Supporting Information

High efficiency pure blue thermally activated delayed fluorescence molecules having 10*H*-phenoxaborin and acridan units

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1. Experimental details

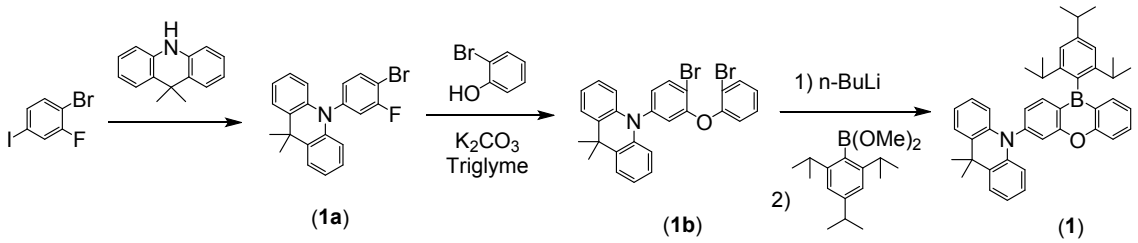
UV-Vis absorption measurements were performed by a Perkin-Elmer Lambda 950-PKA UV-Vis spectrophotometer in the range of 250–800 nm. The photoluminescence spectra were recorded on with a spectrofluorometer (FluoroMax-4, Horiba Jobin Yvon), and the photoluminescence quantum efficiencies were measured using an absolute photoluminescence quantum yield (PLQY) measurement system (C11347 (Quantaurus-QY), Hamamatsu Photonics). The PLQY of the film samples was measured under nitrogen flow. The transient photoluminescence decay characteristics of the solution samples were recorded using a fluorescence lifetime measurement system (C11367-03 (Quantaurus-Tau), Hamamatsu Photonics). The transient photoluminescence decay characteristics of the film samples were recorded under vacuum conditions by using a streak camera (C4334, Hamamatsu Photonics) equipped with a N_2 gas laser (KEN-X, Usho, λ = 337 nm, pulse width ≈ 500 ps, repetition rate = 20 Hz) as the excitation source. Low-temperature measurements were conducted using a cryostat (CRT-006-2000, Iwatani Industrial Gases). The HOMO energy levels of the compounds in film state were determined by atmospheric ultraviolet photoelectron spectroscopy using an AC-3 (Riken Keiki) using 100-nm-thick films deposited by thermal evaporation on quartz substrate under vacuum ($< 1 \times 10^{-3}$ Pa). The 1×10^{-5} M toluene solution was used for UV-Vis absorption and photoluminescence spectra measurement. The 1×10^{-4} M toluene solution was used for PLQY (Φ) measurements for accuracy (S/N ratio) due to the low absorbance at absorption edge, and this solution was degassed with nitrogen bubbling for ca. 15 min prior to measurement. Thin film samples (~100 nm) for the luminescence and photoelectron spectroscopy studies were deposited by thermal evaporation under high vacuum ($< 5 \times 10^{-4}$ Pa) on quartz substrates and ITO substrates, respectively. The OLEDs were fabricated by thermal evaporation onto pre-cleaned indium tin oxide (ITO) glass substrates under high vacuum ($< 5 \times 10^{-4}$ Pa). All organic layers were deposited by rate of 0.05-0.2 nm/sec, while the LiF and Al were deposited by rate of 0.01 nm/sec and 0.1-0.6 nm/sec, respectively. The intersection of the ITO anode and Al cathode gave an active area of 4 mm^2. The current density/voltage/luminance (*J*-*V*-*L*) characteristics were measured using an external quantum efficiency measurement system (C9920-12, Hamamatsu Photonics). All quantum chemical calculations were performed using the Gaussian 03 program package.[1] Geometry optimization was carried out using the B3LYP functional with the 6-31G(d) basis set. Low-lying excited singlet and triplet states were computed using the optimized structures with time-dependent density functional theory (TD-DFT) at the same level.

2. Synthesis of the compounds

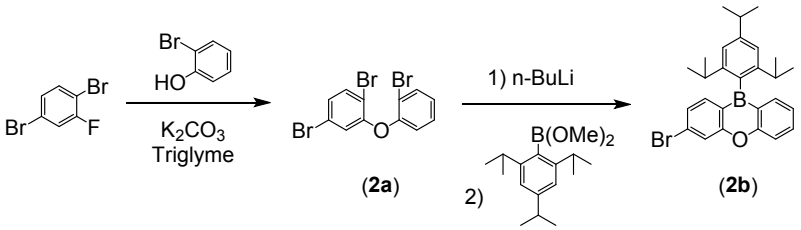
All starting materials were purchased from commercial resources and were used as received. All reactions were carried out under N_2 atmospheres. Melting points were measured using a Melting Point M-565 (Buchi). ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded in $CDCl_3$ with an Avance III 500 spectrometer (Bruker) operating at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS; $\delta = 0$) as the internal reference. ^{1}H NMR spectra data are reported as chemical shift, relative integral, multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant (*J* in

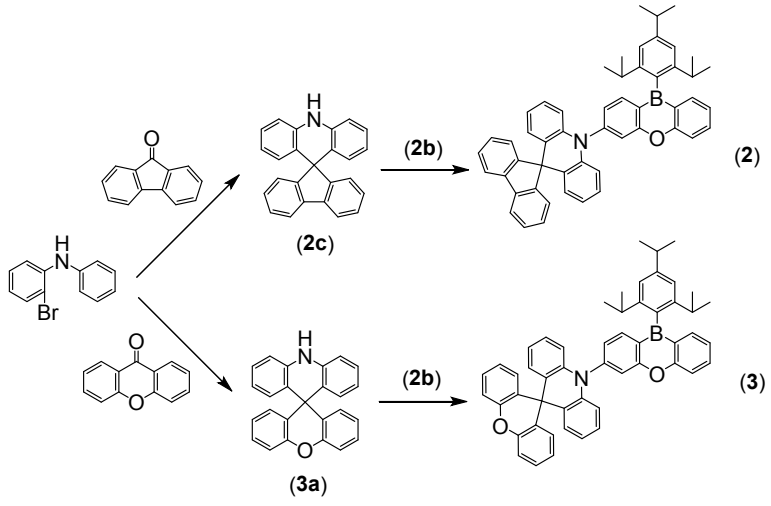
Hz) and assignment. Mass spectra were collected on a JEOL JMS-AX505HA by means of electronic impact at 70 eV ionization energy. Elemental analyses (C, H, N) were carried out with a Yanaco MT-5 CHN corder. 9,9-Dimethylacridan,[2] dimethyl (2,4,6-triisopropylphenyl)boronate,[3] and 2-bromo-*N*-phenylaniline[4] were synthesized according to their corresponding literature.

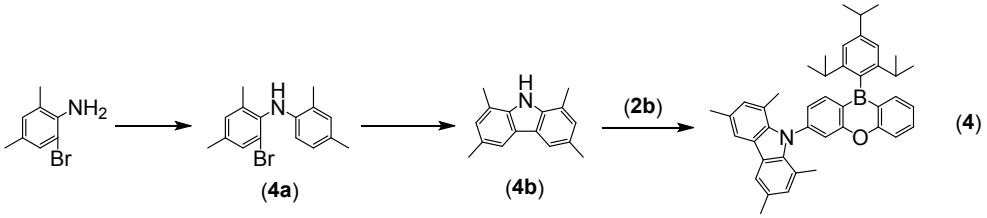
Method A



Method B







Method A

10-(4-Bromo-3-fluorophenyl)-9,9-dimethyl-9,10-dihydroacridine (1a):

A mixture of 1-bromo-2-fluoro-4-iodobenzene(25.3 g, 84 mmol), 9,9-dimethylacridan[2] (17.6 g, 84 mmol), *tert*-BuONa (12.1 g, 126 mmol), CuI (0.32 g, 1.7 mmol), *trans*-1,2-cyclohexanediamine (0.1 mL, 8.4mmol), dioxane (84 mL) was stirred and refluxed for 24 h. After cooling to room temperature, resulting solution was diluted with toluene (500 mL), filtered through a celite and silica gel pad, and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/toluene = 6:4, v/v) and recrystallized from hexane at 5 °C to afford **1a** as a white solid (19.7 g, 61%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.81 (t, 1H, J = 8.0Hz), 7.46 (dd, 2H, J = 7.6, 1.7 Hz), 7.16 (dd, 1H, J = 9.0, 2.3 Hz), 7.06 (ddd, 1H, J = 8.4, 2.3, 1.0 Hz), 7.03-6.92 (m, 4H), 6.27 (dd, 2H, J =8.1, 1.4 Hz), 1.67 (s, 6H).

^{13}C-NMR(125 MHz, $CDCl_3$): δ (ppm) = 161.58, 159.58, 142.14, 142.07, 140.28, 135.49, 130.32, 128.46, 128.43, 126.52, 125.45, 121.19, 119.87, 119.69, 113.91, 109.18, 109.01, 36.01, 31.25.

Elemental analysis (calculated, found for $C_{21}H_{17}NBrF$): C (65.98%, 65.99%), H (4.48%, 4.45%), N (3.66%, 3.62%).

10-(4-Bromo-3-(2-bromophenoxy)phenyl)-9,9-dimethyl-9,10-dihydroacridine (1b):

A mixture of **1a** (7.65 g, 20 mmol), 2-bromophenol (13.8 g, 80 mmol), K_2CO_3 (11.1 g, 80 mmol) and triglyme (triethylene glycol dimethyl ether) (10 mL) was stirred for 72 h at 190 °C. After cooling to room temperature, the resulting product was diluted with toluene (200 mL) and water (200 mL), filtered through a celite and washed with water. The organic layer was dried over $MgSO_4$, filtered through a silica gel pad and concentrated. The crude product was purified by column chromatography on silica gel (hexane/toluene = 6:4, v/v) and washed with hexane to afford **1b** as a white solid (9.40 g, 88%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.89(d, 1H, J = 8.4 Hz), 7.59 (dd, 1H, J = 7.9, 1.5 Hz), 7.42 (dd, 2H, J = 7.7, 1.6 Hz), 7.27 (ddd, 1H, J = 8.2, 7.4, 1.6 Hz), 7.06-6.96 (m, 5H), 6.92 (ddd, 2H, J = 7.6, 7.6, 1.2 Hz), 6.71 (d, 1H, J = 2.3 Hz), 6.28 (dd, 2H, J = 8.2, 1.1 Hz), 1.63 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 155.63, 152.34, 141.62, 140.28, 135.97, 134.28, 129.98, 129.00, 127.30, 126.49, 126.05, 125.42, 121.04, 120.89, 120.84, 114.88, 113.85, 113.30, 35.91, 31.42.

Elemental analysis (calculated, found for $C_{27}H_{21}NBr_2O$): C (60.58%, 60.58%), H (3.95%, 3.96%), N (2.62%, 2.57%).

9,9-Dimethyl-10-(10-(2,4,6-triisopropylphenyl)-10*H*-dibenzo[*b,e*][1,4]oxaborinin-3-yl)-9,10-dihydroacridine (1):

To a stirred solution of **1b** (9.37 g, 17.5 mmol) in Et_2O (175 mL), *n*-BuLi (1.58M in hexane, 22.2 mL, 35 mmol) was added dropwise at 0 °C. After stirring for 10 min, a solution of dimethyl (2,4,6-triisopropylphenyl)boronate[3] (4.83 g, 17.5 mmol) in Et_2O (17.5 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was concentrated and diluted with toluene (100 mL), washed with water, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel

(hexane/toluene = 7:3, v/v) and washed twice with acetonitrile to afford **1** as a pale yellow solid (5.82 g, 56%). This material was sublimed at 220 °C under vacuum (< 1 × 10^{-1} Pa) before device fabrication.
m.p.: 213-216 °C.
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.01 (d, 1H, J = 8.0Hz), 7.83 (dd, 1H, J = 7.6, 1.7 Hz), 7.74 (ddd, 1H, J = 8.6, 7.1, 1.8 Hz), 7.62 (d, 1H, J = 1.8Hz), 7.57 (d, 1H, J = 8.1Hz), 7.48 (dd, 1H, J = 7.6, 1.6 Hz), 7.27 (m, 1H), 7.20 (dd, 1H, J = 8.0, 1.8Hz), 7.10 (s, 2H), 7.03-6.93 (m, 4H), 6.44 (dd, 2H, J = 8.1, 1.4 Hz), 3.00 (sep, 1H, J = 6.9 Hz), 2.40 (sep, 2H, J = 6.7 Hz), 1.71 (s, 6H), 1.36 (d, 6H, J = 7.0 Hz), 1.06-1.01(m, 12H).
^{13}C-NMR(125 MHz, $CDCl_3$): δ (ppm) = 160.43, 158.89, 150.29, 148.64, 147.07, 140.58, 139.29, 136.90, 135.27, 134.73, 130.94, 126.39, 126.183, 125.63, 125.39, 125.17, 124.35, 122.67, 121.10, 120.02, 119.21, 117.45, 114.76, 36.14, 35.44, 34.31, 30.92, 24.40, 24.35, 24.17.
Elemental analysis (calculated, found for $C_{42}H_{44}NBO$): C (85.56%, 85.62%), H (7.52%, 7.57%), N (2.38%, 2.37%).

Method B

1,4-Dibromo-2-(2-bromophenoxy)benzene (2a):
A mixture of 2,5-dibromofluorobenzene (25.4 g, 100 mmol), 2-bromophenol (26.0 g, 150 mmol), K_2CO_3 (27.6 g, 200 mmol) and triglyme (triethylene glycol dimethyl ether) (10mL) was stirred for 72 h at 190 °C. After cooling to room temperature, the resulting product was diluted with toluene (200 mL), filtered through a celite and washed with water. The organic layer was dried over $MgSO_4$, filtered through a silica gel pad and concentrated. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 9:1, v/v) and recrystallized from hexane at 5 °C to afford **2a** as a white solid (50.5 g, 89%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.65 (dd, 1H, J = 8.0, 1.6 Hz), 7.49 (d, 1H, J = 8.5 Hz), 7.30 (ddd, 1H, J = 8.1, 7.5, 1.6 Hz), 7.13 (dd, 1H, J = 8.5, 2.2 Hz), 7.08 (ddd, 1H, J = 8.0, 7.6, 1.4 Hz), 6.94 (dd, 1H, J = 8.2, 1.5 Hz), 6.87 (d, 1H, J = 2.2Hz).
^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 154.24, 152.39, 134.75, 134.18, 128.92, 127.76, 126.04, 121.56, 121.46, 120.60, 114.79, 112.55.
HRMS (*m*/*z*): $[M]^+$ calculated for $C_{12}H_7Br_3O$, 403.8047; found, 403.8047.

3-Bromo-10-(2,4,6-triisopropylphenyl)-10*H*-dibenzo[*b,e*][1,4]oxaborinine (2b):
To a solution of **2a** (32.6 g, 80 mmol) in Et_2O (400 mL), *n*-BuLi (1.6 M in hexane, 103 mL, 164 mmol) was added dropwise at 0 °C. After stirring for 10 min, a solution of dimethyl (2,4,6-triisopropylphenyl)boronate (22.1g, 80 mmol) in Et_2O (40 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was concentrated and diluted with toluene (300 mL), washed with water, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2, = 9:1, v/v) and recrystallized from hexane (50 mL) at 5 °C to afford **2b** as a white solid (16.5g, 45%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.79(d, 1H, J = 1.7Hz), 7.77 (dd, 1H, J = 7.6, 1.7 Hz), 7.73 (ddd, 1H, J = 8.6, 7.1, 1.8 Hz), 7.64(d, 1H, J = 8.1 Hz), 7.57 (d, 1H, J = 8.1 Hz), 7.35 (dd, 1H, J = 8.1, 1.7 Hz), 7.25 (ddd, 1H, J = 7.6, 7.6, 1.0 Hz), 7.06 (s, 2H),

2.98 (sep, 1H, J = 6.9 Hz), 2.26 (sep, 2H, J = 6.8 Hz), 1.35(d, 6H, J = 7.0Hz), 1.00 (m, 12H).
^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 159.05, 158.66, 150.27, 148.70, 142.23, 137.95, 136.86, 134.94, 134.81, 128.77, 125.95, 124.78, 123.80, 122.80, 120.70, 120.01, 117.48, 116.37, 35.87, 34.33, 24.34, 24.33, 24.17.
Elemental analysis (calculated, found for $C_{27}H_{30}BBrO$): C (70.31%, 70.38%), H (6.56%, 6.61%)

10*H*-spiro[acridine-9,9'-fluorene] (2c):
To a solution of 2-bromo-*N*-phenylaniline[4] (24.8 g, 100 mmol) in dry THF (200 mL), *n*-BuLi (1.6 M in hexane, 128 mL, 205 mmol) was added dropwise at -78 °C. After stirring for 1 h, fluorenone (19.8 g, 110 mmol) was added as a powder while stirring the solution at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. After quenching by a small amount of water, the resulting mixture was concentrated and diluted with $CHCl_3$ (500 mL). The solution was washed with water and aqueous phase was extracted twice with $CHCl_3$. A combined $CHCl_3$ solution was dried over $MgSO_4$ and concentrated to afford a hydroxy intermediate. The crude hydroxy intermediate was diluted with $CHCl_3$ (400 mL), and methanesulfonic acid (9.6 g, 100 mmol) was added and then refluxed for 2 h. After cooling to room temperature, the resulting solution was carefully poured into an excess amount of $NaHCO_3$ aqueous solution. The product was extracted by $CHCl_3$, dried over $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 4:6, v/v) and washed with ethanol twice, filtered off, and then dried under reduced pressure to afford **2c** as a pale yellow solid (13.7 g, 41%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.77 (d, 2H, J = 7.6Hz), 7.35 (ddd, 2H, J = 7.5, 7.5, 1.1 Hz), 7.31 (d, 2H, J = 7.6 Hz), 7.20 (ddd, 2H, J = 7.5, 7.5, 1.1 Hz), 7.07 (ddd, 2H, J = 8.6, 8.1, 1.5 Hz), 6.83 (dd, 2H, J = 8.0, 1.1 Hz), 6.58 (ddd, 2H, J = 7.9, 7.9, 1.2 Hz), 6.35 (dd, 2H, J = 7.9, 1.2 Hz), 6.34 (s, 1H).
^{13}C-NMR (125 MHz, DMSO-d_6): δ (ppm) = 155.97, 139.29, 138.53, 128.29, 127.58, 127.44, 126.77, 125.27, 122.96, 120.16, 119.48, 114.23, 56.28.
Elemental analysis (calculated, found for $C_{25}H_{17}N$): C (90.60%, 90.48%), H (5.17%, 5.17%), N (4.23%, 4.22%)

10*H*-spiro[acridine-9,9'-xanthene] (3a):
Following the same manner for **2c**, **3a** was synthesized from 2-bromo-*N*-phenylaniline[4] (12.9 g, 52 mmol) in dry THF (104 mL), *n*-BuLi (1.6 M in hexane, 67 mL, 107 mmol), xanthone (11.2 g, 57 mmol), $MeSO_3H$ (5.0 g, 52 mmol), $CHCl_3$ (520 mL) to afford the desired product as a white solid (13.5 g, 74%).
^{1}H-NMR (500 MHz, DMSO-d_6): δ (ppm) = 9.23 (s, 1H), 7.23-7.14 (m, 4H), 7.02 (ddd, 2H, J = 8.3, 7.0, 1.6 Hz), 6.95 (ddd, 2H, J = 8.00, 6.3, 2.0 Hz), 6.93-6.87 (m, 4H), 6.60 (ddd, 2H, J = 8.1, 7.0, 1.2 Hz), 6.55 (dd, 2H, J = 7.8, 1.6 Hz).
^{13}C-NMR (125 MHz, DMSO-d_6): δ (ppm) = 147.66, 136.93, 131.55, 131.14, 131.05, 127.94, 127.71, 127.21, 123.67, 119.79, 115.61, 113.70, 44.10.
HRMS (*m*/*z*): $[M]^+$ calculated for $C_{25}H_{17}NO$, 347.1310; found, 347.1310.

2-Bromo-*N*-(2,4-dimethylphenyl)-4,6-dimethylaniline (4a):
A mixture of 2-bromo-4,6-dimethylaniline (19.6 g, 98 mmol), 1-iodo-2,4-

dimethylbenzene (25.0 g, 108 mmol), *tert*-BuONa (14.1 g, 147 mmol), $Pd_2(dba)_3$ (0.90 g), and 1,1'-bis(diphenylphosphino)ferrocene (dppf, 1.1 g, 2.0 mmol) in dry toluene (270 mL) was refluxed for 16 h. After cooling to room temperature, the resulting solution was diluted with toluene and filtered through a celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 8:2, v/v) and recrystallized from hexane at 5 °C to afford **4a** (18.7 g, 63%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.30 (dd, 1H, J = 1.3, 0.6 Hz), 7.01-6.95 (m, 2H), 6.79 (ddd, 1H, J = 8.1, 1.4, 0.5 Hz), 6.13 (d, 1H, J = 8.1Hz), 5.17 (s, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 2.12 (s, 3H).
^{13}C-NMR (125 MHz, DMSO-d_6): δ (ppm) = 140.82, 136.78, 136.16, 135.56, 131.21, 131.05, 130.90, 128.81, 126.98, 124.51, 121.38, 113.52, 20.55, 20.50, 19.12, 17.69.
Elemental analysis (calculated, found for $C_{16}H_{18}NBr$): C (63.17%, 63.16%), H (5.96%, 6.01%), N (4.60%, 4.63%).

1,3,6,8-Tetramethyl-9*H*-carbazole (4b):
A mixture of **4a** (18.5 g, 60.8 mmol), K_2CO_3 (16.8 g, 121.6 mmol), $Pd(OAc)_2$ (0.68 g), and tricyclohexylphosphonium tetrafluoroborate (2.24g, 6.08 mmol) in dry *N*,*N*-dimethylacetamide (120 mL) and toluene (120 mL) was refluxed for 6 h. After cooling to room temperature, the resulting mixture was diluted with toluene and filtered through a celite and washed with water to remove *N*,*N*-dimethylacetamide. The solution was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 7:3, v/v) and recrystallized from hexane at 5 °C to afford **4b** (8.91 g, 66%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.66 (d, 2H, J = 0.6 Hz), 7.03 (s, 2H), 2.54 (s, 6H), 2.49 (s, 6H).
^{13}C-NMR (125 MHz, DMSO-d_6): δ (ppm) = 137.56, 127.22, 126.92, 122.46, 119.95, 117.11, 20.96, 17.13.
Elemental analysis (calculated, found for $C_{16}H_{17}N$): C (86.05%, 86.14%), H (7.67%, 7.77%), N (6.27%, 6.30%).

10-(10-(2,4,6-Triisopropylphenyl)-10*H*-dibenzo[*b*,*e*][1,4]oxaborinin-3-yl)-10*H*-spiro[acridine-9,9'-fluorene] (2):
Compound **2** was synthesized from **2b** (2.31 g, 5.0 mmol), **2c** (1.99 g, 6.0 mmol), *tert*-BuONa (0.96 g, 10 mmol), $Pd_2(dba)_3$ (92 mg, 0.10 mmol), P(*t*-Bu)$_3$/HBF_4 (116 mg, 0.40 mmol) and toluene (50 mL). The product was purified by column chromatography (hexane/CH_2Cl_2 = 7:3, v/v), washed with MeCN twice to afford **2** as a pale yellow solid (3.17 g, 89%). This material was sublimed at 260 °C under vacuum (< 1×10^{-1} Pa) before device fabrication.
m.p.: 294-298 °C.
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.12 (d, 1H, J = 7.9 Hz), 7.87 (dd, 1H, J = 7.6, 1.6 Hz), 7.83-7.75 (m, 4H), 7.63(d, 1H, J = 8.1 Hz), 7.46 (d, 2H, J = 7.5 Hz), 7.42-7.34 (m, 3H), 7.33-7.24 (m, 3H), 7.13 (s, 2H), 6.94 (ddd, 2H, J = 8.6, 7.2, 1.6 Hz), 6.62-6.57 (m, 2H), 6.48-6.42 (m, 2H), 3.02 (sep, 1H, J = 6.9 Hz), 2.43 (sep, 2H, J = 6.7 Hz), 1.38 (d, 6H, J = 6.9 Hz), 1.11 (d, 6H, J = 6.8 Hz), 1.09 (d, 6H, J = 6.8 Hz).
^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 160.55, 158.91, 156.41, 150.32, 148.74, 146.68, 140.91, 139.61, 139.26, 136.98, 135.16, 134.90, 128.40, 127.83, 127.63, 127.28,

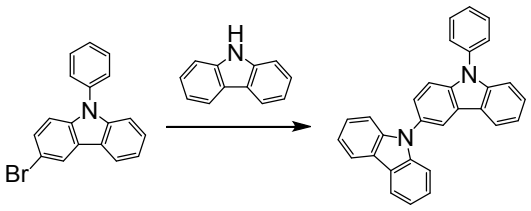
126.19, 125.79, 125.04, 124.97, 122.80, 120.88, 120.22, 120.09, 119.92, 117.50, 114.69, 56.84, 35.52, 34.34, 24.43, 24.37, 24.18.
HRMS (*m*/*z*): $[M]^+$ calculated for $C_{52}H_{46}NBO$, 711.3672; found, 711.3681.

10-(10-(2,4,6-Triisopropylphenyl)-10*H*-dibenzo[*b,e*][1,4]oxaborinin-3-yl)-10*H*-spiro[acridine-9,9'-xanthene] (3):

Compound **3** was synthesized from **2b** (2.31 g, 5.0 mmol), **3a** (1.91 g, 5.5 mmol), *tert*-BuONa (0.96 g, 10 mmol), $Pd_2(dba)_3$ (92 mg, 0.10 mmol), P(*t*-Bu)$_3$/HBF_4 (116mg, 0.40 mmol) and toluene (50 mL). The product was purified by column chromatography (hexane/CH_2Cl_2 =7:3, v/v) and washed with MeCN twice to afford **3** as a pale yellow solid (3.37 g, 93%). This material was sublimed at 260 °C under vacuum (< 1×10^{-1} Pa) before device fabrication.
m.p.: 332-333 °C.
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.11 (d, 1H, J = 7.9 Hz), 7.86 (dd, 1H, J = 7.6, 1.7 Hz), 7.78 (ddd, 1H, J = 8.6, 1.8 Hz), 7.74 (d, 1H, J = 1.8Hz), 7.33-7.28 (m, 2H), 7.22-7.14 (m, 6H), 7.13 (s, 2H), 7.01-6.94 (m, 2H), 6.93-6.85 (m, 4H), 6.70 (ddd, 2H, J = 8.0, 7.1, 1.1 Hz), 6.37 (d, 2H, J = 7.8 Hz), 3.02 (sep, 1H, J = 6.9 Hz), 2.42 (sep, 2H, J = 6.7 Hz), 1.38 (d, 6H, J = 7.0 Hz), 1.10 (d, 6H, J = 6.8 Hz), 1.08 (d, 6H, J = 6.8 Hz).
^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 160.56, 158.89, 150.31, 148.76, 148.50, 146.58, 139.71, 138.80, 136.97, 135.13, 134.92, 132.39, 131.91, 131.34, 129.83, 127.63, 126.98, 126.20, 125.01, 123.68, 122.82, 121.13, 120.33, 120.09, 117.49, 115.97, 114.18, 44.74, 35.52, 34.33, 24.43, 24.36, 24.18.
Elemental analysis (calculated, found for $C_{52}H_{46}NBO_2$): C (85.82%, 85.75%), H (6.37%, 6.31%), N (1.92%, 1.96%).

1,3,6,8-Tetramethyl-9-(10-(2,4,6-triisopropylphenyl)-10*H*-dibenzo[*b,e*][1,4]oxaborinin-3-yl)-9*H*-carbazole (4):

Compound **4** was synthesized from **2b** (2.31 g, 5.0 mmol), **4b** (1.99 g, 6.0 mmol), *tert*-BuONa (0.96g, 10.0 mmol), $Pd_2(dba)_3$ (92 mg, 0.10 mmol), P(*t*-Bu)$_3$/HBF_4 (116 mg, 0.40 mmol) and toluene (50 mL). The product was purified by column chromatography (hexane/CH_2Cl_2 = 7:3, v/v) and washed with MeCN twice to afford **4** as a pale yellow solid (3.17 g, 89%). This material was sublimed at 260 °C under vacuum (< 1×10^{-1} Pa) before device fabrication.
m.p.: 220-225 °C.
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.86 (dd, 1H, J = 7.6, 1.7 Hz), 7.80 (d, 1H, J = 7.9 Hz), 7.78-7.72 (m, 4H), 7.59 (d, 1H, J = 8.1 Hz), 7.33-7.24 (m, 4H), 7.09 (s, 1H), 6.91 (s, 2H), 2.99 (sep, 1H, J = 6.9 Hz), 2.48 (s, 6H), 2.36 (sep, 2H, J = 6.7 Hz), 1.89 (s, 6H), 1.35 (d, 6H, J = 6.9 Hz), 1.07 (d, 6H, J = 6.8 Hz), 1.02 (d, 6H, J = 6.8 Hz).
^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 159.03, 158.35, 150.20, 148.73, 148.03, 139.45, 136.87, 136.61, 135.21, 134.82, 130.29, 129.21, 126.22, 126.08, 125.74, 124.36, 122.81, 121.29, 120.16, 120.05, 117.82, 117.55, 35.52, 34.32, 24.21, 24.17, 21.10, 19.39, 19.23, 24.21, 24.17.
Elemental analysis (calculated, found for $C_{43}H_{46}NBO$): C (85.56%, 85.59%), H (7.68%, 7.74%), N (2.32%, 2.37%).



9-Phenyl-9*H*-3,9'-bicarbazole (CCP):

A mixture of 9-phenyl-3-bromocarbazole (27.7g, 86 mmol), carbazole (15.8 g, 95 mmol), *tert*-BuONa (16.5 g, 172 mmol), $Pd_2(dba)_3$ (1.57 g, 1.7 mmol), and P(*t*-Bu)$_3$/HBF_4 (2.0 g, 6.9 mmol) in dry toluene (344 mL) was refluxed until the reaction was completed. After cooling to room temperature, the resulting solution was filtered through a celite and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/toluene = 65:35, v/v) and recrystallized from toluene/AcOEt to afford the desired product as a white solid. This material was sublimed at 260 °C under vacuum (< 1×10^{-1} Pa) before device fabrication.

m.p.: 172-174 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.29 (dd, 1H, J = 1.95, 0.4 Hz), 8.18 (ddd, 2H, J = 7.75, 0.8, 0.8 Hz), 8.11 (ddd, 1H, J = 7.75, 0.8, 0.8 Hz), 7.69-7.63 (m, 4H), 7.59 (dd, 1H, J = 8.6, 0.4 Hz), 7.56-7.50 (m, 2H), 7.49-7.45 (m, 2H), 7.44-7.37 (m, 4H), 7.35-7.27 (m, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 141.93, 141.65, 140.07, 137.47, 130.09, 129.90, 127.88, 127.22, 126.68, 125.89, 125.54, 124.38, 123.15, 122.96, 120.60, 120.39, 120.31, 119.63, 119.52, 110.89, 110.18, 109.85.

Elemental analysis (calculated, found for $C_{30}H_{20}N_2$): C (88.21%, 88.14%), H (4.93%, 4.85%), N (6.86%, 6.84%).

3. References

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4. DFT calculations for compounds

Table S1. DFT calculations for each moieties.

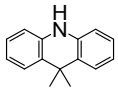
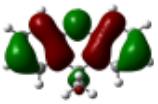
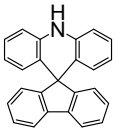
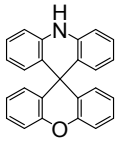
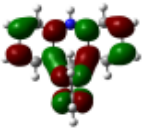
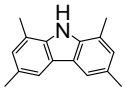
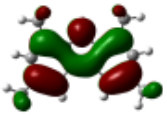
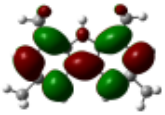
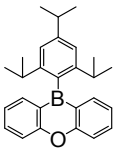
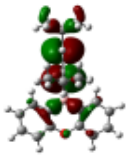
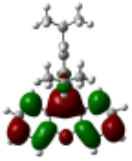
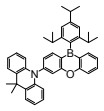
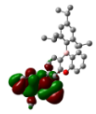
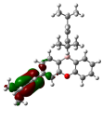
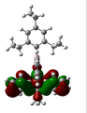
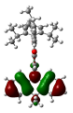
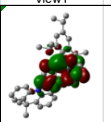
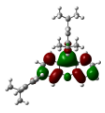
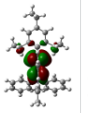
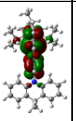
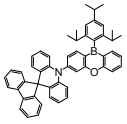
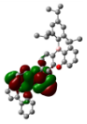
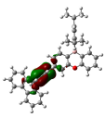
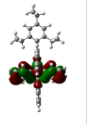
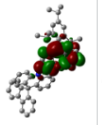
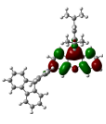
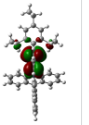
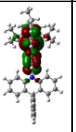
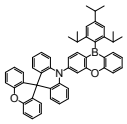
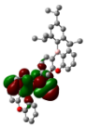
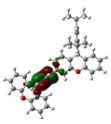
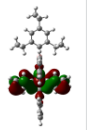
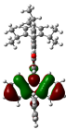
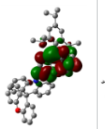
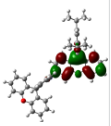
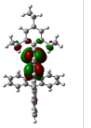
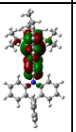
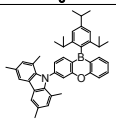
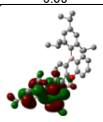
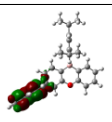
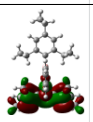
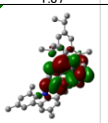
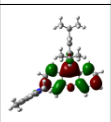
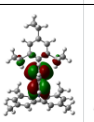
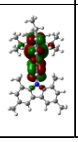
Structure	HOMO(eV)	LUMO(eV)	T_1(eV)	S_1(eV)	ΔE_{ST}(eV)
	 −4.88	 −0.06	3.1902	4.1674	0.9772
	 −4.96	 −0.74	3.0485	3.6131	0.5646
	 −5.03	 −0.74	3.1341	3.8835	0.7494
	 −5.09	 −0.52	3.1590	4.0340	0.8750
	 −5.98	 −1.62	3.1223	3.6091	0.4868

Table S2. DFT calculations for compounds 1-4.

Compound	HOMO(eV)				LUMO(eV)				T_1(eV)	S_1(eV)	ΔE_{ST}(eV)
	view1	view2	view3	view4	view1	view2	view3	view4			
 1	 −4.90				 −1.82				2.5083	2.5181	0.0098
 2	 −4.98				 −1.85				2.5551	2.5649	0.0098
 3	 −5.05				 −1.87				2.5964	2.6061	0.0097
 4	 −5.08				 −1.88				2.6546	2.665	0.0104

5. Photophysical properties data

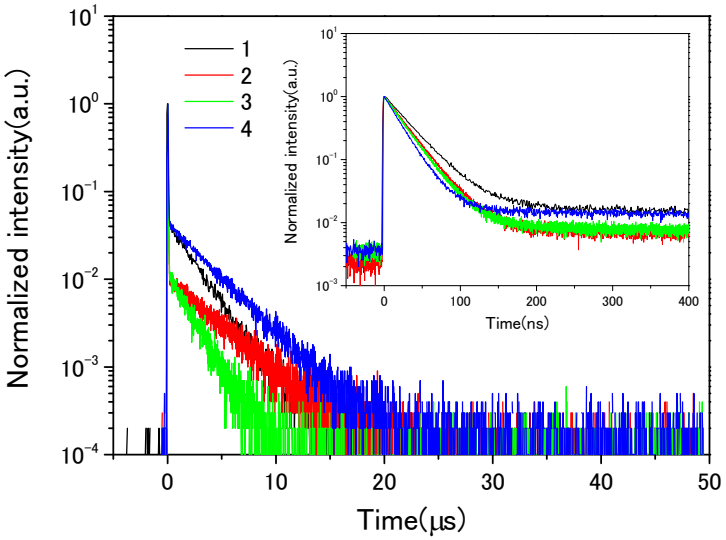


Figure S1. Transient photoluminescence decay curves of the toluene 10^{-4} M solution of **1**(black), **2**(red), **3**(green) and **4**(blue). Inset shows decay curves of their prompt component.

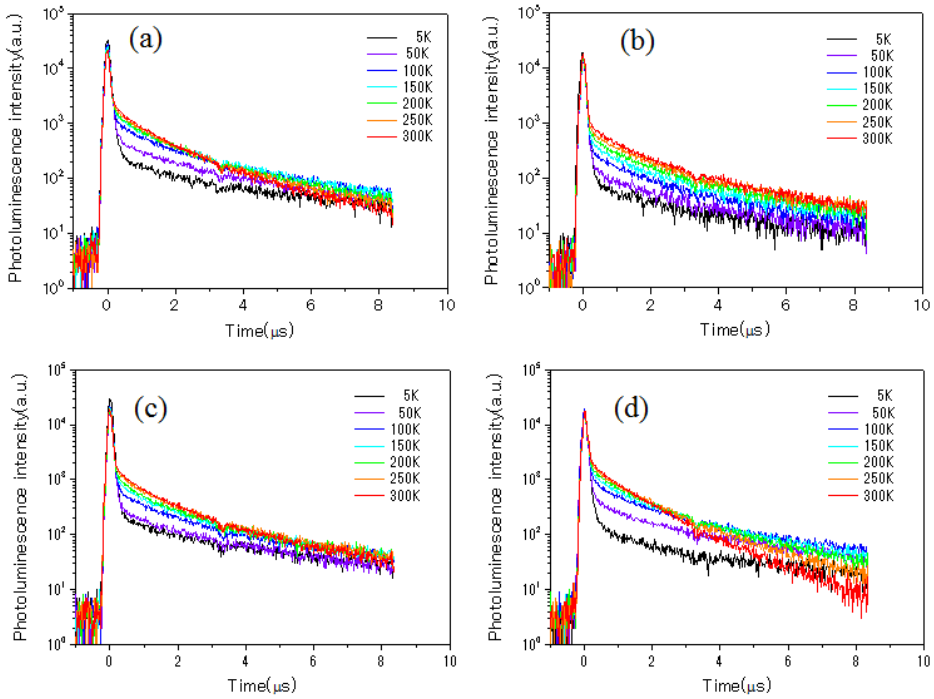


Figure S2. Transient photoluminescence decay curves of the co-deposited film of emitter 20wt%:PPF for **1**(a), **2**(b), **3**(c) and **4**(d).

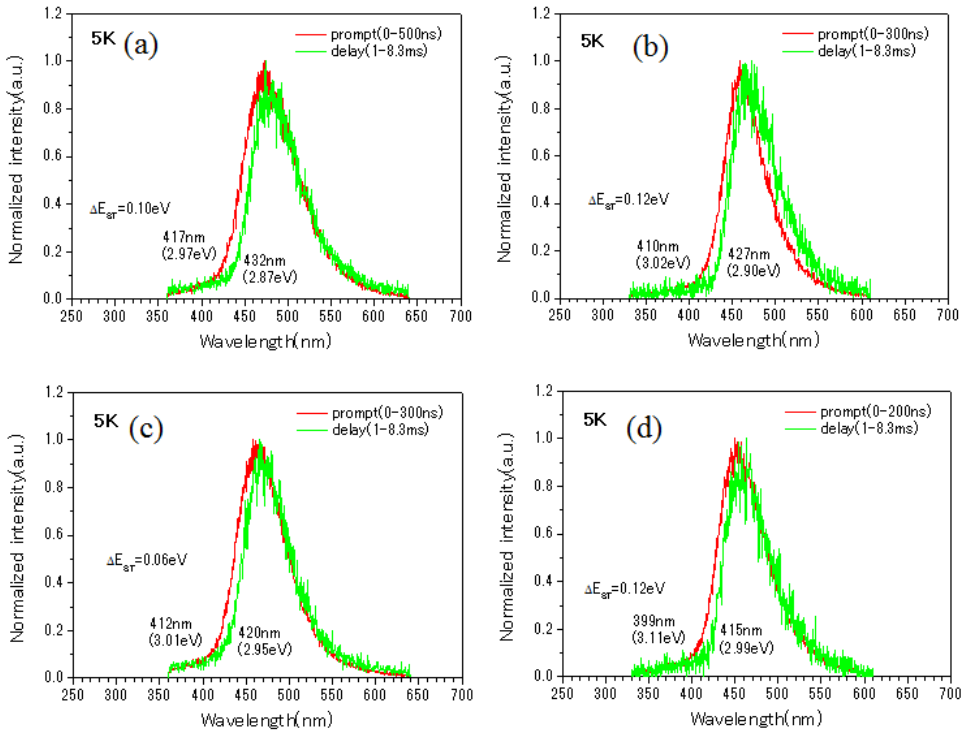


Figure S3. Time resolved photoluminescence spectra of the co-deposited film of emitter 20wt%:PPF for **1**(a), **2**(b), **3**(c) and **4**(d).

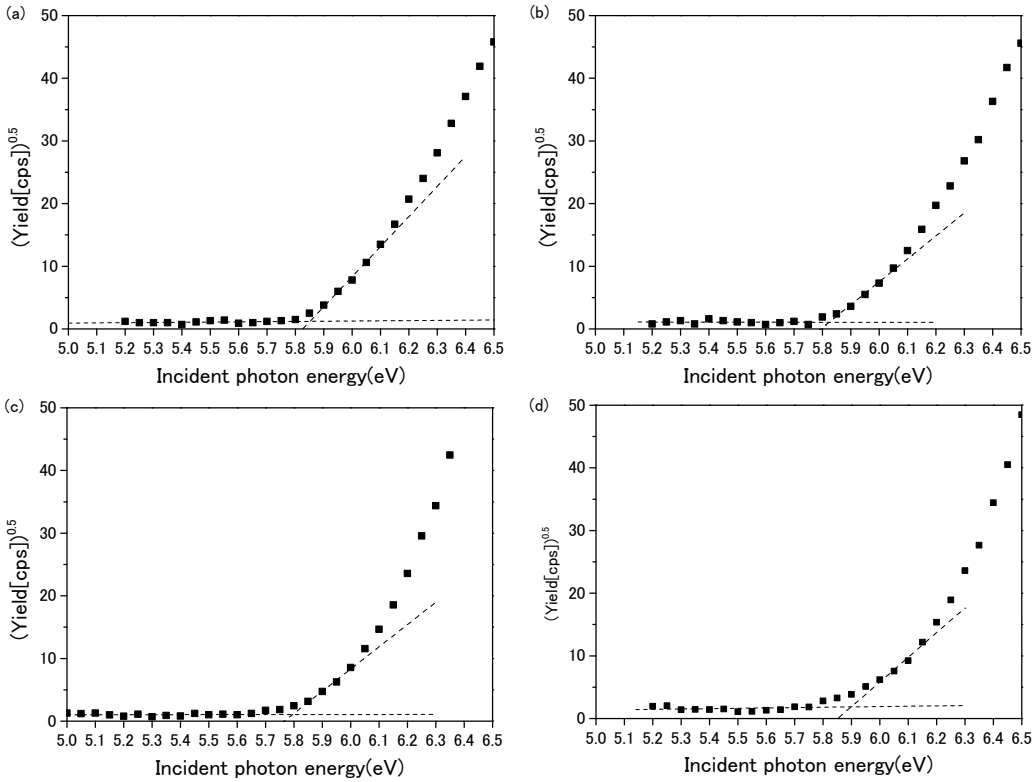
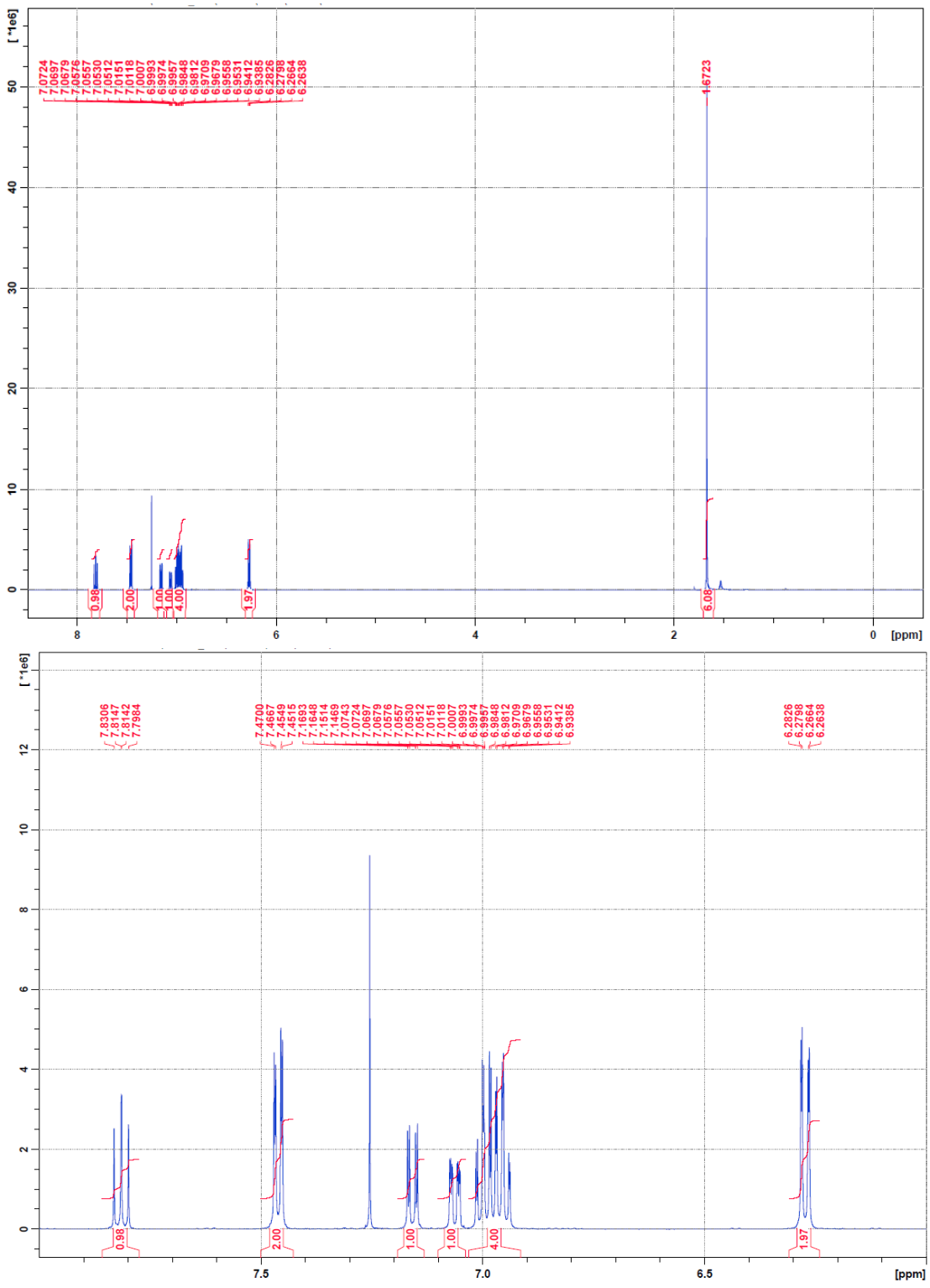


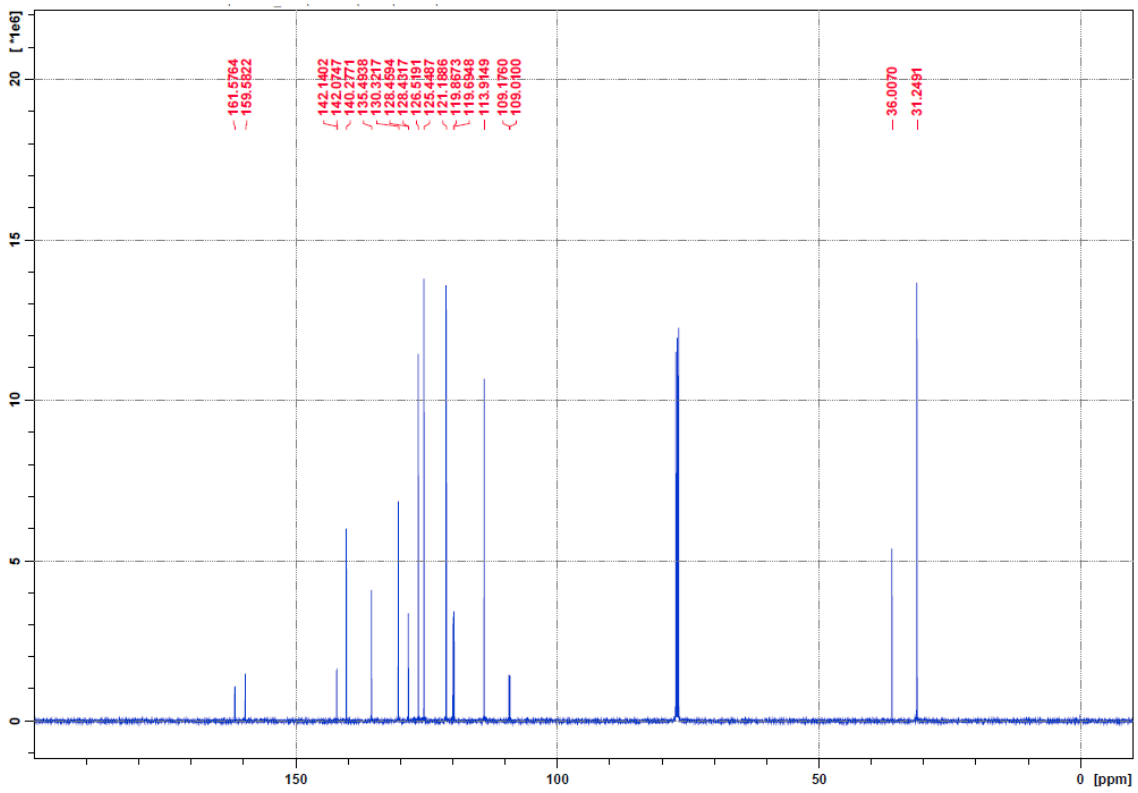
Figure S4. Photoelectron yield spectra of the neat films of **1**(a), **2**(b), **3**(c) and **4**(d).

Figure S5. NMR spectra
Compound 1a
^{1}H-NMR



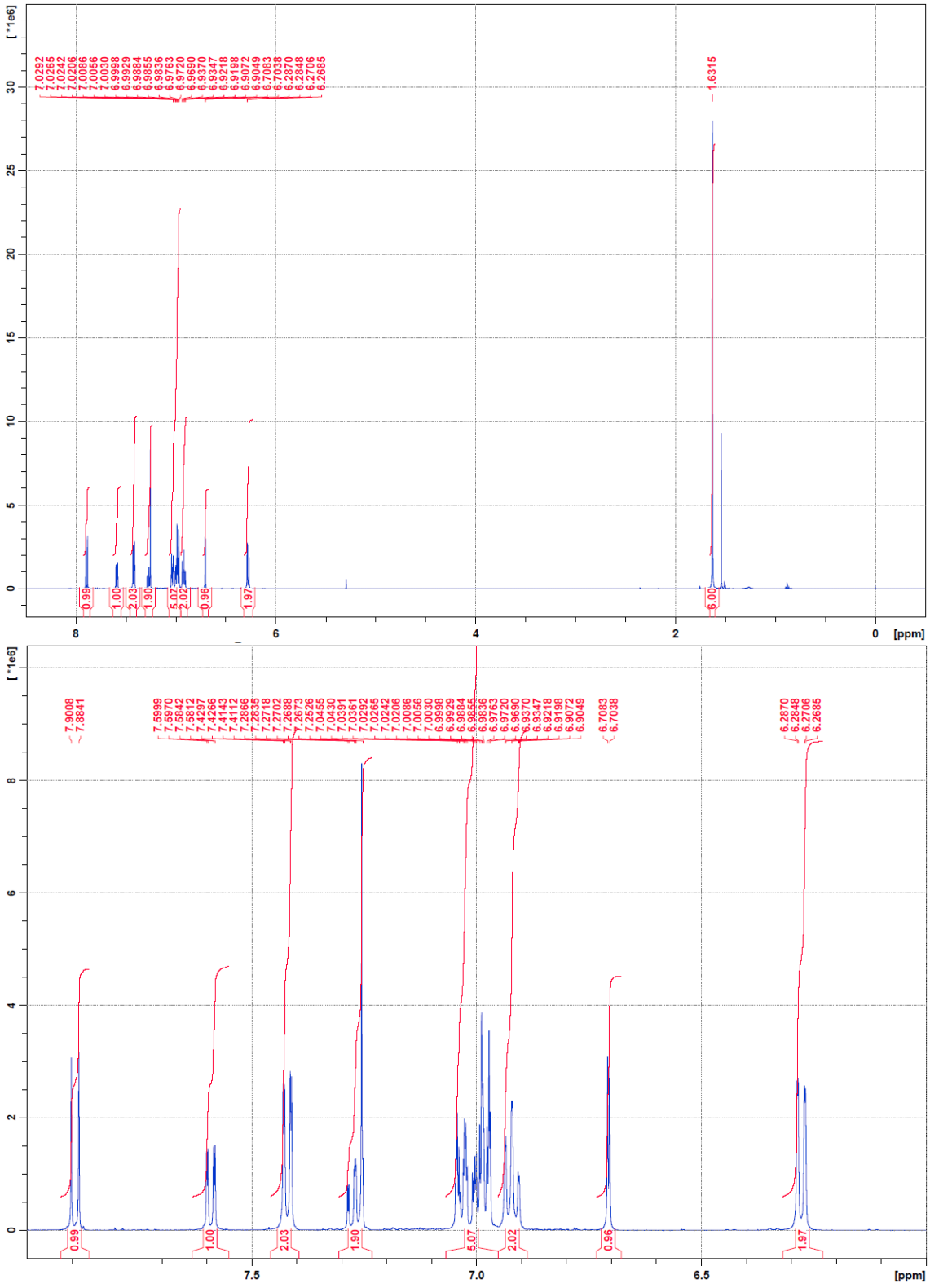
Compound 1a

^{13}C-NMR



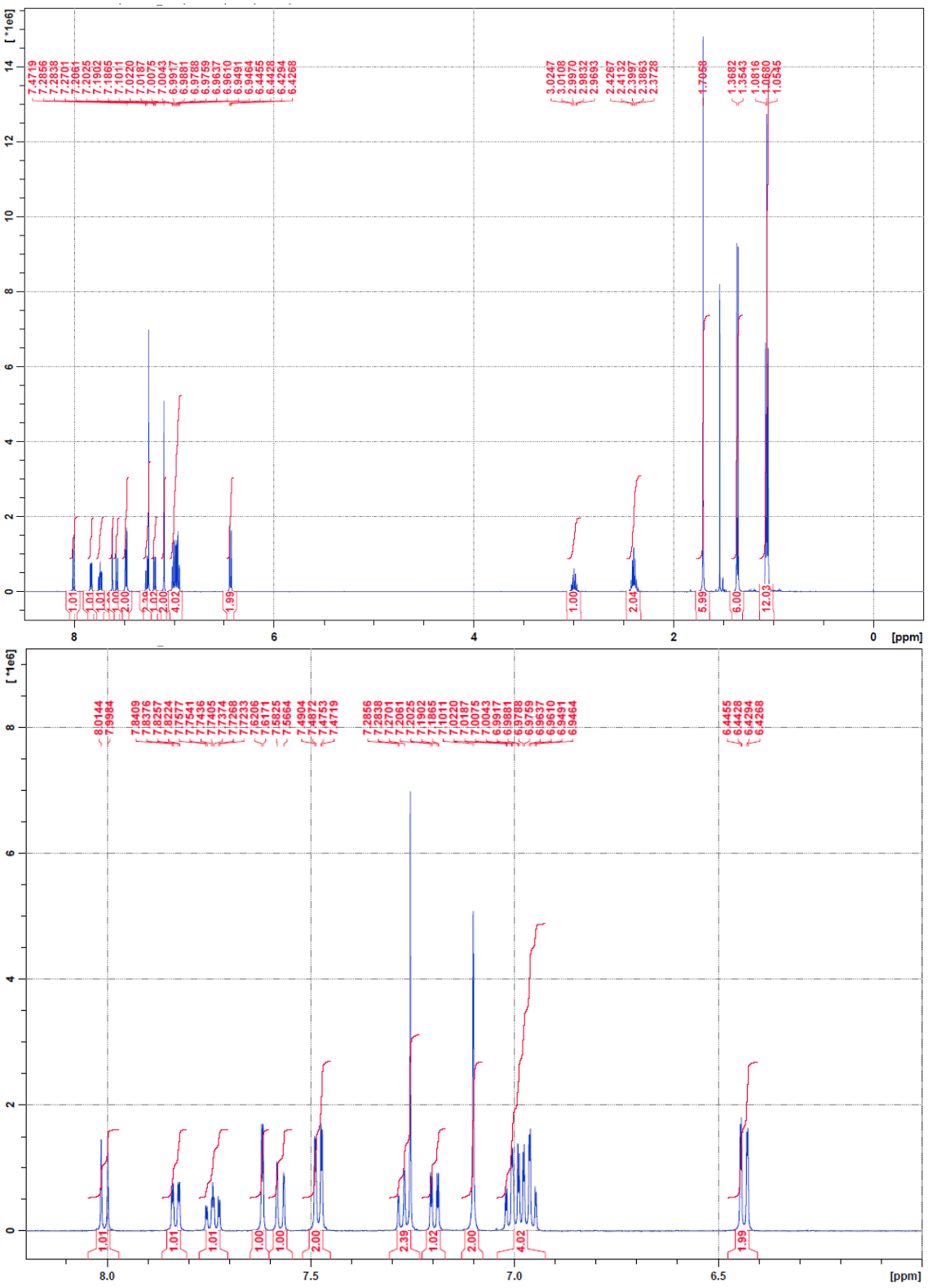
Compound 1b

^{1}H-NMR



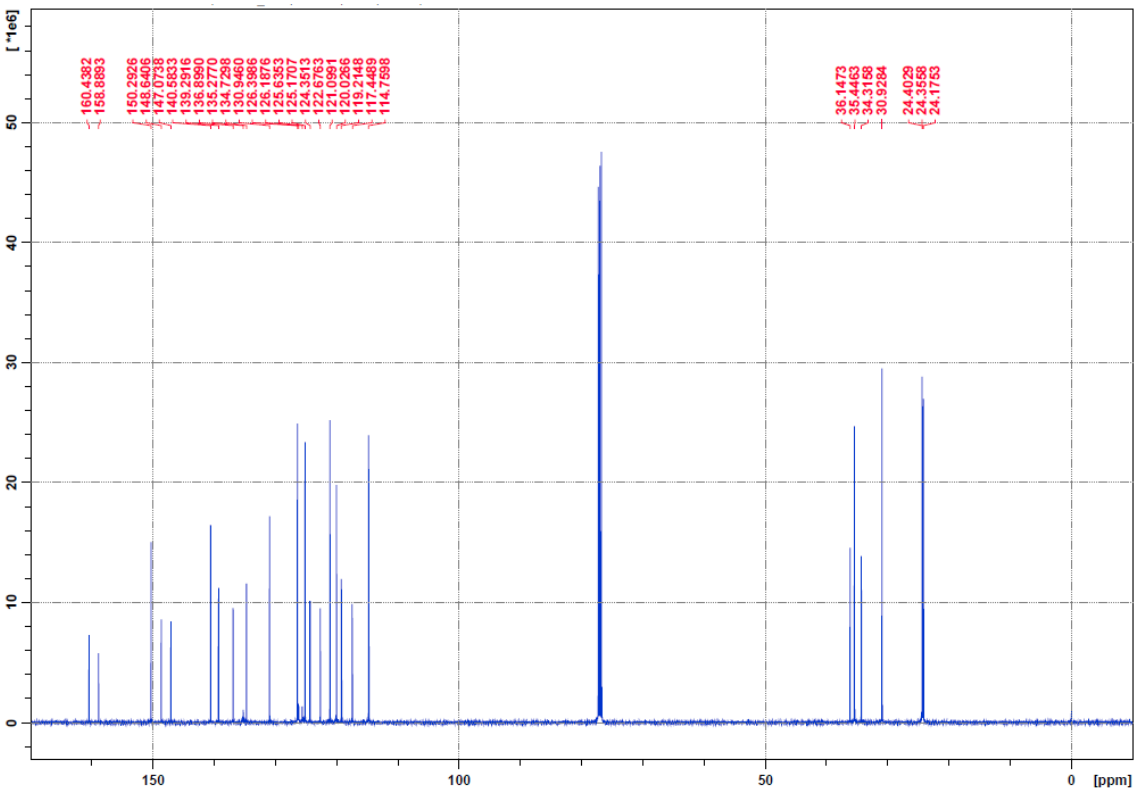
Compound 1

^{1}H-NMR



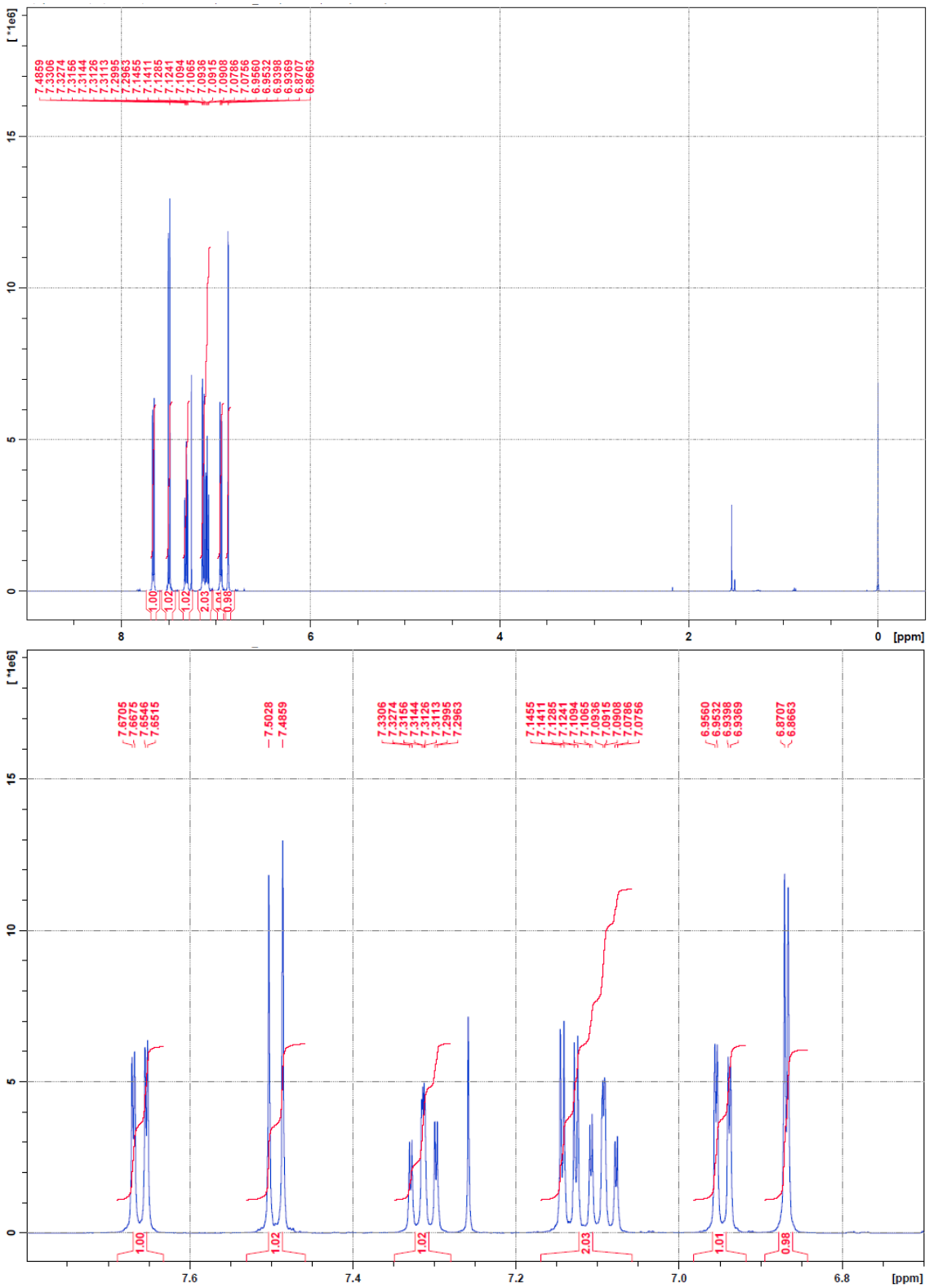
Compound 1

^{13}C-NMR



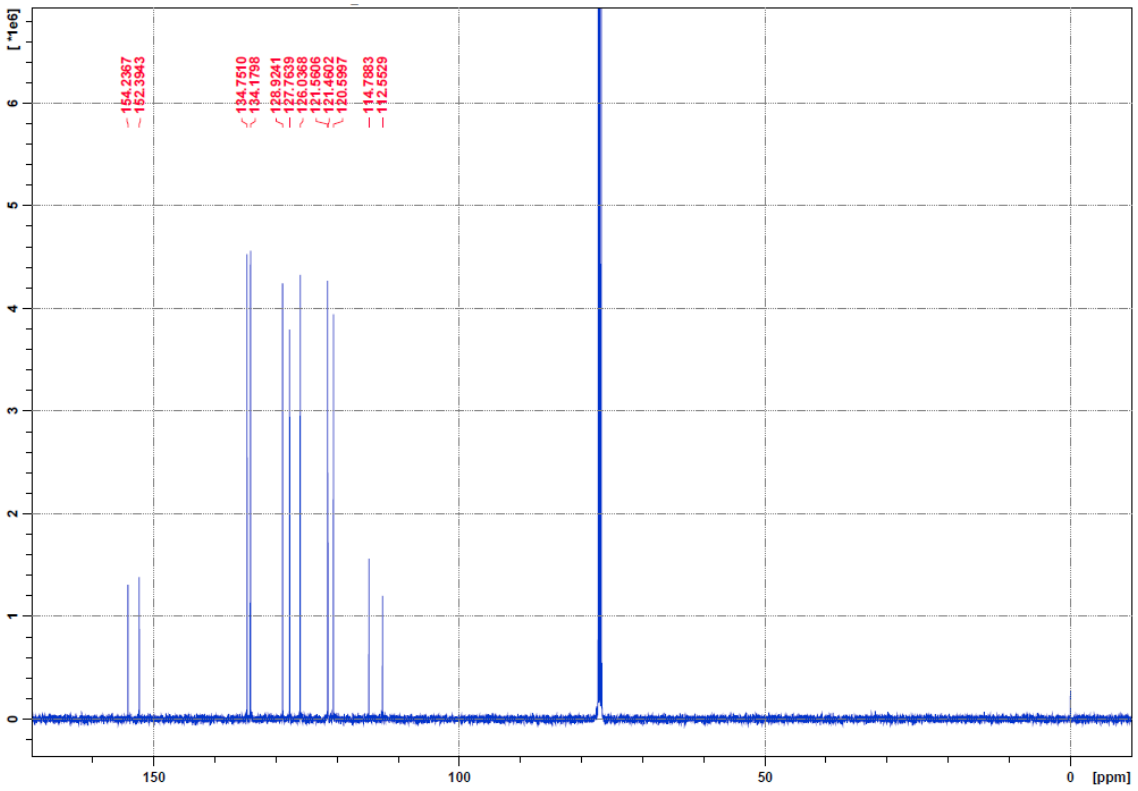
Compound 2a

^{1}H-NMR



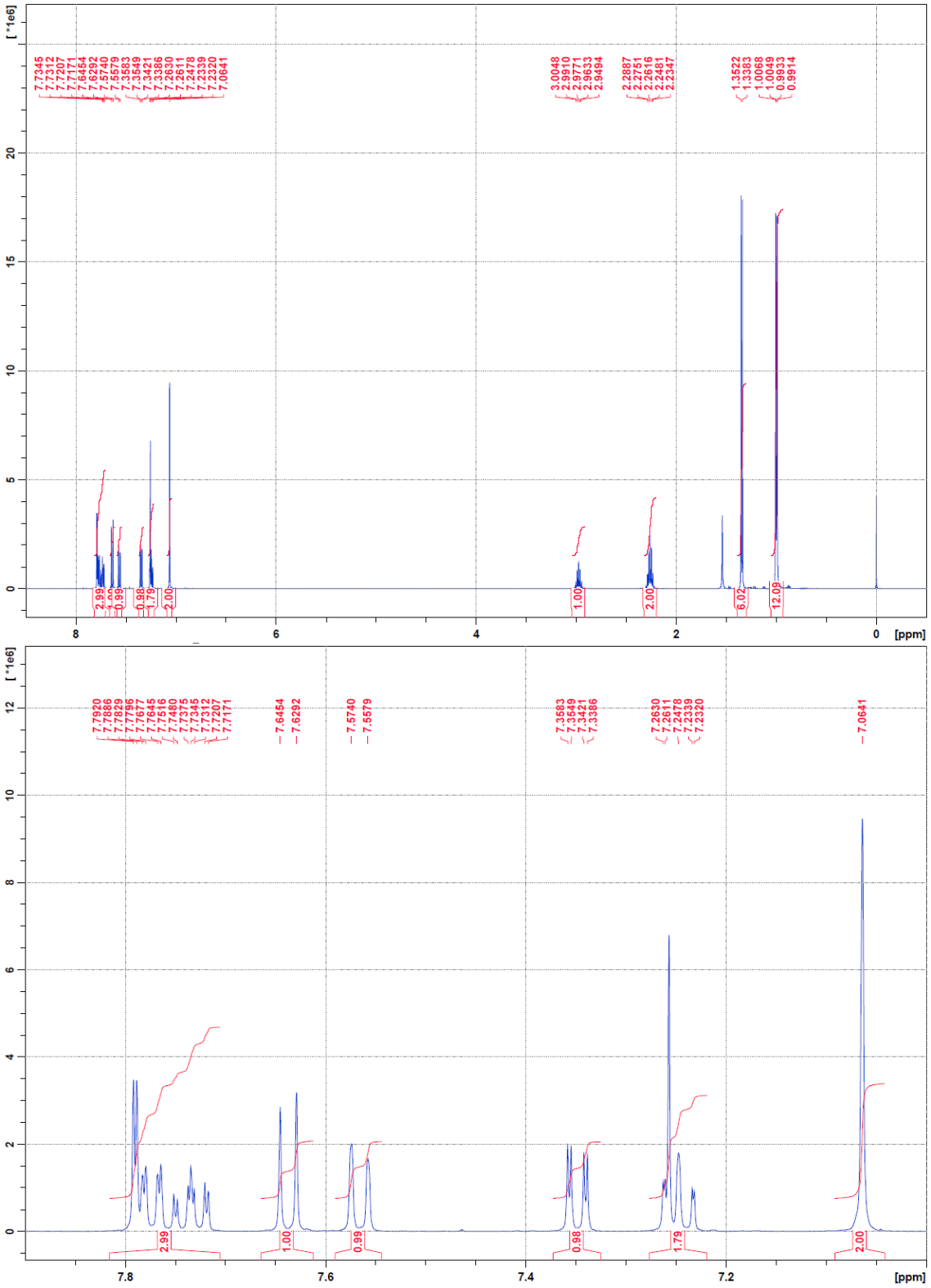
Compound 2a

^{13}C-NMR



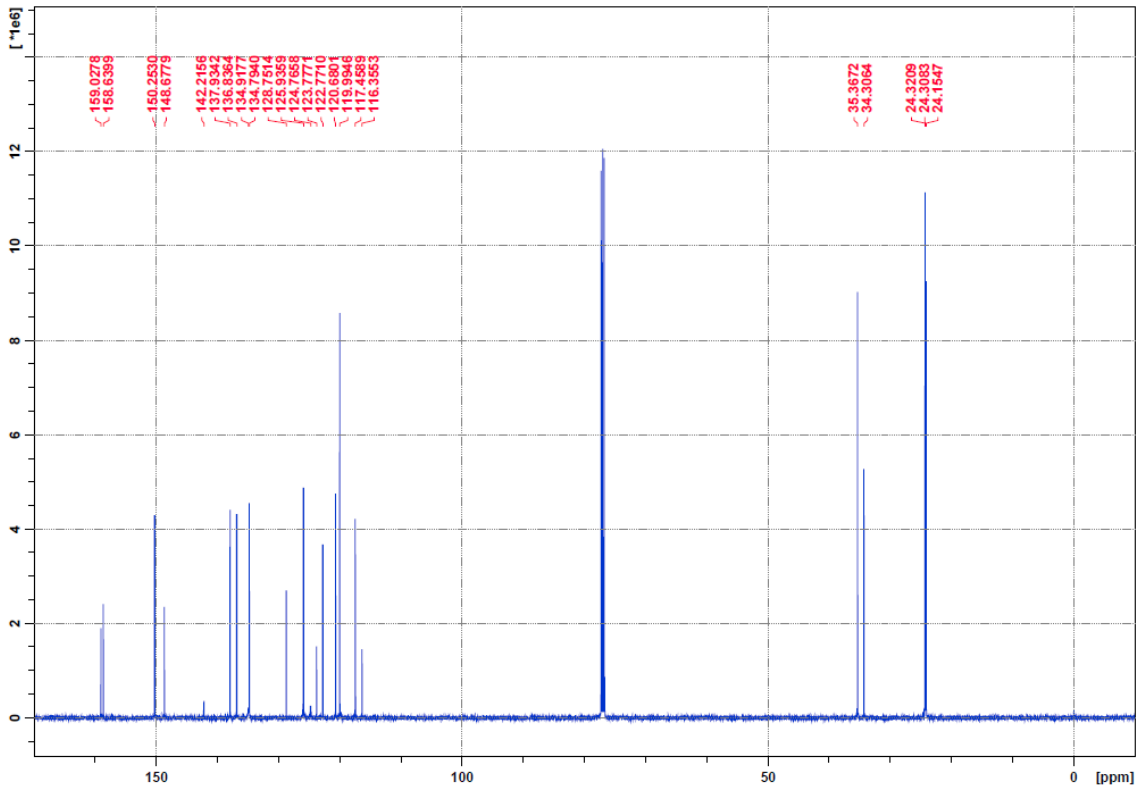
Compound 2b

^{1}H-NMR



Compound 2b

^{13}C-NMR



Compound 2c

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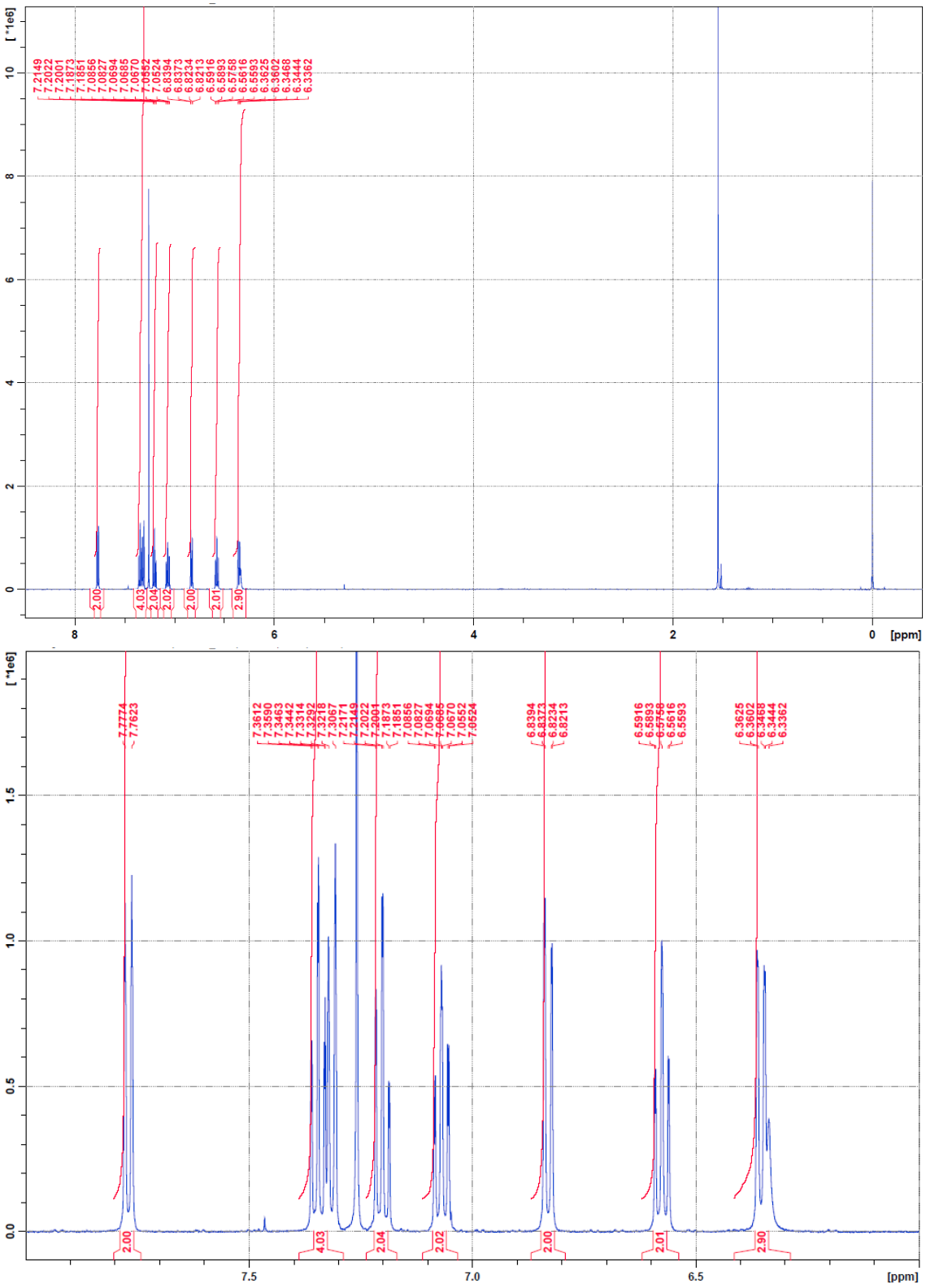
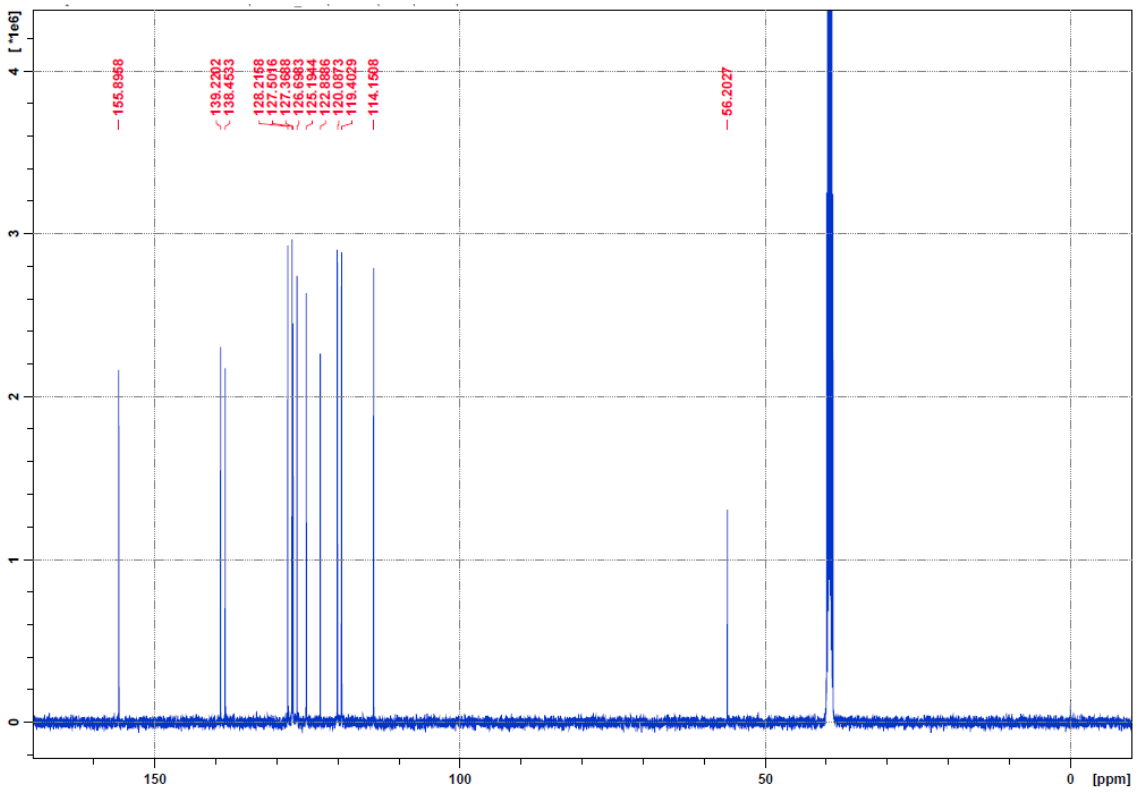


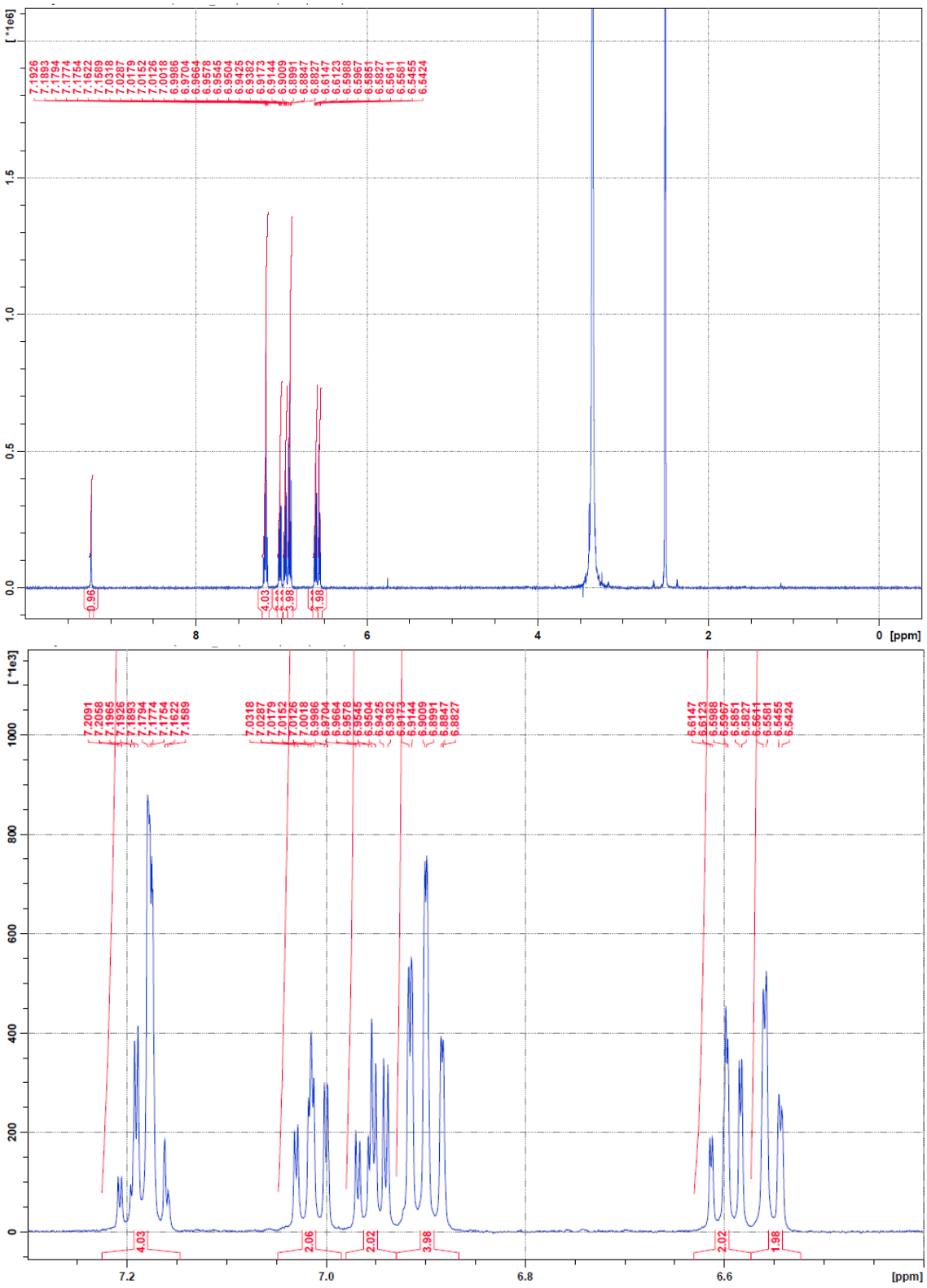
Compound 2c

^{13}C-NMR



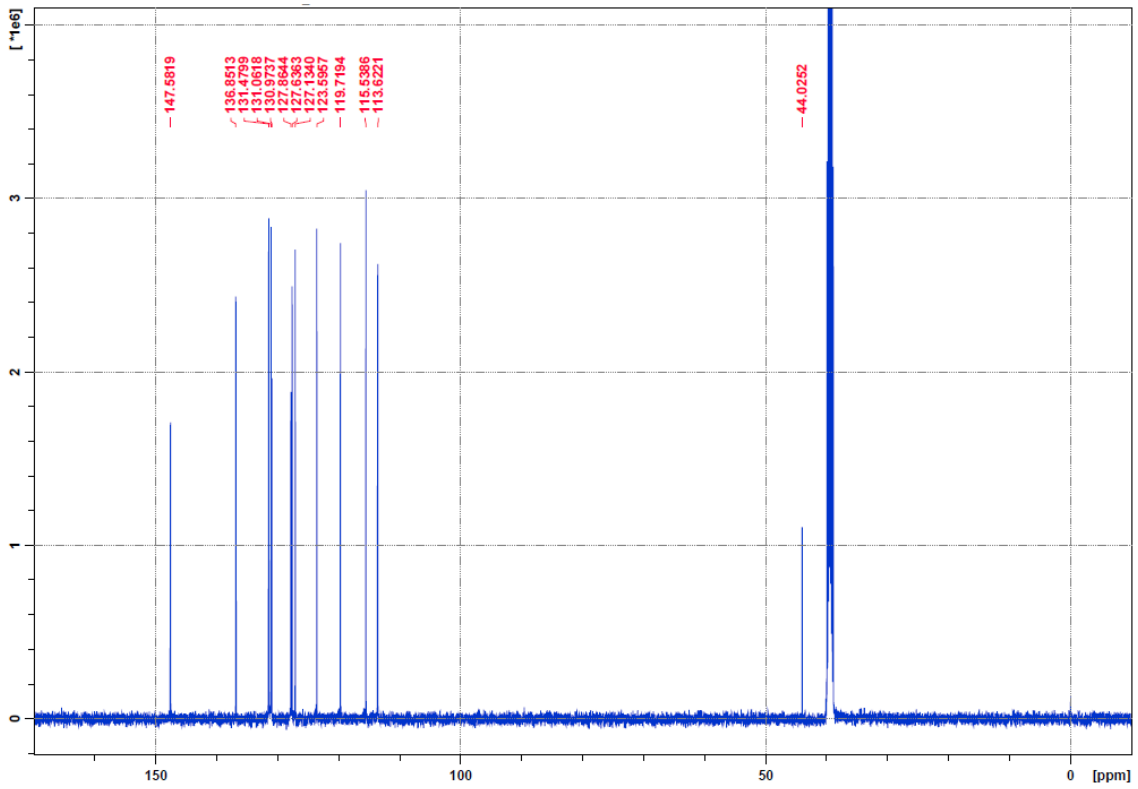
Compound 3a

^{1}H-NMR



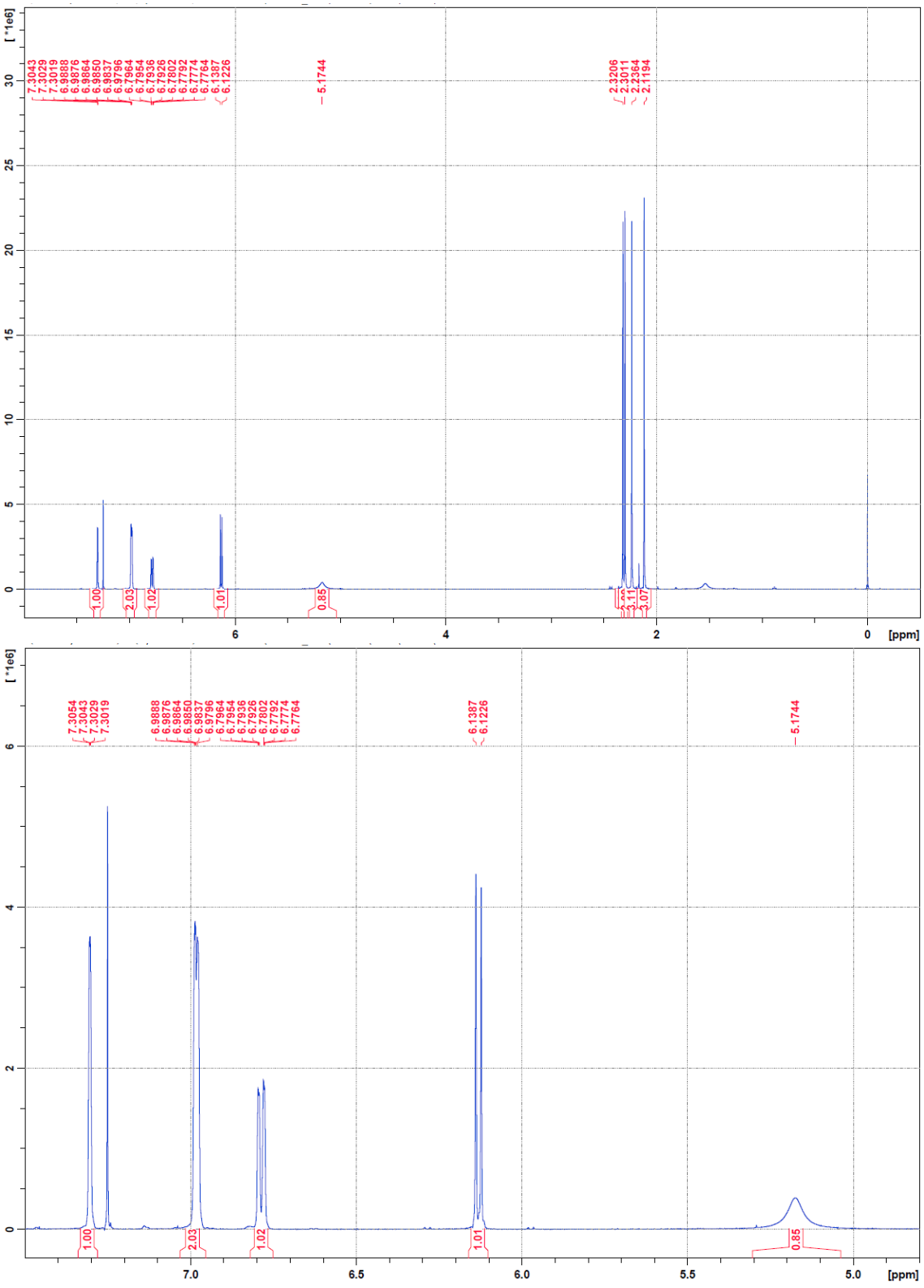
Compound 3a

^{13}C-NMR



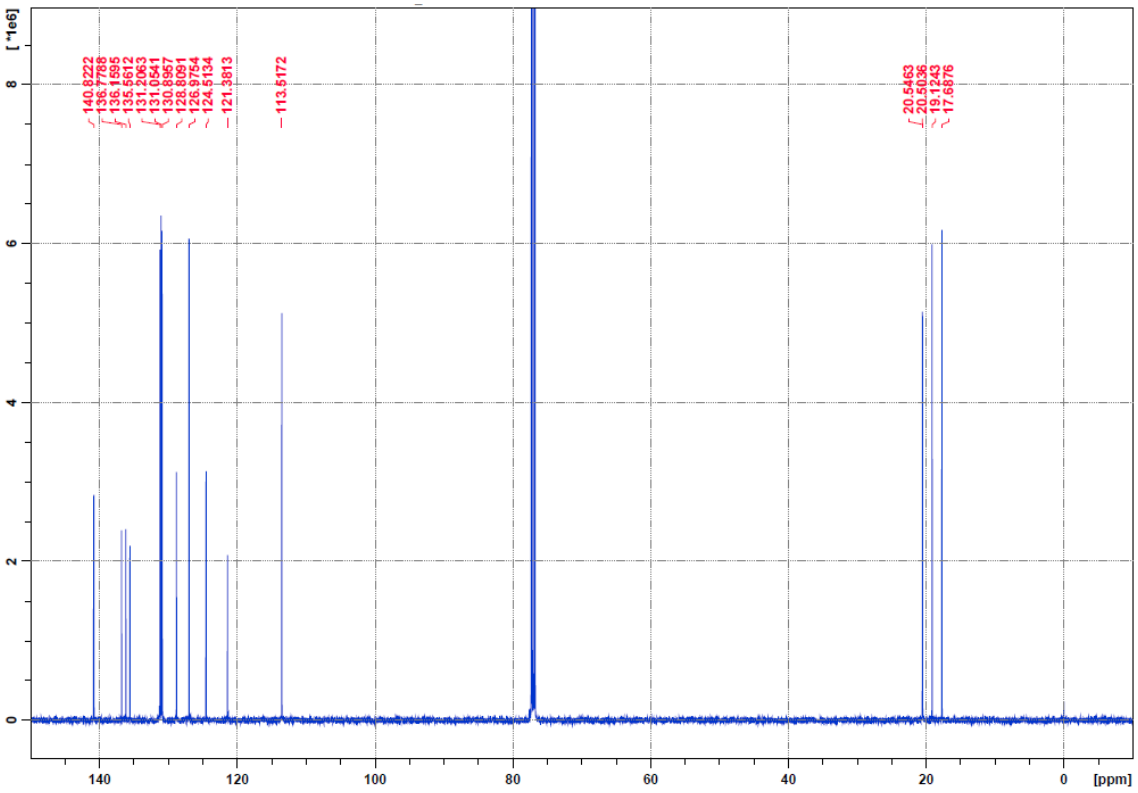
Compound 4a

^{1}H-NMR



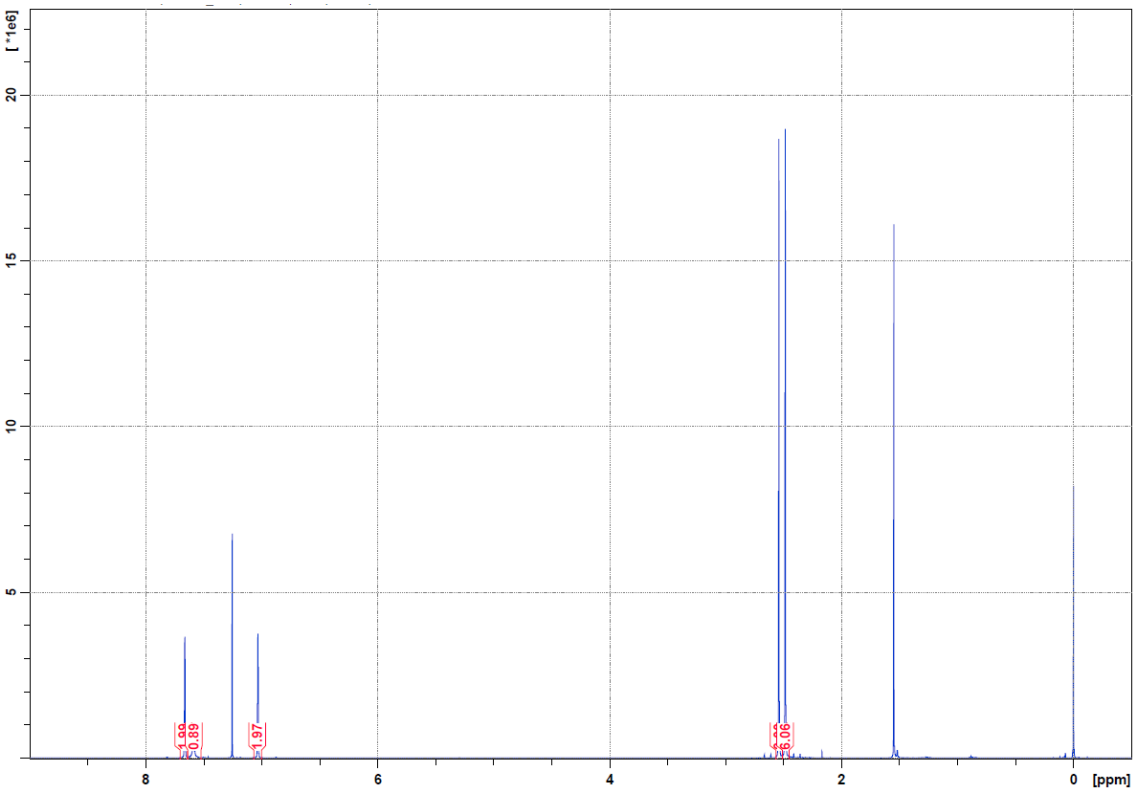
Compound 4a

^{13}C-NMR



Compound 4b

^{1}H-NMR



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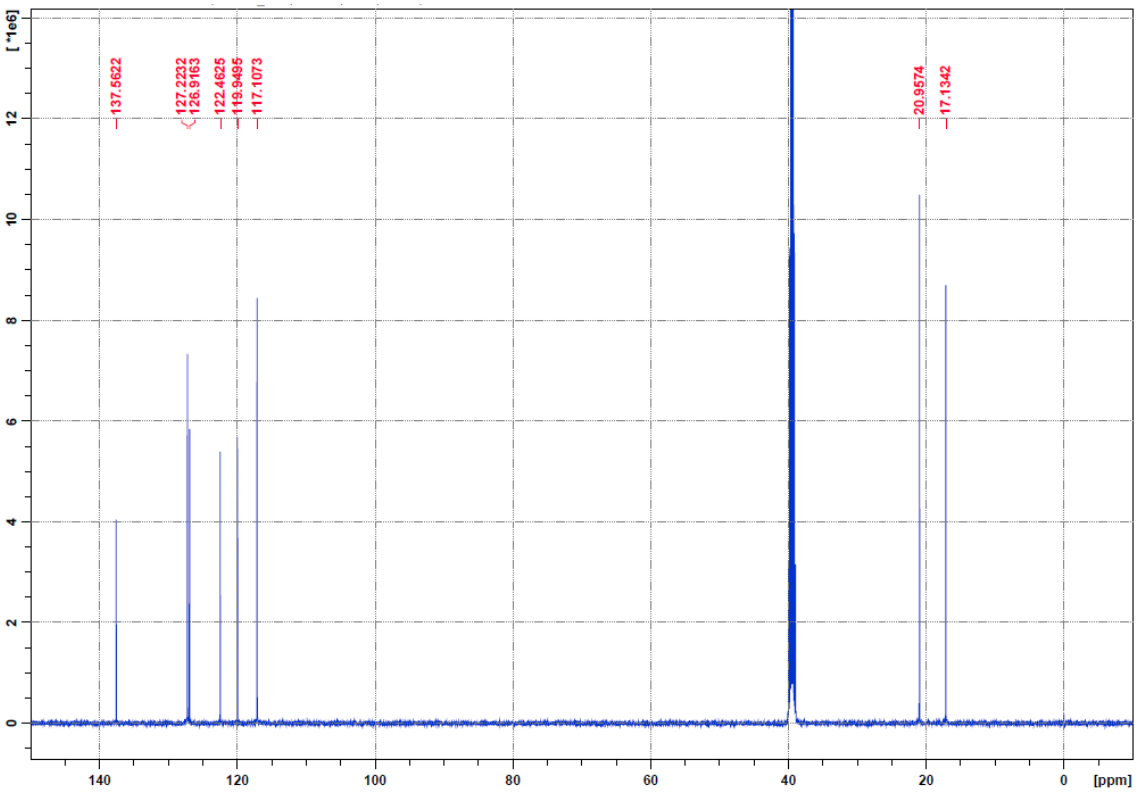
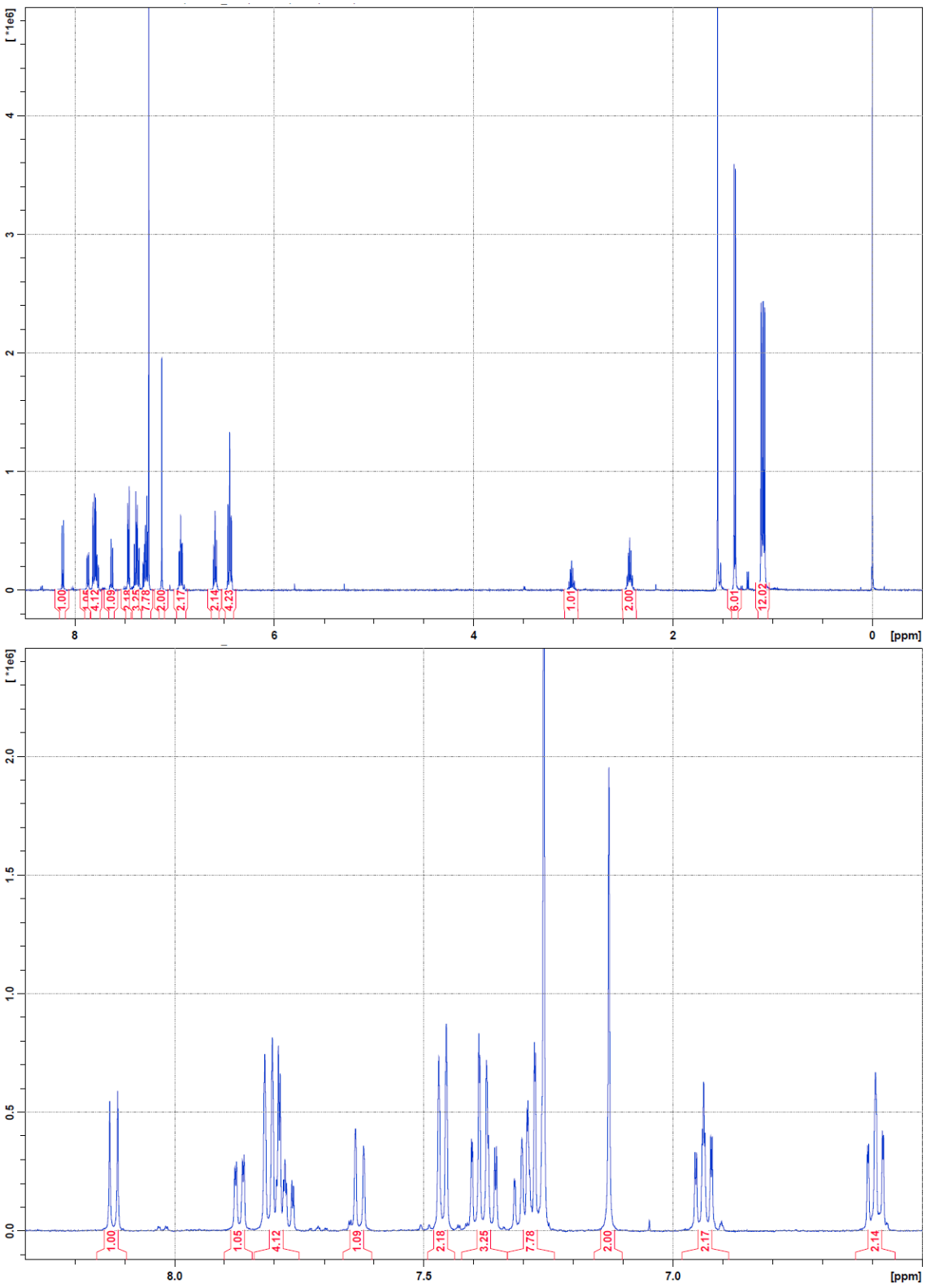


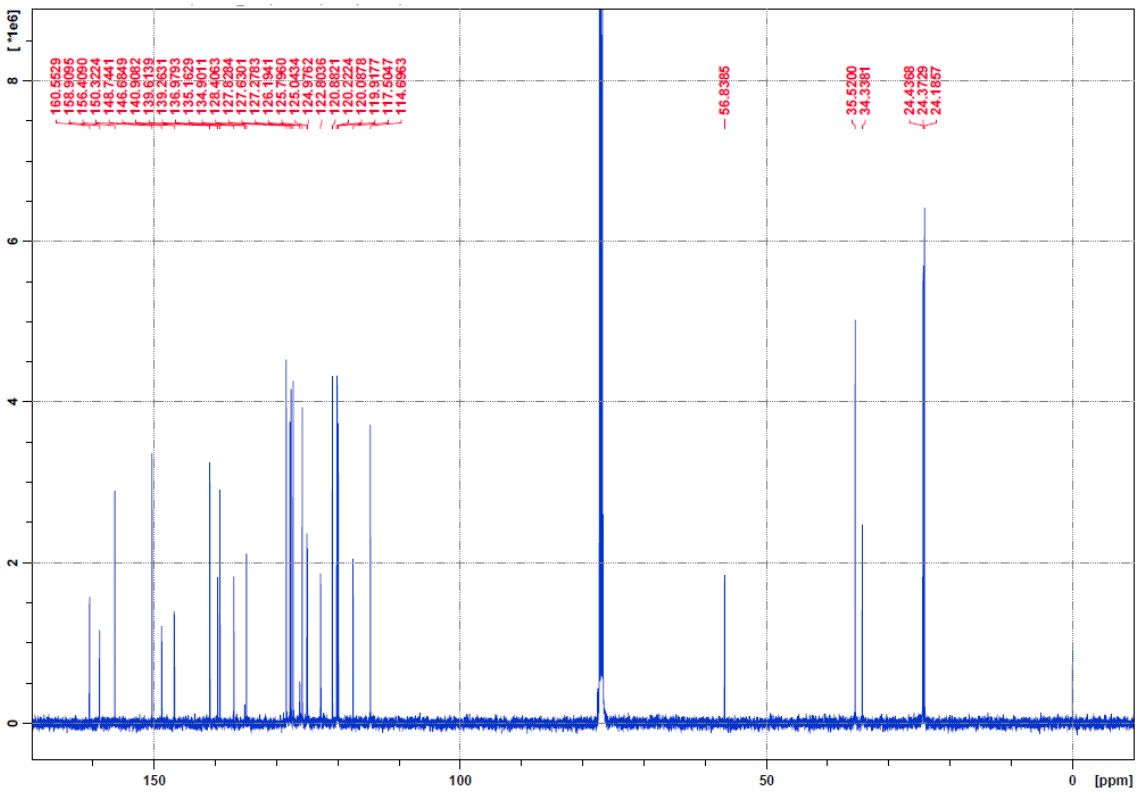
Compound 2

^{1}H-NMR



Compound 2

^{13}C-NMR



Compound 3

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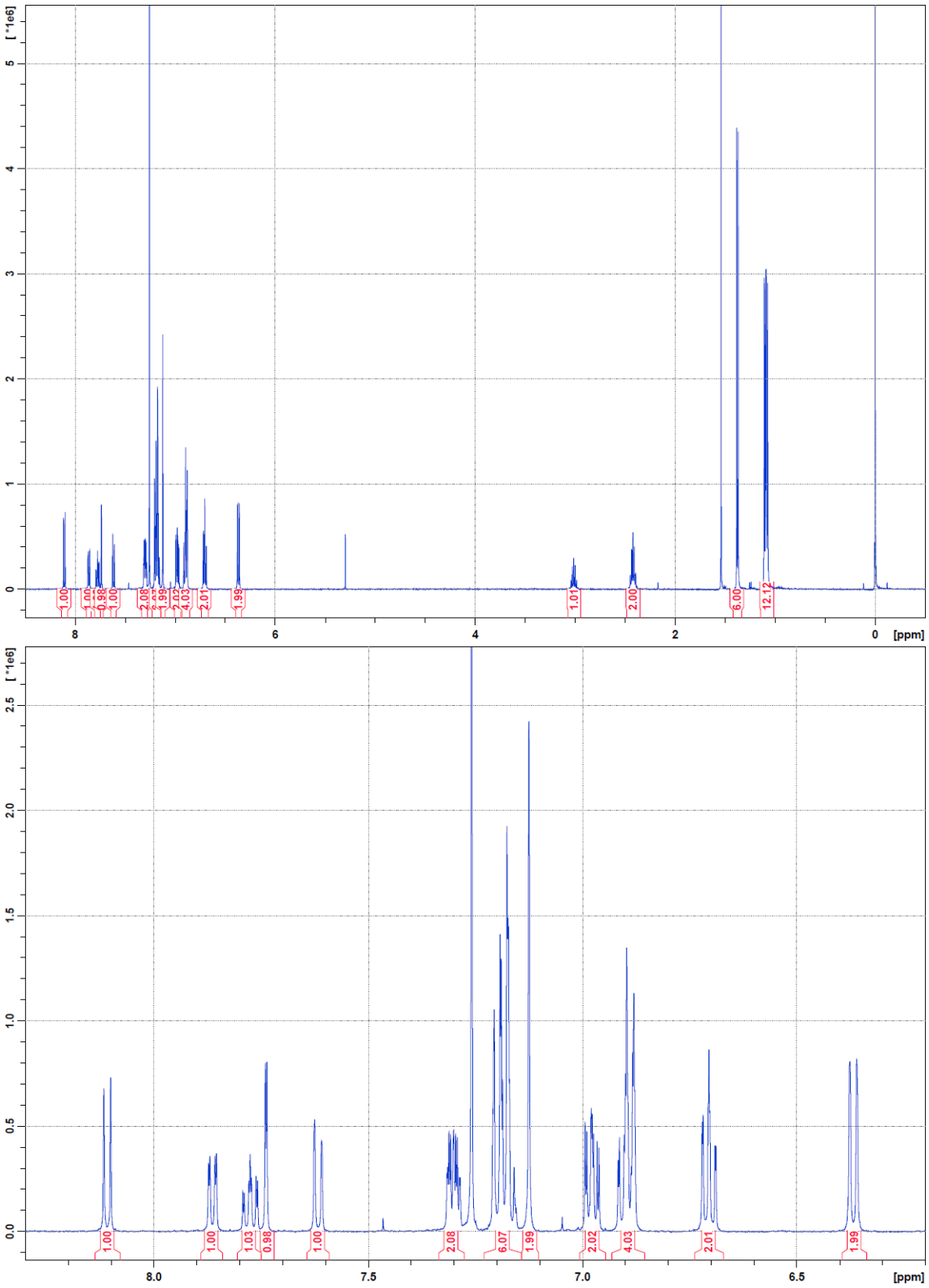
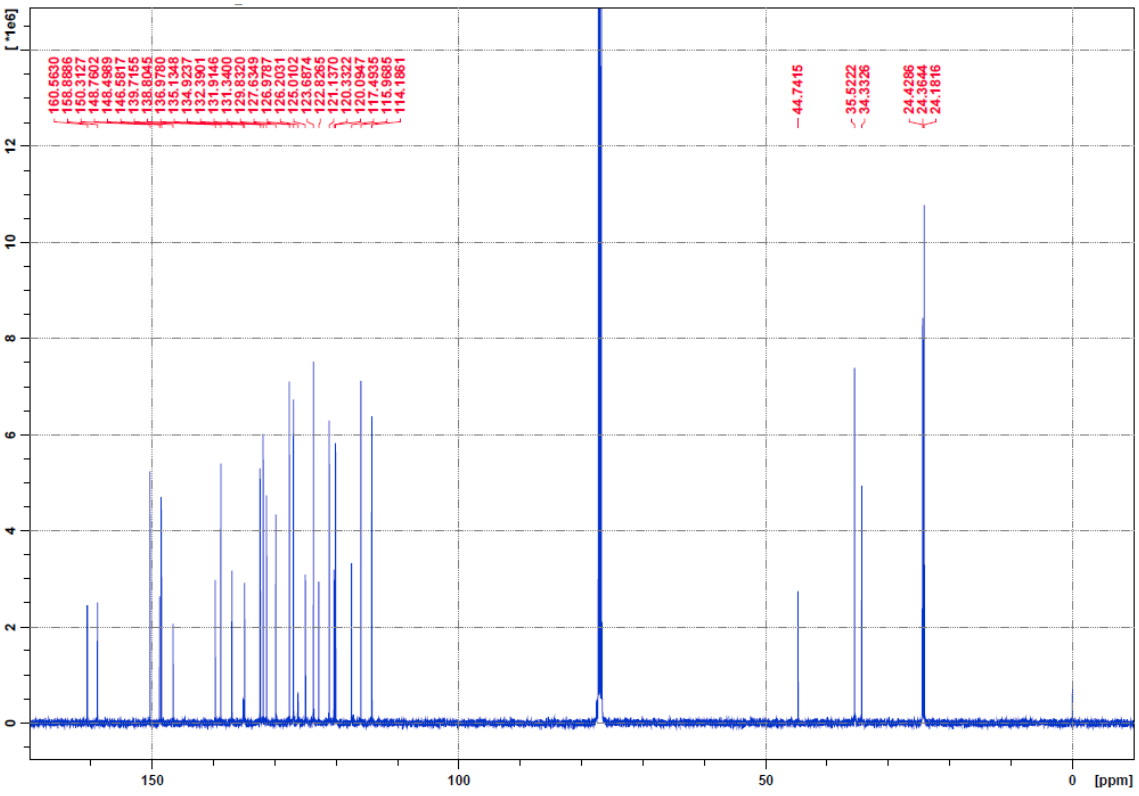


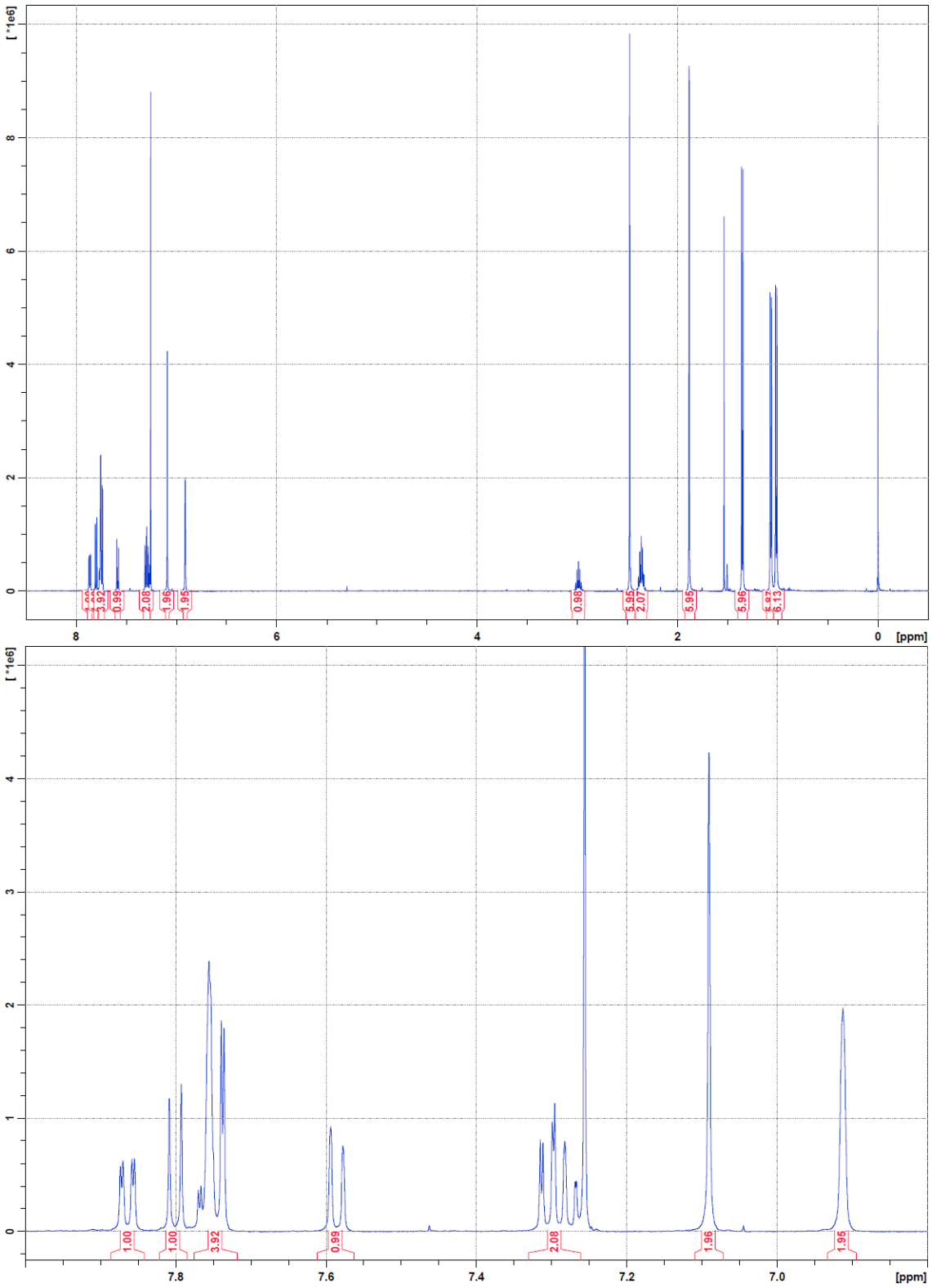
Compound 3

^{13}C-NMR



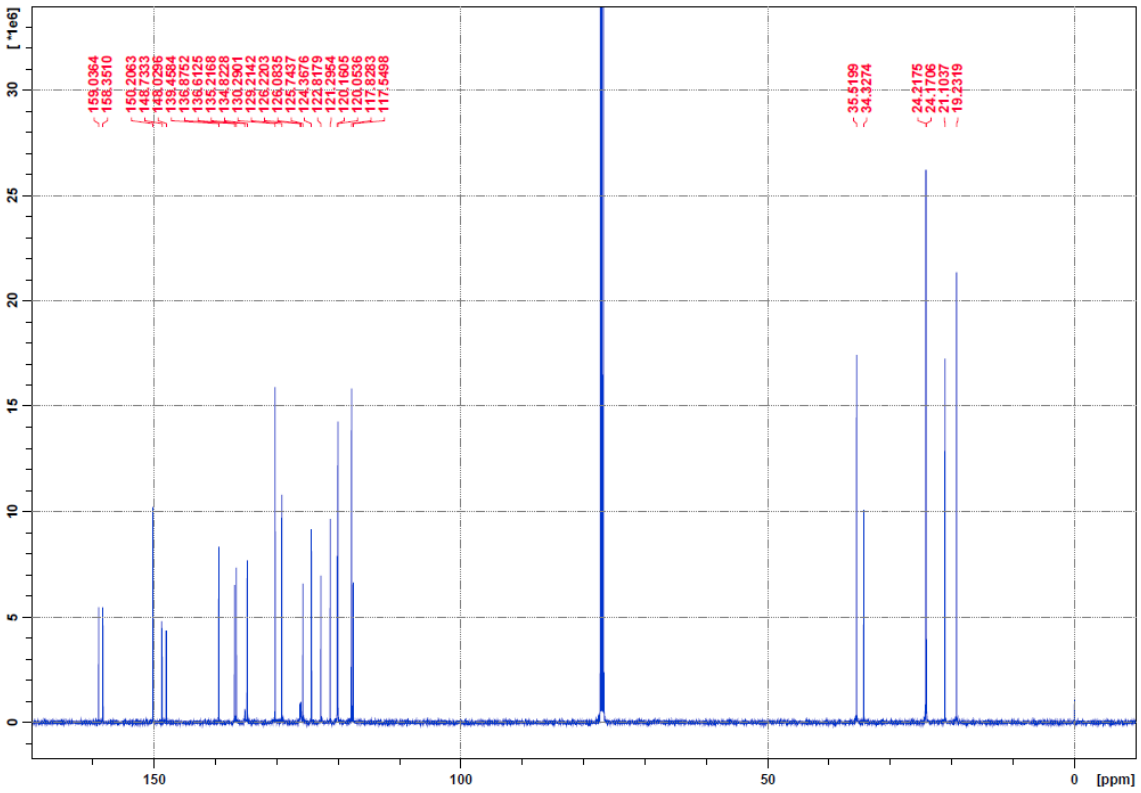
Compound 4

^{1}H-NMR



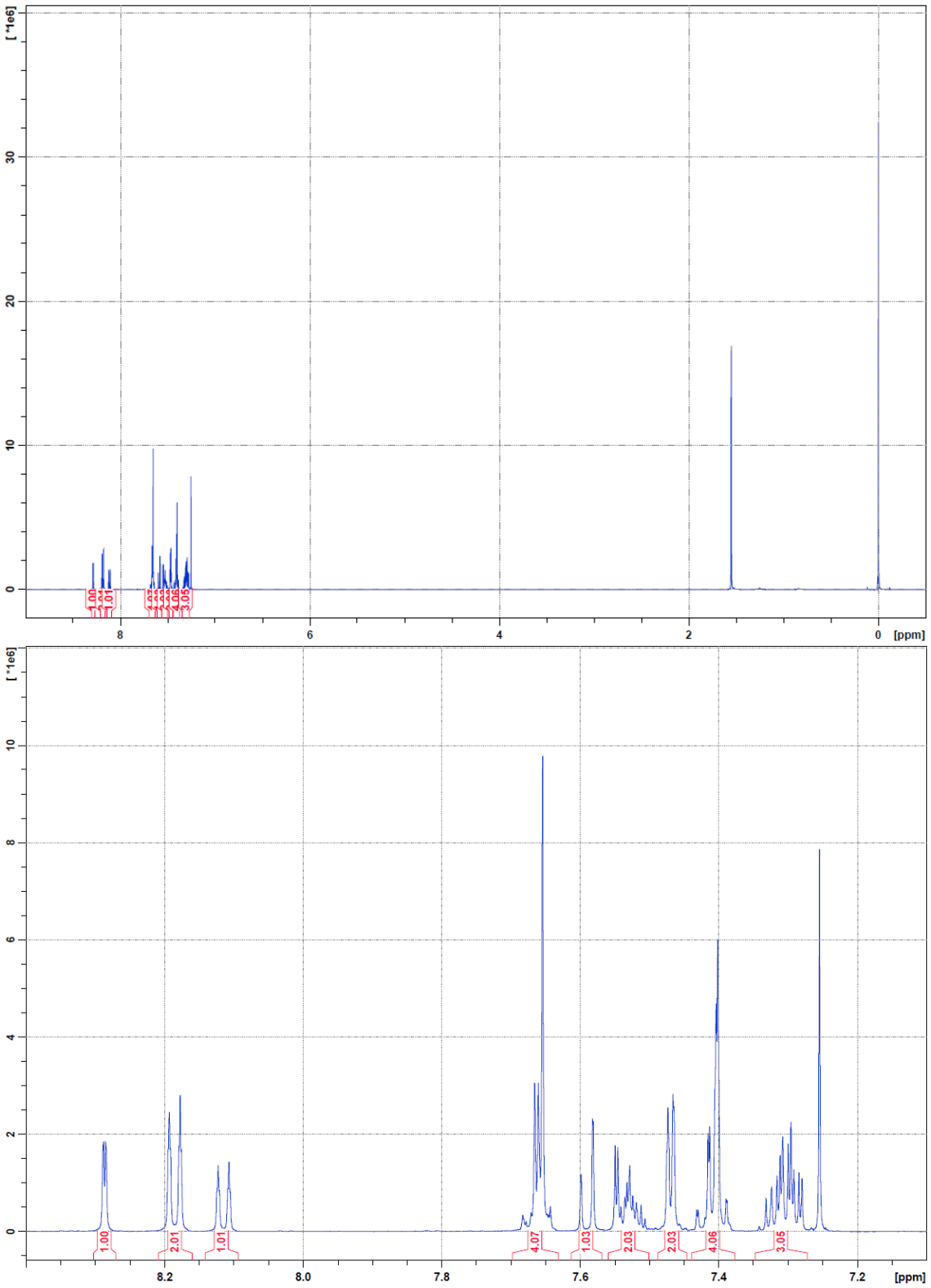
Compound 4

^{13}C-NMR



CCP

^{1}H-NMR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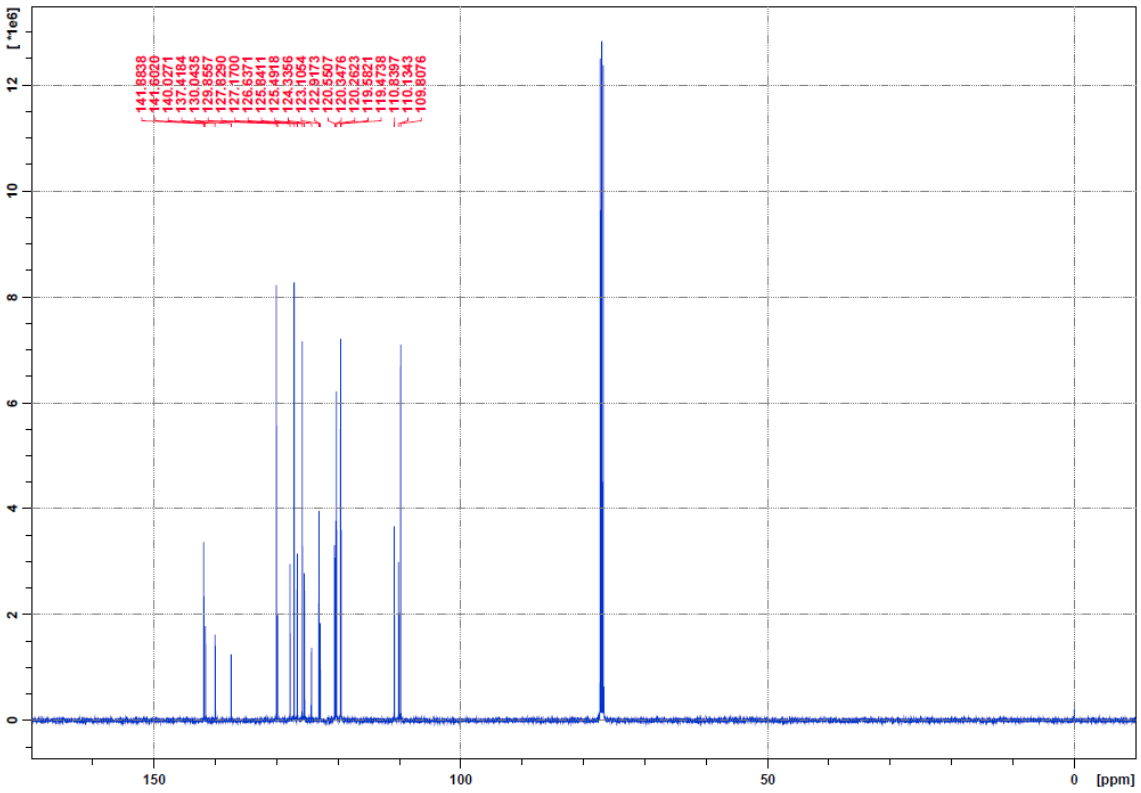
CCP

^{13}C-NMR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