Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Silver-Mediated Oxidative Annulation of N-Arylthio Succinimides with Alkynes: Direct Access to Benzo[*b*]thiophenes

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SUPPORTING INFORMATION

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General Experimental

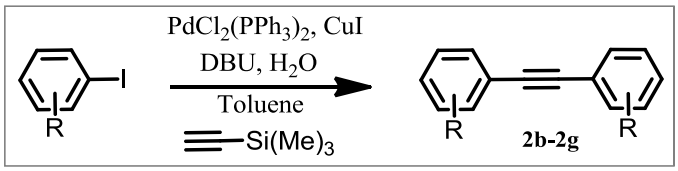
All the reactions were performed in an oven-dried Schlenk flask / pressure tubes under an argon atmosphere. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 Mesh or 230-400 Mesh silica gel eluting with hexane and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber.

Proton, carbon, and fluorine nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded based on the resonating frequencies as follows: (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz) and (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 MHz) having the solvent resonance as internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m =multiplet), coupling constants, *J*, in (Hz), and integration. Data for ^{13}C NMR, ^{19}F NMR were reported in terms of chemical shift (ppm). IR spectra were reported in cm^{-1}. High resolution mass spectra were obtained in ESI mode. LC-MS spectra were obtained with ionization voltage of 70ev; data was reported in theform of *m/z* (intensity relative to base peak = 100). Elemental (C, H, N) analysis were carried out using FLASH EA 1112 analyzer. Melting points were determined by electro-thermal heating and are uncorrected.

Materials: Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Following the standerd procedures, the solvents were dried and stored over molecular sieves under inert gas (nitrogen, argon) atmosphere.[1] Diphenyl acetylene (**2a**), 1-phenyl-1-propyne (**2h**), 1-phenyl-1-hexyne (**2i**), $AgSbF_6$, $AgBF_4$, AgoTf, and KPF_6 were purchased from Sigma Aldrich Ltd, and used as received. Analytical and spectral data of all the known compounds are exactly matching with the reported values.

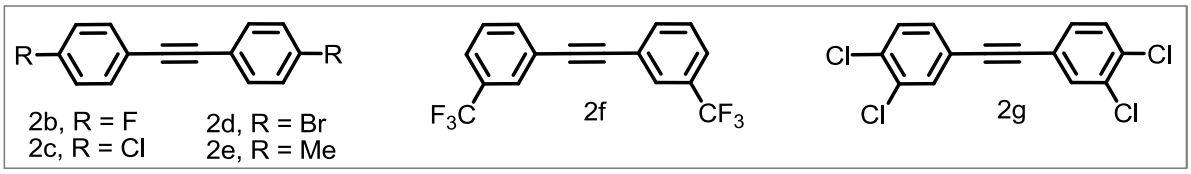
Experimental Procedures:

Perparation of symmetrical diaryl alkynes (2b–g); General Procedure (GP–1):[2]

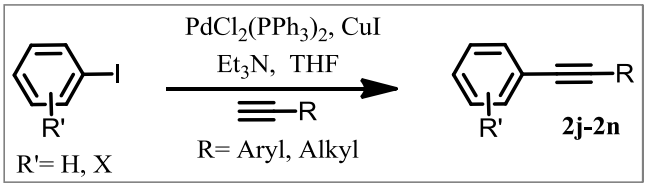


To a mixture of $PdCl_2(PPh_3)_2$ (6.0 mol %), CuI (10 mol %) and aryl iodide (1.0 mmol) in benzene (5.0 mL) was added DBU (6.0 mmol) followed by trimetyhylsilyl acetylene (0.5 mmol) and de-ionized water (40 mol %) under an argon atmosphere at rt. The resulting mixture was heated at 80 ^oC for 18 h in the absence of light. Upon completion, the reaction mixture was cooled to rt and diluted with diethyl ether. The organic layer was washed with water, 10% HCl (2 × 5.0 mL), and brine and dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane /ethyl acetate.

Following this procedure, compounds **2b–g** were prepared.[2] Analytical and spectral data of these compounds are exactly matching with the reported values.



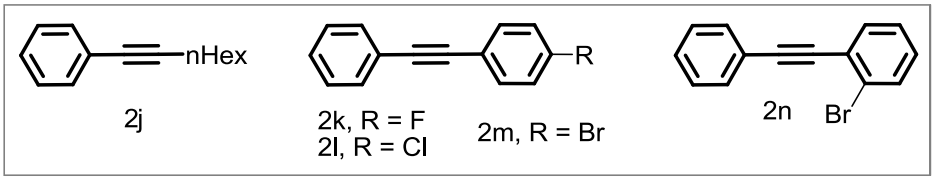
Preparation of unsymmetrical alkynes (2j–n); General Procedure (GP–2):[3]



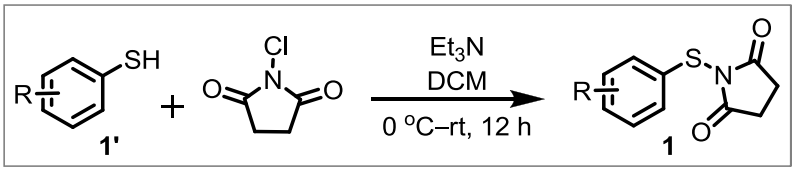
To a mixture of $PdCl_2(PPh_3)_2$ (2.0 mol %), CuI (4.0 mol %) and aryl iodide (1.0 mmol) in THF (5.0 mL) was added Et_3N (3.0 mmol) followed by aryl/alkyl bearing acetylenes (1.0 mmol) under an argon atmosphere at rt. The resulting mixture was heated at 60 ^oC for 16 h in the absence of light. Upon completion, the reaction mixture was cooled to rt and diluted with diethyl ether. The organic layer was washed with water, 10% HCl (2 × 5.0 mL), and brine

and dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane /ethyl acetate.

Following this procedure, compounds **2j-n** were prepared.[3] Analytical and spectral data of these compounds are exactly matching with the reported values.

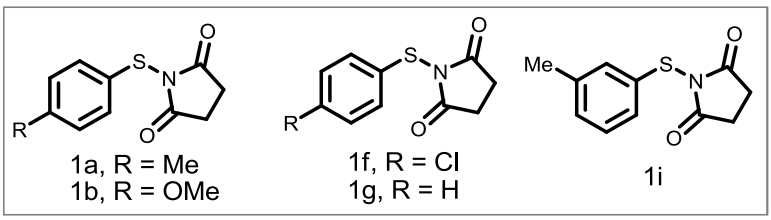


Preparation of N-arylthio succinimide (1): General Procedure (GP–3):[4]

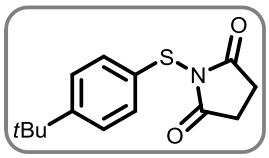


To a solution of N-chlorosuccinimide (NCS) (1.0 equiv) in CH_2Cl_2 (5.0 mL for 2.0 mmol) was added thiophenols (**1′,** 1.0 equiv) and Et_3N (1.0 equiv) drop wise under an argon atmosphere at 0 ^oC. The resulting mixture was stirred for 12 h at rt. After completion, the reaction mixture was quenched with saturated aqueous NH_4Cl solution. The organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (2 times). The combined extracts were washed with brine. The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane /ethyl acetate (4:1).

Following this procedure, the N–arylthio succinamides **1a, 1b**, **1f, 1g** and **1i** were prepared.[4] Analytical and spectral data of these compounds are exactly matching with the reported values.

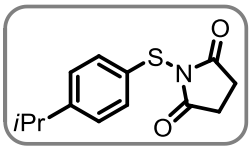


1-(4-*tert*-Butylphenylthio) pyrrolidine-2,5-dione (1c):



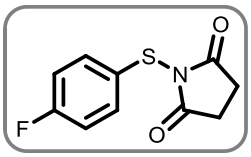
1c colorless solid (765 mg, 48%); mp = 138–139 °C; R_f = 0.38 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.77 (s, 4H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 153.7, 133.2, 130.3, 126.3, 34.7, 31.0, 28.5; IR (KBr) ν_{max} 2958, 1736, 1435, 1298, 1139, 816 cm^{-1}; HRMS (ESI) for $C_{14}H_{18}NO_2S$ $(M+H)^+$: calcd. 264.1058, found 264.1058.

1-(4-*iso*-Propylphenylthio) pyrrolidine-2,5-dione (1d):



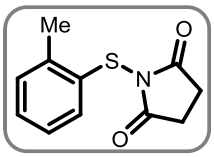
1d colorless solid (812 mg, 51%); mp = 86–87 °C; R_f = 0.43 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 2.92–2.81 (m, 1H), 2.76 (s, 4H), 1.19 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 151.5, 133.6, 130.5, 127.4, 33.9, 28.5, 23.6; IR (KBr) ν_{max} 2958, 1720, 1599, 1353, 1139, 816 cm^{-1}; HRMS (ESI) for $C_{13}H_{16}NO_2S$ $(M+H)^+$: calcd. 250.0902, found 250.0900.

1-(4-Fluorophenylthio) pyrrolidine-2,5-dione (1e):



1e colorless solid (1.9 g, 54%); mp = 162–164 °C; R_f = 0.26 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.68 (m, 2H), 7.04–6.97 (m, 2H), 2.77 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2,163.9 (d, J = 252 Hz), 136.5 (d, J = 9 Hz), 129.0 (d, J = 3 Hz), 116.4 (d, J = 22 Hz), 28.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –108.60; IR (KBr) ν_{max} 3090, 1709, 1479, 1216, 1139 cm^{-1}; HRMS (ESI) for $C_{10}H_9FNO_2S$ $(M+H)^+$: calcd. 226.0338, found 226.0337.

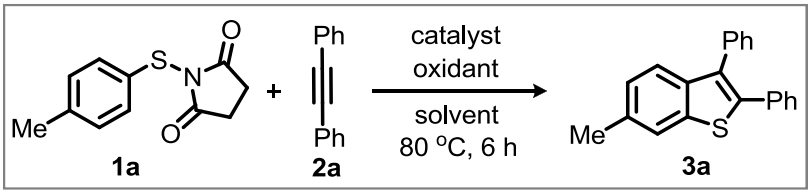
1-(*o*-Tolylthio) pyrrolidine-2,5-dione (1h):



1h colorless solid (2.2 g, 61%); mp = 99–100 °C; R_f = 0.33 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 1H), 7.23–7.16 (m, 2H), 7.15–7.08 (m, 1H), 2.79 (s, 4H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 139.2, 133.0, 131.7, 130.6, 129.4, 126.7, 28.5, 20.2; IR (KBr) ν_{max} 3073, 1726, 1293, 1134, 745 cm^{-1}; HRMS (ESI) for $C_{11}H_{12}NO_2S$ $(M+H)^+$: calcd. 222.0589, found 222.0582.

Reaction optimization.

Table 1: Screening of Catalyst, Oxidant and Solvents.



Entry	Catalyst (30 mol %)	Oxidant (50 mol %)	Solvent (0.5 mL)	yield (%)[b]
1	AgCl	$K_2S_2O_8$	DCE	NR
2	Ag_2CO_3	$K_2S_2O_8$	DCE	NR
3	$AgSbF_6$	Benzoquinone	DCE	22
4	$AgSbF_6$	CuO	DCE	18
5	$AgSbF_6$	CuI	DCE	56
6	$AgSbF_6$	$K_2S_2O_8$	Dioxane	NR
7	$AgSbF_6$	$K_2S_2O_8$	THF	NR
8	$AgSbF_6$	$K_2S_2O_8$	Ph–Cl	NR
9	$AgSbF_6$	$K_2S_2O_8$	Toluene	12
10	$AgSbF_6$	$K_2S_2O_8$	Benzene	9
11	AgSbF6	$K_2S_2O_8$	CH_3NO_2	24

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol). [b]Conversion based on crude ^{1}H NMR of starting material. NR = no reaction

Comparison of structures 3a, X, and 3i.

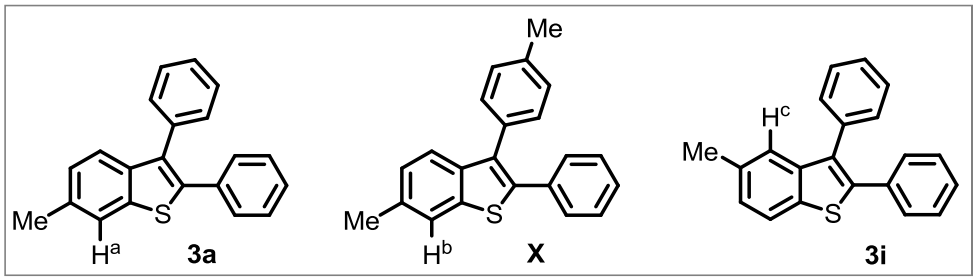


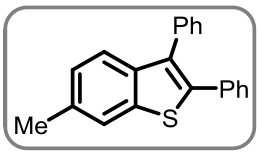
Table 2: The $H^{a/b/c}$ labeled ^{1}H-NMR data for compound 3a, Y, and3i.

S.No	Compound	H^1	ppm	Splitting
1	**3a**	H^a	7.67	singlet
2	**X**	H^b	7.65	singlet
3	**3i**	H^c	7.37-7.44	multiplet

The reaction of N-arylthio succinimide (1) with unactivated alkynes (2); General Procedure (GP–4):

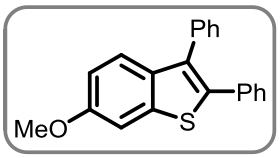
The N-arylthio succinimide (**1**, 0.5 mmol), diphenylacetylene (**2a**, 89 mg, 0.5 mmol) and $K_2S_2O_8$ (68 mg, 0.25 mmol) were taken in a Schlenk tube. Subsequently, $AgSbF_6$ (52 mg, 30 mol %) was introduced in to the flask in a glove box. Solvent 1,2-dichloroethane (2.0 mL) was added to the mixture and the resulting mixture was stirred at 80 ^oC for 6–8 h. Upon completion, the mixture was diluted with CH_2Cl_2 (10 mL) and filterd over a small pad of Celite. Solvent was evaporated under the reduced pressure and the crude residue was purified through slica gel column chromatography using *n*-hexane eluent to give the desired product.

6-Methyl-2,3-diphenylbenzo[*b*]thiophene (3a):



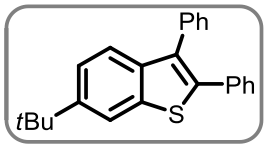
3a colorless solid (96 mg, 64%); mp = 165–167 °C; R_f = 0.46 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.42–7.35 (m, 3H), 7.35–7.28 (m, 4H), 7.25–7.20 (m, 3H), 7.15 (dd, J = 8.4 & 1.2 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ139.1, 138.8, 138.3, 135.7, 134.5, 134.4, 133.0, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 126.1, 123.0, 121.9, 21.5; IR (KBr) ν_{max} 2915, 1589, 1534, 812, 684 cm^{-1}; HRMS (ESI) for $C_{21}H_{16}NaS$ $(M+Na)^+$: calcd. 323.0870, found 323.0876.

6-Methoxy-2,3-diphenylbenzo[*b*]thiophene (3b):



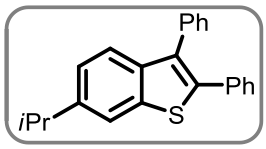
3b Pale yellow solid (79 mg, 50%); mp = 149–150 °C; R_f = 0.16 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.8 Hz, 1H), 7.40–7.28 (m, 8H), 7.23–7.17 (m, 3H), 6.94 (dd, J = 9.0 & 2.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 140.1, 136.8, 135.7, 135.0, 134.4, 132.8, 130.3, 129.4, 128.6, 128.3, 127.4, 127.3, 124.0, 114.4, 104.5, 55.6; IR (KBr) ν_{max} 3019, 1589, 1457, 1276, 1068, 739 cm^{-1}; HRMS (ESI) for $C_{21}H_{16}NaOS$ $(M+Na)^+$: calcd. 339.0820, found 339.0822.

6-*tert*-Butyl-2,3-diphenylbenzo[*b*]thiophene (3c):



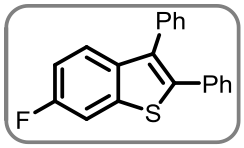
3c colorless solid (131 mg, 76%); mp = 145–146 °C; R_f = 0.5 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.42–7.29 (m, 8H), 7.25–7.20 (m, 3H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 139.0, 138.8, 138.7, 135.7, 134.4, 132.9, 130.4, 129.6, 128.6, 128.3, 127.5, 127.3, 122.8, 122.7, 118.2, 34.9, 31.5; IR (KBr) ν_{max} 2953, 1594, 1441, 1260, 816 cm^{-1}; HRMS (ESI) for $C_{24}H_{22}NaS$ $(M+Na)^+$: calcd. 365.1340, found 365.1340.

6-*iso*-Propyl-2,3-diphenylbenzo[*b*]thiophene (3d):



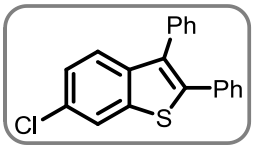
3d colorless solid (118 mg, 72%); mp = 123–124 °C; R_f = 0.4 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 0.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.43–7.35 (m, 3H), 7.34–7.29 (m, 4H), 7.24–7.19 (m, 4H), 3.10–2.98 (m, 1H), 1.32 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 139.1, 138.6, 135.7, 134.4, 133.0, 130.4, 129.6, 128.6, 128.3, 127.5, 127.3, 123.8, 123.1, 119.2, 34.3, 24.2; IR (KBr) ν_{max} 2958, 1594, 1430, 1024, 827 cm^{-1}; HRMS (ESI) for $C_{23}H_{21}S$ $(M+H)^+$: calcd. 329.1364, found 329.1366.

6-Fluoro-2,3-diphenylbenzo[*b*]thiophene (3e):



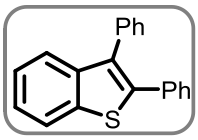
3e colorless solid (92 mg, 60%); mp = 162–163 °C; R_f = 0.44 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.49 (m, 2H), 7.43–7.35 (m, 3H), 7.33–7.27 (m, 4H), 7.26–7.22 (m, 3H), 7.07 (td, J = 9.0 & 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (d, J = 245 Hz), 139.6 (d, J = 10 Hz), 139.0 (d, J = 4 Hz), 137.4, 135.3, 134.0, 132.7, 130.3, 129.5, 128.7, 128.4, 127.8, 127.5, 124.4 (d, J = 9 Hz), 113.3 (d, J = 24 Hz), 108.1 (d, J = 25 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –117.28; IR (KBr) ν_{max} 1589, 1479, 1232, 909, 695 cm^{-1}. HRMS (ESI) for $C_{20}H_{13}FNaS$ $(M+Na)^+$: calcd. 327.0620, found 327.0620.

6-Chloro-2,3-diphenylbenzo[*b*]thiophene (3f):



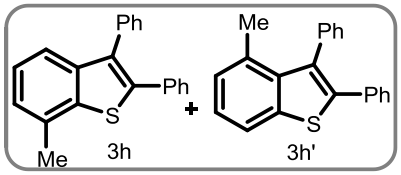
3f colorless crystalline solid (63 mg, 39%); mp = 188–189 °C; R_f = 0.56 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.42–7.36 (m, 3H), 7.33–7.28 (m, 6H), 7.27–7.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.8, 139.4, 135.1, 133.8, 132.9, 130.6, 130.3, 129.5, 128.8, 128.4, 127.9, 127.6, 125.3, 124.2, 121.6; IR (KBr) ν_{max} 1484, 1441, 1101, 789, 690 cm^{-1}; HRMS (ESI) for $C_{20}H_{14}ClS$ $(M+H)^+$: calcd. 321.0505, found 321.0505.

2,3-Diphenylbenzo[*b*]thiophene (3g):



3g colorless crystalline solid (52 mg, 36%); mp = 127–128 °C; R_f = 0.5 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.84 (m, 1H), 7.61–7.56 (m, 1H), 7.41–7.29 (m, 9H), 7.25–7.20 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.5, 138.8, 135.5, 134.2, 133.2, 130.4, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.3, 122.0; IR (KBr) ν_{max} 1435, 1063, 750, 695 cm^{-1}; HRMS (ESI) for $C_{20}H_{15}S$ $(M+H)^+$: calcd. 287.0894, found 287.0887.

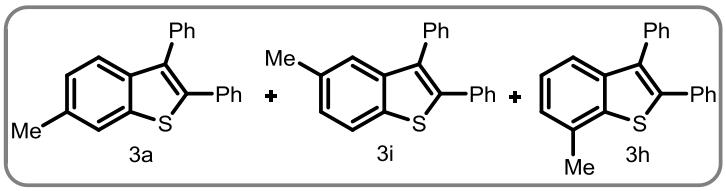
7-Methyl-2,3-diphenylbenzo[*b*]thiophene (3h) and 4-Methyl-2,3-diphenylbenzo[*b*]thiophene (3h'):



Inseparable mixture of **3h**/**3h′** colorless crystalline solid (70:30) (69 mg, 46%); mp = 134–135 °C; R_f = 0.48 (hexane); Peaks for major isomer **3h:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 1H), 7.38–7.29 (m, 6H), 7.26–7.21 (m, 3H), 7.20–7.15 (m, 2H), 7.04 (d, J = 7.2 Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 139.6, 139.2, 138.5, 138.2, 134.4, 131.1, 129.6, 128.6, 128.3, 128.1, 127.9, 127.3, 127.1, 124.1, 120.0, 21.54; Representative peaks for minor isomer **3h':** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 0.4H), 7.38-7.29 (m, 2H), 7.26-7.21 (m, 1H), 7.20-7.15 (m, 0.6H), 2.59 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 135.8, 134.52, 134.47, 134.4, 133.9, 131.6, 130.4, 127.6, 127.4, 127.3, 124.9, 124.8, 121.0, 20.2; IR (KBr) ν_{max} 3051, 1599, 1440, 766, 695 cm^{-1}; MS (EI) *m/z* (%) 301 (M^+ + 1, 100); Anal. Calcd. for $C_{21}H_{16}S$: C, 83.96; H, 5.37; S, 10.67. Found: C, 83.85; H, 5.41; S, 10.56.

Ratio of the both regioisomers **3h:3h'** was determined based on the characteristic Me-H^1 proton integretion. H^1 NMR (400 MHz, $CDCl_3$) H^1 for **3h/3h'**: δ = 1.96 (s, 3H, 70%, major)/2.59 (s, 3H, 30%, minor).

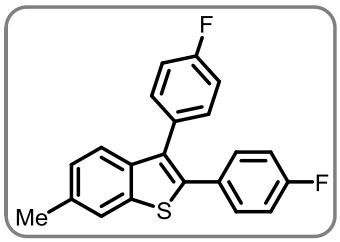
6-Methyl-2,3-diphenylbenzo[*b*]thiophene (3a), 5-Methyl-2,3-diphenylbenzo[*b*]thiophene (3i) and 7-Methyl-2,3-diphenylbenzo[*b*]thiophene (3h):



The reaction between 1-(m-tolylthio)pyrrolidine-2,5-dione **1i** and **2a** under the optimization conditions provided inseparable mixture of **3a, 3i** and **3h** colorless crystalline solid **(50:18:32)** (61 mg, 41%); mp = 132–135 °C; R_f = 0.38 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.0, 4.0 Hz, 1H), 7.64 (bs, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.42–7.28 (m, 16H), 7.26–7.11 (m, 10H), 7.04 (d, J = 7.2 Hz, 1H), [2.46 (s, 3H), 2.39 (s, 1H), 1.96 (s, 2H)]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.7, 139.6, 139.2, 139.1, 138.7, 138.5, 138.3, 138.2, 136.0, 135.7, 134.51, 134.47, 134.45, 134.37, 134.2, 133.0, 132.9, 131.1, 130.44, 130.38, 129.6, 129.55, 129.52, 128.62, 128.59, 128.3, 128.1, 127.9, 127.6, 127.5, 127.4, 127.35, 127.27, 127.1, 126.2, 126.1, 124.1, 123.2, 123.0, 121.9, 121.7, 121.1, 120.0, 21.54 (**3h**), 21.5 (**3a**); IR (KBr) ν_{max} 3052, 1600, 1446, 812, 690 cm^{-1}; HRMS (ESI) for $C_{21}H_{16}NaS$ $(M+Na)^+$: calcd. 323.0870, found 323.0876.

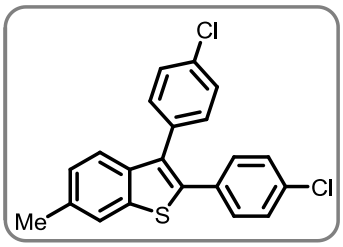
Ratio of the three regioisomers **3a:3i:3h** was determined based on the characteristic Me-H^1 proton integration. H^1 NMR (400 MHz, $CDCl_3$) H^1 for **3a/3i/3h**: δ = 2.46 (s, 3H, 50%, major)/ 2.39 (s, 3H, 18%, minor)/ 1.96 (s, 3H, 32%, minor). The Me peak appeared at 2.46 and 1.96 is matching with the previously observed compound **3a** and **3h,** respectively.

2,3-bis(4-Fluorophenyl)-6-methylbenzo[*b*]thiophene (4a):



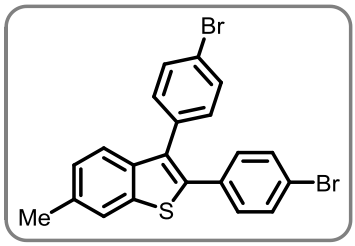
4a colorless crystalline solid (116 mg, 69%); mp = 176–177 °C; R_f = 0.46 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (bs, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.30–7.24 (m, 4H), 7.17 (dd, J = 8.0 & 1.0 Hz, 1H), 7.13–7.08 (m, 2H), 6.98–6.93 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 250 Hz), 162.2 (d, J = 248 Hz), 139.0, 138.5, 137.4, 134.8, 132.0 (d, J = 8 Hz), 131.3 (d, J = 3 Hz), 131.2 (d, J = 8 Hz), 130.3 (d, J = 3 Hz), 126.3, 122.8, 121.9, 115.8 (d, J = 22 Hz), 115.5 (d, J = 23 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.79, –114.43; IR (KBr) ν_{max} 2909, 1604, 1500, 1226, 1018, 837 cm^{-1} ; HRMS (ESI) for $C_{21}H_{14}F_2NaS$ $(M+Na)^+$: calcd. 359.0682, found 359.0679.

2,3-bis(4-Chlorophenyl)-6-methylbenzo[*b*]thiophene (4b):



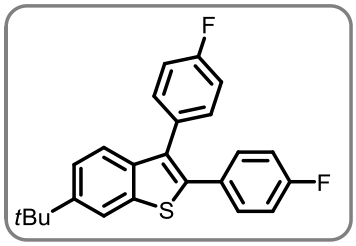
4b colorless crystalline solid (138 mg, 75%); mp = 228–229 °C; R_f = 0.56 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.40–7.37 (m, 2H), 7.26–7.20 (m, 6H), 7.17 (dd, J = 8.5 & 1.0 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.3, 137.3, 135.0, 133.8, 133.5, 132.6, 132.1, 131.6, 130.7, 129.1, 128.7, 126.5, 122.8, 122.0, 21.5; IR (KBr) ν_{max} 2920, 1533, 1495, 1084, 1013, 804 cm^{-1}; HRMS (ESI) for $C_{21}H_{15}Cl_2S$ $(M+H)^+$: calcd. 369.0272, found 369.0269.

2,3-bis(4-Bromophenyl)-6-methylbenzo[*b*]thiophene (4c):



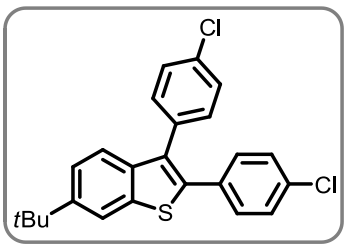
4c colorless crystalline solid (170 mg, 74%); mp = 235–236 °C; R_f = 0.53 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.20–7.13 (m, 5H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.2, 137.3, 135.1, 134.3, 133.0, 132.1, 132.0, 131.9, 131.7, 131.0, 126.5, 122.8, 122.03, 122.00, 121.7, 21.5; IR (KBr) ν_{max} 2920, 1522, 1462, 1232, 1007, 826 cm^{-1}; HRMS (ESI) for $C_{21}H_{14}Br_2SNa$ $(M+Na)^+$: calcd. 478.9081, found 478.9079.

6-*tert*-Butyl-2,3-bis(4-fluorophenyl)benzo[*b*]thiophene (4d):



4d colorless crystalline solid (157 mg, 83%); mp = 168−169 °C; R_f = 0.51 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (bd, J = 1.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.43 (dd, J = 8.5 & 2.0 Hz, 1H), 7.31–7.24 (m, 4H), 7.13–7.08 (m, 2H), 6.99–6.94 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 250 Hz), 162.2 (d, J = 248 Hz), 148.3, 138.9, 138.4, 137.9, 132.0 (d, J = 8 Hz), 131.3 (d, J = 4 Hz), 131.2 (d, J = 8 Hz), 130.3 (d, J = 3 Hz), 122.9, 122.6, 118.2, 115.8 (d, J = 22 Hz), 115.5 (d, J = 22 Hz), 35.0, 31.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.77, −114.45; IR (KBr) ν_{max} 2958, 1605, 1512, 1221, 816 cm^{-1}; HRMS (ESI) for $C_{24}H_{21}F_2S$ $(M+H)^+$: calcd. 379.1332, found 379.1329.

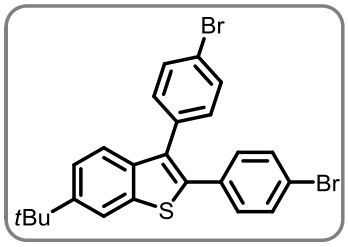
6-*tert*-Butyl-2,3-bis(4-chlorophenyl)benzo[*b*]thiophene (4e):



4e colorless crystalline solid (161 mg, 78%); mp = 233–234 °C; R_f = 0.6 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (bs, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.43 (dd, J = 8.5 & 1.5 Hz, 1H), 7.40–7.37 (m, 2H), 7.26–7.21 (m, 6H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 139.0, 138.1, 137.8, 133.8, 133.5, 132.6, 132.0, 131.6,

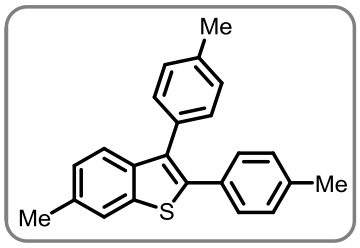
130.7, 129.0, 128.7, 123.0, 122.6, 118.3, 35.0, 31.5; IR (KBr) ν_{max} 2958, 1489, 1259, 1095, 897 cm^{-1}; HRMS (ESI) for $C_{24}H_{20}C_{l2}NaS$ $(M+Na)^+$: calcd. 433.0560, found 433.0553.

6-*tert*-Butyl-2,3-bis(4-bromophenyl)benzo[*b*]thiophene (4f):



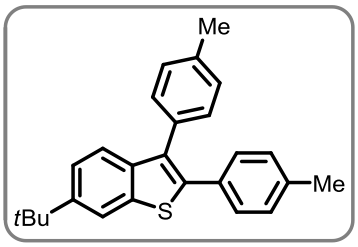
4f colorless crystalline solid (198 mg, 79%); mp = 233–234 °C; R_f = 0.58 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.45–7.36 (m, 3H), 7.22–7.12 (m, 4H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 139.0, 138.1, 137.8, 134.3, 133.8, 133.1, 132.0, 131.9, 131.7, 131.0, 123.1, 122.6, 122.0, 121.7, 118.3, 35.0, 31.5; IR (KBr) ν_{max} 2958, 1467, 1385, 1002, 793 cm^{-1}; HRMS (ESI) for $C_{24}H_{21}Br_2S$ $(M+H)^+$: calcd. 498.9731, found 498.9736.

6-Methyl-2,3-di-*p*-tolylbenzo[*b*]thiophene (4g):



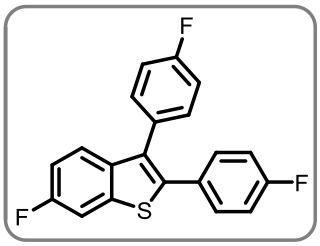
4g colorless crystalline solid (80 mg, 48%); mp = 148–150 °C; R_f = 0.34 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 0.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.25–7.20 (m, 6H), 7.15 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.96, 138.2, 137.3, 136.8, 134.3, 132.8, 132.6, 131.6, 130.2, 129.35, 129.33, 129.0, 126.0, 122.9, 121.8, 21.5, 21.3, 21.2; IR (KBr) ν_{max} 2914, 1561, 1445, 1226, 815 cm^{-1}; MS (EI) *m/z* (%) 329 (M^+ + 1, 100); Anal. Calcd. for $C_{23}H_{20}S$: C, 84.10; H, 6.14; S, 9.76. Found: C, 84.17; H, 6.18; S, 9.69.

6-*tert*-Butyl-2,3-di-*p*-tolylbenzo[*b*]thiophene (4h):



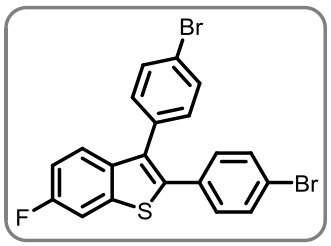
4h colorless crystalline solid (97 mg, 52%); mp = 160–162 °C; R_f = 0.36 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 1.6 Hz, 1H), 7.55 (d, J = 8.4 Hz 1H), 7.41 (dd, J = 8.8 & 1.8 Hz, 1H), 7.25–7.20 (m, 6H), 7.08 (d, J = 7.6 Hz, 2H), 2.43 (s, 3H), 2.34 (s, 3H) 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 138.84, 138.82, 138.6, 137.3, 136.8, 132.8, 132.4, 131.7, 130.2, 129.4, 129.3, 129.0, 122.8, 122.5, 118.1, 34.9, 31.5, 21.3, 21.2; IR (KBr) ν_{max} 2964, 2915, 1517, 1463, 1254, 816 cm^{-1}; HRMS (ESI) for $C_{26}H_{27}S$ $(M+H)^+$: calcd. 371.1833, found 371.1835.

6-Fluoro-2,3-bis(4-fluorophenyl)benzo[*b*]thiophene (4i):



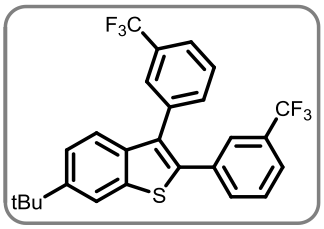
4i colorless crystalline solid (106 mg, 62%); mp = 138–140 °C ; R_f = 0.46 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.5 & 2.5 Hz, 1H), 7.48 (dd, J = 9.0 & 5.0Hz 1H), 7.29–7.22 (m, 4H), 7.14–7.08 (m, 3H), 6.99–6.94 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, J = 250 Hz), 162.3(d, J = 248 Hz), 160.7 (d, J = 247 Hz), 139.5 (d, J = 10 Hz), 138.1 (d, J = 4 Hz), 137.1, 131.9 (d, J = 8 Hz), 131.7, 131.2 (d, J = 8 Hz), 130.9 (d, J = 4 Hz), 129.8 (d, J = 3 Hz), 124.2 (d, J = 9 Hz), 115.9 (d, J = 22 Hz), 115.6 (d, J = 23 Hz), 113.6 (d, J = 24 Hz), 108.2 (d, J = 25 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –113.26, –113.89, –116.84; IR (KBr) ν_{max} 1600, 1506, 1221, 1156, 838 cm^{-1}; HRMS (ESI) for $C_{20}H_{11}F_3NaS$ $(M+Na)^+$: calcd. 363.0431, found 363.0432.

6-Fluoro-2,3-bis(4-bromophenyl)benzo[*b*]thiophene) (4j):



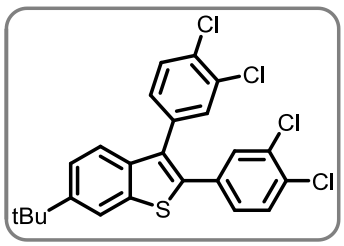
4j light yellow solid (149 mg, 64%); mp = 176–177 °C ; R_f = 0.53 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.53 (m, 3H), 7.49 (dd, J = 9.0 & 5.0Hz 1H), 7.42–7.39 (m, 2H), 7.19–7.13 (m, 4H), 7.10 (td, J = 8.9 & 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8 (d, J = 245 Hz), 139.7 (d, J = 10 Hz), 138.1 (d, J = 4 Hz), 136.9, 133.8, 132.6, 132.2, 131.9, 131.8, 130.9, 124.3 (d, J =9 Hz), 122.3, 122.0, 113.7 (d, J = 24 Hz), 108.3 (d, J = 25 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ –116.26; IR (KBr) ν_{max} 1534, 1457, 1249, 1068, 1002, 805 cm^{-1}; HRMS (ESI) for $C_{20}H_{12}Br_2FS$ $(M+H)^+$: calcd. 460.9010, found. 460.9010.

6-*tert*-Butyl-2,3-bis(3-(trifluoromethyl)phenyl)benzo[*b*]thiophene (4k):



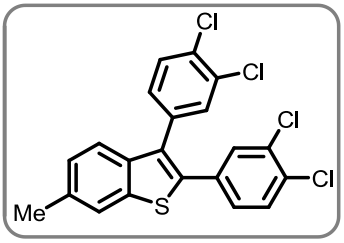
4k colorless crystalline solid (120 mg, 50%); mp = 141–142 °C ; R_f = 0.55 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.73–7.68 (m, 2H), 7.62–7.49 (m, 7H), 7.41 (t, J = 7.75 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 139.2, 137.9, 137.8, 136.0, 134.7, 133.6, 132.7, 132.4, 131.3 (q, J = 32 Hz), 131.0 (q, J = 32 Hz), 129.4, 129.0, 127.1 (q, J = 3.0 Hz), 126.3 (q, J = 3.0 Hz), 125.2 (d, J = 22 Hz), 124.47 (q, J = 4.0 Hz), 123.4, 122.6, 118.4, 35.0, 31.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.78, –63.06; IR (KBr) ν_{max} 2969, 1605, 1358, 1326, 1117, 673 cm^{-1} ; HRMS (ESI) for $C_{26}H_{20}F_6NaS$ $(M+Na)^+$: calcd. 501.1088, found 501.1087.

6-*tert*-Butyl-2,3-bis(3,4-dichlorophenyl)benzo[*b*]thiophene (4l):



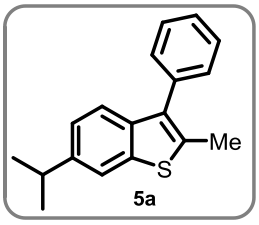
4l pale yellow solid (178 mg, 74%); mp = 144–145 °C ; R_f = 0.63 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (bs, 1H), 7.51–7.44 (m, 5H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.4 & 2.0 Hz, 1H), 7.04 (dd, *J* = 8.4 & 2.0 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 139.1, 137.7, 136.9, 135.0, 133.8, 133.0, 132.8, 132.2, 132.0, 131.8, 131.4, 131.1, 130.9, 130.5, 129.7, 128.6, 123.4, 122.6, 118.4, 35.1, 31.4; IR (KBr) ν_{max} 2964, 1583, 1463, 1134, 1030, 810 cm^{-1}; HRMS (ESI) for $C_{24}H_{19}Cl_4S$ $(M+H)^+$: calcd. 478.9962, found 478.9961.

6-Methyl-2,3-bis(3,4-dichlorophenyl)benzo[*b*]thiophene (4m):



4m colorless crystalline solid (83 mg, 38%); mp = 147–148 °C ; R_f = 0.56 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.47–7.45 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 8.4 & 0.8 Hz, 1H), 7.10 (dd, *J* = 8.0 & 2.0 Hz, 1H), 7.03 (dd, *J* = 8.4 & 2.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 137.8, 136.4, 135.6, 135.0, 133.8, 133.0, 132.8, 132.2, 132.0, 131.9, 131.4, 131.1, 130.9, 130.5, 129.7, 128.6, 126.8, 122.7, 122.1, 21.5; IR (KBr) ν_{max} 2915, 1457, 1123, 1035, 816 cm^{-1}; HRMS (ESI) for $C_{21}H_{13}Cl_4S$ $(M+H)^+$: calcd. 436.9492, found 436.9499.

6-*iso*-Propyl-2-methyl-3-phenylbenzo[*b*]thiophene (5a):

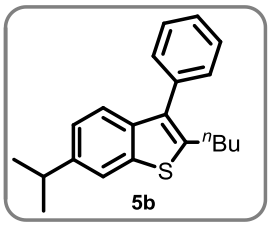


The reaction between 1-(4-*iso*-propylphenylthio)pyrrolidine-2,5-dione (**1d**) and 1-phenyl-1-propyene under the optimized conditions provided **5a** along with an unidentified product. The compounds **5a** and unidentified product are inseparable, forming 4:1 ratio.

5a pale yellow viscous liquid (64 mg, 48%); R_f = 0.52 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.73 (s, 1H), 7.59–7.50 (m, 3H), 7.49–7.45 (m, 3H), 7.25–7.21 (m, 1H), 3.15–3.03 (m, 1H), 2.55 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ144.8, 138.53, 138.46, 135.5, 135.0, 133.5, 130.0, 128.4, 127.1, 123.4, 122.2, 119.2, 34.1, 24.2, 14.4; Representative peaks for the inseparable unidentified product: ^{1}H NMR (400 MHz, $CDCl_3$) δ2.99–2.89 (m, 0.3H), 1.30 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ148.2, 134.3, 128.2, 127.2, 122.7, 121.7, 119.9, 33.7, 23.9; IR (KBr) IR (Neat) ν_{max} 3052, 2958, 2915, 2865, 1600, 1479, 816 cm^{-1}; HRMS (ESI) for $C_{18}H_{19}S$ $(M+H)^+$: calcd. 267.1207, found 267.1209.

The ratio of **5a**:unidentified product (UP) was determined based on the characteristic H^1 proton integretion; δ = 3.15–3.03 (m, 1H, 78%, for **5a**)/ 2.99–2.89 (m, 1H, 22%, minor).

2-Butyl-6-isopropyl-3-phenylbenzo[*b*]thiophene (5b):



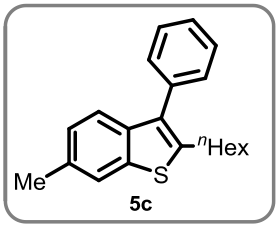
5b

The reaction between 1-(4-*iso*-Propylphenylthio)pyrrolidine-2,5-dione (**1d**) and 1-phenyl-1-hexyne under the optimized conditions provided **5a** along with an unidentified product. The compounds **5a** and unidentified product are inseparable, forming 6:1 ratio.

5b colorless viscous liquid (80 mg, 52%); R_f = 0.64 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 0.8 Hz, 1H), 7.62–7.54 (m, 2H), 7.54–7.47 (m, 4H), 7.31–7.27 (m, 1H), 3.12–3.06 (m, 1H), 2.96 (t, J = 7.6 Hz, 2H), 1.83–1.74 (m, 2H), 1.43 (d, J = 6.8 Hz, 6H), 1.38–1.32 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ144.8, 141.5, 138.6, 138.4, 135.8, 133.2, 130.0, 128.4, 127.1, 123.3, 121.9, 119.3, 34.2, 33.9, 28.5, 24.2, 22.2, 13.8; Representative peaks for the inseparable unidentified product: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.37–7.32 (m, 0.26H), 7.27–7.25 (m, 0.24H), 1.47 (d, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 134.3, 128.2, 126.1, 122.3, 33.7, 23.9; IR (KBr) ν_{max} 3057, 2953, 2865, 1600, 1479, 816, 701 cm^{-1}; ; HRMS (ESI) for $C_{21}H_{25}S$ $(M+H)^+$: calcd. 309.1677, found 309.1673.

The ratio of **5b**:unidentified product (UP) was determined based on the characteristic H^1 proton integretion; δ = 1.43 (d, 6H, 85%, for **5b**)/ 1.47 (d, 6H, 15%, minor).

2-Hexyl-6-methyl-3-phenylbenzo[*b*]thiophene (5c):



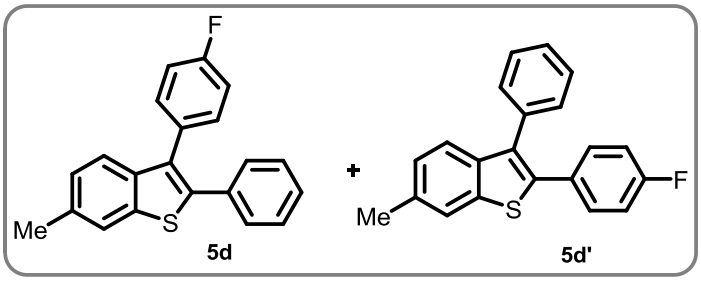
5c

The reaction between 1-(4-*iso*-Propylphenylthio)pyrrolidine-2,5-dione (**1d**) and 1-phenyl-1-octyne under the optimized conditions provided **5a** along with an unidentified product. The compounds **5a** and unidentified product are inseparable, forming 7:1 ratio.

5c as colorless viscous thick liquid (48 mg, 30%); R_f = 0.64 (hexane); Representative peaks for major isomer **5c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ7.63 (bs, 1H), 7.53–7.47 (m, 2H), 7.45–7.36 (m, 4H), 7.15–7.10 (m, 1H), 2.85 (t, J = 7.8 Hz, 2H), 2.48 (s, 3H), 1.74–1.65 (m, 2H), 1.36–1.22 (m, 6H), 0.88 (t, J = 7.0 Hz 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ141.3, 138.4, 138.3, 135.8, 133.6, 133.2, 130.0, 128.4, 127.1, 125.7, 122.1, 121.9, 31.7, 31.5, 28.8, 28.7, 22.5, 21.4, 14.0; Representative peaks for the inseparable unidentified product: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.75–7.70 (m, 0.14H), 2.34 (s, 0.42H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.4, 133.9, 130.2, 130.1, 129.8, 128.5, 21.0; IR (Neat) ν_{max} 2953, 2849, 1468, 810, 706 cm^{-1}; HRMS (ESI) for $C_{21}H_{25}S$ $(M+H)^+$: calcd. 309.1677, found 309.1679.

The ratio of **5c**:unidentified product (UP) was determined based on the characteristic H^1 proton integretion; δ = 2.48 (s, 3H, 88%, for **5c**)/ 2.34 (s, 3H, 12%, minor).

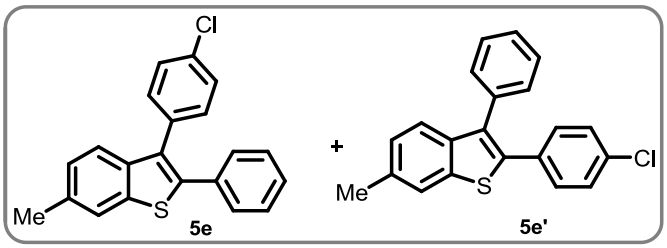
3-(4-Fluorophenyl)-6-methyl-2-phenylbenzo[*b*]thiophene (5d) and **2-(4-Fluorophenyl)-6-methyl-3-phenylbenzo[*b*]thiophene (5d′):**



Inseparable mixture of **5d** and **5d′** colorless crystalline solid (1:1, 89 mg, 56%); mp = 150–151 °C; R_f = 0.46 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.49–7.33 (m, 2H), 7.31–7.21 (m, 6H), 7.18–7.04 (m, 2H), 6.96–6.88 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 250 Hz), 162.1 (d, J = 248 Hz), 139.1, 139.0, 138.6, 137.1, 135.5, 134.6, 134.2, 133.1, 132.0 (d, J = 8 Hz), 131.9, 131.6, 131.2 (d, J = 8 Hz),130.3, 129.5, 128.7, 128.4, 127.6, 127.4, 126.2, 123.0, 122.7, 122.0, 121.9, 115.6 (d, J = 22 Hz), 115.3 (d, J = 22 Hz), 21.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ –114.08, –114.70 (1:1); IR (KBr) ν_{max} 2914, 1599, 1501, 1227, 816, 690 cm^{-1}; HRMS (ESI) for $C_{21}H_{15}FNaS$ $(M+Na)^+$: calcd. 341.0776, found 341.0776.

Both the regioisomeric products **5d** and **5d′** are indistinguishable by 1H NMR, however, the 13C NMR studies clearly reveals the formation of both regioisomers **5d** and **5d′** as inseparable mixture.

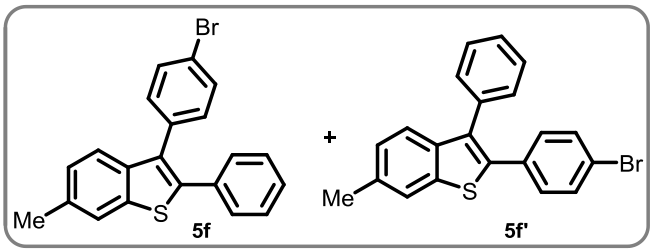
3-(4-Chlorophenyl)-6-methyl-2-phenylbenzo[*b*]thiophene (5e) and **2-(4-Chlorophenyl)-6-methyl-3-phenylbenzo[*b*]thiophene (5e′):**



Inseparable mixture of **5e** and **5e′** colorless crystalline solid (1:1, 97 mg, 58%); mp = 193–195 °C; R_f = 0.5 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65, (s, 1H), 7.45 (d, J = 8.4 Hz 1H), 7.42–7.33 (m, 3H), 7.31–7.22 (m, 4H), 7.19 (bd, J = 4.0 Hz, 2H), 7.17–7.12 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 139.0, 138.8, 138.7, 138.4, 136.8, 135.4, 134.8, 134.7, 134.2, 134.1, 133.53, 133.50, 133.3, 132.9, 131.7, 131.6, 130.7, 130.3, 129.6, 128.9, 128.7, 128.5, 128.4, 127.7, 127.5, 126.3, 123.1, 122.7, 122.0, 121.9, 21.51, 21.50; IR (KBr) ν_{max} 2914, 1594, 1484, 1441, 1227, 1084, 810 cm^{-1}; HRMS (ESI) for $C_{21}H_{15}ClNaS$ $(M+Na)^+$: calcd. 357.0481, found 357.0481.

Both the regioisomeric products **5e** and **5e′** are indistinguishable by 1H NMR, however, the 13C NMR studies clearly reveals the formation of both regioisomers **5e** and **5e′** as inseparable mixture.

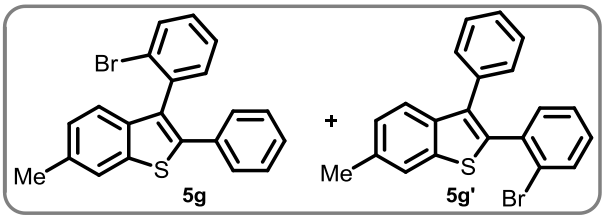
3-(4-Bromophenyl)-6-methyl-2-phenylbenzo[*b*]thiophene (5f) and **2-(4-Bromophenyl)-6-methyl-3-phenylbenzo[*b*]thiophene (5f′):**



Inseparable mixture of **5f** and **5f′** colorless crystalline solid (1:1; 112 mg, 59%); mp = 202–205 °C ; R_f = 0.48 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.53–7.50 (m, 1H), 7.46 (d, J = 8.8 Hz 1H), 7.43–7.34 (m, 3H), 7.32–7.26 (m, 3H), 7.22–7.14 (m, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ139.1, 139.0, 138.8, 138.6, 138.3, 136.8, 135.3, 134.9, 134.7, 134.6, 134.0, 133.5, 133.4, 133.0, 132.1, 131.8, 131.6, 131.5, 131.0, 130.3, 129.8, 129.6, 128.8, 128.5, 127.8, 127.5, 126.3, 123.1, 122.6, 122.0, 121.9, 121.7, 121.4, 21.53, 21.51; IR (KBr) ν_{max} 2909, 1594, 1441, 1238, 1002, 816, 690 cm^{-1}; MS (EI) *m/z* (%) 377 (M^+ – 1, 100); Anal. Calcd. for $C_{21}H_{15}BrS$: C, 66.50; H, 3.99; S, 8.45 Found: C, 66.42; H, 3.91; S, 8.38.

Both the regioisomeric products **5f** and **5f′** are indistinguishable by 1H NMR, however, the 13C NMR studies clearly reveals the formation of both regioisomers **5f** and **5f′** as inseparable mixture.

3-(2-Bromophenyl)-6-methyl-2-phenylbenzo[*b*]thiophene (5g) and **2-(2-Bromophenyl)-6-methyl-3-phenylbenzo[*b*]thiophene (5g′):**



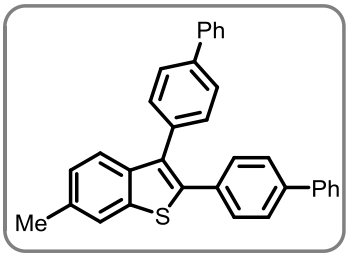
Inseparable mixture of **5g** and **5g′** pale yellow solid (5:1; 119 mg, 63%); mp = 93–94 °C; R_f = 0.4 (hexane); Representative peaks for major isomer **5g:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.69 (m, 2H), 7.39–7.32 (m, 4H), 7.28–7.25 (m, 4H), 7.23–7.18 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ139.4, 138.6, 138.3, 137.1, 134.6, 134.2, 133.0, 132.5, 129.9, 129.3, 128.8, 128.4, 127.7, 127.6, 126.1, 125.0, 122.9, 121.9, 21.56; Representative peaks for minor isomer **5g′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.66 (d, J = 8.4 Hz, 0.19H), 7.59 (dd, J = 8.0 & 1.2 Hz, 0.2H), 7.31–7.28 (m, 1H), 7.18–7.14 (m, 0.38H), 2.53 (s, 0.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 136.8, 135.4, 135.0, 134.8, 133.2, 132.8, 132.0, 129.7, 128.2, 127.1, 126.9, 123.1, 122.0, 21.52; IR (KBr) ν_{max} 2920, 1599, 1430, 1030, 810, 684 cm^{-1}; HRMS (ESI) for $C_{21}H_{19}BrNS$ $(M+NH_4)^+$: calcd. 396.0422, found 396.0422.

The ratio of **5g : 5g'** was determined based on the characteristic H^1 proton integretion; δ = 2.52 (s, 3H, 84%, major)/ 2.53 (s, 3H, 16%, minor).

General procedure for the Suzuki reaction of 4c; Synthesis of 6 (GP 5):[5]

A mixture of compound **4c** (100 mg, 0.218 mmol), phenyl boronic acid (80 mg, 0.655 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013mmol) and Na_2CO_3 (69 mg, 0.654 mmol) in toluene and H_2O (1:1, 3.0 mL) was heated at 80 ^oC for 12h. The reaction mixture was extracted with ethylacetate (3 × 15 mL), dried over Na_2SO_4 and concentrated under vacuum to give a light yellow solid. The crude material was purified by silica gel column chromatograpy eluting with hexane to give compound **6** as colorless crystalline solid.

2,3-di(Biphenyl-4-yl)-6-methylbenzo[*b*]thiophene (6):

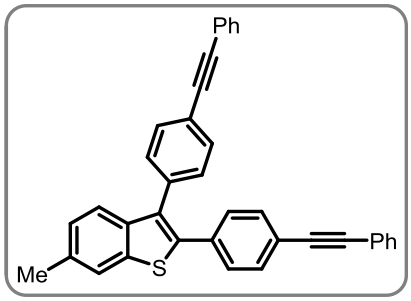


6 colorless crystalline solid (73 mg, 74%); mp = 218–219 °C; R_f = 0.24 (hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.73–7.68 (m, 5H), 7.62–7.57 (m, 3H), 7.54–7.33 (m, 12H), 7.21 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 140.3, 140.2, 140.0, 139.1, 138.8, 138.0, 134.8, 134.6, 133.4, 132.7, 130.8, 129.9, 128.81, 128.76, 127.40, 127.36, 127.3, 127.0, 126.9, 126.2, 123.0, 121.9, 21.5; IR (Neat) ν_{max} 2920, 1643, 1523, 1008, 756, 690 cm^{-1}; HRMS (ESI) for $C_{33}H_{25}S$ $(M+H)^+$: calcd. 453.1677, found 453.1677.

General procedure for the Sonogashira reaction of 4c; Synthesis of 7 (GP 6):[3]

Phenylacetylene (52 µL, 0.479 mmol) was added to a stirred suspension of compound **4c** (100 mg, 0.218 mmol), $PdCl_2(PPh_3)_2$ (15 mg, 0.0218 mmol), CuI (4.0 mg, 0.0218 mmol) and PPh_3 (6.0 mg, 0.0218 mmol) in Et_3N (4 mL) under nitrogen atmosphere. The reaction mixture was heated at 100 ^oC for 48 h. After cooling to room temperature, the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (3 × 15 mL), dried over Na_2SO_4 and concentrated under vacuum to give a light yellow solid. The crude material was purified by silica gel column chromatograpy eluting with hexane/EtOAc (95:5) to give componnd **7** as a pale yellow crystalline solid.

6-Methyl-2,3-bis(4-(phenylethynyl)phenyl)benzo[*b*]thiophene (**7**)**:**

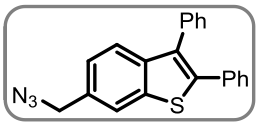


7 yellow solid (66 mg, 60%); mp = 213–215 °C; R_f = 0.2 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.62–7.55 (m, 4H), 7.54–7.48 (m, 3H), 7.44–7.40 (m, 2H), 7.38–7.27 (m, 10H), 7.19 (dd, J = 8.2 & 1.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.3, 138.0, 135.6, 135.0, 134.1, 132.8, 132.0, 131.63, 131.61, 130.4, 129.4, 128.4, 128.3, 126.4, 123.2, 123.1, 122.9, 122.5, 122.4, 122.0, 90.5, 90.1, 89.2, 89.1, 21.5; IR (Neat) ν_{max} 2920, 1594, 1435, 838, 750, 684 cm^{-1}; HRMS (ESI) for $C_{37}H_{25}S$ $(M+H)^+$: calcd. 501.1677, found 501.1677.

General procedure for the benzylic azidation of 3a; Synthesis of 8 (GP 7):[6a, 6b]

A mixture of N-bromosuccinimide (65 mg, 0.36 mmol), AIBN (3 mg, 0.01 mmol), and 6-methyl-2,3-diphenylbenzo[*b*]thiophene **3a** (100 mg, 0.33 mmol) in dry CCL_4 (2.0 mL) were placed in a sealed tube and stirred at room temperature for 18 h. Upon complete consumption of **3a**, the solvent was evaporated and the crude material was subjected to azidation. Accordingly, sodium azide (32 mg, 0.5 mmol) and water-acetone mixture (1:4, 2 mL) was added to the crude material and the resulting mixture was stirred overnight. The solvent was evaporated and the crude mixture was purified by neutral alumina column chromatograpy eluting with hexane/EtOAc (97:3) mixture to provide compound **8** as colorless crystalline solid.

6-(Azidomethyl)-2,3-diphenylbenzo[*b*]thiophene (8):

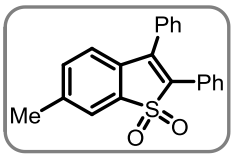


8 colorless crystalline solid (102 mg, 90%); mp = 126–127 °C; R_f = 0.12 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.60 (bd, J = 8.0 Hz, 1H), 7.45–7.22 (m, 11H), 4.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.4, 139.1, 135.2, 134.0, 133.0, 131.8, 130.4, 129.6, 128.7, 128.4, 127.8, 127.5, 124.8, 123.7, 121.8, 54.9; IR (Neat) ν_{max} 3057, 2098, 1441, 1238, 690 cm^{-1}; MS (EI) *m/z* (%) 342 (M^+ + 1, 100); Anal. Calcd. for $C_{21}H_{15}N_3S$: C, 73.87; H, 4.43; N, 12.31; S, 9.39. Found: C, 73.96; H, 4.38; N, 12.25; S, 9.25.

General procedure for the oxidation of benzo[*b*]thiophenes (GP 8):[7]

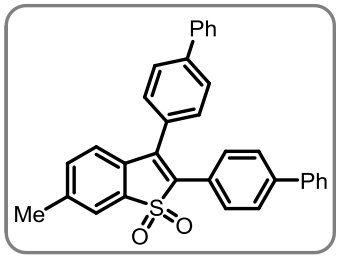
To a solution of **3** (1.0 mmol) in dry CH_2Cl_2 (10 mL) was added *m*-CPBA (1.2 mmol) under an argon atmosphere. The resulting mixture was stirred at room temperature overnight. Upon completion, solvent was evaporated and the crude material was purified by flash column chromatography eluting with hexane/EtOAc 95:5 to give the desired sulfones.

6-Methyl-2,3-diphenylbenzo[*b*]thiophene-1,1-dioxide (10):



10 colorless crystalline solid (503 mg, 91%); mp = 166–168 °C; R_f = 0.44 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.36–7.26 (m, 7H), 7.20–7.15 (m, 3H), 7.10 (d, J = 8.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.7, 138.3, 135.7, 134.5, 134.3, 133.0, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 126.1, 122.9, 121.9, 21.5; IR (Neat) ν_{max} 2350, 1600, 1446, 1238, 1024, 810, 690 cm^{-1}; HRMS (ESI) for $C_{21}H_{16}NaO_2S$ $(M+Na)^+$: calcd. 355.0769, found 355.0770.

2,3-di(Biphenyl-4-yl)-6-methylbenzo[*b*]thiophene-1,1-dioxide (11):



11 yellow color solid (92 mg, 86%); mp = 270–271 °C; R_f = 0.50 (40:10 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.69 (m, 3H), 7.67–7.64 (m, 2H), 7.61–7.53 (m, 6H), 7.50–7.43 (m, 5H), 7.43–7.39 (m, 2H), 7.38–7.33 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 142.1, 141.0, 140.1, 139.9, 137.7, 136.5, 136.2, 134.0, 130.6, 130.0, 129.6, 129.5, 128.9, 128.8, 127.9, 127.8, 127.7, 127.4, 127.0, 126.1, 124.0, 122.2, 21.5; IR (Neat) ν_{max} 2920, 1736, 1484, 1298, 1150, 860, 591cm^{-1}; HRMS (ESI) for $C_{33}H_{24}NaO_2S$ $(M+Na)^+$: calcd. 507.1395, found 507.1388.

References

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2. Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett*. **2002**, *4*, 3199.

3. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

4. Shimada, H.; Kikuchi, S.; Okuda, S.; Haraguchi, K.; Tanaka, H. *Tetrahedron*. **2009**, *65*, 6008.

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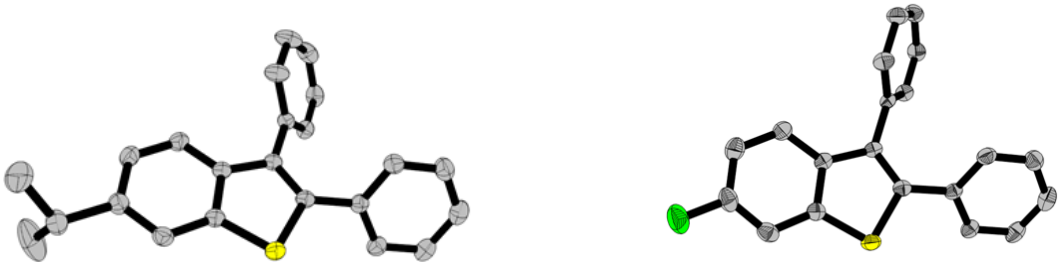
6. (a) Mataka, S.; Liu, G-B.; Sawada, T.; Kurisu, M.; Tashiro, M. *Bulletin of the chemicalsociety of jappan*. **1994**, *67*, 1113. (b) Alvarer, S. G.; Alvarez, M. T. *Synthesis*. **1977**, 413.

7. Furukawa, N.; Hoshiai, H.; Shibutani, T.; Higaki, M.; Iwasaki, F.; Fujihara, H. *Heterocycles*. **1992**, *34*, 1085.

X-ray crystallography: Single crystal X-ray data for the compound **3d** and **3e** were collected using the detector system [λ(Mo-Kα) = 0.71073 Å] at 293K, graphite monochromator with a ω scan width of 0.3°, crystal-detector distance 60 mm, collimator 0.5 mm. The SMART software[1] was used for the intensity data acquisition and the SAINTPLUS Software[1] was used for the data extraction. In each case, absorption correction was performed with the help of SADABS program,[1] an empirical absorption correction using equivalent reflections was performed with the program. The structure was solved using SHELXS-97,[2] and full-matrix least-squares refinement against F^2 was carried out using SHELXL-97.[2] All non-hydrogen atoms were refined anisotropically. Aromatic and methyl hydrogens were introduced on calculated positions and included in the refinement riding on their respective parent atoms.

X-ray crystal structure and data for 3d and 3e:



3d **3e**

Figure 1. Thermal ellipsoidal plot of compound **3d** and **3e** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability level except for the H atoms, which are shown as circles of arbitrary radius**.**

Table 1. Crystal data for 3d and 3e

Compound		
Identification code	**3d**	**3e**
Formula	$C_{23}H_{20}S$	$C_{20}H_{13}FS$
F_w	328.45	304.36
T (K)	296	296
λ (Å)	0.71073	0.71073

Crystal system	triclinic	monoclinic
Space group	P -1	P 21/c
a (Å)	9.756(4)	6.0606(6)
b (Å)	10.716(5)	13.4845(14)
c (Å)	10.881(4)	18.390(2)
α (°)	65.921	90
β (°)	68.070	91.360
γ (°)	63.361	90
V (Å^3)	902.7(7)	1502.5(3)
Z	2	4
ρ_{calcd} (Mg m^{-3})	1.208	1.345
μ (mm^{-1})	0.179	0.219
F (000)	348.0	632
Reflections collected	3777	3446
Unique reflections	2835	1829
Completeness to 2θ (%)	98.7(100.0)	94.0(100)
T_{max}, T_{min}	0.977,0.986	0.974,0.983
GOF (F^2)	1.076	1.012
R1[I>2σ(I)]	0.0453	0.0626
wR2 (all data)	0.1232	0.1349
Diffractometer	Xcalibur Gemini Eos CCD	Xcalibur Gemini Eos CCD
CCDC Number	1479463	1479468

References:

1. Bruker SMART V5.630 and SAINT-PLUS V6.45, Bruker-Nonius Analytical X-ray Systems Inc.: Madison, Wisconsin, USA 2003. SADABS, Empirical absorption correction program, Bruker AXS Inc., Madison, Wisconsin, USA 1997.

2. Sheldrick G M, *Acta Crystallogr* 64A (2008) 112.

tBu
1c
S
N
O
O
7.603
7.601
7.582
7.345
7.324
7.260
2.773
1.268
2.00
2.05
4.07
9.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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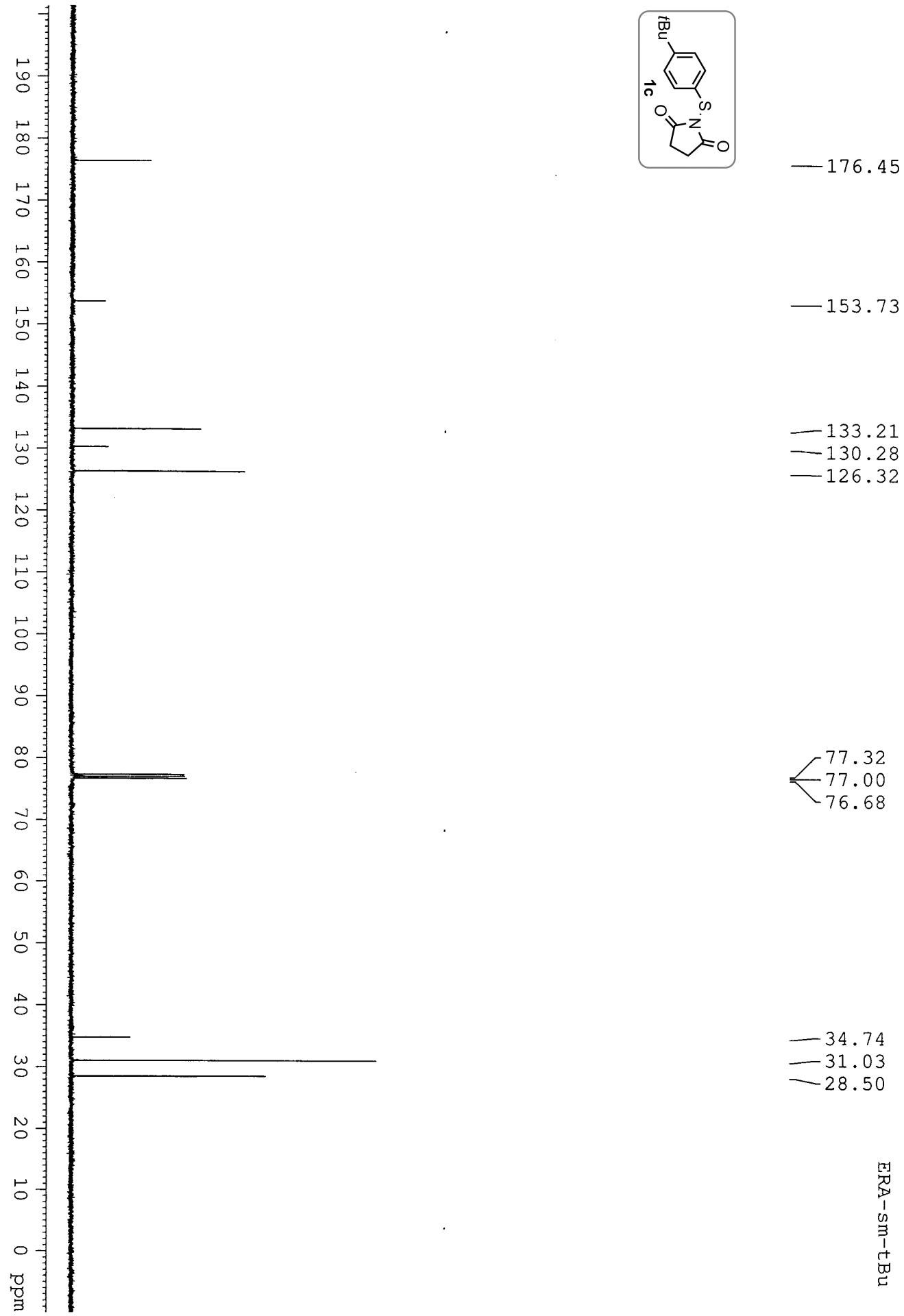
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O
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153.73
133.21
130.28
126.32
77.32
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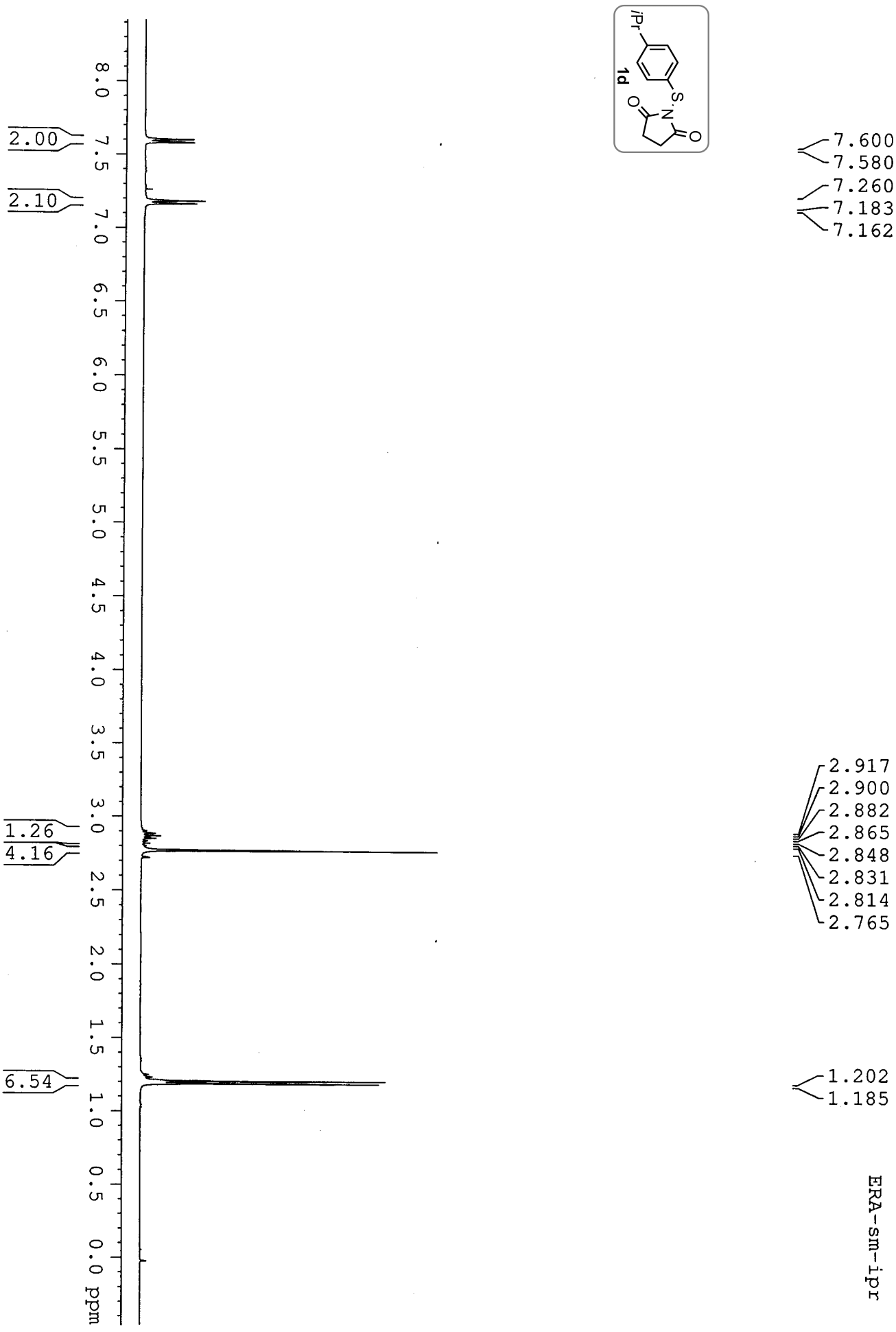
34.74
31.03
28.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
ERA-sm-tBu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2.831
2.814
2.765
1.202
1.185
2.00
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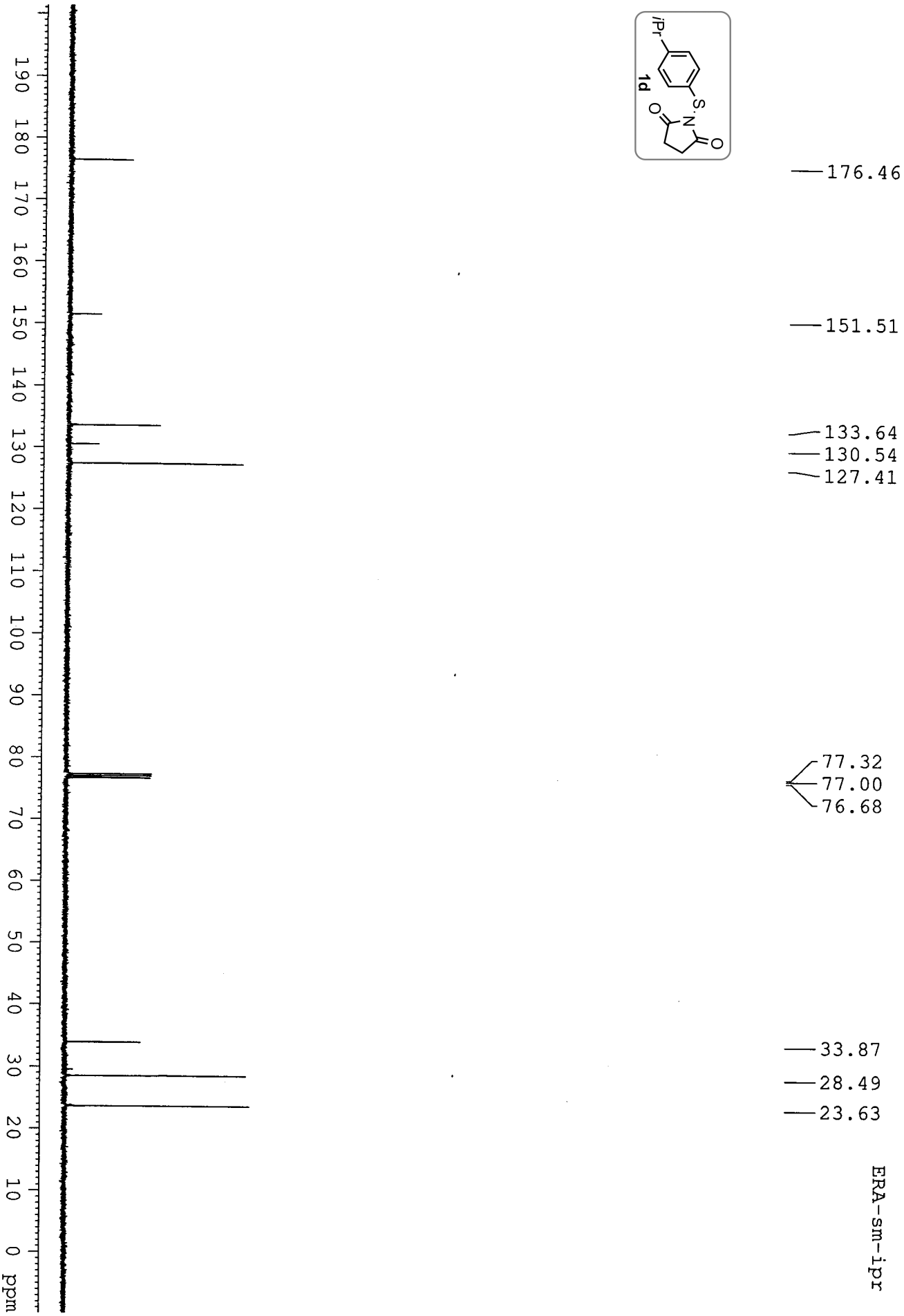
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28.49
23.63
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ERA-sm-ipr

F
S
N
O
O
1e
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7.711
7.702
7.689
7.260
7.025
7.003
6.981
2.772
2.00
2.07
4.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
ERA-sm-P-F

176.25

165.18
162.68

136.54
136.45
129.02
128.99

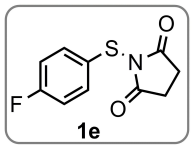
116.55
116.33

77.32
77.00
76.68

28.47

ERA-sm-P-F

ERA-SM-P-F



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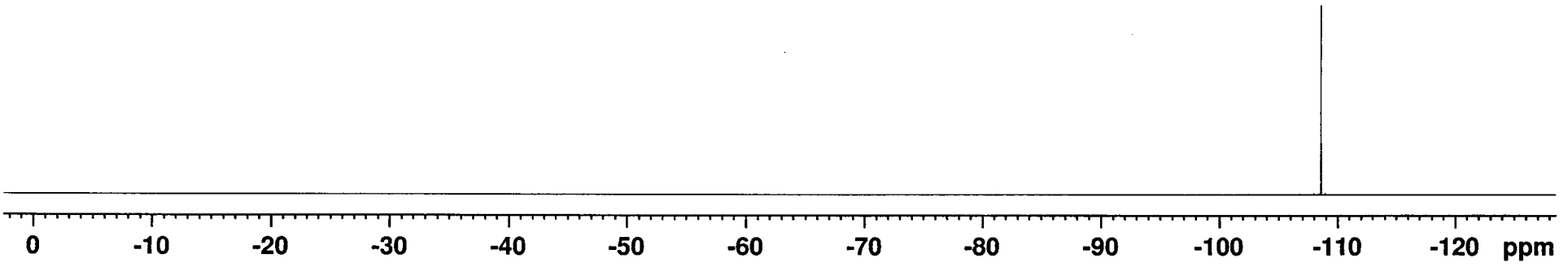

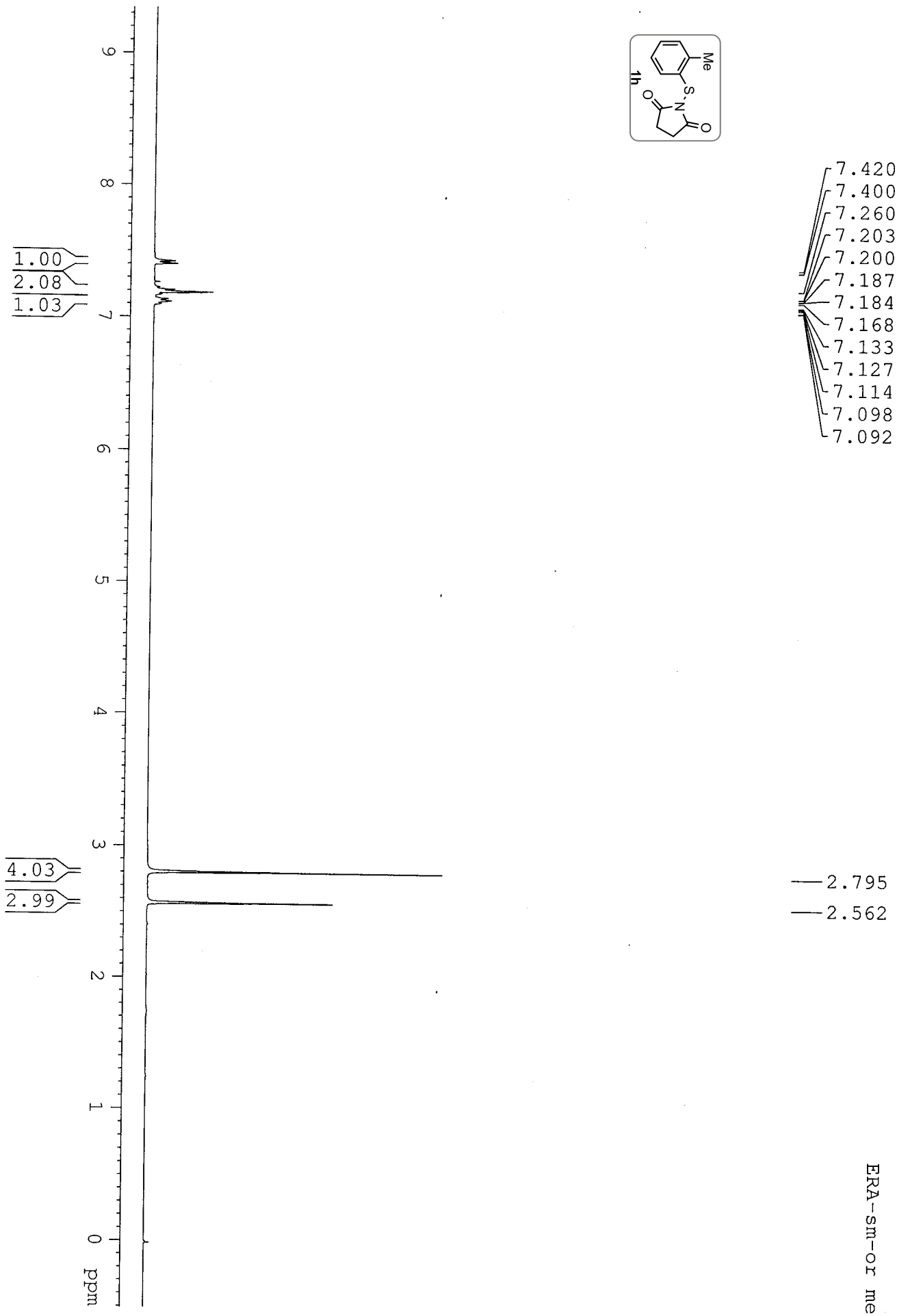
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3
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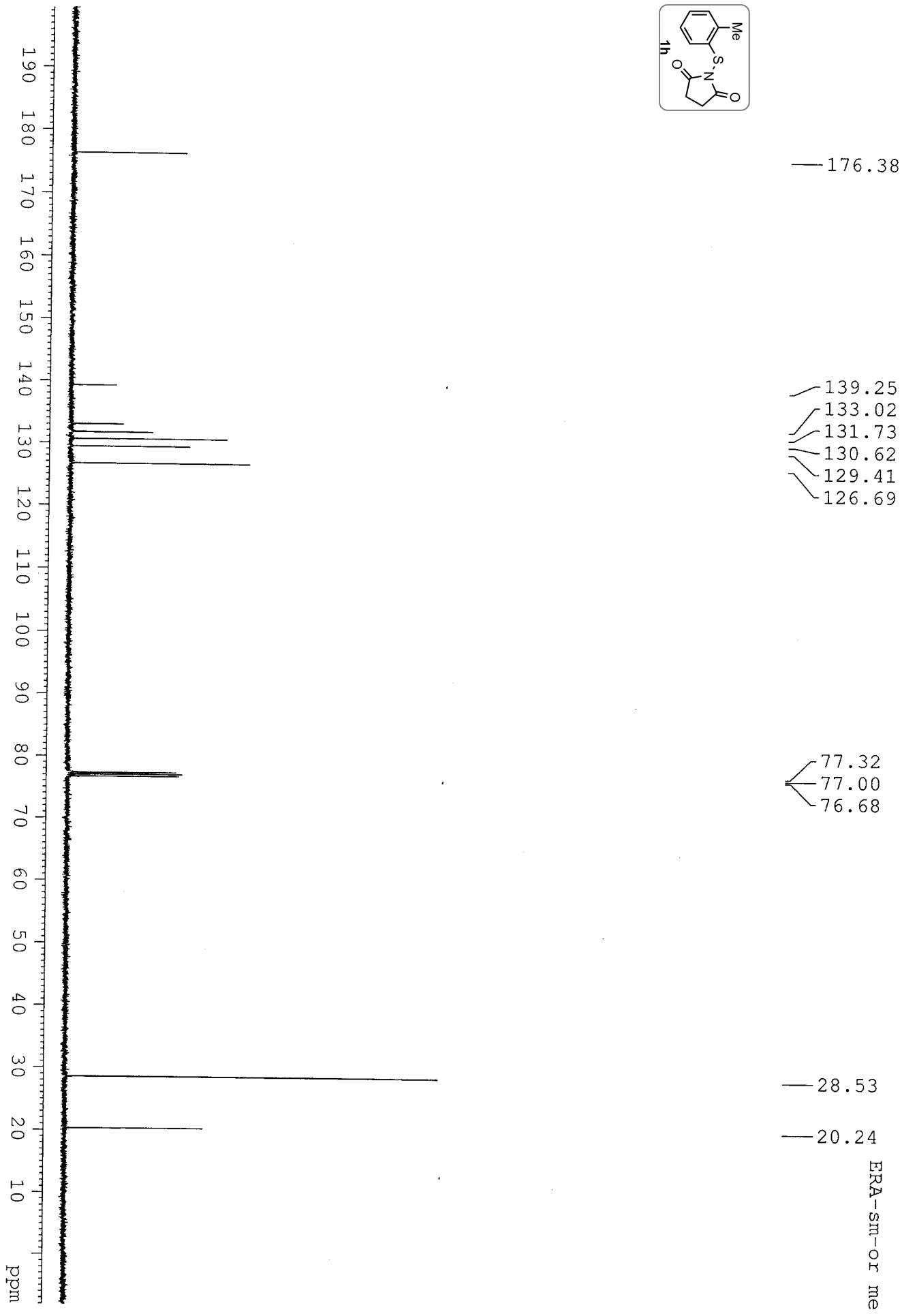
ppm
ERA-sm-or me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50
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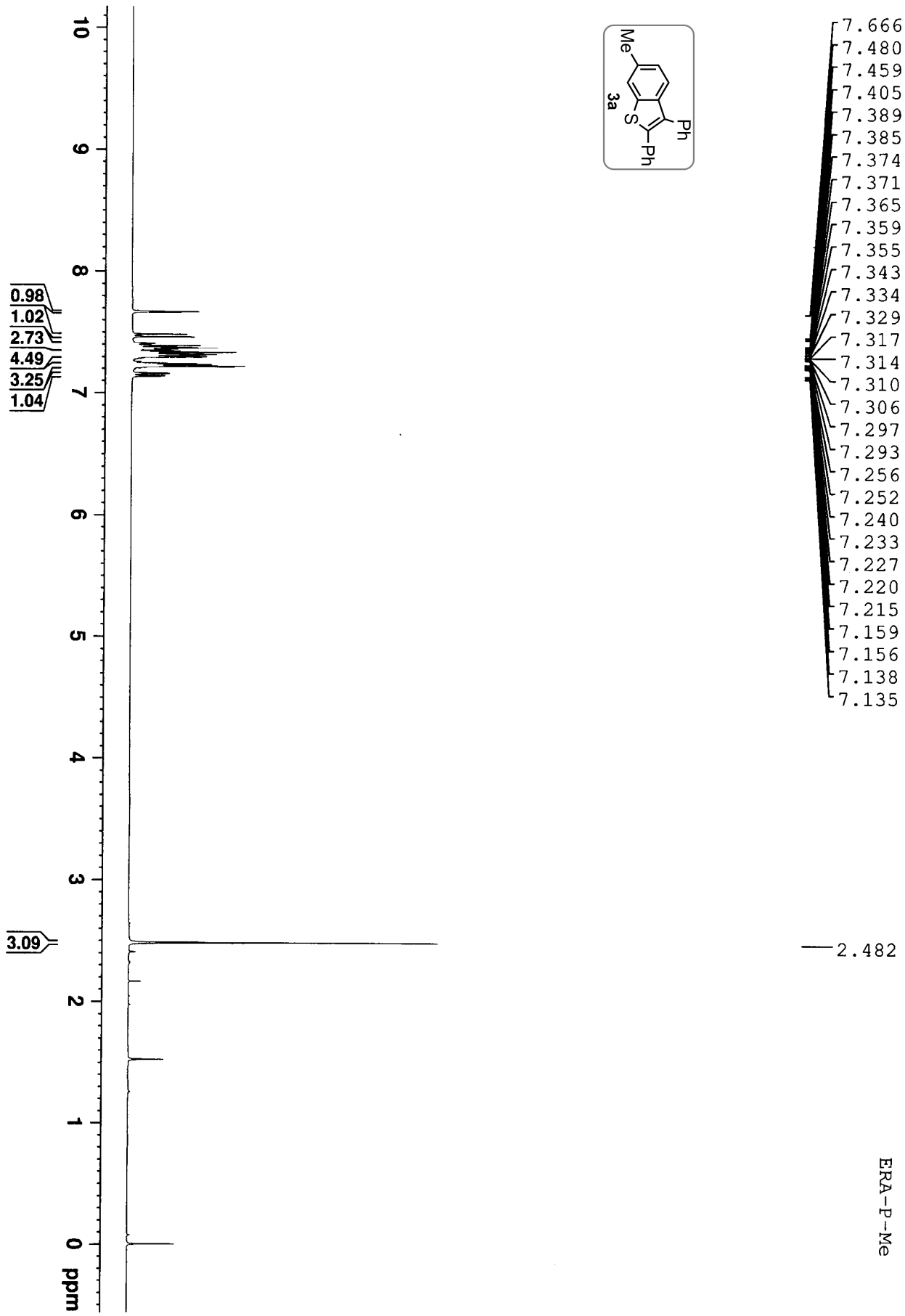
30
20
10
ERA-sm-or me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7.135
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4.49
3.25
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3.09
2.482
10
9
8
7
6
5
4
3
2
1
0 ppm
ERA-P-Me

Me
3a
S
Ph
Ph

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138.76
138.30
135.71
134.53
134.40
133.01
130.39
129.54
128.60
128.29
127.51
127.28
126.14
122.98
121.88

77.32
77.00
76.68

21.50

Me
O
S

ERA-ph-Me

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150
140
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120
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80
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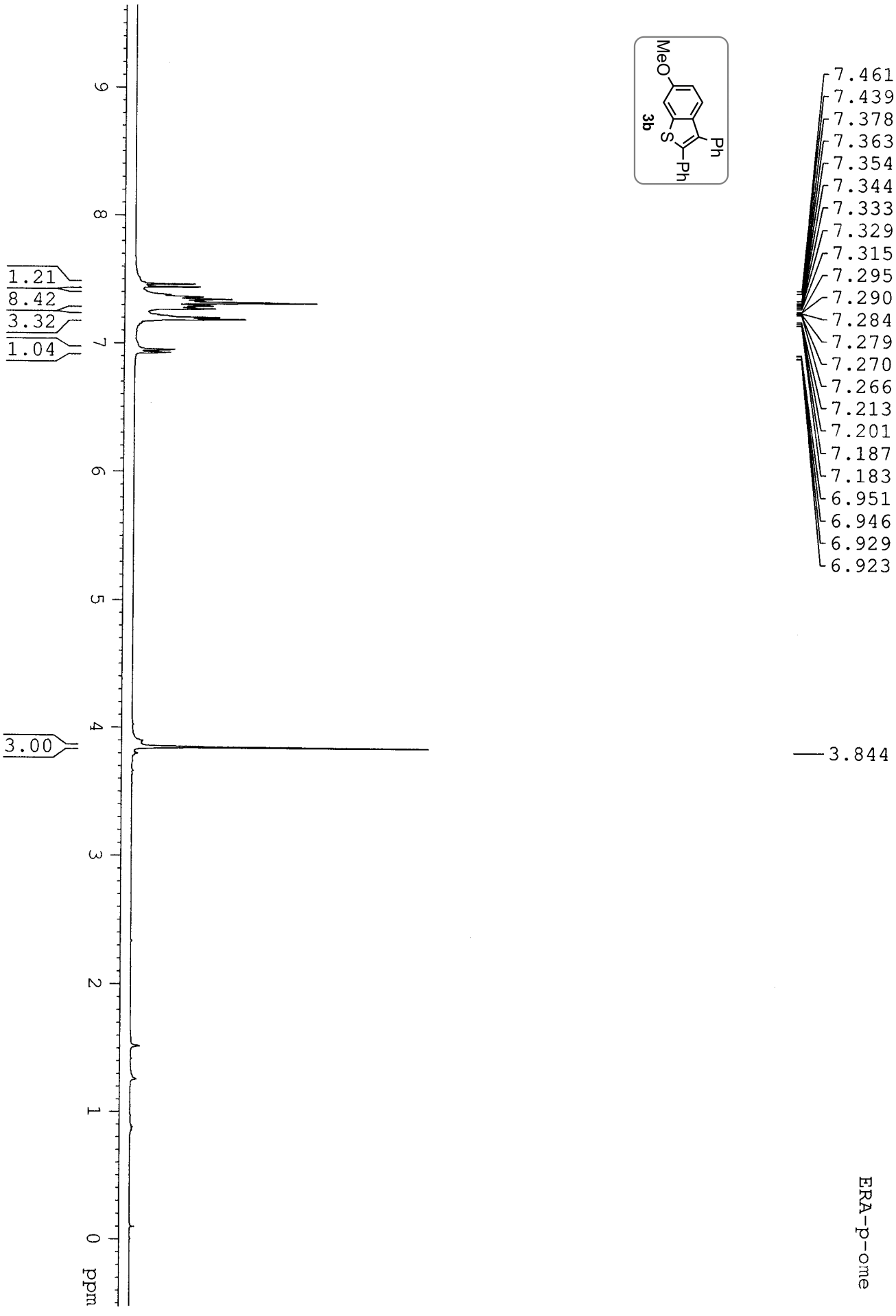
30
20
10
ppm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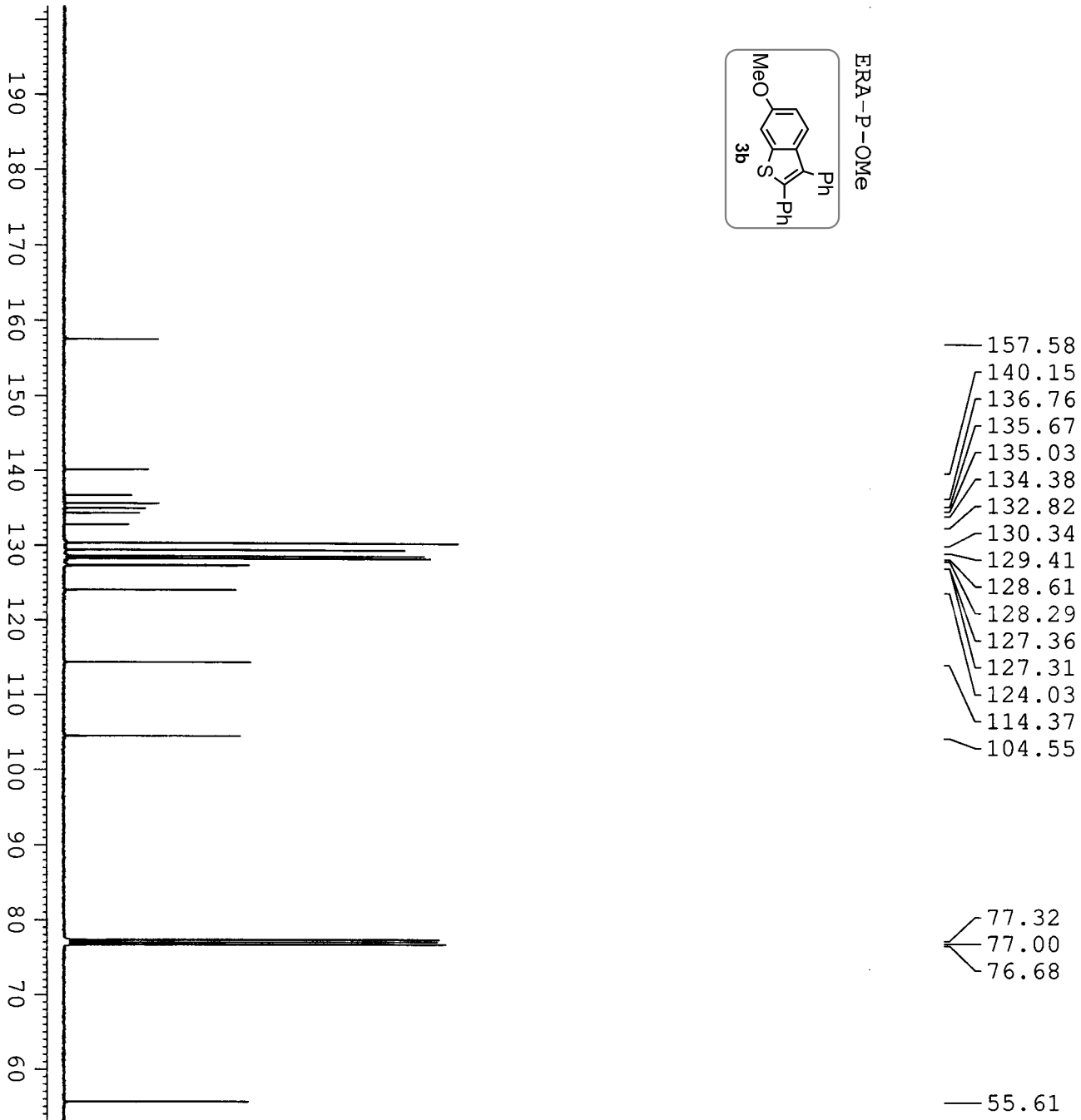
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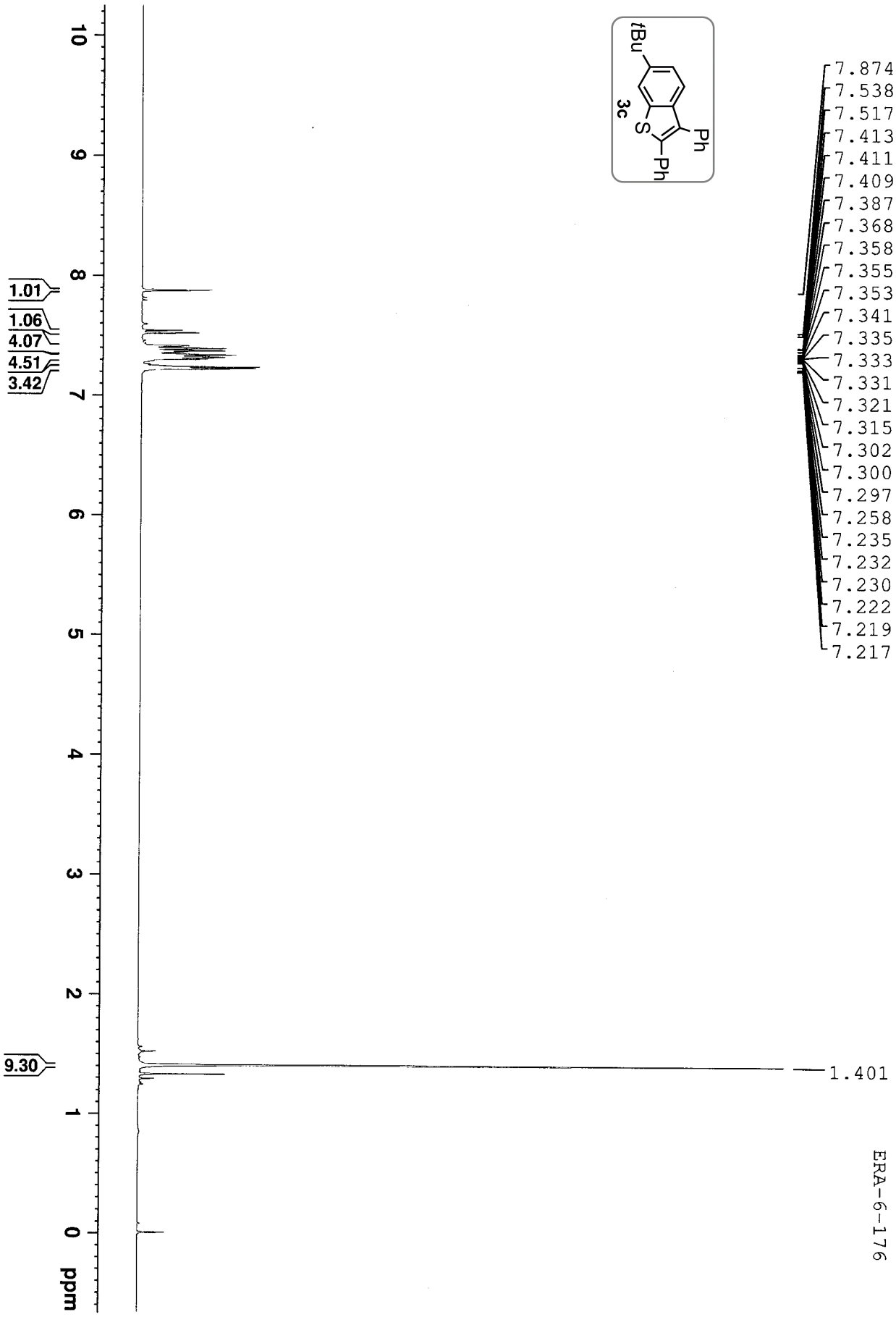
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7.217
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4.07
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tBu
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S
Ph
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127.53
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77.00
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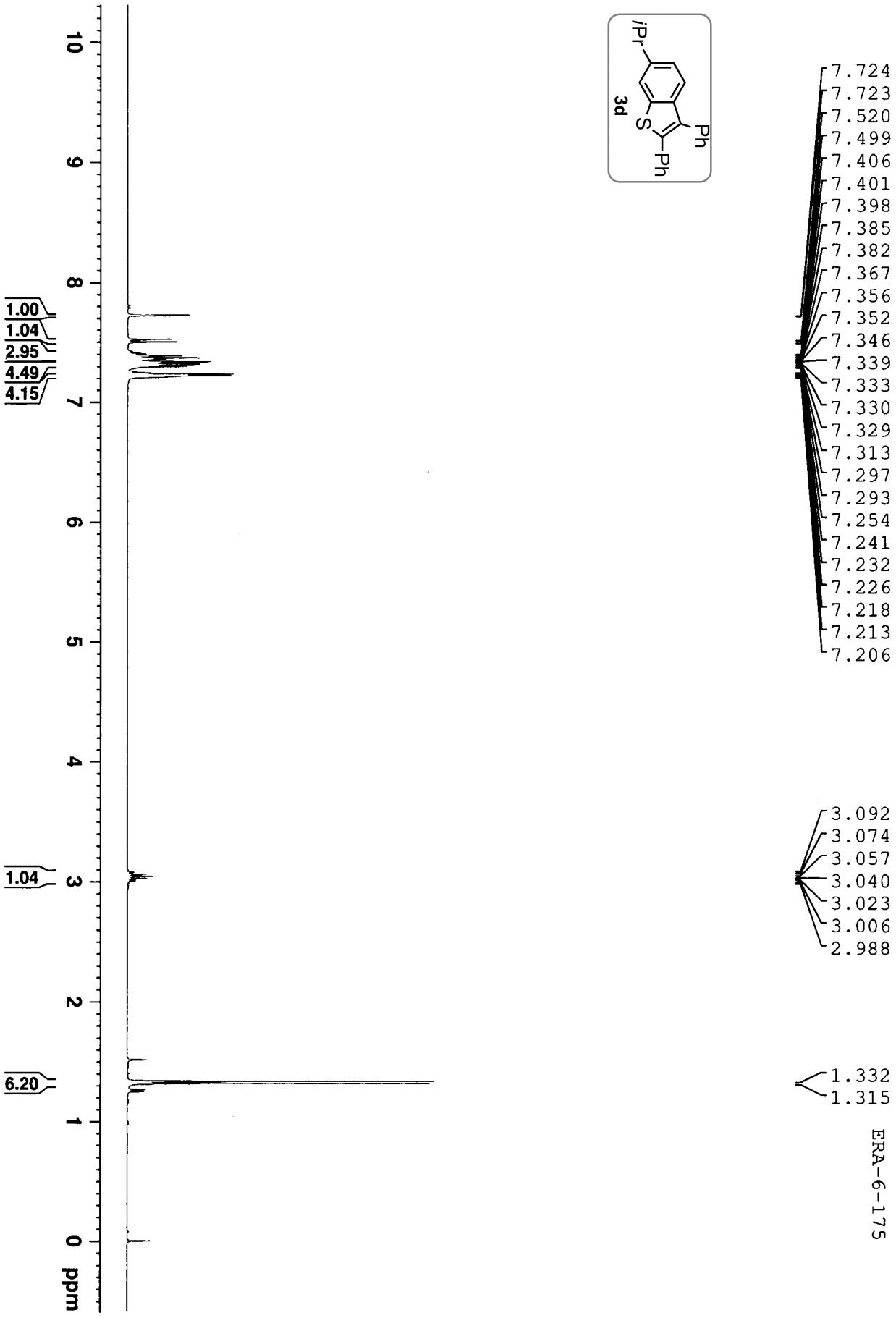
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9
8
7
6
5
4
3
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ERA-6-175

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133.05
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128.30
127.52
127.28
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123.15
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77.00
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34.26

24.20

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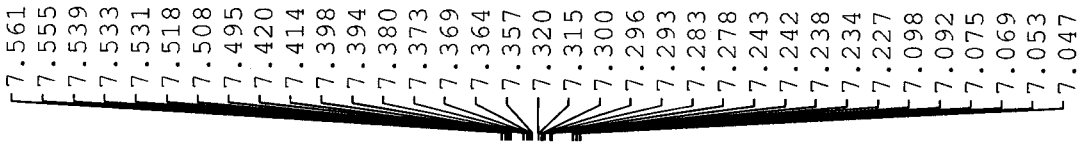
ERA-6-175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7.364
7.357
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7.293
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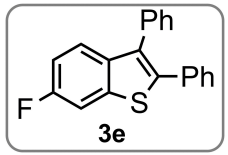
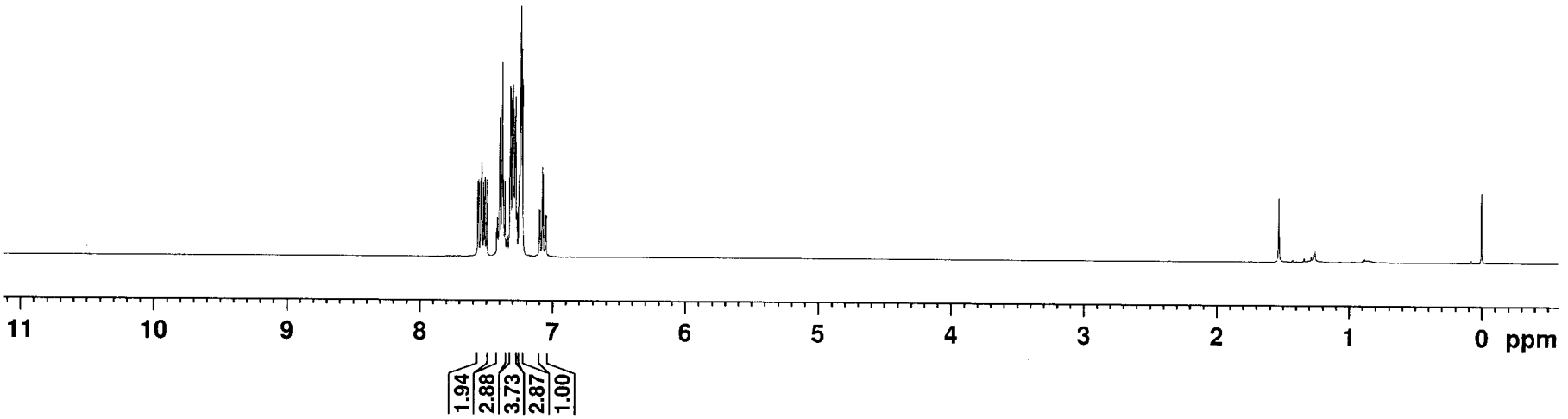
ERA-7-25


Ph
Ph
F
S
3e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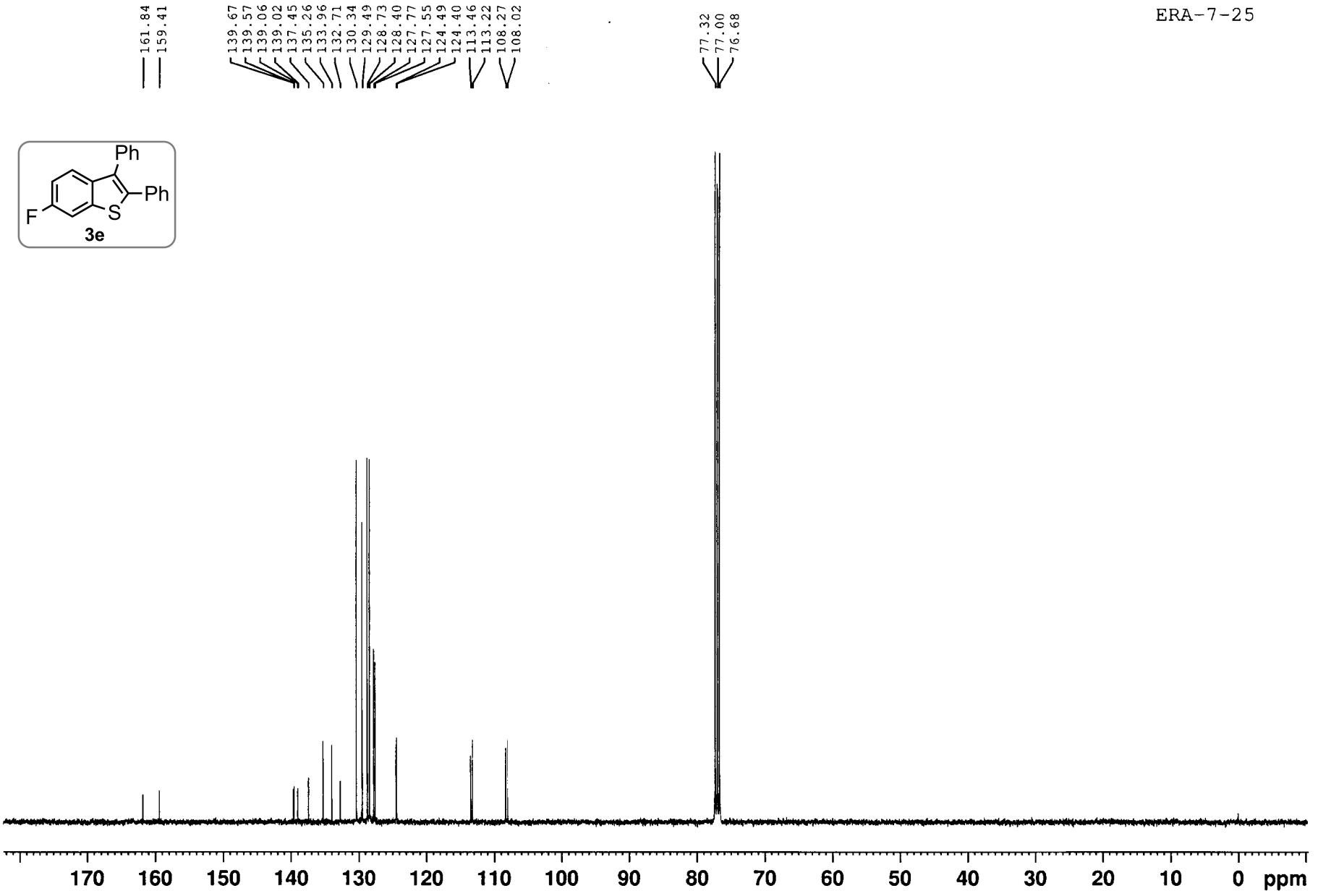
ERA-7-25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127.55
124.49
124.40
113.46
113.22
108.27
108.02
77.32
77.00
76.68
Ph
Ph
F
S
3e
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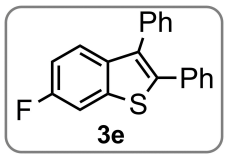
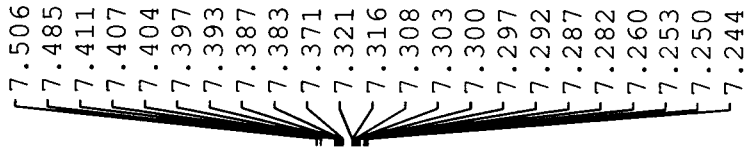


3e

ERA-7-25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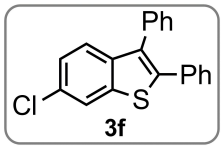
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Cl
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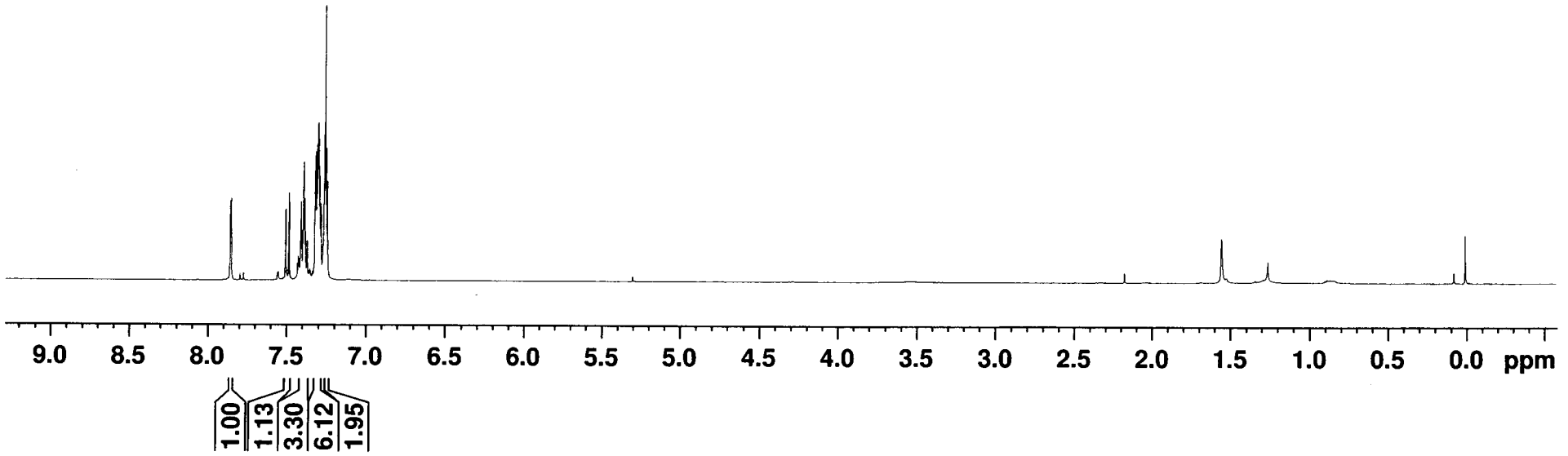
3f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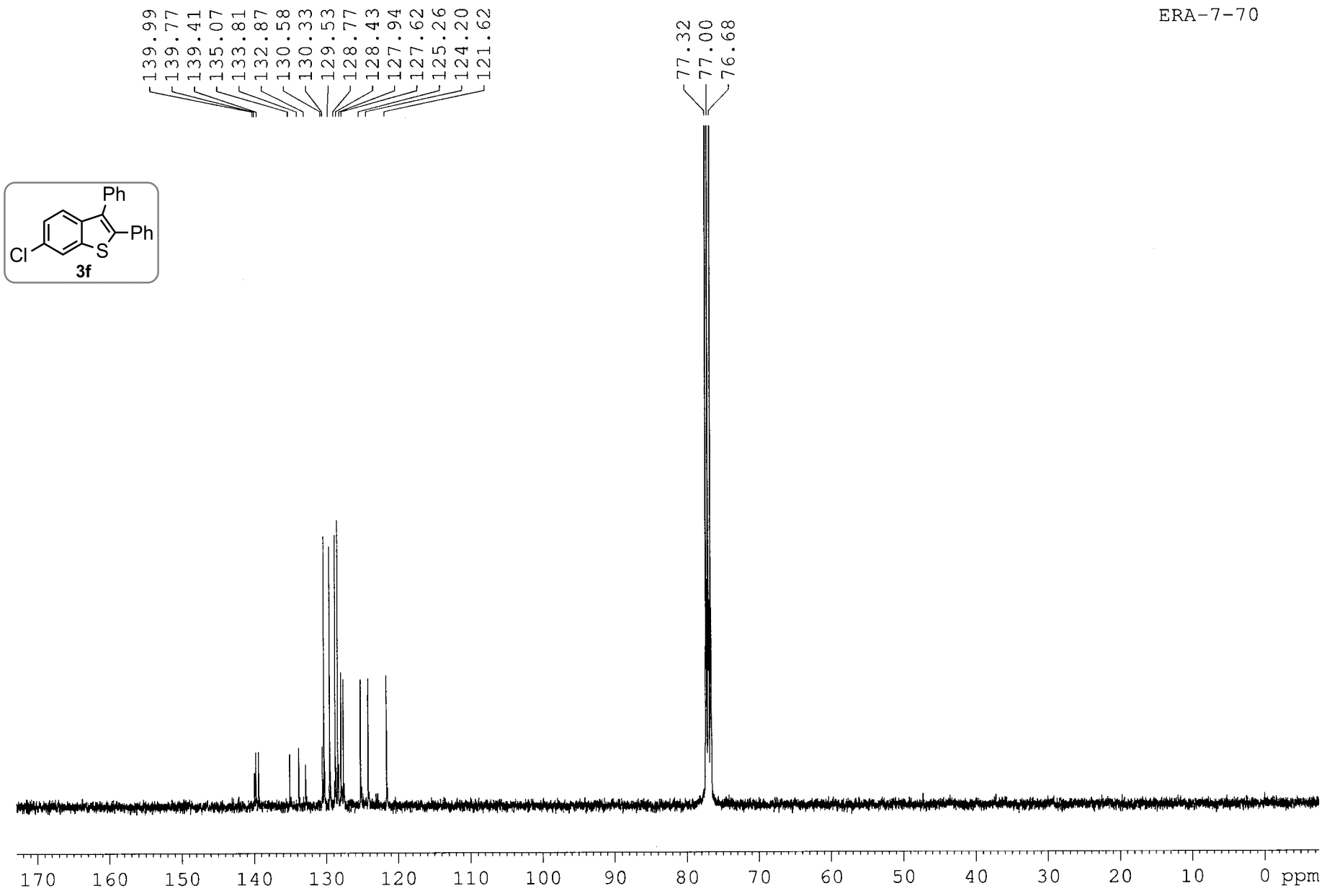
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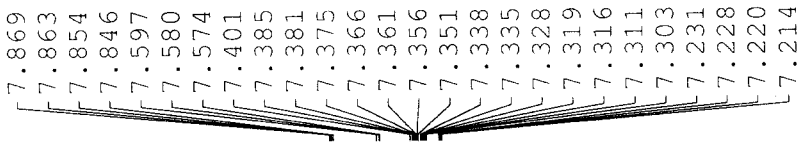
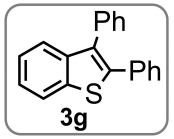
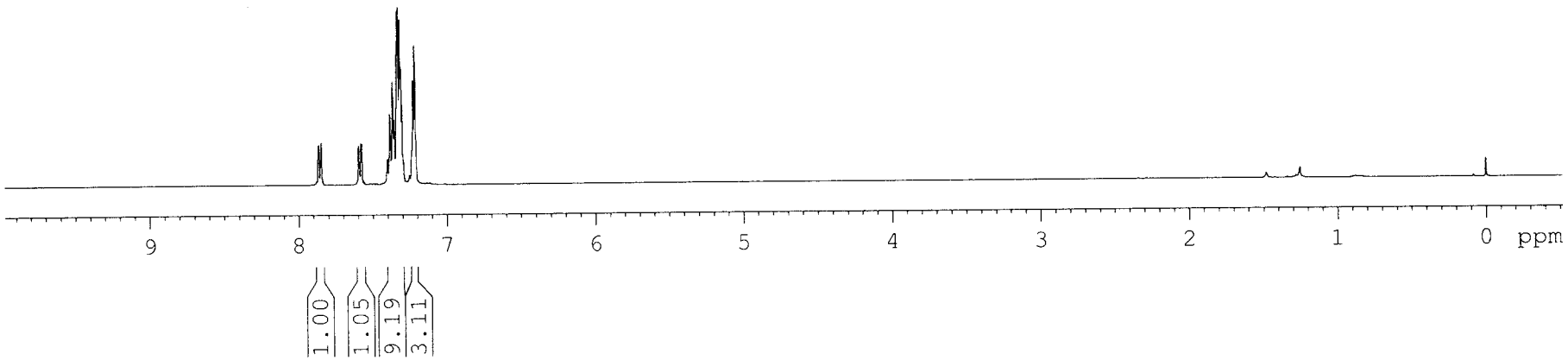
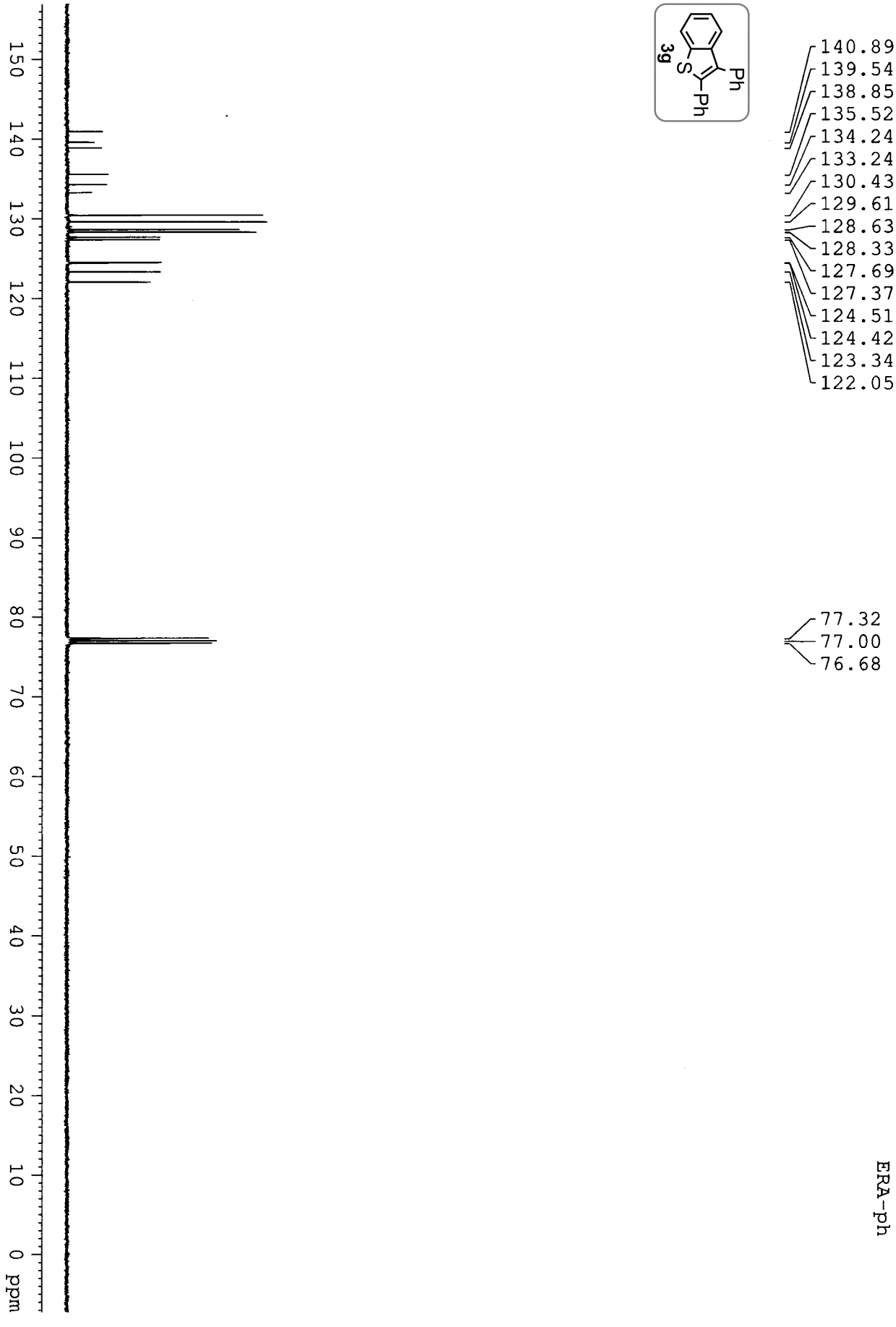
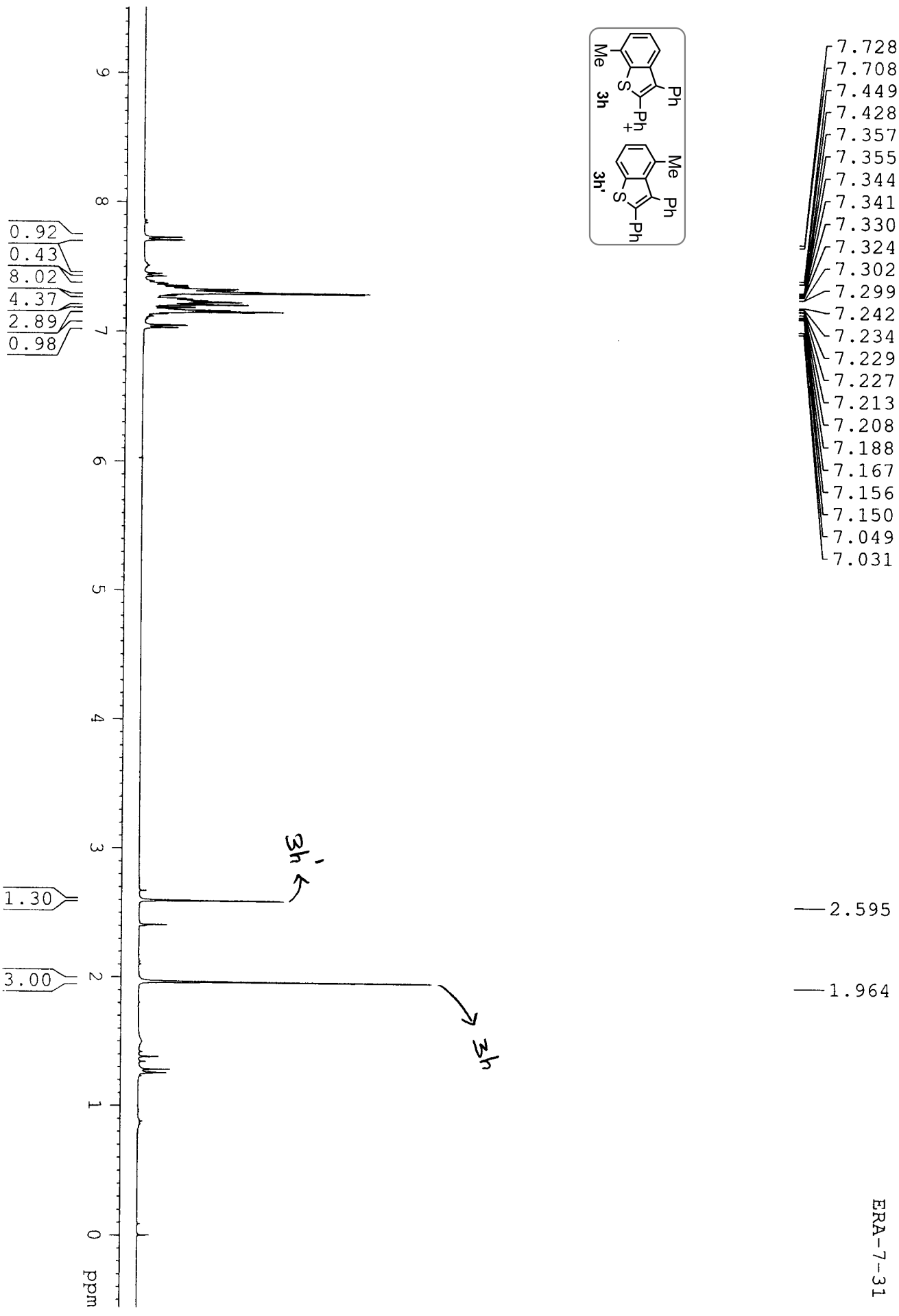
128.43
127.94
127.62
125.26
124.20
121.62
77.32
77.00
76.68
Ph
Ph
Cl
S
3f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.869
7.863
7.854
7.846
7.597
7.580
7.574
7.401
7.385
7.381
7.375
7.366
7.361
7.356
7.351
7.338
7.335
7.328
7.319
7.316
7.311
7.303
7.231
7.228
7.220
7.214


Ph
Ph
S
3g


9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
9.19
3.11


3g
Ph
S
Ph
140.89
139.54
138.85
135.52
134.24
133.24
130.43
129.61
128.63
128.33
127.69
127.37
124.51
124.42
123.34
122.05
77.32
77.00
76.68
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
ERA-ph

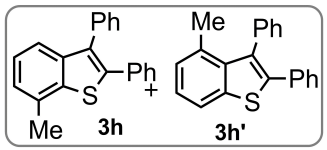

Me
3h
Ph
S
Ph
+
Me
Ph
3h'
S
Ph
7.728
7.708
7.449
7.428
7.357
7.355
7.344
7.341
7.330
7.324
7.302
7.299
7.242
7.234
7.229
7.227
7.213
7.208
7.188
7.167
7.156
7.150
7.049
7.031
0.92
0.43
8.02
4.37
2.89
0.98
1.30
3.00
3h'
3h
2.595
1.964
9
8
7
6
5
4
3
2
1
0
ppm
ERA-7-31

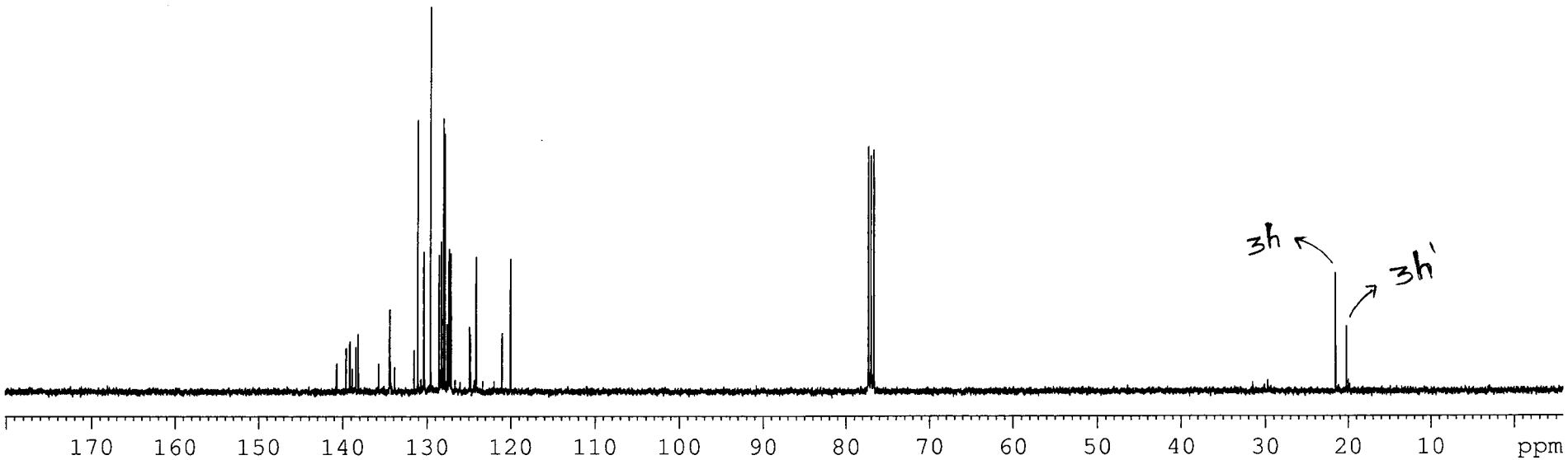
ERA-7-31

140.75
139.63
139.20
138.93
138.47
138.19
135.79
134.52
134.47
134.45
134.37
133.89
131.56
131.10
130.41
129.58
128.58
128.30
128.06
127.87
127.60
127.40
127.35
127.30
127.14
124.94
124.81
124.14
121.05
120.04

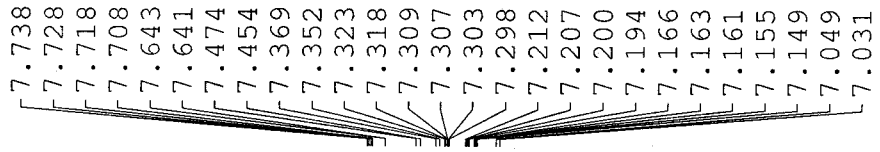
77.32
77.00
76.68

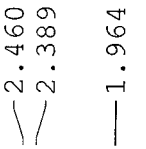
21.54
20.20

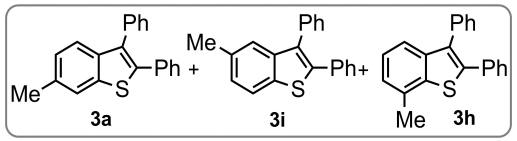


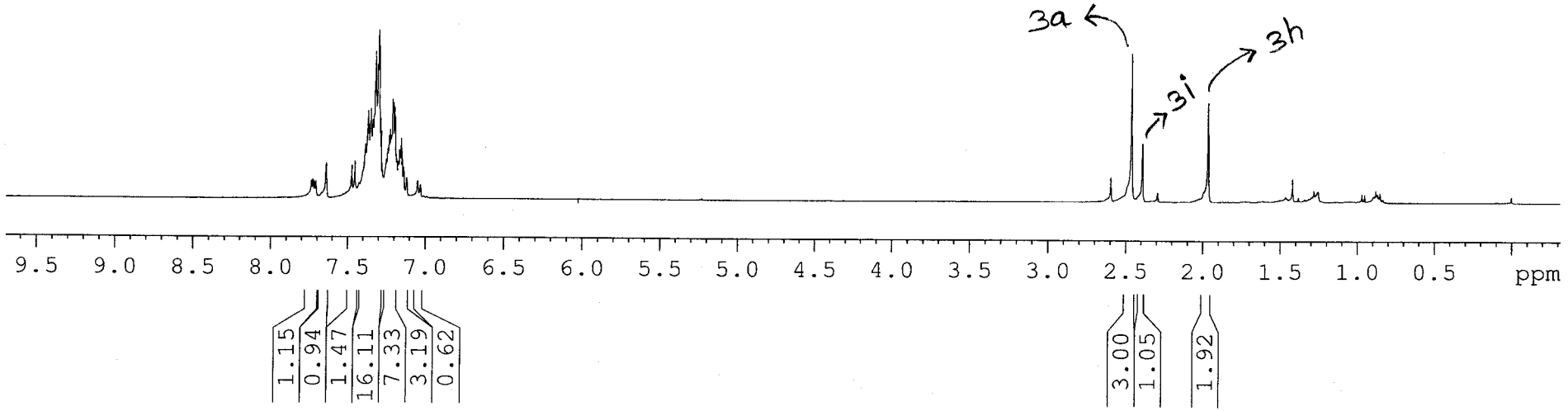


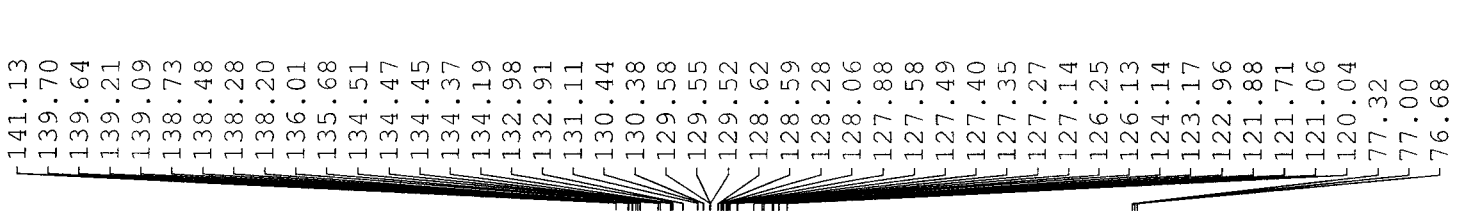
ERA-7-89

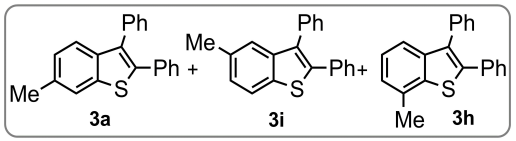

7.738
7.728
7.718
7.708
7.643
7.641
7.474
7.454
7.369
7.352
7.323
7.318
7.309
7.307
7.303
7.298
7.212
7.207
7.200
7.194
7.166
7.163
7.161
7.155
7.149
7.049
7.031

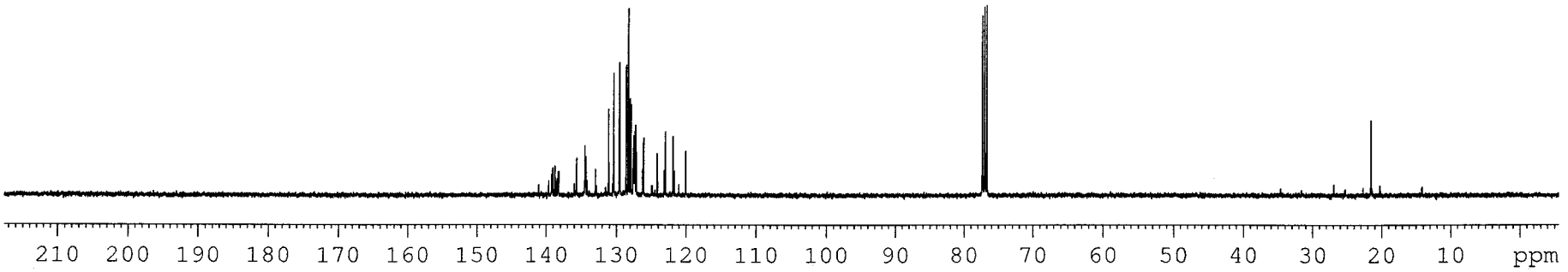

2.460
2.389
1.964

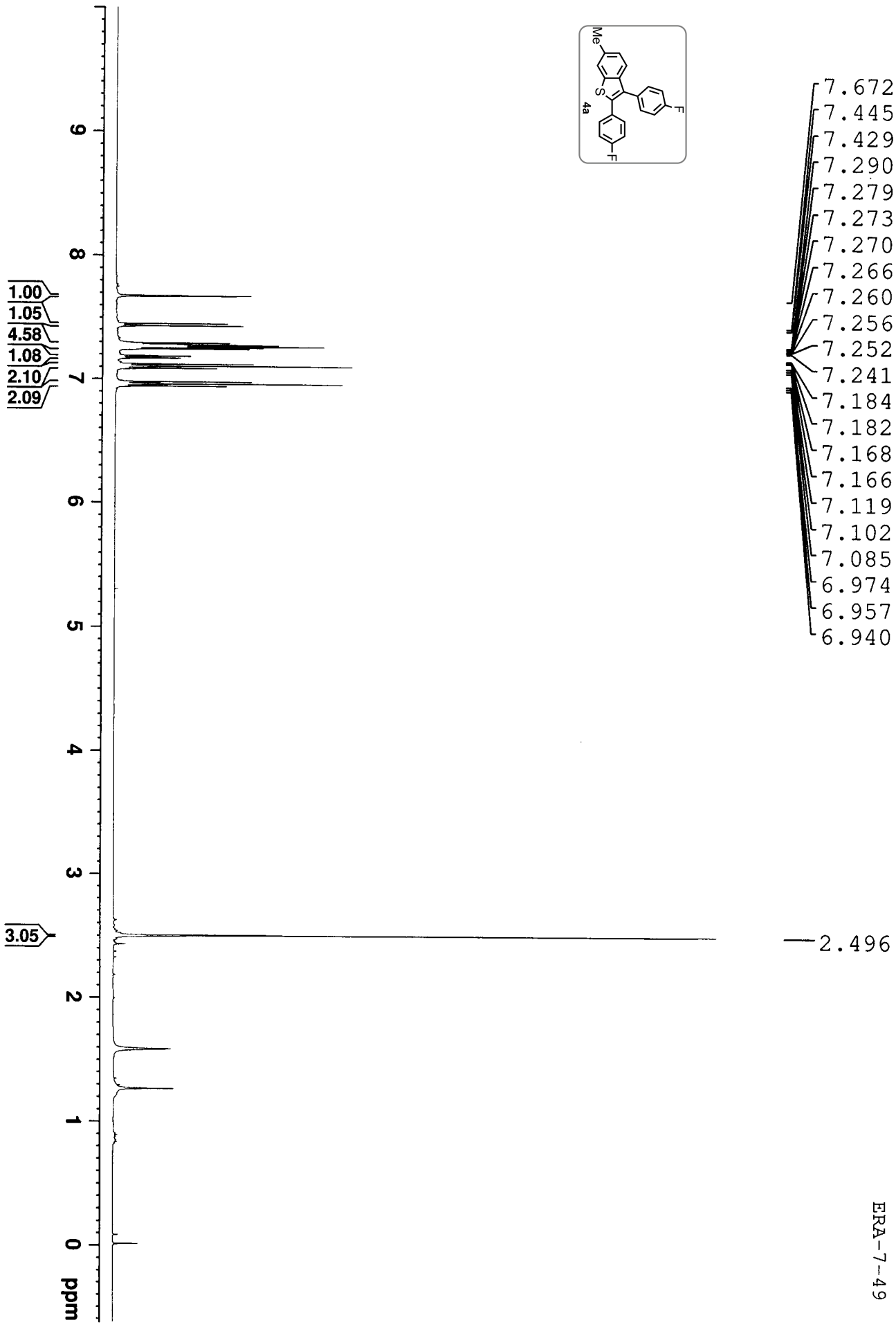

Ph
Me
Ph +
S
3a
Ph
Me
Ph+
S
3i
Ph
Ph
S
Me
3h

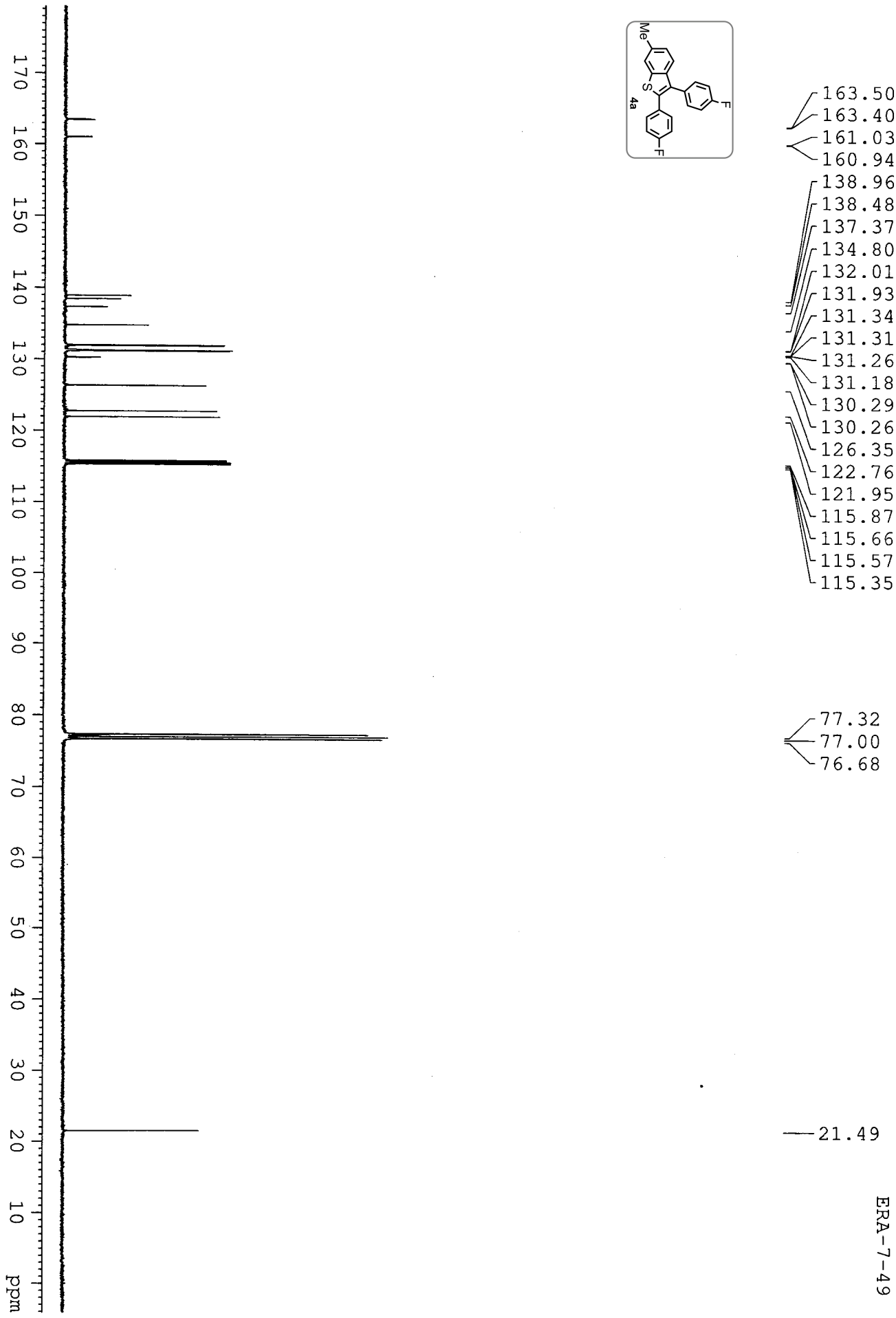

3a
3i
3h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.15
0.94
1.47
16.11
7.33
3.19
0.62
3.00
1.05
1.92

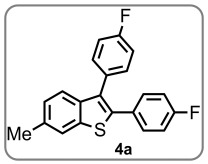

141.13
139.70
139.64
139.21
139.09
138.73
138.48
138.28
138.20
136.01
135.68
134.51
134.47
134.45
134.37
134.19
132.98
132.91
131.11
130.44
130.38
129.58
129.55
129.52
128.62
128.59
128.28
128.06
127.88
127.58
127.49
127.40
127.35
127.27
127.14
126.25
126.13
124.14
123.17
122.96
121.88
121.71
121.06
120.04
77.32
77.00
76.68
3h
3a
21.54
21.50
ERA-7-89


Ph
Me
Ph +
S
3a
Ph
Me
Ph+
S
3i
Ph
Ph
S
Me
3h


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Me
S
4a
F
F
7.672
7.445
7.429
7.290
7.279
7.273
7.270
7.266
7.260
7.256
7.252
7.241
7.184
7.182
7.168
7.166
7.119
7.102
7.085
6.974
6.957
6.940
2.496
1.00
1.05
4.58
1.08
2.10
2.09
3.05
9
8
7
6
5
4
3
2
1
0
ppm
ERA-7-49

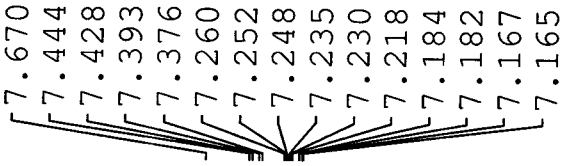

Me
S
4a
F
F
163.50
163.40
161.03
160.94
138.96
138.48
137.37
134.80
132.01
131.93
131.34
131.31
131.26
131.18
130.29
130.26
126.35
122.76
121.95
115.87
115.66
115.57
115.35
77.32
77.00
76.68
21.49
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
ERA-7-49

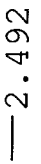


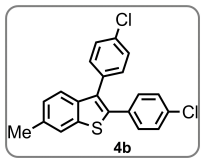
ERA-7-49

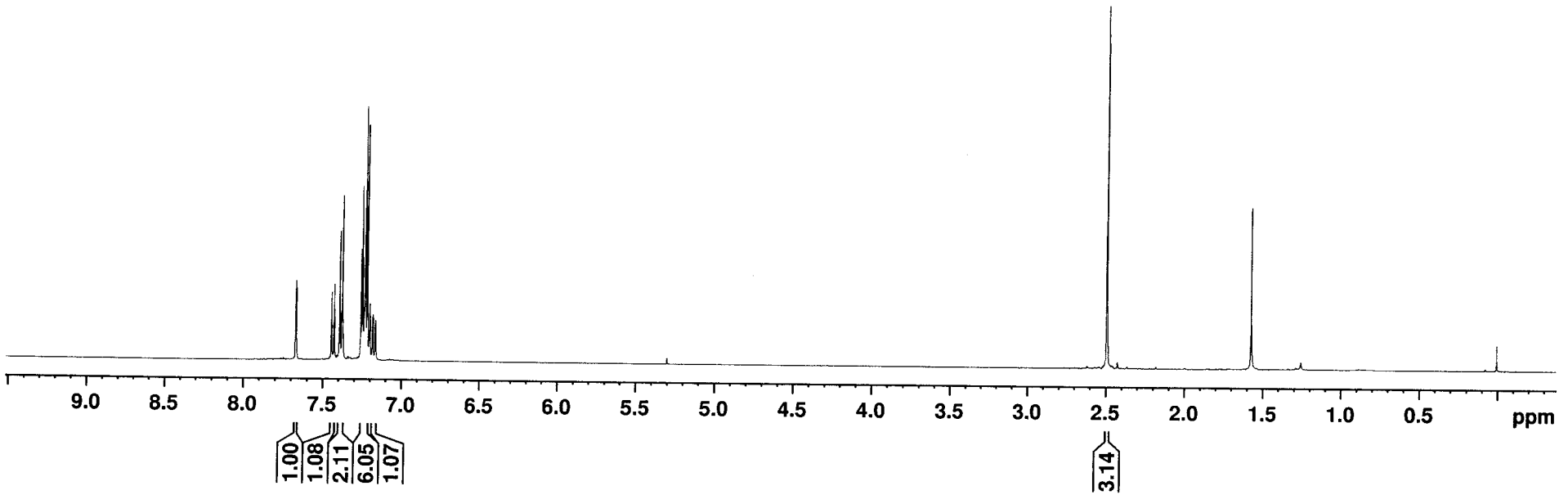
-113.79
-114.43

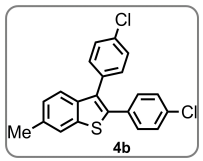
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm


7.670
7.444
7.428
7.393
7.376
7.260
7.252
7.248
7.235
7.230
7.218
7.184
7.182
7.167
7.165

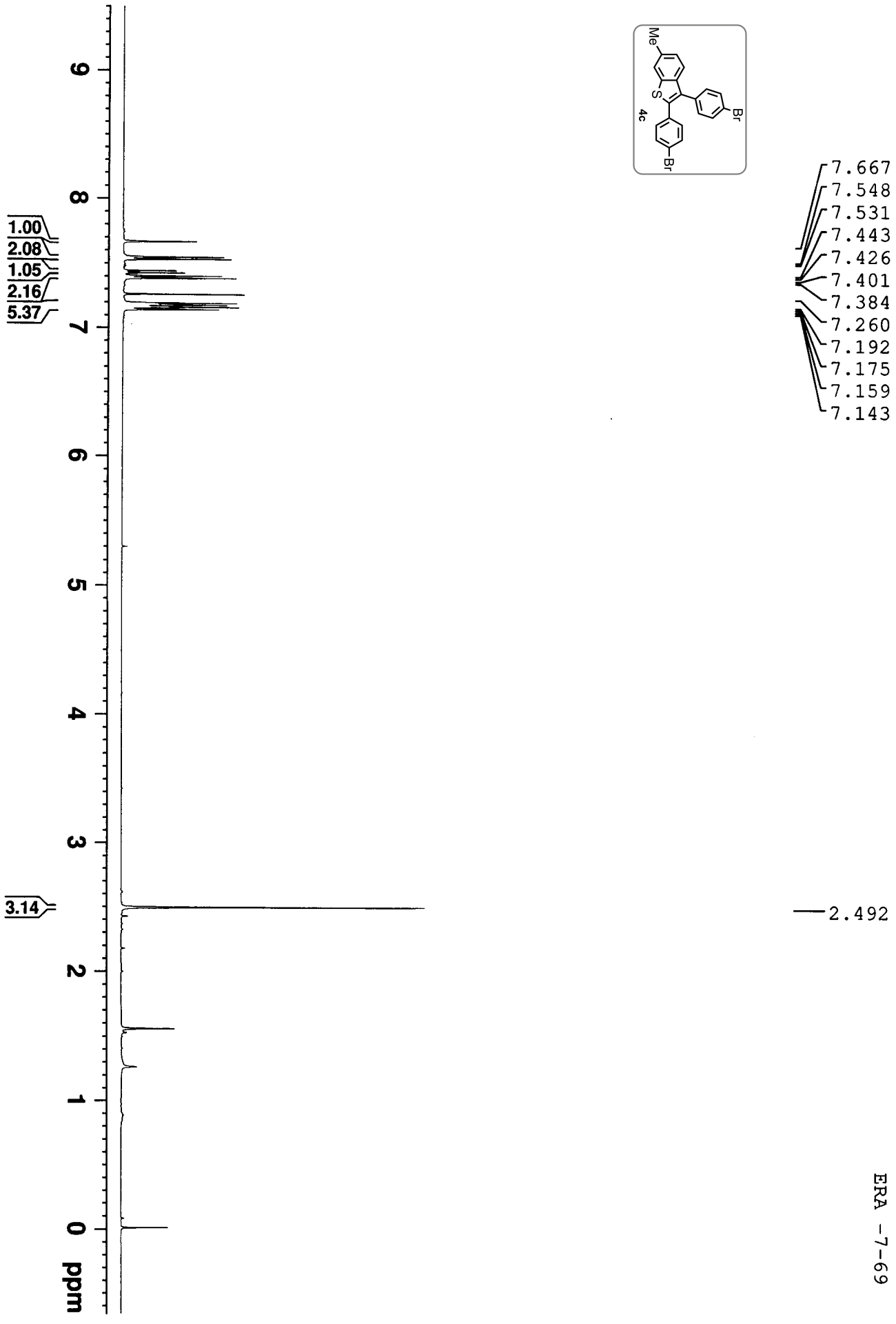

2.492

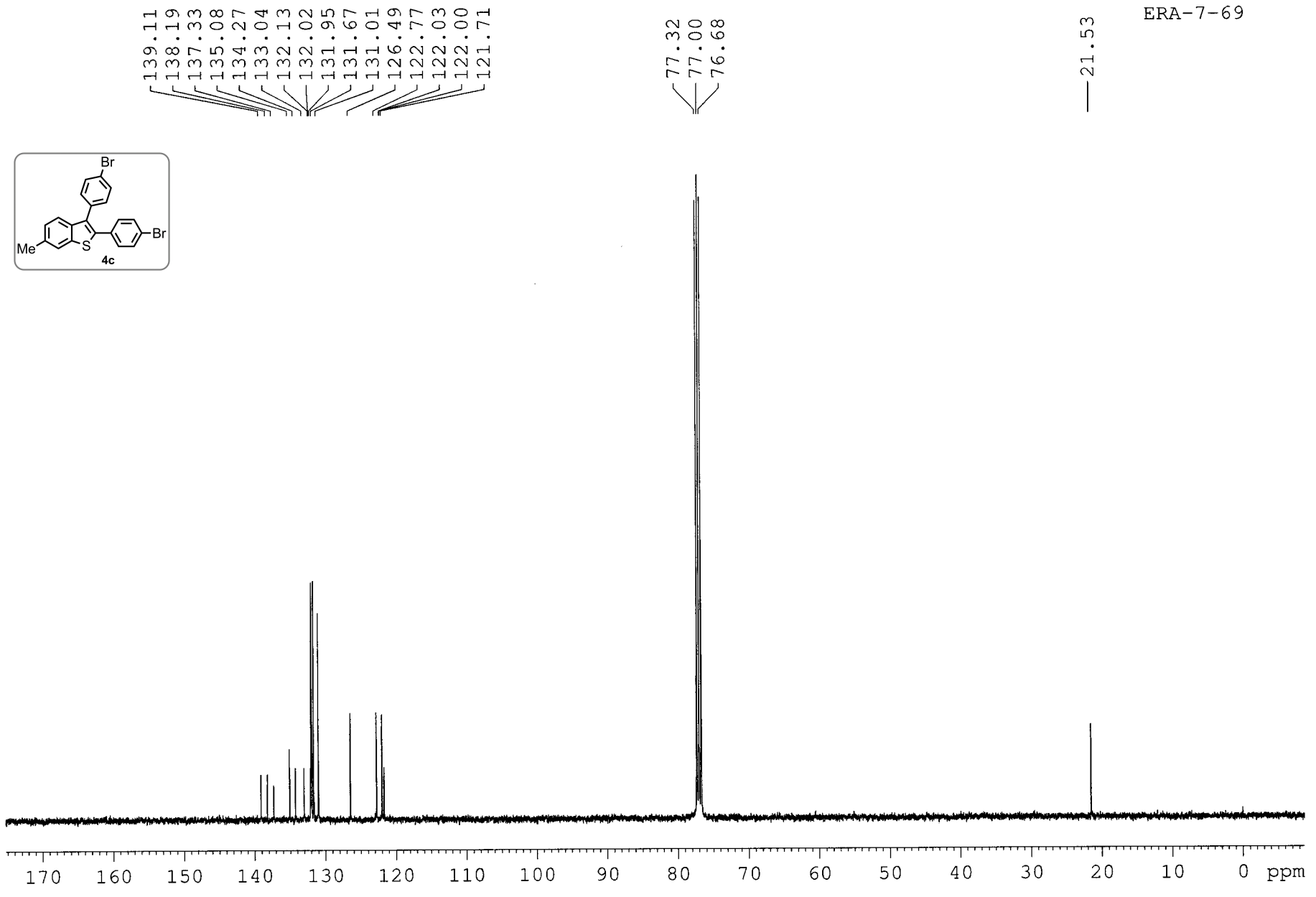

Cl
Me
S
Cl
4b

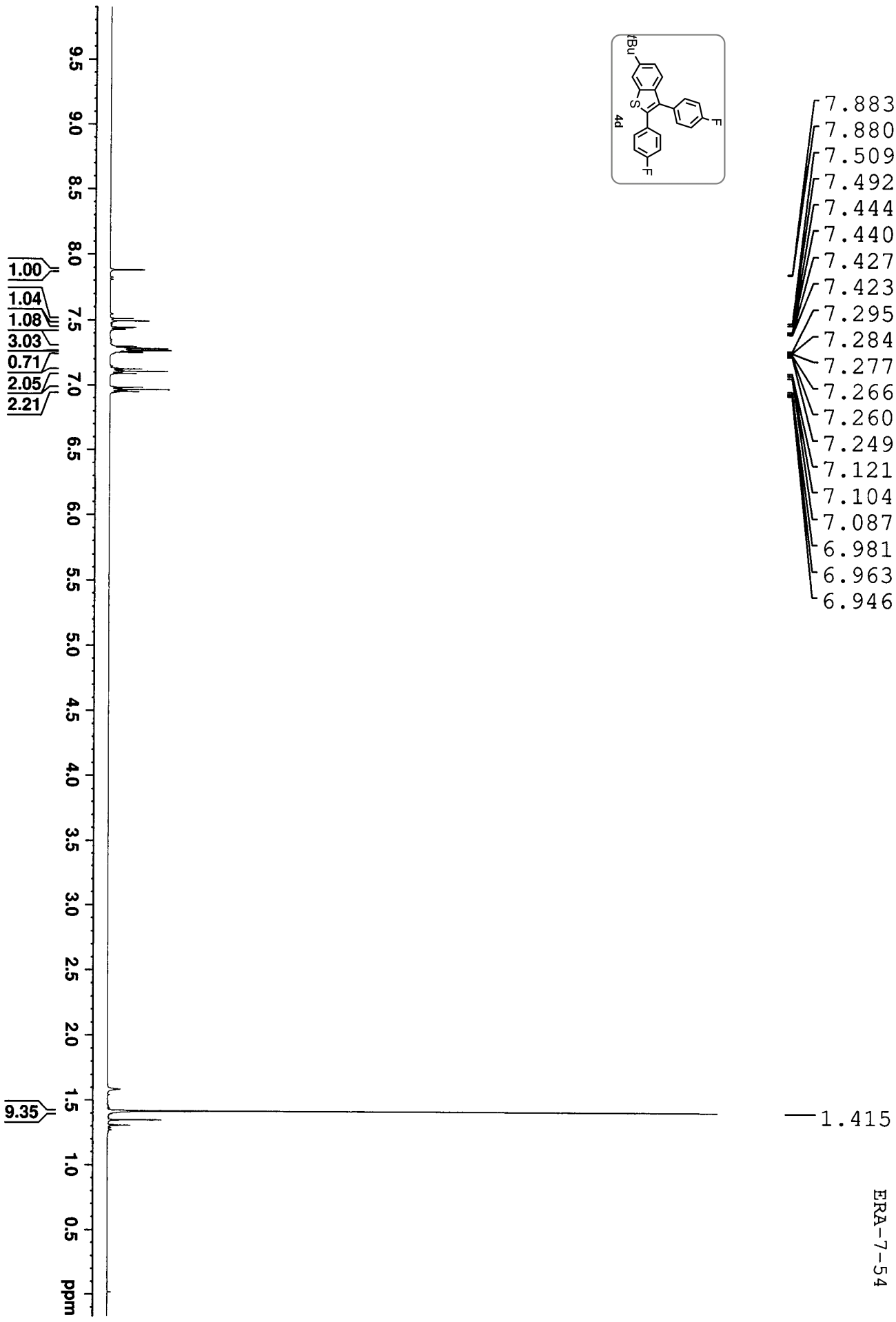

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.08
2.11
6.05
1.07
3.14


Cl
Me
S
Cl
4b

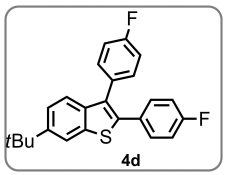
139.09
138.26
137.33
135.03
133.80
133.51
132.60
132.11
131.64
130.72
129.06
128.70
126.46
122.77
121.99
77.32
77.00
76.68
21.52
ERA-7-50
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Me
S
4c
Br
Br
7.667
7.548
7.531
7.443
7.426
7.401
7.384
7.260
7.192
7.175
7.159
7.143
2.492
1.00
2.08
1.05
2.16
5.37
3.14
ppm
ERA -7-69


ERA-7-69
139.11
138.19
137.33
135.08
134.27
133.04
132.13
132.02
131.95
131.67
131.01
126.49
122.77
122.03
122.00
121.71
77.32
77.00
76.68
21.53
Br
Me
S
Br
4c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


tBu
S
F
F
4d
7.883
7.880
7.509
7.492
7.444
7.440
7.427
7.423
7.295
7.284
7.277
7.266
7.260
7.249
7.121
7.104
7.087
6.981
6.963
6.946
1.415
1.00
1.04
1.08
3.03
0.71
2.05
2.21
9.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
ERA-7-54

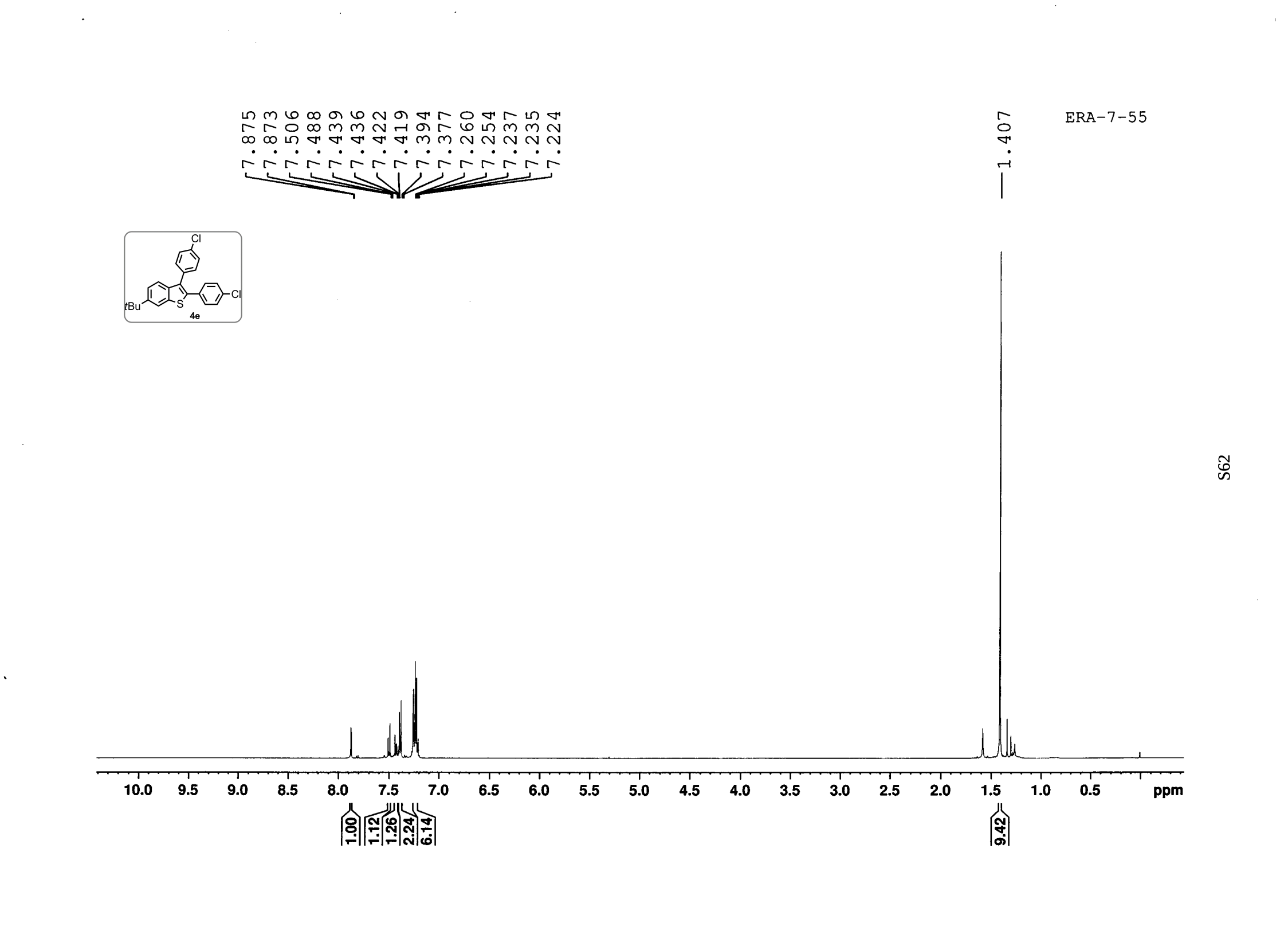
tBu
S
F
F
4d
163.53
163.40
161.06
160.95
148.30
138.87
138.38
137.89
132.00
131.92
131.36
131.32
131.29
131.21
130.34
130.31
122.92
122.62
119.10
118.25
115.87
115.66
115.58
115.37
77.32
77.00
76.68
34.98
31.51
31.25
-0.01
ERA-7-54
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

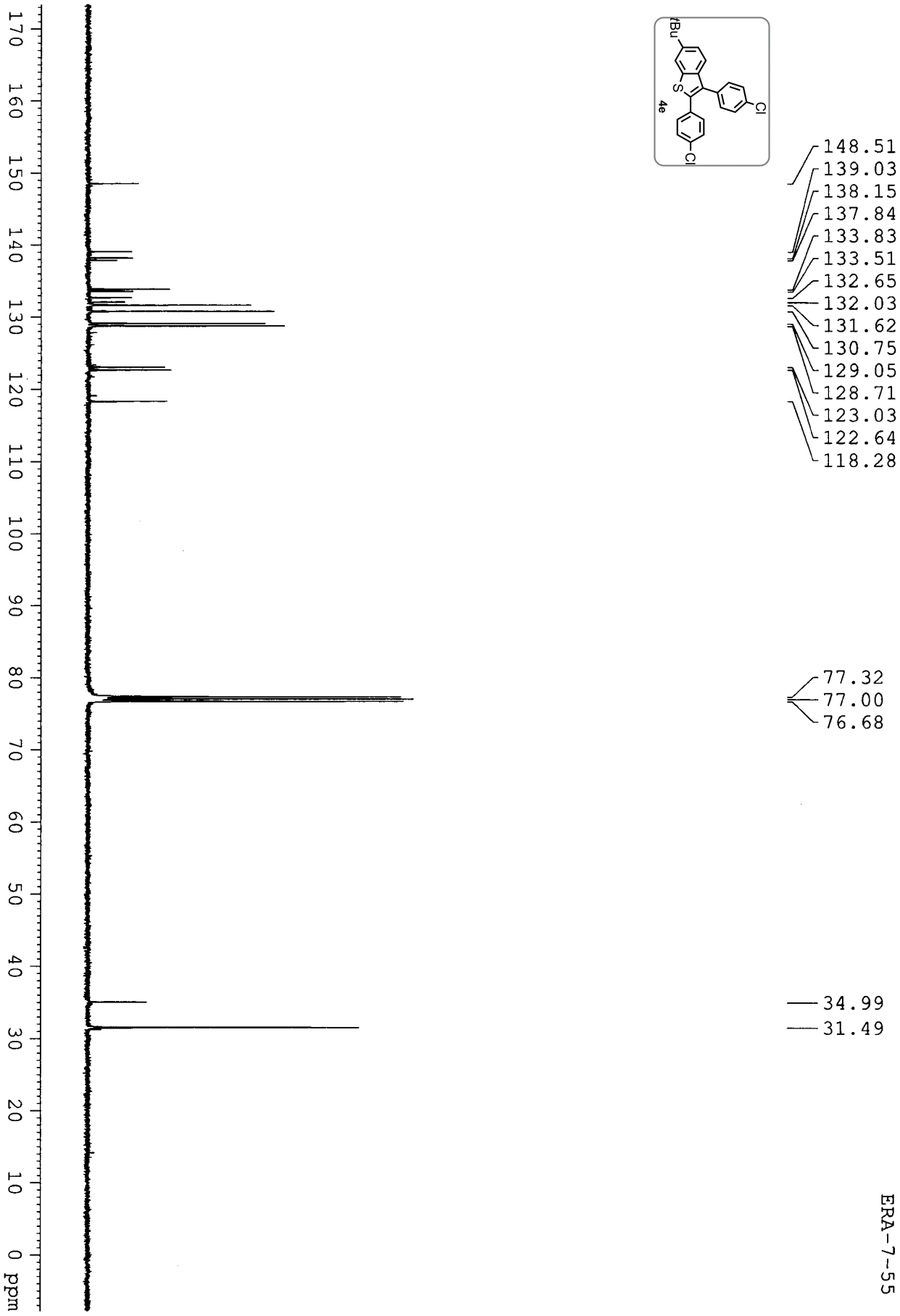


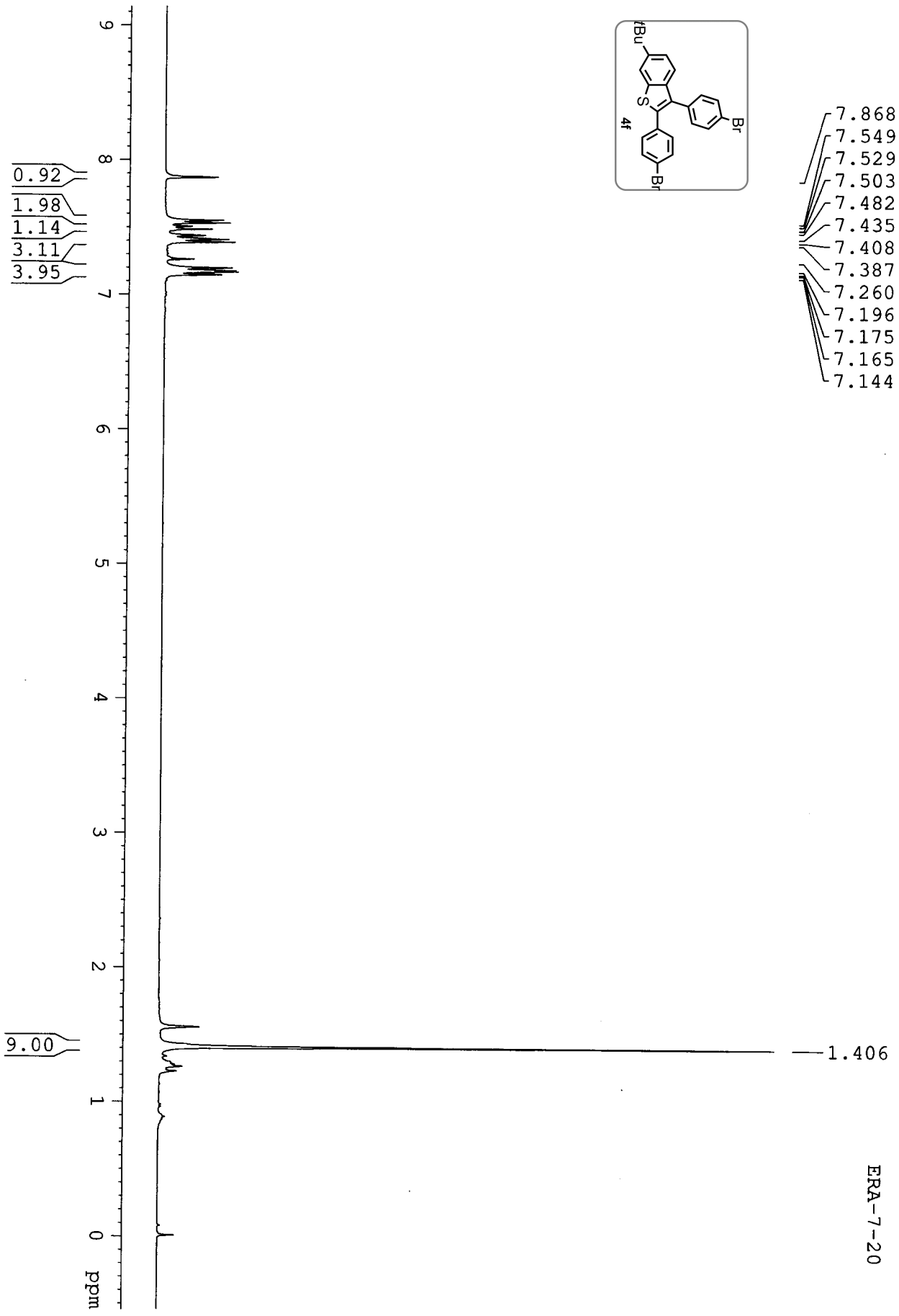
ERA-7-54

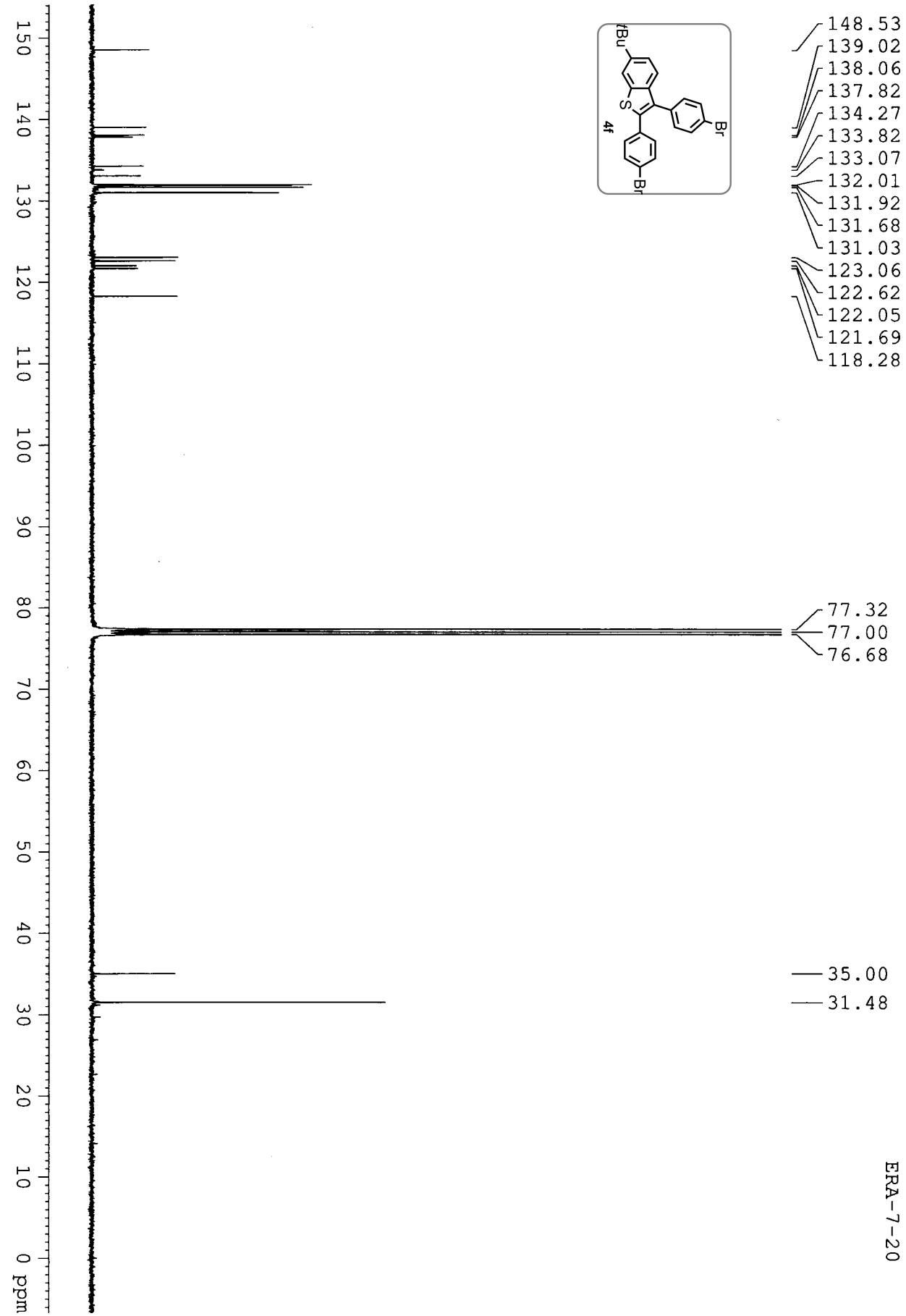
-113.77
-114.45

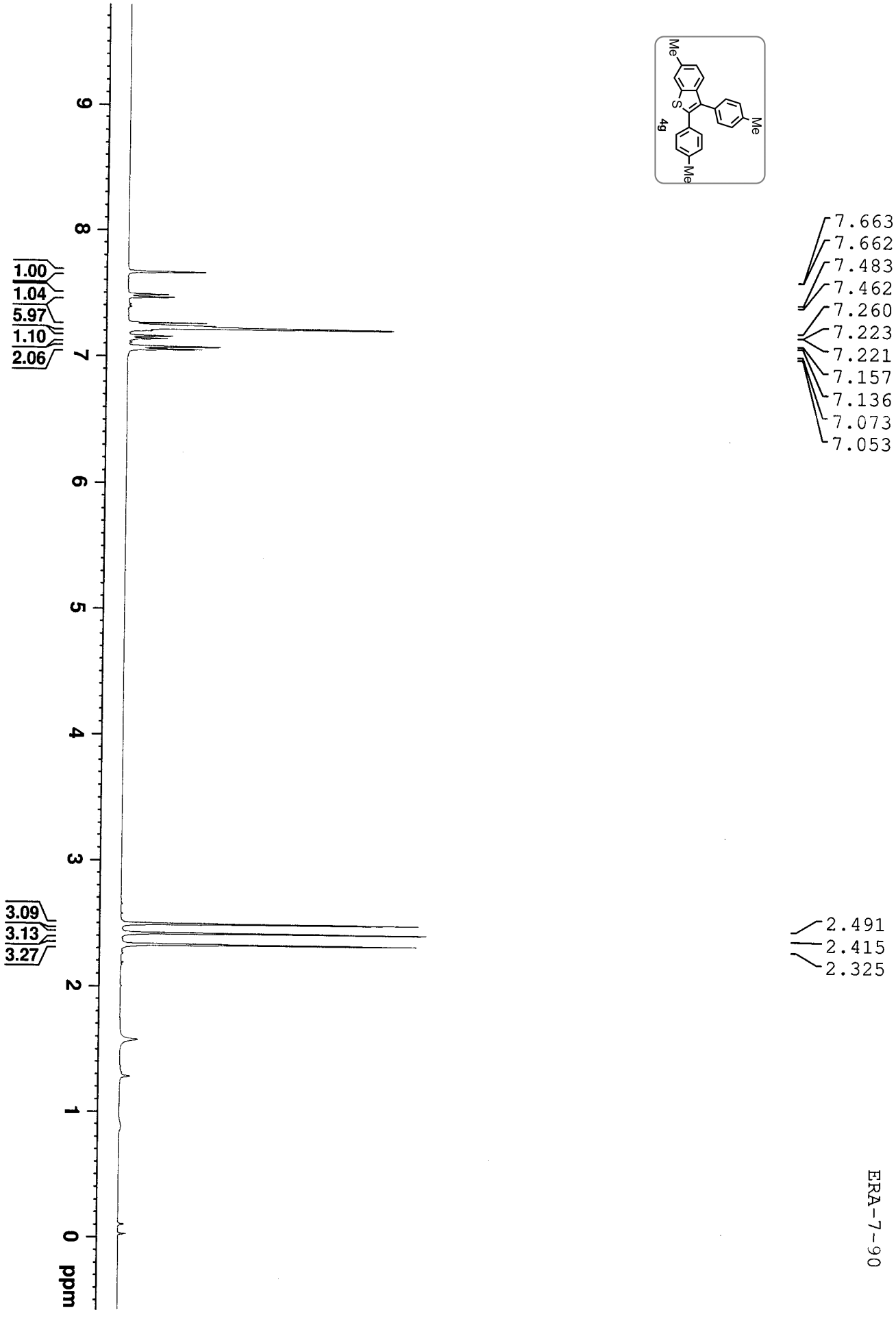
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 ppm

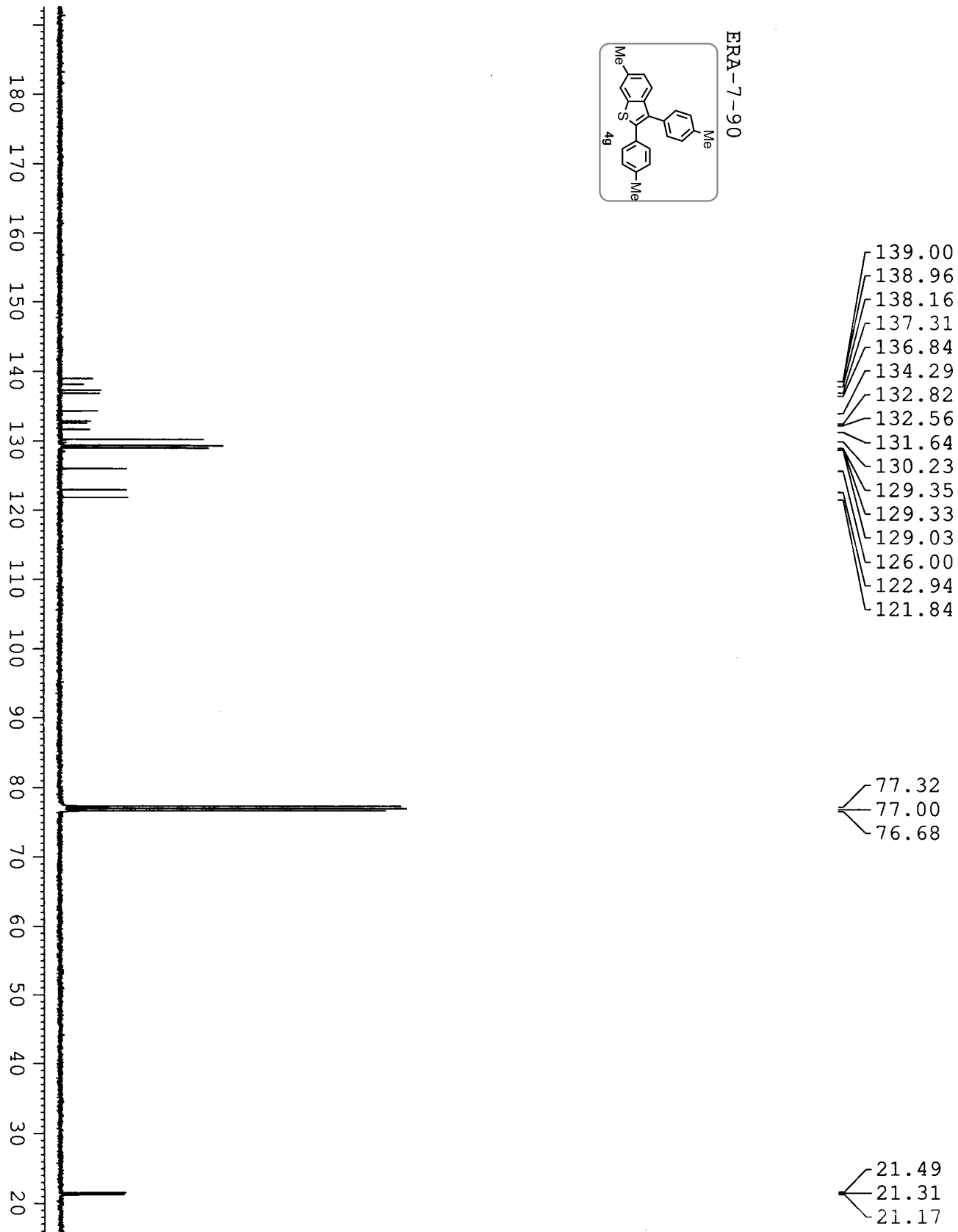

7.875
7.873
7.506
7.488
7.439
7.436
7.422
7.419
7.394
7.377
7.260
7.254
7.237
7.235
7.224
1.407
ERA-7-55
Cl
tBu
S
Cl
4e
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.12
1.26
2.24
6.14
9.42

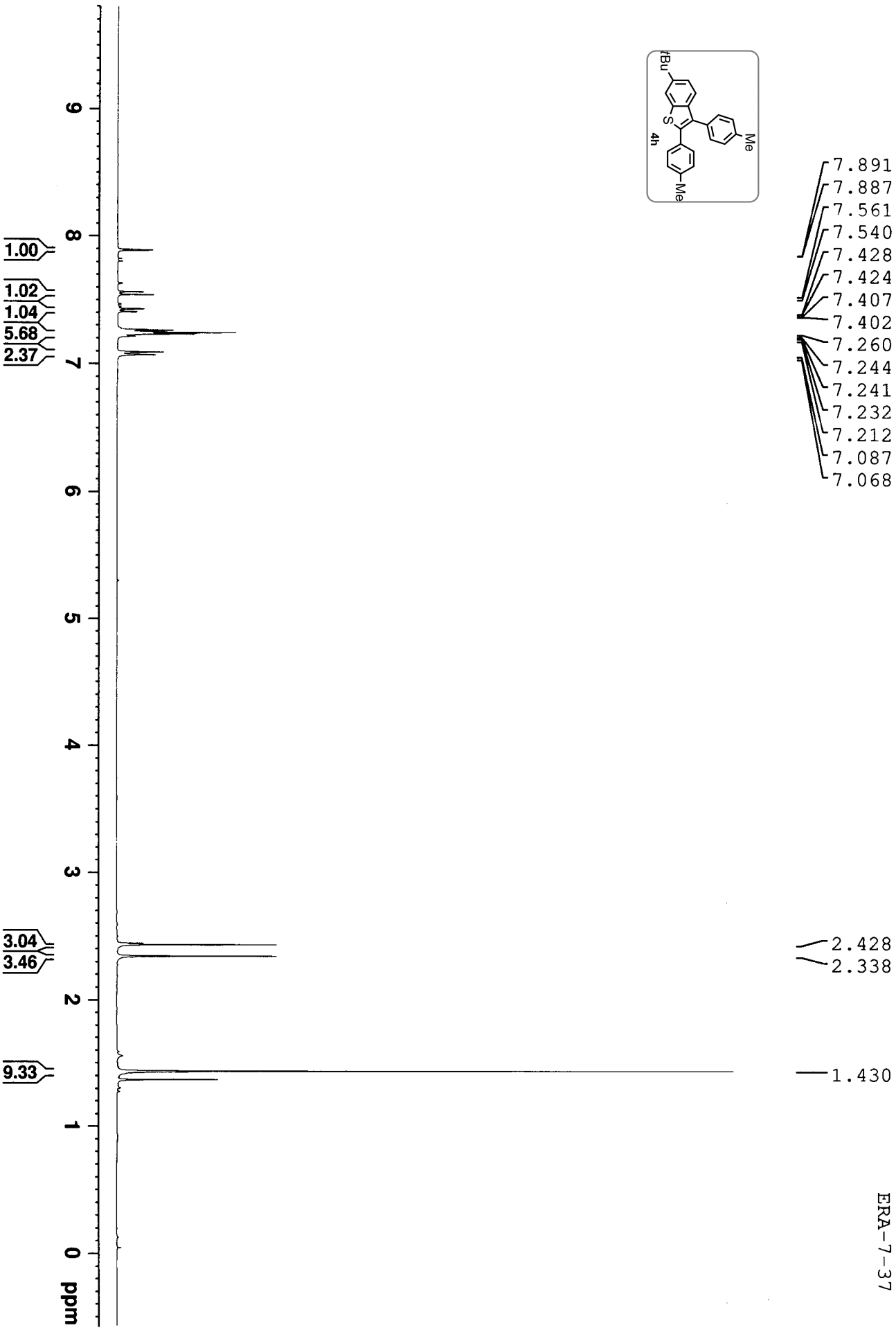

tBu
S
Cl
Cl
4e
148.51
139.03
138.15
137.84
133.83
133.51
132.65
132.03
131.62
130.75
129.05
128.71
123.03
122.64
118.28
77.32
77.00
76.68
34.99
31.49
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
ERA-7-55


0.92
1.98
1.14
3.11
3.95
9.00
1.406
7.868
7.549
7.529
7.503
7.482
7.435
7.408
7.387
7.260
7.196
7.175
7.165
7.144
tBu
S
Br
Br
4f
ppm
ERA-7-20


148.53
139.02
138.06
137.82
134.27
133.82
133.07
132.01
131.92
131.68
131.03
123.06
122.62
122.05
121.69
118.28
77.32
77.00
76.68
35.00
31.48
tBu
S
Br
Br
4f
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
ERA-7-20


Me
S
Me
Me
4g
7.663
7.662
7.483
7.462
7.260
7.223
7.221
7.157
7.136
7.073
7.053
2.491
2.415
2.325
1.00
1.04
5.97
1.10
2.06
3.09
3.13
3.27
9
8
7
6
5
4
3
2
1
0
ppm
ERA-7-90


ERA-7-90
4g
Me
Me
Me
S
139.00
138.96
138.16
137.31
136.84
134.29
132.82
132.56
131.64
130.23
129.35
129.33
129.03
126.00
122.94
121.84
77.32
77.00
76.68
21.49
21.31
21.17
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


tBu
S
4h
Me
Me
7.891
7.887
7.561
7.540
7.428
7.424
7.407
7.402
7.260
7.244
7.241
7.232
7.212
7.087
7.068
2.428
2.338
1.430
1.00
1.02
1.04
5.68
2.37
3.04
3.46
9.33
9
8
7
6
5
4
3
2
1
0
ppm
ERA-7-37

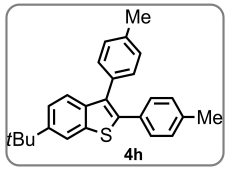
147.74
138.84
138.82
138.65
137.31
136.80
132.79
132.45
131.66
130.19
129.36
129.32
129.02
122.77
122.53
118.12

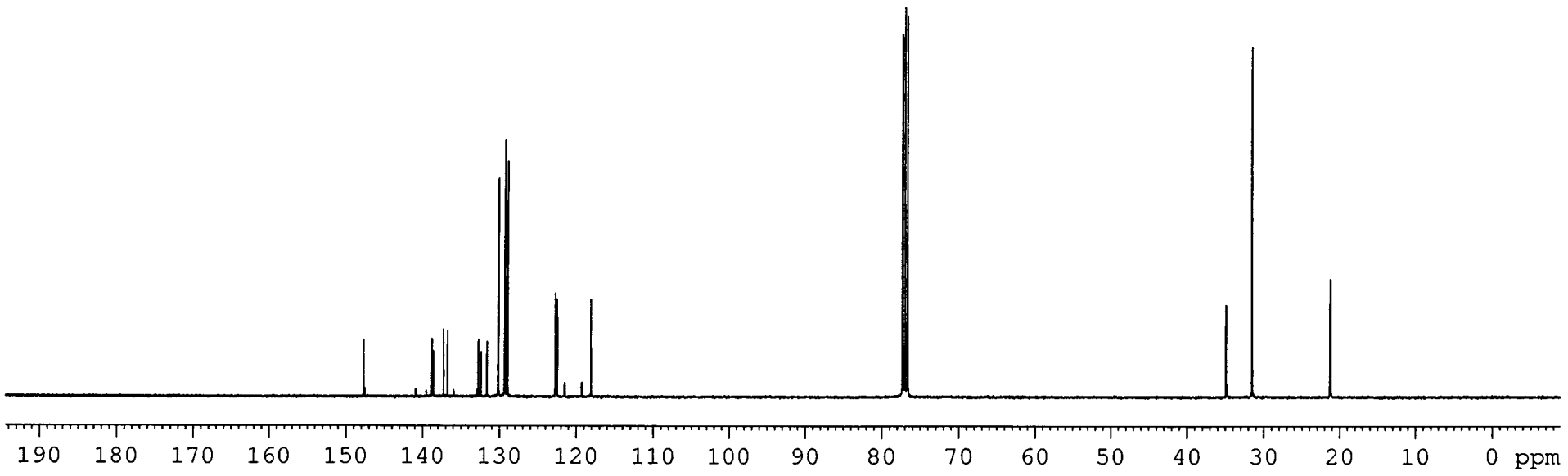
77.32
77.00
76.68

34.90
31.53

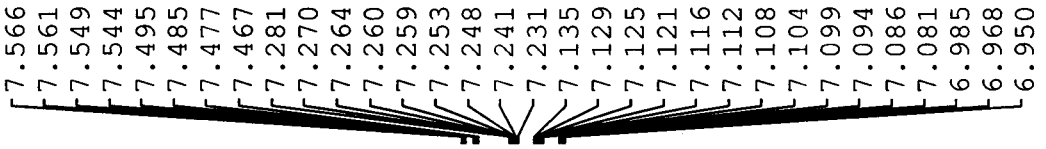
21.32
21.18

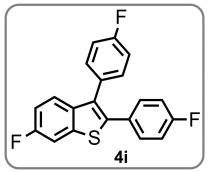
ERA-7-37

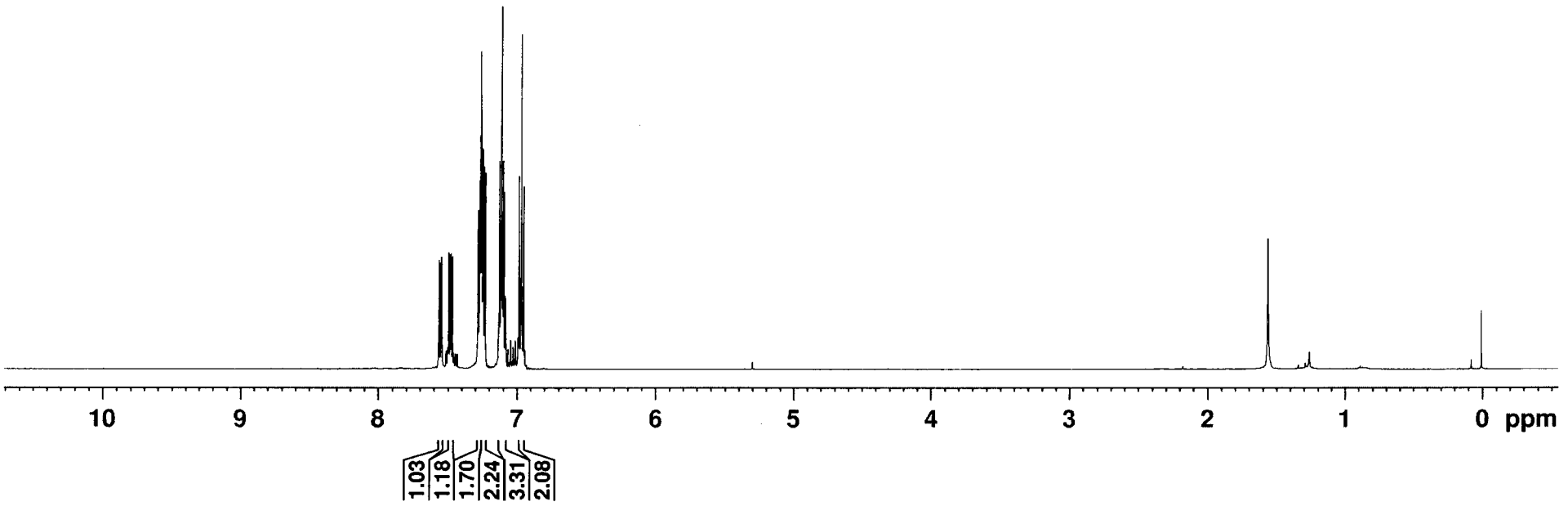


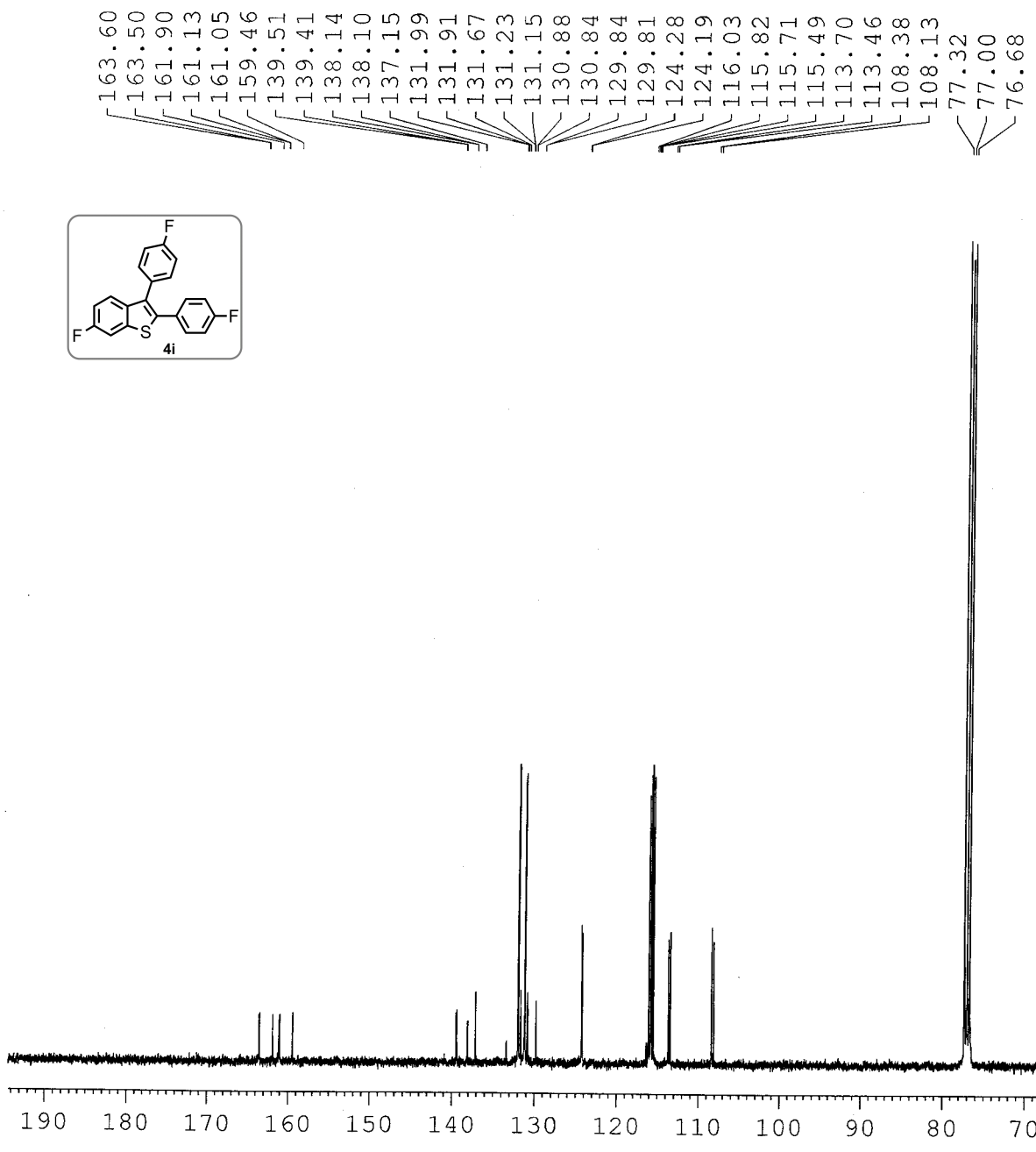


ERA -NA-14

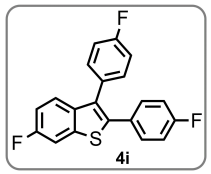

7.566
7.561
7.549
7.544
7.495
7.485
7.477
7.467
7.281
7.270
7.264
7.260
7.259
7.253
7.248
7.241
7.231
7.135
7.129
7.125
7.121
7.116
7.112
7.108
7.104
7.099
7.094
7.086
7.081
6.985
6.968
6.950


F
F
S
F
4i


10
9
8
7
6
5
4
3
2
1
0 ppm
1.03
1.18
1.70
2.24
3.31
2.08

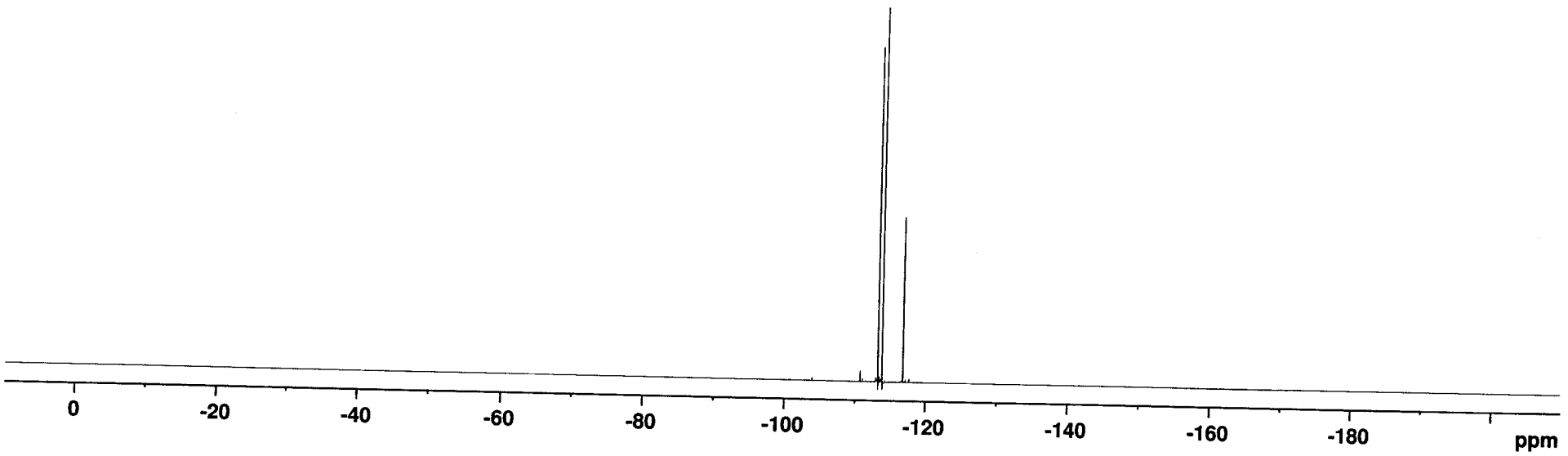

163.60
163.50
161.90
161.13
161.05
159.46
139.51
139.41
138.14
138.10
137.15
131.99
131.91
131.67
131.23
131.15
130.88
130.84
129.84
129.81
124.28
124.19
116.03
115.82
115.71
115.49
113.70
113.46
108.38
108.13
77.32
77.00
76.68
F
F
F
S
4i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

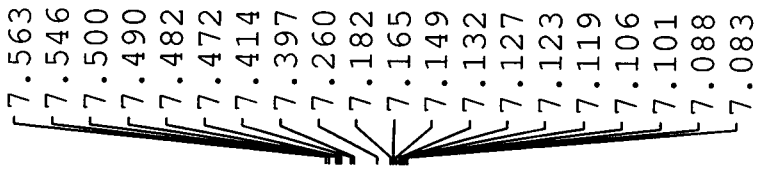
ERA-NA-14

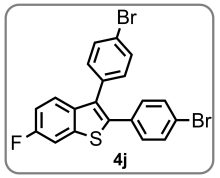


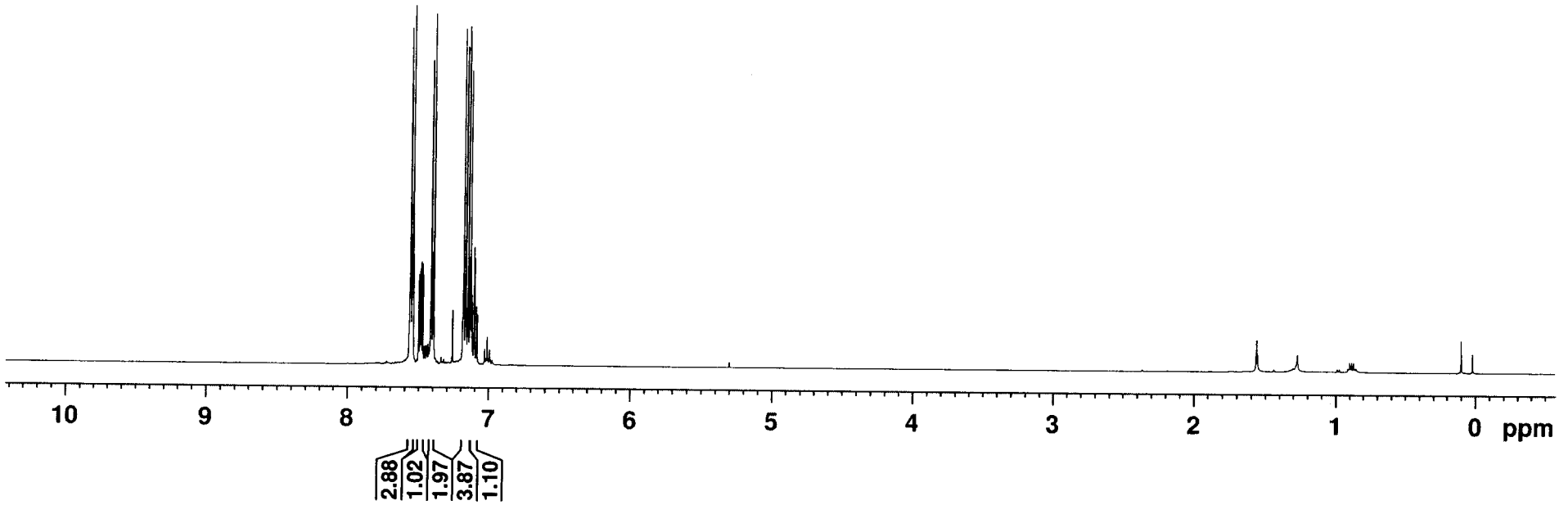
-113.26
-113.89
-116.84

ERA-NA-14-F19



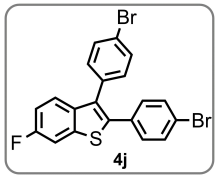

7.563
7.546
7.500
7.490
7.482
7.472
7.414
7.397
7.260
7.182
7.165
7.149
7.132
7.127
7.123
7.119
7.106
7.101
7.088
7.083


Br
F
S
Br
4j

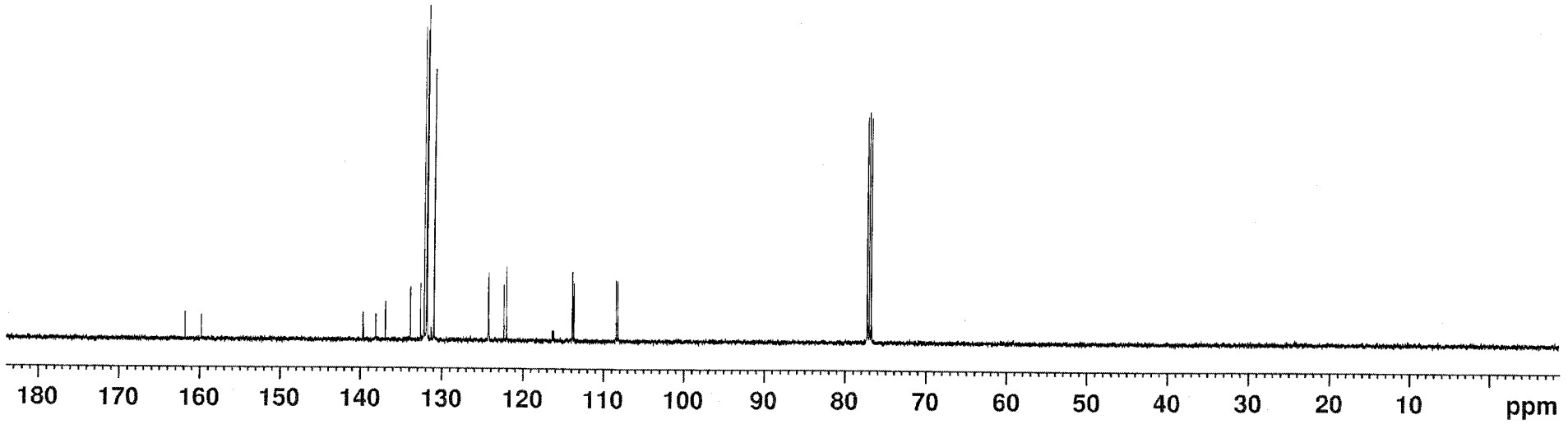

10
9
8
7
6
5
4
3
2
1
0 ppm
2.88
1.02
1.97
3.87
1.10

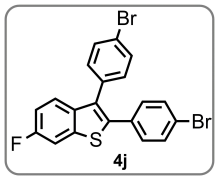
161.77
159.82
139.71
139.62
138.12
138.09
136.89
133.83
132.59
132.16
131.88
131.78
130.93
124.31
124.24
122.36
122.03
113.84
113.65
108.41
108.21

77.25
77.00
76.75



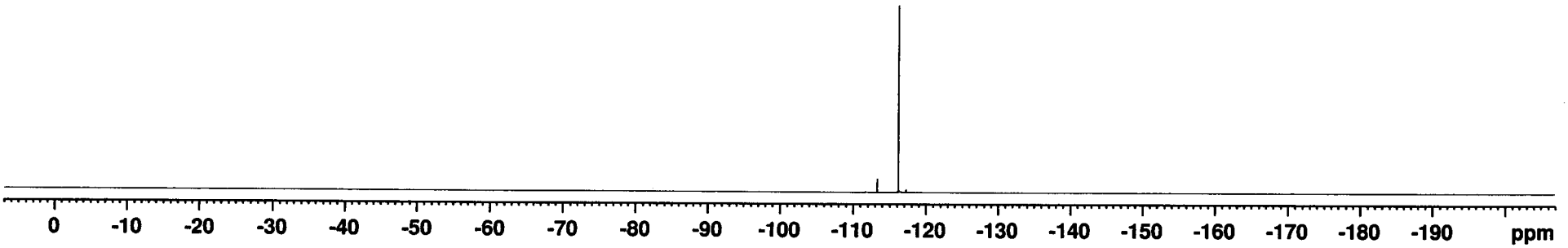
4j

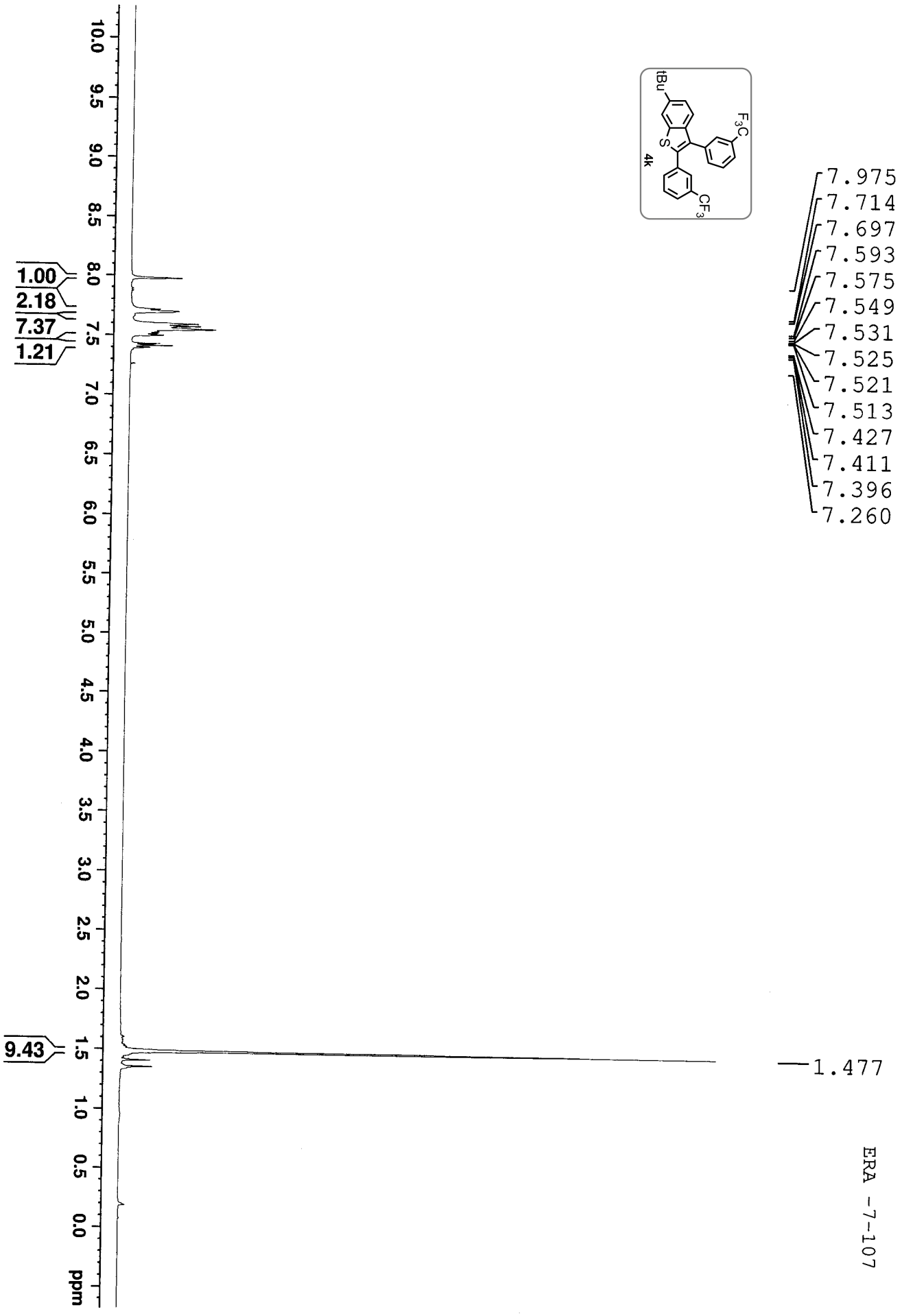




-116.26

ERA-7-124

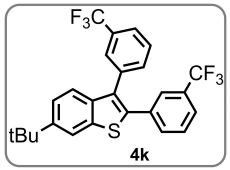


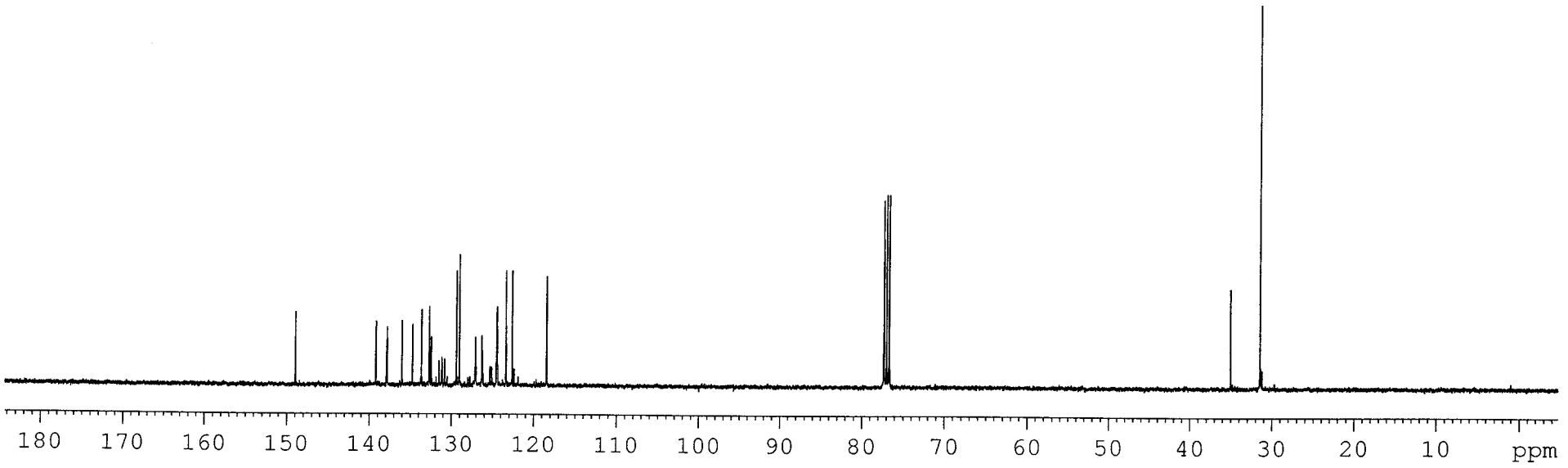

tBu
S
4k
F3C
CF3
7.975
7.714
7.697
7.593
7.575
7.549
7.531
7.525
7.521
7.513
7.427
7.411
7.396
7.260
1.00
2.18
7.37
1.21
9.43
1.477
ERA -7-107
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

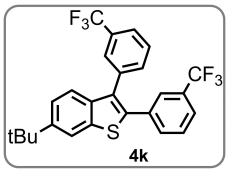
148.95
139.21
137.89
137.82
135.99
134.74
133.65
132.70
132.44
131.82
131.50
131.46
131.18
131.14
130.86
130.82
130.49
129.37
129.02
127.08
127.05
126.28
126.25
125.30
125.08
124.51
124.47
124.43
123.37
122.64
118.41
77.32
77.00
76.68

35.05
31.45

ERA-7-107

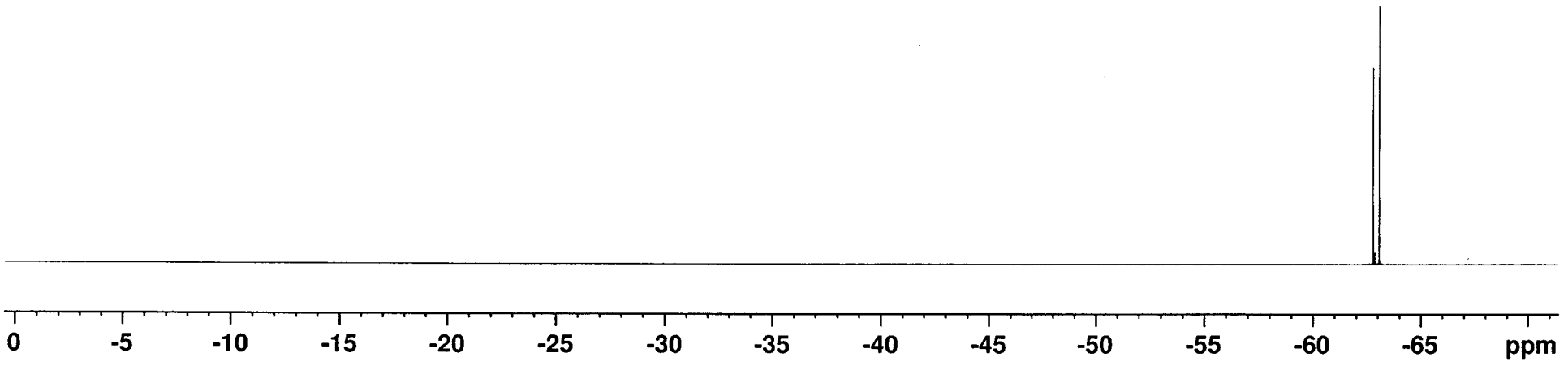


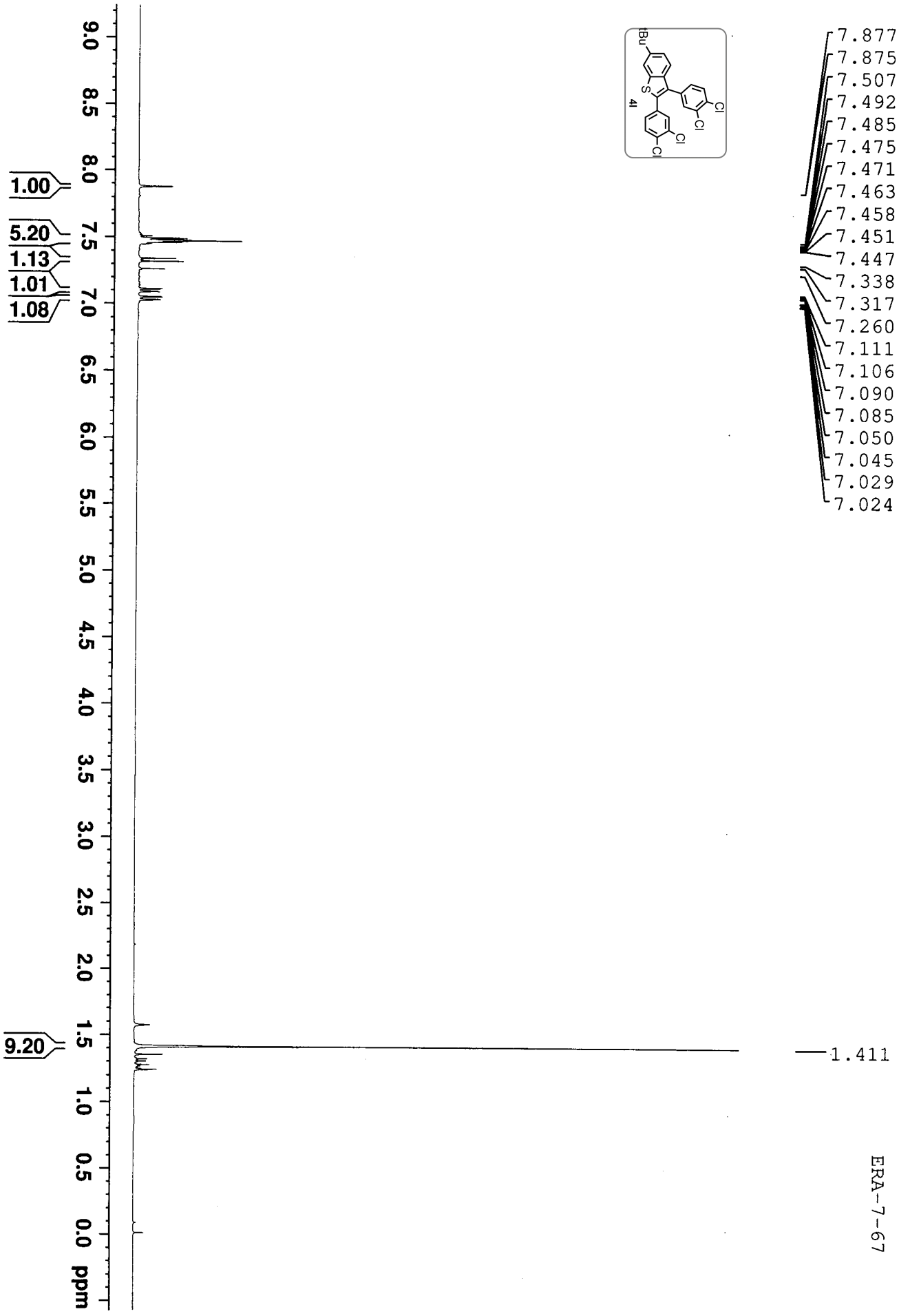


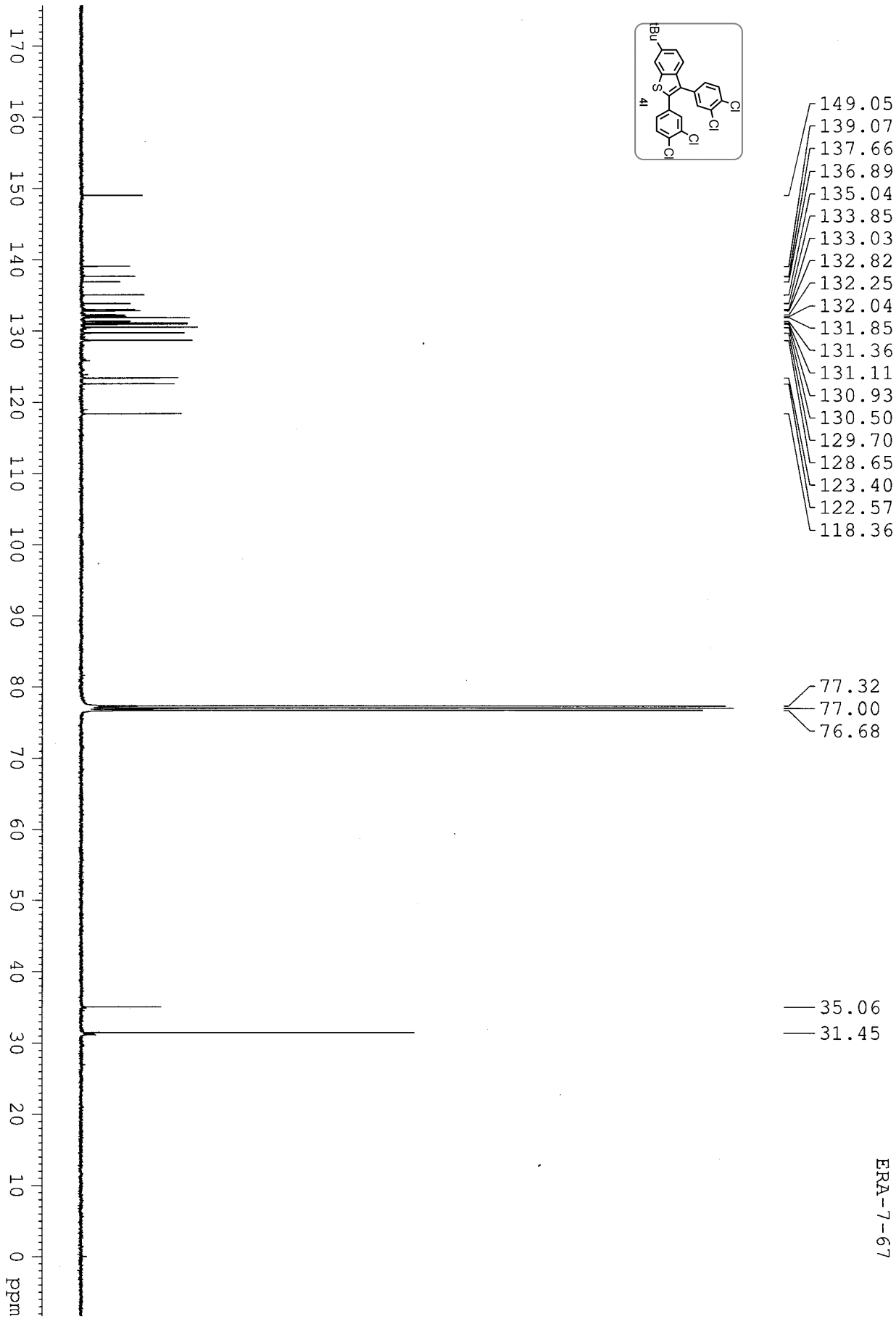


ERA-7-107

-62.78
-63.06

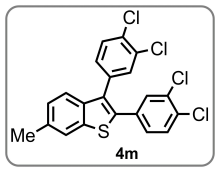



7.877
7.875
7.507
7.492
7.485
7.475
7.471
7.463
7.458
7.451
7.447
7.338
7.317
7.260
7.111
7.106
7.090
7.085
7.050
7.045
7.029
7.024
1.411
1.00
5.20
1.13
1.01
1.08
9.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
ERA-7-67

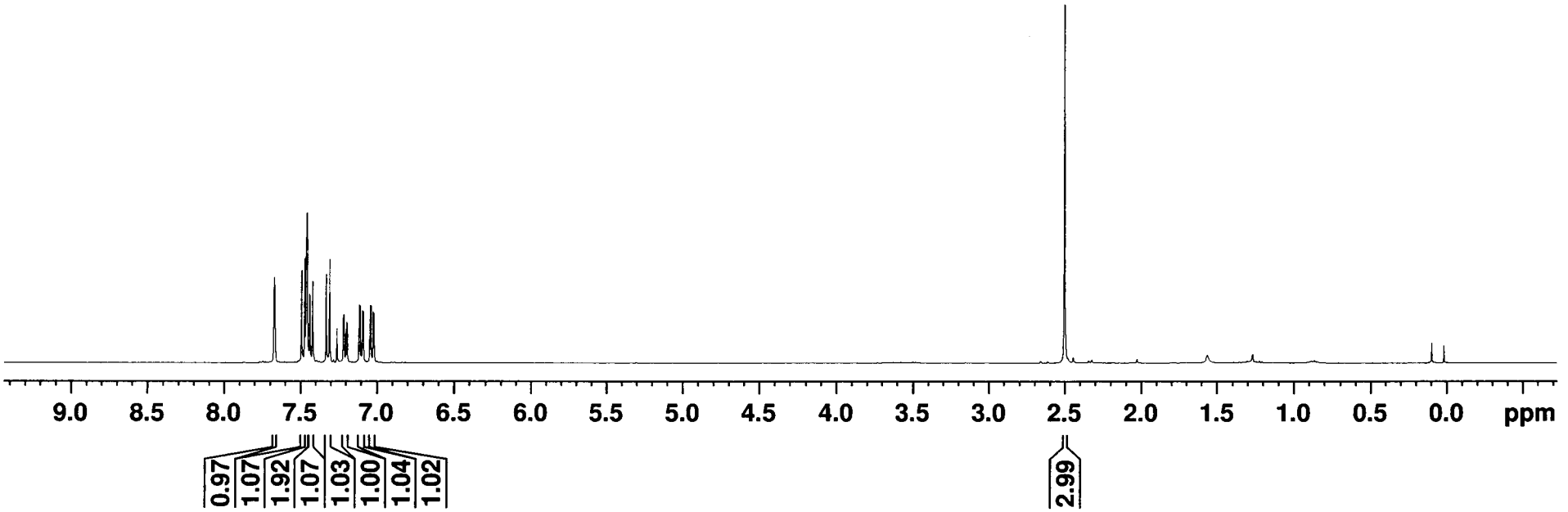

tBu
S
4f
Cl
Cl
Cl
149.05
139.07
137.66
136.89
135.04
133.85
133.03
132.82
132.25
132.04
131.85
131.36
131.11
130.93
130.50
129.70
128.65
123.40
122.57
118.36
77.32
77.00
76.68
35.06
31.45
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
ERA-7-67

7.671
7.494
7.473
7.464
7.461
7.460
7.457
7.441
7.420
7.330
7.309
7.260
7.217
7.215
7.196
7.194
7.114
7.109
7.094
7.089
7.044
7.039
7.023
7.018

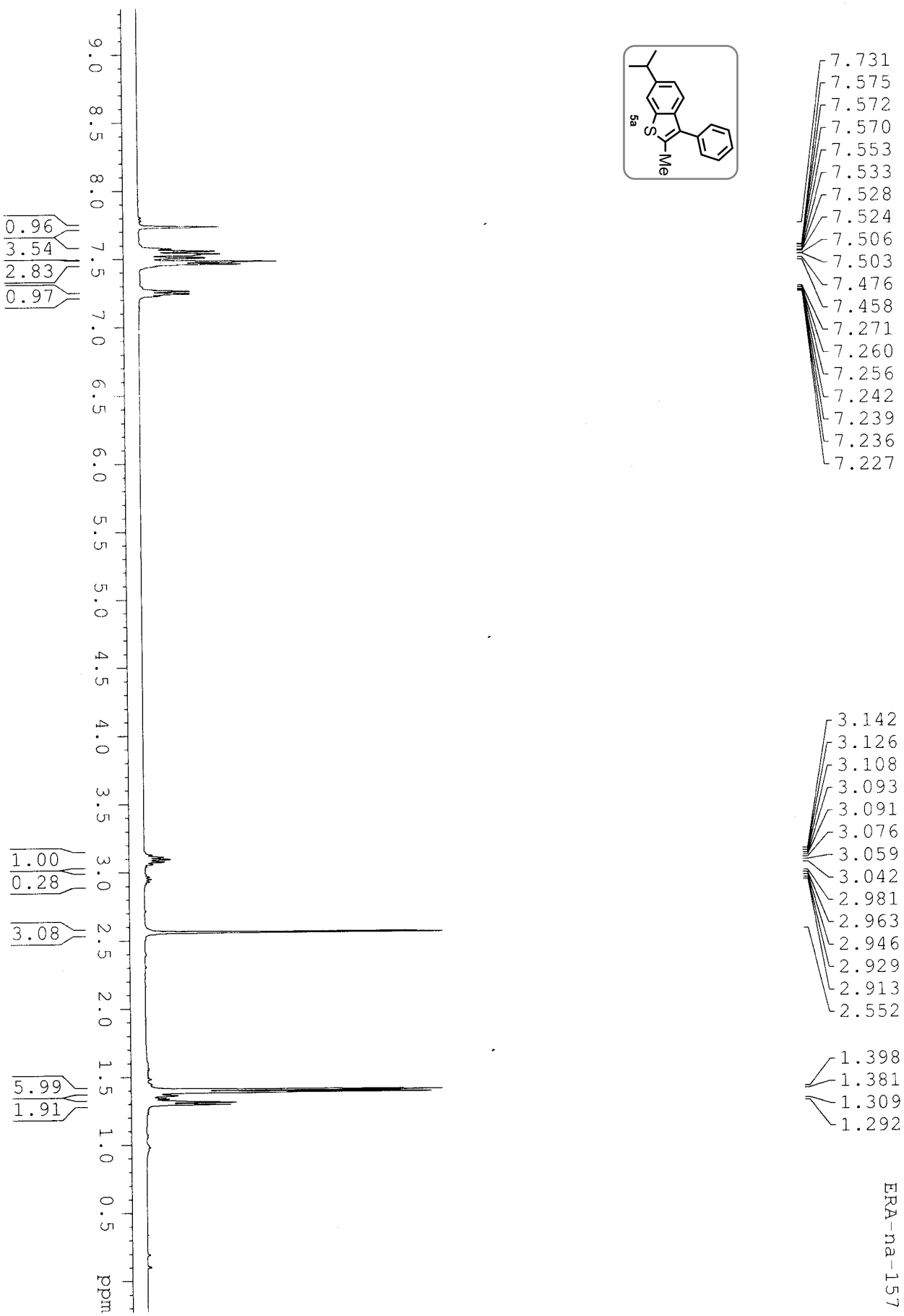
2.503

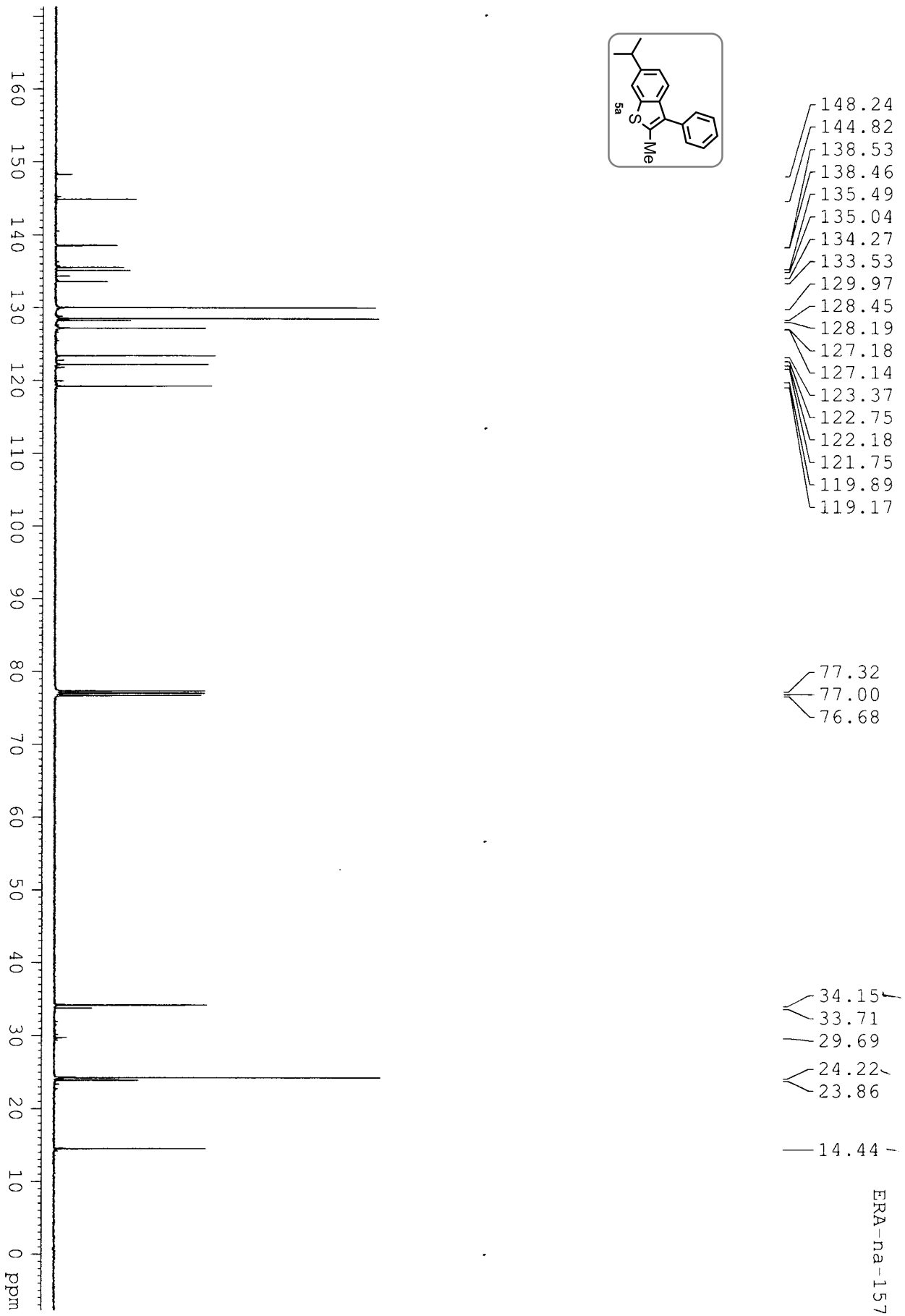


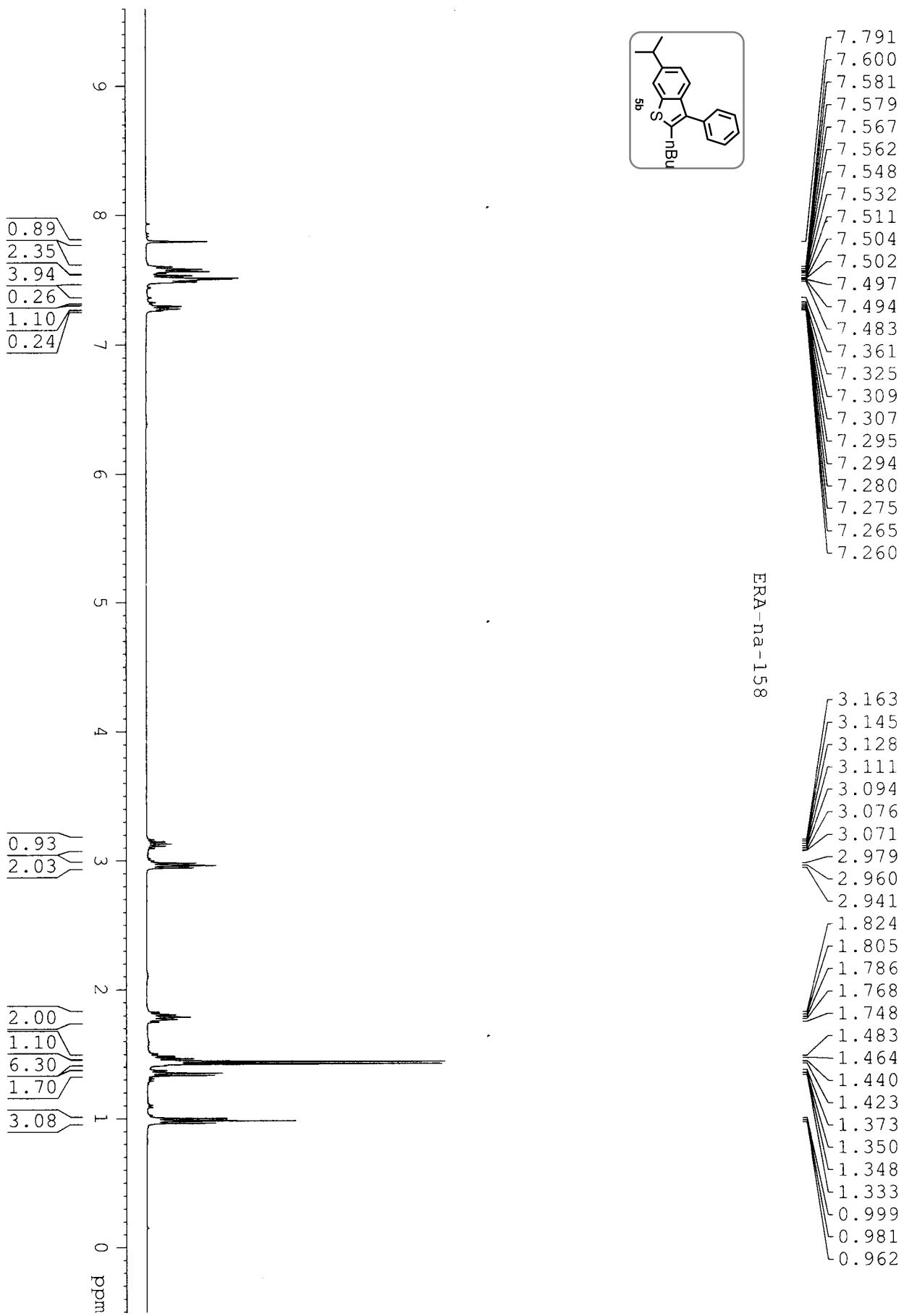
4m



Me
S
Cl
Cl
Cl
4m
139.11
137.79
136.41
135.59
135.04
133.81
133.03
132.81
132.22
132.05
131.87
131.45
131.09
130.92
130.47
129.72
128.61
126.80
122.69
122.07
77.32
77.00
76.68
21.54
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
ERA-7-74


7.731
7.575
7.572
7.570
7.553
7.533
7.528
7.524
7.506
7.503
7.476
7.458
7.271
7.260
7.256
7.242
7.239
7.236
7.227
3.142
3.126
3.108
3.093
3.091
3.076
3.059
3.042
2.981
2.963
2.946
2.929
2.913
2.552
1.398
1.381
1.309
1.292
5a
S
Me
0.96
3.54
2.83
0.97
1.00
0.28
3.08
5.99
1.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
ERA-na-157

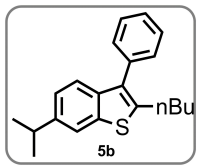

5a
S
Me
148.24
144.82
138.53
138.46
135.49
135.04
134.27
133.53
129.97
128.45
128.19
127.18
127.14
123.37
122.75
122.18
121.75
119.89
119.17
77.32
77.00
76.68
34.15
33.71
29.69
24.22
23.86
14.44
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
ERA-na-157


ERA-na-158
7.791
7.600
7.581
7.579
7.567
7.562
7.548
7.532
7.511
7.504
7.502
7.497
7.494
7.483
7.361
7.325
7.309
7.307
7.295
7.294
7.280
7.275
7.265
7.260
3.163
3.145
3.128
3.111
3.094
3.076
3.071
2.979
2.960
2.941
1.824
1.805
1.786
1.768
1.748
1.483
1.464
1.440
1.423
1.373
1.350
1.348
1.333
0.999
0.981
0.962
0.89
2.35
3.94
0.26
1.10
0.24
0.93
2.03
2.00
1.10
6.30
1.70
3.08
ppm

148.20
144.80
141.51
138.65
138.45
135.77
134.30
133.23
130.02
128.43
128.17
127.14
126.09
123.31
122.29
121.89
119.27

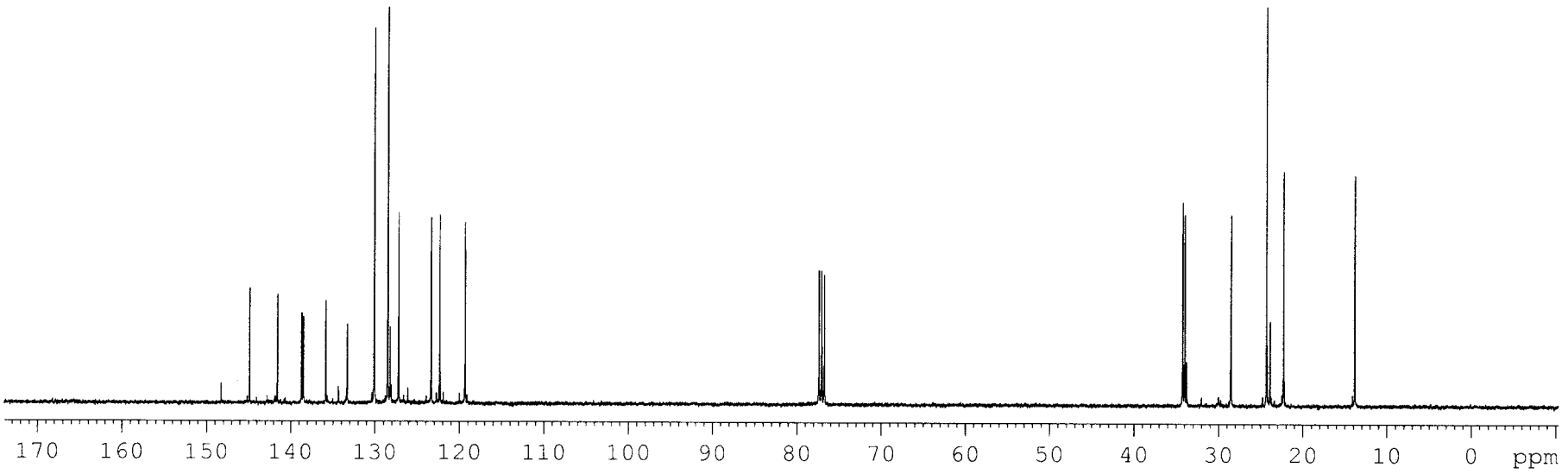
77.32
77.00
76.68

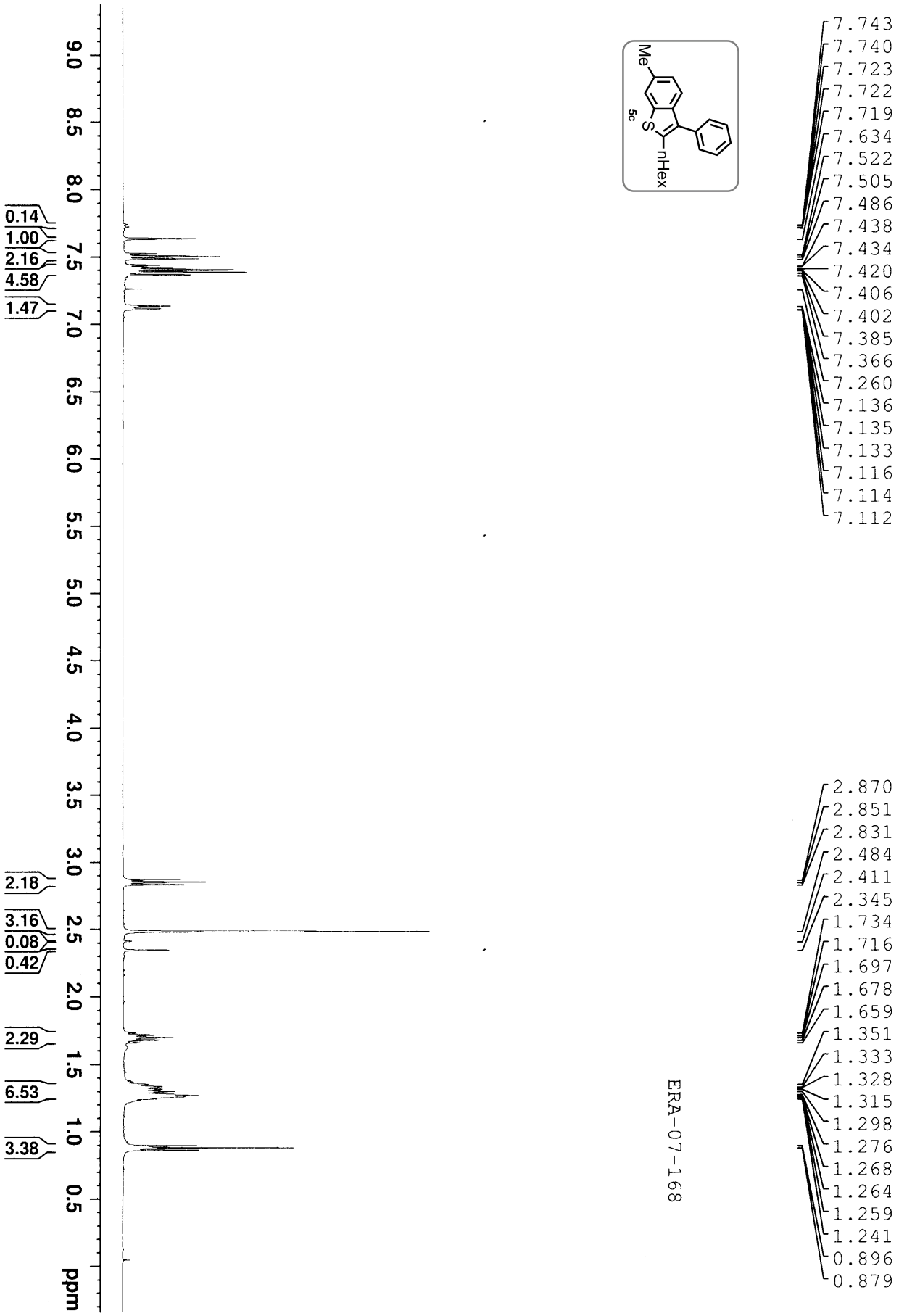
34.18
33.92
33.71
28.47
24.24
23.86
22.24
13.77



5b

ERA-na-158

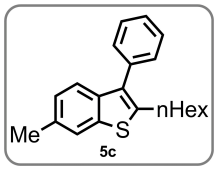



Me
5c
S
nHex
7.743
7.740
7.723
7.722
7.719
7.634
7.522
7.505
7.486
7.438
7.434
7.420
7.406
7.402
7.385
7.366
7.260
7.136
7.135
7.133
7.116
7.114
7.112
2.870
2.851
2.831
2.484
2.411
2.345
1.734
1.716
1.697
1.678
1.659
1.351
1.333
1.328
1.315
1.298
1.276
1.268
1.264
1.259
1.241
0.896
0.879
0.14
1.00
2.16
4.58
1.47
2.18
3.16
0.08
0.42
2.29
6.53
3.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
ERA-07-168

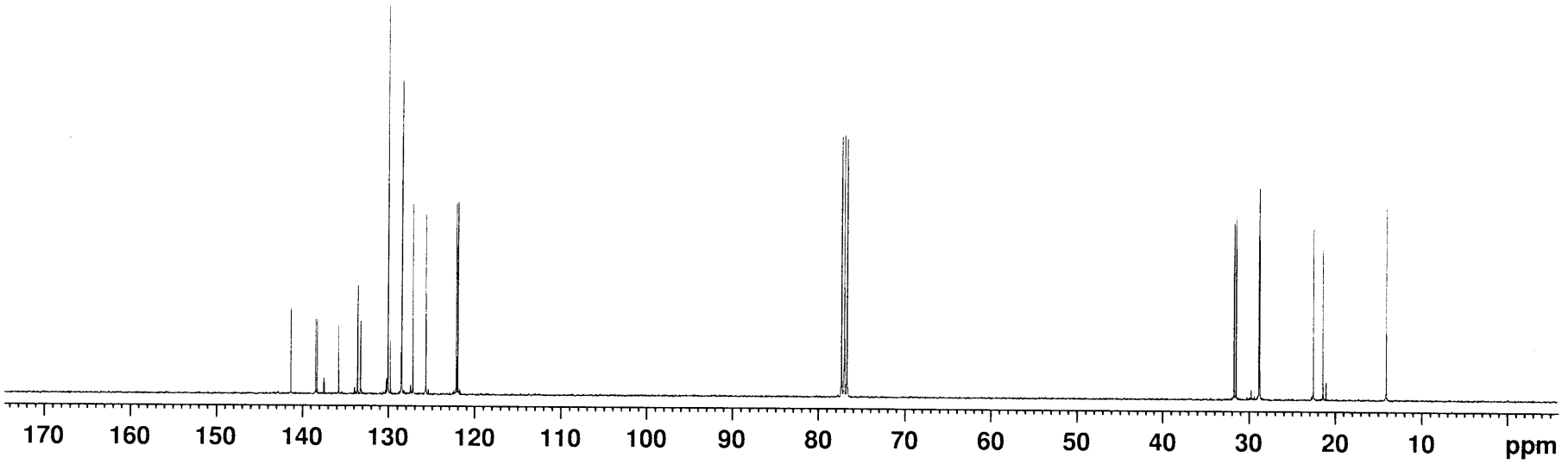
141.30
138.44
138.26
137.46
137.40
135.77
133.90
133.56
133.20
130.20
130.11
130.04
129.76
128.52
128.44
127.15
125.67
122.14
121.93

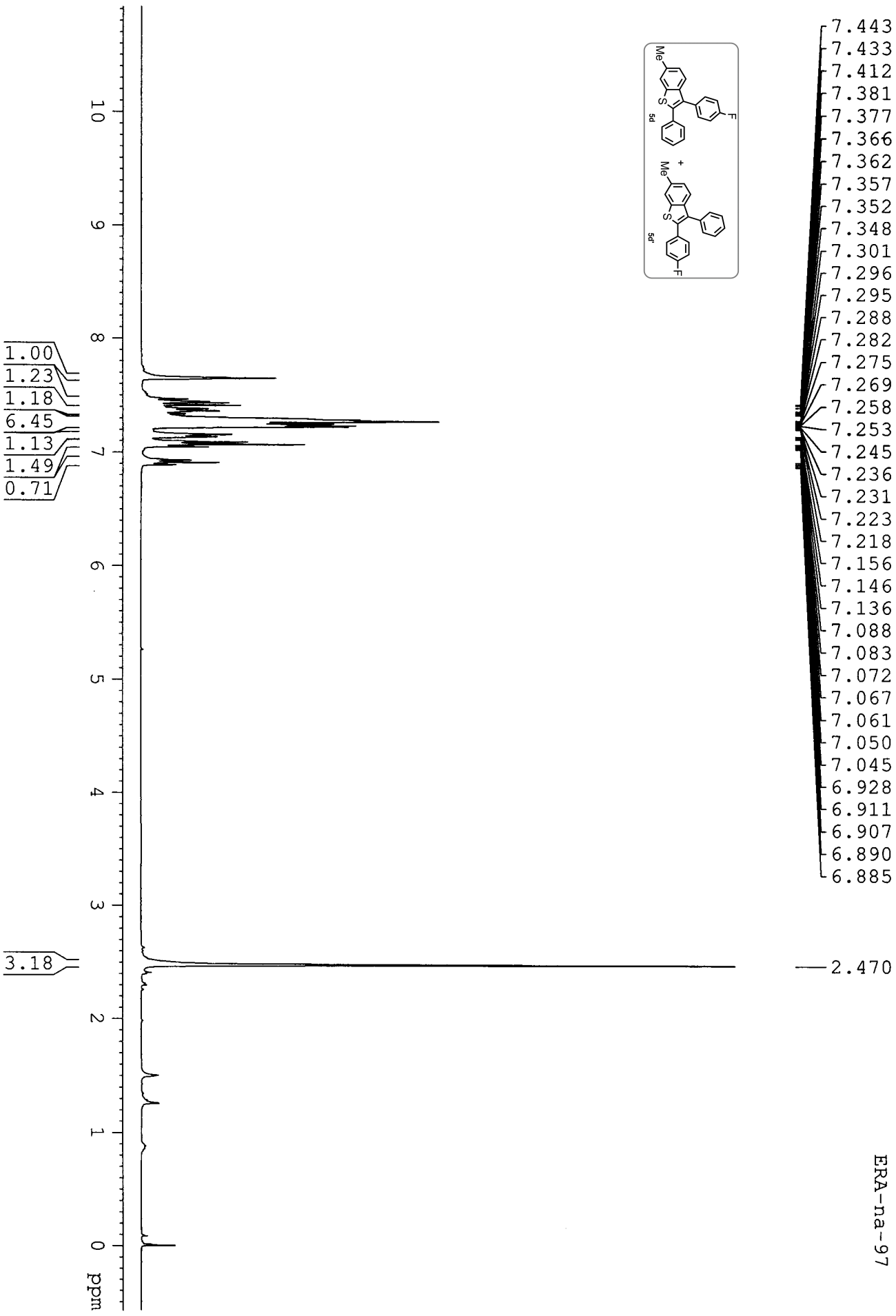
77.32
77.00
76.68

31.69
31.47
28.80
28.71
22.51
21.40
21.03
14.02



ERA-07-168

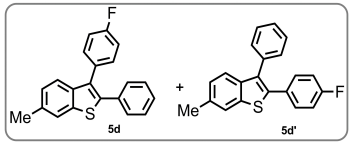


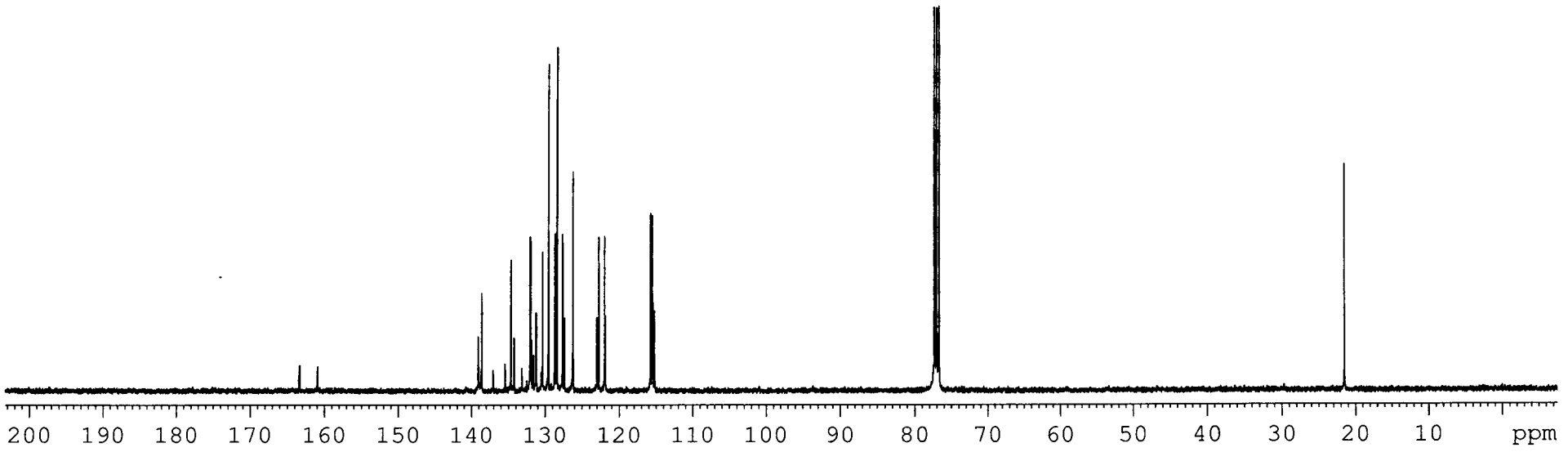

7.443
7.433
7.412
7.381
7.377
7.366
7.362
7.357
7.352
7.348
7.301
7.296
7.295
7.288
7.282
7.275
7.269
7.258
7.253
7.245
7.236
7.231
7.223
7.218
7.156
7.146
7.136
7.088
7.083
7.072
7.067
7.061
7.050
7.045
6.928
6.911
6.907
6.890
6.885
2.470
1.00
1.23
1.18
6.45
1.13
1.49
0.71
3.18
Me
S
5d
F
Me
+
S
5d'
F
10
9
8
7
6
5
4
3
2
1
0
ppm
ERA-na-97

ERA-na-97

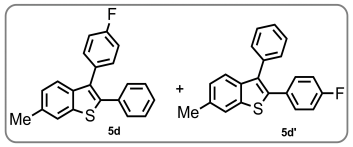
163.43
163.36
160.96
160.91
139.10
138.99
138.61
137.07
135.47
134.65
134.22
133.14
132.04
131.96
131.86
131.59
131.24
131.16
130.35
129.54
128.68
128.38
127.65
127.40
126.24
123.00
122.74
121.96
121.88
115.76
115.55
115.44
115.23
77.32
77.00
76.68

21.49

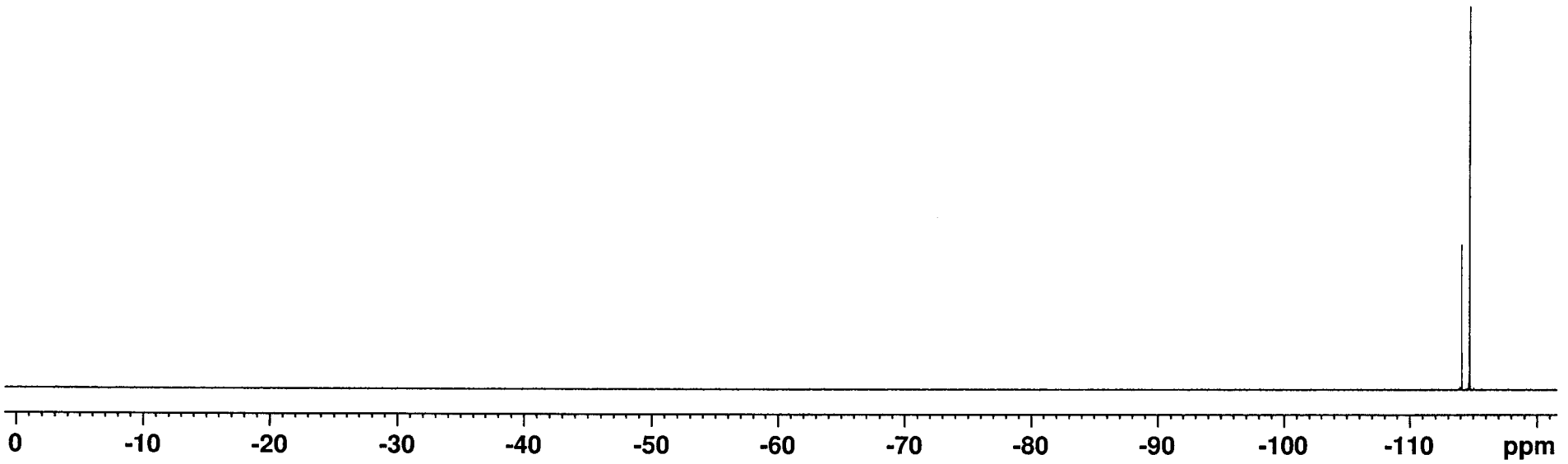




ERA-7-97



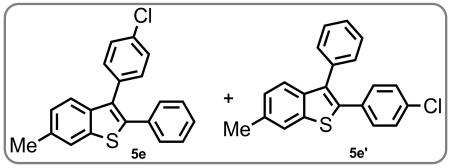
-114.08
-114.70

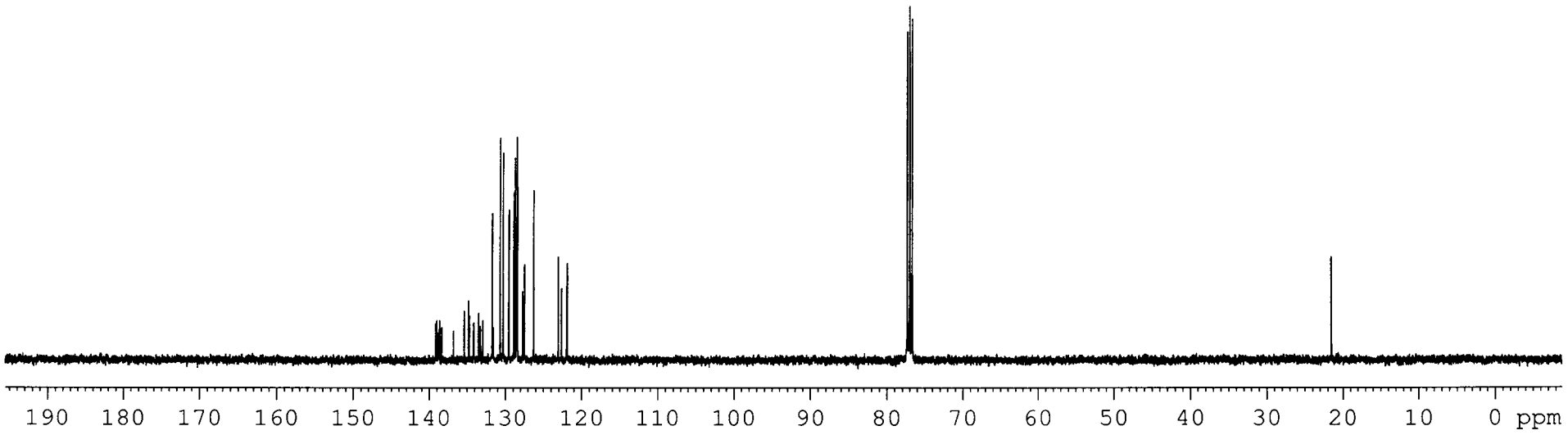


7.646
7.461
7.440
7.416
7.391
7.372
7.364
7.359
7.348
7.338
7.302
7.298
7.286
7.282
7.278
7.273
7.253
7.248
7.235
7.232
7.199
7.189
7.167
7.153
7.133
Me
S
5e
Cl
+
Me
S
5e'
Cl
1.00
0.93
3.00
2.01
2.52
1.91
1.25
3.13
2.471
9
8
7
6
5
4
3
2
1
0
ppm
ERA-na-98

139.16
139.05
138.84
138.66
138.37
136.81
135.39
134.84
134.72
134.16
134.08
133.53
133.50
133.26
132.93
131.73
131.61
130.70
130.30
129.56
128.90
128.74
128.54
128.44
127.74
127.50
126.30
123.08
122.67
121.97
121.90
77.32
77.00
76.68

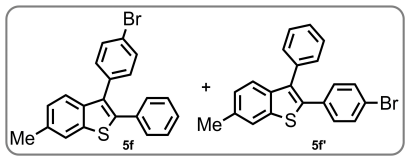
21.51
21.50

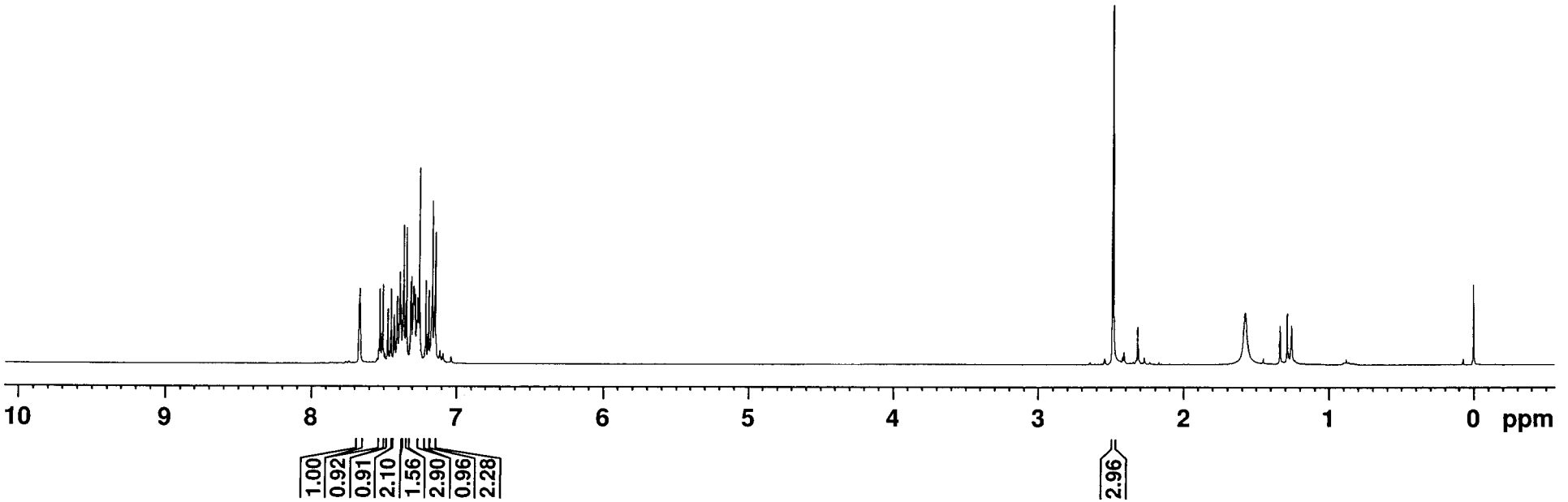


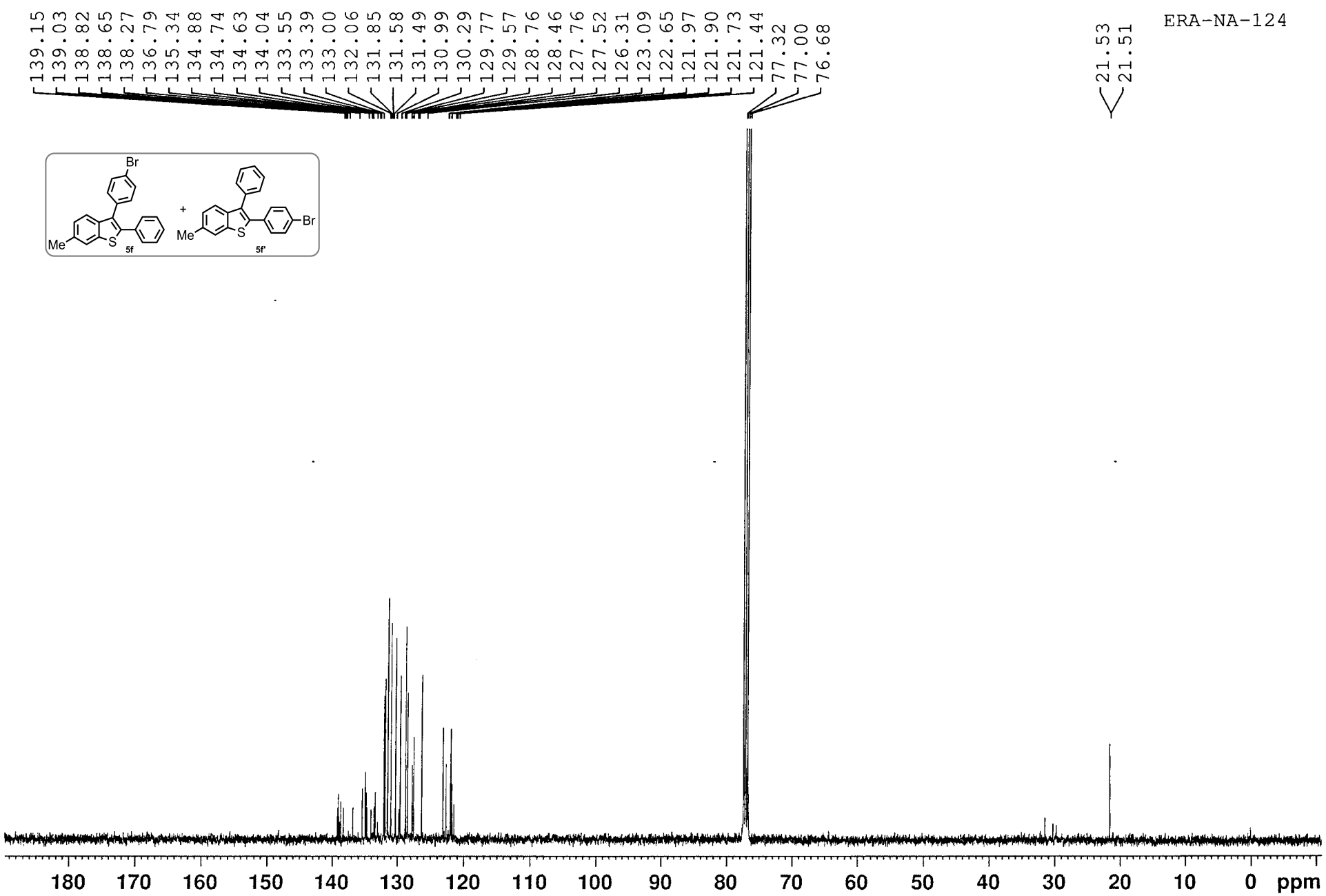


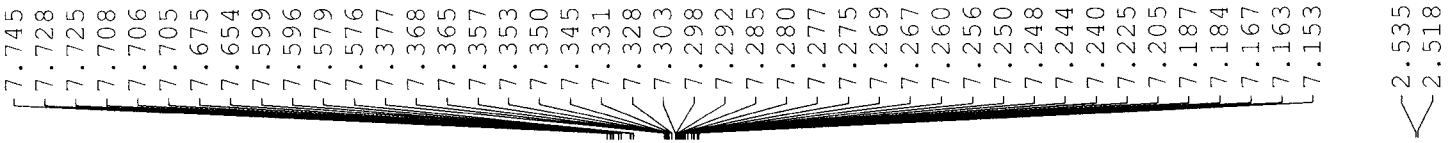
7.665
7.527
7.506
7.472
7.450
7.428
7.408
7.404
7.393
7.390
7.382
7.377
7.365
7.344
7.314
7.310
7.298
7.294
7.290
7.288
7.283
7.268
7.266
7.254
7.249
7.210
7.189
7.166
7.144

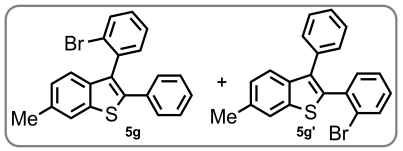
2.486

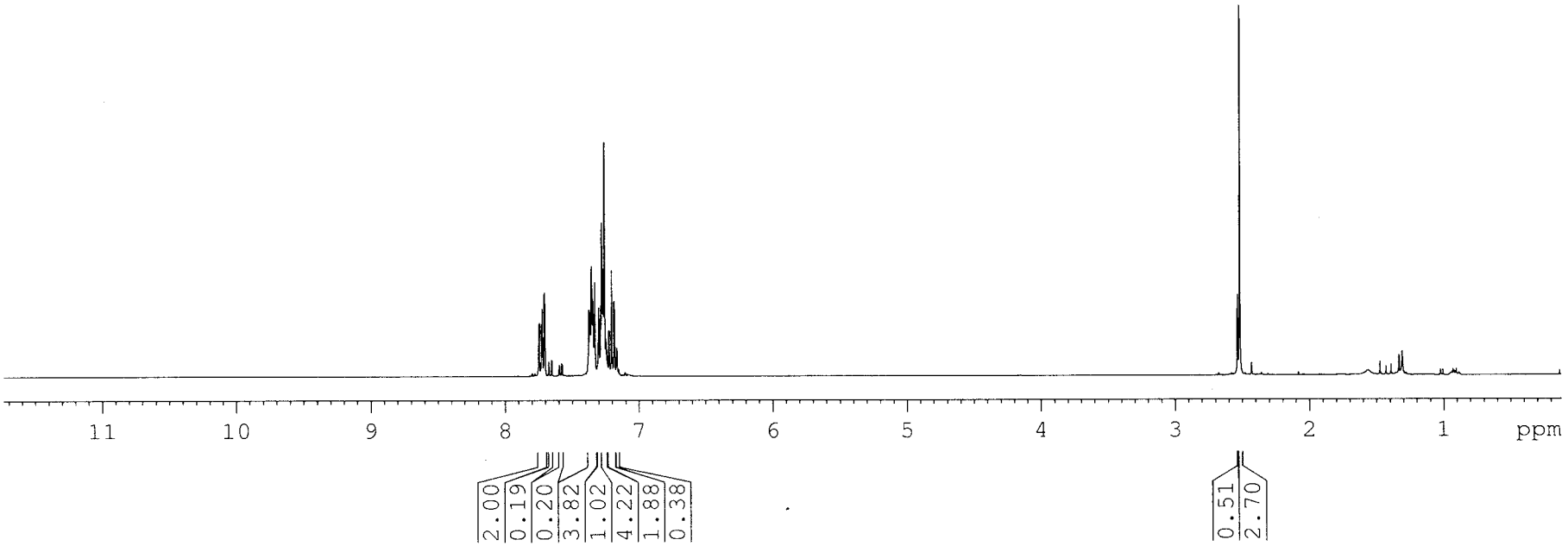





ERA-NA-124
139.15
139.03
138.82
138.65
138.27
136.79
135.34
134.88
134.74
134.63
134.04
133.55
133.39
133.00
132.06
131.85
131.58
131.49
130.99
130.29
129.77
129.57
128.76
128.46
127.76
127.52
126.31
123.09
122.65
121.97
121.90
121.73
121.44
77.32
77.00
76.68
21.53
21.51
Br
Me
S
5f
+
Me
S
Br
5f'
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.745
7.728
7.725
7.708
7.706
7.705
7.675
7.654
7.599
7.596
7.579
7.576
7.377
7.368
7.365
7.357
7.353
7.350
7.345
7.331
7.328
7.303
7.298
7.292
7.285
7.280
7.277
7.275
7.269
7.267
7.260
7.256
7.250
7.248
7.244
7.240
7.225
7.205
7.187
7.184
7.167
7.163
7.153
2.535
2.518

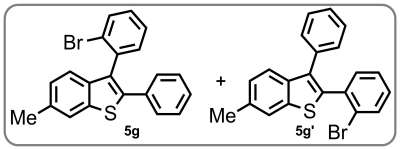

Br
Me
S
5g
+
Me
S
5g'
Br

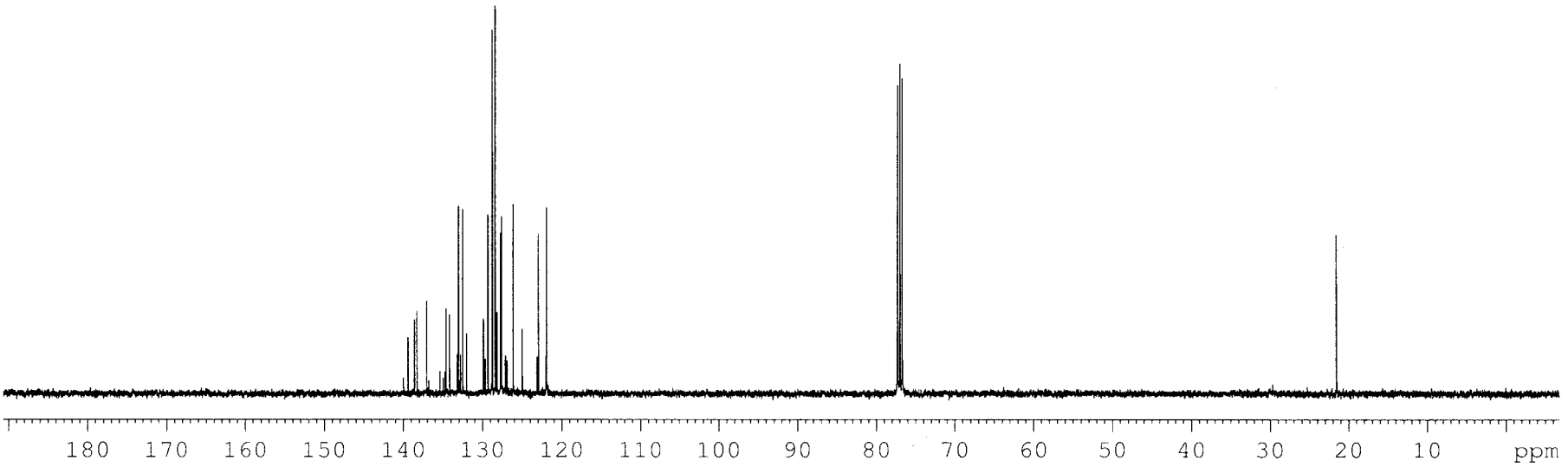

11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
0.19
0.20
3.82
1.02
4.22
1.88
0.38
0.51
2.70

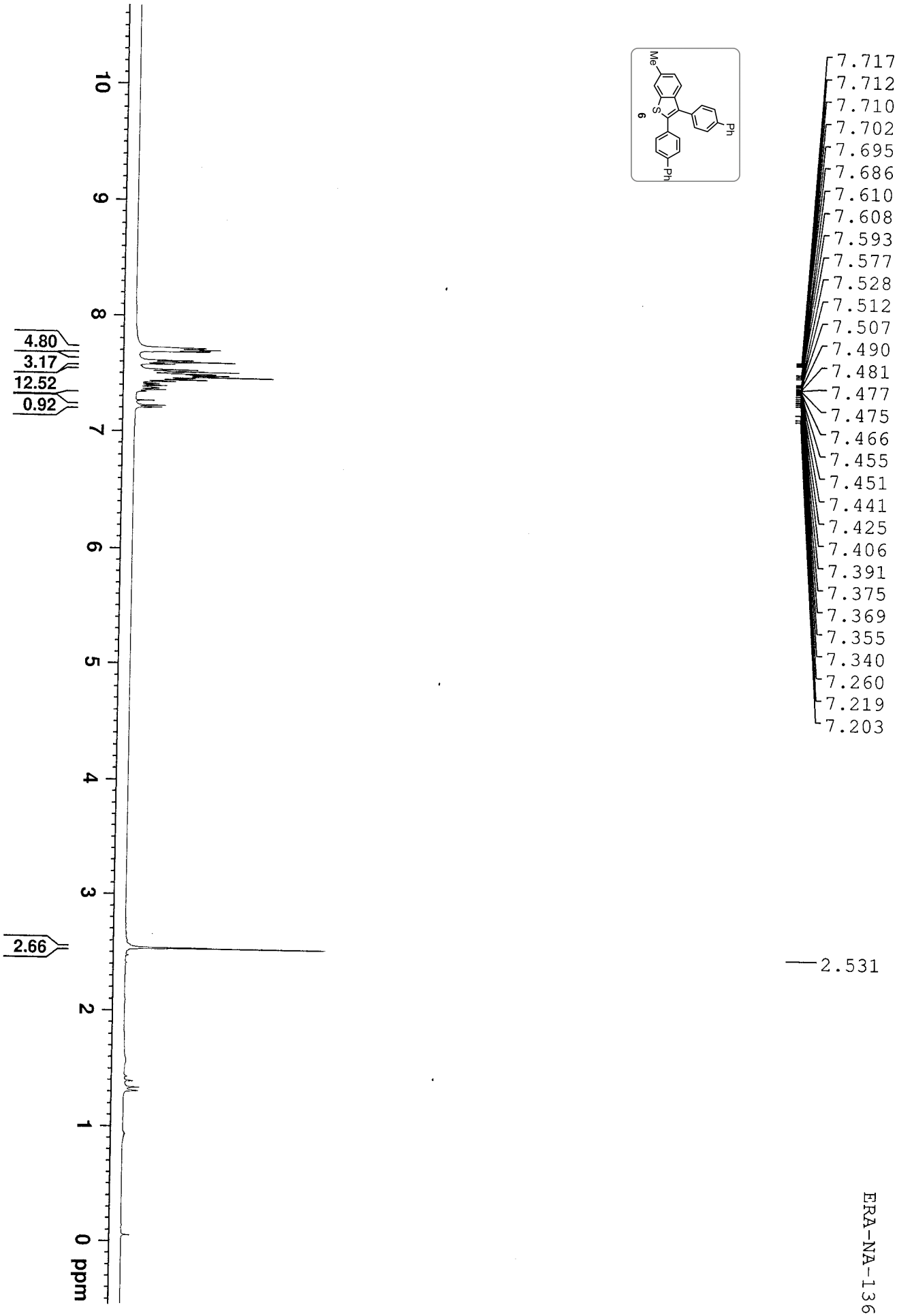
ERA-na-153

139.98
139.41
138.61
138.31
137.08
136.82
135.43
134.98
134.77
134.62
134.17
133.18
133.01
132.77
132.48
132.01
129.91
129.68
129.33
128.80
128.40
128.18
127.71
127.60
127.13
126.89
126.15
125.02
123.15
122.95
121.98
121.91
77.32
77.00
76.68

21.56
21.52



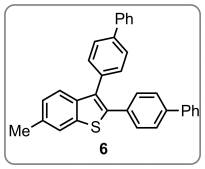



Me
S
6
Ph
Ph
7.717
7.712
7.710
7.702
7.695
7.686
7.610
7.608
7.593
7.577
7.528
7.512
7.507
7.490
7.481
7.477
7.475
7.466
7.455
7.451
7.441
7.425
7.406
7.391
7.375
7.369
7.355
7.340
7.260
7.219
7.203
2.531
4.80
3.17
12.52
0.92
2.66
10
9
8
7
6
5
4
3
2
1
0 ppm
ERA-NA-136

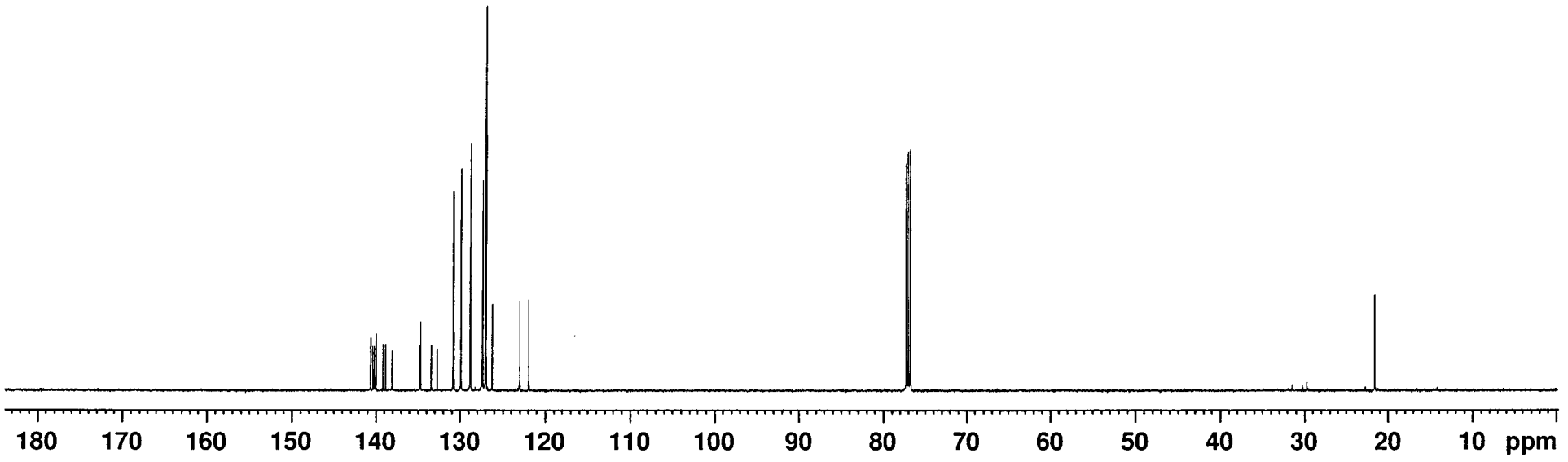
140.62
140.33
140.17
139.96
139.15
138.82
138.04
134.76
134.64
133.39
132.69
130.81
129.86
128.81
128.76
127.40
127.36
127.31
126.98
126.90
126.23
123.01
121.94

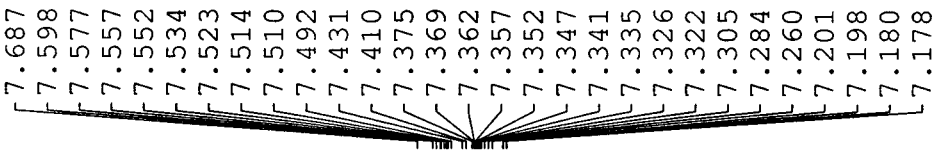
77.25
77.00
76.75

21.52



6




7.687
7.598
7.577
7.557
7.552
7.534
7.523
7.514
7.510
7.492
7.431
7.410
7.375
7.369
7.362
7.357
7.352
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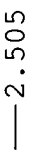
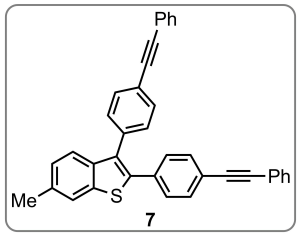
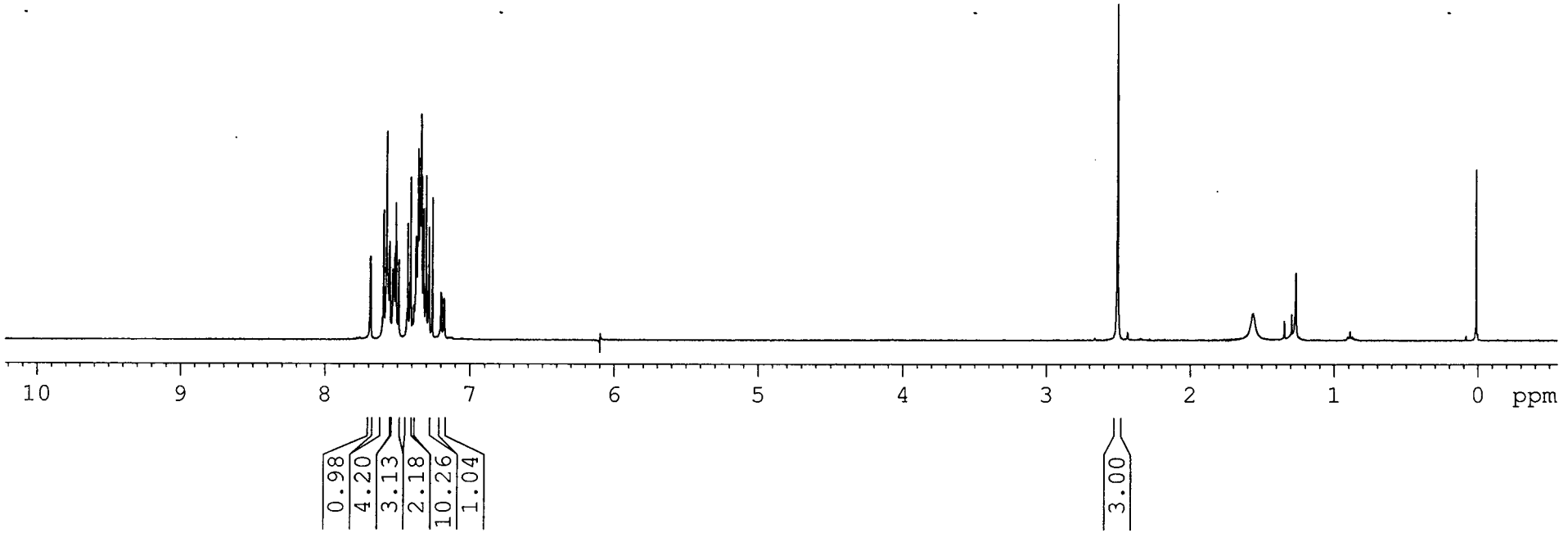
7.326
7.322
7.305
7.284
7.260
7.201
7.198
7.180
7.178


2.505

ERA-na-139


Ph
Me
S
Ph
7


10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
4.20
3.13
2.18
10.26
1.04
3.00

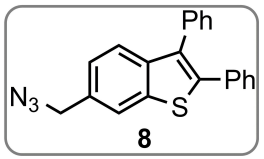
Me
S
Ph
Ph
7
139.25
138.34
137.97
135.60
134.98
134.11
132.83
132.01
131.63
131.61
130.39
129.43
128.37
128.34
126.42
123.21
123.14
122.89
122.54
122.38
122.00
90.53
90.09
89.22
89.10
77.32
77.00
76.68
21.54
ERA-na-139
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

8
N3
S
Ph
Ph
7.832
7.607
7.587
7.385
7.328
7.317
7.250
4.460
0.78
1.00
11.09
1.63
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
ERA-SD-3

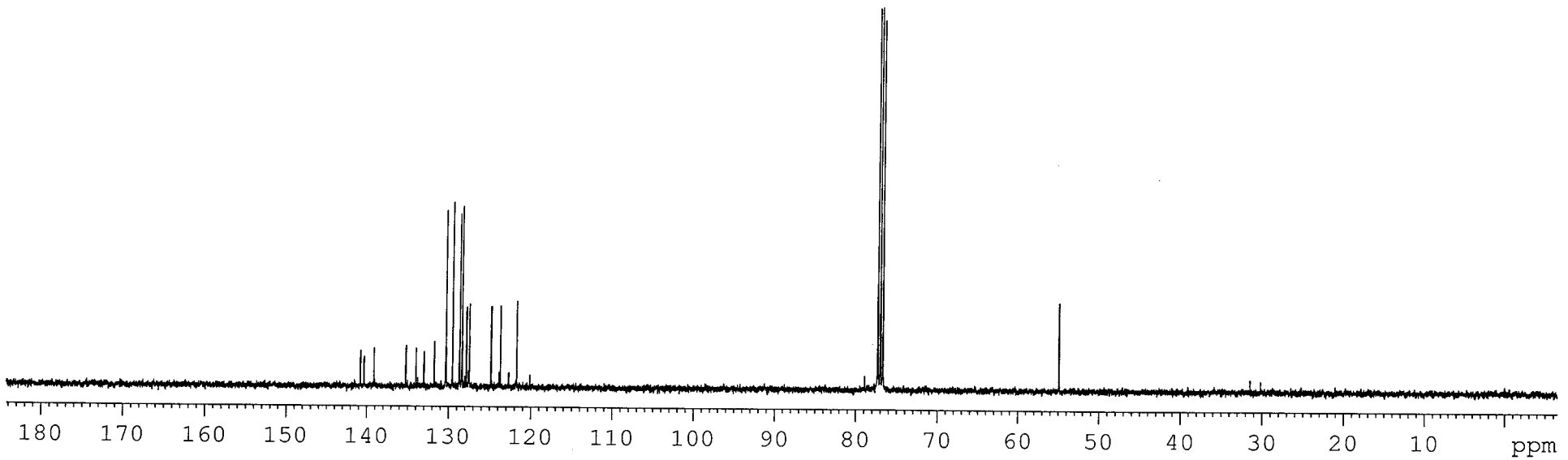
140.84
140.38
139.15
135.25
133.99
133.02
131.77
130.36
129.57
128.70
128.38
127.85
127.50
124.82
123.73
121.76

77.32
77.00
76.68

54.89

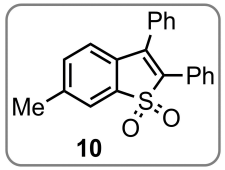


8

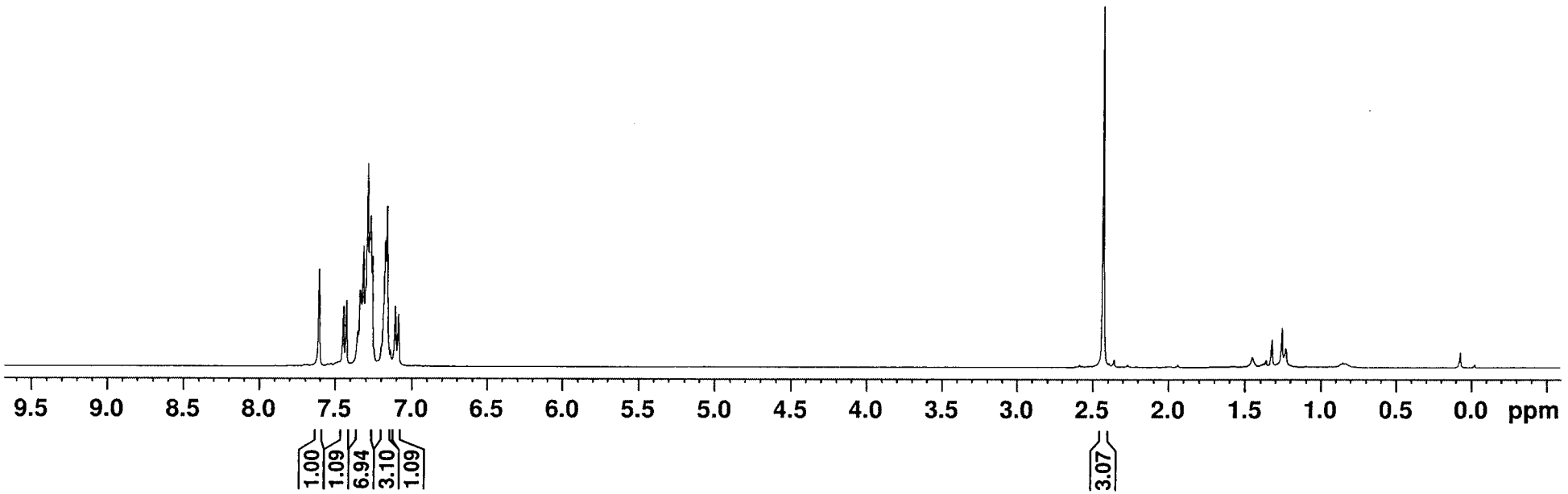


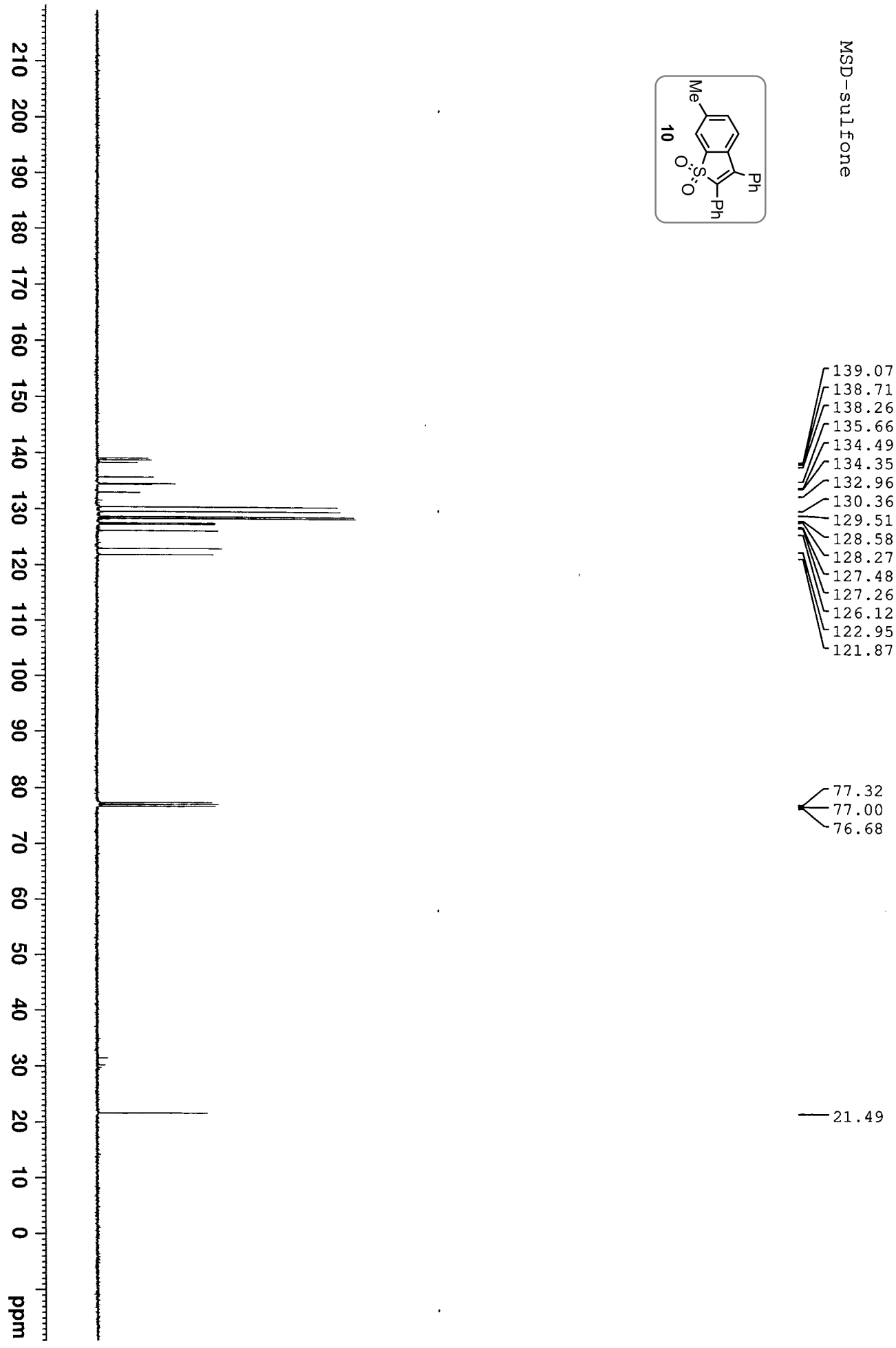
7.607
7.445
7.425
7.338
7.334
7.329
7.318
7.305
7.301
7.291
7.279
7.274
7.272
7.260
7.256
7.177
7.172
7.164
7.159
7.108
7.087

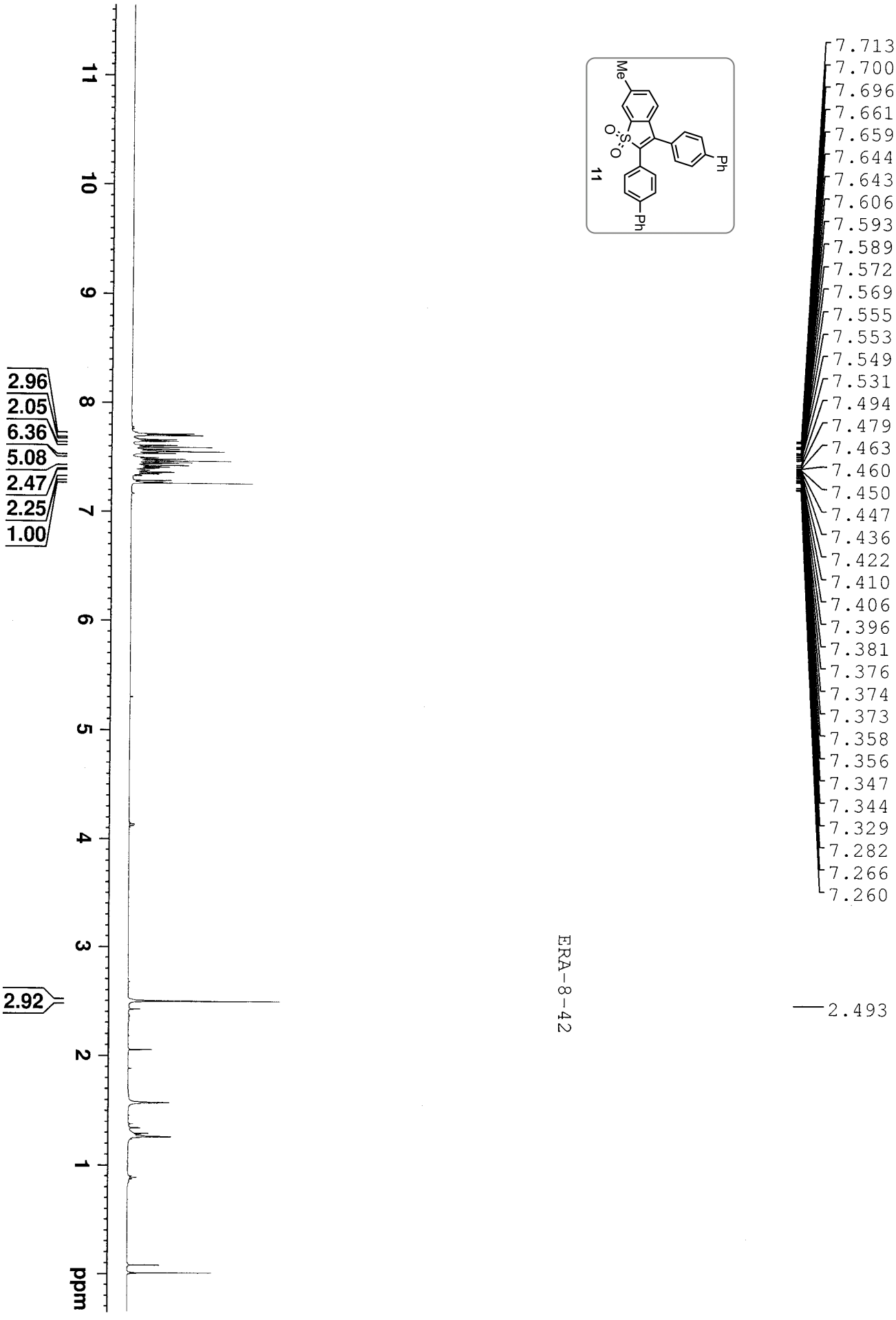
2.426

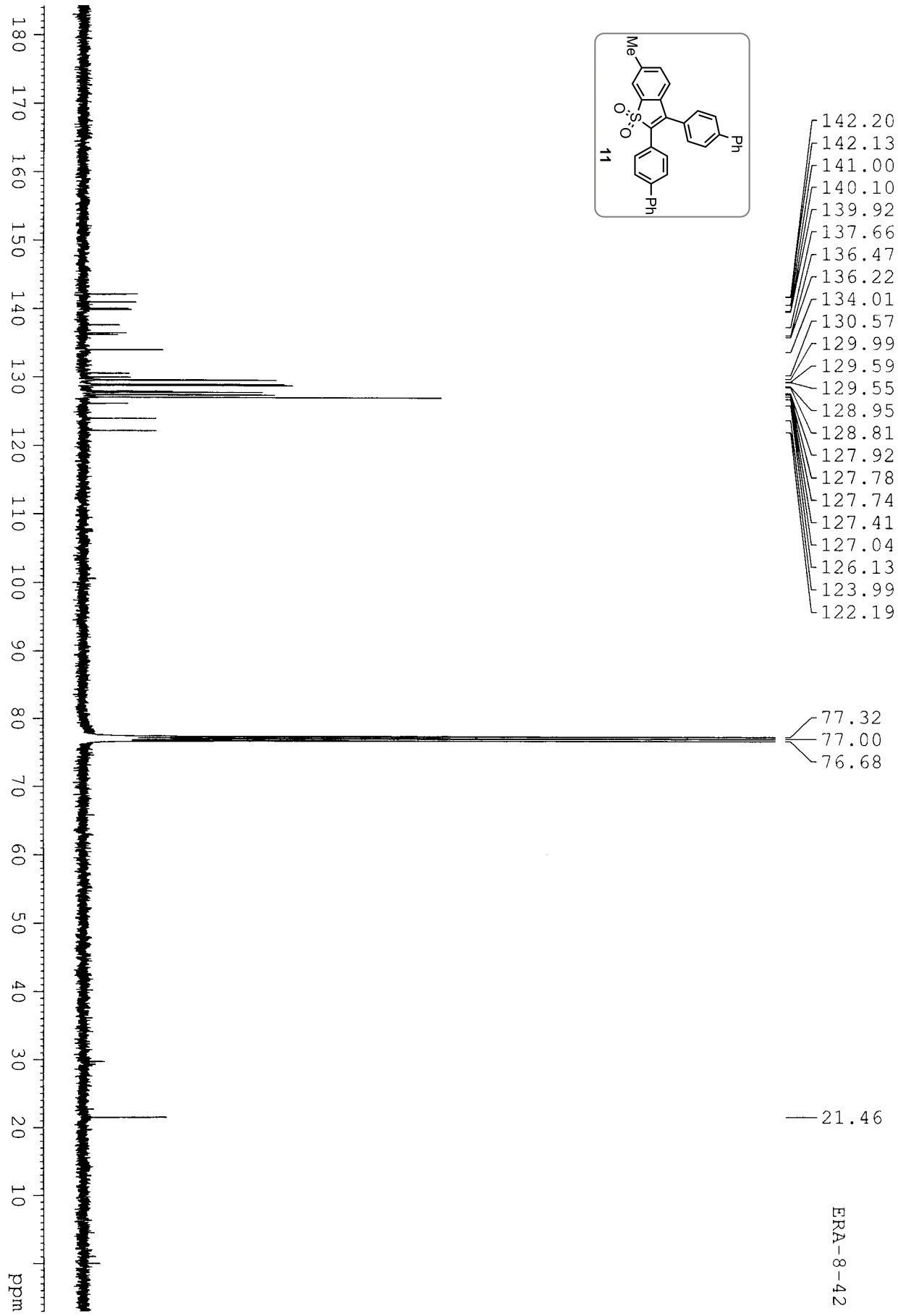


10




MSD-sulfone
10
Me
Ph
Ph
O
S
O
139.07
138.71
138.26
135.66
134.49
134.35
132.96
130.36
129.51
128.58
128.27
127.48
127.26
126.12
122.95
121.87
77.32
77.00
76.68
21.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Me
Ph
Ph
11
7.713
7.700
7.696
7.661
7.659
7.644
7.643
7.606
7.593
7.589
7.572
7.569
7.555
7.553
7.549
7.531
7.494
7.479
7.463
7.460
7.450
7.447
7.436
7.422
7.410
7.406
7.396
7.381
7.376
7.374
7.373
7.358
7.356
7.347
7.344
7.329
7.282
7.266
7.260
2.493
2.96
2.05
6.36
5.08
2.47
2.25
1.00
2.92
ERA-8-42
ppm


Me
Ph
Ph
11
142.20
142.13
141.00
140.10
139.92
137.66
136.47
136.22
134.01
130.57
129.99
129.59
129.55
128.95
128.81
127.92
127.78
127.74
127.41
127.04
126.13
123.99
122.19
77.32
77.00
76.68
21.46
ppm
ERA-8-42