Supporting information for

π-Expanded 1,3-Diketones – Synthesis, Optical Properties and Application in Two-Photon Polymerization

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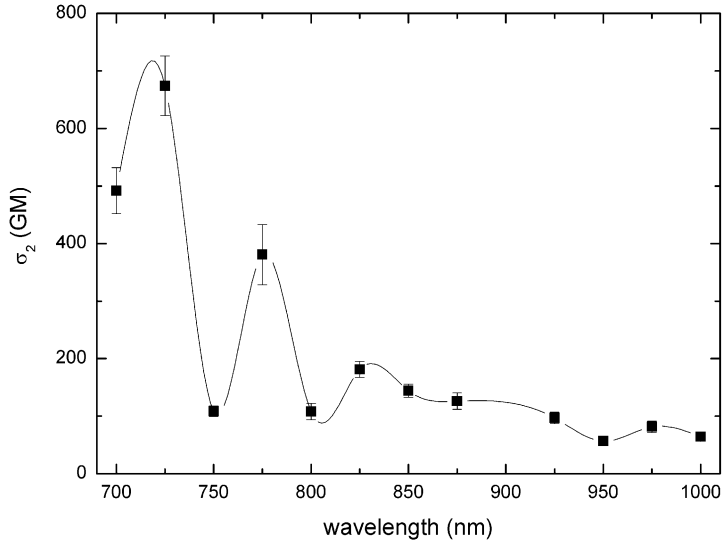

Fig. S1. Two-photon spectrum of dye **6** in DCM (via Z-scan).

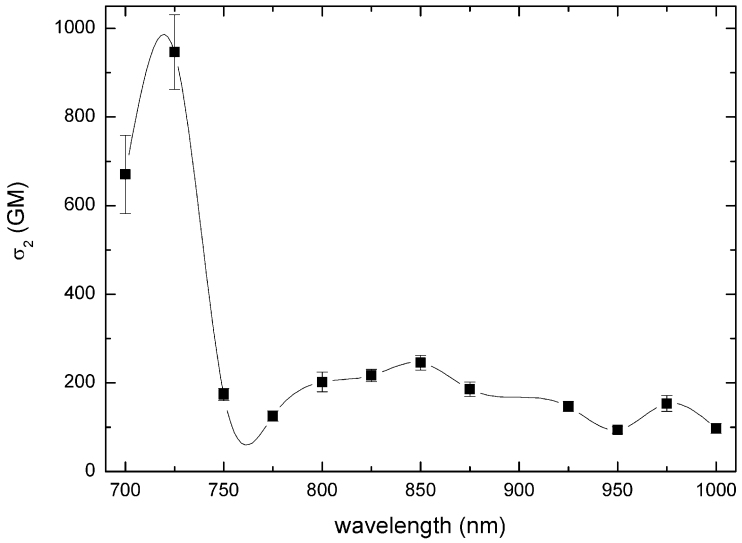

Fig. S2. Two-photon spectrum of dye **7** in DCM (via Z-scan).

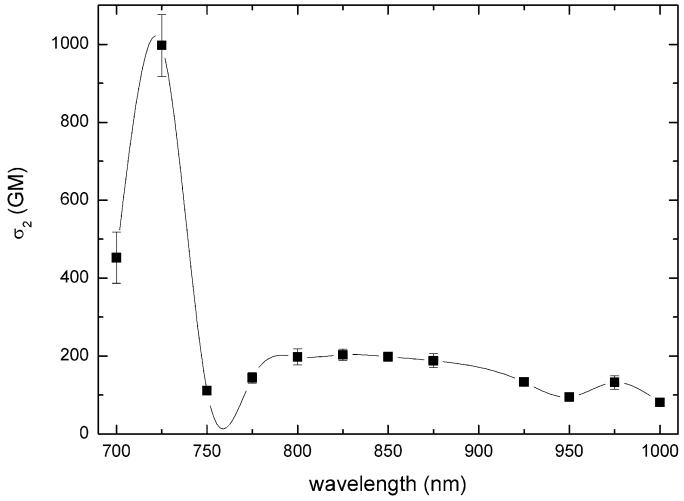

Fig. S3. Two-photon spectrum of dye **10** in DCM (via Z-scan).

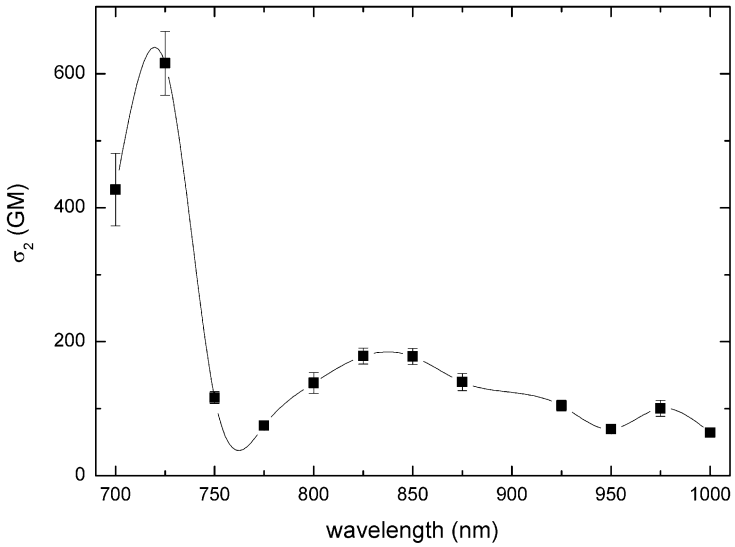

Fig. S4. Two-photon spectrum of dye **16** in DCM (via Z-scan).

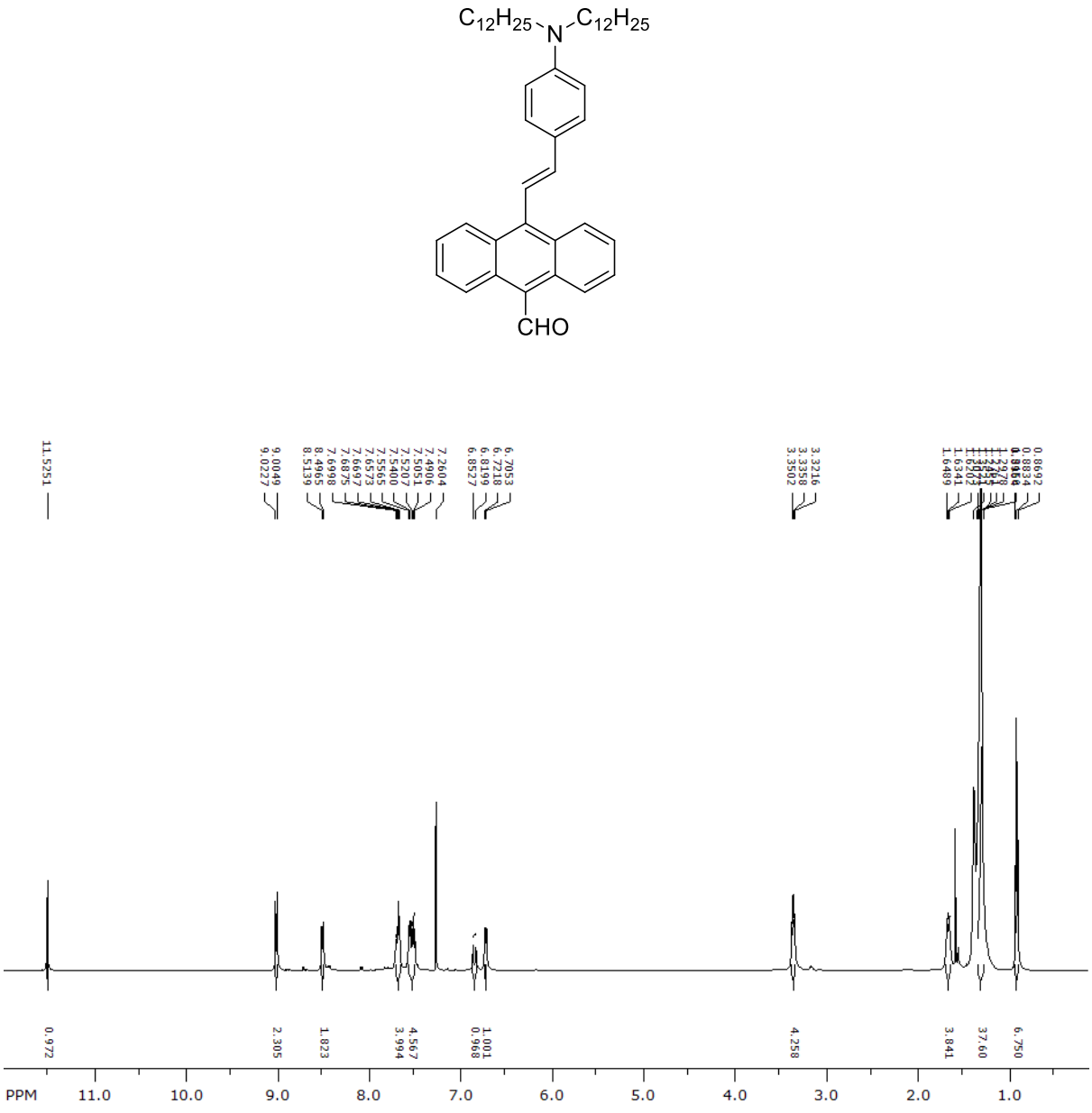

Figure S5.^{1}H NMR spectrum of **3** in $CDCl_3$.

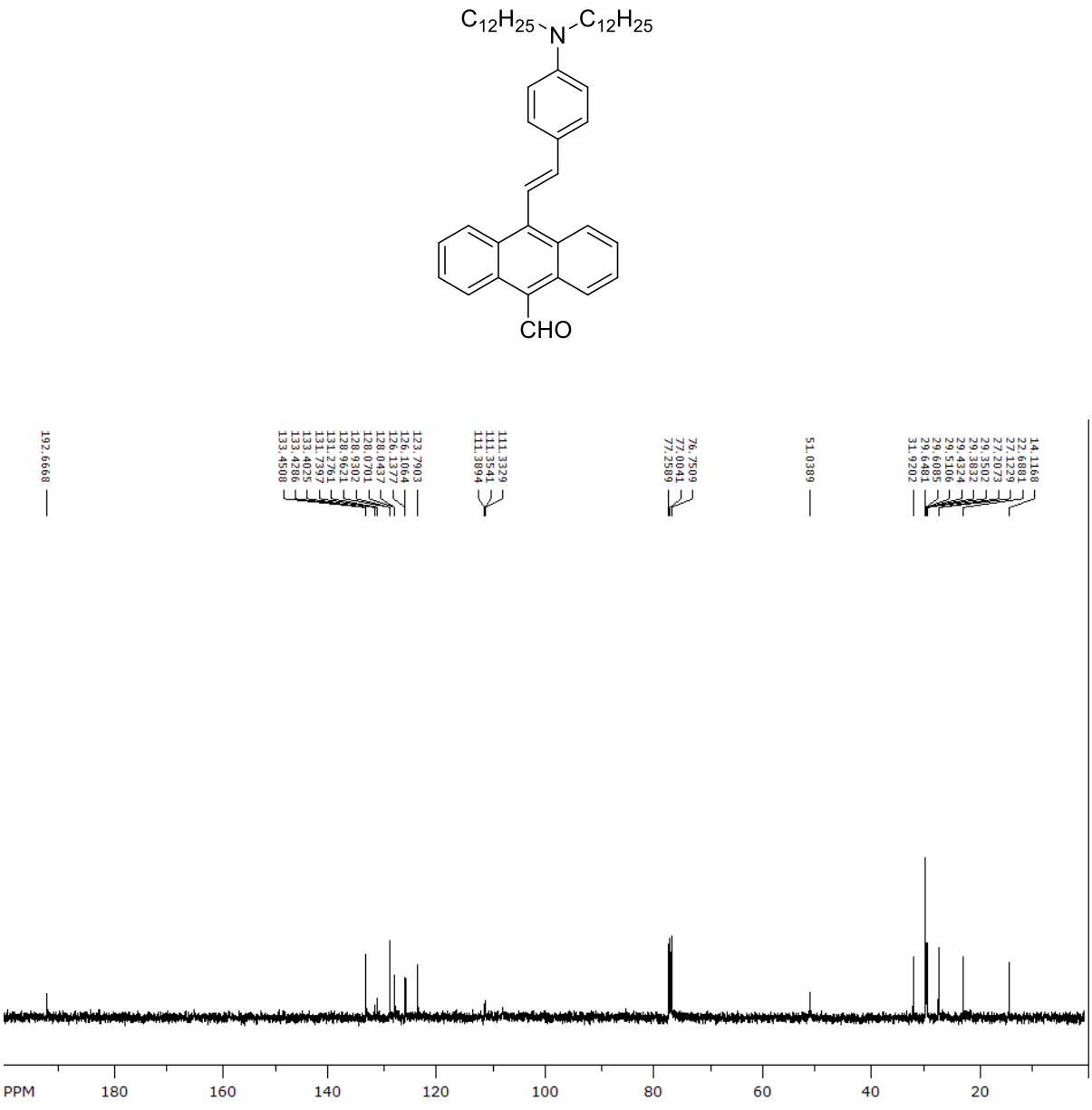

Figure S6.C^{13} NMR spectrum of **3** in $CDCl_3$.

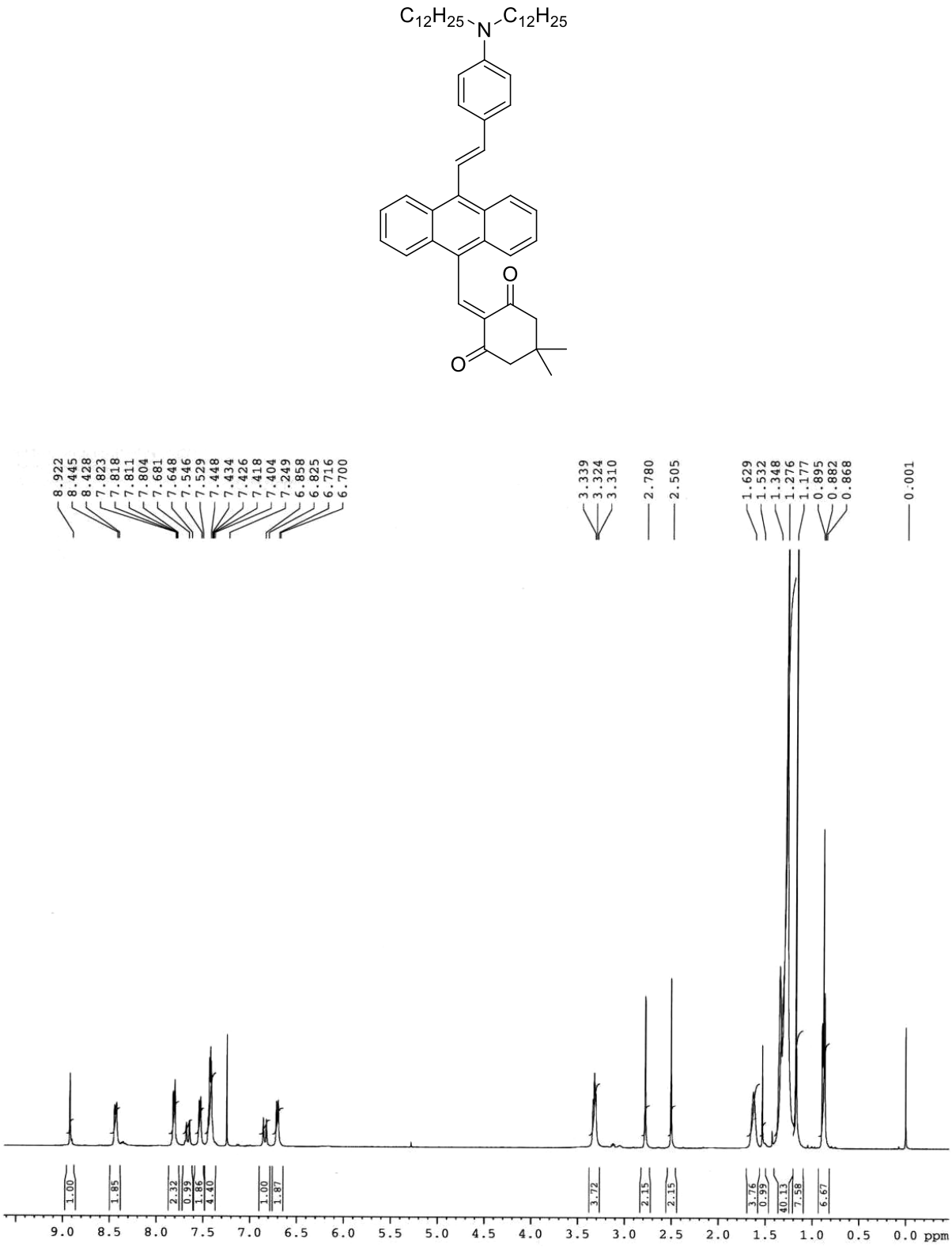

Figure S7. ^{1}H NMR spectrum of **6** in $CDCl_3$

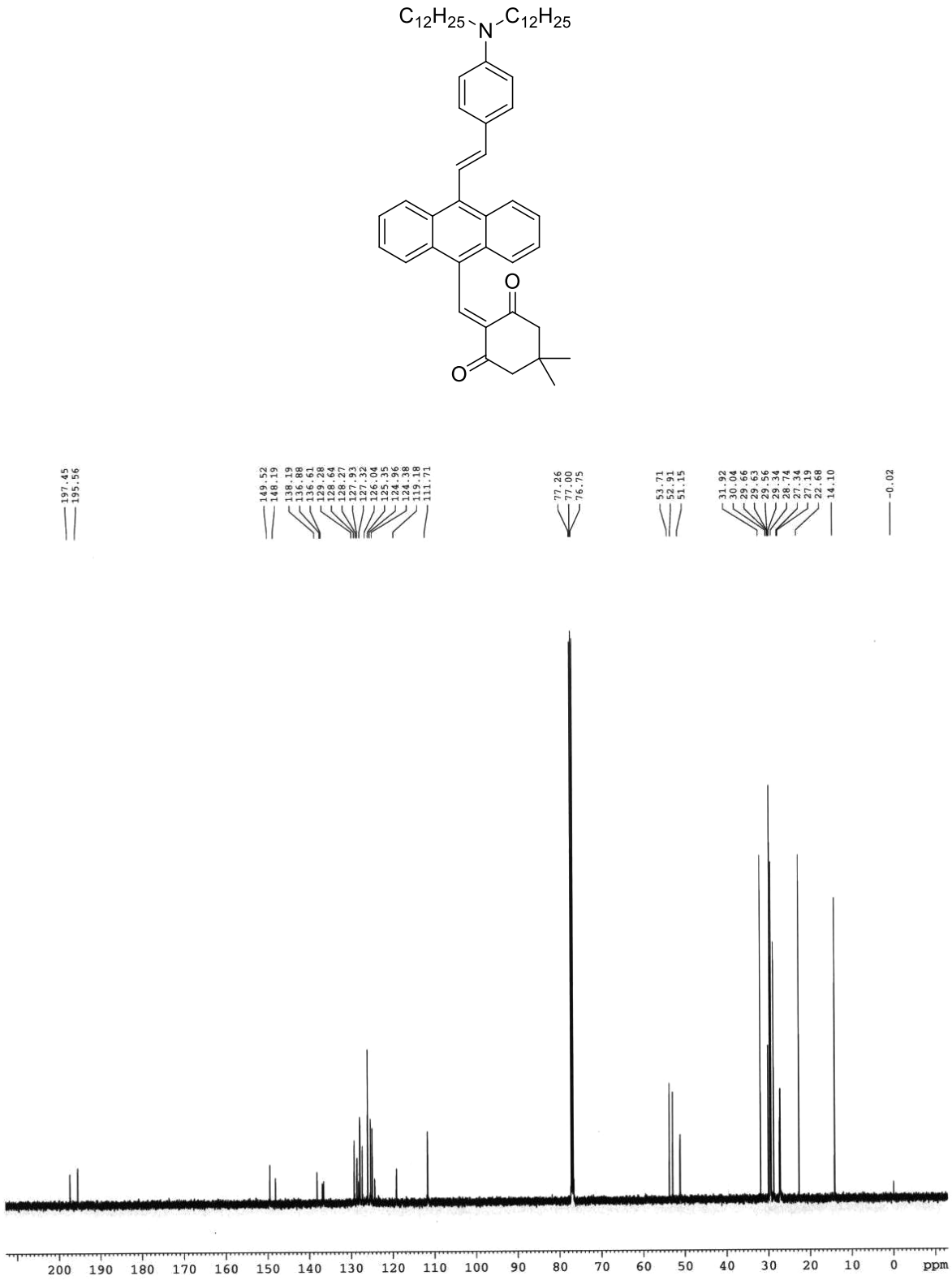

Figure S8.C^{13} NMR spectrum of **6** in $CDCl_3$.

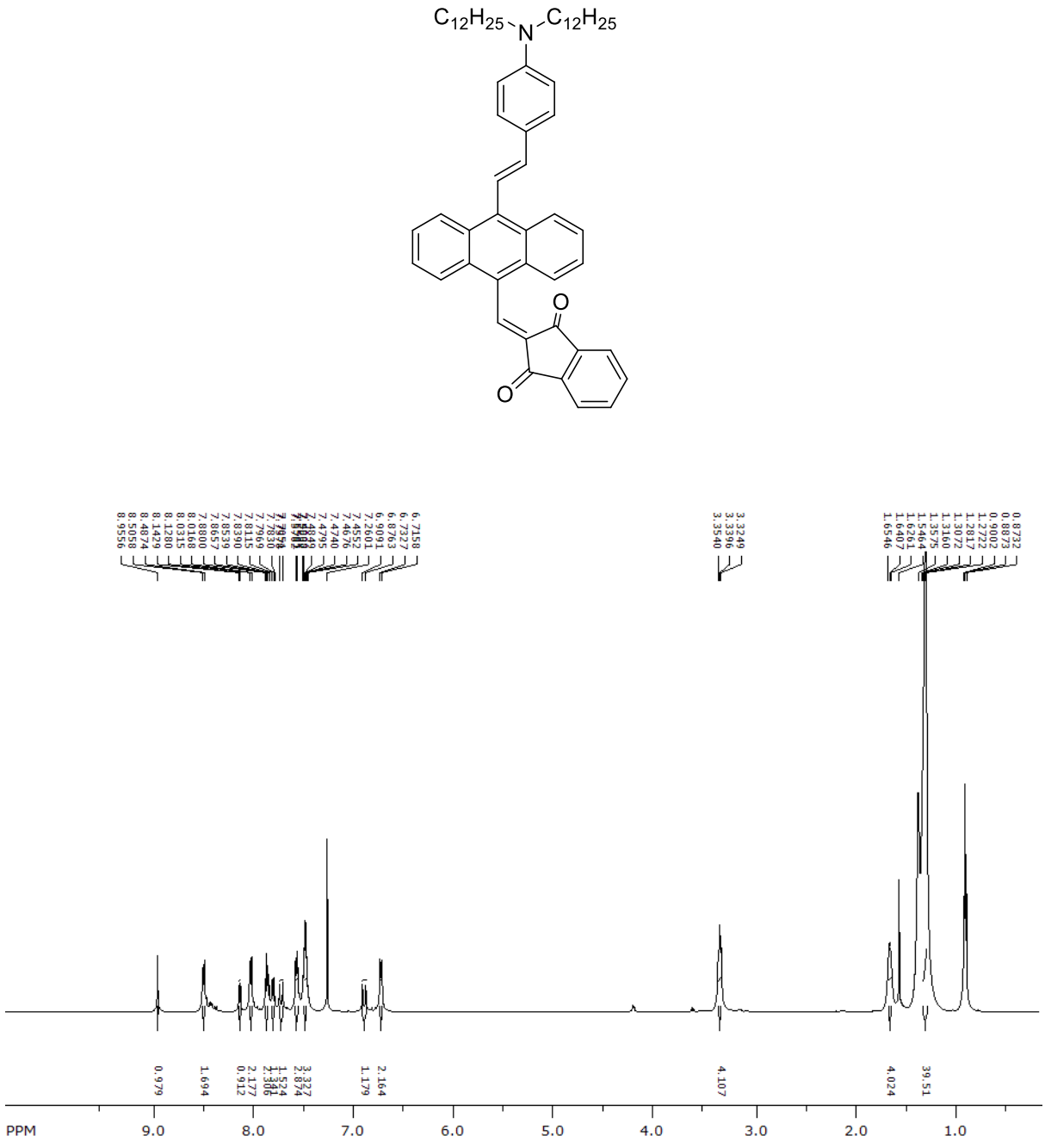

Figure S9. ^{1}H NMR spectrum of **7** in $CDCl_3$

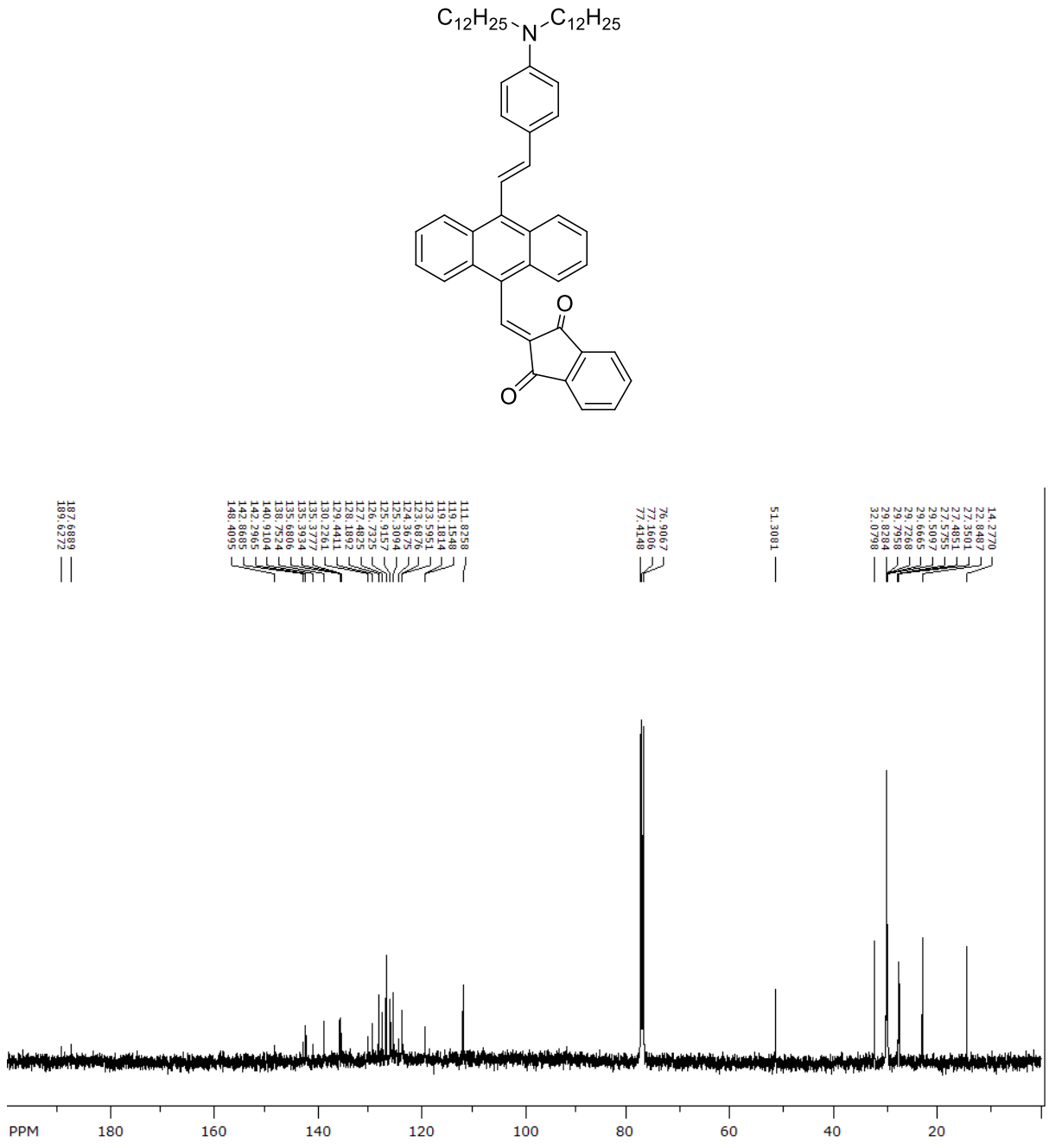

Figure S10.C^{13} NMR spectrum of **7** in $CDCl_3$.

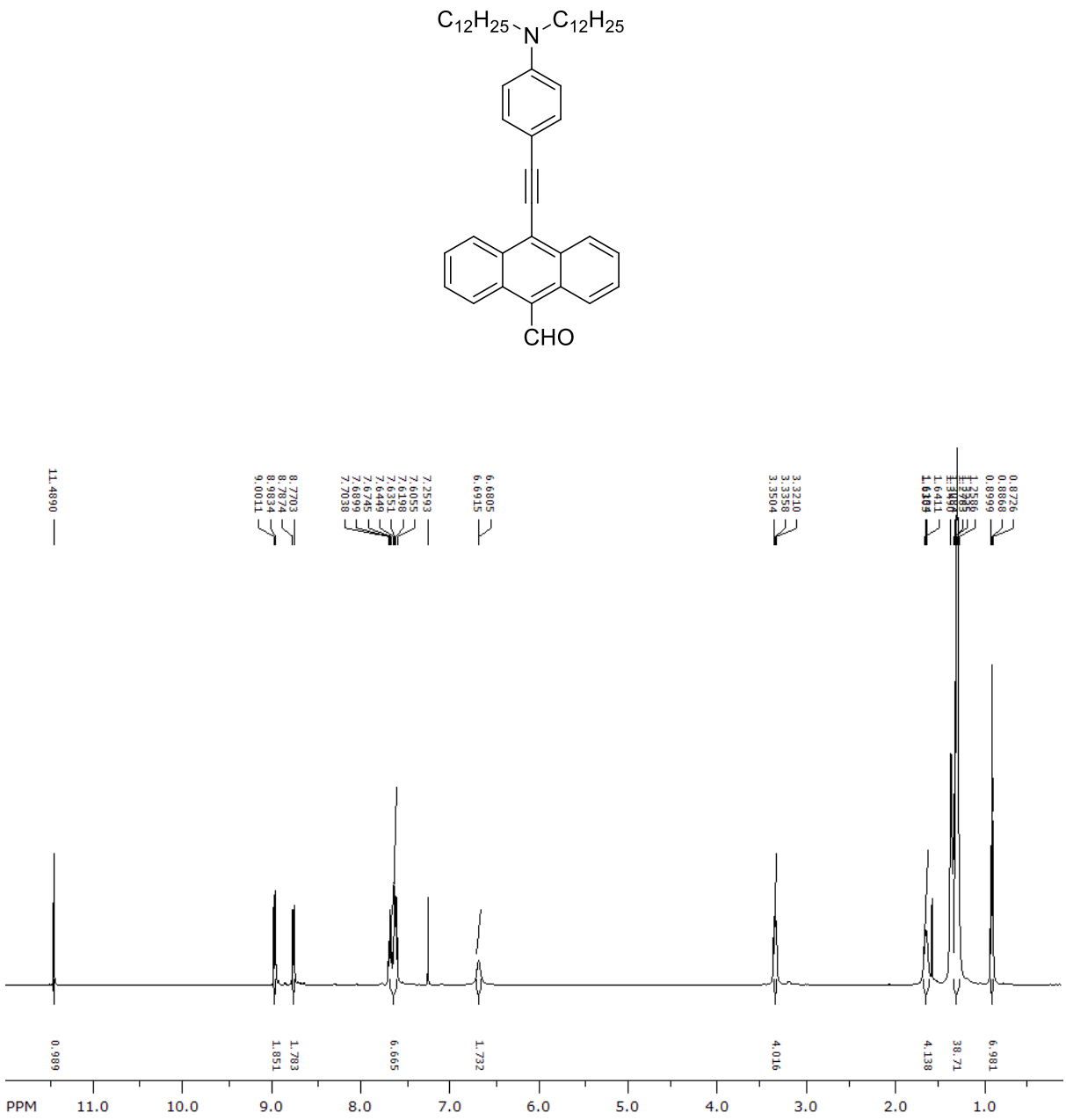

Figure S11. ^{1}H NMR spectrum of **9** in $CDCl_3$

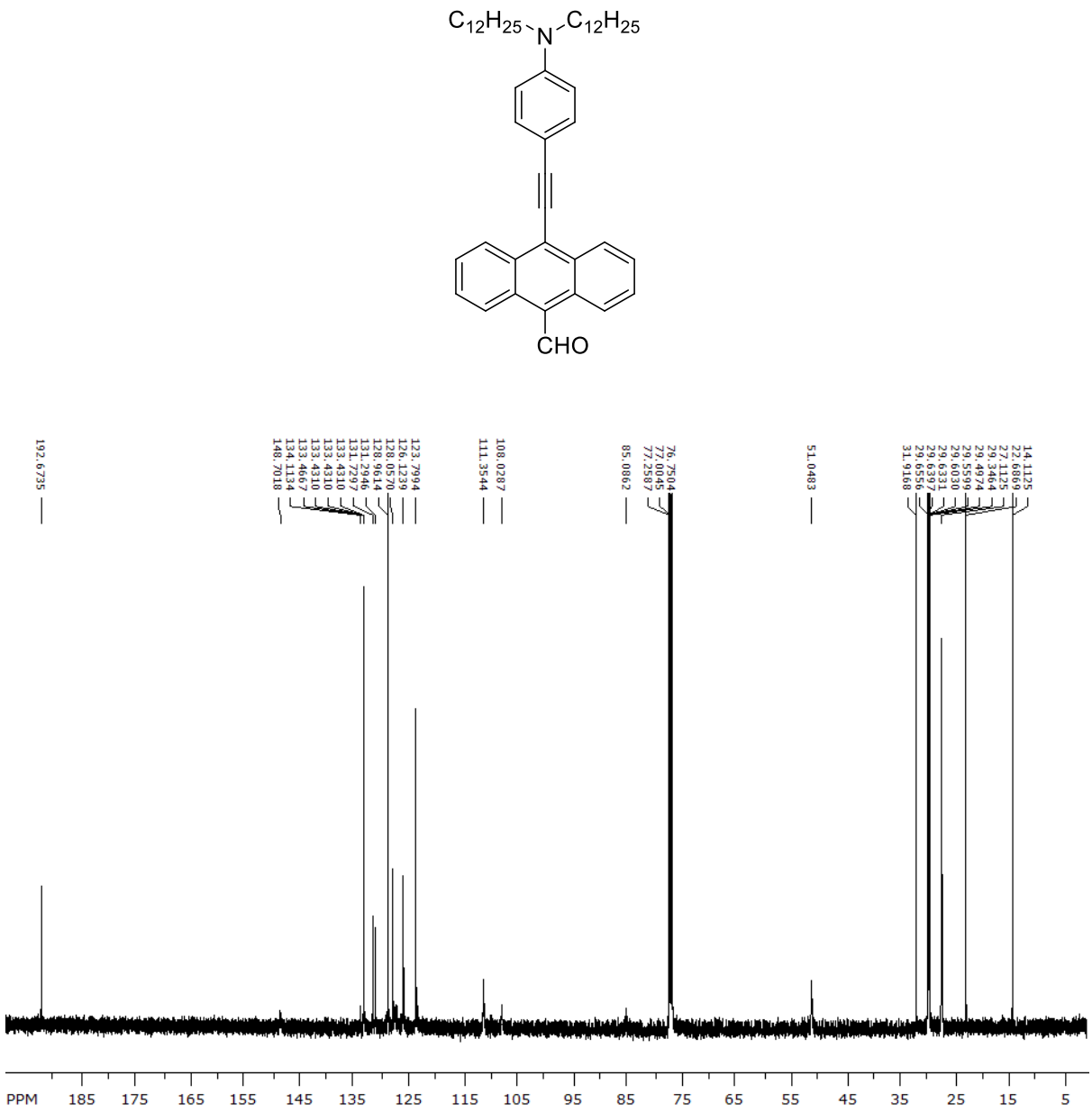

Figure S12.C^{13} NMR spectrum of **9** in $CDCl_3$.

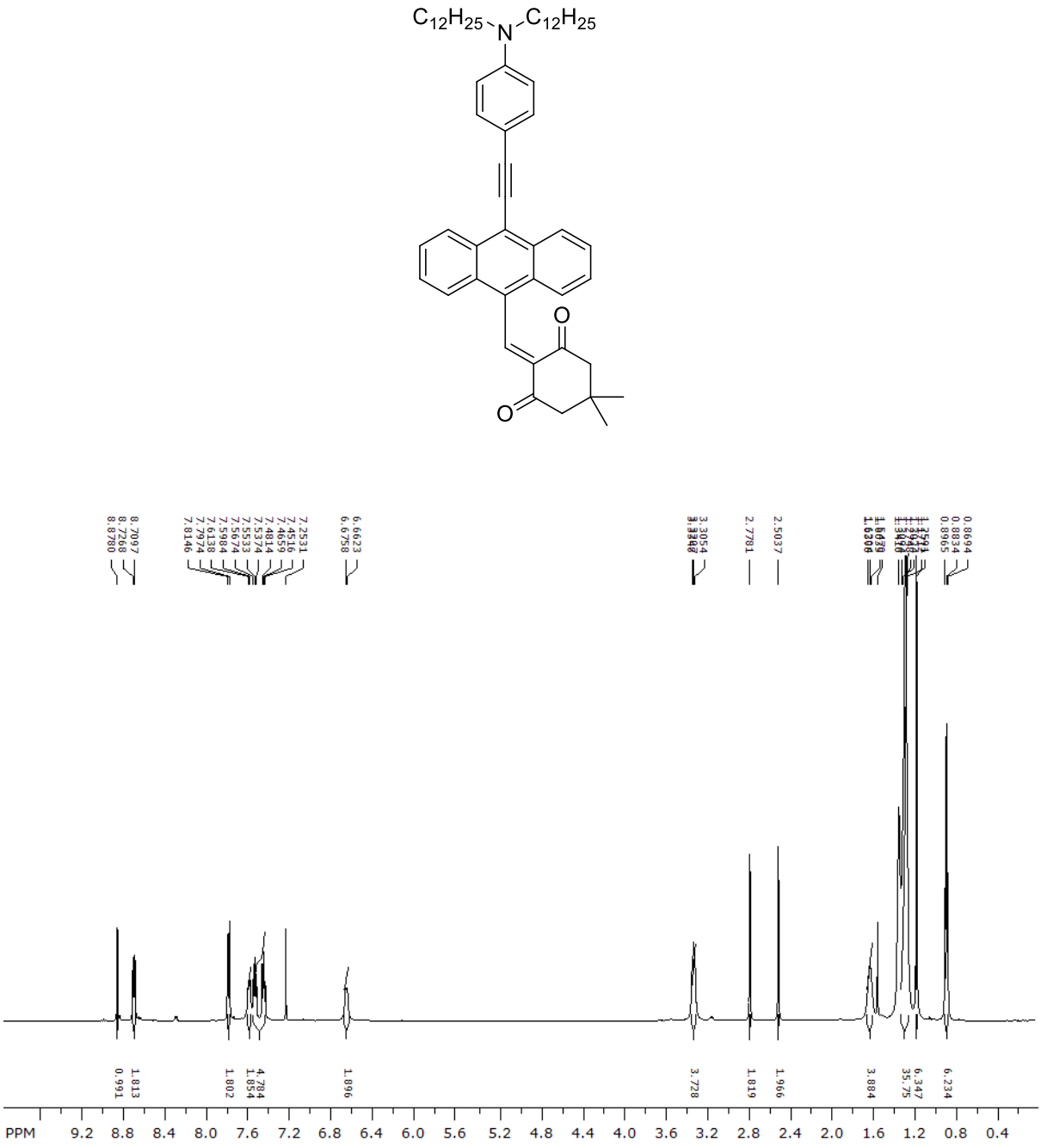

Figure S13.[1]H NMR spectrum of **10** in $CDCl_3$.

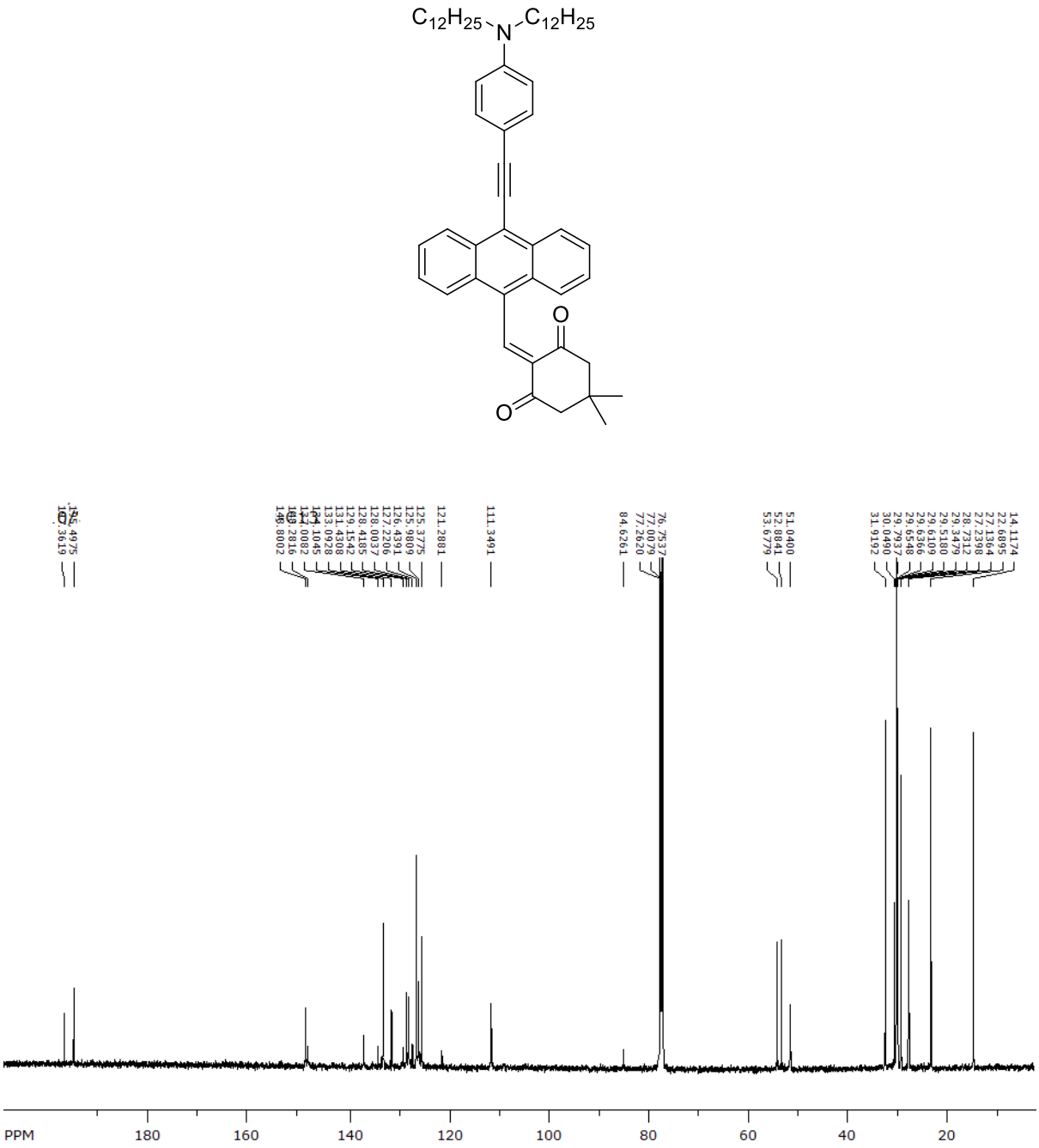

Figure S14.C^{13} NMR spectrum of **10** in $CDCl_3$.

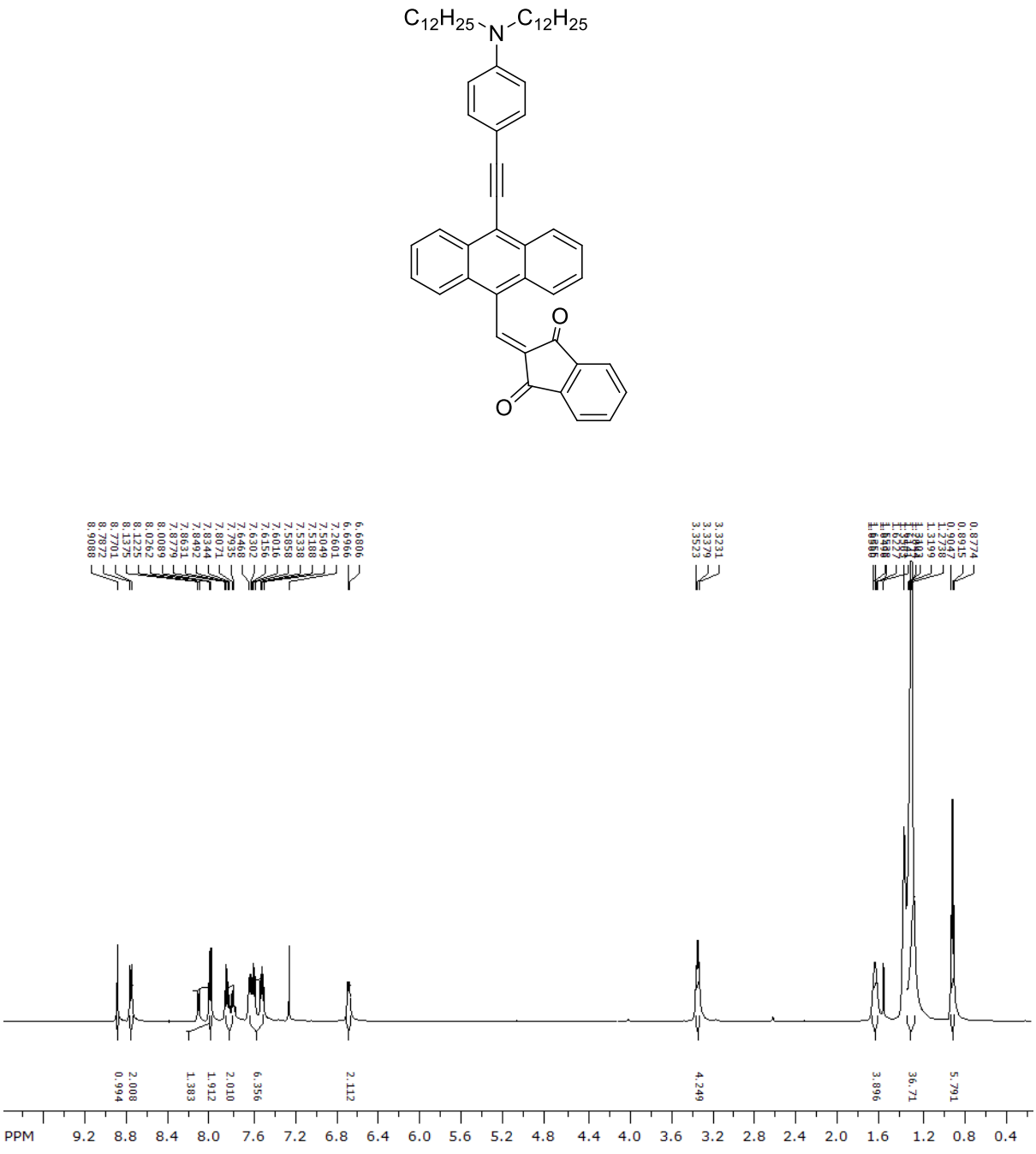

Figure S15.[1]H NMR spectrum of **11** in $CDCl_3$.

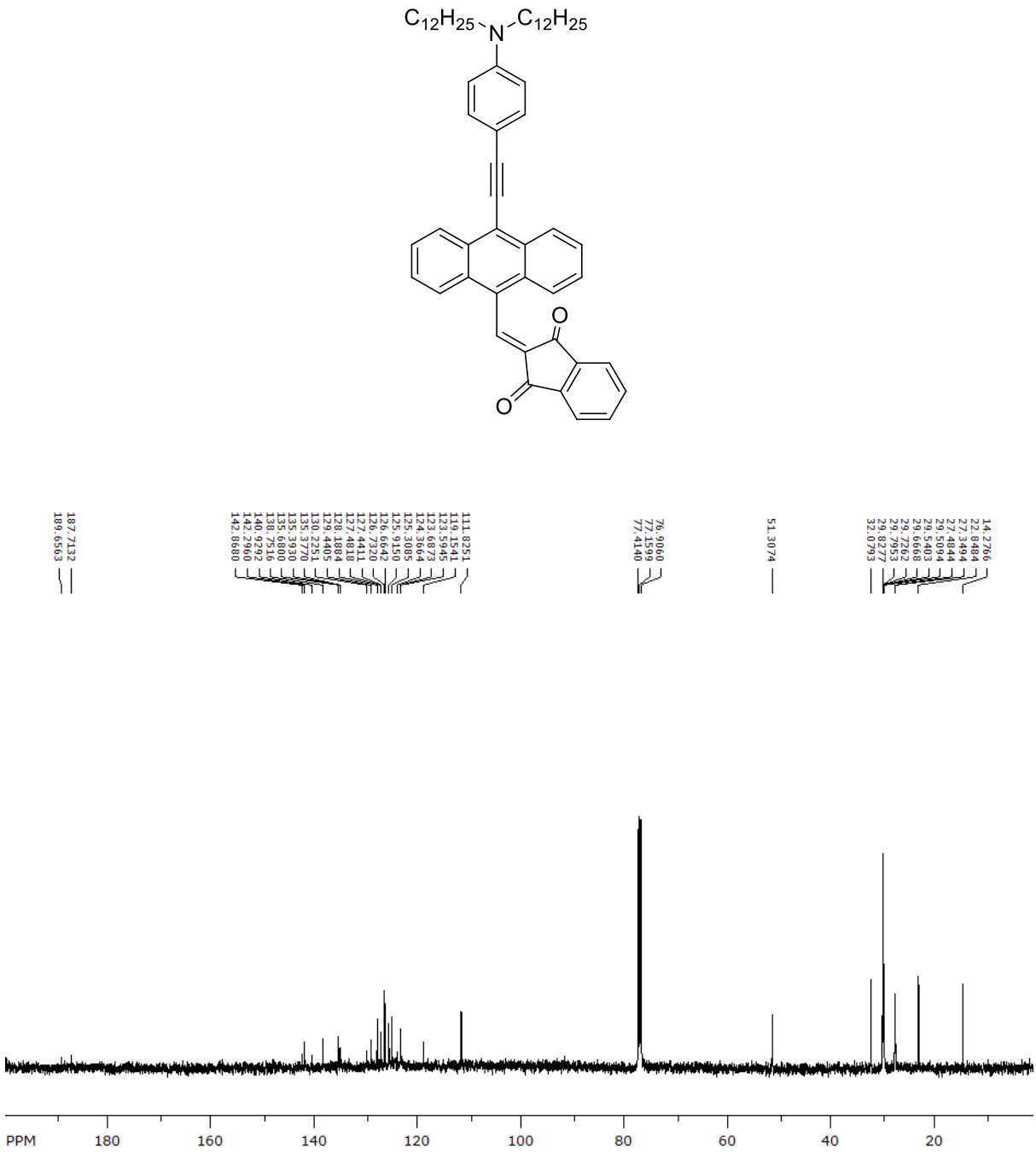

Figure S16.C^{13} NMR spectrum of **11** in $CDCl_3$.

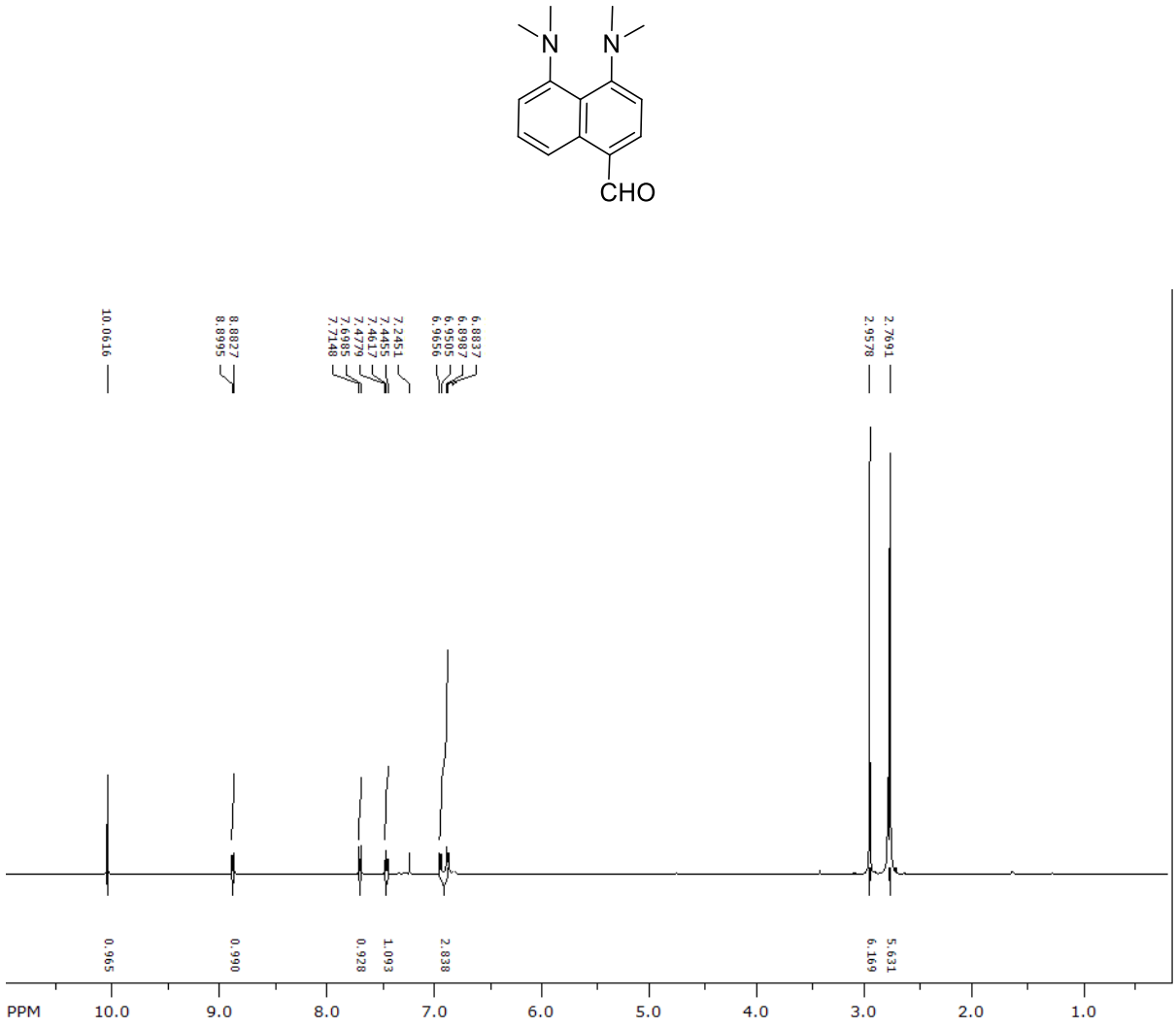

Figure S17. ^{1}H NMR spectrum of **14** in $CDCl_3$.

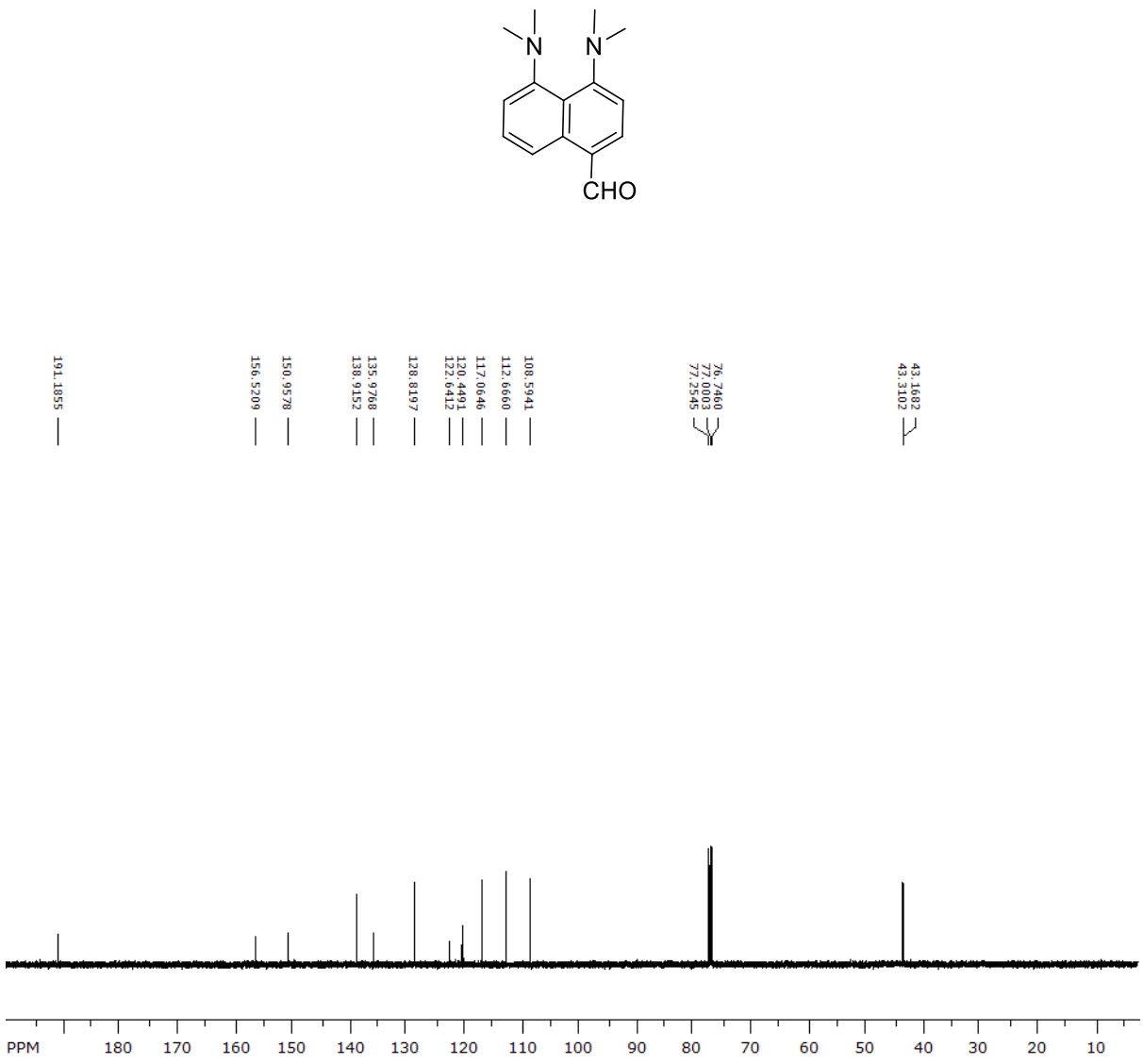

Figure S18.C^{13} NMR spectrum of **14** in $CDCl_3$.

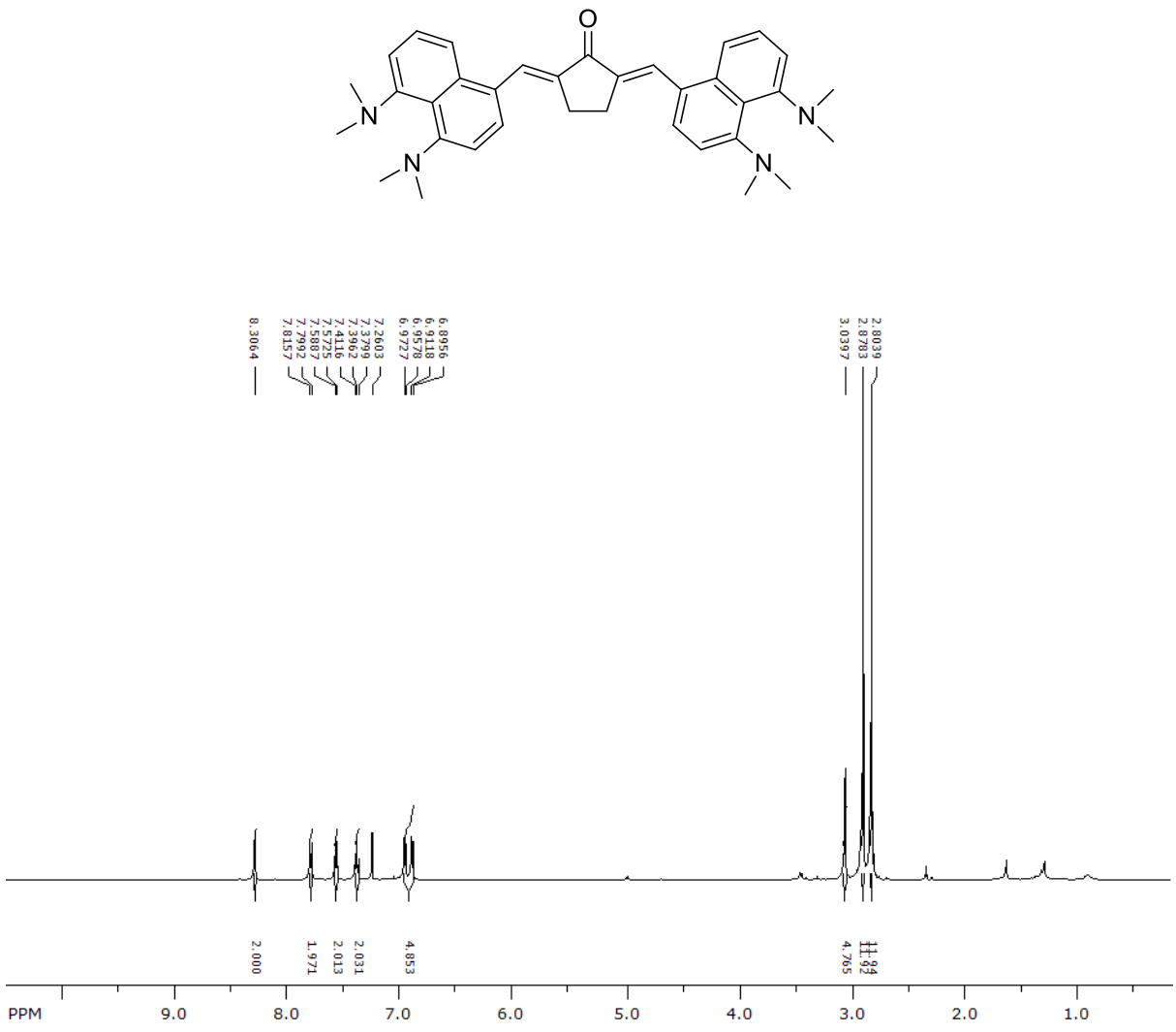

Figure S19.C^{13} NMR spectrum of **16** in $CDCl_3$.

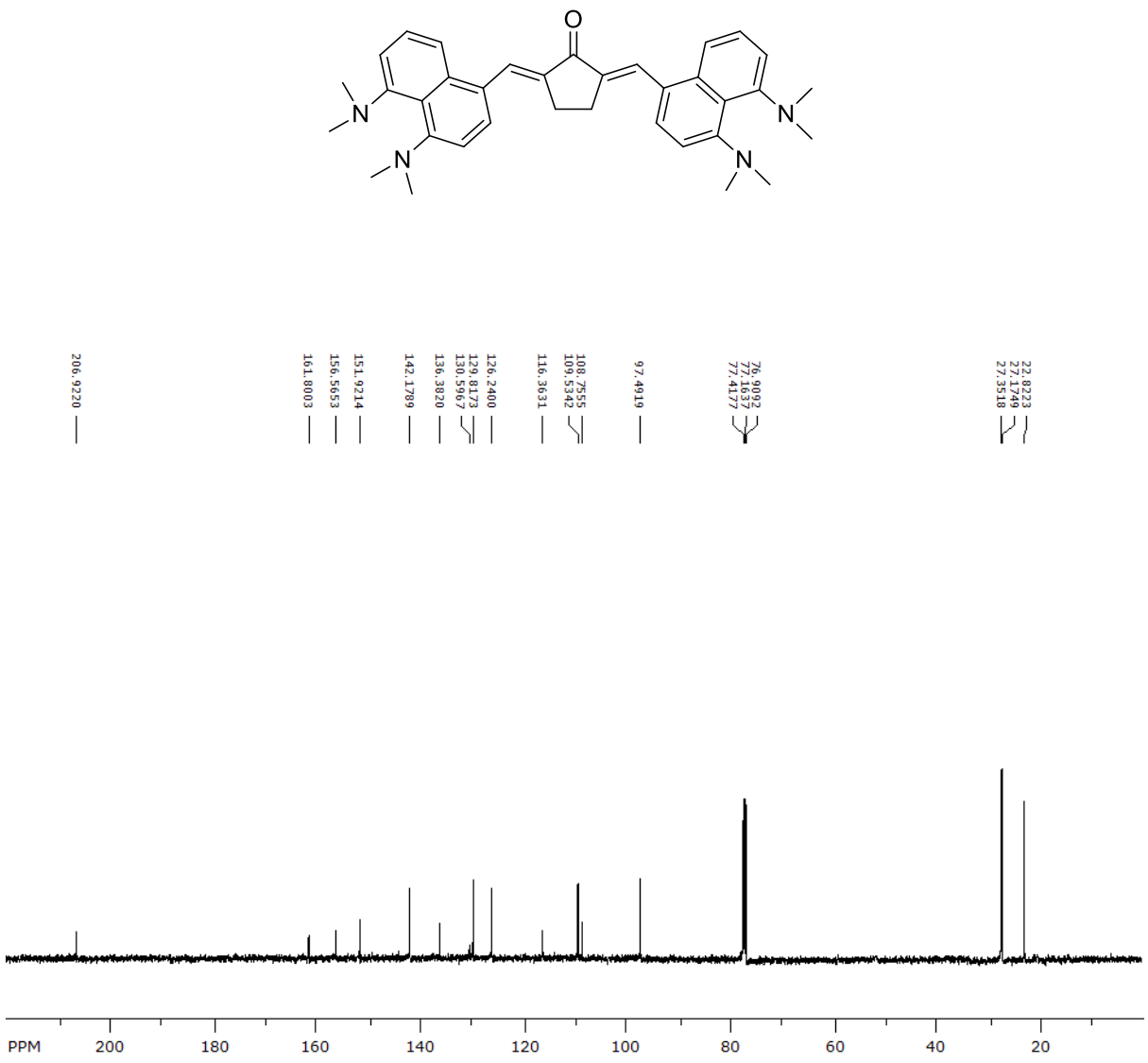

Figure S20.C^{13} NMR spectrum of **16** in $CDCl_3$.

3. Full Gaussian reference.

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

4. Computational details.

Tab.S1.

XYZ coordinates for the DFT B3LYP/6-31G(d,p) optimised structures of 6', 7', 10' and 11'.

molecule 6'; E(RB3LYP) = -1481.41331066 AU

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molecule 7' ; E(RB3LYP) = -1515.90050087 AU

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molecule 10' ; E(RB3LYP) = -1480.17270945 AU

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1	9.345801000	-2.266741000	1.345842000
1	10.774936000	-1.505472000	0.625145000
1	9.521218000	-2.178538000	-0.419850000
1	-7.352122000	-1.005856000	-0.921025000
1	-9.203171000	-0.638978000	1.465067000
1	-8.272427000	-1.602165000	2.622439000
1	-8.476174000	-2.172469000	0.958040000
1	-7.728187000	1.383759000	1.963510000
1	-5.969491000	1.277417000	1.822206000
1	-6.800878000	0.417645000	3.122400000
1	-7.949955000	0.591403000	-0.488153000
1	-6.017316000	-2.390862000	0.738734000

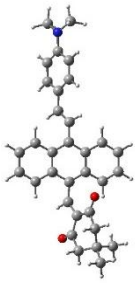
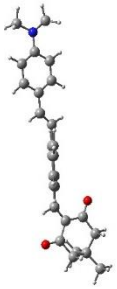
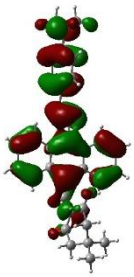
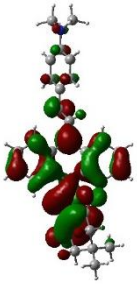
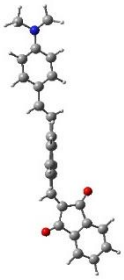
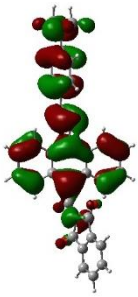
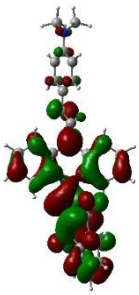
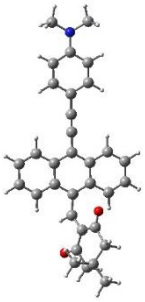
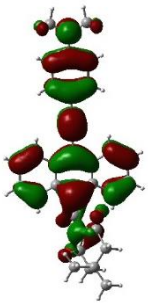
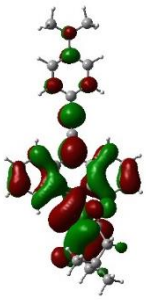
molecule 11'; E(RB3LYP) = -1514.65976084 AU

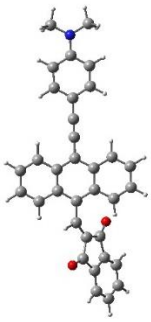
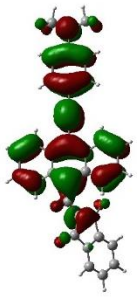
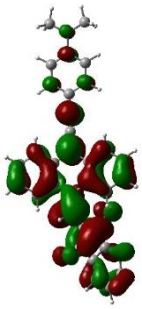
8	3.631862000	-1.447772000	1.188687000
6	8.012786000	-1.815539000	1.879428000
6	8.753488000	-0.892295000	1.123730000
6	6.618914000	-1.859168000	1.796814000

6	8.117054000	0.009508000	0.267641000
6	5.988872000	-0.961874000	0.939374000
6	6.728277000	-0.039857000	0.186650000
6	4.524559000	-0.800019000	0.665313000
6	5.796745000	0.799511000	-0.623032000
6	4.414154000	0.309491000	-0.326634000
6	-9.937601000	0.546218000	0.915919000
6	-7.752976000	-0.422568000	0.357682000
6	-6.914379000	-1.519143000	0.037148000
6	-7.136098000	0.843690000	0.514729000
6	-5.548933000	-1.352866000	-0.123312000
6	-4.935709000	-0.091674000	0.028730000
6	-3.536955000	0.073728000	-0.132579000
6	2.064930000	-1.678693000	-1.359205000
6	1.309039000	-0.554208000	-0.908554000
6	1.901594000	0.718737000	-0.671043000
6	-0.115383000	-0.721969000	-0.771969000
6	-0.935002000	0.387262000	-0.421291000
6	-0.351897000	1.673018000	-0.232045000
6	1.070623000	1.837126000	-0.359920000
6	1.475838000	-2.892128000	-1.600844000
6	-0.689929000	-2.004668000	-1.015817000
6	-2.332299000	0.217374000	-0.269201000
6	-1.154890000	2.804355000	0.094930000
6	1.611503000	3.137657000	-0.113891000
6	0.806096000	4.207195000	0.186527000
6	-0.598050000	4.041592000	0.291189000
6	0.080659000	-3.065647000	-1.411072000
6	3.331555000	0.966968000	-0.816334000
6	-5.769652000	0.998827000	0.352749000
7	-9.115368000	-0.580611000	0.508581000

6	-9.708180000	-1.904828000	0.426161000
8	6.106791000	1.714285000	-1.371025000
1	-9.528368000	-2.366217000	-0.553037000
1	-10.787031000	-1.823697000	0.561110000
1	-9.319172000	-2.584571000	1.197615000
1	3.600446000	1.860560000	-1.383264000
1	6.033196000	-2.565746000	2.376222000
1	8.535418000	-2.504134000	2.537003000
1	9.836072000	-0.881690000	1.210133000
1	8.675615000	0.731515000	-0.319543000
1	-4.934030000	-2.212984000	-0.368608000
1	-2.225382000	2.660275000	0.187320000
1	2.684825000	3.282071000	-0.147097000
1	1.248883000	5.183900000	0.357964000
1	-1.227302000	4.891497000	0.537470000
1	-5.327925000	1.982053000	0.480207000
1	3.125219000	-1.558043000	-1.533176000
1	-7.333433000	-2.509730000	-0.086526000
1	2.080856000	-3.725538000	-1.945240000
1	-1.761411000	-2.114941000	-0.894167000
1	-0.375457000	-4.033461000	-1.596612000
1	-7.729403000	1.713368000	0.767263000
1	-9.877260000	1.370216000	0.193871000
1	-10.979159000	0.228821000	0.970088000
1	-9.649373000	0.937981000	1.901812000

Tab.S2. The properties of **6'**, **7'**, **10'** and **11'** molecules calculated by DFT B3LYP/6-31G(d,p) method.

molecule	some features of geometry		HOMO	LUMO	S_0 -> S_i transition energy ΔE[nm]	osc. strength f
6' 		<(AN_{pl}, DMA_{pl}) 57.1^0 d($H^{C=C}$, H^{AN}) 2.151, 2.367 d(H_{AN}, O=C) 2.722			**574.69** 470.81 435.06 411.07 375.46	**0.5451** 0.0009 0.0030 0.0896 0.0019
7' 		<(AN_{pl}, DMA_{pl}) 57.0^0 d($H^{C=C}$, H^{AN}) 2.138, 2.349 d(H_{AN}, O=C) 2.767			**585.93** 477.76 473.35 427.12 419.53	**0.6350** 0.0075 0.0036 0.0007 0.0967
10' 		<(AN_{pl}, DMA_{pl}) 0.5^0 d(H_{AN}, O=C) 2.789			**590.82** 450.95 448.69 417.65 383.61	**0.7430** 0.0405 0.0020 0.0718 0.0023

11' 		<(AN$_{pl}$, DMA$_{pl}$) 0.9^0 d(H$_{AN}$, O=C) 2.721			**596.16** 476.73 454.68 434.83 426.04	**0.8468** 0.0034 0.0223 0.0019 0.0899