Supplementary Material

Synthesis and structural elucidation of 2,3-dimethylnaphthazarin ester derivatives

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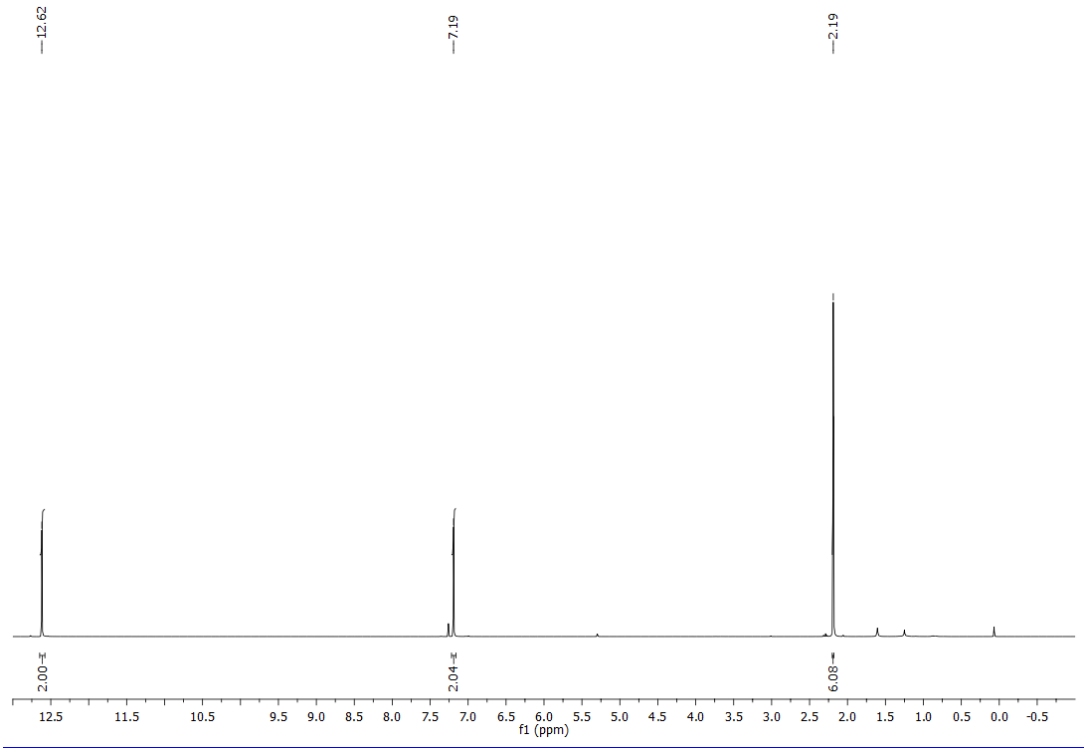
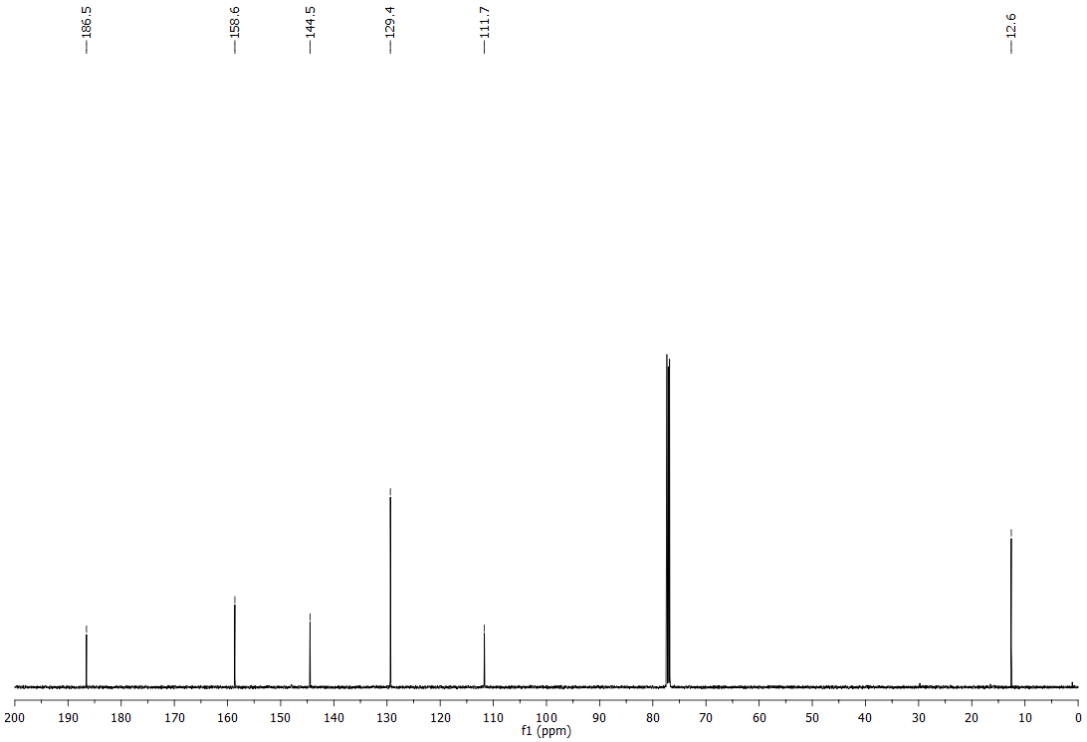
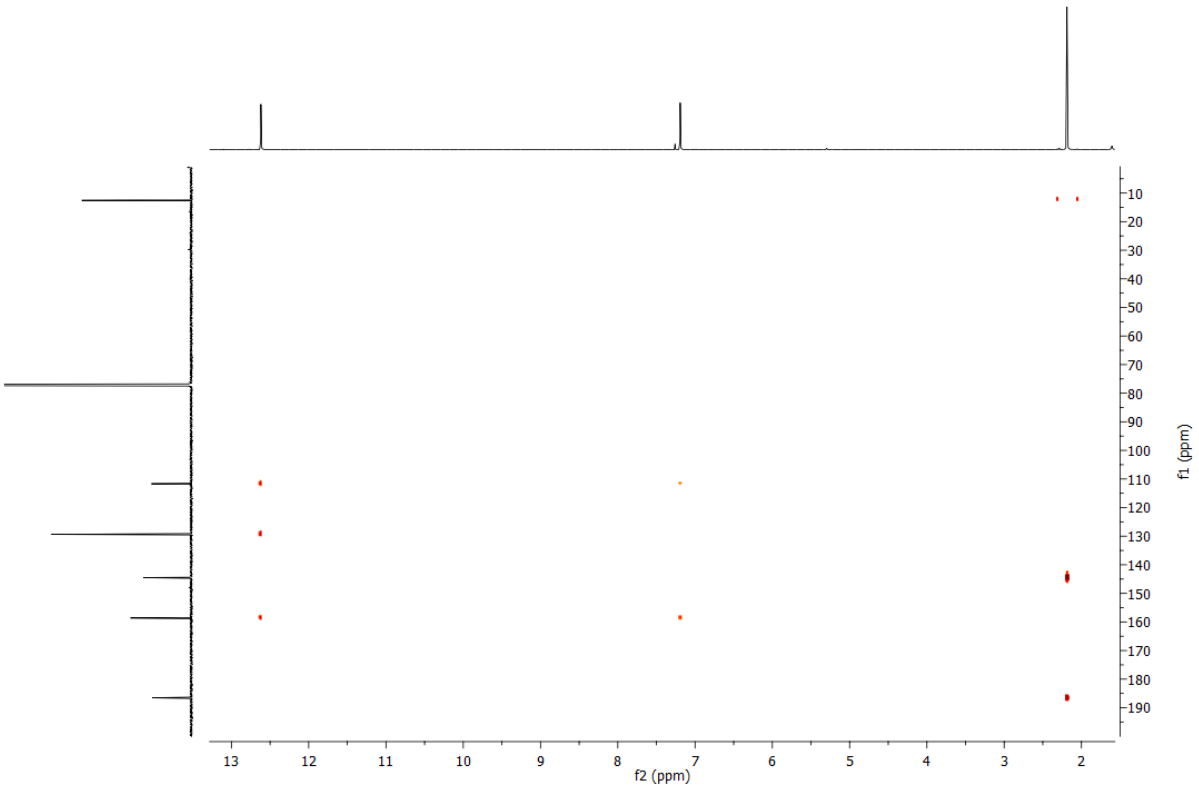


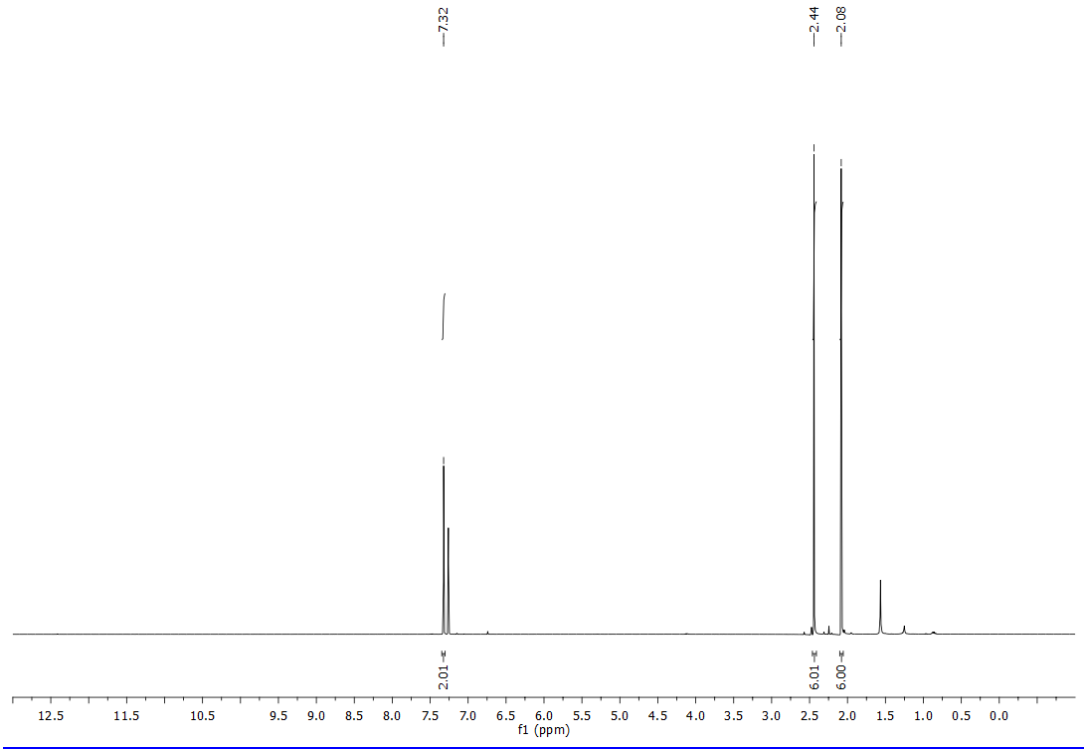
Spectrum 1. ^{1}H NMR spectrum of 2,3-Dimethylnapthazarine (DMN) **3** ($CDCl_3$, 500 MHz).



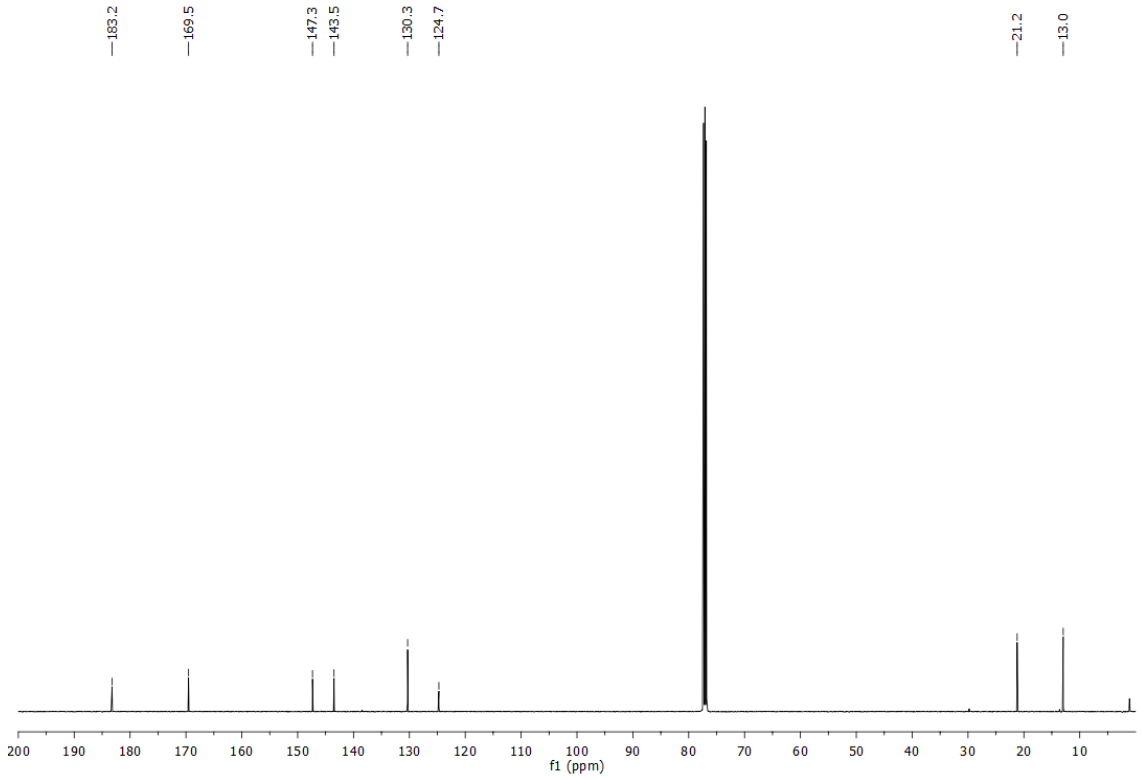
Spectrum 2. ^{13}C NMR spectrum of 2,3-Dimethylnapthazarine (DMN) **3** ($CDCl_3$, 125 MHz).



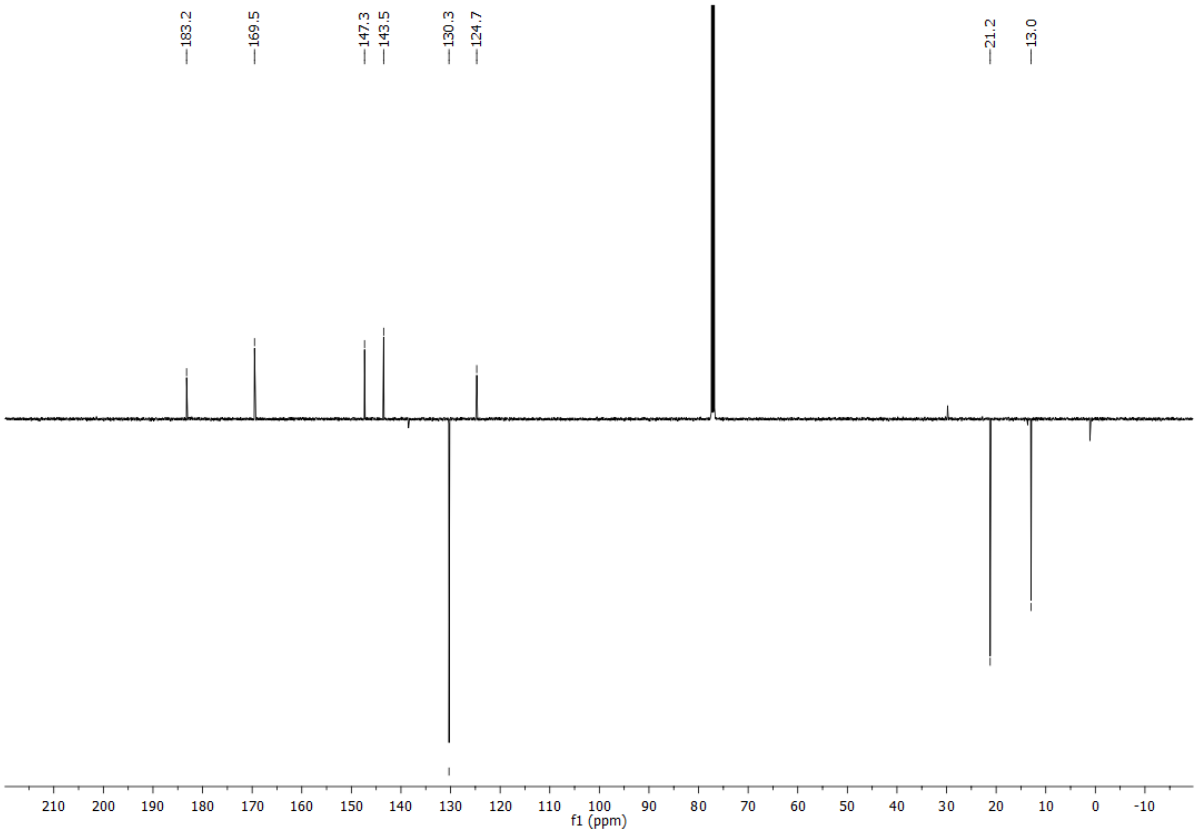
Spectrum 3. HMBC NMR spectrum of 2,3-Dimethylnapthazarine (DMN) **3** in $CDCl_3$.



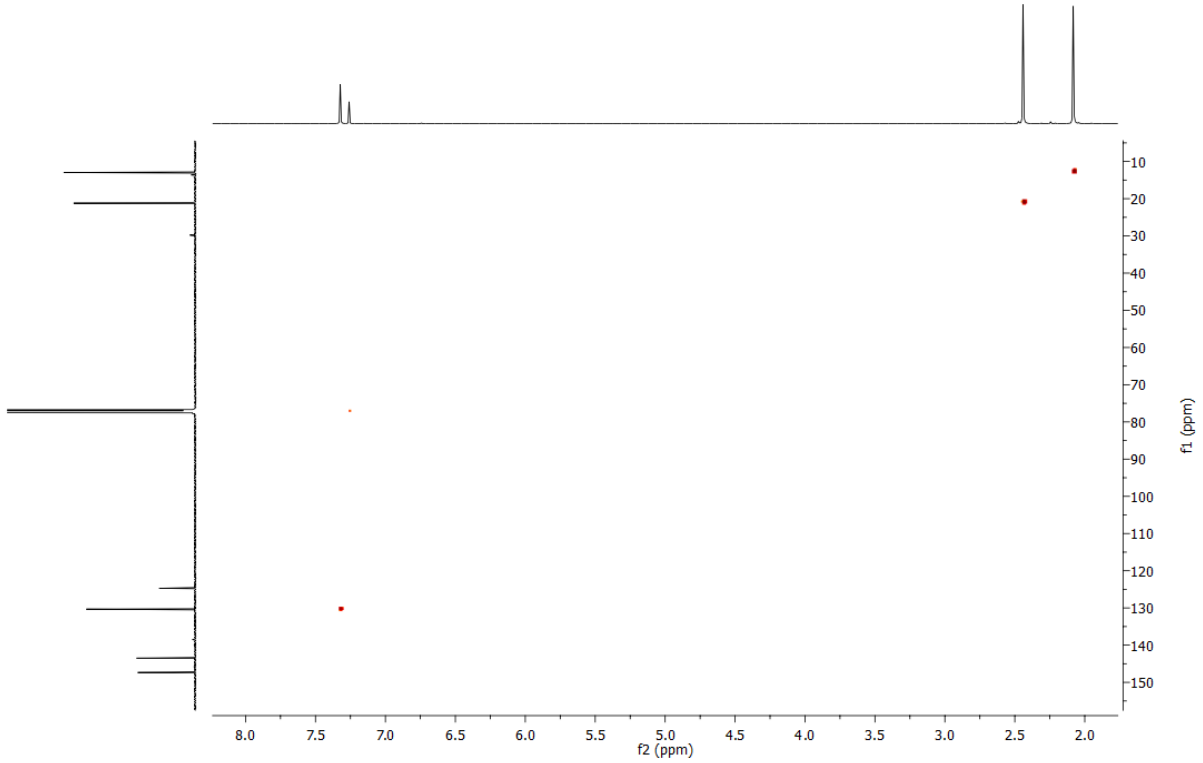
Spectrum 4. ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 500 MHz).



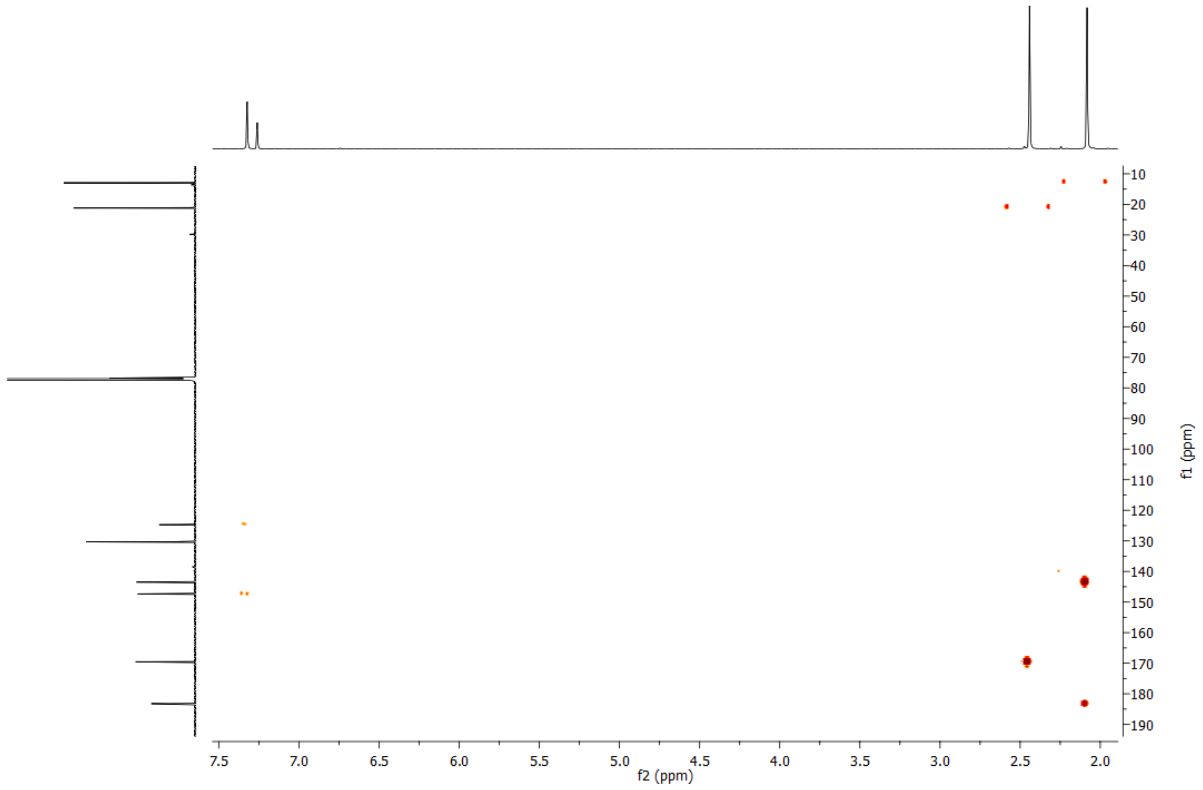
Spectrum 5. ^{13}C NMR spectrum of compound **5** ($CDCl_3$, 125 MHz).



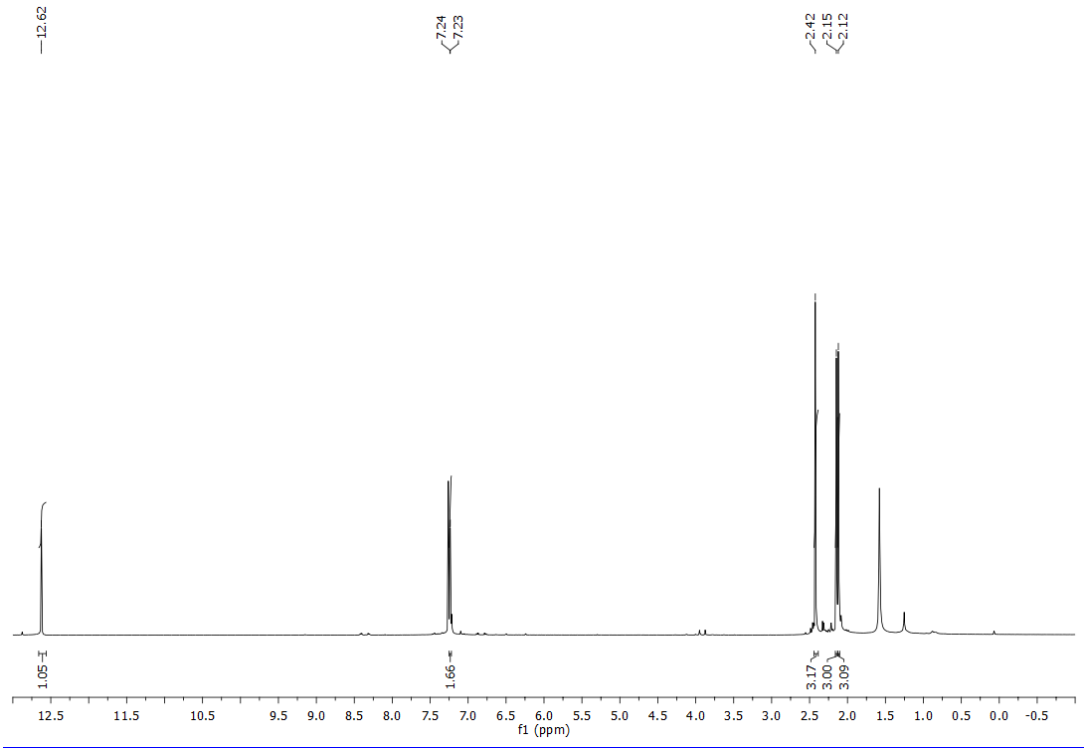
Spectrum 6. APT NMR spectrum of compound **5** ($CDCl_3$, 125 MHz).



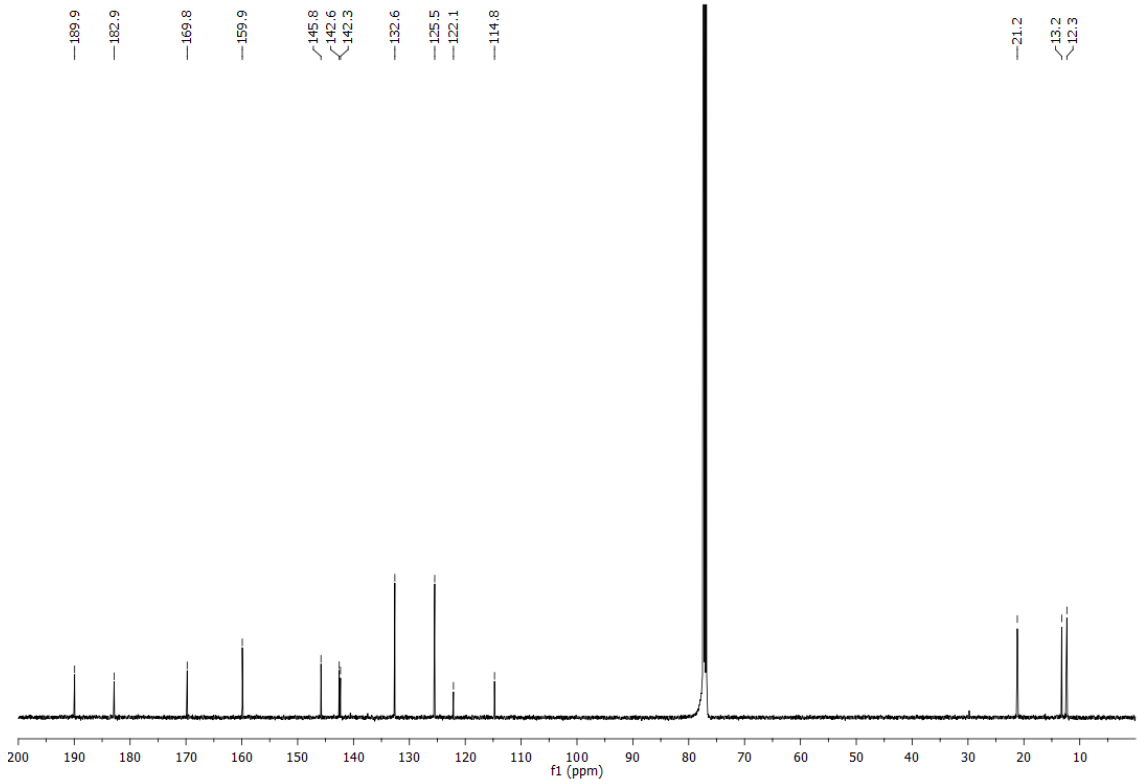
Spectrum 7. HSQC NMR spectrum of compound **5** in $CDCl_3$.



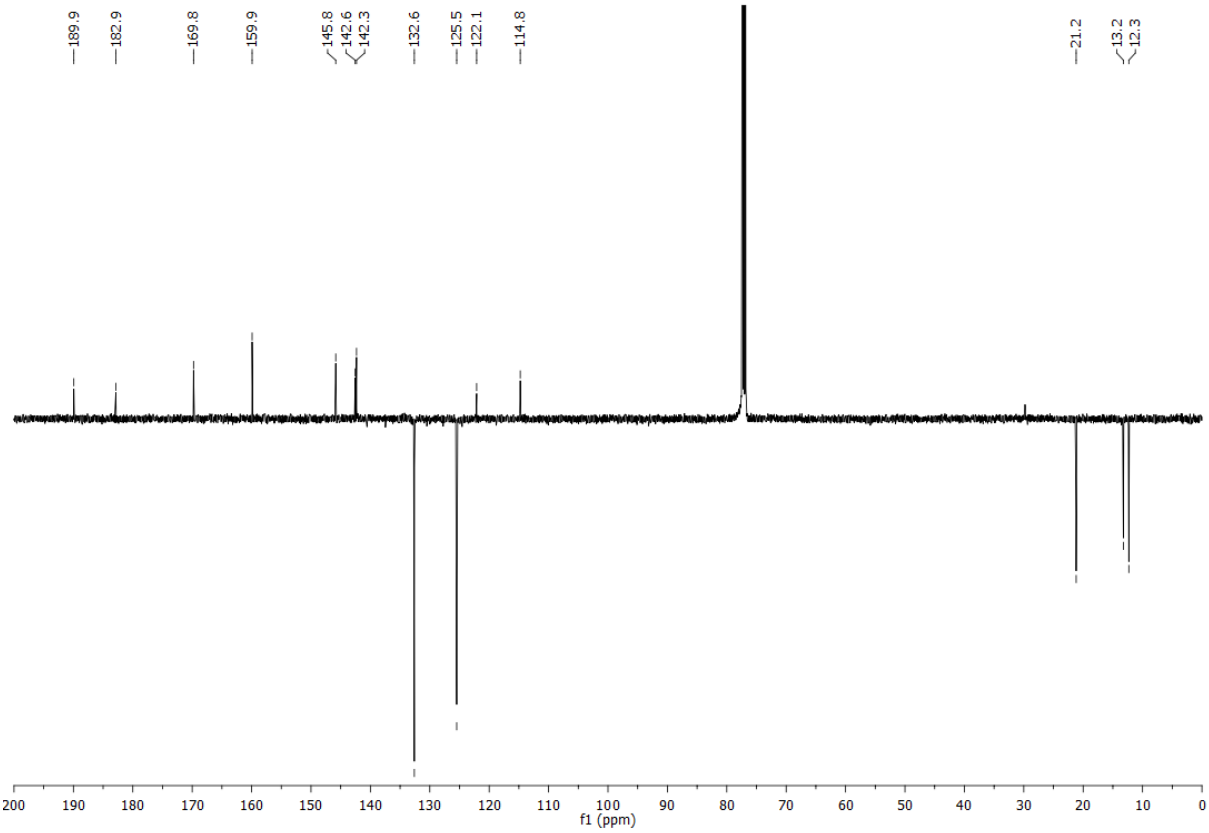
Spectrum 8. HMBC NMR spectrum of compound **5** in $CDCl_3$.



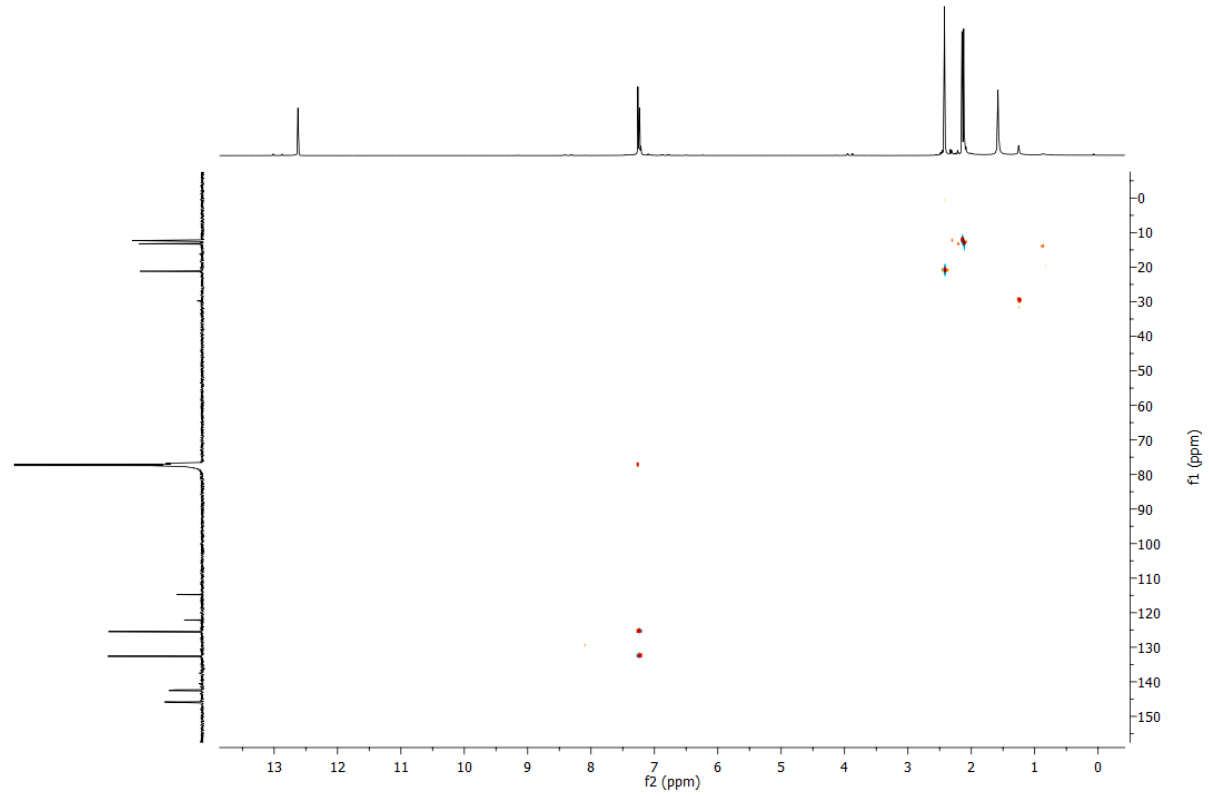
Spectrum 9. ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 500 MHz).



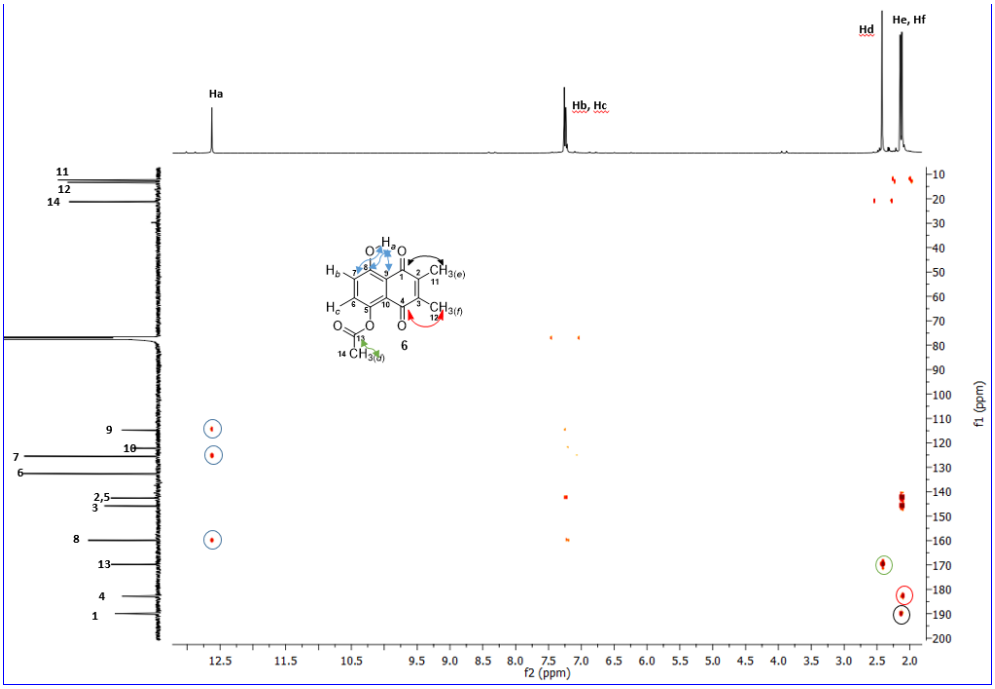
Spectrum 10. ^{13}C NMR spectrum of compound **6** ($CDCl_3$, 125 MHz)



Spectrum 11. APT NMR spectrum of compound **6** ($CDCl_3$, 125 MHz).

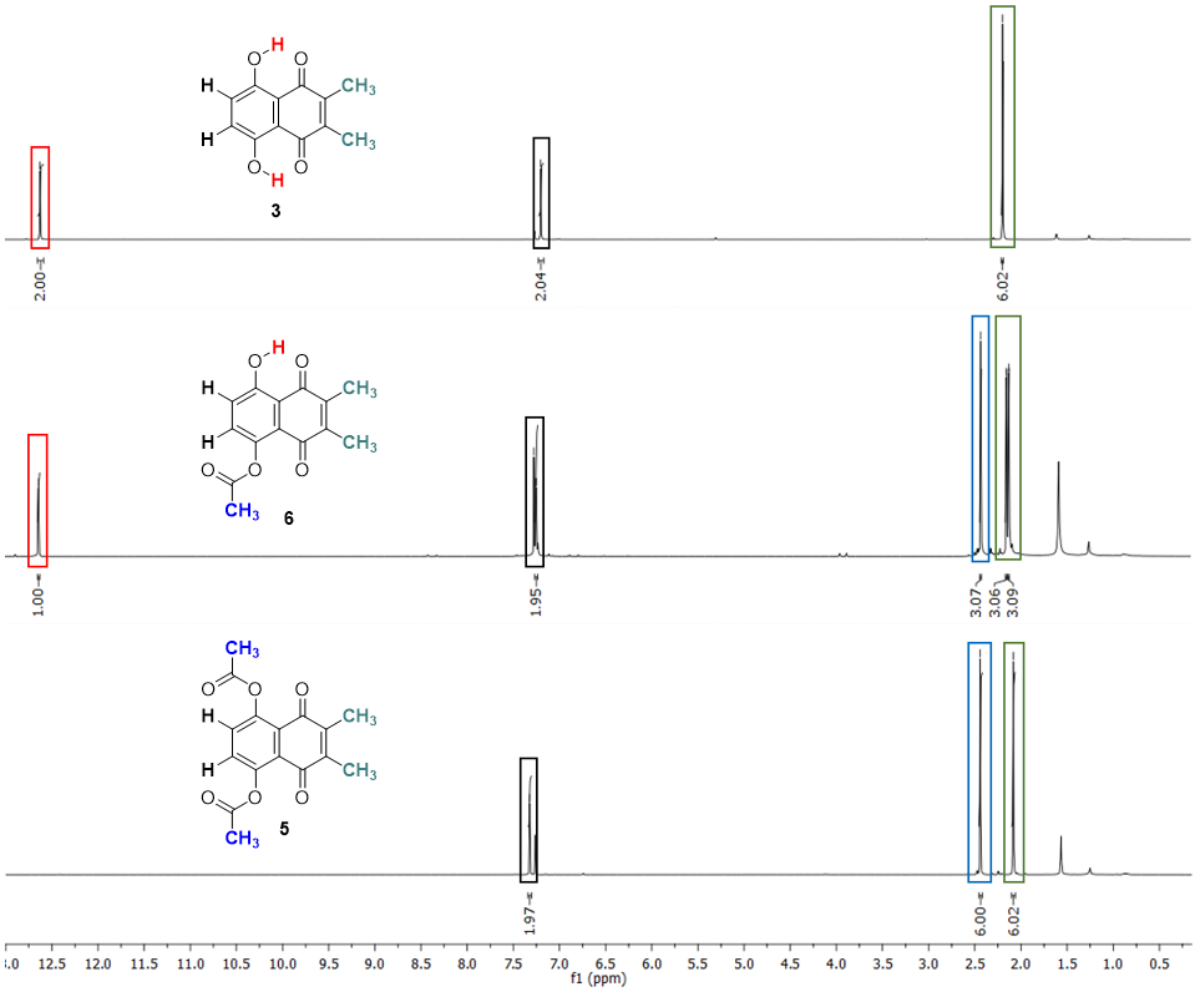


Spectrum 12. HSQC NMR spectrum of compound **6** in $CDCl_3$.

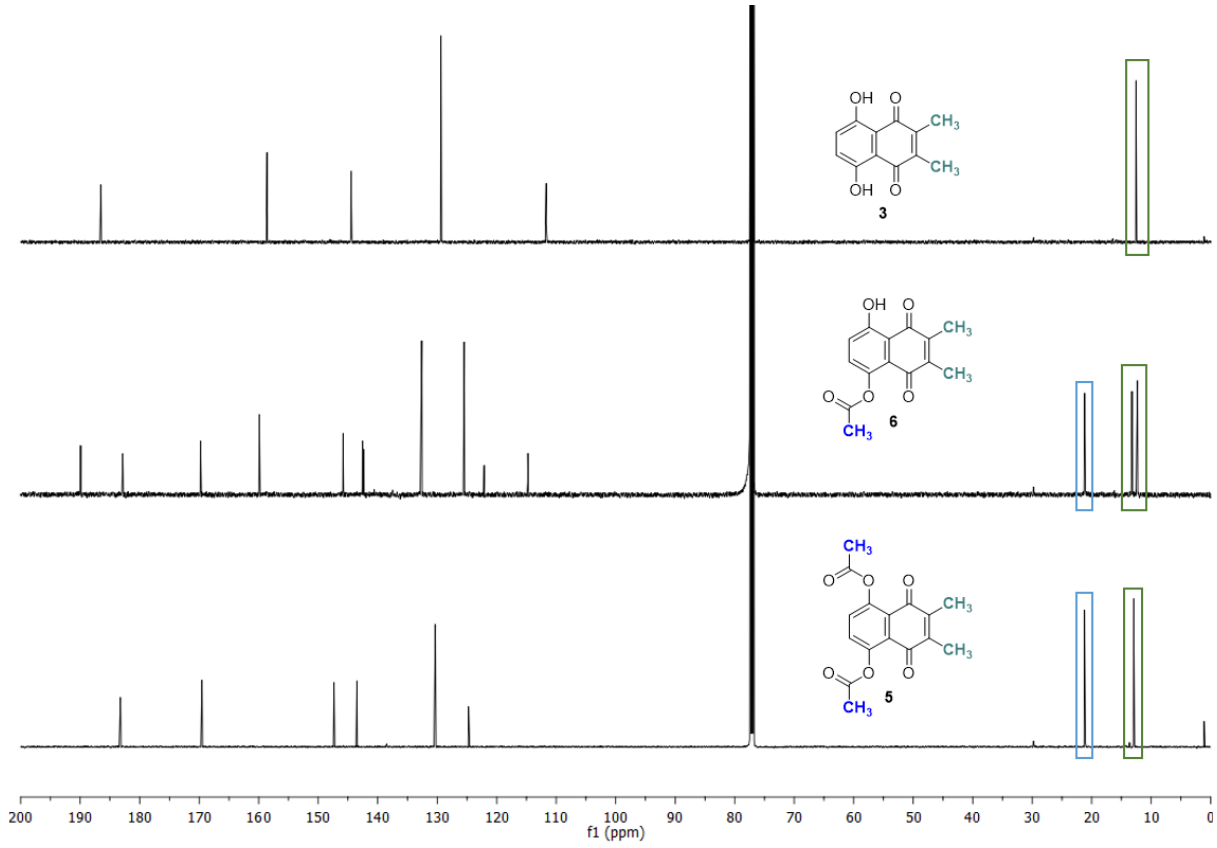


Spectrum 13. HMBC NMR spectrum of compound **6** in $CDCl_3$.

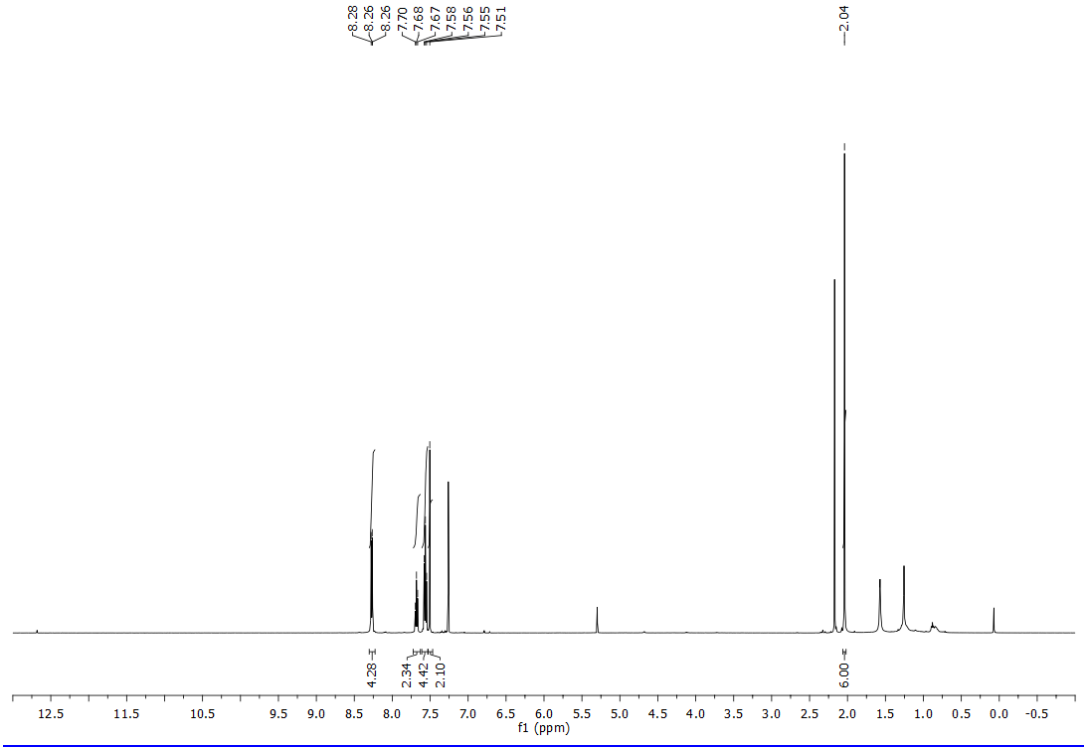
As shown in Spectrum 13, based on the analysis of the cross-peak signals observed in the two-dimensional HMBC spectrum of mono-ester **6,** the connectivity of phenolic ***Ha*** proton with C7, C8, and C9 was established. It was found that both of the methyl group protons ***He*** and ***Hf*** at the quinonoid ring show connection with carbonyl carbons C1 and C4, respectively, and the methyl protons ***Hd*** of the acetyl group has cross-peak with acetyl ester carbonyl carbon C13.



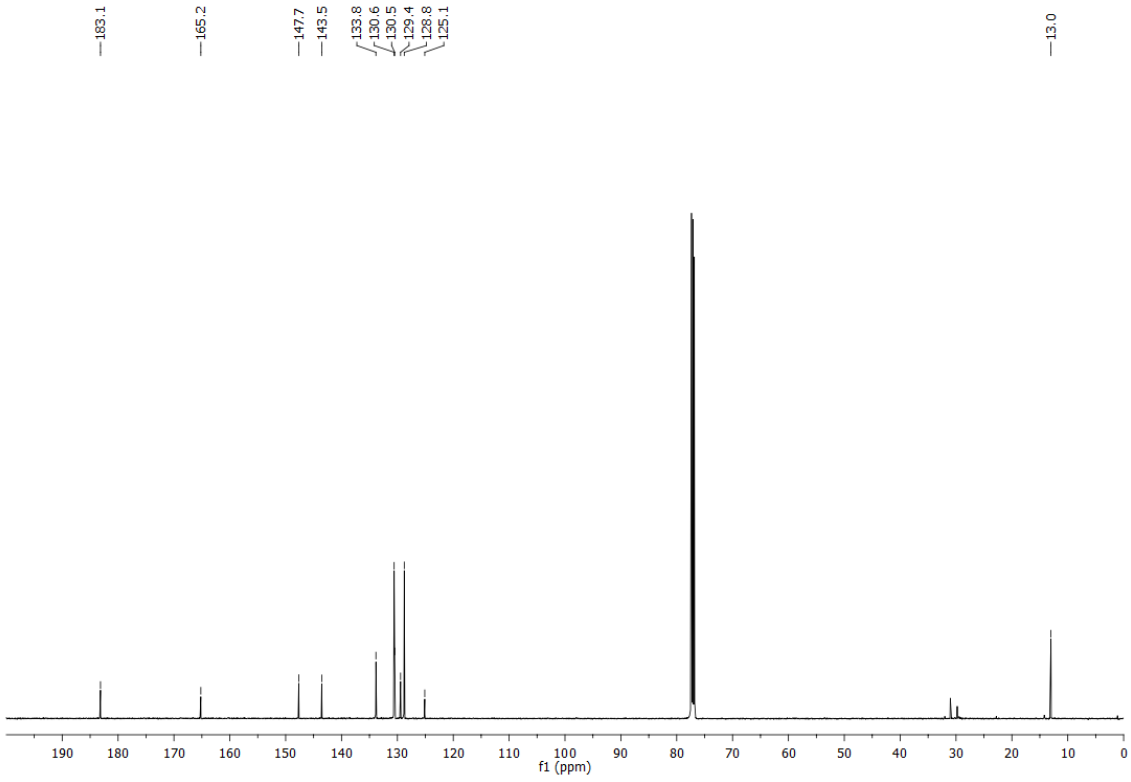
Spectrum 14. Comparison of the ^{1}H NMR spectra of compounds- DMN **3**, mono-acetyl DMN **6**, bis-acetyl DMN **5** ($CDCl_3$, 500 MHz).



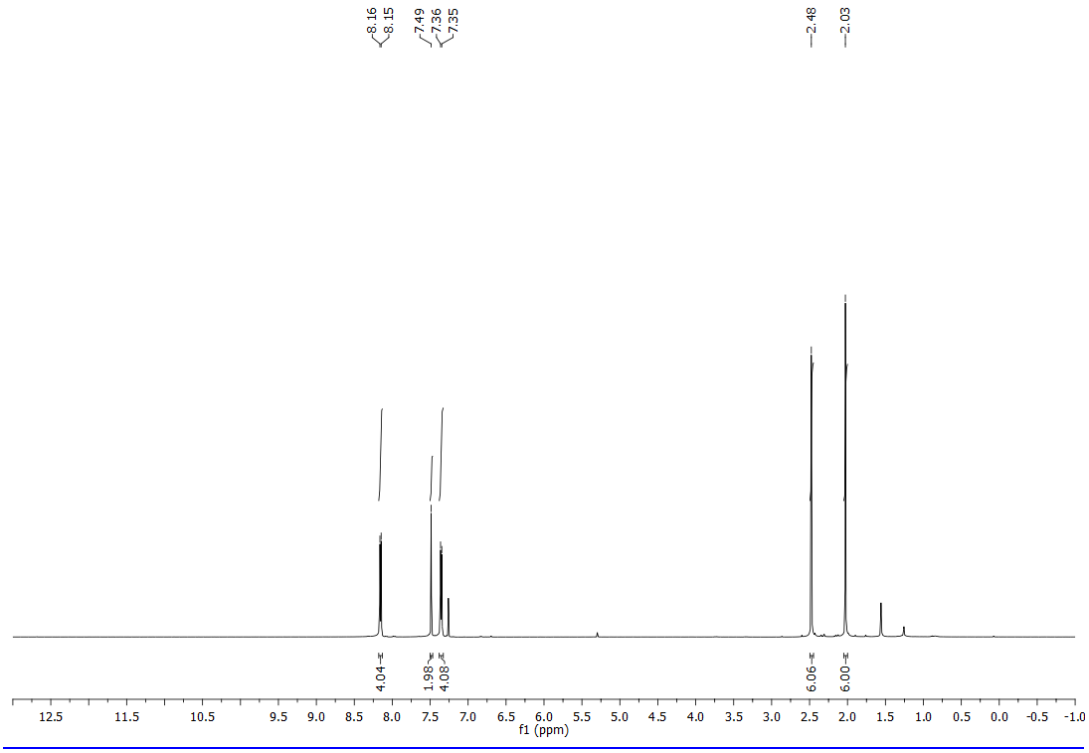
Spectrum 15. Comparison of the ^{13}C NMR spectra of compounds- DMN **3**, mono-acetyl DMN **6**, bis-acetyl DMN **5** ($CDCl_3$, 125 MHz).



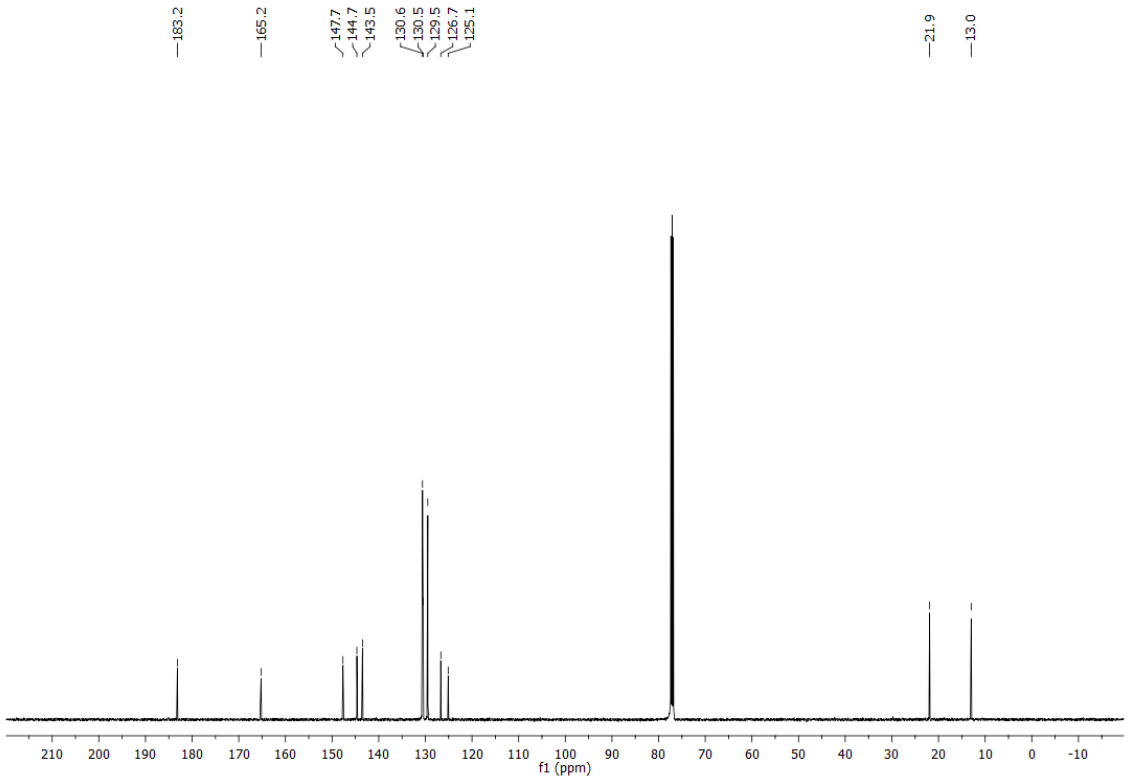
Spectrum 16. ^{1}H NMR spectrum of compound **12** ($CDCl_3$, 500 MHz).



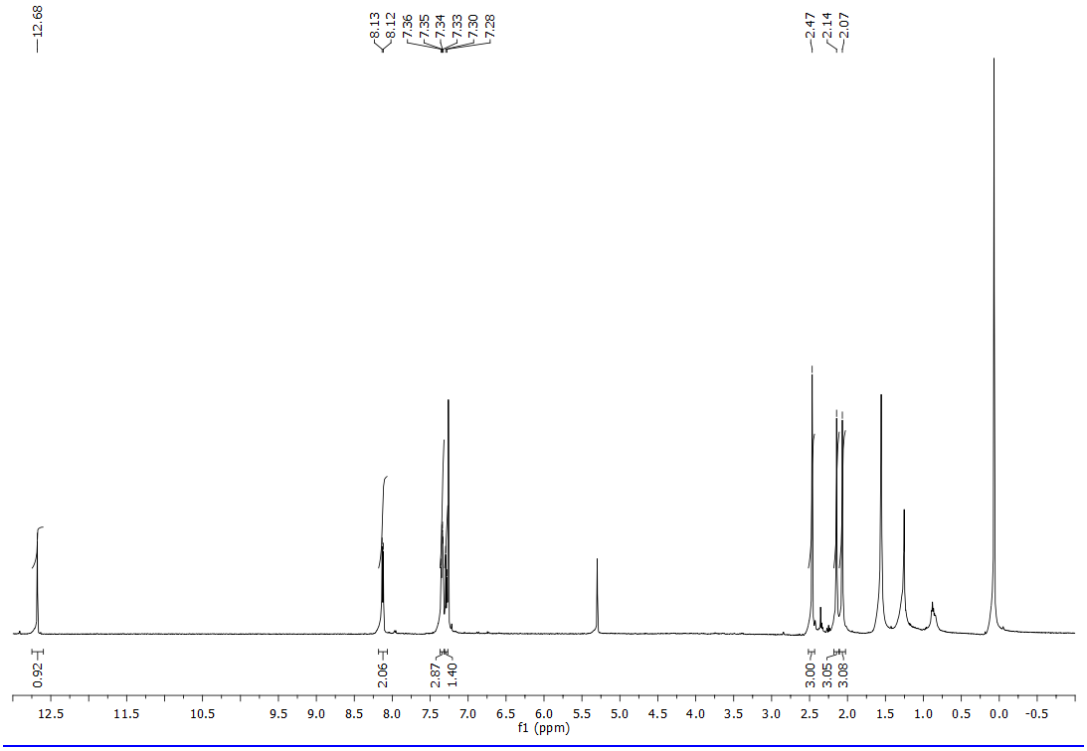
Spectrum 17. ^{13}C NMR spectrum of compound **12** ($CDCl_3$, 125 MHz).



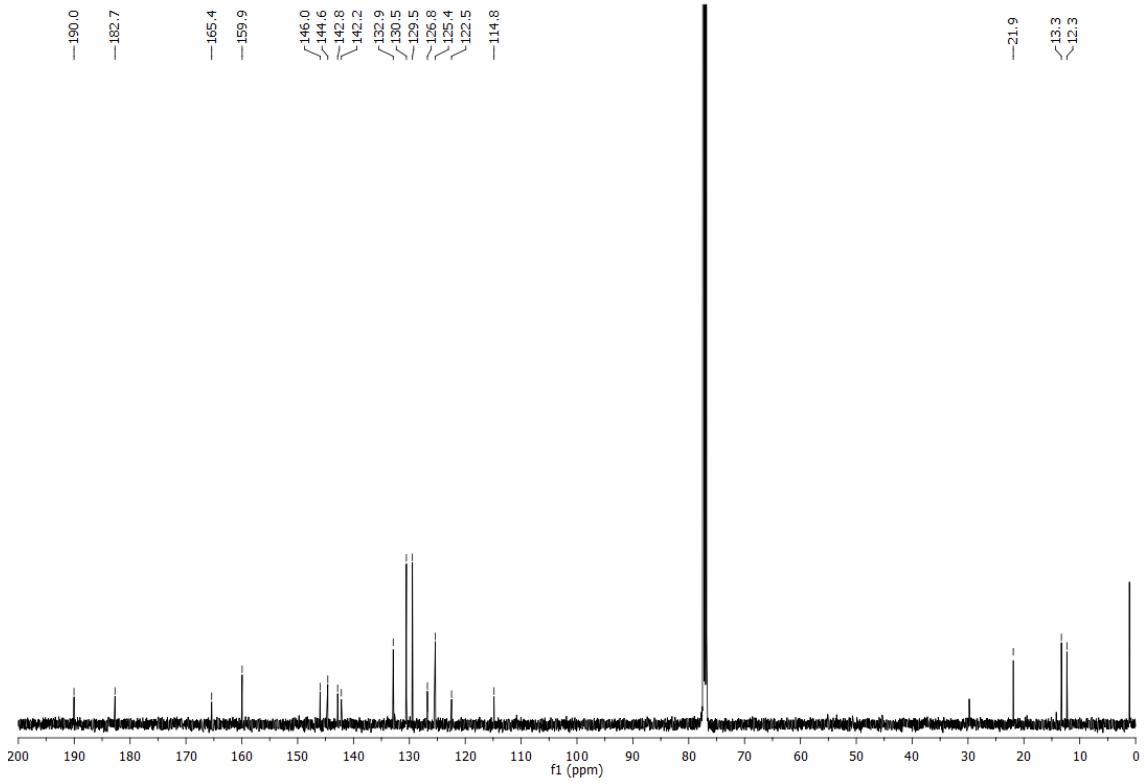
Spectrum 18. ^{1}H NMR spectrum of compound **13** ($CDCl_3$, 500 MHz).



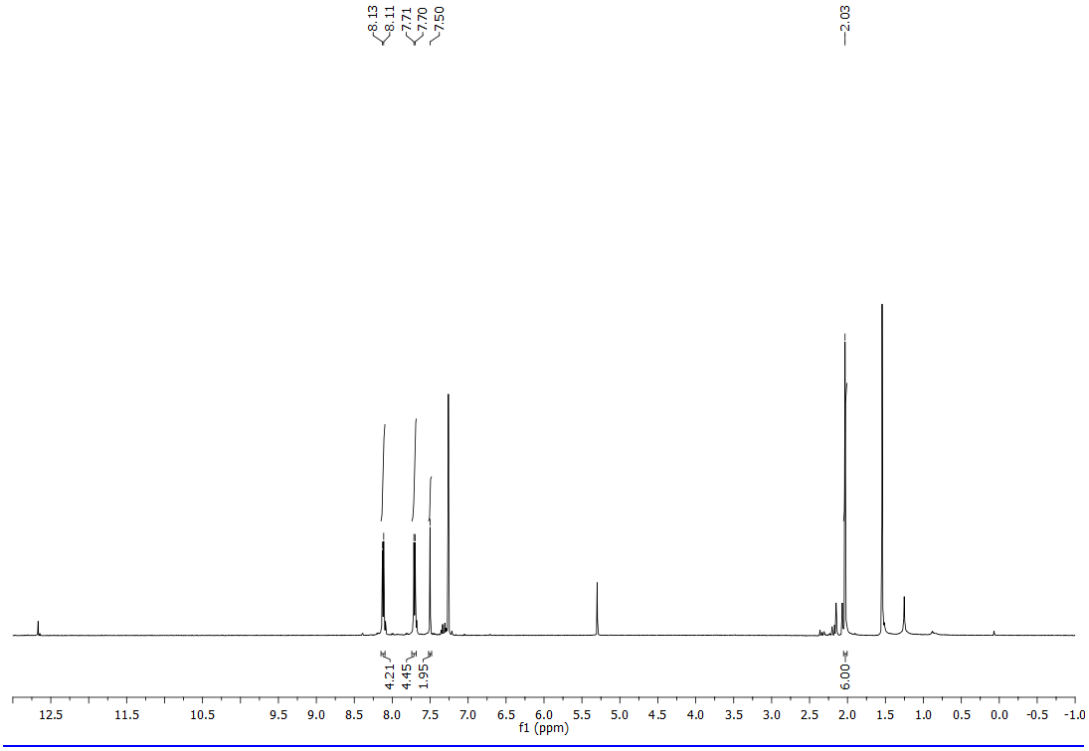
Spectrum 19. ^{13}C NMR spectrum of compound **13** ($CDCl_3$, 125 MHz).



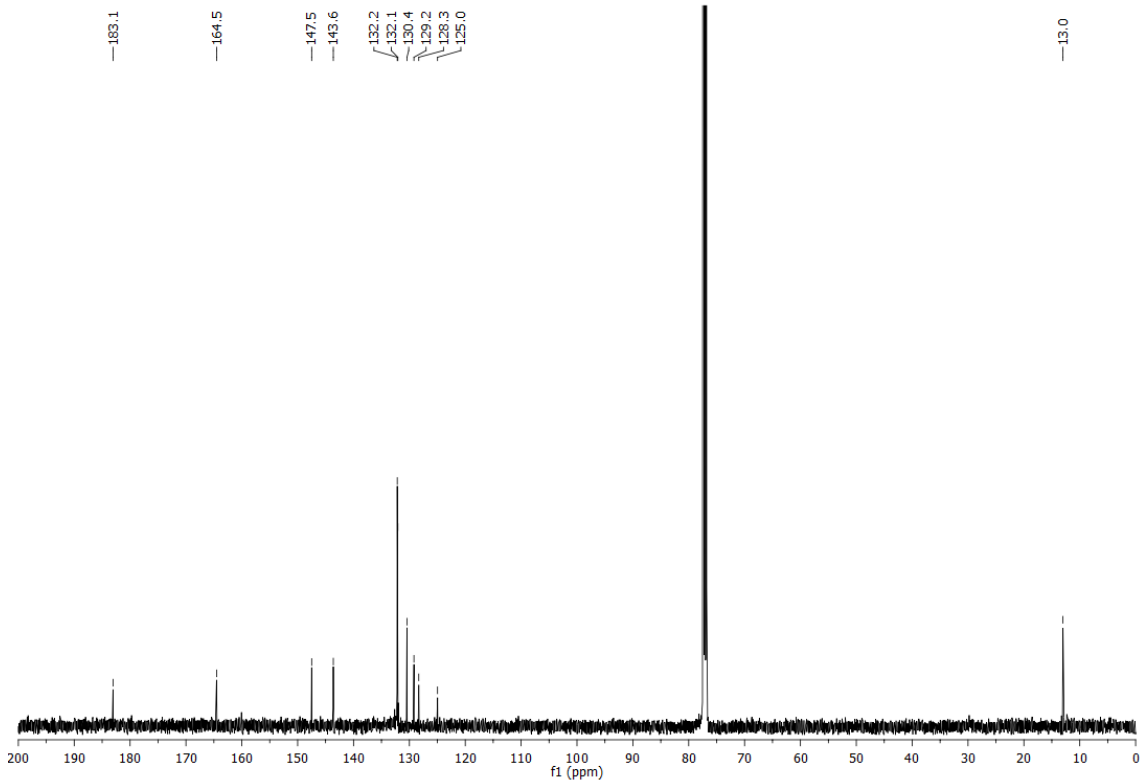
Spectrum 20. ^{1}H NMR spectrum of compound **17** ($CDCl_3$, 500 MHz).



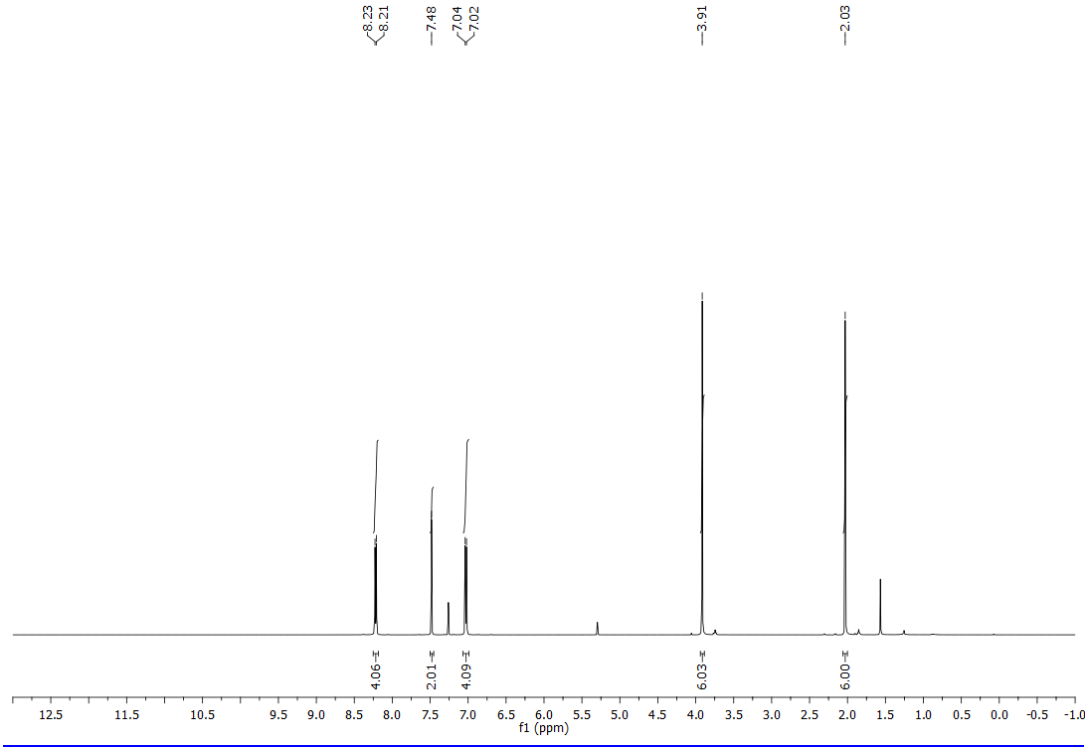
Spectrum 21. ^{13}C NMR spectrum of compound **17** ($CDCl_3$, 125 MHz).



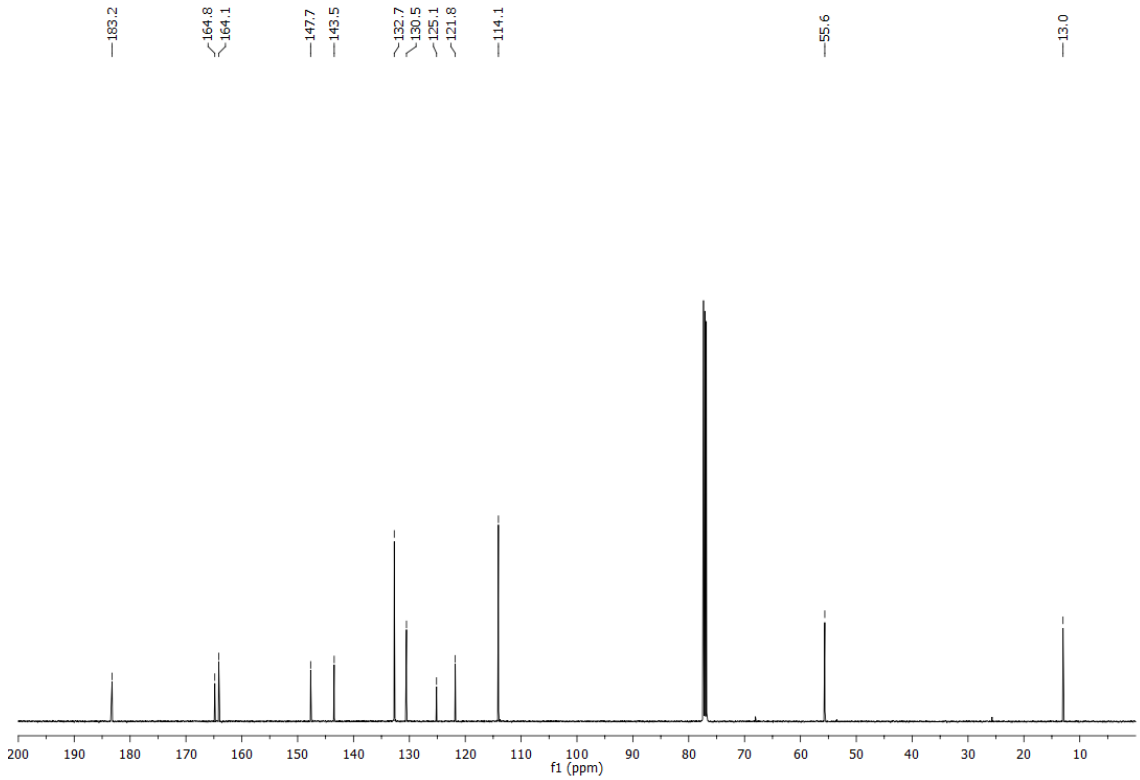
Spectrum 22. ^{1}H NMR spectrum of compound **14** ($CDCl_3$, 500 MHz).



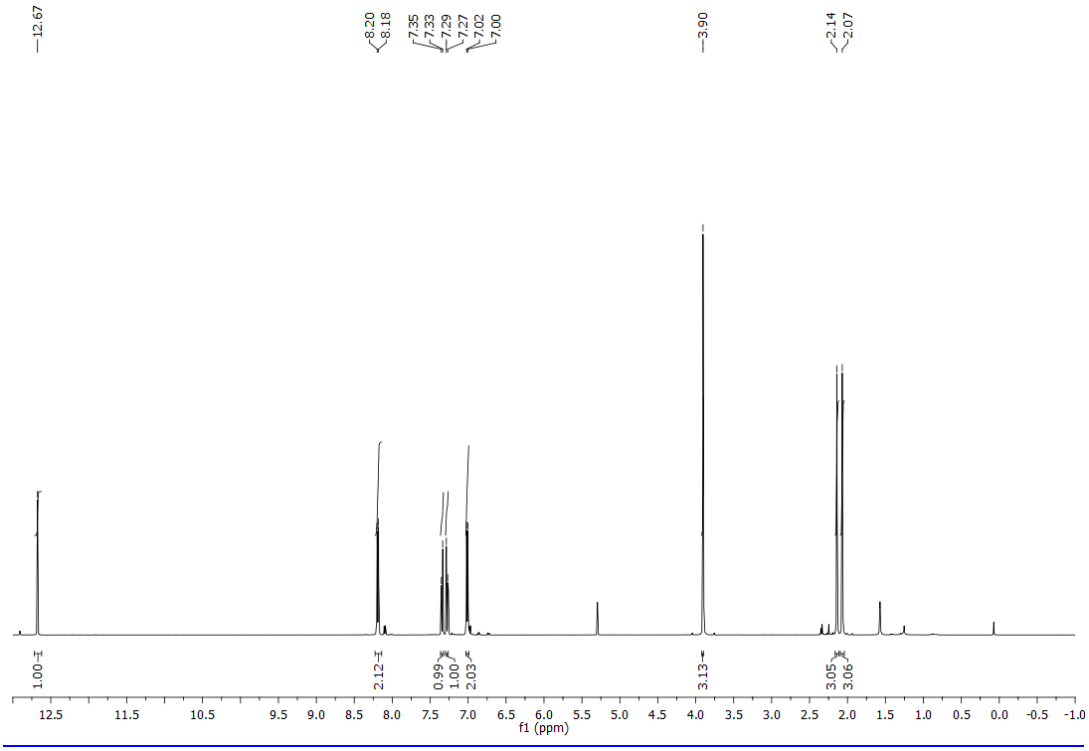
Spectrum 23. ^{13}C NMR spectrum of compound **14** ($CDCl_3$, 125 MHz).



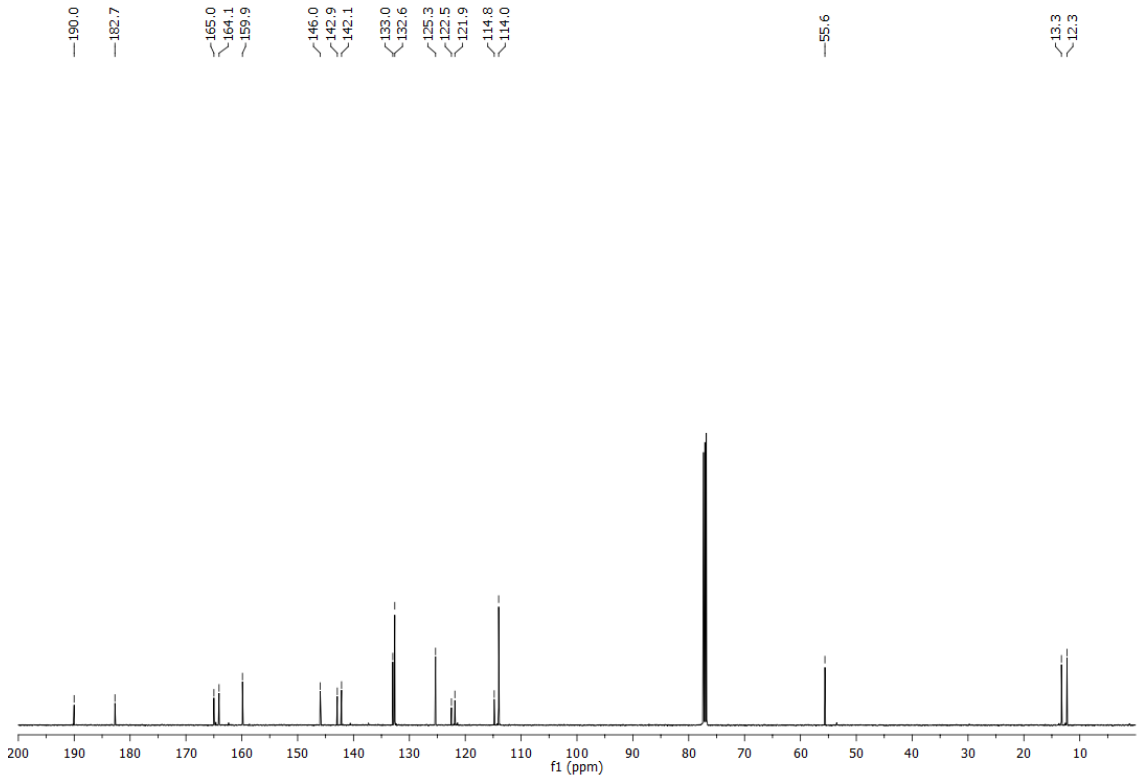
Spectrum 24. ^{1}H NMR spectrum of compound **15** ($CDCl_3$, 500 MHz).



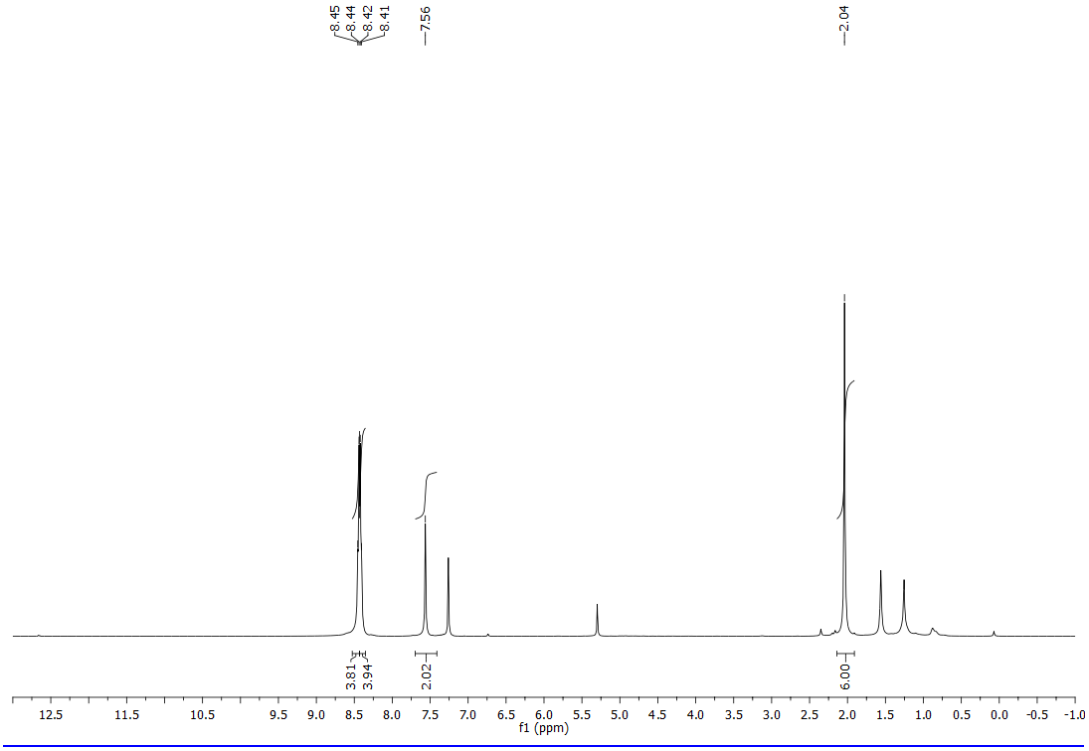
Spectrum 25. ^{13}C NMR spectrum of compound **15** ($CDCl_3$, 125 MHz).



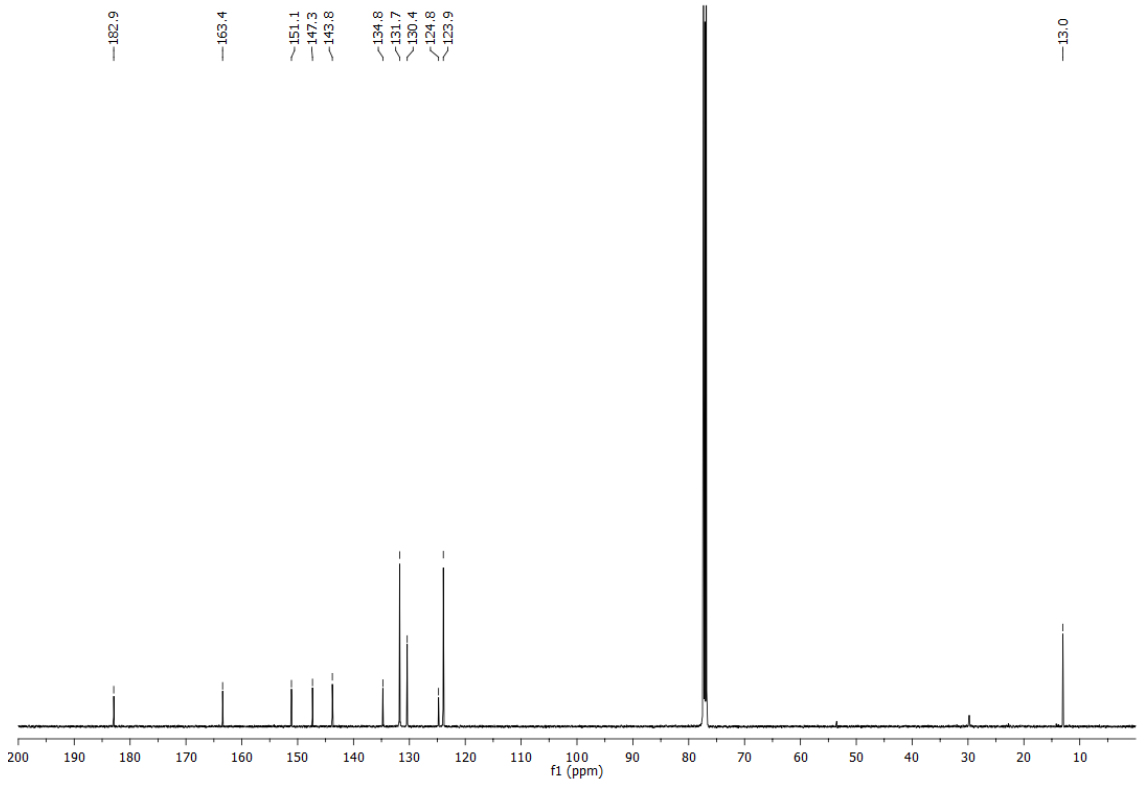
Spectrum 26. ^{1}H NMR spectrum of compound **18** ($CDCl_3$, 500 MHz).



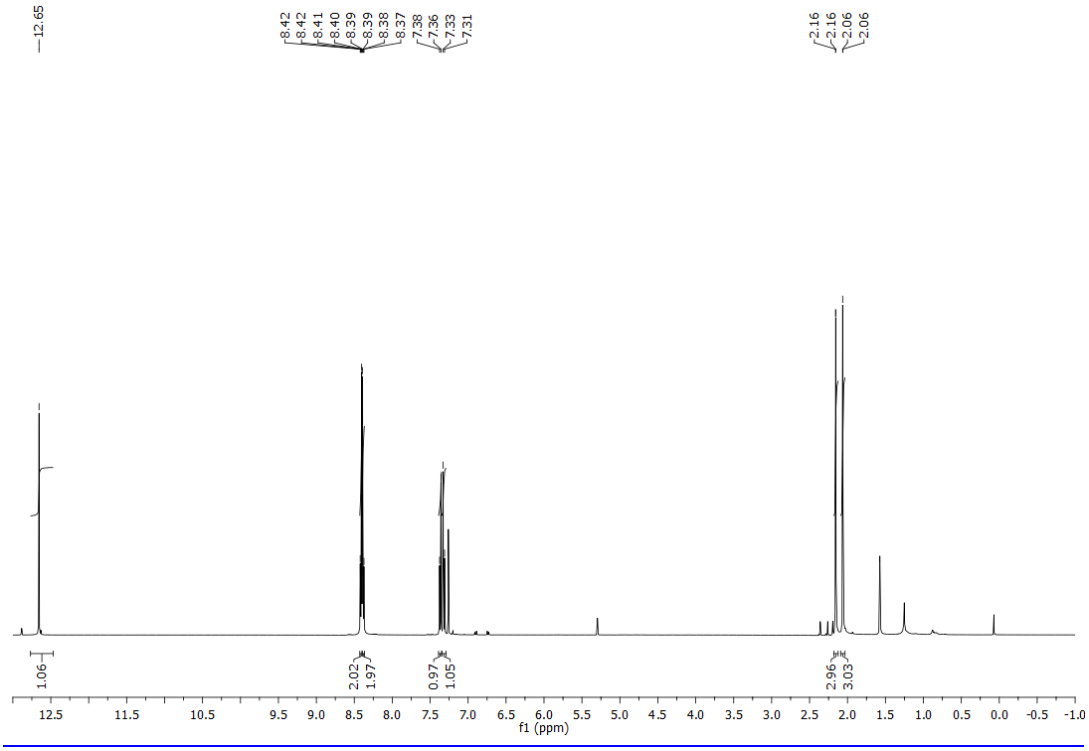
Spectrum 27. ^{13}C NMR spectrum of compound **18** ($CDCl_3$, 125 MHz).



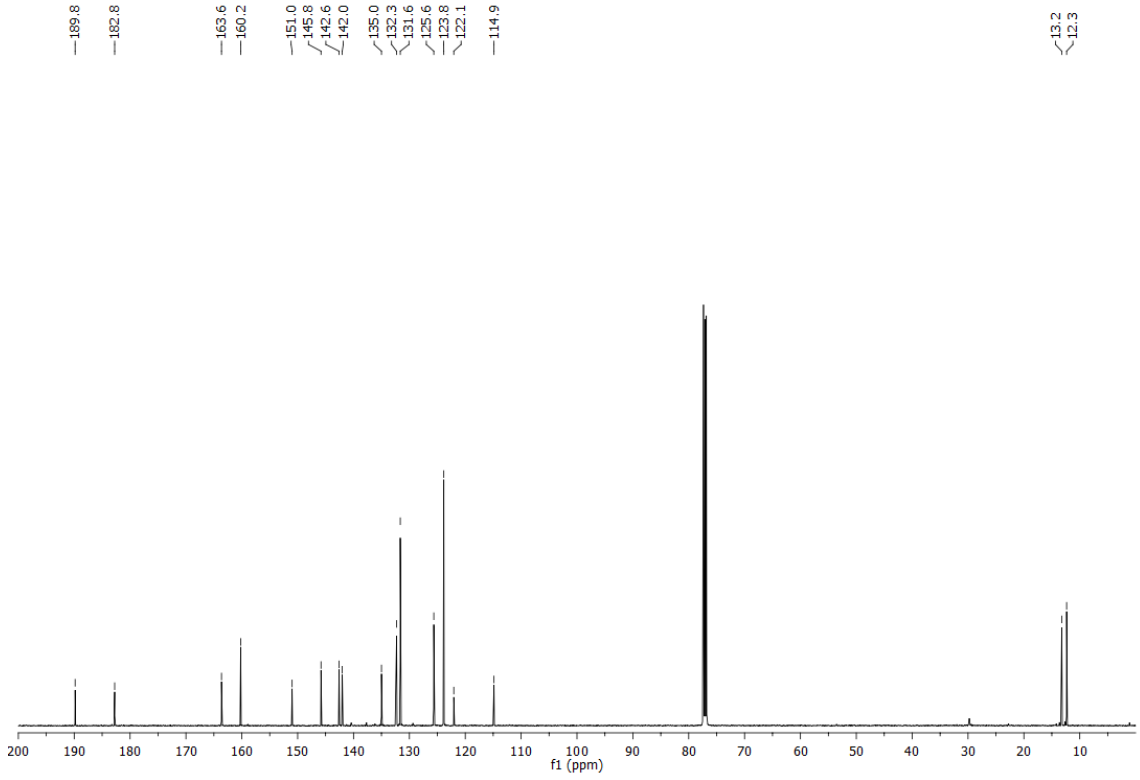
Spectrum 28. ^{1}H NMR spectrum of compound **16** ($CDCl_3$, 500 MHz).



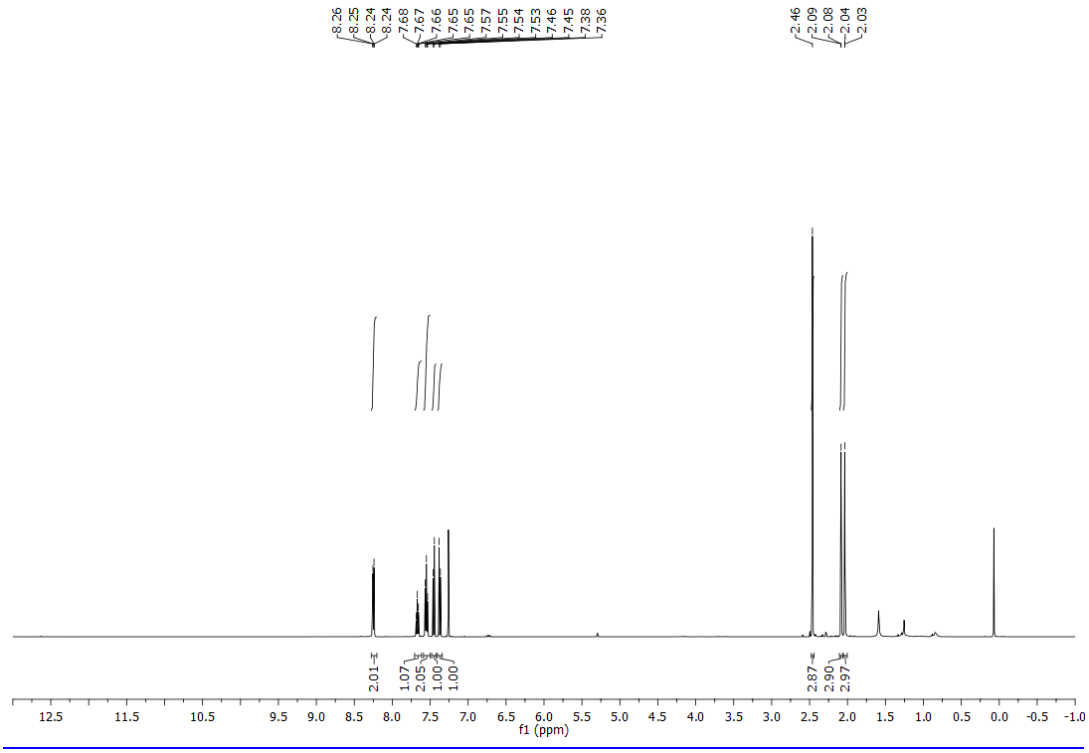
Spectrum 29. ^{13}C NMR spectrum of compound **16** ($CDCl_3$, 125 MHz**).**



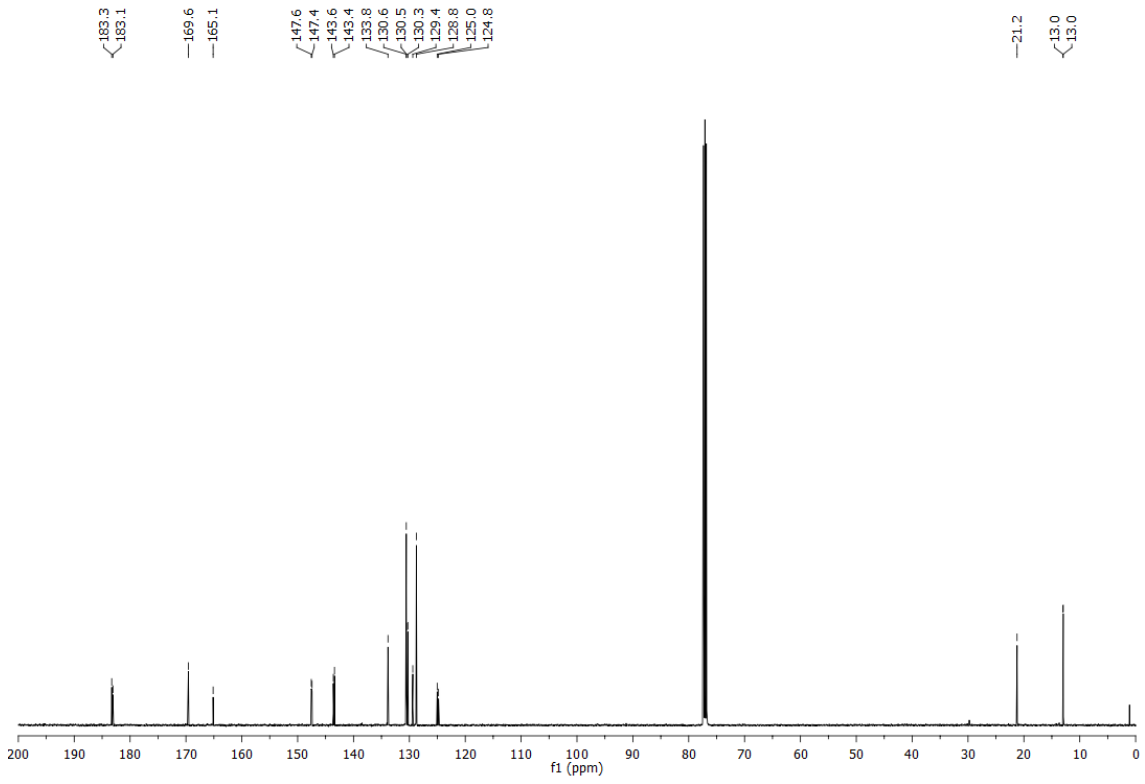
Spectrum 30. ^{1}H NMR spectrum of compound **19** ($CDCl_3$, 500 MHz).



Spectrum 31. ^{13}C NMR spectrum of compound **19** ($CDCl_3$, 125 MHz).



Spectrum 32. ^{1}H NMR spectrum of compound **20** ($CDCl_3$, 500 MHz).



Spectrum 33. ^{13}C NMR spectrum of compound **20** ($CDCl_3$, 125 MHz).

2. X-ray crystallographic data and structure refinement

Single crystal X-ray diffraction experiments were performed on a Bruker APEX II QUAZAR three-circle diffractometer using using monochromatized Mo-Kα X-radiation (λ = 0.71073 Å). Indexing, data collection, data reduction[1] and absorption correction[2] were carried out using APEX2.[3] All crystal structures were solved using SHELXT[4] and then refined by full-matrix least-squares refinements on F^2 using the SHELXL[5] in Olex2 Software Package.[6]

1. SAINT, version 8.34A, Bruker, 2013, Bruker AXS Inc., Madison, WI
2. SADABS, version2014/5, Bruker, 2014, Bruker AXS Inc., Madison, WI
3. APEX2, version 2014.11-0, Bruker, 2014, Bruker AXS Inc., Madison, WI
4. Sheldrick, G. M. *Acta Crystallogr. Sect. A. Found Crystallogr.* **2015**, *71*, 3.
5. Sheldrick, G. M. *Acta Crystallogr. Sect. C. Struct. Chem.* **2015**, *71*, 3.
6. Dolomanov, O.V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.

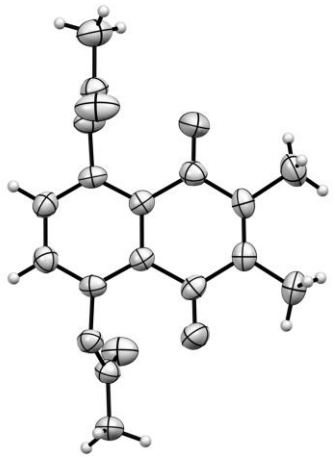


Figure S1: Molecular structure of **5** (CCDC 1948087). H atoms are drawn as circles with small radii.

Bond precision: C-C = 0.0075 A Wavelength=0.71073

Cell: a=5.7287(7) b=12.7981(14) c=19.345(2)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1418.3(3)	1418.3(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C16 H14 O6	C16 H14 O6
Sum formula	C16 H14 O6	C16 H14 O6
Mr	302.27	302.27
Dx,g cm-3	1.416	1.416
Z	4	4
Mu (mm-1)	0.109	0.109
F000	632.0	632.0
F000'	632.40	
h,k,lmax	6,15,23	6,15,23
Nref	2506[1481]	2478
Tmin,Tmax	0.992,0.995	
Tmin'	0.946	

Correction method= Not given

Data completeness= 1.67/0.99 Theta(max)= 25.021

R(reflections)= 0.0539(1503) wR2(reflections)= 0.1326(2478)

S = 1.015 Npar= 203

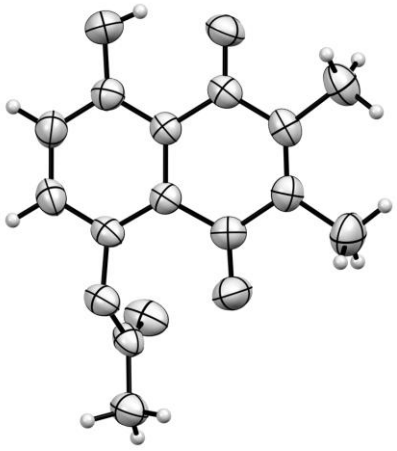


Figure S2: Molecular structure of **6** (CCDC 1946392). H atoms are drawn as circles with small radii.

Bond precision: C-C = 0.0040 A Wavelength=0.71073

Cell: a=14.9268(18) b=5.1190(7) c=15.6899(19)
alpha=90 beta=91.397(8) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1198.5(3)	1198.5(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C14 H12 O5	C14 H12 O5
Sum formula	C14 H12 O5	C14 H12 O5
Mr	260.24	260.24
Dx,g cm-3	1.442	1.442
Z	4	4
Mu (mm-1)	0.110	0.110
F000	544.0	544.0
F000'	544.34	
h,k,lmax	17,6,18	17,6,18
Nref	2117	2118
Tmin,Tmax	0.989,0.994	
Tmin'	0.930	

Correction method= Not given

Data completeness= 1.000 Theta(max)= 25.011

R(reflections)= 0.0534(1329) wR2(reflections)= 0.1538(2118)

S = 1.031 Npar= 176

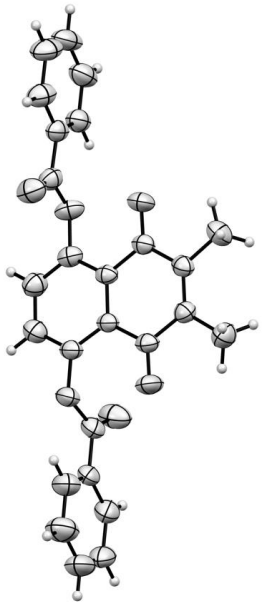


Figure S3: Molecular structure of **12** (CCDC 2048115). H atoms are drawn as circles with small radii.

Bond precision:	C-C = 0.0035 A	Wavelength=0.71073	
Cell:	a=13.910(3)	b=9.6029(18)	c=15.476(3)
	alpha=90	beta=99.855(3)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2036.7(7)	2036.8(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H18 O6	C26 H18 O6
Sum formula	C26 H18 O6	C26 H18 O6
Mr	426.40	426.40
Dx,g cm-3	1.391	1.391
Z	4	4
Mu (mm-1)	0.099	0.099
F000	888.0	888.0
F000'	888.50	
h,k,lmax	18,12,20	18,12,20
Nref	4666	4648
Tmin,Tmax	0.982,0.991	
Tmin'	0.944	

Correction method= Not given

Data completeness= 0.996 Theta(max)= 27.483

R(reflections)= 0.0558(2315) wR2(reflections)= 0.1615(4648)

S = 1.023 Npar= 291

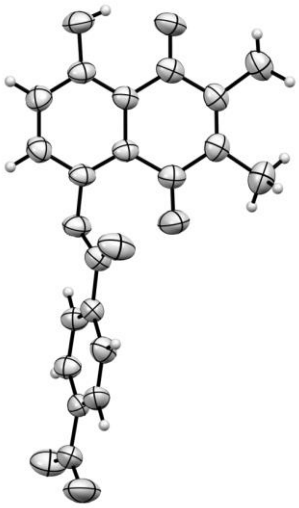


Figure S4: Molecular structure of **19** (CCDC 2184617). H atoms are drawn as circles with small radii.

Bond precision: C-C = 0.0039 A Wavelength=0.71073

Cell: a=7.456(2) b=8.851(3) c=12.875(4)
alpha=97.571(7) beta=100.670(7) gamma=99.575(7)
Temperature: 273 K

	Calculated	Reported
Volume	811.7(4)	811.6(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H13 N O7	C19 H13 N O7
Sum formula	C19 H13 N O7	C19 H13 N O7
Mr	367.30	367.30
Dx,g cm-3	1.503	1.503
Z	2	2
Mu (mm-1)	0.117	0.117
F000	380.0	380.0
F000'	380.24	
h,k,lmax	8,10,15	8,10,15
Nref	2868	2852
Tmin,Tmax	0.972,0.991	
Tmin'	0.965	

Correction method= Not given

Data completeness= 0.994 Theta(max)= 25.026

R(reflections)= 0.0478(1964) wR2(reflections)= 0.1422(2852)

S = 1.030 Npar= 247

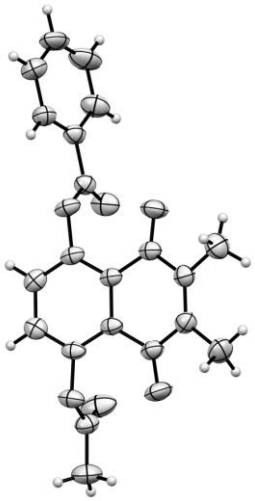


Figure S5: Molecular structure of **20** (CCDC 2184607). H atoms are drawn as circles with small radii.

Bond precision: C-C = 0.0022 A Wavelength=0.71073

Cell: a=9.5232(13) b=7.9089(11) c=23.314(3)
alpha=90 beta=93.868(2) gamma=90
Temperature: 299 K

	Calculated	Reported
Volume	1752.0(4)	1752.0(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H16 O6	C21 H16 O6
Sum formula	C21 H16 O6	C21 H16 O6
Mr	364.34	364.34
Dx,g cm-3	1.381	1.381
Z	4	4
Mu (mm-1)	0.102	0.102
F000	760.0	760.0
F000'	760.45	
h,k,lmax	12,10,30	12,10,30
Nref	4015	4003
Tmin,Tmax	0.971,0.976	
Tmin'	0.971	

Correction method= Not given

Data completeness= 0.997 Theta(max)= 27.483

R(reflections)= 0.0453(3323) wR2(reflections)= 0.1247(4003)

S = 1.028 Npar= 247