Supporting Information

Trityl-based alkoxyamines as potential NMP controllers and spin-labels.

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Table 1SI. Simulation parameters of EPR spectra for Figures 2SI and 3SI

Biradical	T, K	J, G	ΔJ, G	biradical lwpp[a,b], G	free trityl lwpp[a,c], G	free nitroxide lwpp[a,c], G	a_n, G	a_p, G
1•	273	55	30	1.5	0.45[d]	1.5	15.4[e]	-
	283	61	24	1.2				
	293	62	25.5	1.2				
	303	63	30	1.2				
	313	67	30	1				
	323	70	30	1				
	333	70	40	0.8				
	343	75	40	0.8				
	353	75	40	0.8				
3•	283	160	130	1	0.45[d]	2	13.6[f]	44.9[f]
	293	160	130	1				
	303	170	130	1				
	313	180	150	1				
	323	200	150	1				
	333	220	150	1				

[a] lwpp – peak-to-peak line width; [b] Lorentzian line shape; [c] Gaussian line shape. [d] g = 2.00281. [e] g = 2.00595. [f] g = 2.0058

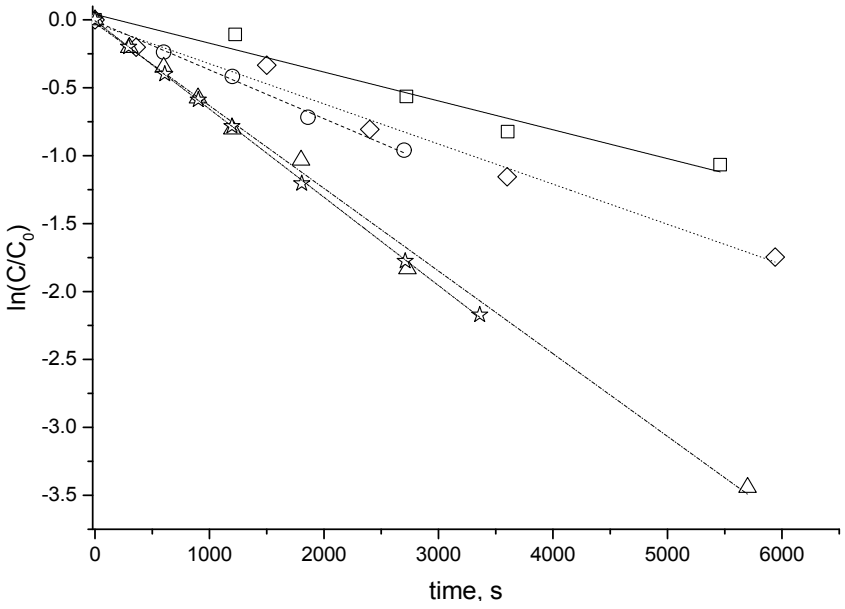
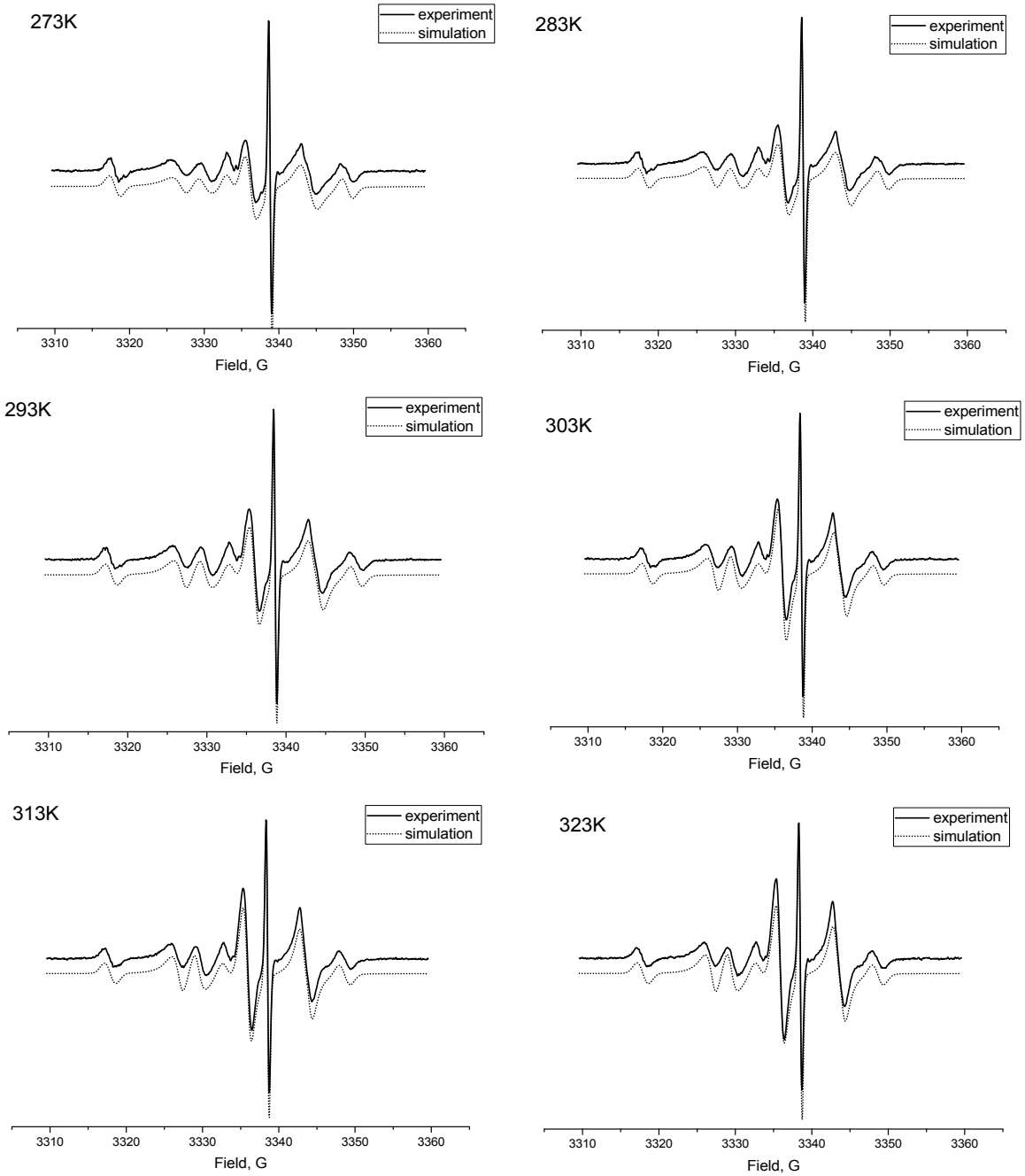
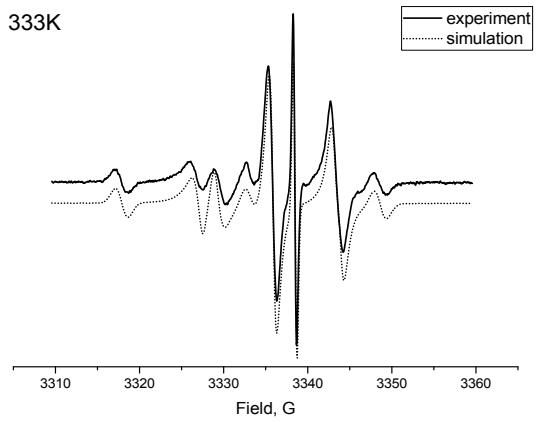
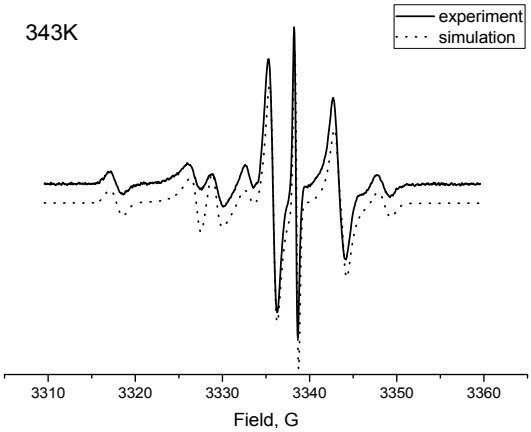


Figure 1SI. Kinetics of alkoxyamine homolysis: ◊ – ***1*** at 398K; □ – ***2*** at 353K; ○ – ***3*** at 373K; Δ – ***4*** at 373K, star – ***5*** at 373K

Figure 2SI. The temperature dependence of the EPR signal from the reaction mixture of ***2*** (after thermolysis at 373K for 5h): full line – experimental spectrum; dotted line – simulated spectrum




333K
experiment
simulation
3310
3320
3330
3340
3350
3360
Field, G


343K
experiment
simulation
3310
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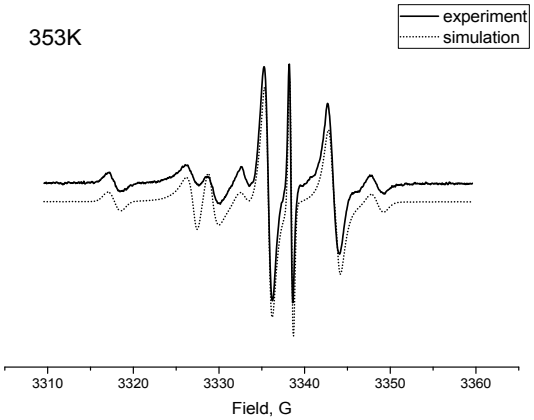
Field, G


353K
experiment
simulation
3310
3320
3330
3340
3350
3360
Field, G

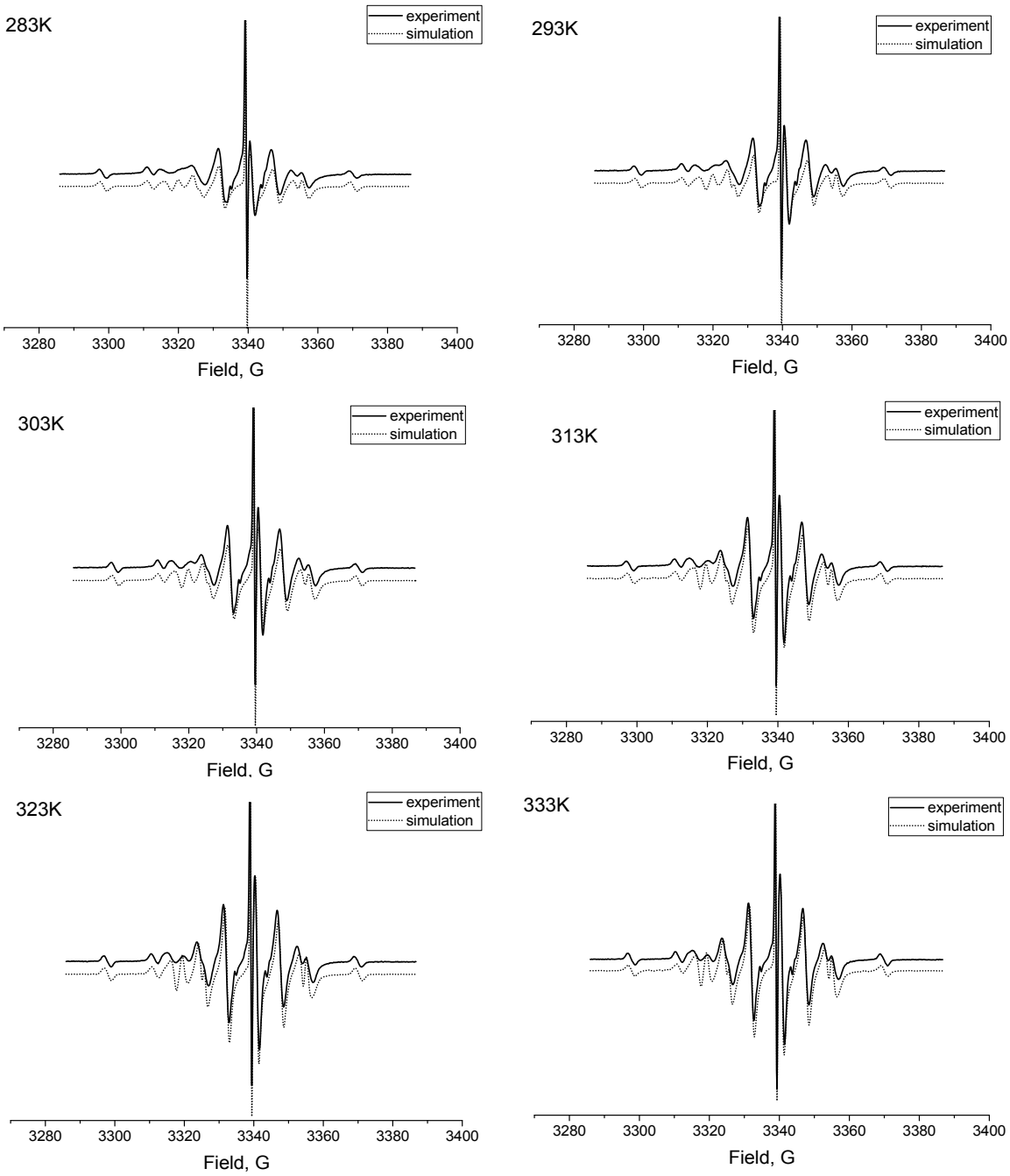


Figure 3SI. The temperature dependence of the EPR signal from the reaction mixture of ***3*** (after thermolysis at 373K for 5h): full line – experimental spectrum; dotted line – simulated spectrum

Figure 4SI. ^{1}H-NMR and ^{13}C-NMR spectral data for alkoxyamine 6

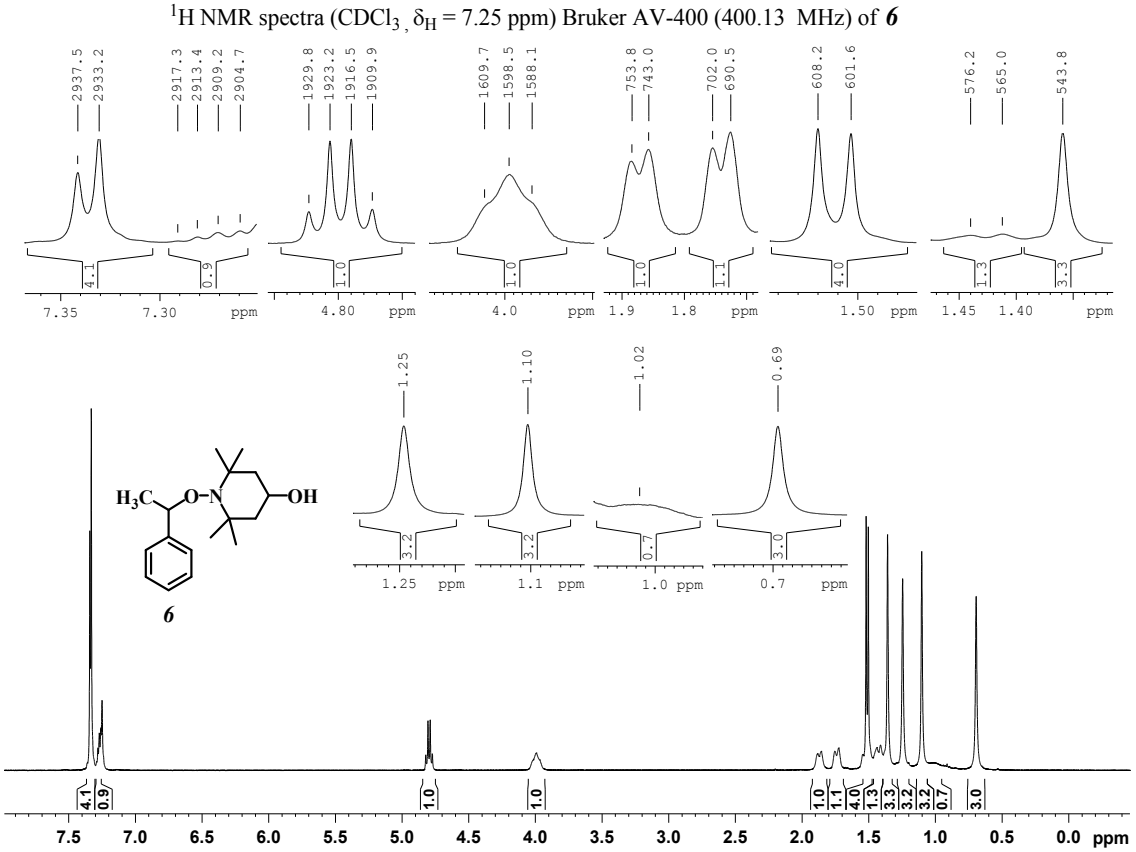


Figure S4.1 ^{1}H-NMR spectral data for alkoxyamine **6**

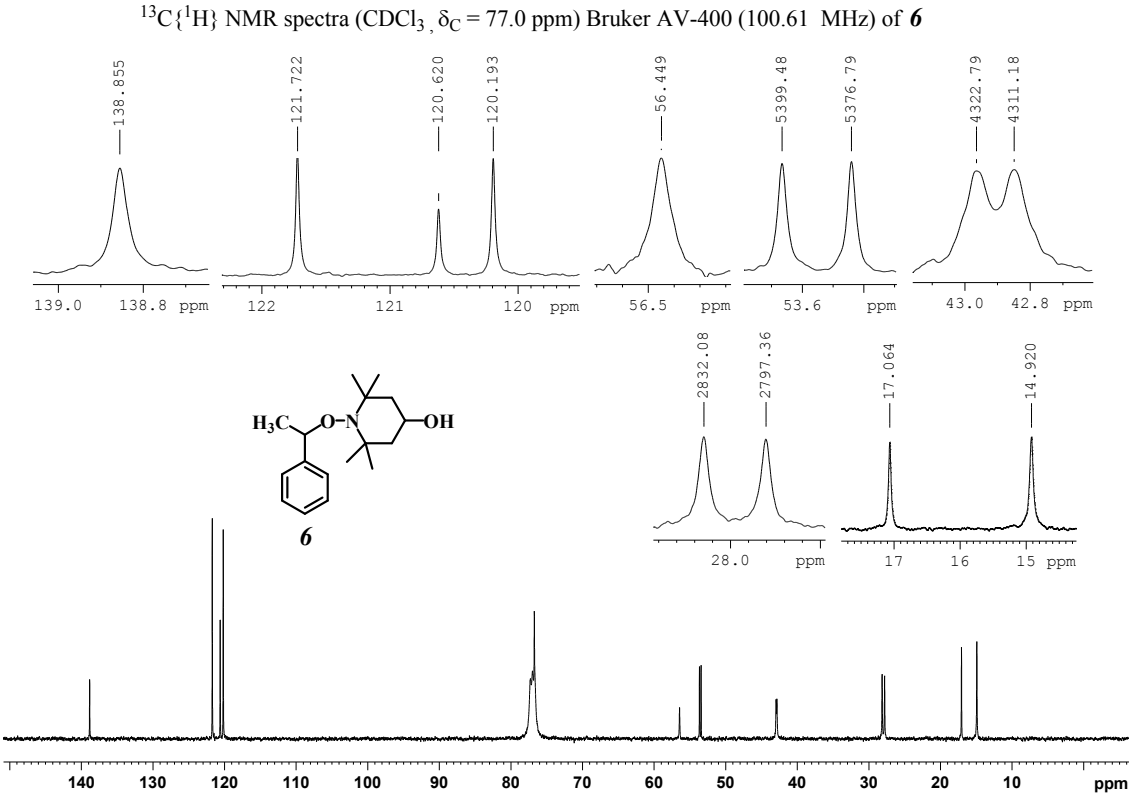


Figure S4.2 ^{13}C-NMR spectral data for alkoxyamine **6**

Figure 5SI. HR MS, ^{1}H-,^{13}C-NMR and FT IR spectral data for alkoxyamine 7

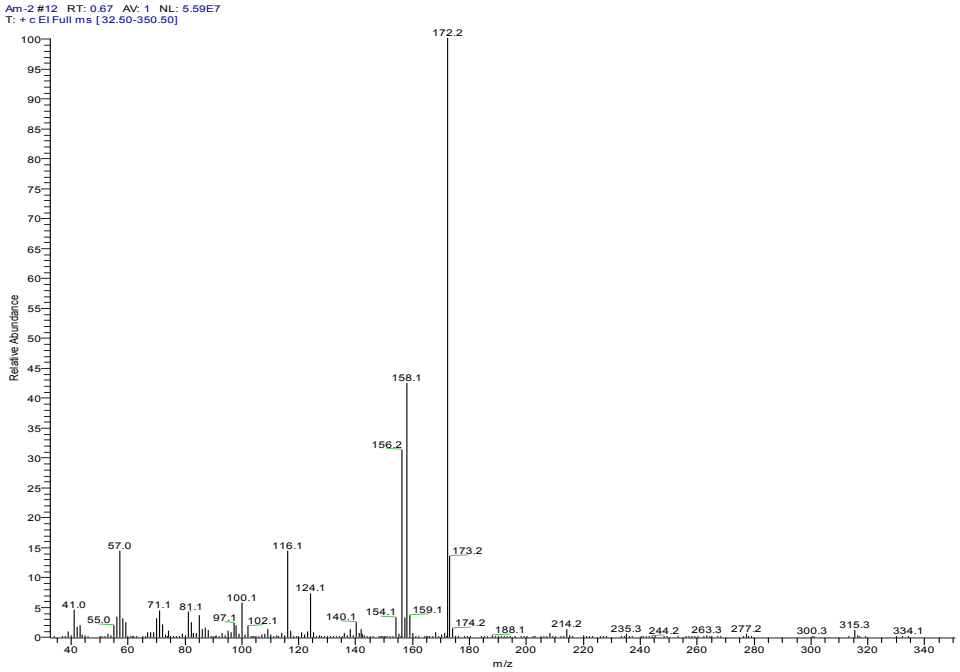


Figure S5.1 HR MS (ESI) spectrum of alkoxyamine **7**: calcd. for $C_{17}H_{33}O_4N$ [M^+] 315.2404, found 315.2408

^{1}H NMR spectra ($CDCl_3$, δ_H = 7.25 ppm) Bruker AV-400 (400.13 MHz) of ***7***

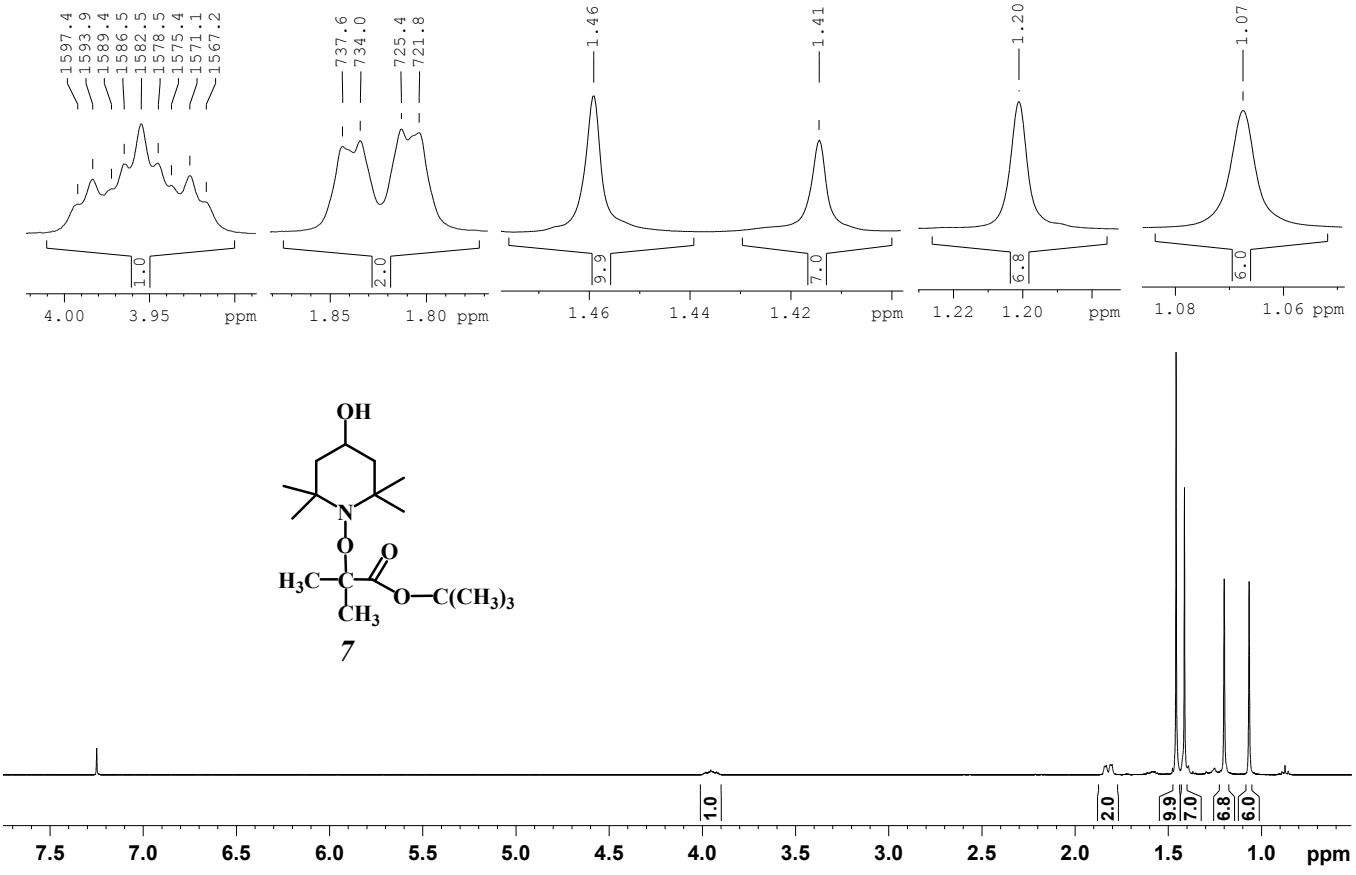


Figure S5.2 ^{1}H-NMR spectral data for alkoxyamine **7**

$^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, δ_C = 77.0 ppm) Bruker AV-400 (100.61 MHz) of ***7***

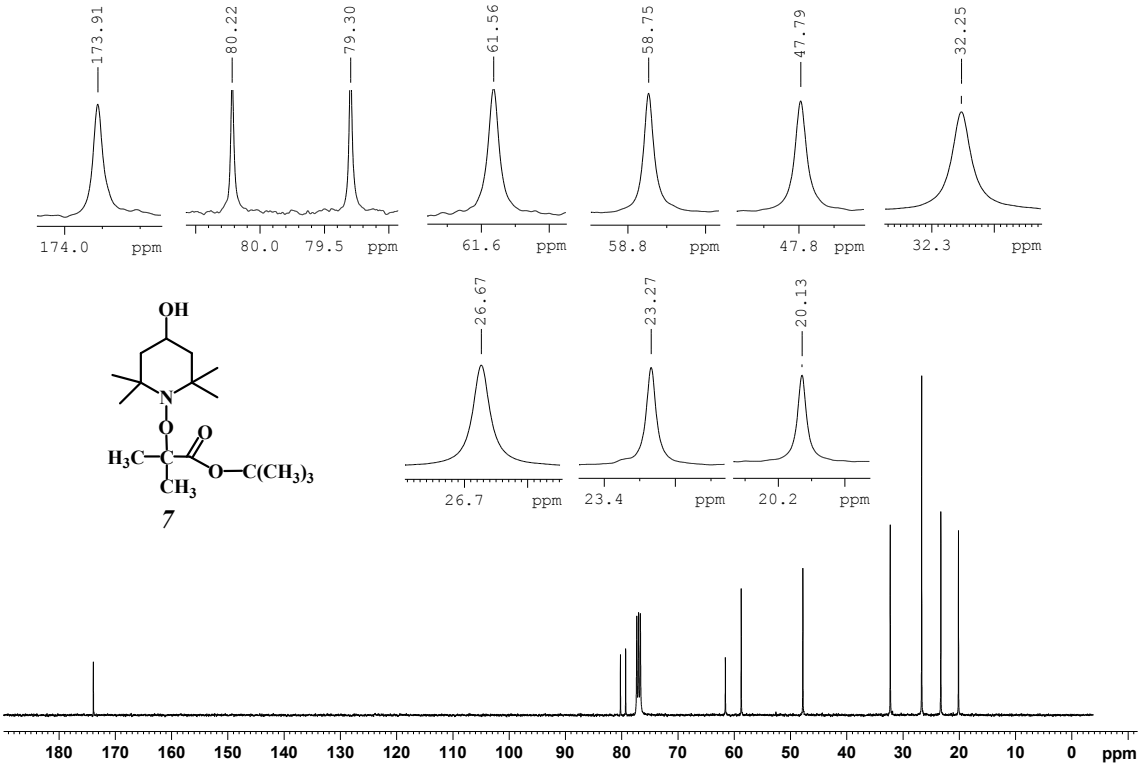
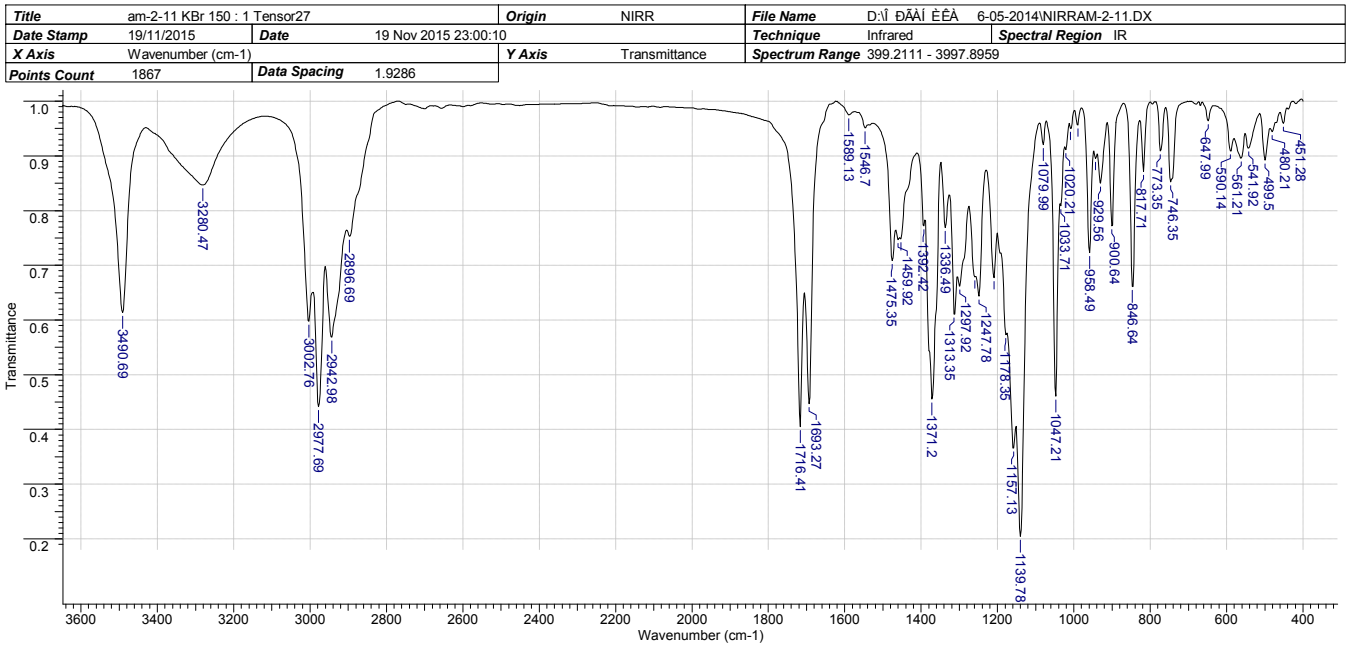


Figure S5.3 ^{13}C-NMR spectral data for alkoxyamine **7**



No	cm-1	T	Intensity	No	cm-1	T	Intensity	No	cm-1	T	Intensity	No	cm-1	T	Intensity
1	451.28	0.959	VW	13	929.56	0.850	W	25	1209.20	0.677	M	37	1589.13	0.975	VW
2	480.21	0.944	VW	14	943.06	0.895	W	26	1247.78	0.644	M	38	1693.27	0.447	S
3	499.50	0.892	W	15	958.49	0.723	M	27	1259.35	0.678	M	39	1716.41	0.405	S
4	541.92	0.914	W	16	989.35	0.956	VW	28	1297.92	0.662	M	40	2896.69	0.753	M
5	561.21	0.896	W	17	1008.63	0.950	VW	29	1313.35	0.610	M	41	2942.98	0.569	M
6	590.14	0.909	W	18	1020.21	0.912	W	30	1336.49	0.769	W	42	2977.69	0.442	S
7	647.99	0.964	VW	19	1033.71	0.809	W	31	1371.20	0.455	S	43	3002.76	0.597	M
8	746.35	0.852	W	20	1047.21	0.460	S	32	1392.42	0.772	W	44	3280.47	0.847	W
9	773.35	0.909	W	21	1079.99	0.920	W	33	1452.20	0.748	M	45	3490.69	0.613	M
10	817.71	0.871	W	22	1139.78	0.204	VS	34	1459.92	0.747	M				
11	846.64	0.661	M	23	1157.13	0.365	S	35	1475.35	0.708	M				
12	900.64	0.772	W	24	1178.35	0.573	M	36	1546.70	0.951	VW				

Figure S5.4 FT IR (KBr) spectrum of alkoxyamine **7**

Figure 6SI. HR MS(ESI), EPR, and FT IR spectral data for trityl 1

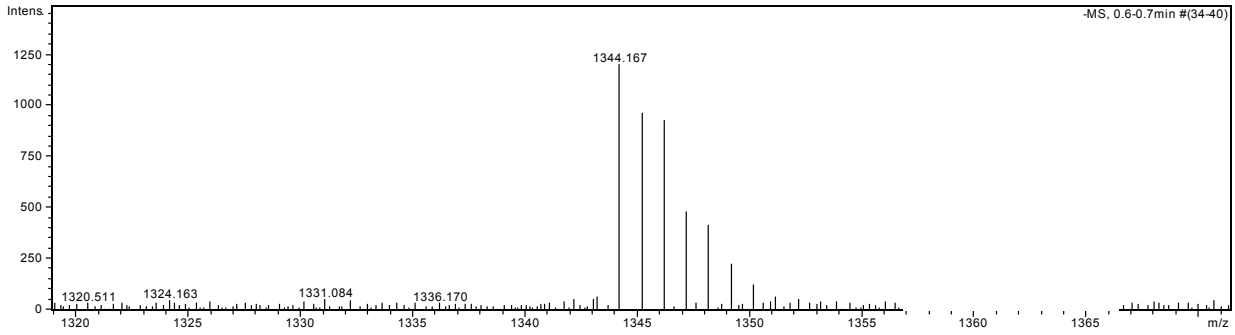


Figure S6.1.1 MS(ESI) spectrum of trityl **1**: calcd. for $C_{61}H_{70}NO_9S_{12}$ [M^-] 1344.1699, found 1344.167

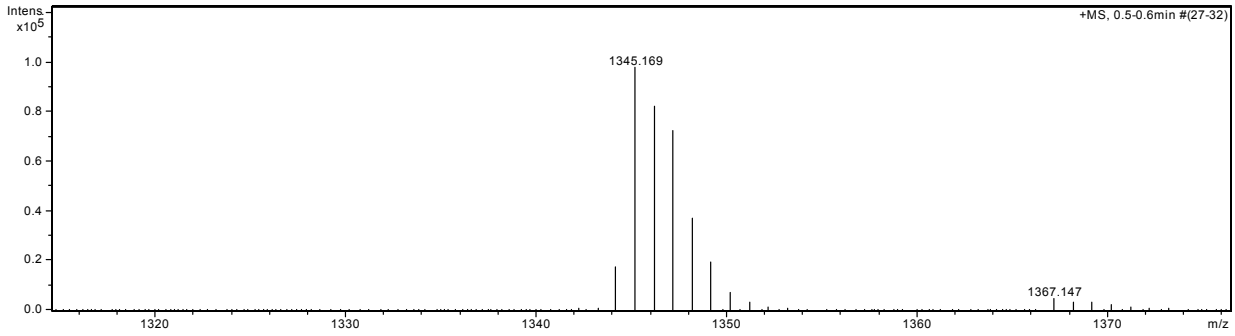


Figure S6.1.2 MS(ESI) spectrum of trityl **1**: calcd. $C_{61}H_{71}NO_9S_{12}$ for [$M+H^+$] 1345.1777, found 1345.169

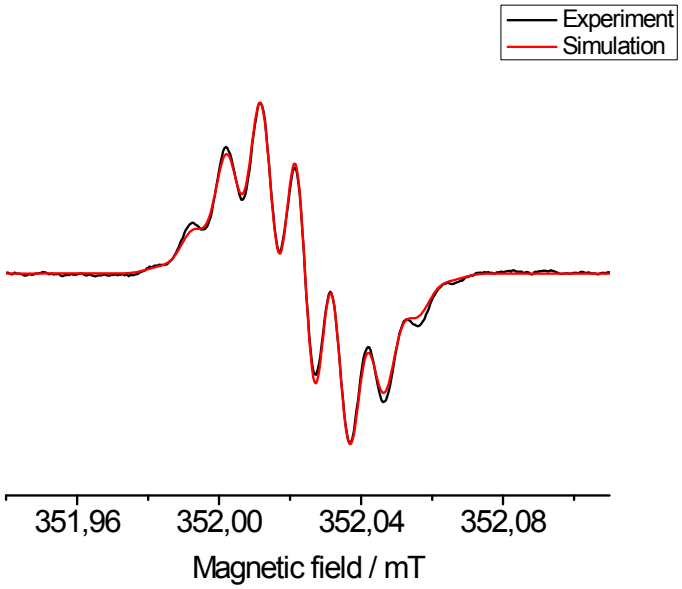


Figure S6.2. EPR for 0.5 mM deoxygenated solution in DCM: multiplet, α_H=9.4 μT, linewidth (Gauss) 8.7 μT, g = 2.00280

15 Feb 2016

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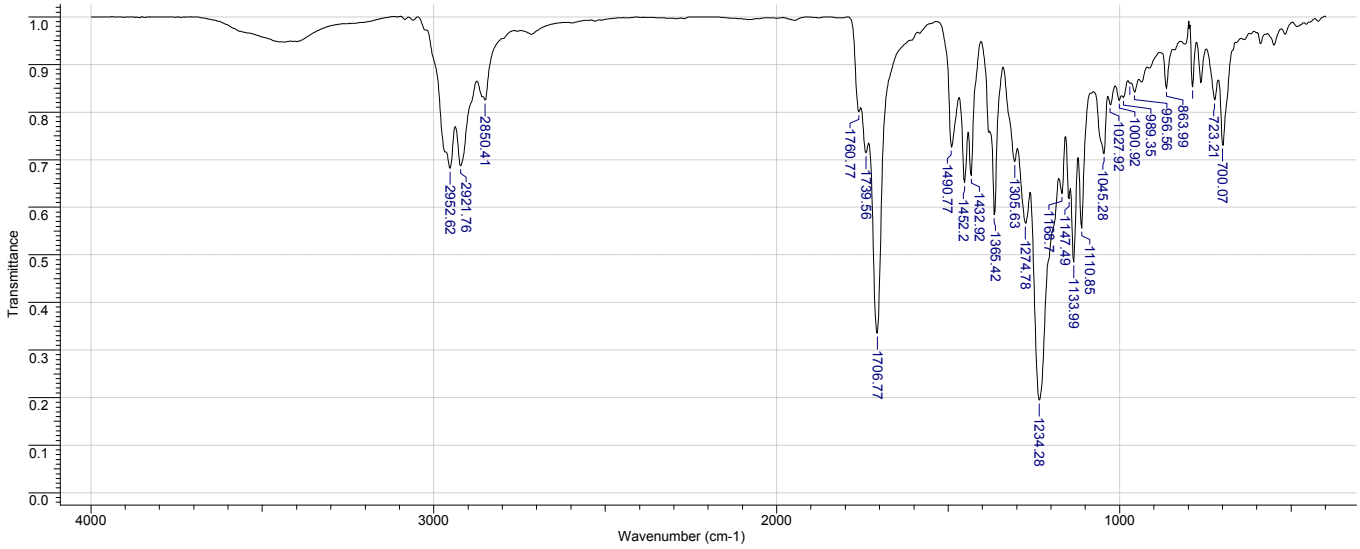
X Axis	Wavenumber (cm-1)		***Y Axis***	Transmittance	***Spectrum Range*** 399.2111 - 3997.8959
Points Count	1867	***Data Spacing*** 1.9286			



No	cm-1	T	FWHH	Asym	Intensity
1	2952.62	0.682	-	-	M
2	2921.76	0.687	-	-	M
3	2850.41	0.825	-	-	W
4	1760.77	0.800	-	-	W
5	1739.56	0.715	-	-	M
6	1706.77	0.336	-1.00	0.00	S
7	1490.77	0.726	-	-	M
8	1452.20	0.652	-	-	M
9	1432.92	0.667	-	-	M

No	cm-1	T	FWHH	Asym	Intensity
10	1365.42	0.584	-	-	M
11	1305.63	0.696	-	-	M
12	1274.78	0.566	-	-	M
13	1234.28	0.195	-1.00	0.00	VS
14	1168.70	0.629	-	-	M
15	1147.49	0.618	-	-	M
16	1133.99	0.486	-	-	S
17	1110.85	0.556	-	-	M
18	1045.28	0.713	-	-	M

No	cm-1	T	FWHH	Asym	Intensity
19	1027.92	0.816	-	-	W
20	1000.92	0.825	-	-	W
21	989.35	0.831	-	-	W
22	970.06	0.861	-	-	W
23	956.56	0.842	-	-	W
24	863.99	0.849	-1.00	0.00	W
25	786.85	0.853	-1.00	0.00	W
26	723.21	0.825	-	-	W
27	700.07	0.730	-1.00	0.00	M

Figure S6.3 FT IR (KBr) spectrum of trityl **1**

Figure 7SI. HR MS(ESI), EPR, and FT IR spectral data for trityl 2

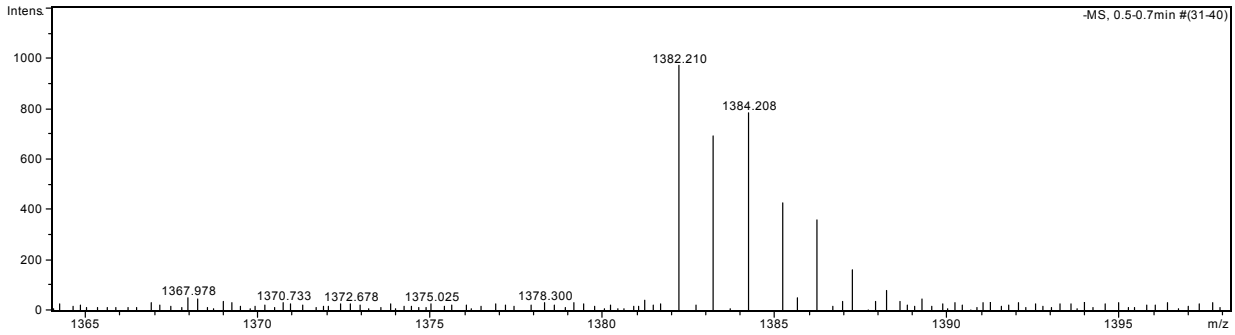


Figure S7.1.1. HR MS (ESI) spectrum of trityl **2**: calcd. for $C_{61}H_{76}NO_{11}S_{12}$ [M^-] 1382.2067, found 1382.210

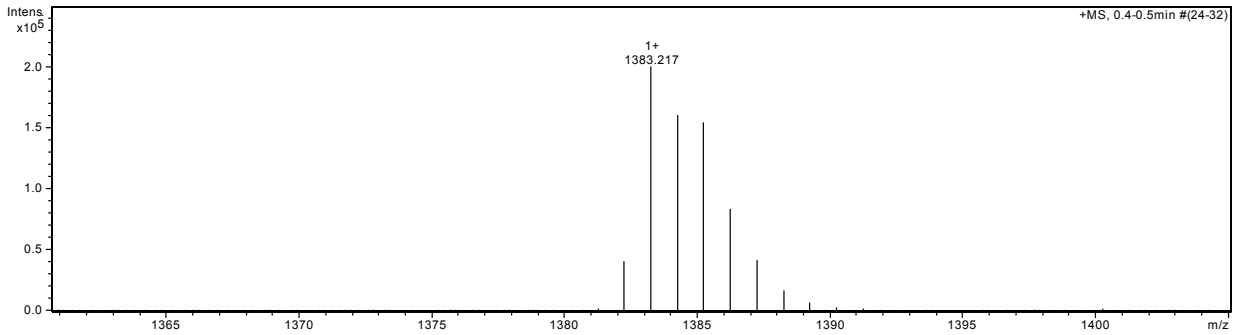


Figure S7.1.2. HR MS (ESI) spectrum of trityl **2**: calcd. for $C_{61}H_{77}NO_{11}S_{12}$ [$M+H^+$] 1383.2145, found 1383.217

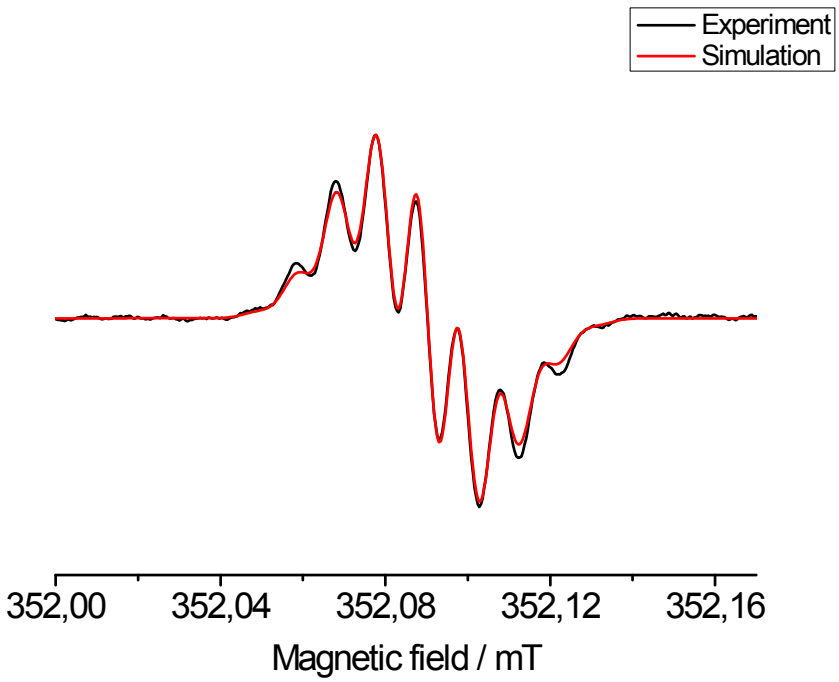
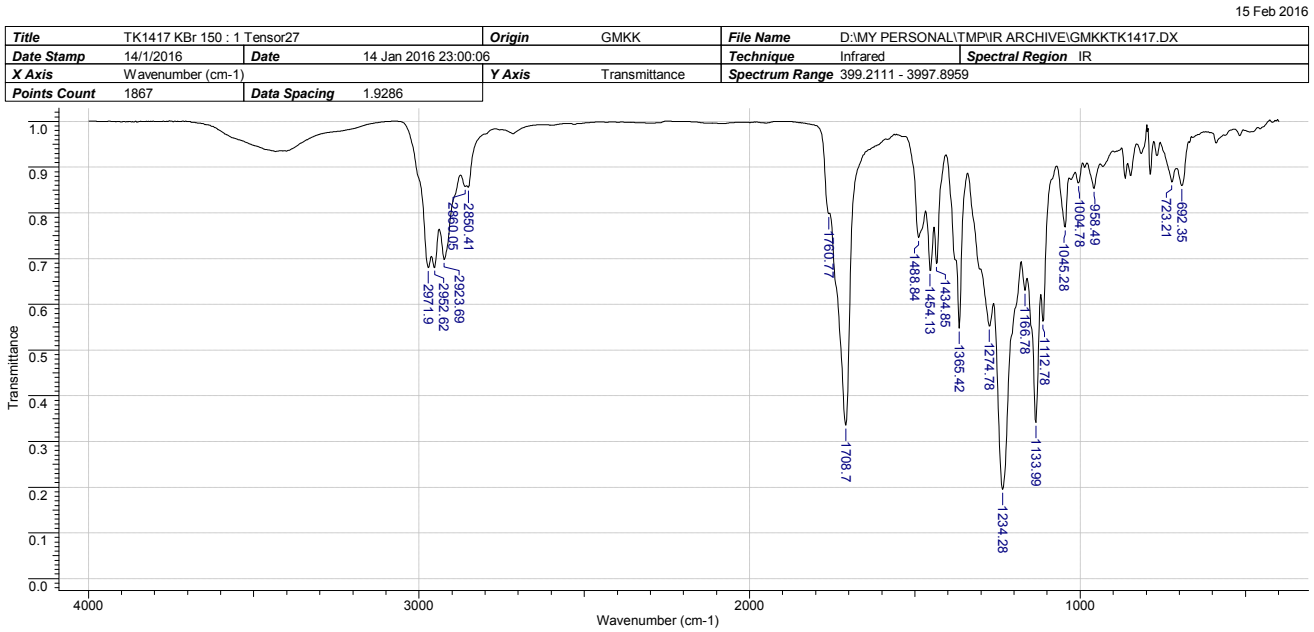


Figure S7.2. EPR for 0.5 mM deoxygenated solution in DCM: multiplet, α_H=9.4 μT, linewidth (Gauss) 8.5 μT, g = 2.00280



No	cm-1	T	FWHH	Asym	Intensity
1	2971.90	0.680	-	-	M
2	2952.62	0.681	-	-	M
3	2923.69	0.698	-	-	M
4	2860.05	0.857	-	-	W
5	2850.41	0.856	-	-	W
6	1760.77	0.799	-	-	W
7	1708.70	0.335	-1.00	0.00	S
8	1488.84	0.746	-	-	M
9	1454.13	0.674	-	-	M
10	1434.85	0.689	-	-	M
11	1365.42	0.548	-	-	M

No	cm-1	T	FWHH	Asym	Intensity
12	1274.78	0.552	-	-	M
13	1234.28	0.195	-1.00	0.00	VS
14	1166.78	0.631	-	-	M
15	1133.99	0.341	-1.00	0.00	S
16	1112.78	0.563	-	-	M
17	1045.28	0.769	-1.00	0.00	W
18	1004.78	0.865	-	-	W
19	958.49	0.854	-	-	W
20	723.21	0.867	-	-	W
21	692.35	0.860	-	-	W

Figure S7.3 FT IR (KBr) spectrum of trityl **2**

Figure 8SI. HR MS(ESI), EPR, and FT IR spectral data for trityl 3

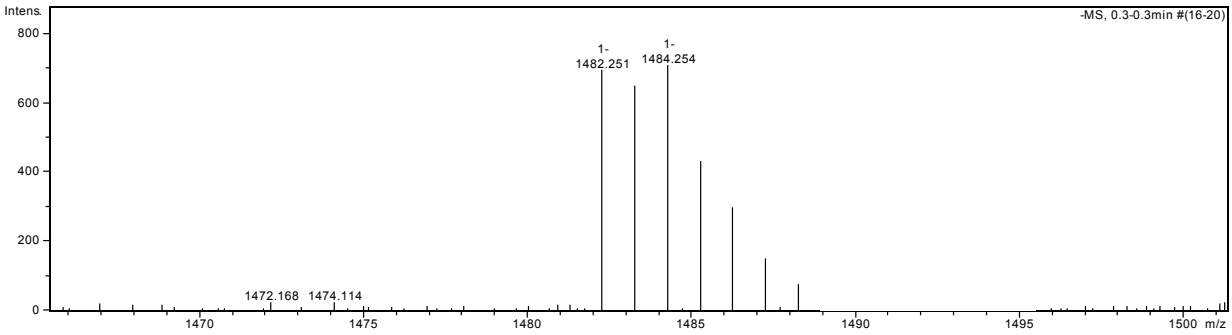


Figure S8.1.1 HR MS (ESI) spectrum of trityl **3**: calcd. for $C_{65}H_{81}NO_{12}PS_{12}$ [M^-] 1482.2145, found 1482.251.

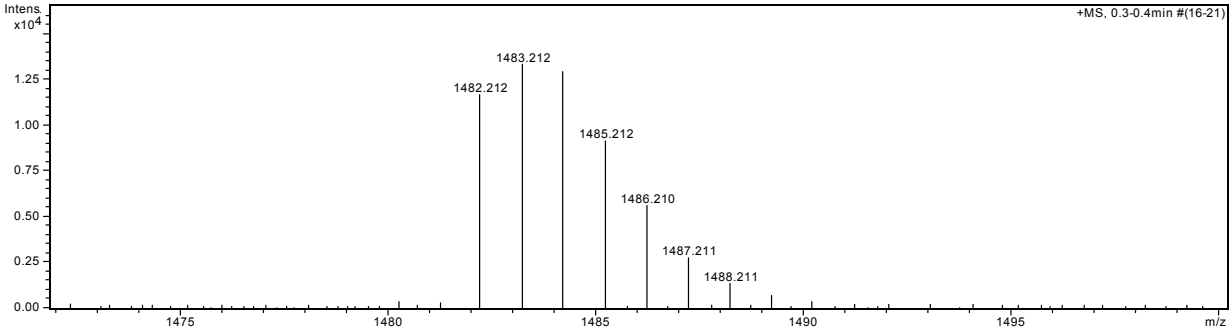


Figure S8.1.2. HR MS (ESI) spectrum of trityl **3**: calcd. for $C_{65}H_{82}NO_{12}PS_{12}$ [$M+H^+$] 1483.2223, found 1483.212.

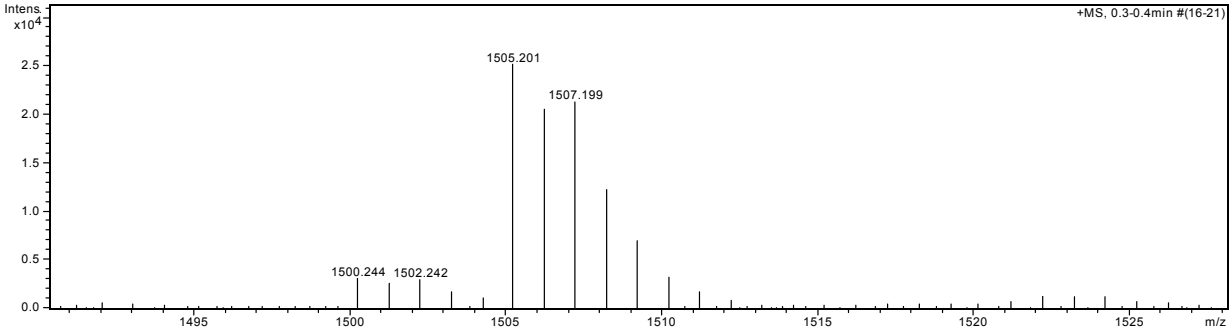


Figure S8.1.3. HR MS (ESI) spectrum of trityl **3**: calcd. for $C_{65}H_{85}N_2O_{12}PS_{12}$ [$M+NH_4^+$] 1500.2489, found 1500.244; calcd. for $C_{65}H_{81}NNaO_{12}PS_{12}$ [$M+Na^+$] 1505.2043, found 1505.201.

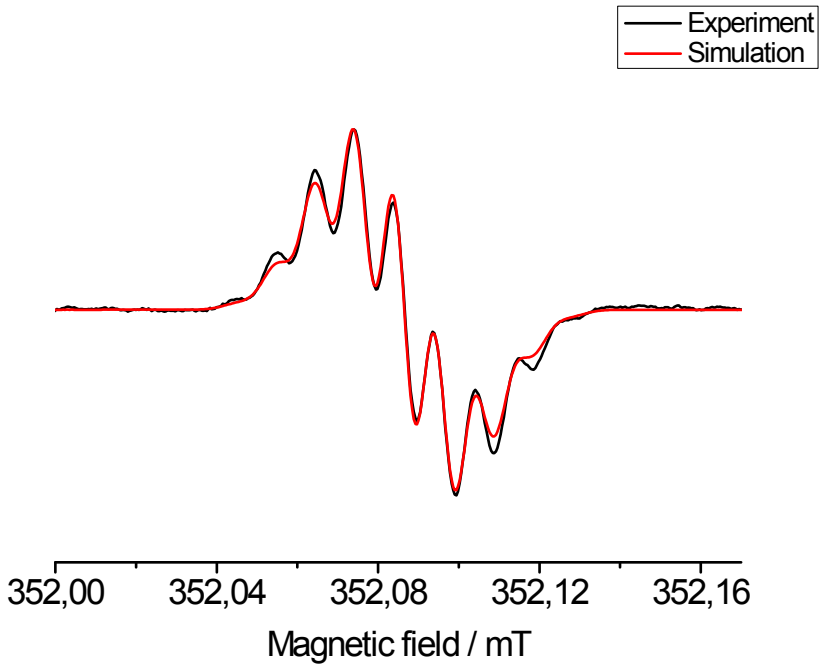


Figure S8.2. EPR for 0.5 mM deoxygenated solution in DCM: multiplet, α_H=9.4 μT, linewidth (Gauss) 8.7 μT, g = 2.00280

15 Feb 2016

Title	TK1399 KBr 150 : 1 Tensor27	**Origin**	GMKK	**File Name**	D:\MY PERSONAL\TMP\IR ARCHIVE\GMKKTK1399.DX
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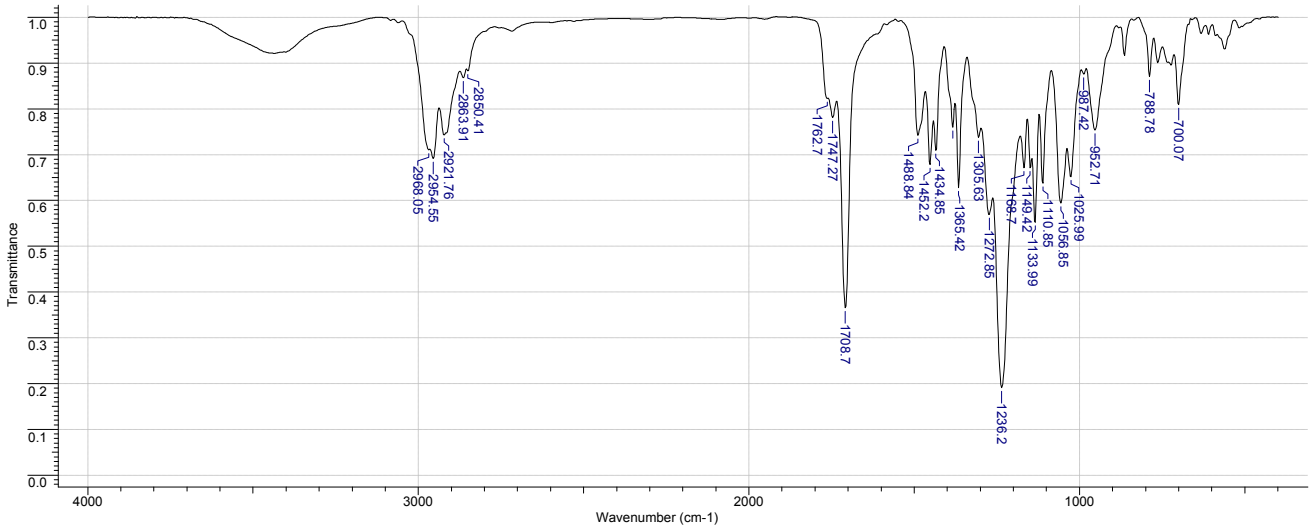
X Axis	Wavenumber (cm-1)	**Y Axis**	Transmittance	**Spectrum Range**	399.2111 - 3997.8959
Points Count	1867	**Data Spacing**	1.9286		



No	cm-1	T	FWHH	Asym	Intensity
1	2968.05	0.710	-	-	M
2	2954.55	0.691	-	-	M
3	2921.76	0.743	-	-	M
4	2863.91	0.868	-	-	W
5	2850.41	0.883	-	-	W
6	1762.70	0.823	-	-	W
7	1747.27	0.781	-	-	W
8	1708.70	0.365	-1.00	0.00	S
9	1488.84	0.742	-	-	M

No	cm-1	T	FWHH	Asym	Intensity
10	1452.20	0.678	-	-	M
11	1434.85	0.709	-	-	M
12	1382.77	0.760	-	-	W
13	1365.42	0.628	-1.00	0.00	M
14	1305.63	0.738	-	-	M
15	1272.85	0.569	-	-	M
16	1236.20	0.191	-1.00	0.00	VS
17	1168.70	0.672	-	-	M
18	1149.42	0.671	-	-	M

No	cm-1	T	FWHH	Asym	Intensity
19	1133.99	0.553	-	-	M
20	1110.85	0.637	-	-	M
21	1056.85	0.594	-	-	M
22	1025.99	0.652	-	-	M
23	987.42	0.876	-	-	W
24	952.71	0.754	-1.00	0.00	M
25	788.78	0.871	-1.00	0.00	W
26	700.07	0.810	-1.00	0.00	W

Figure S8.3 FT IR (KBr) spectrum of trityl **3**

Figure 9SI. HR MS(ESI), EPR, and FT IR spectral data for trityl 4

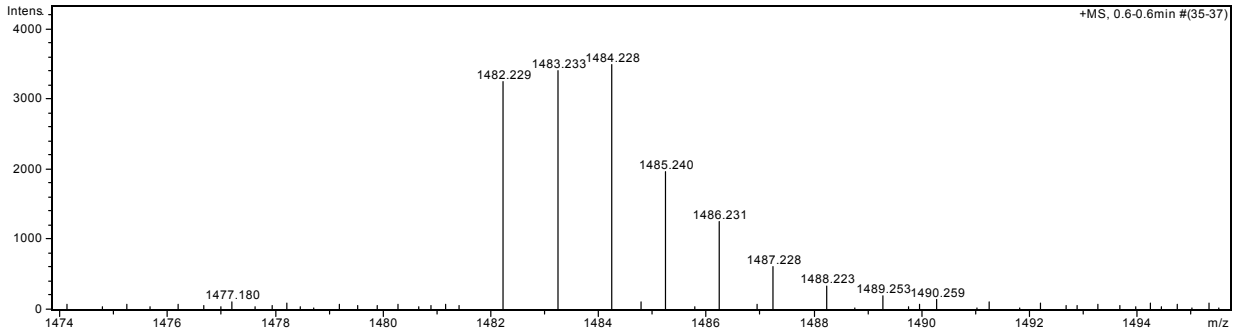


Figure S9.1.1. HR MS (ESI) spectrum of trityl **4**: calcd. for $C_{65}H_{83}N_2O_{11}PS_{12}$ [M+H$^+$] 1482.2383, found 1482.229

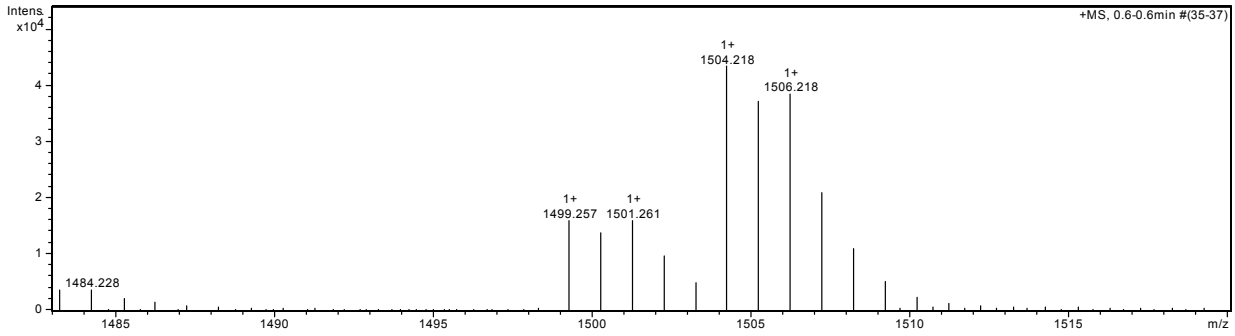


Figure S9.1.2. HR MS (ESI) spectrum of trityl **4**: calcd. for $C_{65}H_{86}N_3O_{11}PS_{12}$ [M+NH$_4^+$] 1499.2648, found 1499.257; calcd. for $C_{65}H_{82}N_2NaO_{11}PS_{12}$ [M+Na$^+$] 1504.2202, found 1504.218.

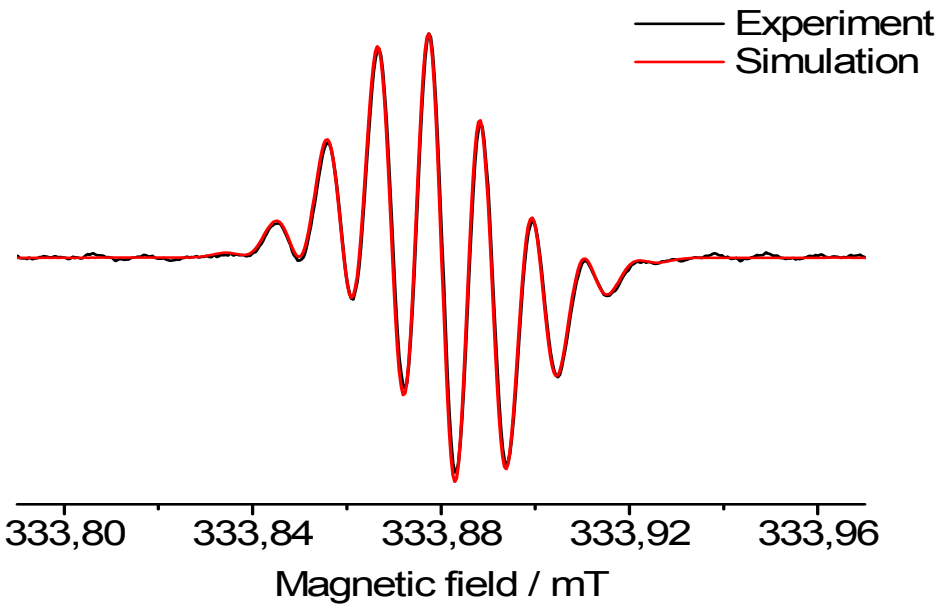
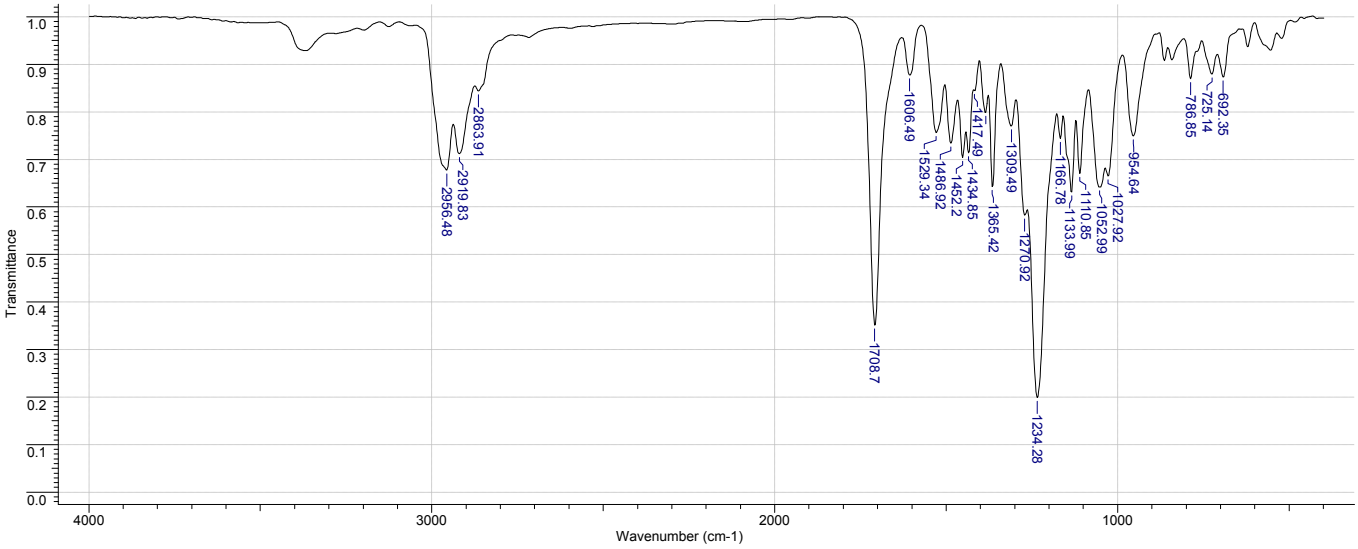


Figure S9.2. EPR for 0.5 mM deoxygenated solution of trityl **4** in DCM: multiplet, α_H= 10.6 μT, linewidth (Gauss) 7.3 μT, g = 2.00281

16 Feb 2016

Title	TK1421 KBr 150 : 1 Tensor27			***Origin***	GMKK	***File Name***	D:\MY PERSONAL\TMP\IR ARCHIVE\GMKKTK1421.DX
Date Stamp	15/2/2016	***Date***	15 Feb 2016 23:00:10			***Technique***	Infrared ***Spectral Region*** IR
X Axis	Wavenumber (cm-1)			***Y Axis***	Transmittance	***Spectrum Range***	399.2111 - 3997.8959
Points Count	1867	***Data Spacing***	1.9286				



No	cm-1	T	FWHH	Asym	Intensity
1	2956.48	0.678	-	-	M
2	2919.83	0.712	-	-	M
3	2863.91	0.844	-	-	W
4	1708.70	0.351	-1.00	0.00	S
5	1606.49	0.877	448.71	-2.80	W
6	1529.34	0.757	-	-	M
7	1486.92	0.734	-	-	M
8	1452.20	0.704	-	-	M
9	1434.85	0.713	-	-	M
10	1417.49	0.845	-	-	W
11	1384.70	0.799	-	-	W
12	1365.42	0.643	-1.00	0.00	M

No	cm-1	T	FWHH	Asym	Intensity
13	1309.49	0.770	-	-	W
14	1270.92	0.583	-	-	M
15	1234.28	0.199	-1.00	0.00	VS
16	1166.78	0.744	-	-	M
17	1133.99	0.631	-	-	M
18	1110.85	0.670	-	-	M
19	1052.99	0.642	-	-	M
20	1027.92	0.665	-	-	M
21	954.64	0.749	-1.00	0.00	M
22	786.85	0.870	-	-	W
23	725.14	0.879	-	-	W
24	692.35	0.873	-	-	W

Figure S9.3 FT IR (KBr) spectrum of trityl **4**

Figure 10SI. HR MS(ESI), EPR, and FT IR spectral data for trityl 5

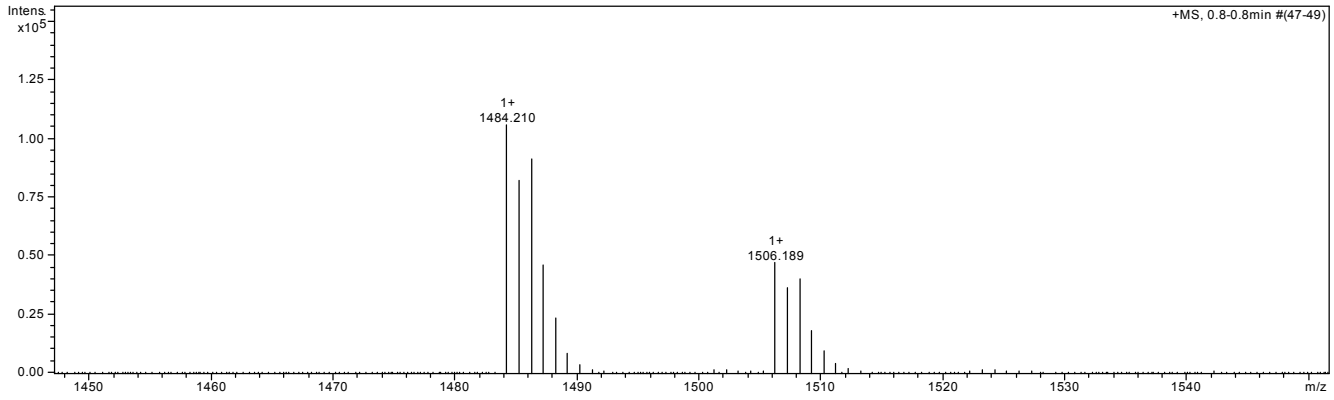


Figure S10.1.1. HR MS (ESI) spectrum of trityl **5**: calcd. for $C_{64}H_{81}N_2O_{12}PS_{12}$ [M+H$^+$] 1484.2176, found 1484.210; calcd. for $C_{64}H_{80}N_2NaO_{12}PS_{12}$ [M+Na$^+$] 1506.1995, found 1506.189.

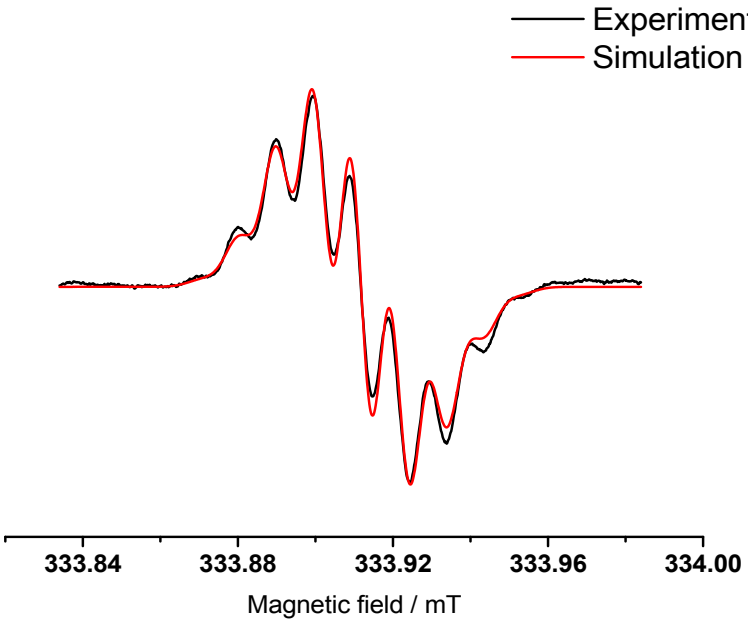
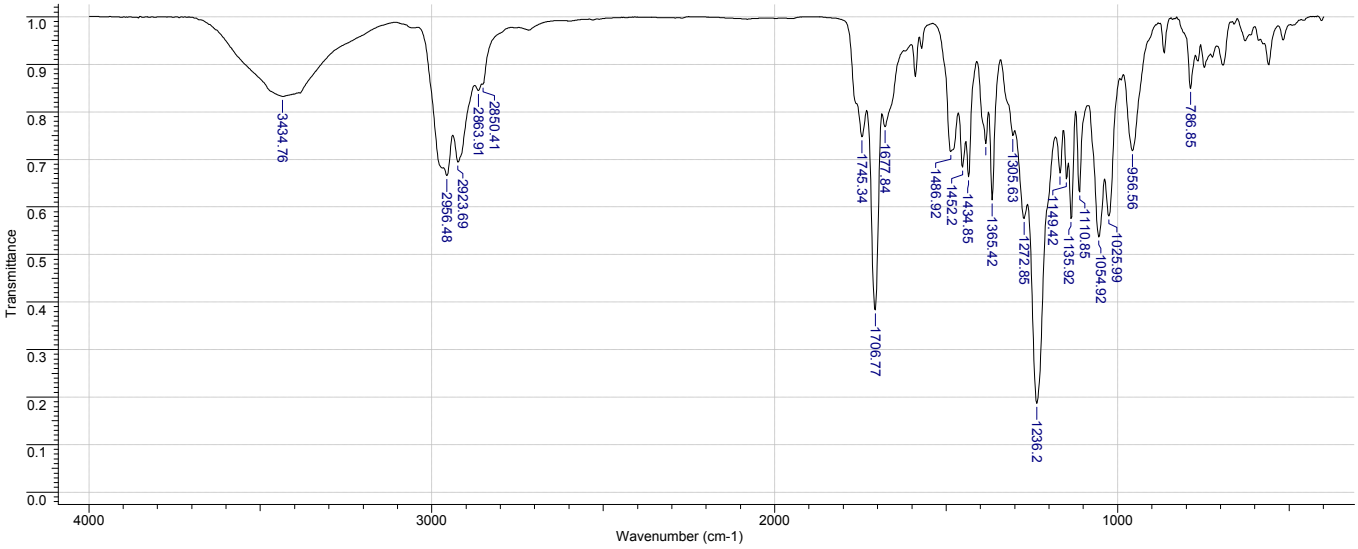


Figure S10.2. EPR for 0.5 mM deoxygenated solution of **5** in DCM: multiplet (splitting on 8 protons in groups of 3H, 3H, 2H), α_{H1}= 9.0 μT, α_{H2}= 9.5 μT, α_{H3}= 9.8 μT (respectively), linewidth (Gauss) 8.6 μT, *g* = 2.00281

30 Jun 2016

Title	PO-1789-2 KBr 150:1 Tensor27	***Origin***	GMKK	***File Name***	H:\GMKKPO-1789-2.DX
Date Stamp	14/4/2016	***Date***	14 Apr 2016 23:00:12	***Technique***	Infrared
X Axis	Wavenumber (cm-1)	***Y Axis***	Transmittance	***Spectrum Range***	399.2111 - 3997.8959
Points Count	1867	***Data Spacing***	1.9286		



No	cm-1	T	FWHH	Asym	Intensity	No	cm-1	T	FWHH	Asym	Intensity
1	3434.76	0.832	-1.00	0.00	W	13	1365.42	0.614	-1.00	0.00	M
2	2956.48	0.666	-	-	M	14	1305.63	0.750	-	-	M
3	2923.69	0.694	-	-	M	15	1272.85	0.575	-	-	M
4	2863.91	0.845	-	-	W	16	1236.20	0.187	-1.00	0.00	VS
5	2850.41	0.858	-	-	W	17	1168.70	0.671	-	-	M
6	1745.34	0.747	-	-	M	18	1149.42	0.659	-	-	M
7	1706.77	0.383	-1.00	0.00	S	19	1135.92	0.575	-	-	M
8	1677.84	0.768	-	-	W	20	1110.85	0.631	-1.00	0.00	M
9	1486.92	0.716	-	-	M	21	1054.92	0.537	-	-	M
10	1452.20	0.683	-	-	M	22	1025.99	0.581	-	-	M
11	1434.85	0.663	-	-	M	23	956.56	0.718	-1.00	0.00	M
12	1384.70	0.733	-	-	M	24	786.85	0.849	-	-	W

Figure S10.3 FT IR (KBr) spectrum of trityl **5**

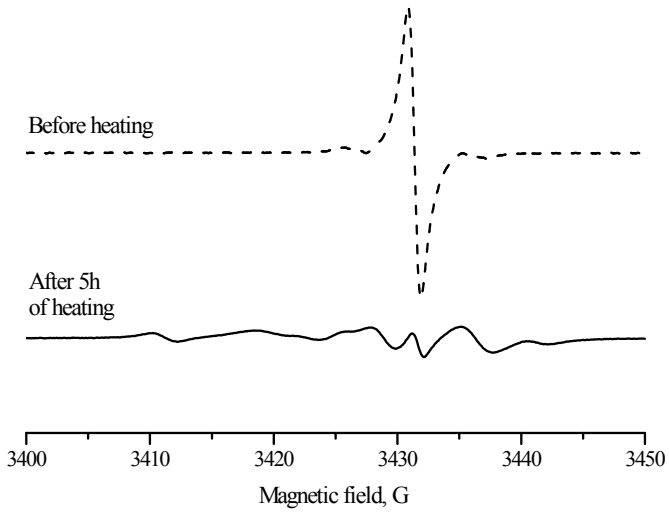


Figure 11SI. Livingness of polymer initiated with 1