

Palladium catalyzed template directed C-5 selective olefination of thiazoles

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Crystallographic data

Sample preparation.

5 mg of each compound **3af**, **3ah**, **3bd** and **3cj** were taken into a 5 mL glass vials separately and dissolved in minimal amount of ethyl acetate followed by n-hexane was added to the all vials. Vials were capped loosely and kept for slow evaporation. After 4 – 6 days single crystals were obtained and then subjected to X-ray diffraction.

DMAP appended T6 (D): The purified compound obtained from the reaction mixture was taken into a 5 mL glass vial and dissolved in hot toluene and acetonitrile. Then this vial was kept into a 20 mL glass vial. Then 5 mL of n-hexane was added to the 20 mL vial and the vial was capped tightly. With this vapor diffusion technique, after 5 days single crystal was obtained.

Quinaldine appended T6: 10 mg of template **T6** and 5 μ L of quinaldine were taken into a 10 mL reaction tube containing stirring bar. The mixture was then dissolved in minimal amount of dichloromethane and kept for stirring for 10 min. After that the solvent was removed under reduced pressure. The solid compound was then taken into a 10 mL glass vial (3 sets) and crystallized following the above method for compound **D**.

Crystallographic data collection.

X-ray diffraction data were recorded on a Rigaku Saturn-724+ CCD single-crystal X-ray diffractometer using Mo-K α radiation as X-ray source. Data collection was performed using Crystal Clear-SM Expert software. Standard ω -scan technique was used for data collection. The structures were determined by the direct method using SHELXT2014 and refined by full matrix least squares with SHELXL-2014, refining on F².¹ Data were corrected for Lorentz and polarization effects, and all non-hydrogen atoms were refined anisotropically. Remaining hydrogen atoms were incorporated in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. Hydrogen atoms were included as per the riding model in the refinement process.

1. (a) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, A64, 112–122. (b) Program for Crystal Structure Solution and Refinement; University of Goettingen: Goettingen, Germany, 1997. (c) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8

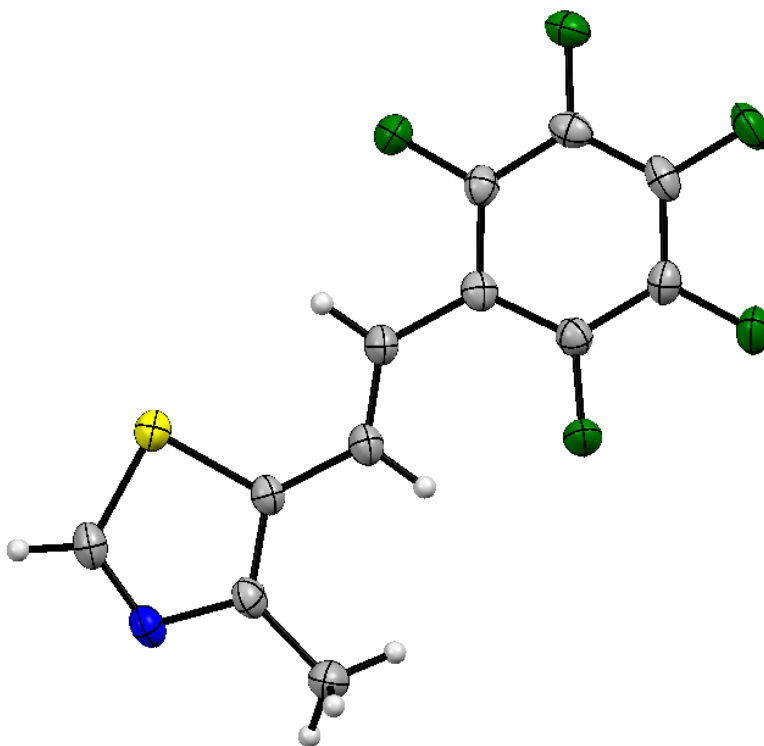


Figure S1. X-ray structure of **3af** (CCDC 1899792). Ellipsoids are drawn at 50% probability level.

Cell:	a = 7.4999(2)	b = 10.9169(6)	c = 14.4193(7)
	Alpha = 78.395(4)	beta = 81.878(3)	gamma = 82.656(3)
Temperature:	150 K		
	Calculated	Reported	
Volume	1138.83(9)	1138.82(9)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Data completeness = 0.999	Theta (max) = 24.999		
R (reflections) = 0.0544 (3418)	wR2 (reflections) = 0.1755 (3997)		

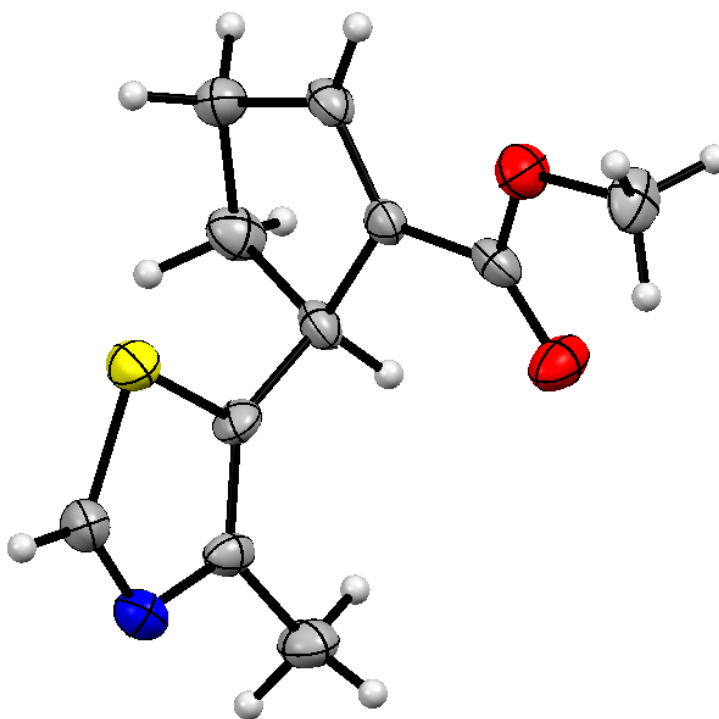


Figure S2. X-ray structure of **3ah** (**CCDC 1899793**). Ellipsoids are drawn at 50% probability level.

Cell:	$a = 11.2985(15)$	$b = 6.4748(9)$	$c = 15.103(2)$
	$\alpha = 90$	$\beta = 104.709(15)$	$\gamma = 90$

Temperature: 150 K

	Calculated	Reported
Volume	1068.7(3)	1068.6(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Data completeness = 0.998		Theta (max) = 24.999
R (reflections) = 0.0705 (1123)		wR2 (reflections) = 0.1860 (1881)

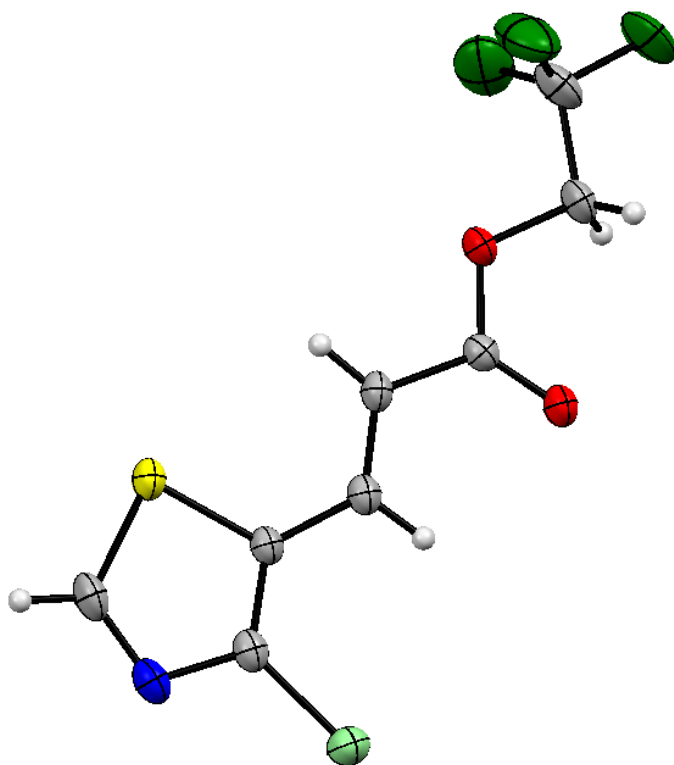


Figure S3. X-ray structure of **3bd** (**CCDC 1899794**). Ellipsoids are drawn at 50% probability level.

Cell:	a=8.2188(5)	b=19.2559(9)	c=6.6689(4)
	Alpha = 90	beta = 90	gamma = 90

Temperature: 293 K

	Calculated	Reported
Volume	1055.42(10)	1055.42(10)
Space group	P b c m	P b c m
Hall group	-P 2c 2b	-P 2c 2b
Data completeness = 0.997		Theta (max) = 24.986
R (reflections) = 0.0369 (875)		wR2 (reflections) = 0.0941 (1013)

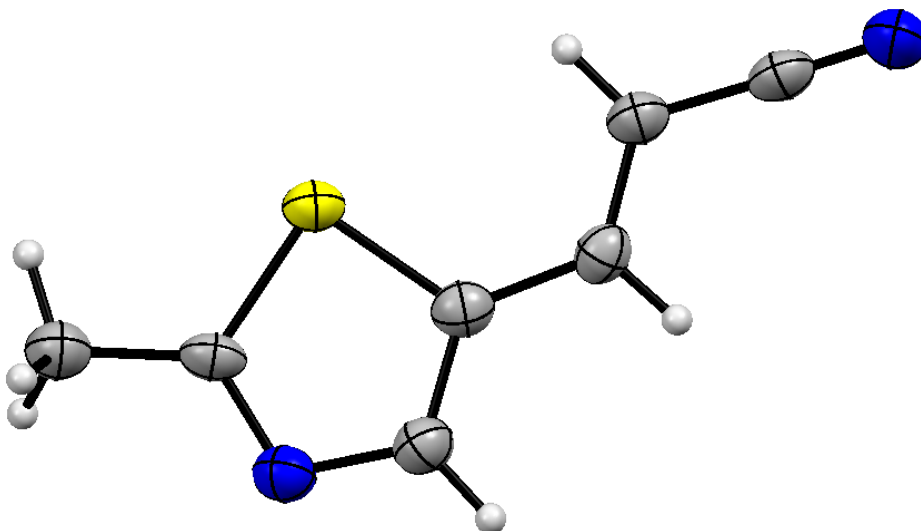


Figure S4. X-ray structure of **3cj** (**CCDC 1899795**). Ellipsoids are drawn at 50% probability level.

Cell:	$a=3.9295(4)$	$b=18.2181(16)$	$c=10.247(1)$
	$\alpha=90$	$\beta=97.120(9)$	$\gamma=90$

Temperature: 150 K

	Calculated	Reported
Volume	727.91(12)	727.90(13)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Data completeness = 1.000	Theta (max) = 24.991	
R (reflections) = 0.0734 (1100)	wR2 (reflections) = 0.1772 (1288)	

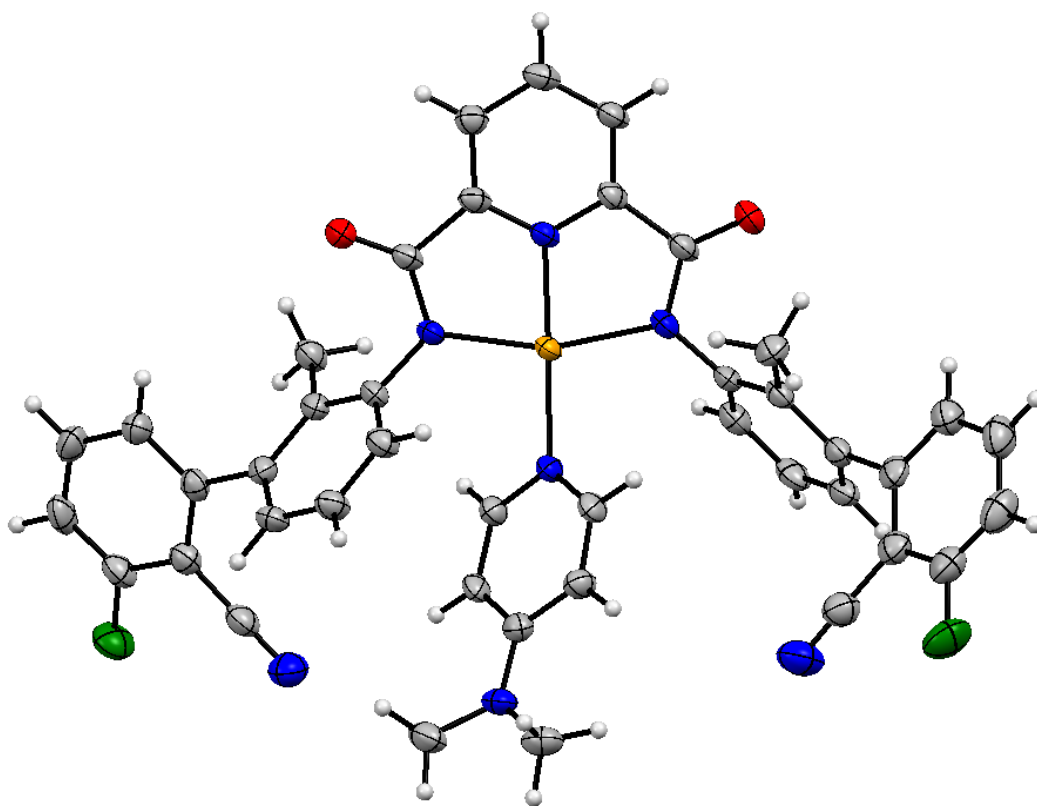


Figure S5. X-ray structure of **DMAP appended T6 (D)** (**CCDC 1846055**). Ellipsoids are drawn at 50% probability level.

Cell:	$a = 8.7124(4)$	$b = 28.1168(10)$	$c = 15.7854(5)$
	$\alpha = 90$	$\beta = 94.165(4)$	$\gamma = 90$

Temperature: 150 K

	Calculated	Reported
Volume	3856.7(3)	3856.7(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc

Data completeness = 0.998

Theta (max) = 24.997

R (reflections) = 0.0471 (5394)

wR2 (reflections) = 0.1102 (6791)

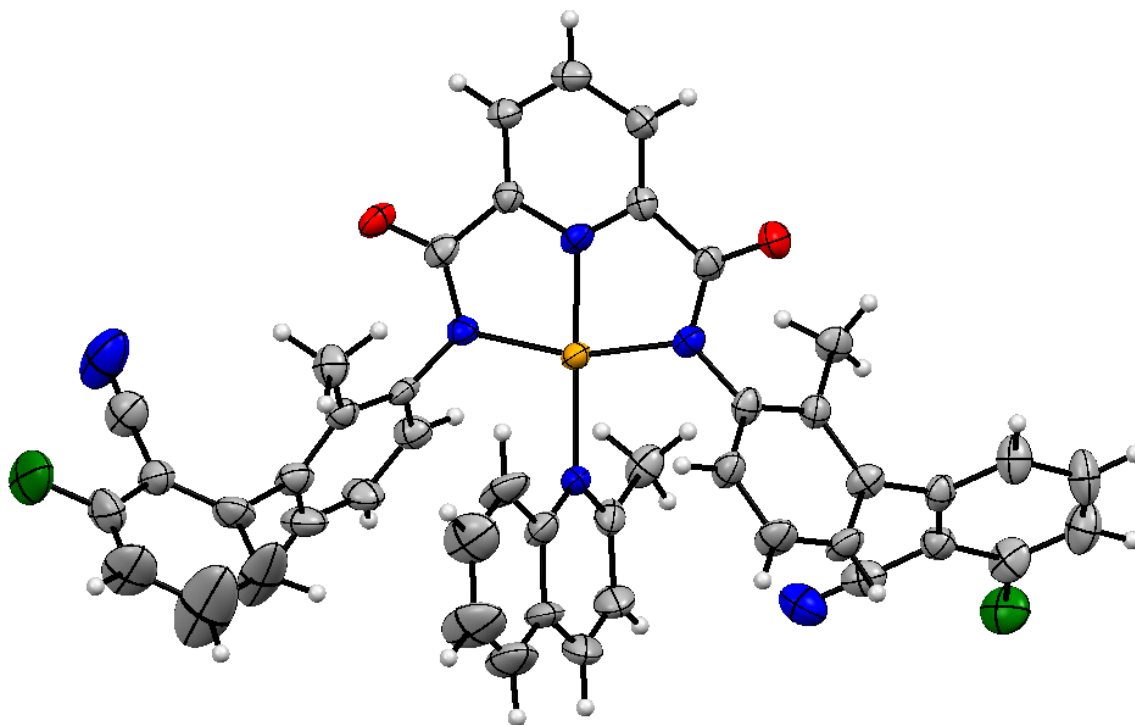


Figure S6. X-ray structure of quinaldine appended T6 (CCDC 1899987). Ellipsoids are drawn at 50% probability level.

Cell:	$a = 20.8007(15)$	$b = 14.1869(11)$	$c = 15.5305(14)$
	$\alpha = 90$	$\beta = 92.242(8)$	$\gamma = 90$

Temperature: 150 K

	Calculated	Reported
Volume	4579.5(6)	4579.5(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Data completeness = 1.000	Theta (max) = 25.000	
R (reflections) = 0.0650 (5638)	wR2 (reflections) = 0.2454 (8063)	

ESI-MS study

0.05 mmol of each T6 and thiazole were transferred to a clean reaction tube containing magnetic stirring bar. Then 1 mL DCM was added to it and kept stirring for 30 min at room temperature. After that DCM was removed under vacuuo and dissolved in CH₃CN followed by ESI-MS was recorded.

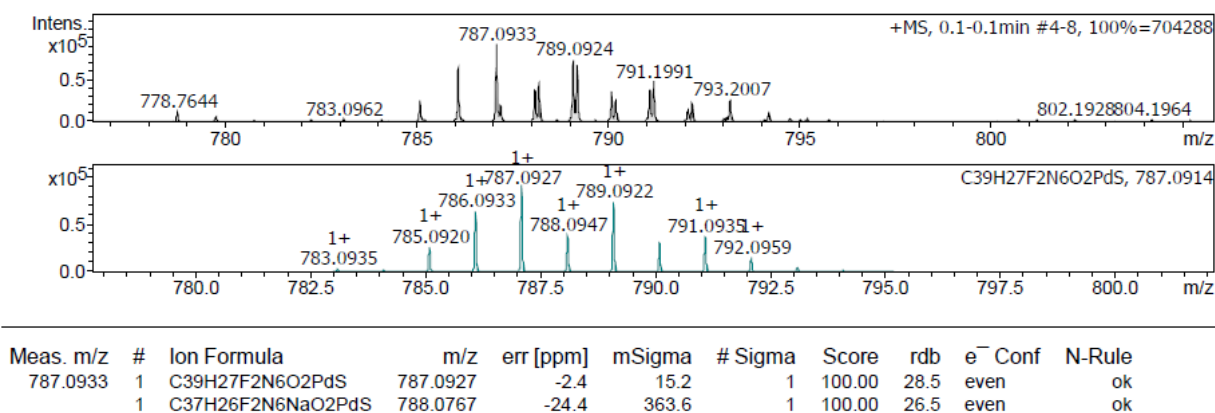
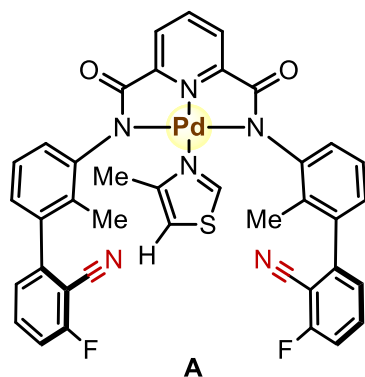


Figure S7. ESI-MS spectra of **A** (manuscript, Figure 2), thiazole appended T6.

NMR Spectra

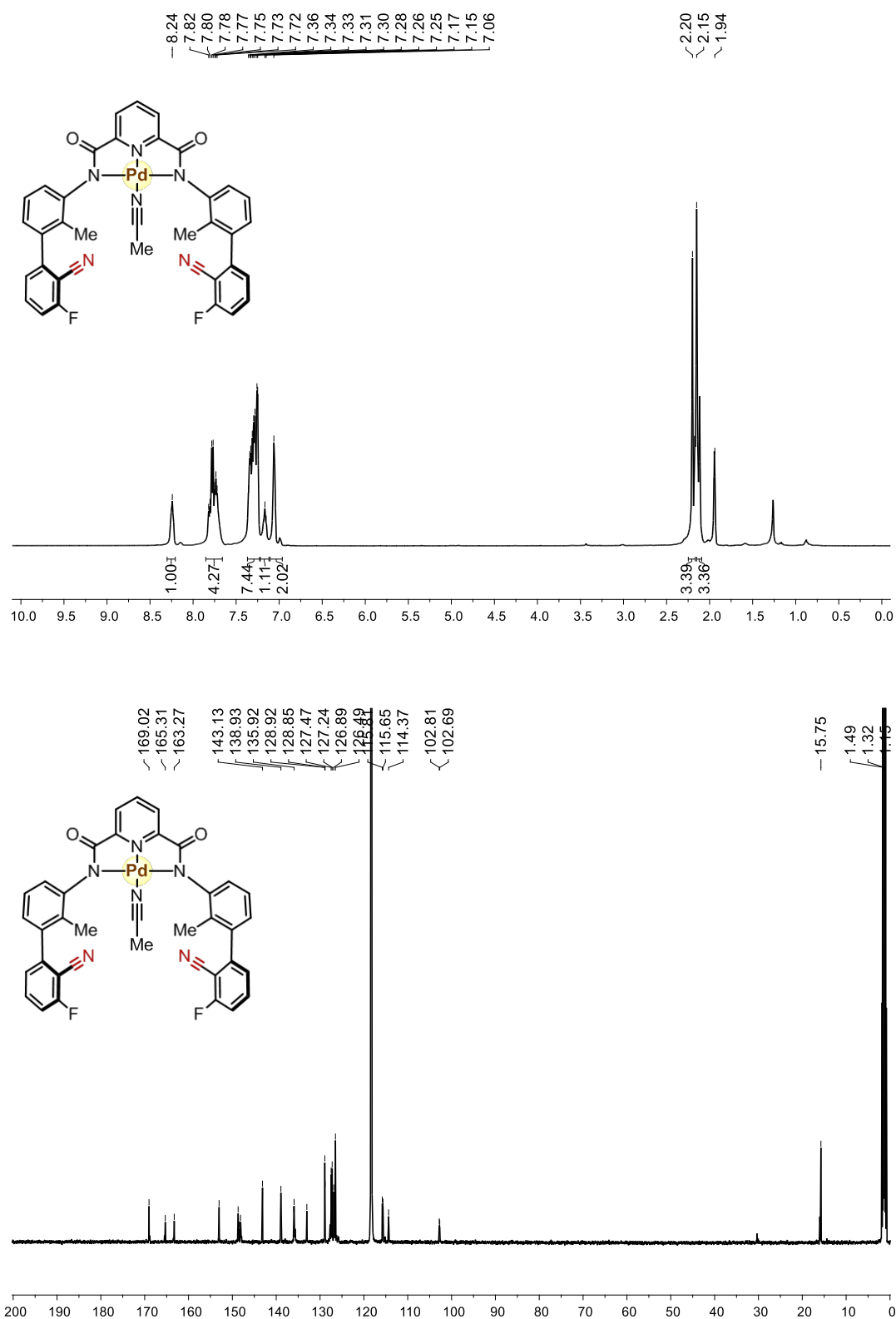


Figure S8. ¹H (top) and ¹³C (bottom) NMR of T6.

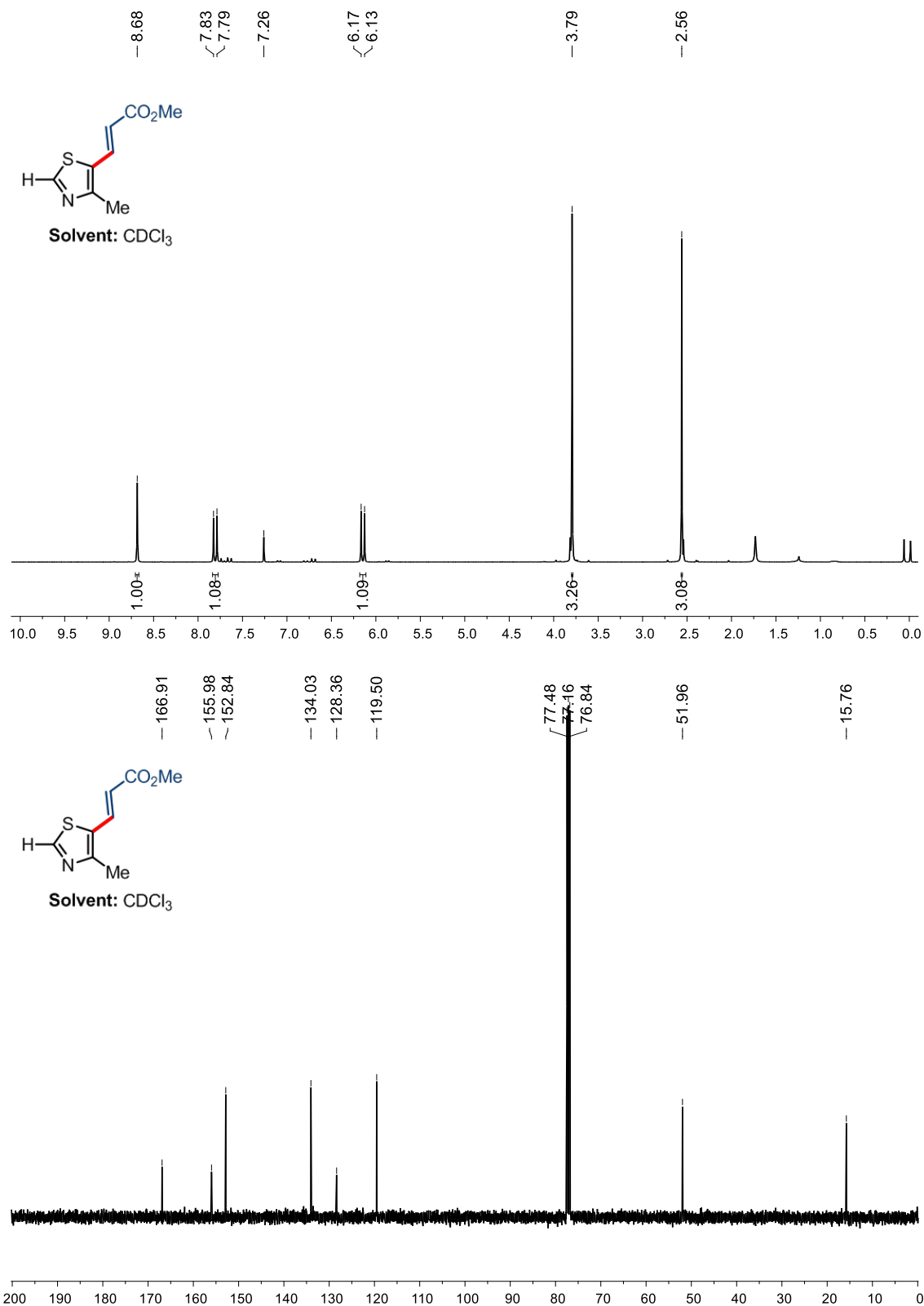


Figure S9. ¹H (top) and ¹³C (bottom) NMR of **3aa**.

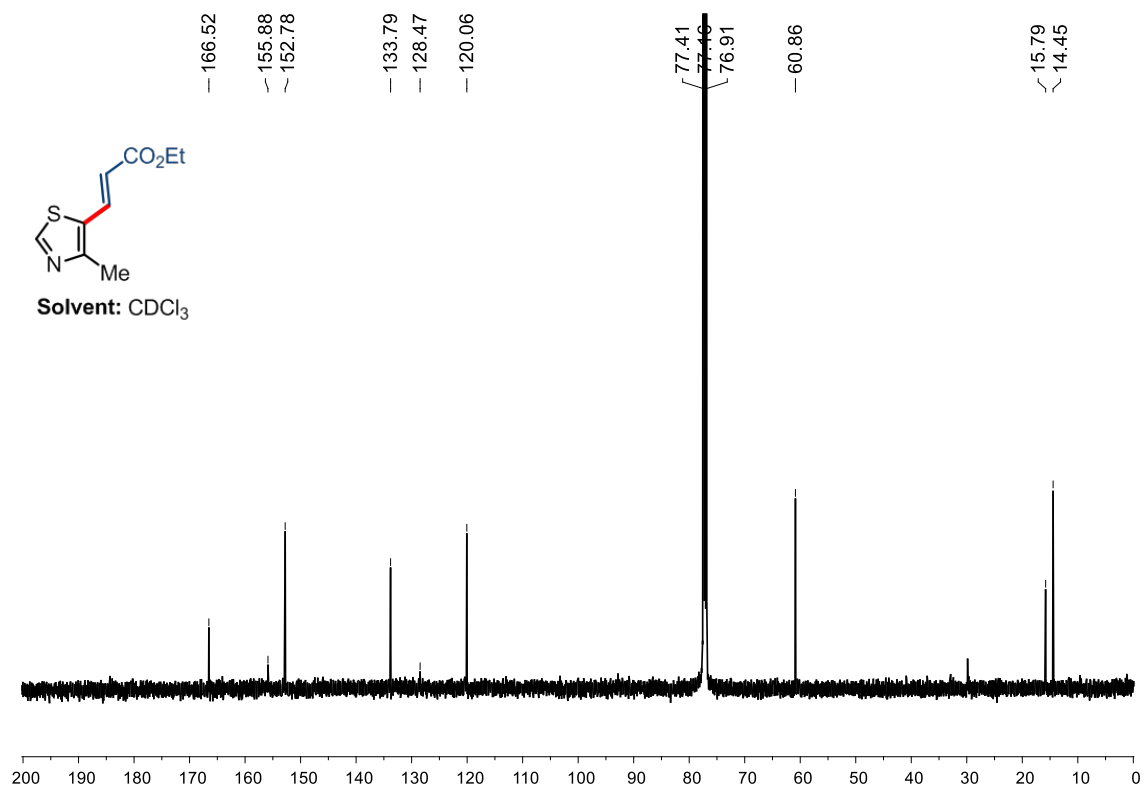
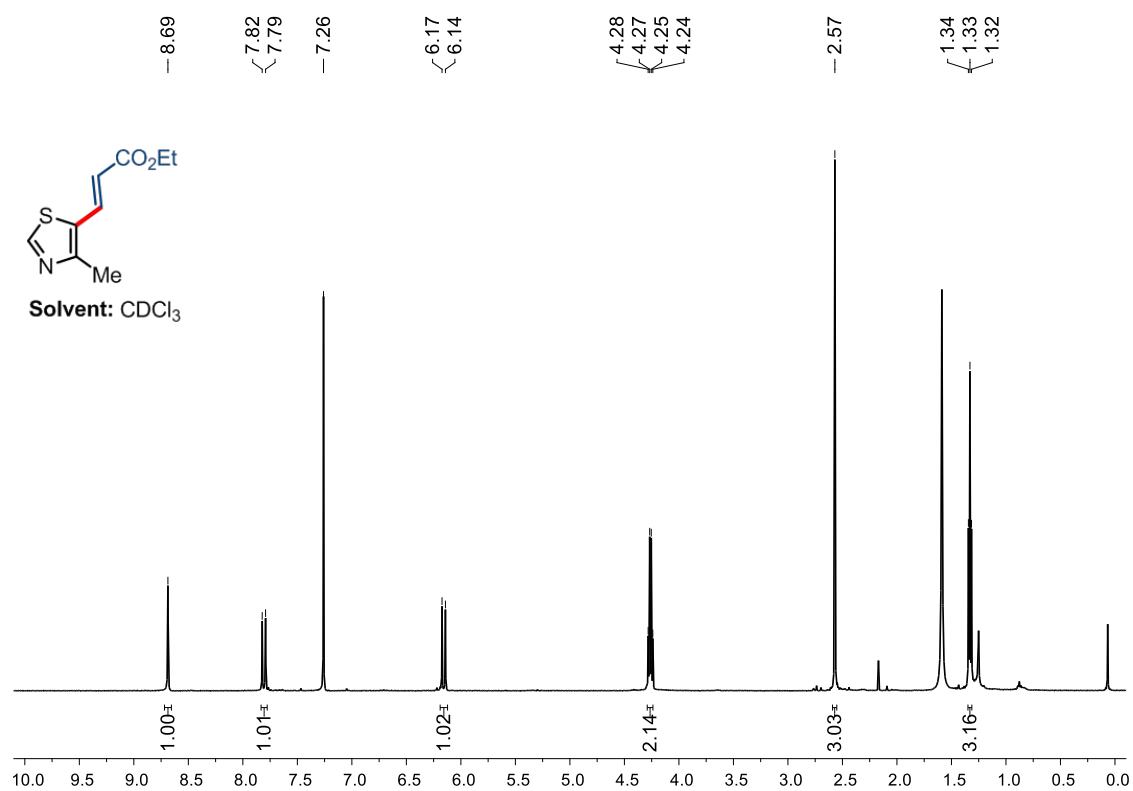


Figure S10. ¹H (top) and ¹³C (bottom) NMR of **3ab**.

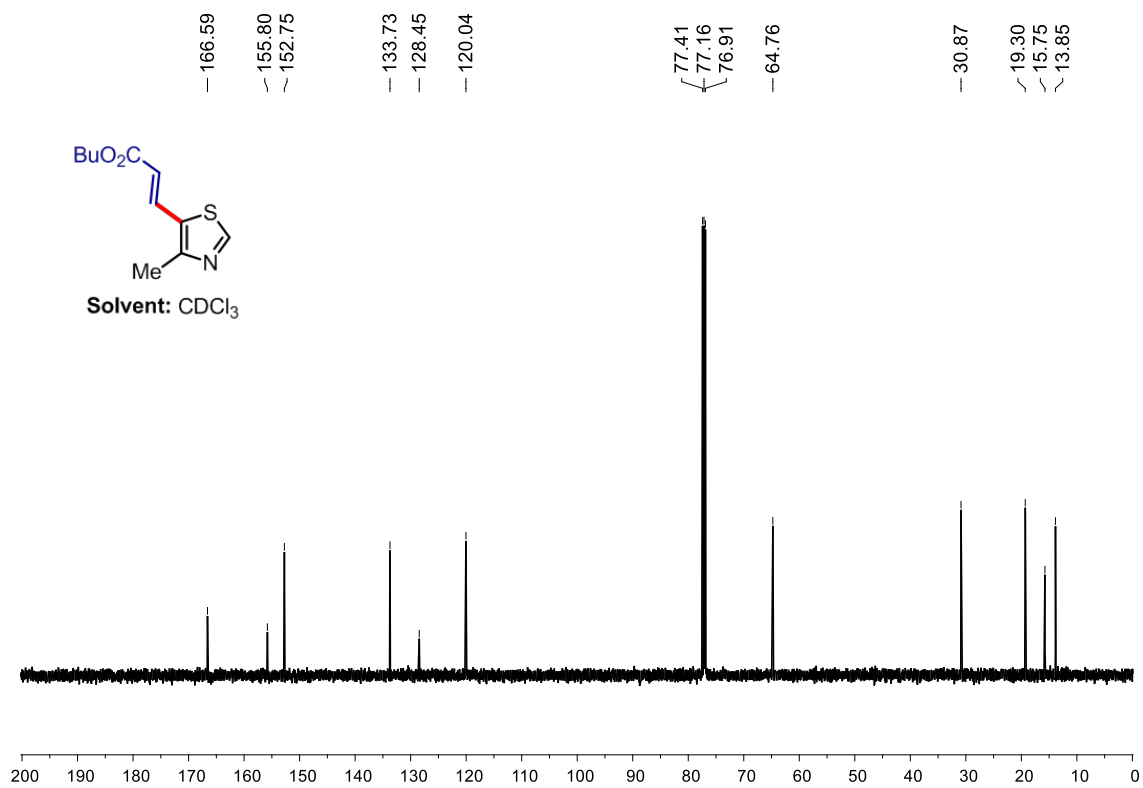
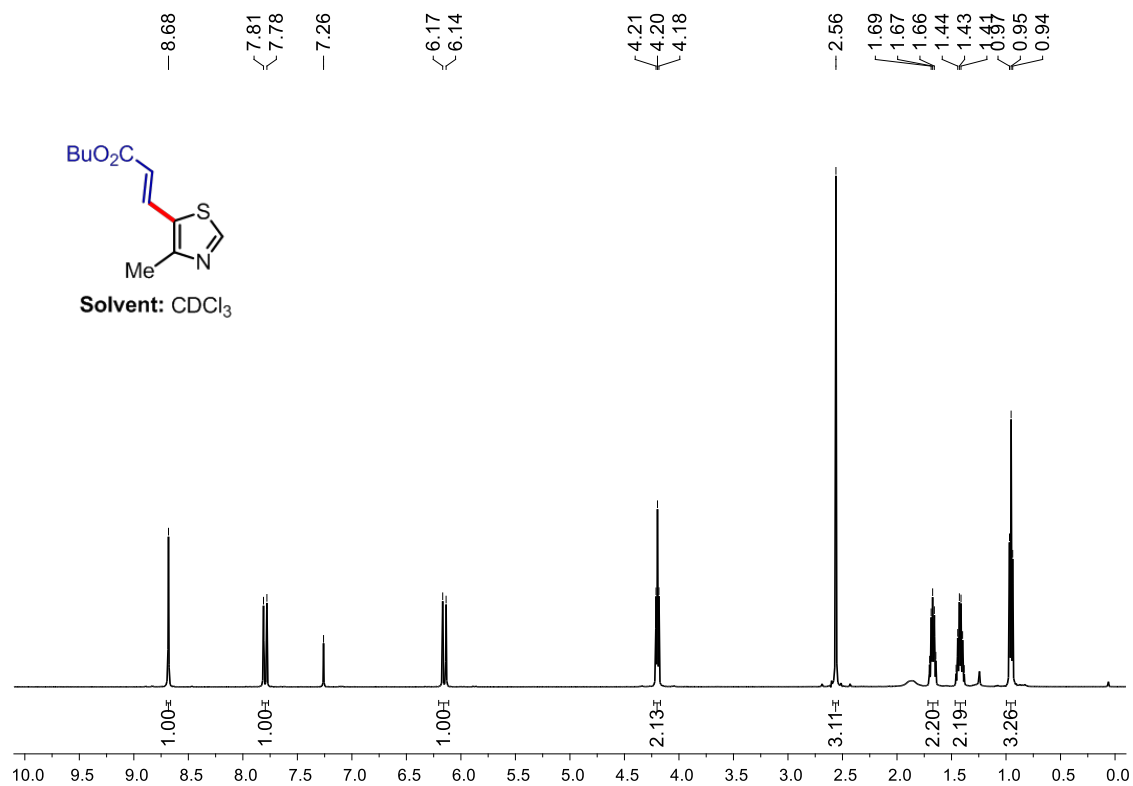


Figure S11. ^1H (top) and ^{13}C (bottom) NMR of **3ac**.

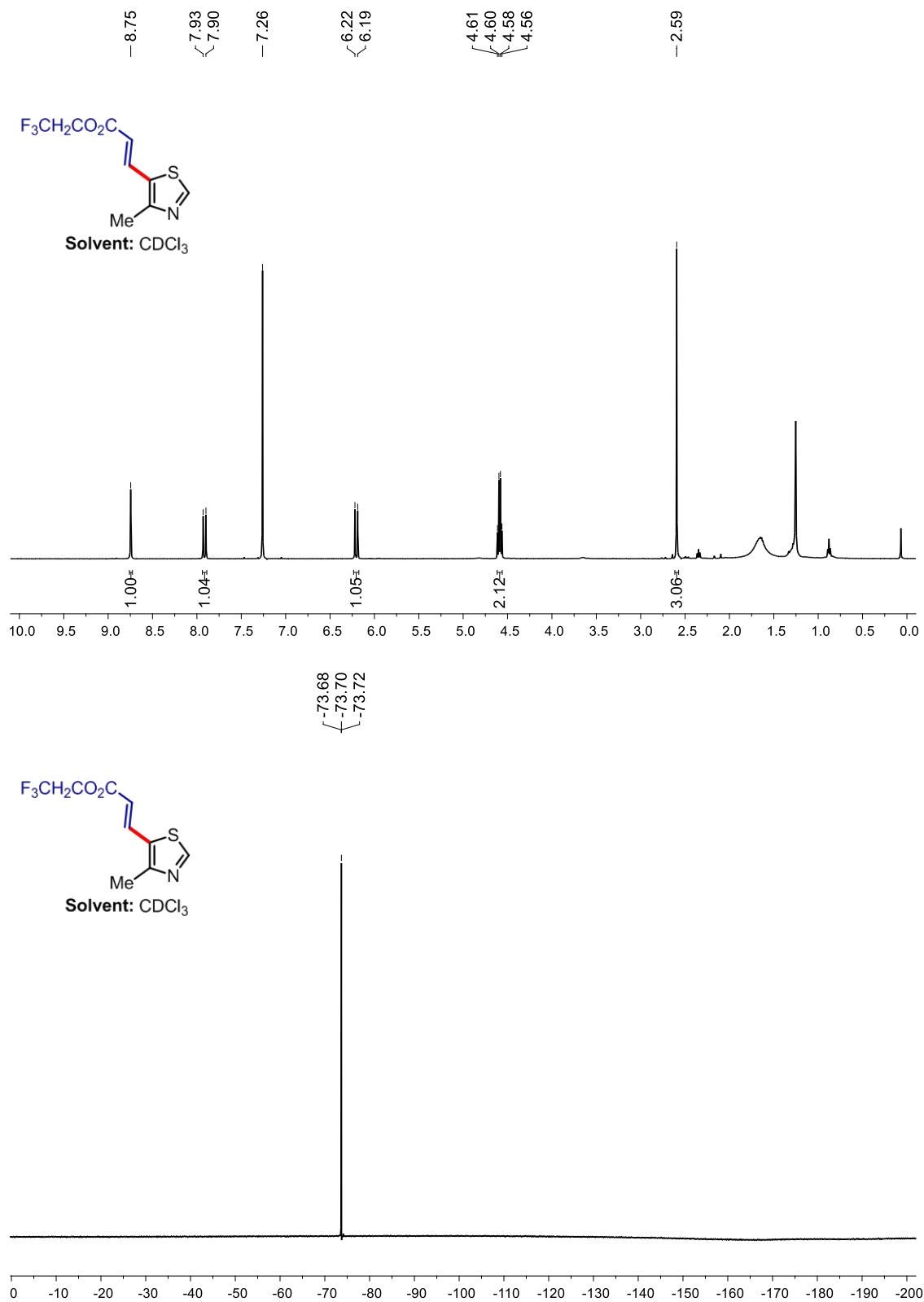


Figure S12. ¹H (top) and ¹⁹F (bottom) NMR of **3ad**.

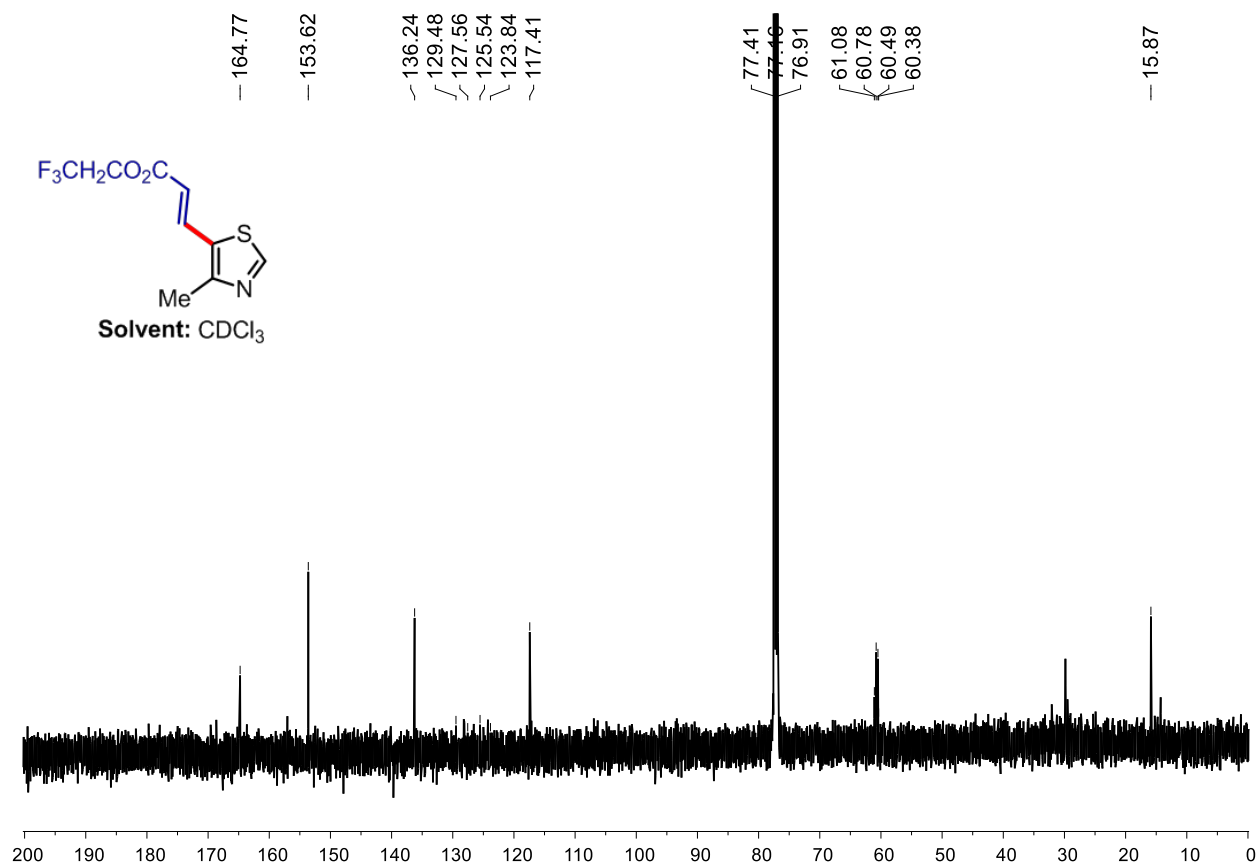


Figure S13. ¹³C NMR of 3ad.

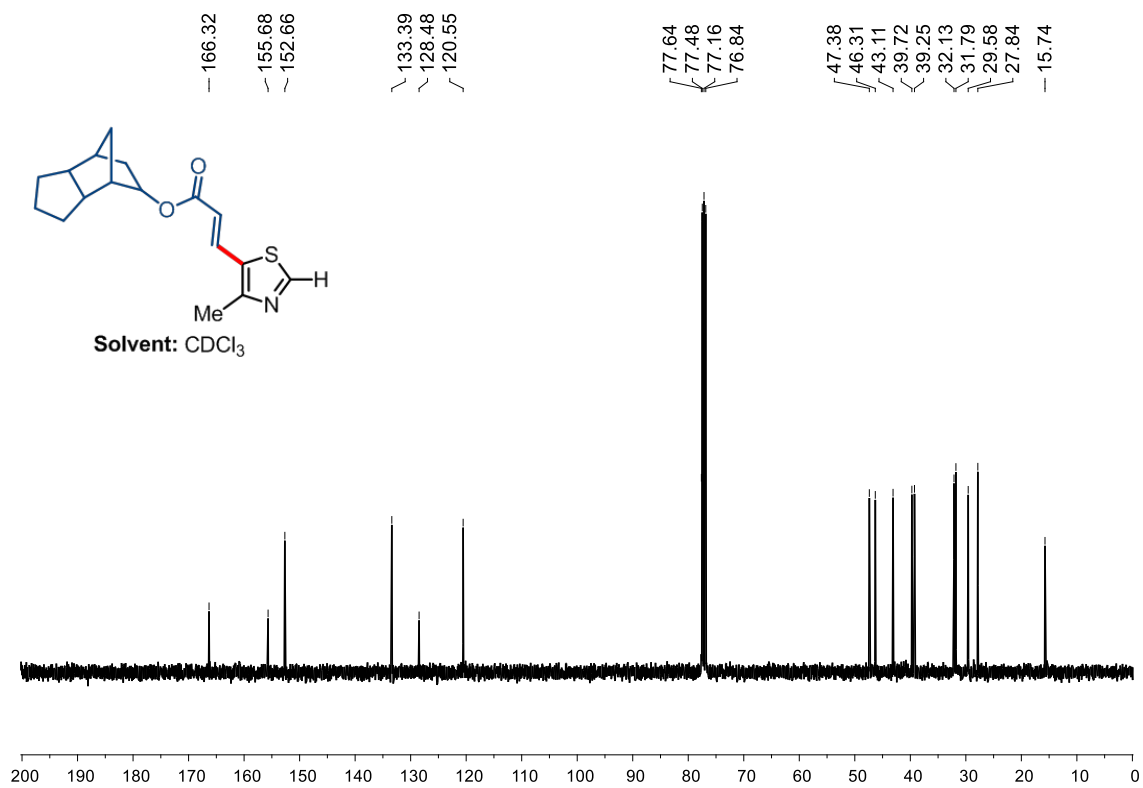
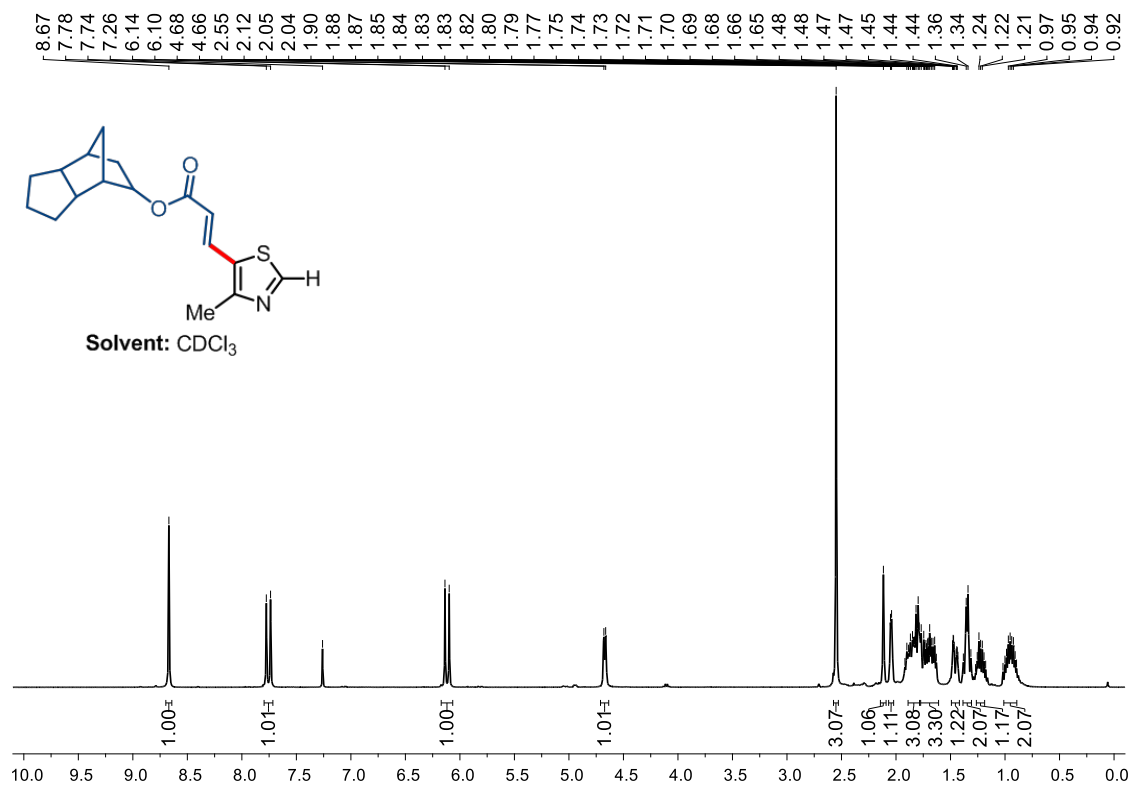


Figure S14. ^1H (top) and ^{13}C (bottom) NMR of **3ae**.

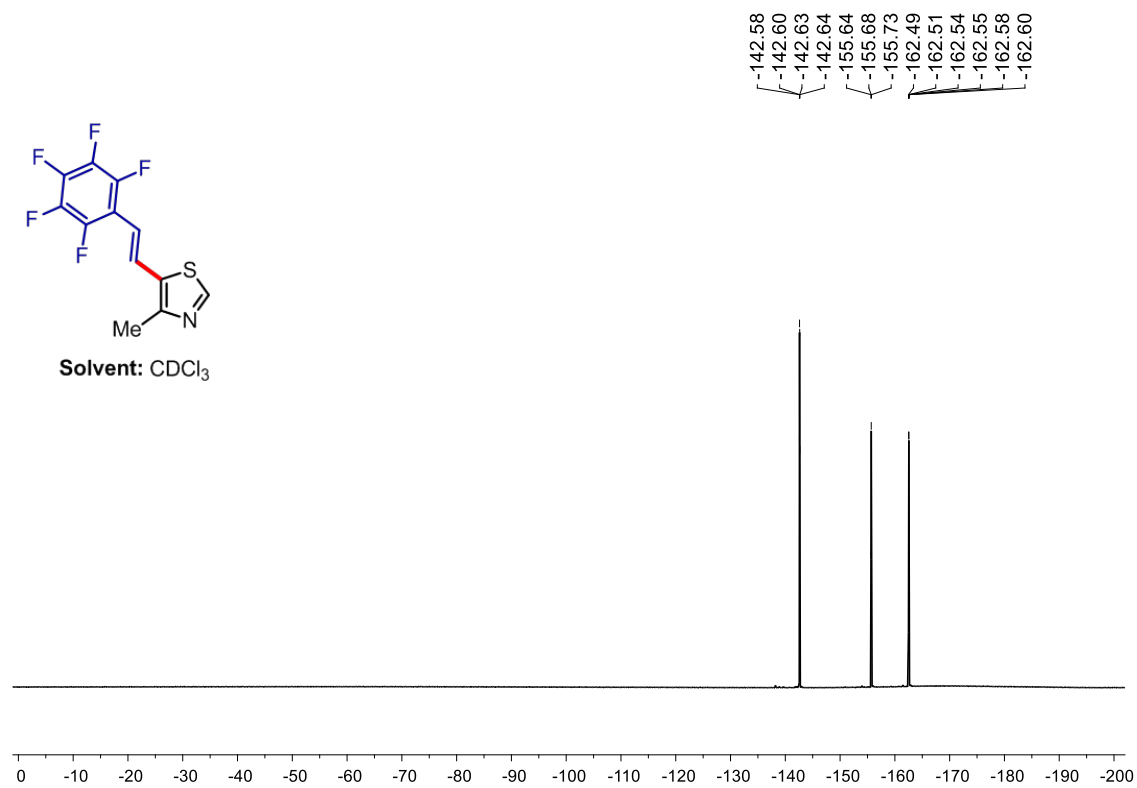
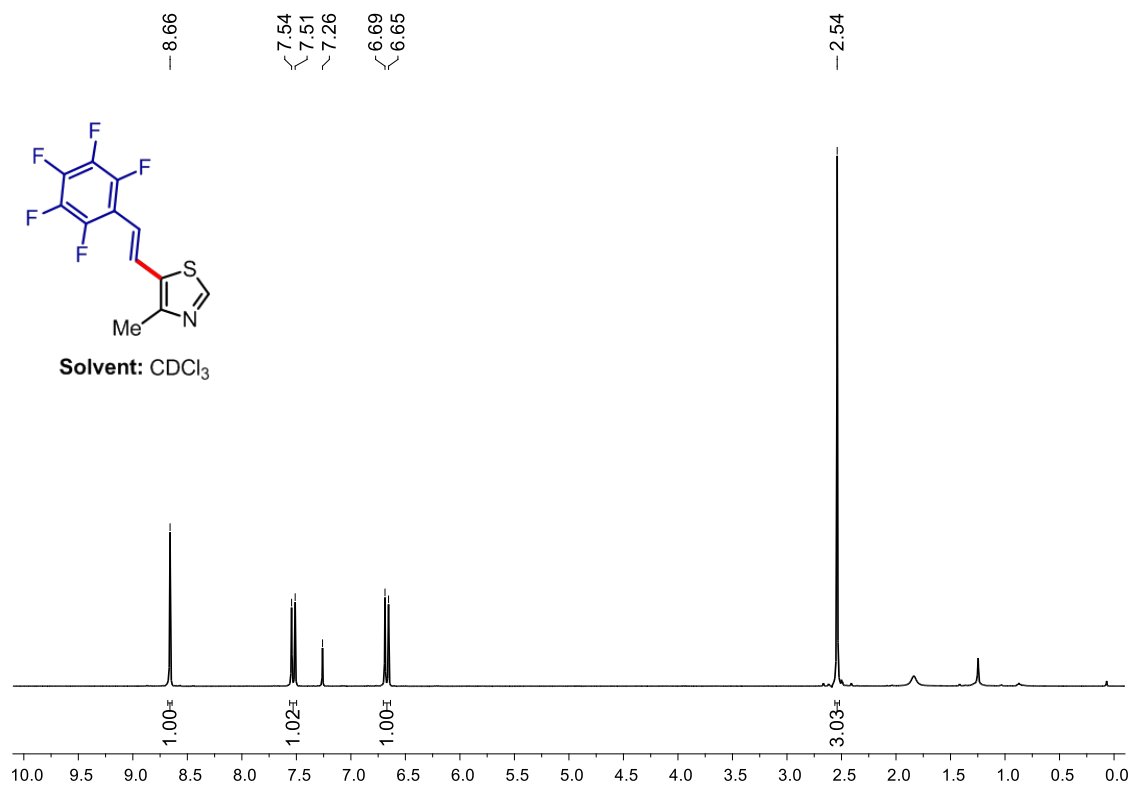


Figure S15. ¹H (top) and ¹⁹F (bottom) NMR of **3af**.

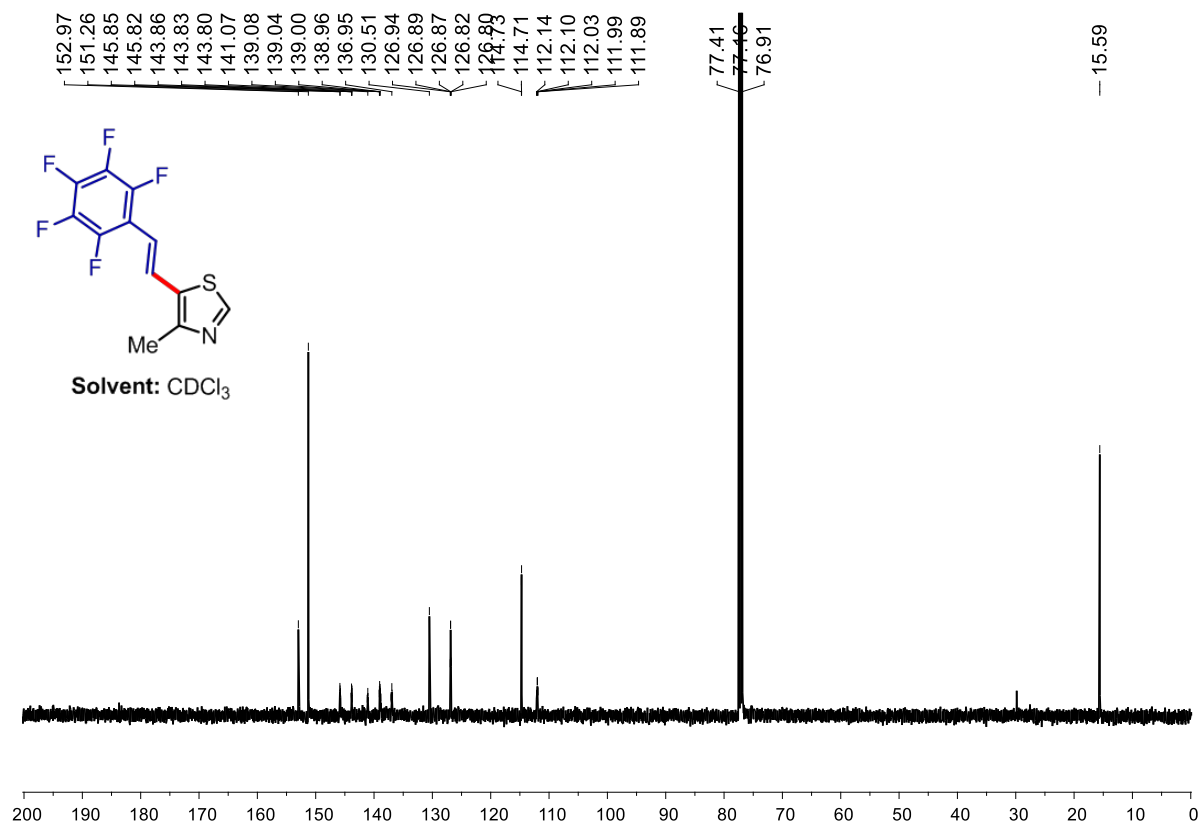


Figure S16. ¹³C NMR of 3af.

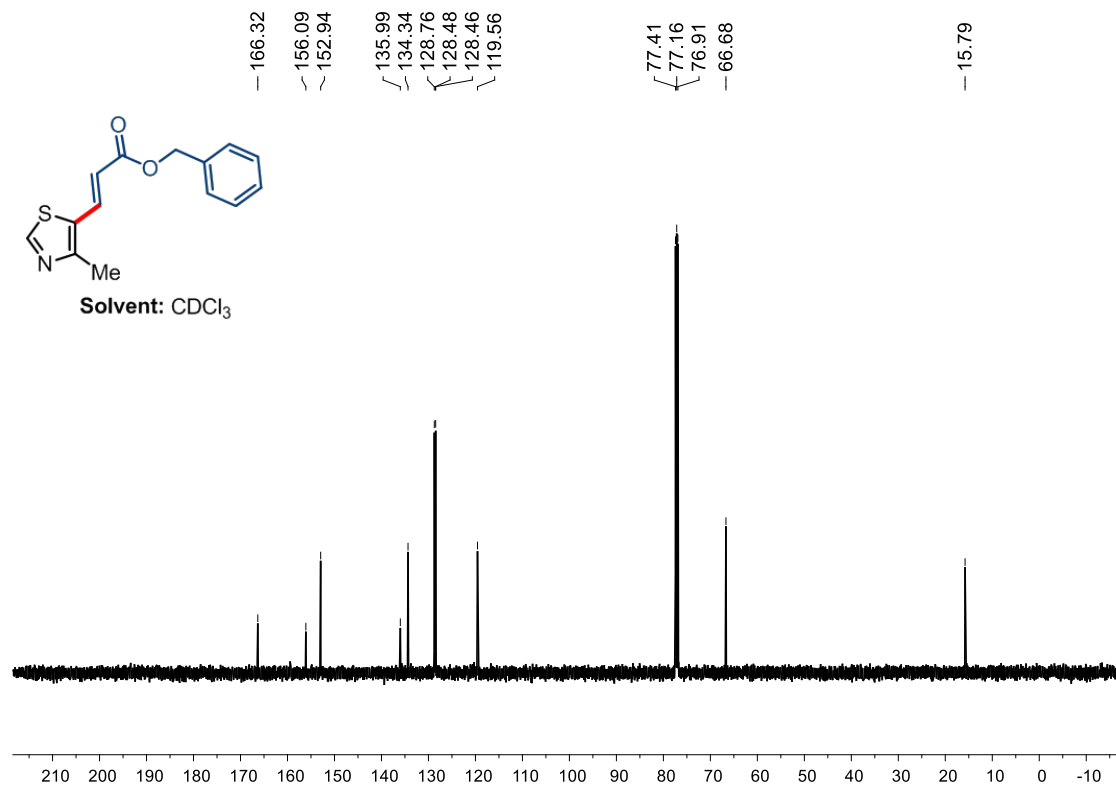
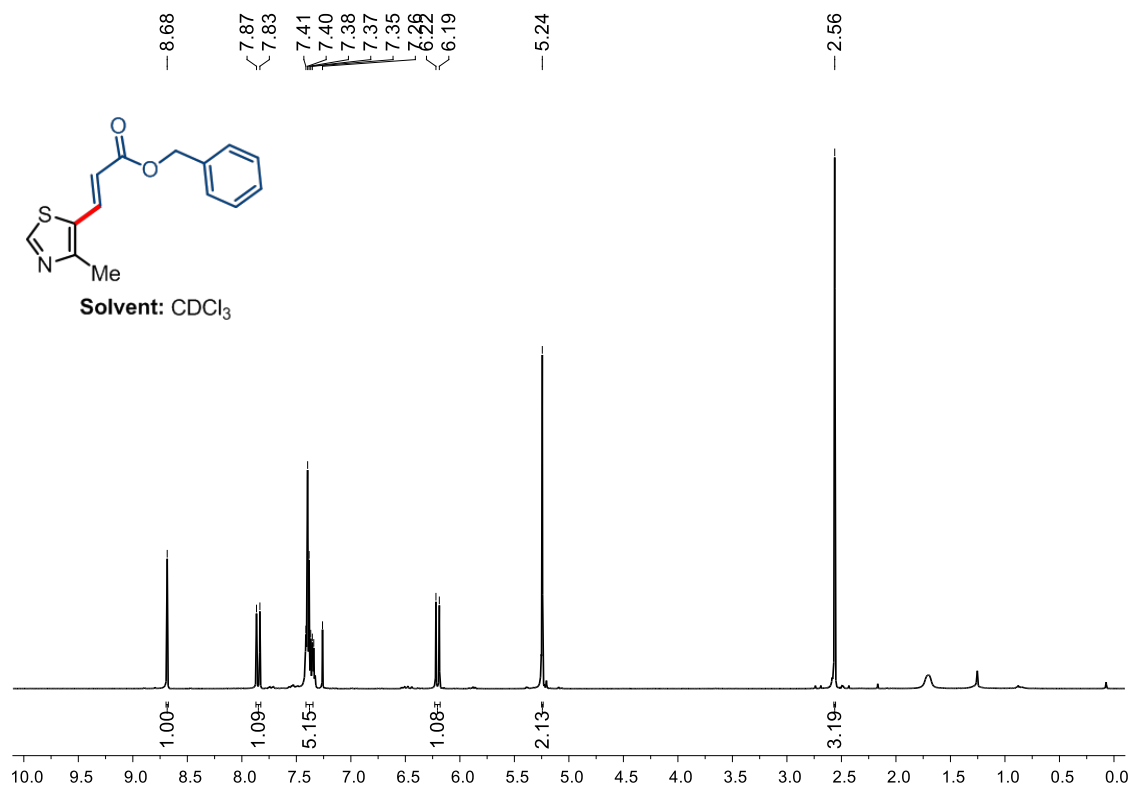


Figure S17. ¹H (top) and ¹³C (bottom) NMR of **3ag**.

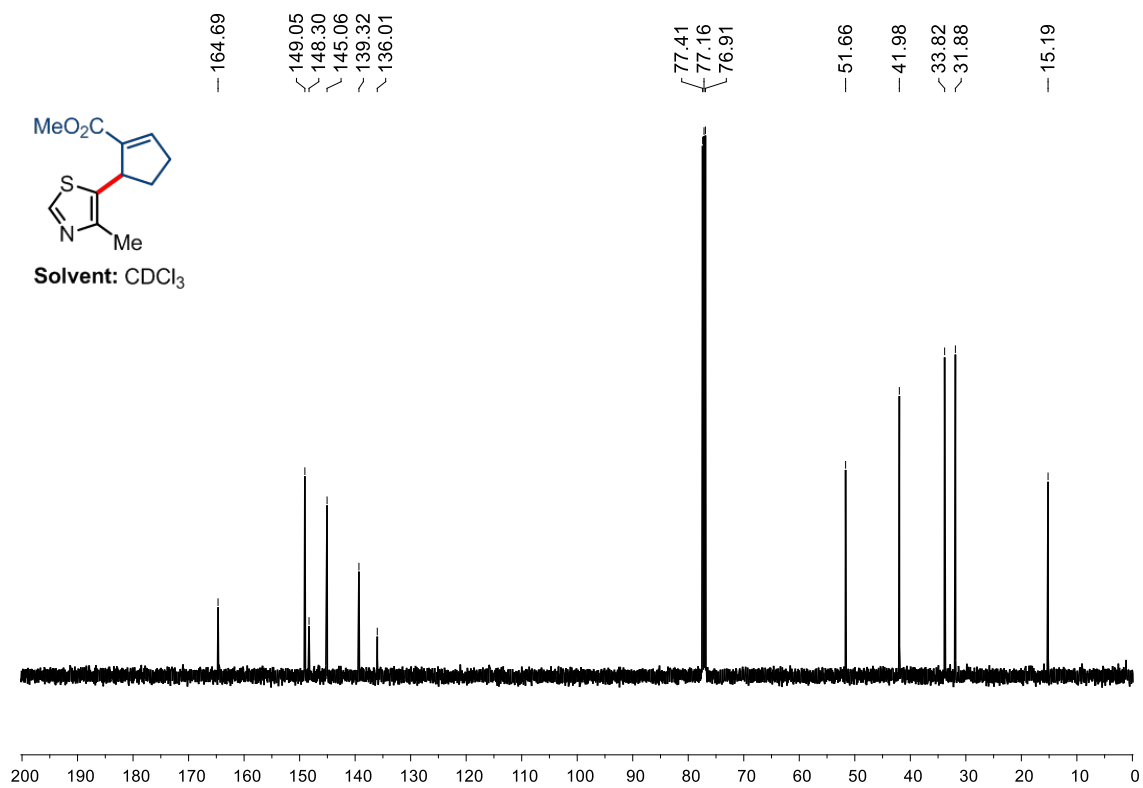
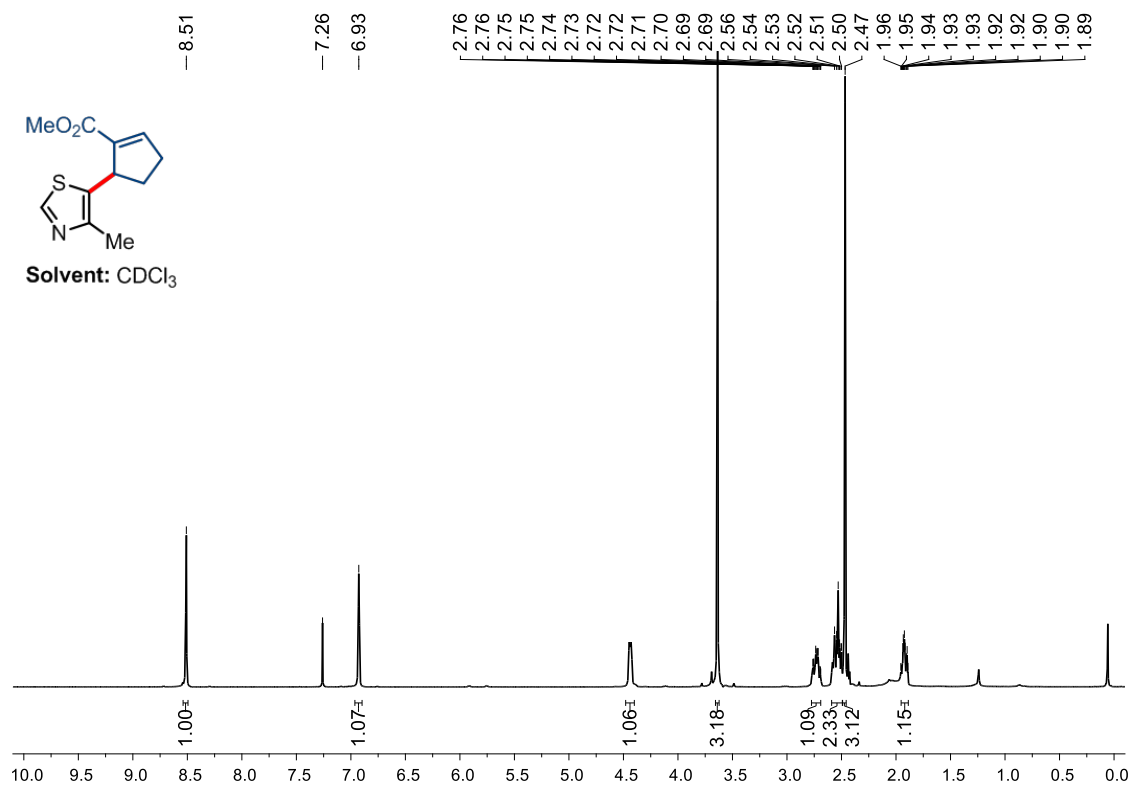


Figure S18. ¹H (top) and ¹³C (bottom) NMR of **3ah**.

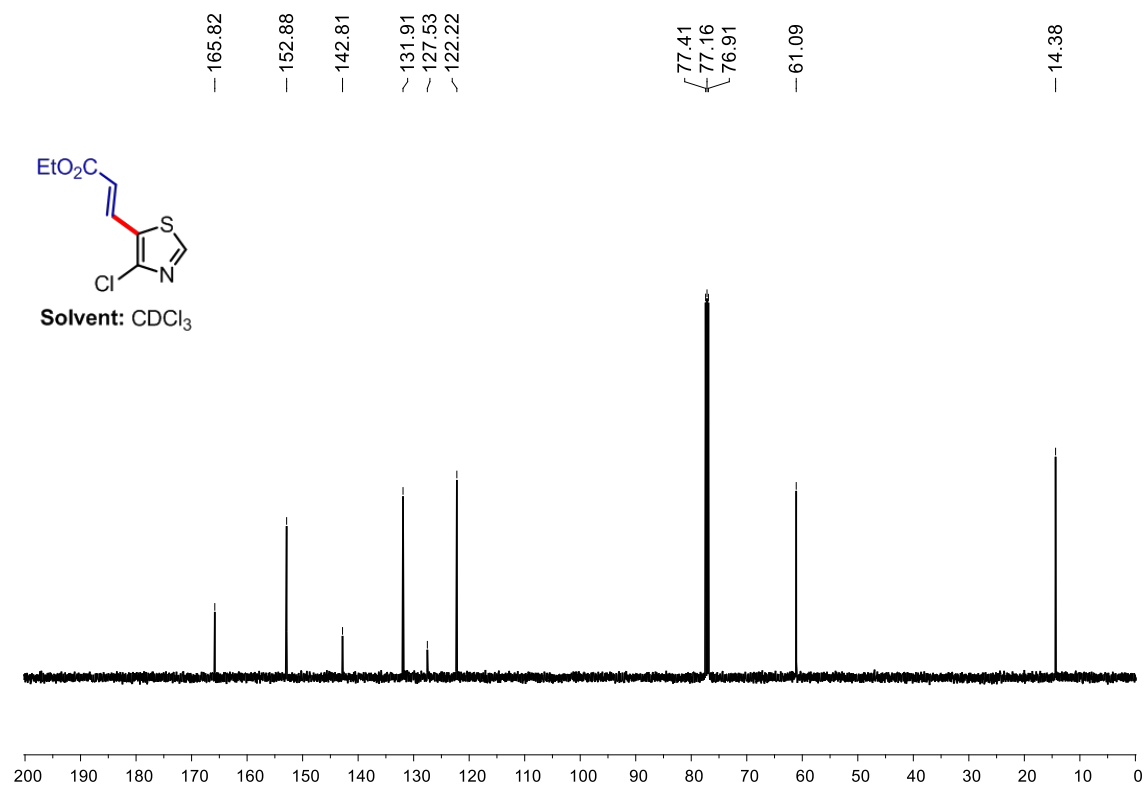
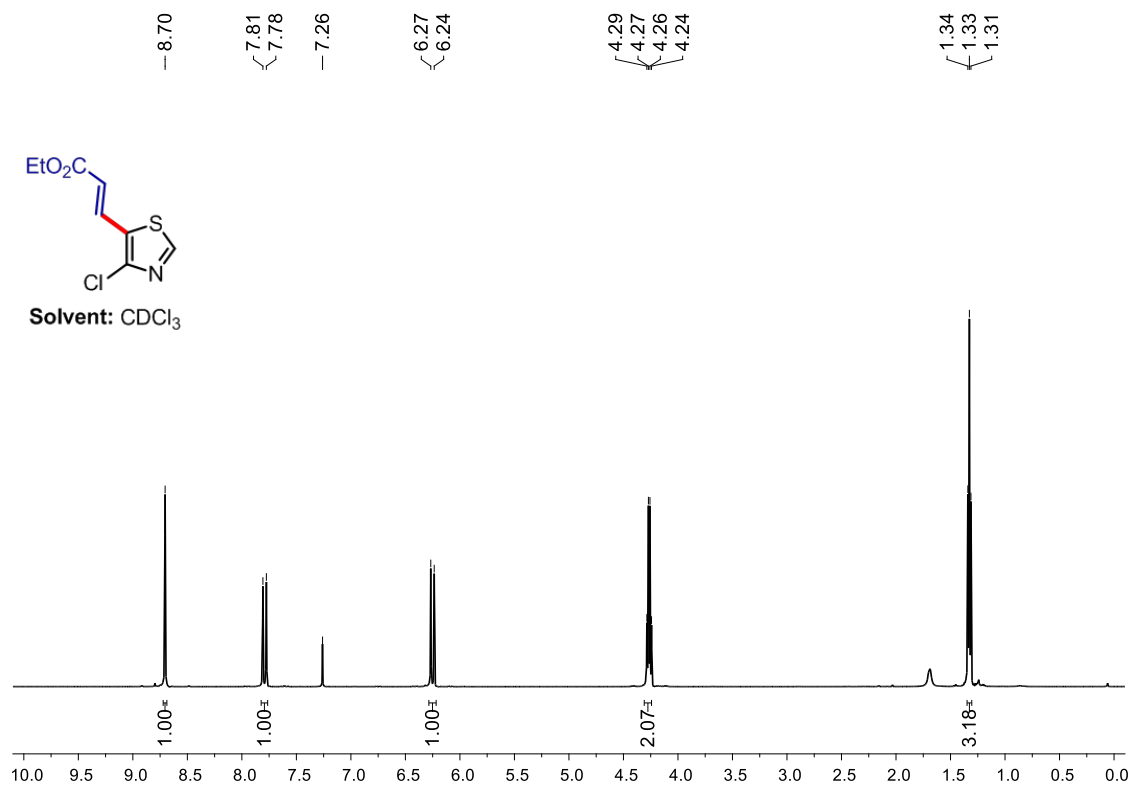


Figure S19. ¹H (top) and ¹³C (bottom) NMR of **3bb**.

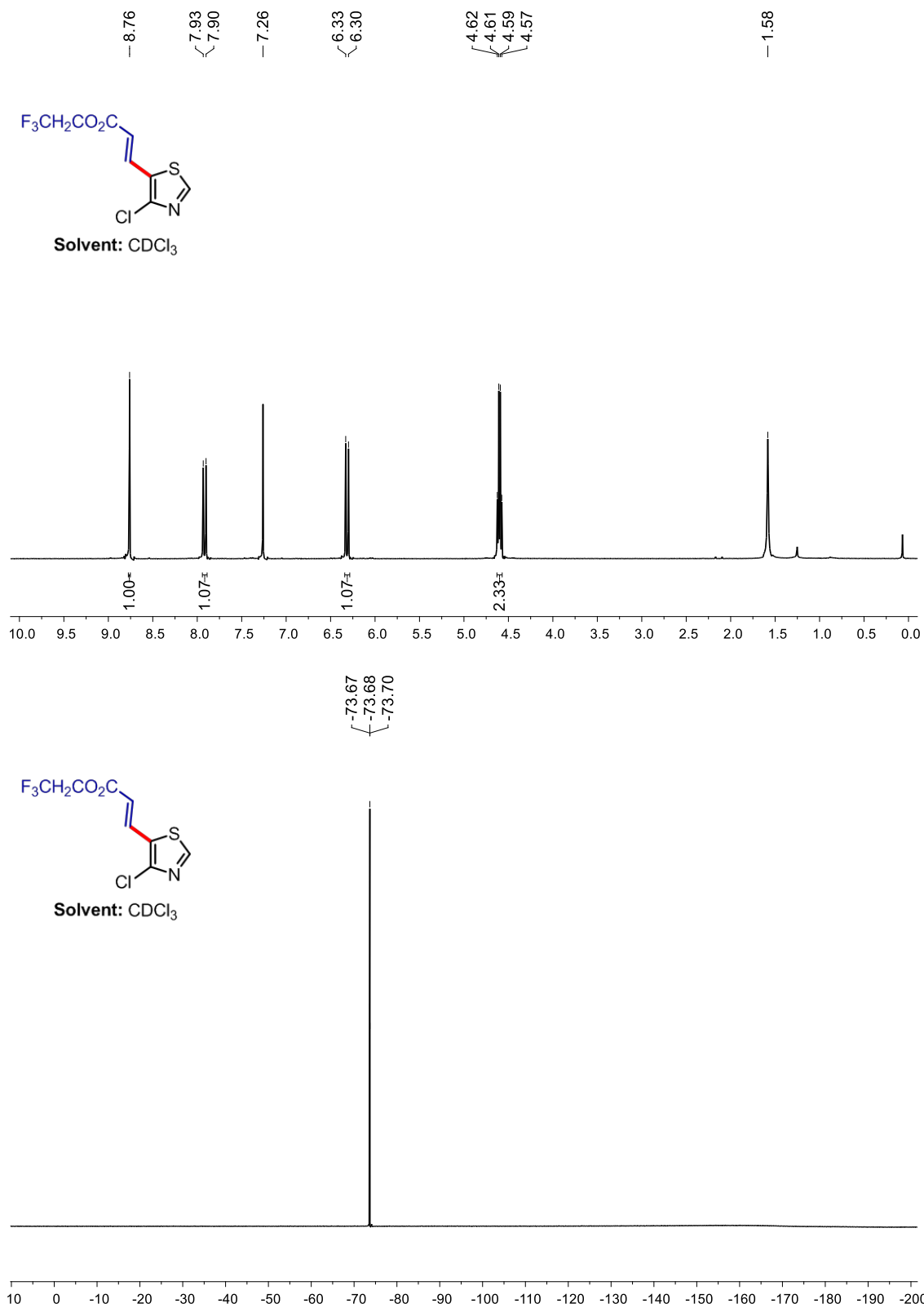


Figure S20. ¹H (top) and ¹⁹F (bottom) NMR of **3bd**.

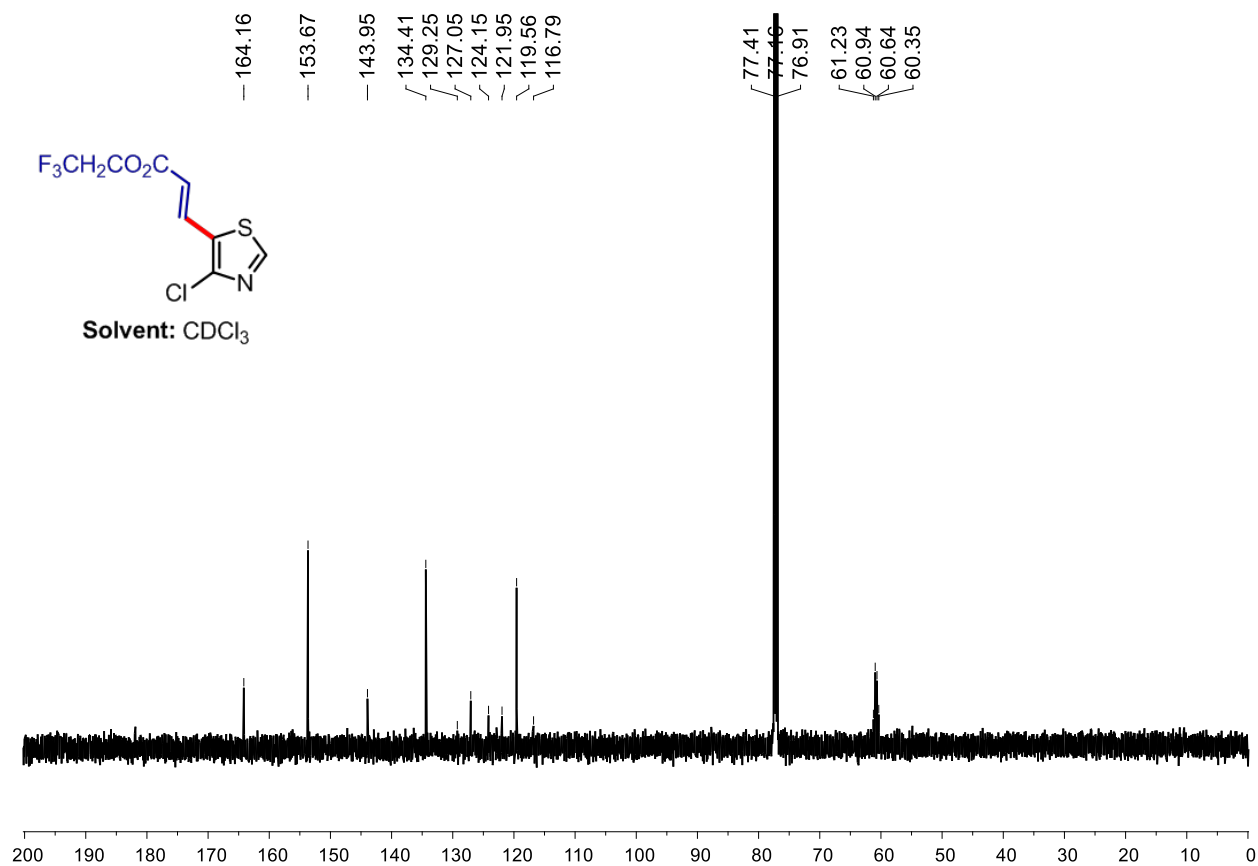


Figure S21. ^{13}C NMR of 3bd.

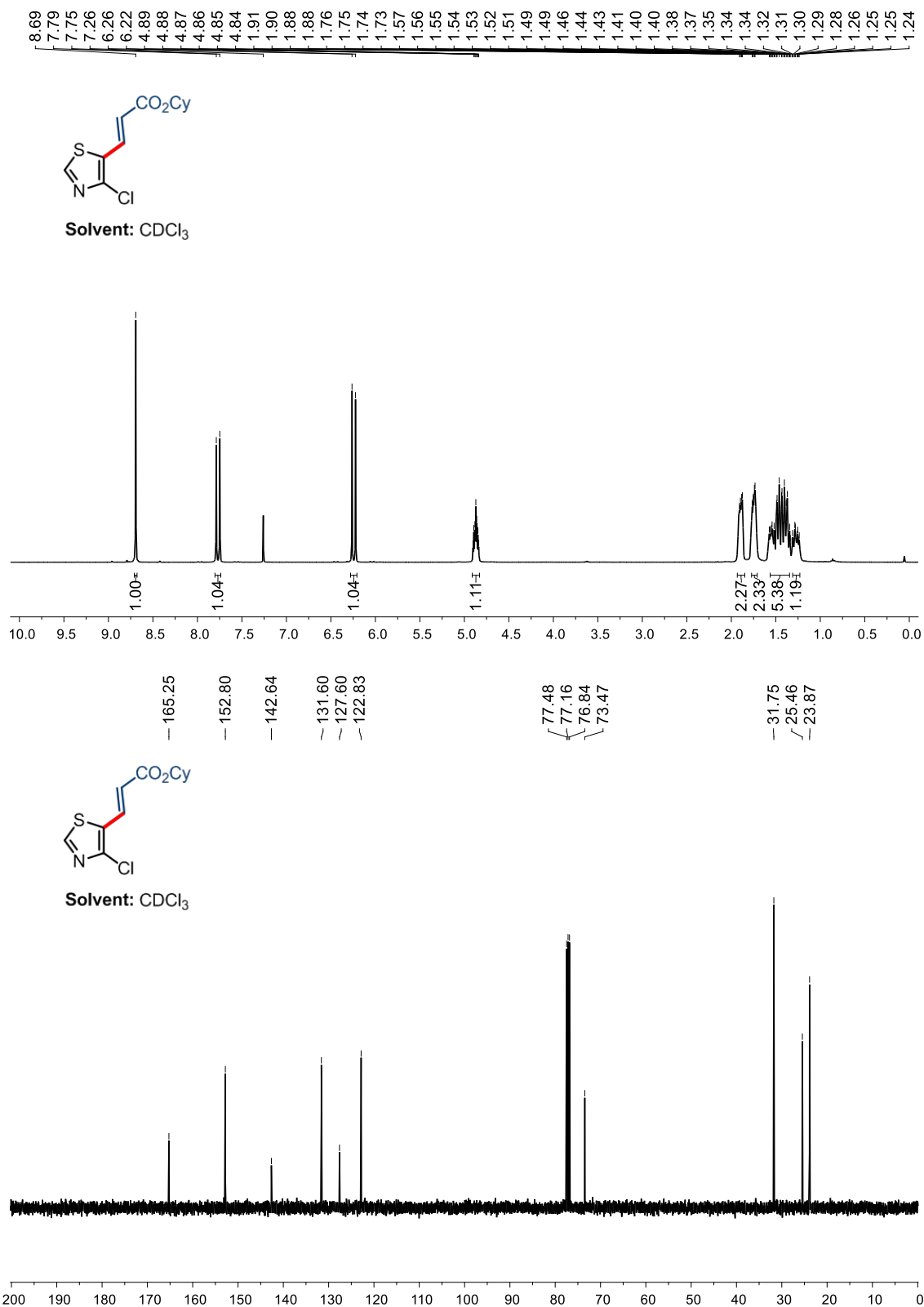


Figure S22. ¹H (top) and ¹³C (bottom) NMR of **3bi**.

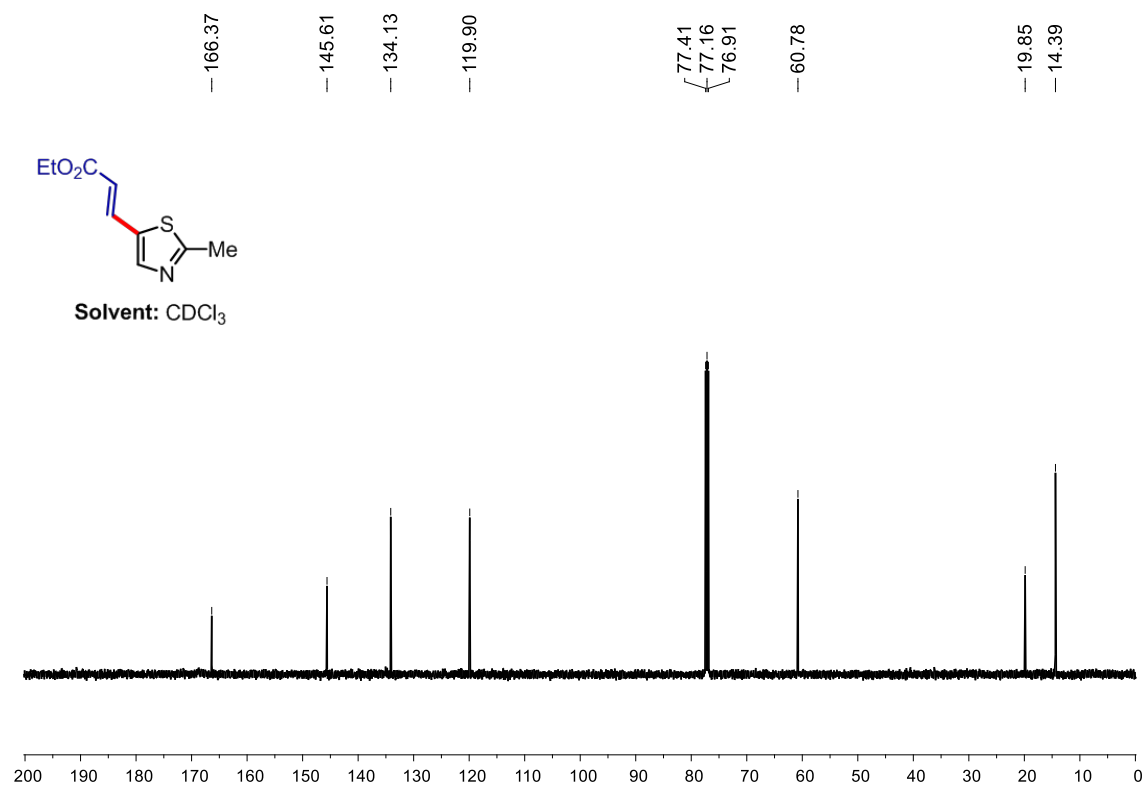
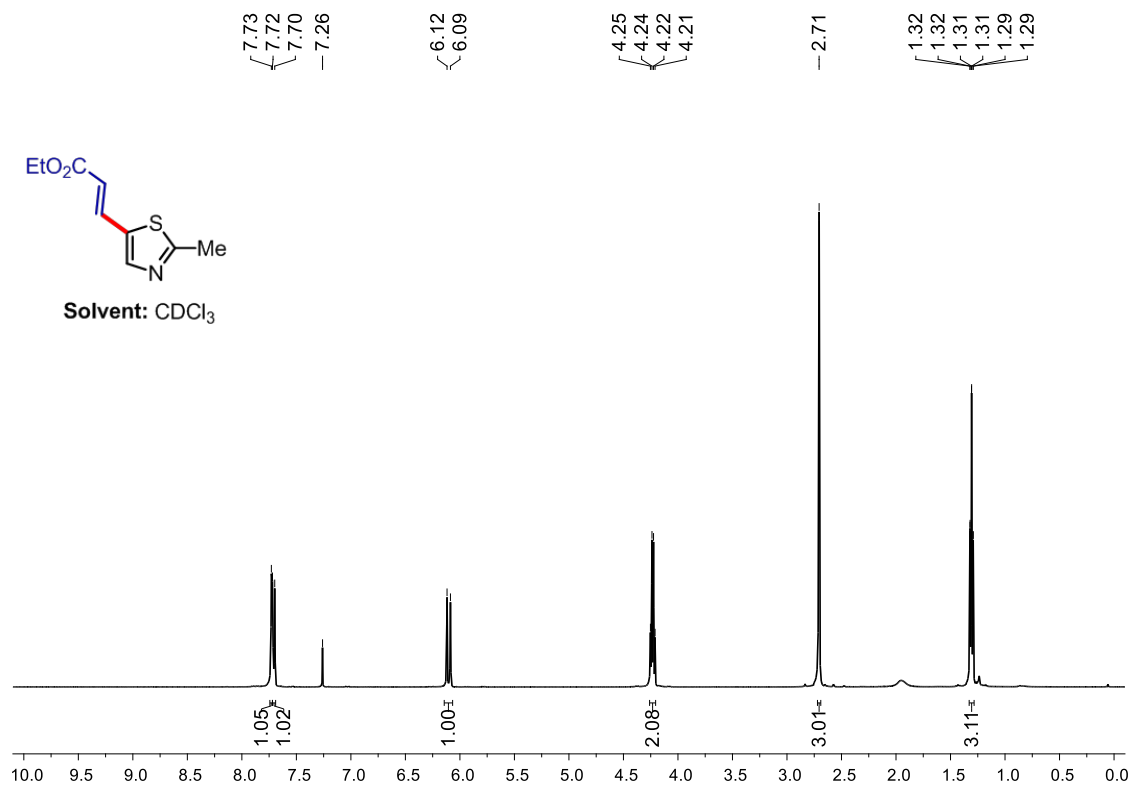


Figure S23. ¹H (top) and ¹³C (bottom) NMR of **3cb**.

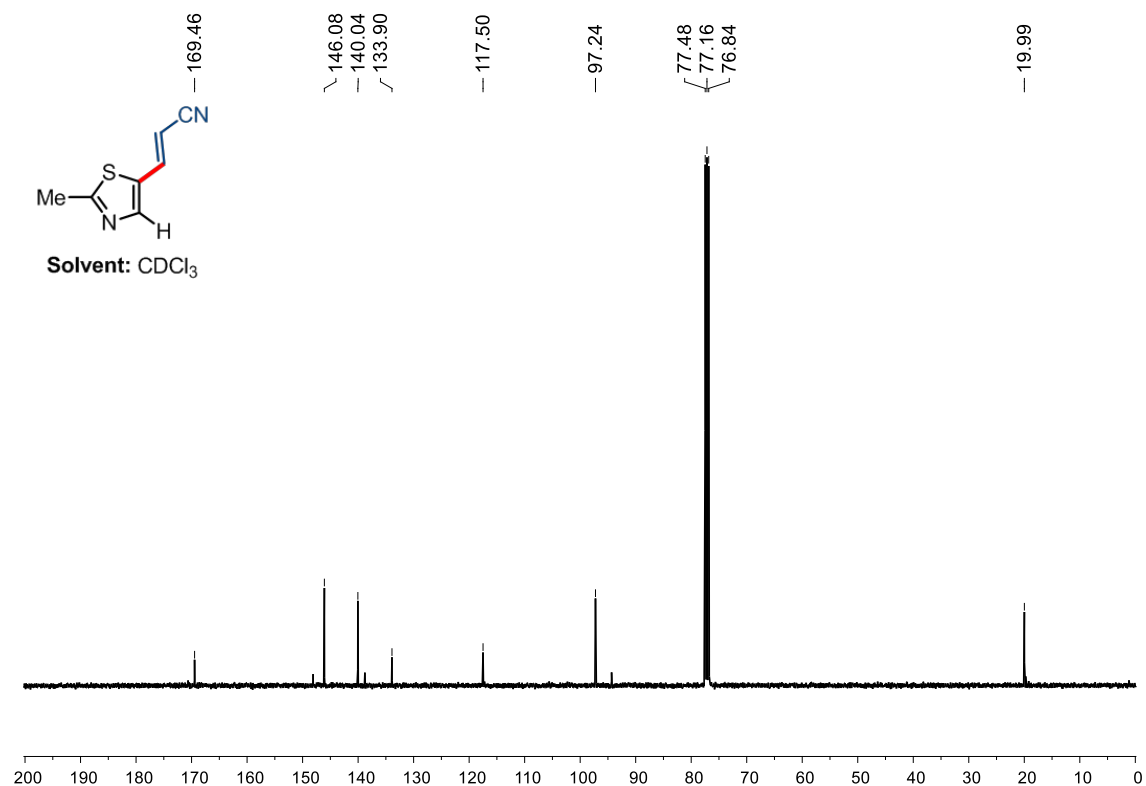
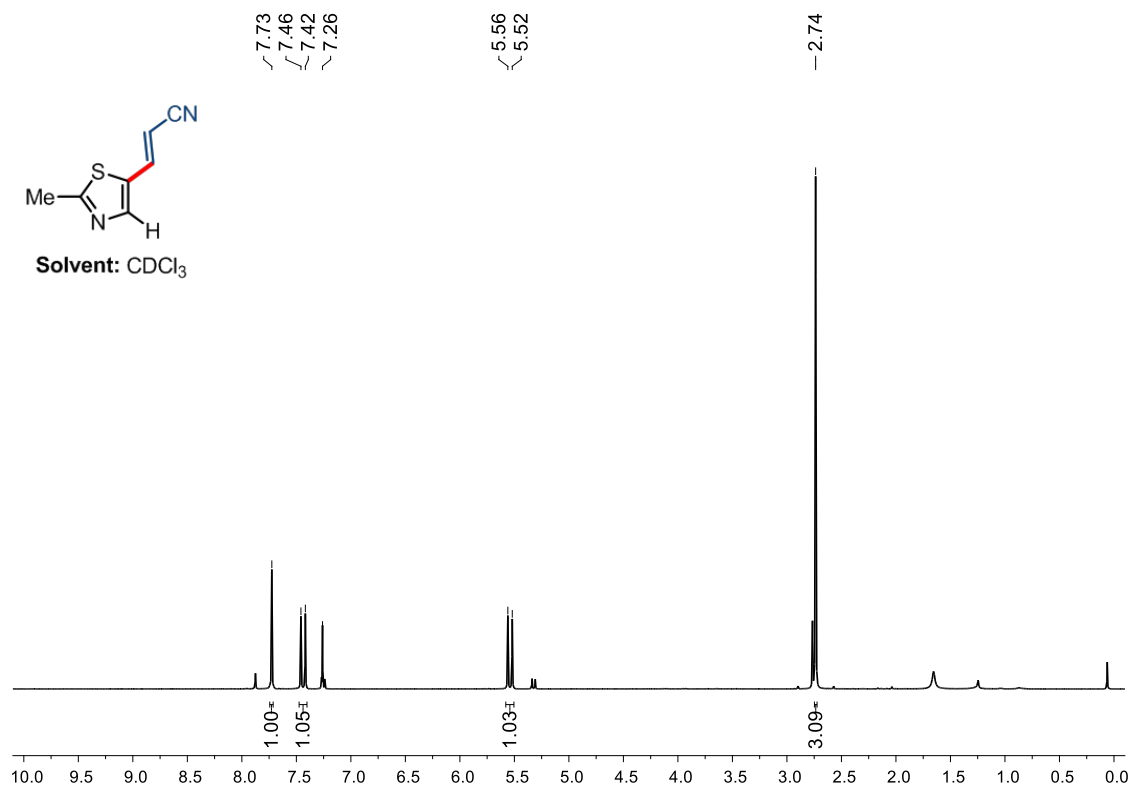


Figure S24. ¹H (top) and ¹³C (bottom) NMR of **3cj**.

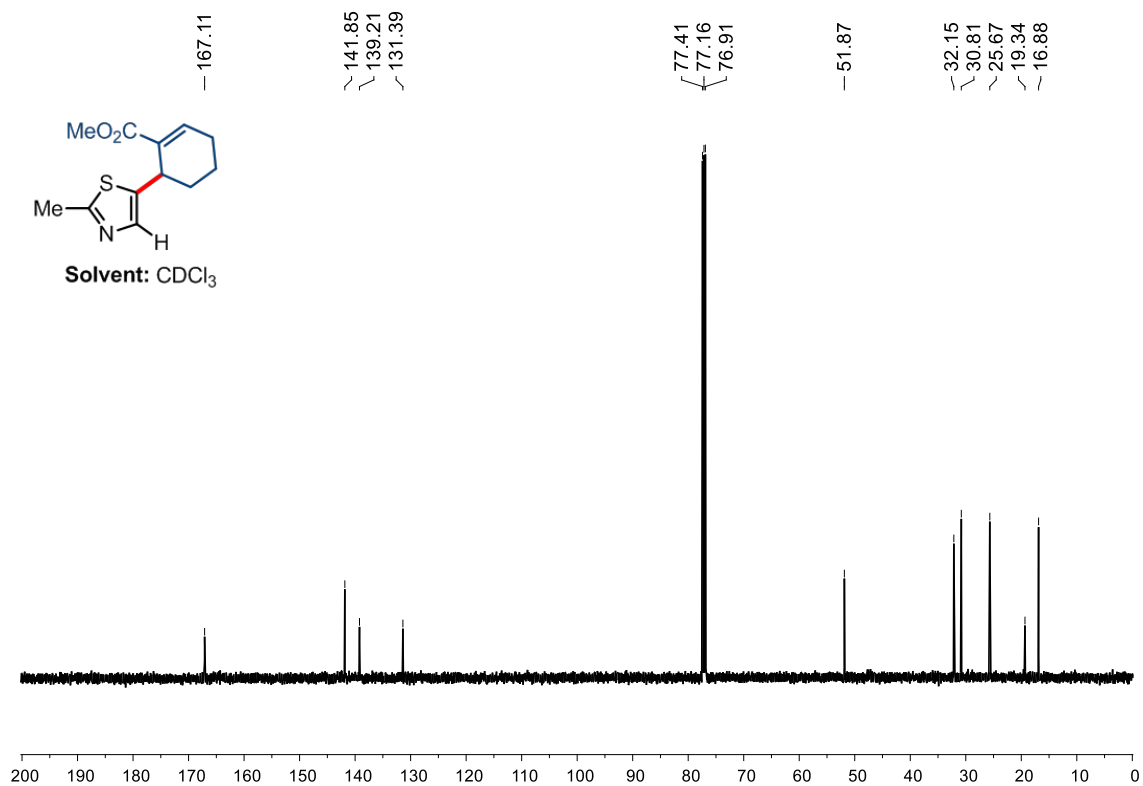
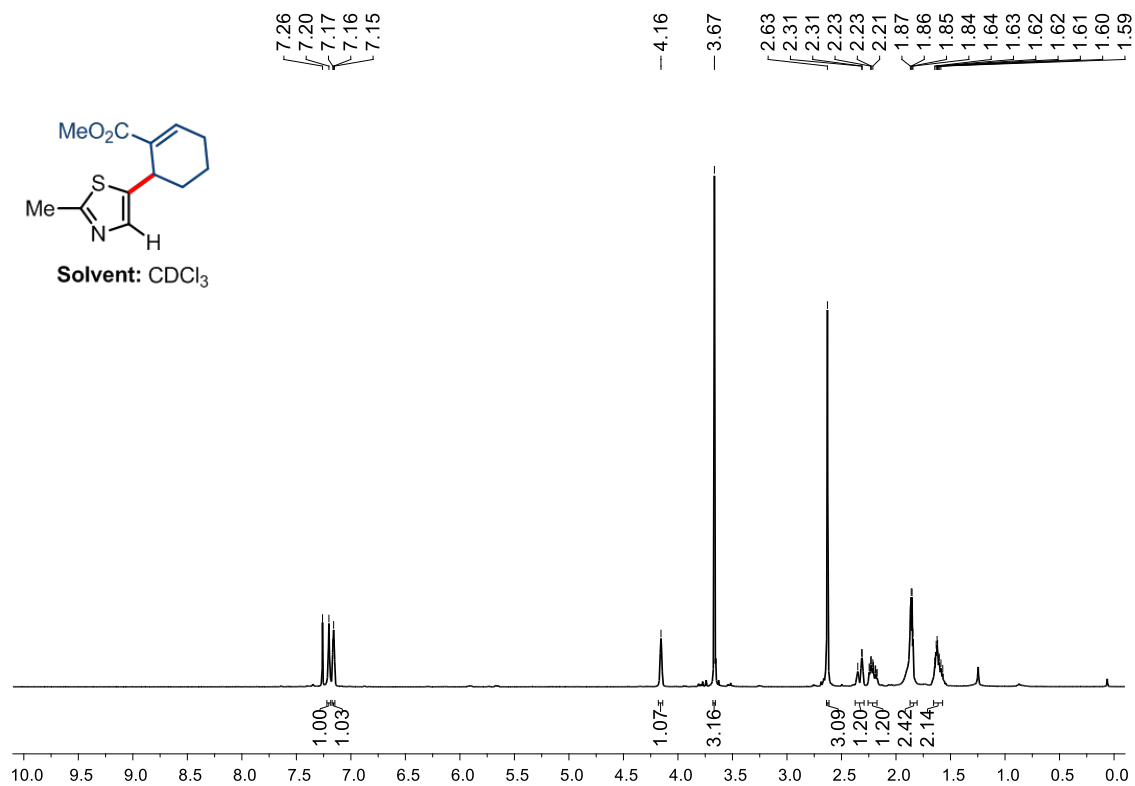


Figure S25. ¹H (top) and ¹³C (bottom) NMR of **3ck**.

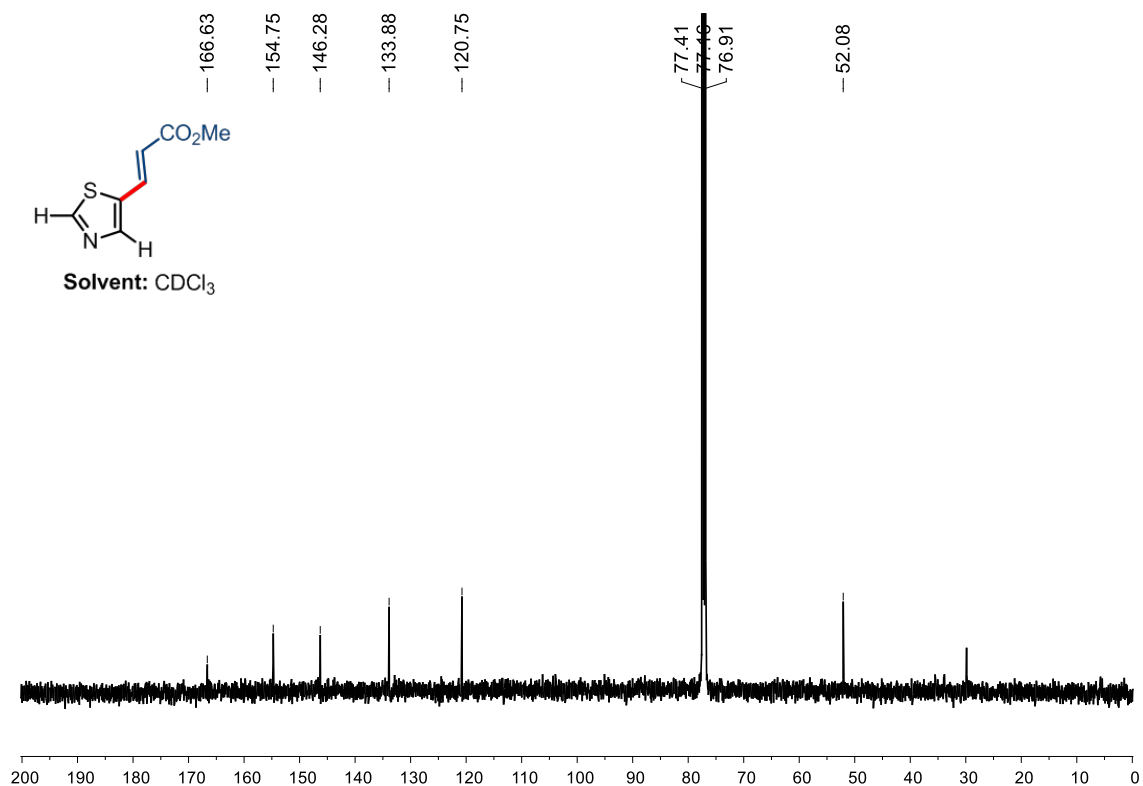
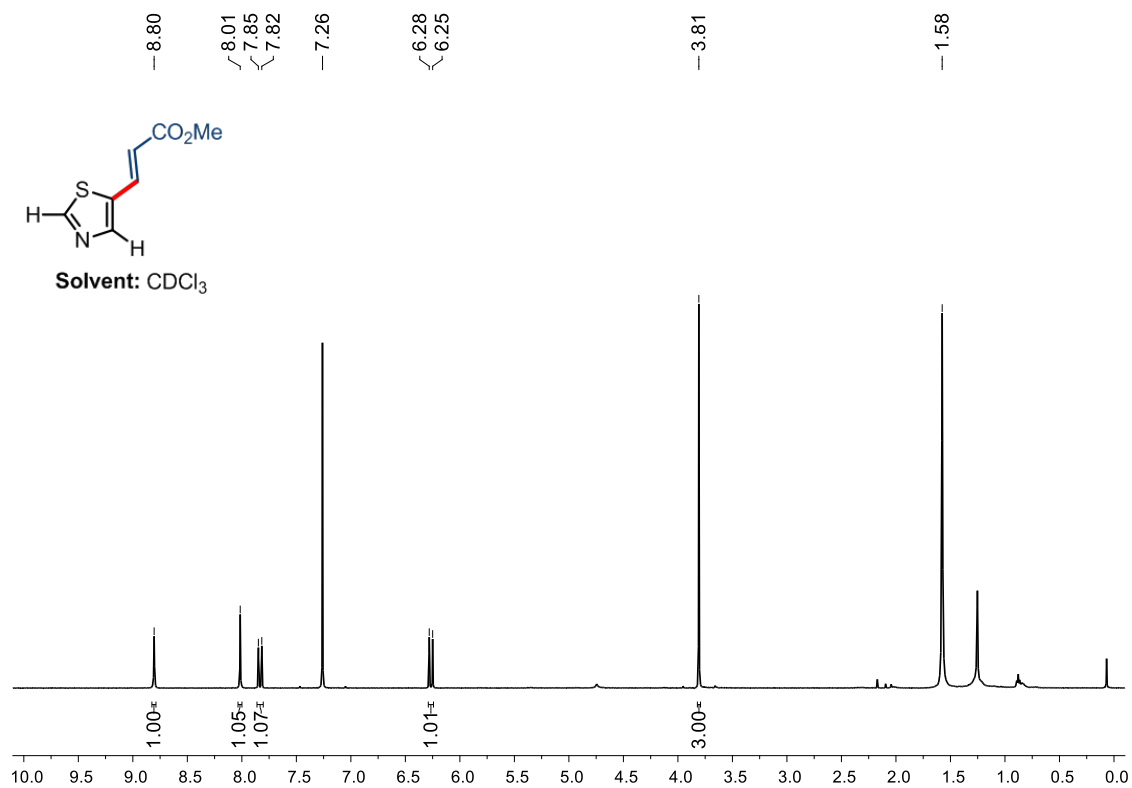


Figure S26. ¹H (top) and ¹³C (bottom) NMR of **3da**.

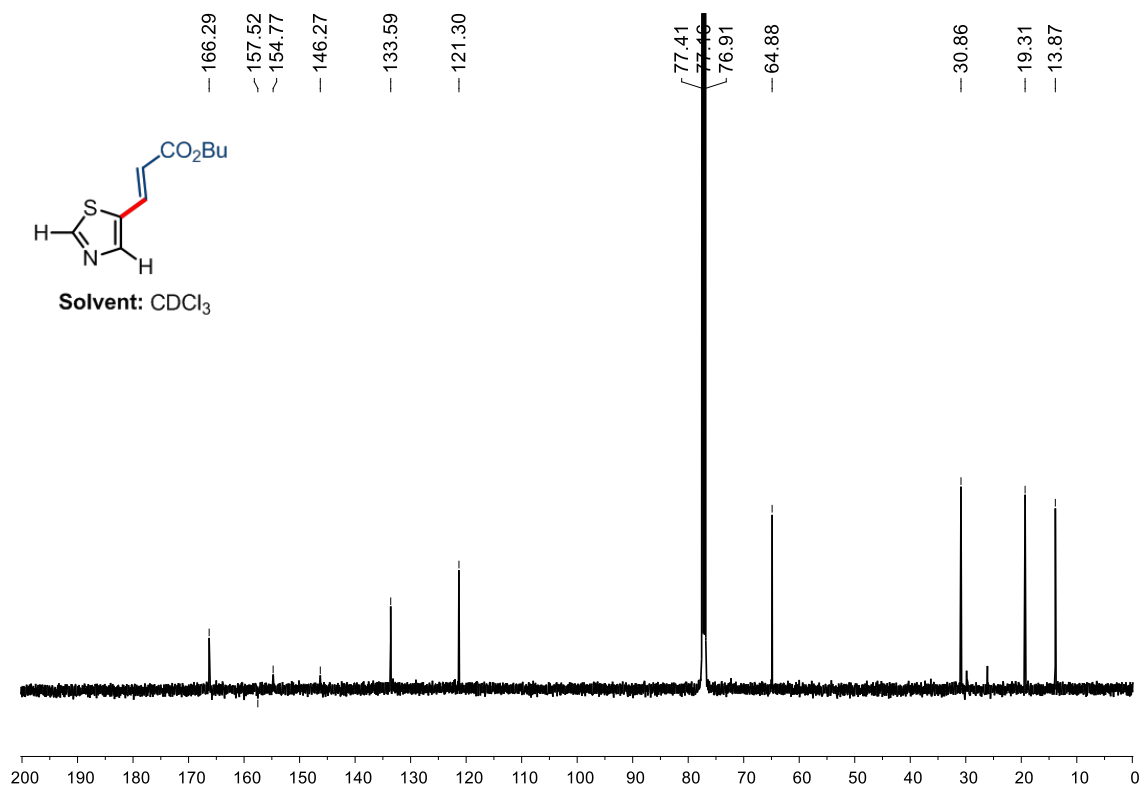
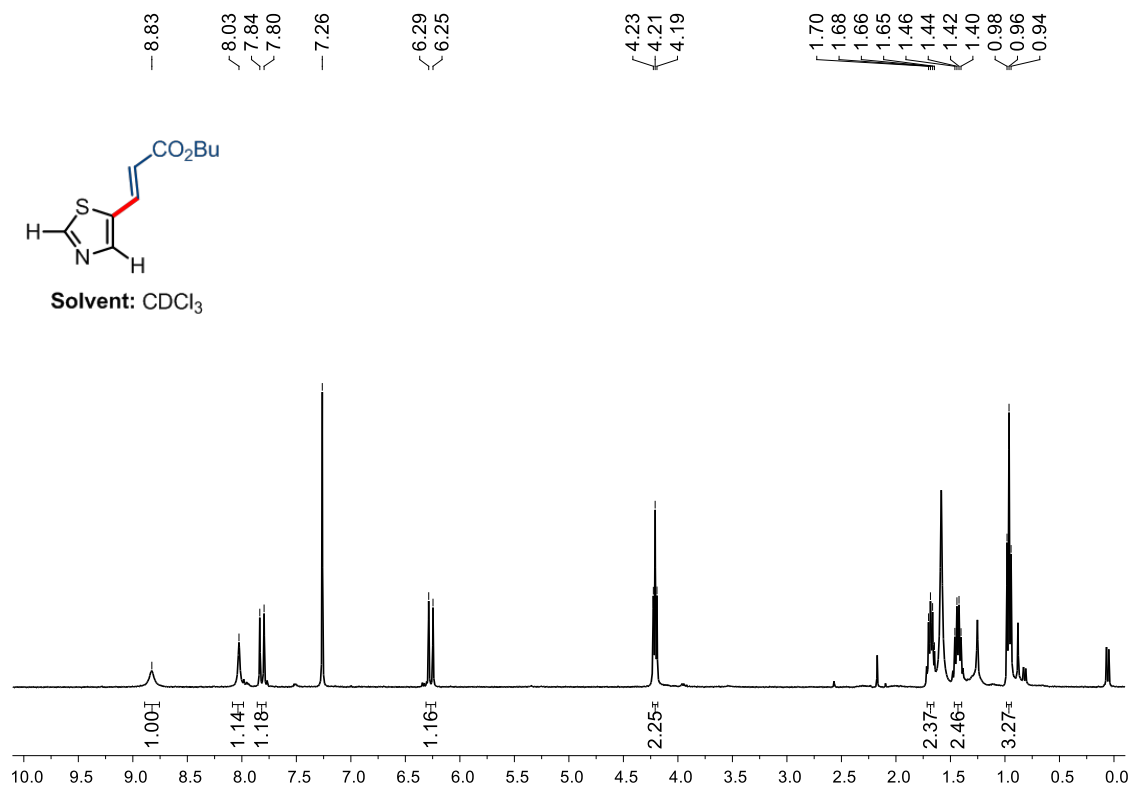


Figure S27. ^1H (top) and ^{13}C (bottom) NMR of **3dc**.

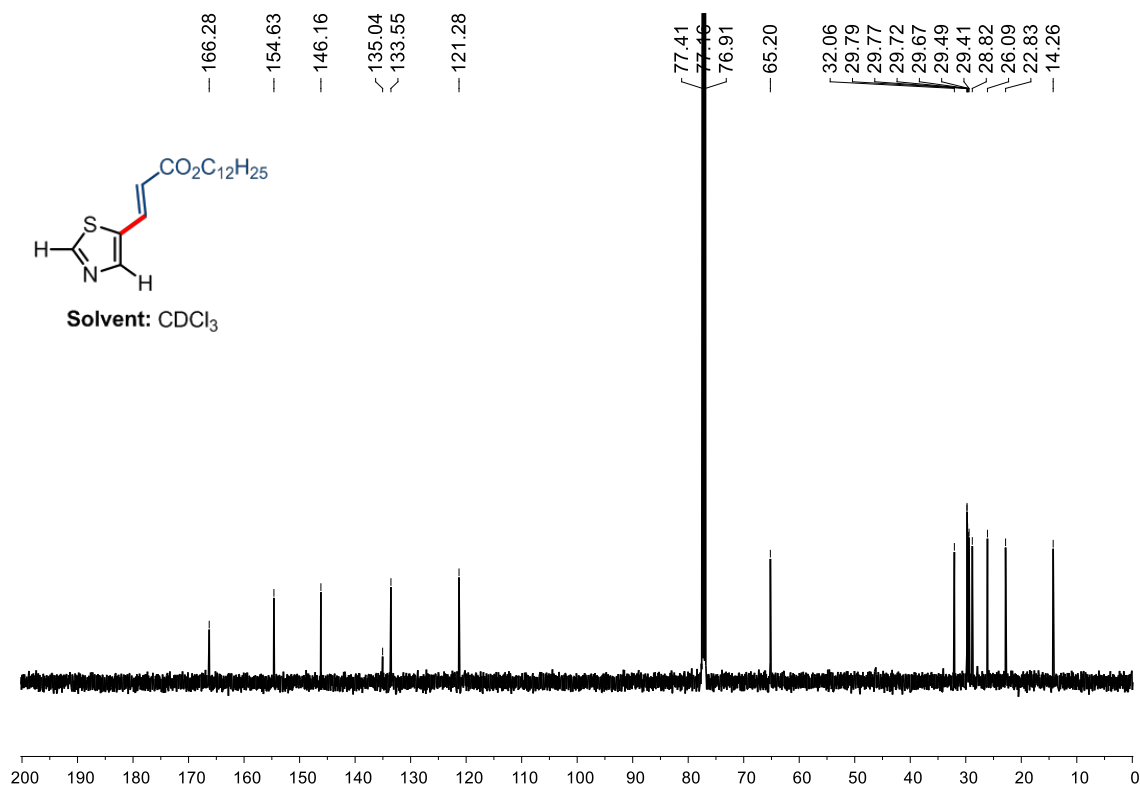
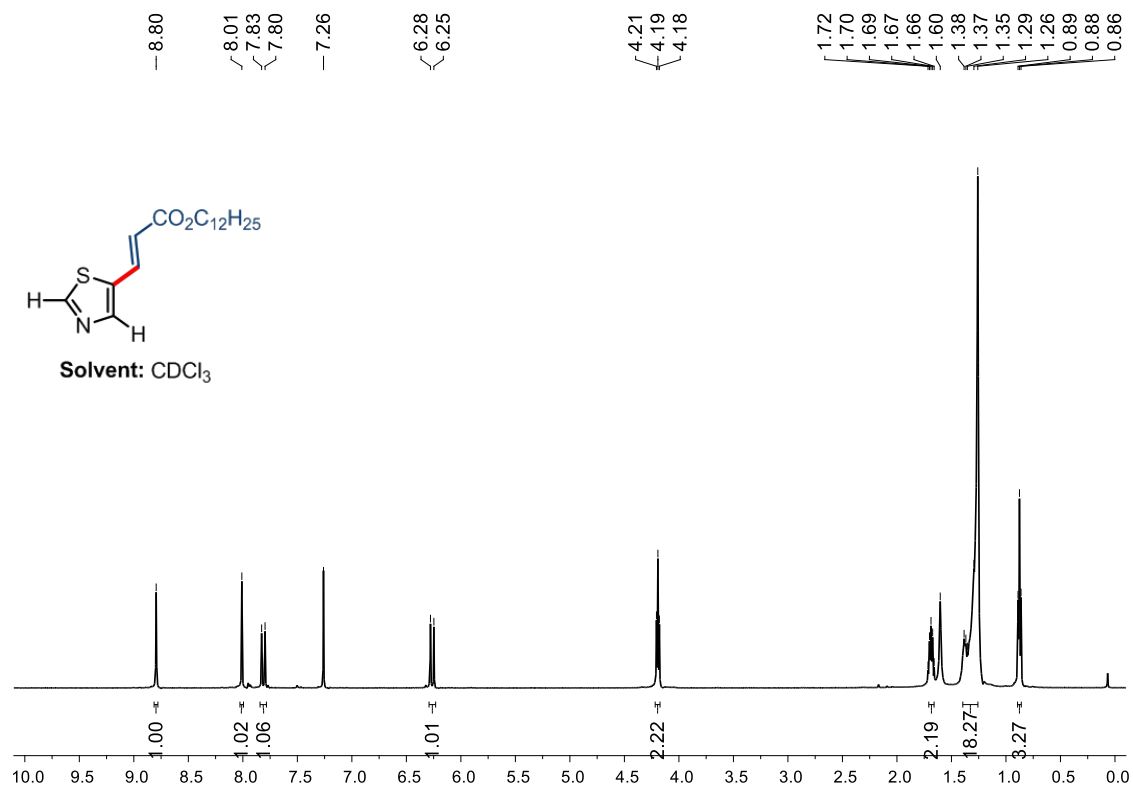


Figure S28. ^1H (top) and ^{13}C (bottom) NMR of 3dl.

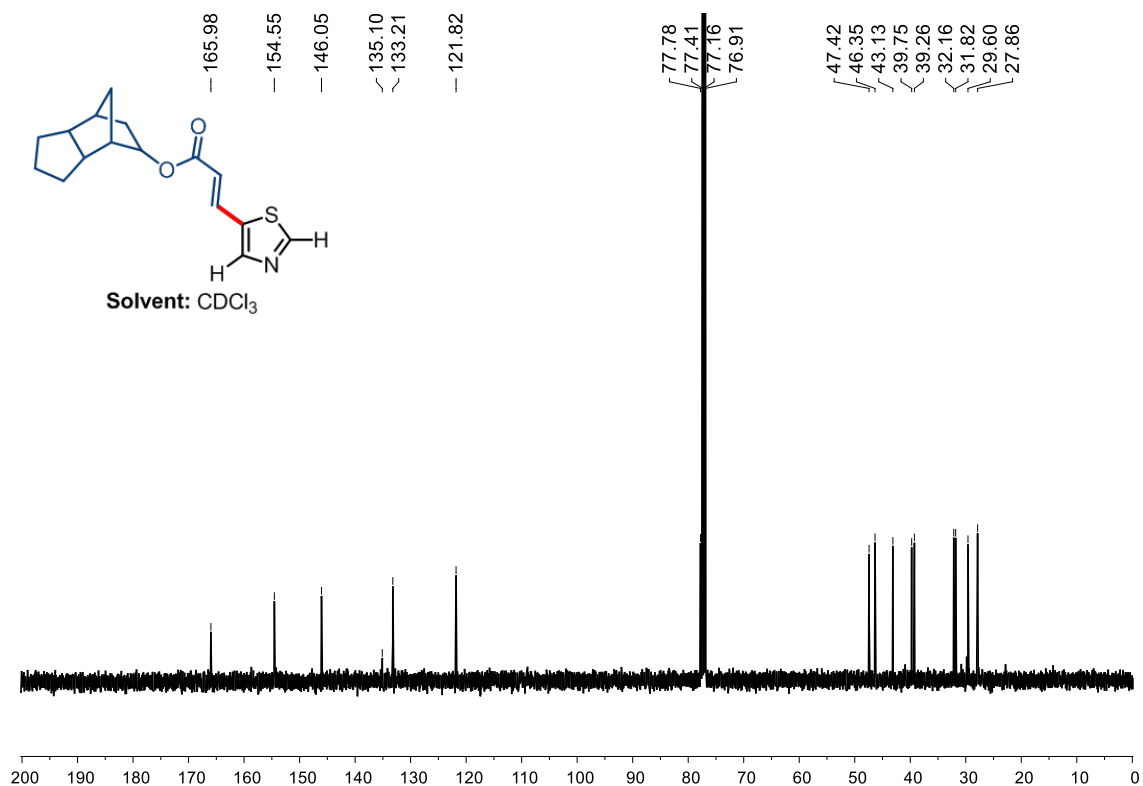
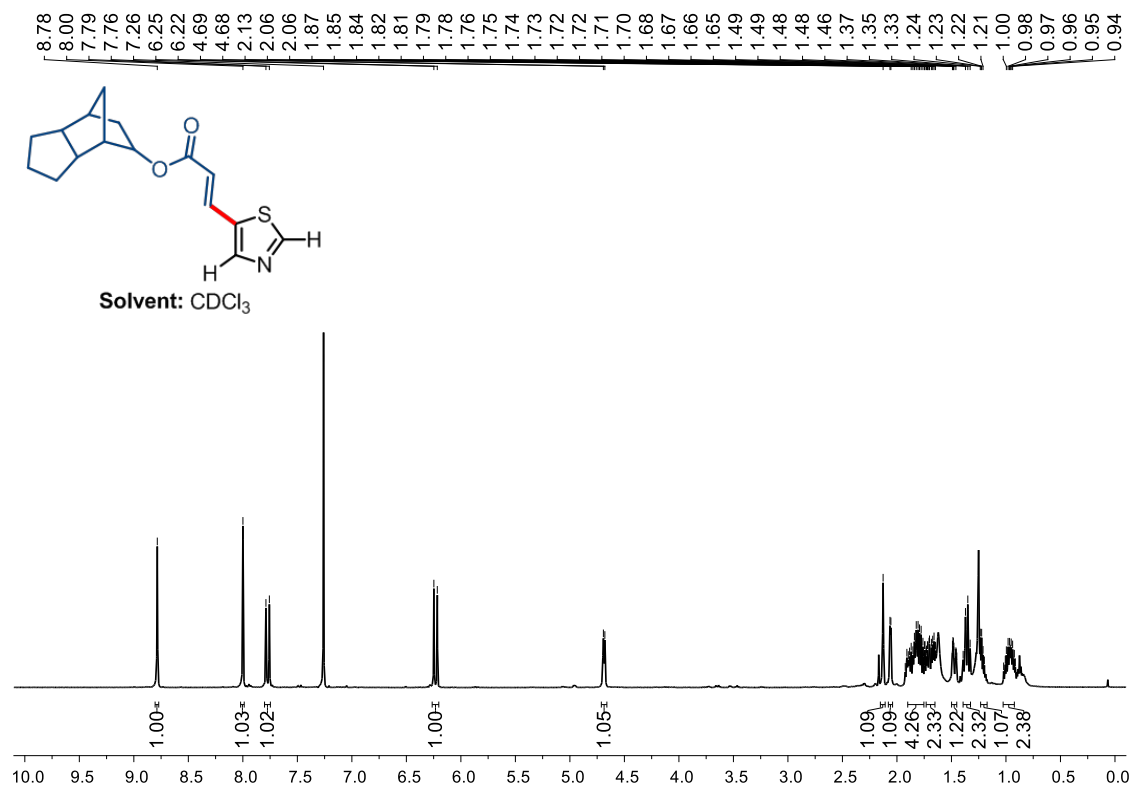


Figure S29. ^1H (top) and ^{13}C (bottom) NMR of **3de**.

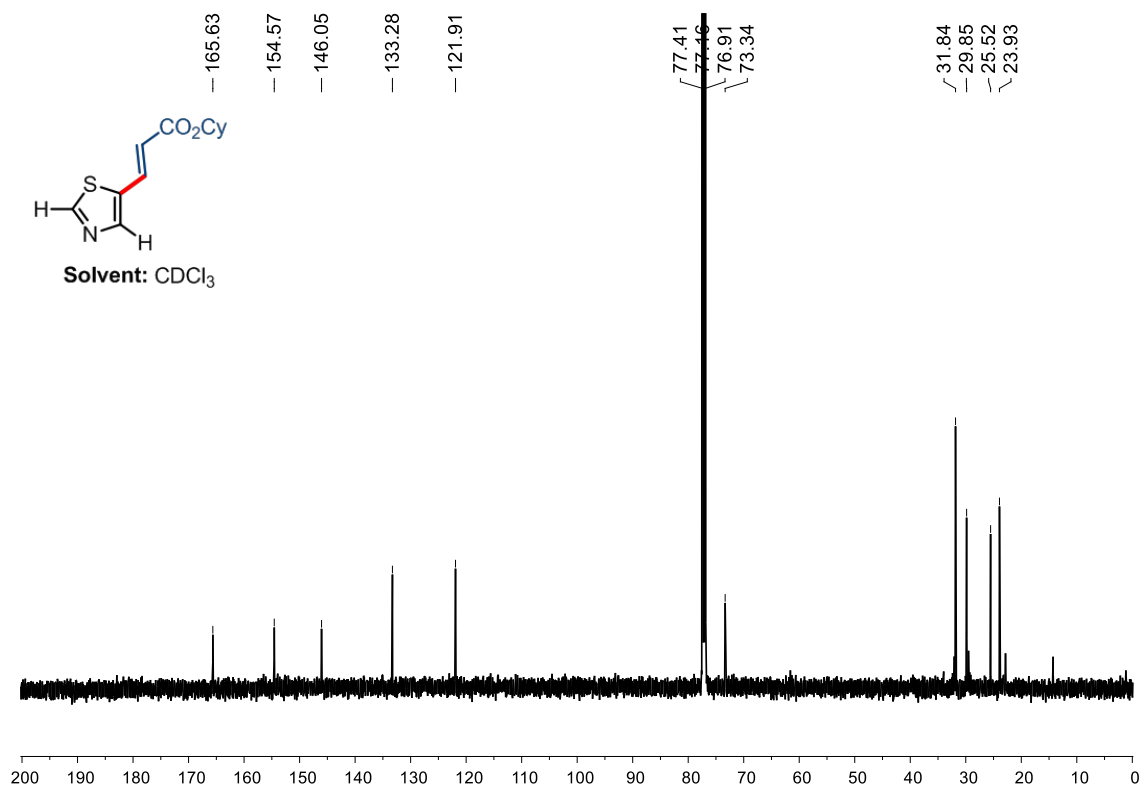
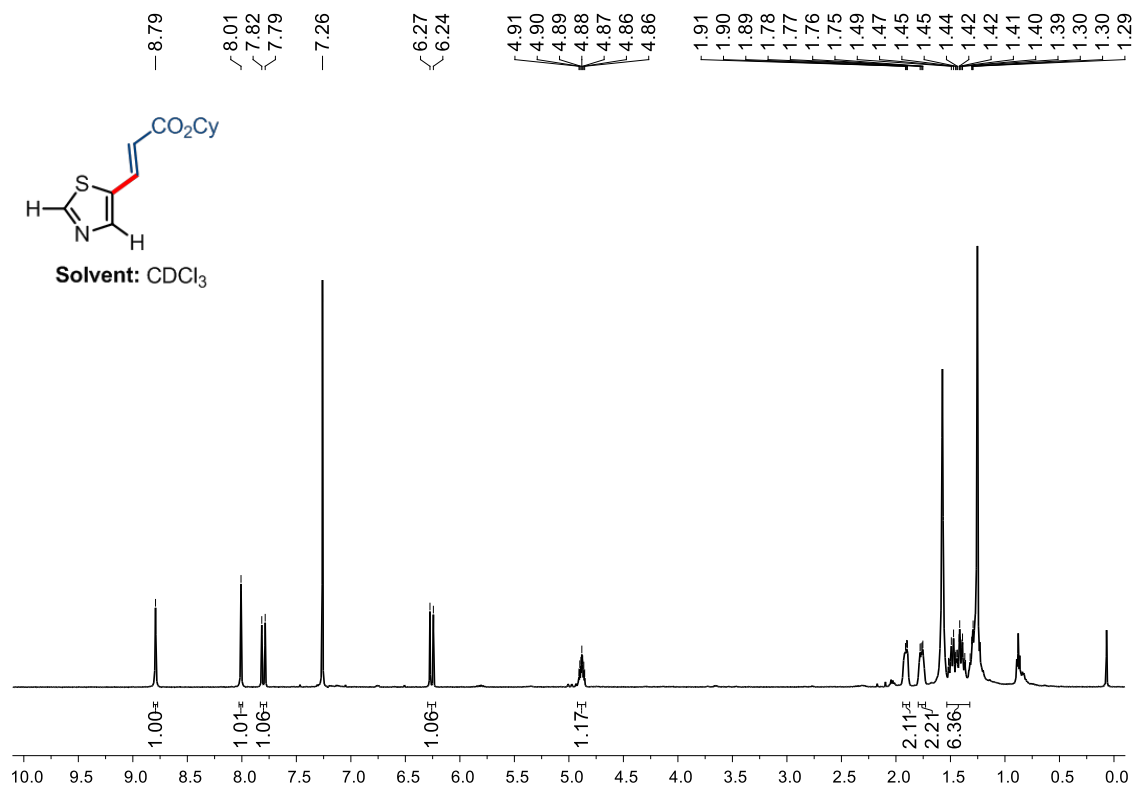


Figure S30. ¹H (top) and ¹³C (bottom) NMR of 3di.

Mass spectra

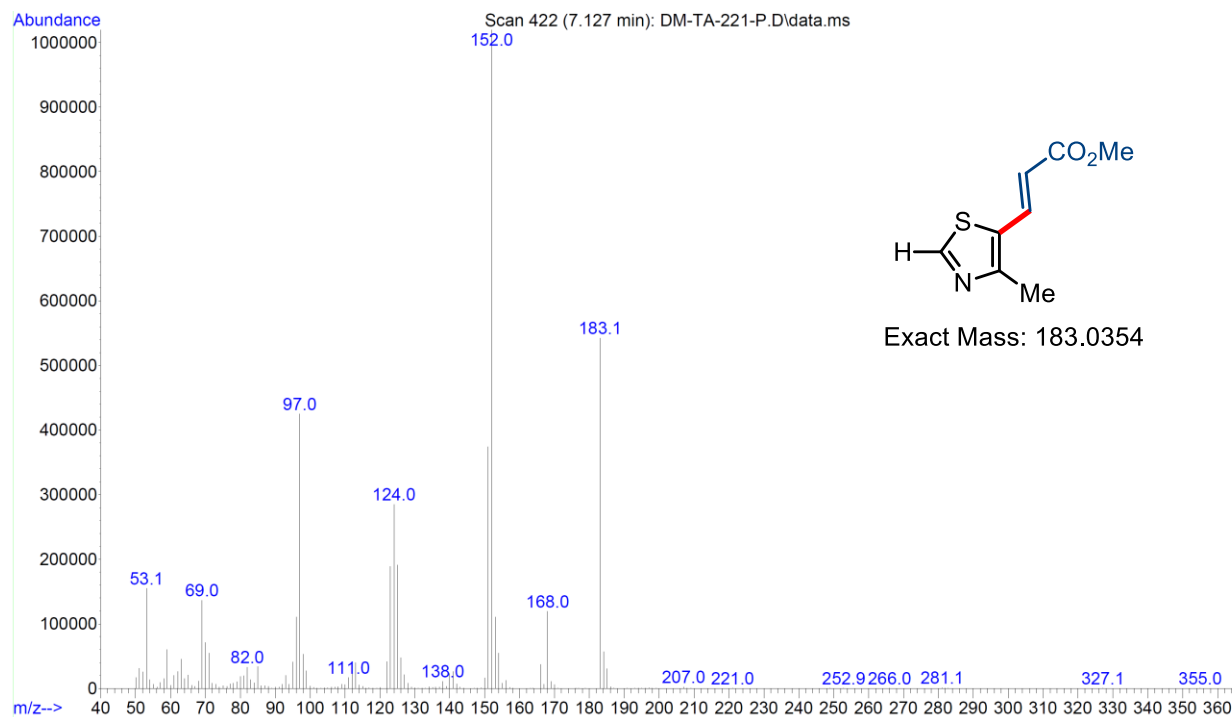


Figure S31. EI-MS of 3aa.

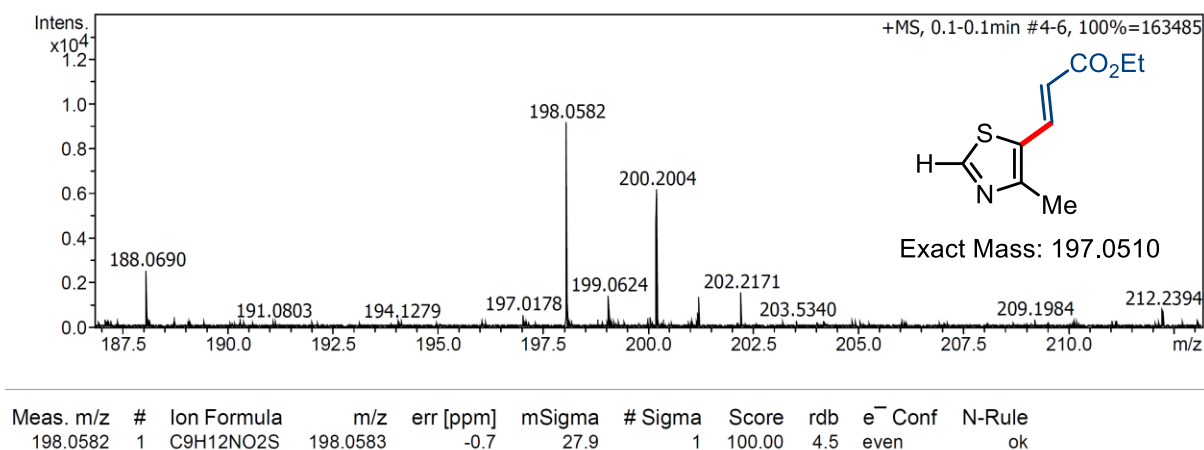


Figure S32. ESI-MS of 3ab.

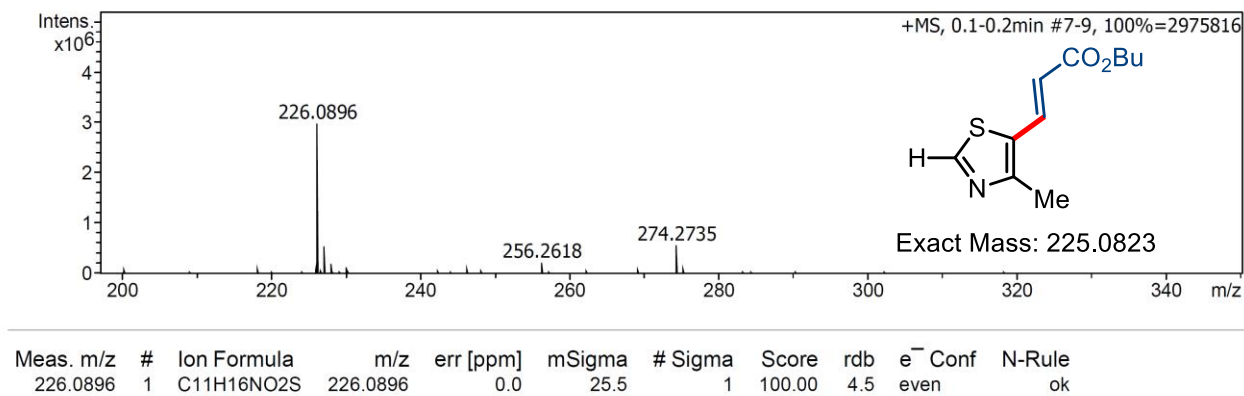


Figure S33. ESI-MS of 3ac.

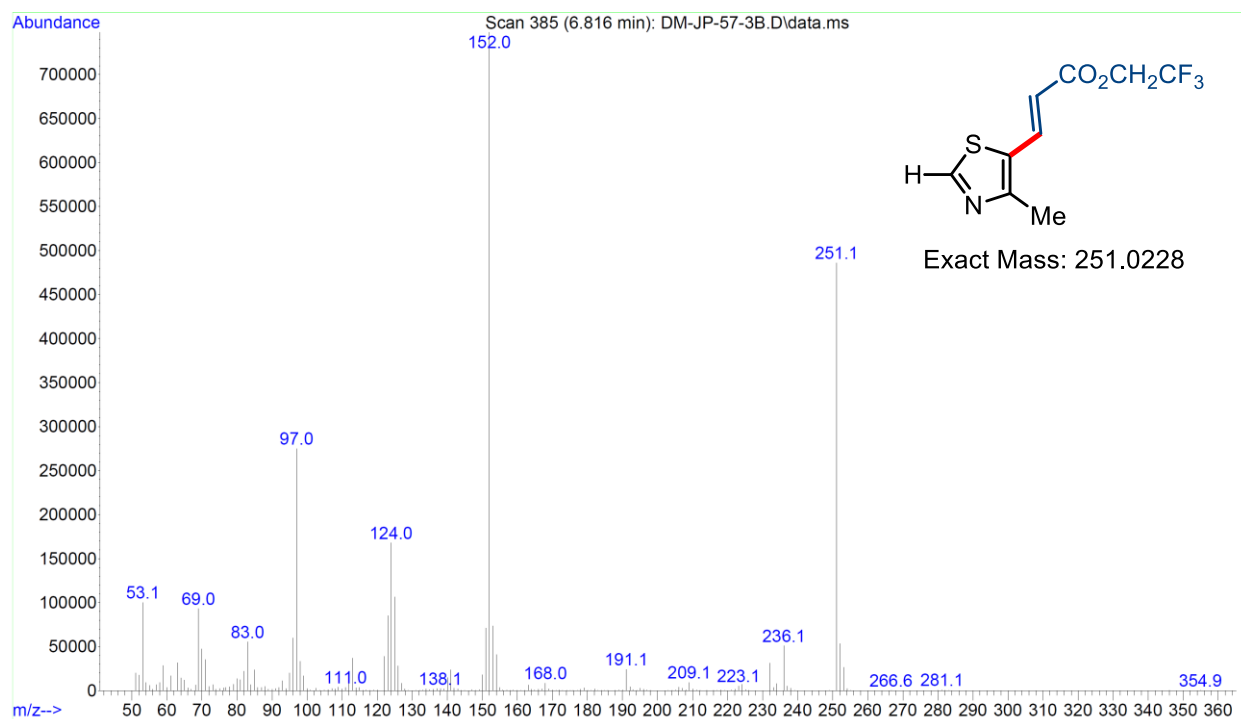


Figure S34. EI-MS of 3ad.

Sample Name	JP2-57-3B	Position	P1F1	Instrument Name	QTOF	User Name	LCMSQTOF-PC\admin
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	JP2-57-3B.d	ACQ Method	2MINS DIRECT MS.m	Comment		Acquired Time	4/23/2019 8:34:04 PM

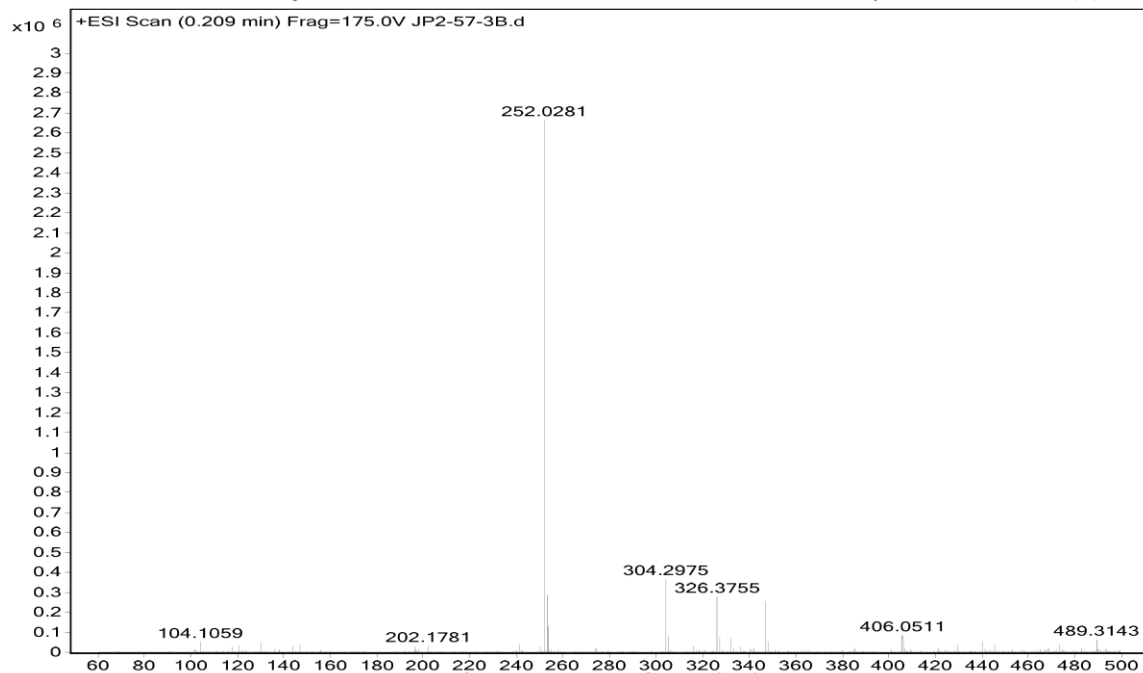


Figure S35. ESI-MS of 3ad.

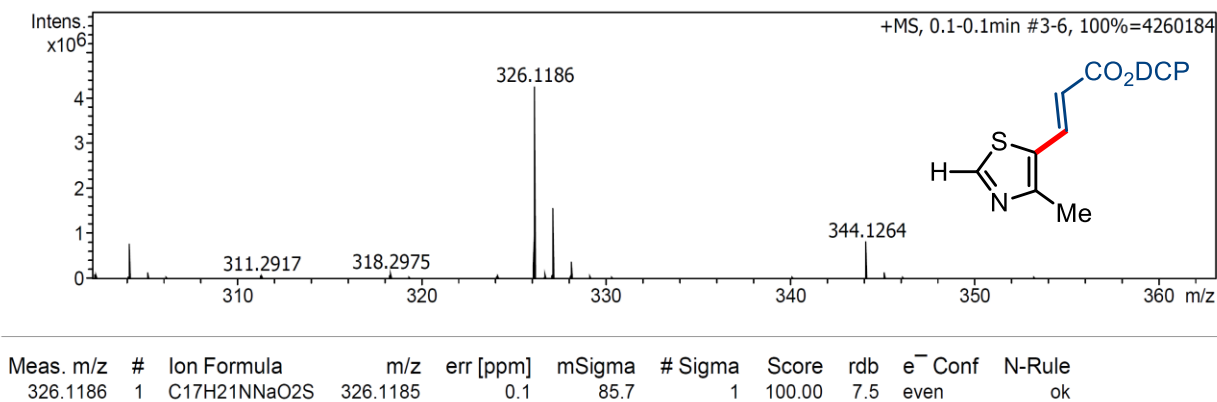


Figure S36. ESI-MS of 3ae.

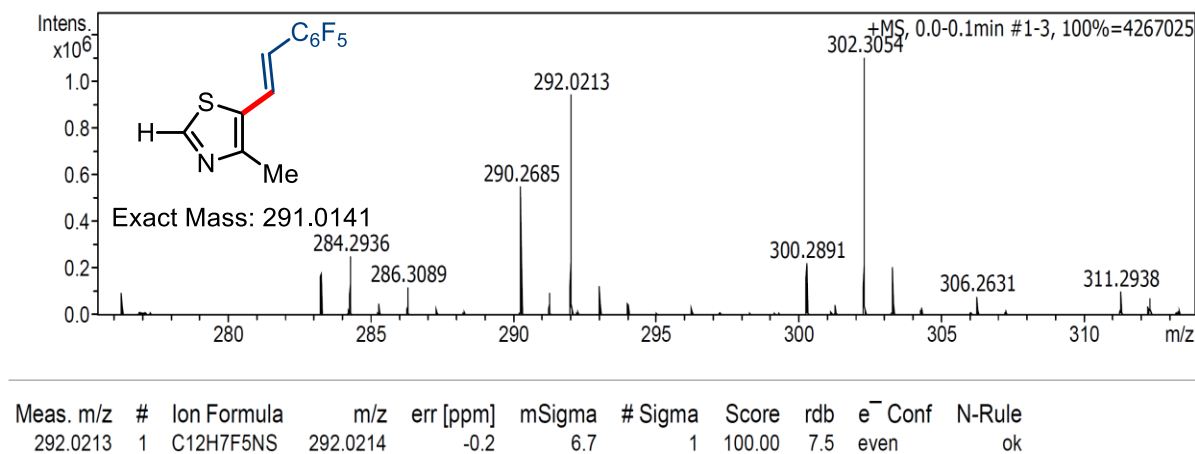


Figure S37. ESI-MS of 3af.

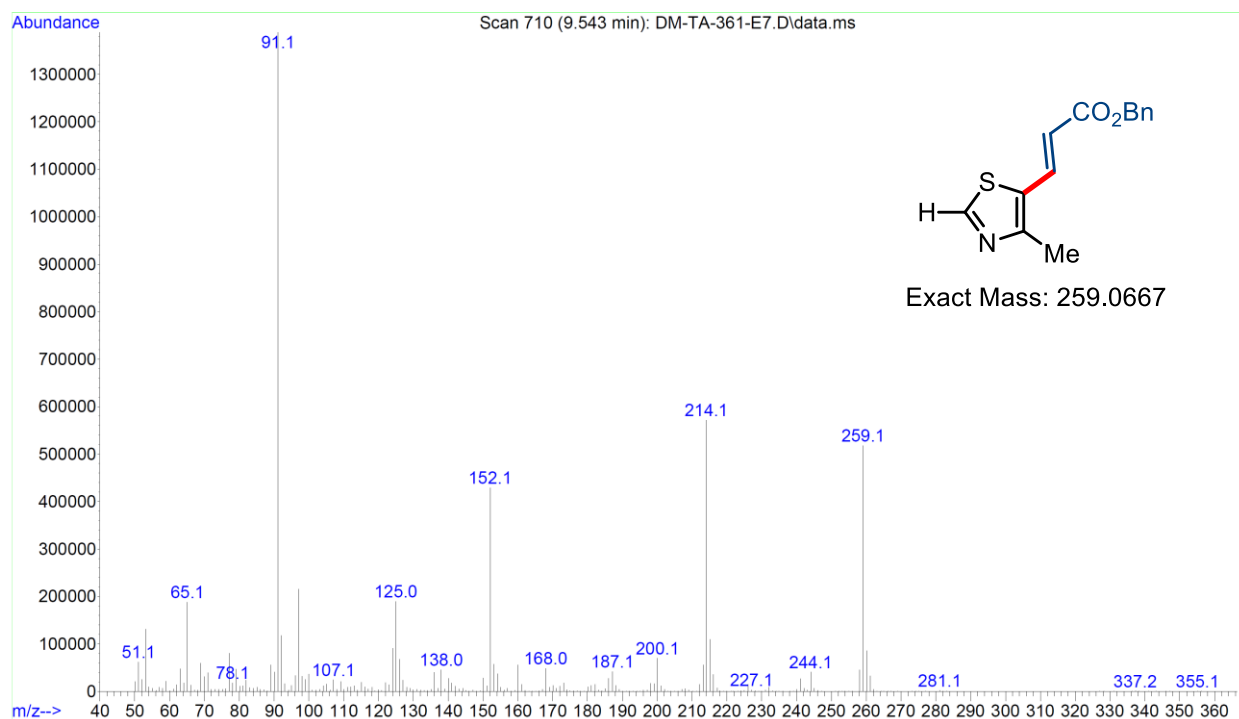


Figure S38. EI-MS of 3ag.

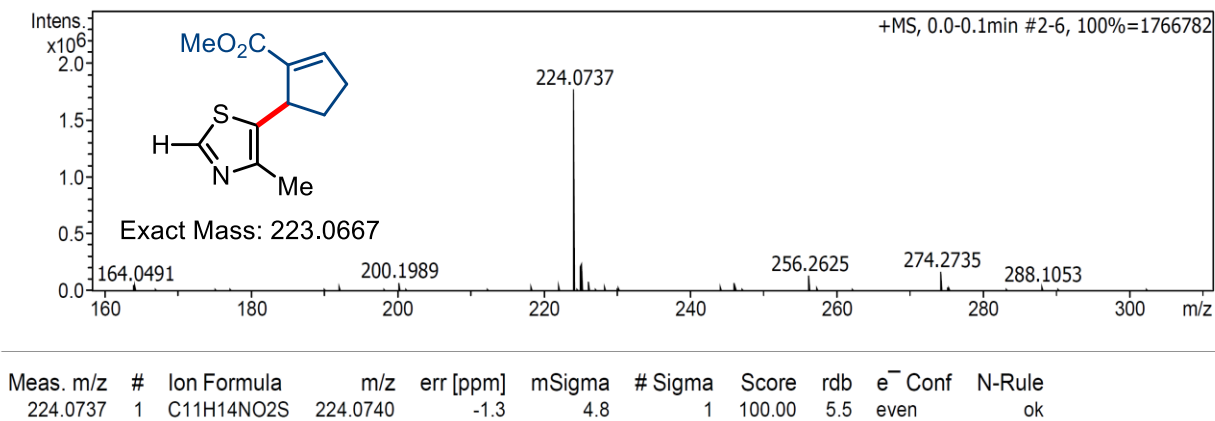


Figure S39. ESI-MS of 3ah.

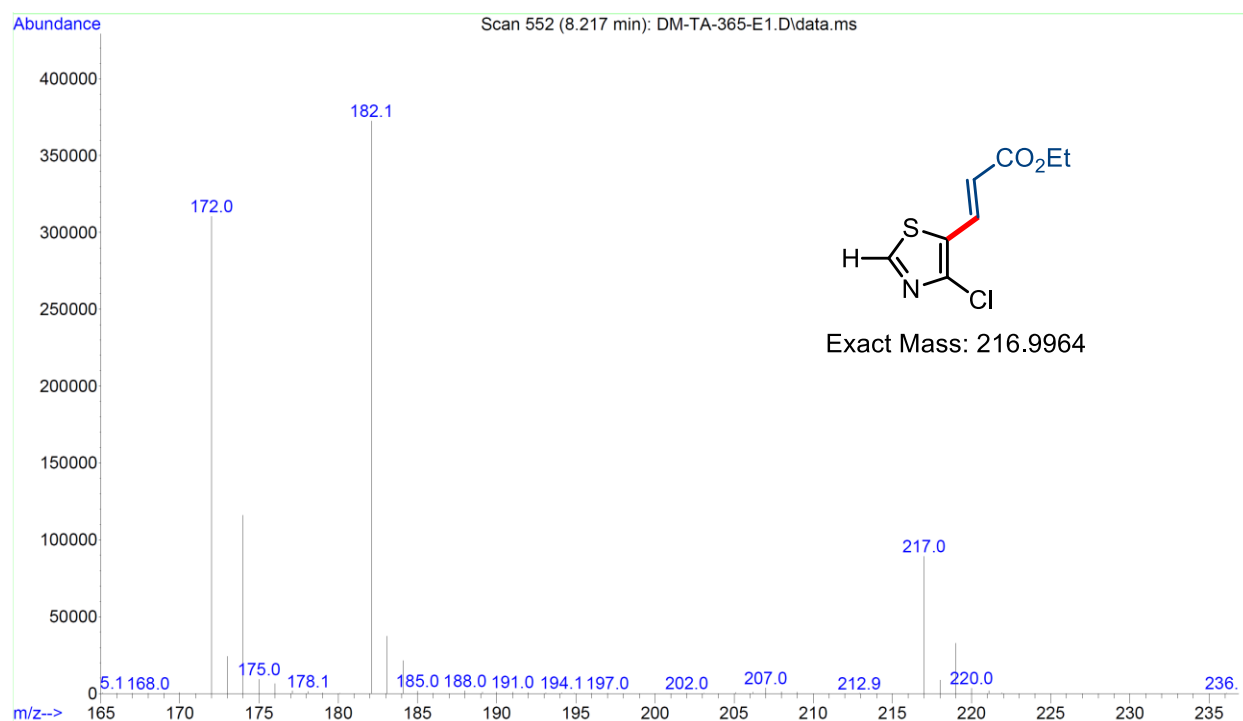


Figure S40. EI-MS of 3bb.

Sample Name	TA-365-E1	Position	P1F4	Instrument Name	QTOF	User Name	LCMSQTOF-PC\admin
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TA-365-E1.d	ACQ Method	2MINS DIRECT MS.m	Comment		Acquired Time	4/23/2019 8:19:27 PM

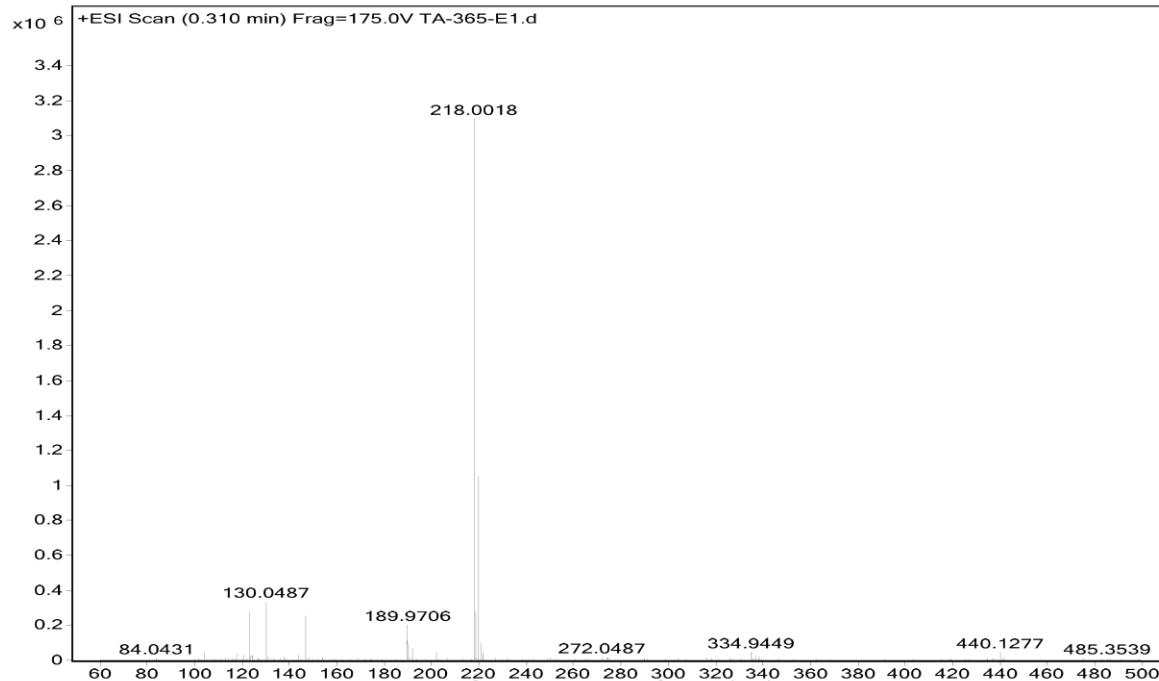


Figure S41. ESI-MS of 3bb.

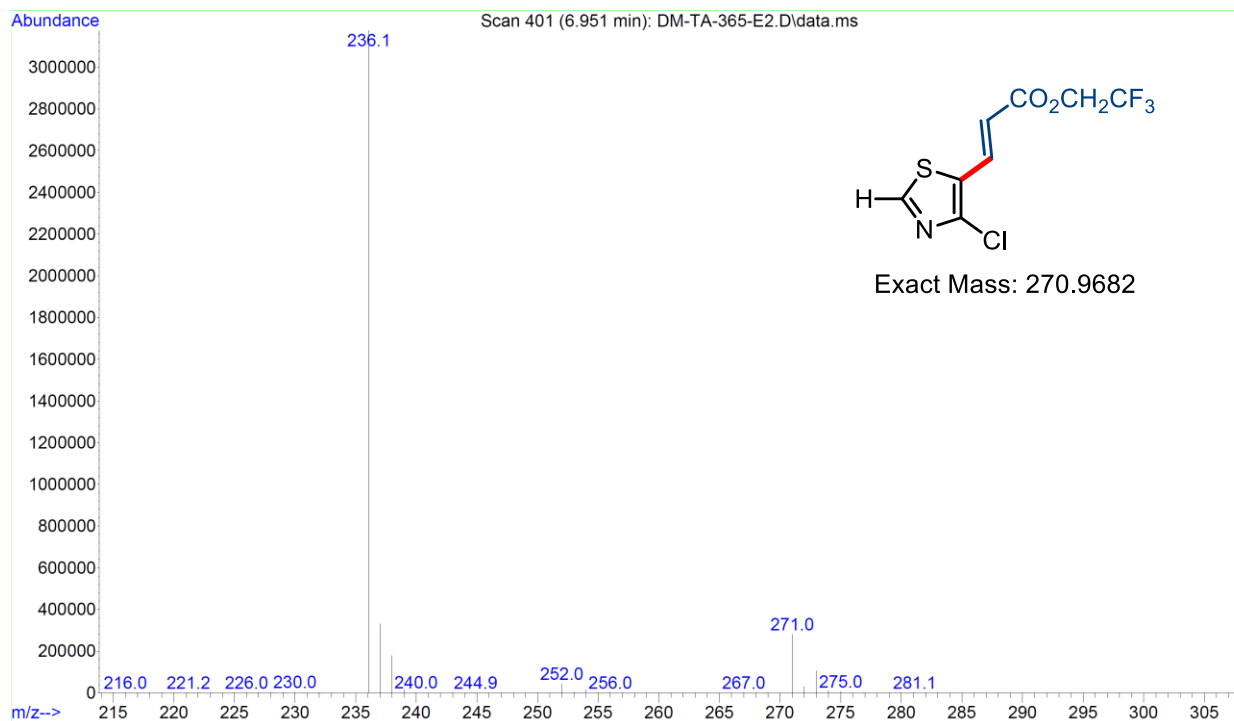


Figure S42. EI-MS of 3bd.

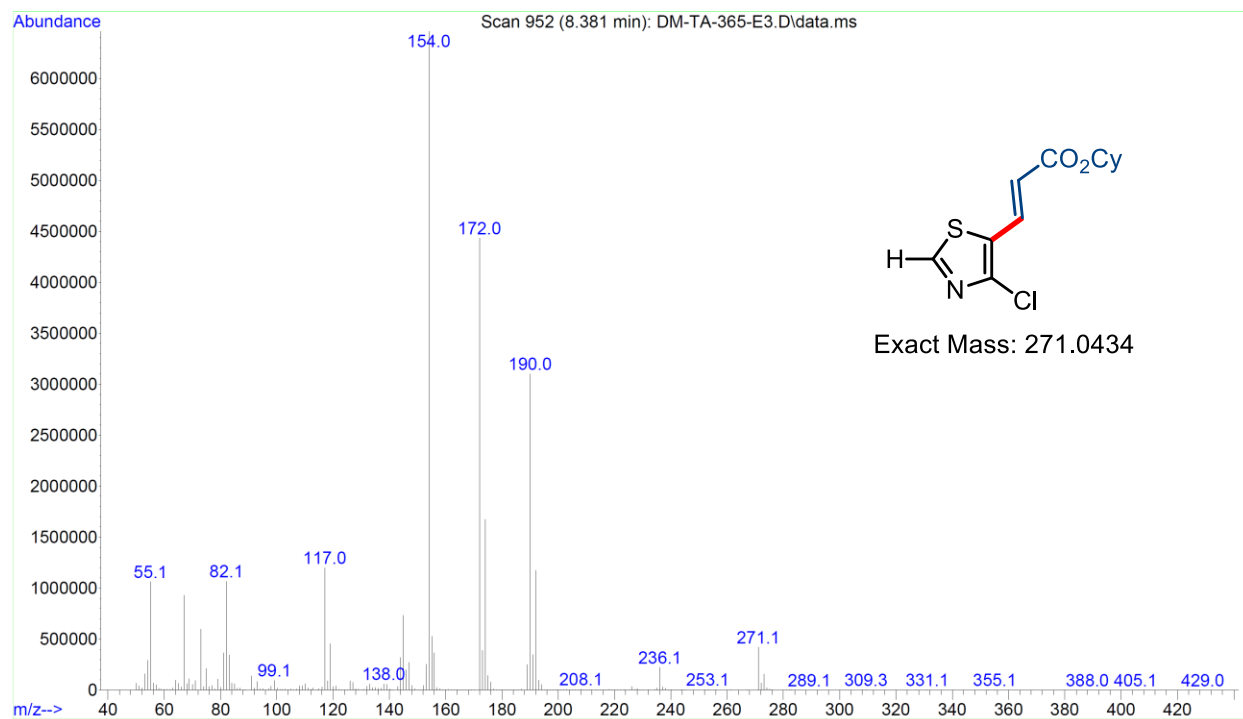


Figure S43. EI-MS of 3bi.

Sample Name	TA-365-E3	Position	P1F5	Instrument Name	QTOF	User Name	LCMSQTOF-PC\admin
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TA-365-E3.d	ACQ Method	2MINS DIRECT MS.m	Comment		Acquired Time	4/23/2019 8:15:33 PM

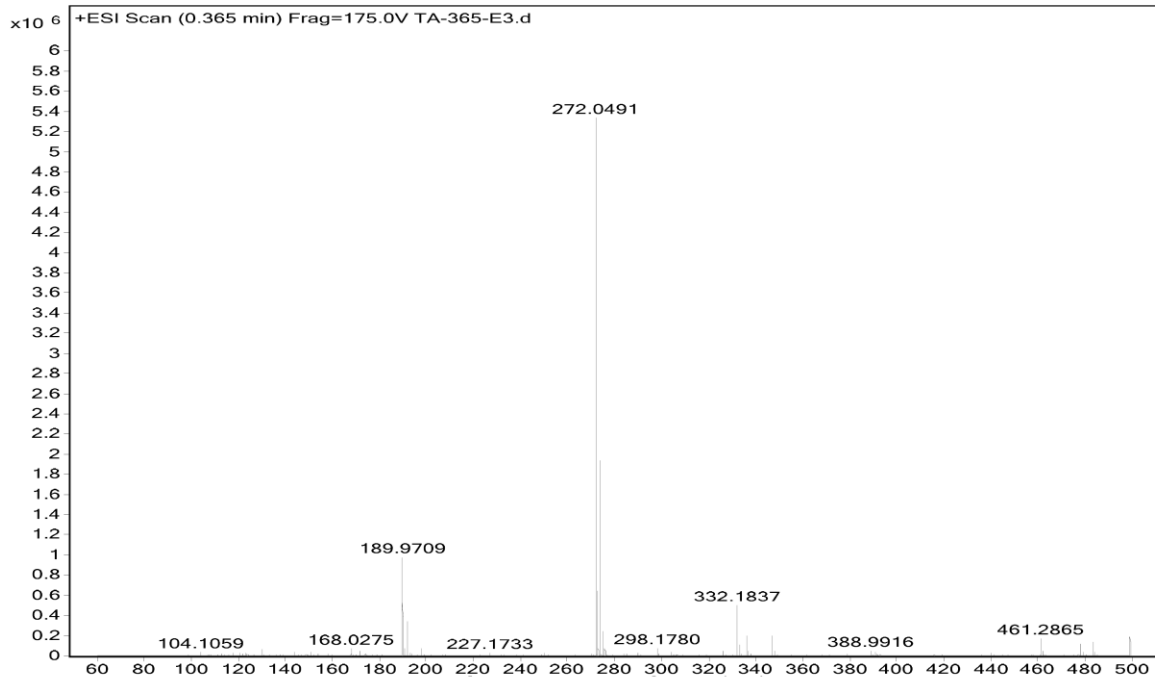


Figure S44. ESI-MS of 3bi.

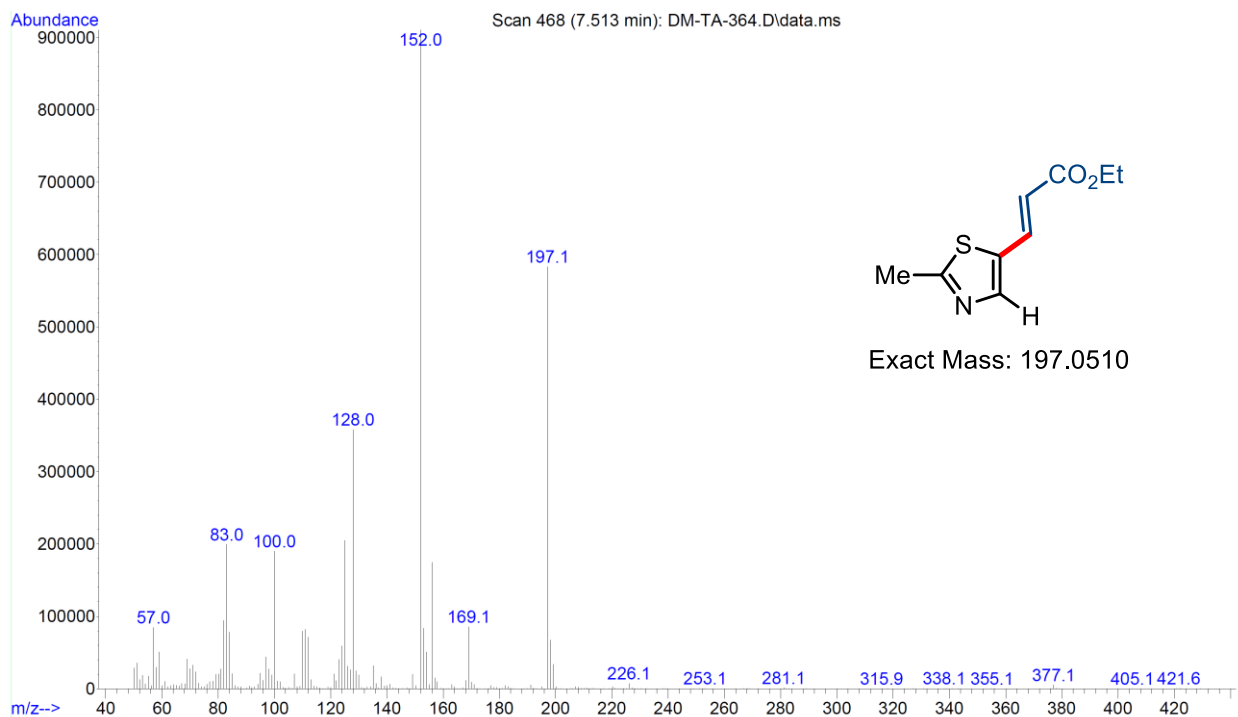


Figure S45. EI-MS of 3cb.

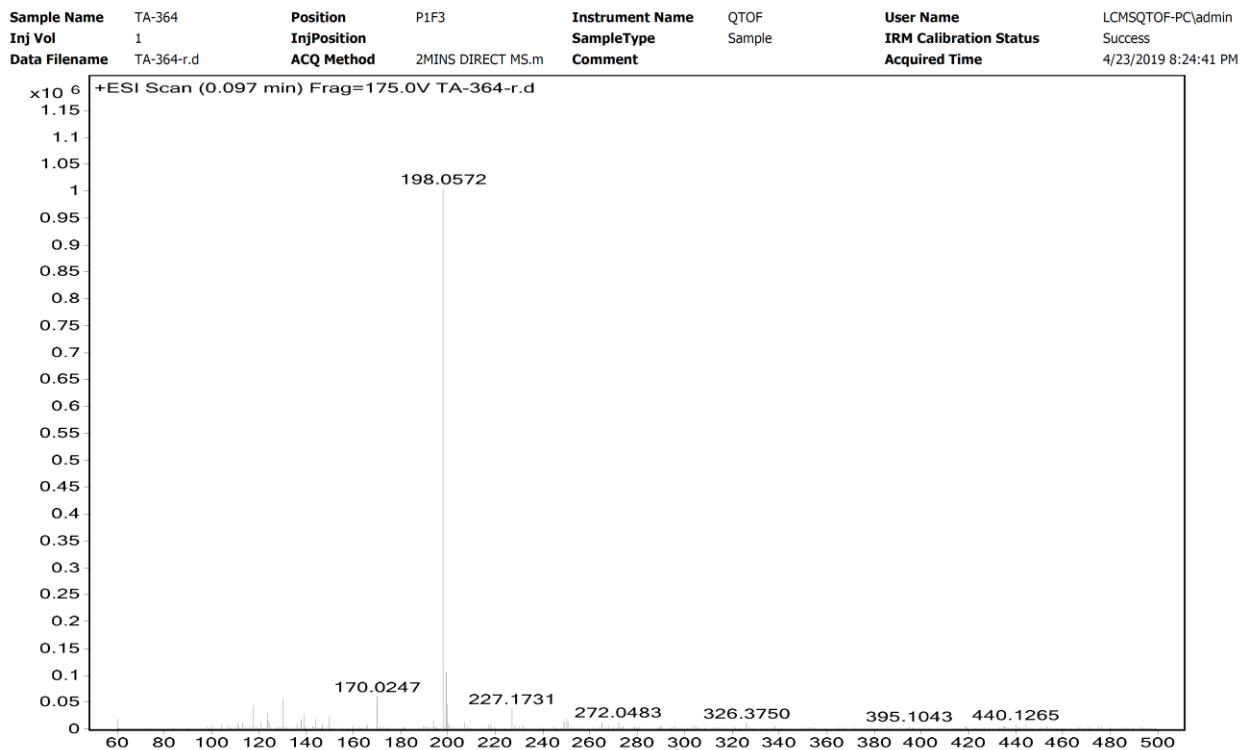


Figure S46. ESI-MS of 3cb.



Figure S47. EI-MS of **3cj**.

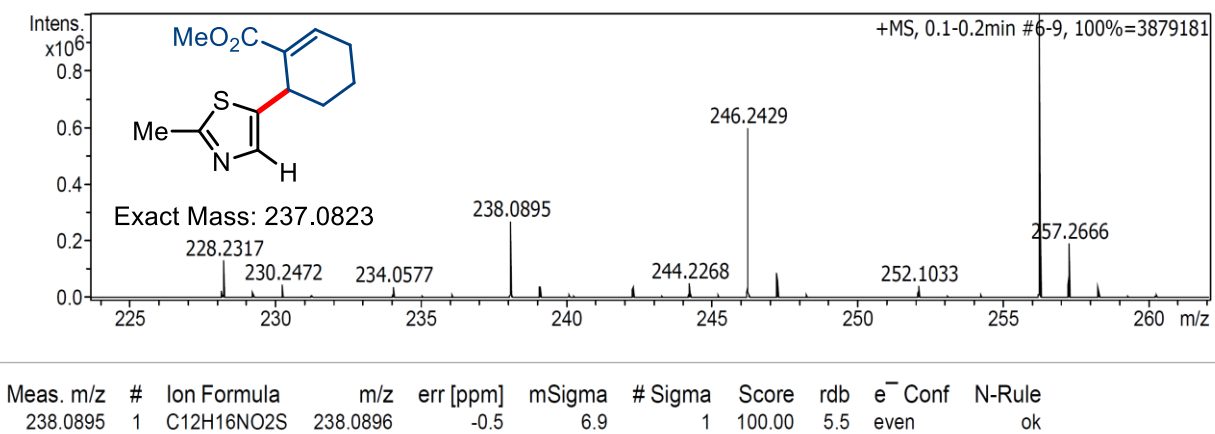


Figure S48. ESI-MS of **3ck**.

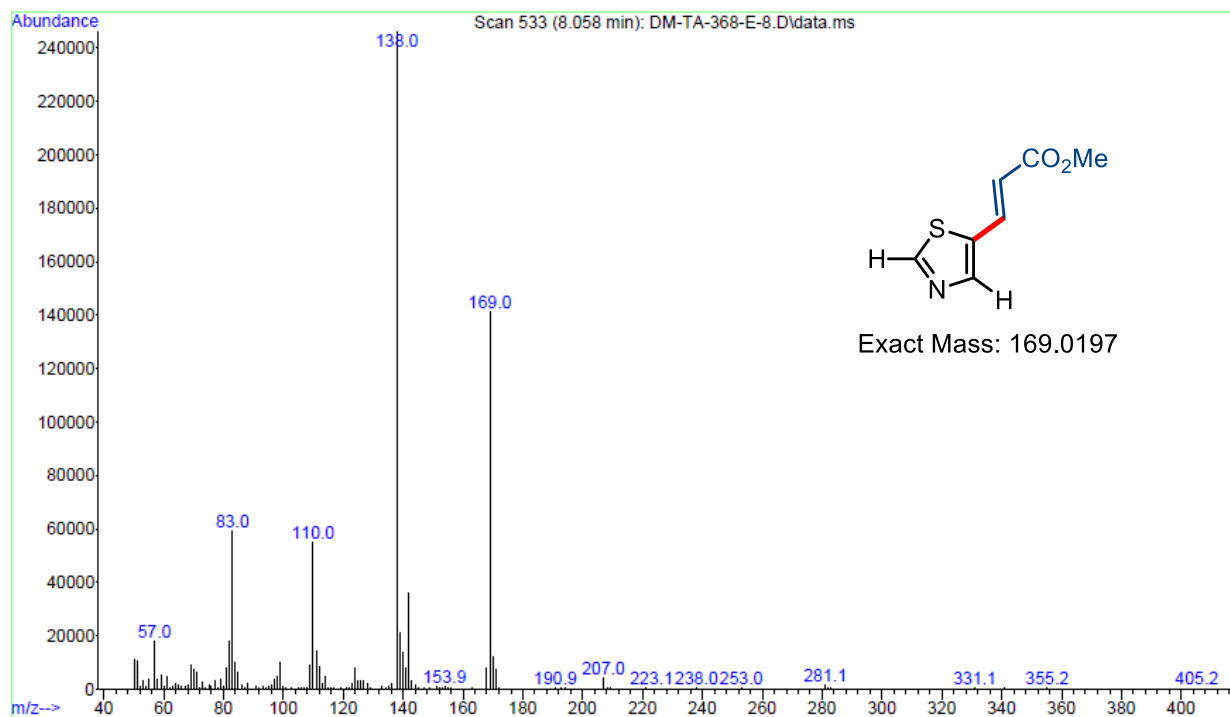


Figure S49. EI-MS of 3da.

Sample Name	TA-368-E8	Position	P1F2	Instrument Name	QTOF	User Name	LCMSQTOF-PC\admin
Inj Vol	3	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TA-368-E8.d	ACQ Method	2MINS DIRECT MS.m	Comment		Acquired Time	4/23/2019 7:54:12 PM

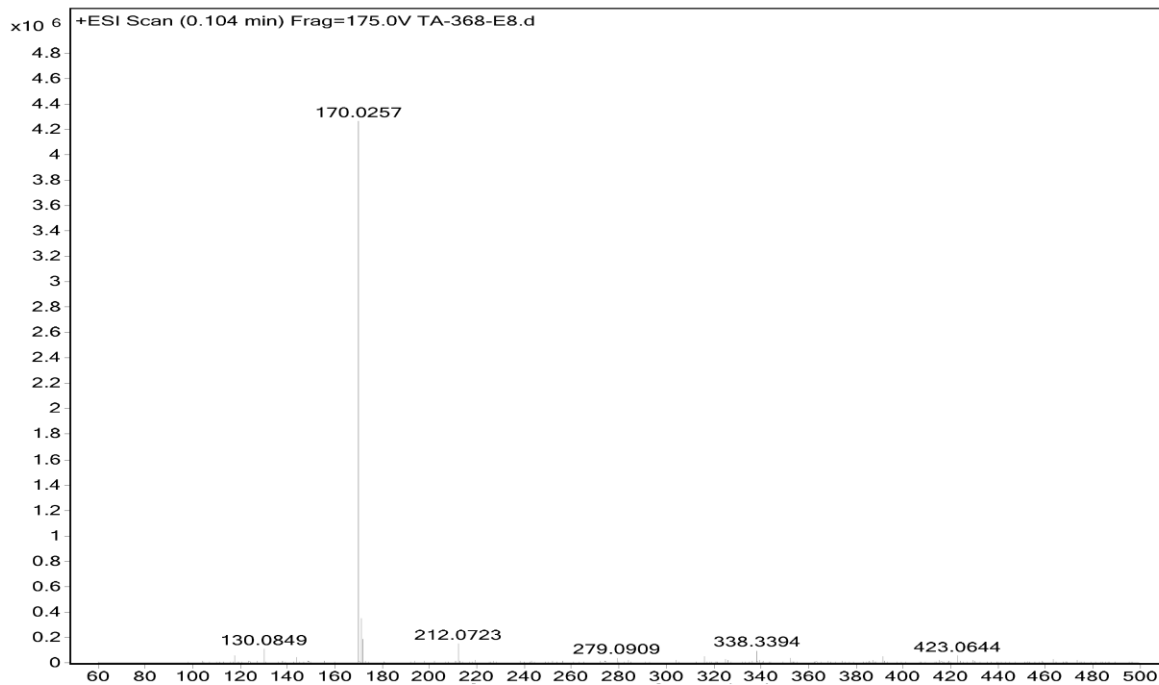


Figure S50. ESI-MS of 3da.

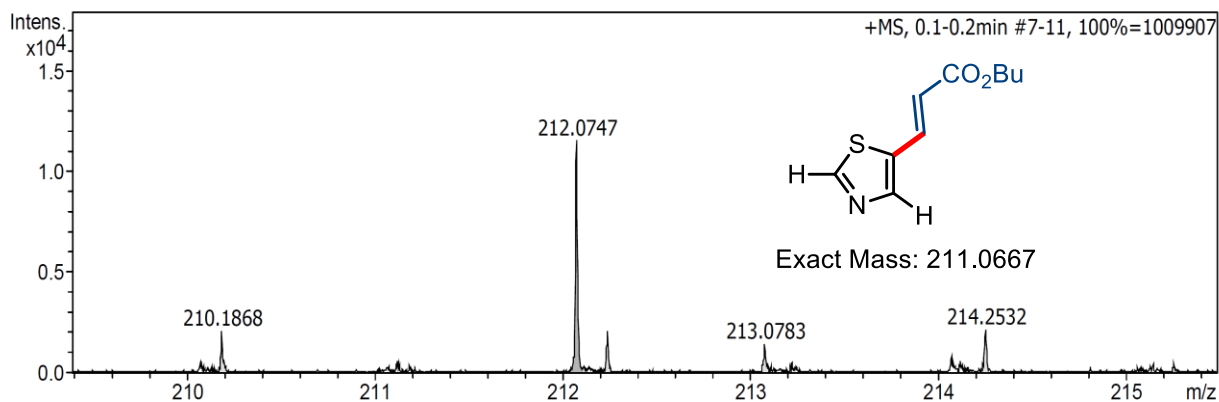
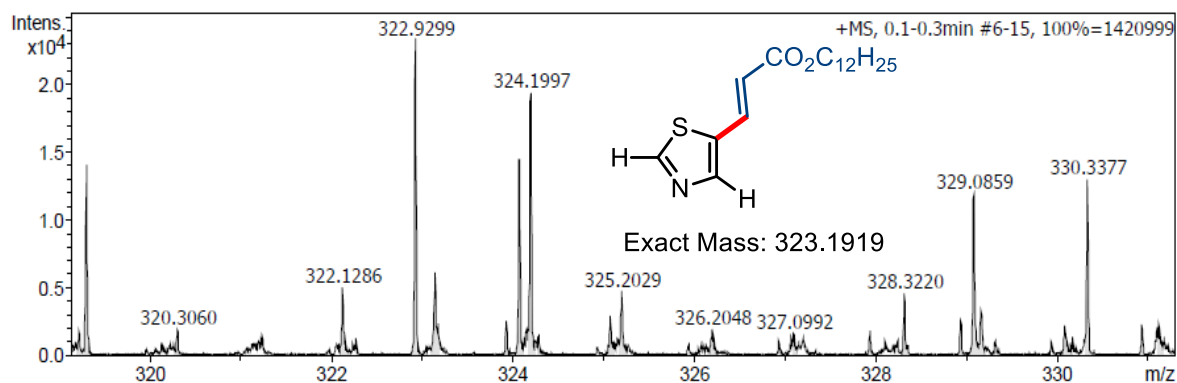


Figure S51. ESI-MS of 3dc.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
324.1997	1	C ₁₈ H ₃₀ NO ₂ S	324.1992	1.7	23.4	1	100.00	4.5	even	ok

Figure S52. ESI-MS of 3dl.

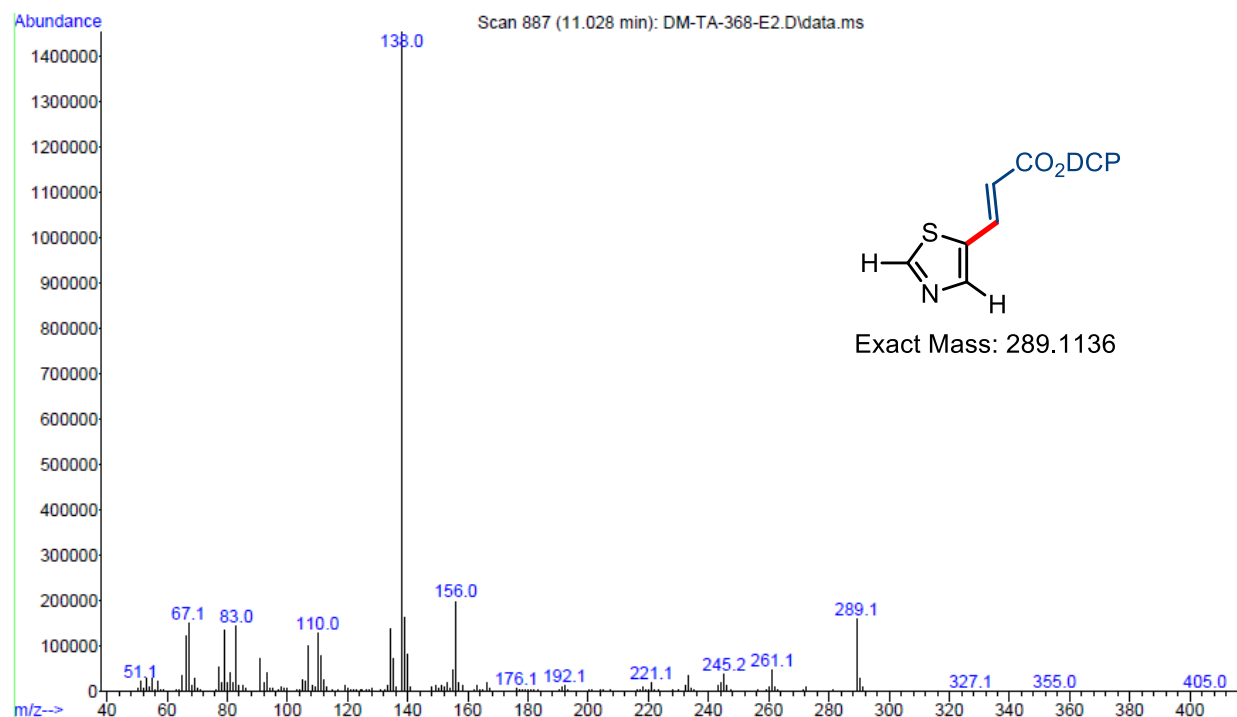


Figure S53. EI-MS of 3de.

Sample Name	TA-368-E2	Position	P1F6	Instrument Name	QTOF	User Name	LCMSQTOF-PC\admin
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TA-368-E2.d	ACQ Method	2MINS DIRECT MS.m	Comment		Acquired Time	4/23/2019 8:11:15 PM

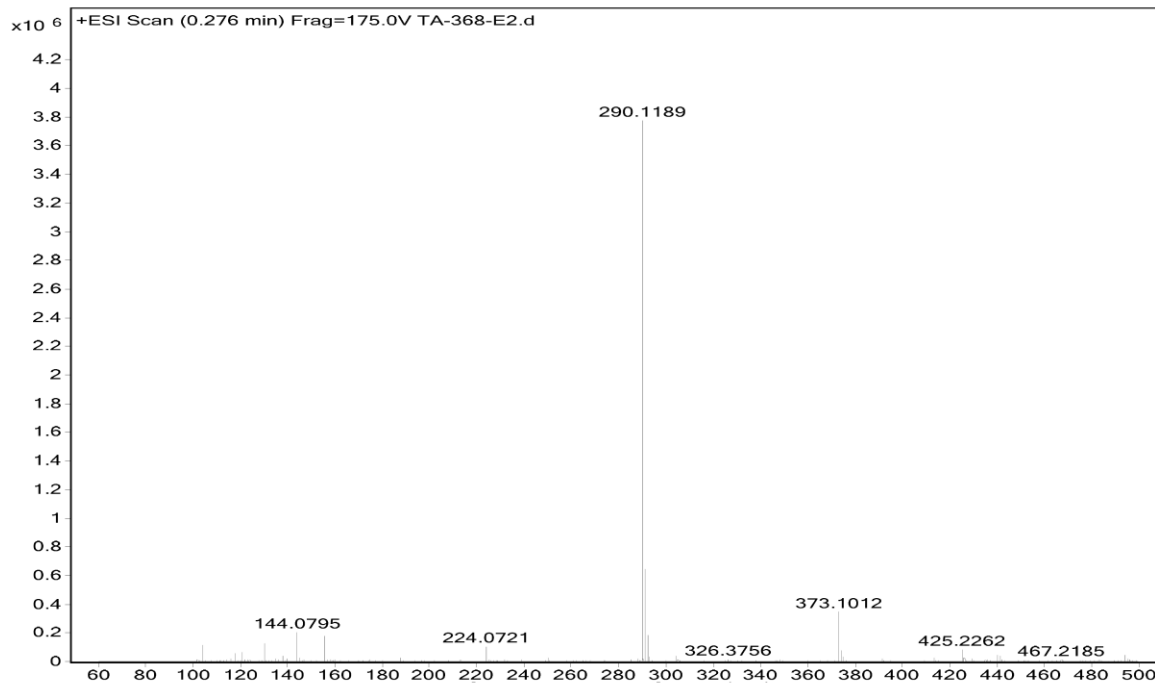


Figure S54. ESI-MS of 3de.

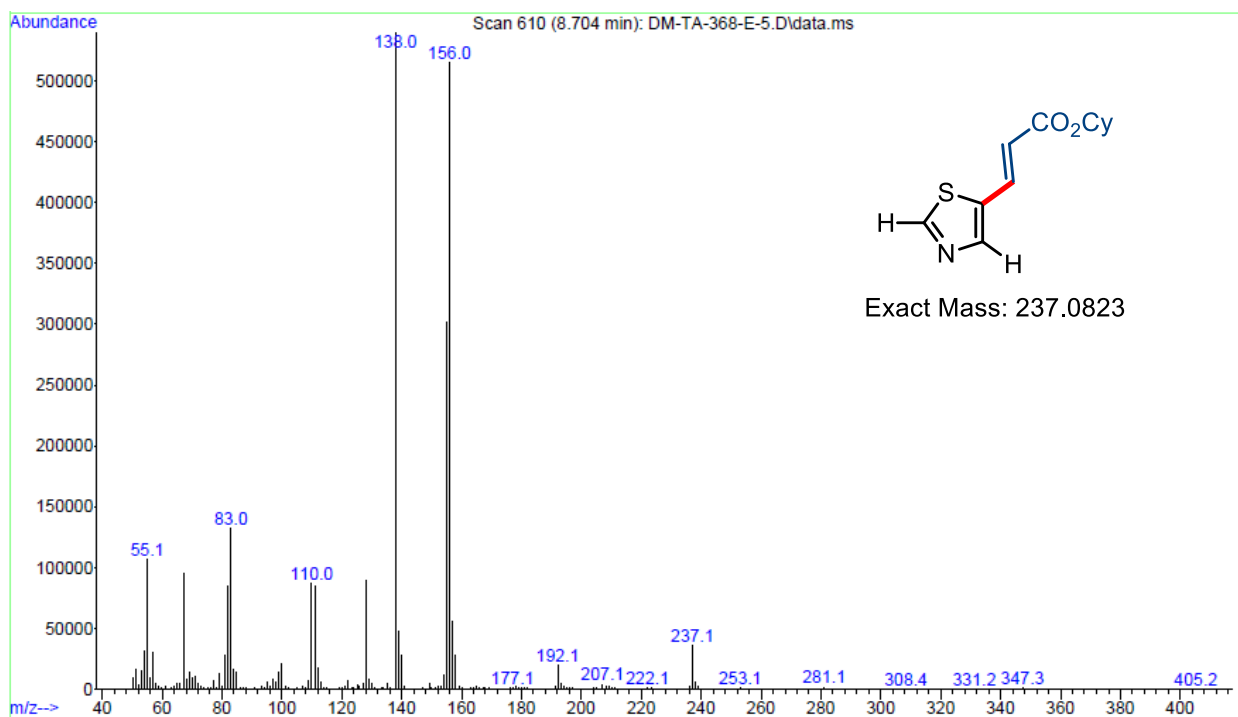


Figure S55. EI-MS of 3di.

Sample Name	TA-368-E5	Position	P1F7	Instrument Name	QTOF	User Name	LCMSQTOF-PC\admin
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TA-368-E5.d	ACQ Method	2MINS DIRECT MS.m	Comment		Acquired Time	4/23/2019 8:03:44 PM

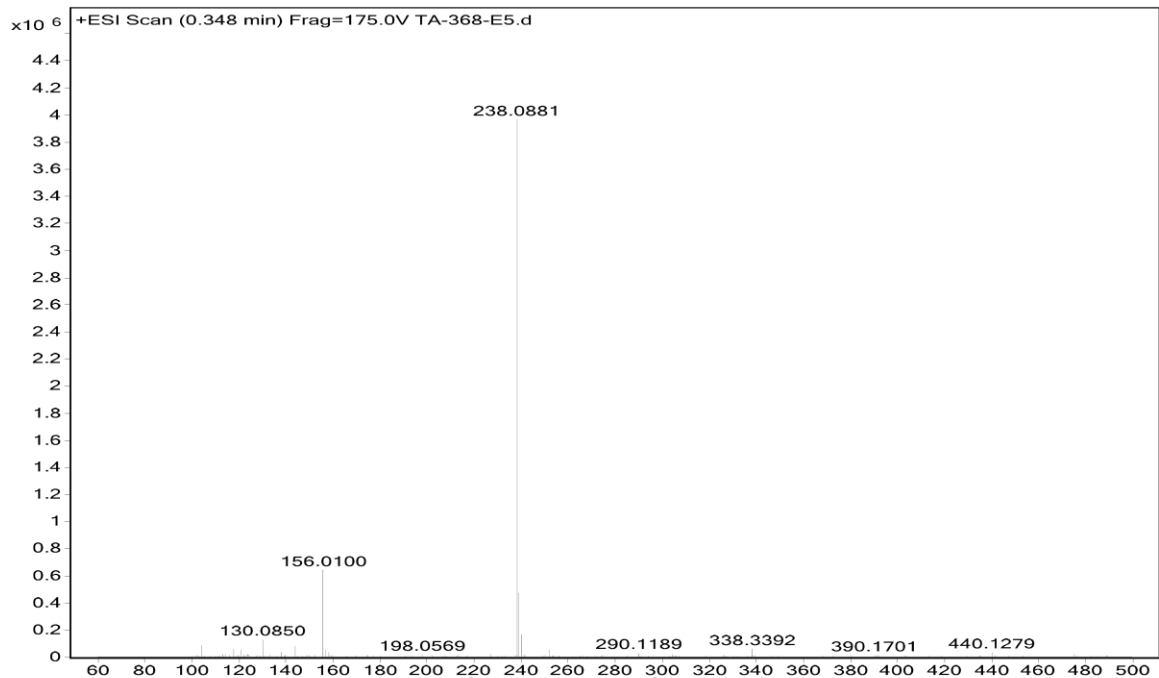


Figure S56. ESI-MS of 3di.