Electronic Supplementary Material (ESI) for RSC Advances.

Macrocyclic pentamers functionalised around their periphery as potential building blocks

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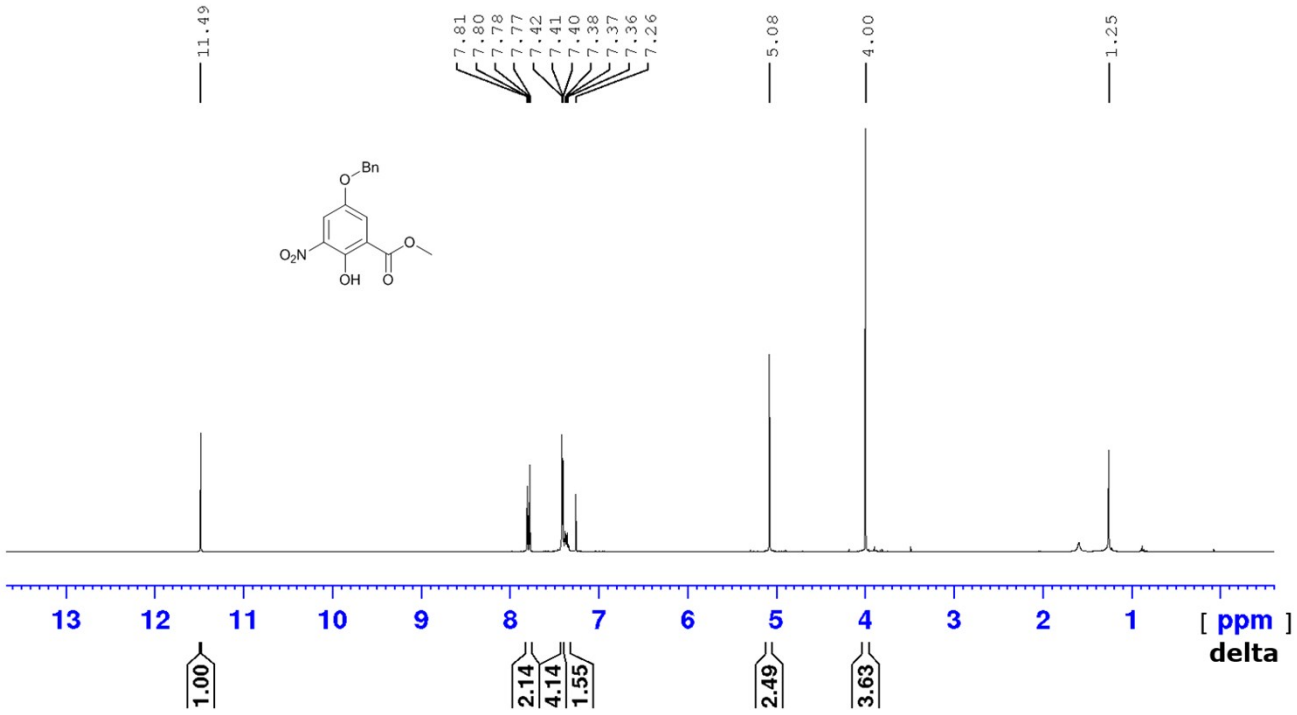


Fig S1 ^{1}H NMR spectrum of **8** in $CDCl_3$

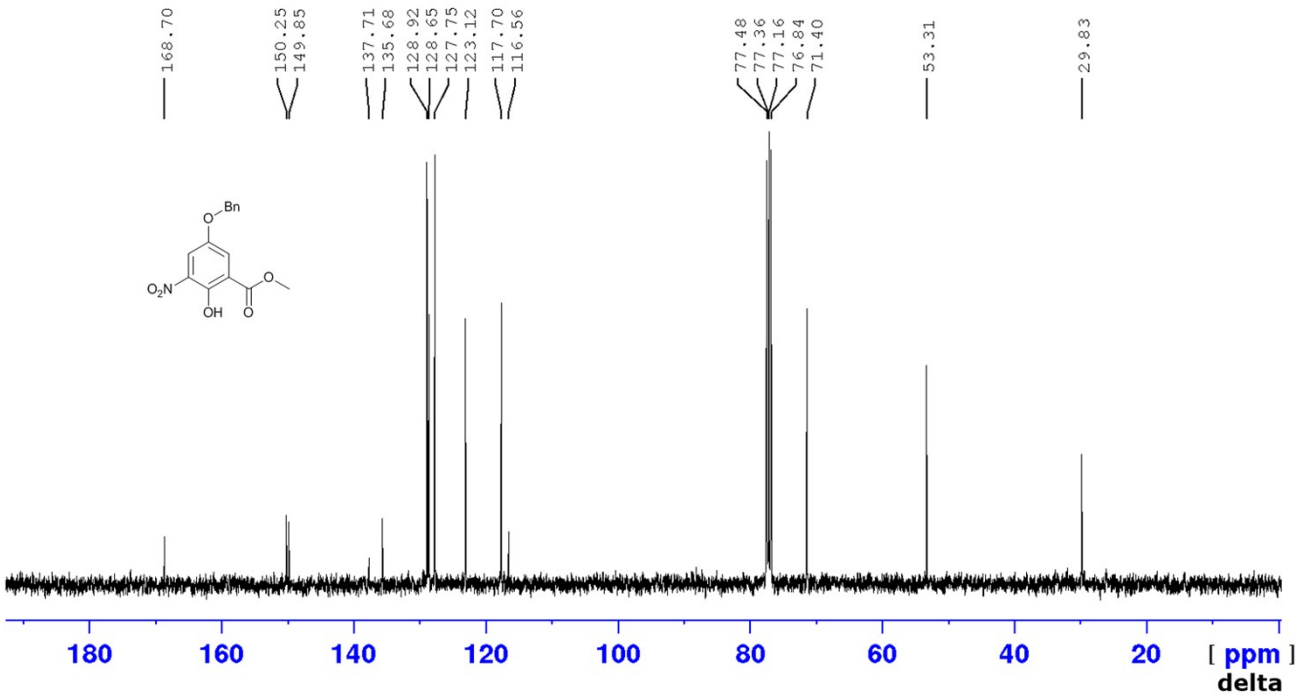


Fig S2 ^{13}C NMR spectrum of **8** in $CDCl_3$

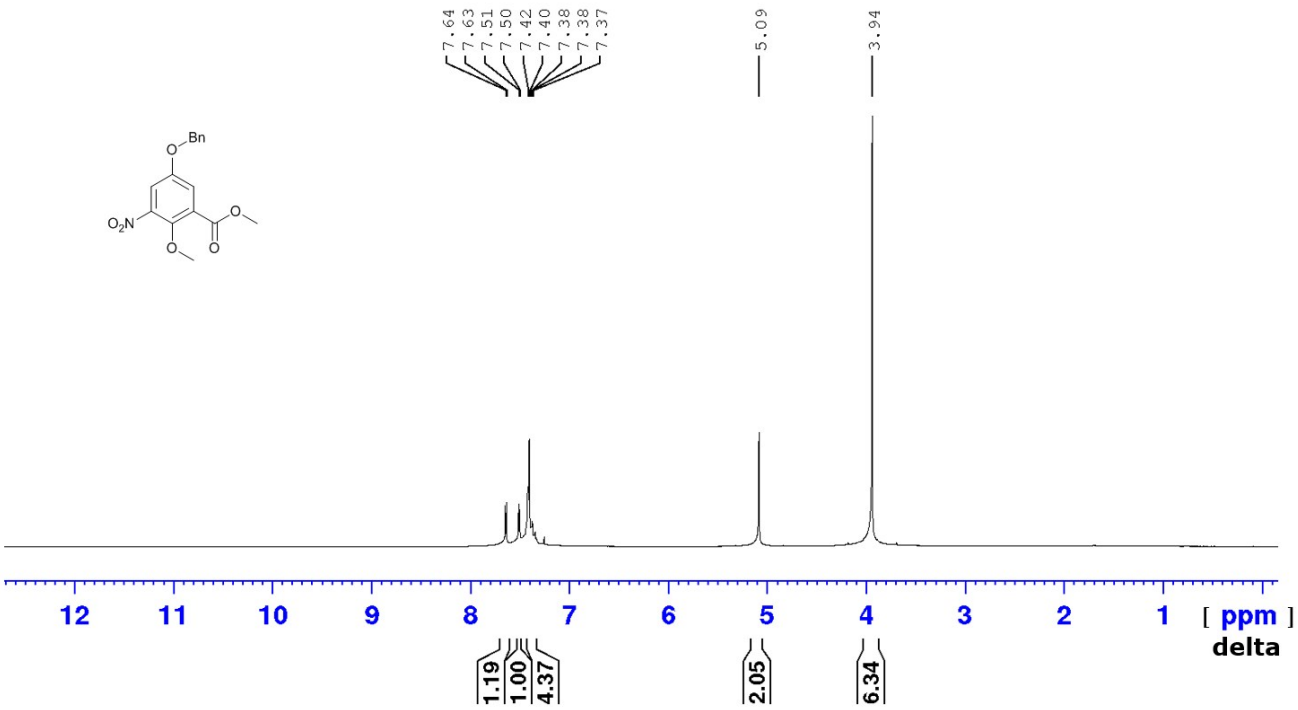


Fig S3 ^{1}H NMR spectrum of **9** in $CDCl_3$

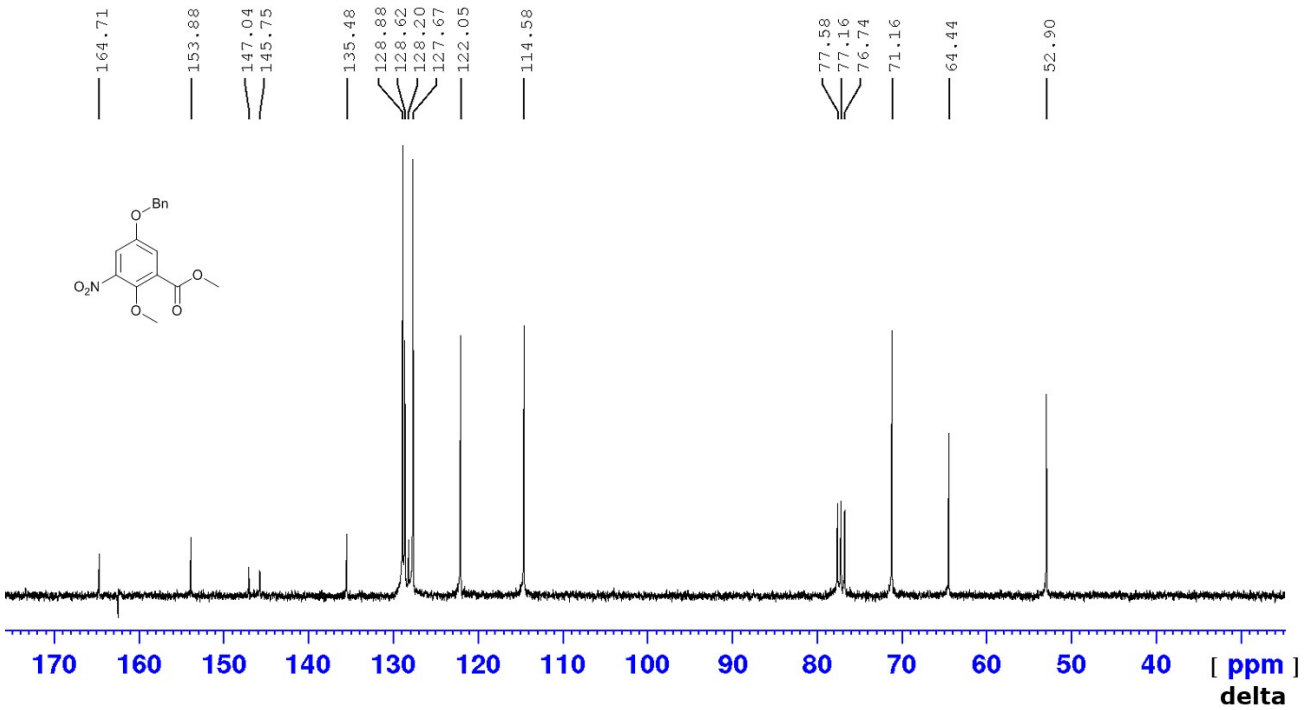


Fig S4 ^{13}C NMR spectrum of **9** in $CDCl_3$

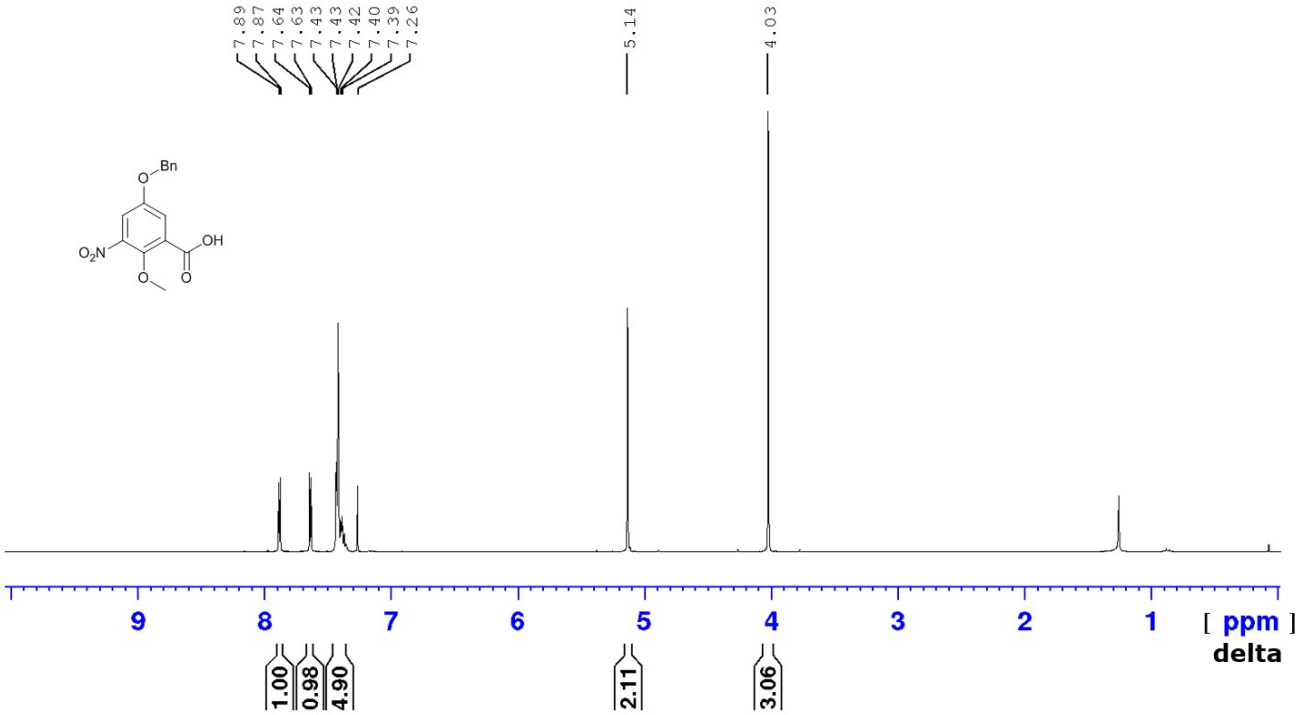


Fig S5 ^{1}H NMR spectrum of **10** in $CDCl_3$

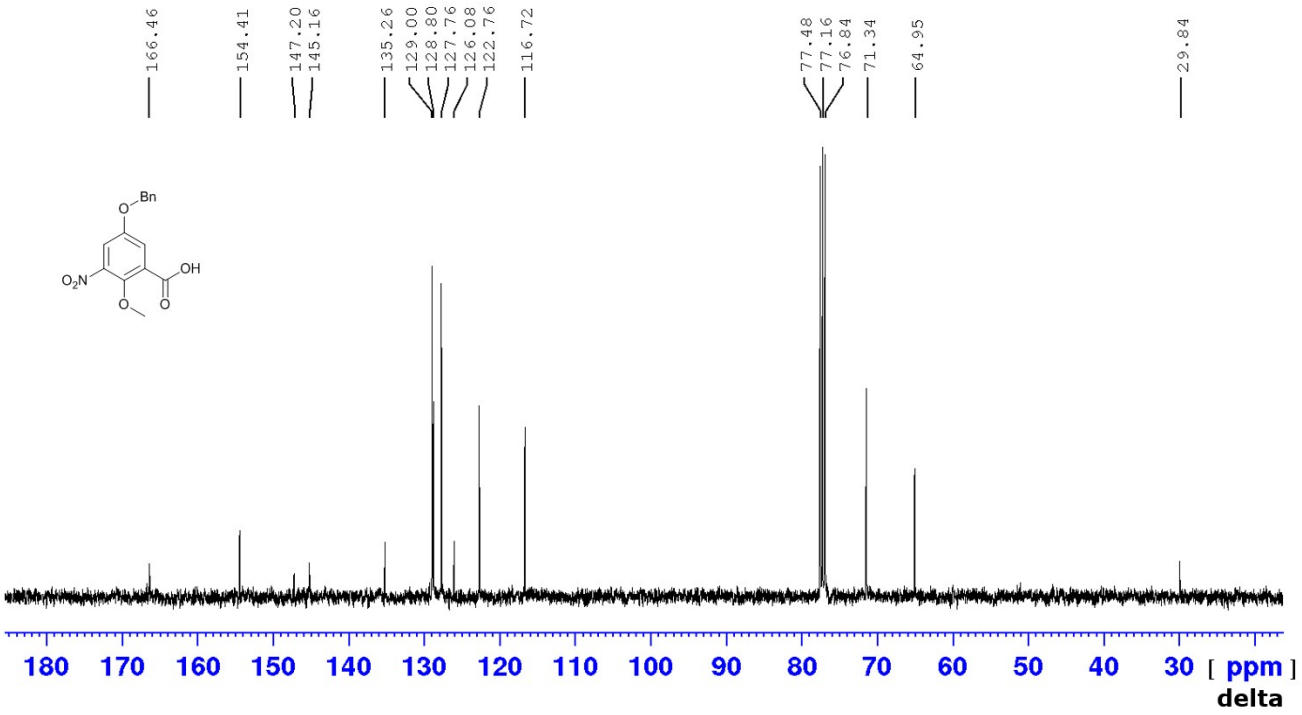


Fig S6 ^{13}C NMR spectrum of **10** in $CDCl_3$

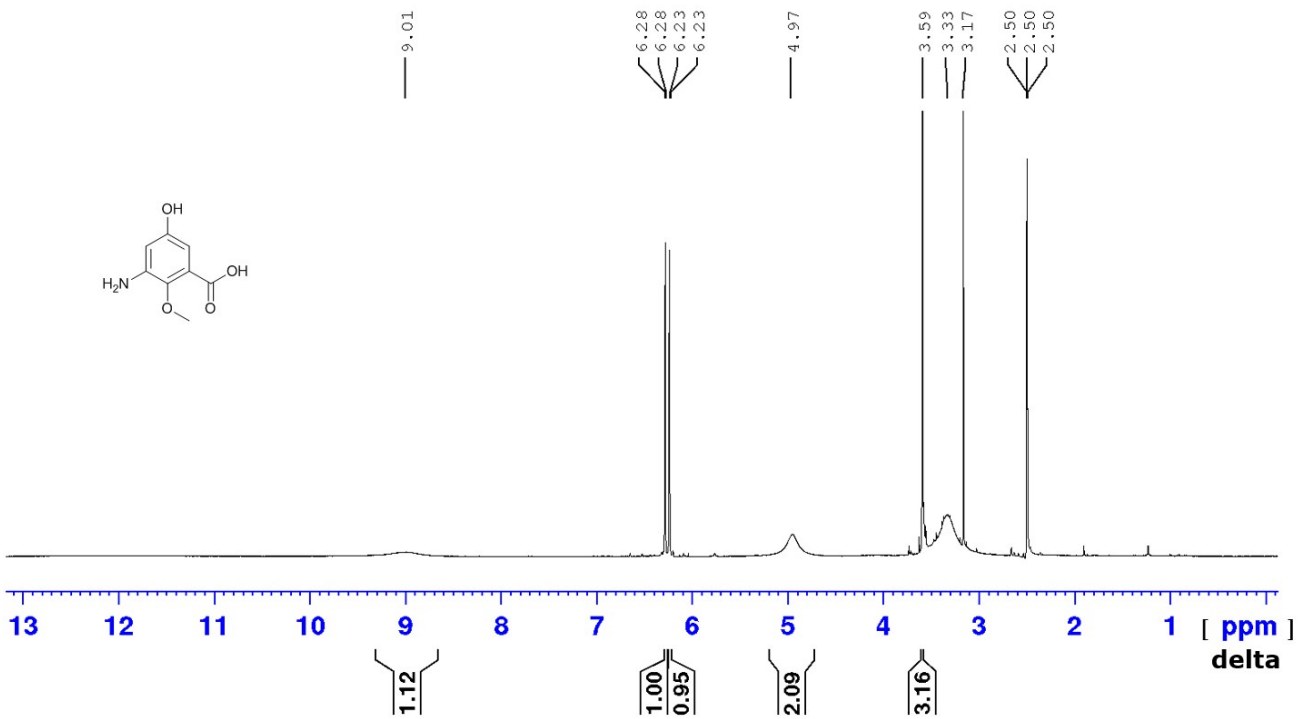


Fig S7 ^{1}H NMR spectrum of **11** in DMSO-d_6

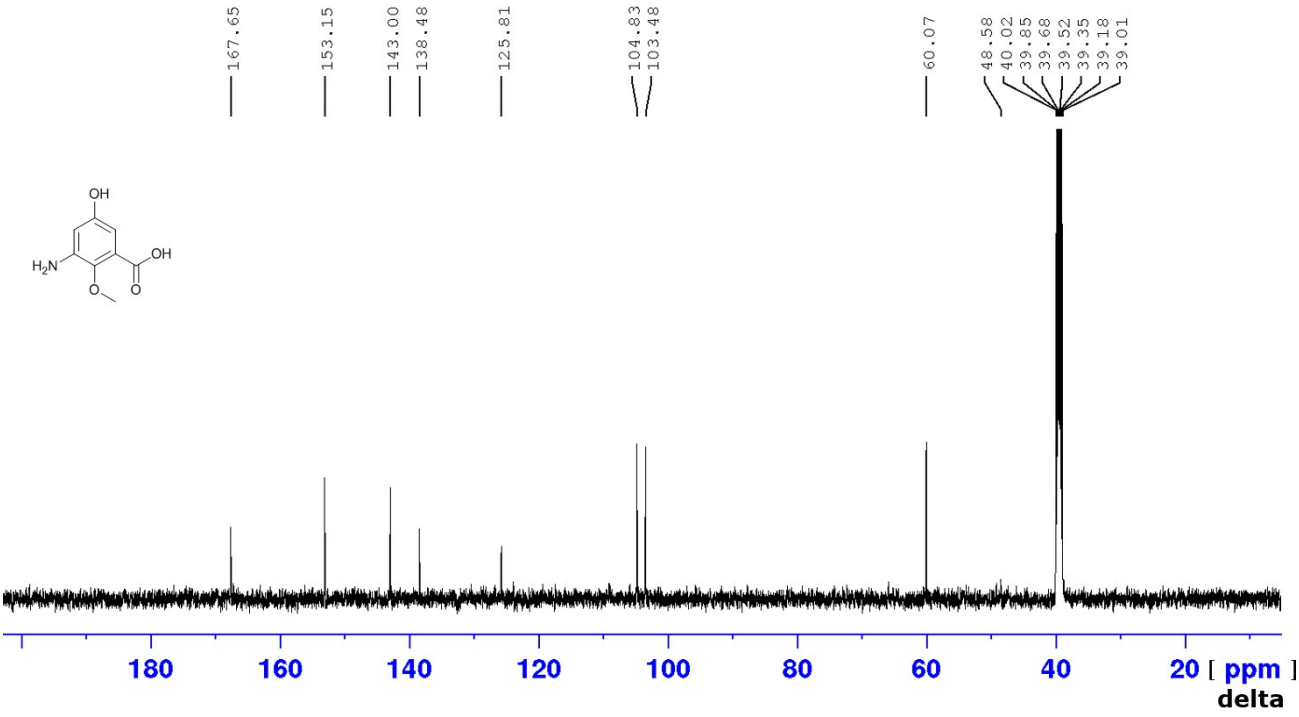


Fig S8 ^{13}C NMR spectrum of **11** in DMSO-d_6

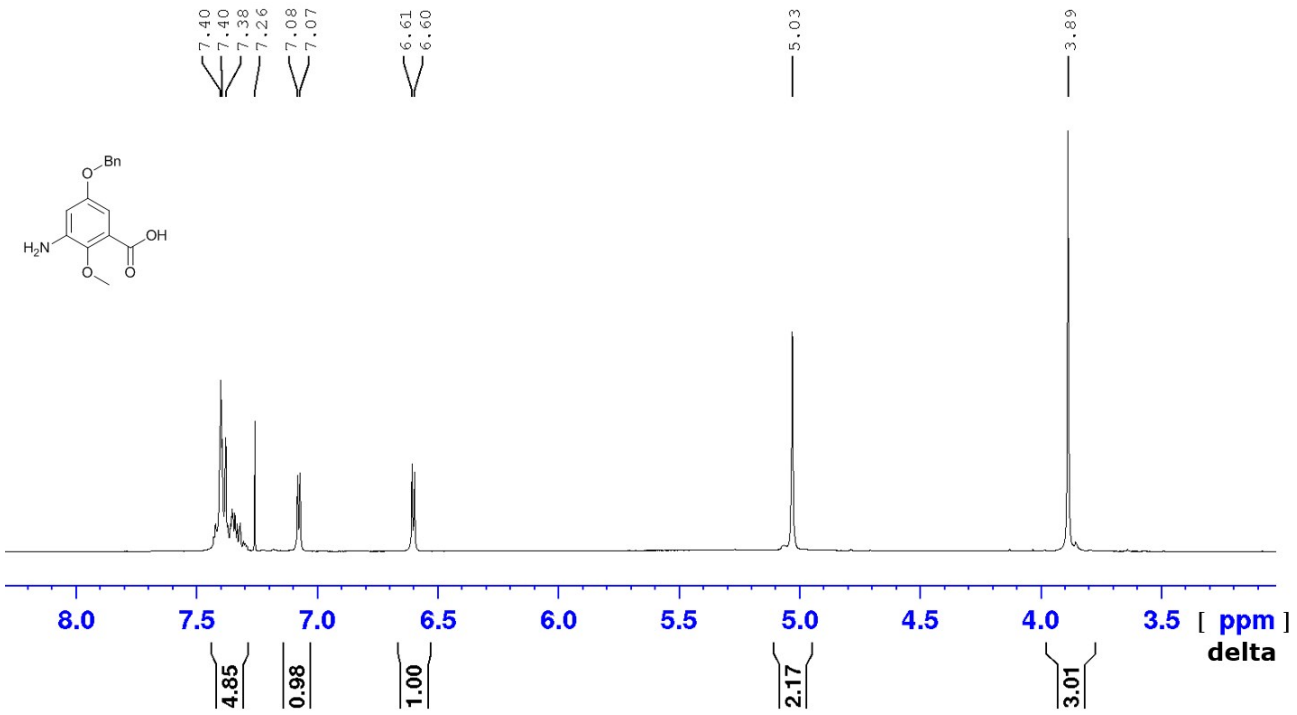


Fig S9 ^{1}H NMR spectrum of **12** in $CDCl_3$

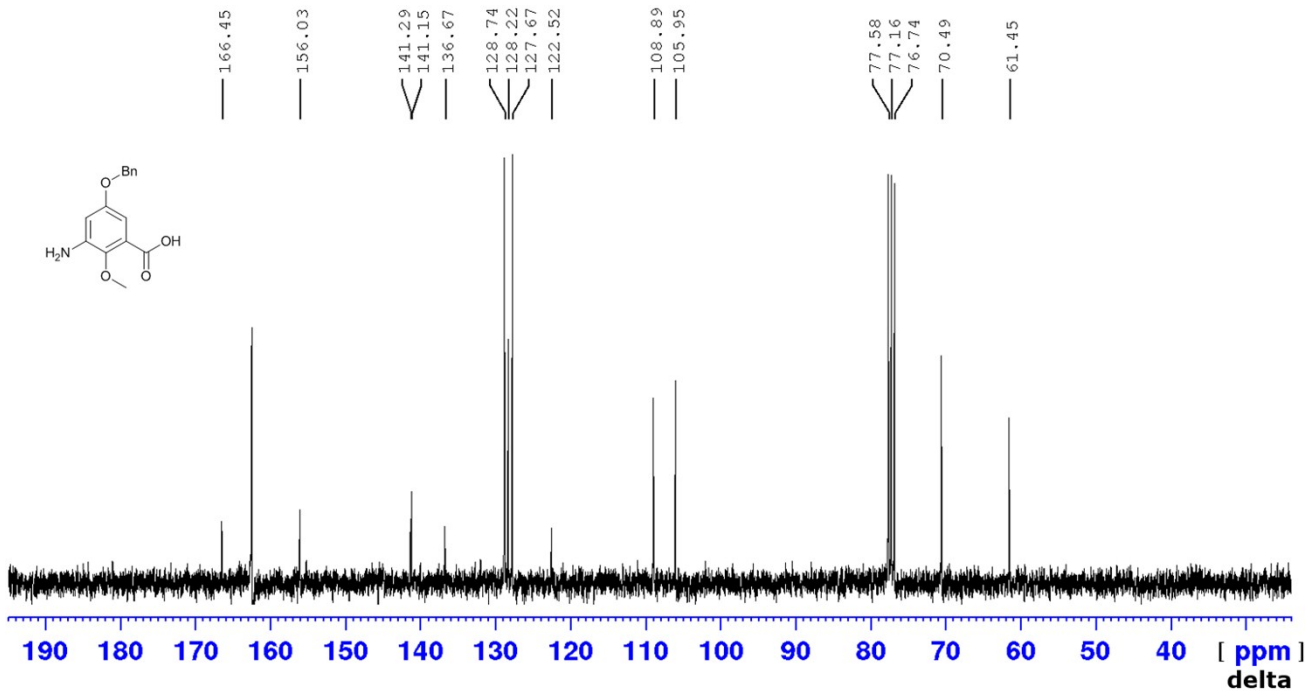
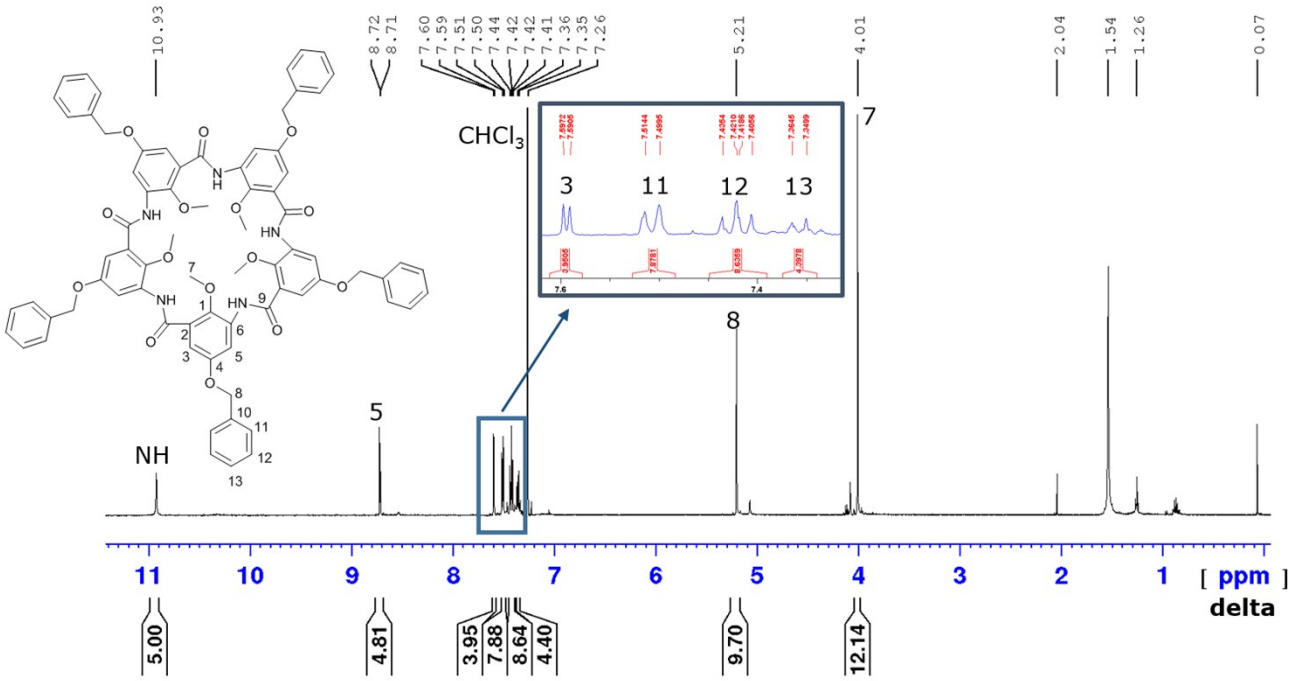


Fig S10 ^{13}C NMR spectrum of **12** in $CDCl_3$



FigS 11 ^{1}H NMR spectrum of **1** in $CDCl_3$

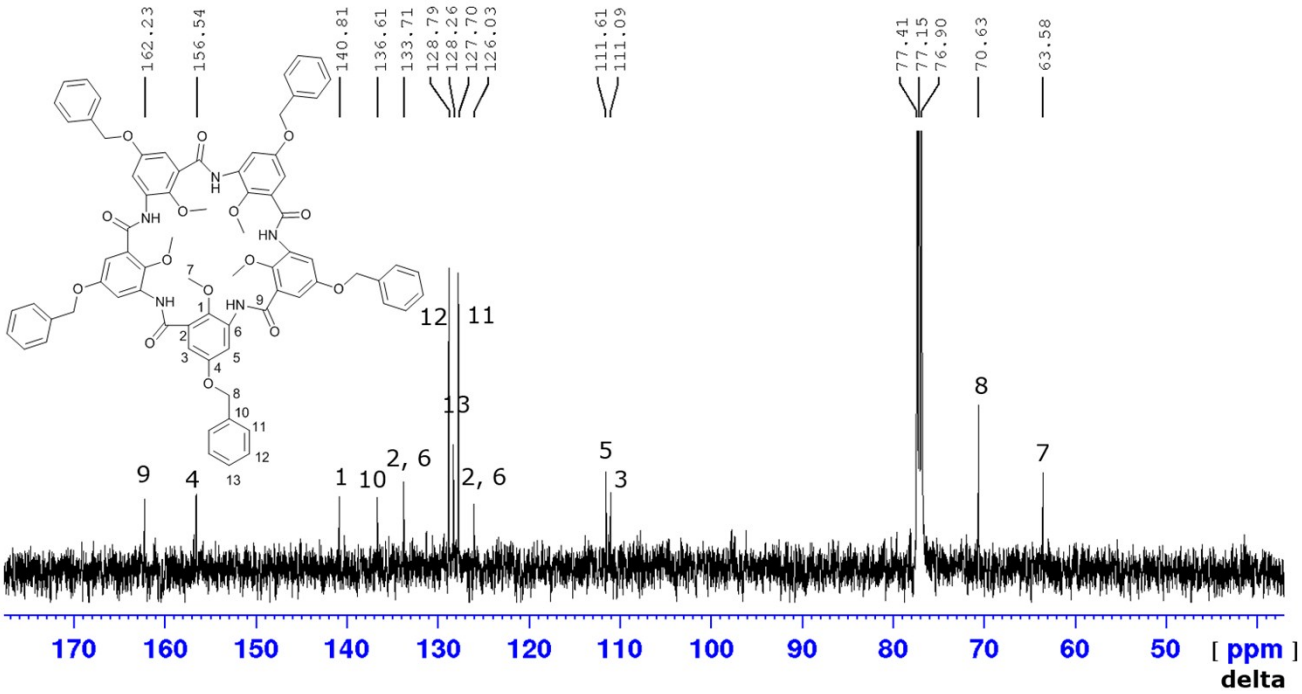


Fig S12 ^{13}C NMR spectrum of **1** in $CDCl_3$

1 was symmetric since only eight sets of signals were observed in 1H NMR spectrum. Assignments were achieved via the following steps. First, the proton signals of NH and H7 for the amide and internal methoxy could be assigned unambiguously to the

singlets at 10.93ppm and 4.01 ppm by comparison with the peaks for all the other amide and internal methoxy protons of other methoxy pentamers which were observed between 10.8 – 11.0 ppm and 4.10 – 4.00 ppm, respectively.[1, 2] The proton signal of H8 for the methylene of benzyl could also be assigned unambiguously to the singlet at 5.20 ppm due to peaks for all the protons of benzyl-containing monomers (**8**, **9**, **10** and **12**) observed between 5.02 – 5.13 ppm. The integrations for Ha, H7 and H8 also matched 5, 10 and 15 protons, respectively. The carbon signal at 162.22 ppm could also be assigned unambiguously to C9 by comparison with the carbonyl carbons of other methoxy pentamers observed between 162.91 – 162.33 ppm.[1, 2] The carbon signals of C7 and C8 were assigned at 63.57 ppm and 70.62 ppm, respectively according to correlation in the HSQC spectrum. Based on integration of 5 protons and correlation in the COSY spectrum, the downfield doublet at 8.72 ppm was assigned to H3 or H5 and the doublet at 7.59 ppm was definitely assigned to the other pair. According to correlation between the carbon signal of C9 and the proton signal of H3 in the HMBC spectrum, the 63 doublets at 8.72 ppm and 7.59 ppm were assigned to H5 and H3, respectively as correlation between C9 and H3 and no correlation between C9 and H5 were observed. Therefore, the other proton signal at 7.59 ppm could be assigned to H5. Based on the HSQC spectrum, the carbon signals at 111.09 ppm and 111.60 ppm could be assigned to C3 and C5, respectively and correlation between Ha and C5 in the HMBC spectrum also agreed. The proton signals in the aromatic region (7.5 ppm) could be assigned to the benzyl protons. Based on integration of 5H, the doublet at 7.36 ppm could be assigned to H13. The carbon signal of C13 was at 128.25 ppm according to correlation in the HSQC spectrum. The other doublet at 7.51 ppm could be assigned to H11 which was integrated 10 H. The carbon signal of C11 was at 127.70 ppm according to correlation in the HSQC spectrum. The remaining triplet at 7.43 ppm could be assigned to H12 which was also integrated 10 protons. The carbon signal of C12 was at 128.78 ppm according to correlation in the HSQC spectrum. The remaining quaternary carbons (C1, C2, C4, C6 and C10) were assigned according to the HMBC spectrum. Based on correlation between the signals of H3, H5 and H7 and the signal of C1, the carbon signal at 140.81 ppm could be assigned to C1. The carbon signal at 136.61 ppm was assigned to C10 due to correlation between the signals of H8 and H12 and the signal of C10. Based on correlation between the signals of H3, H5 and H8 and the signal of C4, the carbon signal at 156.54 ppm could be assigned to C4 although the correlation between the signals of H3 and H5 and the signal of C4 were insufficiently strong. The last two signals for quaternary carbons at 133.70 ppm and

126.02 ppm were C2 or C6. Due to no correlation signals observed in the HMBC spectrum, C2 and C6 could not be assigned.

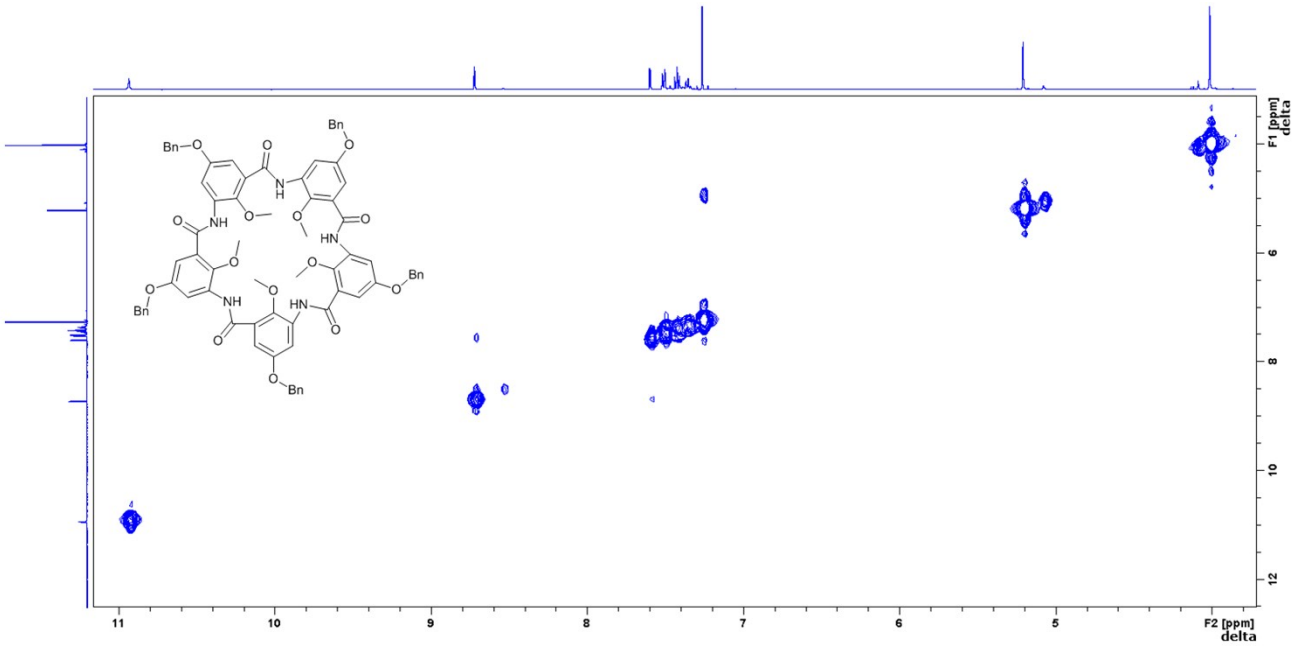


Fig S13 COSY spectrum of **1** in $CDCl_3$

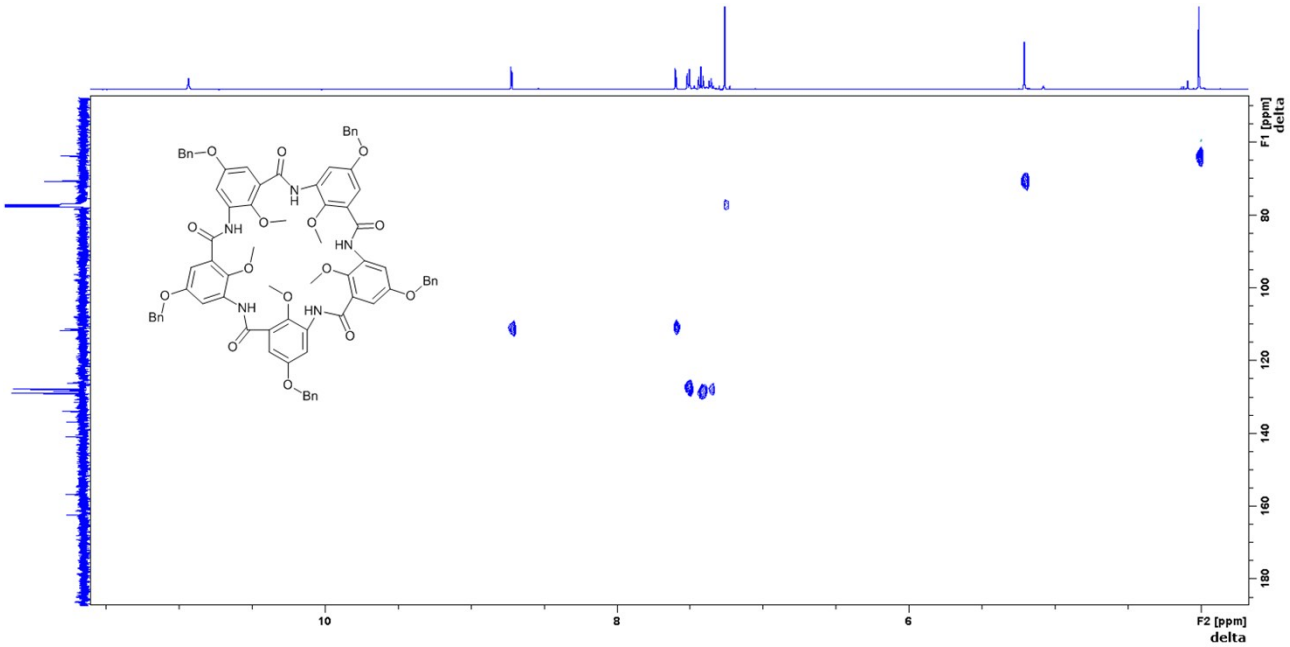


Fig S14 HSQC spectrum of **1** in $CDCl_3$

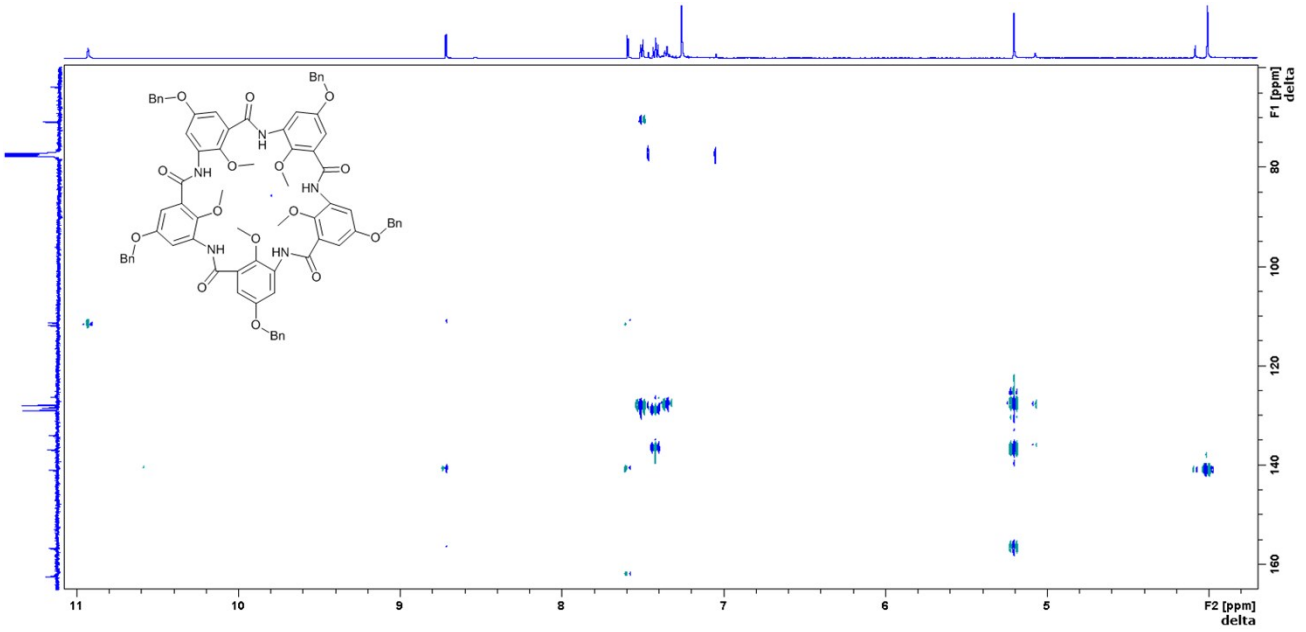


Fig S15 HMBC spectrum of **1** in $CDCl_3$

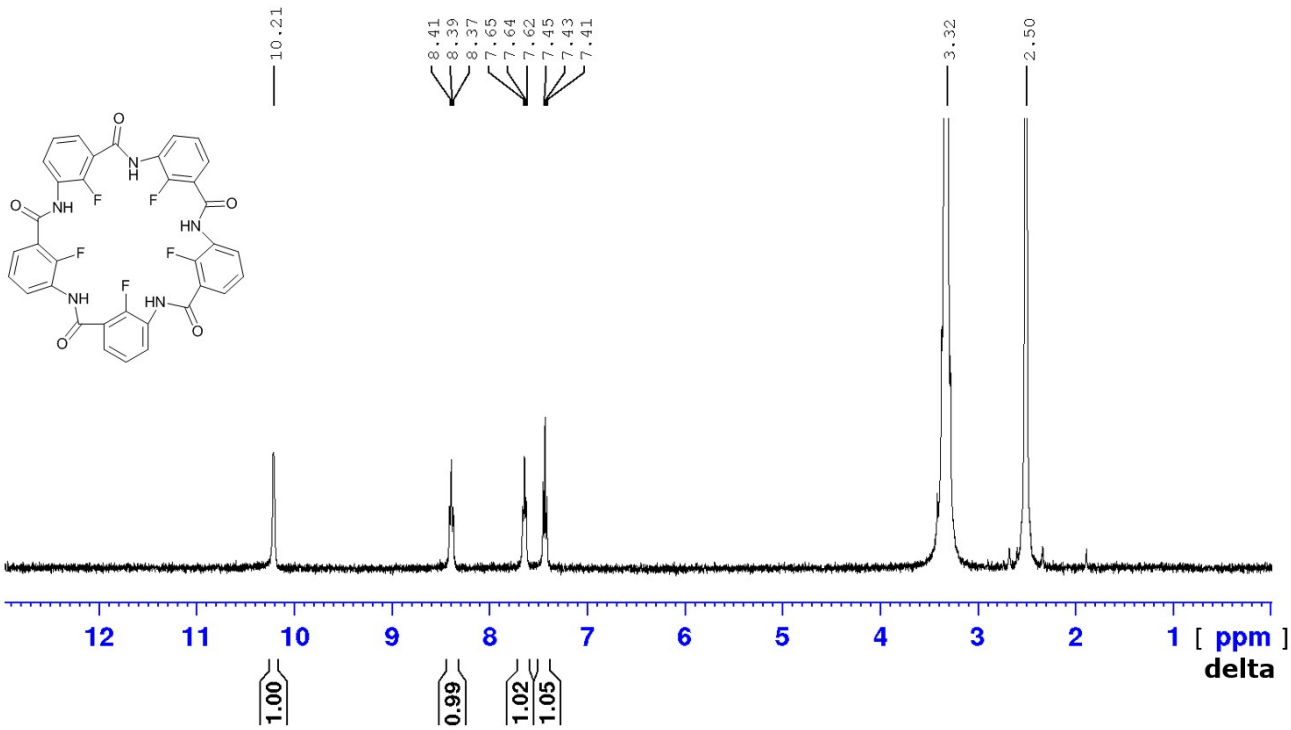


Fig S16 ^{1}H NMR spectrum of **3** in DMSO-d_6

Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Akld University\2014\Nick 03\14-03-31\Seong000005.d	Acquisition Date	31/03/2014 6:00:24 p.m.
Method	130822 - Low.m	Operator	Nick
Sample Name	seong 159	Instrument / Ser#	micrOTOF-Q 10191
Comment	Sample diluted 2uL in 1mL MeOH Sample diluted 100uL in 1mL MeOH CCE = 4		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
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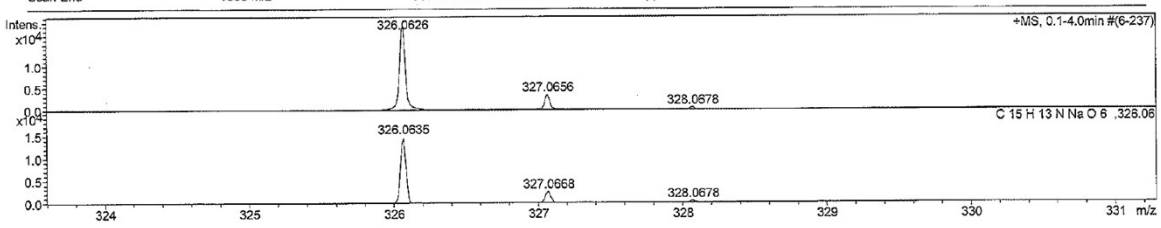
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
326.0626	1	C 15 H 13 N Na O 6	100.00	326.0635	0.9	2.8	5.6	9.5	even	ok

Fig S17 ESI-MS of **8**

Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Akld University\2014\Nick 03\14-03-31\Seong000001.d	Acquisition Date	31/03/2014 5:18:24 p.m.
Method	130822 - Low.m	Operator	Nick
Sample Name	seong 160	Instrument / Ser#	micrOTOF-Q 10191
Comment	Sample diluted 2uL in 1mL MeOH CCE = 4		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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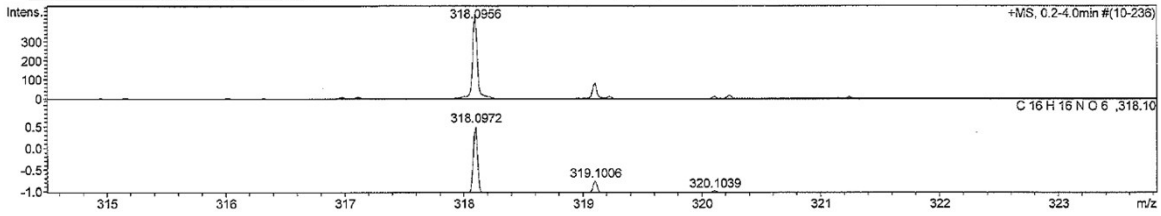
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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	2	C 17 H 15 N 2 Na O 3	55.13	318.0975	1.9	5.8	111.2	11.0	odd	ok

Fig S18 ESI-MS of **9**

Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

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Method	130822 - Low.m	Operator	Nick
Sample Name	seong 160	Instrument / Ser#	micrOTOF-Q 10191
Comment	Sample diluted 2uL in 1mL MeOH CCE = 4		

Acquisition Parameter

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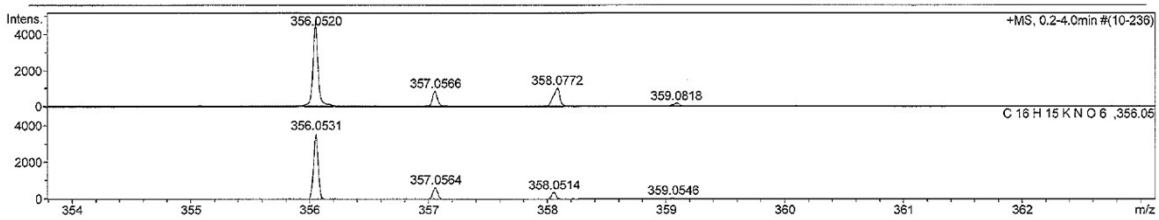
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



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	2	C 17 H 14 K N 2 Na O 3	79.74	356.0534	1.4	3.9	84.0	11.0	odd	ok
	3	C 18 H 12 O 8	18.52	356.0527	0.7	1.9	107.9	13.0	odd	ok
	4	C 16 H 10 N 3 O 7	16.93	356.0513	-0.7	-1.8	110.1	13.5	even	ok
	5	C 19 H 11 N Na O 5	13.99	356.0529	1.0	2.7	110.5	14.5	even	ok
	6	C 17 H 9 N 4 Na O 4	17.23	356.0516	-0.4	-1.1	112.3	15.0	odd	ok
	7	C 17 H 6 N 7 O 3	14.34	356.0527	0.7	1.9	112.9	18.5	even	ok
	8	C 18 H 5 N 8 Na	10.49	356.0529	1.0	2.7	116.0	20.0	odd	ok

Fig S19 ESI-MS of **9**

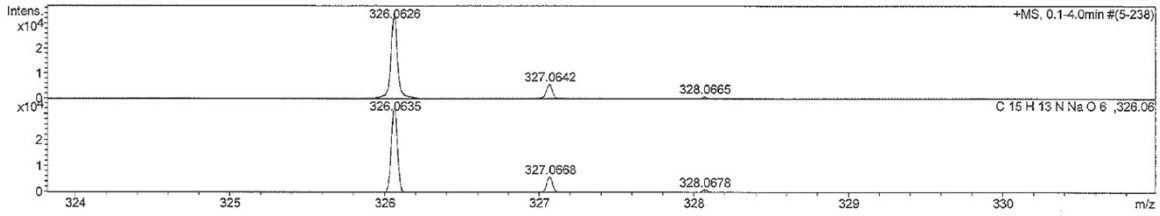
Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Akld University\2014\Nick 04\14-04-02\Seong000003.d	Acquisition Date	2/04/2014 1:04:27 p.m.
Method	130822 - Low.m	Operator	Nick
Sample Name	seong 161	Instrument / Ser#	micrOTOF-Q 10191
Comment	Sample dissolved in 1mL MeOH Sample diluted 2uL in 1mL MeOH CCE = 8		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 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	150.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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	2	C 14 H 14 O 9	100.00	326.0632	0.6	2.0	9.0	8.0	odd	ok

Fig S20 ESI-MS of **10**

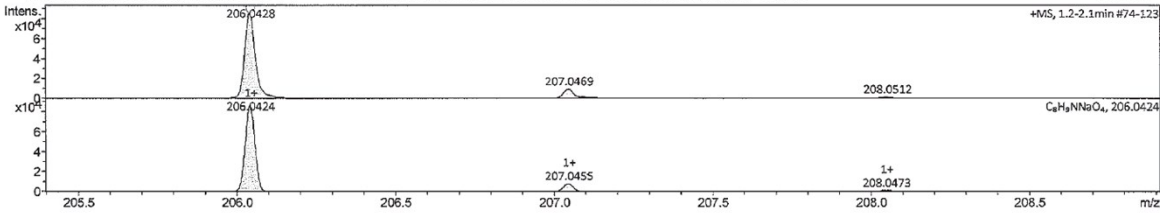
Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Bruker\Data\Tony14\Tony07\14-07-16\run1\seong162_RA4_01_403.d	Acquisition Date	7/16/2014 1:17:53 PM
Method	may2014 - low - hplc.m	Operator	Tony
Sample Name	seong162	Instrument / Ser#	micrOTOF-Q 228888.10191
Comment	Sample in 2mg/mL MeCN/MeOH Sample diluted 5uL in 1mL MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 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	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
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	2	C6H4N7O2	206.0421	-3.2	12.9	2	89.85	8.5	even	ok
	3	C7H10O7	206.0421	-3.2	18.7	3	80.07	3.0	odd	ok
	1	C8H9NNaO4	206.0424	-1.8	11.5	1	100.00	4.5	even	ok

Fig S21 ESI-MS of **11**

Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

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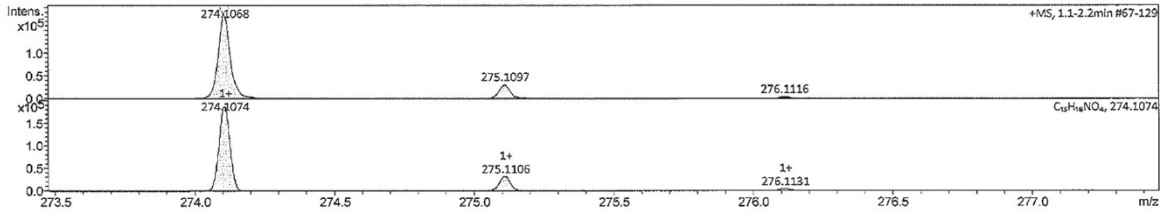
Method	may2014 - low - hplc.m	Operator	Tony
Sample Name	seong162-3	Instrument / Ser#	micrOTOF-Q 228888.10191
Comment	Sample dissolved in 1mL MeOH @ 2mg/mL Sample diluted 3uL in 1mL MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 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	150.0 Vpp	Set Divert Valve	Waste



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	2	C15H16NO4	274.1074	2.3	3.7	2	100.00	8.5	even	ok
	1	C13H14N4O3	274.1060	2.6	3.4	1	95.31	9.0	odd	ok
	2	C15H16NO4	274.1074	2.3	3.7	2	100.00	8.5	even	ok
	1	C14H13N5Na	274.1063	1.6	6.3	1	100.00	10.5	even	ok
	2	C16H15N2NaO	274.1077	-3.3	11.4	2	72.51	10.0	odd	ok

Fig S22 ESI-MS of **12**

Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

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Comment	Sample dissolved in MeCN @ 2mg/ml Sample diluted 3ul in 1ml MeCN		

Acquisition Parameter

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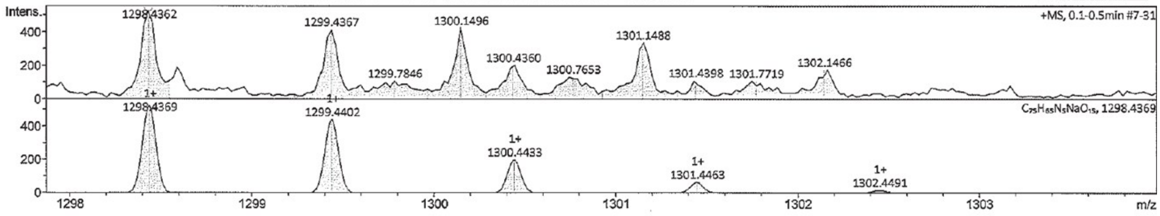
Scan End	3000 m/z	Set Collision Cell RF	1600.0 Vpp	Set Divert Valve	Waste		



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1298.4362	1	C75H65N5NaO15	1298.4369	0.6	42.5	1	100.00	45.5	even	ok

Fig S23 ESI-MS of **1**

Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

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Method	May2014 Wide.m	Operator	Tony
Sample Name	seong185a	Instrument / Ser#	micrOTOF-Q 228888.10191
Comment	Sample dissolved in 0.2ml MeOH Sample diluted 10ul in 0.5ml MeOH fast forward		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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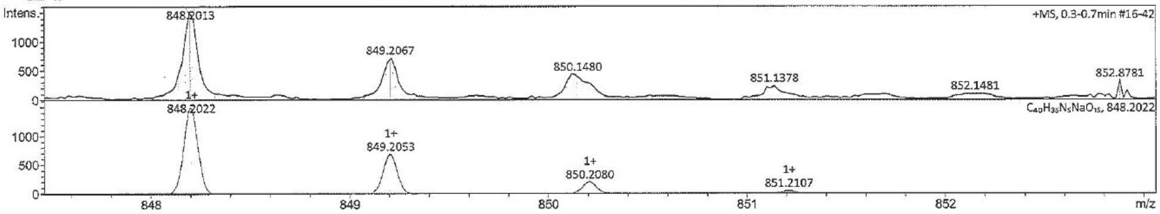

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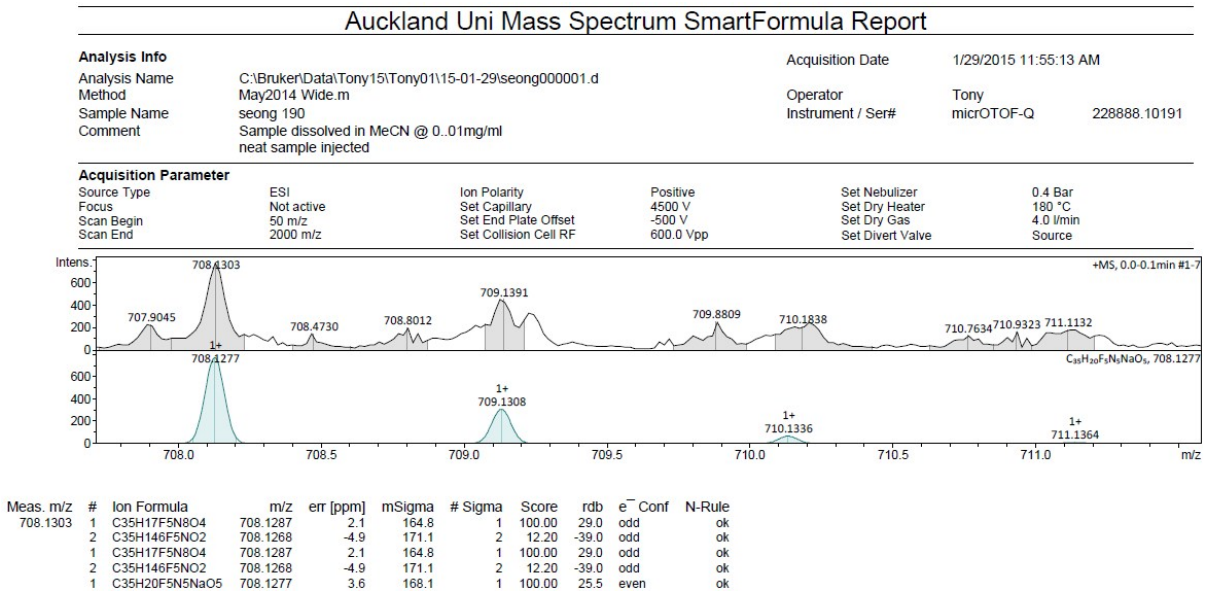
	2	C40H22N19O5	848.2046	3.9	78.7	2	29.51	39.5	even	ok
	1	C40H32N8O14	848.2032	-2.3	78.0	1	100.00	29.0	odd	ok
	2	C40H22N19O5	848.2046	3.9	78.7	2	29.51	39.5	even	ok
	1	C40H32N8O14	848.2032	-2.3	78.0	1	100.00	29.0	odd	ok
	2	C40H22N19O5	848.2046	3.9	78.7	2	29.51	39.5	even	ok
	1	C40H35N5NaO15	848.2022	-1.1	79.5	1	100.00	25.5	even	ok
	2	C40H25N16NaO6	848.2035	-2.6	79.5	2	40.46	36.0	odd	ok

Fig S24 ESI-MS of **2**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
708.1303	1	C35H17F5N8O4	708.1287	2.1	164.8	1	100.00	29.0	odd	ok
	2	C35H146F5NO2	708.1268	-4.9	171.1	2	12.20	-39.0	odd	ok
	1	C35H17F5N8O4	708.1287	2.1	164.8	1	100.00	29.0	odd	ok
	2	C35H146F5NO2	708.1268	-4.9	171.1	2	12.20	-39.0	odd	ok
	1	C35H20F5N5NaO5	708.1277	3.6	168.1	1	100.00	25.5	even	ok

Fig S25 ESI-MS of **3**

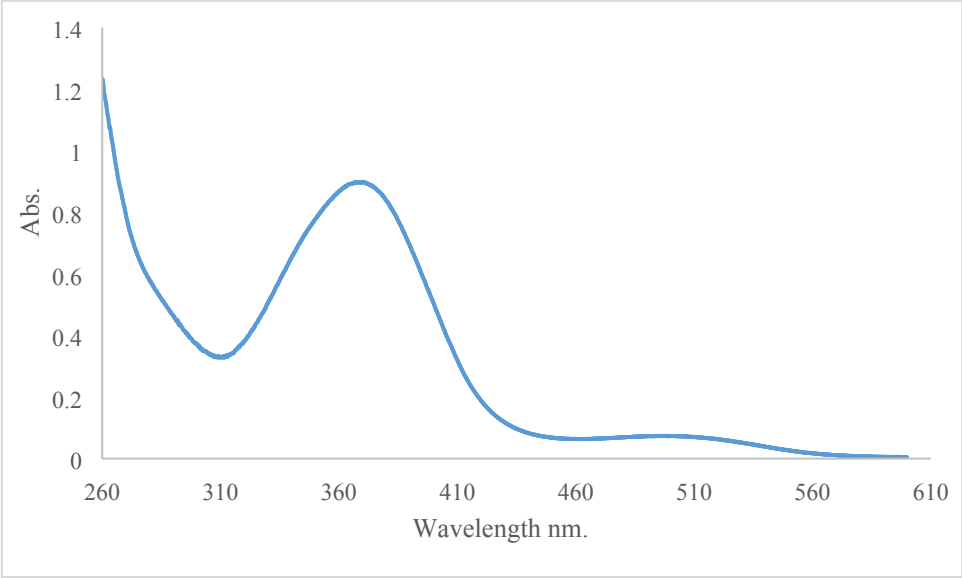


Fig S26 UV-Vis spectrum of **8** (2.7 x 10^{-4} mol.L^{-1} in DMSO)

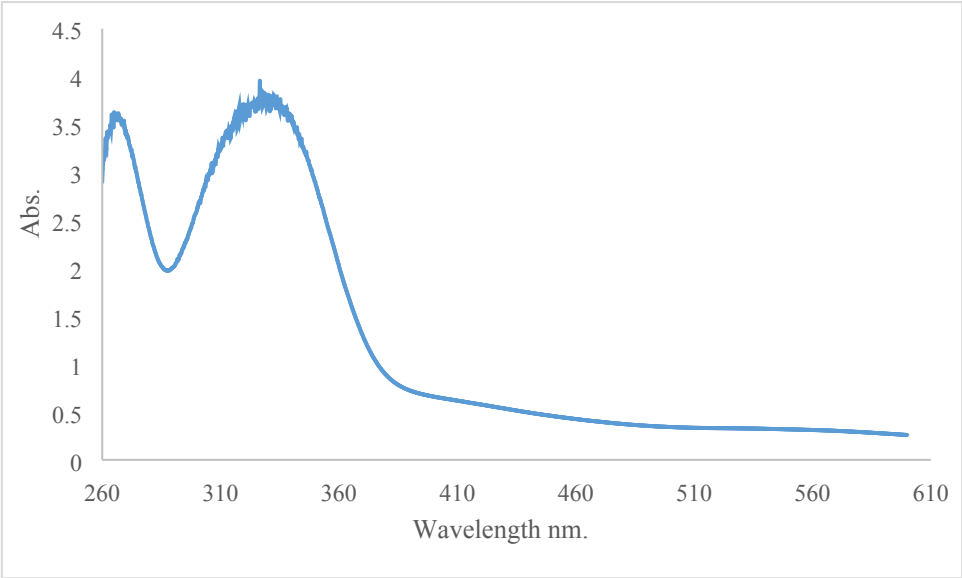


Fig S27 UV-Vis spectrum of **11** (9.1 x 10^{-4} mol.L^{-1} in DMSO)

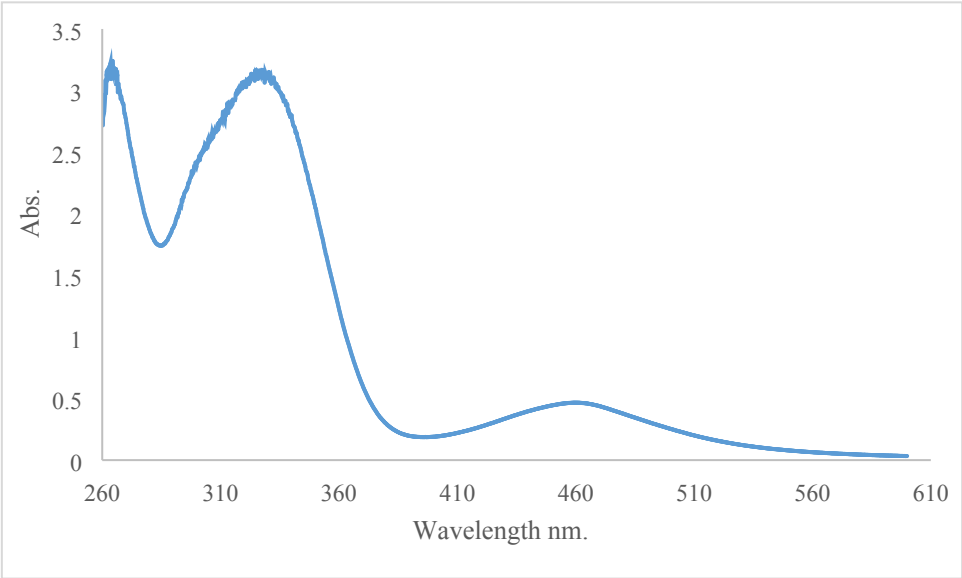


Fig S28 UV-Vis spectrum of **12** (9.7 x 10^{-4} mol.L^{-1} in DMSO)

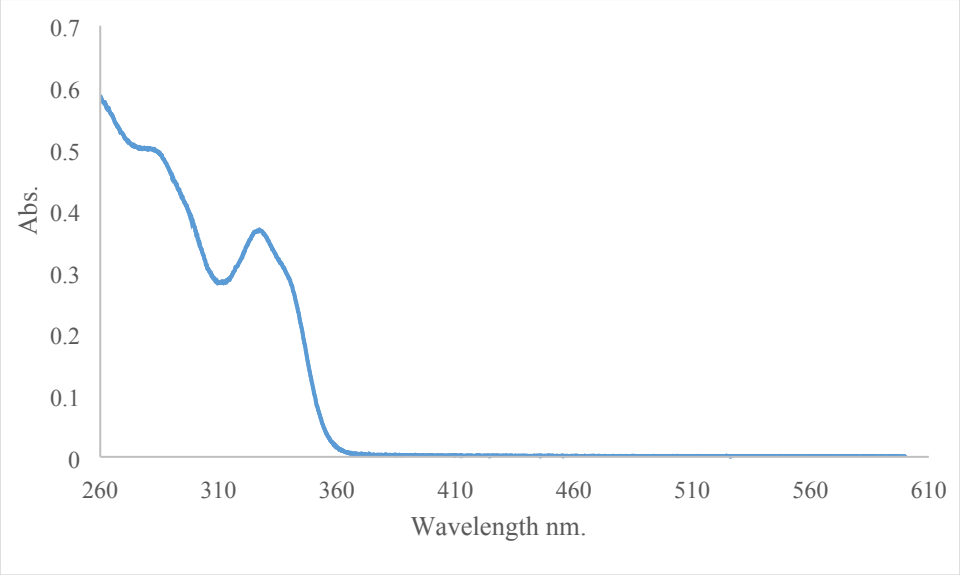


Fig S29 UV-Vis spectrum of **1** (2.6 x 10^{-5} mol.L^{-1} in DMSO)

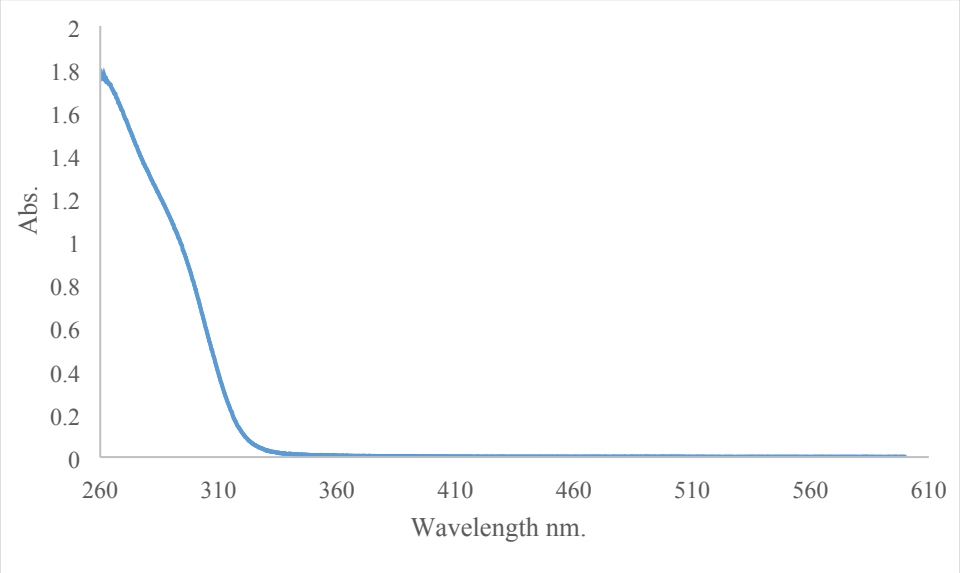


Fig S30 UV-Vis spectrum of **3** (7.3 x 10^{-5} mol.L^{-1} in DMSO)

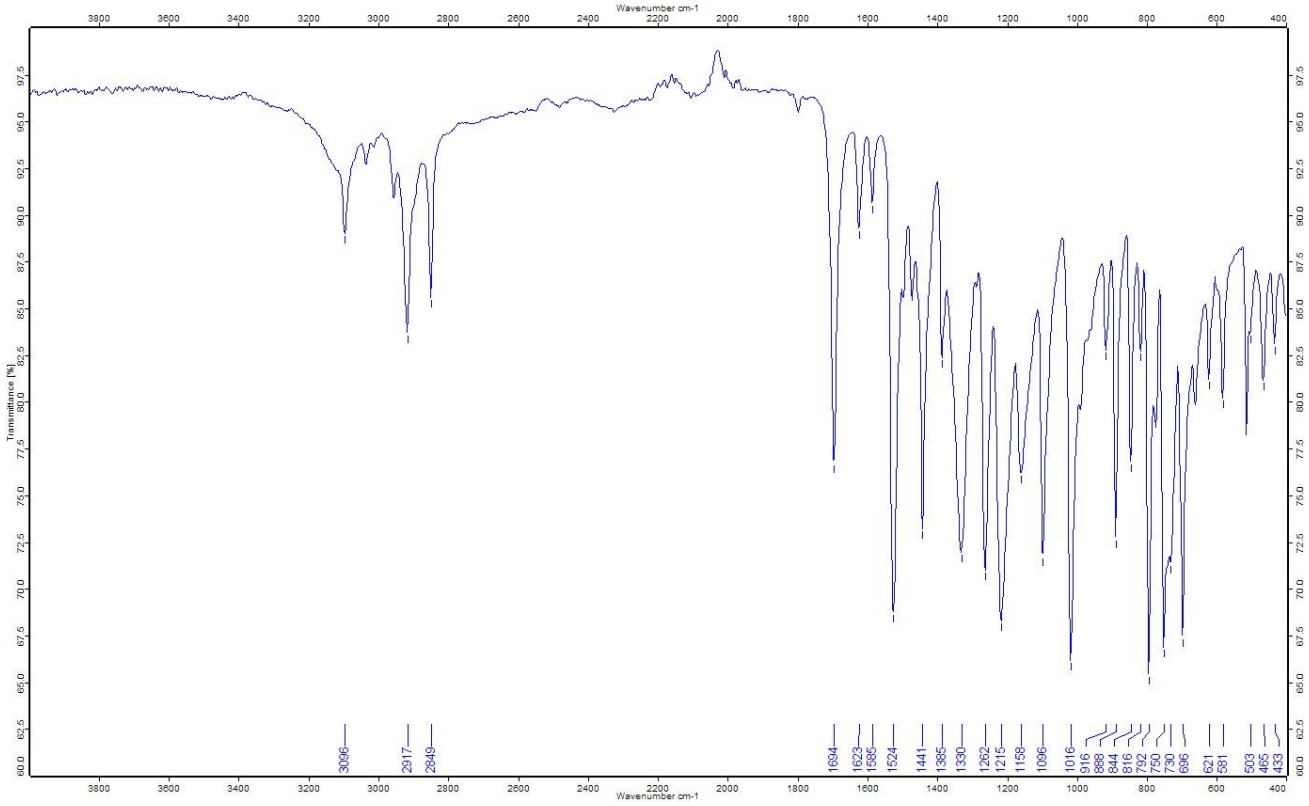


Fig S31 IR spectrum of **8**

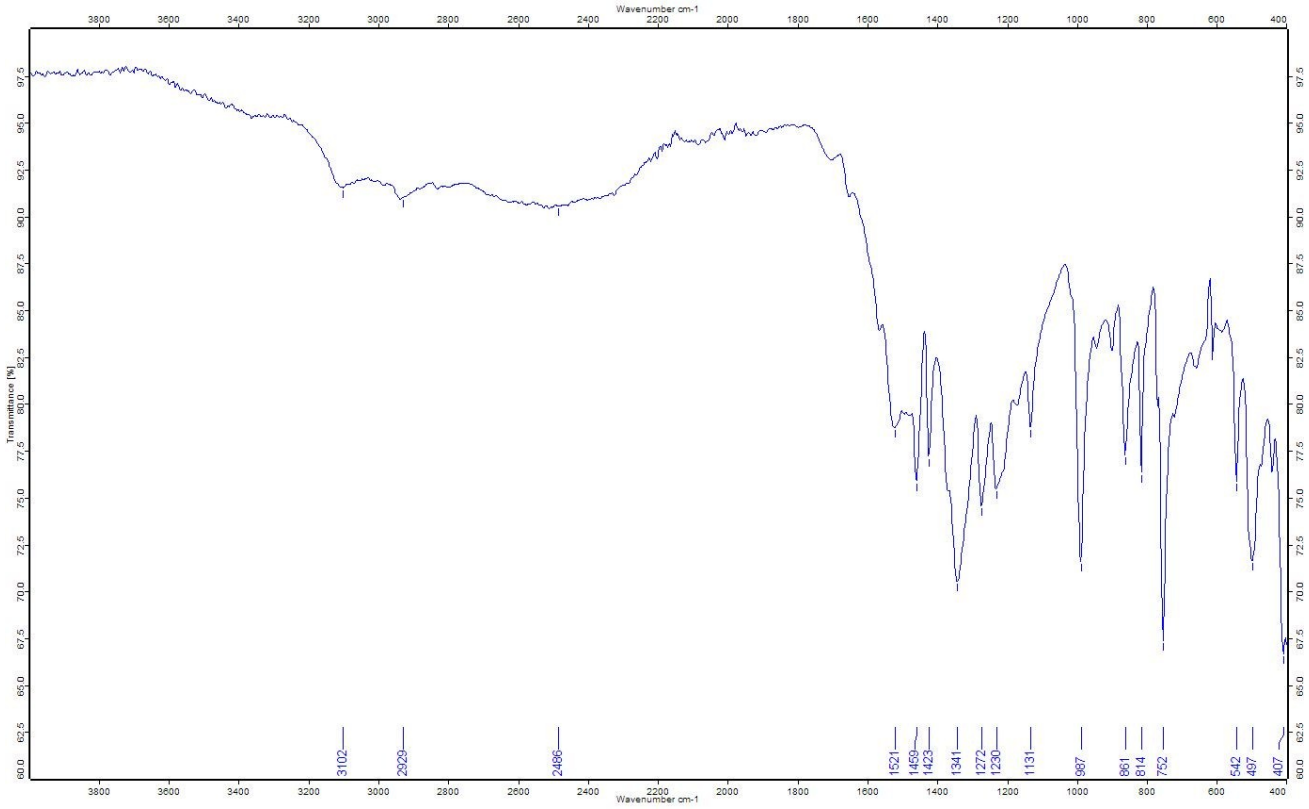


Fig S32 IR spectrum of **11**

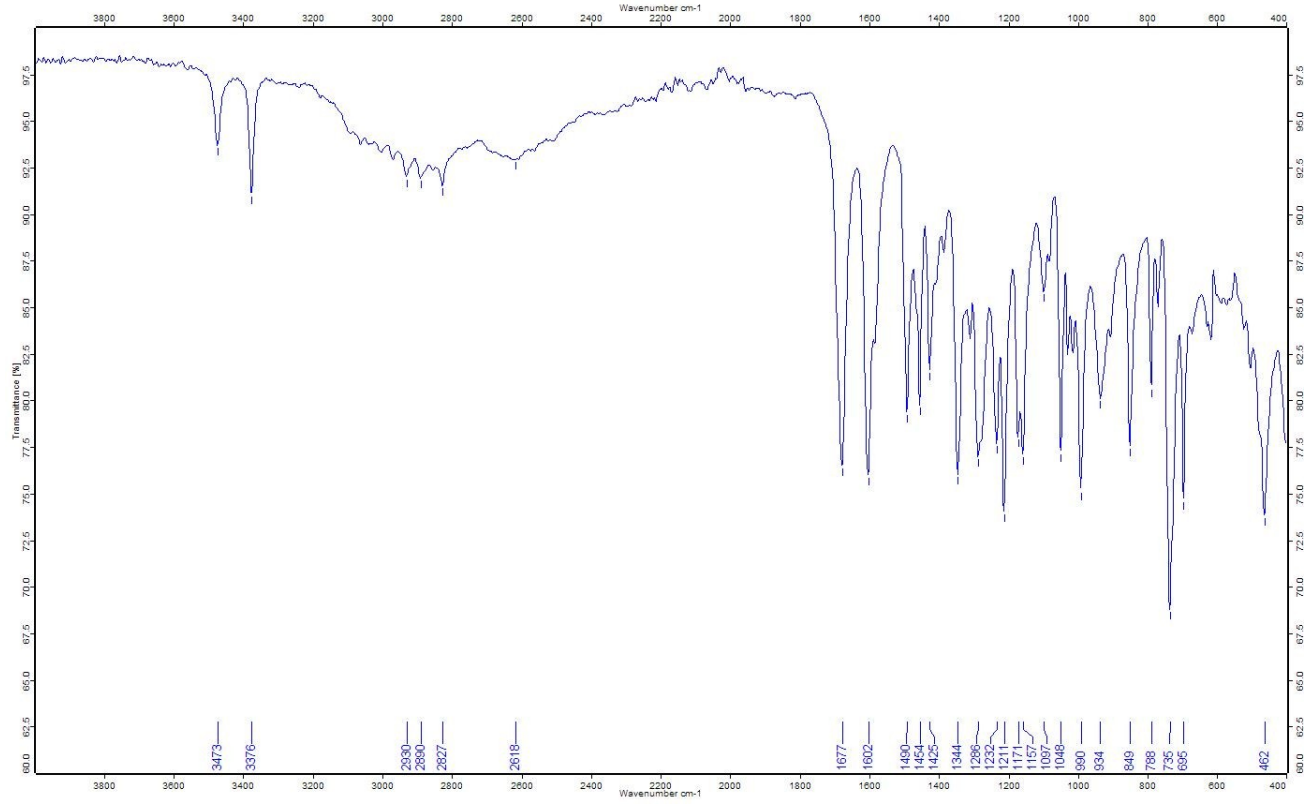


Fig S33 IR spectrum of **12**

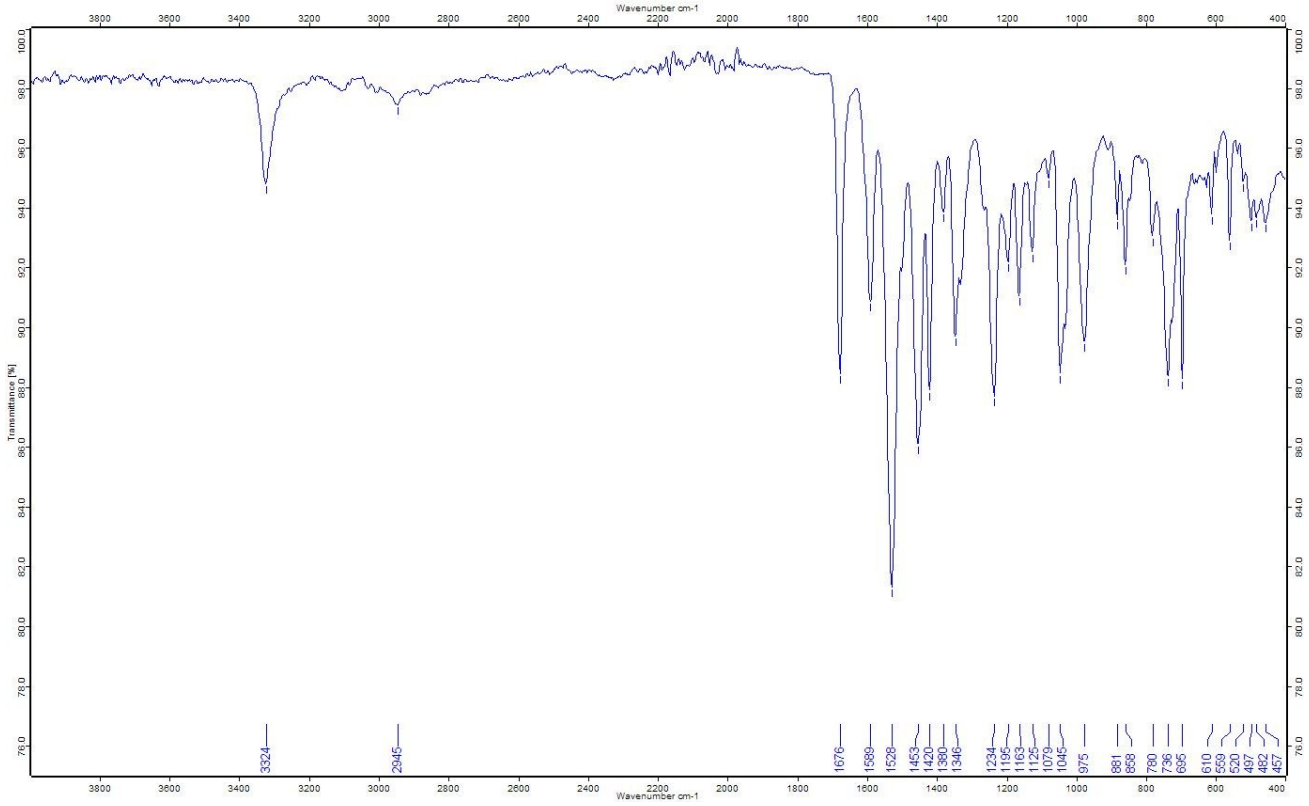


Fig S34 IR spectrum of **1**

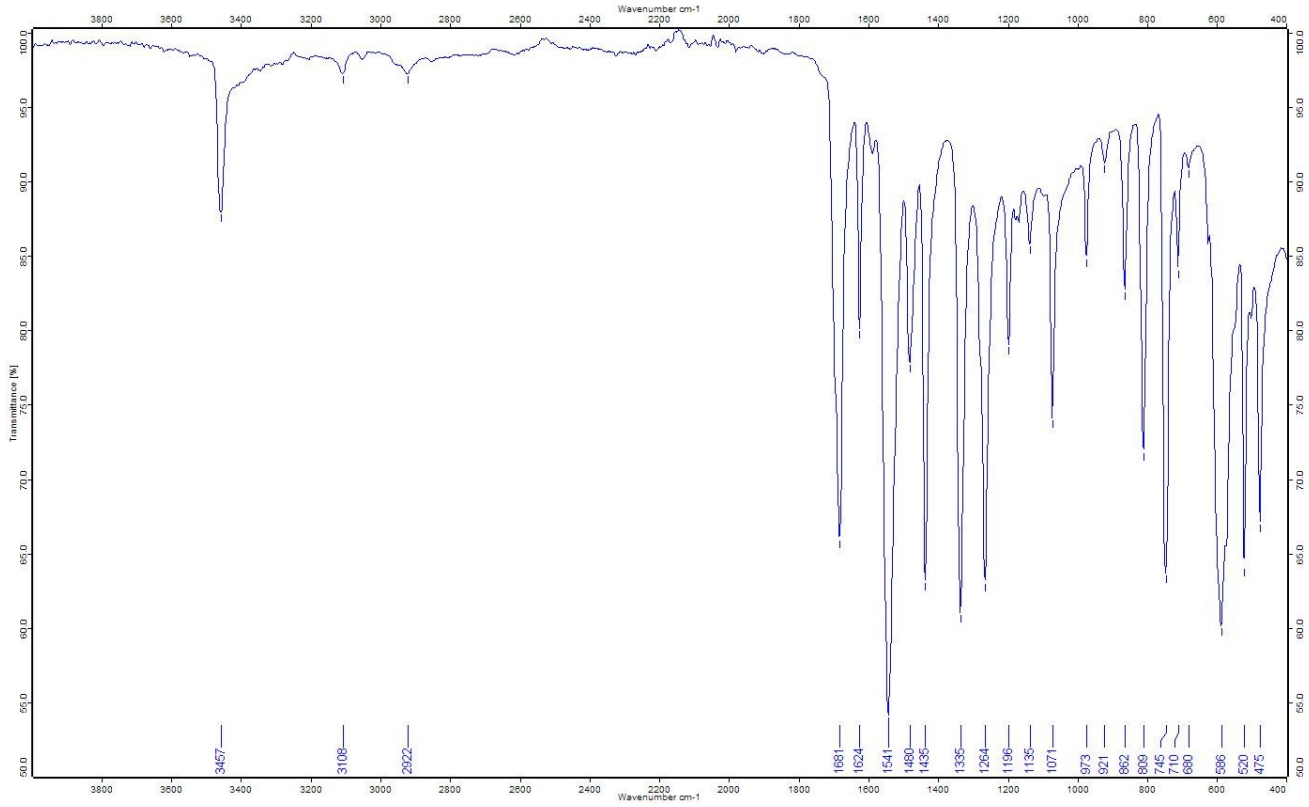


Fig S35 IR spectrum of **3**

References

1. B. Qin, C. Sun, Y. Liu, J. Shen, R. Ye, J. Zhu, X.-F. Duan and H. Zeng, *Org. Lett.*, 2011, **13**, 2270-2273.
2. B. Qin, X. Chen, X. Fang, Y. Shu, Y. K. Yip, Y. Yan, S. Pan, W. Q. Ong, C. Ren, H. Su and H. Zeng, *Org. Lett.*, 2008, **10**, 5127-5130.