Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

An insight into regioselectivity in the formation of ruthenacycle

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1. Time course for reaction of 1-cyclohexylhex-1-yne (2h) with methyl (*E*)-penta-2,4-dienoate (3a)

1-Cyclohexylhex-1-yne (**2h**) (23.0 µl, 0.119 mmol) was placed in an NMR tube under nitrogen atmosphere, and C_6D_6 (600 µL) was added. To the solution was added methyl (*E*)-penta-2,4-dienoate (**3a**) (14.0 µL, 0.117 mmol) by a hypodermic syringe at room temperature. [Ru(η^6-naphthalene)(η^4-1,5-cod)] (**1**) (3.97 mg, 0.0118 mmol) was added in the solution under nitrogen atmosphere. The mixture was allowed to react at room temperature for 210 min, during which the reaction was monitored by ^{1}H NMR spectroscopy. In order to determine the yield of the product, dibenzyl (5.21 mg, 0.0286 mmol) was added into the solution as an internal standard.

The time course of this reaction was shown Fig S1. The time course curves for the catalytic reaction of **2h** with **3a** the **4ha**/**5ha** ratio is almost constant. According to these facts, formation of **4ha** and **5ha** was considered to be a parallel reaction.

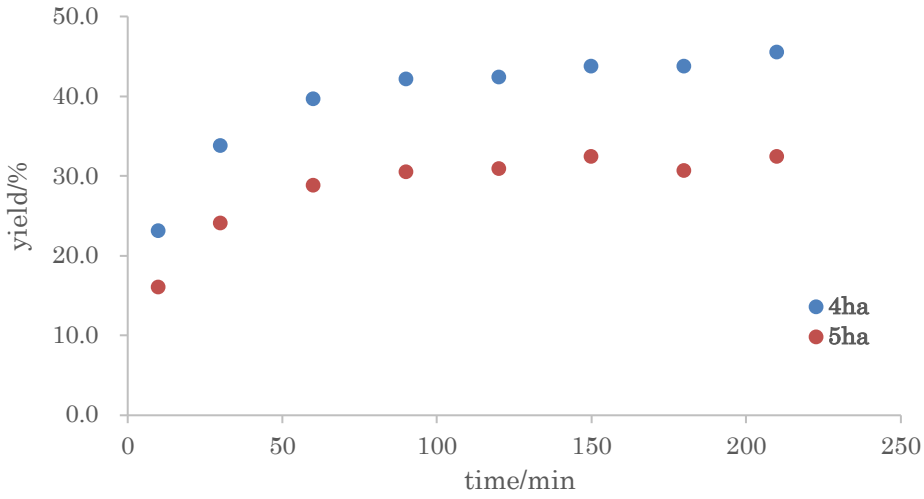


Figure S1. Time course for reaction of 2h with 3a giving 4ha and 5ha.

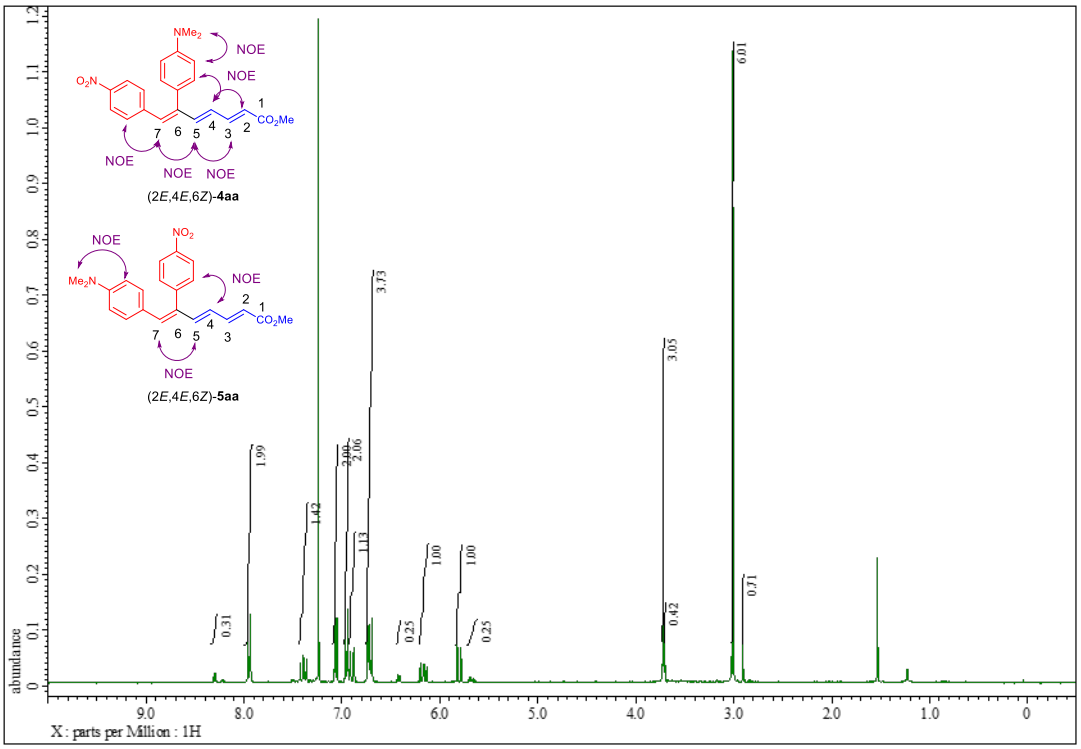


Figure S2. ^{1}H NMR Spectrum of 4aa and 5aa in $CDCl_3$.

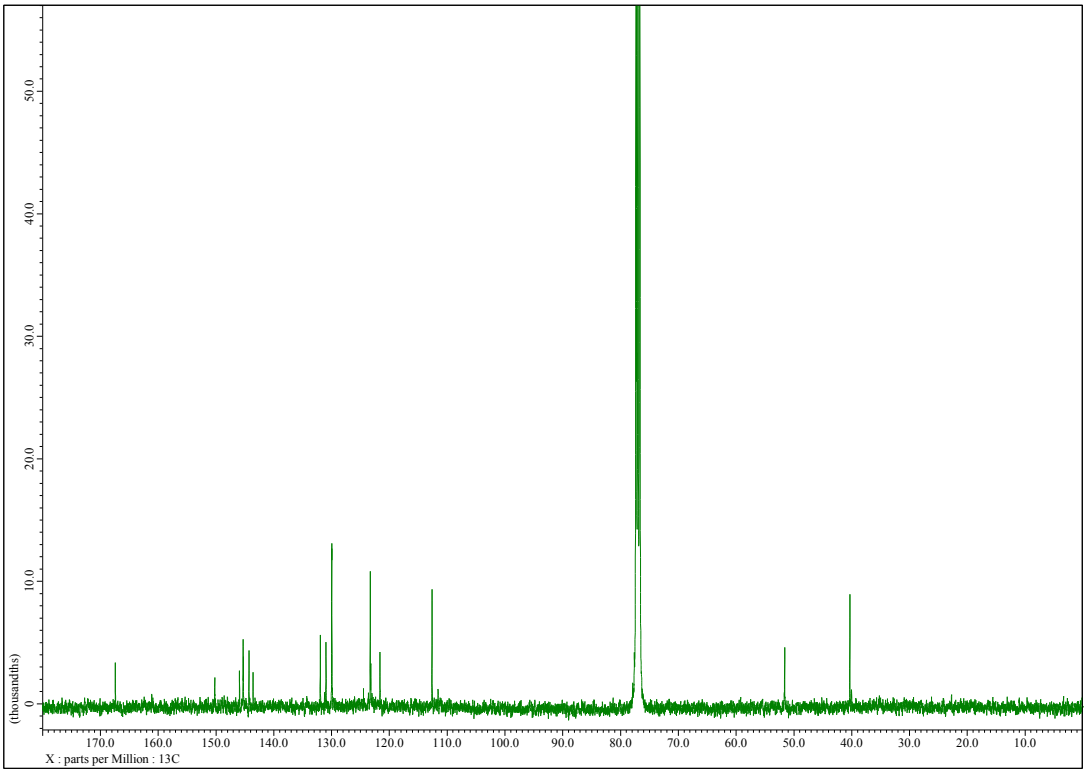


Figure S3. $^{13}C\{^{1}H\}$ NMR Spectrum of 4aa and 5aa in $CDCl_3$.

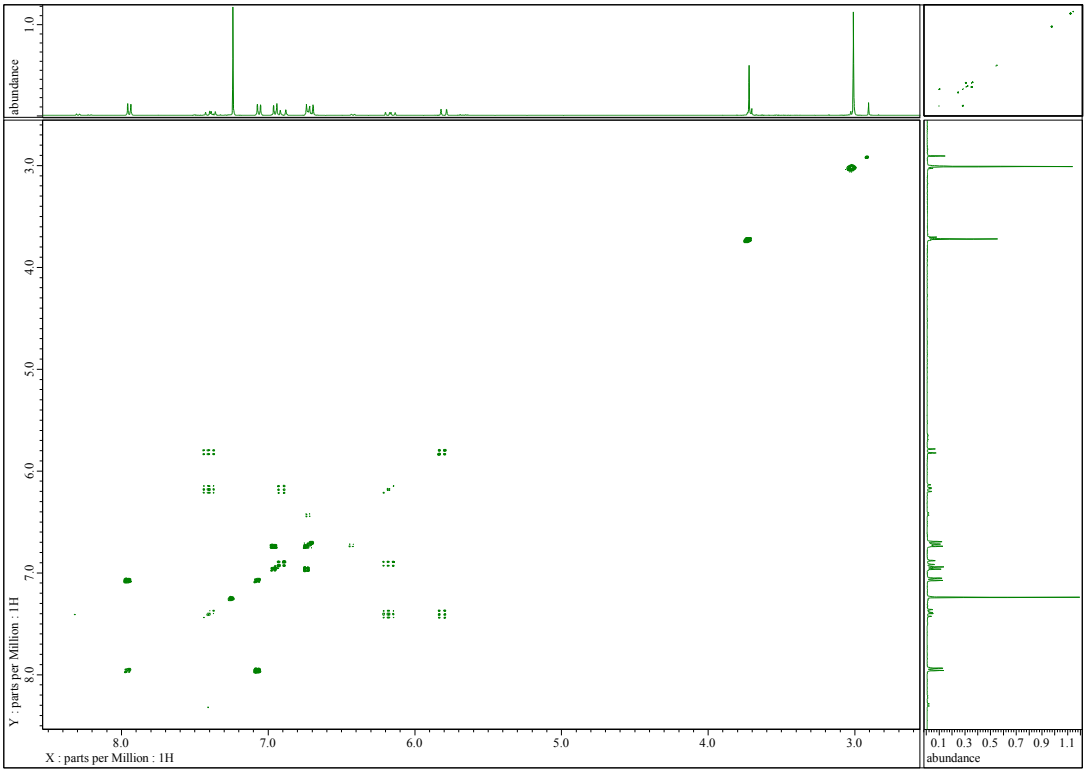


Figure S4. ^{1}H-^{1}H COSY NMR Spectrum of 4aa and 5aa in $CDCl_3$.

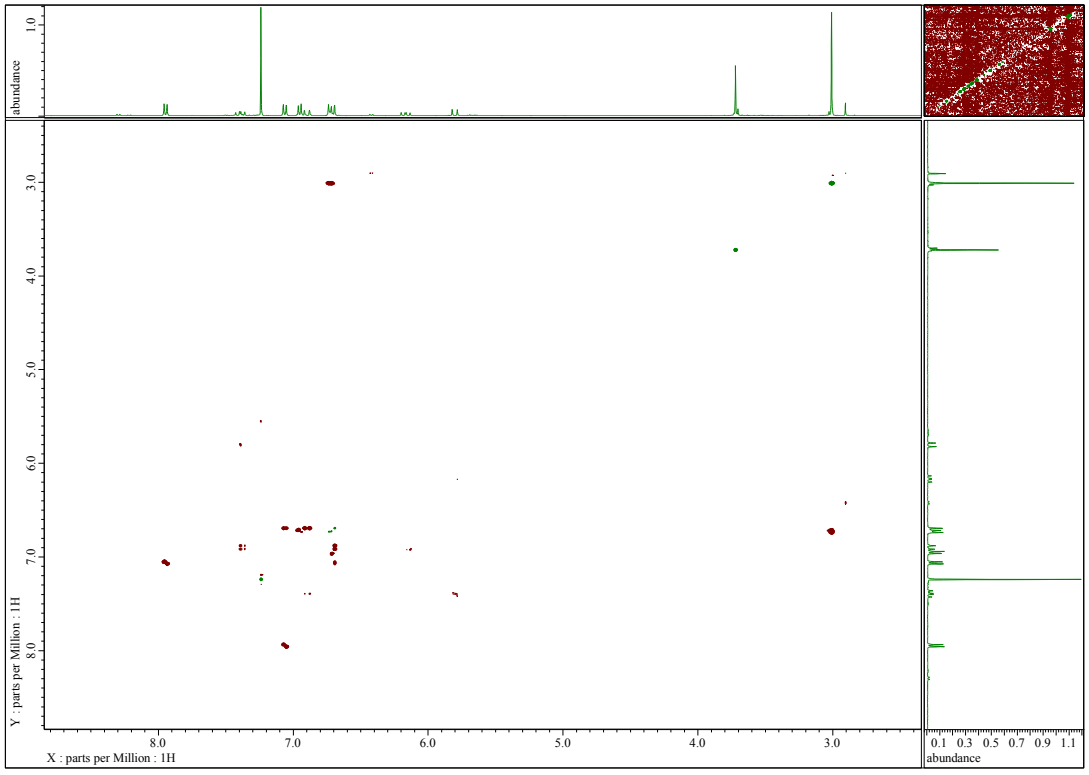


Figure S5. ^{1}H-^{1}H pNOESY NMR Spectrum of 4aa and 5aa in $CDCl_3$.

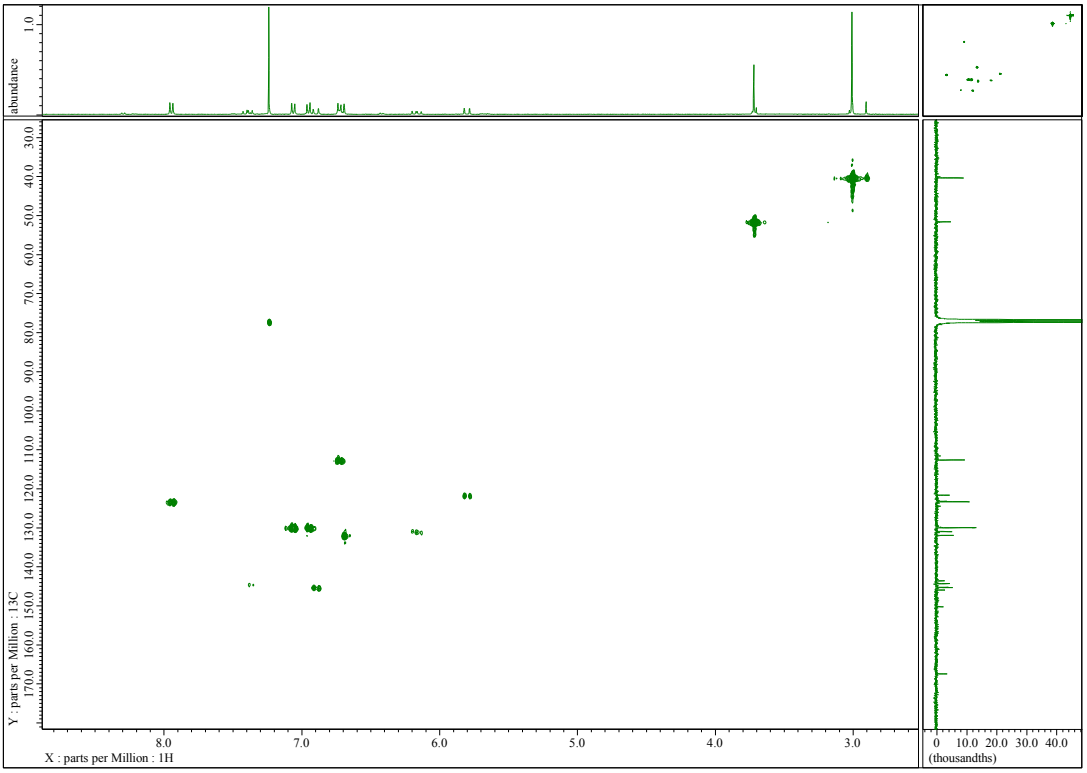
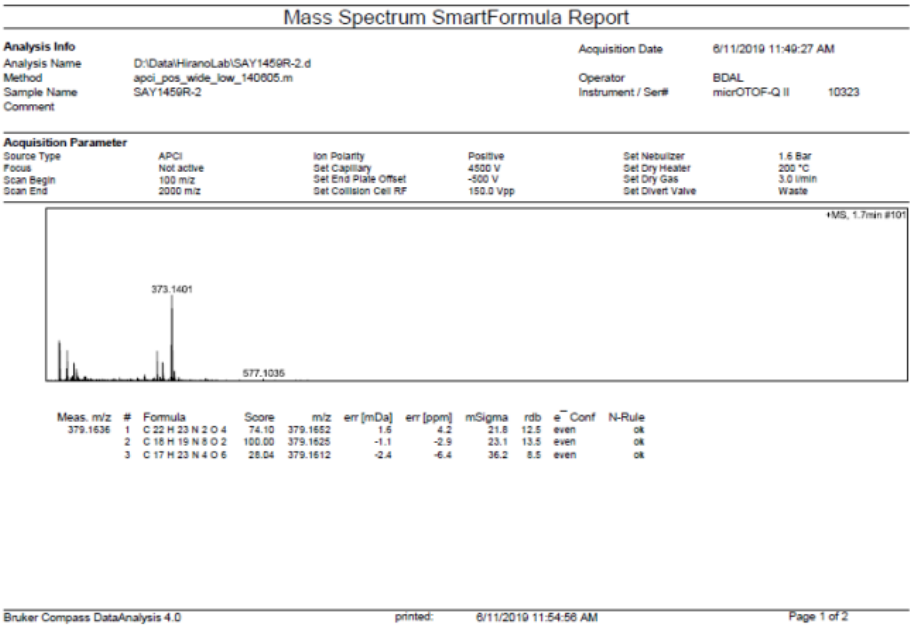


Figure S6. ^{13}C-^{1}H Correlation Spectrum of 4aa and 5aa in $CDCl_3$.



Mass Spectrum SmartFormula Report

Analysis Info

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Comment		Instrument / Ser#	micrOTOF-Q II 10323

Acquisition Parameter

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	2	C 18 H 19 N 8 O 2	100.00	379.1625	-1.1	-2.9	23.1	13.5	even	ok
	3	C 17 H 23 N 4 O 6	28.04	379.1612	-2.4	-6.4	36.2	8.5	even	ok

Figure S7-1. HRMS (APCI) data for 4aa and 5aa.

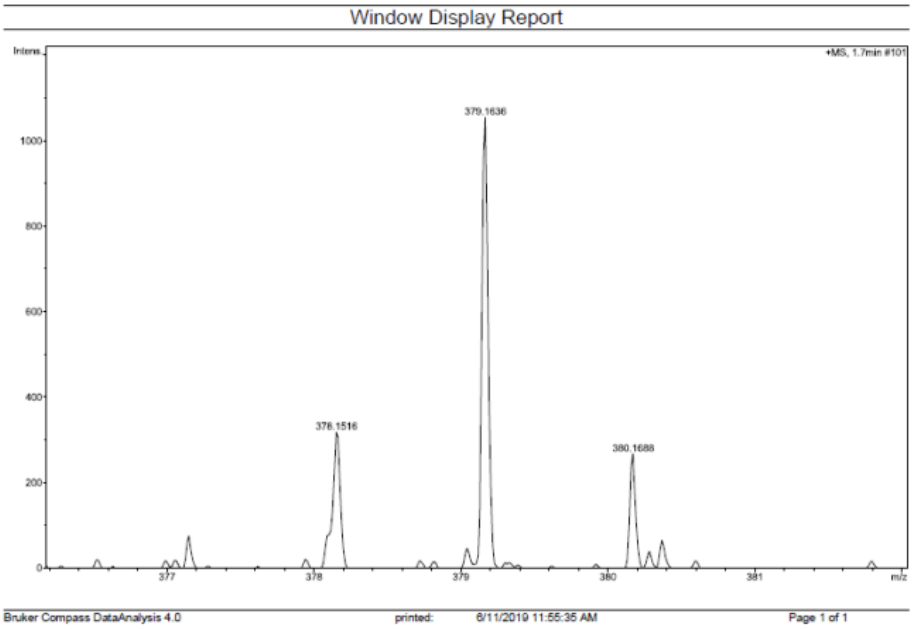


Figure S7-2. HRMS (APCI) data for 4aa and 5aa.

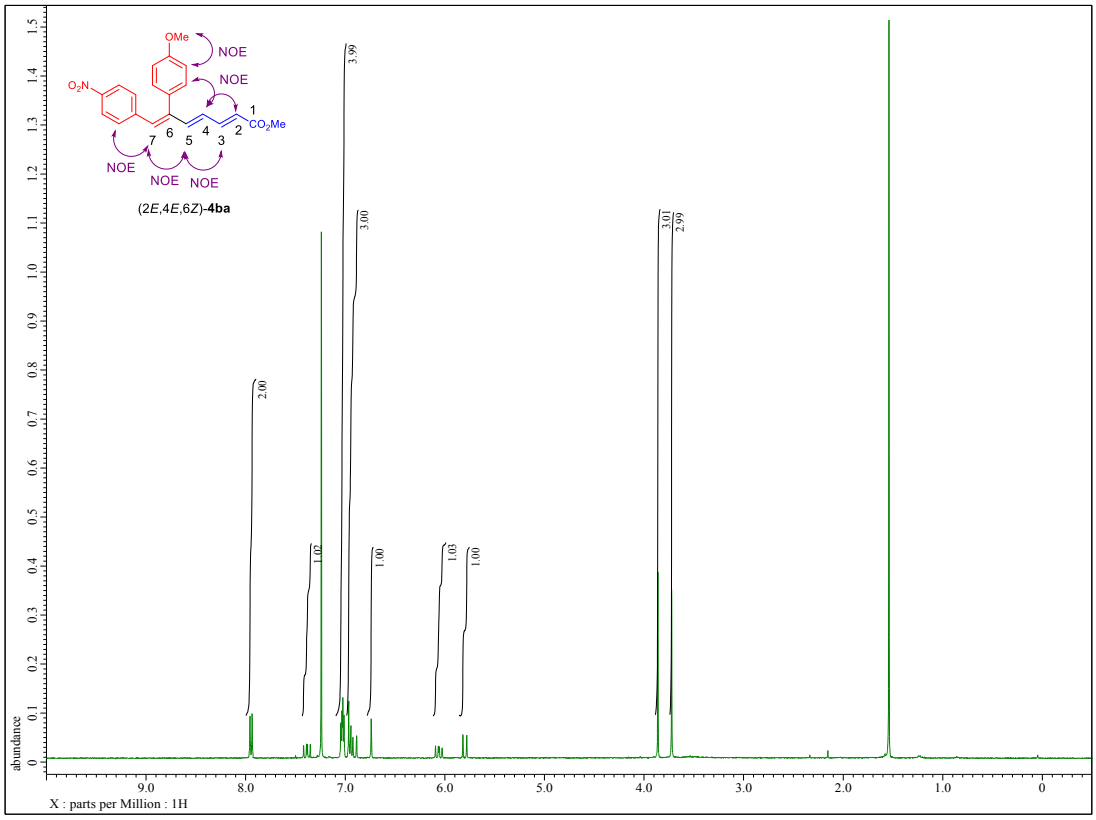


Figure S8. ^{1}H NMR Spectrum of 4ba in $CDCl_3$.

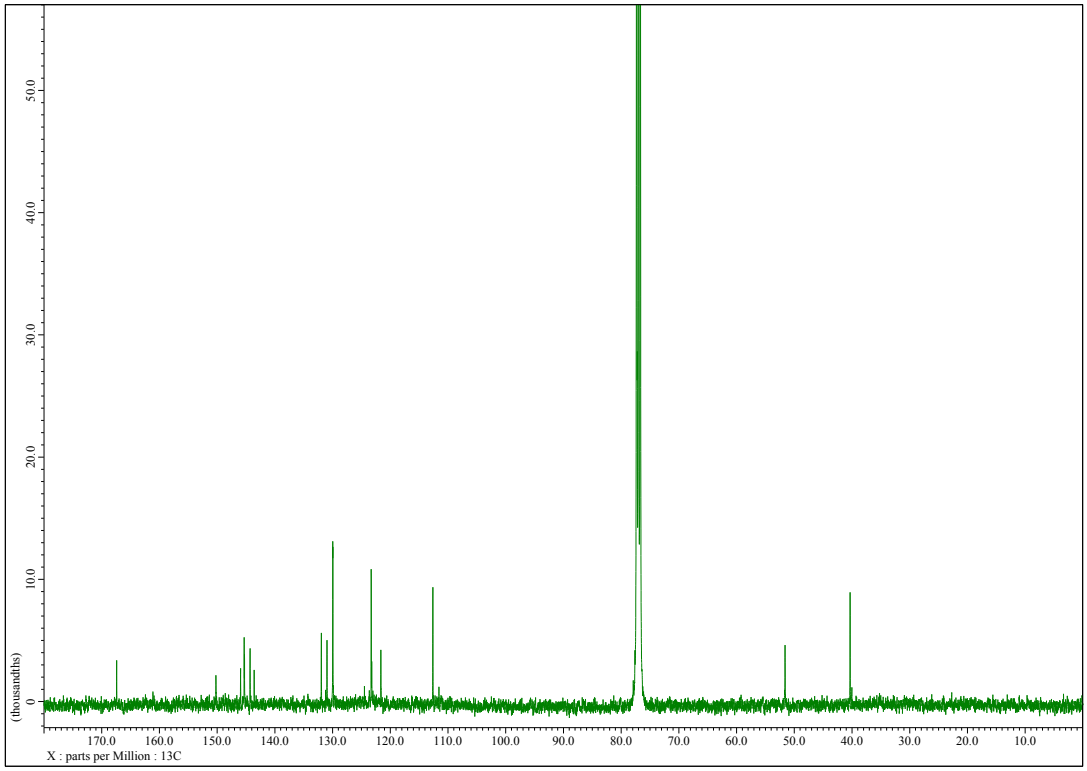


Figure S9. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ba in $CDCl_3$.

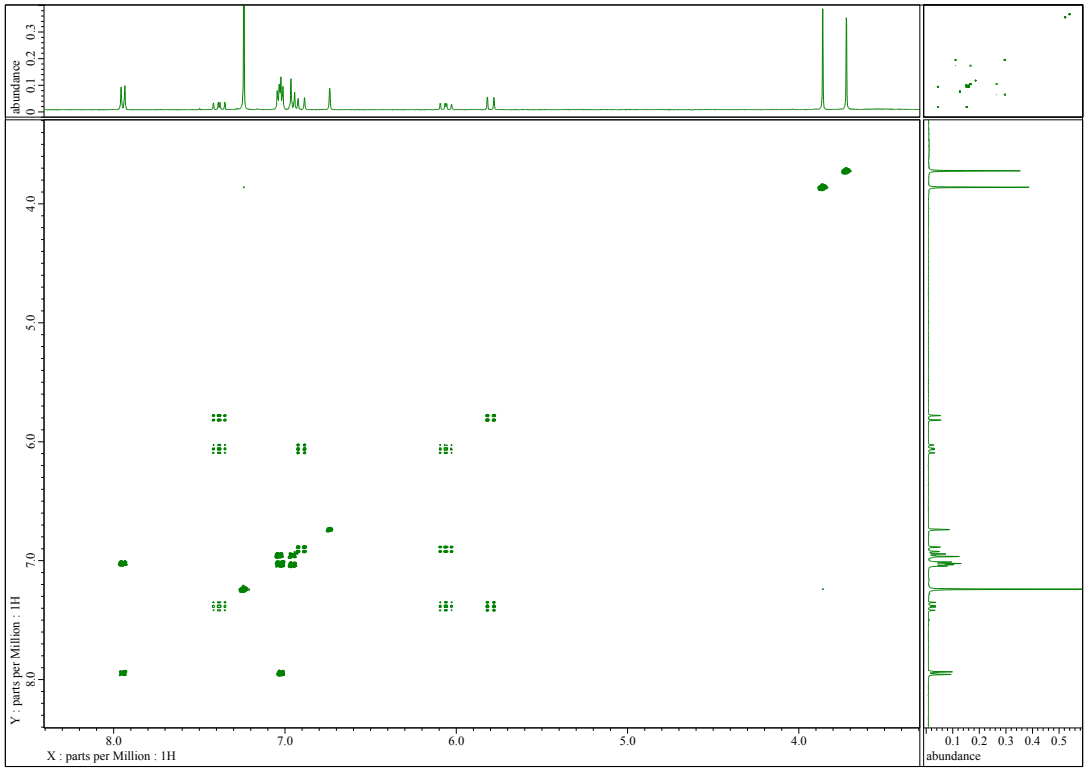


Figure S10. ^{1}H-^{1}H COSY NMR Spectrum of 4ba in $CDCl_3$.

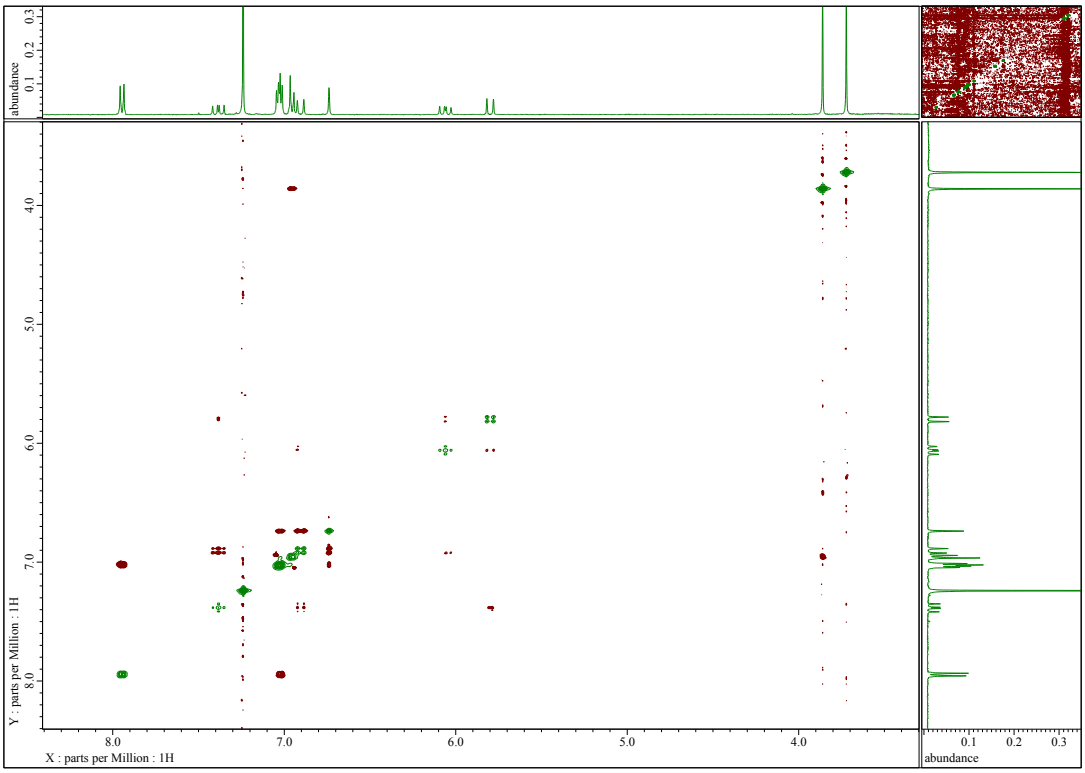


Figure S11. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ba in $CDCl_3$.

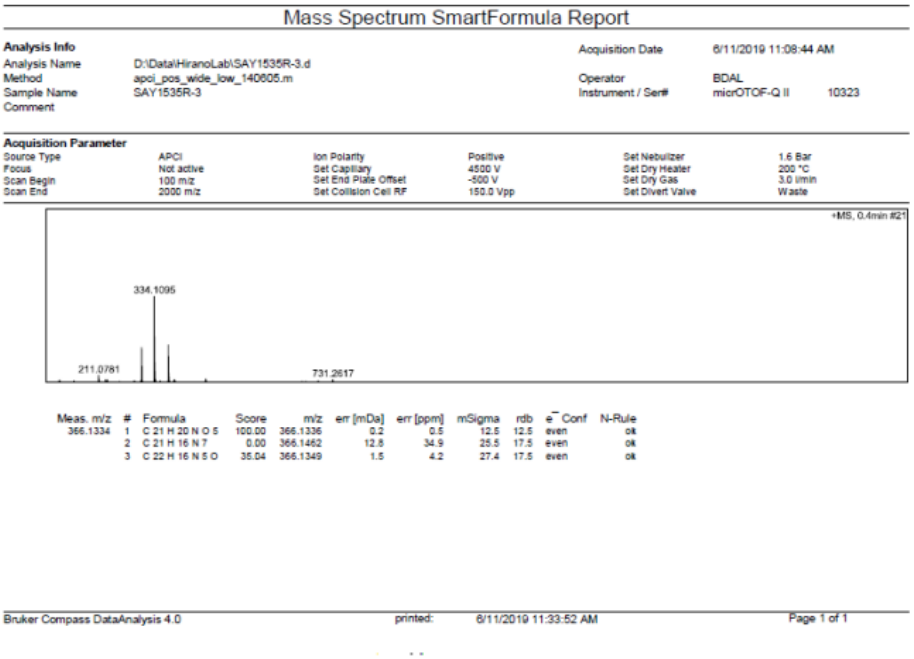


Figure S12-1. HRMS (APCI) data for 4ba.

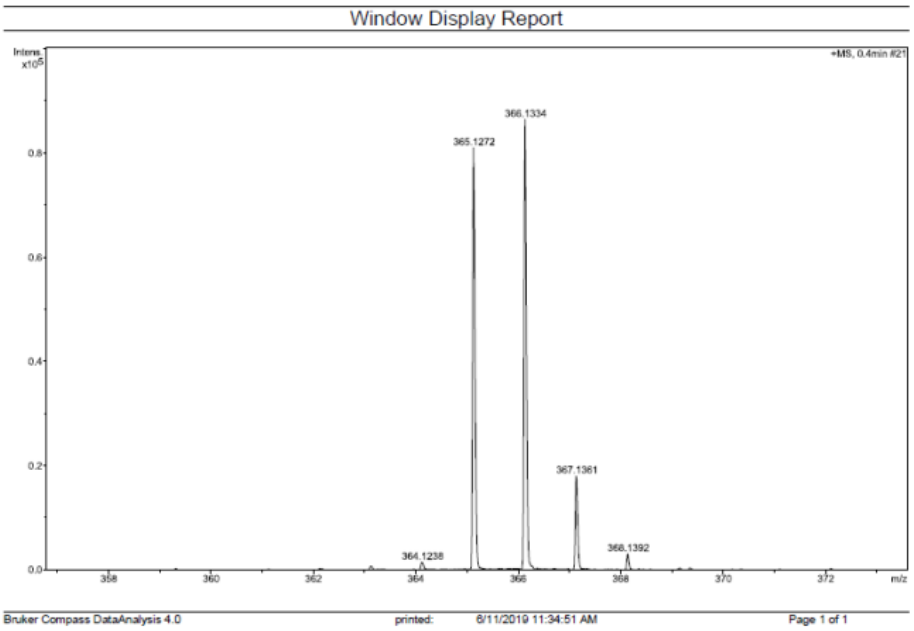


Figure S12-2. HRMS (APCI) data for 4ba.

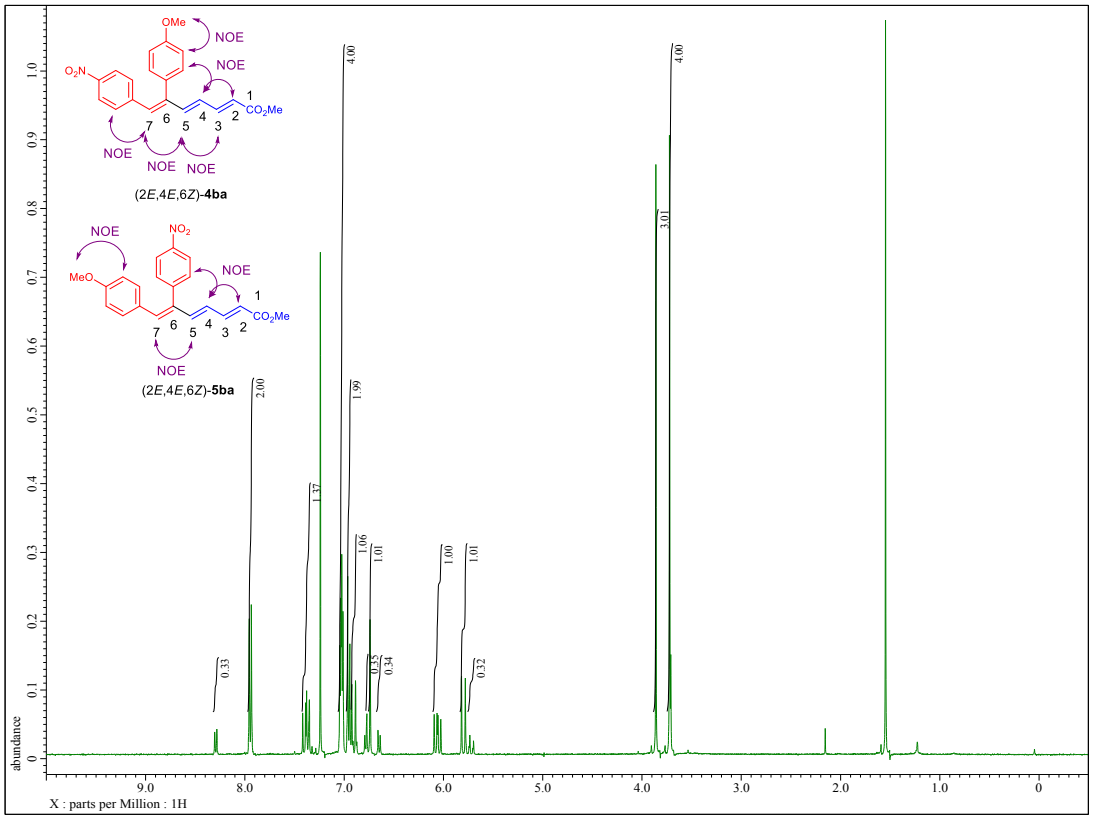


Figure S13. ^{1}H NMR Spectrum of 4ba and 5ba in $CDCl_3$.

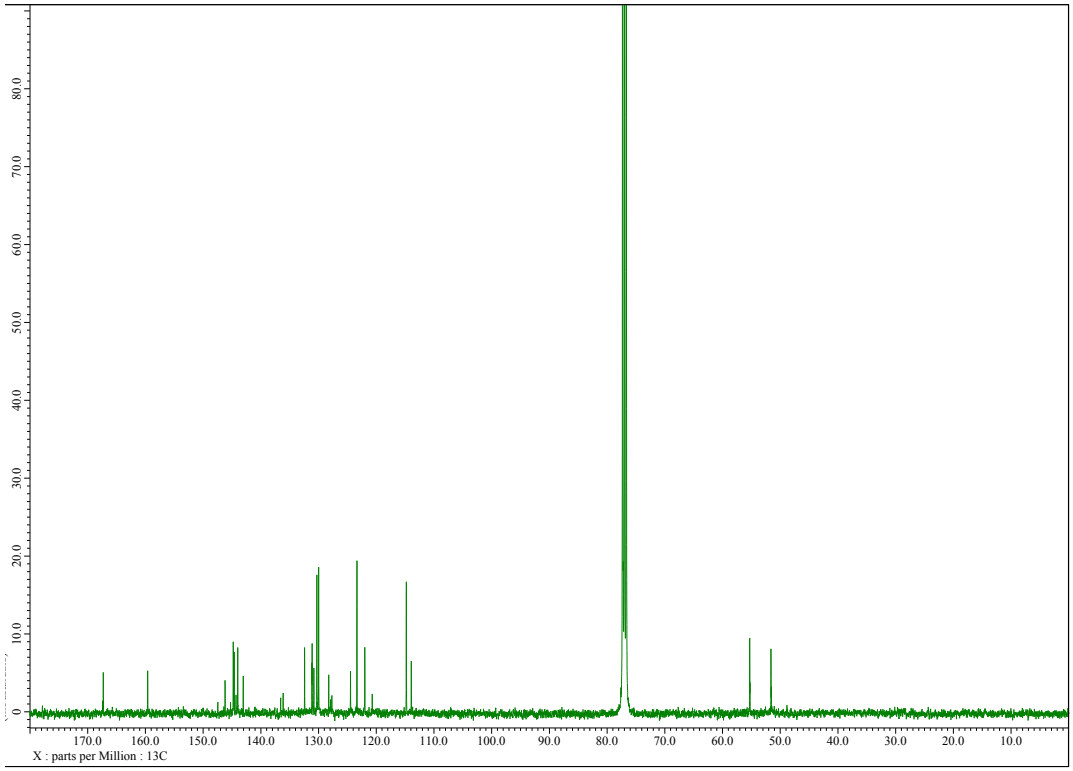


Figure S14. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ba and 5ba in $CDCl_3$.

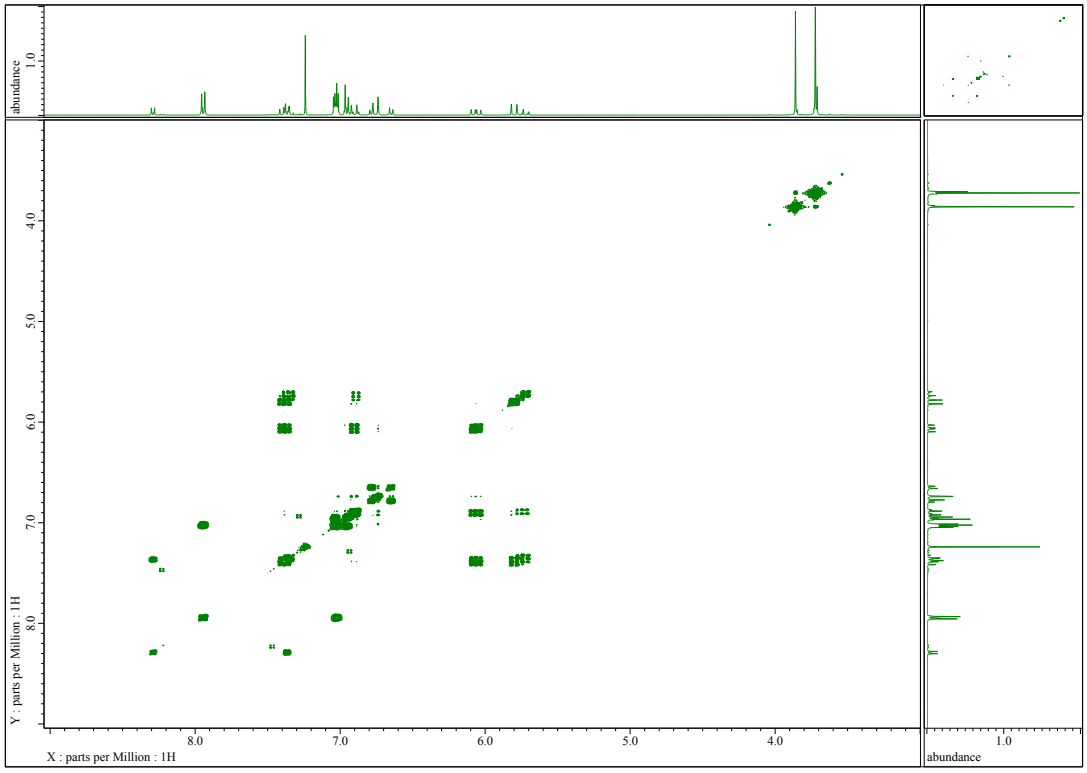


Figure S15. ^{1}H-^{1}H COSY NMR Spectrum of 4ba and 5ba in $CDCl_3$.

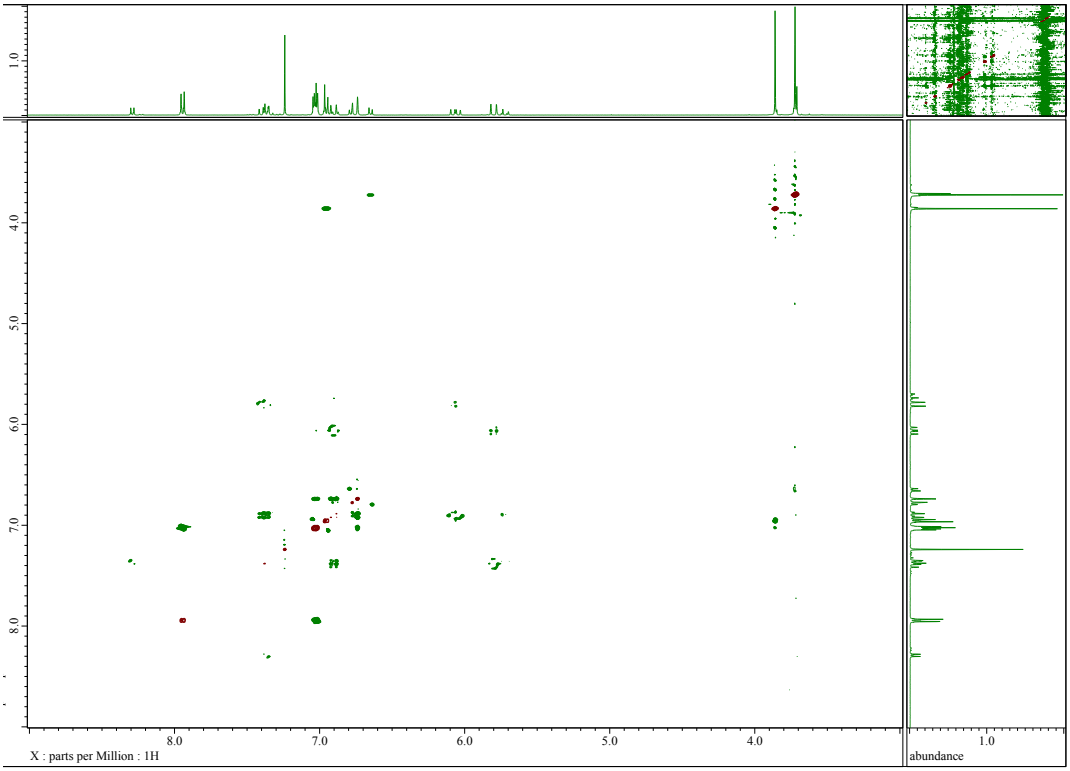


Figure S16. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ba and 5ba in $CDCl_3$.

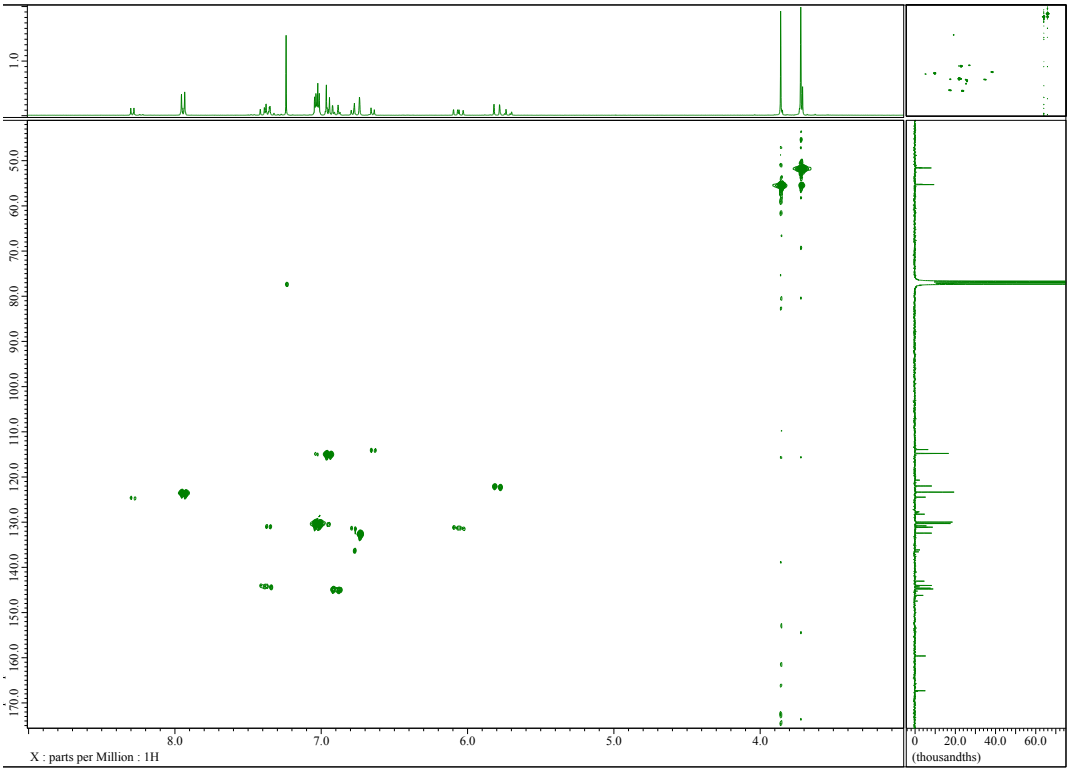


Figure S17. ^{13}C-^{1}H Correlation Spectrum of 4ba and 5ba in $CDCl_3$.

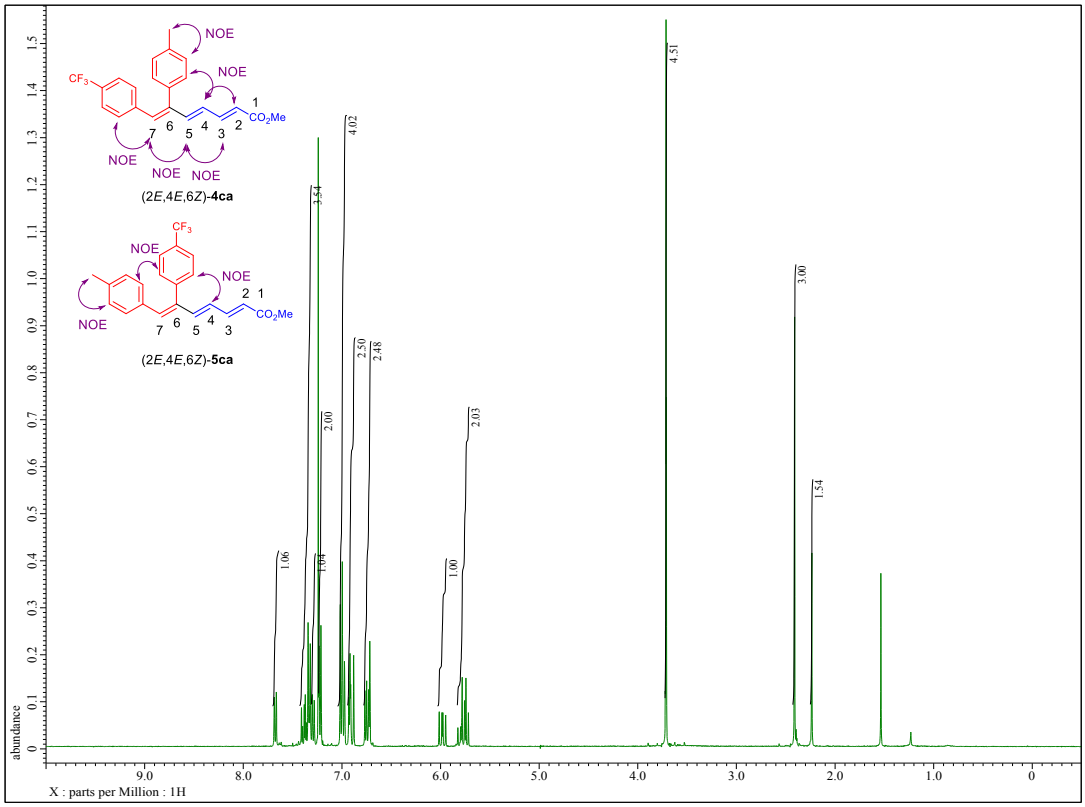


Figure S18. ^{1}H NMR Spectrum of 4ca and 5ca in $CDCl_3$.

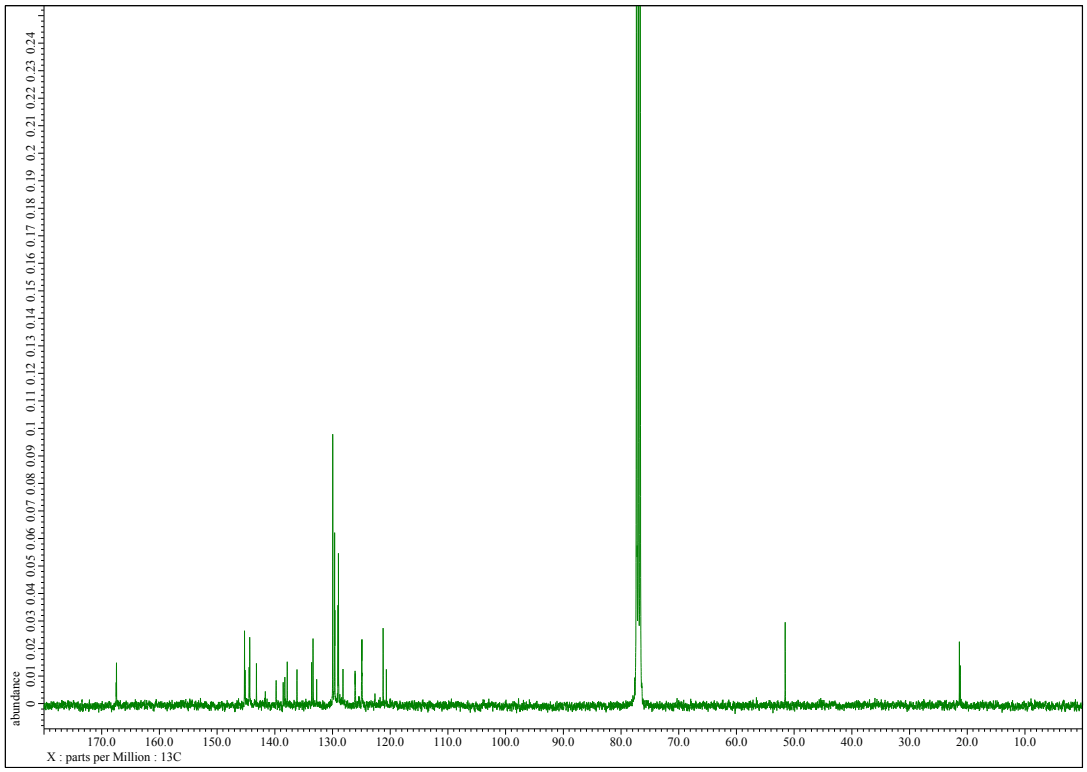


Figure S19. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ca and 5ca in $CDCl_3$.

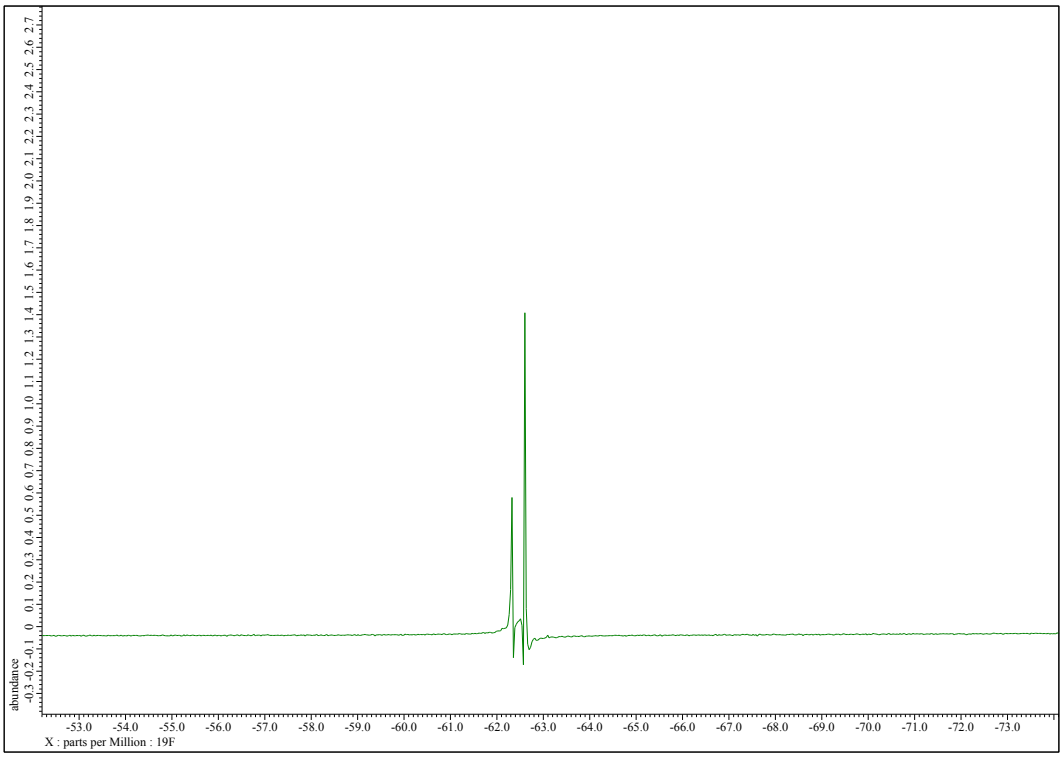


Figure S20. $^{19}F\{^{1}H\}$ NMR Spectrum of 4ca and 5ca in $CDCl_3$.

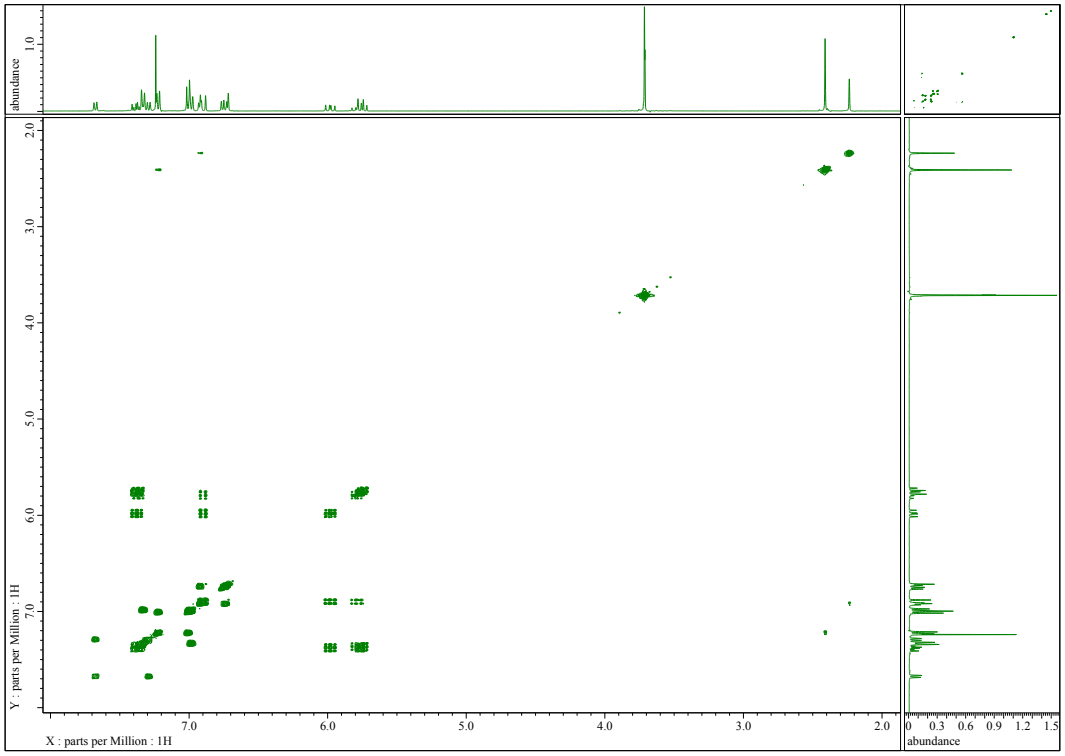


Figure S21. ^{1}H-^{1}H COSY NMR Spectrum of 4ca and 5ca in $CDCl_3$.

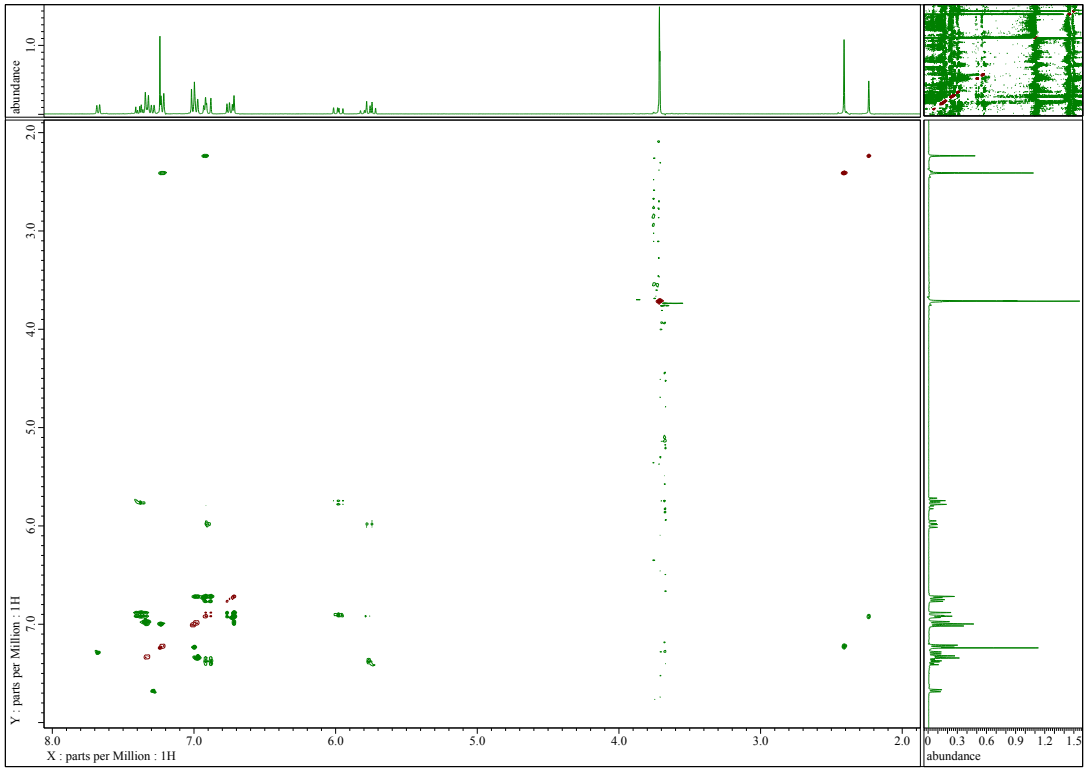


Figure S22. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ca and 5ca in $CDCl_3$.

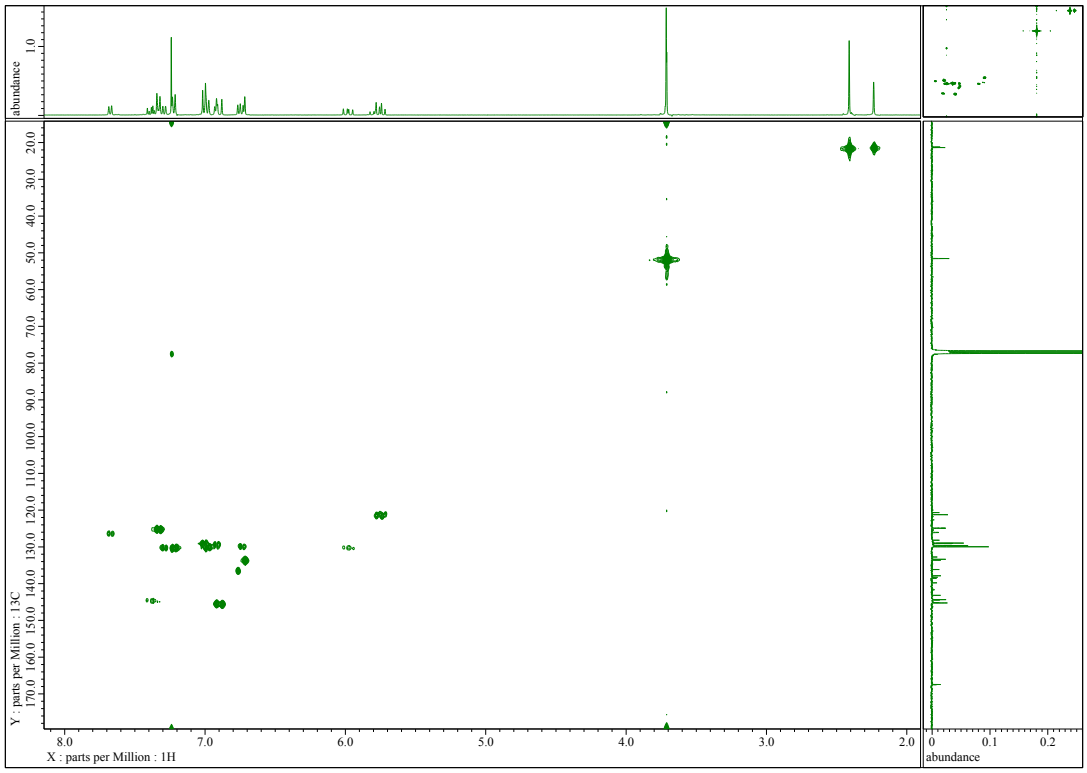


Figure S23. ^{13}C-^{1}H Correlation Spectrum of 4ca and 5ca in $CDCl_3$.

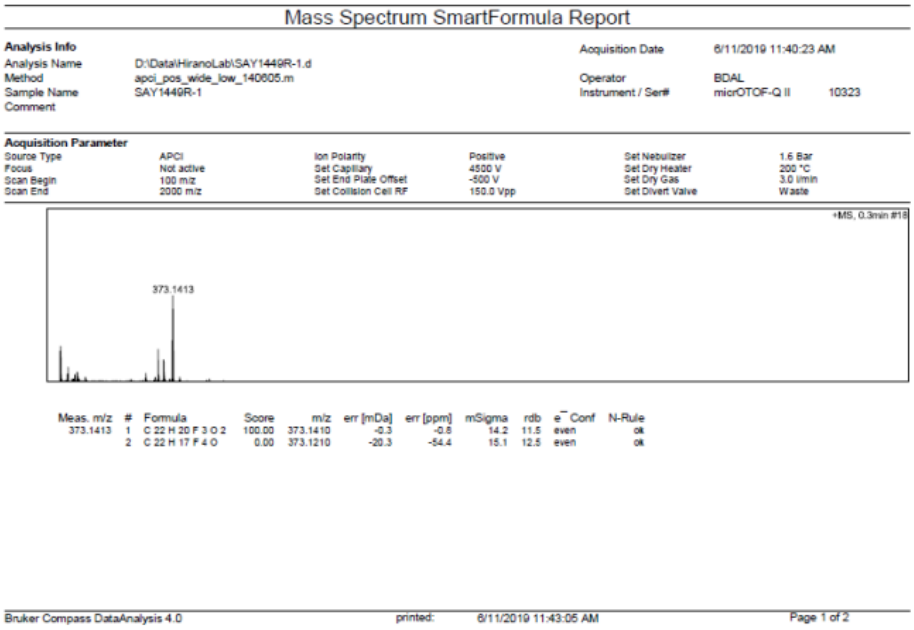


Figure S24. HRMS (APCI) data for 4ca and 5ca.

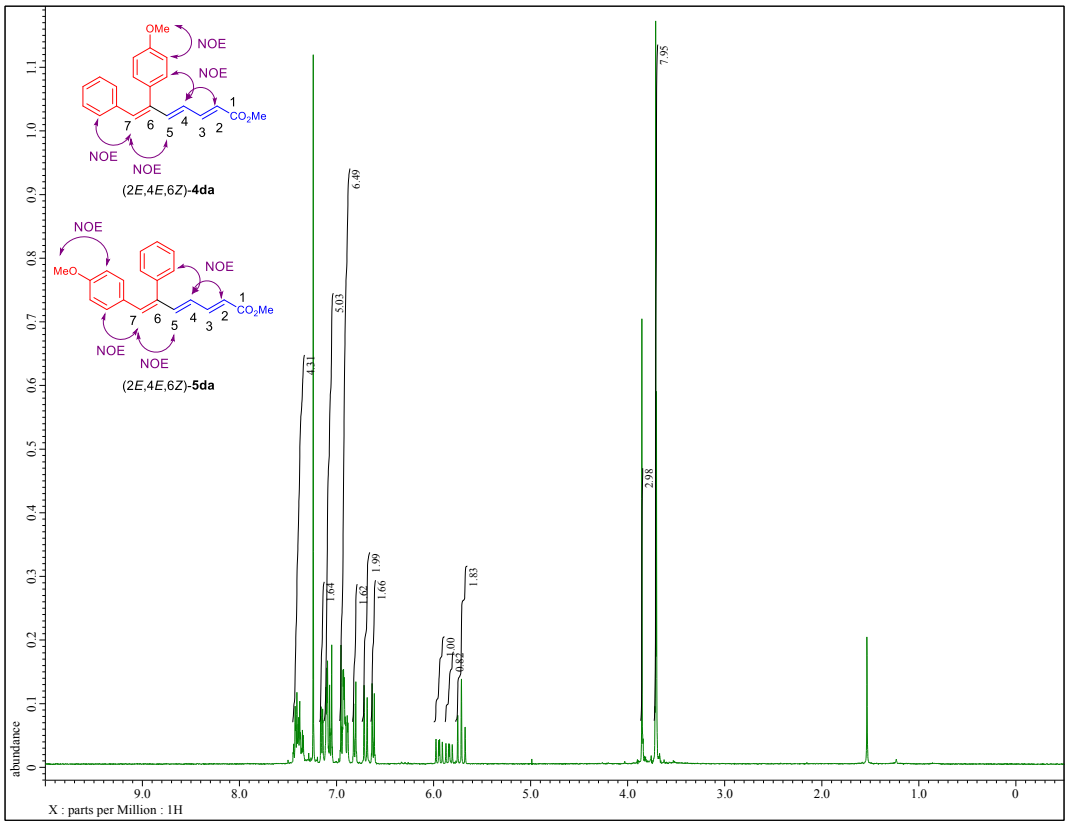


Figure S25. ^{1}H NMR Spectrum of 4da and 5da in $CDCl_3$.

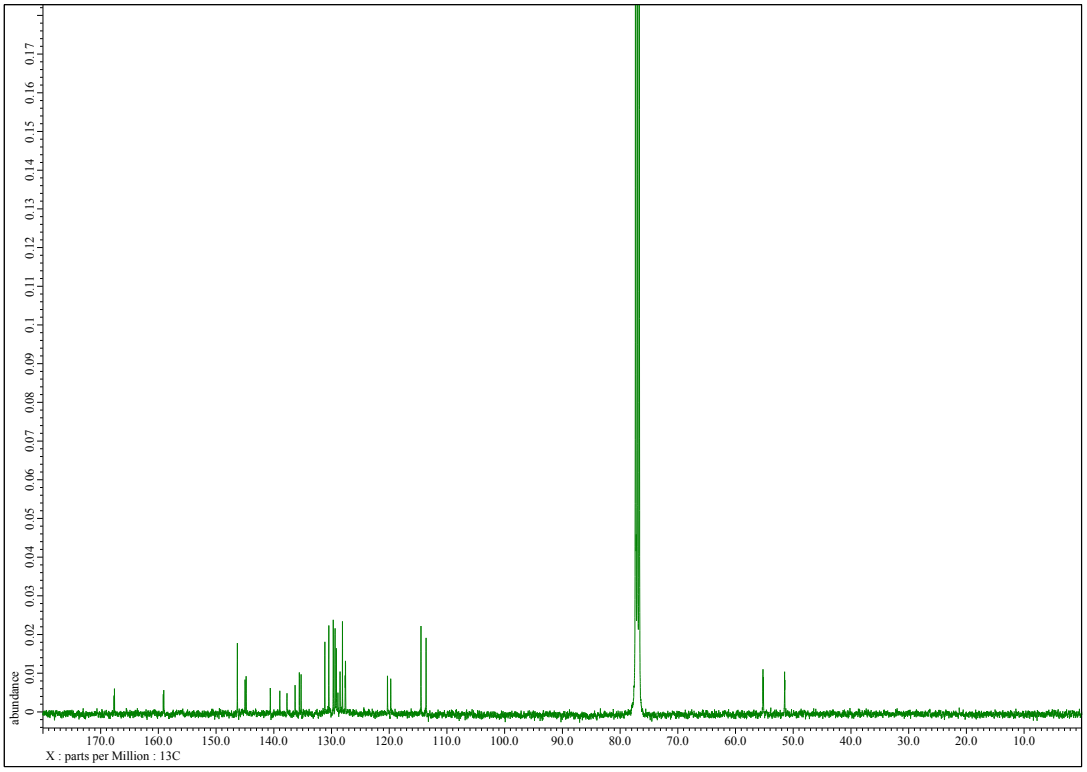


Figure S26. $^{13}C\{^{1}H\}$ NMR Spectrum of 4da and 5da in $CDCl_3$.

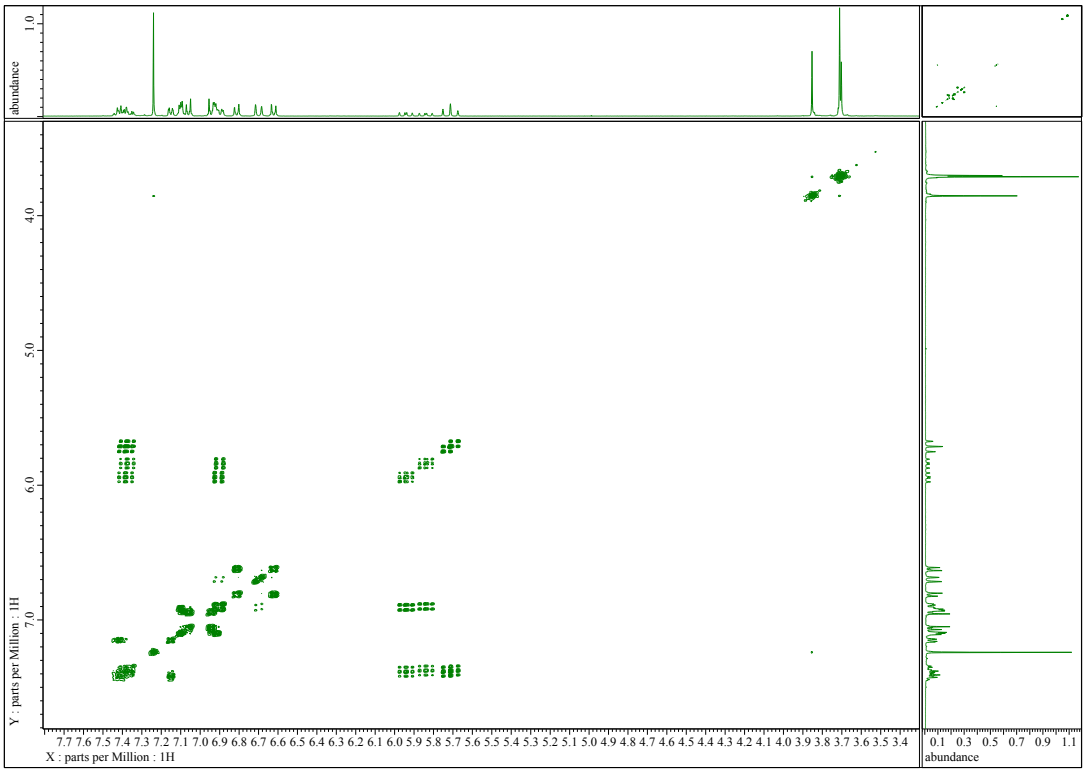


Figure S27. ^{1}H-^{1}H COSY NMR Spectrum of 4da and 5da in $CDCl_3$.

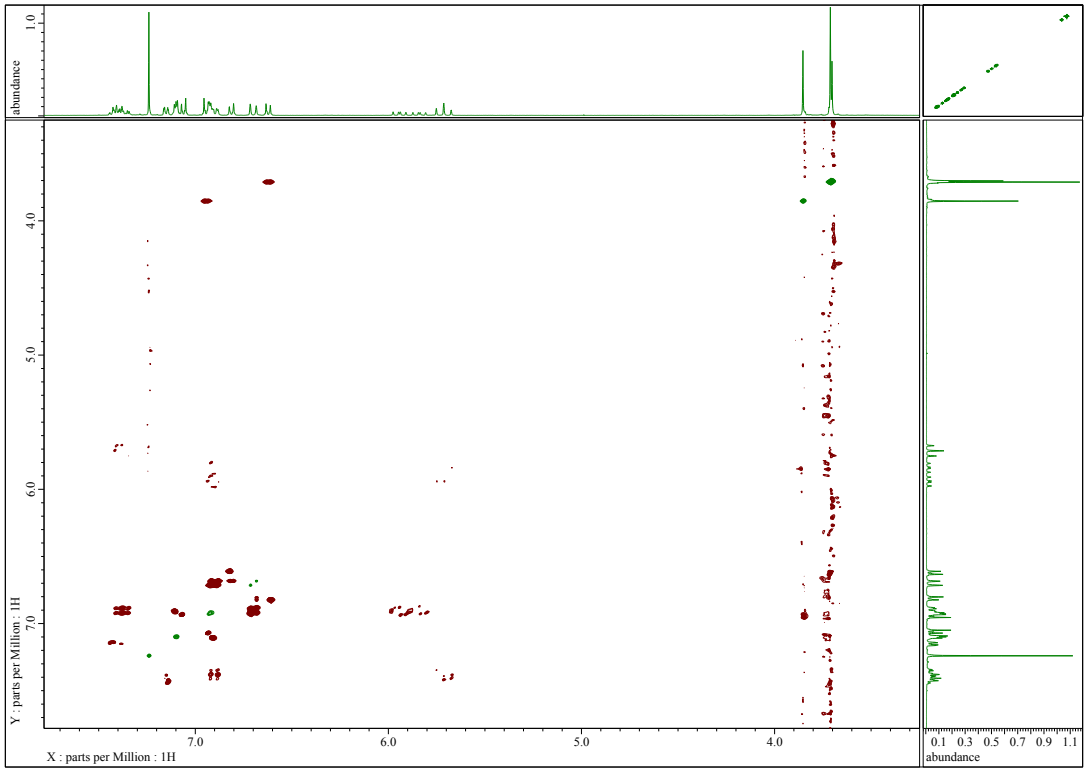


Figure S28. ^{1}H-^{1}H pNOESY NMR Spectrum of 4da and 5da in $CDCl_3$.

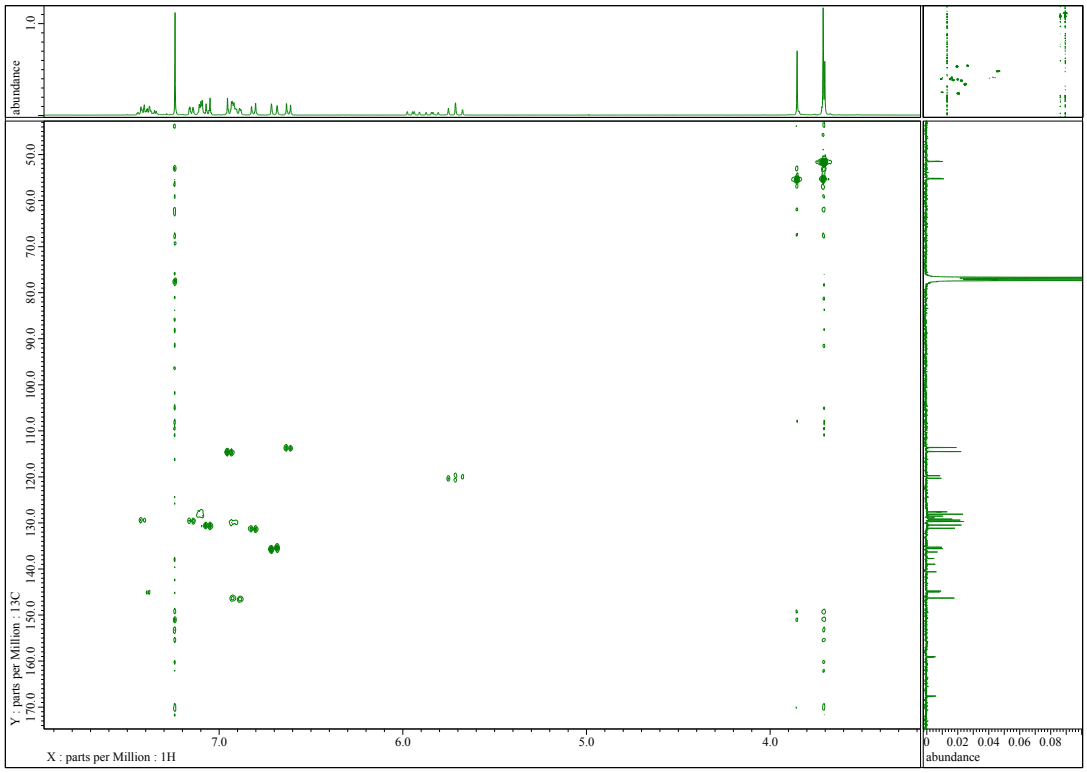


Figure S29. ^{13}C-^{1}H Correlation Spectrum of 4da and 5da in $CDCl_3$.

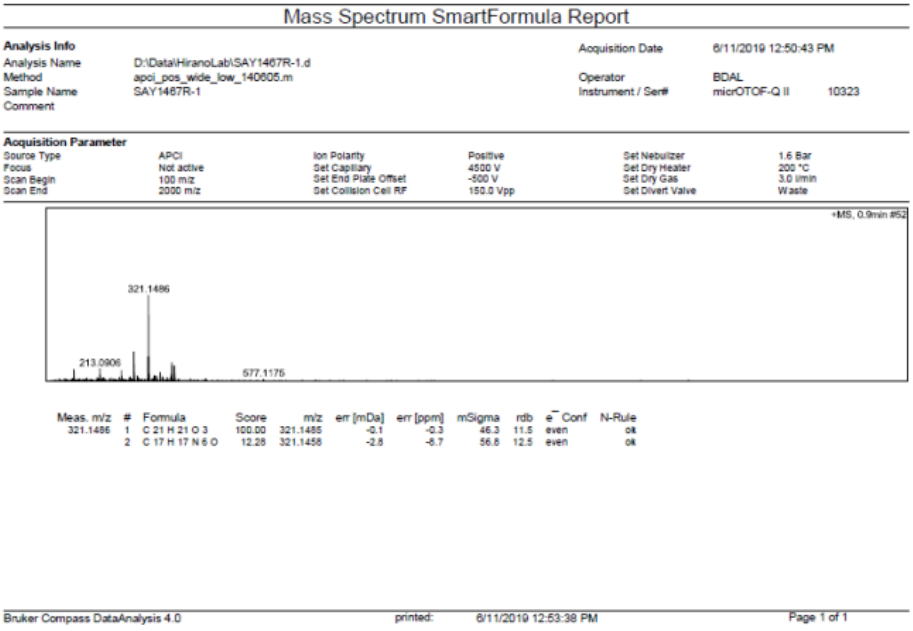


Figure S30. HRMS (APCI) data for 4da and 5da.

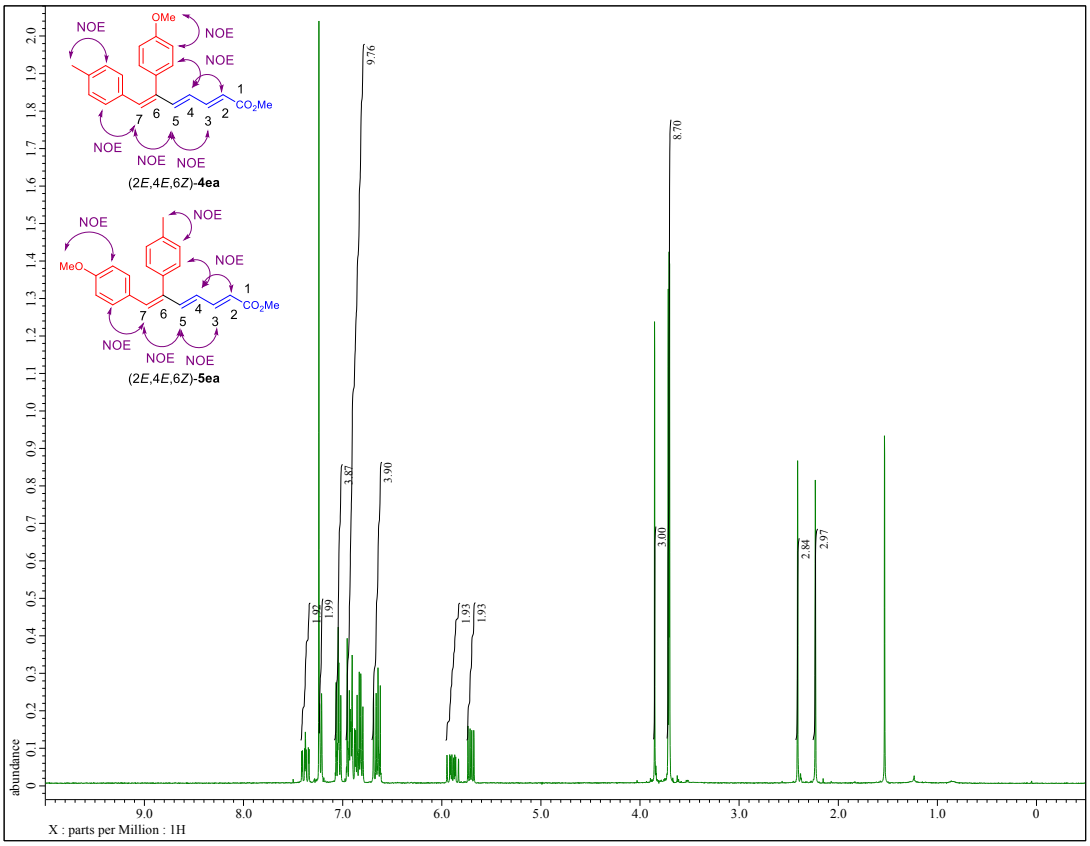


Figure S31. ^{1}H NMR Spectrum of 4ea and 5ea in $CDCl_3$.

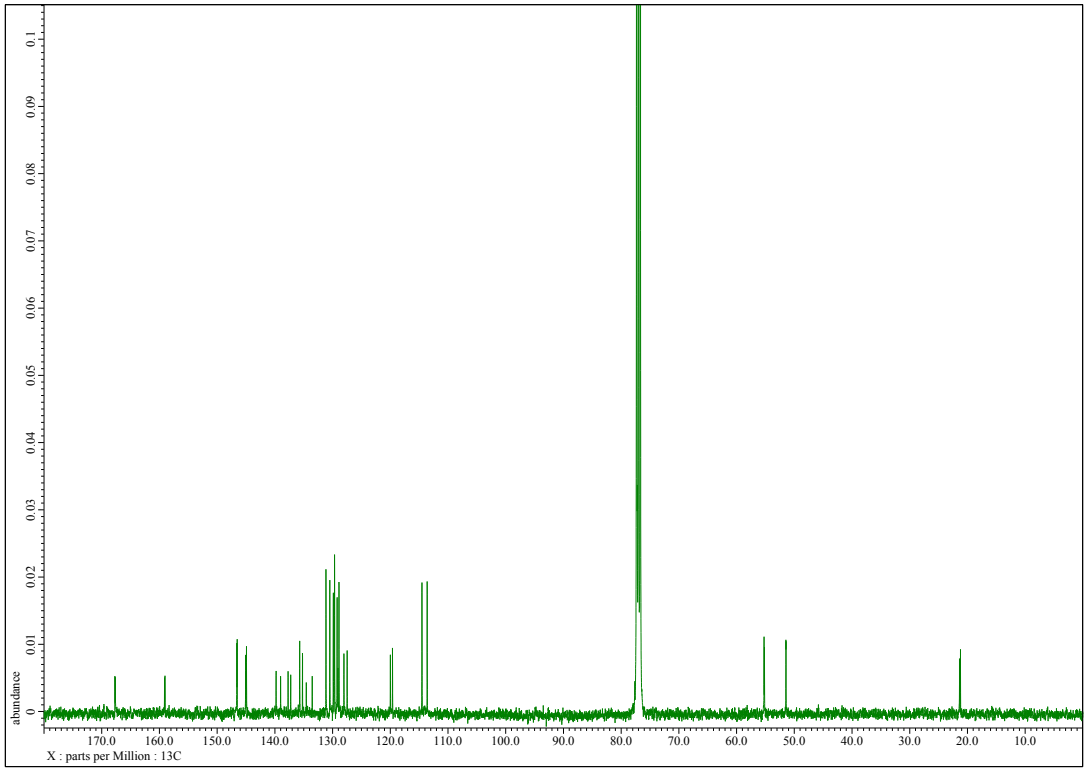


Figure S32. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ea and 5ea in $CDCl_3$.

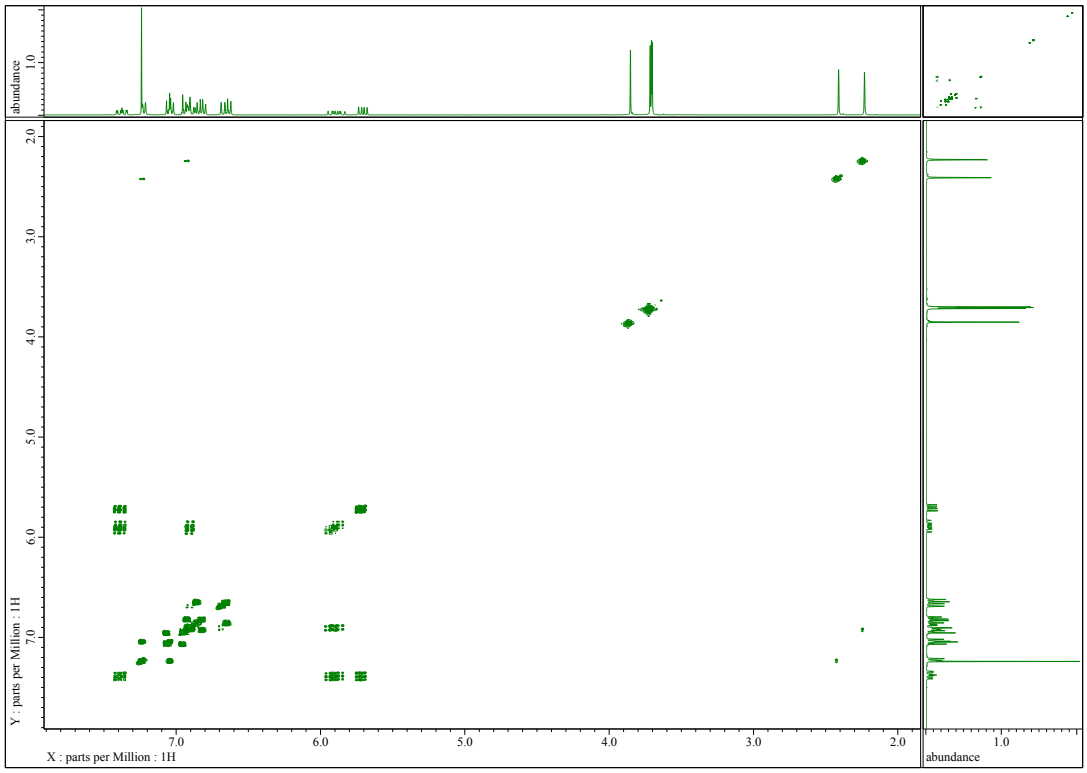


Figure S33. ^{1}H-^{1}H COSY NMR Spectrum of 4ea and 5ea in $CDCl_3$.

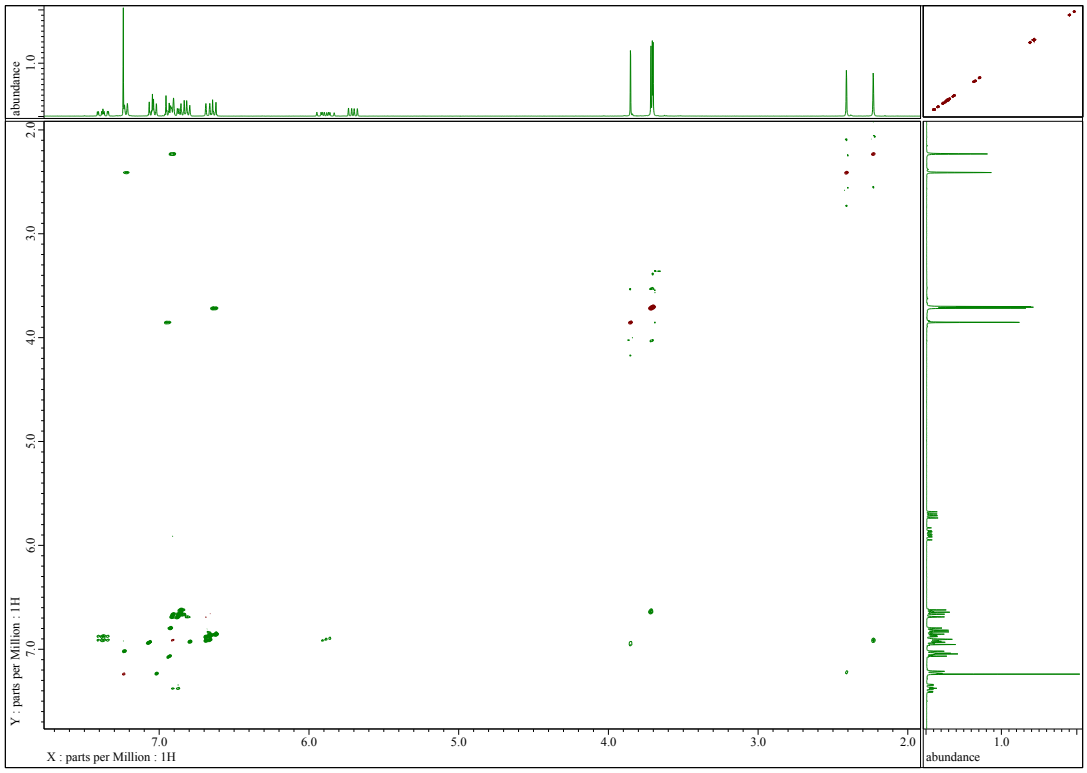


Figure S34. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ea and 5ea in $CDCl_3$.

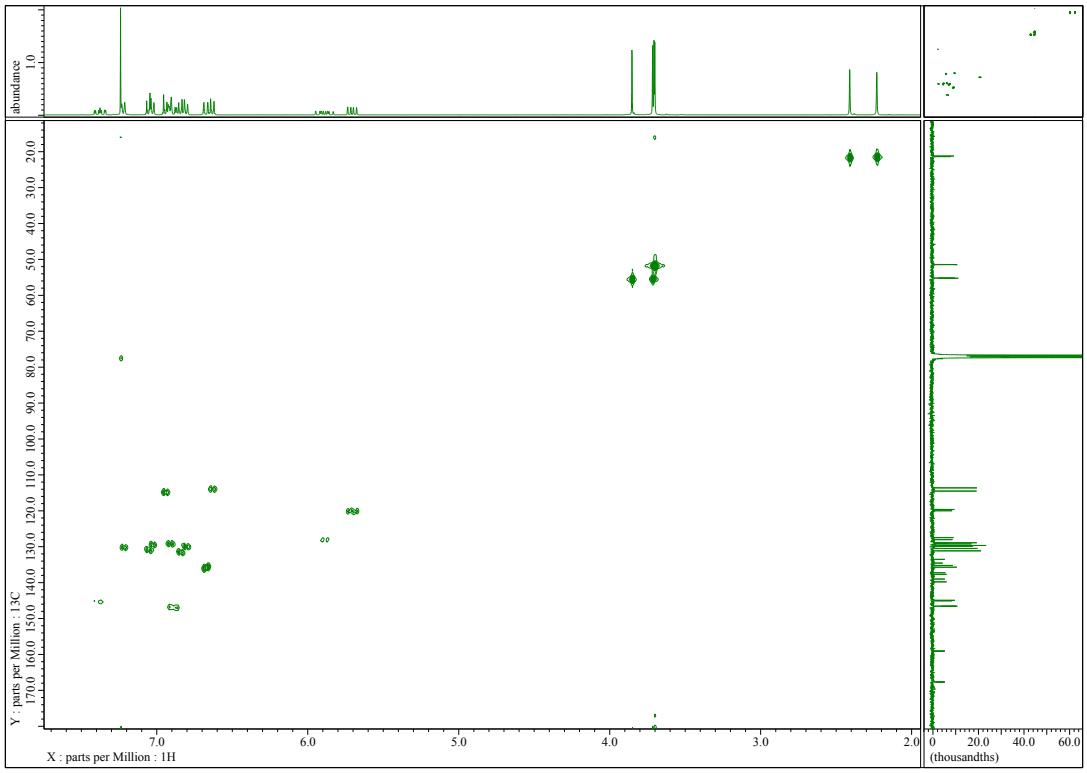


Figure S35. ^{13}C-^{1}H Correlation Spectrum of 4ea and 5ea in $CDCl_3$.

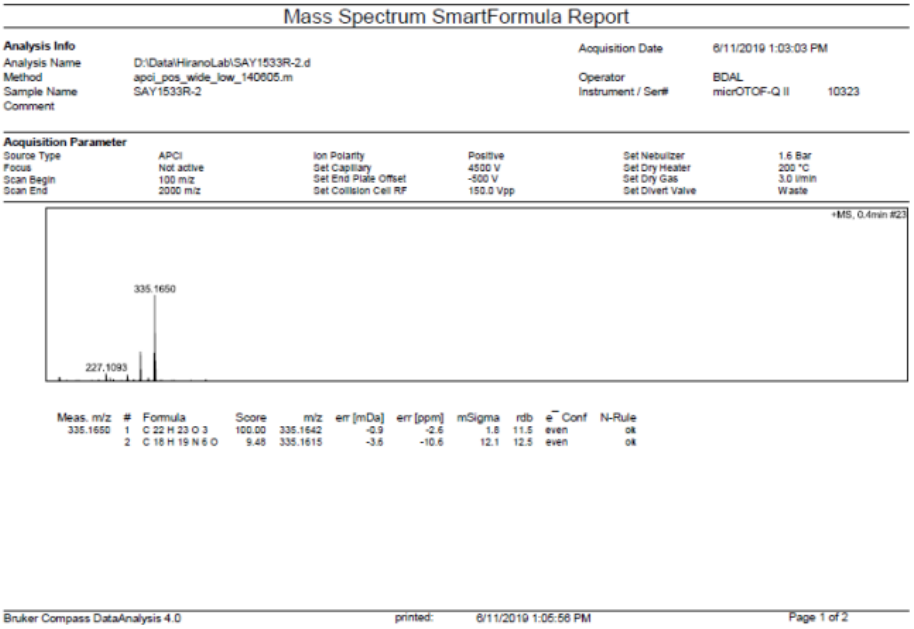


Figure S36. HRMS (APCI) data for 4ea and 5ea in $CDCl_3$.

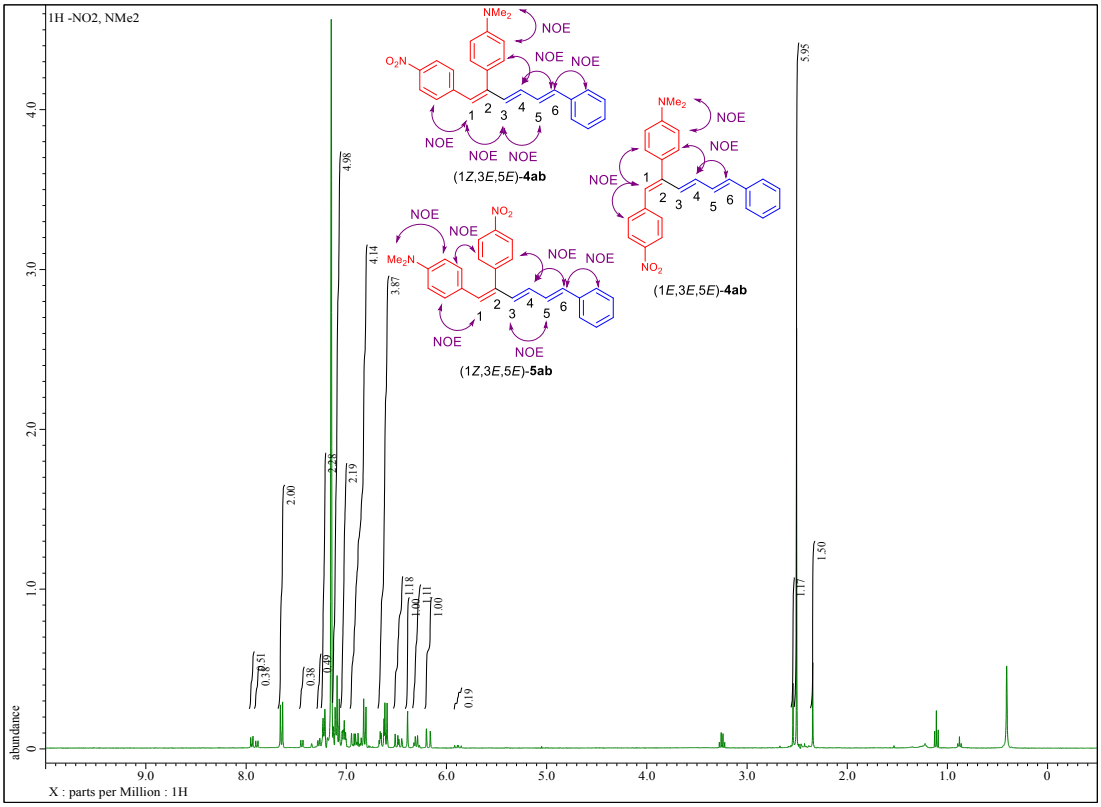


Figure S37. ^{1}H NMR Spectrum of 4ab and 5ab in C_6D_6.

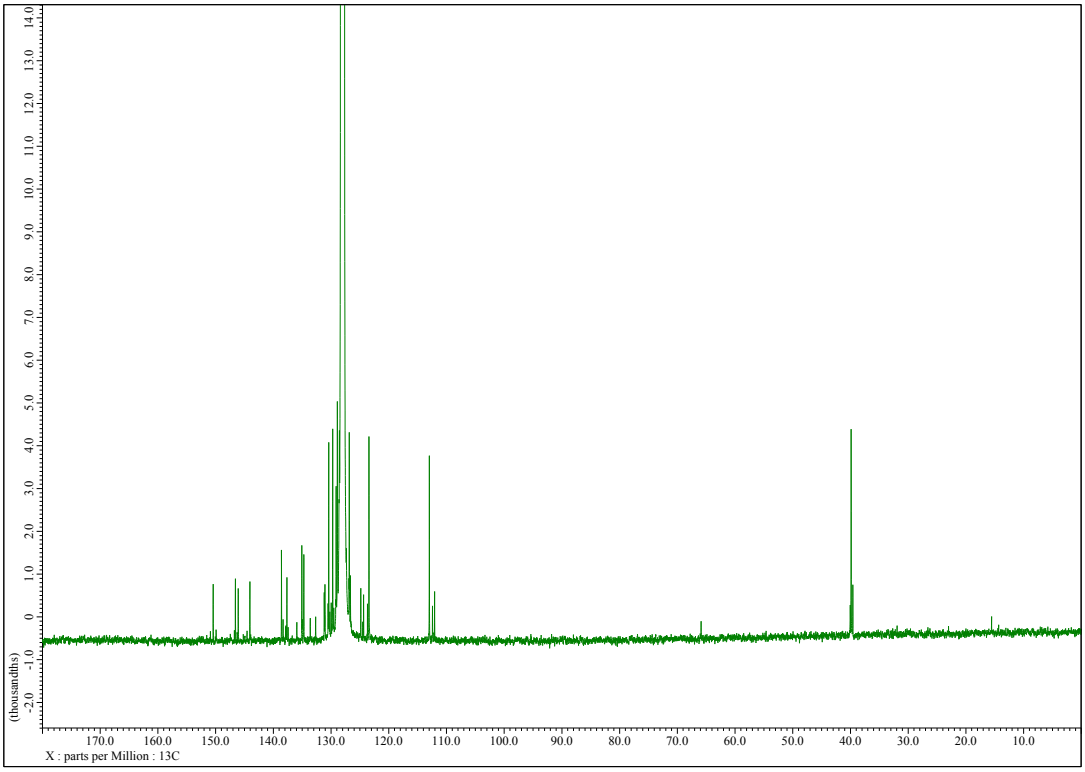


Figure S38. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ab and 5ab in C_6D_6.

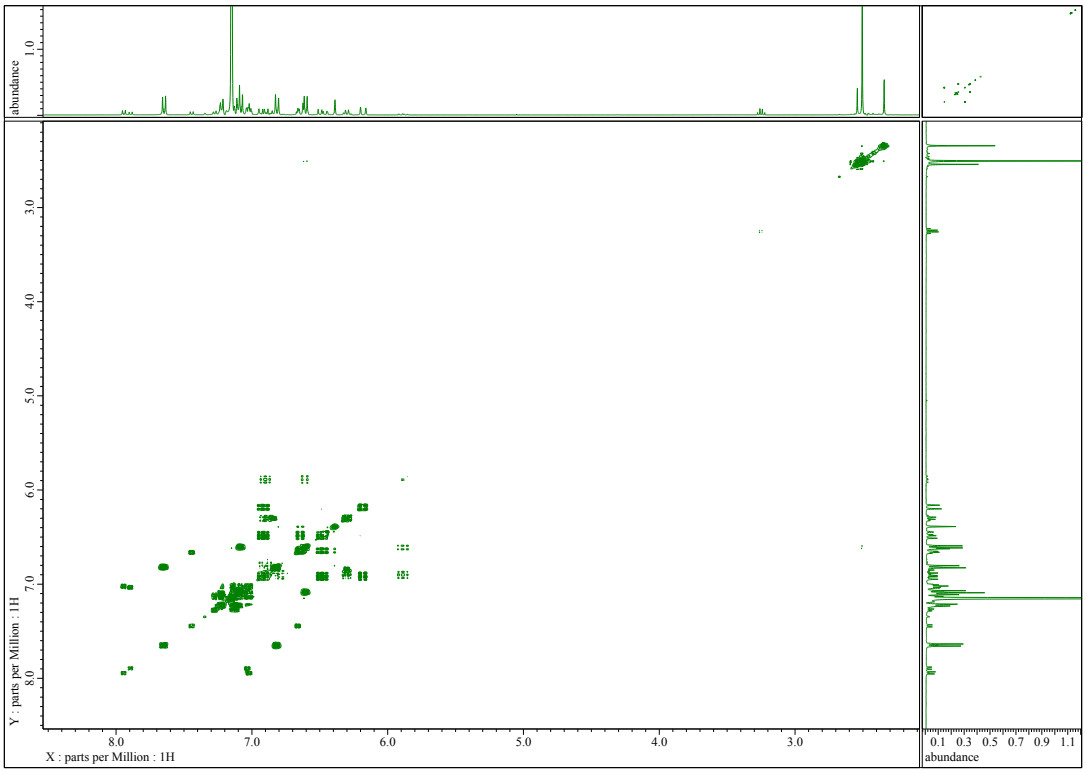


Figure S39. ^{1}H-^{1}H COSY NMR Spectrum of 4ab and 5ab in C_6D_6.

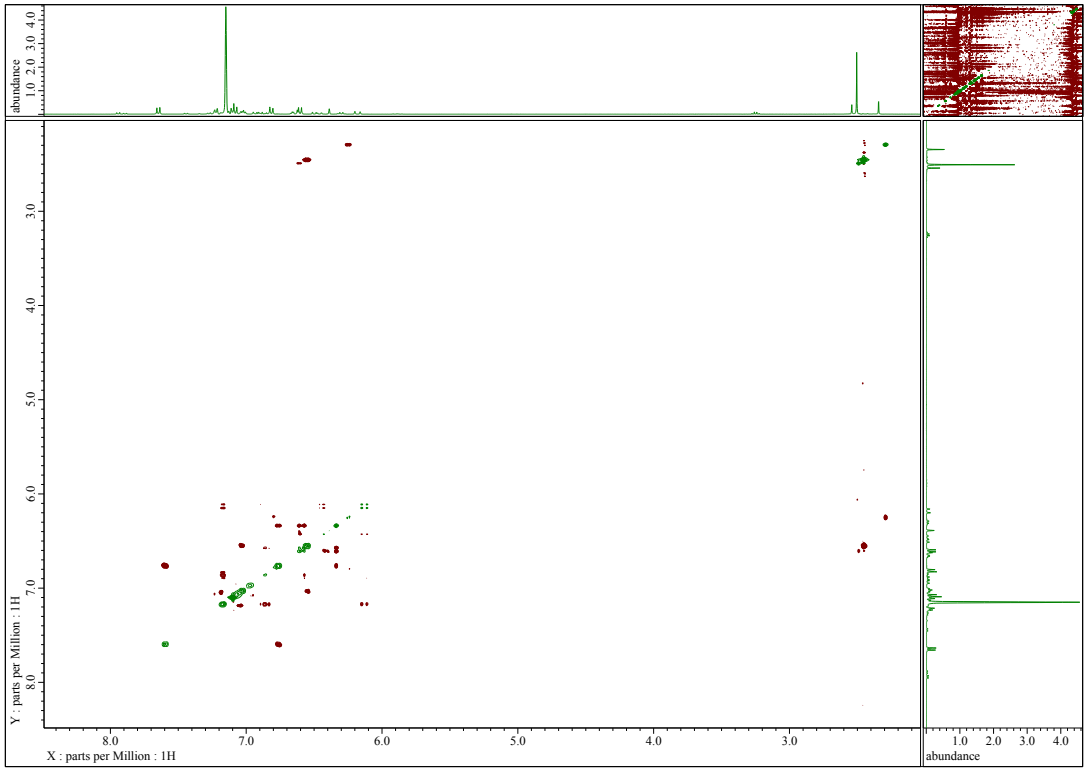


Figure S40. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ab and 5ab in C_6D_6.

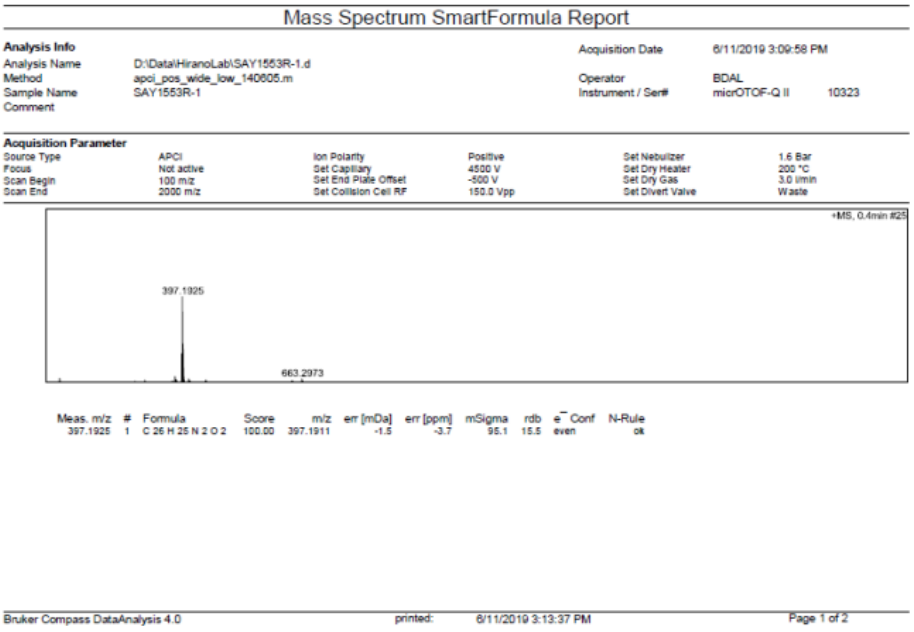


Figure S41. HRMS (APCI) data for 4ab and 5ab.

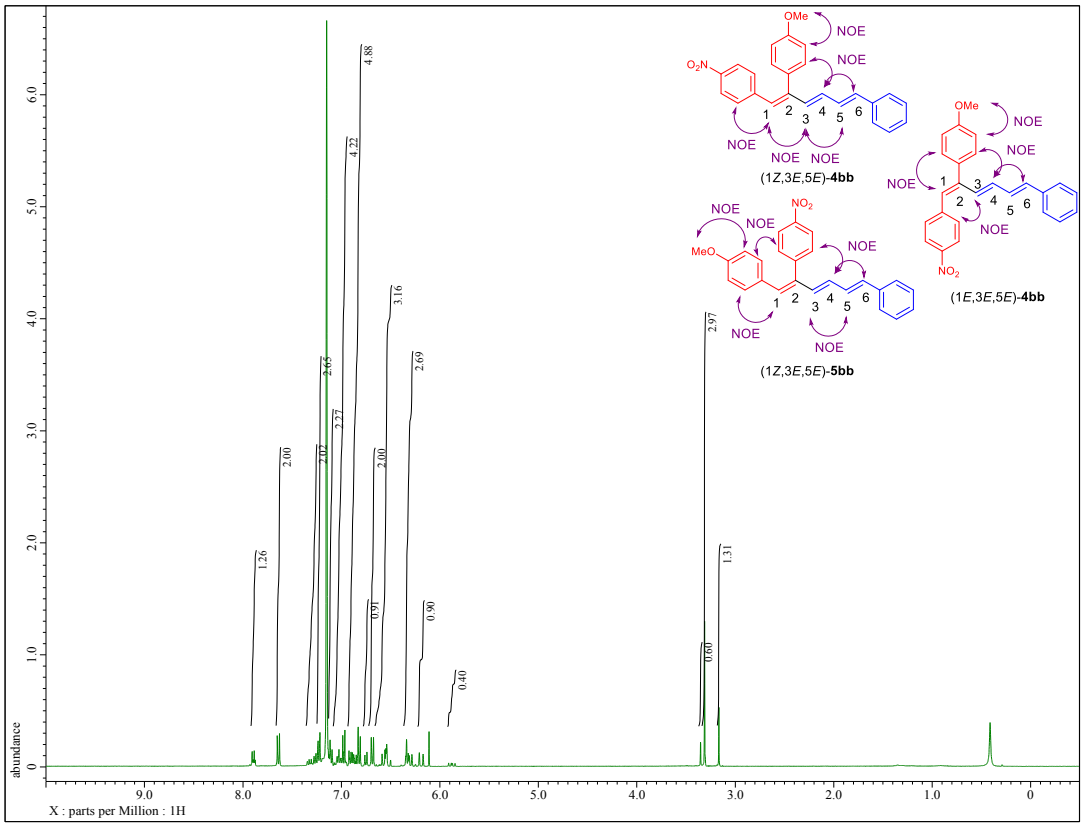


Figure S42. ^{1}H NMR Spectrum of 4bb and 5bb in C_6D_6.

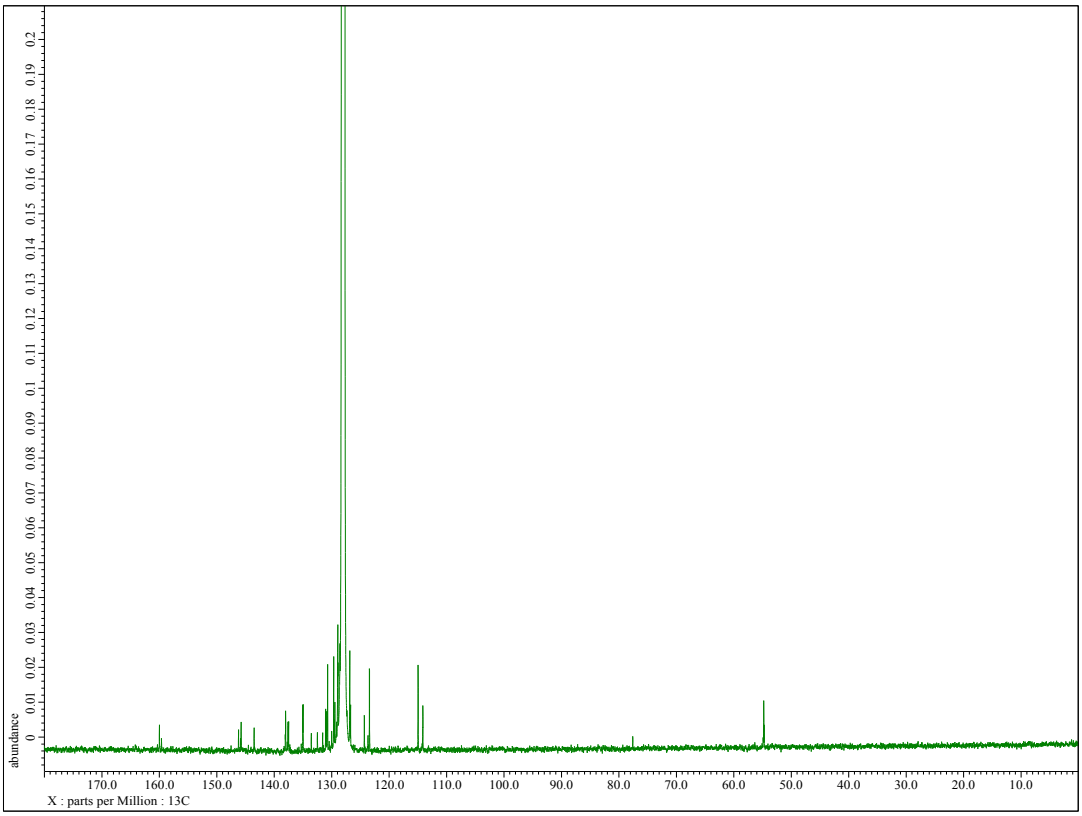


Figure S43. $^{13}C\{^{1}H\}$ NMR Spectrum of 4bb and 5bb in C_6D_6.

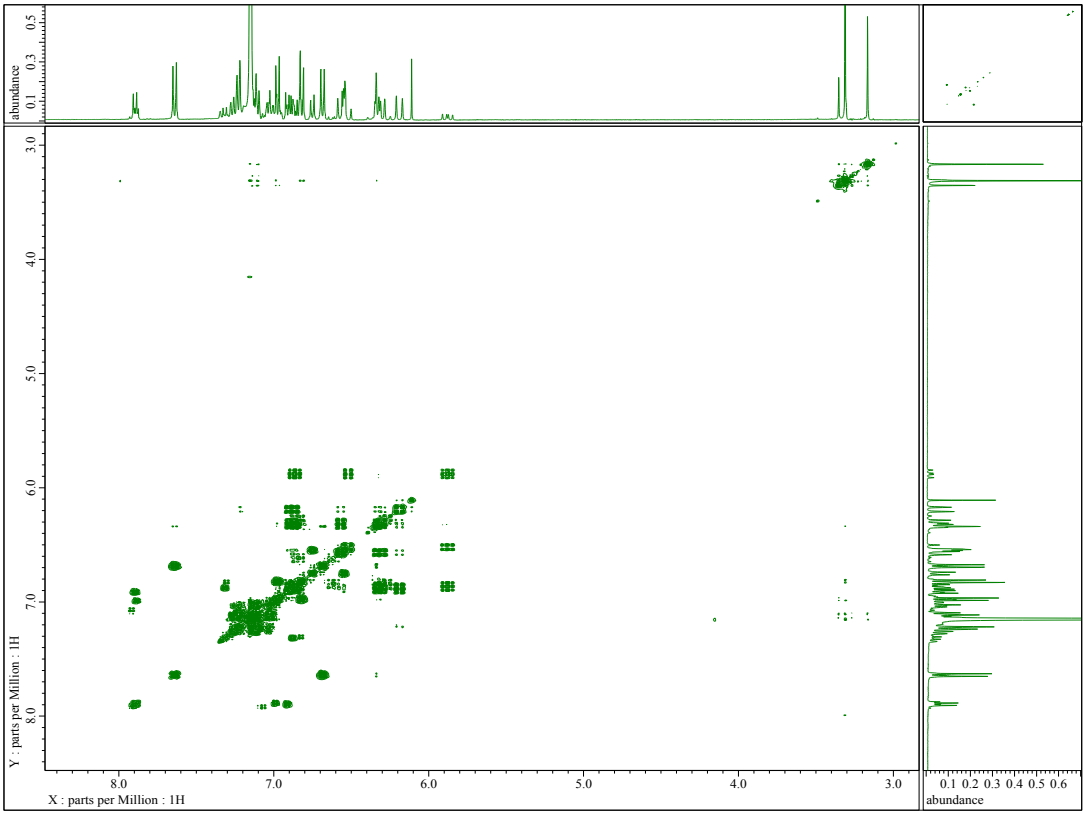


Figure S44. ^{1}H-^{1}H COSY NMR Spectrum of 4bb and 5bb in C_6D_6.

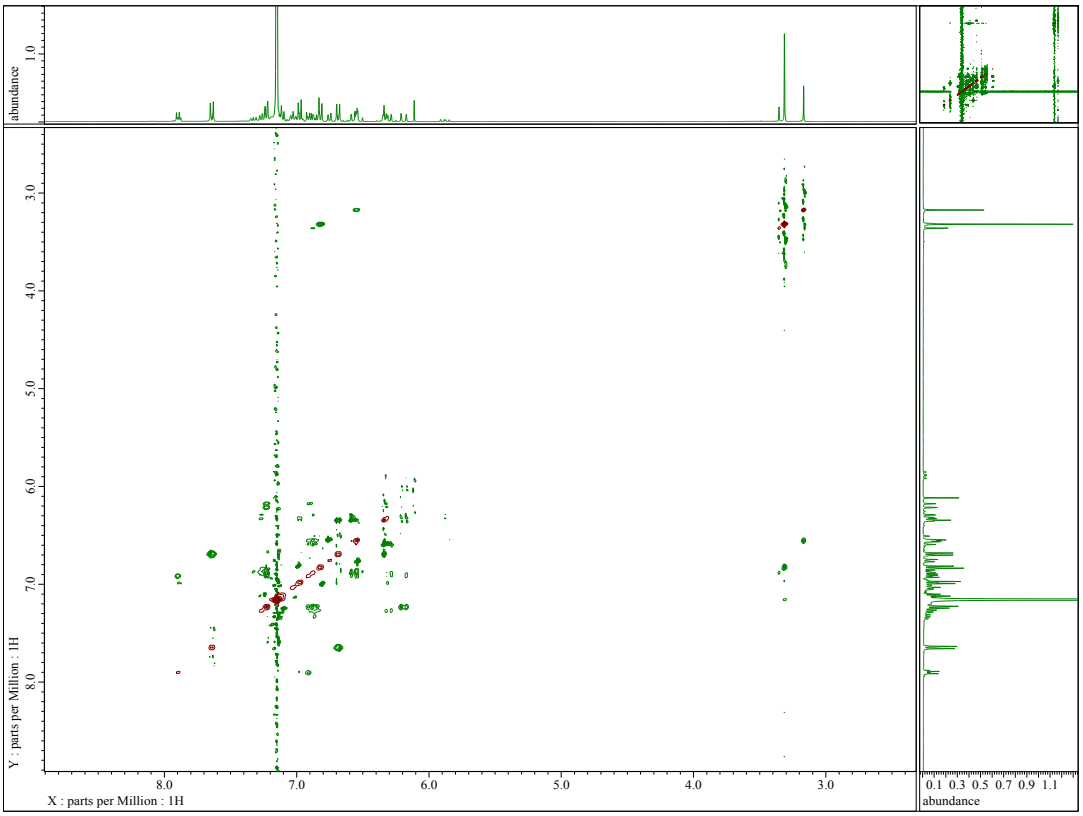


Figure S45. ^{1}H-^{1}H pNOESY NMR Spectrum of 4bb and 5bb in C_6D_6.

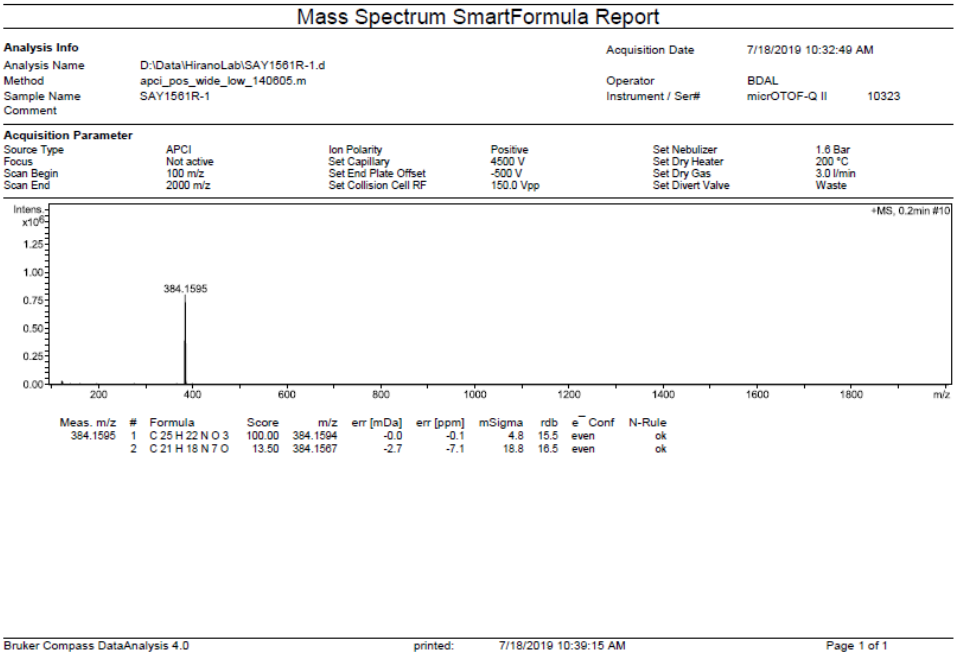


Figure S46. HRMS (APCI) data for 4bb and 5bb.

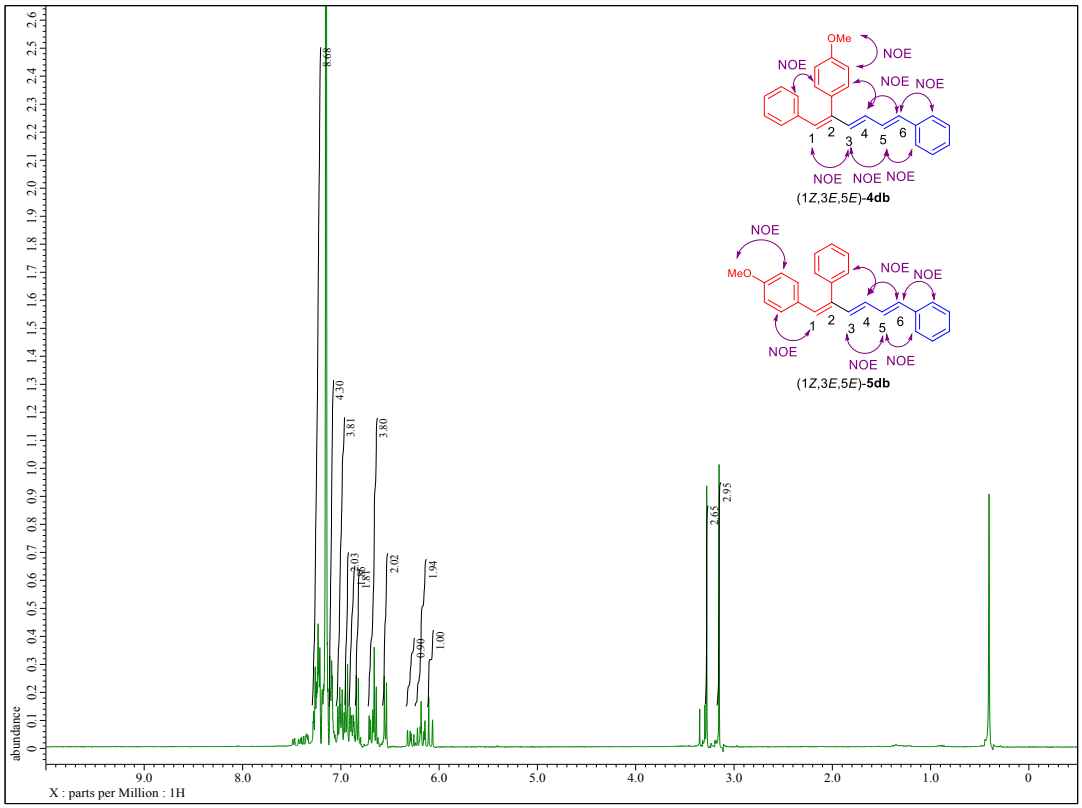


Figure S47. ^{1}H NMR Spectrum of 4db and 5db in C_6D_6.

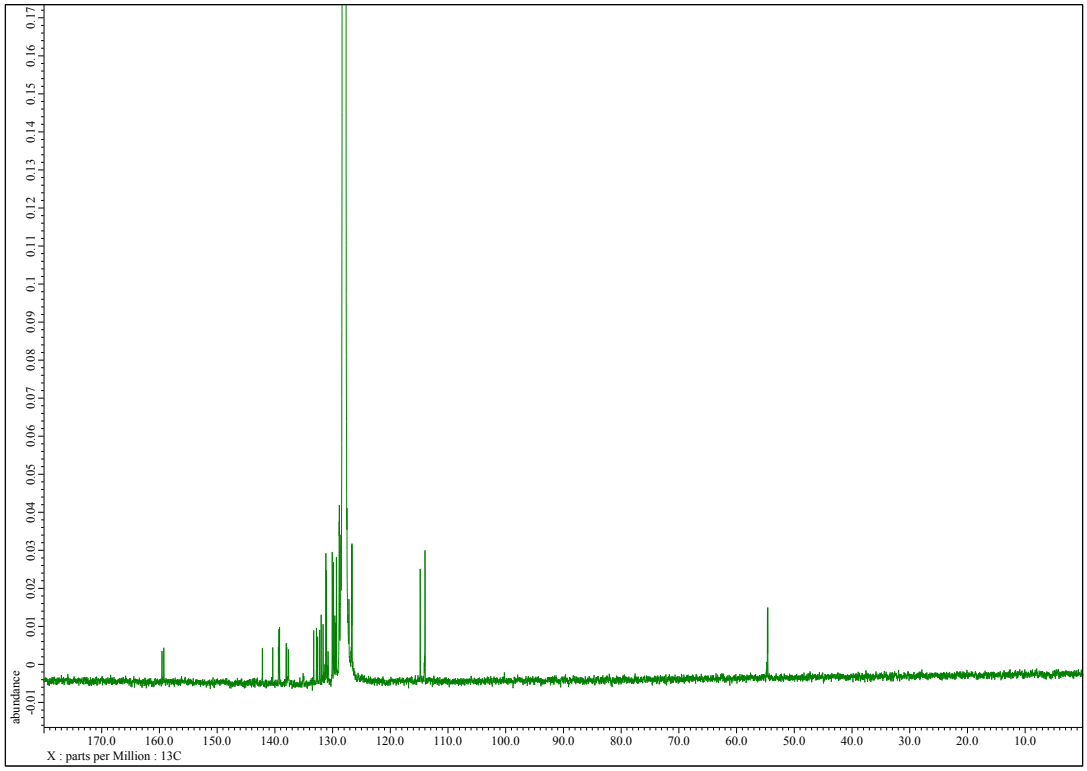


Figure S48. $^{13}C\{^{1}H\}$ NMR Spectrum of 4db and 5db in C_6D_6.

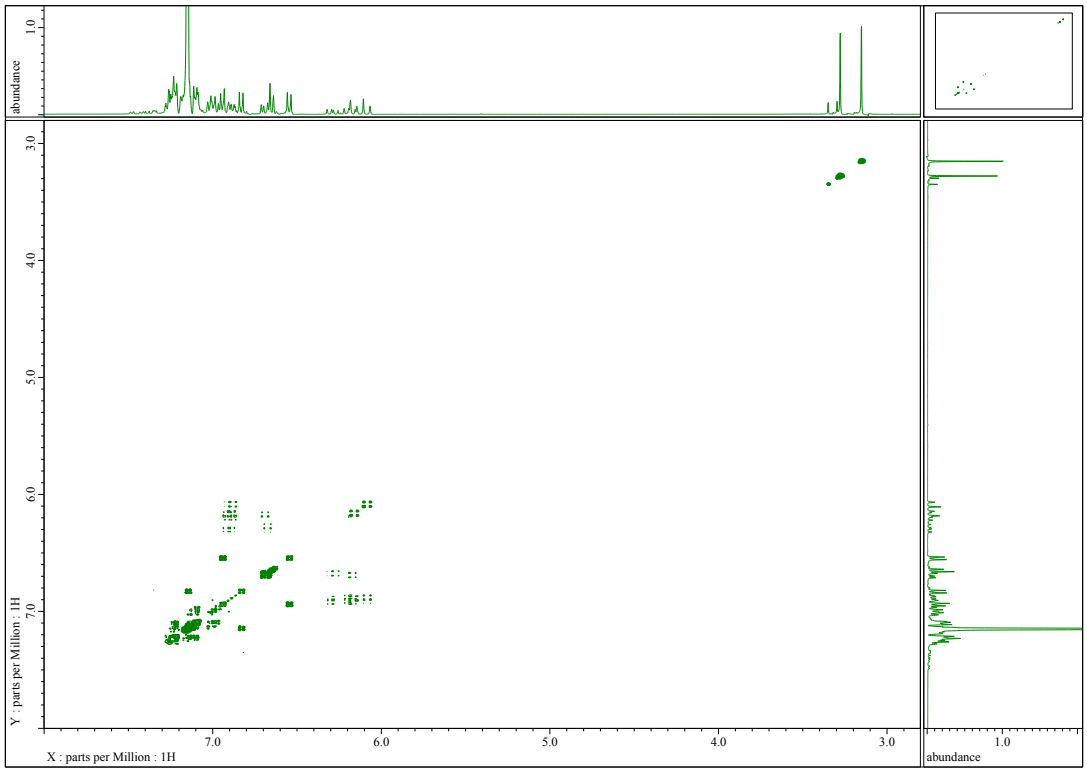


Figure S49. ^{1}H-^{1}H COSY NMR Spectrum of 4db and 5db in C_6D_6.

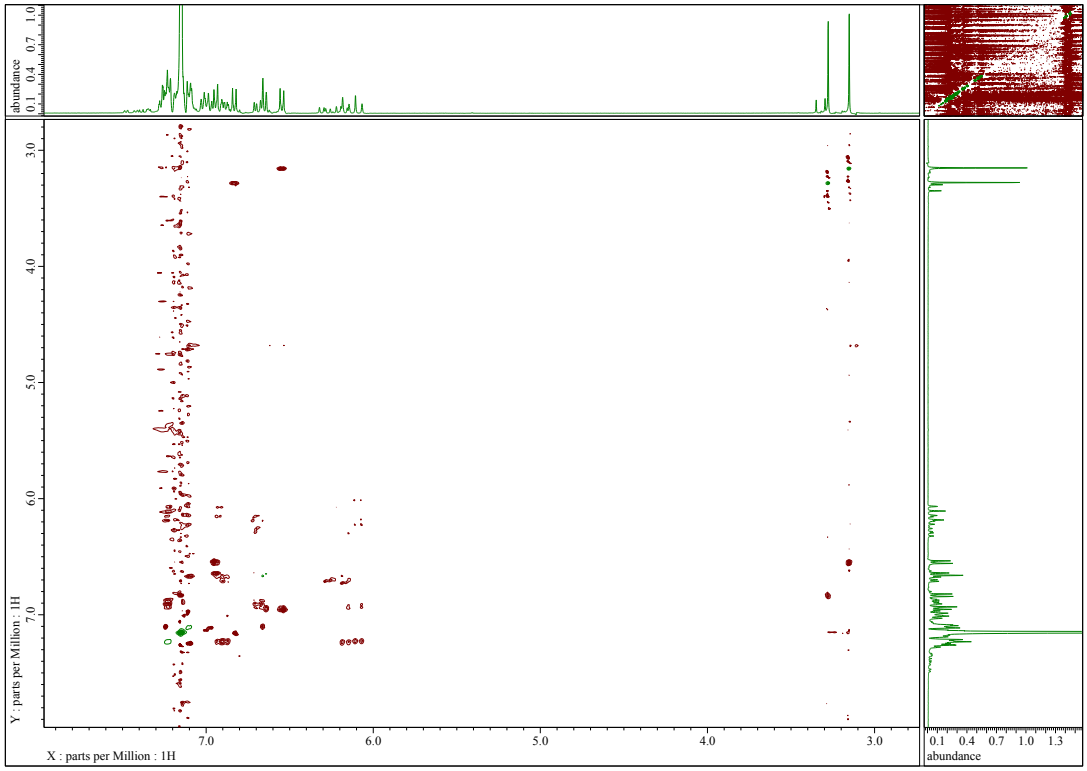


Figure S50. ^{1}H-^{1}H NOESY NMR Spectrum of 4db and 5db in C_6D_6.

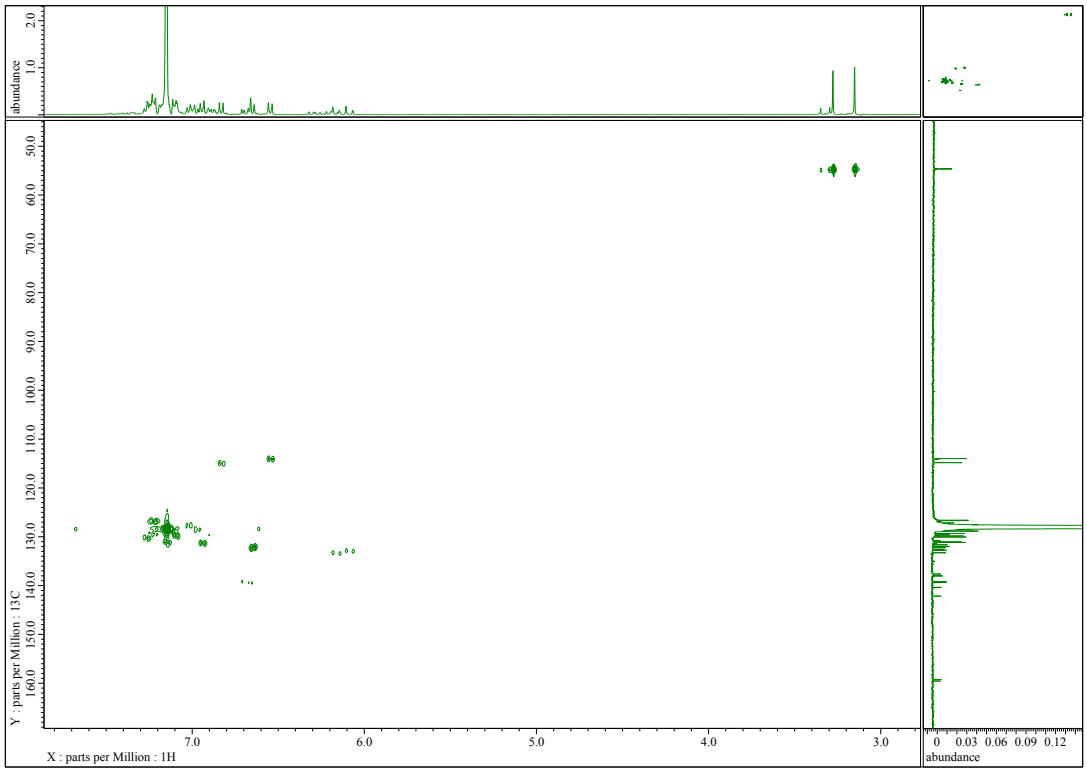


Figure S51. ^{13}C-^{1}H Correlation Spectrum of 4db and 5db in C_6D_6.

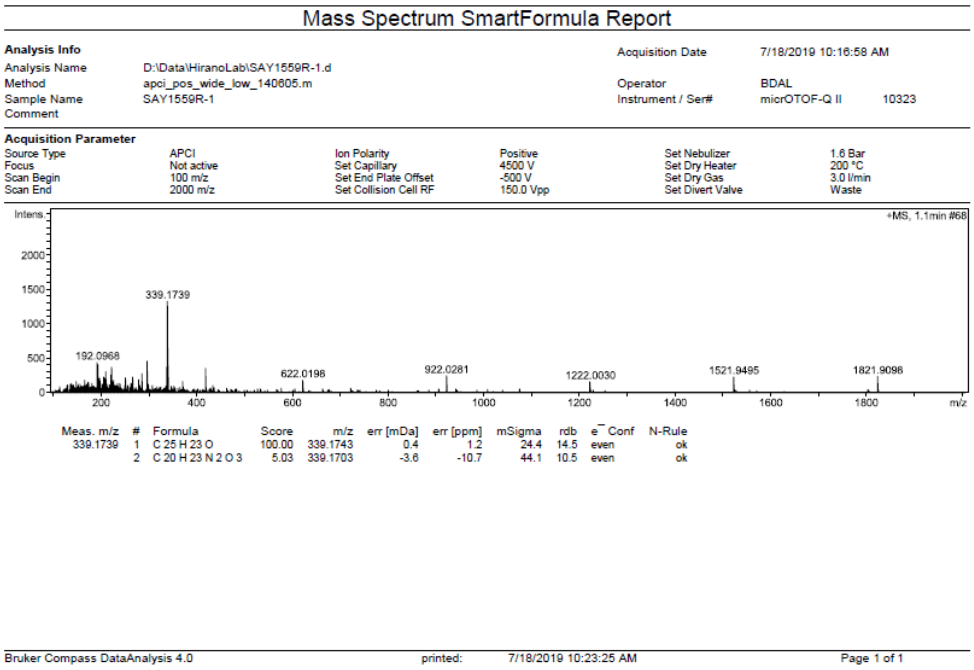


Figure S52. HRMS (APCI) data for 4db and 5db.

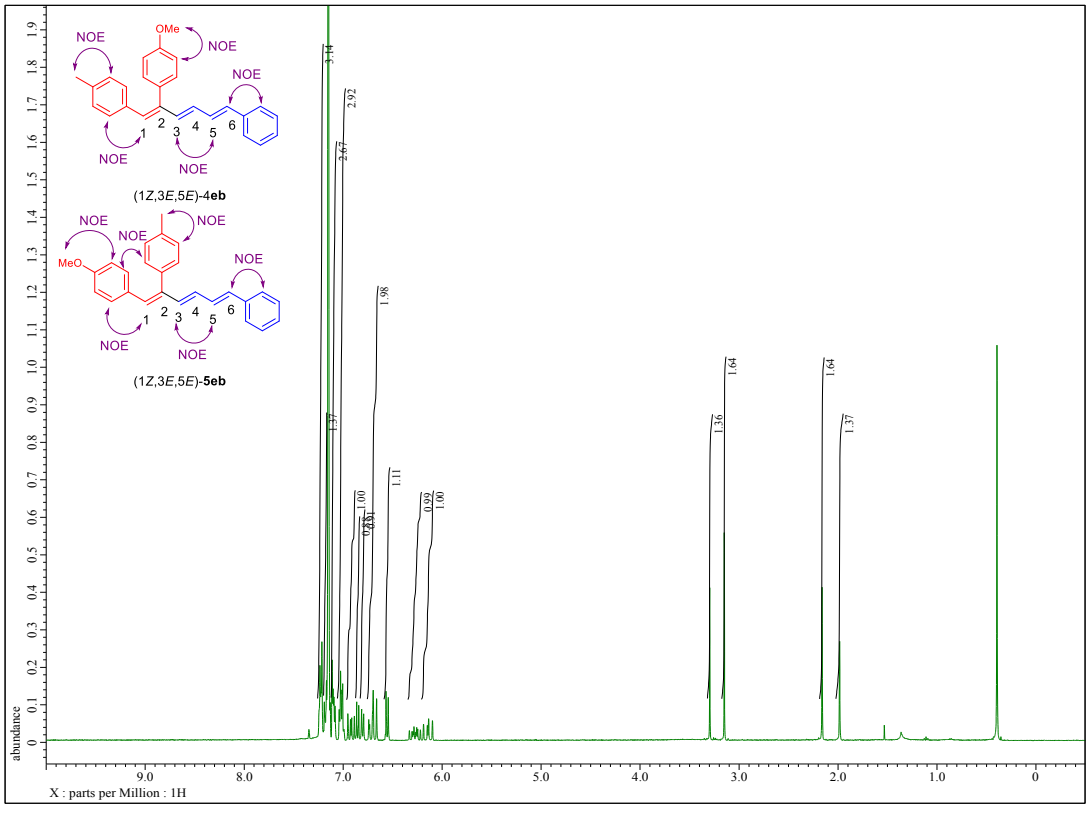


Figure S53. ^{1}H NMR Spectrum of 4eb and 5eb in C_6D_6.

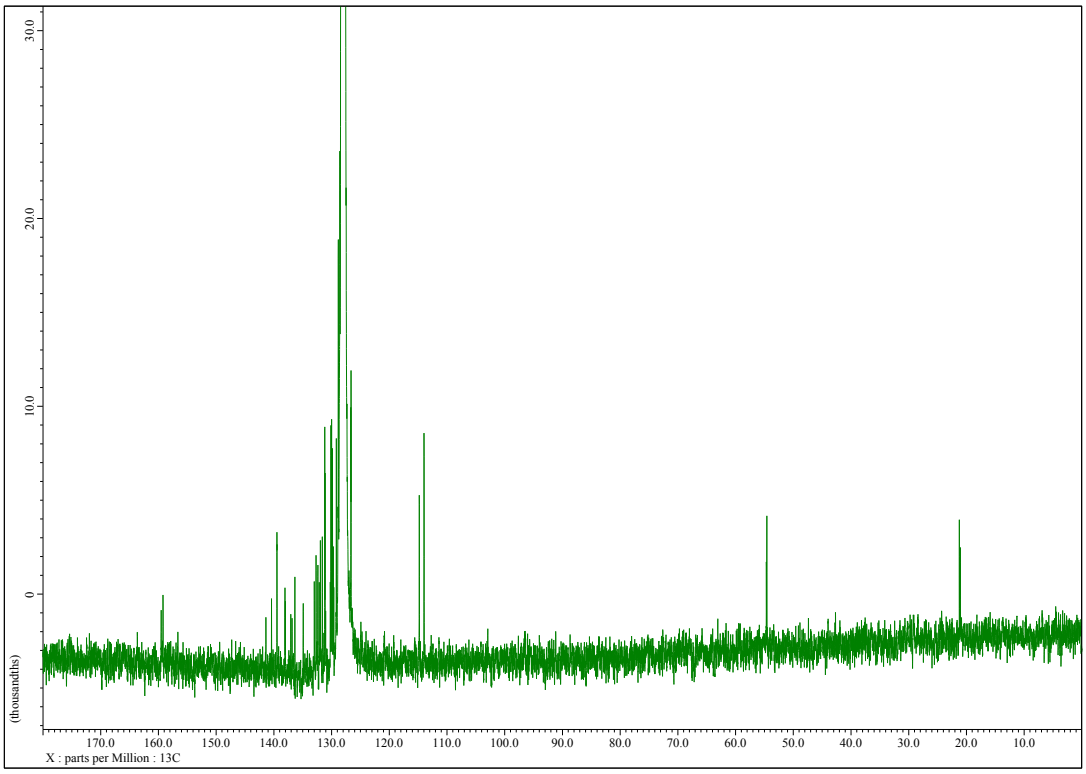


Figure S54. $^{13}C\{^{1}H\}$ NMR Spectrum of 4eb and 5eb in C_6D_6.

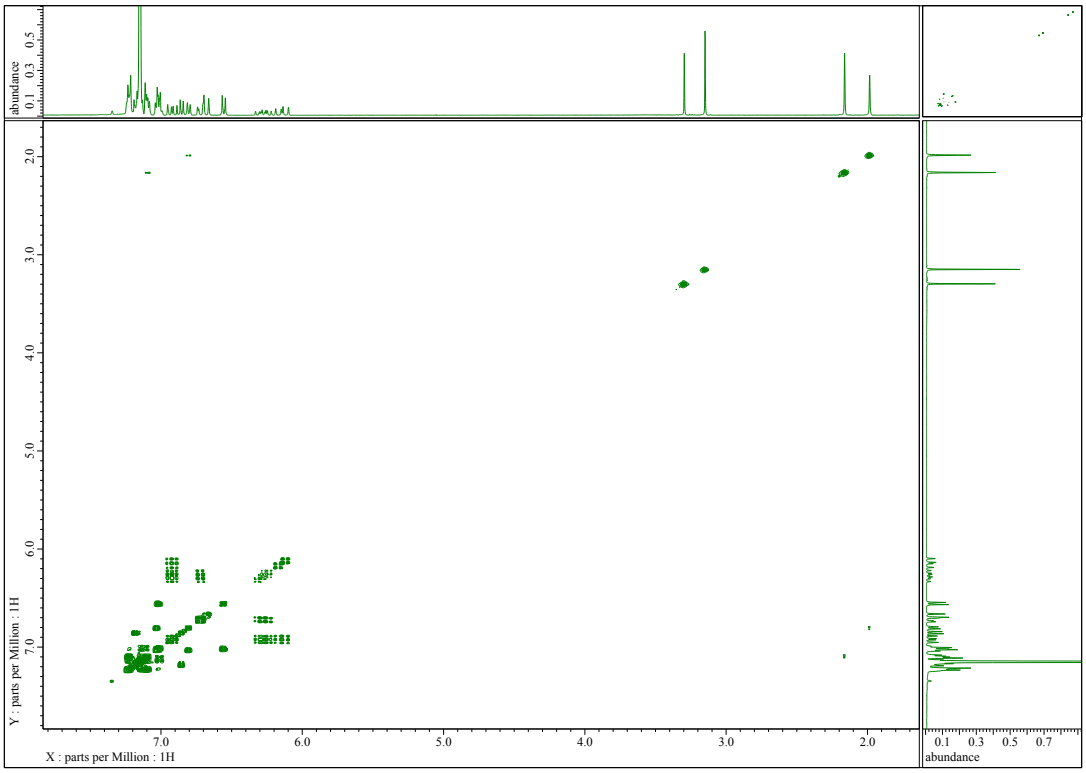


Figure S55. ^{1}H-^{1}H COSY NMR Spectrum of 4eb and 5eb in C_6D_6.

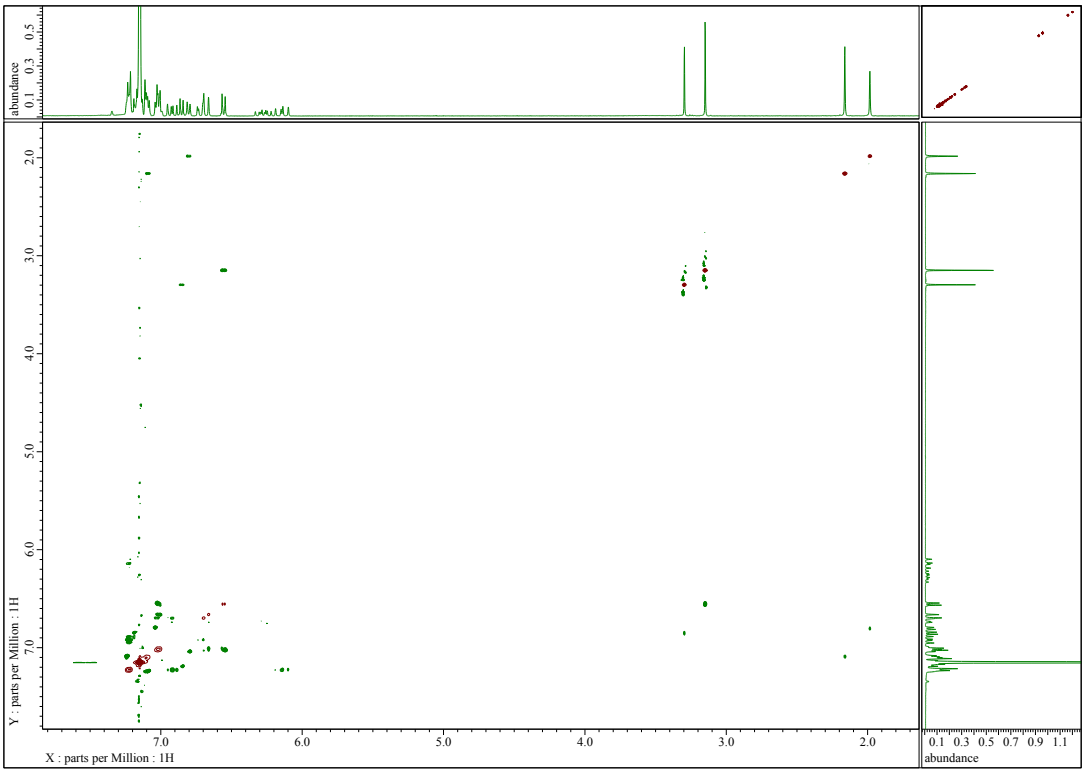


Figure S56. ^{1}H-^{1}H NOESY NMR Spectrum of 4eb and 5eb in C_6D_6.

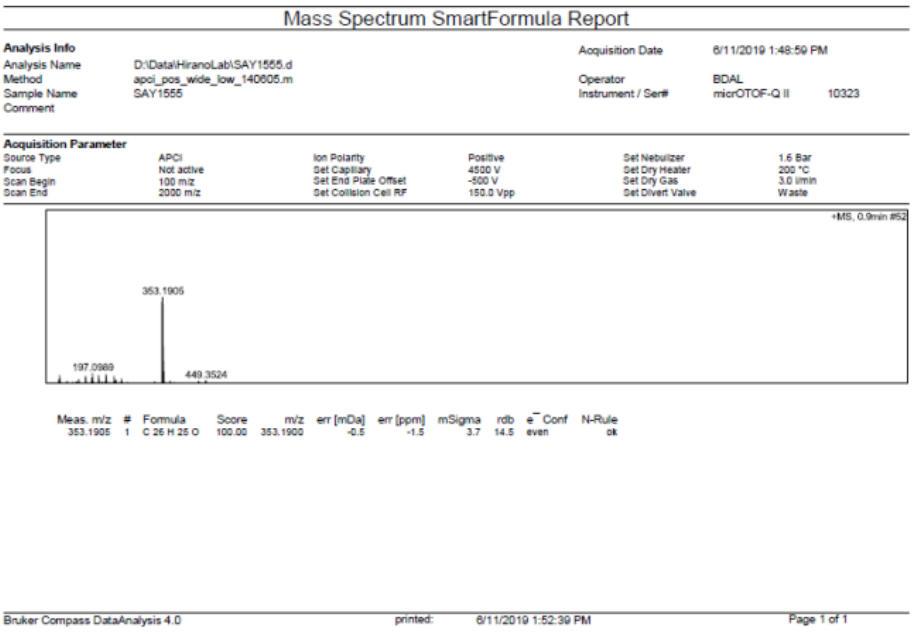


Figure S57. HRMS (APCI) data for 4eb and 5eb.

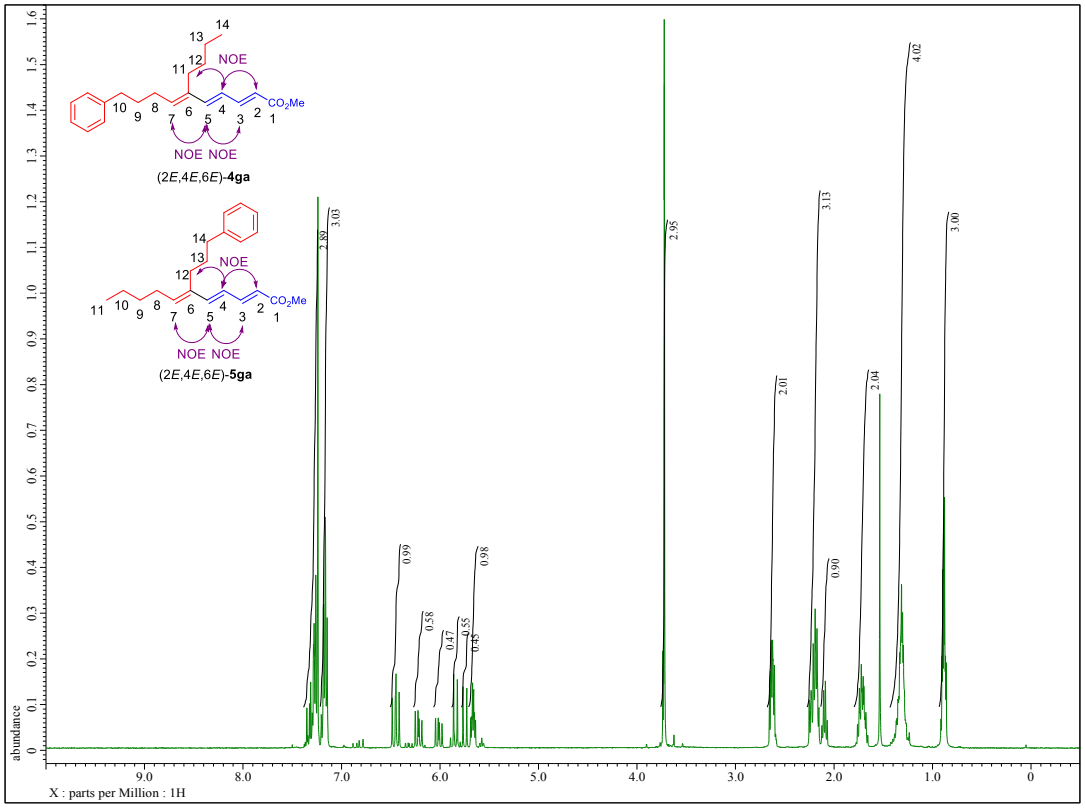


Figure S58. ^{1}H NMR Spectrum of 4ga and 5ga in $CDCl_3$.

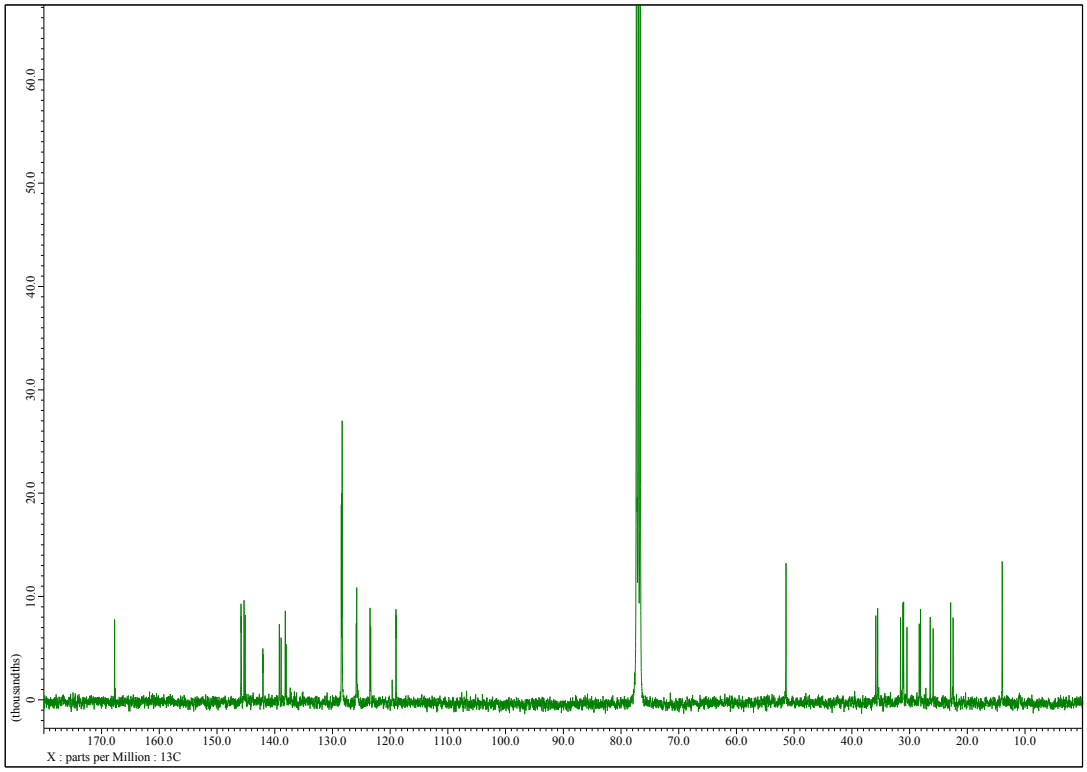


Figure S59. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ga and 5ga in $CDCl_3$.

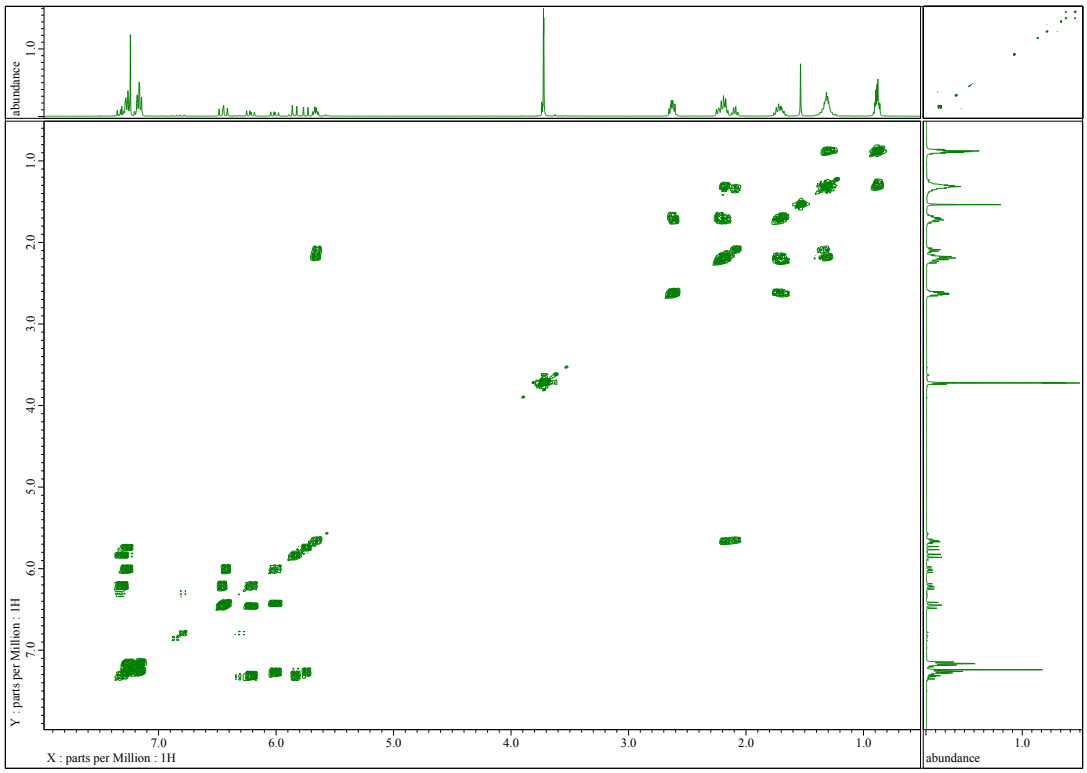


Figure S60. ^{1}H-^{1}H COSY NMR Spectrum of 4ga and 5ga in $CDCl_3$.

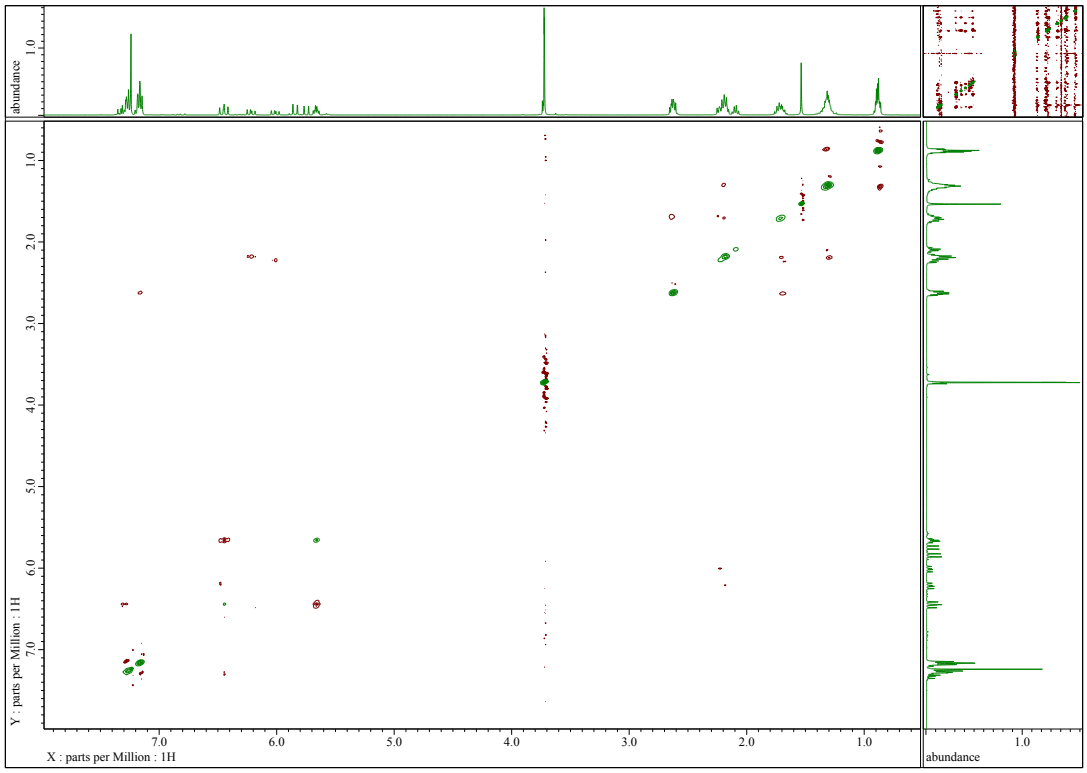


Figure S61. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ga and 5ga in $CDCl_3$.

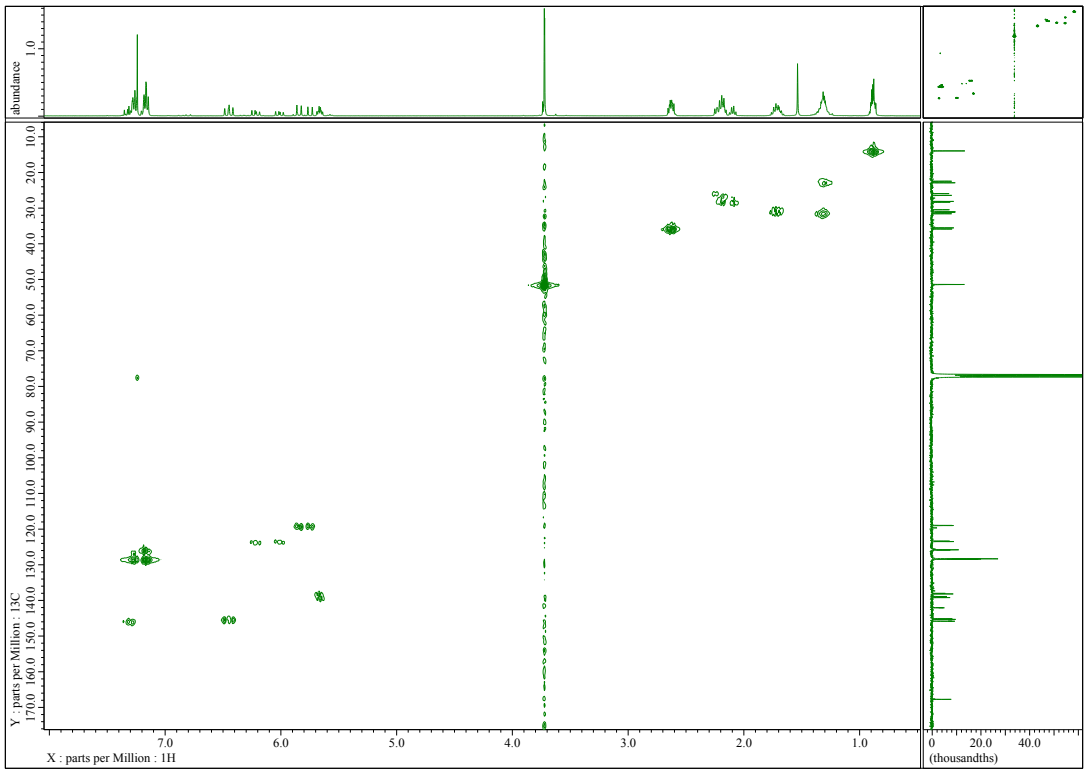


Figure S62. ^{13}C-^{1}H Correlation Spectrum of 4ga and 5ga in $CDCl_3$.

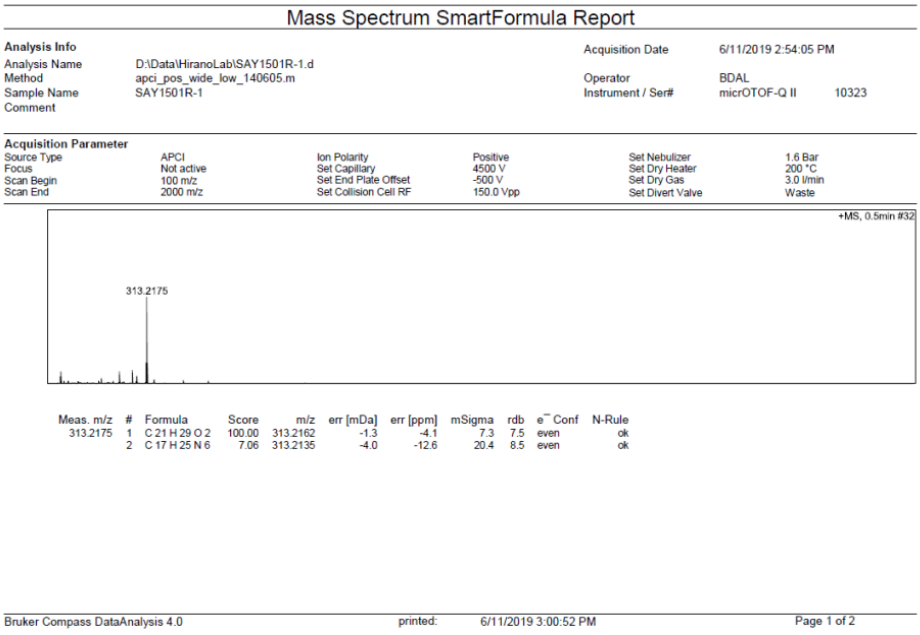


Figure S63. HRMS (APCI) data for 4ga and 5ga.

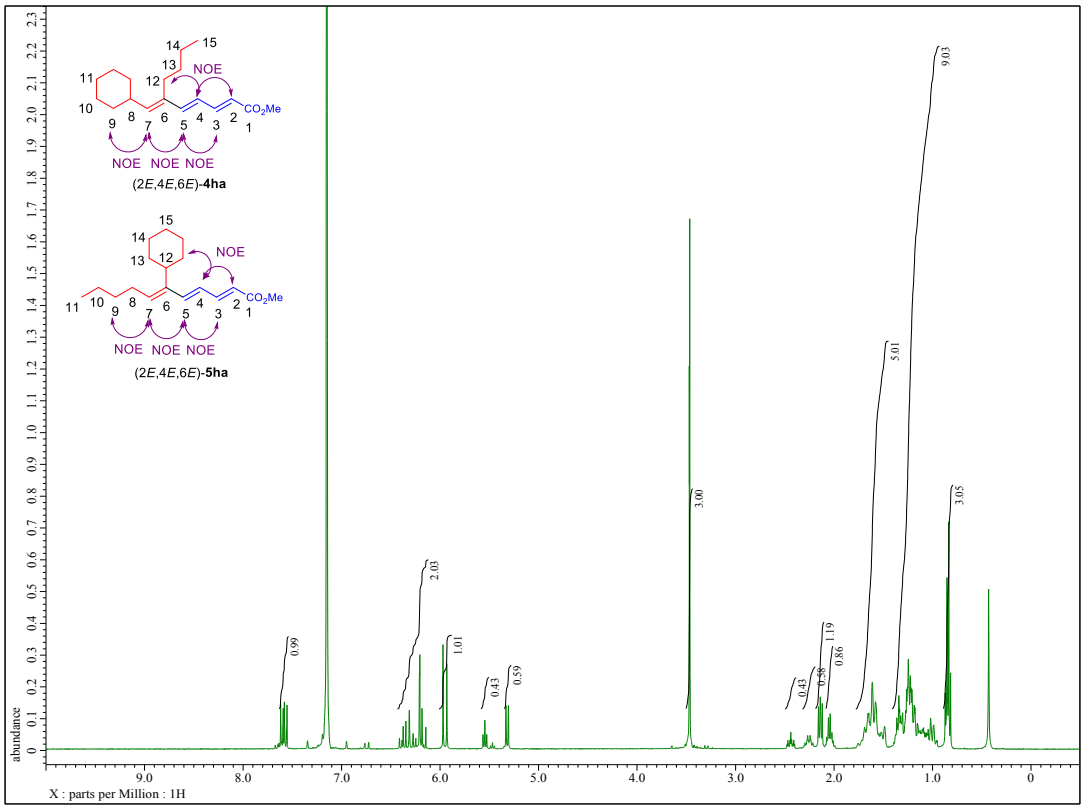


Figure S64. ^{1}H NMR Spectrum of 4ha and 5ha in C_6D_6.

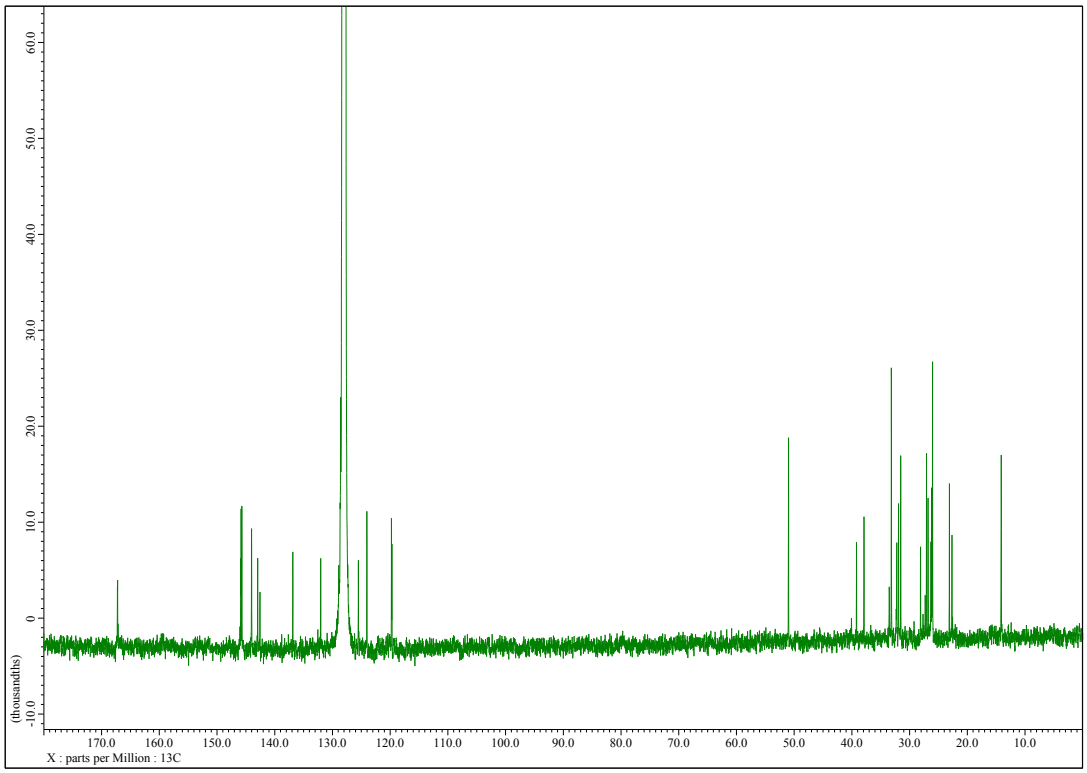


Figure S65. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ha and 5ha in C_6D_6.

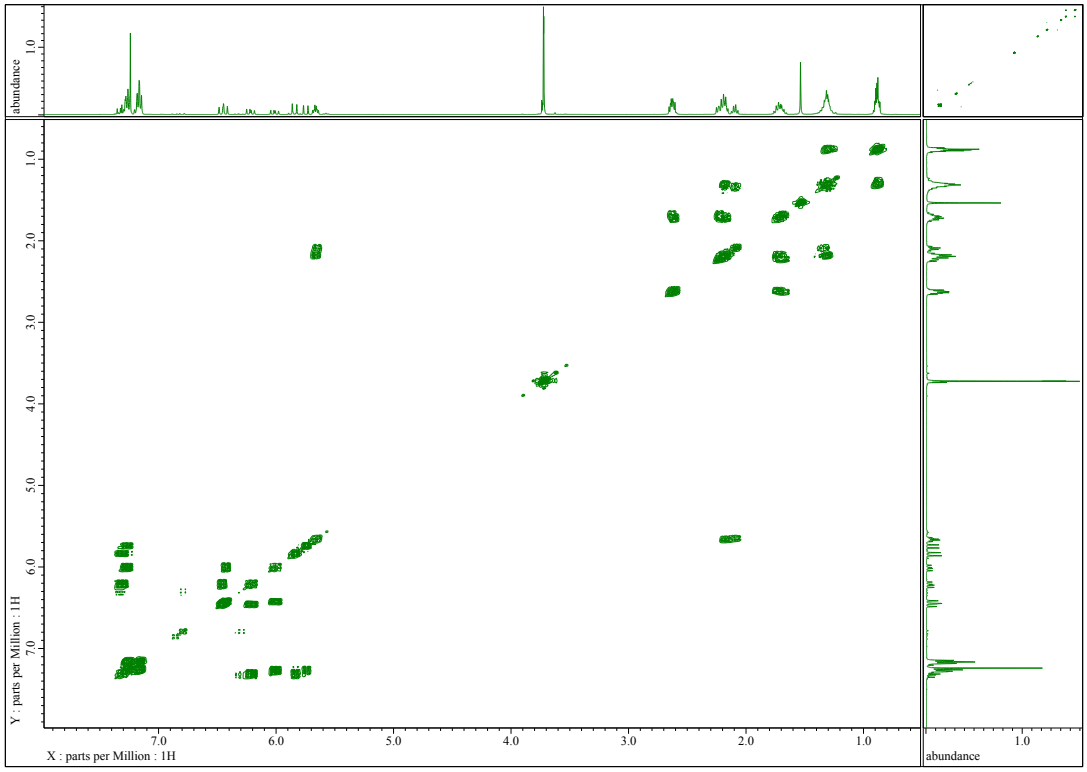


Figure S66. ^{13}C-^{1}H Correlation Spectrum of 4ea and 5ea in C_6D_6.

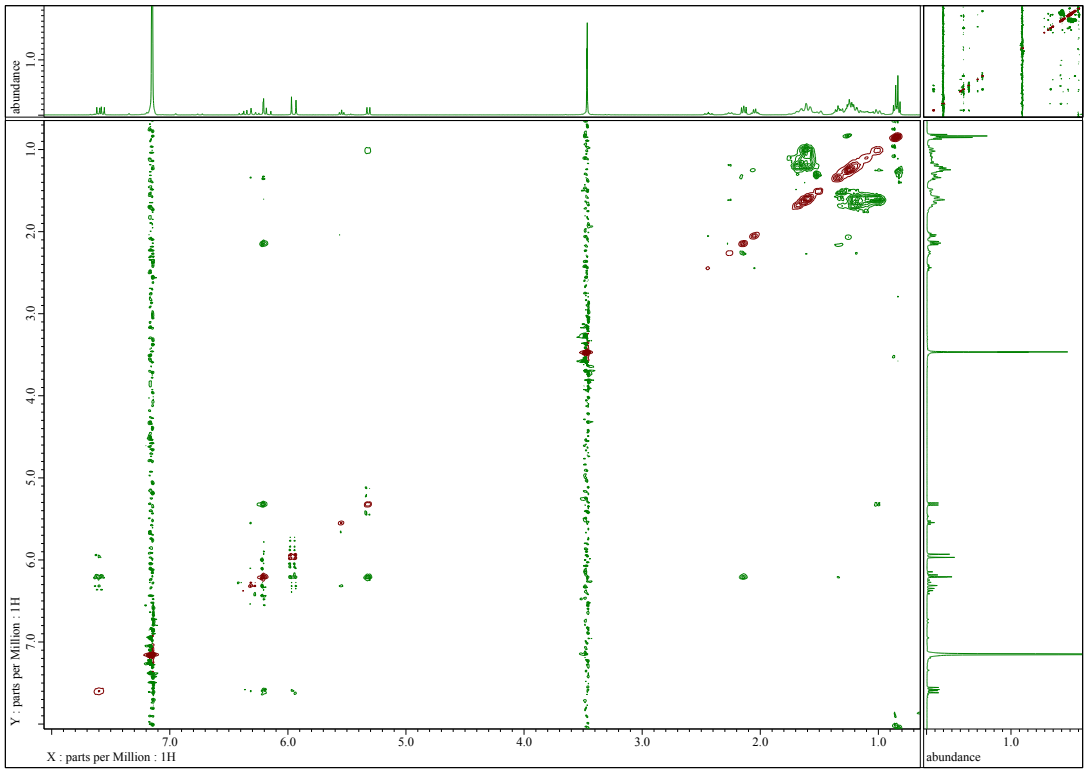


Figure S67. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ha and 5ha in C_6D_6.

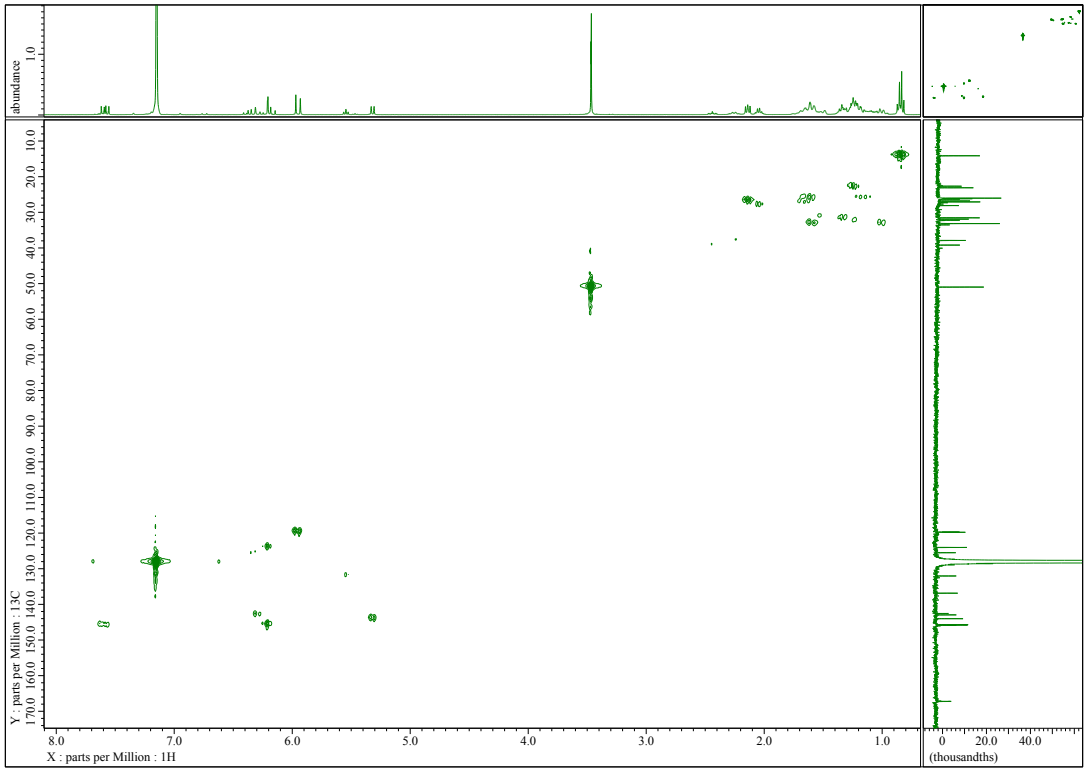


Figure S68. ^{13}C-^{1}H Correlation Spectrum of 4ha and 5ha in C_6D_6.

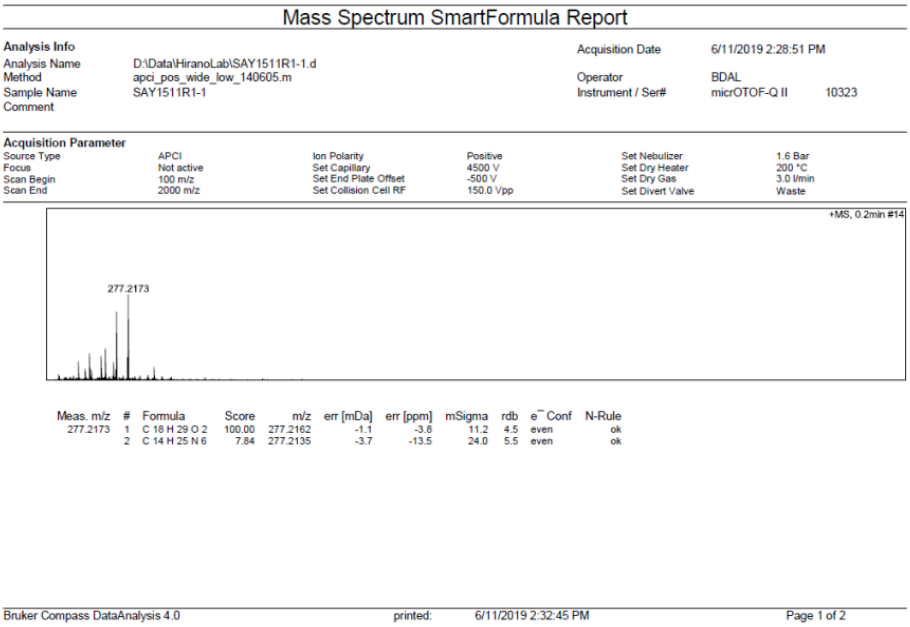


Figure S69. HRMS (APCI) data for 4ha and 5ha.

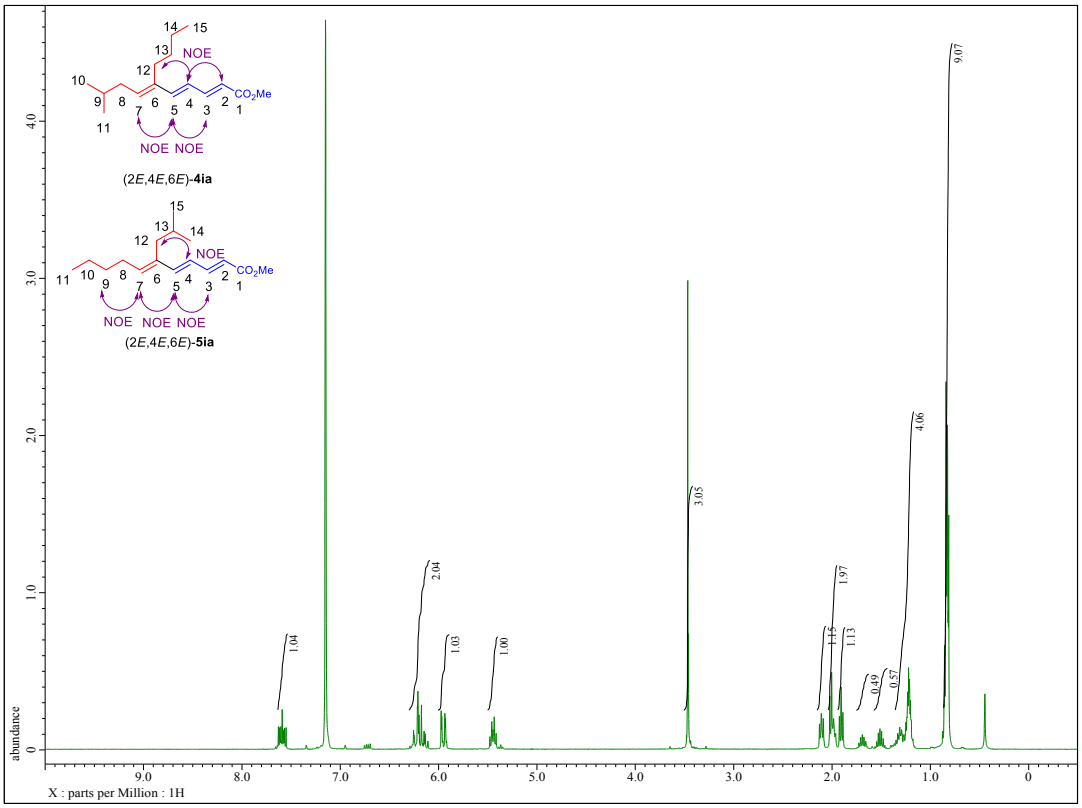


Figure S70. ^{1}H NMR Spectrum of 4ia and 5ia in C_6D_6.

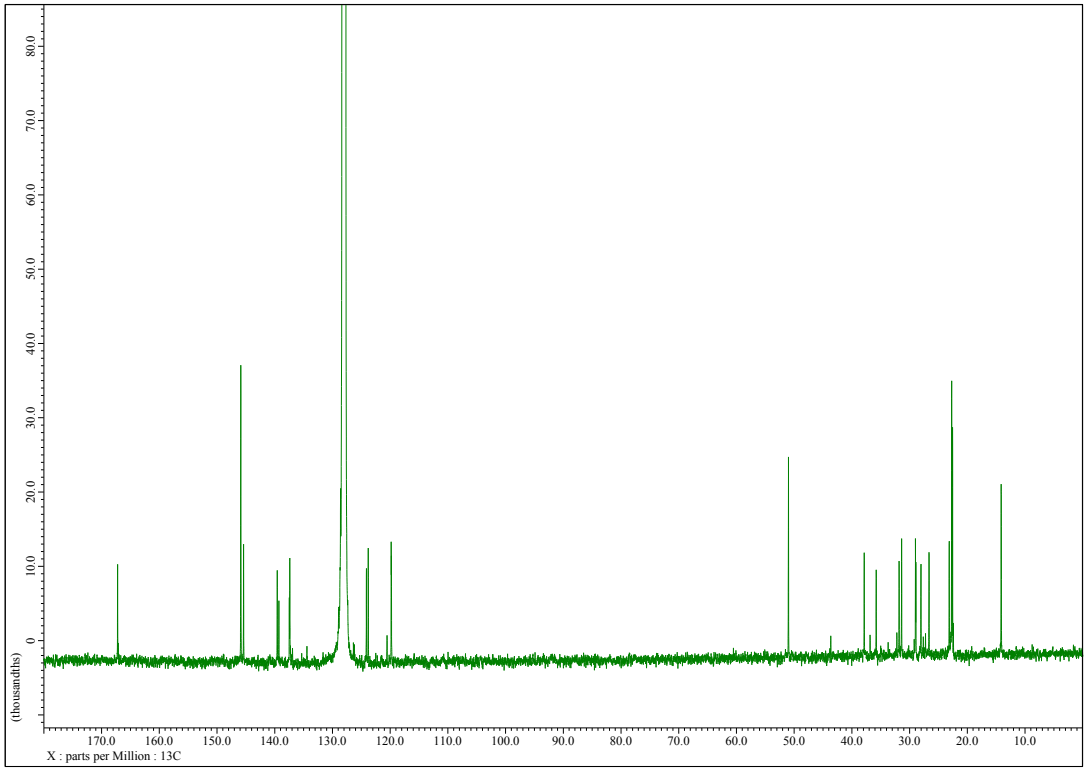


Figure S71. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ia and 5ia in C_6D_6.

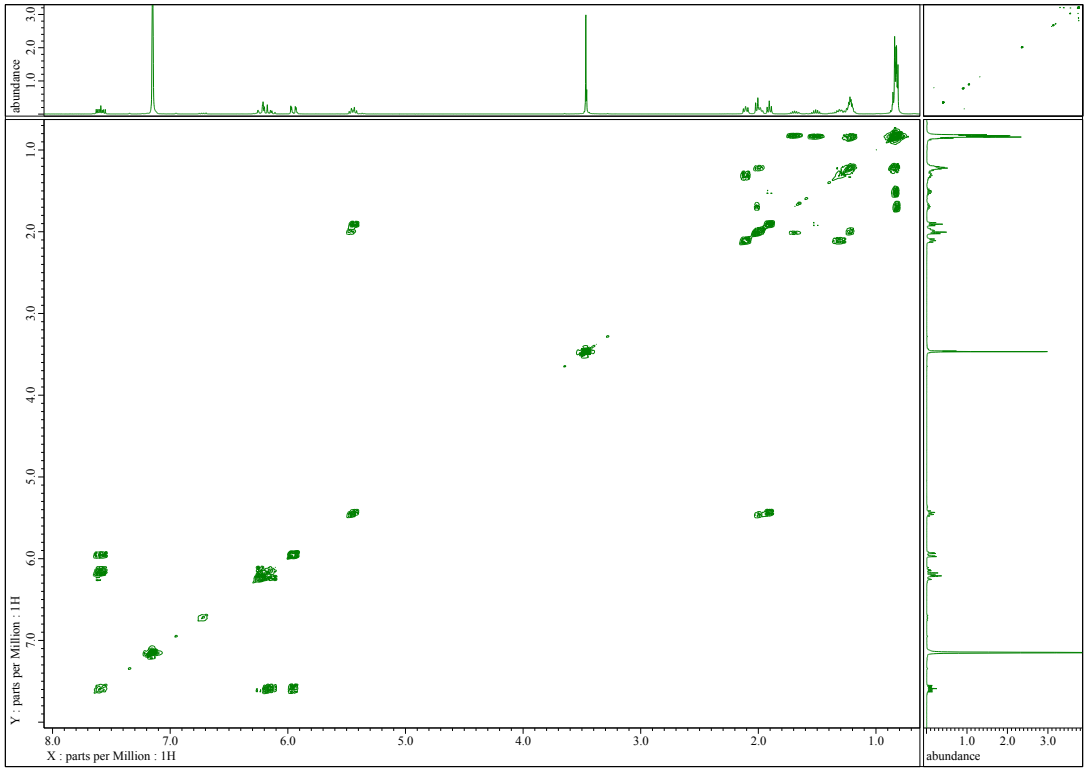


Figure S72. ^{1}H-^{1}H COSY NMR Spectrum of 4ia and 5ia in C_6D_6.

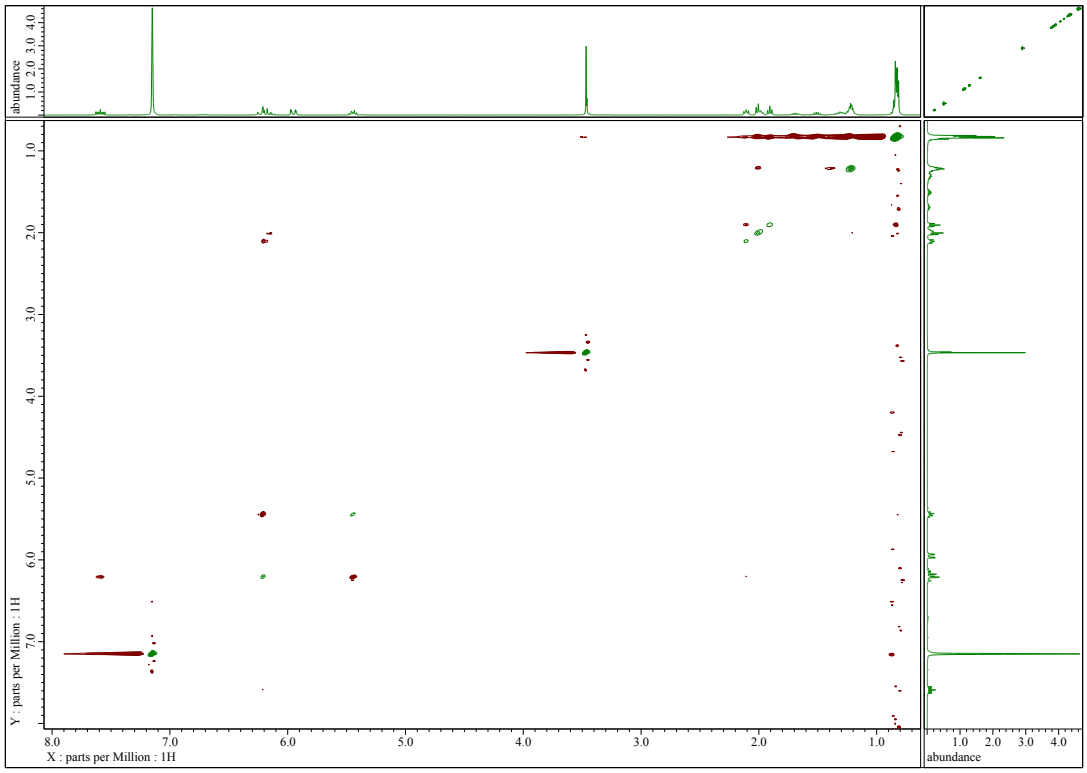


Figure S73. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ia and 5ia in C_6D_6.

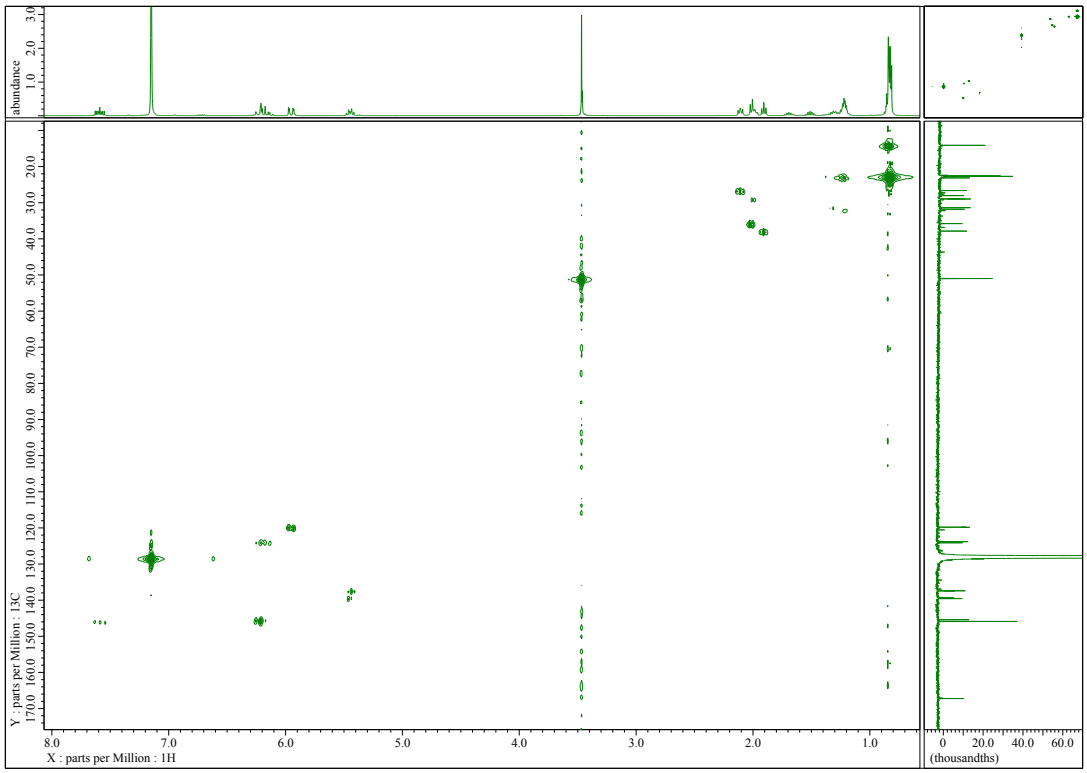


Figure S74. ^{13}C-^{1}H Correlation Spectrum of 4ia and 5ia in C_6D_6.

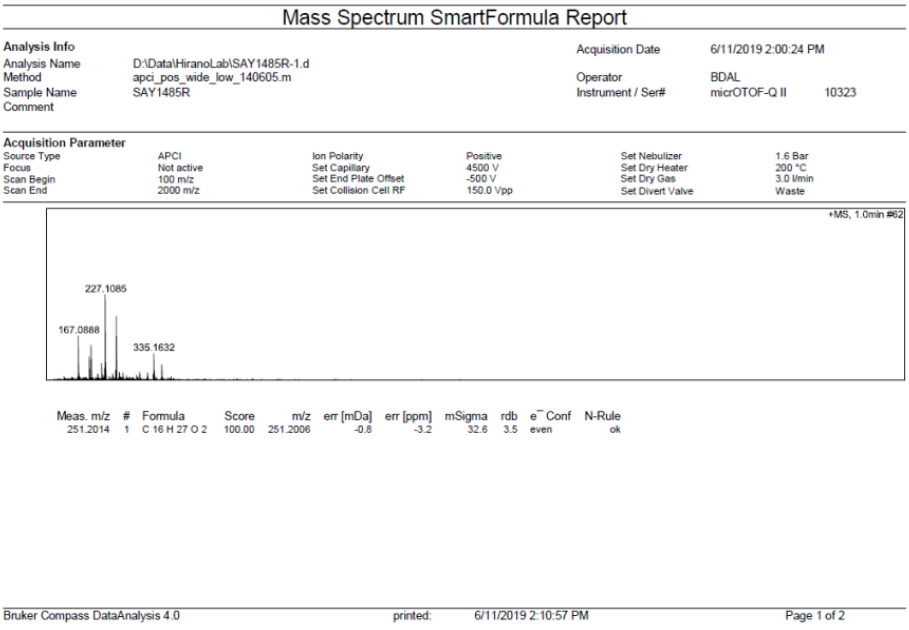


Figure S75-1. HRMS (APCI) data for 4ia and 5ia.

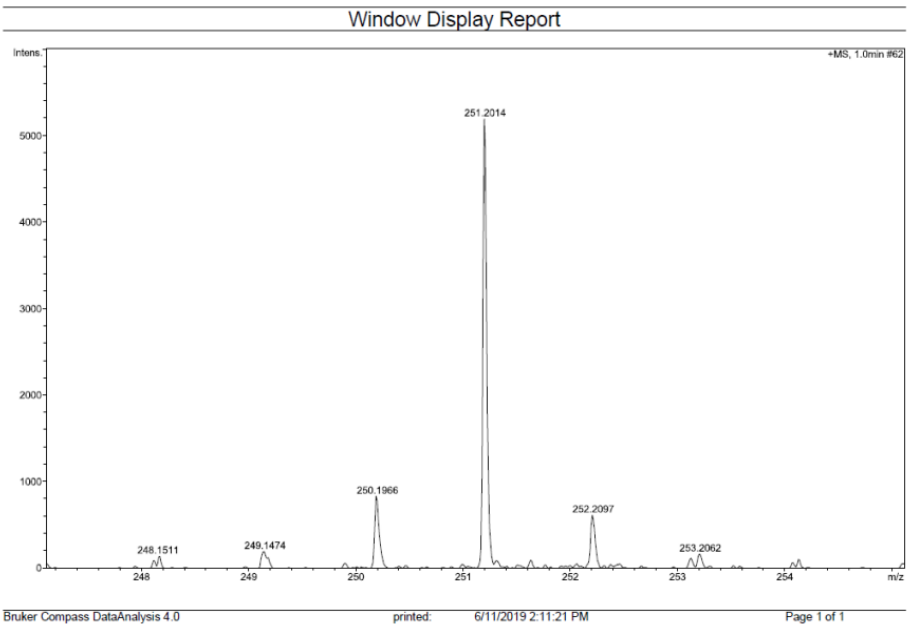


Figure S75-2. HRMS (APCI) data for 4ia and 5ia.

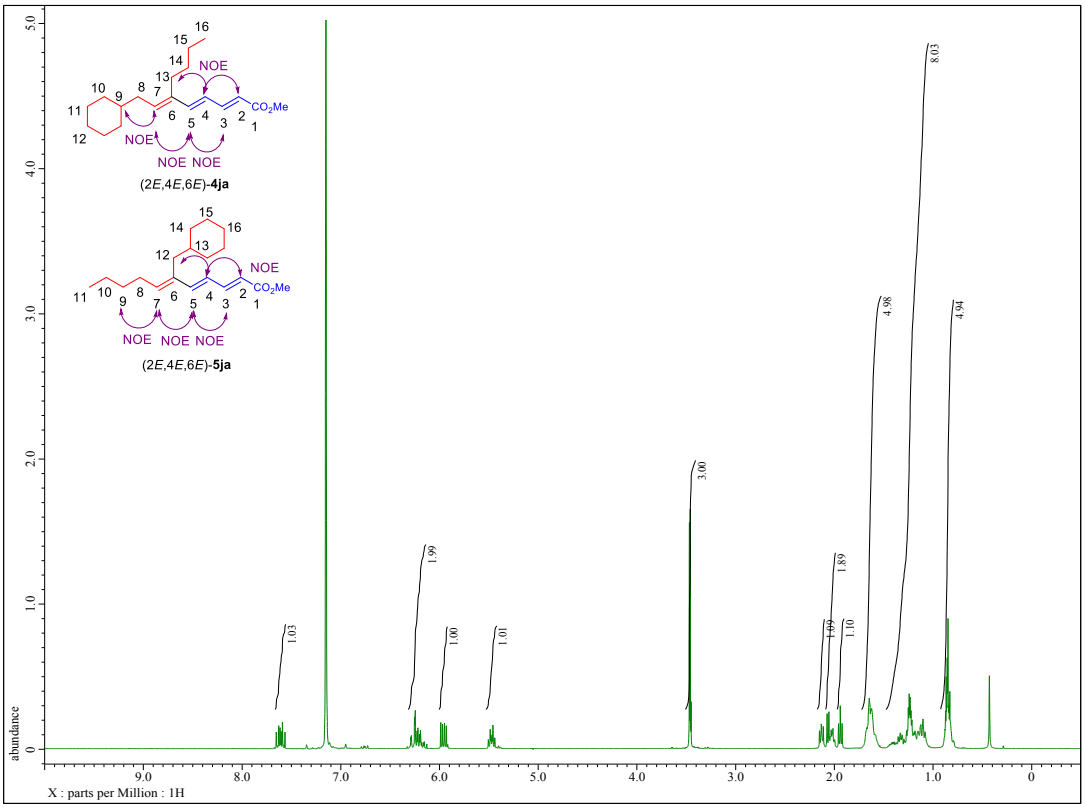


Figure S76. ^{1}H NMR Spectrum of 4ja and 5ja in C_6D_6.

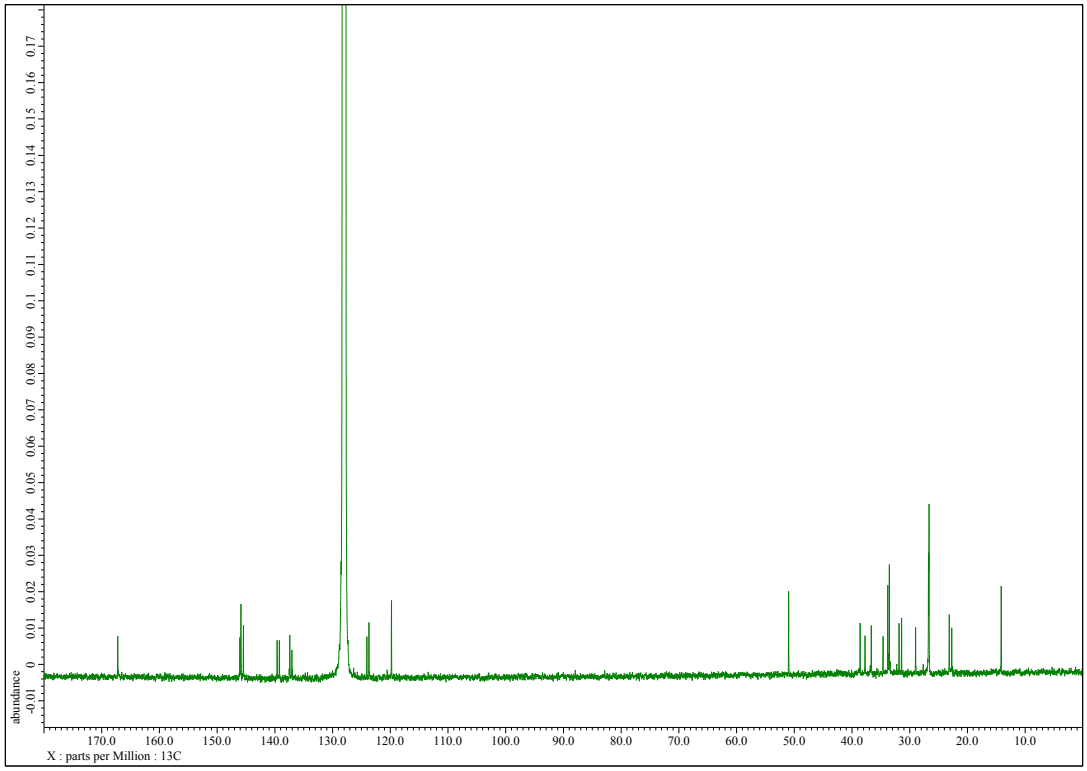


Figure S77. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ja and 5ja in C_6D_6.

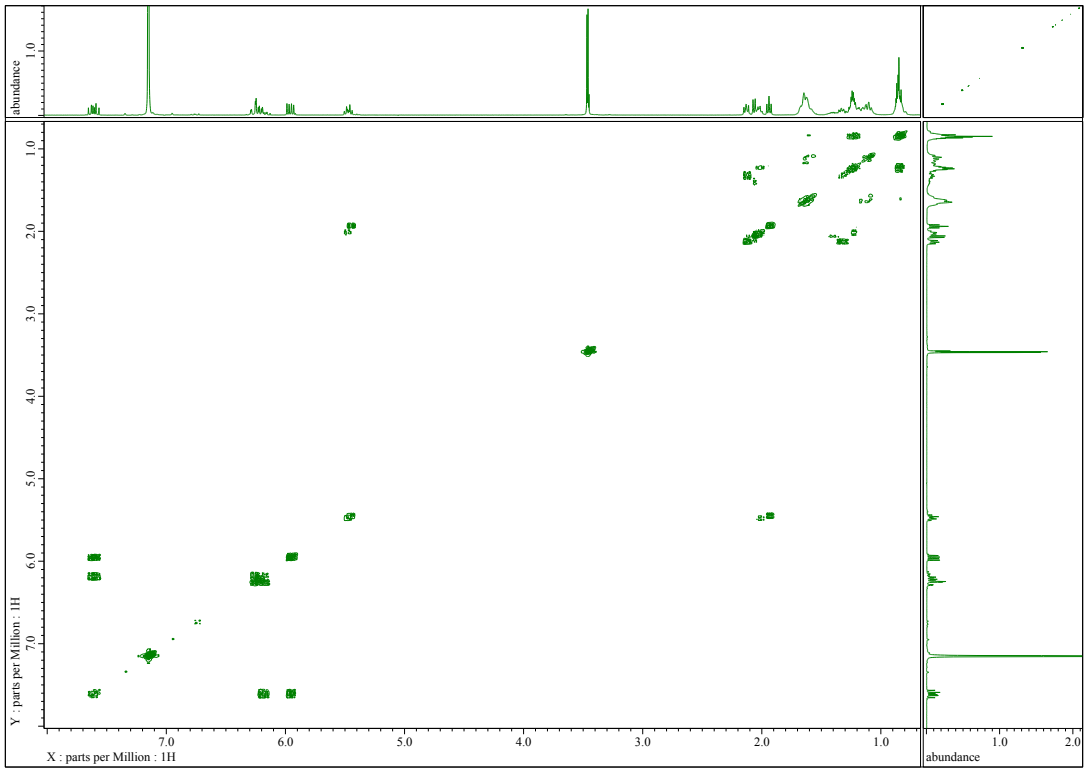


Figure S78. ^{1}H-^{1}H COSY NMR Spectrum of 4ja and 5ja in C_6D_6.

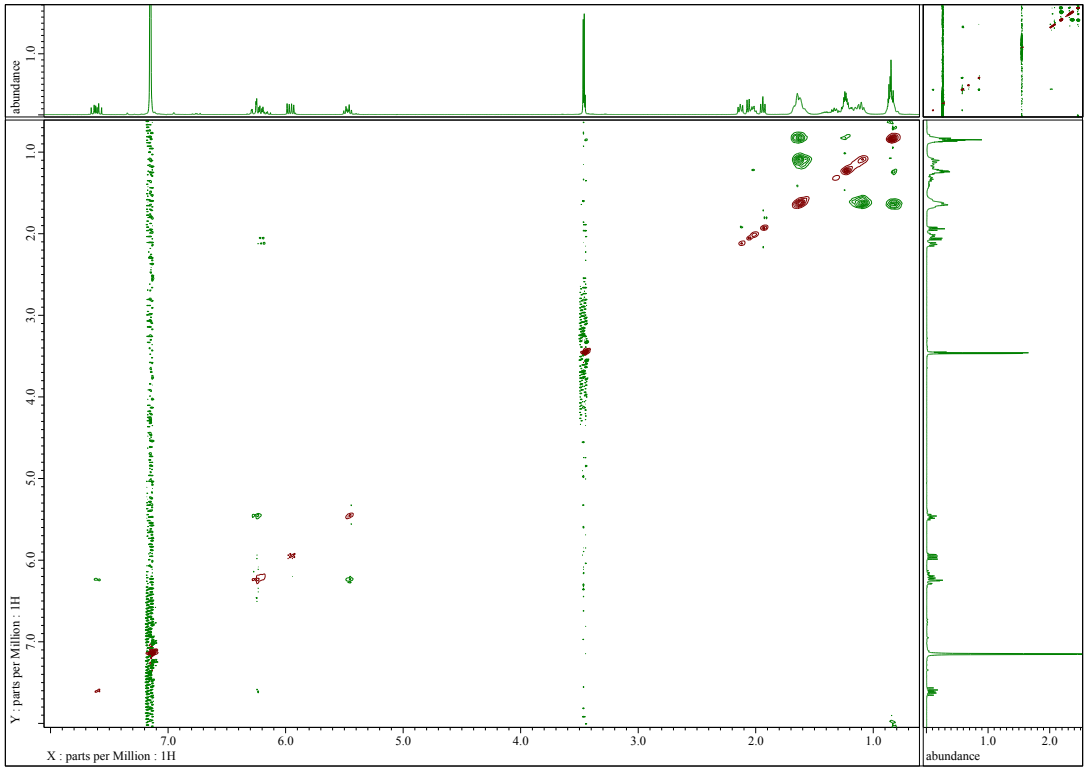


Figure S79. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ja and 5ja in C_6D_6.

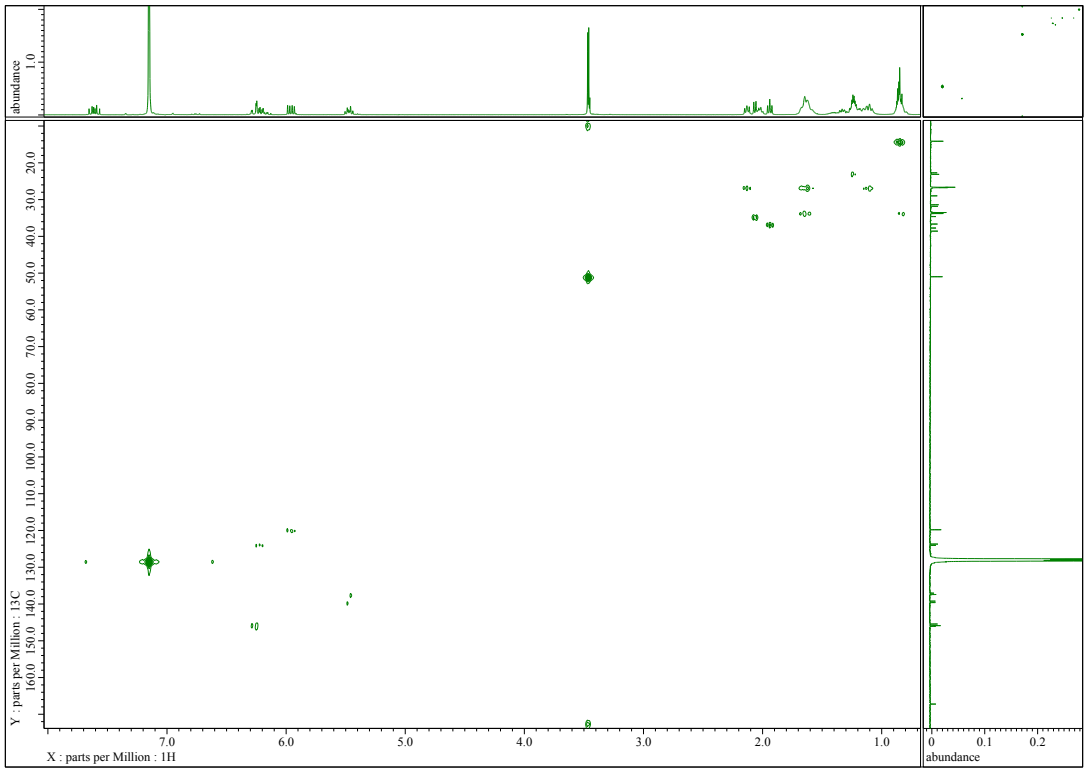
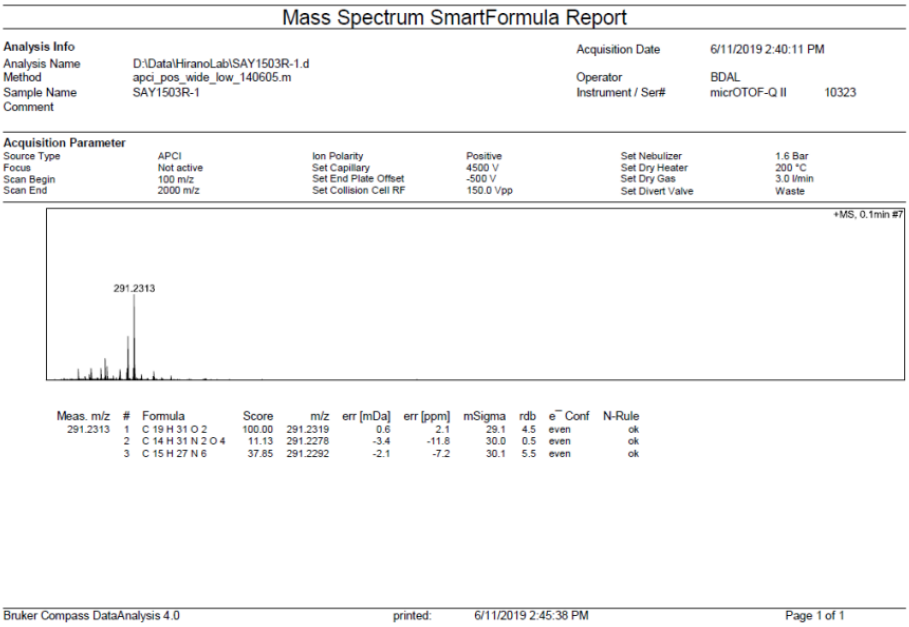


Figure S80. ^{13}C-^{1}H Correlation Spectrum of 4ja and 5ja in C_6D_6.



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	SAY1503R-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

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Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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	2	C 14 H 31 N 2 O 4	11.13	291.2278	-3.4	-11.8	30.0	0.5	even	ok
	3	C 15 H 27 N 6	37.85	291.2292	-2.1	-7.2	30.1	5.5	even	ok

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Figure S81. HRMS (APCI) data for 4ja and 5ja.

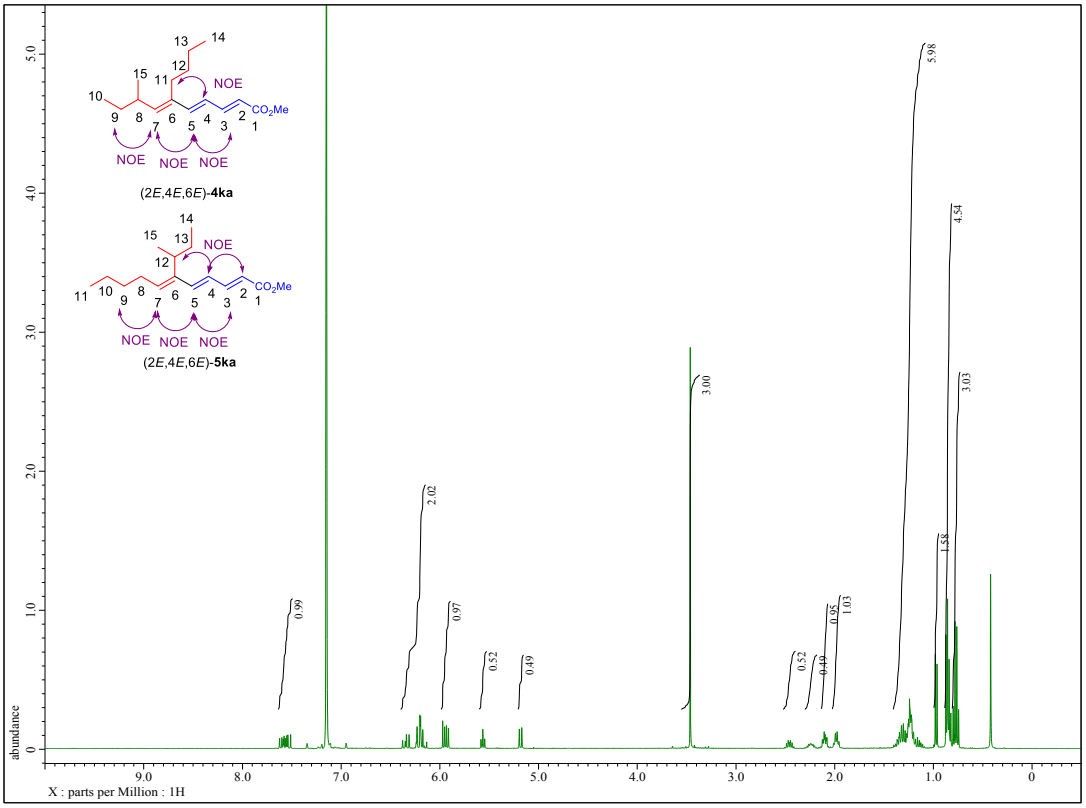


Figure S82. ^{1}H NMR Spectrum of 4ka and 5ka in C_6D_6.

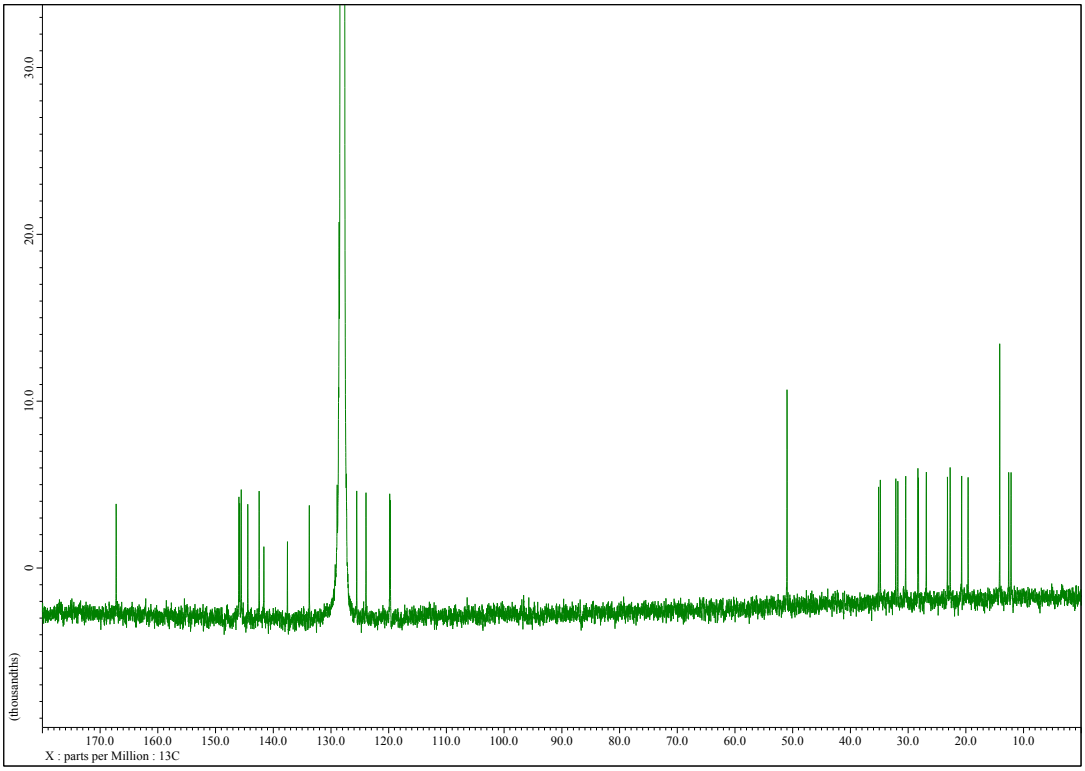


Figure S83. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ka and 5ka in C_6D_6.

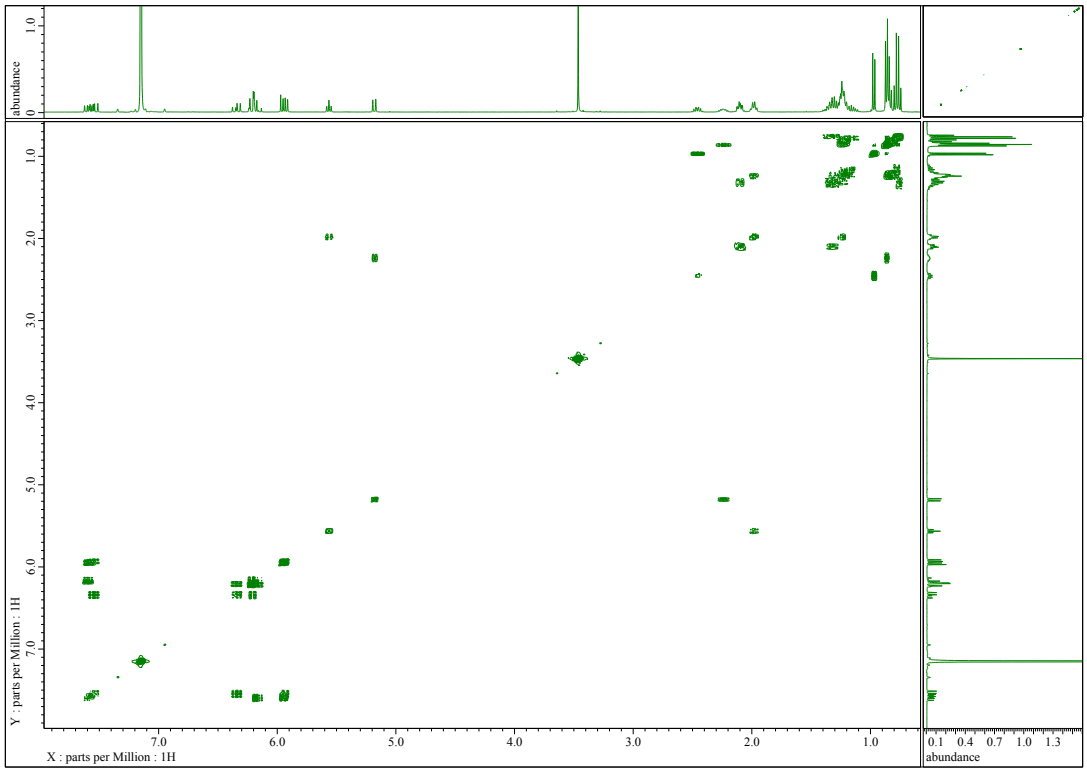


Figure S84. ^{1}H-^{1}H COSY NMR Spectrum of 4ka and 5ka in C_6D_6.

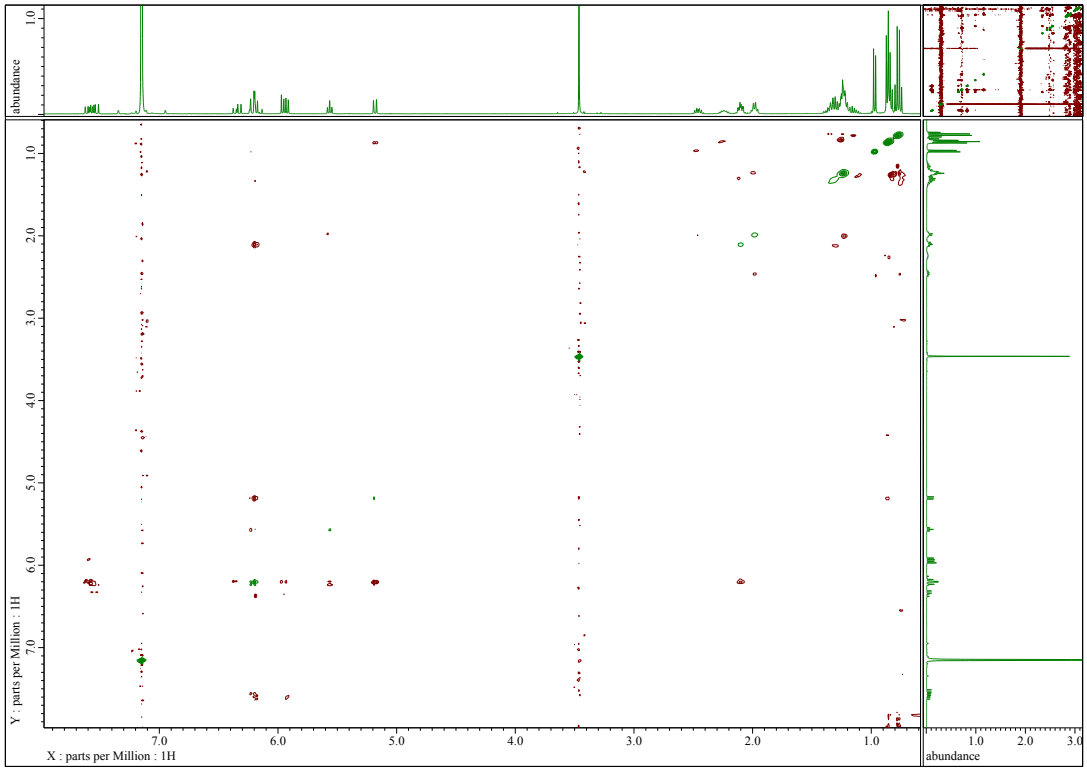


Figure S85. ^{1}H-^{1}H pNOESY NMR Spectrum of 4ka and 5ka in C_6D_6.

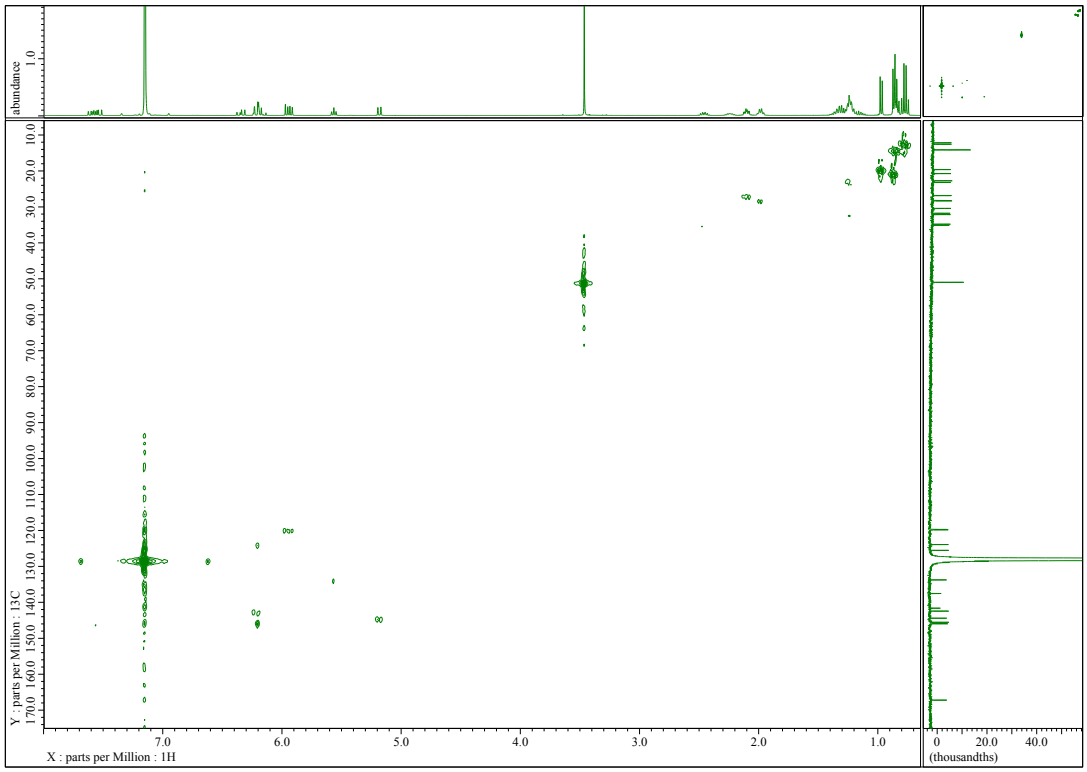
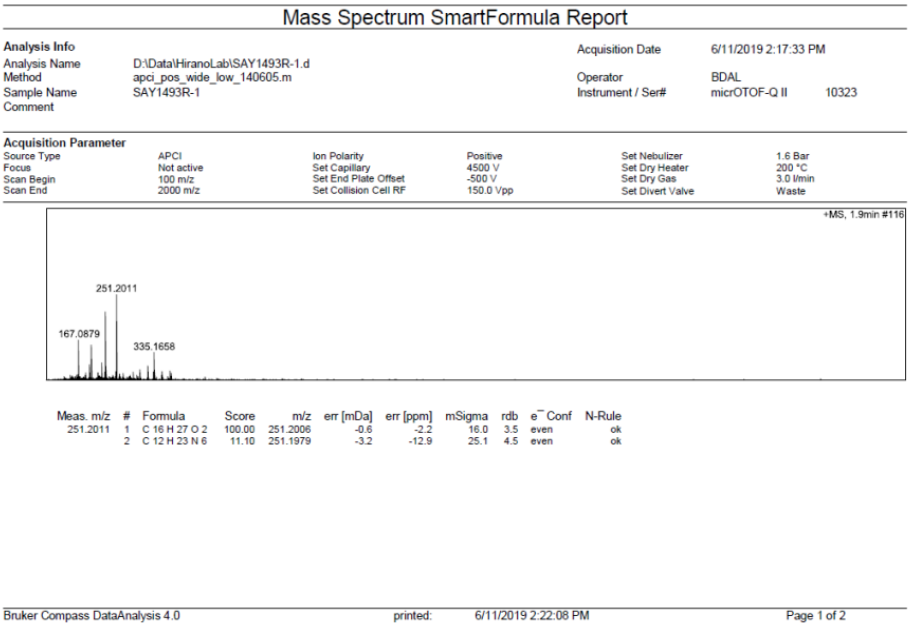


Figure S86. ^{13}C-^{1}H Correlation Spectrum of 4ka and 5ka in C_6D_6.



Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	SAY1493R-1	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

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Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

+MS, 1.9min #116

251.2011
167.0879
335.1658

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Figure S87. HRMS (APCI) data for 4ka and 5ka.

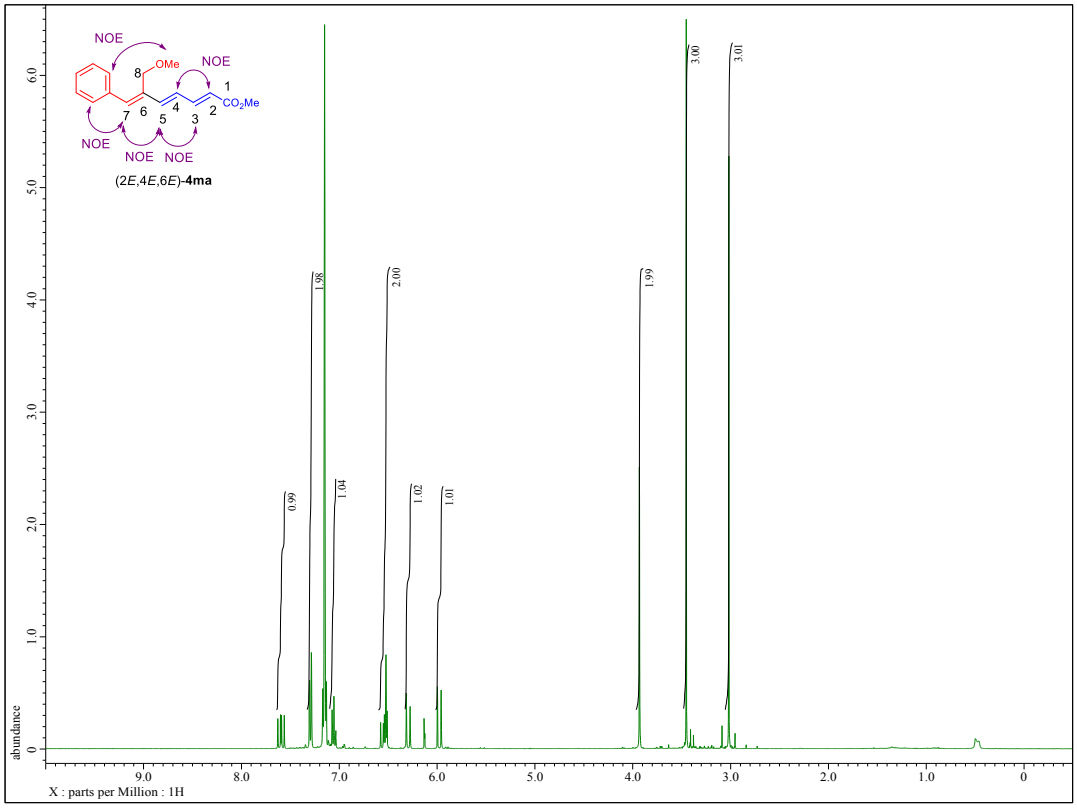


Figure S88. ^{1}H NMR Spectrum of 4ma in C_6D_6.

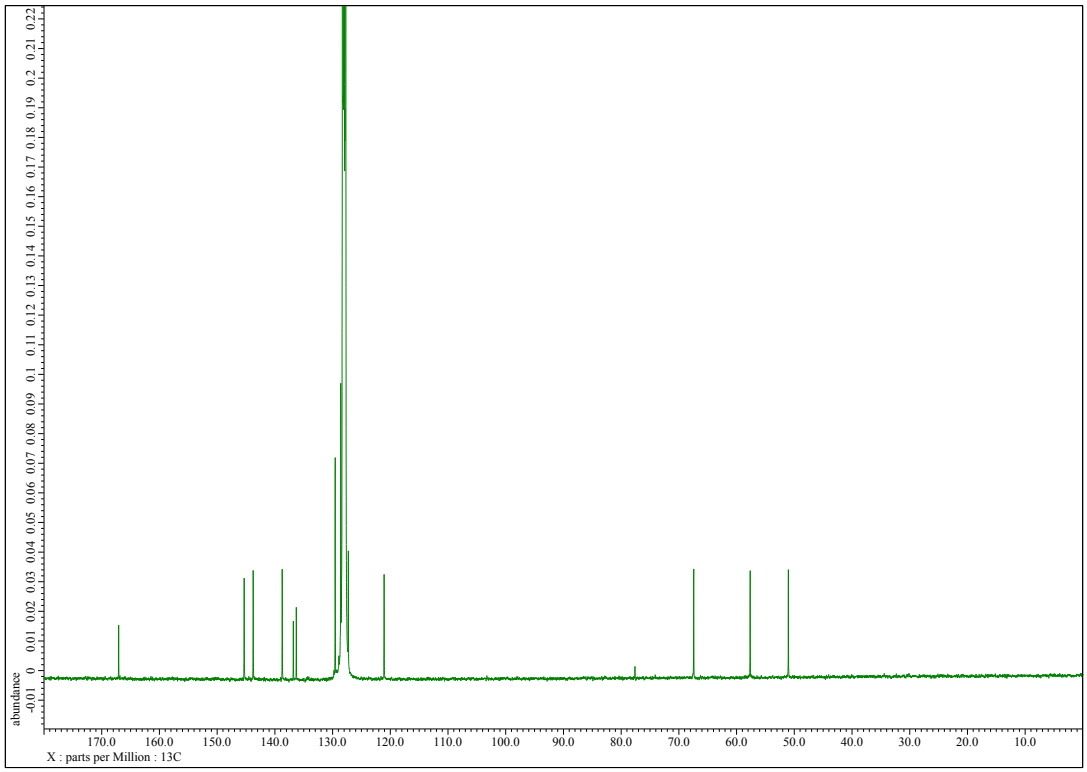


Figure S89. $^{13}C\{^{1}H\}$ NMR Spectrum of 4ma in C_6D_6.

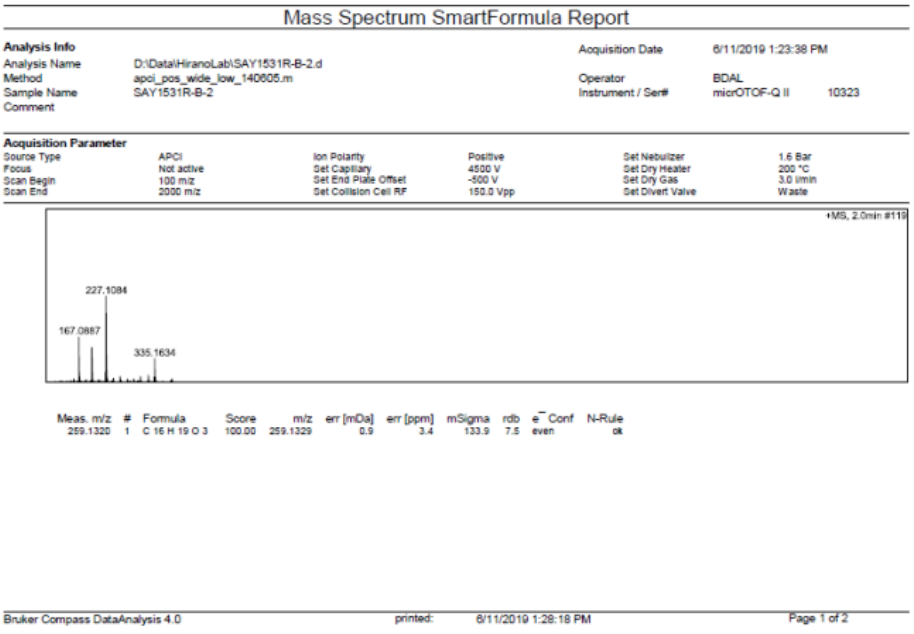


Figure S90-1. HRMS (APCI) data for 4ma.

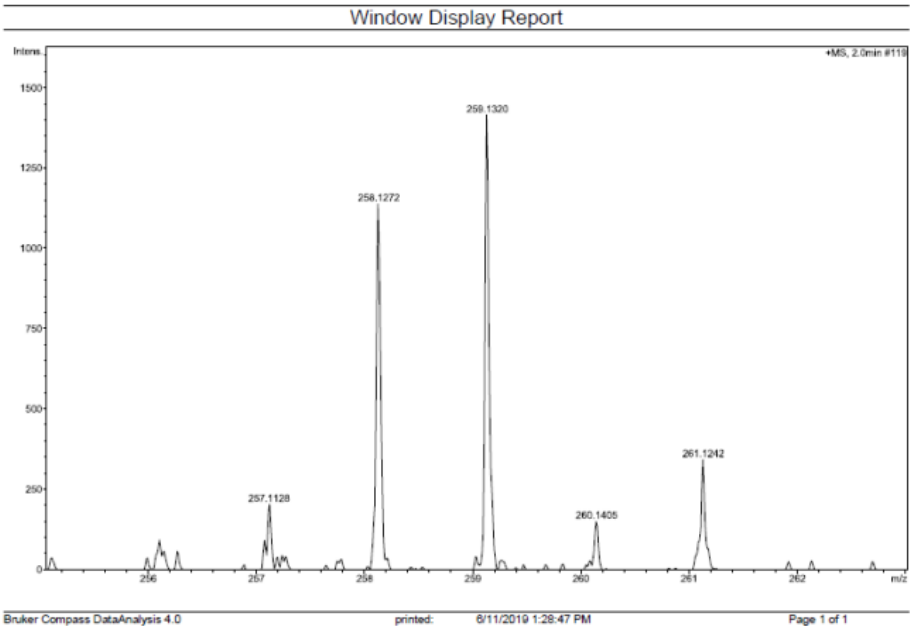


Figure S90-2. HRMS (APCI) data for 4ma.

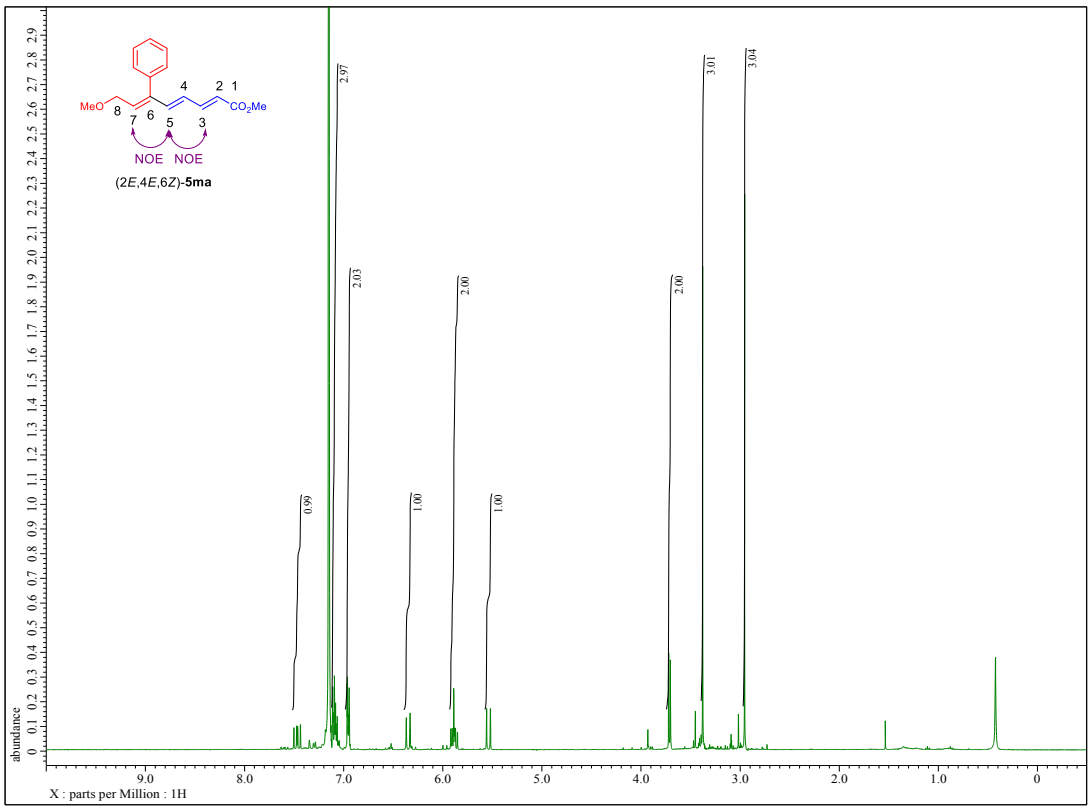


Figure S91. ^{1}H NMR Spectrum of 5ma in C_6D_6.

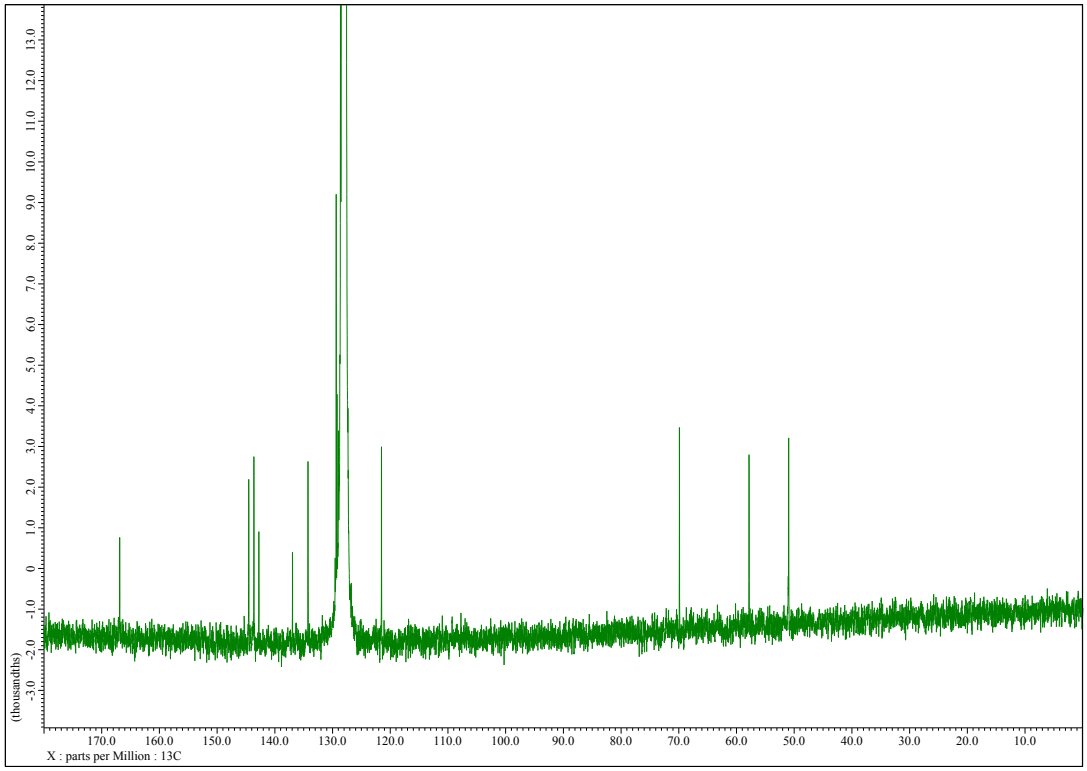


Figure S92. $^{13}C\{^{1}H\}$ NMR Spectrum of 5ma in C_6D_6.

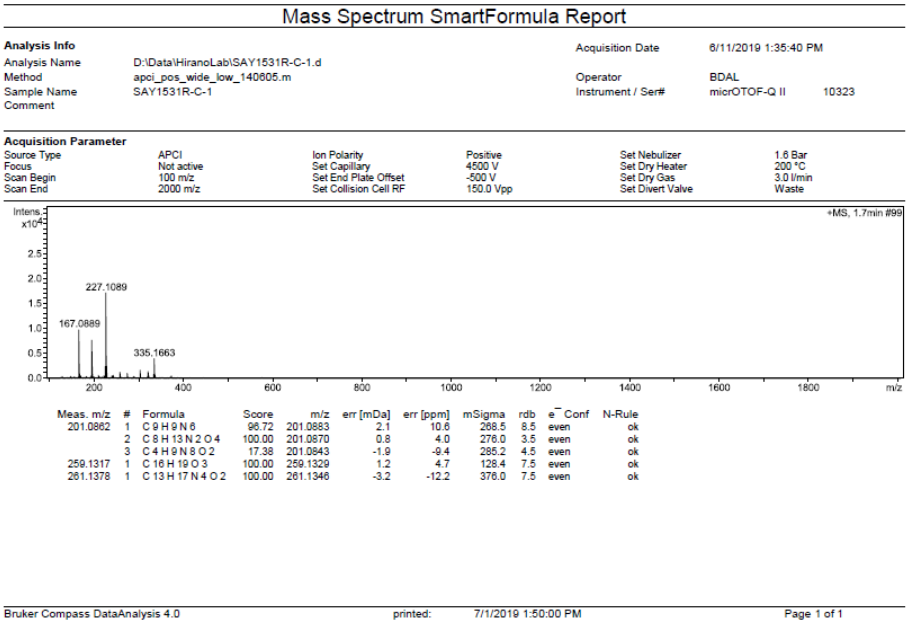


Figure S93-1. HRMS (APCI) data for 5ma.

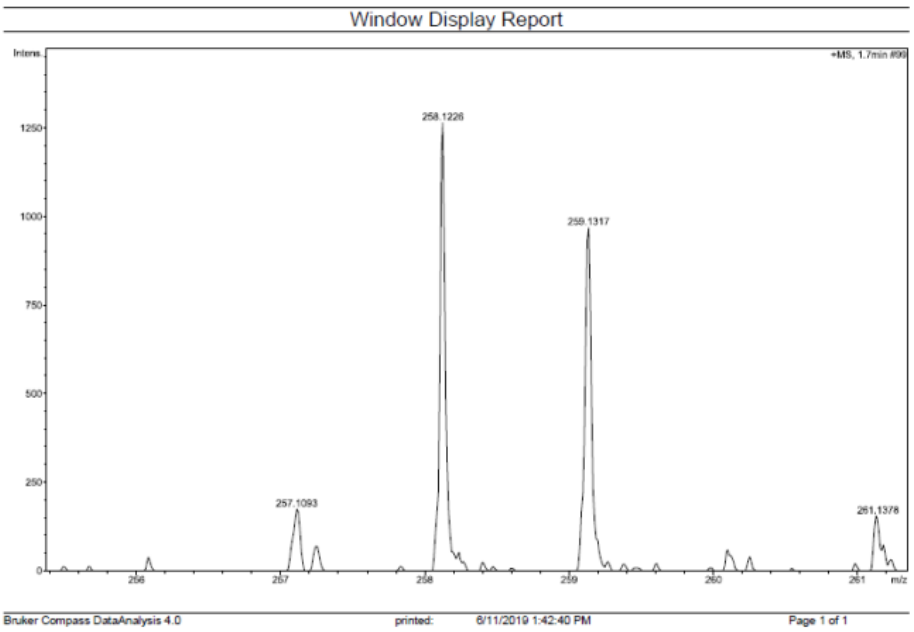


Figure S93-2. HRMS (APCI) data for 5ma.

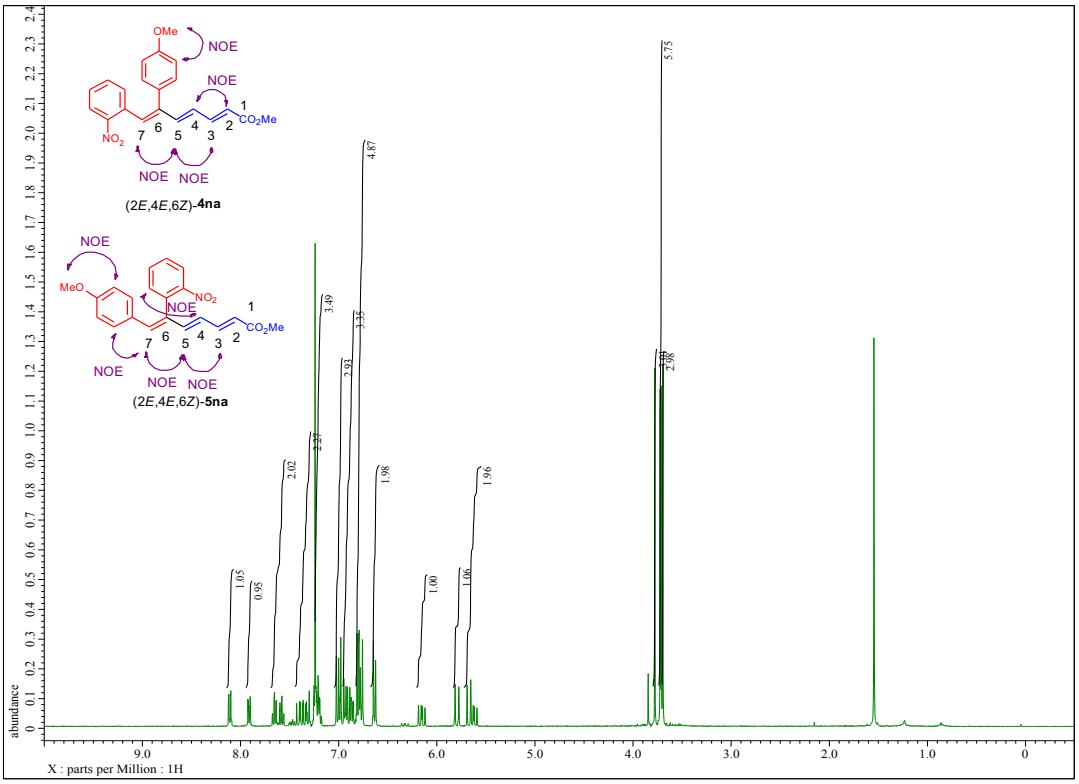


Figure S94. ^{1}H NMR Spectrum of 4na and 5na in $CDCl_3$.

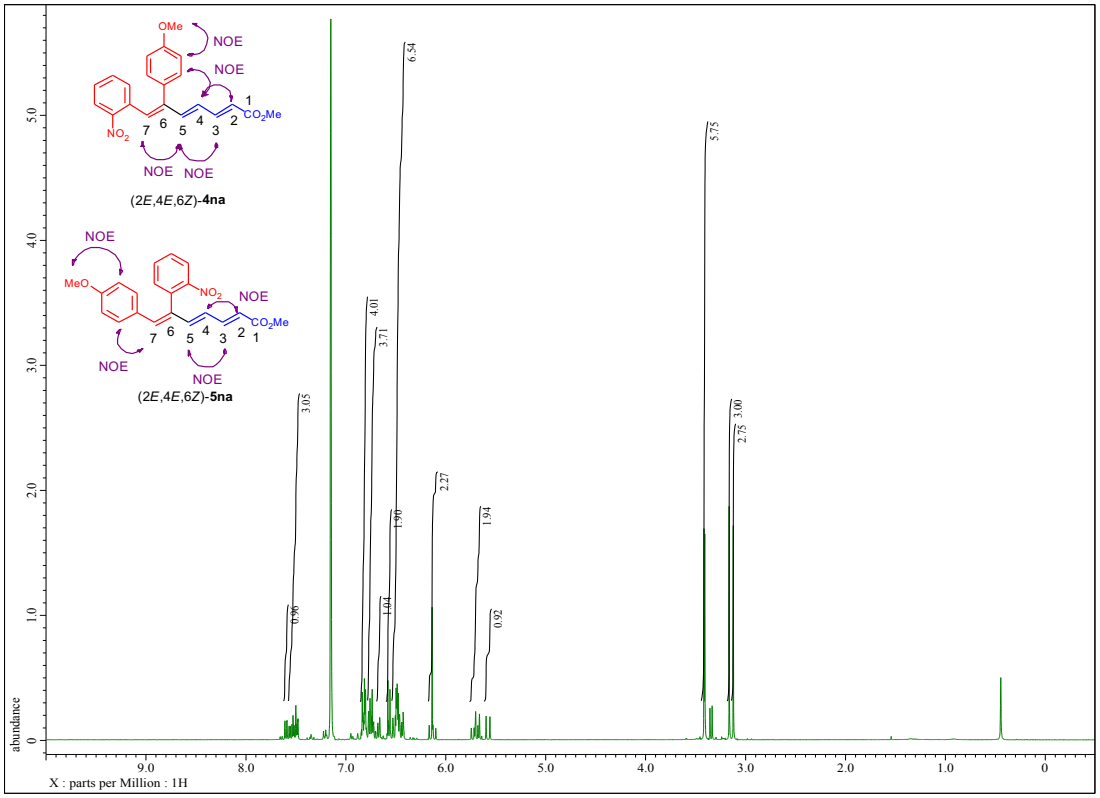


Figure S95. ^{1}H NMR Spectrum of 4na and 5na in C_6D_6.

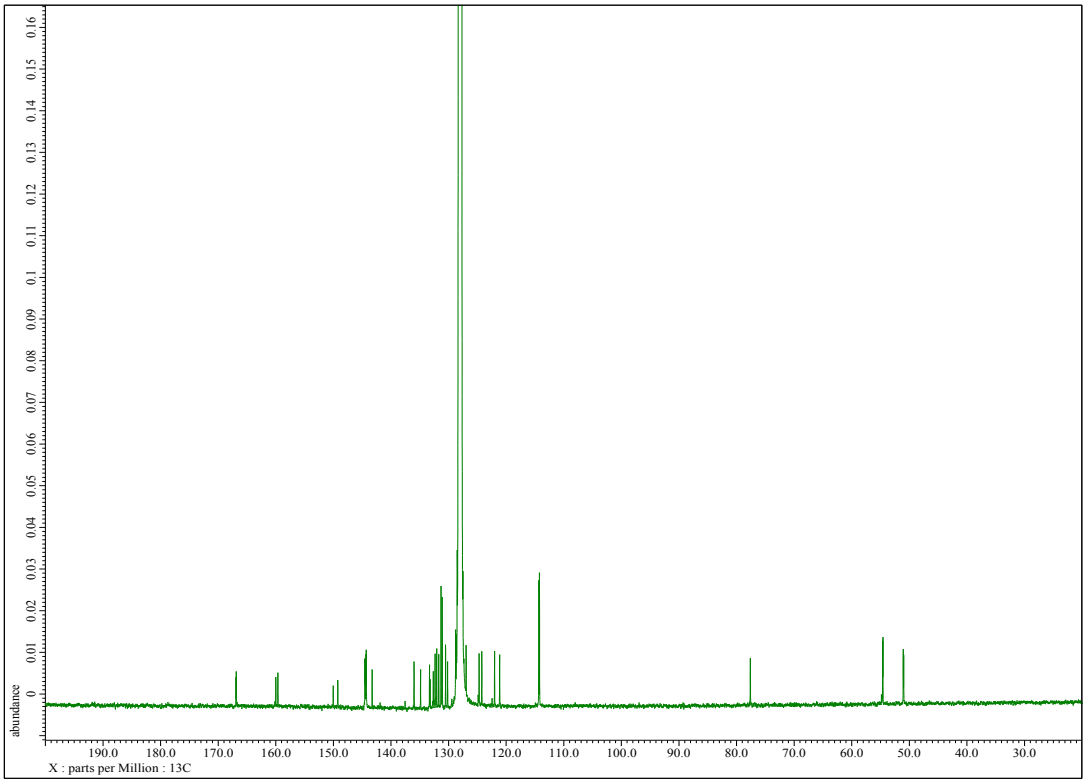


Figure S96. $^{13}C\{^{1}H\}$ NMR Spectrum of 4na and 5na in C_6D_6.

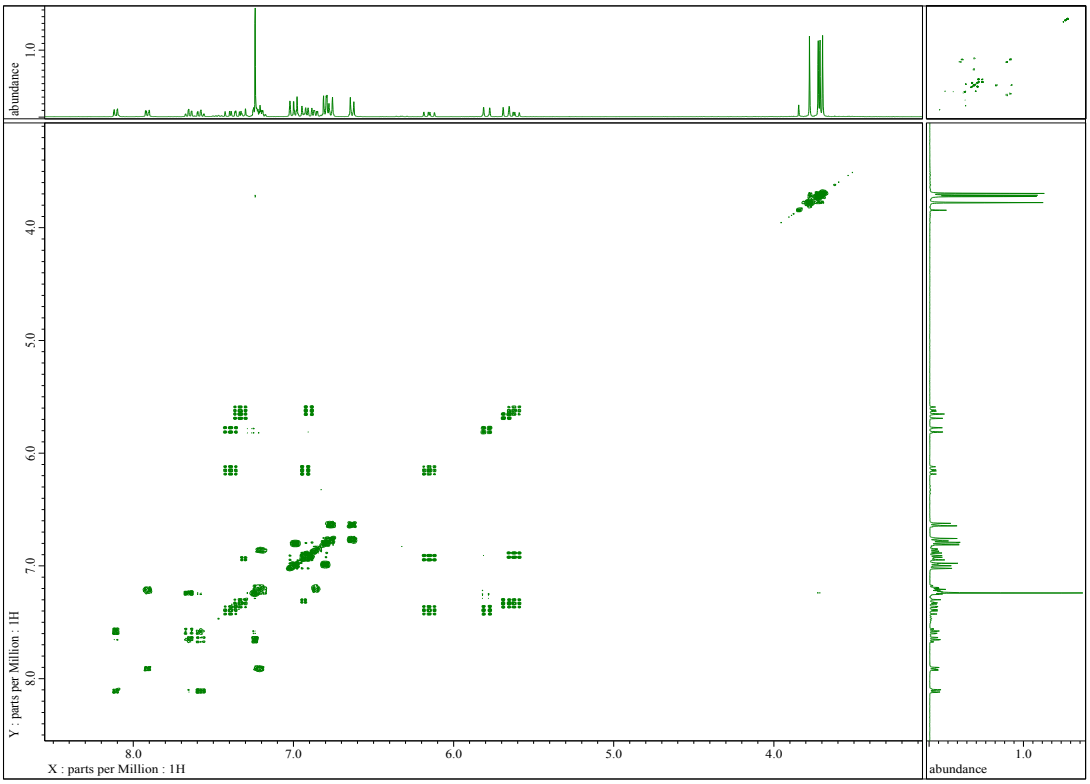


Figure S97. ^{1}H-^{1}H COSY NMR Spectrum of 4na and 5na in $CDCl_3$.

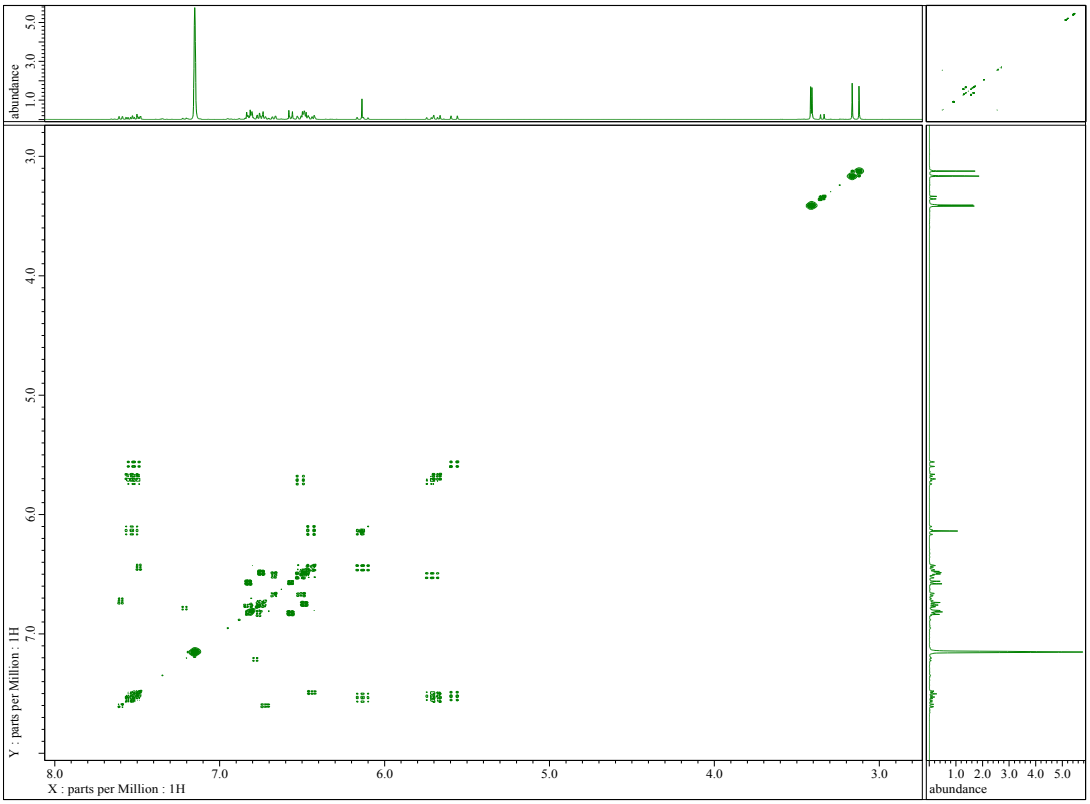


Figure S98. ^{1}H-^{1}H COSY NMR Spectrum of 4na and 5na in C_6D_6.

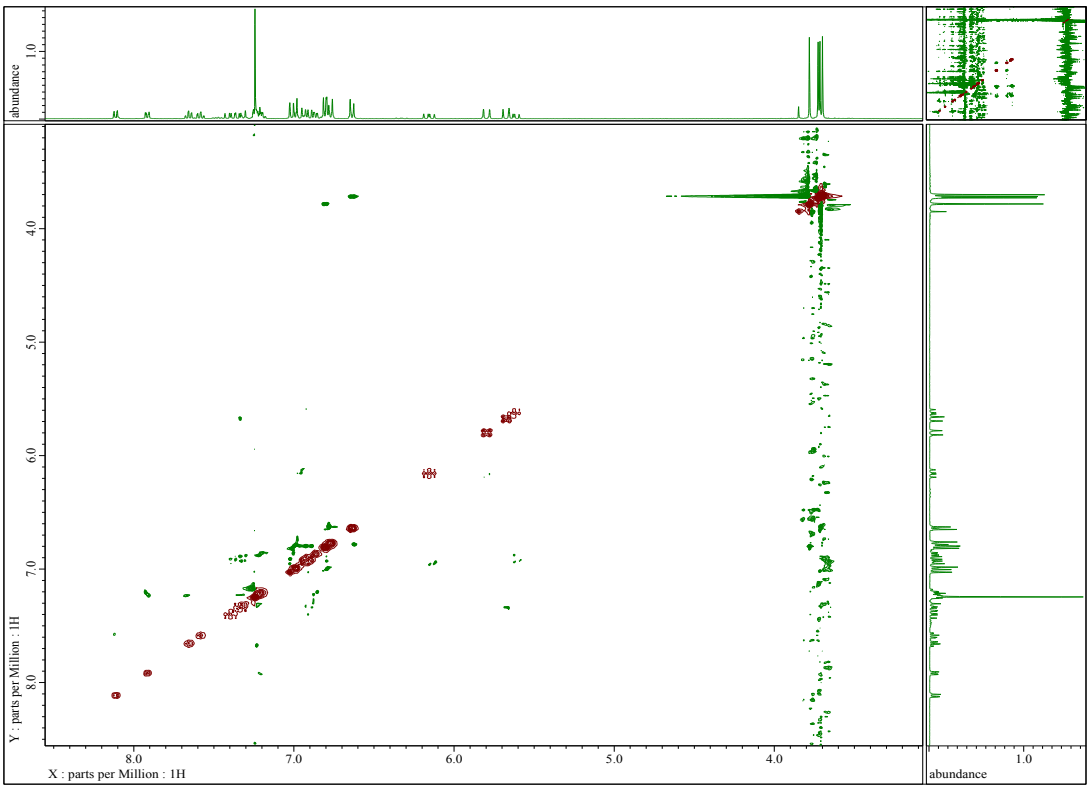


Figure S99. ^{1}H-^{1}H pNOESY NMR Spectrum of 4na and 5na in $CDCl_3$.

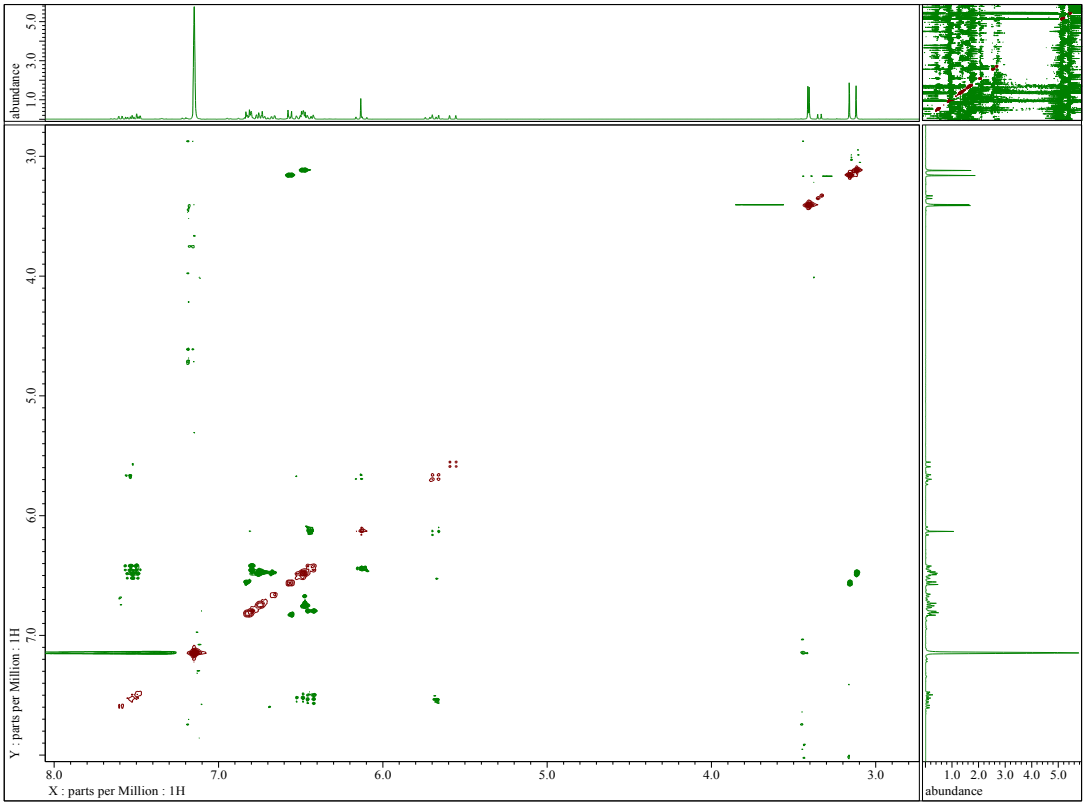


Figure S100. ^{1}H-^{1}H pNOESY NMR Spectrum of 4na and 5na in C_6D_6.

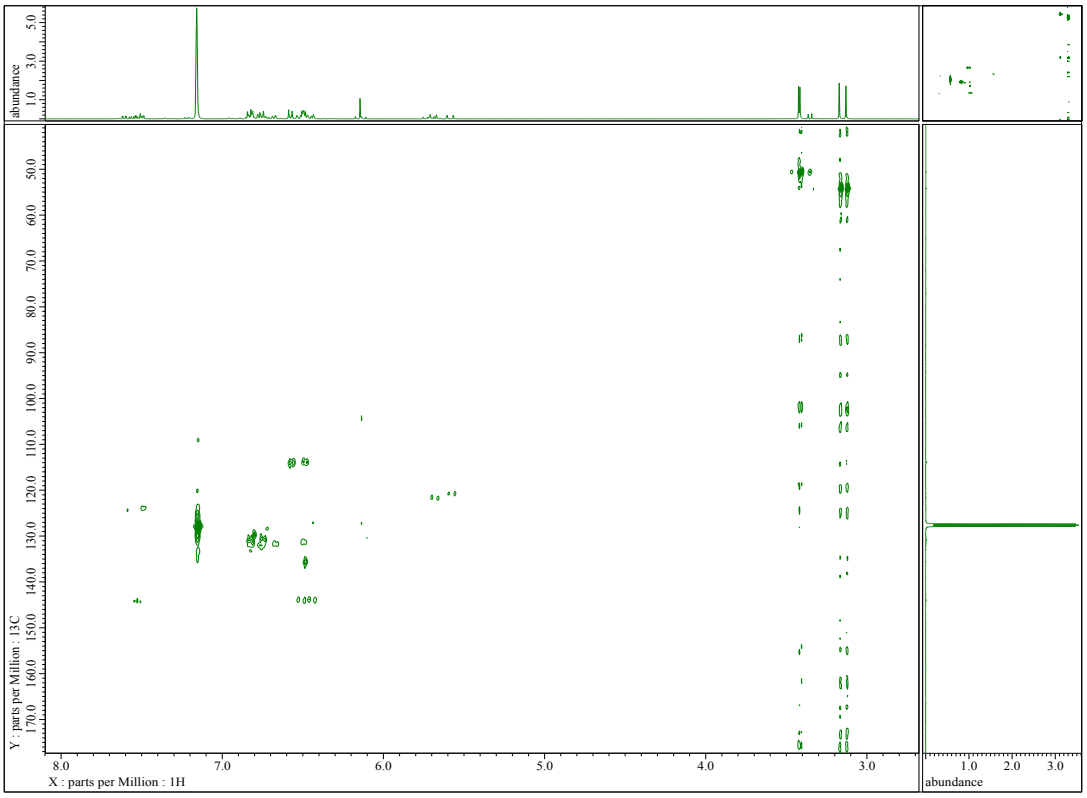
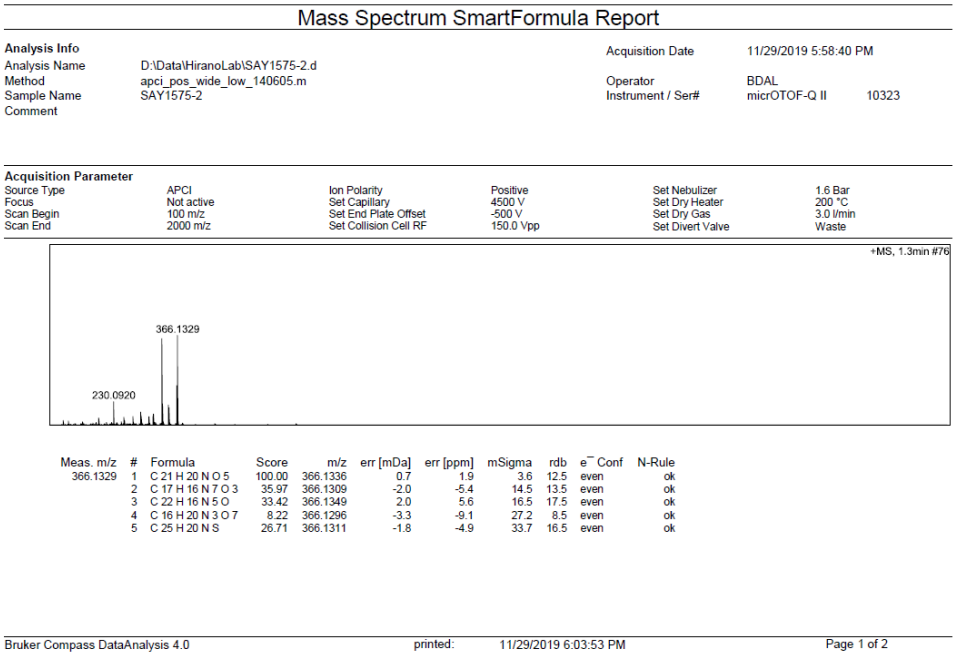


Figure S101. ^{13}C-^{1}H Correlation Spectrum of 4na and 5na in C_6D_6.



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\HiranoLab\SAY1575-2.d	Acquisition Date	11/29/2019 5:58:40 PM
Method	apci_pos_wide_low_140605.m	Operator	BDAL
Sample Name	SAY1575-2	Instrument / Ser#	micrOTOF-Q II 10323
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
366.1329	1	C 21 H 20 N O 5	100.00	366.1336	0.7	1.9	3.6	12.5	even	ok
	2	C 17 H 16 N 7 O 3	35.97	366.1309	-2.0	-5.4	14.5	13.5	even	ok
	3	C 22 H 16 N 5 O	33.42	366.1349	2.0	5.6	16.5	17.5	even	ok
	4	C 16 H 20 N 3 O 7	8.22	366.1296	-3.3	-9.1	27.2	8.5	even	ok
	5	C 25 H 20 N S	26.71	366.1311	-1.8	-4.9	33.7	16.5	even	ok

Figure S102. HRMS (APCI) data for 4na and 5na