Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

A Route to Hydroxylfluorenes: TsOH-Mediated Reactions of 1,3-diketones with Propargylic Alcohols

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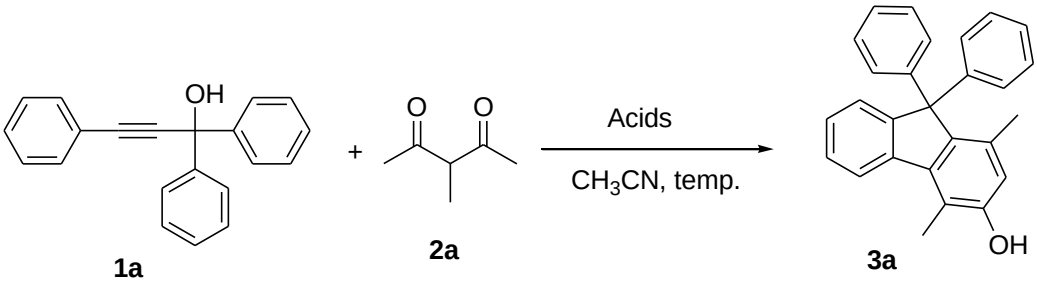
Content

Table S1. Optimization of the Reaction Conditions

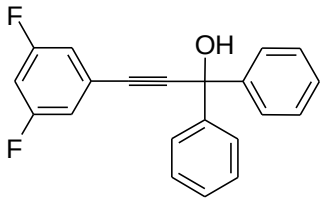


1a **2a** **3a**

Entry[a]	Acids	Temp.	yield of **3a**[b]
1	TsOH (0.1 eq)	60 ^oC	60%
2	TsOH (0.5 eq)	60 ^oC	64%
3	***TsOH (1.0 eq)***	***60 ^oC***	***75%***
4	TsOH (2.0 eq)	60 ^oC	67%
5	TsOH (0.1 eq)	rt	trace
6	MsOH (1.0 eq)	60 ^oC	65%
7	TsOH (1.0 eq)	60 ^oC	52%[c]
8	Conc. H_2SO_4 (1.0 eq)	60 ^oC	-
9	Conc. HCl (1.0 eq)	60 ^oC	-

[a]All of reactions were carried out with **1a** (0.3 mmol), **2a** (0.36 mmol) in CH_3CN (3 mL)
[b]Isolated yields.[C]The ratio of **1a**/**2a** was 1.2/1

Figures of ^{1}H and ^{13}C NMR Spectra:



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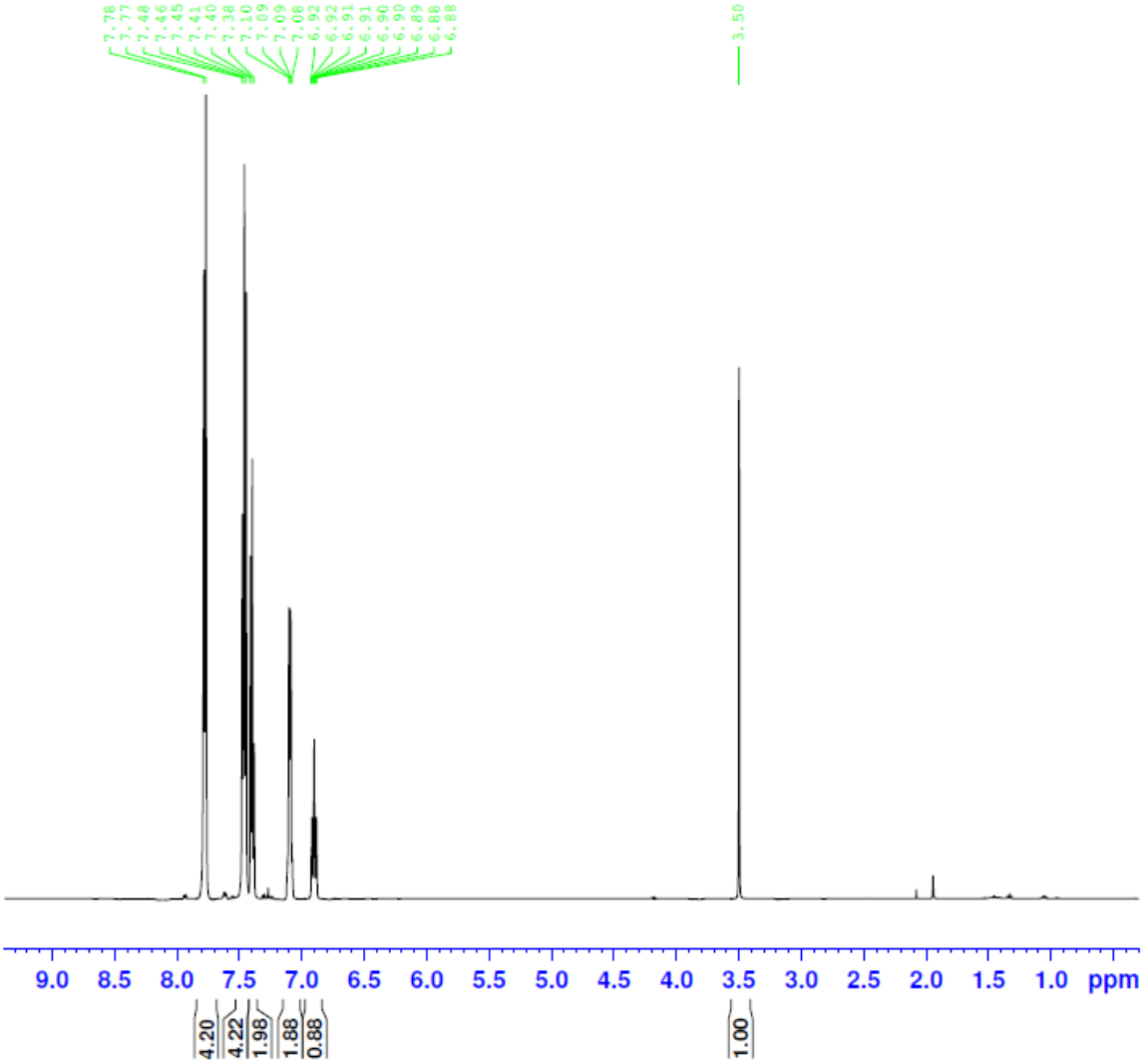

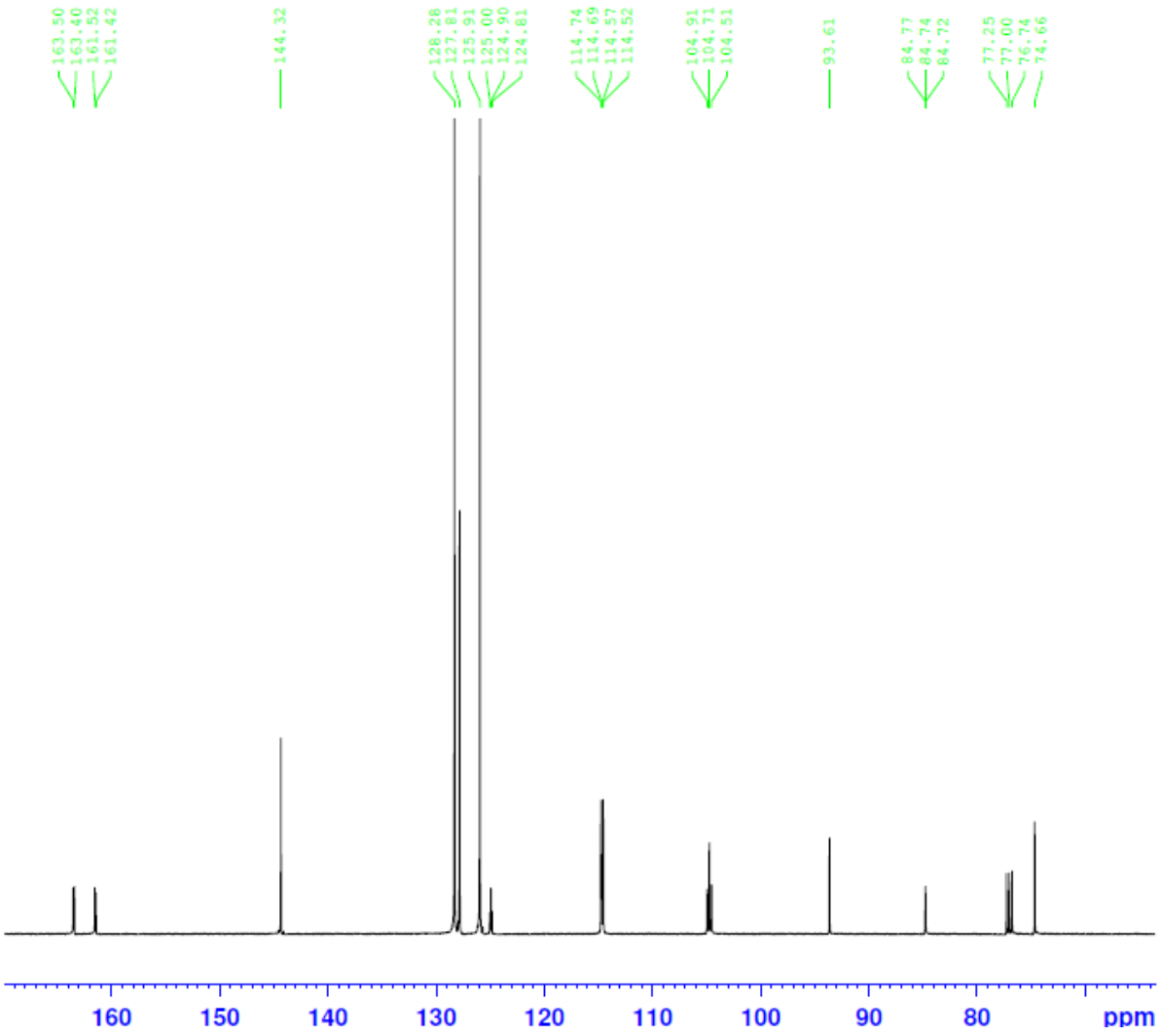

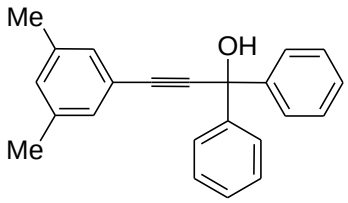

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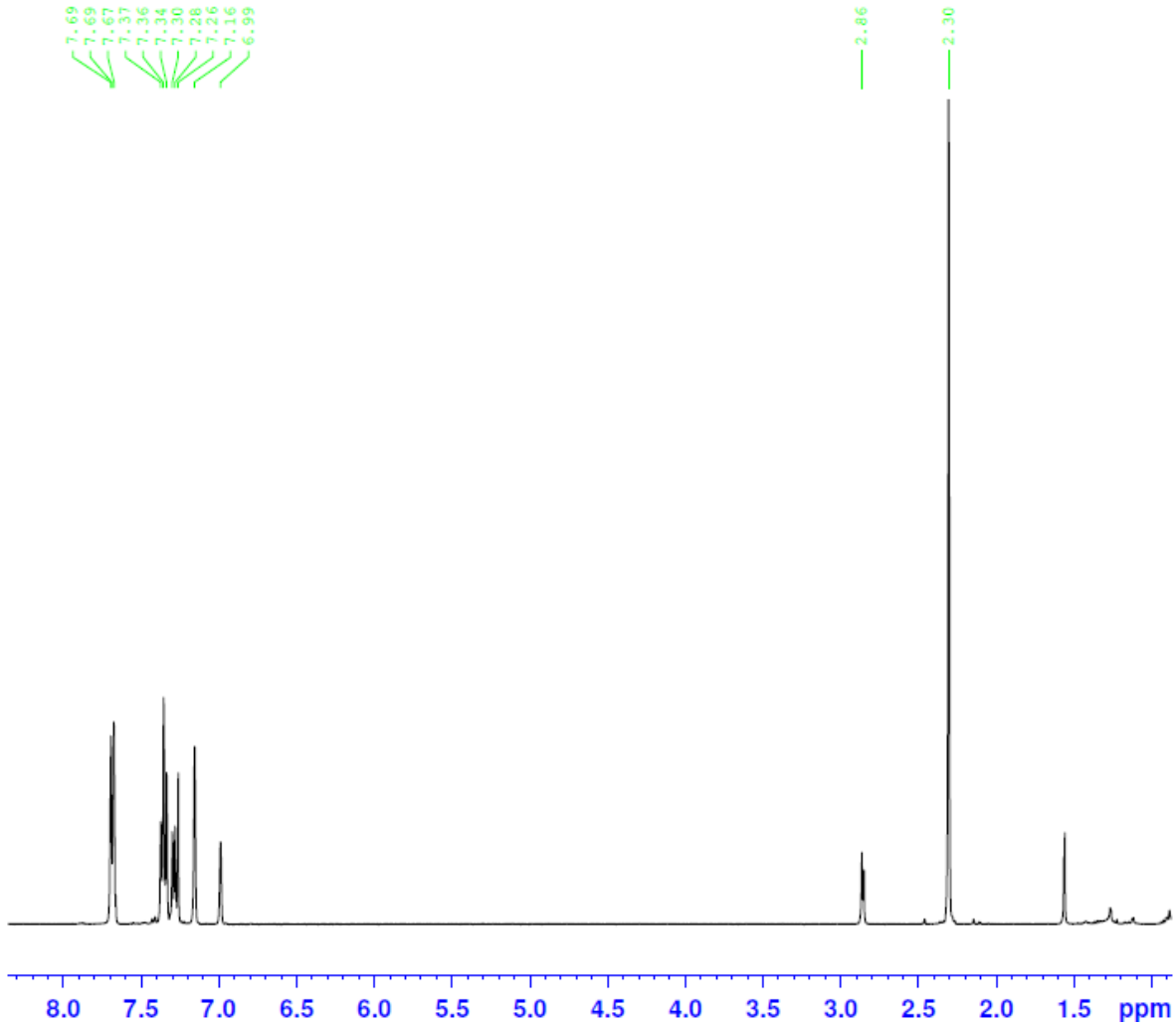
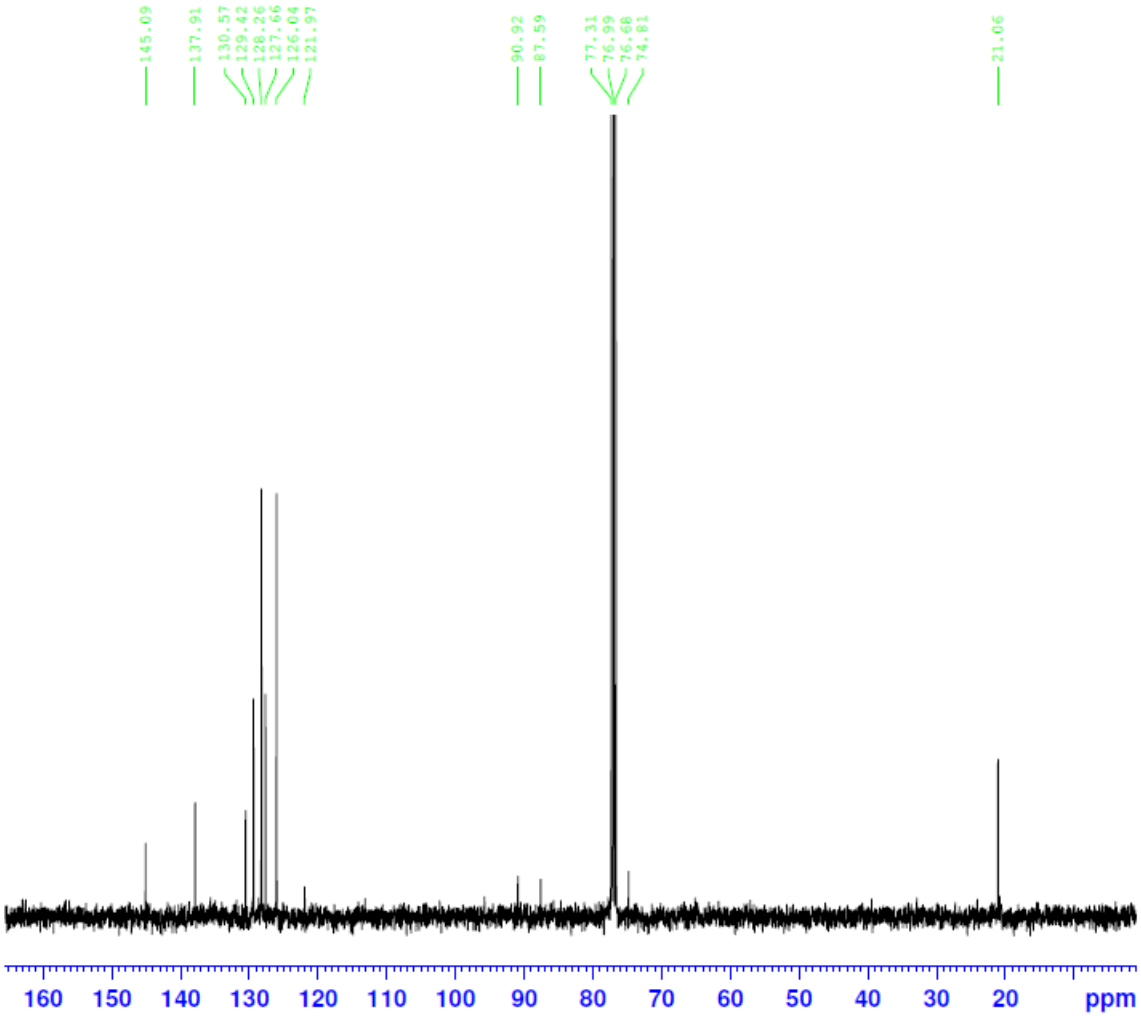
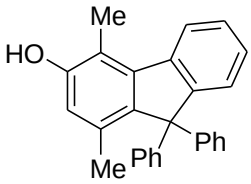
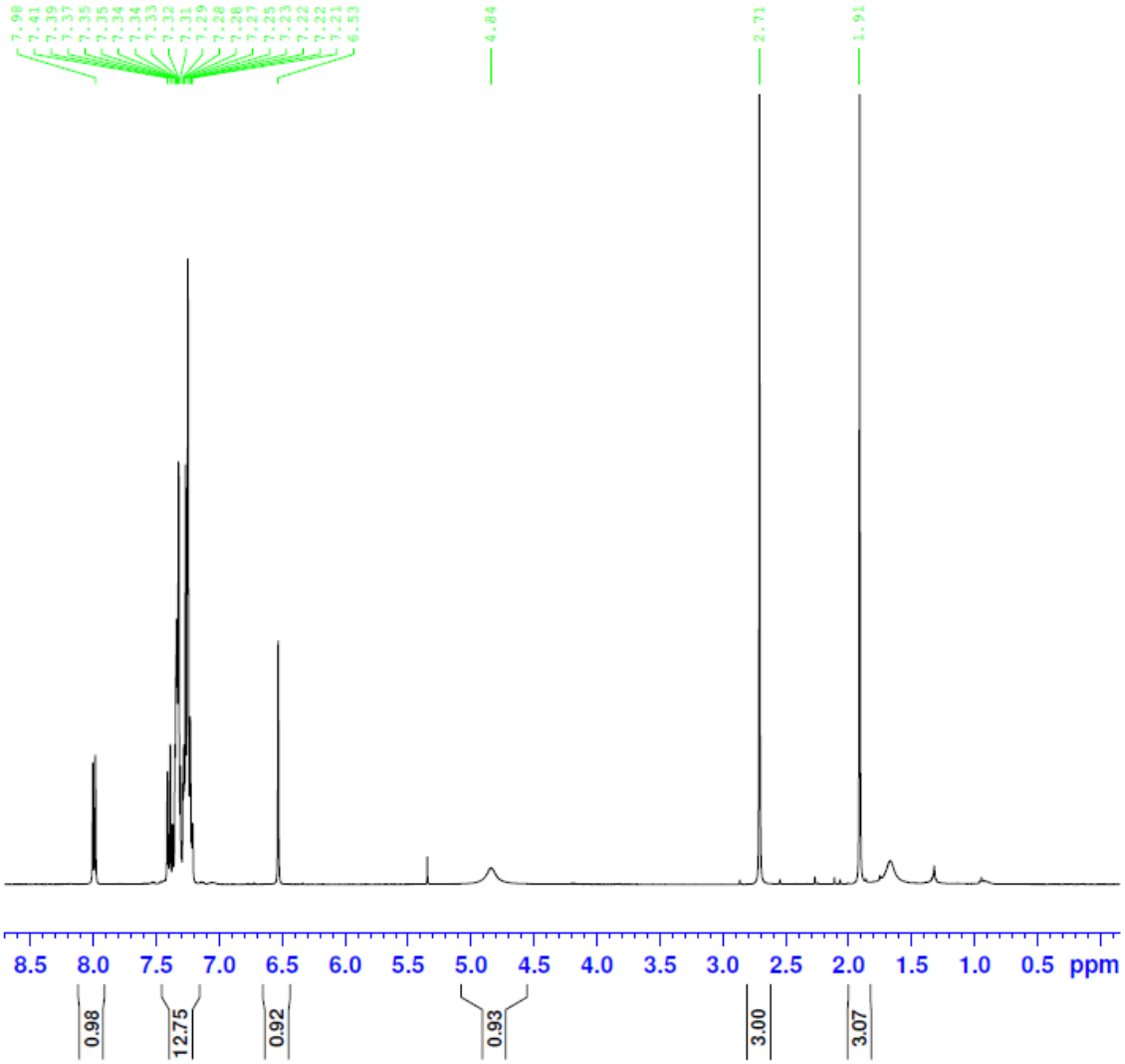
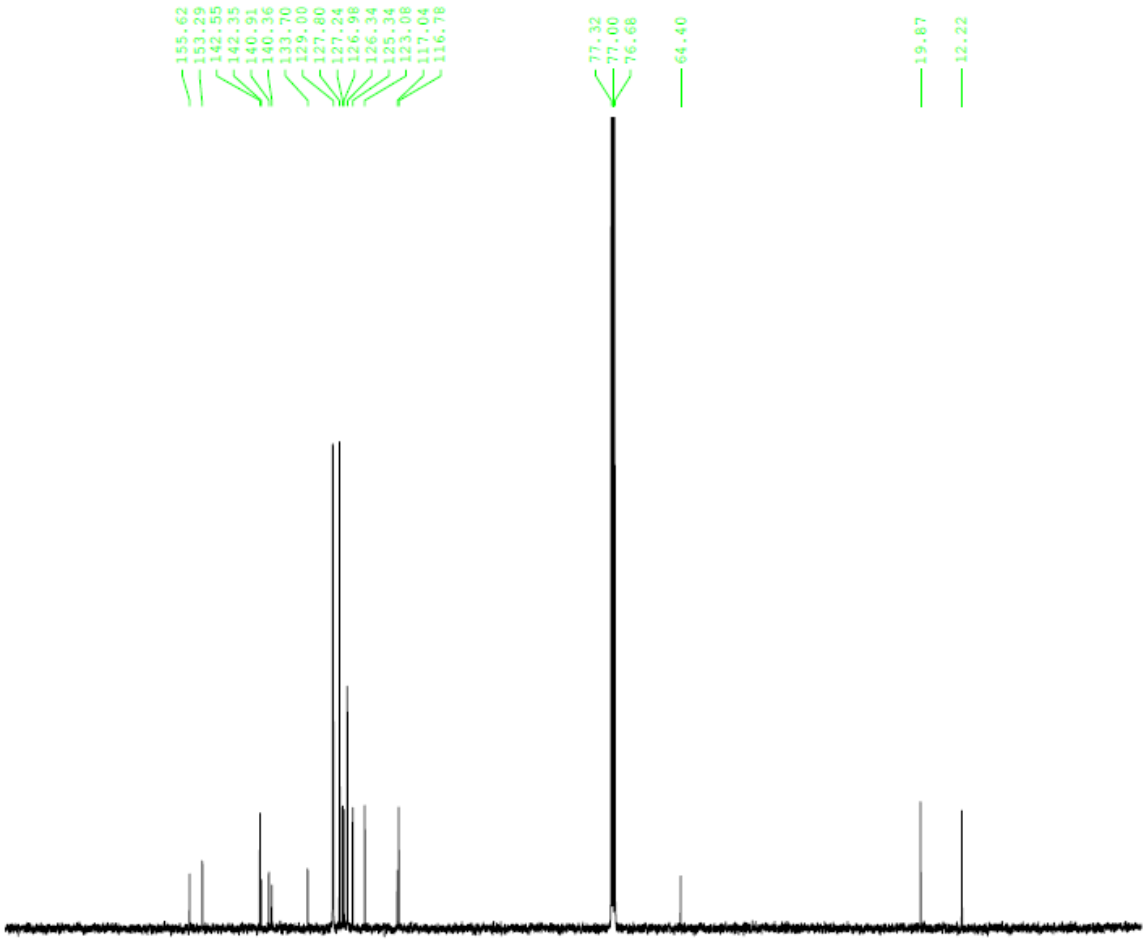




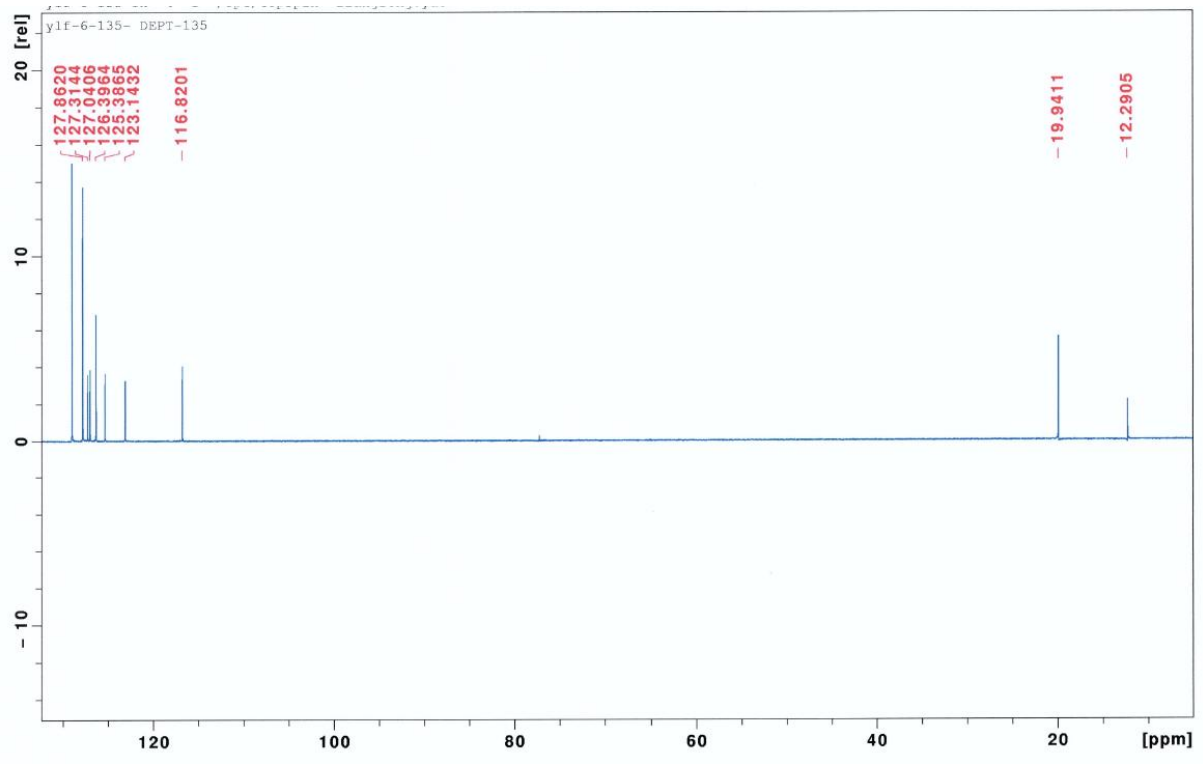


3a





DEPT 135 spectrum of **3a**



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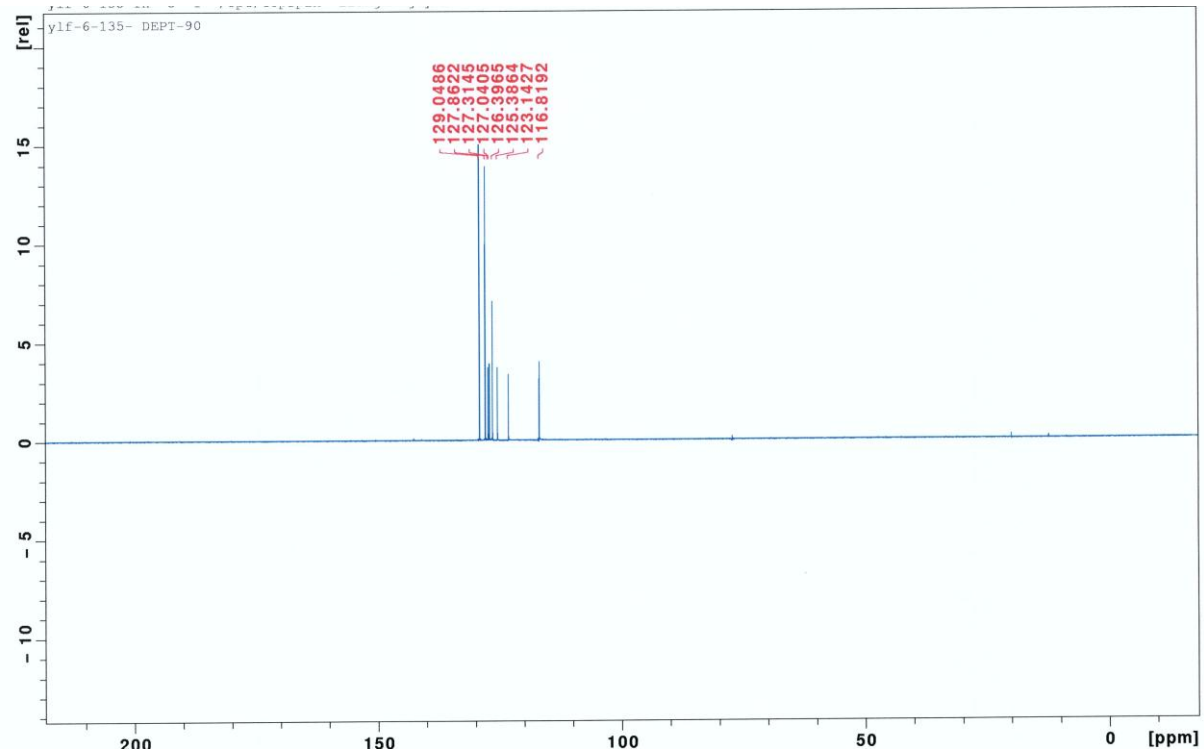

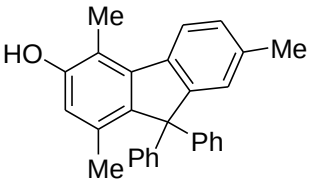

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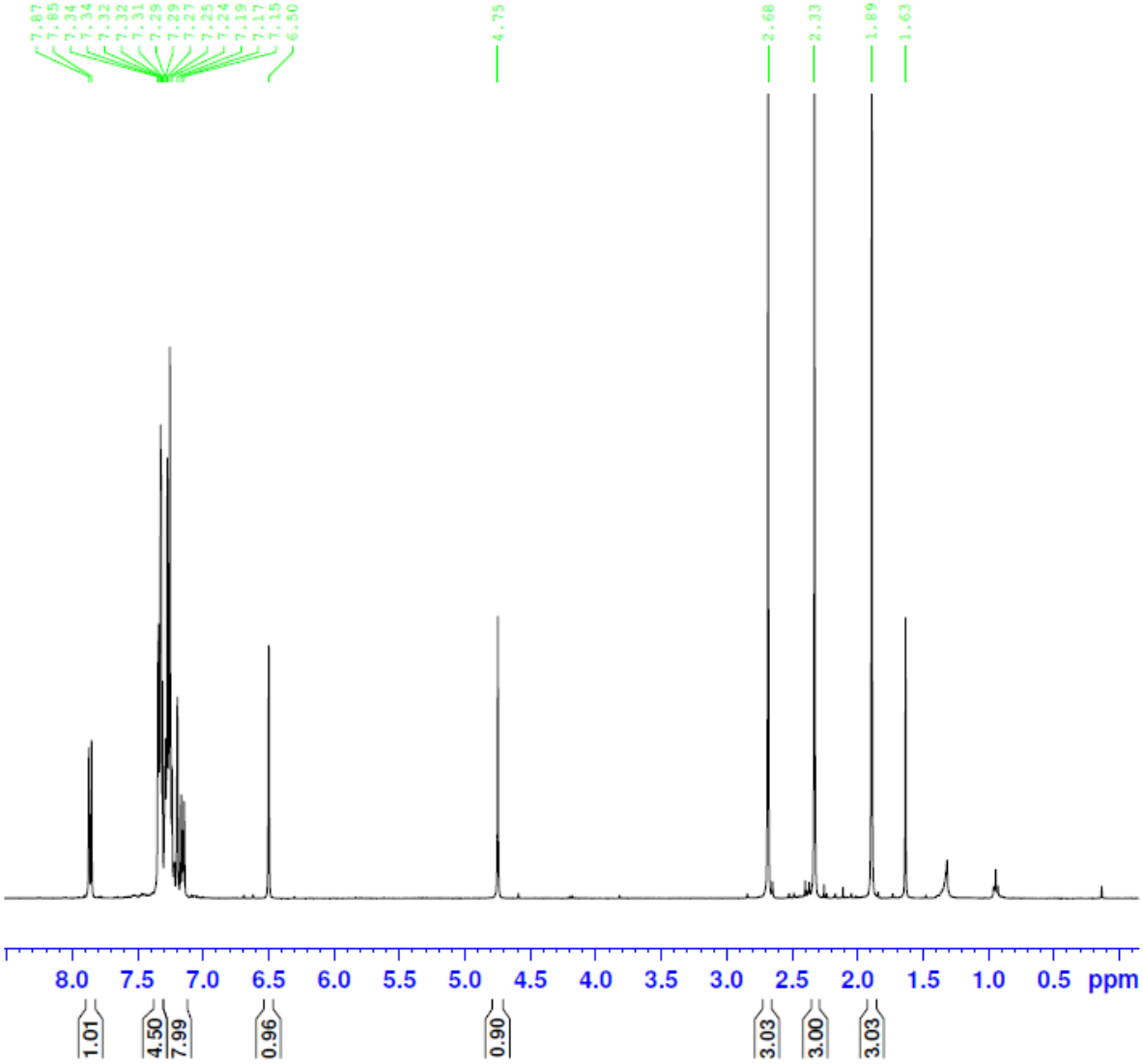

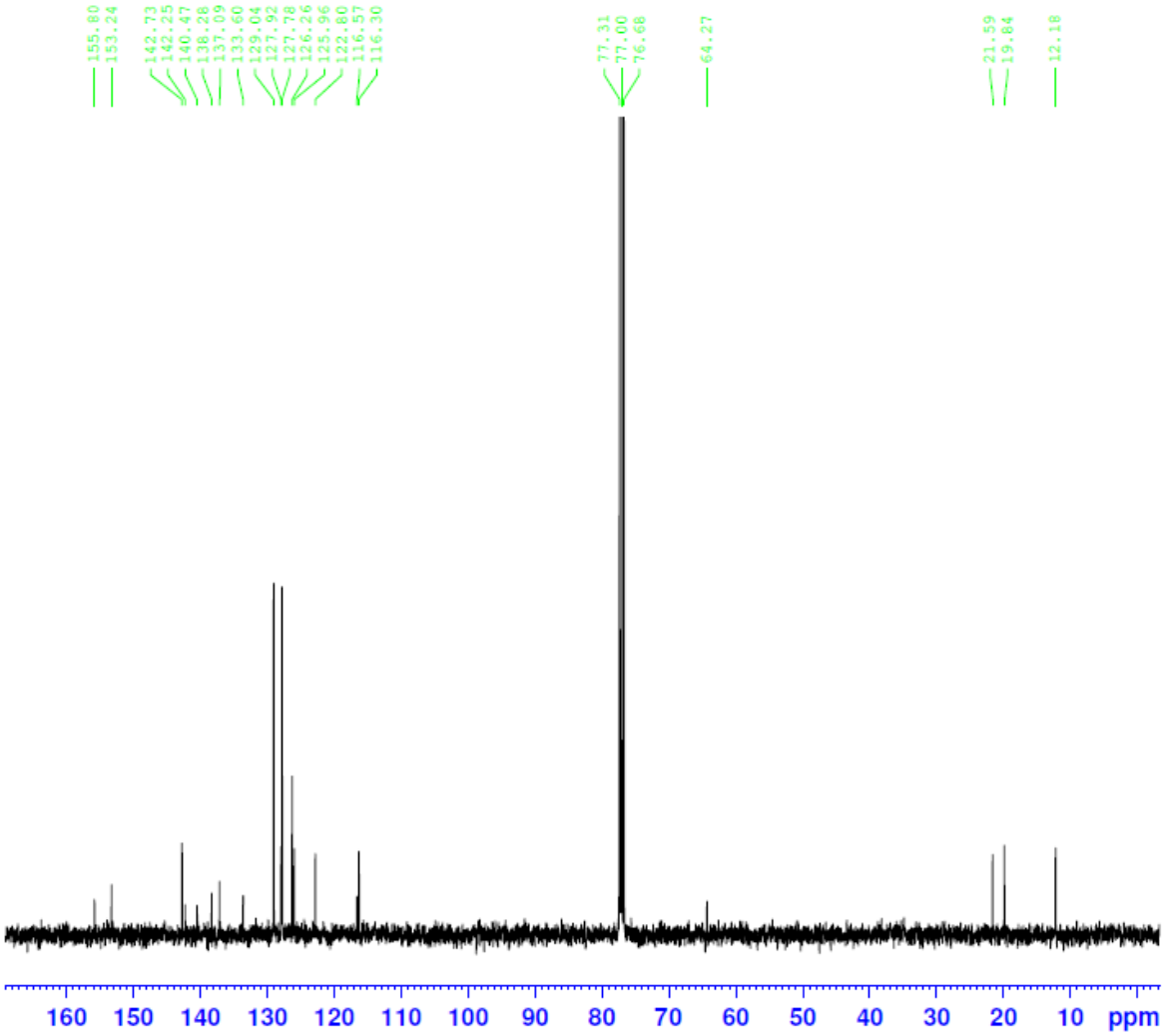

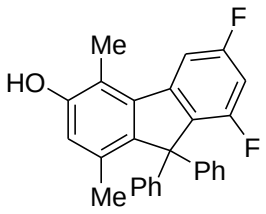

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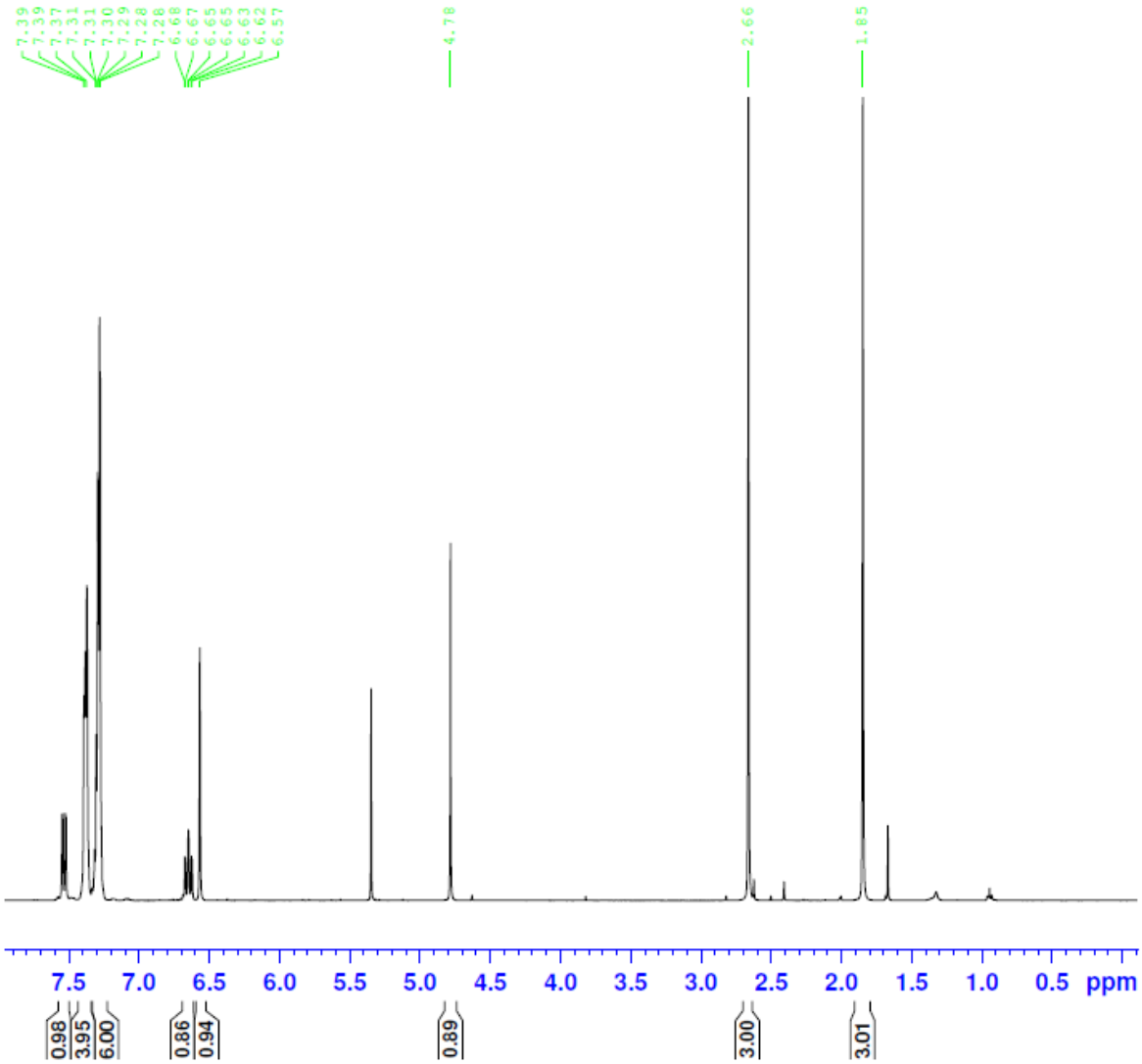

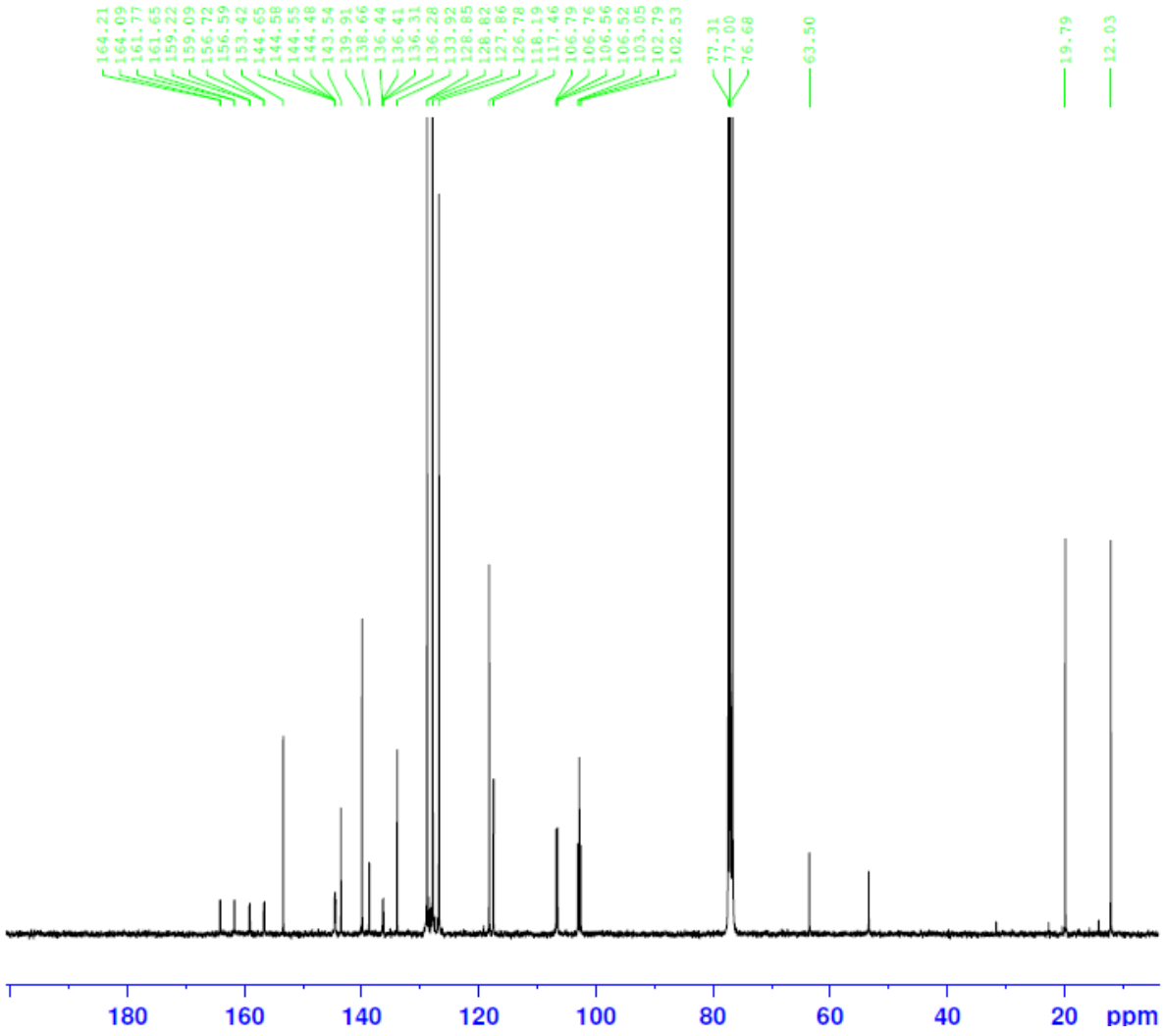

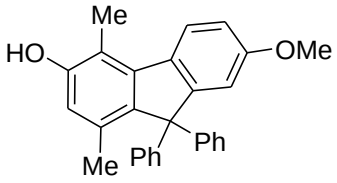

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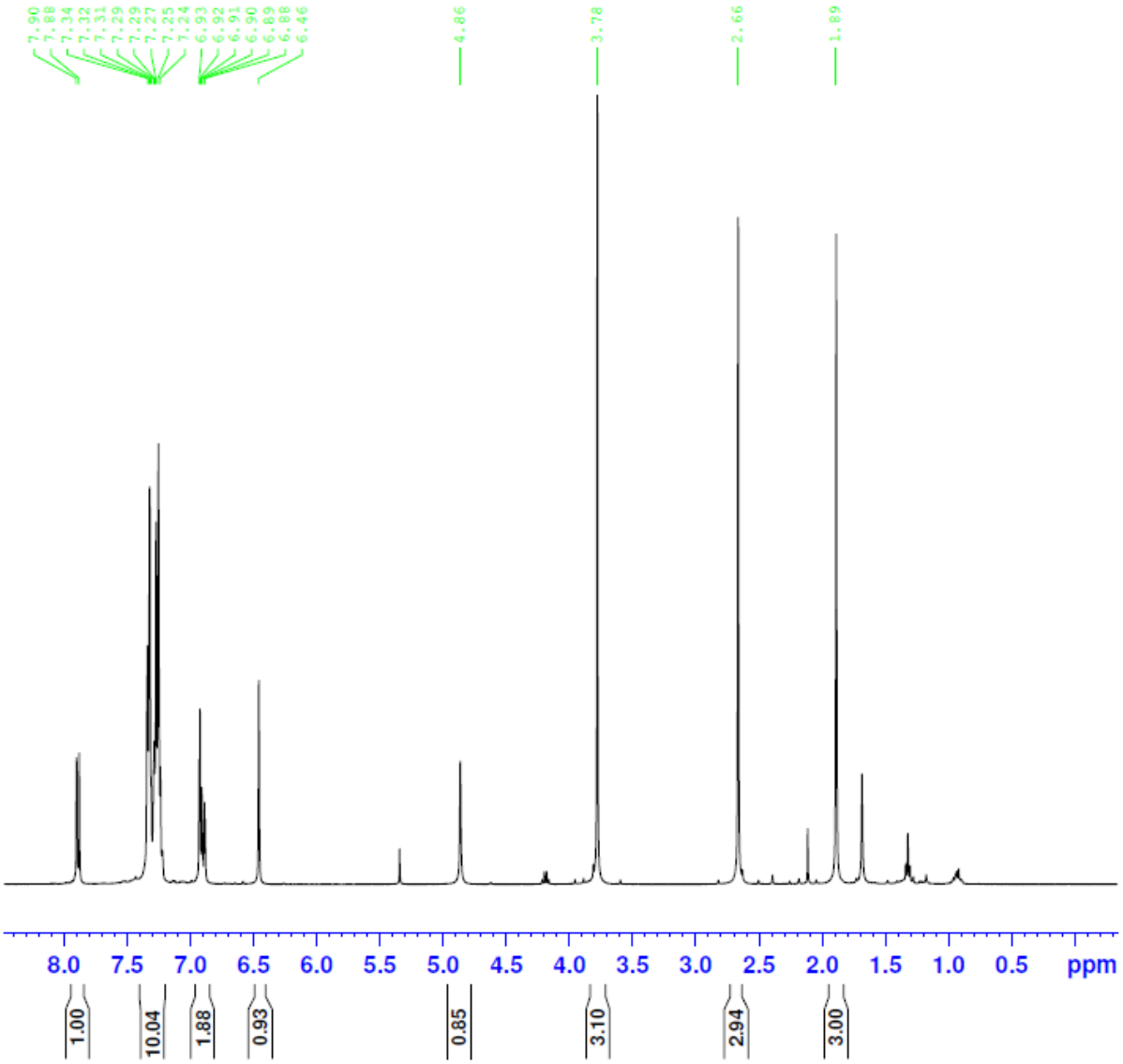

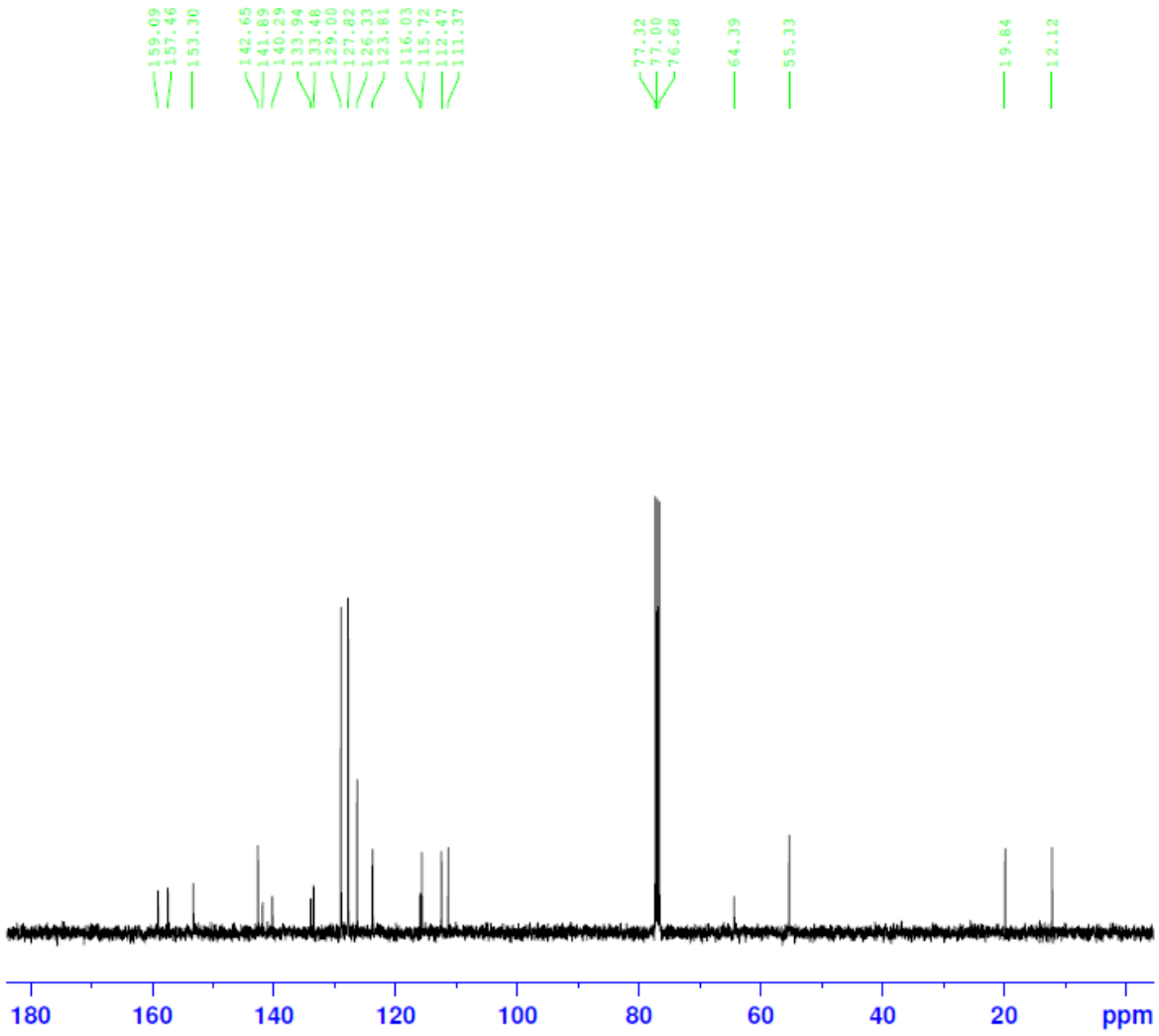

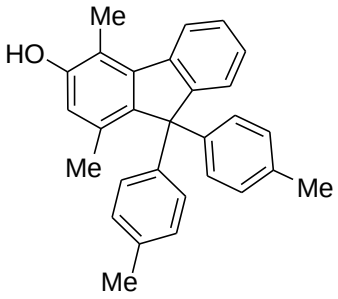

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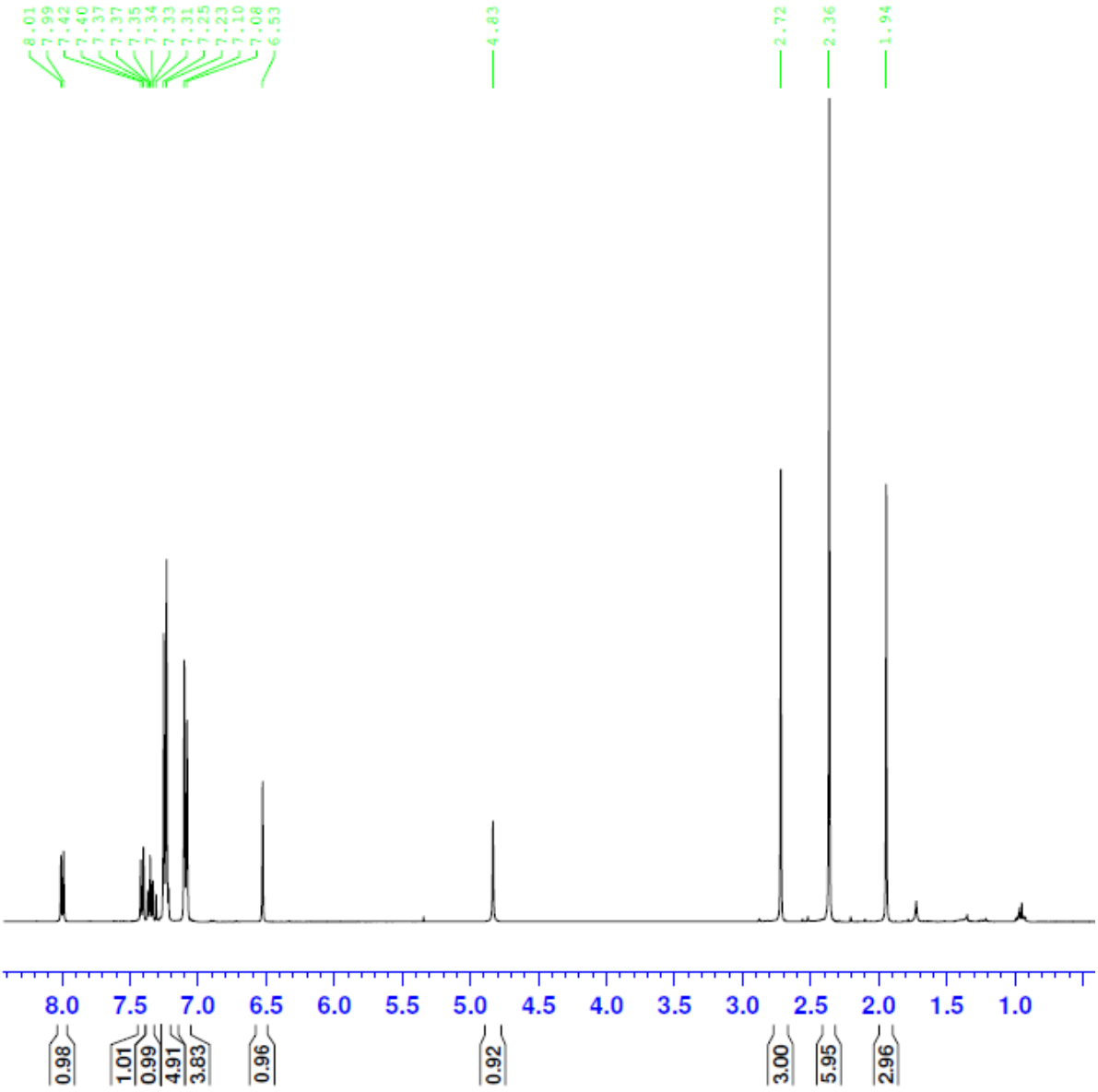

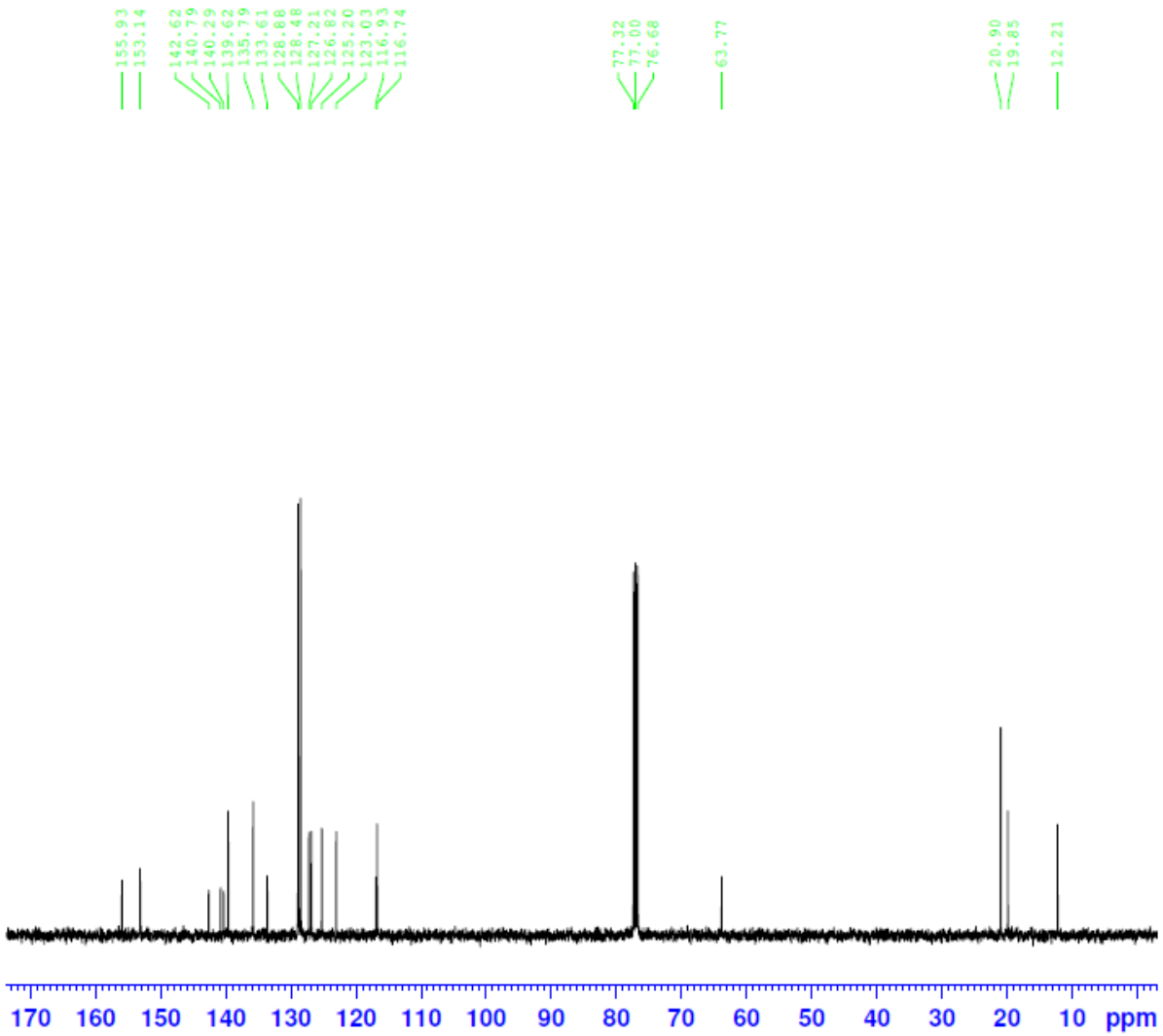

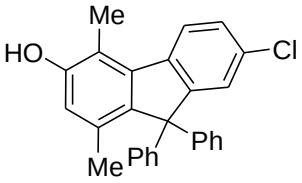

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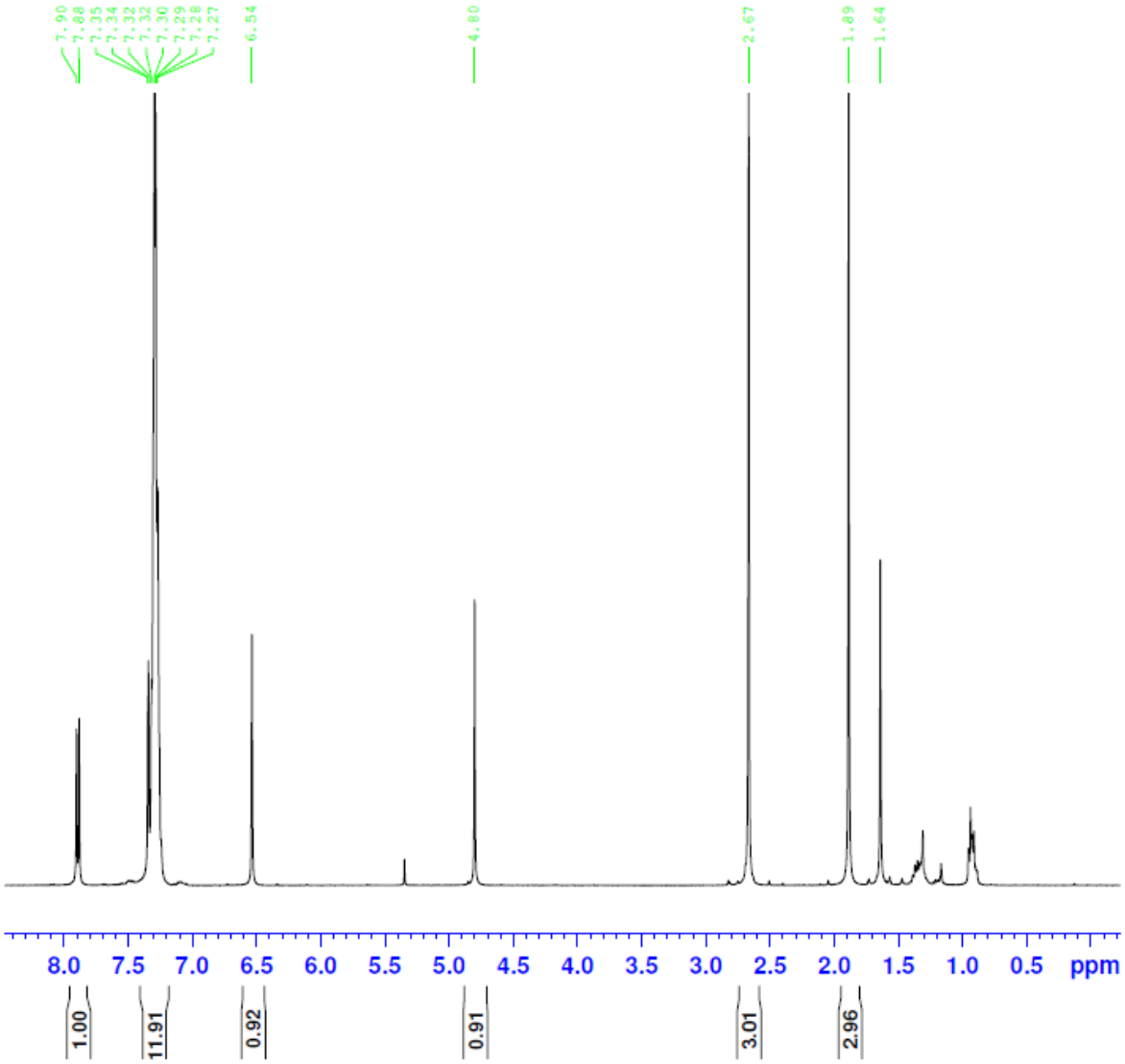

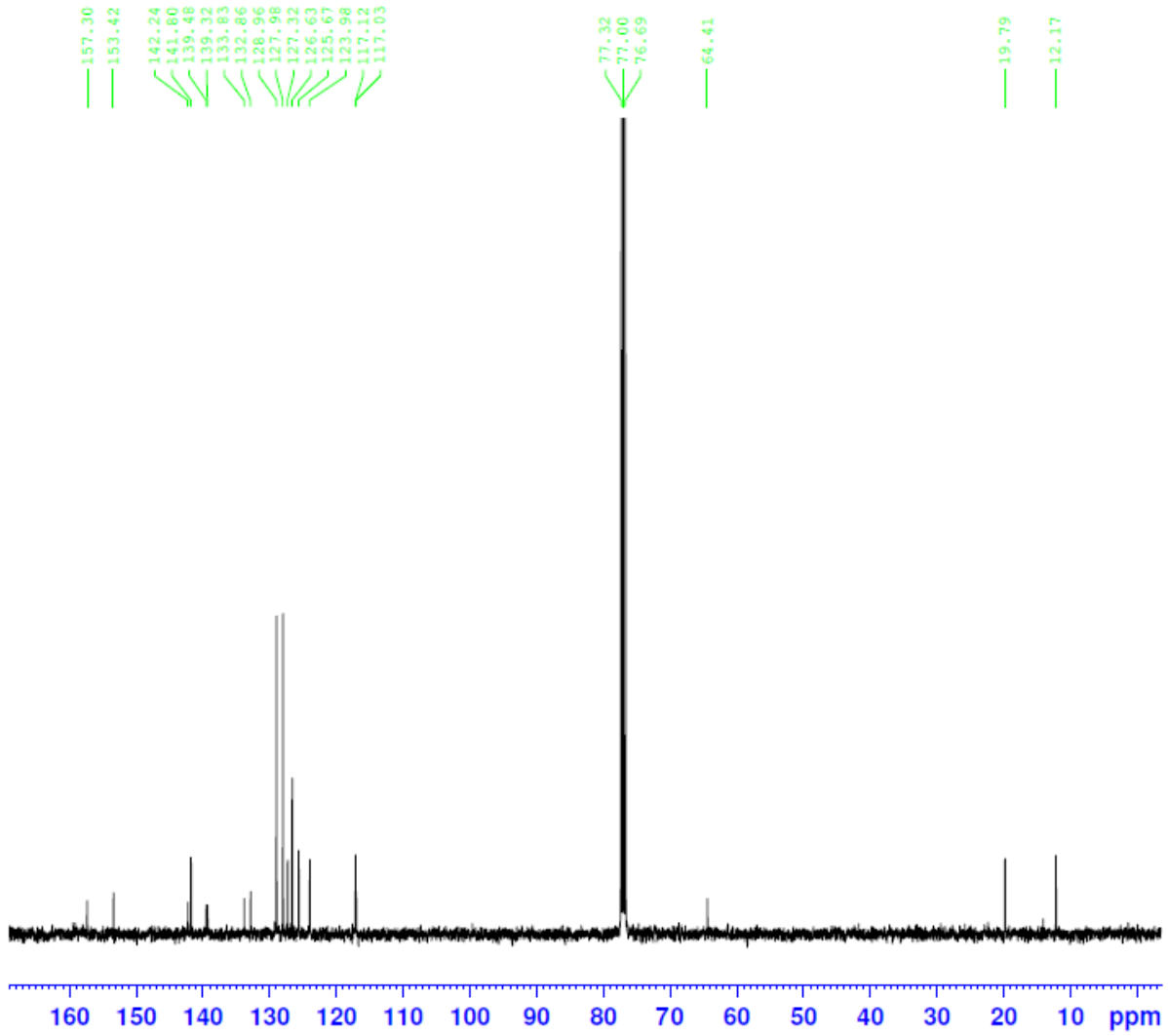

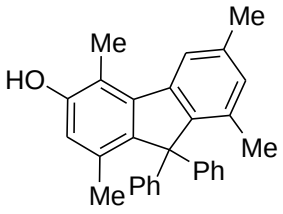

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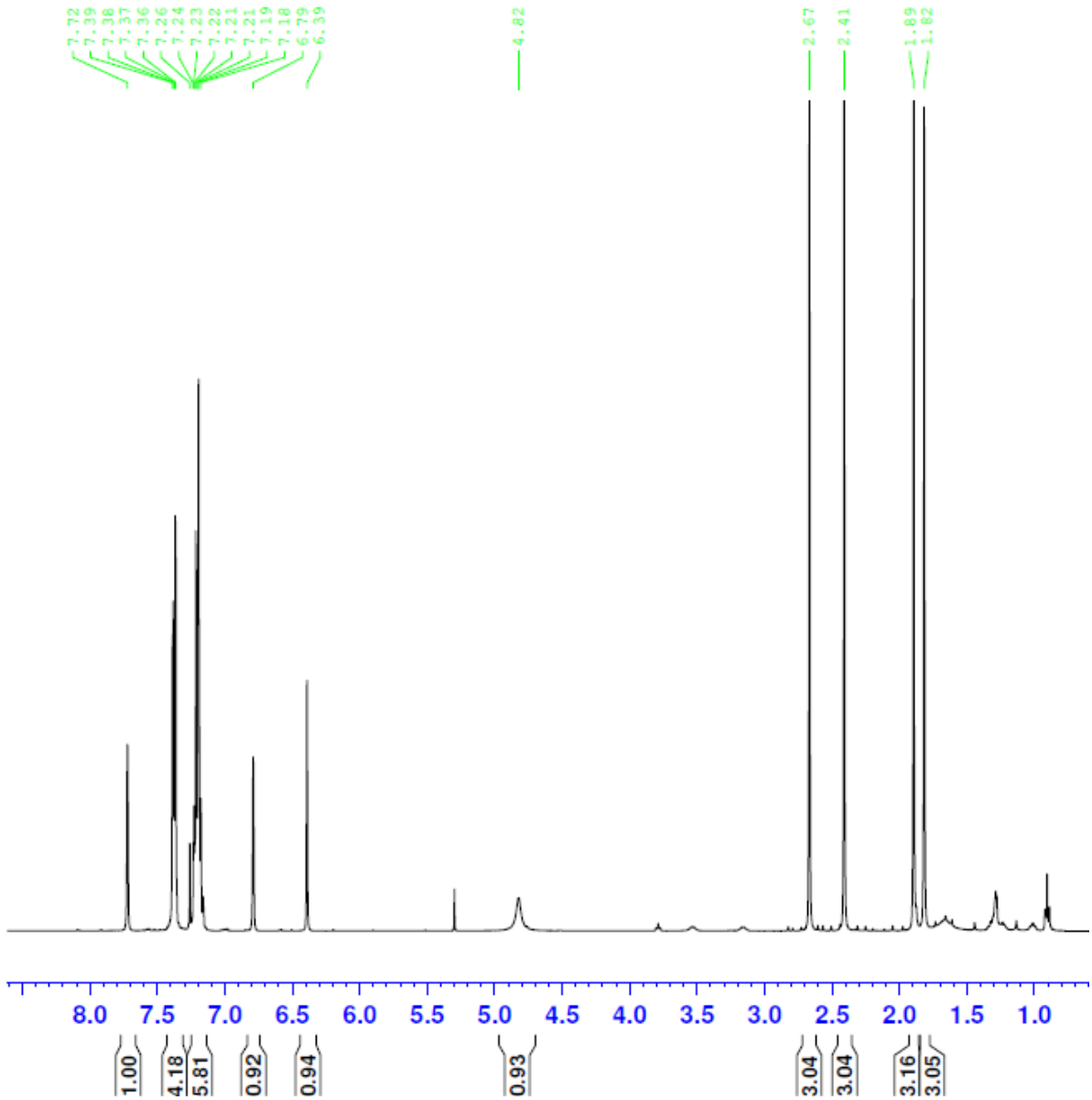

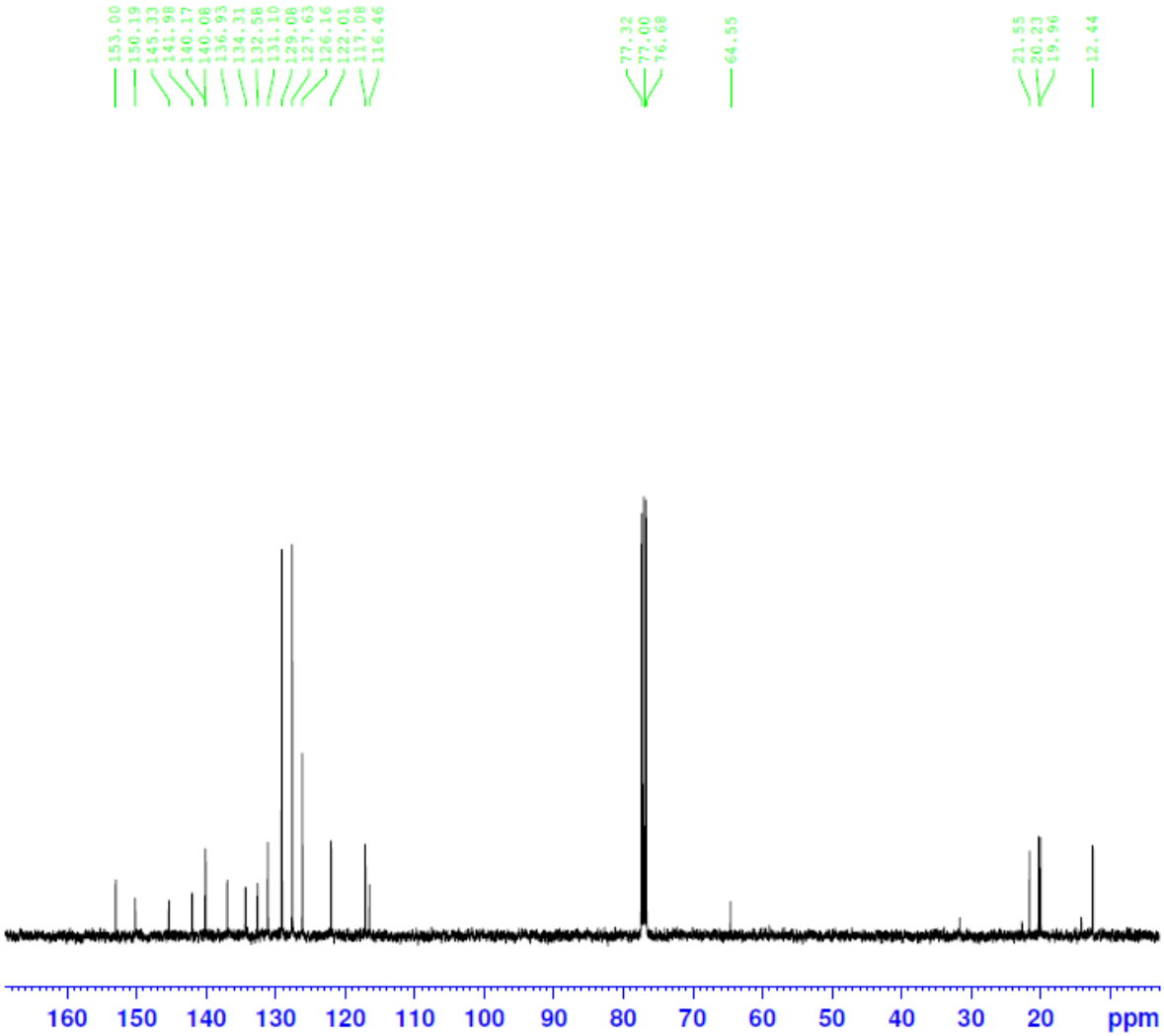

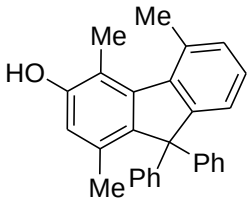

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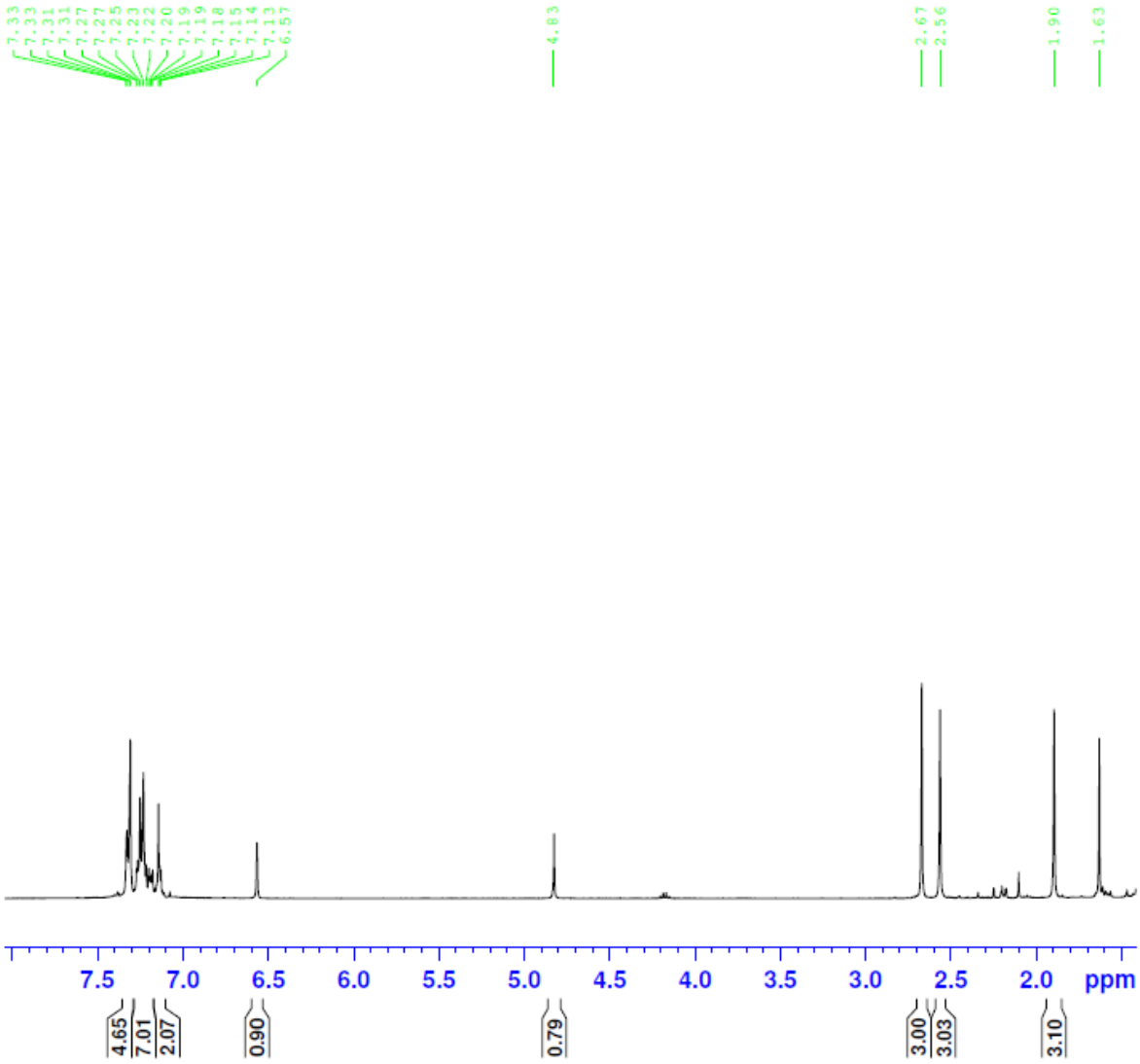
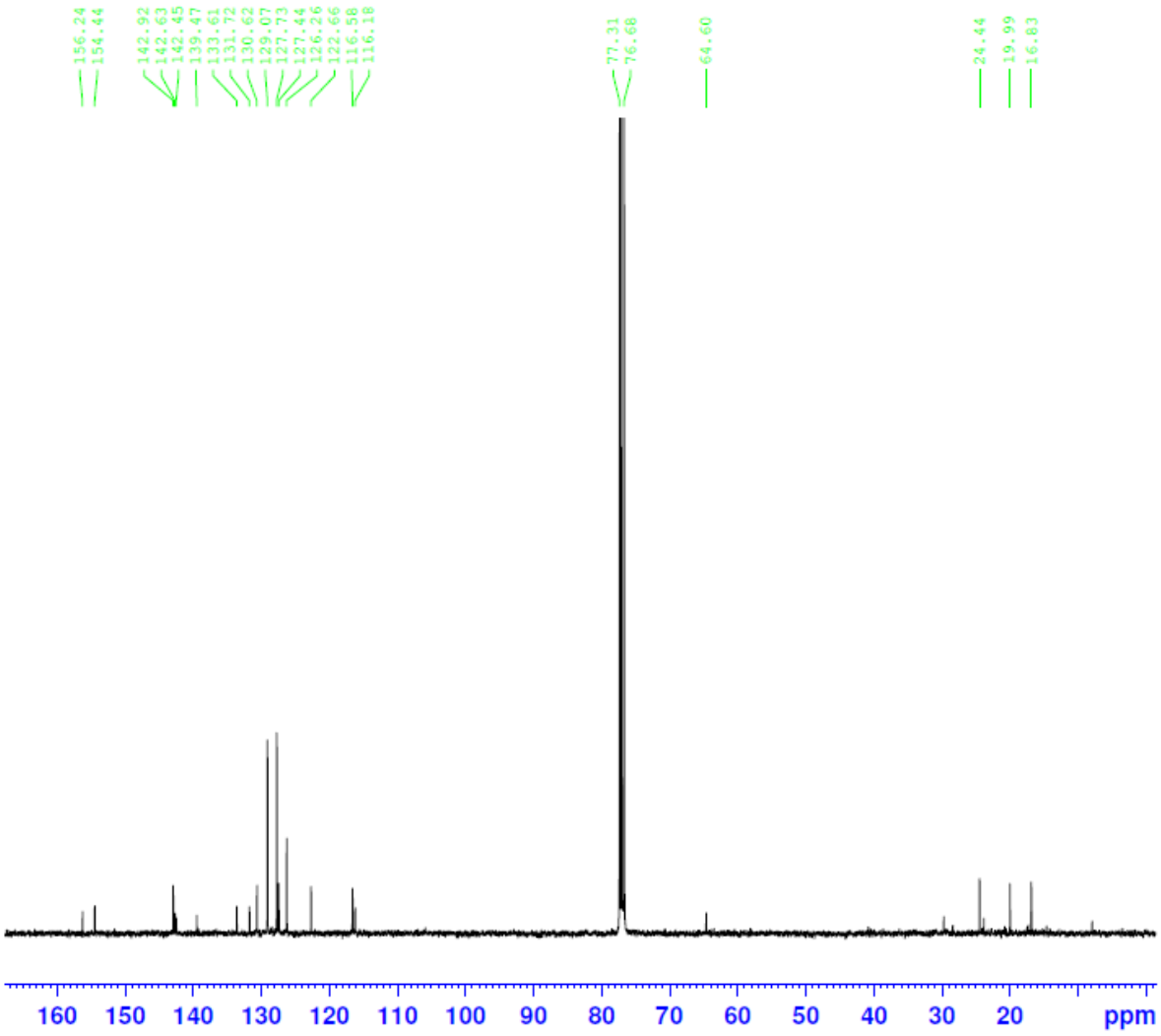
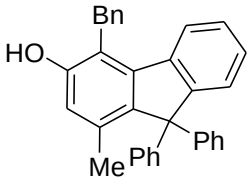
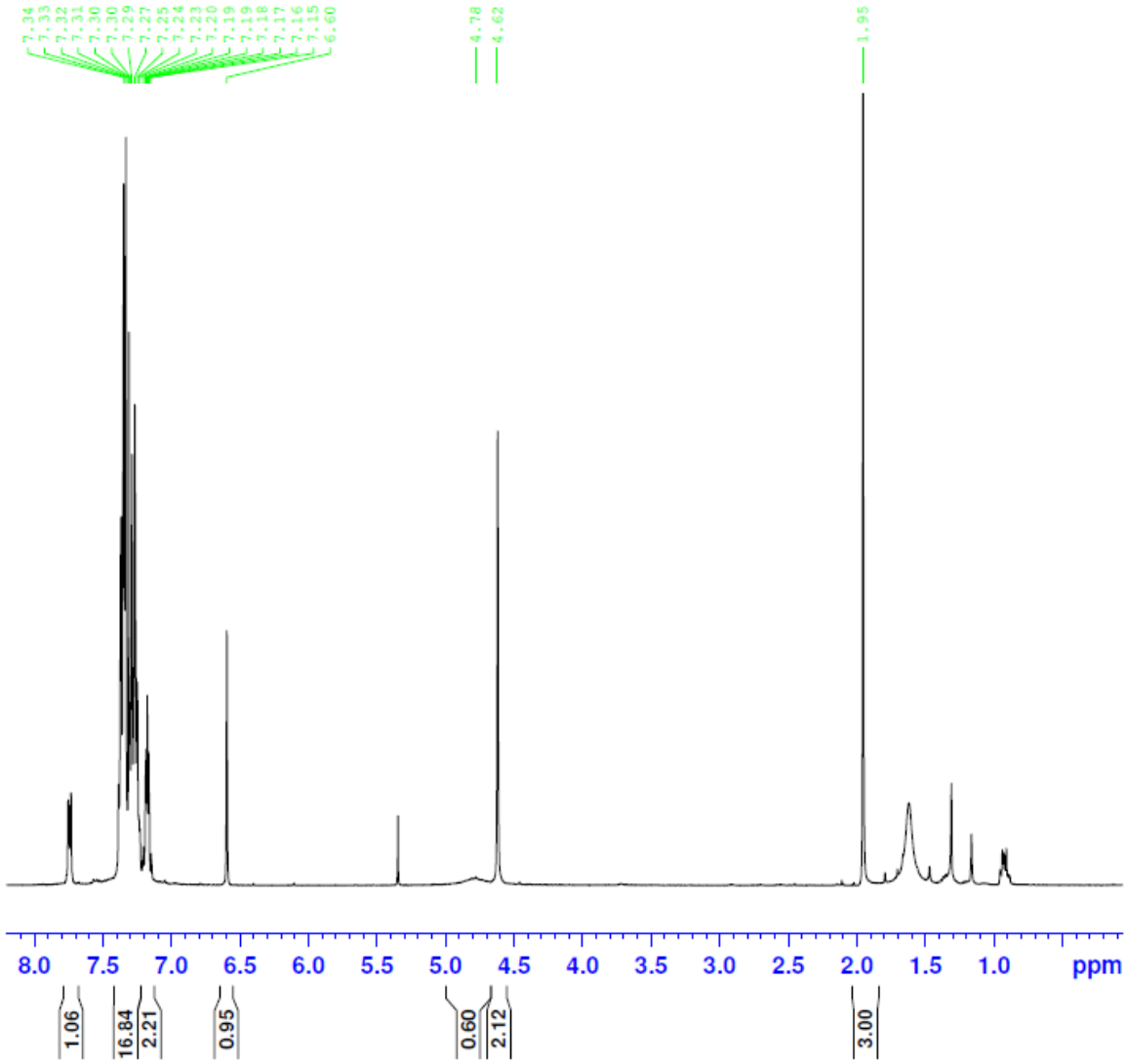
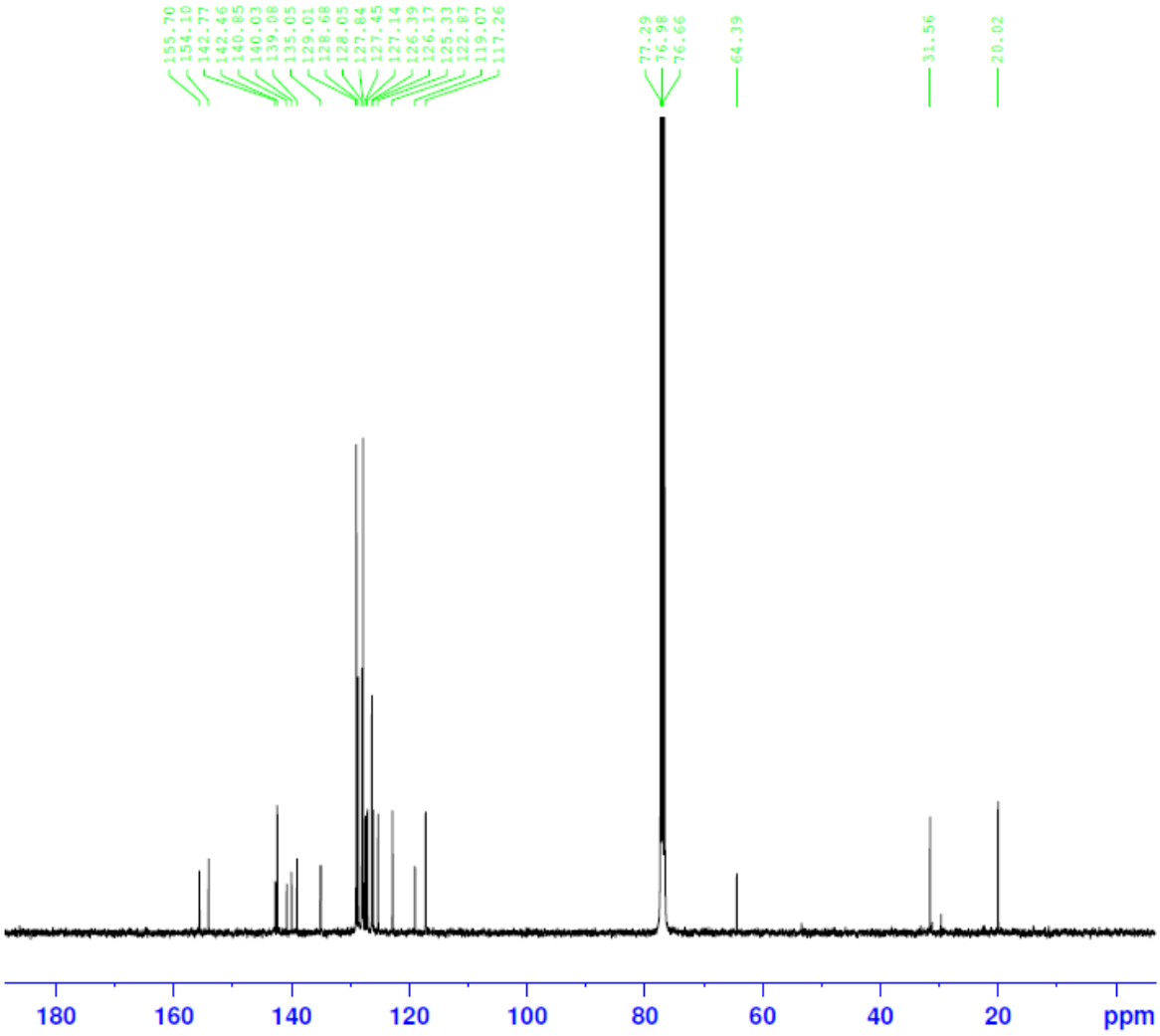




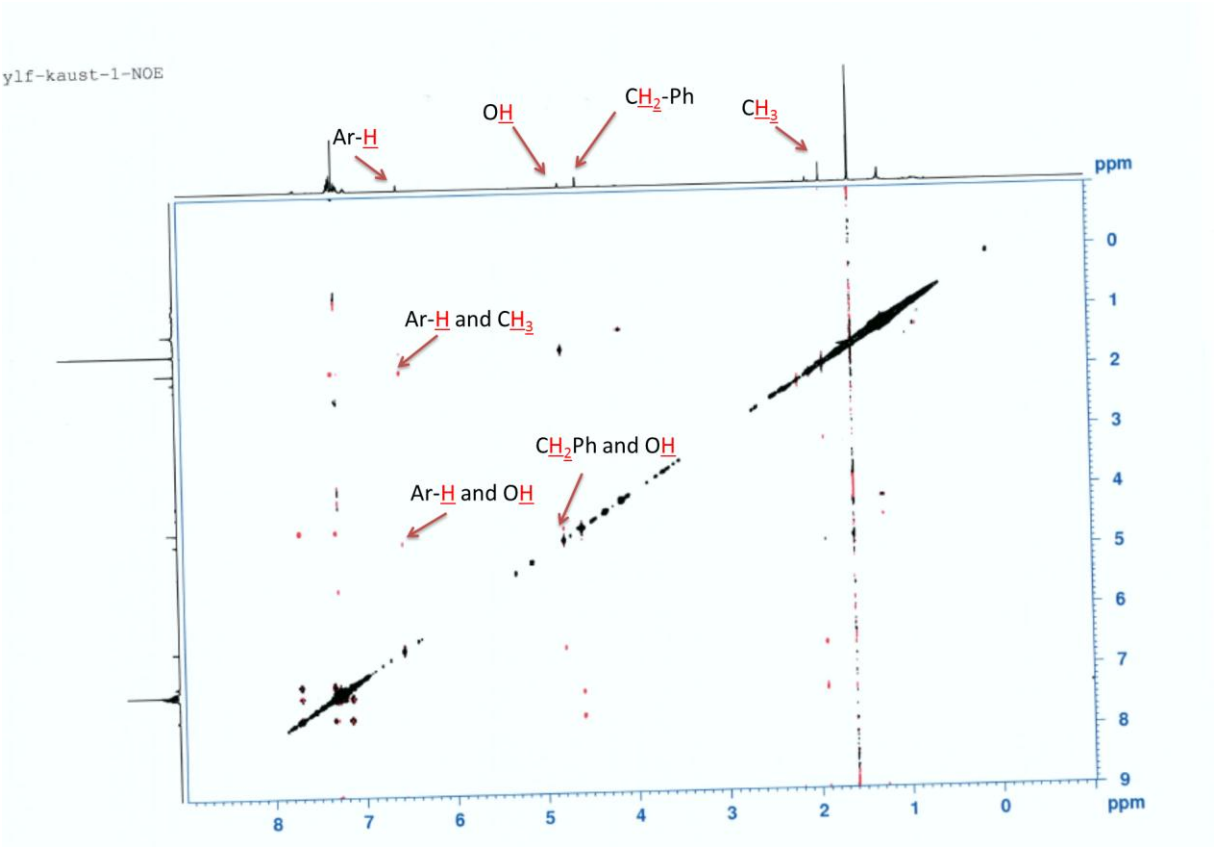


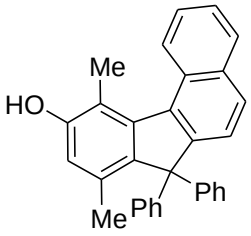
3i





NOESY study of **3i**





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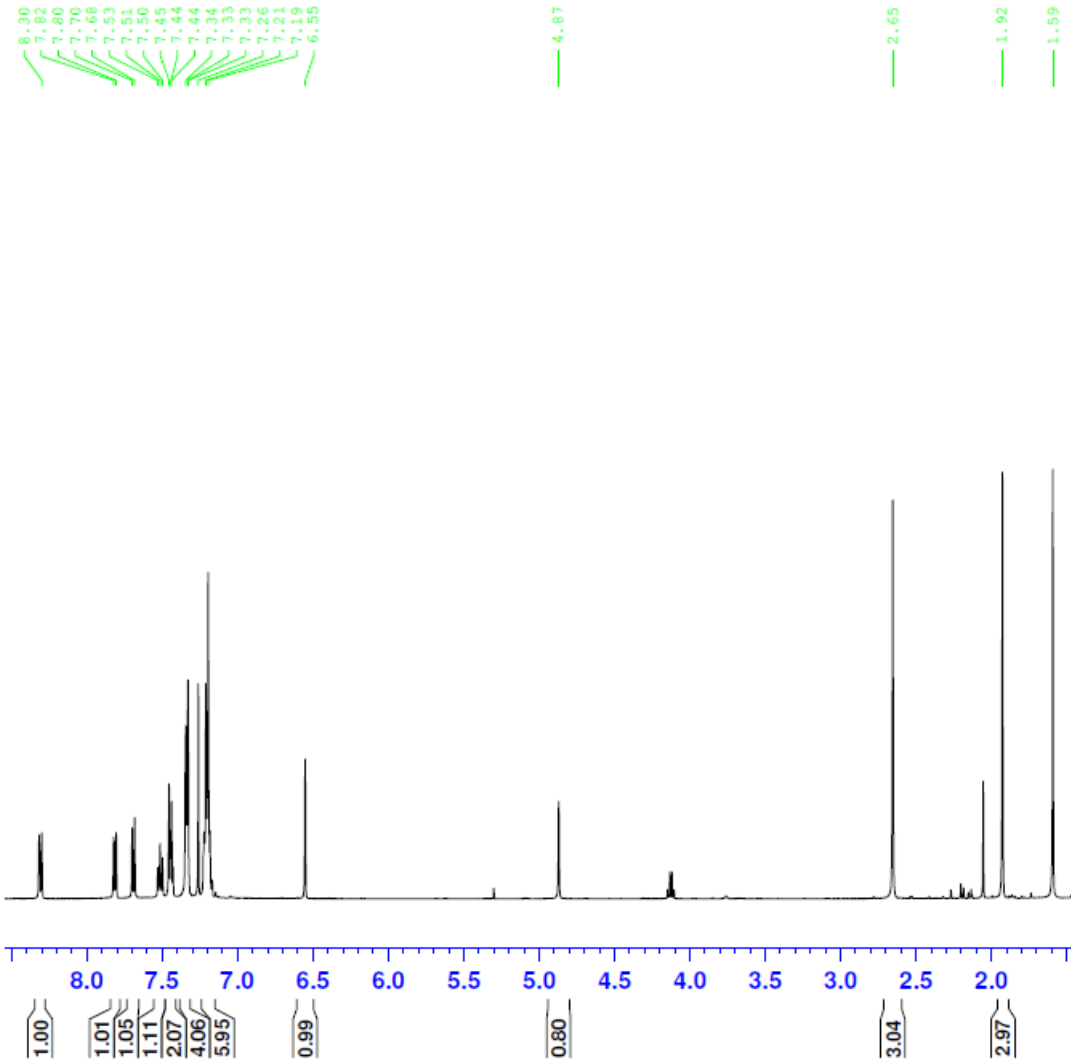

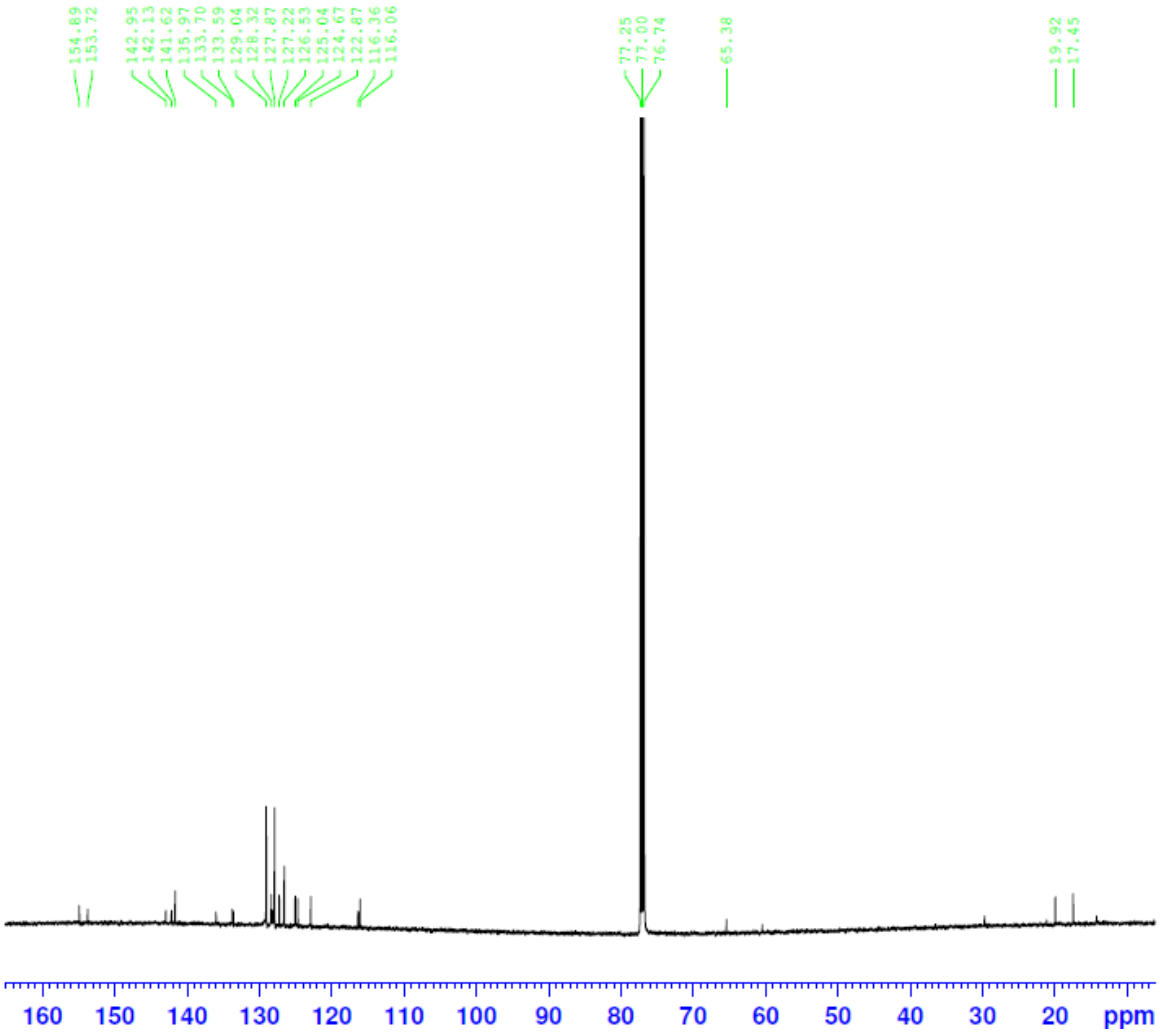

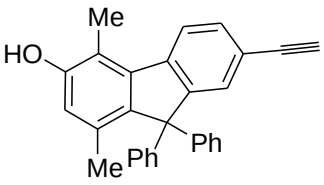

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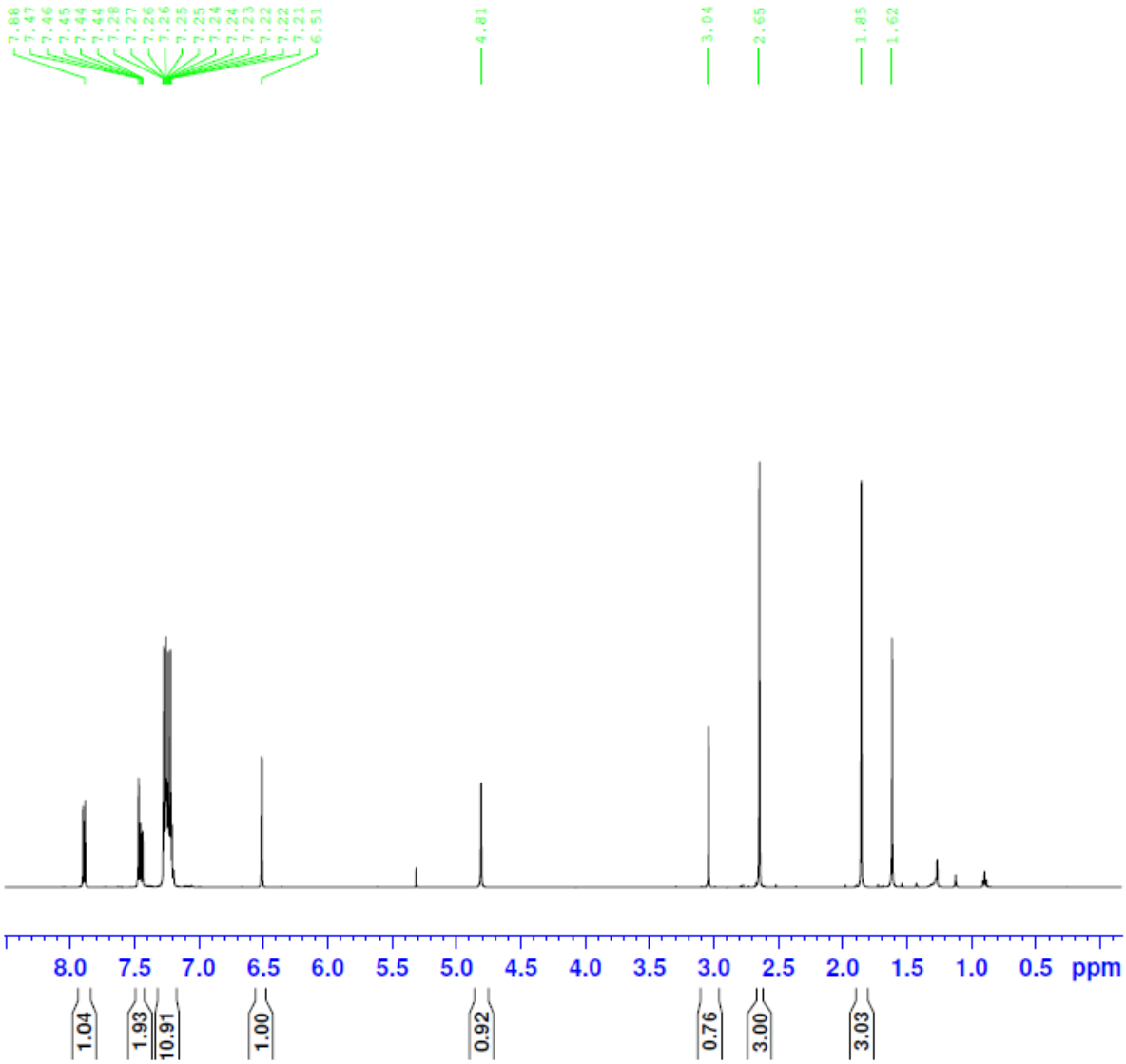

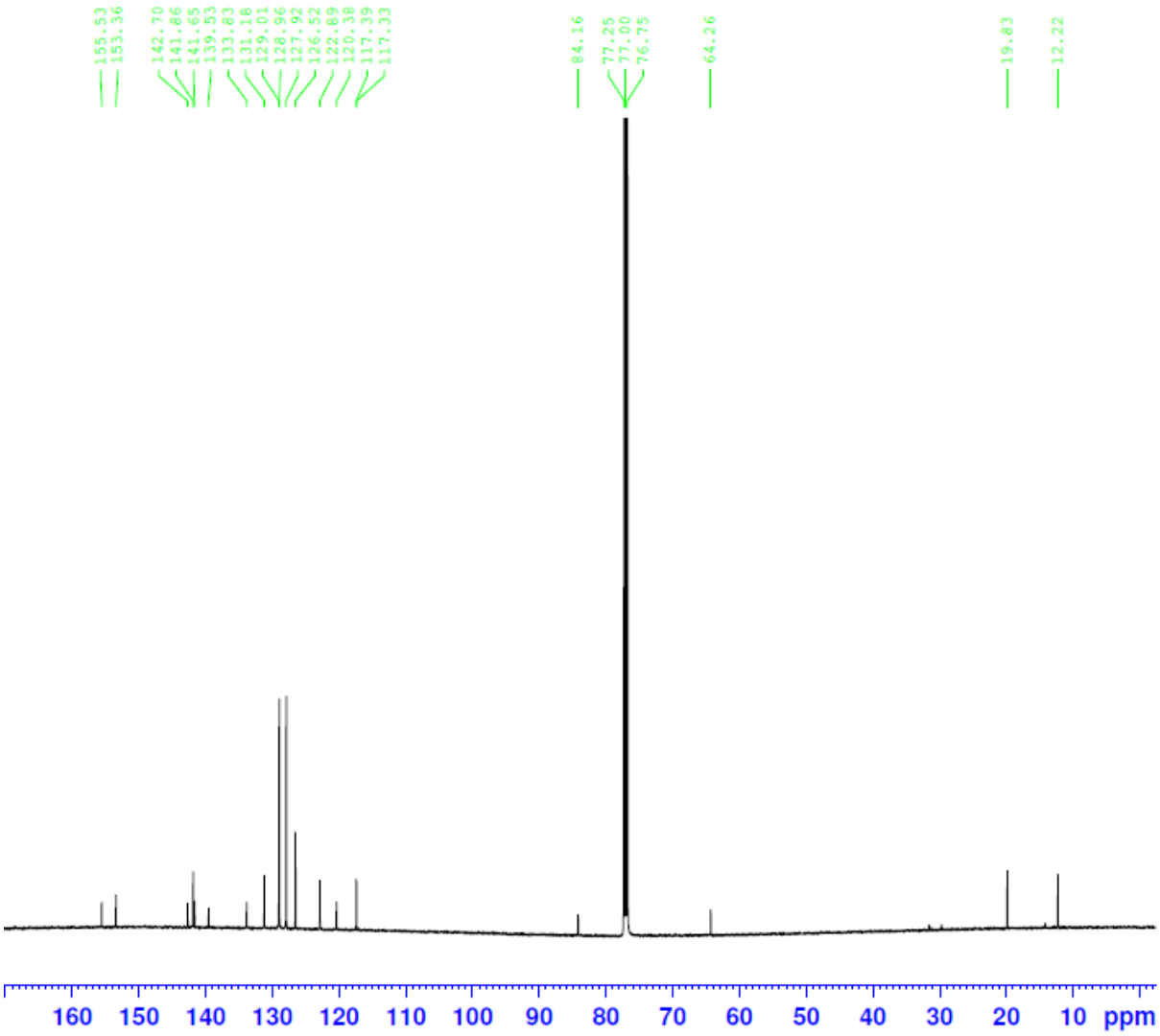

1. Figure of X-ray data of compound 3a

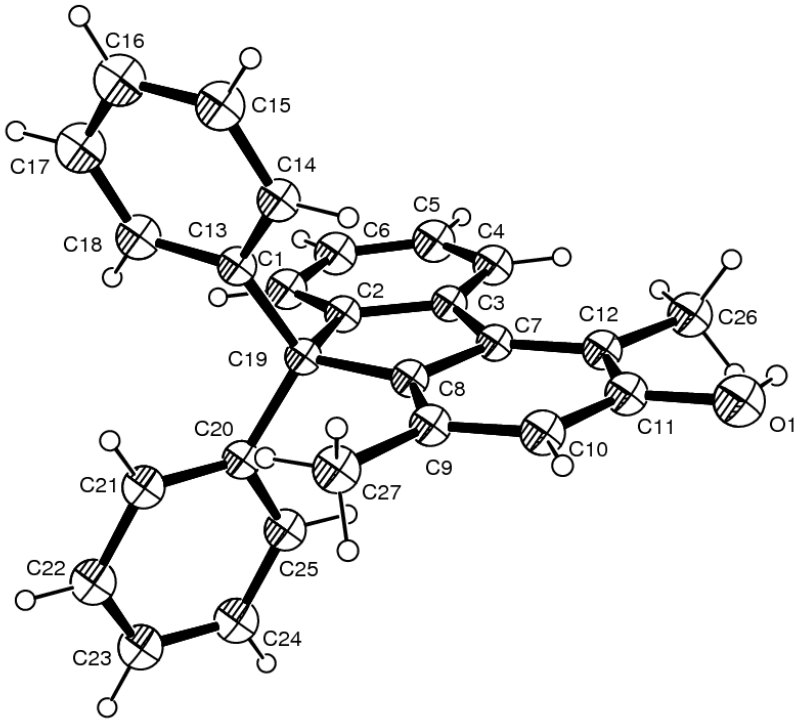

Table 1. Crystal Data and Structure Refinement for Compound **3a**

Empirical formula	$C_{27}H_{22}O$
Formula weight	362.45
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 8.8927 (7) Å alpha = 64.309 (7)°
	b =11.1096 (9) Å beta = 75.677 (6)°
	c = 11.2148 (7) Å gamma = 87.598 (7)°
Volume, Z	964.69 (12) $Å^3$, 2
ρcalc / mg mm^{-3}	1.248
μ / mm^{-1}	3.261
F(000)	384.0

Crystal size / mm^3	0.30 × 0.20 × 0.10
2ɵ range for data collection	5.8 to 50.0°
Index ranges	$-10 \leq h \leq 9$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
Reflections collected	6725
Independent reflections	3395 [R(int) = 0.020]
Data / restraints / parameters	3390/0/253
Goodness-of-fit on F^2	0.780
Final R indices [I>2σ (I)]	R1 = 0.065, wR2 = 0.194
R indices (all data)	R1 = 0.077, wR2 = 0.209
Largest diff. peak/hole / e $Å^{-3}$	0.362/-0.408

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C17	0.8100 (4)	−0.0329 (3)	0.3183 (4)	0.0666 (10)
H17	0.8546	−0.1146	0.3466	0.080*
C16	0.7141 (4)	−0.0039 (4)	0.2312 (4)	0.0686 (10)
H16	0.6939	−0.0654	0.2005	0.082*
C7	0.8330 (3)	0.5233 (3)	0.2054 (3)	0.0368 (6)
C19	0.8212 (3)	0.2887 (3)	0.3639 (3)	0.0373 (6)
C8	0.7335 (3)	0.4152 (3)	0.3119 (3)	0.0379 (6)
C3	0.9919 (3)	0.4780 (3)	0.1847 (3)	0.0376 (6)
C9	0.5746 (3)	0.4301 (3)	0.3538 (3)	0.0427 (6)
C20	0.8116 (3)	0.2374 (3)	0.5177 (3)	0.0402 (6)
C13	0.7742 (3)	0.1820 (3)	0.3240 (3)	0.0395 (6)
C10	0.5220 (3)	0.5543 (3)	0.2851 (3)	0.0497 (7)
H10	0.4170	0.5673	0.3103	0.060*
C2	0.9880 (3)	0.3442 (3)	0.2787 (3)	0.0386 (6)

C11	0.6218 (4)	0.6602 (3)	0.1795 (3)	0.0469 (7)
C12	0.7801 (3)	0.6487 (3)	0.1369 (3)	0.0421 (6)
O1	0.5624 (3)	0.7813 (2)	0.1130 (3)	0.0675 (7)
H1A	0.6327	0.8345	0.0528	0.101*
C14	0.6782 (3)	0.2089 (3)	0.2362 (3)	0.0462 (7)
H14	0.6328	0.2902	0.2075	0.055*
C27	0.4614 (3)	0.3183 (3)	0.4672 (3)	0.0548 (8)
H27A	0.5157	0.2394	0.5040	0.082*
H27B	0.3822	0.2996	0.4315	0.082*
H27C	0.4142	0.3446	0.5381	0.082*
C21	0.7321 (3)	0.1179 (3)	0.6196 (3)	0.0498 (7)
H21	0.6797	0.0639	0.5964	0.060*
C4	1.1340 (3)	0.5438 (3)	0.0948 (3)	0.0497 (7)
H4	1.1384	0.6324	0.0304	0.060*
C25	0.8846 (4)	0.3166 (3)	0.5576 (3)	0.0507 (7)
H25	0.9368	0.3979	0.4916	0.061*
C18	0.8403 (4)	0.0584 (3)	0.3637 (3)	0.0540 (8)
H18	0.9058	0.0375	0.4219	0.065*
C6	1.2633 (4)	0.3458 (4)	0.1972 (3)	0.0599 (9)
H6	1.3549	0.3023	0.2015	0.072*
C26	0.8837 (4)	0.7671 (3)	0.0233 (3)	0.0558 (8)
H26A	0.9887	0.7421	0.0070	0.084*
H26B	0.8797	0.8393	0.0491	0.084*
H26C	0.8486	0.7954	−0.0585	0.084*
C22	0.7300 (4)	0.0781 (3)	0.7561 (3)	0.0581 (8)
H22	0.6772	−0.0026	0.8229	0.070*
C15	0.6487 (4)	0.1170 (4)	0.1906 (3)	0.0594 (9)
H15	0.5840	0.1373	0.1318	0.071*

C23	0.8049 (4)	0.1566 (4)	0.7928 (3)	0.0601 (9)
H23	0.8043	0.1290	0.8840	0.072*
C1	1.1232 (3)	0.2783 (3)	0.2866 (3)	0.0511 (7)
H1	1.1203	0.1899	0.3510	0.061*
C5	1.2671 (4)	0.4764 (4)	0.1024 (3)	0.0594 (8)
H5	1.3614	0.5201	0.0422	0.071*
C24	0.8812 (4)	0.2771 (4)	0.6935 (3)	0.0592 (8)
H24	0.9305	0.3319	0.7179	0.071*

Atomic displacement parameters (Å ^{2})

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C17	0.069 (2)	0.0474 (18)	0.084 (2)	0.0045 (16)	−0.0075 (19)	−0.0355 (18)
C16	0.072 (2)	0.065 (2)	0.077 (2)	−0.0144 (18)	−0.0004 (19)	−0.0473 (19)
C7	0.0400 (14)	0.0404 (14)	0.0369 (13)	0.0039 (11)	−0.0129 (11)	−0.0216 (11)
C19	0.0358 (13)	0.0398 (14)	0.0374 (13)	0.0029 (11)	−0.0110 (11)	−0.0172 (11)
C8	0.0371 (14)	0.0441 (14)	0.0386 (13)	0.0034 (11)	−0.0120 (11)	−0.0223 (12)
C3	0.0359 (13)	0.0453 (14)	0.0366 (13)	0.0017 (11)	−0.0103 (11)	−0.0218 (11)
C9	0.0377 (14)	0.0519 (16)	0.0455 (15)	0.0055 (12)	−0.0100 (12)	−0.0281 (13)
C20	0.0385 (14)	0.0440 (15)	0.0395 (14)	0.0087 (11)	−0.0123 (11)	−0.0187 (12)
C13	0.0363 (13)	0.0421 (14)	0.0378 (13)	−0.0006 (11)	−0.0059 (11)	−0.0169 (11)
C10	0.0383 (15)	0.0597 (18)	0.0598 (18)	0.0136 (13)	−0.0142 (13)	−0.0341 (15)

C2	0.0356 (13)	0.0455 (15)	0.0392 (13)	0.0046 (11)	−0.0115 (11)	−0.0215 (12)
C11	0.0520 (17)	0.0445 (15)	0.0547 (17)	0.0153 (13)	−0.0222 (14)	−0.0276 (13)
C12	0.0483 (16)	0.0419 (15)	0.0429 (14)	0.0065 (12)	−0.0160 (12)	−0.0227 (12)
O1	0.0688 (15)	0.0507 (13)	0.0779 (16)	0.0222 (11)	−0.0244 (12)	−0.0222 (12)
C14	0.0431 (15)	0.0522 (16)	0.0439 (15)	−0.0015 (12)	−0.0090 (12)	−0.0222 (13)
C27	0.0394 (15)	0.066 (2)	0.0552 (18)	0.0012 (14)	−0.0040 (13)	−0.0268 (15)
C21	0.0467 (16)	0.0528 (17)	0.0459 (16)	−0.0008 (13)	−0.0134 (13)	−0.0168 (13)
C4	0.0442 (16)	0.0545 (17)	0.0451 (16)	−0.0027 (13)	−0.0062 (12)	−0.0192 (13)
C25	0.0589 (18)	0.0488 (16)	0.0479 (16)	0.0015 (14)	−0.0150 (14)	−0.0234 (14)
C18	0.0544 (18)	0.0478 (17)	0.0632 (19)	0.0079 (14)	−0.0183 (15)	−0.0258 (15)
C6	0.0373 (16)	0.078 (2)	0.066 (2)	0.0133 (15)	−0.0165 (14)	−0.0319 (18)
C26	0.063 (2)	0.0449 (16)	0.0529 (18)	0.0067 (14)	−0.0168 (15)	−0.0143 (14)
C22	0.0503 (17)	0.065 (2)	0.0424 (16)	0.0054 (15)	−0.0097 (13)	−0.0096 (15)
C15	0.0558 (19)	0.075 (2)	0.0565 (18)	−0.0112 (16)	−0.0110 (15)	−0.0376 (17)
C23	0.0571 (19)	0.086 (2)	0.0382 (16)	0.0159 (17)	−0.0161 (14)	−0.0269 (16)
C1	0.0405 (15)	0.0580 (18)	0.0545 (17)	0.0106 (13)	−0.0160 (13)	−0.0230 (14)
C5	0.0377 (16)	0.078 (2)	0.0592 (19)	−0.0024 (15)	−0.0039 (14)	−0.0305 (18)

C24	0.068 (2)	0.070 (2)	0.0531 (18)	0.0081 (17)	−0.0209 (16)	−0.0371 (17)

Geometric parameters (Å , °)

C17—C18	1.378 (5)	C20—C25	1.389 (4)
C17—C16	1.379 (5)	C13—C14	1.388 (4)
C16—C15	1.372 (5)	C13—C18	1.400 (4)
C7—C12	1.397 (4)	C10—C11	1.391 (4)
C7—C8	1.405 (4)	C2—C1	1.383 (4)
C7—C3	1.477 (4)	C11—O1	1.382 (3)
C19—C8	1.532 (4)	C11—C12	1.389 (4)
C19—C2	1.535 (4)	C12—C26	1.507 (4)
C19—C13	1.540 (4)	C14—C15	1.384 (4)
C19—C20	1.545 (4)	C21—C22	1.392 (4)
C8—C9	1.401 (4)	C4—C5	1.374 (4)
C3—C2	1.396 (4)	C25—C27	1.384 (4)
C3—C4	1.398 (4)	C6—C5	1.374 (5)
C9—C10	1.386 (4)	C6—C1	1.388 (4)
C9—C27	1.509 (4)	C22—C23	1.367 (5)
C20—C21	1.390 (4)	C23—C24	1.379 (5)

C18—C17—C16	120.5 (3)	C14—C13—C19	121.7 (2)
C15—C16—C17	119.2 (3)	C18—C13—C19	120.8 (2)
C12—C7—C8	122.4 (2)	C9—C10—C11	121.8 (3)
C12—C7—C3	129.4 (2)	C1—C2—C3	120.7 (3)
C8—C7—C3	108.2 (2)	C1—C2—C19	128.0 (2)
C8—C19—C2	100.6 (2)	C3—C2—C19	111.2 (2)
C8—C19—C13	112.2 (2)	O1—C11—C12	118.3 (3)

C2—C19—C13	107.3 (2)	O1—C11—C10	119.3 (3)
C8—C19—C20	111.1 (2)	C12—C11—C10	122.4 (3)
C2—C19—C20	110.0 (2)	C11—C12—C7	115.9 (3)
C13—C19—C20	114.6 (2)	C11—C12—C26	120.3 (3)
C9—C8—C7	120.5 (2)	C7—C12—C26	123.8 (3)
C9—C8—C19	128.2 (2)	C15—C14—C13	121.3 (3)
C7—C8—C19	111.2 (2)	C20—C21—C22	120.8 (3)
C2—C3—C4	119.2 (3)	C5—C4—C3	119.4 (3)
C2—C3—C7	108.5 (2)	C24—C25—C20	121.3 (3)
C4—C3—C7	132.3 (3)	C17—C18—C13	121.3 (3)
C10—C9—C8	117.1 (3)	C5—C6—C1	120.2 (3)
C10—C9—C27	119.7 (3)	C23—C22—C21	120.6 (3)
C8—C9—C27	123.2 (3)	C16—C15—C14	120.6 (3)
C21—C20—C25	117.6 (3)	C22—C23—C24	119.4 (3)
C21—C20—C19	124.3 (2)	C2—C1—C6	119.2 (3)
C25—C20—C19	118.1 (2)	C6—C5—C4	121.2 (3)
C14—C13—C18	117.1 (3)	C23—C24—C25	120.2 (3)

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.