

Supplementary Data

Synthesis, Chemo-selective Properties of Substituted 9-Aryl-9H-fluorenes from Triarylcarbinols and Enantiomercal Kinetics of Chiral 9-Methoxy-11-(naphthalen-1-yl)-11H-benzo[a]fluorene

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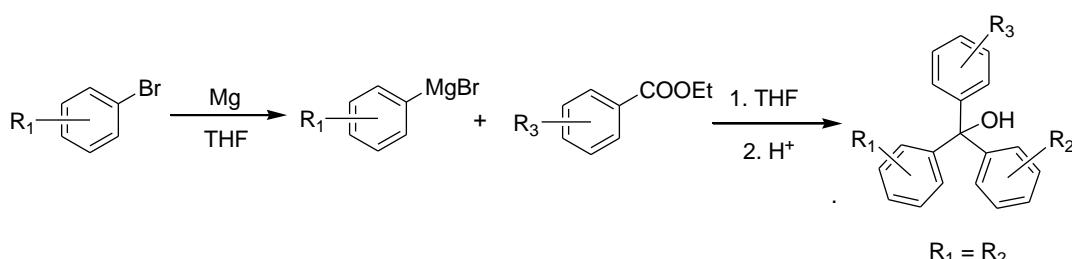
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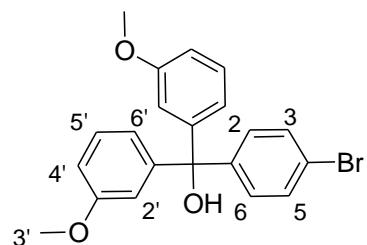
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I. General Procedure for Preparation of **1c**, **1d**, **1e**, **1g**, **1h**, **1k**, **1l** (except **1i**).^[S1]



A mixture of bromoarene (32.0 mmol) and 20 mL of anhydrous THF is added to magnesium (2.30 g, 96.0 mmol), and the flask warmed gently until the reaction start. A mixture of bromoarene (64.0 mmol) and 40 mL of anhydrous THF is run in at such a rate as to cause vigorous refluxing, the mixture is warmed to refluxing for two hours, in order to dissolve all the magnesium. The reaction was cooled to room temperature, aromatic ester (40.0 mmol) is added into the Grignard solution, and the mixture is warmed to reflux over night. The reaction mixture is cooled in an ice-salt bath and then added slowly, with constant stirring, into 60 mL saturated NH₄Cl aqueous solution. The mixture is distilled to remove THF and stream-distilled to remove biphenyl and unchanged bromobenzene. The product is filtered, washed with water, and recrystallized from ethanol and water.

(4-Bromophenyl)bis(3-methoxyphenyl)methanol (**1c**)



Colorless solid; m.p. 127-128 °C; $R_f = 0.43$ (petroleum ether/ethyl acetate = 4/1); product 1.41 g (yield 35.3%).

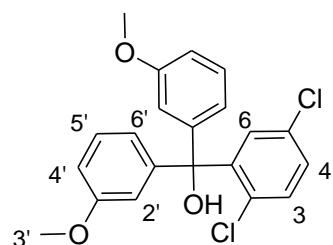
¹H NMR (300 MHz, CDCl₃, TMS): $\delta = 7.42$ (d, 2H, $J = 8.7$ Hz; H-3, 5), 7.23 (t, 2H, $J = 8.7$ Hz; H-5'), 7.18 (d, 2H, $J = 8.7$ Hz; H-2, 6), 6.84 (s, 2H; H-2'), 6.84-6.78 (m, 4H; H-4', 6'), 3.75 (s, 6H; H-3').

¹³C NMR (75 MHz): $\delta = 159.2, 147.8, 145.5, 130.1, 129.6, 129.0, 121.4, 120.3, 113.8, 112.5, 81.5, 55.1$.

FT-IR (cm⁻¹): $\nu_{\text{max}}(\text{KBr}/\text{cm}^{-1})$, 3554, 2969, 1597, 1484, 1421, 1321, 1286, 1251, 1166, 1137, 1072, 1042, 1022, 1010, 934, 865, 833, 775, 704.

Anal. Calc. for C₂₁H₁₉BrO₃: C, 63.17; H, 4.80. Found: C, 63.13; H, 4.69.

(2,5-Dichlorophenyl)bis(3-methoxyphenyl)methanol (**1d**)

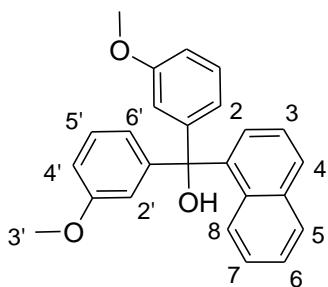


Colorless solid; m.p. 42-44 °C; R_f = 0.53 (petroleum ether/ethyl acetate = 4/1); product 6.59 g (yield 42.3%).

^1H NMR (300 MHz, CDCl₃, TMS): δ = 7.32 (d, 1H, J = 8.4 Hz; H-3), 7.24 (t, 2H, J = 8.4 Hz; H-5'), 7.23 (dd, 1H, J = 8.4, 2.1 Hz; H-4), 6.89 (t, 2H, J = 2.1 Hz; H-2'), 6.85 (dd, 2H, J = 8.4, 2.1 Hz; H-4'), 6.76 (d, 2H, J = 8.4 Hz; H-6'), 6.74 (d, 2H, J = 2.1 Hz, H-6), 3.78 (s, 6H; H-3').

^{13}C NMR (75 MHz): δ = 159.4, 146.2, 145.3, 132.5, 132.2, 131.4, 131.3, 129.0, 120.1, 113.4, 112.8, 82.1, 55.1. FT-IR (cm⁻¹): ν_{max} (KBr/cm⁻¹), 3445, 2956, 1599, 1559, 1487, 1457, 1289, 1250, 1105, 1047, 776, 758, 699, 553. HRMS (EI): m/z calcd for C₂₁H₁₈Cl₂O₃[M⁺]: 388.0633; found: 388.0659.

Bis(3-methoxyphenyl)(naphthalen-1-yl)methanol (**1e**)



Colorless solid; m.p. 71-73 °C; R_f = 0.42 (petroleum ether/ethyl acetate = 4/1); product 6.04 g (yield 62.7%).

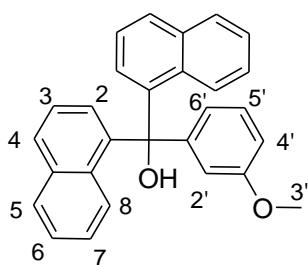
^1H NMR (300 MHz, CDCl₃, TMS): δ = 8.11 (d, 1H, J = 8.7 Hz; H-8), 7.85-7.78 (m, 2H; H-4, 5), 7.39 (td, 1H, J = 8.8, 0.9 Hz; H-6), 7.31-7.27 (m, 1H; naphthalen H), 7.22 (t, 2H, J = 8.1 Hz; H-5') 7.17-7.12 (m, 1H; naphthalen H), 6.95 (t, 2H, J = 2.1 Hz; H-2'), 6.88 (dd, 2H, J = 7.5, 0.9 Hz; naphthalen H), 6.84-6.81 (m, 3H; H-6', naphthalen 2-H), 3.74 (s, 6H; H-3').

^{13}C NMR (75 MHz): δ = 159.3, 148.4, 141.7, 134.8, 131.1, 129.3, 128.9, 128.1, 127.8, 125.6, 125.2, 124.2, 120.3, 113.6, 113.5, 112.3, 83.1, 55.1.

FT-IR (cm⁻¹): ν_{max} (KBr/cm⁻¹), 3454, 2935, 1597, 1486, 1463, 1432, 1316, 1289, 1250, 1143, 1040, 865, 781, 760, 700.

HRMS (EI): m/z calcd for C₂₅H₂₂O₃[M]⁺: 370.1569; found: 370.1575.

(3-Methoxyphenyl)dinaphthalen-1-ylmethanol (**1g**)



Colorless solid; m.p. = 206-207 °C; R_f = 0.63 (petroleum ether/ethyl acetate = 4/1); product 4.06 g (yield 52.1)..

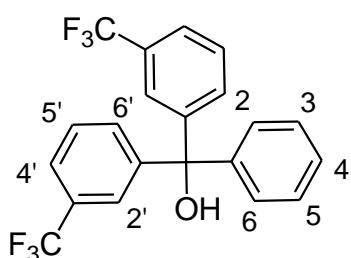
¹H NMR (300M Hz, CDCl₃, TMS): δ = 8.26 (brs), 2H; H-8), 7.87 (d, 2H, *J* = 8.1 Hz; H-5), 7.80 (d, 2H, *J* = 8.1 Hz; H-4), 7.41 (td, 2H, *J* = 7.5, 0.9 Hz; H-6), 7.28 (t, 2H, *J* = 7.5 Hz; H-7), 7.23-7.18 (m, 3H, H-3, 5'), 7.05 (s, 1H; H-2'), 6.88-6.82 (m, 4H, H-2, 4' 6'), 3.75 (s, 6H; H-3').

¹³C NMR (75M Hz): 159.4, 148.6, 141.9, 135.0, 131.2, 129.4, 129.2, 128.9, 128.8, 128.4, 128.2, 125.5, 124.3, 120.5, 113.9, 112.1, 85.1, 55.1.

FT-IR (cm⁻¹): ν_{max} (KBr/cm⁻¹), 3412, 3043, 1582, 1504, 1482, 1434, 1393, 1284, 1237, 1160, 1019, 875, 833, 806, 793, 776, 698, 560.

Anal. Calc. for C₂₈H₂₂O₂: C, 86.13; H, 5.68. Found: C, 86.21; H, 5.47.

phenylbis(3-(trifluoromethyl)phenyl)methanol (**1j**)



Colorless oil; R_f = 0.30 (petroleum ether/ethyl acetate = 10/1); product 1.68 g (yield 42.4%).

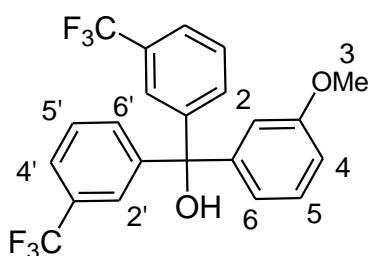
¹H NMR (300M Hz, CDCl₃, TMS): δ = 7.68 (s, 2H, H-2'), 7.57 (d, 2H; *J* = 6.3 Hz; H-4'), 7.48-7.43 (m, 4H; H-5', 6'), 7.36 (m, 1H; H-4), 7.34 (d, 2H, *J* = 2.4 Hz; H-2, 6) 7.22-7.18 (m, 2H; H-3, 5), 2.91 (s, 1H; -OH).

¹³C NMR (75M Hz): δ = 146.1, 144.5, 130.3, 129.4 (t, *J* = 31.9), 127.5, 127.5, 127.1, 126.7, 124.9, 123.4, 123.3, 121.3, 80.6.

FT-IR (cm⁻¹): ν_{max} (KBr/cm⁻¹), 3454, 3076, 2926, 1492, 1446, 1330, 1168, 1120, 1076, 806, 703, 675.

Anal. Calc. for C₂₁H₁₄F₆O: C, 63.64; H, 3.56. Found: C, 63.69; H, 3.47.

(3-methoxyphenyl)bis(3-(trifluoromethyl)phenyl)methanol (**1k**)



Colorless solid; m.p. = 73-74 °C; R_f = 0.43 (petroleum ether/ethyl acetate = 10/1); product 1.59 g (yield 37.3%).

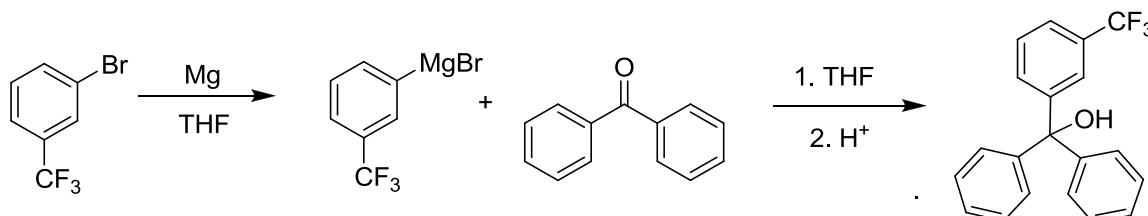
¹H NMR (300M Hz, CDCl₃, TMS): δ = 7.68 (s, 2H, H-2'), 7.57 (d, 2H; *J* = 6.3 Hz; H-4'), 7.47-7.41 (m, 4H; H-5', 6'), 7.27 (t, 1H; *J* = 8.1 Hz; H-5), 6.87 (dd, 1H, *J* = 8.1, 2.1 Hz; H-4), 6.78 (t, 1H; *J* = 2.1 Hz; H-2), 6.75 (d, 1H; *J* = 7.5 Hz; H-6), 3.75 (s, 3H; -OMe), 2.92 (s, 1H; -OH).

¹³C NMR (75M Hz): δ = 159.6, 147.2, 147.0, 131.3, 130.4 (t, J = 31.7), 129.6, 128.8, 128.6, 124.5, 124.3, 120.1, 114.0, 113.1, 81.4, 55.2.

FT-IR (cm^{-1}): $\nu_{\text{max}}(\text{KBr}/\text{cm}^{-1})$, 3507, 2955, 1597, 1489, 1470, 1437, 1330, 1255, 1164, 1123, 1076, 1034, 809, 771, 705.

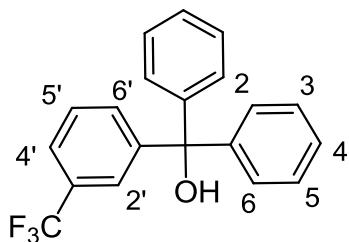
Anal. Calc. for C₂₂H₁₆F₆O₂: C, 61.98; H, 3.78. Found: C, 61.93; H, 3.87.

II. Procedure for Preparation of **1i**



A mixture of 1-bromo-3-(trifluoromethyl)benzene (4.95, 22.0 mmol) and 40 mL of anhydrous THF is added one third to magnesium (0.53g, 22.0 mmol), and the flask warmed gently until the reaction start. The residual mixture of benzophenone and anhydrous THF is run in at such a rate as to cause vigorous refluxing, the mixture is warmed to refluxing for two hours, in order to dissolved all the magnesium. The reaction was cooled to room temperature, 20.0 mmol of benzophenone is added into the Grinard solution, the mixture is warmed to reflux over night. The reaction mixture is cooled in an ice-salt bath and then added slowly, with constant stirring, into 16 mL saturated NH₄Cl aqueous solution. The mixture is distilled to remove THF and stream-distilled to remove biphenyl and unchanged bromobenzene. The crude product was purified by column chromatography with silica gel using CH₂Cl₂ as eluant to afford pure product.

diphenyl(3-(trifluoromethyl)phenyl)methanol (**1i**)



Colorless oil; R_f = 0.41 (petroleum ether/ethyl acetate = 10/1); product 2.71g (yield 41.3 %).

¹H NMR (300M Hz, CDCl₃, TMS): δ = 7.75 (s, 1H, H-2'), 7.58 (d, 1H; J = 7.8 Hz; H-4'), 7.51-7.44 (m, 2H; H-5', 6'), 7.39-7.27 (m, 10H; H-2, 3, 4, 5, 6), 2.98 (s, 1H; -OH).

¹³C NMR (75M Hz): δ = 147.9, 146.3, 131.5, 128.9, 128.8, 128.3, 127.9, 127.7, 124.5, 124.5, 124.2, 124.1, 81.9.

FT-IR (cm^{-1}): $\nu_{\text{max}}(\text{KBr}/\text{cm}^{-1})$, 3449, 2925, 2855, 1448, 1167, 1128, 1076, 1018, 804, 755, 702, 661.

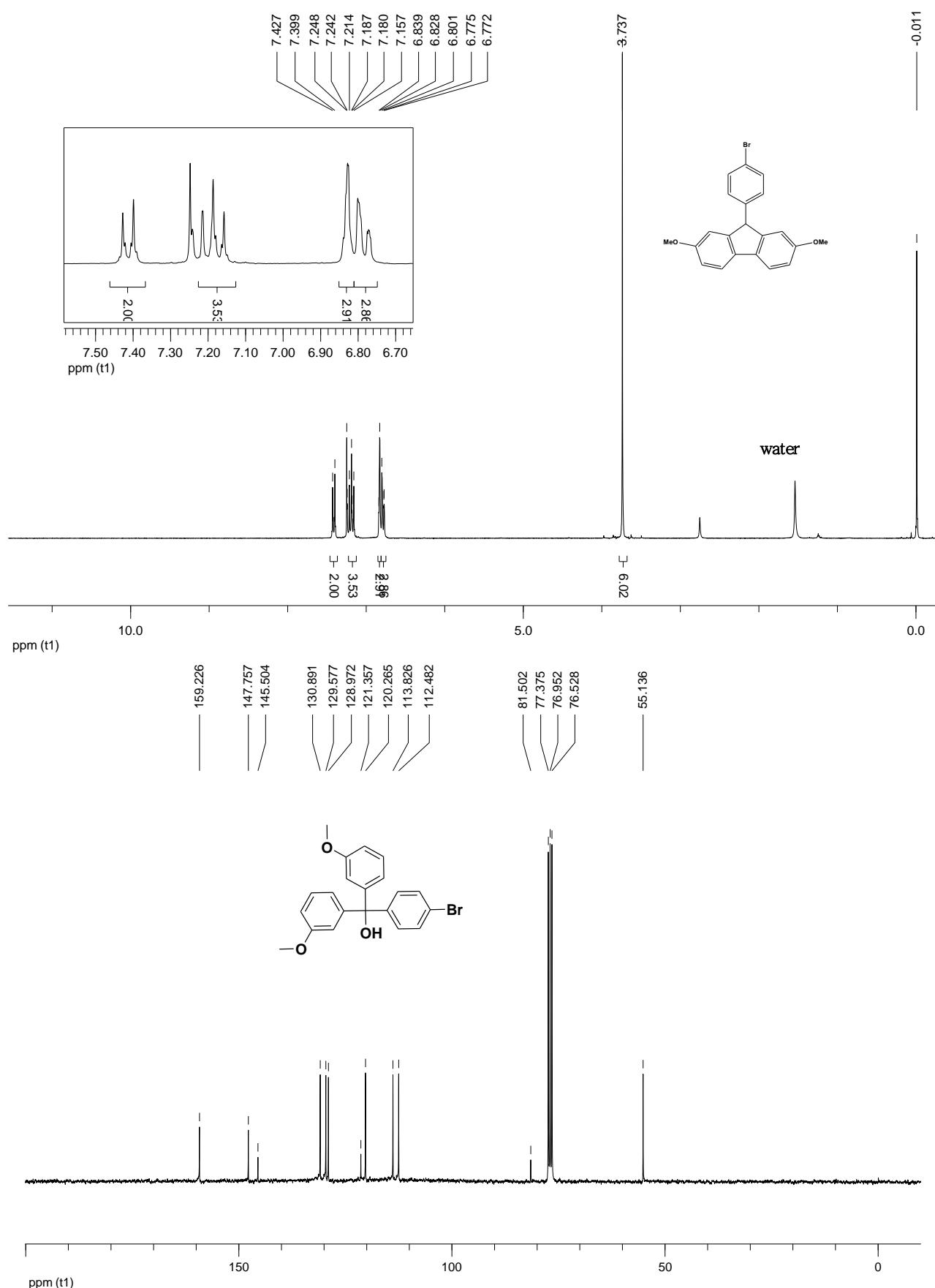
Anal. Calc. for C₂₀H₁₅F₃O: C, 73.16; H, 4.60. Found: C, 73.07; H, 4.71.

References

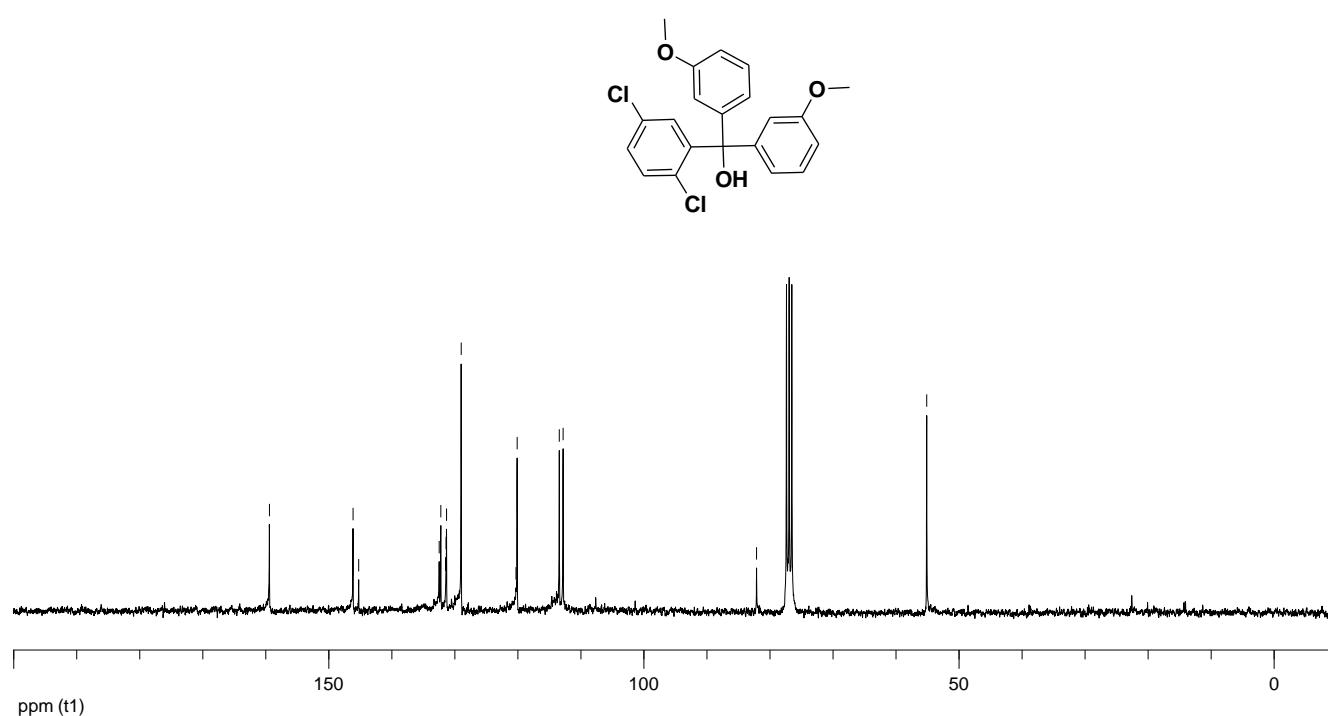
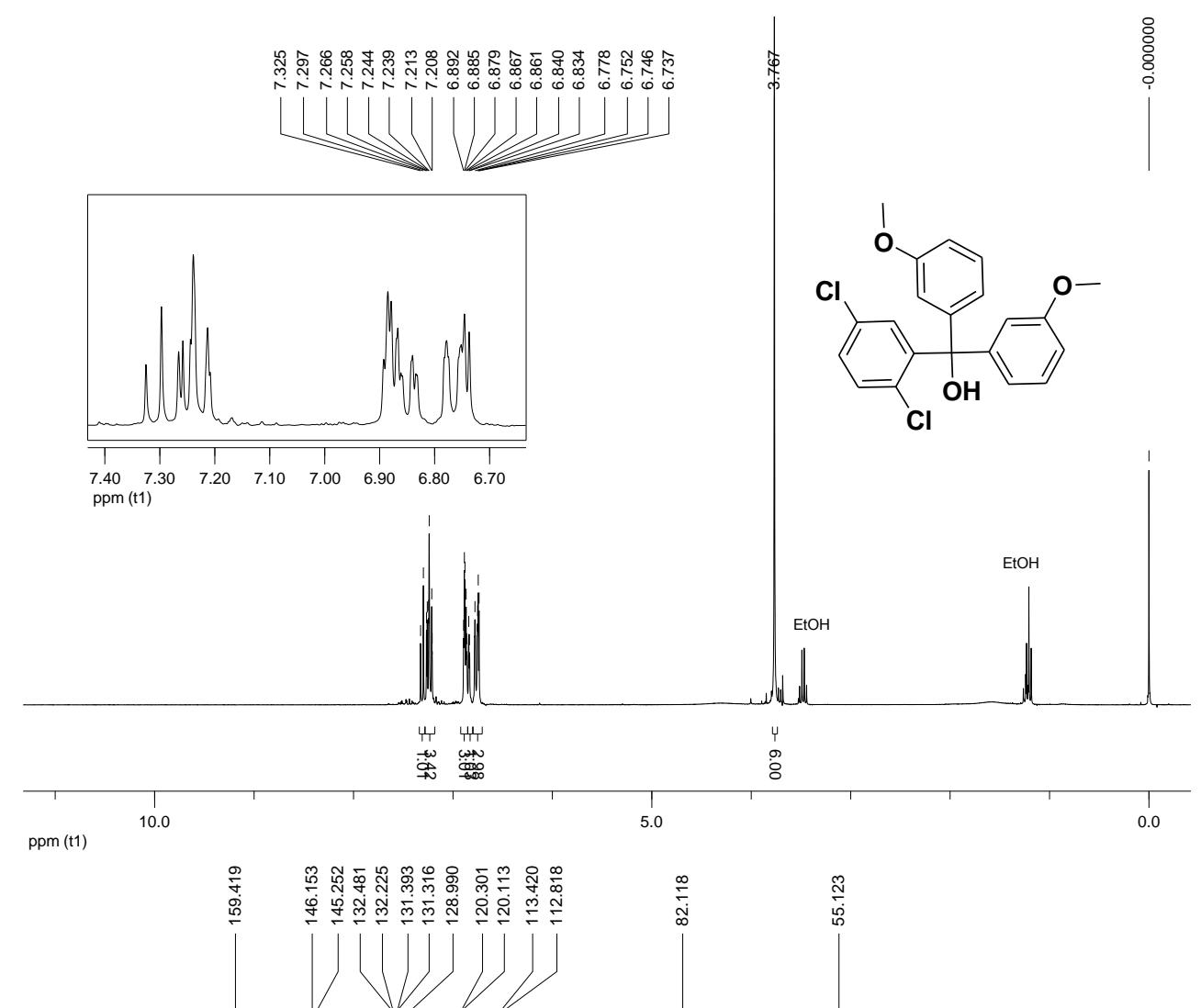
[S1] Bachmann, W. E., Hetzner, H. P. *Org. Synth.* **1955**, Coll. Vol. 3, 839.

III. NMR Spectral Characterization (^1H and ^{13}C NMR for **1c, **1d**, **1e**, **1g**, **1i**, **1j**, **1k**, **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, and **3a**)**

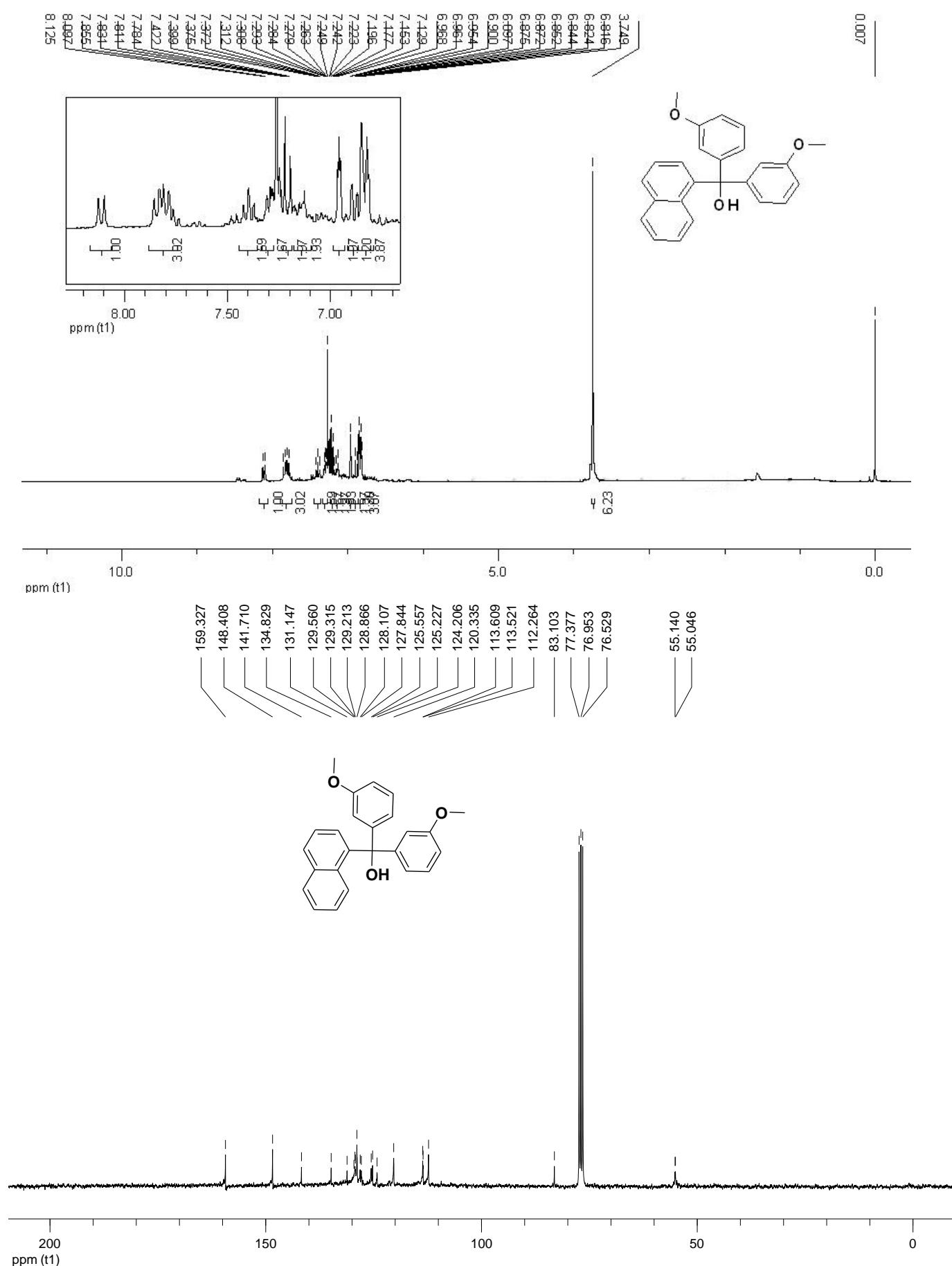
1c in CDCl_3



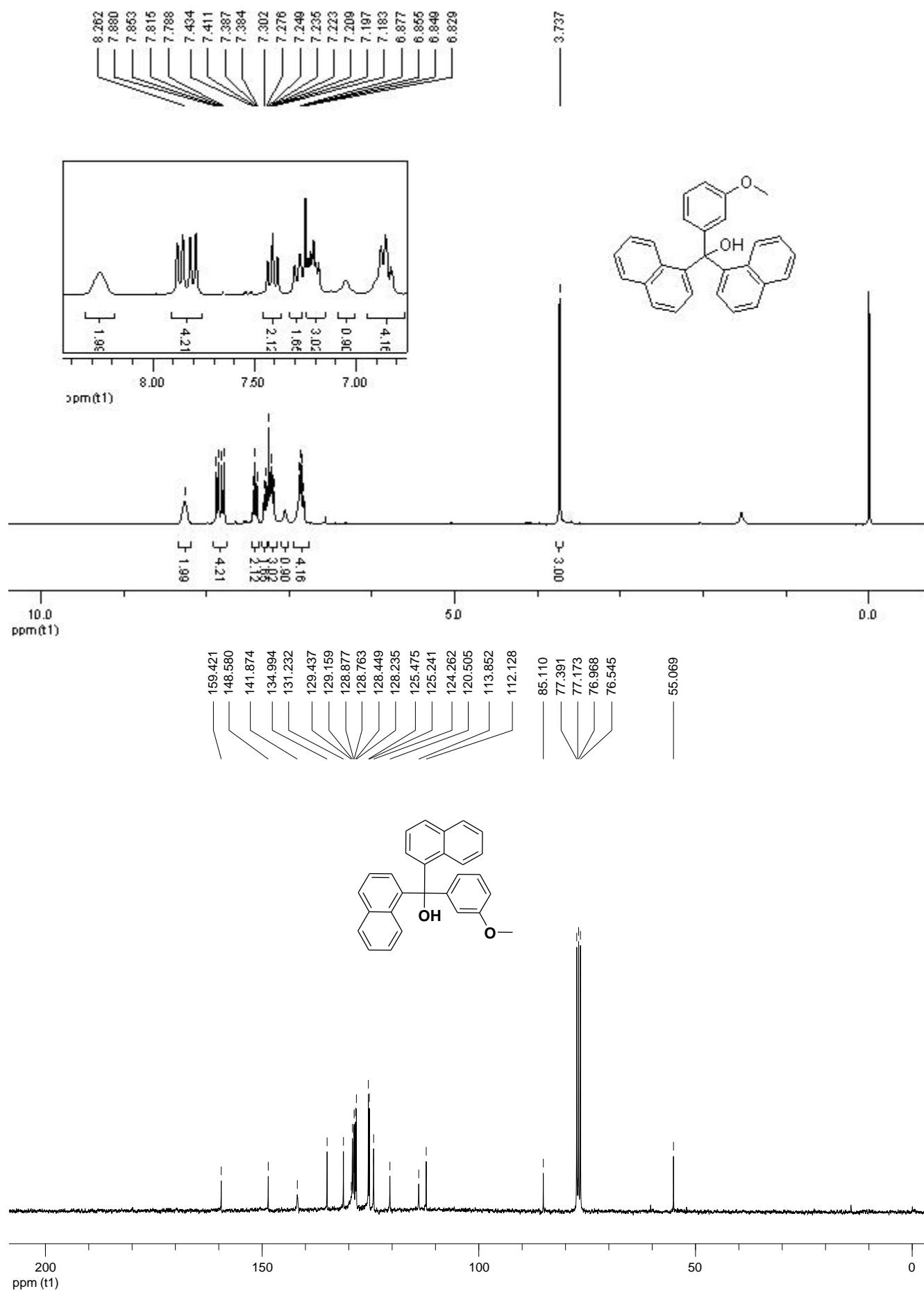
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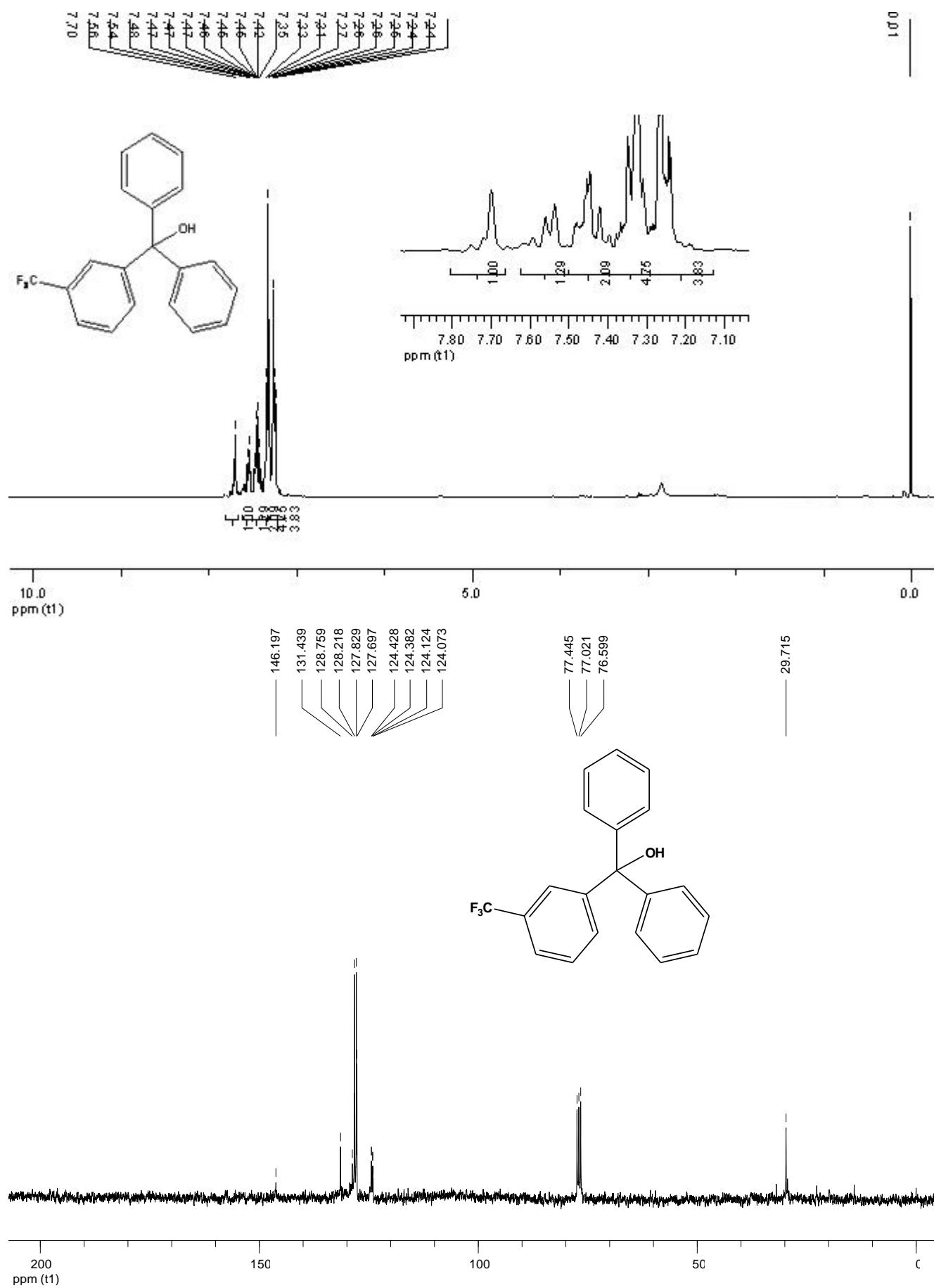
1e in CDCl_3



1g in CDCl_3



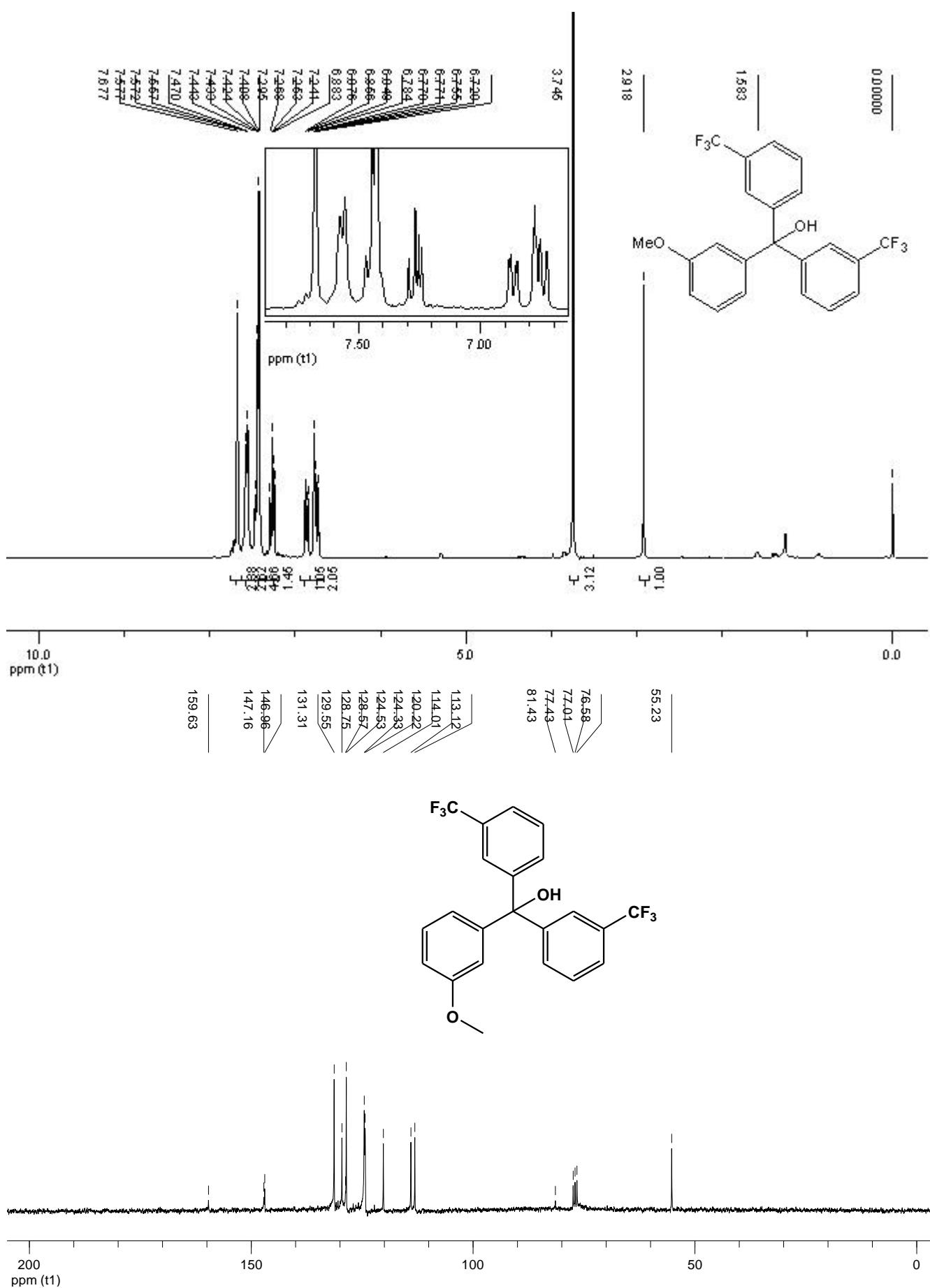
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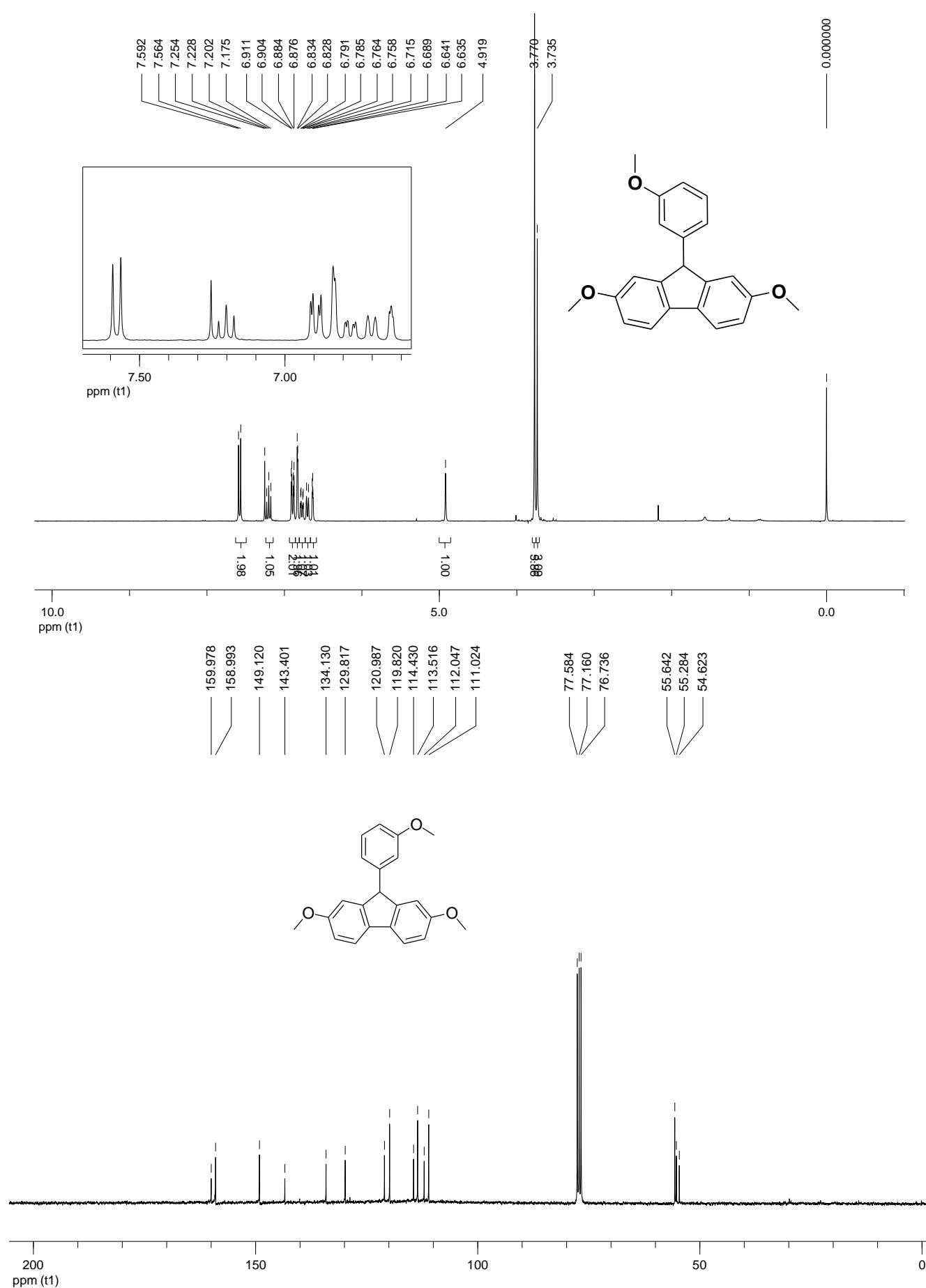
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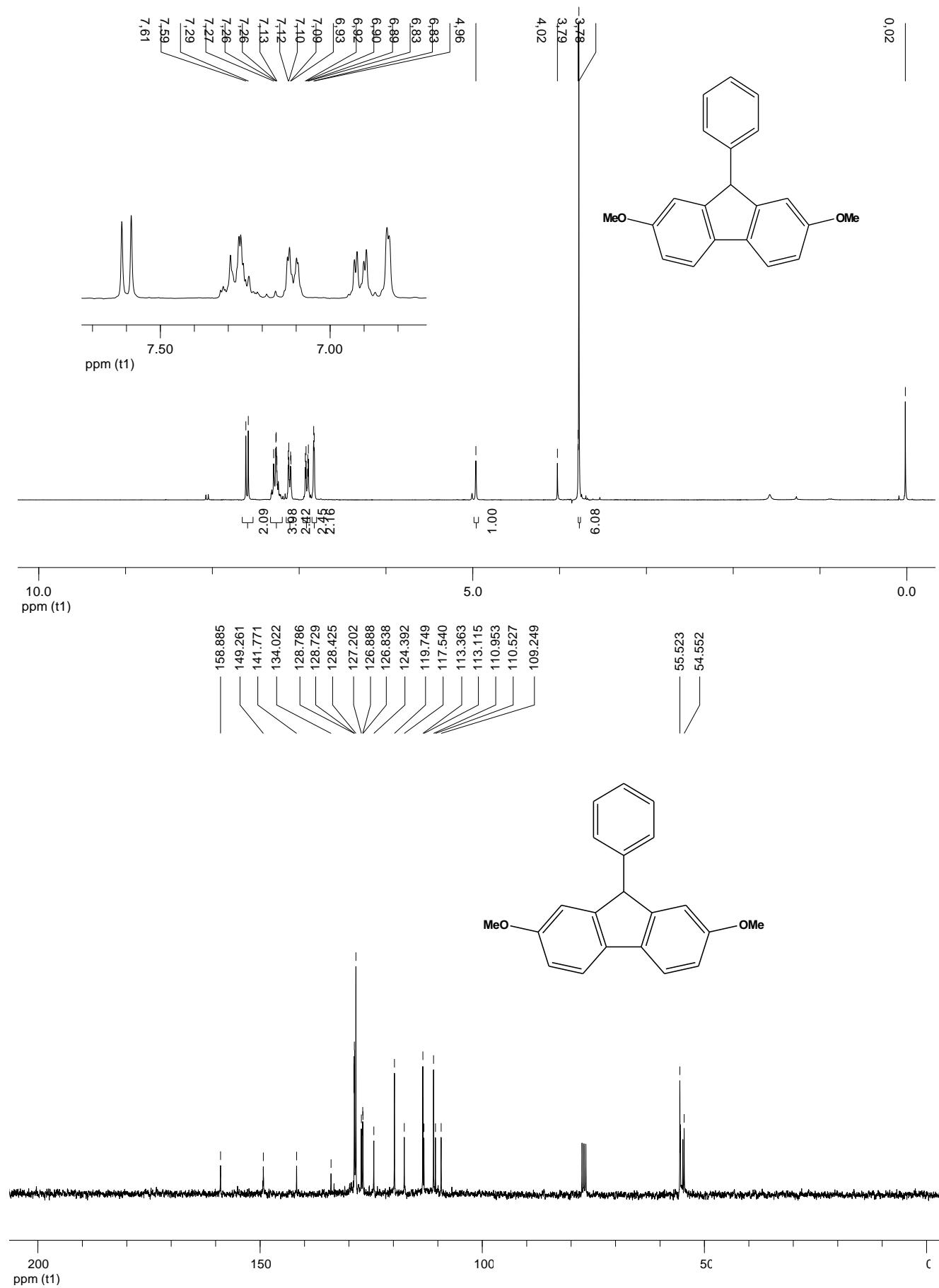
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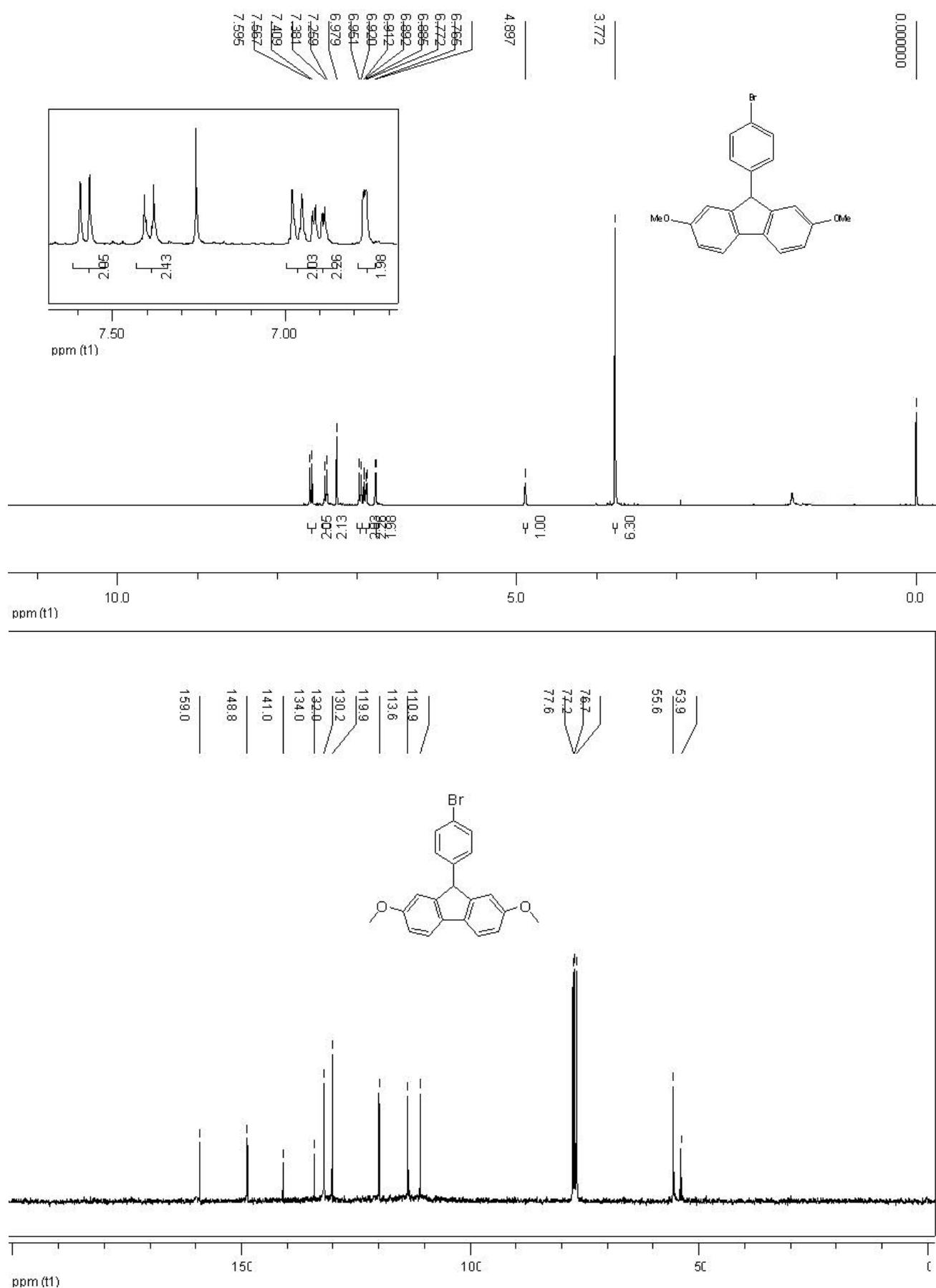
• 2a in CDCl₃



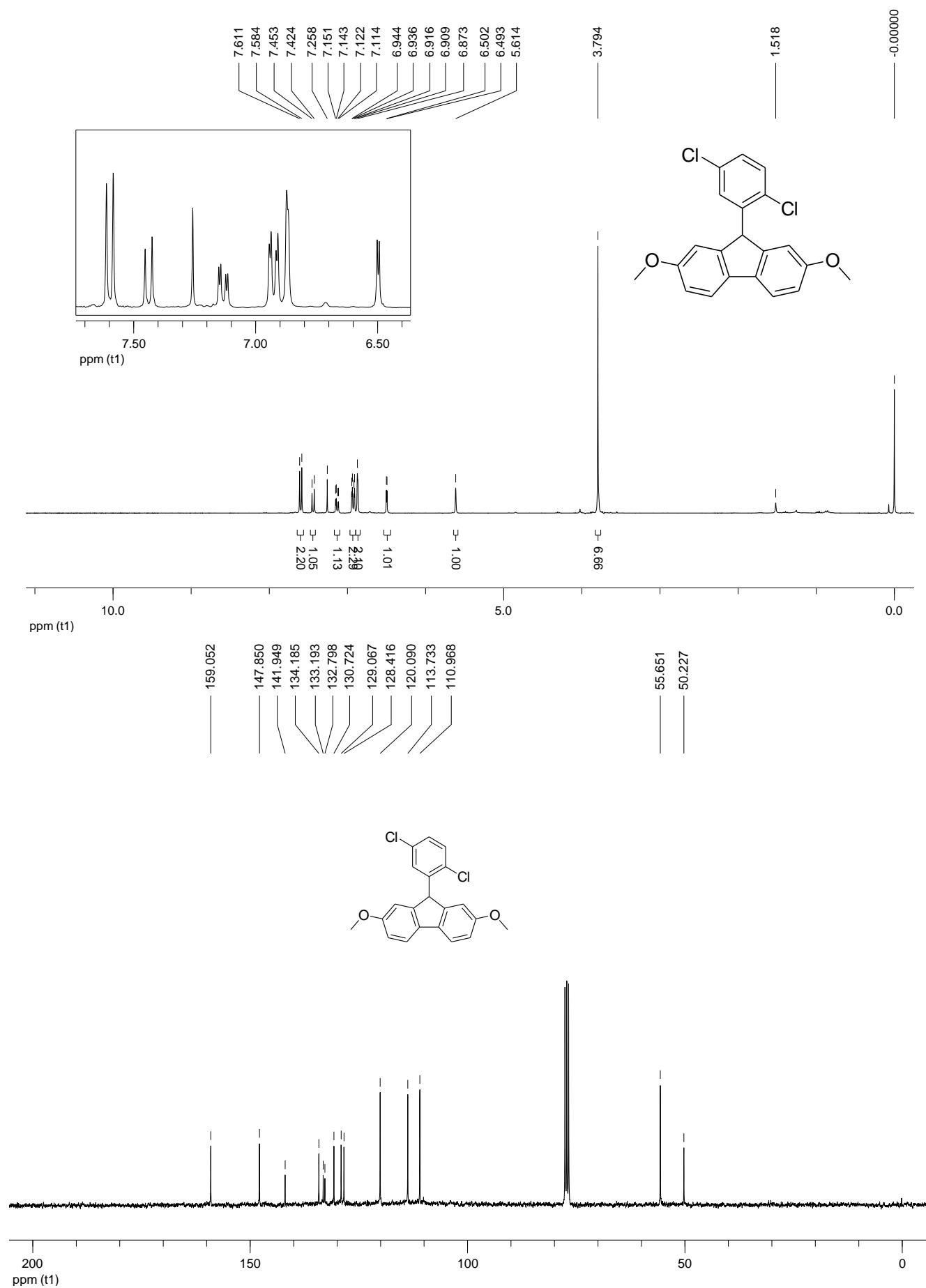
2b in CDCl₃



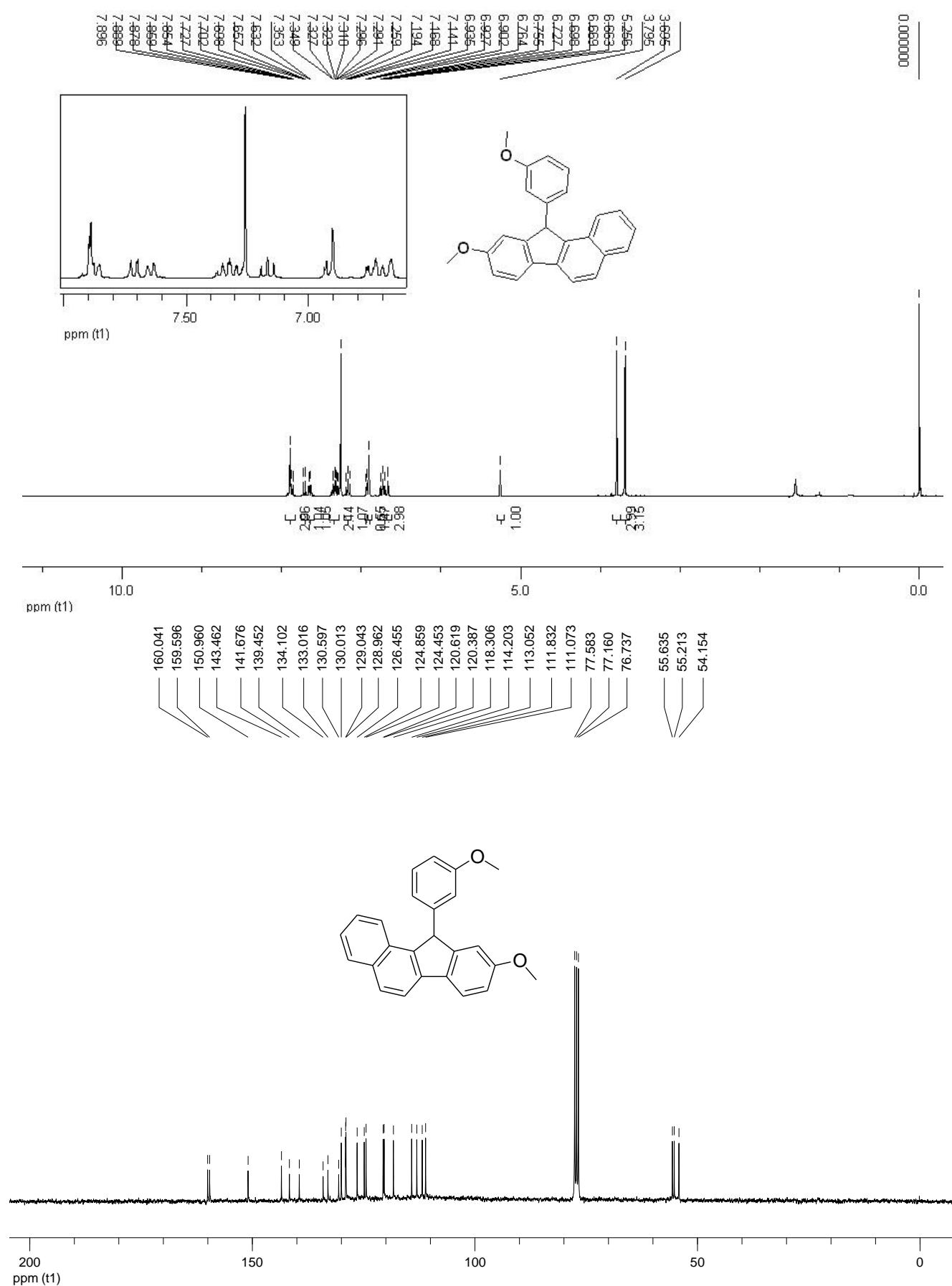
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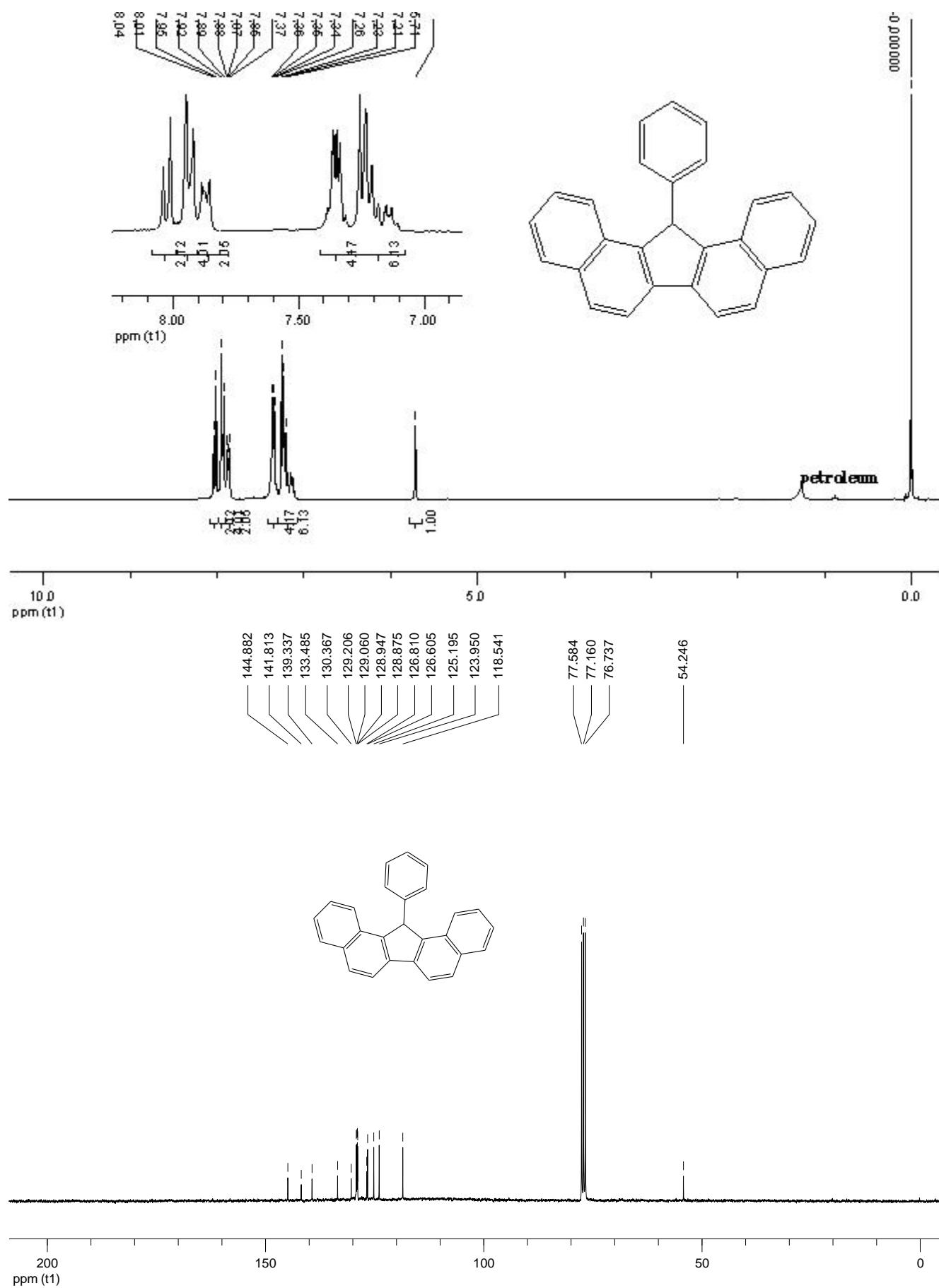
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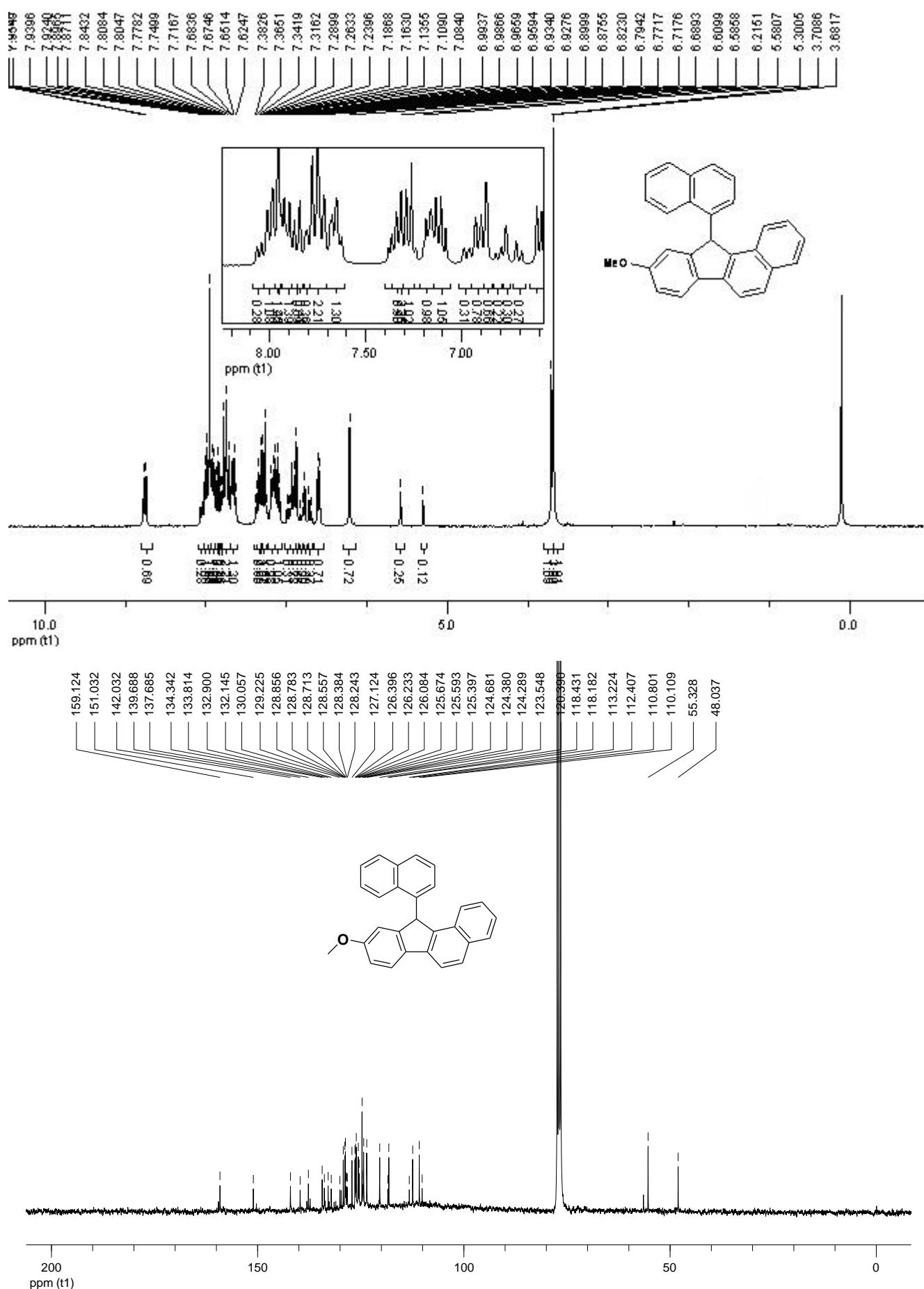
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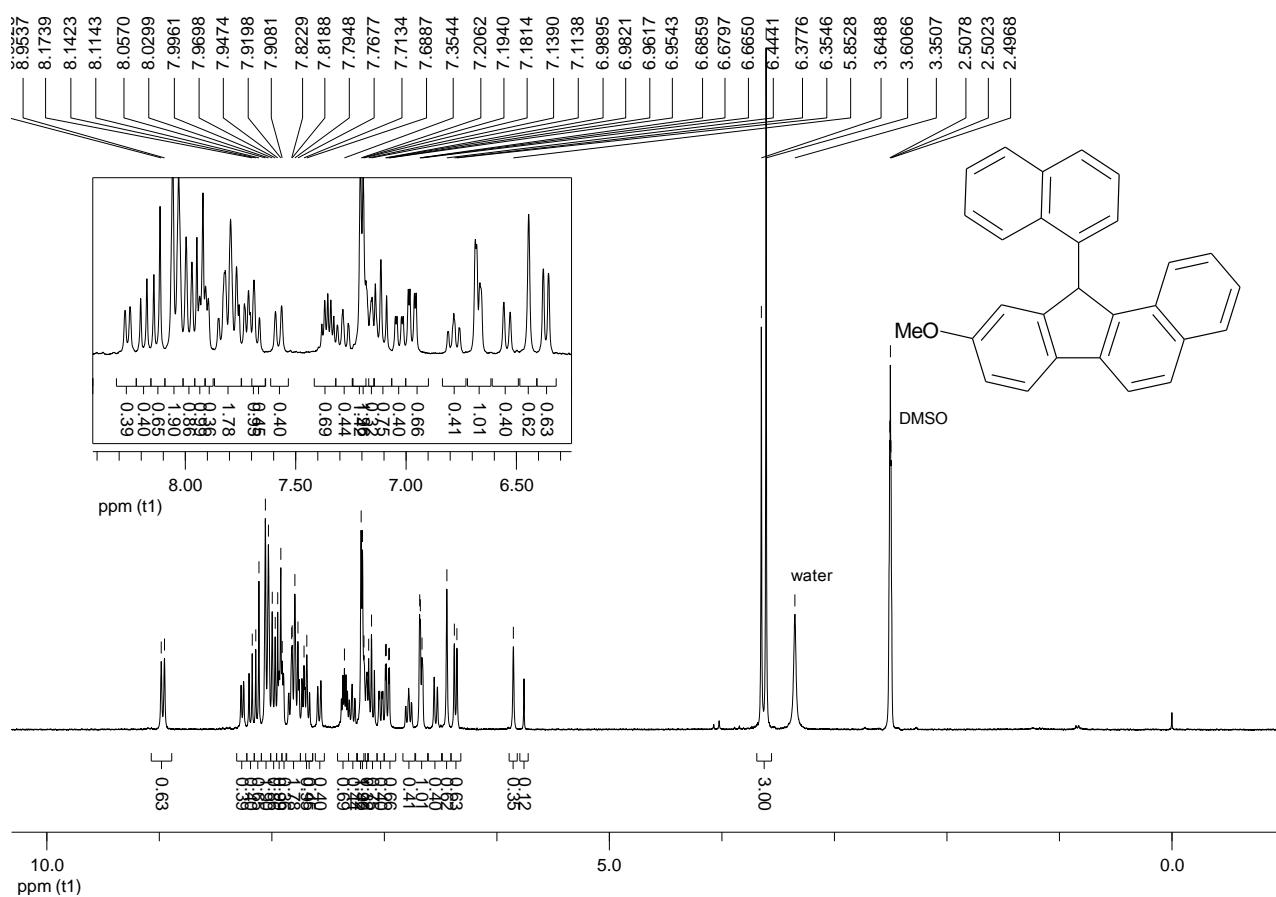
2f in CDCl_3



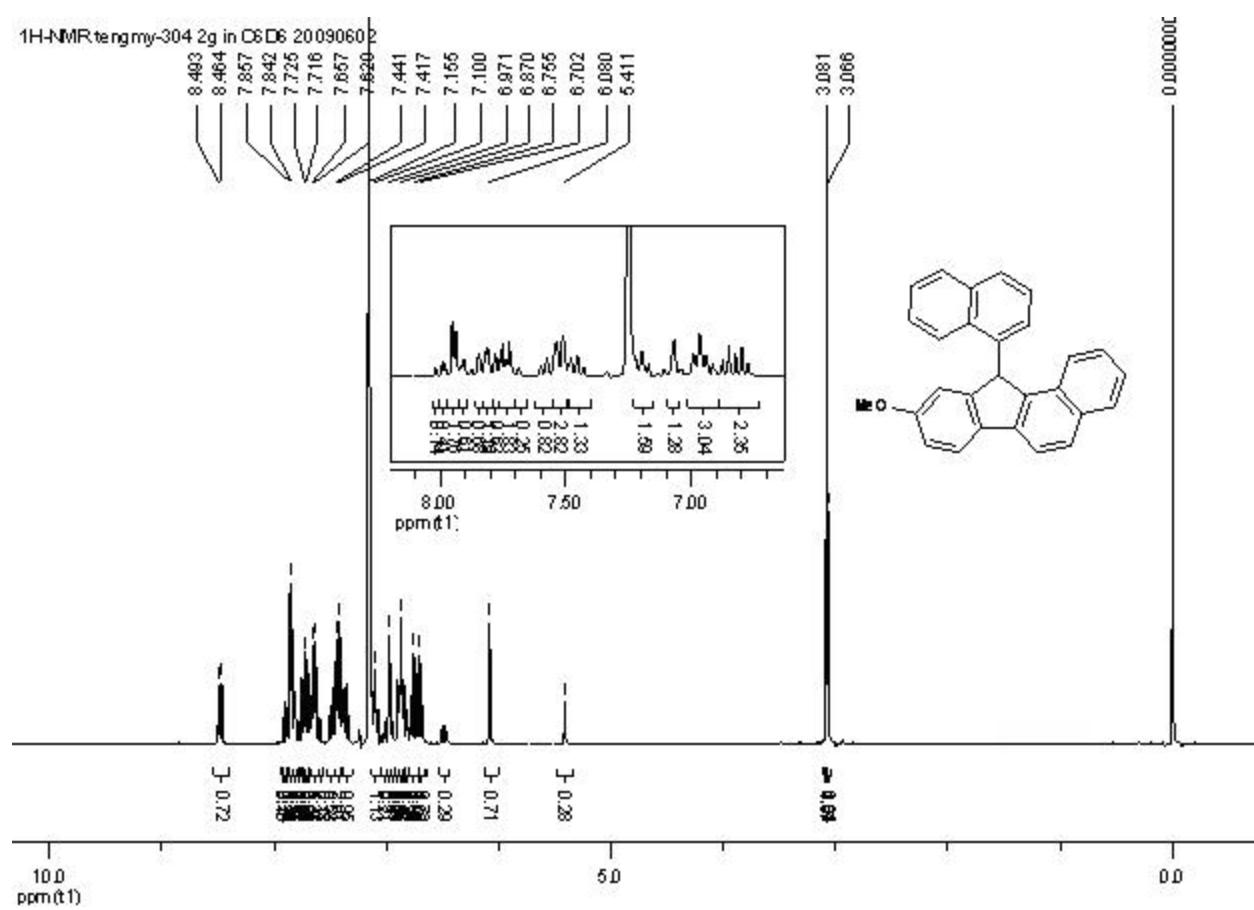
2g in CDCl₃



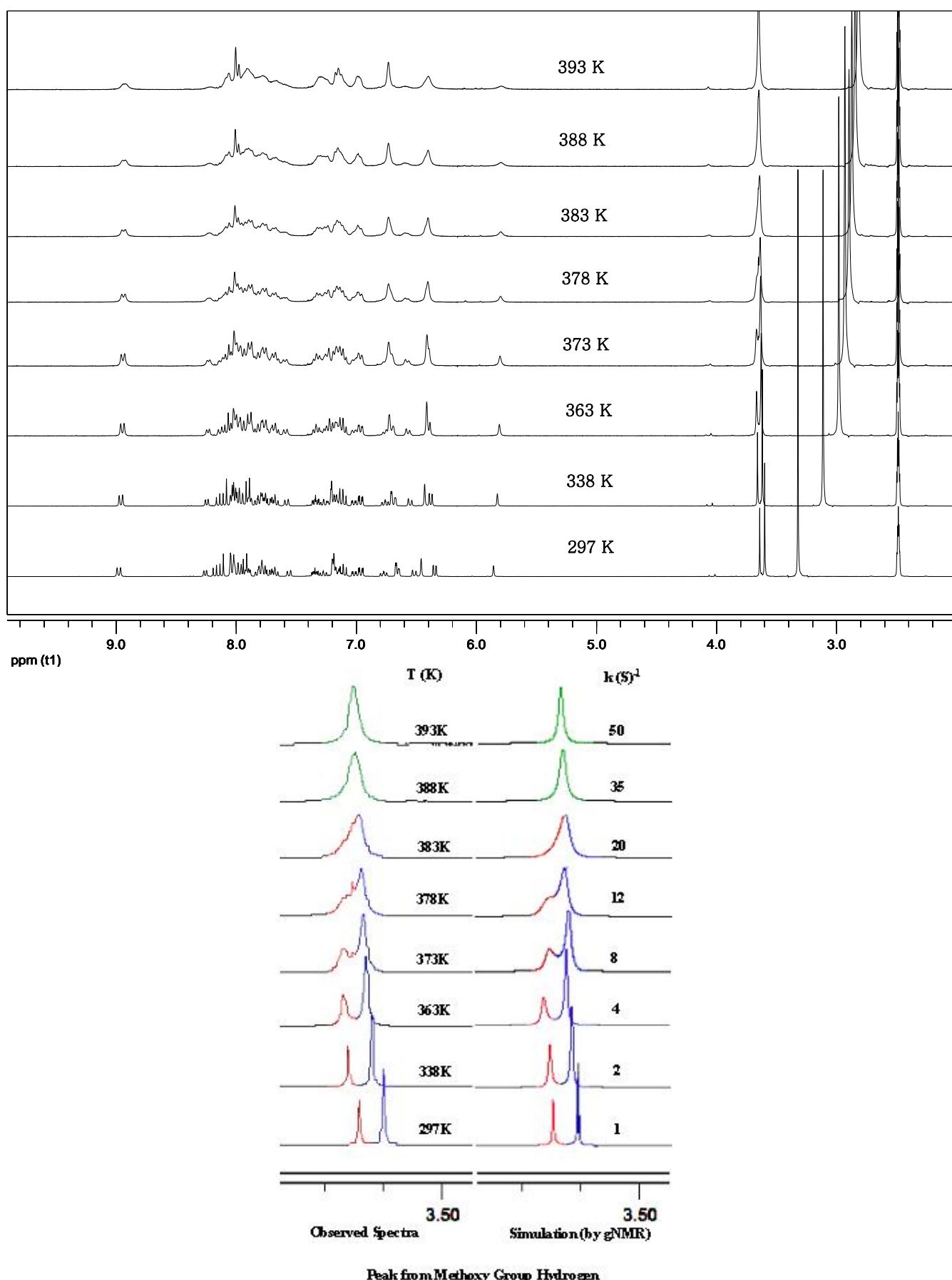
2g in DMSO-d₆



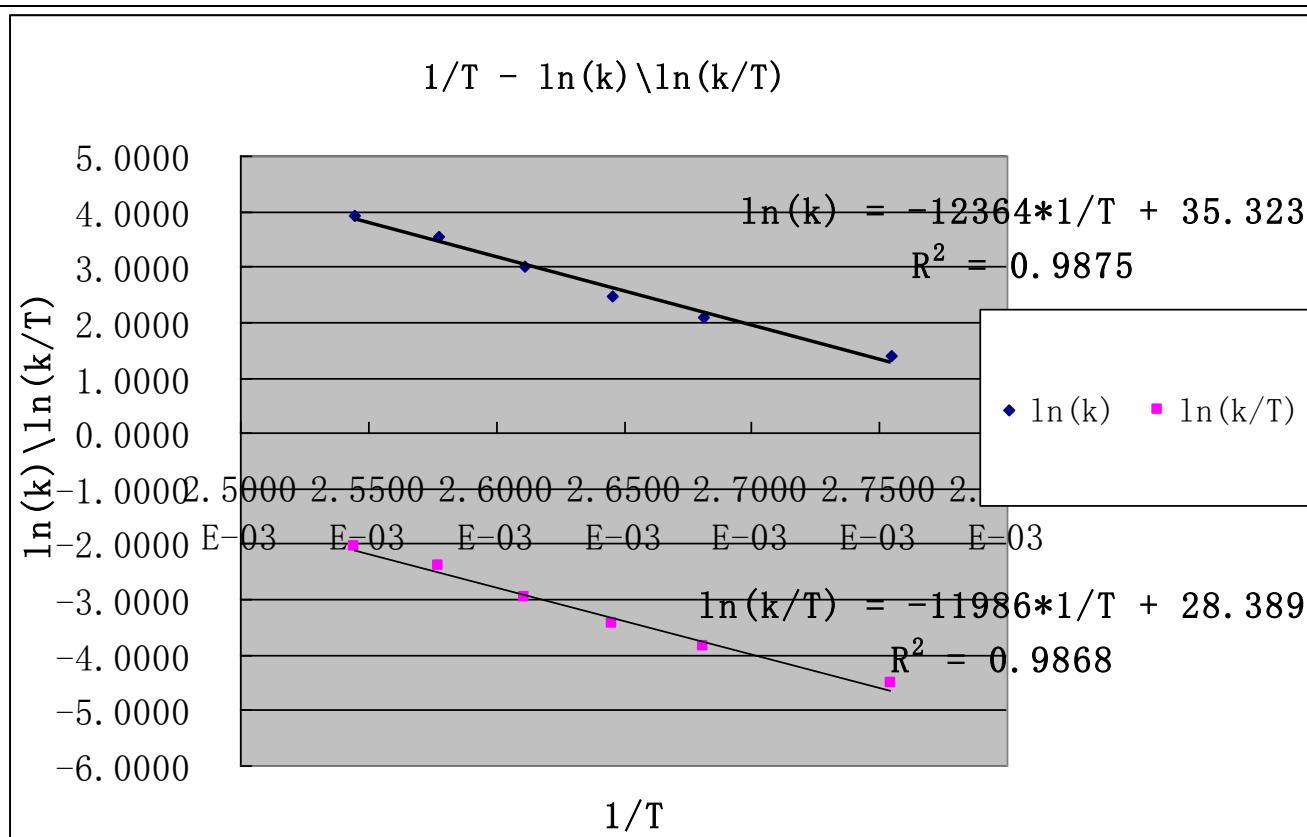
2g in benzene-d₆



IV. Variable-temperature ^1H NMR and Eyring Plot Analysis of $2\text{g}'$ and $2\text{g}''$ (300 MHz, DMSO)



T (K)	rate constant k/S ⁻¹	1/T (K ⁻¹)	1/T × 1000	ln(k)	ln(k/T)	ΔG [‡] (J/mol)
3.630E+02	4.000E+00	2.7548E-03	2.7548209	1.3863	-4.50811	8.5313E+04
3.730E+02	8.000E+00	2.6810E-03	2.6809651	2.0794	-3.84214	8.5598E+04
3.780E+02	1.200E+01	2.6455E-03	2.6455026	2.4849	-3.44999	8.5513E+04
3.830E+02	2.000E+01	2.6110E-03	2.6109661	2.9957	-2.9523	8.5059E+04
3.880E+02	3.500E+01	2.5773E-03	2.5773196	3.5553	-2.40566	8.4406E+04
3.930E+02	5.000E+01	2.5445E-03	2.5445293	3.9120	-2.06179	8.4370E+04



$\ln(k) = \ln A - E_a/RT$	R	$8.314E+0$
	E_a/R	12364
	$-\Delta H^\ddagger/R$	$E_a \text{ (J/mol)}$
		102.794E+3

$$\ln(k/T) = 23.76 + \Delta S^\ddagger/8.31 - \Delta H^\ddagger/(8.31T) \quad \Delta H^\ddagger \text{ (J/mol)} \quad 99651.60$$

$$\Delta G^\ddagger = (23.76 - \ln(k/T)) * R * T$$

$$\Delta G^\ddagger = aT(10.319 - \log(k/T))$$

$$a = 1.914 * 0.01 \quad (\Delta G^\ddagger \text{ in kJ/mol})$$

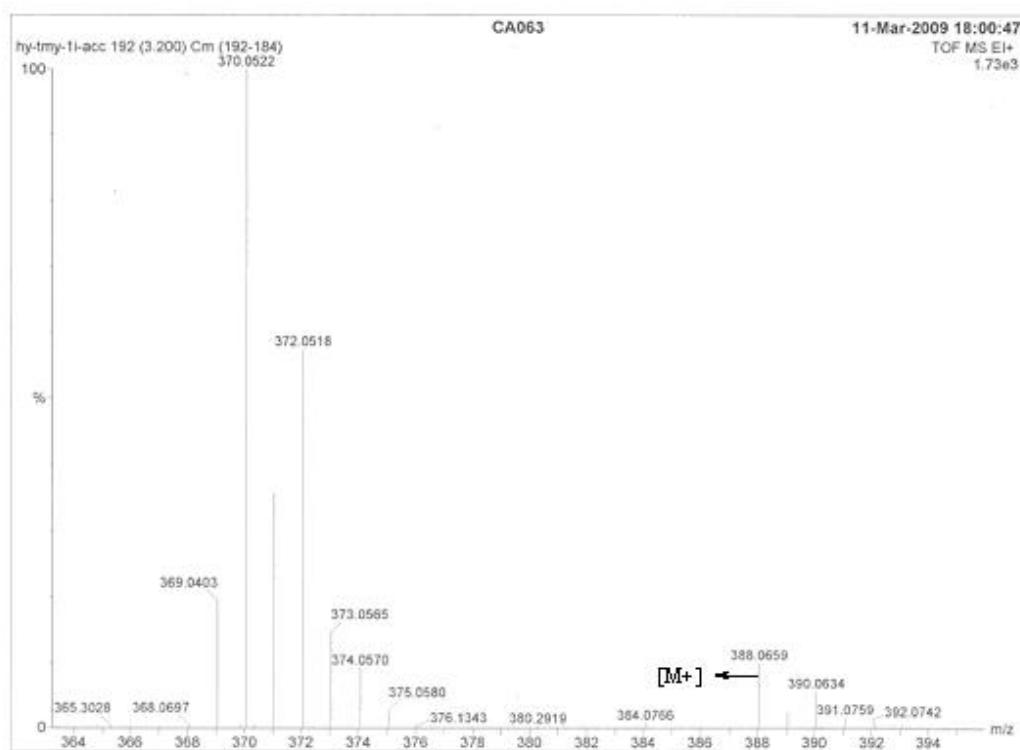
$$a = 1.914 * 10 \quad (\Delta G^\ddagger \text{ in J/mol})$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

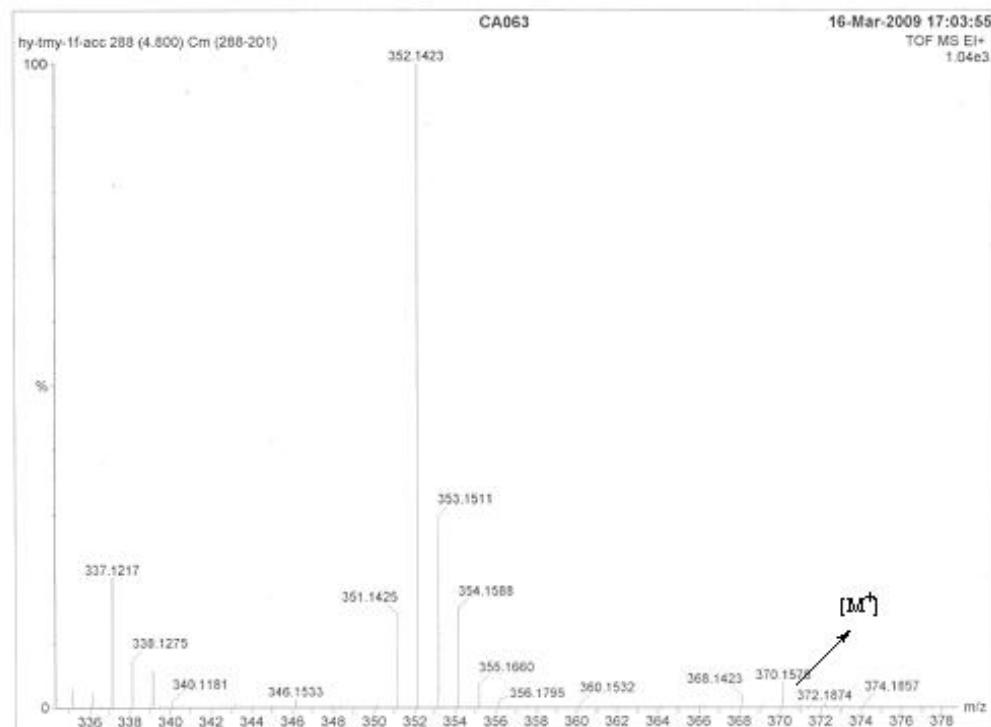
$$\Delta S^\ddagger \text{ (J/mol*K)} \quad 37.6783112 \quad (T = 373K)$$

V. MS Spectra

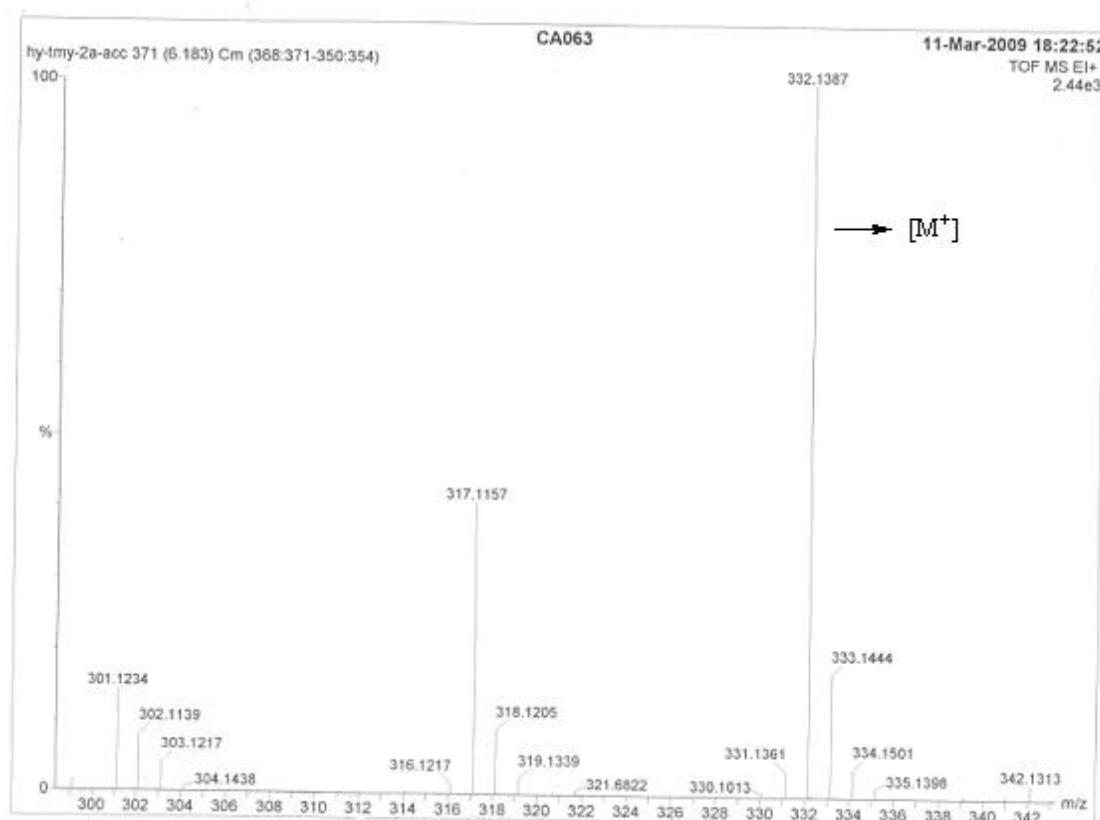
1d



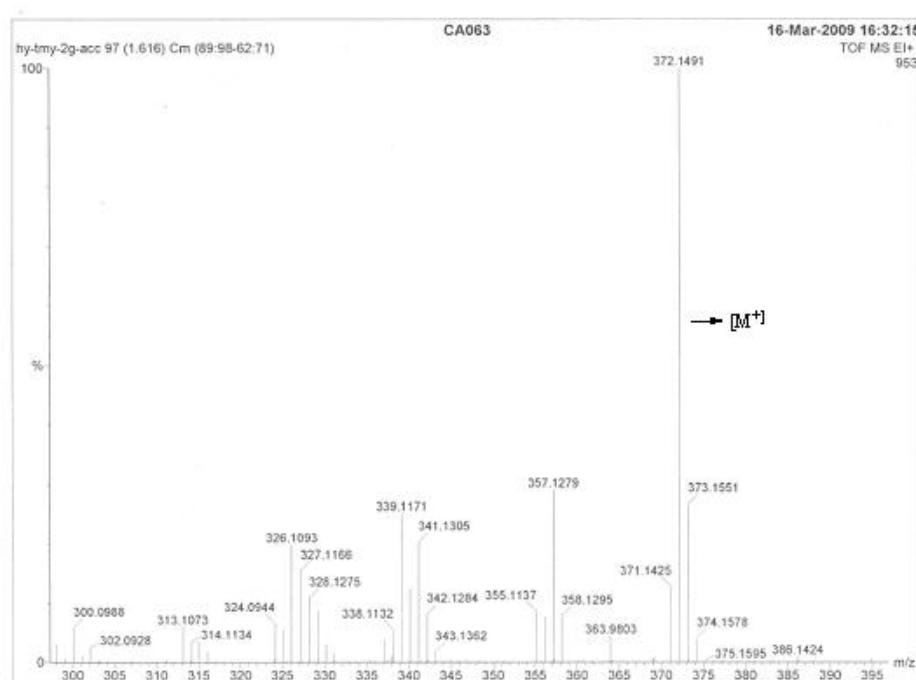
1e



2a



2g



VI. HPLC of 2g.

Page 1 of 1

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Sample Number	:	Study	:
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Sample Volume	: 1.000000 ul	Dilution Factor	: 1.00
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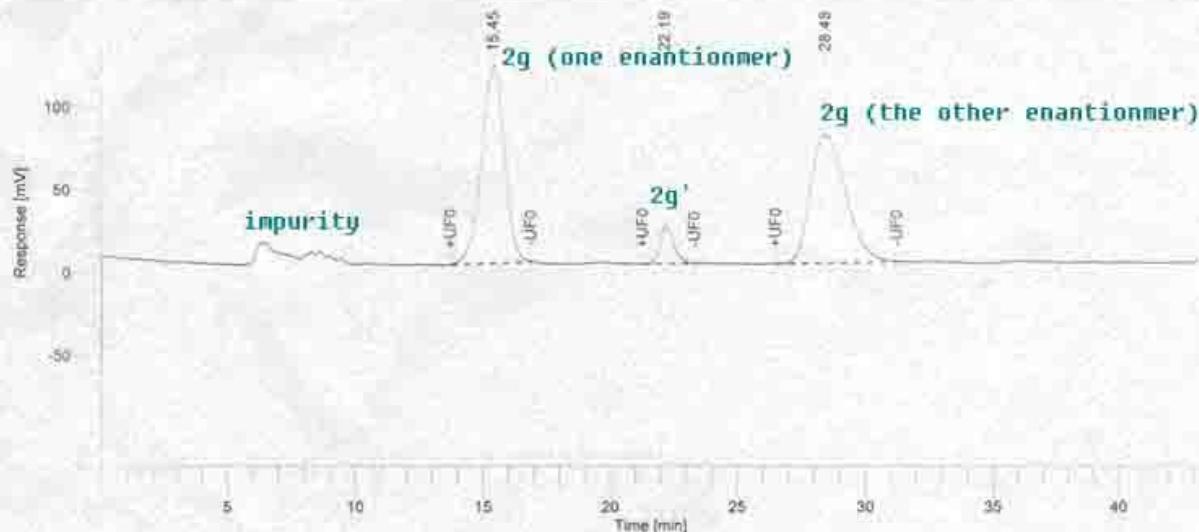
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Calib Method : D:\hufeng\method\lmyod-98-2-0-5-223-90-600 from D:\hufeng\result\lmy-0417-01.rst [Editing in Progress]

Report Format File: D:\hufeng\method\lmyod-98-2-0-5-223-90-600.rpt

Sequence File: C:\PenExe\TcWS\Ver6.2.0\Examples\lmy-0417-01.seq



HPLC REPORT

HPLC REPORT

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Raw Amount	Adjusted Amount
1		15.453	14366224.62	232329.56	47.39	47.39	14.3662	14.3662
2		22.192	1685759.38	44837.12	5.56	5.56	1.6858	1.6858
3		28.480	14263720.87	151019.25	47.05	47.05	14.2637	14.2637
30315704.87			428185.93	100.00	100.00	30.3157	30.3157	

Missing Component Report

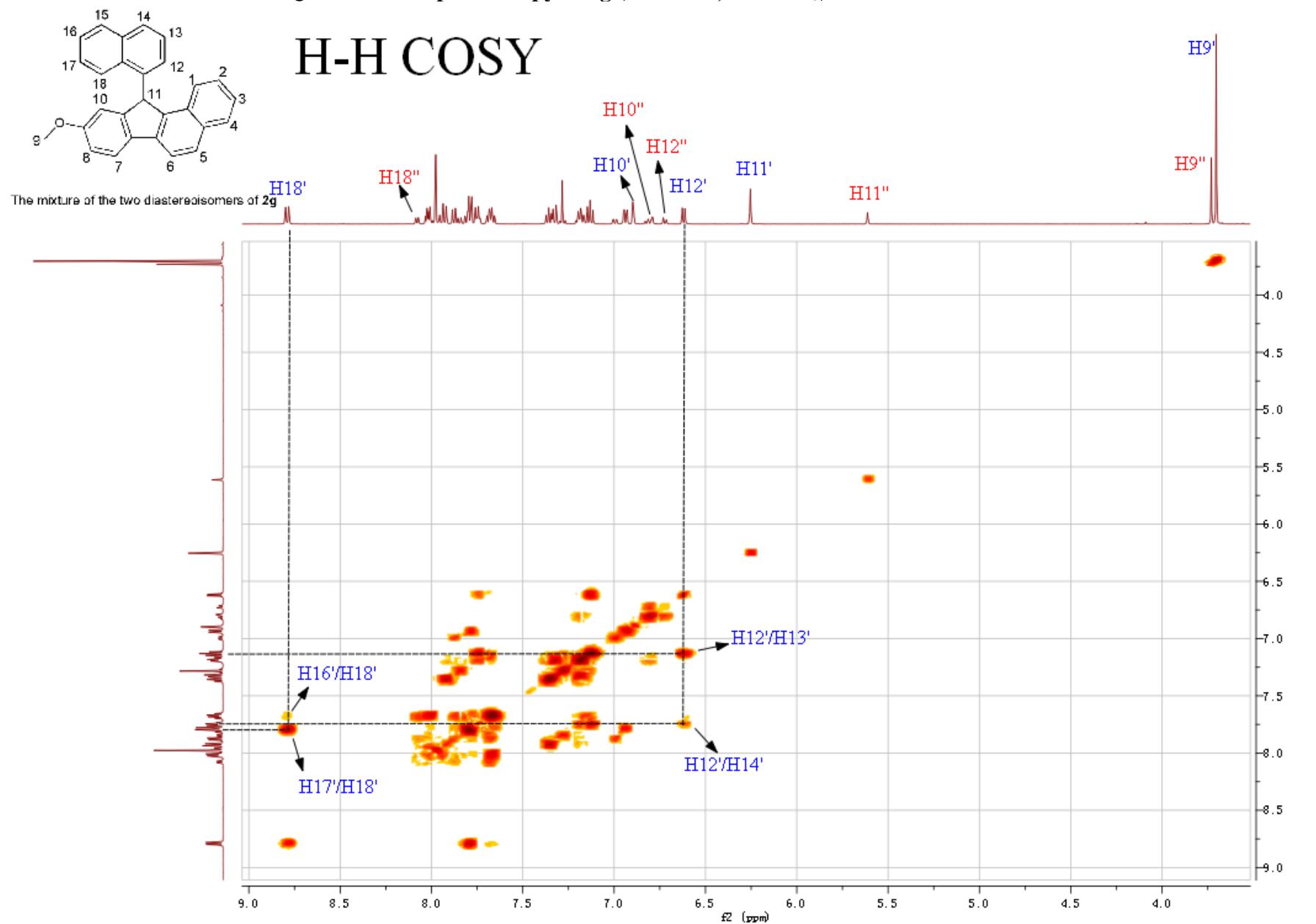
Component Expected Retention (Calibration File)

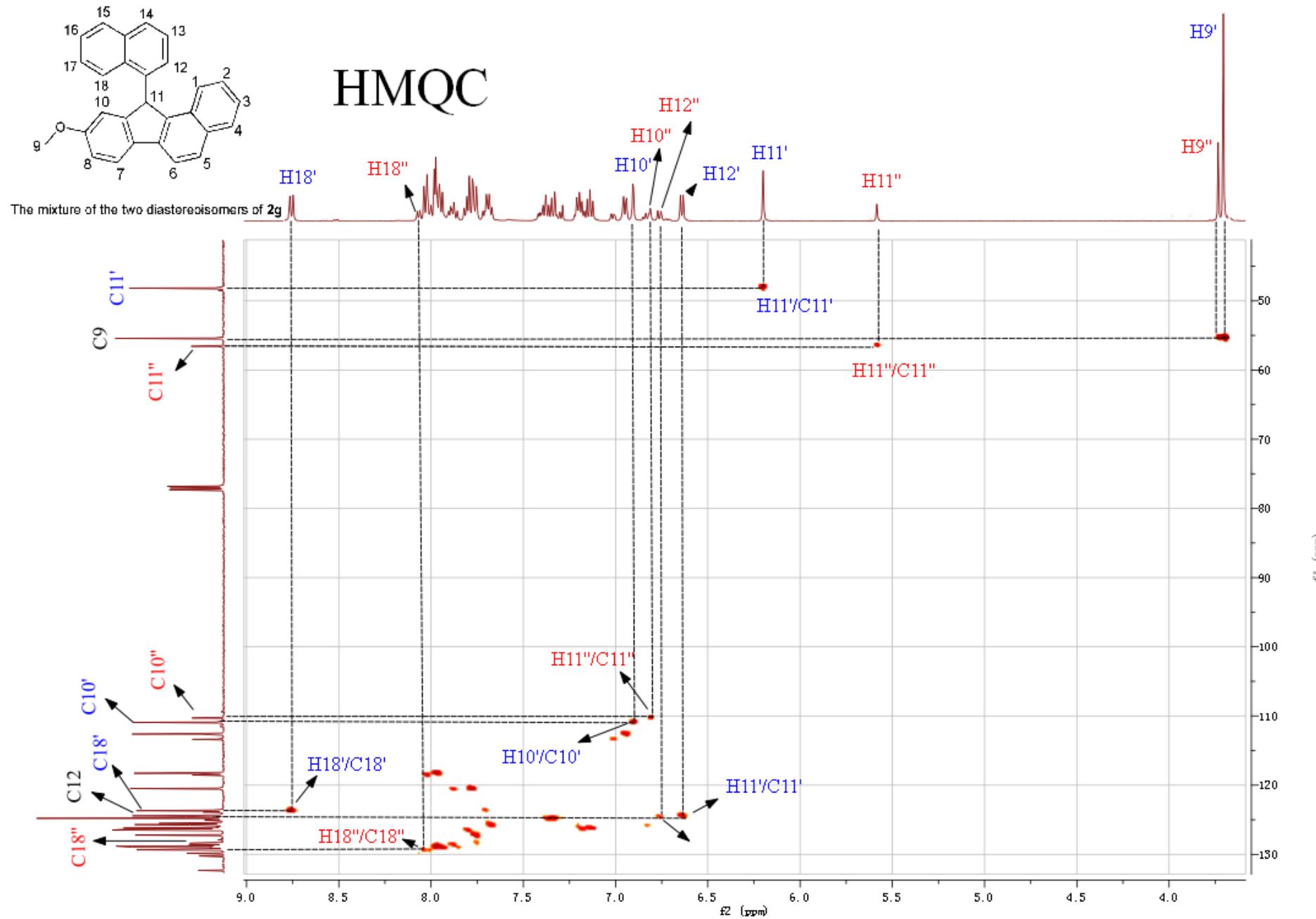
All components were found

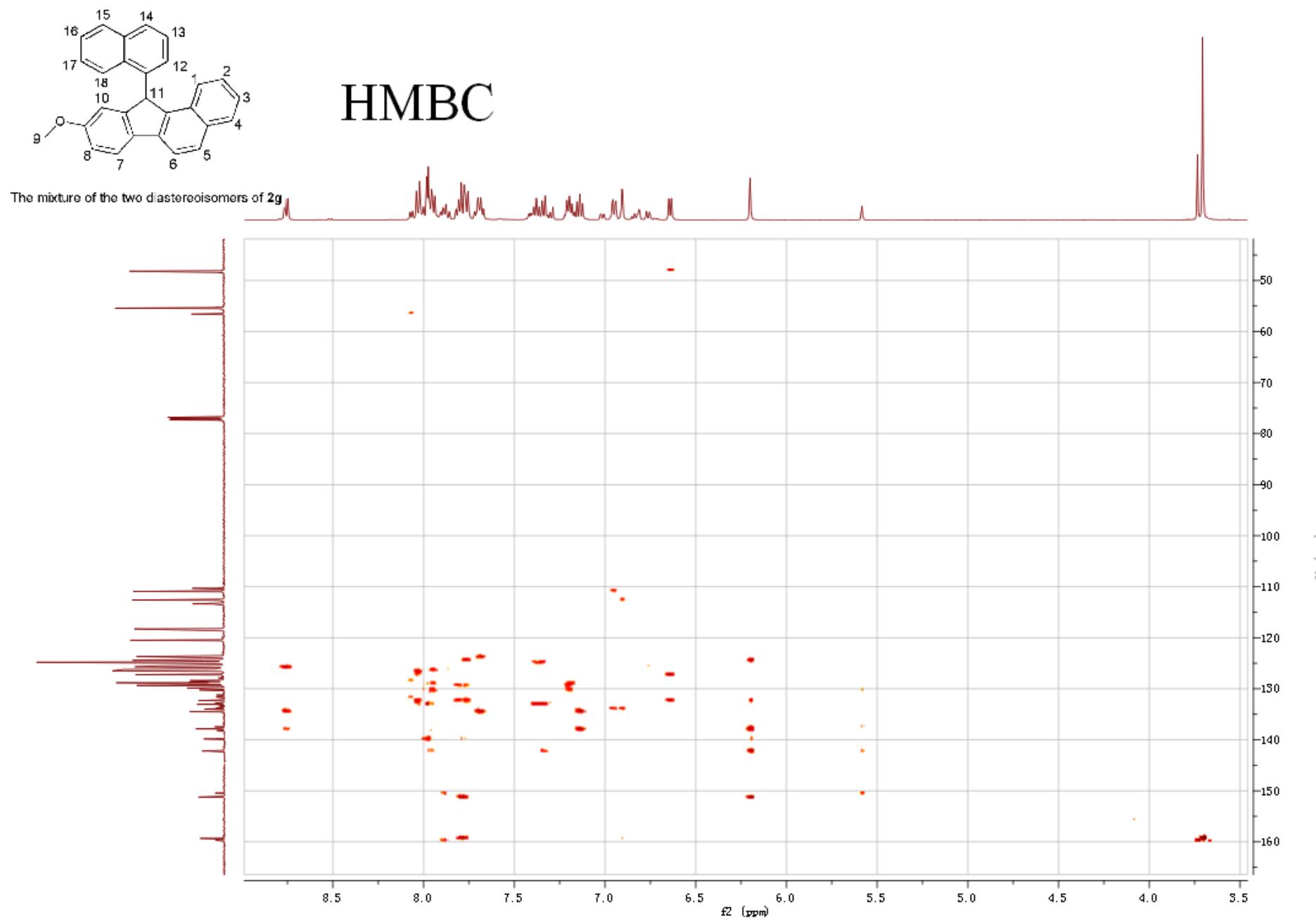
ANALYZED BY

DATE

VII. H-H COSY/HMBC/HMQC 2D NMR Spectroscopy of 2g (500M Hz, in CDCl₃).







Reference

[S1]. Bachmann, W. E.; Hetzner H. P. *Org. Synth.* **1955**, Coll. Vol. 3, 839-840.