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Supporting Information

Accessing Improbable Foldamer Shapes with Strained Macrocycles

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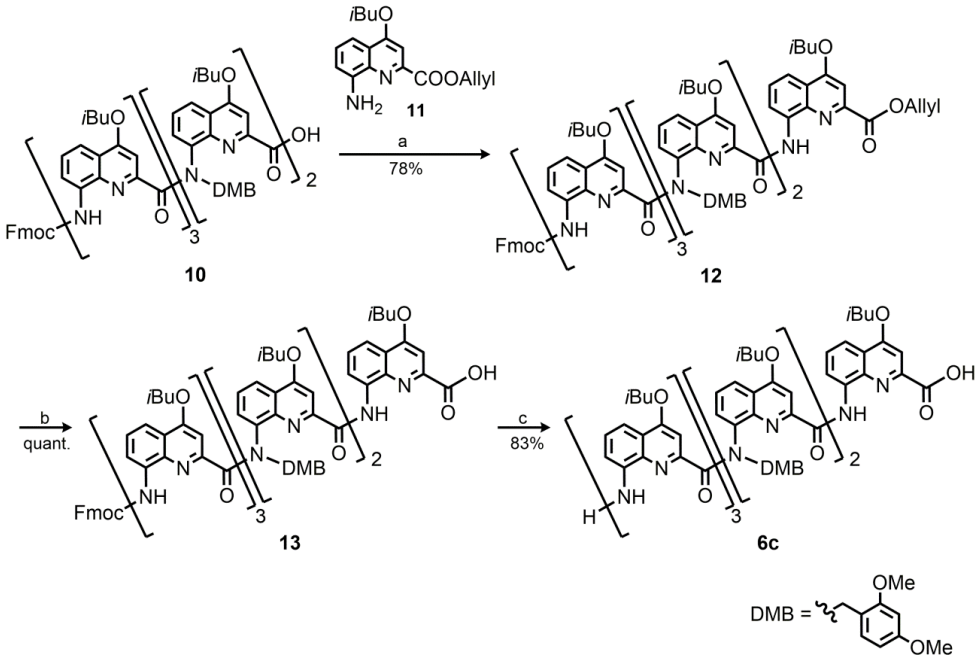
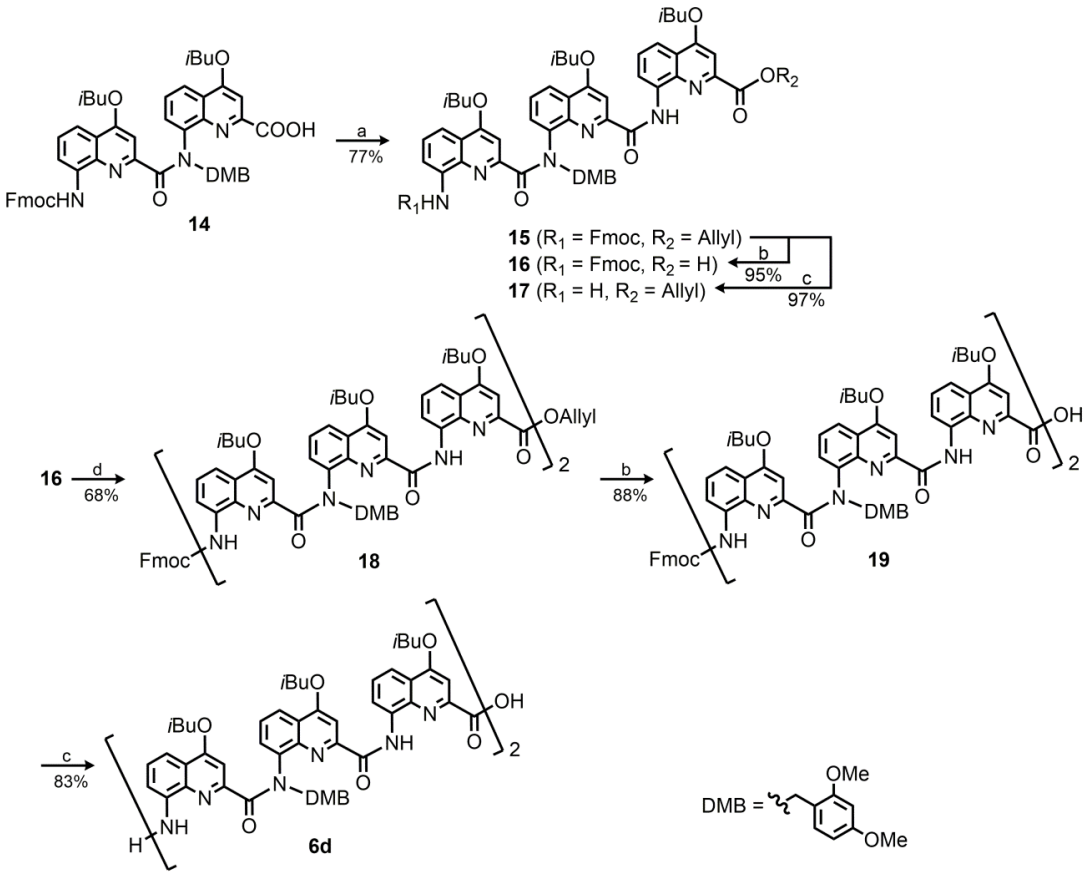
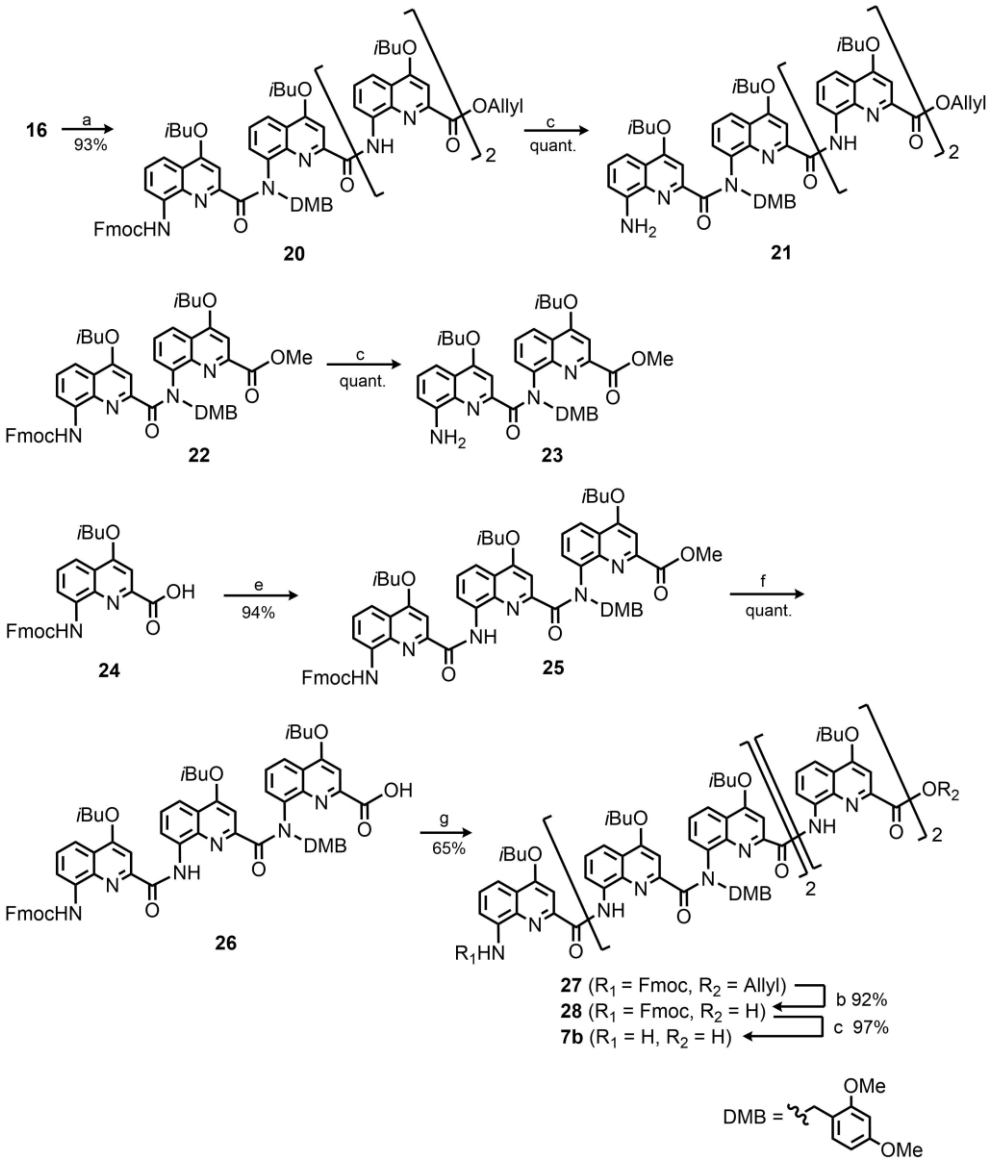
1) Synthetic schemes



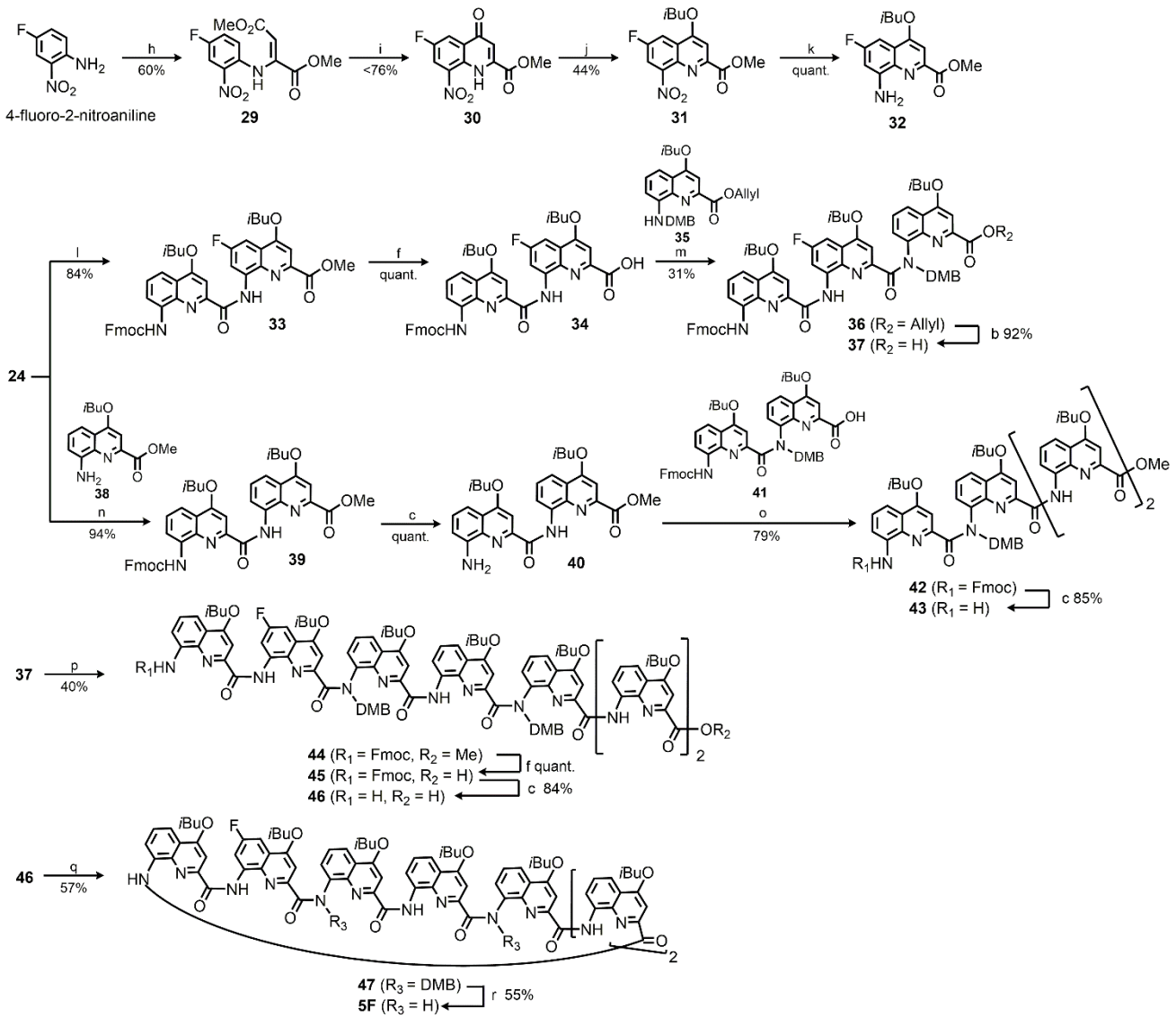
Scheme S1. Synthesis of **6c** a) Ghosez's reagent, **11**, DIPEA, $CHCl_3$. b) $Pd(PPh_3)_4$, $PhSiH_3$, DCM. c) DBU, DCM.



Scheme S2. Synthesis of **6d** a) Ghosez's reagent, **11**, DIPEA, $CHCl_3$. b) $Pd(PPh_3)_4$, $PhSiH_3$, DCM. c) DBU, DCM. d) Ghosez's reagent, **17**, DIPEA, $CHCl_3$.



Scheme S3. Synthesis of **7b** a) Ghosez's reagent, **11**, DIPEA, $CHCl_3$. c) DBU, DCM. e) $(COCl)_2$, **23**, DIPEA, $CHCl_3$. f) LiI, AcOEt, 80°C. g) Ghosez's reagent, **21**, DIPEA, $CHCl_3$.



Scheme S4. Synthesis of **7b** h) dimethylacetylene dicarboxylate, MeOH, reflux. i) diphenylether, reflux. j) *i*BuOH, DIAD, PPh_3, THF. k) Pd/C, H_2, MeOH. l) $(COCl)_2$, **32**, DIPEA, $CHCl_3$. m) $(COCl)_2$, **35**, DIPEA, $CHCl_3$. n) $(COCl)_2$, **38**, DIPEA, $CHCl_3$. o) Ghosez's reagent, **41**, DIPEA, $CHCl_3$. p) Ghosez's reagent, **43**, DIPEA, $CHCl_3$. q) PPh_3, trichloroacetonitrile, DIPEA, $CHCl_3$. r) TFA (neat), 60°C.

2) NMR studies

For the structural elucidation of **4**, 1D and 2D NMR spectra were recorded on a Bruker Avance III Nanobay NMR spectrometer (Bruker BioSpin) operating at 400,13MHz for ^{1}H observation using a 5mm dual SmartProbe with gradient, and on a Bruker Avance NEO NMR spectrometer (Bruker BioSpin) operating at 700,15MHz for ^{1}H observation and 176,05MHz for ^{13}C observation equipped with a 5mm TXI probe with gradient. All NMR experiments were performed at 258K. For ^{1}H NMR experiment at 400MHz, a single pulse sequence was recorded with 10µs for 90° pulse, a sweep width of 10kHz, a recycling delay of 2s, a number of 32 scans. 2D ^{1}H-^{1}H COSY and ^{1}H-^{1}H ROESY NMR spectra were recorded with 10µs for hard pulse, a sweep width of 6kHz, a recycling delay of 2s and respectively 16 and 80 scans. The number of points was 2048 and 128 or 256 complex points in the direct and indirect acquisition. For ^{1}H NMR experiment at 700MHz, a single pulse sequence was recorded with 8µs for 90° pulse, a sweep width of

11,4kHz, a recycling delay of 2s, a number of 24 scans. 2D ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC NMR spectra were performed with 8µs and 12µs for respectively 1H and 13C hard pulse, a sweep width of 11,4kHz and 29,1kHz or 38,8kHz, a recycling delay of 2s and respectively 32 and 96 scans, a long-range coupling constant of 8Hz for HMBC. The number of points was 2048 and 256 complex points in the direct and indirect acquisition. All NMR data had processed with Topspin software (Bruker BioSpin).

For the investigation of the fluxional behavior of **5F**, ^{1}H and ^{19}F NMR spectra were recorded on a Bruker Avance III Nanobay NMR spectrometer (Bruker BioSpin) operating respectively at 400,13MHz and 376,50MHz for ^{1}H and ^{19}F observation, using a 5mm dual SmartProbe with gradient. All NMR experiments were performed at 323K. For ^{1}H NMR experiment, a single pulse sequence was recorded with 10µs for 90° pulse, a sweep width of 6,8kHz, a recycling delay of 2s, a number of 8 scans. For 19F NMR experiment, a single pulse sequence with proton decoupling were performed with 18µs for hard pulse, a sweep width of 5,6kHz, a recycling delay of 20s and 128 scans. For 2D ^{19}F-^{19}F EXSY NMR spectra, a conventional NOESY with proton decoupling during acquisition was acquired at 2 mixing time at 0 and 300ms. All acquisition parameters were 18µs of hard pulse, a relaxation delay of 2s, a sweep width of 5,3kHz, 128 scans, an acquisition time of 0,194s. The number of points was 2048 and 344 complex points in the direct and indirect acquisition. All NMR data had processed with Topspin software (Bruker BioSpin) and EXSYcalc software (Mestrelab Research)

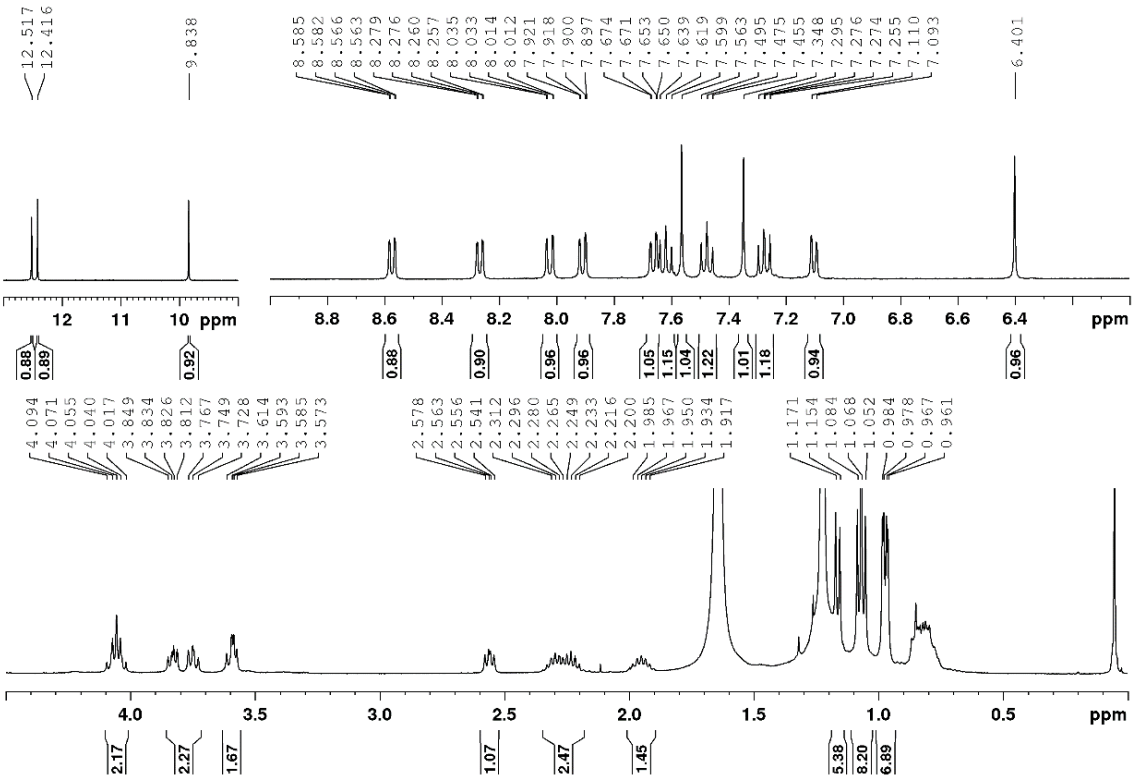


Figure S1. ^{1}H NMR spectrum (700 MHz) of **4** in CD_2Cl_2 at 258 K.

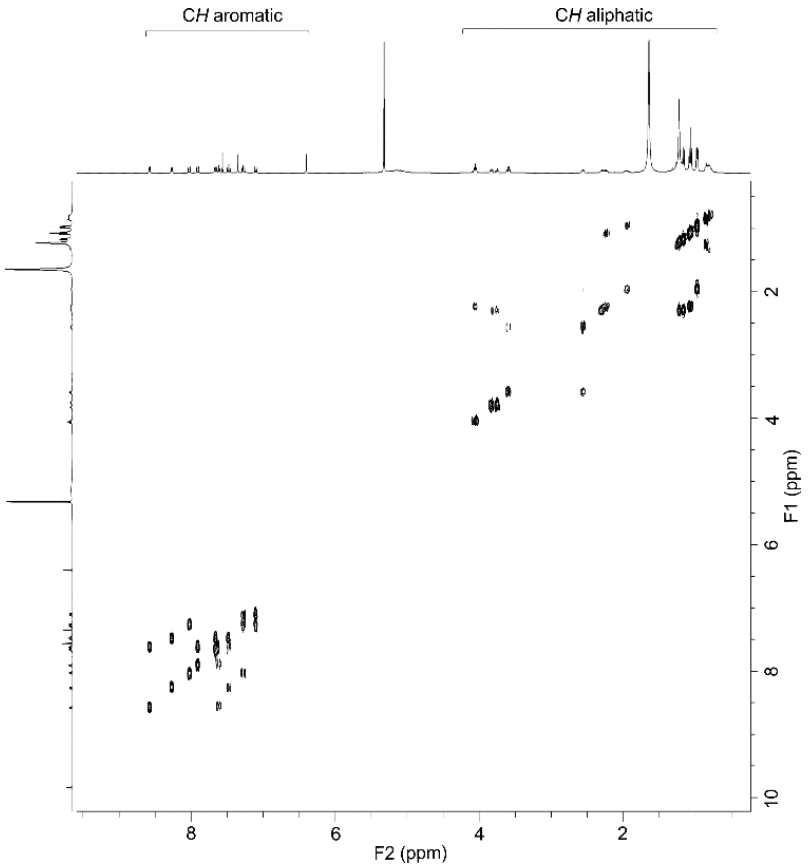


Figure S2. Part of the ^{1}H-^{1}H COSY NMR (400 MHz, 258K) of **4** at 1 mM in CD_2Cl_2.

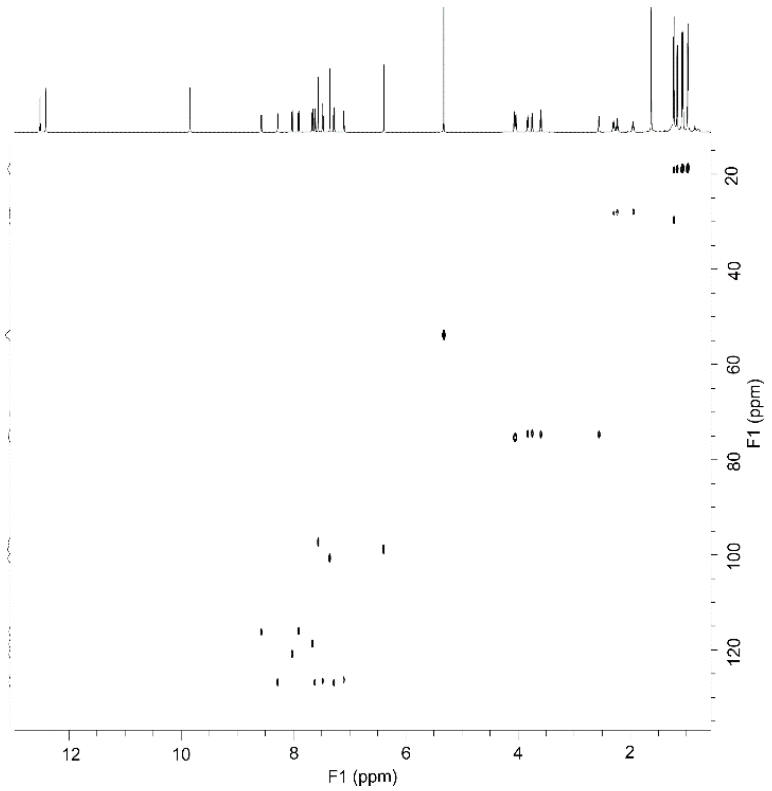


Figure S3. Part of the ^{1}H-^{13}C HSQC NMR (700 MHz, 258K) of **4** at 2 mM in CD_2Cl_2.

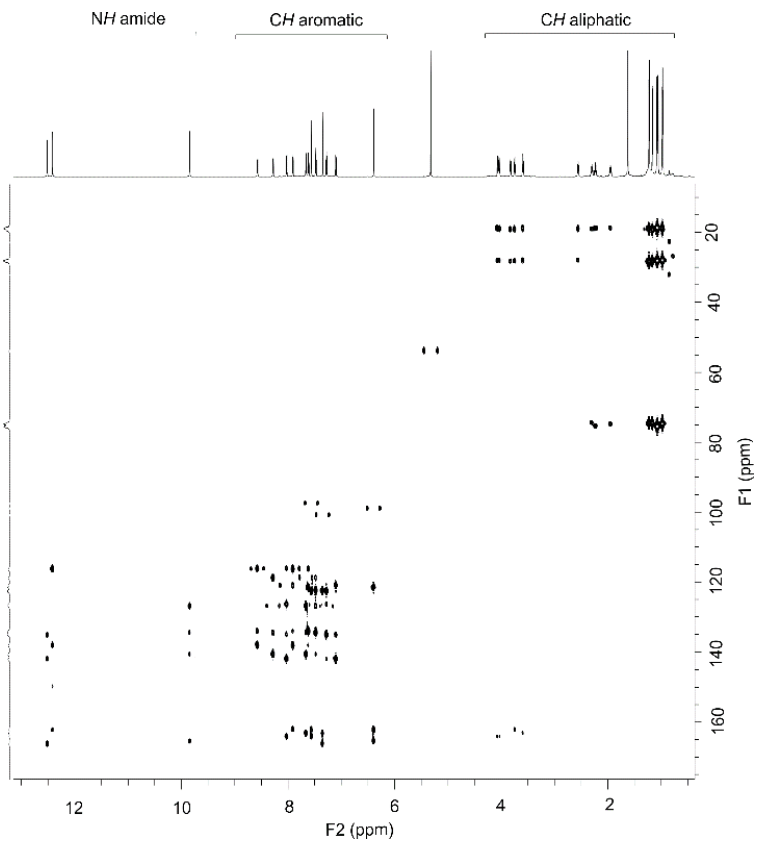


Figure S4. Part of the ^{1}H-^{13}C HMBC NMR (700 MHz, 258K) of **4** at 2 mM in CD_2Cl_2.

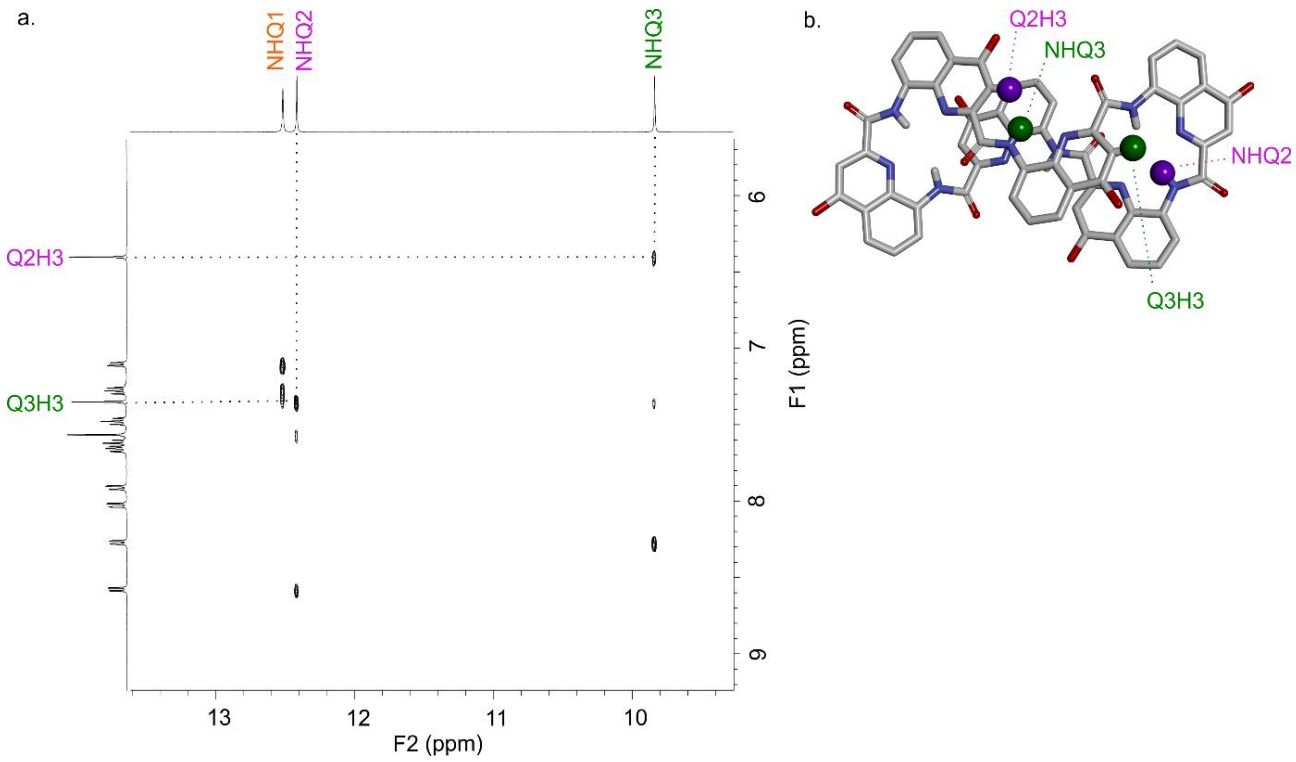
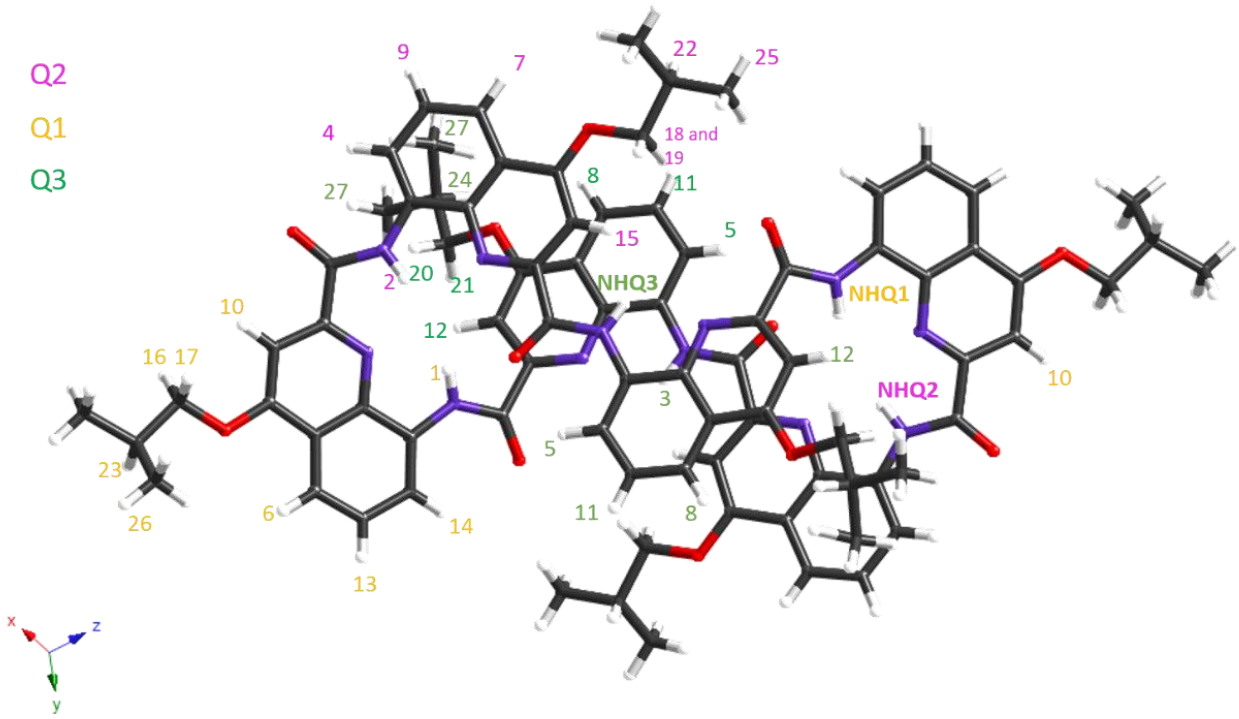


Figure S5: a) Part of the ^{1}H-^{1}H ROESY NMR (400 MHz, 258K, mixing time = 300 ms) of **4** at 1 mM in CD_2Cl_2. Noticeable NOE are highlighted with dashed lines. d) Structure of **4**. Remarkable interaction are shown with colored balls.

Table S1. Assignment of the ^{1}H and ^{13}C chemical shifts of **4** in CD_2Cl_2.

	^{1}H δ (ppm)		^{13}C δ (ppm)
Q1-NH1	12.52		
Q2-NH2	12.42		
Q3-NH3	9.84		
Q2-H4	8.57	Q2-C4	116.2
Q3-H5	8.27	Q3-C5	126.8
Q1-H6	8.02	Q1-C6	120.9
Q2-H7	7.91	Q2-C7	116.1
Q3-H8	7.66	Q3-C8	118.7
Q2-H9	7.62	Q2-C9	126.9
Q1-H10	7.56	Q1-C10	97.3
Q3-H11	7.47	Q3-C11	126.5
Q3-H12	7.35	Q3-C12	100.7
Q1-H13	7.27	Q1-C13	126.9
Q1-H14	7.10	Q1-C14	126.4
Q2-H15	6.40	Q2-C15	98.9
Q1-H16 / H17	4.04 / 4.07	Q1-C	75.4
Q2-H18 / H19	3.75 / 3.83	Q2-C	74.5
Q3-H20 / H21	2.56 / 3.59	Q3-C	74.7
Q2-H22	2.30	Q2-C22	28.2
Q1-H23	2.23	C23	28.0
Q3-H24	1.95	Q3-C24	27.9
Q2-H25	1.16 / 1.22	Q2-C25	19.1
Q1-H26	1.06 / 1.08	C26	18.7
Q3-H27	0.97	Q3-C27	18.7
		Q1-CO	162.2
		Q2-CO	165.4
		Q3-CO	166.2



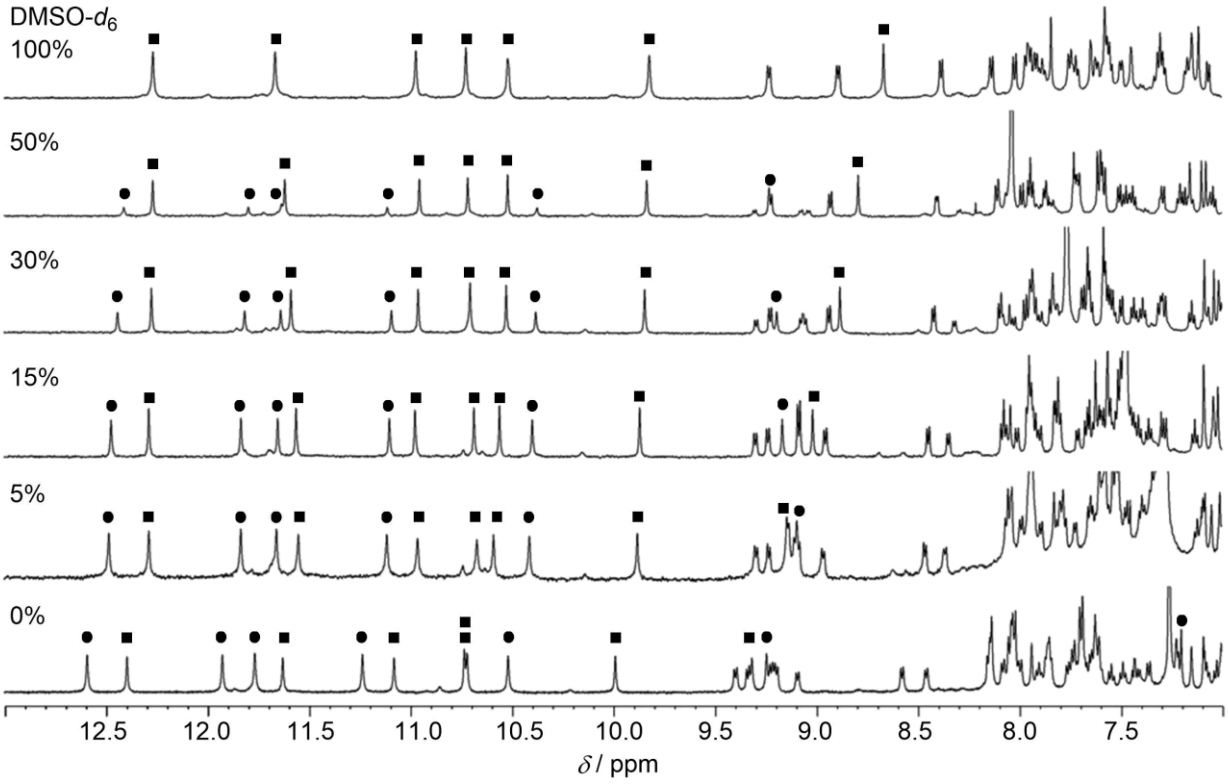


Figure S6. ^{1}H NMR (600 MHz) spectra of **5** at 298 K in DMSO-d_6/$CDCl_3$ mixture solvents.

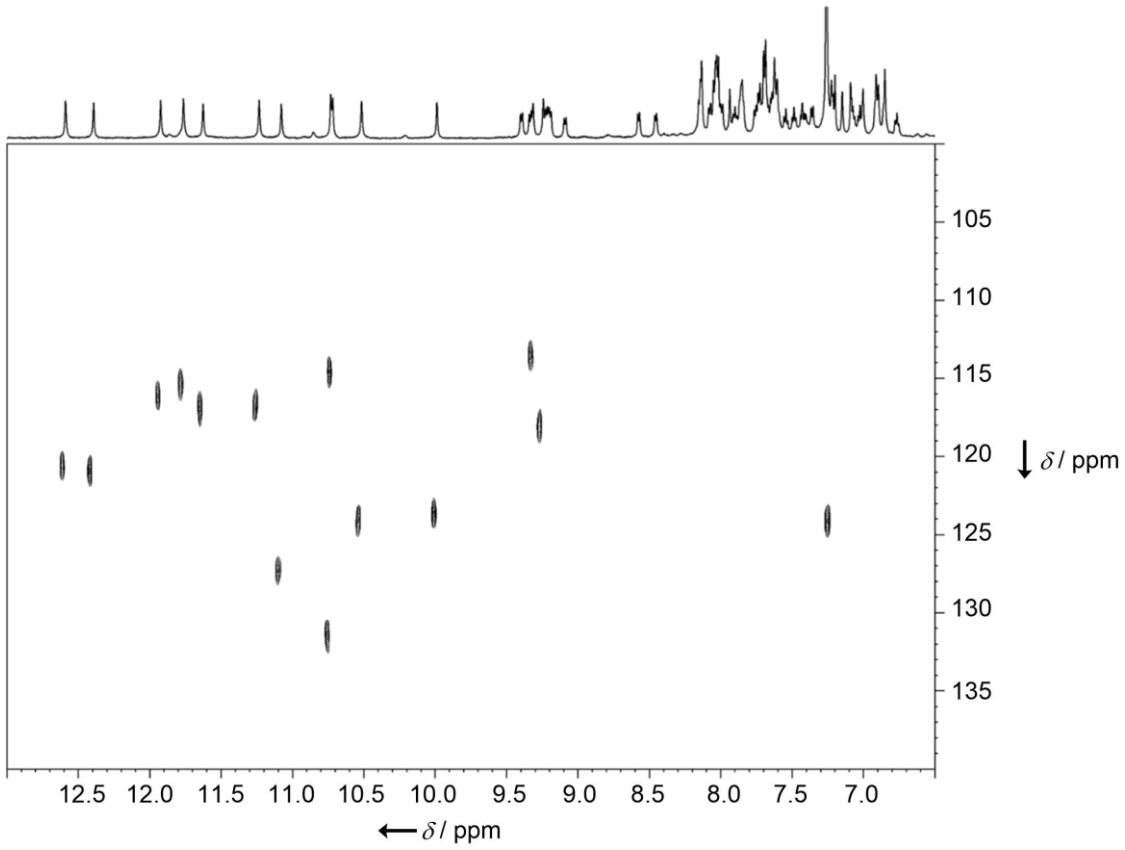


Figure S7. ^{1}H-^{15}N HSQC spectrum (700 MHz) of **5** in $CDCl_3$ at 298 K.

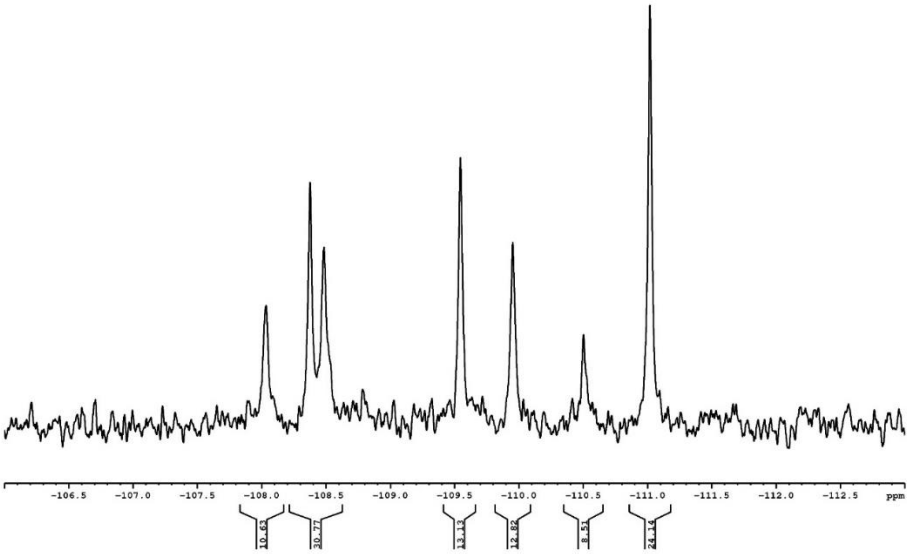


Figure S8. ^{19}F {^{1}H} NMR spectrum (376.5 MHz) of **5F** at 1 hour after solubilization in DMSO-d_6 at 323 K.

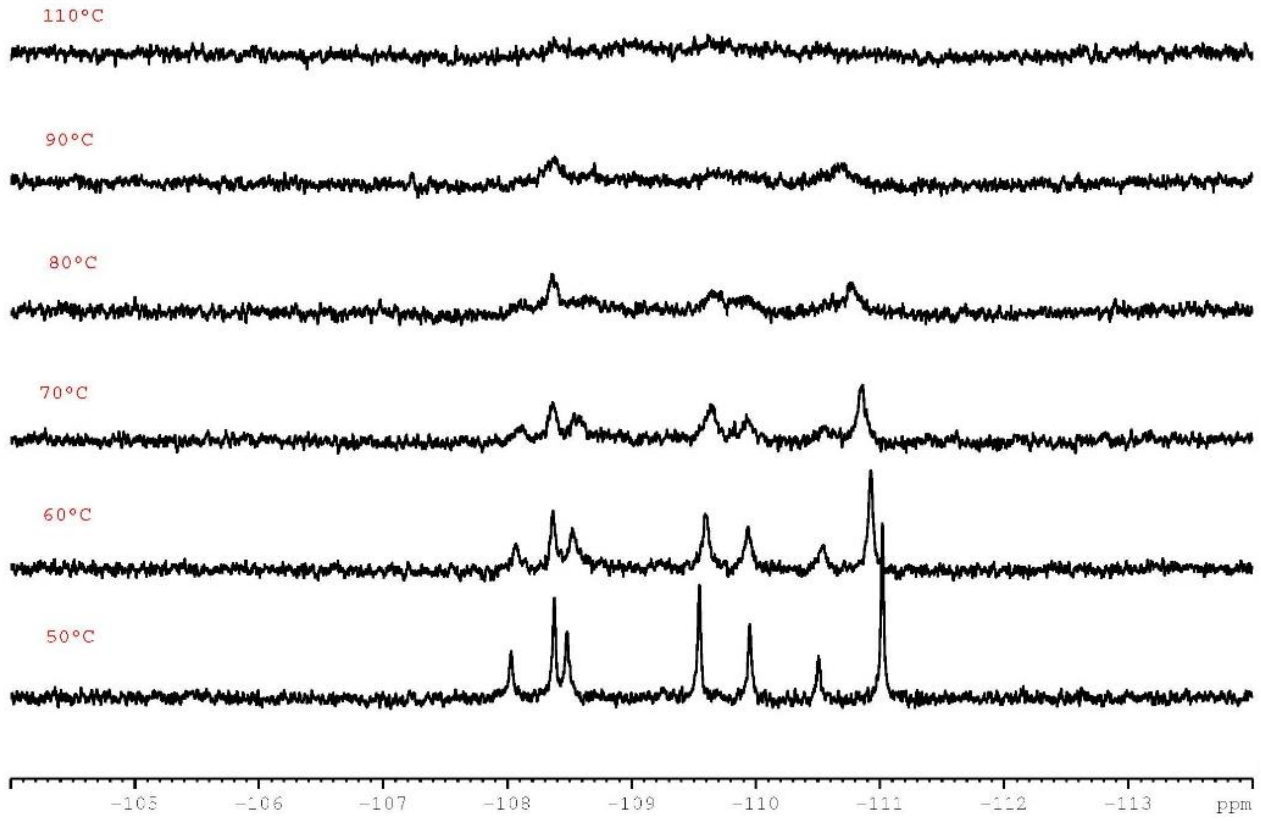


Figure S9. Variable temperature (323 to 383 K) ^{19}F {^{1}H} NMR spectra (376.5 MHz) of **5F** in DMSO-d_6.

3) Chemical shift values prediction

Chemical shift values were calculated using density functional (DFT) methods recommended by Rablen et al. based on a study using a test set of 80 organic molecules.[1] Initial structures of different conformations are snapshots from MD simulations and are then fully optimized in gas phase at the B3LYP/6-31G(d) level of theory. The nuclear magnetic shielding tensors were then calculated at the WP04/cc-pvdz or WP04/6-31G++(d,p) level with implicit solvent chloroform using the PCM model. Chemical shifts were then obtained as δ = (31.844 - isotropic magnetic shielding)/1.0205 for WP04/cc-pvdz and δ = (31.934 - isotropic magnetic shielding)/1.0424 for WP04/6-31G++(d,p), respectively.

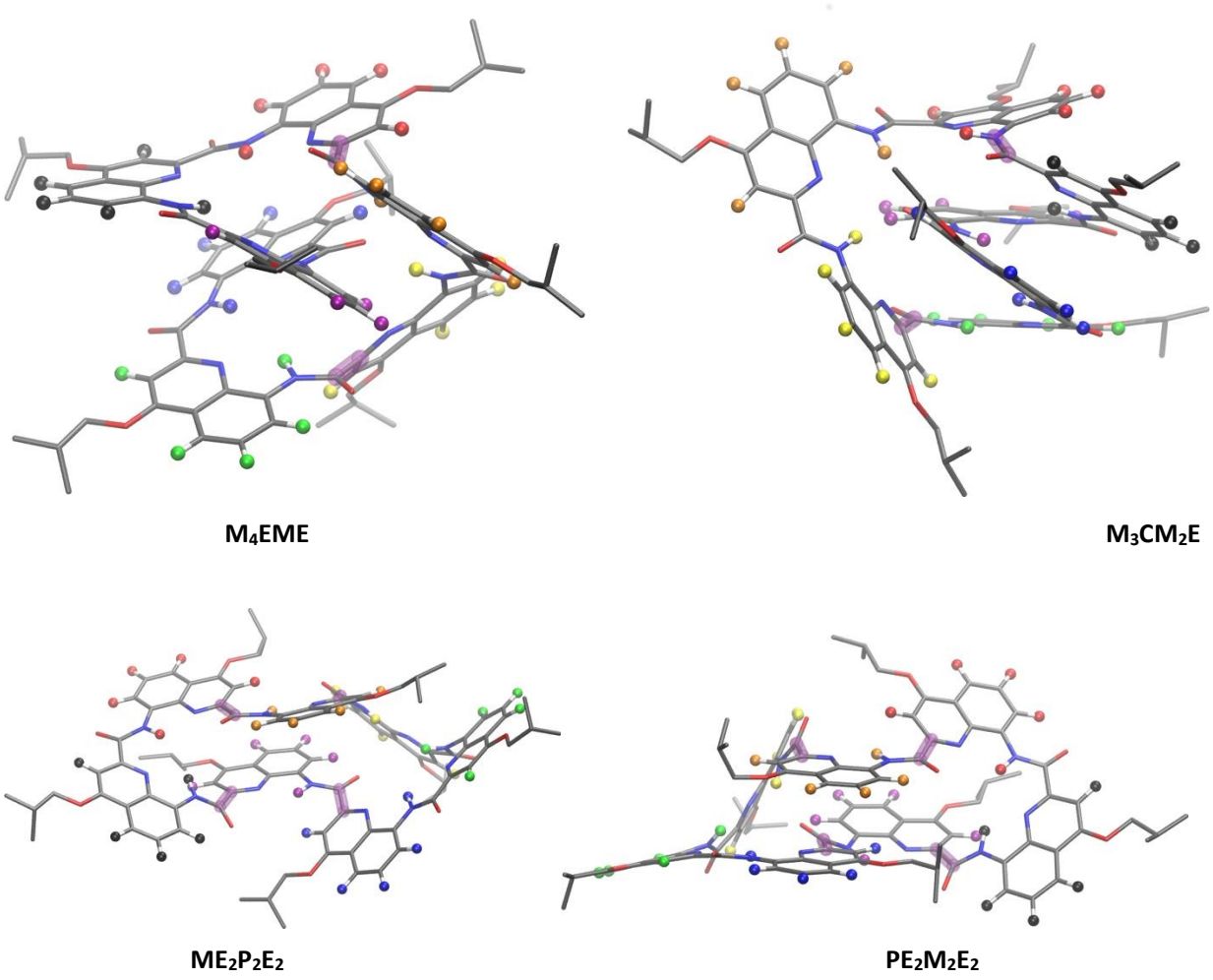


Figure S10. Optimized conformations and color coding of quinoline rings of heptamer **5**. **M_4EME** (top left) is the crystal conformation also predicted as the major conformation in simulations with two flipped Aryl-CO torsions at n and n+2, (highlighted by purple tube). **M_3CM_2E** (top right) is a conformation with a cis amide and one flipped Aryl-CO torsion, at n (cis amide) and n+3 (flipped Aryl-CO) (highlighted by purple tube). The view of **M_3CM_2E** structure on the right side was rotated roughly 180 degrees (around the helix axis) with respect to the **M_4EME** view in order to show the cis amide. **$ME_2P_2E_2$** and **$PE_2M_2E_2$** (bottom) are likely intermediates along the interconversion of degenerate states, not stable conformers, but they were nevertheless considered for chemical shift calculations.

Table S2. Calculated chemical shift values of the conformers of heptamer **5** shown in Figure S10.

	B3LYP/6-31G(d)//WP04/cc-pvdz				B3LYP/6-31G(d)//WP04/6-31G++(d,p)			
Proton	**M_4EME**	**M_3CM_2E**	**$ME_2P_2E_2$[a]**	**$PE_2M_2E_2$[a]**	**M_4EME**	**M_3CM_2E**	**$ME_2P_2E_2$[a]**	**$PE_2M_2E_2$[a]**
NH-1 (red)	9.87	**8.05 (cis)**	11.90	10.88	10.32	**8.05 (cis)**	12.78	10.86
NH-2 (orange)	9.64	10.42	9.71	9.93	9.47	10.00	9.70	10.06
NH-3 (yellow)	10.65	11.29	10.16	10.39	10.58	11.67	10.03	10.75
NH-4 (green)	9.50	9.26	9.31	9.74	9.25	9.84	9.96	9.88
NH-5 (blue)	10.82	10.71	10.78	11.08	11.04	11.15	11.36	12.00
NH-6 (purple)	9.78	10.70	9.93	10.04	10.05	10.88	10.39	10.22
NH-7 (black)	10.39	9.65	10.33	10.27	10.85	9.60	10.61	10.42
Q1-H3	6.53	6.93	6.83	6.82	6.91	5.98	6.96	6.55
Q1-H5	7.89	7.08	8.00	7.83	7.79	7.04	8.05	7.91
Q1-H6	7.47	6.42	7.66	7.57	8.08	6.59	7.32	7.32
Q1-H7	9.06	5.80	8.72	8.75	9.19	5.56	8.66	9.13
Q2-H3	7.42	8.04	7.01	6.92	7.28	8.09	7.01	6.99
Q2-H5	7.89	8.20	7.56	6.76	8.03	8.08	7.57	6.18
Q2-H6	7.30	7.56	7.20	7.02	7.27	7.25	7.23	6.40
Q2-H7	7.59	7.97	8.37	8.21	7.48	7.77	8.52	8.32
Q3-H3	6.30	6.38	7.61	8.08	6.33	6.68	7.43	8.43
Q3-H5	7.84	7.63	8.22	8.26	7.90	7.54	8.49	8.43
Q3-H6	7.53	7.39	7.85	7.69	7.33	7.13	8.03	7.92
Q3-H7	8.29	8.59	9.45	9.52	8.54	8.43	9.41	9.59
Q4-H3	6.97	7.20	8.02	8.02	7.01	7.10	8.43	8.31
Q4-H5	7.58	7.52	8.37	8.09	7.71	7.68	8.24	8.22
Q4-H6	7.14	7.04	7.66	7.60	7.36	6.66	7.27	7.53
Q4-H7	8.33	7.40	7.89	8.49	8.50	7.27	8.06	8.67
Q5-H3	5.51	7.31	7.00	6.89	5.14	7.30	7.07	7.02
Q5-H5	7.76	7.34	7.98	7.91	8.45	7.52	8.15	7.76
Q5-H6	7.50	6.90	7.59	7.63	8.20	8.01	7.50	7.03
Q5-H7	8.33	7.37	9.29	9.38	8.36	7.52	9.30	8.95
Q6-H3	7.60	6.54	6.82	6.77	7.72	6.56	6.88	6.79
Q6-H5	7.24	7.65	7.51	7.31	7.34	7.96	7.55	7.39
Q6-H6	6.53	7.63	7.24	6.15	6.30	7.60	7.45	6.04
Q6-H7	9.48	8.75	7.74	6.59	9.13	8.40	7.60	6.66
Q7-H3	7.41	6.54	7.44	7.43	8.06	6.85	7.02	7.66
Q7-H5	7.94	7.69	8.02	8.05	8.10	7.92	8.32	8.03
Q7-H6	7.47	7.48	7.63	7.64	7.40	7.60	7.83	7.41
Q7-H7	9.20	8.39	8.74	8.71	9.01	8.46	8.76	8.81

[a] $ME_2P_2E_2$ and $PE_2M_2E_2$ are in principle enantiomeric conformers, but the energy optimization produced two slightly different local minima, hence the different chemical shift values.

4) Crystallographic analysis

X-ray crystallographic data for compounds **8d**, **9b** and **4** were collected at Ochanomizu University. The low diffracting colorless prismatic crystal (0.200 × 0.150 × 0.150 mm^3) of **8d,** obtained from chloroform/methanol, yellow plate crystal (0.200 × 0.100 × 0.100 mm^3) of **9b**, obtained from chloroform/acetonitrile/methanol and yellow needle crystal (0.100 × 0.010 × 0.010 mm^3) of **4**, obtained from chloroform/methanol were immersed in Paraton-N oil and placed in the N_2 cold stream at 93 K. The diffraction experiment was performed in a Bruker APEX2 system (APEX II CCD detector, MoKα: λ = 0.71073 Å). Absorption correction was performed by a multi scan method implemented in SADABS.[2] Structure solution and refinement were performed by using SHELXT-2018/2[3] and SHELXL-2018/3.[4] All non-hydrogen atoms were refined anisotropically.

For **8d**, hydrogen atoms bonding to nitrogen or oxygen atoms were found by the Fourier map and refined isotropically. Other hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The methanol molecule was firstly refined with the free variable and finally fixed with the site occupancy factor of 100%. Disordered isobutyl moieties (C11-C14 and O2, and C26-C28) were refined with PART n/-n. The occupancy factors were as follows, C11A-C14A and O2A: 76%, C11B-C14B and O2B: 24%, C26A-C28A: 71% and C26B-C28B: 29%. SIMU was applied to C12B, C13B and C14B.

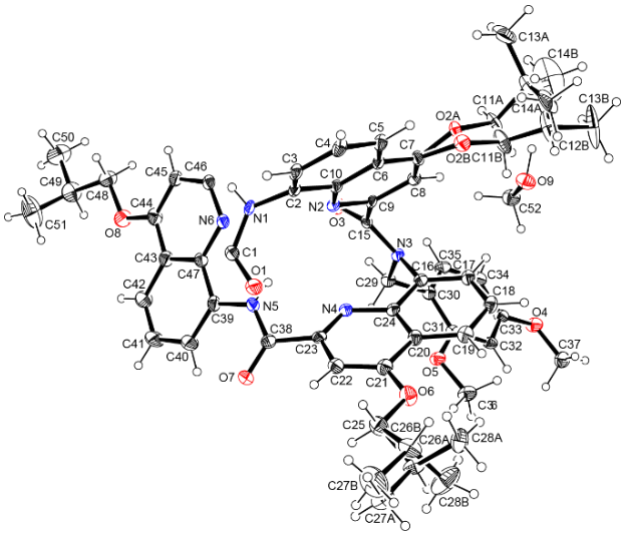


Figure S11. Ortep drawing of **8d**. (asymmetric unit, 50% probability)

For **9b**, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonding to nitrogen atoms were found by the Fourier map and refined isotropically. Other hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 147, 23, 43 and 83) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The disordered quinoline ring and isobutyloxy moiety (C1-C13, N1 and O1) were refined with PART, SAME and EADP. Occupancy ratio A/B was 76/24. SIMU was applied to C11B, C12B and C13B. The methanol molecules were refined with free variables, partly combined with PART, SADI and EADP. Each occupancy was as follows, C117 and O19: 89%, C118 and O21: 30%, C119 and O22: 43%. In the final stage of refinement, PLATON/SQUEEZE[5] was applied to unidentified residual electron density. The result showed 49 electrons and 148 $Å^3$ void volume in the asymmetric unit.

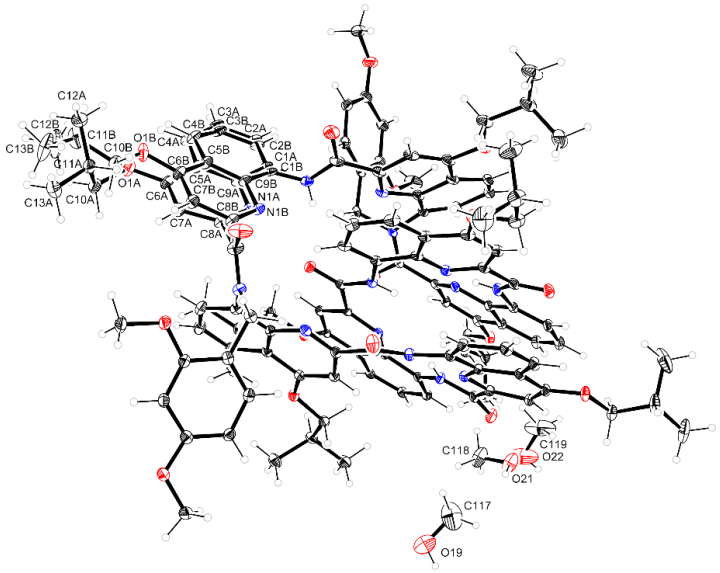


Figure S12. Ortep drawing of **9b**. (30% probability)

For **4**, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms binding nitrogen atoms (N3 and N5) were found by the Fourier map and refined isotropically. Other hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The disordered isobutyloxy moiety (C39, C40, C41, C42 and O6) was refined with PART and restrained with SAME. Occupancy ratio of A/B was 52/48. The violently disordered chloroform molecules (C43A, Cl1A, Cl2A, Cl3A, and C43B, Cl1B, Cl2B and Cl3B) were refined with free variables and occupancy was 36% for A and 21% for B respectively. These molecules were restrained with SAME and constrained with EADP.

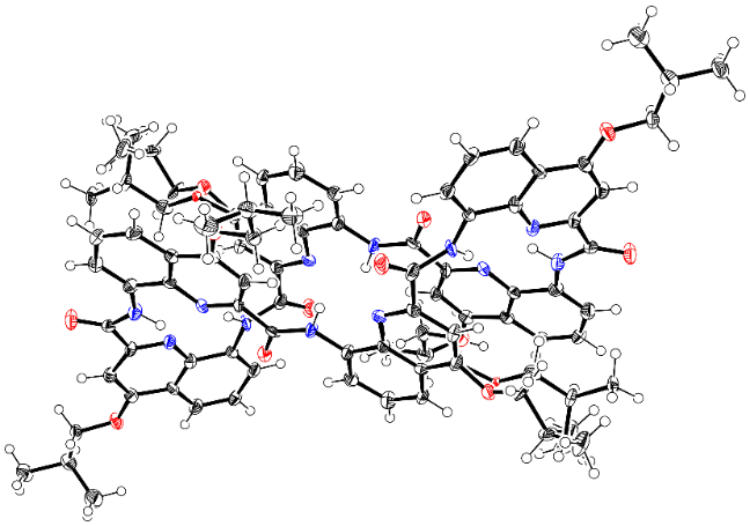


Figure S13. Ortep drawing of **4**. (50% probability. Solvent molecules were omitted for clarity.)

X-ray crystallographic data for compounds **8c** and **5** were collected at SPring-8. The low diffracting colorless plate crystal (0.10 × 0.04 × 0.01 mm^3) of **8c**, which was obtained from chloroform/methanol, and colorless needle crystal (0.10 × 0.04 × 0.03 mm^3) of **5**, which was obtained from chloroform/methanol were immersed in Paraton-N oil and placed in the N_2 cold stream at 100 K. X-ray diffraction images of the crystal were collected using a Rayonix MX225

CCD area detector with synchrotron radiation at a wavelength of 0.85 Å at the BL38B1 station of SPring-8 (Hyogo, Japan). Images were processed using software HKL2000 (HKL Research). Structure solution and refinement were performed by using SHELXT-2014/5[3] and SHELXL-2017/1[4]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms (including amide N–H) were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23 and 43) with Uiso values constrained to 1.2/1.5 Ueq of their parent atoms. In the case of compound **7c**, disordered isobutyl moieties were refined with some restraints and constraints. A pair, C11–C14 and C11B–C14B were applied with PART, SAME and EADP. The occupancies of these moieties were refined with free variables in course of refinements and finally 68/32 ratio. C38–C41 were applied with DELU. A pair of C75–C78 and C75B–C78B were applied with PART, SAME, ISOR, DFIX, DANG and EADP. The occupancies of these moieties were refined with free variables in course of refinements and finally 60/40 ratio. The solvent chloroform was refined with DELU and its occupancy was refined with free variables to be 41%. In the case of compound **5**, DELU was applied to an isobutoxyl moiety (C11–C14 and O2)

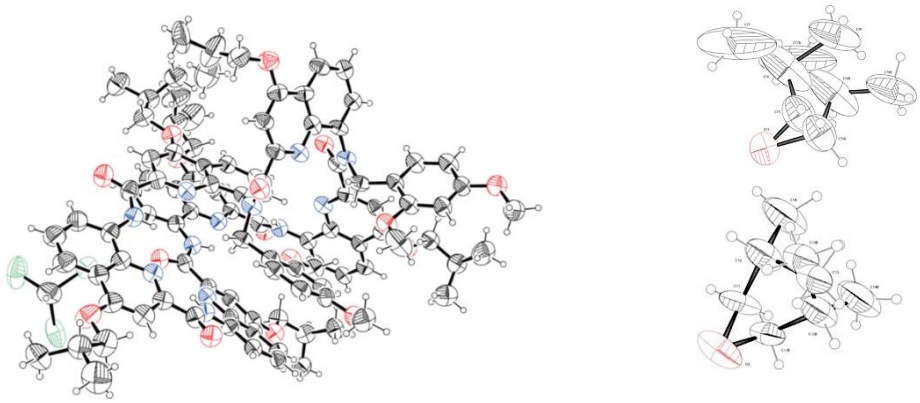


Figure S14. Ortep drawing of compound **8c**. (30% probability) Left: Asymmetric unit. (Minor disordered parts are omitted for clarity.) Right: two pairs of disordered isobutyl groups: (C11–C14 and C11B–C14B) and (C75–C78 and C75B–C78B).

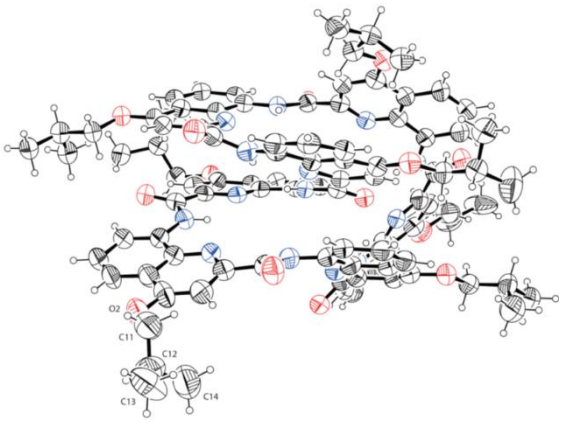


Figure S15. Ortep drawing of compound **5**. (30% probability).

For **5F**. A low-diffracting, colorless, needle crystal (0.30 × 0.05 × 0.05 mm^3), obtained from $CHCl_3$/*n*-hexane was immersed in Paraton-N oil and placed in the N_2 cold stream at 130 K. The X-ray diffraction measurement for **5F** was

carried out on a Rigaku FRX rotating anode (2.9 kW) diffractometer at the IECB x-ray facility (CNRS UMS 3033 – INSERM US001). The CuKα (λ = 1.54184 Å) radiation monochromated with high flux Osmic Varimax HF mirrors was used for data collection. The x-ray source is equipped with a Dectris Pilatus 200K detector and partial chi goniometer. The crystal was kept at 130 K during data collection. The Rigaku CrystalClear suite[6] was used to index and integrate data with a multiscan absorption correction. Structure solution and refinement were performed using SHELXT-2018/3[3] and SHELXL-2018/3[4]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on the calculated positions using a riding model (AFIX 13, 137, 23, 33 and 43) with U_{iso} values constrained to 1.2/1.5 U_{eq} of their parent atoms. The disorder including fluorine atom (C6A, F1A, C48A / C6B, F1B, C48B) could be refined with PART, SUMP, SIMU, EADP, EXYZ and DFIX. Occupancy ratio of A/B was ca. 70/30. Some appropriate restraints (SIMU, DELU, RIGU, SADI, DANG and FLAT) were applied in the structure refinement. In the final stage of refinement, PLATON/SQUEEZE[5] was applied to unidentified residual electron density. The result showed 243 electrons and 658 Å^3 void volume in the asymmetric unit.

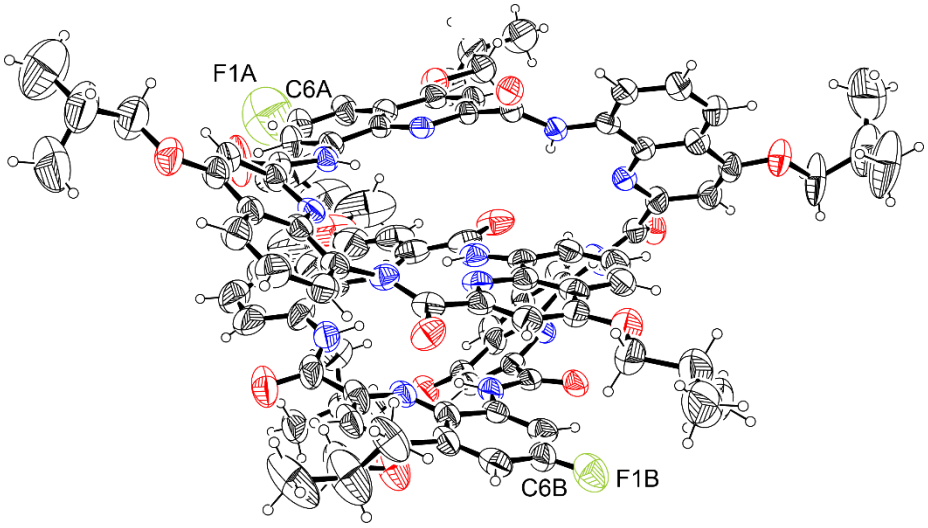


Figure S16. Ortep drawing of compound **5F** (30% probability).

Table S3. Crystallographic data for **8c**, **8d**, **9b**, **4**, **5** and **5F**.

	8c*	**8d***	**4***	**9b***	**5**	**5F**
chemical formula	$C_{102.41}H_{104.41}Cl_{1.23}N_{12}O_{16}$	$C_{104}H_{112}N_{12}O_{18}$	$C_{85.14}H_{85.14}Cl_{3.41}N_{12}O_{12}$	$C_{117.62}H_{124.49}N_{14}O_{19.62}$	$C_{98}H_{98}N_{14}O_{14}$	$C_{98}H_{97}FN_{14}O_1$
FW, g/mol	1803.00	1818.05	1589.35	2048.22	1695.90	1713.89
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	P-1	$P2_1/c$	$P2_1/n$	$I\,2/a$
a, Å	17.678(4)	32.719(6)	8.602(4)	18.1053(11)	19.856(4)	33.2315(11)
b, Å	14.216(3)	17.980(4)	12.502(6)	21.5495(14)	18.444(4)	18.4232(5)
c, Å	37.768(8)	16.476(3)	18.968(9)	28.1674(18)	24.271(5)	37.3484(16)
α, *deg*	90	-	93.218(8)	-	90	90
β, *deg*	96.69(3)	101.043(3)	91.180(7)	98.8050(10)	96.39(3)	113.309(4)
γ, *deg*	90	-	103.516(9)	-	90	90
V, Å^3	9427(3)	9513(3)	1979.0(16)	10860.3(12)	8833(3)	20999.6(14)
Z	4	4	1	4	4	8
D(calcd.), g/cm^3	1.298	1.250	1.334	1.253	1.275	1.084
temp. (K)	100	93	93	93	100	130
uniq, refl. / total no. of	5004/20779	4633/20956	3172/10270	19499/84110	5454/22852	7560/89857
R_1 ($I > 2\sigma(I)$) [a]	0.1144	0.1945	0.0881	0.0789	0.1313	0.1294
wR_2 (all data) [b]	0.2901	0.2192	0.2216	0.1899	0.3666	0.3831
restraints/ parameters	76/1259	108/614	12/587	1493/45	8/1150	1435/1169
GooF on F^2 [c]	1.067	1.041	1.031	1.029	1.100	1.635
CCDC#	2059866	2059868	2059869	2059870	2059871	2063705

[a] $R1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$

[b] $wR2 = [\Sigma[w(F_0^2-F_c^2)^2/\Sigma[w(F_0^2)^2]^{1/2}$, where $w = 1/\sigma^2(F_0^2)+(aP)^2+bP$, $P = (F_0^2+2F_c^2)/3$

[c] GooF = $[\Sigma[w(F_0^2-F_c^2)^2]/(n-p)]^{1/2}$, where n = no. of reflections and p = no. of refined parameters.

[*] including solvent molecules

5) Synthetic procedures

General. Unless otherwise noted, the original materials were used directly from commercial supplies without any purification. Dry dichloromethane, chloroform, diisiopropylethylamine were distilled from CaH_2 prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker DMX 300 and Bruker Avance 600 spectrometer using residual solvent resonances (chloroform (7.26 ppm) and DMSO (2.50 ppm)) as the internal reference peak. Mass spectral data were obtained on a Bruker Daltonics micro TOF-2focus in the positive ion detection mode.

Synthesis of Compound **12**: A solution of acid **10**[7] (200 mg, 0.11 mmol) in dry chloroform (1 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (26 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **11**[7] (30 mg, 0.9 eq.) and dry DIPEA (37 μL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **12** as yellow solid (58.0 mg, 78%). ^1H NMR (600 MHz, $CDCl_3$) δ 12.61 (s, 1 H), 11.43 (s, 1 H), 11.21 (s, 1 H), 9.26 (d, *J* = 7.6 Hz, 1 H), 8.87 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.57 (s, 1 H), 8.51 (d, *J* = 7.6 Hz, 1 H), 8.05 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.98 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.97 (d, *J* = 7.2 Hz, 1 H), 7.91 (s, 1 H), 7.76 (m, 4 H), 7.66-7.56 (m, 6 H), 7.48 (s, 1 H), 7.46 (br, 1 H), 7.44 (s, 1 H), 7.39 (m, 3 H), 7.32 (t, *J* = 7.0 Hz, 1 H), 7.25-7.13 (m, 9 H), 7.07 (dd, *J* = 7.2, 1.2 Hz, 1 H), 6.85 (t, *J* = 7.0 Hz, 1 H), 6.80 (s, 1 H), 6.74 (t, *J* = 7.2 Hz, 1 H), 6.73 (s, 1 H), 6.44 (dd, *J* = 8.3, 1.2 Hz, 1 H), 6.32 (dd, *J* = 7.6, 1.2 Hz, 1 H), 6.24 (d, *J* = 1.3 Hz, 1 H), 6.22 (d, *J* = 7.3 Hz, 1 H), 5.66 (m, 2 H), 5.58 (d, *J* = 15.4 Hz, 1 H), 5.30 (m, 1 H), 4.85 (d, *J* = 15.2 Hz, 1 H), 4.77 (dd, *J* = 13.3, 5.4 Hz, 1 H), 4.63 (d, *J* = 13.1 Hz, 1 H), 4.62 (d, *J* = 10.3 Hz, 1 H), 4.50 (dd, *J* = 8.8, 6.0 Hz, 1 H), 4.43 (d, *J* = 17.2 Hz, 1 H), 4.27 (t, *J* = 8.4 Hz, 1 H), 4.14-3.98 (m, 12 H), 3.90 (dd, *J* = 9.1, 6.2 Hz, 1 H), 3.79 (dd, *J* = 9.0, 6.2 Hz, 1 H), 3.74 (s, 3 H), 3.74-3.62 (m, 4 H), 3.65 (s, 3 H), 3.44 (s, 3 H), 3.12 (dd, *J* = 9.1, 7.1 Hz, 1 H), 2.87 (dd, *J* = 9.0, 6.8 Hz, 1 H), 2.57 (m, 1 H), 2.28 (m, 2 H), 2.18 (m, 1 H), 2.08 (m, 1 H), 1.94 (s, 3 H), 1.58 (m, 1 H), 1.32 (d, *J* = 6.7 Hz, 3 H), 1.29 (d, *J* = 6.7 Hz, 3 H), 1.13 (m, 15 H), 1.04 (d, *J* = 6.7 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 0.51 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 169.0, 165.9, 164.8, 164.0, 163.7, 163.4, 162.9, 162.9, 162.6, 161.2, 160.2, 159.9, 159.8, 158.9, 158.2, 155.9, 153.0, 151.6, 151.5, 150.6, 149.9, 149.6, 144.3, 143.9, 143.6, 143.0, 141.4, 141.2, 141.1, 140.2, 140.1, 138.4, 137.2, 137.0, 134.9, 134.7, 133.9, 133.4, 132.5, 132.0, 131.5, 130.9, 129.8, 128.6, 127.7, 127.5, 127.3, 126.7, 126.6, 125.9, 125.3, 125.2, 123.5, 123.0, 122.4, 122.3, 120.7, 120.3, 119.8, 119.7, 119.2, 119.1, 119.0, 118.1, 117.7, 117.3, 116.9, 116.6, 116.4, 115.2, 115.0, 114.4, 104.0, 103.5, 101.9, 101.6, 101.4, 100.7, 99.5, 98.9, 98.4, 97.9, 97.8, 75.8, 75.4, 75.2, 75.1, 74.9, 73.9, 67.1, 66.0, 55.4, 55.3, 55.2, 54.9, 54.7, 53.7, 48.7, 47.2, 46.7, 28.4, 28.3, 28.1, 28.0, 27.6, 19.7, 19.6, 19.5, 19.4, 19.2 19.1, 18.9. HRMS (ESI+) m/z calcd for $C_{120}H_{121}N_{12}O_{19}$ $[M+H]^+$ 2033.8865, found 2033.8871.

Synthesis of Compound **13**: To a solution of **12** (49.5 mg, 0.024 mmol) in dry dichloromethane (0.5 mL), phenylsilane (10 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (2.8 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **13** as yellow solid (48.6 mg, quant.). ^1H NMR (600 MHz, $CDCl_3$) δ 12.63 (s, 1 H), 11.56 (s, 1 H), 11.15 (s,

1 H), 9.28 (d, *J* = 7.5 Hz, 1 H), 9.08 (d, *J* = 7.6 Hz, 1 H), 8.56 (s, 1 H), 8.48 (d, *J* = 7.4 Hz, 1 H), 8.05 (d, *J* = 8.3 Hz, 2 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 7.92 (s, 1 H), 7.78 (m, 2 H), 7.74 (d, *J* = 8.6 Hz, 1 H), 7.70 (s, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 7.1 Hz, 1 H), 7.51 (s, 1 H), 7.43 (s, 1 H), 7.38 (m, 3 H), 7.32 (m, 3 H), 7.24 (m, 1 H), 7.21 (m, 1 H), 7.20 (m, 2 H), 7.15 (t, *J* = 7.4 Hz, 1 H), 7.04 (d, *J* = 7.3 Hz, 2 H), 6.84 (s, 1 H), 6.84 (t, *J* = 8.0 Hz, 1 H), 6.76 (t, *J* = 7.3 Hz, 1 H), 6.62 (s, 1 H), 6.46 (d, *J* = 2.2 Hz, 1 H), 6.41 (d, *J* = 8.3 Hz, 1 H), 6.20 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.06 (d, *J* = 7.0 Hz, 1 H), 5.73 (d, *J* = 14.4 Hz, 1 H), 5.62 (t, *J* = 7.9 Hz, 1 H), 5.59 (d, *J* = 2.3 Hz, 1 H), 4.83 (d, *J* = 14.5 Hz, 1 H), 4.58 (d, *J* = 13.0 Hz, 1 H), 4.53 (dd, *J* = 8.8, 6.2 Hz, 1 H), 4.30 (t, *J* = 7.7 Hz, 1 H), 4.10 (m, 3 H), 4.03-3.96 (m, 4 H), 3.91 (m, 1 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.81 (m, 3 H), 3.75 (m, 2 H), 3.64 (s, 3 H), 3.01 (t, *J* = 8.6 Hz, 1 H), 2.96 (t, *J* = 8.6 Hz, 1 H), 2.60 (m, 1 H), 2.33-2.23 (m, 3 H), 2.09 (m, 1 H), 1.80 (s, 3 H), 1.70 (m, 1 H), 1.36 (d, *J* = 6.7 Hz, 3 H), 1.35 (d, *J* = 6.7 Hz, 3 H), 1.20 (d, *J* = 6.5 Hz, 3 H), 1.19 (d, *J* = 6.5 Hz, 3 H), 1.13 (m, 12 H), 0.97 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H), 0.66 (d, *J* = 6.7 Hz, 3 H), 0.60 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 169.1, 167.2, 164.8, 164.0, 163.7, 163.4, 163.2, 162.8, 161.3, 160.7, 160.6, 158.8, 158.8, 154.0, 153.0, 151.6, 151.5, 150.1, 149.9, 149.6, 144.3, 143.9, 143.2, 142.8, 141.2, 141.1, 140.4, 140.1, 139.4, 138.3, 137.1, 136.9, 134.7, 134.5, 134.2, 133.7, 133.4, 132.3, 131.6, 130.0, 128.2, 127.9, 127.7, 127.6, 127.3, 126.7, 126.6, 125.8, 125.3, 125.2, 124.2, 123.1, 122.9, 122.3, 122.2, 120.6, 120.5, 120.3, 119.8, 119.7, 118.8, 117.4, 117.3, 117.2, 116.9, 116.8, 116.4, 115.1, 114.9, 114.5, 104.0, 103.5, 101.7, 101.0, 99.7, 99.5, 99.0, 98.6, 98.4, 97.5, 75.7, 75.5, 75.4, 74.2, 74.8, 73.9, 67.1, 55.7, 55.4, 55.2, 53.4, 50.0, 47.5, 46.7, 28.5, 28.3, 28.2, 28.2, 28.1, 27.8, 19.7, 19.6, 19.5, 19.4, 19.3, 19.3, 19.2, 19.2, 19.1, 19.0. HRMS (ESI+) m/z calcd for $C_{117}H_{117}N_{12}O_{19}$ $[M+H]^+$ 1993.8552, found 1993.8567.

Synthesis of Compound **15**: A solution of acid **14**[7] (457.8 mg, 0.52 mmol) in dry chloroform (4 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (0.12 mL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **11** (153.0 mg, 0.9 eq.) and dry DIPEA (0.46 mL, 5 eq.) in dry chloroform (4 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **15** as yellow solid (455.8 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.84 (s, 1 H), 8.92 (dd, *J* = 7.7, 1.1 Hz, 1 H), 8.12 (br, 1 H), 8.06 (s, 1 H), 8.02 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.87 (d, *J* = 7.7 Hz, 1 H), 7.81 (t, *J* = 8.2 Hz, 2 H), 7.71 (d, *J* = 7.3 Hz, 1 H), 7.65 (m, 3 H), 7.57 (d, *J* = 7.2 Hz, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.49 (s, 1 H), 7.47 (s, 1 H), 7.43 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.26 (m, 2 H), 7.08 (br, 1 H), 6.99 (s, 1 H), 6.43 (m, 2 H), 6.00 (m, 2 H), 5.26 (dd, *J* = 17.2, 1.5 Hz, 1 H), 5.11 (dd, *J* = 10.3, 1.3 Hz, 1 H), 4.92 (m, 2 H), 4.85 (dd, *J* = 13.0, 6.0 Hz, 1 H), 4.65 (dd, *J* = 10.6, 6.7 Hz, 1 H), 4.48 (br, 1 H), 4.36 (t, *J* = 6.8 Hz, 1 H), 4.08 (d, *J* = 6.3 Hz, 2 H), 3.92 (d, *J* = 6.7 Hz, 2 H), 3.73 (s, 3 H), 3.62 (s, 3 H), 3.32 (dd, *J* = 8.8, 6.5 Hz, 1 H), 2.92 (dd, *J* = 8.8, 6.8 Hz, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 1.86 (m, 1 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.07 (d, *J* = 6.7 Hz, 3 H), 1.06 (d, *J* = 6.7 Hz, 3 H), 0.78 (d, *J* = 6.7 Hz, 3 H), 0.76 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 165.8, 163.4, 163.0, 162.8, 161.7, 160.2, 158.5, 153.9, 153.3, 150.8, 149.6, 144.1, 143.9, 143.1, 141.6, 141.4, 140.1, 136.3, 135.2, 132.4, 131.0, 128.0, 127.9, 127.8, 127.3, 127.3, 127.0, 126.5, 125.2, 125.1, 122.9, 122.3, 120.7, 120.2, 119.0, 118.7, 118.5, 116.6, 114.8, 114.7, 104.2, 101.6, 101.1, 98.6, 98.3, 75.3, 75.2, 74.2, 66.8, 55.4, 55.2, 49.3, 47.4, 28.4, 28.2, 27.9, 19.4, 19.4, 19.1, 19.0. HRMS (ESI+) m/z calcd for $C_{69}H_{69}N_6O_{11}$ $[M+H]^+$ 1157.5019, found 1157.5007.

Synthesis of Compound **16**: To a solution of **15** (180.0 mg, 0.16 mmol) in dry dichloromethane (1.5 mL), phenylsilane (44 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (7.4 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **16** as yellow solid (164.7 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.44 (s, 1 H), 9.03 (d, *J* = 7.6 Hz, 1 H), 8.14 (br, 2 H), 8.11 (d, *J* = 8.2 Hz, 1 H), 7.83 (d, *J* = 7.3 Hz, 2 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.78 (s, 1 H), 7.68 (m, 2 H), 7.60 (d, *J* = 7.4 Hz, 1 H), 7.53 (d, *J* = 8.3 Hz, 1 H), 7.51 (s, 1 H), 7.45 (m, 4 H), 7.38 (t, *J* = 7.1 Hz, 1 H), 7.34 (s, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.28 (br, 1 H), 7.01 (br, 1 H), 6.34 (m, 2 H), 5.79 (d, *J* = 14.6 Hz, 1 H), 4.95 (d, *J* = 14.6 Hz, 1 H), 4.66 (dd, *J* = 10.5, 6.3 Hz, 1 H), 4.46 (br, 1 H), 4.25 (t, *J* = 6.5 Hz, 1 H), 4.12 (m, 2 H), 3,93 (t, *J* = 6.6 Hz, 1 H), 3.90 (t, *J* = 6.5 Hz, 1 H), 3.71 (s, 3 H), 3.52 (s, 3 H), 3.37 (t, *J* = 6.8 Hz, 1 H), 3.17 (t, *J* = 7.2 Hz, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 1.88 (m, 1 H), 1.15 (d, *J* = 6.7 Hz, 6 H), 1.07 (d, *J* = 6.7 Hz, 3 H), 1.06 (d, *J* = 6.7 Hz, 3 H), 0.77 (d, *J* = 6.7 Hz, 3 H), 0.74 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 167.1, 163.3, 163.2, 163.1, 161.9, 160.6, 158.8, 153.1, 152.3, 150.1, 149.3, 143.9, 143.7, 142.8, 142.3, 141.5, 141.3, 139.5, 136.5, 134.7, 134.5, 131.6, 127.9, 127.8, 127.2, 127.1, 126.3, 124.9, 124.9, 123.0, 122.7, 120.9, 120.3, 120.2, 120.2, 120.1, 117.4, 117.2, 115.0, 114.5, 104.0, 101.5, 101.2, 98.9, 98.3, 75.4, 75.2, 74.4, 66.6, 55.2, 55.2, 49.7, 47.1, 28.1, 28.1, 27.7, 19.2, 19.0, 18.9. HRMS (ESI+) m/z calcd for $C_{66}H_{65}N_6O_{11}$ $[M+H]^+$ 1117.4706, found 1117.4687.

Synthesis of Compound **17**: To a solution of **15** (180.0 mg, 0.16 mmol) in dry dichloromethane (0.5 mL), DBU (27.8 mg, 3.9 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **17** as yellow solid (141.0 mg, 97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.81 (s, 1 H), 8.93 (d, *J* = 7.6 Hz, 1 H), 8.02 (d, *J* = 7.1 Hz, 1 H), 8.00 (d, *J* = 7.2 Hz, 1 H), 7.68 (d, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 8.1 Hz, 1 H), 7.57 (s, 1 H), 7.48 (s, 1 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 7.35 (t, *J* = 8.1 Hz, 1 H), 7.19 (d, *J* = 7.4 Hz, 1 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 6.96 (s, 1 H), 6.57 (d, *J* = 7.4 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.34 (d, *J* = 2.3 Hz, 1 H), 5.97 (d, *J* = 15.1 Hz, 1 H), 5.95 (m, 1 H), 5.23 (dd, *J* = 17.2, 1.3 Hz, 1 H), 5.09 (d, *J* = 10.4 Hz, 1 H), 4.99 (d, *J* = 15.2 Hz, 1 H), 4.85 (dd, *J* = 13.1, 5.9 Hz, 1 H), 4.75 (dd, *J* = 13.1, 6.0 Hz, 1 H), 4.07 (d, *J* = 5.2 Hz, 2 H), 3.99 (d, *J* = 6.5 Hz, 4 H), 3.74 (s, 3 H), 3.53 (s, 3 H), 3.39 (dd, *J* = 8.8, 6.5 Hz, 1 H), 3.01 (dd, *J* = 8.8, 6.8 Hz, 1 H), 2.32 (m, 1 H), 2.23 (m, 1 H), 1.88 (m, 1 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 1.09 (d, *J* = 6.7 Hz, 3 H), 0.81 (d, *J* = 6.7 Hz, 3 H), 0.80 (d, *J* = 6.7 Hz ,3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 165.6, 163.4, 163.0, 162.6, 161.4, 159.9, 158.4, 152.3, 151.0, 149.2, 143.9, 143.7, 143.2, 140.1, 136.5, 135.1, 132.3, 131.2, 127.7, 125.6, 126.3, 122.9, 122.2, 121.3, 120.2, 119.1, 118.6, 118.5, 116.5, 110.1, 109.4, 103.9, 101.4, 100.6, 98.6, 98.0, 75.1, 75.1, 74.0, 66.7, 55.2, 55.0, 49.1, 28.2, 28.1, 27.8, 19.3, 19.2, 19.2, 19.1, 18.9. HRMS (ESI+) m/z calcd for $C_{54}H_{59}N_6O_9$ $[M+H]^+$ 935.4338, found 935.4319.

Synthesis of Compound **18:** A solution of acid **16** (150.0 mg, 0.13 mmol) in dry chloroform (1 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (30 μL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **17** (112.0 mg, 0.9 eq.) and

dry DIPEA (0.1 mL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **18** as yellow solid (166.4 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.05 (s, 1 H), 10.98 (s, 1 H), 10.82 (s, 1 H), 9.17 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.87 (dd, *J* = 7.7, 1.1 Hz, 1 H), 8.52 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.23 (dd, *J* = 8.3, 1.2 Hz, 1 H), 8.00 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.87 (s, 1 H), 7.85 (d, *J* = 7.9 Hz, 1 H), 7.79 (t, *J* = 8.0 Hz. 1 H), 7.74 (s, 1 H), 7.72 (d, *J* = 8.6 Hz, 1 H), 7.71 (d, *J* = 8.6 Hz, 1 H), 7.61-7.54 (m, 4 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.48 (d, *J* = 7.6 Hz, 1 H), 7.39 (m, 2 H), 7.35 (m, 4 H), 7.30 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 7.18 (s, 1 H), 7.13 (m, 2 H), 7.04 (t, *J* = 7.9 Hz, 1 H), 6.98 (d, *J* = 7.0 Hz, 1 H), 6.78 (s, 1 H), 6.51 (d, *J* = 8.3 Hz, 1 H), 6.06 (dd, *J* = 8.4, 2.3 Hz, 1 H), 5.97 (d, *J* = 2.3 Hz, 1 H), 5.82 (d, *J* = 2.3 Hz, 1 H), 5.69 (m, 2 H), 5.58 (dd, *J* = 8.3, 7.4 Hz, 1 H), 5.29 (d, *J* = 14.6 Hz, 1 H), 5.26 (d, *J* = 14.3 Hz, 1 H), 4.98 (d, *J* = 9.4 Hz, 1 H), 4.94 (dd, *J* = 17.2, 1.5 Hz, 1 H), 4.89 (d, *J* = 14.2 Hz, 1 H), 4.62 (m, 2 H), 4.36 (d, *J* = 5.9 Hz, 1 H), 4.35 (d, *J* = 6.1 Hz, 1 H), 4.29-4.23 (m, 4 H), 4.16 (dd, *J* = 8.8, 6.5 Hz, 1 H), 4.12-4.02 (m, 4 H), 3.75 (d, *J* = 6.5 Hz, 2 H), 3.64 (s, 3 H), 3.40 (d, *J* = 14.5 Hz, 1 H), 3.30 (s, 3 H), 3.28 (m, 2 H), 3.12 (s, 3 H), 2.94 (s, 3 H), 2.85 (dd, *J* = 8.6, 6.8 Hz, 1 H), 2.45 (m, 1 H), 2.32 (m, 2 H), 2.10 (m, 1 H), 1.90 (m, 1 H), 1.71 (m, 1 H), 1.25 (m, 6 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.25 (d, *J* = 6.5 Hz, 3 H), 1.11 (d, *J* = 6.5 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.7 Hz, 3 H), 0.60 (d, *J* = 6.7 Hz, 3 H), 0.52 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 168.3, 166.4, 163.8, 163.6, 163.5, 163.4, 163.2, 162.5, 162.4, 161.6, 161.0, 159.8, 159.6, 158.5, 158.0, 154.1, 153.5, 153.2, 152.7, 150.5, 150.3, 149.8, 144.0, 143.8, 143.5, 143.1, 142.4, 141.7, 141.5, 141.3, 140.1, 139.4, 137.2, 136.3, 135.0, 135.0, 134.3, 133.9, 132.6, 132.4, 131.5, 128.7, 127.9, 127.8, 127.5, 127.5, 127.2, 126.6, 126.5, 126.0, 125.4, 125.1, 125.0, 123.1, 122.6, 122.2, 121.9, 120.6, 120.4, 120.1, 120.1, 119.7, 119.4, 118.9, 118.3, 118.0, 118.0, 117.4, 117.1, 116.7, 115.6, 114.7, 114.5, 103.4, 103.3, 101.9, 101.3, 100.8, 100.4, 98.9, 98.2, 97.6, 97.3, 75.6, 75.3, 75.3, 74.9, 74.2, 74.1, 66.7, 66.3, 55.2, 54.9, 54.7, 54.5, 48.2, 47.7 47.2, 28.4, 28.3, 28.3, 28.1, 28.0, 27.7, 19.5, 19.5, 19.5, 19.4, 19.4, 19.4, 19.4, 19.3, 19.3, 19.1, 18.8, 18.8. HRMS (ESI+) m/z calcd for $C_{120}H_{121}N_{12}O_{19}$ $[M+H]^+$ 2033.8865, found 2033.8883.

Synthesis of Compound **19**: To a solution of **18** (137.9 mg, 0.068 mmol) in dry dichloromethane (1 mL), phenylsilane (19 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (3.1 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **19** as yellow solid (118.4 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.11 (s, 1 H), 11.18 (s, 1 H), 10.96 (s, 1 H), 9.26 (d, *J* = 7.6 Hz, 1 H), 9.00 (d, *J* = 7.7 Hz, 1 H), 8.54 (d, *J* = 7.6 Hz, 1 H), 8.25 (d, *J* = 8.3 Hz, 1 H), 8.10 (d, *J* = 7.3 Hz, 1 H), 8.10 (br, 1 H), 7.95 (s, 1 H), 7.88 (s, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H), 7.82 (m, 2 H), 7.74 (s, 1 H), 7.71 (t, *J* = 7.9 Hz, 2 H), 7.67 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.4 Hz, 1 H), 7.54 (d, *J* = 7.4 Hz, 1 H), 7.50 (d, *J* = 8.3 Hz, 1 H), 7.45 (d, *J* = 8.5 Hz, 1 H), 7.38-7.30 (m, 5 H), 7.26 (m, 1 H), 7.23 (s, 2 H), 7.22 (br, 1 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 7.10 (s, 2 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 6.9 Hz, 1 H), 6.80 (s, 1 H), 6.78 (br, 1 H), 6.55 (d, *J* = 8.3 Hz, 1 H), 6.08 (dd, *J* = 8.3, 2.2 Hz, 1 H), 5.91 (d, *J* = 2.2 Hz, 1 H), 5.89 (dd, *J* = 8.5, 2.3 Hz, 1 H), 5.81 (d, *J* = 2.3 Hz, 1 H), 5.65 (t, *J* = 8.0 Hz, 1 H), 5.45 (d, *J* = 14.5 Hz, 1 H), 5.29 (d, *J* = 14.2 Hz, 1 H), 4,98 (d, *J* = 14.5 Hz, 1 H), 4.58 (dd, *J* = 10.6, 6.7 Hz, 1 H), 4.40 (br, 1 H), 4.33 (dd, *J* = 8.6, 6.7 Hz, 1 H), 4.27 (m, 4 H), 4.12 (m, 3 H), 4.05 (dd, *J* = 8.6, 6.8 Hz, 1 H), 3.74 (d, *J* = 6.4 Hz, 2 H), 3.66

(s, 3 H), 3.47 (s, 3 H), 3.35 (m, 2 H), 3.19 (dd, *J* = 8.6, 6.8 Hz, 1 H), 3.05 (s, 3 H), 3.01 (s, 3 H), 2.44 (m, 1 H), 2.32 (m, 2 H), 2.07 (m, 1 H), 1.94 (m, 1 H), 1.80 (m, 1 H), 1.25 (m, 6 H), 1.17 (m, 6 H), 1.14 (d, *J* = 6.7 Hz, 3 H), 1.12 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 6 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.68 (d, *J* = 6.7 Hz, 6 H).^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 168.6, 167.1, 164.0, 163.7, 163.5, 163.4, 163.2, 163.2, 162.7, 161.6, 161.2, 159.9, 159.8, 158.5, 158.1, 153.5, 153.2, 152.3, 152.2, 150.7, 150.1, 149.0, 144.0, 143.8, 143.1, 142.7, 141.8, 141.4, 141.3, 149.5, 139.5, 139.2, 137.3, 136.4, 135.0, 134.7, 134.3, 134.1, 132.2, 131.8, 128.1, 127.8, 127.8, 127.7, 127.7, 127.4, 127.2, 127.2, 126.8, 126.5, 126.3, 125.2, 125.1, 125.0, 123.0, 122.7, 121.7, 120.7, 120.6, 120.5, 120.3, 120.1, 120.1, 119.8, 119.0, 117.9, 117.6, 117.3, 117.2, 116.2, 115.5, 114.8, 114.5, 103.3, 103.2, 101.8, 100.9, 100.8, 100.2, 98.8, 98.2, 97.7, 97.6, 75.6, 75.5, 75.3, 75.9, 74.2, 74.2, 66.8, 55.2, 55.1, 54.6, 54.5, 48.2, 47.7, 47.2, 28.4, 28.3, 28.3, 28.1, 28.0, 27.8, 19.5, 19.4, 19.4, 19.3, 19.3, 19.3, 19.1, 19.0, 18.9. HRMS (ESI+) m/z calcd for $C_{117}H_{117}N_{12}O_{19}$ $[M+H]^+$ 1993.8552, found 1993.8558.

Synthesis of Compound **6c**: To a solution of **13** (43.4 mg, 0.022 mmol) in dry dichloromethane (0.5 mL), DBU (13.2 mg, 3.9 eq.) in dry dichloromethane (0.5 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by GPC to give **6c** as yellow solid (29.8 mg, 83%).^{1}H NMR (600 MHz, $CDCl_3$) δ 12.44 (s, 1 H), 11.55 (s, 1 H), 10.85 (s, 1 H), 9.27 (dd, *J* = 7.6, 1.1 Hz, 1 H), 9.09 (d, *J* = 6.8 Hz, 1 H), 8.43 (d, *J* = 6.6 Hz, 1 H), 8.05 (dd, *J* = 8.3, 1.2 Hz, 1 H), 8.00 (dd, *J* = 8.3, 1.1 Hz, 1 H), 7.82 (s, 1 H), 7.79 (dd, *J* = 7.4, 1.2 Hz, 1 H), 7.74 (m, 2 H), 7.71 (s, 1 H), 7.71 (m, 1 H), 7.69 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.62 (t, *J* = 8.0 Hz, 2 H), 7.57 (s, 1 H), 7.54 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.51 (s, 1 H), 7.34-7.27 (m, 4 H), 7.07 (m, 3 H), 6.91 (d, *J* = 8.3 Hz, 1 H), 6.72 (s, 1 H), 6.38 (d, *J* = 2.2 Hz, 1 H), 6.33 (dd, *J* = 8.4, 2.3 Hz, 1 H), 6.14 (m, 2 H), 6.02 (dd, *J* = 7.5, 1.1 Hz, 1 H), 5.71 (d, *J* = 2.5 Hz, 1 H), 5.69 (d, *J* = 15.1 Hz, 1 H), 6.49 (t, *J* = 8.1 Hz, 1 H), 4.89 (d, *J* = 14.3 Hz, 1 H), 4.74 (d, *J* = 13.7 Hz, 1 H), 4.31 (dd, *J* = 8.8, 6.4 Hz, 1 H), 4.16 (dd, *J* = 8.7, 7.2 Hz, 1 H), 4.10 (m, 5 H), 3.90 (dd, *J* = 8.9, 6.3 Hz, 1 H), 3.85 (d, *J* = 6.6 Hz, 2 H), 3.82 (m, 1 H), 3.76 (s, 6 H), 3.69 (m, 2 H), 3.68 (s, 3 H), 3.60 (d, *J* = 13.7 Hz, 1 H), 3.05 (t, *J* = 6.8 Hz, 1 H), 2.99 (t, *J* = 6.7 Hz, 1 H), 2.43 (m, 1 H), 2.32 (m, 2 H), 2.26 (m, 1 H), 2.15 (s, 3 H), 2.08 (m, 1 H), 1.71 (m, 1 H), 1.24 (d, *J* = 6.7 Hz, 6 H), 1.17 (m, 12 H), 1.13 (d, *J* = 6.7 Hz, 6 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H), 0.68 (d, *J* = 6.7 Hz, 3 H), 0.62 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 169.4, 167.2, 164.2, 163.7, 163.7, 163.5, 163.4, 163.3, 161.5, 160.9, 160.7, 159.9, 158.9, 158.6, 154.2, 151.5, 150.1, 149.5, 148.6, 143.6, 143.2, 142.6, 140.7, 140.0, 139.3, 138.4, 137.3, 137.1, 135.0, 134.6, 133.8, 131.7, 131.5, 130.0, 127.9, 127.8, 127.8, 127.7, 127.4, 126.0, 124.4, 123.3, 123.1, 122.3, 122.2, 120.7, 120.6, 120.5, 119.8, 119.0, 117.7, 117.4, 117.4, 116.7, 116.3, 116.2, 110.3, 109.9, 103.9, 103.6, 101.7, 101.4, 99.9, 99.3, 98.6, 98.4, 97.8, 75.5, 75.5, 75.2, 74.9, 74.0, 55.6, 55.4, 55.3, 53.8, 49.9, 47.7, 28.4, 28.3, 28.3, 28.2, 28.1, 27.8, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.2, 19.2, 19.1. HRMS (ESI+) m/z calcd for $C_{102}H_{107}N_{12}O_{17}$ $[M+H]^+$ 1771.7872, found 1771.7914.

Synthesis of Compound **6d:** To a solution of **19** (108.4 mg, 0.054 mmol) in dry dichloromethane (0.5 mL), DBU (15.6 mg, 3.9 eq.) in dry dichloromethane (0.5 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by GPC to give **6d** as yellow solid (80.7 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.08 (s, 1 H), 11.11 (s, 1 H),

10.92 (s, 1 H), 9.26 (d, *J* = 7.6 Hz, 1 H), 8.97 (dd, *J* = 7.7, 1.1 Hz, 1 H), 8.40 (d, *J* = 7.6 Hz, 1 H), 8.23 (dd, *J* = 8.3, 1.0 Hz, 1 H), 8.10 (dd, *J* = 8.3, 1.0 Hz, 1 H), 8.00 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.95 (s, 1 H), 7.84 (s, 1 H), 7.84 (t, *J* = 8.0 Hz, 1 H), 7.75 (s, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.6 Hz, 1 H), 7.34-7.28 (m, 3 H), 7.20 (s, 1 H), 7.18 (d, *J* = 8.3 Hz, 1 H), 7.15 (s, 1 H), 7.07-7.01 (m, 4 H), 6.81 (m, 2 H), 6.76 (dd, *J* = 7.6, 1.1 Hz, 1 H), 6.52 (d, *J* = 6.5 Hz, 1 H), 6.06 (dd, *J* = 8.3, 2.3 Hz, 1 H), 5.84 (dd, *J* = 8.5, 2.3 Hz, 1 H), 5.79 (d, *J* = 2.3 Hz, 1 H), 5.69 (d, *J* = 2.3 Hz, 1 H), 5.63 (t, *J* = 8.2 Hz, 1 H), 5.50 (d, *J* = 14.5 Hz, 1 H), 5.30 (d, *J* = 14.2 Hz, 1 H), 4.98 (d, *J* = 14.4 Hz, 1 H), 4.41 (dd, *J* = 8.8, 6.6 Hz, 1 H), 4.24 (dd, *J* = 6.4, 1.5 Hz, 2 H), 4.16 (dd, *J* = 8.8, 6.7 Hz, 1 H), 4.13 (d, *J* = 6.5 Hz, 2 H), 3.77 (d, *J* = 14.1 Hz, 1 H), 3.73 (d, *J* = 6.4 Hz, 2 H), 3.64 (s, 3 H), 3.45 (s, 3 H), 3.18 (m, 2 H), 3.04 (dd, *J* = 8.6, 6.6 Hz, 1 H), 3.03 (s, 3 H), 2.79 (s, 3 H), 2.45-2.33 (m, 3 H), 2.05 (m, 1 H), 1.96 (m, 1 H), 1.78 (m, 1 H), 1.24 (d, *J* = 6.7 Hz, 3 H), 1.23 (d, *J* = 6.7 Hz, 3 H), 1.16 (m, 12 H), 0.93 (m, 12 H), 0.65 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.2, 164.1, 163.8, 163.4, 163.3, 163.2, 163.1, 162.6, 161.4, 161.1, 160.0, 159.5, 158.6, 157.9, 152.2, 152.1, 151.9, 151.0, 150.2, 149.0, 143.9, 143.8, 142.7, 142.3, 140.6, 139.6, 139.4, 137.3, 136.7, 135.0, 134.7, 134.0, 132.3, 132.1, 128.8, 127.8, 127.7, 127.5, 126.8, 125.9, 125.3, 123.2, 123.1, 122.7, 121.7, 121.3, 120.9, 120.5, 120.4, 119.8, 119.4, 118.2, 117.5, 117.4, 117.2, 116.3, 115.3, 110.1, 109.4, 103.1, 101.9, 101.0, 100.6, 100.0, 98.8, 98.1, 97.7, 97.4, 75.6, 75.5, 75.4, 75.0, 74.3, 74.2, 55.2, 55.1, 54.6, 54.1, 48.5, 47.8, 28.4, 28.3, 28.1, 28.0, 27.8, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 18.9, 18.9. HRMS (ESI+) m/z calcd for $C_{102}H_{107}N_{12}O_{17}$ $[M+H]^+$ 1771,7872, found 1771.7828.

Synthesis of Compound **8c**: **6c** (26 mg, 0.015 mmol) and triphenylphosphine (14.8 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (5.6 μL, 4 eq.) and dry DIPEA (14 μL, 6 eq.) were added. The mixture was stirred at rt for 4.5 h. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) and GPC to give **8c** as white solid (33.1 mg, 26%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.20 (s, 1 H), 11.86 (s, 1 H), 11.56 (s, 1 H), 9.20 (d, *J* = 6.8 Hz, 1 H), 9.01 (s, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.26 (d, *J* = 7.4 Hz, 1 H), 8.13 (m, 2 H), 8.05 (d, *J* = 8.1 Hz, 1 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 7.97 (m, 2 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.81 (t, *J* = 8.1 Hz, 1 H), 7.65 (m, 6 H), 7.53 (m, 2 H), 7.48 (t, *J* = 7.9 Hz, 2 H), 7.43 (m, 2 H), 7.34 (d, *J* = 6.8 Hz, 1 H), 7.23 (m, 3 H), 7.11 (d, *J* = 8.2 Hz, 1 H), 7.04 (t, *J* = 8.0 Hz, 1 H), 6.83 (s, 1 H), 6.73 (m, 5 H), 6.30 (d, *J* = 7.1 Hz, 1 H), 6.29 (s, 1 H), 6.23 (m, 1 H), 6.15 (d, *J* = 2.3 Hz, 1 H), 6.12 (dd, *J* = 8.4, 2.3 Hz, 1 H), 6.04 (dd, *J* = 8.3, 2.3 Hz, 1 H), 5.97 (d, *J* = 2.3 Hz, 1 H), 5.47 (m, 3 H), 4.36 (m, 2 H), 4.21-4.12 (m, 6 H), 4.07-4.00 (m, 5 H), 3.91 (m, 2 H), 3.82 (m, 2 H), 3.64 (s, 3 H), 3.64 (s, 3 H), 3.39 (s, 3 H), 2.75 (s, 3 H), 2.37-2.25 (m, 3 H), 2.08 (m, 2 H), 1.96 (m, 1 H), 1.17 (m, 18 H), 0.95 (m, 12 H), 0.84 (d, *J* = 6.7 Hz, 3 H), 0.75 (d, *J* = 6.7 Hz, 3 H). minor peaks: (major: minor = 2:1) 11.71 (s, 1 H), 11.64 (s, 1 H), 9.90 (s, 1 H), 9.47 (s, 1 H), 9.37 (d, *J* = 6.8 Hz, 1 H), 8.68 (d, *J* = 7.2 Hz, 1 H), 8.52 (d, *J* = 7.6 Hz, 1 H), 8.32 (d, *J* = 6.9 Hz, 1 H), 8.20 (t, *J* = 7.6 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 1 H), 7.78-7.68 (m, 6 H), 7.20 (t, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 8.5 Hz, 1 H), 6.89 (s, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 6.52 (s, 1 H), 6.19 (d, *J* = 2.3 Hz, 1 H), 5.82 (d, *J* = 13.8 Hz, 2 H), 5.37 (d, *J* = 17.9 Hz, 2 H), 4.83 (d, *J* = 17.8 Hz, 2 H), 3.70 (m, 4 H), 3.65 (s, 3 H), 3.64 (s, 3 H), 3.41 (s, 3 H), 2.74 (s, 3 H), 2.31 (m, 3 H), 2.15 (m, 1 H), 1.85 (m, 3 H), 1.58 (m, 1 H), 1.17 (m, 18 H), 1.04 (m, 6 H), 1.00 (d, *J* = 6.7 Hz, 3 H), 0.95 (m, 6 H), 0.87 (m, 3 H), 0.82 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 170.2, 169.9, 167.2, 166.5, 165.6, 165.3, 165.1, 164.3, 164.1, 163.9, 163.4, 163.4, 163.3, 163.0, 162.9, 162.8, 162.6, 162.6, 162.1, 162.0, 161.9, 160.9, 160.0, 159.8, 159.3, 158.4,

158.1, 157.5, 155.8, 155.6, 155.3, 154.0, 153.2, 153.0, 152.4, 151.9, 151.5, 151.0, 150.9, 150.4, 145.6, 143.9, 143.1, 143.1, 142.2, 141.9, 141.3, 140.9, 140.4, 140.3, 140.0, 139.9, 139.7, 137.9, 137.1, 136.5, 135.8, 135.7, 135.1, 135.0, 134.7, 134.4, 134.4, 134.1, 133.1, 131.6, 130.7, 130.3, 129.5, 128.0, 127.8, 127.6, 127.3, 127.2, 126.7, 126.6, 126.5, 126.4, 126.0, 126.0, 125.6, 125.5, 125.3, 124.9, 123.7, 123.5, 122.9, 122.7, 122.5, 122.4, 122.4, 122.3, 122.1, 122.0, 122.0, 121.9, 121.8, 121.7, 120.7, 120.5, 120.3, 120.0, 119.4, 118.7, 118.6, 118.5, 118.5, 118.3, 118.2, 118.1, 118.0, 117.7, 117.1, 116.9, 116.3, 115.1, 103.5, 103.0, 102.8, 101.3, 100.5, 100.3, 100.2, 99.0, 98.6, 98.6, 98.5, 98.5, 98.1, 97.6, 97.3, 75.5, 75.4, 75.3, 75.1, 75.1, 74.9, 74.7, 74.7, 74.6, 73.9, 55.3, 55.3, 55.3, 55.2, 55.0, 54.0, 52.8. 52.3, 50.5, 49.8, 48.7, 29.8, 28.4, 28.4, 28.4, 28.3, 28.3, 28.2, 28.1, 28.1, 28.0, 27.9, 19.5, 19.4, 19.4, 19.4, 19.3, 19.3, 19.3, 19.2, 19.2, 19.2, 19.1, 19.1, 18.8. HRMS (ESI+) m/z calcd for $C_{102}H_{105}N_{12}O_{16}$ $[M+H]^+$ 1753.7766, found 1753.7774.

Synthesis of Compound **8d**: **6d** (30.4 mg, 0.017 mmol) and triphenylphosphine (17.9 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (6.8 μL, 4 eq.) and dry DIPEA (17 μL, 6 eq.) were added. The mixture was stirred at rt overnight. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed in *vacuo*, the residue was purified by GPC and PLC to give **8d** as yellow solid (10.7 mg, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.31 (s, 1 H), 10.13 (s, 1 H), 9.02 (br, 1 H), 7.96 (d, *J* = 7.3 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 7.59 (s, 1 H), 7.45 (d, *J* = 8.2 Hz, 1 H), 7.15 (d, *J* = 8.3 Hz, 1 H), 7.08 (t, *J* = 7.4 Hz, 1 H), 6.88 (t, *J* = 7.7 Hz, 1 H), 6.84 (br, 1 H), 6.65 (br, 1 H), 6.34 (s, 1 H), 5.87 (d, *J* = 8.2 Hz, 1 H), 5.86 (s, 1 H), 5.17 (d, *J* = 14.3 Hz, 1 H), 4.81 (d, *J* = 14.3 Hz, 1 H), 4.38 (t, *J* = 8.4 Hz, 1 H), 4.08 (dd, *J* = 8.8, 6.3 Hz, 1 H), 3.77 (m, 2 H), 3.64 (br, 1 H), 3.57 (dd, *J* = 8.9, 6.4 Hz, 1 H), 3.52 (s, 3 H), 2.84 (s, 3 H), 2.36 (m, 1 H), 2.17 (m, 1 H), 2.07 (m, 1 H), 1.26 (d, *J* = 6.7 Hz, 3 H), 1.25 (d, *J* = 6.7 Hz, 3 H), 1.14 (d, *J* = 6.7 Hz, 3 H), 1.11 (d, *J* = 6.7 Hz, 3 H), 1.10 (d, *J* = 6.8 Hz, 3 H), 0.99 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 162.1, 160.8, 159.9, 158.5, 153.7, 151.8, 151.7, 143.5, 141.4, 140.9, 139.0, 136.0, 133.9, 132.4, 128.7, 128.1, 126.9, 125.5, 125.2, 122.6, 122.1, 120.6, 120.0, 118.2, 118.0, 117.9, 116.3, 103.4, 101.4, 100.7, 98.9, 97.5, 74.9, 74.5, 55.2, 54.4, 47.2, 28.6, 28.2, 28.2, 19.7, 19.6, 19.5, 19.4, 19.2. HRMS (ESI+) m/z calcd for $C_{102}H_{105}N_{12}O_{16}$ $[M+H]^+$ 1753.7766, found 1753.7798.

Synthesis of Compound **4**: Trifluoroacetic acid (0.5 mL) was added to **8d** (11.1 mg, 6.3 μmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC to give **4** as yellow solid (6.1 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.49 (s, 4 H), 9.83 (s, 2 H), 8.60 (d, *J* = 7.5 Hz, 2 H), 8.28 (d, *J* = 7.5 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.59 (t, *J* = 8.0 Hz, 2 H), 7.57 (s, 2 H), 7.44 (t, *J* = 7.9 Hz, 2 H), 7.37 (s, 2 H), 7.27 (t, *J* = 7.7 Hz, 2 H), 7.19 (d, *J* = 7.3 Hz, 2 H), 6.55 (s, 2 H), 4.07 (t, *J* = 8.9 Hz, 2 H), 4.02 (t, *J* = 6.8 Hz, 2 H), 4.01 (t, *J* = 6.6 Hz, 2 H), 3.81 (t, *J* = 5.8 Hz, 2 H), 3.77 (t, *J* = 7.0 Hz, 2 H), 3.62 (t, *J* = 8.1 Hz, 2 H), 2.64 (t, *J* = 6.7 Hz, 2 H), 2.26 (m, 4 H), 1.95 (m, 2 H), 1.21 (d, *J* = 6.7 Hz, 6 H), 1.16 (d, *J* = 6.7 Hz, 6 H), 1.07 (m, 12 H), 0.99 (m, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 165.8, 164.3, 163.3, 162.9, 162.3, 154.5, 152.1, 150.1, 142.4, 141.2, 138.5, 135.1, 134.7, 134.4, 127.6, 127.3, 127.1, 126.9, 126.5, 123.1, 122.6, 121.8, 121.2, 118.9, 116.5, 116.2, 110.9, 99.5, 97.8, 75.5, 74.8, 70.7, 29.8, 28.3, 28.2, 19.6, 19.4, 19.3, 19.2.HRMS (ESI+) m/z calcd for $C_{84}H_{85}N_{12}O_{12}$ $[M+H]^+$ 1453.6404, found 1453.6393.

Synthesis of Compound **20**: A solution of acid **16** (200 mg, 0.18 mmol) in dry chloroform (1.5 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (40 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **11** (51.2 mg, 0.9 eq.) and dry DIPEA (0.15 mL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **20** as yellow solid (178 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.01 (s, 1 H), 11.90 (s, 1 H), 8.99 (m, 2 H), 8.08 (d, *J* = 8.1 Hz, 1 H), 7.88 (s, 1 H), 7.76 (m, 3 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.2 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 8.2 Hz, 1 H), 7.49 (s, 1 H), 7.47 (d, *J* = 8.3 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.28 (br, 1 H), 7.24 (m, 1 H). 7.20 (br, 1 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 6.98 (m, 2 H), 6.94 (d, *J* = 8.2 Hz, 1 H), 6.87 (br, 1 H), 6.82 (s, 1 H), 6.20 (dd, *J* = 8.3, 2.2 Hz, 1 H), 6.10 (d, *J* = 2.1 Hz, 1 H), 5.67 (m, 1 H), 5.28 (d, *J* = 14.9 Hz, 1 H), 5.17 (dd, *J* = 17.2, 1.4 Hz, 1 H), 4.88 (d, *J* = 10.4 Hz, 1 H), 4.53 (m, 2 H), 4.41 (dd, *J* = 13.4, 5.7 Hz, 1 H), 4.37 (br, 1 H), 4.29 (t, *J* = 7.0 Hz, 1 H), 4.18 (m, 2 H), 3.96 (t, *J* = 8.6 Hz, 1 H), 3.93 (t, *J* = 6.5 Hz, 1 H), 3.82 (t, *J* = 6.4 Hz, 1 H), 3.77 (t, *J* = 6.5 Hz, 1 H), 3.70 (s, 3 H), 3.42 (br, 1 H), 3.33 (br, 1 H), 3.27 (s, 3 H), 3.30 (br, 1 H), 2.36 (br, 1 H), 2.20 (m, 2 H), 1.92 (m, 1 H), 1.19 (m, 6 H), 1.10 (m, 12 H), 0.88 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.3, 163.8, 163.6, 163.4, 163.0, 162.3, 161.7, 159.9, 158.0, 153.2, 151.9, 151.0, 146.2, 144.0, 143.9, 142.7, 141.4, 141.4, 139.4, 139.4, 136.2, 135.2, 135.1, 134.2, 131.3, 130.6, 128.2, 127.9, 127.8, 127.3, 127.2, 126.5, 125.2, 125.1, 122.7, 122.6, 121.8, 120.6, 120.2, 120.1, 119.3, 118.5, 118.4, 118.3, 118.1, 116.8, 115.8, 114.7, 114.6, 103.6, 100.8, 100.5, 100.0, 98.3, 97.8, 77.4, 77.2, 76.9, 75.5, 75.2, 74.9, 74.3, 66.9, 66.2, 55.3, 54.7, 48.6, 47.2, 28.3, 28.3, 28.2, 28.0, 19.4, 19.4, 19.4, 19.3, 19.1. HRMS (ESI+) m/z calcd for $C_{83}H_{82}N_8NaO_{13}$ $[M+Na]^+$ 1421.5894, found 1421.5854.

Synthesis of Compound **21**: To a solution of **20** (170 mg, 0.12 mmol) in dry dichloromethane (1 mL), DBU (19.2 mg, 3.9 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **21** as yellow solid (155 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.07 (s, 1 H), 11.87 (s, 1 H), 9.06 (d, *J* = 7.4 Hz, 1 H), 8.94 (d, *J* = 7.2 Hz, 1 H), 8.06 (d, *J* = 8.3, 0.9 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 7.83 (s, 1 H), 7.71 (s, 1 H), 7.67 (t, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.49 (t, *J* = 7.9 Hz, 1 H), 7.16 (d, *J* = 8.3 Hz, 1 H), 7.11 (d, *J* = 7.9 Hz, 1 H), 6.98 (m, 2 H), 6.83 (s, 1 H), 6.74 (s, 1 H), 6.70 (d, *J* = 7.1 Hz, 1 H), 6.44 (d, *J* = 7.1 Hz, 1 H), 6.15 (dd, *J* = 8.3, 2.2 Hz, 1 H), 5.95 (d, *J* = 2.1 Hz, 1 H), 5.73 (m, 1 H), 5.37 (d, *J* = 14.6 Hz, 1 H), 5.23 (d, *J* = 15.8 Hz, 1 H), 4.95 (d, *J* = 9.6 Hz, 1 H), 4.54 (m, 2 H), 4.14 (d, *J* = 6.4 Hz, 2 H), 4.08 (d, *J* = 6.6 Hz, 2 H), 3.68 (m, 1 H), 3.67 (s, 3 H), 3.59 (br, 2 H), 3.49 (dd, *J* = 8.8, 6.6 Hz, 1 H), 3.35 (t, *J* = 7.2 Hz, 1 H), 3.05 (s, 3 H), 2.31 (m, 2 H), 2.15 (m, 1 H), 2.02 (m. 1 H), 1.15 (m, 12 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 1.09 (d, *J* = 6.7 Hz, 1 H). 0.98 (d, *J* = 6.7 Hz, 3 H), 0.95 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 164.7, 163.9, 163.8, 163.4, 163.2, 162.0, 161.3, 159.7, 158.1, 152.0, 151.1, 151.0, 146.2, 143.8, 143.8, 142.9, 139.5, 139.2, 136.2, 135.3, 135.1, 131.6, 127.9, 127.6, 127.4, 126.7, 126.1, 122.8, 122.6, 121.4, 121.1, 119.6, 118.8, 118.6, 118.6, 118.0, 116.7, 115.7, 109.8, 109.4, 103.6, 100.7, 100.4, 99.9, 98.3, 97.6, 75.4, 75.3, 74.6, 74.3, 66.2, 55.2, 54.4, 48.2, 28.3, 28.3, 28.3, 28.1, 19.4, 19.4, 19.2. HRMS (ESI+) m/z calcd for $C_{68}H_{73}N_8O_{11}$ $[M+H]^+$ 1177.5393, found 1177.5368.

Synthesis of Compound **23**: To a solution of **22**[7] (427 mg, 0.48 mmol) in dichloromethane (4 mL), DBU (0.07 mL, 1 eq.) was added. The mixture was stirred for 15 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **23** as yellow solid (330 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.53 (dd, *J* = 7.4, 1.3 Hz, 1 H), 3.39-3.31 (m, 4 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 6.61 (d, *J* = 7.5 Hz, 1 H), 6.39 (dd, *J* = 8.3, 2.3 Hz, 1 H), 6.29 (d, *J* = 2.4 Hz, 1 H), 5.65 (d, *J* = 15.9 Hz, 1 H), 5.03 (d, *J* = 15.3 Hz, 1 H), 4.11 (br, 1 H), 4.04 (s, 3 H), 3.91 (d, *J* = 6.5 Hz, 3 H), 3.75 (s, 3 H), 3.69 (br, 1 H), 3.51 (s, 3 H), 2.18 (m, 2 H), 1.06 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ166.6, 162.6, 161.6, 160.1, 158.5, 152.7, 148.3, 144.5, 144.1, 131.1, 127.8, 126.9, 126.8, 123.0, 121.7, 120.3, 118.6, 110.2, 109.5, 104.1, 101.4, 100.7, 98.1, 75.1, 74.7, 55.4, 55.1, 52.9, 28.2, 28.2, 19.3, 19.3. HRMS (ESI+) m/z calcd for $C_{38}H_{43}N_4O_7$ $[M+H]^+$ 667.3126, found 667.3111.

Synthesis of Compound **25**: A solution of acid **24**[8] (219 mg, 0.45 mmol) in dry $CHCl_3$ (2 mL) was cooled to 0°C. Oxalyl chloride (0.12 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **23** (303 mg, 0.9 eq.) and dry DIPEA (0.40 mL, 5 eq.) in dry $CHCl_3$ (0.5 mL). The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **25** as white solid (560 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.39 (s, 1 H), 9.52 (s, 1 H), 8.72 (d, *J* = 7.0 Hz, 1 H), 8.60 (d, *J* = 7.1 Hz, 1 H), 8.04 (d, *J* = 7.7 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.77 (s, 1 H), 7.71 (m, 3 H), 7.63 (d, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.52 (d, 8.5 Hz, 1 H), 7.43 (m, 2 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.34 (s, 1 H), 7.27 (t, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 7.03 (s, 1 H), 6.77 (t, *J* = 7.4 Hz, 1 H), 6.20 (dd, *J* = 8.5, 2.3 Hz, 1 H), 6.15 (t, *J* = 7.9 Hz, 1 H), 6.08 (d, *J* = 2.3 Hz, 1 H), 5.62 (d, *J* = 15 Hz, 1 H), 5.13 (d, *J* = 15 Hz, 1H), 4.75 (m, 1 H), 4.54 (m, 2 H), 4.19 (d, *J* = 6.5 Hz, 2 H), 4.00 (s, 3 H), 3.90 (m, 1 H), 3.71 (dd, *J* = 6.4, 2.2 Hz, 2 H), 3.68 (m, 1 H), 3.65 (s, 3 H), 3.32 (s, 3 H), 2.38 (m, 1 H), 2.15 (m ,1 H), 2.08 (m, 1 H), 1.21 (d, *J* = 6.5 Hz, 6 H), 1.04 (d, *J* = 6.6 Hz, 3 H), 1.03 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 166.3, 163.8, 162.6, 162.0, 161.4, 159.8, 158.2, 155.0, 153.8, 150.6, 147.2, 144.7, 143.9, 143.8, 142.3, 141.4, 141.2, 137.5, 137.3, 134.8, 133.9, 131.6, 128.1, 127.6, 127.5, 127.3, 126.9, 126.7, 126.5, 126.1, 125.7, 125.4, 122.4, 122.3, 120.8, 119.9, 119.9, 119.8, 117.5, 116.6, 116.5, 116.0, 115.5, 103.7, 102.7, 100.3, 99.3, 97.6, 75.6, 74.9, 74.8, 68.1, 55.3, 55.0, 52.8, 48.3, 46.8, 28.4, 28.2, 28.1, 19.5, 19.4, 19.4, 19.3, 19.3. HRMS (ESI+) m/z calcd for $C_{67}H_{67}N_6O_{11}$ $[M+H]^+$ 1131.4862, found 1131.4842.

Synthesis of Compound **26**: The mixture of **25** (232 mg, 0.20 mmol) and LiI (140 mg, 4.9 eq.) in degassed ethyl acetate (3 mL) was heated to 80°C overnight. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with 5% citric acid aq. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3 / 7) to give **26** as yellow solid (291 mg, quant.). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.38 (s, 1 H), 9.55 (s, 1 H), 8.72 (s, 1 H), 8.61 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.06 (d, *J* = 7.4 Hz, 1 H), 7.78 (s, 1 H), 7.74-7.67 (m, 6 H), 7.61 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.54 (d, *J* = 8.5 Hz, 1 H), 7.49 (d, *J*

= 7.5 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.22 (s, 1 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.07 (s, 1 H), 6.99 (t, *J* = 6.9 Hz, 1 H), 6.87 (t, *J* = 7.4 Hz, 1 H), 6.28 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.24 (dd, *J* = 8.3, 7.6 Hz, 1 H), 5.89 (d, *J* = 2.3 Hz, 1 H), 5.80 (d, *J* = 13.9 Hz, 1 H), 4.82 (d, *J* = 13.9 Hz, 1 H), 4.76 (m, 2 H), 4.53 (t, *J* = 7.7 Hz, 1 H), 4.19 (t, *J* = 6.0 Hz, 2 H), 3.88 (dd, *J* = 8.9, 6.7 Hz, 1 H), 3.79 (dd, *J* = 8.8, 6.4 Hz, 1 H), 3.76 (dd, *J* = 6.7, 2.9 Hz, 2 H), 3.64 (s, 3 H), 2.95 (s, 3 H), 2.39 (m, 1 H), 2.12 (m, 2 H), 1.23 (d, *J* = 6.7 Hz, 3 H), 1.22 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 6.7 Hz, 3 H), 1.04 (d, *J* = 6.7 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 164.2, 163.9, 163.5, 162.4, 162.3, 160.4, 158.6, 153.7, 153.7, 150.5, 145.6, 144.5, 143.7, 142.8, 141.5, 141.4, 141.3, 137.4, 137.4, 134.7, 133.9, 132.8, 129.3, 128.2, 127.5, 127.5, 127.0, 126.9, 126.8, 126.8, 125.5, 125.4, 122.4, 122.4, 120.8, 120.4, 119.9, 119.9, 117.2, 116.7, 116.0, 115.6, 103.8, 101.4, 99.2, 98.2, 98.1, 75.6, 75.4, 75.2, 68.2, 55.4, 54.8, 48.7, 47.0, 28.4, 28.1, 28.0, 19.4, 19.3, 19.2, 19.2. HRMS (ESI+) m/z calcd for $C_{66}H_{65}N_6O_{11}$ $[M+H]^+$ 1117.4706, found 1117.4679.

Synthesis of Compound **27**: A solution of acid **26** (76.6 mg, 0.069 mmol) in dry chloroform (1 mL) was cooled to 0°C. 1-Chloro-*N*,*N*,2-trimethyl-1-propenylamine (15 μL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum line. To the resulting acid chloride, a solution of **21** (72.6 mg, 0.9 eq.) and dry DIPEA (22 μL, 5 eq.) in dry chloroform (1 mL) was added. The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **27** as yellow solid (90.9 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major/Minor 1/ Minor 2 = 10/ 5/ 1) Major δ 11.87 (s, 1 H), 11.40 (s, 1 H), 11.20 (s, 1 H), 10.98 (s, 1 H), 9.54 (s, 1 H), 9.18 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.81 (d, *J* = 7.6 Hz, 1 H), 8.68 (dd, *J* = 7.8, 1.2 Hz, 1 H), 8.65 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.52 (dd, *J* = 7.2, 1.2 Hz, 1 H), 8.09 (m, 2 H), 7.97 - 7.54 (m, 23 H), 7.51 - 7.27 (m, 14 H), 7.16 (s, 1 H), 7.16 (br, 1 H), 7.10 (m, 2 H), 7.05 (s, 1 H), 7.04 - 6.99 (m, 4 H), 6.78 (s, 1 H), 6.69 (t, *J* = 7.4 Hz, 1 H), 6.63 (s, 1 H), 6.57 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.06 (d, *J* = 1.2 Hz, 1 H), 6.02 (br, 1 H), 5.94 (m, 1 H), 5.52 (m, 2 H), 5.27 (m, 2 H), 4.99 (m, 3 H), 4.90 (d, *J* = 7.8 Hz, 1 H), 4.29-4.06 (m, 18 H), 3.95 (m, 1 H), 3.82-3.68 (m, 13 H), 3.21 (m, 2 H), 3.43 (s, 3 H), 2,90 (m, 1 H), 2.70 (br, 1 H), 2.65 (m, 1 H), 2.42 -2.04 (m, 6 H), 1.66 (m, 1 H), 1.22 -1.17 (m, 28 H), 1.16-1.12 (m, 22 H), 0.98 (d, *J* = 6.7 Hz, 6 H), 0.76 (d, *J* = 6.7 Hz, 3 H), 0.72 (d, *J* = 6.7 Hz, 1 H), 0.63 (d, *J* = 6.7 Hz, 3 H), 0.52 (d, *J* = 6.7 Hz, 3 H). Minor 1 δ 11.50 (s, 1 H), 11.36 (s. 1 H), 11.06 (s, 1 H), 10.80 (s, 1 H), 9.31 (s, 1 H), 9.08 (s, 1 H), 9.01 (d, *J* = 7.4 Hz, 1 H), 8.55 (m, 2 H), 8.45 (br, 1 H), 8.16 (d, *J* = 7.4 Hz, 1 H), 8.12 (br, 1 H), 6.71 (s, 1 H), 6.49 (d, *J* = 6.4 Hz, 1 H), 6.28 - 6.11 (m, 8 H), 5.13 (m, 3 H), 4.82 (d, *J* = 7.4 Hz, 1 H), 4.76 (m, 2 H), 4.67 (m, 2 H), 4.54 (m, 2 H), 3.16 (s, 3 H). Minor 2 δ 11.81 (s, 1 H), 11.48 (s, 1 H), 11.22 (s, 1 H), 10.74 (s, 1 H), 9.16 (d, *J* = 8.0 Hz, 1 H), 8.73 (m, 2 H), 8.35 (d, *J* = 6.4 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.04 (d, *J* = 8.4 Hz, 2 H), 6.97-6.89 (m, 16 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.7, 168.1, 164.9, 164.0, 163.8, 163.7, 163.6, 163.5, 163.2, 162.8, 162.5, 162.3, 162.2, 161.4, 160.7, 159.6, 159.3, 157.8, 157.5, 156.2, 154.9, 153.5, 152.7, 151.4. 150.6, 150.2, 146.2, 144.8, 144.6, 143.7, 143.2, 141.2, 141.0, 140.8, 140.1, 139.6, 139.3, 137.4, 136.9, 135.1, 134.9, 134.8, 134.3, 134.2, 133.8, 133.3, 132.7, 131.5, 131.4, 127.9, 127.7, 127.5, 127.3, 127.2, 127.0, 126.8, 126.6, 126.6, 126.4, 126.2, 126.0, 125.7, 125.6, 125.4, 125.3, 124.9, 122.9, 122.7, 122.4, 122.3, 122.2, 122.1, 121.4, 121.1, 120.9, 120.7, 120.6, 120.0, 119.9, 119.5, 119.4, 119.4, 119.2, 119.1, 118.4, 118.2, 117.3, 117.0, 116.9, 116.8, 116.5, 116.4, 116.2, 116.1, 116.1, 115.8, 115.6, 115.0, 105.0, 104.1, 102.5, 102.0, 101.7, 100.9,100.3, 100.2, 100.1, 99.3, 99.1, 98.5, 98.2, 98.0, 97.0, 75.6, 75.4, 75.4, 74.8, 74.7, 74.2, 73.8, 67.6, 66.9, 66.1, 66.0, 55.6, 55.4, 55.0, 55.0, 54.7, 54.1, 53.6, 53.2, 47.5, 46.5, 45.8,

45.0, 29.8, 28.4, 28.4, 28.3, 28.2, 28.2, 28.2, 28.1, 27.7, 27.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.2, 19.2. HRMS (ESI+) m/z calcd for $C_{134}H_{134}N_{14}NaO_{21}$ $[M+Na]^+$ 2297.9740, found 2297.9738.

Synthesis of Compound **28**: To a solution of **27** (125 mg, 0.055 mmol) in dry dichloromethane (1 mL), phenylsilane (16 μL, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (1.3 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/*n*-hexane = 3/7) to give **28** as yellow solid (113 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major and three kinds of minor) Major δ 11.59 (s, 1 H), 11.89 (s, 1 H), 11.34 (s, 1 H), 11.00 (s, 1 H), 9.53 (s, 1 H), 9.08 (d, *J* = 7.0 Hz, 1 H), 8.80 (d, *J* = 7.4 Hz, 1 H), 8.73 (d, *J* = 7.8 Hz, 1 H), 8.68 (dd, *J* = 7.4, 1.2 Hz, 1 H), 8.52 (dd, *J* = 7.2, 1.2 Hz, 1 H), 8.10 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.08 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.03 (s, 1 H), 7.94 (m, 2 H), 7.82 - 7.32 (m, 36 H), 7.14 (m, 6 H), 7.02 (m, 5 H), 6.78 (s, 1 H), 6.64 (s, 1 H), 6.51 (dd, *J* = 6.8, 1.2 Hz, 1 H), 6.29 - 6.11 (m, 5 H), 6.03 (d, *J* = 1.2 Hz, 1 H), 5.93 (dd, *J* = 6.8, 8.0 Hz, 1 H), 5.40 (d, *J* = 14.4 Hz, 1 H), 5.23 (s, 1 H), 5.06 (d, *J* = 13.6 Hz, 1 H), 4.93 (d, *J* = 13.6 Hz, 1 H), 4.83 (m, 2 H), 4.33 (m, 1 H), 4.24 - 3.95 (m, 18 H), 3.89 - 3.67 (m, 12 H), 3.84 (s, 3 H), 3.73 (s, 3 H), 3.40 (s, 3 H), 2.46 - 1.64 (m, 7 H), 1.26 - 1.10 (m, 54 H), 1.03 (m, 5 H), 0.99 (d, *J* = 6.7 Hz, 9 H), 0.90 (m, 7 H), 0.77 (m, 10 H), 0.65 (d, *J* = 6.7 Hz, 5 H), 0.54 (d, *J* = 6.7 Hz, 3 H). Minor δ 11.79 (s, 1 H), 11.55 (s, 1 H), 11.34 (s, 2 H), 11.26 (m, 3 H), 11.17 (s, 1 H), 11.03 (s, 1 H), 10.90 (s, 1 H), 10.80 (s, 1 H), 10.62 (s, 1 H), 10.53 (s, 1 H), 9.33 (s, 1 H), 9.27 (d, *J* = 6.8 Hz, 1 H), 9.15 (br, 1 H), 9.00 (d, *J* = 6.8 Hz, 1 H), 8.90 (d, *J* = 6.6 Hz, 1 H), 8.64 (m, 2 H), 8.53 (t, *J* = 6.6 Hz, 1 H), 8.44 (br, 1 H), 8.41 (d, *J* = 6.4 Hz, 1 H), 8.18 (d, *J* = 7.0 Hz, 1 H), 5.74 (d, *J* = 13.1 Hz, 1 H), 5.66 (m, 2 H), 5.59 (d, *J* = 13.1 Hz, 1 H), 5.22 (d, *J* = 1.2 Hz, 1 H), 5.16 (br, 1 H), 3.60 (s, 3 H), 3.45 (s, 3 H), 3.29 (s, 3 H), 3.25 (s, 3 H), 3.19 (m, 1 H), 3.15 (s, 1 H), 2.92 (m, 1 H), 2.67 (m, 1 H), 0.35 (d, *J* = 6.7 Hz, 3 H).^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.6, 168.4, 164.0, 163.9, 163.8, 163.7, 163.6, 163.5, 163.4, 163.4, 163.2, 163.2, 163.1, 162.8, 162.6, 162.5, 162.2, 161.4, 160.9, 159.5, 159.4, 157.7, 157.2, 156.0, 154.8, 154.4, 153.4, 151.6, 151.5, 150.5, 150.1, 145.3, 144.8, 144.5, 144.3, 143.5, 143.1, 141.3, 141.1, 140.9, 140.7, 140.2, 139.7, 139.0, 137.9, 137.3, 136.9, 134.9, 134.7, 134.6, 134.3, 134.1, 133.7, 133.3, 133.0, 132.5, 128.1, 127.9, 127.5, 127.5, 127.3, 127.2, 127.0, 126.8, 126.6, 126.6, 126.5, 126.2, 126.0, 125.6, 125.6, 125.4, 125.2, 124.8, 122.9, 122.6, 122.3, 122.1, 122.0, 121.9, 121.2, 120.7, 120.7, 120.0, 119.8, 119.6, 119.5, 119.4, 119.3, 119.2, 118.2, 117.4, 116.9, 116.6, 116.4, 116.4, 116.2, 116.2, 116.0, 115.6, 104.9, 102.5, 101.6, 100.8, 99.8, 99.3, 99.2, 98.5, 98.2, 97.9, 97.4, 97.1, 75.6, 75.5, 75.4, 75.4, 74.3, 74.8, 74.6, 74.3, 73.7, 66.7, 55.5, 55.5, 55.4, 55.2, 55.2, 55.0, 55.0, 54.8, 54.8, 54.7, 54.5, 54.1, 53.5, 53.3, 53.2, 47.7, 46.5, 45.8, 44.8, 28.4, 28.3, 28.2, 28.0, 27.6, 27.5, 19.5, 19.4, 19.4, 19.4, 19.4, 19.3, 19.3, 19.3, 19.3, 19.2, 19.2, 19.1, 19.1, 18.9, 18.7. HRMS (ESI+) m/z calcd for $C_{131}H_{131}N_{14}O_{21}$ $[M+H]^+$ 2235.9608, found 2235.9597.

Synthesis of Compound **7b:** To a solution of **28** (113 mg, 0.05 mmol) in dry dichloromethane (1 mL), DBU (7.5 mg, 1.0 eq.) was added. The mixture was stirred for 10 min. The organic layer was washed with a 5% citric acid aqueous solution and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **7b** as yellow solid (85.5 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major and three kinds of minor) (Major) δ 12.76 (s, 1 H), 12.37 (s, 1 H), 11.62 (s, 1 H), 11.06 (s, 1 H), 9.43 (d, *J* = 7.8 Hz, 1 H), 9.10 (d, *J* = 8.0 Hz, 1 H), 9.05 (d, *J* = 6.8 Hz, 1 H), 8.99 (t, *J* = 7.6 Hz, 1 H), 8.72 (d, *J* = 8.0 Hz, 1 H), 8.67 (m, 2 H),

8.64 (m, 2 H), 8.33 (m, 2 H), 8.01 - 7.95 (m, 8 H), 7.90 (s, 1 H), 7.87 - 7.27 (m, 40 H), 7.02 (m, 2 H), 6.97 - 6.92 (m, 3 H), 6.87 (m, 2 H), 6.79 (m, 2 H), 6.74 (s, 1 H), 6.71 (t, *J* = 7.4 Hz, 1 H), 6.66 (m, 1 H), 6.57 - 6.48 (m, 6 H), 6.08 (d, *J* = 1.2 Hz, 1 H), 6.06 (dd, *J* = 7.0, 1.2 Hz, 1 H), 5.98 (d, *J* = 1.2 Hz, 1 H), 5.79 (d, *J* = 14.0 Hz, 1 H), 5.39 (m, 2 H), 4.88 (m, 3 H), 4.63 (br, 3 H), 4.44 (br, 1 H), 4.32 (m, 4 H), 4.24 - 4.08 (m, 18 H), 3.90 (m, 10 H), 3.81 - 3.76 (m, 6 H), 3.62 (m, 3 H), 3.53 (s, 5 H), 3.11 (s, 3 H), 3.03 (s, 3 H), 2.74 (m, 3 H), 2.58 (t, *J* = 6.4 Hz, 2 H), 2.55 (s, 1 H), 2.48 (m, 1 H), 2.38 - 2.27 (m, 13 H), 2.17 - 1.52 (m, 15 H), 1.29 - 1.09 (m, 74 H), 1.05 - 0.78 (m, 40 H), 0.68 (m, 8 H), 0.57 (m, 9 H), 0.52 (d, *J* = 6.7 Hz, 3 H). (Minor) δ 11.91 (s, 1 H), 11.82 (s, 1 H), 11.80 (s, 1 H), 11.59 (s, 1 H), 11.55 (s, 1 H), 11.48 (s, 1 H), 11.40 (s, 1 H), 11.32 (s, 1 H), 11.28 (s, 1 H), 11.08 (s, 1 H), 10.63 (br, 1 H), 9.16 (br, 1 H), 8.89 (d, *J* = 7.8 Hz, 1 H), 8.58 (d, *J* = 7.8 Hz, 1 H), 8.54 (d, *J* = 7.8 Hz, 1 H), 8.46 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 7.6 Hz, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 7.13 (s, 1 H), 6.33 (d, *J* = 6.8 Hz, 1 H), 6.29 (d, *J* = 1.2 Hz, 1 H), 6.22 (dd, *J* = 7.4, 1.2 Hz, 1 H), 5.99 (d, *J* = 7.4 Hz, 1 H), 5.90 (d, *J* = 1.2 Hz, 1 H), 5.67 (d, *J* = 1.2 Hz, 1 H), 5.1 (dd, *J* = 6.8, 1.2 Hz, 1 H), 5.57 (d, *J* = 13.0 Hz, 1 H), 5.44 (d, *J* = 1.2 Hz, 1 H), 5.42 (s, 1 H), 5.32 (d, *J* = 13.8 Hz, 1 H), 5.23 (br, 1 H), 5.04 (d, *J* = 14.2 Hz, 1 H), 4.97 (d, *J* = 14.8 Hz, 1 H), 3.50 (t, *J* = 6.4 Hz, 1 H), 3.47 (s, 3 H), 3.28 (s, 3 H), 3.27 (s, 3 H), 3.18 (s, 3 H), 0.48 (d, *J* = 6.7 Hz, 3 H).^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.4, 169.1, 168.7, 166.4, 165.3, 164.5, 164.2, 164.1, 163.8, 163.7, 163.6, 163.5, 163.5, 163.4, 163.3, 163.3, 163.2, 163.1, 163.0, 162.9, 162.7, 162.6, 162.4, 162.2, 161.9, 161.7, 161.3, 160.9, 160.9, 159.8, 159.7, 159.5, 159.3, 159.3, 158.5, 157.3, 157.2, 156.1, 155.8, 155.3, 152.8, 151.6, 150.6, 148.9, 148.2, 148.2, 146.3, 145.0, 145.0, 144.8, 143.6, 143.0, 141.7, 140.2, 140.2, 140.0, 140.0, 139.9, 139.3, 138.9, 138.8, 138.5, 138.3, 137.2, 136.9, 136.8, 135.4, 135.4, 135.2, 134.9, 134.7, 134.4, 134.3, 134.2, 134.1, 133.5, 133.2, 133.1, 128.4, 128.1, 128.0, 127.6, 127.4, 127.3, 126.9, 126.7, 126.5, 126.4, 126.3, 126.2, 126.1, 125.9, 123.9, 123.2, 123.1, 123.0, 122.9, 122.8, 122.6, 122.5, 122.3, 122.2, 122.1, 122.0, 121.8, 121.7, 121.5, 121.3, 120.9, 120.9, 120.7, 120.5, 120.3, 120.2, 120.0, 119.2, 119.0, 118.6, 118.5, 118.4, 118.3, 118.2, 117.9, 117.7, 117.5, 117.1, 117.0, 116.5, 116.4, 116.2, 116.0, 115.9, 115.8, 115.5, 115.1, 110.6, 110.4, 109.9, 109.3, 109.1, 108.7, 108.6, 104.2, 104.0, 103.4, 103.2, 102.6, 102.2, 102.0, 101.3, 101.2, 100.9, 100.8, 100.3, 99.8, 99.6, 99.6, 98.9, 98.8, 98.6, 98.6, 98.4, 98.3, 98.2, 98.0, 97.5, 97.3, 97.2, 97.1, 96.3, 77.4, 77.2, 77.0, 75.6, 75.4, 75.3, 75.1, 74.9, 74.8, 74.5, 74.4, 74.0, 73.6, 70.7, 55.6, 55.5, 55.3, 55.2, 55.2, 55.1, 55.0, 54.9, 54.8, 54.7, 54.2, 53.8, 53.6, 53.5, 50.5, 49.5, 28.4, 28.3, 28.3, 28.1, 28.1, 27.7, 27.6, 19.5, 19.5, 19.5, 19.4, 19.4. 19.3, 19.3, 19.2, 19.2, 19.1, 19.1, 19.0, 18.9, 18.8, 18.7, 18.6. HRMS (ESI+) m/z calcd for $C_{116}H_{121}N_{14}O_{19}$ $[M+H]^+$ 2013.8927, found 2013.8982.

Synthesis of Compound **9b**: **7b** (30.0 mg, 0.015 mmol) and triphenylphosphine (15.6 mg, 4 eq.) were mixed in dry chloroform (1 mL) and then trichloroacetonitrile (6.4 μL, 4 eq.) and dry DIPEA (15 μL, 6 eq.) were added. The mixture was stirred at rt overnight. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC and PLC to give **9b** as yellow solid (23.9 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) (Major : Minor = 5 : 3) (Major)δ 11.70 (s, 1 H), 11.27 (s, 1 H), 10.34 (s, 1 H), 10.29 (s, 1 H), 9.44 (d, *J* = 8.2 Hz, 1 H), 9.18 (s, 1 H), 8.30 (dd, *J* = 1.9, 8.2 Hz, 1 H), 8.24 (dd, *J* = 1.0, 7.8 Hz, 1 H), 8.19 (m, 2 H), 8.09 (m, 1 H), 8.00 (dd, *J* = 2.2, 8.4 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 2 H), 7.93 (d, *J* = 8.2 Hz, 1 H), 7.82-7.63 (m, 10 H), 7.57-7.50 (m, 3 H), 7.42 (m, 4 H), 7.37 (d, *J* = 2.2 Hz, 2 H), 7.21 (m, 2 H), 7.15 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.11 (dd. *J* = 2.0, 8.0 Hz, 1 H), 7.07 (m, 2 H), 6.98 (dd, *J* = 6.8, 7.8 Hz, 1 H), 6.92 (d, *J* = 7.2 Hz, 1 H), 6.72 (s, 1 H), 6.57 (s, 1 H), 6.48 (s, 1 H), 6.21 (m,

2 H), 6.14 (d, *J* = 2.3 Hz, 1 H), 6.08 (s, 1 H), 6.01 (m, 2 H), 5.98 (d, *J* = 2.0 Hz, 1 H), 5.79 (m, 2 H), 5.70 (d, *J* = 13.6 Hz, 1 H), 5.53 (m, 2 H), 4.38 (m, 1 H), 4.33 (m, 1 H), 4.24-4.06 (m, 10 H), 4.02 (m, 1 H), 3.96 (m, 1 H), 3.90 (m, 1 H), 3.84 (m, 3 H), 3.76 (m, 1 H), 3.59 (s, 3 H), 3.52 (m, 6 H), 3.17 (s, 3 H), 2.48-2.32 (m, 7 H), 1.32 (d, *J* = 6.6 Hz, 3 H), 1.23 (m, 24 H), 1.10 (d, *J* = 6.6 Hz, 3 H), 1.03 (d, *J* = 6.6 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H), 0.80 (d, *J* = 6.6 Hz, 3 H). (Minor) δ 12.22 (s, 1 H), 11.89 (s, 1 H), 11.70 (s, 1 H), 10.86 (s, 1 H), 10.82 (s, 1 H), 9.37 (d, *J* = 8.2 Hz, 1 H), 8.67 (d, *J* = 7.8 Hz, 1 H), 8.63 (d, *J* = 7.8 Hz, 1 H), 8.55 (d, *J* = 7.8 Hz, 1 H), 8.36 (br, 1 H), 8.09 (m, 1 H), 7.33 (d, *J* = 8.4 Hz, 1 H), 6.77 (t, *J* = 7.4 Hz, 1 H), 6.69 (t, *J* = 7.0 Hz, 1 H), 6.37 (d, *J* = 7.8 Hz, 1 H), 6.09 (d, *J* = 7.8 Hz, 1 H), 5.91 (s, 1 H), 5.86 (d, *J* = 2.3 Hz, 1 H), 5.38 (d, *J* = 12.6 Hz, 1 H), 5.24 (d, *J* = 13.0 Hz, 1 H), 4.75 (d, *J* = 12.8 Hz, 1 H), 3.43 (s, 3 H), 3.42 (s, 3 H), 2.82 (s, 3 H), 2.37 (s, 3 H), 1.25 (m, 30 H), 0.89 (m, 6 H), 0.73 (d, *J* = 6.6 Hz, 3 H), 0.70 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 167.7, 167.4, 167.0, 165.3, 164.9, 163.9, 163.5, 163.4, 163.3, 163.0, 162.8, 162.7, 162.6, 162.1, 162.1, 162.0, 161.9, 161.6, 161.2, 161.1, 160.9, 160.8, 160.6, 160.0, 160.0, 159.8, 159.6, 158.9, 158.8, 158.5, 158.3, 157.7, 155.0, 154.3, 152.5, 151.7, 151.0, 150.9, 150.7, 150.6, 150.1, 149.7, 147.3, 145.3, 144.6, 144.3, 144.2, 142.4, 141.5, 141.2, 139.1, 138.5, 138.5, 138.1, 137.9, 137.9, 137.4, 136.8, 136.1, 135.3, 134.6, 134.4, 134.1, 134.0, 133.8, 133.4, 133.3, 133.0, 132.7, 132.3, 131.6, 130.8, 130.7, 130.5, 130.1, 129.7, 129.0, 128.6, 126.7, 126.6, 126.5, 126.4, 126.3, 126.1, 125.9, 125.7, 125.6, 123.4, 123.0, 122.8, 122.7, 122.6, 122.6, 122.5, 122.5, 122.4, 122.4, 122.0, 121.9, 121.0, 120.9, 120.8, 120.7, 120.7, 120.6, 120.0, 119.3, 118.8, 118.7, 118.5, 118.0, 117.9, 117.7, 117.4, 117.0, 116.8, 116.6, 116.3, 116.1, 116.1, 116.0, 115.7, 104.1, 103.8, 103.4, 103.2, 102.7, 102.6, 101.7, 101.4, 100.9, 99.8, 99.8, 99.3, 98.5, 98.0, 98.0, 97.8, 97.8, 97.7, 97.7, 96.9, 96.9, 75.8, 75.6, 75.4, 75.3, 75.2, 75.1, 75.1, 75.0, 74.4, 73.9, 73.8, 73.4, 70.6, 55.2, 55.1, 55.1, 54.8, 54.3, 53.8, 47.8, 47.6, 47.5, 46.8, 29.8, 28.6, 28.4, 28.4, 28.3, 28.3, 28.2, 28.0, 27.6, 27.5, 27.4, 19.8, 19.8, 19.6, 19.6, 19.6, 19.5, 19.5, 19.4, 19.4, 19.3, 19.3, 19.3, 19.2, 19.1, 19.1, 19.0, 18.9, 18.9, 18.5, 18.5, 19.3, 18.1. HRMS (ESI+) m/z calcd for $C_{116}H_{119}N_{14}O_{18}$ $[M+H]^+$ 1995.8821, found 1995.8845.

Synthesis of Compound **5**: Trifluoroacetic acid (1 mL) was added to **9b** (10.0 mg, 5 μmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC to give **5** as yellow solid (5.8 mg, 68%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.26 (s, 1 H), 11.64 (s, 1 H), 10.98 (s, 1 H), 10.72 (s, 1 H), 10.51 (s, 1 H), 9.81 (s, 1 H), 9.23 (d, *J* = 7.3 Hz, 1 H), 8.89 (d, *J* = 7.7 Hz, 1 H), 8.69 (s, 1 H), 8.38 (d, *J* = 7.4 Hz, 1 H), 8.13 (d, *J* = 8.3 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 7.94 (m, 3 H), 7.87 (t, *J* = 8.0 Hz, 1 H), 7.84 (s, 1 H), 7.73 (m, 2 H), 7.64 (s, 1 H), 7.62 (d, *J* = 8.2 Hz, 1 H), 7.58 (m, 3 H), 7.51 (d, *J* = 7.4 Hz, 1 H), 7.42 (s, 1 H), 7.29 (m, 2 H), 7.15 (m, 4 H), 6.72 (s, 1 H), 5.63 (t, *J* = 7.8 Hz, 1 H), 4.88 (s, 1 H), 4.35 (m, 4 H), 4.25 (t, *J* = 7.2 Hz, 1 H), 4.21 (t, *J* = 8.1 Hz, 1 H), 4.13 (t, *J* = 6.7 Hz, 1 H), 4.05 (m, 2 H), 3.94 (t, *J* = 6.8 Hz, 1 H), 3.37 (m, 2 H), 3.14 (t, *J* = 6.9 Hz, 1 H), 2.71 (t, *J* = 7.0 Hz, 1 H), 2.38 (m, 3 H), 2.25 (m, 3 H), 2.05 (m, 1 H), 1.28 (d, *J* = 6.6 Hz, 3 H), 1.24 (d, *J* = 6.6 Hz, 3 H), 1.22 (d, *J* = 6.6 Hz, 6 H), 1.14 (m, 18 H), 1.08 (d, *J* = 6.6 Hz, 3 H), 1.07 (d, *J* = 6.6 Hz, 3 H), 0.34 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 165.2, 164.5, 164.5, 164.3, 164.2, 164.2, 163.6, 163.3, 163.2, 163.0, 162.8, 162.6, 162.5, 162.4, 162.2, 162.1, 161.9, 161.6, 161.5, 161.2, 156.1, 153.1, 152.9, 152.5, 151.4, 151.4, 151.2, 150.7, 150.6, 150.4. 150.1, 149.2, 148.8, 142.5, 141.3, 140.7, 140.2, 139.9, 139.3, 139.1, 138.9, 138.7, 138.0, 137.5, 137.4, 137.0, 136.1, 135.9, 135.6, 135.4, 135.2, 134.9, 134.6, 134.4, 134.0, 133.8, 133.3, 132.5, 132.3, 132.2, 131.2, 127.9, 127.8, 127.6, 128.3, 126.7, 126.3, 126.1, 124.0, 122.6, 122.5, 122.1, 121.9, 121.8, 121.6, 121.5, 121.3, 120.6,

119.5, 119.3, 119.1, 118.6, 118.2, 117.4, 117.2, 117.0, 116.9, 116.7, 116.6, 116.5, 116.4, 116.3, 116.0, 115.7, 103.4, 102.3, 101.5, 100.2, 100.0, 99.7, 99.6, 99.3, 99.2, 98.6, 98.5, 97.8, 96.9, 75.7, 75.6, 75.5, 75.1, 75.0, 74.7, 74.5, 74.4, 74.3, 73.9, 70.6, 29.8, 28.4, 28.3, 28.2, 28.1, 27.9, 27.6, 19.6, 19.5, 19.4, 19.4, 19.3, 19.2, 19.1, 19.0, 18.8, 18.7, 18.4. HRMS (ESI+) m/z calcd for $C_{98}H_{99}N_{14}O_{14}$ $[M+H]^+$ 1695.7460, found 1695.7437.

Synthesis of Compound **33**: A solution of acid **24** (195 mg, 0.40 mmol) in dry $CHCl_3$ (2 mL) was cooled to 0°C. Oxalyl chloride (0.1 mL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1 mL) and added to a solution of **32**[9] (116 mg, 1.0 eq.) and dry DIPEA (0.3 mL, 5 eq.) in dry $CHCl_3$ (1 mL). The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / petroleum ether = 1 / 5) to give **33** as white solid (251 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.52 (s, 1 H), 9.31 (s, 1 H), 8.76 (dd, *J* = 2.8, 10.4 Hz, 1 H), 8.44 (d, *J* = 7.4 Hz, 1 H), 7.96 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.77 (s, 1 H), 7.60 (m, 4 H), 7.43 (m, 3 H), 7.22 (t, *J* = 7.5 Hz, 2 H), 6.82 (dt, *J* = 1.0, 7.5 Hz, 2 H), 4.50 (d, *J* = 7.5 Hz, 2 H), 4.14 (m, 3 H), 3.96 (s, 3 H), 3.95 (d, *J* = 6.4 Hz, 2 H), 2.23 (m, 2 H), 1.17 (d, *J* = 6.7 Hz, 6 H), 1.12 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 164.0, 163.7, 163.1, 162.7, 162.7, 160.5, 153.8, 150.0, 146.9, 146.9, 143.7, 141.3, 138.2, 136.9, 136.8, 136.8, 134.8, 127.9, 127.6, 126.9, 125.2, 123.3, 123.1, 122.6, 119.9, 117.4, 115.8, 108.2, 107.8, 102.3, 100.2, 99.9, 99.1, 75.6, 75.5, 67.6, 53.0, 47.1, 28.3, 28.2, 19.4, 19.3. HRMS (ESI+) m/z calcd for $C_{44}H_{42}FN_4O_7$ $[M+H]^+$ 757.3032, found 757.3014.

Synthesis of Compound **34**: The mixture of **33** (160 mg, 0.21 mmol) and LiI (226 mg, 8 eq.) in degassed ethyl acetate (3 mL) was heated to 80°C overnight. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with 5% citric acid aq. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by middle pressure column chromatography (silica gel, ethyl acetate/ petroleum ether = 1 / 1) to give **34** as yellow solid (225 mg, quant.).^{1}H NMR (300 MHz, $CDCl_3$) δ 11.91 (s, 1 H), 8.94 (s, 1 H), 8.79 (dd, *J* = 2.8, 10.5 Hz, 1 H), 7.90 (dd, *J* = 1.3, 8.4 Hz, 1 H), 7.75 (s, 1 H), 7.70 (d, *J* = 7.6 Hz, 2 H), 7.53 (m, 5 H), 7.29 (t, *J* = 7.4 Hz, 2 H), 7.05 (t, *J* = 7.2 Hz, 2 H), 4.64 (d, *J* = 7.4 Hz, 2 H), 4.29 (t, *J* = 7.0 Hz, 1 H), 4.10 (d, *J* = 6.2 Hz, 2 H), 4.00 (d, *J* = 6.5 Hz, 2 H), 2.34 (m, 2 H), 1.18 (d, *J* = 6.7 Hz, 6 H), 1.13 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 163.1, 162.9, 162.4, 162.3, 159.8, 149.3, 146.0, 144.0, 141.2, 137.4, 136.3, 136.1, 135.7, 134.3, 127.5, 127.4, 126.9, 125.3, 122.6, 122.5, 122.0, 119.9, 115.2, 101.1, 100.0, 99.7, 98.7, 75.4, 75.1, 67.7, 47.0, 29.8, 28.2, 19.3, 19.3. HRMS (ESI+) m/z calcd for $C_{43}H_{40}FN_4O_7$ $[M+H]^+$ 743.2876, found 743.2854.

Synthesis of Compound **36**: A solution of acid **34** (157 mg, 0.21 mmol) in dry $CHCl_3$ (1.5 mL) was cooled to 0°C. Oxalyl chloride (0.05 mL, 3 eq.) was added. The solution was stirred at rt for 1 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (0.6 mL) and added to a solution of **35**[7] (107 mg, 1.1 eq.) and dry DIPEA (0.16 mL, 5 eq.) in dry $CHCl_3$ (0.6 mL). The mixture was stirred overnight. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate / petroleum ether = 1 / 5) to give **36**

as white solid (77 mg, 31%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.33 (s, 1 H), 9.48 (s, 1 H), 8.74 (d, *J* = 7.6 Hz, 1 H), 8.42 (dd, *J* = 2.6, 10.5 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.75-7.38 (m, 11 H), 7.27 (m, 1 H), 7.18 (t, *J* = 7.4 Hz, 1 H), 7.04 (m, 2 H), 6.80 (t, *J* = 7.4 Hz, 1 H), 6.15 (m, 4 H), 5.69 (d, *J* = 7.4 Hz, 1 H), 5.63 (d, *J* = 9.6 Hz, 1 H), 5.40 (d, *J* = 10.3 Hz, 1 H), 5.13 (d, *J* = 15 Hz, 1 H), 4.98-4.51 (m, 6 H), 4.18 (d, *J* = 6.4 Hz, 2 H), 3.87 (m, 1 H), 3.74 (m, 4 H), 3.64 (s, 3 H), 3.34 (s, 3 H), 2.35 (m, 2 H), 2.11 (m, 1 H), 1.24 (m, 6 H), 1.04 (d, *J* = 6.7 Hz, 6 H), 0.97 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 165.3, 163.9, 162.8, 162.3, 162.0, 161.0, 161.0, 159.8, 159.1, 158.1, 154.1, 153.7, 150.1, 147.3, 144.6, 143.9, 143.8, 142.5, 141.4, 141.2, 137.5, 135.7, 135.5, 134.8, 134.2, 131.7, 131.5, 128.2, 127.4, 127.3, 126.9, 126.7, 126.1, 125.6, 125.4, 122.4, 122.3, 121.4, 121.2, 119.8, 119.7, 118.5, 117.5, 116.7, 115.5, 107.0, 106.6, 103.8, 103.4, 100.3, 99.9, 99.6, 99.2, 97.6, 75.6, 74.9, 68.1, 66.1, 55.2, 55.0, 48.5, 46.9, 29.8, 29.7, 29.5, 29.4, 28.3, 28.1, 28.1, 19.4, 19.3, 19.2. HRMS (ESI+) m/z calcd for $C_{69}H_{68}FN_6O_{11}$ $[M+H]^+$ 1175.4925, found 1175.4920.

Synthesis of Compound **37**: To a solution of **36** (77 mg, 0.066 mmol) in dry dichloromethane (1 mL), phenylsilane (14 mg, 1.7 eq.) and Tetrakis(triphenylphosphine)palladium(0) (2 mg, 2 mol%) were added. The mixture was stirred for 1 h. The organic layer was washed with sat. NH_4Cl aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by middle pressure column chromatography (silica gel, ethyl acetate) to give **37** as yellow solid (68 mg, 92%).^{1}H NMR (600 MHz, $CDCl_3$) δ 11.36 (s, 1 H), 9.50 (s, 1 H), 8.72 (d, *J* = 7.3 Hz, 1 H), 8.41 (dd, *J* = 2.7, 10.4 Hz, 1 H), 8.07 (d, *J* = 7.7 Hz, 1 H), 7.77-7.50 (m, 9 H), 7.27 (m, 4 H), 7.10 (s, 1 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 6.91 (t, *J* = 7.5 Hz, 1 H), 6.29 (m, 2 H), 5.92 (d, *J* = 2.2 Hz, 1 H), 5.81 (d, *J* = 13.7 Hz, 1 H), 4.83 (d, *J* = 13.8 Hz, 1 H), 4.79 (d, *J* = 7.5 Hz, 2 H), 4.53 (t, *J* = 7.3 Hz, 1 H), 4.19 (d, *J* = 6.4 Hz, 2 H), 3.92-3.78 (m, 4 H), 3.65 (s, 3 H), 2.98 (s, 3 H), 2.39 (m, 1 H), 2.14 (m, 2 H), 1.23 (m, 6 H), 1.05 (d, *J* = 6.7 Hz, 6 H), 0.99 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 164.1, 164.0, 163.5, 162.6, 160.4, 158.6, 153.7, 152.9, 150.0, 145.8, 144.5, 143.7, 142.8, 141.5, 141.4, 141.3, 137.4, 135.7, 134.7, 134.4, 132.7, 132.3, 132.1, 129.3, 128.7, 128.5, 128.4, 127.5, 127.5, 126.9, 126.8, 125.3, 122.5, 122.4, 121.3, 120.3, 119.9, 117.2, 116.8, 115.6, 107.3, 106.9, 103.9, 102.1, 100.0, 99.6, 99.2, 98.2, 98.1, 75.6, 75.5, 75.3, 68.2, 55.3, 54.8, 48.6, 47.0, 30.4, 29.8, 29.4, 28.4, 28.1, 28.0, 19.4, 19.2.
HRMS (ESI+) m/z calcd for $C_{66}H_{64}FN_6O_{11}$ $[M+H]^+$ 1135.4612, found 1135.4578.

Synthesis of Compound **39**: A solution of acid **24** (1.130 g, 2.34 mmol) in dry $CHCl_3$ (7 mL) was cooled to 0°C. Oxalyl chloride (0.6 mL, 3 eq.) were added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum line. The resulting acid chloride was dissolved in dry $CHCl_3$ (15 mL) and added to a solution of **38**[10] (585 mg, 0.9 eq.) and dry DIPEA (2.0 mL, 5 eq.) in dry $CHCl_3$ (2 mL). The mixture was stirred for 17h. The organic layer was washed with water, sat. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flush column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 10) to give **39** as yellow solid (1.481 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.52 (s, 1 H), 9.36 (s, 1 H), 8.95 (dd, *J* = 1.2, 7.6 Hz, 1 H), 8.44 (d, *J* = 7.2 Hz, 1 H), 8.01 (dd, *J* = 1,2, 8.5 Hz, 1 H), 7.96 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.81 (s, 1 H), 7.72 (t, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 7.7 Hz, 2 H), 7.58 (d, *J* = 8.1 Hz, 1 H), 7.44 (m, 3 H), 7.21 (t, *J* = 7.4 Hz, 2 H), 6.81 (dt, *J* = 1.0, 7.5 Hz, 2 H), 4.49 (d, *J* = 7.6 Hz, 2 H), 4.16 (m, 3 H), 3.97 (d, *J* = 6.0 Hz, 2 H), 3.96 (s, 3 H), 2.30 (m, 2 H), 1.17 (d, *J* = 6.7 Hz, 6 H), 1.12 (d, *J* = 6.7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 163.9, 163.2, 162.9, 153.8, 150.4, 147.6, 143.7, 141.2, 134.9, 134.8, 128.5, 127.7, 127.6, 126.9, 125.2, 122.5, 119.9, 117.6, 117.3, 116.3, 115.8, 101.7, 99.1, 75.5, 75.4, 67.5, 53.0, 47.1,

28.3, 28.3, 27.0, 19.4, 19.3. HRMS (ESI+) m/z calcd for $C_{44}H_{43}N_2O_7$ $[M+H]^+$ 739.3132, found 739.3165.

Synthesis of Compound **40**: To a solution of **39** (100 mg, 0.14 mmol) in dichloromethane (1.5 mL), DBU (0.02 mL, 1 eq.) was added. The mixture was stirred for 15 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) to give **40** as yellow solid (74 mg, quant.).^{1}H NMR (300 MHz, $CDCl_3$) δ 12.69 (s, 1 H), 9.05 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.76 (s, 1 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.56 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.56 (s, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.00 (dd, *J* = 7.5, 1.2 Hz, 1 H), 5.52 (br, 2 H), 4.10 (s, 3 H), 4.10 (d, *J* = 6.5 Hz, 2 H), 4.06 (d, *J* = 6.5 Hz, 2 H), 2.31 (m, 2 H), 1.17 (d, *J* = 5.2 Hz, 6 H), 1.14 (d, *J* = 5.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 163.2, 163.1, 162.9, 148.2, 146.7, 144.8, 139.5, 137.4, 135.2, 128.4, 128.1, 123.0, 122.1, 117.1, 115.6, 110.9, 109.5, 101.3, 98.2, 75.1, 75.0, 52.9, 28.3, 19.4, 19.3. HRMS (ESI+) m/z calcd for $C_{29}H_{33}N_4O_5$ $[M+H]^+$ 517.2451, found 517.2439.

Synthesis of Compound **42**: A solution of acid **41**[7] (300 mg, 0.34 mmol) in dry $CHCl_3$ (3 mL) was cooled to 0°C. 1-Chloro-*N*, *N*, 2-trimethyl-1-propenylamine (80 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (1.5 mL) and added to a solution of **40** (170 mg, 0.9 eq.) and dry DIPEA (0.44 mL, 5 eq.) in dry $CHCl_3$ (1.5 mL). The mixture was stirred for 15 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 3) to give **42** as white solid (329 g, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.12 (s, 1 H), 11.94 (s, 1 H), 8.98 (t, *J* = 7.3 Hz, 2 H), 8.08 (d, *J* = 7.4 Hz, 1 H), 7.90 (s, 1 H), 7.83 (br, 1 H), 7.74 (m, 4 H), 7.69 (d, *J* = 8.3 Hz, 1 H), 7.65 (t, *J* = 8.0 Hz, 1 H), 7.58-7.47 (m, 6 H), 7.38 (m, 2 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 7.5 Hz, 1 H), 7.00 (s, 1 H), 6.93 (m, 2 H), 6.83 (br, 1 H), 6.81 (s, 1 H), 6.20 (dd, *J* = 2.3, 8.4 Hz, 1 H), 6.09 (m, 1 H), 5.31 (d, *J* = 14.9 Hz, 1 H), 4.55 (dd, *J* = 6.9, 10.4 Hz, 1 H), 4.37 (br, 1 H), 4.29 (t, *J* = 6.8 Hz, 1 H), 4.18 (m, 2 H), 3.97 (m, 1 H), 3.92 (m, 1 H), 3.81 (br, 1 H), 3.76 (br, 1 H). 3.71 (s, 3 H), 3.61 (s, 3 H), 3.34 (t, *J* = 7.3 Hz, 1 H), 3.20 (s, 3 H), 2.37 (m, 1 H), 2.21 (m, 2 H), 1.93 (m, 1 H), 1.17 (m, 6 H), 1.16-1.07 (m, 12 H), 0.90 (d, *J* = 6.6 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3, 163.7, 163.6, 163.5, 163.1, 162.4, 161.7, 160.0, 158.0, 153.2, 151.8, 150.8, 146.2, 144.0, 143.9, 142.7, 142.6, 141.5, 141.4, 139.5, 139.4, 136.2, 135.1, 135.0, 128.2, 127.9, 127.8, 127.5, 127.3, 1227.2, 126.5, 125.2, 125.1, 122.7, 121.9, 120.6, 120.2, 120.1, 119.4, 118.4, 118.2, 118.1, 117.0, 115.8, 114.7, 114.6, 193.6, 100.8, 100.5, 99.9, 98.2, 97.8, 75.5, 75.3, 74.9, 74.3, 68.9, 55.3, 54.6, 52.9, 48.5, 47.2, 28.3, 28.3, 28.0, 19.4, 19.4, 19.4, 19.3, 19.1. HRMS (ESI+) m/z calcd for $C_{81}H_{81}N_8O_{13}$ $[M+H]^+$ 1373.5923, found 1373.5955.

Synthesis of Compound **43**: To a solution of **42** (196.8 mg, 0.14 mmol) in dry dichloromethane (1 mL), DBU (35.6 mg, 3.9 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by open column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **43** as yellow solid (139.9 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.14 (s, 1 H), 12.00 (s, 1 H), 9.06 (d, *J* = 7.5 Hz, 1 H), 8.94 (d, *J* = 8.0 Hz, 1 H), 8.06 (d, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.85 (s, 1 H), 7.76 (s, 1 H), 7.66 (t, *J* = 7.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.48

(d, *J* = 6.7 Hz, 1 H), 7.14 (m, 2 H), 6.99 (m, 2 H), 6.83 (s, 1 H), 6.75 (s, 1 H), 6.65 (d, *J* = 7.8 Hz, 1 H), 6.45 (d, *J* = 7.8 Hz, 1 H), 6.16 (d, *J* = 6.7 Hz, 1 H), 5.94 (d, *J* = 2.3 Hz, 1 H), 5.40 (d, *J* = 12.6 Hz, 1 H), 4.20 (br, 1 H), 4.13 (dd, *J* = 6.5, 8.2 Hz, 4 H), 3.68 (m, 6 H), 3.64 (m, 1 H), 3.51 (m, 2 H), 3.38 (m, 1 H), 2.98 (s, 3 H), 2.32 (m, 2 H), 2.15 (m, 1 H), 2.04 (m, 1 H), 1.16 (m, 12 H), 1.08 (m, 6 H), 1.00 (d, *J* = 6.6 Hz, 3 H), 0.97 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 165.8, 163.9, 163.6, 163.5, 163.3, 162.0, 161.2, 159.7, 158.0, 151.9, 150.9, 146.0, 143.8, 143.8, 142.8, 139.6, 139.1, 136.1, 135.1, 135.0, 131.7, 127.9, 127.4, 126.7, 126.2, 122.8, 122.6, 121.4, 121.1, 119.7, 118.9, 118.5, 118.0, 116.8, 115.7, 109.8, 109.4, 103.5, 100.7, 100.4, 99.8, 98.2, 97.5, 75.4, 75.4, 74.6, 74.3, 55.2, 54.3, 52.9, 48.0, 28.3, 28.2, 28.1, 19.4, 19.4, 19.2. HRMS (ESI+) m/z calcd for $C_{66}H_{71}N_8O_{11}$ $[M+H]^+$ 1151.5237, found 1151.5232.

Synthesis of Compound **44**: A solution of acid **37** (68 mg, 0.06 mmol) in dry $CHCl_3$ (0.6 mL) was cooled to 0°C. 1-Chloro-*N*, *N*, 2-trimethyl-1-propenylamine (15 μL, 3 eq.) was added. The solution was stirred at rt for 2 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry $CHCl_3$ (0.6 mL) and added to a solution of **43** (80 mg, 0.9 eq.) and dry DIPEA (45 μL, 5 eq.). The mixture was stirred for 15 h. The organic layer was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel, ethyl acetate / petroleum ether = 1 / 3) to give **44** as yellow solid (39 mg, 40%). ^{1}H NMR (30 MHz, $CDCl_3$) Minor : Major = 0.7 : 1 (Minor) δ 11.50 (s, 1 H), 11.33 (s, 1 H), 11.03 (s, 1 H), 10.94 (s, 1 H), 5.74 (d, *J* = 13.5 Hz, 1 H). (Major) δ 11.92 (s, 1 H), 11.70 (s, 1 H), 11.19 (s, 1 H), 10.94 (s, 1 H), 9.48 (s, 1 H), 9.18 (m, 2 H), 9.02 (m, 1 H), 8.82 (d, *J* = 7.8 Hz, 1 H), 8.70 (m, 2 H), 8.39 (m, 3 H), 8.11 - 6.07 (m, 70 H), 5.97 (t, *J* = 8.0 Hz, 1 H), 5.85 (d, *J* = 8.3 Hz, 1 H), 5.53 - 4.75 (m, 10 H), 4.53 (m, 3 H), 4.22 - 3.19 (m, 53 H), 2.89 (m, 1 H), 2.69 (m, 3 H), 2.40 - 1.79 (m, 30 H), 0.99 - 0.53 (m, 47 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 169.4, 168.4, 168.1, 166.0, 165.8, 164.4, 164.0, 163.9, 163.6, 163.5, 163.4, 163.1, 163.0, 162.7, 162.6, 162.4, 162.2, 161.9, 161.4, 161.0, 161.0, 160.9, 160.2, 159.7, 159.4, 159.1, 158.7, 157.7, 157.4, 157.2, 156.2, 154.1, 153.5, 153.4, 152.5, 151.7, 151.3, 151.1, 150.3, 150.1, 146.1, 146.0, 144.9, 144.7, 144.5, 144.3, 143.6, 143.4, 143.1, 141.3, 141.2, 141.0, 140.8, 140.2, 139.8, 139.4, 139.3, 139.2, 138.9, 137.4, 135.6, 135.4, 135.1, 135.0, 134.8, 134.4, 134.3, 134.0, 133.5, 133.4, 132.7, 131.5, 130.0, 128.1, 127.8, 127.5, 127.4, 127.2, 127.0, 126.8, 126.6, 126.5, 126.4, 126.2, 125.9, 125.7, 125.6, 125.3, 124.9, 123.0, 122.8, 122.6, 122.5, 122.4, 122.3, 122.1, 121.6, 121.3, 121.2, 121.0, 120.8, 120.0, 119.7, 119.5, 119.2, 119.1, 118.6, 118.1, 117.2, 117.1, 116.9, 116.7, 116.4, 116.1, 115.6, 115.1, 106.7, 106.3, 105.1, 104.2, 102.4, 101.0, 100.3, 100.1, 100.0, 99.8 ,99.3, 99.1, 98.8, 98.5, 98.3, 98.0, 97.2, 97.0, 75.6, 75.4, 74.9, 74.6, 74.3, 73.9, 67.6, 66.7, 55.6, 55.4, 55.1, 55.0, 54.9, 54.1, 53.5, 53.1, 52.9, 52.7, 49.3, 47.7, 46.5, 45.6, 45.0, 32.0, 30.4, 29.8, 29.6, 29.5, 29.4, 29.3, 29.1, 28.4, 28.3, 28.2, 28.2, 28.1, 27.7, 27.5, 22.8, 19.5, 19.4, 19.4, 19.3, 19.2, 19.2, 19.0, 18.9, 18.7, 18.6. HRMS (ESI+) m/z calcd for $C_{132}H_{132}FN_{14}O_{21}$ $[M+H]^+$ 2267.9670, found 2267.9658.

Synthesis of Compound **45**: The mixture of **44** (55 mg, 0.02 mmol) and LiI (16 mg, 5 eq.) in degassed ethyl acetate (1 mL) was heated to 80°C overnight. After quenching the reaction mixture with water, the solution was washed with 5% $NaHSO_3$ aq. and acidified with 5% citric acid aq. Then the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the residue was purified by middle pressure column chromatography (silica gel, ethyl acetate) to give **45** as yellow solid (64 mg, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.59 (s, 1 H), 11.34 (s, 1 H), 11.16 (s, 1 H), 10.96 (s, 1 H), 9.47 (s, 1 H), 9.06 (d, *J* = 8.0 Hz, 1 H), 9.00

(m, 1 H), 8.80 (d, *J* = 7.8 Hz, 1 H), 8.70 (m, 2 H), 8.30 (dd, *J* = 1.0, 8.8 Hz, 1 H), 8.11 - 6.75 (m, 63 H), 6.64 (s, 1 H), 6.48 (m, 2 H), 6.19(m, 7 H), 5.92 (t, *J* = 8.0 Hz, 1 H), 5.54 (dd, *J* = 1.0, 7.8 Hz, 1 H), 5.54 - 4.78 (m, 9 H), 4.21 (m, 6 H), 3.80 (m, 19 H), 3.44 - 3.15 (m, 11 H), 3.02 - 2.56 (m, 6 H), 2.31 (m, 12 H), 2.03 (m, 5 H), 1.84 (m, 3 H), 1.18 - 0.52 (m, 62 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 171.2, 169.6, 168.3, 168.3, 163.9, 163.8, 163.7, 163.6, 163.4, 163.3, 163.1, 162.6, 162.1, 161.0, 160.9, 160.2, 159.6, 159.4, 159.0, 157.7, 157.2, 155.9, 154.0, 153.3, 151.6, 151.5, 150.2, 150.0, 145.3, 144.6, 144.4, 144.3, 143.6, 143.4, 143.1, 141.2, 141.0, 140.9, 140.6, 140.1, 139.7, 139.0, 137.9, 137.3, 135.9, 135.5, 135.3, 134.8, 134.6, 134.4, 134.2, 133.9, 133.3, 133.0, 132.4, 131.3, 131.2, 130.2, 130.0, 128.0, 127.8, 127.4, 127.2, 126.9, 126.6, 126.4, 125.9, 125.5, 125.4, 125.1, 124.8, 122.8, 122.7, 122.5, 122.4, 122.2, 122.0, 121.9, 121.4, 121.2, 121.1, 120.7, 120.2, 119.8, 119.4, 119.2, 119.0, 118.2, 117.3, 116.8, 116.5, 116.5, 116.3, 116.2, 115.5, 106.6, 106.2, 104.9, 104.2, 102.5, 102.3, 100.8, 100.0, 99.8, 99.7, 99.2, 98.7, 98.4, 98.1, 97.8, 97.3, 77.5, 77.0, 76.6, 75.6, 75.4, 74.8, 74.3, 73.8, 60.4, 55.4, 54.9, 54.9, 53.1, 33.7, 31.9, 30.3, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 28.3, 28.2, 28.0, 27.6, 27.4, 24.8, 22.7, 21.1, 19.3, 19.2, 19.2, 19.1, 18.9, 18.8, 18.6, 14.2, 14.1 . HRMS (ESI+) m/z calcd for $C_{131}H_{130}FN_{14}O_{21}$ $[M+H]^+$ 2252.9514, found 2252.9517.

Synthesis of Compound **46**: To **45** (64 mg, 0.02 mmol), DBU (8 mg, 2.2 eq.) in dry dichloromethane (1 mL) was added. The mixture was stirred for 10 min. The organic layer was washed with 5% citric acid aq. and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by GPC to give **45** as yellow solid (41 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) The ratio of minor conformer was not unclear. The minor signals overlap major ones. (Minor) δ 11.78 (m), 11.56 - 11.26 (m), 10.61 (br). (Major) δ 12.73 (s, 1 H), 12.34 (s, 1 H), 11.61 (s, 1 H), 11.04 (s, 2 H), 9.42 (d, *J* = 8.0 Hz, 1 H), 9.00 (m, 5 H), 8.67 - 8.29 (m, 10 H), 8.19 - 6.47 (m, 105 H), 6.03 (m, 6 H), 5.30 (m, 5 H), 4.86- 4.58 (m, 9 H), 4.20 - 3.04 (m, 105 H), 2.30 (m, 22 H), 2.16 (m, 18 H), 1.61 (m, 16 H), 0.99 - 0.49 (m, 111 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 168.8, 166.3, 165.2, 164.5, 164.0, 163.8, 163.4, 163.3, 163.2, 162.8, 162.4, 162.2, 161.8, 161.6, 160.9, 159.7, 159.4, 159.3, 158.4, 157.2, 156.0, 152.7, 151.6, 150.5, 147.6, 146.2, 144.9, 143.5, 141.6, 139.9, 139.2, 138.8, 138.4, 136.8, 135.8, 135.3, 135.1, 134.8, 134.6, 134.1, 133.2, 128.5, 128.1, 127.8, 127.5, 127.2, 126.9, 126.6, 126.2, 125.7, 123.8, 123.0, 122.8, 122.7, 122.5, 122.2, 121.7, 121.5, 120.8, 120.5, 120.0, 119.5, 118.8, 118.3, 117.9, 117.0, 116.2, 115.9, 115.7, 109.9, 108.6, 103.4, 103.2, 102.1, 101.9, 100.8, 99.7, 99.5, 99.0, 98.8, 98.7, 98.2, 97.9, 97.2, 97.0, 75.6, 75.4, 75.1, 74.8, 74.4, 55.5, 55.4, 55.2, 55.1, 54.9, 54.8, 54.6, 53.7, 53.5, 29.7, 29.4, 28.3, 28.2, 28.1, 19.4, 19.3, 19.3, 19.2, 19.2, 19.1, 19.0. HRMS (ESI+) m/z calcd for $C_{116}H_{120}FN_{14}O_{19}$ $[M+H]^+$ 2031.8833, found 72031.8845.

Synthesis of Compound **47**: **46** (41 mg, 0.02 mmol) and triphenylphosphine (21 mg, 4 eq.) were mixed in dry chloroform (1.2 mL) and then trichloroacetonitrile (8.5 μL, 4 eq.) and dry DIPEA (21 μL, 6 eq.) were added. The mixture was stirred at rt for overnight. The mixture was washed with sat. NH_4Cl aq., sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous $MgSO_4$. After the solvent was removed *in vacuo*, The residue was purified by GPC to give **47** as white solid (20 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$) Minor : Major = 1 : 3 (Minor) δ 12.22 (s, 1 H), 11.86 (s, 1 H), 11.69 (s, 1 H), 10.89 (s, 1 H), 10.79 (s, 1 H), 9.10 (t, *J* = 8.0 Hz, 1 H), 8.66 (d, *J* = 7.5 Hz, 1 H), 8.52 (m, 3 H), 6.36 (d, *J* = 7.0 Hz, 1 H),2.85 (s, 3 H), 0.45 (d, *J* = 6.7 Hz, 3 H), 0.28 (d, *J* = 6.7 Hz, 3 H). (Major) δ 11.65 (s, 1 H), 11.10 (s, 1 H), 10.25 (s, 1 H), 10.24 (s, 1 H), 9.40 (dd, *J* = 1.0, 7.5 Hz, 1 H),

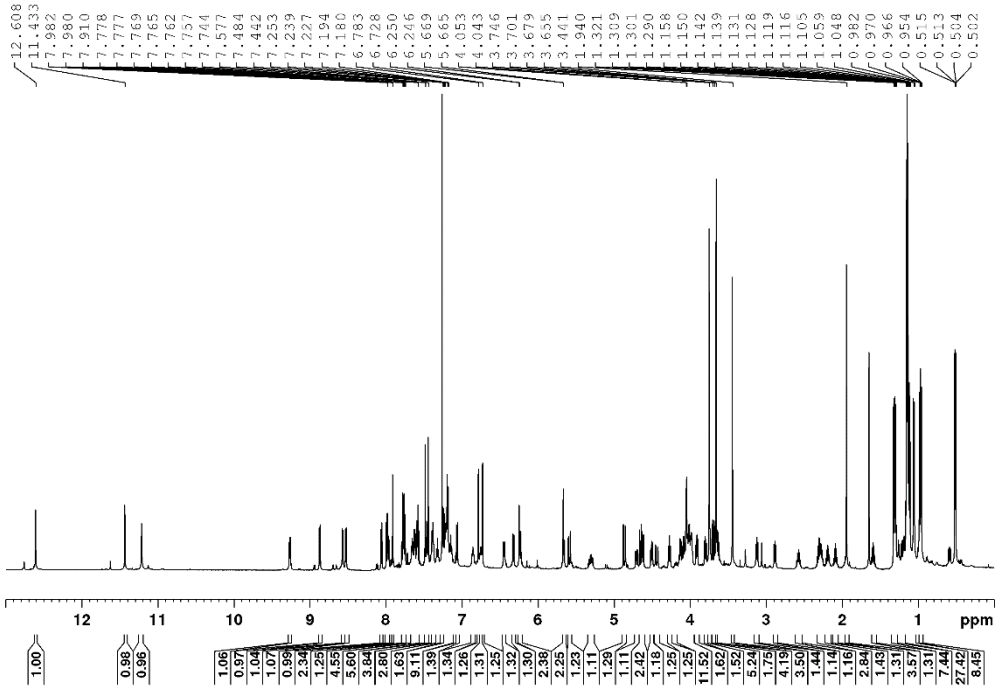
9.31 (s, 1 H), 8.25 - 7.27 (m, 28 H), 7.24 - 6.91 (m, 10 H), 6.76 (s, 1 H), 6.59 (s, 1 H), 6.51 (s, 1 H), 6.21 (m, 3 H), 6.08 (s, 1 H), 5.98 (m, 3 H), 5.91 - 5.69 (m, 4 H), 5.53 (m, 2 H), 5.29 (s, 1 H), 4.40 - 3.38 (m, 16 H), 3.58 (s, 3 H), 3.57 (s, 3 H), 3.52 (s, 3 H), 3.16 (s, 3 H), 2.40 (m, 8 H), 1.87 (m, 7 H), 1.24 (m, 62 H), 0.84 (m, 16 H), 0.34 (d, *J* = 6.7 Hz, 3 H), 0.19 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 166.9, 164.8, 163.6, 162.8, 162.1, 162.0, 161.9, 161.9, 161.3, 161.1, 160.6, 160.0, 159.6, 158.9, 158.6, 157.6, 152.9, 150.9, 150.6, 150.4, 150.0, 147.0, 144.7, 144.4, 142.6, 138.1, 138.0, 137.8, 137.5, 136.2, 135.2, 135.0, 133.9, 133.6, 133.3, 132.9, 132.7, 132.4, 131.0, 130.7, 130.5, 130.3, 128.9, 127.9, 126.5, 125.9, 125.6, 123.3, 123.0, 122.9, 122.5, 122.4, 122.3, 121.9, 121.0, 120.9, 120.0, 119.2, 118.5, 118.4, 118.1, 117.3, 116.6, 115.8, 103.5, 103.4, 103.3, 101.5, 99.8, 99.3, 98.3, 97.7, 97.0, 75.8, 75.6, 75.4, 75.1, 73.9, 73.4, 55.2, 55.1, 55.1, 54.8, 29.8, 28.6, 28.4, 28.4, 28.3, 28.0, 27.5, 19.8, 19.7, 19.6, 19.5, 19.5, 19.4, 19.3, 19.2, 19.0, 18.4, 18.1. HRMS (ESI+) m/z calcd for $C_{116}H_{118}FN_{14}O_{18}$ $[M+H]^+$ 2013.8727, found 2013.8711.

Synthesis of Compound **5F**: Trifluoroacetic acid (1 mL) was added to **47** (20 mg, 9.9 μmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. $NaHCO_3$ aq. and extracted with chloroform. The organic layer was washed with brine, and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was purified by GPC to give **5F** as yellow solid (9.3 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.66 (m, 1 H), 12.57 (m, 1 H), 11.98 - 11.02 (m, 6 H), 10.66 (m, 3 H), 9.98 (m, 1 H), 9.23 (m, 7 H), 8.56 (m, 2 H), 8.15 - 6.76 (m, 56 H), 6.12 - 5.84 (m, 4 H), 5.15 (m, 1 H), 4.24 - 2.82 (m ,36 H), 2.31 (m, 12 H), 0.87 - 0.39 (m, 58 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 165.1, 164.5, 164.4, 164.3, 164.1, 164.1, 164.0, 163.5, 163.5, 163.2, 163.1, 162.9, 162.7, 162.5, 162.4, 162.3, 162.3, 162.1, 162.0, 161.5, 161.4, 161.1, 155.9, 153.0, 152.4, 151.3, 151.0, 150.5, 150.3, 150.0, 142.4, 141.2, 140.6, 140.1, 139.8, 139.1, 138.9, 138.8, 138.6, 138.5, 137.9, 137.4, 137.4, 136.8, 136.0, 135.8, 135.5, 135.3, 135.1, 134.8, 134.6, 134.3, 133.9, 133.6, 133.2, 132.4, 131.1, 127.8, 127.7, 127.4, 127.3, 127.0, 126.7, 126.6, 126.3, 126.0, 122.4, 121.8, 121.6, 121.5, 121.4, 121.1, 120.4, 119.4, 119.2, 119.0, 118.6, 118.1, 117.3, 117.2, 116.9, 116.8, 116.6, 116.5, 116.4, 116.3, 116.2, 116.1, 115.6, 115.3, 115.0, 114.8, 103.3, 102.1, 101.4, 100.1, 99.9, 99.6, 99.5, 99.2, 99.1, 98.5, 98.4, 97.7, 96.8, 75.6, 75.4, 75.0, 74.9, 74.6, 74.5, 74.3, 74.2, 73.8, 29.7, 28.3, 28.2, 28.1, 28.0, 27.8, 27.5, 19.4, 19.4, 19.3, 19.1, 19.0, 18.8, 18.7, 18.6, 18.3. HRMS (ESI+) m/z calcd for $C_{98}H_{98}FN_{14}O_{14}$ $[M+H]^+$ 1713.7365, found 1713.7336.

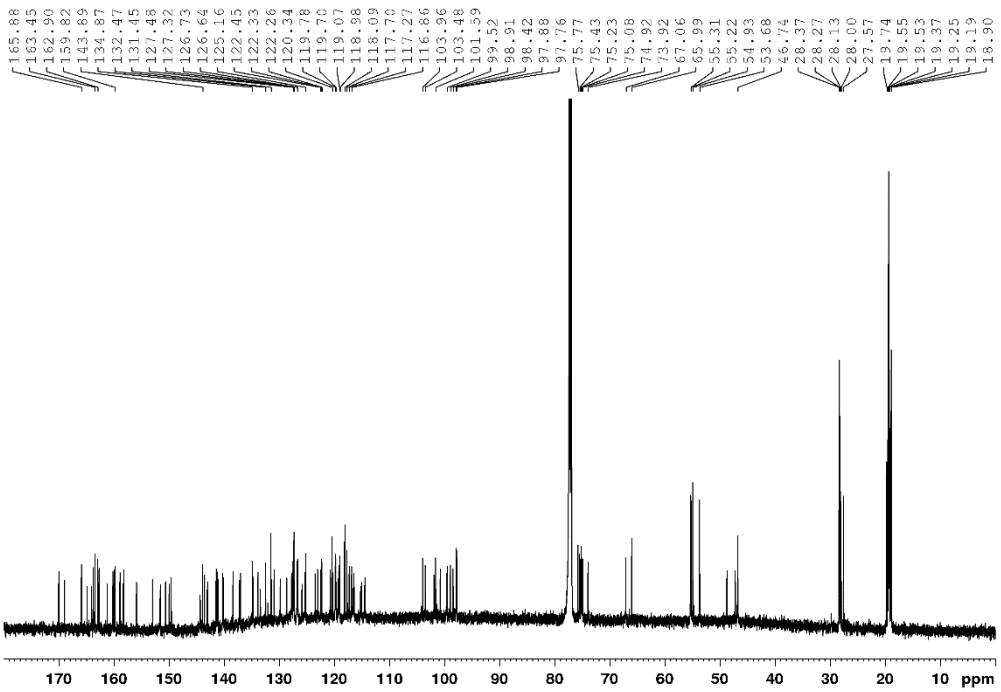
6) ^{1}H and ^{13}C NMR spectra of new compounds

Compound **12**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

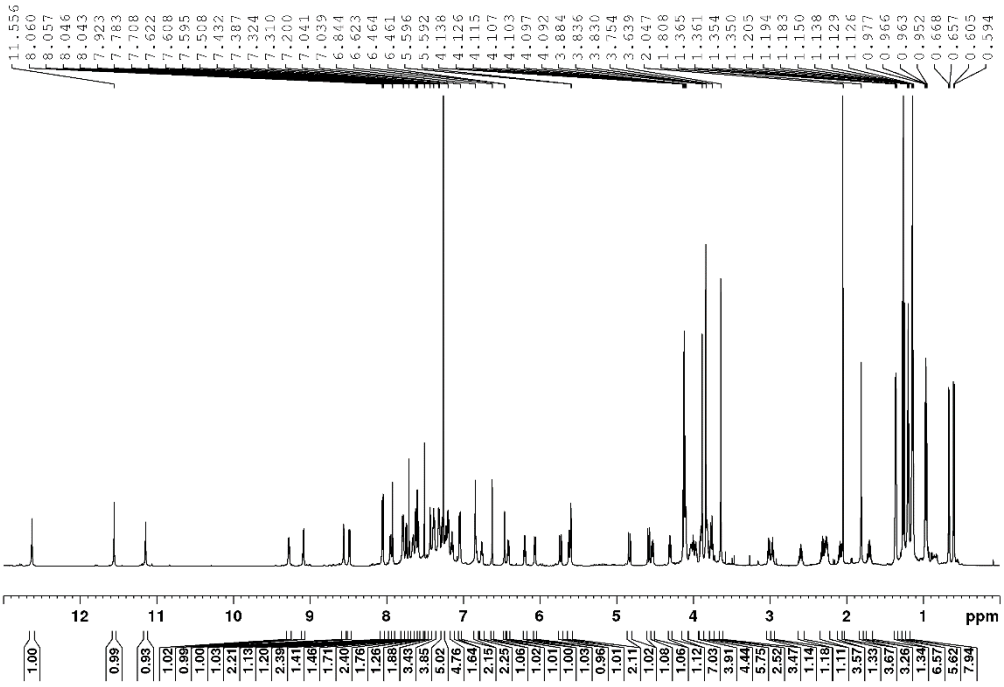


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

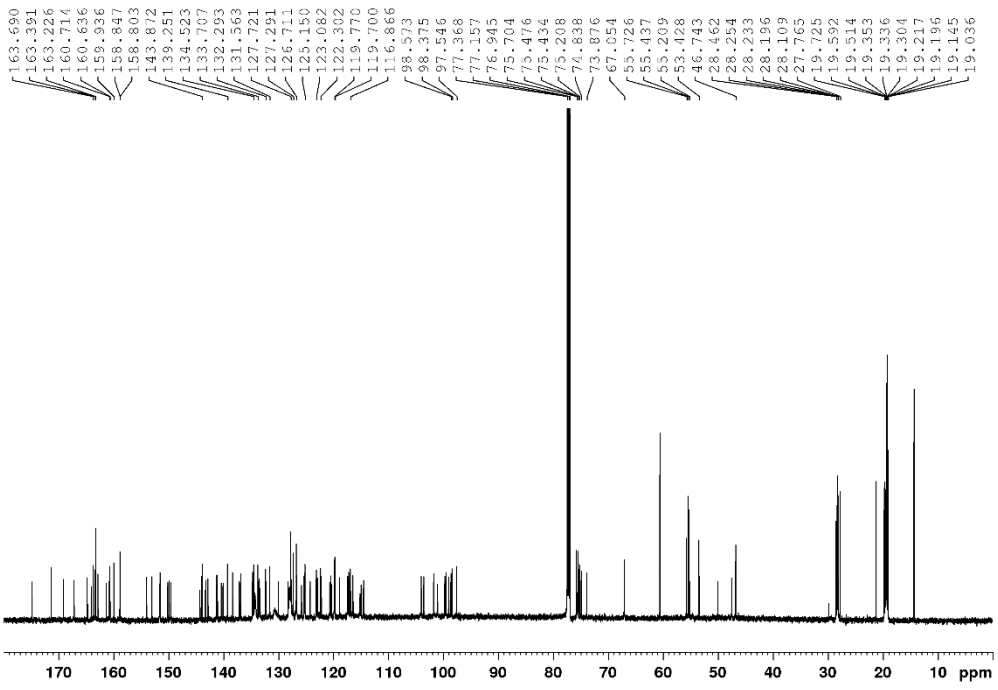


Compound **13**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

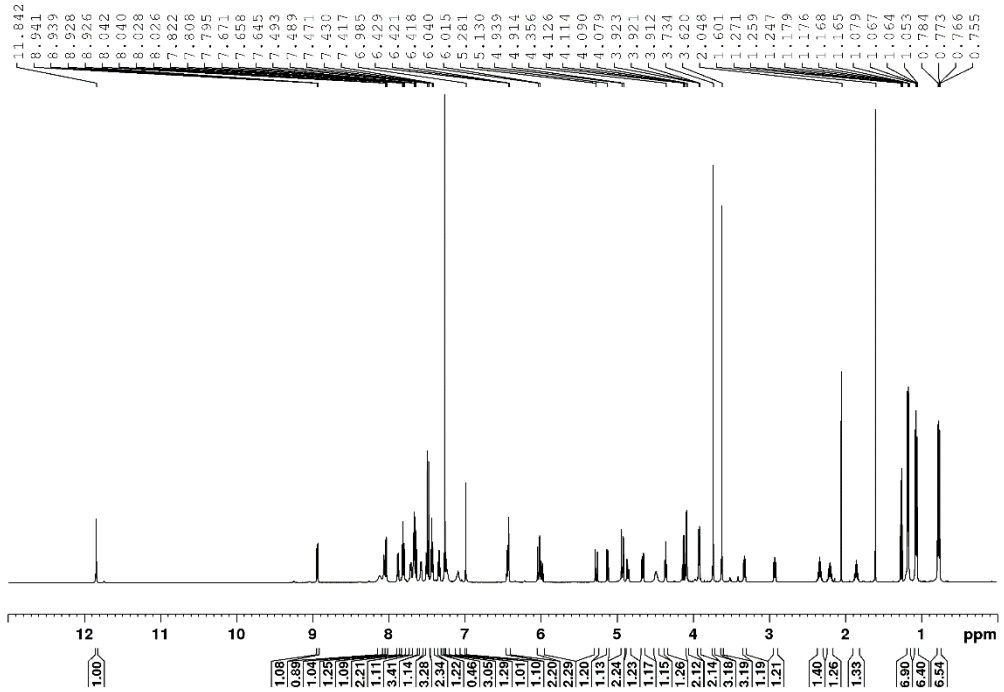


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

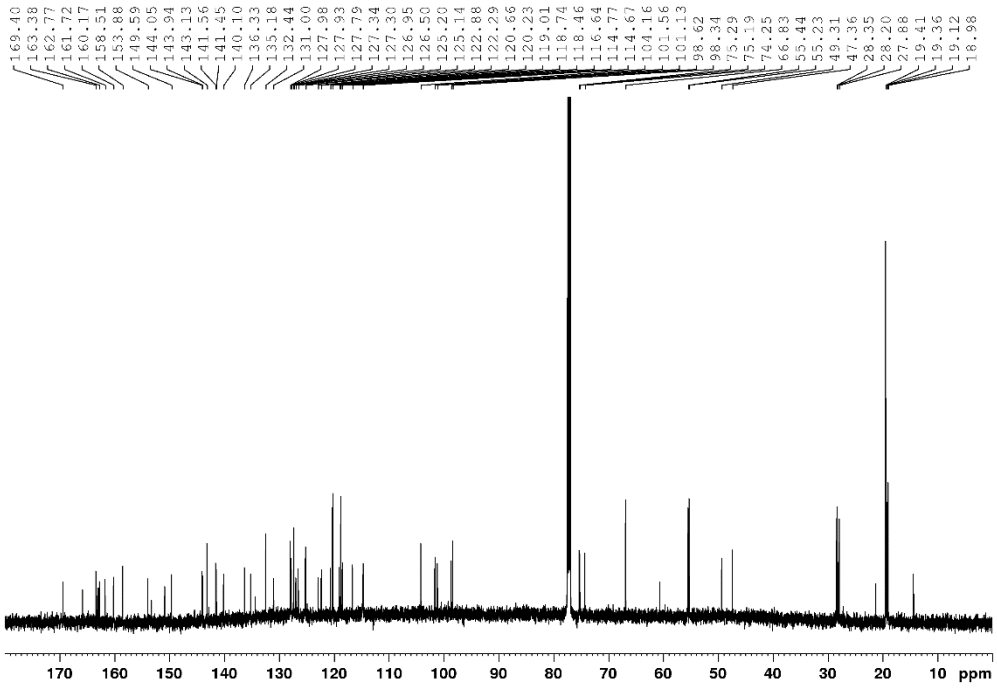


Compound **15**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

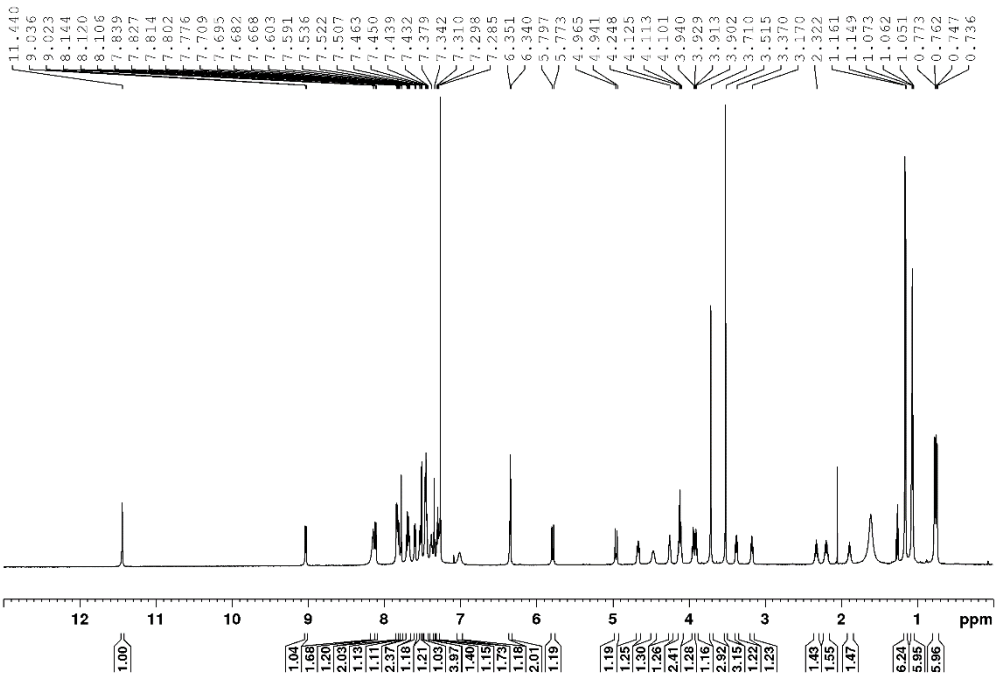


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

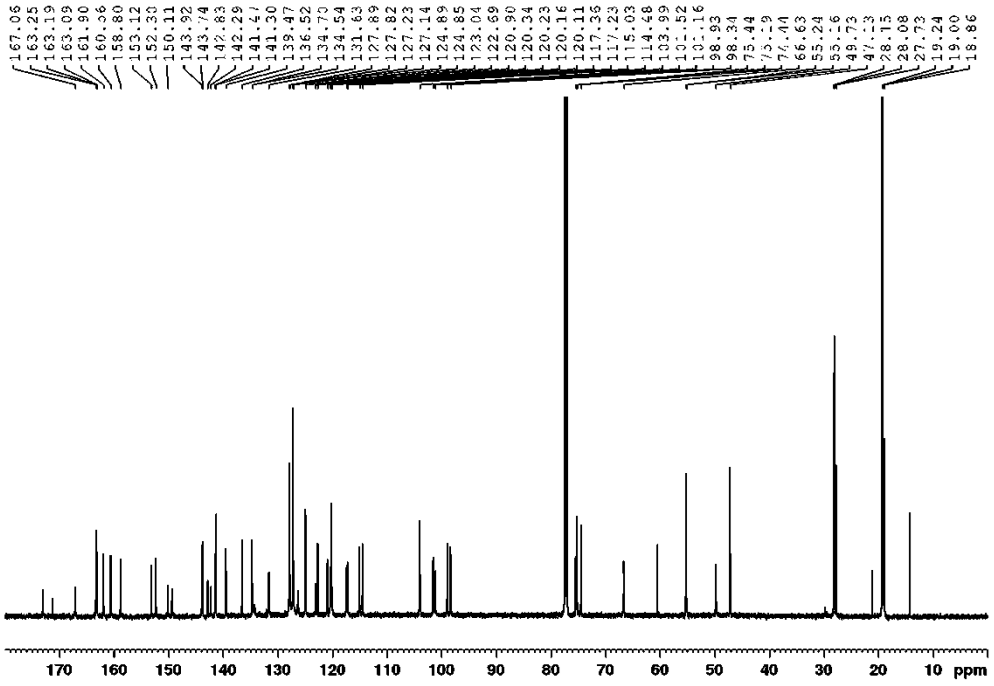


Compound **16**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

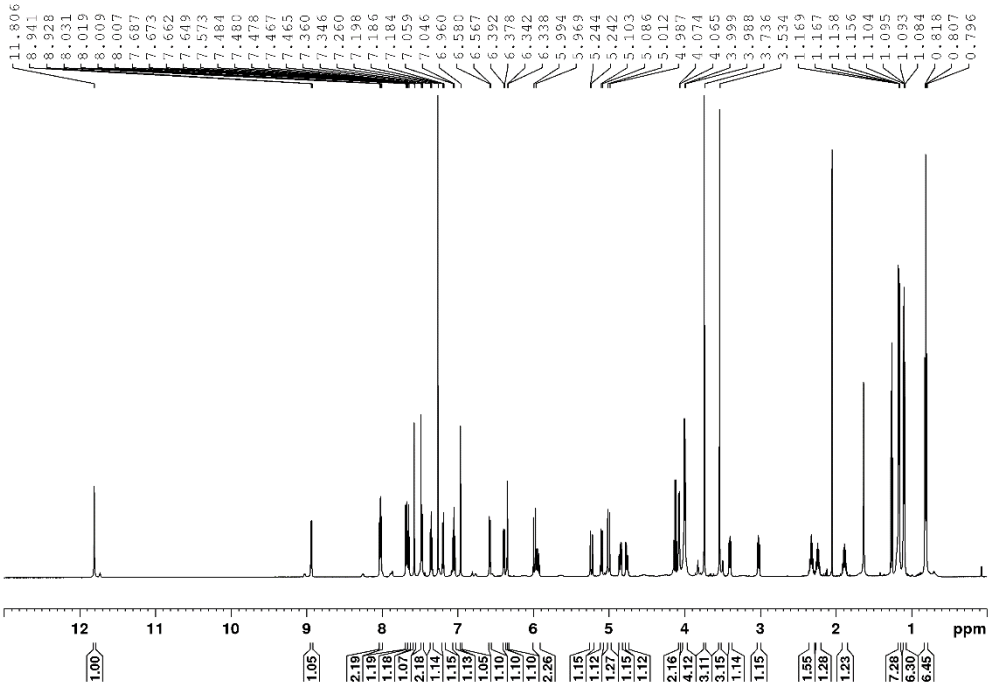


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

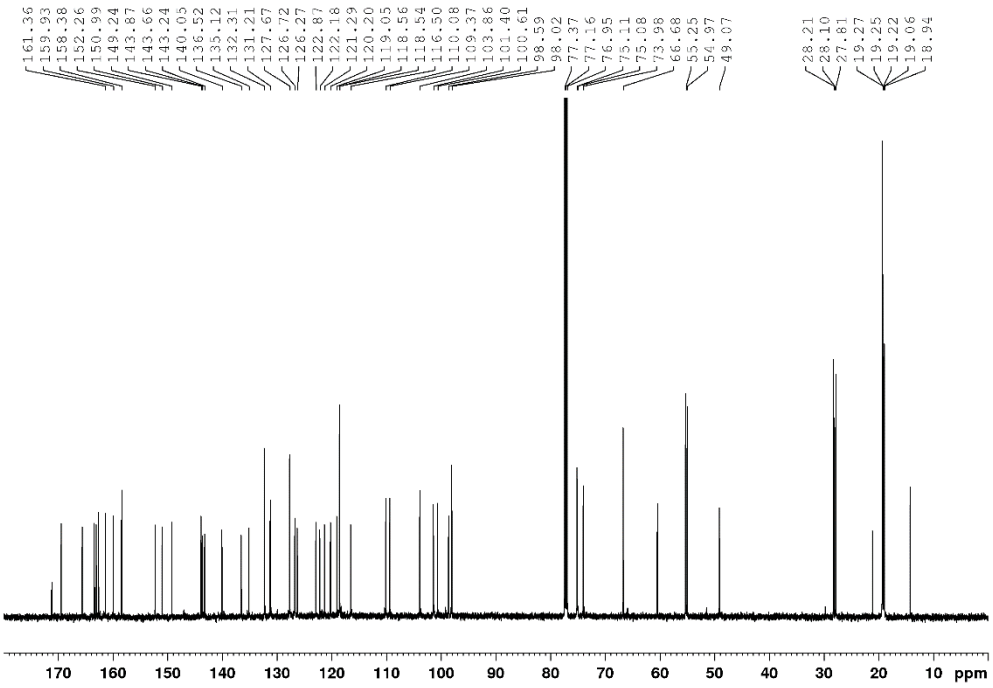


Compound **17**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

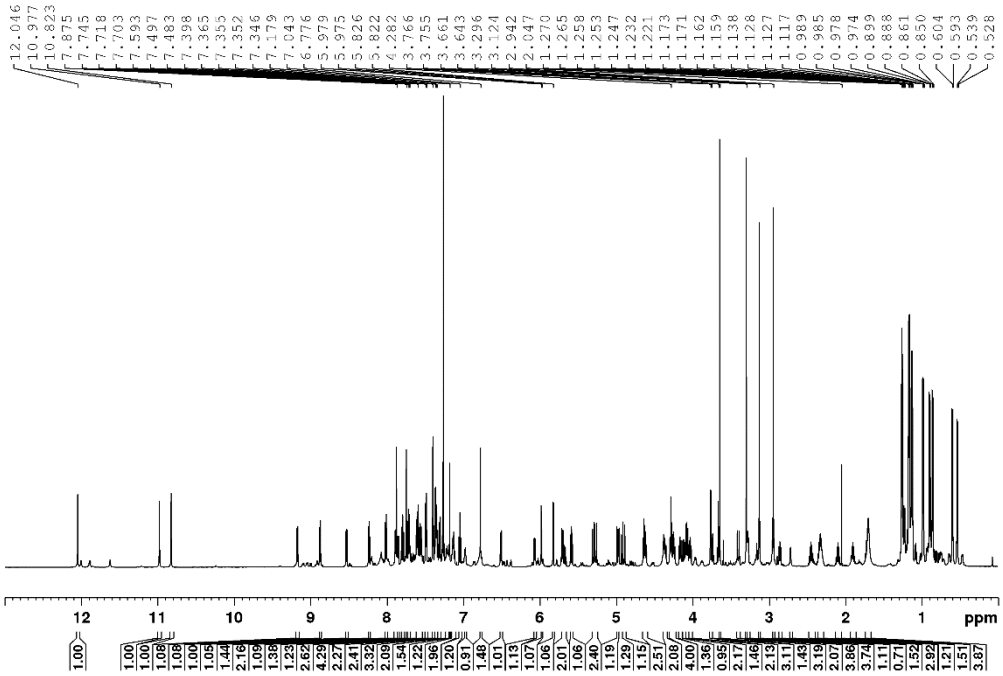


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

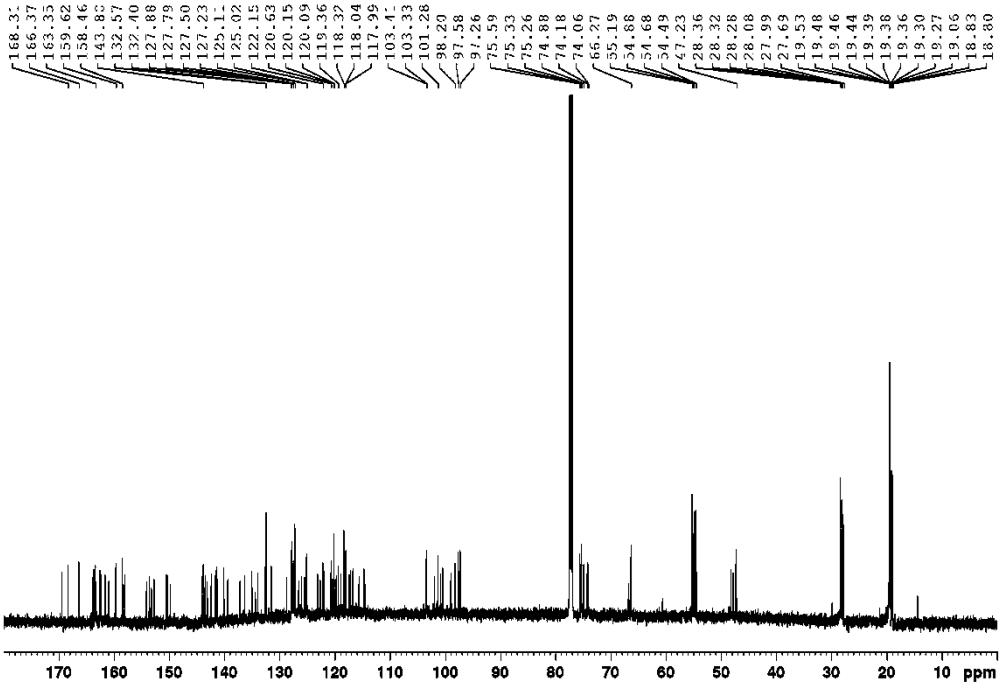


Compound **18**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

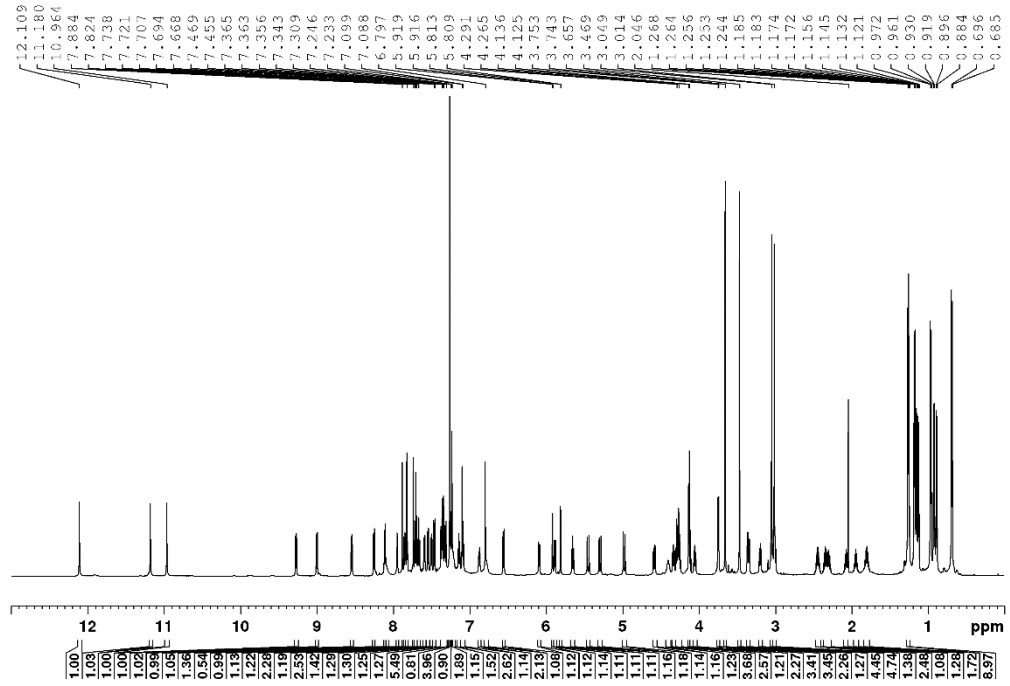


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

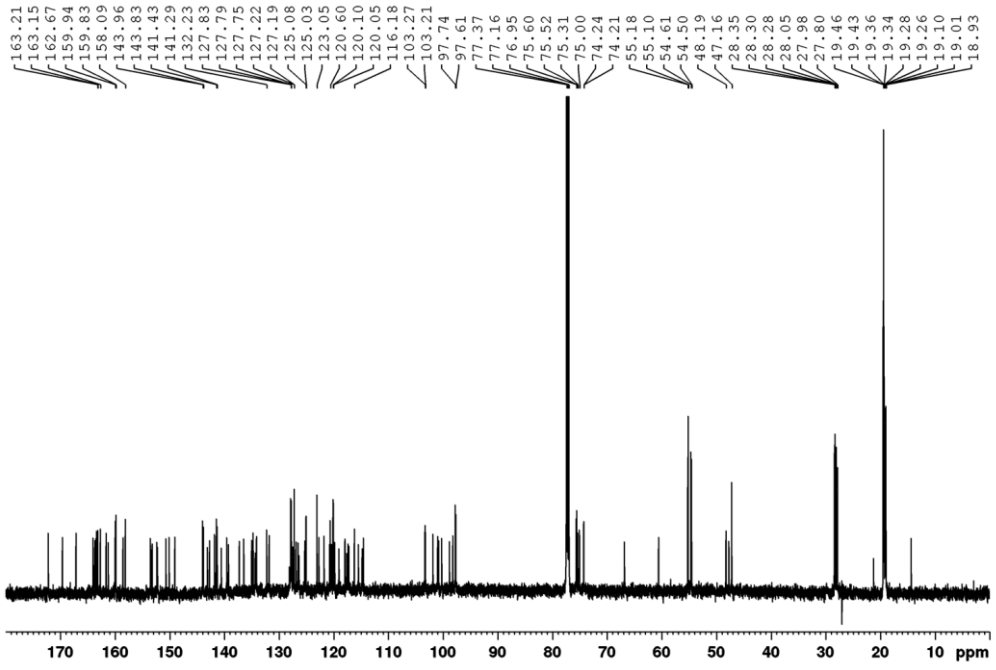


Compound **19**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

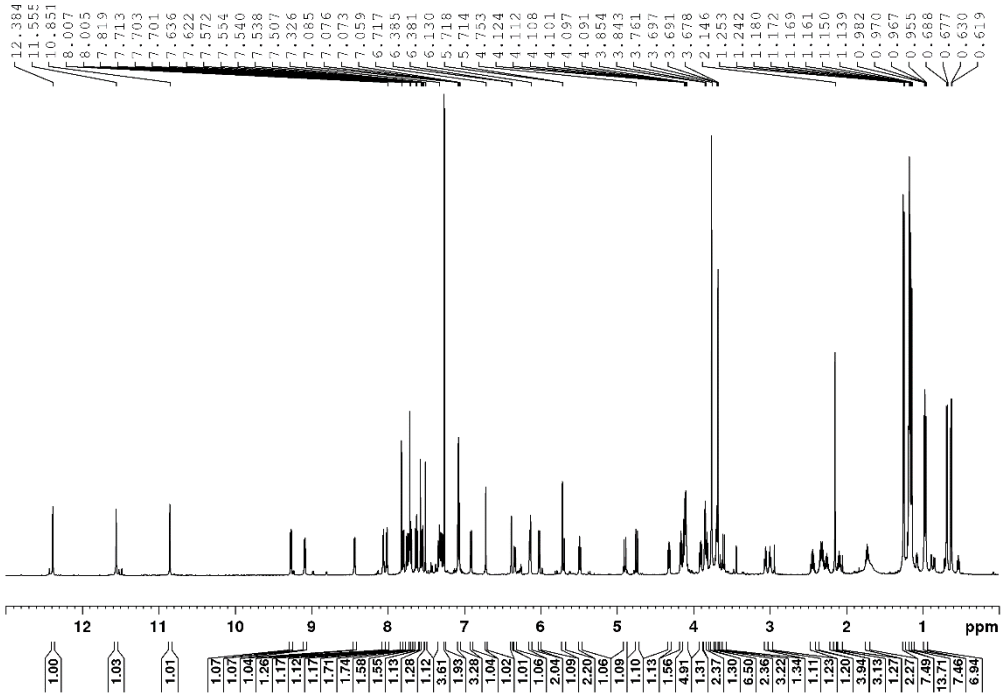


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

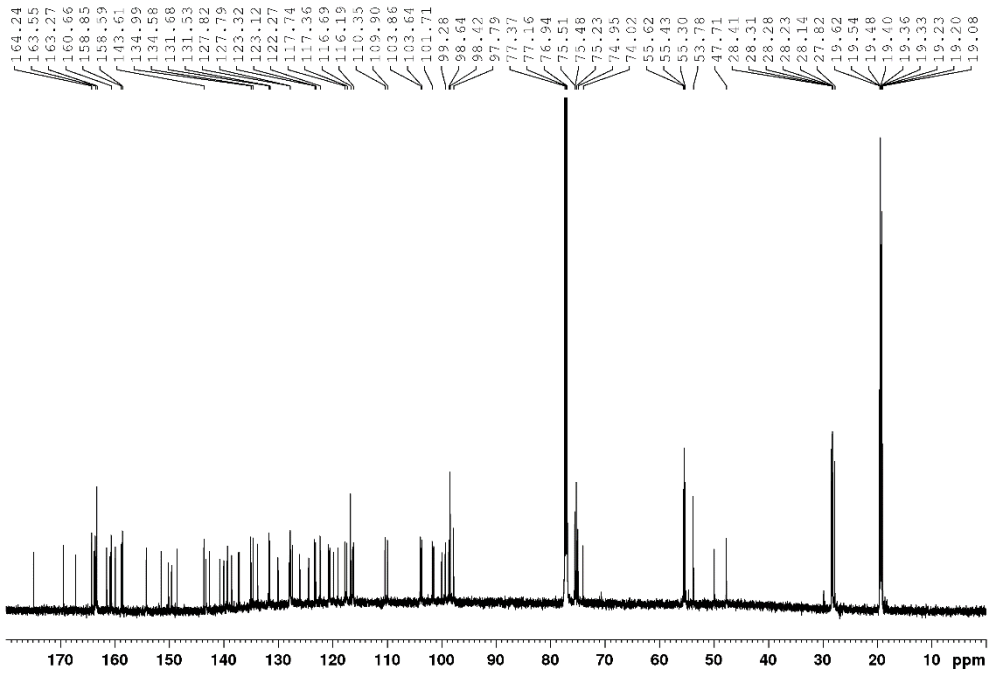


Compound **6c**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

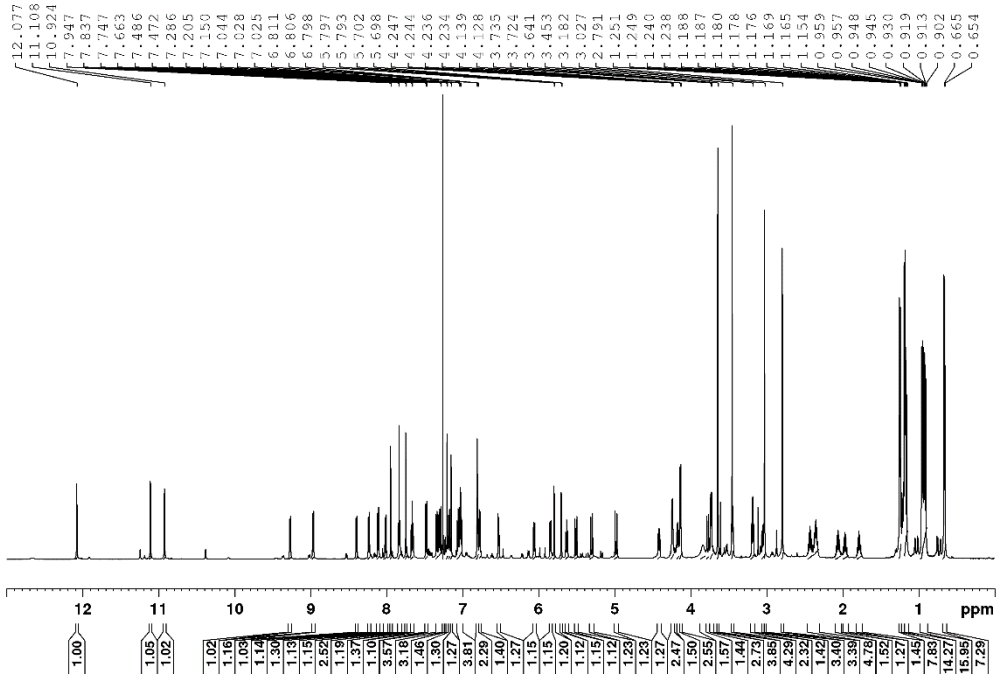


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

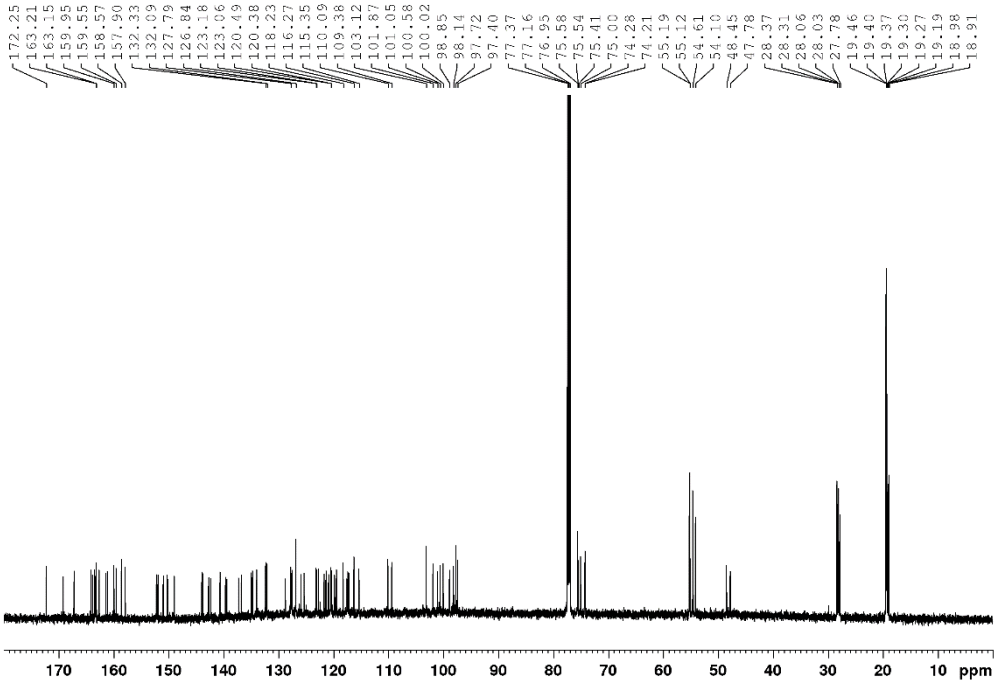


Compound **6d**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

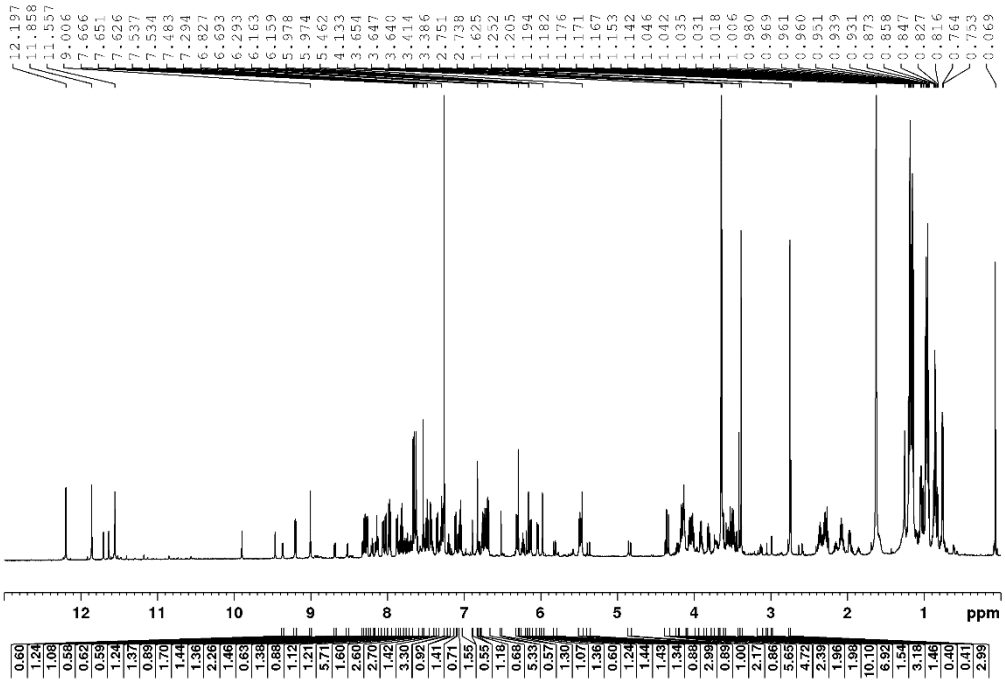


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

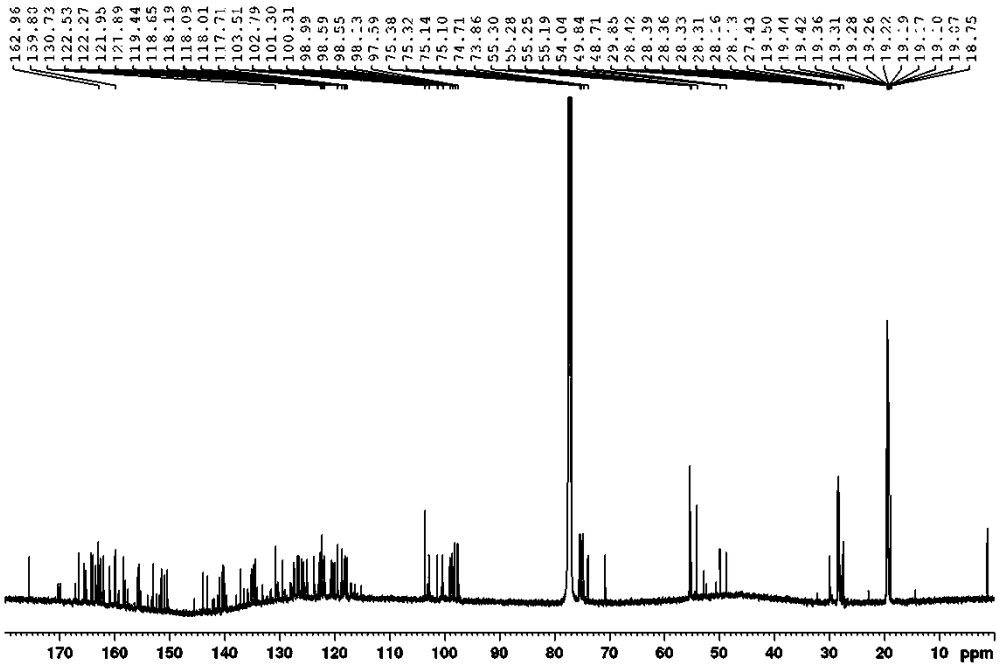


Compound **8c**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

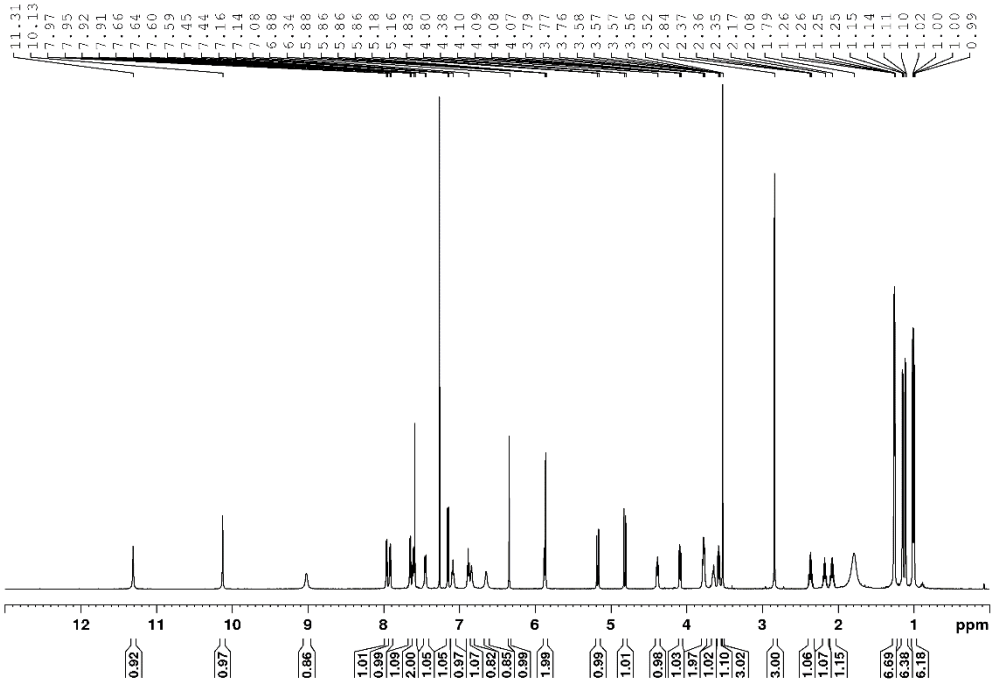


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

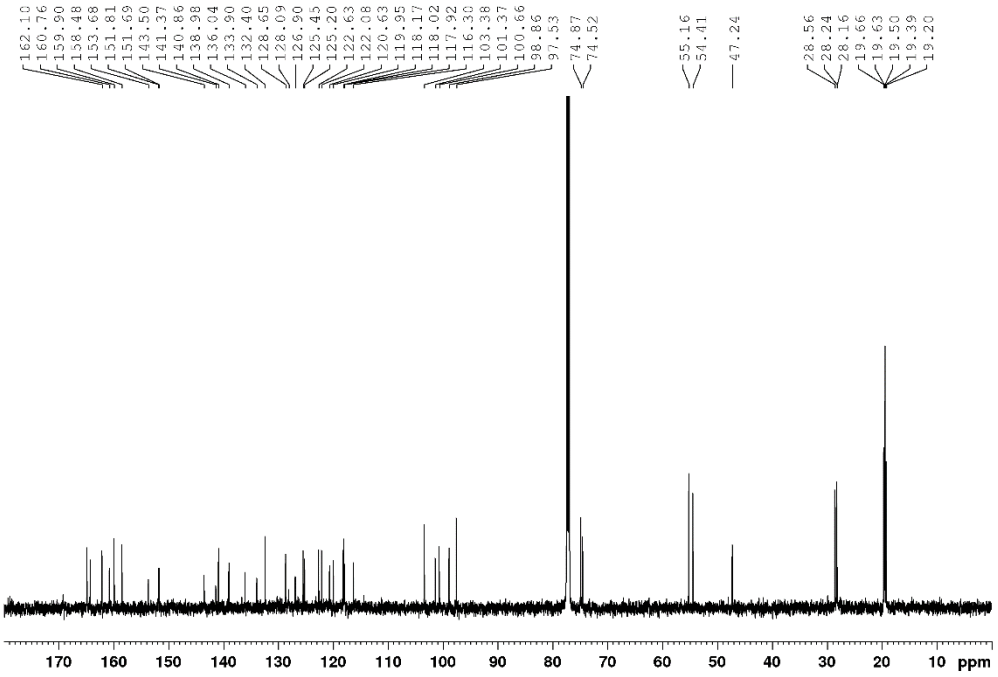


Compound **8d**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

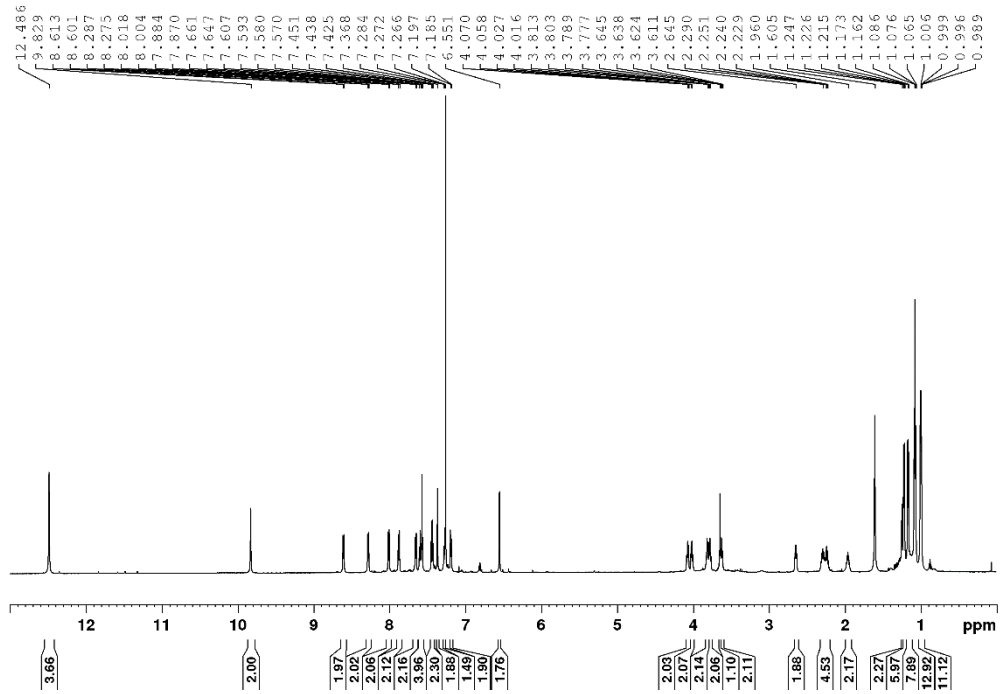


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

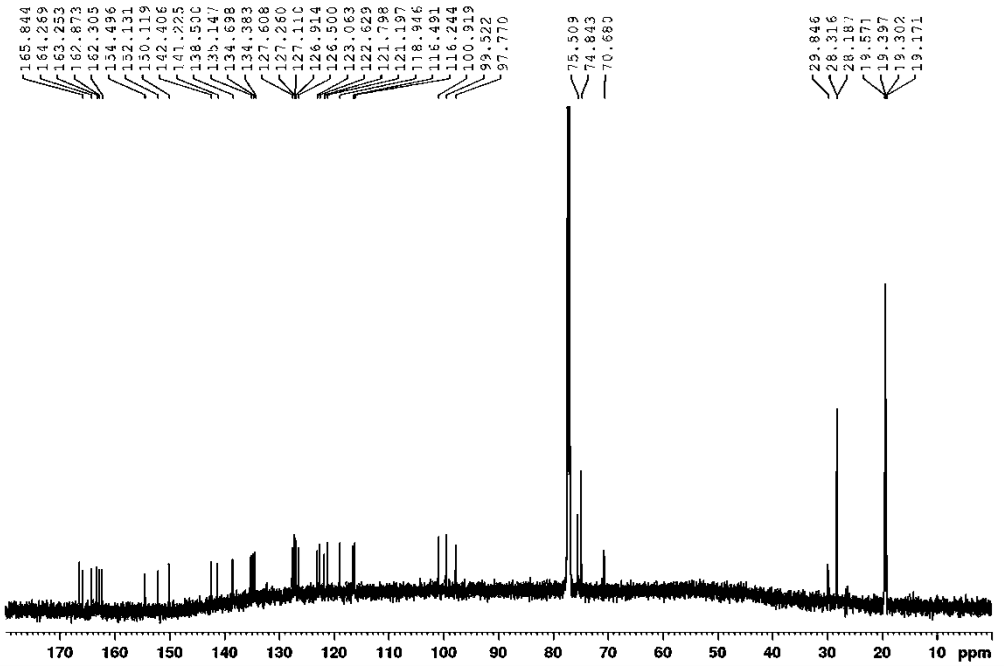


Compound **4**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

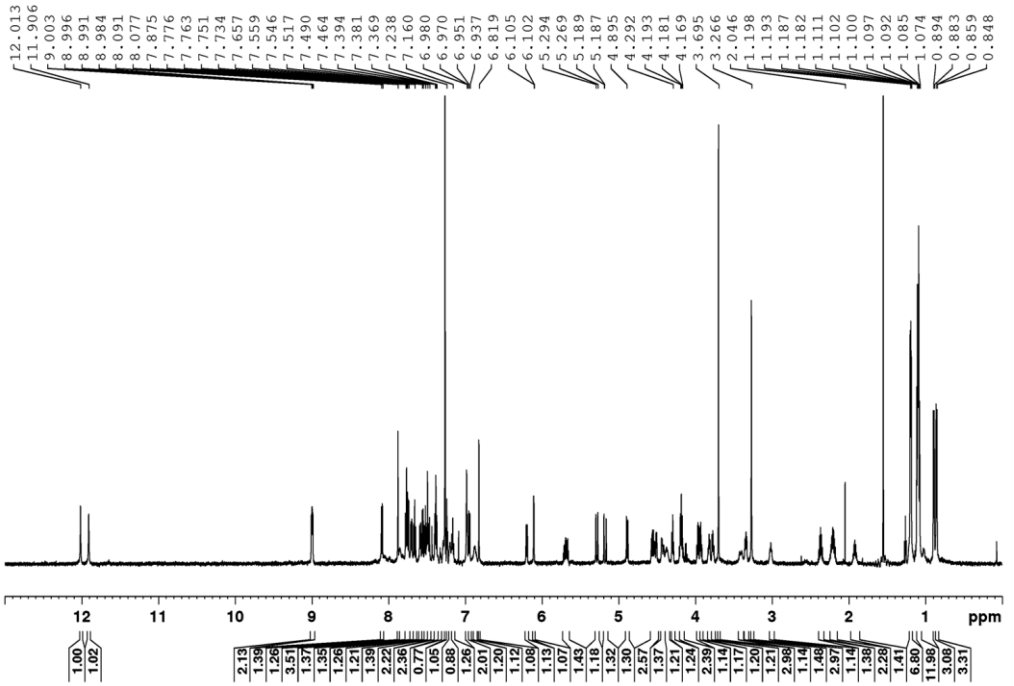


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

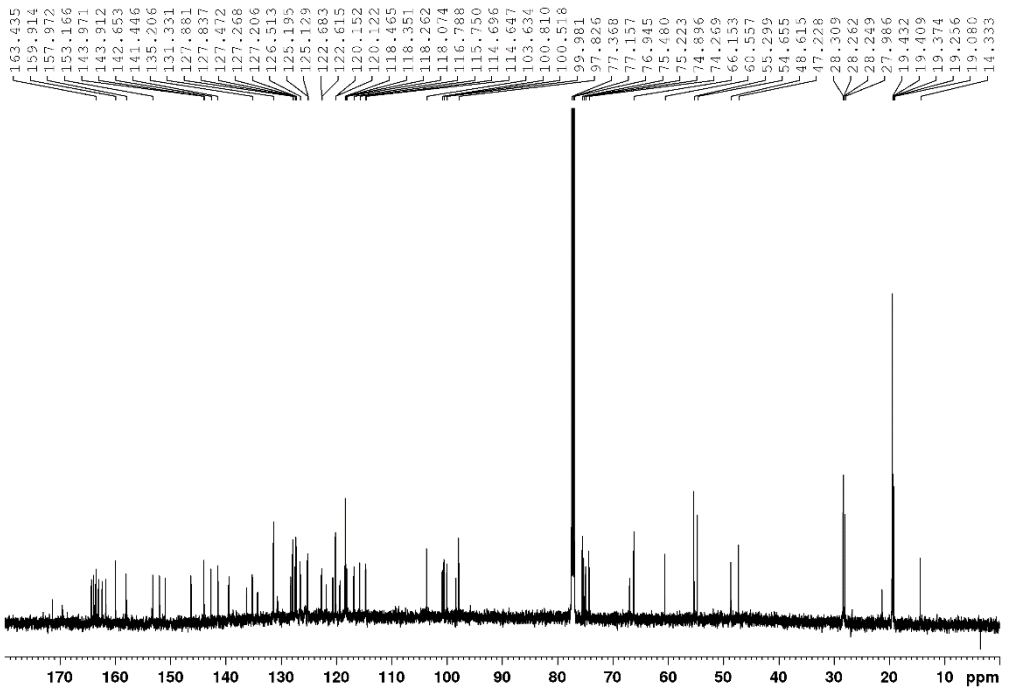


Compound **20**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

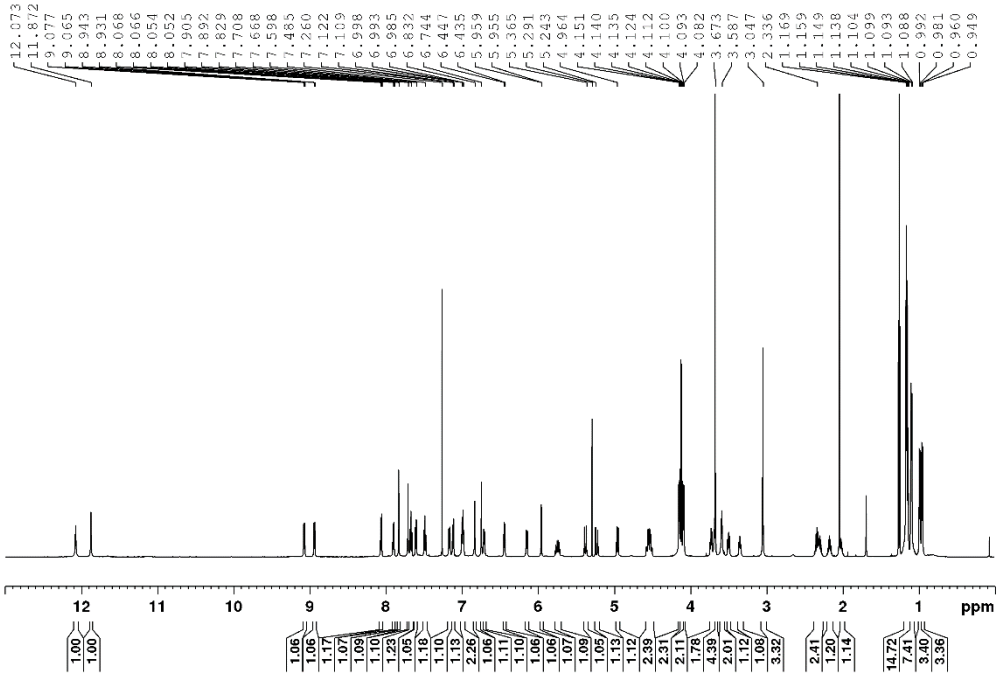


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

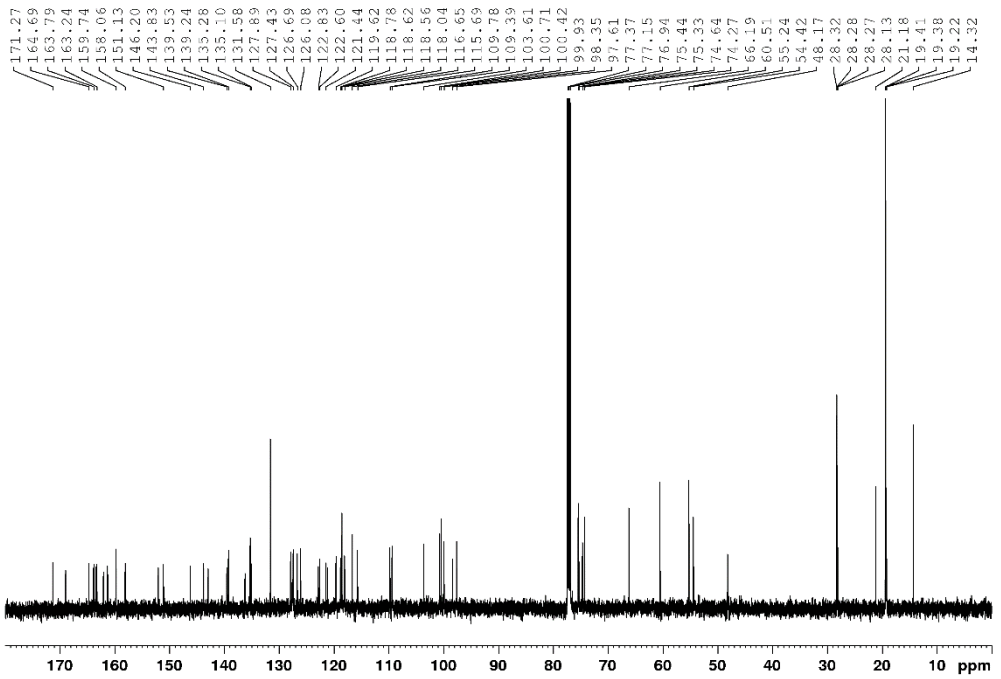


Compound **21**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

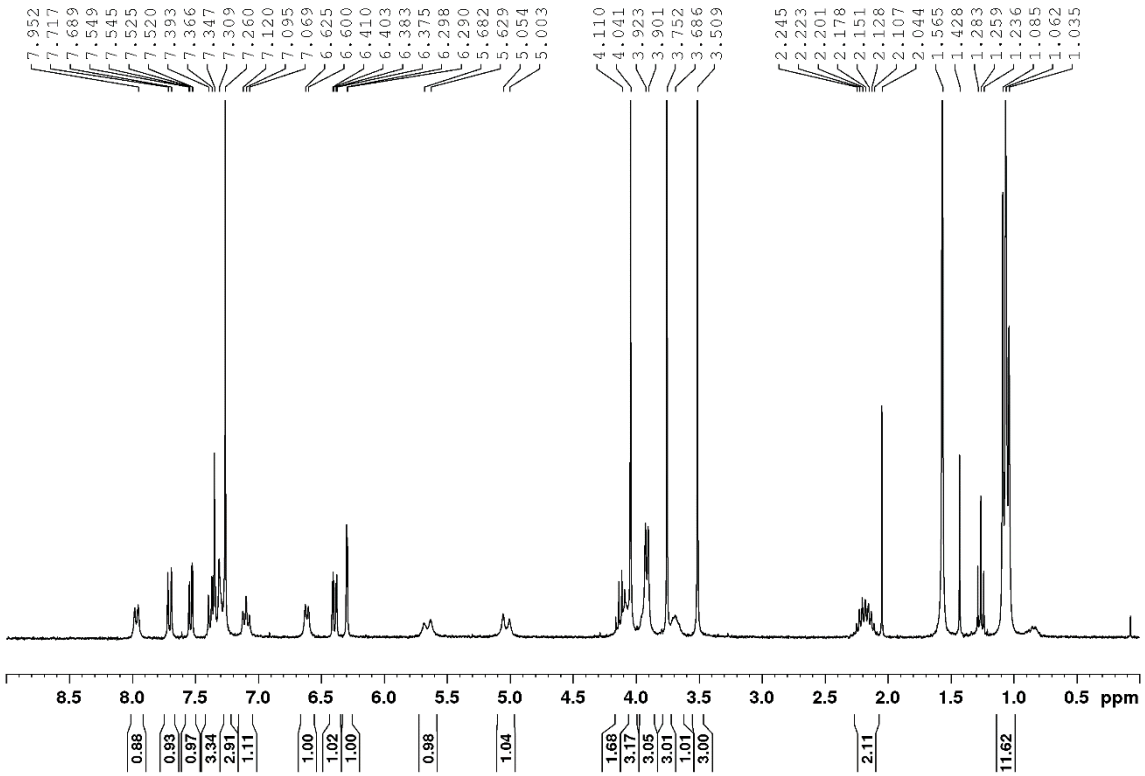


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

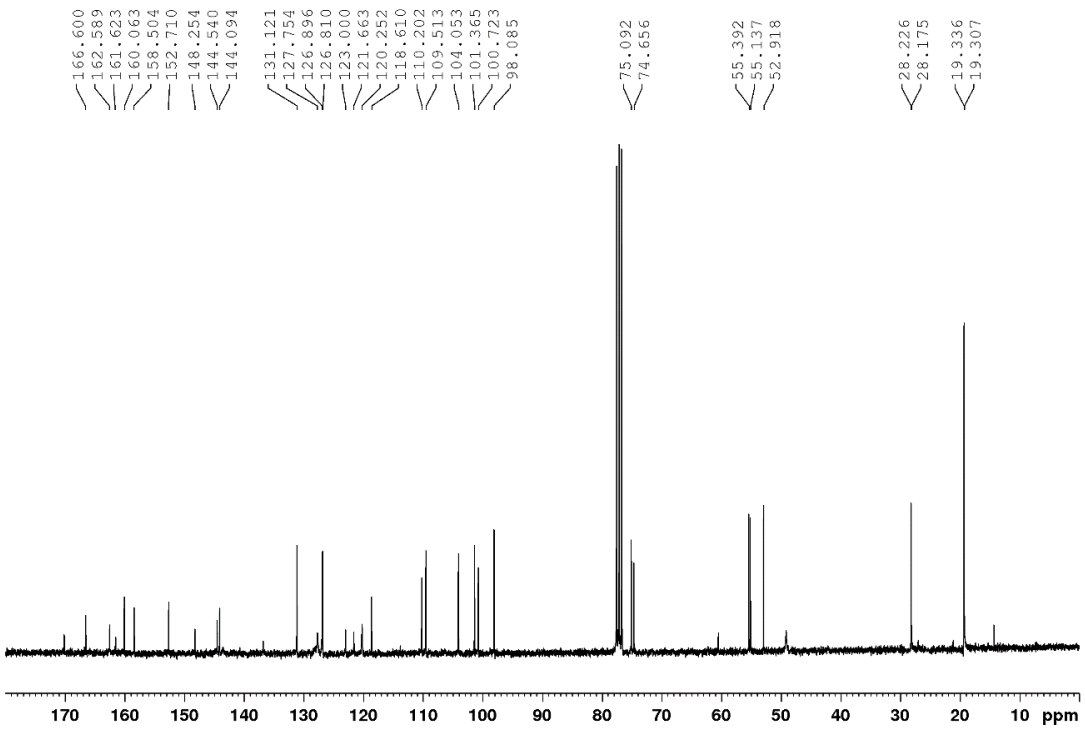


Compound **23**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

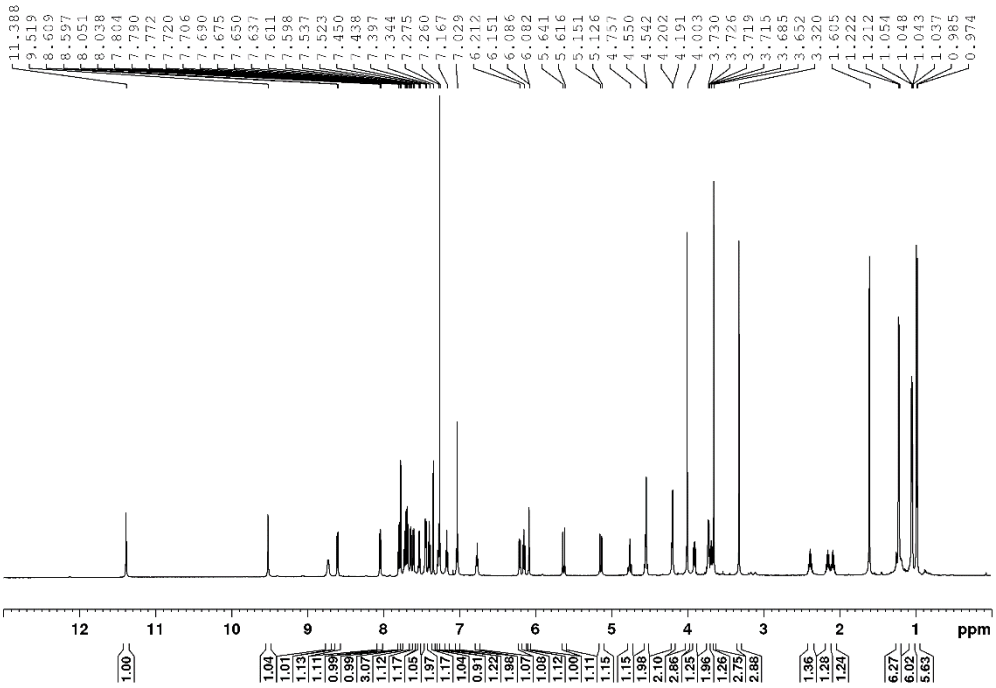


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

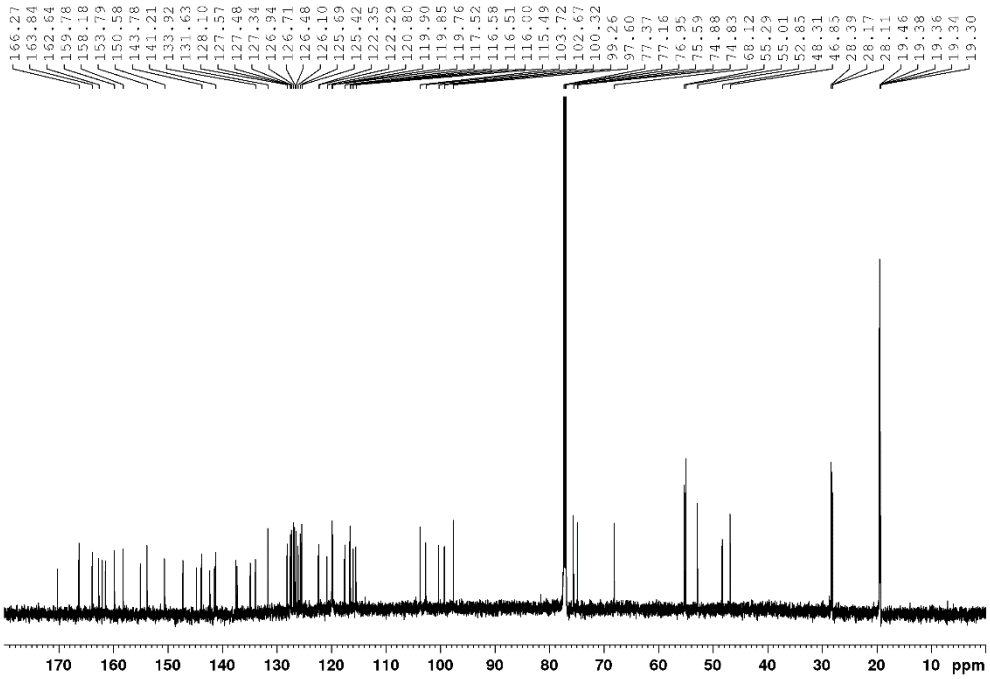


Compound **25**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

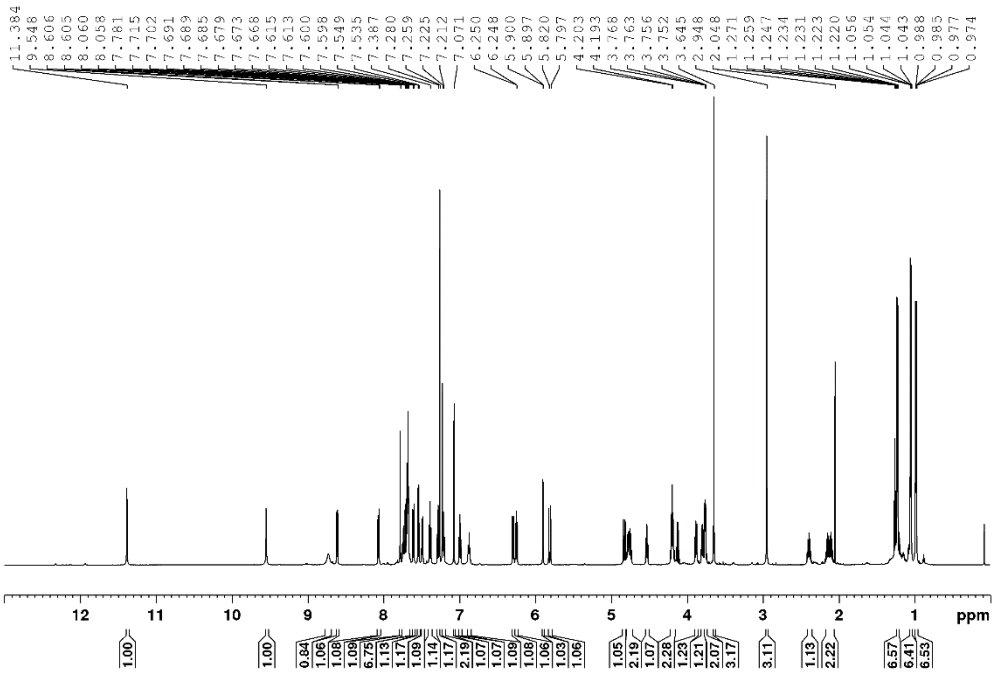


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

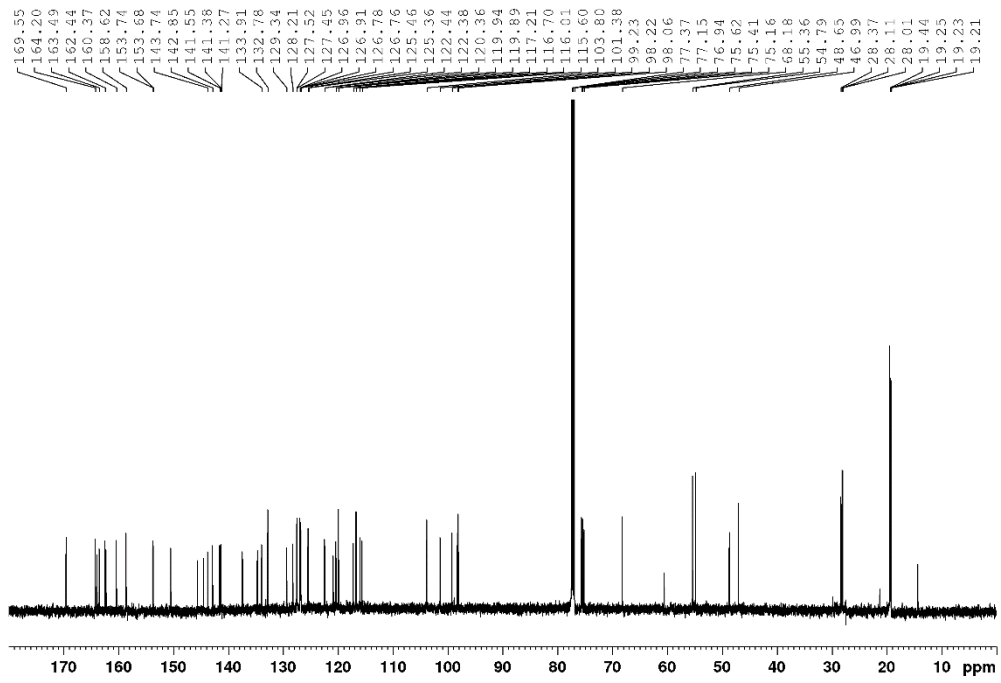


Compound **26**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

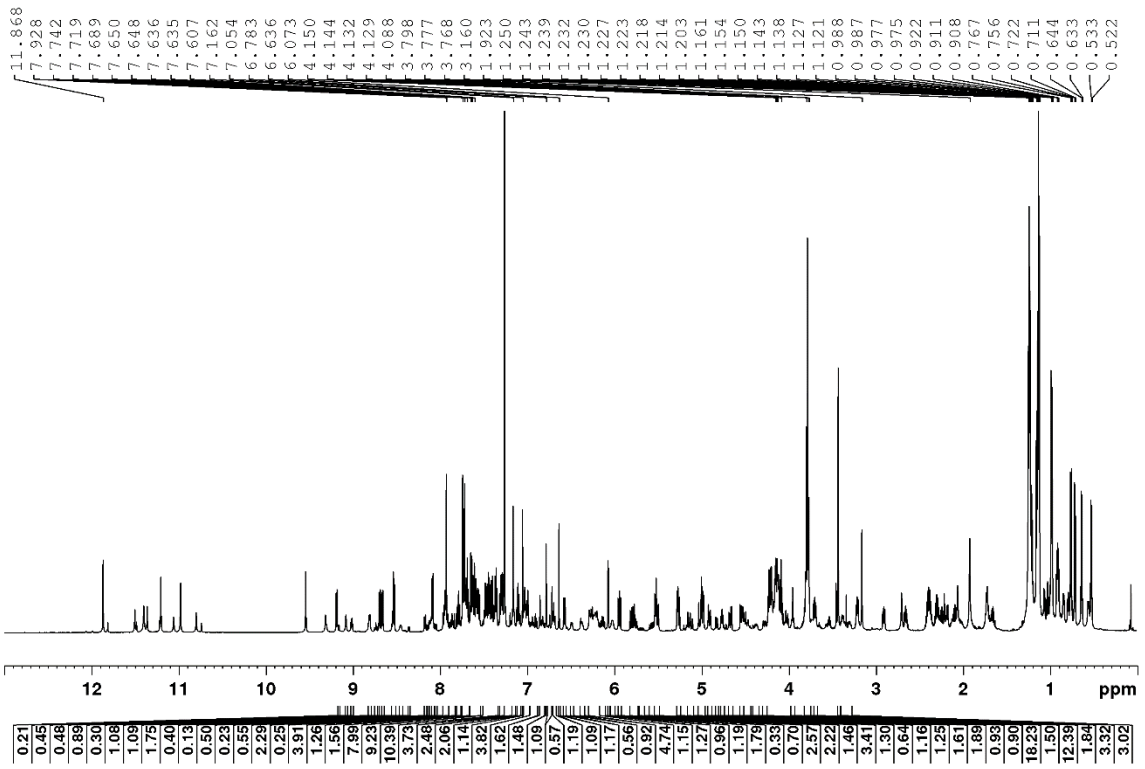


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

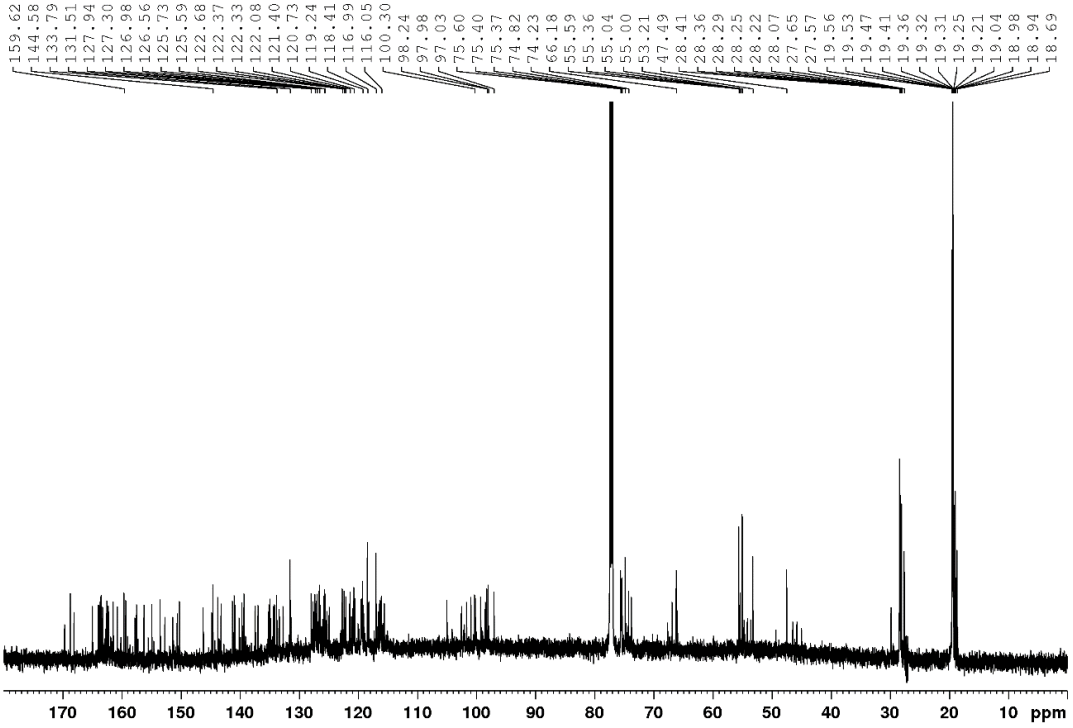


Compound **27**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

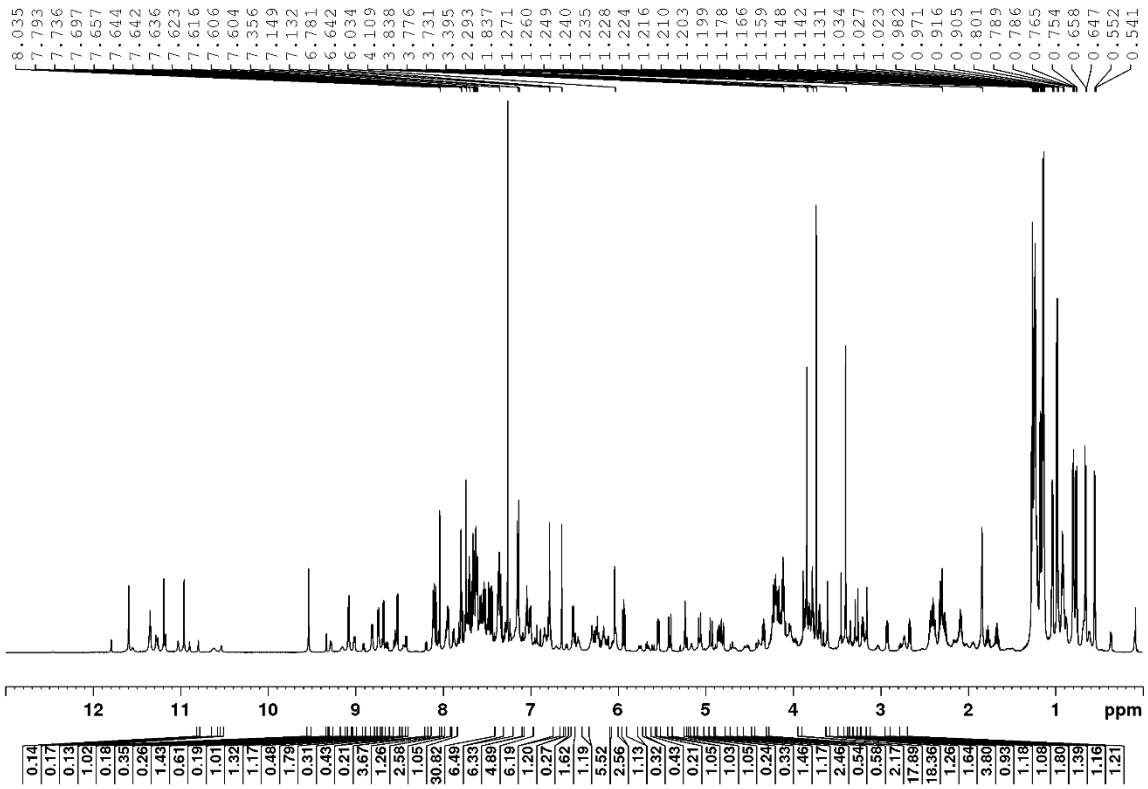


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

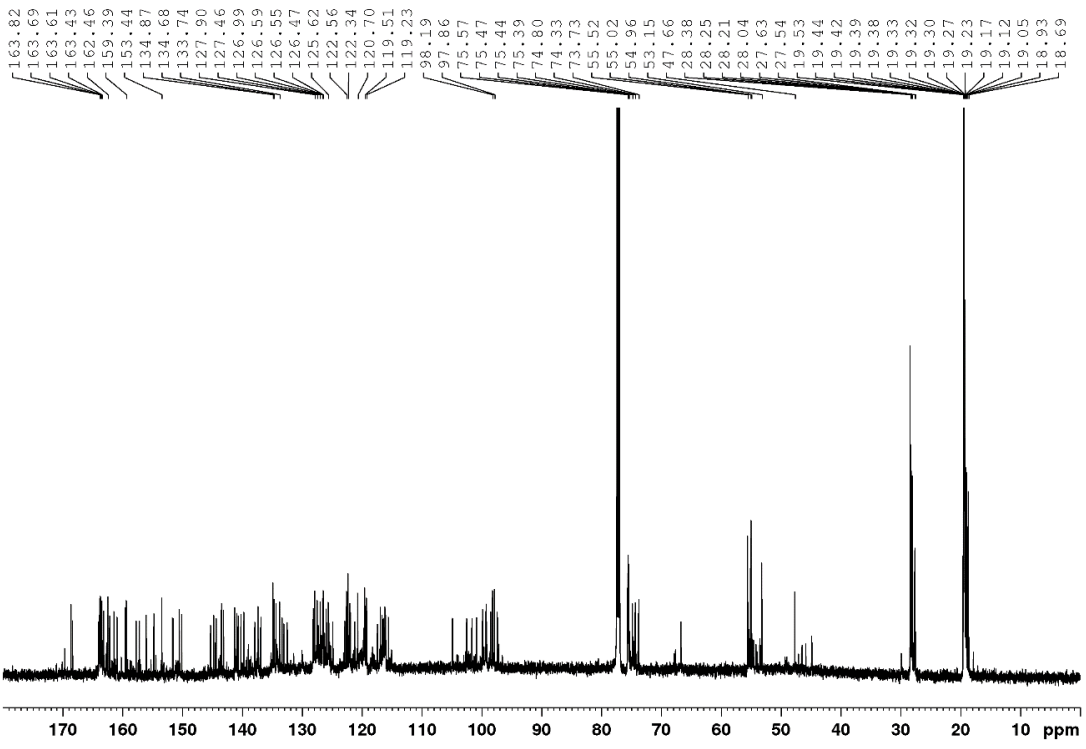


Compound **28**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

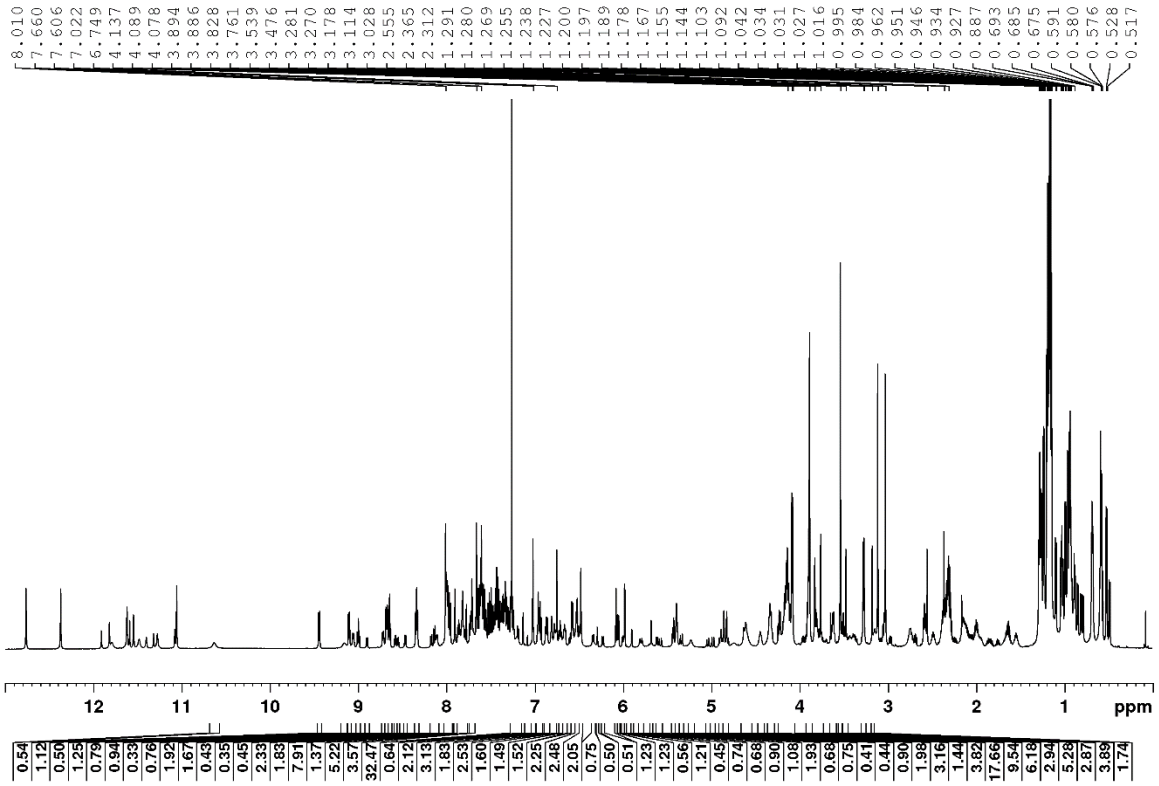


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

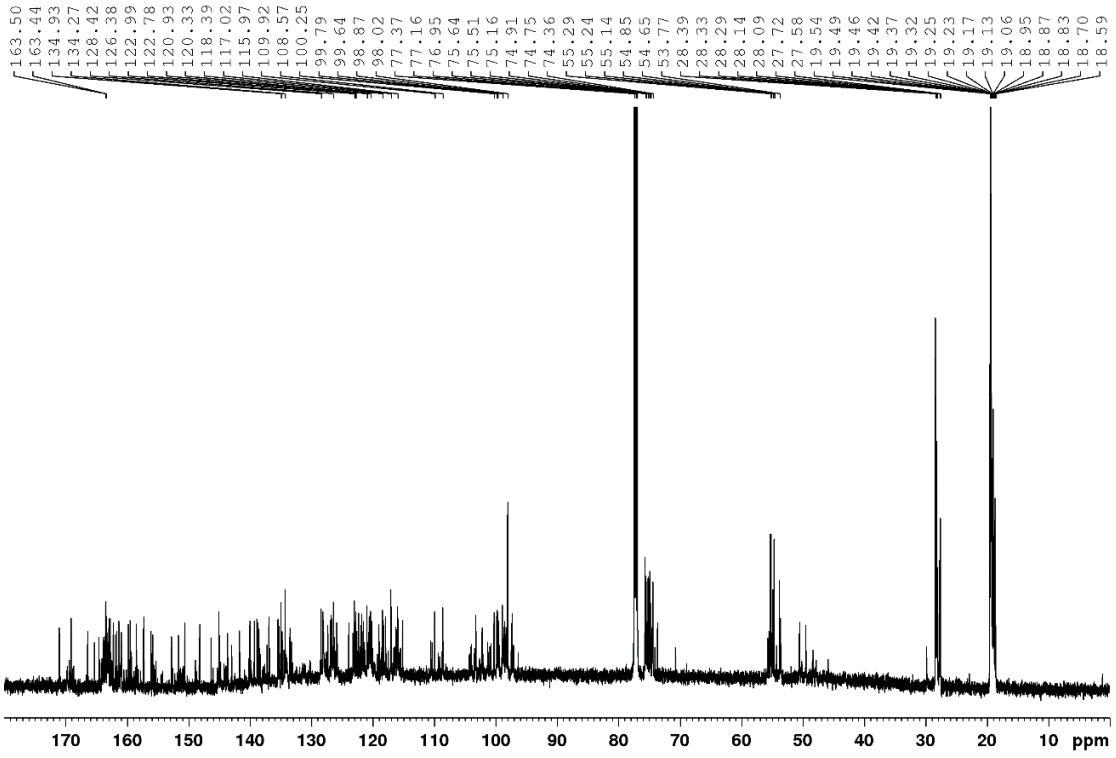


Compound **7b**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

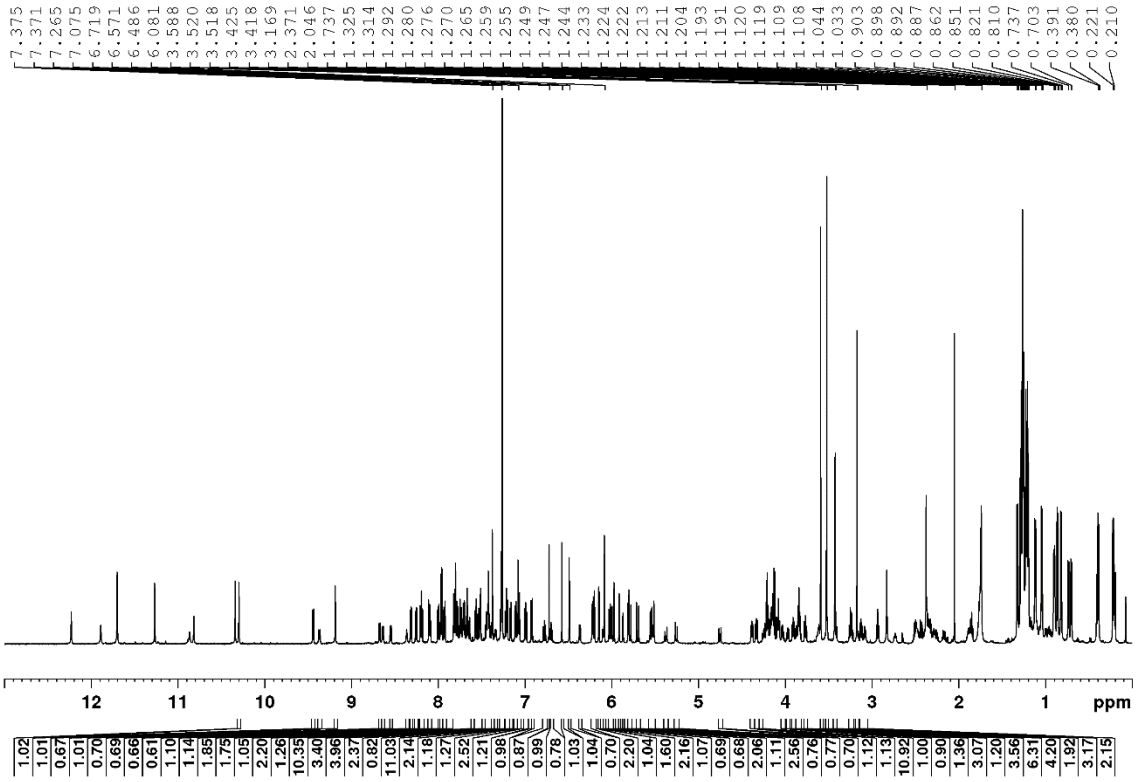


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

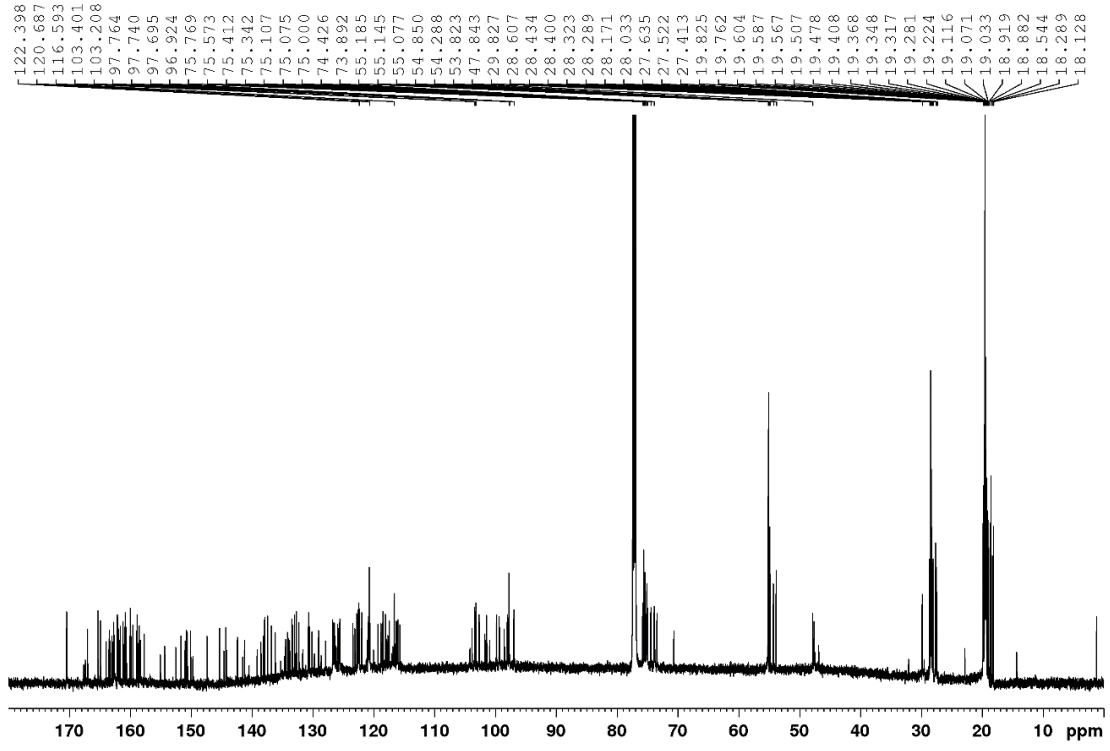


Compound **9b**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

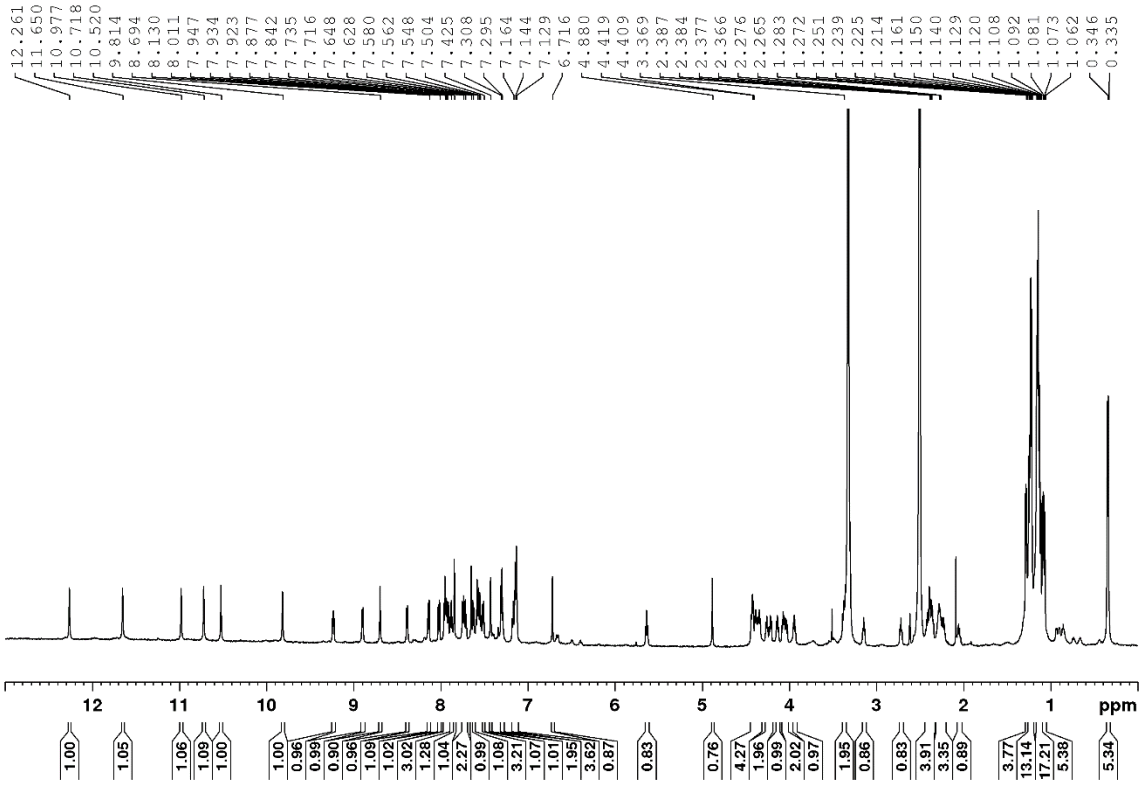


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

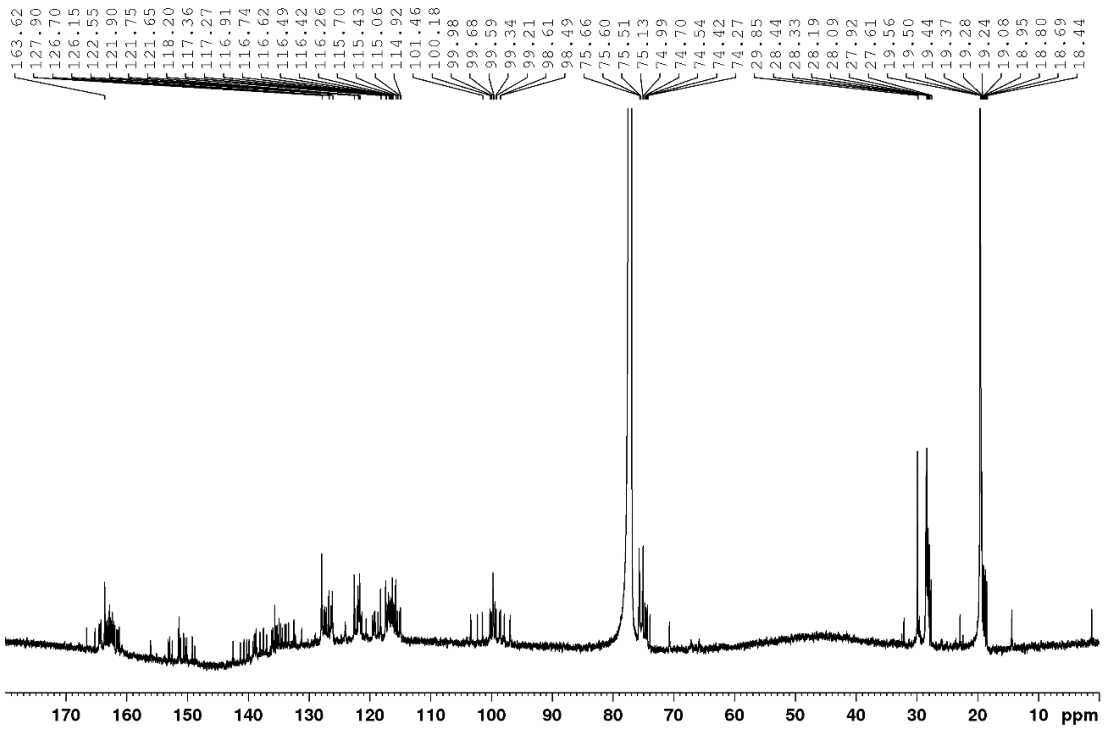


Compound **5**

^{1}H NMR (600 MHz, DMSO-d_6, 25℃)

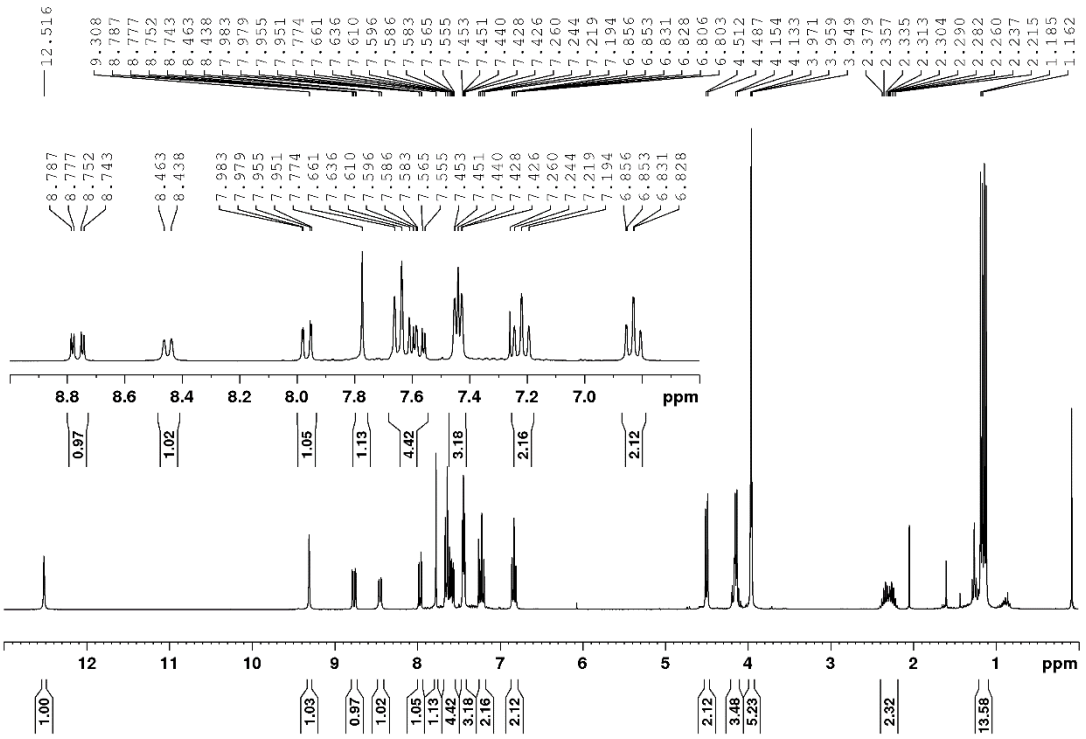


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

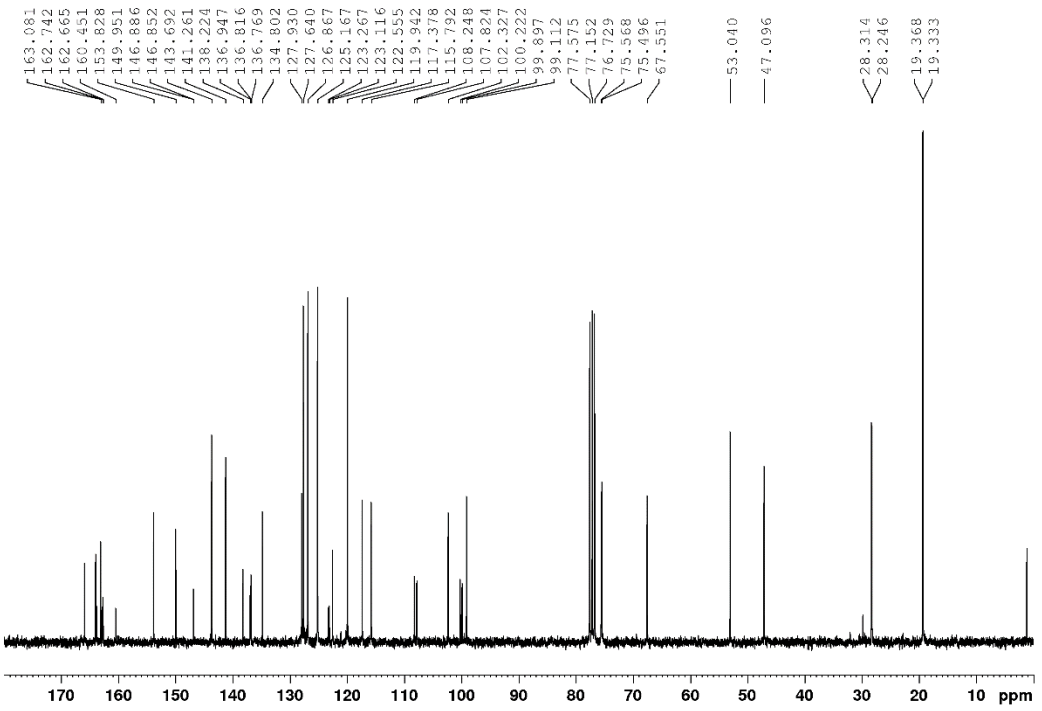


Compound **33**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

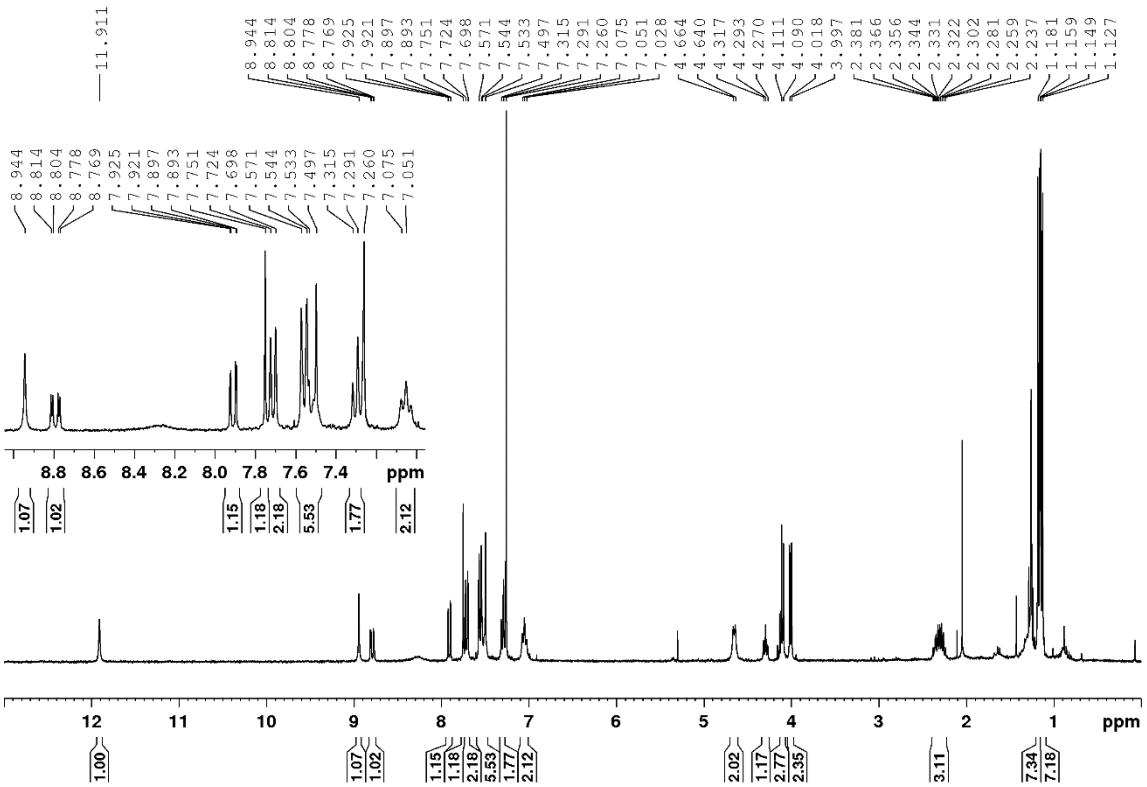


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

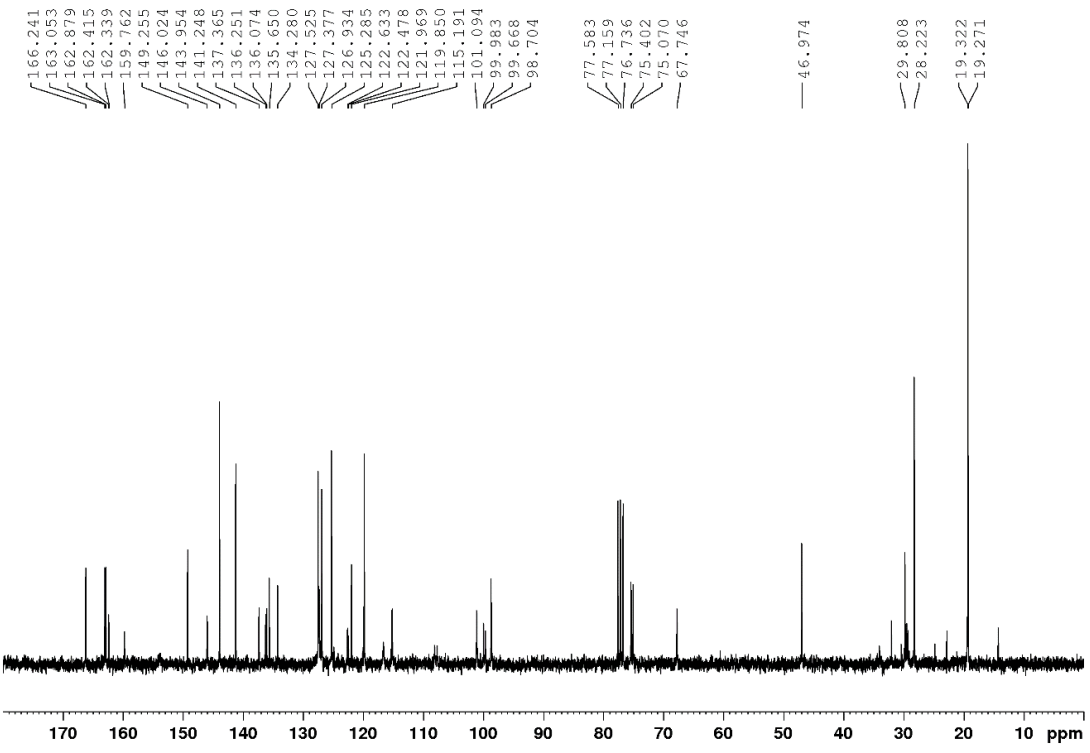


Compound **34**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

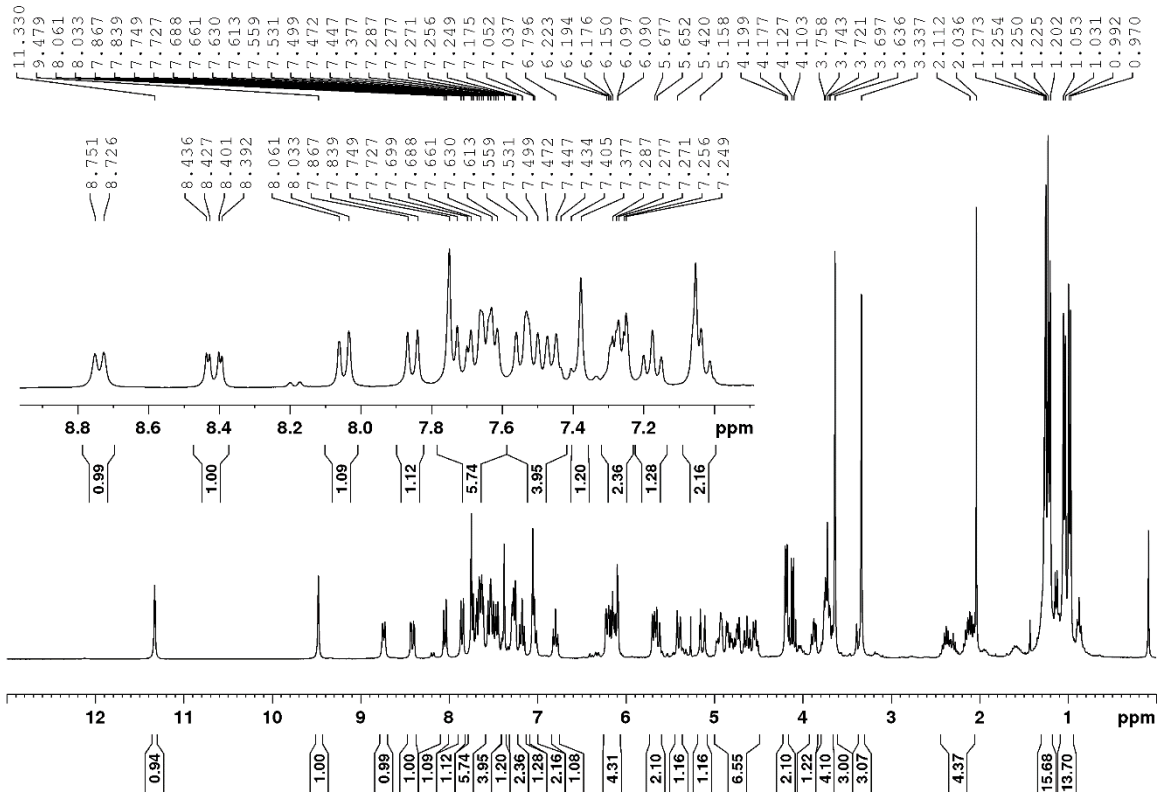


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

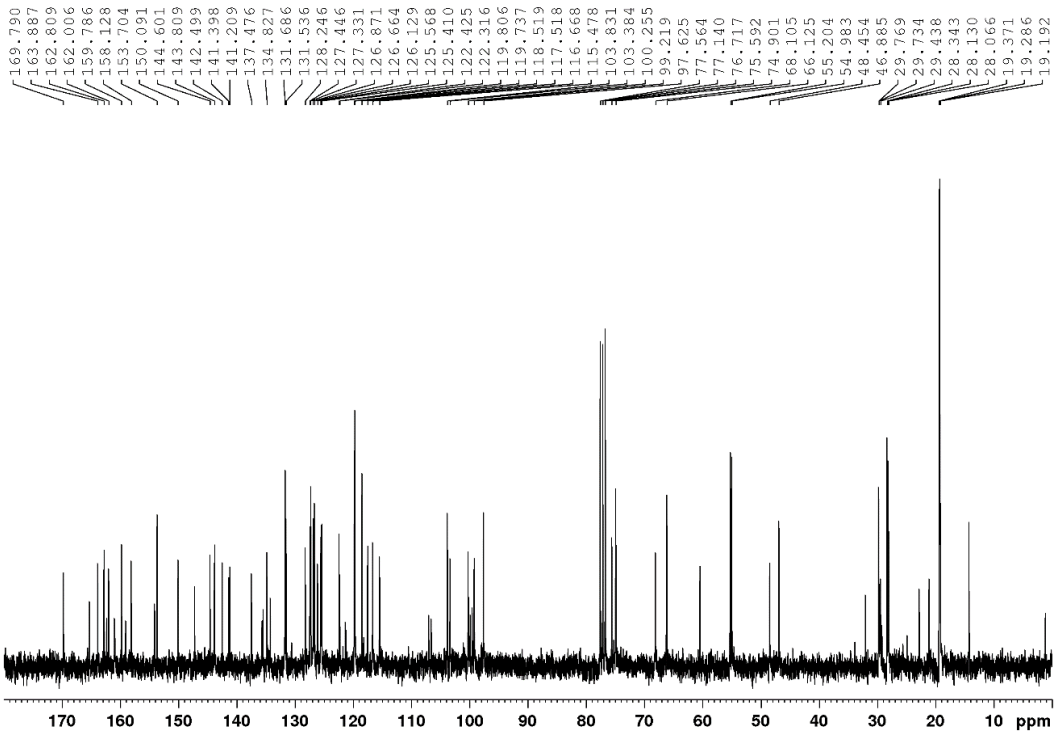


Compound **36**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

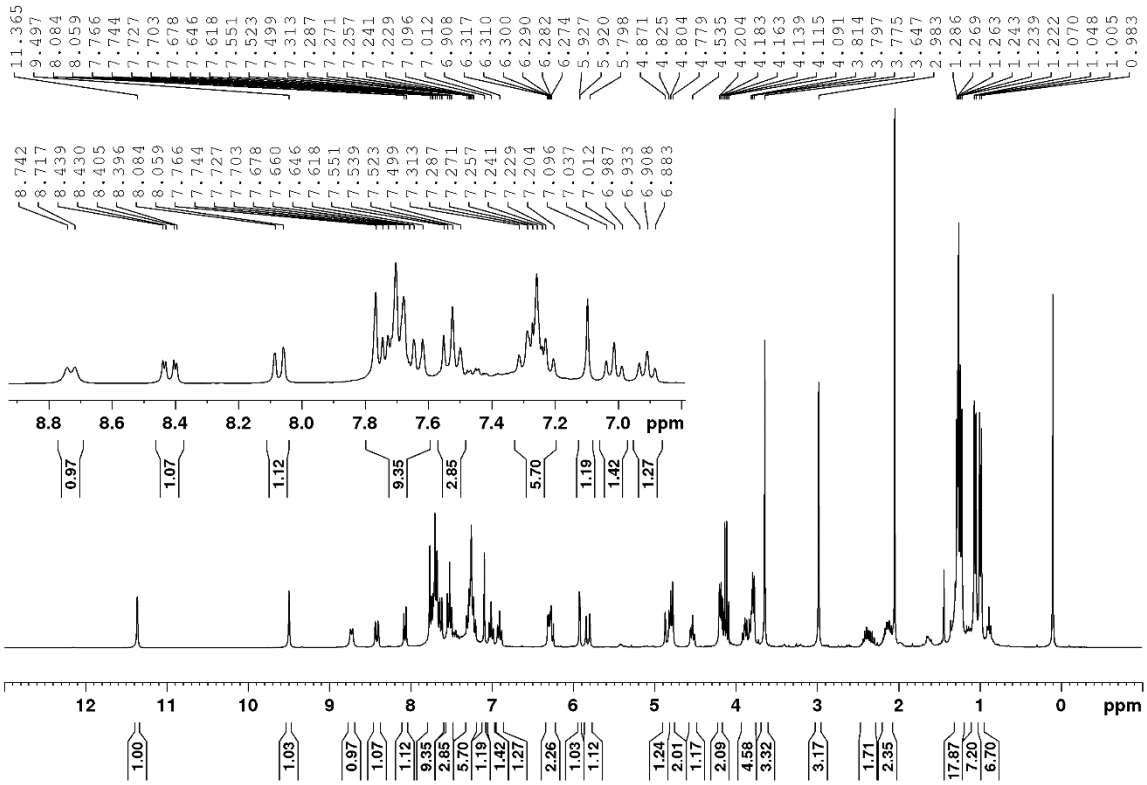


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

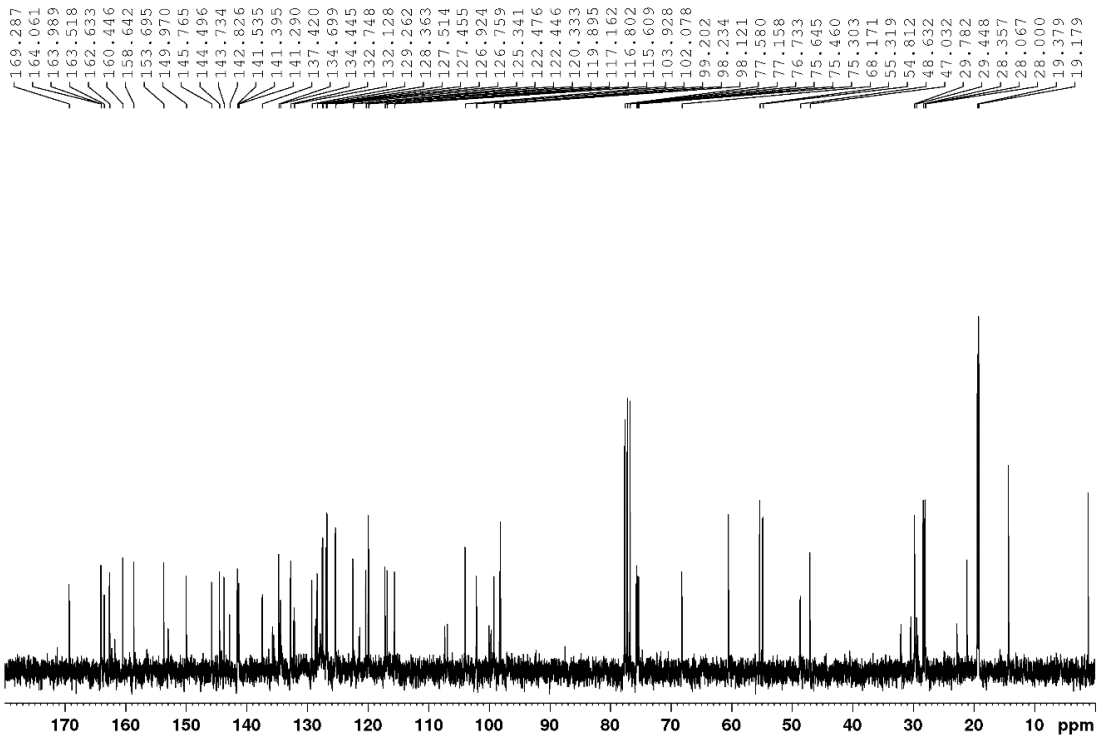


Compound **37**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

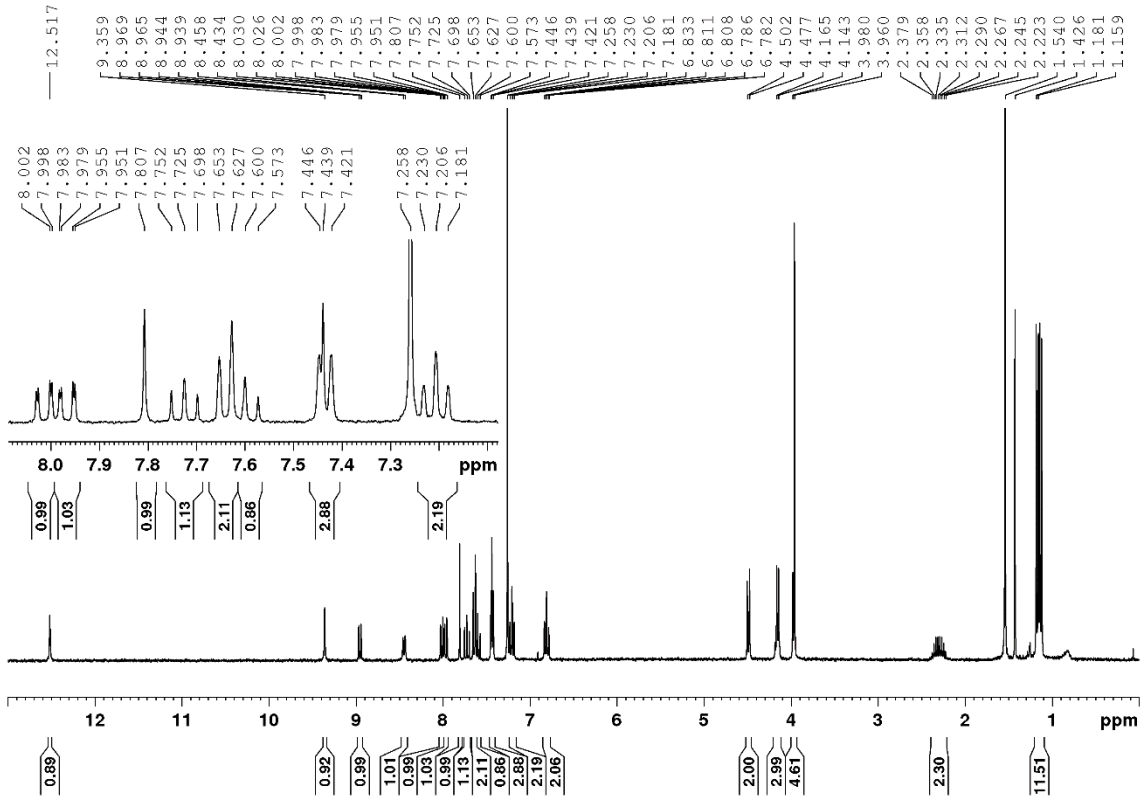


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

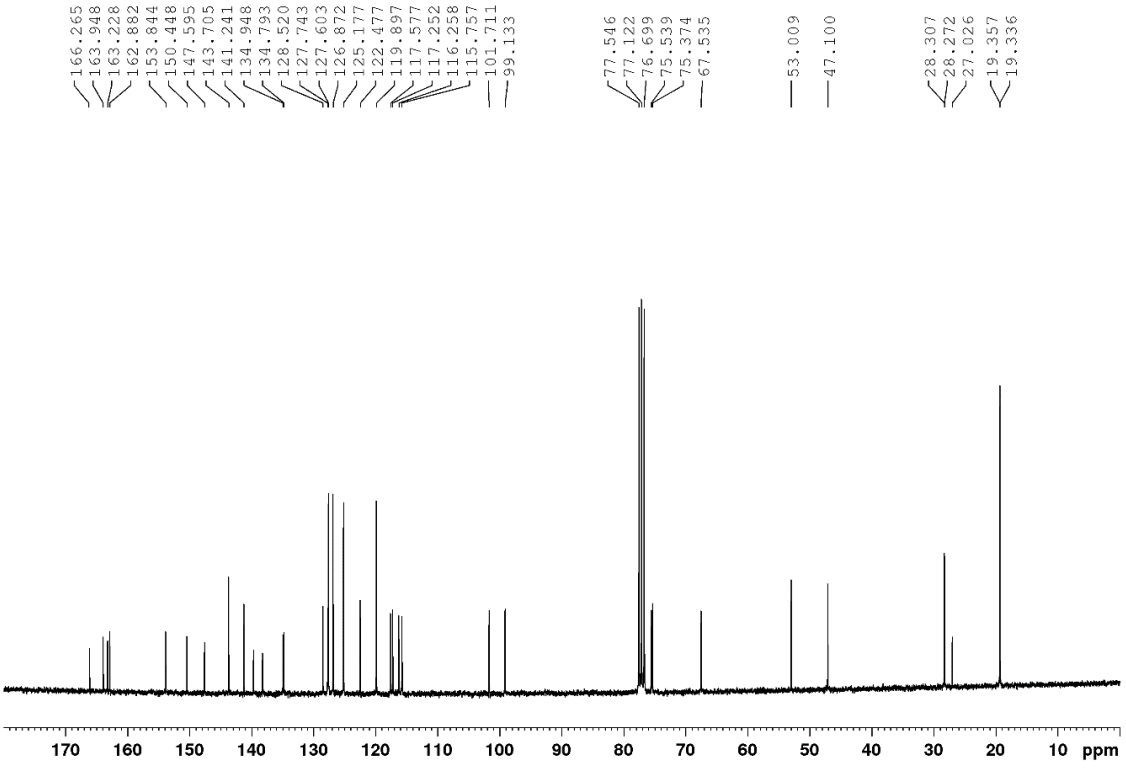


Compound **39**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

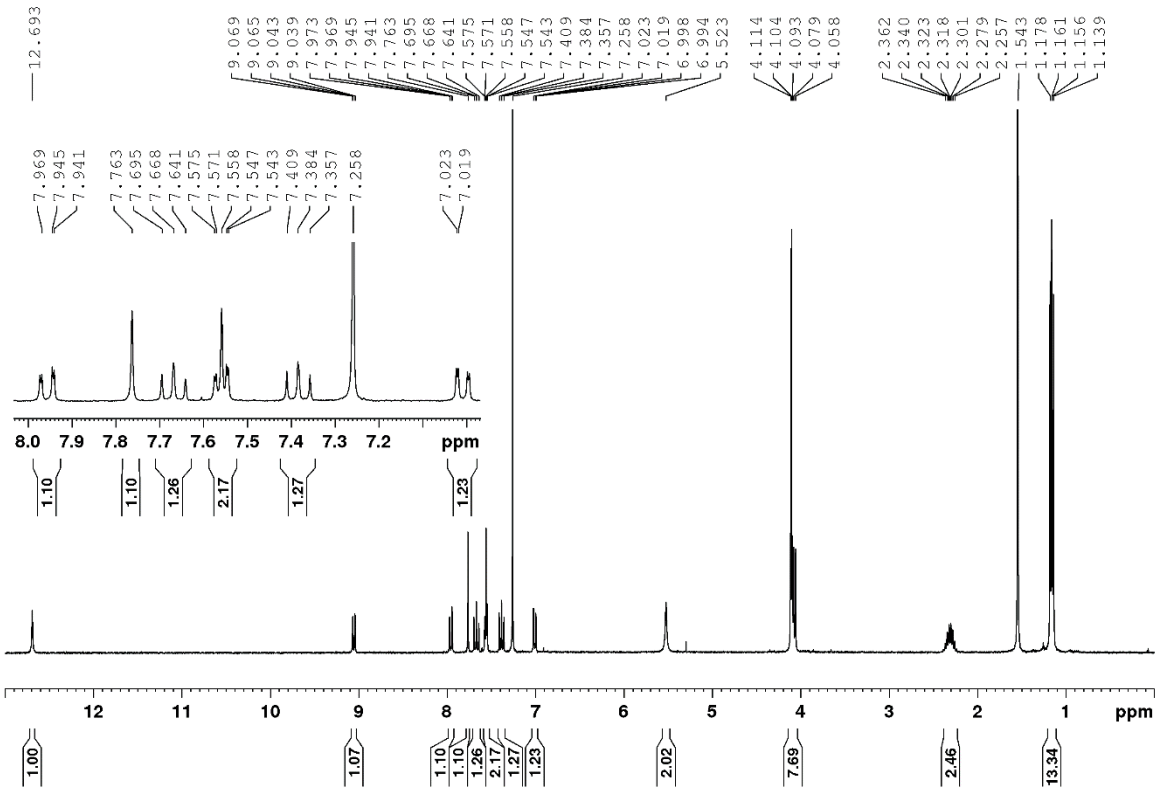


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

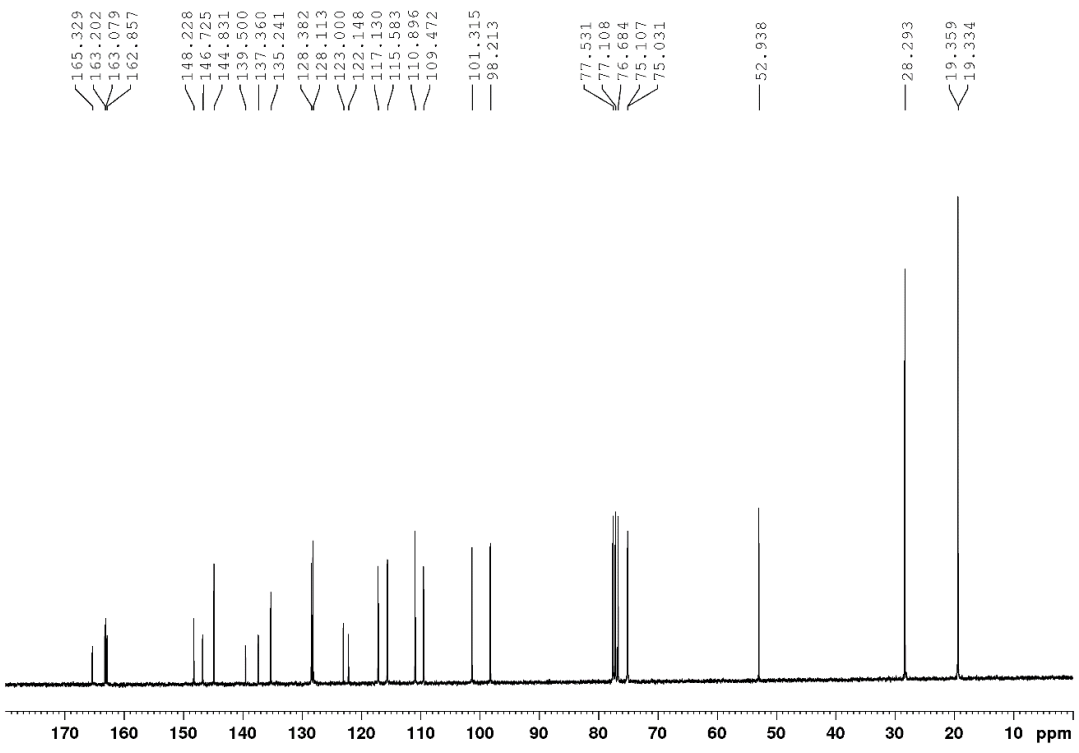


Compound **40**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

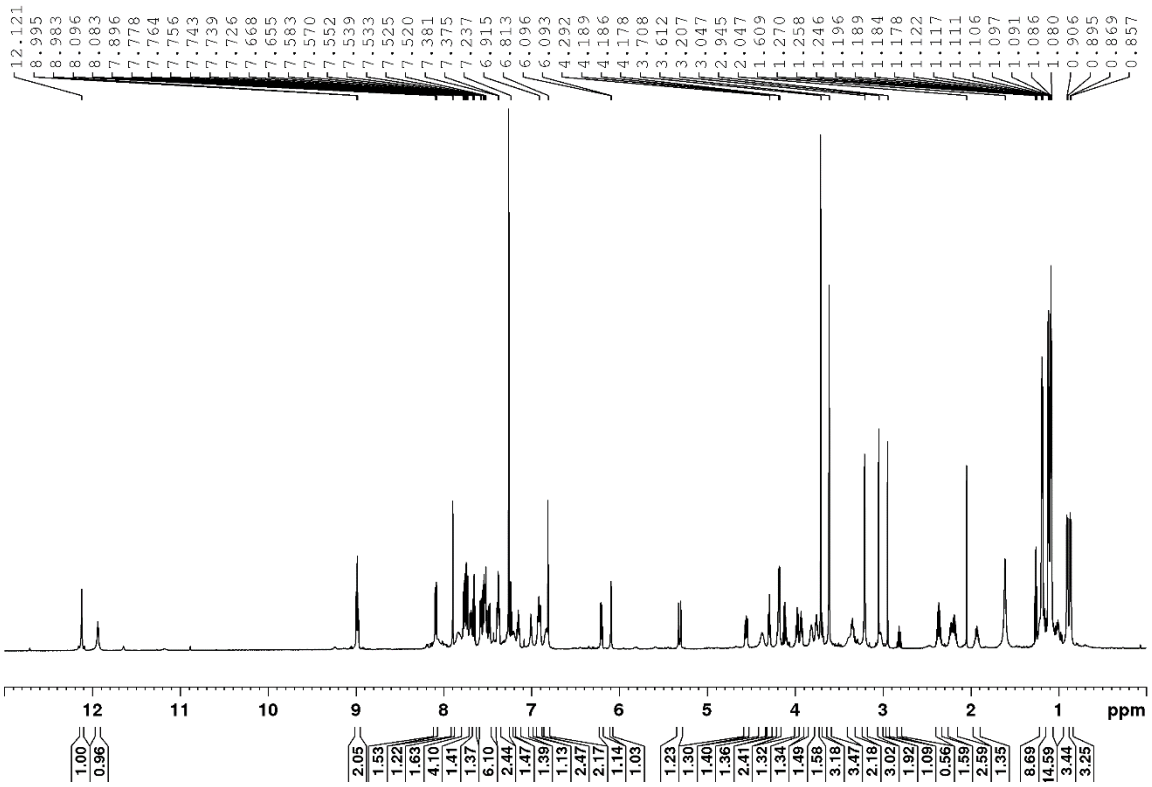


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

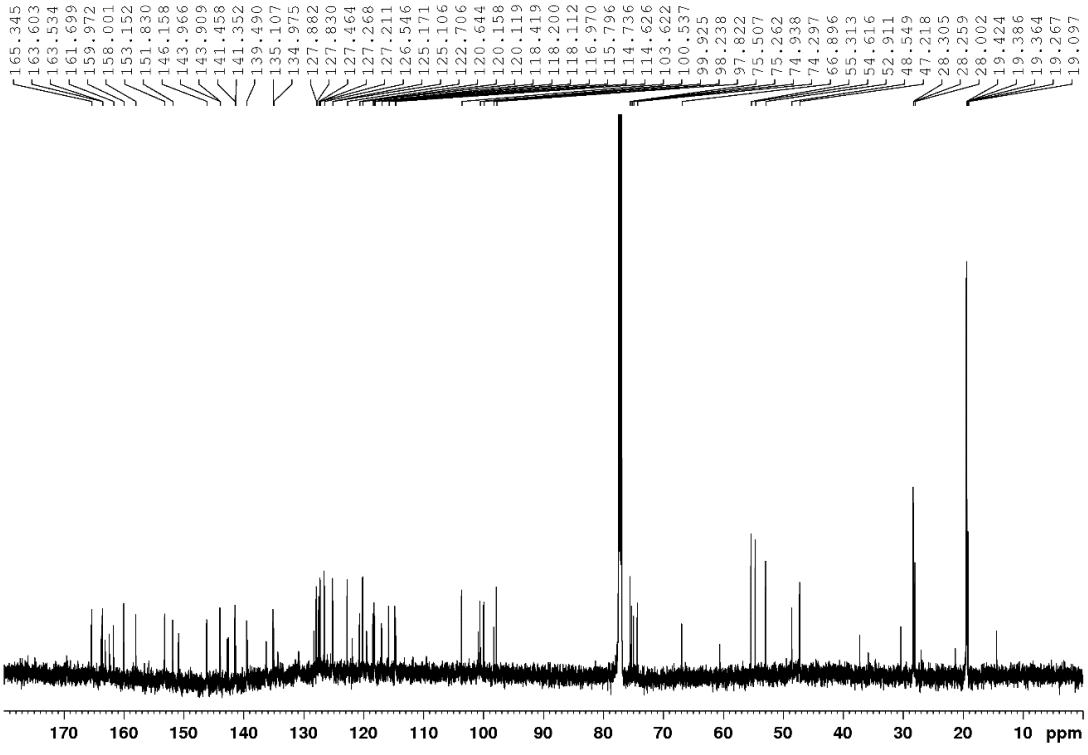


Compound **42**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

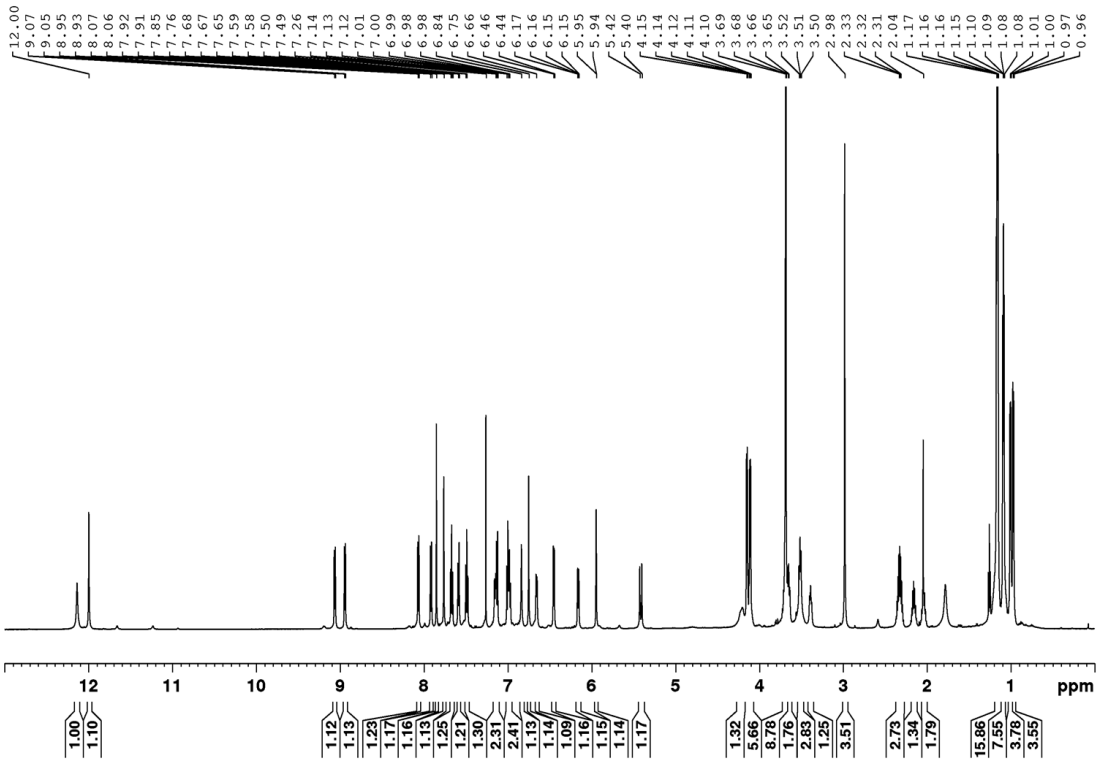


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

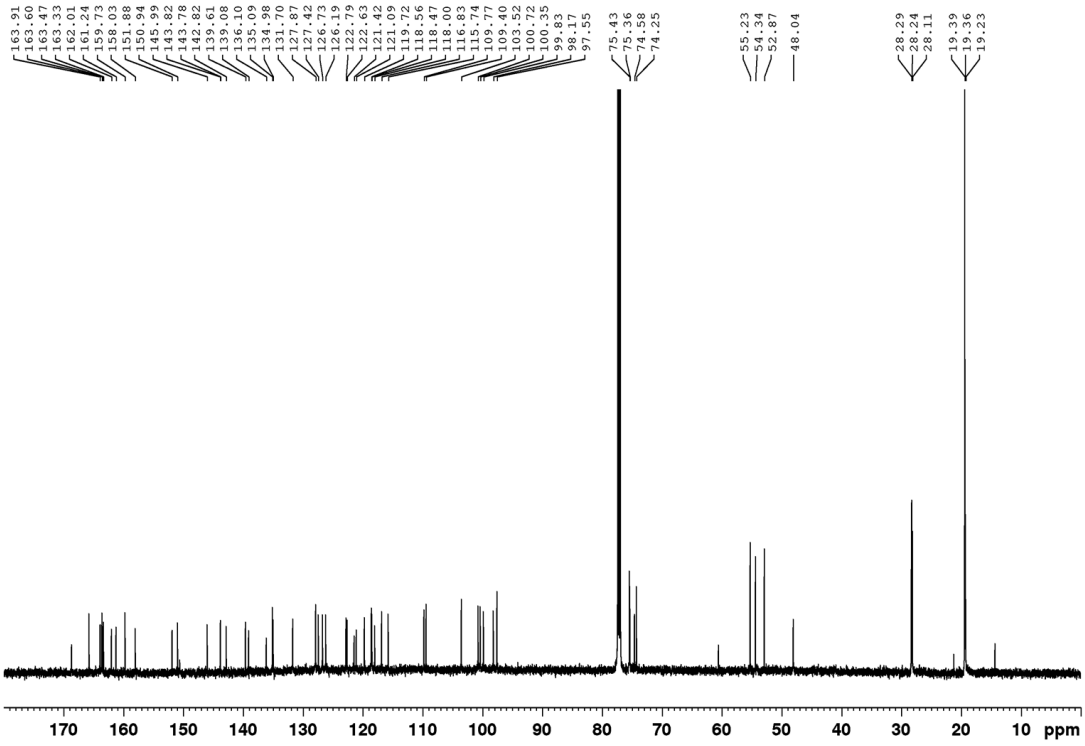


Compound **43**

^{1}H NMR (600 MHz, $CDCl_3$, 25℃)

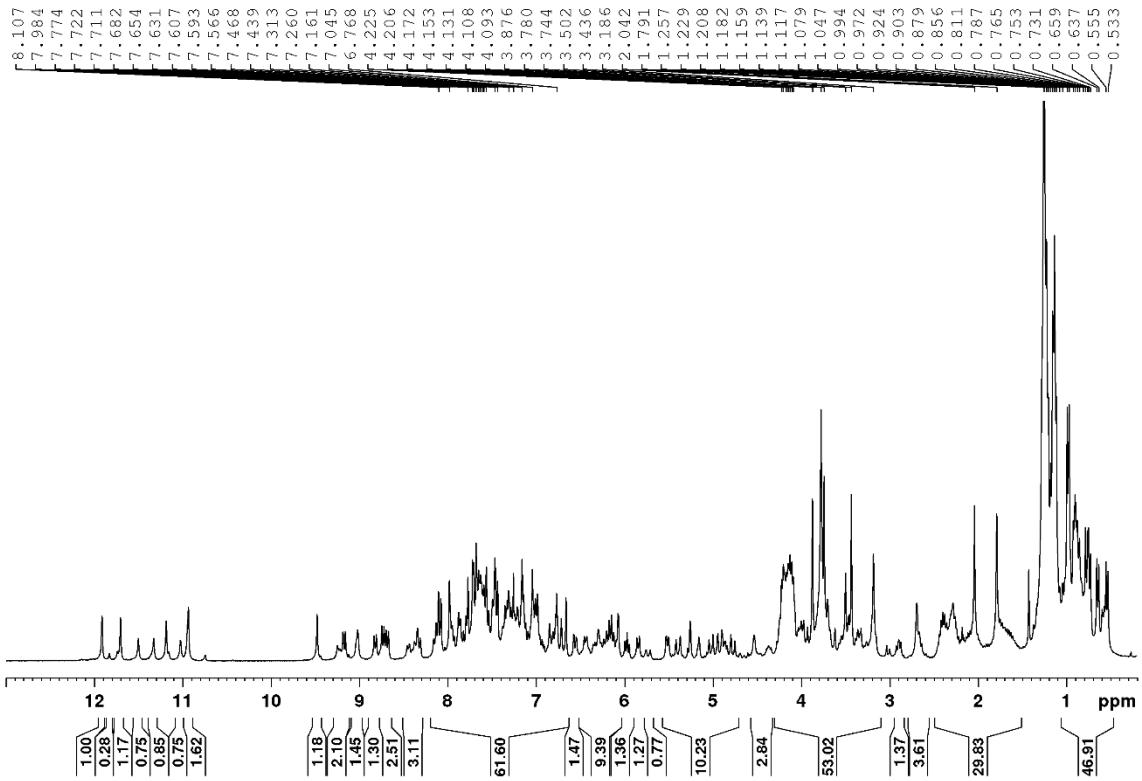


^{13}C NMR (150 MHz, $CDCl_3$, 25℃)

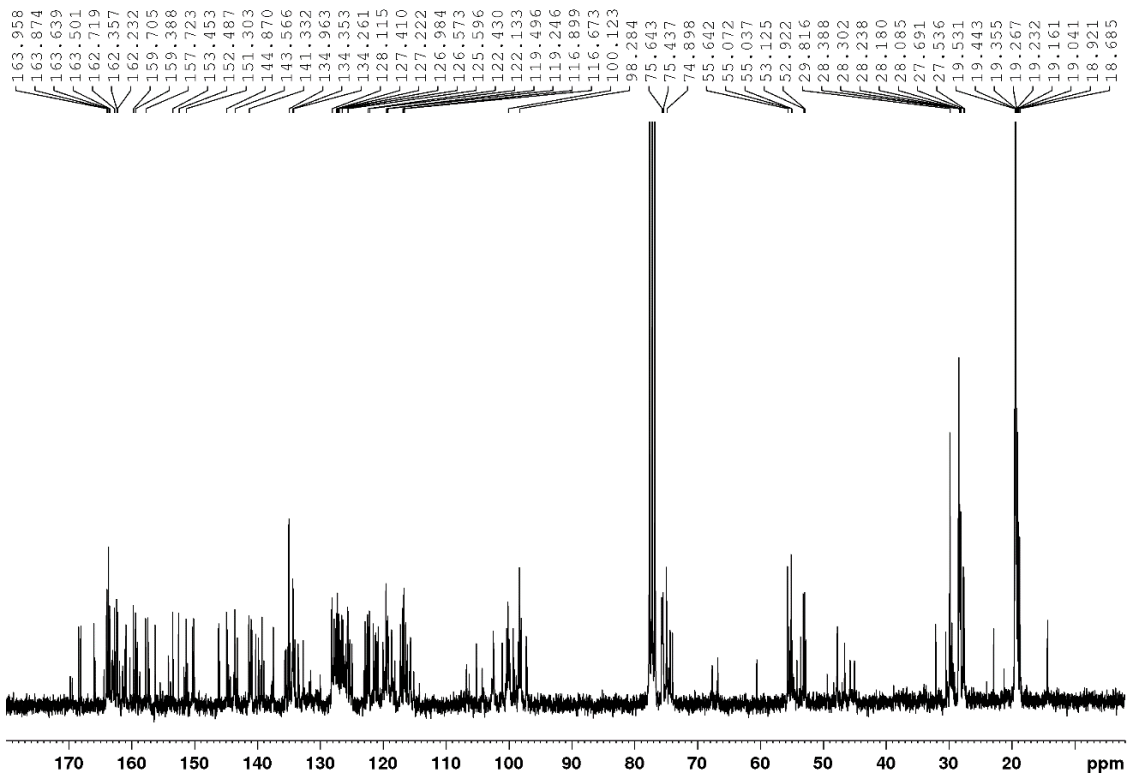


Compound **44**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

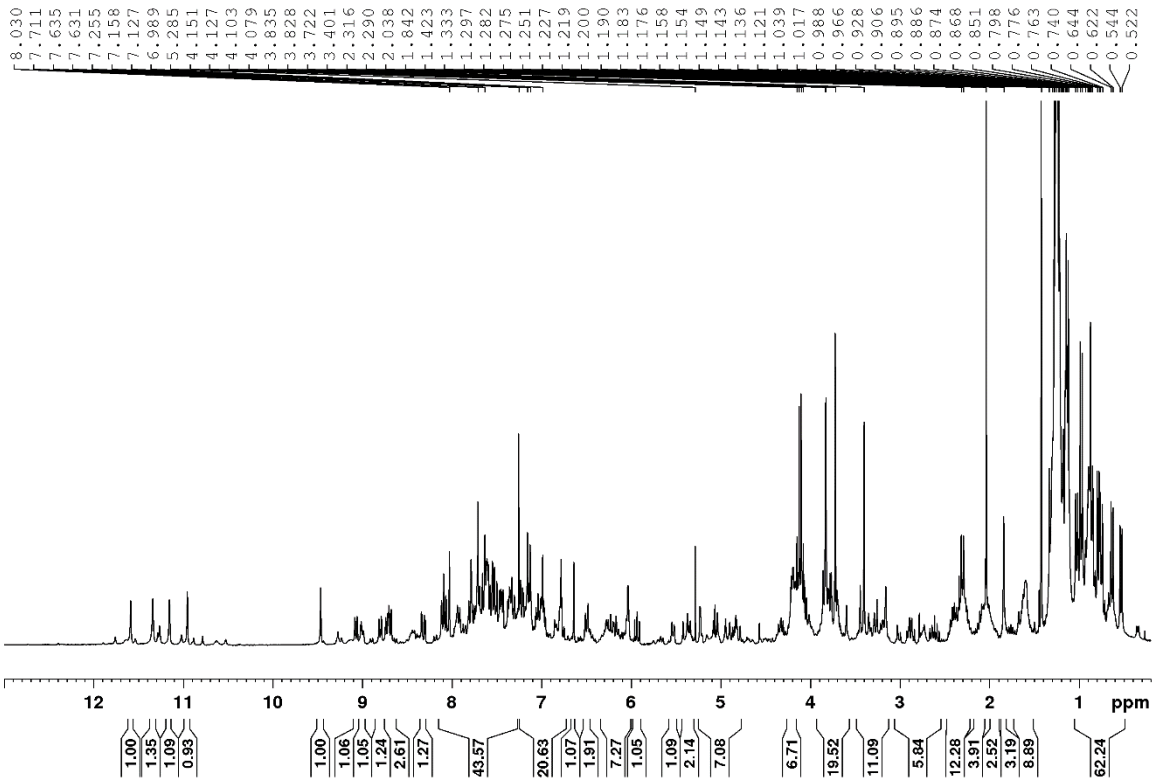


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

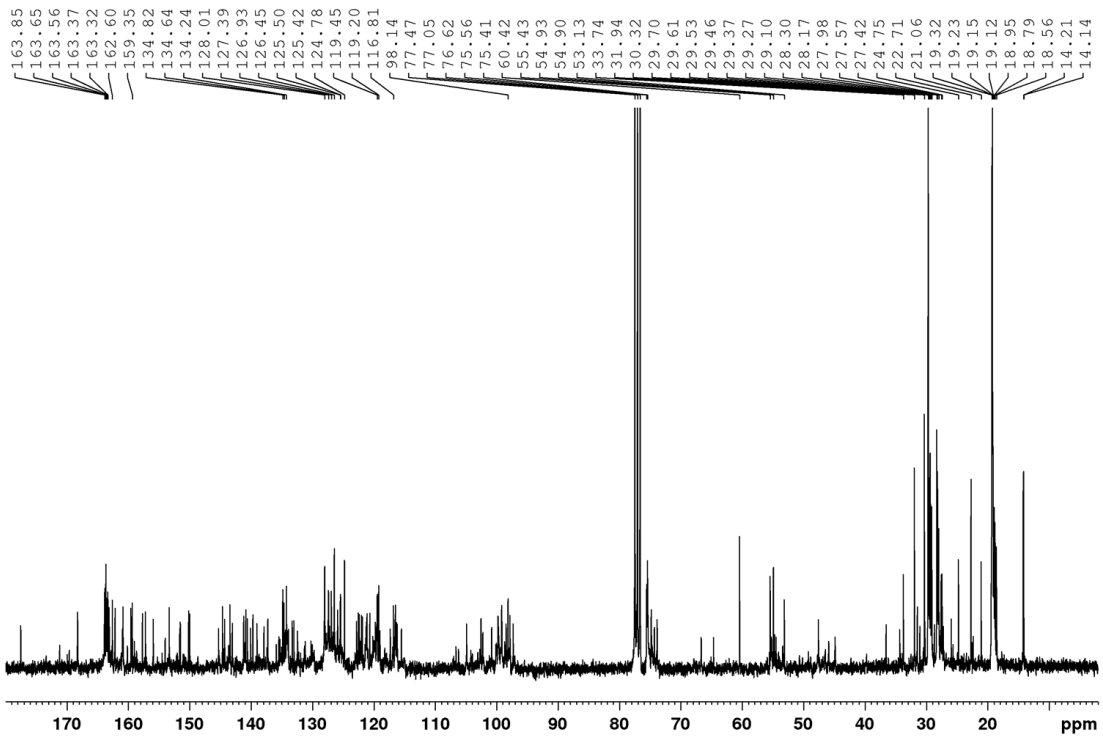


Compound **45**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

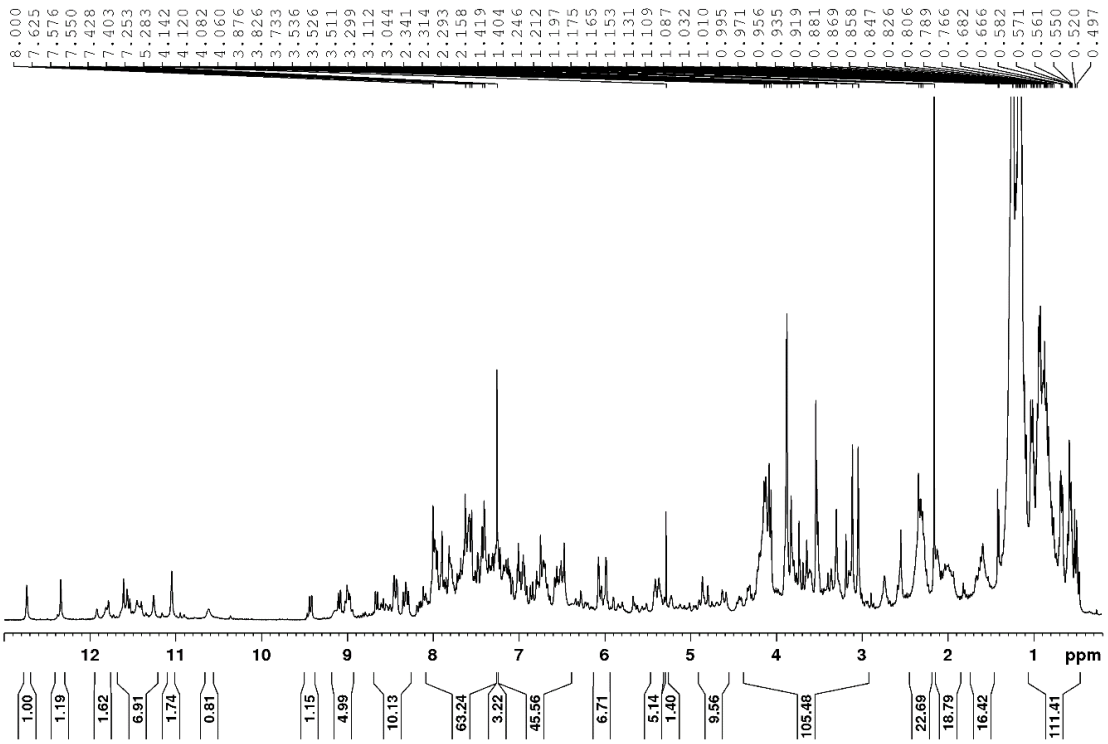


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

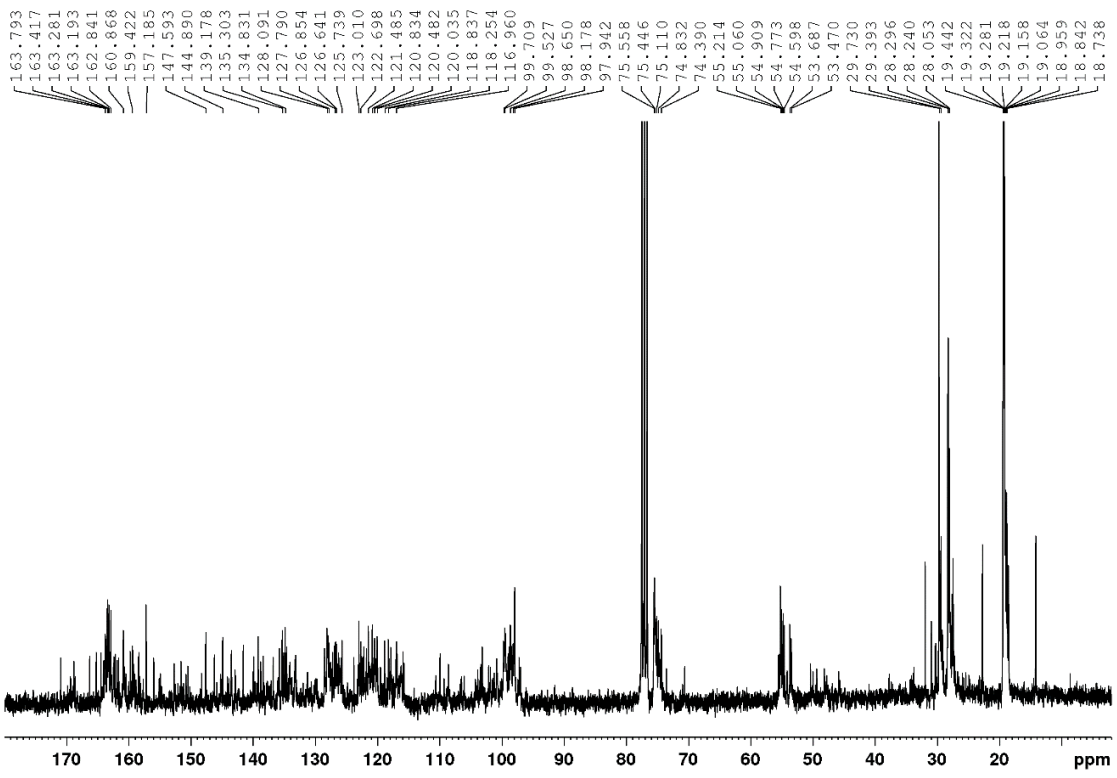


Compound **46**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

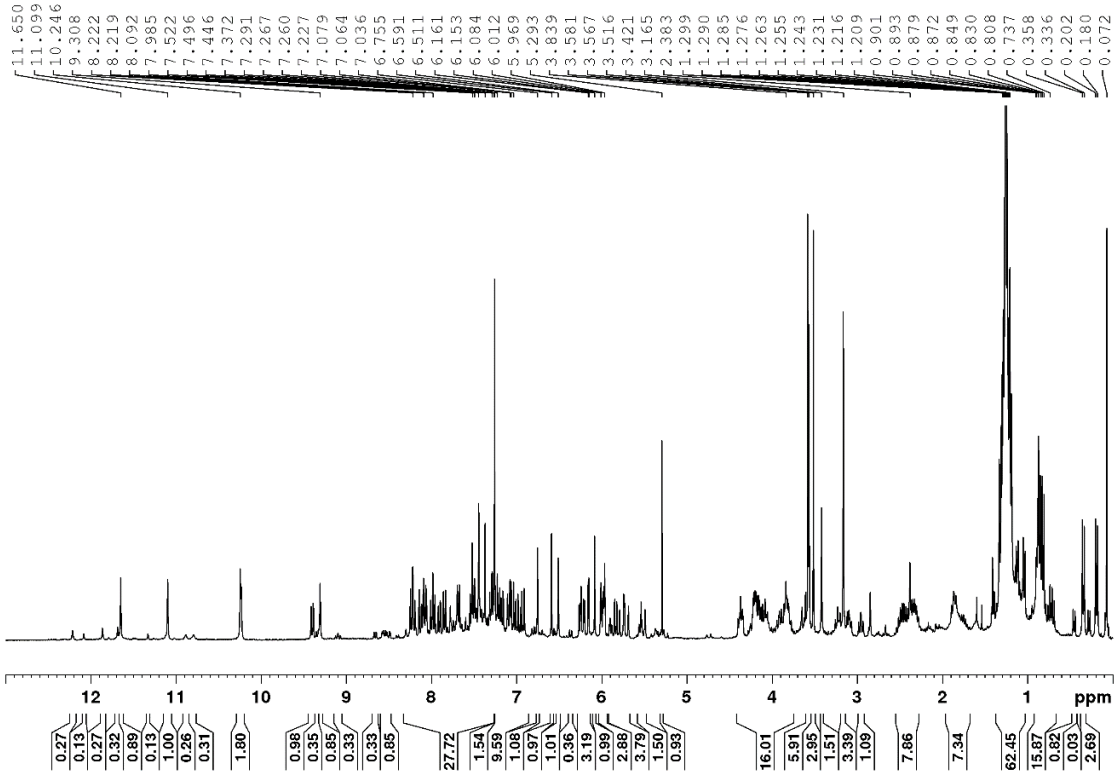


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

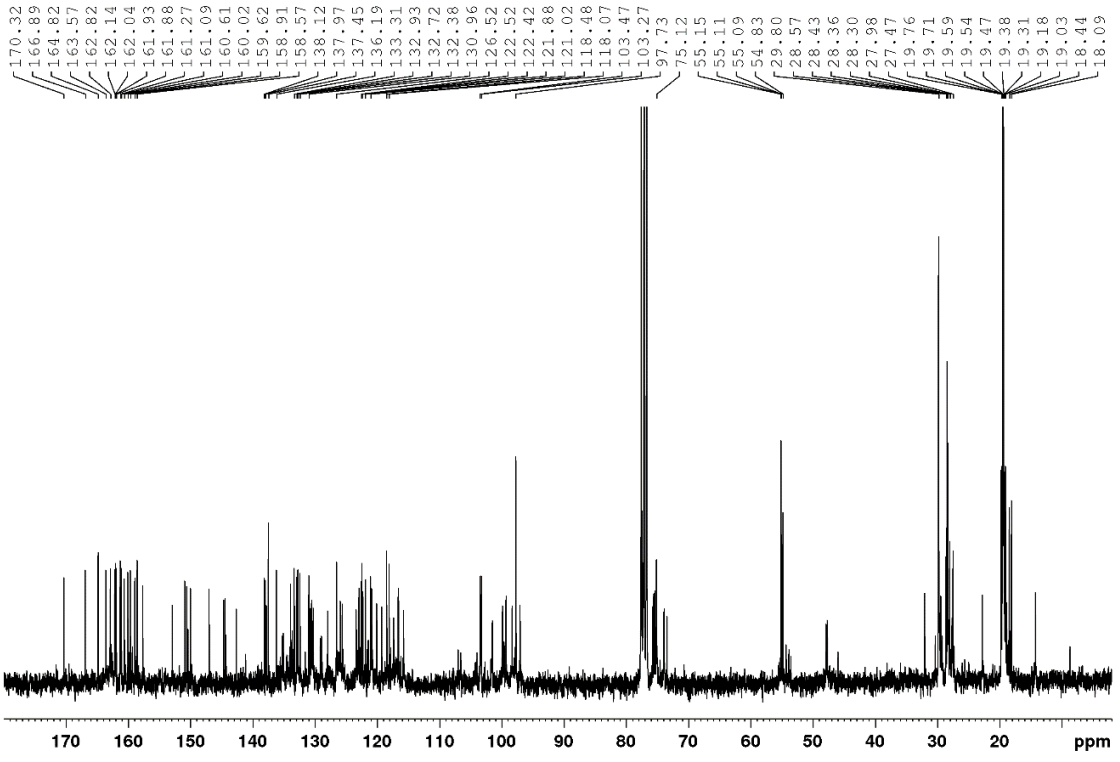


Compound **47**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)

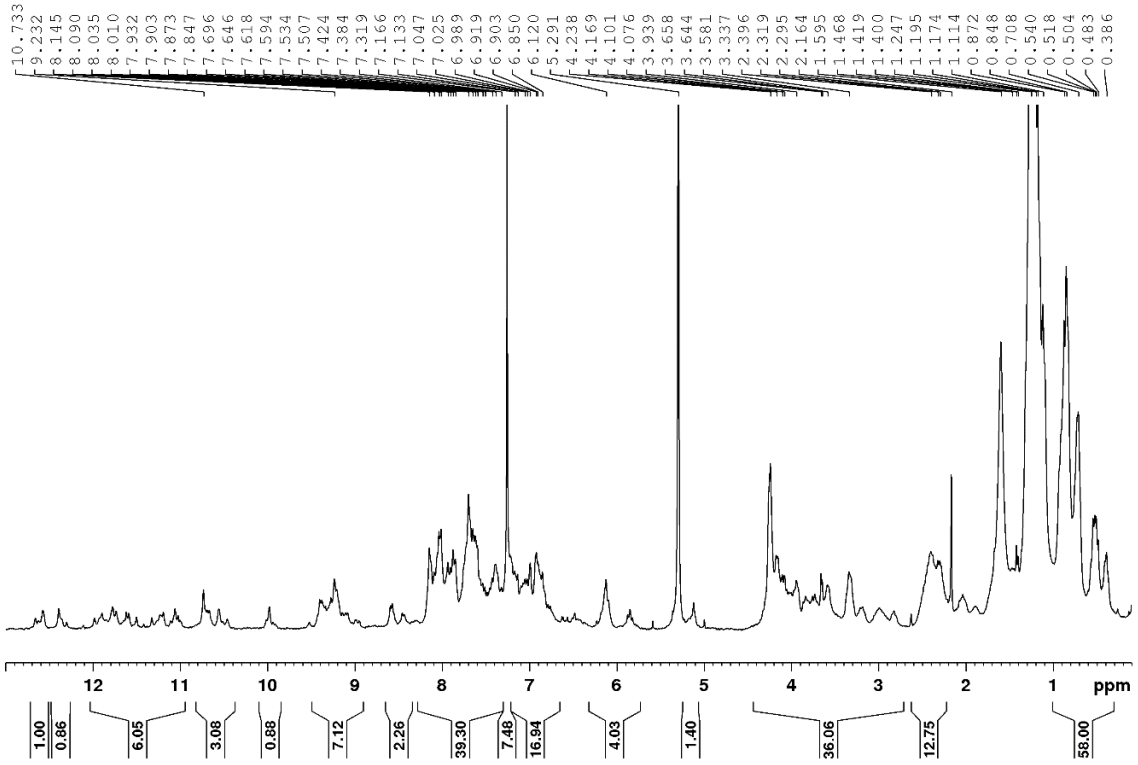


^{13}C NMR (75 MHz, $CDCl_3$, 25℃)

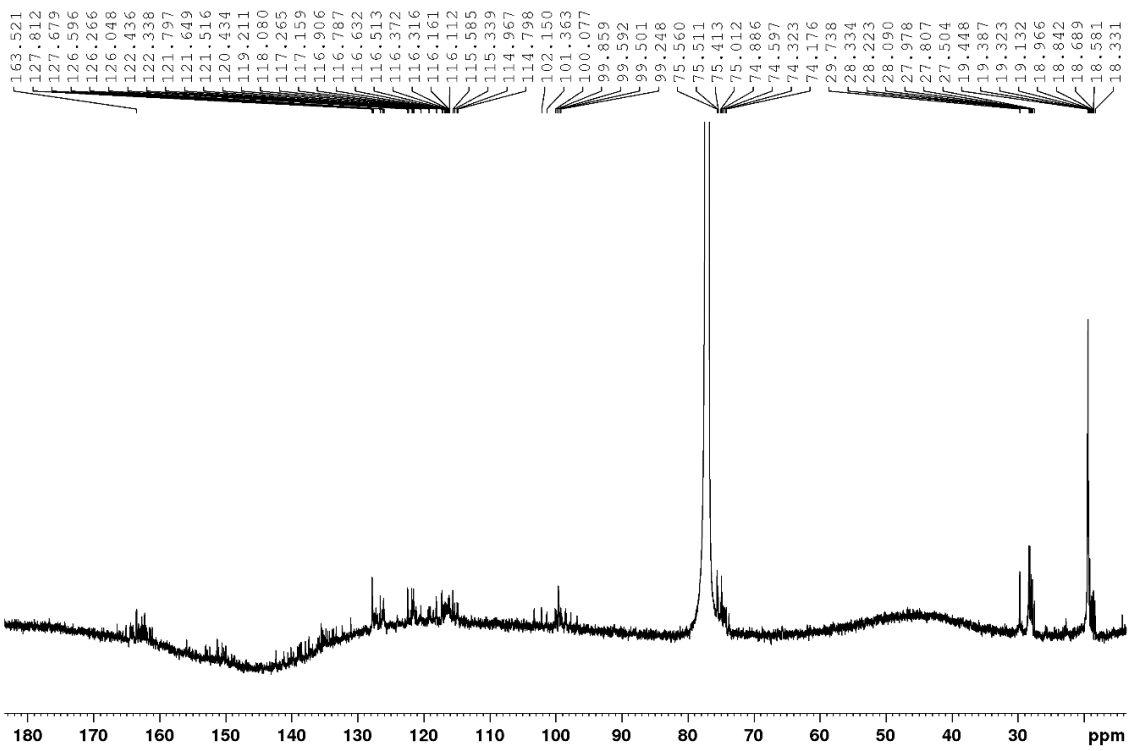


Compound **5F**

^{1}H NMR (300 MHz, $CDCl_3$, 25℃)



^{13}C NMR (75 MHz, $CDCl_3$, 25℃)



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