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Supporting Information

For

A new skeletal rearrangement of 1, 7-dimethyl Cookson's cage dione catalyzed by Lewis acid

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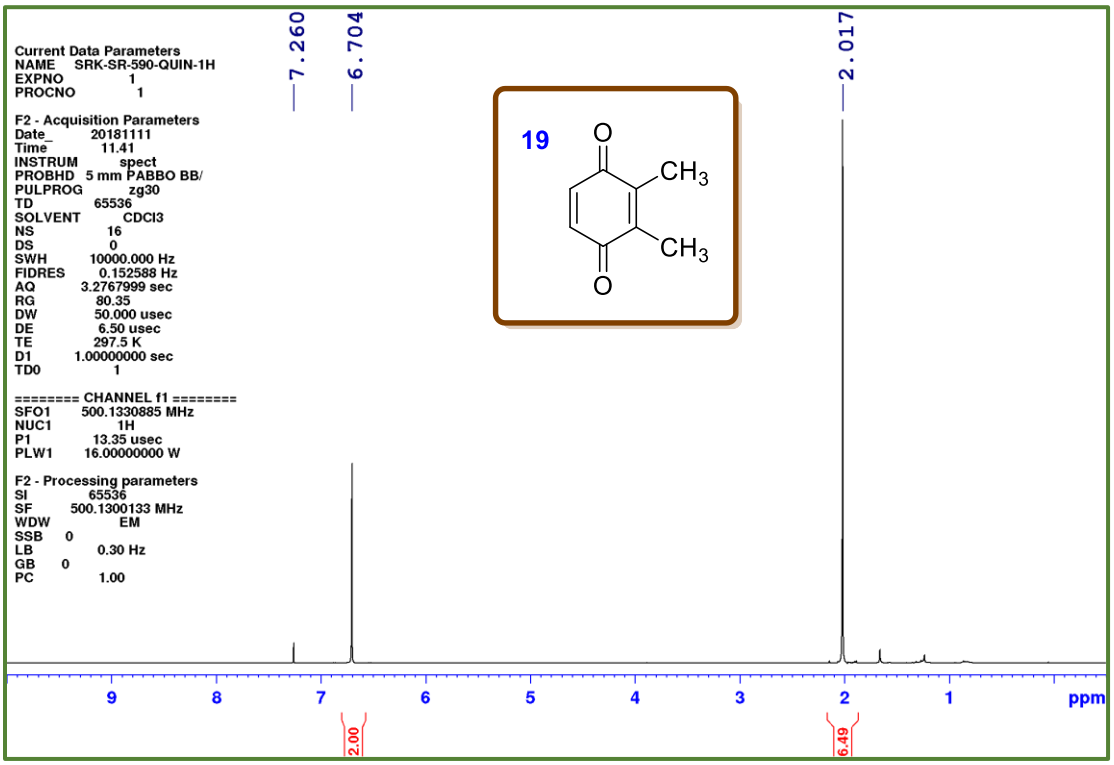
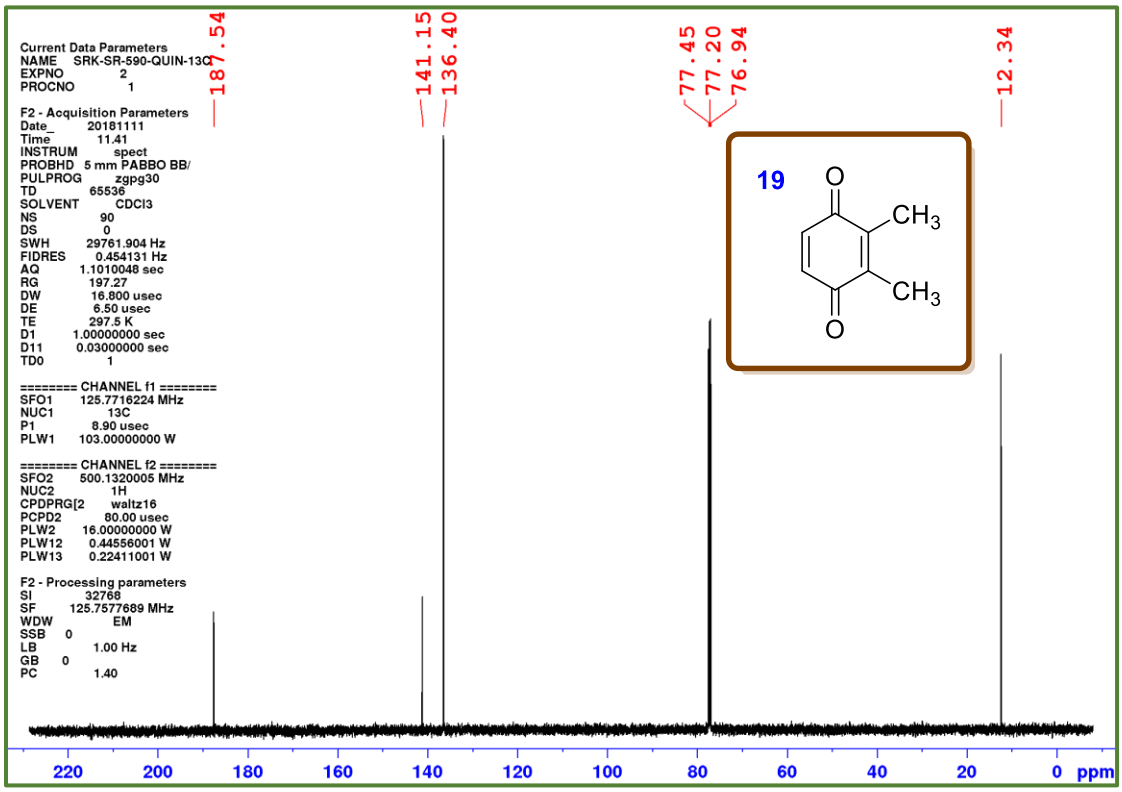
Copies of ^{1}H, ^{13}C and ^{13}C-APT & DEPT-135 NMR spectra

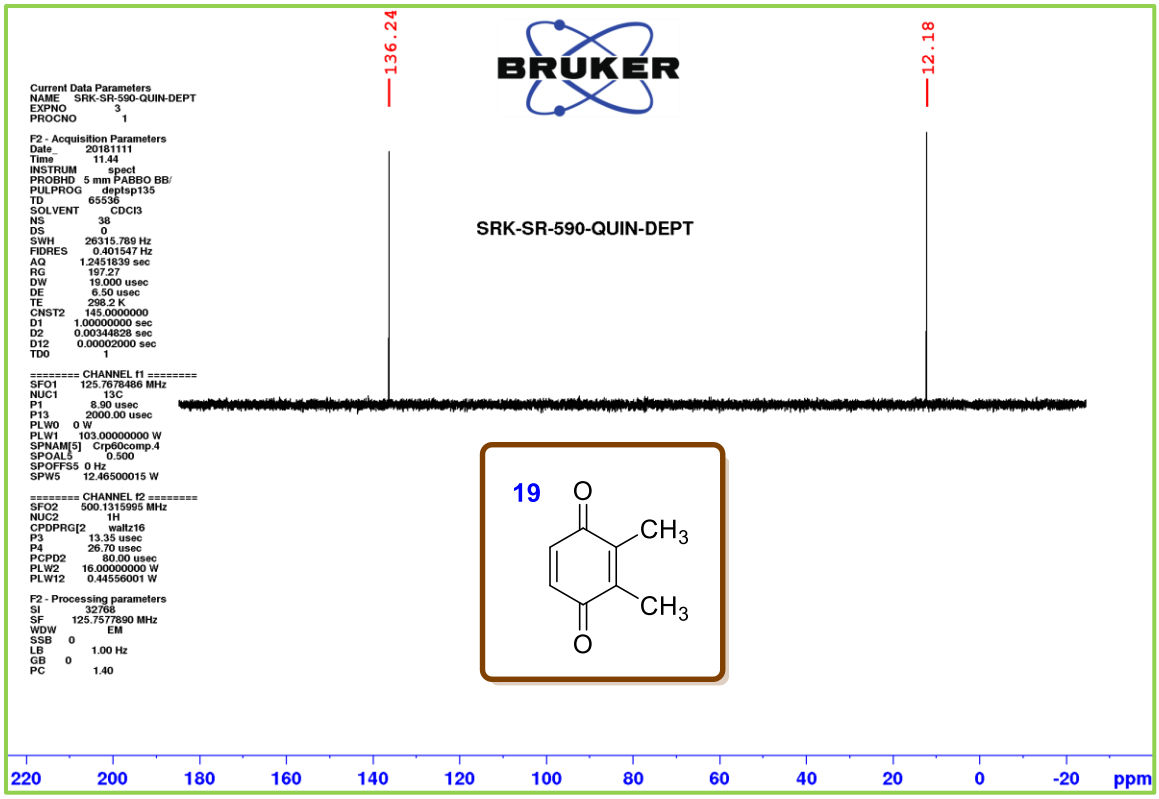
^{1}H NMR of Compound 19 (500 MHz, $CDCl_3$)



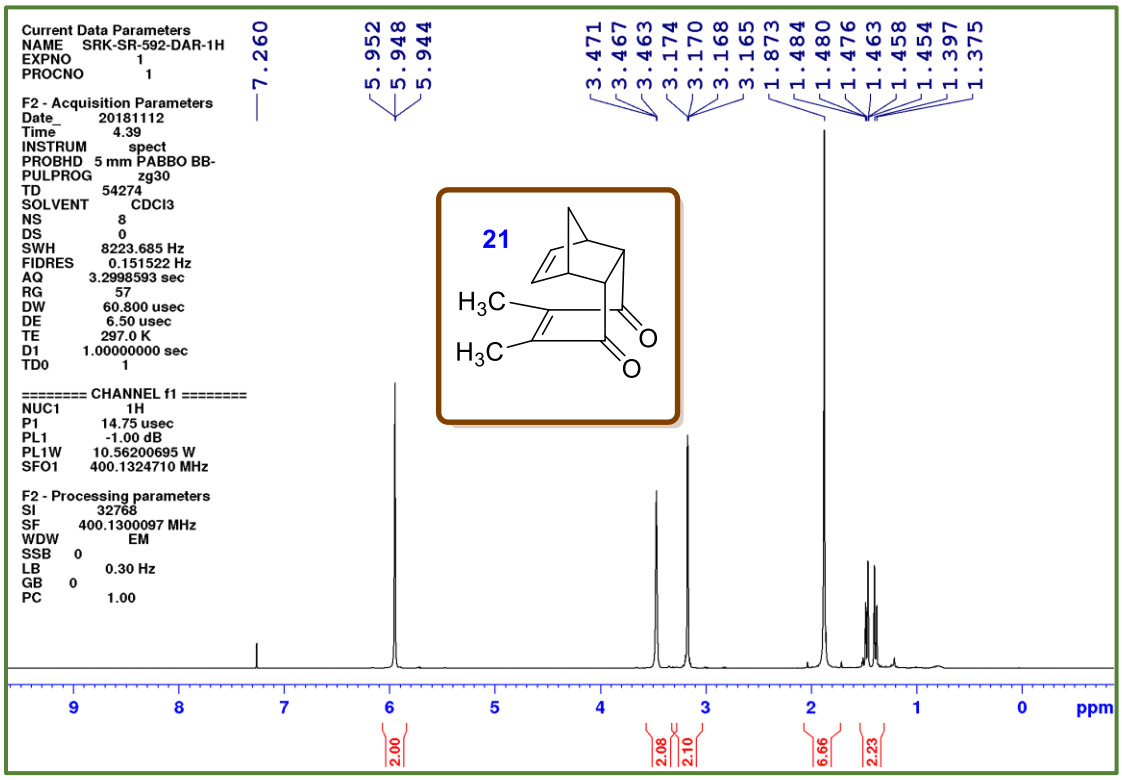
^{13}C NMR of Compound 19 (125.7 MHz, $CDCl_3$)



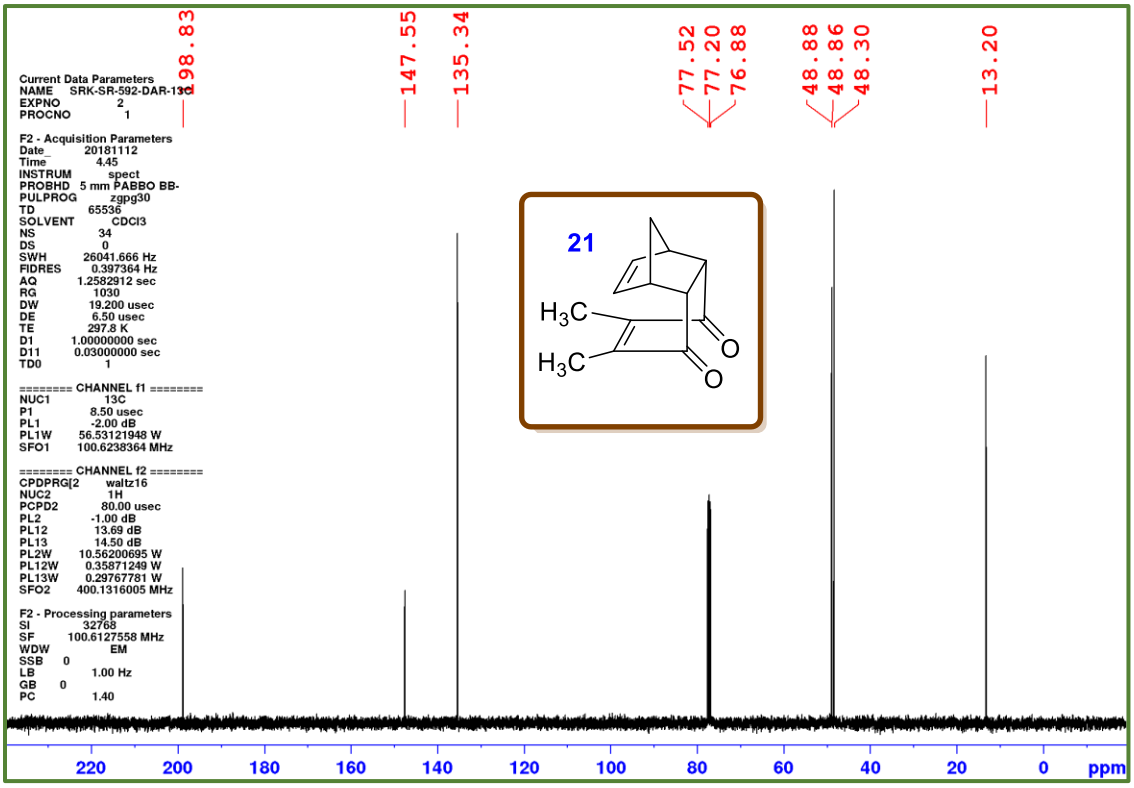
DEPT 135 NMR of Compound 19 (125.7 MHz, $CDCl_3$)



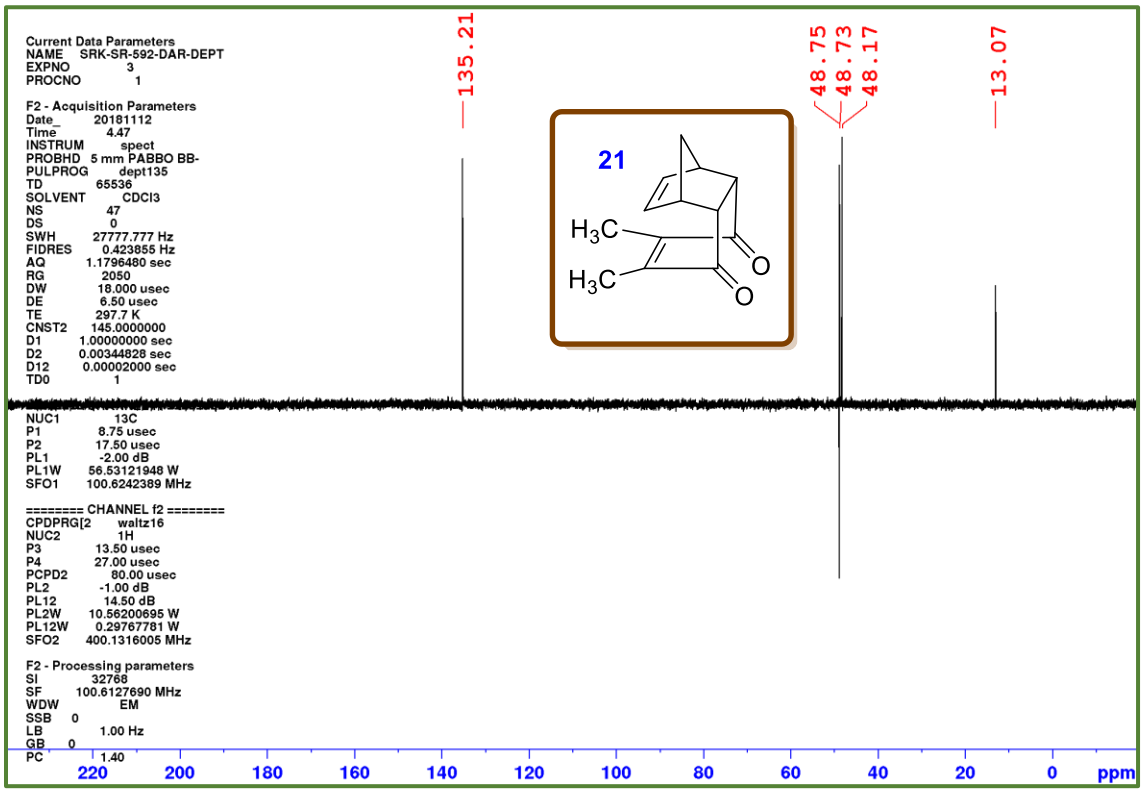
^{1}H NMR of Compound 21 (400 MHz, $CDCl_3$)



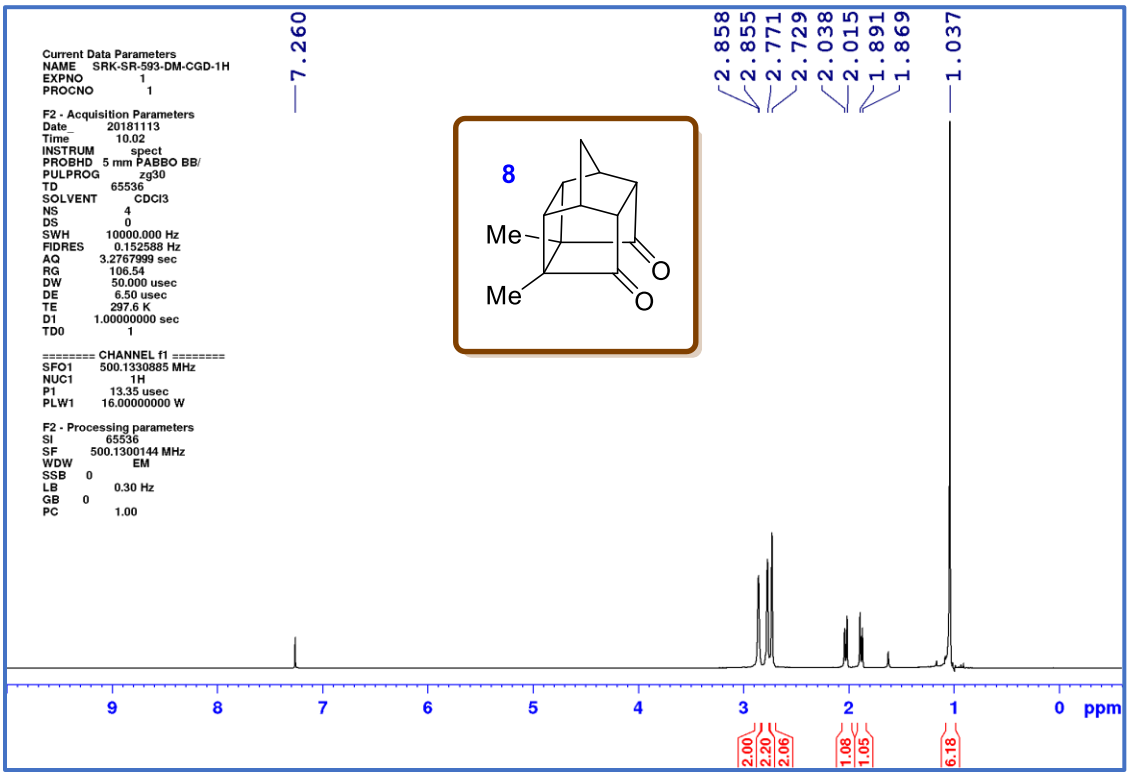
^{13}C NMR of Compound 21 (100.6 MHz, $CDCl_3$)



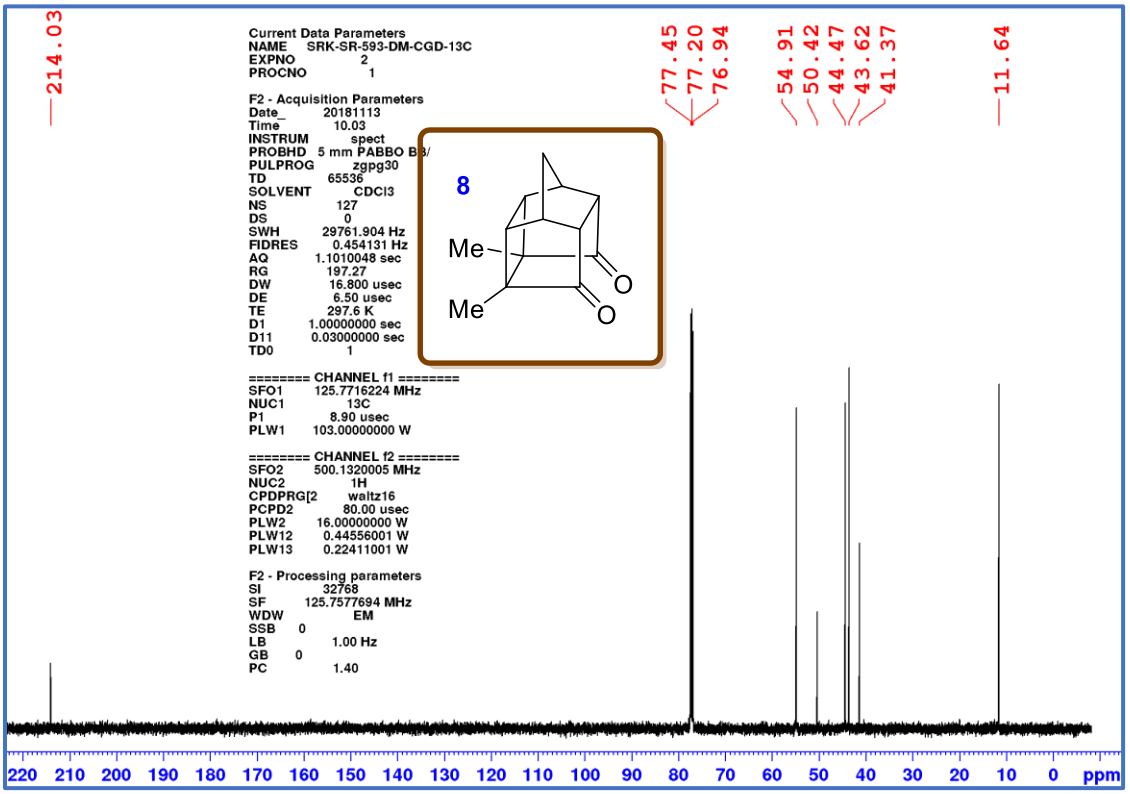
DEPT 135 NMR of Compound 21 (100.6 MHz, $CDCl_3$)



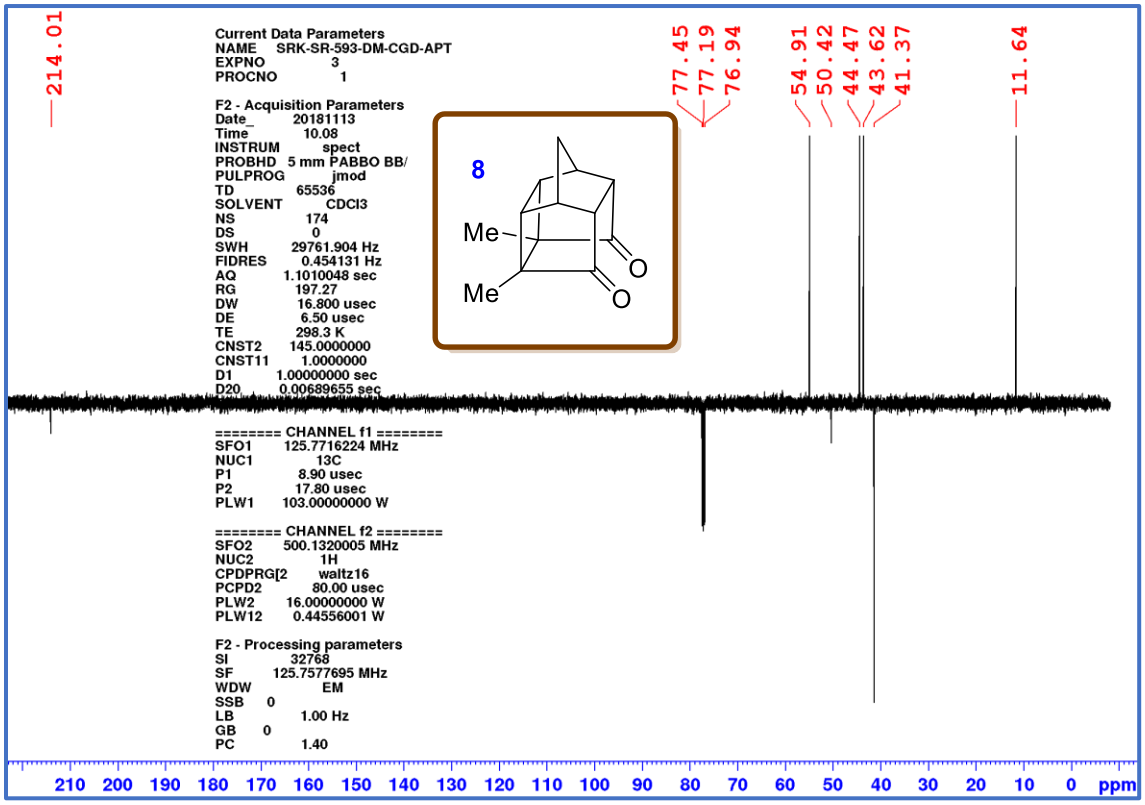
^{1}H NMR of Compound 8 (500 MHz, $CDCl_3$)



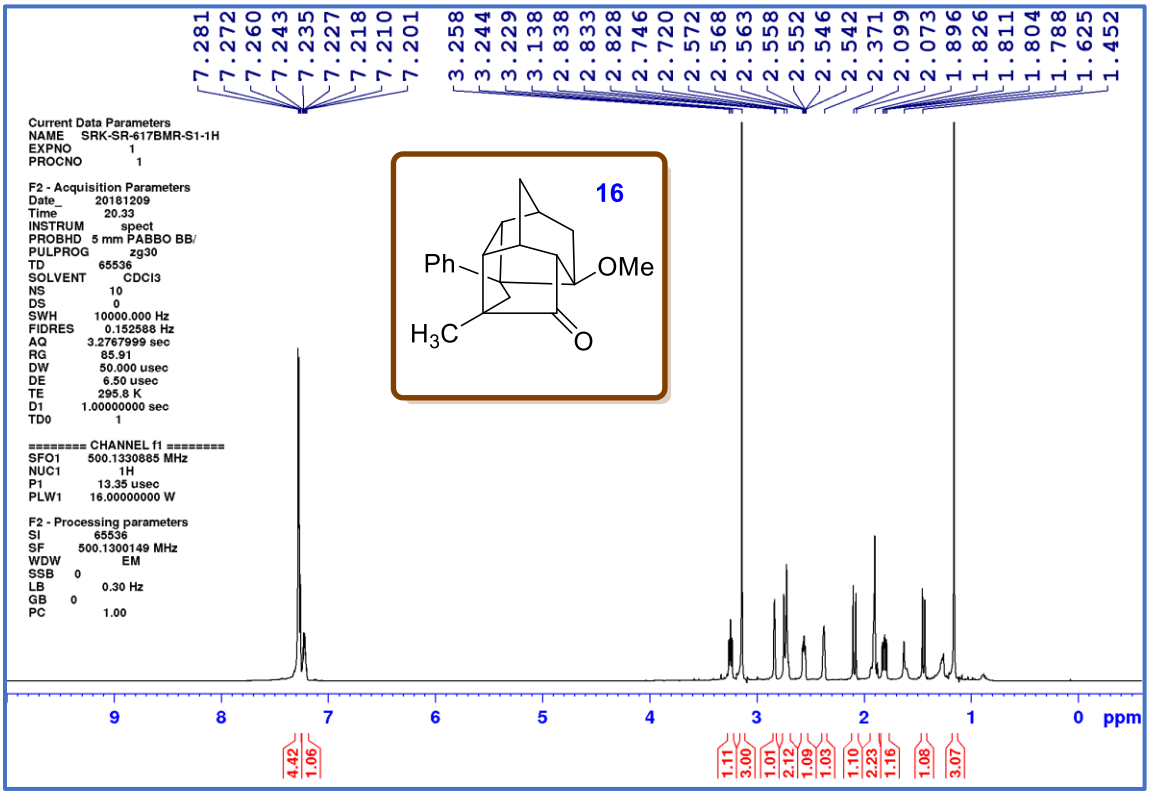
^{13}C NMR of Compound 8 (125.7 MHz, $CDCl_3$)



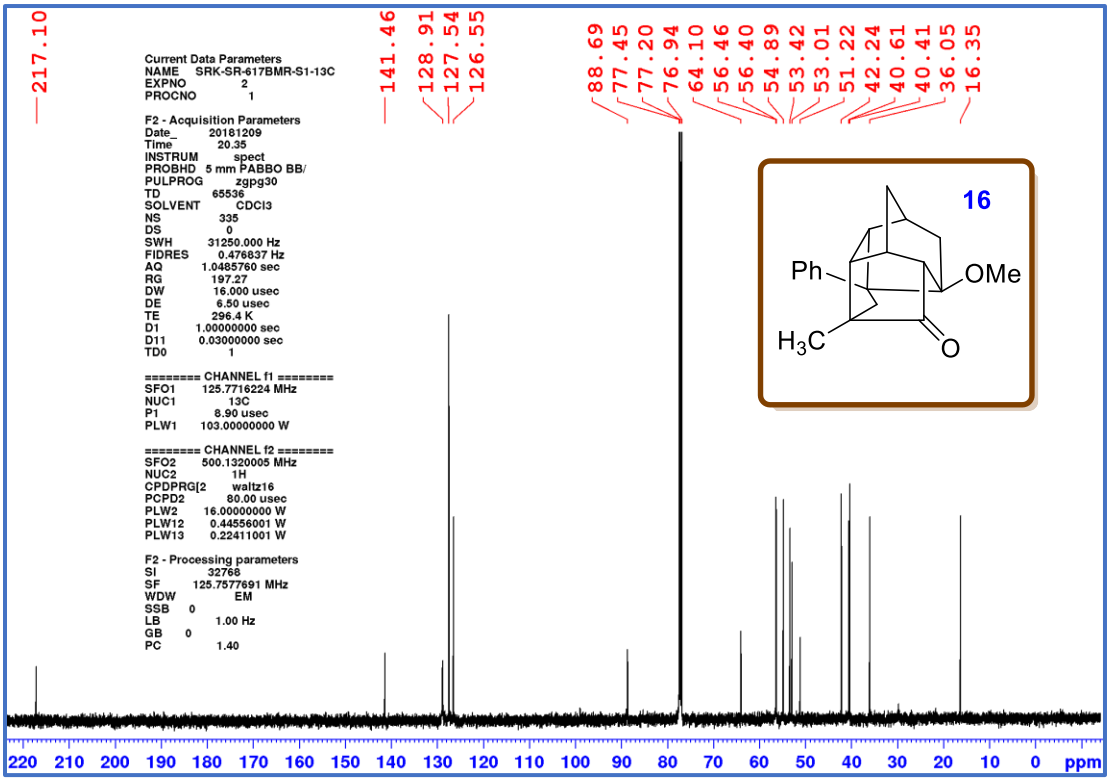
APT 135 NMR of Compound 8 (125.7 MHz, $CDCl_3$)



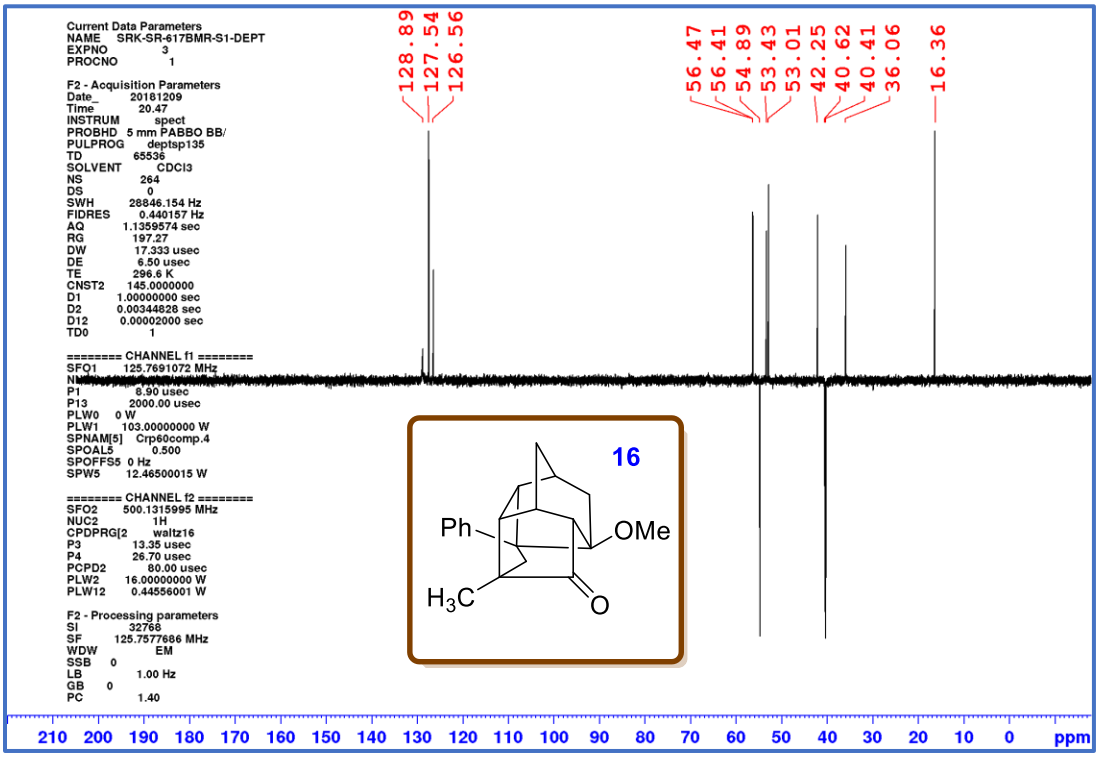
^{1}H NMR of Compound 16 (500 MHz, $CDCl_3$)



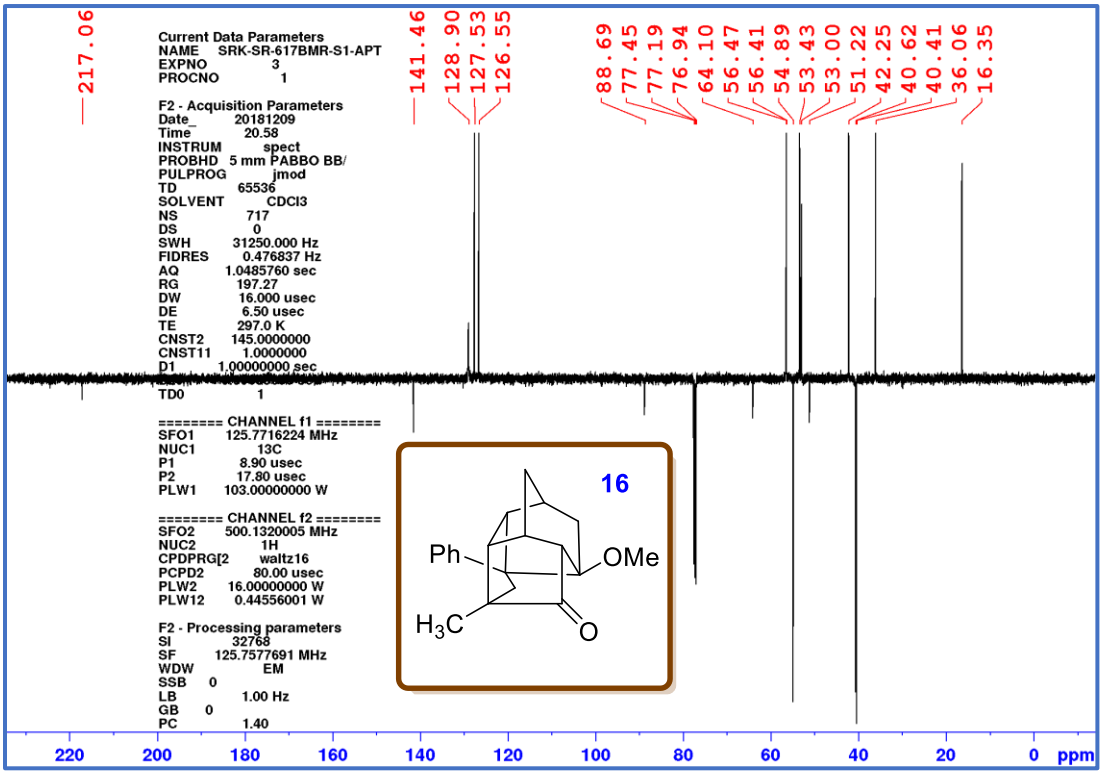
^{13}C NMR of Compound 16 (125.7 MHz, $CDCl_3$)



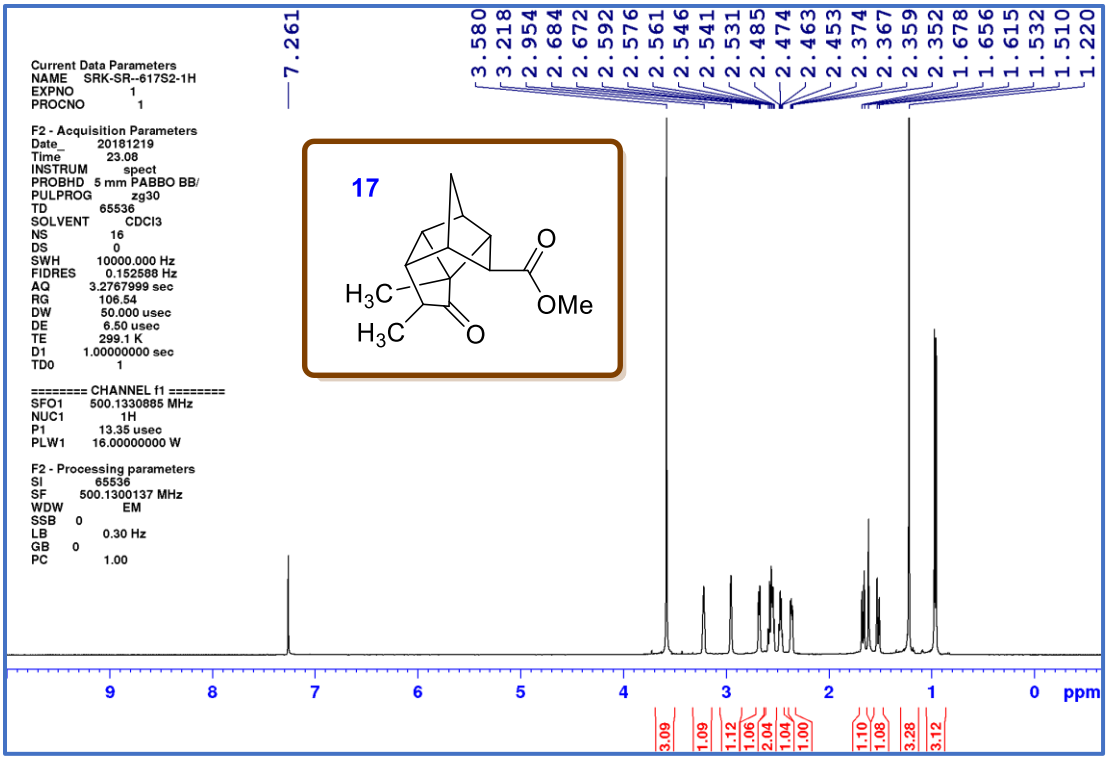
DEPT 135 NMR of Compound 16 (125.7 MHz, $CDCl_3$)



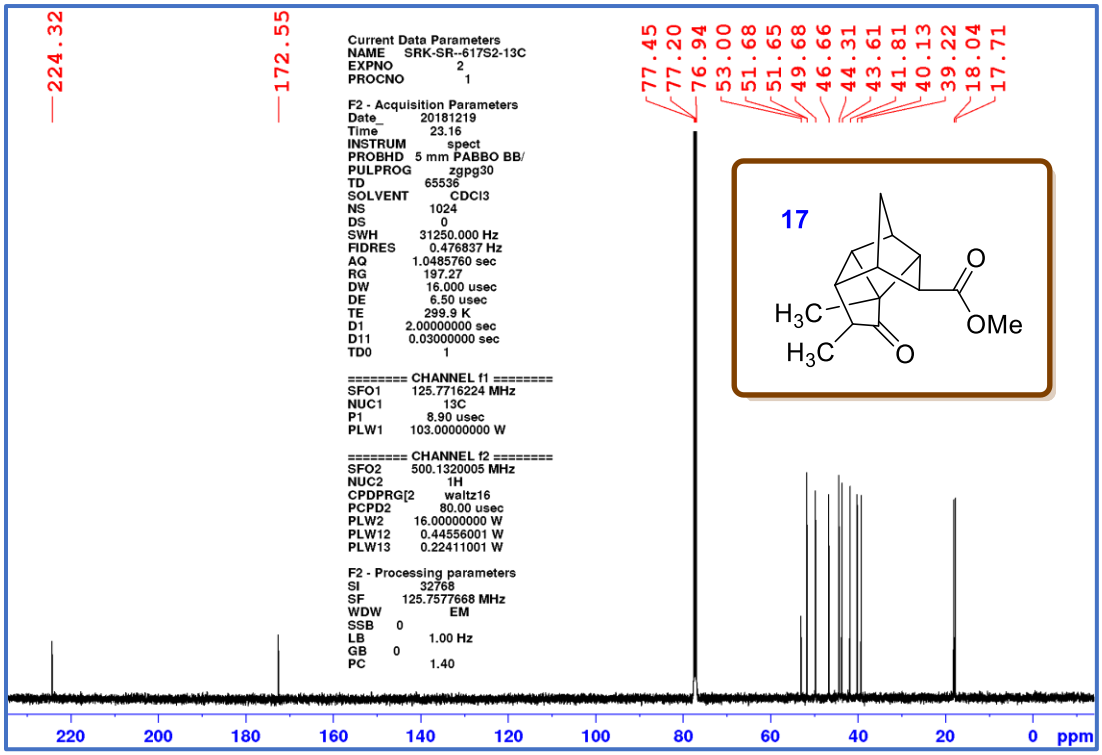
APT NMR of Compound 16 (125.7 MHz, $CDCl_3$)



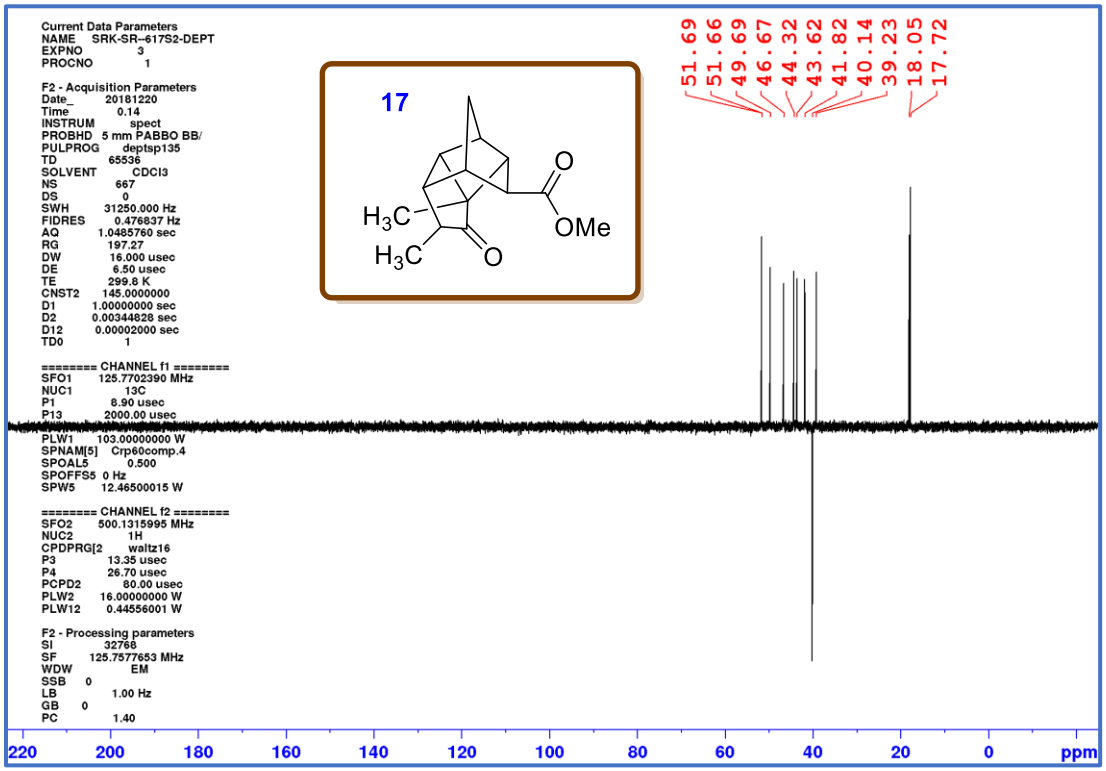
^{1}H NMR of Compound 17 (500 MHz, $CDCl_3$)



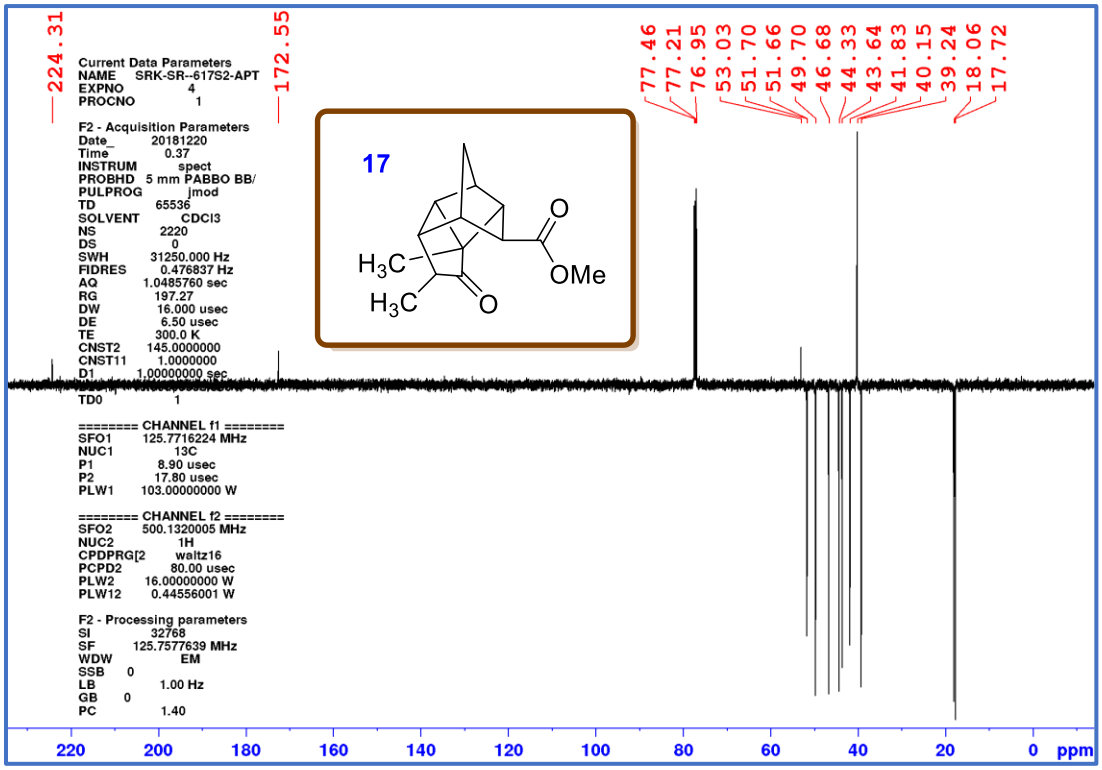
^{13}C NMR of Compound 17 (125.7 MHz, $CDCl_3$)



DEPT 135 NMR of Compound 17 (125.7 MHz, $CDCl_3$)



APT NMR of Compound 17 (125.7 MHz, $CDCl_3$)



Mass spectra of compound 16

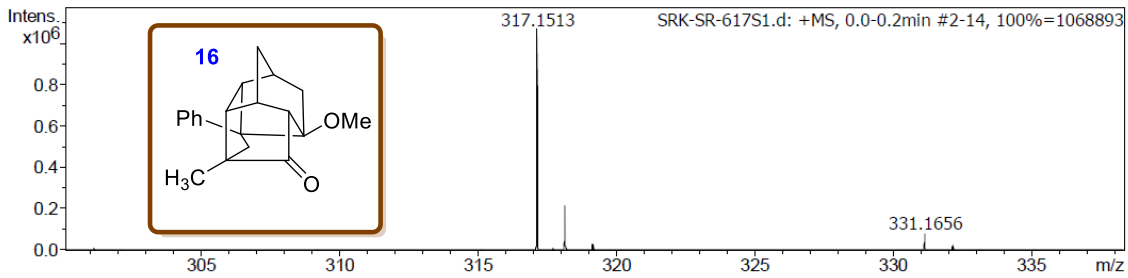
DEPARTMENT OF CHEMISTRY, I.I.T.(B)

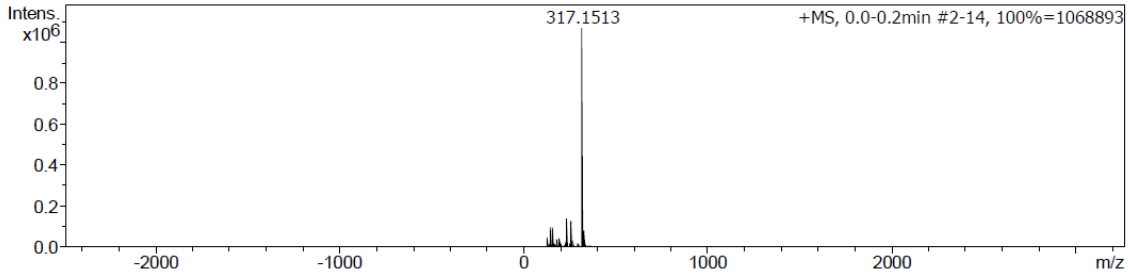
Analysis Info

Analysis Name	D:\Data\DEC 2018\SRK-SR-617S1.d	Acquisition Date	12/20/2018 11:26:44 PM
Method	Tune_pos_NAICSI-500a.m	Operator	MR IN
Sample Name	SRK-SR-617S1	Instrument	maXis impact 282001.00081
Comment	C20H22O2		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Source





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
317.1513	1	C20H22NaO2	317.1512	0.3	10.8	1	100.00	9.5	even	ok

Mass spectra of compound 17

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

Analysis Name	D:\Data\DEC 2018\SRK-SR-617S2.d	Acquisition Date	12/20/2018 11:19:28 PM
Method	Tune_pos_NAICSI-500a.m	Operator	MR IN
Sample Name	SRK-SR-617S2	Instrument	maXis impact 282001.00081
Comment	C14H18O3		

Acquisition Parameter

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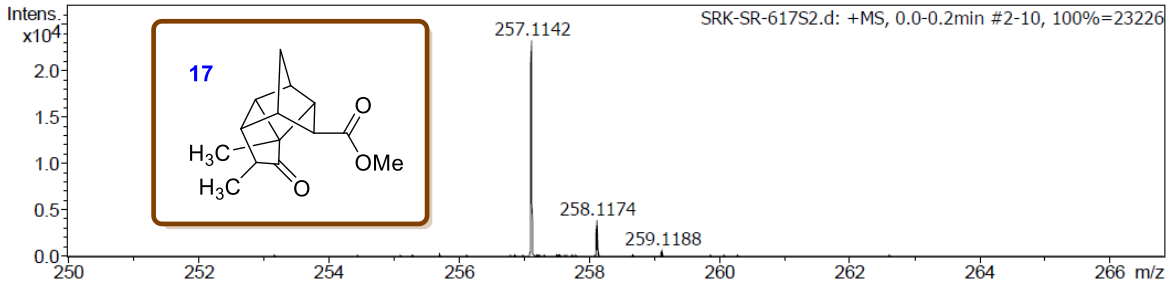
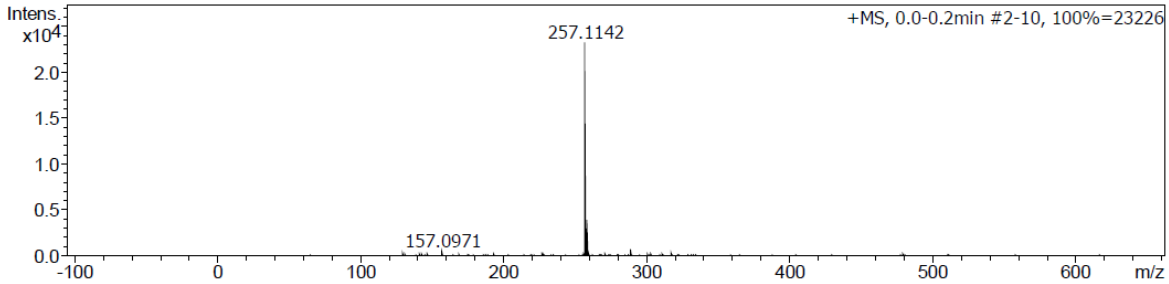
Scan End	1000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Source

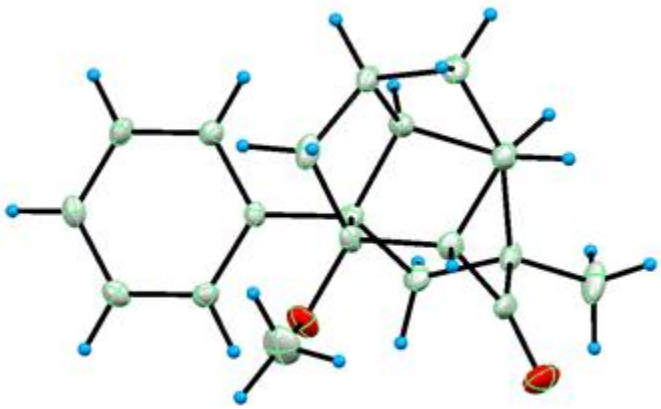




Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
257.1142	1	C14H18NaO3	257.1148	2.3	9.7	1	100.00	5.5	even	ok

X-ray crystal structure and data for compounds 16 and 17(CCDC- 1907857 and 1908339)

X-ray single crystal structure and refinement data for compound 16



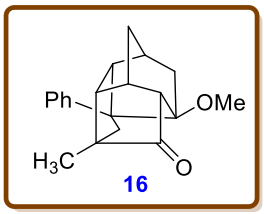
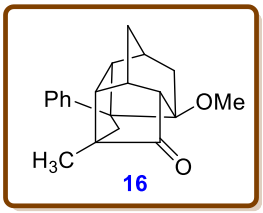


Figure S1: ORTEP representation of the compound **16** with thermal ellipsoids drawn at 20% probability level.

The X-ray structure of compound **16** was determined by single-crystal X-ray diffraction studies. Single crystals of compound **16** were obtained from EtOAc in petroleum ether solvent at room temperature. Crystal data was collected with graphite monochromatized $M_0K\alpha$ radiation (λ = 0.71073) on a Rigaku Saturn 724+ diffractometer using ω scans at temperature 293 K. The structures were solved by direct methods using Olex-2[1] and ShelXL- 97[2] and refined by full-matrix least-square minimisation based on F^2. ORTEPs were drawn using Mercury program[3] and ORTEP-3.[4] X-ray crystallographic data and refinement parameters for compound **16** provided in the below tables and are deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC No: **CCDC-1907857**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. X-ray crystallographic data and refinement parameters for compound **16** **(CCDC 1907857)**



Identification code	SRK-SR-617-S1_Mo
Empirical formula	$C_{80}H_{88}O_8$
Formula weight	1177.50
Temperature	150 K
Crystal system	Triclinic

Space group	P-1	
Hall group	-P 1	
Unit cell dimensions	a = 12.1732 (5) $Å^3$	α = 106.423 (3) °
	b = 12.4347 (4) $Å^3$	β = 90.464 (3) °
	c = 21.2275 (7) $Å^3$	γ = 90.866 (3) °
Volume	3081.50 (19) $Å^3$	
Z	2	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient (μ)	0.080 mm^{-1}	
Absorption correction	Multi-Scan	
Bond precision C–C	0.0046 A	
Max. and min. transmission	1.000 and 0.821	
F (000)	1264.0	
Crystal size	0.22 × 0.15 × 0.12 mm^3	
Crystal colour, shape	Colourless, Black	
Index ranges	$-14 \leq h \leq 10$, $-14 \leq k \leq 14$, $-25 \leq l \leq 24$	
Theta range for data collection	3.416 to 50°	
Reflections collected	19146	
Wavelength	0.71073 Å	
Independent reflections	10620 [$R_{(int)}$ = 0.0737]	
Completeness to θ = 25.00°	97.7%	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	10620/0/801	
Goodness-of-fit on F^2	1.043	
Final *R* indices [*I* >2sigma (*I*)]	R1 = 0.0689, ωR2 = 0.1438	
R indices (all data)	R1 = 0.1132, ωR2 = 0.1835	
Largest diff. peak and hole	0.29 and -0.34 e. $Å^{-3}$	

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for SRK-SR-617-S1_Mo. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O6	3948.2(17)	3763.2(16)	828.0(11)	29.6(5)
O8	1040.0(17)	-1269.4(16)	818.0(11)	30.8(6)
O2	-4342.4(19)	3267.3(17)	4282.6(12)	36.2(6)
O7	2641.4(19)	-663.4(17)	2347.9(11)	36.0(6)
O4	-1024.1(17)	8528.5(16)	4193.2(11)	32.3(6)
O5	2302.8(19)	4328.6(17)	2313.5(11)	35.9(6)
O3	-2602(2)	7437(2)	2705.3(12)	50.6(7)
O1	-3133(2)	2538(2)	2683.1(12)	53.2(8)
C15	-2954(2)	2436(2)	5135.9(15)	21.1(7)
C20	-2850(2)	3600(2)	5391.2(16)	25.6(7)
C16	-3023(3)	1808(2)	5582.7(15)	27.5(8)
C66	2489(2)	-3566(2)	1577.8(16)	25.3(7)
C41	634(3)	2537(3)	1905.7(16)	32.2(8)
C65	2053(2)	-3986(2)	863.2(15)	24.4(7)
C11	-4158(2)	2099(2)	4106.7(15)	23.3(7)
C18	-2909(2)	3467(2)	6501.8(16)	28.5(8)
C12	-4205(3)	1588(2)	3341.6(16)	28.6(8)
C74	2417(3)	-1572(2)	1966.0(16)	27.5(8)
C70	244(2)	-3189(2)	739.9(17)	28.3(7)
C62	3212(2)	-2480(2)	1637.2(15)	23.6(7)
C17	-2996(3)	2317(3)	6262.3(16)	29.5(8)
C77	2168(3)	-3460(3)	-1488.4(16)	29.5(8)
C79	1997(2)	-4192(2)	-558.3(15)	25.1(7)
C50	4738(3)	1874(2)	778.2(17)	29.8(8)
C51	3831(2)	2731(2)	993.5(15)	24.1(7)
C80	2125(2)	-3127(2)	-121.0(15)	23.7(7)
C24	-1921(2)	6908(2)	4411.7(15)	21.9(7)
C23	-3056(2)	6970(3)	4119.1(16)	27.6(8)
C5	-3054(3)	611(2)	4173.2(15)	25.3(7)
C31	-977(2)	7338(2)	4036.6(15)	22.6(7)
C4	-3014(2)	1895(2)	4402.9(16)	23.1(7)
C63	3258(2)	-2397(2)	925.6(15)	25.2(7)
C42	1751(2)	2484(2)	1592.1(15)	22.7(7)
C7	-3980(3)	311(2)	3139.1(16)	28.7(8)
C10	-4912(3)	1383(3)	4404.8(16)	32.6(8)
C48	4196(3)	837(3)	925.2(17)	29.9(8)
C55	2900(2)	1857(2)	-132.0(15)	22.1(7)

C61	4319(3)	-2397(3)	1984.8(17)	33.9(8)
C67	1414(2)	-3162(2)	1943.6(16)	27.0(7)
C35	-1870(2)	7446(2)	5153.2(16)	24.2(7)
C69	777(3)	-4205(2)	901.7(16)	28.4(8)
C3	-2049(3)	2209(2)	4025.3(16)	28.9(8)
C64	2172(2)	-2932(2)	620.0(15)	22.6(7)
C68	586(3)	-4081(3)	1630.3(16)	31.8(8)
C58	2918(3)	1509(2)	-1503.4(16)	29.7(8)
C39	-2101(2)	9056(2)	6096.2(16)	26.9(7)
C30	15(3)	6839(3)	4279.6(17)	33.9(8)
C6	-2801(2)	360(2)	3428.7(15)	23.4(7)
C38	-1842(3)	8433(3)	6525.0(17)	32.0(8)
C75	2262(3)	-2226(2)	-391.5(16)	28.4(8)
C59	3078(3)	627(3)	-1238.8(17)	31.5(8)
C40	-2114(2)	8572(2)	5425.8(16)	25.7(7)
C56	2753(2)	2748(2)	-409.2(16)	27.7(8)
C29	-363(3)	5599(3)	4134.9(17)	34.6(8)
C33	-2266(3)	6921(3)	3072.9(16)	31.1(8)
C22	-2955(3)	6212(3)	3407.4(17)	31.1(8)
C72	1285(3)	-2057(2)	1747.2(16)	26.8(7)
C76	2271(3)	-2394(3)	-1061.3(17)	32.2(8)
C78	2021(3)	-4358(3)	-1232.5(16)	29.8(8)
C27	-1071(3)	5505(2)	3094.5(16)	30.1(8)
C45	3676(2)	2973(2)	1754.8(15)	25.0(7)
C32	-1097(3)	6808(3)	3285.1(16)	31.7(8)
C8	-4623(3)	-361(3)	3511.4(16)	34.9(9)
C53	1728(2)	2554(2)	875.8(15)	22.5(7)
C52	2822(2)	2055(2)	604.2(15)	20.7(7)
C71	1150(2)	-2296(2)	985.8(16)	25.7(7)
C57	2770(3)	2580(3)	-1082.5(16)	30.9(8)
C60	3079(3)	798(2)	-559.7(15)	26.3(7)
C9	-4303(3)	261(2)	4216.4(16)	30.2(8)
C36	-1609(3)	6829(3)	5587.2(17)	30.6(8)
C19	-2823(2)	4108(2)	6063.9(16)	27.6(7)
C47	2925(2)	1004(2)	849.4(15)	24.0(7)
C73	4(3)	-745(3)	945(2)	44.9(10)
C26	-2112(3)	5309(3)	3466.3(16)	29.5(8)
C54	5001(3)	4306(3)	962(2)	45.7(10)
C46	2543(3)	3429(2)	1939.9(16)	27.0(7)
C37	-1600(3)	7310(3)	6264.2(17)	36.5(9)
C49	4357(3)	974(3)	1662.4(16)	31.9(8)
C43	2458(2)	1423(2)	1551.8(16)	25.4(7)

C2	-2241(3)	1427(3)	3321.2(16)	28.6(8)
C25	-1653(3)	5654(2)	4177.3(16)	27.1(7)
C44	3521(3)	1867(2)	1952.8(16)	27.6(7)
C13	-3187(3)	1961(2)	3061.8(15)	31.5(8)
C28	-162(3)	5025(3)	3409.6(17)	37.9(9)
C14	-5422(3)	3606(3)	4151(2)	51.0(11)
C21	-4045(3)	5775(3)	3061.3(19)	48.1(10)
C1	-1226(3)	1254(3)	2888.8(18)	48.6(11)
C34	-65(3)	9092(3)	4059(2)	51.5(11)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for SRK-SR-617-S1_Mo. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O6	28.9(12)	25.4(11)	35.1(14)	10.0(10)	0.0(10)	-5.4(9)
O8	29.1(12)	27.2(11)	38.5(15)	12.8(11)	3.5(11)	8.3(10)
O2	39.3(14)	29.1(12)	37.8(15)	5.0(11)	-8.7(11)	13.6(10)
O7	42.4(14)	29.7(12)	31.8(15)	2.2(11)	-1.5(12)	-0.1(11)
O4	34.9(13)	24.1(10)	38.2(15)	9.1(10)	8.6(11)	-4.5(10)
O5	40.4(14)	29.5(12)	34.0(15)	2.6(11)	3.4(12)	1.4(10)
O3	74.0(19)	47.7(15)	36.4(17)	21.8(13)	-5.7(14)	12.9(14)
O1	84(2)	48.8(15)	34.0(16)	23.9(13)	-6.2(14)	-14.3(14)
C15	19.6(16)	23.7(14)	19.0(18)	4.7(13)	1.5(13)	-0.5(12)
C20	27.5(18)	26.4(15)	26(2)	11.7(14)	1.0(15)	3.0(13)
C16	34.5(19)	24.9(15)	23(2)	7.4(14)	2.6(15)	-1.6(14)
C66	26.7(18)	24.3(15)	25.0(19)	7.1(14)	0.0(14)	1.2(13)
C41	32.7(19)	36.0(17)	30(2)	12.8(16)	5.1(16)	2.2(15)
C65	26.0(17)	21.6(14)	24.8(19)	5.3(14)	-1.5(14)	-1.5(13)
C11	25.8(17)	25.1(15)	18.2(18)	5.2(13)	-5.7(14)	4.5(13)
C18	25.6(18)	32.0(16)	24.1(19)	1.3(15)	1.5(15)	4.2(14)
C12	28.7(18)	31.9(16)	26(2)	9.0(15)	-2.6(15)	1.0(14)
C74	35.1(19)	24.8(16)	21.4(19)	4.8(15)	4.1(15)	-1.0(14)
C70	22.7(17)	35.2(17)	26(2)	7.9(15)	-2.4(14)	-2.8(14)
C62	22.5(17)	28.7(15)	19.2(18)	6.2(14)	-4.3(13)	-1.9(13)
C17	35.7(19)	34.1(17)	19.7(19)	8.9(15)	2.3(15)	1.2(15)
C77	28.4(18)	41.5(18)	19.1(19)	9.9(16)	-1.7(14)	-5.7(15)
C79	25.7(17)	24.7(15)	26(2)	9.1(14)	-1.9(14)	0.4(13)
C50	23.5(17)	33.8(17)	31(2)	6.5(15)	1.5(15)	1.4(14)
C51	26.2(17)	22.8(14)	23.1(19)	6.4(14)	-1.5(14)	1.0(13)
C80	18.6(16)	28.0(15)	25.1(19)	8.5(14)	-0.7(14)	0.2(13)

C24	20.9(16)	25.3(15)	21.4(18)	9.1(14)	2.8(14)	5.8(13)
C23	24.5(17)	31.7(16)	27(2)	8.5(15)	2.3(15)	2.0(14)
C5	28.9(18)	21.8(15)	25.2(19)	6.7(14)	1.7(15)	-0.2(13)
C31	24.6(17)	21.0(14)	21.2(18)	4.5(13)	-0.7(14)	-1.2(13)
C4	19.6(16)	22.7(14)	27.5(19)	8.1(14)	1.7(14)	-1.3(12)
C63	29.0(18)	21.7(14)	23.7(19)	4.8(14)	-0.4(14)	-3.0(13)
C42	18.6(16)	24.1(15)	25.1(19)	6.2(14)	4.4(14)	1.9(12)
C7	33.3(19)	30.0(16)	23.2(19)	8.4(15)	-2.1(15)	-4.4(14)
C10	21.6(18)	49(2)	24(2)	4.5(16)	2.0(15)	-4.5(15)
C48	29.6(18)	29.1(16)	33(2)	10.5(15)	4.5(16)	10.1(14)
C55	18.1(16)	24.8(15)	22.0(18)	4.1(14)	1.3(13)	2.0(12)
C61	35(2)	36.2(18)	28(2)	5.3(16)	-2.4(16)	-4.4(15)
C67	29.0(18)	32.0(16)	19.3(18)	6.6(14)	-0.7(14)	-3.7(14)
C35	20.5(16)	26.9(15)	27(2)	11.2(14)	1.1(14)	1.0(13)
C69	28.0(18)	27.5(16)	31(2)	9.9(15)	-2.9(15)	-4.8(14)
C3	27.0(18)	30.5(16)	29(2)	8.4(15)	3.4(15)	-6.2(14)
C64	28.1(17)	20.6(14)	19.1(18)	5.6(13)	-0.5(14)	0.4(13)
C68	29.7(18)	35.5(17)	32(2)	12.8(16)	-2.2(16)	-6.1(15)
C58	32.1(19)	36.0(17)	21.7(19)	9.0(15)	1.7(15)	6.3(15)
C39	25.9(18)	25.6(15)	27(2)	3.3(14)	2.5(15)	1.3(13)
C30	24.5(18)	41.6(19)	30(2)	1.2(16)	1.3(16)	5.6(15)
C6	28.6(17)	25.9(15)	14.8(17)	4.3(13)	-1.0(14)	3.9(13)
C38	36(2)	34.9(17)	23(2)	3.8(15)	2.9(16)	6.2(15)
C75	29.7(18)	24.4(15)	31(2)	7.9(15)	-1.5(15)	-3.5(14)
C59	36(2)	27.0(16)	31(2)	6.1(15)	8.9(16)	7.7(14)
C40	24.6(17)	24.6(15)	28(2)	7.6(14)	4.0(14)	2.5(13)
C56	29.6(18)	24.9(15)	30(2)	9.4(15)	3.7(15)	5.4(14)
C29	37(2)	35.9(18)	31(2)	8.4(16)	-1.9(16)	16.0(16)
C33	46(2)	31.5(17)	14.8(19)	4.4(15)	-5.1(16)	7.0(16)
C22	26.8(18)	34.3(17)	32(2)	9.3(16)	-5.3(15)	0.0(14)
C72	27.0(18)	31.2(16)	22.5(19)	7.6(15)	0.7(15)	1.9(14)
C76	37(2)	37.3(18)	28(2)	18.1(16)	0.8(16)	-3.6(15)
C78	35.2(19)	28.5(16)	23(2)	3.6(15)	0.0(15)	-3.3(14)
C27	38(2)	28.8(16)	21.5(19)	4.1(15)	2.3(15)	6.2(15)
C45	24.9(17)	27.6(15)	19.2(18)	1.6(14)	-0.5(14)	-2.2(13)
C32	35(2)	32.7(17)	29(2)	11.7(16)	8.7(16)	0.3(15)
C8	38(2)	31.7(17)	32(2)	4.6(16)	6.5(17)	-11.8(15)
C53	20.6(16)	23.9(15)	22.3(18)	5.3(14)	0.5(14)	3.2(13)
C52	22.3(16)	19.2(14)	20.6(18)	5.6(13)	-1.5(13)	2.9(12)
C71	24.8(17)	23.4(15)	30(2)	9.8(14)	-0.3(15)	0.5(13)
C57	34.8(19)	34.4(17)	30(2)	18.7(16)	6.4(16)	8.3(15)
C60	30.4(18)	26.7(15)	22.5(19)	7.9(14)	0.9(15)	3.7(14)

C9	39(2)	29.3(16)	20.4(19)	4.7(14)	3.0(15)	-11.0(15)
C36	33.9(19)	28.2(16)	30(2)	8.9(15)	-0.2(16)	7.6(14)
C19	26.3(18)	23.7(15)	32(2)	5.9(15)	-2.4(15)	1.3(13)
C47	27.4(17)	18.9(14)	25.4(19)	5.8(13)	-1.7(14)	-0.2(13)
C73	39(2)	37.3(19)	57(3)	10.3(19)	0.2(19)	11.4(17)
C26	31.1(18)	27.4(16)	31(2)	8.7(15)	4.3(16)	-0.4(14)
C54	42(2)	37.6(19)	58(3)	14.9(19)	4(2)	-13.7(17)
C46	33.4(19)	27.2(16)	22.0(19)	9.2(15)	1.7(15)	1.5(14)
C37	50(2)	38.7(18)	24(2)	14.3(16)	2.6(17)	7.4(17)
C49	30.0(19)	36.8(18)	33(2)	17.0(16)	-2.2(16)	6.4(15)
C43	23.3(17)	26.5(15)	28(2)	10.5(14)	0.6(14)	-0.7(13)
C2	28.5(18)	35.8(17)	18.9(19)	4.0(15)	4.8(15)	-8.8(14)
C25	33.0(19)	27.4(16)	22.4(19)	9.5(14)	0.5(15)	4.6(14)
C44	29.0(18)	34.9(17)	20.4(19)	10.3(15)	-2.1(14)	2.6(14)
C13	53(2)	26.3(16)	14.2(18)	5.1(14)	-0.7(16)	-8.1(16)
C28	38(2)	34.3(18)	38(2)	3.6(17)	3.8(18)	11.8(16)
C14	45(2)	50(2)	59(3)	16(2)	-2(2)	23.7(19)
C21	41(2)	60(2)	40(3)	10(2)	-11.8(19)	-4.2(19)
C1	39(2)	66(2)	32(2)	-0.6(19)	14.8(18)	-17.4(19)
C34	46(2)	36.5(19)	72(3)	16(2)	18(2)	-14.2(18)

Table S4. Bond Lengths for SRK-SR-617-S1_Mo.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O6	C51	1.428(3)	C31	C30	1.517(4)
O6	C54	1.428(4)	C31	C32	1.549(4)
O8	C71	1.427(3)	C4	C3	1.535(4)
O8	C73	1.421(4)	C63	C64	1.526(4)
O2	C11	1.415(3)	C42	C53	1.548(4)
O2	C14	1.435(4)	C42	C46	1.523(4)
O7	C74	1.215(4)	C42	C43	1.568(4)
O4	C31	1.425(3)	C7	C6	1.550(4)
O4	C34	1.425(4)	C7	C8	1.516(4)
O5	C46	1.216(3)	C10	C9	1.542(4)
O3	C33	1.214(4)	C48	C47	1.578(4)
O1	C13	1.221(4)	C48	C49	1.536(4)
C15	C20	1.398(4)	C55	C56	1.406(4)
C15	C16	1.391(4)	C55	C52	1.516(4)
C15	C4	1.511(4)	C55	C60	1.393(4)
C20	C19	1.389(4)	C67	C68	1.512(4)
C16	C17	1.402(4)	C67	C72	1.554(4)

C66	C65	1.545(4)
C66	C62	1.575(4)
C66	C67	1.544(4)
C41	C42	1.513(4)
C65	C69	1.579(4)
C65	C64	1.544(4)
C11	C12	1.568(4)
C11	C4	1.577(4)
C11	C10	1.530(4)
C18	C17	1.377(4)
C18	C19	1.389(4)
C12	C7	1.553(4)
C12	C13	1.501(4)
C74	C62	1.516(4)
C74	C72	1.512(4)
C70	C69	1.549(4)
C70	C71	1.533(4)
C62	C63	1.545(4)
C62	C61	1.519(4)
C77	C76	1.381(4)
C77	C78	1.384(4)
C79	C80	1.392(4)
C79	C78	1.387(4)
C50	C51	1.528(4)
C50	C48	1.549(4)
C51	C45	1.571(4)
C51	C52	1.567(4)
C80	C64	1.523(4)
C80	C75	1.404(4)
C24	C23	1.522(4)
C24	C31	1.574(4)
C24	C35	1.527(4)
C24	C25	1.538(4)
C23	C22	1.545(4)
C5	C4	1.531(4)
C5	C6	1.556(4)
C5	C9	1.586(4)
C35	C40	1.393(4)
C35	C36	1.392(4)
C69	C68	1.531(4)
C3	C2	1.549(4)
C64	C71	1.573(4)
C58	C59	1.382(4)
C58	C57	1.393(4)
C39	C38	1.389(4)
C39	C40	1.379(4)
C30	C29	1.546(4)
C6	C2	1.557(4)
C38	C37	1.385(4)
C75	C76	1.377(4)
C59	C60	1.396(4)
C56	C57	1.385(4)
C29	C25	1.576(5)
C29	C28	1.526(5)
C33	C22	1.526(4)
C33	C32	1.510(5)
C22	C26	1.562(4)
C22	C21	1.528(5)
C72	C71	1.565(4)
C27	C32	1.556(4)
C27	C26	1.550(4)
C27	C28	1.504(5)
C45	C46	1.512(4)
C45	C44	1.557(4)
C8	C9	1.522(4)
C53	C52	1.525(4)
C52	C47	1.545(4)
C36	C37	1.392(5)
C47	C43	1.549(4)
C26	C25	1.545(5)
C49	C44	1.518(4)
C43	C44	1.549(4)
C2	C13	1.512(5)
C2	C1	1.527(4)

Table S5. Bond Angles for SRK-SR-617-S1_Mo.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C54	O6	C51	115.9(2)	C4	C3	C2	102.6(2)
C73	O8	C71	116.3(2)	C65	C64	C71	97.1(2)
C11	O2	C14	116.5(3)	C80	C64	C65	116.2(2)
C31	O4	C34	116.4(2)	C80	C64	C63	112.6(2)
C20	C15	C4	120.8(3)	C80	C64	C71	113.5(3)
C16	C15	C20	117.3(3)	C63	C64	C65	103.9(2)
C16	C15	C4	121.9(2)	C63	C64	C71	112.3(2)
C19	C20	C15	121.3(3)	C67	C68	C69	100.8(2)
C15	C16	C17	121.6(3)	C59	C58	C57	119.1(3)
C65	C66	C62	107.7(2)	C40	C39	C38	120.9(3)
C67	C66	C65	100.5(2)	C31	C30	C29	100.9(3)
C67	C66	C62	106.1(2)	C5	C6	C2	107.6(2)
C66	C65	C69	106.8(2)	C7	C6	C5	100.6(2)
C64	C65	C66	102.5(2)	C7	C6	C2	105.9(2)
C64	C65	C69	105.9(2)	C37	C38	C39	118.5(3)
O2	C11	C12	110.8(2)	C76	C75	C80	121.2(3)
O2	C11	C4	108.6(2)	C58	C59	C60	120.7(3)
O2	C11	C10	117.4(2)	C39	C40	C35	121.6(3)
C12	C11	C4	111.6(2)	C57	C56	C55	121.4(3)
C10	C11	C12	107.6(2)	C30	C29	C25	104.1(2)
C10	C11	C4	100.4(2)	C28	C29	C30	107.8(3)
C17	C18	C19	119.3(3)	C28	C29	C25	103.5(3)
C7	C12	C11	111.4(2)	O3	C33	C22	126.5(3)
C13	C12	C11	108.2(3)	O3	C33	C32	128.5(3)
C13	C12	C7	97.8(2)	C32	C33	C22	105.0(3)
O7	C74	C62	127.1(3)	C23	C22	C26	103.9(3)
O7	C74	C72	127.3(3)	C33	C22	C23	103.6(2)
C72	C74	C62	105.5(2)	C33	C22	C26	101.4(2)
C71	C70	C69	100.3(2)	C33	C22	C21	114.7(3)
C74	C62	C66	101.0(2)	C21	C22	C23	115.0(3)
C74	C62	C63	103.3(2)	C21	C22	C26	116.5(3)
C74	C62	C61	114.4(3)	C74	C72	C67	97.1(2)
C63	C62	C66	103.8(2)	C74	C72	C71	110.1(2)
C61	C62	C66	117.3(3)	C67	C72	C71	111.3(2)
C61	C62	C63	115.0(3)	C75	C76	C77	120.9(3)
C18	C17	C16	120.0(3)	C77	C78	C79	120.5(3)
C76	C77	C78	118.8(3)	C26	C27	C32	98.0(2)
C78	C79	C80	121.4(3)	C28	C27	C32	115.3(3)
C51	C50	C48	100.6(2)	C28	C27	C26	103.8(3)

O6	C51	C50	117.4(2)
O6	C51	C45	109.9(2)
O6	C51	C52	108.9(2)
C50	C51	C45	108.5(3)
C50	C51	C52	100.7(2)
C52	C51	C45	111.1(2)
C79	C80	C64	122.3(3)
C79	C80	C75	117.1(3)
C75	C80	C64	120.5(3)
C23	C24	C31	113.0(2)
C23	C24	C35	112.8(2)
C23	C24	C25	103.9(3)
C35	C24	C31	113.0(2)
C35	C24	C25	115.8(2)
C25	C24	C31	97.3(2)
C24	C23	C22	102.9(2)
C4	C5	C6	102.3(2)
C4	C5	C9	105.8(2)
C6	C5	C9	106.2(3)
O4	C31	C24	108.6(2)
O4	C31	C30	117.7(3)
O4	C31	C32	110.3(2)
C30	C31	C24	100.4(2)
C30	C31	C32	108.5(2)
C32	C31	C24	110.9(2)
C15	C4	C11	111.4(2)
C15	C4	C5	116.7(2)
C15	C4	C3	114.0(3)
C5	C4	C11	97.6(2)
C5	C4	C3	103.9(2)
C3	C4	C11	112.0(2)
C64	C63	C62	103.7(2)
C41	C42	C53	114.5(3)
C41	C42	C46	114.4(3)
C46	C45	C51	109.6(3)
C46	C45	C44	97.1(2)
C44	C45	C51	111.4(2)
C31	C32	C27	111.9(3)
C33	C32	C31	109.5(2)
C33	C32	C27	97.8(3)
C7	C8	C9	100.8(2)
C52	C53	C42	103.4(2)
C55	C52	C51	113.2(2)
C55	C52	C53	112.6(2)
C55	C52	C47	115.8(2)
C53	C52	C51	112.4(2)
C53	C52	C47	104.2(2)
C47	C52	C51	97.5(2)
O8	C71	C70	117.0(3)
O8	C71	C64	108.8(2)
O8	C71	C72	110.2(2)
C70	C71	C64	100.6(2)
C70	C71	C72	109.0(2)
C72	C71	C64	110.9(3)
C56	C57	C58	120.2(3)
C55	C60	C59	121.0(3)
C10	C9	C5	104.3(2)
C8	C9	C5	104.1(2)
C8	C9	C10	107.9(3)
C35	C36	C37	121.7(3)
C20	C19	C18	120.5(3)
C52	C47	C48	105.7(2)
C52	C47	C43	101.7(2)
C43	C47	C48	107.0(3)
C27	C26	C22	106.6(2)
C25	C26	C22	107.7(2)
C25	C26	C27	99.8(3)
O5	C46	C42	126.7(3)

C41	C42	C43	117.6(2)	O5	C46	C45	128.1(3)
C53	C42	C43	103.5(2)	C45	C46	C42	105.1(2)
C46	C42	C53	103.5(2)	C38	C37	C36	120.3(3)
C46	C42	C43	101.6(2)	C44	C49	C48	101.0(2)
C6	C7	C12	98.4(2)	C47	C43	C42	108.4(2)
C8	C7	C12	115.3(3)	C44	C43	C42	105.7(2)
C8	C7	C6	103.3(3)	C44	C43	C47	100.7(2)
C11	C10	C9	100.8(2)	C3	C2	C6	104.1(2)
C50	C48	C47	104.3(2)	C13	C2	C3	103.5(2)
C49	C48	C50	107.3(3)	C13	C2	C6	102.0(2)
C49	C48	C47	103.8(2)	C13	C2	C1	114.0(3)
C56	C55	C52	120.3(2)	C1	C2	C3	114.5(3)
C60	C55	C56	117.5(3)	C1	C2	C6	117.0(3)
C60	C55	C52	122.2(3)	C24	C25	C29	105.8(2)
C66	C67	C72	98.5(2)	C24	C25	C26	102.2(2)
C68	C67	C66	103.8(2)	C26	C25	C29	107.3(2)
C68	C67	C72	115.1(3)	C49	C44	C45	114.6(2)
C40	C35	C24	121.2(3)	C49	C44	C43	103.7(3)
C36	C35	C24	121.7(3)	C43	C44	C45	98.4(2)
C36	C35	C40	117.1(3)	O1	C13	C12	127.3(3)
C70	C69	C65	104.3(2)	O1	C13	C2	127.0(3)
C68	C69	C65	104.0(3)	C12	C13	C2	105.7(2)
C68	C69	C70	107.4(3)	C27	C28	C29	100.8(3)

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for SRK-SR-617-S1_Mo.

Atom	*x*	*y*	*z*	U(eq)
H20	-2795.79	4051.98	5098.74	31
H16	-3090.21	1014.88	5423.47	33
H66	2871.12	-4152.37	1732.8	30
H41A	295.94	3254.12	1921.71	48
H41B	717.49	2470.6	2352.7	48
H41C	165.48	1920.11	1645.75	48

H65	2452.63	-4648.33	588.66	29
H18	-2906.68	3817.28	6961.7	34
H12	-4894.88	1774.78	3139.33	34
H70A	102.02	-3336.88	262.77	34
H70B	-449.39	-2977.16	980.77	34
H17	-3037.96	1869.43	6557.54	35
H77	2197.76	-3573.56	-1949.68	35
H79	1890.4	-4818.39	-391.78	30
H50A	5421.4	2115.19	1039.63	36
H50B	4900.55	1730.08	305.57	36
H23A	-3228.98	7749.14	4126.49	33
H23B	-3631.42	6681.1	4358.95	33
H5	-2536.04	252.38	4417.82	30
H63A	3316.24	-1604.96	918.89	30
H63B	3889.99	-2811.15	689.94	30
H7	-4010.86	-33.94	2652.71	34
H10A	-5659.21	1302.29	4206.92	39
H10B	-4962.75	1696.07	4887.17	39
H48	4463.62	107.21	638.68	36
H61A	4217.45	-2506.3	2420.26	51
H61B	4651.96	-1655.82	2031.87	51
H61C	4802.31	-2976.86	1726.38	51
H67	1486.5	-3030.73	2429.21	32
H69	519.86	-4944.75	606.33	34
H3A	-1335.63	2060.42	4209.32	35
H3B	-2070	3007.72	4032.7	35
H68A	-173.82	-3851.4	1758.56	38
H68B	744.12	-4783.49	1743.35	38
H58	2908.54	1386.94	-1965.88	36
H39	-2271.03	9826.24	6266.95	32
H30A	152.48	7185.6	4754.67	41
H30B	683.11	6917.42	4032.67	41
H6	-2379.16	-341.55	3247.36	28
H38	-1830.36	8768.66	6986.49	38
H75	2351	-1487.05	-107.36	34
H59	3188.21	-104.53	-1522.14	38
H40	-2294.22	9016.25	5143.34	31
H56	2640.1	3480.67	-128.63	33
H29	-23.55	5204.41	4436.36	42
H72	687.08	-1579.5	1993.68	32
H76	2347.8	-1768.23	-1231.65	39
H78	1936.61	-5094.48	-1520.48	36

H27	-1132.52	5151.01	2609.69	36
H45	4272.2	3469.59	2015.07	30
H32	-552.09	7128.73	3034.12	38
H8A	-4391.04	-1152.13	3393.51	42
H8B	-5423.68	-334.89	3433.88	42
H53A	1102.45	2112.69	625	27
H53B	1674.64	3341.29	862.68	27
H57	2680.12	3196.68	-1257.8	37
H60	3202.91	184.12	-386.72	32
H9	-4425.8	-193.53	4530.79	36
H36	-1432.19	6060.75	5416.75	37
H19	-2745.98	4899.95	6225.9	33
H47	2530.64	326.04	564.76	29
H73A	-574.88	-1265.89	711.6	67
H73B	6.5	-70.88	791.84	67
H73C	-134.42	-535.15	1417.54	67
H26	-2410.58	4523.04	3318.45	35
H54A	5563.28	3803.8	718.46	69
H54B	5164.23	4491.07	1433.47	69
H54C	4999.74	4995.34	824.7	69
H37	-1427.07	6867.09	6548.71	44
H49A	4189.81	266.6	1772.32	38
H49B	5113.34	1231.38	1812.15	38
H43	2060.89	827.79	1698	30
H25	-1975.06	5208.45	4458.24	32
H44	3427.85	1998.27	2436.17	33
H28A	570.54	5227.36	3273.04	46
H28B	-232.73	4199.59	3307.56	46
H14A	-5536.72	3441.75	3675.76	77
H14B	-5494.56	4412.68	4356.97	77
H14C	-5971.99	3194.66	4331.41	77
H21A	-4448.7	5358.21	3317.07	72
H21B	-3902.55	5277.57	2622.36	72
H21C	-4482.97	6408.13	3022.24	72
H1A	-987.35	1973.13	2826.89	73
H1B	-1405.32	724.41	2460.93	73
H1C	-633.89	953.33	3100.91	73
H34A	96.67	8825.72	3589.57	77
H34B	557.52	8938	4313.97	77
H34C	-189.41	9901.72	4181.55	77

X-ray single-crystal structure and refinement data for compound 17

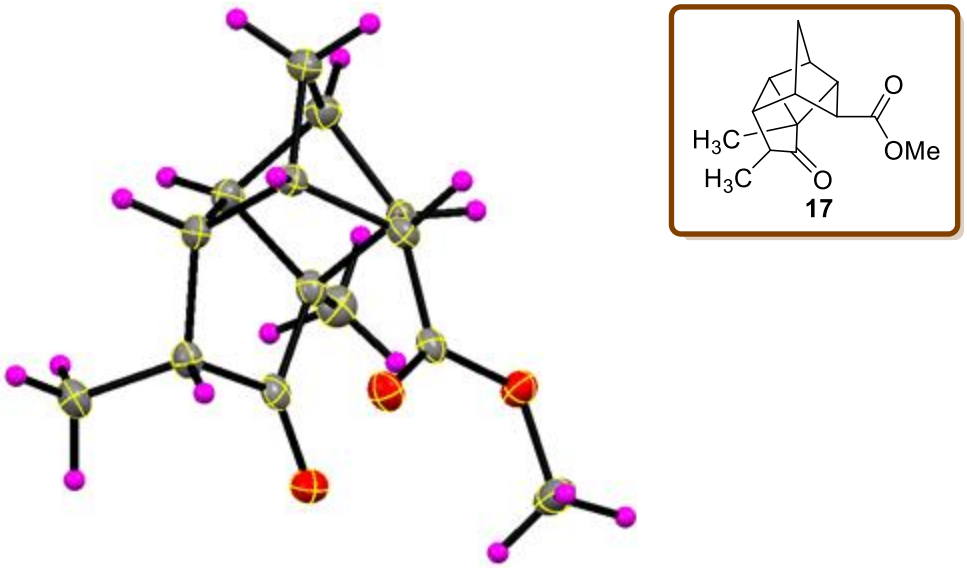
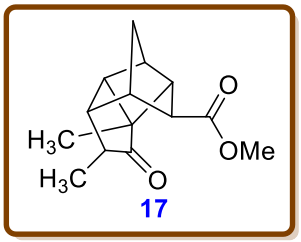


Figure S2: ORTEP representation of compound **17** with thermal ellipsoids drawn at 20% probability level.

The X-ray structure of compound **17** was determined by single-crystal X-ray diffraction studies. Single crystals of compound **17** were obtained from $CHCl_3$ in petroleum ether solvent at room temperature. Crystal data was collected with graphite monochromatized $M_0K\alpha$ radiation (λ = 0.71073) on a Rigaku Saturn 724+ diffractometer using ω scans at temperature 293 K. The structures were solved by direct methods using Olex-2[1] and ShelXL- 97[2] and refined by full-matrix least-square minimisation based on F^2. ORTEPs were drawn using Mercury program[3] and ORTEP-3.[4] X-ray crystallographic data and refinement parameters for compound **17** provided in the below tables and are deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC No: **CCDC-1908339**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S7. X-ray crystallographic data and refinement parameters for compound **17** **(CCDC 1908339)**



Identification code	SRK-SR-617-S2_Mo	
Empirical formula	$C_{14}H_{18}O_8$	
Formula weight	234.30	
Temperature	150 K	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Hall group	-P 2ybc	
Unit cell dimensions	a = 6.5860 (4) Å^3	α = 90 °
	b = 17.7133 (10) Å^3	β = 92.235 (7) °
	c = 10.0216 (8) Å^3	γ = 90 °
Volume	1168.22 (13) Å^3	
Z	4	
Density (calculated)	1.3320 Mg/m^3	
Absorption coefficient (μ)	0.092 mm^{-1}	
Absorption correction	Multi-Scan	
Bond precision C–C	0.0034 A	
Max. and min. transmission	1.000 and 0.783	
F (000)	504.3	
Crystal size	0.2 × 0.15 × 0.08 mm^3	
Crystal colour, shape	Colourless, Black	
Index ranges	$-9 \leq h \leq 8$, $-22 \leq k \leq 25$, $-14 \leq l \leq 13$	
Theta range for data collection	3.416 to 50°	
Reflections collected	6157	
Wavelength	0.71073 Å	
Independent reflections	1987 [$R_{(int)}$ = 0.0517]	
Completeness to θ = 24.99°	99.8%	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1987/0/157	

Goodness-of-fit on F^2	1.041
Final *R* indices [*I* >2sigma (*I*)]	R1 = 0.0558, ωR2 = 0.1268
R indices (all data)	R1 = 0.0777, ωR2 = 0.1468
Largest diff. peak and hole	0.34 and -0.33 e. $Å^{-3}$

Table S8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for SRK-SR-617-S2_Mo. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O3	3519(2)	7963.4(9)	7507.4(18)	27.3(5)
O1	5134(2)	6473.3(10)	9588.4(18)	28.4(5)
O2	6500(2)	7424.3(9)	7048.1(18)	26.5(5)
C8	1081(4)	6107.6(15)	5008(3)	26.6(6)
C14	4462(4)	7473.4(14)	6971(3)	21.8(6)
C7	1267(3)	6711.7(14)	6116(2)	22.9(6)
C10	3833(4)	6264.4(13)	8778(3)	22.4(6)
C9	3574(3)	6861.8(13)	6091(2)	21.1(6)
C11	1616(3)	6527.7(14)	8738(3)	24.0(6)
C1	5572(4)	5051.7(15)	8025(3)	30.4(7)
C4	2604(4)	5566.9(14)	5673(3)	26.0(6)
C12	562(4)	6154.0(16)	9896(3)	31.1(7)
C13	7503(4)	8004.6(15)	7848(3)	34.9(7)
C2	4110(3)	5691.6(13)	7672(2)	22.6(6)
C3	4428(3)	6053.4(13)	6262(3)	21.8(6)
C6	783(3)	6242.7(14)	7371(3)	23.6(6)
C5	1945(4)	5489.1(14)	7133(3)	24.7(6)

Table S9. Anisotropic Displacement Parameters (Å^2×10^3) for SRK-SR-617-S2_Mo. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O3	30.0(9)	24.2(9)	28.0(11)	2.7(8)	6.3(8)	-1.1(8)
O1	28.0(10)	33.7(10)	23.4(11)	-0.8(8)	-1.2(8)	-1.6(8)
O2	23.2(9)	25.1(9)	31.1(11)	-1.1(7)	1.1(8)	-4.0(8)
C8	25.8(13)	32.8(14)	21.3(15)	-3.4(11)	0.2(11)	-1.4(12)
C14	24.4(13)	23.7(13)	17.5(14)	0.3(10)	3.4(11)	5.4(11)
C7	21.7(13)	28.8(13)	18.3(14)	-0.6(10)	0.3(11)	-0.2(11)

C10	26.1(13)	23.4(13)	18.0(14)	-2.5(10)	3.8(11)	7.3(10)
C9	25.5(13)	20.7(12)	17.2(14)	0.8(10)	3.1(11)	1.0(10)
C11	22.7(12)	25.5(13)	24.2(15)	0.8(10)	5.3(11)	0.0(11)
C1	32.4(14)	26.1(14)	32.6(16)	1.5(11)	-0.4(12)	4.8(12)
C4	29.2(13)	25.0(13)	23.8(15)	-3.4(11)	2.1(11)	-2.5(11)
C12	31.4(14)	38.5(15)	24.0(16)	-3.8(12)	8.2(12)	-1.6(12)
C13	28.1(14)	35.5(15)	40.6(19)	-6.1(12)	-2.3(13)	-12.1(14)
C2	22.5(12)	23.4(13)	22.1(14)	0.3(10)	2.4(11)	5.8(11)
C3	22.4(12)	22.2(12)	21.3(14)	-0.7(10)	6.4(11)	-1.9(11)
C6	18.3(11)	30.1(14)	22.4(15)	-2.0(10)	2.6(10)	-1.6(11)
C5	27.0(13)	23.5(13)	23.7(15)	-4.8(10)	2.5(11)	0.8(11)

Table S10. Bond Lengths for SRK-SR-617-S2_Mo.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C14	1.206(3)	C10	C2	1.519(3)
O1	C10	1.215(3)	C9	C3	1.546(3)
O2	C14	1.344(3)	C11	C12	1.526(3)
O2	C13	1.447(3)	C11	C6	1.540(3)
C8	C7	1.543(3)	C1	C2	1.520(3)
C8	C4	1.522(3)	C4	C3	1.574(3)
C14	C9	1.501(3)	C4	C5	1.548(4)
C7	C9	1.544(3)	C2	C3	1.573(3)
C7	C6	1.551(3)	C2	C5	1.547(3)
C10	C11	1.532(3)	C6	C5	1.562(3)

Table S11. Bond Angles for SRK-SR-617-S2_Mo.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	O2	C14	114.77(19)	C5	C4	C8	105.4(2)
C4	C8	C7	95.10(19)	C5	C4	C3	86.14(18)
O2	C14	O3	123.5(2)	C1	C2	C10	114.9(2)
C9	C14	O3	125.8(2)	C3	C2	C10	114.05(19)
C9	C14	O2	110.6(2)	C3	C2	C1	114.1(2)
C9	C7	C8	99.11(19)	C5	C2	C10	105.93(19)
C6	C7	C8	101.49(19)	C5	C2	C1	118.4(2)
C6	C7	C9	109.82(18)	C5	C2	C3	86.22(18)
C11	C10	O1	124.8(2)	C4	C3	C9	101.33(18)

C2	C10	O1	126.1(2)	C2	C3	C9	114.6(2)
C2	C10	C11	109.0(2)	C2	C3	C4	89.27(18)
C7	C9	C14	118.4(2)	C11	C6	C7	117.92(19)
C3	C9	C14	118.15(19)	C5	C6	C7	102.49(19)
C3	C9	C7	101.13(19)	C5	C6	C11	104.85(19)
C12	C11	C10	108.0(2)	C2	C5	C4	91.19(18)
C6	C11	C10	103.3(2)	C6	C5	C4	103.1(2)
C6	C11	C12	112.2(2)	C6	C5	C2	101.47(19)
C3	C4	C8	107.5(2)				

Table S12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for SRK-SR-617-S2_Mo.

Atom	*x*	*y*	*z*	U(eq)
H8a	-302(4)	5890.4(15)	4912(3)	32.0(7)
H8b	1522(4)	6294.7(15)	4135(3)	32.0(7)
H7	391(3)	7167.2(14)	5964(2)	27.5(7)
H9	3848(3)	7014.4(13)	5154(2)	25.3(7)
H11	1529(3)	7090.2(14)	8796(3)	28.8(7)
H1a	6913(8)	5260.7(16)	8273(17)	45.6(10)
H1b	5063(14)	4765(6)	8779(11)	45.6(10)
H1c	5680(20)	4717(6)	7253(6)	45.6(10)
H4	2936(4)	5093.9(14)	5182(3)	31.2(7)
H12a	680(20)	5604.2(16)	9823(9)	46.7(10)
H12b	1204(16)	6322(7)	10743(3)	46.7(10)
H12c	-877(7)	6296(7)	9866(10)	46.7(10)
H13a	7010(20)	8501.8(16)	7557(12)	52.3(11)
H13b	7210(20)	7929(6)	8790(4)	52.3(11)
H13c	8974(4)	7976(7)	7739(14)	52.3(11)
H3	5777(3)	5958.6(13)	5868(3)	26.2(7)
H6	-711(3)	6146.7(14)	7399(3)	28.3(7)
H5	1322(4)	5003.7(14)	7420(3)	29.6(7)

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Appendix I

Table S13. ***Reactions of Cage dione 8 with BF_3.MeOH in different solvents (chlorobenzene, anisole, toluene and isopropyl benzene (Cumene)***

S.NO	**Cage compound**	**Solvents**	**Conditions**	**Observations**
1	Compound **8** (Cage dione)	chlorobenzene	100-110 °C (6-8 h) 130-140 °C (24 h)	Ketoester **17** (**solid**) Unidentified rearranged product **(Colourless liquid)**
2	Compound **8** (Cage dione)	Methoxybenzene (Anisole)	110-120 °C (6 h)	1] Mixture of compound (similar product such as compound **16**) 2] other unidentified solvent inserted rearranged product **(both are colourless liquids)**
3	Compound **8** (Cage dione)	Toluene	120-130 °C (overnight)	unidentified rearranged product **(colourless liquid)**
4	Compound **8** (Cage dione)	Cumene (Isopropyl benzene)	150-160 °C (12 h)	Complex mixture

We did BF_3.MeOH rearrangement with some other substituted aromatics such as chlorobenzene, toluene, and methoxybenzene and isopropyl benzene under different reaction conditions (shown in Table S13). We observed ketoester **17** with chlorobenzene at **100-110 °C (6-8 h)** and also identified another rearranged product (colourless liquid) at **130-140 °C (24 h)** unable to identify by spectroscopic data in pure form. As well as in the case of methoxy benzene with substituted

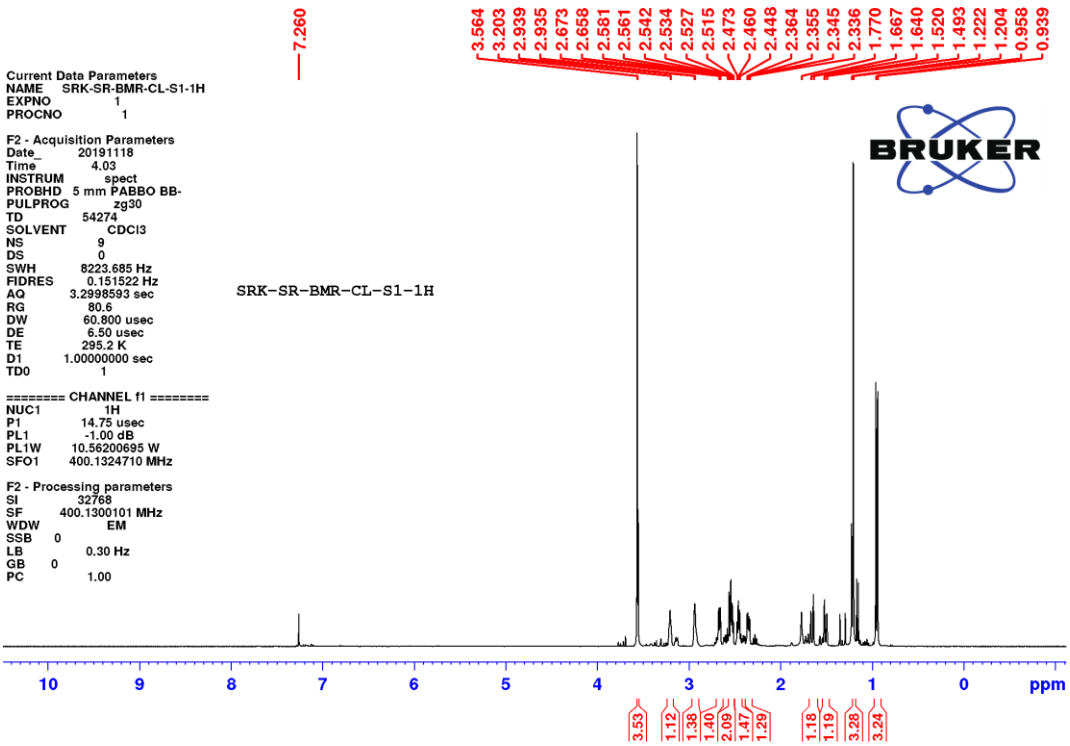
cage dione at **110-120 °C (6 h)** we got methoxy benzene inserted product (with mixture) and this structural data appearance like compound **16**. We have attached here the spectral data of methoxybenzene inserted cage compound (NMR and GC data) and also identified another rearranged product (colourless liquid) which was unable to identify by spectroscopic data. Whereas the other substituted aromatic compound such as toluene, we observed some other unidentified rearrangement product (mixture) by spectral data with solvent incorporation (colourless liquid). Along similar lines, rearrangement of cage dione **8** with BF_3.MeOH/isopropyl benzene (Cumene) at 150 °C produces the complex mixture of products (Table S13). The spectral data was recorded in all cases (attached with this doc as appendix II). It is very difficult to isolate single products with **toluene** and **anisole** through column chromatography (Attached complex spectra as appendix II).

In similar fashion, we optimized the reaction conditions in different temperatures upto 90-120 °C under benzene in BF_3.MeOH complex. In this conditions we got similar products reported earlier (compound **16** and **17**). Whereas the temperature beyond 120 °C, we observed some other rearranged products (colourless liquids) which are difficult to characterize from spectroscopic data (complex spectra).

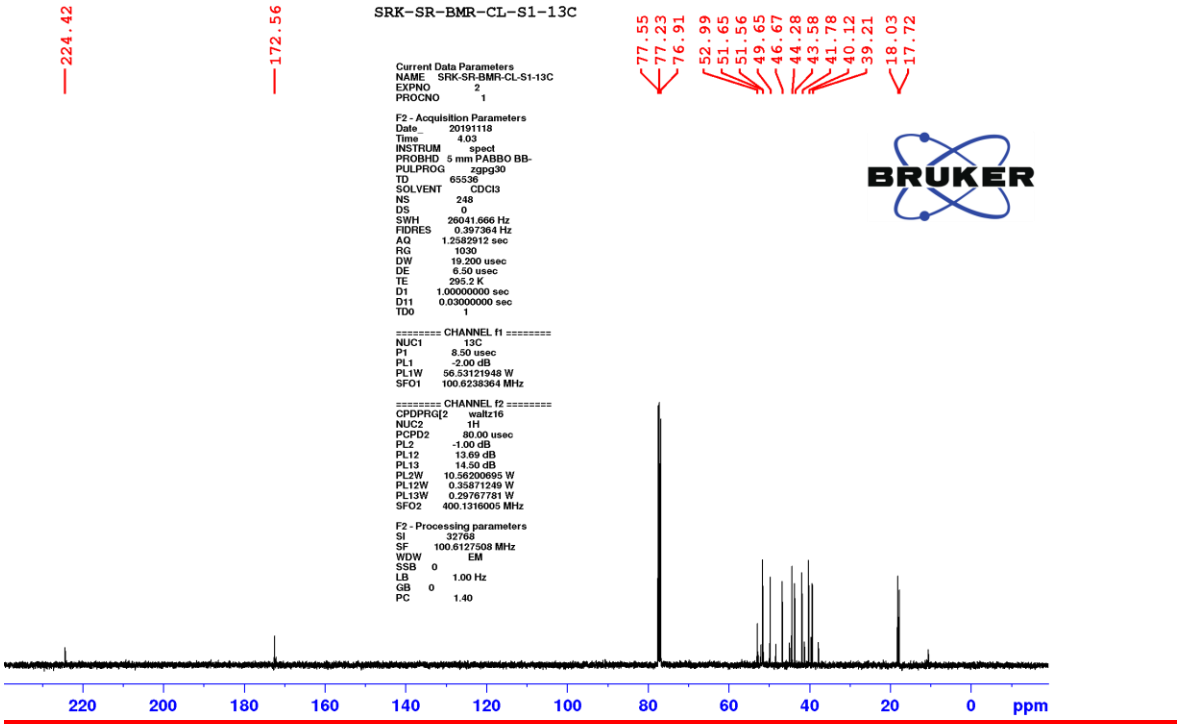
Appendix II

Spectroscopic details (plots)

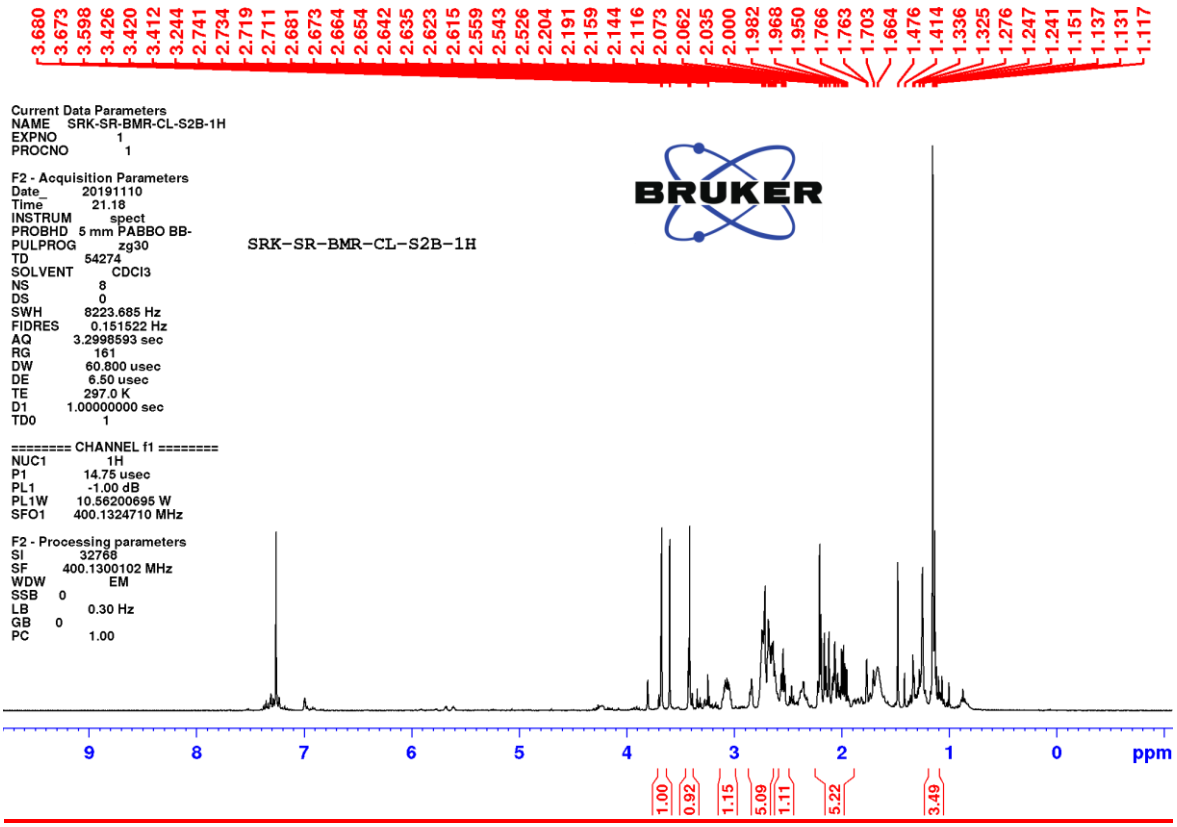
Reaction of Cage dione 8 with BF_3.MeOH in chlorobenzene (1H NMR of spot1, data consistent with compound 17)



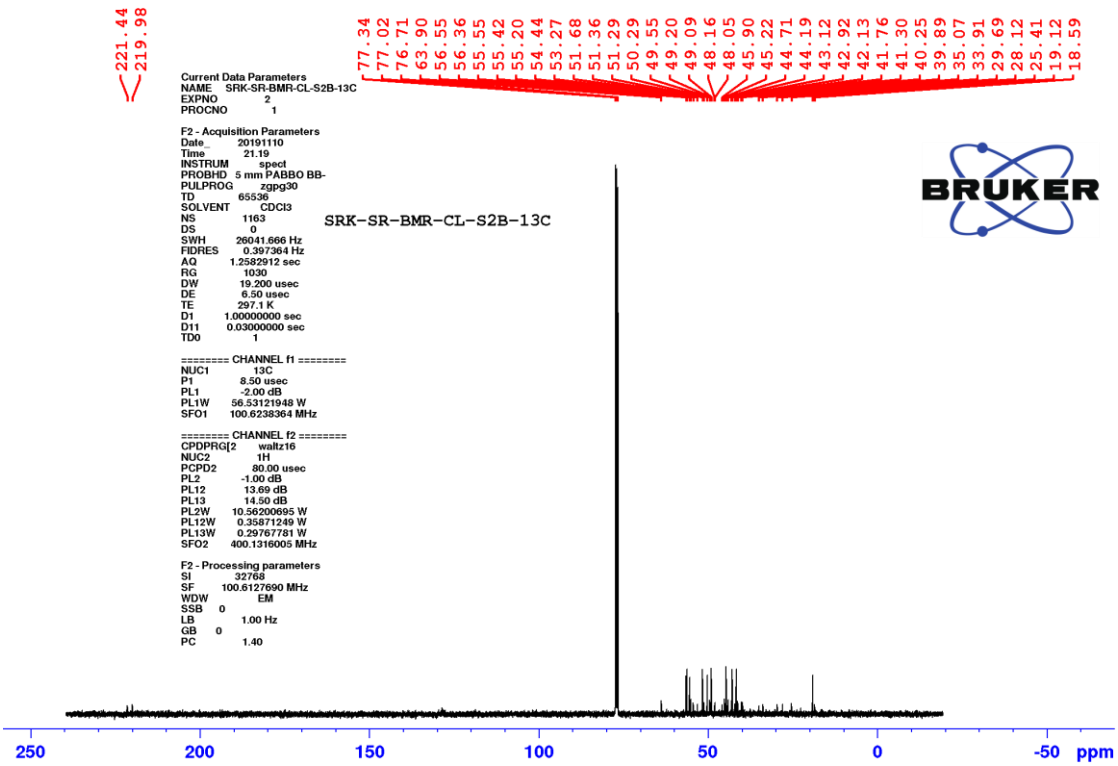
Reaction of Cage dione 8 with BF_3.MeOH in chlorobenzene (^{13}C NMR of spot 1, data consistent with compound 17)



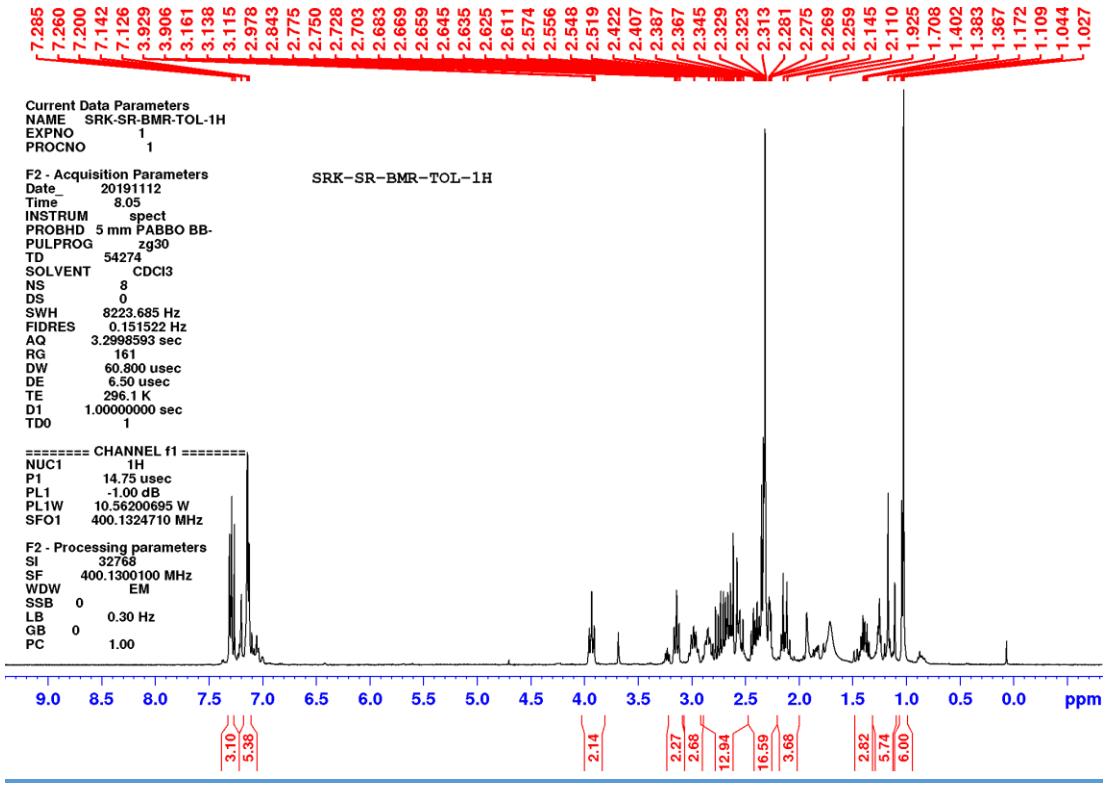
Reaction of Cage dione 8 with BF_3.MeOH in chlorobenzene (^{1}H NMR of spot2)



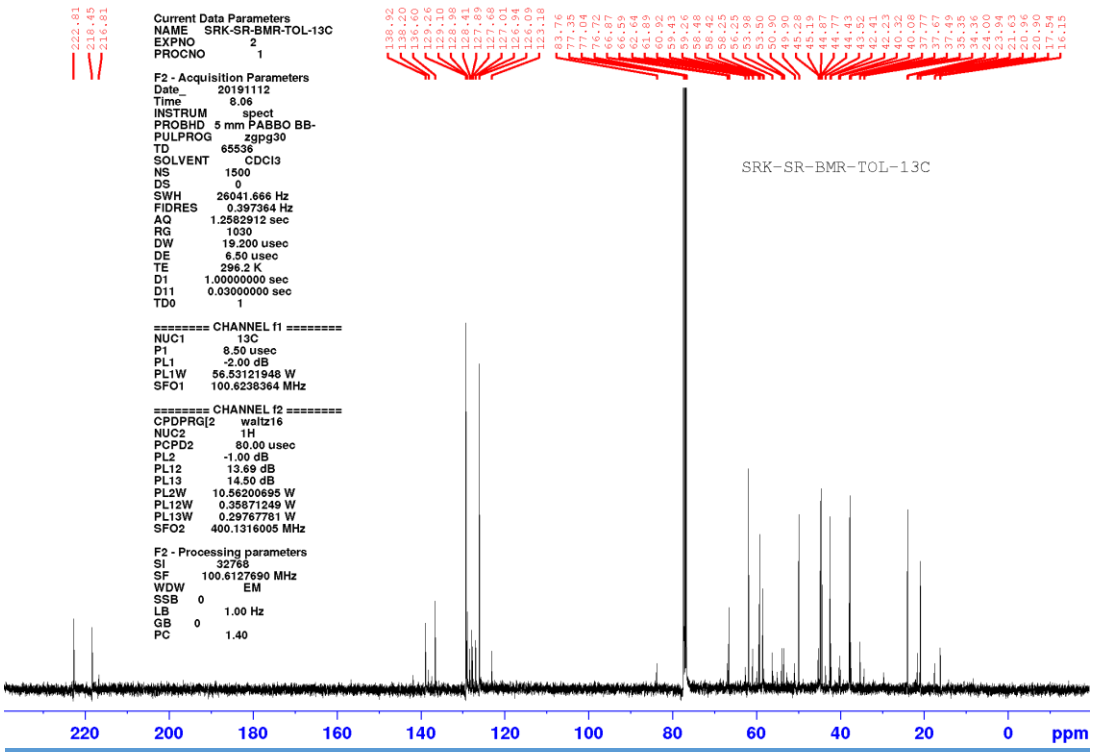
Reaction of Cage dione 8 with BF_3.MeOH in chlorobenzene (^{13}C NMR of spot2)



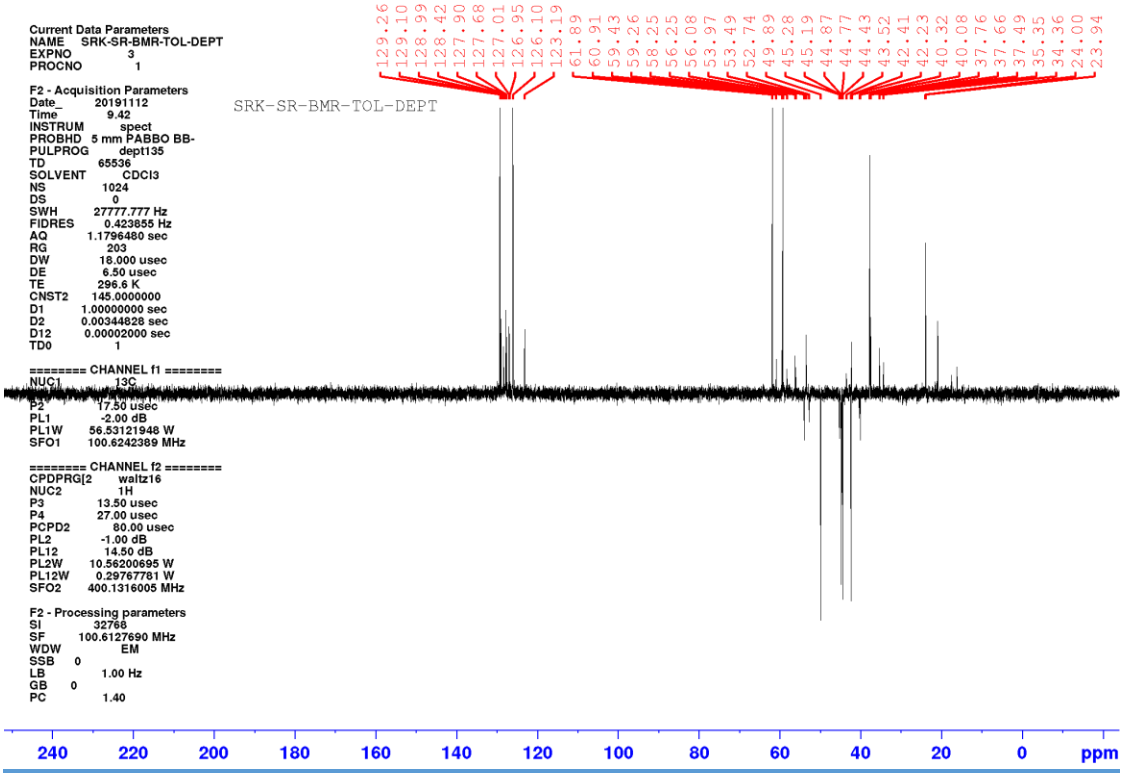
Reaction of Cage dione 8 with BF_3.MeOH in toluene (^{1}H NMR)



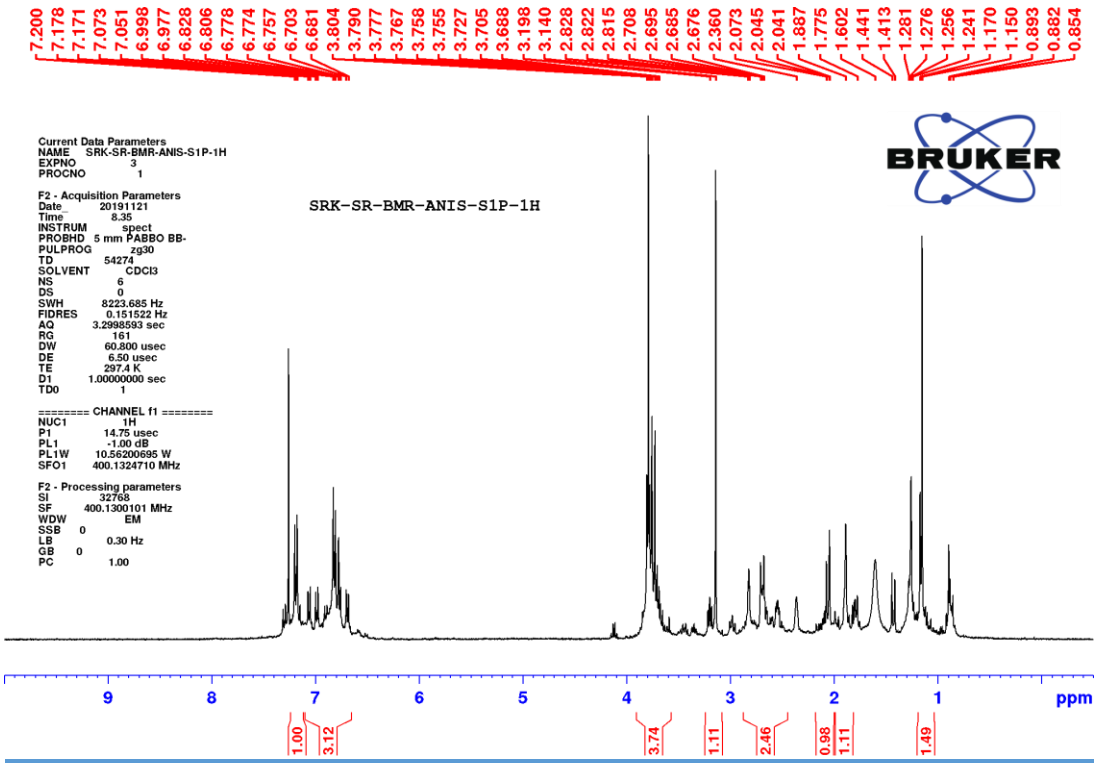
Reaction of Cage dione 8 with BF_3.MeOH in toluene (^{13}C NMR)



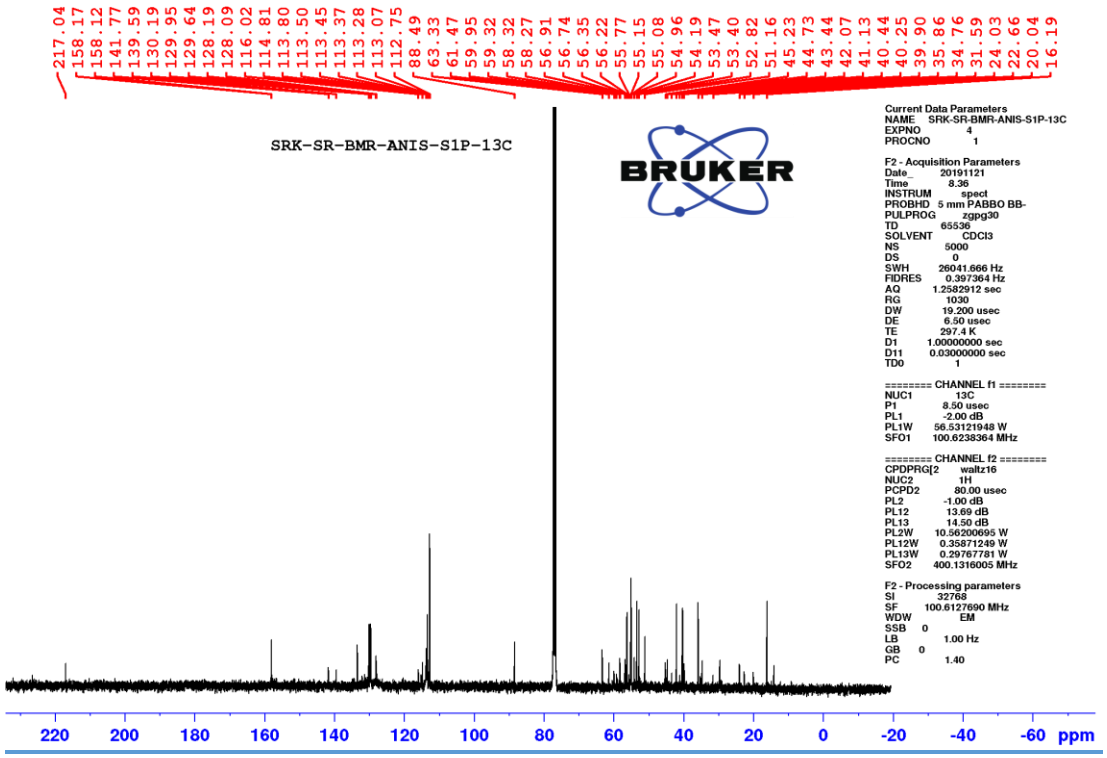
Reaction of Cage dione 8 with BF_3.MeOH in toluene (DEPT 135 NMR)



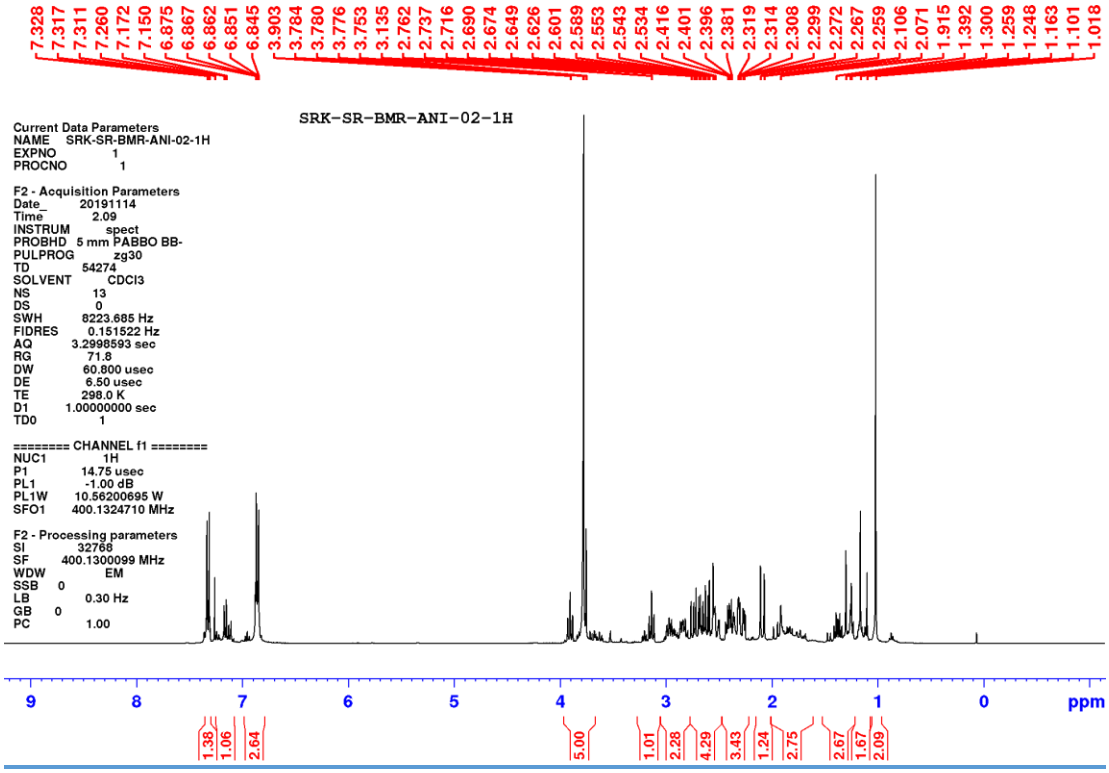
Reaction of Cage dione 8 with BF_3.MeOH in Anisole (^{1}H NMR-spot1)



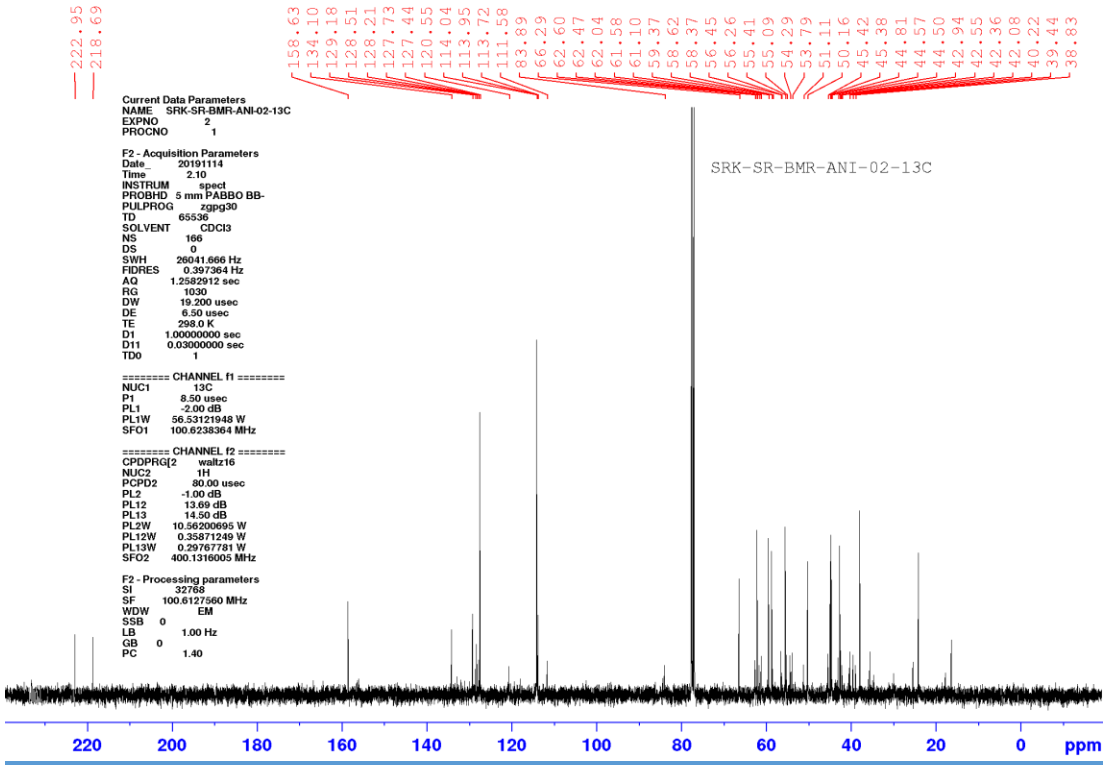
Reaction of Cage dione 8 with BF_3.MeOH in Anisole (^{13}C NMR-spot1)



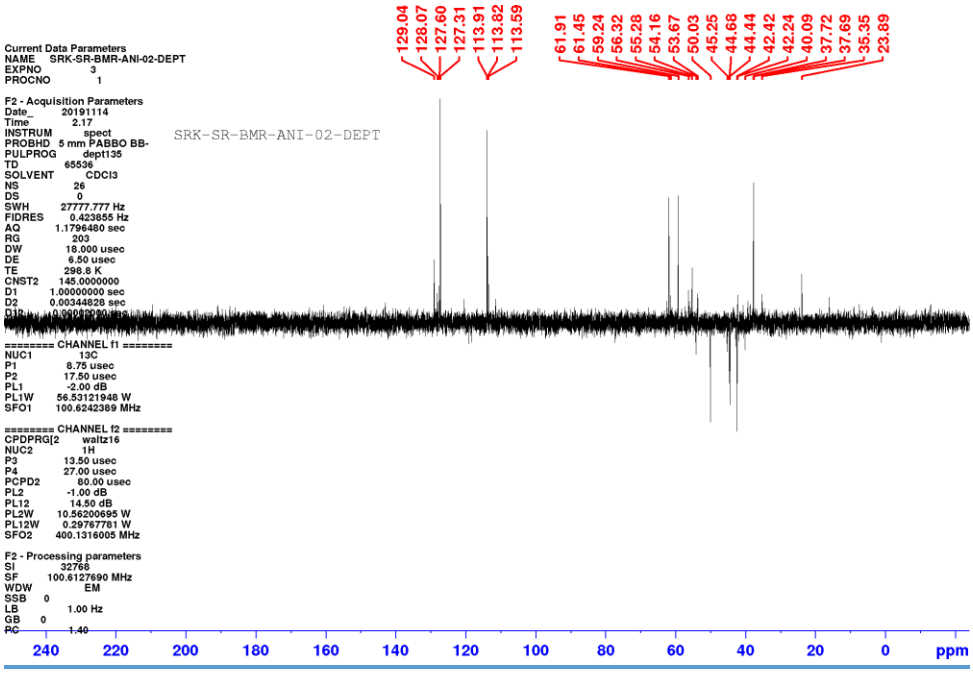
Cage dione 8 with Anisole (^{1}H NMR-spot2)



Reaction of Cage dione 8 with BF_3.MeOH in Anisole (^{13}C NMR-spot2)



Reaction of Cage dione 8 with BF_3.MeOH in toluene (DEPT 135 NMR-spot2)



Reaction of Cage dione 8 with BF_3.MeOH in toluene (GC Data)

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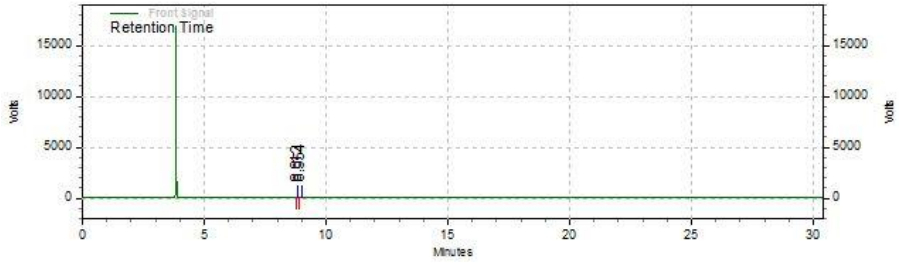
Printed: 26-Nov-19 5:31:59 PM



Front Signal
Results

Retention Time	Area	Area %	Height	Height %
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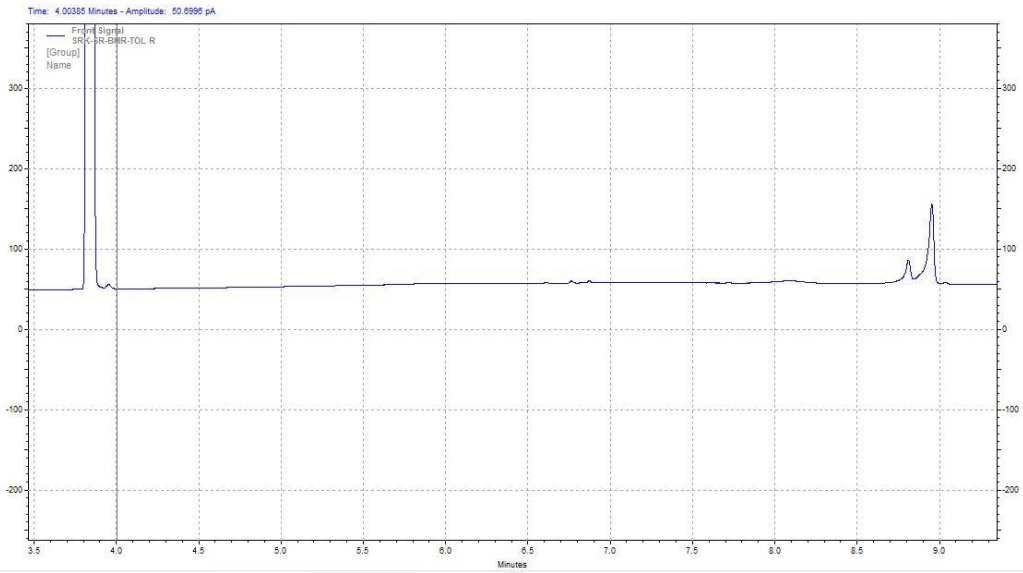

Reaction of Cage dione 8 with BF_3.MeOH in Anisole (GC Data)

Area % Report

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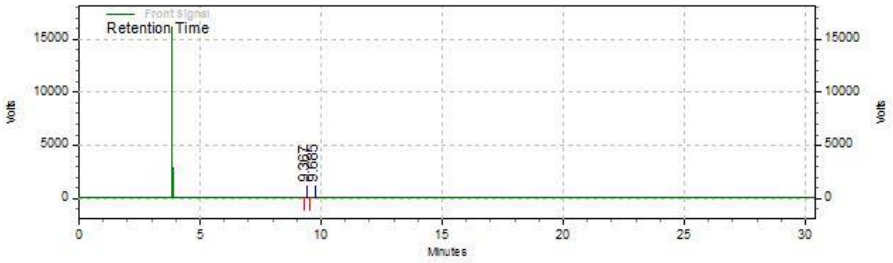

Front Signal
Results

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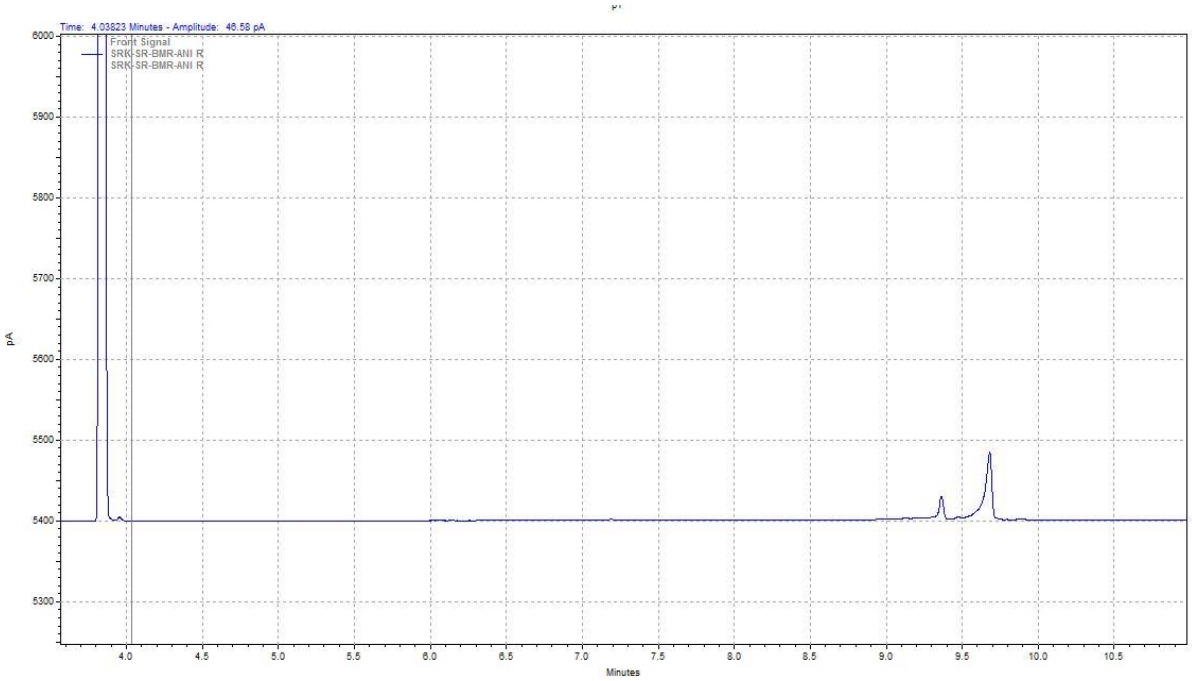
Time: 4.03823 Minutes - Amplitude: 46.58 pA
Front Signal
SRK-SR-BMR-ANI R
SRK-SR-BMR-ANI R
pA
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Minutes