Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of Dibenzoxanthene and Acridine Derivatives Catalyzed by 1,3-Disulfonic Acid Imidazolium Carboxylate Ionic Liquids

Arup Kumar Dutta, Pinky Gogoi and Ruli Borah*

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General Information

All chemicals were purchased from chemical suppliers and used without any purification. Thin layer chromatography was monitored on glass plate using Merck silica gel. The ^{1}HNMR and ^{13}CNMR were run on a JEOL 400 MHz spectrometer (ŭ in ppm) in DMSO-d_6 and $CDCl_3$ solvents. FT-IR spectra were recorded on a Nicolet Impact-410 spectrometer. The Hammett plot of the ILs was measured on an UV 2550 spectrophotometer using 4-nitroaniline as basic indicator. The p*K*a of the ionic liquids were determined by digital pH meter 802. The thermal stability of the three ionic liquids was performed on Shimadzu TGA 50. Perkin Elmer 20 analyzer was utilized for elemental analysis of all compounds. Melting points were recorded on a Buchi-545 apparatus. The ^{1}H NMR and ^{13}C NMR spectra of new ionic liquids and selected dibenzoxanthene **4** and 1,8-dioxo-octahydroacridine derivatives **5** were included in supplimentary file.

Spectral data of ionic liquids 1, 2 and 3

[DISM][CH_3COO]$^-$ (**1**): Light reddish oil, 98 % yield; FT-IR (KBr) : 3556, 3453, 3217, 1709, 1644, 1592, 1435, 1180, 1048, 878, 764, 586 cm^{-1}; ^{1}H NMR(DMSO-d6, 400 MHz): ŭ 14.17(s, 1H), 11.30 (s, 1H), 8.91 (s,1H), 7.53(s, 2H),1.79 (s, 3H) ; ^{13}C NMR (DMSO-d6, 100 MHz):ŭ 172.6, 134.7,119.8,21.5; CHN analysis(%): $C_5H_8O_8S_2N_2$,Cal. C 20.83, H 2.80, N 9.70; Found C 20.91, H 2.84, N 9.73.

[DISM][CCl_3COO]$^-$ (**2**): Dark reddish oil, 100 % yield; FT-IR (KBr): 3416, 3316, 1748, 1639, 1591, 1433, 1192, 1048, 876, 764, 688, 585 cm^{-1}; ^{1}H NMR(DMSO-d6, 400 MHz): ŭ 14.2(s, 1H); 12.77 (s,1H), 8.87(s, 1H), 7.46(s, 2H), ^{13}C NMR (DMSO-d6, 100 MHz): ŭ 163.05, 134.5, 120.03, 79.6 ;CHN analysis(%): $C_5H_5O_8S_2N_2Cl_3$,Cal. C 15.35; H 1.27, N 7.15; Found C 15.38, H1.30, N 7.19.

[DSIM][CF_3COO]$^-$ (**3**) : Reddish oil, 100 % yield; FT-IR (KBr) : 3531, 3420, 1751, 1640, 1588, 1432, 1178, 1054, 875, 765, 694, 587 cm^{-1}; ^{1}H NMR(DMSO-d6, 400 MHz): ŭ 14.14(s, 1H), 13.42 (s,1H), 8.89(s, 1H), 7.48(s, 2H); ^{13}C NMR (DMSO-d6, 100 MHz): ŭ 158.6, 134.2, 134.6, 119.7, 62.4 ; CHN analysis(%): $C_5H_5O_8S_2N_2F_3$,Cal. C 17.69, H 1.51, N 8.16; Found C17.72, H 1.54, N 8.19.

Spectral data of new derivatives of 1,8-dioxo-decahydroacrdine (4) and dibenzoxanthene (5)

[1] 3,4,6,7-Tetrahydro-3,3,6,6-tetramethylacridine-1,8(2*H*,5*H*,9*H*,10*H*)-dione (table 3, entry 6 , **4f** ,new): White ; FT-IR (KBr) cm^{-1} : 3432, 2962, 2880, 1609, 1376, 1239, 1246, 1151, 1083, 1026, 873, 809 ; ^{1}H NMR ($CDCl_3$, 400 MHz): ŭ 3.16 (s, 2H), 2.29(s, 8H), 1.05 (s, 12 H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) : ŭ 189.5, 113.5, 46.0, 31.8, 29.5, 27.1, 15.9; CHN analysis (%) : $C_{17}H_{23}NO_2$, Cal. C 74.73,H 8.42 ,N 5.13 ; Found C 74.71 , H 8.44, N 5.15.

[2] Decahydro-3,3,6,6-tetramethyl-9-(naphthalen-2-yl)acridine-1,8(5*H*,8a*H*)-dione (table 3, entry 7**, 4g,** new)**:** Grey ; FT-IR (KBr) cm^{-1} : 3768, 2956, 2875, 1666, 1462, 1361, 1195, 1144, 999, 928, 800, 698; ^{1}H NMR ($CDCl_3$, 400 MHz):ŭ 8.81(s, 1H),7.75(d, *J*=8.2Hz,1H), 7.62-7.60(m, 2H), 7.44(m, 1H), 7.30 (m,1H), 7.20(s, 1H), 5.52(s, 1H), 2.5(s, 4H), 2.22-2.06(m, 4H), 1.19(s, 6H), 0.95 (s, 6H);^{13}C NMR ($CDCl_3$, 100 MHz) : ŭ 196.7, 162.2, 133.6, 131.7, 128.2, 127.5, 125.9, 125.7, 124.9, 116.9, 50.7, 41.0, 32.3, 29.4, 27.4; CHN analysis (%) : $C_{27}H_{29}NO_2$, Cal. C 81.2,. H 7.27, N 3.51; Found C 81.18, H 7.3, N 3.50.

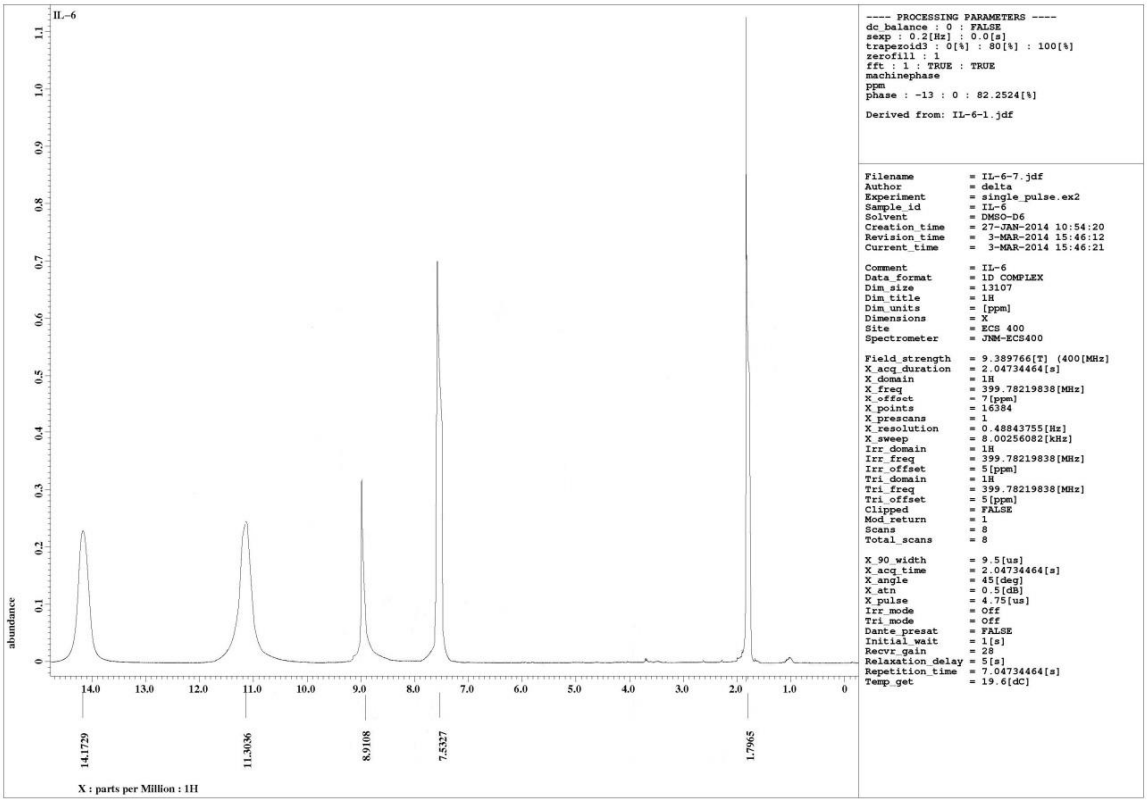
[3] 3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-styrylacridine-1,8 (2*H*,5*H*,9*H*,10*H*)-dione) (table 3, entry 8, **4h**): Grey ; FT-IR (KBr) cm^{-1} : 3429, 2934, 1640, 1628, 1540, 1392, 1078, 1026, 874, 773; ^{1}H NMR ($CDCl_3$, 400 MHz):ŭ 7.22-7.27 (m, 5H), 6.27-6.31(m, 2H), 4.41(d, *J*= 5.5 Hz,1H), 2.44(s, 4H), 2.29(s, 4H), 1.12(s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) :ŭ 196.5, 163.1, 137.2, 131.3, 130.4, 128.3, 127.1, 126.3, 50.8, 40.9, 32.2, 29.2, 27.9, 27.6; CHN analysis (%) : $C_{25}H_{29}NO_2$, Cal. C 80, H 7.73,N 3.73; Found C 80.12, H 7.76, N 3,75.

[4] 14-Dihydro-dibenzo[a,j] xanthene (table 4, entry 6, **5f** ,new): White **;** FT-IR (KBr) cm^{-1} : 3057, 1589, 1510, 1455, 1396, 1240, 1171, 1069, 955, 854, 802, 744; ^{1}H NMR ($CDCl_3$, 400 MHz):ŭ 8.02 (d, *J*=8.2Hz,2H), 7.85(d, *J*=7.8Hz,2H), 7.76(d, *J*=9.2Hz,2H), 7.63(m,2H), 7.46(t, *J*=7.3Hz,2H), 7.31(d, *J*=8.7Hz,2H), 4.56(s,2H) ; ^{13}C NMR ($CDCl_3$, 100 MHz) :ŭ 147.9, 132.2, 130.2, 128.5, 128.4, 126.8, 124.2, 122.4, 117.8, 111.0, 22.4; CHN analysis (%) : $C_{21}H_{14}O$, Cal. C 89.36, H 4.97; Found C 89.38, H 5.01.

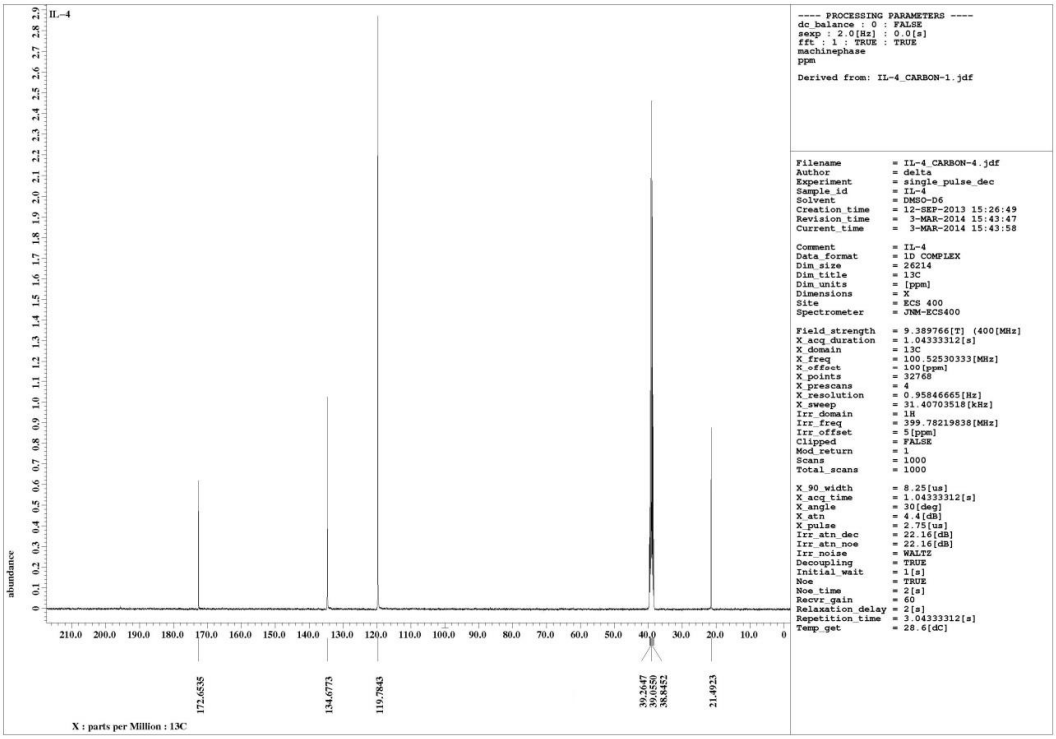
[5] 14-Naphthyl-14*H*-dibenzo [a.j] xanthene(table 4,entry 7, **5g** ,new) :Brown solid ; FT-IR (KBr) cm^{-1} : 3058, 2378, 1591, 1509, 1398, 1356, 1242, 1158, 1070, 959, 807, 739; ^{1}H NMR ($CDCl_3$, 400 MHz): ŭ 8.47 (d, *J*=8.7Hz,2H),8.01 (s,1H),7.75-7.78(m,5H), 7.48-7.58(m, 7H), 7.27-7.37(m,4 H), 6.63(s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) :ŭ 148.7, 142.3, 133, 132, 131.1, 128.9, 128.8, 127.8, 127.4, 126.8, 126.5, 124.2, 122.7, 117.9, 117, 38.3; CHN analysis (%): $C_{31}H_{20}O$, Cal. C, 91.18, H 4.9; Found C 91.16, H 4.93.

Spectra of ionic liquids:

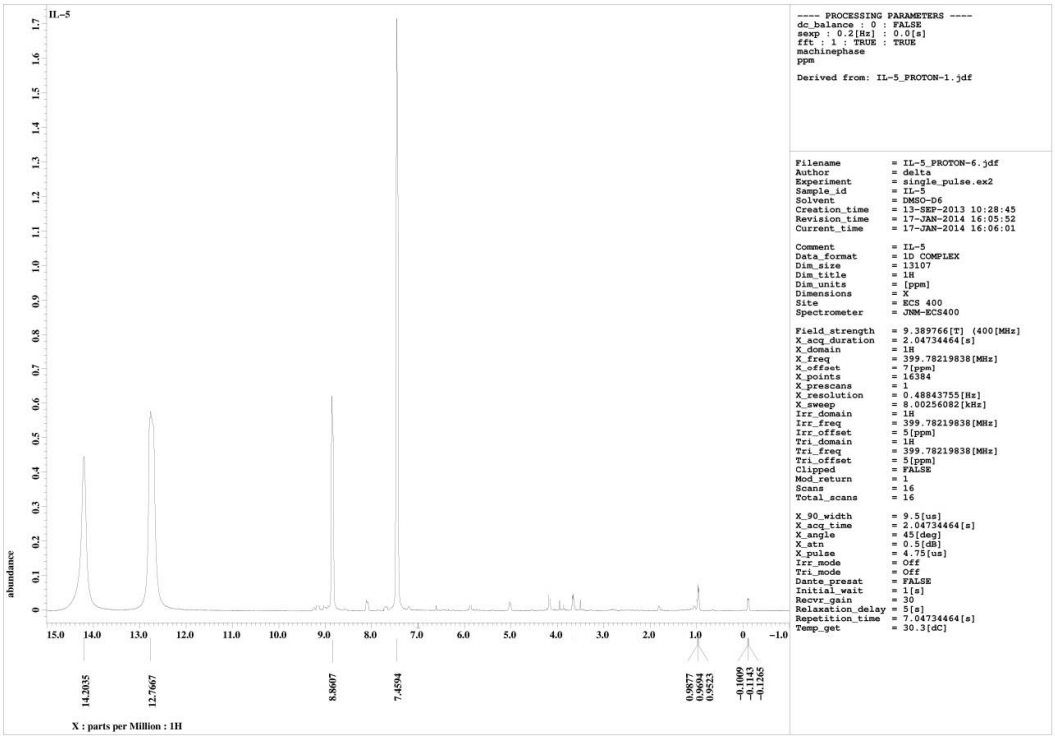
^{1}H NMR [DSIM][CH_3COO]$^-$ **1**



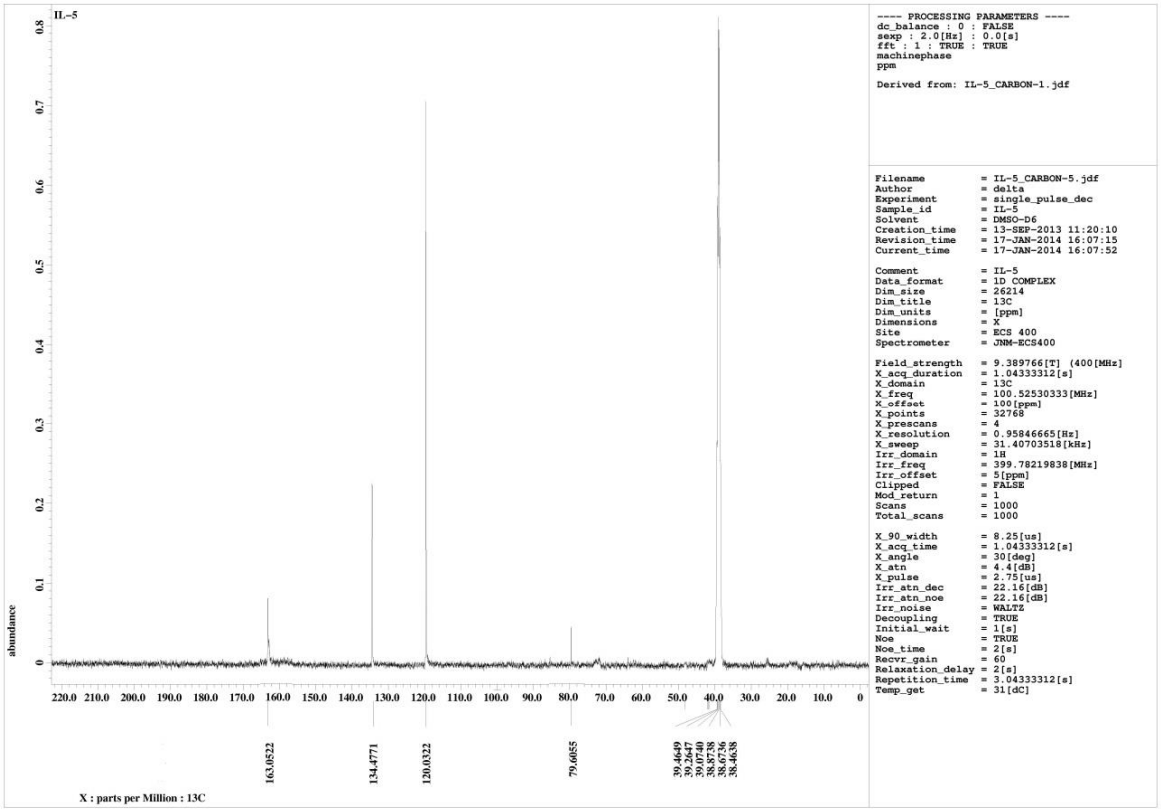
^{13}C NMR [DSIM][CH_3COO]$^-$ **1**



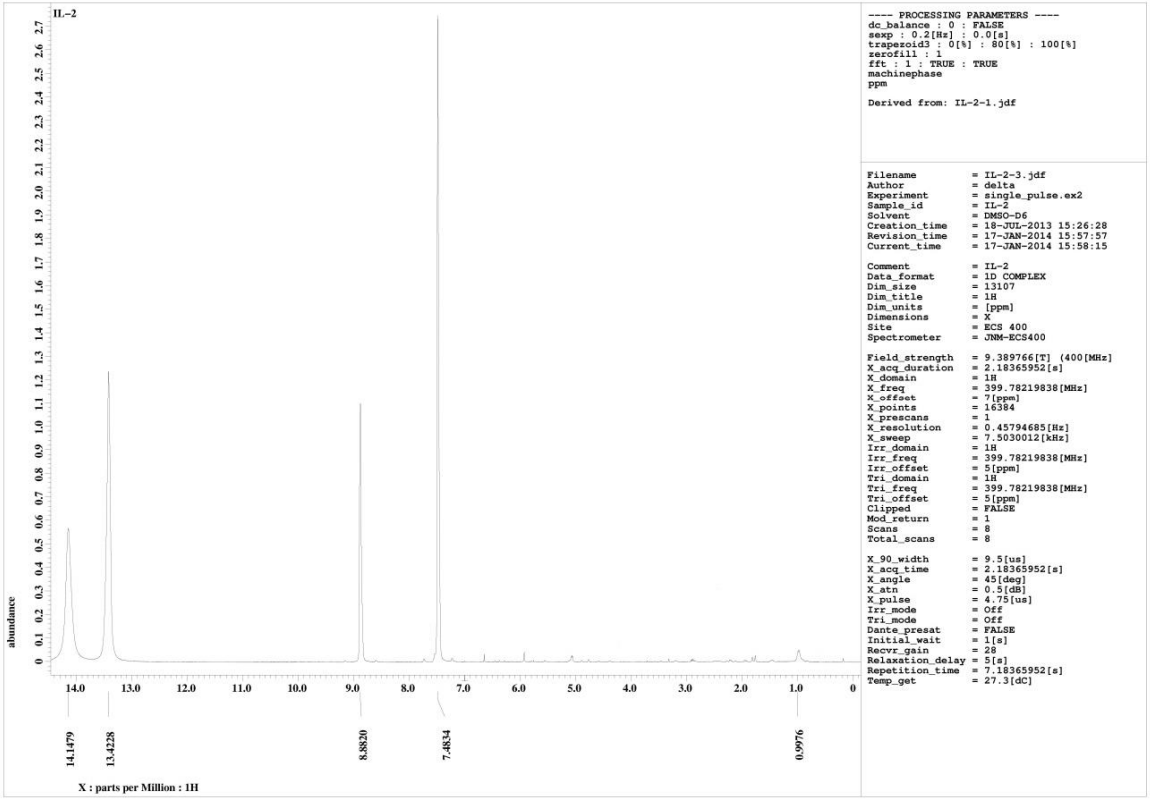
^{1}H NMR [DSIM][CCl_3COO]$^{-}$ **2**



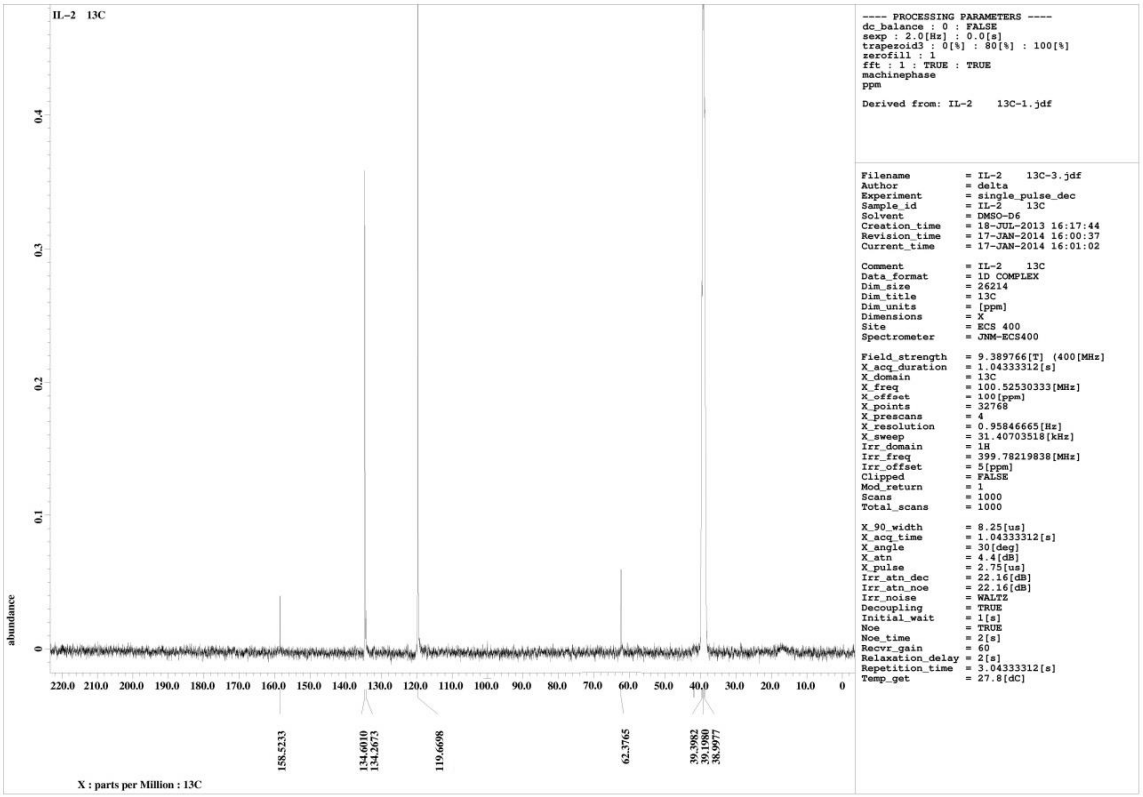
^{13}C NMR [DSIM][CCl_3COO]$^-$



^{1}H NMR [DSIM][CF_3COO]$^{-}$ **3**

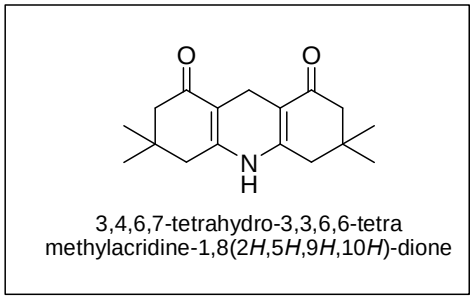


^{13}C NMR [DSIM][CF_3COO]$^-$



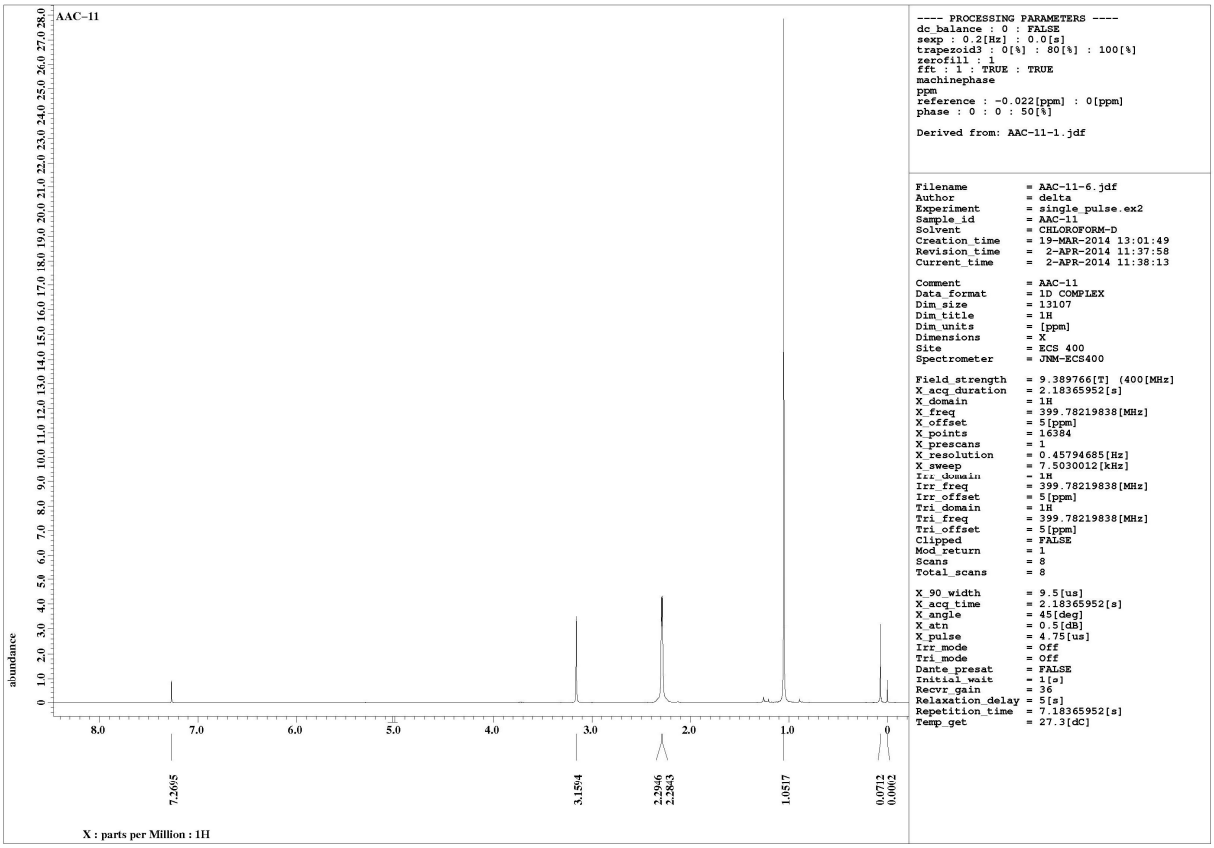
Spectra of 1, 8-dioxooctahydroacridine 4 and dibenzoxanthene derivatives 5 :

Table 3, entry 6 **4f**

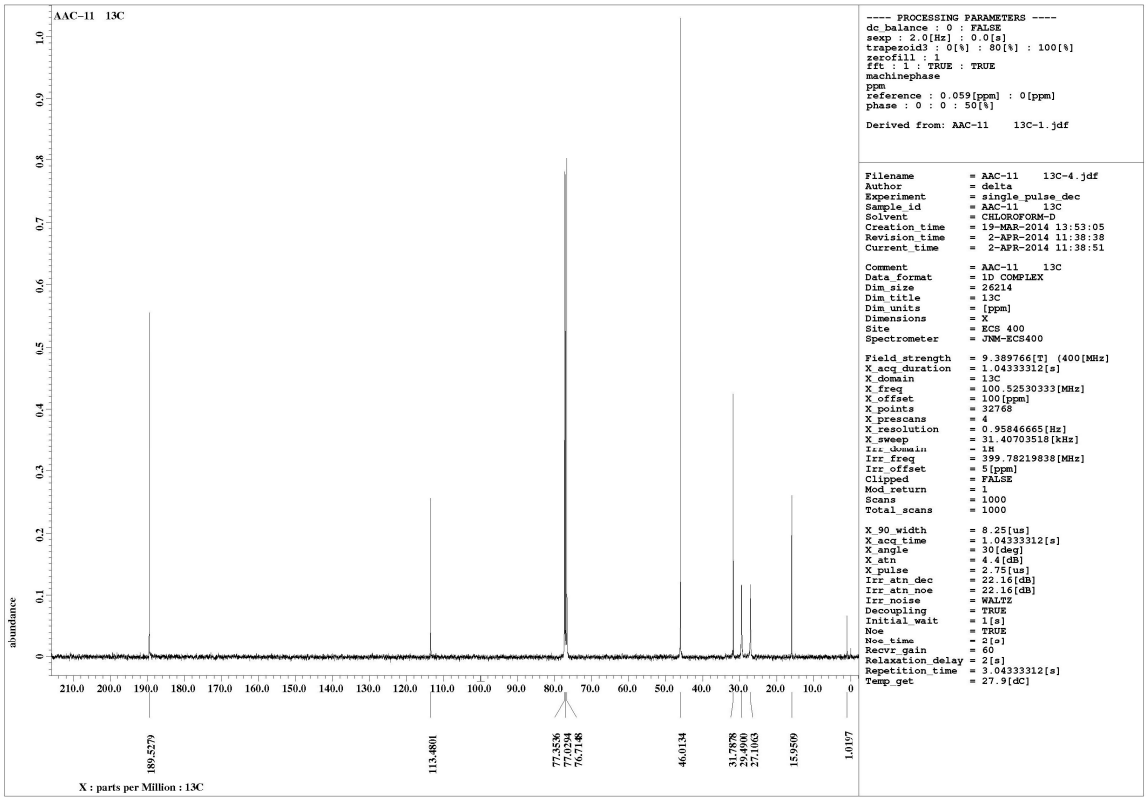


3,4,6,7-tetrahydro-3,3,6,6-tetra methylacridine-1,8(2*H*,5*H*,9*H*,10*H*)-dione

^{1}H-NMR



^{13}C-NMR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29.4990
27.1063
15.9509
1.0197
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ppm
reference : 0.059[ppm] : 0[ppm]
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X_sweep = 31.40703518[kHz]
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X_angle = 30[deg]
X_atn = 4.4[dB]
X_pulse = 2.75[us]
Irr_atn_dec = 22.16[dB]
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Irr_noise = WALTZ
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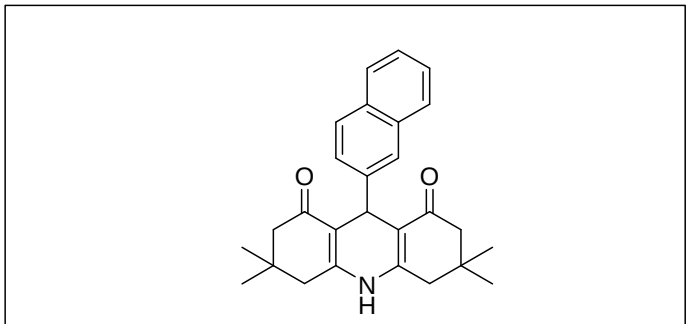
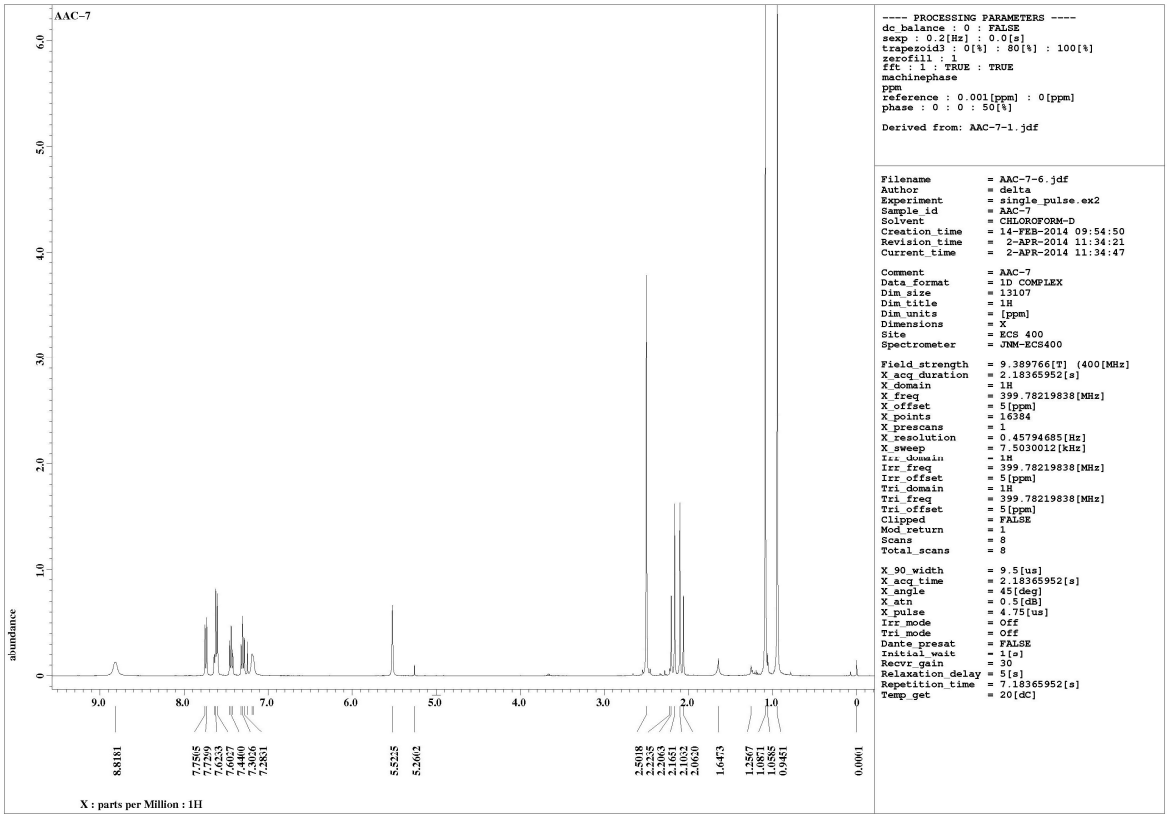
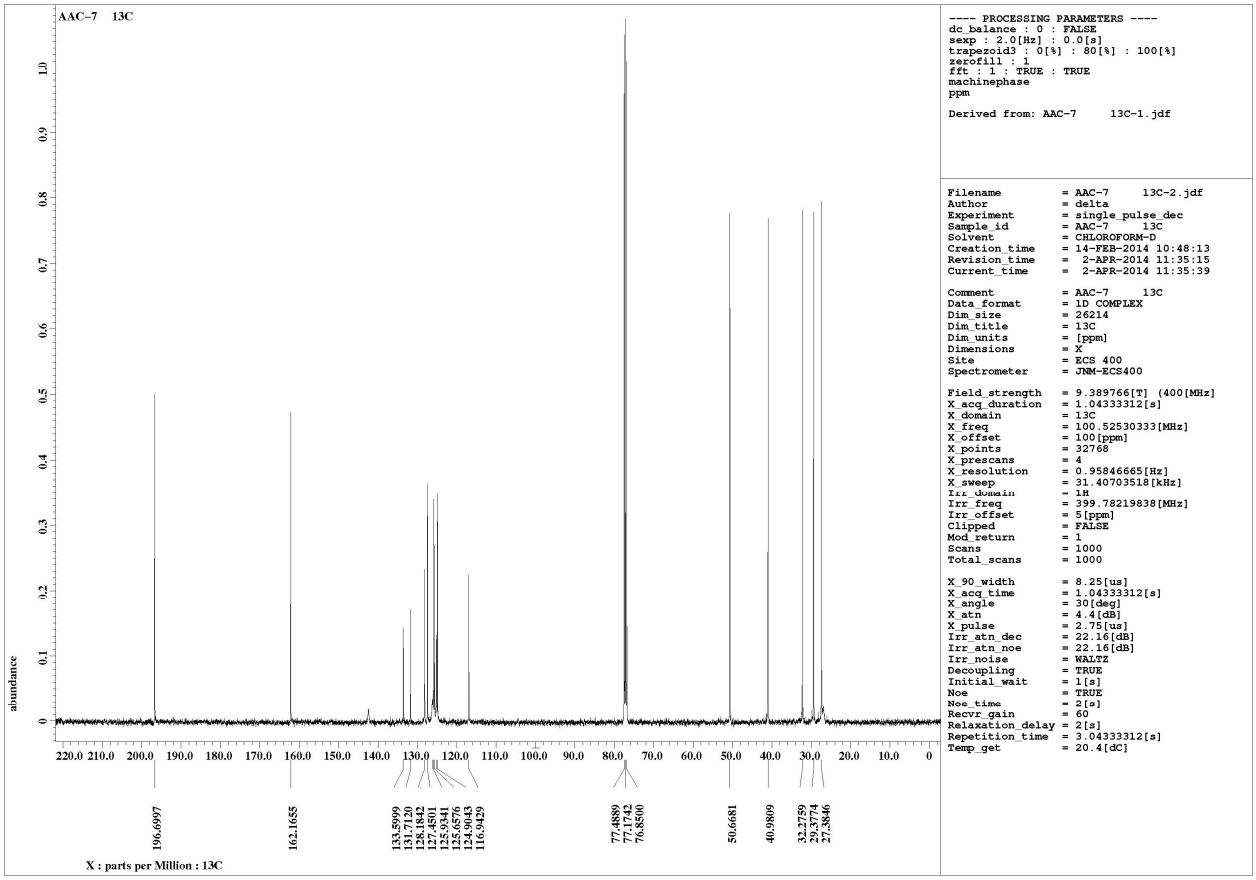


3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(naphthalen-2-yl) acridine-1,8(2*H*,5*H*,9*H*,10*H*)-dione

^{1}H-NMR



^{13}C-NMR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0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
196.6997
162.1655
133.5999
131.7120
128.1842
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32.2759
29.3774
27.3846
X : parts per Million : 13C
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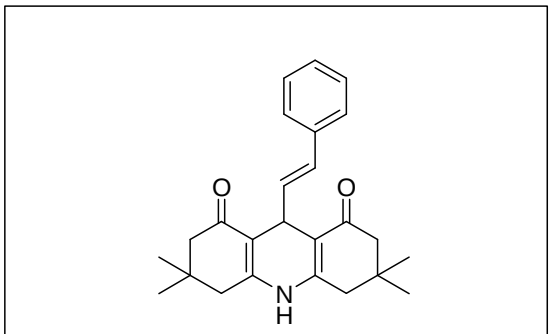
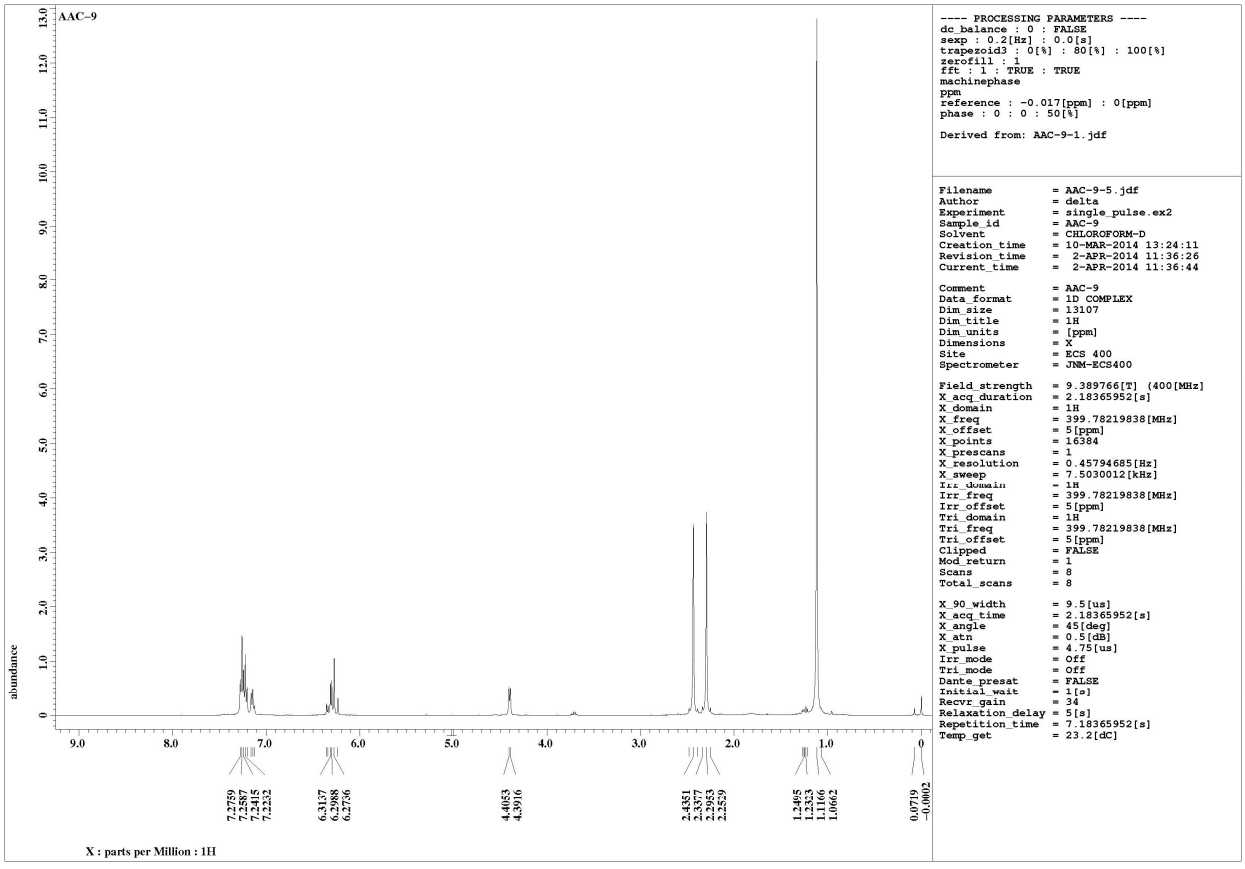
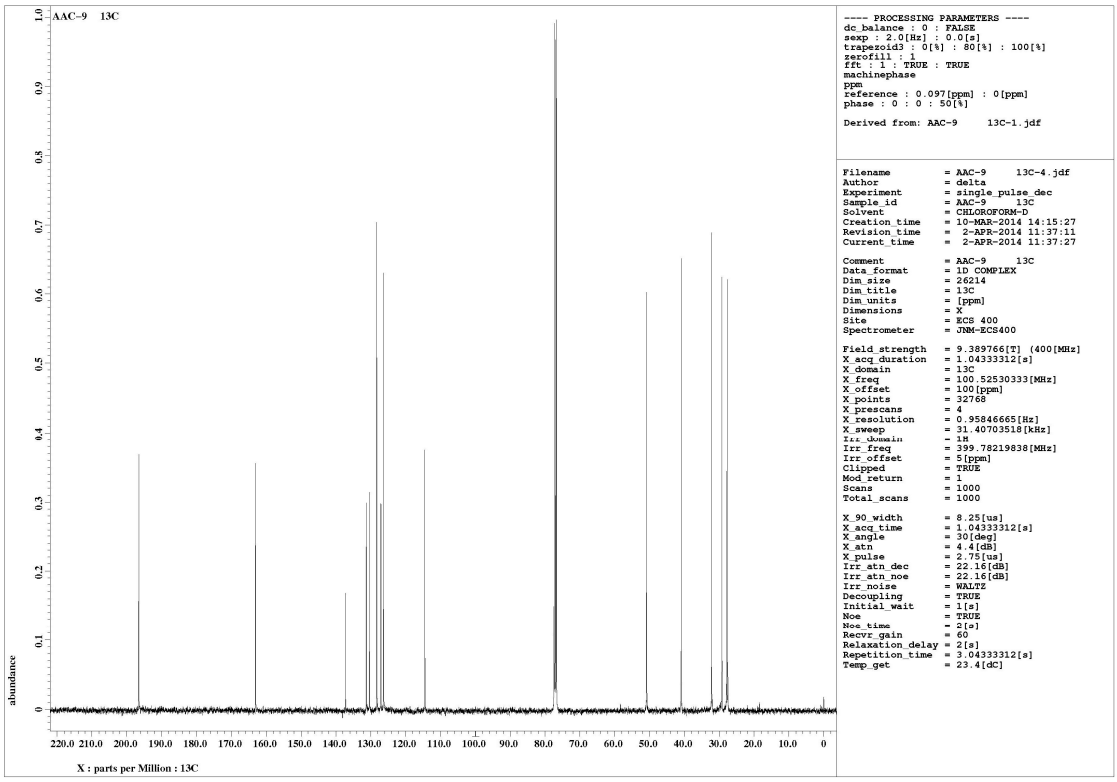


3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-
9-styrylacridine-1,8(2*H*,5*H*,9*H*,10*H*)-dione

^{1}H-NMR



^{13}C-NMR


AAC-9 13C
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ppm
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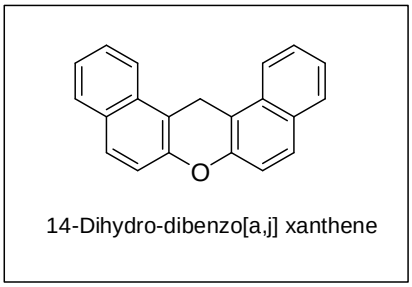
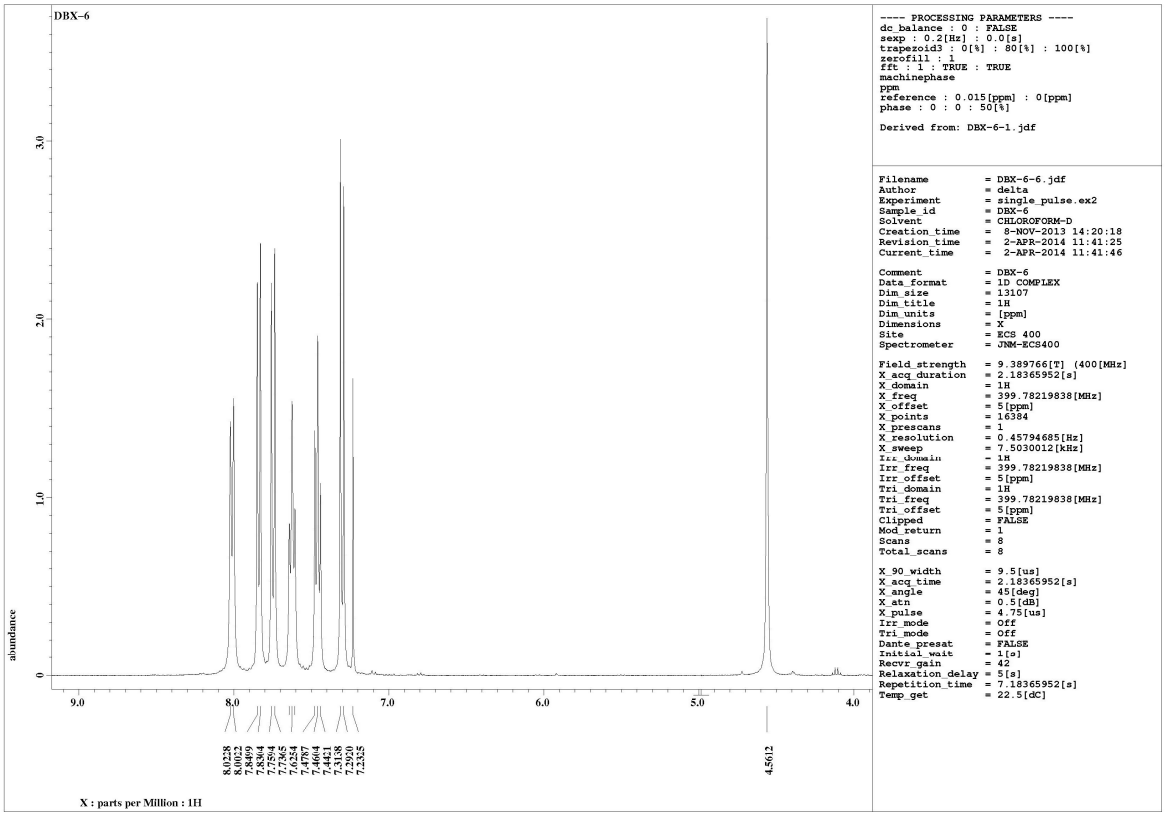
Table 4, entry 6, **5f**

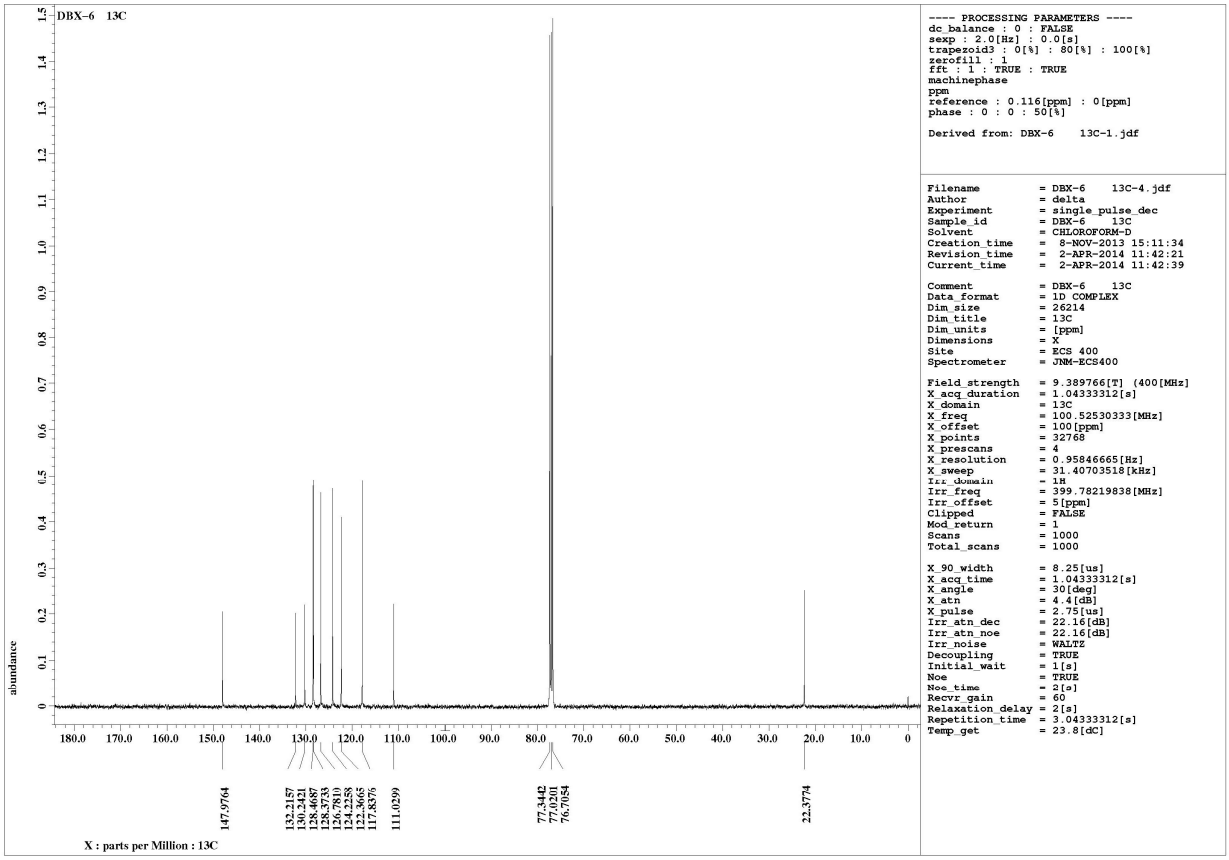


14-Dihydro-dibenzo[a,j] xanthene

^{1}H-NMR



^{13}C-NMR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147.9764
133.2157
130.7431
130.4687
128.3733
126.7810
124.2258
122.3665
117.8375
111.0299
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77.0301
76.7054
22.3774
X : parts per Million : 13C
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ppm
reference : 0.116[ppm] : 0[ppm]
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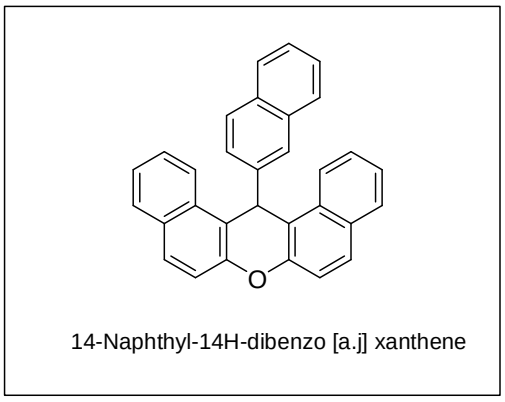
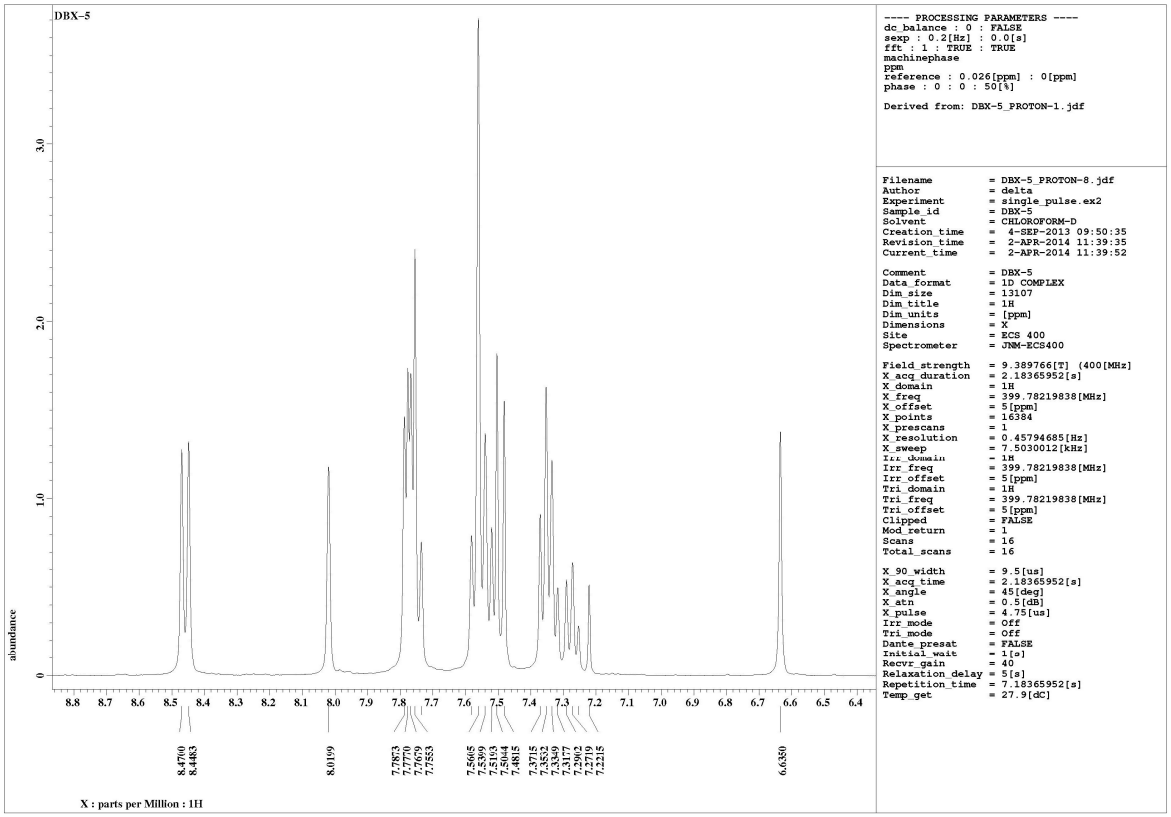
Site = ECS 400
Spectrometer = JNM-ECS400
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 8.25[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.4[dB]
X_pulse = 2.75[us]
Irr_atn_dec = 22.16[dB]
Irr_atn_noe = 22.16[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 23.8[dC]

Table 4, entry 7, **5g**

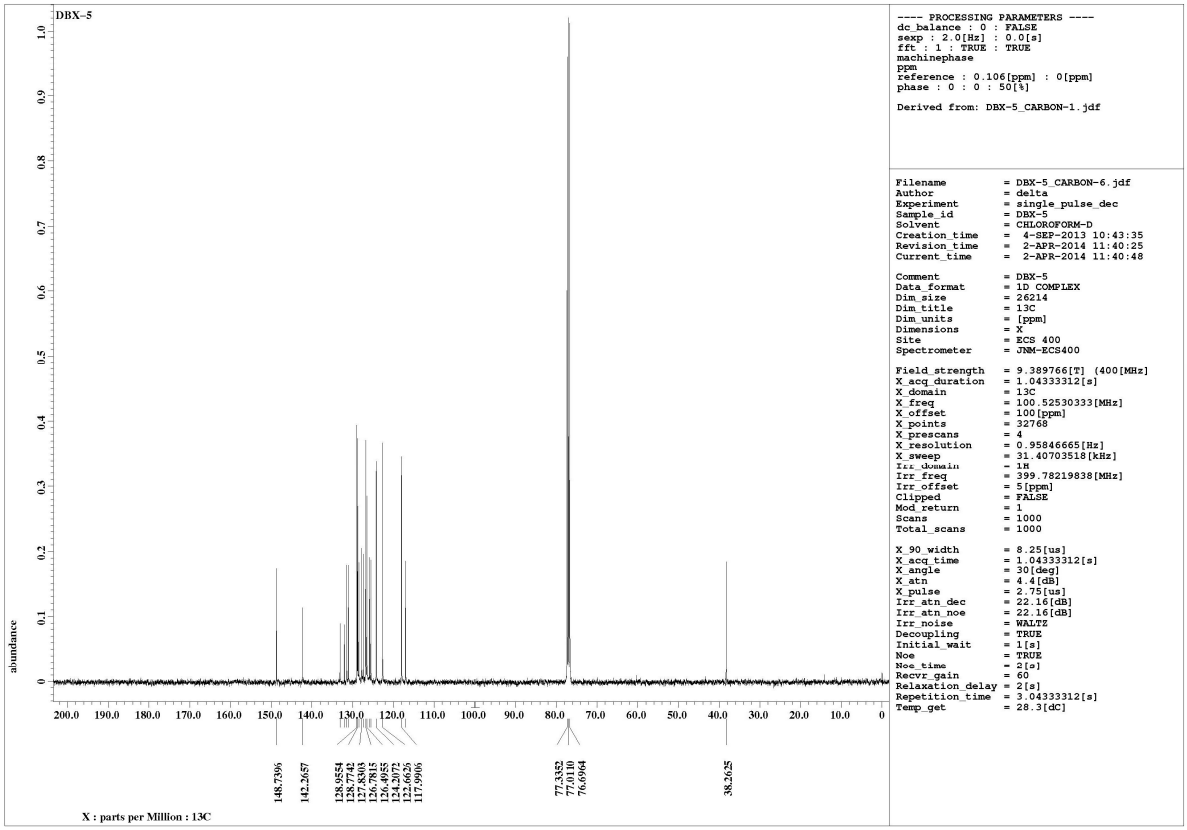


14-Naphthyl-14H-dibenzo [a.j] xanthene

^{1}H-NMR



^{13}C-NMR


DBX-5
abundance
X : parts per Million : 13C
148.7396
142.2657
128.9554
128.7742
127.8303
126.7815
126.4955
124.2072
122.6625
117.9906
77.3352
77.0110
76.6964
38.2625
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
fft : 1 : TRUE : TRUE
machinephase
ppm
reference : 0.106[ppm] : 0[ppm]
phase : 0 : 0 : 50[%]
Derived from: DBX-5_CARBON-1.jdf
Filename = DBX-5_CARBON-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = DBX-5
Solvent = CHLOROFORM-D
Creation_time = 4-SEP-2013 10:43:35
Revision_time = 2-APR-2014 11:40:25
Current_time = 2-APR-2014 11:40:48
Comment = DBX-5
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECS 400
Spectrometer = JNM-ECS400
Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain = 13C
X_freq = 100.52530333[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.95846665[Hz]
X_sweep = 31.40703518[kHz]
Irr_domain = 1H
Irr_freq = 399.78219838[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 8.25[us]
X_acq_time = 1.04333312[s]
X_angle = 30[deg]
X_atn = 4.4[dB]
X_pulse = 2.75[us]
Irr_atn_dec = 22.16[dB]
Irr_atn_noe = 22.16[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 3.04333312[s]
Temp_get = 28.3[dC]