Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Asymmetric Total Syntheses of Aspilactonol F, Aspiketolactonol and Synthetic Studies Toward Diplofuranoxin

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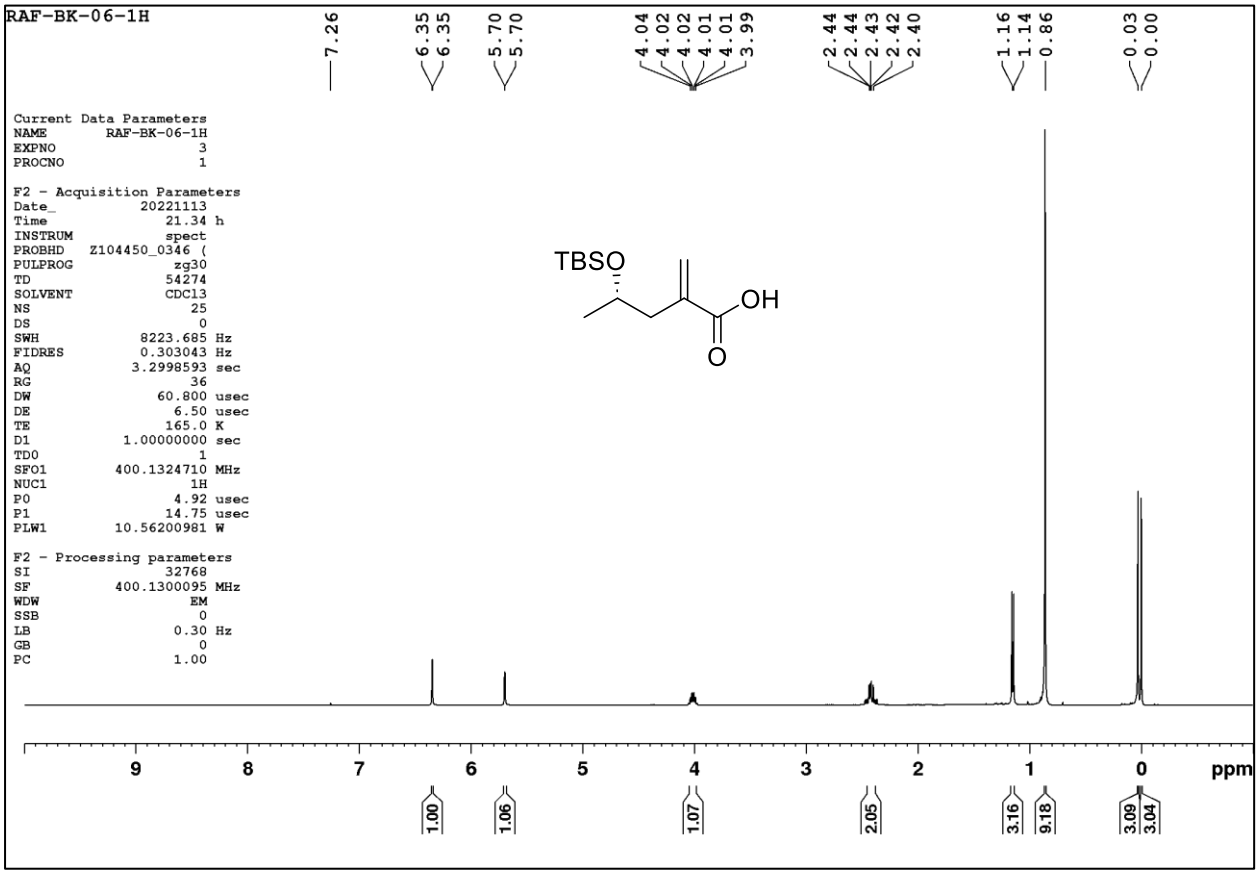
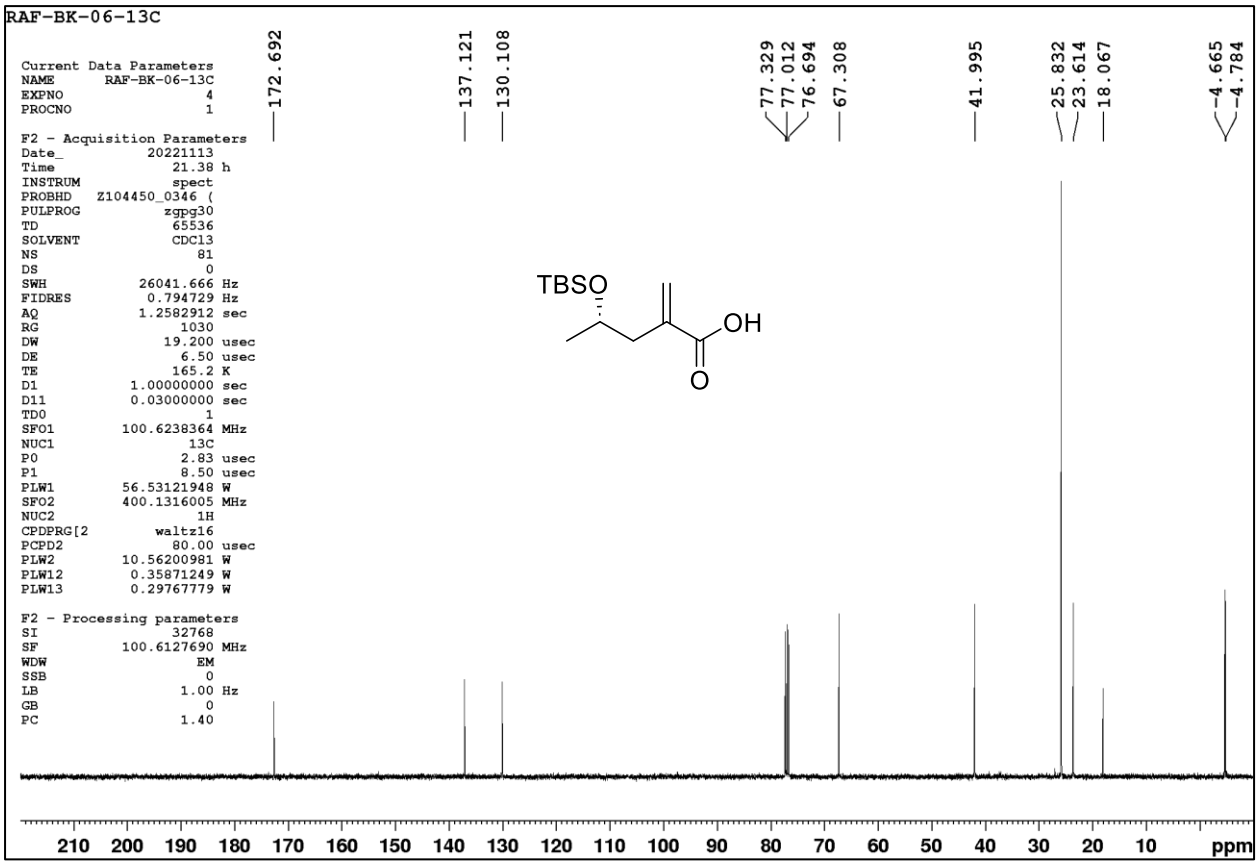
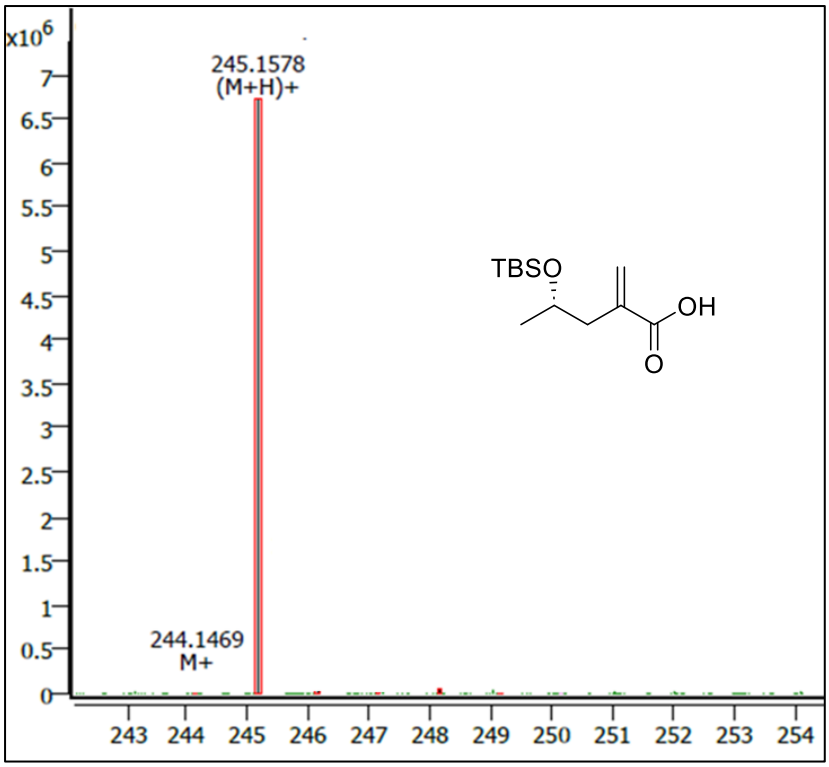
^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **3**

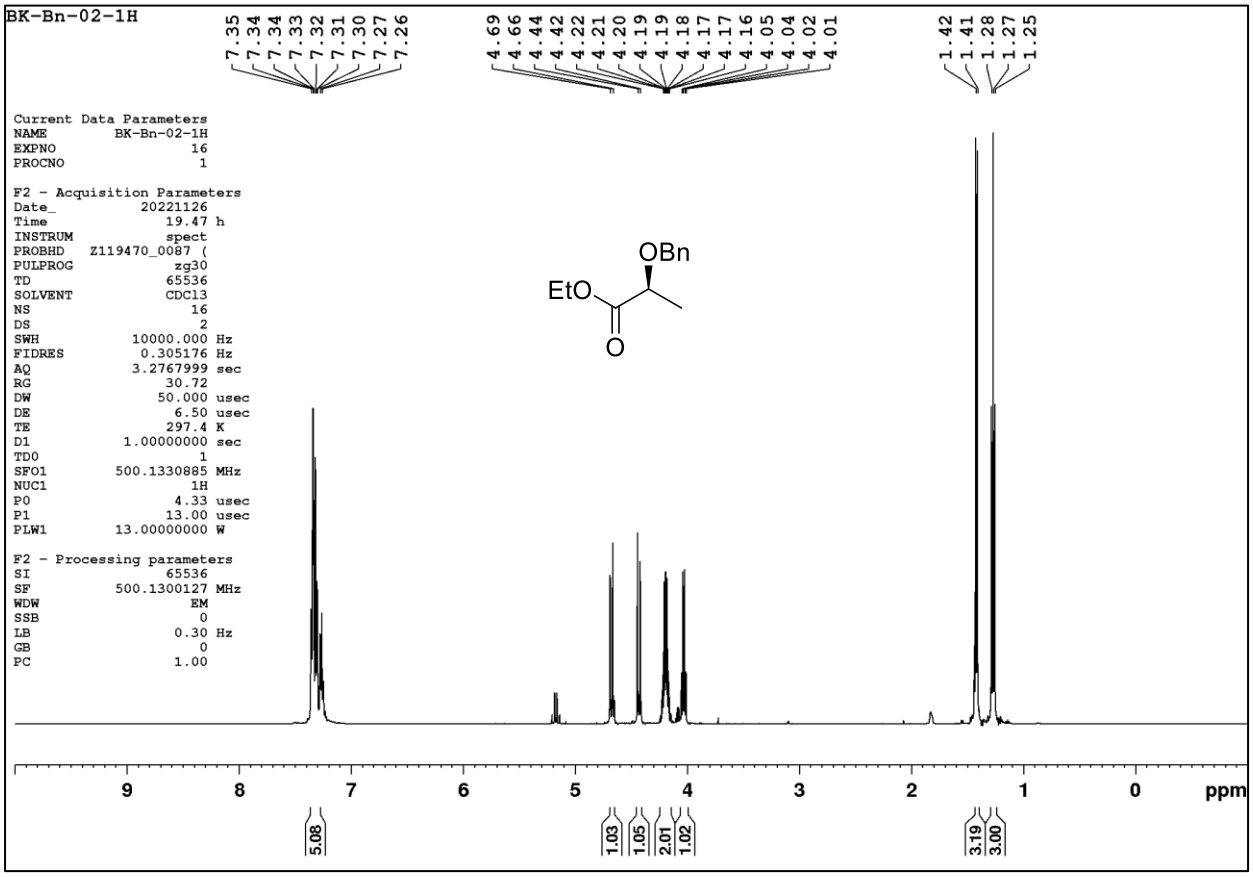


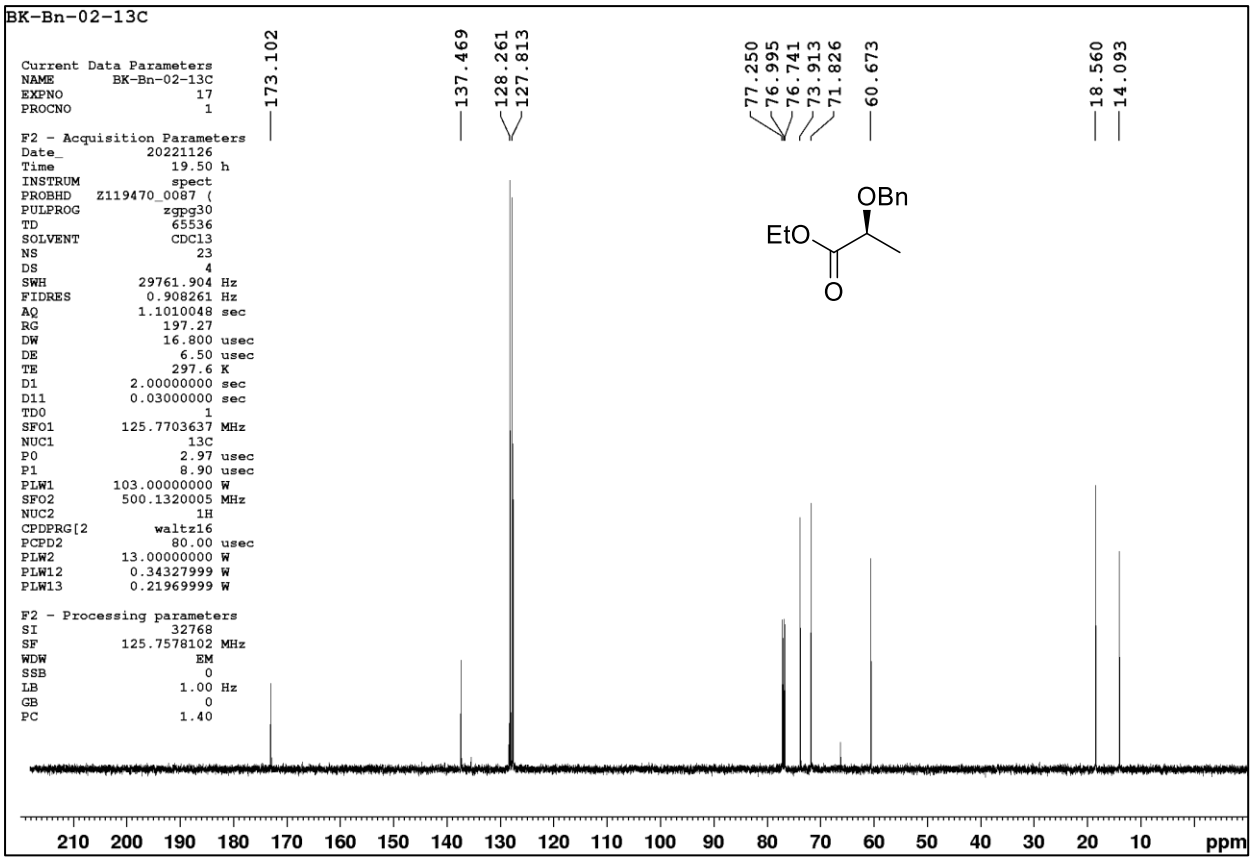


3: HRMS (Q–TOF) *m/z:* [M + H] $^{+}$ Calcd for $C_{12}H_{25}O_3Si$ 245.1568; Found 245.1578.

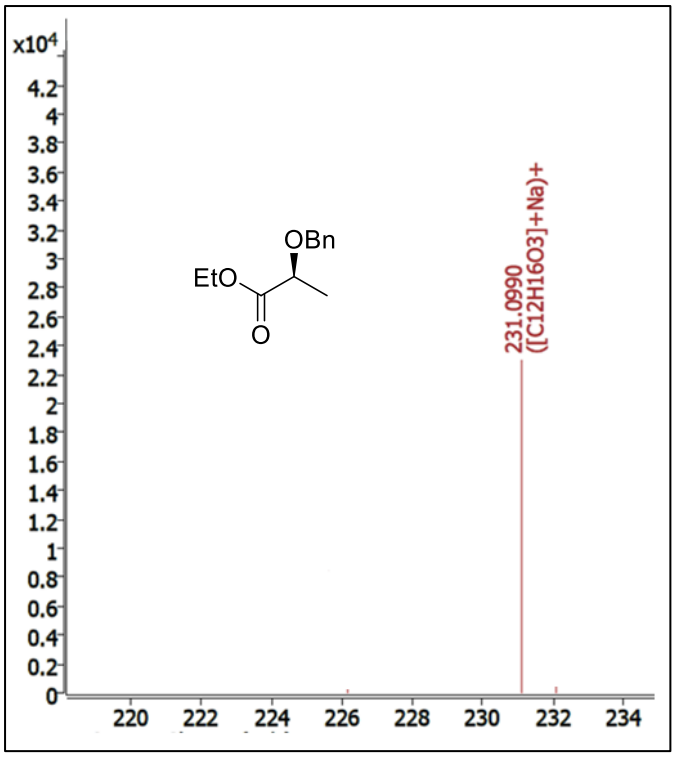


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **11**

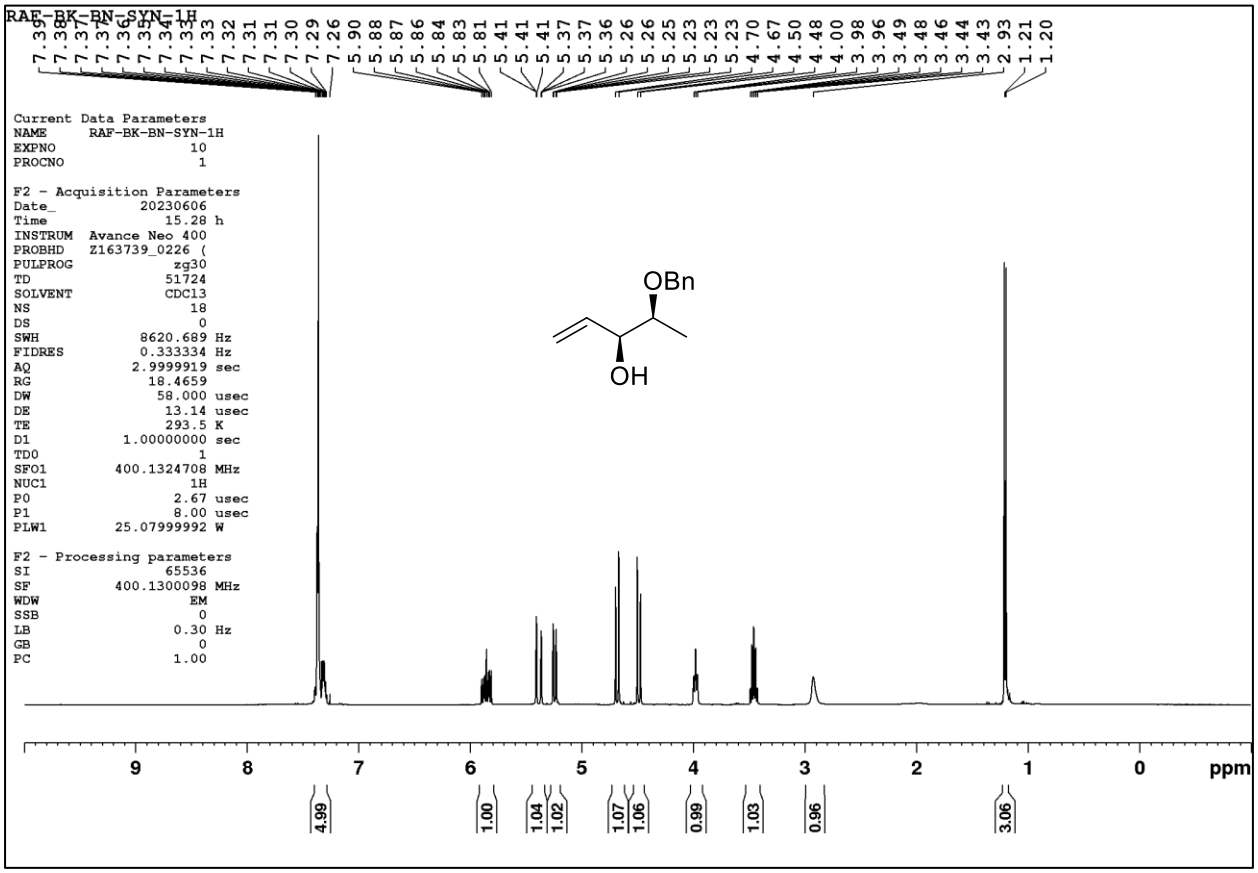


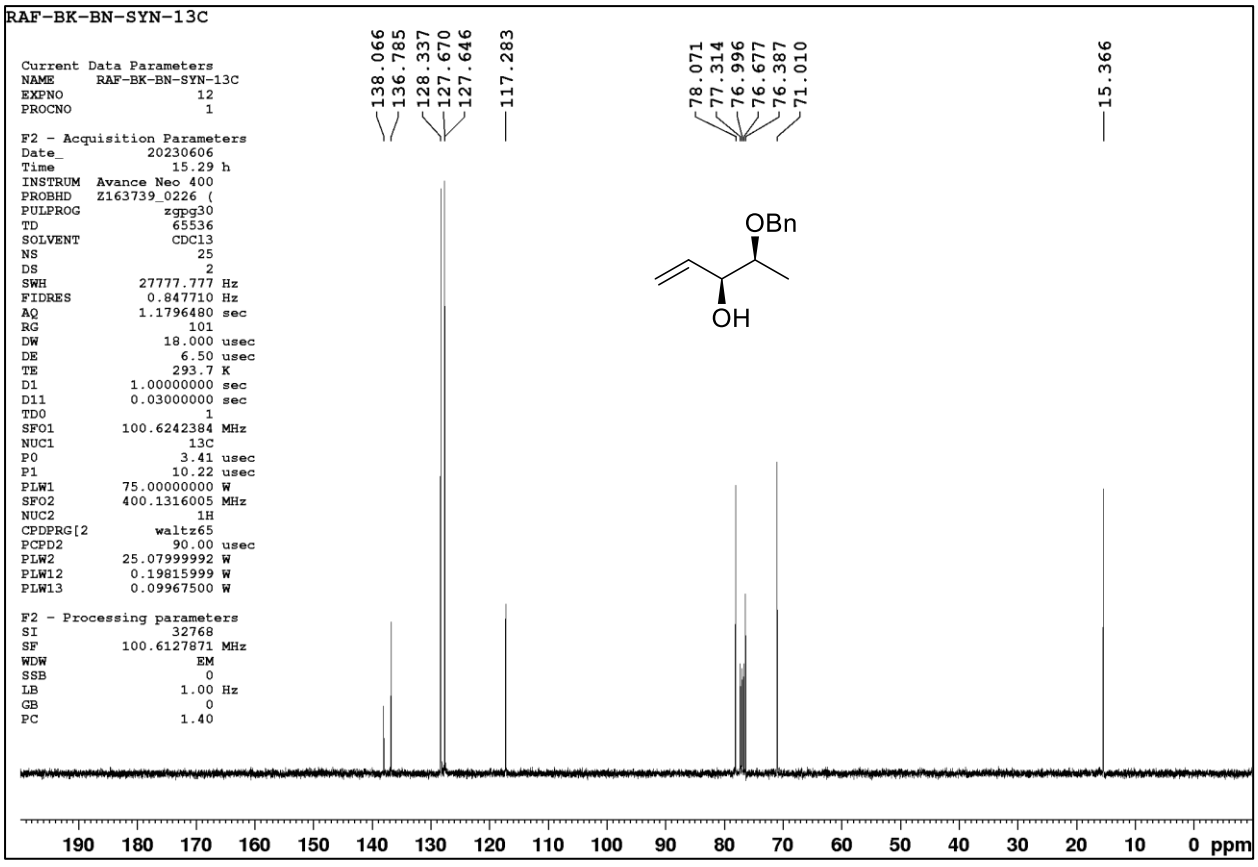


11: HRMS (Q–TOF) *m/z:* $[M + Na]^+$ Calcd for $C_{12}H_{16}O_3Na$ 231.0992; Found 209.0990.

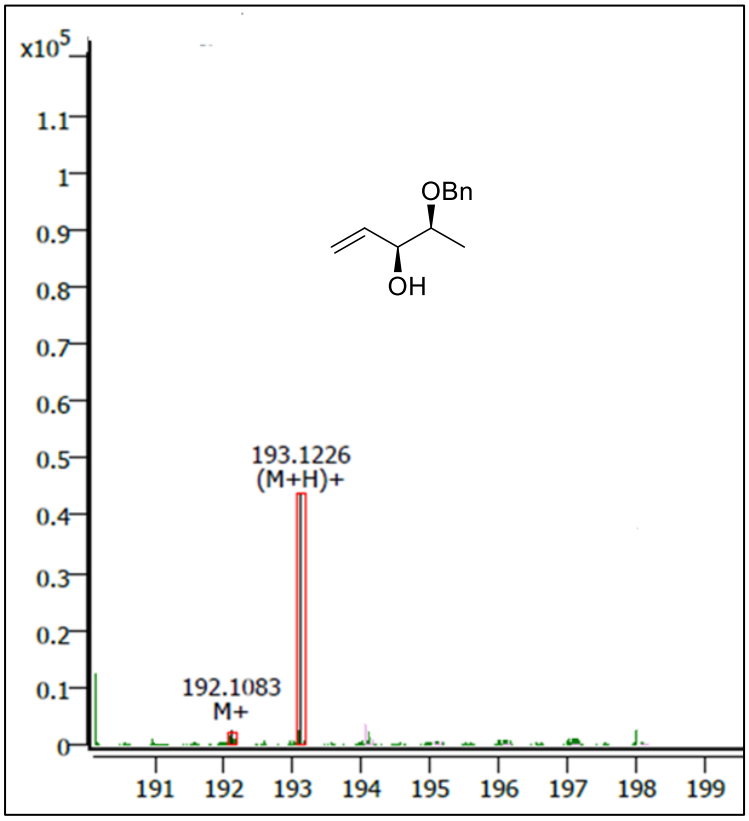


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4a**

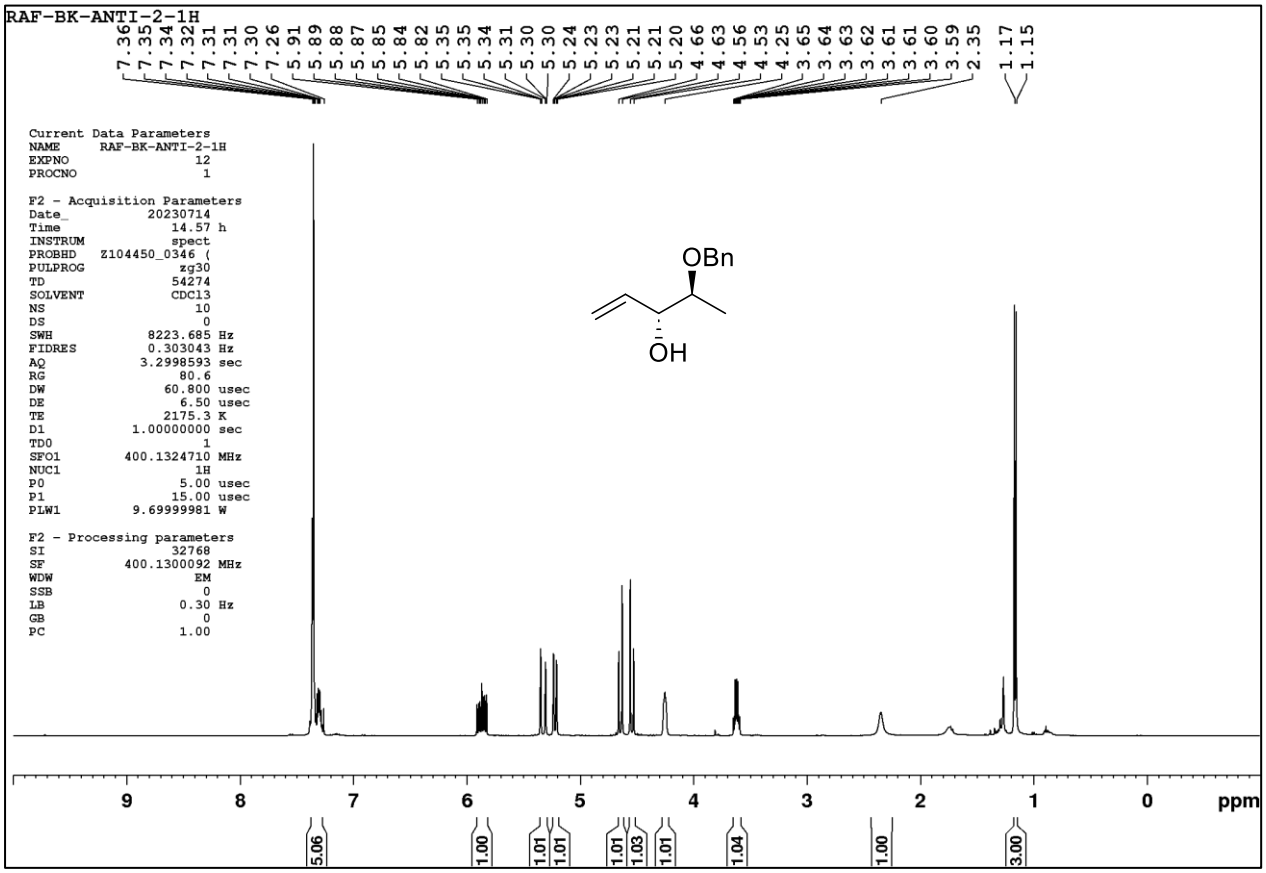


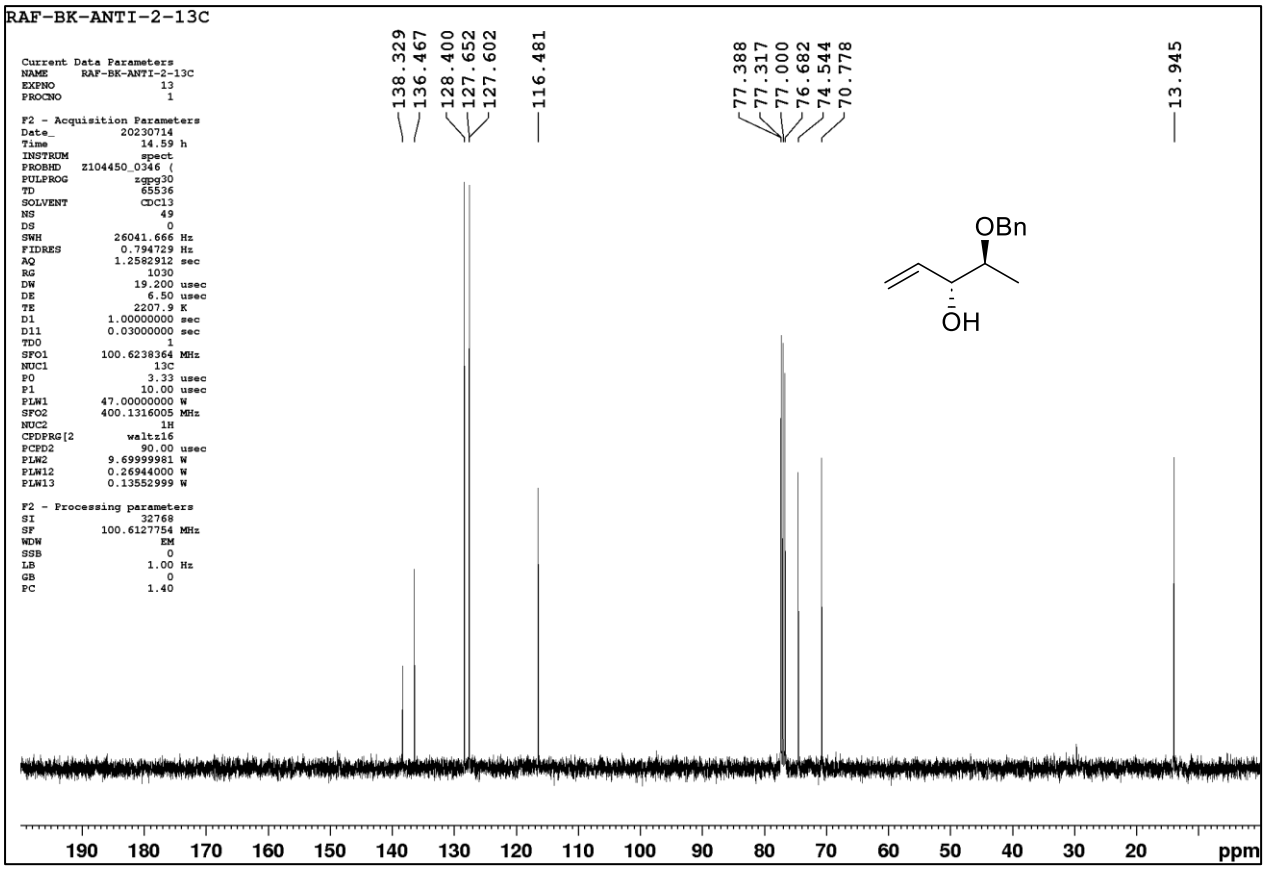


4a: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{12}H_{17}O_2$ 193.1224; Found 193.1226.

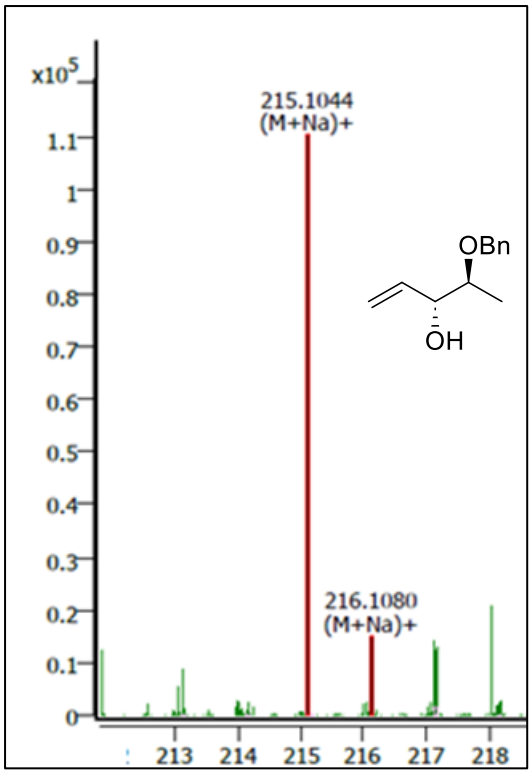


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **4b**

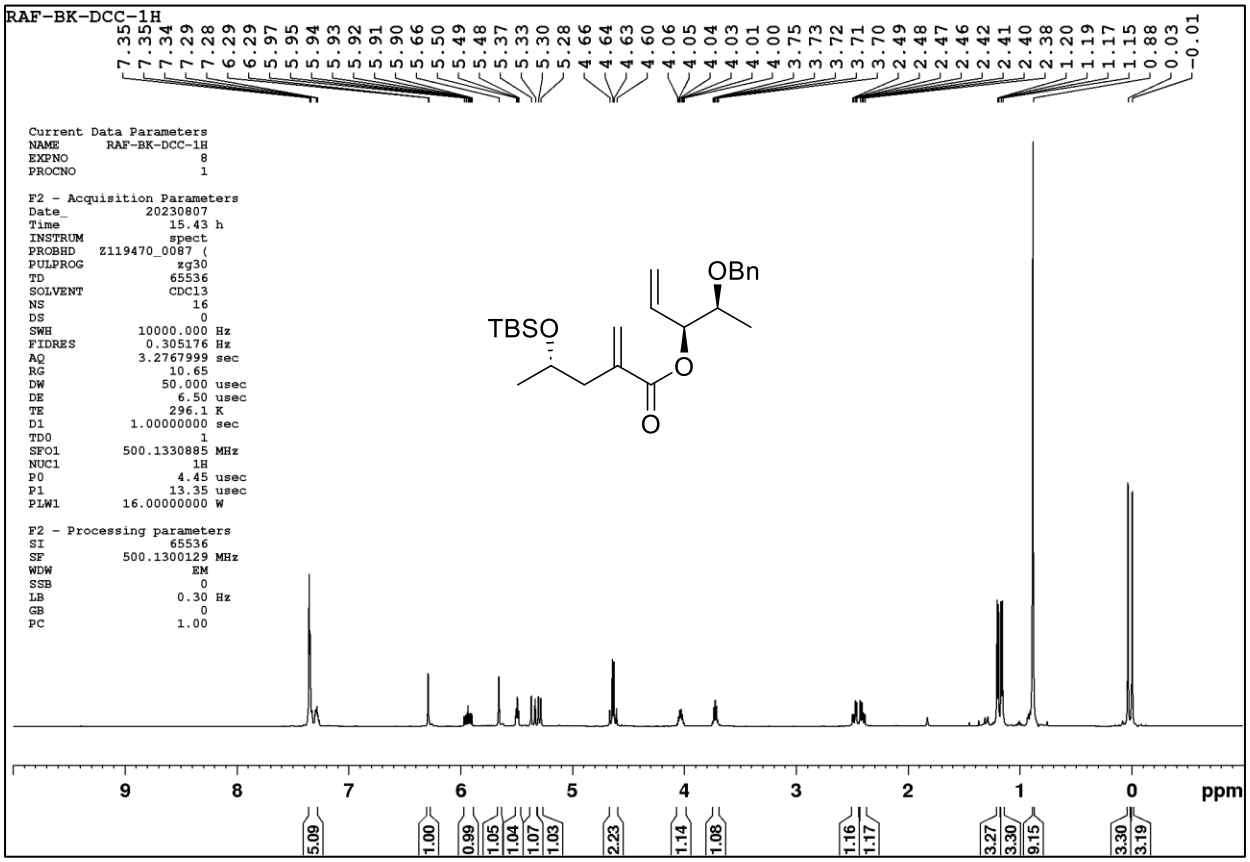


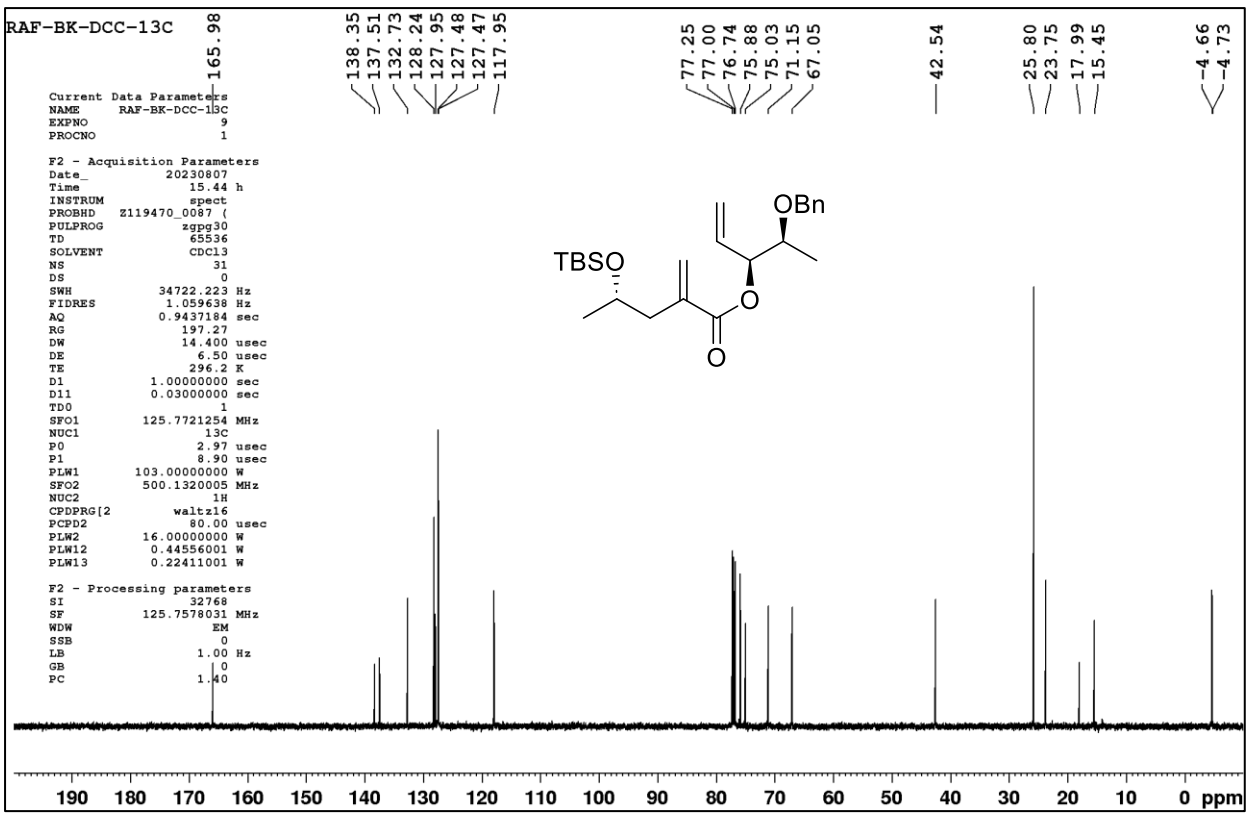


4b: HRMS (Q–TOF) *m/z:* $[M + Na]^+$ Calcd for $C_{12}H_{16}O_2Na$ 215.1043; Found 215.1044.

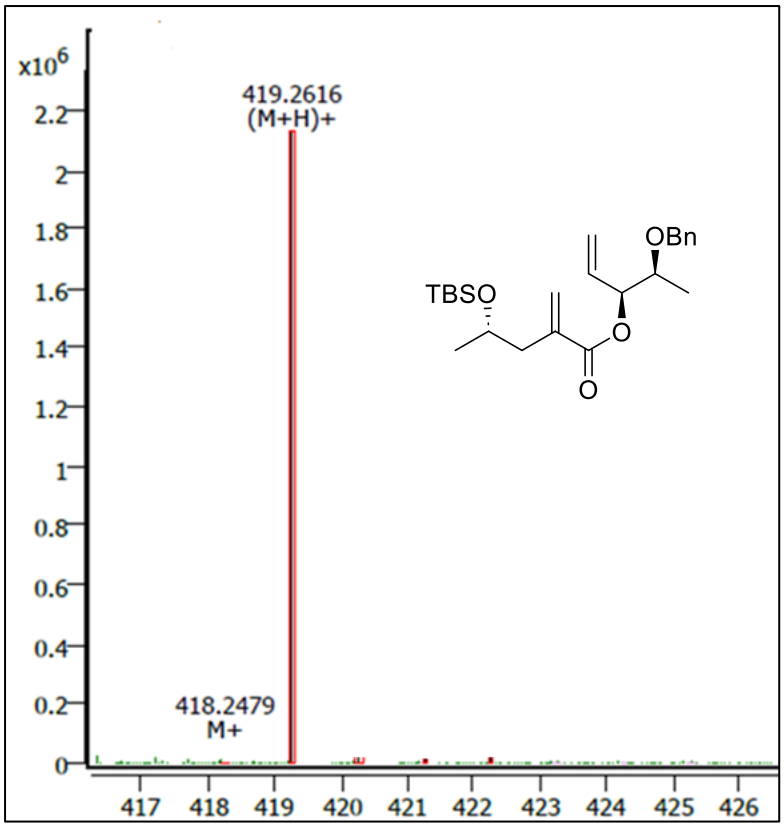


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **12a**

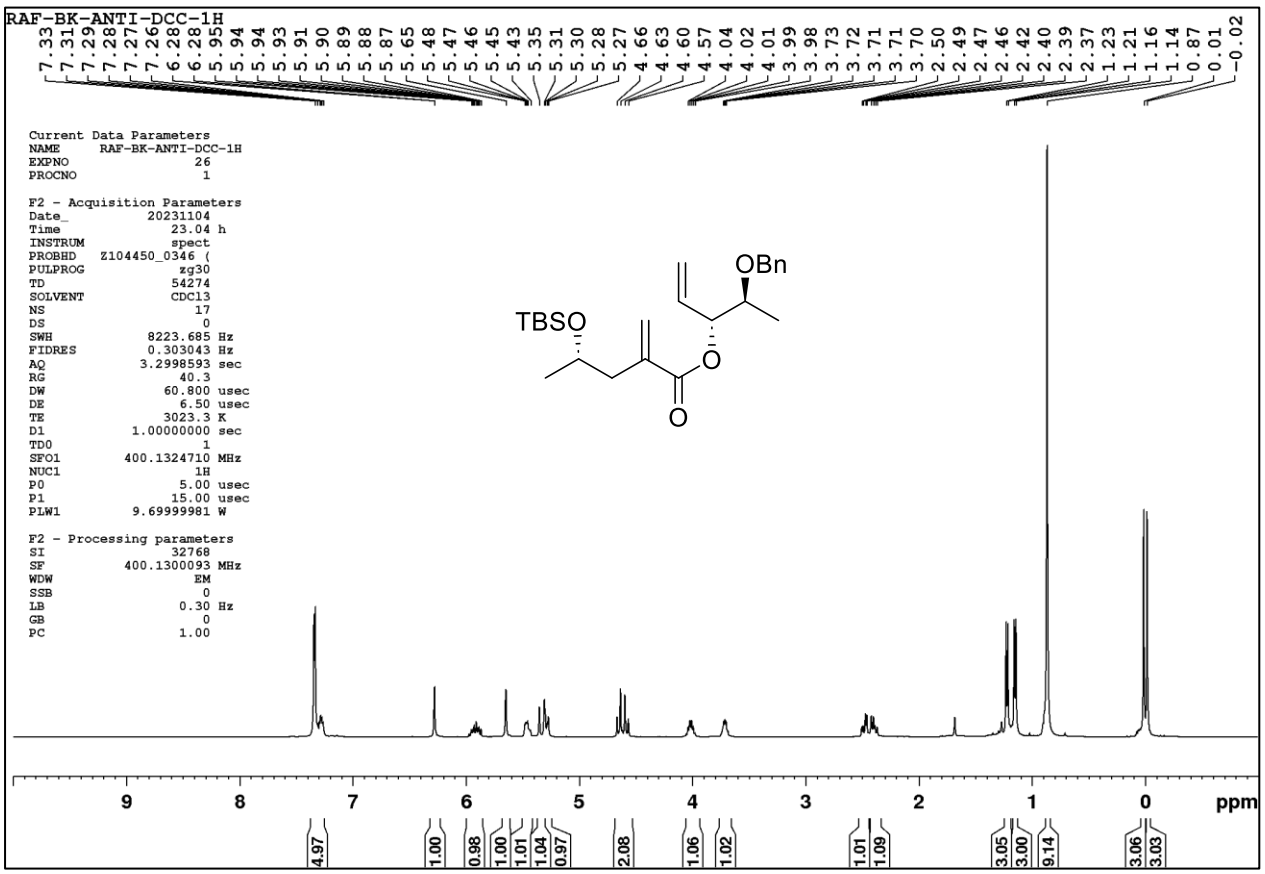


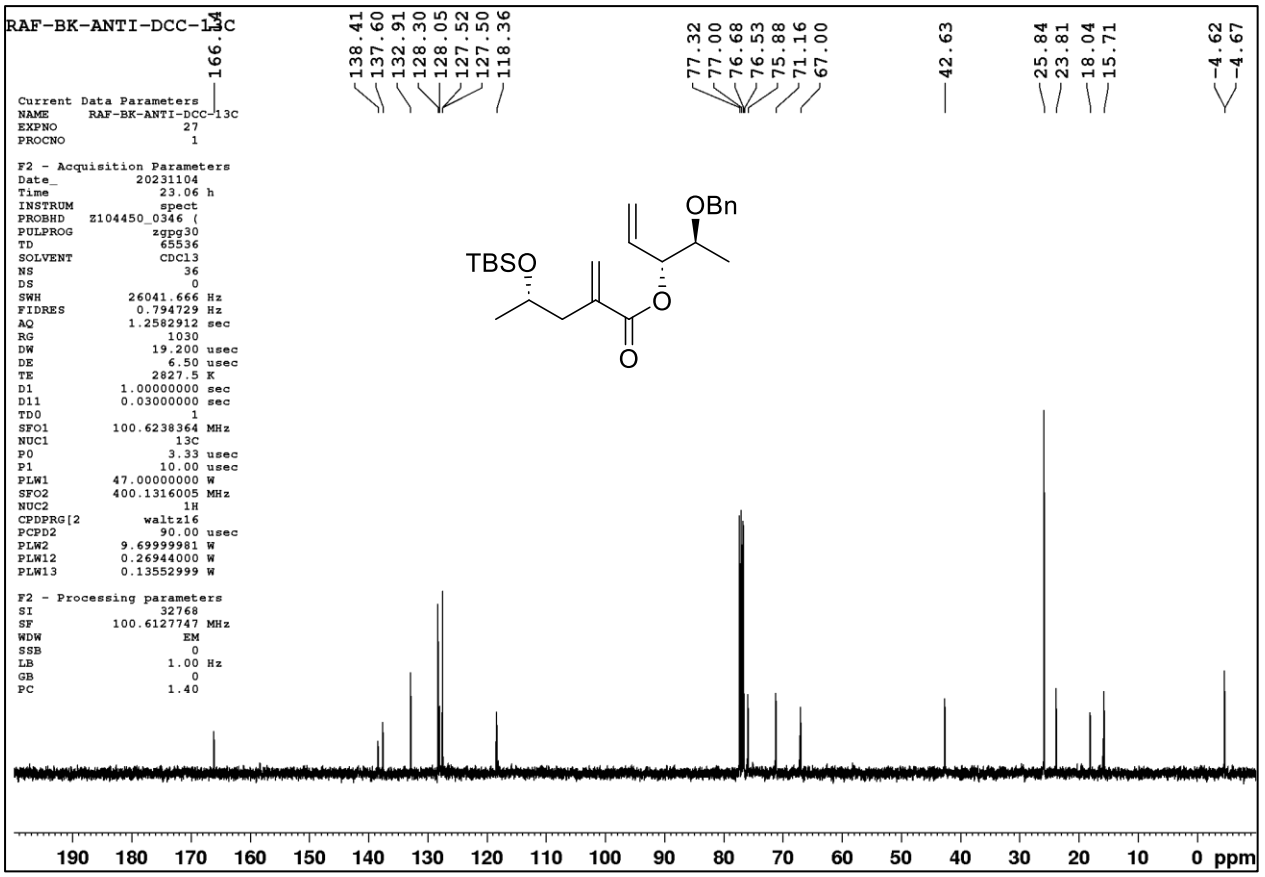


12a: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{24}H_{39}O_4Si$ 419.2613; Found 419.2616.

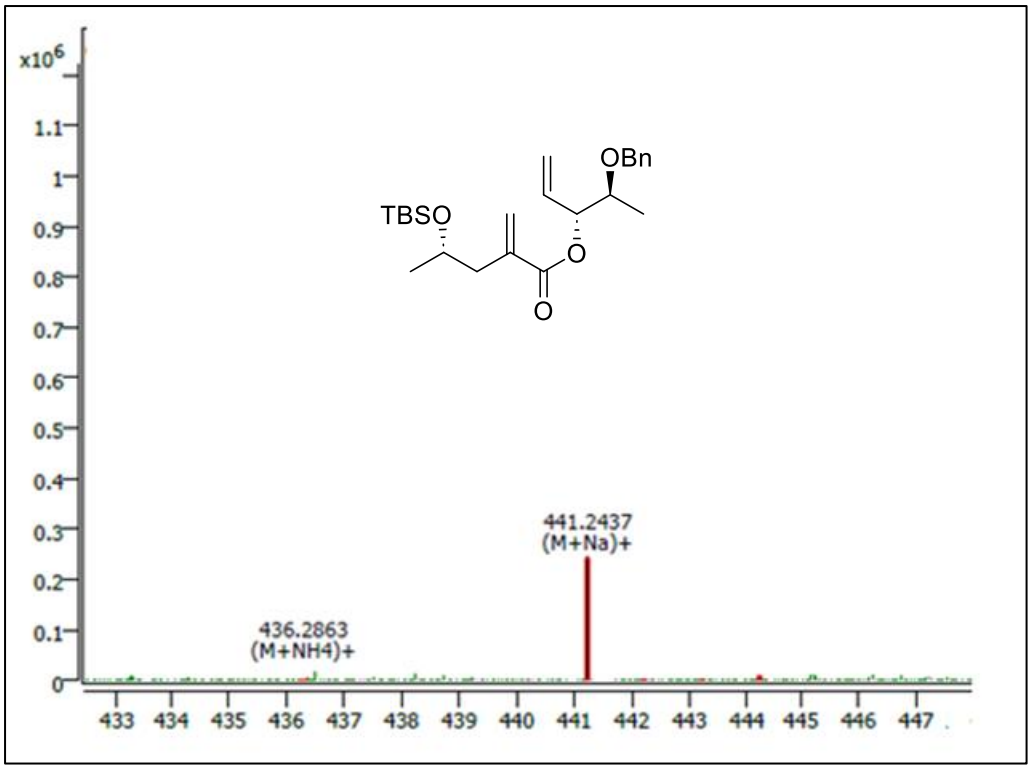


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **12b**

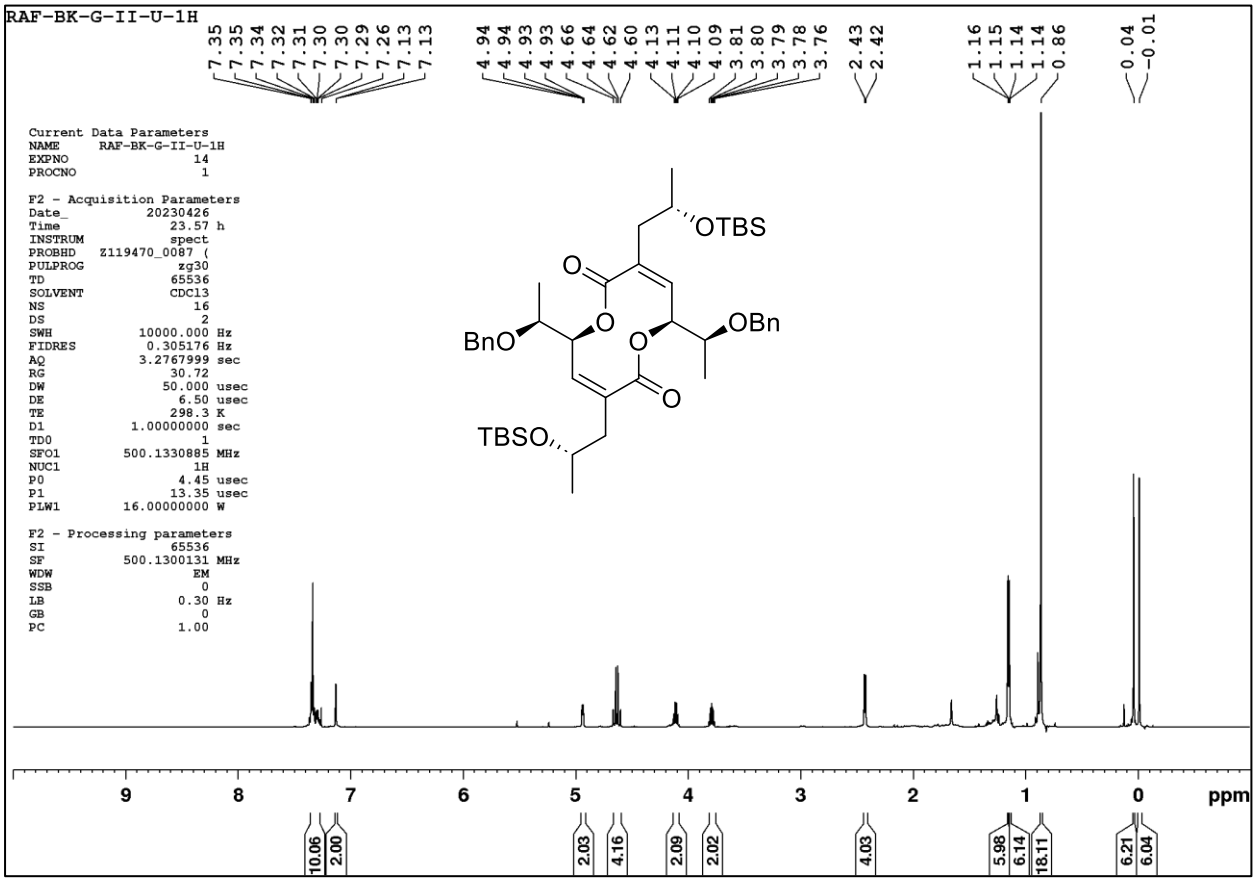


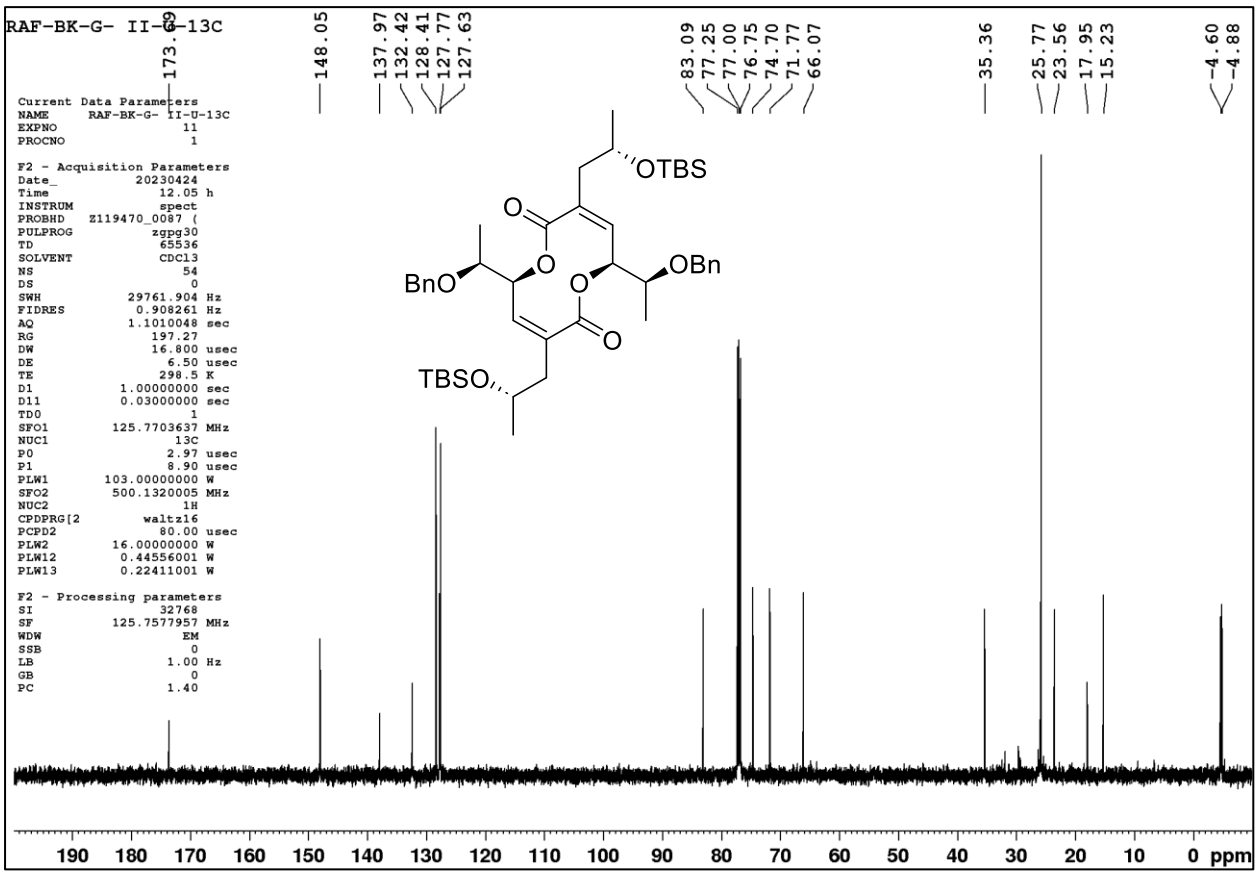


12b: HRMS (Q–TOF) *m/z:* [M + Na] $^{+}$ Calcd for $C_{24}H_{38}O_4SiNa$ 441.2432; Found 441.2437.

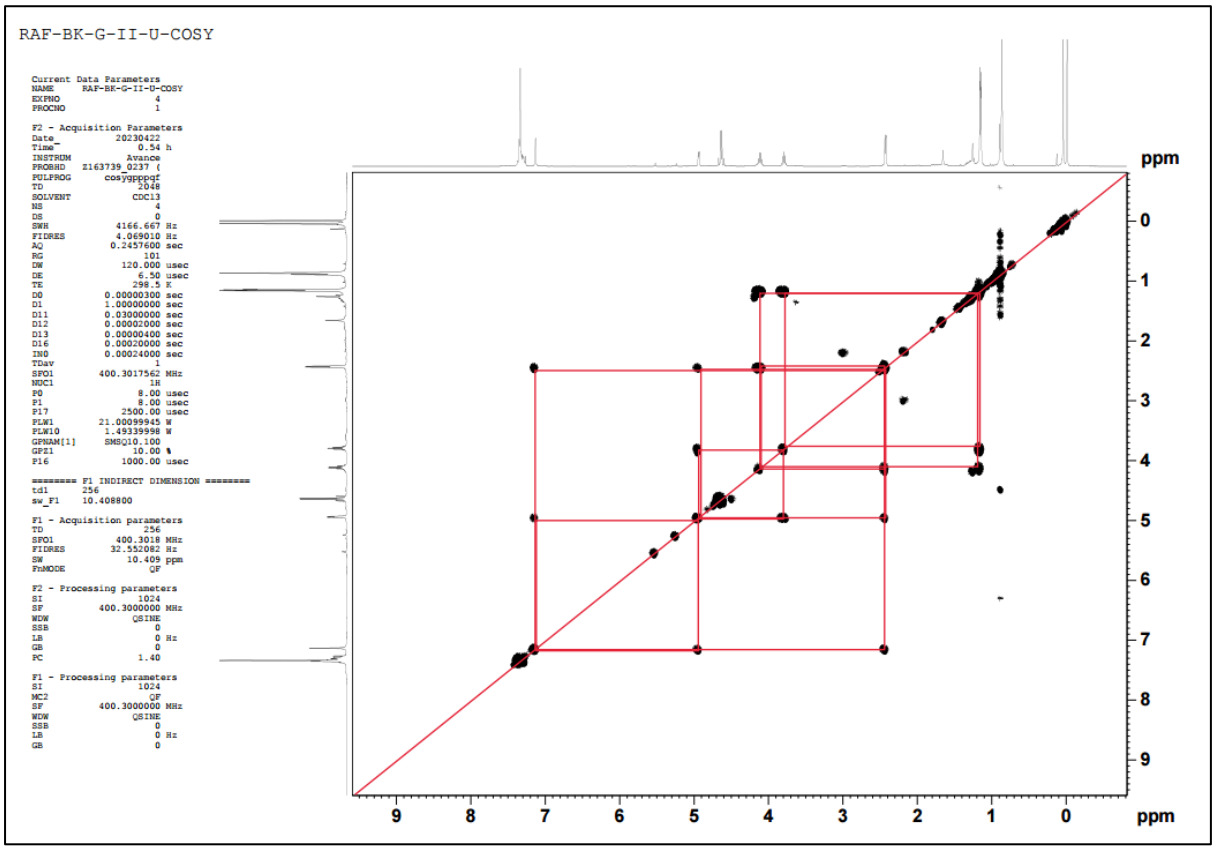


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **13**

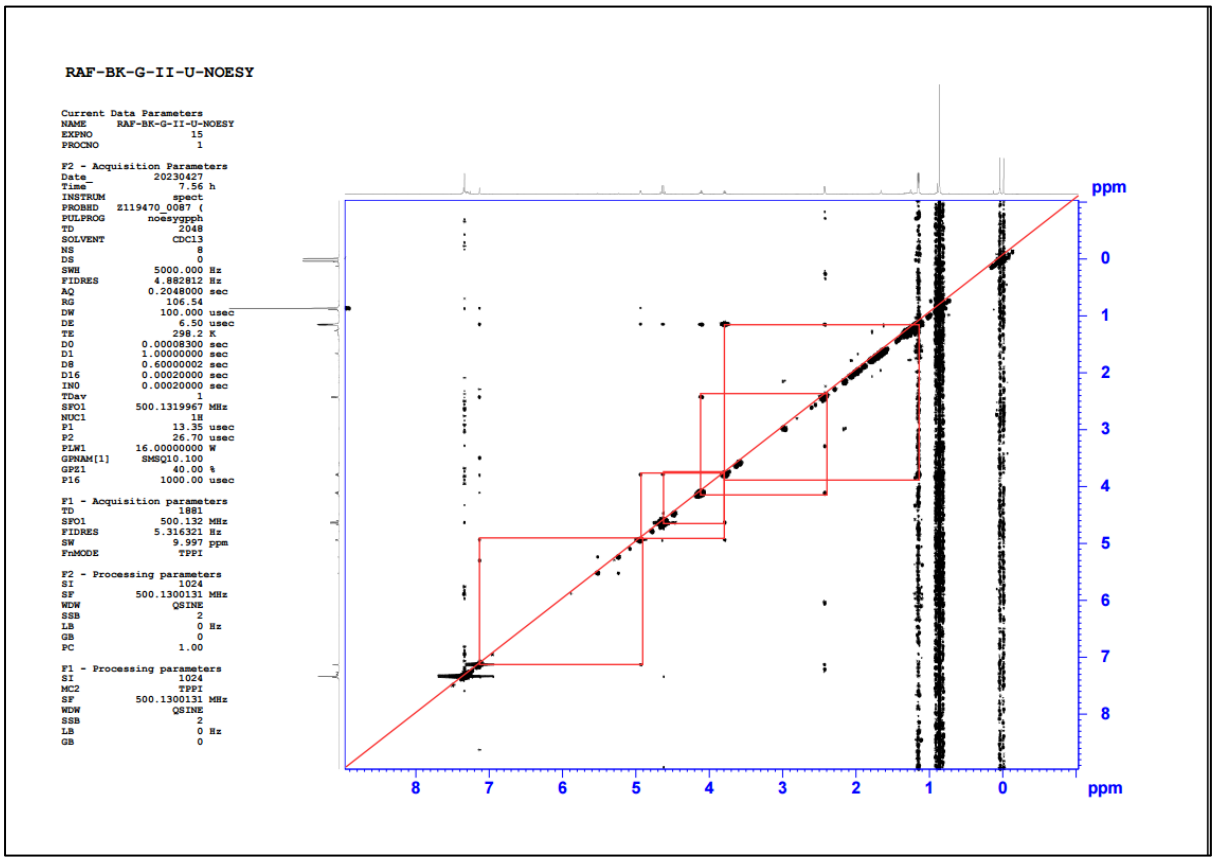




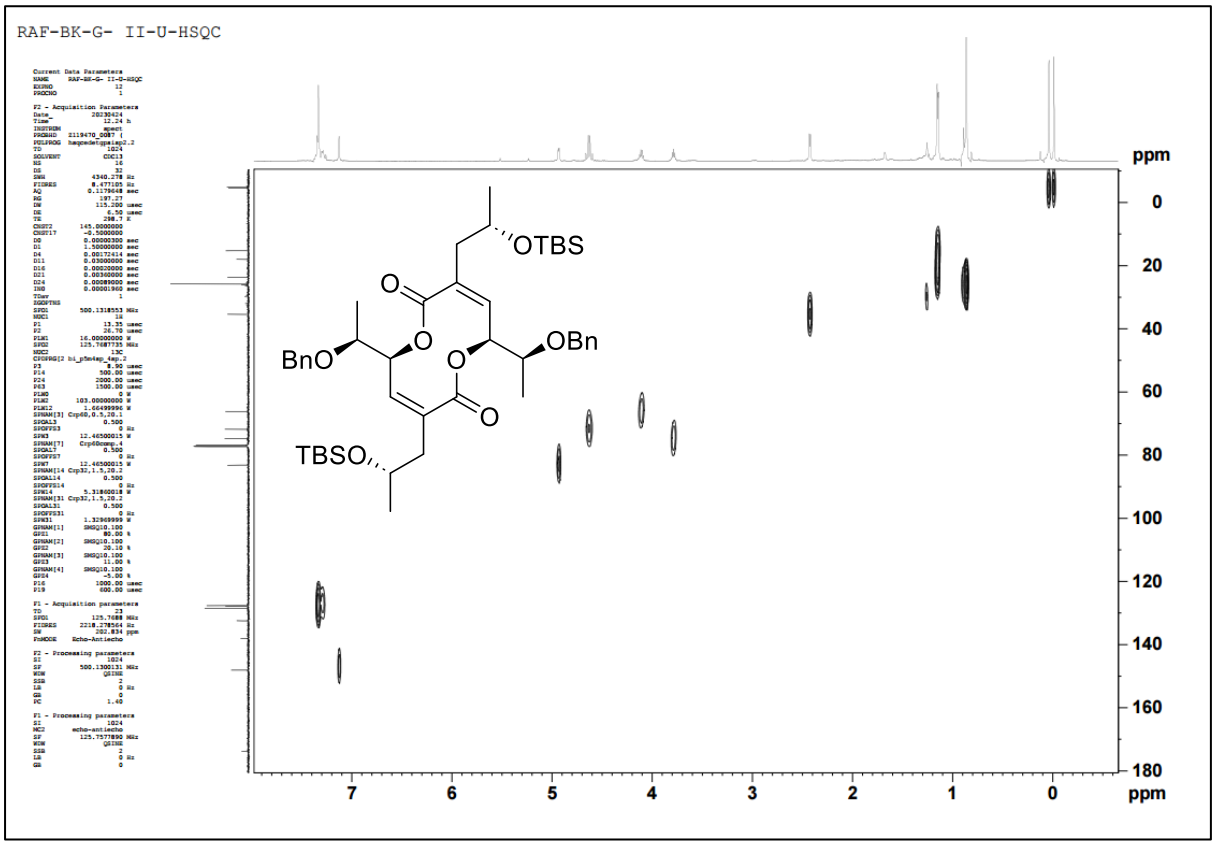
H-H COSY spectra of compound **13**



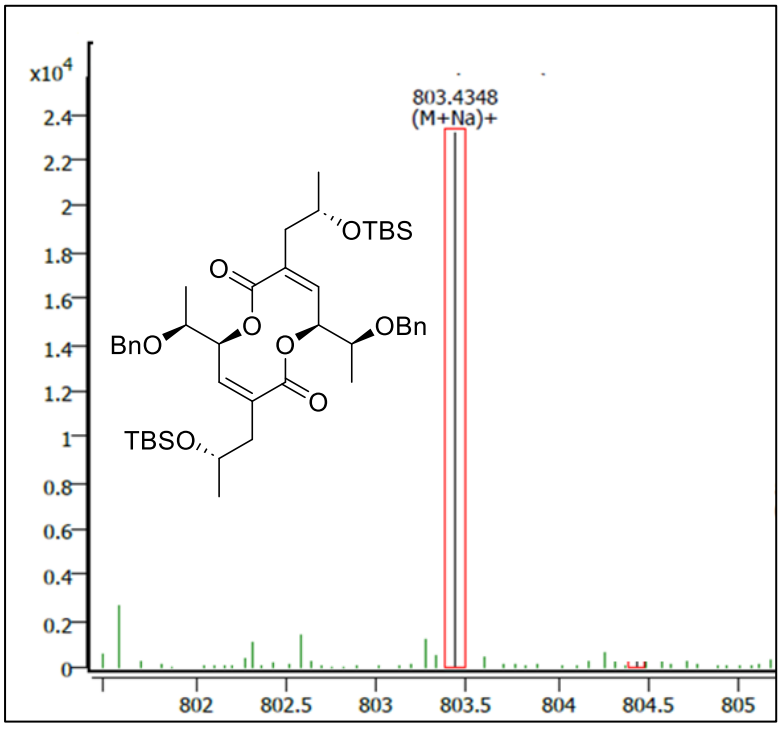
NOESY spectra of compound **13**



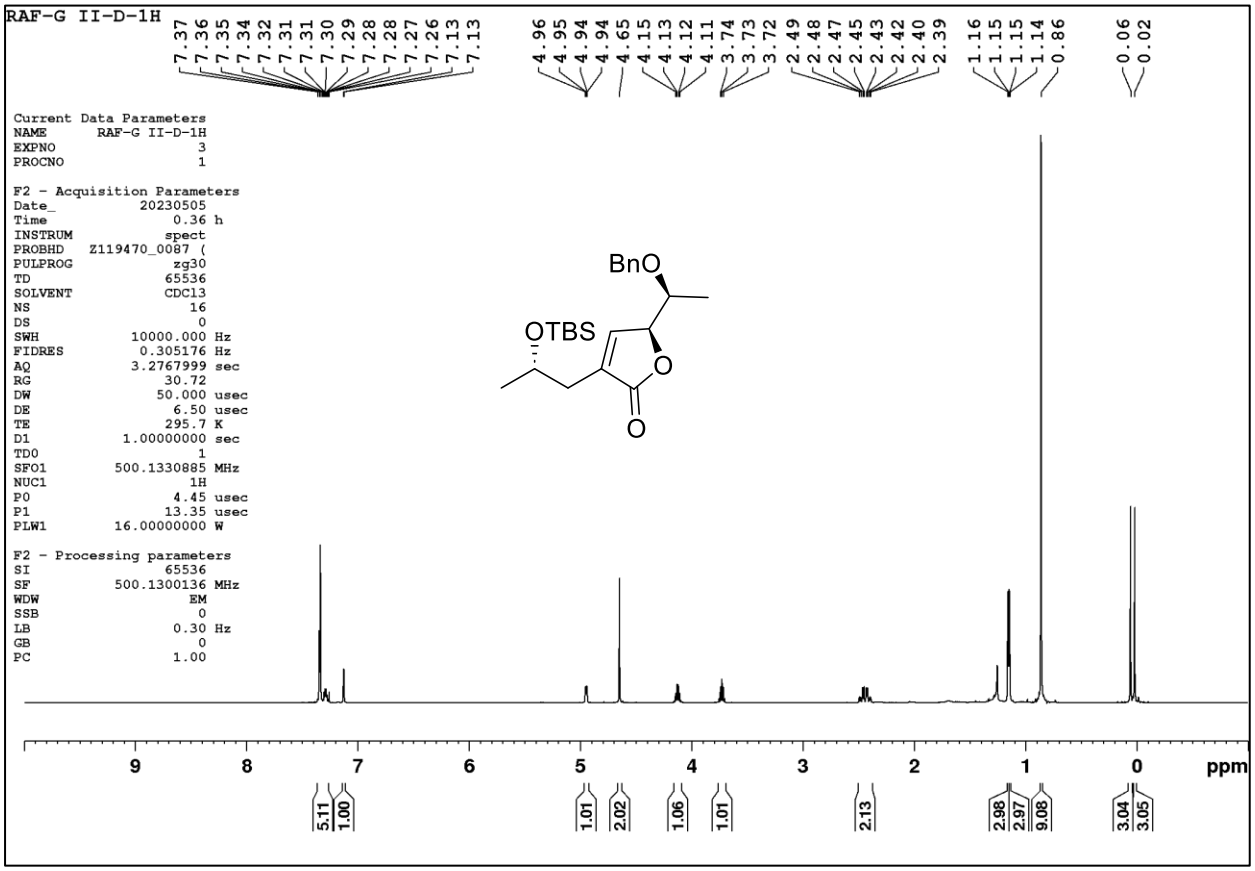
HSQC spectra of compound **13**

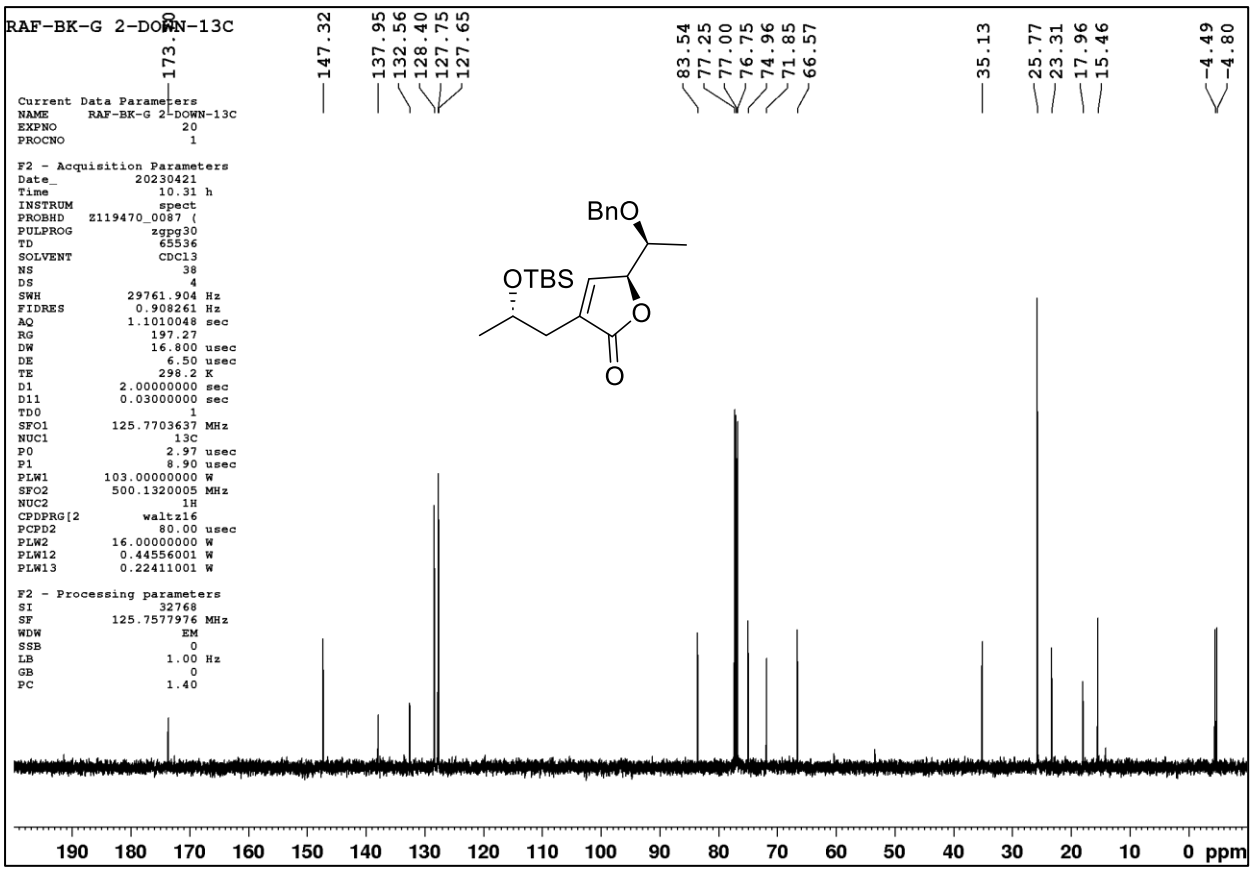


13: HRMS (Q–TOF) *m/z:* [M + Na]$^+$ Calcd for $C_{44}H_{68}O_8Si_2Na$ 803.4345; Found 803.4348.

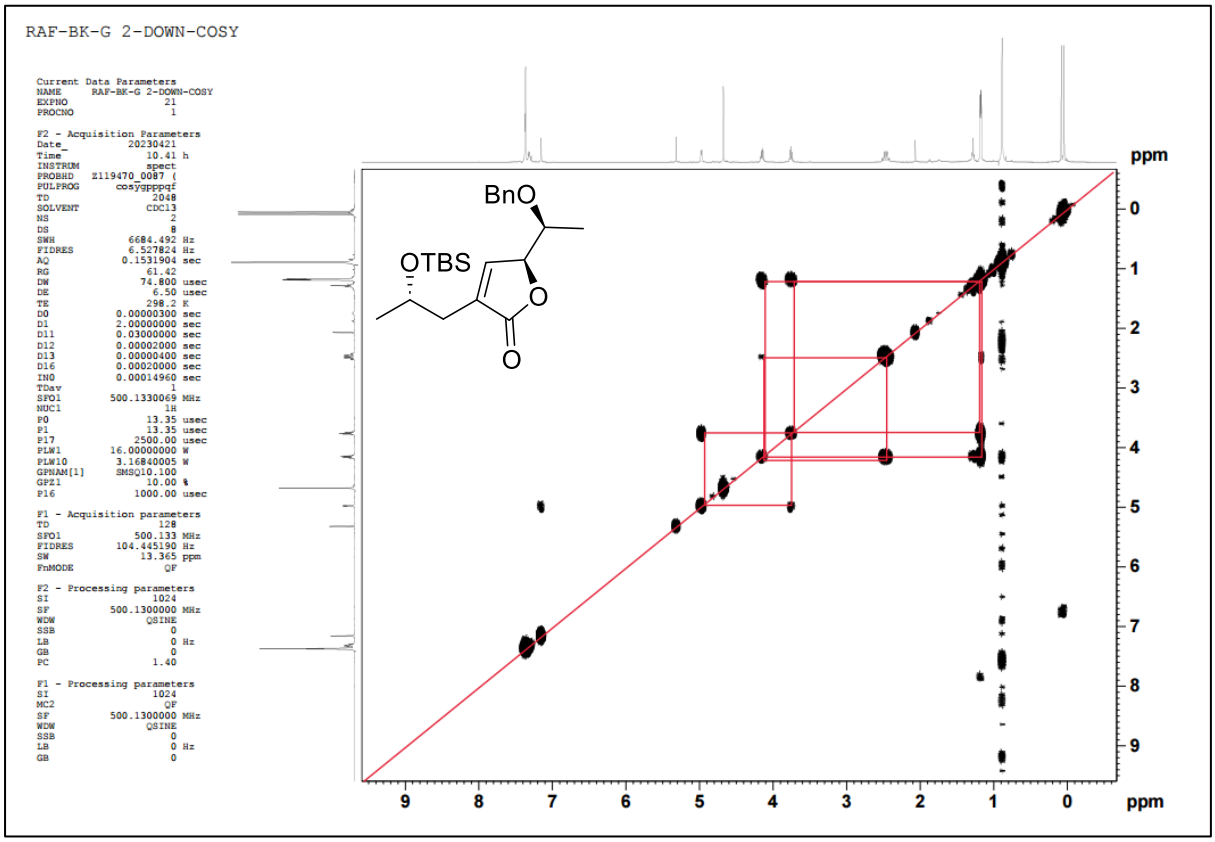


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **2a**

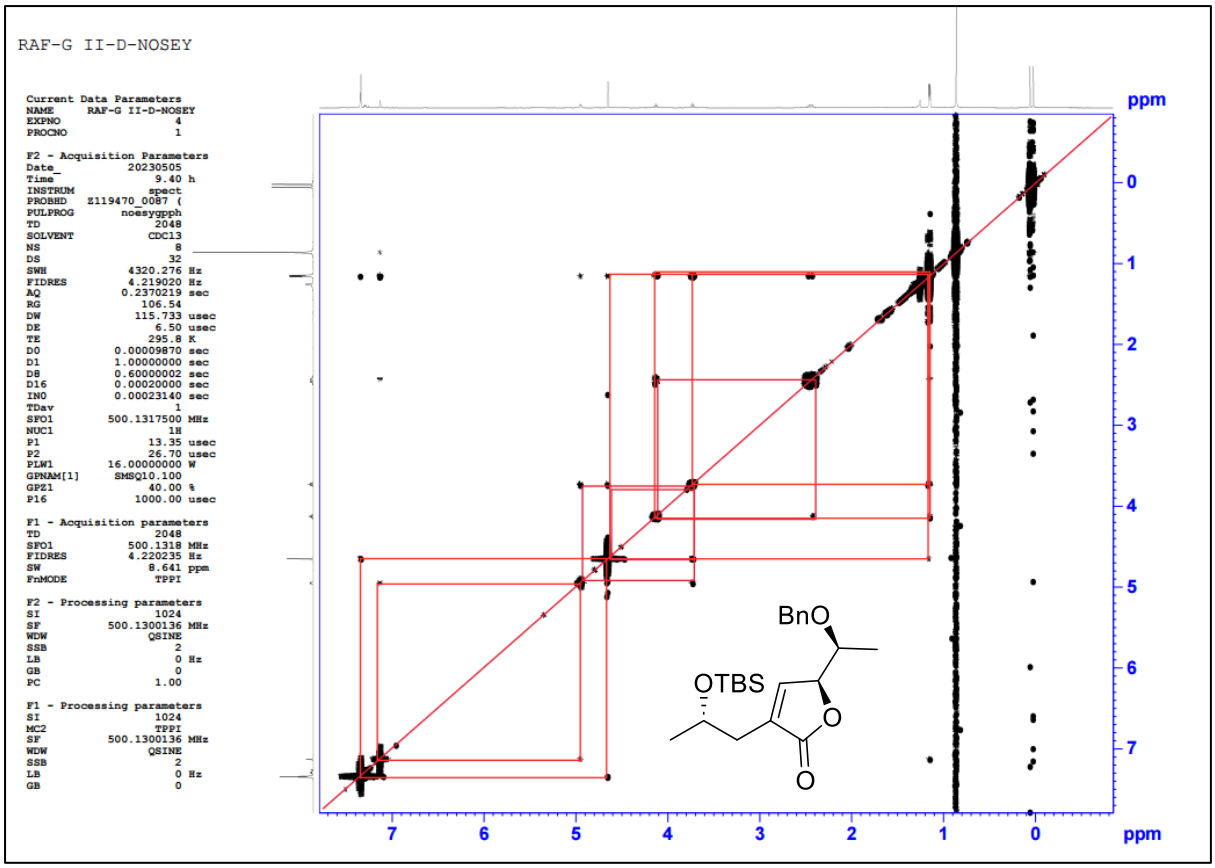




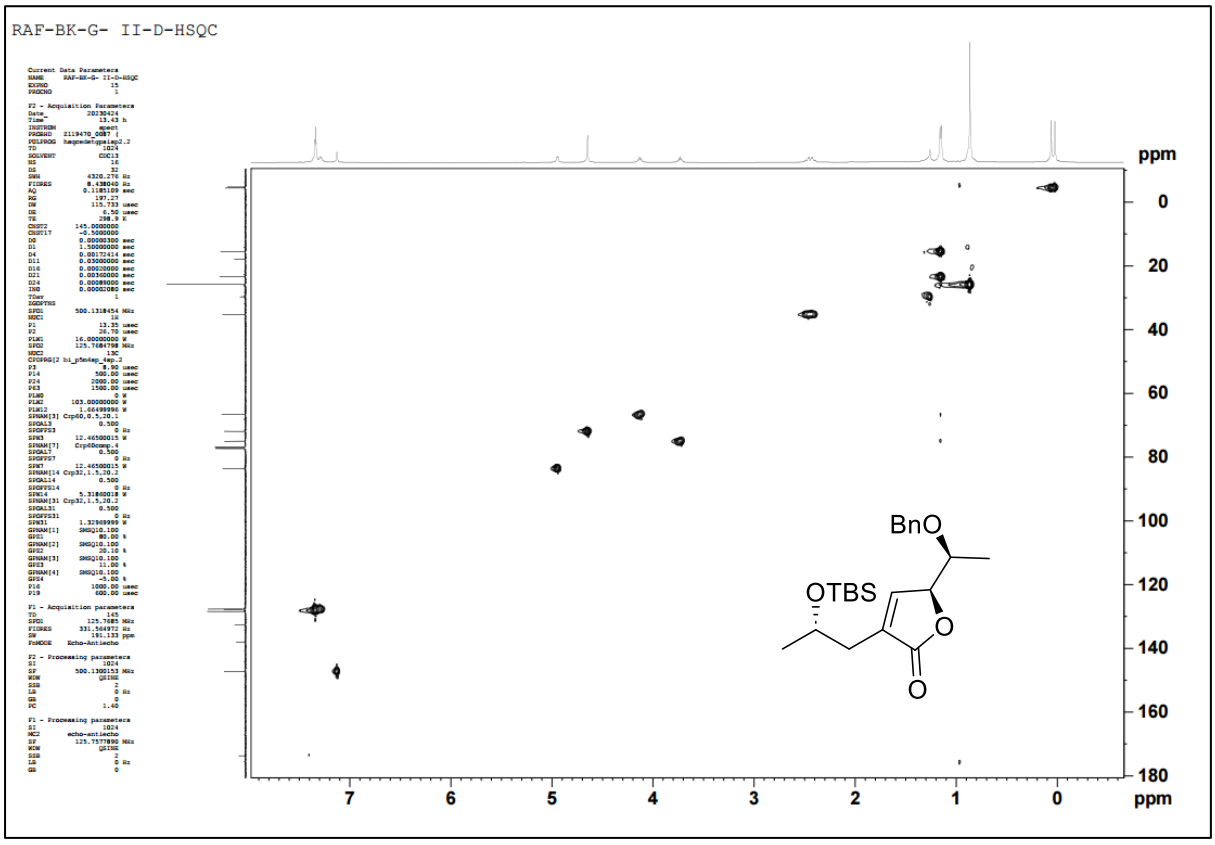
H-H COSY spectra of compound **2a**



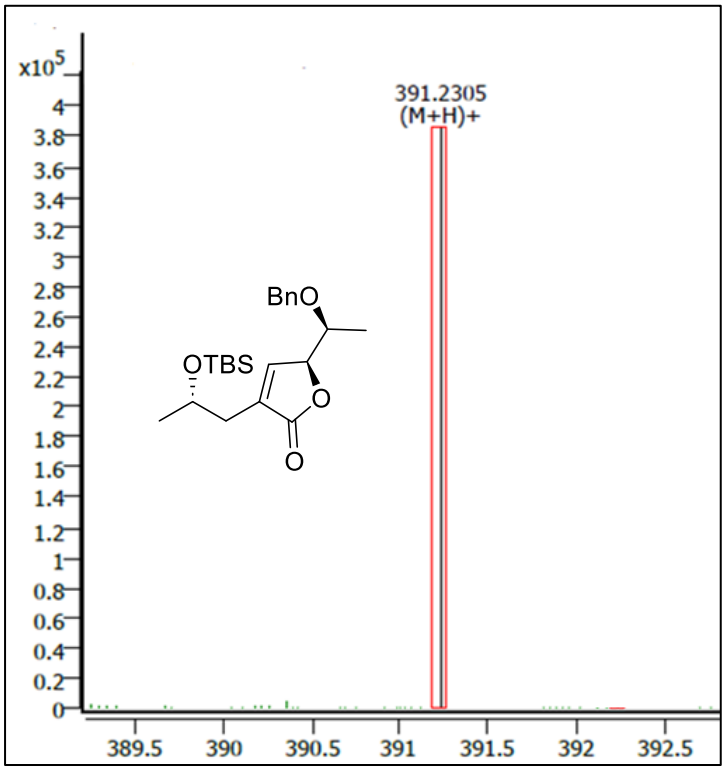
NOESY spectra of compound **2a**



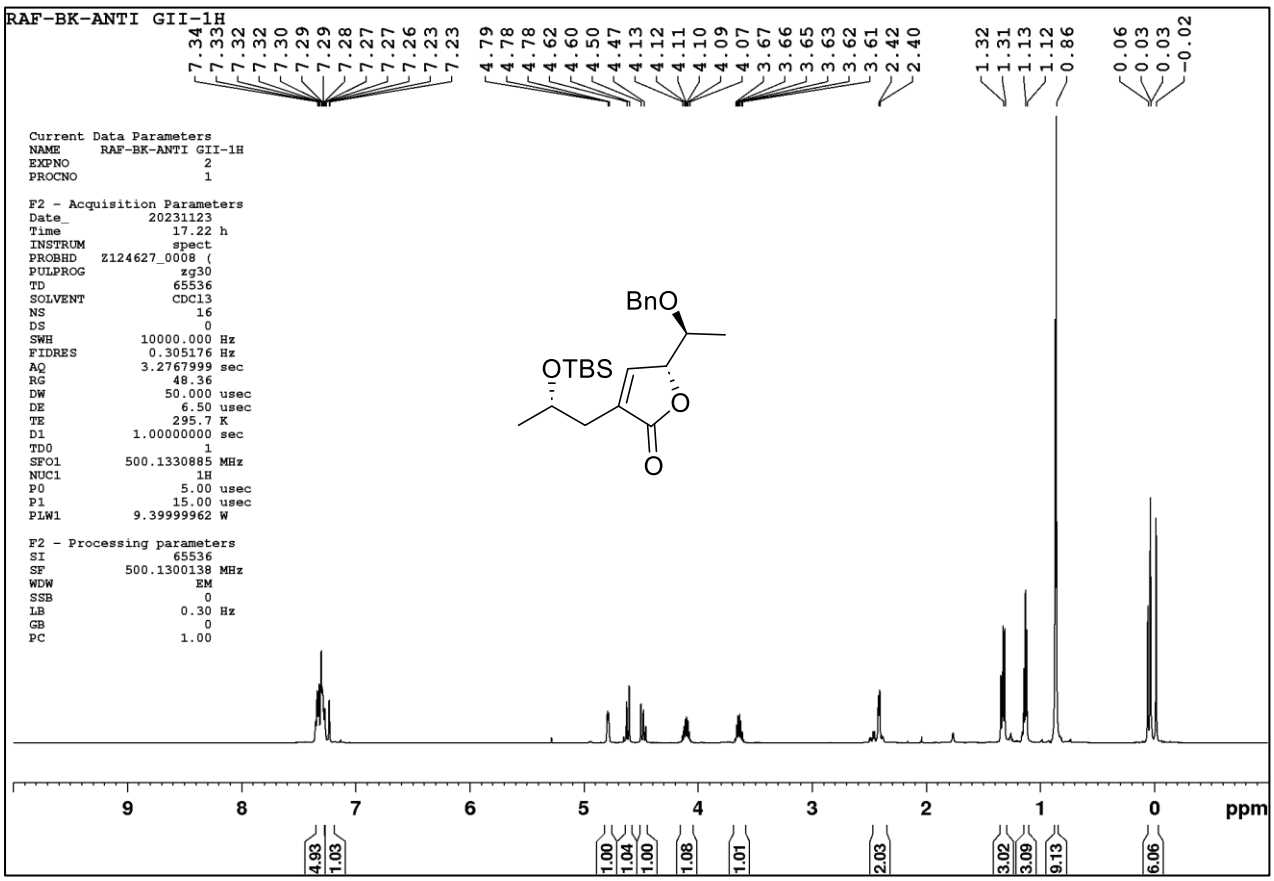
HSQC spectra of compound **2a**

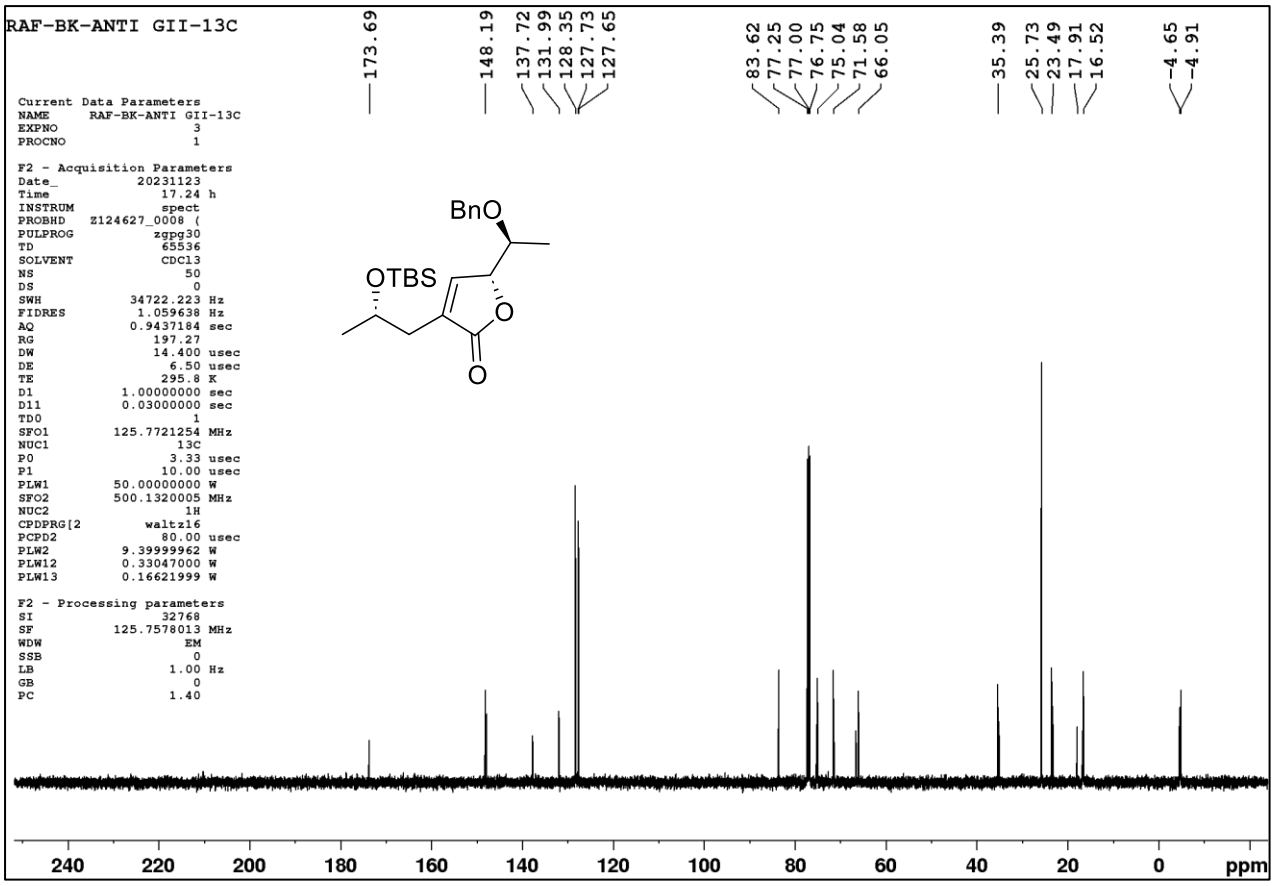


2a: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{35}O_4Si$ 391.2300; Found 391.2305.

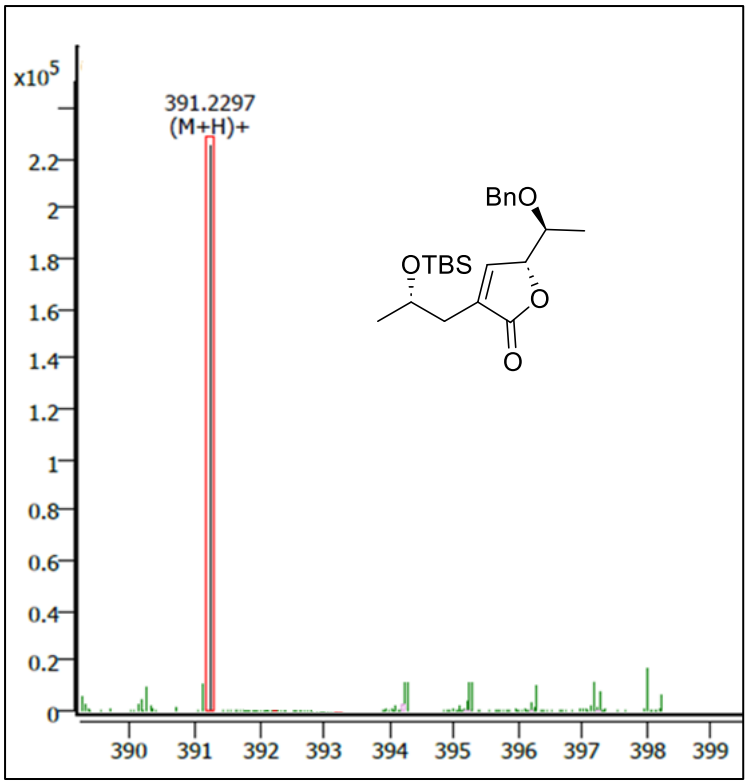


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **2b**

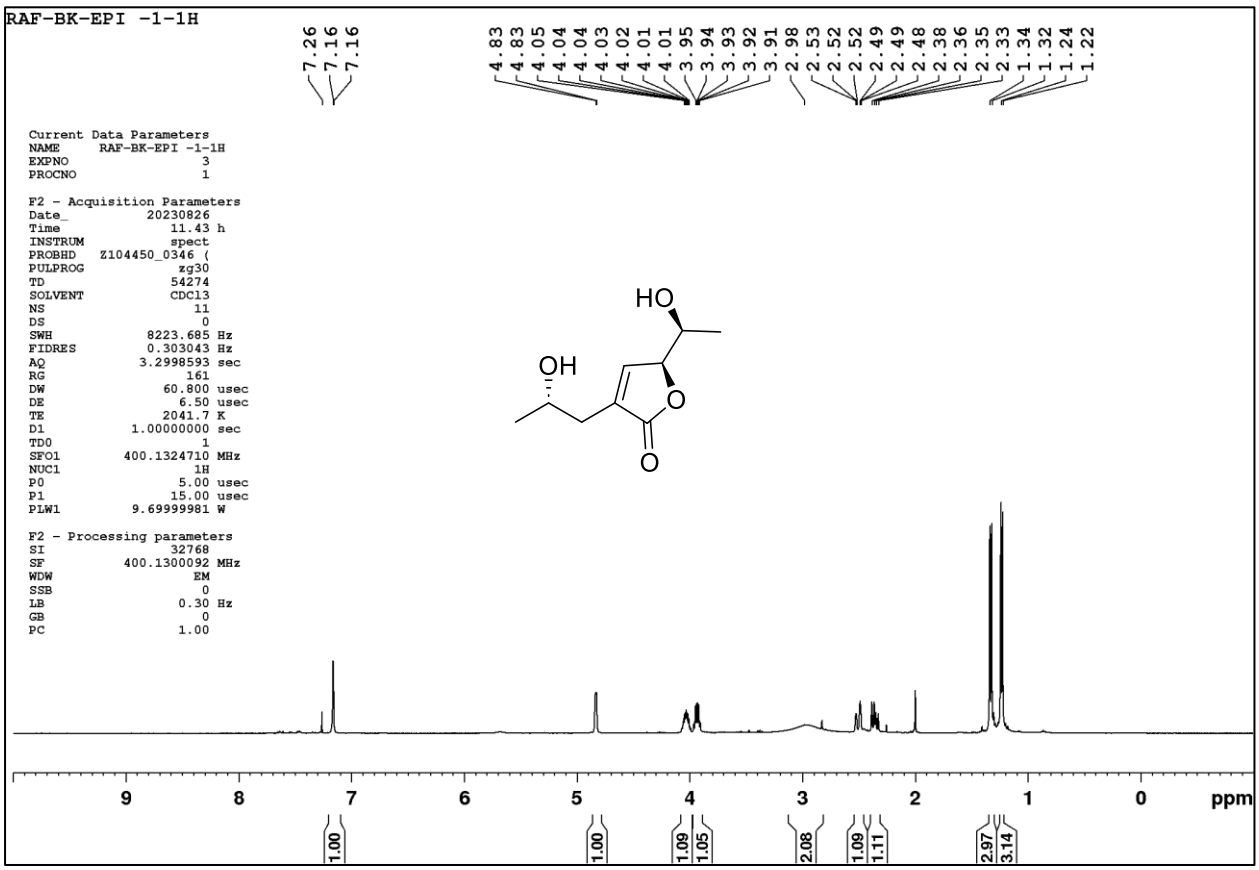


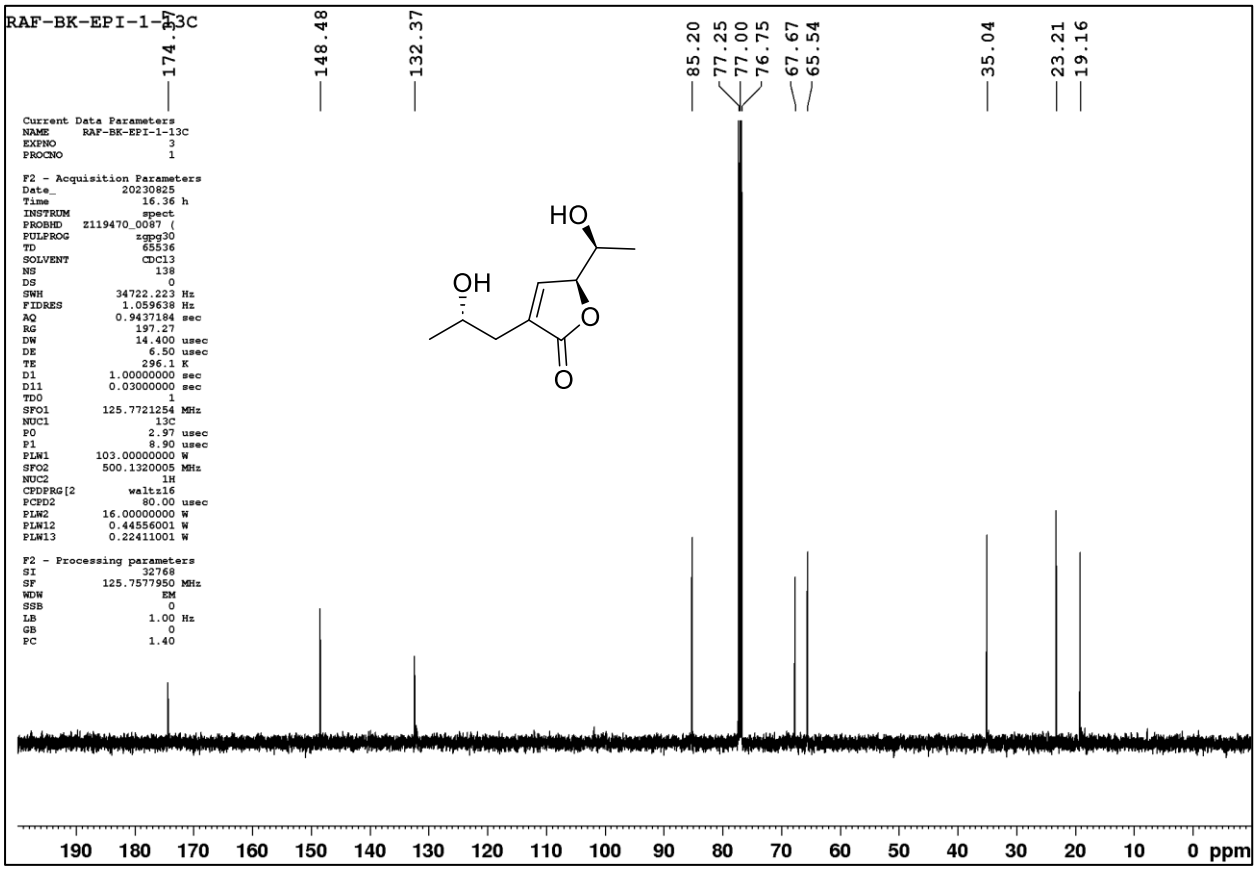


2b: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{22}H_{35}O_4Si$ 391.2300; Found 391.2297.

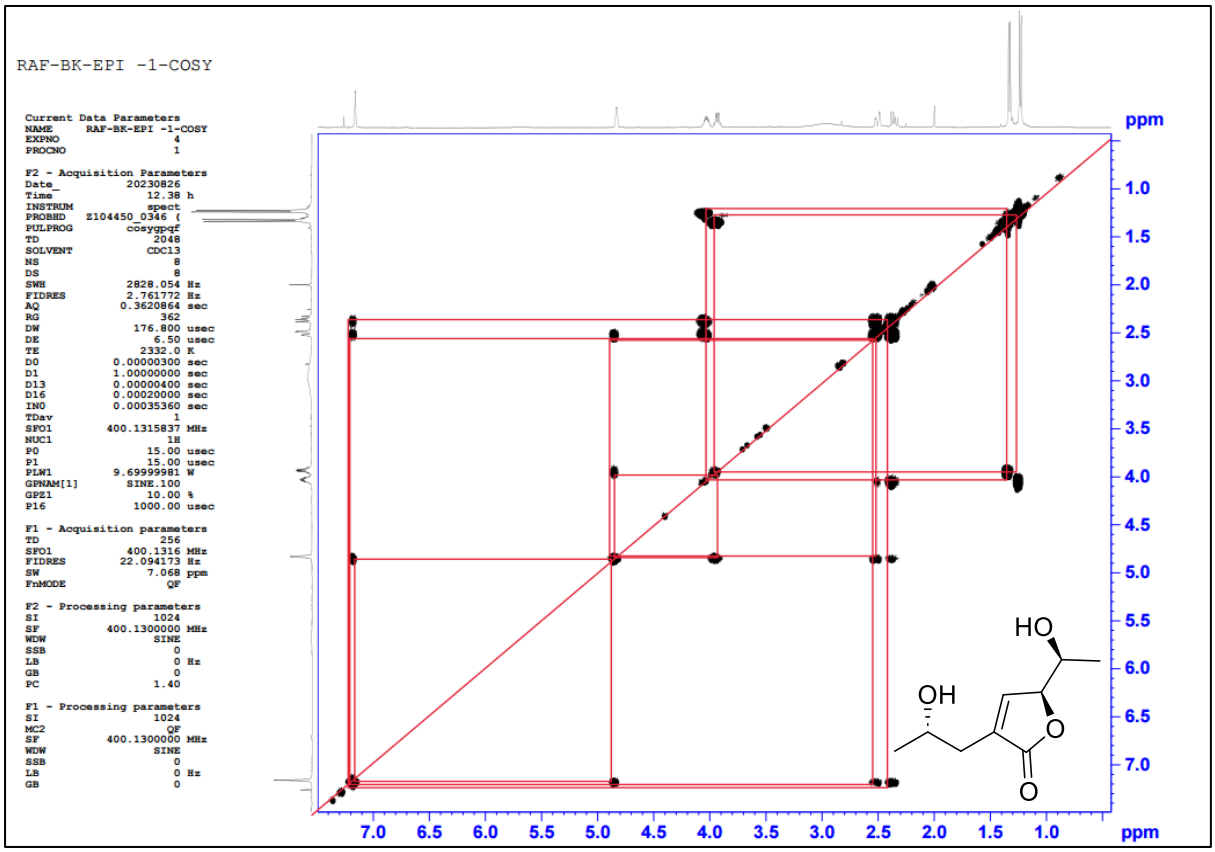


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **1a'**

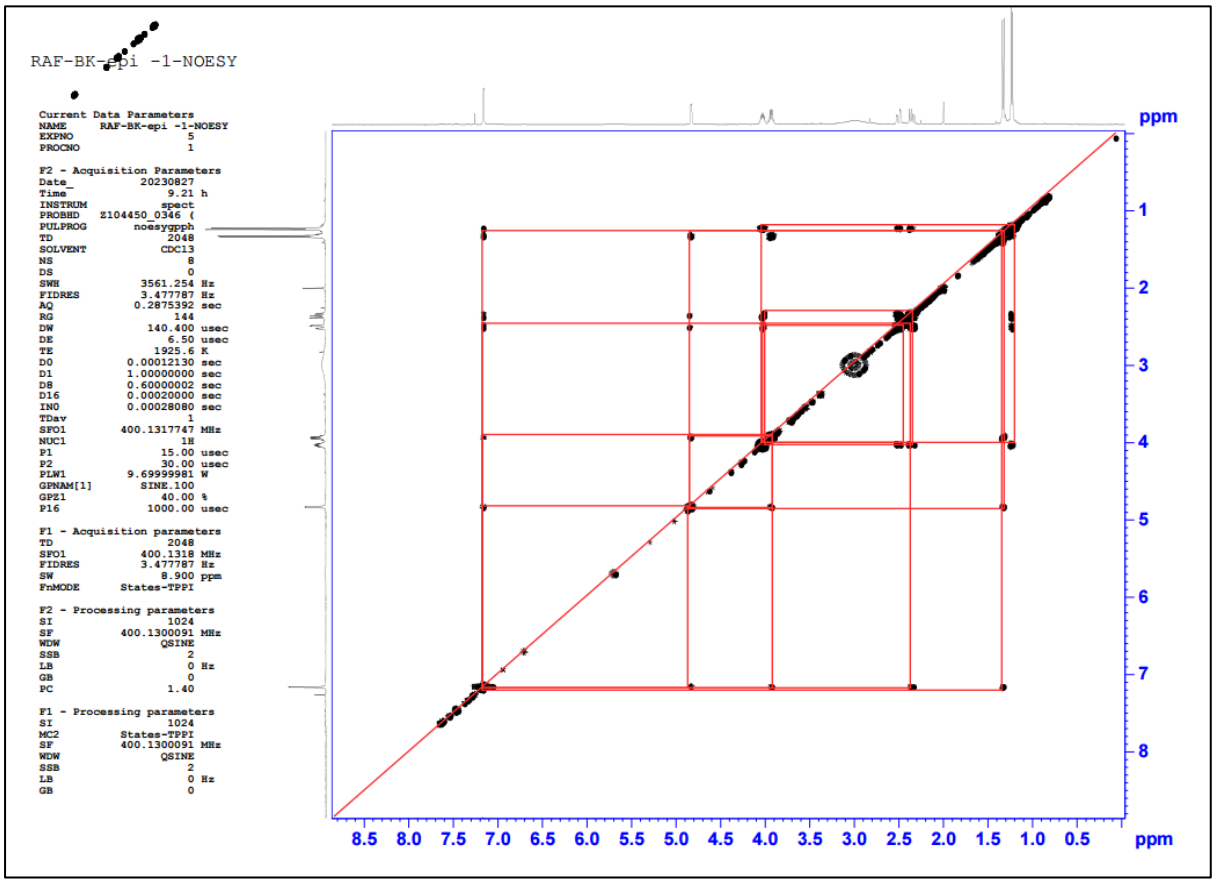




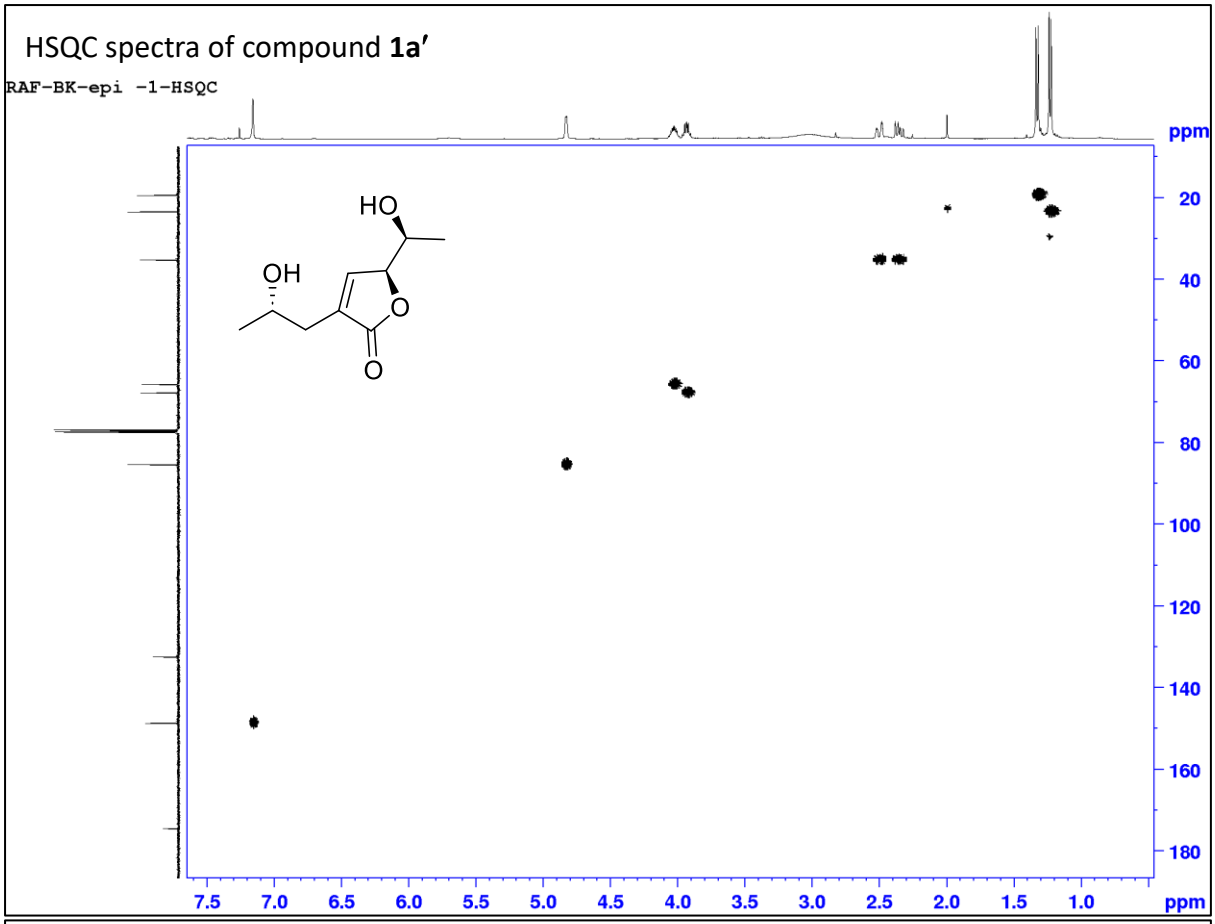
H-H COSY spectra of compound **1a′**



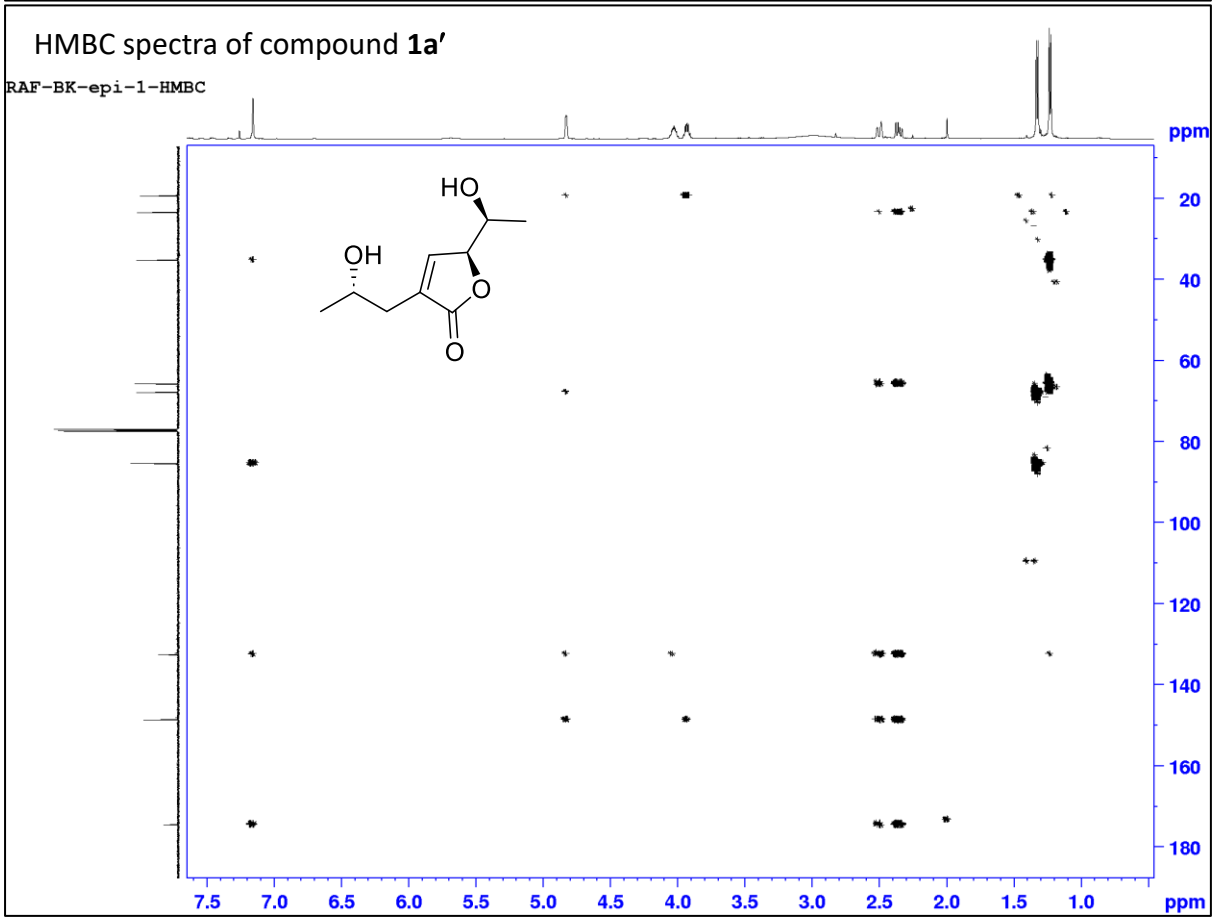
NOESY spectra of compound **1a′**



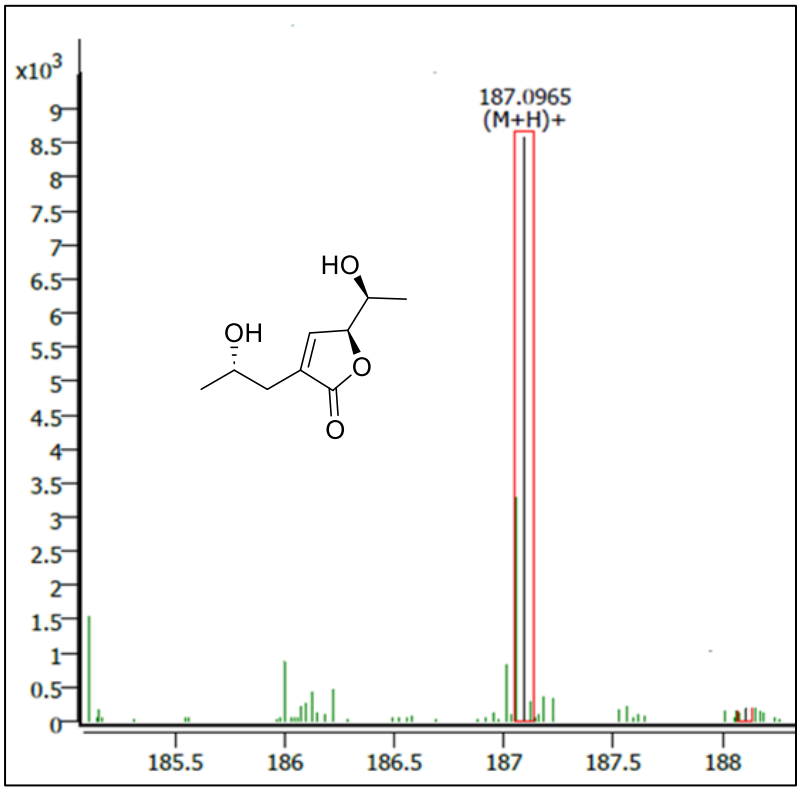
HSQC spectra of compound **1a'**



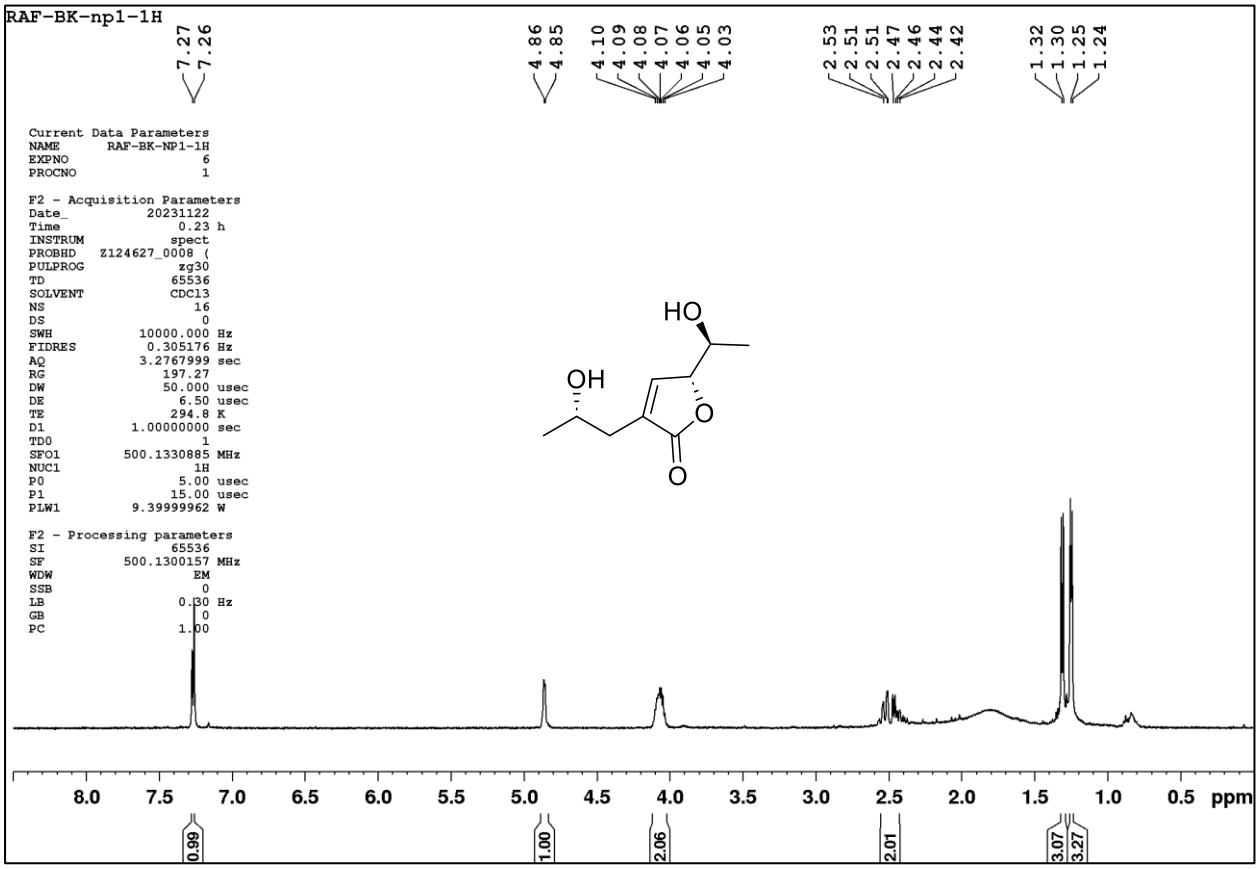
HMBC spectra of compound **1a'**

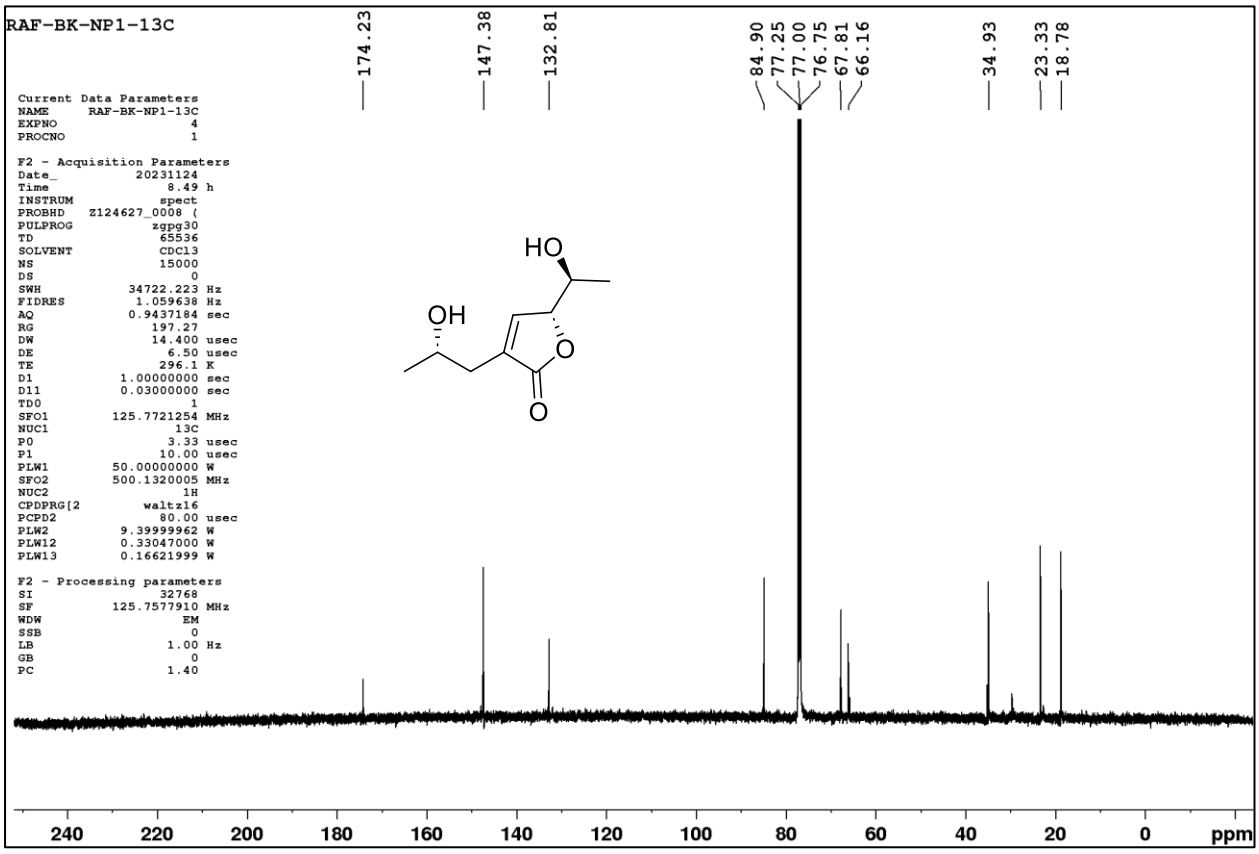


1a′: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_9H_{15}O_4$ 187.0965; Found 187.0965.

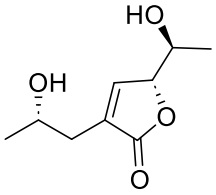


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **1a**

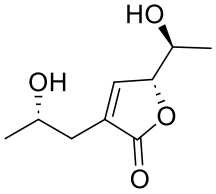




^{1}H NMR Comparison data of compound **1a**: Isolated and our work



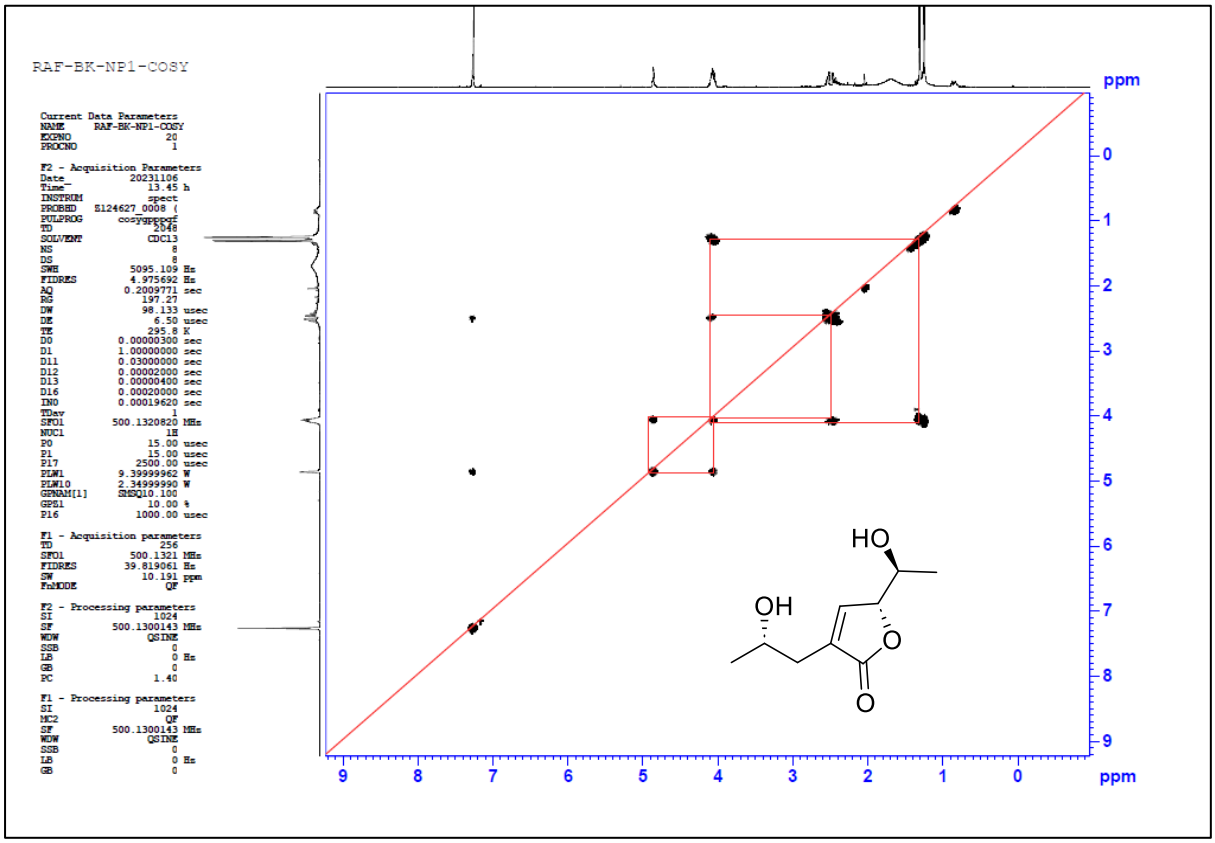
^{1}H NMR (500 MHz, $CDCl_3$) Isolated by Yurchenko *Mar. Drugs*, 2019, 17, 579	**^{1}H NMR (500 MHz, $CDCl_3$) Our work**
7.27 (d, *J* = 1.4 Hz, 1H)	7.27 (s, 1H)
4.85 (dd, *J* = 4.4, 1.4 Hz, 1H)	4.86 (d, *J* = 5.0 Hz, 1H)
4.08 (m, 1H)	4.11–4.02 (m, 2H)
4.05 (qd, *J* = 6.4, 4.4 Hz, 1H)	
2.52 (ddt, *J* = 15.0, 3.8, 1.4 Hz, 1H)	2.57–2.37 (m, 2H)
2.45 (ddt, *J* = 15.0, 7.8, 1.4 Hz, 1H)	
1.31 (d, *J* = 6.4 Hz, 3H)	1.30 (d, *J* = 6.7 Hz, 3H)
1.25 (d, *J* = 6.3 Hz, 3H)	1.25 (d, *J* = 6.2 Hz, 3H)



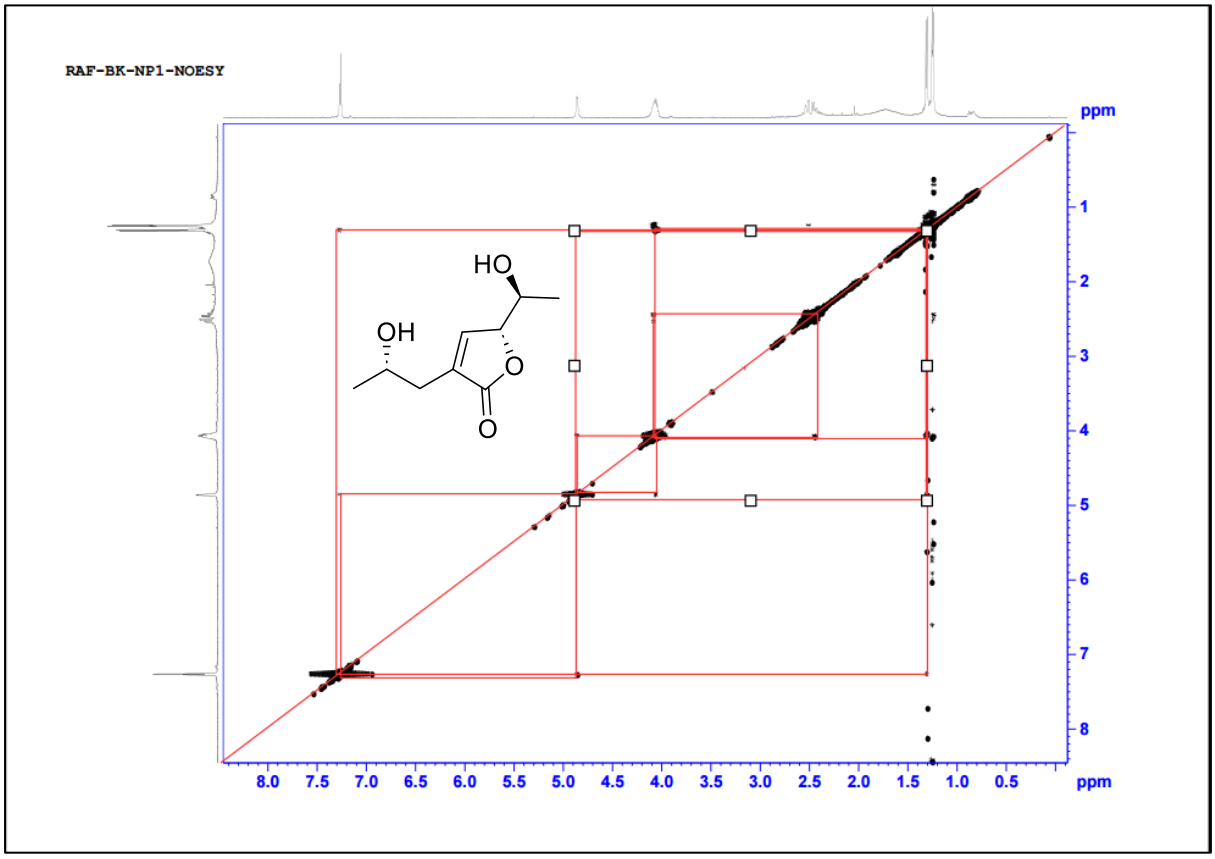
^{13}C NMR Comparison data of compound **1a**: Isolated and our work

^{13}C NMR (125 MHz, $CDCl_3$) Isolated by Yurchenko *Mar. Drugs*, 2019, 17, 579.	**^{13}C NMR (125 MHz, $CDCl_3$) Our work**
174.2	174.2
147.4	147.4
132.8	132.8
84.9	84.9
67.8	67.8
66.2	66.2
34.9	34.9
23.3	23.3
18.8	18.8

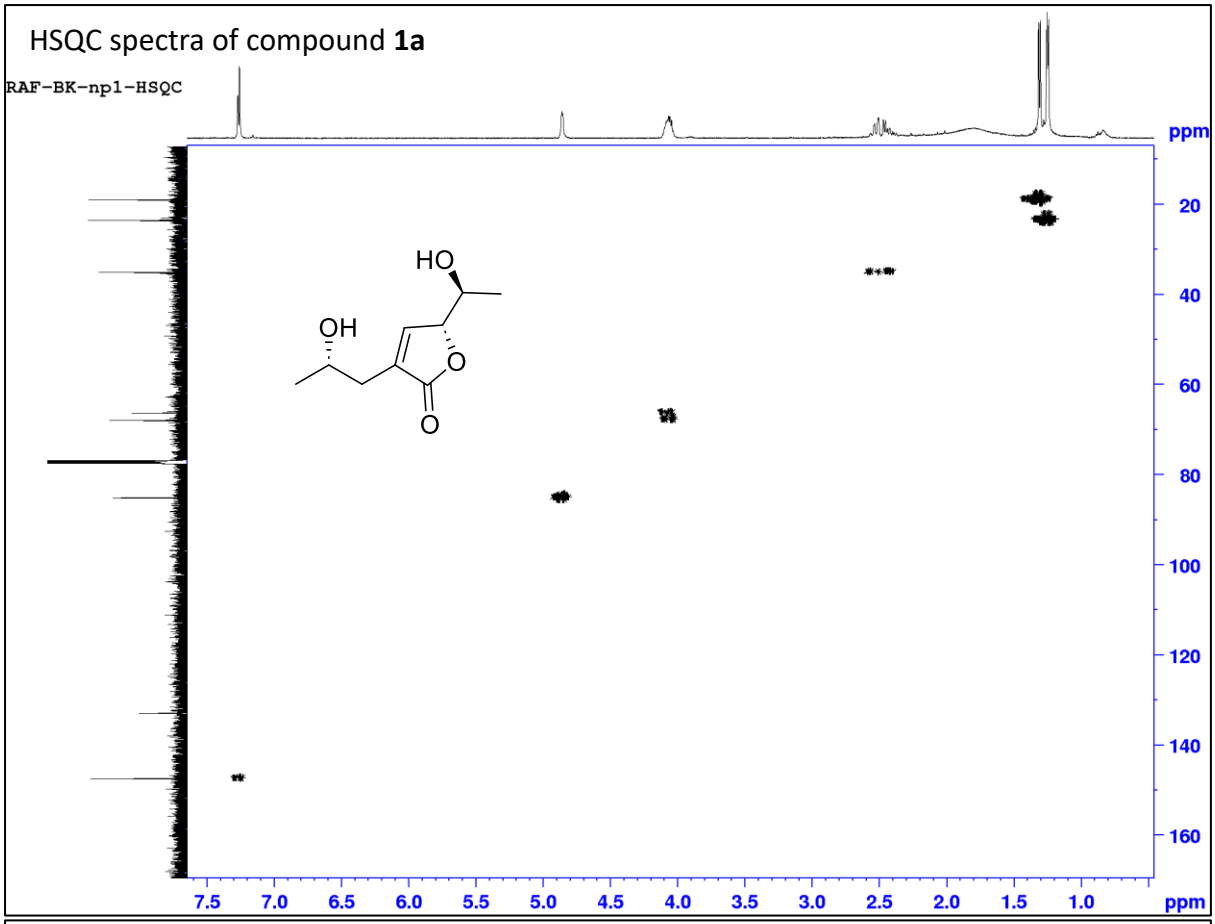
H-H COSY spectra of compound **1a**



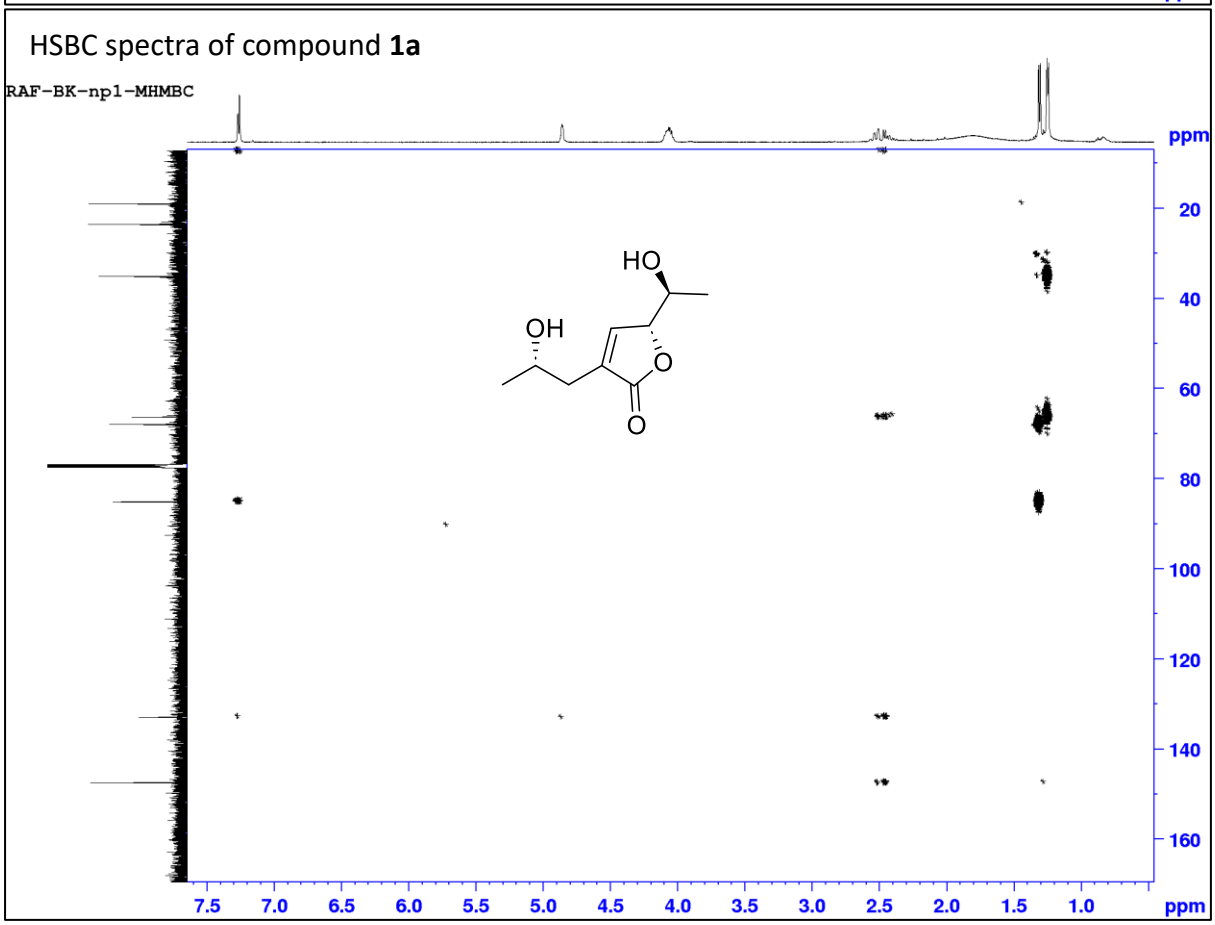
NOESY spectra of compound **1a**



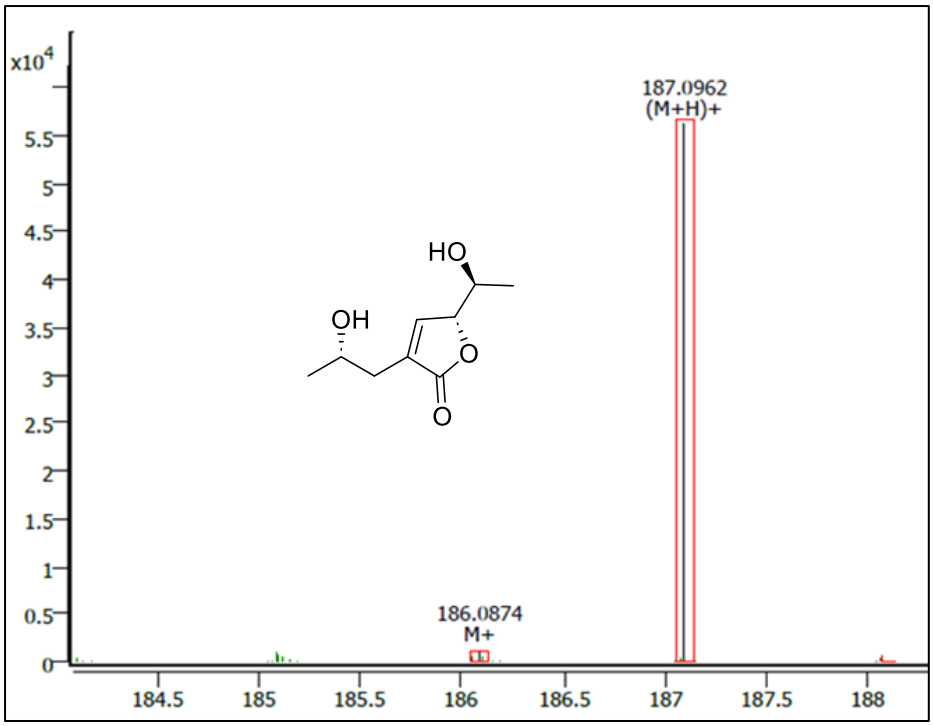
HSQC spectra of compound **1a**



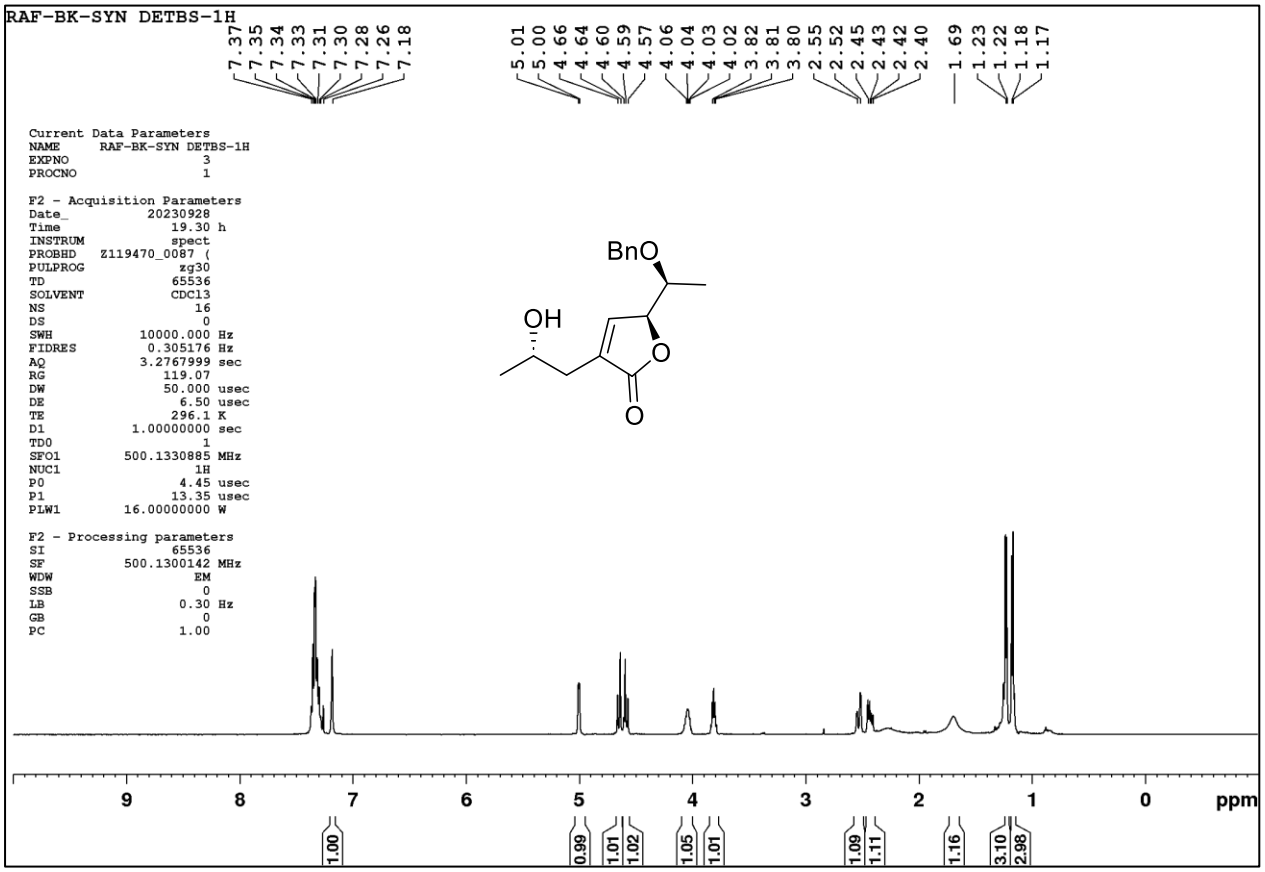
HSBC spectra of compound **1a**

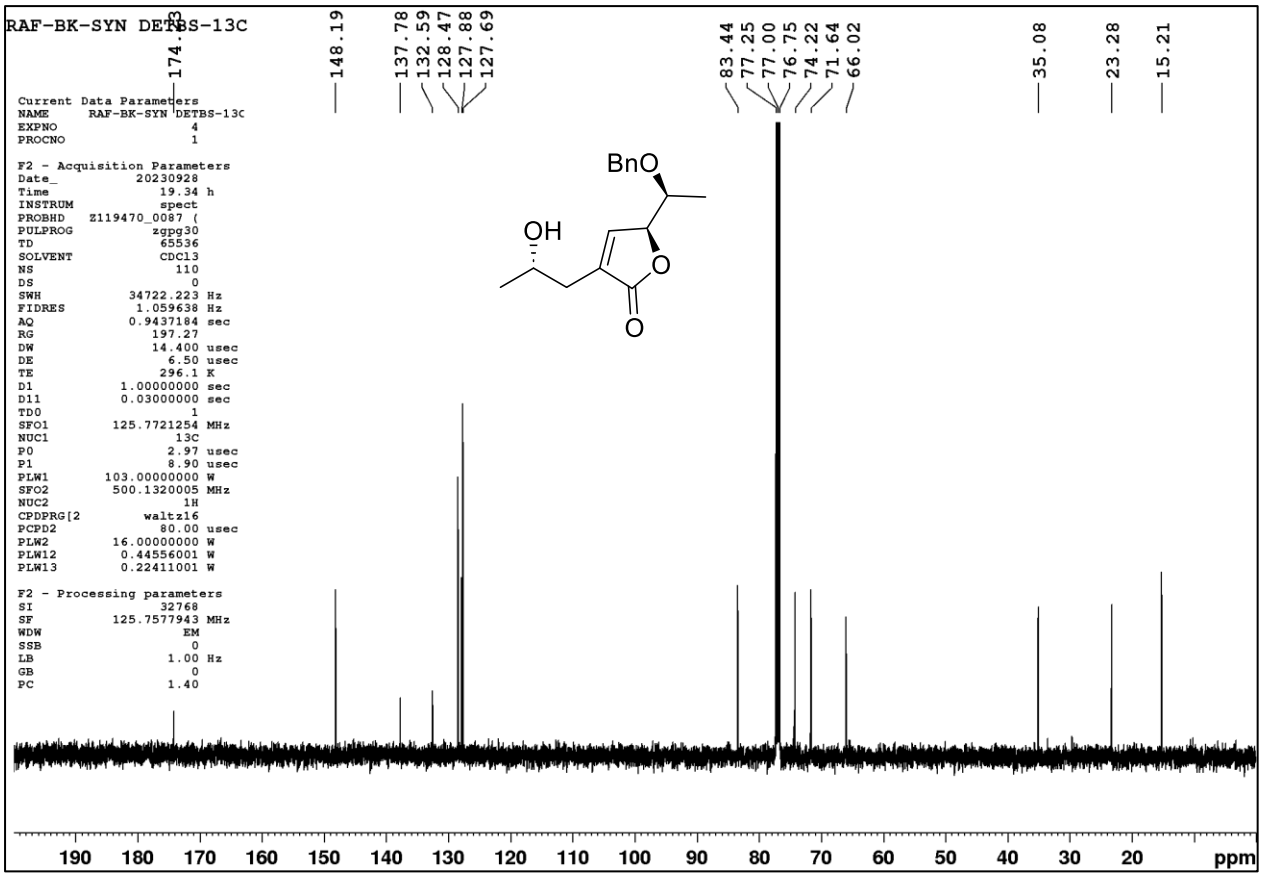


1a: HRMS (Q–TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{15}O_4$ 187.0965; Found 187.0962.

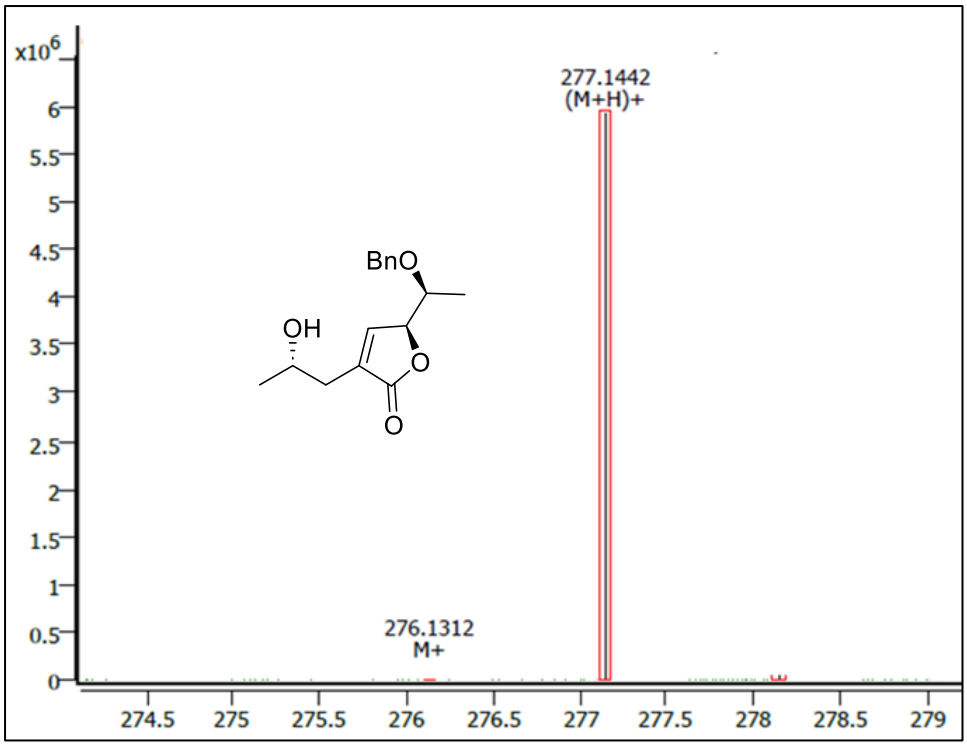


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **14a**

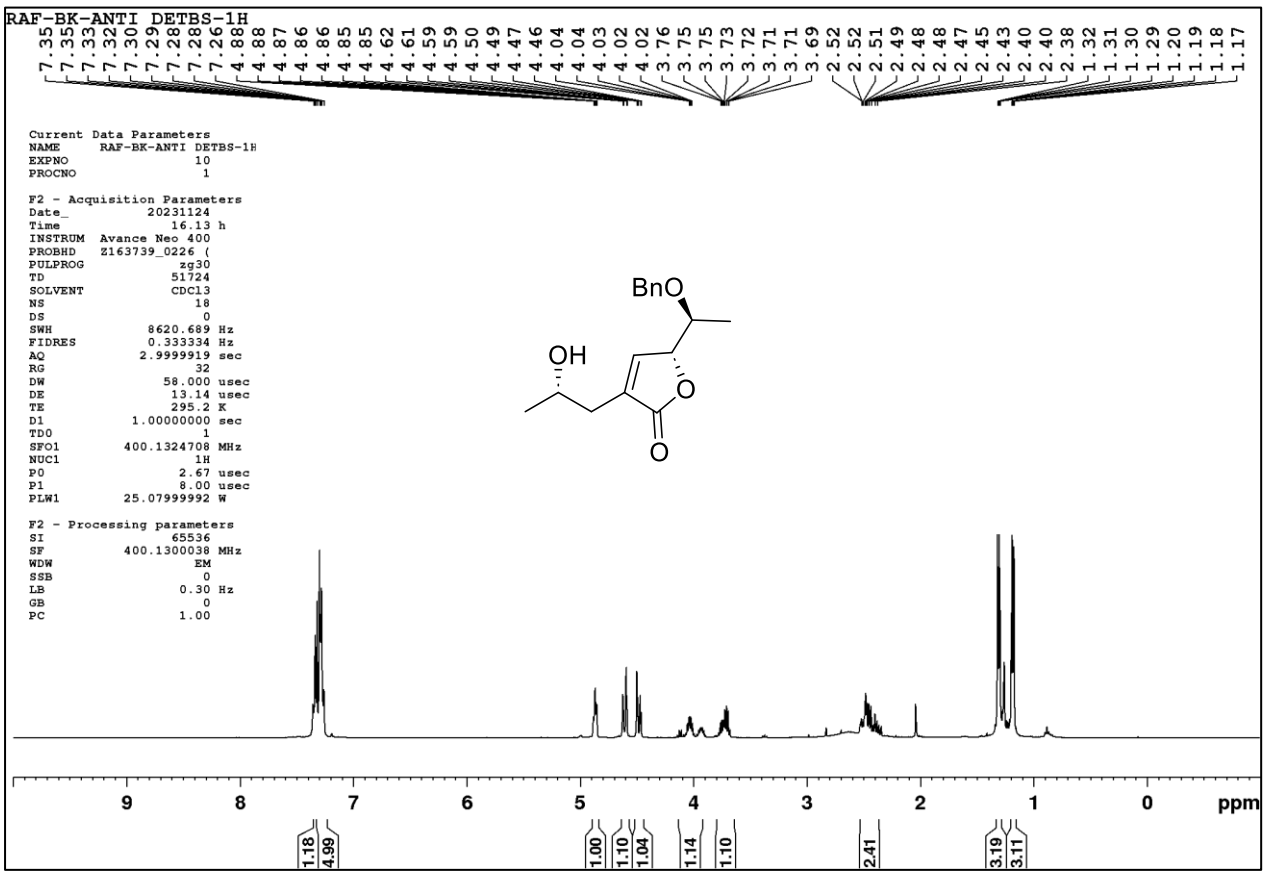


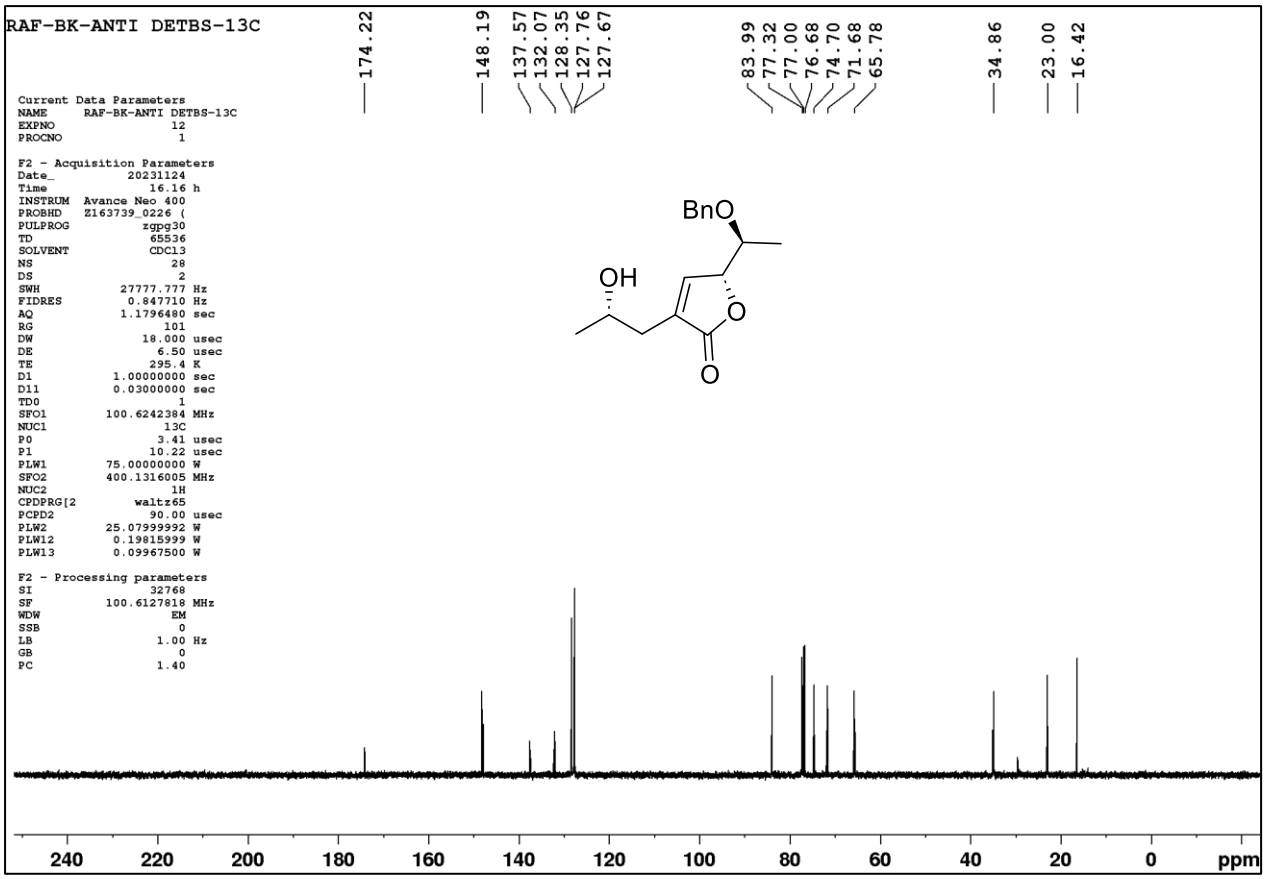


14a: HRMS (Q–TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{21}O_4$ 277.1435; Found 277.1442.

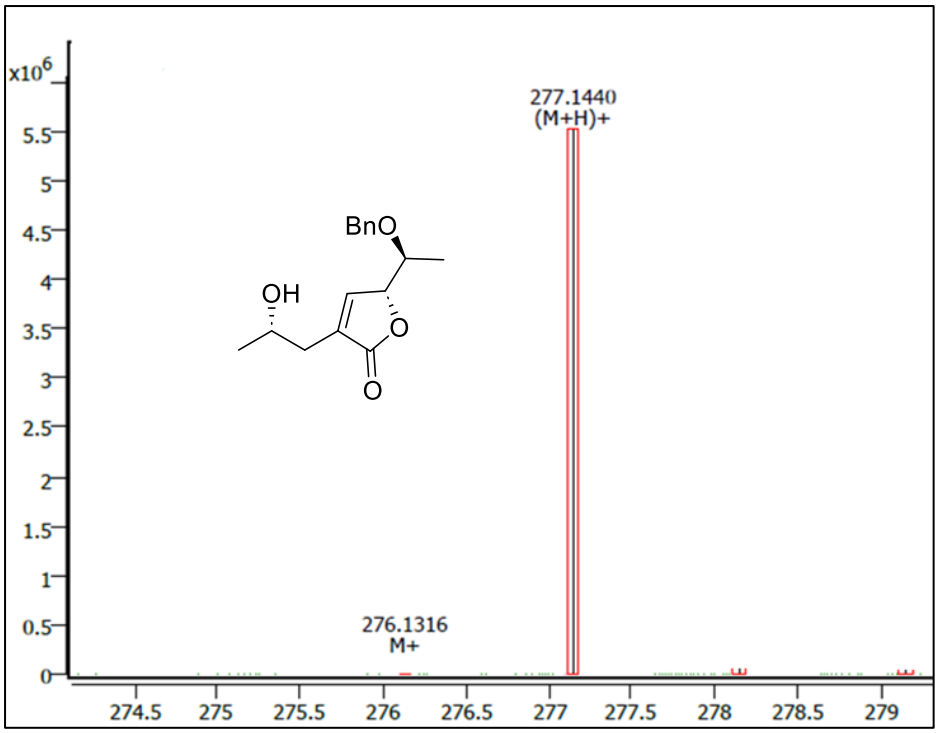


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **14b**

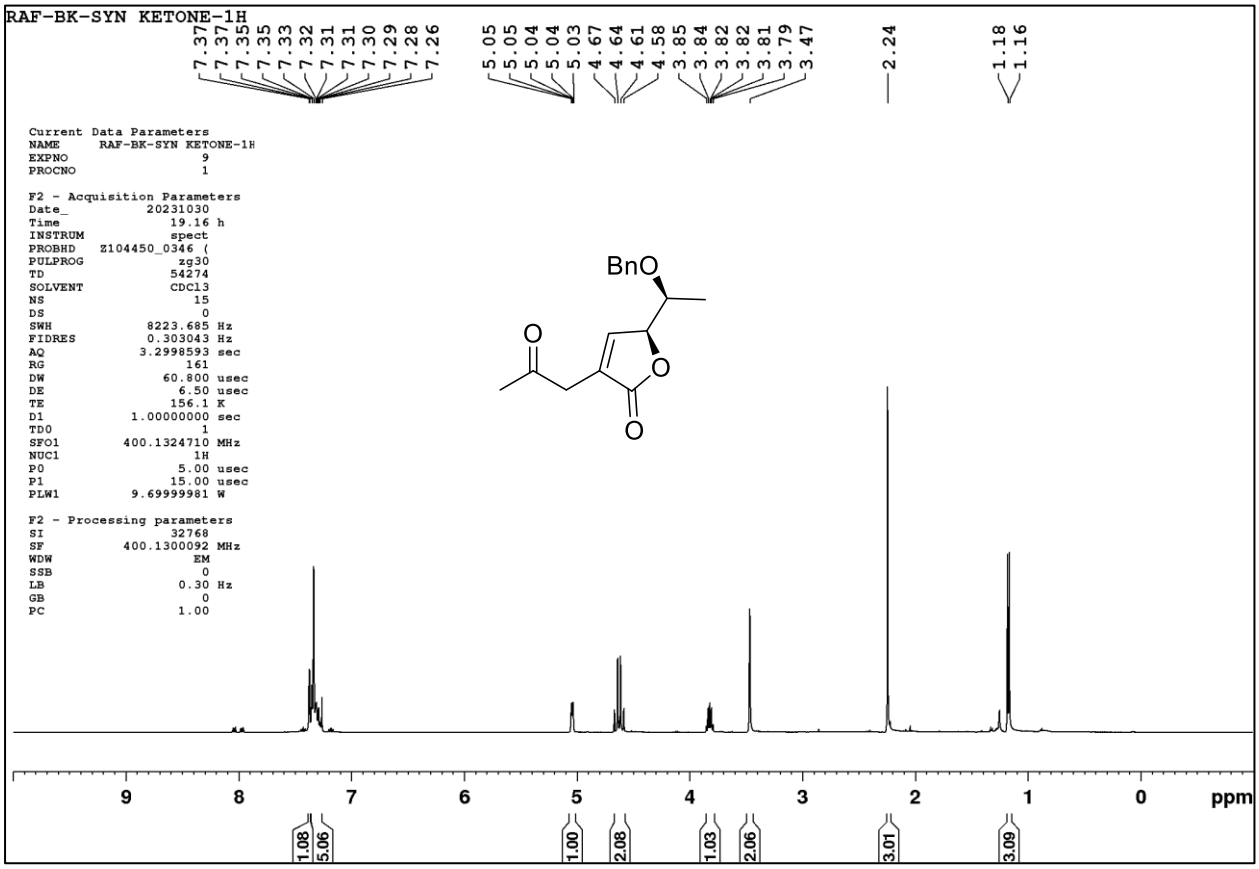


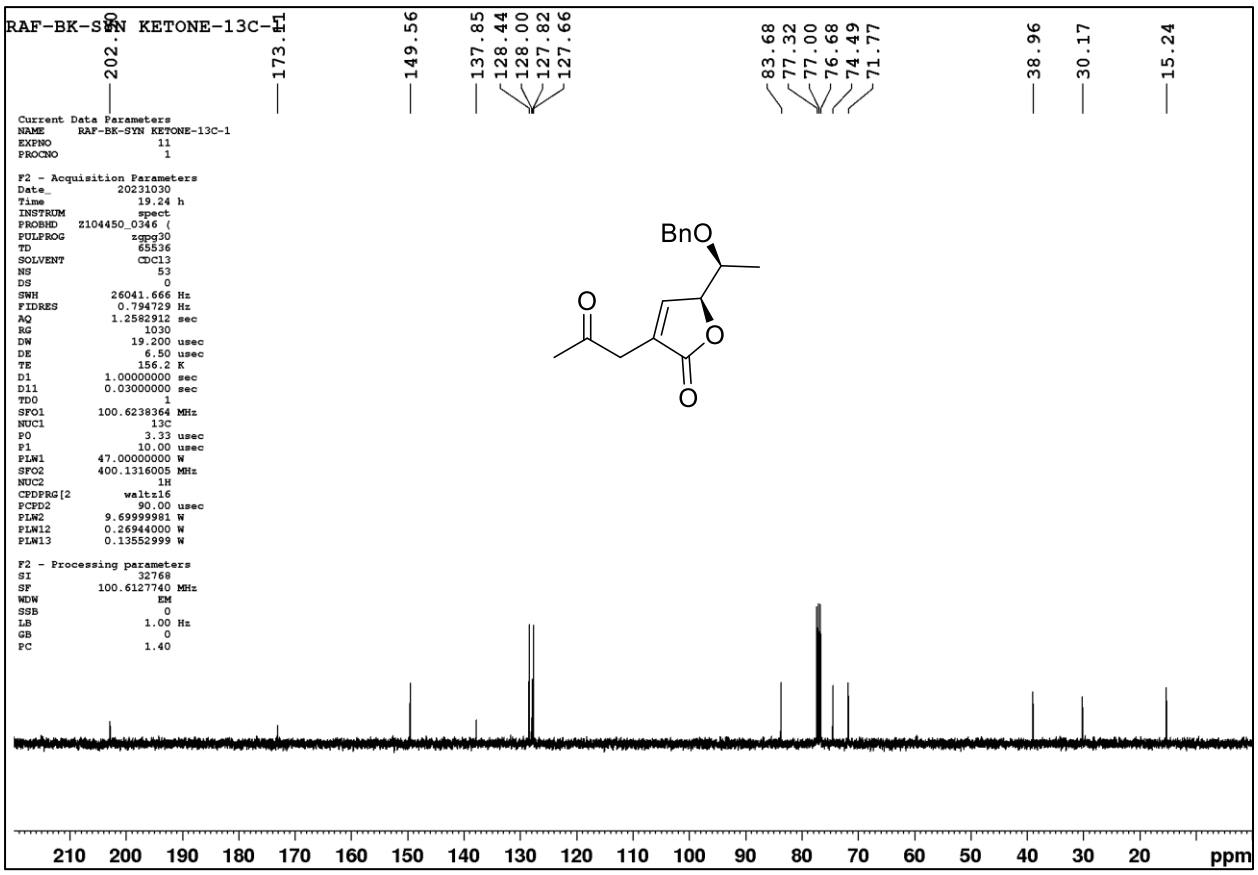


14b: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{21}O_4$ 277.1435; Found 277.1440.

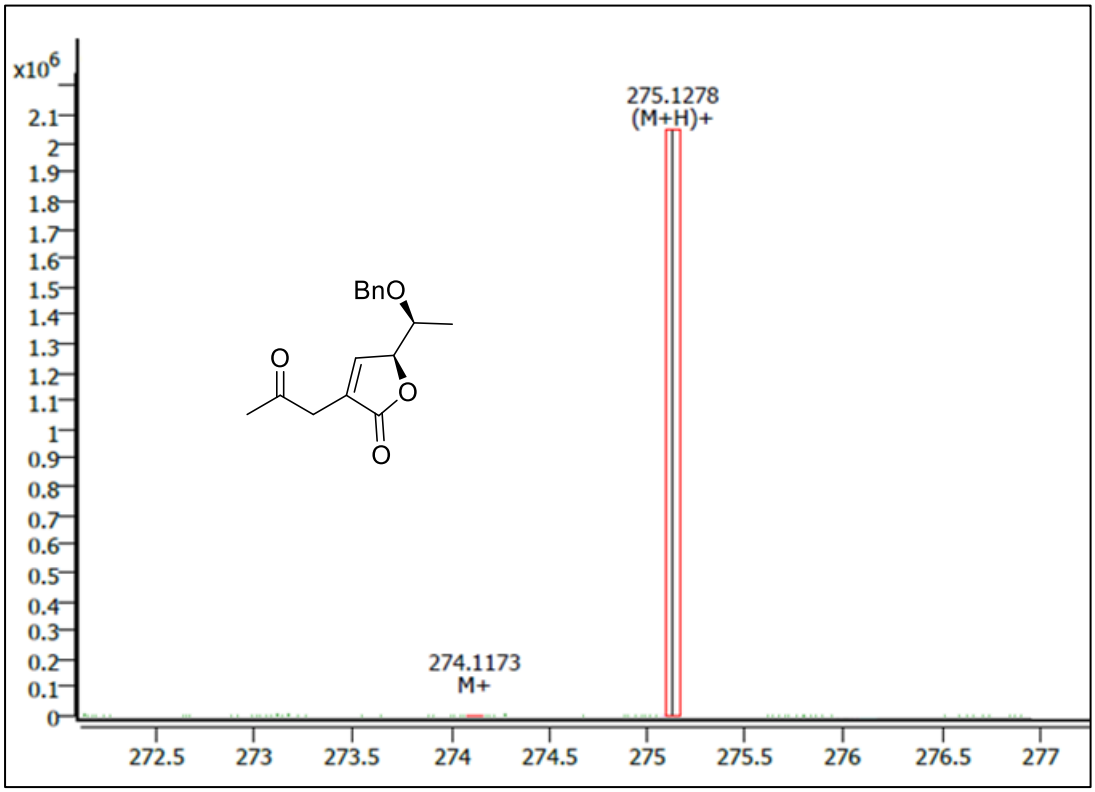


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **15a**

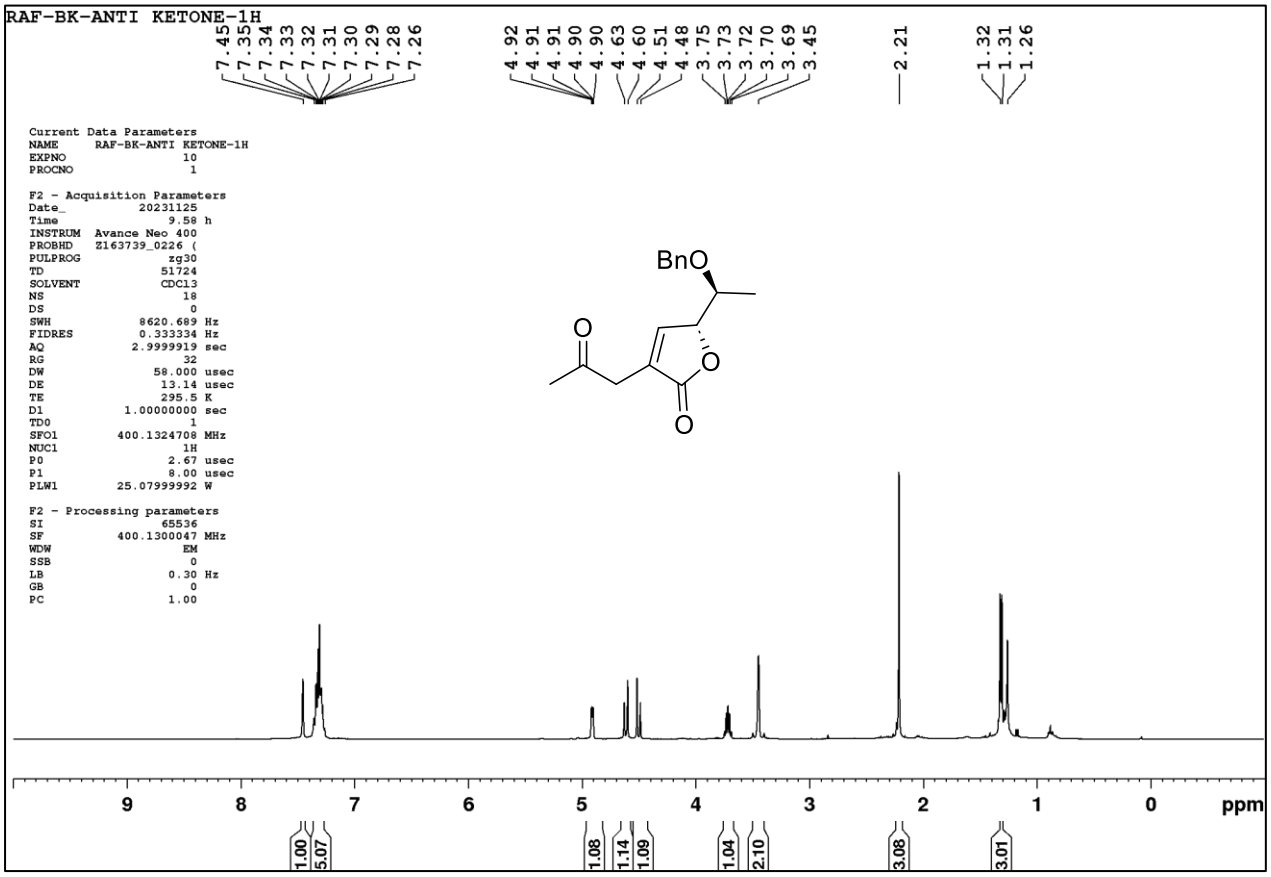


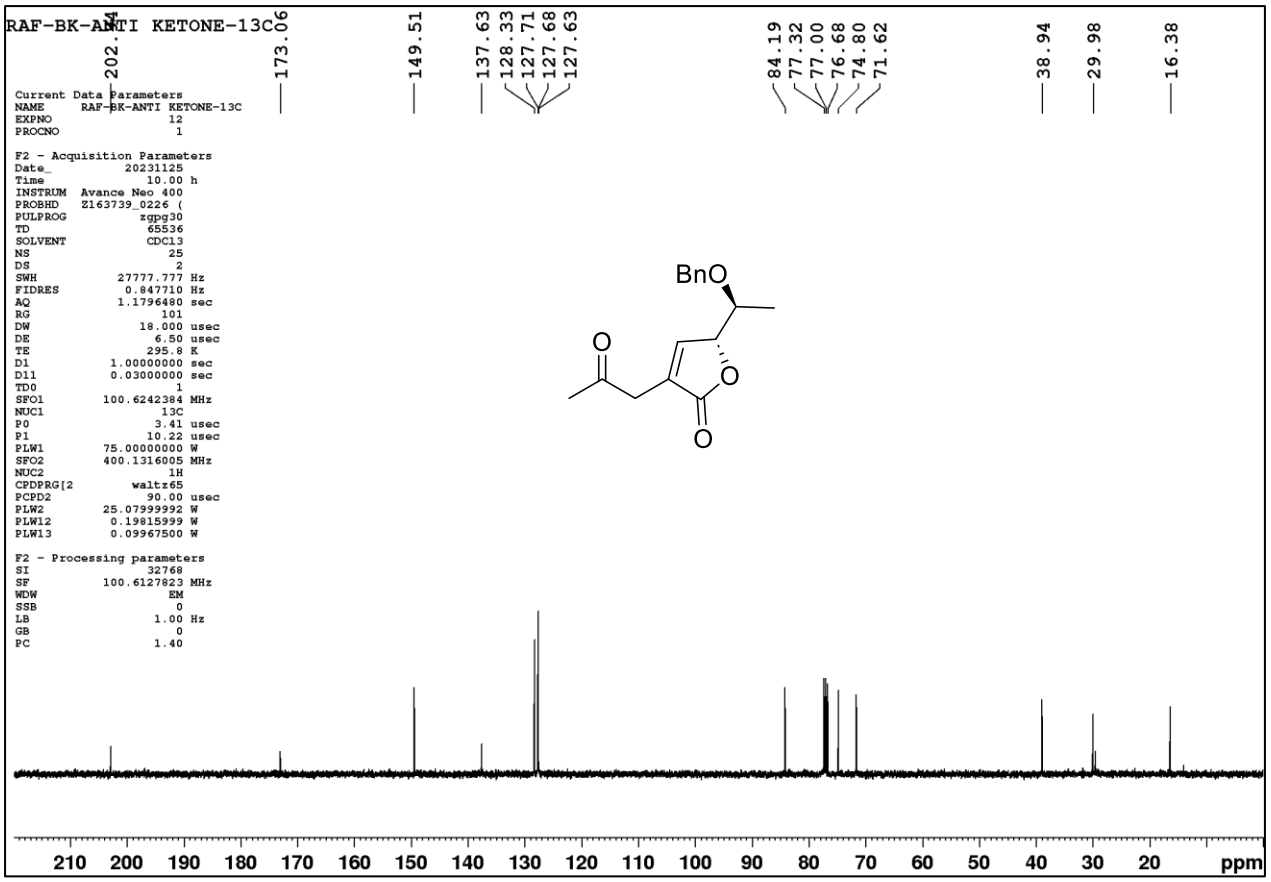


15a: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{19}O_4$ 275.1278; Found 275.1278.

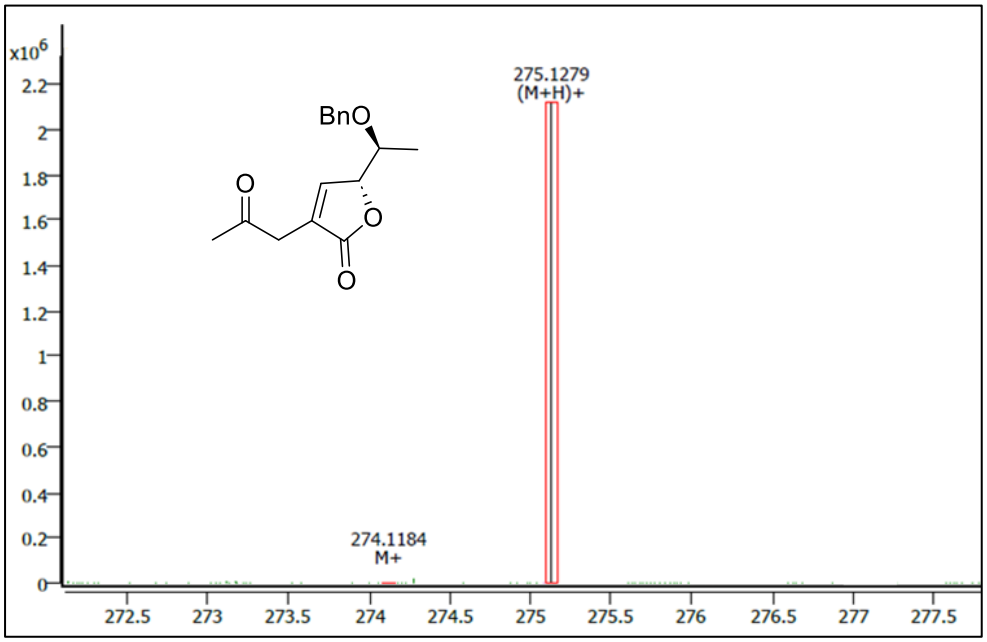


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **15b**

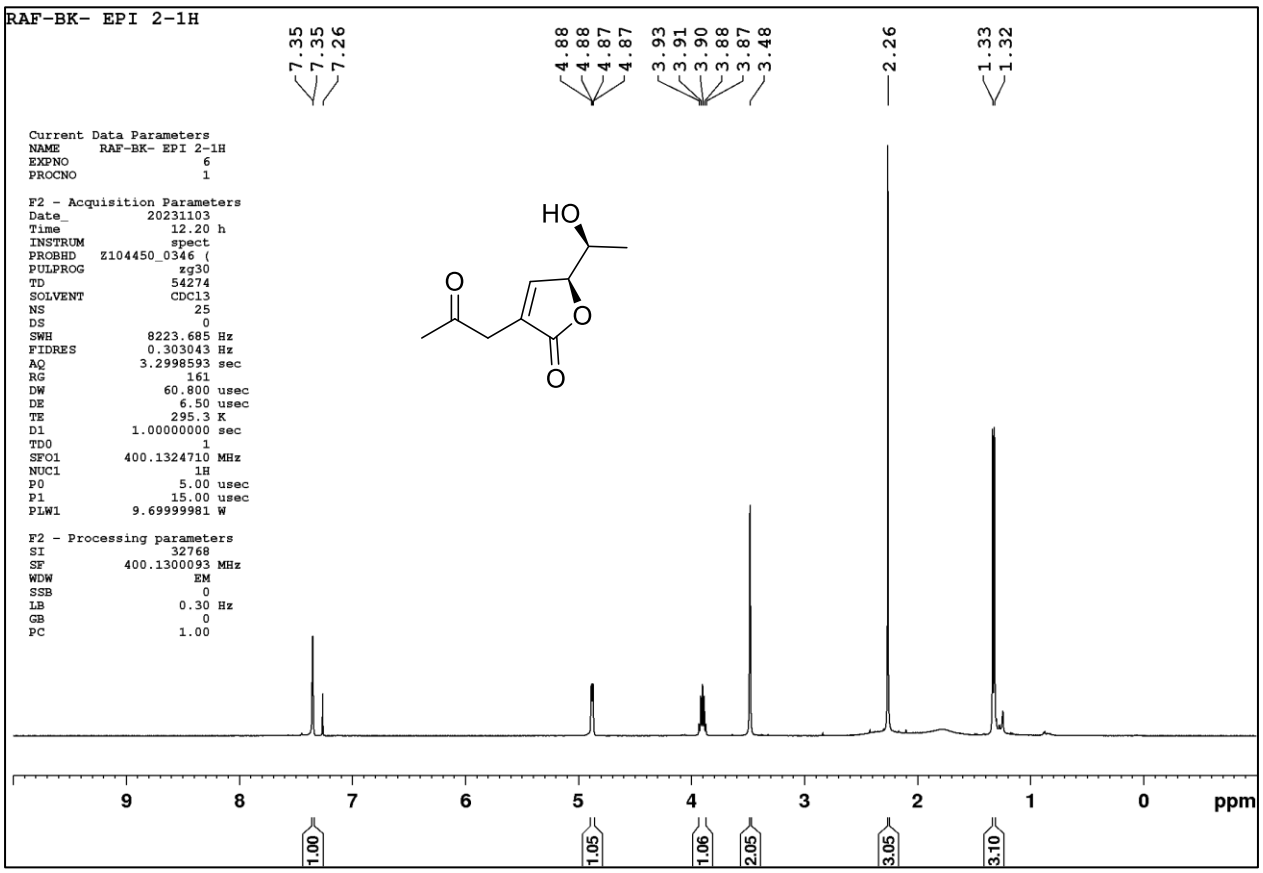


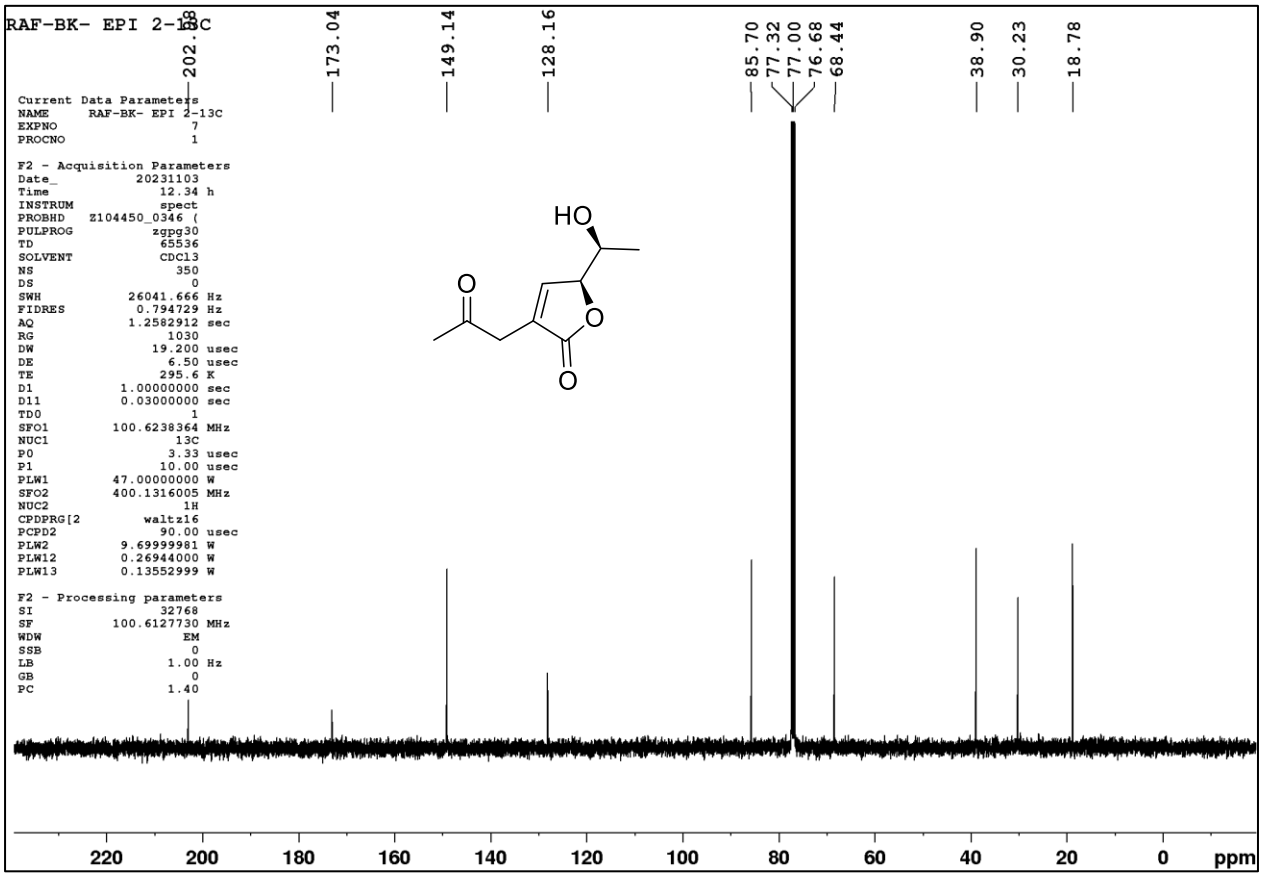


15b: HRMS (Q–TOF) *m/z:* $[M + H]^+$ Calcd for $C_{16}H_{19}O_4$ 275.1278; Found 275.1279.

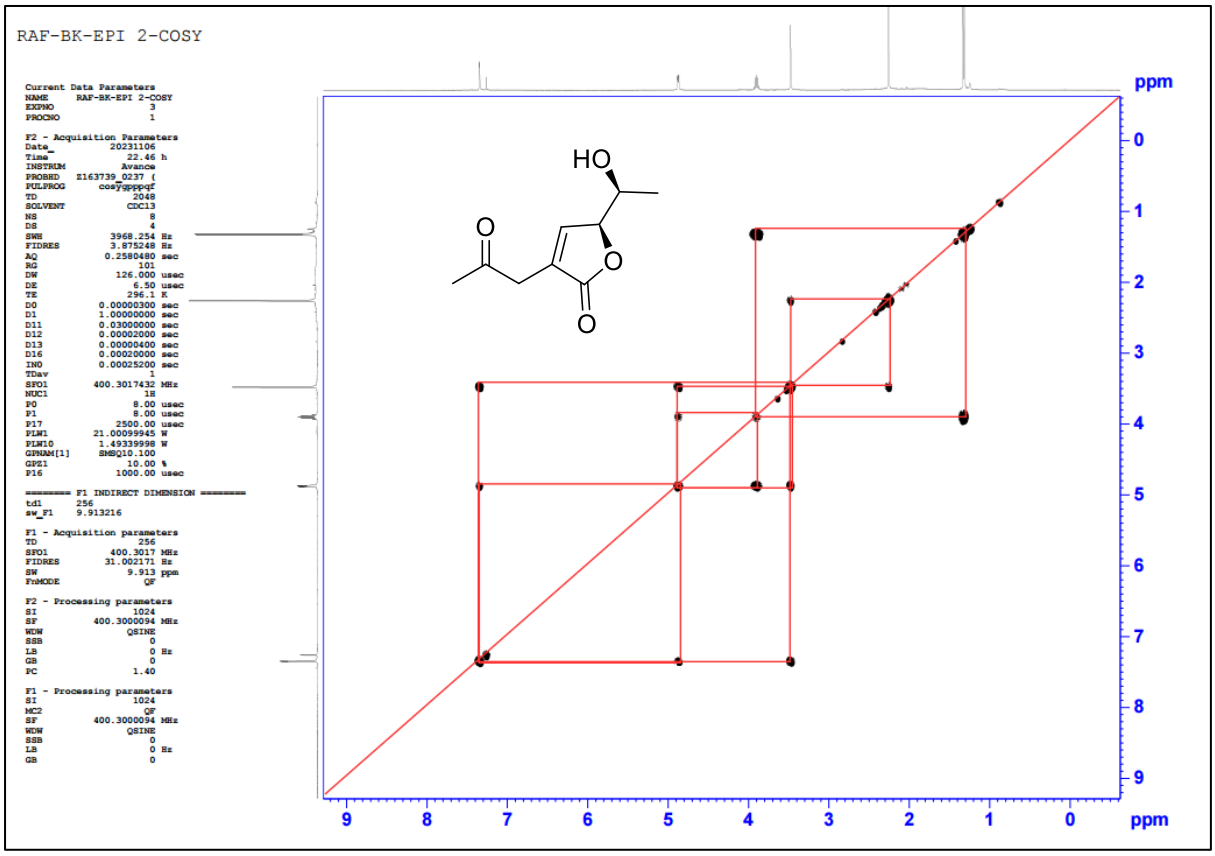


^{1}H NMR (400 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound **1b'**

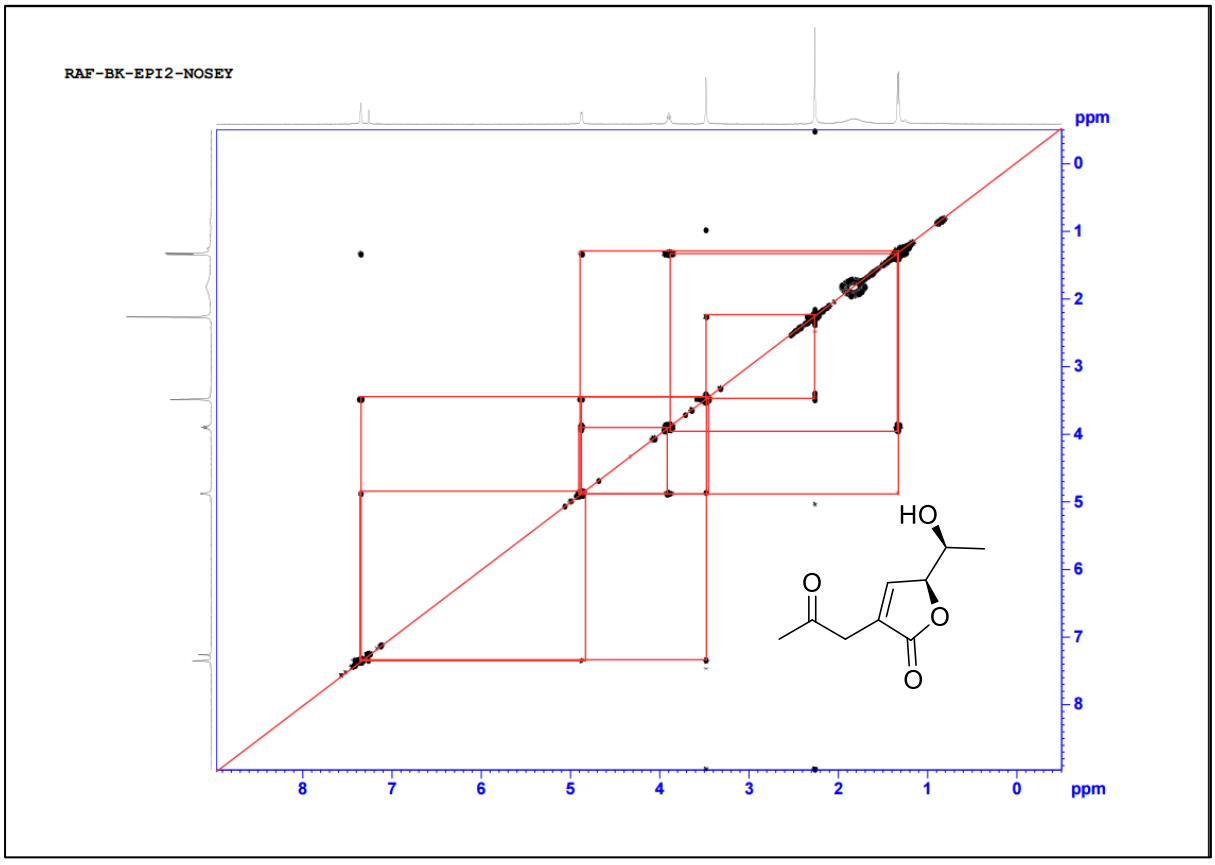




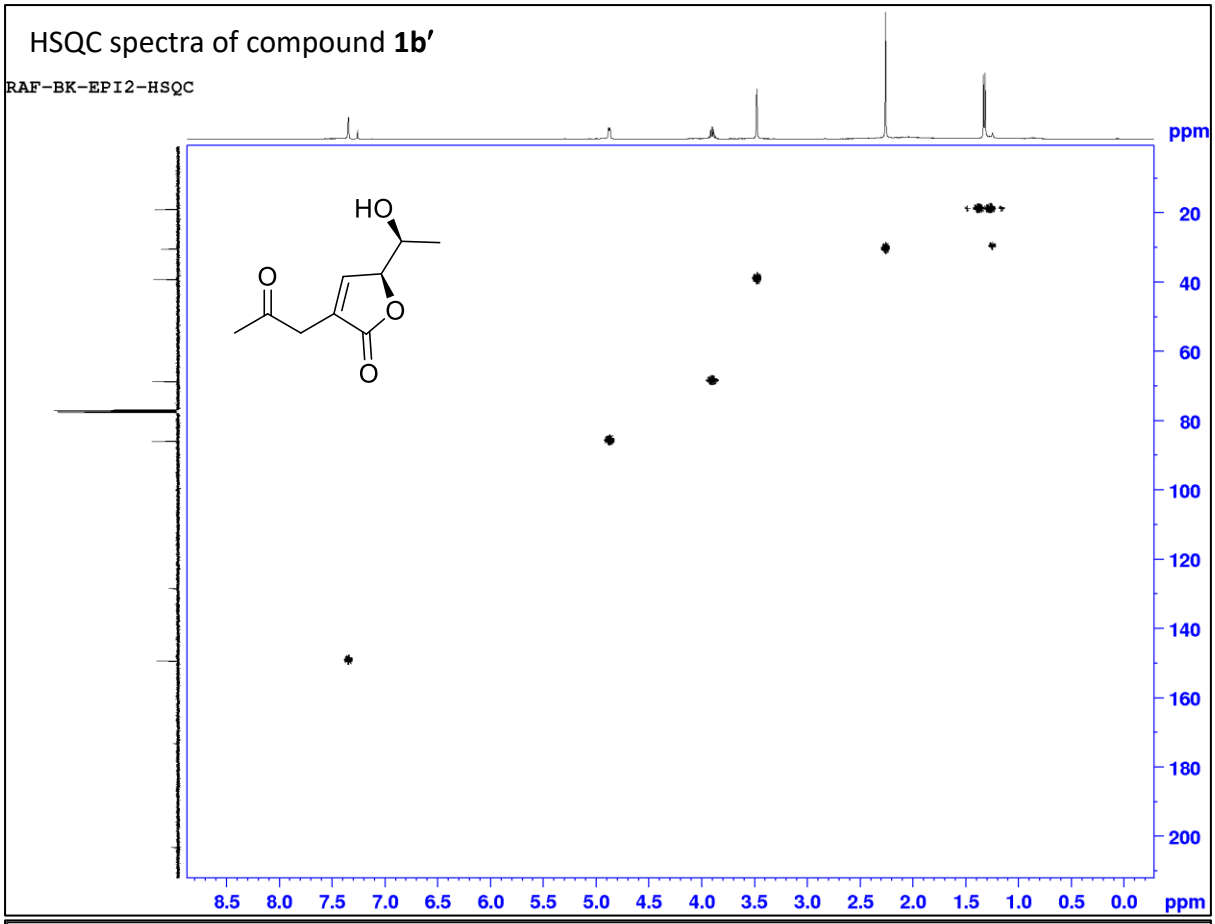
H-H COSY spectra of compound **1b′**



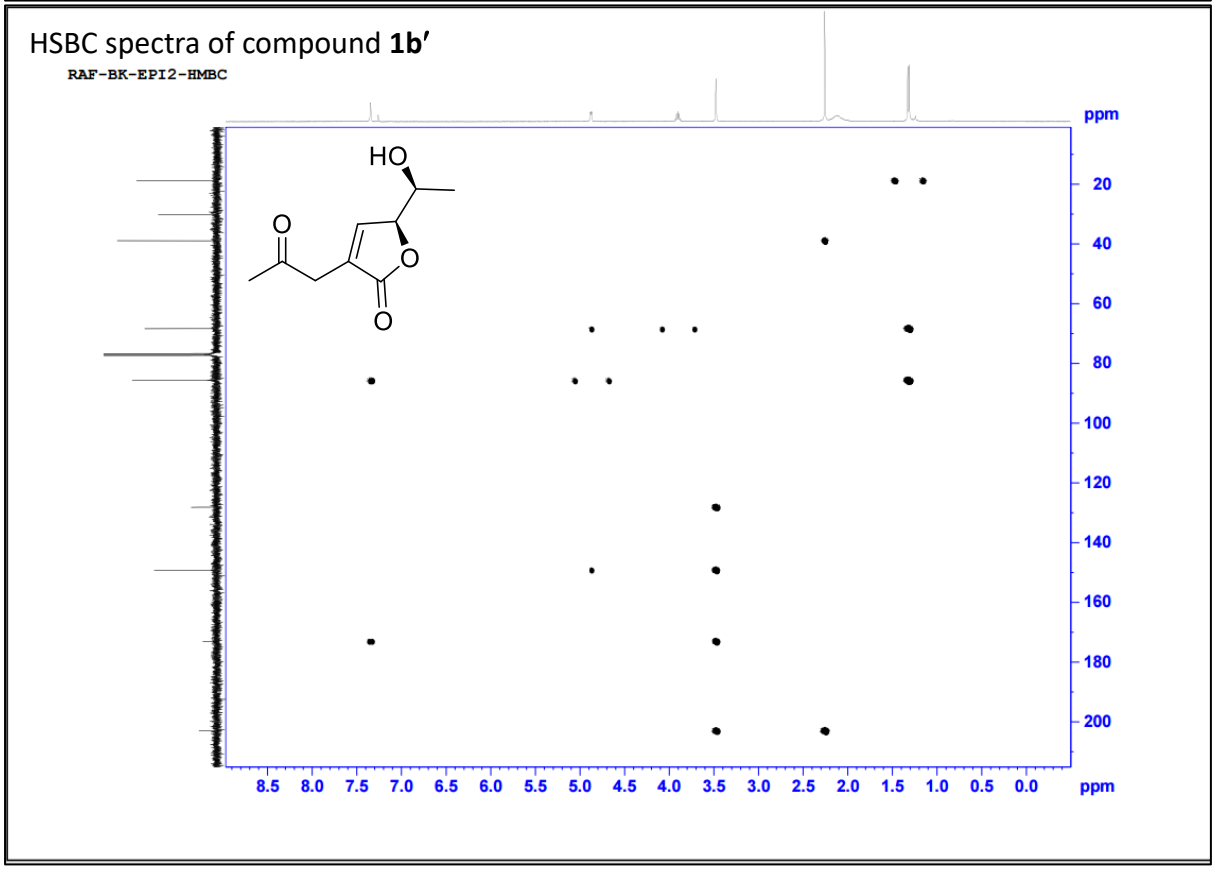
NOESY spectra of compound **1b′**



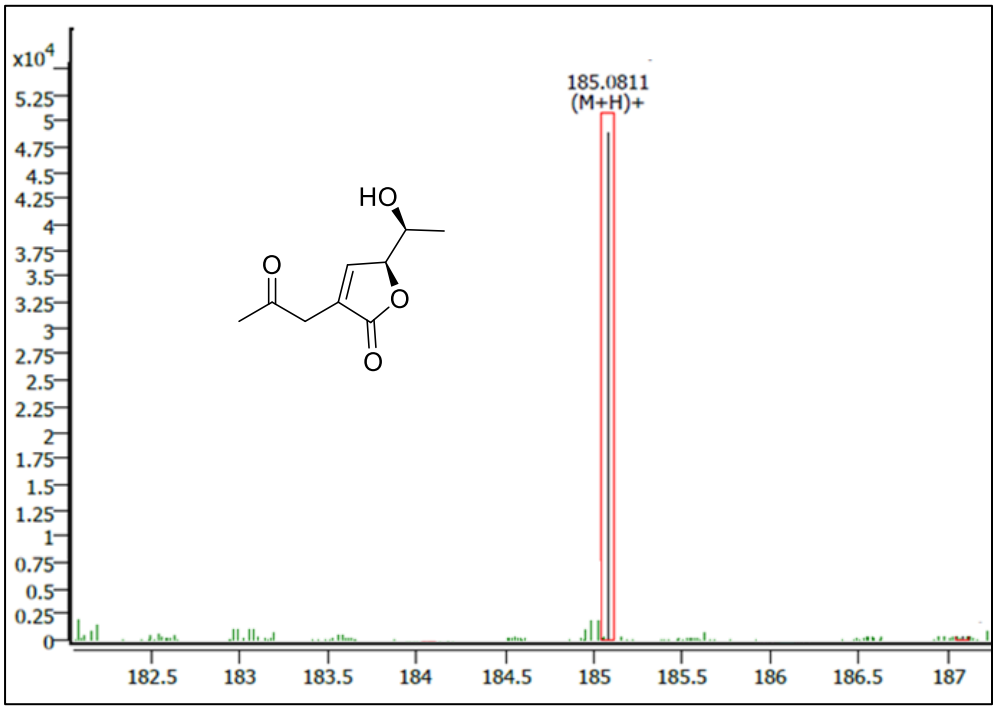
HSQC spectra of compound **1b′**



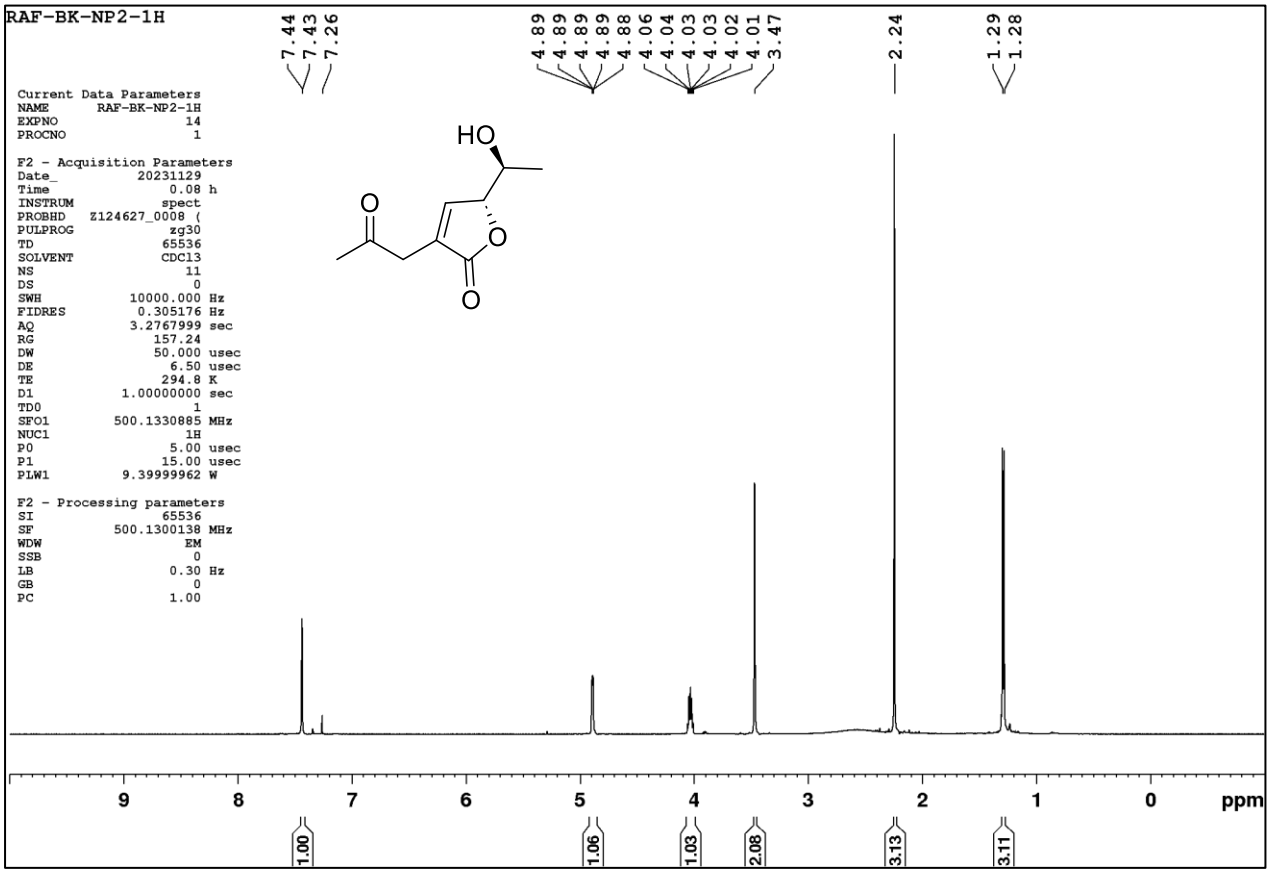
HSBC spectra of compound **1b′**

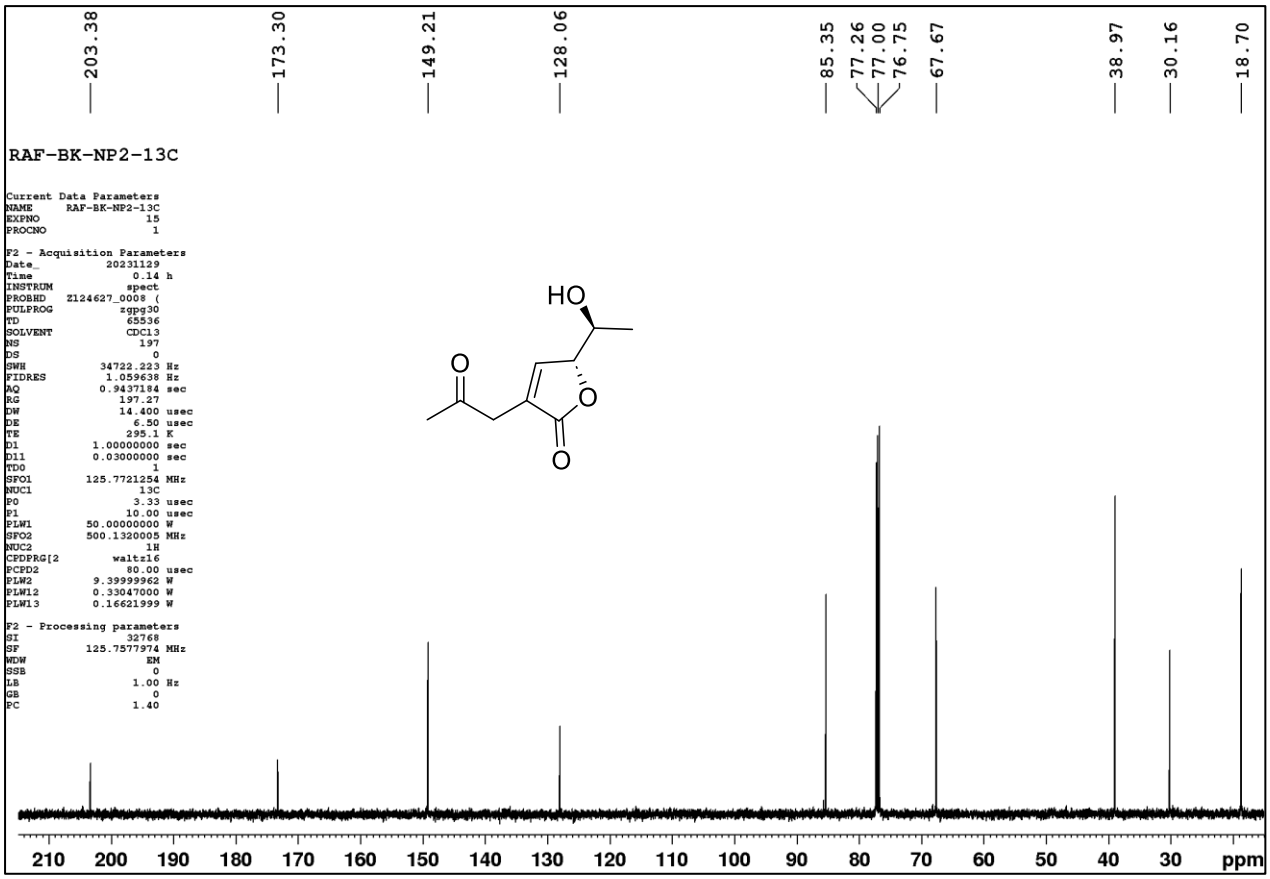


1b′: HRMS (Q–TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{13}O_4$ 185.0809; Found 185.0811.

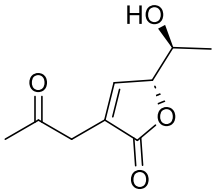


^{1}H NMR (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) of compound **1b**



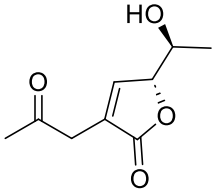


^{1}H NMR Comparison data of compound **1b**: Isolated and our work



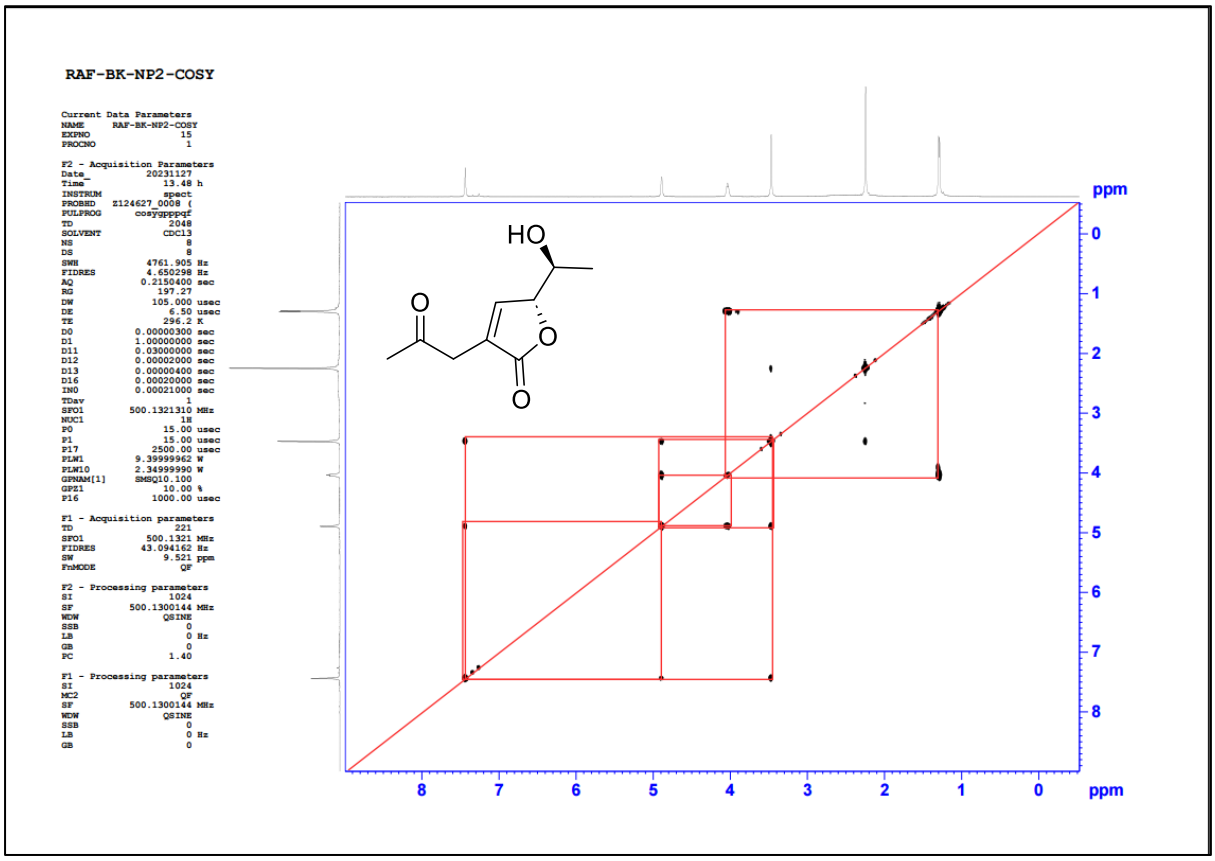
^{1}H NMR (400 MHz, $CDCl_3$) Isolated by Cui *Mar. Drugs,* 2014, 12, 3116	**^{1}H NMR (500 MHz, $CDCl_3$) Our work**
7.43 (q, *J* = 1.4 Hz, 1H)	7.43 (d, *J* = 1.1 Hz, 1H)
4.88 (dq, *J* = 4.7, 1.4 Hz, 1H)	4.88 (dq, *J* = 3.0, 1.4 Hz, 1H)
4.02 (dq, *J* = 6.5, 4.7 Hz, 1H)	4.06–3.99 (m, 1H)
3.46 (t, *J* = 1.4 Hz, 2H)	3.47 (s, 2H)
2.24 (s, 3H)	2.24 (s, 3H)
1.28 (d, *J* = 6.6 Hz, 3H)	1.28 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR Comparison data of compound **1b**: Isolated and our work

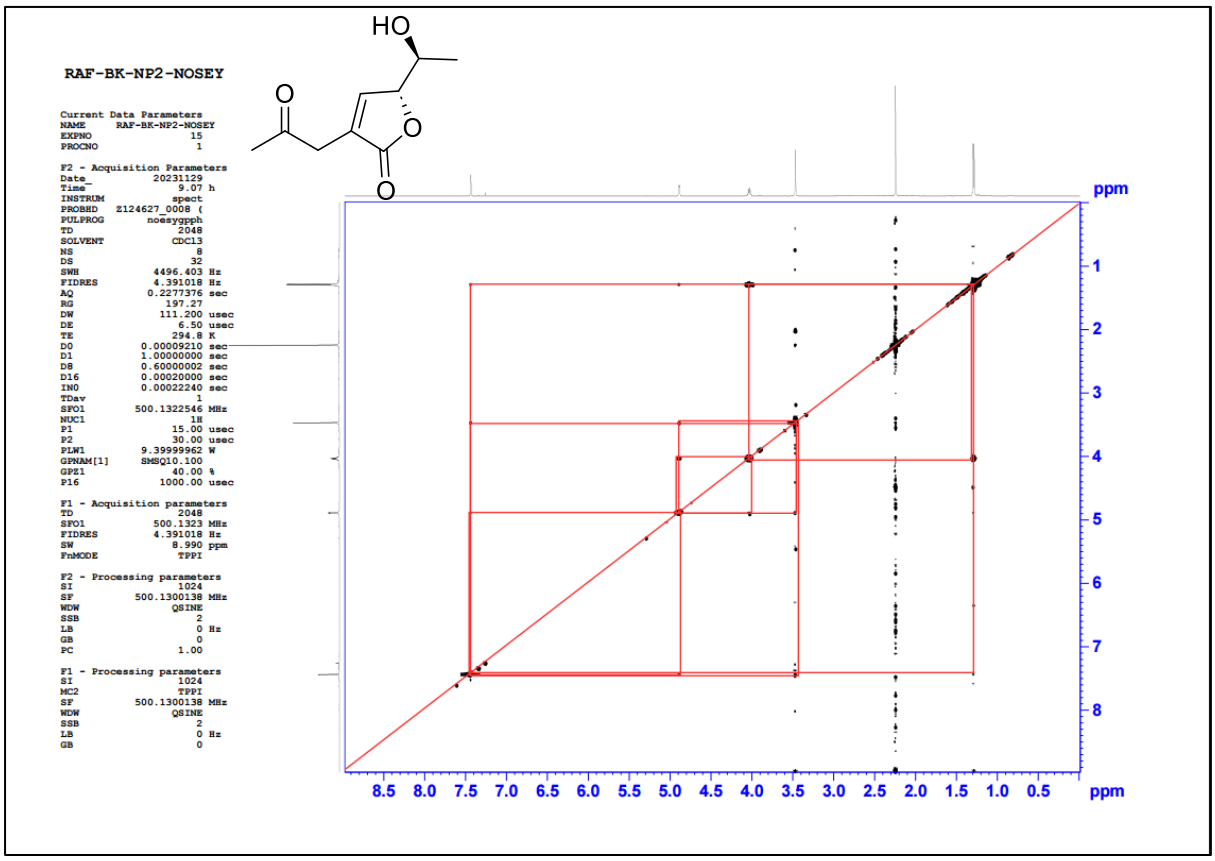


^{13}C NMR (100 MHz, $CDCl_3$) Isolated by Cui *Mar. Drugs,* 2014, 12, 3116	**^{13}C NMR (125 MHz, $CDCl_3$) Our work**
203.6	203.4
173.5	173.3
149.4	149.2
128.2	128.1
85.5	85.4
67.8	67.7
39.1	39.0
30.3	30.2
18.9	18.7

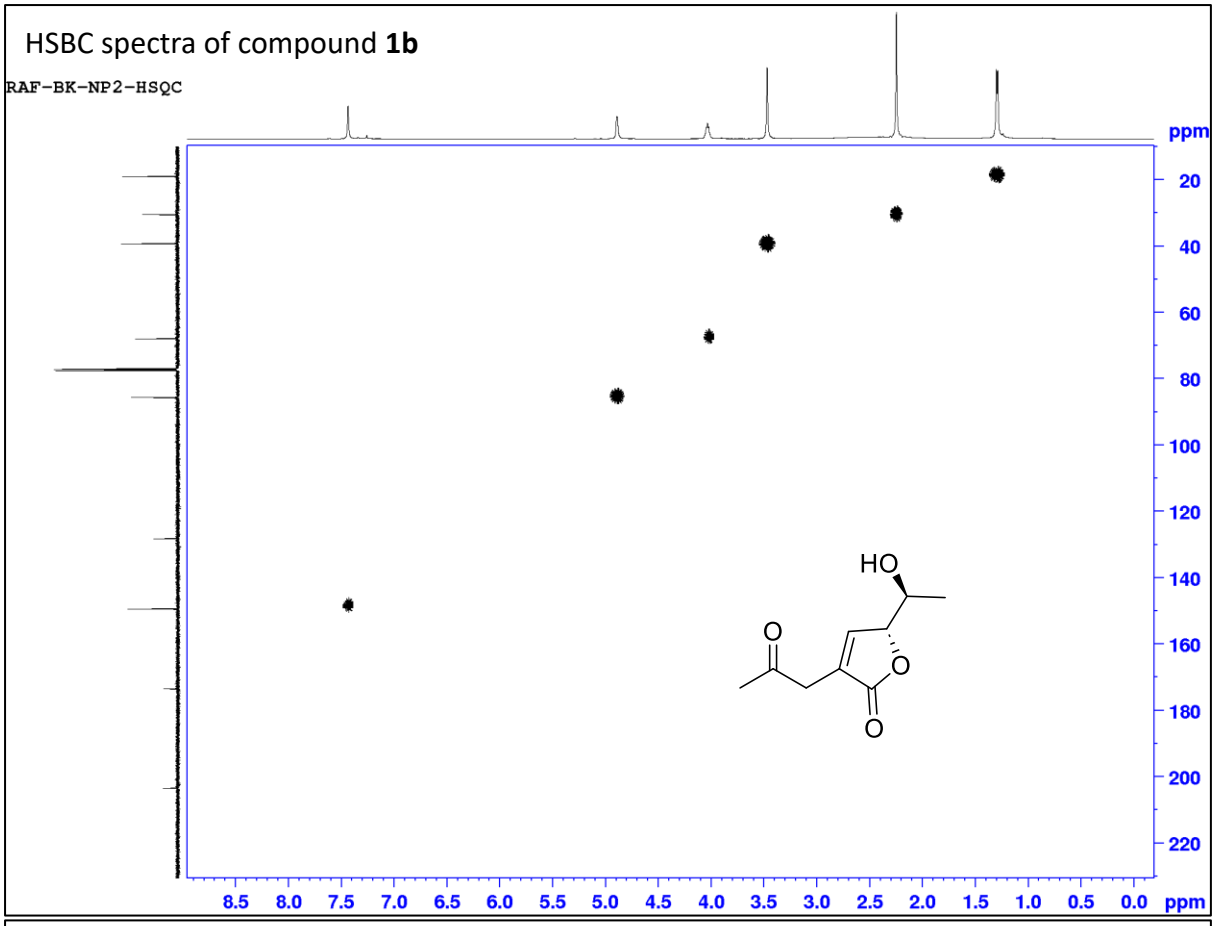
H-H COSY spectra of compound **1b**



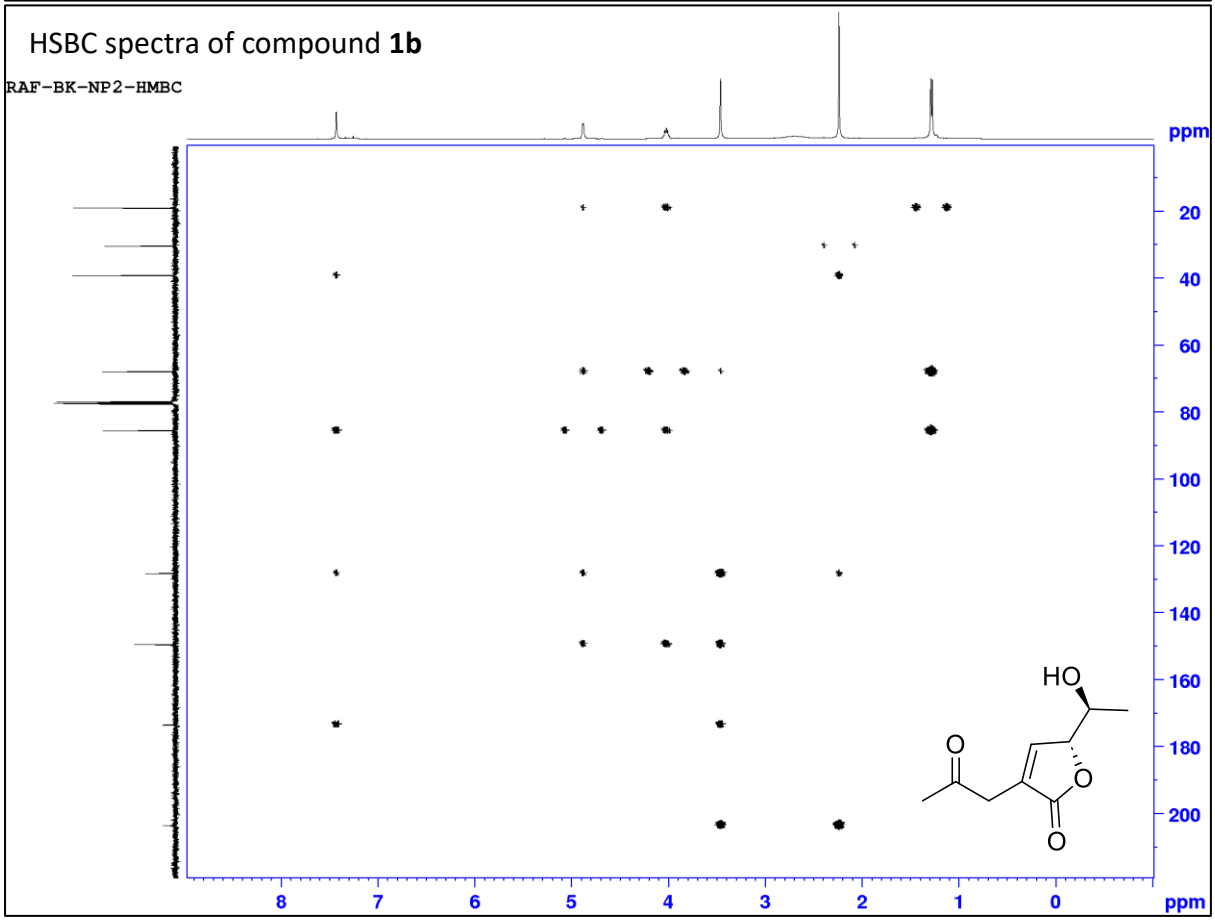
NOESY spectra of compound **1b**



HSBC spectra of compound **1b**



HSBC spectra of compound **1b**



1b: HRMS (Q–TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{13}O_4$ 185.0809; Found 185.0812.