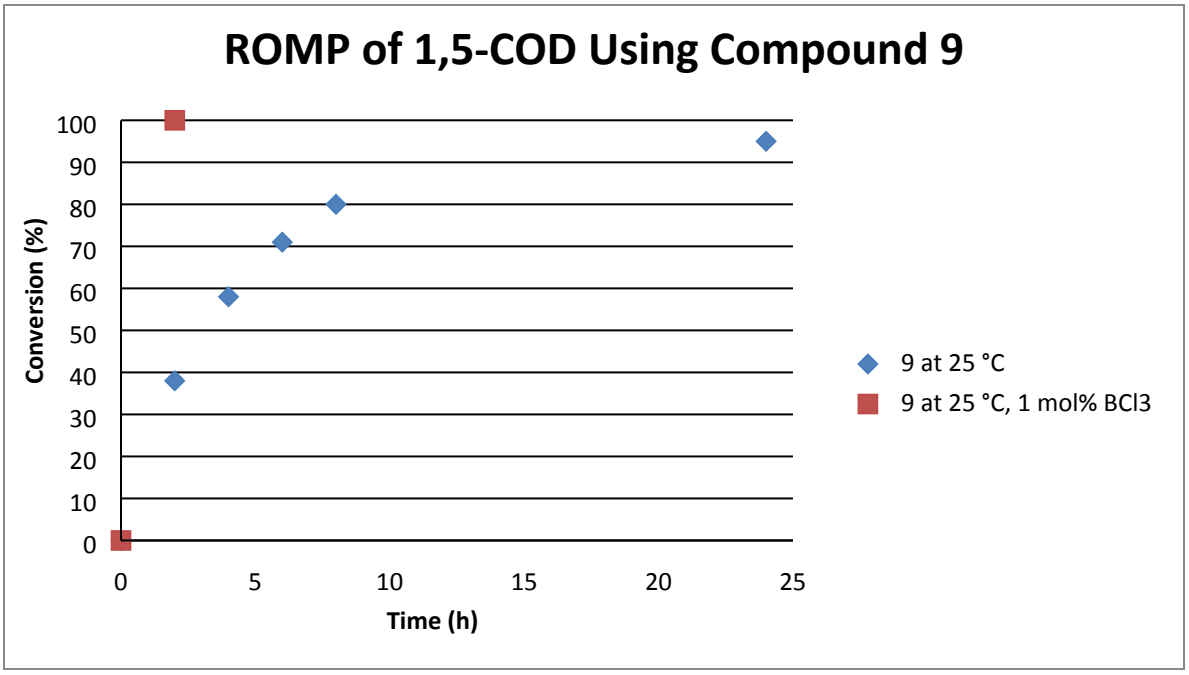


Figure S8. Plot of Catalysis for ROMP of 1,5-COD with **9**.

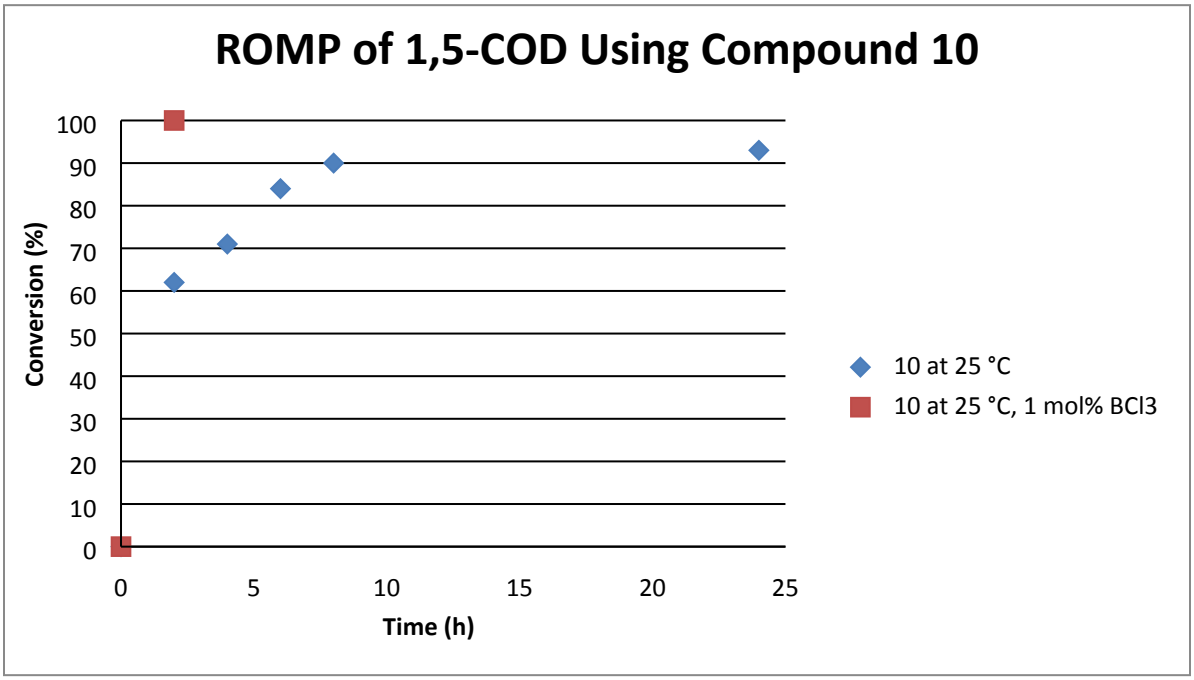


Figure S9. Plot of Catalysis for ROMP of 1,5-COD with **10**.

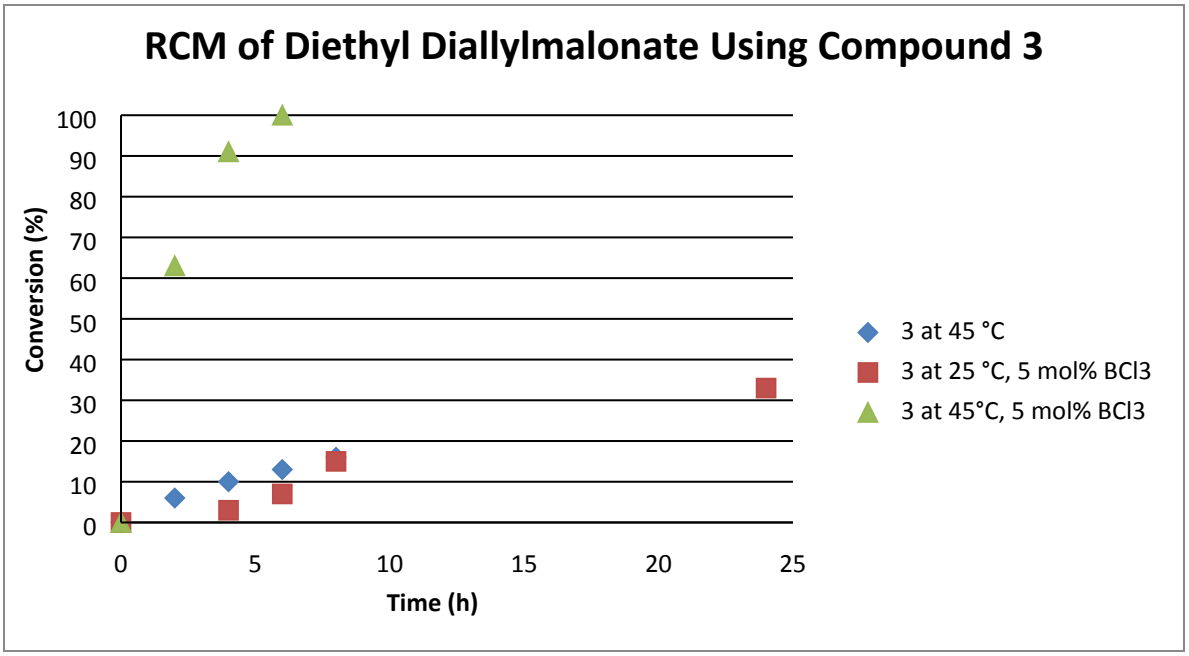


Figure S10. Plot of Catalysis for RCM of Diethyl Diallylmalonate with **3**.

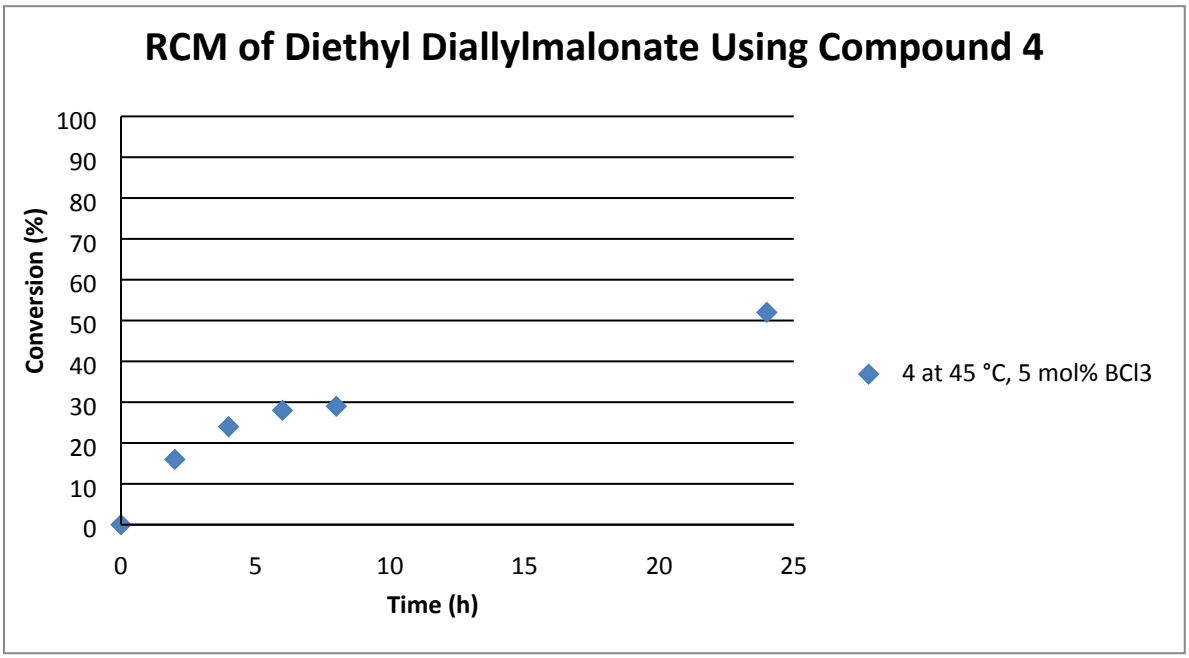


Figure S11. Plot of Catalysis for RCM of Diethyl Diallylmalonate with **4**.

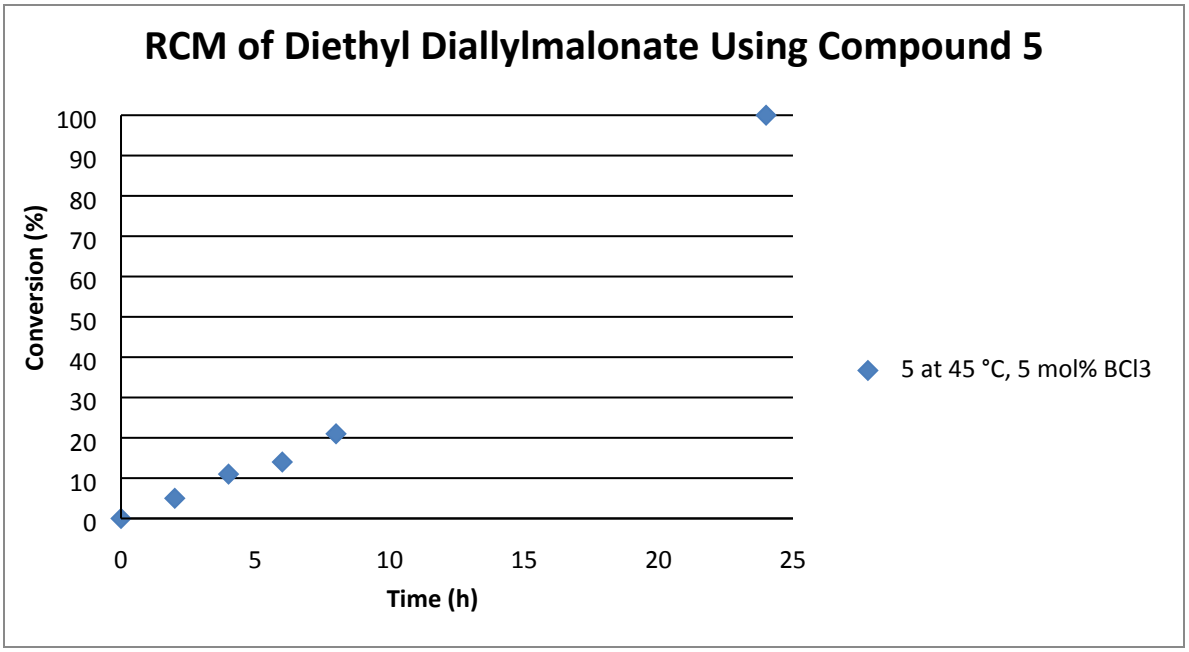


Figure S12. Plot of Catalysis for RCM of Diethyl Diallylmalonate with **5**.

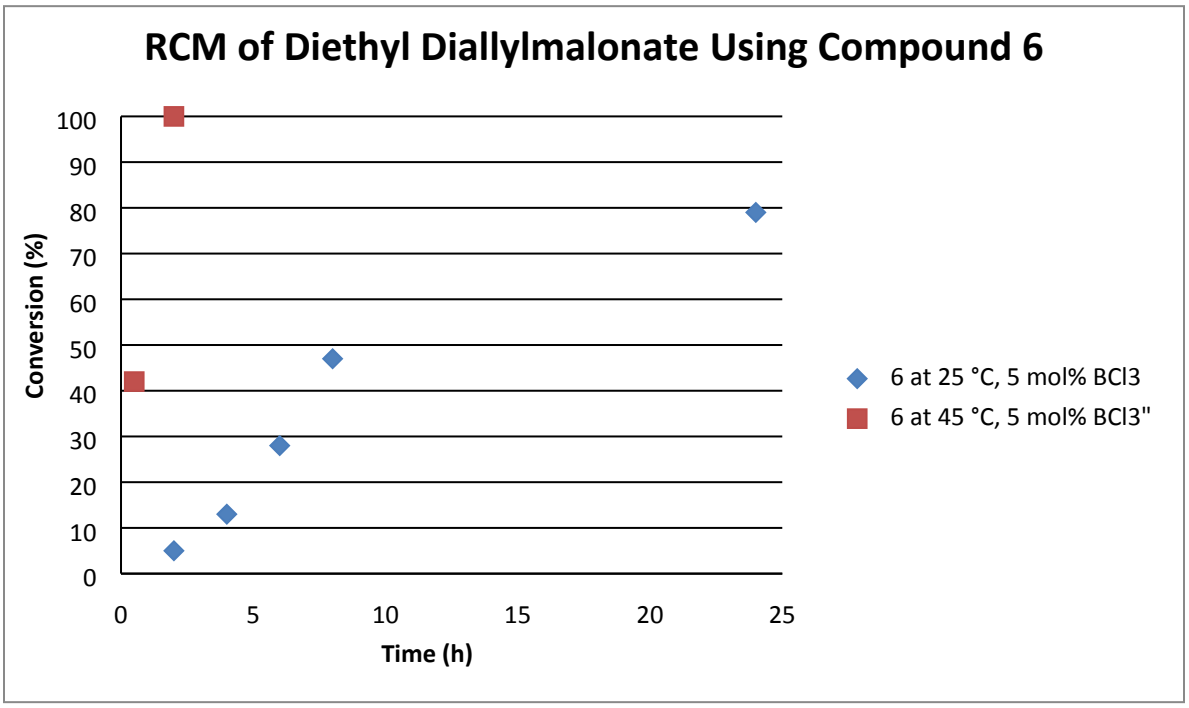


Figure S13. Plot of Catalysis for RCM of Diethyl Diallylmalonate with **6**.

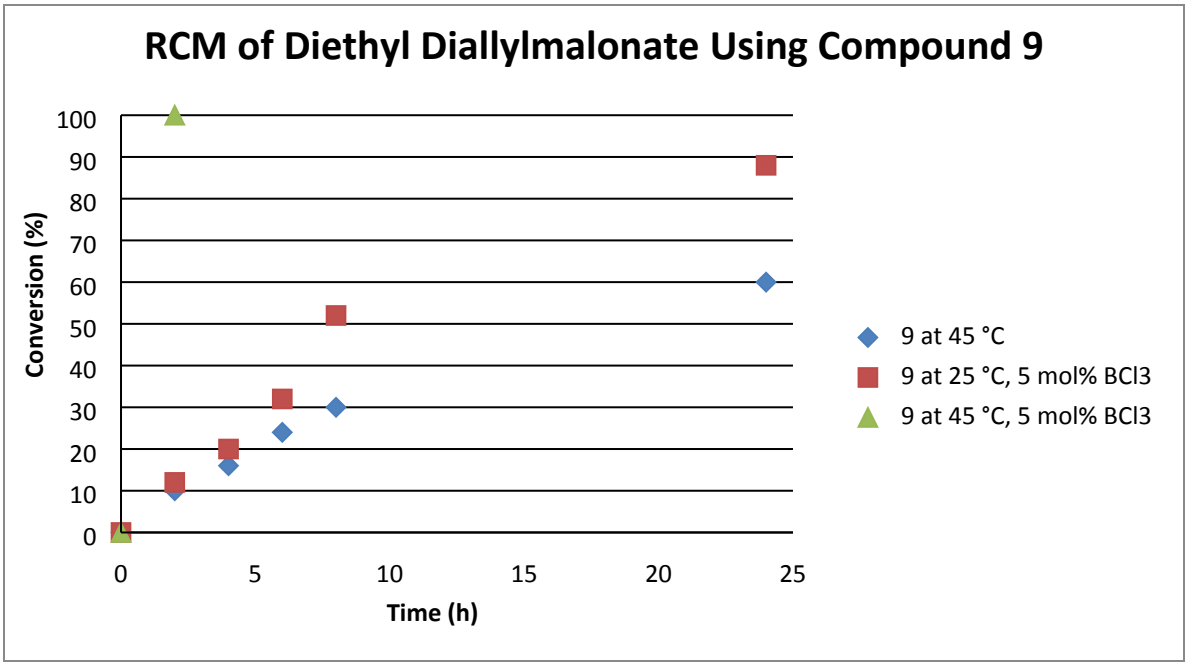


Figure S14. Plot of Catalysis for RCM of Diethyl Diallylmalonate with **9**.

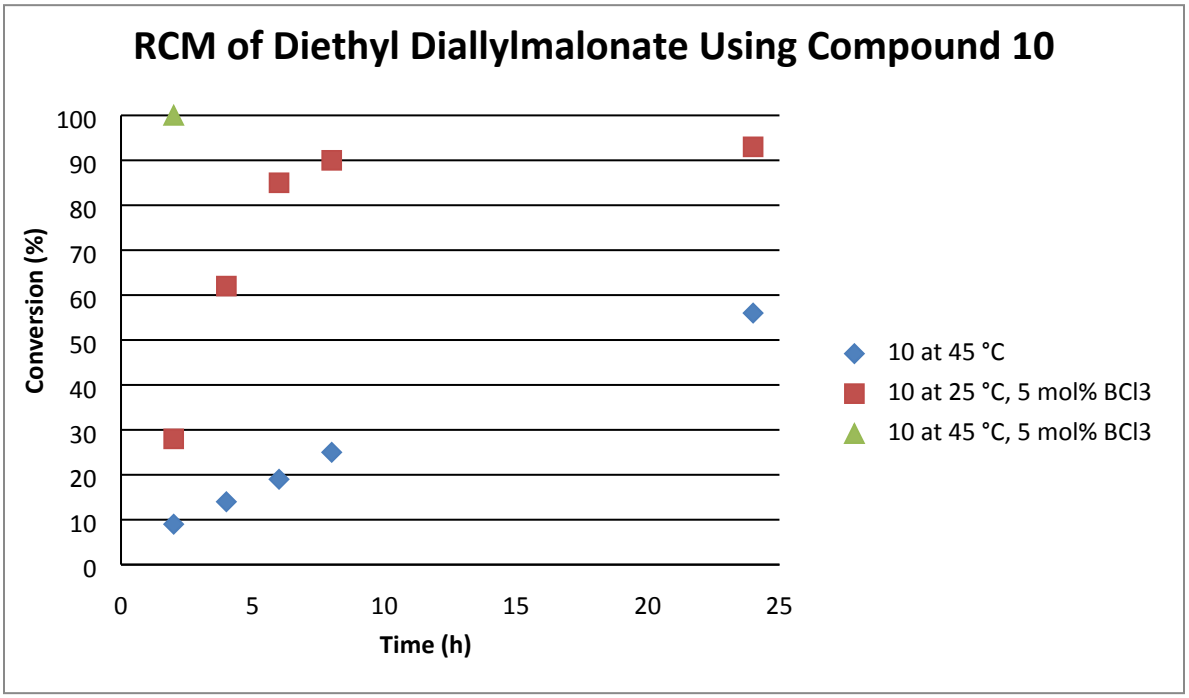


Figure S15. Plot of Catalysis for RCM of Diethyl Diallylmalonate with **10**.

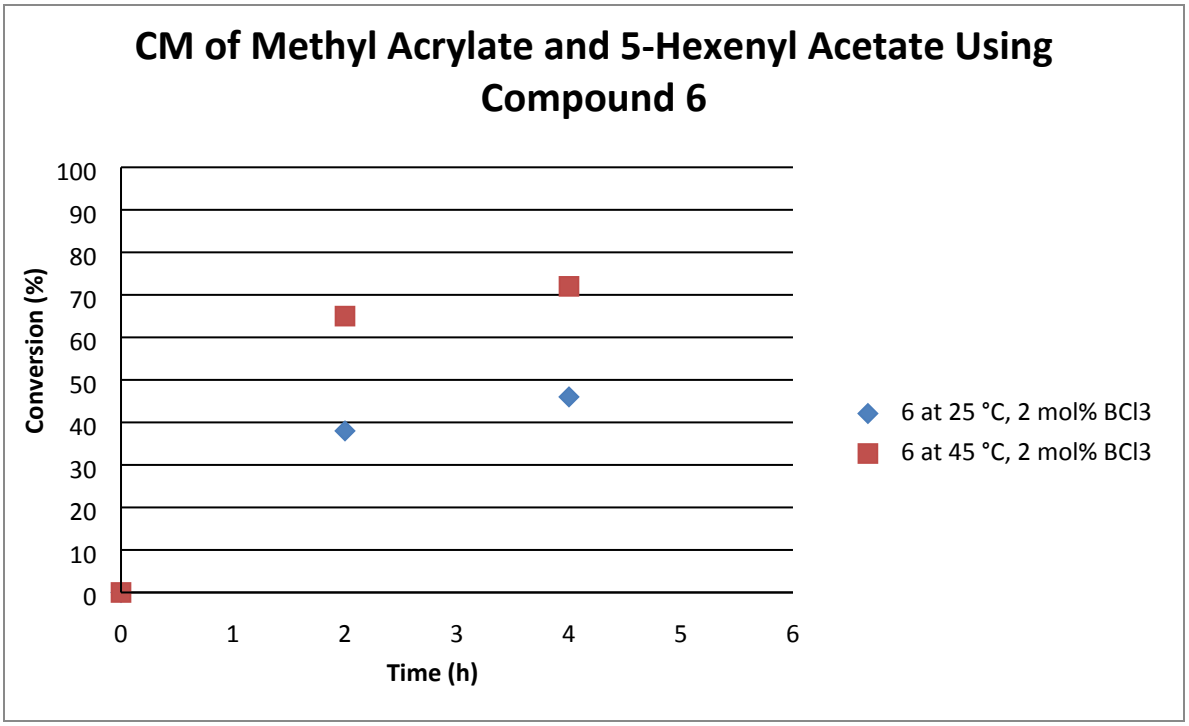


Figure S16. Plot of Catalysis for CM of 5-Hexenyl Acetate and Methyl Acrylate with **6**.

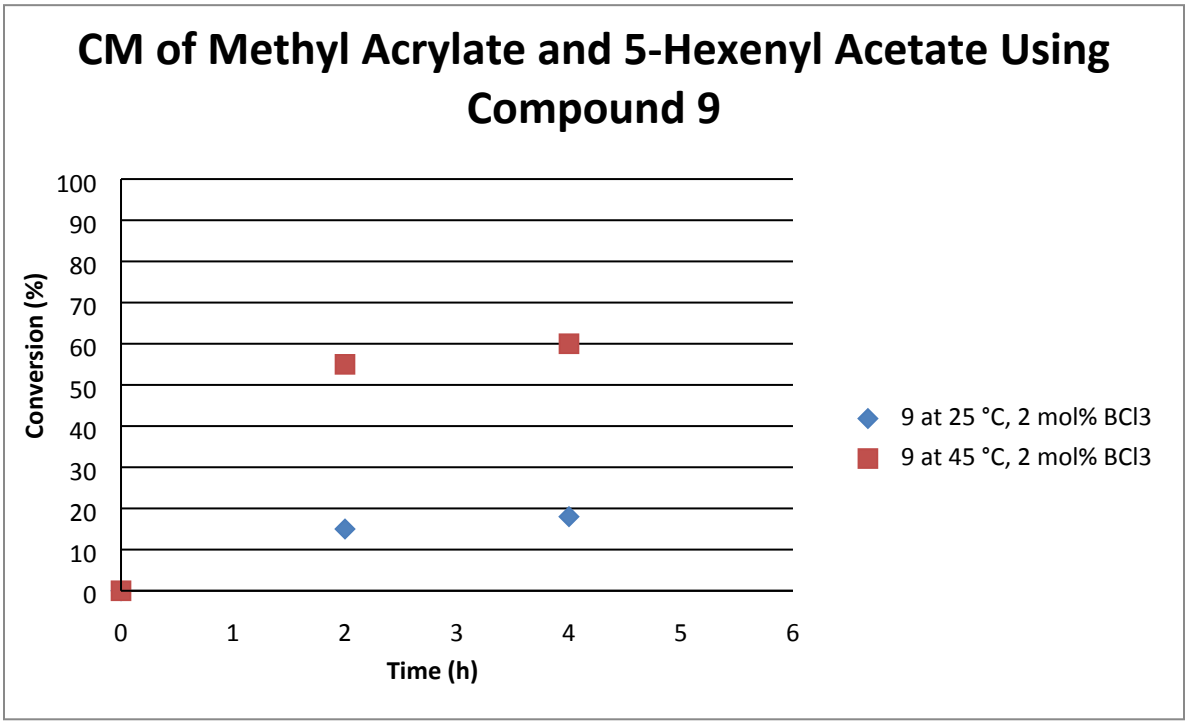


Figure S17. Plot of Catalysis for CM of 5-Hexenyl Acetate and Methyl Acrylate with **9**.

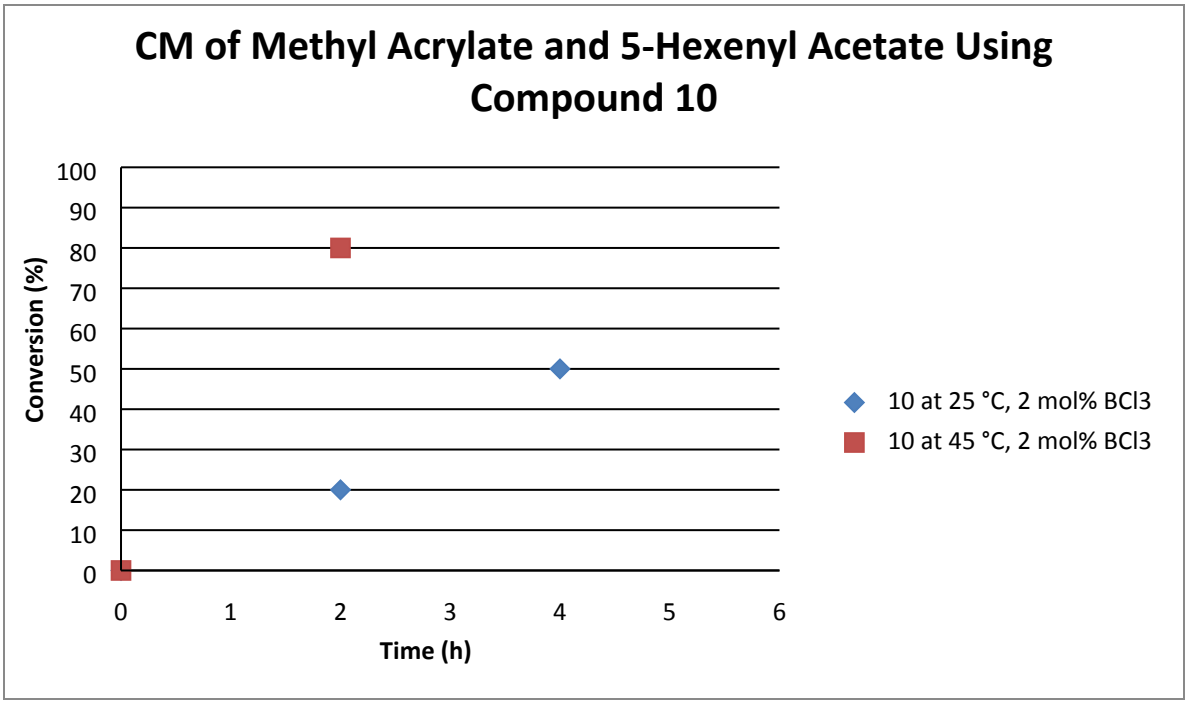


Figure S18. Plot of Catalysis for CM of 5-Hexenyl Acetate and Methyl Acrylate with **10**.

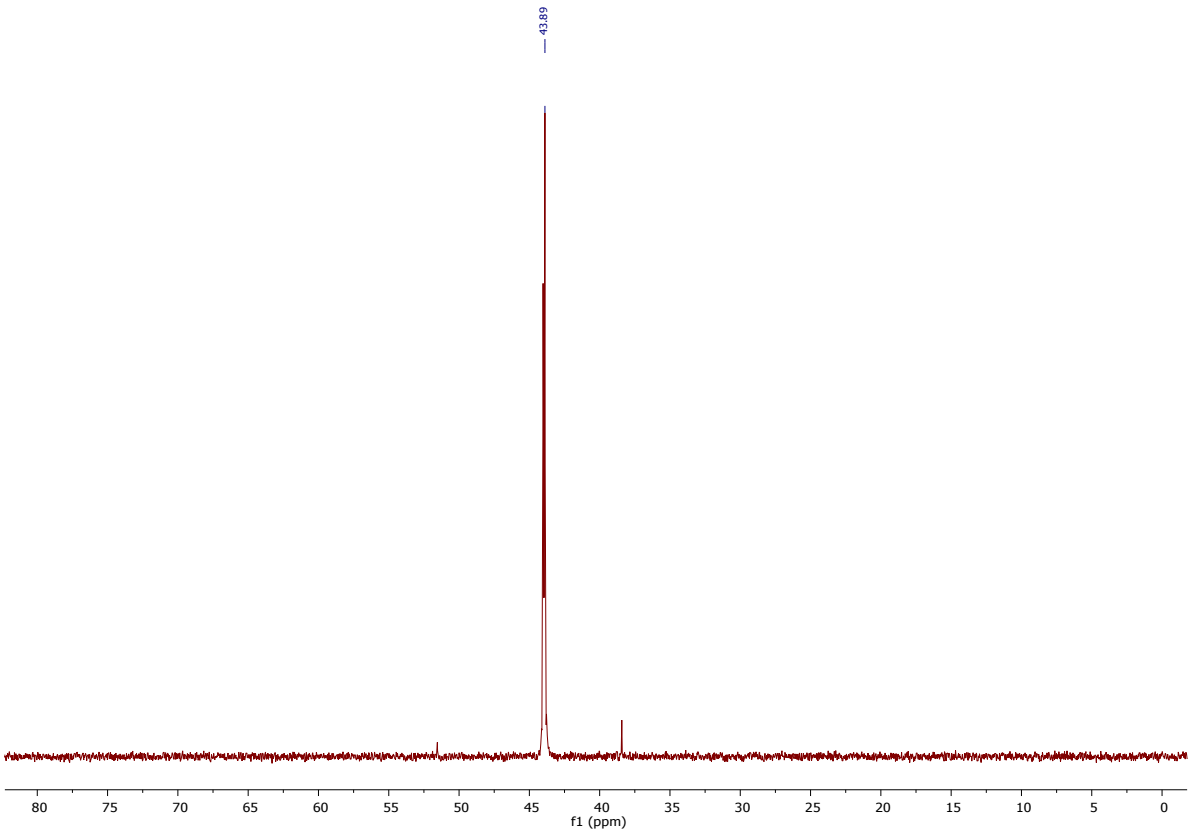


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **1**.

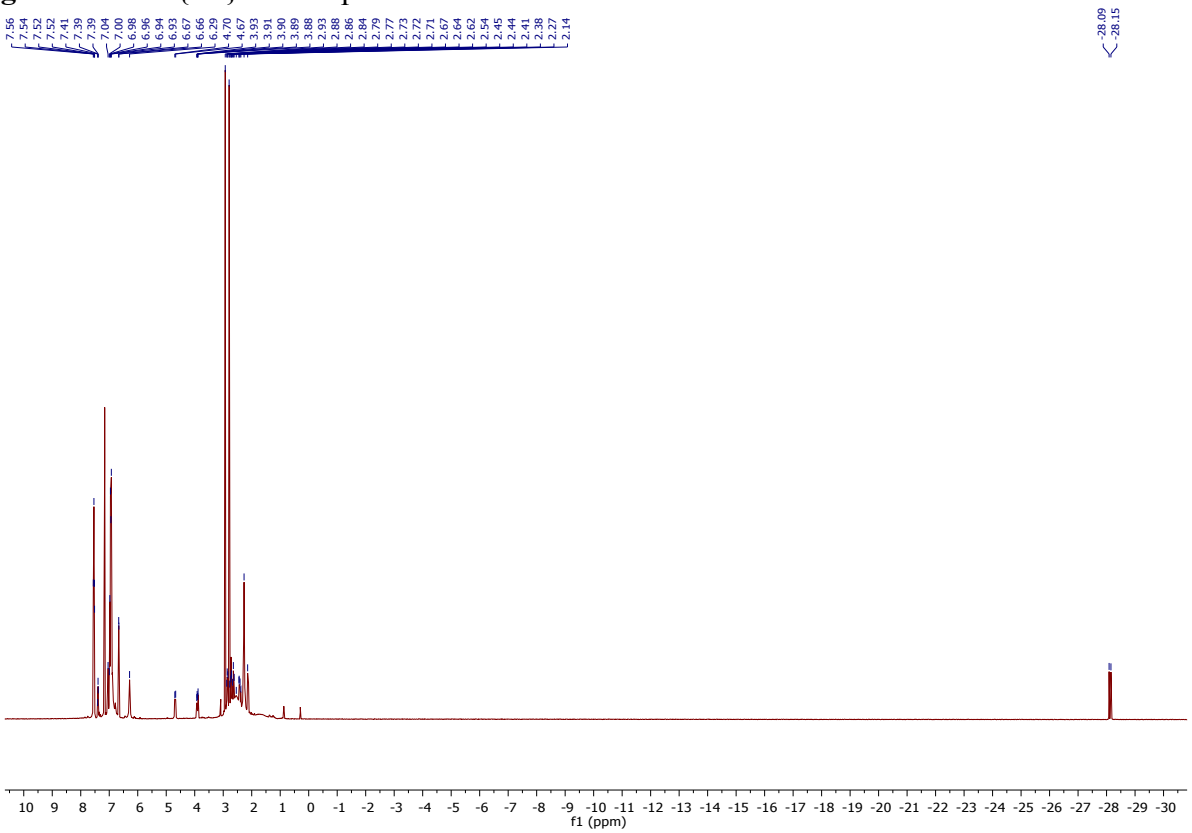


Figure S20. ^{1}H NMR spectrum of **1**.

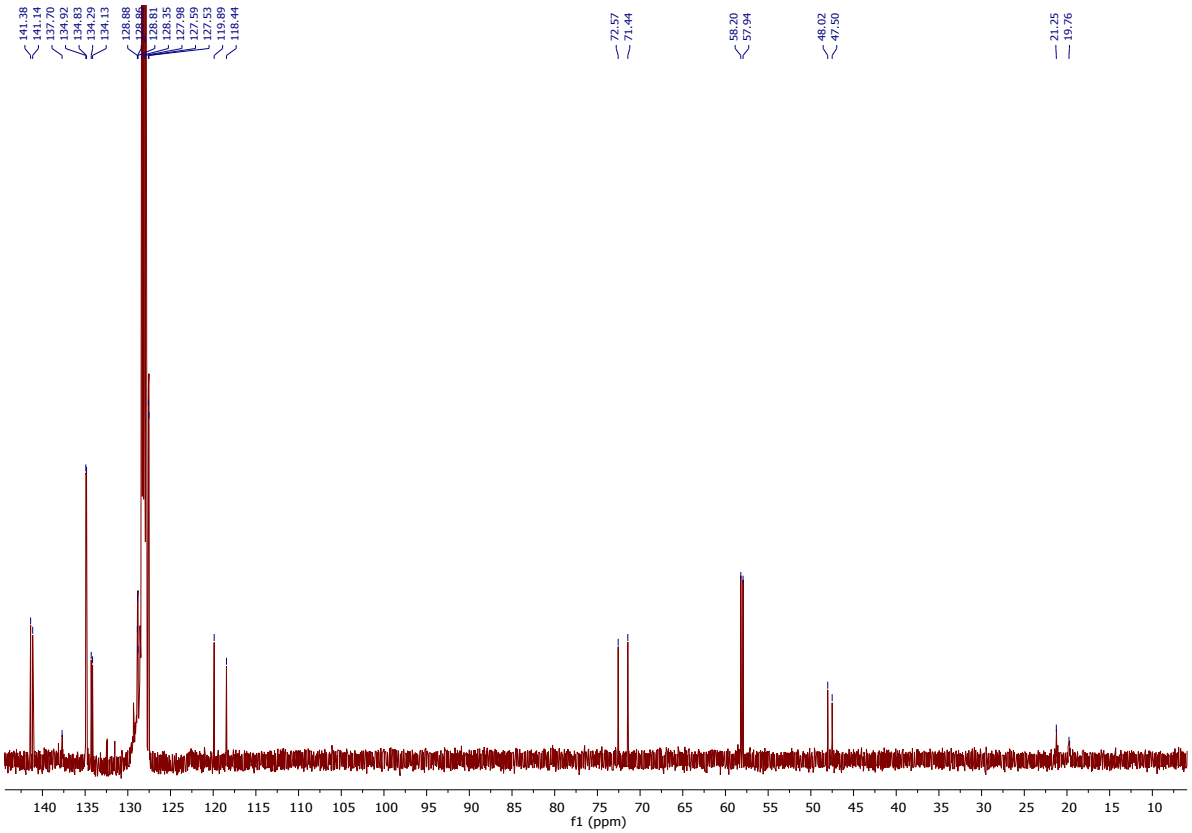


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **1**.

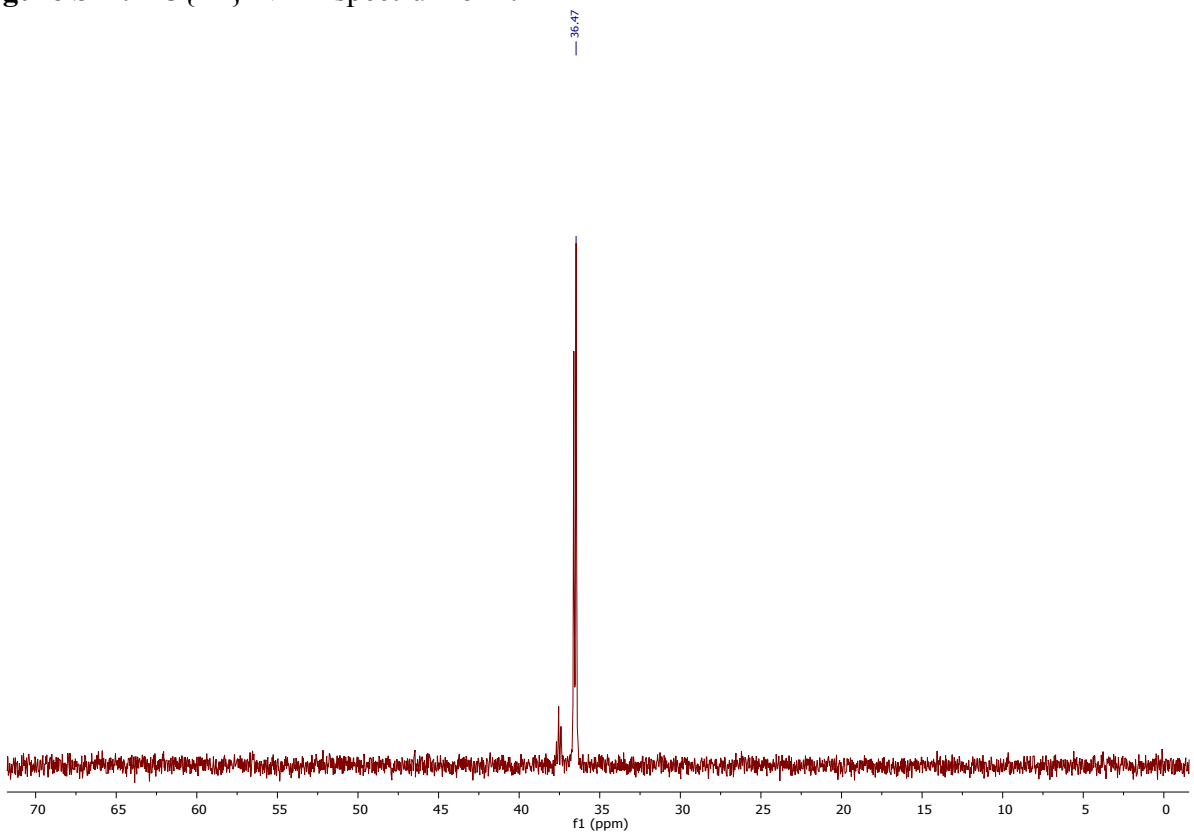


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **2**.

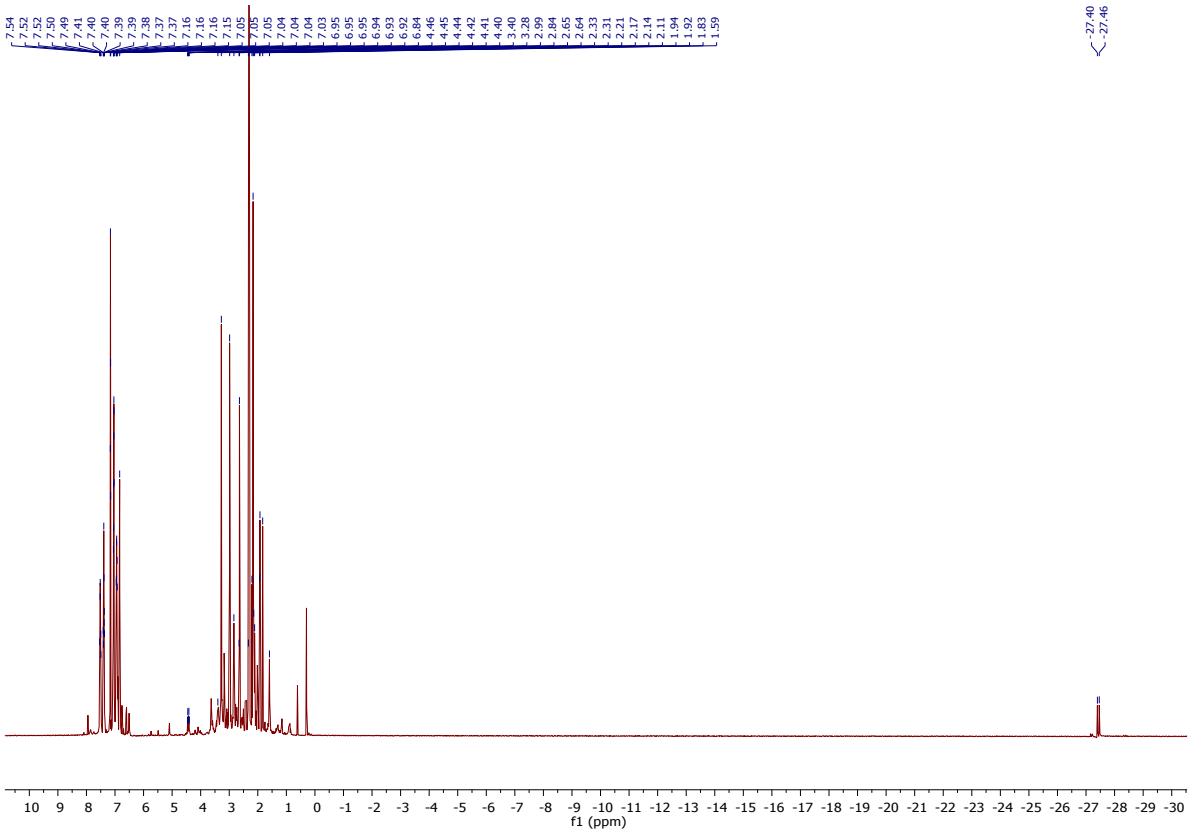


Figure S23. ^{1}H NMR spectrum of **2**.

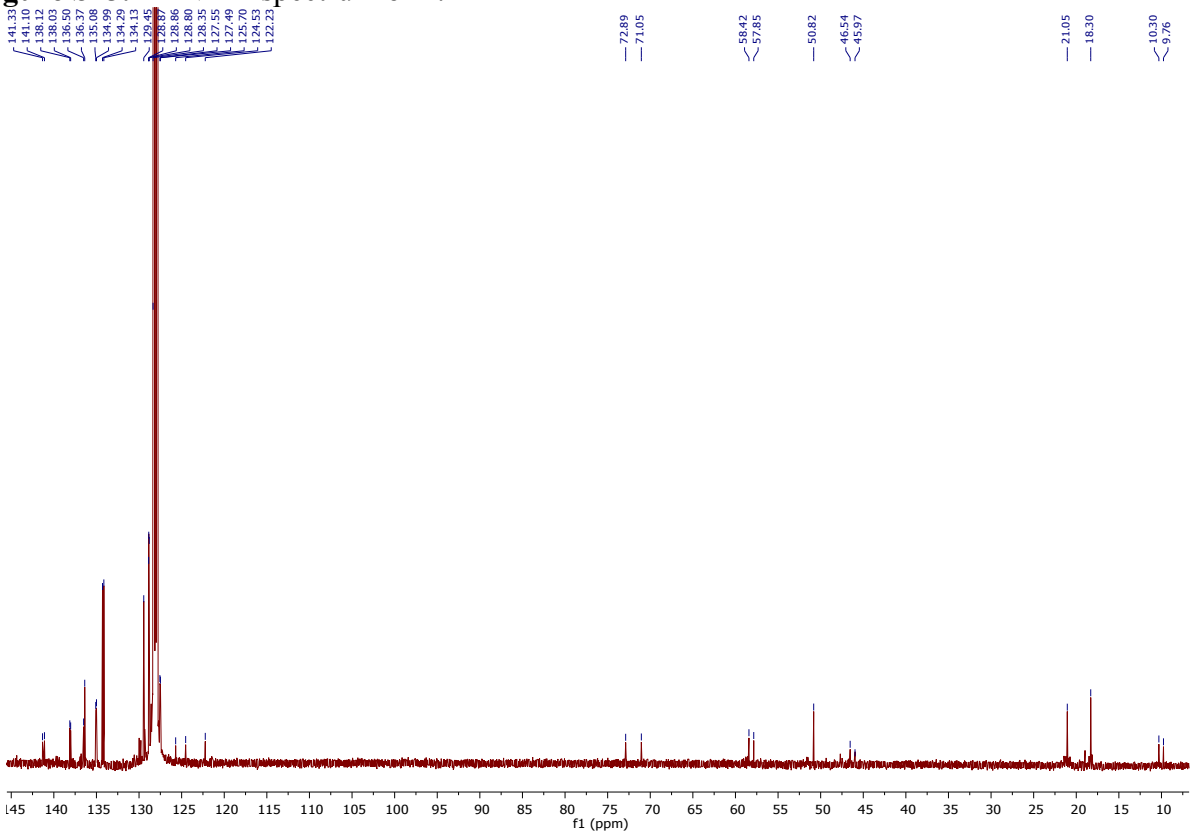


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

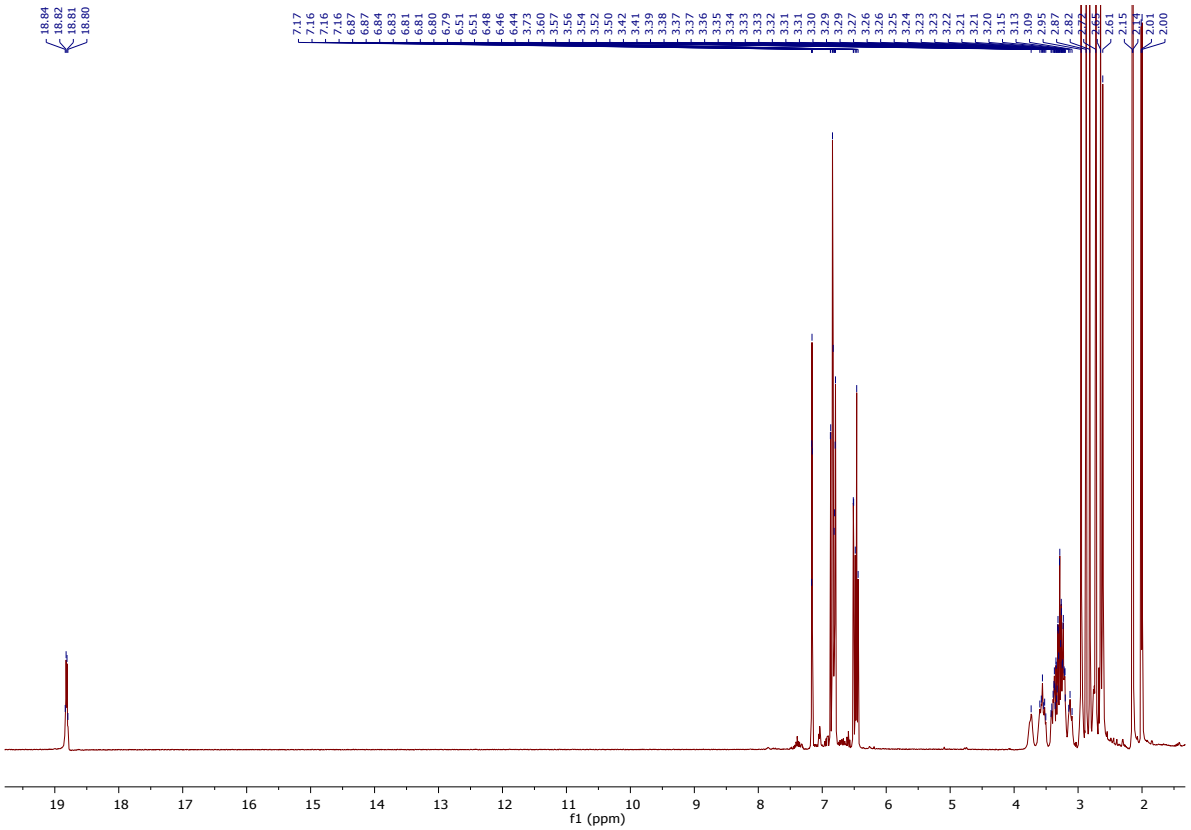


Figure S25. ^{1}H NMR spectrum of **3**.

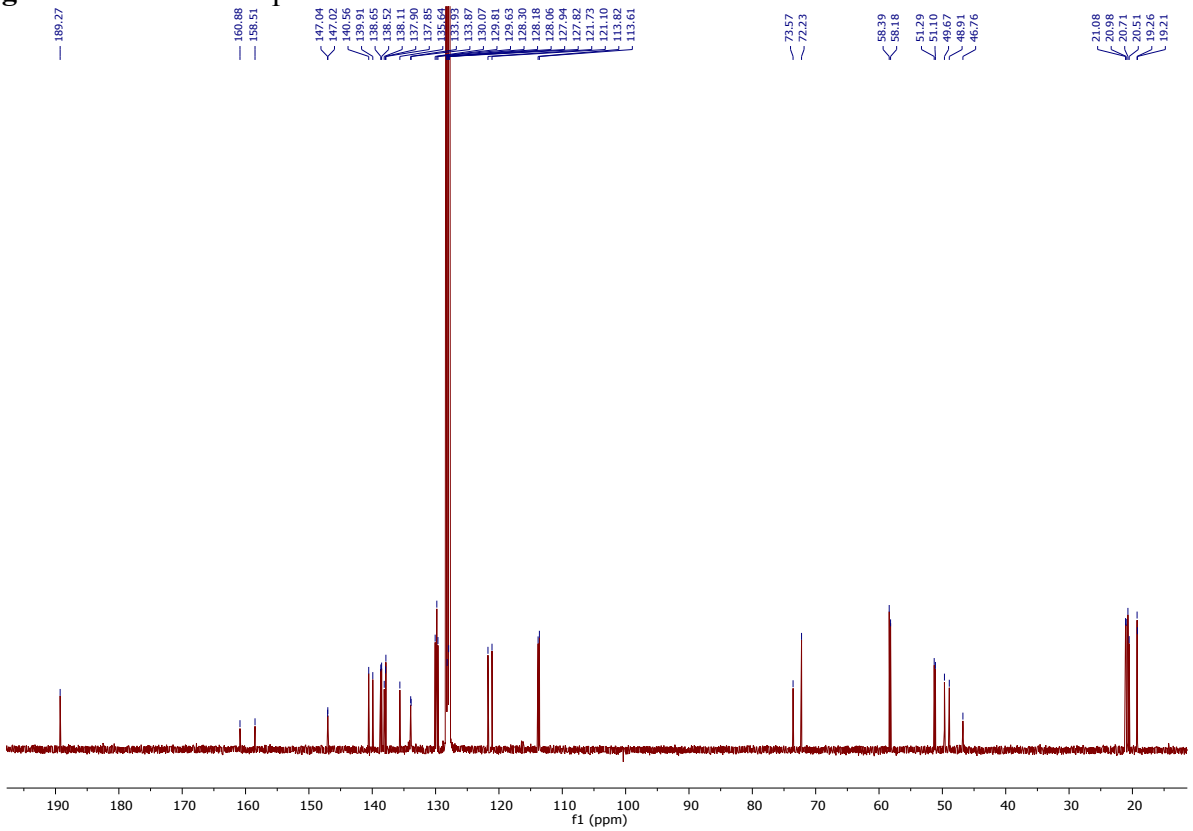


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

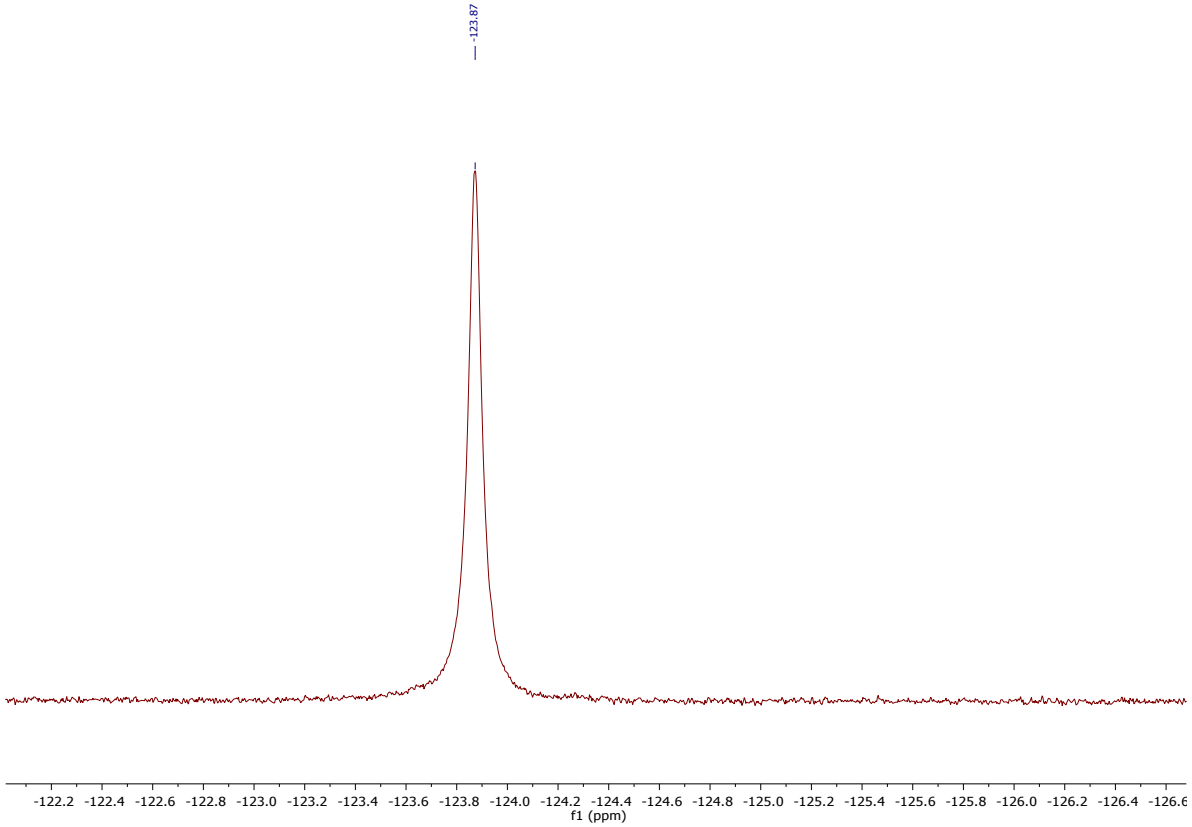


Figure S27. $^{19}F\{^{1}H\}$ NMR spectrum of **3**.

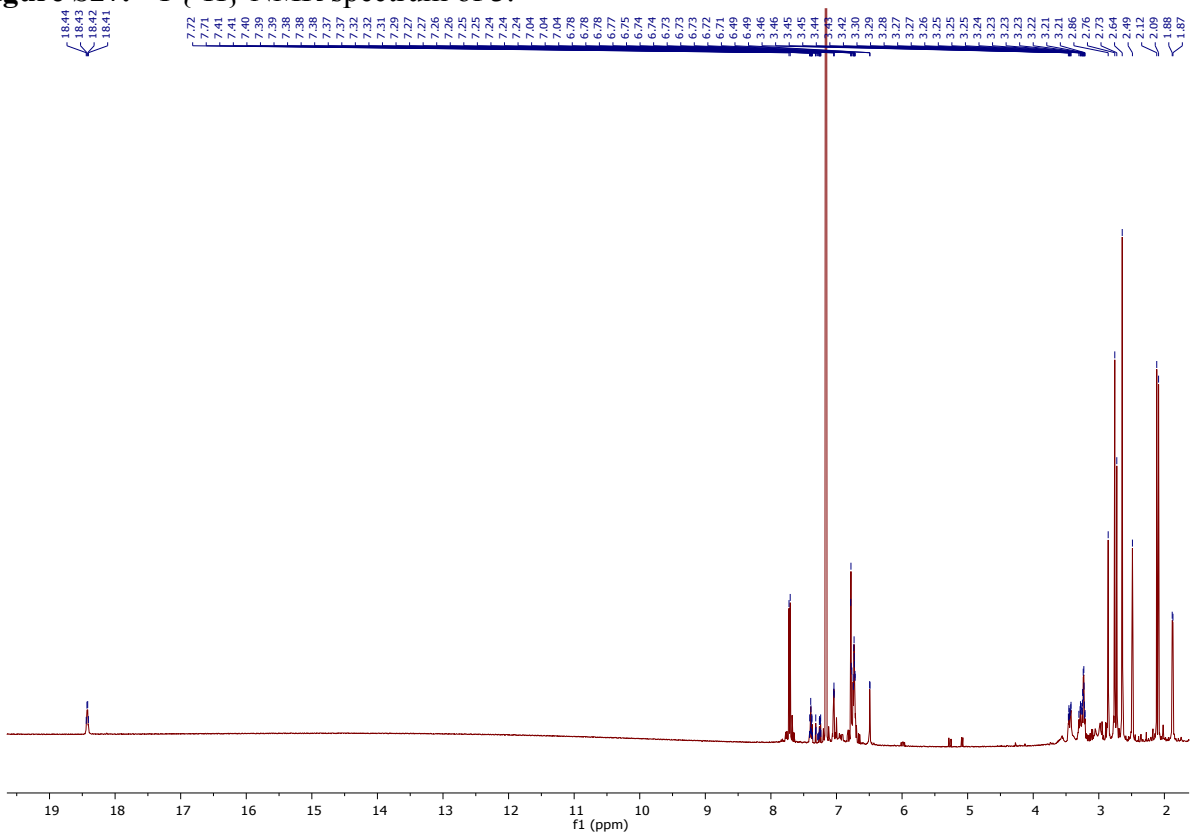


Figure S28. ^{1}H NMR spectrum of **4**.

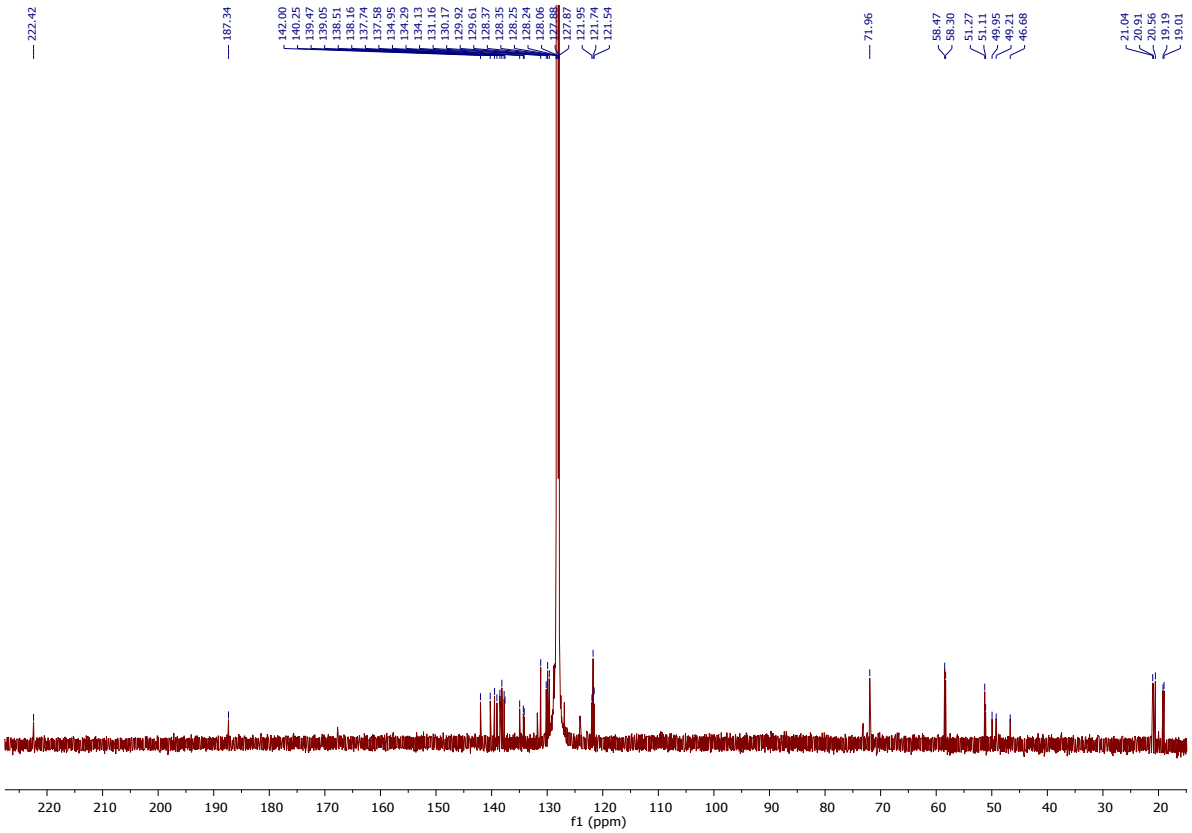


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

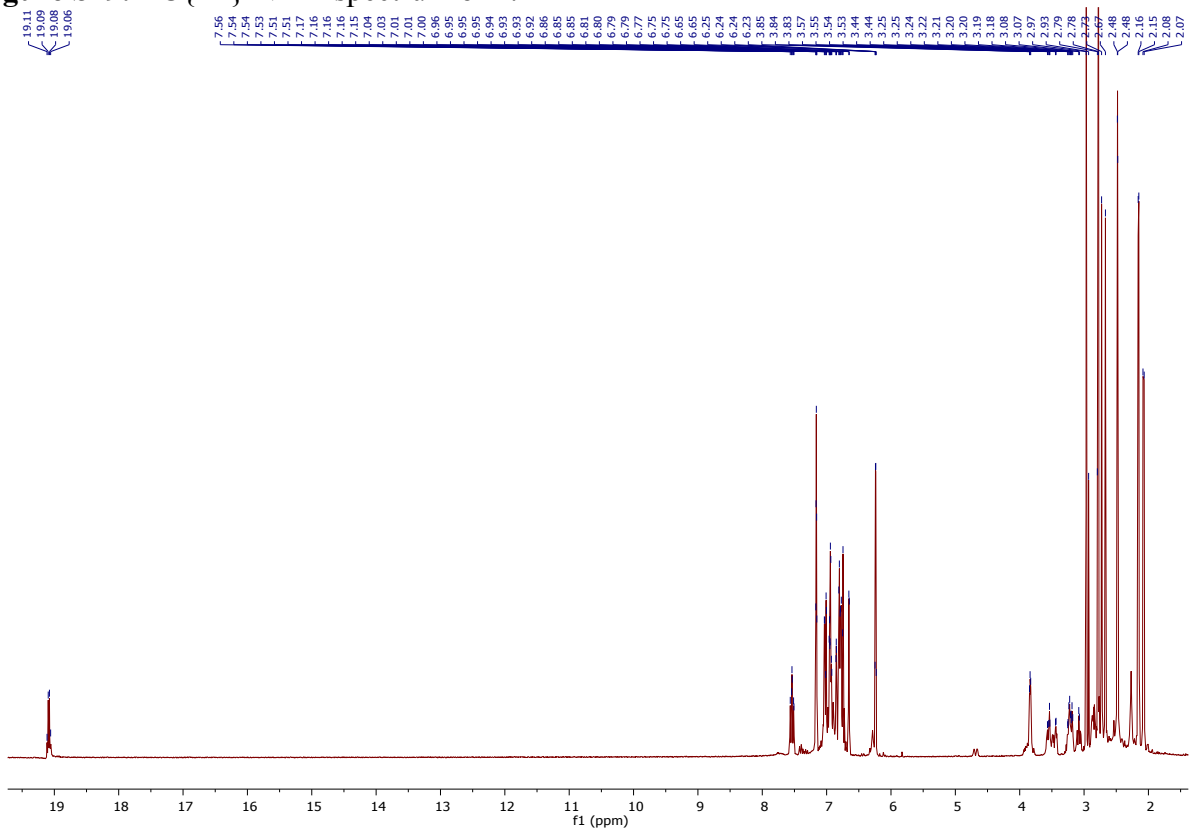


Figure S30. ^{1}H NMR spectrum of **5**.

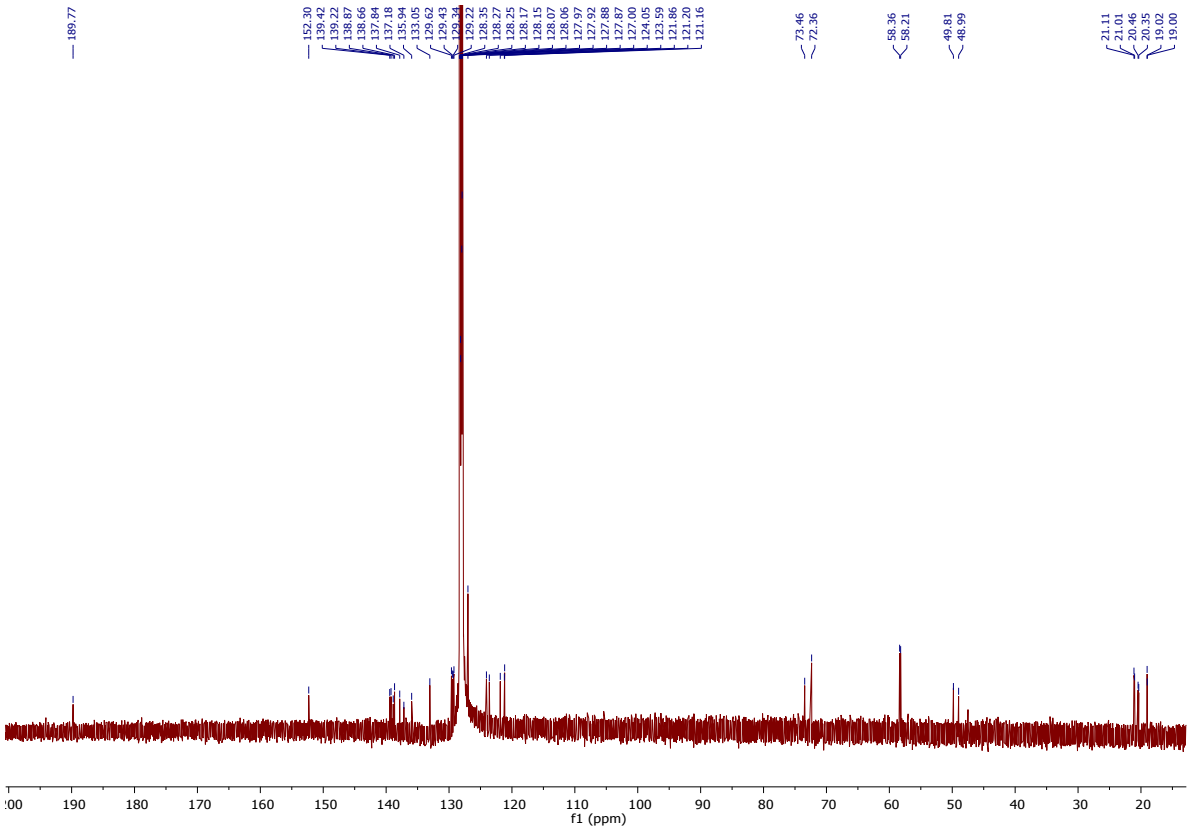


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

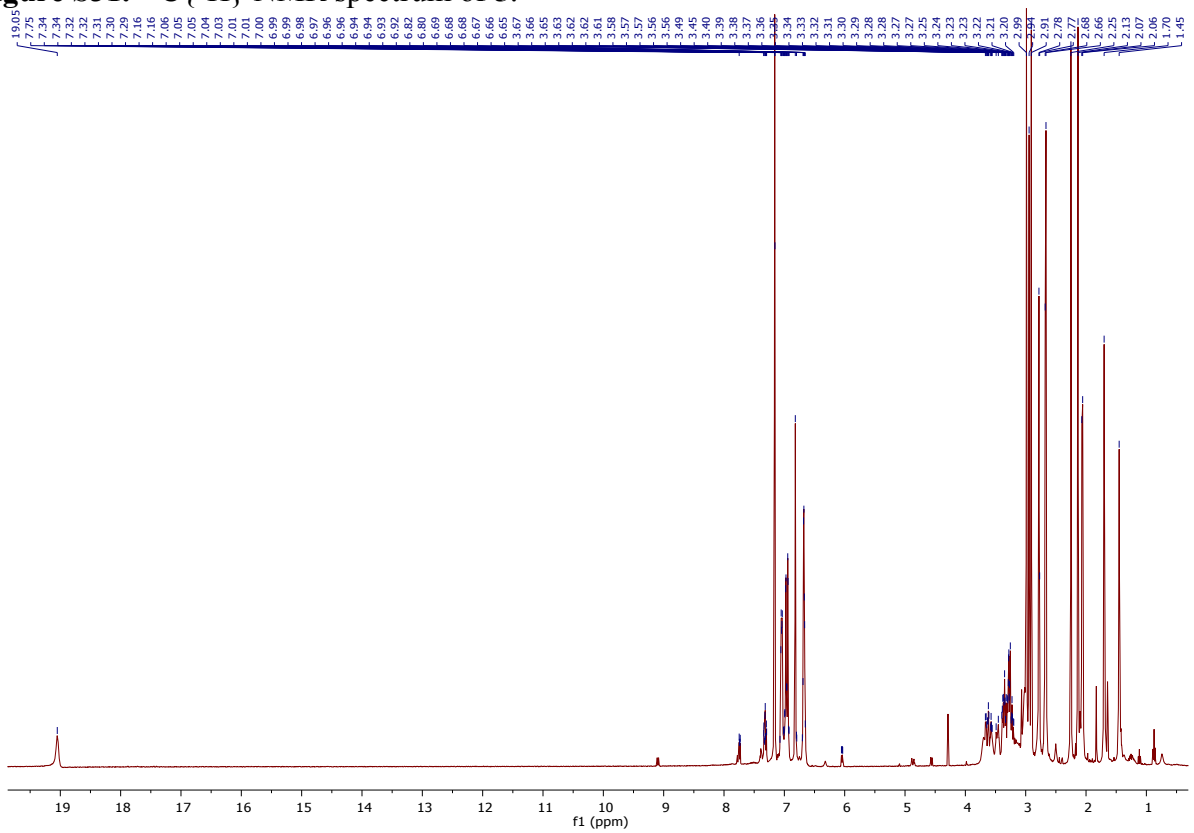


Figure S32. ^{1}H NMR spectrum of **6**.

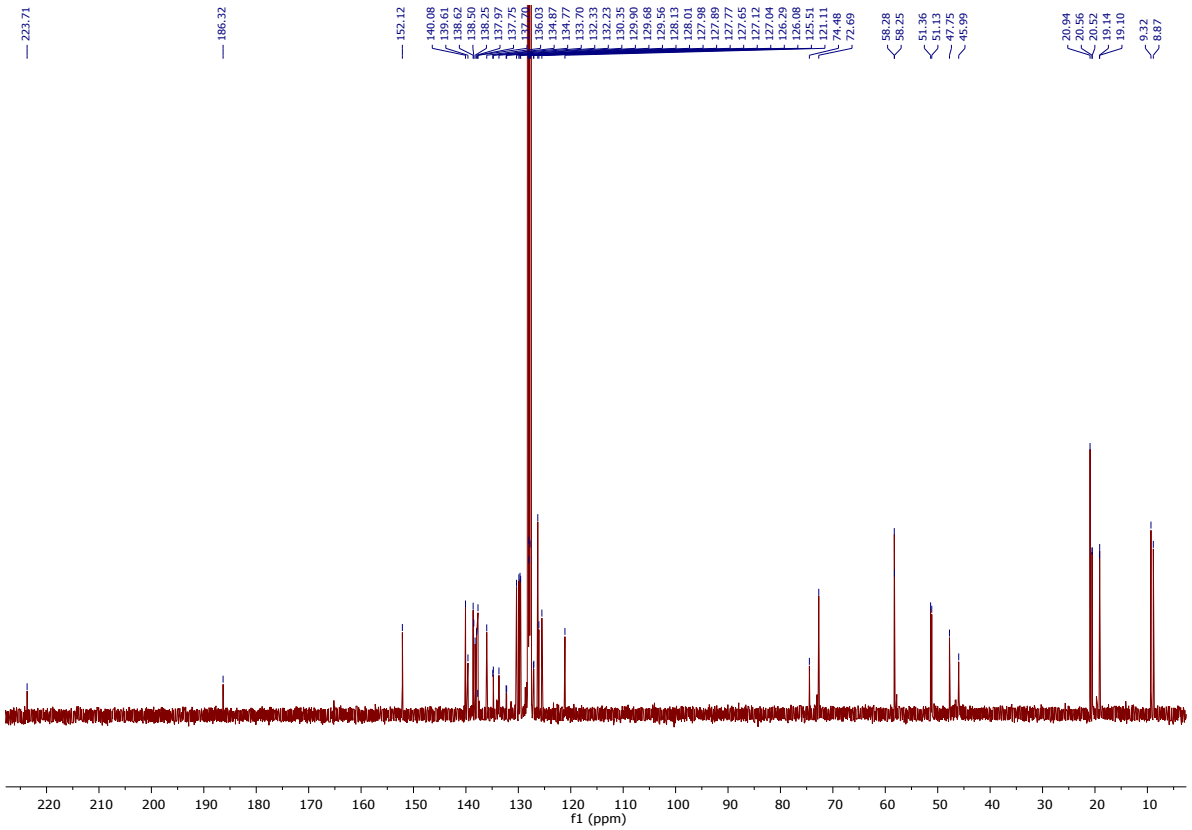


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

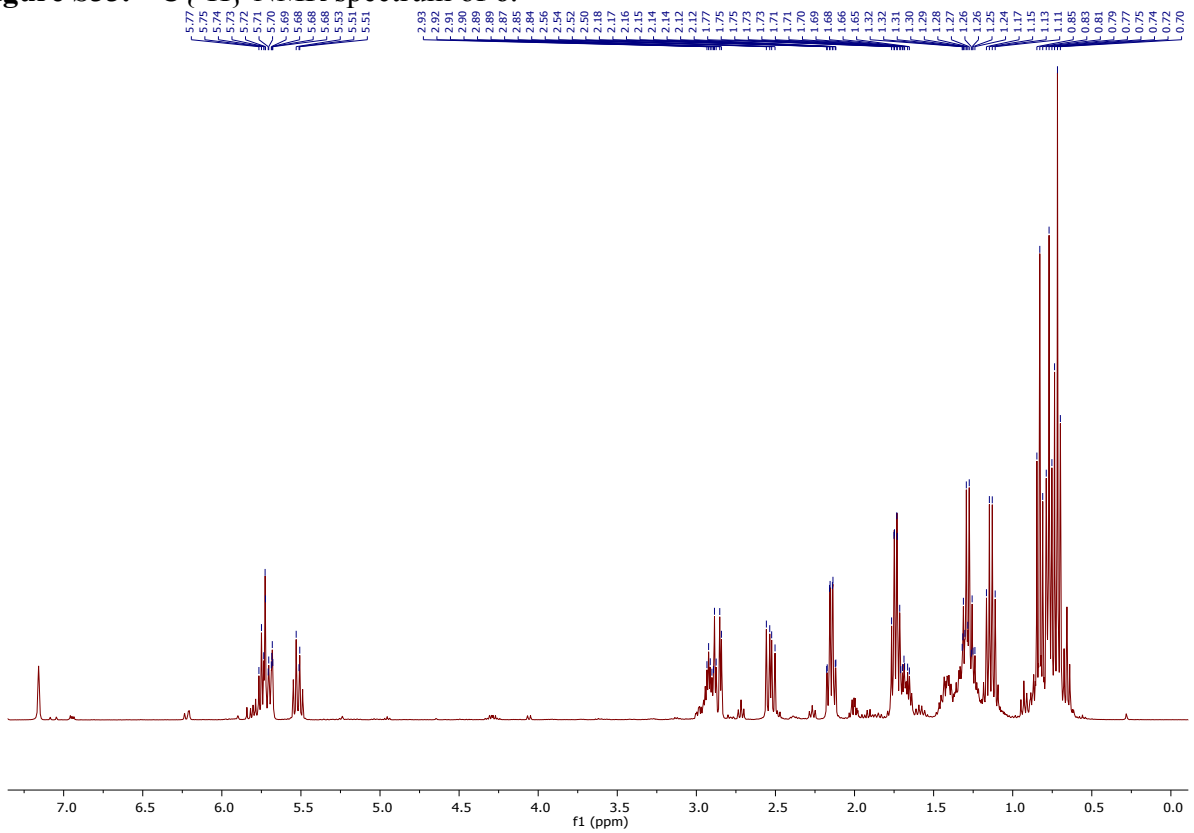


Figure S34. ^{1}H NMR spectrum of **7**.

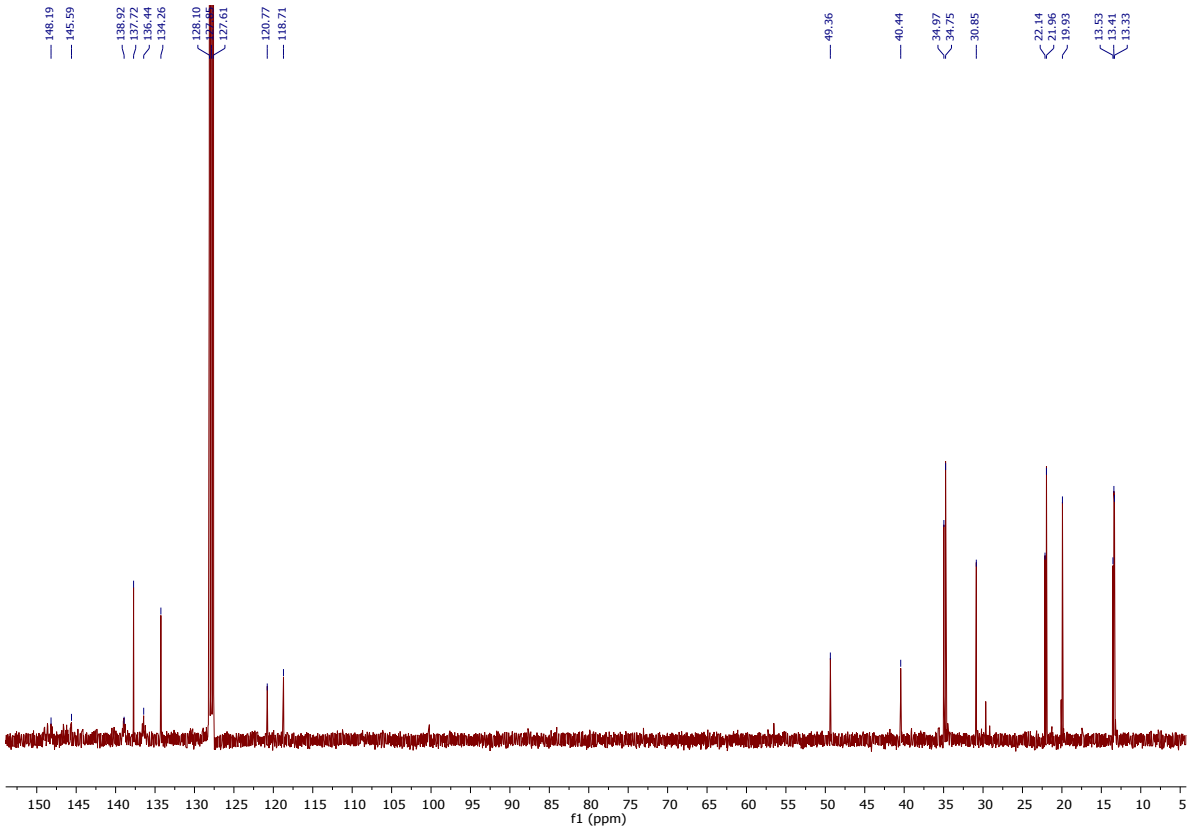


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **7**.

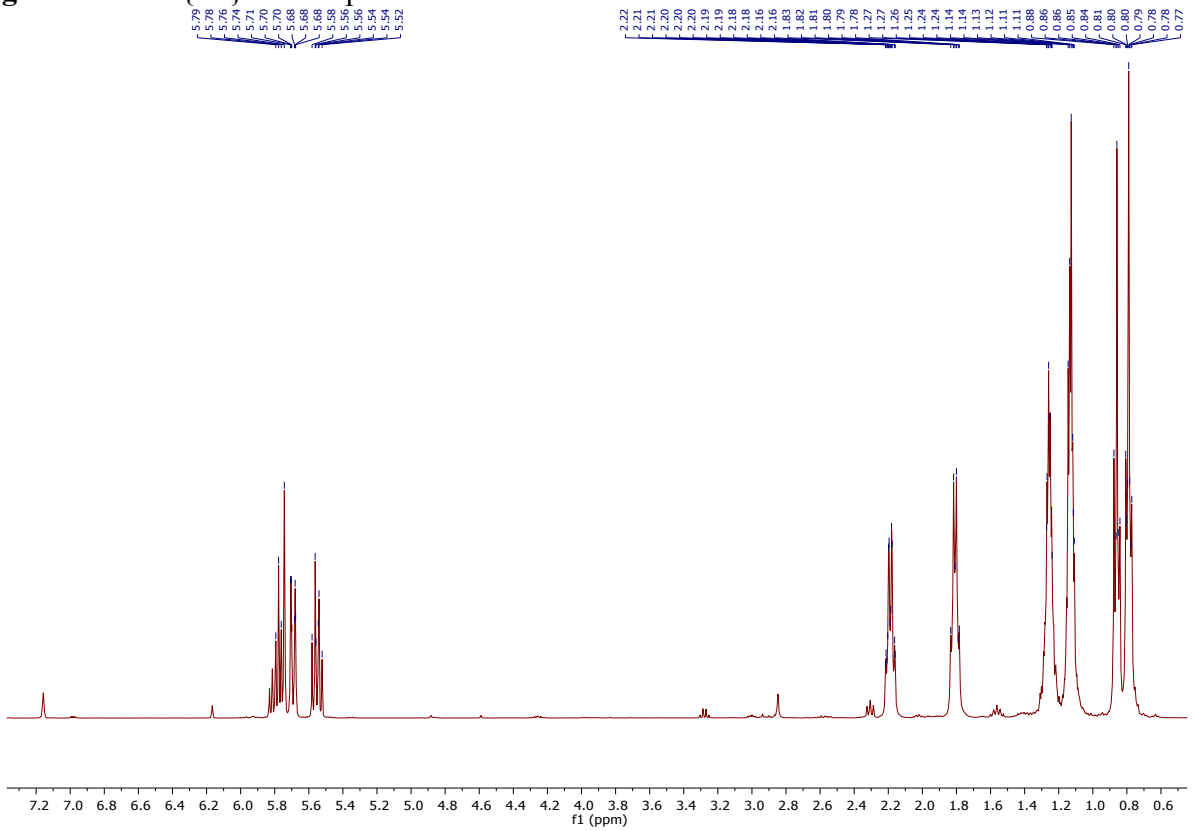


Figure S36. ^{1}H NMR spectrum of **8**.

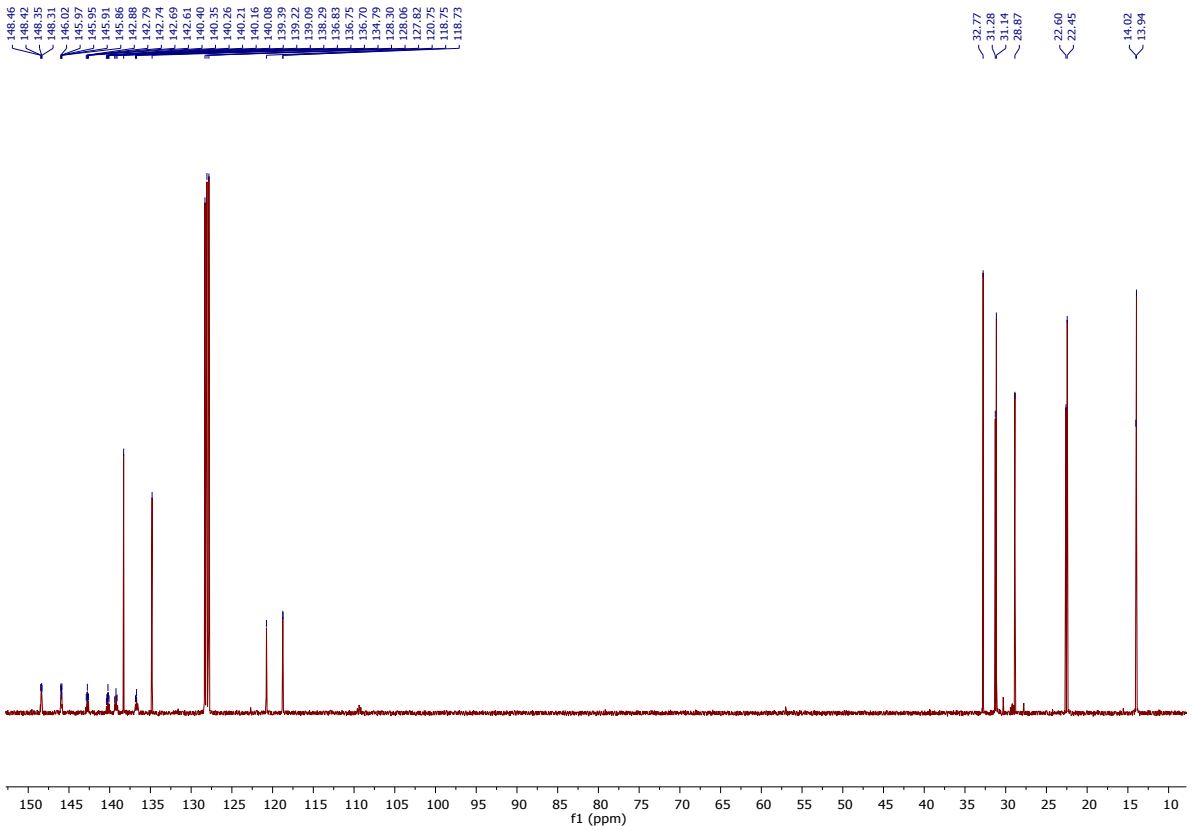


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **8**.

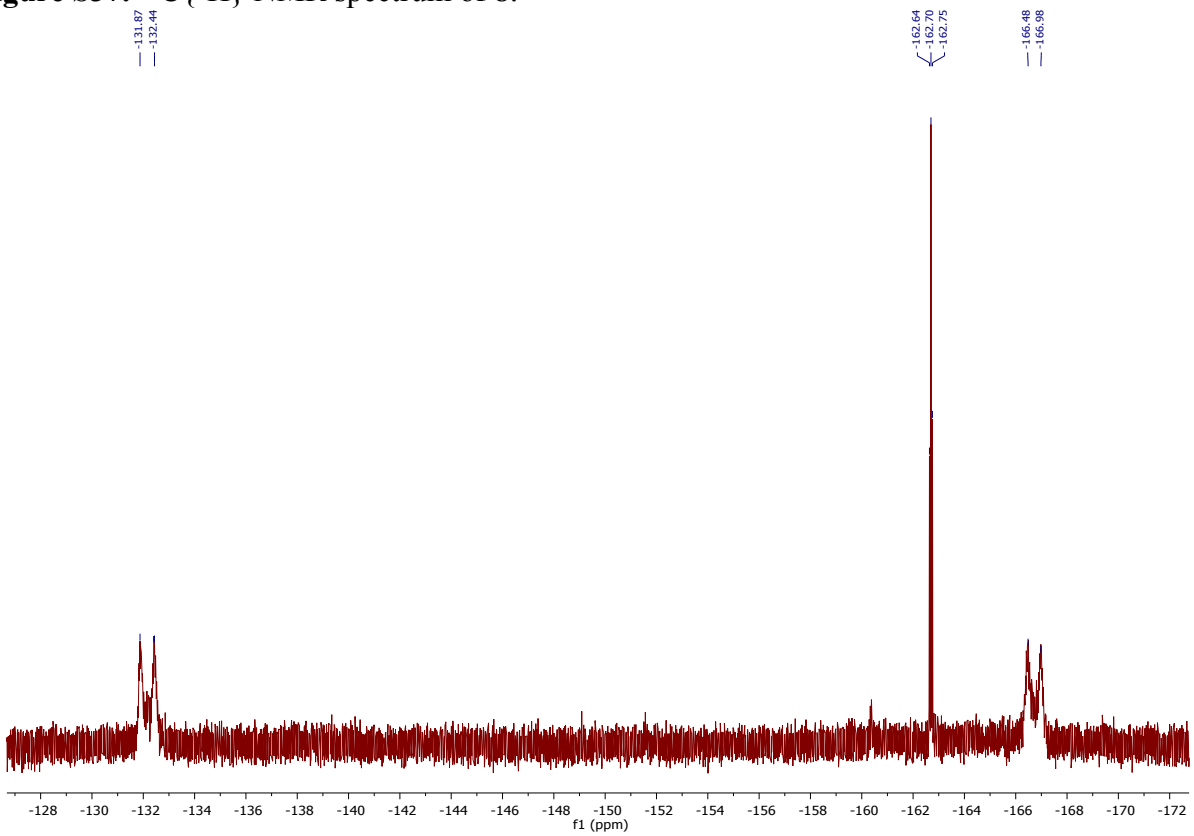


Figure S38. $^{19}F\{^{1}H\}$ NMR spectrum of **9**.

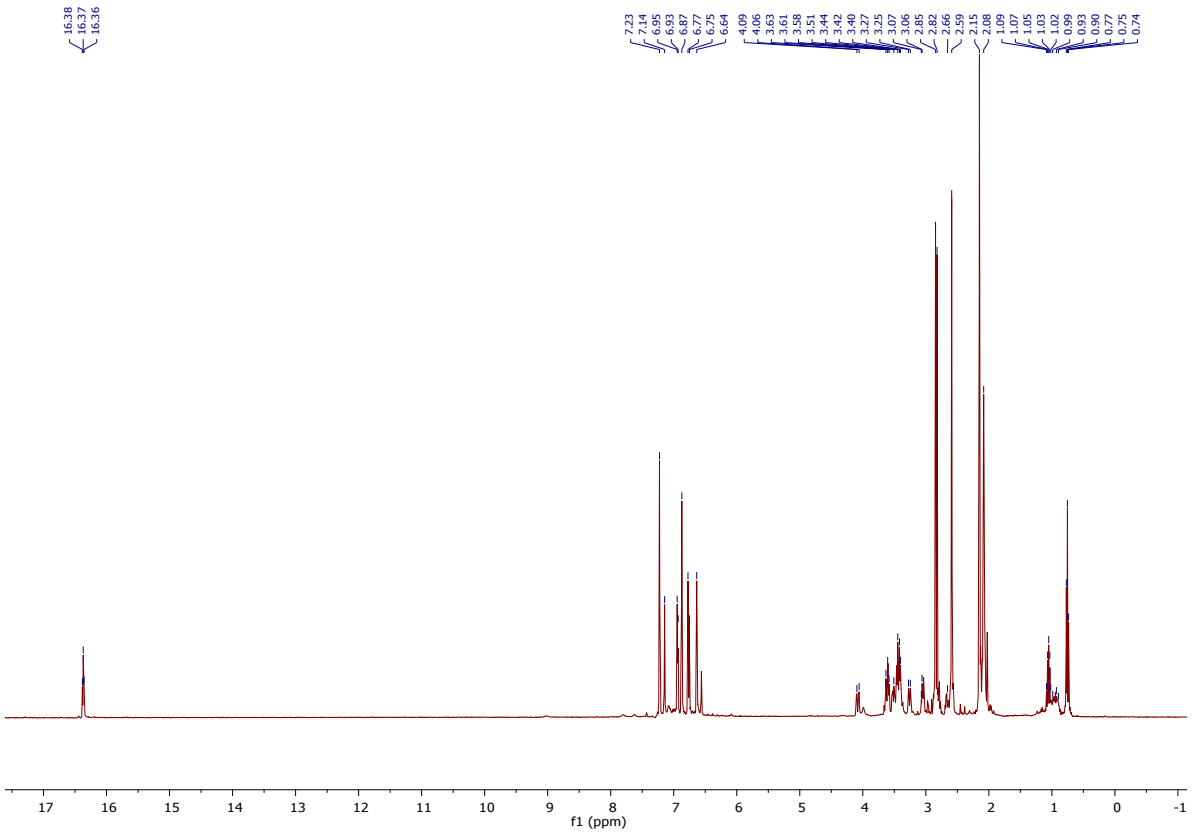


Figure S39. ^{1}H NMR spectrum of **9**.

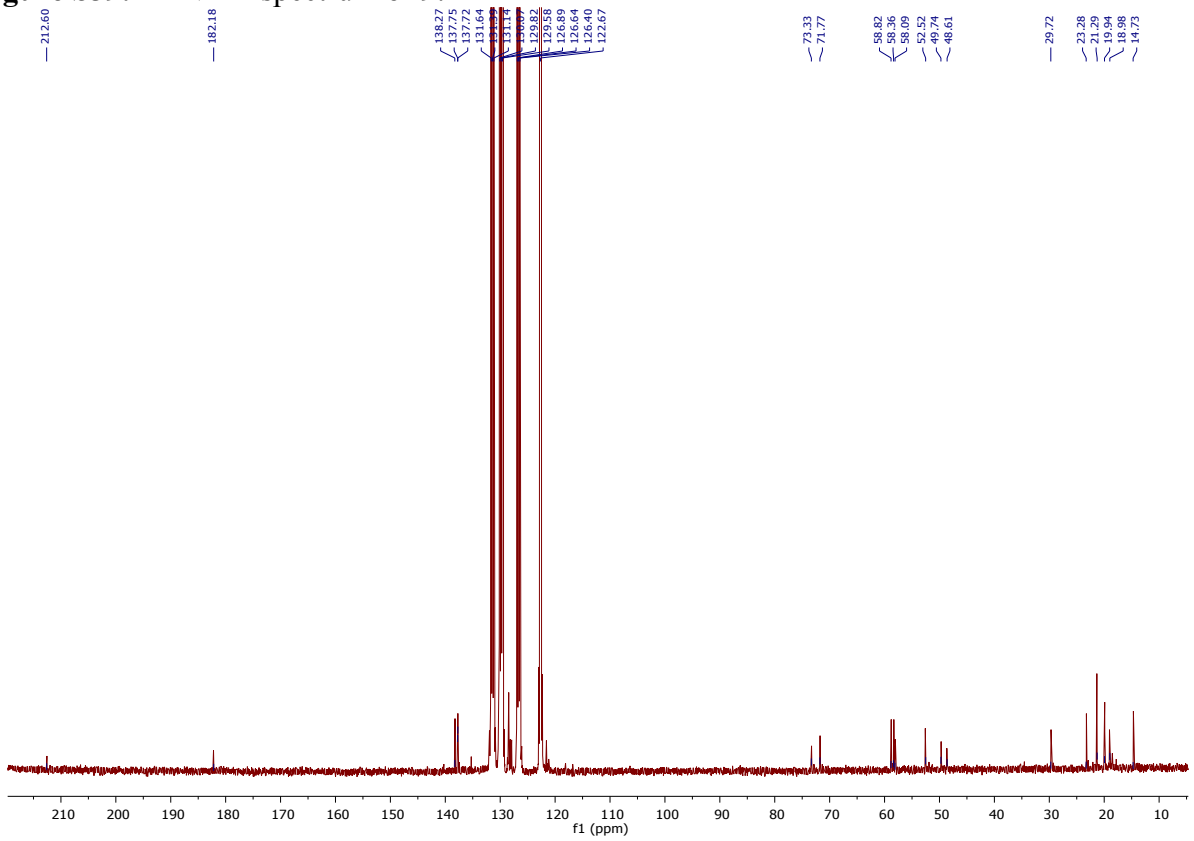


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **9**.

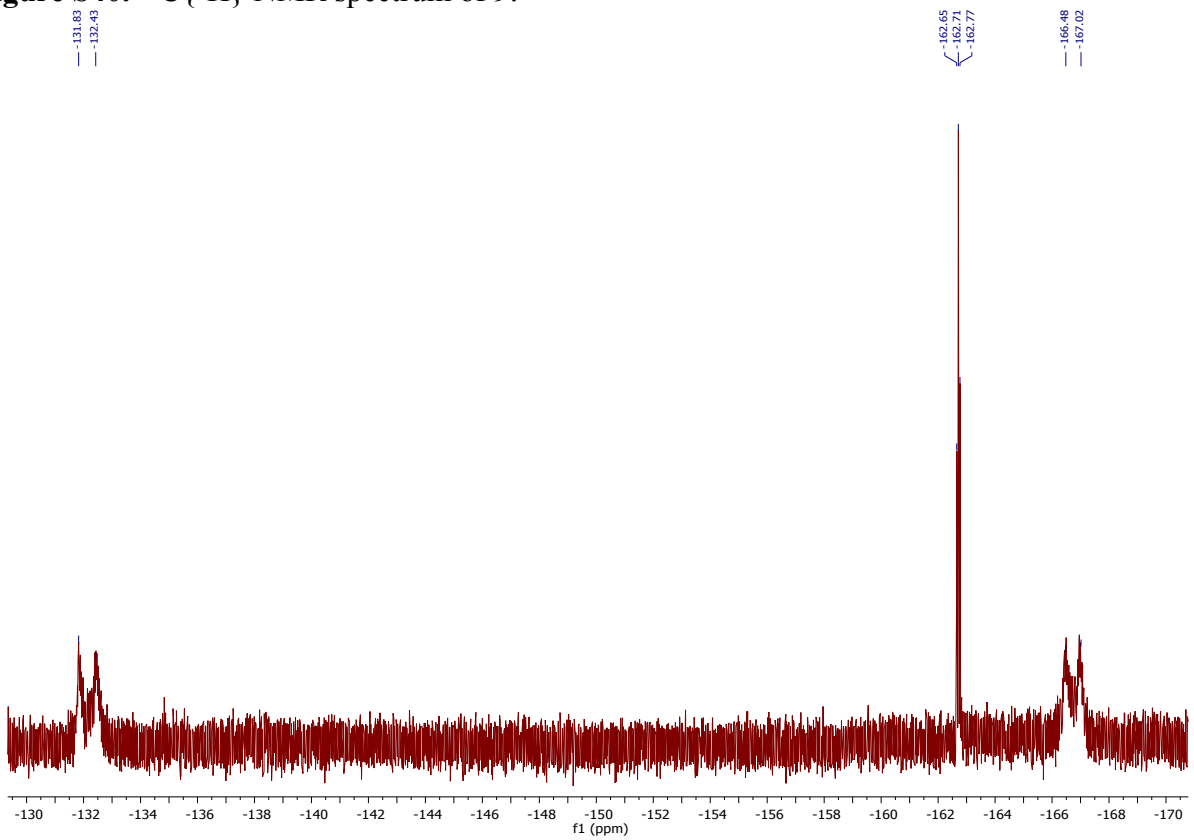


Figure S41. $^{19}F\{^{1}H\}$ NMR spectrum of **10**.

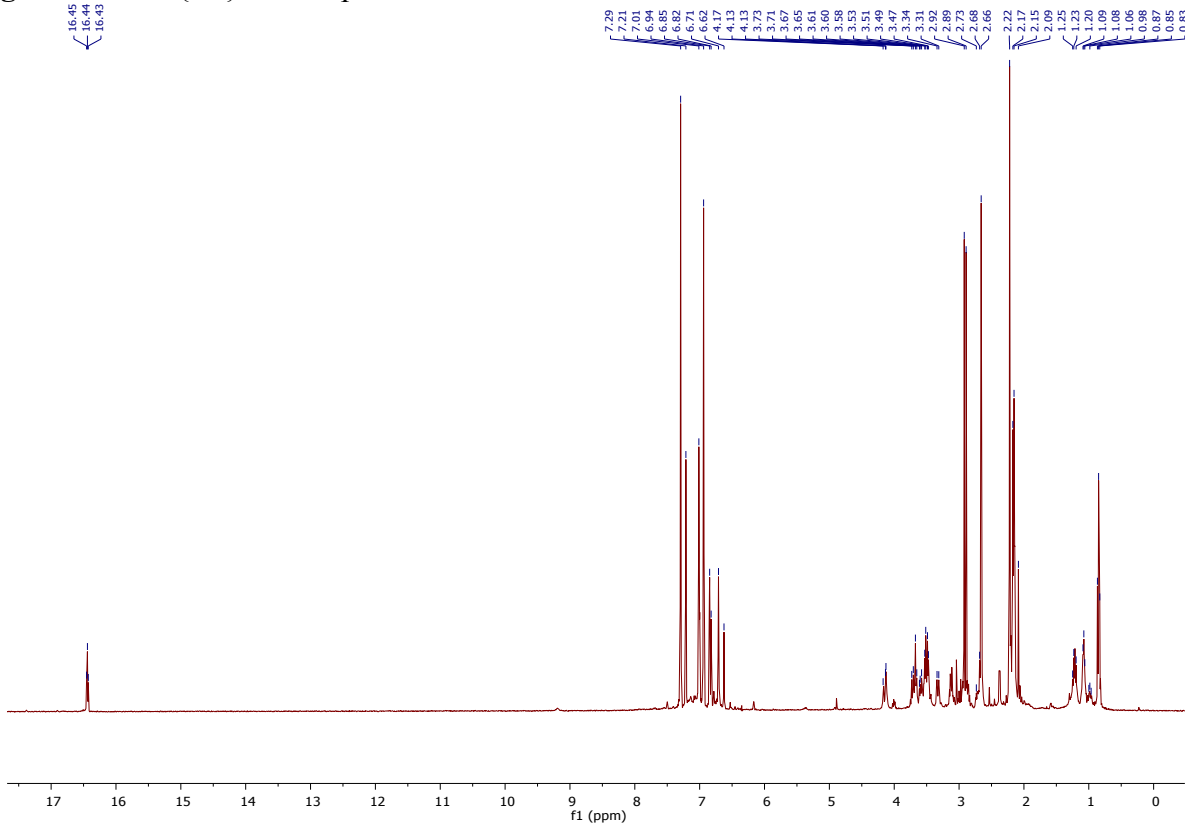


Figure S42. ^{1}H NMR spectrum of **10**.

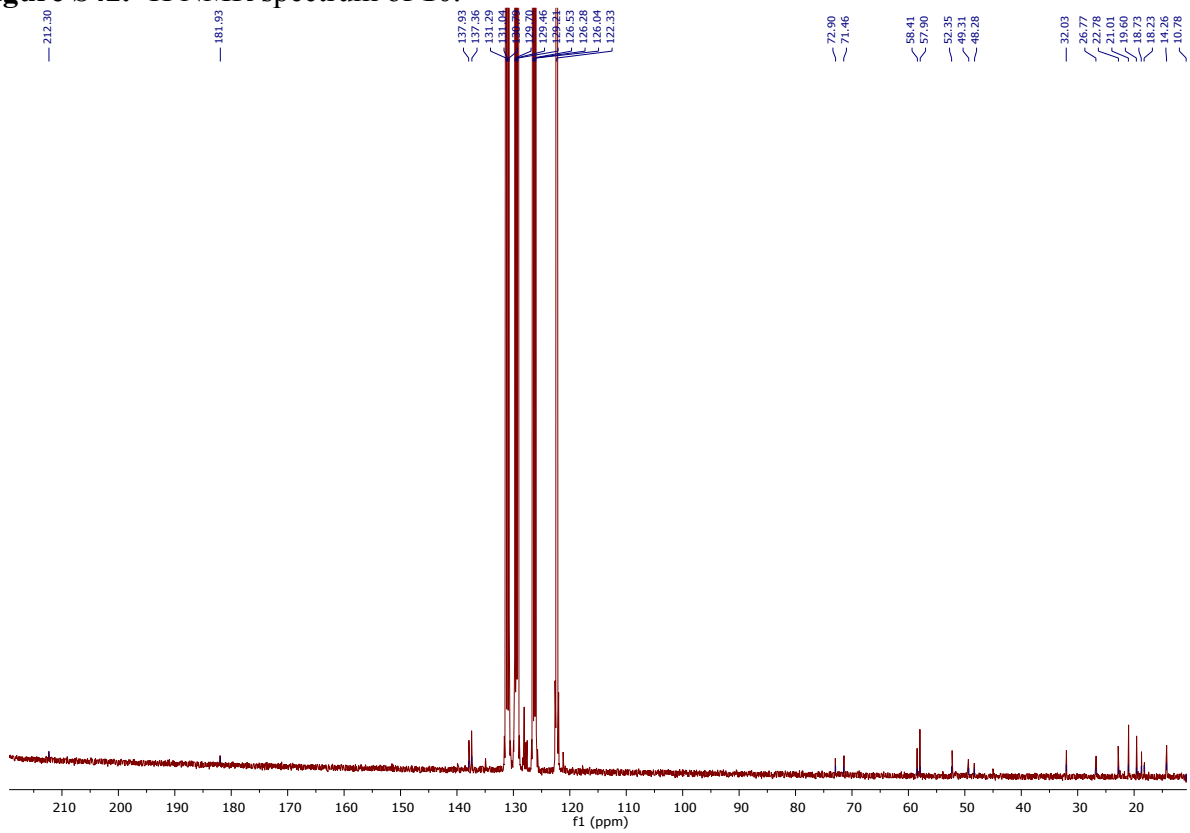


Figure S43. ^{13}C{^{1}H} NMR spectrum of **10**.

Table S1. Crystallographic Parameters for **1-3**, **5**, and **6**.

	1	**2•1.5(C_7H_8)•0.5(C_5H_{12})**	**3**	**5**	**6**
Formula	$C_{48}H_{56}ClN_4O_2PRu$	$C_{63}H_{80}ClN_4O_2PRu$	$C_{38}H_{50}ClFN_4O_2RuS$	$C_{38}H_{49}ClN_4O_2RuS$	$C_{40}H_{55}ClN_4O_2RuS$
wt	888.46	1092.80	782.41	762.39	792.46
Cryst. syst.	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	P-1	P-1	Pbca
a(Å)	13.9645(12)	14.687(2)	8.8552(11)	8.7968(3)	25.5160(18)
b(Å)	17.4923(14)	16.729(2)	11.8620(15)	11.7375(4)	8.8783(6)
c(Å)	18.6694(18)	24.285(3)	19.312(3)	19.4493(7)	38.627(3)
α(deg)	90.00	90.00	80.115(7)	79.242(2)	90.00
β(deg)	107.017(3)	101.749(8)	89.229(6)	88.387(1)	90.00
γ(deg)	90.00	90.00	69.025(6)	68.968(1)	90.00
V(Å^3)	4360.7(7)	5841.9(14)	1863.5(4)	1839.81(11)	8750.6(11)
Z	4	4	2	2	8
d(calc) gcm^{-3}	1.353	1.243	1.394	1.376	1.203
R(int)	0.0431	0.0870	0.0646	0.0608	0.1370
μ, mm^{-1}	0.501	0.387	0.592	0.594	0.502
Total data	10004	13365	8517	8388	7699
>2σ(F_O^2)	7963	8756	6283	6011	5084
Variables	518	704	430	421	439
R (>2σ)	0.0338	0.0479	0.0486	0.0480	0.0655
R_w	0.0836	0.1244	0.1172	0.1107	0.1399
GOF	1.019	1.010	1.032	1.024	1.082