Synthesis of Polycyclic Aromatics and Heteroaromatics via Electrophilic Cyclization

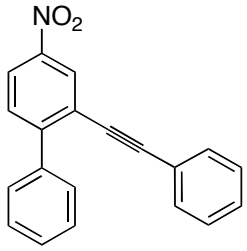
Tuanli Yao, Marino A. Campo and Richard C. Larock*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Supporting Information

General. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz. Thin-layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) and a basic $KMnO_4$ solution [3 g of $KMnO_4$ + 20 g of K_2CO_3 + 5 mL of NaOH (5%) + 300 mL of H_2O]. All melting points are uncorrected. All reagents were used directly as commercially obtained unless otherwise noted. Compounds **1**, **2**, **6-17**, **32-37**, and **49-56** were reported in our earlier communication.[1]

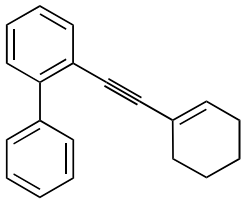
General procedure for preparation of the 2-(arylethynyl)biphenyls. To a solution of the corresponding aryl iodide (1.0 mmol) and the terminal alkyne (1.2 mmol, 1.2 equiv) in Et_3N (4 mL), were added $PdCl_2(PPh_3)_2$ (14 mg, 2 mol %) and CuI (2 mg, 1 mol %). The resulting mixture was then heated under an N_2 atmosphere at 55 °C for 3 h. The mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the corresponding product.



18

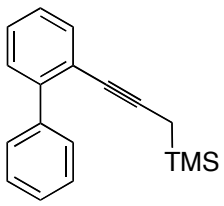
2-Phenylethynyl-4-nitrobiphenyl (18). 2-Iodo-4-nitrobiphenyl and phenylacetylene were employed. Purification by flash chromatography (10:1 hexane/EtOAc) afforded 254 mg (85%) of the product as a yellow solid: mp 129-130 ºC; ^{1}H NMR ($CDCl_3$) δ 7.31-

7.38 (m, 5H), 7.48-7.55 (m, 3H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.67-7.71 (m, 2H), 8.21 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.50 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 87.4, 94.7, 122.6, 123.2, 123.5, 128.0, 128.5, 128.7, 129.1, 129.2, 129.4, 130.6, 131.8, 138.7, 147.0, 150.0; IR (neat, cm^{-1}) 3630, 1514, 1343; HRMS Calcd for $C_{20}H_{13}NO_2$: 299.0946. Found: 299.0950.



20

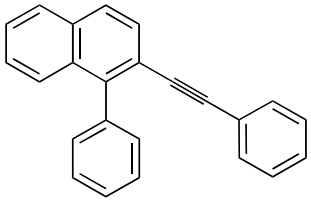
2-(Cyclohex-1-en-1ylethynyl)biphenyl (20). 2-Iodobiphenyl and 1-ethynylcyclohexene were employed. Purification by flash chromatography (40:1 hexane/EtOAc) afforded 146 mg (70%) of the product as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 1.53-1.65 (m, 4H), 2.07-2.13 (m, 4H), 6.03-6.06 (m, 1H), 7.26-7.47 (m, 6H), 7.53-7.57 (m, 1H), 7.62-7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 22.5, 26.0, 29.0, 86.9, 94.4, 121.2, 122.3, 127.2, 127.5, 128.0, 128.2, 129.59, 129.61, 133.0, 135.1, 140.9, 143.7; IR (neat, cm^{-1}) 3059, 3023, 2931, 2199, 1475; HRMS Calcd for $C_{20}H_{18}$: 258.1409. Found: 258.1412.



26

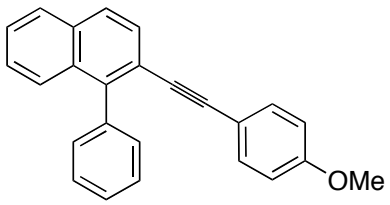
[3-(Biphenyl-2-yl)prop-2-ynyl](trimethyl)silane (26). 2-Iodobiphenyl and prop-2-ynyl(trimethyl)silane were employed. Purification by flash chromatography (30:1

hexane/EtOAc) afforded 128 mg (49%) of the product as a clear liquid: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9H), 1.59 (s, 2H), 7.24-7.34 (m, 4H), 7.37-7.41 (m, 2H), 7.48-7.51 (m, 1H), 7.54-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -1.9, 8.3, 78.9, 91.5, 123.2, 126.9, 127.1, 127.2, 127.9, 129.3, 129.5, 133.2, 141.2, 143.4; IR (neat, cm^{-1}) 3060, 2955, 2205, 1476, 1249; HRMS Calcd for $C_{18}H_{20}Si$: 264.1334. Found: 264.1339.



28

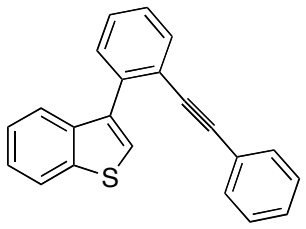
1-Phenyl-2-(phenylethynyl)naphthalene (28). 2-Iodo-1-phenylnaphthalene and phenylacetylene were employed. Purification by flash chromatography (40:1 hexane/EtOAc) afforded 301 mg (99%) of the product as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.16-7.21 (m, 2H), 7.23-7.27 (m, 3H), 7.38-7.44 (m, 1H), 7.47-7.55 (m, 5H), 7.65-7.70 (m, 2H), 7.82-7.89 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 90.2, 93.4, 120.4, 123.7, 126.6, 126.7, 126.9, 127.68, 127.7, 128.18, 128.22, 128.23, 128.4, 128.6, 130.9, 131.6, 132.4, 133.4, 139.2, 143.3; IR (neat, cm^{-1}) 3056, 1950, 1598, 1505, 1490; HRMS Calcd for $C_{24}H_{16}$: 304.1252. Found: 304.1257.



30

2-[(4-Methoxyphenyl)ethynyl]-1-phenylnaphthalene (30). 2-Iodo-1-phenylnaphthalene and *p*-methoxyphenyl acetylene were employed. Purification by flash

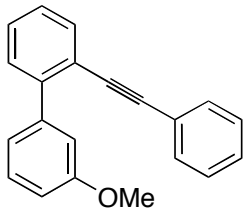
chromatography (20:1 hexane/EtOAc) afforded 276 mg (82%) of the product as a white solid: mp 109-111 ºC; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 6.82 (dd, *J* = 2.1, 6.9 Hz, 2H), 7.17 (dd, *J* = 2.1, 6.9 Hz, 2H), 7.34-7.57 (m, 7H), 7.68-7.74 (m, 2H), 7.84-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 55.4, 88.9, 93.5, 114.1, 115.7, 120.7, 126.4, 126.6, 126.8, 127.60, 127.62, 128.1, 128.2, 128.4, 130.9, 132.4, 133.0, 133.1, 139.3, 142.8, 159.7; IR (neat, cm^{-1}) 3055, 2956, 2836, 2207, 1605, 1511; HRMS Calcd for $C_{25}H_{18}O$: 334.1358. Found: 334.1365.



40

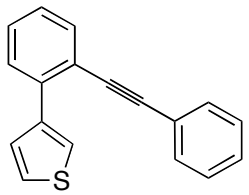
3-[2-(Phenylethynyl)phenyl]-benzothiophene (40). To a solution of 2-bromophenyl phenyl acetylene (1.5 mmol, 386 mg) and 1-benzothien-3-ylboronic acid (320 mg, 1.2 equiv) in 7.5 mL of DME were added $Pd(dba)_2$ (43.2 mg, 5 mol %), PPh_3 (39 mg, 10 mol %) and CsF (456 mg, 2.0 equiv). The resulting mixture was heated under an N_2 atmosphere at 100 °C for 24 h. The mixture was cooled to room temperature and diluted with 70 mL of ether, washed with 25 mL of satd NaCl, dried ($MgSO_4$) and filtered. The solvent was evaporated under reduced pressure and the residue was chromatographed using 50:1 hexane/EtOAc to afford 145 mg (31%) of the product as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.02-7.08 (m, 2H), 7.18-7.24 (m, 3H), 7.36-7.48 (m, 4H), 7.52-7.56 (m, 1H), 7.63 (s, 1H), 7.70-7.74 (m, 1H), 7.76-7.80 (m, 1H), 7.94-7.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 89.3, 93.3, 122.9, 123.3, 123.4, 123.8, 124.3, 124.5, 125.6, 127.8, 128.3,

128.4, 128.5, 130.3, 131.5, 132.9, 136.5, 138.3, 138.7, 140.2; IR (neat, cm^{-1}) 3057, 1597, 1492, 1441; HRMS Calcd for $C_{22}H_{14}S$: 310.0816. Found: 310.0821.



43

3'-Methoxy-2-(phenylethynyl)biphenyl (43). This alkyne was prepared from 2-(phenylethynyl)phenylboronic acid and 3-iodoanisole by following the same procedure as compound **40** at 80 °C. 2-(Phenylethynyl)phenylboronic acid (133 mg, 0.6 mmol), 1-methoxy-3-iodobenzene (126 mg, 0.9 equiv), $Pd(dba)_2$ (14.4 mg, 0.05 equiv), PPh_3 (13 mg, 0.1 equiv), CsF (182 mg, 2.0 equiv) and DME (2.5 mL) afforded, after purification by flash column chromatography (silica gel, 20:1 hexane/EtOAc), 76 mg (50%) of the indicated compound **43** as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.97-7.00 (m, 1H), 7.26-7.33 (m, 5H), 7.36-7.49 (m, 6H), 7.67-7.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 55.5, 89.6, 92.7, 113.7, 115.0, 121.8, 122.2, 123.7, 127.4, 128.4, 128.5, 128.8, 129.2, 129.7, 131.7, 133.2, 142.2, 144.0, 159.4; IR (neat, cm^{-1}) 3058, 3023, 2955, 2936, 2833, 1599, 1581, 1490; HRMS Calcd for $C_{21}H_{16}O$: 284.1201. Found: 284.1206.

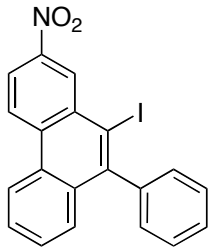


46

3-[2-(Phenylethynyl)phenyl]thiophene (46). This alkyne was prepared from 2-bromophenyl phenyl acetylene and 3-thiopheneboronic acid by following the same

procedure as compound **40** at 90 °C. 1-Bromo-2-(phenylethynyl)benzene (257 mg, 1 mmol), 3-thiopheneboronic acid (154 mg, 1.2 equiv), $Pd(dba)_2$ (24 mg, 0.05 equiv), PPh_3 (22 mg, 0.1 equiv), CsF (304 mg, 2.0 equiv) and DME (4 mL) afforded, after purification by flash column chromatography (silica gel, 20:1 hexane/EtOAc), 235 mg (90%) of the indicated compound **46** as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.26-7.39 (m, 6H), 7.42-7.44 (m, 2H), 7.48-7.50 (m, 1H), 7.53 (dd, *J* = 0.9, 3.9 Hz, 1H), 7.61-7.64 (m, 1H), 7.70 (dd, *J* = 0.9, 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 89.7, 92.7, 121.2, 123.5, 123.7, 124.8, 127.0, 128.3, 128.4, 128.6, 128.7, 129.1, 131.5, 133.3, 138.2, 141.0; IR (neat, cm^{-1}) 3103, 3058, 3028, 1597, 1492, 1442; HRMS Calcd for $C_{18}H_{12}S$: 260.0660. Found: 260.0663.

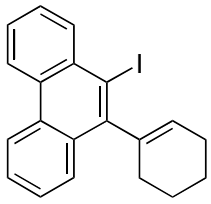
General procedure for the electrophilic cyclization of 2-(arylethynyl)biphenyls by ICl. To a solution of 2-(arylethynyl)biphenyl (0.30 mmol) in CH_2Cl_2 (3 mL) under N_2 was added ICl (1.2 equiv) in CH_2Cl_2 (0.5 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with 25 mL of satd aq $Na_2S_2O_3$, dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.



19

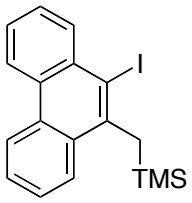
10-Iodo-2-nitro-9-phenylphenanthrene (19). Purification by flash chromatography (7:1 hexane/EtOAc) afforded 112 mg (88%) of the product as a yellow solid: mp 182-183 ºC; ^{1}H NMR ($CDCl_3$) δ 7.25-7.30 (m, 2H), 7.44-7.62 (m, 5H), 7.75 (dt, *J* = 1.2, 7.8

Hz, 1H), 8.45 (td, *J* = 2.7, 9.0 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.81 (dd, *J* = 3.3, 9.3 Hz, 1H), 9.42 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 105.5, 121.3, 123.8, 124.7, 128.3, 128.5, 128.9, 129.28, 129.33, 129.4, 129.8, 131.1, 132.9, 133.8, 134.8, 144.8, 147.2, 148.0; IR (neat, cm^{-1}) 3080, 3059, 3025, 1577, 1515, 1345; HRMS Calcd for $C_{20}H_{12}INO_2$: 424.9913. Found: 424.9921.



21

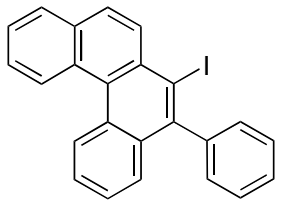
9-(Cyclohex-1-en-1-yl)-10-iodophenanthrene (21). Purification by flash chromatography (50:1 hexane/EtOAc) afforded 79 mg (70%) of the product as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.85-2.01 (m, 4H), 2.19-2.26 (m, 1H), 3.35-2.48 (m, 3H), 5.71-5.74 (m, 1H), 7.54-7.60 (m, 1H), 7.62-7.70 (m, 3H), 8.06 (dd, *J* = 0.9, 8.1 Hz, 1H), 8.41-8.46 (m, 1H), 8.61-8.64 (m, 1H), 8.69 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.3, 23.2, 25.7, 29.5, 105.4, 122.8, 123.0, 127.2, 127.28, 127.33, 128.0, 128.2, 129.2, 130.5, 130.7, 131.4, 132.8, 134.5, 142.4, 147.2; IR (neat, cm^{-1}) 3067, 3025, 2926, 1562, 1482, 1445; HRMS Calcd for $C_{20}H_{17}I$: 384.0375. Found: 384.0380.



27

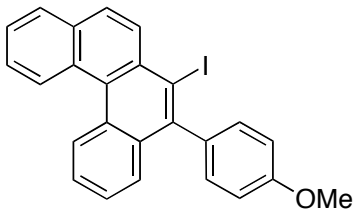
[(10-Iodo-9-phenanthryl)methyl](trimethyl)silane (27). Purification by flash chromatography (50:1 hexane/EtOAc) afforded 54 mg (50%) of the product as a white

solid: mp 70-72 ºC; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 3.24 (s, 2H), 7.56-7.71 (m, 4H), 8.09 (dd, *J* = 0.8, 8.1 Hz, 1H), 8.39-8.42 (m, 1H), 8.58-8.62 (m, 1H), 8.70-8.73 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 0.00, 31.1, 106.0, 122.2, 122.9, 125.9, 126.54, 126.57, 126.64, 127.5, 129.2, 130.1, 130.7, 133.0, 134.2, 141.8; IR (neat, cm^{-1}) 3068, 2951, 1562, 1485, 1445; HRMS Calcd for $C_{18}H_{19}ISi$: 390.0301. Found: 390.0310.



29

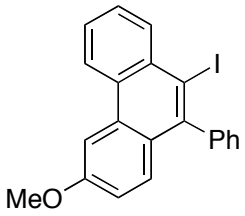
6-Iodo-5-phenylbenzo[*c*]phenanthrene (29). Purification by flash chromatography (3:1 hexane/CH_2Cl_2) afforded 61 mg (48%) of the product as a white solid: mp 159-160 ºC; ^{1}H NMR ($CDCl_3$) δ 7.32-7.36 (m, 2H), 7.44-7.47 (m, 1H), 7.52-7.60 (m, 4H), 7.62-7.70 (m, 3H), 7.95 (d, *J* = 9.0 Hz, 1H), 8.03-8.07 (m, 1H), 8.43 (m, *J* = 9.0 Hz, 1H), 9.04 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 106.4, 126.4, 126.6, 126.7, 126.8, 128.1, 128.3, 128.4, 128.6, 128.67, 128.71, 128.8, 129.0, 129.6, 130.1, 130.3, 131.2, 132.2, 133.4, 133.8, 145.2, 145.4; IR (neat, cm^{-1}) 3057, 1599, 1503, 1488; HRMS Calcd for $C_{24}H_{15}I$: 430.0219. Found: 430.0228.



31

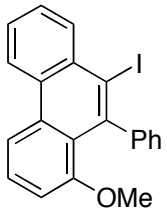
5-(4-Methoxyphenyl)-6-iodobenzo[*c*]phenanthrene (31). Purification by flash chromatography (20:1 hexane/ EtOAc) afforded 134 mg (97%) of the product as a green solid: mp 186-187 ºC; ^{1}H NMR ($CDCl_3$) δ 3.94 (s, 3H), 7.10 (d, *J* = 4.5 Hz, 2H), 7.23-

7.26 (m, 2H), 7.42-7.47 (m, 1H), 7.57-7.69 (m, 4H), 7.94 (d, J = 9.0 Hz, 1H), 8.02-8.06 (m, 1H), 8.42 (d, J = 9.0 Hz, 1H), 9.01-9.05 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 55.6, 107.3, 114.1, 126.4, 126.6, 126.7, 126.8, 128.41, 128.44, 128.61, 128.64, 128.8, 129.0, 129.7, 130.2, 131.3, 131.5, 132.4, 133.75, 133.80, 138.0, 145.0, 159.4; IR (neat, cm^{-1}) 3065, 2961, 2838, 1607, 1510, 1247; HRMS Calcd for $C_{25}H_{17}IO$: 460.0324. Found: 460.0334.



44

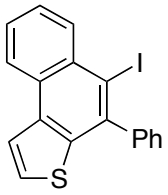
9-Iodo-3-methoxy-10-phenylphenanthrene (44). Purification by flash chromatography (30:1 hexane/ EtOAc) afforded 83 mg (66%) of the product as a white solid: mp 136-138 ºC; ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 3H), 7.05 (dd, J = 2.5, 9.3 Hz, 1H), 7.26-7.35 (m, 3H), 7.51-7.58 (m, 3H), 7.68-7.71 (m, 2H), 8.09 (d, J = 2.4 Hz, 1H), 8.43-8.47 (m, 1H), 8.59-8.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 55.7, 103.3, 104.3, 117.0, 122.9, 127.3, 127.5, 128.0, 128.4, 128.7, 130.2, 130.4, 130.5, 132.0, 133.0, 134.9, 145.3, 145.7, 158.9; IR (neat, cm^{-1}) 3056, 3025, 2957, 2933, 2834, 1613, 1576, 1519; HRMS Calcd for $C_{21}H_{15}IO$: 410.0168. Found: 410.0175.



45

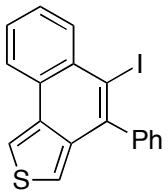
9-Iodo-1-methoxy-10-phenylphenanthrene (45). Purification by flash chromatography (30:1 hexane/ EtOAc) afforded 26 mg (20%) of the product as a light

yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 3H), 6.94 (d, *J* = 7.8 Hz, 1H), 7.18-7.21 (m, 2H), 7.37-7.46 (m, 3H), 7.58-7.69 (m, 3H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.48-8.52 (m, 1H), 8.64-8.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 56.2, 109.5, 110.0, 115.8, 123.4, 123.5, 126.5, 127.4, 127.6, 128.0, 128.5, 129.0, 130.4, 132.7, 133.0, 135.3, 142.9, 151.1, 156.6; IR (neat, cm^{-1}) 3056, 3021, 2929, 1601, 1575, 1455; HRMS Calcd for $C_{21}H_{15}IO$: 410.0168. Found: 410.0172.



47

5-Iodo-4-phenylnaphtho[2,1-*b*]thiophene (47). Purification by flash chromatography (20:1 hexane/ EtOAc) afforded 58 mg (50%) of the product as a light yellow solid: mp 98-99 ºC; ^{1}H NMR ($CDCl_3$) δ 7.41-7.44 (m, 2H), 7.54-7.58 (m, 4H), 7.63-7.68 (m, 2H), 8.01 (d, *J* = 5.4 Hz, 1H), 8.30-8.35 (m, 1H), 8.43-8.49 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 101.18, 122.2, 124.2, 127.3, 127.4, 127.9, 128.8, 128.9, 129.0, 129.6, 132.8, 134.4, 136.3, 139.7, 141.2, 144.8; IR (neat, cm^{-1}) 3102, 3059, 3025, 1551, 1492, 1442; HRMS Calcd for $C_{18}H_{11}IS$: 385.9626. Found: 385.9633.



48

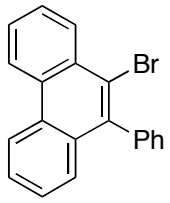
5-Iodo-4-phenylnaphtho[1,2-*c*]thiophene (48). Purification by flash chromatography (20:1 hexane/ EtOAc) afforded 43 mg (37%) of the product as a white solid: mp 149-150 ºC; ^{1}H NMR ($CDCl_3$) δ 7.36-7.40 (m, 2H), 7.52-7.67 (m, 6H), 7.81 (s, 1H), 8.12-8.17 (m,

1H), 8.40-8.44 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 101.1, 121.4, 124.0, 127.6, 127.7, 128.1, 129.0, 129.4, 132.9, 133.8, 134.5, 135.2, 138.2, 140.4, 144.1 (one sp^2 carbon missing due to overlap); IR (neat, cm^{-1}) 3057, 3022, 1554, 1496; HRMS Calcd for $C_{18}H_{11}IS$: 385.9626. Found: 385.9632.

General procedure for the electrophilic cyclization of 2-(1-alkynyl)biphenyls by I_2. To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in CH_2Cl_2 (3 mL) was added I_2 (3.0 equiv) and $NaHCO_3$ (3.0 equiv) at room temperature. The reaction mixture was stirred at room temperature for 24 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq $Na_2S_2O_3$ (25 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.

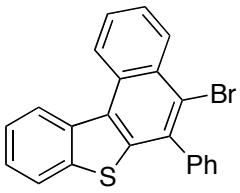
9-Iodo-10-phenylphenanthrene (2). Purification by flash chromatography (50:1 hexane/EtOAc) afforded 92 mg (80%) of the product as a white solid with a melting point and spectral properties identical to those previously reported.[2]

General procedure for the electrophilic cyclization of 2-(1-alkynyl)biphenyls by NBS. To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in CH_2Cl_2 (3 mL) was added NBS (1.2 equiv) and silica gel (50 mg) at room temperature. The reaction mixture was stirred at room tempature for 144 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq $Na_2S_2O_3$ (25 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.



3

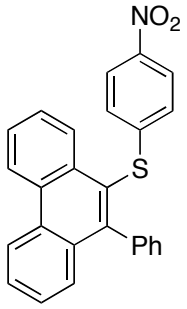
9-Bromo-10-phenylphenanthrene (3). Purification by flash chromatography (40:1 hexane/EtOAc) afforded 86 mg (86%) of the product as a white solid: mp 108-109 ºC; ^{1}H NMR ($CDCl_3$) δ 7.34-7.38 (m, 2H), 7.41-7.47 (m, 2H), 7.50-7.60 (m, 3H), 7.64-7.77 (m, 3H), 8.53-8.57 (m, 1H), 8.72-8.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 122.9, 123.8, 127.1, 127.3, 127.7, 127.9, 128.0, 128.2, 128.7, 129.2, 129.3, 130.2, 130.7, 131.2, 132.9, 139.9, 141.3; IR (neat, cm^{-1}) 3070, 3058, 3027, 1583, 1567, 1484; HRMS Calcd for $C_{20}H_{15}Br$: 332.0201. Found: 332.0209.



41

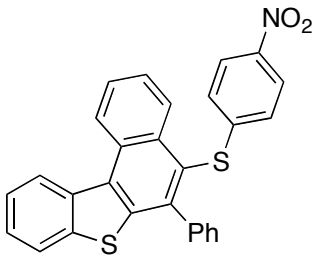
5-Bromo-6-phenylbenzo[*b*]naphtha[1,2-*d*]thiophene (41). Purification by flash chromatography (40:1 hexane/EtOAc) afforded 102 mg (88%) of the product as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.46-7.53 (m, 3H), 7.54-7.63 (m, 4H), 7.68-7.74 (m, 1H), 7.78-7.83 (m, 1H), 7.88 (dd, J = 7.8, 0.6 Hz, 1H), 8.64 (dd, J = 8.4, 1.2 Hz, 1H), 8.86 (d, J = 8.1 Hz, 1H), 9.07 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 122.7, 123.3, 123.6, 125.1, 125.3, 125.8, 126.5, 127.9, 128.9, 129.0, 129.70, 129.74, 130.9, 131.0, 136.4, 136.6, 140.6, 141.0, 141.4; IR (neat, cm^{-1}) 3059, 2921, 1558, 1494, 1442; HRMS Calcd for $C_{22}H_{13}BrS$: 387.9921. Found: 387.9930.

General procedure for the electrophilic cyclization of 2-(1-alkynyl)biphenyls by *p*-$O_2NC_6H_4SCl$. To a solution of 2-(1-alkynyl)biphenyl (0.30 mmol) in CH_2Cl_2 (3 mL) was added *p*-$O_2NC_6H_4SCl$ (1.2 equiv) at room temperature. The reaction mixture was stirred for 0.5 h unless otherwise indicated. The reaction mixture was then diluted with diethyl ether (50 mL), washed with satd aq NH_4Cl (25 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column.



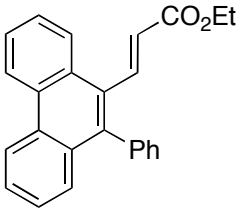
4

9-(4-Nitrophenylsulfenyl)-10-phenylphenanthrene (4). Purification by flash chromatography (30:1 hexane/EtOAc) afforded 112 mg (92%) of the product as a yellow solid: mp 192-193 ºC; ^{1}H NMR ($CDCl_3$) δ 6.94-6.98 (m, 2H), 7.20-7.24 (m, 2H), 7.39-7.47 (m, 3H), 7.50-7.54 (m, 2H), 7.71-7.64 (m, 1H), 7.72-7.79 (m, 2H), 7.93 (dt, *J* = 9.3, 2.1 Hz, 2H), 8.46 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.83 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 123.0, 123.4, 124.1, 125.0, 125.9, 127.3, 127.4, 127.8, 128.1, 128.3, 128.4, 128.6, 129.2, 129.4, 131.3, 131.6, 131.7, 132.3, 139.9, 145.1, 148.0, 149.2; IR (neat, cm^{-1}) 3066, 3024, 2834, 1610; HRMS Calcd for $C_{26}H_7NO_2S$: 407.0980. Found: 407.0989.



42

5-(4-Nitrophenylthio)-6-phenylbenzo[*b*]naphtha[1,2-*d*]thiophene (42). Purification by flash chromatography (9:1 hexane/EtOAc) afforded 101 mg (91%) of the product as a yellow solid: mp > 215 ºC (decomposed); ^{1}H NMR ($CDCl_3$) δ 6.93-6.97 (m, 2H), 7.34-7.38 (m, 2H), 7.43-7.57 (m, 4H), 7.61-7.68 (m, 2H), 7.79-7.85 (m, 1H), 7.92-7.95 (m, 3H), 8.63 (dd, *J* = 8.7, 0.9 Hz, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 9.17 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 123.4, 124.2, 125.5, 125.6, 126.0, 126.5, 126.9, 128.03, 128.04, 128.7, 129.0, 129.0, 131.2, 131.7, 132.8, 136.6, 139.9, 141.3, 141.4, 143.3, 145.2, 149.1 (two sp^2 carbons missing due to overlap); IR (neat, cm^{-1}) 3060, 2924, 1579, 1513, 1336; HRMS Calcd for $C_{28}H_{17}NO_2S_2$: 463.0701 Found: 463.0713.



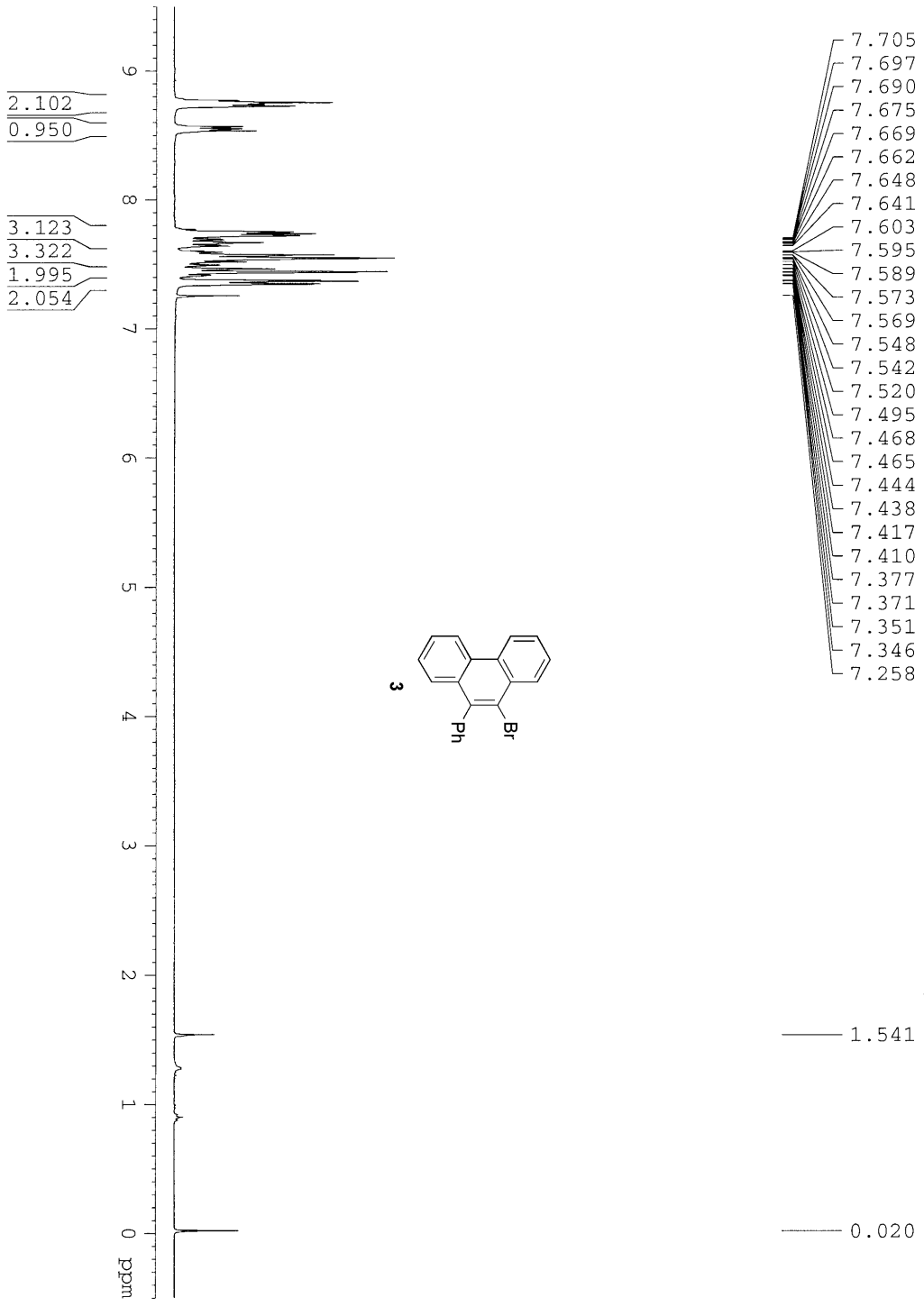
57

Ethyl (2*E*)-3-(10-phenyl-9-phenanthryl)acrylate (57). To a solution of 9-iodo-10-phenylphenanthrene (0.20 mmol) and ethyl acrylate (1.0 mmol, 5.0 equiv) in DMF (0.8 mL) were added $Pd(OAc)_2$ (2.2 mg, 5 mol %), *n*-Bu_4NCl (0.20 mmol, 1 equiv) and $NaHCO_3$ (0.5 mmol, 2.5 equiv). The resulting mixture was heated under a N_2 atmosphere at 100 °C for 3 d. The mixture was cooled to room temperature and diluted with 70 mL

of ether, washed with 25 mL of satd aq NaCl, dried ($MgSO_4$) and filtered. The solvent was evaporated under reduced pressure. The residue was chromatographed using 7:1 hexane/EtOAc to afford 69.0 mg (98%) of the product as a yellow solid: mp 135-136 ºC; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, *J* = 7.1 Hz, 3H), 4.20 (q, *J* = 6.9 Hz, 2H), 6.02 (d, *J* = 16.2 Hz, 1H), 7.26-7.31 (m, 2H), 7.44-7.55 (m, 5H), 7.62-7.75 (m, 3H), 7.88 (d, *J* = 16.2 Hz, 1H), 8.23 (dd, *J* = 1.2, 8.1 Hz, 1H), 8.73-8.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5, 60.7, 122.7, 123.2, 126.1, 126.5, 127.0, 127.1, 127.31, 127.34, 127.8, 128.3, 128.6, 129.9, 130.2, 130.4, 130.6, 130.9, 131.7, 138.3, 139.0, 143.5, 166.6; IR (neat, cm^{-1}) 3066, 2982, 1712, 1642, 1488; HRMS Calcd for $C_{25}H_{20}O_2$: 352.1463. Found: 352.1469.

References

1. Yao, T. Campo, M. A.; Larock, R. C. *Org. Lett.* **2004**, *6*, 2677.
2. Campo, M. A.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3675.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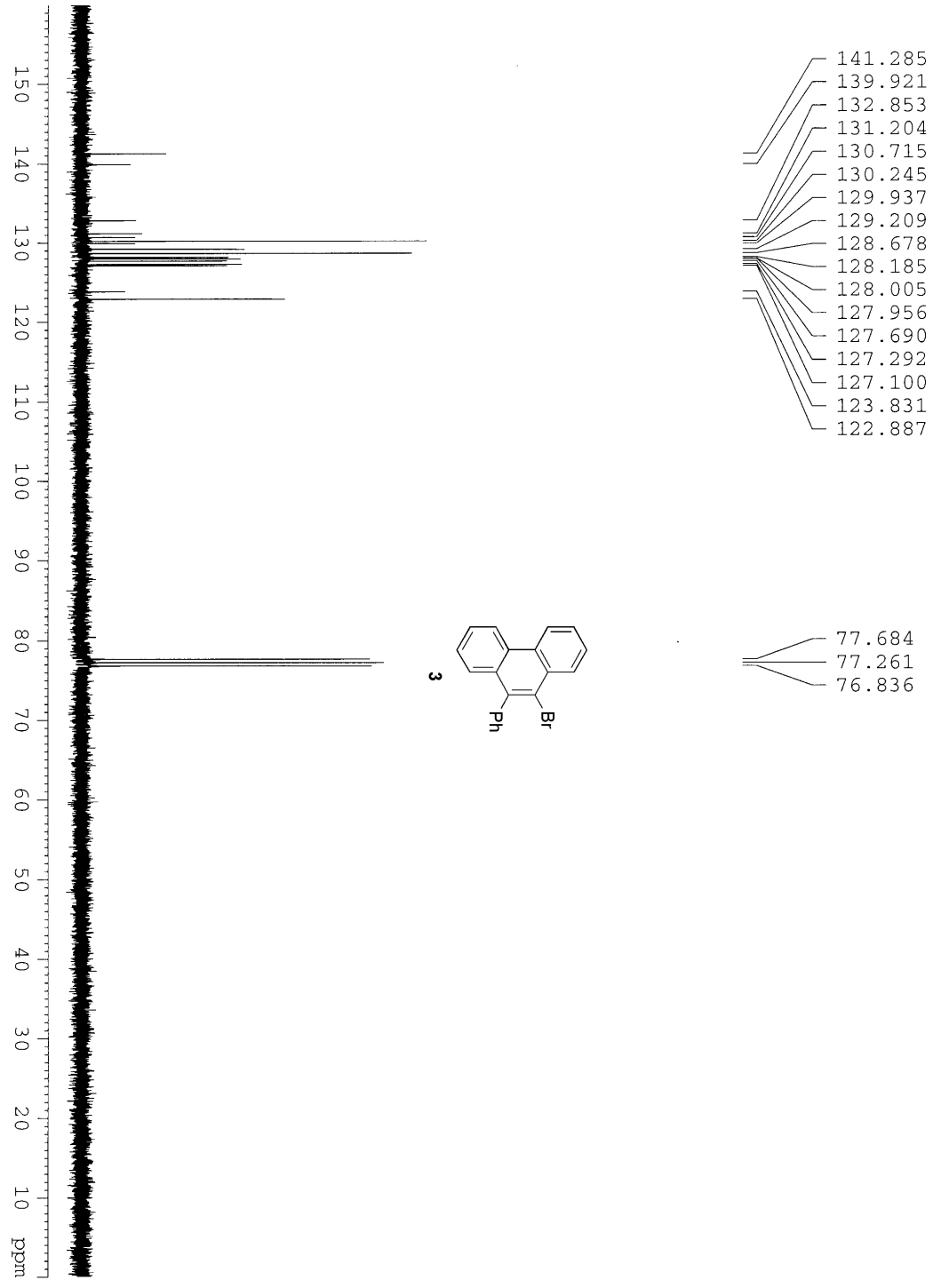
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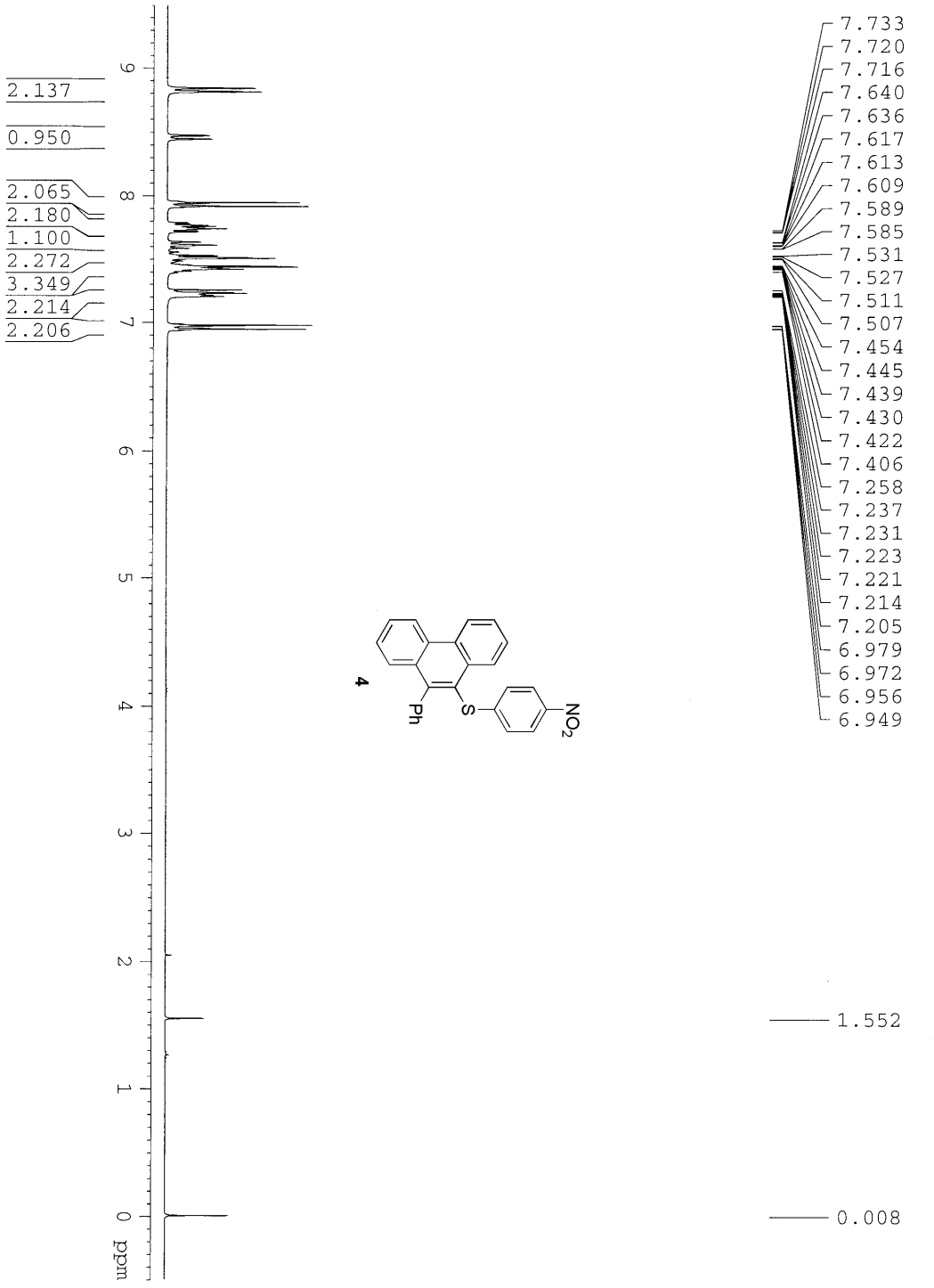
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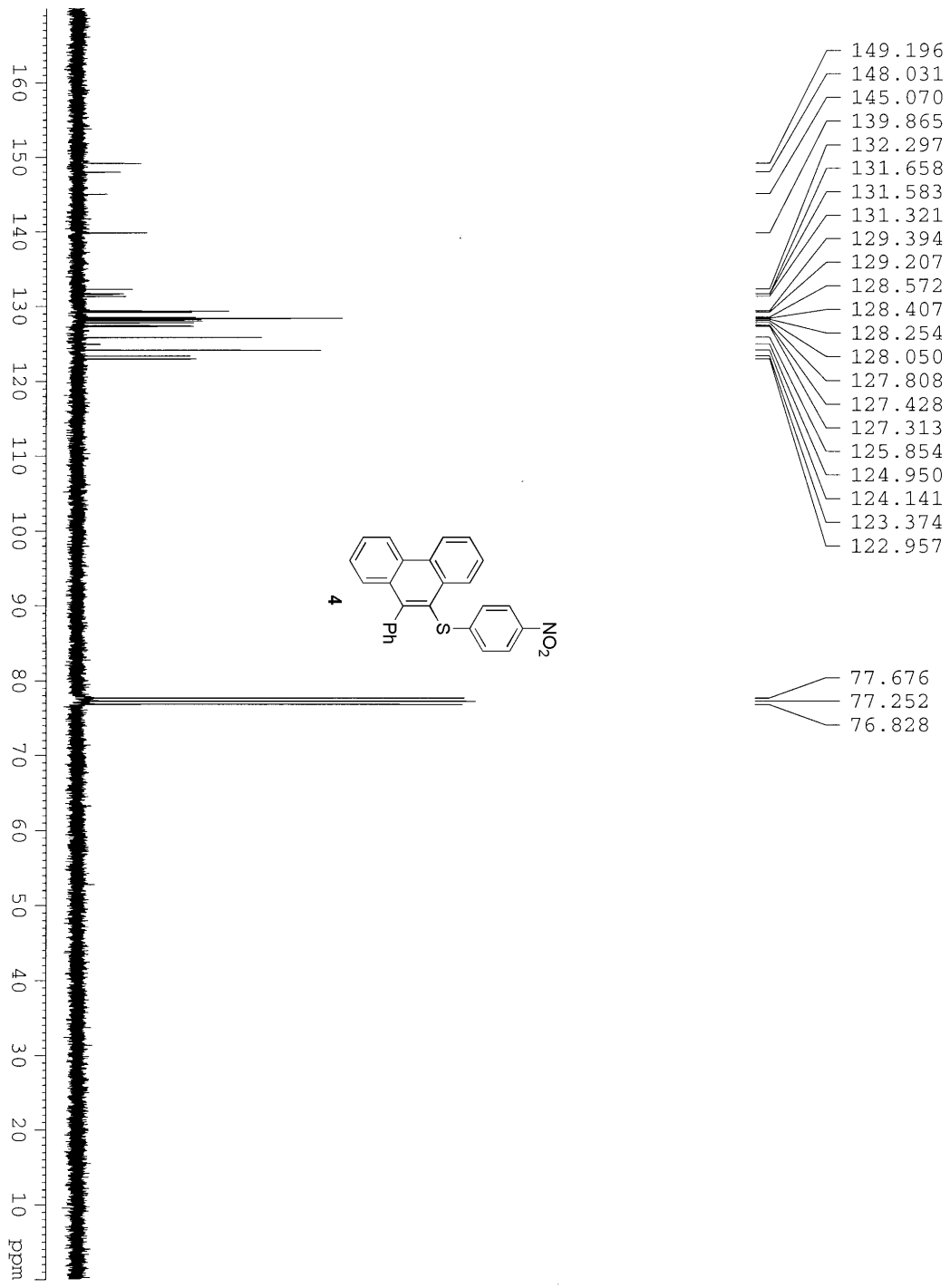
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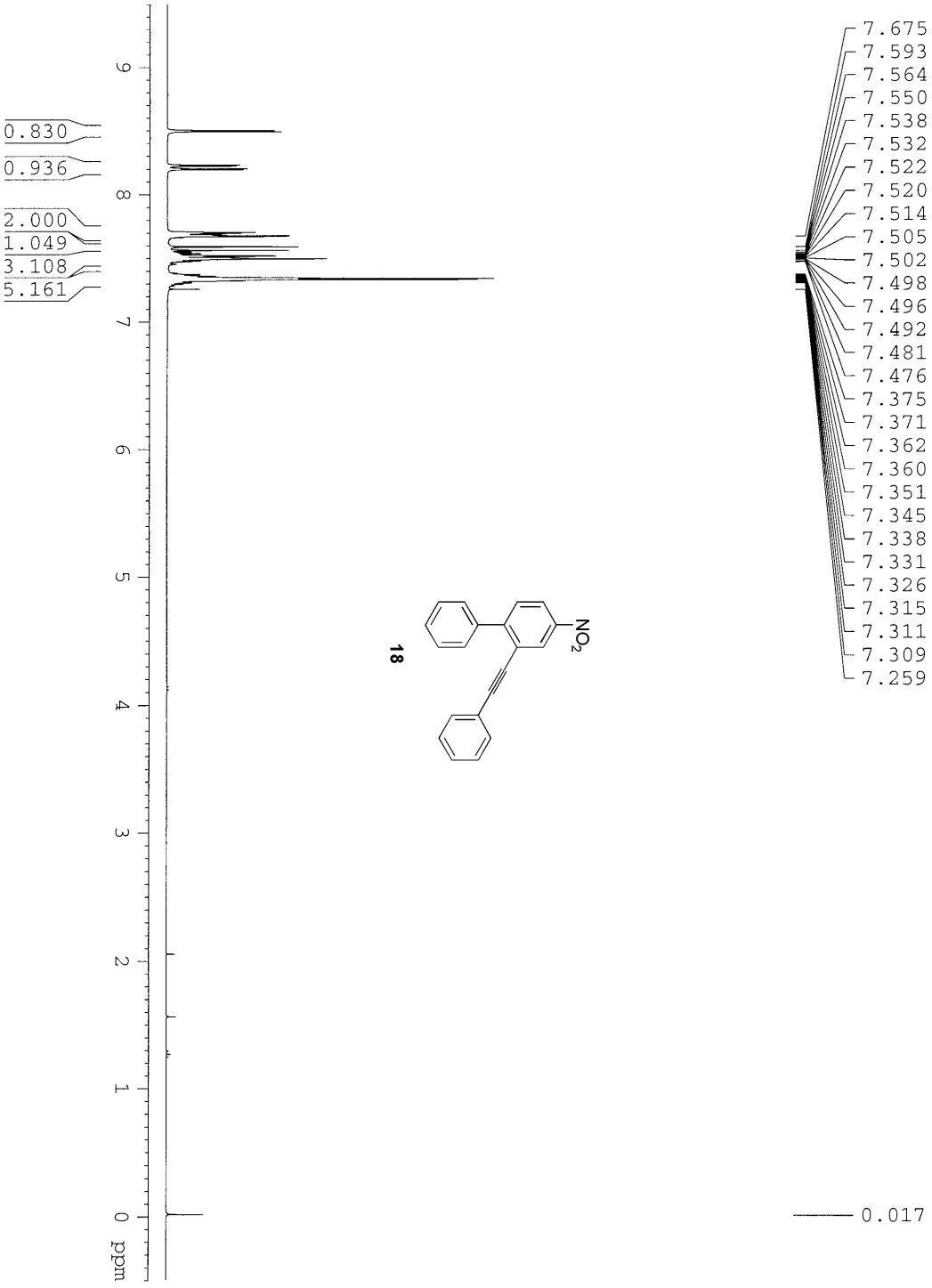
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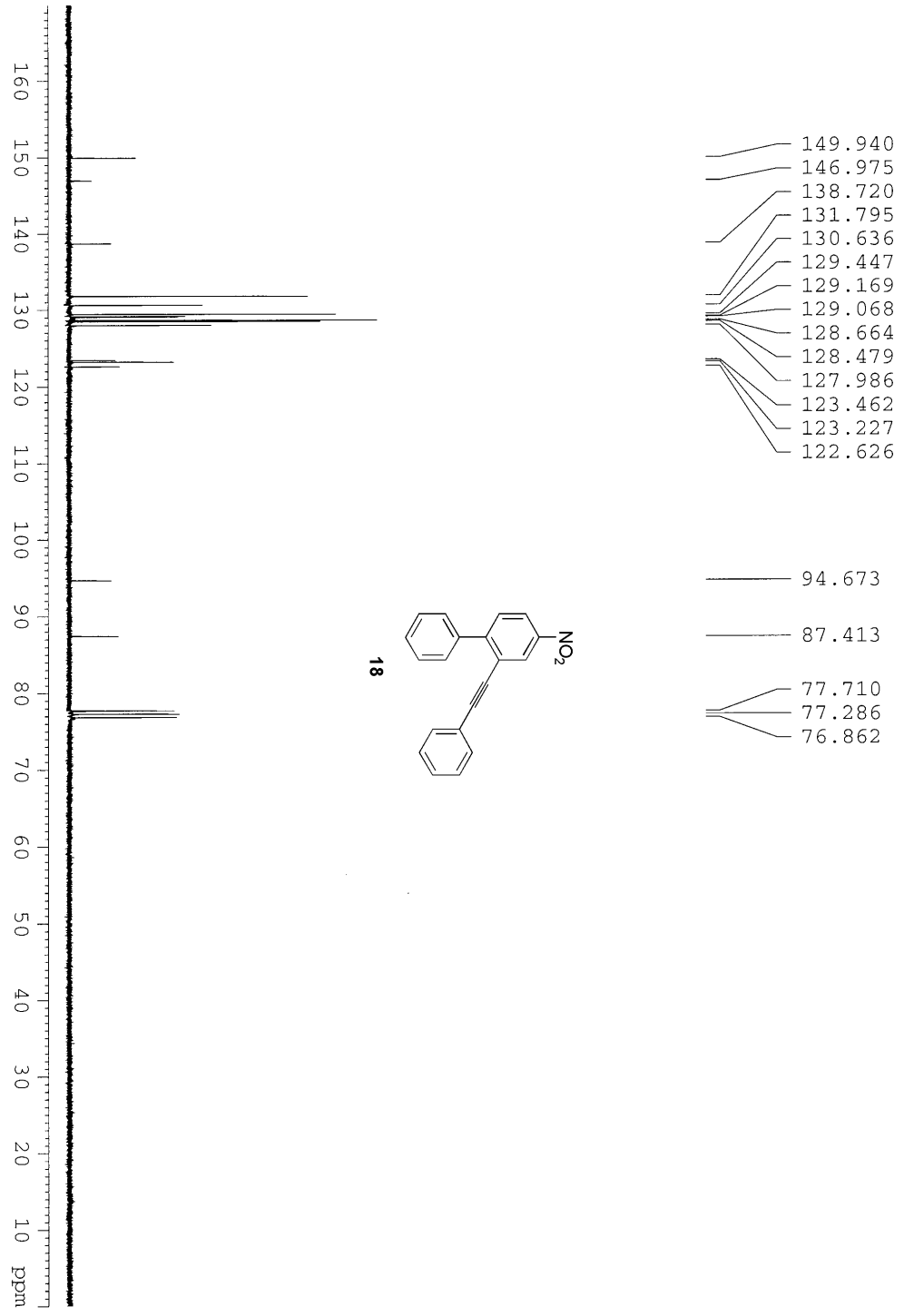
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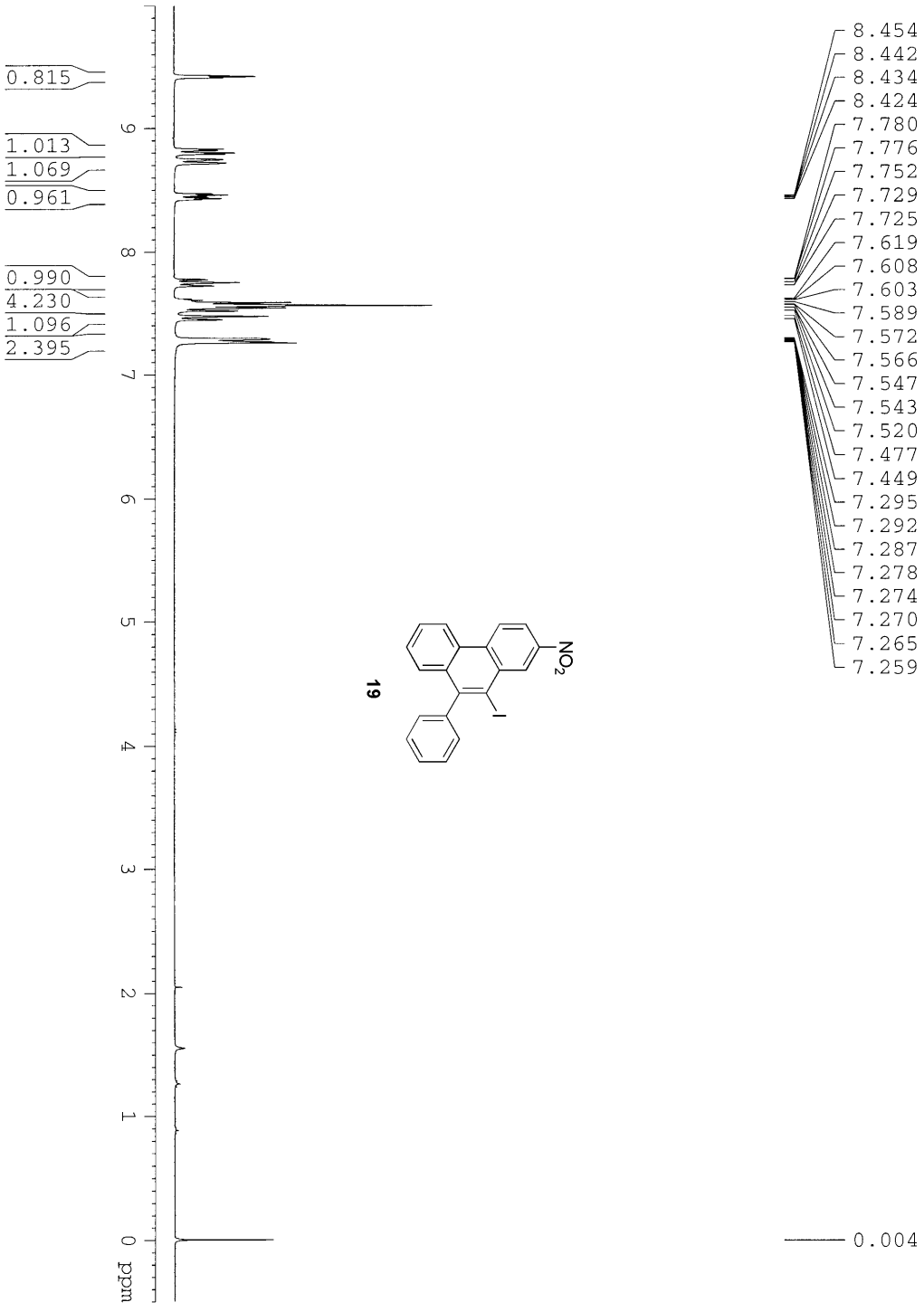
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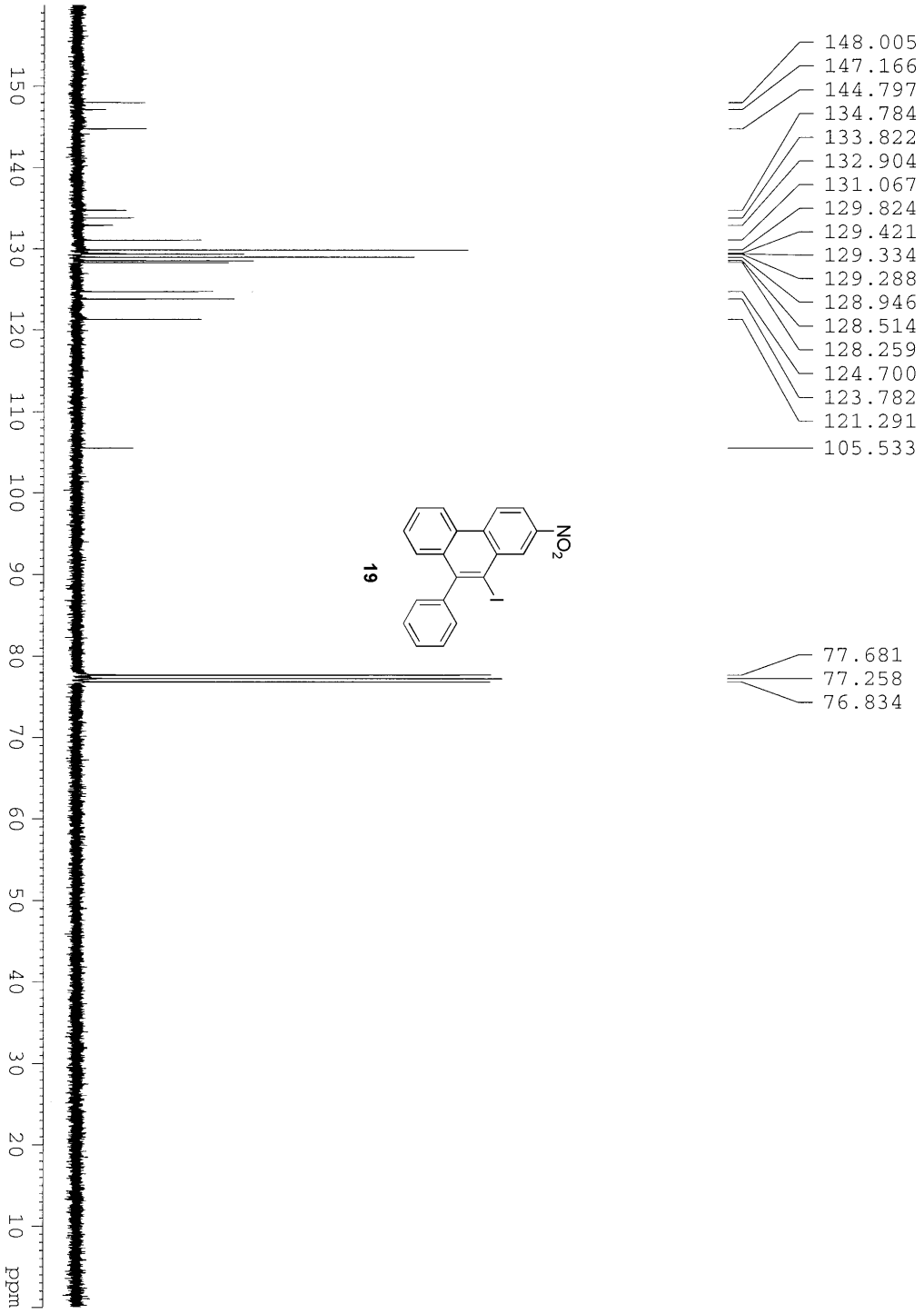
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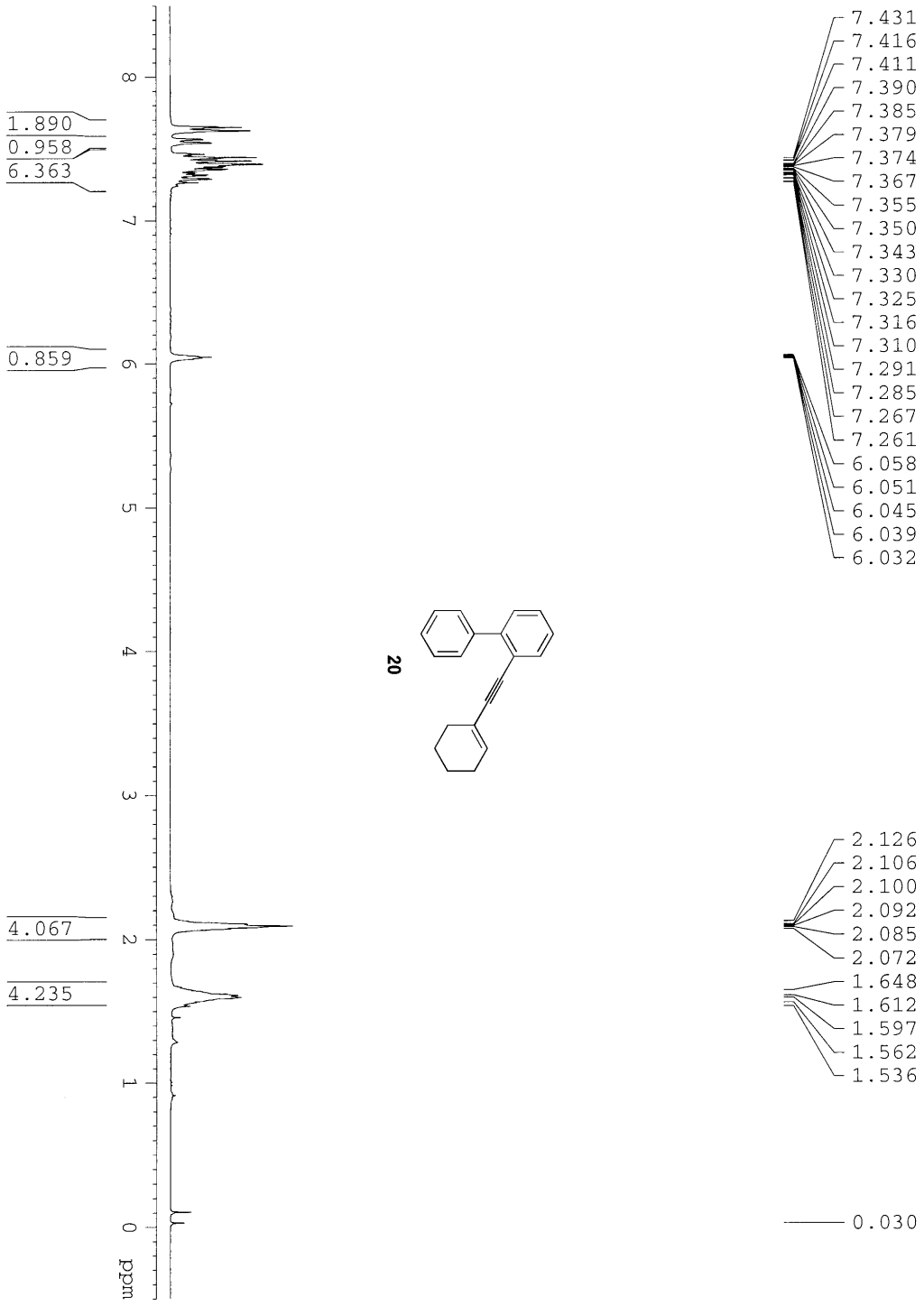
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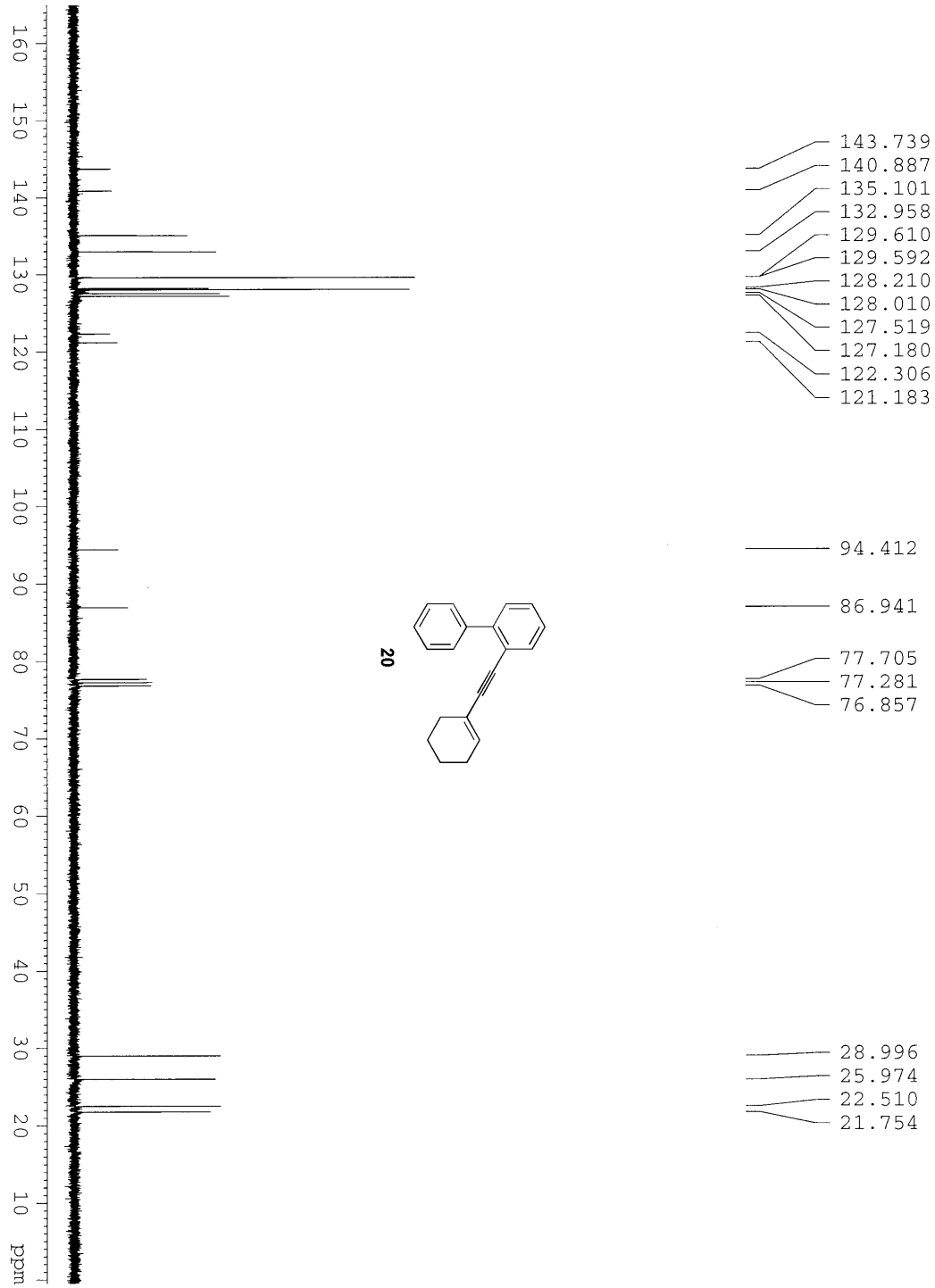
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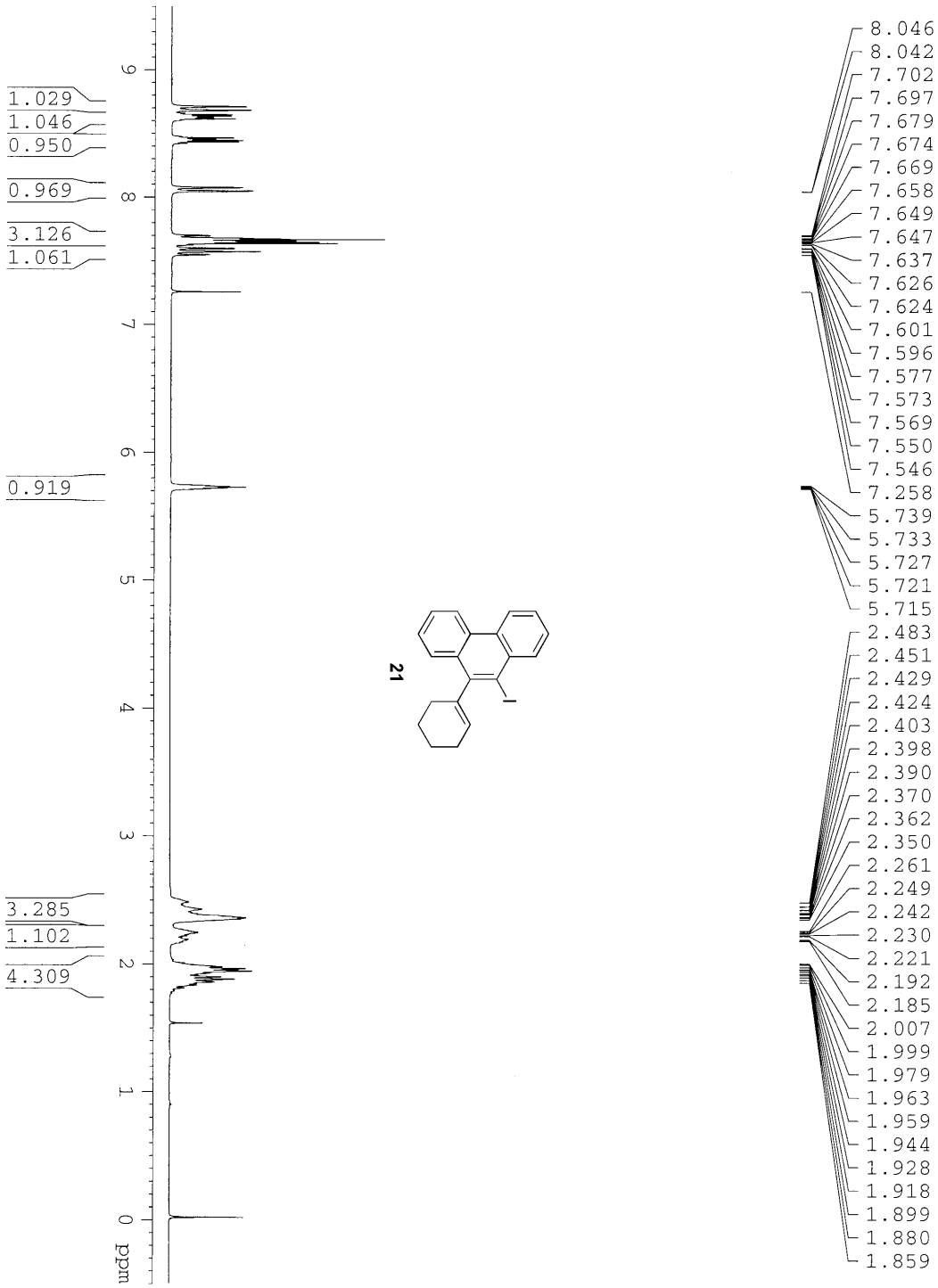
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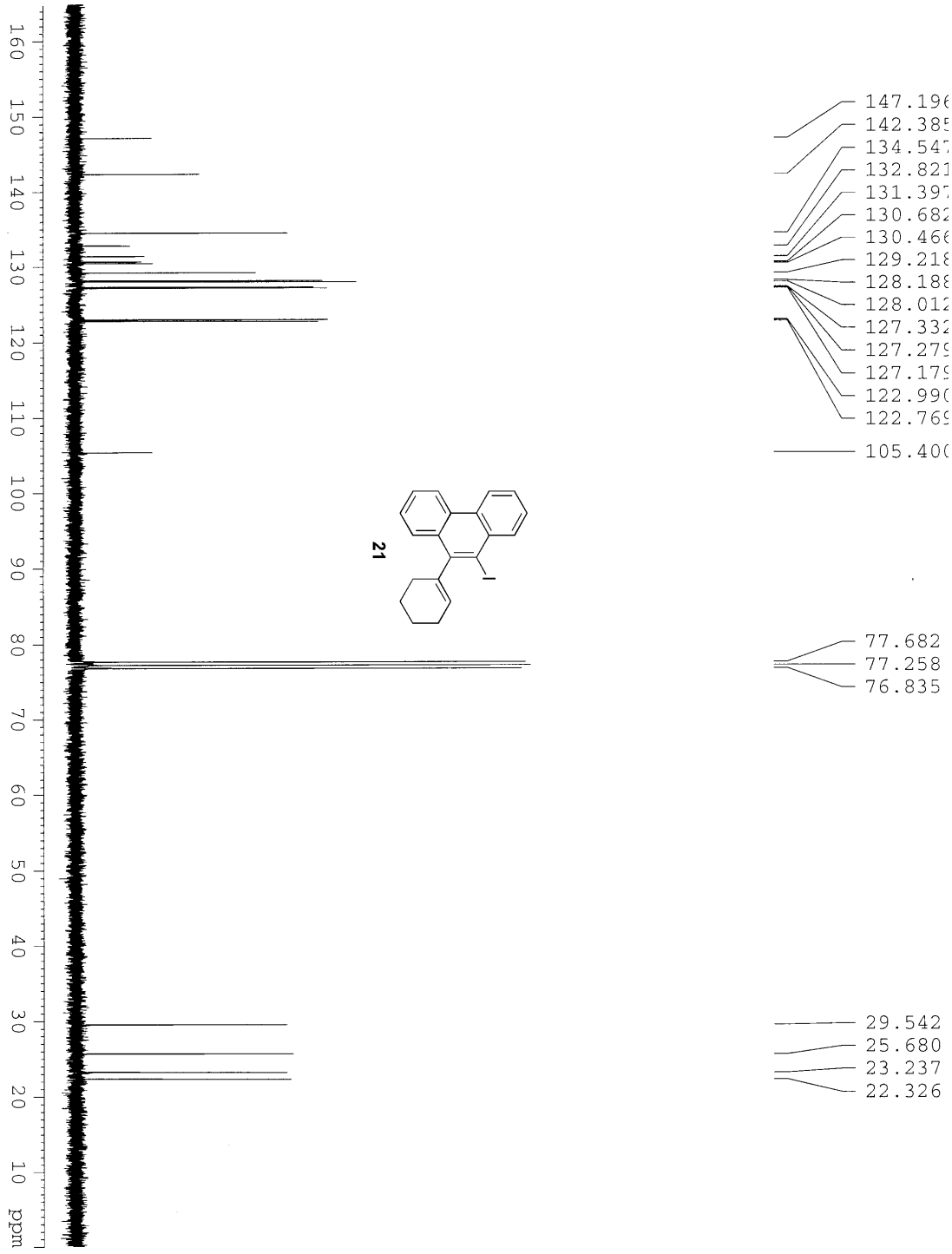
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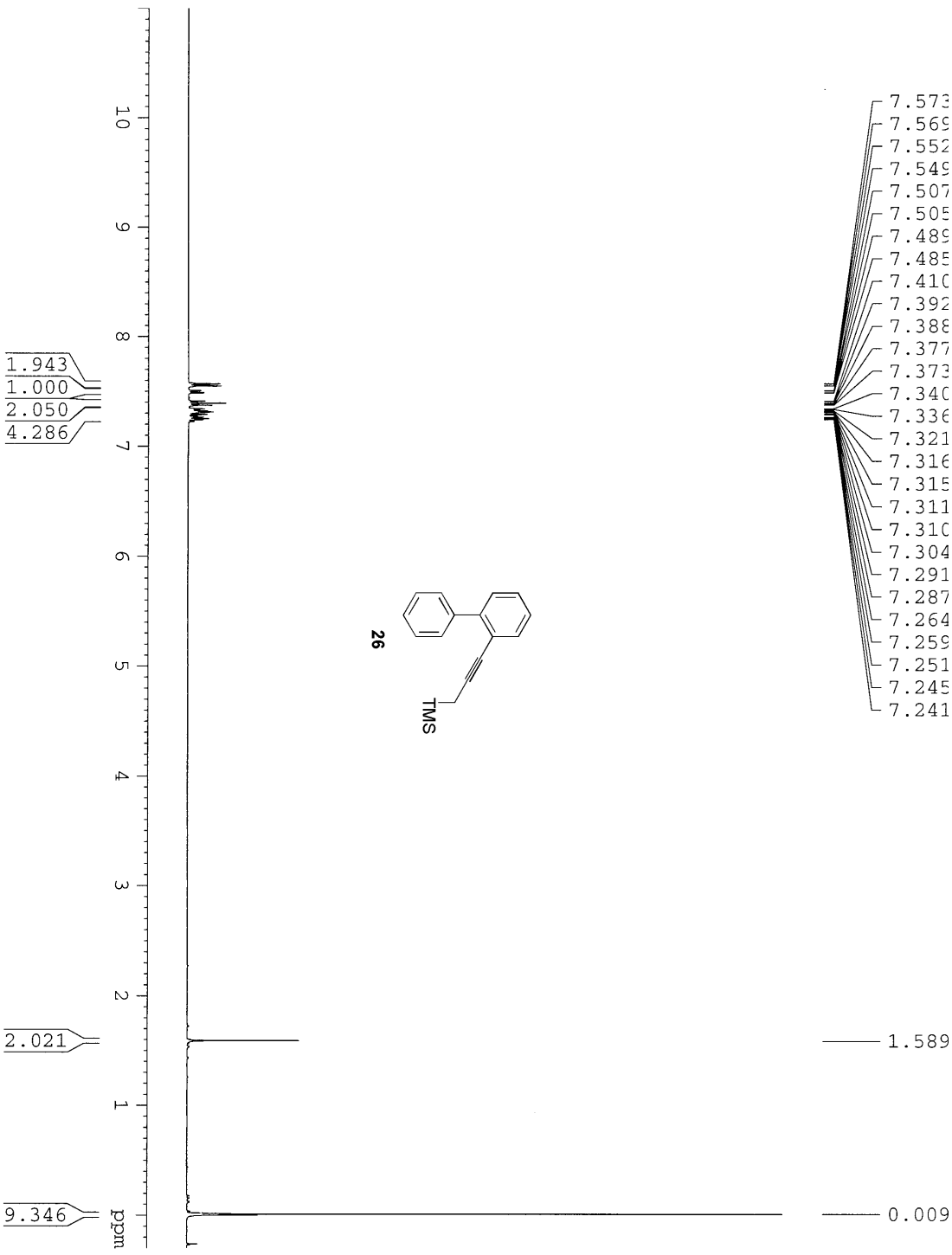
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7.505
7.489
7.485
7.410
7.392
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7.340
7.336
7.321
7.316
7.315
7.311
7.310
7.304
7.291
7.287
7.264
7.259
7.251
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2.021
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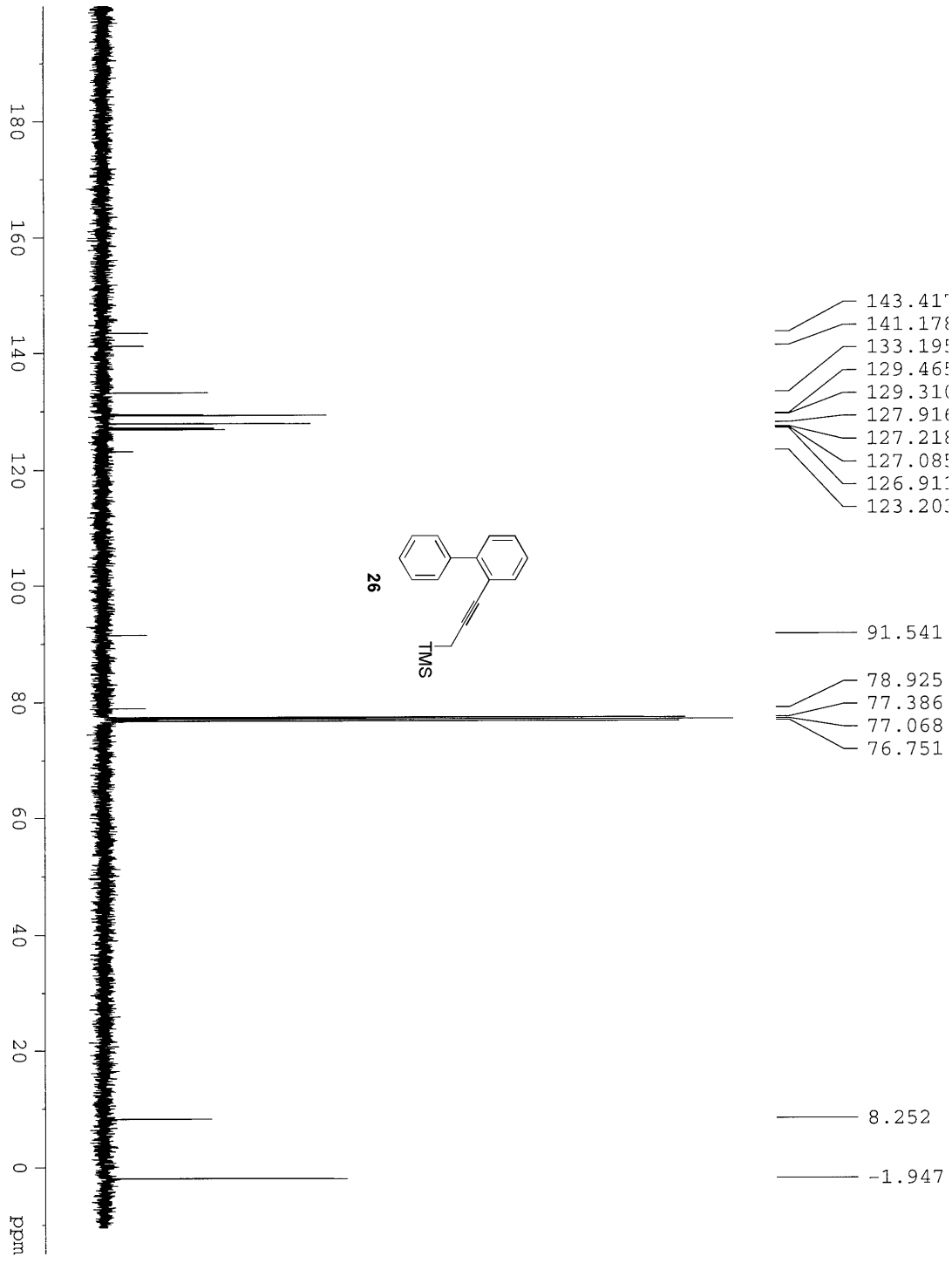
26
TMS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ppm
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TMS
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129.31
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123.20
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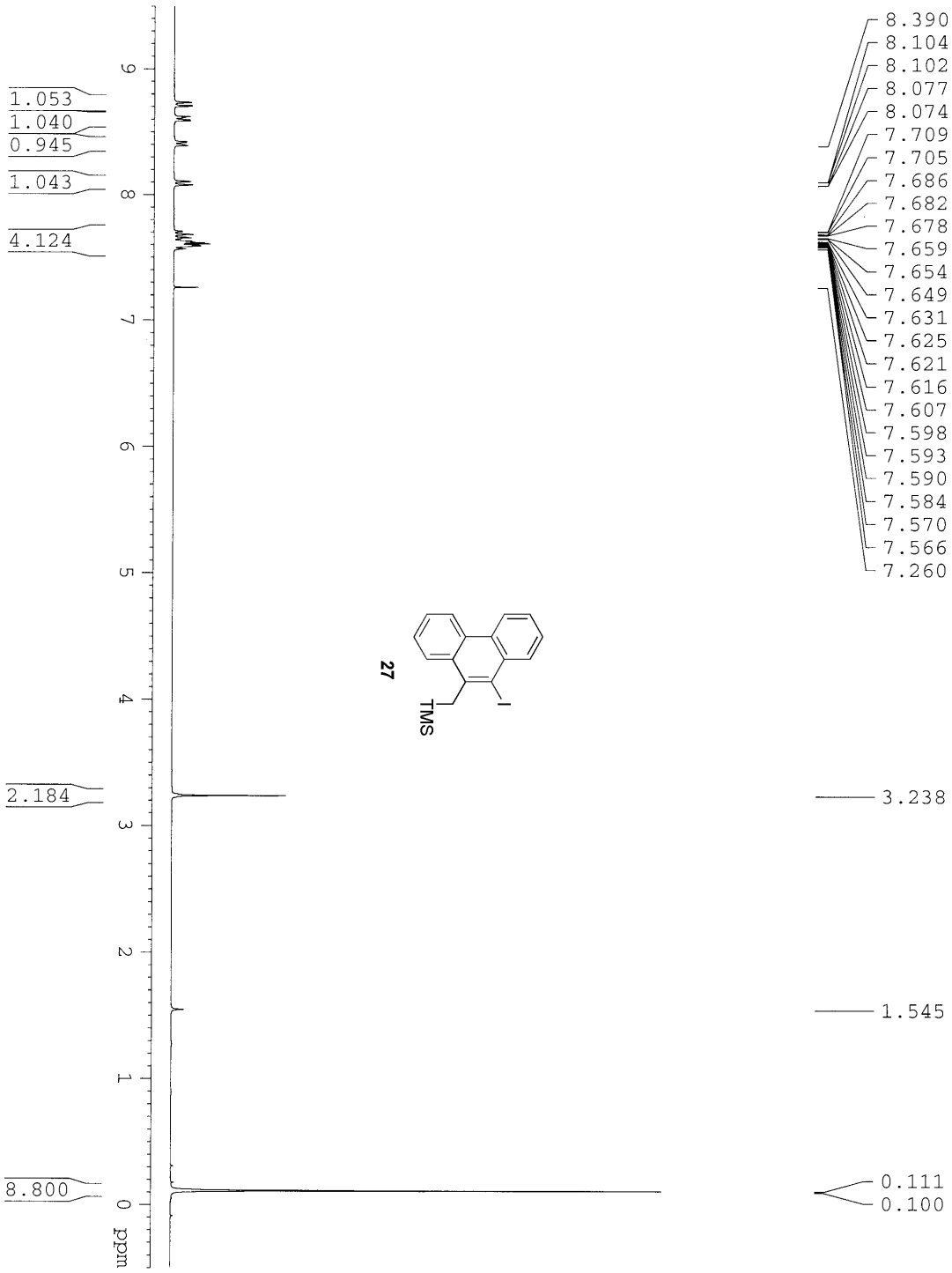
-1.947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7.659
7.654
7.649
7.631
7.625
7.621
7.616
7.607
7.598
7.593
7.590
7.584
7.570
7.566
7.260
1.053
1.040
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TMS
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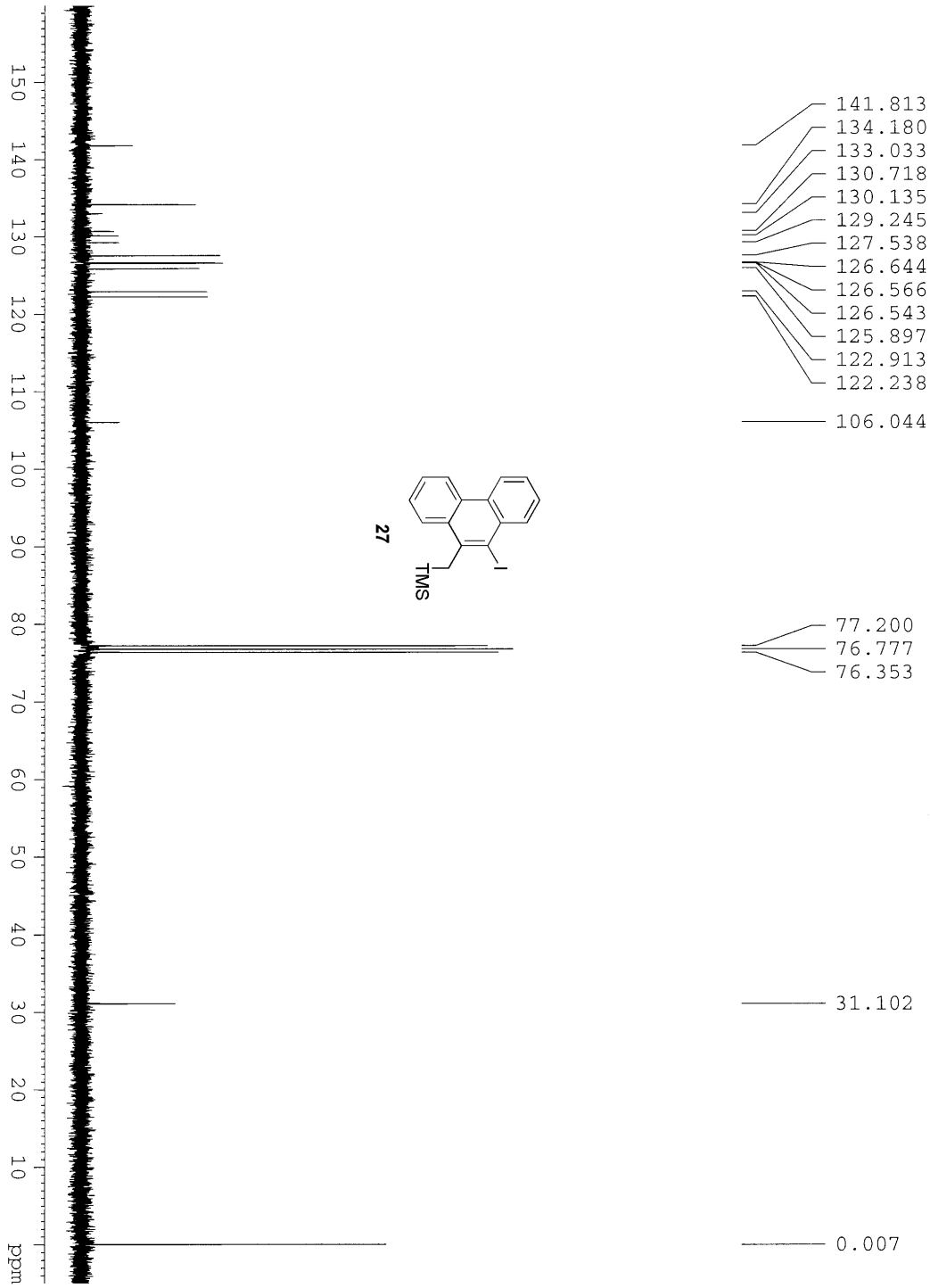
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122.238
106.044
77.200
76.777
76.353
31.102
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TMS
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140
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110
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30
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10
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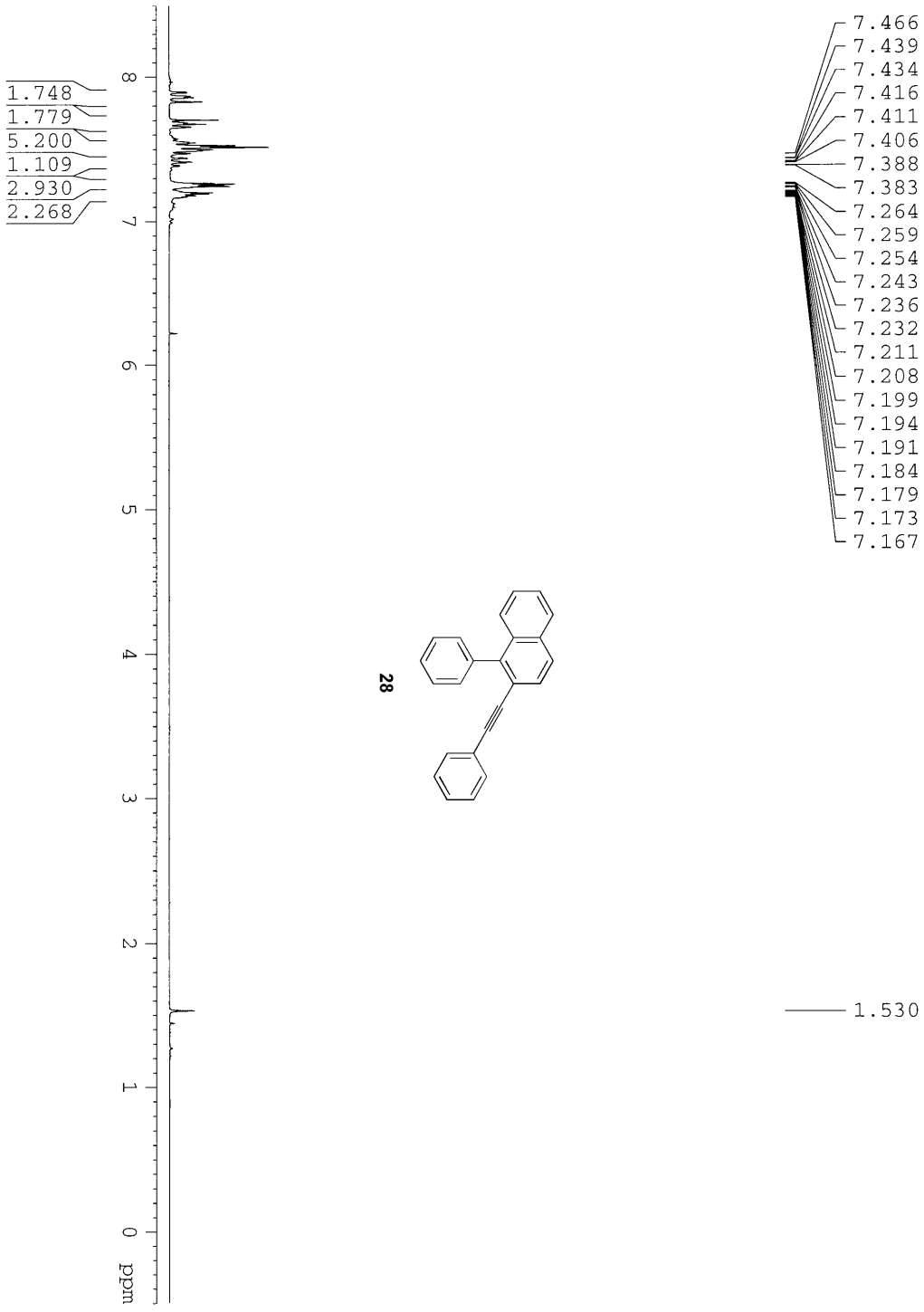
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5.200
1.109
2.930
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8
7
6
5
4
3
2
1
0
ppm
7.466
7.439
7.434
7.416
7.411
7.406
7.388
7.383
7.264
7.259
7.254
7.243
7.236
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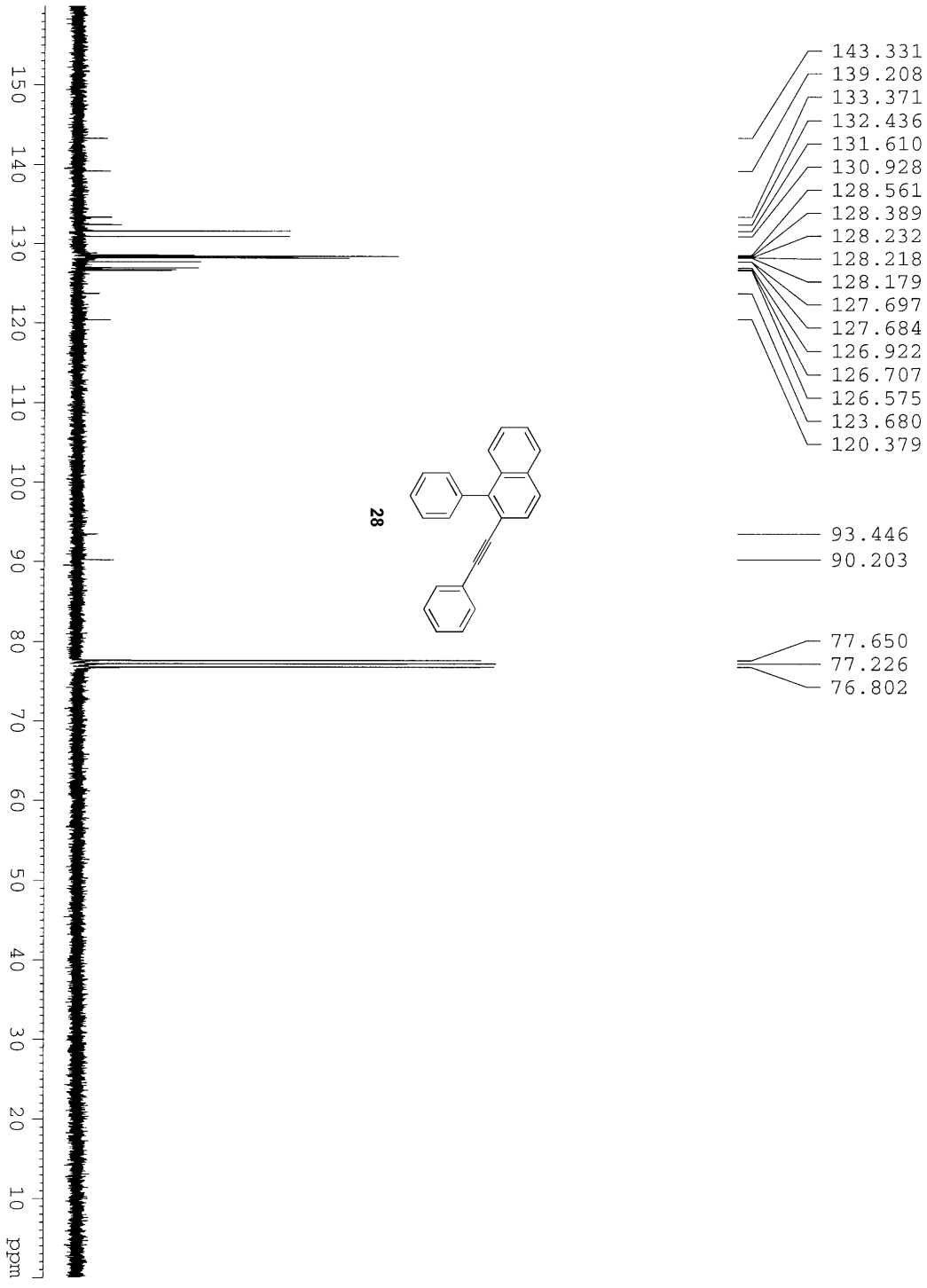
7.208
7.199
7.194
7.191
7.184
7.179
7.173
7.167
1.530

28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70
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40
30
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10
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28
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139.208
133.371
132.436
131.610
130.928
128.561
128.389
128.232
128.218
128.179
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126.707
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123.680
120.379
93.446
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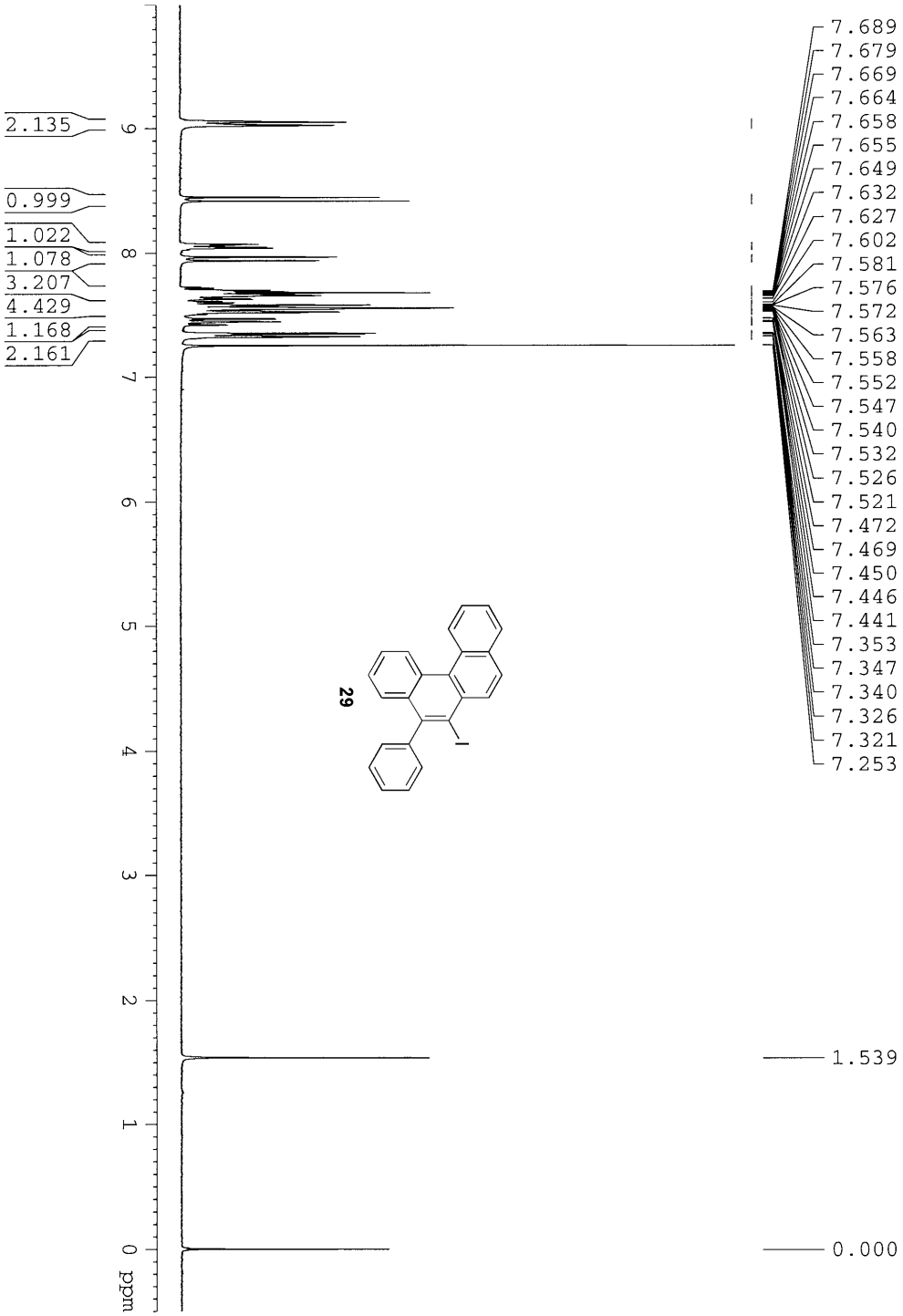
77.226
76.802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1.022
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4.429
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2.161
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7.679
7.669
7.664
7.658
7.655
7.649
7.632
7.627
7.602
7.581
7.576
7.572
7.563
7.558
7.552
7.547
7.540
7.532
7.526
7.521
7.472
7.469
7.450
7.446
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7.353
7.347
7.340
7.326
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7.253
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I
1.539
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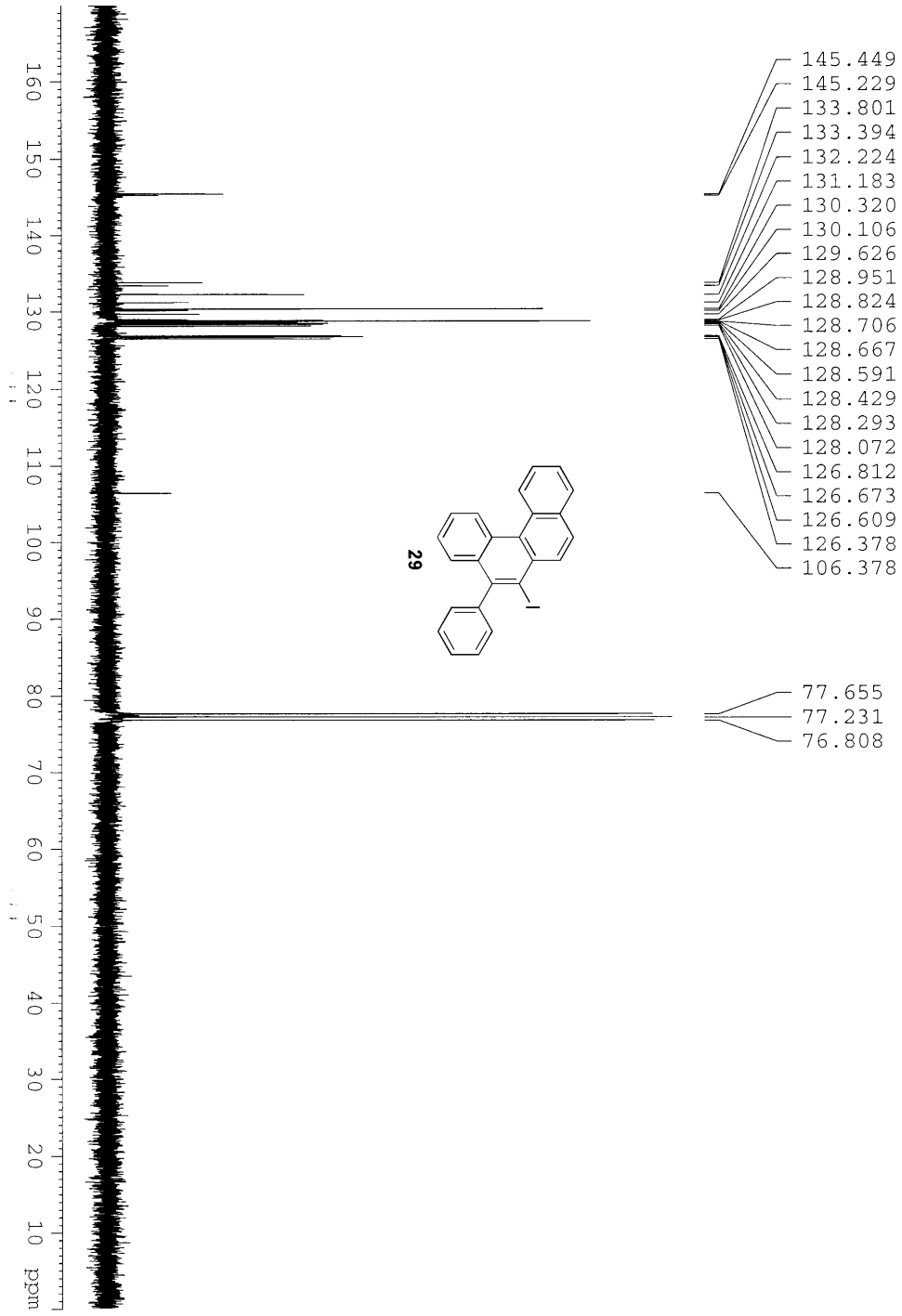
ppm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145.229
133.801
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131.183
130.320
130.106
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128.824
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128.667
128.591
128.429
128.293
128.072
126.812
126.673
126.609
126.378
106.378
77.655
77.231
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29
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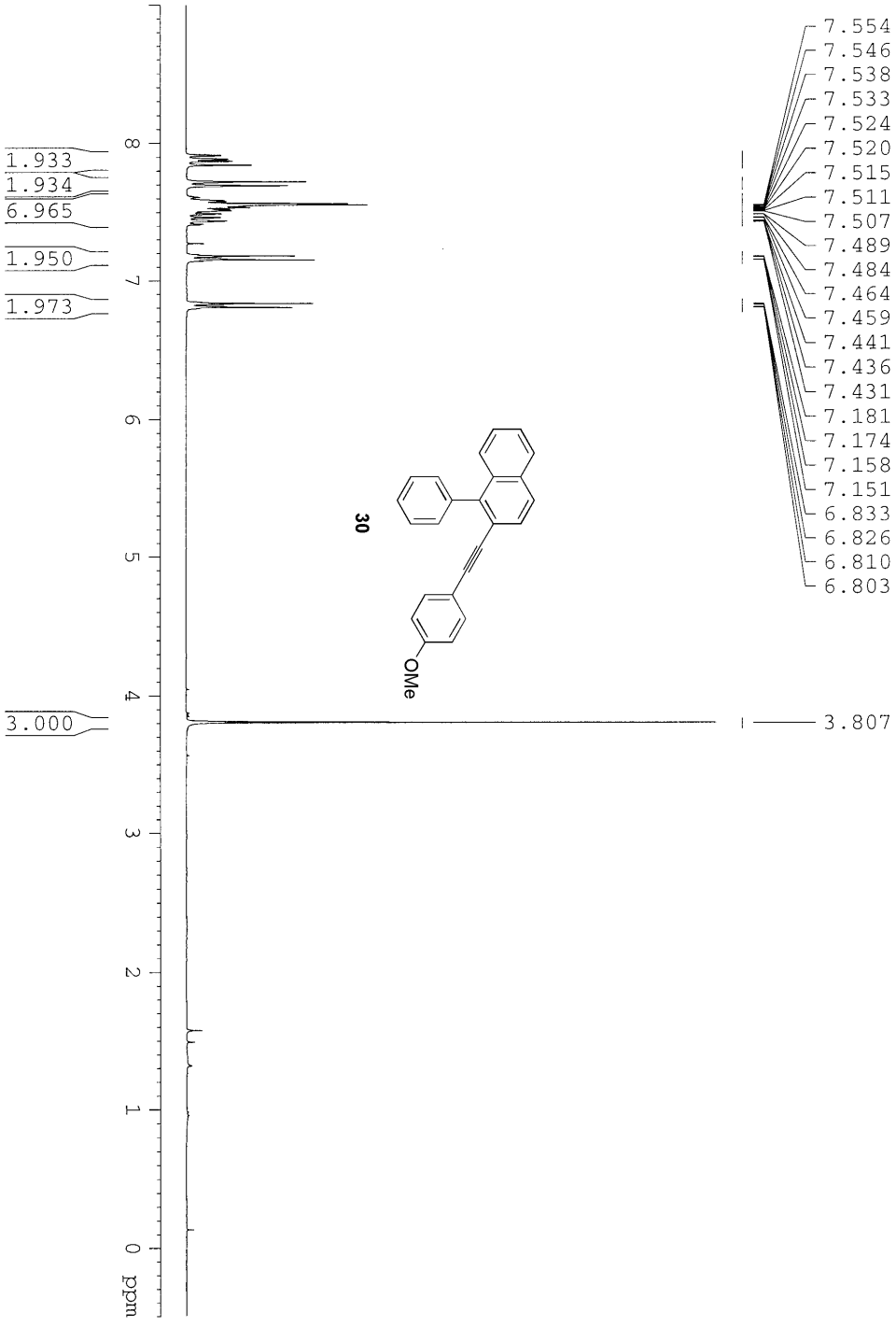
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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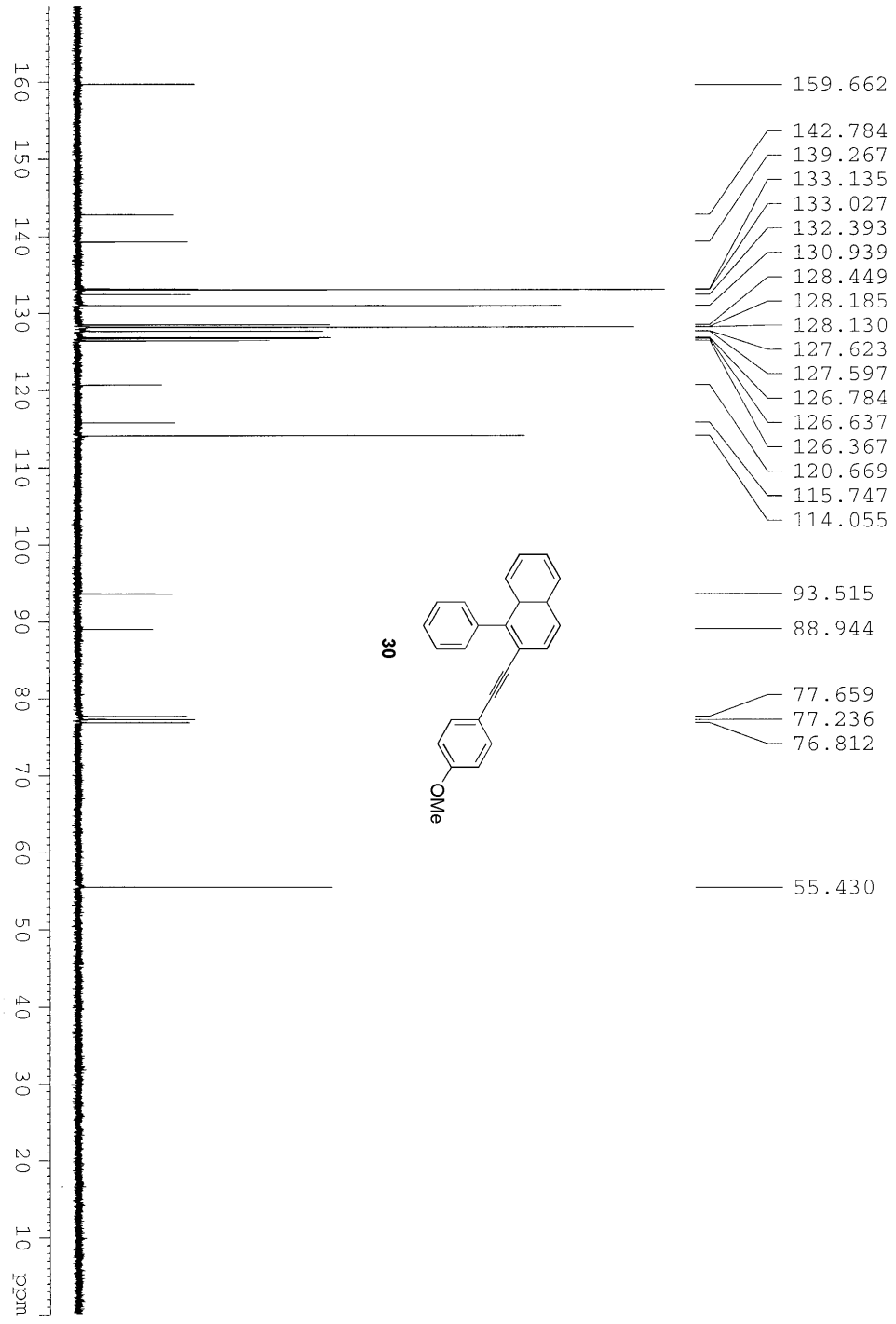
1.934
6.965
1.950
1.973
3.000
7.554
7.546
7.538
7.533
7.524
7.520
7.515
7.511
7.507
7.489
7.484
7.464
7.459
7.441
7.436
7.431
7.181
7.174
7.158
7.151
6.833
6.826
6.810
6.803
3.807
30
OMe
ppm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142.784
139.267
133.135
133.027
132.393
130.939
128.449
128.185
128.130
127.623
127.597
126.784
126.637
126.367
120.669
115.747
114.055
93.515
88.944
77.659
77.236
76.812
55.430
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OMe
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150
140
130
120
110
100
90
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70
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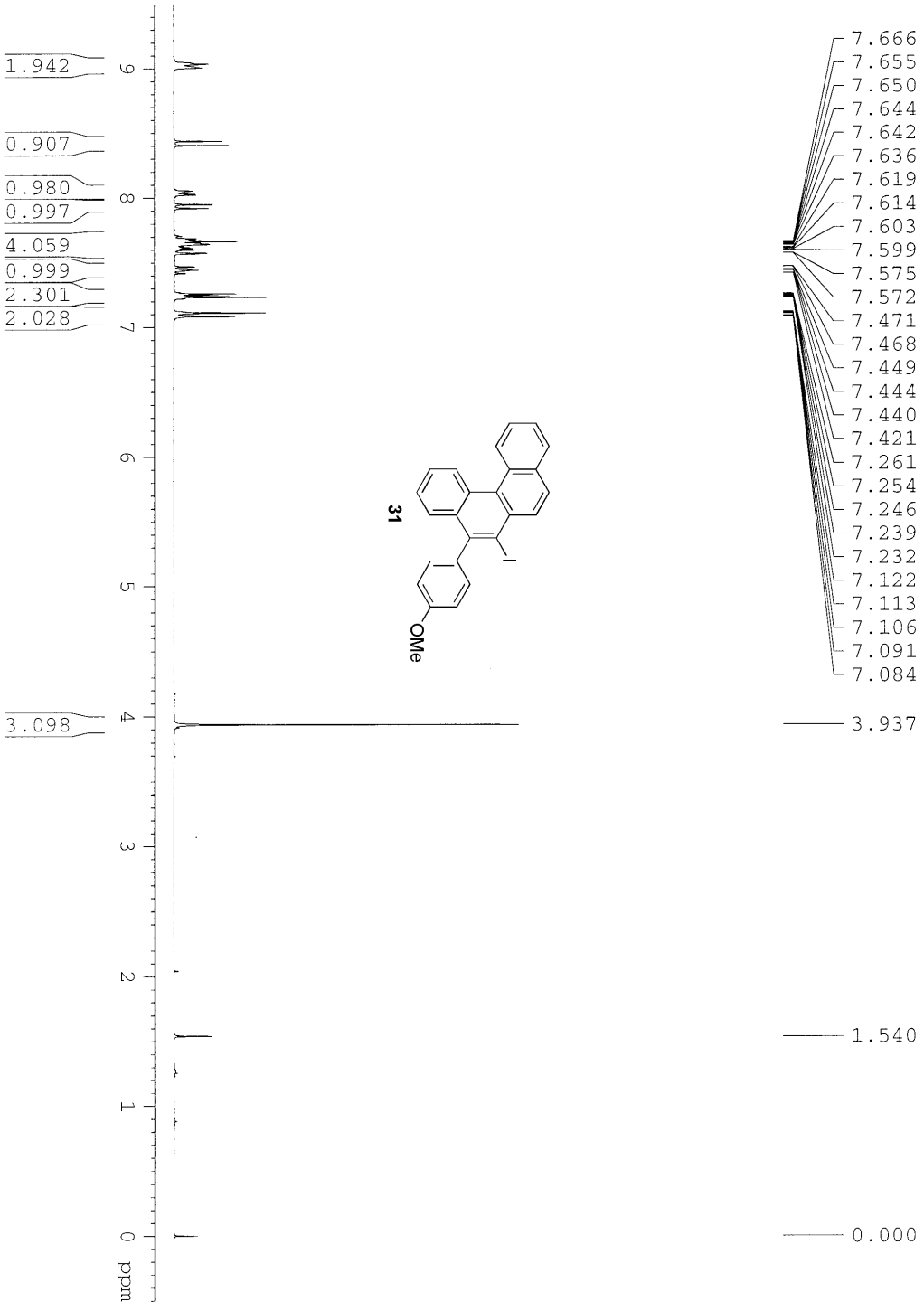
30
20
10
ppm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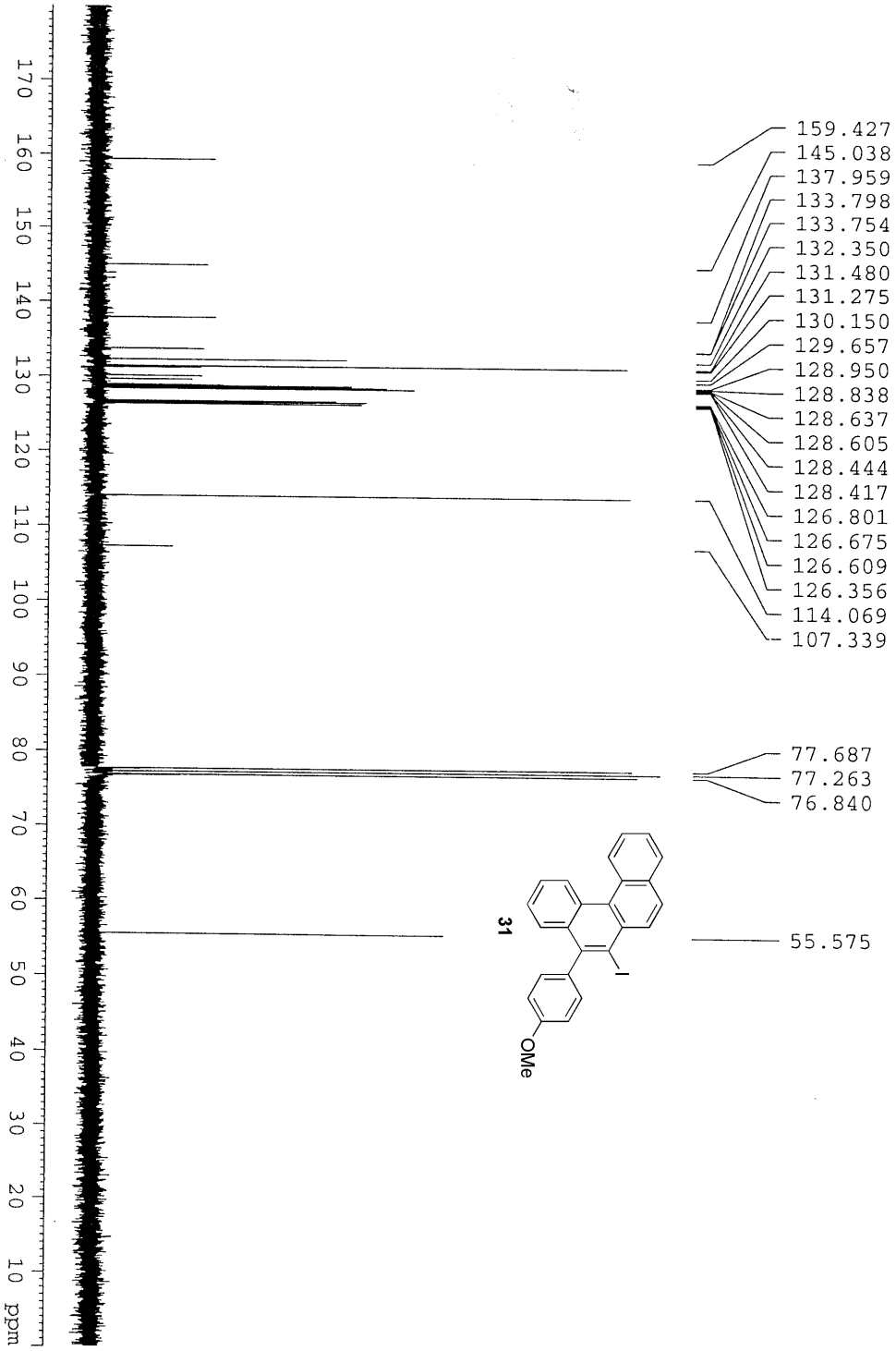
0.980
0.997
4.059
0.999
2.301
2.028
3.098
9
8
7
6
5
4
3
2
1
0
ppm
31
I
OMe
7.666
7.655
7.650
7.644
7.642
7.636
7.619
7.614
7.603
7.599
7.575
7.572
7.471
7.468
7.449
7.444
7.440
7.421
7.261
7.254
7.246
7.239
7.232
7.122
7.113
7.106
7.091
7.084
3.937
1.540
0.000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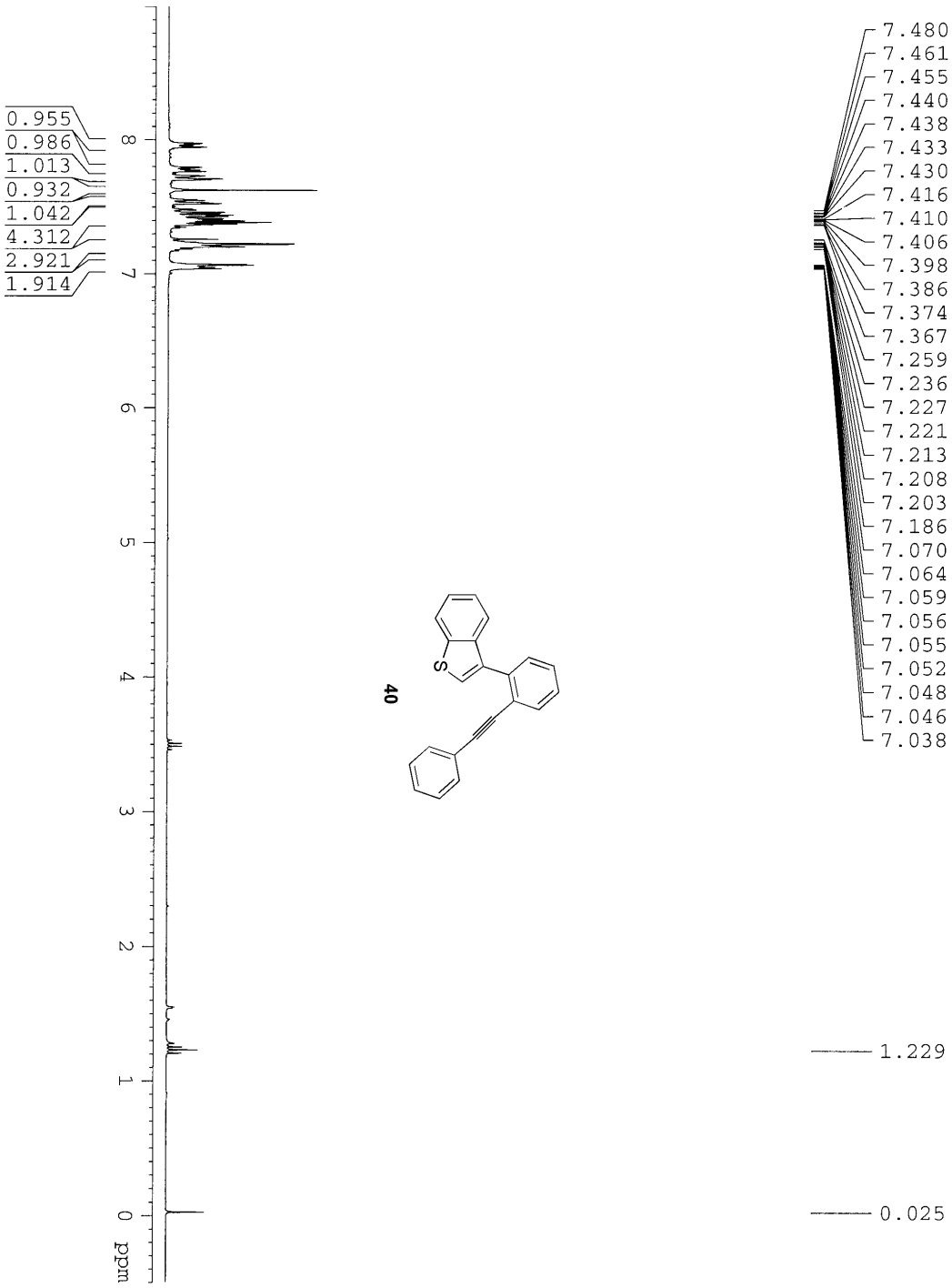
133.754
132.350
131.480
131.275
130.150
129.657
128.950
128.838
128.637
128.605
128.444
128.417
126.801
126.675
126.609
126.356
114.069
107.339
77.687
77.263
76.840
55.575
31
I
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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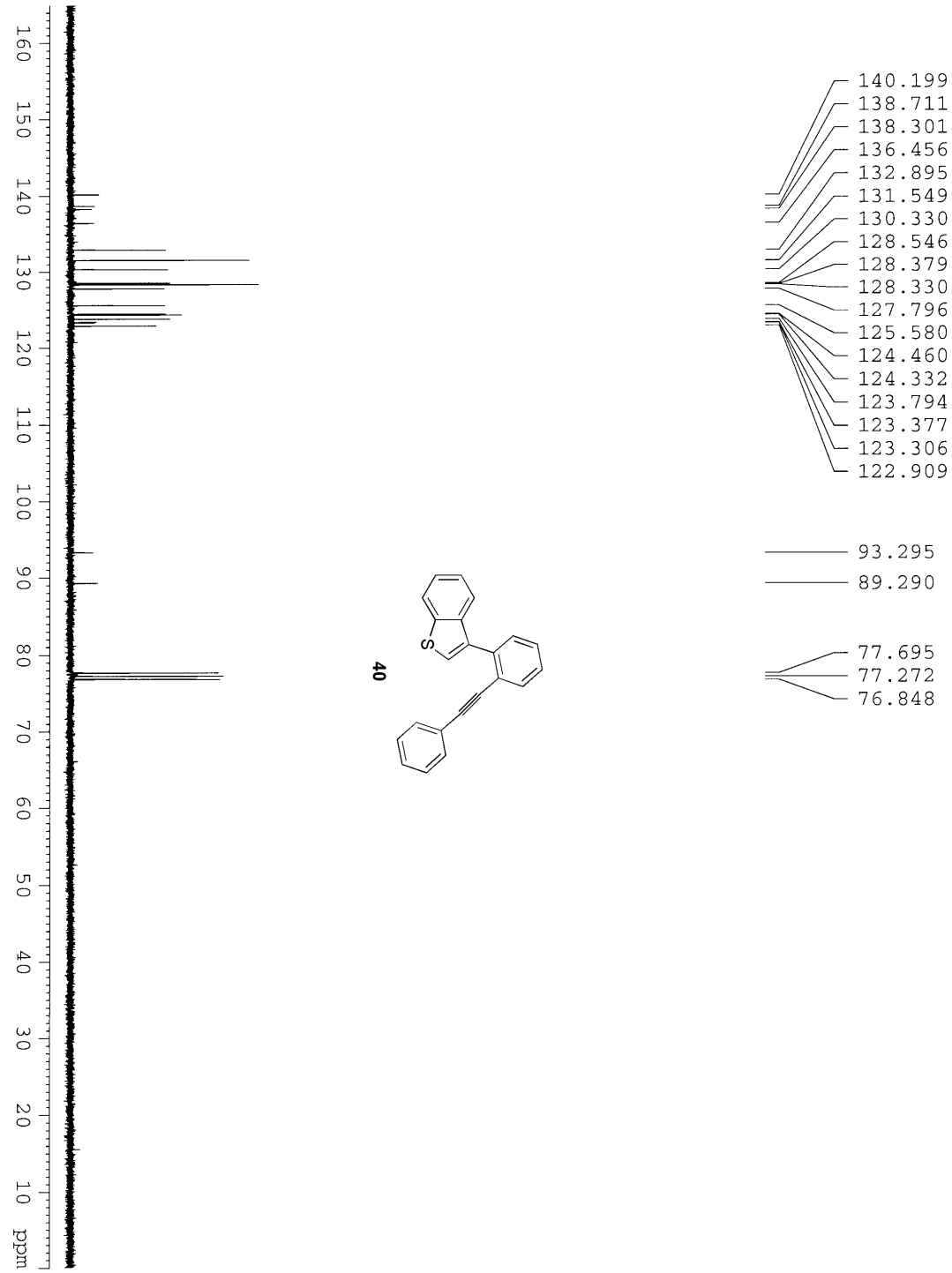
1.013
0.932
1.042
4.312
2.921
1.914
8
7
6
5
4
3
2
1
0
ppm
40
S
7.480
7.461
7.455
7.440
7.438
7.433
7.430
7.416
7.410
7.406
7.398
7.386
7.374
7.367
7.259
7.236
7.227
7.221
7.213
7.208
7.203
7.186
7.070
7.064
7.059
7.056
7.055
7.052
7.048
7.046
7.038
1.229
0.025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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
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138.711
138.301
136.456
132.895
131.549
130.330
128.546
128.379
128.330
127.796
125.580
124.460
124.332
123.794
123.377
123.306
122.909
93.295
89.290
77.695
77.272
76.848
S
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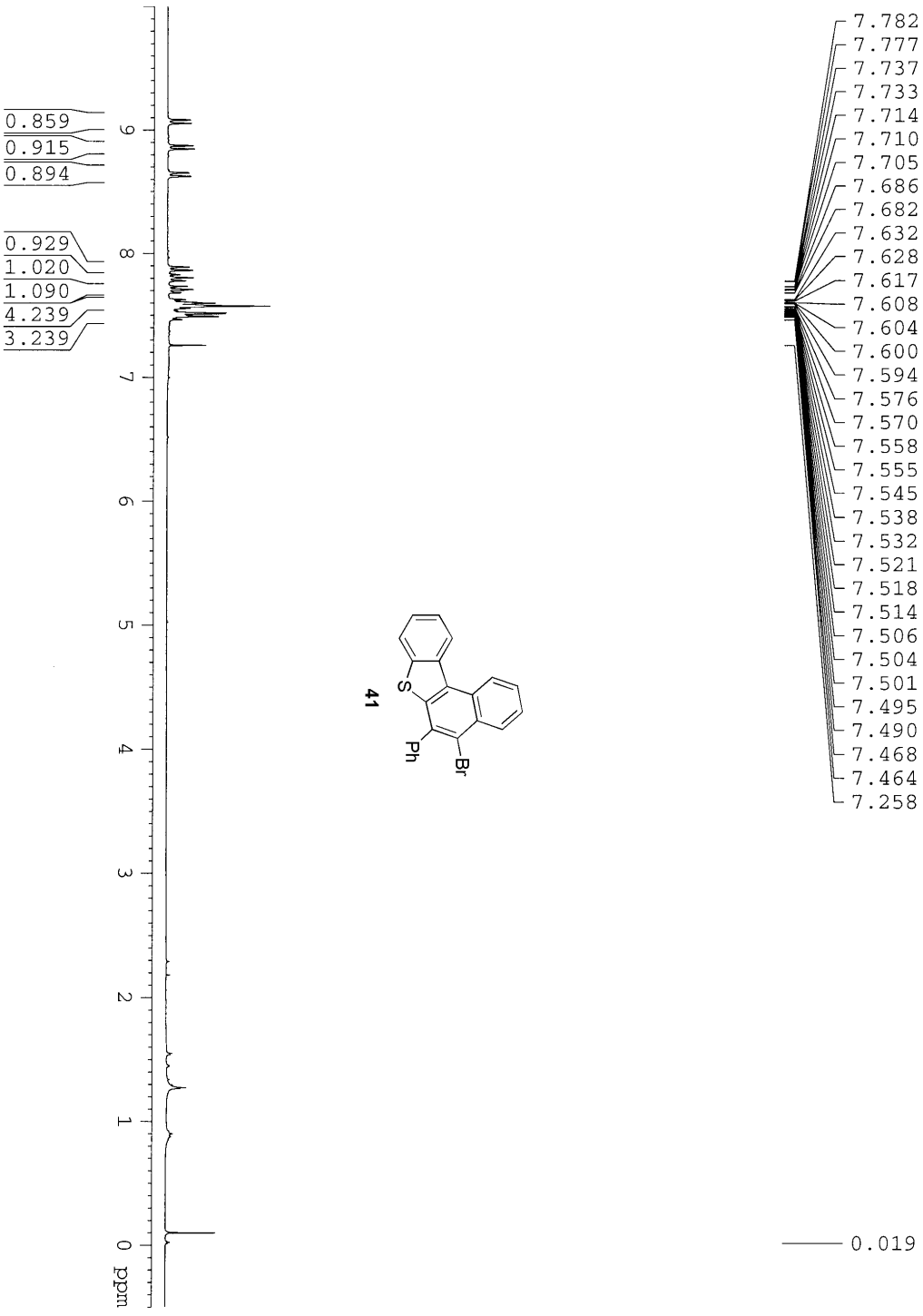
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0.894
0.929
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1.090
4.239
3.239
9
8
7
6
5
4
3
2
1
0 ppm
41
S
Ph
Br
7.782
7.777
7.737
7.733
7.714
7.710
7.705
7.686
7.682
7.632
7.628
7.617
7.608
7.604
7.600
7.594
7.576
7.570
7.558
7.555
7.545
7.538
7.532
7.521
7.518
7.514
7.506
7.504
7.501
7.495
7.490
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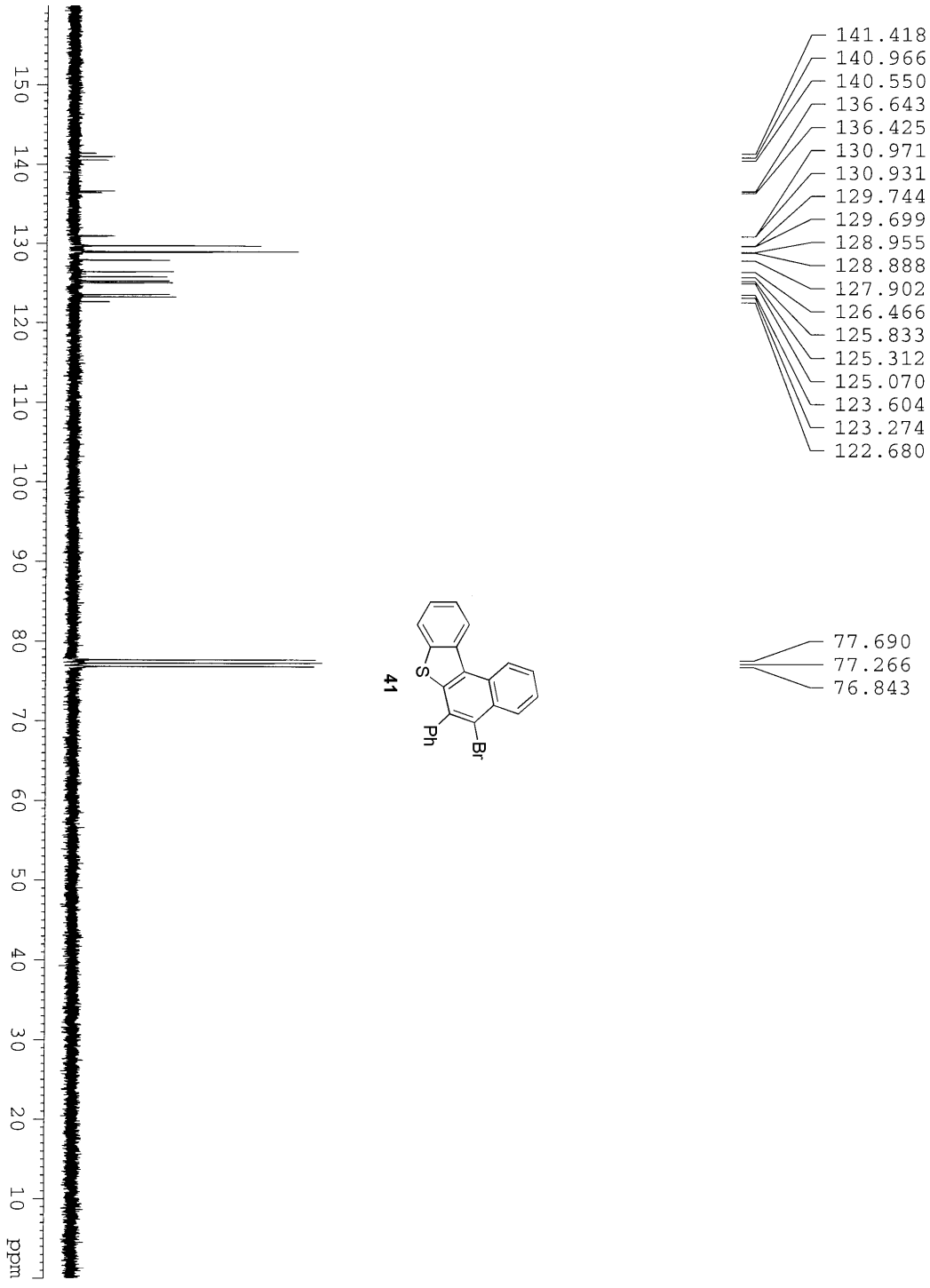
7.464
7.258
0.019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130.971
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129.744
129.699
128.955
128.888
127.902
126.466
125.833
125.312
125.070
123.604
123.274
122.680
77.690
77.266
76.843
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Ph
Br
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20
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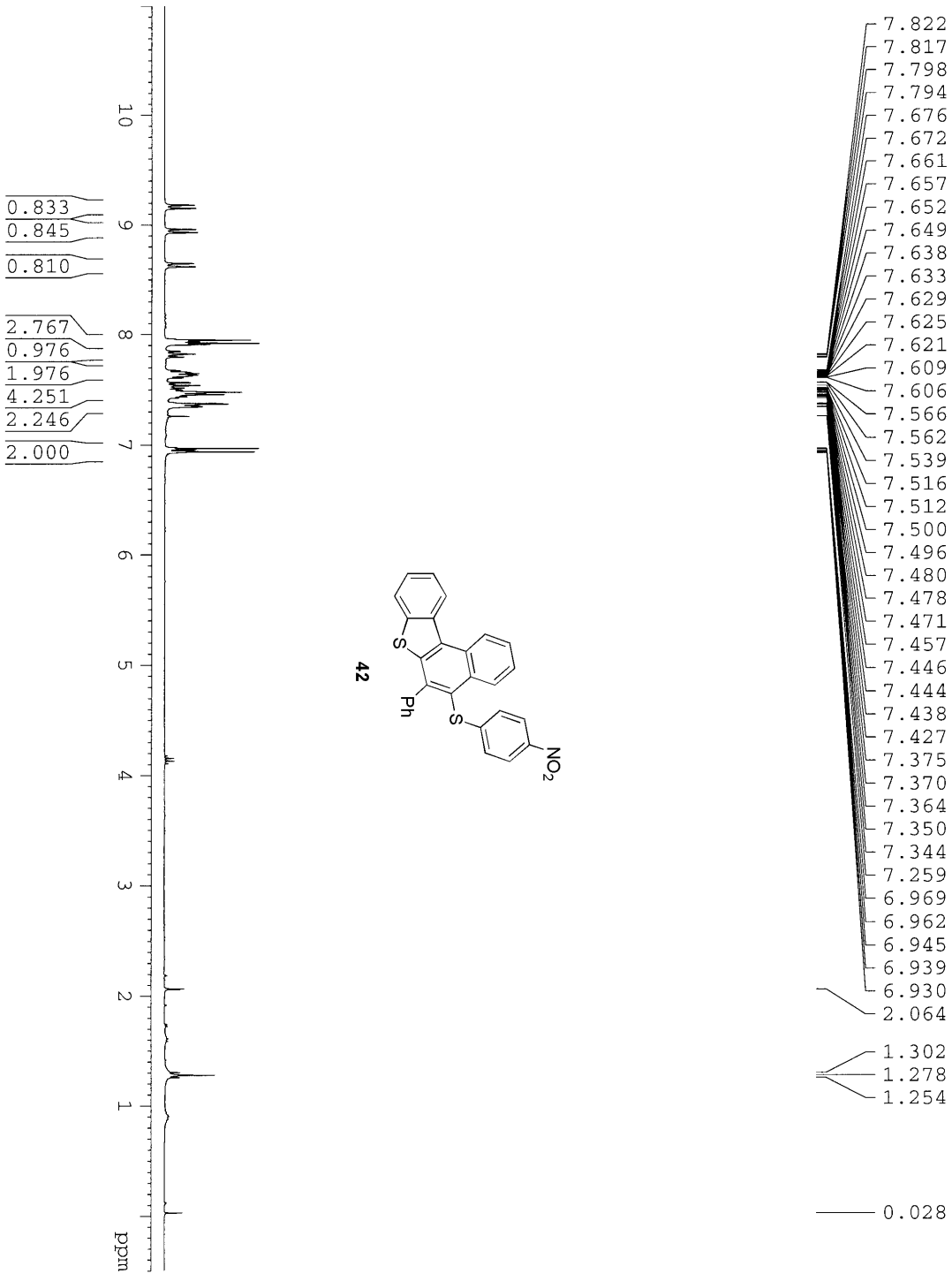
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2.246
2.000
10
9
8
7
6
5
4
3
2
1
ppm
7.822
7.817
7.798
7.794
7.676
7.672
7.661
7.657
7.652
7.649
7.638
7.633
7.629
7.625
7.621
7.609
7.606
7.566
7.562
7.539
7.516
7.512
7.500
7.496
7.480
7.478
7.471
7.457
7.446
7.444
7.438
7.427
7.375
7.370
7.364
7.350
7.344
7.259
6.969
6.962
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1.278
1.254
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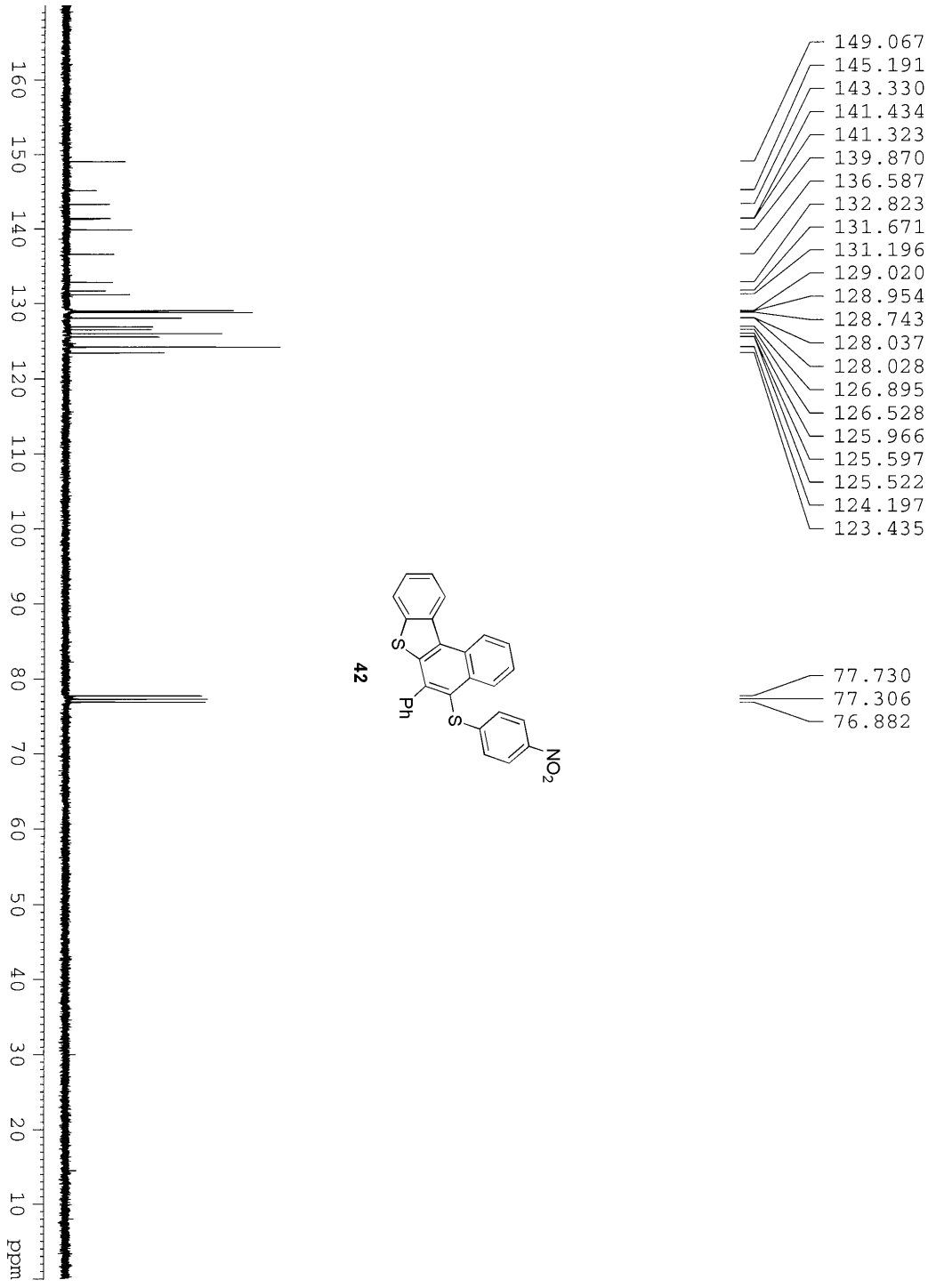
Ph
S
NO2

42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140
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120
110
100
90
80
70
60
50
40
30
20
10
ppm
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143.330
141.434
141.323
139.870
136.587
132.823
131.671
131.196
129.020
128.954
128.743
128.037
128.028
126.895
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125.522
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123.435
77.730
77.306
76.882
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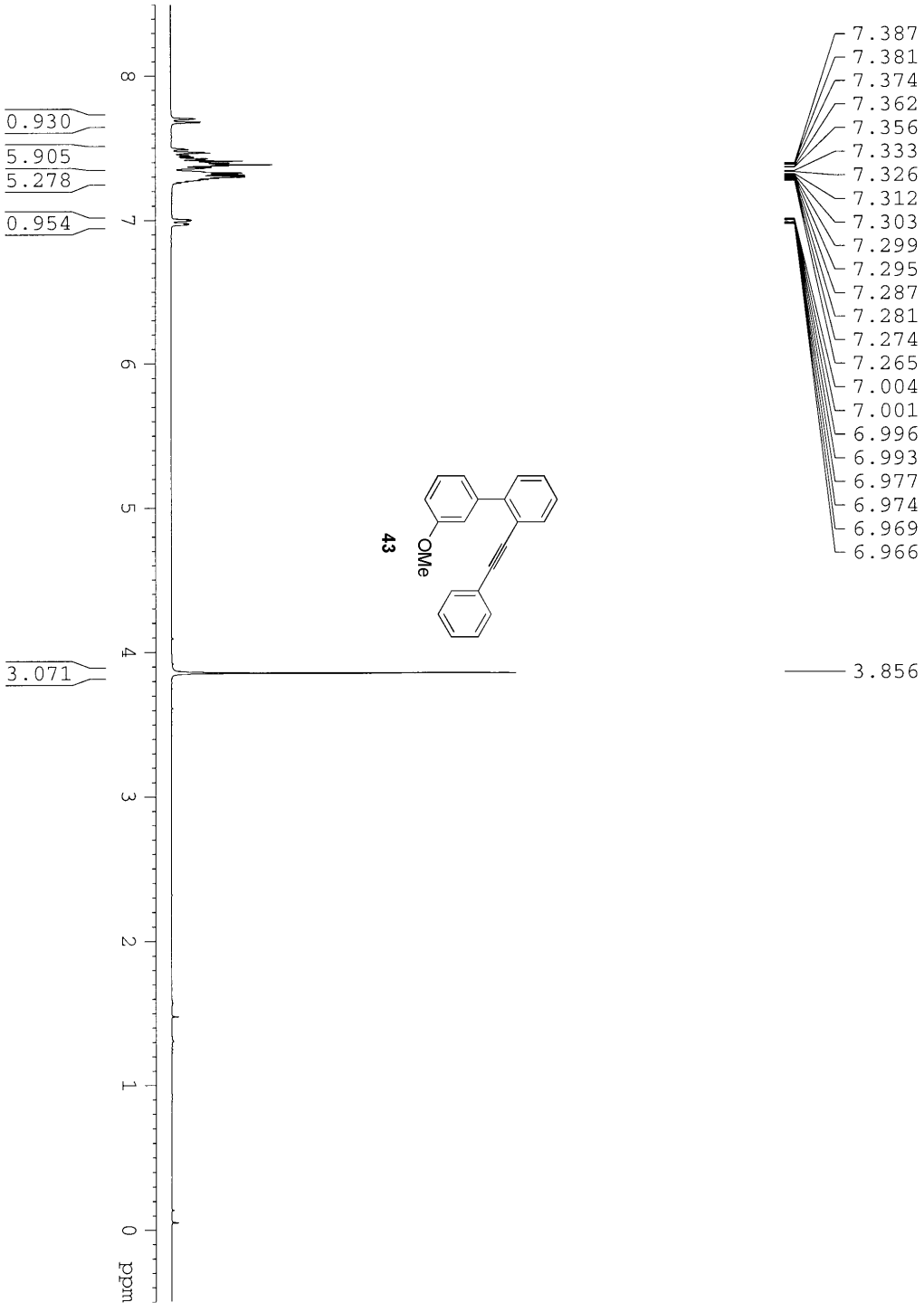
Ph
S
NO2

42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5.905
5.278
0.954
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8
7
6
5
4
3
2
1
0
ppm
OMe
43
7.387
7.381
7.374
7.362
7.356
7.333
7.326
7.312
7.303
7.299
7.295
7.287
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7.001
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6.993
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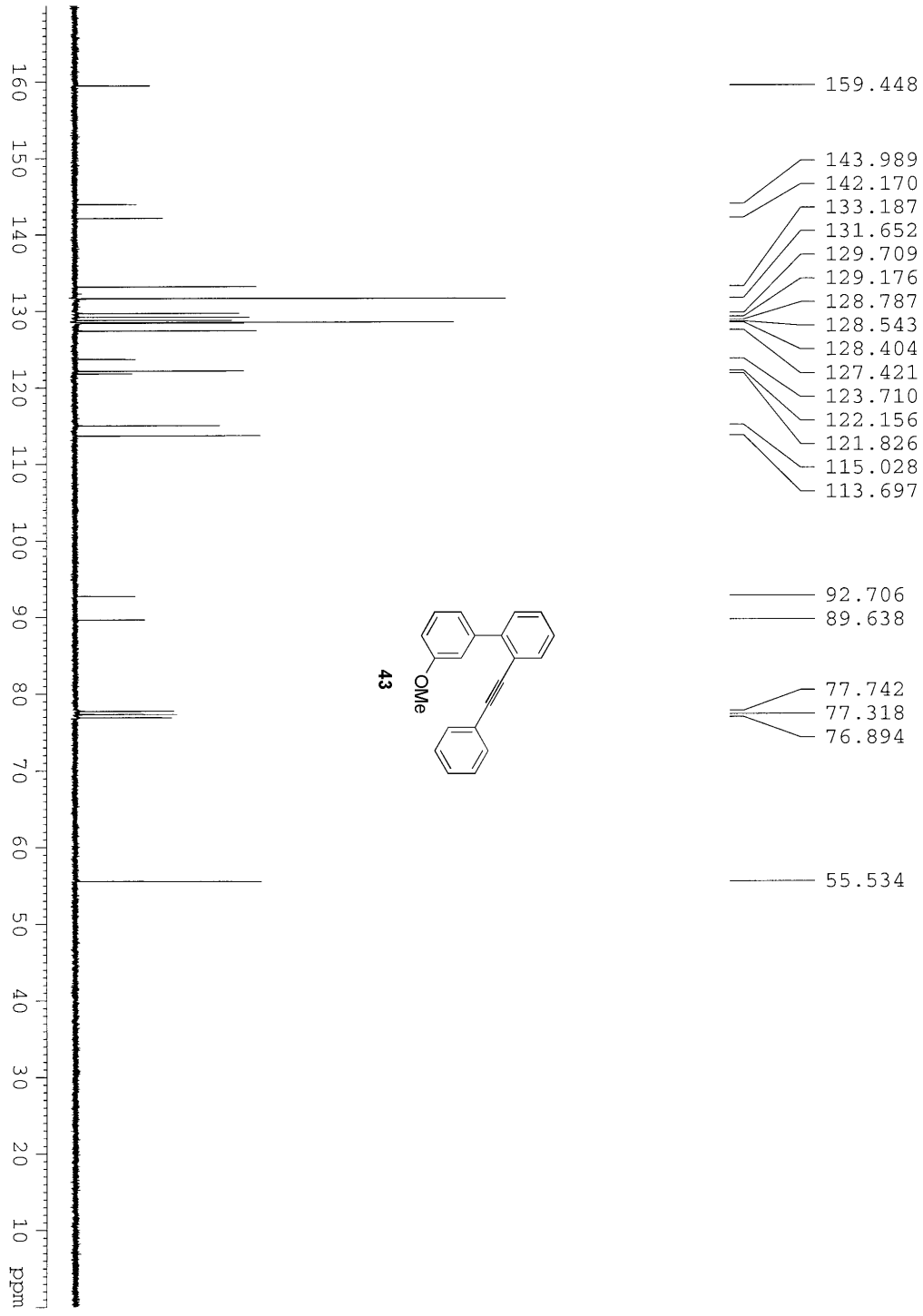
6.974
6.969
6.966
3.856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128.787
128.543
128.404
127.421
123.710
122.156
121.826
115.028
113.697
92.706
89.638
77.742
77.318
76.894
55.534
OMe
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150
140
130
120
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100
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30
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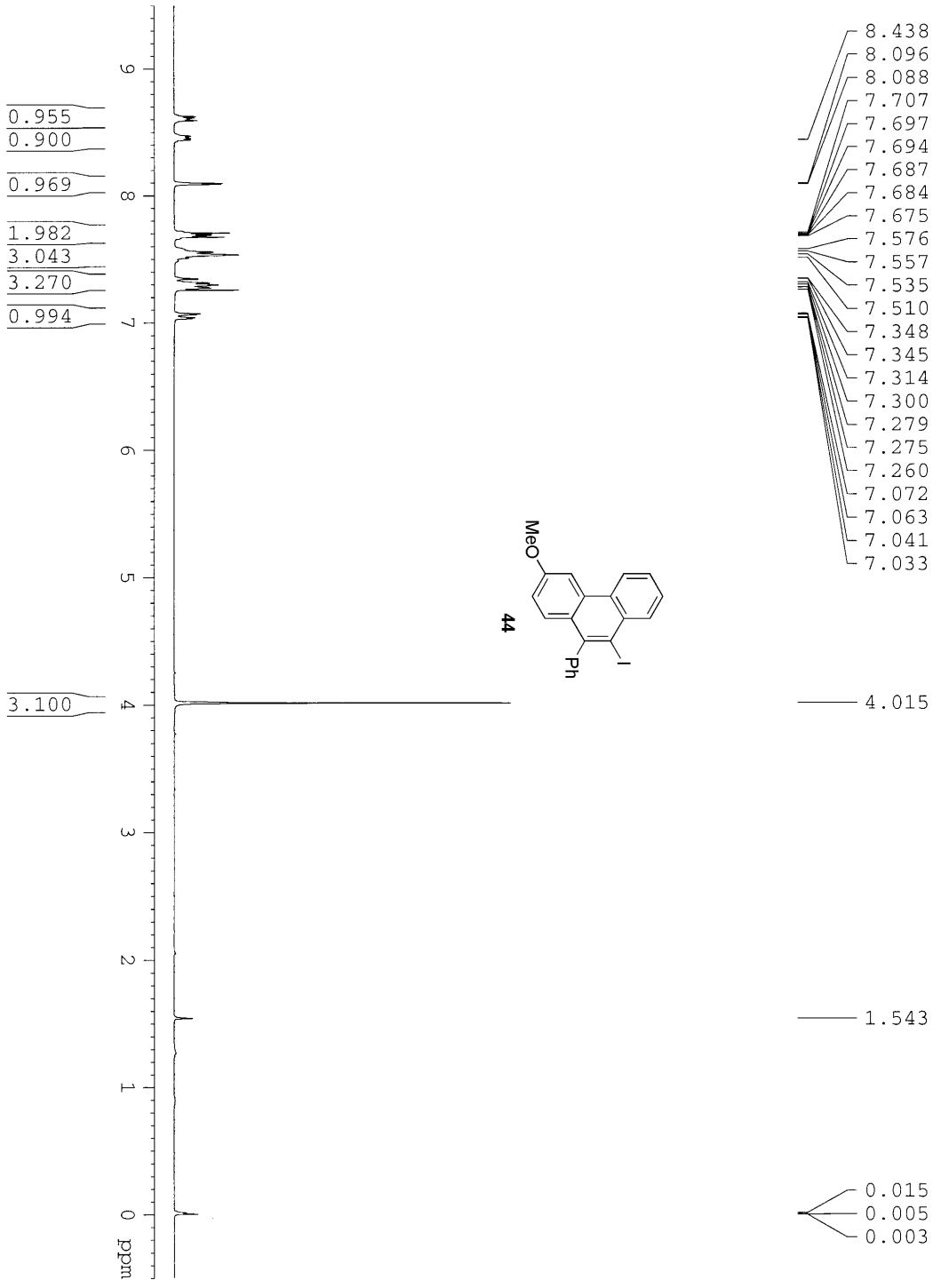
10
ppm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0.994
3.100
9
8
7
6
5
4
3
2
1
0
ppm
MeO
Ph
I
44
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8.096
8.088
7.707
7.697
7.694
7.687
7.684
7.675
7.576
7.557
7.535
7.510
7.348
7.345
7.314
7.300
7.279
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7.260
7.072
7.063
7.041
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4.015
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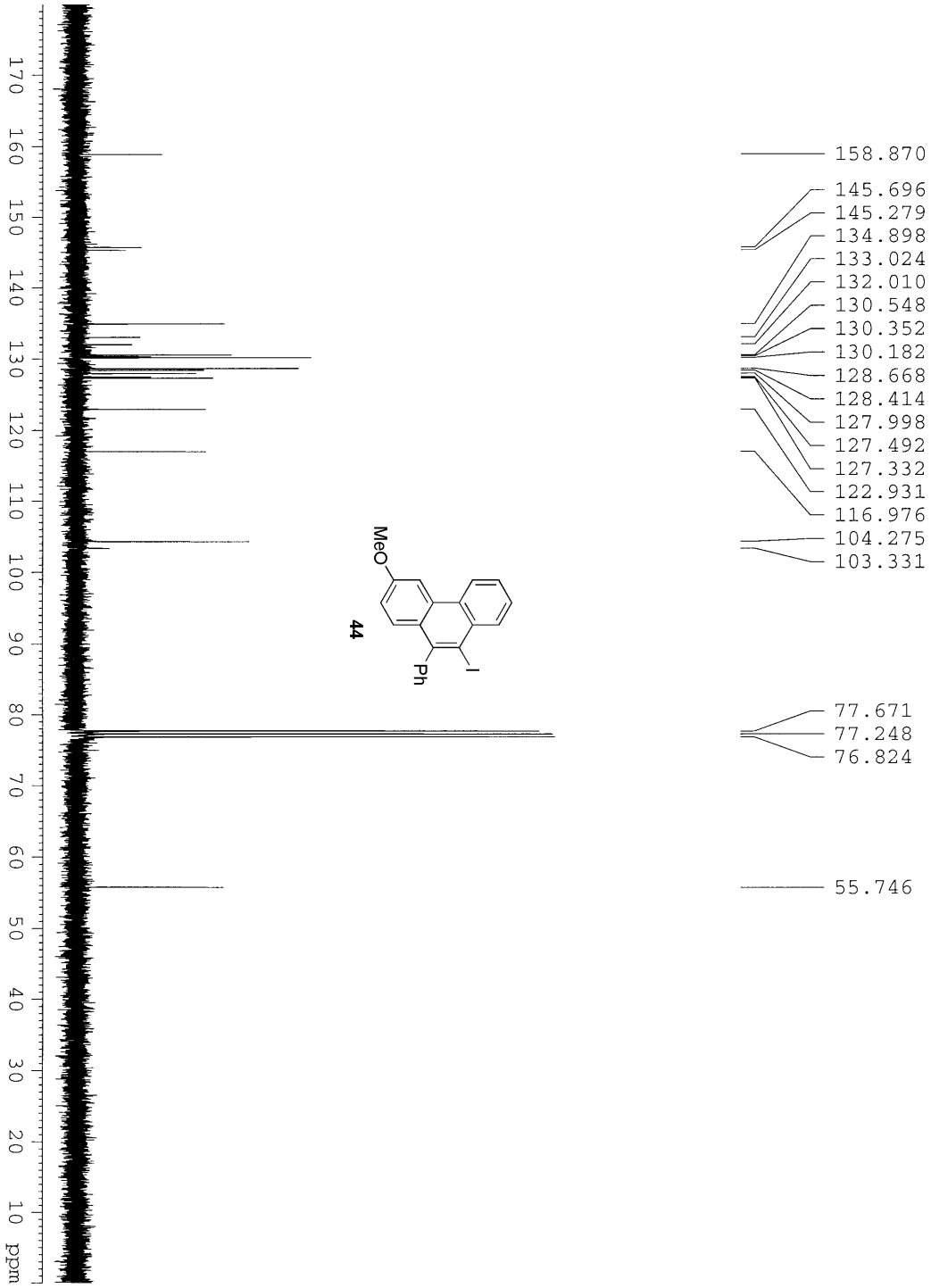
0.005
0.003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145.279
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132.010
130.548
130.352
130.182
128.668
128.414
127.998
127.492
127.332
122.931
116.976
104.275
103.331
77.671
77.248
76.824
55.746
MeO
Ph
I
44
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140
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120
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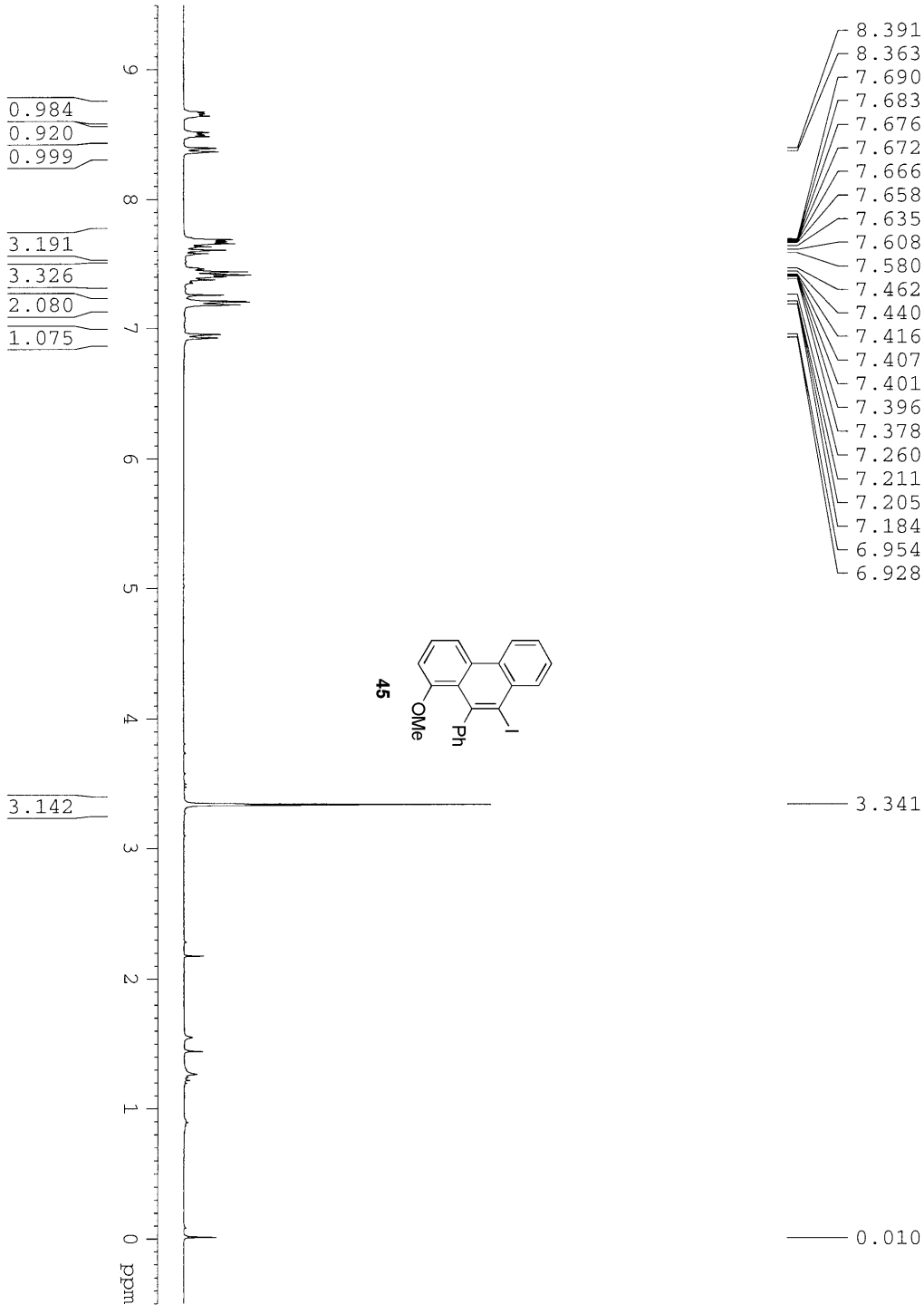
30
20
10
ppm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7.683
7.676
7.672
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7.658
7.635
7.608
7.580
7.462
7.440
7.416
7.407
7.401
7.396
7.378
7.260
7.211
7.205
7.184
6.954
6.928
0.984
0.920
0.999
3.191
3.326
2.080
1.075
3.142
3.341
0.010
OMe
Ph
I
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8
7
6
5
4
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2
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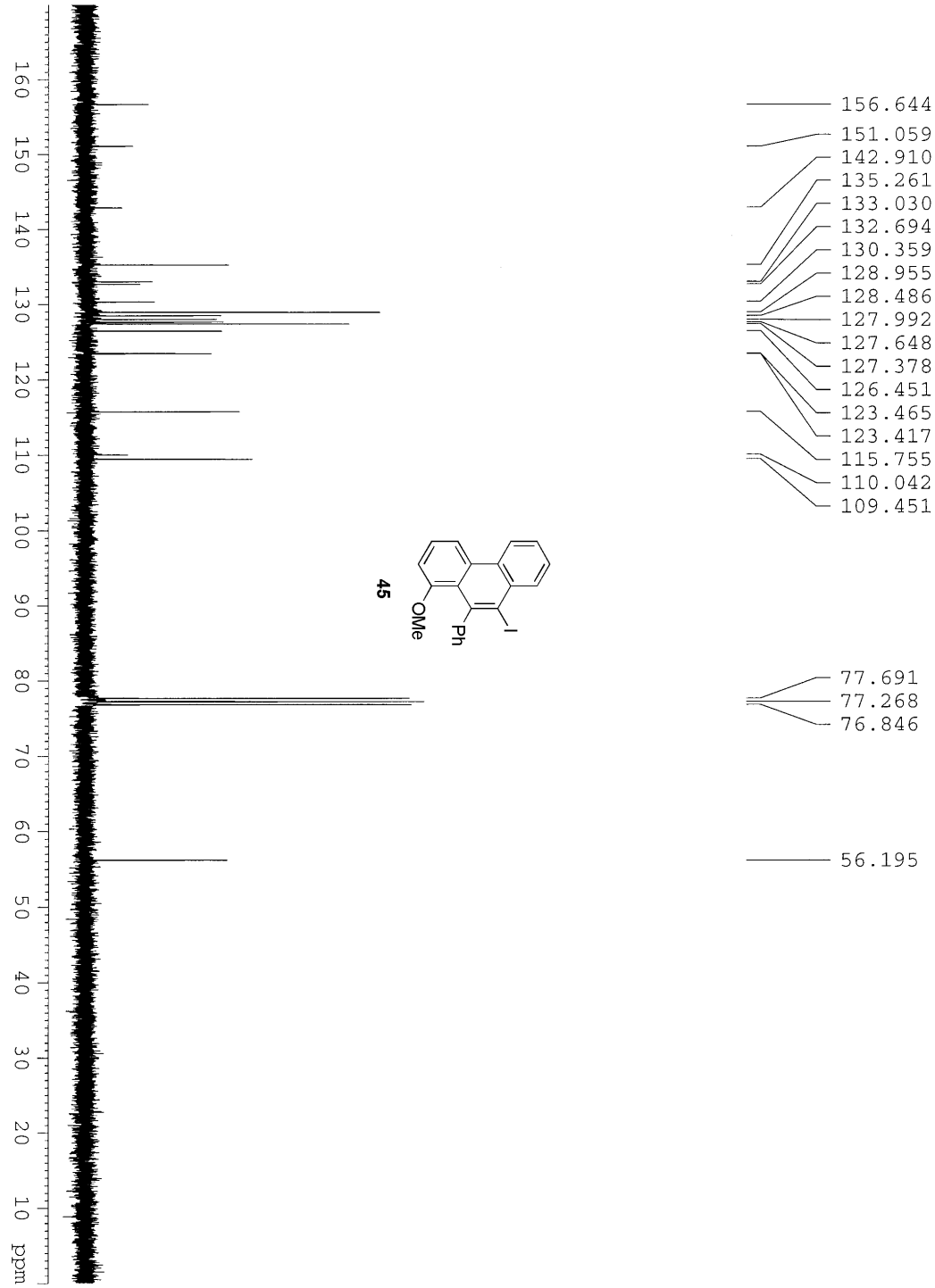
0
ppm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142.910
135.261
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132.694
130.359
128.955
128.486
127.992
127.648
127.378
126.451
123.465
123.417
115.755
110.042
109.451
77.691
77.268
76.846
56.195
45
OMe
Ph
I
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150
140
130
120
110
100
90
80
70
60
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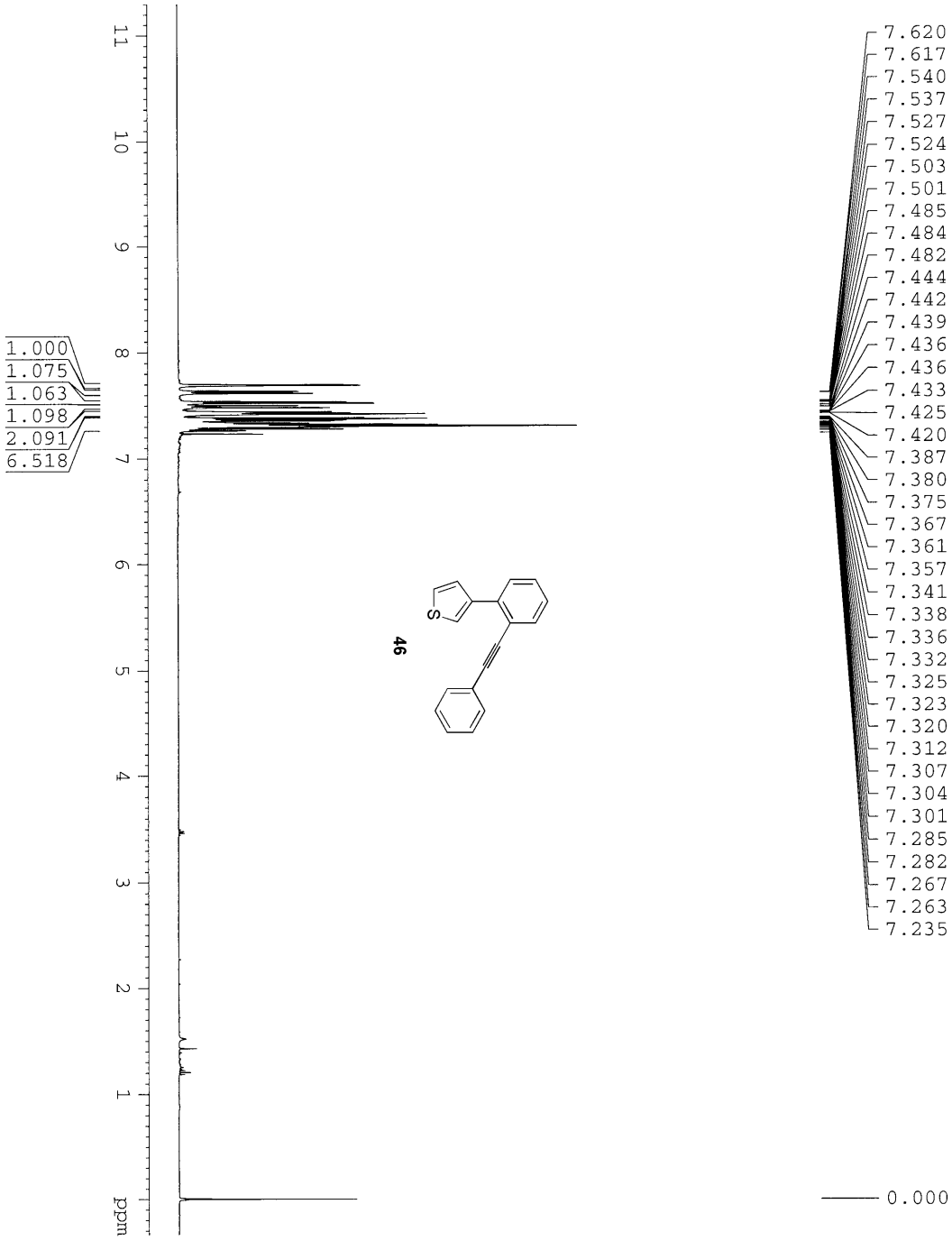
30
20
10
ppm


1.000
1.075
1.063
1.098
2.091
6.518
11
10
9
8
7
6
5
4
3
2
1
ppm
S
46
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7.617
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7.537
7.527
7.524
7.503
7.501
7.485
7.484
7.482
7.444
7.442
7.439
7.436
7.436
7.433
7.425
7.420
7.387
7.380
7.375
7.367
7.361
7.357
7.341
7.338
7.336
7.332
7.325
7.323
7.320
7.312
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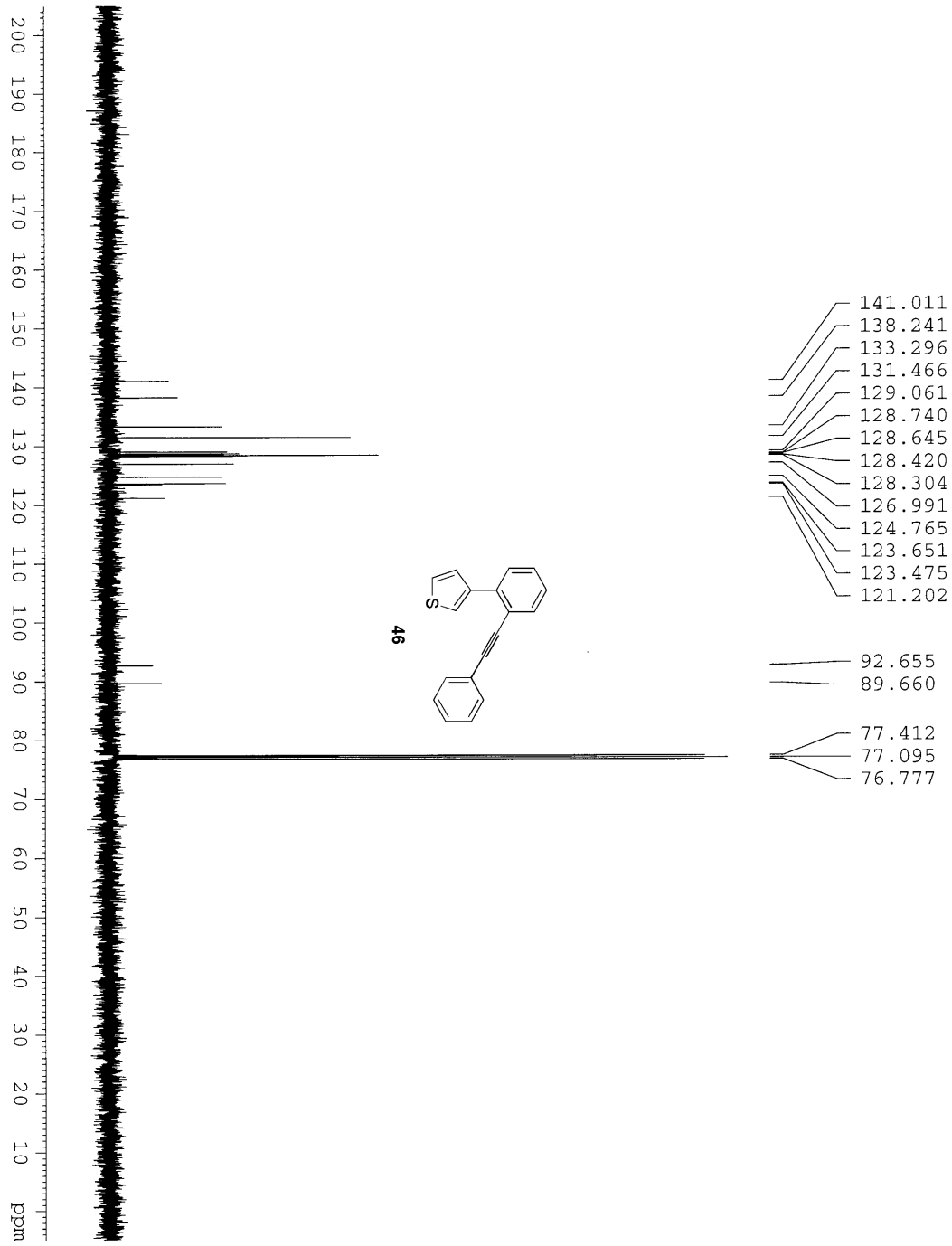
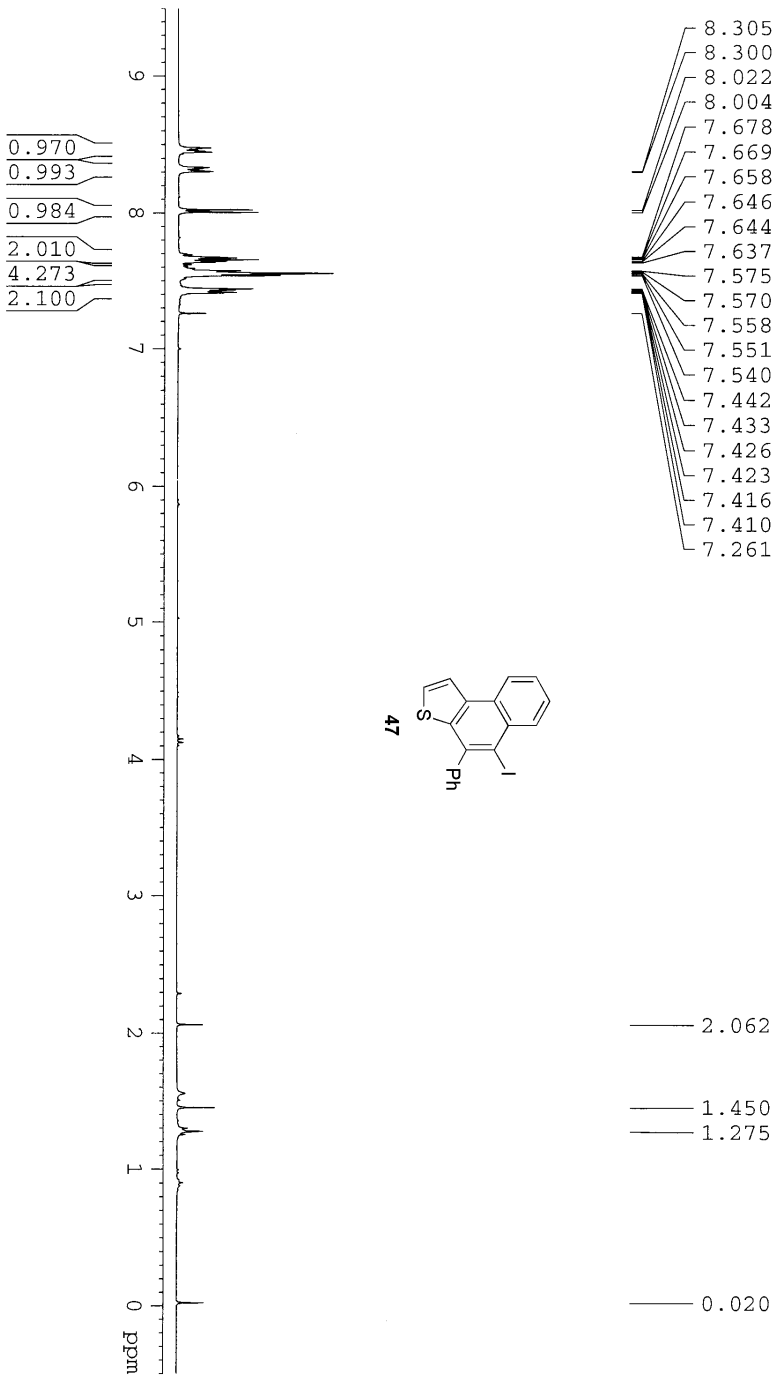
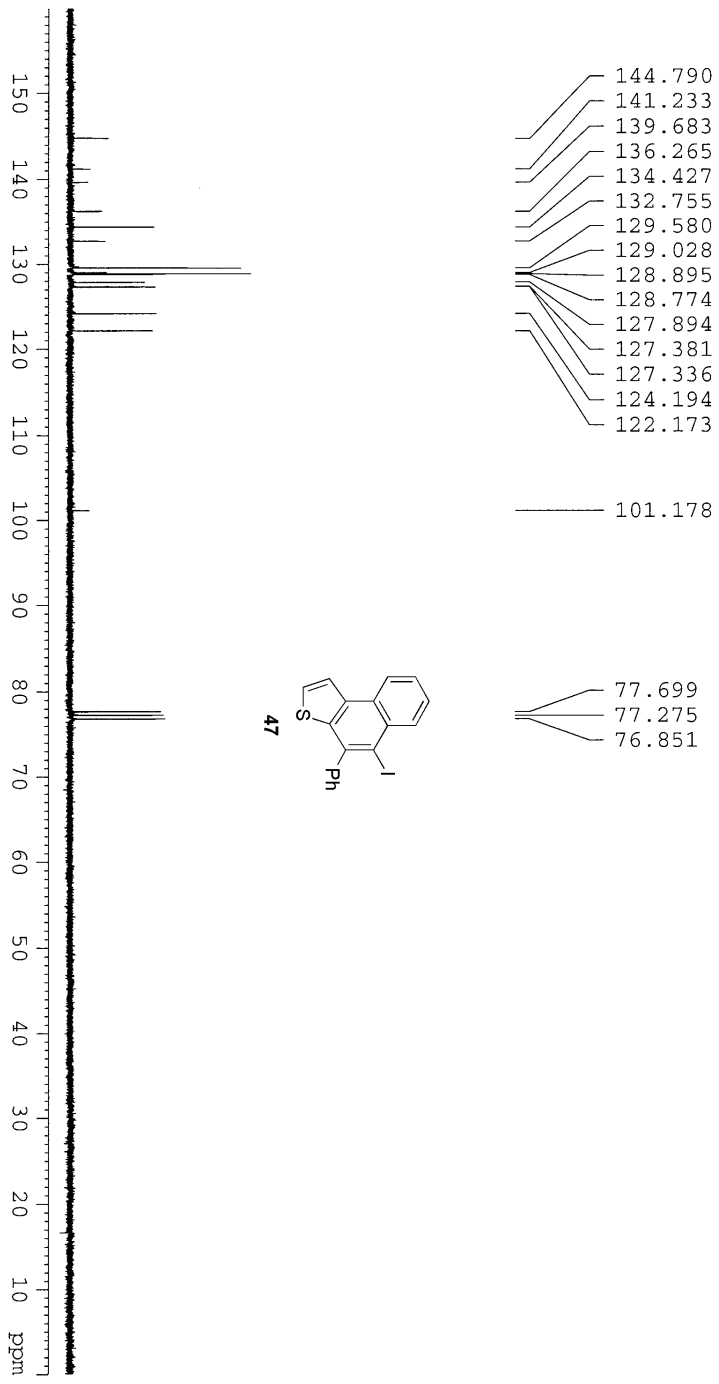
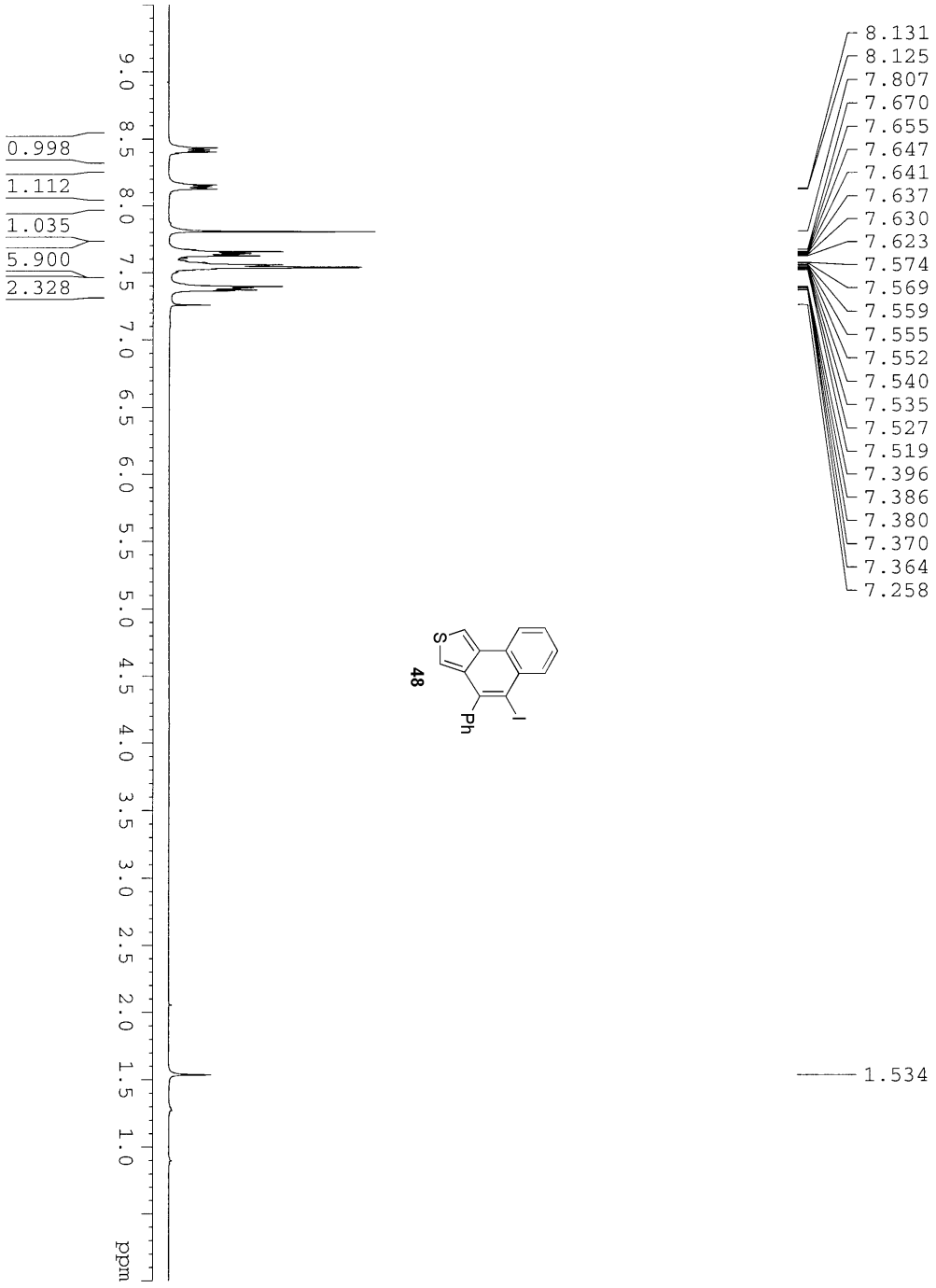
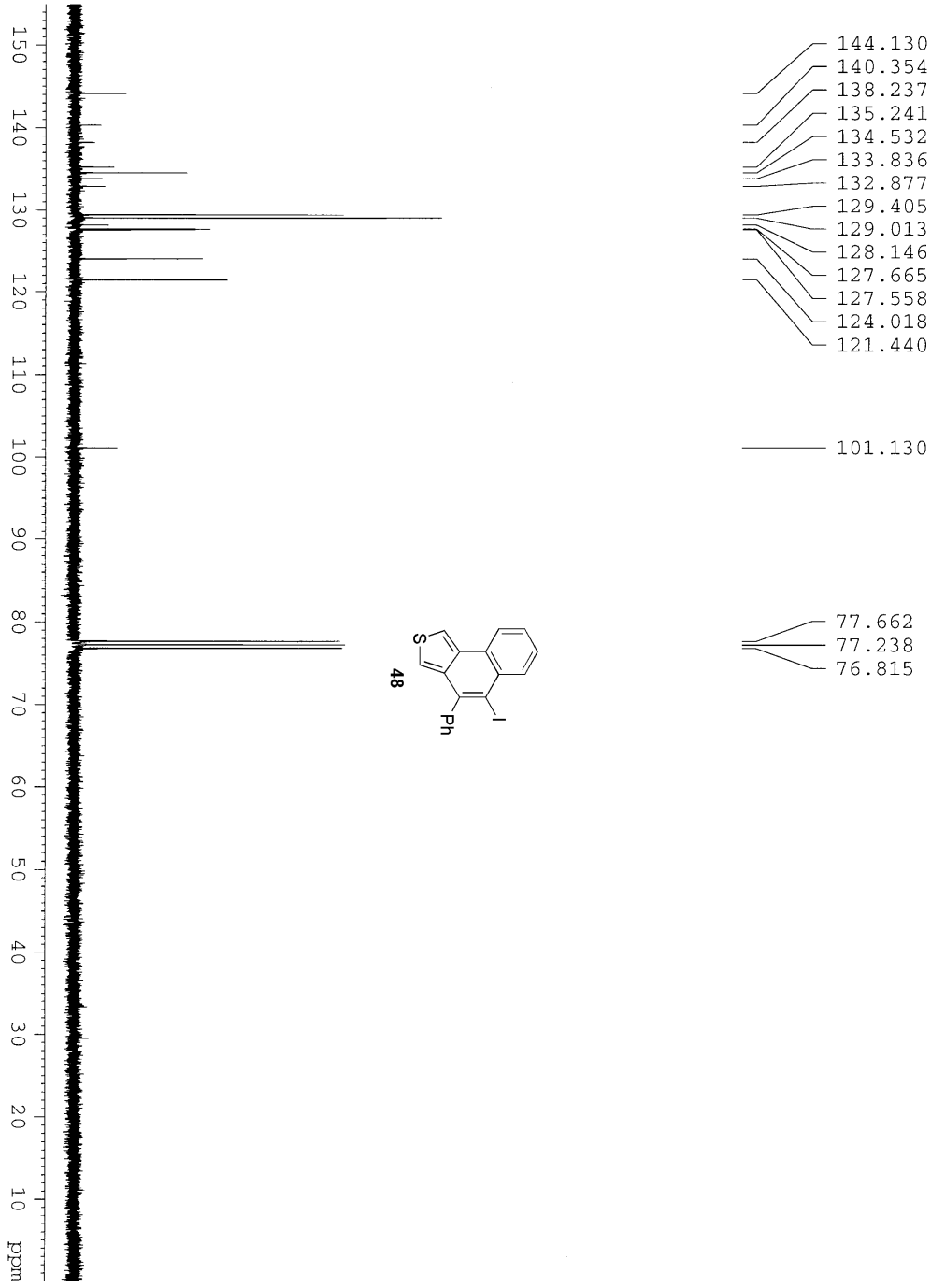
7.304
7.301
7.285
7.282
7.267
7.263
7.235
0.000

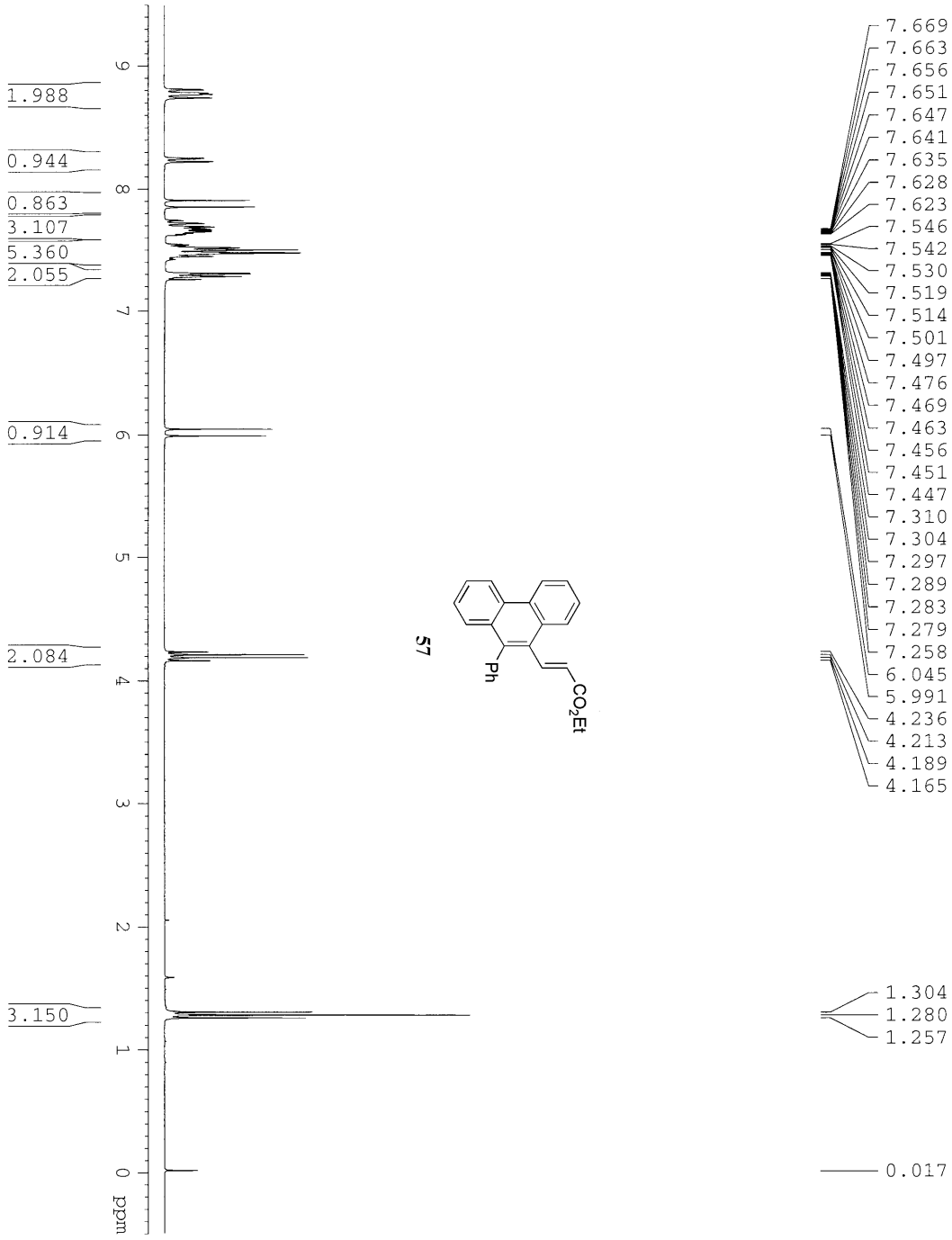

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
141.011
138.241
133.296
131.466
129.061
128.740
128.645
128.420
128.304
126.991
124.765
123.651
123.475
121.202
92.655
89.660
77.412
77.095
76.777
S
46

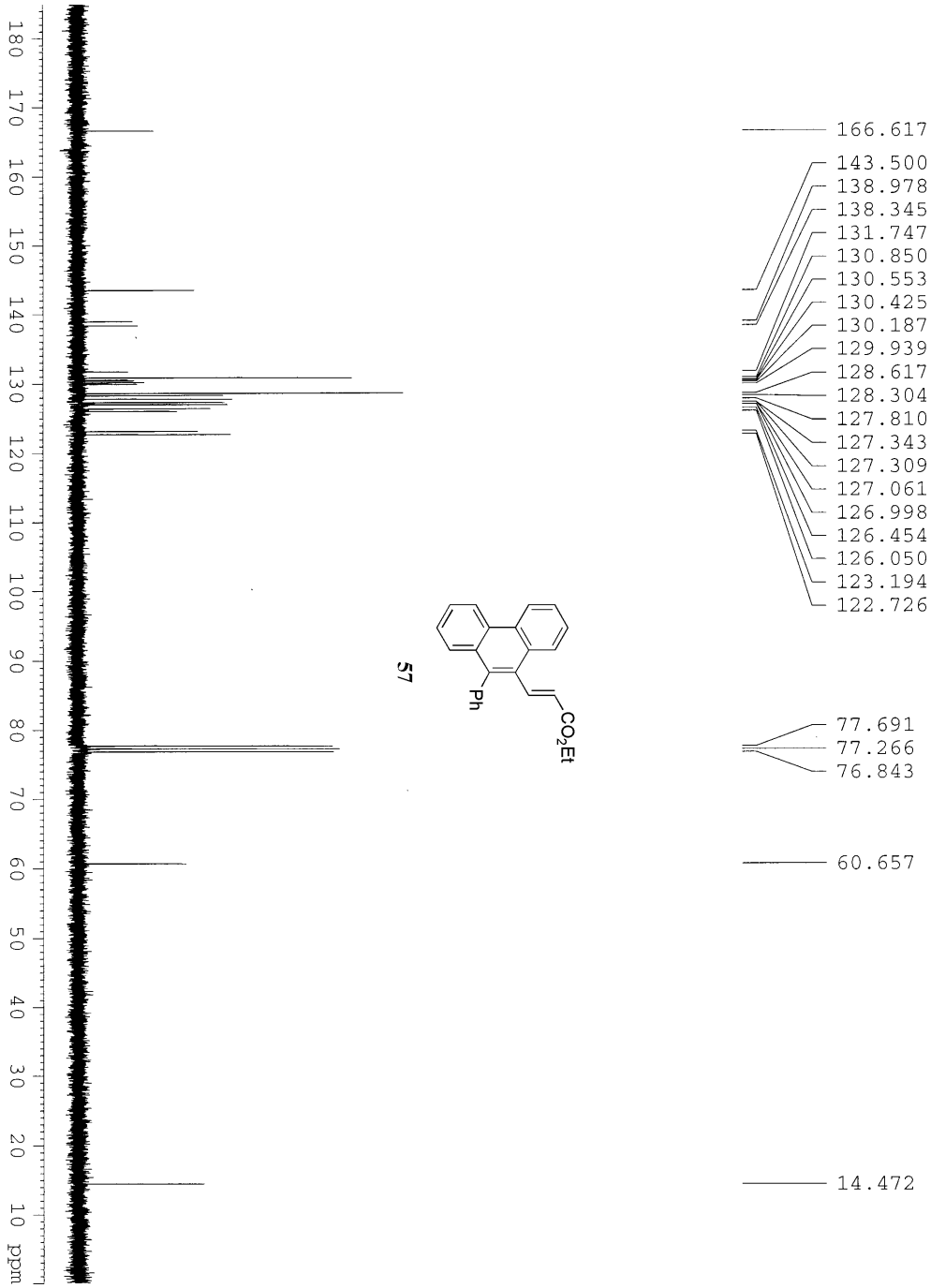

0.970
0.993
0.984
2.010
4.273
2.100
8.305
8.300
8.022
8.004
7.678
7.669
7.658
7.646
7.644
7.637
7.575
7.570
7.558
7.551
7.540
7.442
7.433
7.426
7.423
7.416
7.410
7.261
S
Ph
I
47
2.062
1.450
1.275
0.020
ppm


144.790
141.233
139.683
136.265
134.427
132.755
129.580
129.028
128.895
128.774
127.894
127.381
127.336
124.194
122.173
101.178
77.699
77.275
76.851
47
S
Ph
I
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.131
8.125
7.807
7.670
7.655
7.647
7.641
7.637
7.630
7.623
7.574
7.569
7.559
7.555
7.552
7.540
7.535
7.527
7.519
7.396
7.386
7.380
7.370
7.364
7.258
1.534
0.998
1.112
1.035
5.900
2.328
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
ppm
S
Ph
I
48


144.130
140.354
138.237
135.241
134.532
133.836
132.877
129.405
129.013
128.146
127.665
127.558
124.018
121.440
101.130
77.662
77.238
76.815
S
Ph
I
48
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


1.988
0.944
0.863
3.107
5.360
2.055
0.914
2.084
3.150
9
8
7
6
5
4
3
2
1
0
ppm
57
Ph
CO2Et
7.669
7.663
7.656
7.651
7.647
7.641
7.635
7.628
7.623
7.546
7.542
7.530
7.519
7.514
7.501
7.497
7.476
7.469
7.463
7.456
7.451
7.447
7.310
7.304
7.297
7.289
7.283
7.279
7.258
6.045
5.991
4.236
4.213
4.189
4.165
1.304
1.280
1.257
0.017


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
166.617
143.500
138.978
138.345
131.747
130.850
130.553
130.425
130.187
129.939
128.617
128.304
127.810
127.343
127.309
127.061
126.998
126.454
126.050
123.194
122.726
77.691
77.266
76.843
60.657
14.472
Ph
CO2Et

57