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Supporting Information

First *in situ* vesicular self-assembly of 'binols' generated by two-component aerobic oxidation reaction

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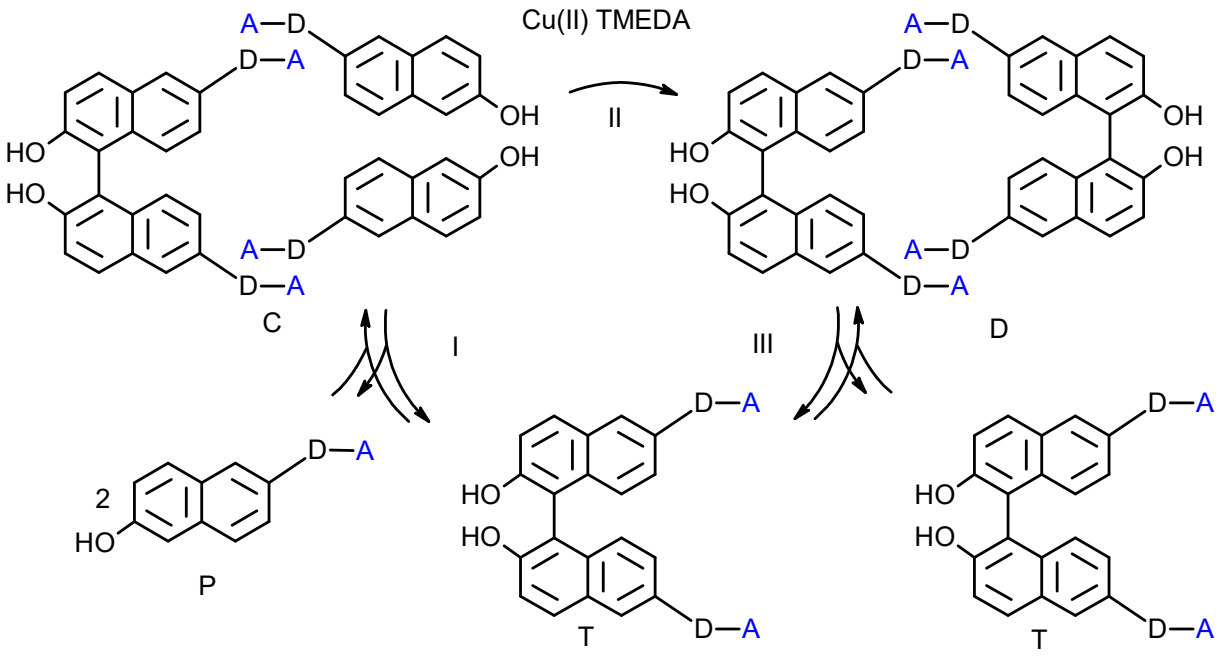


Scheme S1: Model schematic representation of self-replication of binols where the D::::A represents donor-acceptor noncovalent interactions

Study of Gelation Property:

The compounds (**2b-d**) attached with long alkyl chain to binol system are excellent gelator for the mixed solvents basically in alkane solvents; here very little amount of chloroform is used only to solubilize i.e. to make a super saturated solution during gel formation. A survey of CGC values show that compound **2d** is the best gelator among all.

Gelation Study in Cyclohexane/Chloroform (6:1 V/V):

All the gels were thermo-reversible in nature. Hence the gel to sol transition temperature T_{gel} were plotted against the gelator concentration (mM). With increase in the concentration of the gelator the T_{gel} increased indicating stronger intermolecular interactions and increased branching at higher concentrations.

Entry	Conc.(%w/v)	*Tgel* (^{o}C) of compound **2b**	*Tgel* (^{o}C) of compound **2c**	*Tgel* (^{o}C) of compound **2d**
1	0.833	54	55	58
2	1.00	58	60	65
3	1.25	63	65	70
4	1.66	70	73	74
5	2.5	77	80	84

Thermodynamic parameters Calculation:

Various thermodynamic parameters (ΔH^{o}, ΔS^{o} and ΔG^{o}) during gel to sol phase transitions were calculated from the variation of T_{gel} with concentrations. The positive free energy changes (ΔG^{o} values) obtained in both of the cases studied during gel to sol transition indicated the stability of the gels. The free energy changes during gel to sol transition of compound **2b-d** in cyclohexane/$CHCl_3$ (6:1 v/v) were calculated as

Calculation:

The thermo-reversibility of a gel can be expressed as:

Gel→liquid

The equilibrium constant can be expressed as ;

K_{eqm} = [Gelator]/ [Gel]

Assuming unit activity of the gel, the equilibrium constant can be expressed as :

K = [Gelator]

The Gibbs free energy change (ΔG°) during gel melting can be obtained by the following equation

$\Delta G^{\circ} = - RTlnK = \Delta H^{\circ} - T\Delta S^{\circ}$

Hence, lnK = -ΔH° /RT + ΔS° /R

The gel melting temperature (T_{gel}) increases with increasing concentration of the " gelator".

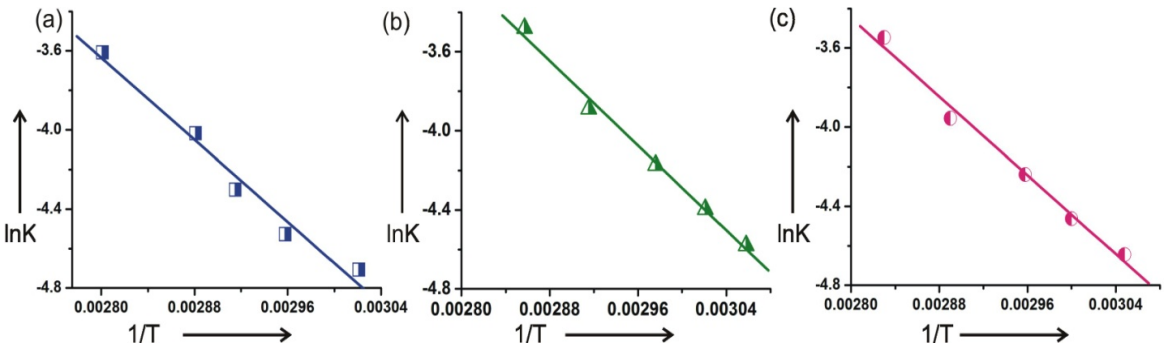


Figure S1. Plot of lnK vs 1/T where T is the gel to sol transition temperature T_{gel} (a) **2b**, (b) **2c**, (c) **2d**

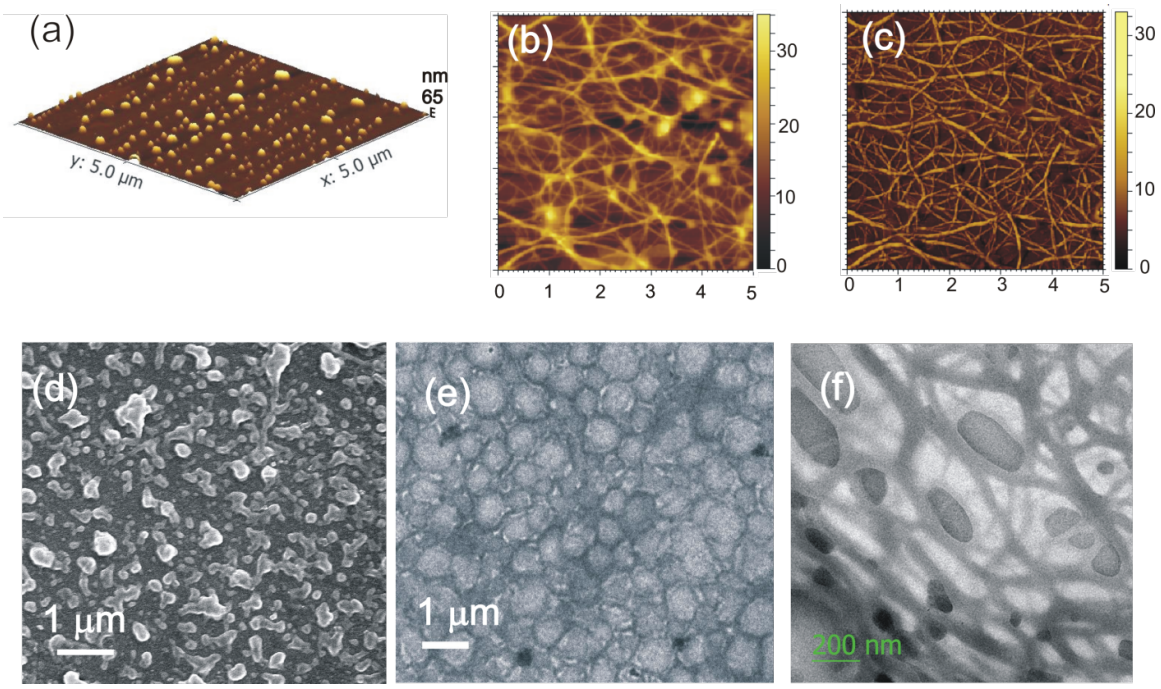


Figure S2. (a) AFM images of 0.12 % (w/v) **2c** in 6:1 cyclohexane-chloroform , (b,c) AFM images of 0.14% (w/v) **2d** in 6:1 heptane-chloroform and octane-chloroform, (d) SEM image of (0.11% w/v) 2d in (6:1 v/v) chloroform/dodecane and **(e,f)** TEM images of 0.10 % (w/v) **2d** in 6:1 cyclohexane-chloroform .Samples were collected after 4h on a glass plate, dried slowly and then under reduced pressure and sputter coated with Au for 60 s and analyzed.

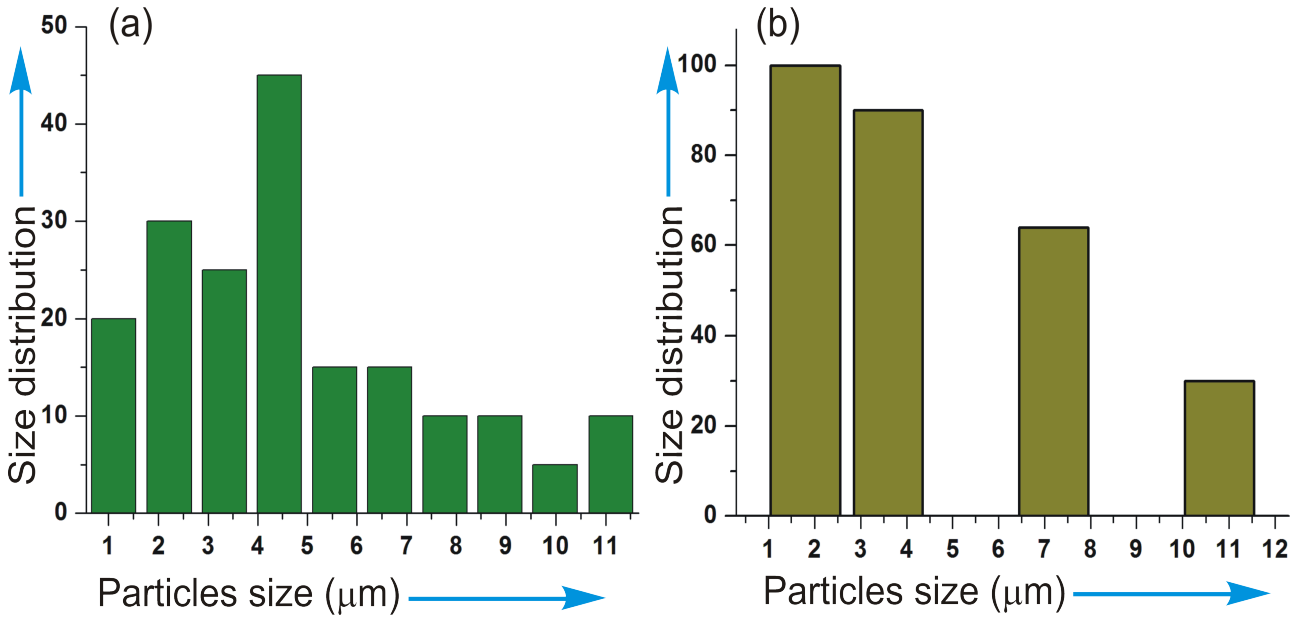


Figure S3. Histogram from OPM (a) 3.2 % of **2c** in 5:1 (v/v) DMSO-Water; (b) 3.25 % of **2d** in 5:1 (v/v) DMSO-Water

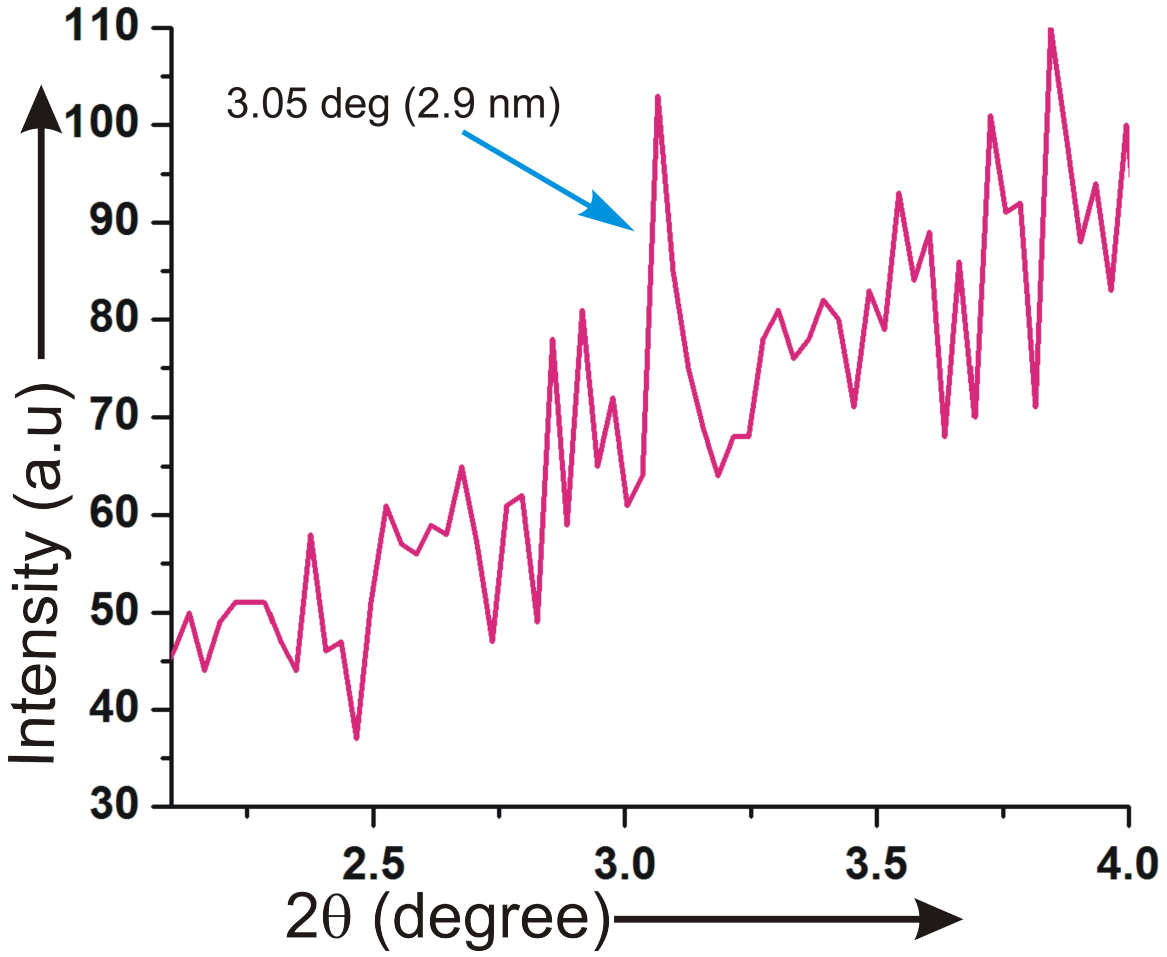


Figure S4. X-ray diffraction studies of the self-assemblies of **2c** (0.11% w/v) in DMSO-water (5:1 v/v).

DLS studies: Dynamic light scattering (DLS) studies were carried out in a Zetasizer Nanoseries instrument (Model Nano ZS90). In all the cases studied, polydisperse self-assemblies of varied diameters were observed. For **2c** (0.10% w/v) and **2d** (0.10% w/v) in cyclohexane-chloroform (6:1 v/v), average size of 310.8 nm and 151.5 nm respectively were observed. For the self-assemblies of **2d** (0.10% w/v) in octane-chloroform (6:1), the average size was 75.3 nm.

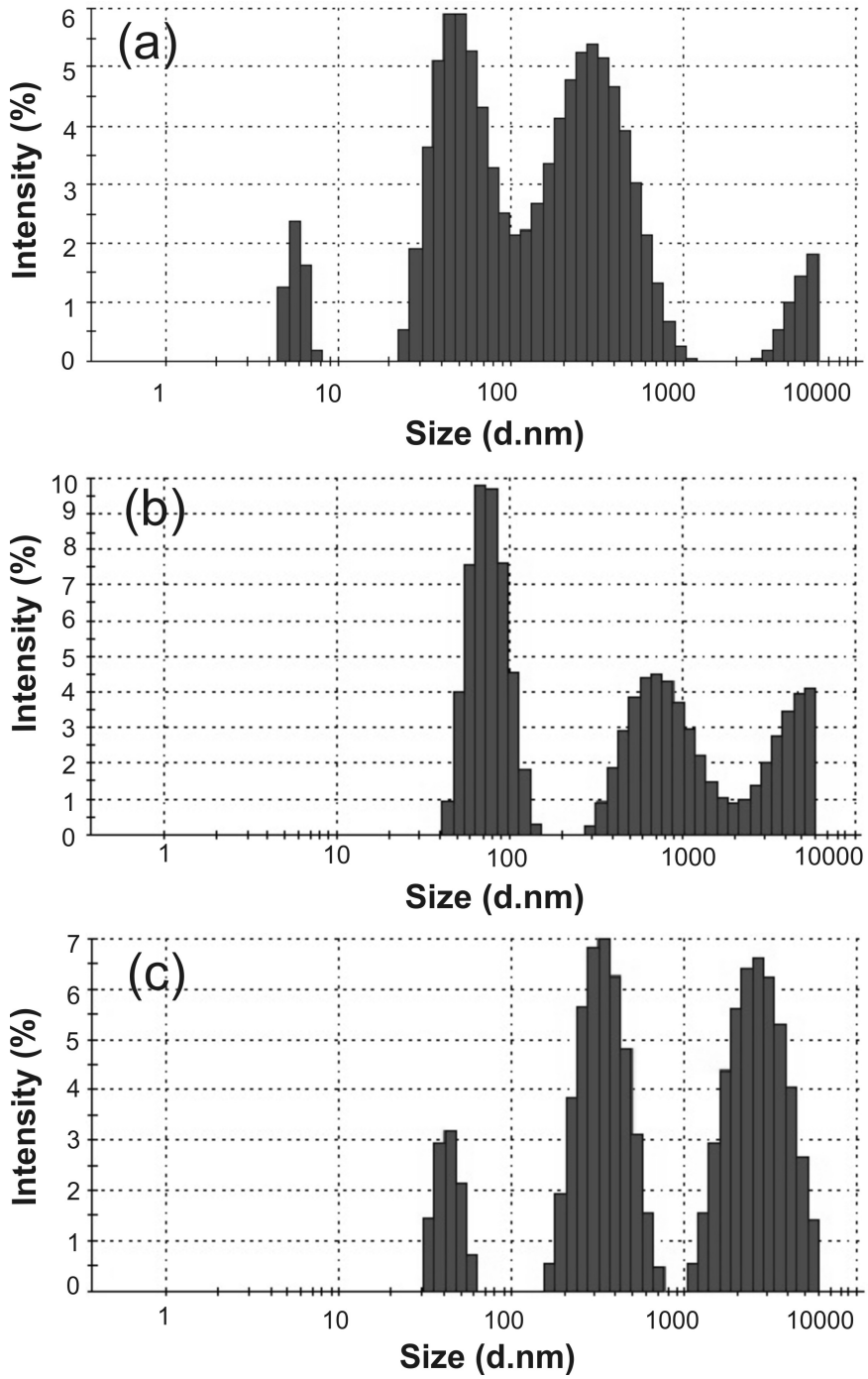


Figure S5. Dynamic light scattering (DLS) studies of **(a) 2d** in 6:1 (v/v) n-octane-chloroform (0.10% w/v), (b) **2d** in 6:1 (v/v) cyclohexane-chloroform (0.10% w/v), (c) **2c** in 6:1 (v/v) cyclohexane-chloroform (0.10 % w/v)

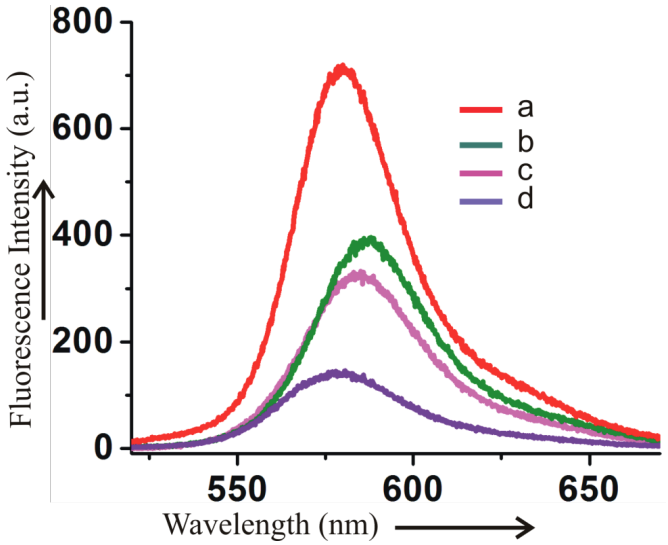


Figure S6. Fluorescence emission spectra (λ_{max} 510 nm) of release of encapsulated Rho-B by sonication at different duration of sonication time, a = 45 min, b = 30 min, c = 15 min, (d) encapsulated Rho-B inside the vesicular self-assemblies of **2d** after 24 h.

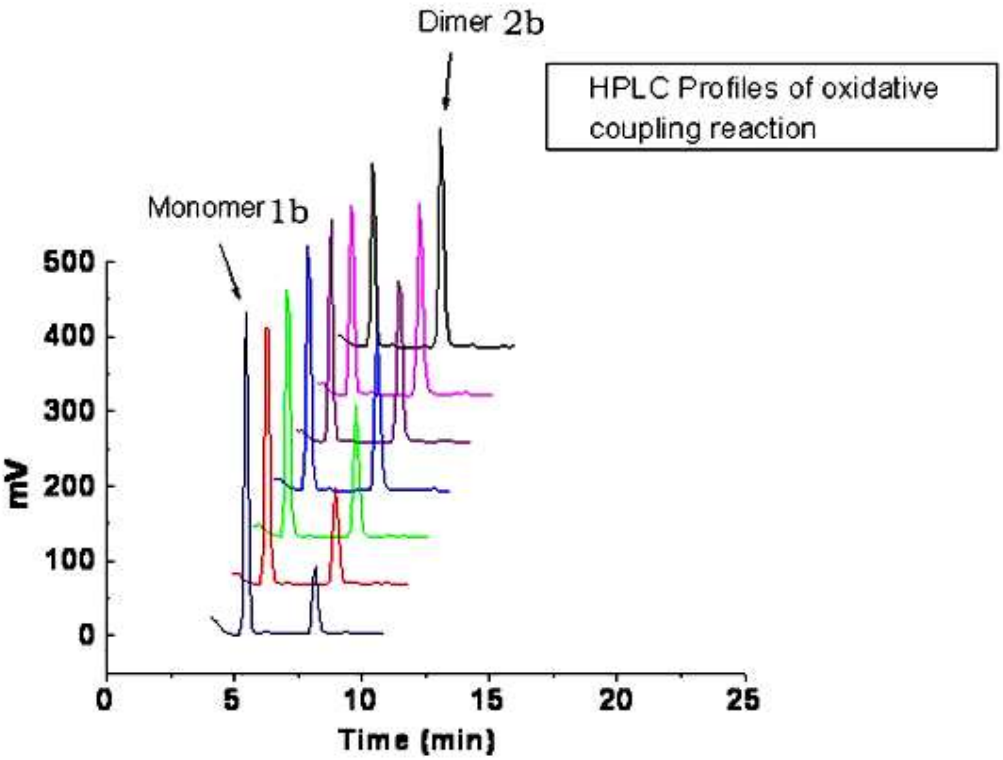
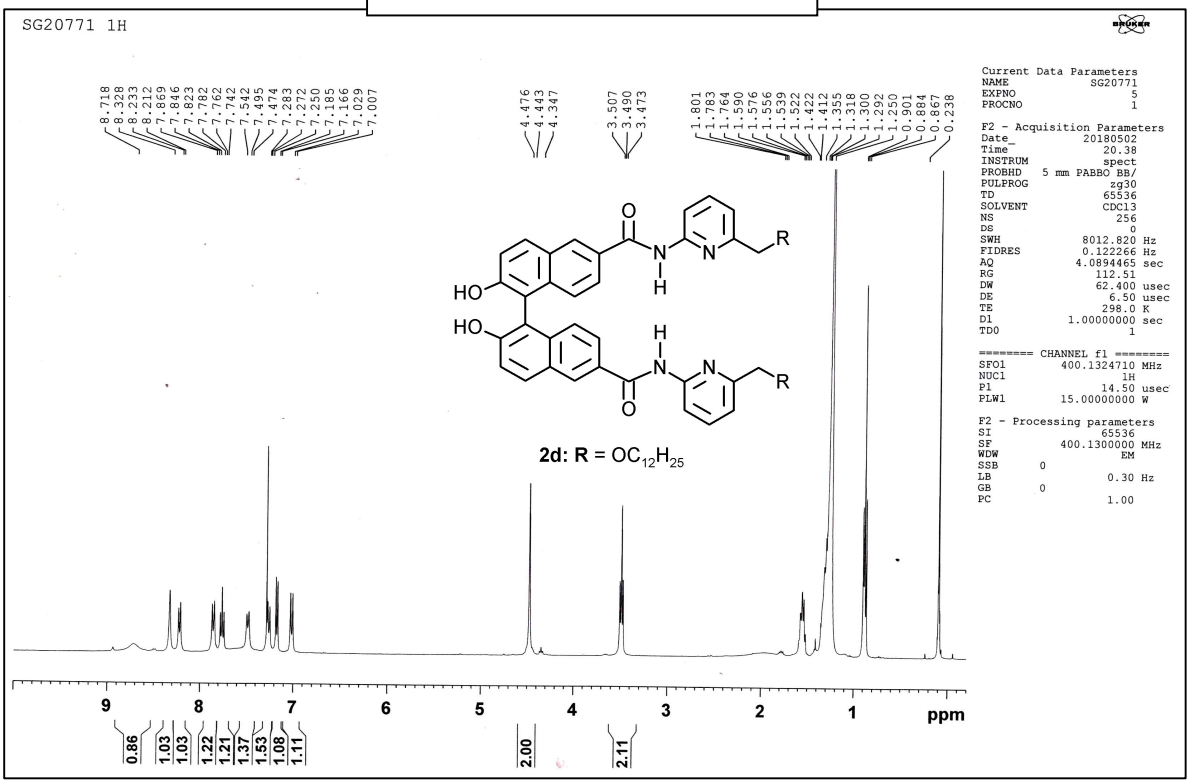
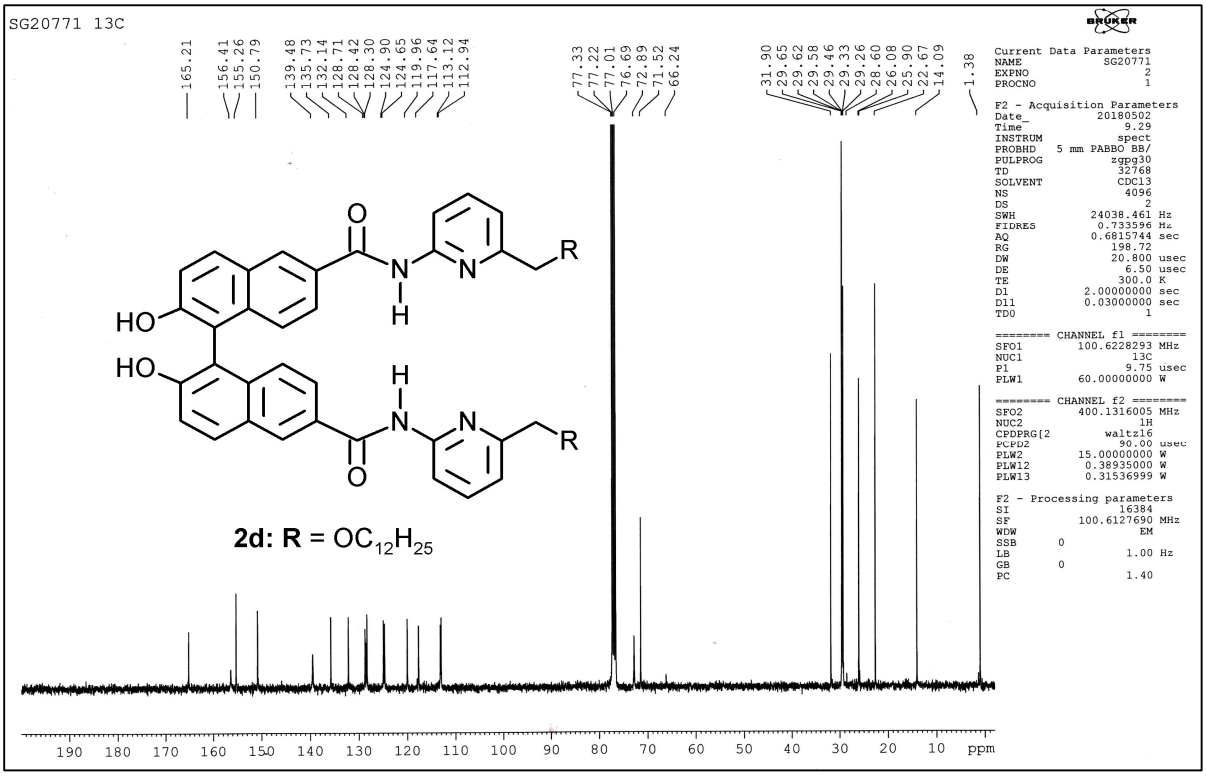


Figure 7: HPLC profiles for the oxidative coupling of **1b** to **2b**. Aliquots were collected at 10 min time intervals. Increase in the concentration of the dimer **2b** was observed with concomitant decrease of the monomer **1b** at the initial stage of the reaction. The reaction mixture became heterogeneous after about an hour.

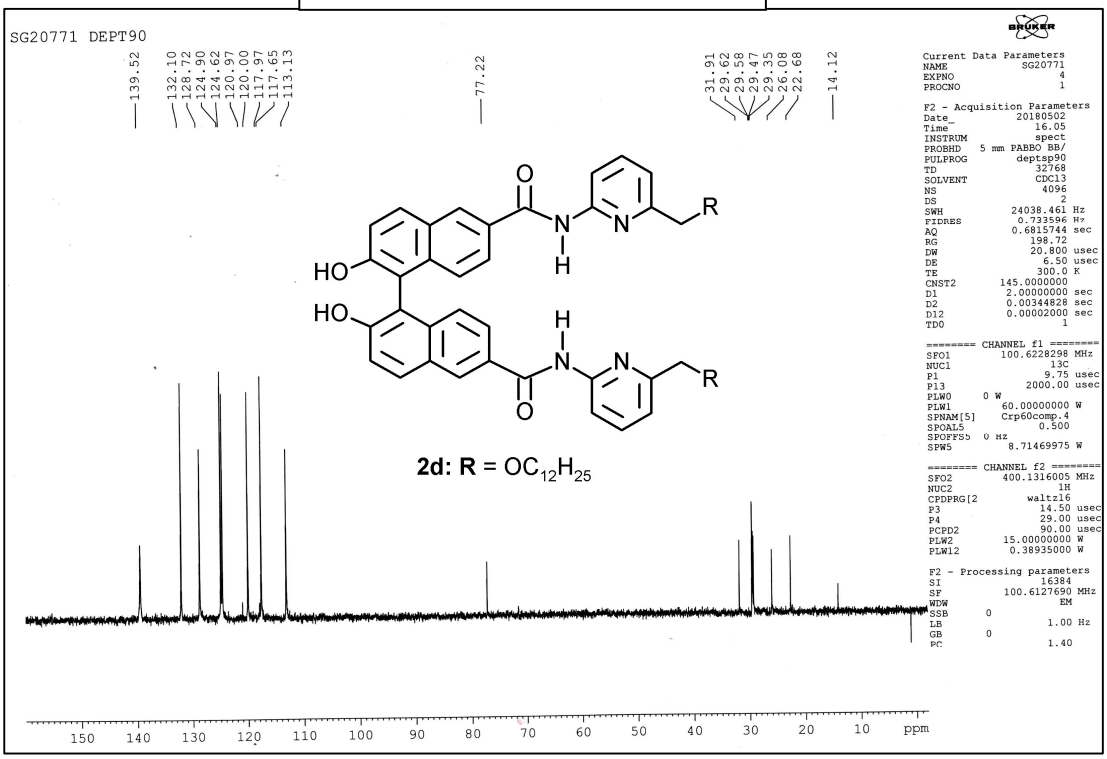
^{1}H-NMR, $CDCl_3$ (400 MHz)



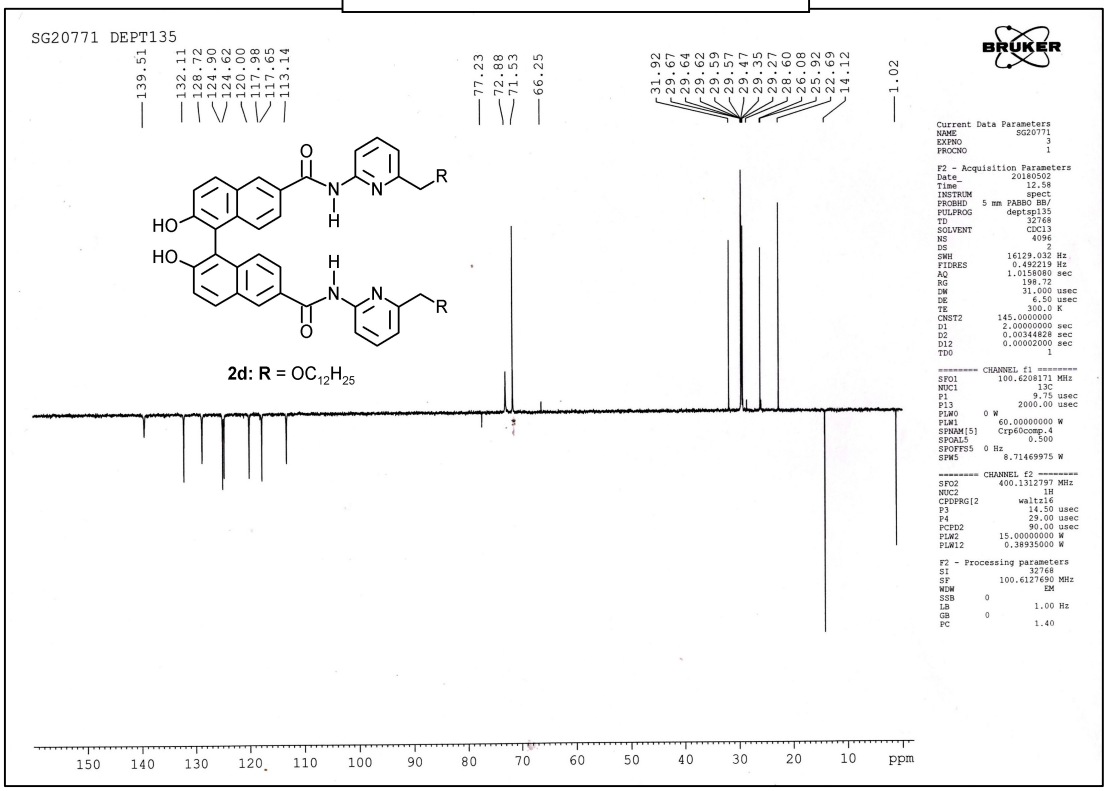
^{13}C-NMR, $CDCl_3$ (100 MHz)



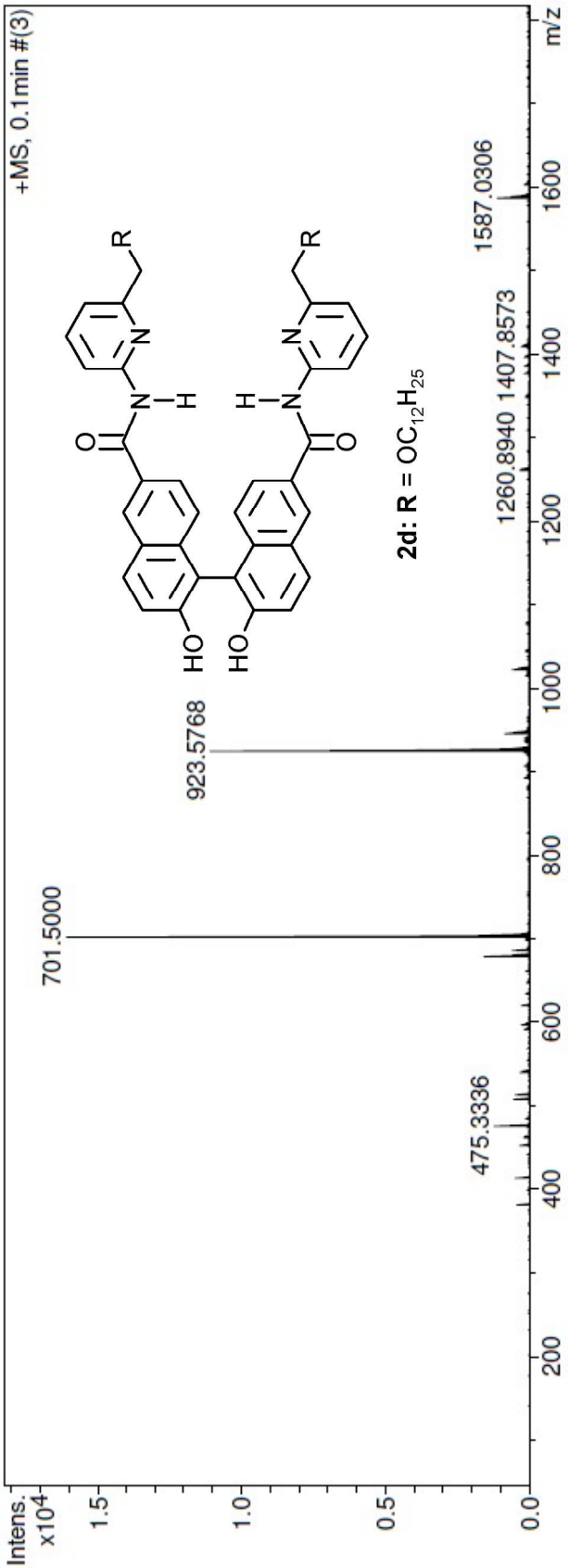
DEPT-90, $CDCl_3$ (100 MHz)



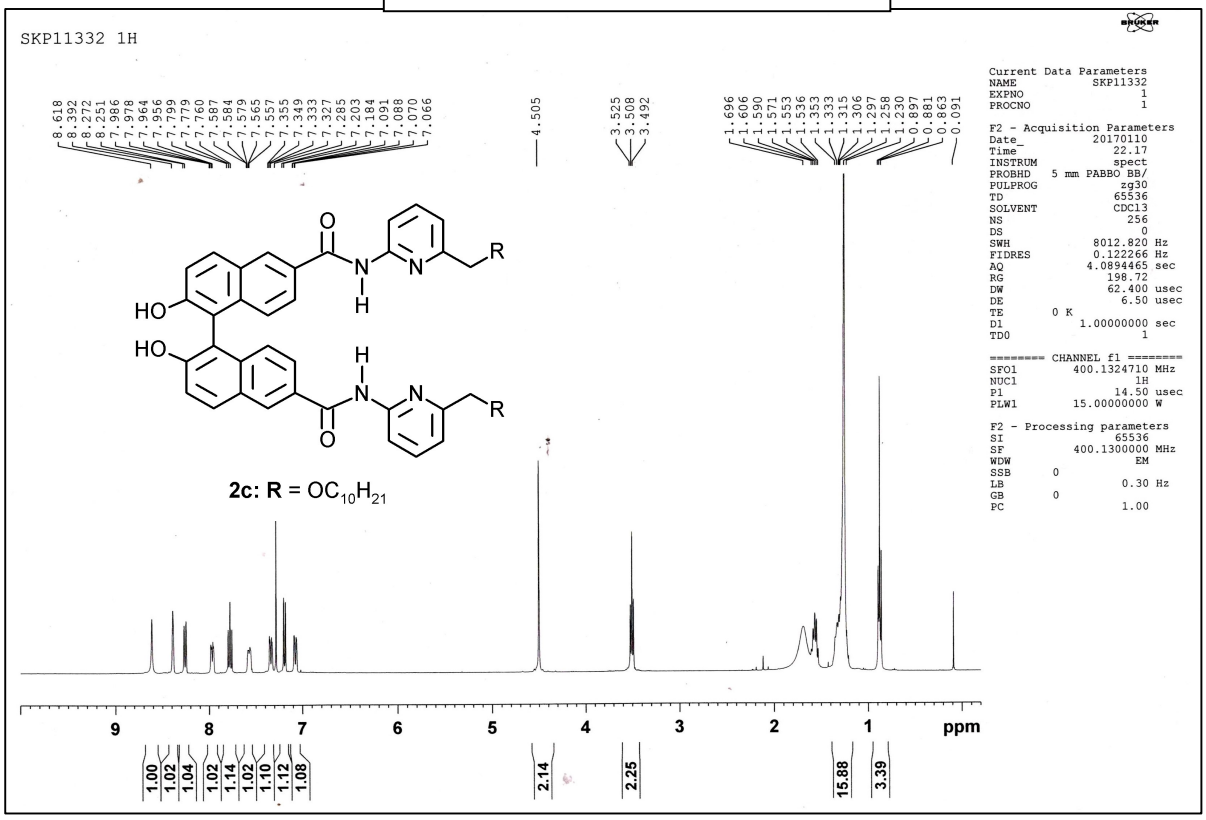
DEPT-135, $CDCl_3$ (100 MHz)



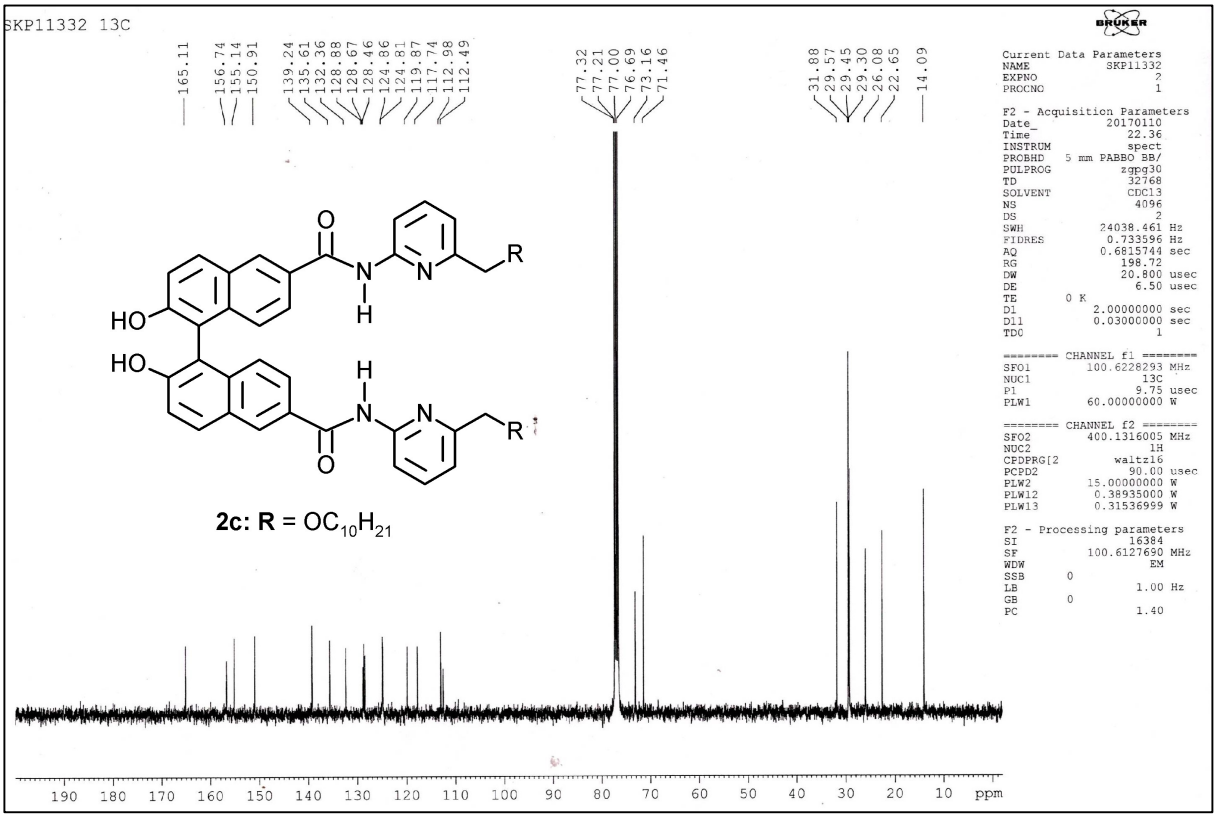
HRMS


+MS, 0.1min #(3)
Intens.
x10^4
1.5
1.0
0.5
0.0
200
400
600
800
1000
1200
1400
1600
m/z
701.5000
475.3336
923.5768
1260.8940
1407.8573
1587.0306
HO
HO
O
O
N
H
R
2d: R = OC12H25

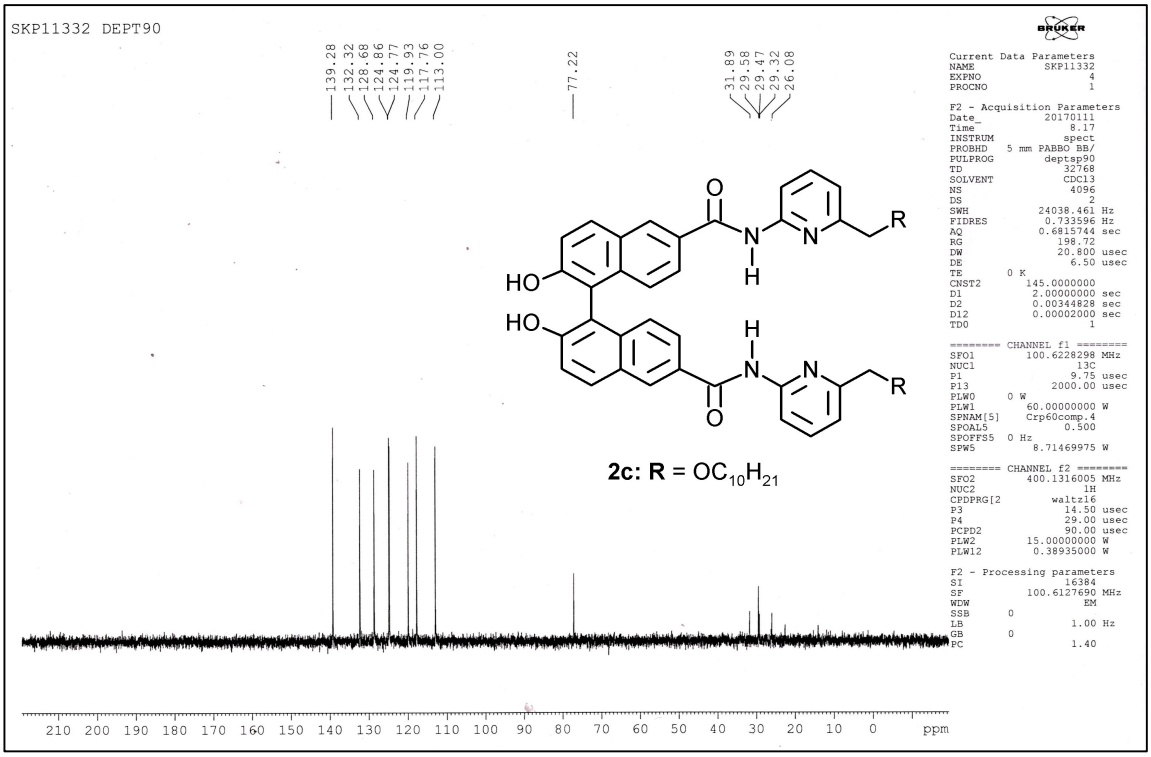
^{1}H-NMR, $CDCl_3$ (400 MHz)



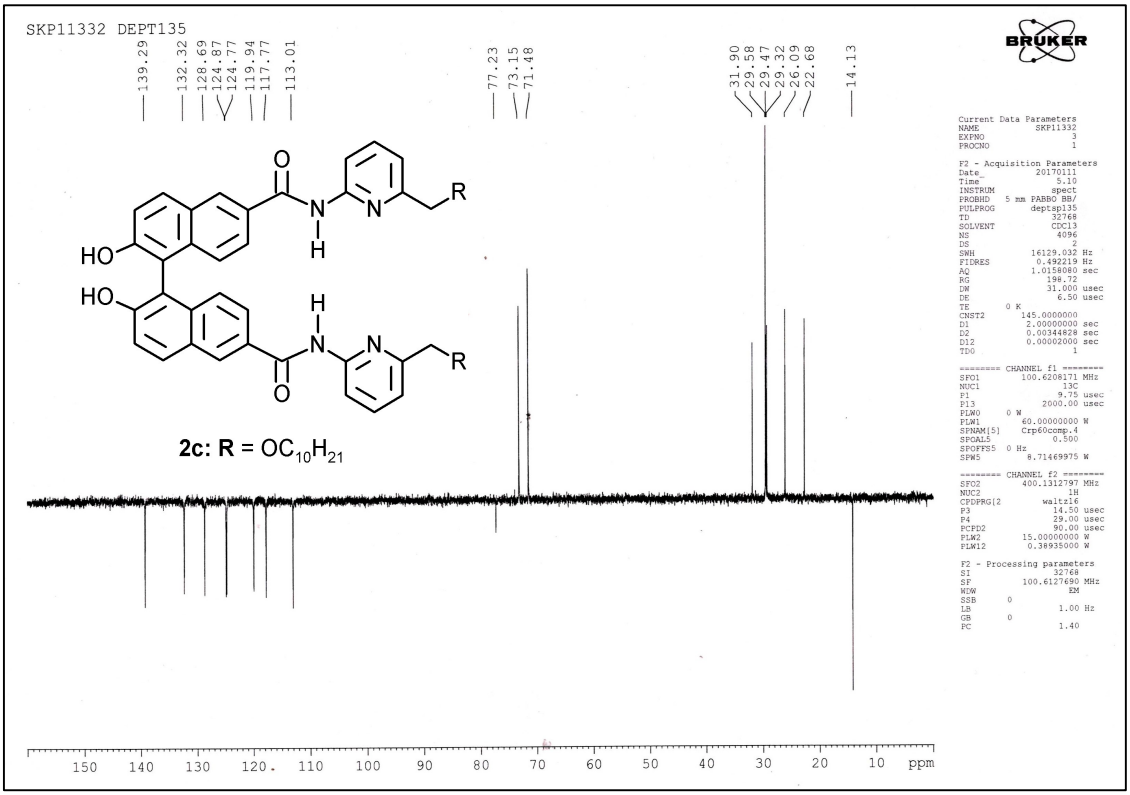
^{13}C-NMR, $CDCl_3$ (100 MHz)

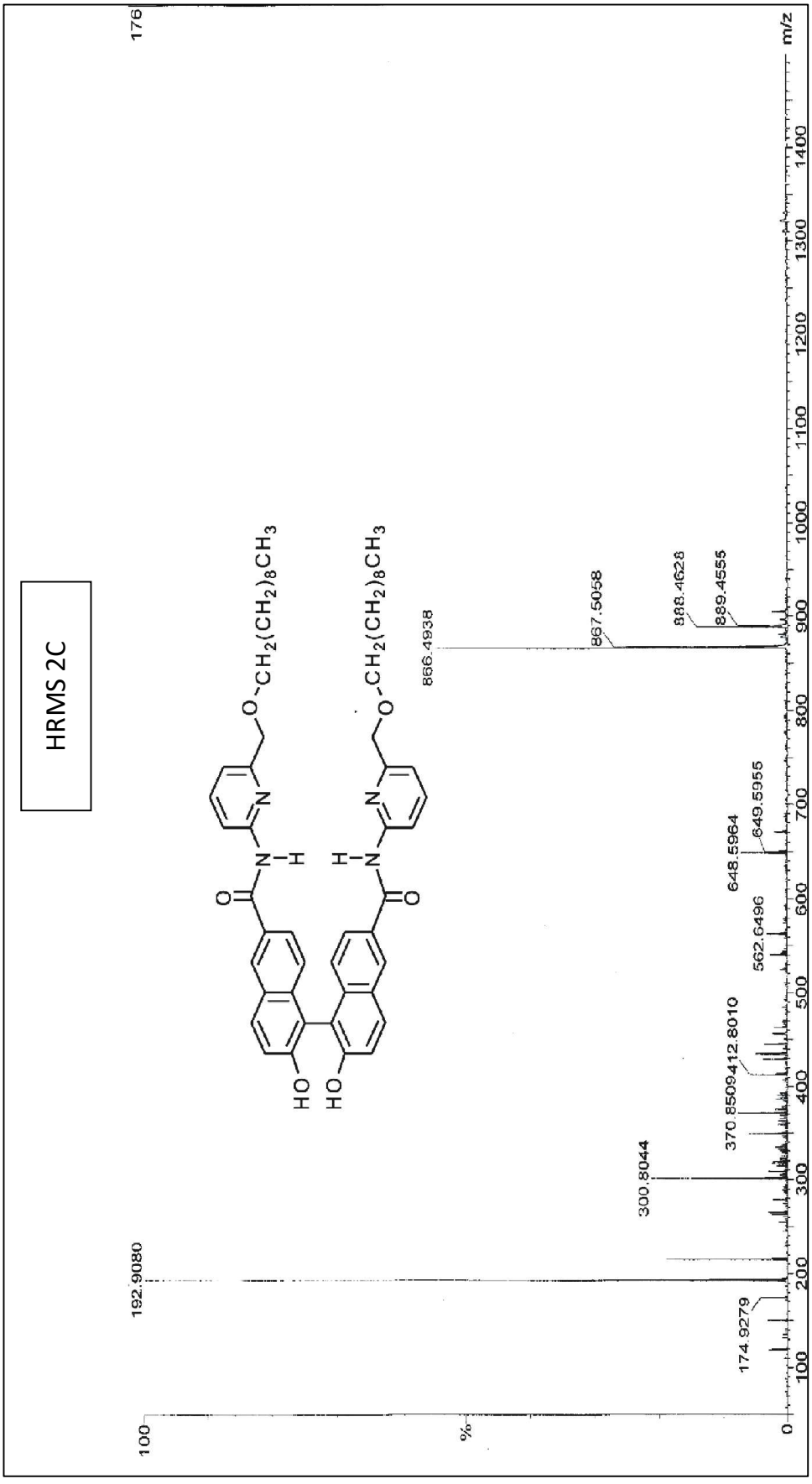


DEPT-90, $CDCl_3$ (100 MHz)

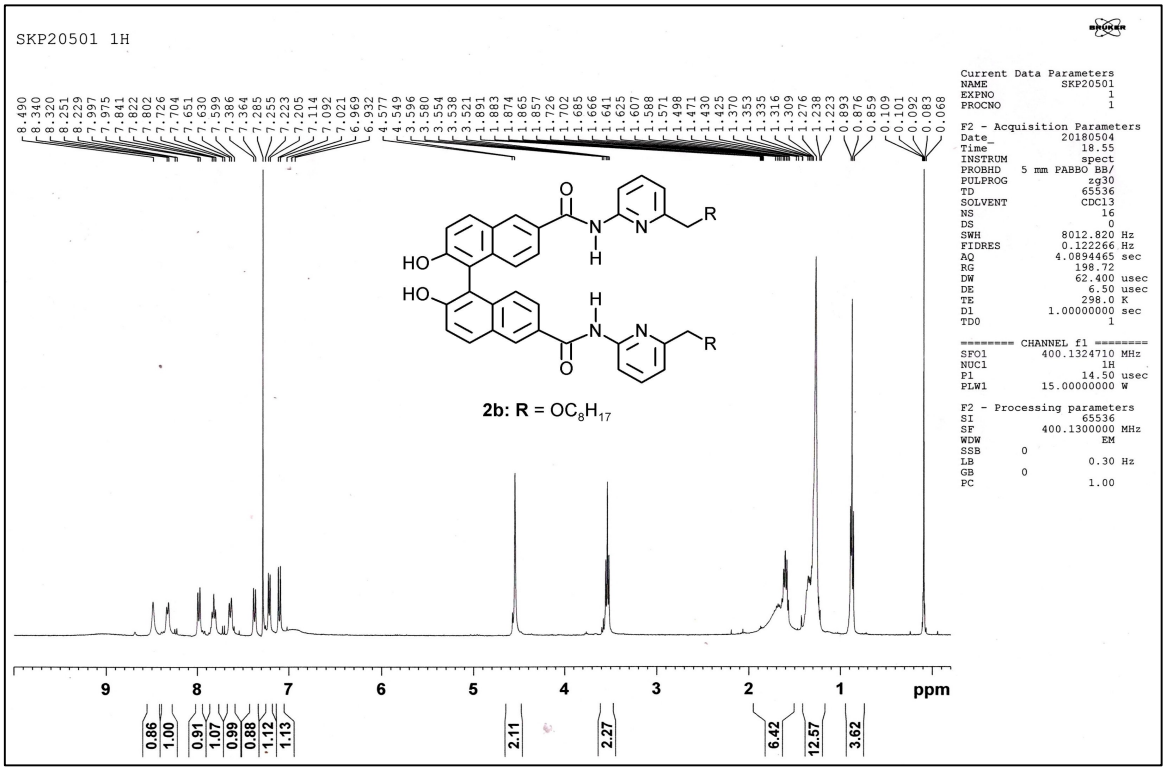


DEPT-135, $CDCl_3$ (100 MHz)

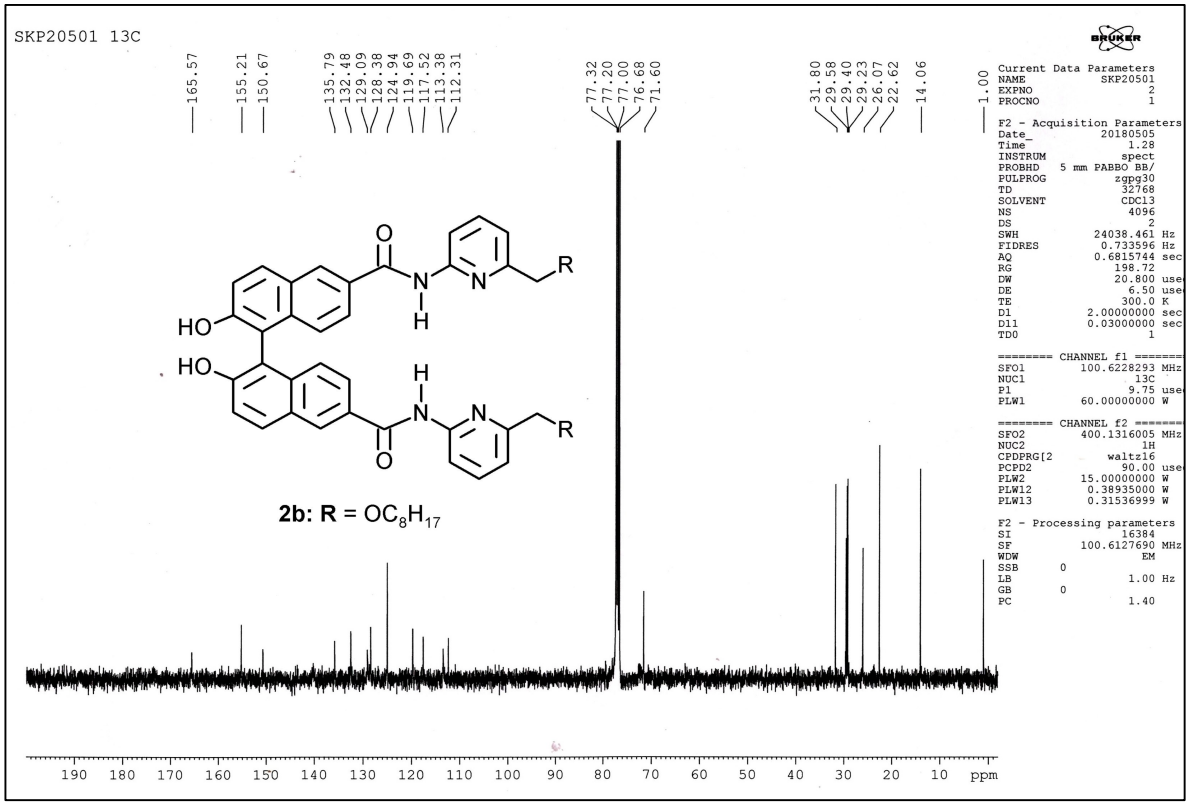



HRMS 2C
176
192.9080
174.9279
300.8044
370.8509
412.8010
562.6496
648.5964
649.5955
866.4938
867.5058
888.4628
889.4555
100
%
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
m/z
HO
HO
O
N
H
O
CH2(CH2)8CH3

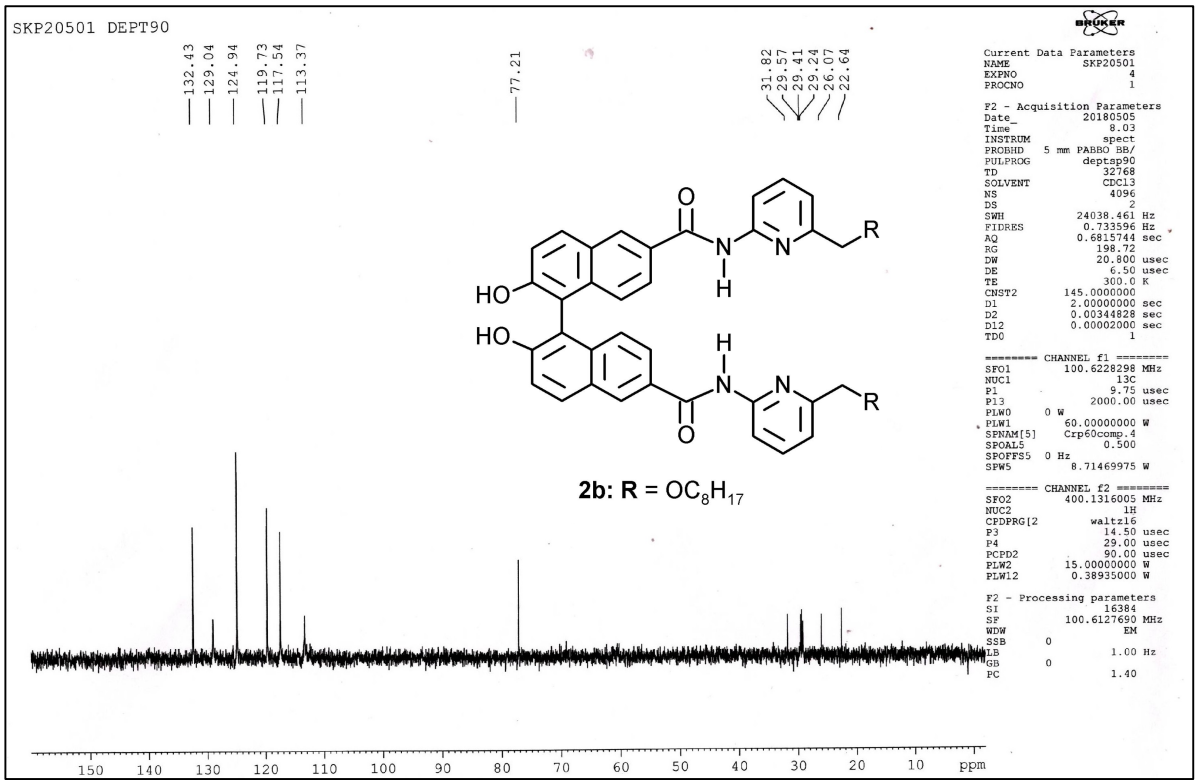
1H-NMR, $CDCl_3$ (100 MHz)



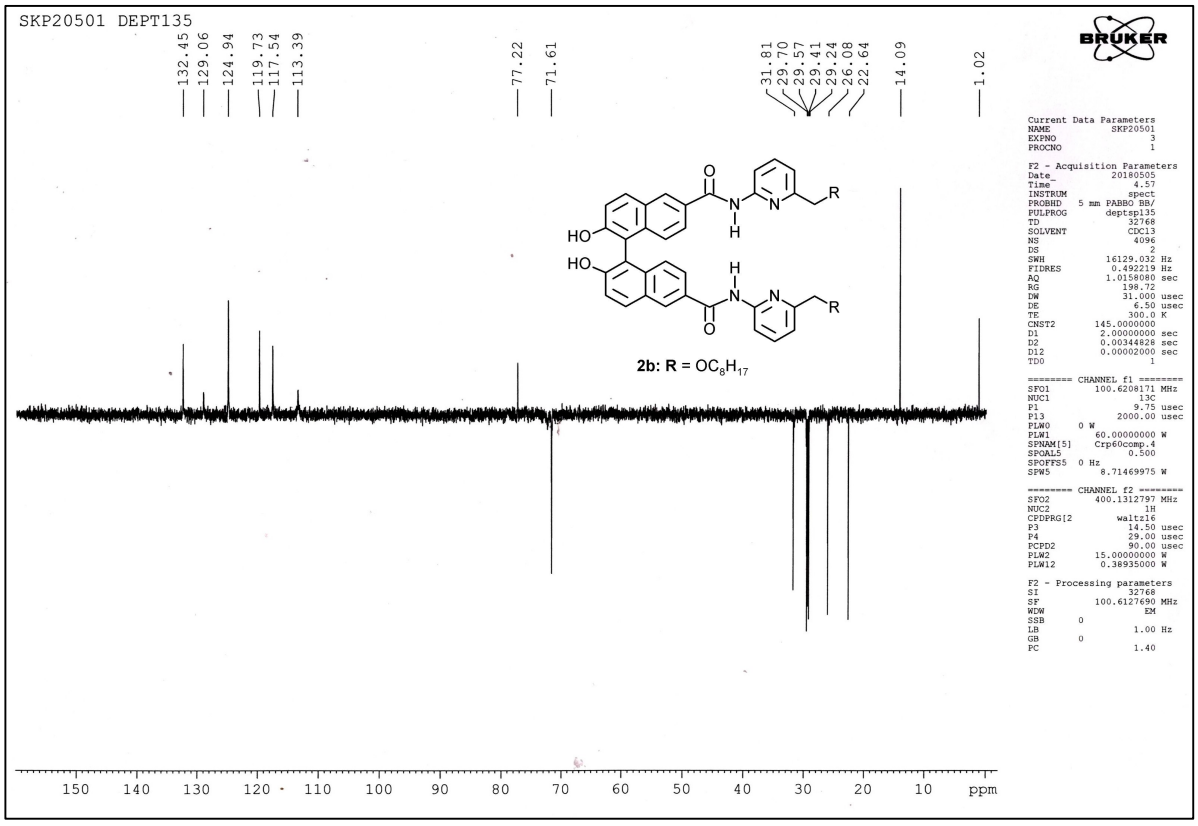
^{13}C-NMR, $CDCl_3$ (100 MHz)



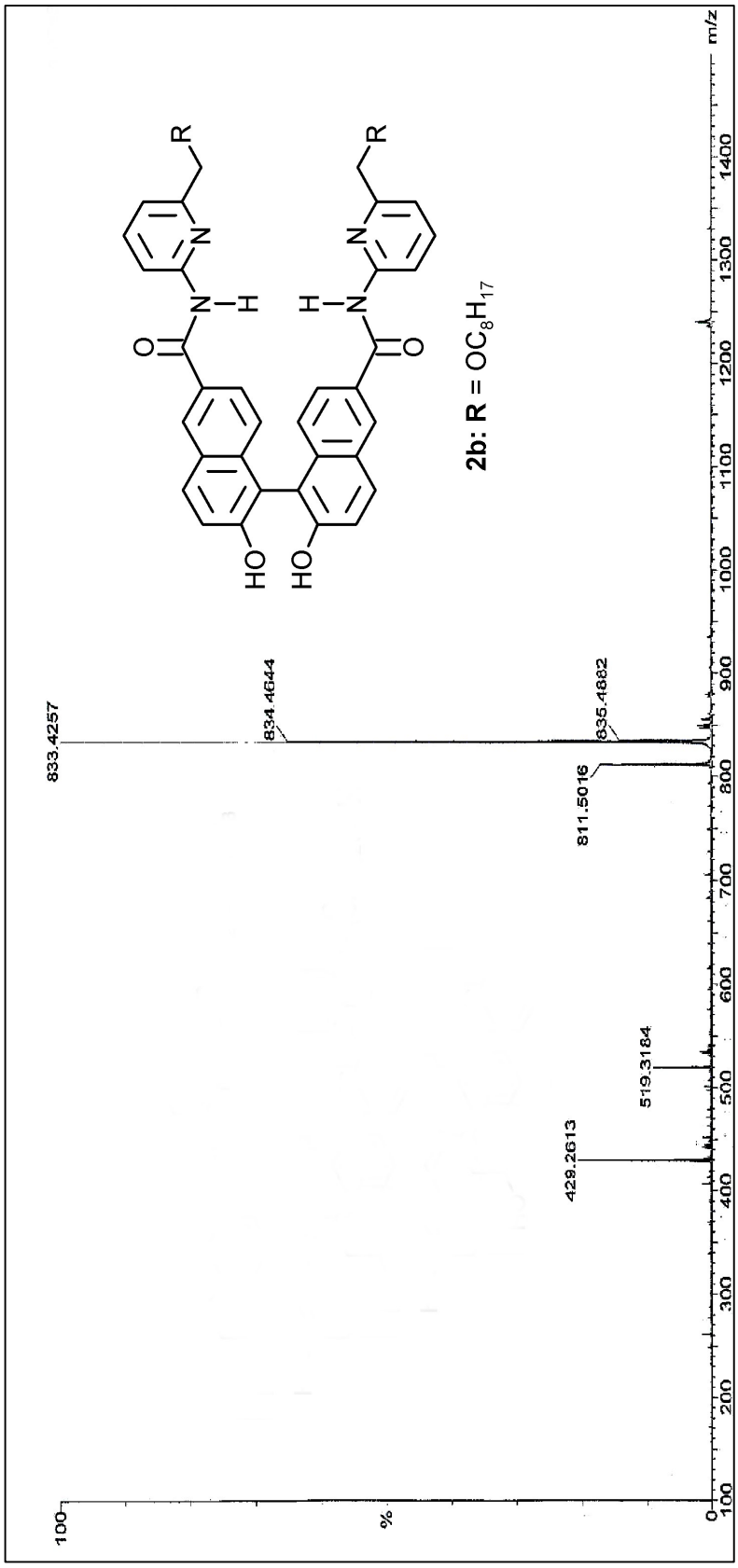
DEPT-90, $CDCl_3$ (100 MHz)



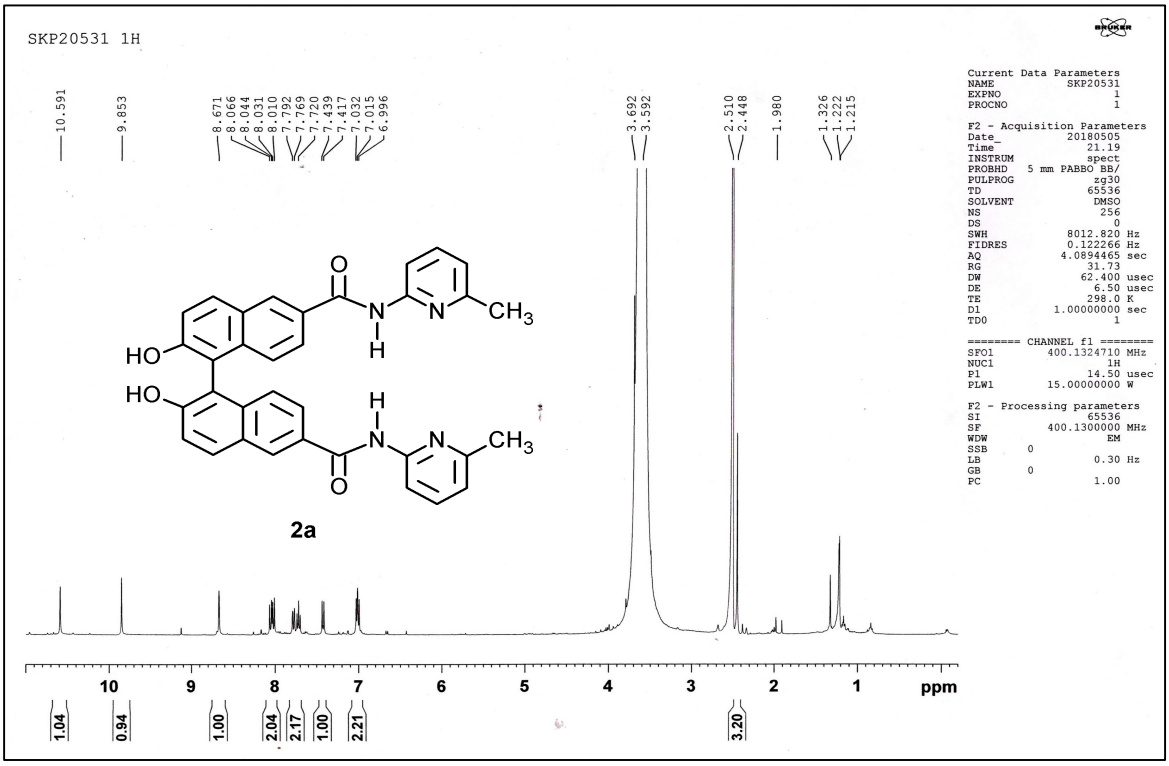
DEPT-135, $CDCl_3$ (100 MHz)



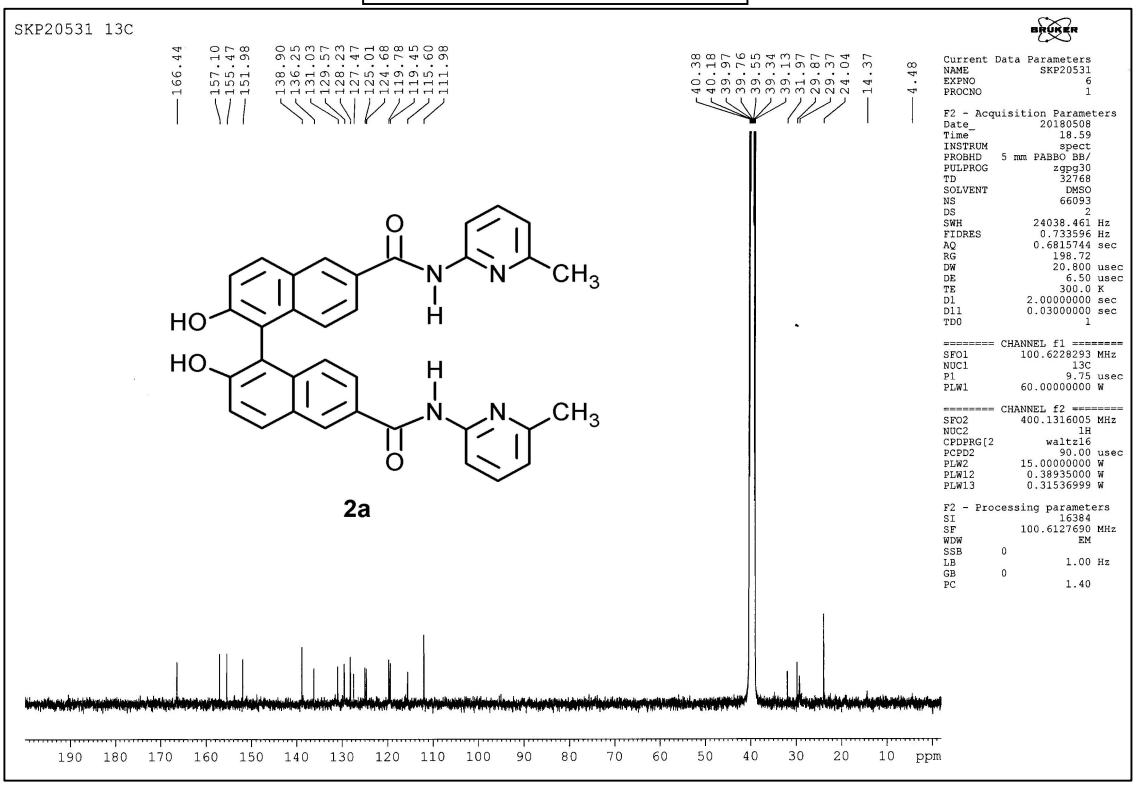
HRMS


2b: R = OC_8H_{17}
833.4257
834.4644
835.4882
811.5016
519.3184
429.2613
100
%
0
m/z

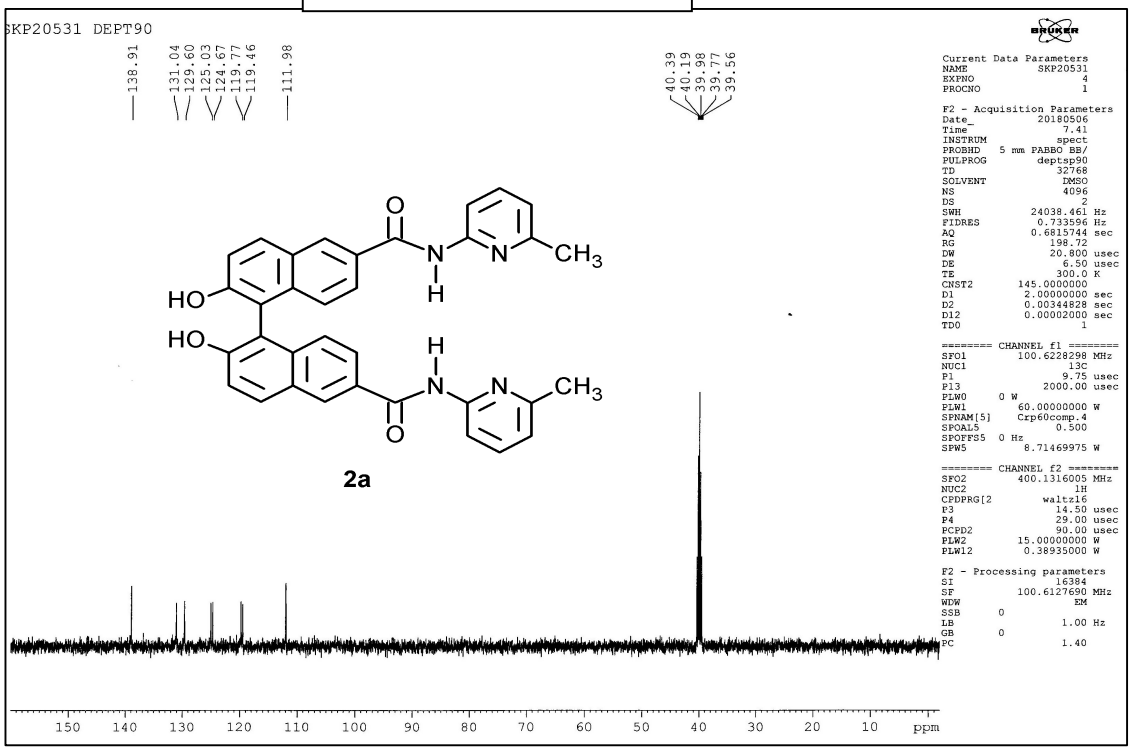
^{1}H-NMR, DMSO-d_6 (400 MHz)



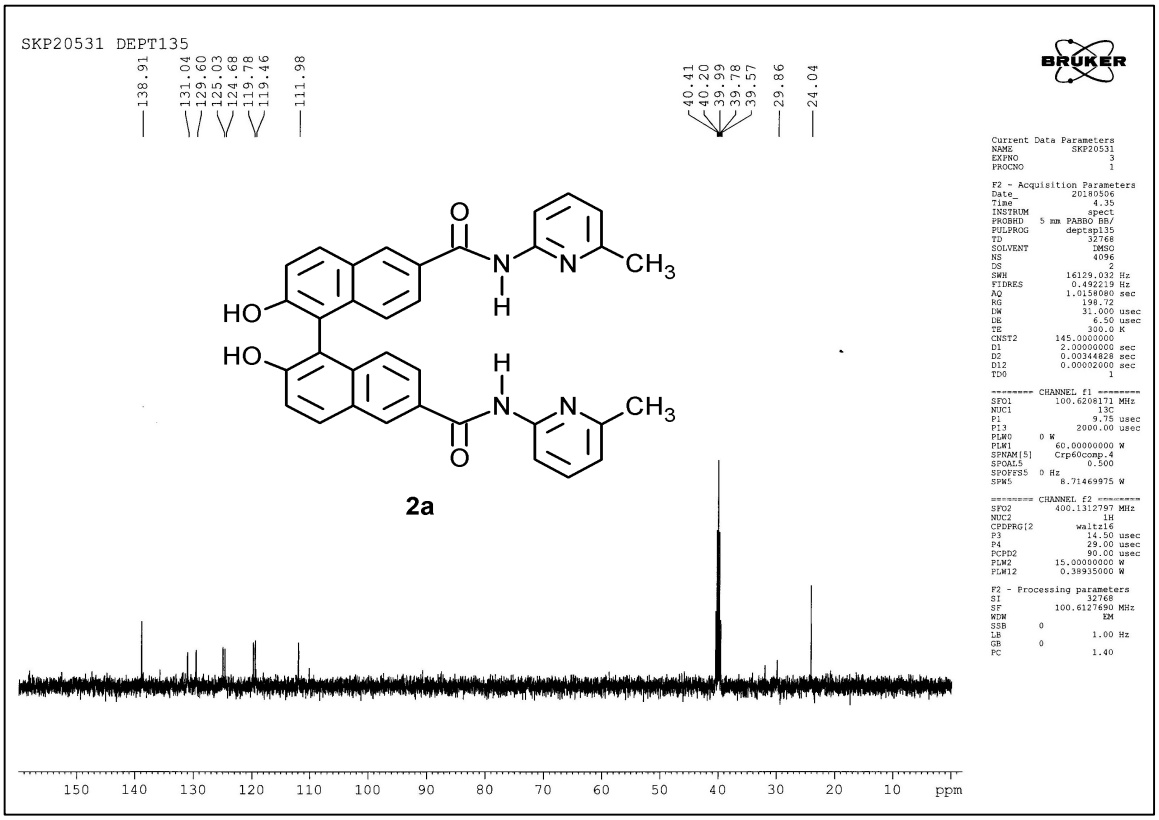
^{13}C-NMR, DMSO-d_6 (100 MHz)



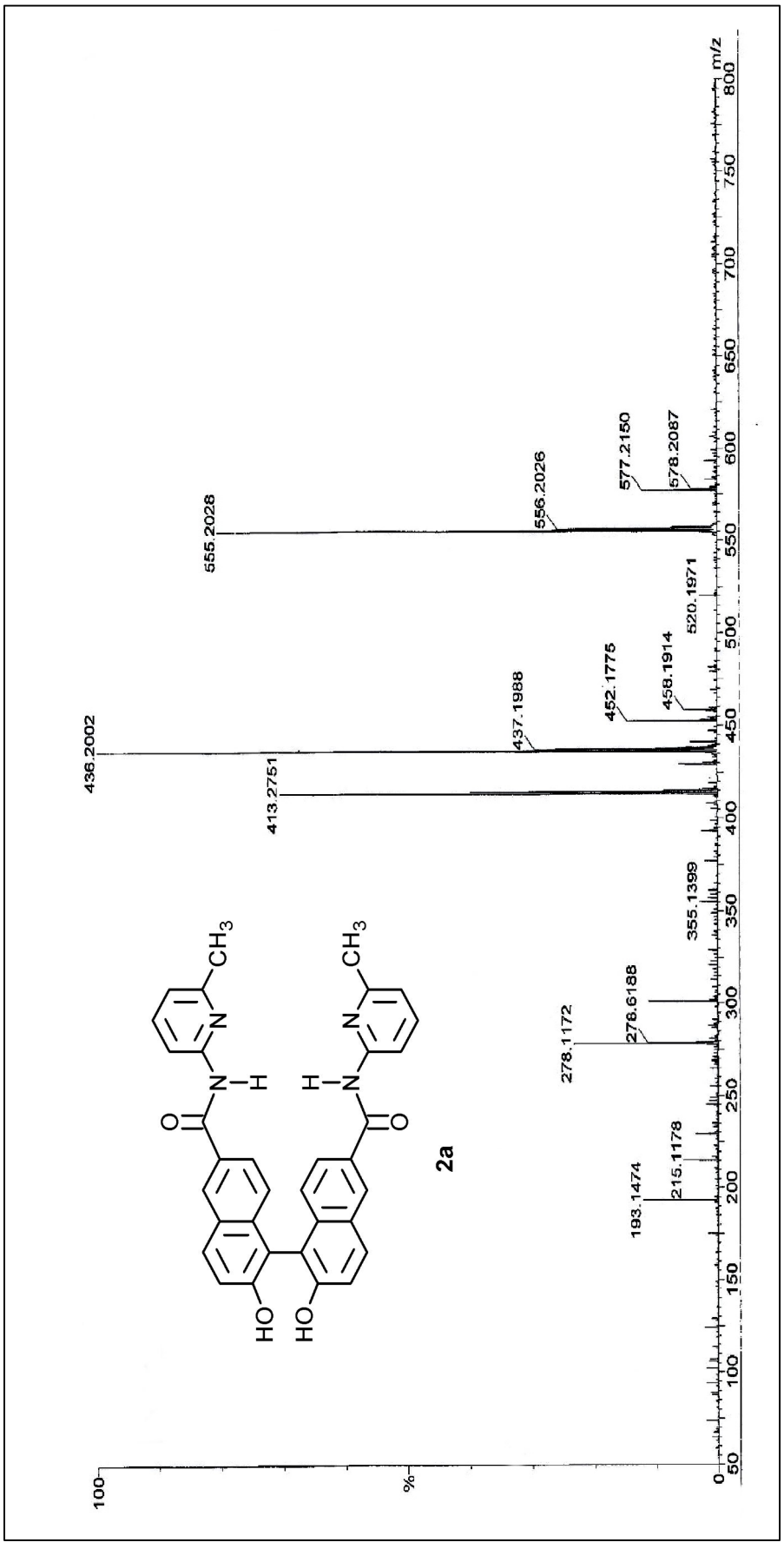
DEPT-90, DMSO-d_6 (100 MHz)



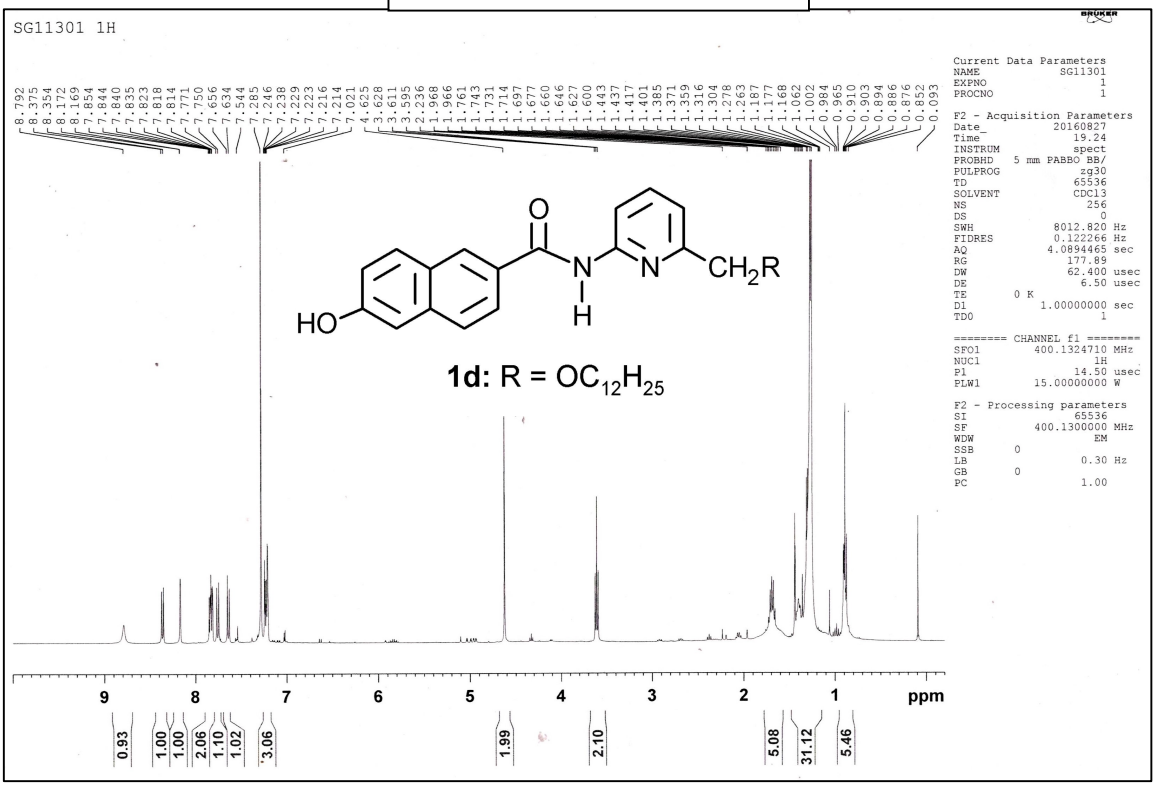
DEPT-135, DMSO-d_6 (100MHz)



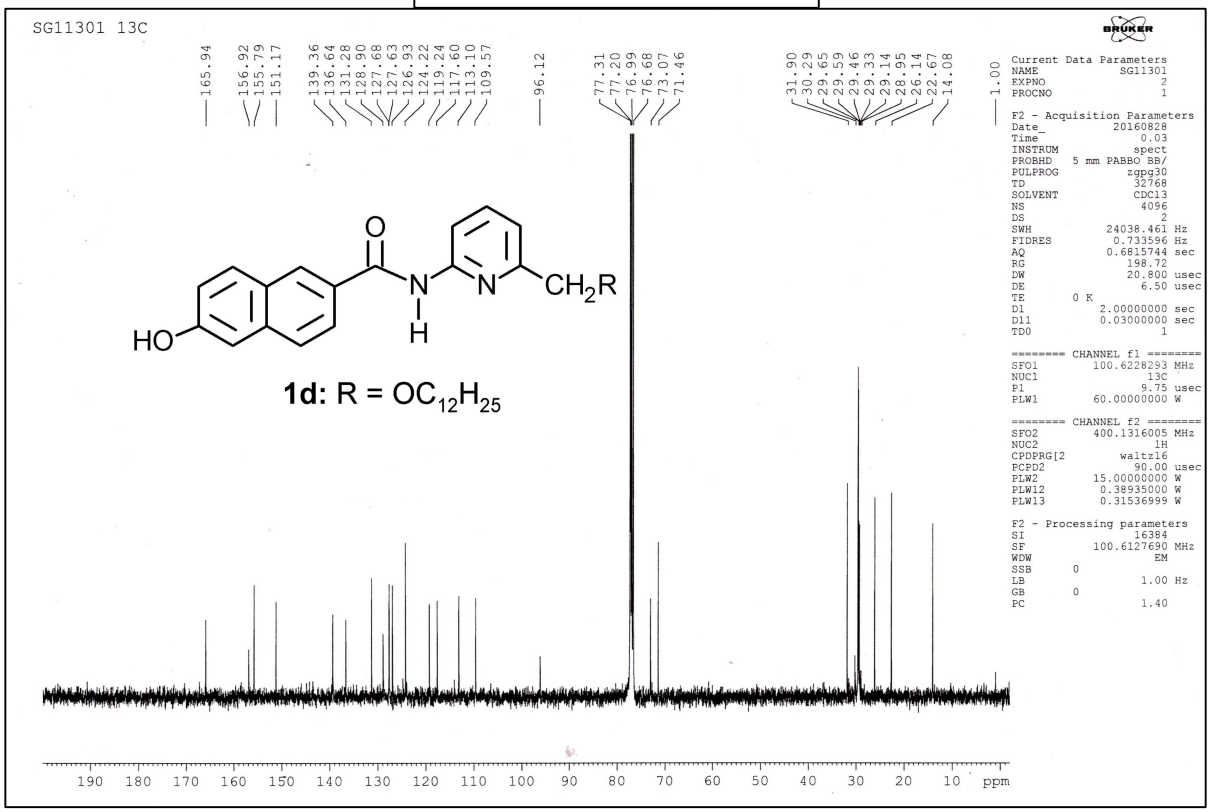
HRMS


100
%
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z
436.2002
413.2751
437.1988
452.1775
458.1914
520.1971
555.2028
556.2026
577.2150
578.2087
355.1399
276.6188
278.1172
215.1178
193.1474
HO
HO
N
H
O
CH3
2a

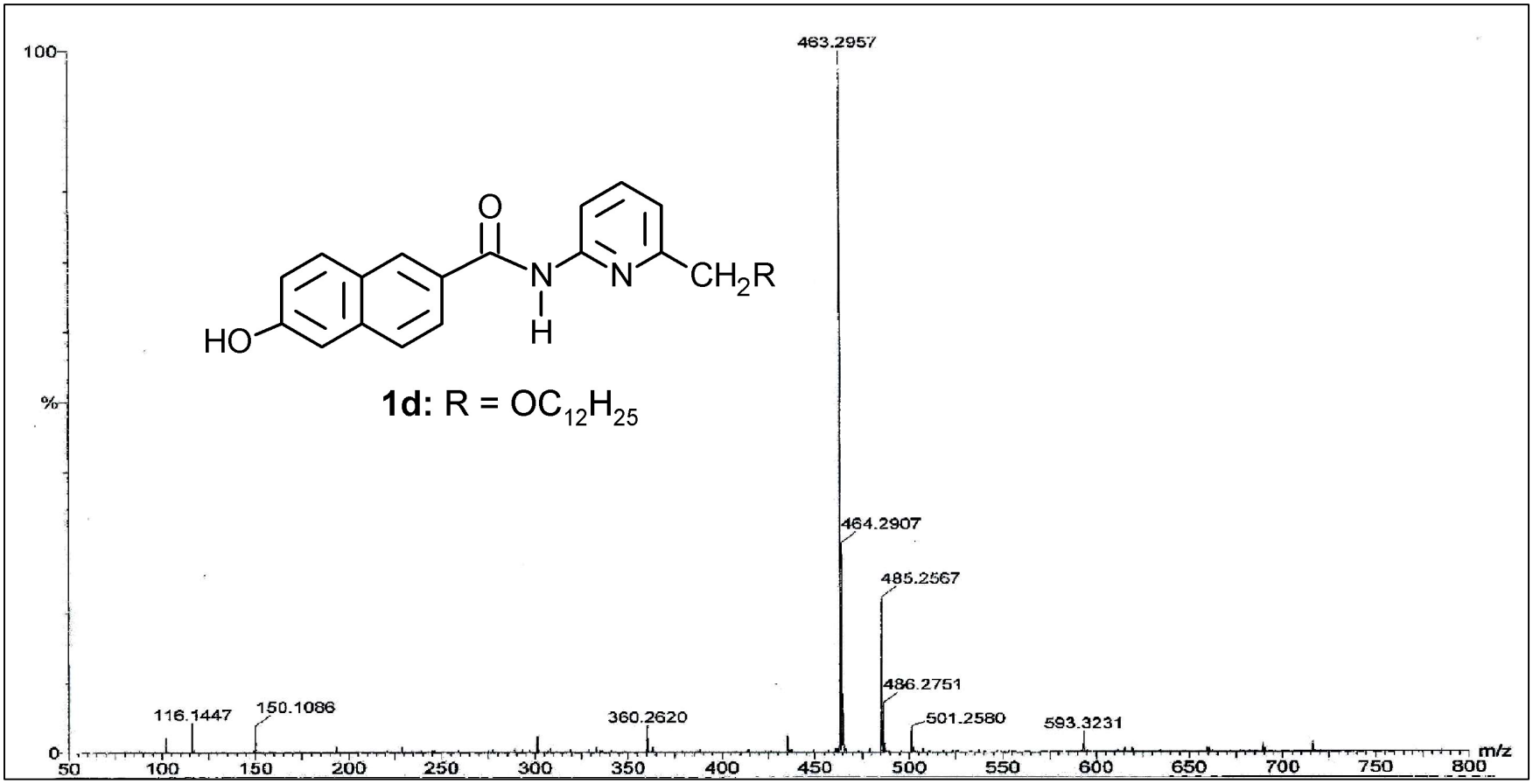
^{1}H-NMR, $CDCl_3$ (400 MHz)



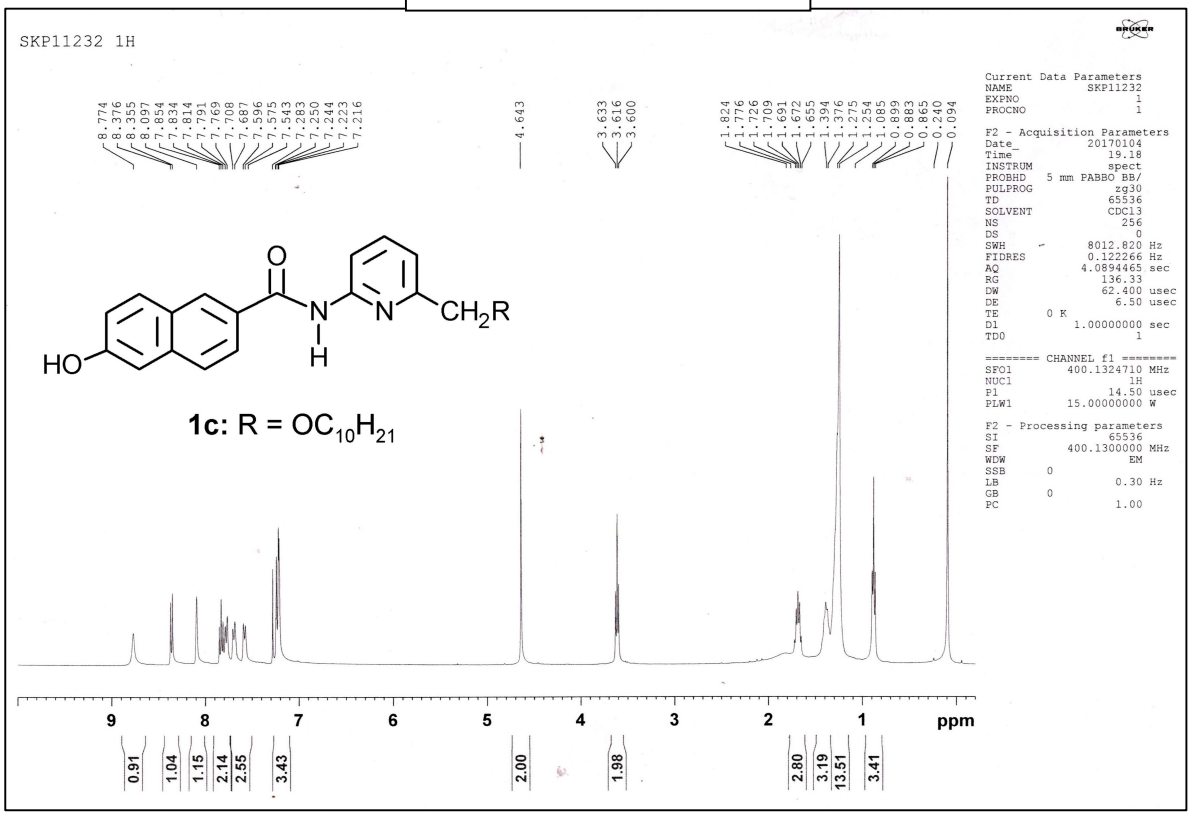
^{13}C-NMR, $CDCl_3$ (100 MHz)



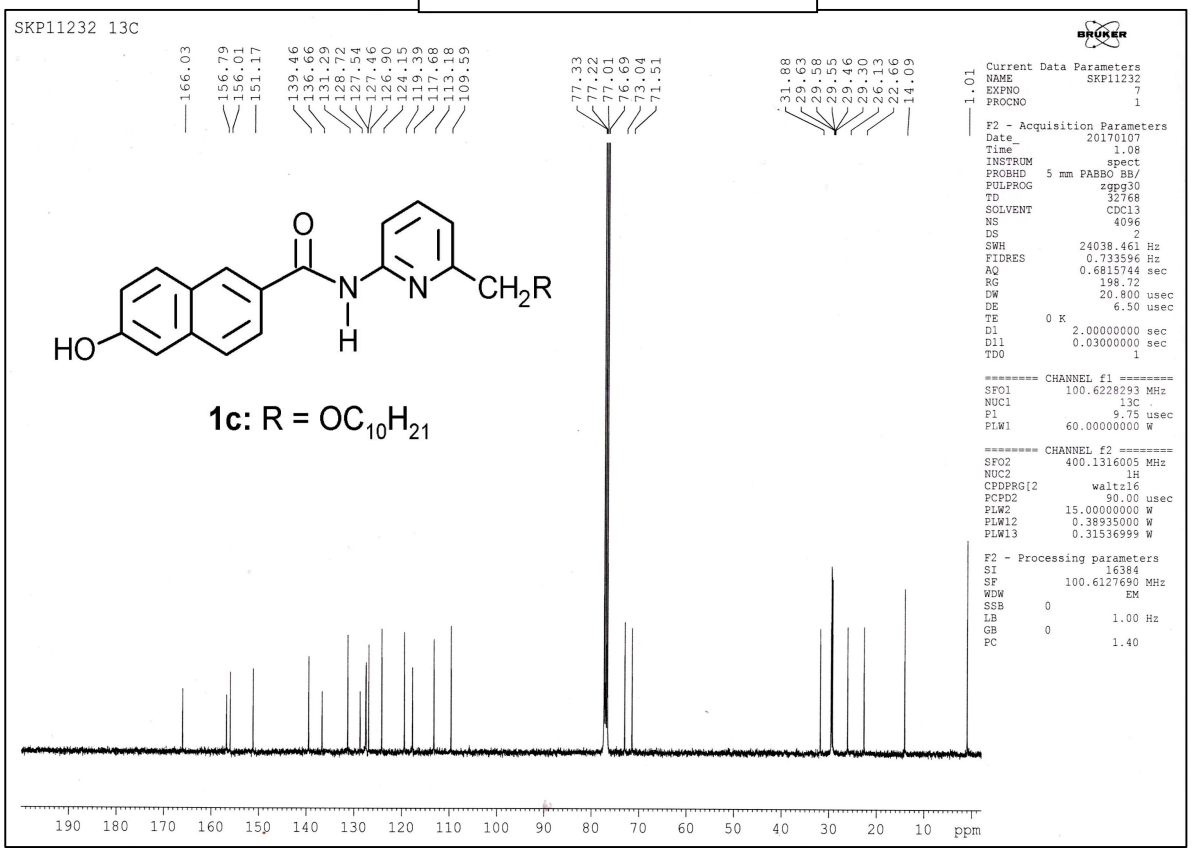
HRMS


100
%
0
463.2957
464.2907
485.2567
486.2751
501.2580
593.3231
116.1447
150.1086
360.2620
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z
HO
O
N
H
N
CH2R
1d: R = OC12H25

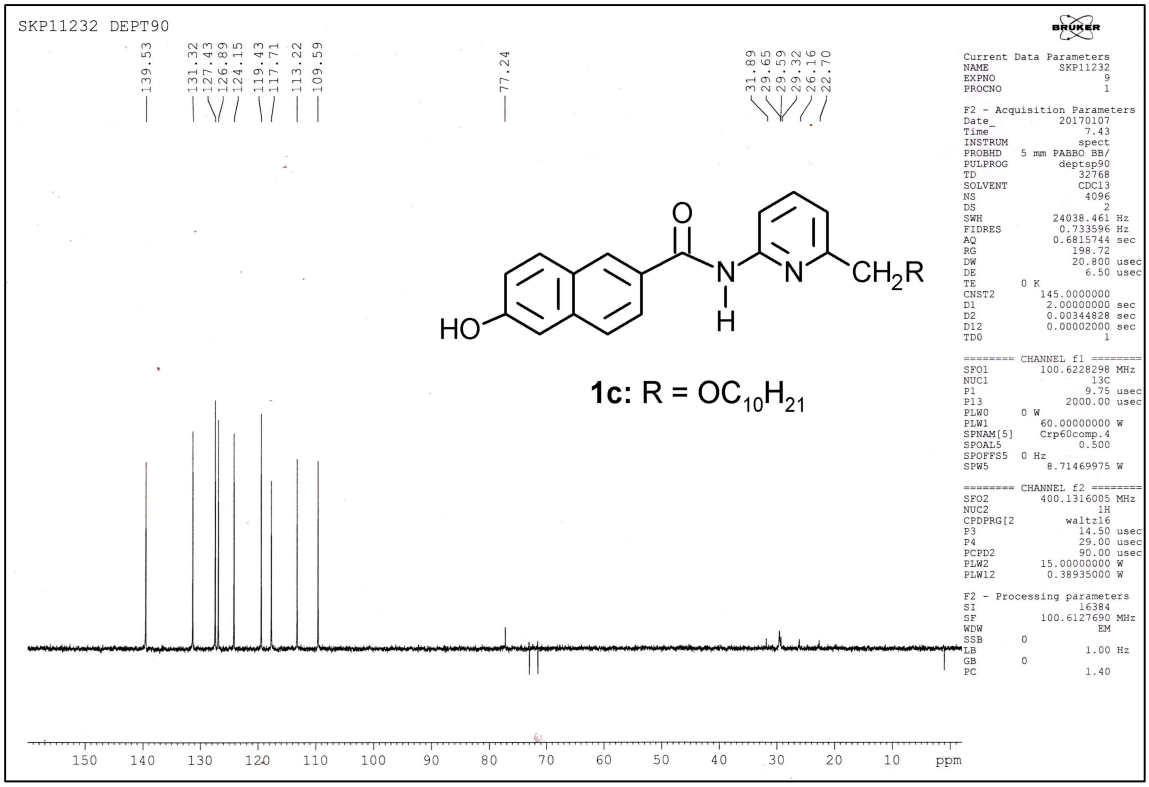
1H-NMR, $CDCl_3$ (400 MHz)



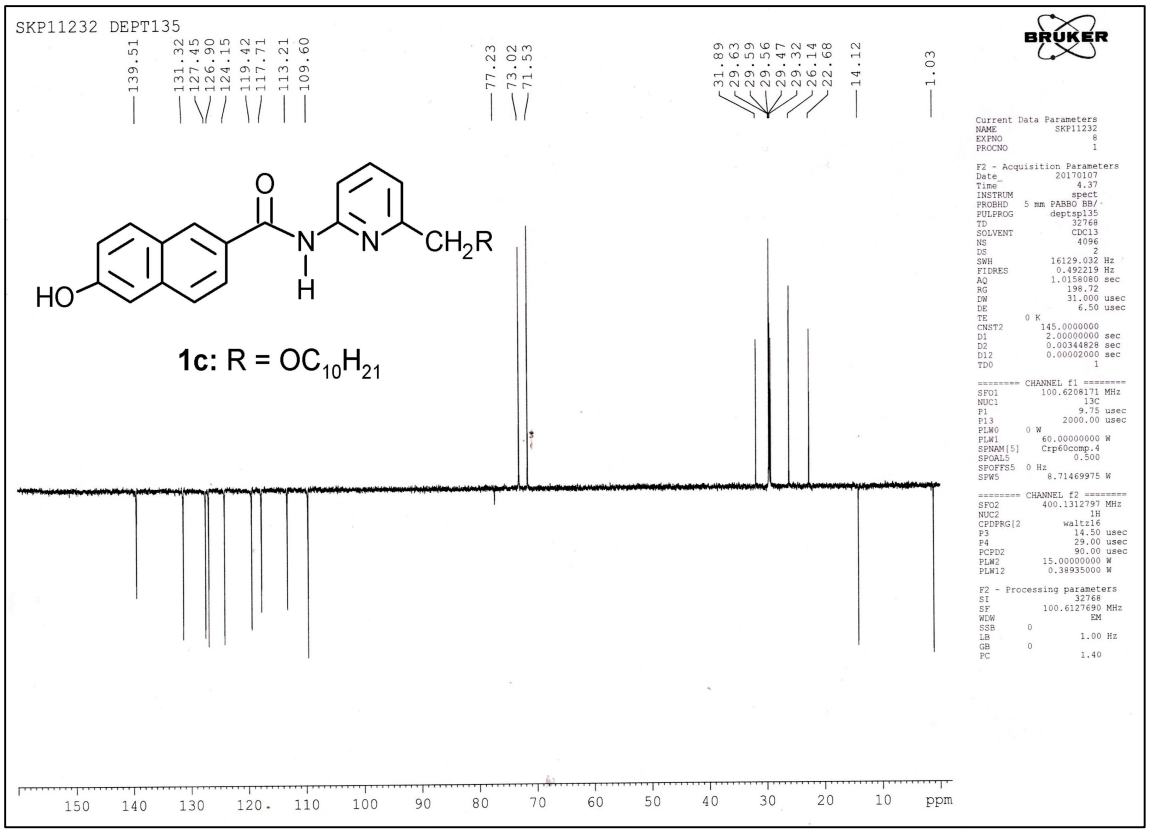
13C-NMR, $CDCl_3$ (100 MHz)



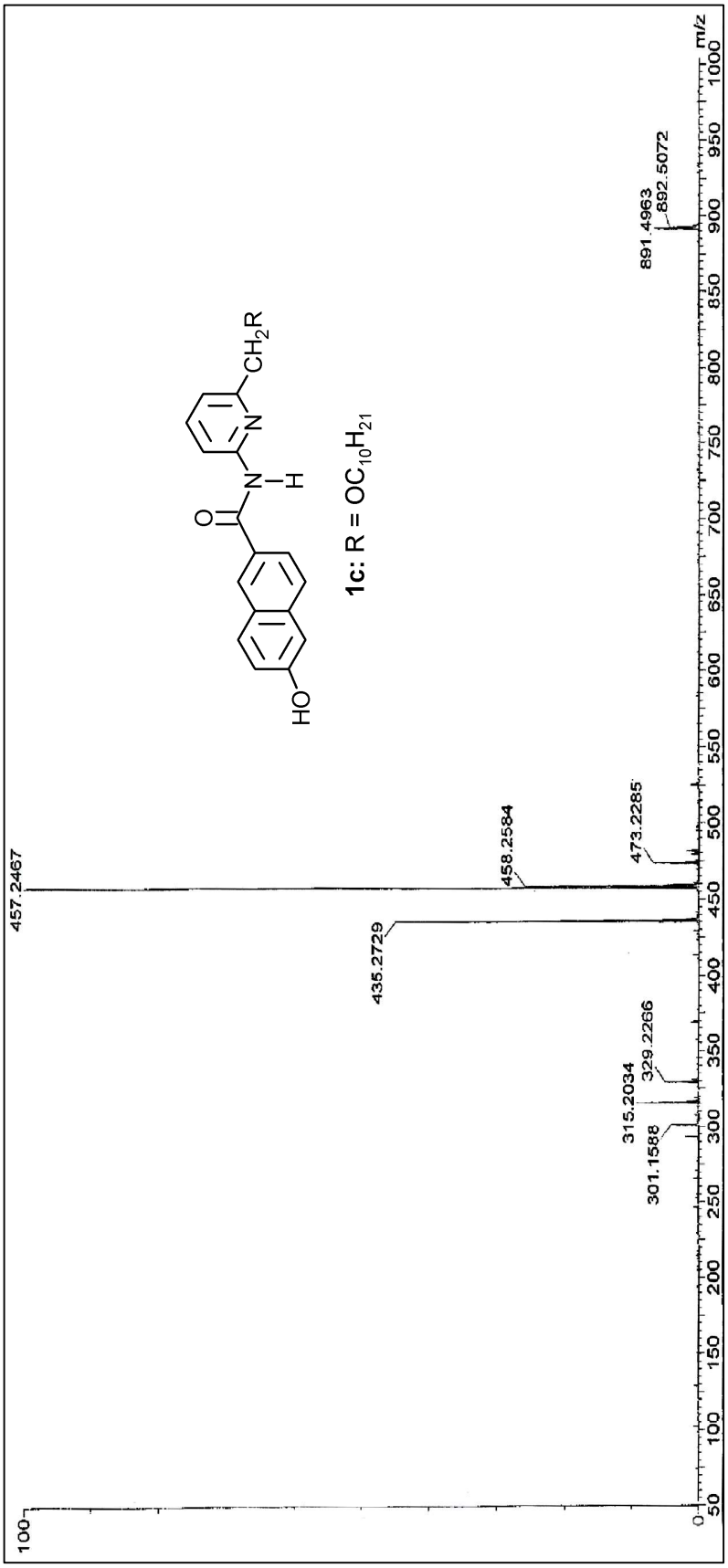
DEPT-90, $CDCl_3$ (100MHz)



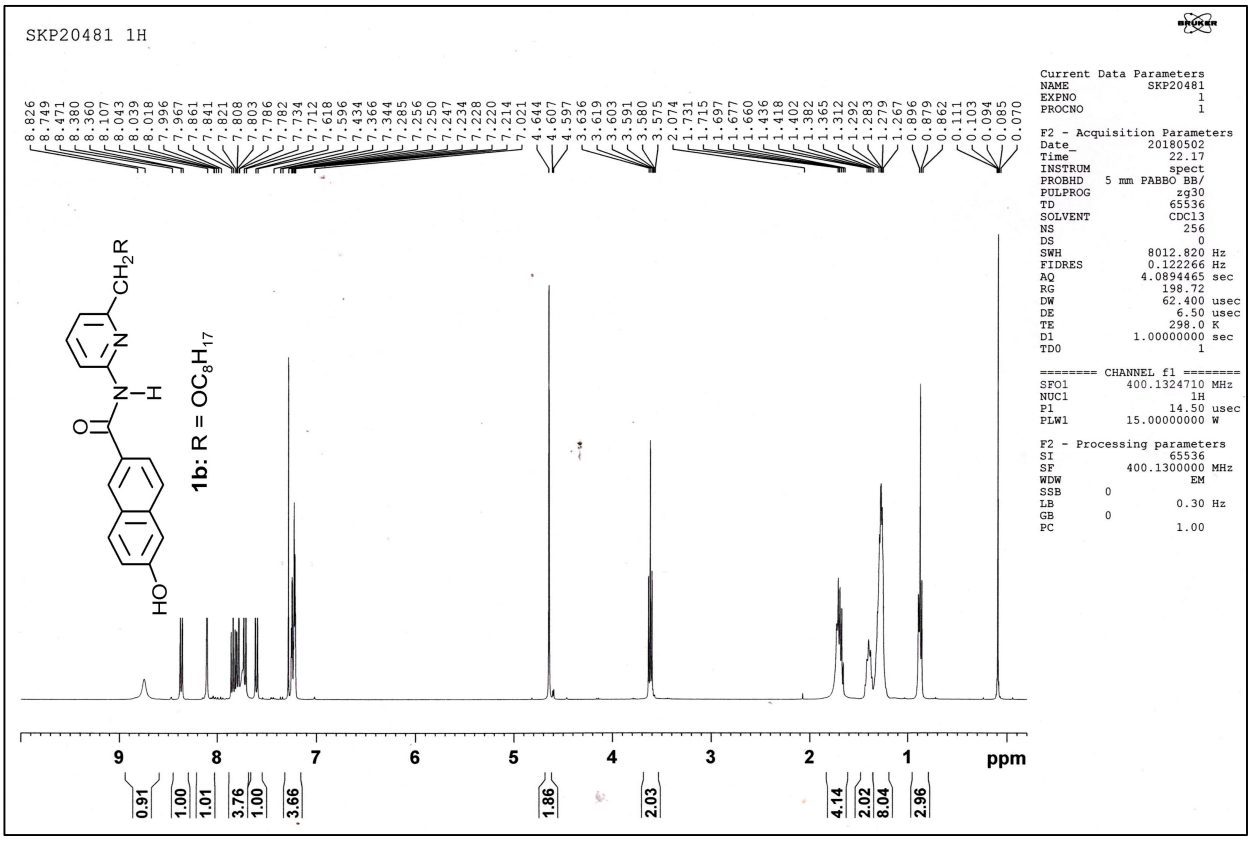
DEPT-135, CDCl3 (100MHz)



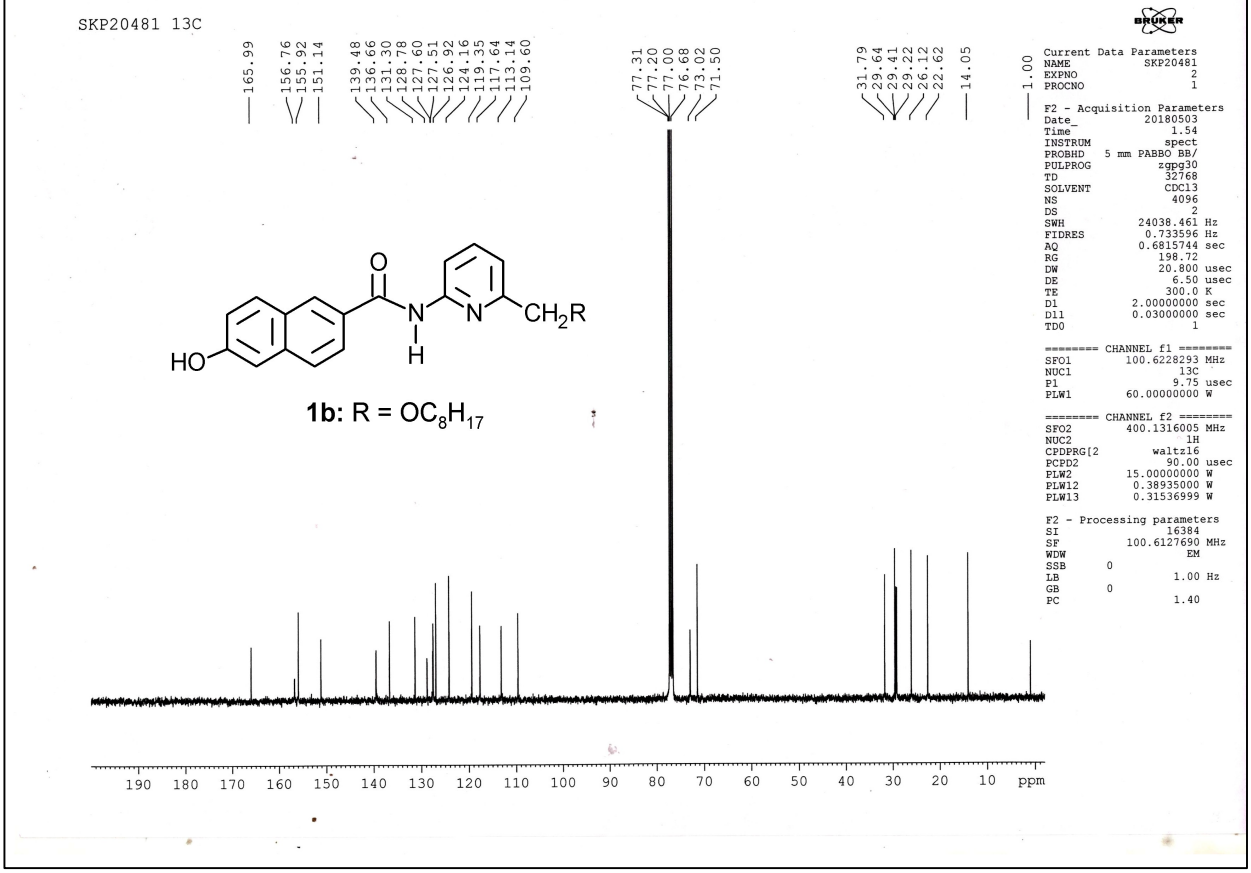
HRMS


1c: R = OC10H21
HO
O
N
H
N
CH2R
100
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z
457.2467
458.2584
473.2285
435.2729
329.2266
315.2034
301.1588
891.4963
892.5072

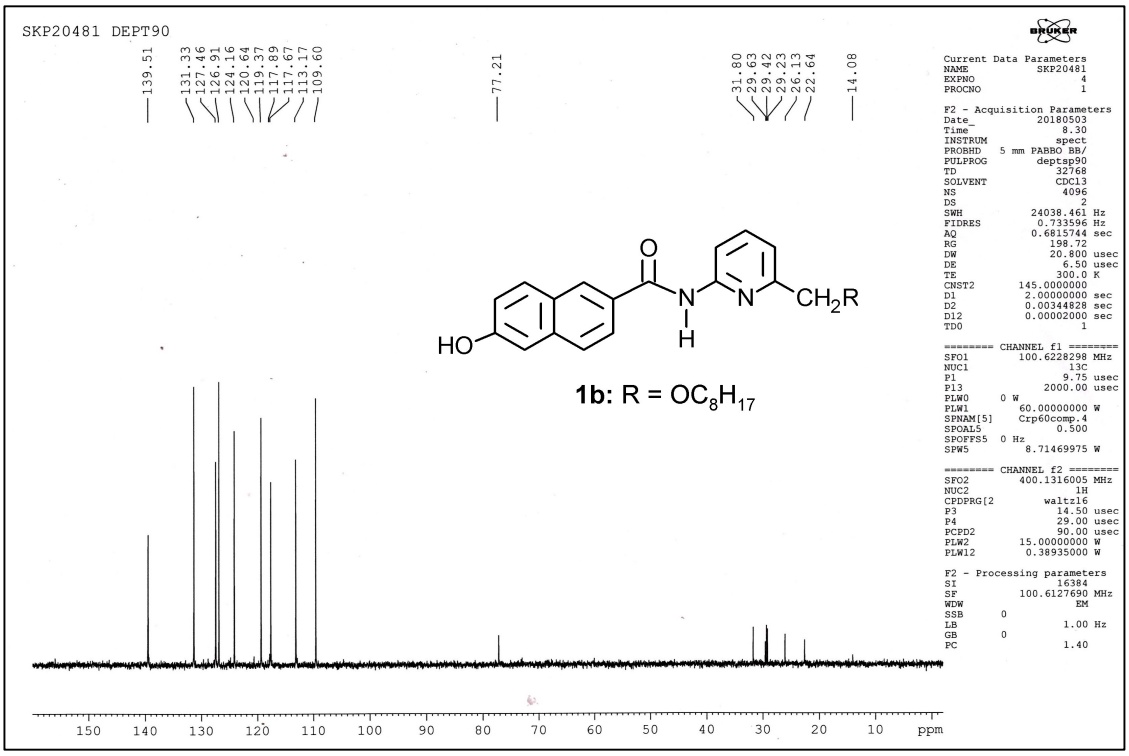
^{1}H-NMR 400 MHz($CDCl_3$)



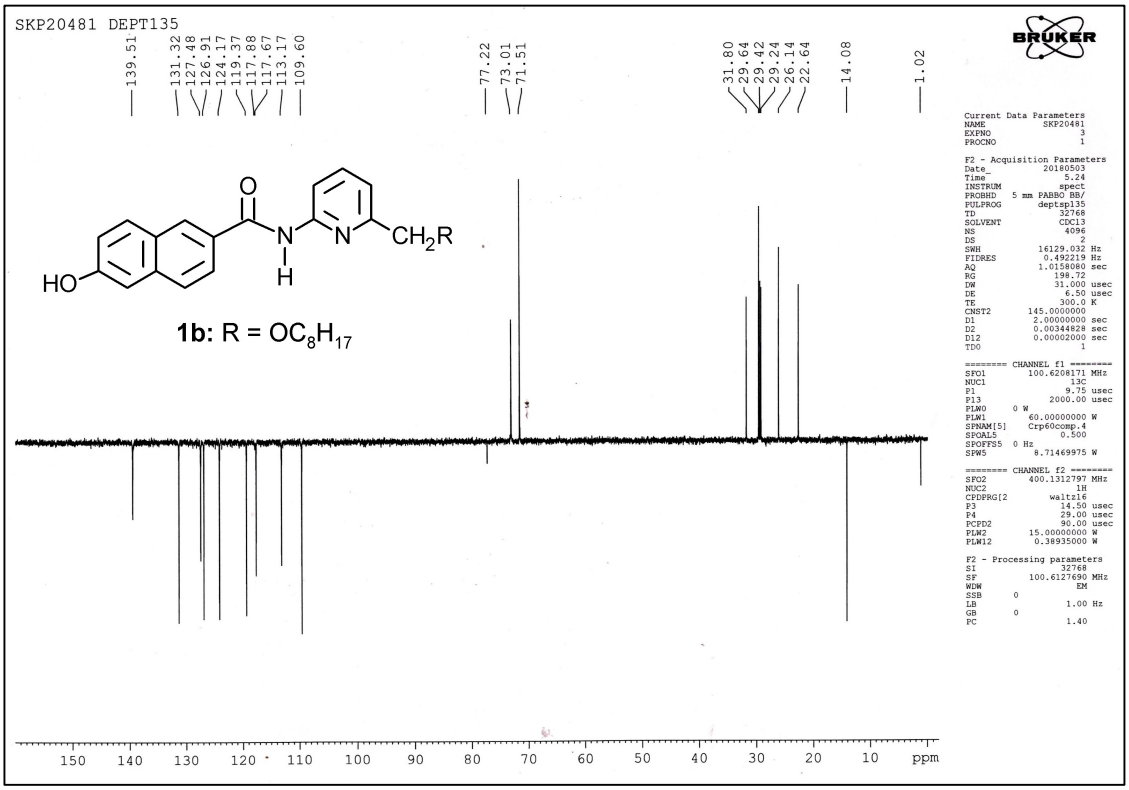
13C-NMR, CDCl3 (100MHz)



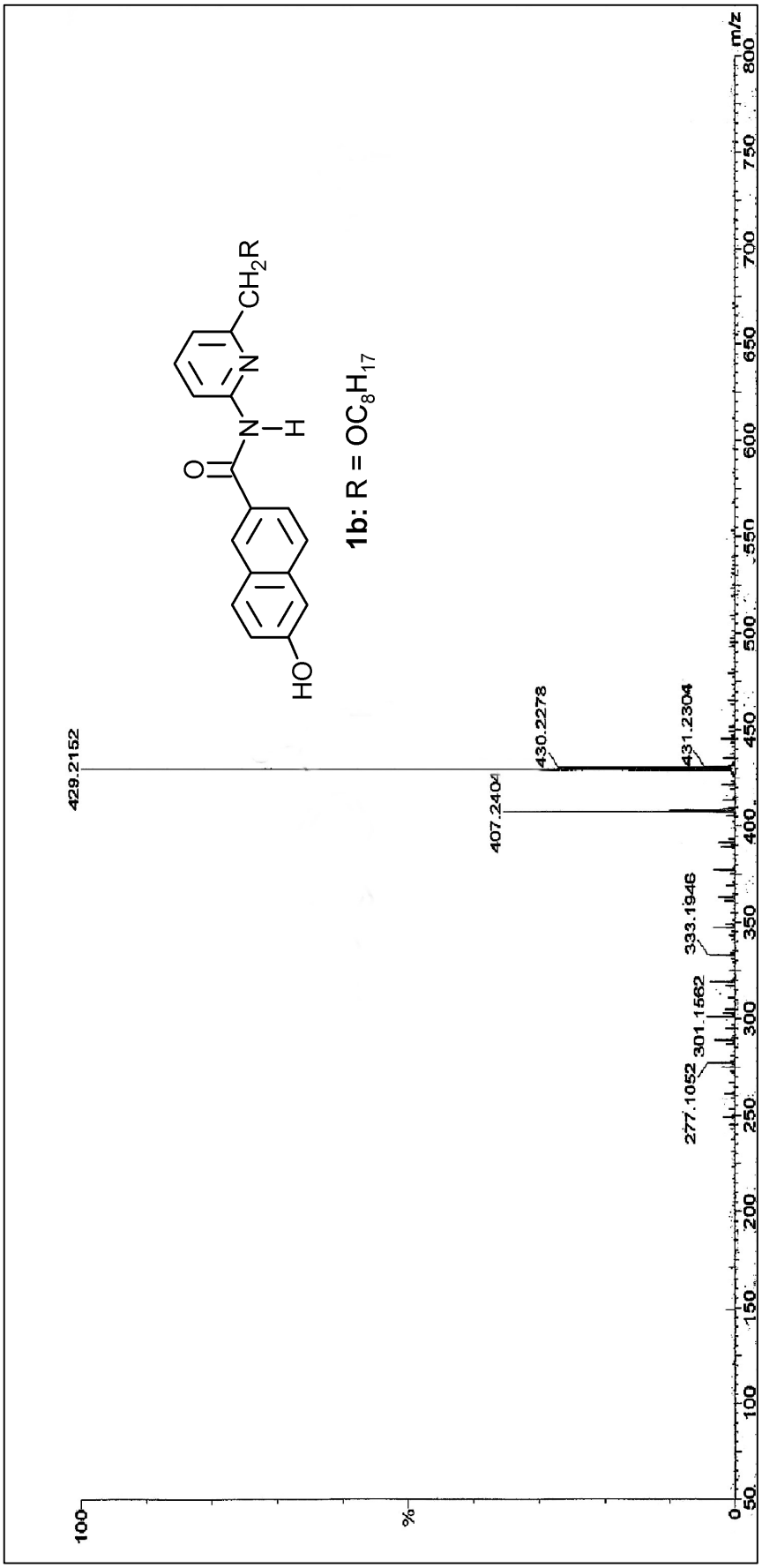
DEPT-90, CDCl3 (100 MHz)



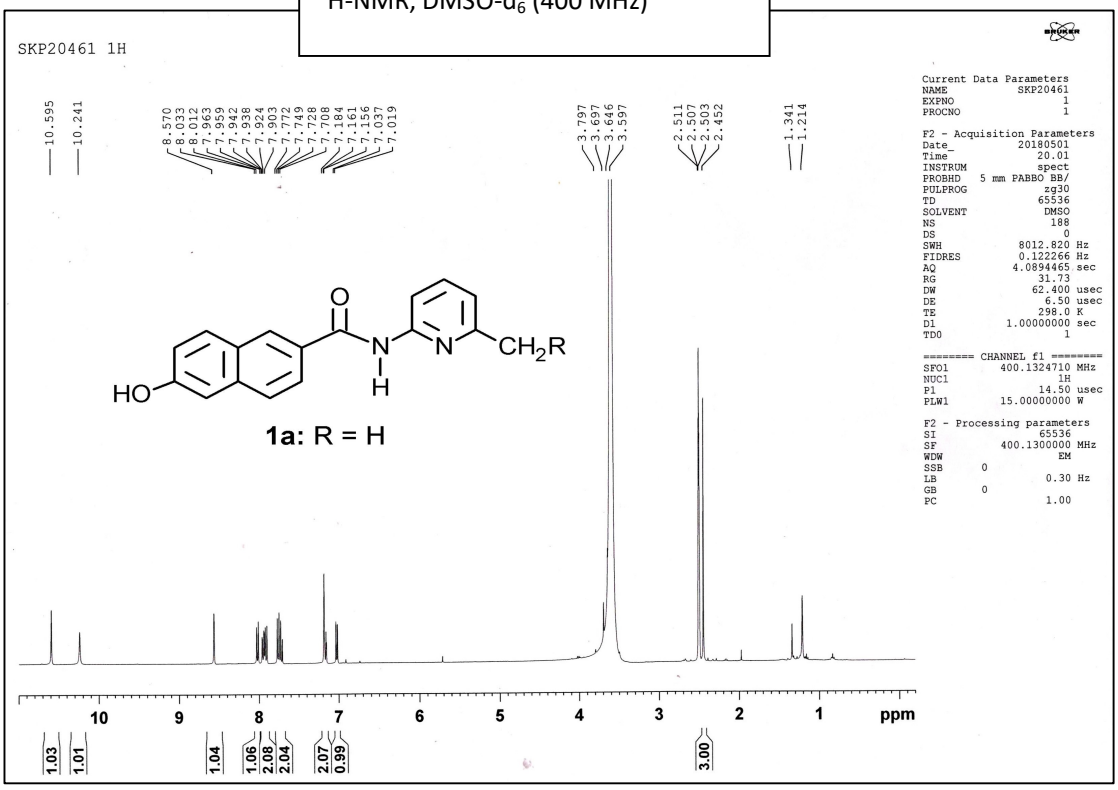
DEPT-135, CDCl3 (100 MHz)



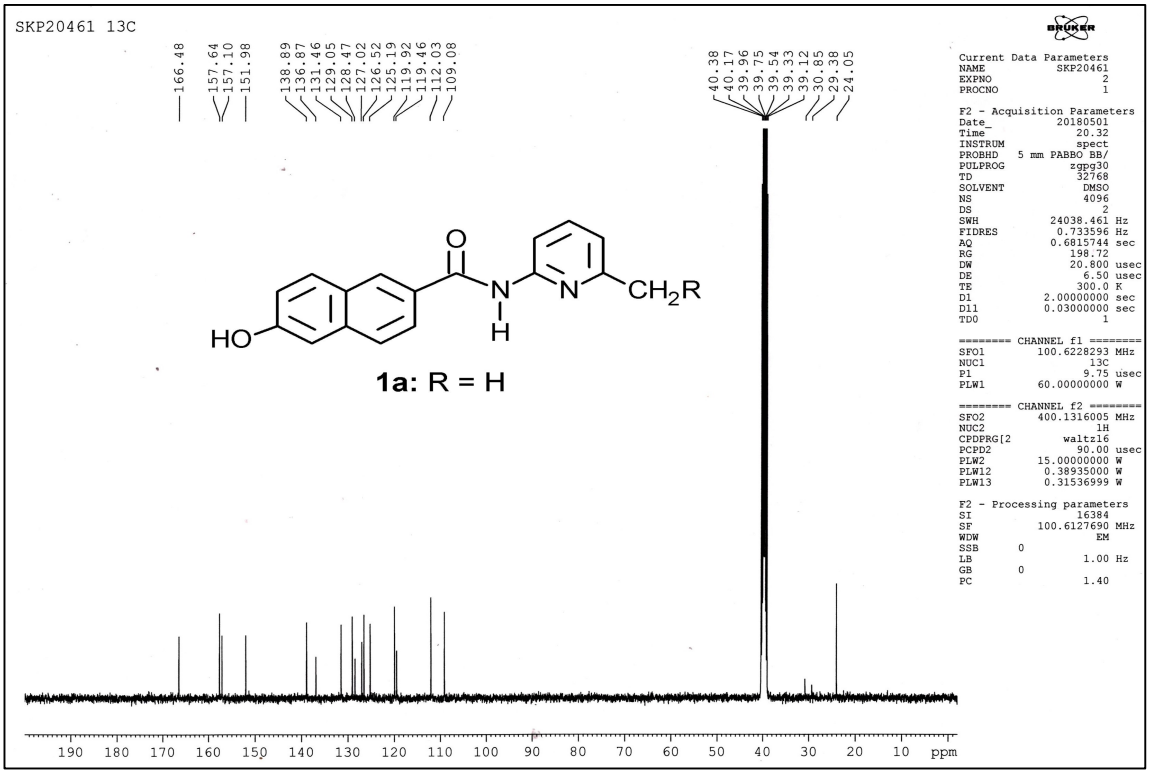
HRMS


CH2R
N
N
H
O
HO
1b: R = OC8H17
429.2152
430.2278
431.2304
407.2404
333.1946
301.1562
277.1052
100
%
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z

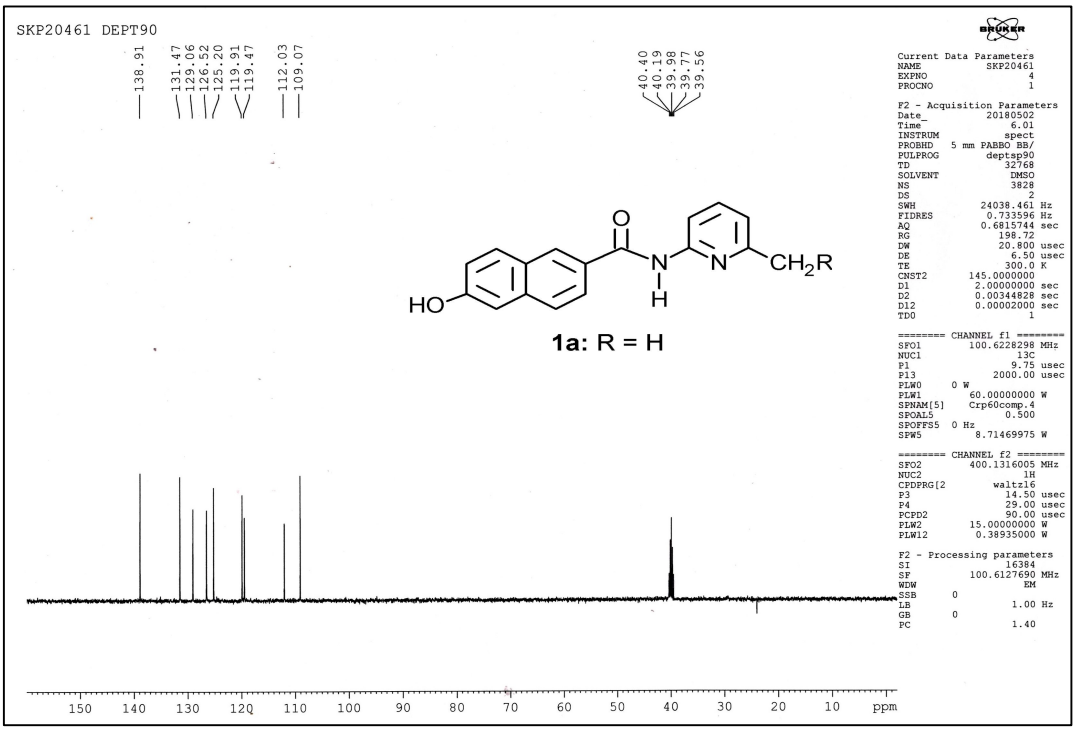
^{1}H-NMR, DMSO-d_6 (400 MHz)



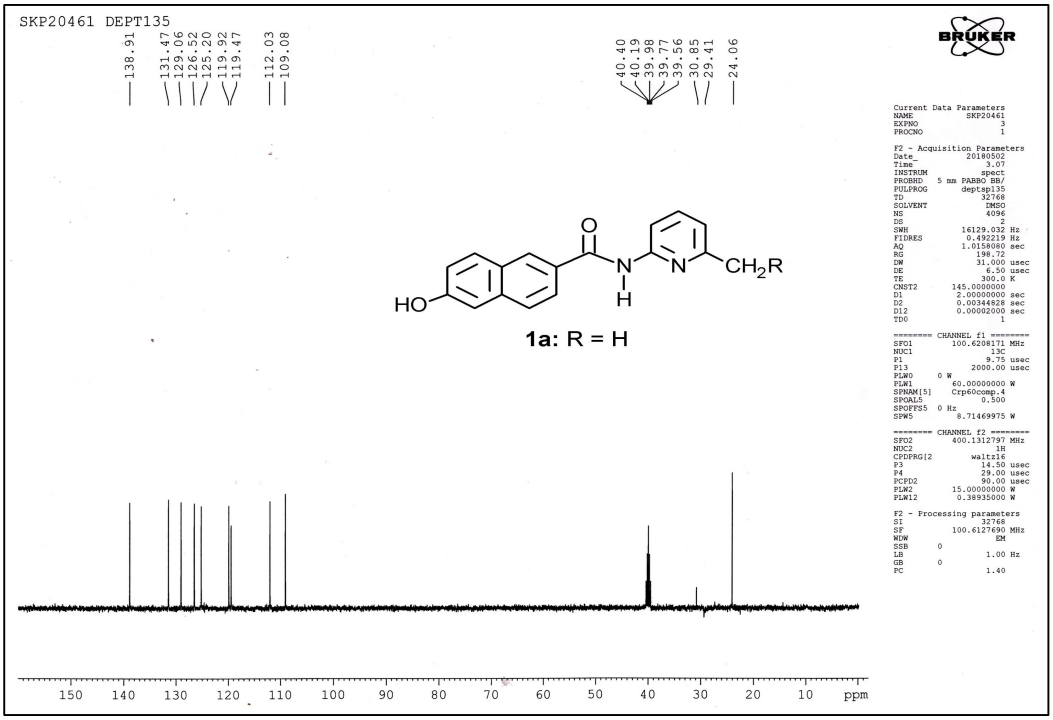
^{13}C-NMR, DMSO-d_6 (100 MHz)



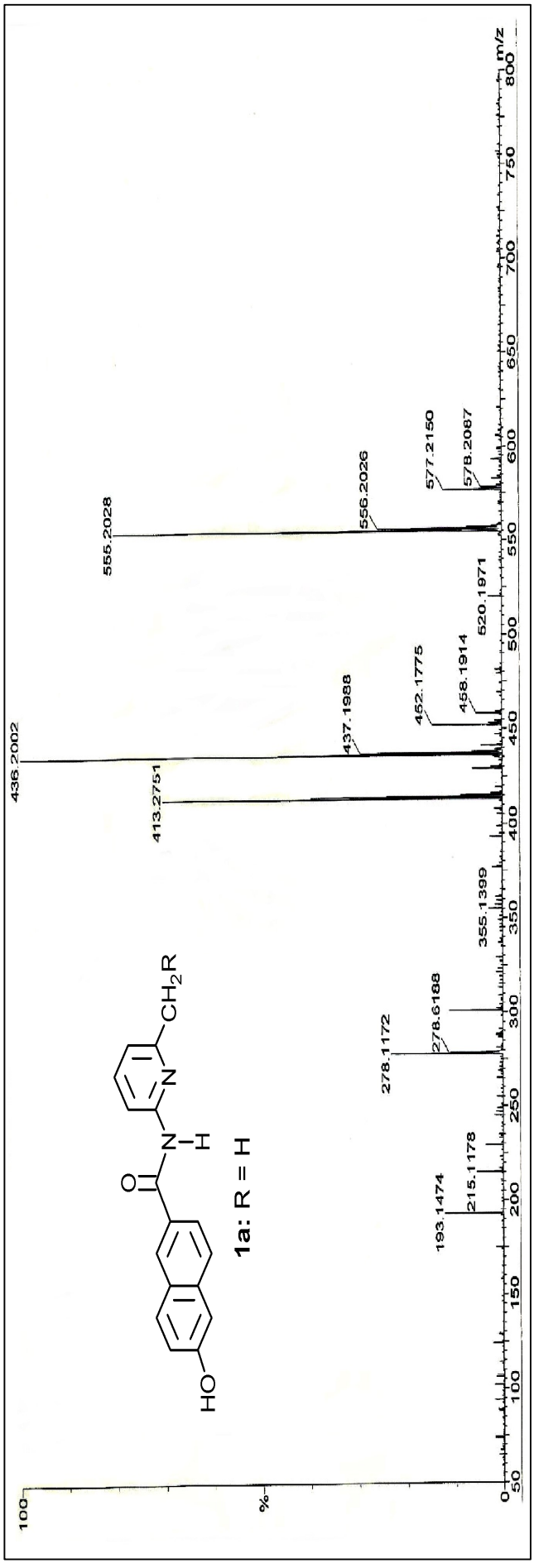
DEPT-90, DMSO-d_6



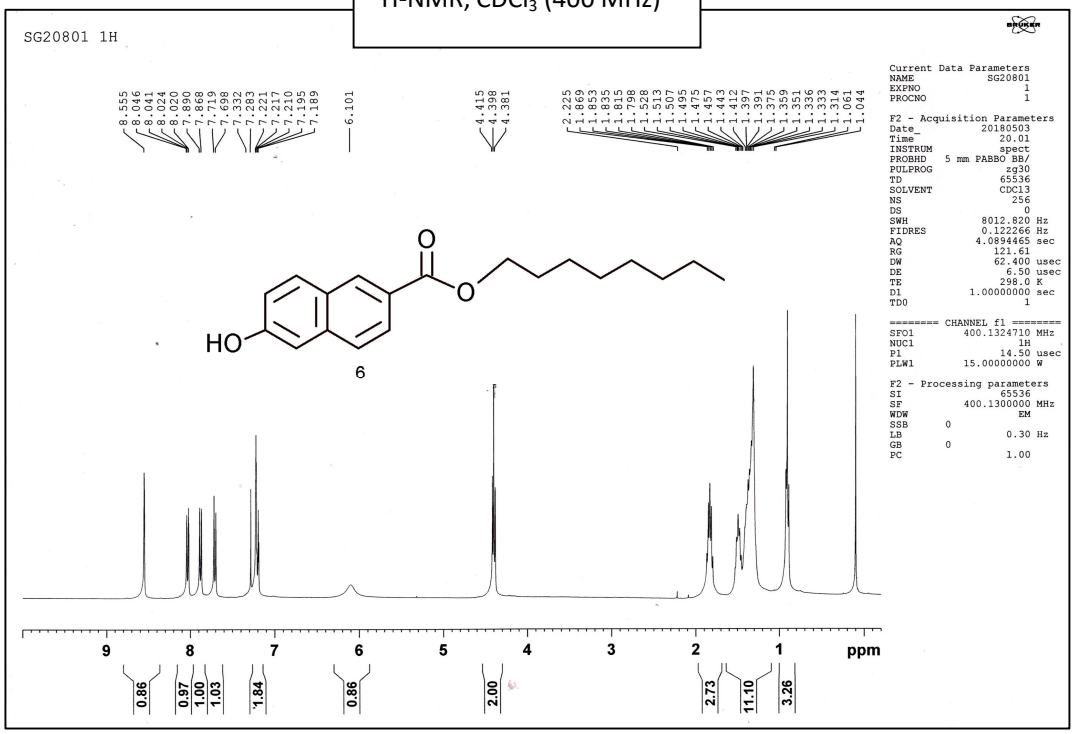
DEPT-135, DMSO-d_6



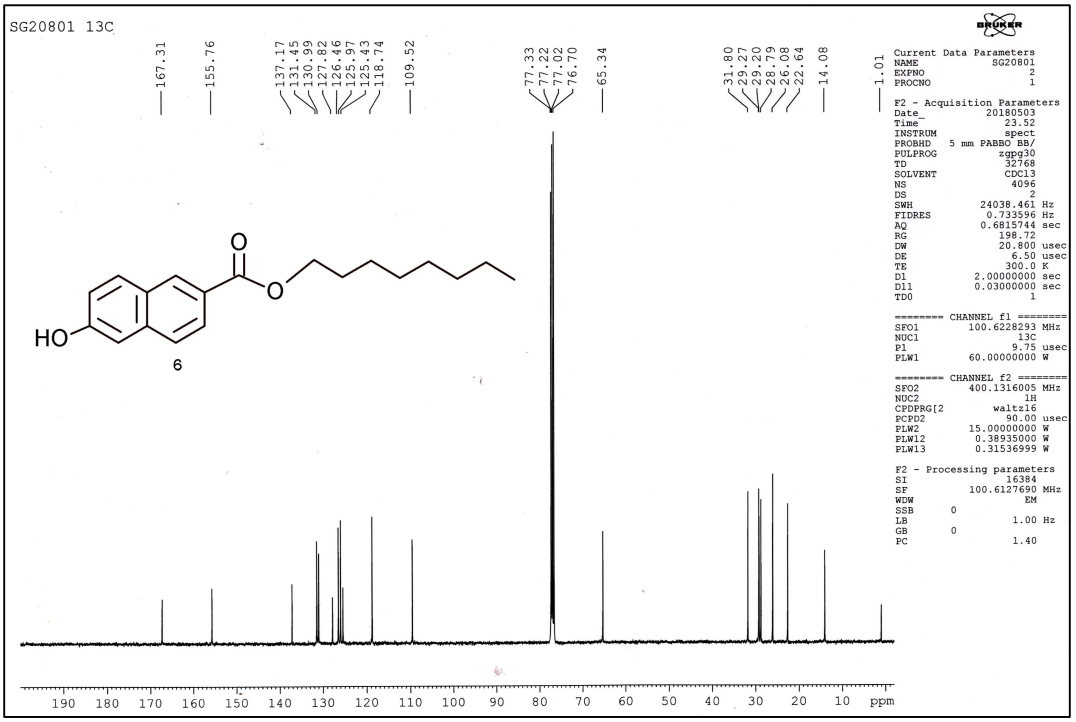
HRMS


100
%
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z
436.2002
413.2751
555.2028
437.1988
556.2026
452.1775
577.2150
458.1914
578.2087
520.1971
355.1399
278.1172
278.6188
193.1474
215.1178
O
N
H
CH2R
HO
1a: R = H

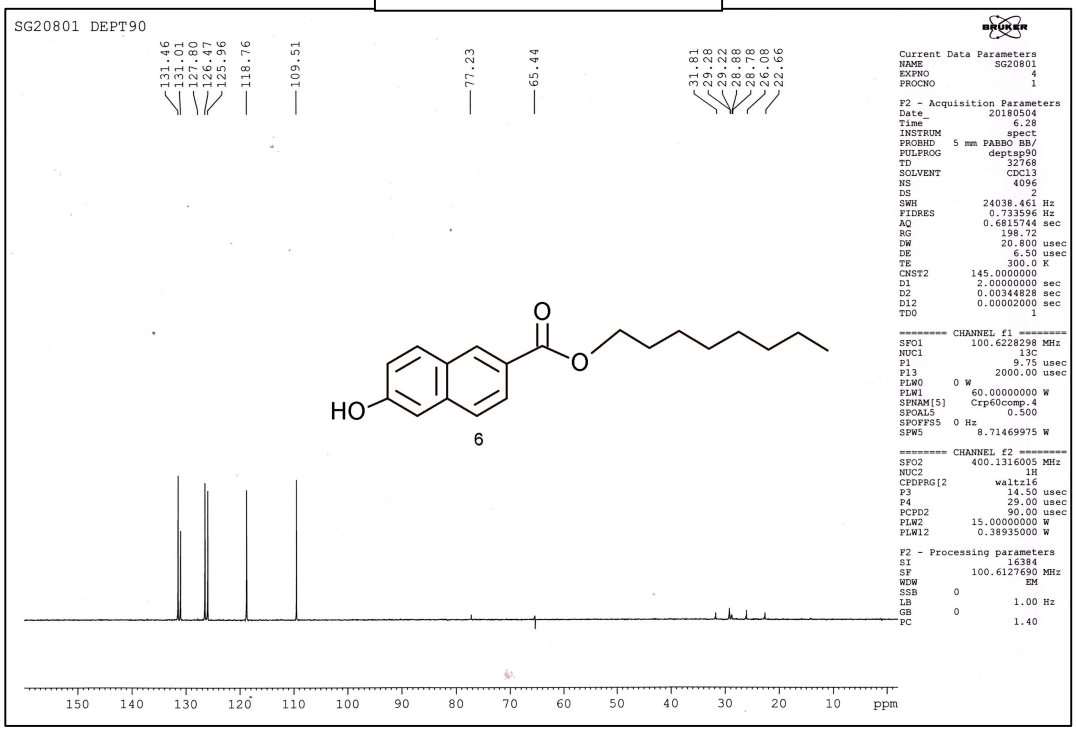
^{1}H-NMR, $CDCl_3$ (400 MHz)



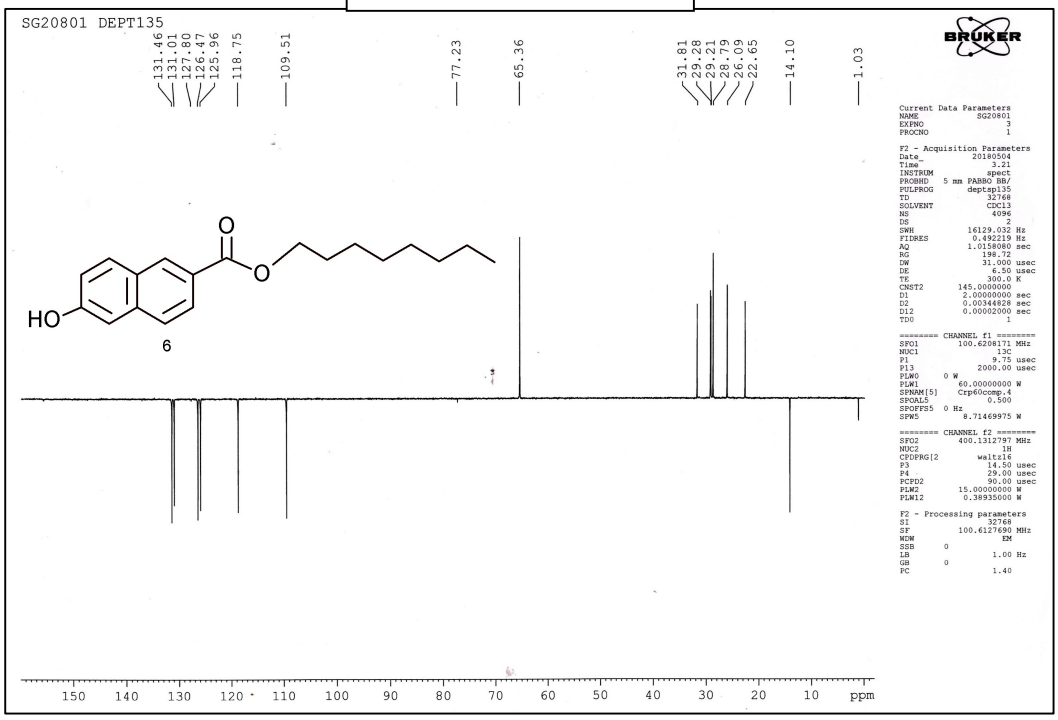
^{13}C-NMR, $CDCl_3$ (100 MHz)



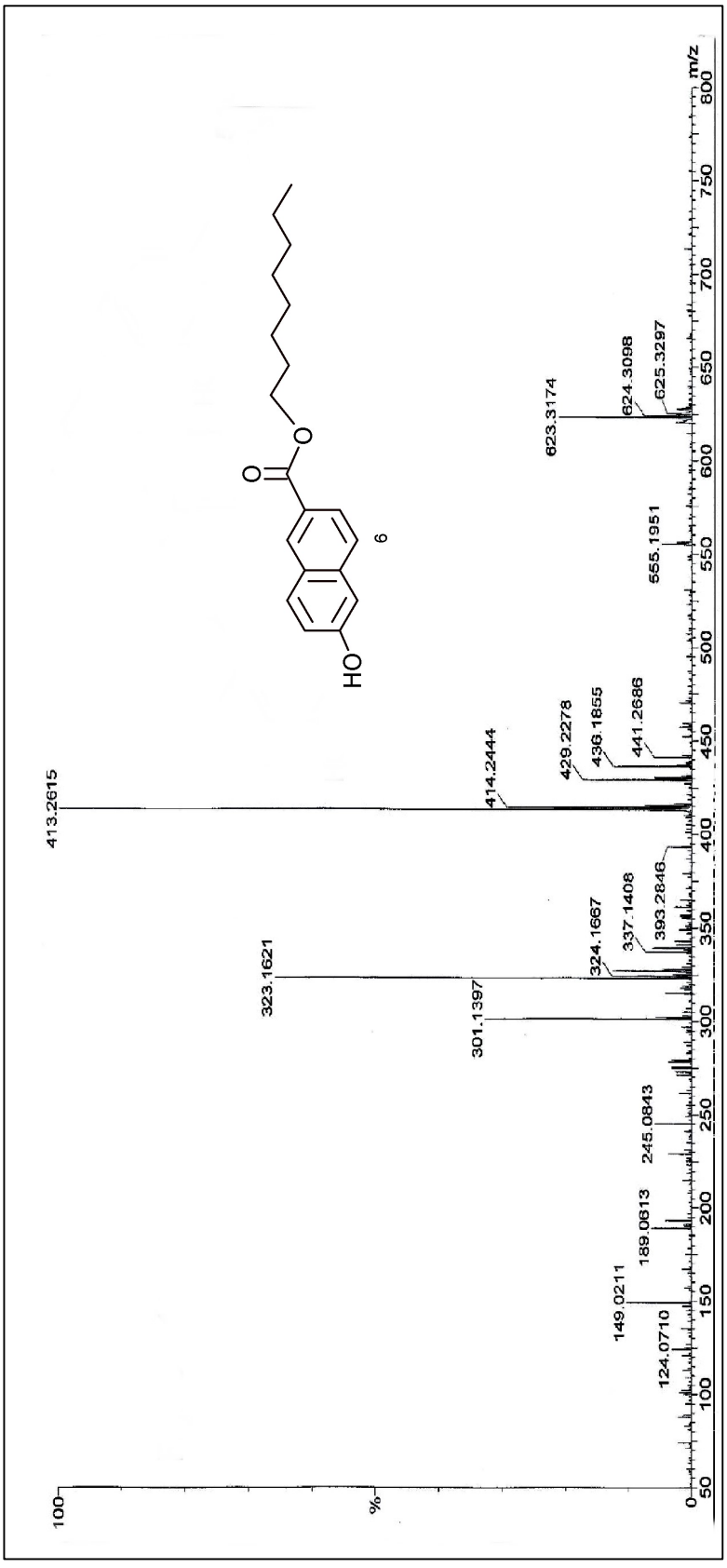
DEPT-90, $CDCl_3$ (400 MHz)



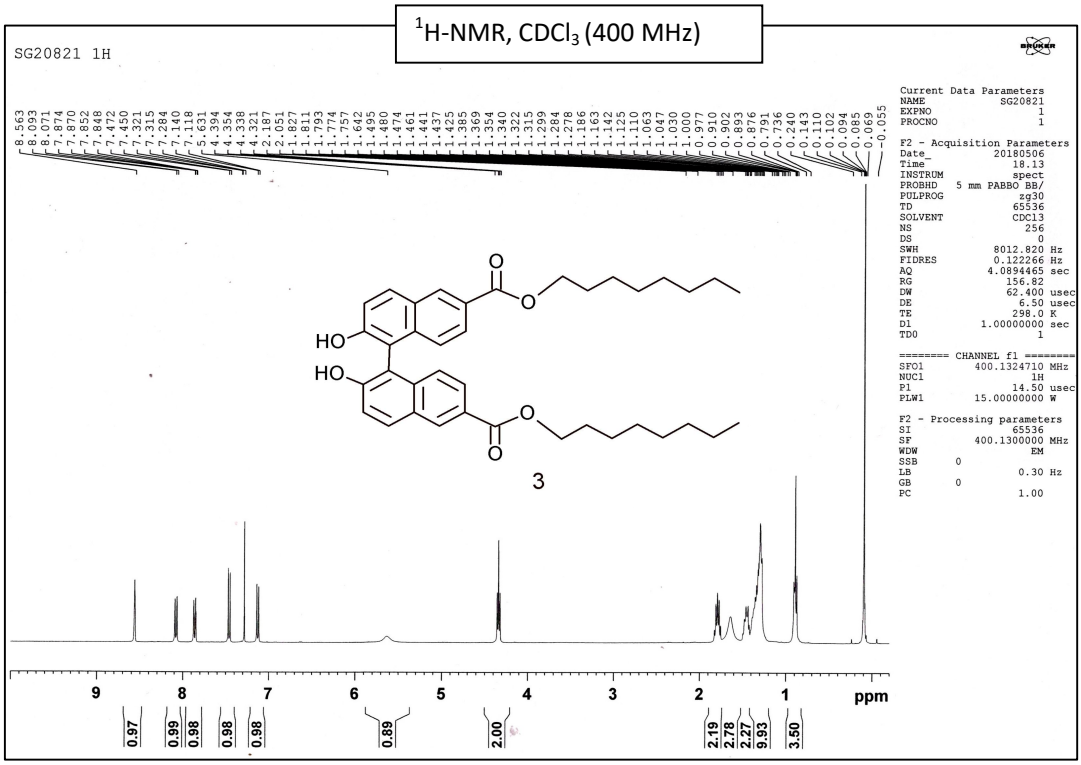
DEPT-135, $CDCl_3$ (400 MHz)



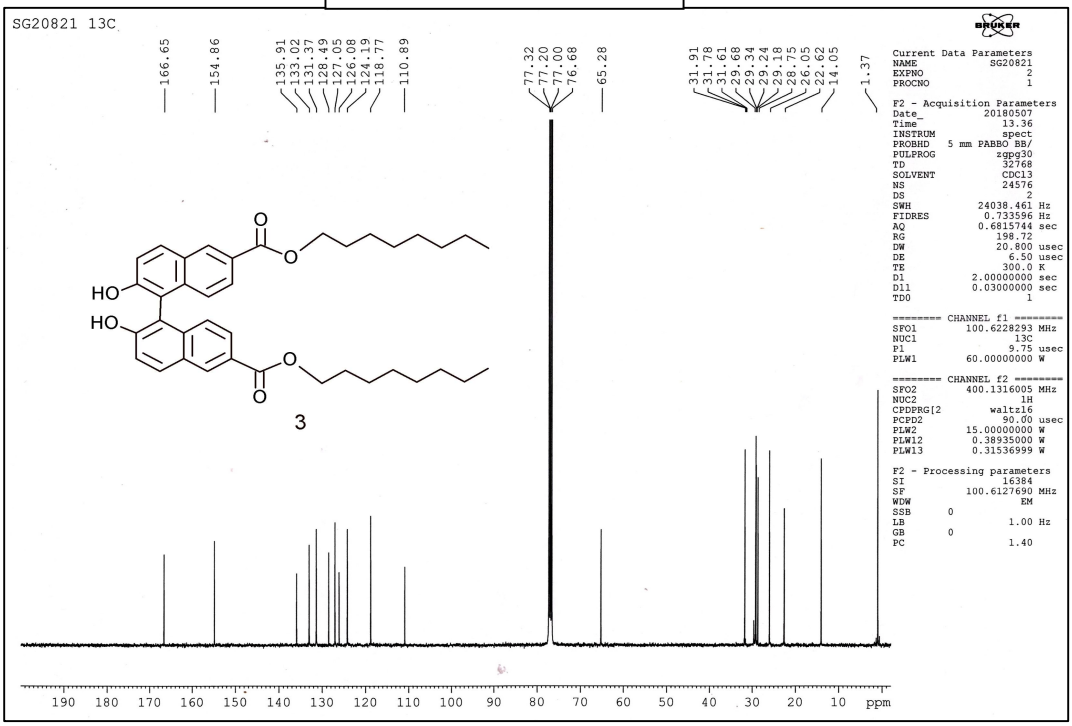
HRMS


HO
O
O
6
100
%
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z
124.0710
149.0211
189.0813
245.0843
301.1397
323.1621
324.1667
337.1408
393.2846
413.2615
414.2444
429.2278
436.1855
441.2686
555.1951
623.3174
624.3098
625.3297

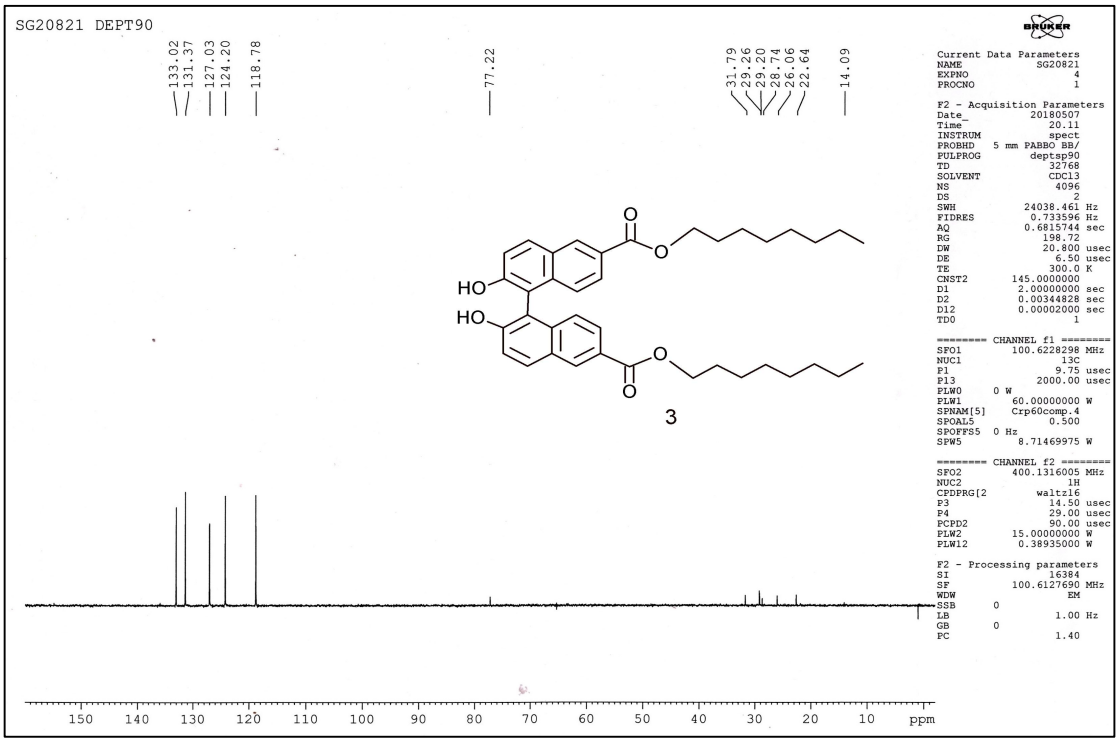
^{1}H-NMR, $CDCl_3$ (400 MHz)



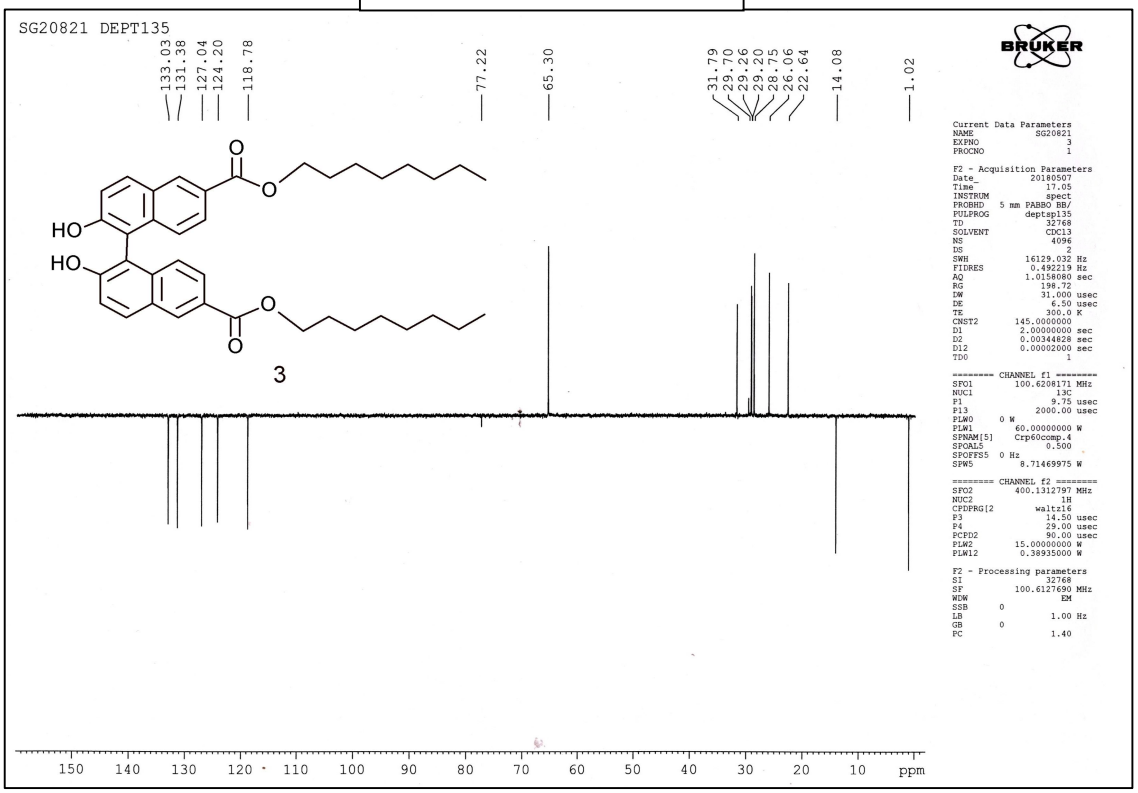
^{13}C-NMR, $CDCl_3$ (100 MHz)



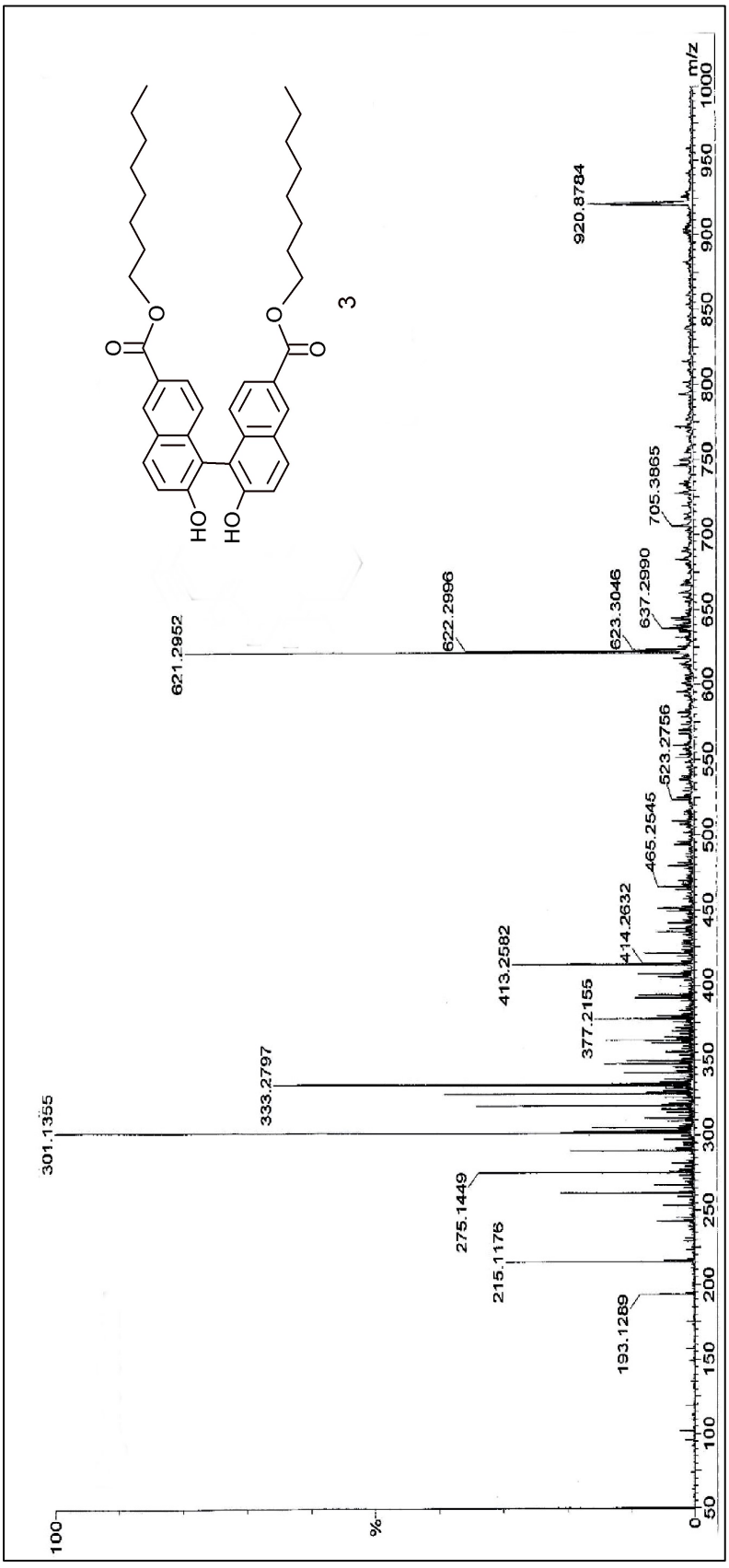
DEPT-90, $CDCl_3$ (100 MHz)



DEPT-135, $CDCl_3$ (100 MHz)



HRMS


HO
HO
O
O
O
O
3
100
%
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
m/z
301.1355
333.2797
377.2155
413.2582
414.2632
465.2545
523.2756
621.2952
622.2996
623.3046
637.2990
705.3865
920.8784
193.1269
215.1176
275.1449