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Supporting Information

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3-Boryl-2,2'-Bithiophene as a Versatile Core Skeleton for Full-Color Highly Emissive Organic Solids

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General. Melting points (mp) were measured on a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL AL-400 spectrometer in $CDCl_3$ or (400 MHz for ^{1}H, 100 MHz for ^{13}C, 128 MHz for ^{11}B). UV-vis absorption spectra and fluorescence spectra measurement were performed with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in degassed spectral grade solvents. Quantum yields were determined with a Hamamatsu C9920-01 calibrated integrating sphere system. Time-resolved fluorescence spectra were measured using a Hamamatsu C4780 system equipped with a PLP-10 picosecond light pulser (LED wavelengths: 375 or 405 nm). Thermogravimetric analysis (TGA) was carried out with a Seiko TGA 6200 at a heating rate of 5 °C/min under nitrogen. Cyclic Voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurement was carried out under argon atmosphere using THF solutions of samples with a concentration of 1 mM and 0.1M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia). Preparative gel permeation chromatography (GPC) was performed with a JAI LC–918 chromatograph equipped with JAIGEL 1H and 2H column. 2-(2’,6’-dimethoxybiphenyl)dicyclohexylphosphine (S-Phos)[1] was purchased from Aldrich and used as received. All reactions were carried out under argon atmosphere.

Computation Method. All calculations were conducted using the Gaussian 03 program.[2]

3-Dimesitylboryl-2,2’-bithiophene (1). To a solution of 3-bromo-2,2’-bithiophene (3.49 g, 13.7 mmol) in ether (20 mL) was added a hexane solution of *n*BuLi (1.6 M, 9.0 mL, 14.4 mmol) dropwise at –78 ºC. The mixture was stirred at the same temperature for 3 h. A solution of dimesitylboron fluoride (4.05 g, 15.1 mmol) in ether (20 mL) was added to the reaction mixture via syringe. The reaction mixture was gradually warmed to room temperature and stirred overnight. After addition of water (20 mL), the organic layer was separated and the aqueous layer was extracted with hexane for three times. The combined organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (7/1 hexane/toluene, R_f = 0.40), followed by recrystallization from a hexane/toluene mixed solvent to afford 3.59 g (8.68 mmol) of **1** in 63% yield as yellow solids: mp 129–130 ºC; ^{1}H NMR ($CDCl_3$) δ 2.02 (s, 12H), 2.21 (s, 6H), 6.65 (s, 4H), 6.67 (dd, J_{HH} = 5.2, 3.6 Hz, 1H), 6.75 (dd, J_{HH} = 3.6, 1.2 Hz, 1H), 6.89 (d, J_{HH} = 4.8 Hz, 1H), 7.03 (dd, J_{HH} = 5.2, 1.2 Hz, 1H), 7.19 ppm (d, J_{HH} = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.0, 124.6, 126.2, 126.7, 127.0, 128.1, 135.1, 136.5, 138.6, 140.6, 142.2, 146.0, 147.7 ppm; ^{11}B NMR ($CDCl_3$) δ 69.2 ppm. Anal. Calcd for $C_{26}H_{27}BS_2$: C, 75.35; H, 6.57. Found: C, 75.10; H, 6.53.

The compound **1** is stable under the acidic and basic conditions. The treatment of chloroform solution of **1** with a 1N HCl aqueous solution or a 1N NaOH aqueous solution resulted in no change, as confirmed by the ^{1}H NMR spectrum.

5,5’-Dibromo-3-dimesitylboryl-2,2’-bithiophene (2). A solution of **1** (1.66 g, 4.00 mmol) and *N*-bromosuccinimide (1.49 g, 8.40 mmol) in dichloromethane (10 mL) was stirred at room temperature for 12 h. After addition of water (10 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane for three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (5/1 hexane/CH_2Cl_2, R_f = 0.68) to afford 2.26 g, (3.95 mmol) of **2** in 99% yield as yellow solids: mp 174–175 ºC; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 12H), 2.24 (s, 6H), 6.45 (d, J_{HH} = 4.0 Hz, 1H), 6.61 (d, J_{HH} = 4.0 Hz, 1H), 6.69 (s, 4H), 6.85 ppm (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.1, 111.9, 113.2, 127.5, 128.2, 129.5, 136.7, 137.1, 139.3, 140.6, 141.5, 145.6, 149.3 ppm; ^{11}B NMR ($CDCl_3$) δ 70.0 ppm. Anal. Calcd for $C_{26}H_{25}BBr_2S_2$: C, 54.57; H, 4.40. Found: C, 54.30; H, 4.48.

5,5’-Dimesityl-3-dimesitylboryl-2,2’-bithiophene (3). A mixture of **2** (286 mg, 0.50 mmol), mesitylboronic acid (328 mg, 2.0 mmol), $Pd_2(dba)_3$·$CHCl_3$ (10.5 mg, 0.01 mmol), S-Phos (17.6 mg, 0.04 mmol), and K_3PO_4 (640 mg, 3.0 mmol) in 4 mL of toluene was stirred at 50 ºC for 36 h. After addition of water (10 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane for three times. The combined organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (10/1 hexane/dichloromethane, R_f = 0.38) to afford 166 mg (0.26 mmol) of **3** in 51% yield as green solids: mp 167–168 ºC; ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 6H), 2.09 (s, 12H), 2.17 (s, 6 H), 2.19 (s, 6H), 2.28 (s, 3H), 2.29 (s, 3H), 6.41 (d, J_{HH} = 3.4 Hz, 1H), 6.56 (s, 1H), 6.65 (s, 4H), 6.85 (d, J_{HH} = 3.4 Hz, 1H), 6.88 (s, 2H), 6.90 ppm (s, 2H); ^{13}C NMR ($CDCl_3$) δ 20.5, 20.8, 21.05, 21.15, 23.1, 126.6, 126.7, 127.9, 128.0, 128.2, 130.5, 130.7, 134.6, 136.7, 137.78, 137.80, 137.9, 138.3, 138.4, 140.6, 140.7, 142.4(br), 142.7, 146.7, 148.2 ppm (br); ^{11}B NMR ($CDCl_3$) δ 68.5 ppm; HRMS (FAB): 650.3223 (M^+); Calcd for $C_{44}H_{47}BS_2$: 650.3212.

5,5'-Diphenyl-3-dimesitylboryl-2,2'-bithiophene (4). A mixture of **2** (286 mg, 0.50 mmol), phenylboronic acid (243 mg, 2.0 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (10.9 mg, 0.01 mmol), S-Phos (17.0 mg, 0.04 mmol), and K_3PO_4 (638 mg, 3.0 mmol) in toluene (5 mL) was stirred at 50 ºC for 12 h. After addition of water (10 mL), the organic layer was separated and the aqueous layer was extracted with dichloromethane for three times. The combined organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (5/1 hexane/dichloromethane, R_f = 0.40) and GPC to afford 265 mg (0.46 mmol) of **4** in 93% yield as yellow solids: mp 118–120 ºC; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 12H), 2.20 (s, 6H), 6.69 (s, 4H), 6.78 (d, J_{HH} = 4.0 Hz, 1H), 6.89 (d, J_{HH} = 4.0 Hz, 2H), 7.12 (s, 1H), 7.34 (s, 2H), 7.34 (d, 7.2 Hz, 4H), 7.41 (d, 7.2 Hz, 2H), 7.56 ppm (d, 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.1, 123.0, 125.6, 125.9, 127.4, 127.5, 127.9, 128.2, 128.78, 128.81, 130.8, 133.8, 134.3, 136.1, 138.9, 140.8, 142.3 (br), 143.1, 145.1, 145.3, 149.0 ppm (br); ^{11}B NMR ($CDCl_3$) δ 69.0 ppm; HRMS (FAB): 566.2283 (M^+); Calcd for $C_{38}H_{35}BS_2$: 566.2273.

5,5'-Bis[4-(*N*-carbazolyl)phenyl]-3-dimesitylboryl-2,2'-bithiophene (5). To a solution of 4-*N*-carbazolyl-iodobenzene (299 mg, 0.81 mmol) in ether (5 mL) was added a hexane solution of *n*-BuLi (1.6 M, 0.56 mL, 0.90 mmol) dropwise at –78 ºC. The mixture was stirred at the same temperature for 1 h. Tributyltin chloride (293 mg, 0.90 mmol) was added to the reaction mixture via syringe. The reaction mixture was gradually warmed to room temperature and stirred overnight. After the solvent was removed under reduced pressure, the mixture was dissolved with 5 mL of THF and added to a mixture of **2** (172 mg, 0.30 mmol), $Pd_2dba_3 \cdot CHCl_3$ (6.2 mg, 0.003 mmol), and trifurylphosphine (5.6 mg, 0.024 mmol) in 5 mL of THF via cannula. The reaction mixture was refluxed for 30 h. After the solvent was removed under reduced pressure, the mixture was purified by a silica gel column chromatography (4/1 hexane/dichloromethane, R_f = 0.25) to afford 85 mg (0.095 mmol) of **5** in 32% yield as yellow solids: mp >300 ºC; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 12H), 2.20 (s, 6H), 6.75 (s, 4H), 6.89 (d, J_{HH} = 3.6 Hz, 1H), 7.03 (d, J_{HH} = 3.6 Hz, 1H), 7.25 (s, 1H), 7.30 (td, J_{HH} = 8.4 Hz, 3.6 Hz, 4H), 7.42 (t, J_{HH} = 8.4 Hz, 4H), 7.44 (d, J_{HH} = 8.4 Hz, 4H), 7.57 (d, J_{HH} = 8.4 Hz, 4H), 7.65 (d, J_{HH} = 8.4 Hz, 2H), 7.81 (d, J_{HH} = 8.4 Hz, 2H), 8.15 ppm (dd, 8.4 Hz, 3.6 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.2, 109.7, 109.8, 120.06, 120.08, 120.4, 123.47, 123.48, 123.52, 126.0, 126.9, 127.0, 127.2, 127.3, 127.4, 128.2, 128.3, 131.4 132.9, 133.3, 136.5, 136.9, 139.1, 140.7, 140.9, 142.2, 144.2, 145.4, 149.3 ppm (br); ^{11}B NMR ($CDCl_3$) δ 67.5 ppm; HRMS (FAB): 896.3441 (M^+); Calcd for $C_{62}H_{49}BN_2S_2$: 896.3430.

5,5'-Bis[4-(*N,N*-diphenylamino)phenyl]-3-dimesitylboryl-2,2'-bithiophene (6). To a solution of 4-(*N,N*-diphenylamino)bromobenzene (341 mg, 1.05 mmol) in THF (10 mL) was added a hexane solution of *n*-BuLi (1.6 M, 0.69 mL, 1.10 mmol) dropwise at –78 ºC. The mixture was stirred at the same temperature for 1 h. Tributyltin chloride (358 mg, 1.10 mmol) was added to the reaction mixture via syringe. The reaction mixture was gradually warmed to room temperature and stirred for 3 h. The mixture was transferred to a mixture of **2** (286 mg, 0.50 mmol), $Pd_2dba_3 \cdot CHCl_3$ (21.3 mg, 0.021 mmol), and trifurylphosphine (19.5 mg, 0.083 mmol) in THF (5 mL) via cannula. The reaction mixture was refluxed for 61 h. After the solvent was removed under reduced pressure, the mixture was dissolved into $CHCl_3$ and washed with water (40 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography (4/1 hexane/chloroform, R_f = 0.23) to afford 238 mg (0.26 mmol) of **6** in 53% yield as reddish orange solids: mp 134–135 ºC; ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 12H), 2.20 (s, 6H), 6.69 (s, 4H), 6.74 (d, J_{HH} = 3.9 Hz, 1H), 6.80 (d, J_{HH} = 3.9 Hz, 1H), 7.01–7.06 (m, 8H), 7.03 (s, 1H), 7.09 (d, J_{HH} = 7.6 Hz, 4H), 7.11 (d, J_{HH} = 7.6 Hz, 4H), 7.23–7.29 (m, 10H), 7.41 ppm (d,

J_{HH} = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.1, 122.2, 123.0, 123.1, 123.5, 123.7, 124.4, 124.5, 126.4, 126.6, 127.8, 128.0, 128.2, 128.3, 129.27, 129.30, 130.0, 135.4, 138.8, 140.8, 142.3 (br), 142.6, 144.7, 144.9, 147.2, 147.2, 147.4, 147.5, 148.7 ppm (br); ^{11}B NMR ($CDCl_3$) δ 68.5 ppm; HRMS (FAB): 900.3754 (M^+); Calcd for $C_{62}H_{53}BN_2S_2$: 900.3743.

5,5”’-Bis(*N*,*N*-diphenylamino)-4’-dimesitylboryl-2,2’:5’,2”:5”,2”’-quaterthiophene (7). To a solution of 2-(*N,N*-diphenylamino)thiophene (528 mg, 2.10 mmol) in THF (10 mL) was added a hexane solution of *n*-BuLi (1.6 M, 1.4 mL, 2.2 mmol) dropwise at –78 ºC. The mixture was stirred at the same temperature for 20 min and was warmed to 0 °C. After stirring for 2 h, tributyltin chloride (293 mg, 0.90 mmol) was added to the mixture via syringe. The reaction mixture was gradually warmed to room temperature and stirred overnight. The obtained mixture was added to a mixture of **2** (573 mg, 1.00 mmol), $Pd_2dba_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), and trifurylphosphine (18.6 mg, 0.08 mmol) in THF (15 mL) via cannula. The reaction mixture was refluxed for 14 h. After addition of water (40 mL), the organic layer was separated and the aqueous layer was extracted with chloroform for three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography (3/1 hexane/dichloromethane, R_f = 0.24) to afford 681 mg (0.75 mmol) of **7** in 75% yield as red solids: mp 100–102 ºC; ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 12H), 2.19 (s, 6H), 6.54 (d, J_{HH} = 3.9 Hz, 1H), 6.57 (d, J_{HH} = 3.7 Hz, 1H), 6.61 (d, J_{HH} = 3.7 Hz, 1H), 6.63 (d, J_{HH} = 3.7 Hz, 1H), 6.67 (s, 4H), 6.75 (d, J_{HH} = 3.9 Hz, 1H), 6.79 (s, 1H), 6.91 (d, J_{HH} = 3.9 Hz, 1H), 7.01-7.07 (m, 4H), 7.13-7.17 (m, 8H), 7.24-7.30 ppm (m, 8H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.1, 120.9, 121.2, 122.0, 122.6, 122.69, 122.75, 123.2, 123.3, 127.6, 128.3, 129.2, 130.2, 130.8, 130.9, 134.8, 136.6, 138.6, 139.0, 140.8, 142.1 (br), 143.6, 147.6, 148.6 (br), 150.68, 150.72 ppm; ^{11}B NMR ($CDCl_3$) δ 70.9 ppm; HRMS (FAB): 912.2887 (M^+); Calcd for $C_{52}H_{49}BN_2S_4$: 912.2872.

X-Ray Crystal Structure Analysis of 1. Single crystals of **1** suitable for X-ray crystal analysis were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **1**. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 7590 reflections were measured at a maximum 2*q* angle of 50.0°, of which 3893 were independent reflections (R_{int} = 0.0251). The structure was solved by direct methods (SHELXS-97[3]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[3]). One thiophene ring (S2, C5, C6, C7, and C8) is disordered and solved using appropriate disordered models. Thus, two sets of thiophene rings, *i.e.*, (S2A, C5, C6A, C7A, C8A) and (S2B, C5, C6B, C7B, C8B), were placed and their occupancies were refined to be 0.73 and 0.27, respectively. The two sets of disordered thiophene rings (S2A, C5, C6A, C7A, C8A) and (S2B, C5, C6B, C7B, C8B) were restrained by SADI, DELU, and DFIX (S2B–C5) instructions during refinement. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{26}H_{27}BS_2$; FW = 414.41, crystal size 0.20 × 0.15 × 0.05 mm^3, Triclinic, *P*–1, *a* = 8.514(2) Å, *b* = 11.325(3) Å, *c* = 11.991(3) Å, *a* = 83.960(7)°, *b* = 83.873(7)°, *g* = 79.621(7)°, *V* = 1126.4(4) $Å^3$, Z = 2, D_c = 1.222 g cm^{-3}. The refinement converged to R_1 = 0.0407, wR_2 = 0.1066 ($I > 2\sigma(I)$), GOF = 1.082.

X-Ray Crystal Structure Analysis of 8. Single crystals of **8** suitable for X-ray crystal analysis were obtained by slow diffusion of hexane into a solution of **8** in dichrolomethane. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 16099 reflections were measured at a maximum 2*q* angle of 51.0°, of which 8276 were independent reflections (R_{int} = 0.0345). The structure was solved by direct methods (SHELXS-97[3]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[3]). Two sets of two independent molecules are included in a lattice. The thiophene ring consisting S4, C31, C32, C33, C34, and C35 in one molecule is disordered and solved using appropriate models. Thus, two sets of thiophene rings, *i.e.*, (S4A, C31, C32, C33, C34A) and (S4B, C31, C32, C33, C34B), were placed and their occupancies were refined to be 0.58 and 0.42, respectively. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{26}H_{27}BS_2$; FW = 414.41, crystal size 0.20 × 0.20 × 0.20 mm^3, Triclinic, P–1, a = 8.5599(2) Å, b = 10.6718(2) Å, c = 25.4636(6) Å, a = 91.4862(7)°, b = 91.3853(9)°, g = 100.562(2)°, V = 2284.92(9) Å^3, Z = 4, D_c = 1.205 g cm^{-3}. The refinement converged to R_1 = 0.1067, wR_2 = 0.2543 ($I > 2\sigma(I)$), GOF = 1.198.

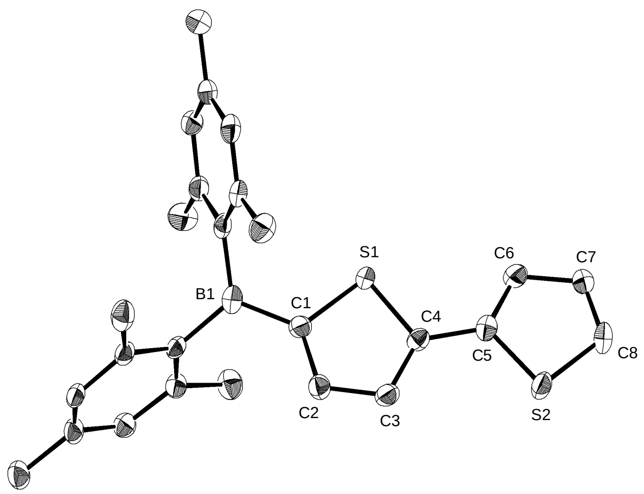

Figure S1. ORTEP drawing of **8**. One of two independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The dihedral angle between the mean planes of (S1, C1, C2, C3, C4) and (S2, C5, C6, C7. C8) is 9.85°.

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[1] T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685.

[2] Gaussian 03 (Revision C.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2004**.

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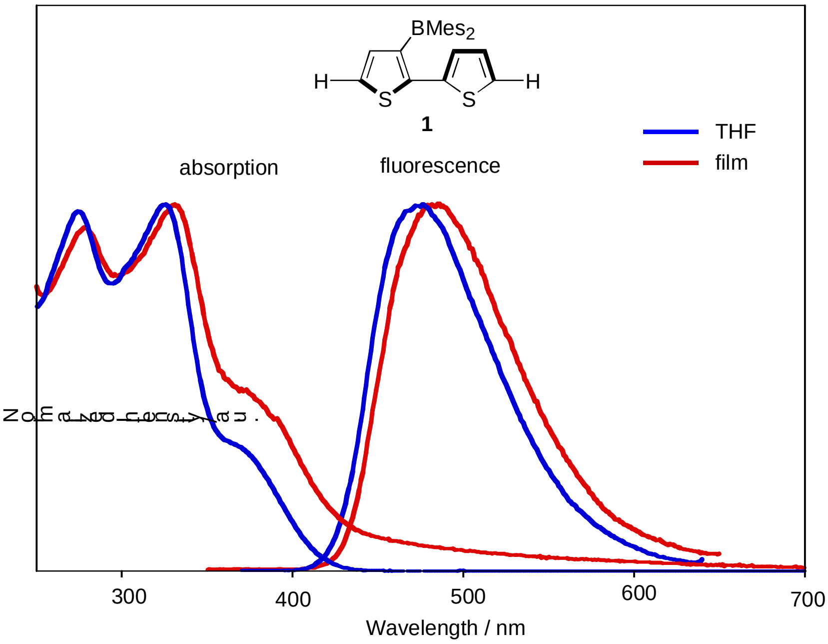


Figure S2. UV-vis absorption and fluorescence spectra of **1** in THF and in the solid state (spin-coated film).

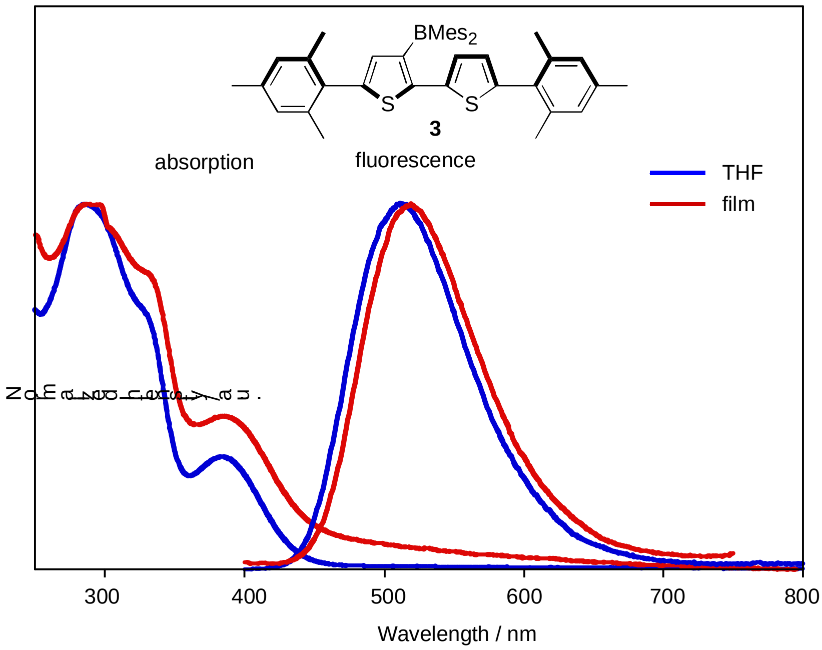


Figure S3. UV-vis absorption and fluorescence spectra of **3** in THF and in the solid state (spin-coated film).

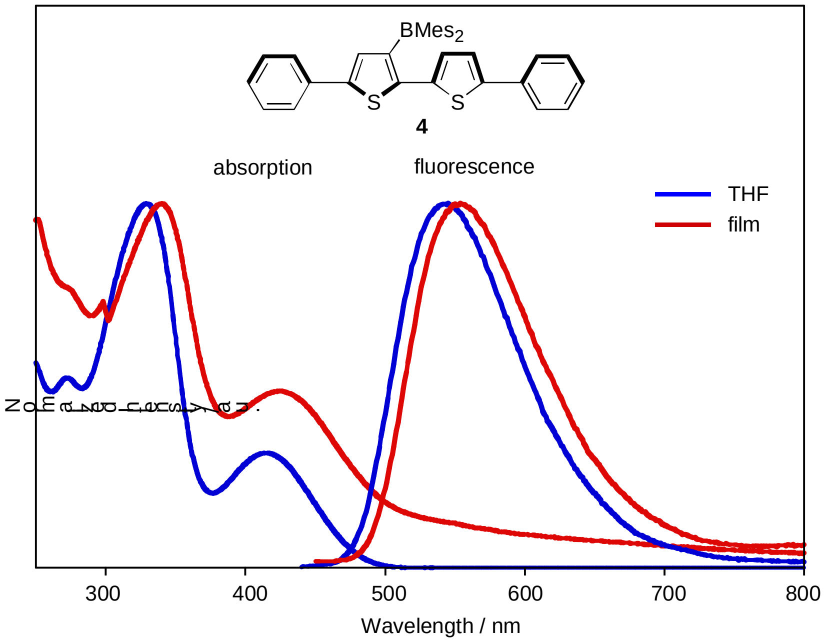


Figure S4. UV-vis absorption and fluorescence spectra of **4** in THF and in the solid state (spin-coated film).

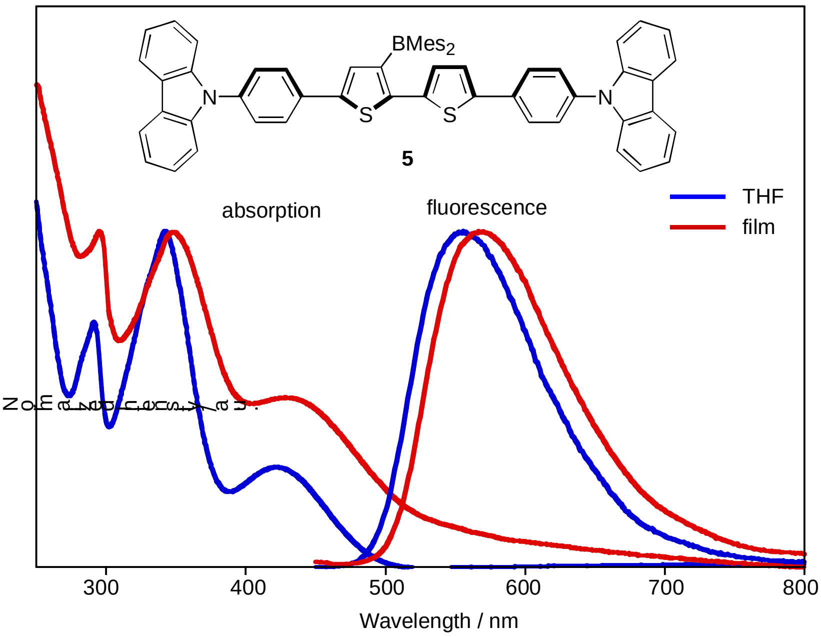


Figure S5. UV-vis absorption and fluorescence spectra of **5** in THF and in the solid state (spin-coated film).

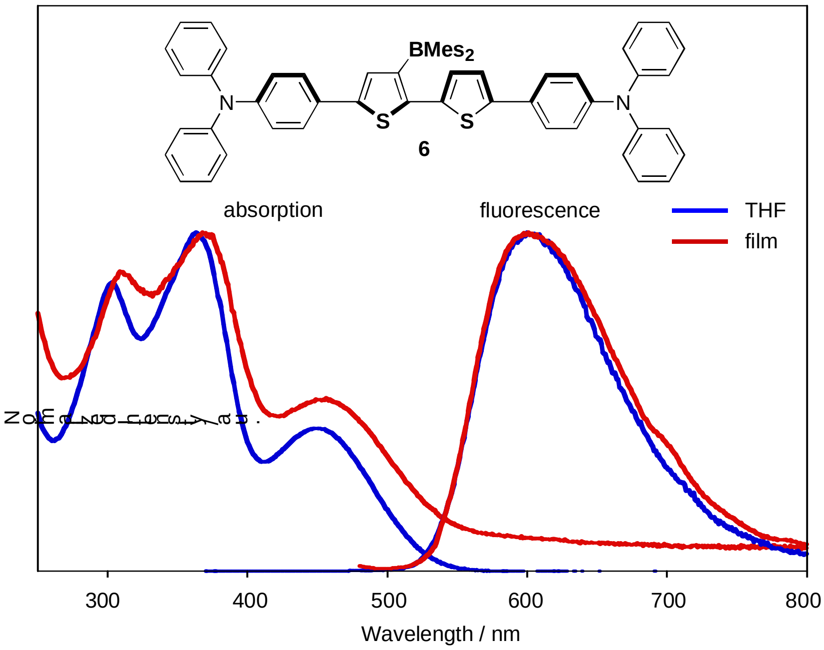


Figure S6. UV-vis absorption and fluorescence spectra of **6** in THF and in the solid state (spin-coated film).

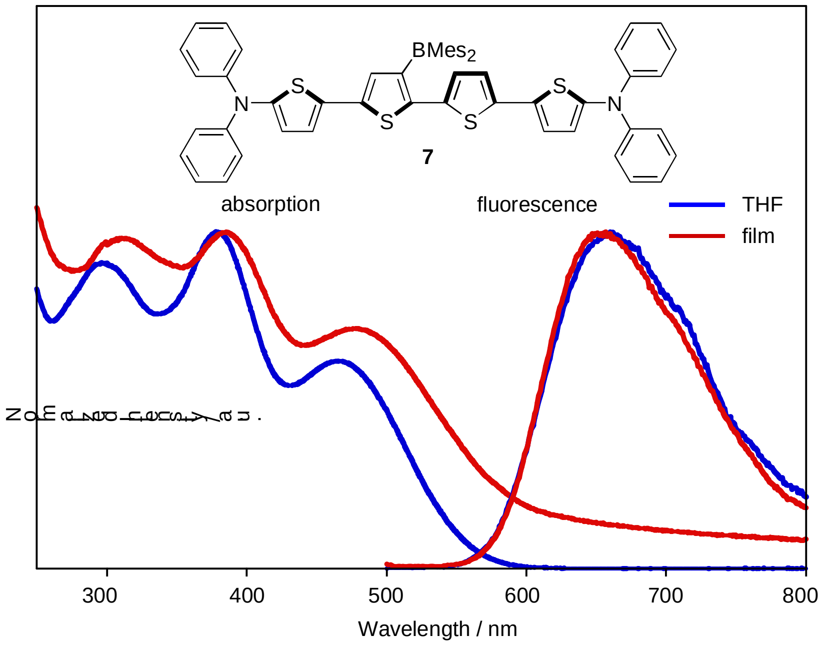


Figure S7. UV-vis absorption and fluorescence spectra of **7** in THF and in the solid state (spin-coated film).

Pictures of the Spin-Coated Films

Figure S8. The pictures of the spin-coated films of **1**, and **3-7** under irradiation of a black light at 365 nm. The spin-coated films were prepared from THF solutions (10^{-3} M).

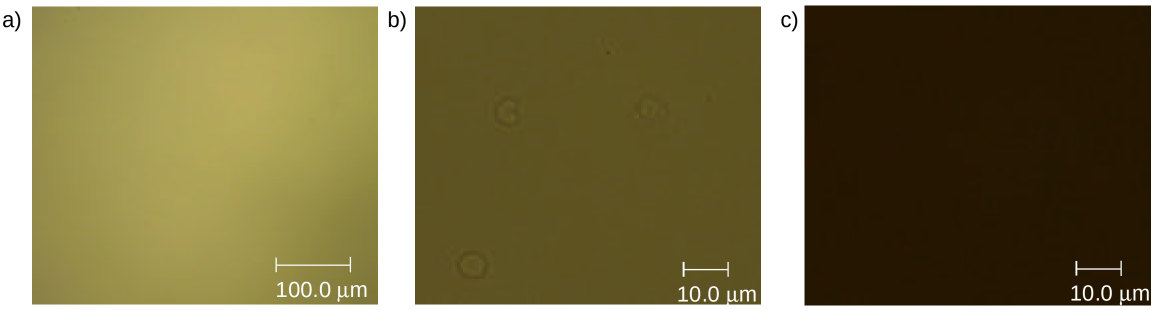


Figure S9. Optical micrographs of the spin-coated film of **1** a) (× 500), b) (× 3000), and c) with crossed polarizers (× 3000). The film was prepared from a THF solution (10^{-3} M). The optical polarization microscope image indicates that the homogeneous amorphous thin film forms even in the case of crystalline compound **1**.

Table S1. Photophysical Data of **1** in Various Solvents and in the Solid State

	l_{abs}/nm[a]	l_{em}/nm[b]	F_{F}[c]
Cyclohexane	378	457	0.52
Benzene	377	467	0.75
THF	371	477	0.66
MeOH	375	478	0.57
Film[d]	386	486	0.55

[a]Only the longest absorption maxima are shown. [b]Excited at the longest absorption maxima. [c]Absolute fluorescence quantum yield determined by a calibrated integrating sphere system. [d]Spin-coated film prepared from a THF solution.

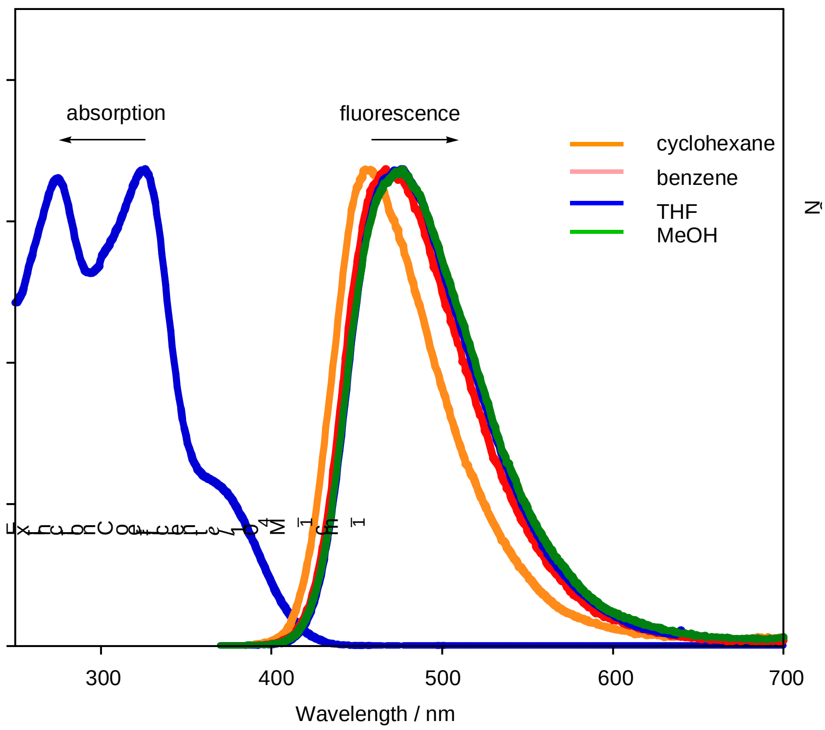


Figure S10. UV-vis absorption and fluorescence spectra of **1** in various solvents.

Table S2. Photophysical Data of **6** in Various Solvents and in the Solid State

	l_{abs}/nm[a]	l_{em}/nm[b]	F_{F}[c]
Cyclohexane	443	572	0.92
Benzene	450	591	0.96
THF	449	600	0.90
MeOH	441	605	0.59
Film[d]	456	601	0.60

[a]Only the longest absorption maxima are shown. [b]Excited at the longest absorption maxima. [c]Absolute fluorescence quantum yield determined by a calibrated integrating sphere system. [d]Spin-coated film prepared from a THF solution.

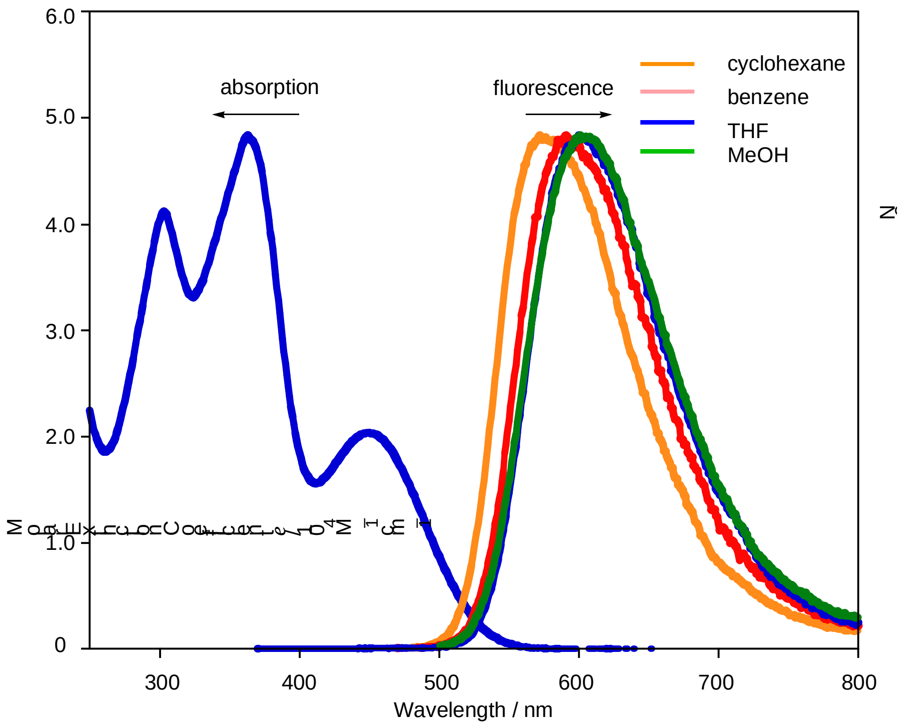


Figure S11. UV-vis absorption and fluorescence spectra of **6** in various solvents.

Table S3. Photophysical Data of **7** in Various Solvents and in the Solid State

	l_{abs}/nm[a]	l_{em}/nm[b]	F_F[c]
Cyclohexane	459	622	0.36
Benzene	467	642	0.41
THF	465	660	0.38
MeOH	458	663	0.25
Film[d]	479	657	0.30

[a]Only the longest absorption maxima are shown. [b]Excited at the longest absorption maxima. [c]Absolute fluorescence quantum yield determined by a calibrated integrating sphere system. [d]Spin-coated film prepared from a THF solution.

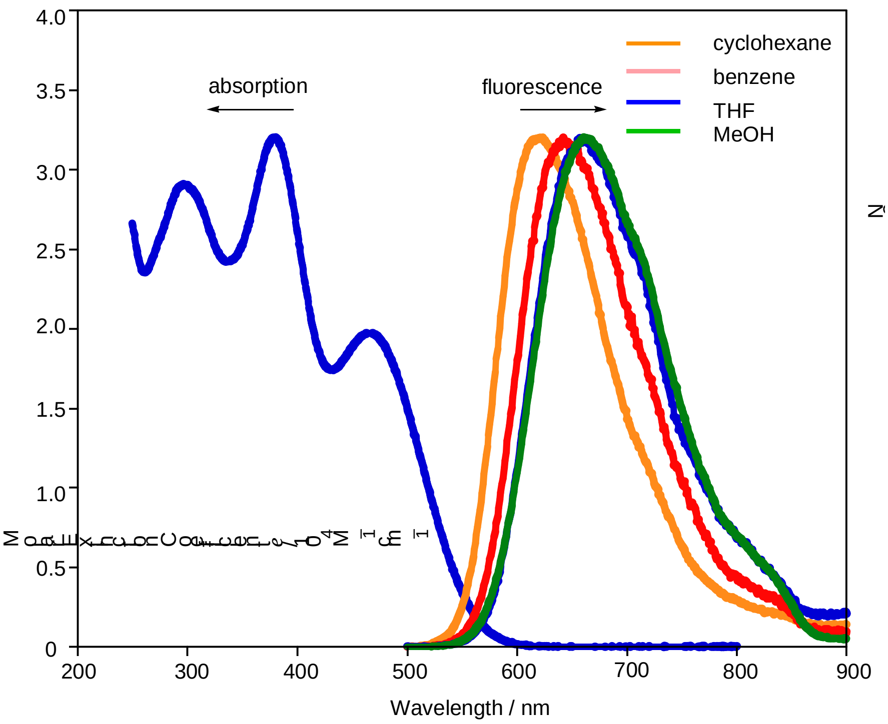


Figure S12. UV-vis absorption and fluorescence spectra of **7** in various solvents.

Thermogravimetric Analysis (TGA)

Table S4. Thermogravical analysis (TGA) Data of **1**, and **3–7**.

Compd	T_{d5} (°C)[a]	T_{d10} (°C)[b]	Compd	T_{d5} (°C)[a]	T_{d10} (°C)[b]
1	210	224	**5**	415	425
3	309	323	**6**	416	486
4	301	320	**7**	385	397

[a]Temperature at which 5% weight loss was recorded on TGA at a heating rate of 5 °C/min under nitrogen. [b]Temperature at which 10% weight loss was recorded on

Cyclic Voltammetry

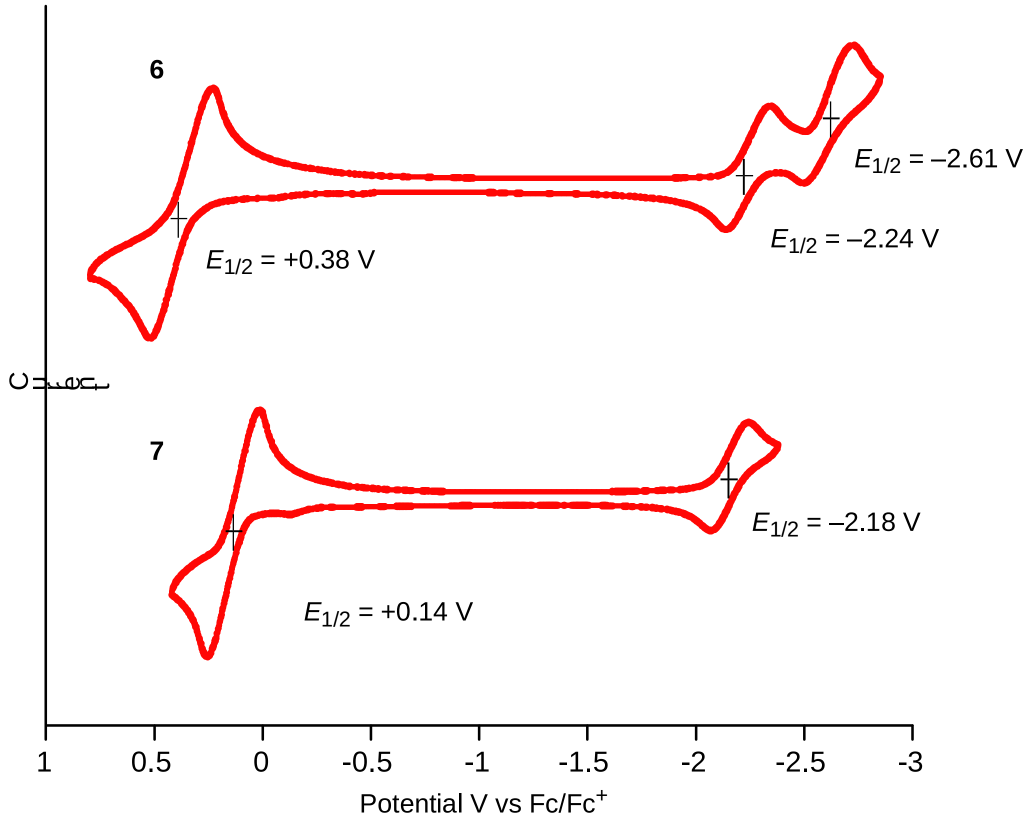


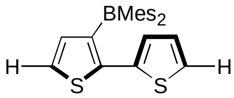
Figure S13. Cyclic voltammograms of **6** and **7** in THF, measured with n-$Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrode at a scan rate of 100 mV s^{-1}.

Theoretical Calculations

Table S5. Calculated HOMO,[a] LUMO,[a] and Lowest Excitation Energies[b]

Compd	HOMO /eV[a]	LUMO /eV[a]	Transition /eV[b]	Main CI coefficient [b]	Oscillator Strength f[b]
1	–5.59	–1.77	3.18 (390 nm)	0.66 (HOMO→LUMO)	0.0726
8	–5.61	–1.98	3.24 (382 nm)	0.61 (HOMO→LUMO)	0.5473

[a]Calculated at the B3LYP/6-31G(d) level. [b]Calculated at the B3LYP/6-31G(d) level using the TD-DFT method.



1

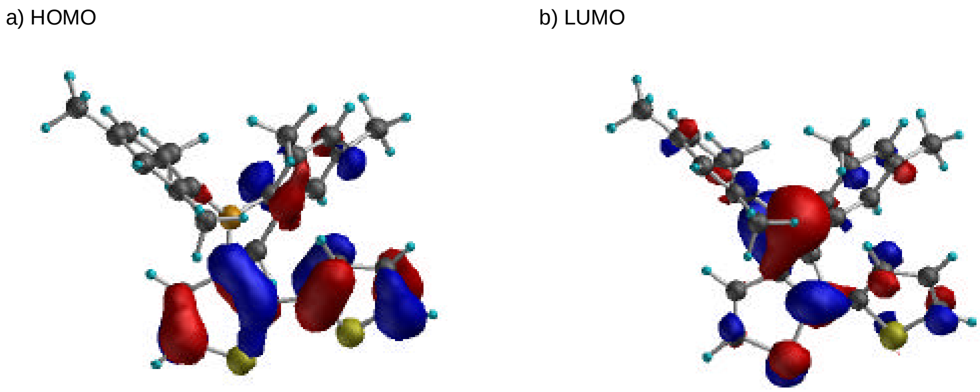
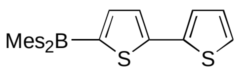


Figure S14. Pictorial presentation of (a) HOMO and (b) LUMO of **1** calculated at the B3LYP/6-31G(d) level.



8

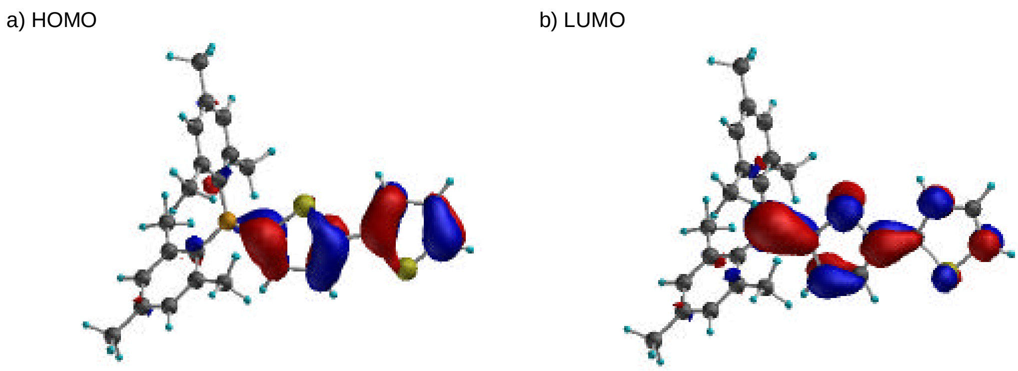
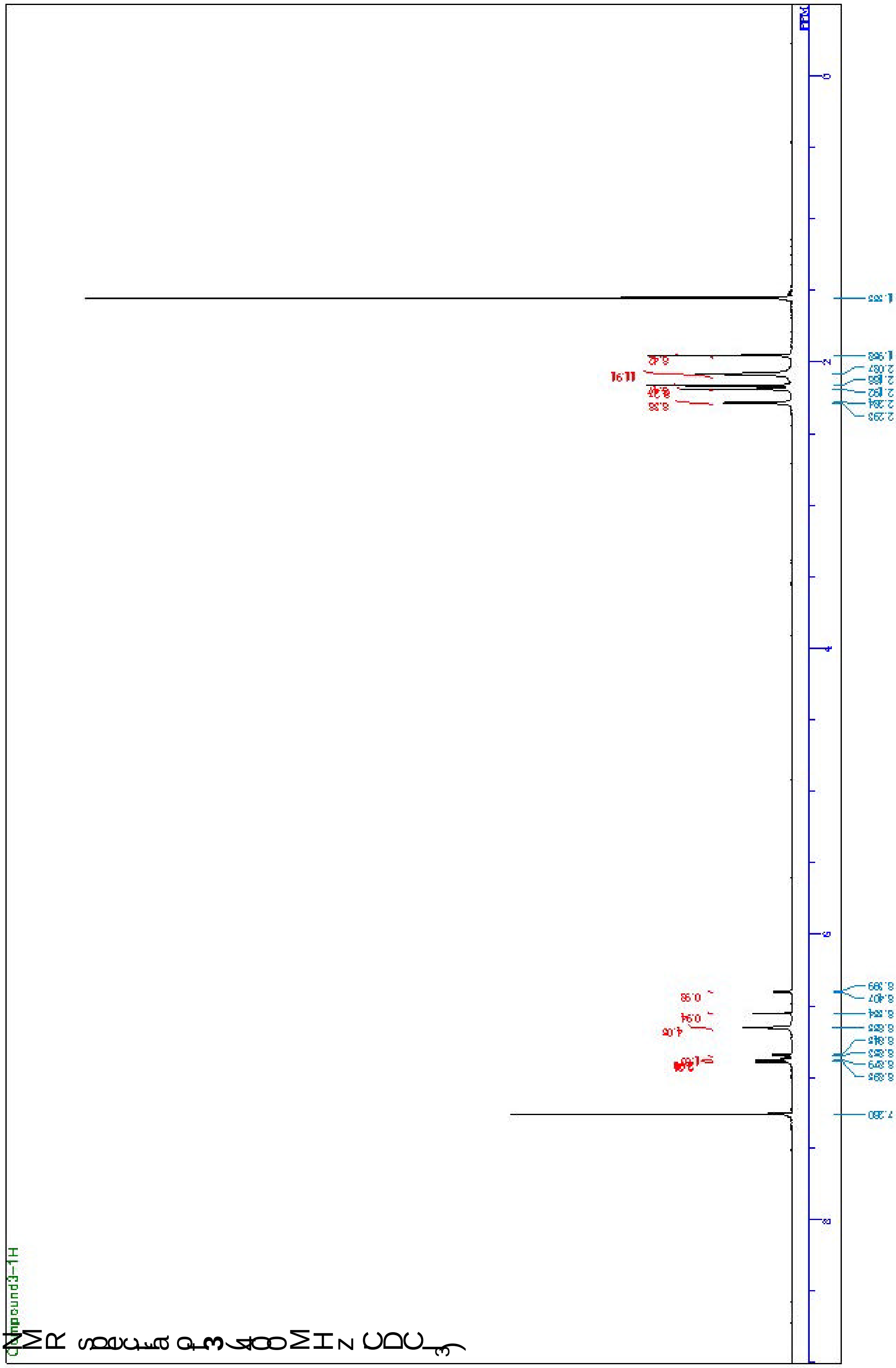
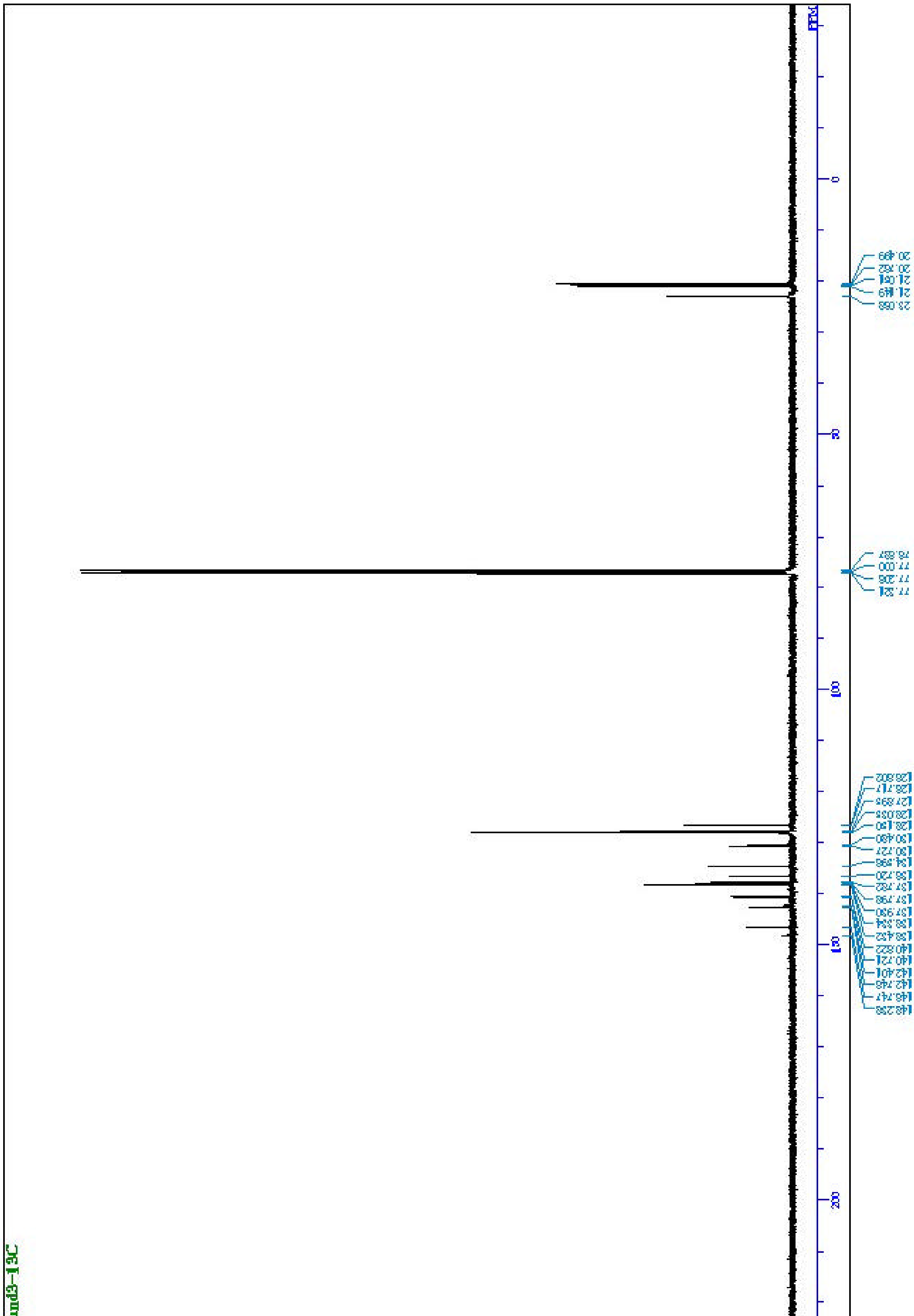
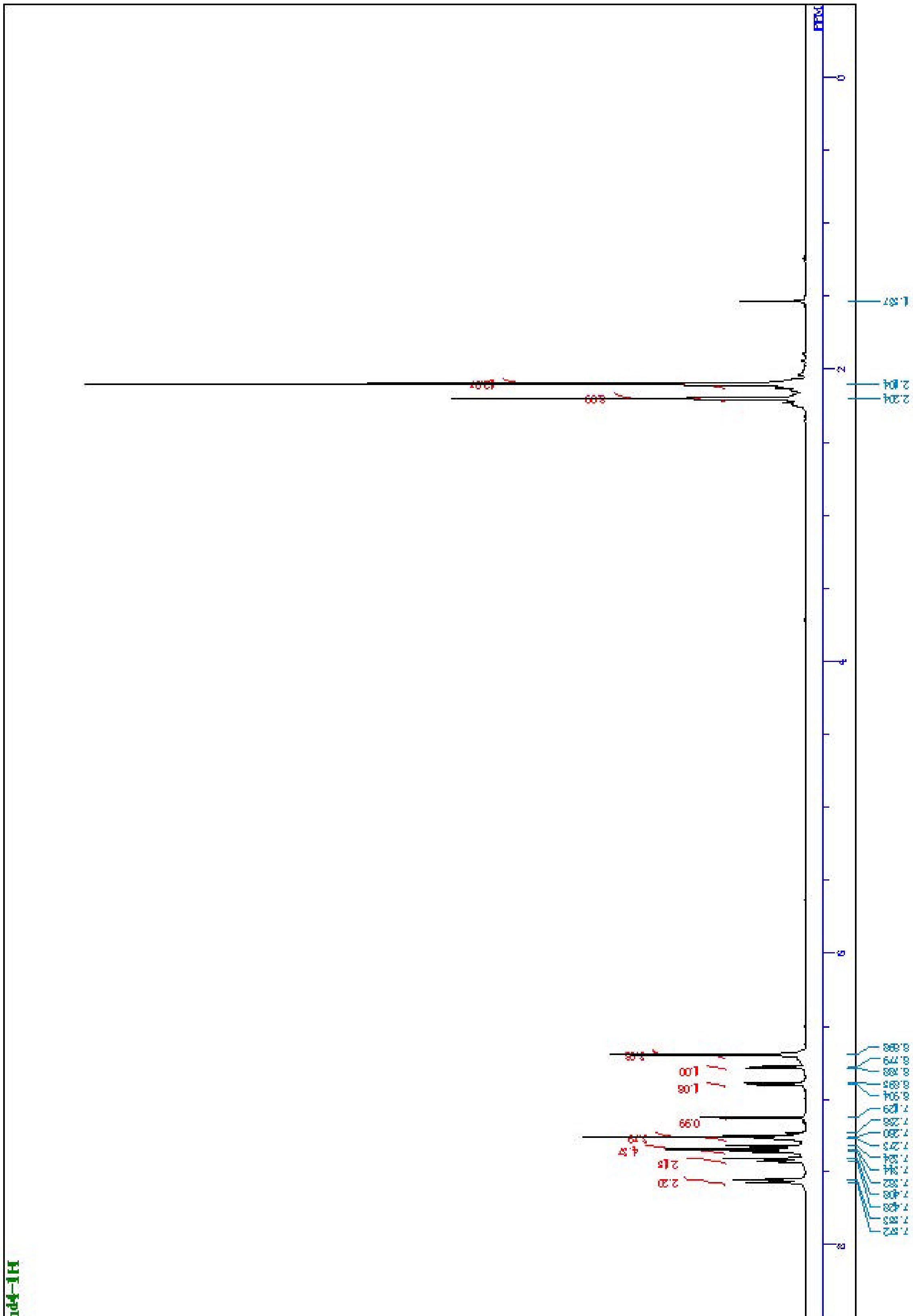


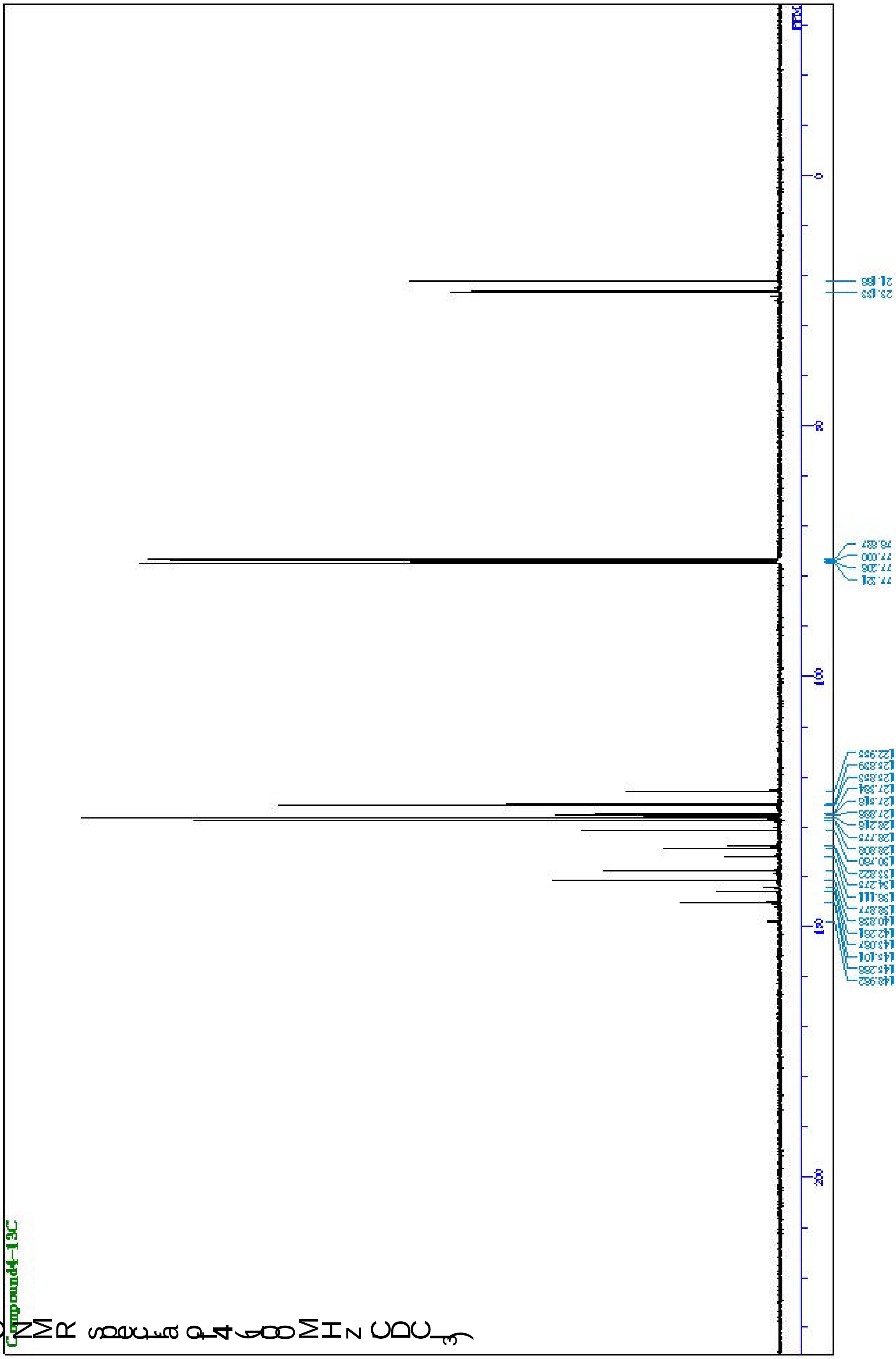
Figure S15. Pictorial presentation of (a) HOMO and (b) LUMO of **8** calculated at the B3LYP/6-31G(d) level.



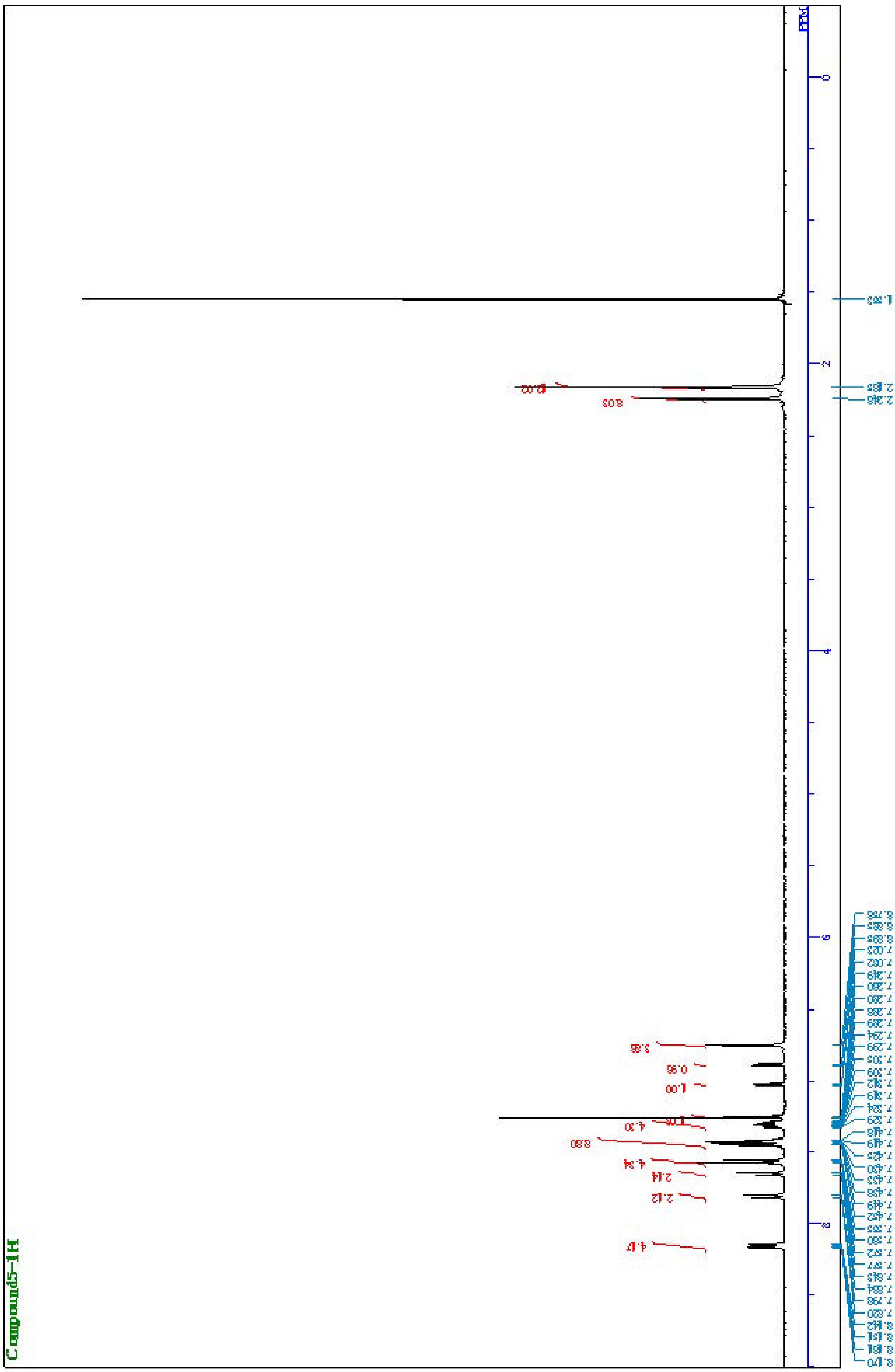
^1H NMR spectra of **3** (400 MHz, $CDCl_3$)

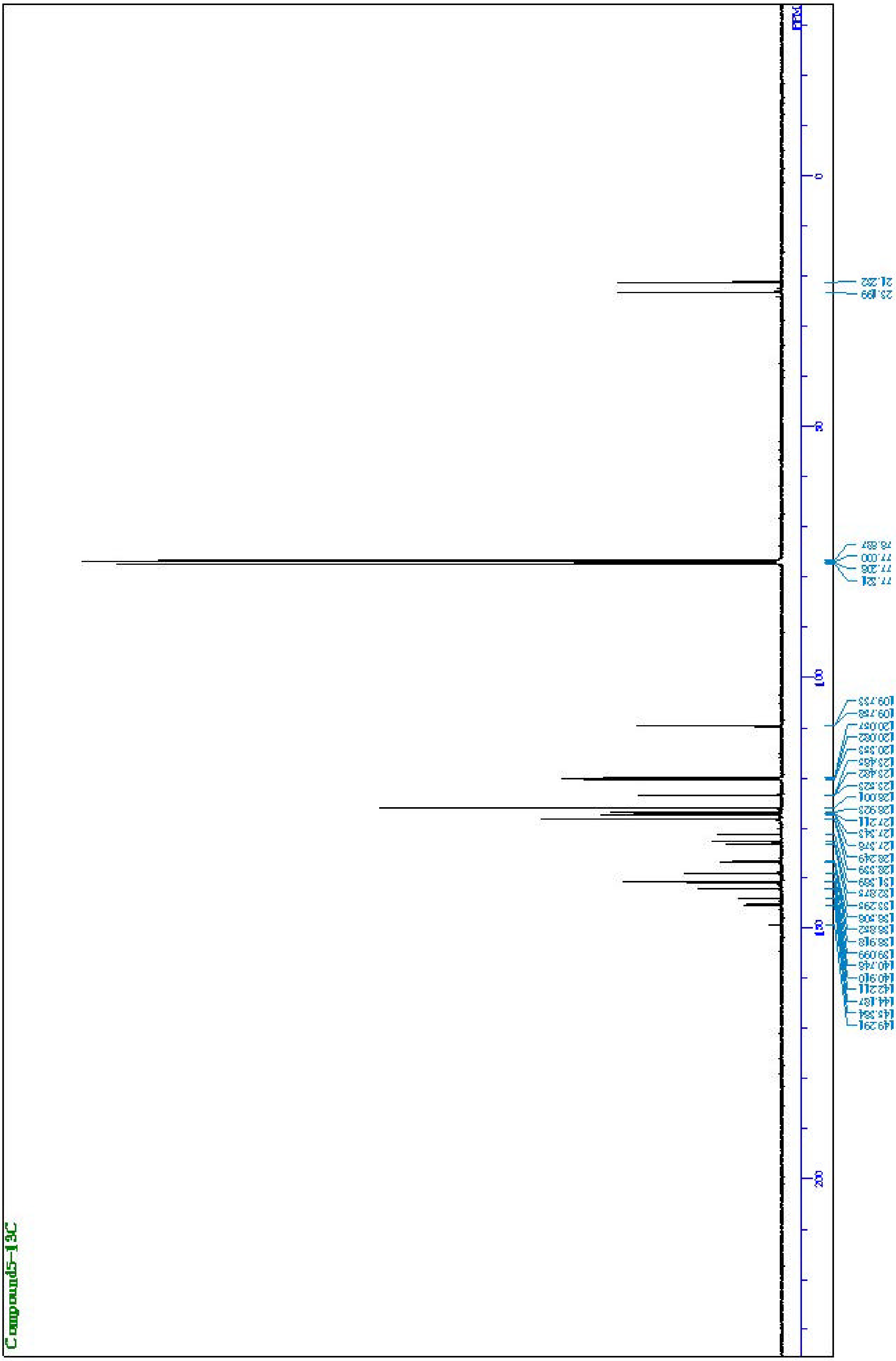

Compound3-13C

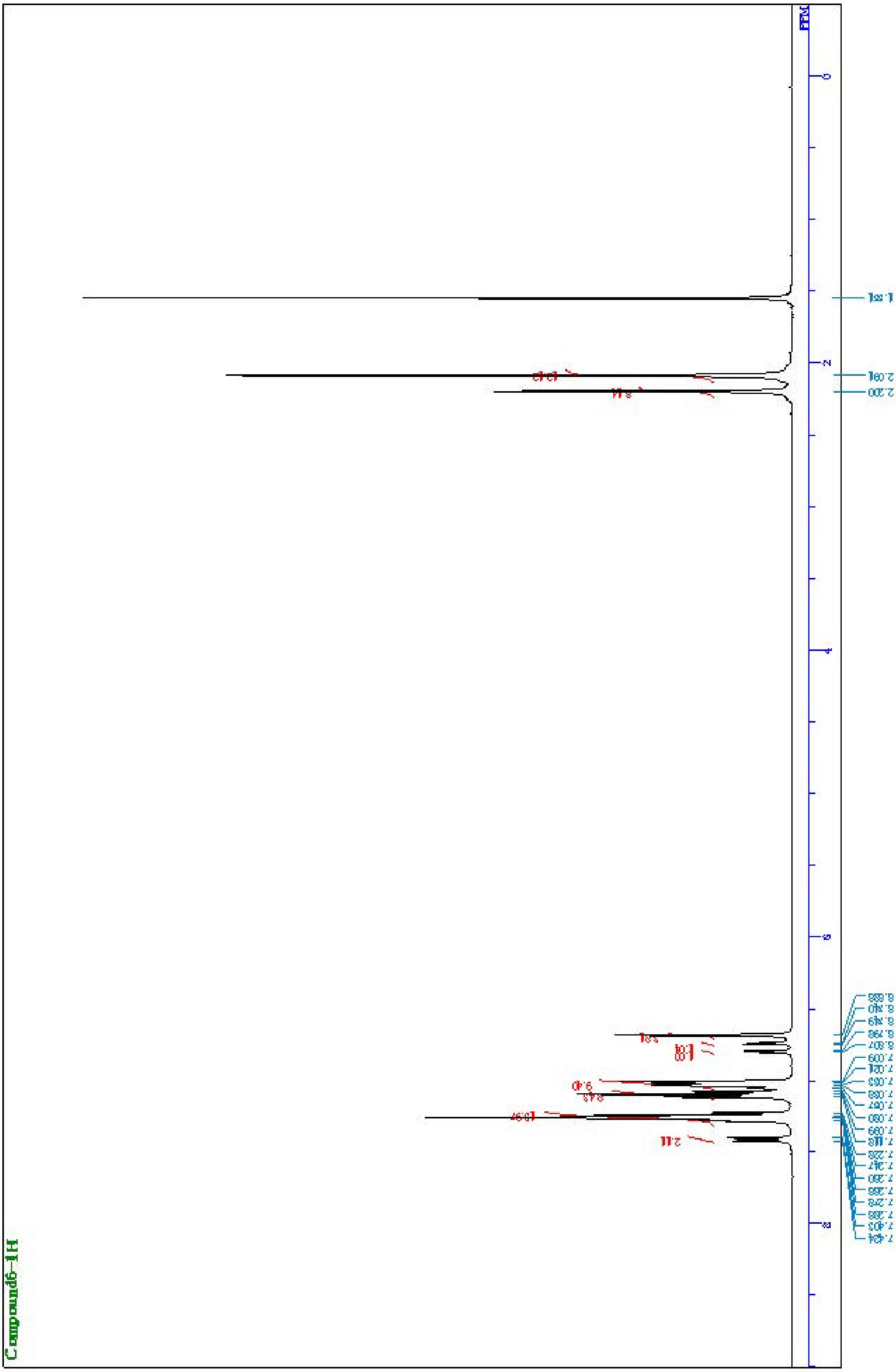

Compound4-1H

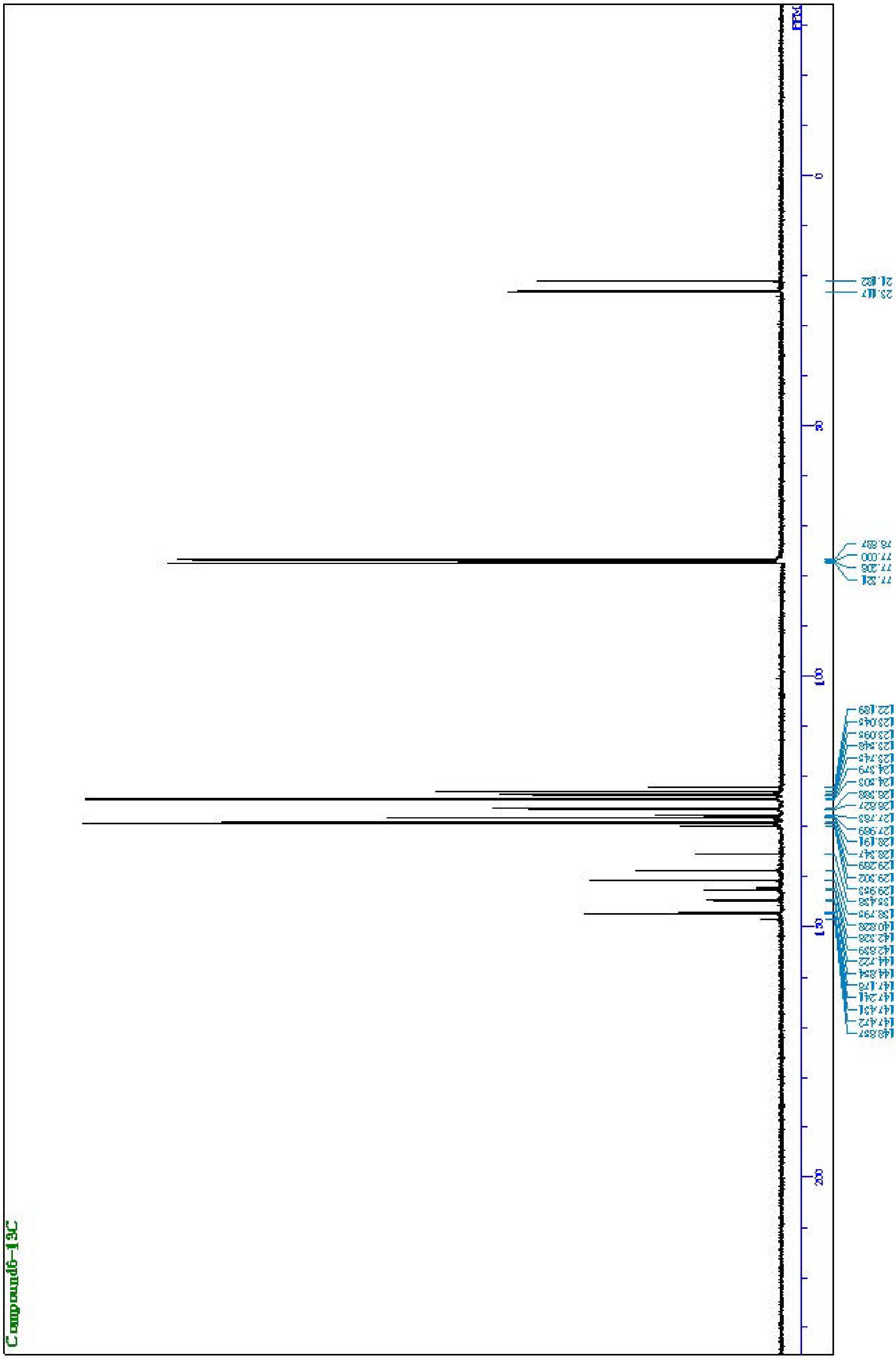


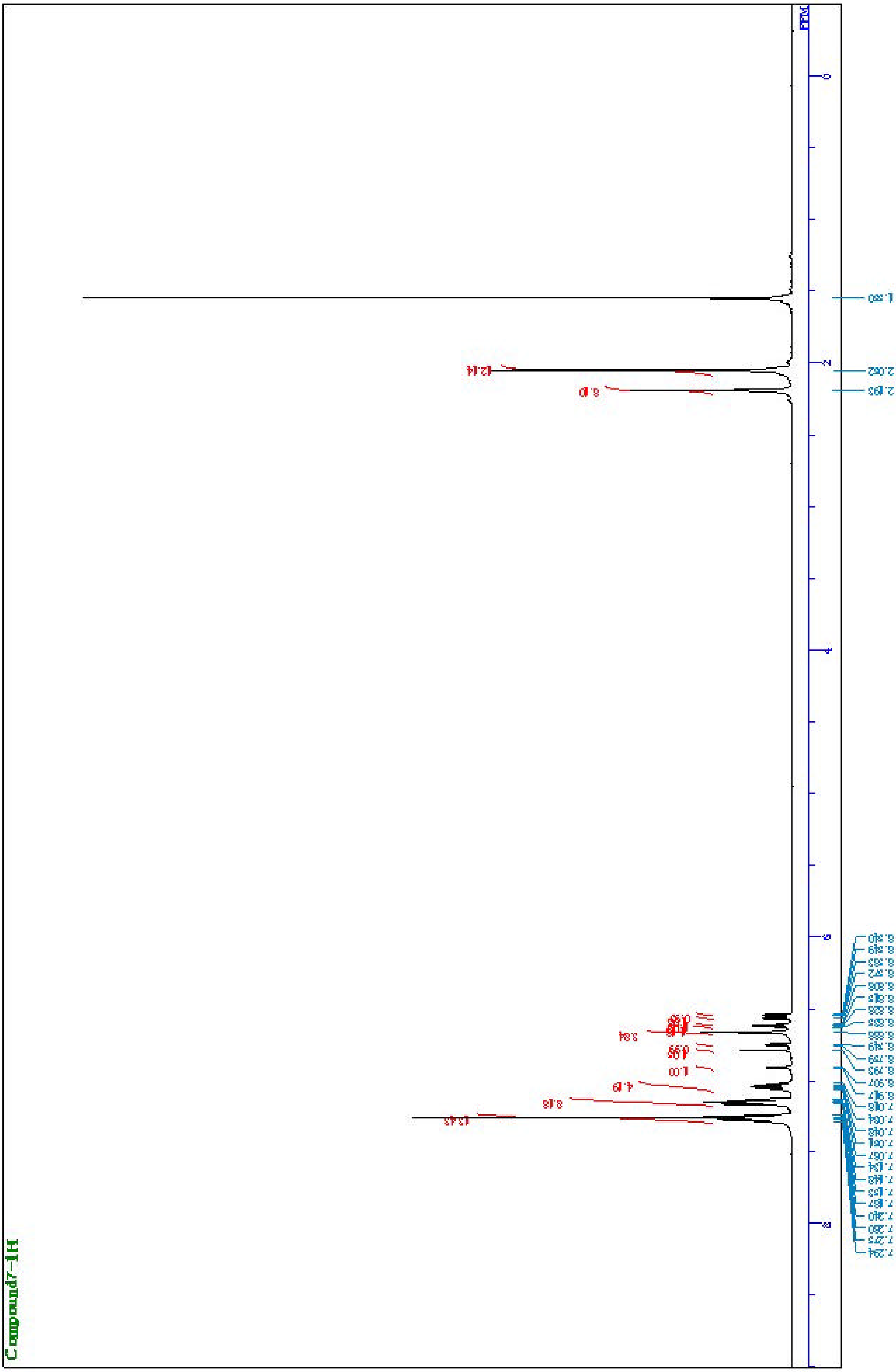
^{13}C NMR spectra (400 MHz, $CDCl_3$)

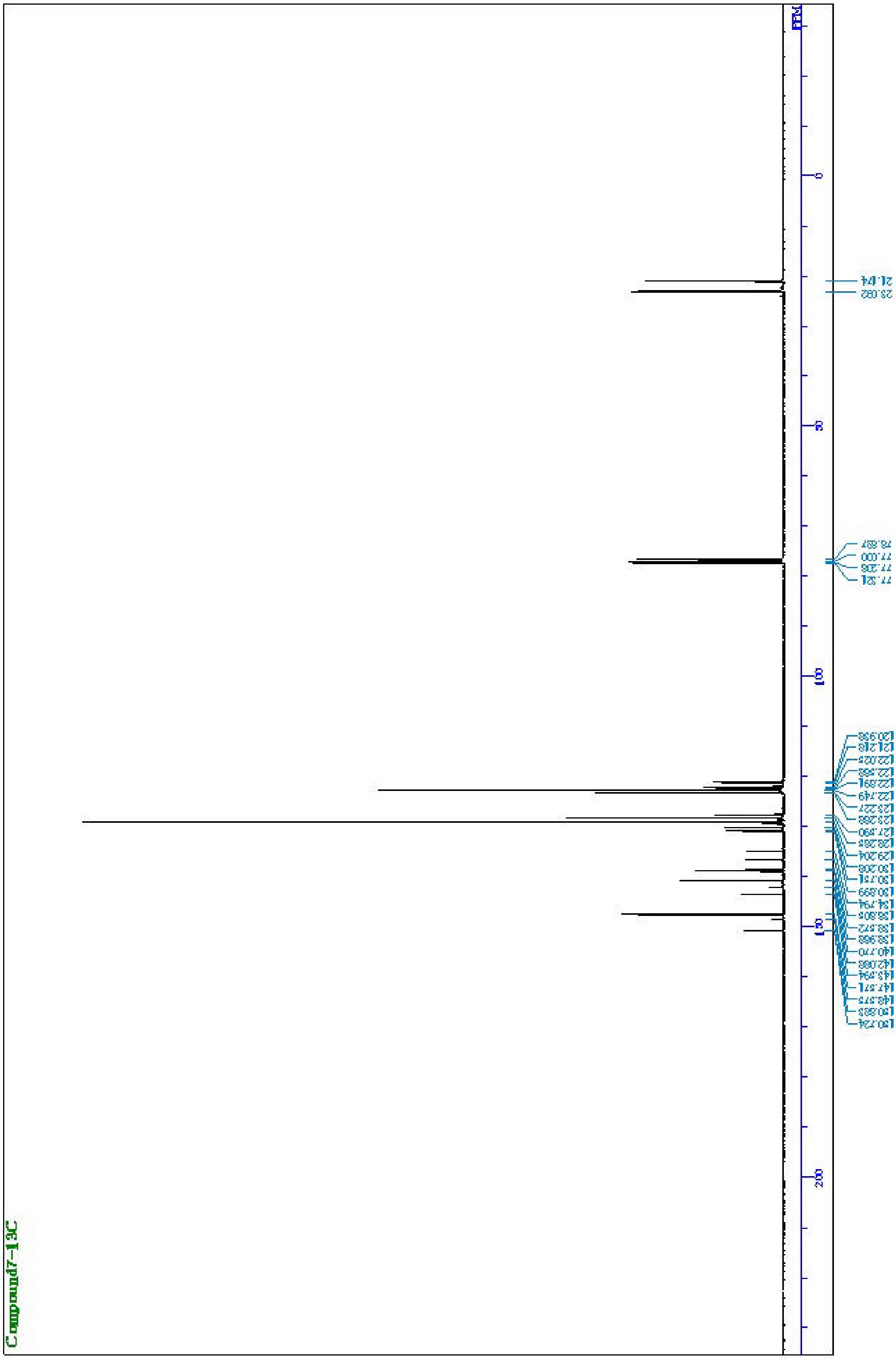

Compound5-1H
ppm


Compound5-13C


Compound6-1H


Compound6-13C


Compound7-1H
PPM
1.880
2.062
2.193


Compound7-13C