Supporting Information

New Journal of Chemistry

Metal-Free Annulative Hydrosulfonation of Propiolate Esters: Synthesis of 4-Sulfonates of Coumarins and Butenolides

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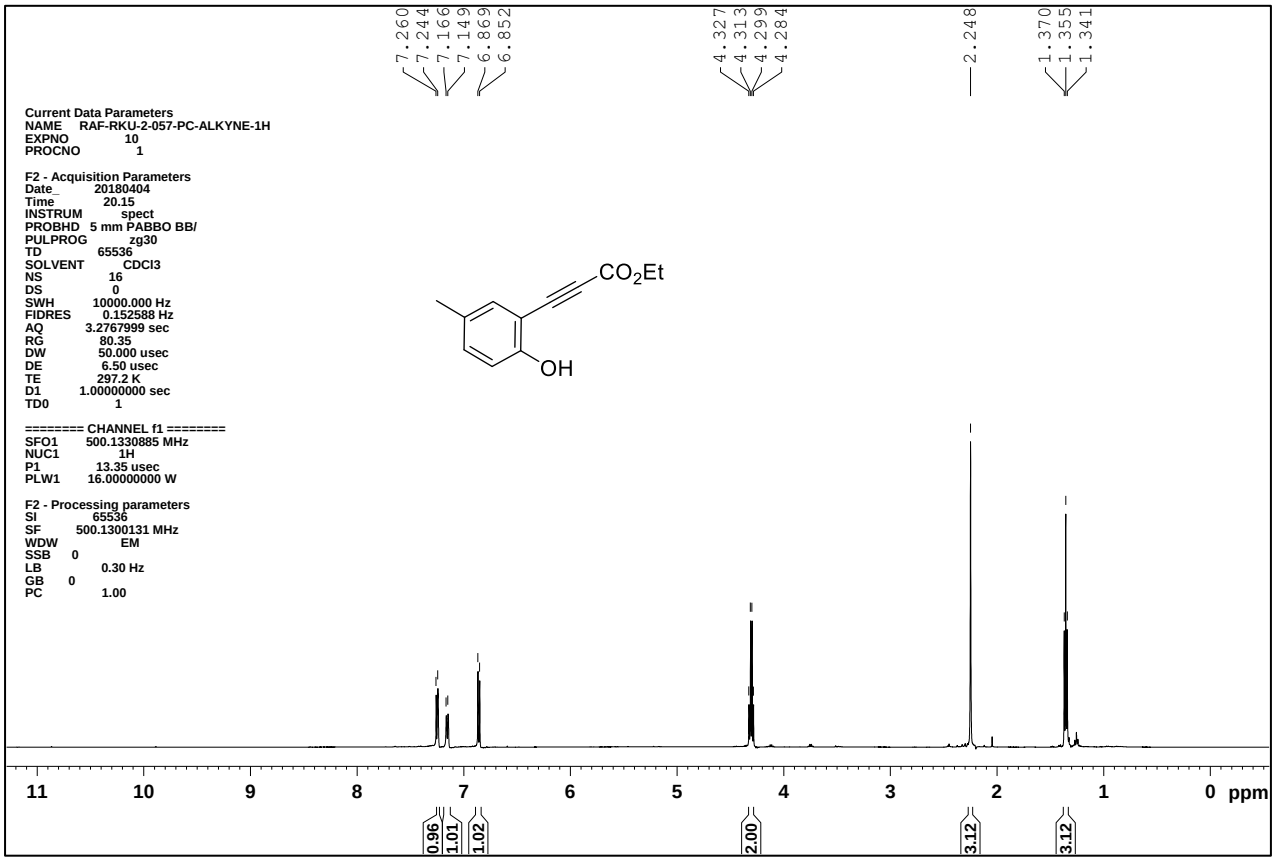
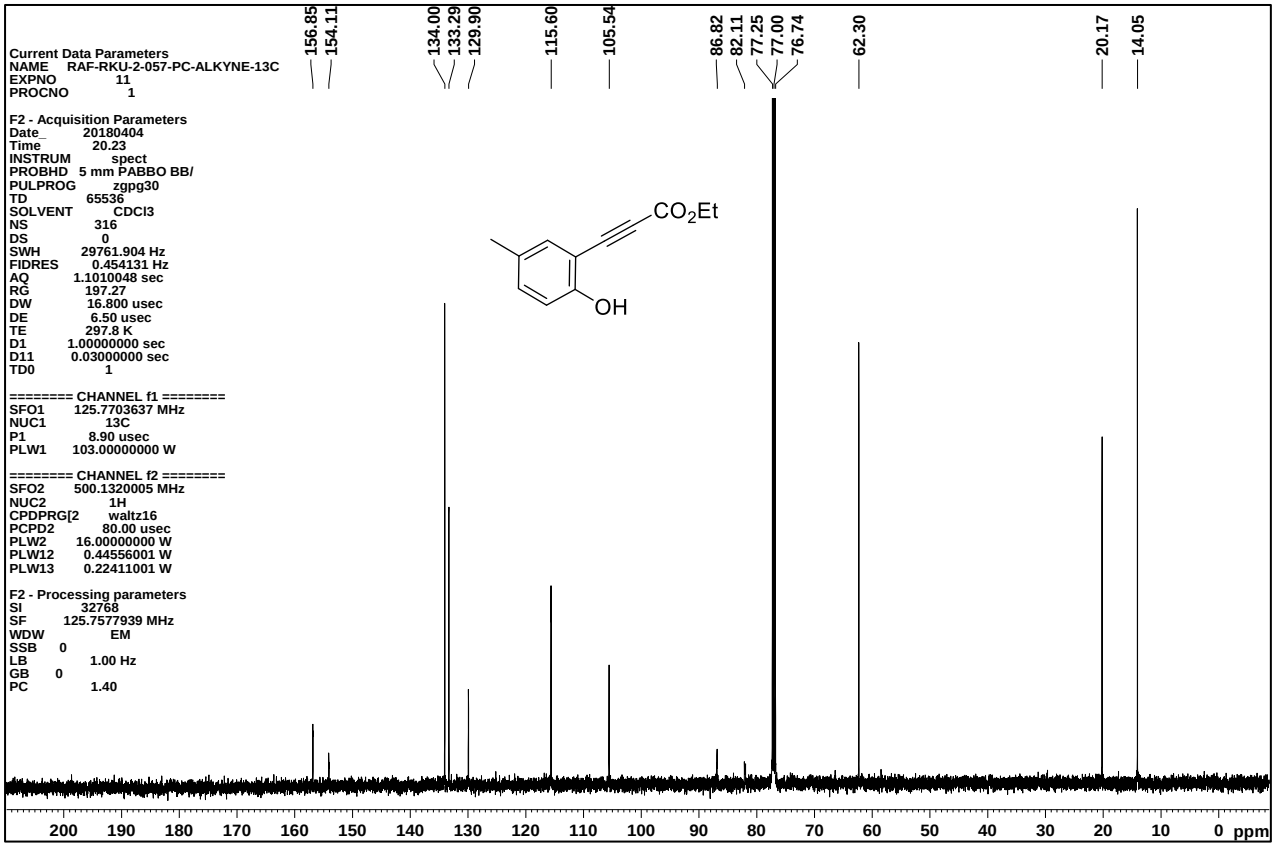
Table of Contents

^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **6a**





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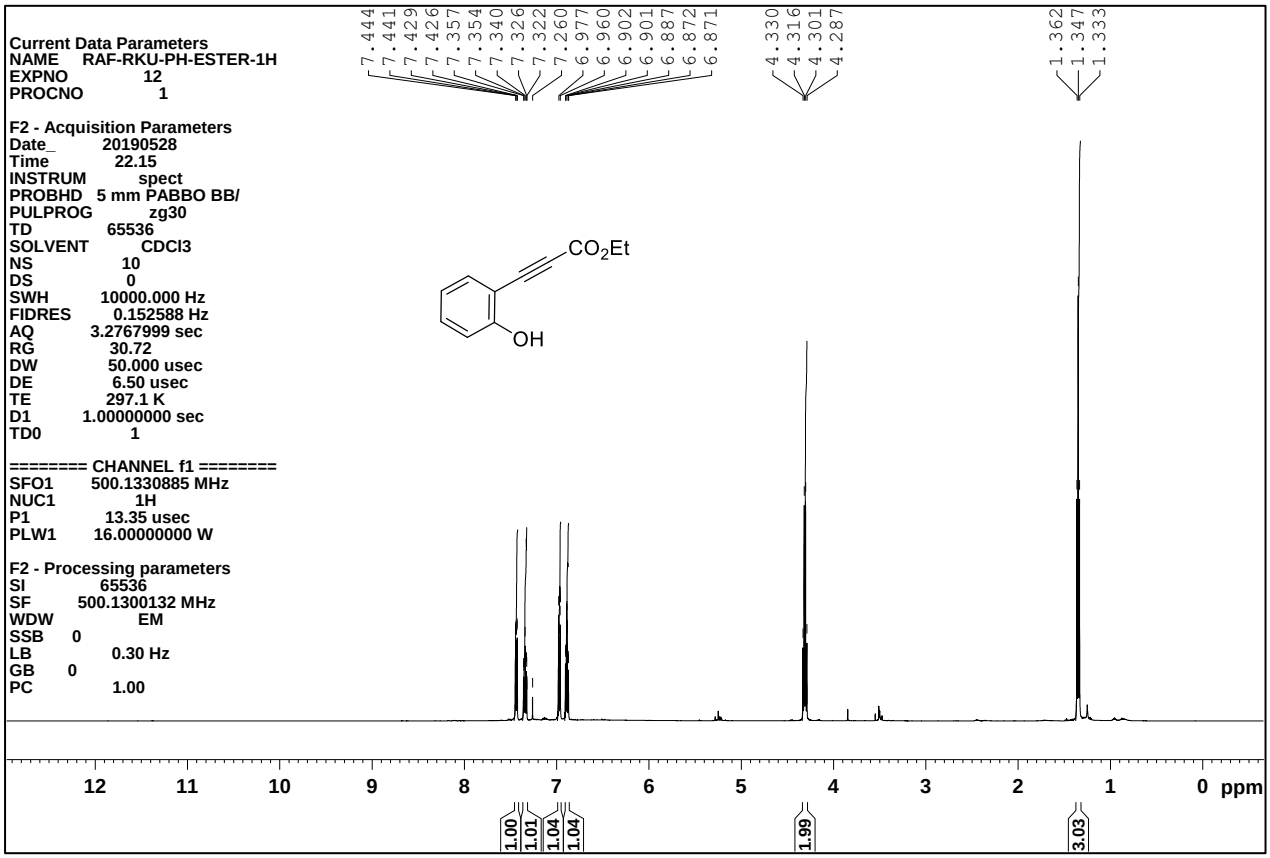

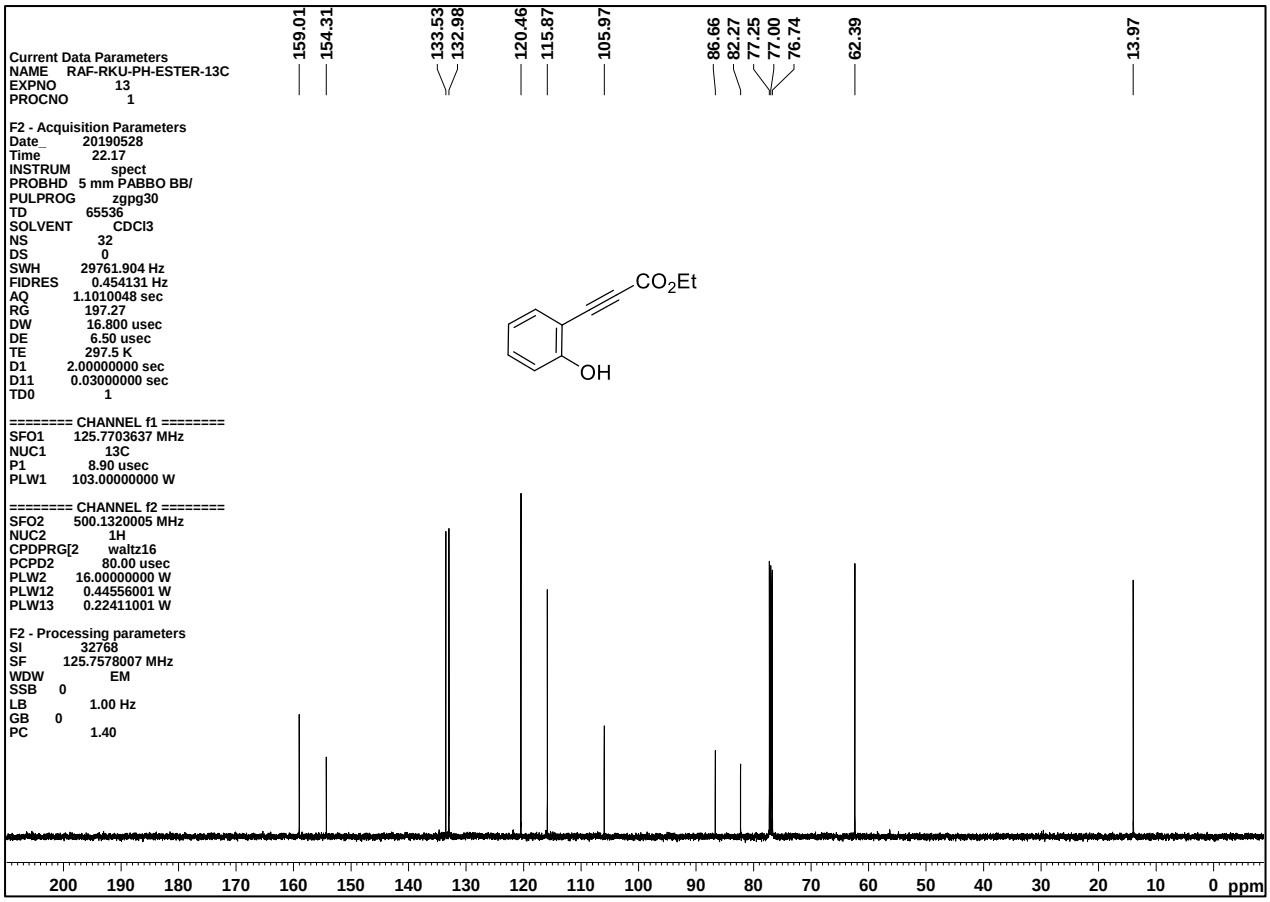

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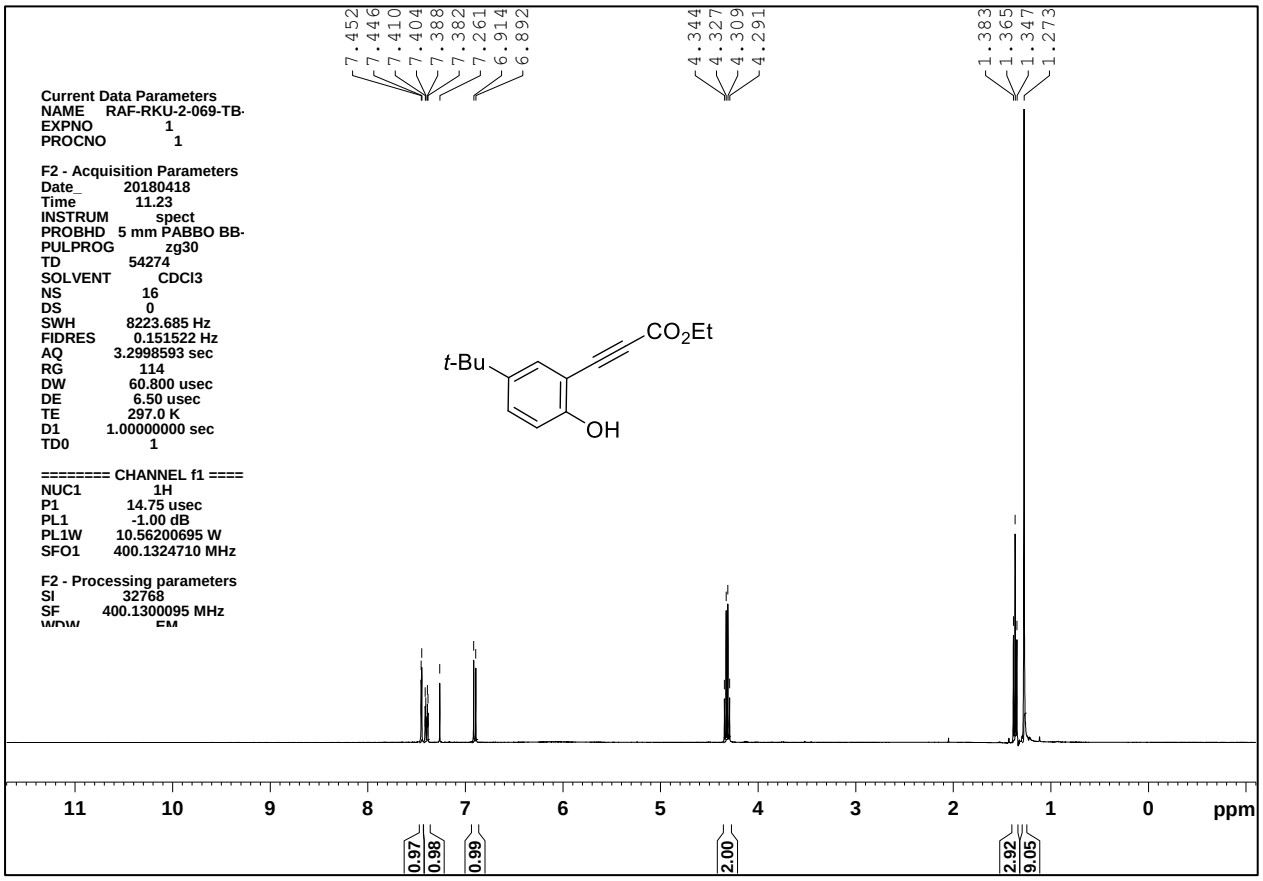

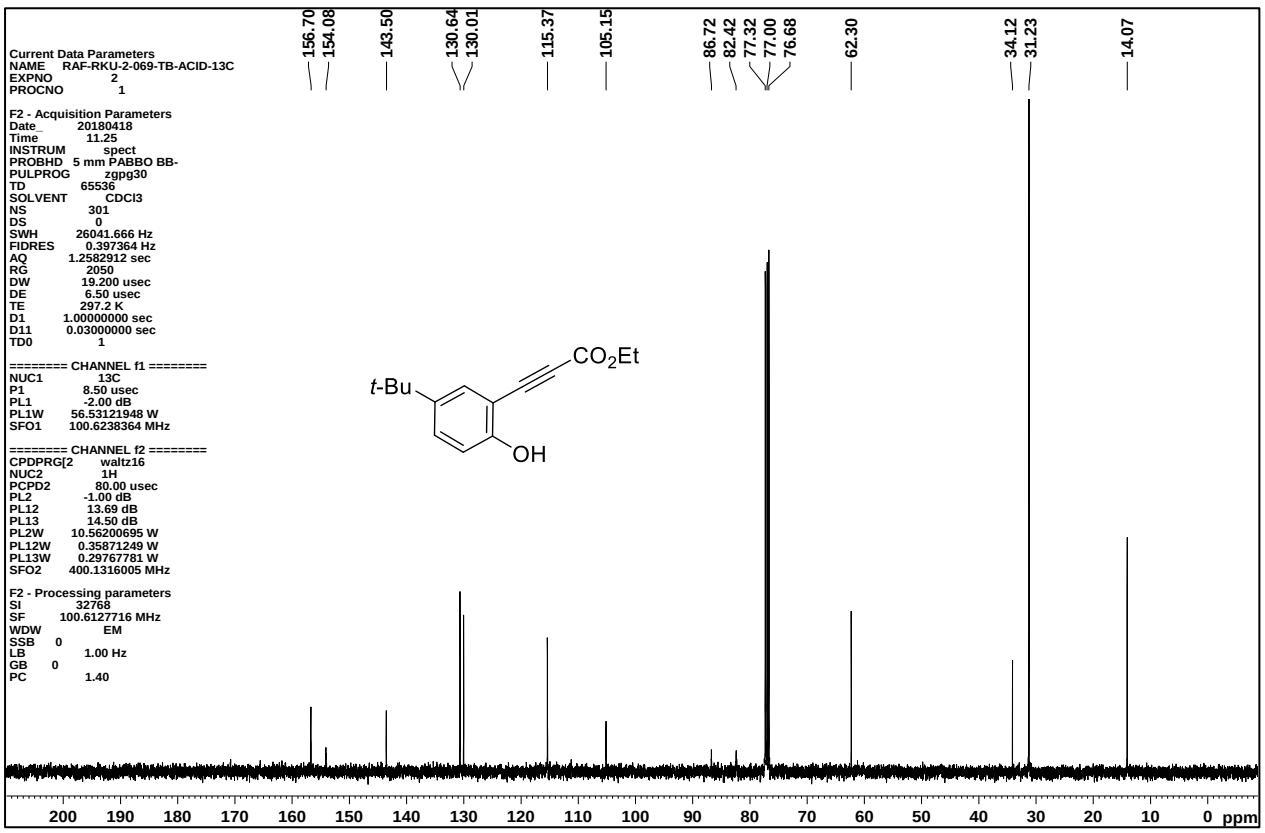

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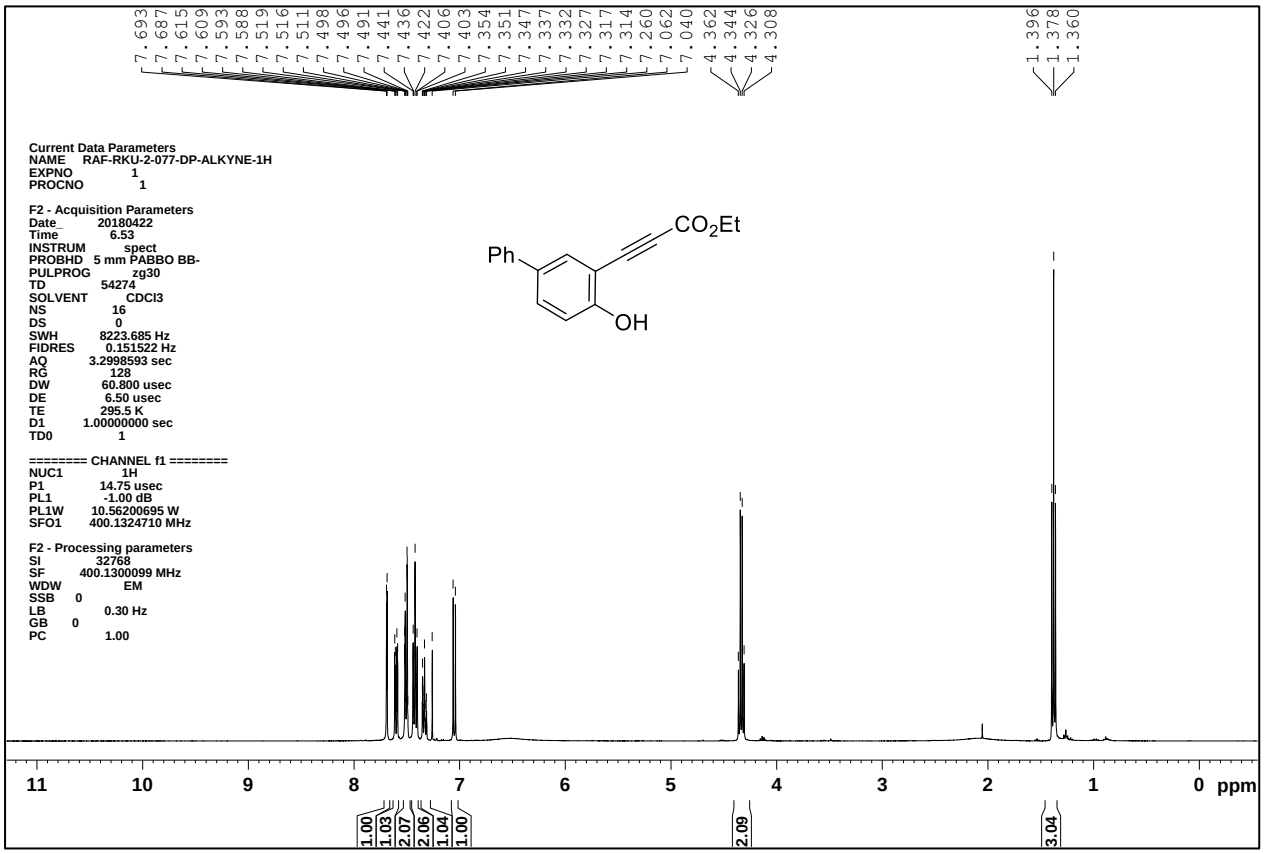

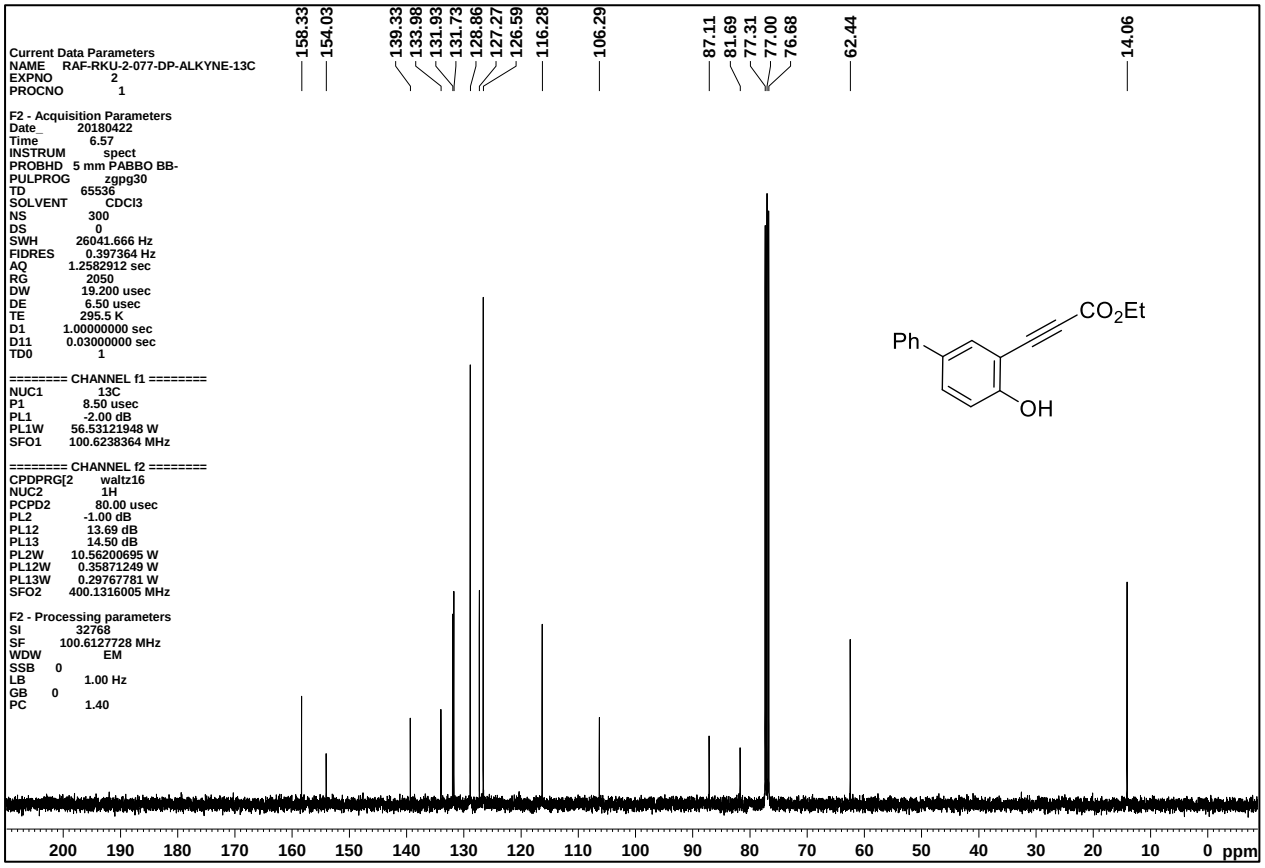

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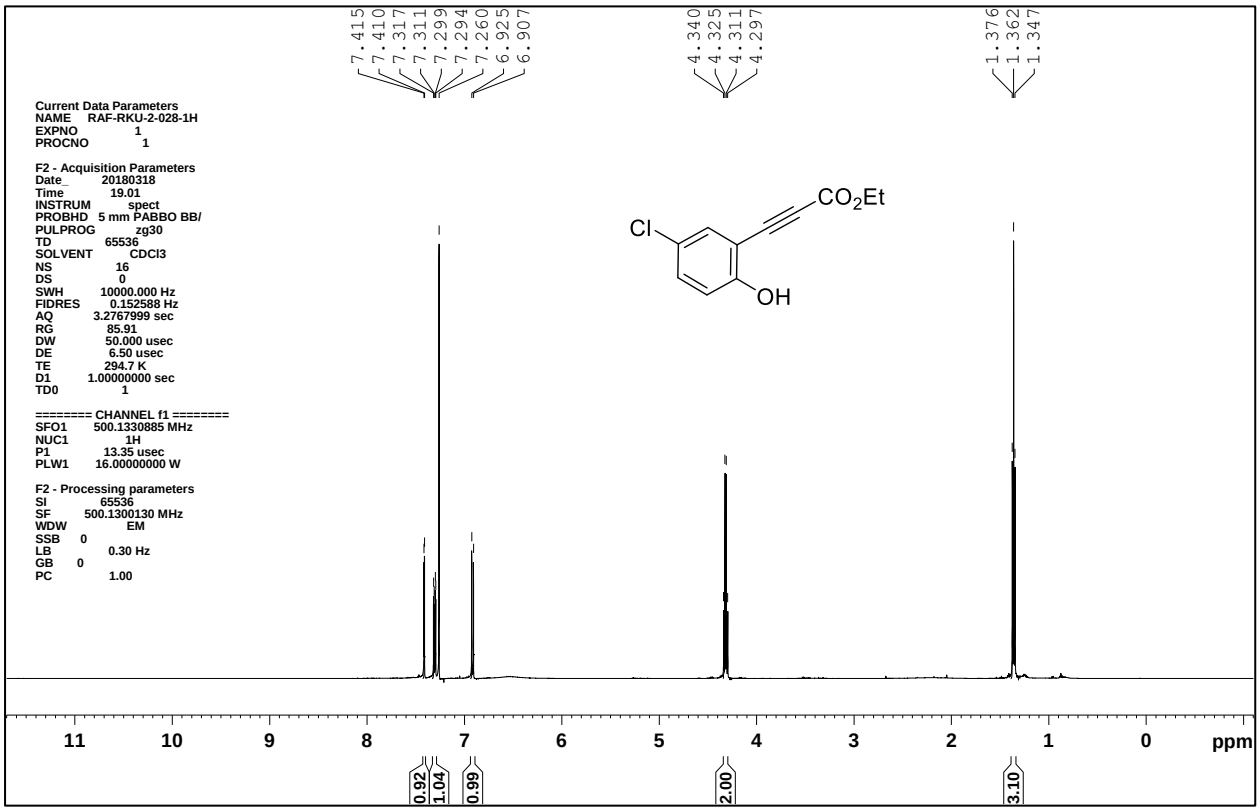

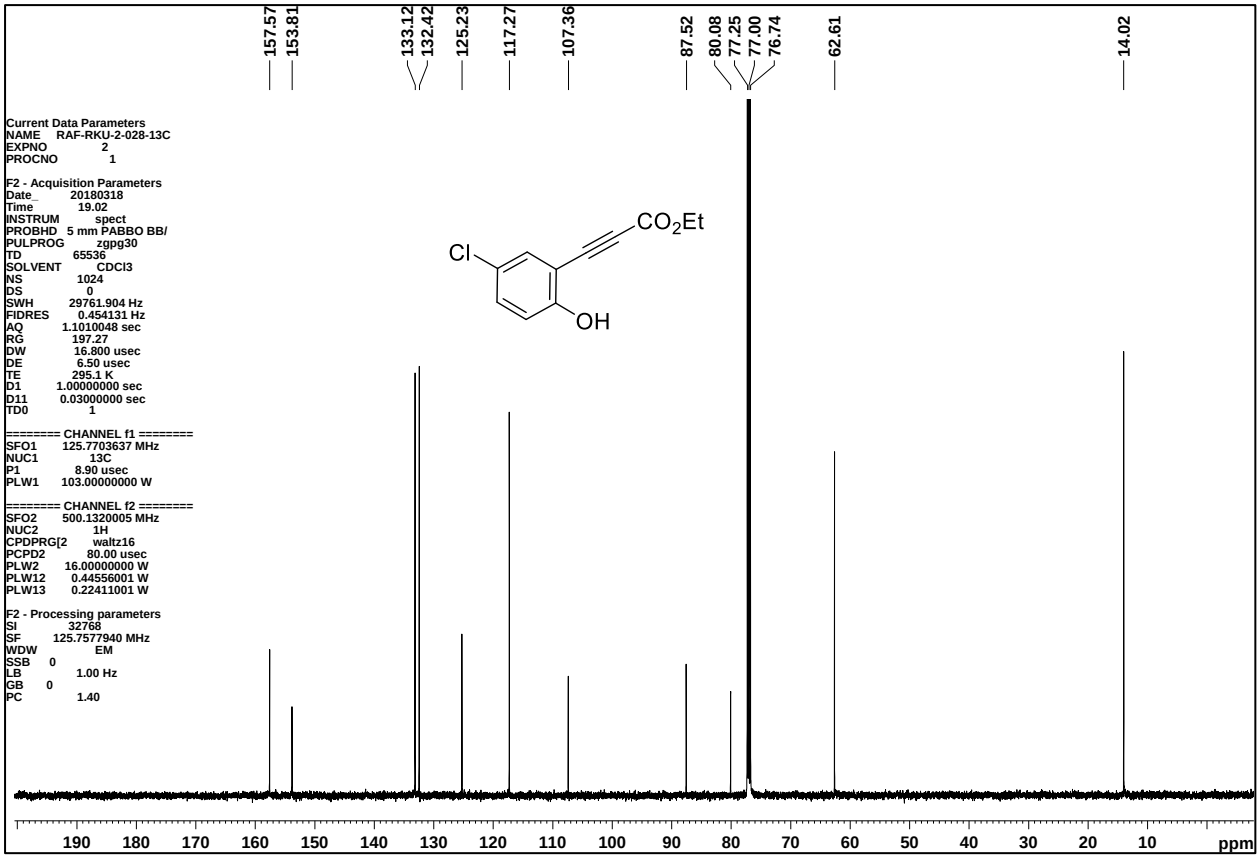

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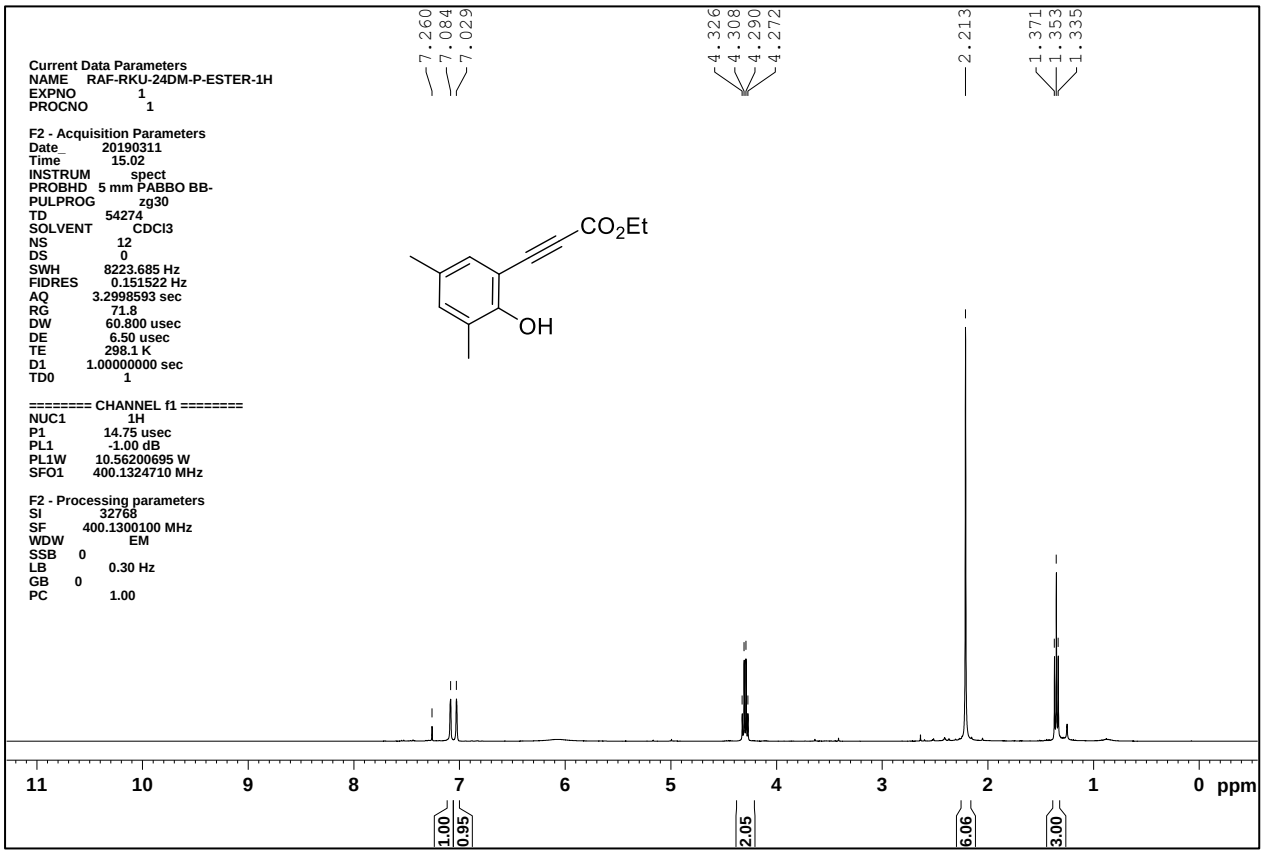

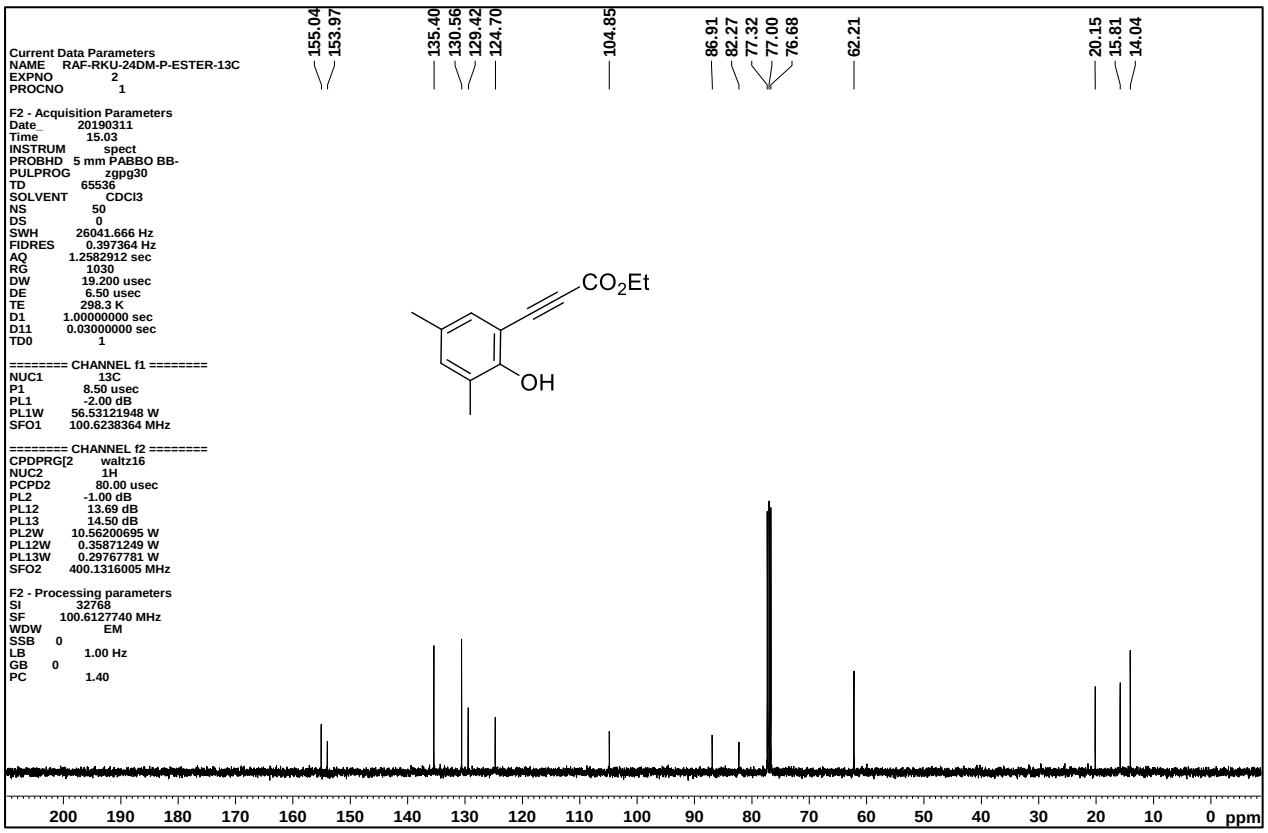

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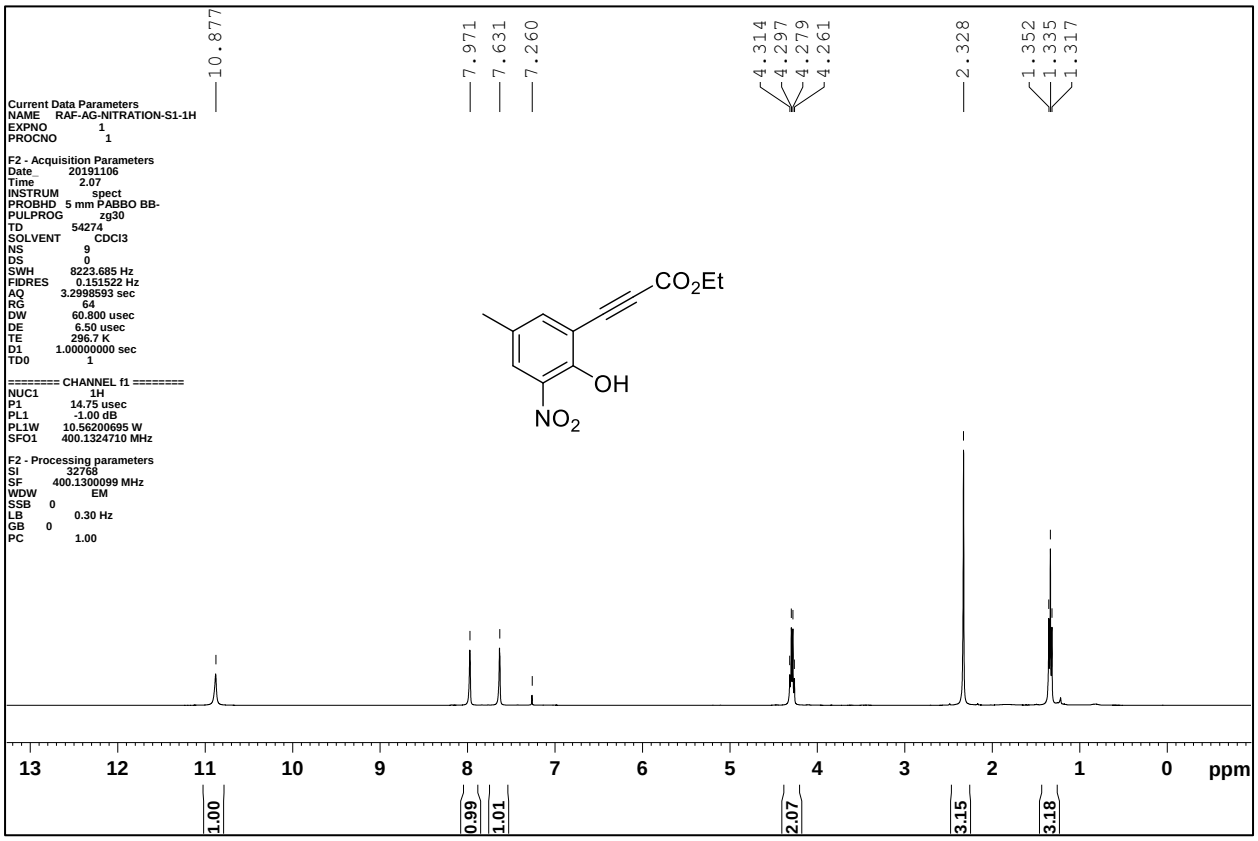

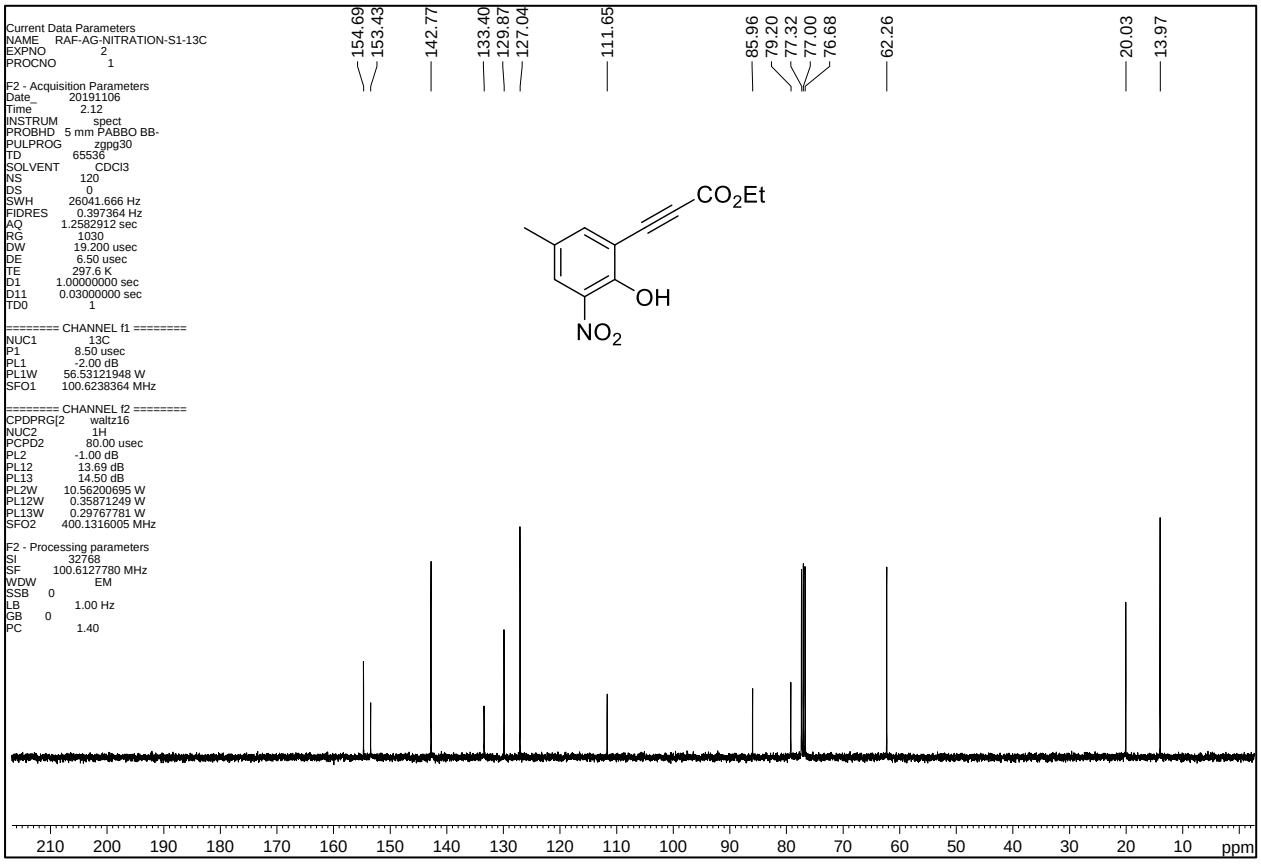

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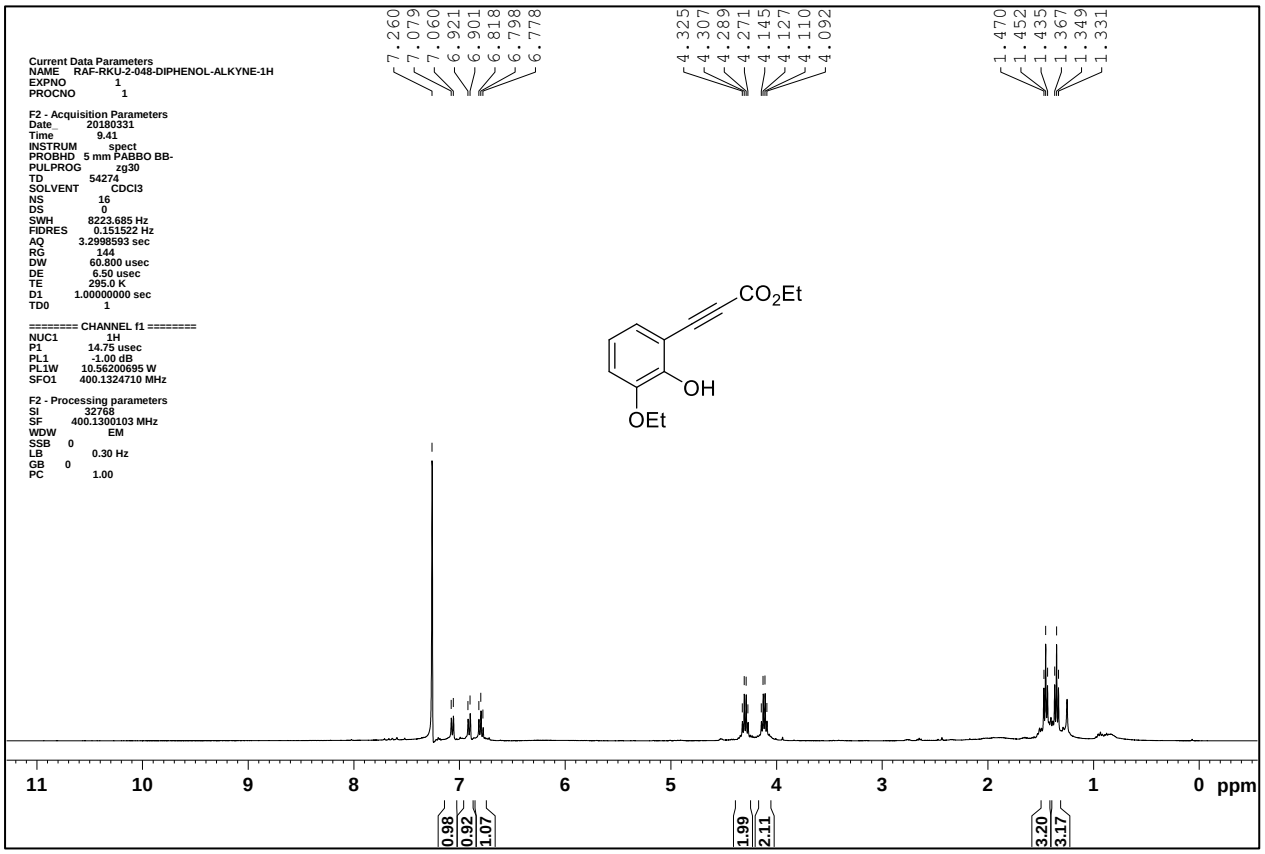

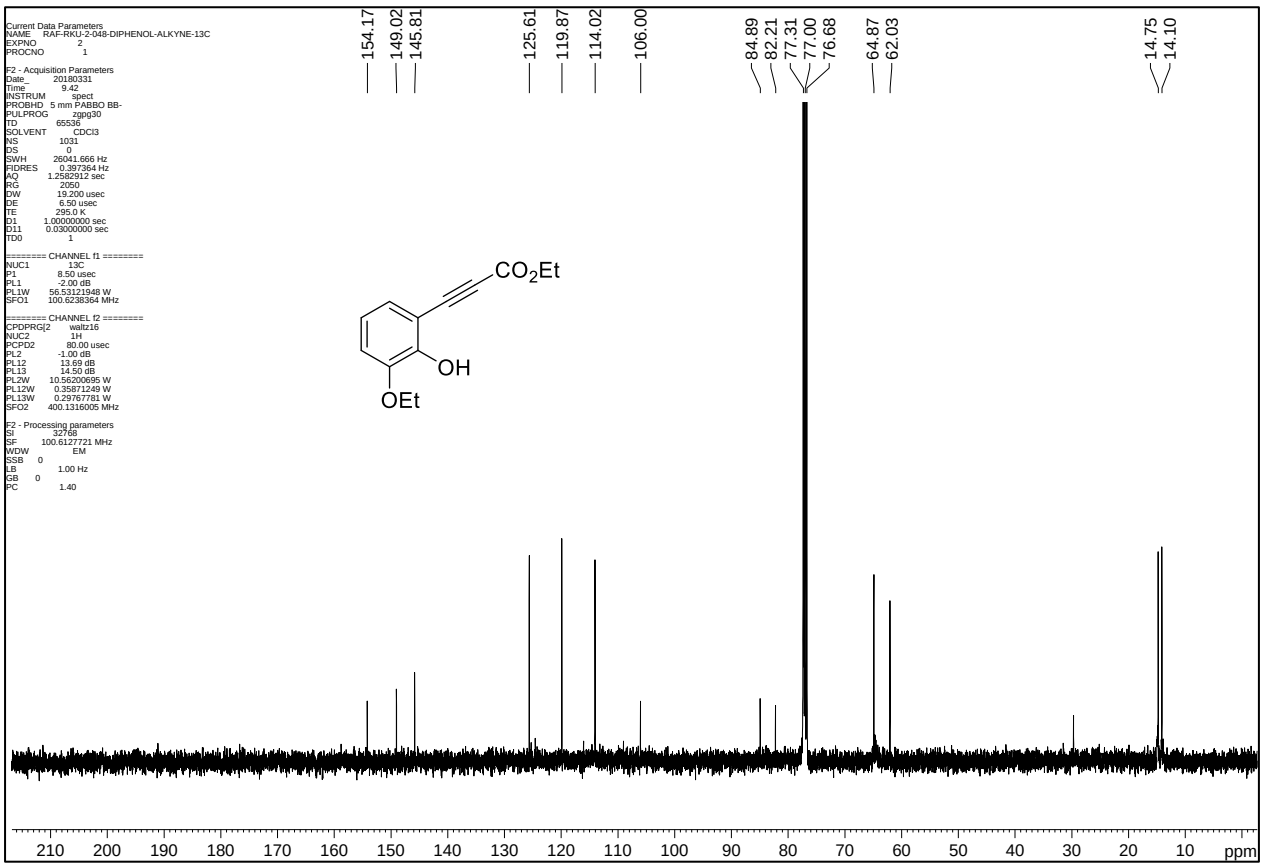

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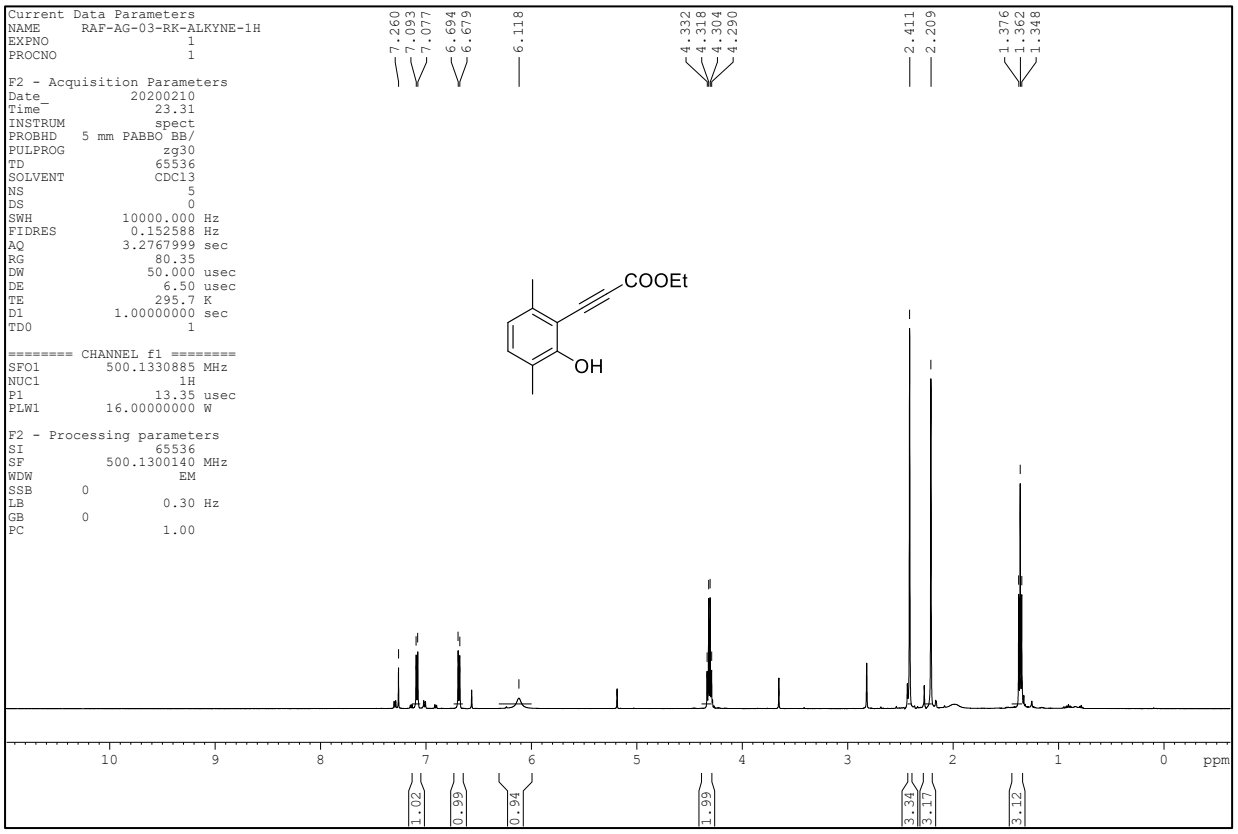

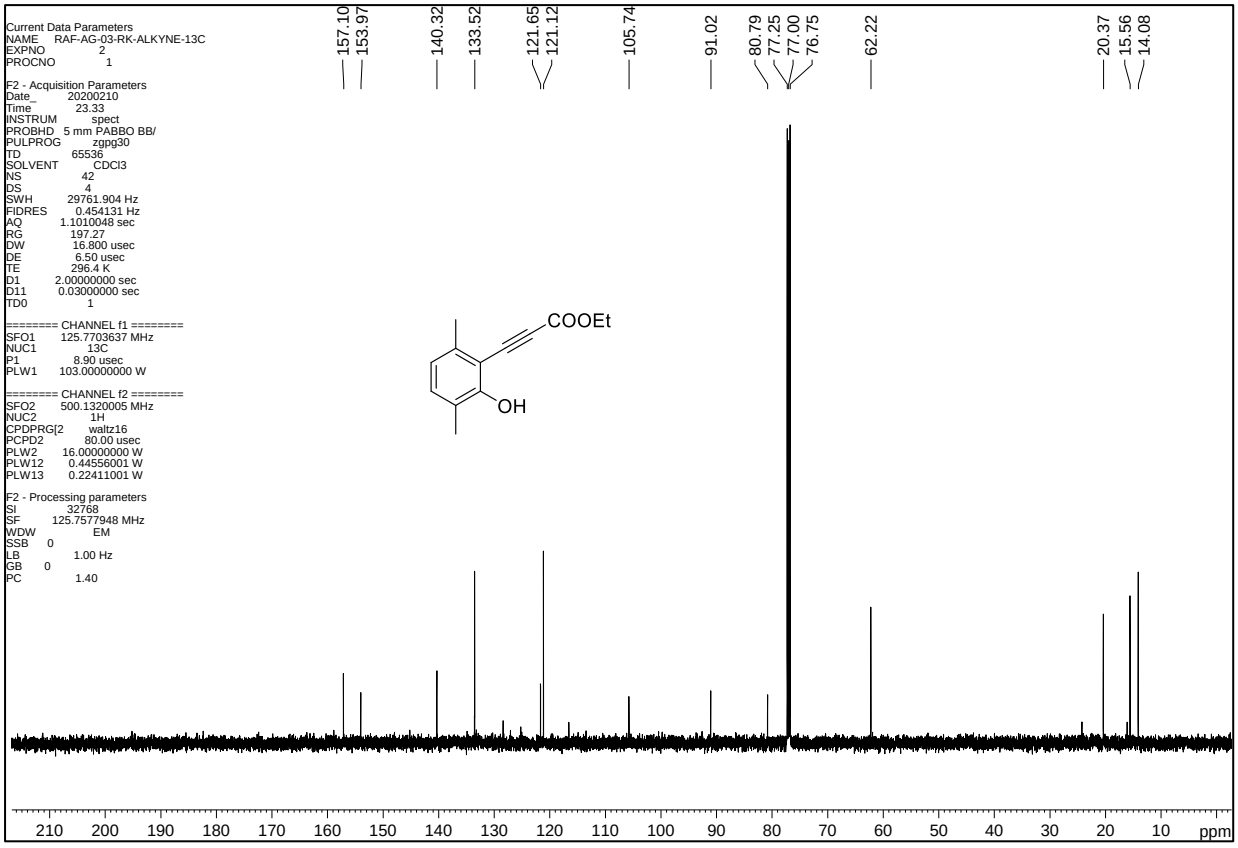

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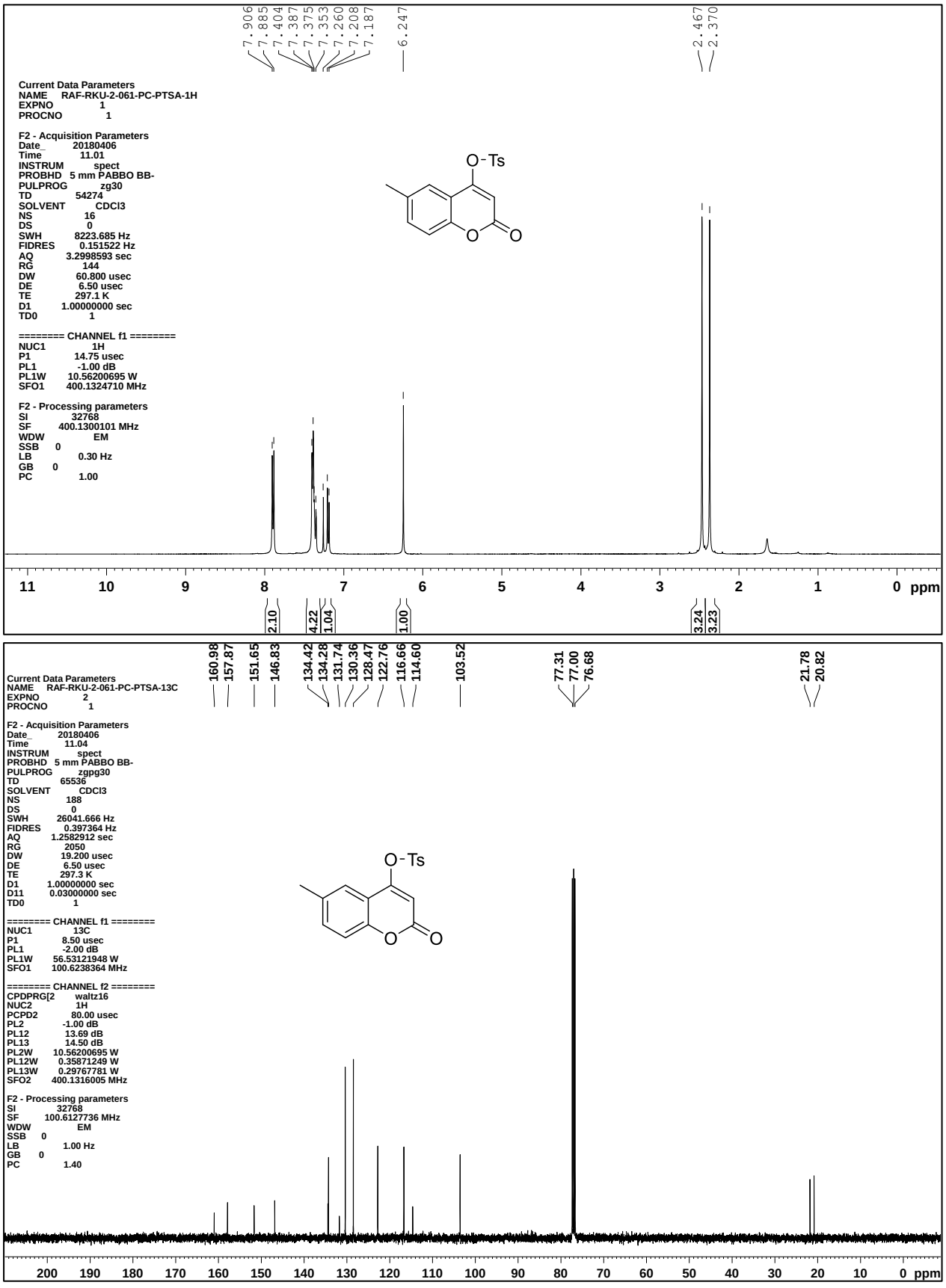

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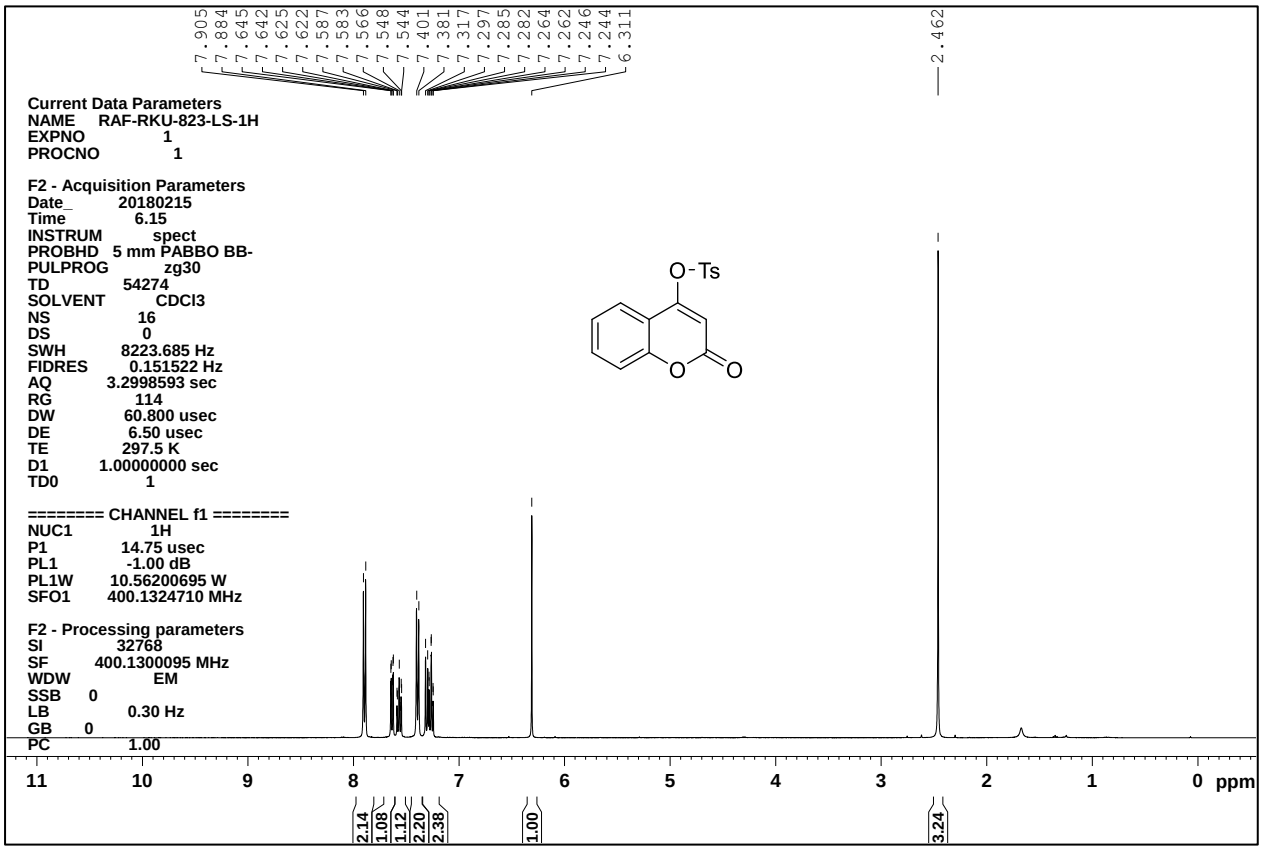

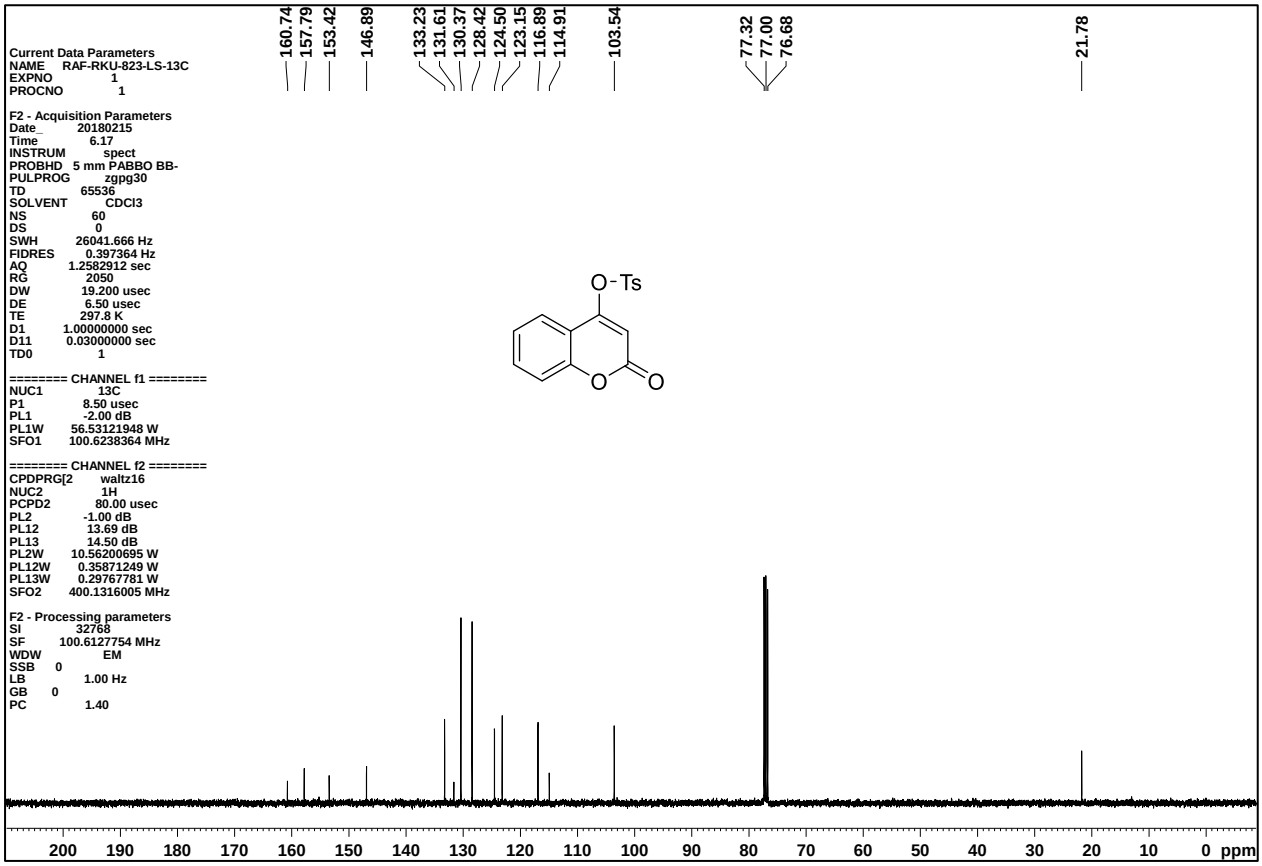

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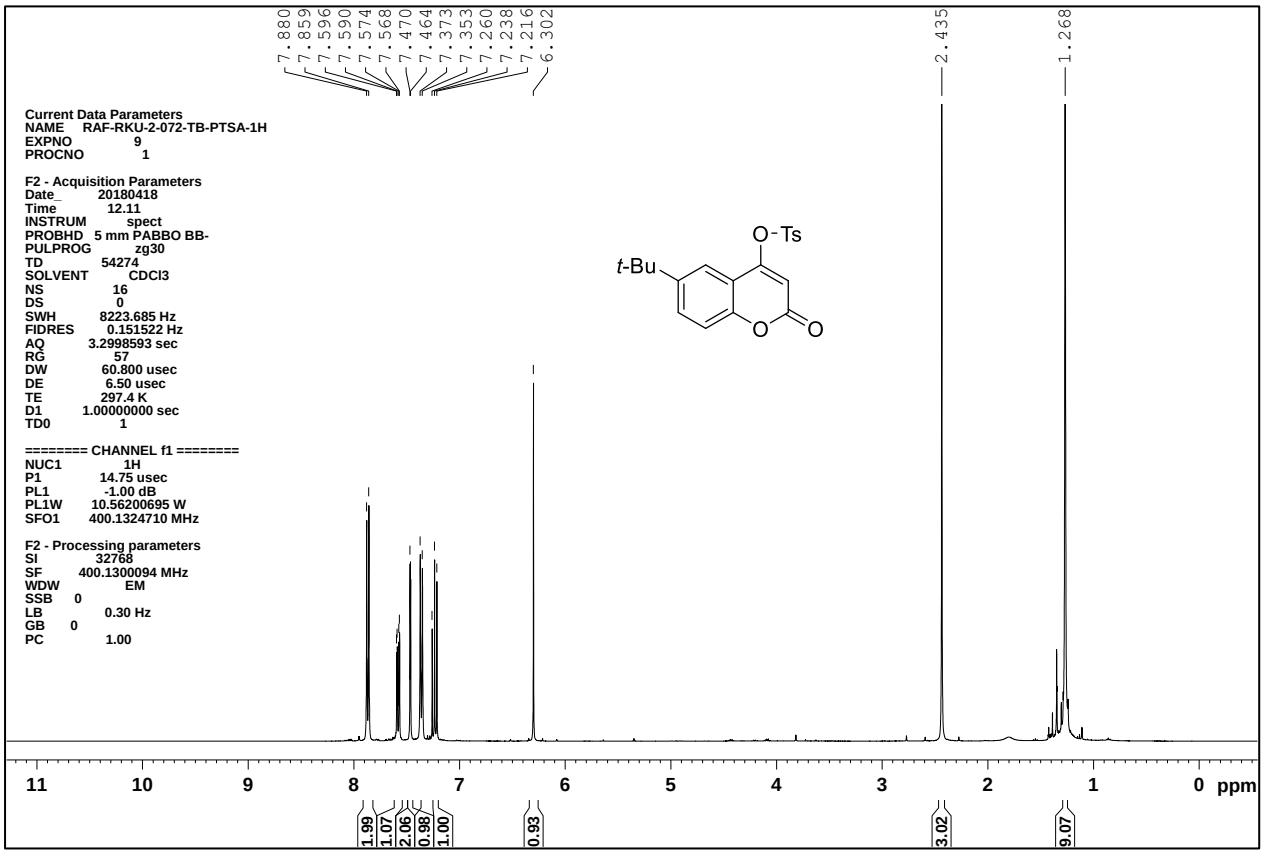

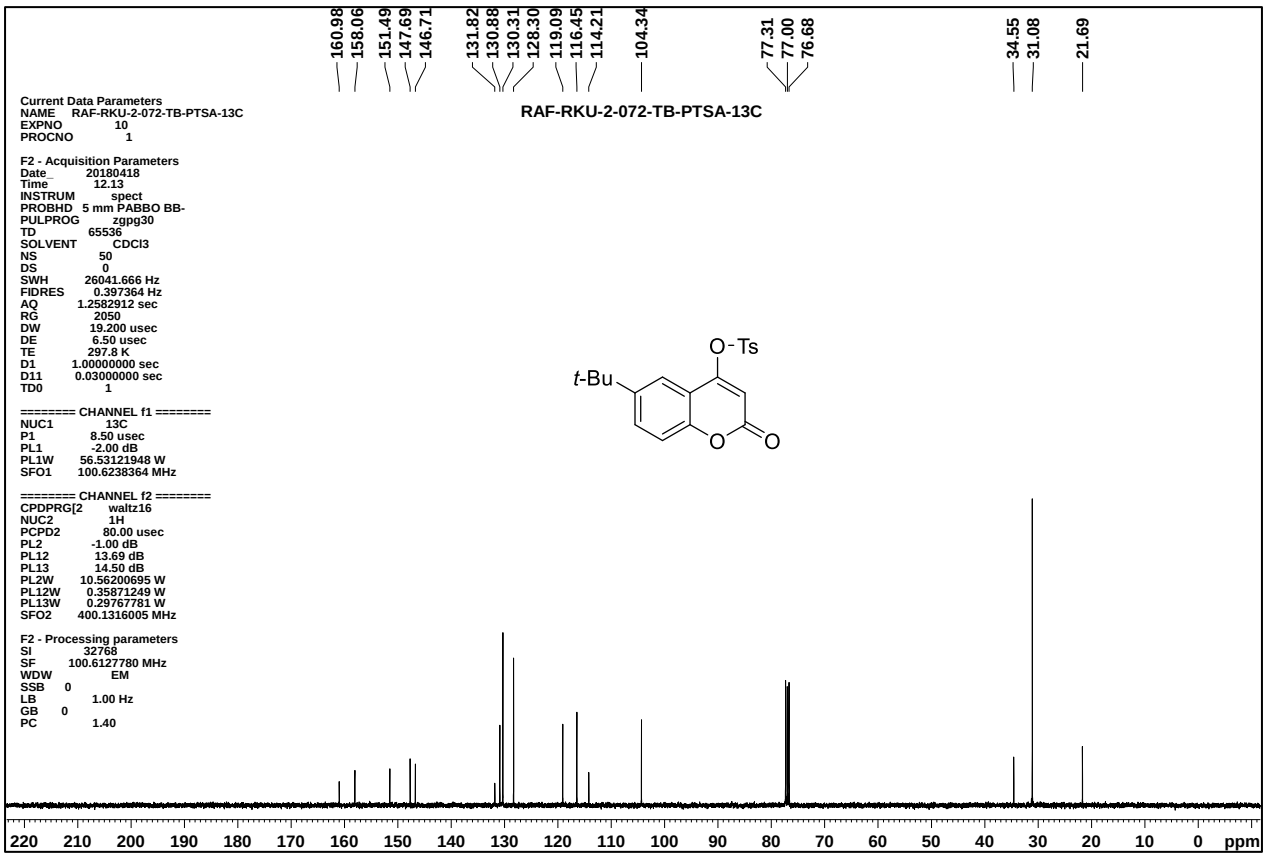

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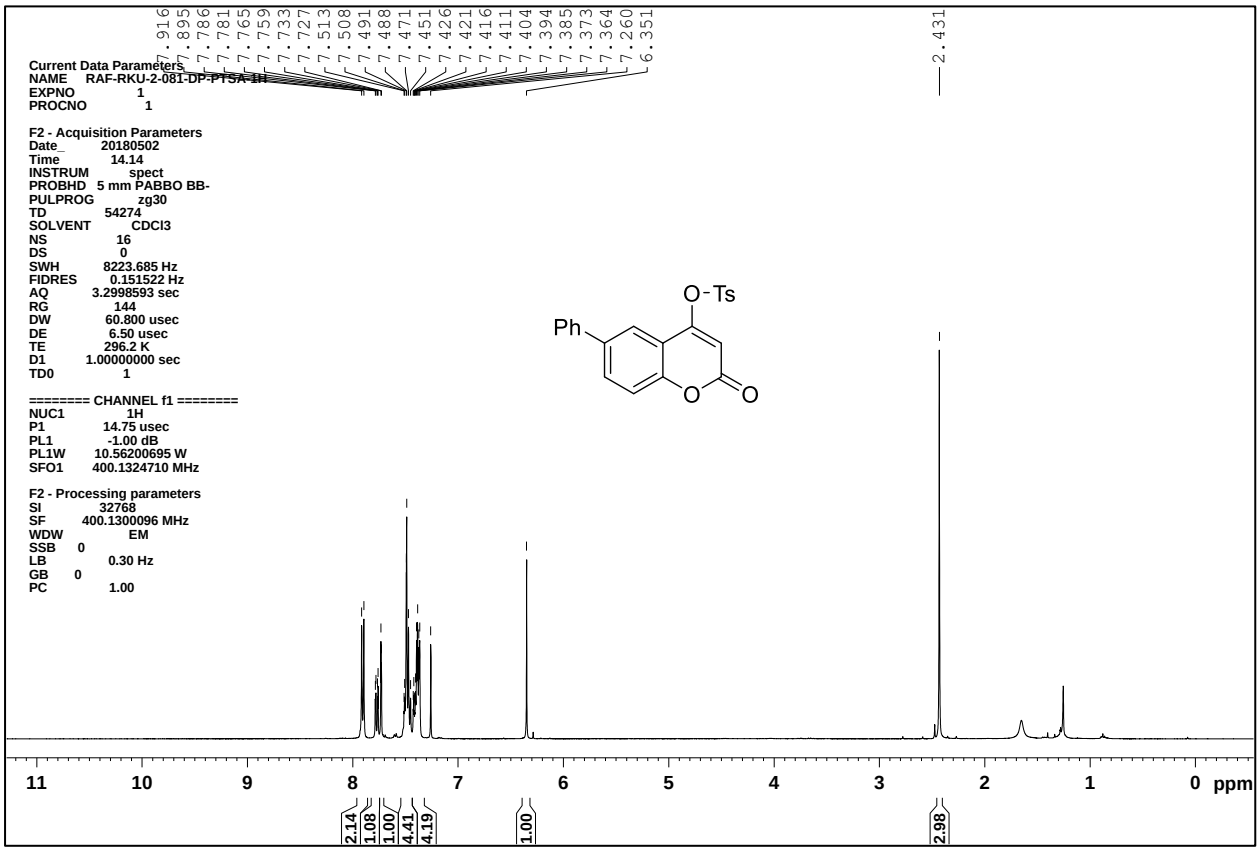
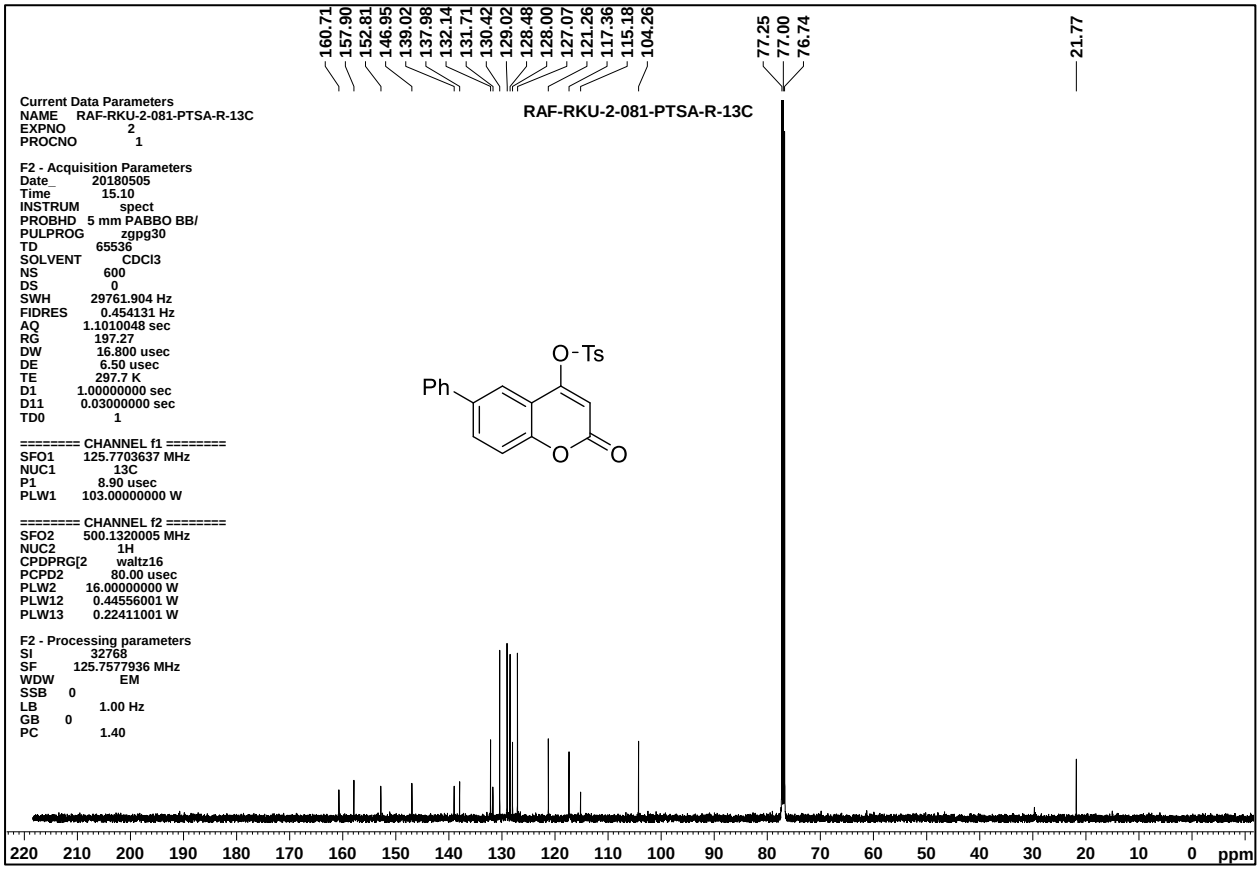
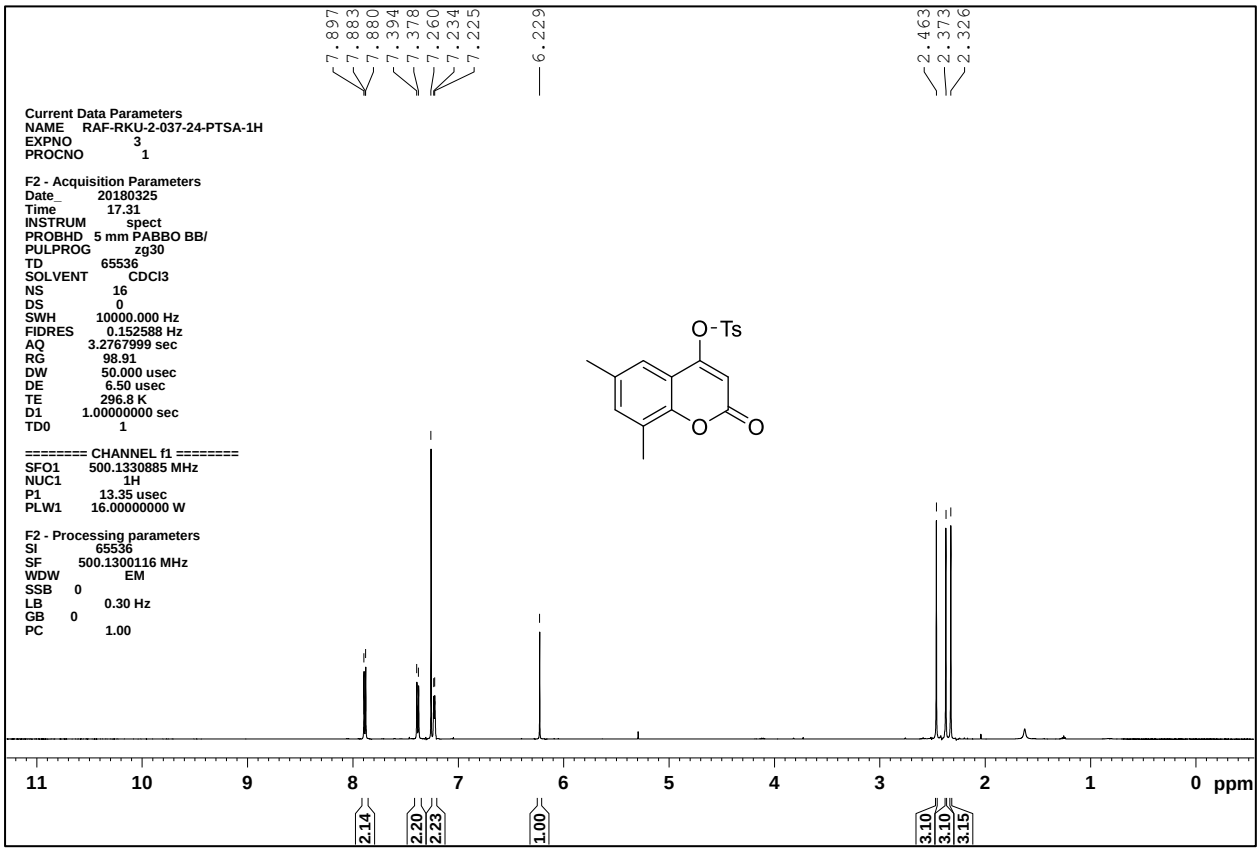
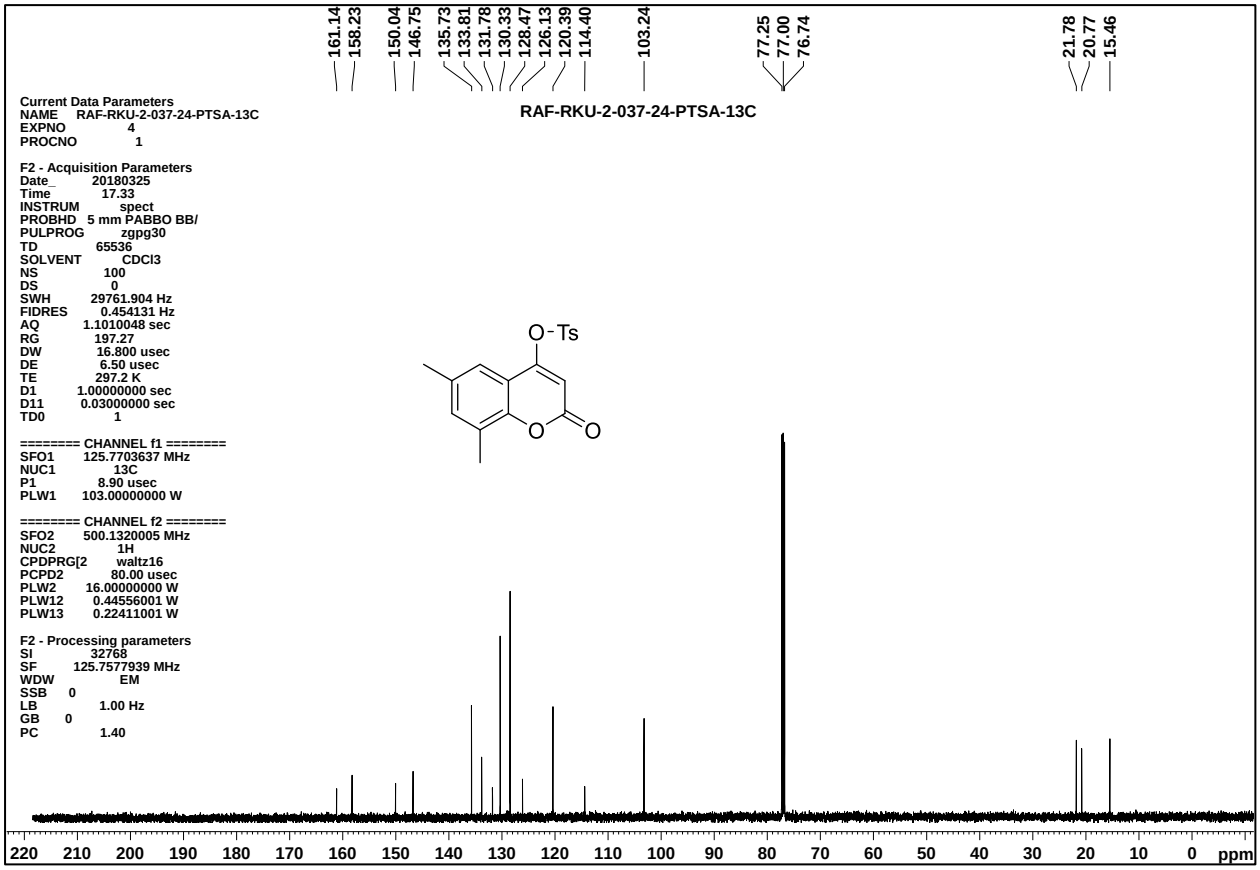


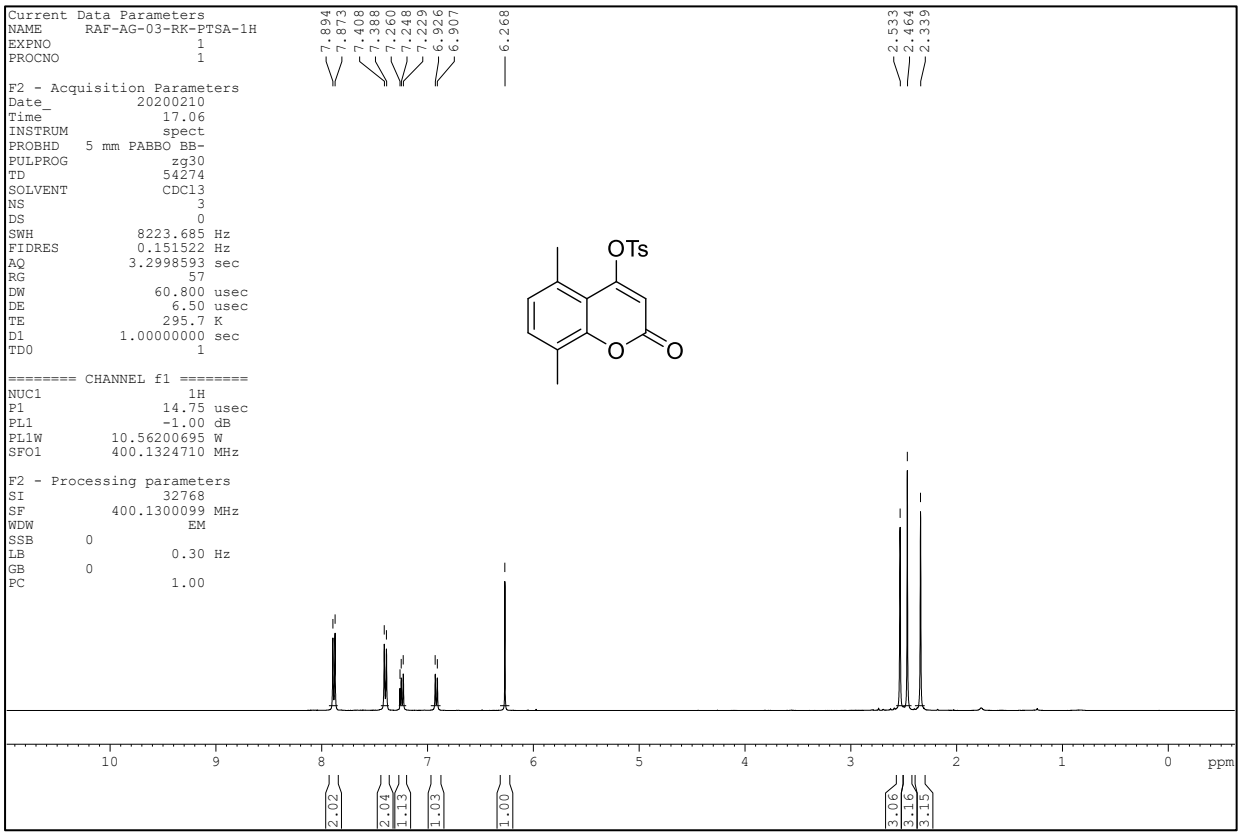


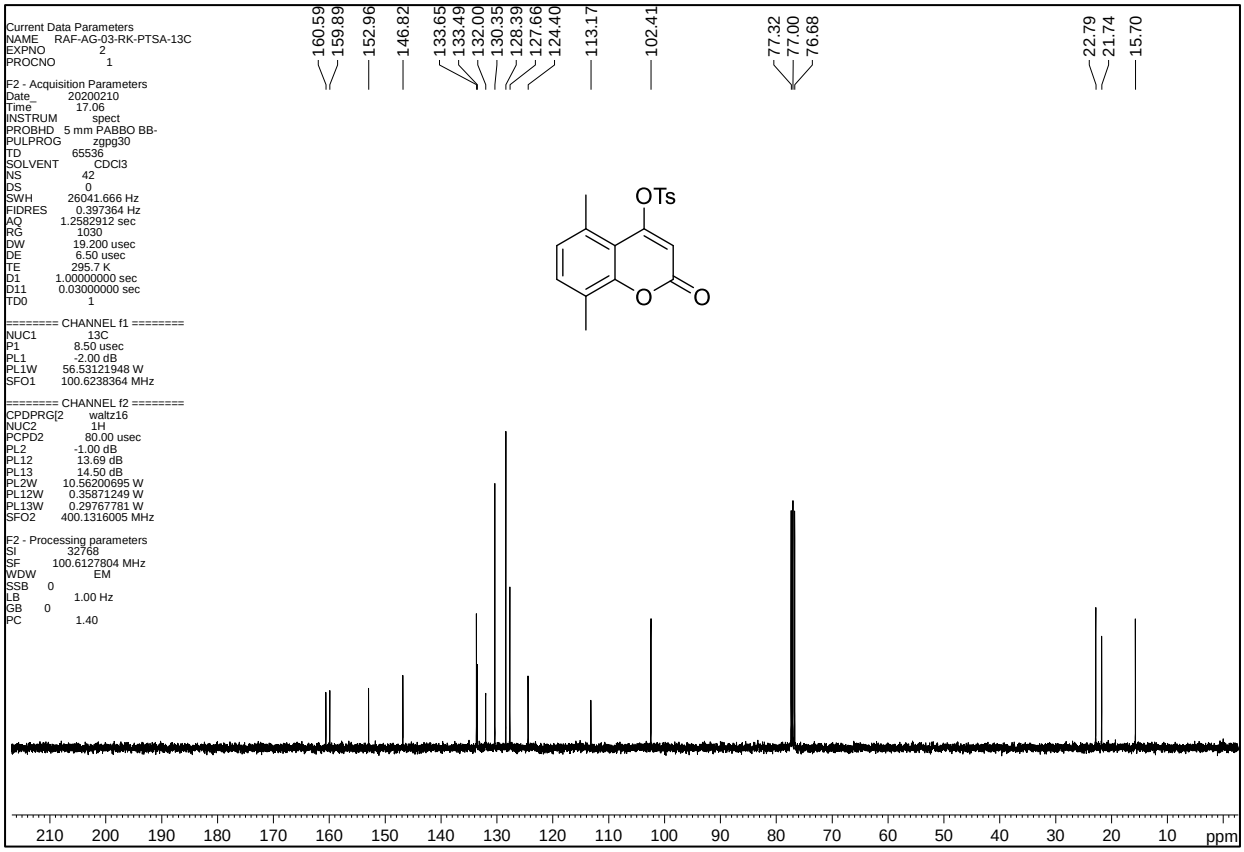
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **5f**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **5i**





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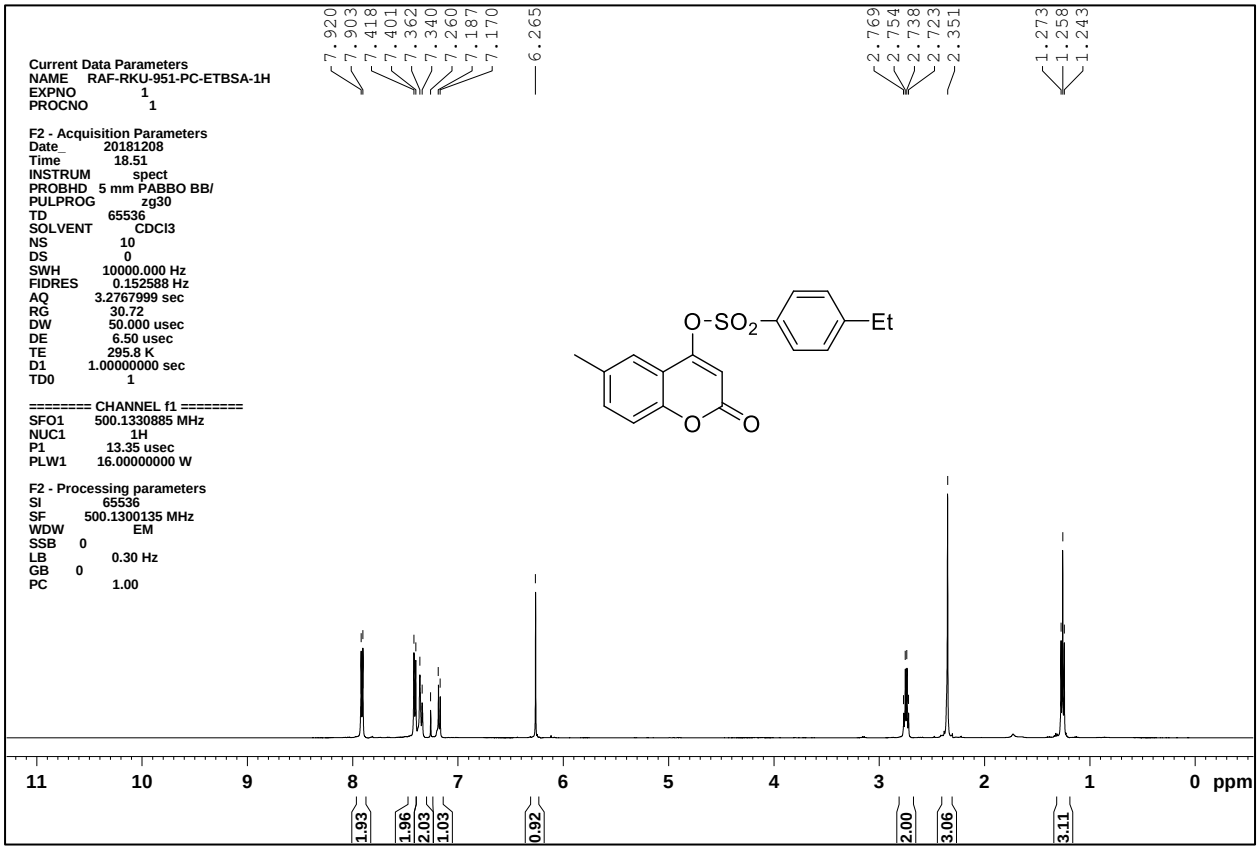

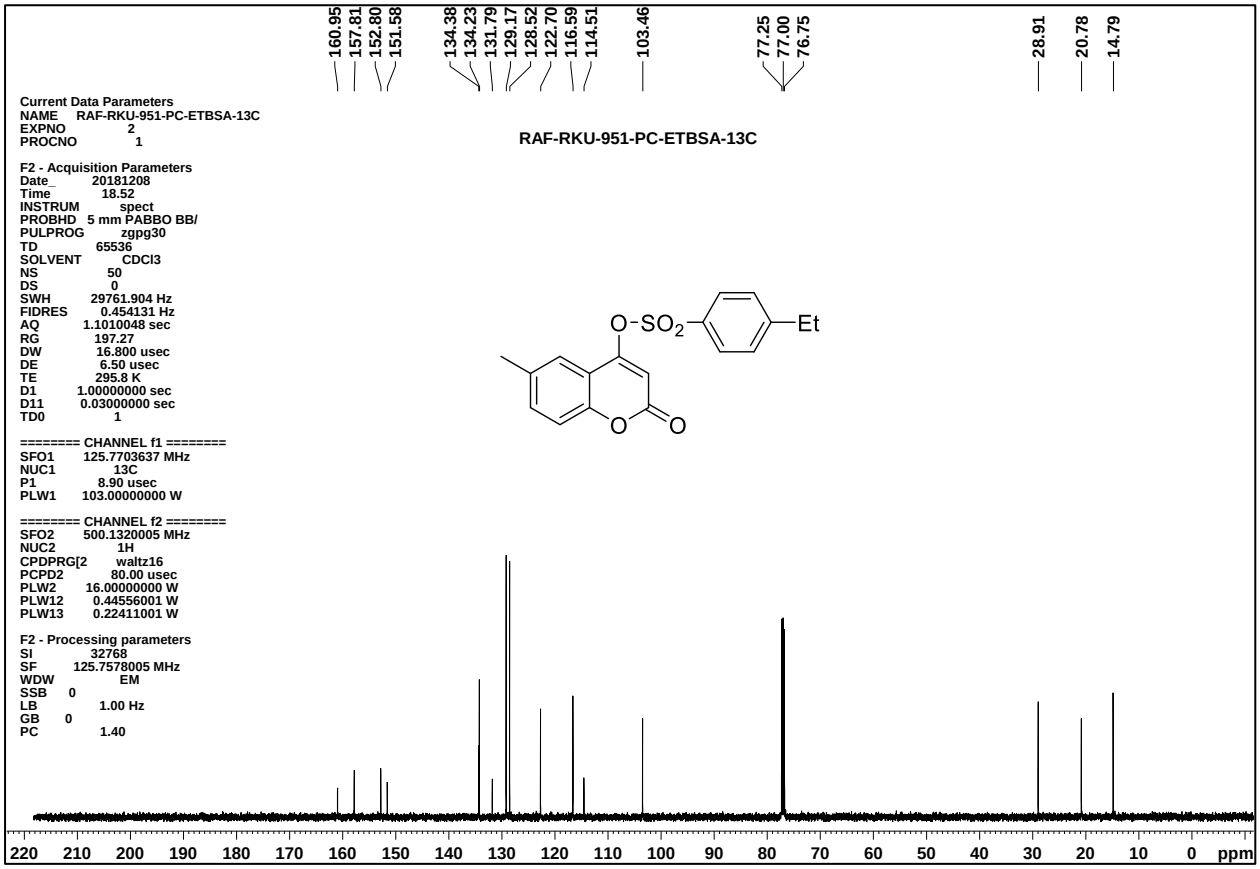

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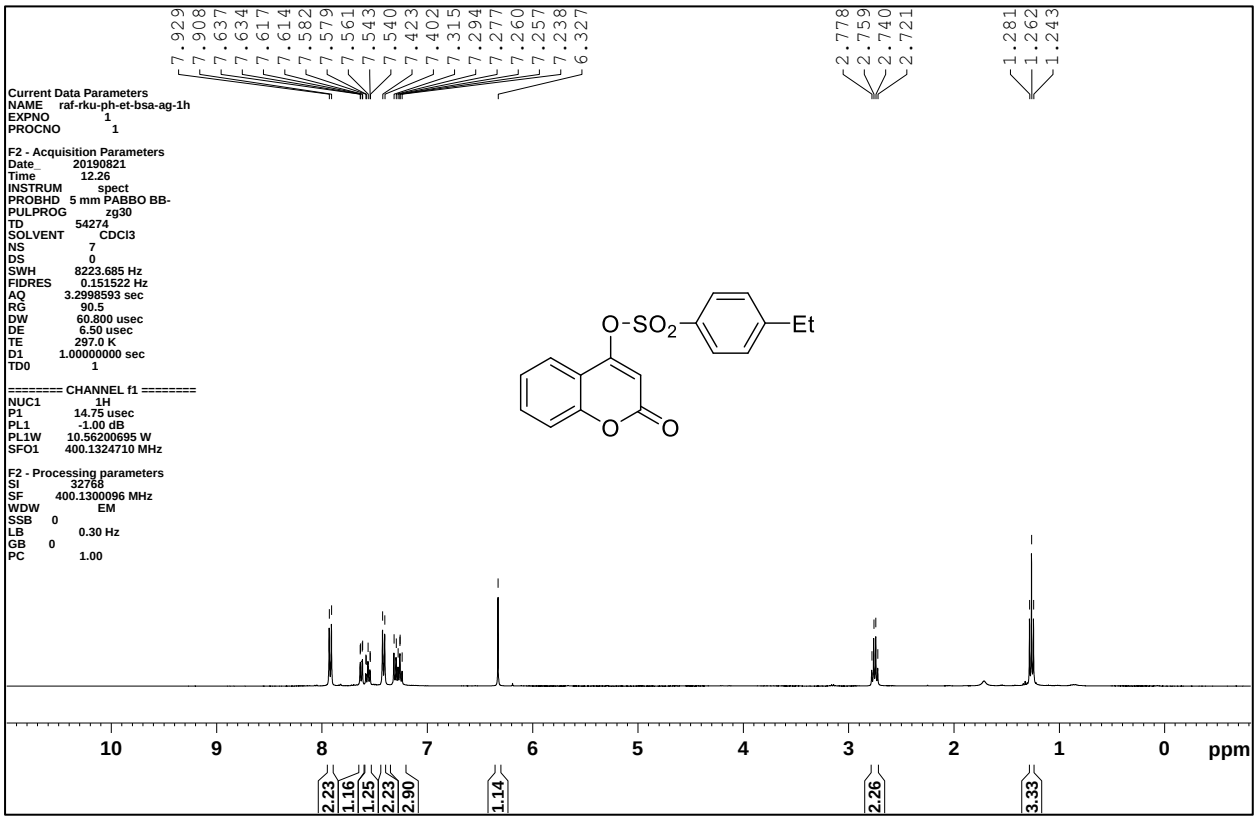

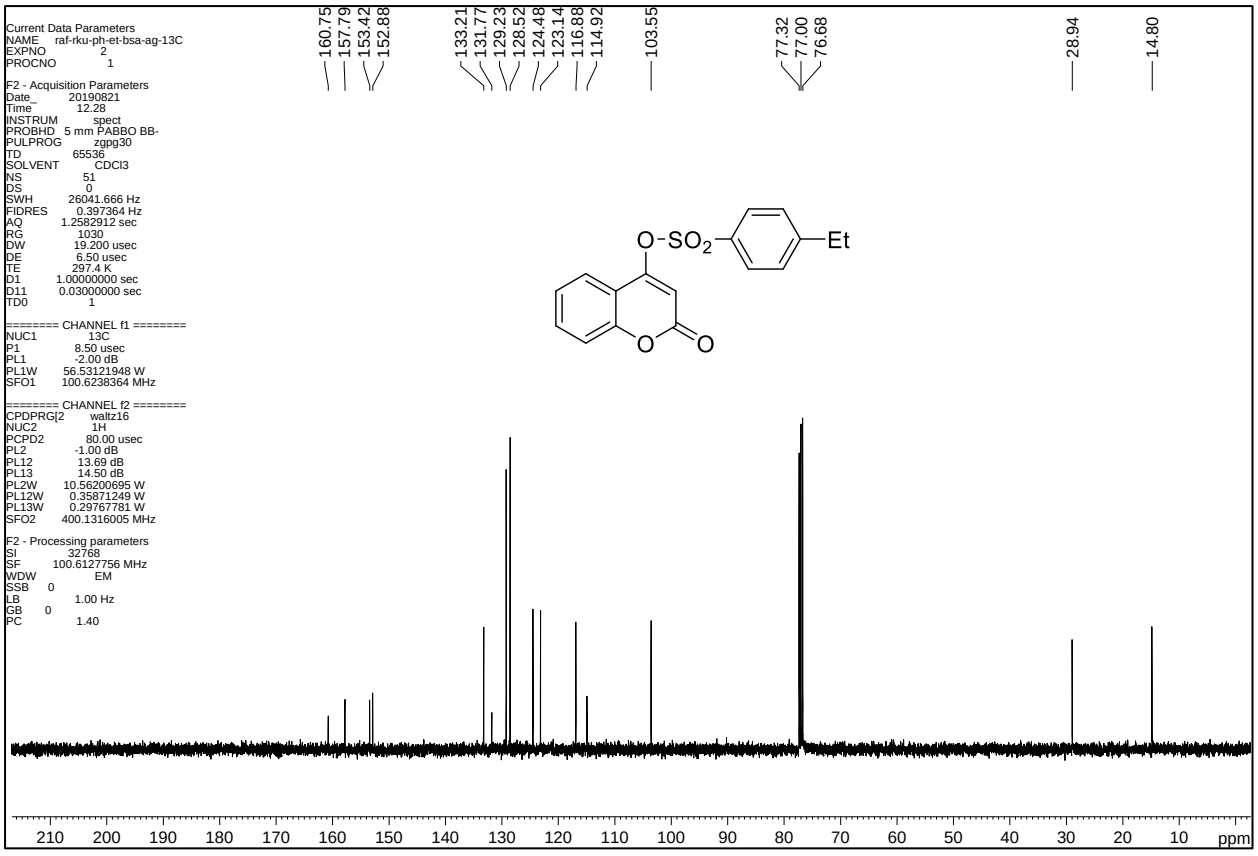

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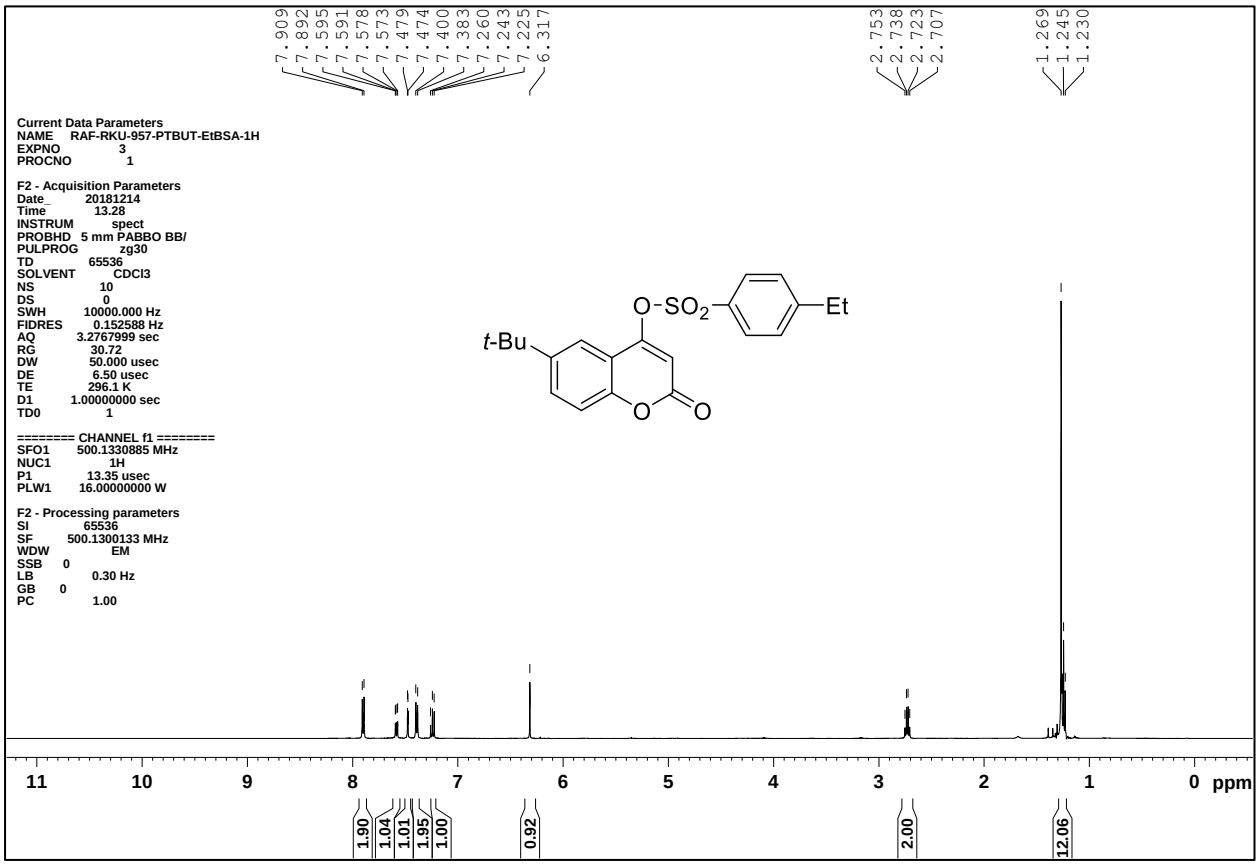

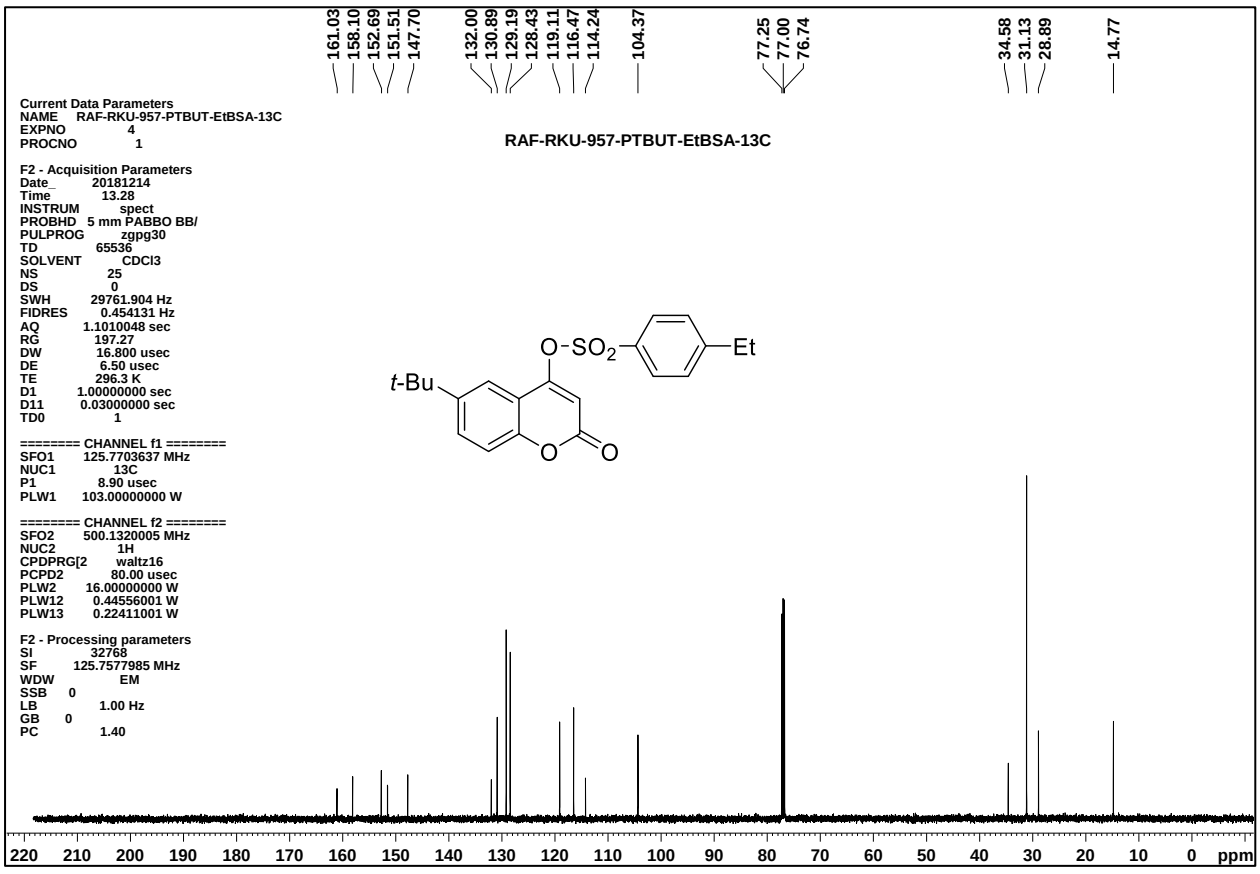

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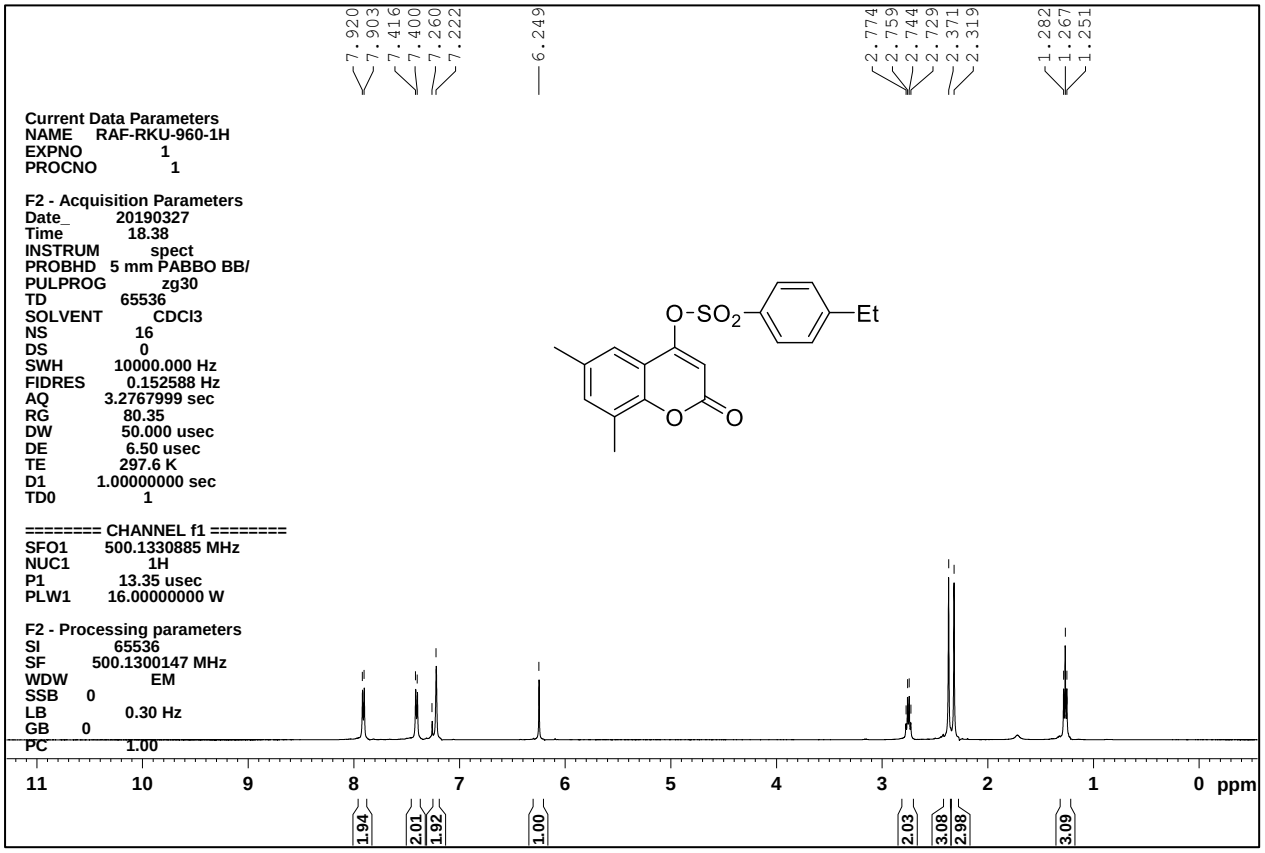

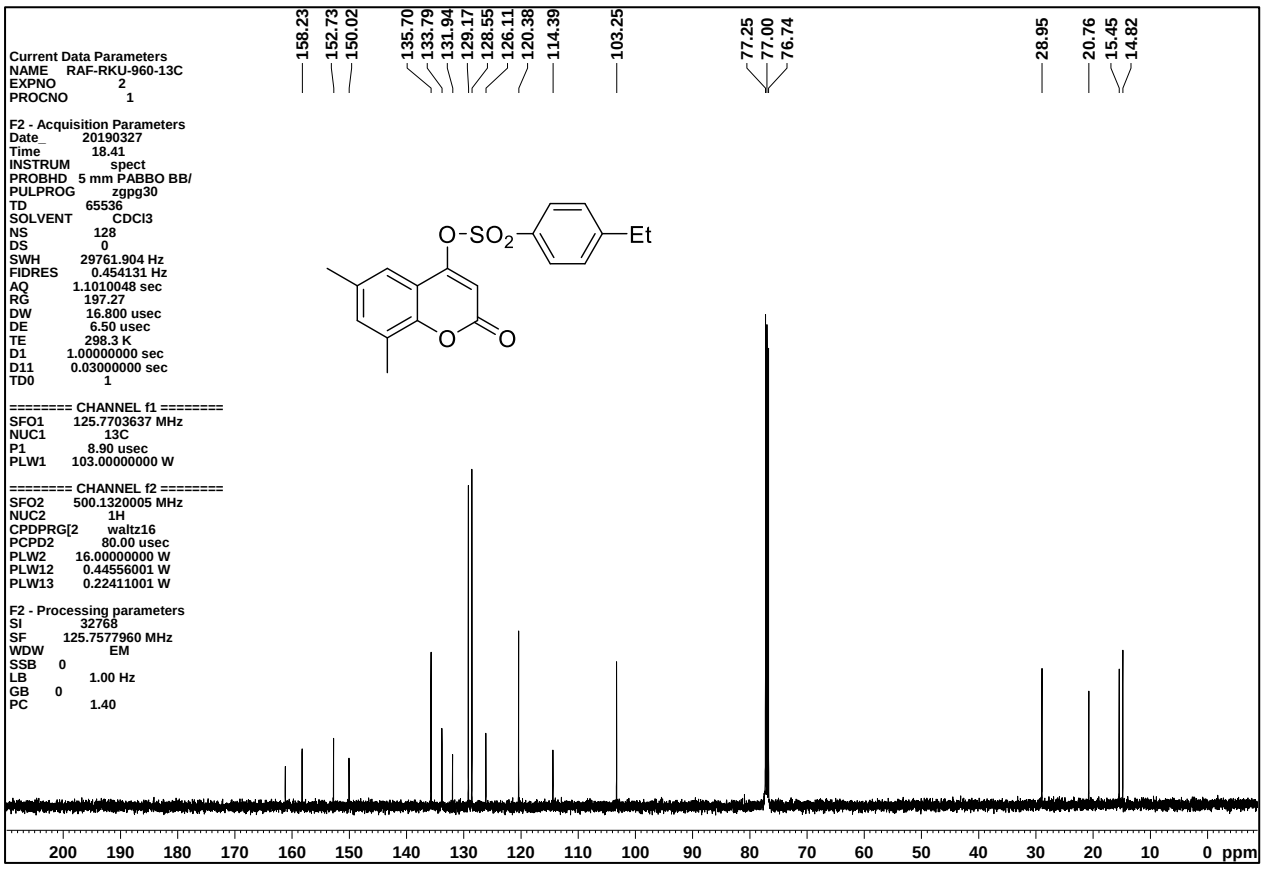

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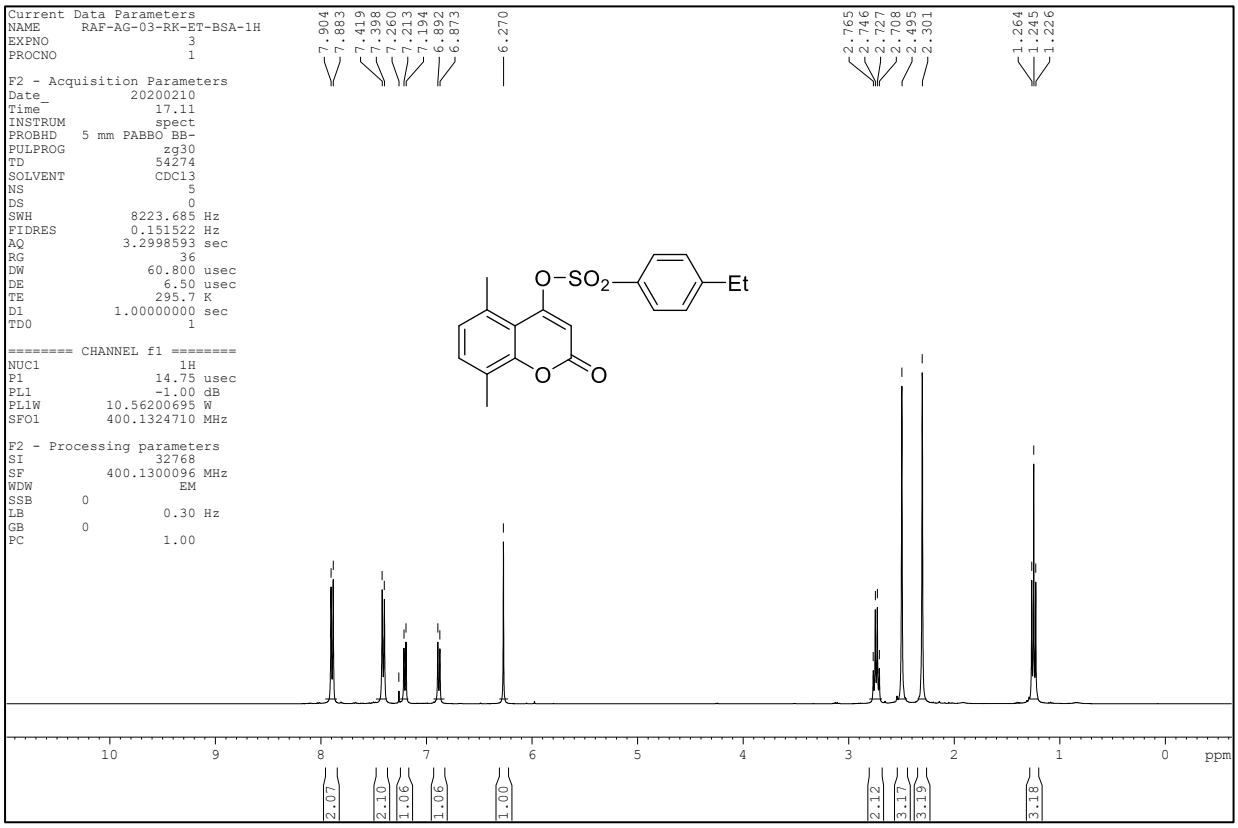

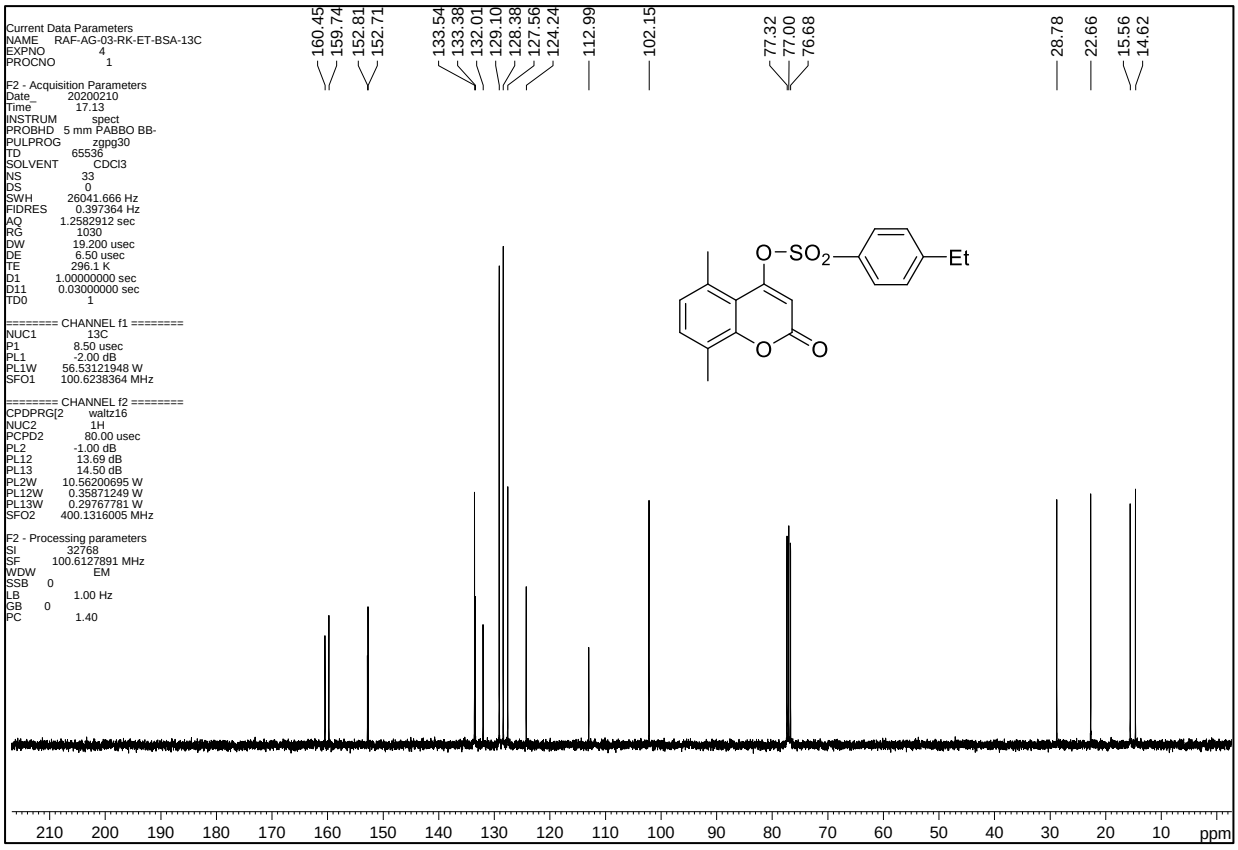

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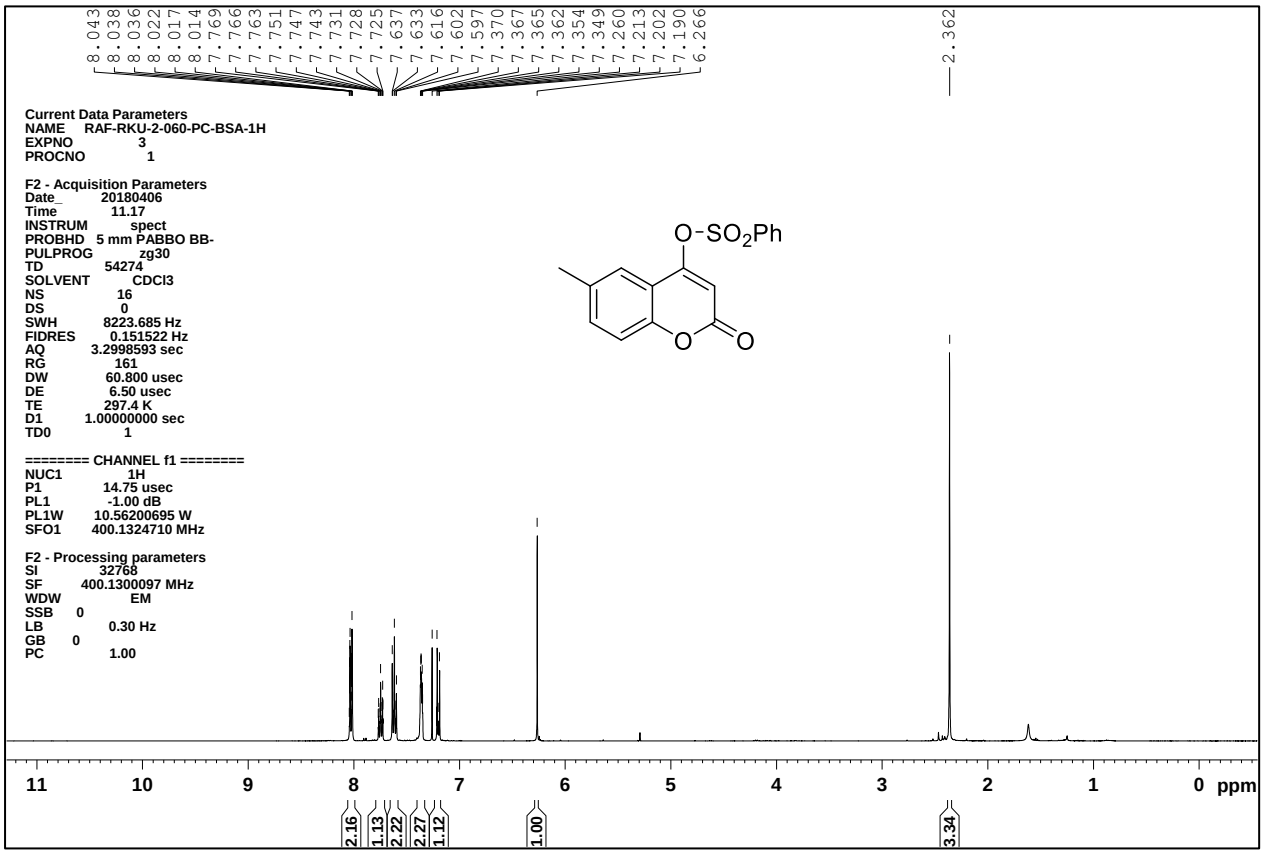

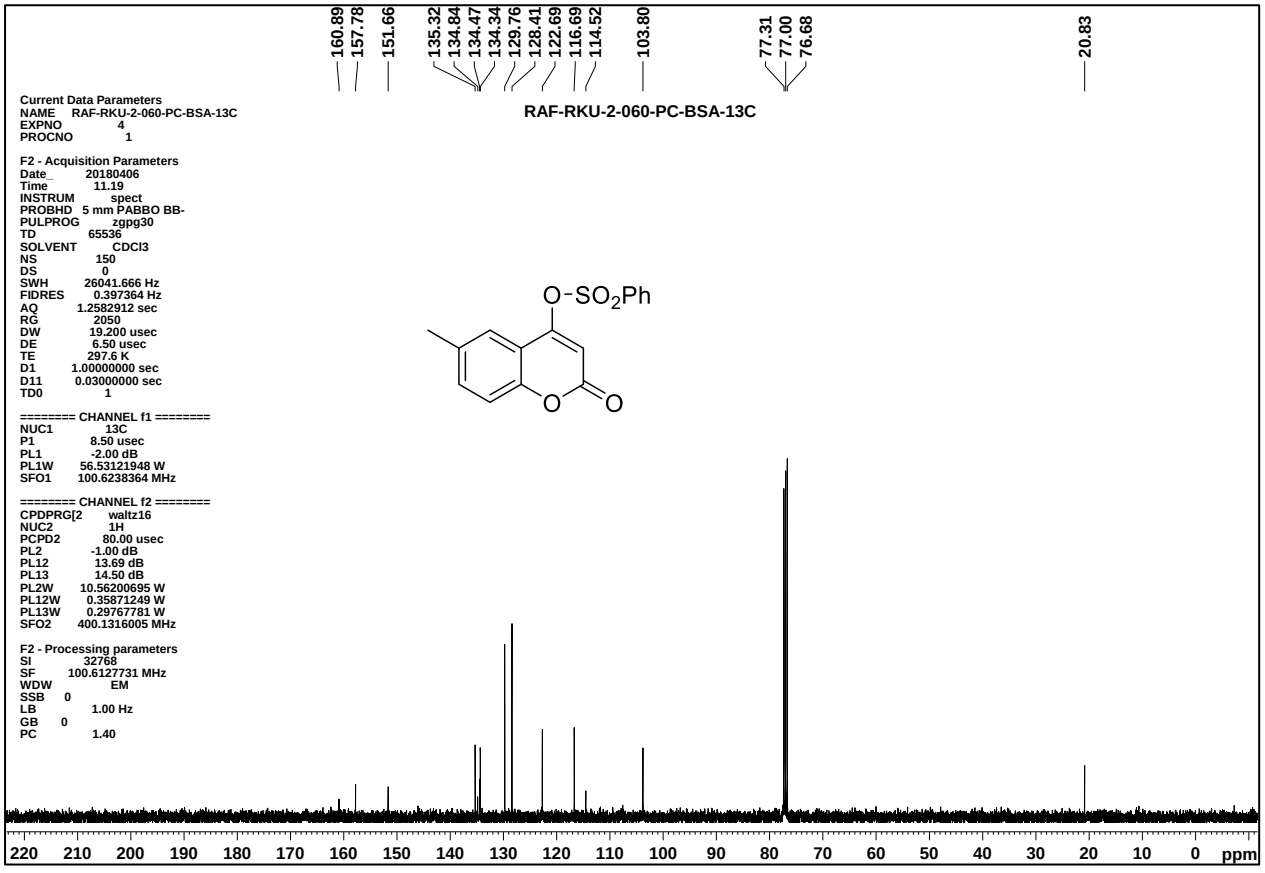

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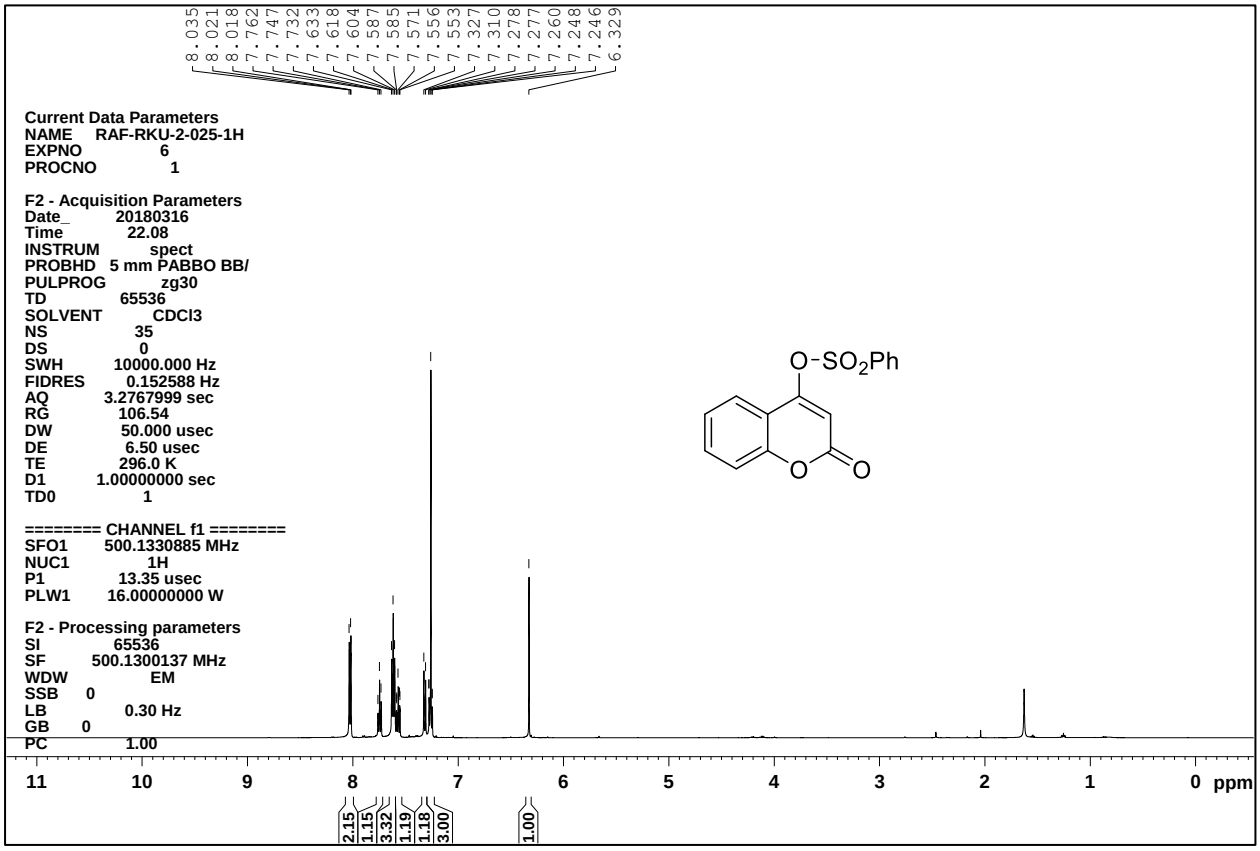

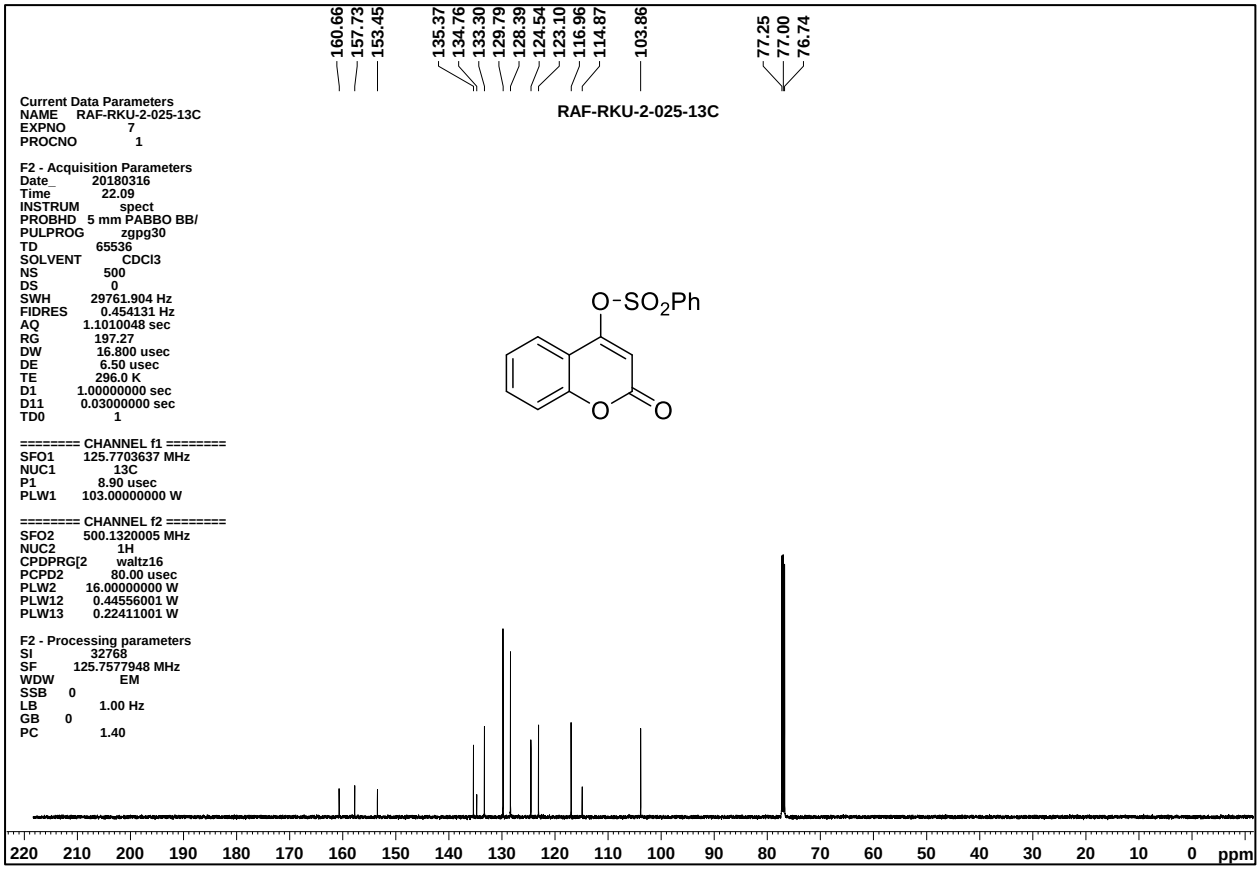

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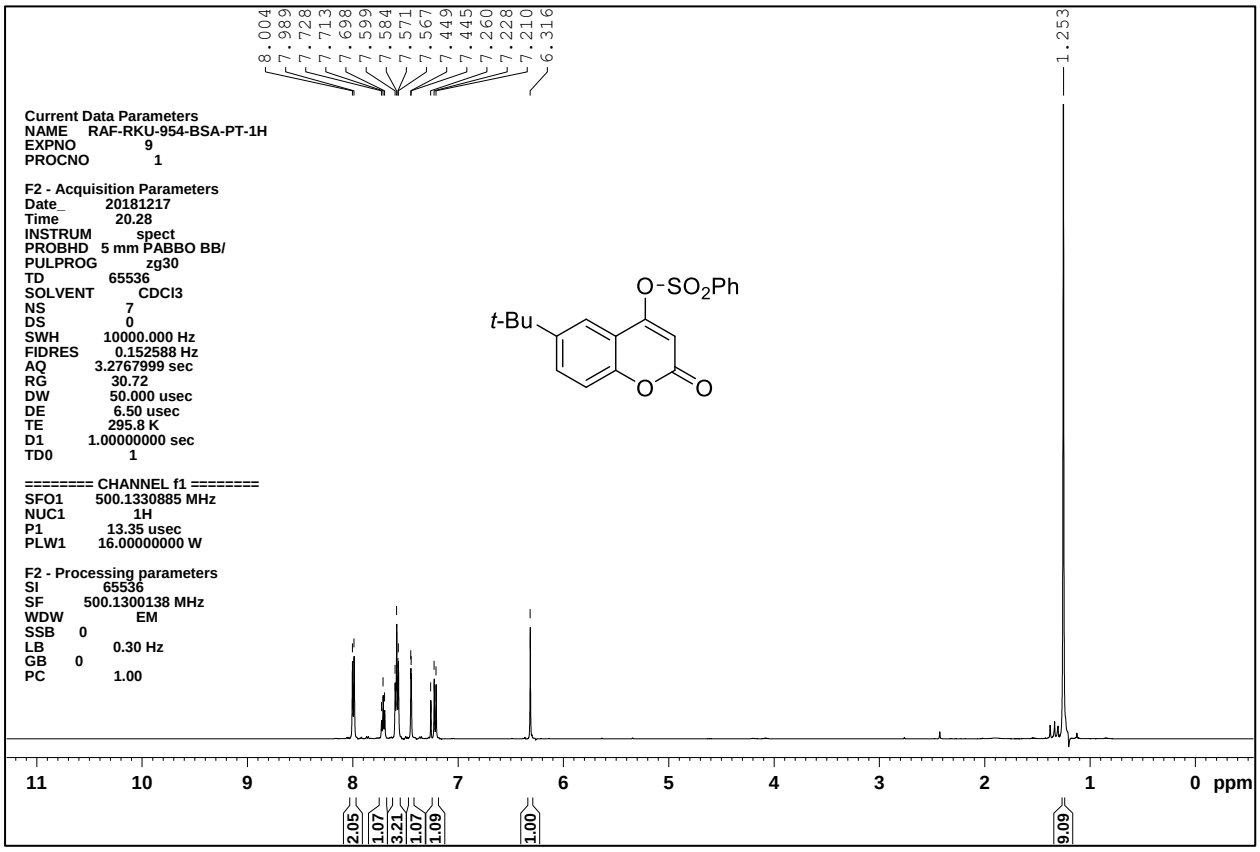

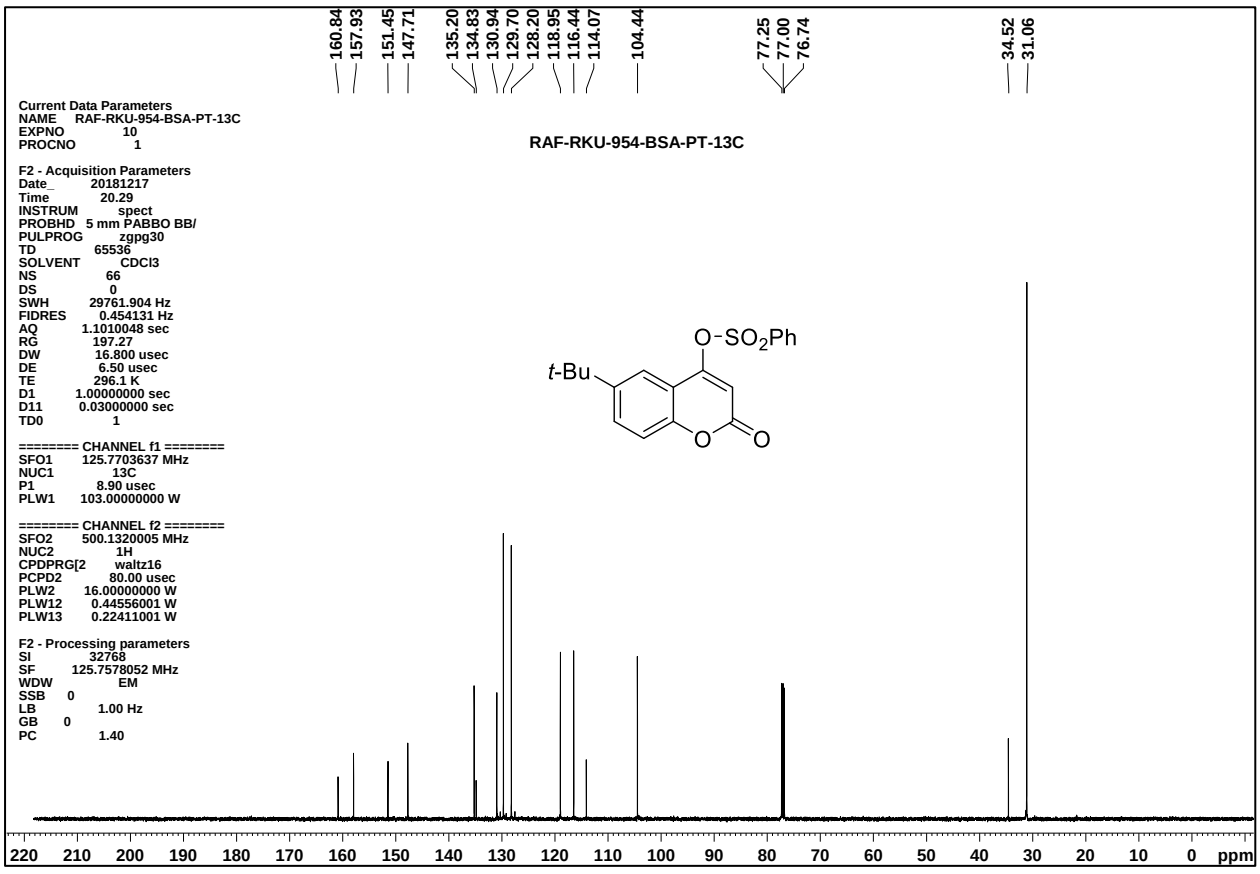

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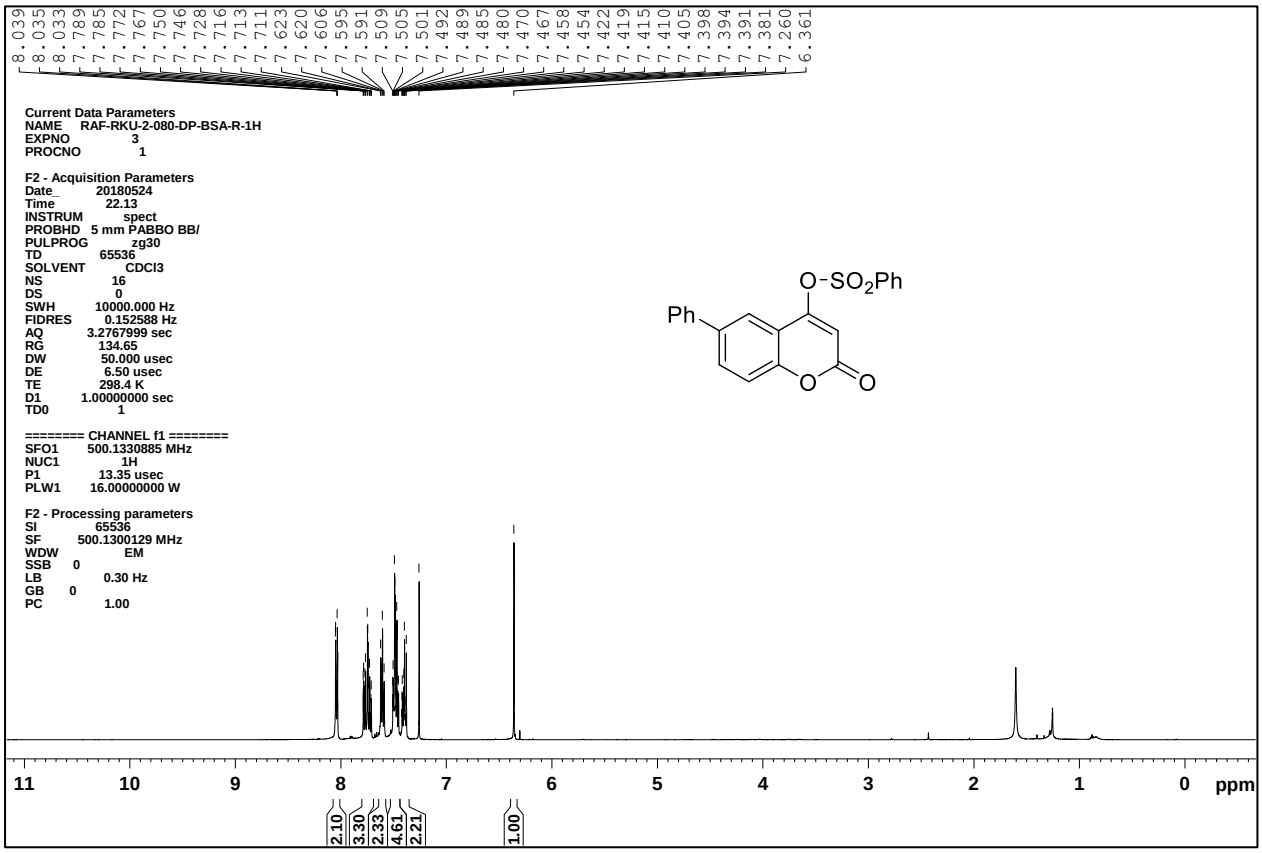

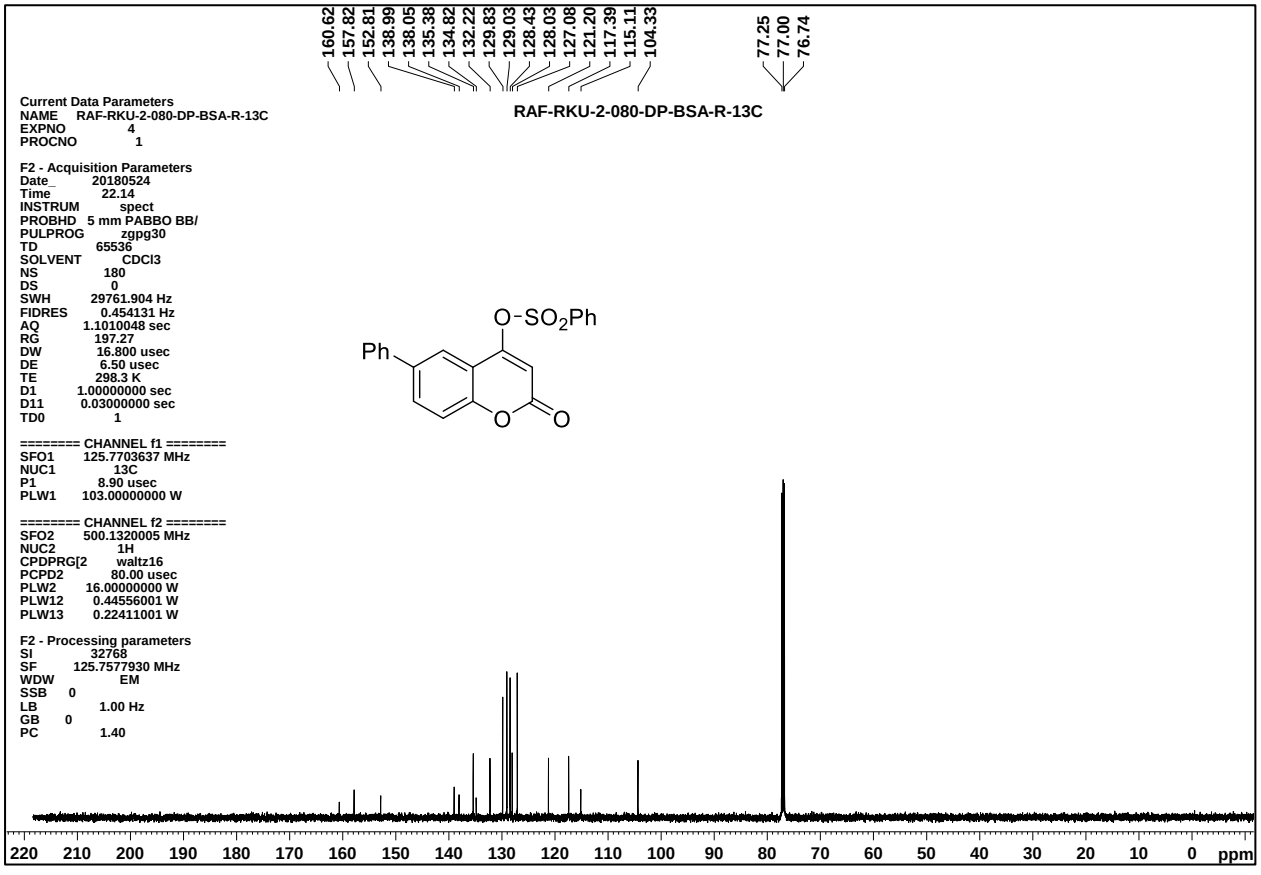

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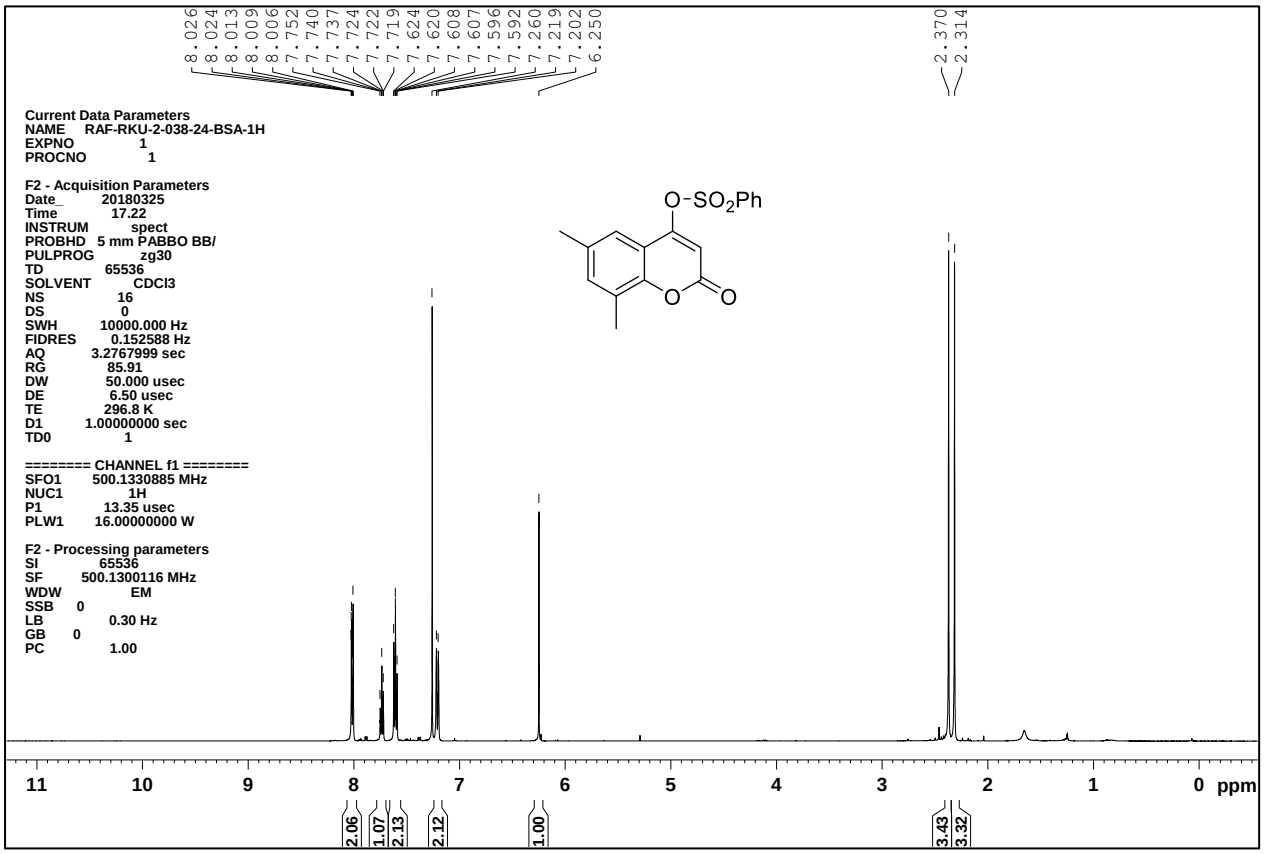

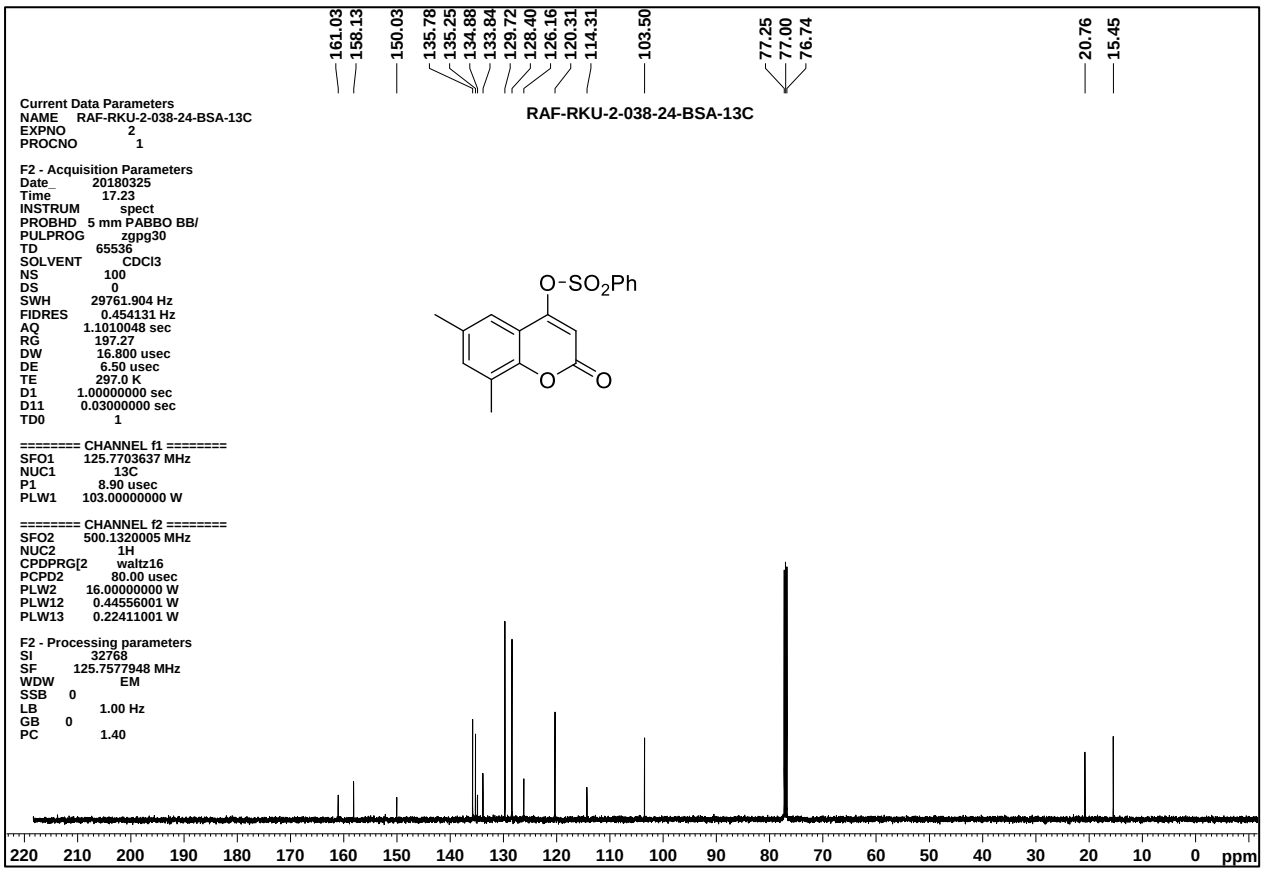

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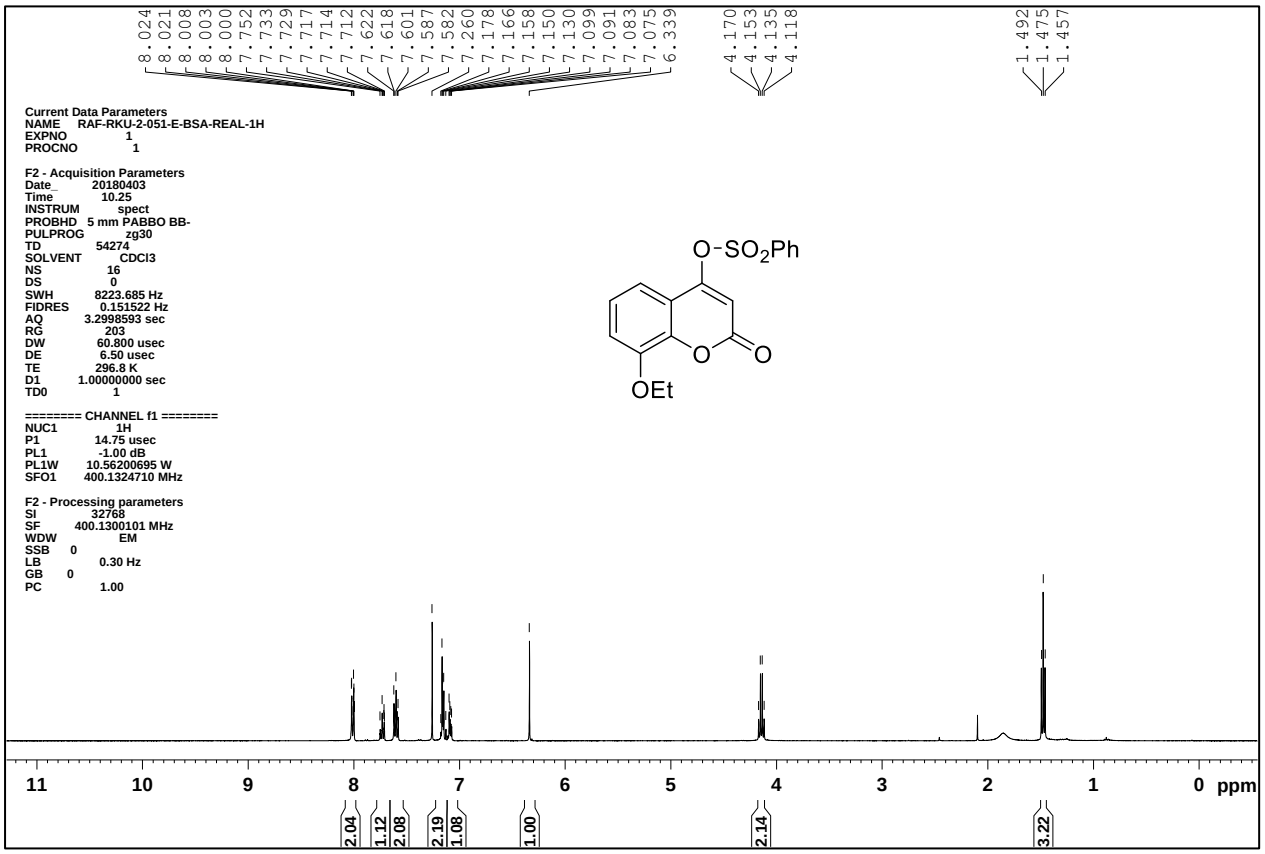

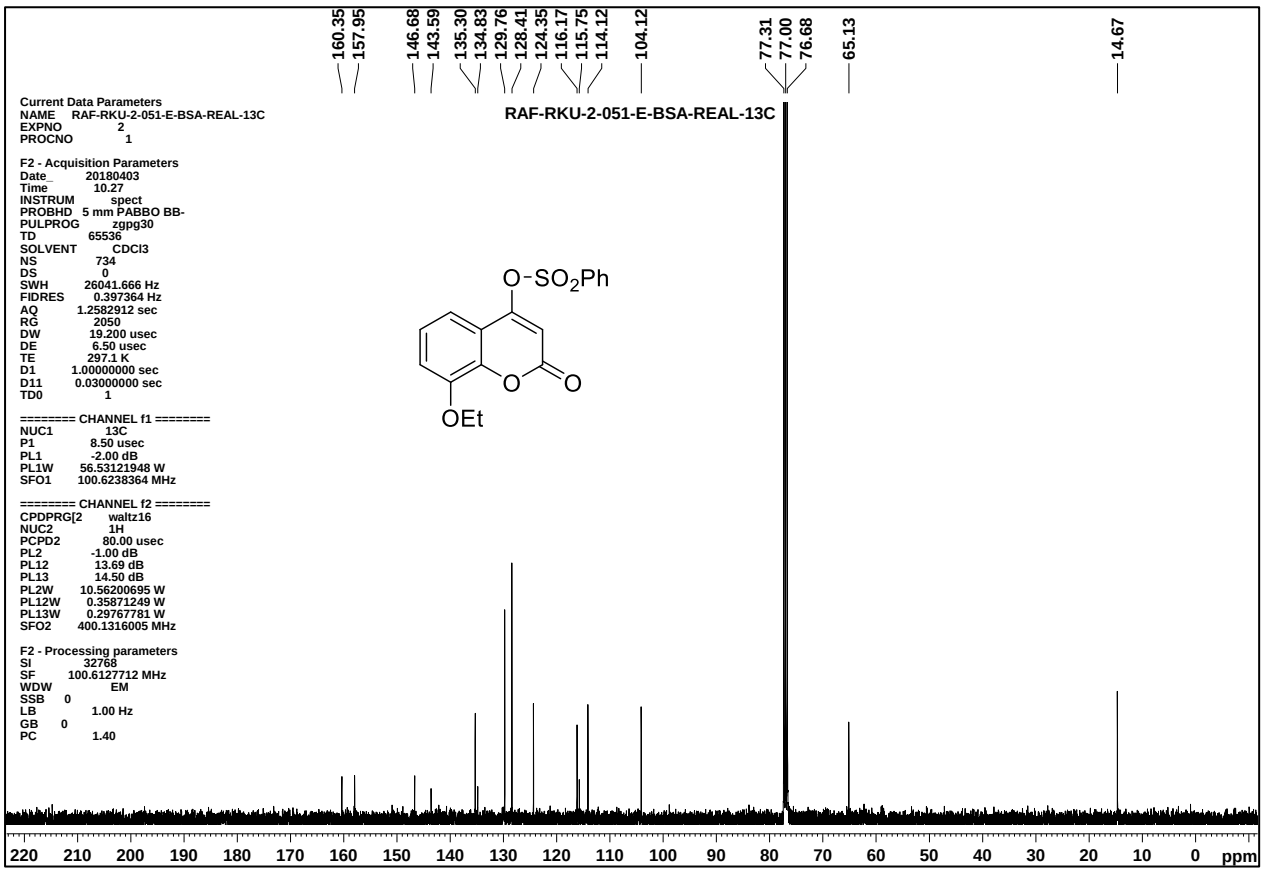

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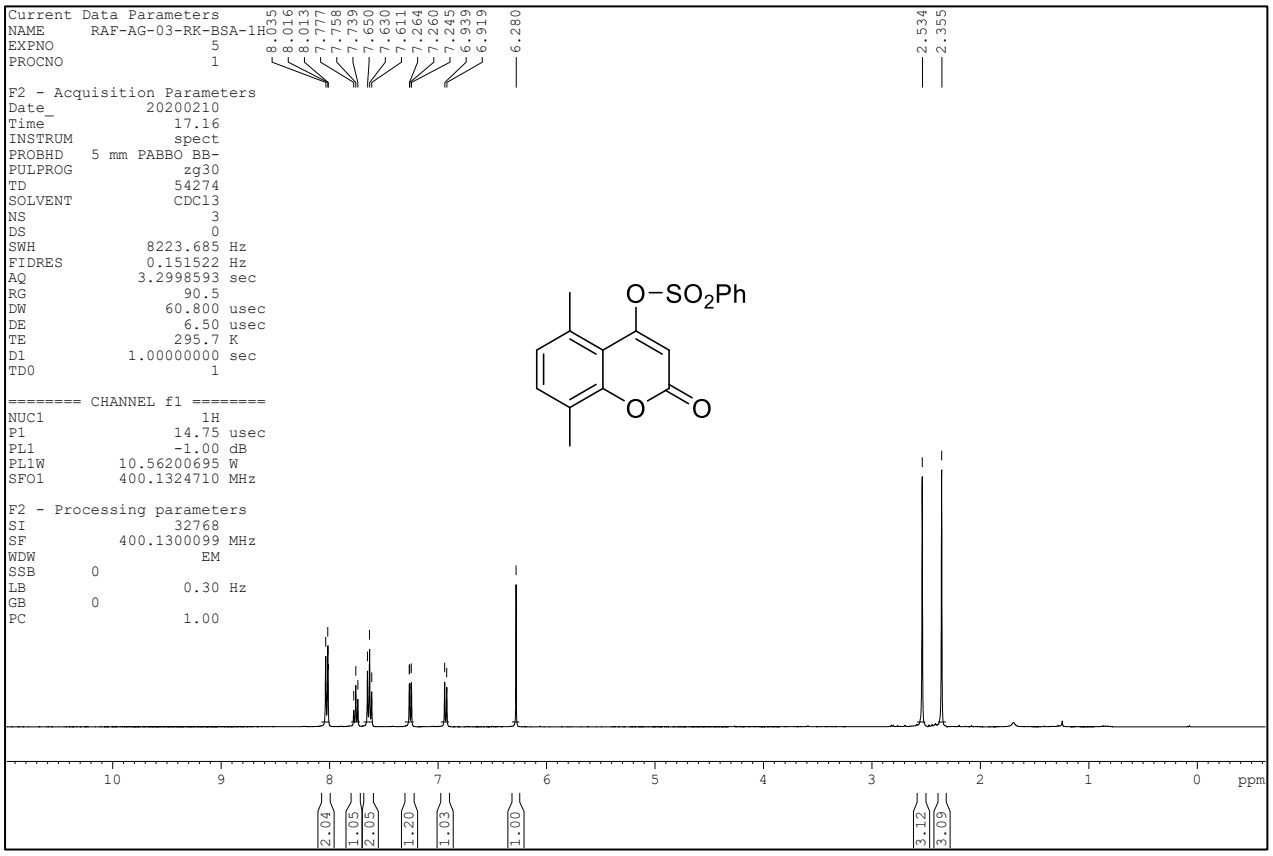
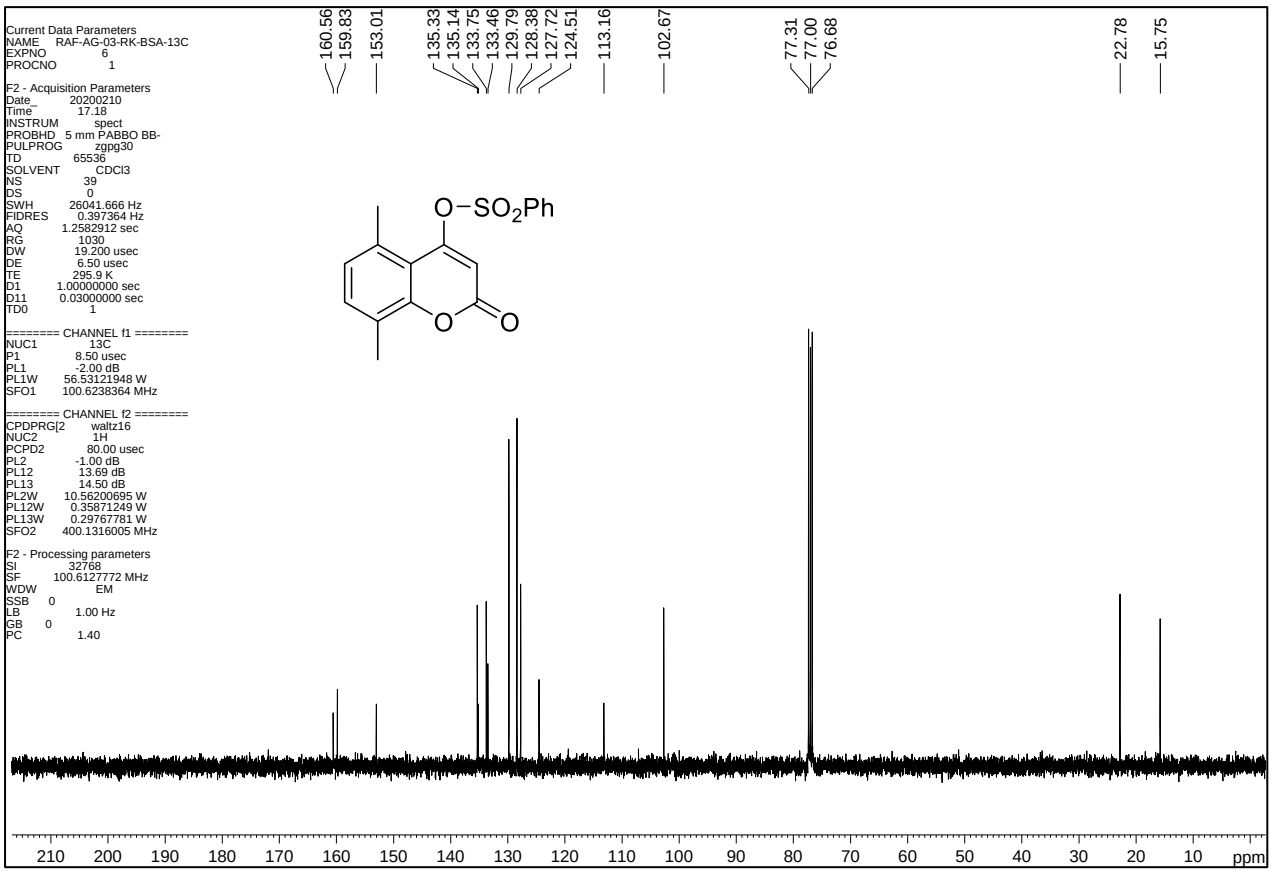
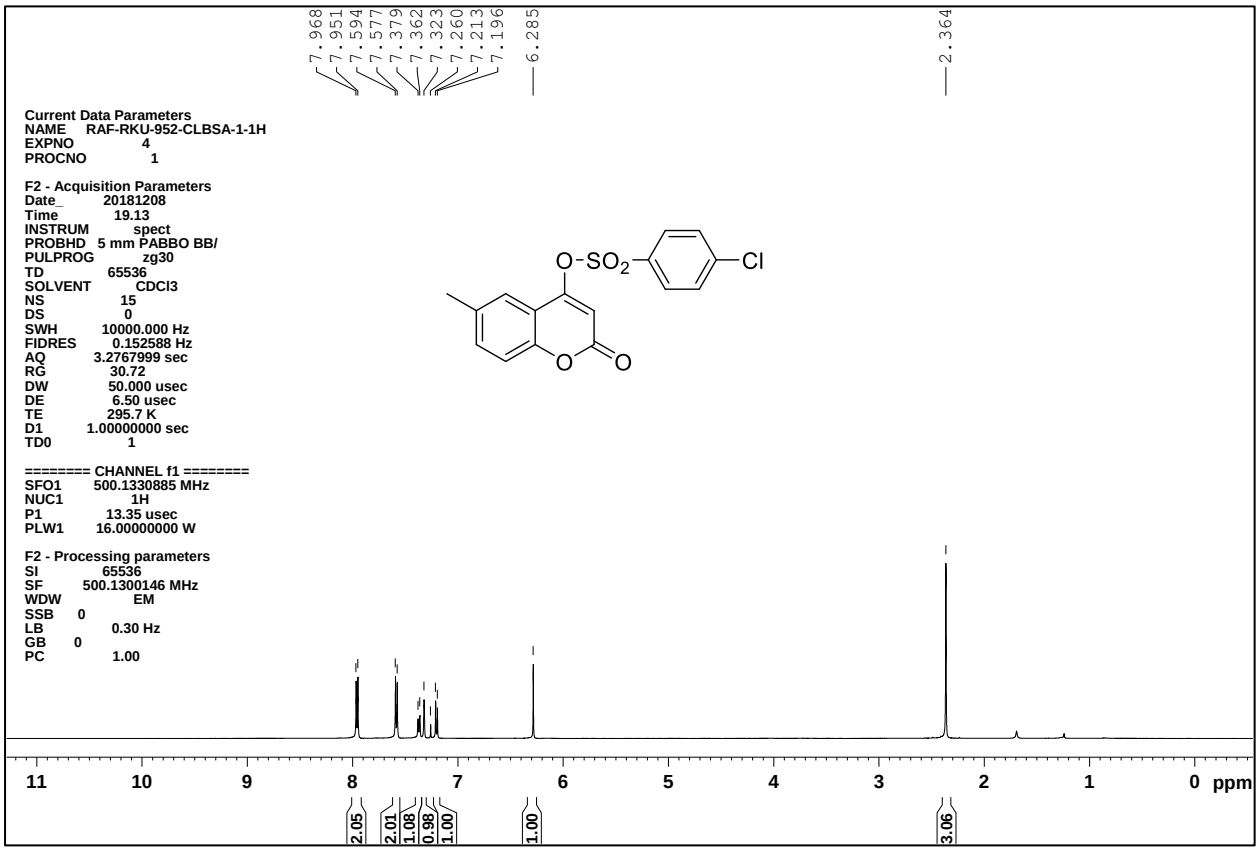
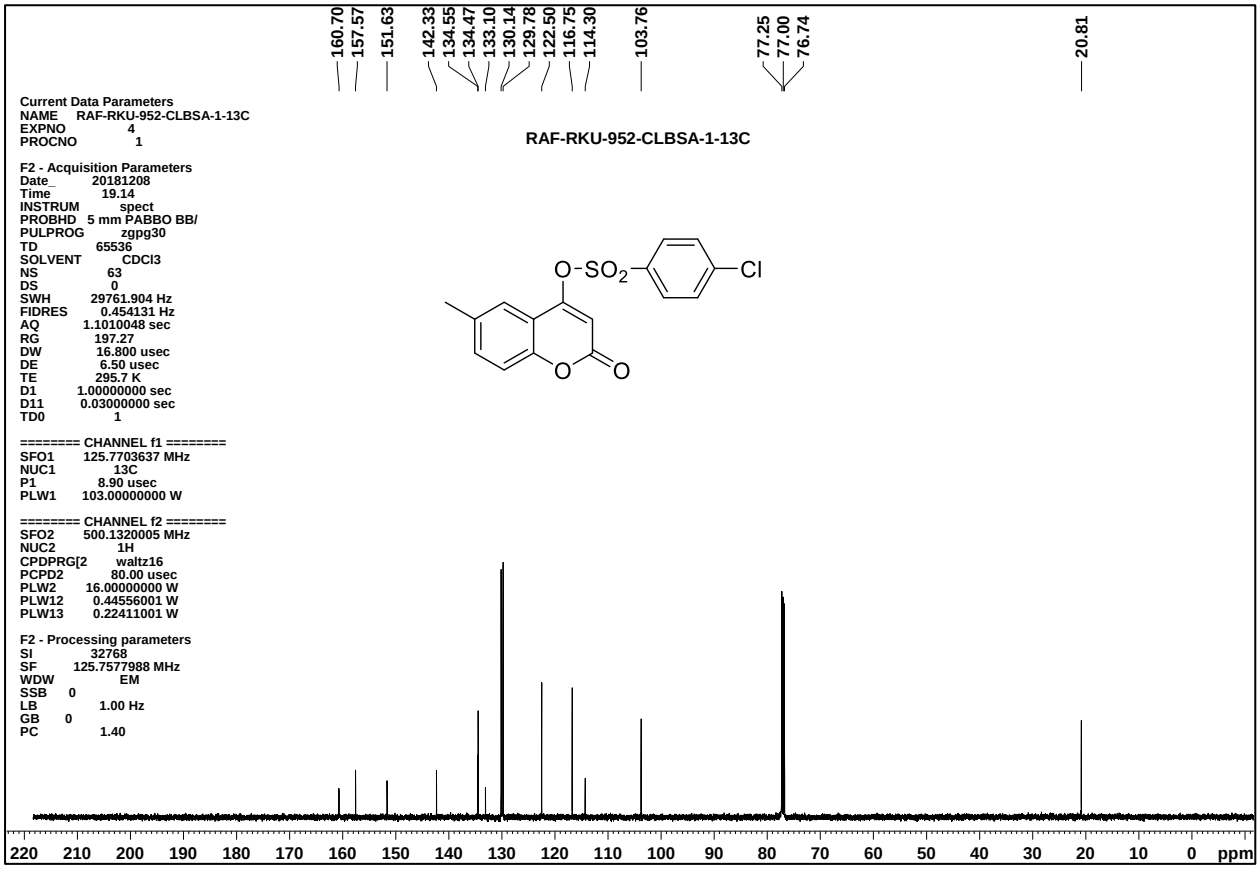


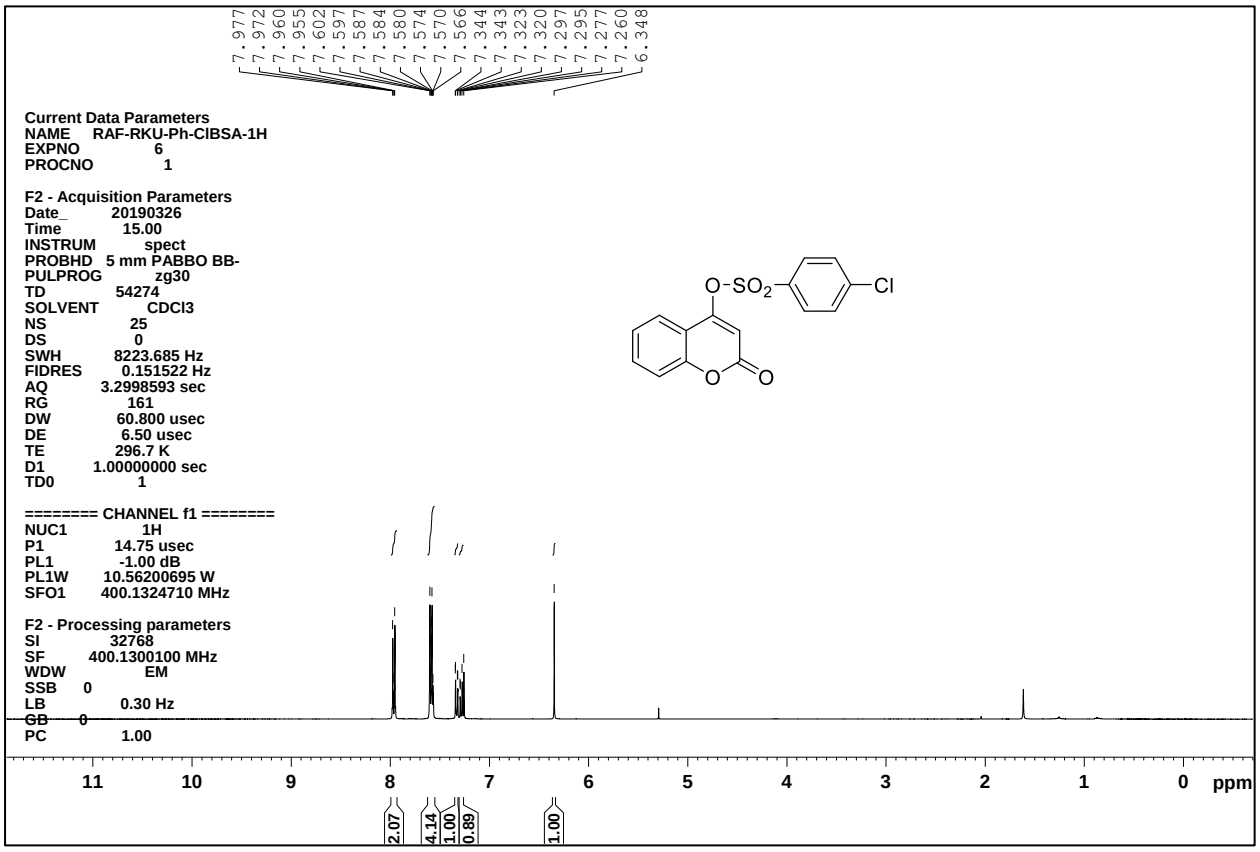


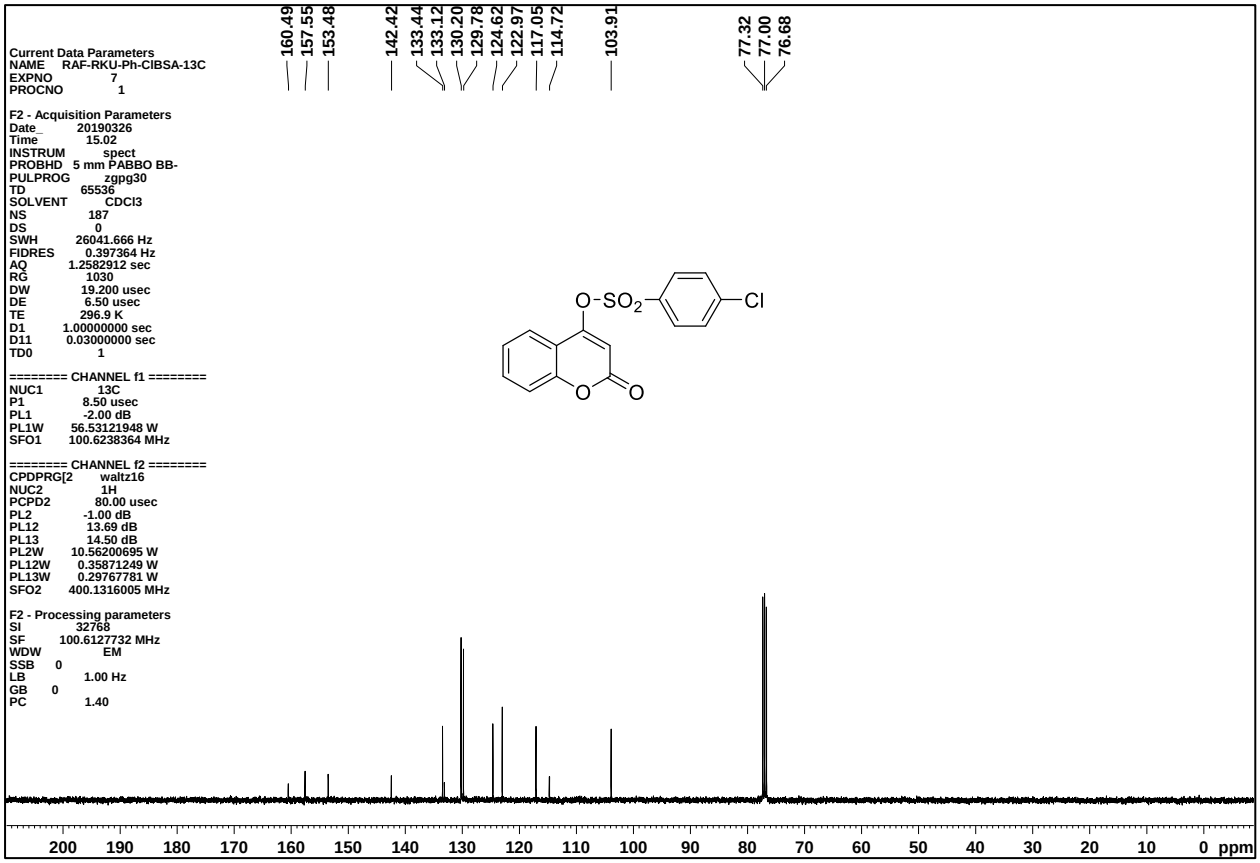
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **9a**



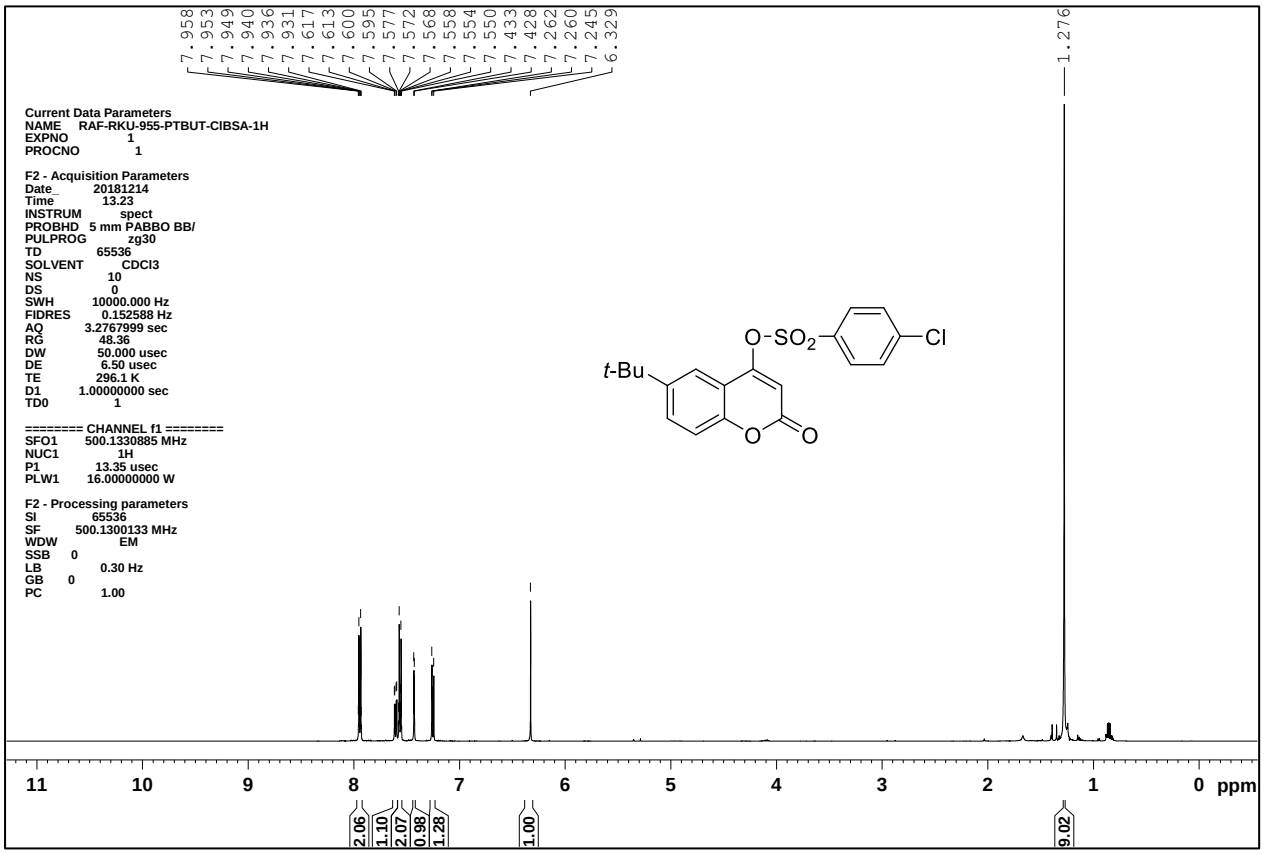


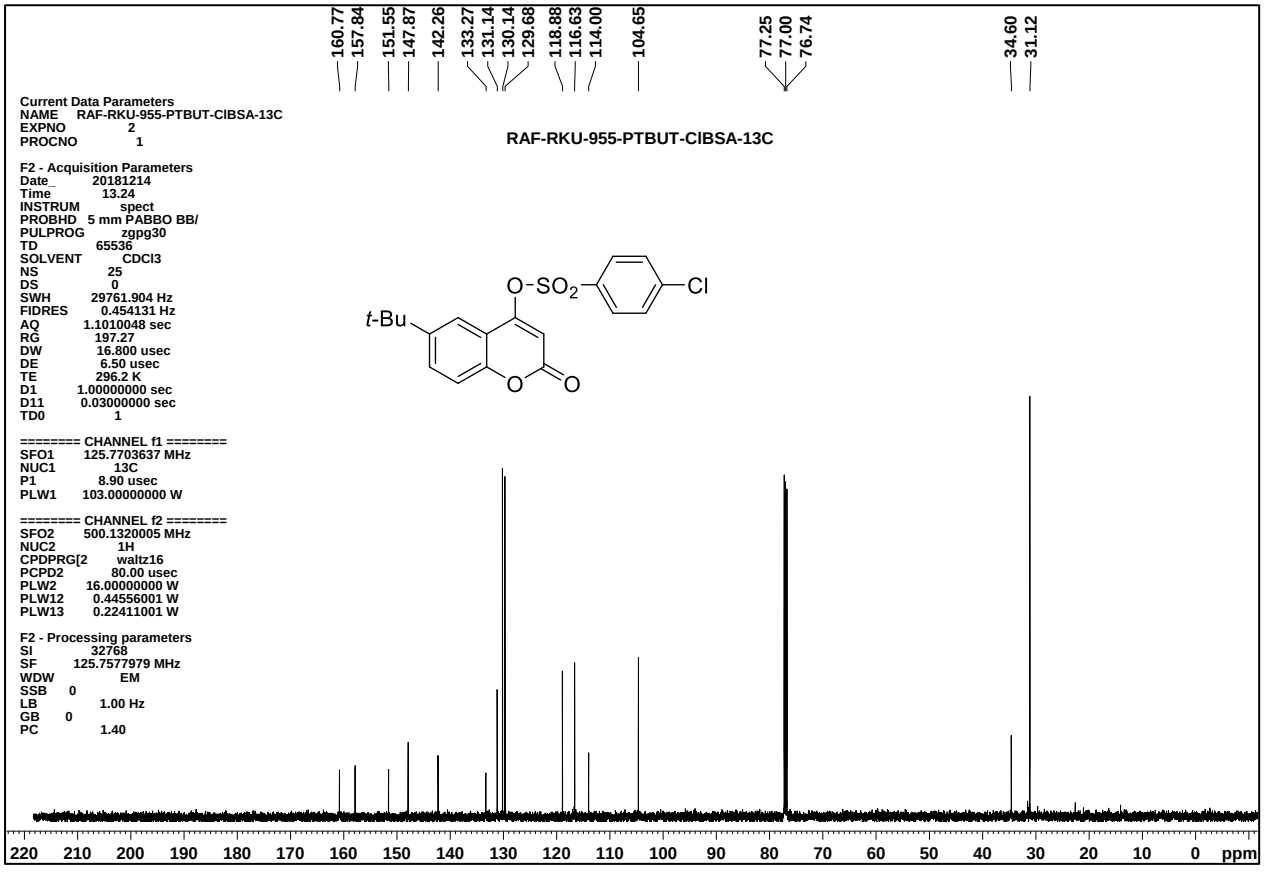
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **9b**



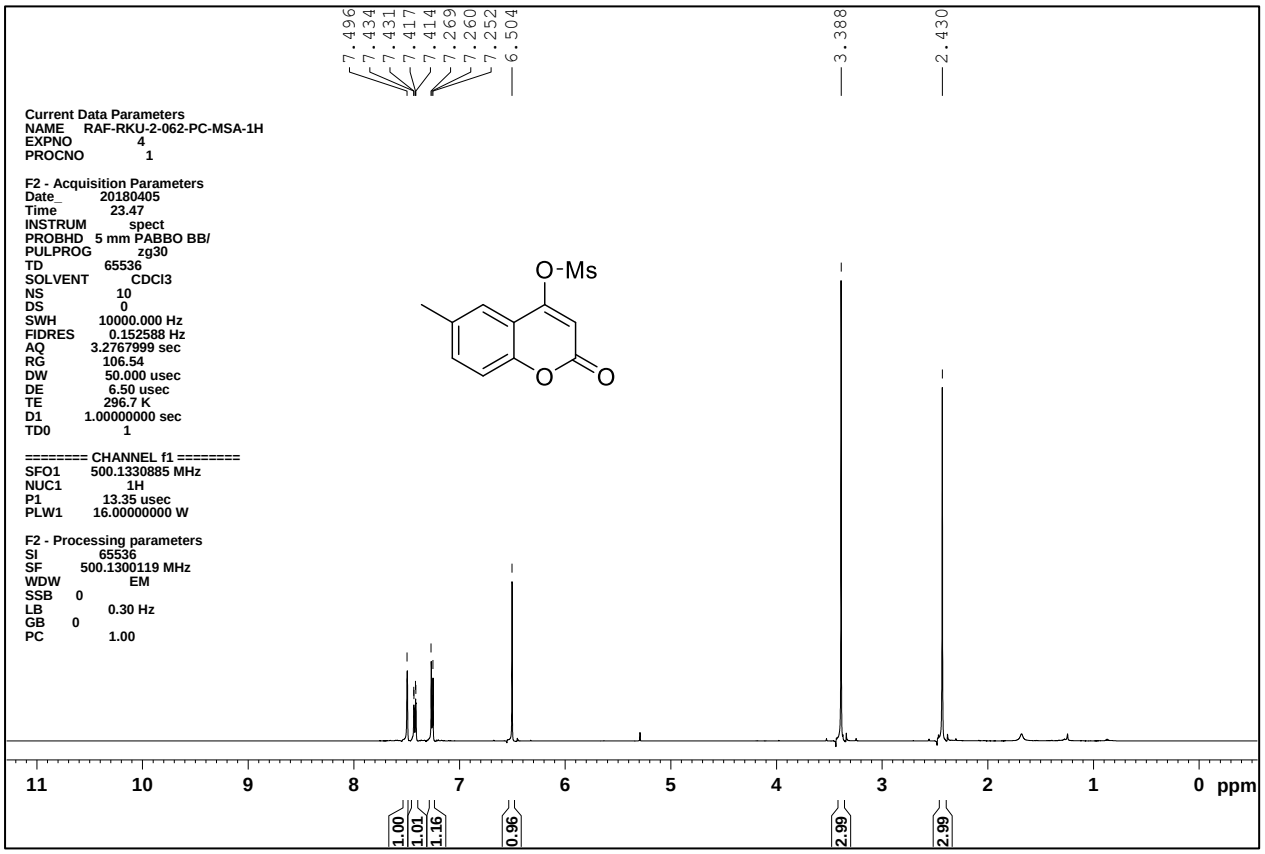


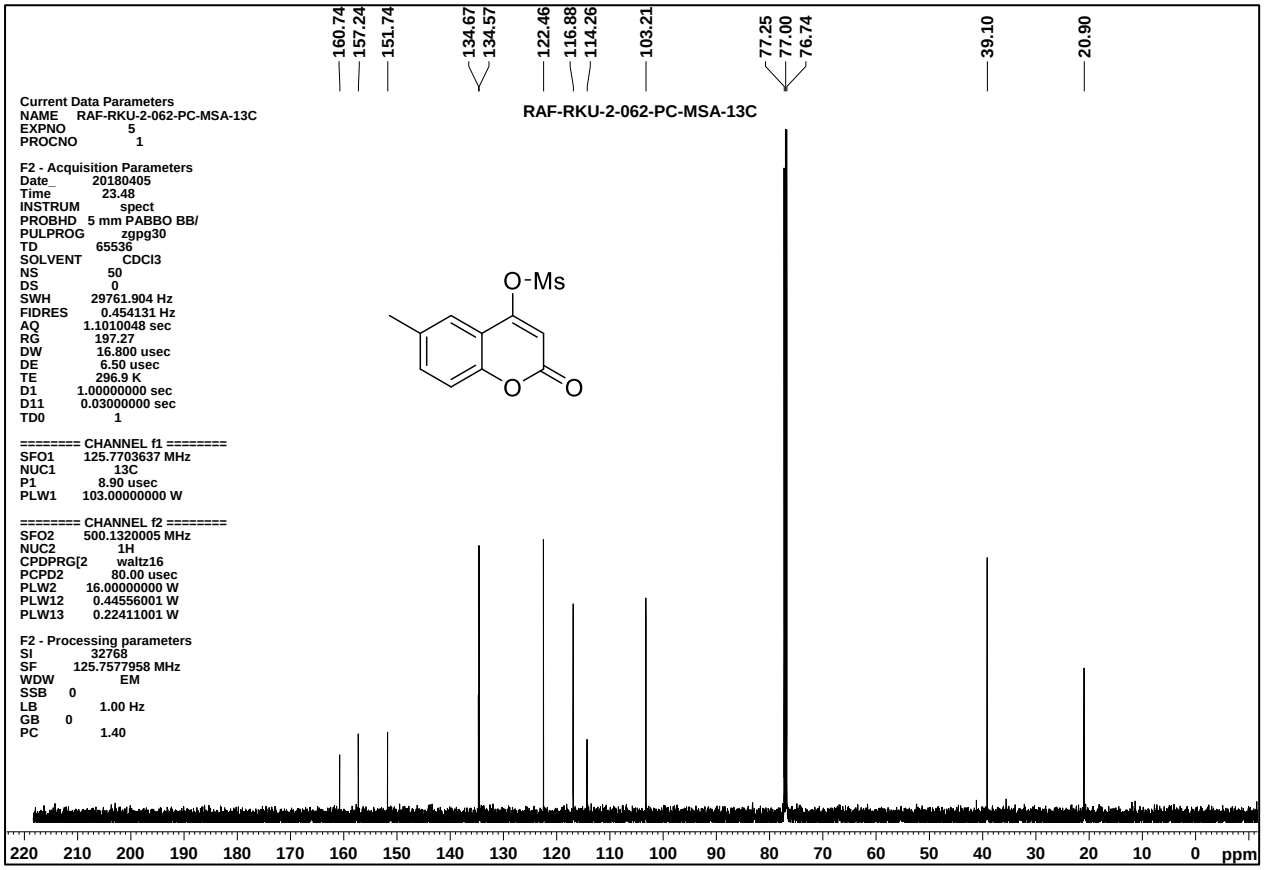
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **9c**



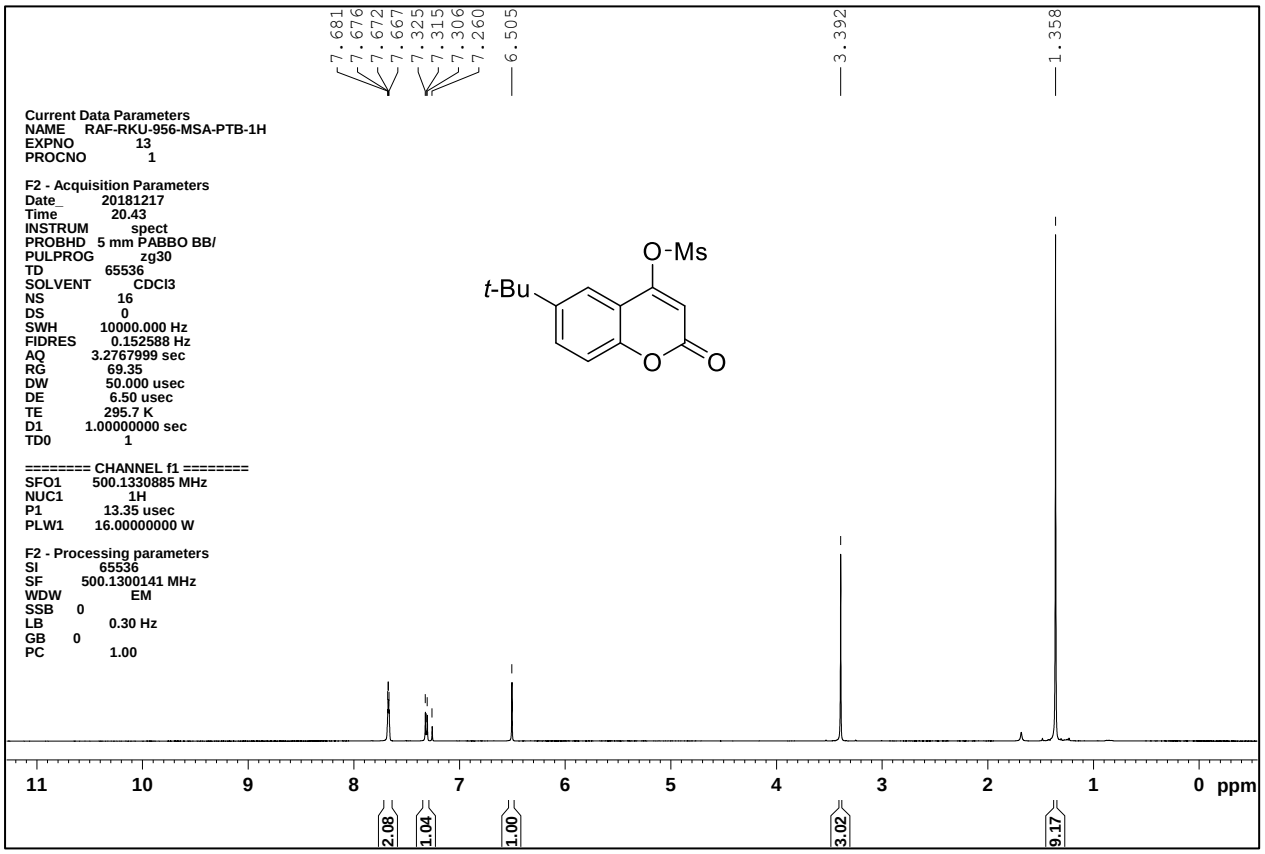


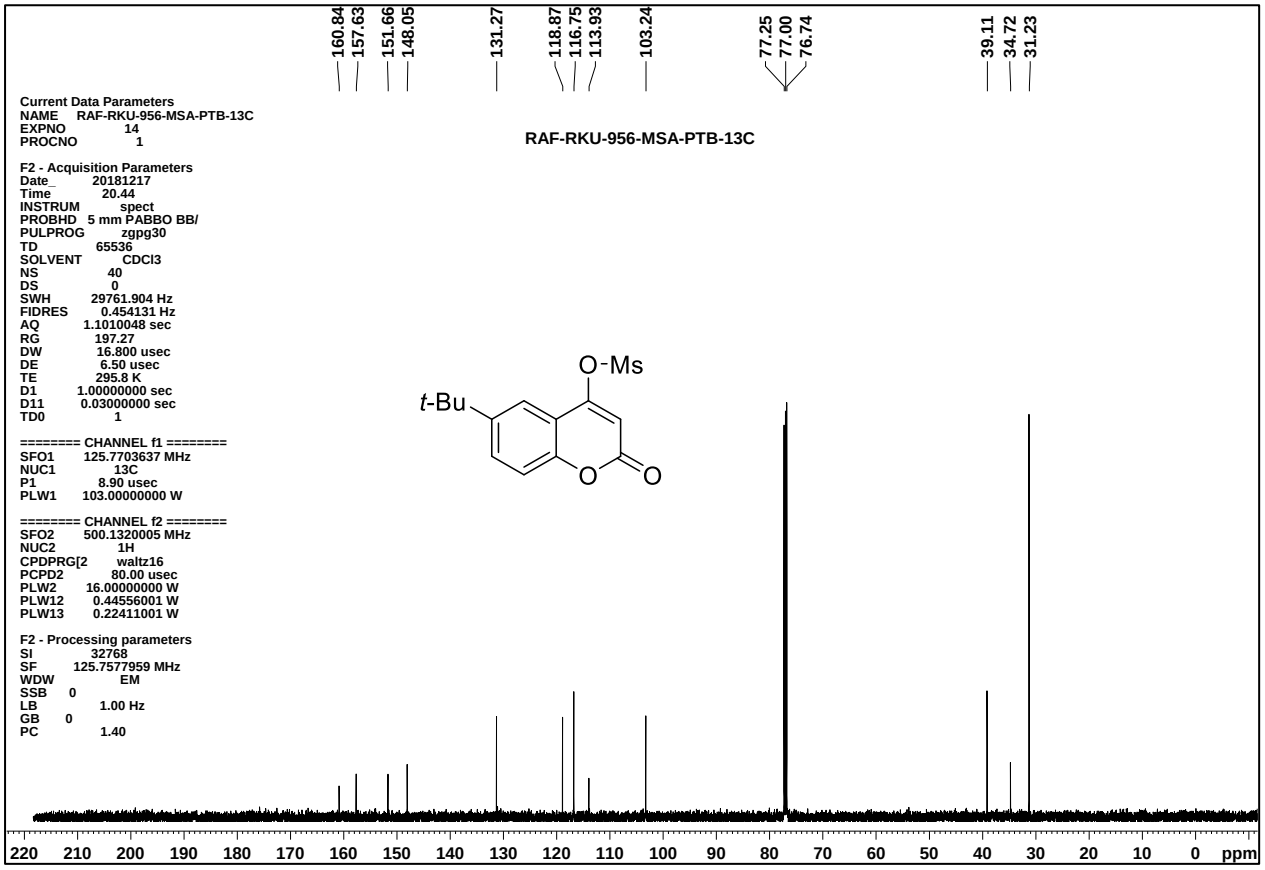
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **10a**



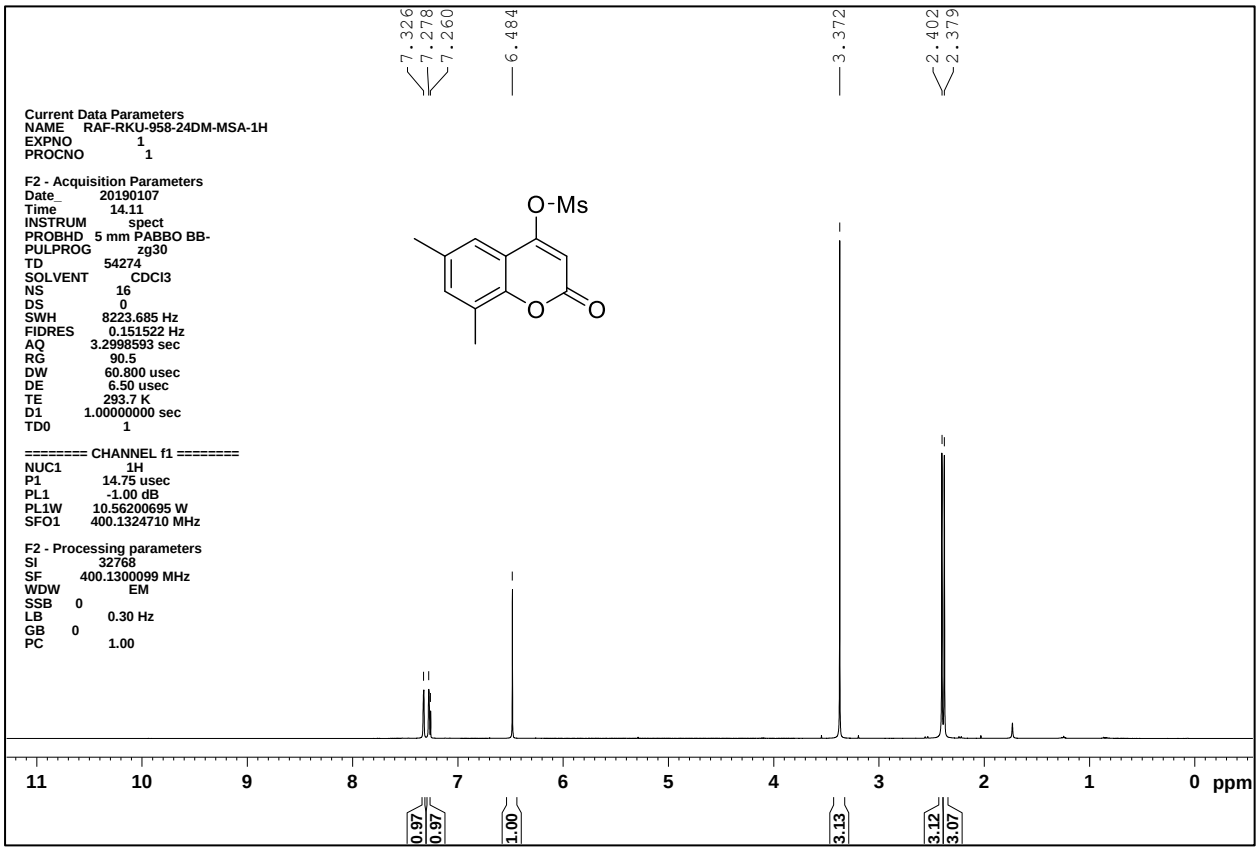


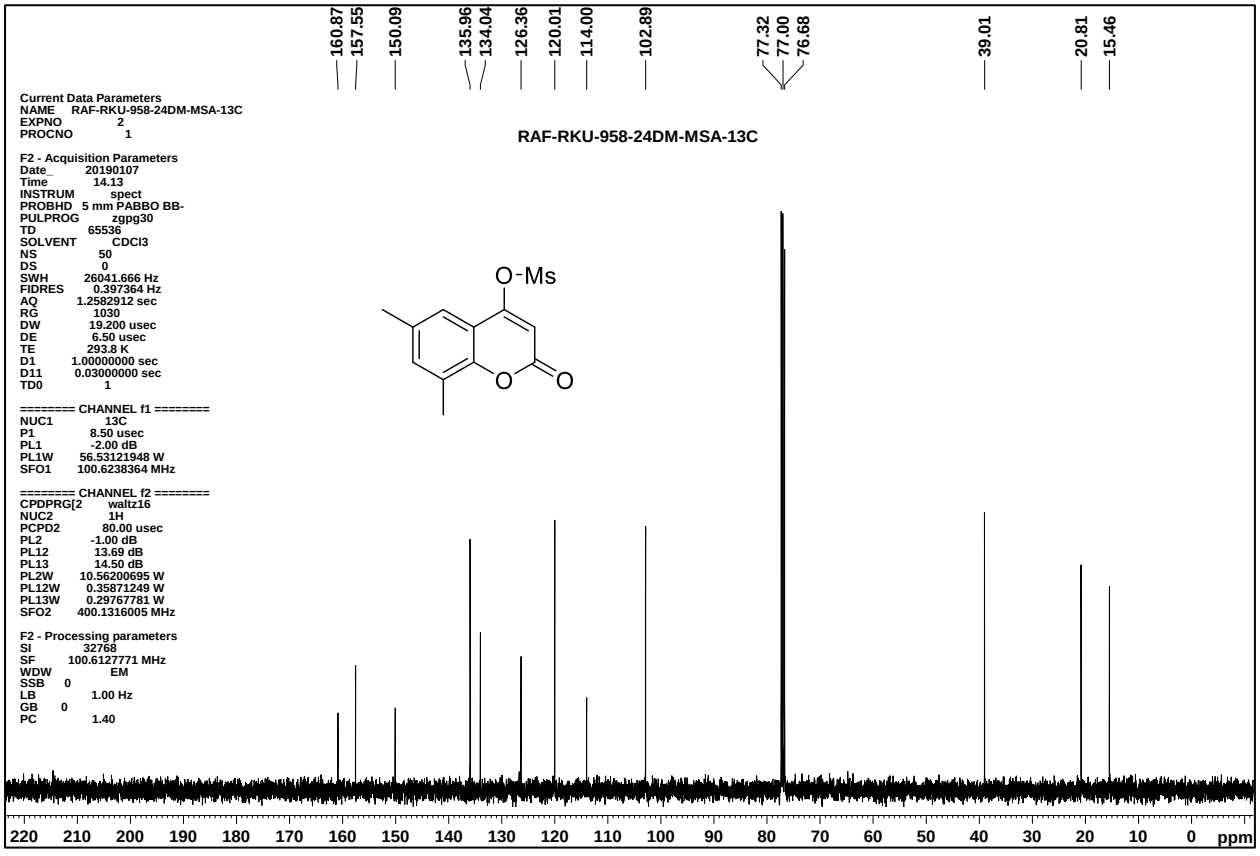
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **10c**



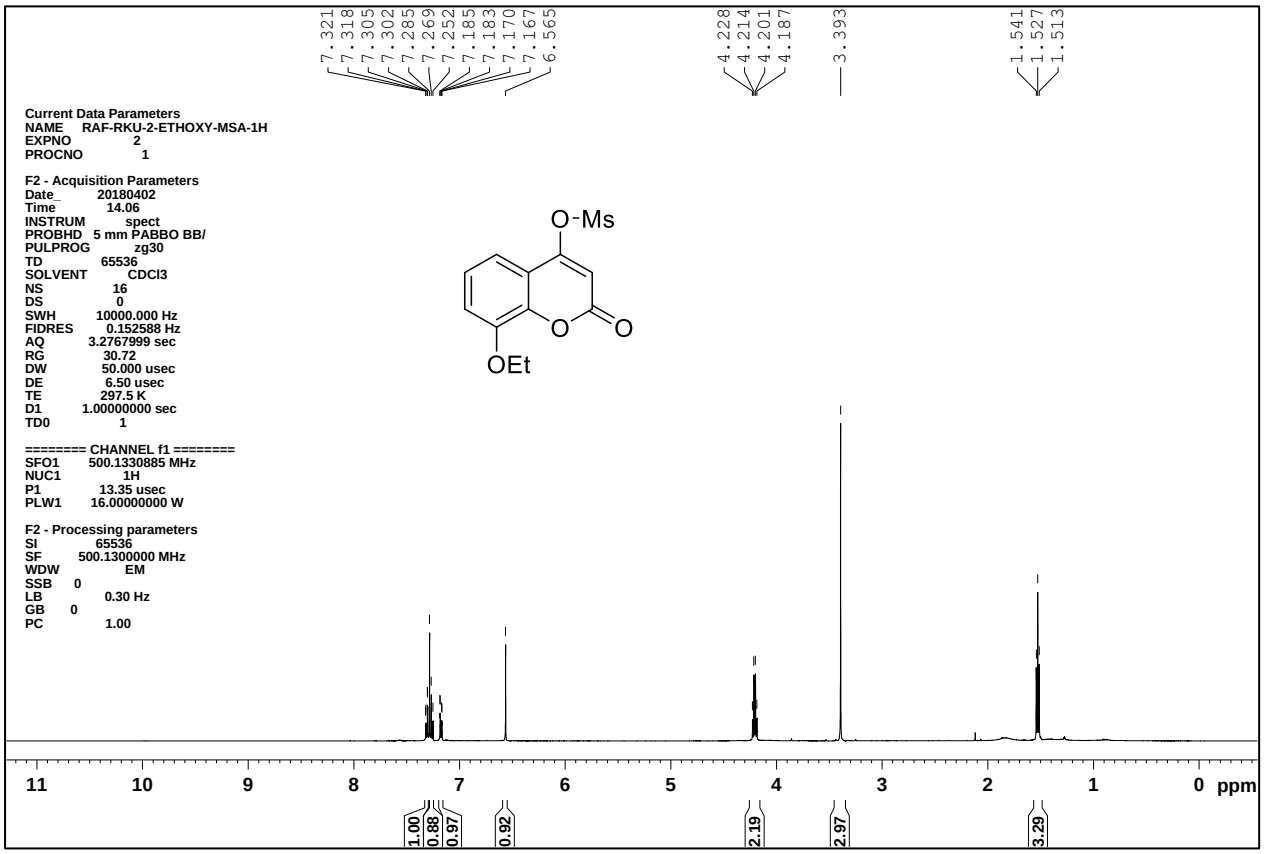


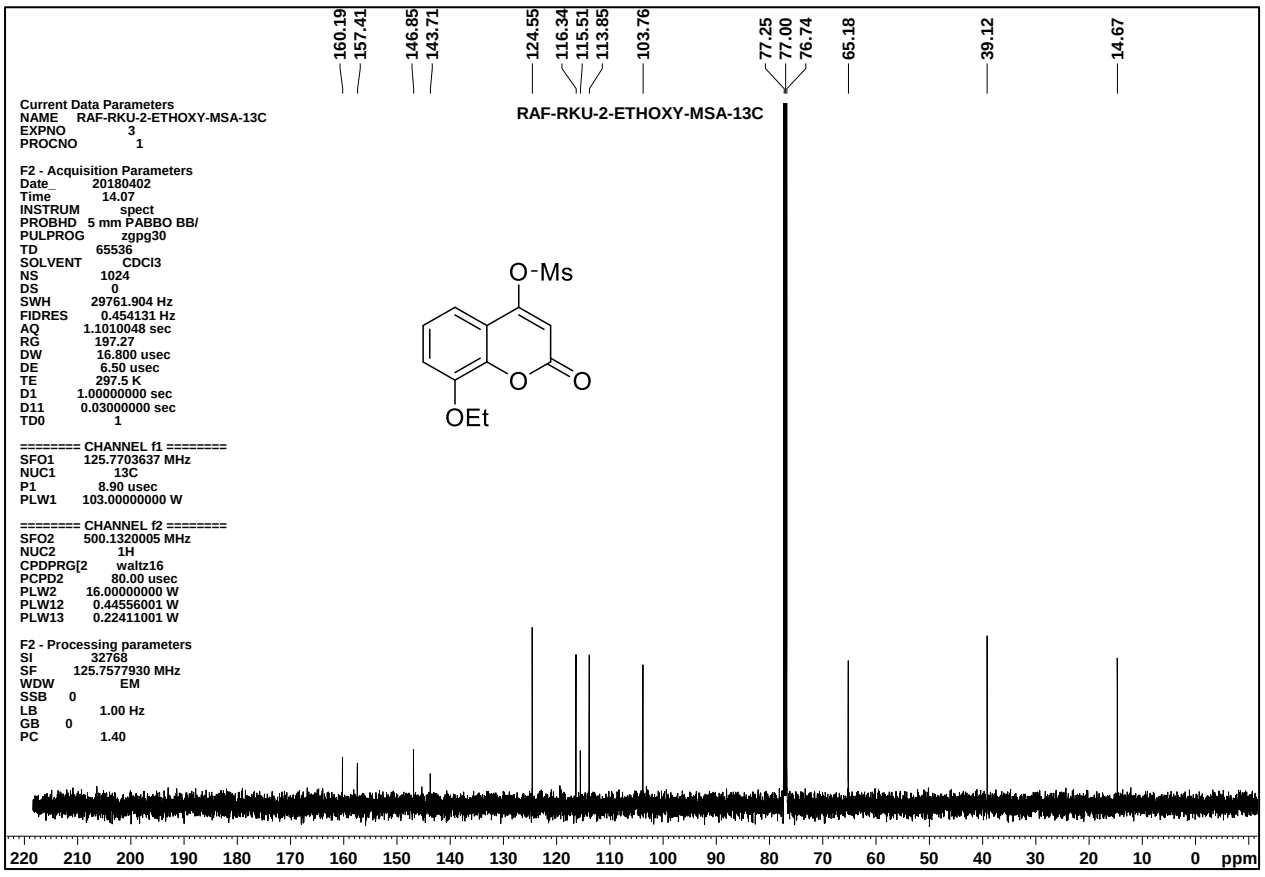
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **10f**



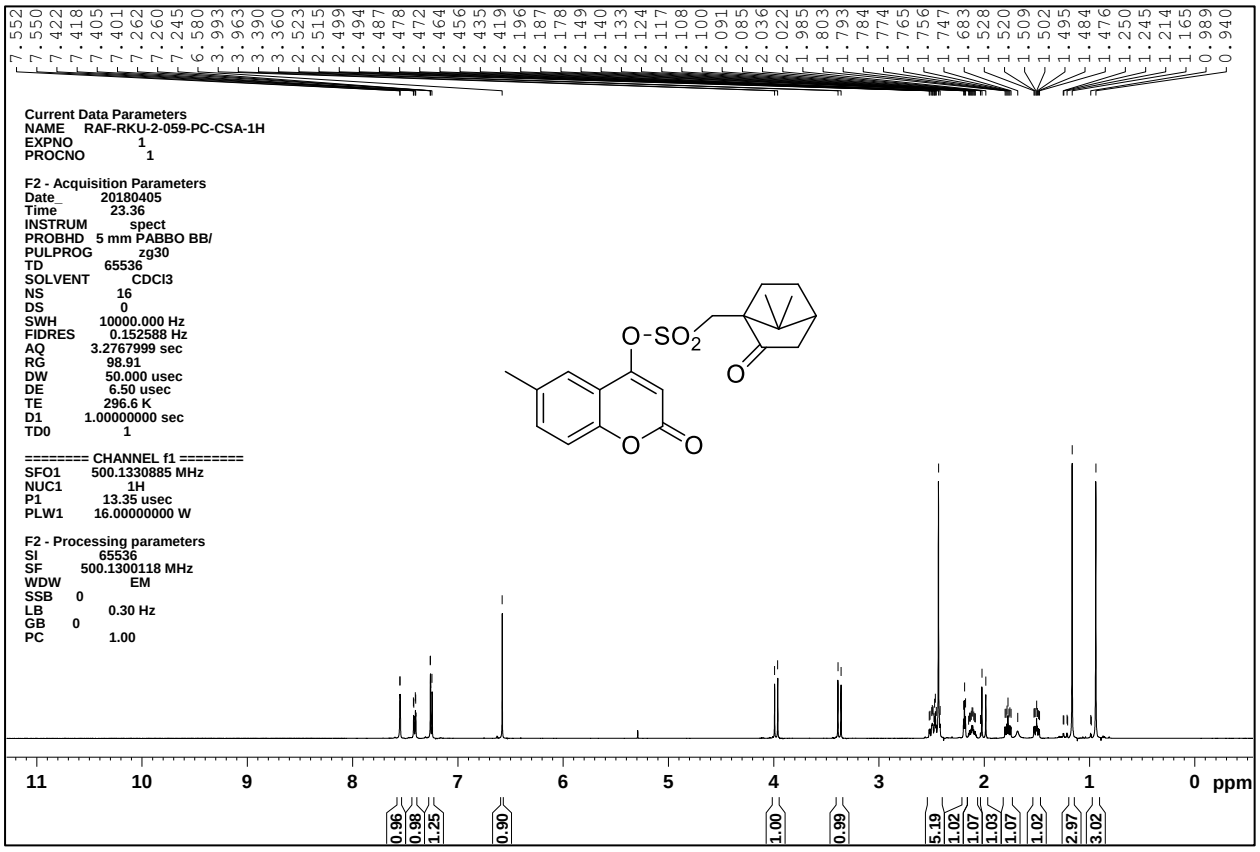


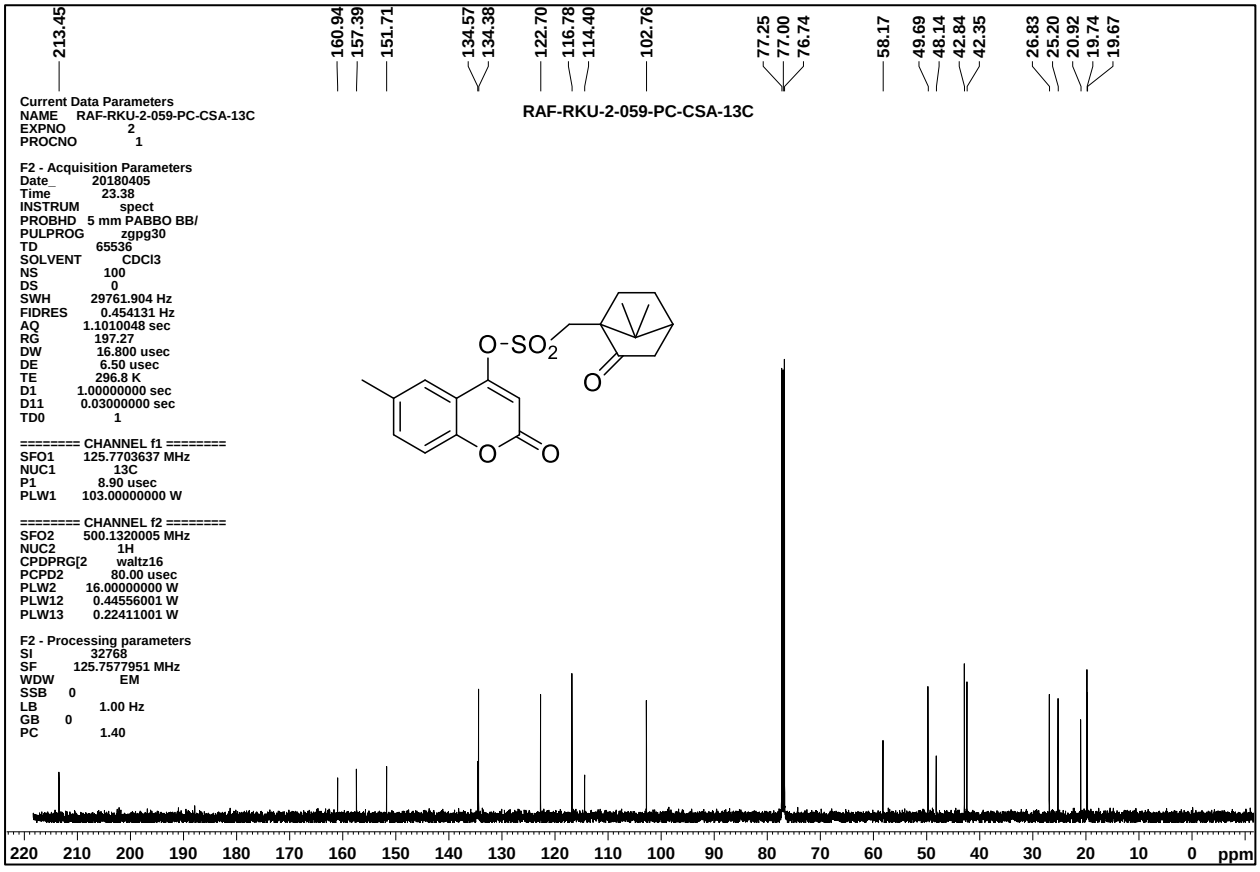
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **10h**



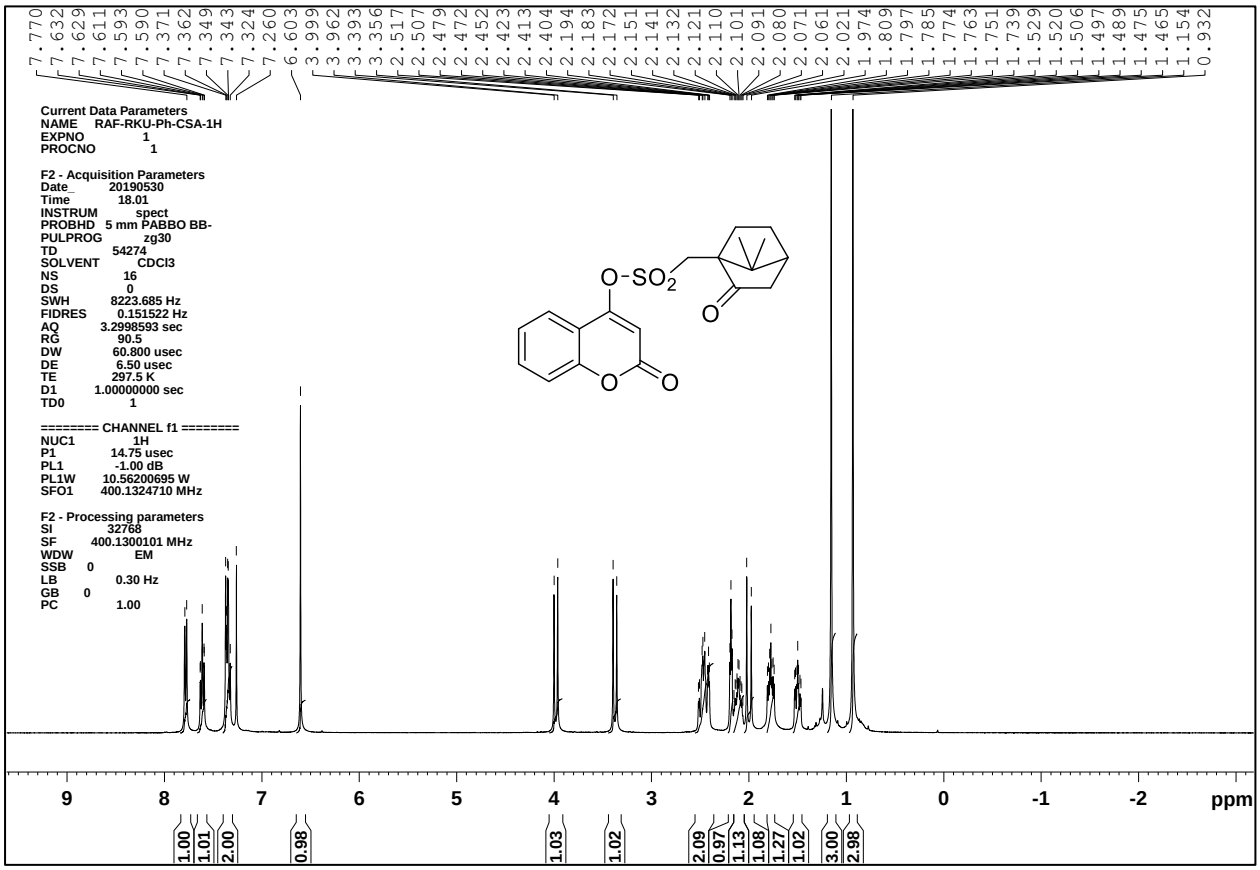


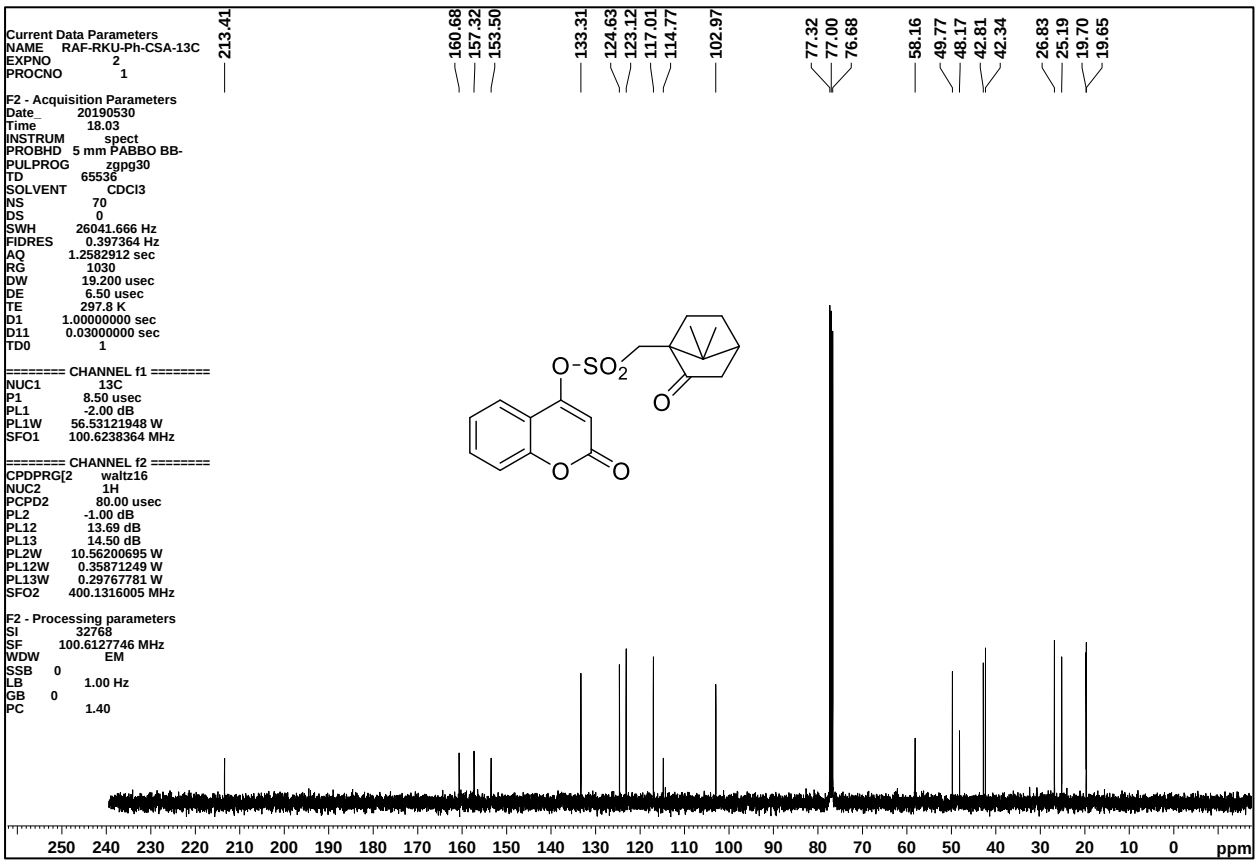
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **11a**



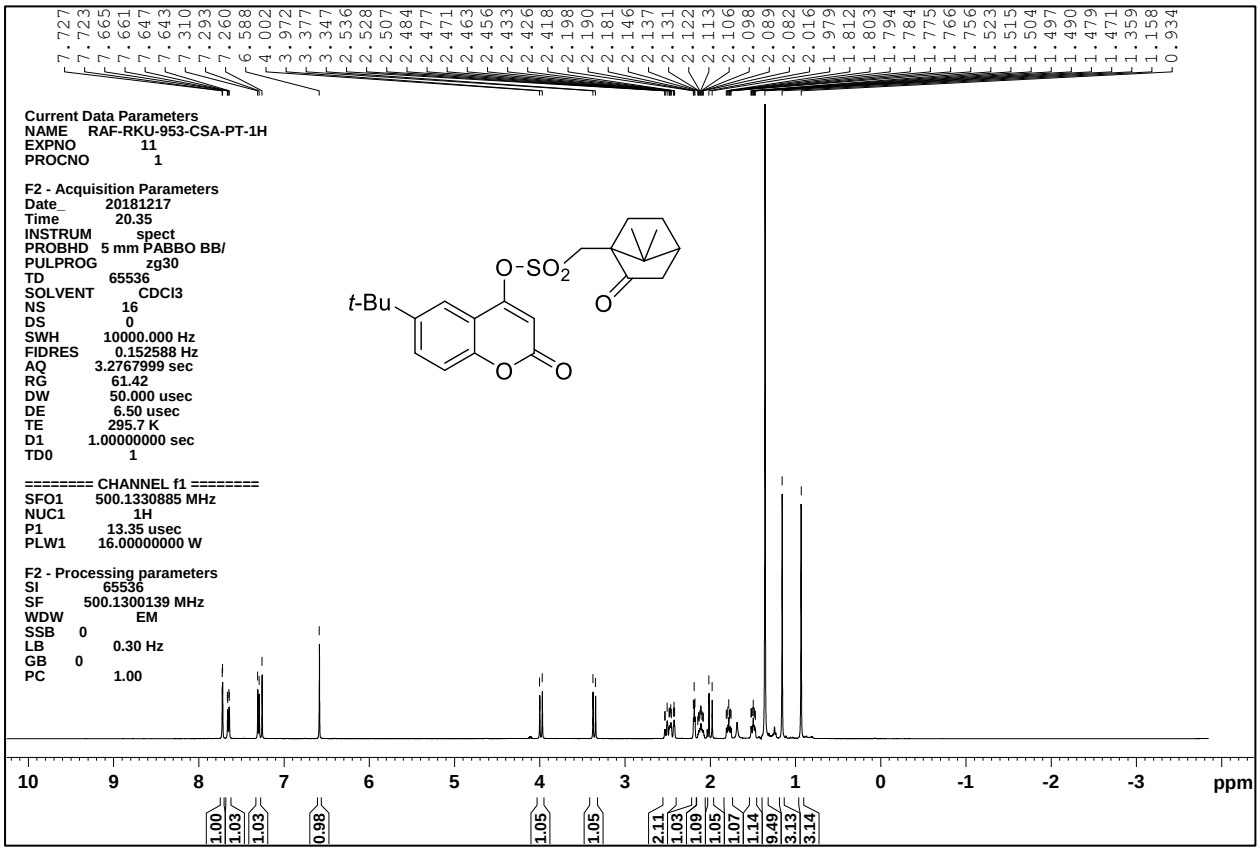


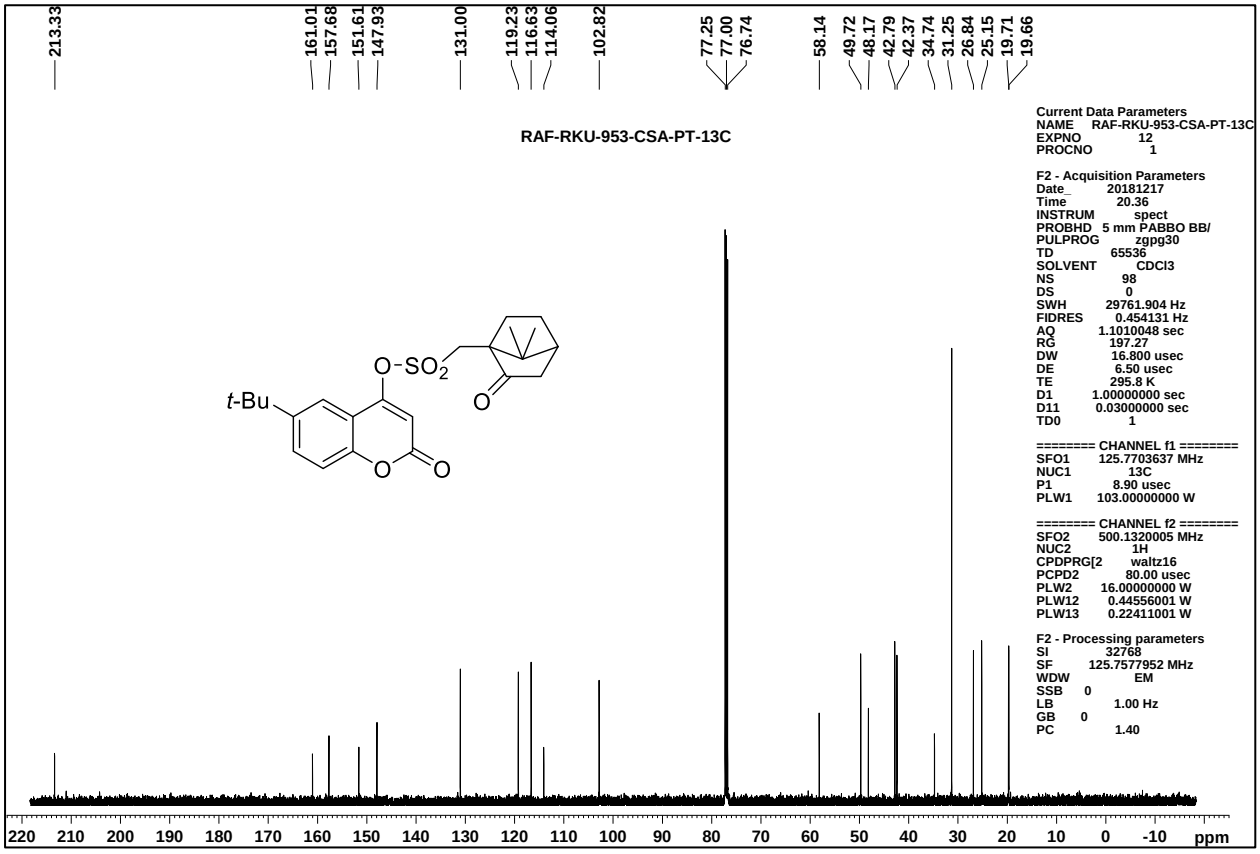
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **11b**



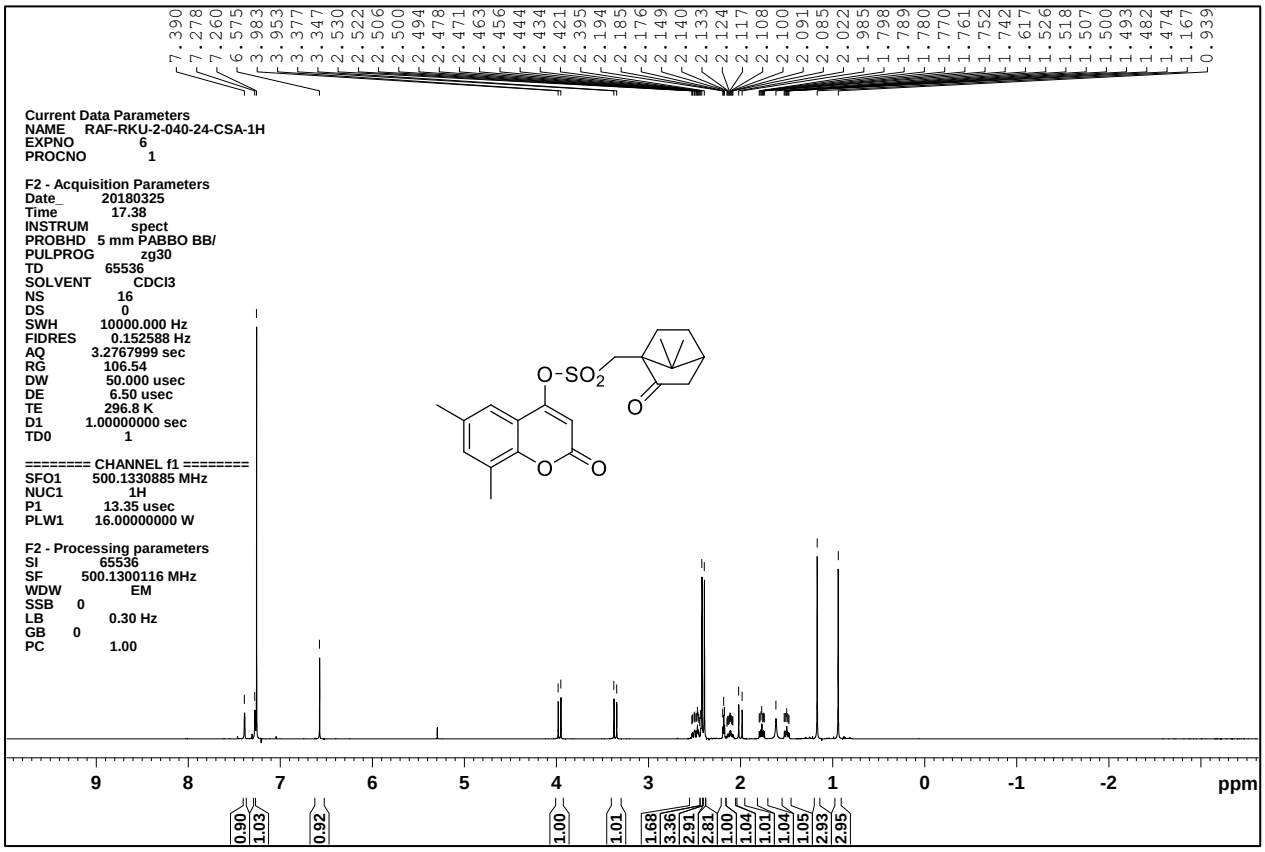


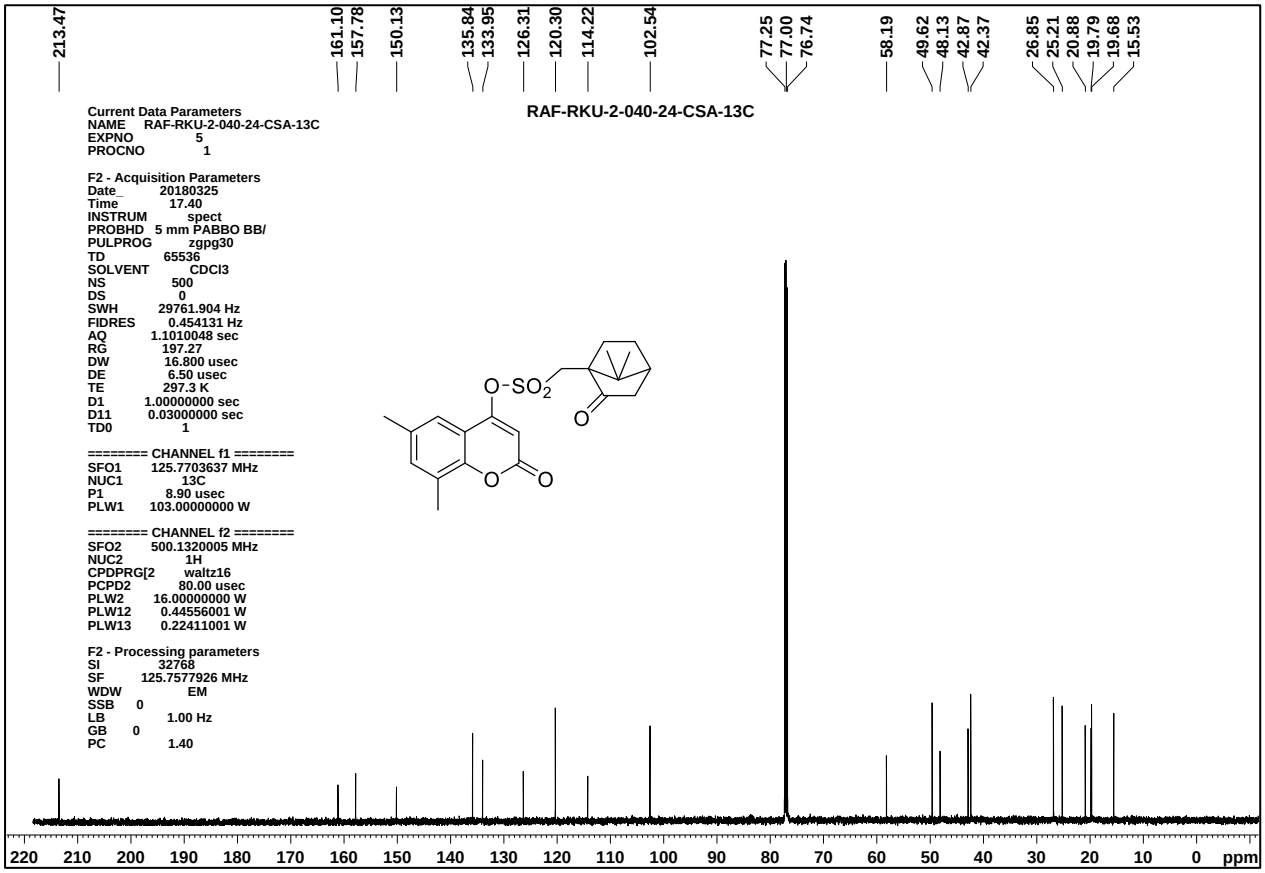
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **11c**



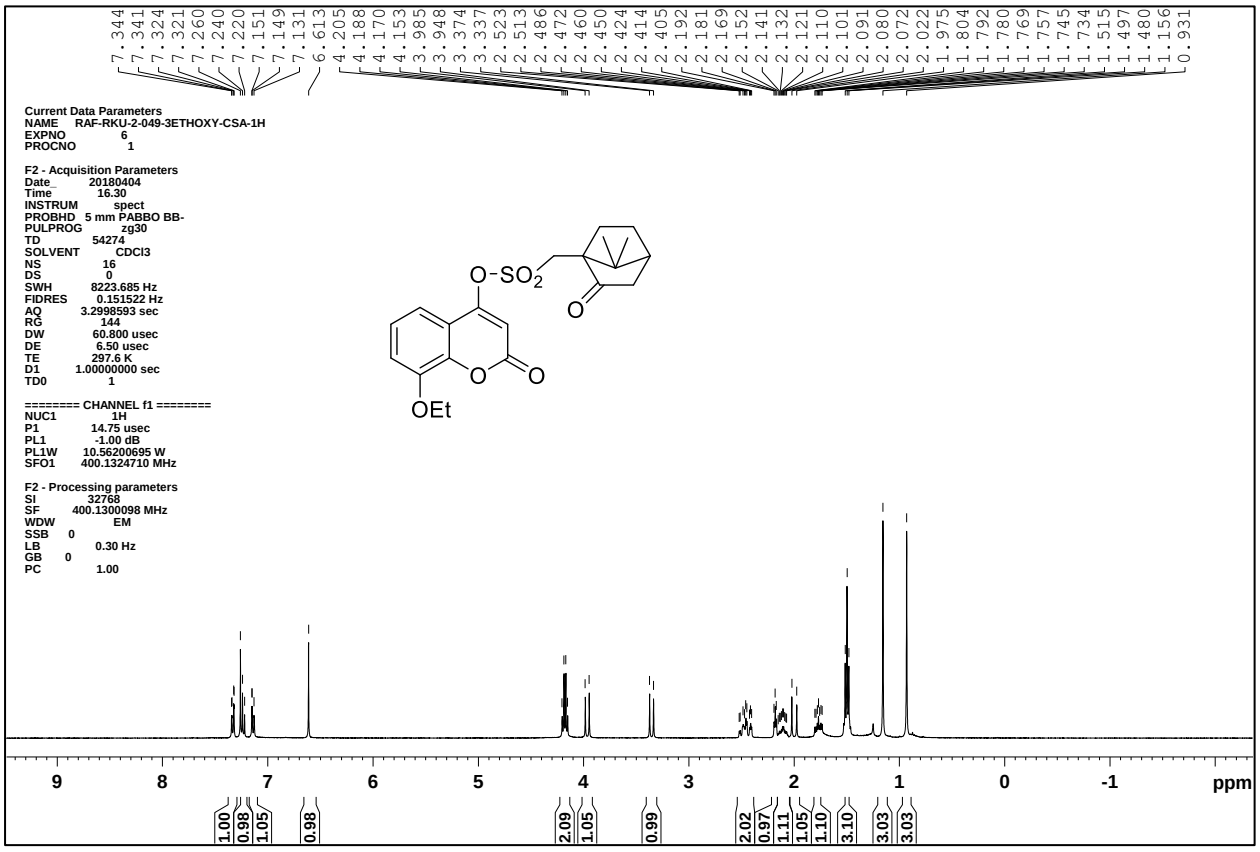


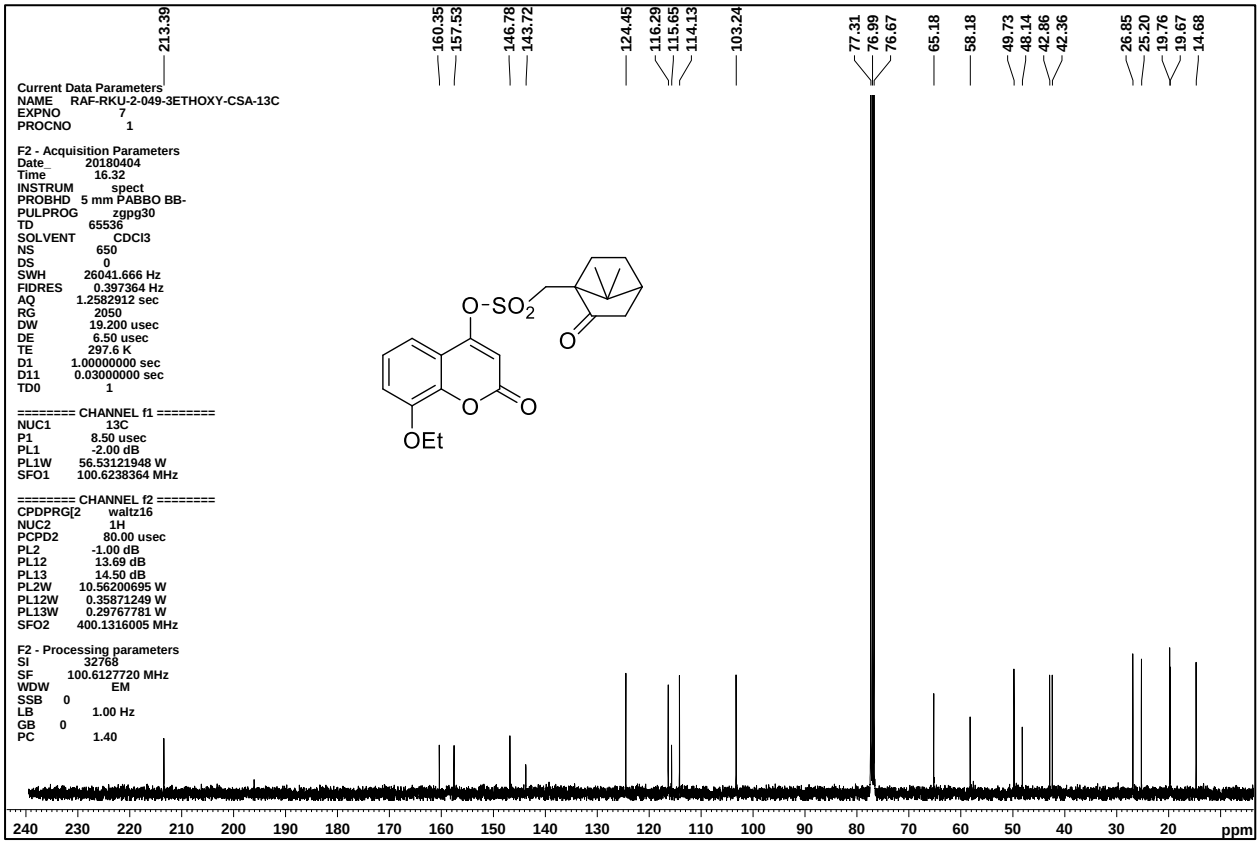
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **11f**



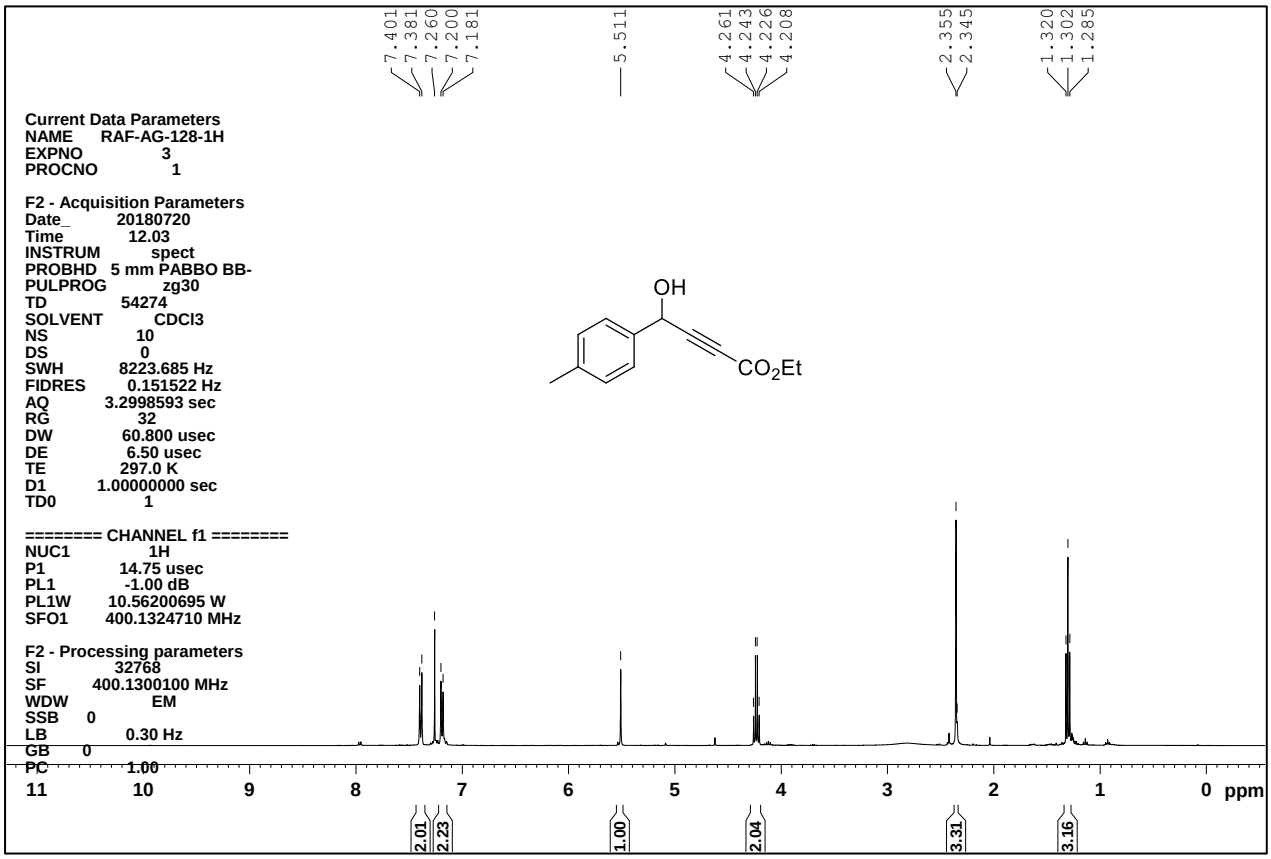


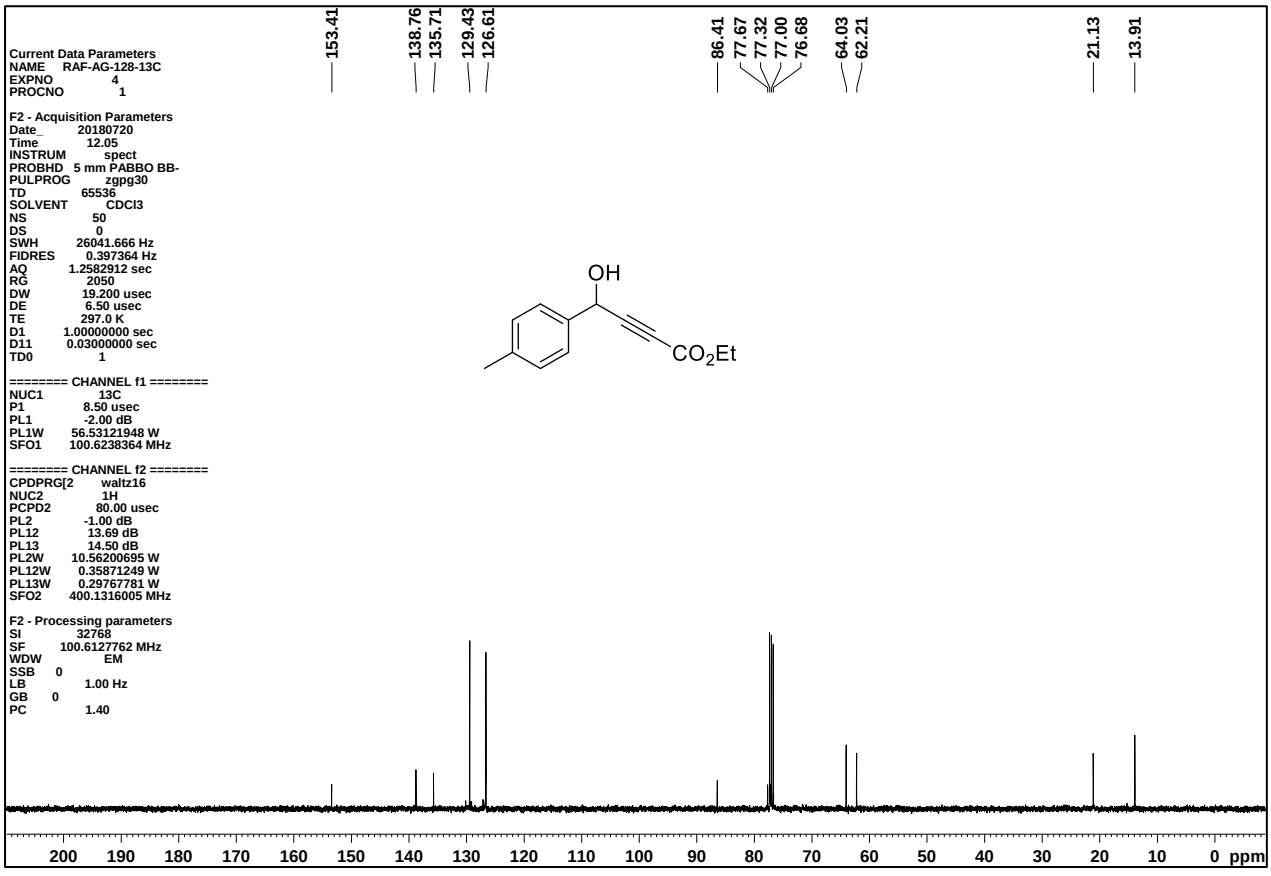
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **11h**



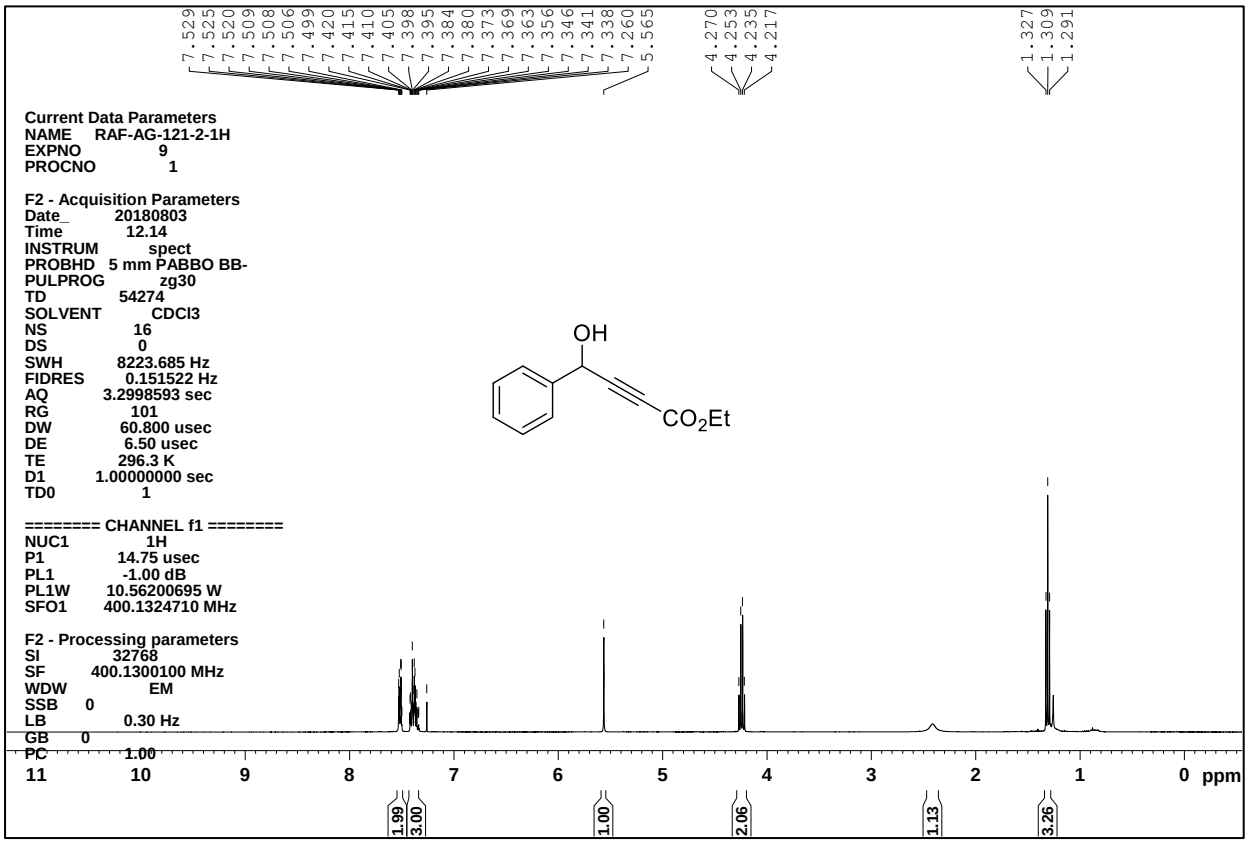


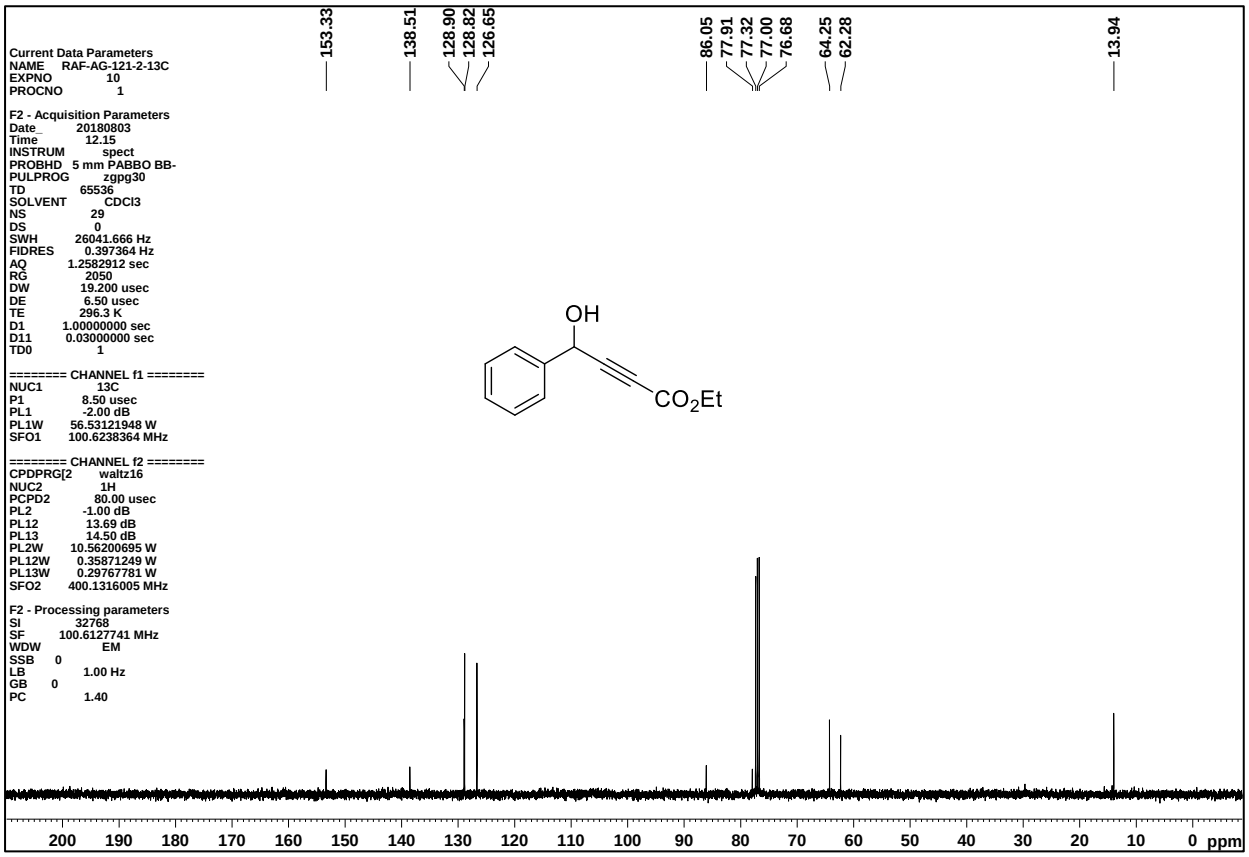
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12a**



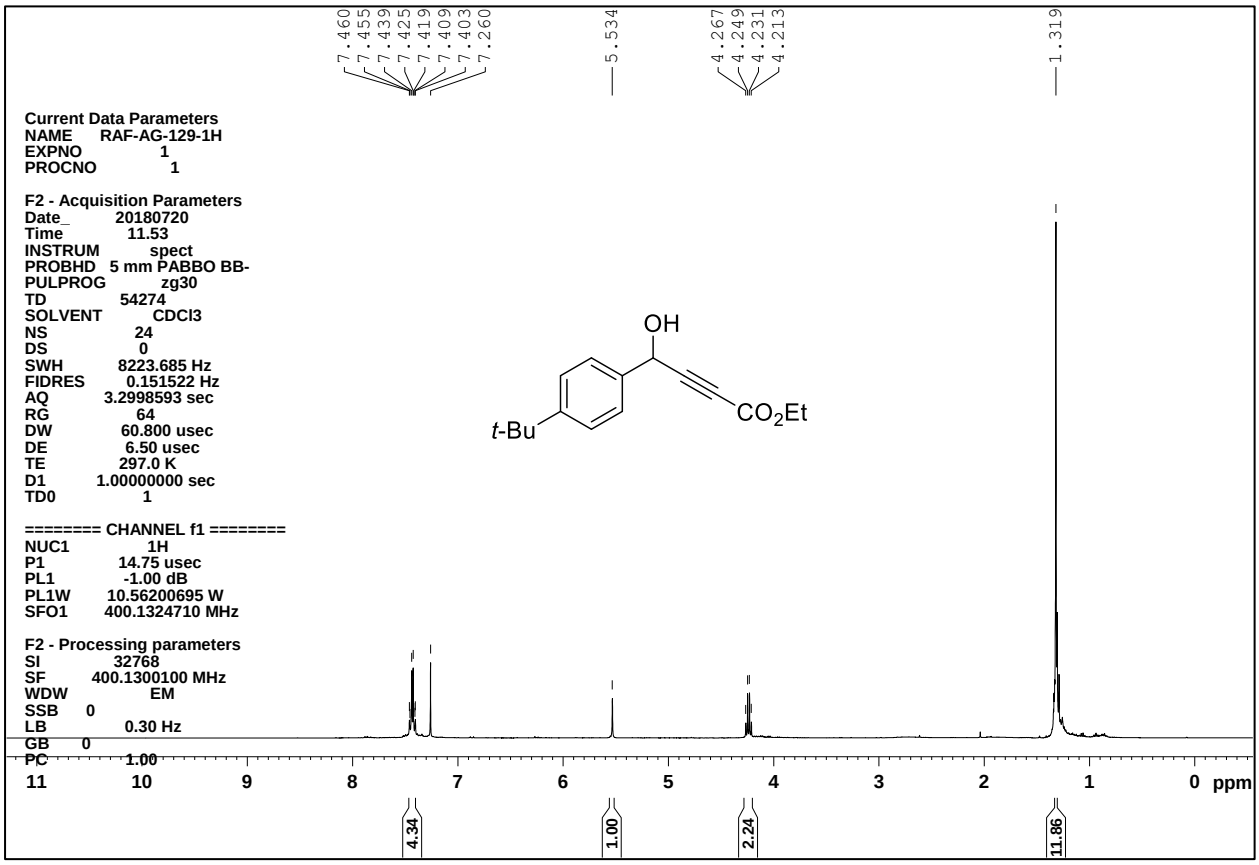


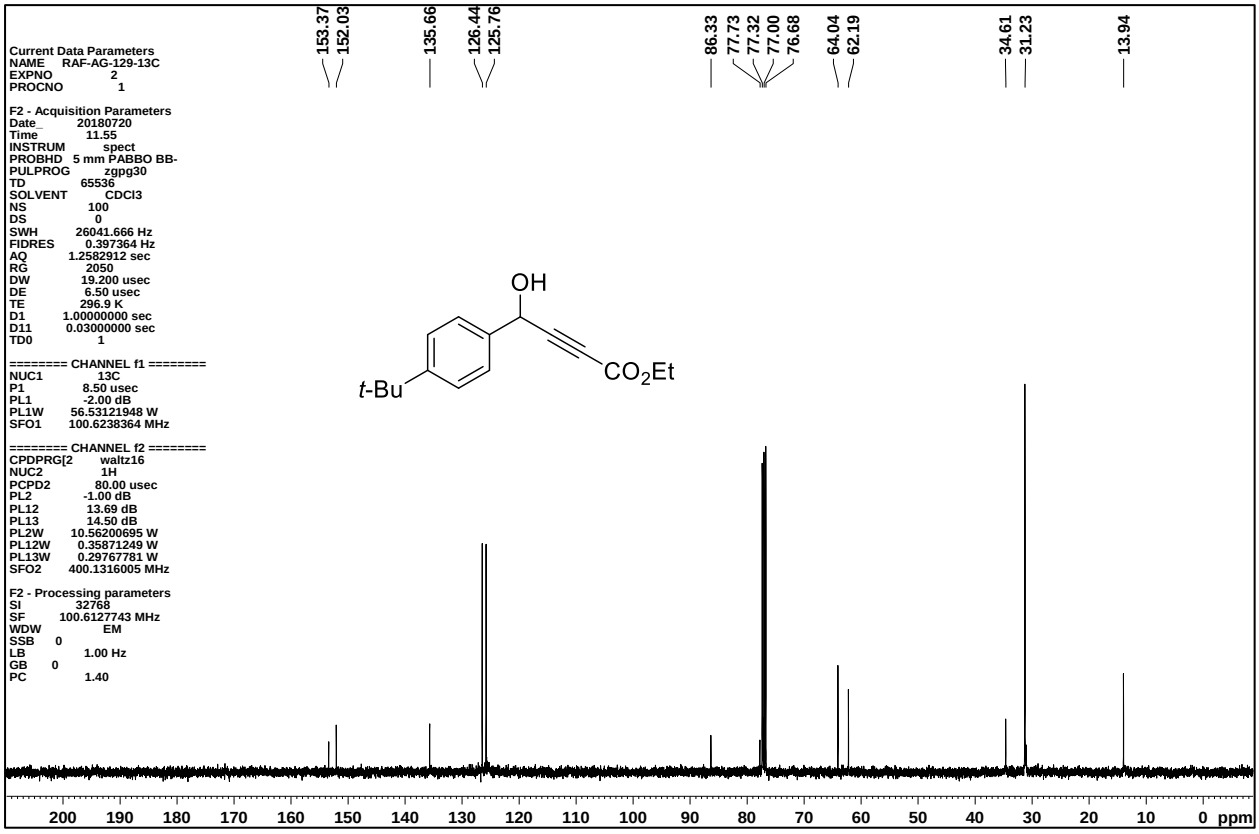
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12b**



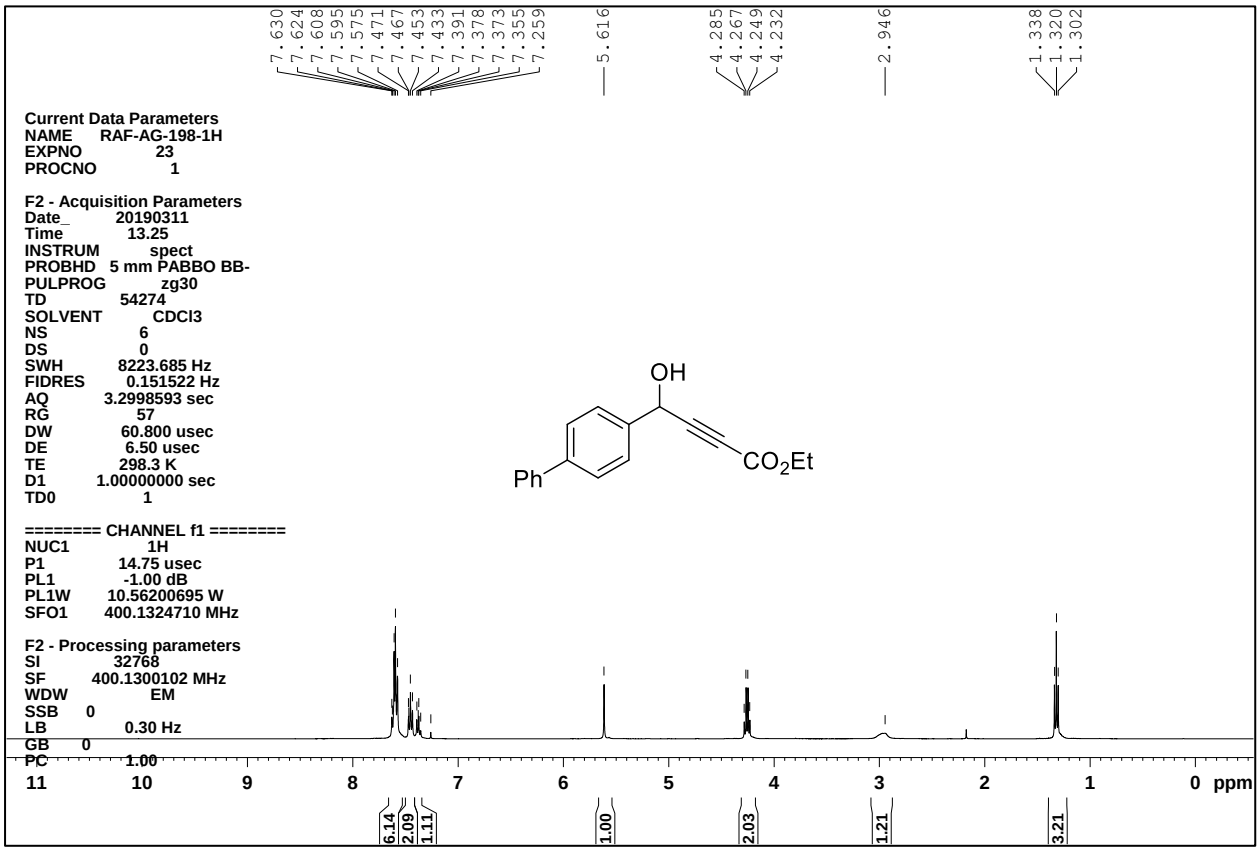


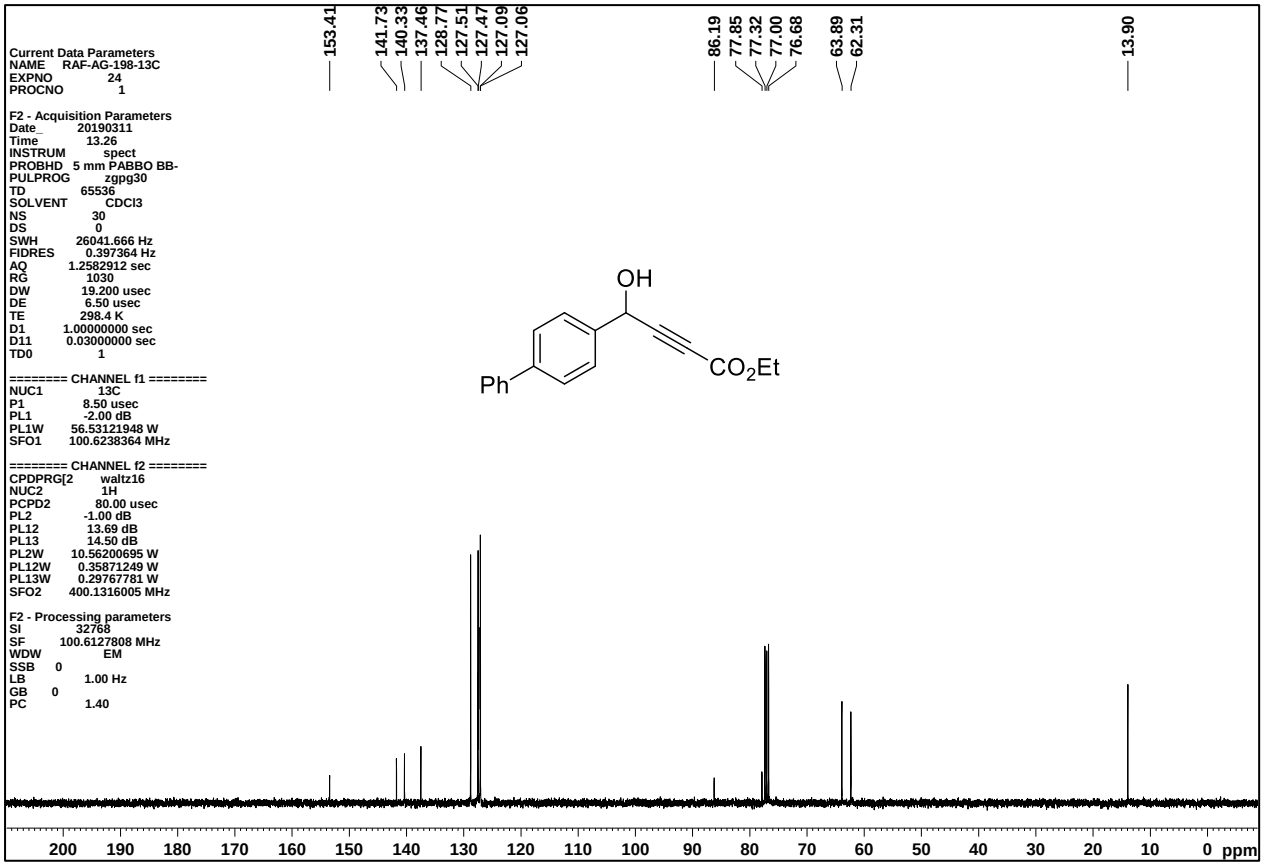
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of of **12c**



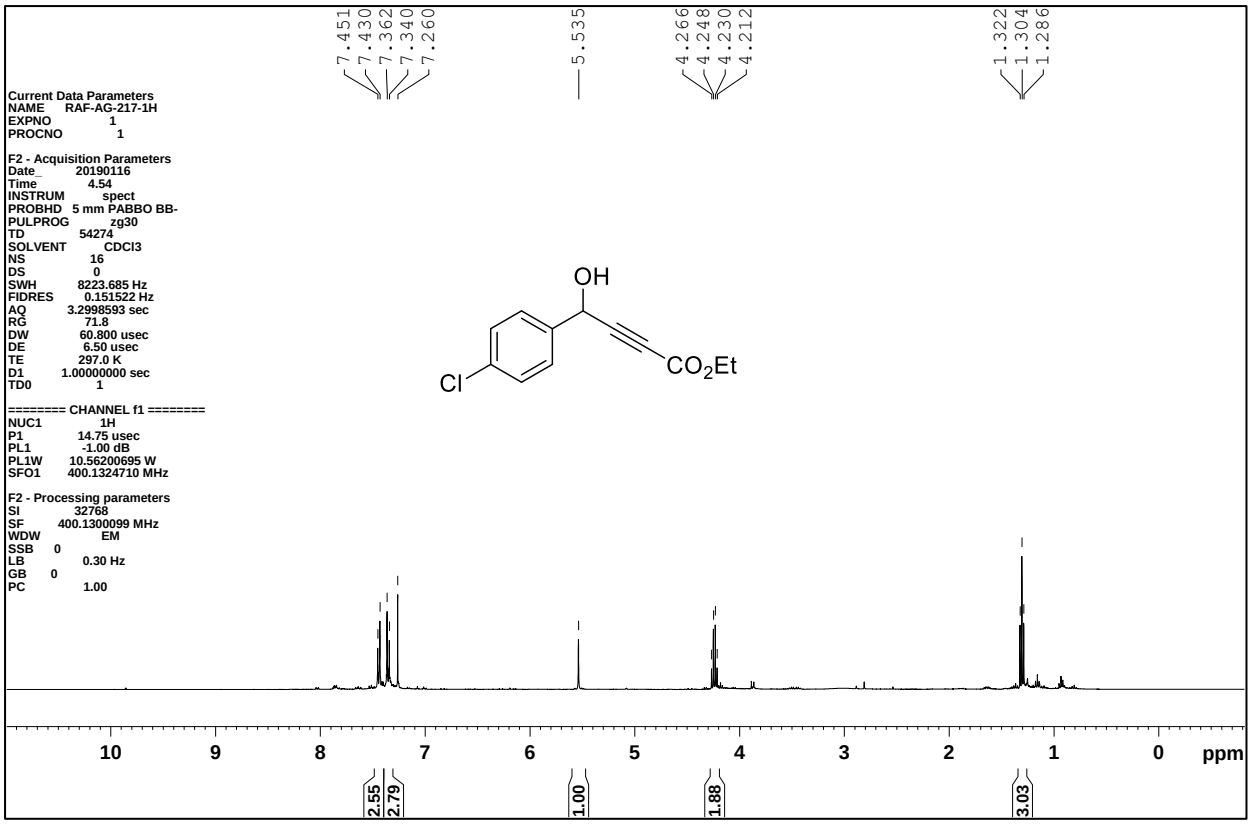


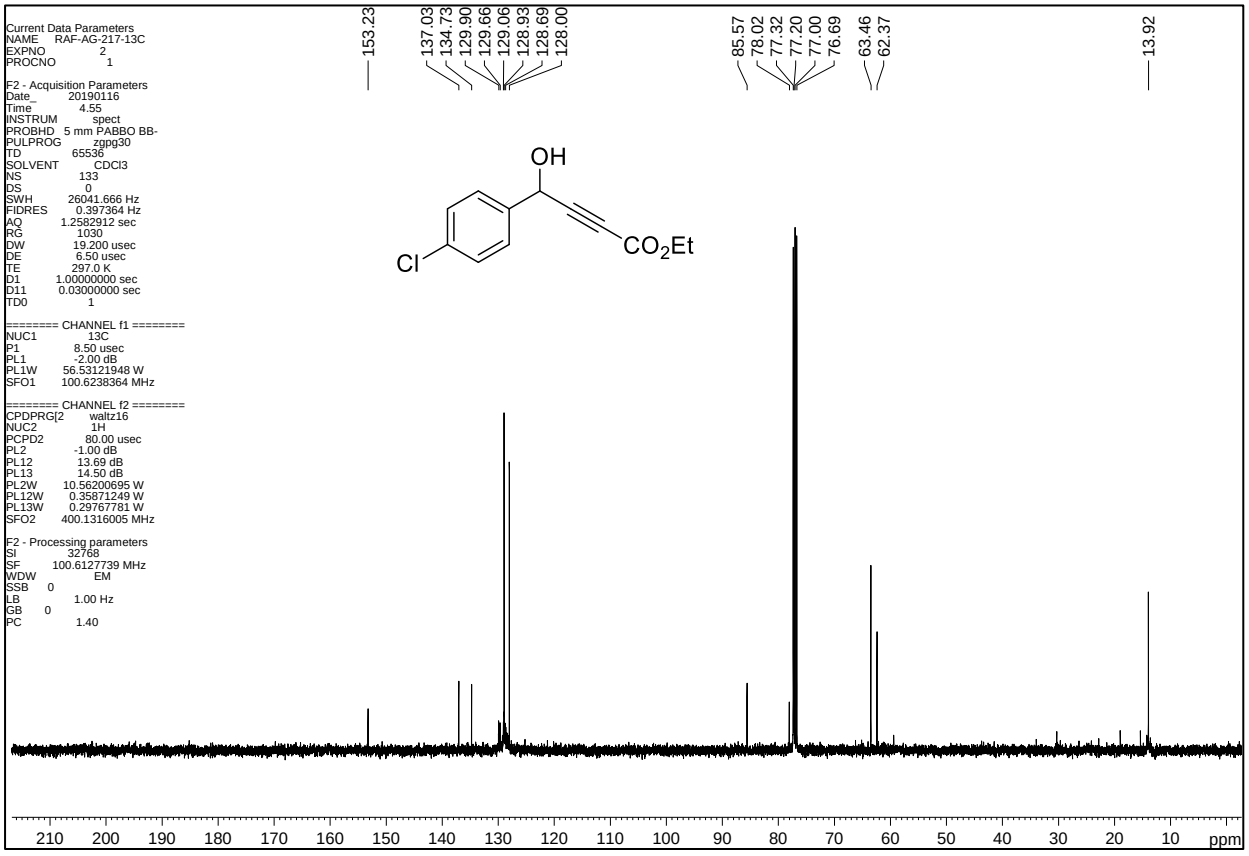
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12d**



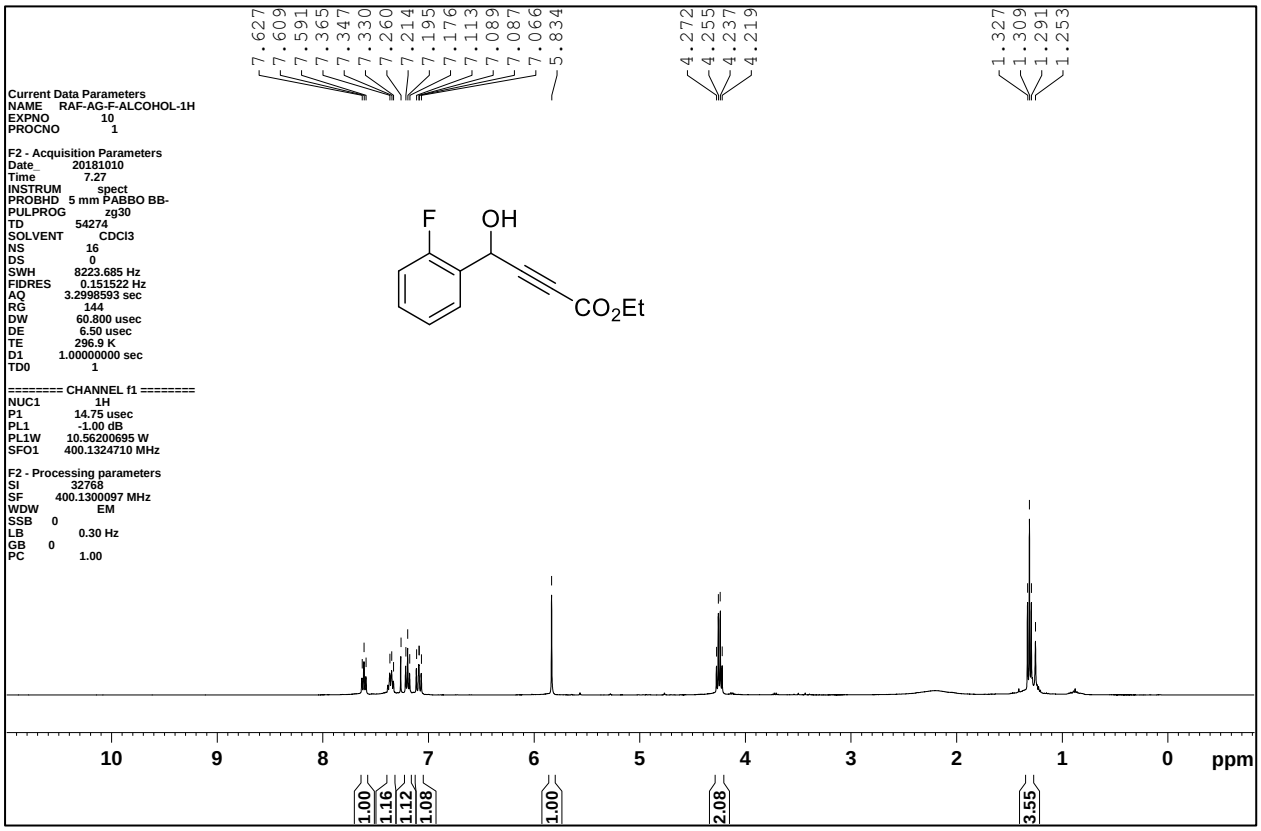


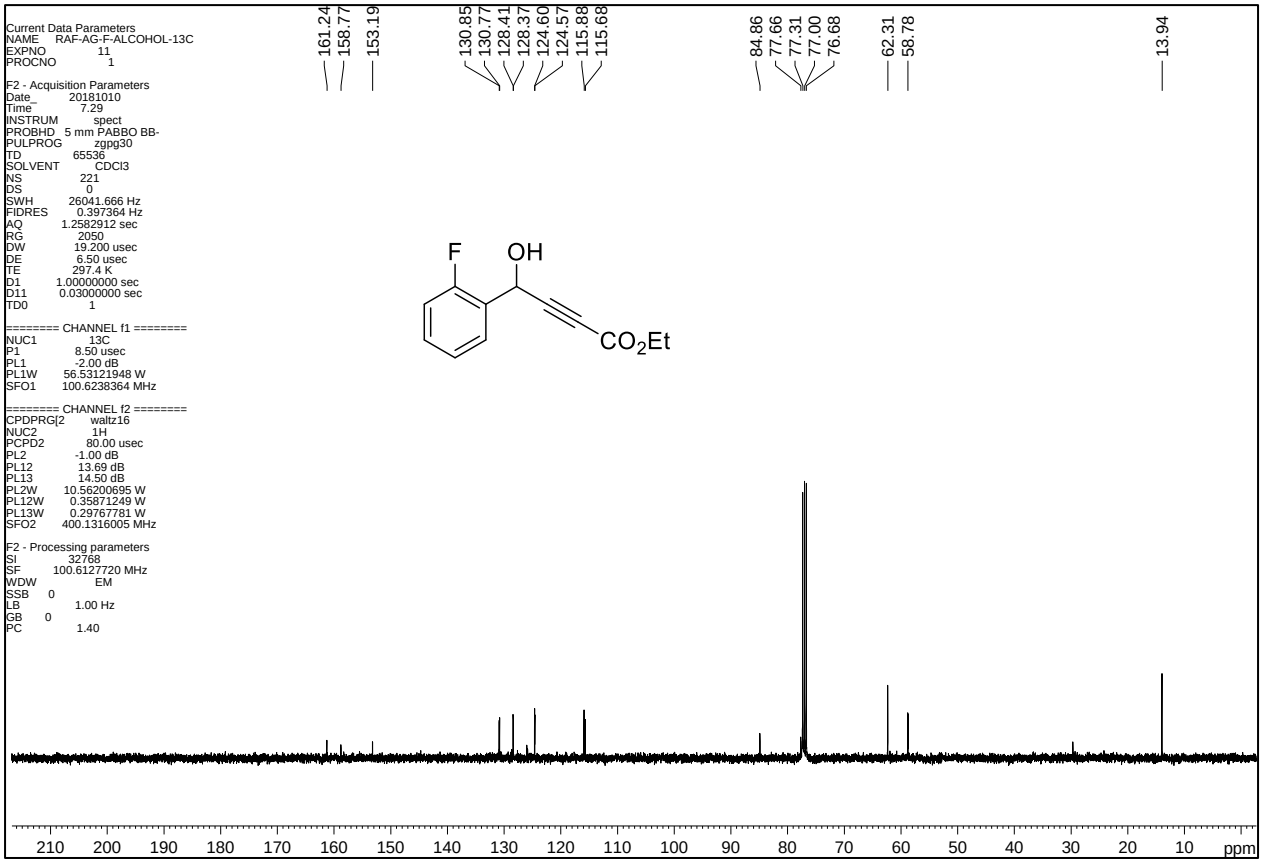
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12e**



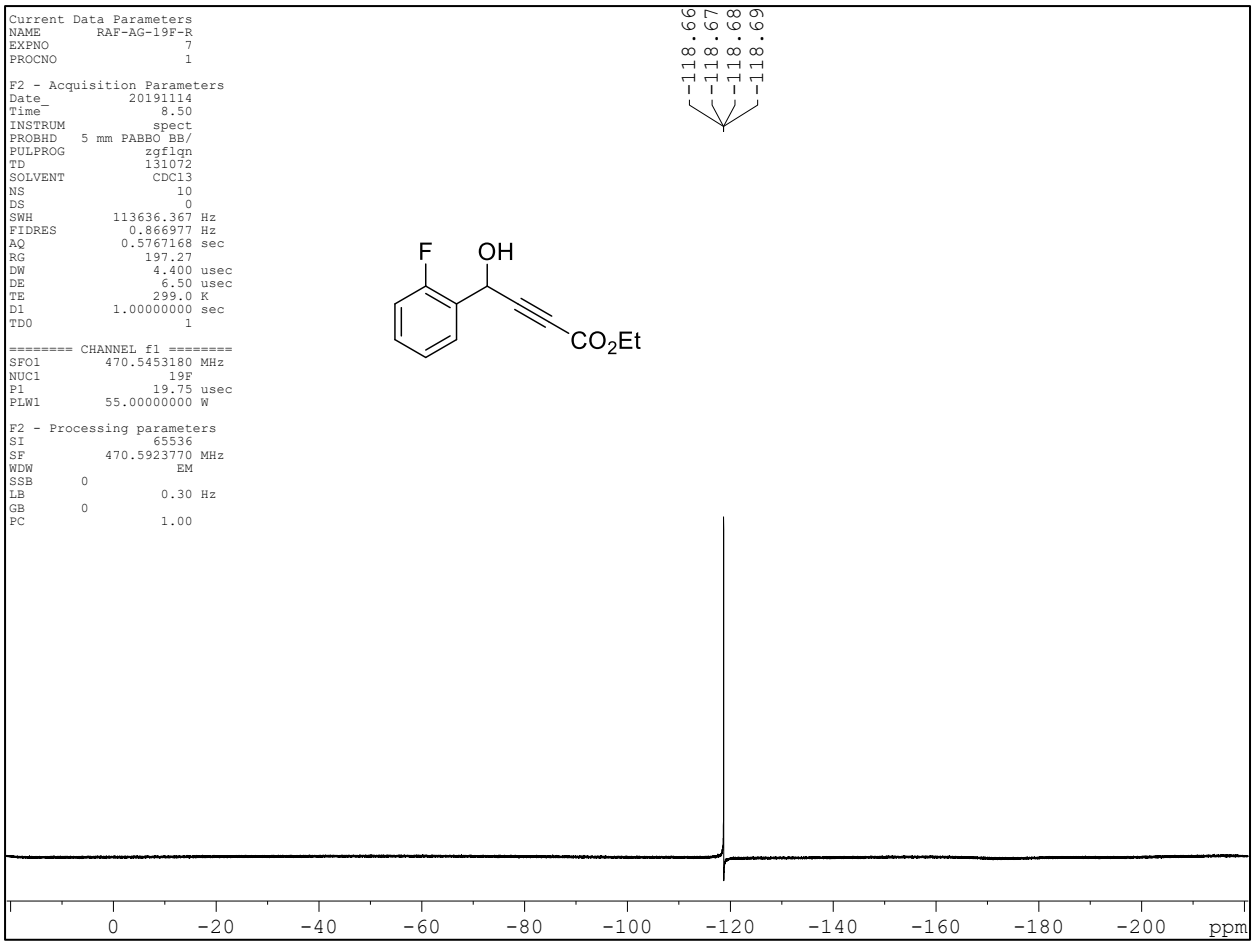


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12f**

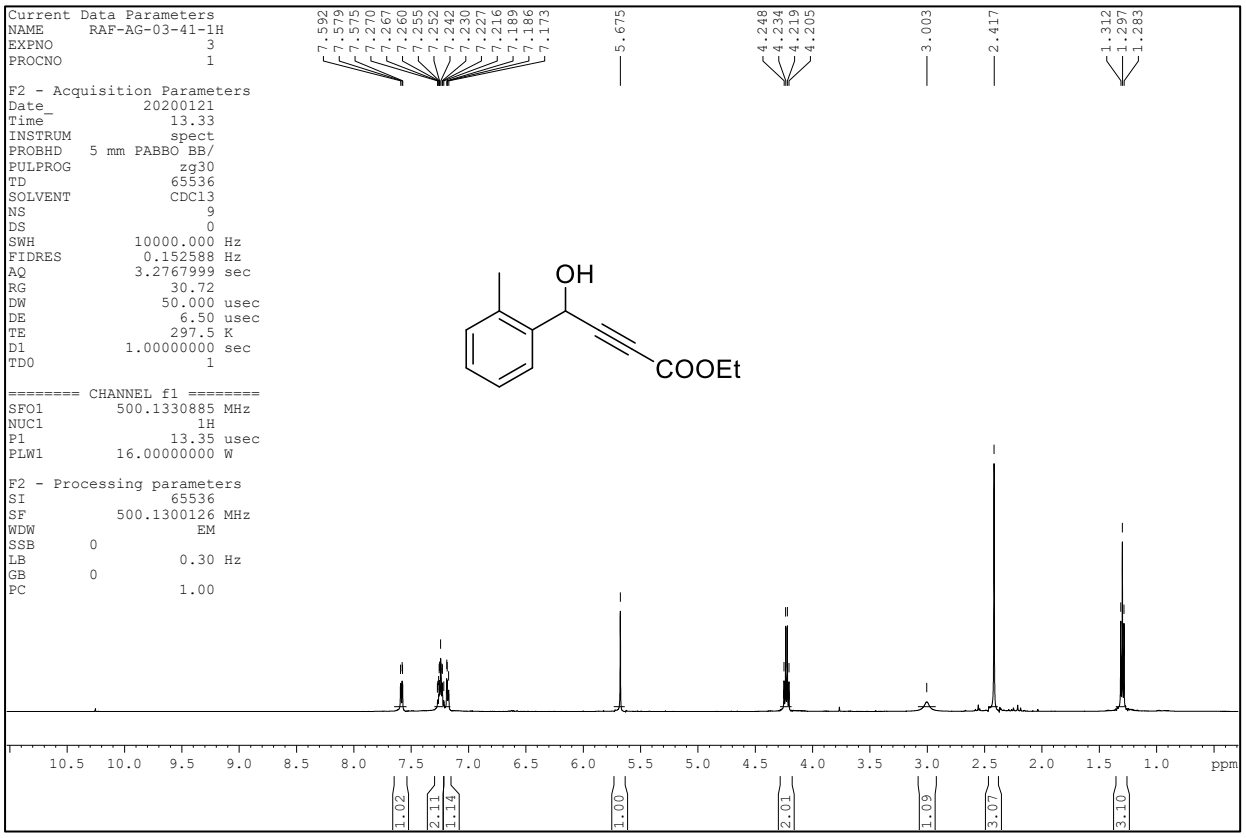


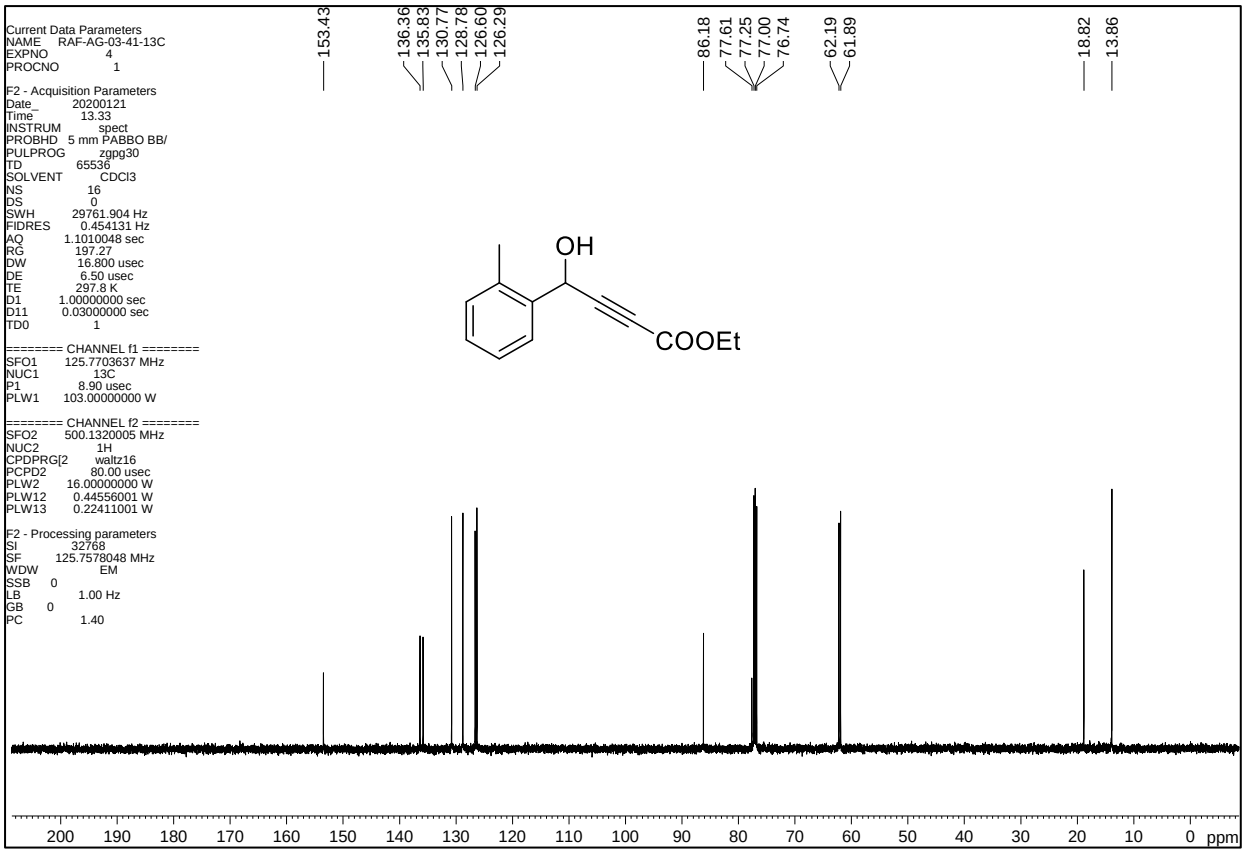


^{19}F NMR (471 MHz, $CDCl_3$) of **12f**

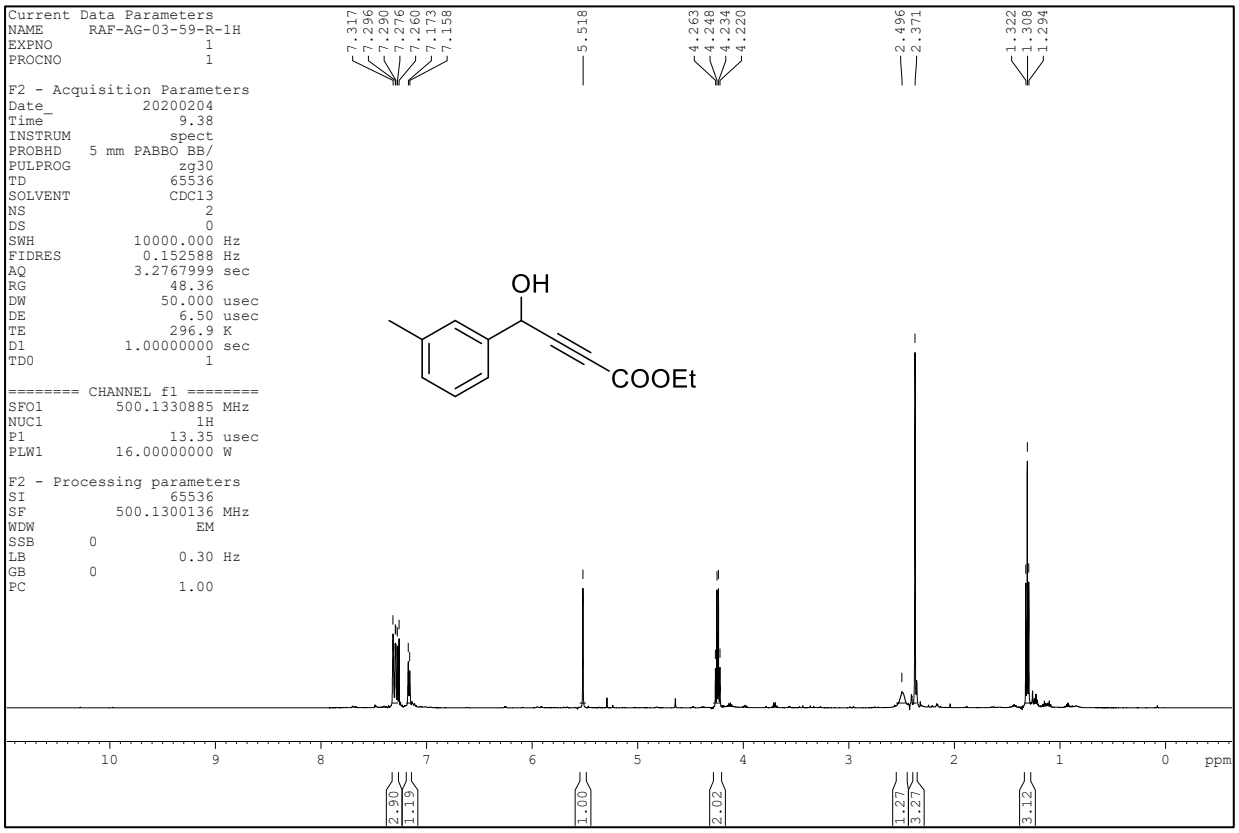


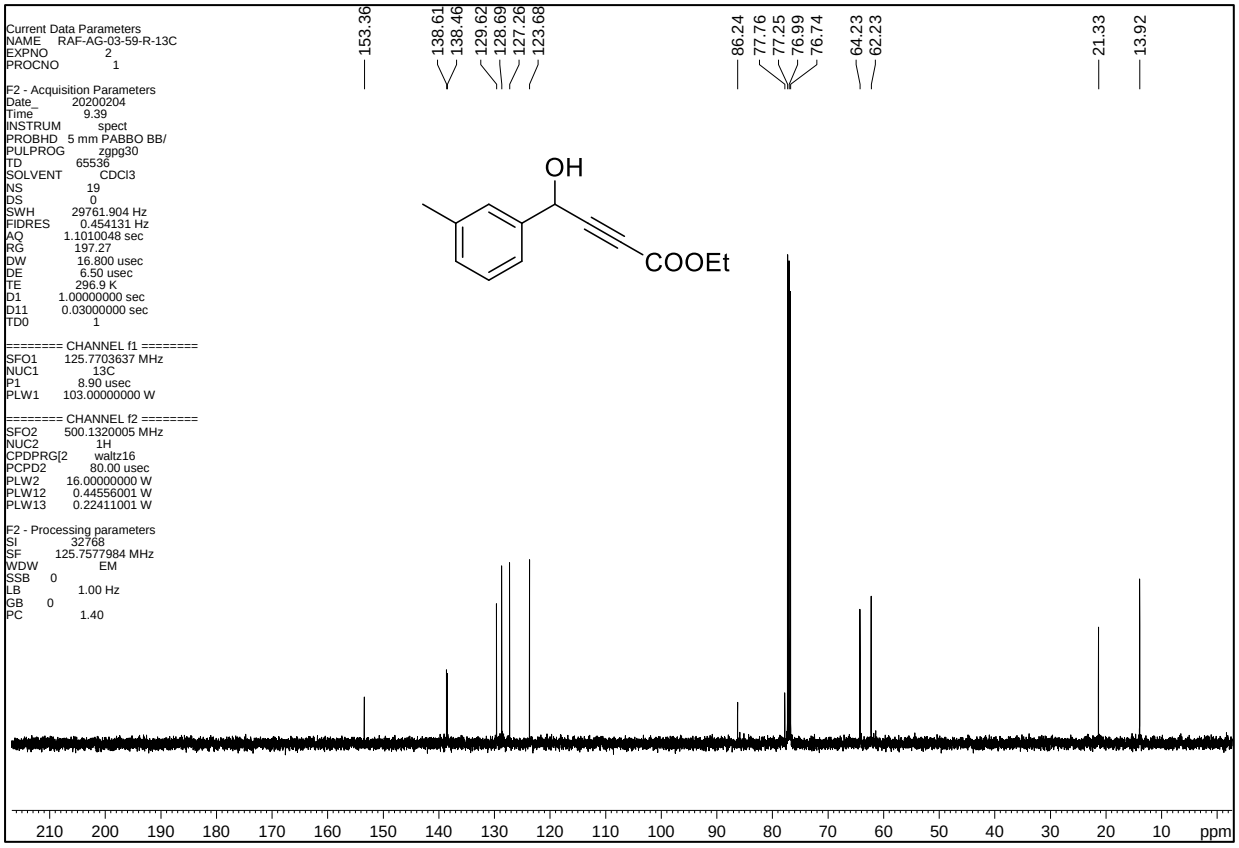
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **12g**



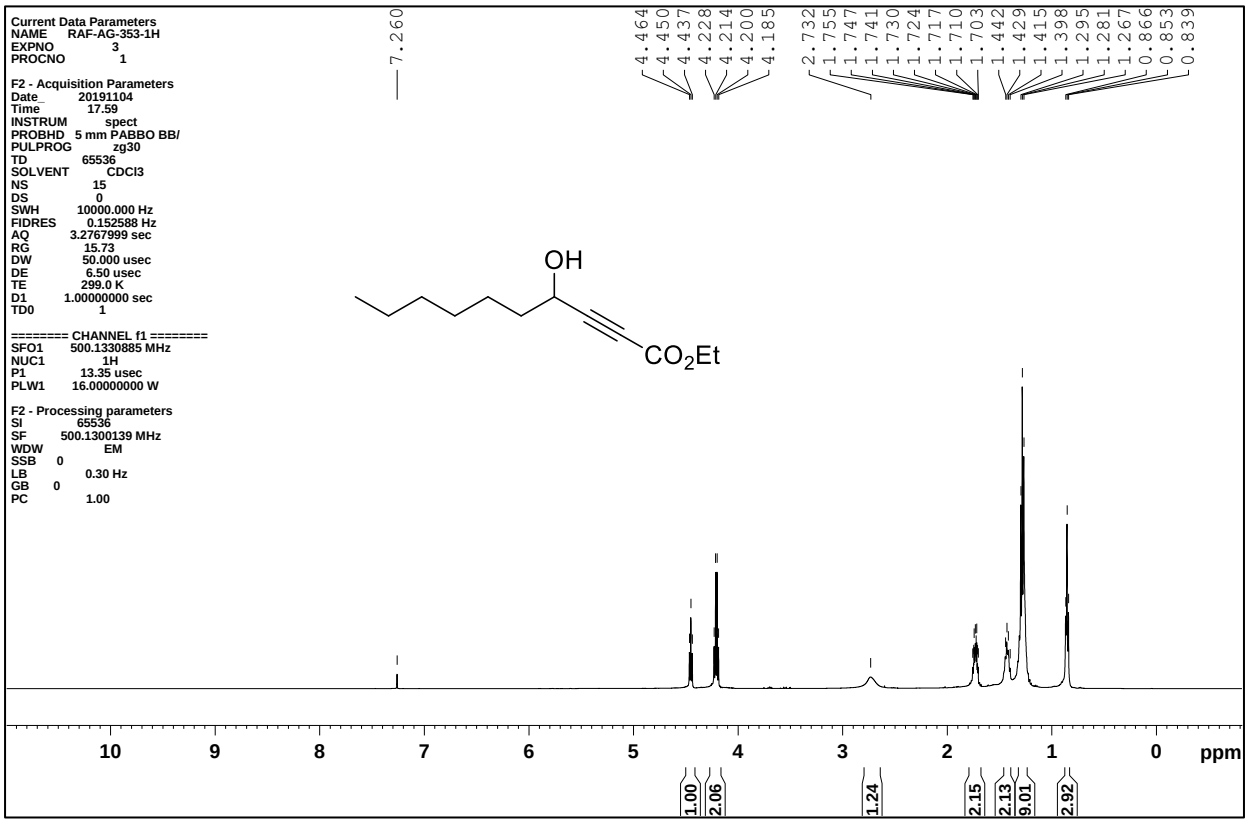


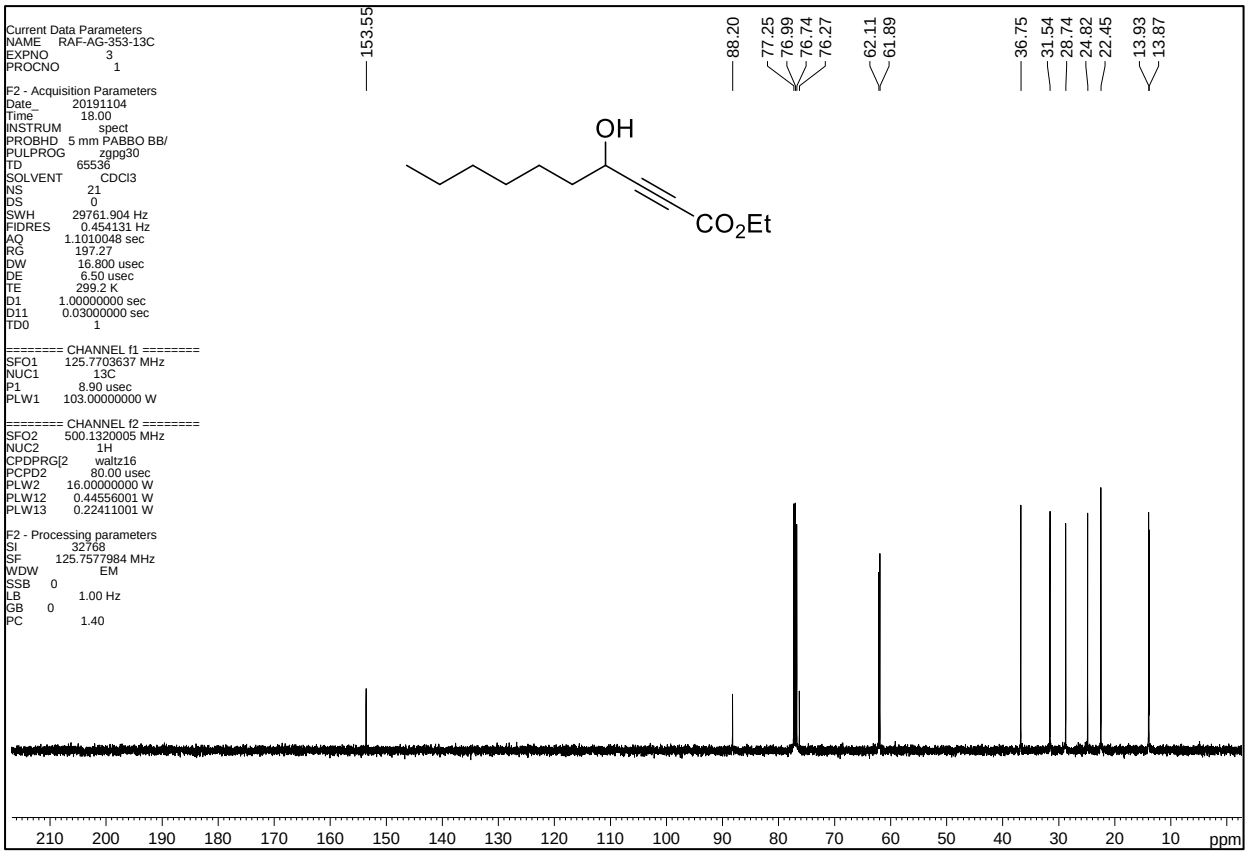
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **12h**



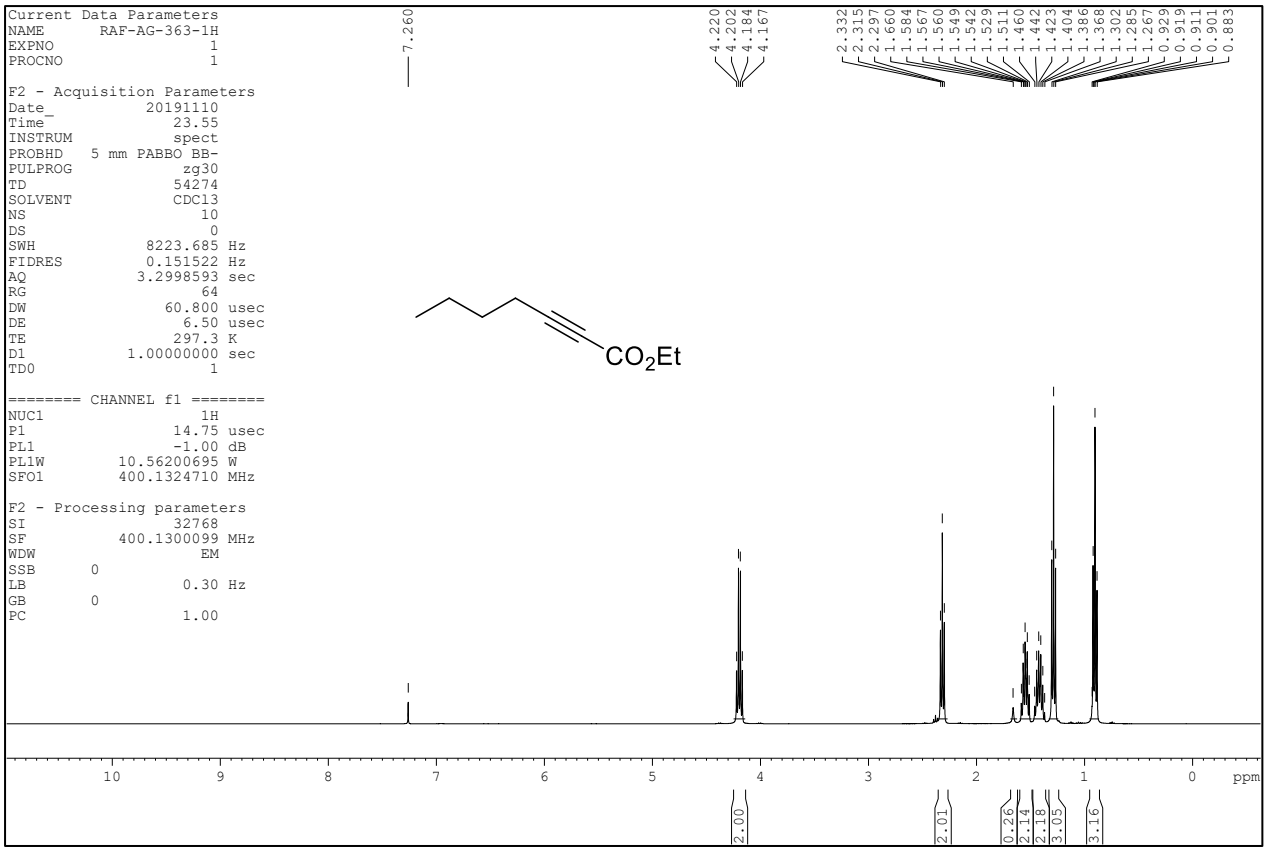


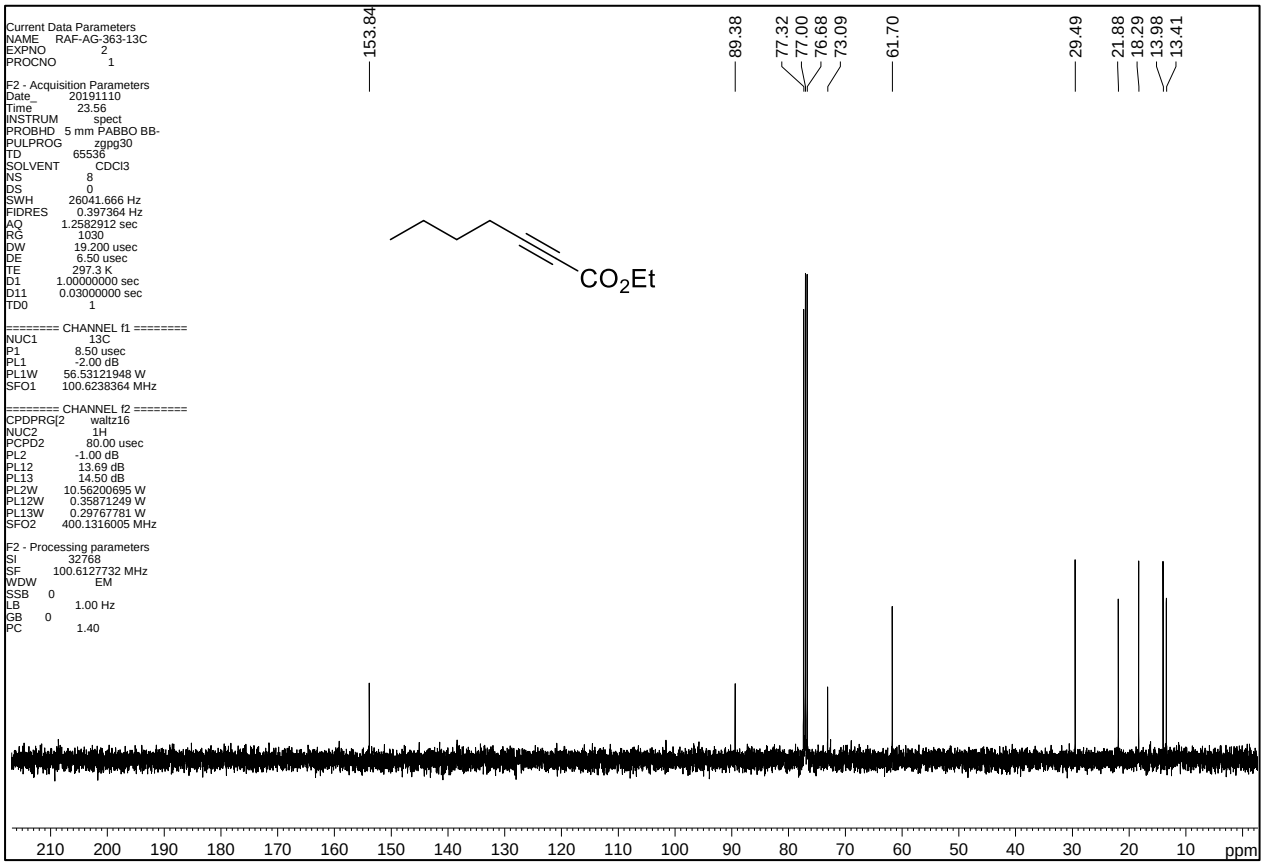
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **12i**



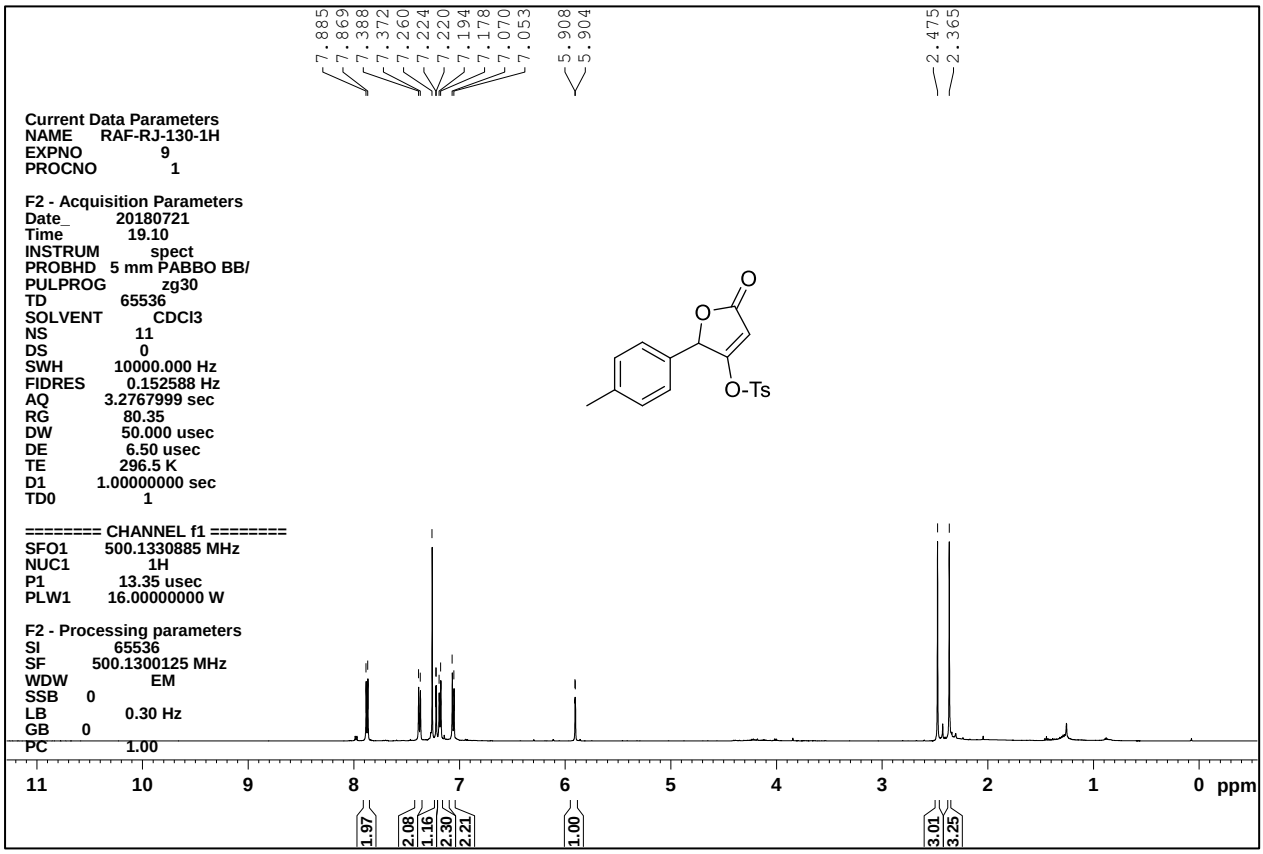


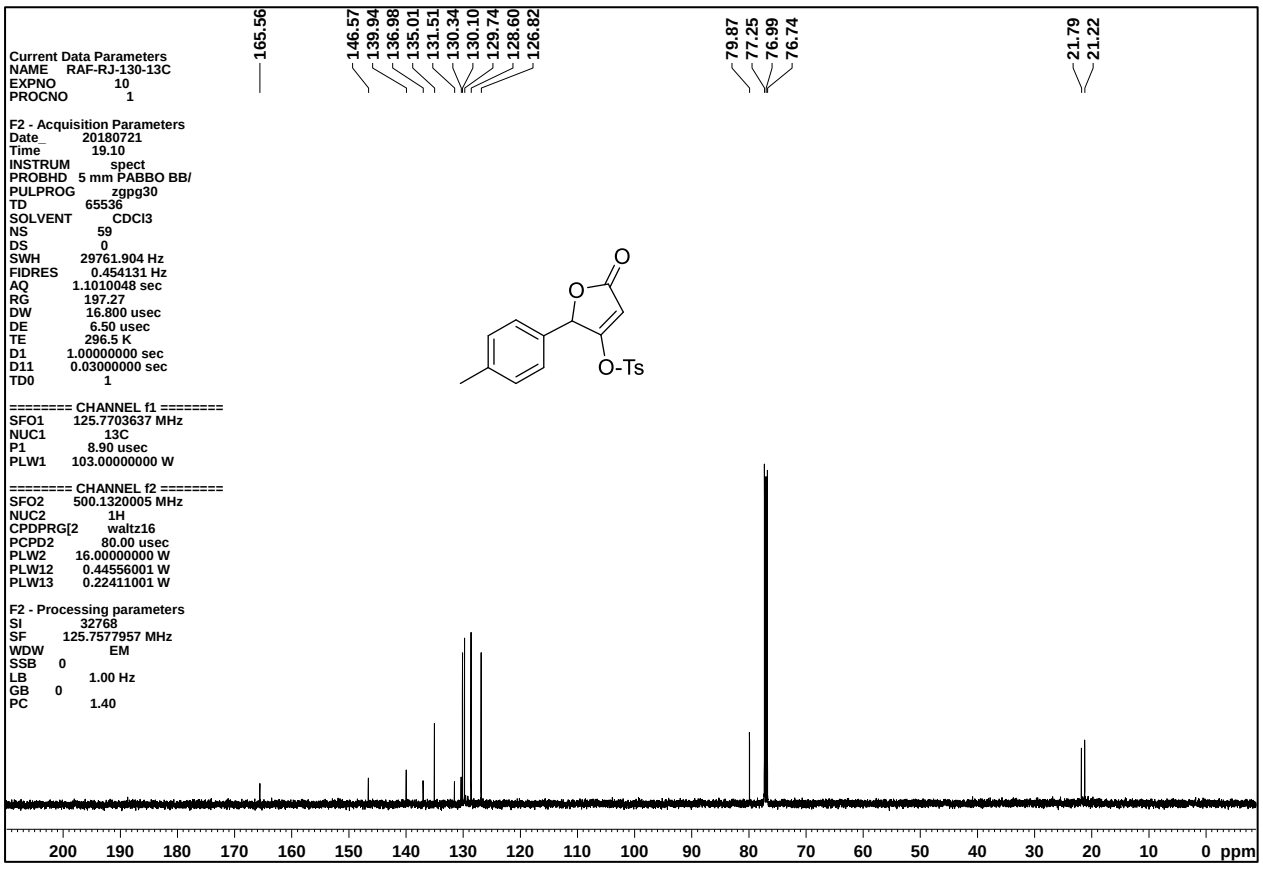
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **12j**



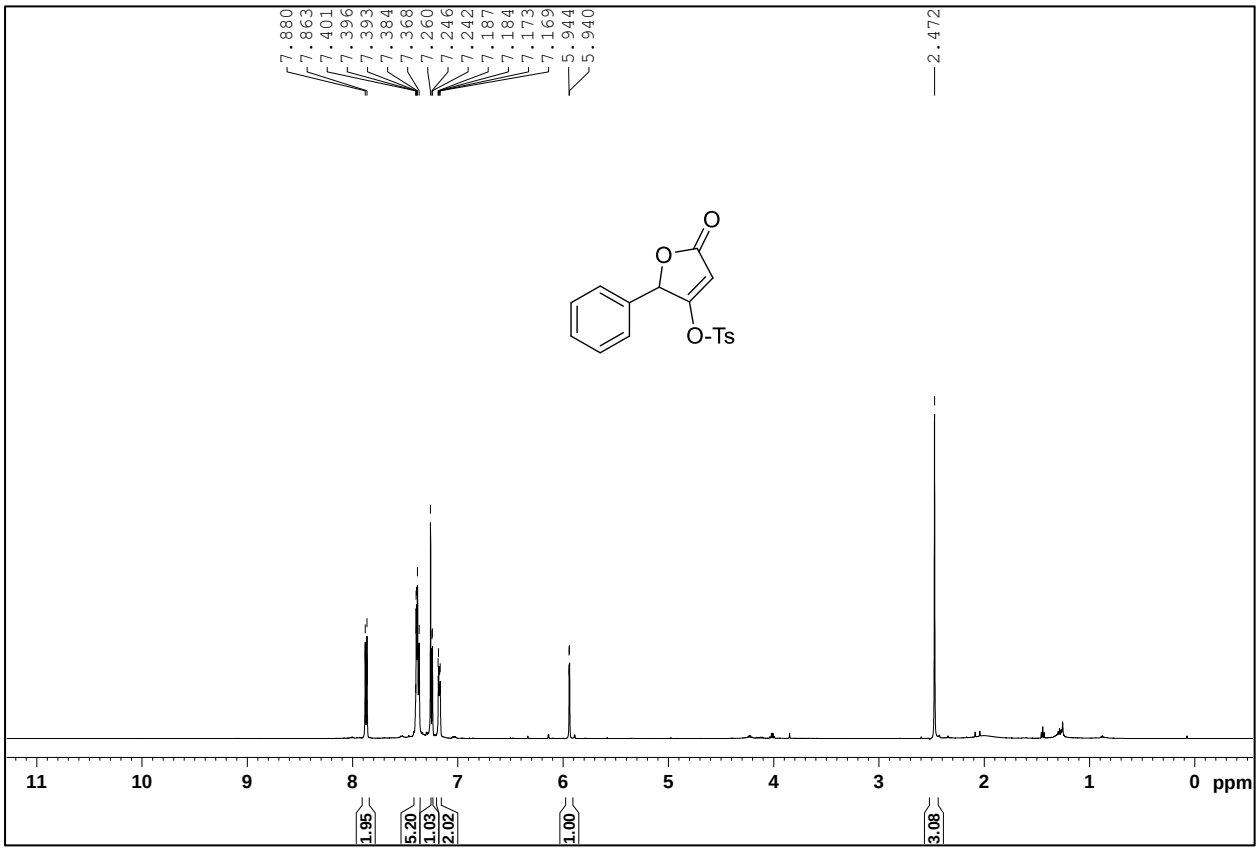


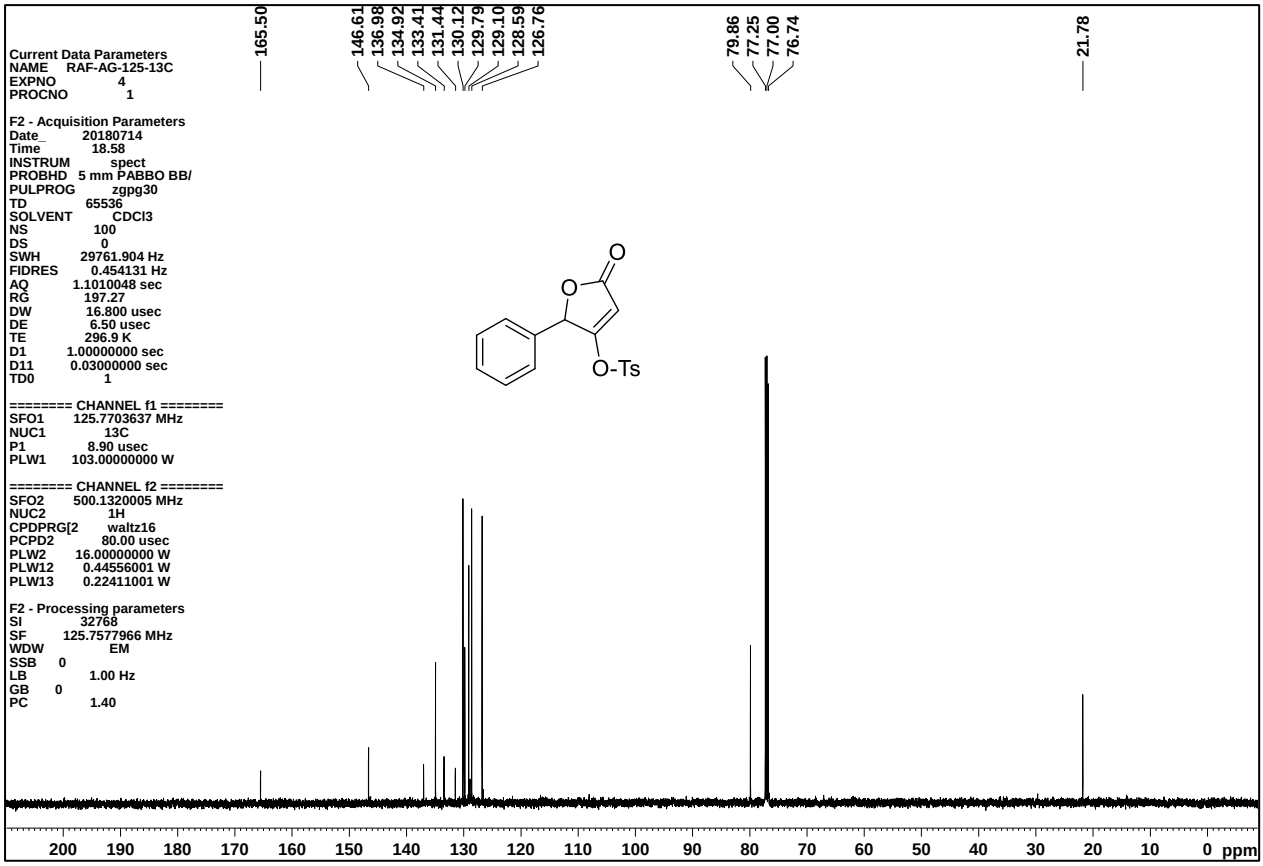
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13a**



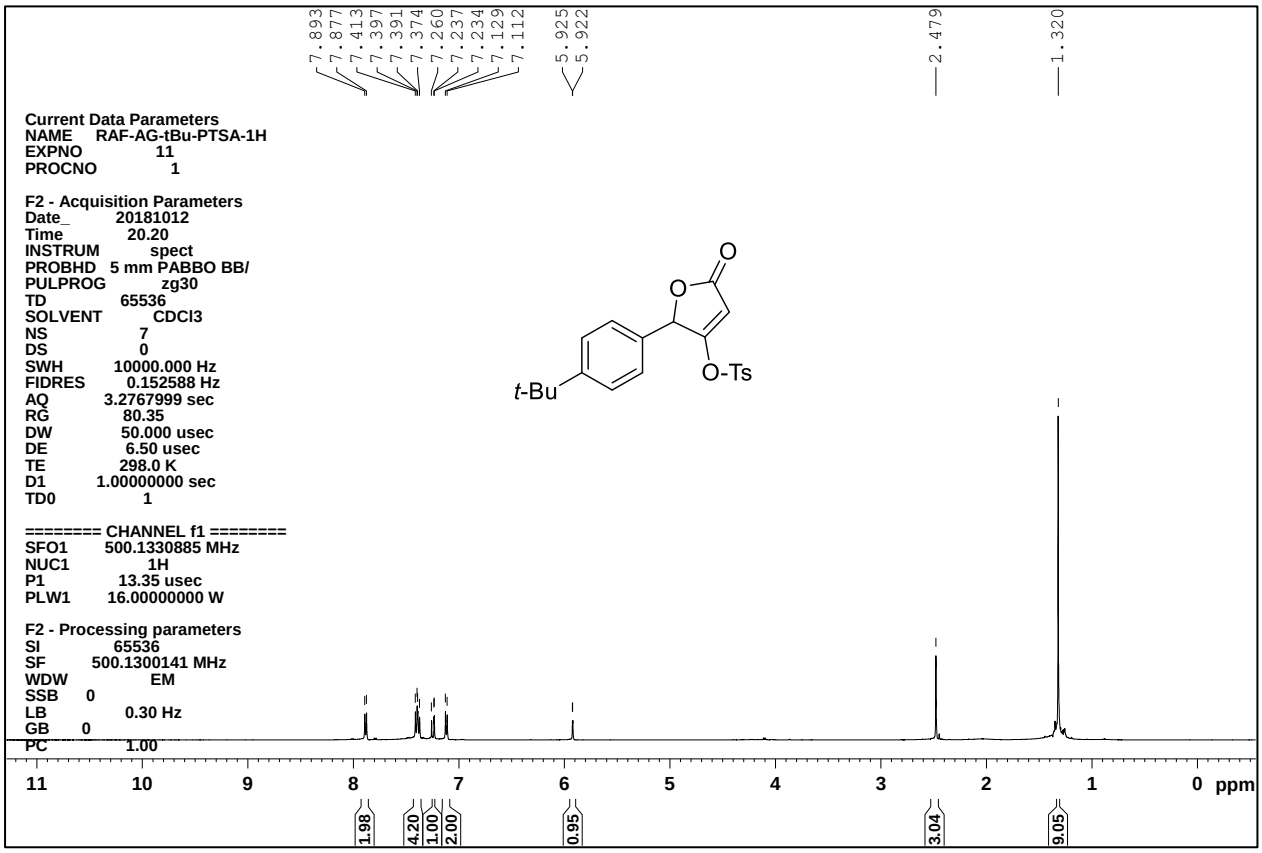


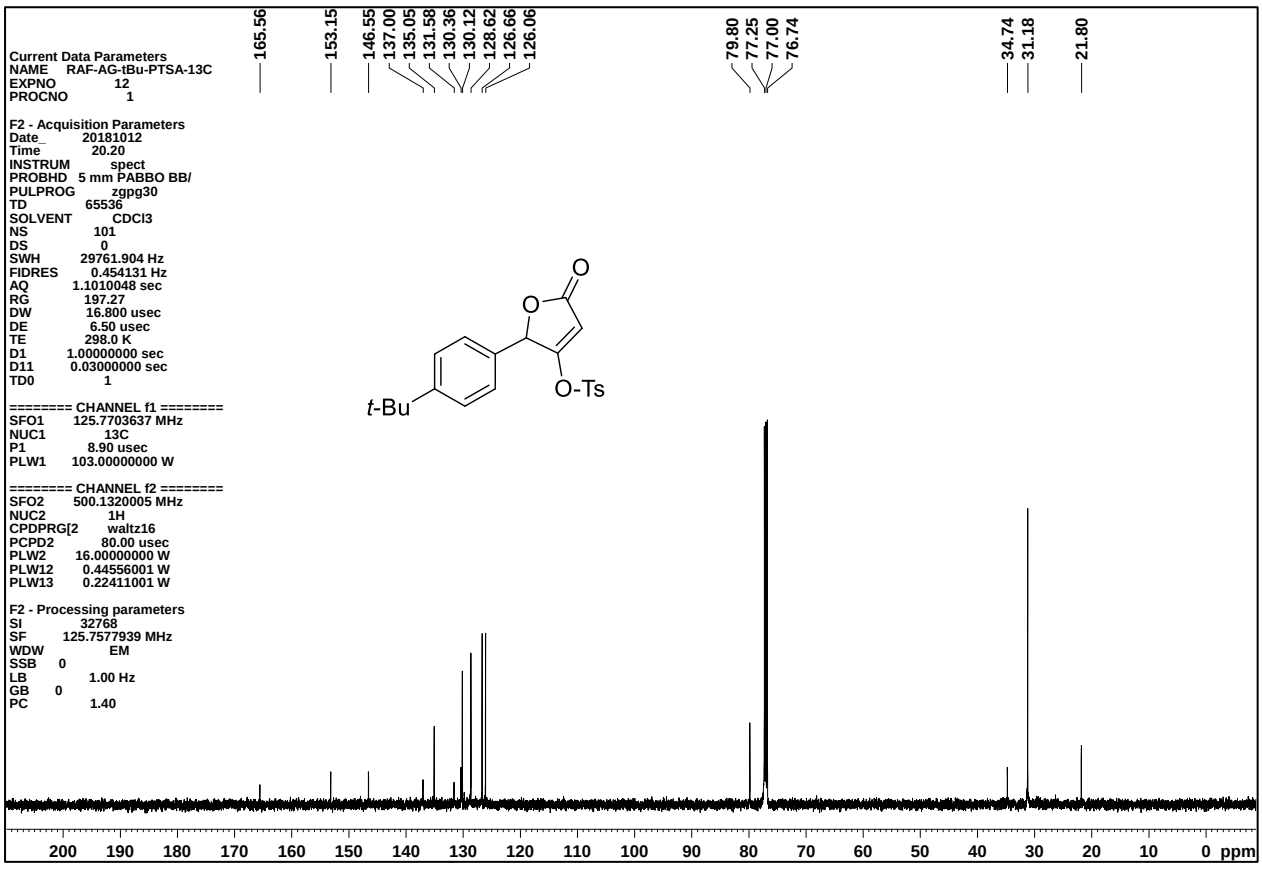
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13b**



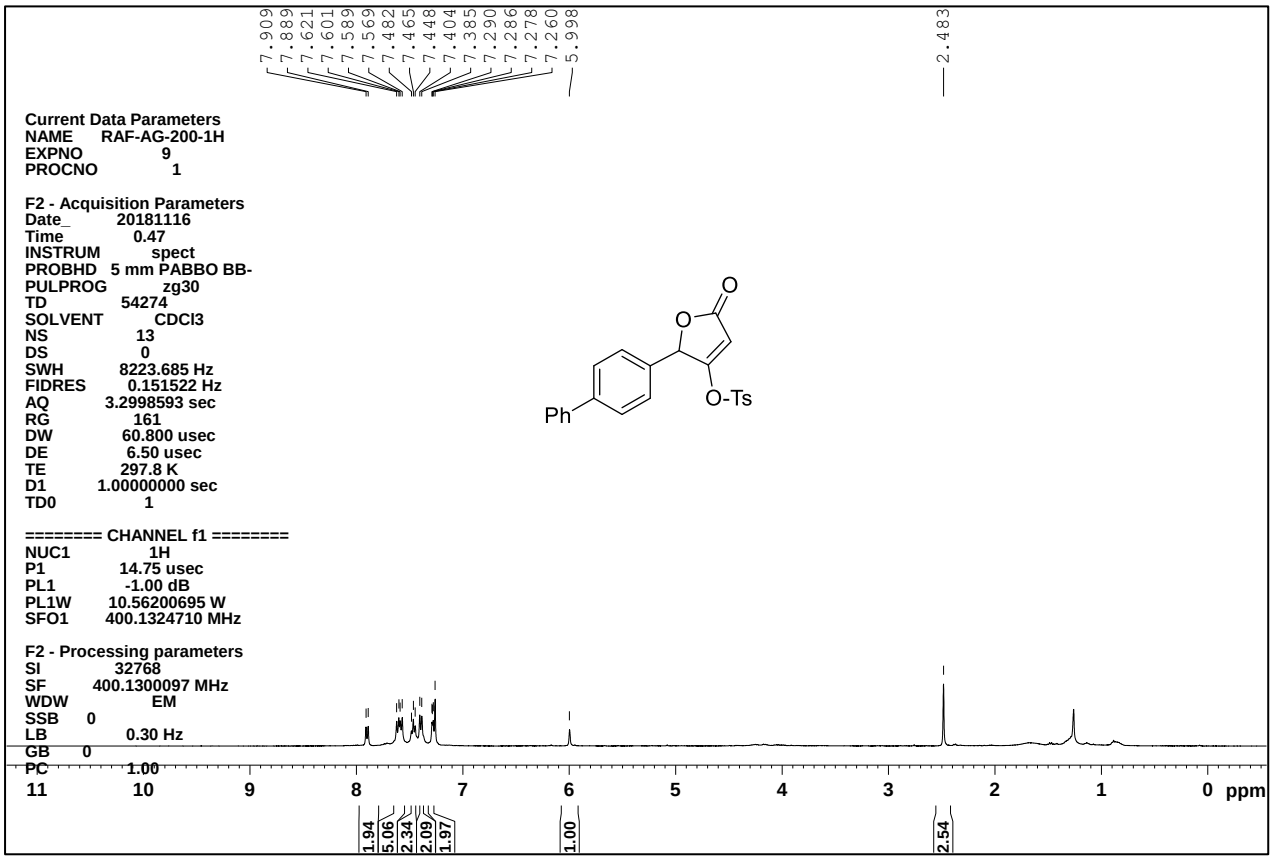


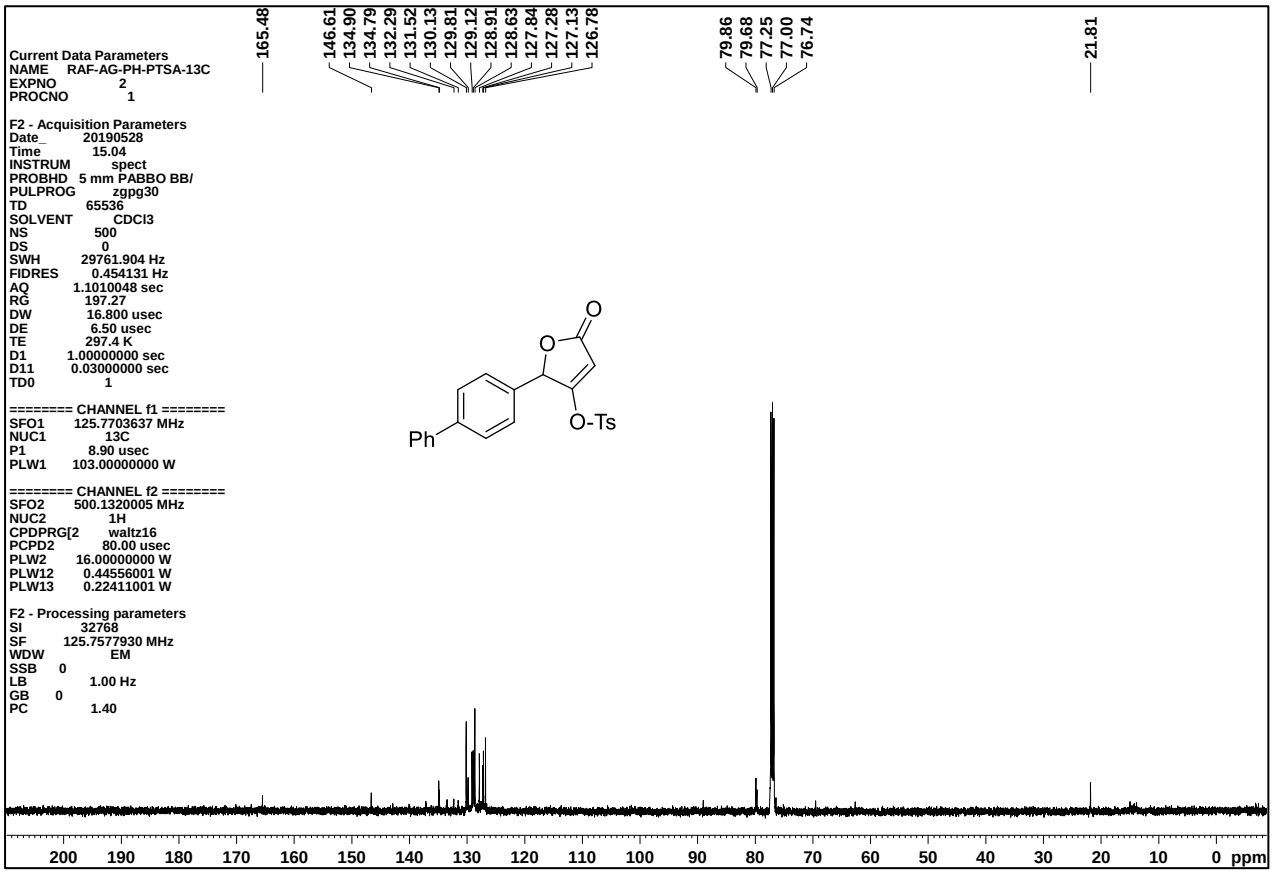
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13c**



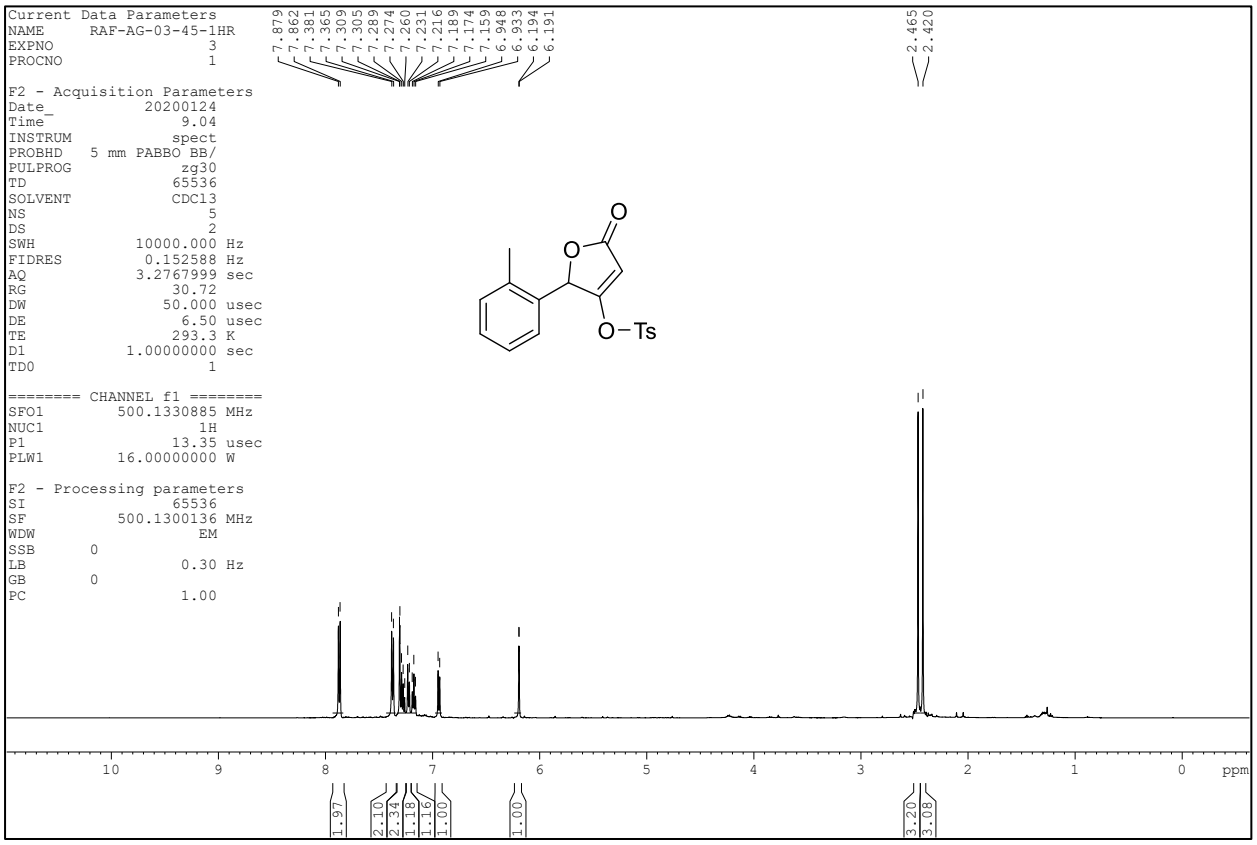


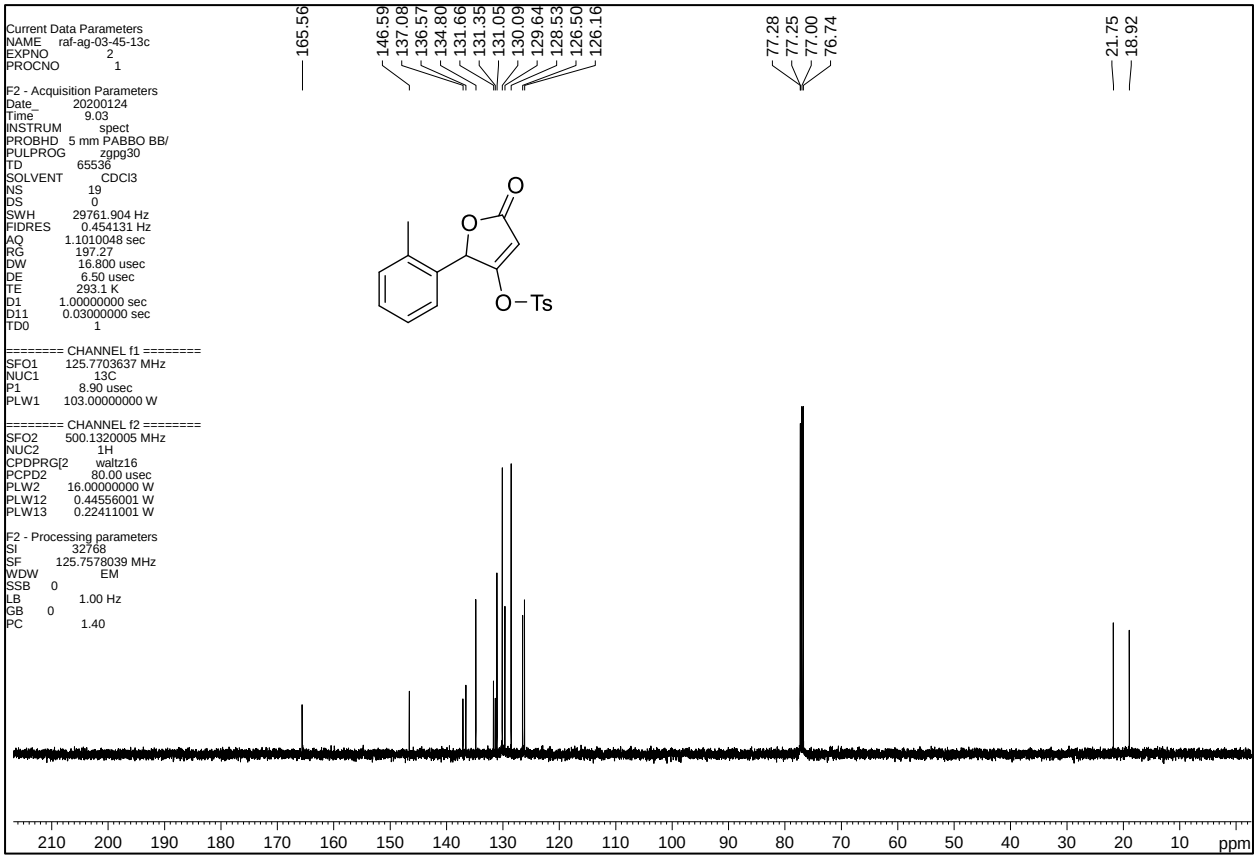
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13d**



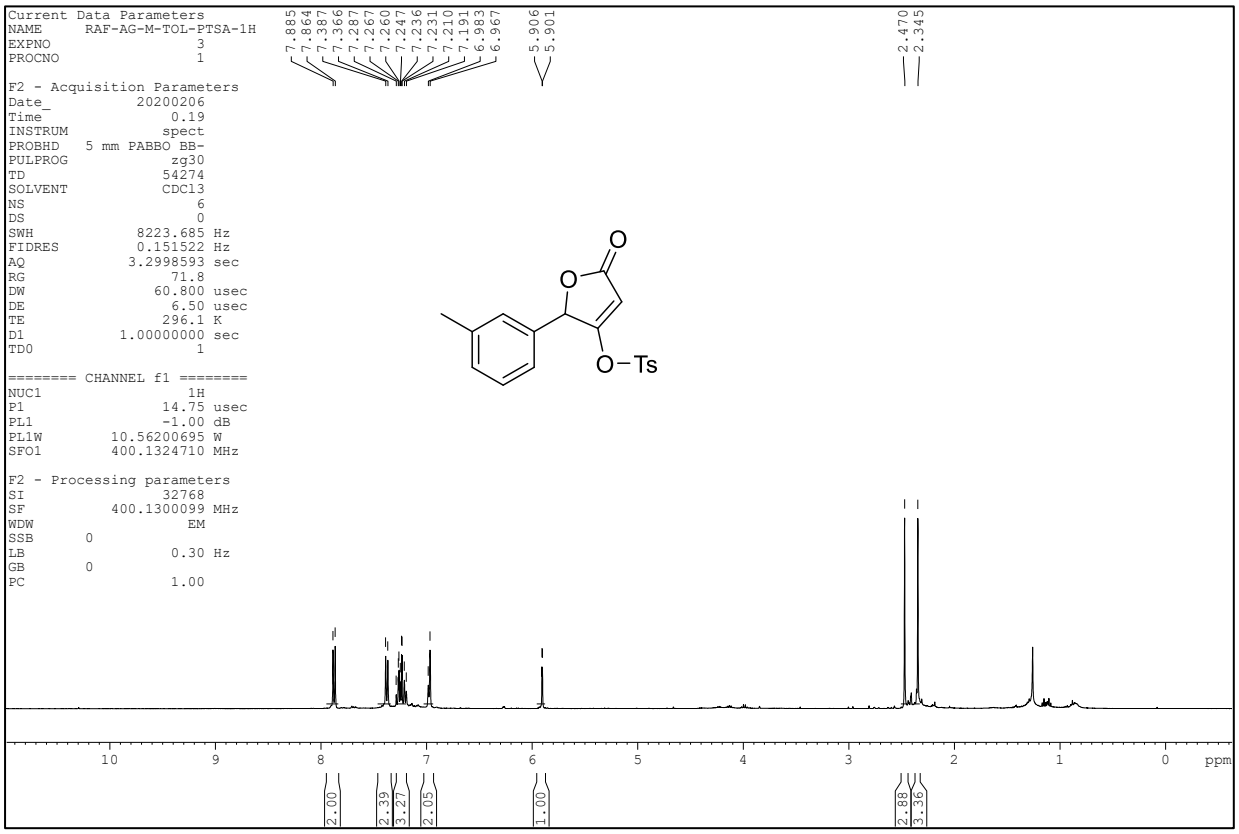


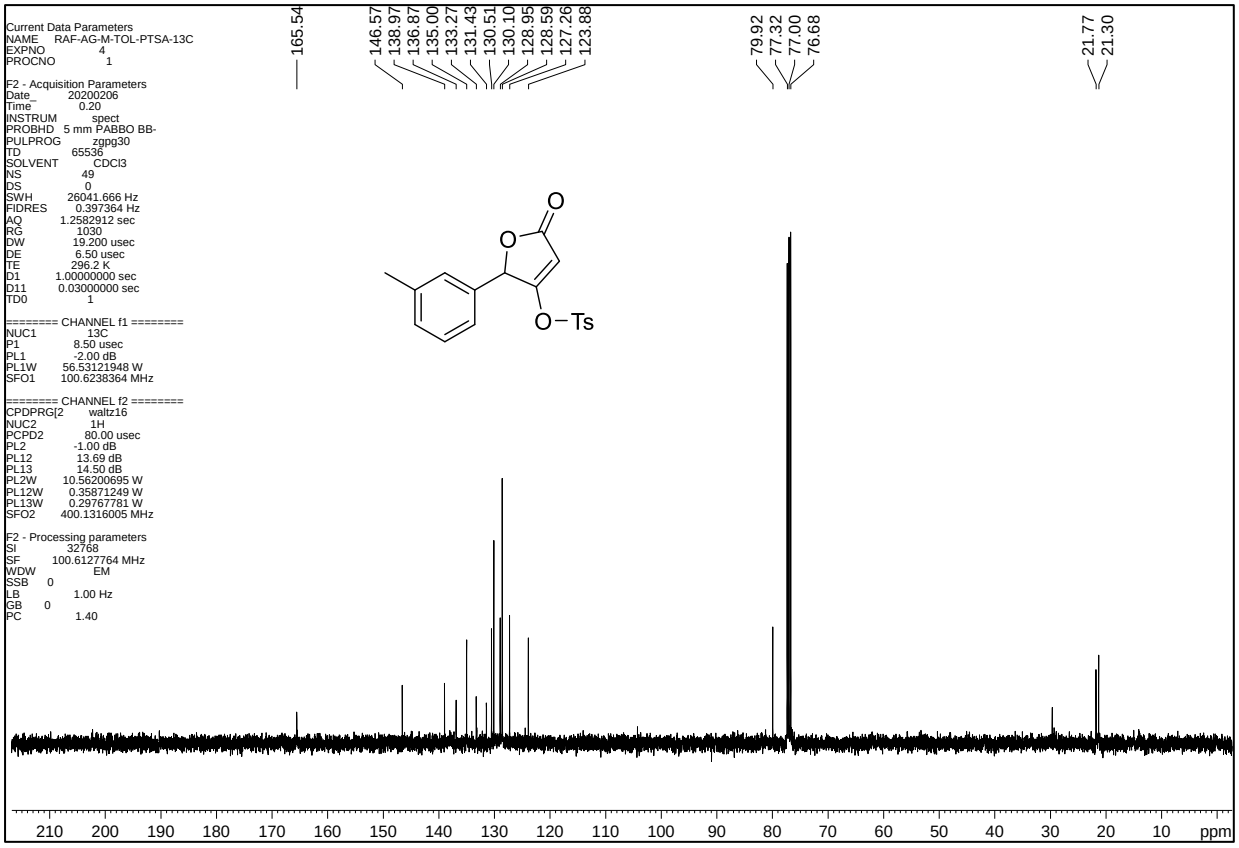
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **13g**



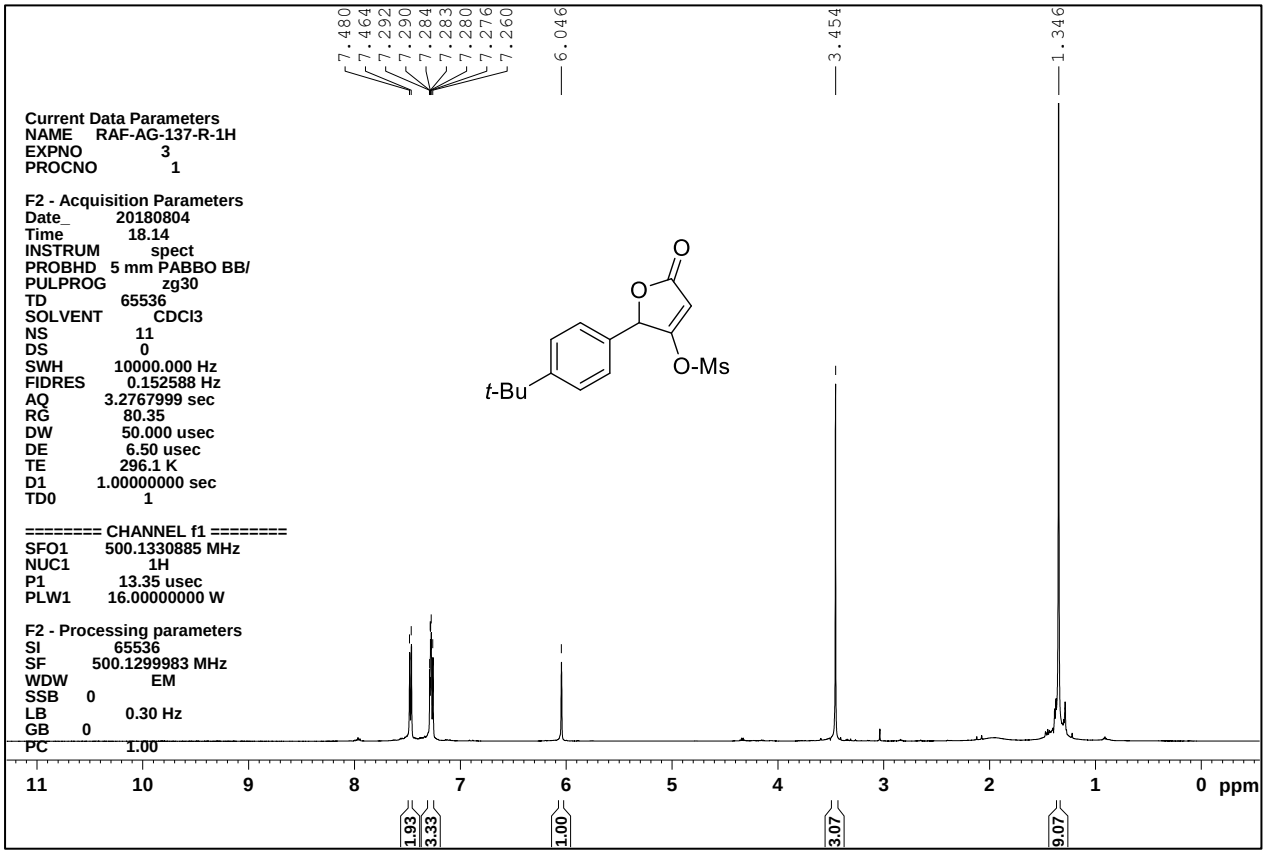


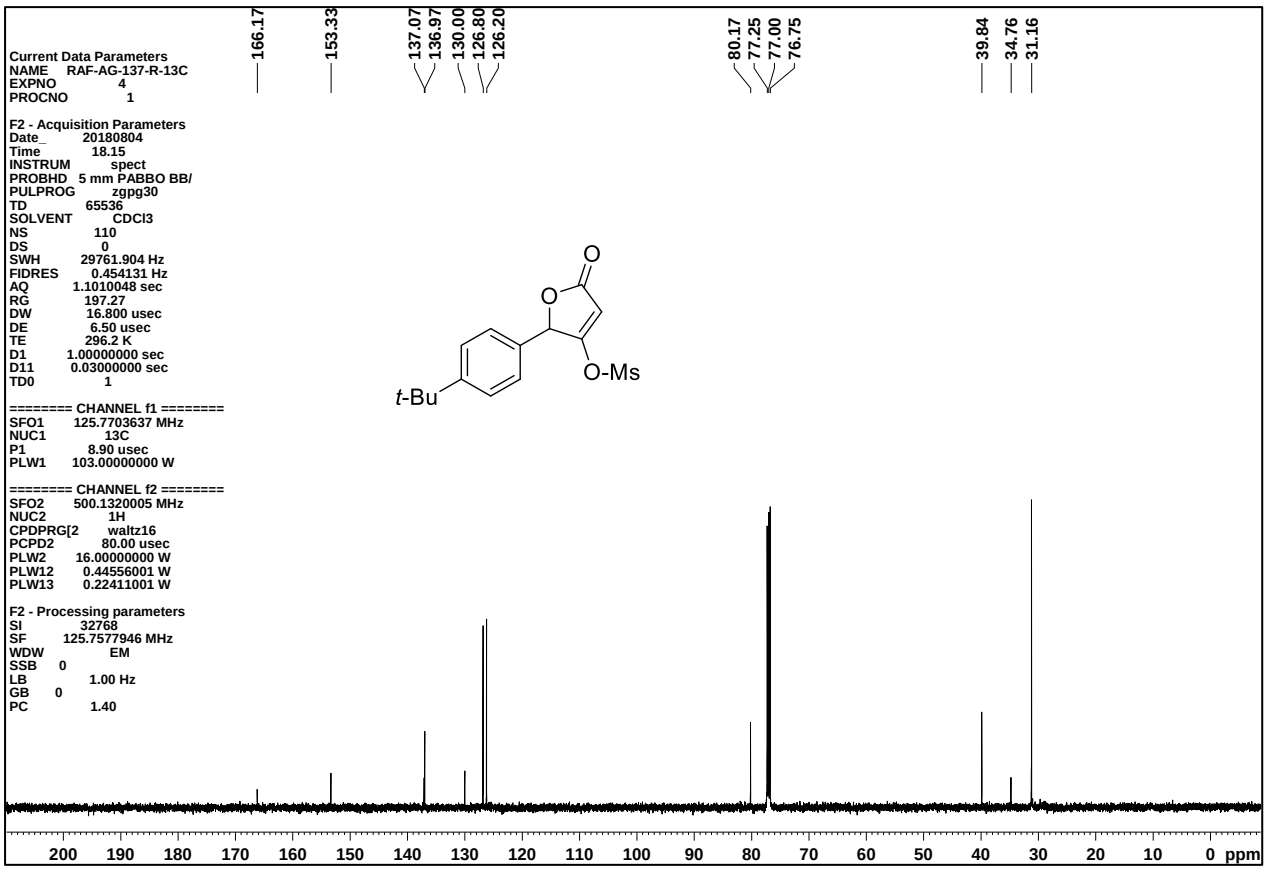
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **13h**



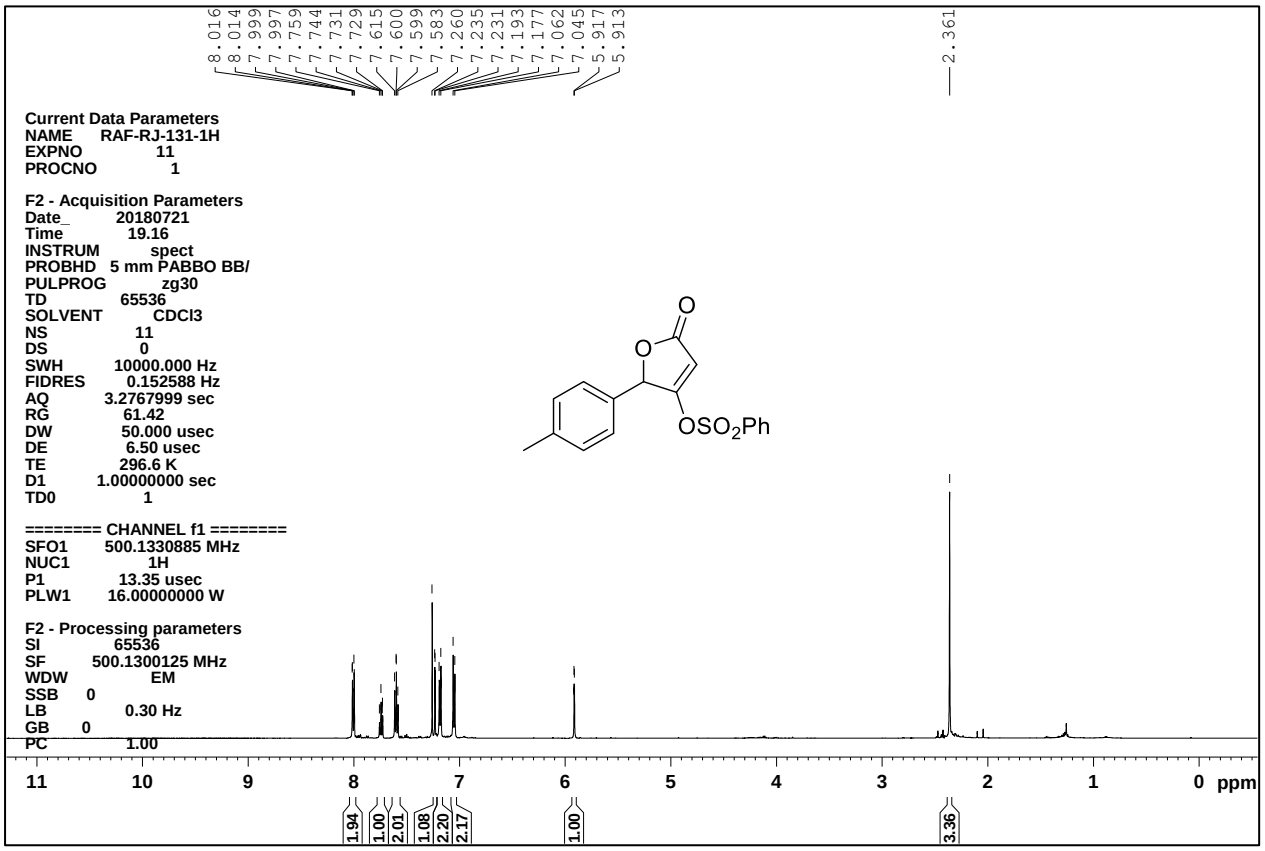


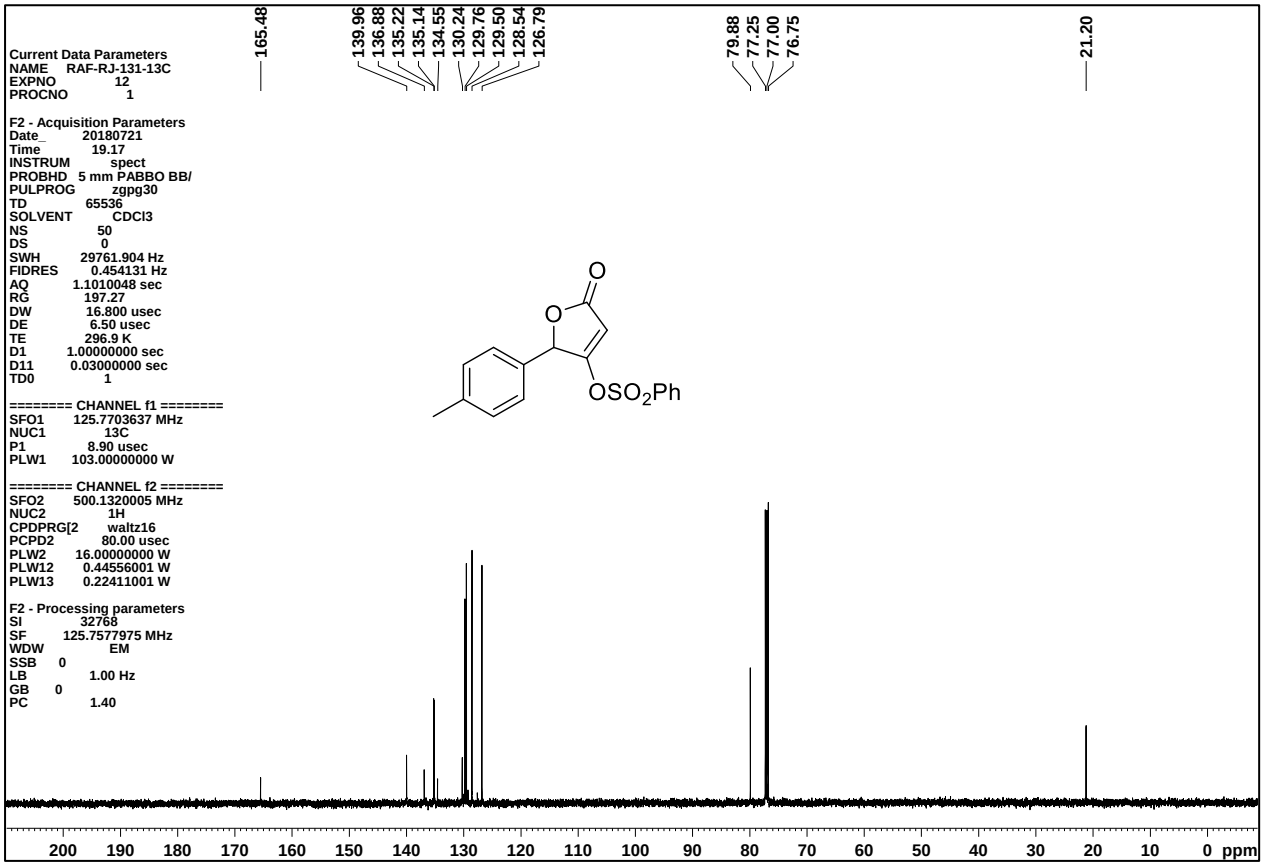
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **14**



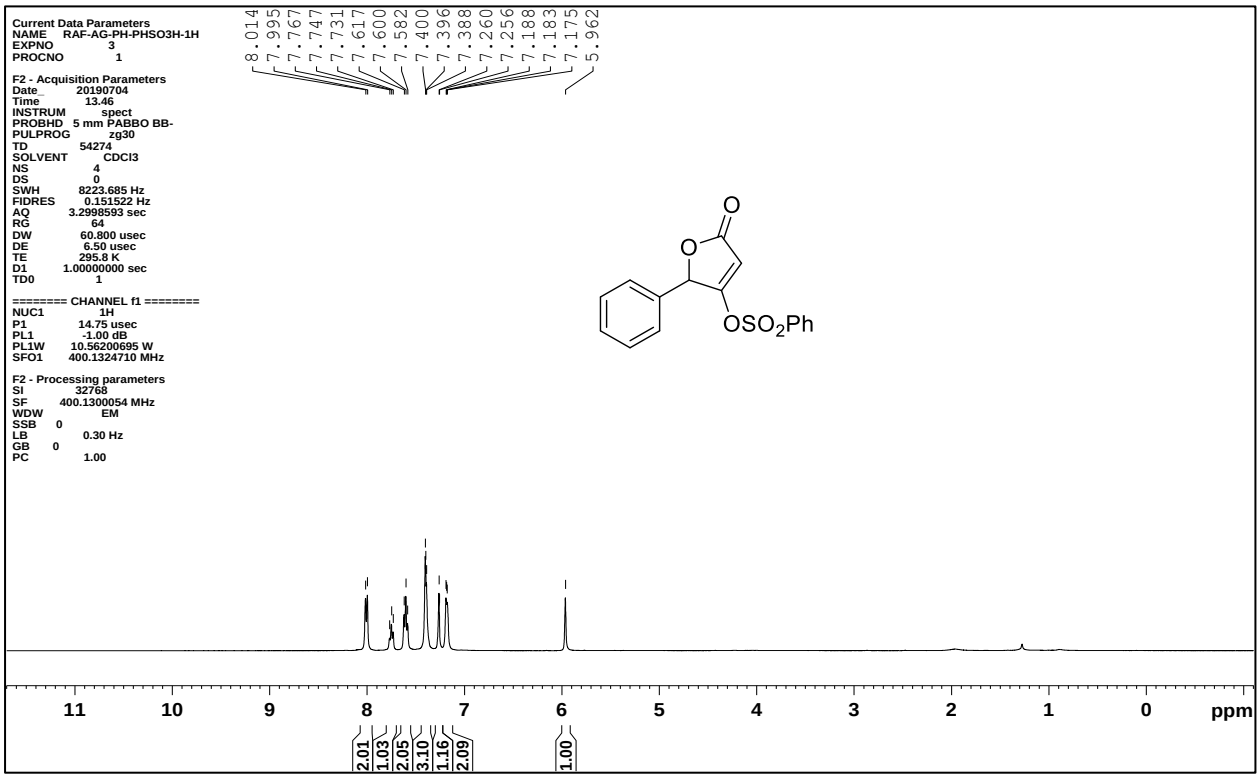


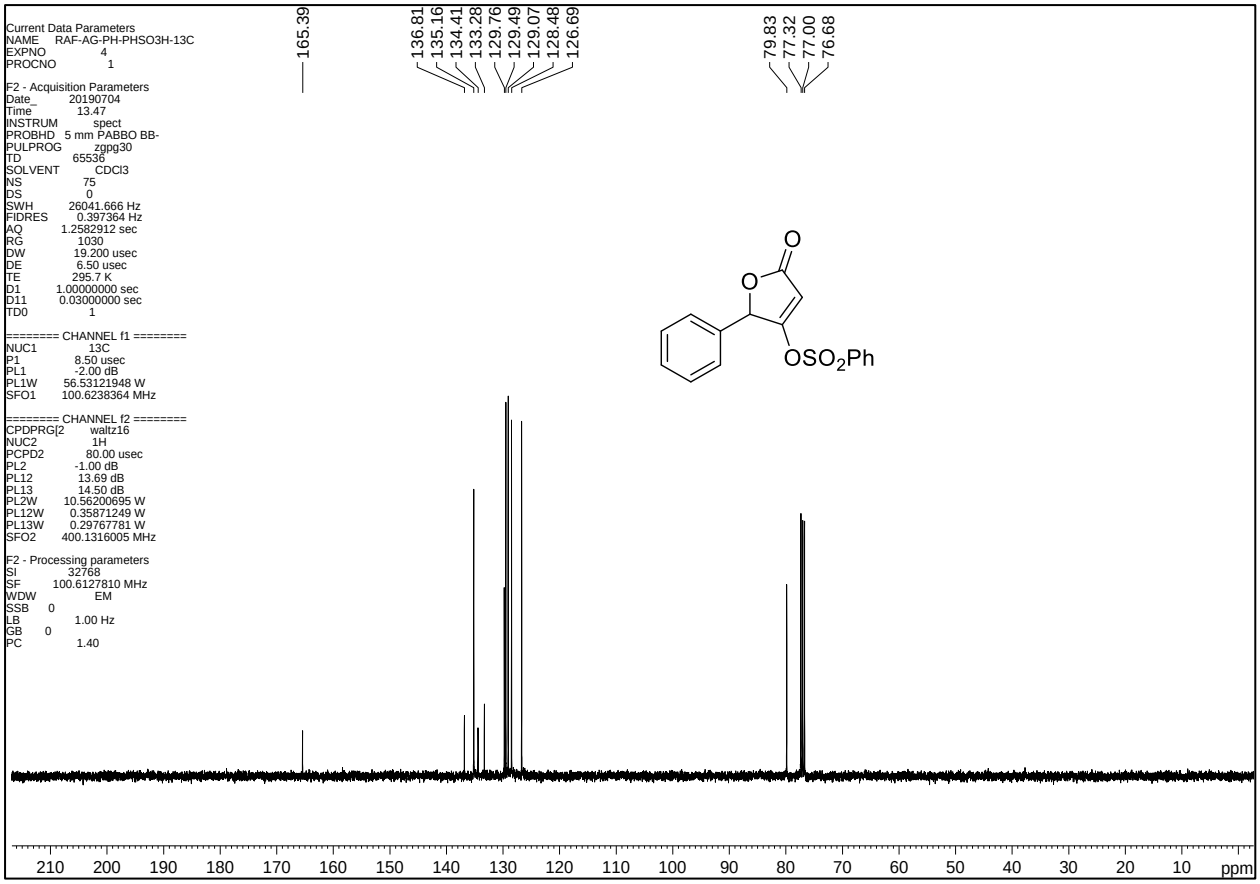
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **15a**



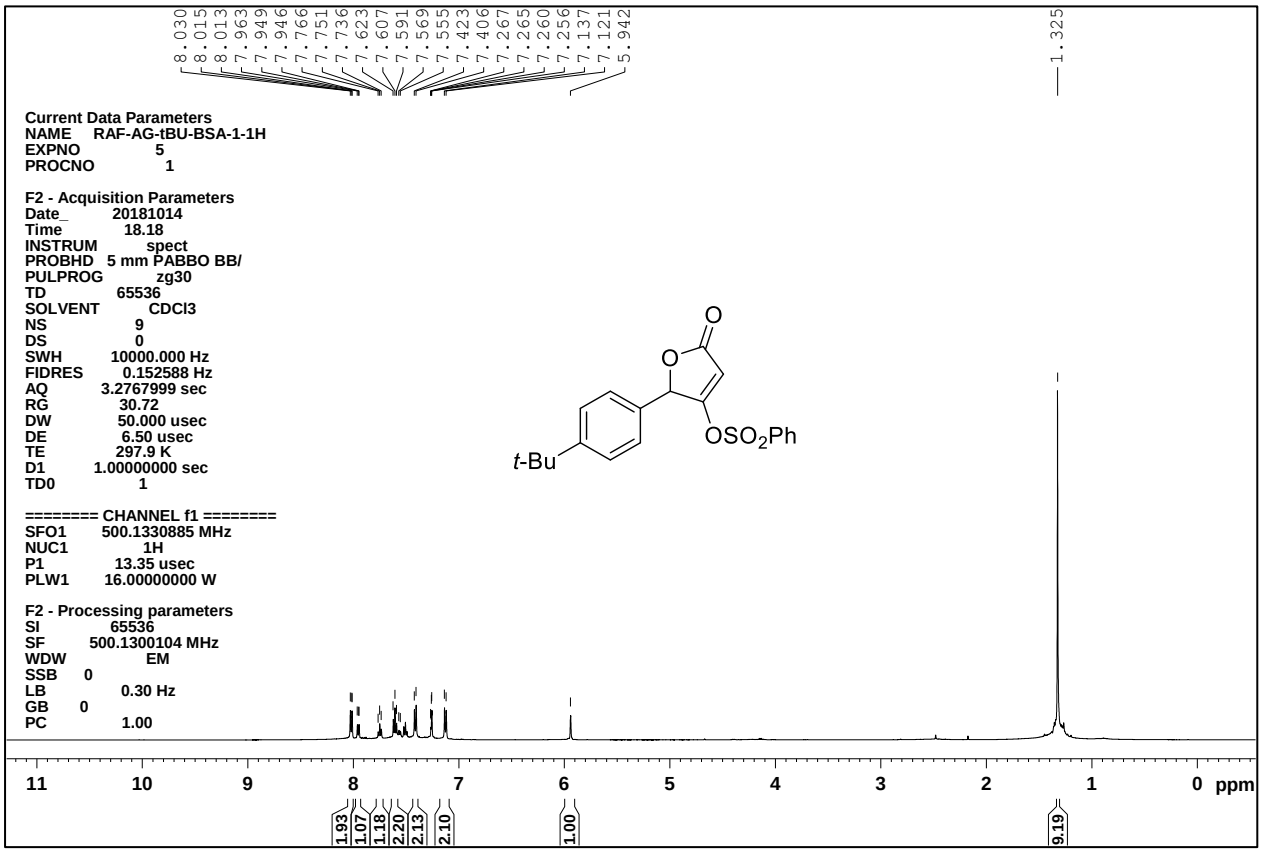


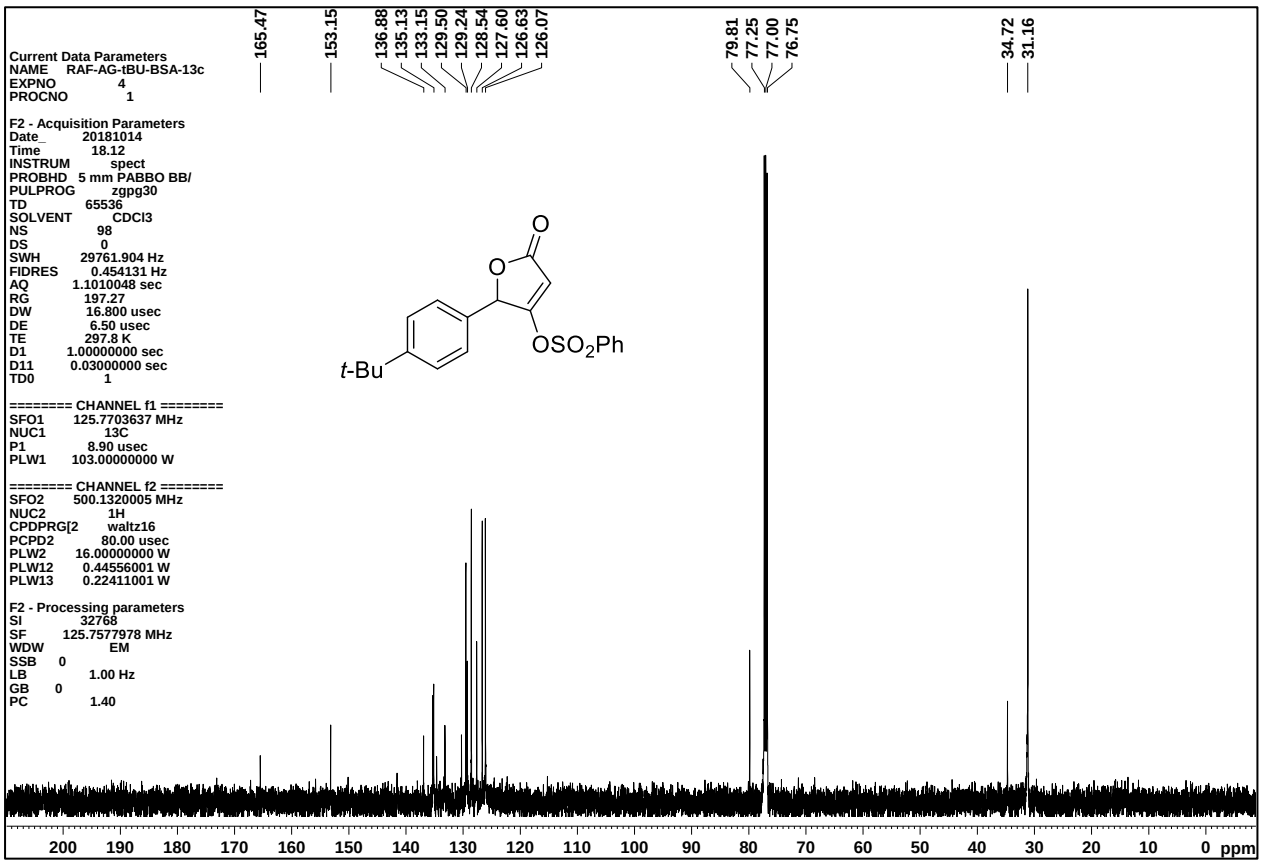
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound **15b**



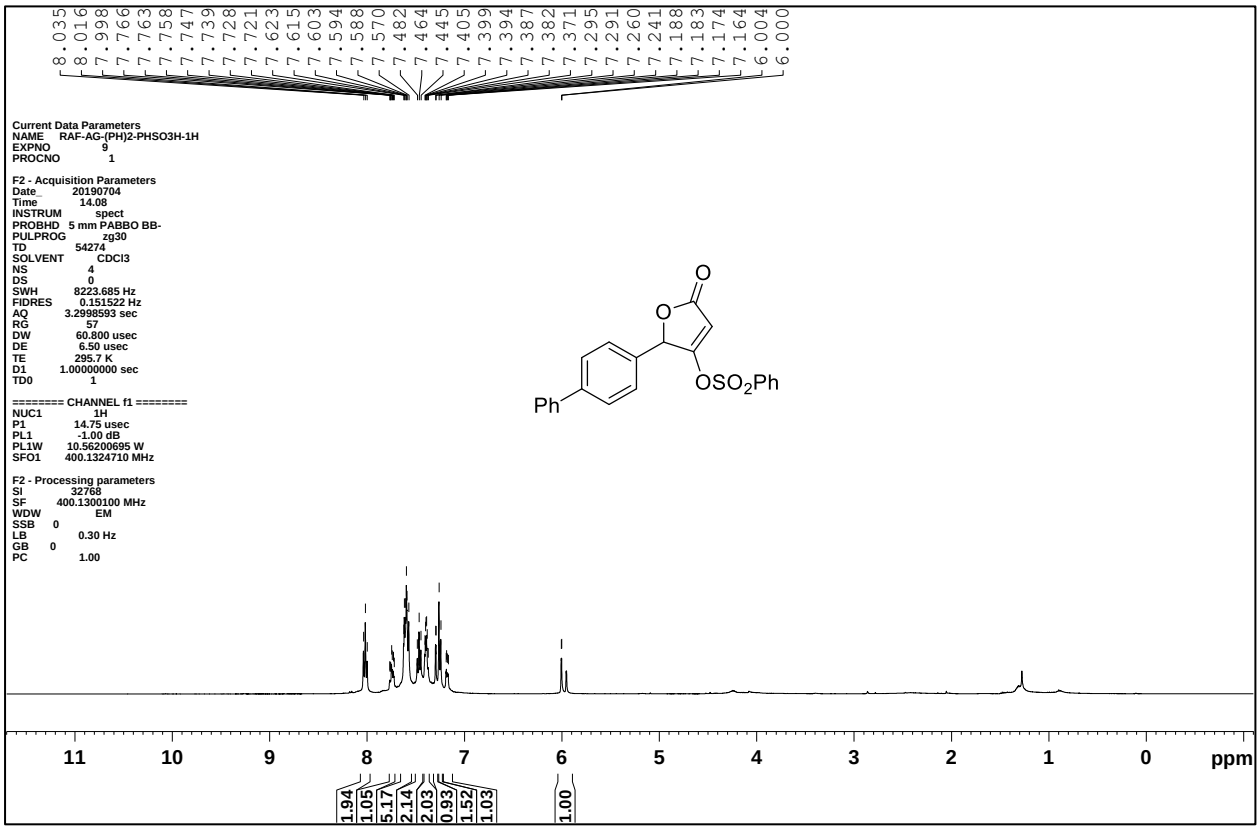


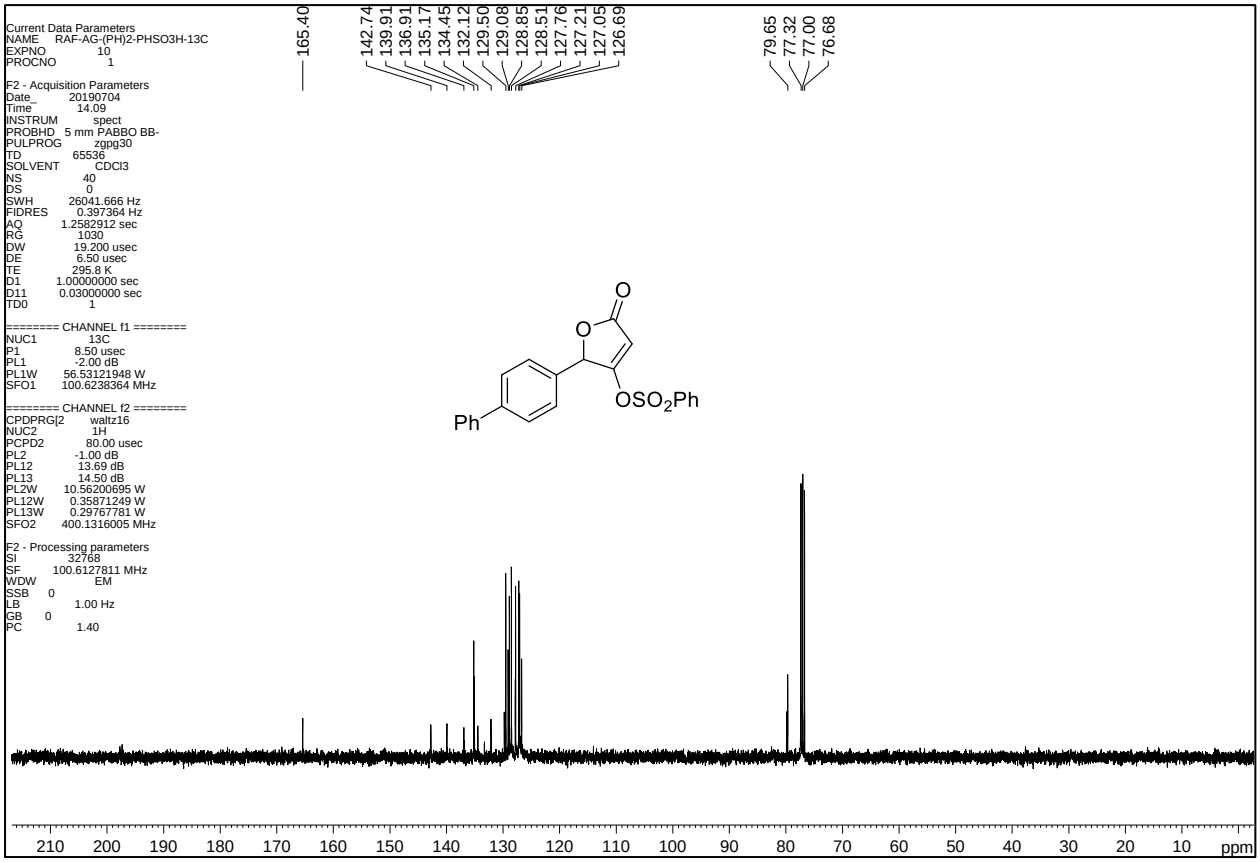
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **15c**



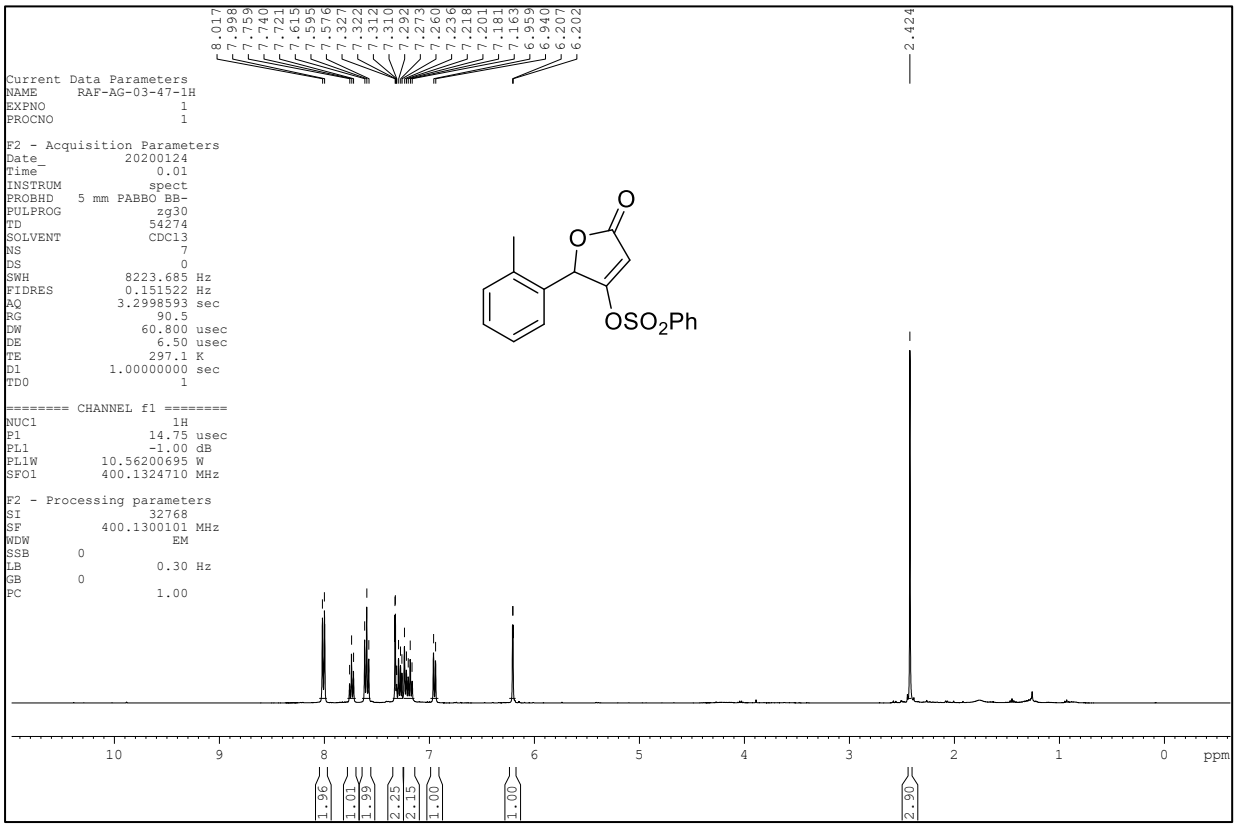


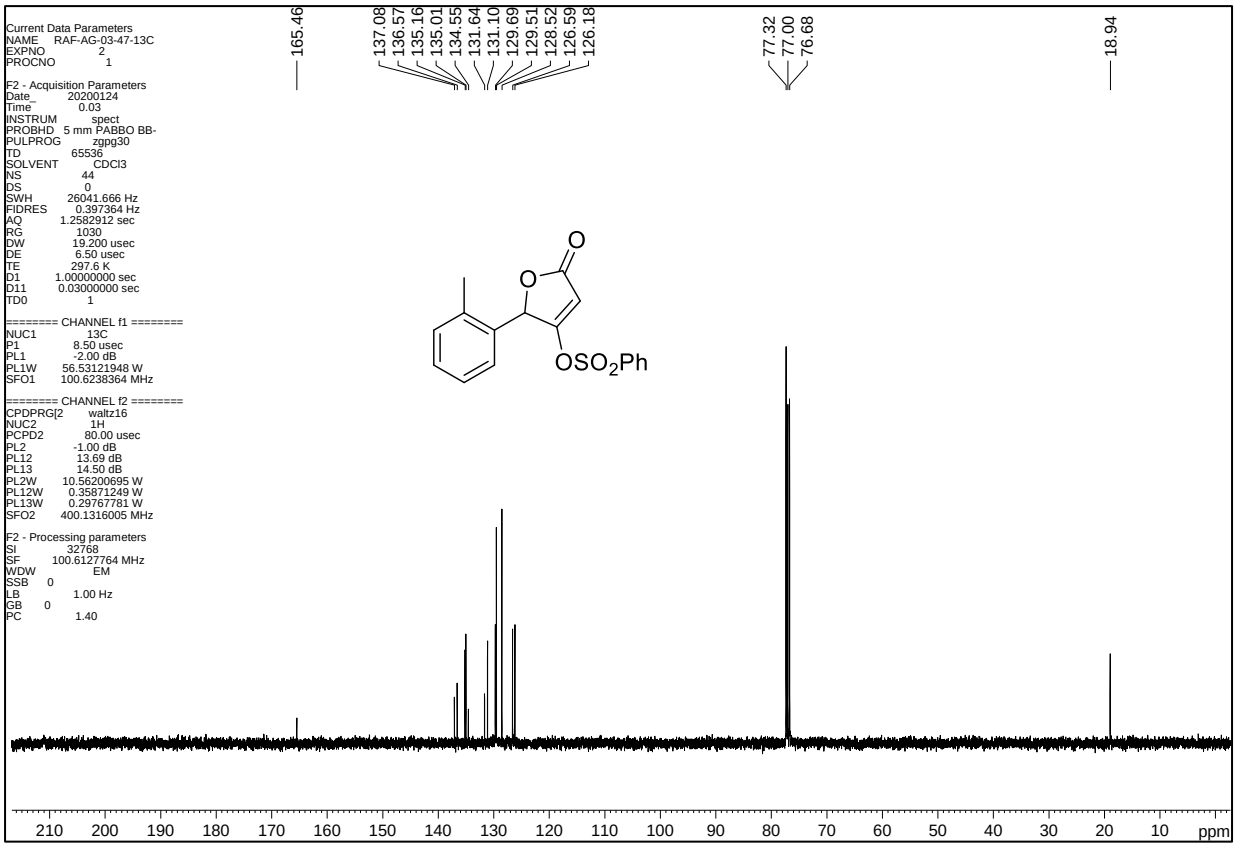
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound **15d**



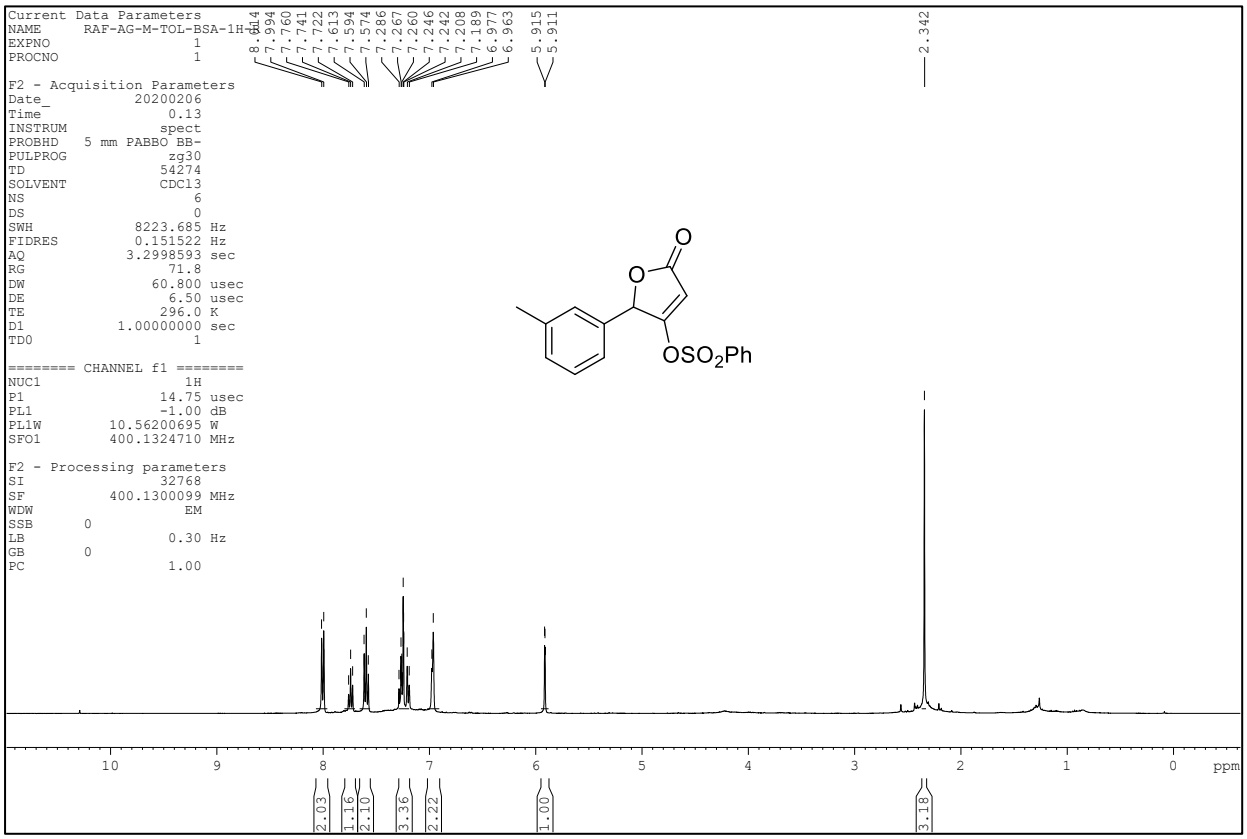


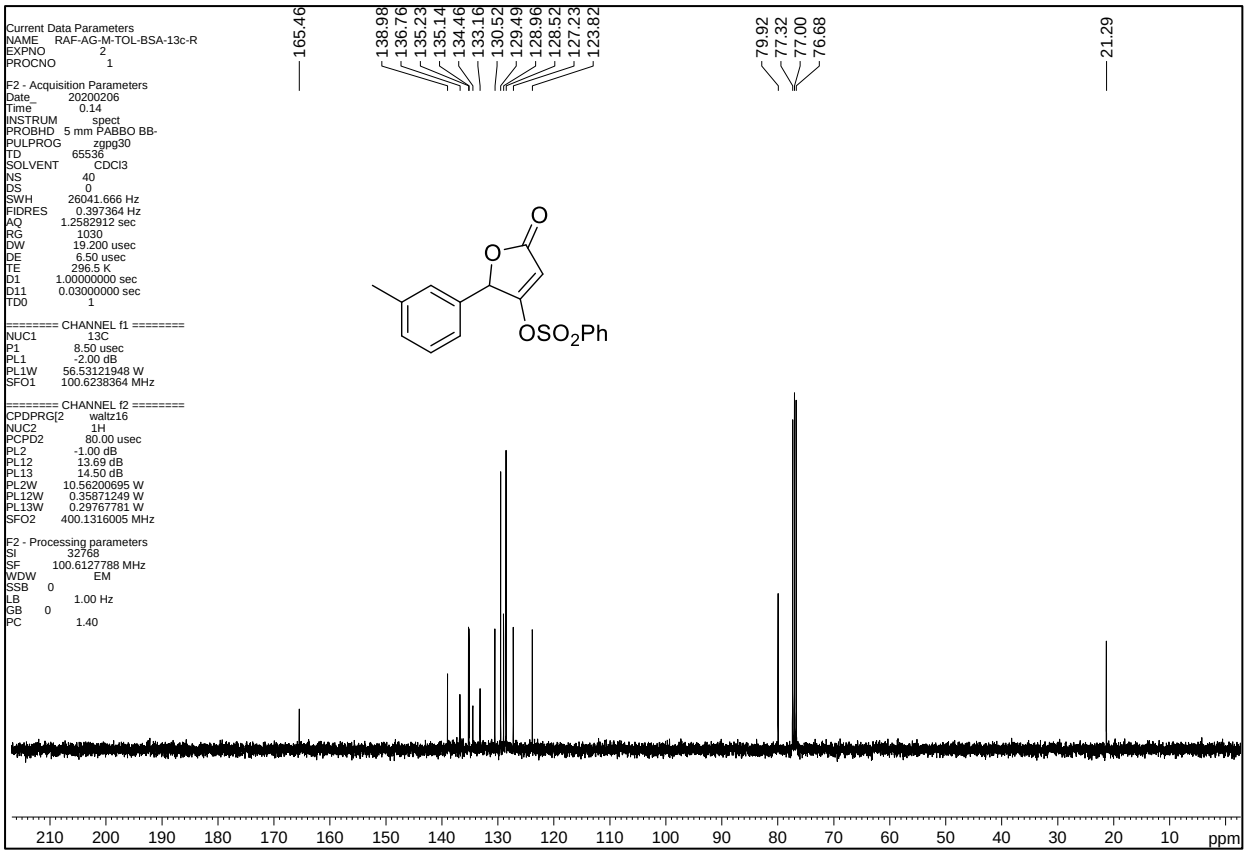
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **15g**



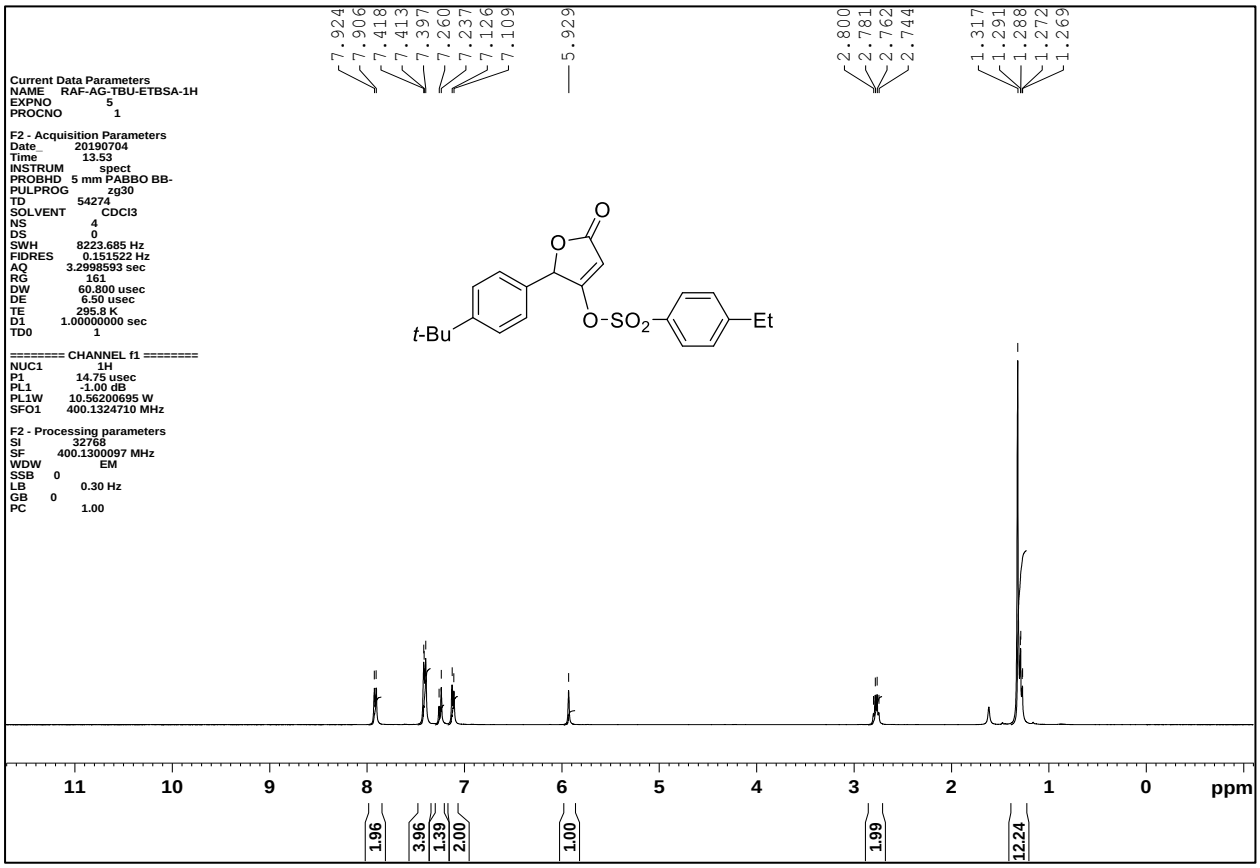


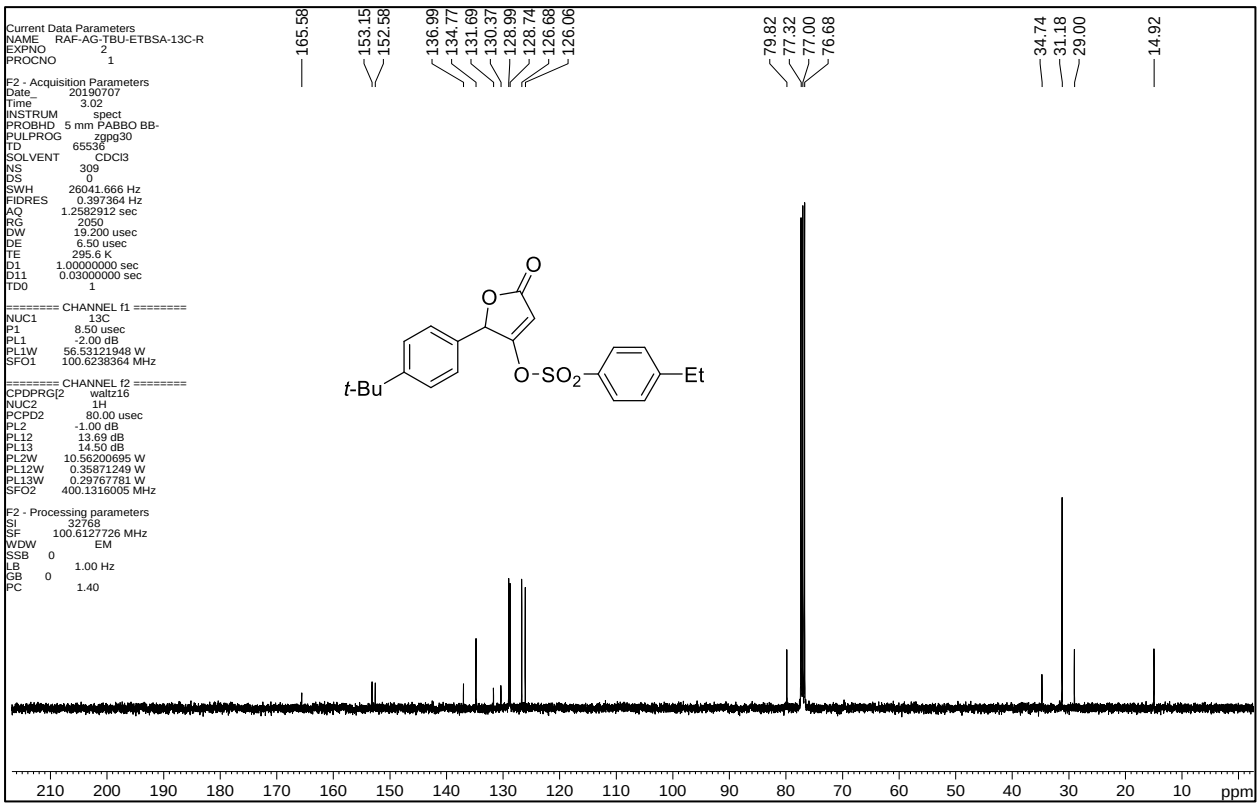
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **15h**



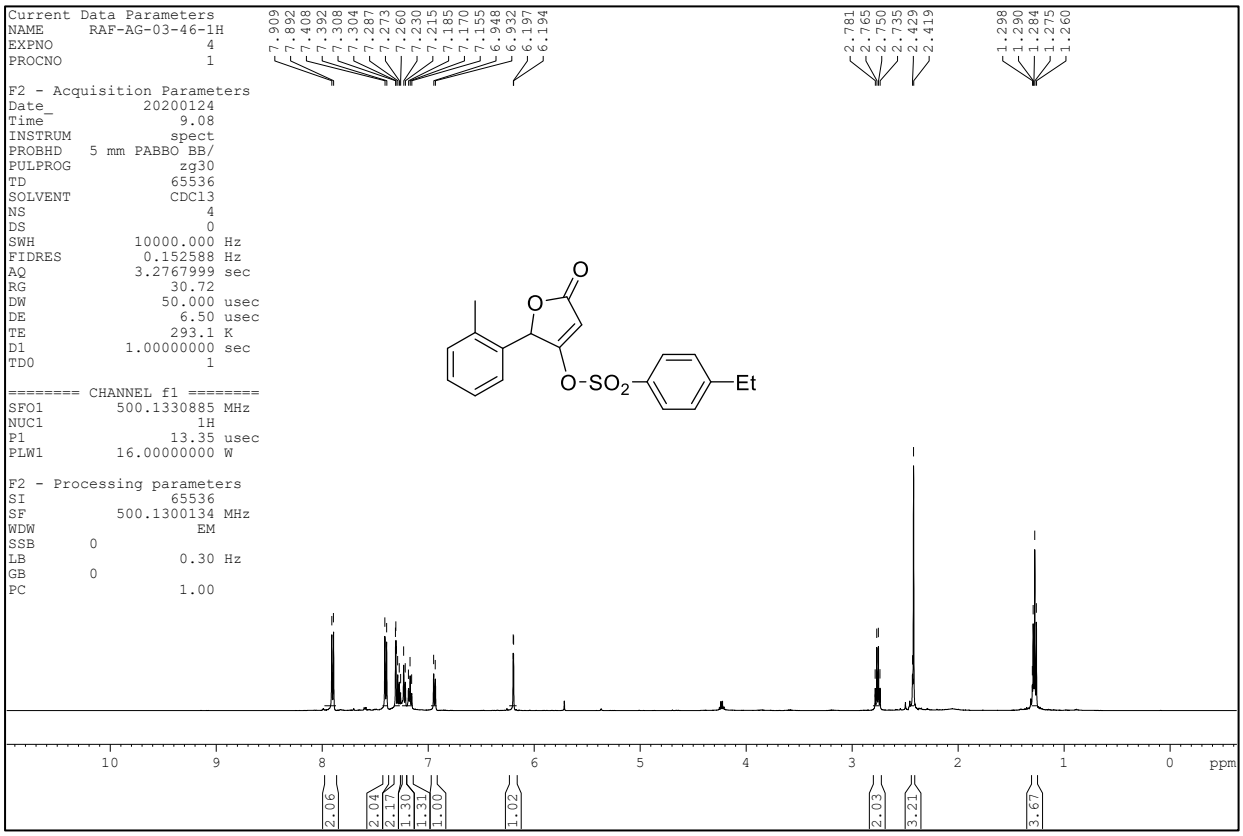


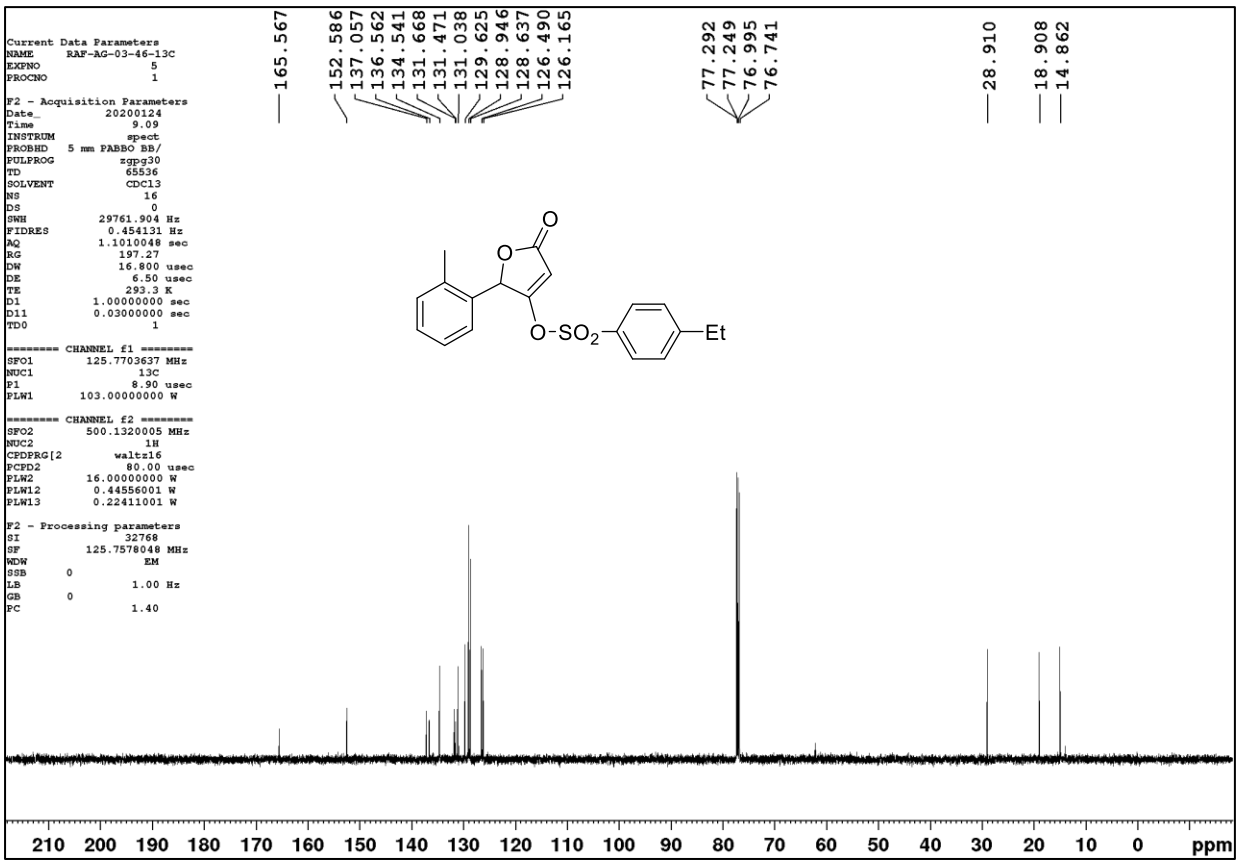
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of compound **16c**



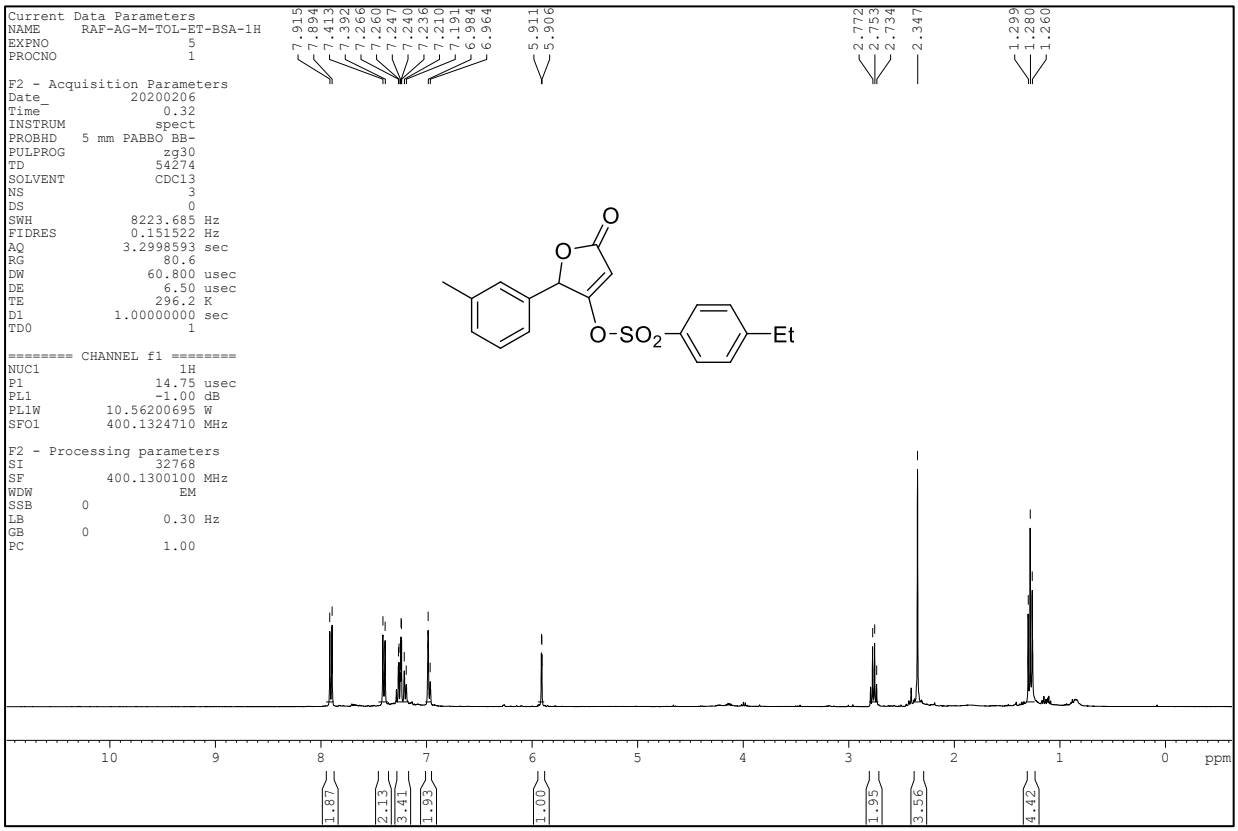


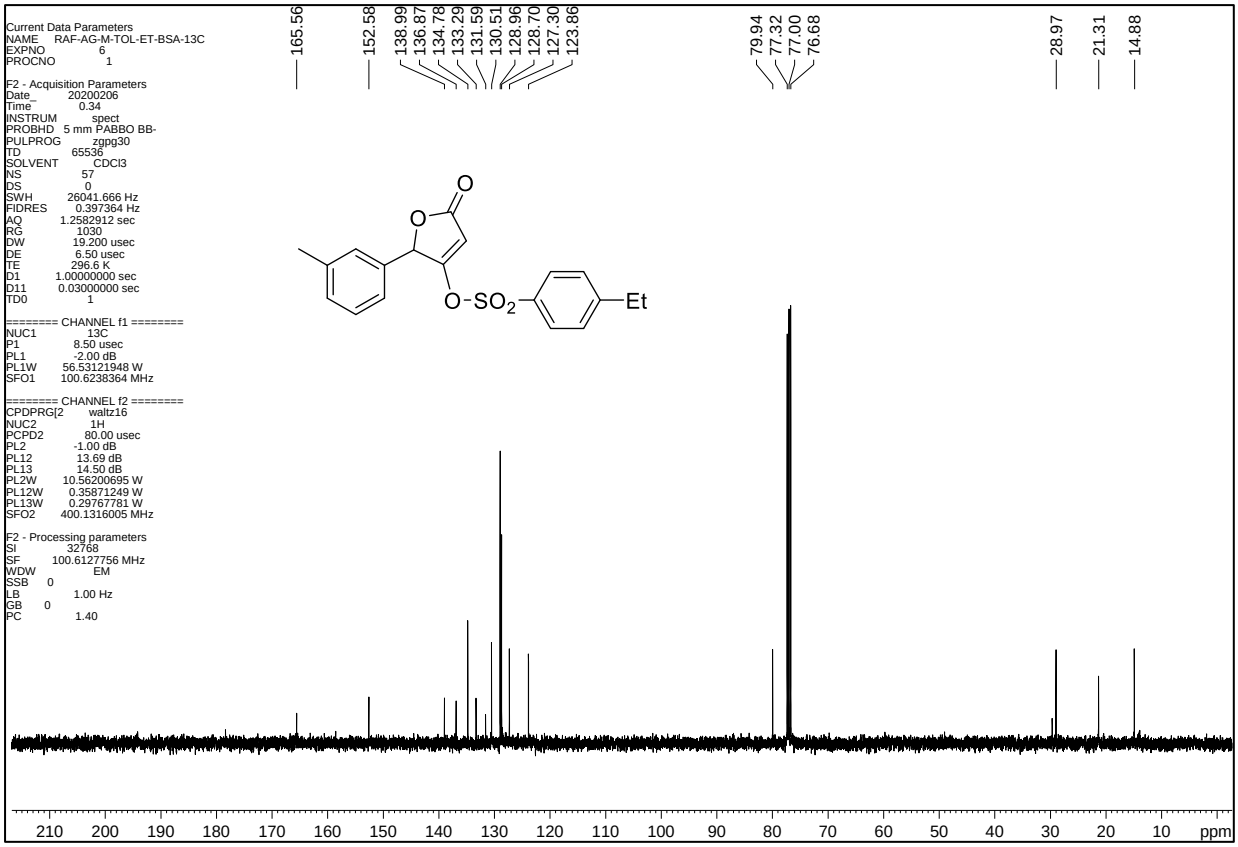
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **16g**



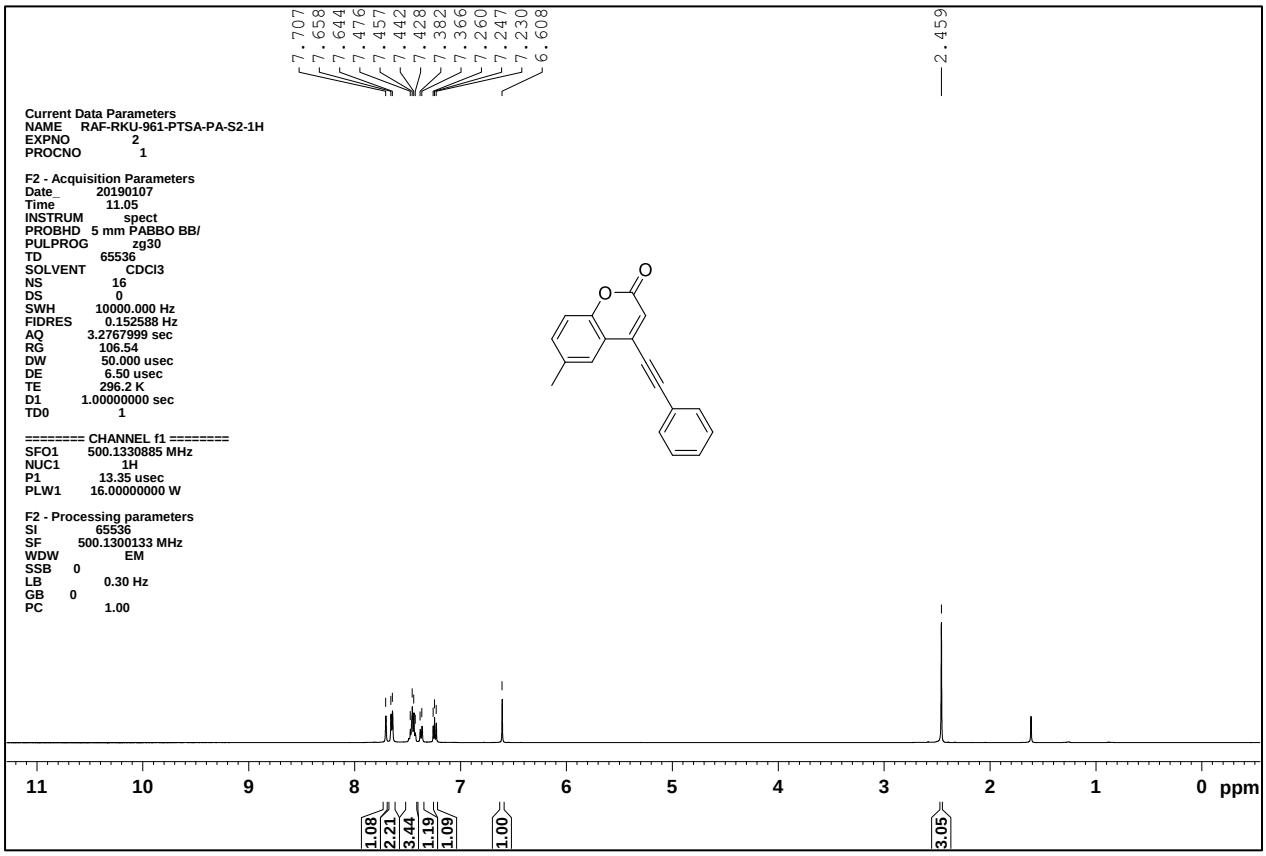


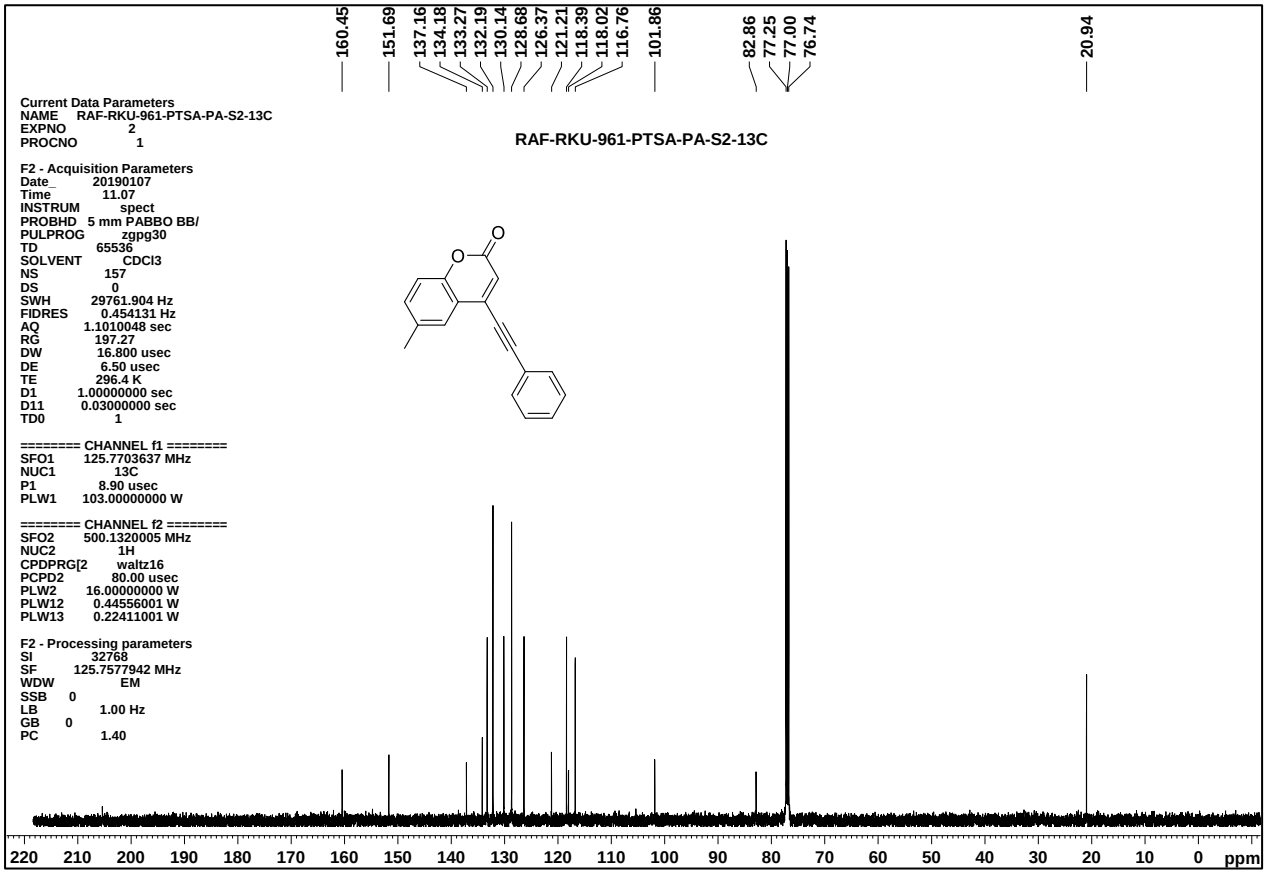
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **16h**



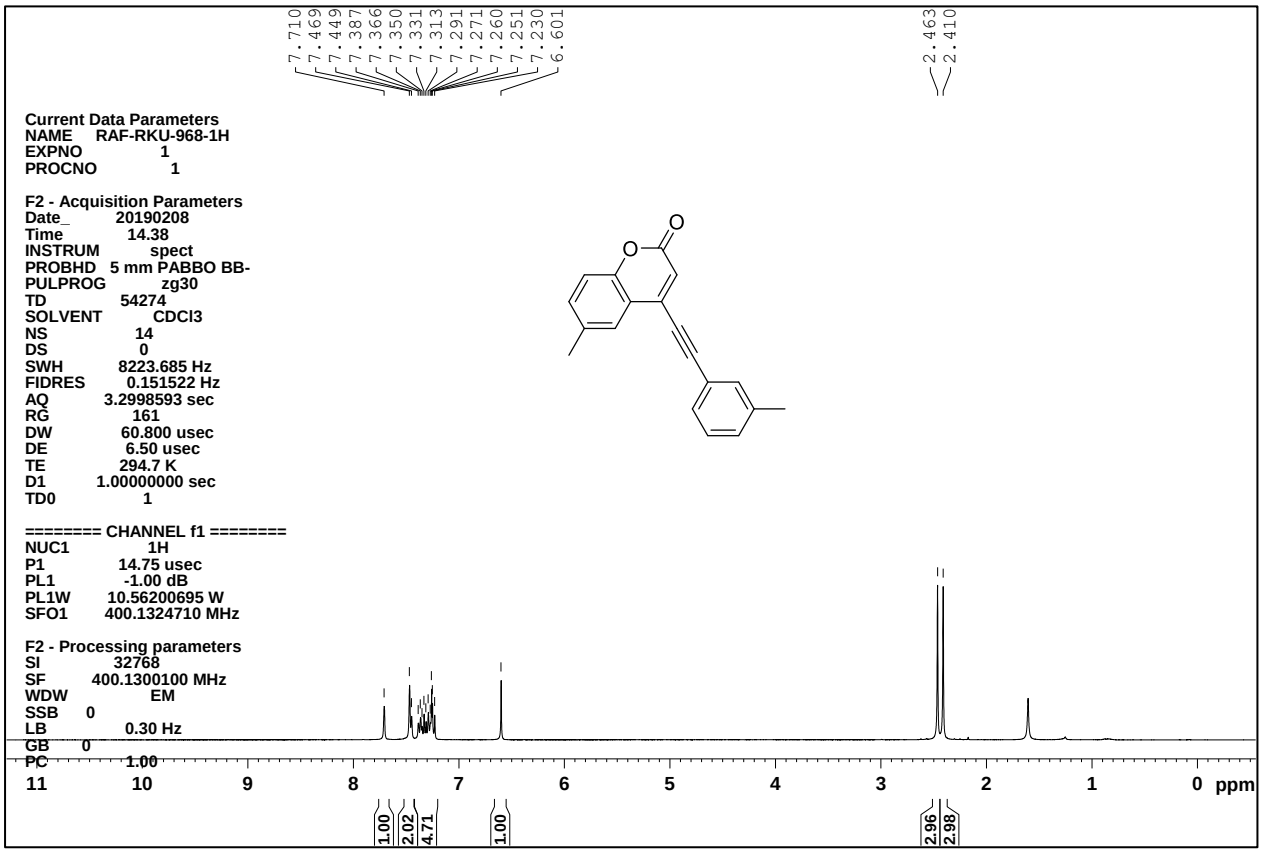


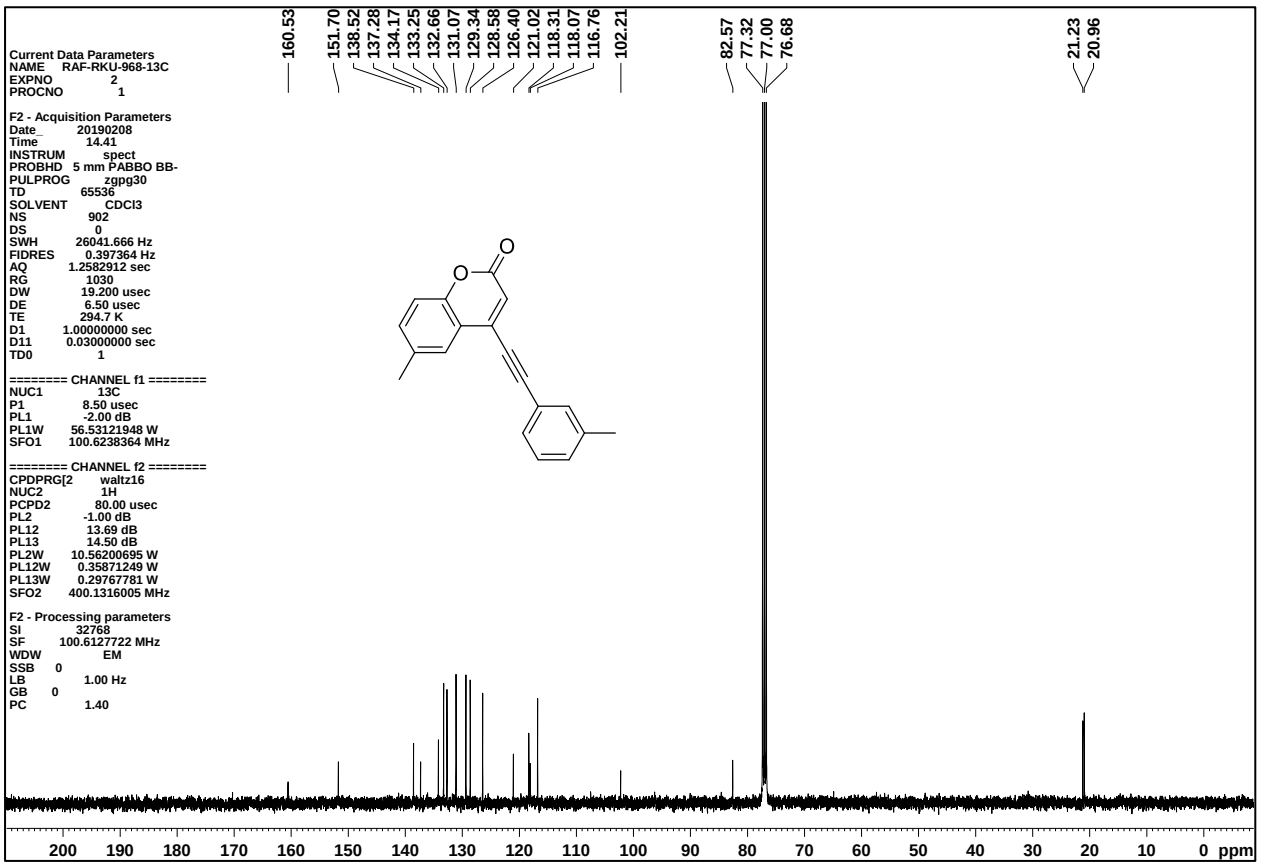
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **18a**



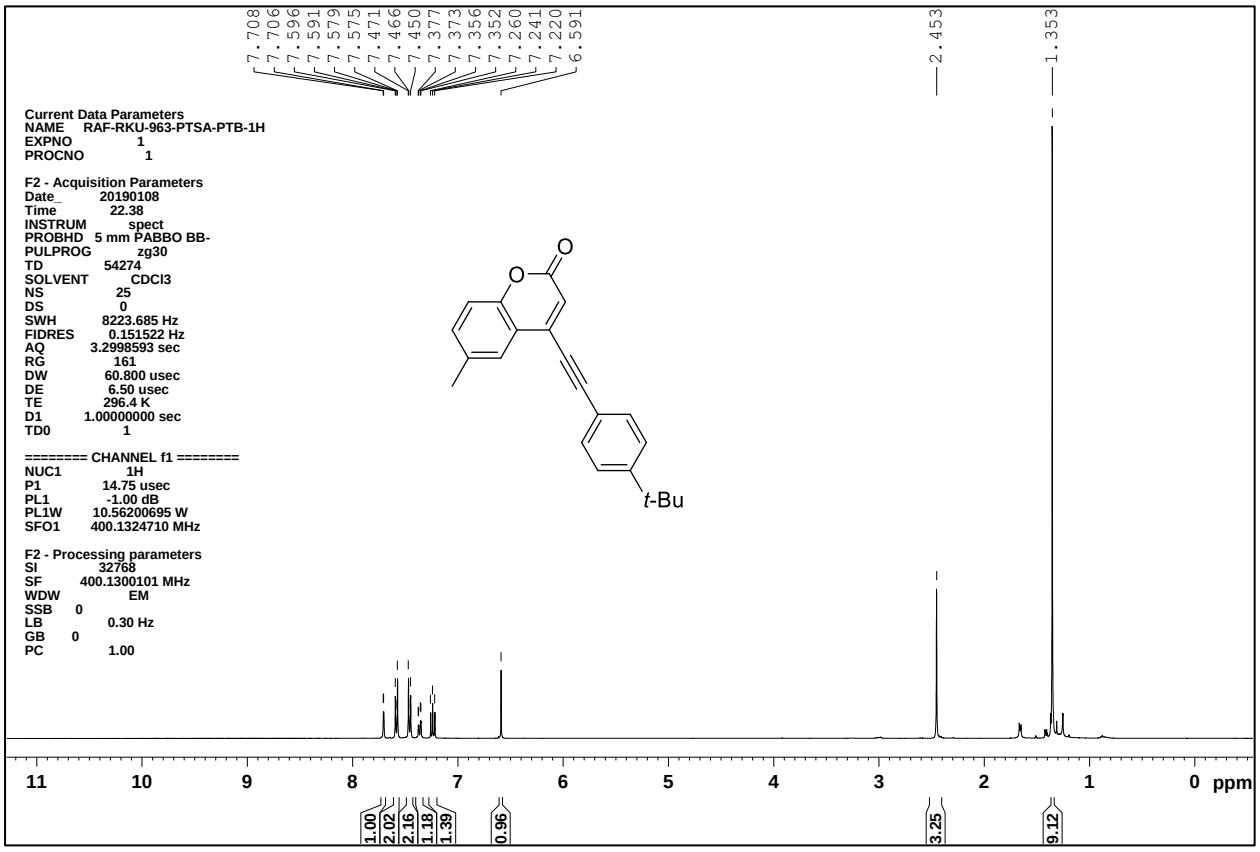


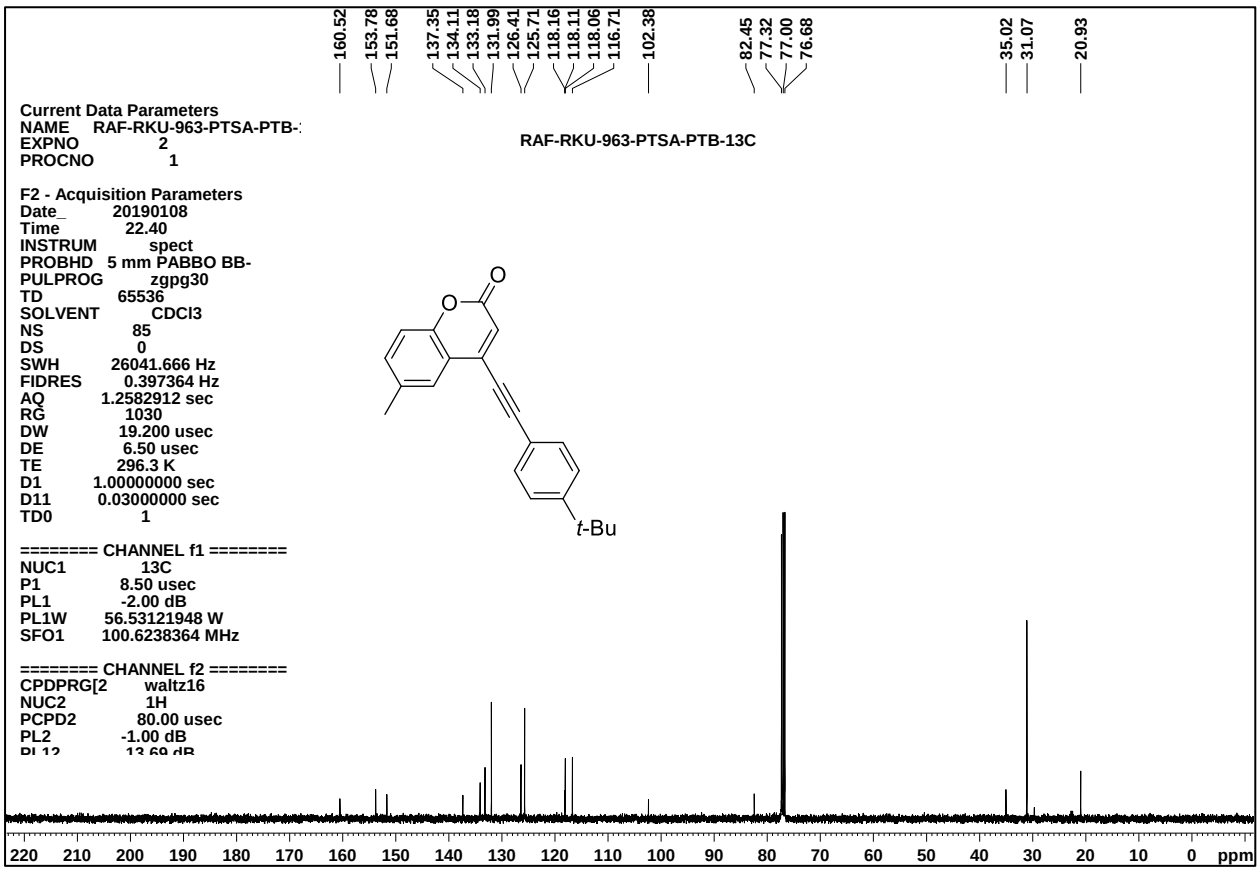
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18b**



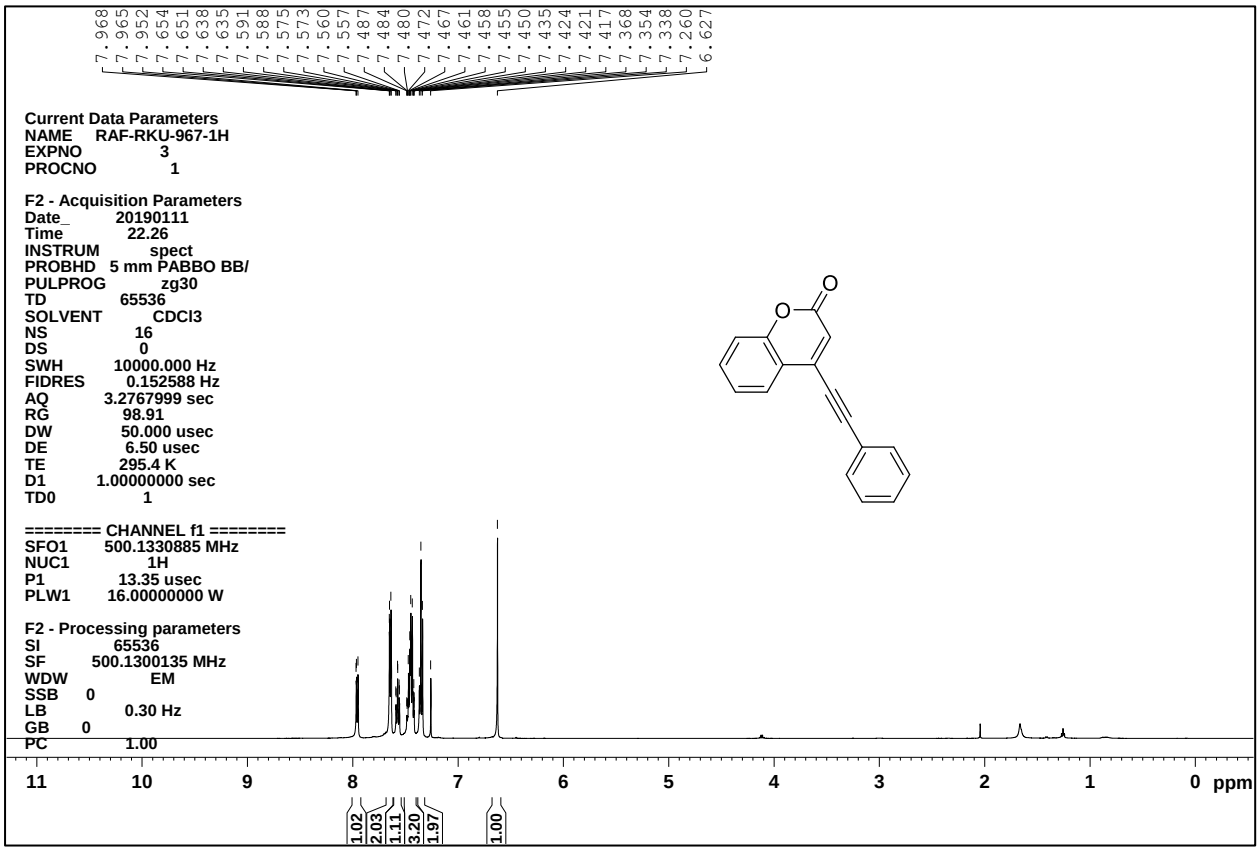


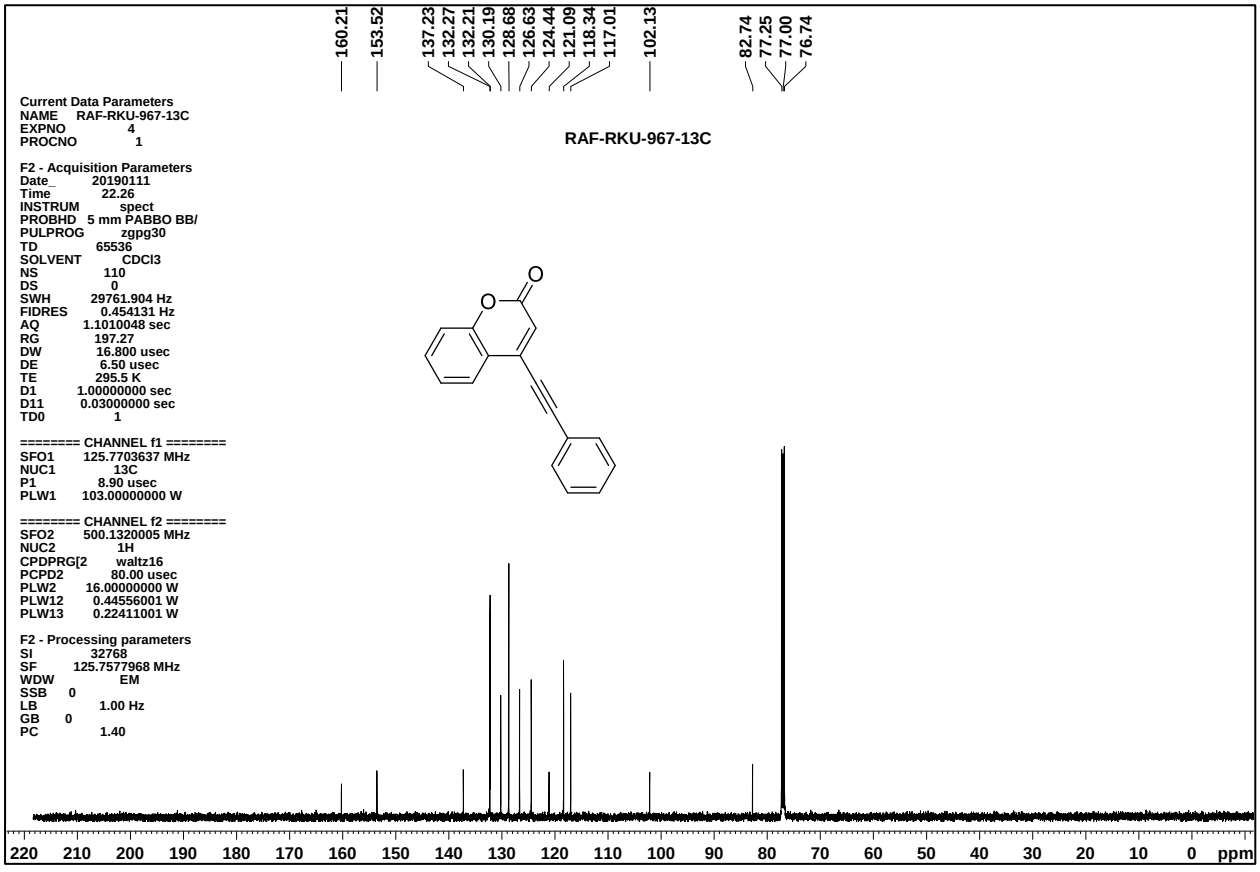
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18c**



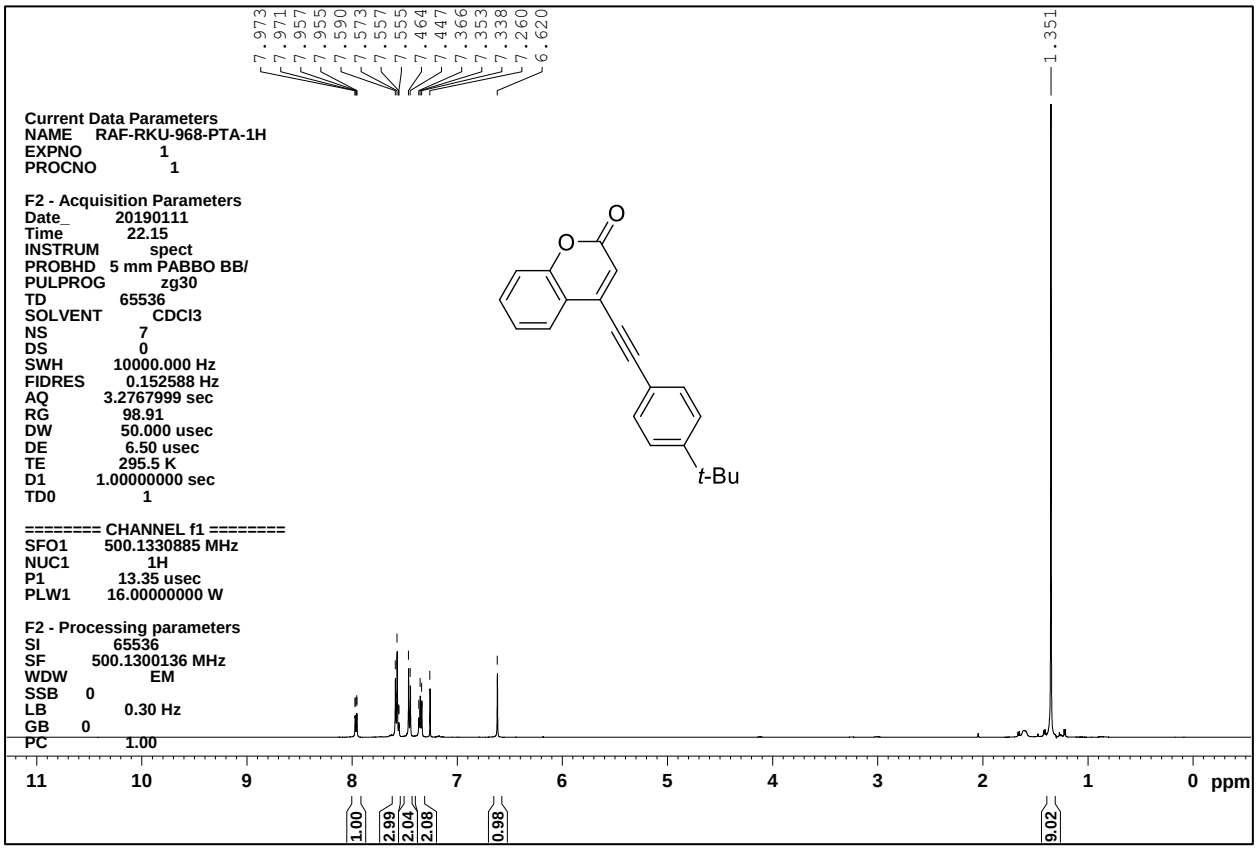


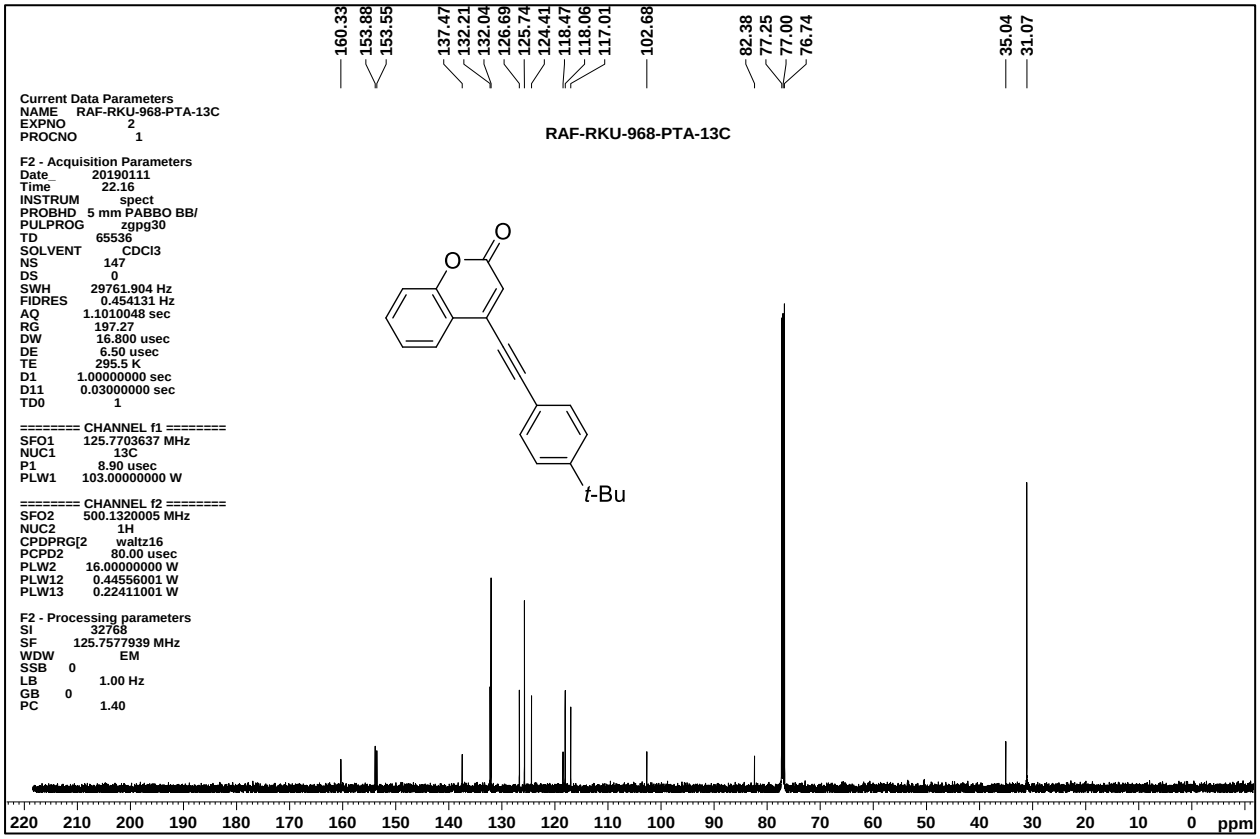
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **18d**



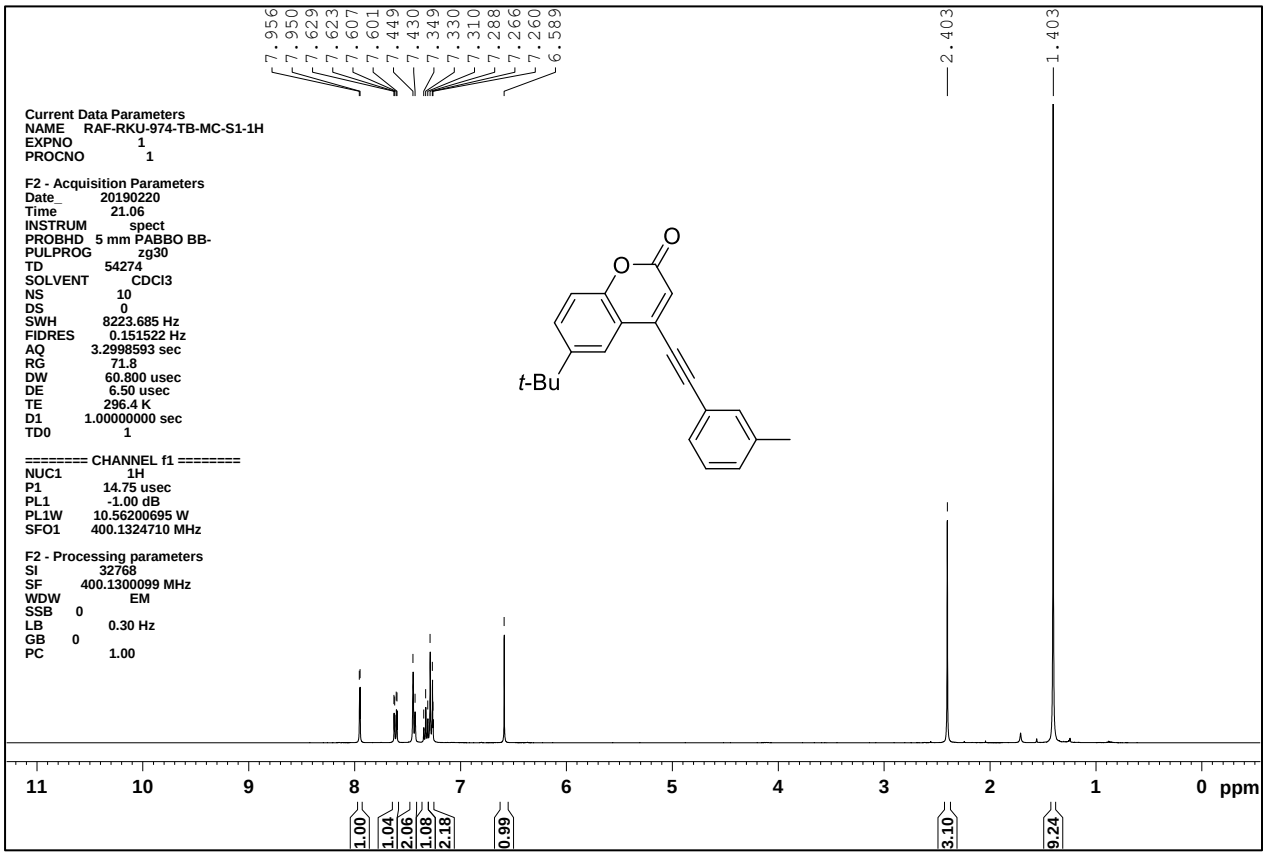


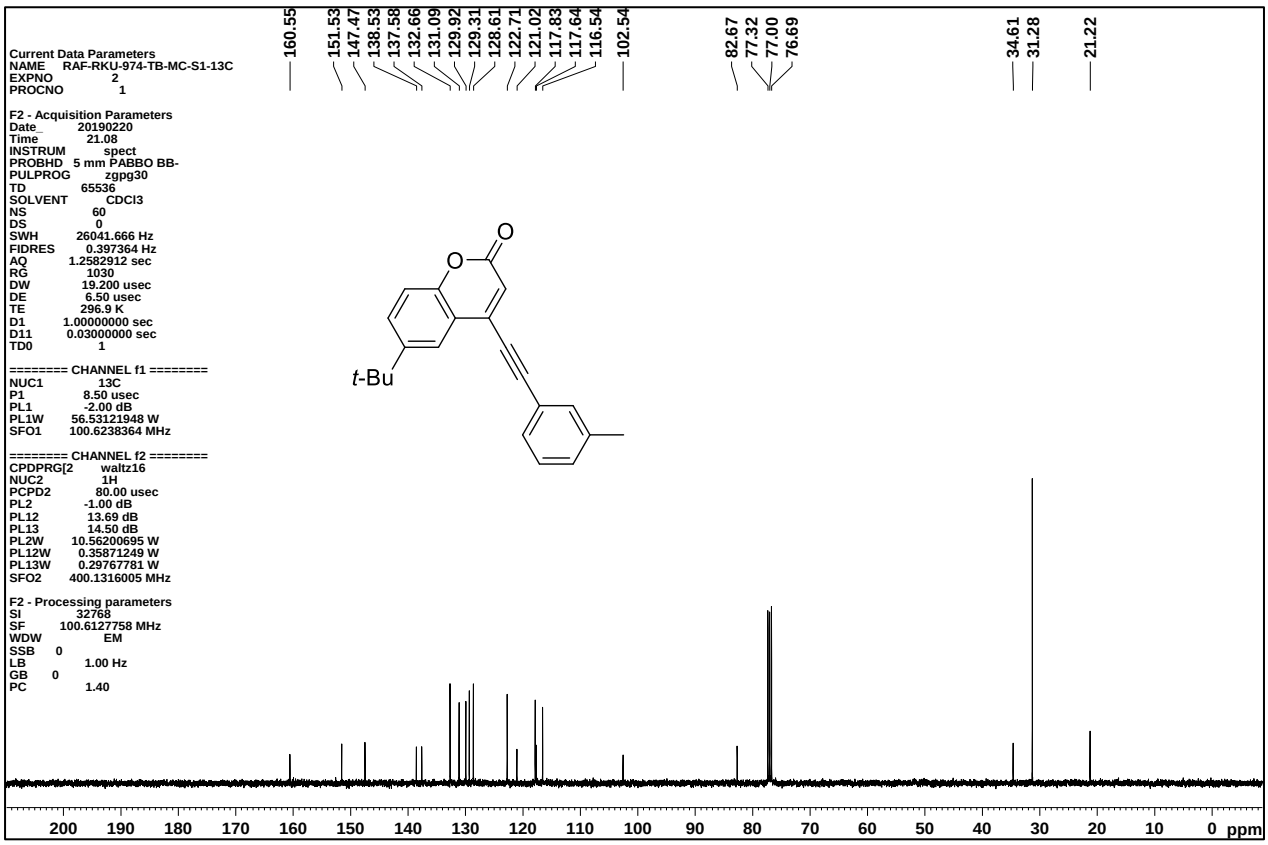
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **18e**



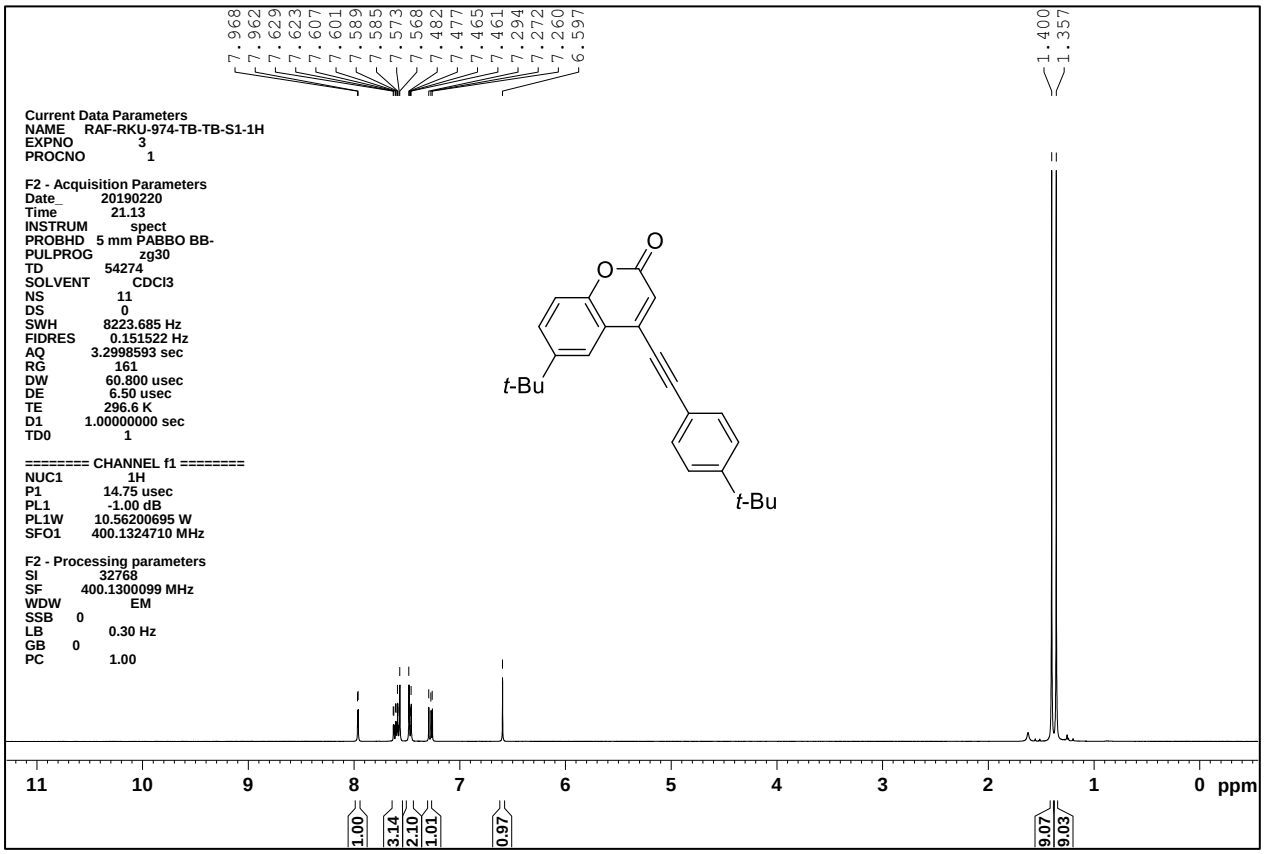


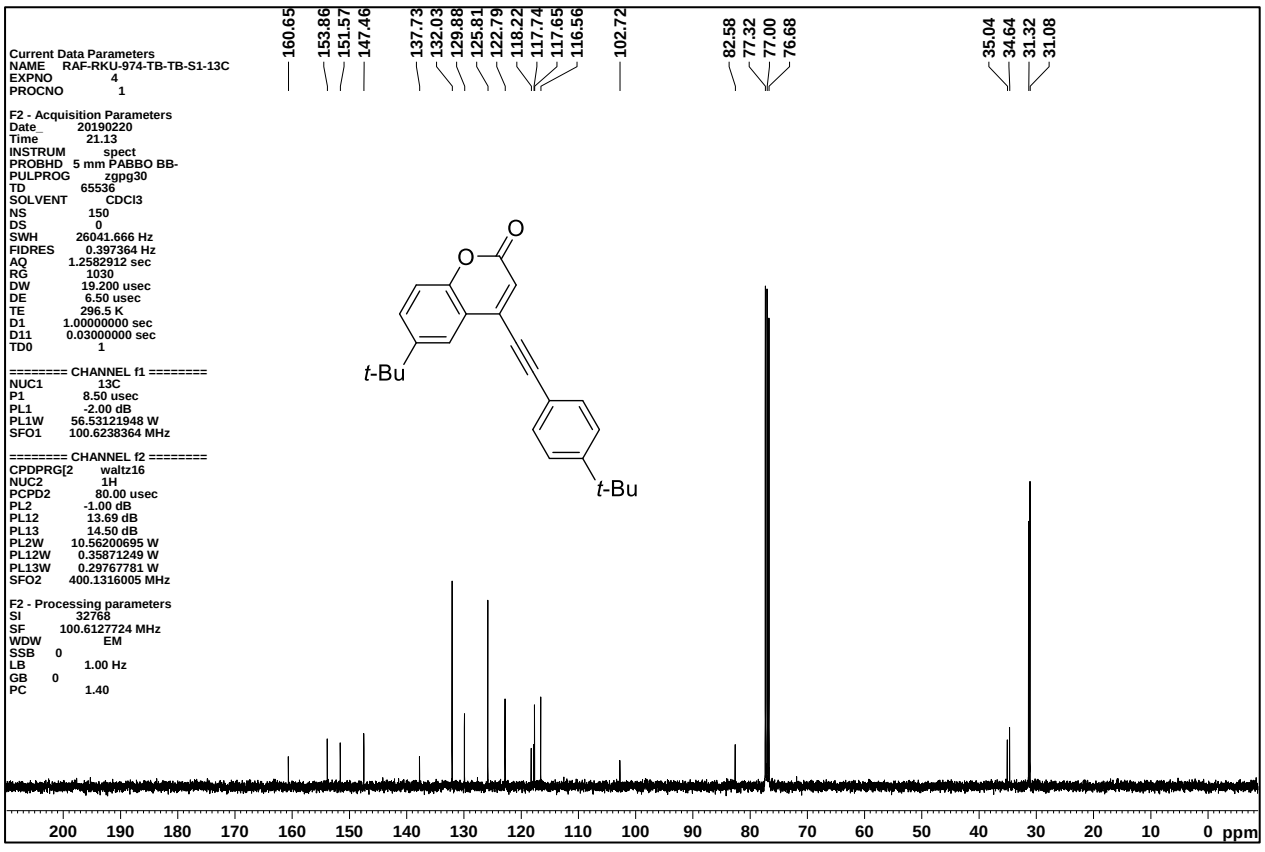
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18f**



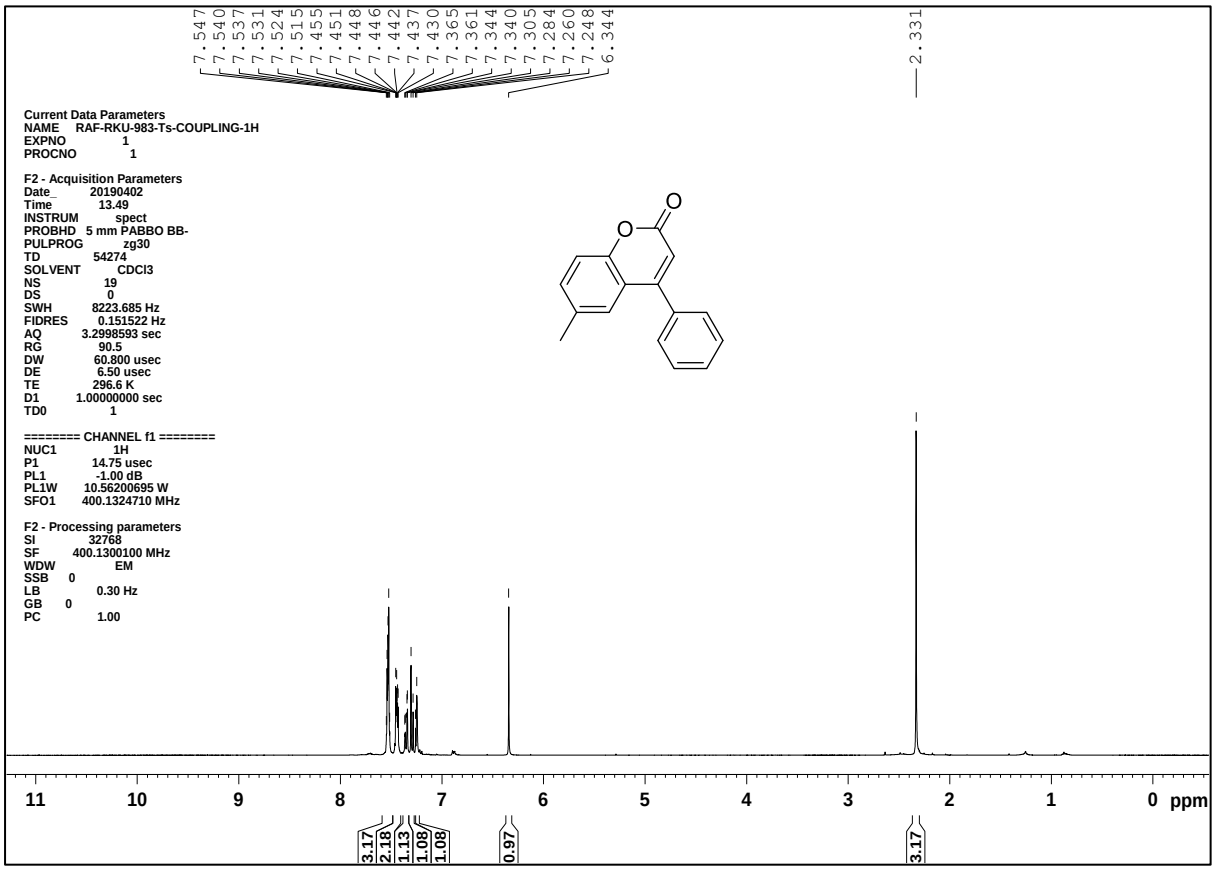


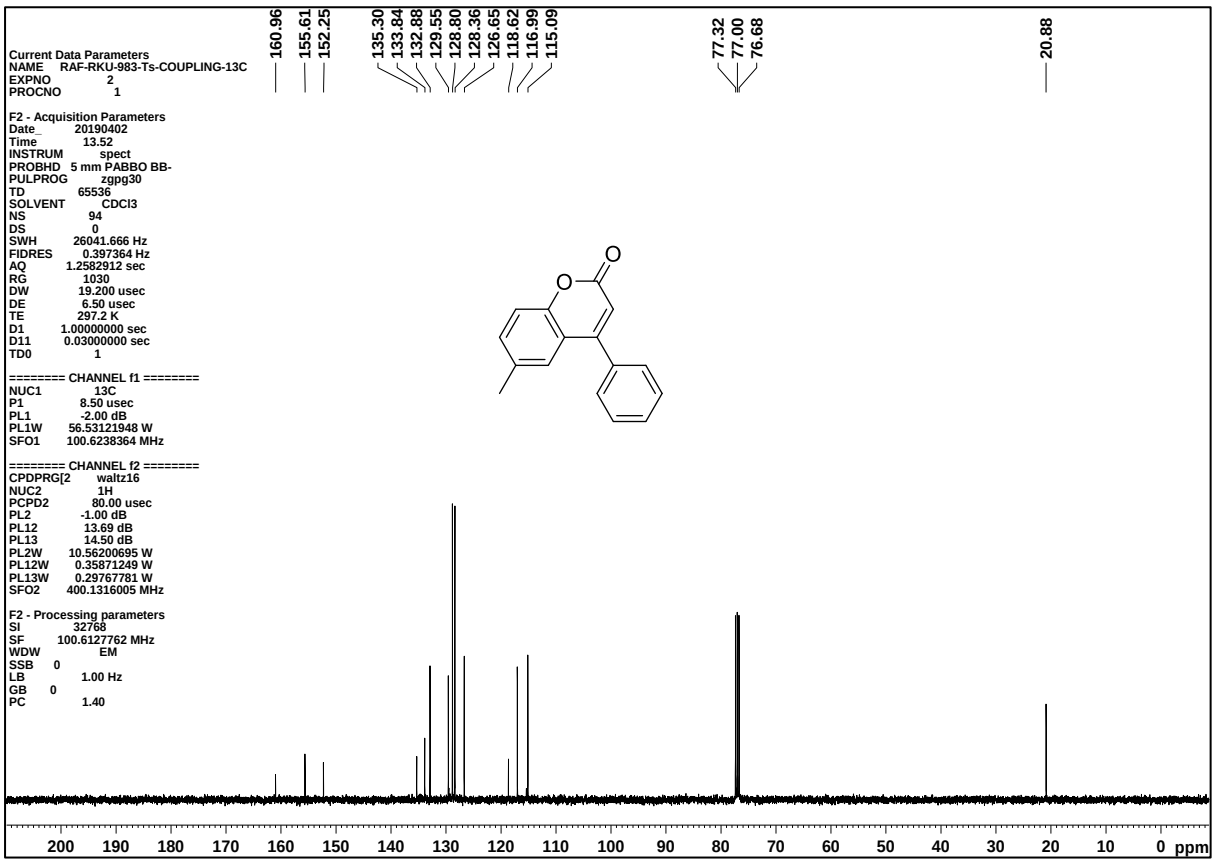
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **18g**



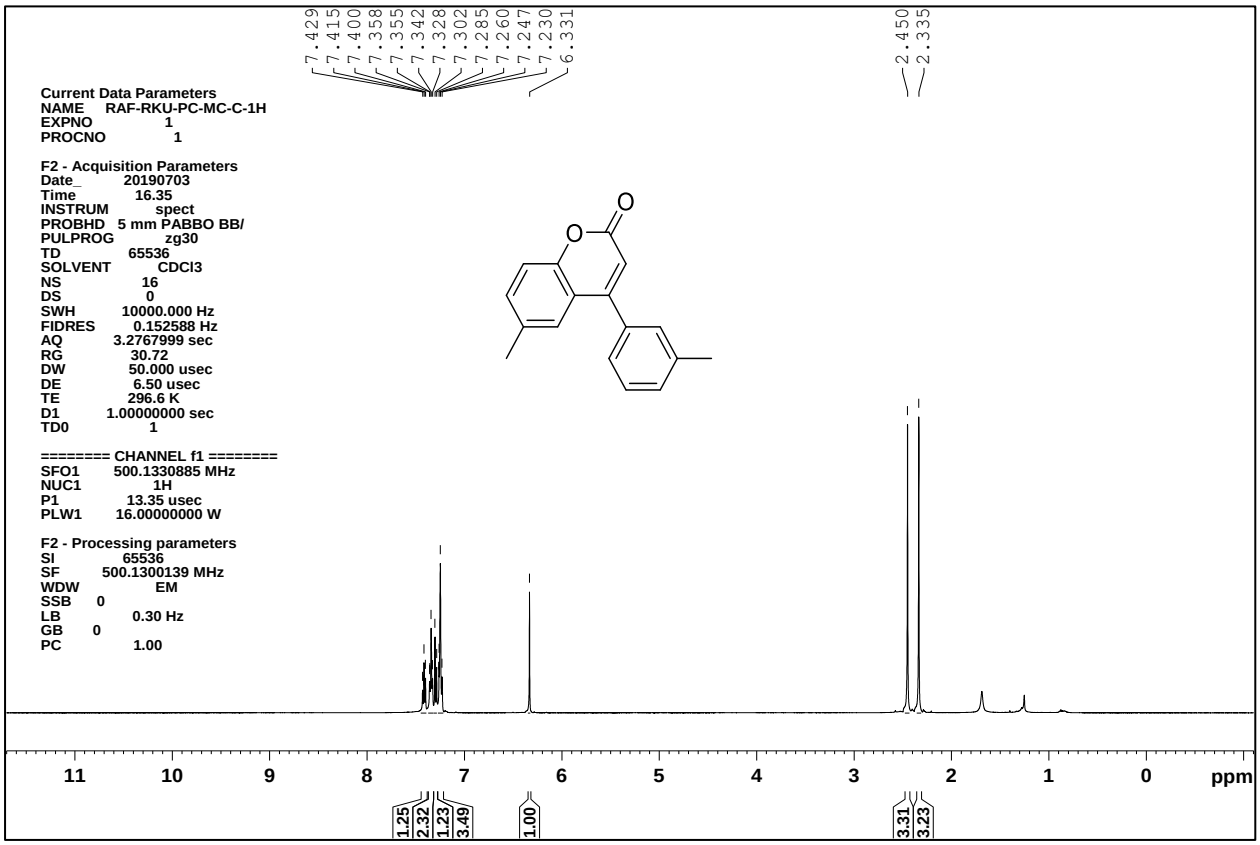


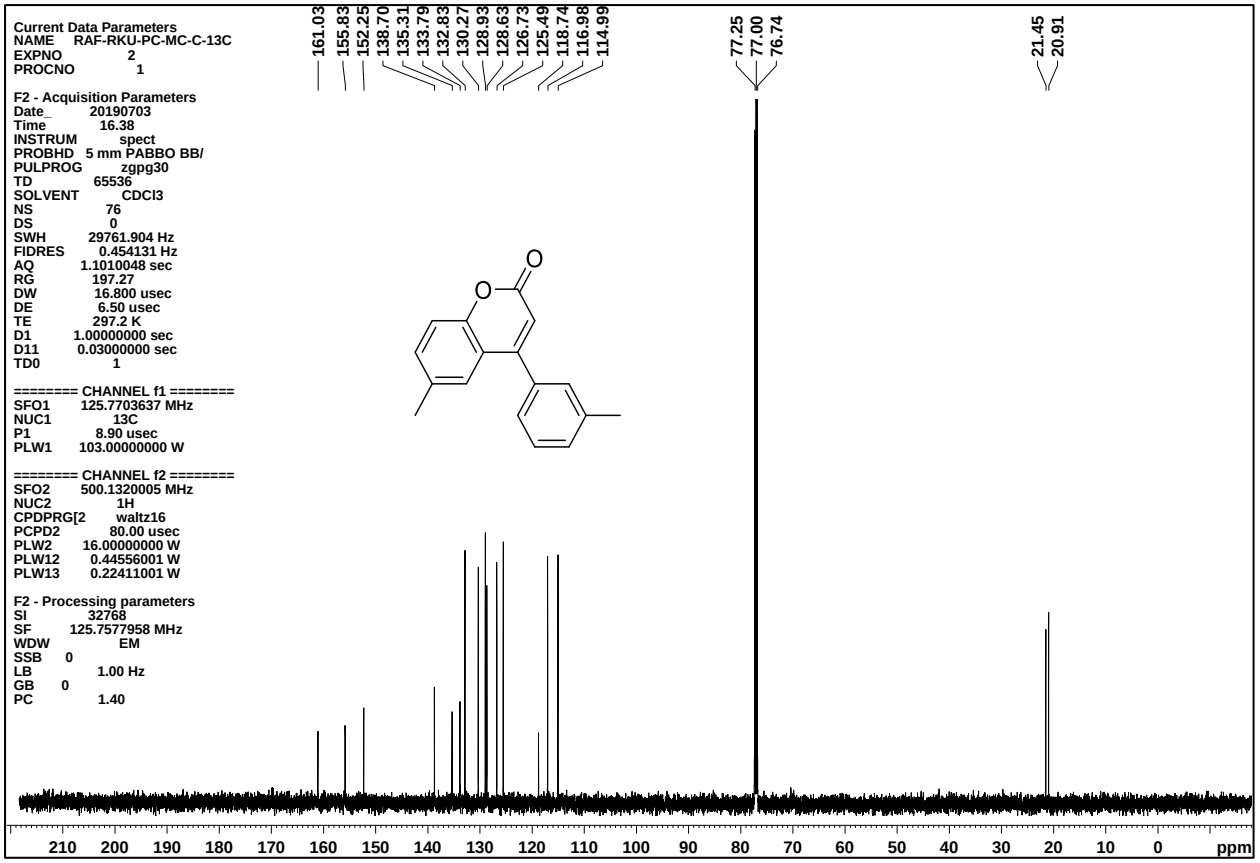
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **20a**



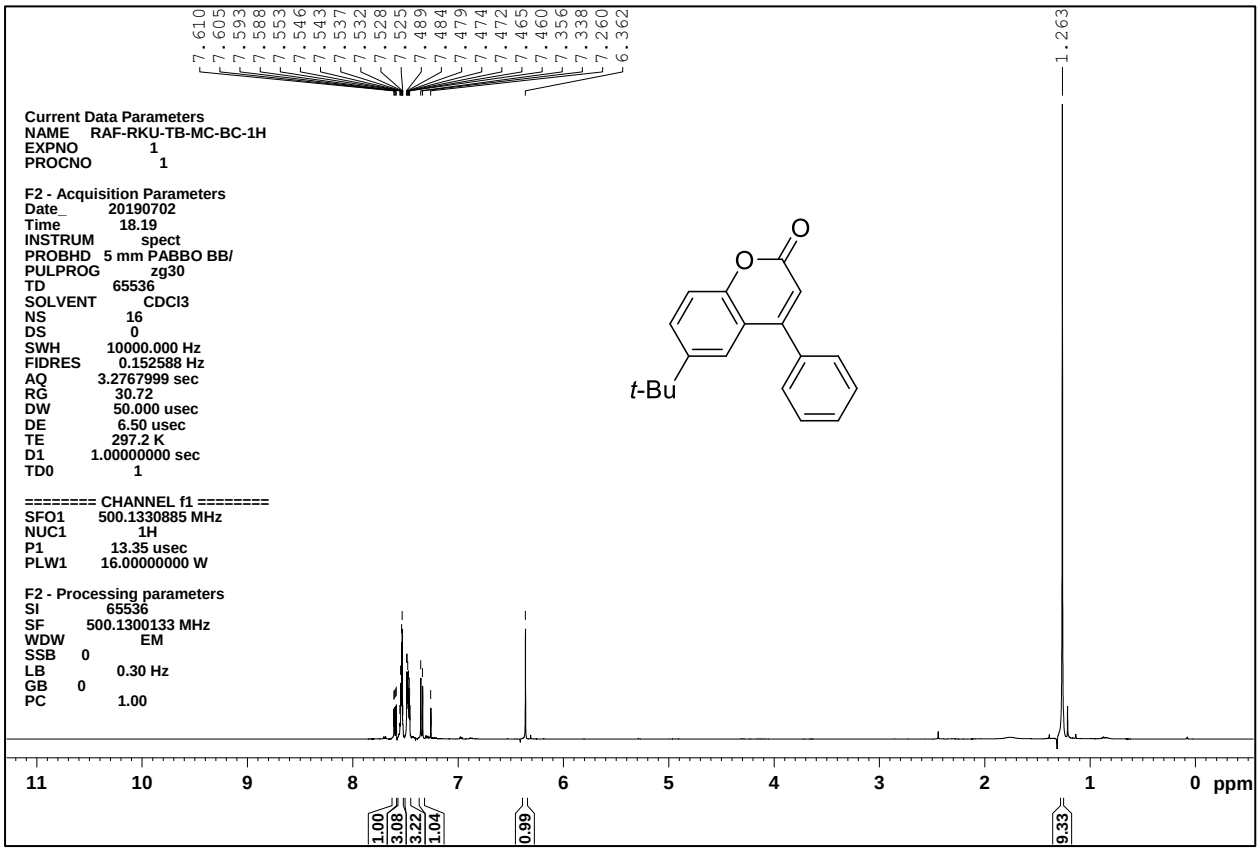


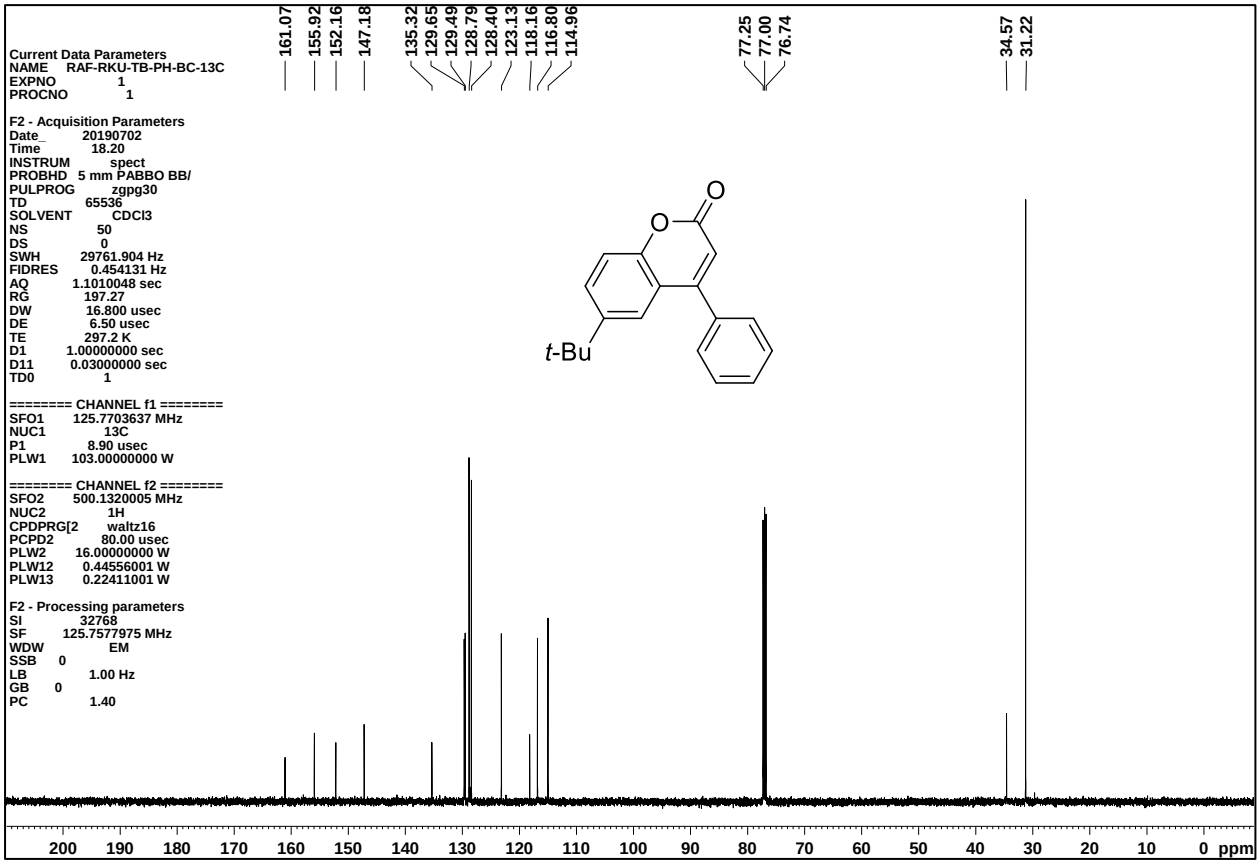
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **20b**



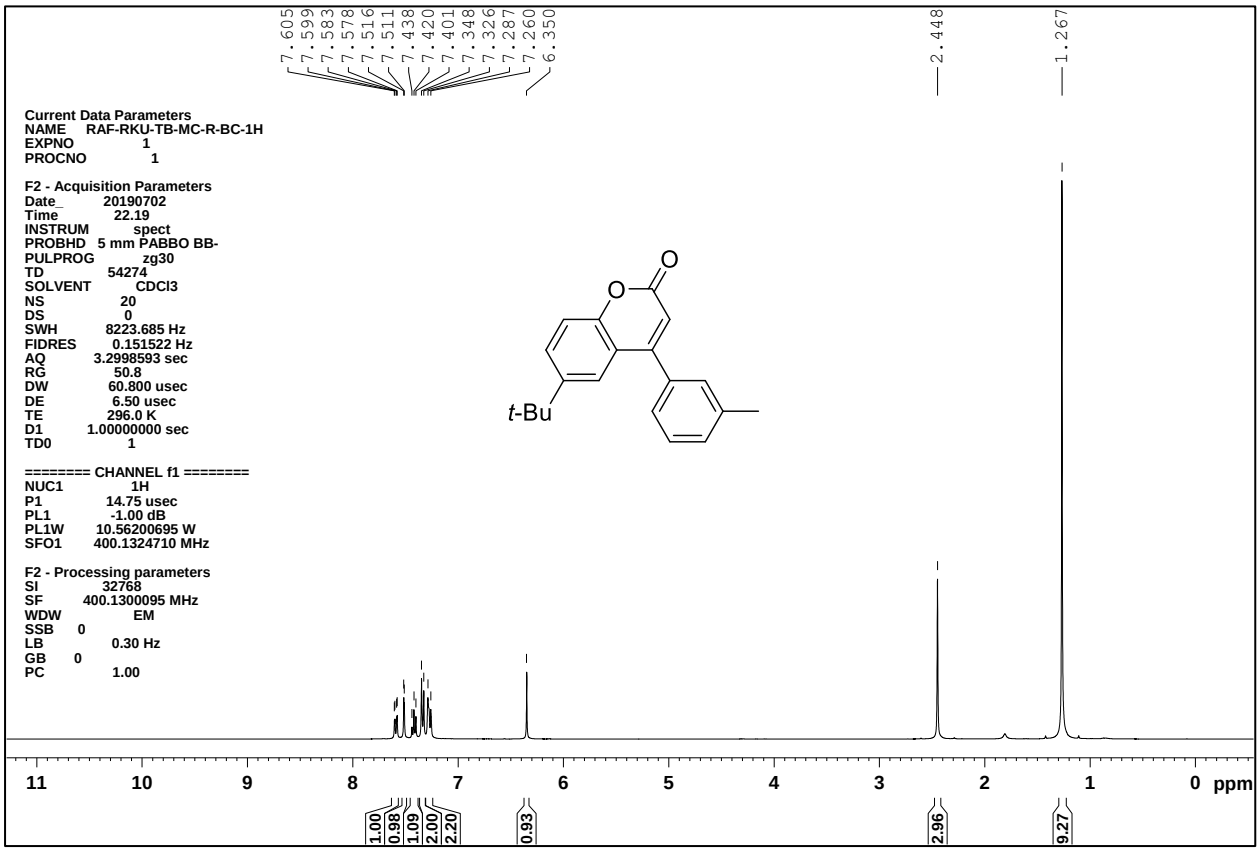


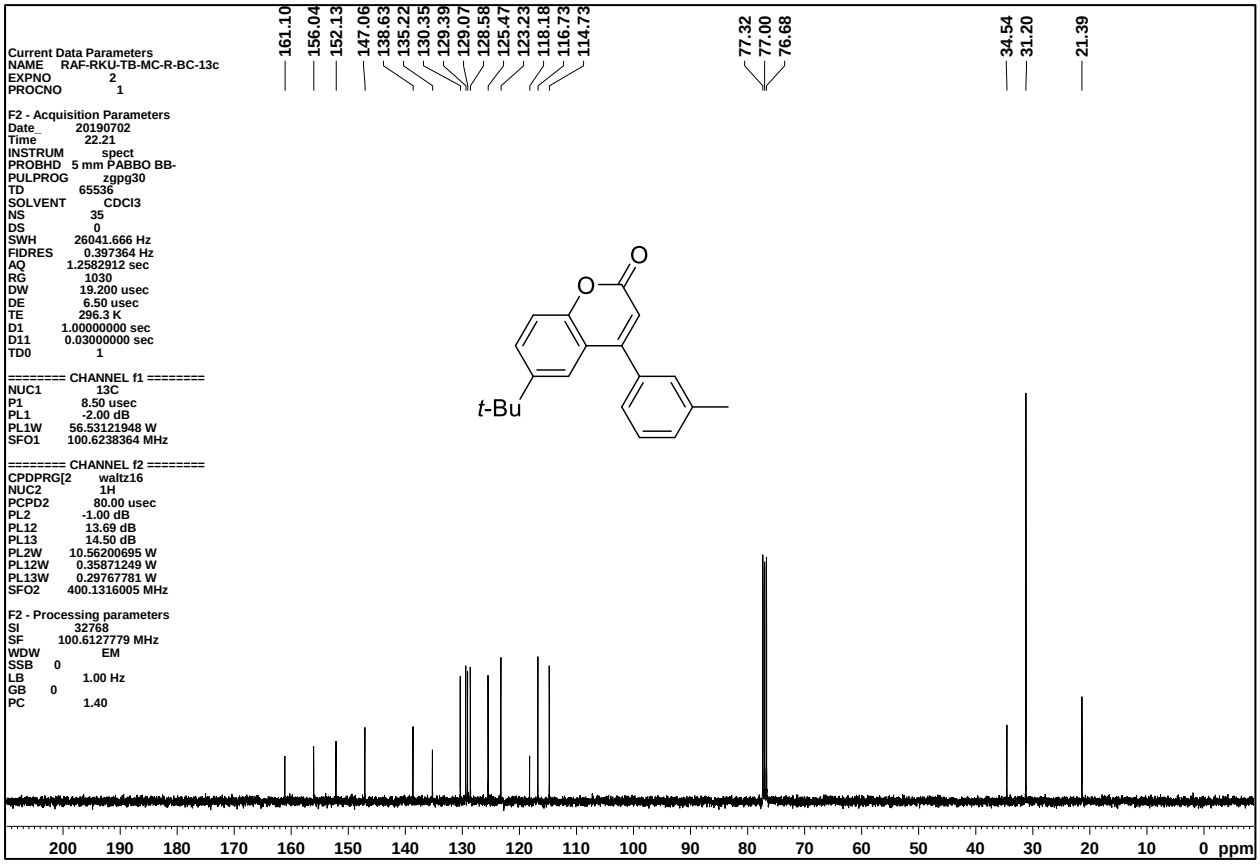
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **20c**



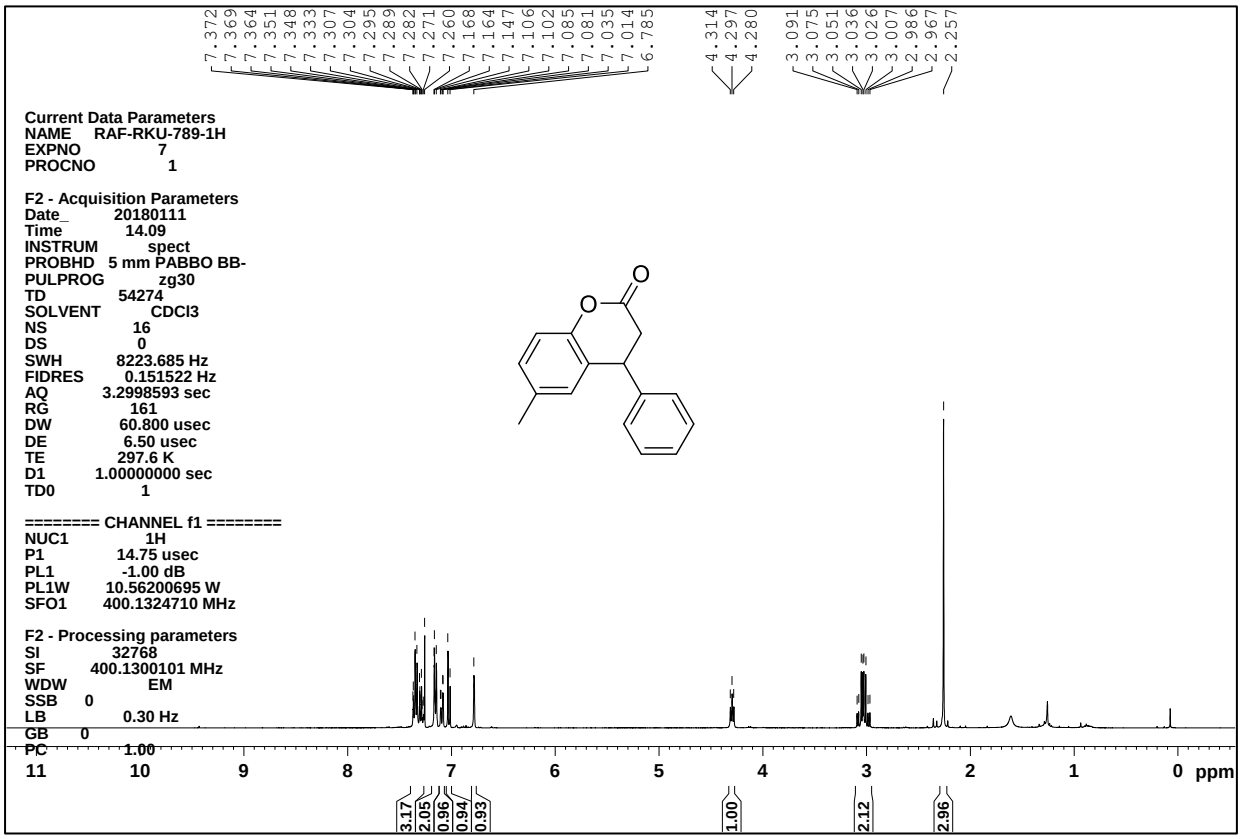


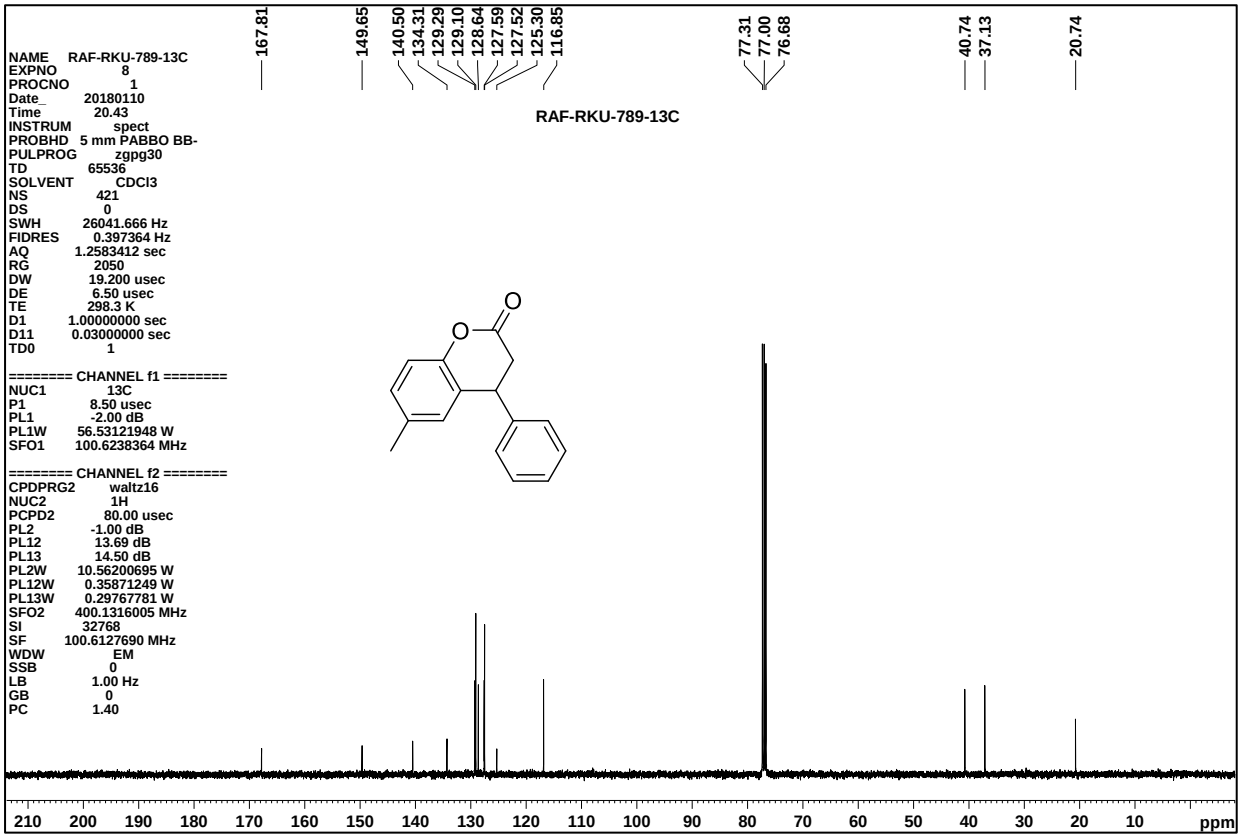
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **20d**



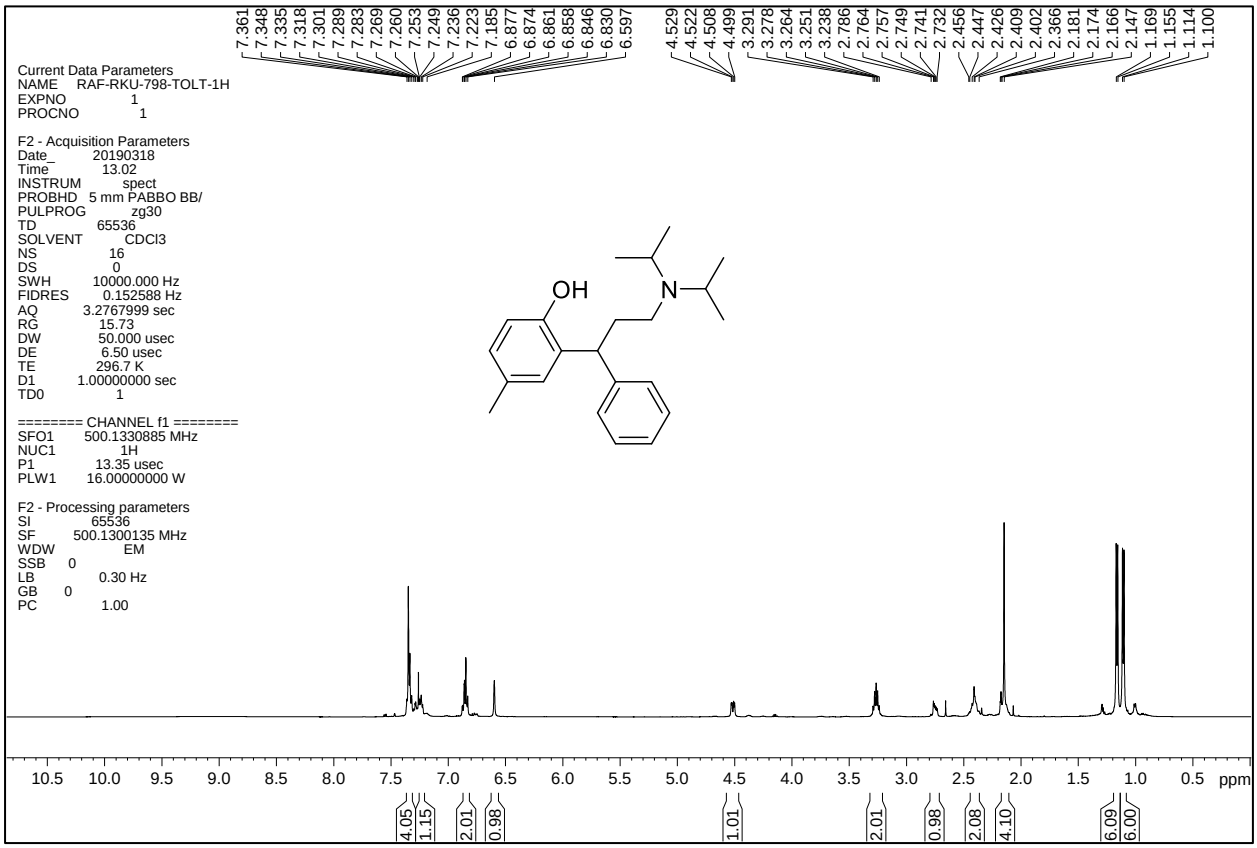


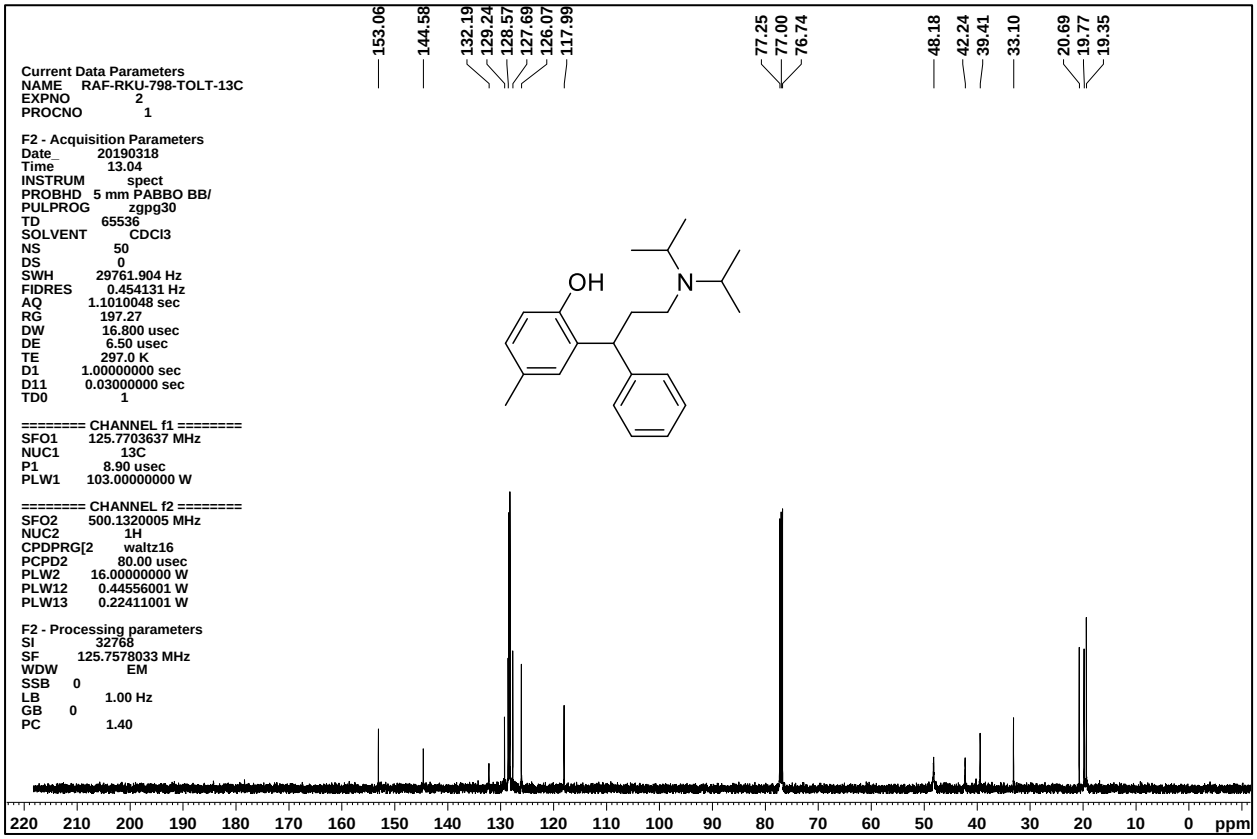
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **21**



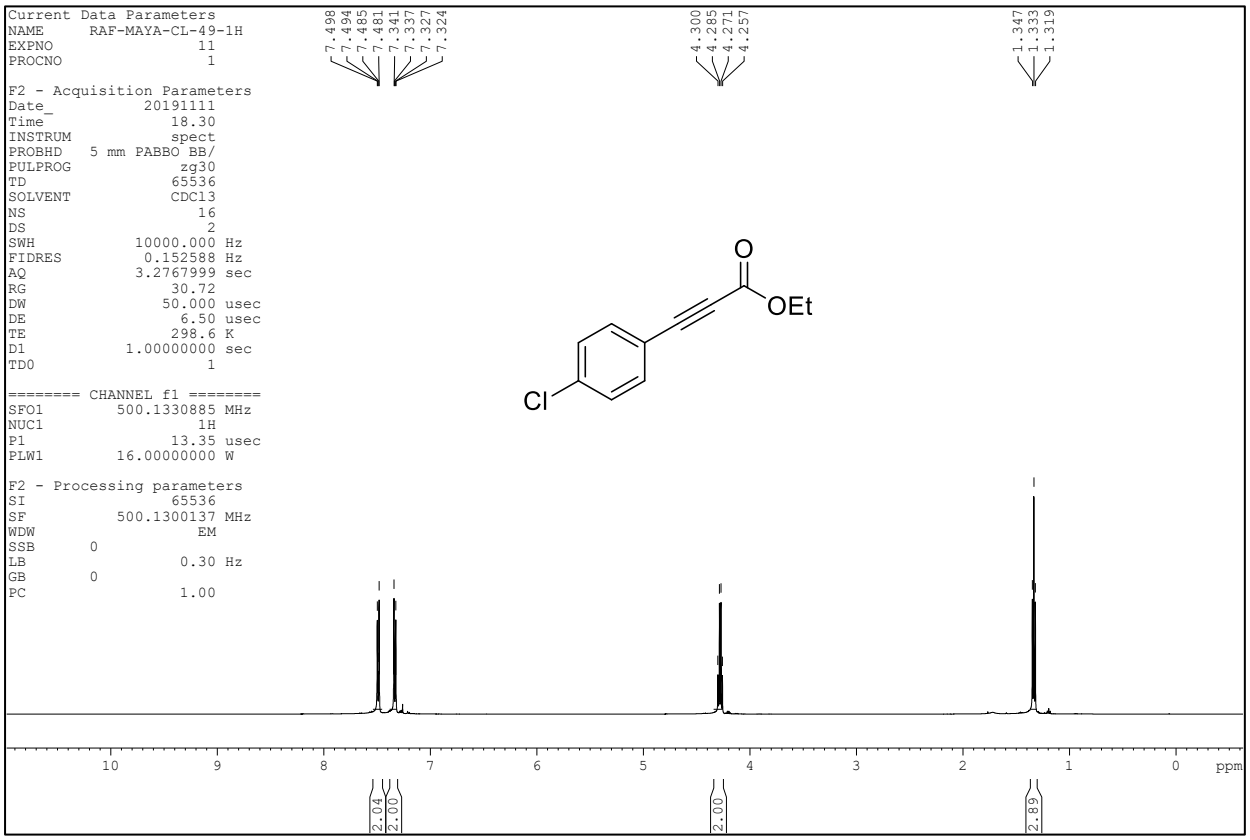


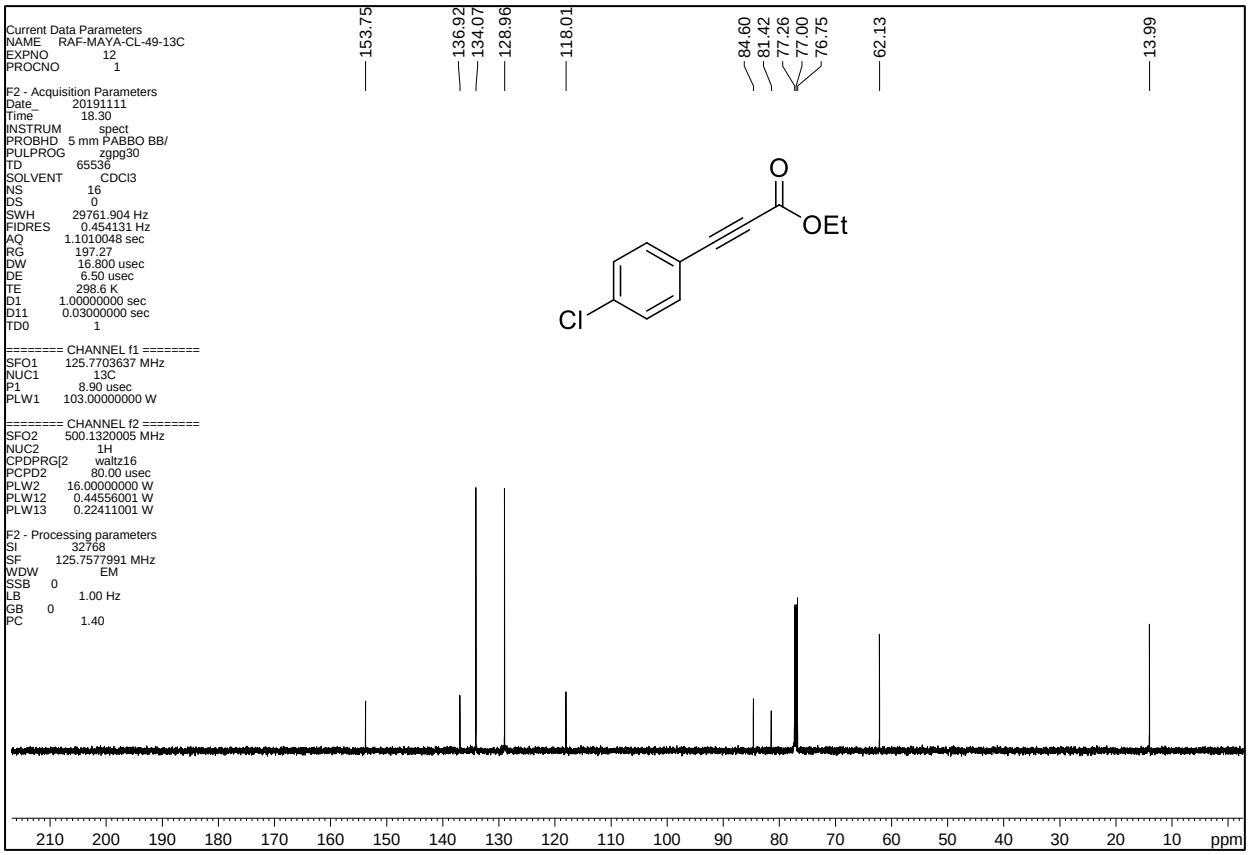
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **22**



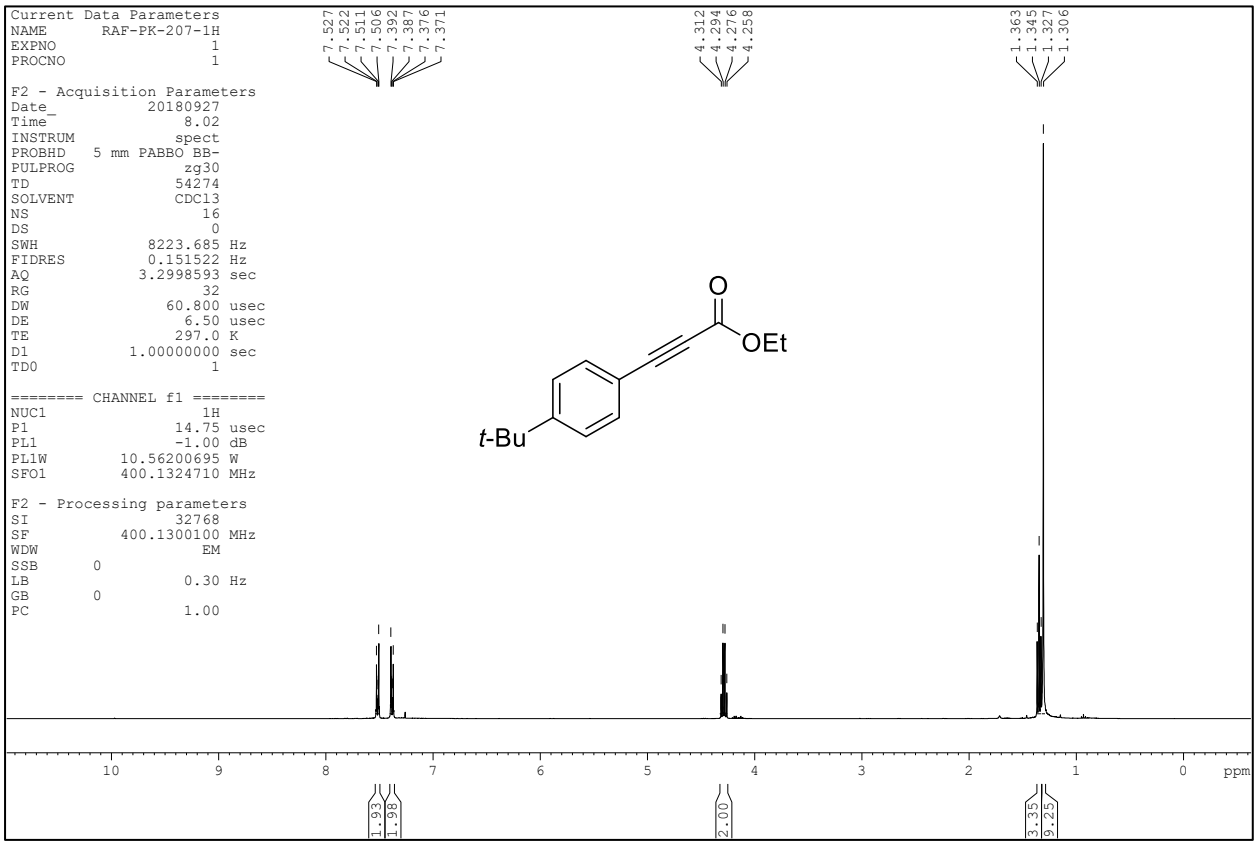


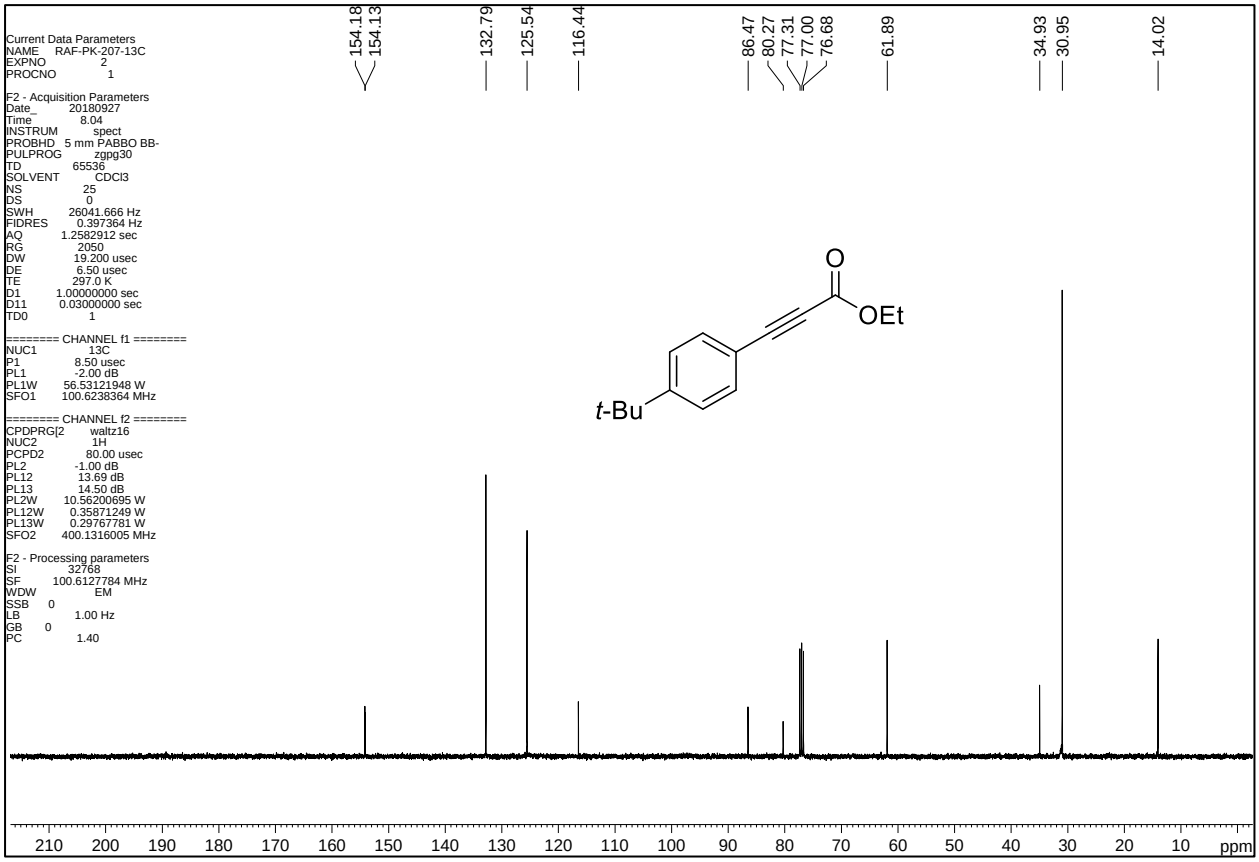
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of **23a**



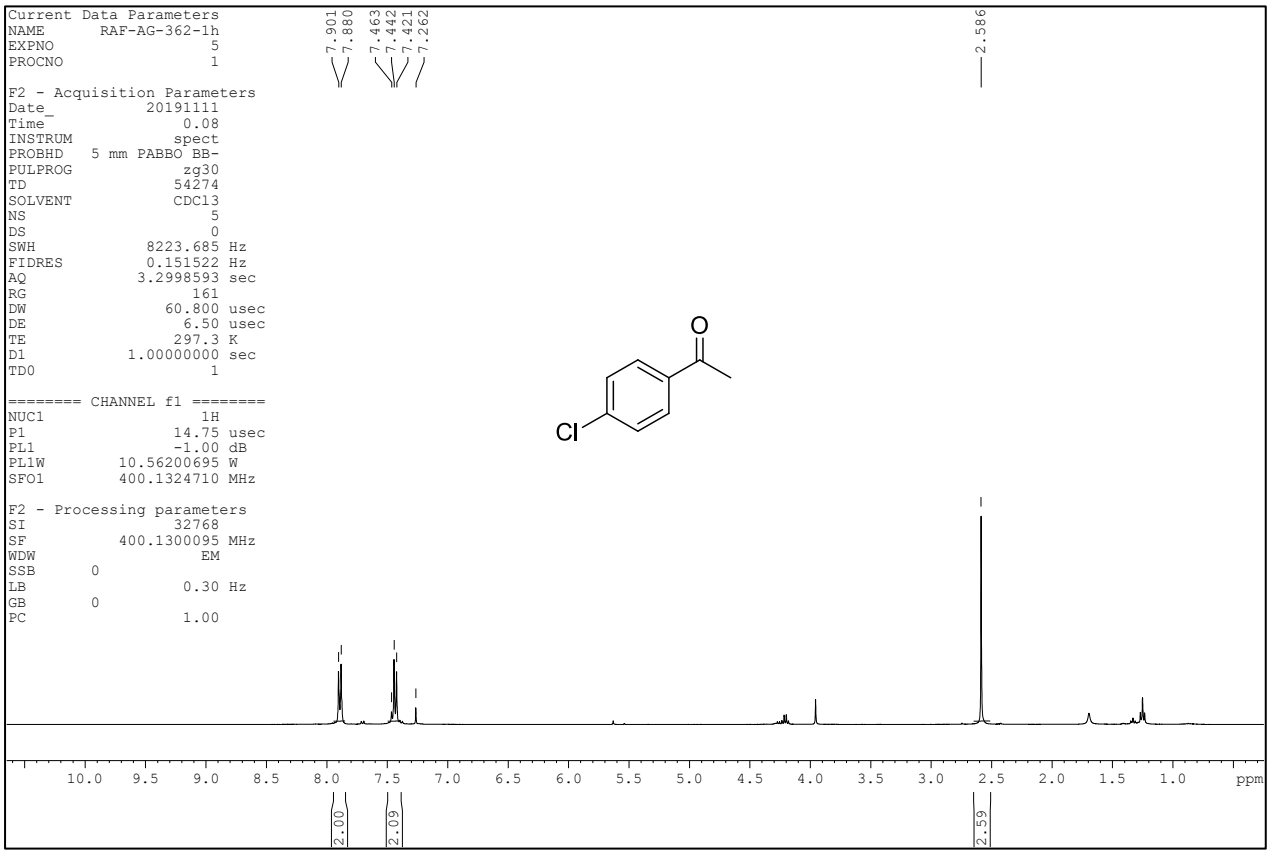


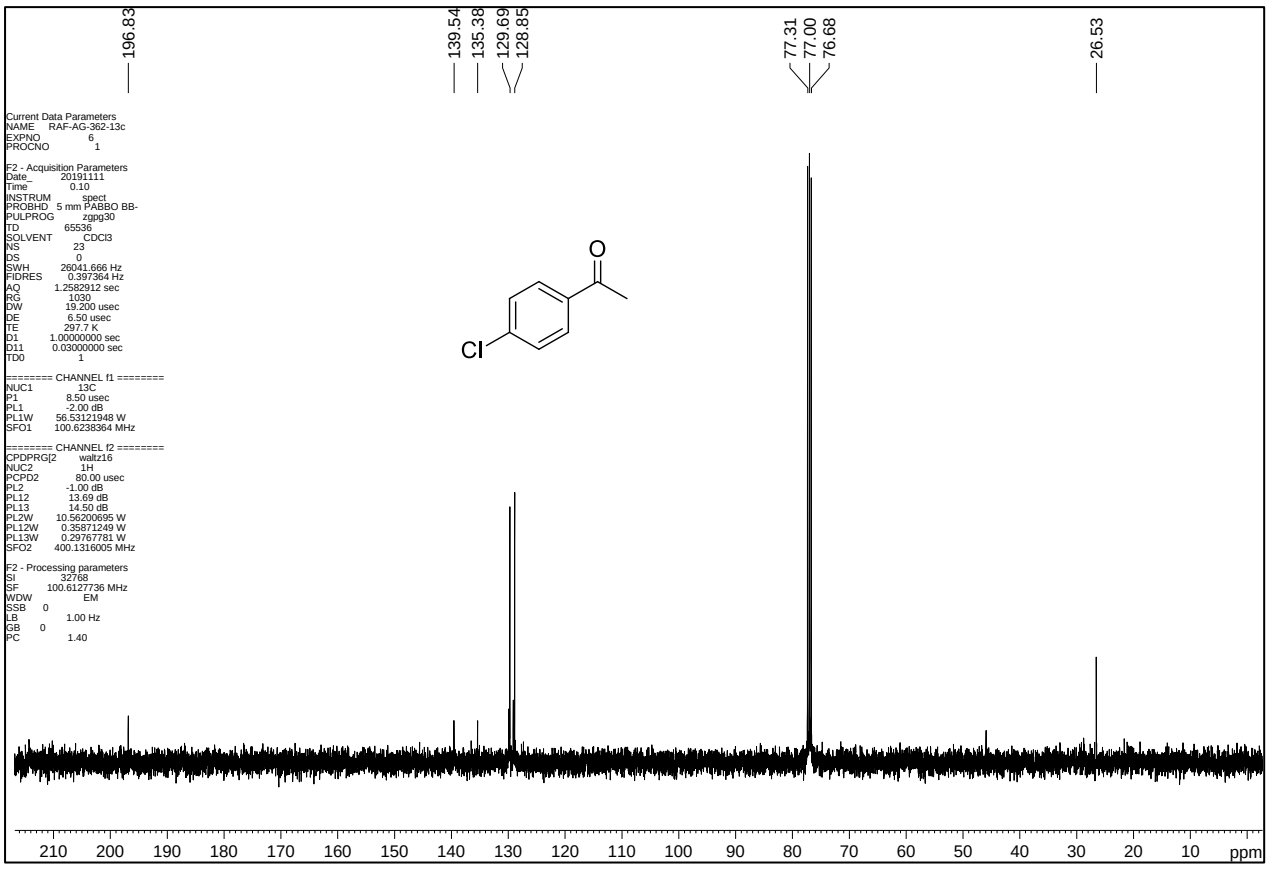
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **23b**



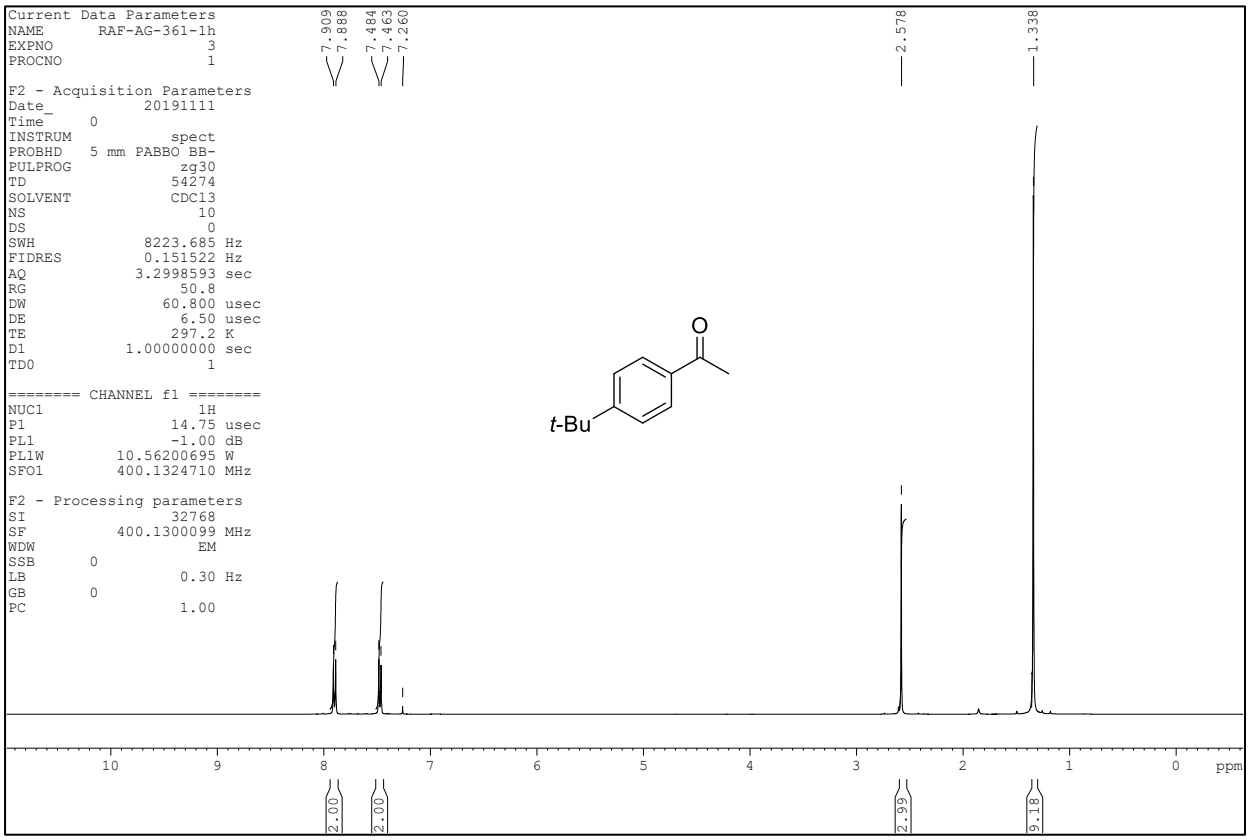


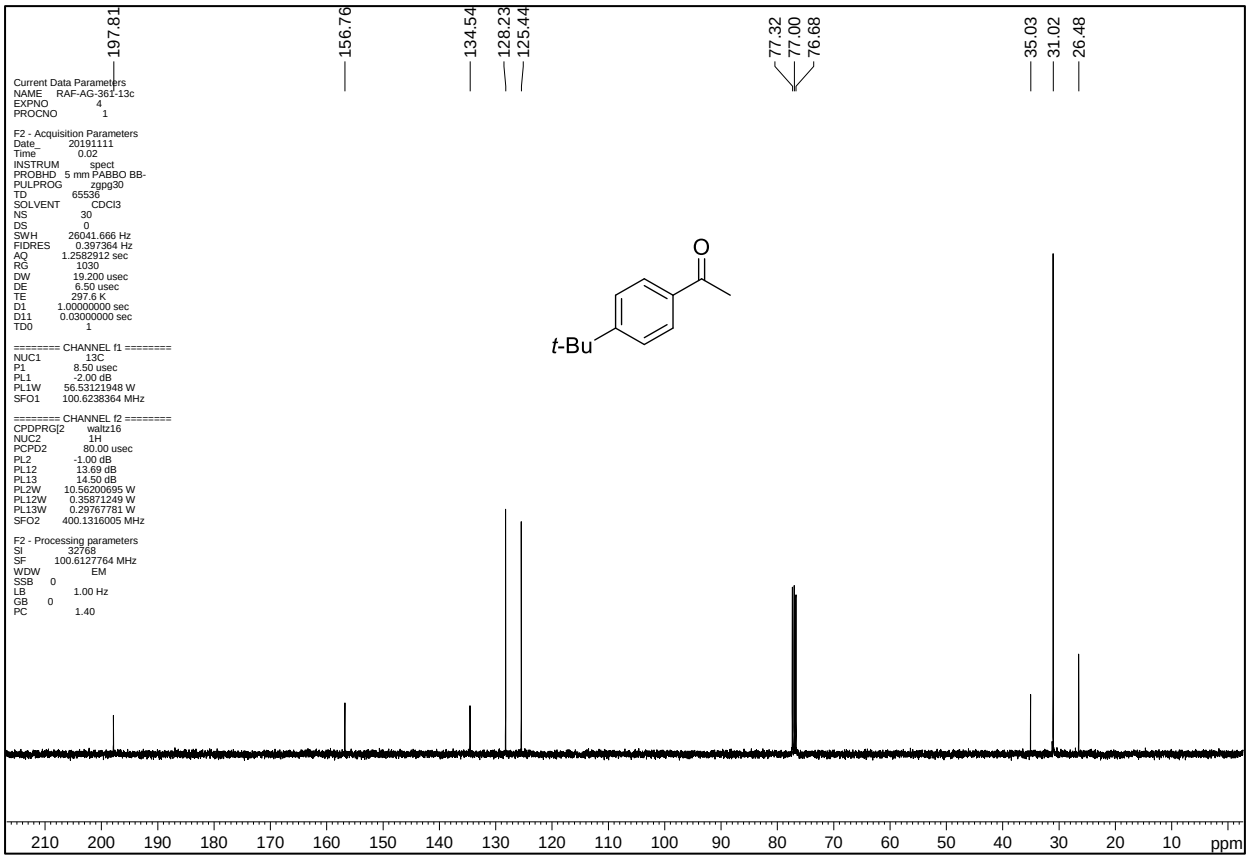
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **24a**



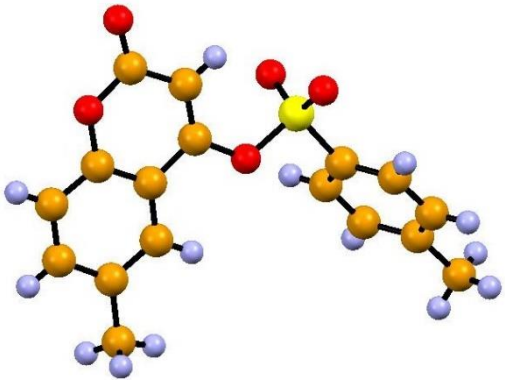


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of **24b**





XRD parameters of **5a**



CCDC	1942552
Empirical formula	$C_{11.33}H_{9.33}O_{3.33}S_{0.67}$
Formula weight	220.23
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.5139(6)
b/Å	11.8830(8)
c/Å	13.6051(9)
α/°	90
β/°	103.300(6)
γ/°	90
Volume/Å^3	1496.86(18)
Z	6
ρ_{calc}g/cm^3	1.466
μ/mm^{-1}	0.240
F(000)	688.0
Crystal size/mm^3	0.20 × 0.12 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.606 to 49.992
Index ranges	$-11 \leq h \leq 7$, $-13 \leq k \leq 10$, $-16 \leq l \leq 16$
Reflections collected	4668
Independent reflections	2559 [R_{int} = 0.0496, R_{sigma} = 0.0758]
Data/restraints/parameters	2559/0/210
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1310
Largest diff. peak/hole / e Å^{-3}	0.29/-0.57

Table 1 Bond Lengths for **5a.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S01	O002	1.624(2)	C00A	C00G	1.389(4)
S01	O003	1.420(2)	C00A	C00N	1.386(4)
S01	O004	1.427(2)	C00B	C00D	1.399(4)
S01	C00I	1.744(3)	C00C	C00N	1.513(4)
O002	C007	1.383(3)	C00D	C00J	1.391(4)
O005	C00H	1.372(3)	C00E	C00M	1.378(4)
O005	C00J	1.385(3)	C00F	C00H	1.443(4)
O006	C00H	1.213(4)	C00G	C00I	1.386(4)
C007	C00D	1.444(4)	C00I	C00K	1.388(4)
C007	C00F	1.343(4)	C00J	C00M	1.384(4)
C008	C009	1.513(4)	C00K	C00L	1.378(4)
C008	C00B	1.381(4)	C00L	C00N	1.380(4)
C008	C00E	1.396(4)			

Table 2 Bond Angles for **5a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O002	S01	C00I	98.40(12)	C00M	C00E	C008	122.0(3)
O003	S01	O002	108.45(12)	C007	C00F	C00H	121.4(3)
O003	S01	O004	118.86(14)	C00I	C00G	C00A	118.5(3)
O003	S01	C00I	110.85(14)	O005	C00H	C00F	117.3(3)
O004	S01	O002	107.03(12)	O006	C00H	O005	117.3(3)
O004	S01	C00I	111.15(13)	O006	C00H	C00F	125.4(3)
C007	O002	S01	121.07(18)	C00G	C00I	S01	119.1(2)
C00H	O005	C00J	121.6(2)	C00G	C00I	C00K	121.4(3)
O002	C007	C00D	113.5(2)	C00K	C00I	S01	119.4(2)
C00F	C007	O002	125.4(3)	O005	C00J	C00D	122.0(3)
C00F	C007	C00D	121.2(3)	C00M	C00J	O005	116.9(3)
C00B	C008	C009	121.2(3)	C00M	C00J	C00D	121.1(3)
C00B	C008	C00E	118.2(3)	C00L	C00K	C00I	118.5(3)
C00E	C008	C009	120.6(3)	C00K	C00L	C00N	121.7(3)
C00N	C00A	C00G	121.1(3)	C00E	C00M	C00J	118.8(3)
C008	C00B	C00D	121.2(3)	C00A	C00N	C00C	120.2(3)
C00B	C00D	C007	124.8(3)	C00L	C00N	C00A	118.7(3)
C00J	C00D	C007	116.5(3)	C00L	C00N	C00C	121.0(3)
C00J	C00D	C00B	118.8(3)				