Supporting Information

Direct Synthesis of Phenanthrenyl Triflates from 1-Biphenylyl-2-diazo-2-aryl Ketones and Triflic Anhydride

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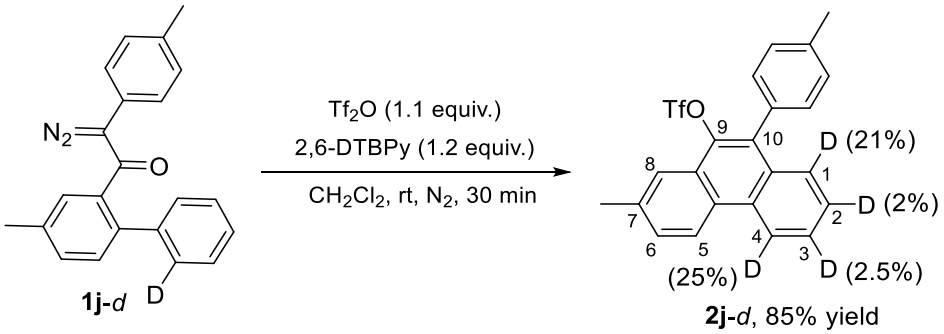
Table of Contents

1 General information

Unless otherwise noted, all reactions were carried out in oven-dried 25 mL Schlenk tubes under a nitrogen atmosphere. Solvents were purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR), a Varian DLG400 spectrometer (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR), a Bruker Avance III-500 spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR), and a Bruker Avance NEO 600 NMR Spectrometer (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR); All chemical shifts were reported in ppm (δ) relative to the internal standard TMS (0 ppm). The coupling constants J are given in Hz. The peak patterns are indicated below: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS EURO (Thermo Nicolet) FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on either an LTQ Orbitrap XL (Thermo Scientific) mass spectrometer or a G6224A (Agilent Technologies) mass spectrometer. TLC was carried out on SiO_2 (silica gel 60 F254, Bide Pharmatech Ltd.), and the spots were located with UV light. Column chromatography was carried out on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., LTD.) or basic aluminium oxide (200–300 mesh, Sinopharm Group Co. LTD). Melting points were determined using a micro-melting point apparatus and were uncorrected. Unless otherwise noted, starting materials are commercially available.

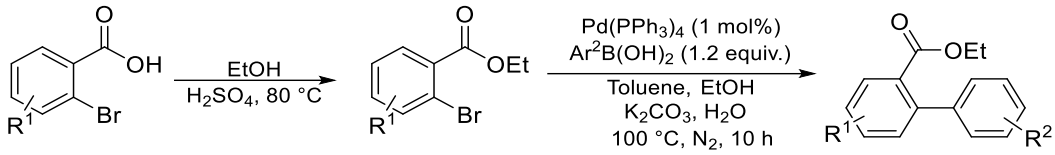
2 Details of Deuterium labeling experiments



Product **2j**-*d* (ca. 50% D) was obtained in 85% yield when the reaction of deuterated **1j**-*d* (>99% D) was conducted under the standard reaction conditions. The ^{2}H and ^{1}H NMR spectroscopy were used to determine the deuterium distribution in product **2j**-*d*, and the results showed that the deuterium incorporation at C1 and C4 are almost the same (21% and 25%, respectively). The result of hydrogen-deuterium (H-D) exchange indicates that the transformation occurs via an intramolecular hydrogen migration process.

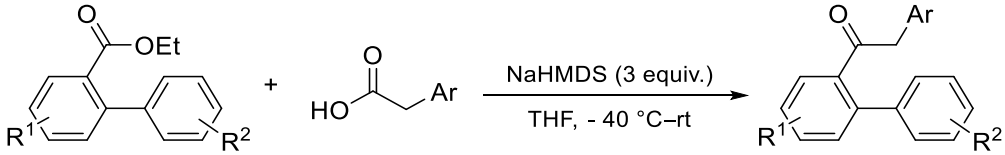
3 General procedure for preparation of diazoketones

3.1 General procedure for preparation of ethyl 1-([1,1'-biaryl]-2-yl)-2-arylethan-1-ones



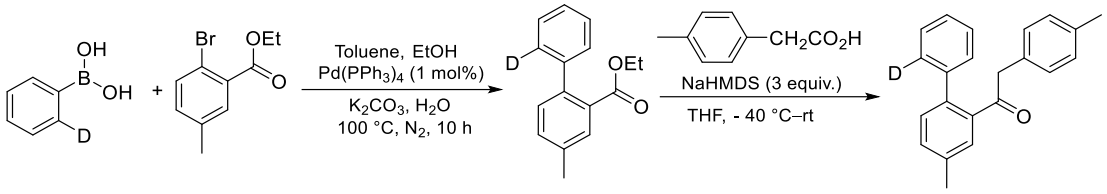
A 100 mL flask equipped with a magnetic stir bar was charged with 2-bromoarylic acid (10 mmol), ethanol (50 ml), and concentrated sulfuric acid (1 mL). The resulting reaction mixture was stirred and heated to 80 °C in an oil bath for 5 h. The reaction progress was monitored by TLC. After completion of the reaction, the resulting solution was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was used in the next step without further purification.

In the next step, a Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), ethyl 2-bromoaroate (10 mmol), arylboronic acid (12 mmol), and K_2CO_3 (1.38 g, 10 mmol), toluene (40 mL), ethanol (2 mL), and deionized water (2 mL) under a nitrogen atmosphere. The resulting reaction mixture was stirred and heated to 100 °C in an oil bath for 10 h. The reaction progress was monitored by TLC. After reaction completion, the aqueous phase was separated and extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain the corresponding ethyl 2-aryl-1-aroate.



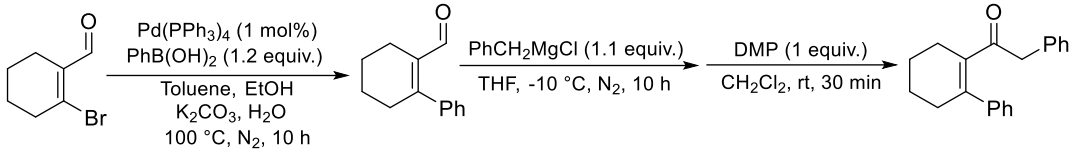
A Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with ethyl 2-aryl-1-aroate (8.0 mmol) and arylacetic acid (8.0 mmol), dry THF (20 mL) under a nitrogen atmosphere. After the mixture was cooled to -40 °C, NaHMDS (2.5 M in THF, 10 mL) was added dropwise, and the temperature was slowly warmed to room temperature over 10 h. The mixture was quenched with saturated aqueous NH_4Cl solution, and the residue was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain the corresponding 1-([1,1'-biaryl]-2-yl)-2-arylethan-1-one.

3.2 Procedure for preparation of 1-(4-methyl-[1,1'-biphenyl]-2-yl-2'-d)-2-(p-tolyl)ethan-1-one



1-(4-methyl-[1,1'-biphenyl]-2-yl-2'-d)-2-(p-tolyl)ethan-1-one was synthesized by the same method for preparation of 1-([1,1'-biaryl]-2-yl)-2-arylethan-1-ones using 2-deuteriophenylboronic acid as starting material.[1]

3.3 Procedure for preparation of 2-phenyl-1-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one



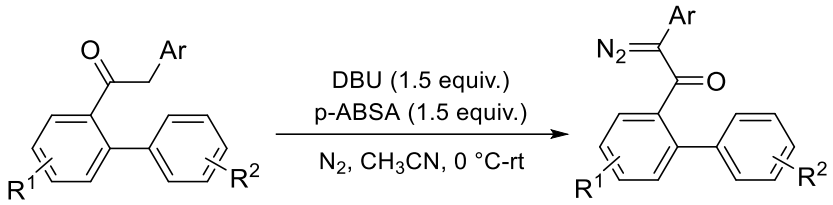
A Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (116 mg, 0.2 mmol), 2-bromocyclohex-1-ene-1-carbaldehyde[2] (20 mmol), phenylboronic acid (12 mmol), and K_2CO_3 (1.38 g, 10 mmol), toluene (40 mL), ethanol (2 mL), and deionized water (2 mL) under a nitrogen atmosphere. The resulting reaction mixture was stirred and heated to 100 °C in an oil bath for 10 h. The reaction progress was monitored by TLC. After reaction completion, the aqueous phase was separated and extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain 3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde.

A Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with 3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (5.0 mmol) and dry THF (10 mL) under a nitrogen atmosphere. After the mixture was cooled to -10 °C, $PhCH_2MgCl$ (1 M in THF, 5.5 mL) was added dropwise, and the temperature was slowly warmed to room temperature over 10 h. The mixture was quenched with saturated aqueous NH_4Cl solution, and the residue was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was used in the next step without further purification.

In the next step, a 100 mL flask equipped with a magnetic stir bar was charged with the residue of previous step and CH_2Cl_2 (20.0 mL). Dess-Martin periodinane (5 mmol, 2.2 g) was added in small portions, and the mixture was stirred at room temperature for 30 min. The reaction progress was monitored by TLC. After reaction completion, the mixture was quenched with saturated aqueous $Na_2S_2O_3$, and the residue was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified

by silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain 2-phenyl-1-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one.

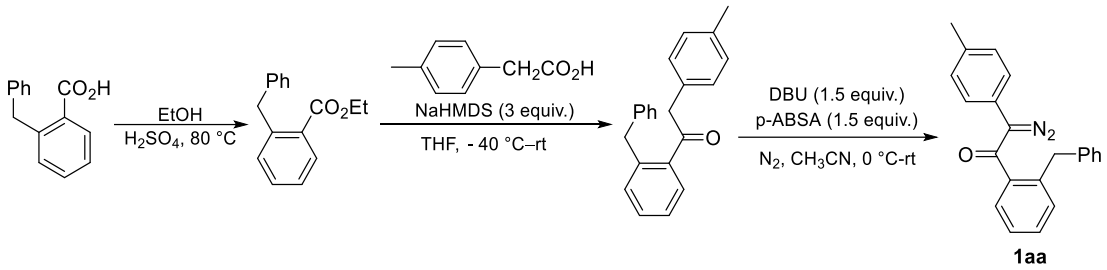
3.4 Procedure for preparation of diazoketones 1a–1z and 1j-*d*



In a glove box, an oven-dried 50 mL flask equipped with a Teflon-coated magnetic stir bar was charged with 1-([1,1'-biaryl]-2-yl)-2-arylethan-1-one (4.0 mmol), 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 1.44 g, 6.0 mmol), and acetonitrile (10.0 mL). Then, the flask was sealed with a rubber septum. The flask was taken out of the glove box and cooled to 0 °C with an ice bath. Subsequently, DBU (0.92 g, 6.0 mmol in 3 mL acetonitrile) was added dropwise under N_2 atmosphere, and the mixture was slowly warmed to room temperature overnight. The solvent was removed under reduced pressure, maintaining the temperature below 25 °C. The resulting residue was purified by column chromatography (eluent: hexane/CH_2Cl_2 = 1:1) on basic aluminium oxide to afford the corresponding diazoketone.

It is worth noting that diazoketone **1y** was synthesized via this procedure using 2-phenyl-1-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one as substrate.

3.5 Procedure for preparation of diazoketone 1aa

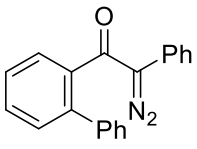


1aa

1-(2-benzylphenyl)-2-(*p*-tolyl)ethan-1-one was synthesized by the same method for preparation of 1-([1,1'-biaryl]-2-yl)-2-arylethan-1-one using 2-benzylbenzoic acid as starting material. Diazoketone **1aa** was synthesized by the same method for preparation of diazoketone **1a**.

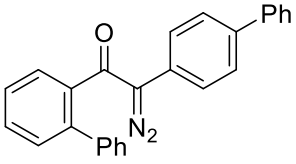
3.6 Characterization data of diazoketones

1-([1,1'-biphenyl]-2-yl)-2-diazo-2-phenylethan-1-one (1a)[3]



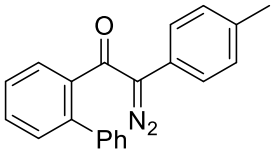
0.84 g, 70% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 1H), 7.56–7.41 (m, 3H), 7.41–6.76 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 139.9, 139.2, 137.8, 130.8, 129.8, 128.8, 128.3, 128.2, 127.93, 127.89, 126.8, 125.60, 125.55, 75.2.

1-([1,1'-biphenyl]-2-yl)-2-([1,1'-biphenyl]-4-yl)-2-diazoethan-1-one (1b)



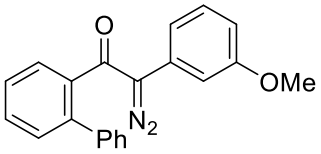
1.30 g, 87% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.32 (m, 8H), 7.34–7.10 (m, 10H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.6, 140.3, 139.9, 139.6, 139.2, 137.8, 130.9, 129.9, 128.9, 128.8, 128.4, 128.3, 128.0, 127.6, 127.5, 127.0, 125.9, 124.4, 75.2; IR (KBr): ν_{max} 3058, 2924, 2074, 1579, 1487, 1345, 1234, 1179, 1112, 1075, 835, 764, 743, 671 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{26}H_{19}O^+$ 347.1430, found 347.1427.

1-([1,1'-biphenyl]-2-yl)-2-diazo-2-(p-tolyl)ethan-1-one (1c)



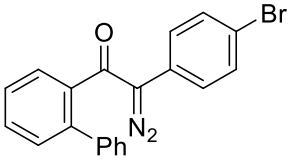
0.66 g, 53% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.5, 1.6 Hz, 1H), 7.62–7.32 (m, 9H), 7.23–7.01 (m, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.7, 139.9, 139.3, 138.0, 136.8, 130.8, 129.8, 129.6, 128.8, 128.6, 128.4, 128.3, 128.0, 125.7, 122.3, 75.1, 21.2; IR (neat): ν_{max} 3022, 2925, 2849, 2076, 1844, 1718, 1597, 1511, 1489, 1274, 1062, 859, 812, 699 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{21}H_{17}O^+$ 285.1274, found 285.1273.

1-([1,1'-biphenyl]-2-yl)-2-diazo-2-(3-methoxyphenyl)ethan-1-one (1d)



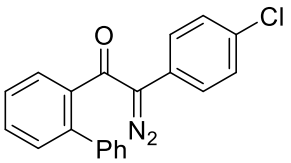
0.97 g, 74% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 1H), 7.53–7.23 (m, 8H), 7.19–6.14 (m, 4H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.5, 159.9, 139.9, 139.2, 137.9, 130.8, 129.8, 129.7, 128.8, 128.3, 128.2, 127.93, 127.89, 126.9, 117.7, 112.7, 111.1, 75.4, 55.2; IR (neat): ν_{max} 3061, 2840, 2077, 1577, 1492, 1352, 1231, 1180, 1036, 806, 776, 744, 699, 688 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - N_2)^+$ $C_{21}H_{16}O_2Na^+$ 323.1043, found 323.1039.

1-([1,1'-biphenyl]-2-yl)-2-(4-bromophenyl)-2-diazoethan-1-one (1e)



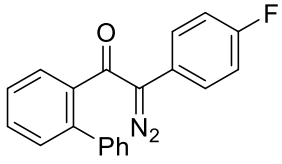
1.21 g, 80% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.39 (m, 2H), 7.37–7.10 (m, 9H), 7.11–6.03 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.3, 139.9, 139.1, 137.5, 131.9, 131.0, 129.8, 128.7, 128.4, 128.2, 128.0, 126.9, 124.7, 120.5, 74.8; IR (neat): ν_{max} 3059, 2924, 2077, 1622, 1489, 1343, 1305, 1274, 1178, 1078, 852, 744, 700 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{20}H_{14}{}^{79}BrO^+$ 349.0223, found 349.0218.

1-([1,1'-biphenyl]-2-yl)-2-(4-chlorophenyl)-2-diazoethan-1-one (1f)



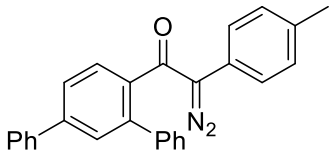
1.05 g, 79% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 1H), 7.40–7.37 (m, 1H), 7.36–6.74 (m, 11H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.3, 139.9, 139.1, 137.5, 132.5, 130.9, 129.8, 128.9, 128.7, 128.4, 128.2, 128.0, 126.6, 124.2, 74.7; IR (neat): ν_{max} 3059, 2077, 1898, 1578, 1492, 1342, 1275, 1233, 1179, 853, 824, 699, 662, 494 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - N_2)^+$ $C_{20}H_{14}{}^{35}ClONa^+$ 341.0704, found 341.0702.

1-([1,1'-biphenyl]-2-yl)-2-diazo-2-(4-fluorophenyl)ethan-1-one (1g)



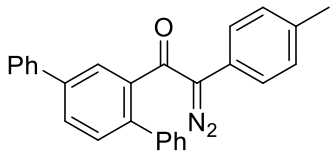
1.05 g, 83% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H), 7.39–7.00 (m, 9H), 6.79 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.5, 161.6 (d, J = 247.5 Hz), 139.9, 139.2, 137.6, 130.9, 129.8, 128.8, 128.4, 128.2, 128.0, 127.6, 121.4, 115.8 (d, J = 22.0 Hz), 74.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.29; IR (neat): ν_{max} 3061, 2928, 2077, 1508, 1474, 1285, 1262, 1233, 1180, 1162, 1100, 1073, 698, 670 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{20}H_{14}FO^+$ 289.1023, found 289.1019.

1-([1,1':3',1''-terphenyl]-4'-yl)-2-diazo-2-(p-tolyl)ethan-1-one (1h)



1.09 g, 70% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.54 (m, 5H), 7.51–7.22 (m, 8H), 7.21–6.66 (m, 4H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.4, 143.6, 140.6, 140.0, 139.4, 136.9, 136.8, 129.6, 129.1, 128.9, 128.6, 128.4, 128.2, 128.1, 127.3, 126.6, 125.8, 122.4, 75.2, 21.2; IR (KBr): ν_{max} 3031, 2954, 2074, 1621, 1511, 1344, 1180, 1074, 912, 870, 812, 698, 497 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{27}H_{21}O^+$ 361.1587, found 361.1584.

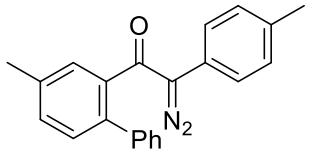
1-([1,1':4',1''-terphenyl]-2'-yl)-2-diazo-2-(p-tolyl)ethan-1-one (1i)



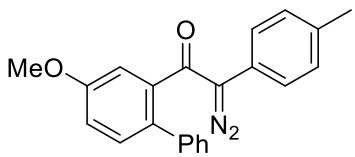
1.18 g, 76% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 2.8 Hz, 1H), 7.69 (dd, J = 8.0, 2.0 Hz, 1H), 7.62 (d, J = 7.6 Hz, 2H), 7.57–6.77 (m, 13H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.5, 140.8, 139.7, 138.9, 138.8, 138.4, 136.9, 130.4, 129.6, 129.3, 129.1, 128.8, 128.5, 128.0, 128.0, 127.2, 126.9, 125.8, 122.3, 75.1, 21.2; IR (KBr): ν_{max} 3028, 2955, 2075, 1512, 1450, 1342, 1231, 1174, 1077, 815, 758, 699 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{27}H_{21}O^+$ 361.1587, found 361.1585.

2-diazo-1-(4-methyl-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)ethan-1-one (1j)

1.12 g, 86% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 3H), 7.18–7.02 (m, 6H), 7.02–6.78 (m, 3H), 2.25 (s, 3H), 2.12 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.8, 139.2, 137.9, 137.8, 137.1, 136.7, 131.6, 129.7, 129.5, 128.8, 128.7, 128.3, 127.7, 125.7, 122.4, 74.9, 21.13, 21.08; IR (neat): ν_{max} 3022, 2916, 2860, 2074, 1512, 1479, 1339, 1284, 1236, 1208, 1074, 811, 733 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{19}O^+$ 299.1430, found 299.1431.



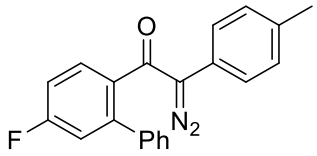
2-diazo-1-(4-methoxy-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)ethan-1-one (1k)



0.70 g, 51% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.22 (m, 7H), 7.14–6.77 (m, 5H), 3.77 (s, 3H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.7, 159.3, 139.0, 138.8, 136.8, 132.4, 131.1, 129.5,

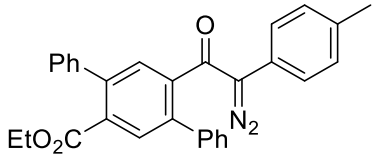
128.7, 128.3, 127.5, 125.6, 122.3, 117.1, 112.8, 75.0, 55.5, 21.1; IR (KBr): ν_{max} 3054, 2074, 1625, 1512, 1251, 1222, 1185, 1083, 837, 812, 771, 706, 573 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{19}O_2^+$ 315.1380, found 315.1380.

2-diazo-1-(5-fluoro-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)ethan-1-one (1l)



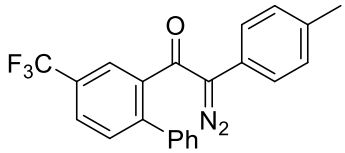
0.99 g, 75% yield; Orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.7, 5.5 Hz, 1H), 7.51–7.19 (m, 5H), 7.19–6.73 (m, 6H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 189.5, 163.7 (d, J = 251.0 Hz), 142.6 (d, J = 8.2 Hz), 138.1, 136.9, 134.1 (d, J = 3.3 Hz), 130.6 (d, J = 9.1 Hz), 129.5, 128.6, 128.4, 125.8, 122.1, 116.5 (d, J = 22.0 Hz), 115.0 (d, J = 21.6 Hz), 75.2, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.13; IR (KBr): ν_{max} 3028, 2924, 2074, 1583, 1570, 1512, 1480, 1344, 1283, 1115, 1065, 896, 811, 698 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{21}H_{16}FO^+$ 303.1180, found 303.1178.

ethyl 5'-(2-diazo-2-(p-tolyl)acetyl)-[1,1':4',1''-terphenyl]-2'-carboxylate (1m)



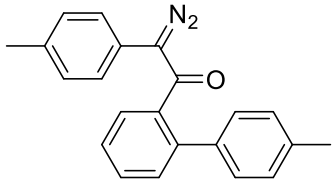
1.66 g, 90% yield; Orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.49 (s, 1H), 7.47–7.13 (m, 10H), 7.10–6.64 (m, 3H), 3.99 (q, J = 7.1 Hz, 2H), 2.15 (s, 3H), 0.88 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 189.2, 168.1, 141.9, 140.2, 140.0, 138.7, 138.0, 137.1, 133.4, 131.2, 130.5, 129.6, 128.8, 128.5, 128.2, 127.7, 125.7, 121.9, 75.1, 61.3, 21.1, 13.7; IR (KBr): ν_{max} 3027, 2981, 2924, 2077, 1624, 1577, 1446, 1385, 1227, 1047, 910, 853 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{30}H_{25}O_3^+$ 433.1798, found 433.1794.

2-diazo-2-(p-tolyl)-1-(5-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethan-1-one (1n)



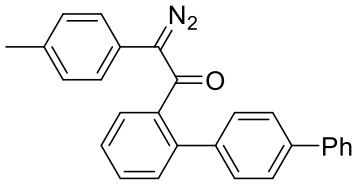
1.16 g, 76% yield; Orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.61–6.52 (m, 10H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 143.3, 138.4, 137.9, 137.2, 130.4, 130.0, 129.6, 128.8 (q, J = 20.8 Hz), 128.7, 128.6, 127.3 (q, J = 3.7 Hz) 125.6 (q, J = 3.9 Hz), 123.9 (q, J = 272.5 Hz), 121.7, 75.2, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47; IR (neat): ν_{max} 3030, 2924, 2078, 1567, 1414, 1327, 1283, 1169, 1127, 1084, 910, 767, cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{16}F_3O^+$ 353.1148, found 353.1145.

2-diazo-1-(4'-methyl-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)ethan-1-one (1o)



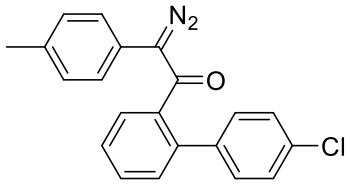
0.89 g, 68% yield; Orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 1H), 7.35–7.31 (m, 1H), 7.30–7.05 (m, 5H), 7.04–6.89 (m, 5H), 2.17 (s, 3H), 2.15 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.8, 139.9, 137.9, 137.7, 136.8, 136.4, 130.7, 129.8, 129.5, 129.1, 128.7, 128.2, 127.7, 125.7, 122.4, 74.9, 21.2, 21.1; IR (KBr): ν_{max} 3024, 2921, 2077, 1635, 1513, 1343, 1234, 1180, 856, 812, 758, 697 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{19}O^+$ 299.1430, found 299.1429.

1-([1,1':4',1''-terphenyl]-2-yl)-2-diazo-2-(p-tolyl)ethan-1-one (1p)



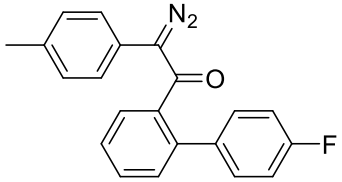
1.26 g, 81% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.37 (m, 5H), 7.36–6.99 (m, 9H), 6.98–6.66 (m, 3H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.7, 140.6, 140.5, 139.5, 138.3, 138.0, 136.9, 130.8, 129.8, 129.6, 129.3, 128.9, 128.4, 128.0, 127.6, 127.1, 127.0, 125.8, 122.4, 75.1, 21.2; IR (KBr): ν_{max} 3027, 2922, 2074, 1628, 1511, 1474, 1344, 1233, 1178, 812, 753, 696 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{27}H_{21}O^+$ 361.1587, found 361.1582.

1-(4'-chloro-[1,1'-biphenyl]-2-yl)-2-diazo-2-(p-tolyl)ethan-1-one (1q)



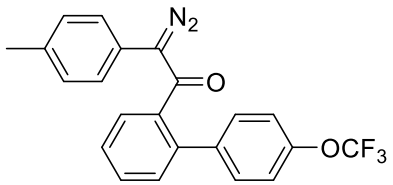
0.97 g, 70% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 1H), 7.52–7.39 (m, 2H), 7.39–7.16 (m, 5H), 7.16–6.48 (m, 4H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.3, 138.5, 137.8, 137.7, 137.0, 134.1, 130.8, 130.0, 129.7, 129.6, 128.5, 128.3, 128.3, 125.7, 122.0, 75.1, 21.1; IR (KBr): ν_{max} 3028, 2077, 1620, 1577, 1474, 1343, 1232, 1176, 908, 758, 733 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{21}H_{16}O^{35}Cl^+$ 319.0884, found 319.0885.

2-diazo-1-(4'-fluoro-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)ethan-1-one (1r)



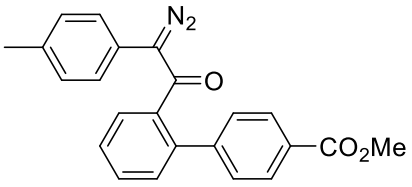
1.02 g, 77% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.46 (m, 4H), 7.45–7.29 (m, 2H), 7.26–6.79 (m, 6H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.5, 162.7 (d, J = 247.4 Hz), 138.7, 137.9, 137.0, 135.3, 130.7, 130.4 (d, J = 8.2 Hz), 129.7, 129.6, 128.2, 128.0, 125.6, 122.1, 115.3 (d, J = 21.5 Hz), 75.1, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.14; IR (KBr): ν_{max} 3027, 2922, 2074, 1621, 1513, 1345, 1179, 1095, 858, 812, 761 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{21}H_{16}FO^+$ 303.1180, found 303.1179.

2-diazo-2-(p-tolyl)-1-(4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-yl)ethan-1-one (1s)



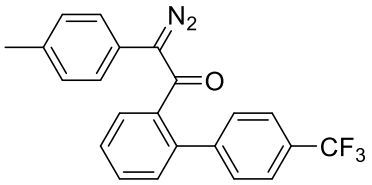
0.73 g, 46% yield; Orange solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1H), 7.60–5.47 (m, 11H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 190.3, 149.0, 138.4, 138.0, 137.9, 137.0, 130.8, 130.1, 129.6, 129.5, 128.3, 125.8, 122.0, 120.7, 120.5 (q, J = 257.2 Hz), 75.1, 21.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -57.76; IR (KBr): ν_{max} 3030, 2924, 2074, 1720, 1513, 1476, 1345, 1258, 1006, 764, 688 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{16}F_3O_2^+$ 369.1097, found 369.1102.

methyl 2'-(2-diazo-2-(p-tolyl)acetyl)-[1,1'-biphenyl]-4-carboxylate (1t)



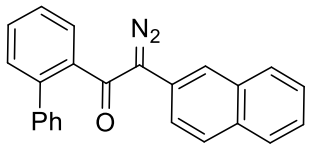
0.77 g, 52% yield; Orange solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 7.9 Hz, 2H), 7.68–7.17 (m, 6H), 7.15–6.58 (m, 4H), 3.80 (s, 3H), 2.19 (s, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 190.1, 166.7, 143.8, 138.7, 137.9, 136.9, 130.8, 129.7, 129.5, 128.8, 128.6, 128.3, 125.6, 121.9, 75.2, 52.1, 21.1; IR (KBr): ν_{max} 2950, 2852, 2074, 1720, 1512, 1435, 1345, 1281, 1180, 1112, 862, 753, 700, 611 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{23}H_{19}O_3^+$ 343.1329, found 343.1333.

2-diazo-2-(p-tolyl)-1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethan-1-one (1u)



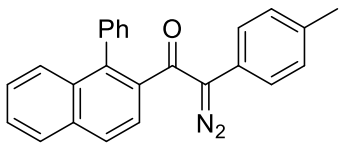
0.85 g, 56% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.14 (m, 8H), 7.07–6.36 (m, 4H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 143.0, 138.4, 137.9, 137.1, 130.9, 129.7, 129.6, 129.1, 128.7, 128.4, 125.8, 125.2 (q, J = 3.7 Hz), 124.2 (q, J = 271.9 Hz), 121.9, 75.2, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48; IR (KBr): ν_{max} 3029, 2923, 2075, 1722, 1512, 1479, 1325, 1283, 1237, 1166, 1069, 765, 675, 609 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{16}F_3O^+$ 353.1148, found 353.1148.

1-([1,1'-biphenyl]-2-yl)-2-diazo-2-(naphthalen-2-yl)ethan-1-one (1v)



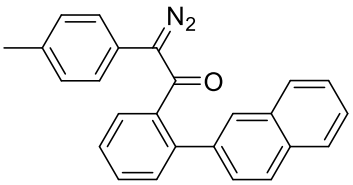
0.56 g, 40% yield; Orange oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24–7.74 (m, 4H), 7.70–7.60 (m, 2H), 7.60–6.90 (m, 10H); $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO) δ 190.1, 139.7, 139.2, 137.8, 133.4, 131.9, 131.5, 130.2, 128.9, 128.85, 128.81, 128.52, 128.49, 128.4, 128.05, 127.98, 127.1, 126.6, 124.0, 123.27, 123.18, 75.5; IR (neat): ν_{max} 3025, 2921, 2077, 1621, 1512, 1480, 1343, 1282, 1041, 915, 815, 766 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{24}H_{17}O^+$ 321.1274, found 321.1267.

2-diazo-1-(1-phenylnaphthalen-2-yl)-2-(p-tolyl)ethan-1-one (1w)



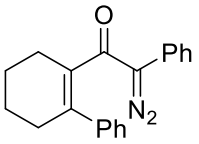
1.03 g, 71% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.37–7.12 (m, 7H), 6.89 (s, 4H), 2.08 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 190.7, 137.3, 136.9, 136.7, 136.0, 134.4, 131.8, 130.4, 129.6, 128.7, 128.4, 128.24, 128.20, 127.1, 127.0, 126.9, 125.7, 124.0, 122.2, 75.2, 21.2; IR (KBr): ν_{max} 3057, 2077, 1597, 1578, 1505, 1473, 1328, 1267, 1231, 1175, 813, 743, 699 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{25}H_{19}O^+$ 335.1430, found 335.1429.

2-diazo-1-(2-(naphthalen-2-yl)phenyl)-2-(p-tolyl)ethan-1-one (1x)



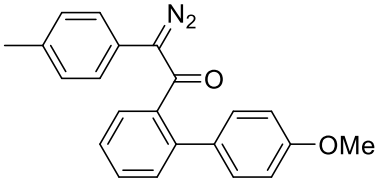
0.58 g, 40% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.58 (m, 4H), 7.49 (d, J = 6.6 Hz, 1H), 7.46–7.17 (m, 6H), 7.08–6.64 (m, 4H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.7, 139.8, 138.1, 136.8, 133.3, 132.7, 132.3, 130.8, 130.1, 129.4, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 126.9, 126.3, 125.8, 122.1, 75.1, 21.0; IR (neat): ν_{max} 3055, 2924, 2074, 1511, 1486, 1345, 1265, 1179, 863, 697 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{25}H_{19}O^+$ 335.1430, found 335.1424.

2-diazo-2-phenyl-1-(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)ethan-1-one (1y)



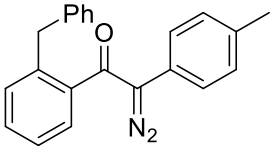
0.62 g, 51% yield; Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–6.87 (m, 10H), 2.46–2.26 (m, 4H), 1.89–1.63 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 193.0, 140.8, 139.9, 134.0, 128.6, 128.0, 127.9, 127.4, 126.6, 125.8, 125.5, 74.0, 30.5, 27.3, 22.7, 22.0; IR (neat): ν_{max} 3057, 2858, 2073, 1620, 1496, 1362, 1325, 1285, 1230, 1170, 753, 720 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{20}H_{19}O^+$ 275.1430, found 275.1425.

2-diazo-1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-2-(p-tolyl)ethan-1-one (1z)



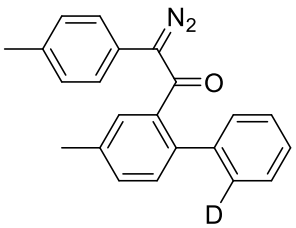
1.15 g, 84% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 1H), 7.38–6.81 (m, 9H), 6.73 (d, J = 8.2 Hz, 2H), 3.61 (s, 3H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 191.0, 159.5, 139.5, 137.8, 136.8, 131.6, 130.6, 130.0, 129.6, 129.5, 128.2, 127.4, 125.7, 122.3, 113.9, 74.9, 55.3, 21.1; IR (KBr): ν_{max} 3034, 2958, 2834, 2072, 1613, 1514, 1444, 1345, 1283, 1249, 1179,1034, 856, 763 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{19}O_2^+$ 315.1380, found 315.1376.

1-(2-benzylphenyl)-2-diazo-2-(p-tolyl)ethan-1-one (1aa)



0.94 g, 72% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–6.91 (m, 13H), 3.99 (s, 2H), 2.21 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.2, 140.4, 139.3, 138.7, 136.9, 131.1, 130.3, 129.7, 129.2, 128.4, 126.8, 126.4, 126.3, 125.6, 122.2, 74.9, 38.9, 21.2; IR (KBr): ν_{max} 3061, 3026, 2920, 2077, 1512, 1453, 1344, 1243, 1176, 1060, 861, 698, 668 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H - N_2)^+$ $C_{22}H_{19}O^+$ 299.1430, found 299.1434.

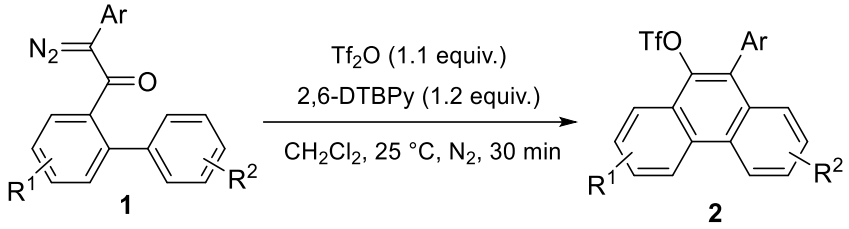
2-diazo-1-(4-methyl-[1,1'-biphenyl]-2-yl-2'-d)-2-(p-tolyl)ethan-1-one (1j-d)



1.06 g, 81% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 1.8 Hz, 2H), 7.28–7.10 (m, 5H), 7.10–6.46 (m, 4H), 2.32 (s, 3H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.9, 139.1, 137.84, 137.76, 137.1, 136.8, 131.5, 129.6, 129.5, 128.71, 128.66, 128.2, 128.1, 127.6, 125.7, 122.3, 74.9, 21.1, 21.0; IR (KBr): ν_{max} 3024, 2921, 2073, 1512,

1464, 1379, 1284, 1263, 1208, 1163, 811, 777, 633 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - N_2)^+$ $C_{22}H_{17}DONa^+$ 322.1313, found 322.1311.

4 Procedure for obtaining products 2a–2z, 2z′, 2aa and 2j-*d*

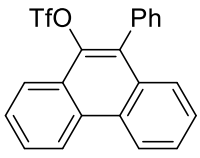


An oven-dried Schlenk tube equipped with a magnetic stir bar was charged successively with 2,6-DTBPy (1.2 mmol, 229 mg), diazoketone (1.0 mmol), and CH_2Cl_2 (5.0 mL) under nitrogen atmosphere. After the resulting mixture was stirred at 25 ºC for 1 min, trifluoromethanesulfonic anhydride (Tf_2O, 1.1 mmol, 310 mg) was added, and the mixture was stirred at 25 ºC for 30 min. The mixture was quenched with saturated aqueous $NaHCO_3$ solution (2.0 mL), and the residue was extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over anhydrious Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified via silica gel column chromatography (eluent: hexane) to afford the corresponding phenanthrenyl triflate.

Diazoketone **1z** reacted with Tf_2O to afford phenanthrenyl triflate **2z** along with spirocyclic compound **2z'**. It is worth noting that diazoketone **1aa** with benzyl group reacted to afford dibenzocycloheptene derivative **2aa**.

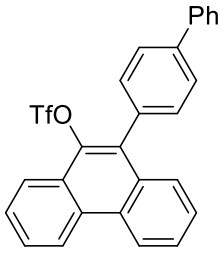
4.1 Characterization data of 2a–2z, 2z′ and 2aa

10-phenylphenanthren-9-yl trifluoromethanesulfonate (2a)[4]



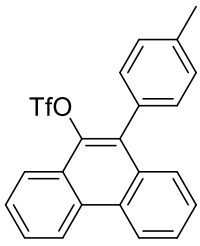
378 mg, 94% yield; White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.75–8.65 (m, 2H), 8.39–8.13 (m, 1H), 7.81–7.68 (m, 2H), 7.70–7.58 (m, 2H), 7.58–7.41 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.2, 133.5, 131.9, 131.6, 131.5, 131.3, 129.8, 128.7, 128.5, 128.1, 128.01, 127.96, 127.7, 127.5, 125.8, 122.9, 122.8, 122.7, 118.3 (q, J = 320.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.74.

10-([1,1'-biphenyl]-4-yl)phenanthren-9-yl trifluoromethanesulfonate (2b)



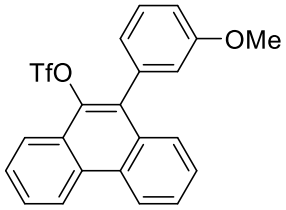
392 mg, 82% yield; White solid; Mp 206.9–207.6 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.65–8.61 (m, 2H), 8.29–8.10 (m, 1H), 7.77–7.53 (m, 8H), 7.50–7.24 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.5, 141.3, 140.7, 132.4, 131.7, 131.6, 131.5, 129.9, 129.0, 128.1, 128.03, 128.01, 127.8, 127.7, 127.6, 127.25, 127.16, 125.9, 123.0, 122.9, 122.8, 118.3 (q, J = 320.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.65; IR (KBr): ν_{max} 3079, 3031, 1600, 1448, 1408, 1286, 1136, 1008, 953, 839, 763, 726, 613, 506 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{27}H_{17}F_3O_3S^+$ 478.0845, found 478.0842.

10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2c)



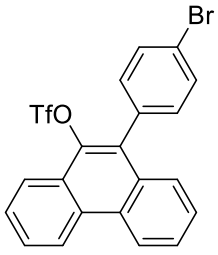
304 mg, 73% yield; White solid; Mp 163.2–164.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94–8.61 (m, 2H), 8.50–8.30 (m, 1H), 7.94–7.68 (m, 4H), 7.61–7.57 (m, 1H), 7.47 (s, 4H), 2.59 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.3, 138.6, 132.0, 131.8, 131.5, 131.2, 130.5, 129.9, 129.2, 128.1, 128.0, 127.9, 127.7, 127.5, 125.9, 122.9, 122.8, 122.7, 118.4 (q, J = 320.7 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.61; IR (KBr): ν_{max} 3054, 1510, 1489, 1404, 1265, 1199, 1138, 1002, 934, 862, 759, 744, 705, 644 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{22}H_{15}F_3O_3S^+$ 416.0689, found 416.0691.

10-(3-methoxyphenyl)phenanthren-9-yl trifluoromethanesulfonate (2d)



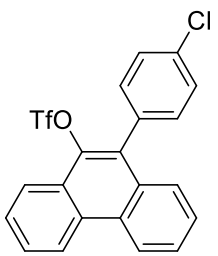
333 mg, 77% yield; White solid; Mp 167.3–168.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72–8.70 (m, 1H), 8.68 (d, J = 8.4 Hz, 1H), 8.30–8.27 (m, 1H), 7.74–7.71 (m, 2H), 7.68–7.64 (m, 2H), 7.50 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.44 (dd, J = 8.4, 7.4 Hz, 1H), 7.06 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 7.02 (dd, J = 2.5, 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 159.7, 141.1, 134.7, 131.7, 131.54, 131.51, 129.8, 129.6, 128.1, 128.07, 128.0, 127.7, 127.5, 125.8, 123.7, 122.9, 122.78, 122.76, 118.3 (q, J = 320.8 Hz), 116.7, 114.6, 55.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -73.61; IR (KBr): ν_{max} 3002, 2946, 1600, 1577, 1416, 1209, 1133, 1048, 1010, 825, 758, 623, 582 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{22}H_{15}F_3O_4SNa^+$ 455.0535, found 455.0537.

10-(4-bromophenyl)phenanthren-9-yl trifluoromethanesulfonate (2e)



424 mg, 88% yield; White solid; Mp 159.1–160.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85–8.61 (m, 2H), 8.35 (dd, J = 6.2, 3.3 Hz, 1H), 7.85–7.68 (m, 5H), 7.64 (dd, J = 8.3, 1.5 Hz, 1H), 7.61–7.53 (m, 1H), 7.39 (d, J = 8.4 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.1, 133.0, 132.5, 131.8, 131.6, 131.2, 130.6, 129.9, 128.3, 128.1, 127.9, 127.69, 127.65, 125.7, 123.2, 123.0, 122.9, 122.8, 118.3 (q, J = 320.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.59; IR (KBr): ν_{max} 3081, 2925, 1603, 1489, 1448, 1407, 1216, 1135, 1004, 933, 834, 751, 725, 633, 508 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{21}H_{12}{}^{79}BrF_3O_3S^+$ 479.9637, found 479.9630.

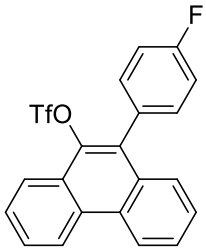
10-(4-chlorophenyl)phenanthren-9-yl trifluoromethanesulfonate (2f)



406 mg, 93% yield; White solid; Mp 148.6–149.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74–8.71 (m, 2H), 8.28–8.26 (m, 1H), 7.78–7.67 (m, 3H), 7.59–7.50 (m, 4H), 7.39 (d, J = 8.5 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 135.0, 132.7, 132.0, 131.6, 131.3, 130.6, 129.9, 128.9, 128.3, 128.1, 127.9, 127.68, 127.66, 125.7, 123.0, 122.9, 122.8, 118.3 (q, J = 320.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.63; IR (KBr): ν_{max} 3087, 3063, 1592, 1489, 1407, 1265, 1138,

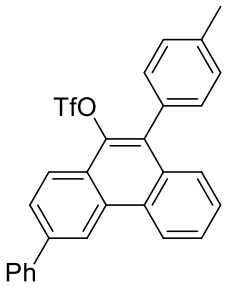
1004, 836, 763, 631, 505, 438 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{21}H_{12}{}^{35}ClF_3O_3S^+$ 436.0142, found 436.0142.

10-(4-fluorophenyl)phenanthren-9-yl trifluoromethanesulfonate (2g)



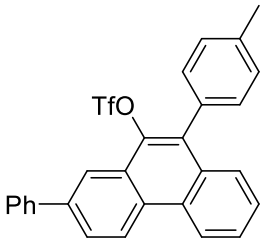
336 mg, 80% yield; White solid; Mp 149.2–150.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.84–8.69 (m, 2H), 8.45–8.29 (m, 1H), 7.88–7.74 (m, 2H), 7.73 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.50 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.33 (dd, *J* = 8.5, 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.3 Hz), 141.4, 133.1 (d, *J* = 8.3 Hz), 131.6, 131.5, 130.8, 129.9, 129.4 (d, *J* = 3.5 Hz), 128.2, 128.0, 127.8, 127.7, 127.6, 125.7, 123.0, 122.9, 122.8, 118.4 (q, *J* = 320.6 Hz), 115.7 (d, *J* = 21.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.67, -112.63; IR (KBr): ν_{max} 3084, 2928, 1604, 1508, 1410, 1212, 1017, 840, 818, 797, 760, 633 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{21}H_{12}F_4O_3S^+$ 420.0438, found 420.0437.

6-phenyl-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2h)



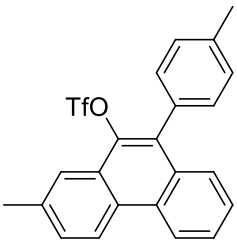
305 mg, 62% yield; White solid; Mp 200.2–201.4 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 1.7 Hz, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.78 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.53–7.46 (m, 2H), 7.36–7.30 (m, 3H), 7.27–7.17 (m, 5H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.2, 140.8, 140.7, 138.6, 132.1, 131.9, 131.8, 131.2, 130.4, 129.9, 129.2, 129.1, 128.2, 128.0, 127.71, 127.68, 127.6, 127.3, 125.0, 123.3, 122.8, 121.3, 118.4 (q, *J* = 320.8 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56; IR (KBr): ν_{max} 3040, 2022, 1600, 1402, 1204, 1138, 1003, 829, 817, 700, 642, 596, 507, 426 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{28}H_{19}F_3O_3S^+$ 492.1002, found 492.0999.

7-phenyl-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2i)



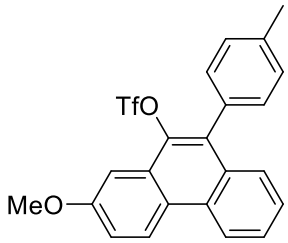
369 mg, 75% yield; White solid; Mp 185.2–186.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.47–8.34 (m, 3H), 7.70 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.43–7.39 (m, 1H), 7.34–7.26 (m, 3H), 7.22–7.15 (m, 5H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.4, 140.5, 140.1, 138.6, 132.4, 131.8, 131.1, 130.51, 130.48, 129.7, 129.3, 129.2, 128.1, 128.0, 127.8, 127.43, 127.41, 127.1, 126.3, 123.6, 122.9, 120.7, 118.5 (q, *J* = 320.9 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56; IR (KBr): ν_{max} 3034, 2925, 1600, 1515, 1483, 1452, 1405, 1204, 1137, 1008, 934, 826, 635, 598, 514 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{28}H_{19}F_3O_3S^+$ 492.1002, found 492.1005.

7-methyl-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2j)



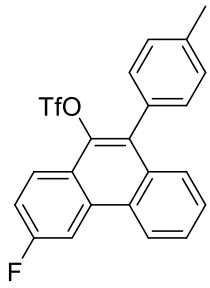
379 mg, 88% yield; White solid; Mp 158.1–159.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8.3 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.02 (s, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.55 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.46–7.35 (m, 2H), 7.32 (s, 4H), 2.52 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.3, 138.5, 138.0, 132.0, 131.4, 131.2, 130.6, 129.9, 129.7, 129.4, 129.2, 128.0, 127.6, 127.0, 125.9, 122.9, 122.6, 122.2, 118.5 (q, J = 320.7 Hz), 21.8, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.60; IR (KBr): ν_{max} 3026, 2924, 1400, 1230, 1208, 1184, 1135, 919, 829, 816, 760, 600, 511 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{23}H_{17}F_3O_3S^+$ 430.0845, found 430.0844.

7-methoxy-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2k)



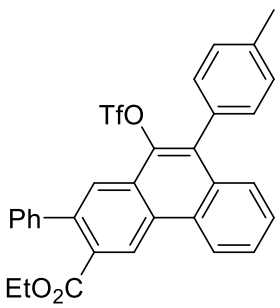
429 mg, 96% yield; White solid; Mp 194.6–195.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67–8.46 (m, 2H), 7.73–7.51 (m, 3H), 7.48–7.22 (m, 6H), 3.95 (s, 3H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.4, 141.0, 138.5, 132.5, 131.0, 130.7, 130.5, 129.9, 129.2, 128.0, 127.7, 127.2, 126.4, 125.7, 124.7, 122.2, 118.9, 118.3 (q, J = 320.8 Hz) 102.8, 55.5, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.73; IR (KBr): ν_{max} 3048, 2969, 1623, 1519, 1465, 1453, 1411, 1204, 1143, 1037, 949, 835, 802, 573, 505 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{18}F_3O_4S^+$ 447.0872, found 447.0869.

6-fluoro-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2l)



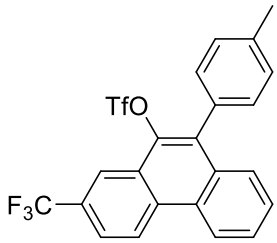
343 mg, 79% yield; White solid; Mp 206.9–207.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.3 Hz, 1H), 8.38 (dd, J = 10.8, 2.5 Hz, 1H), 8.30 (dd, J = 9.1, 5.5 Hz, 1H), 7.82–7.67 (m, 2H), 7.64–7.47 (m, 2H), 7.47–7.30 (m, 4H), 2.54 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 248.7 Hz), 140.7, 138.6, 133.3 (d, J = 8.7 Hz), 132.3, 131.3 (d, J = 2.6 Hz), 131.1, 130.1, 129.2, 129.1, 128.2, 128.0, 127.7, 125.3 (d, J = 9.1 Hz), 123.0, 122.6, 118.2 (q, J = 322.2.0 Hz), 116.9 (d, J = 24.0 Hz), 108.3 (d, J = 22.9 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.65, -111.04; IR (KBr): ν_{max} 2926, 1605, 1511, 1499,1430, 1401, 1210, 1126, 1002, 935, 902, 871, 819, 768, 617 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{22}H_{14}F_4O_3S^+$ 434.0594, found 434.0593.

ethyl 2-phenyl-9-(p-tolyl)-10-(((trifluoromethyl)sulfonyl)oxy)phenanthrene-3-carboxylate (2m)



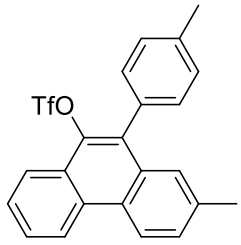
395 mg, 70% yield; White solid; Mp 181.9–182.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.69 (d, J = 8.3 Hz, 1H), 8.18 (s, 1H), 7.72–7.54 (m, 2H), 7.47–7.28 (m, 6H), 7.25 (s, 2H), 4.09 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.8, 141.1, 140.9, 140.6, 138.8, 134.4, 132.0, 131.2, 130.9, 130.1, 129.8, 129.7, 129.2, 128.6, 128.34, 128.31, 128.25, 127.9, 127.6, 127.3, 125.5, 124.7, 123.0, 118.3 (q, J = 320.7 Hz), 61.5, 21.4, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.56; IR (KBr): ν_{max} 3031, 2978, 1722, 1603, 1396, 1282, 1209, 1130, 1009, 830, 764, 713, 701, 601, 488 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{31}H_{24}F_3O_5S^+$ 565.1291, found 565.1300.

10-(p-tolyl)-7-(trifluoromethyl)phenanthren-9-yl trifluoromethanesulfonate (2n)



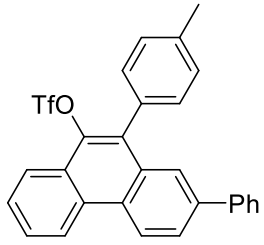
373 mg, 77% yield; White solid; Mp 188.2–189.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.7 Hz, 1H), 8.70 (d, J = 8.3 Hz, 1H), 8.65 (s, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.85–7.70 (m, 2H), 7.66–7.62 (m, 1H), 7.54–7.32 (m, 4H), 2.58 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.6, 139.0, 133.8, 133.3, 132.5, 131.0, 129.9, 129.7 (q, J = 33.3 Hz), 129.3, 129.0, 128.6, 128.3, 128.2, 125.4, 124.1 (q, J = 273.7 Hz), 123.9, 123.8 (q, J = 3.4 Hz), 123.1, 120.3(q, J = 3.3 Hz), 118.4 (q, J = 320.8 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.47, -73.45; IR (KBr): ν_{max} 2928, 2854, 1639, 1515, 1411, 1368, 1337, 1286, 1214, 1132, 1082, 1029, 826, 765 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{23}H_{14}F_6O_3S^+$ 484.0562, found 484.0559.

2-methyl-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2o)



314 mg, 73% yield; Colorless oil; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.70 (dd, J = 7.3, 2.1 Hz, 1H), 8.60 (d, J = 8.5 Hz, 1H), 8.21 (dd, J = 7.2, 2.3 Hz, 1H), 7.88–7.63 (m, 2H), 7.51 (dd, J = 8.6, 2.0 Hz, 1H), 7.43 (s, 1H), 7.40–7.26 (m, 4H), 2.48 (s, 3H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 141.3, 138.6, 137.7, 131.8, 131.7, 131.4, 131.1, 130.4, 129.5, 129.1, 127.9, 127.6, 127.43, 127.38, 125.3, 122.72, 122.67, 122.4, 118.3 (q, J = 320.3 Hz), 21.4, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.66; IR (neat): ν_{max} 2923, 2852, 1666, 1511, 1425, 1211, 1138, 1044, 880, 822, 755, 597, 574, 502 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{23}H_{17}F_3O_3S^+$ 430.0845, found 430.0848.

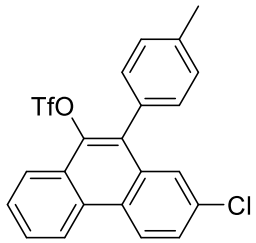
2-phenyl-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2p)



345 mg, 70% yield; White solid; Mp 180.4–181.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 8.6, 6.1 Hz, 2H), 8.11 (d, J = 7.9 Hz, 1H), 7.71 (s, 1H), 7.63 (dd, J = 8.6, 2.0 Hz, 1H), 7.56–7.42 (m, 2H), 7.32 (d, J = 7.5 Hz, 2H), 7.25–7.09 (m, 7H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.7, 140.4, 140.2, 138.7, 132.22, 132.17, 131.3, 131.2, 130.3, 129.4, 129.04,

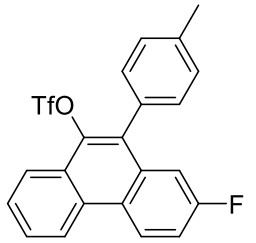
128.85, 128.1, 127.9, 127.8, 127.4, 126.9, 126.0, 125.9, 123.5, 123.0, 122.8, 118.4 (q, J = 320.7 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.55; IR (KBr): ν_{max} 3022, 2923, 1614, 1600, 1512, 1482, 1405, 1205, 1172, 1005, 843, 753, 728, 596, 509 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{28}H_{19}F_3O_3S^+$ 492.1002, found 492.1006.

2-chloro-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2q)



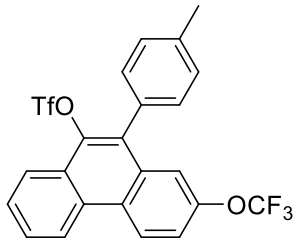
302 mg, 67% yield; White solid; Mp 168.1–169.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57–8.48 (m, 2H), 8.24–8.22 (m, 1H), 7.71–7.65 (m, 2H), 7.60 (d, J = 2.2 Hz, 1H), 7.53 (dd, J = 8.9, 2.2 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 138.9, 133.7, 133.0, 131.2, 131.0, 130.9, 129.7, 129.4, 128.3, 128.1, 127.1, 125.7, 124.3, 122.8, 118.3 (q, J = 320.7 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.59; IR (KBr): ν_{max} 3025, 2922, 2849, 1604, 1511, 1481, 1397, 1212, 1136, 1004, 862, 755, 697 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{22}H_{14}{}^{35}ClF_3O_3S^+$ 450.0299, found 450.0300.

2-fluoro-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2r)



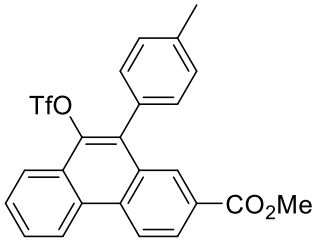
91 mg, 21% yield; White solid; Mp 178.5–179.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, J = 9.2, 5.5 Hz, 1H), 8.51 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 9.0 Hz, 1H), 7.71–7.57 (m, 2H), 7.38–7.15 (m, 6H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J = 247.5 Hz), 142.1, 138.9, 133.6 (d, J = 8.8 Hz), 131.4 (d, J = 4.0 Hz), 131.1, 130.9, 129.9, 129.4, 128.3, 127.7, 126.4 (d, J = 2.0 Hz), 125.4, 125.2 (d, J = 8.8 Hz), 122.8, 122.7, 118.3 (q, J = 230.1 Hz), 116.6 (d, J = 23.9 Hz), 112.7 (d, J = 23.1 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.62, -112.28; IR (KBr): ν_{max} 3025, 2928, 1620, 1539, 1513, 1450, 1230, 1143, 1107, 873, 822, 757, 509 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{22}H_{14}F_4O_3S^+$ 434.0594, found 434.0592.

10-(p-tolyl)-2-(trifluoromethoxy)phenanthren-9-yl trifluoromethanesulfonate (2s)



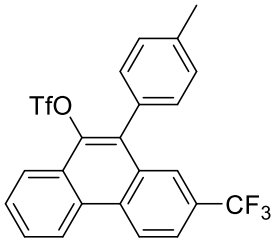
430 mg, 86% yield; White solid; Mp 141.6–142.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 9.7 Hz, 1H), 8.49–8.36 (m, 1H), 8.21–8.06 (m, 1H), 7.69–7.50 (m, 2H), 7.47–7.33 (m, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.2 (q, J = 2.0 Hz), 142.2, 139.0, 133.0, 131.5, 130.9, 130.8, 129.6, 129.4, 128.4, 128.2, 125.9, 124.9, 122.91, 122.86, 120.7, 120.6 (q, J = 258.6 Hz), 119.2, 118.3 (q, J = 322.2 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.72, -73.66; IR (KBr): ν_{max} 2919, 1621, 1515, 1422, 1212, 1136, 1003, 917, 819, 777, 756, 727, 704 cm^{-1}; HRMS(ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{15}F_6O_4S^+$ 501.0590, found 501.0589.

methyl 10-(p-tolyl)-9-(((trifluoromethyl)sulfonyl)oxy)phenanthrene-2-carboxylate (2t)



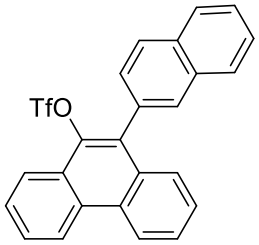
270 mg, 57% yield; White solid; Mp 210.2–211.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, J = 8.4 Hz, 2H), 8.44 (s, 1H), 8.38–8.15 (m, 2H), 7.97–7.71 (m, 2H), 7.58–7.33 (m, 4H), 3.94 (s, 3H), 2.55 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.7, 141.7, 138.9, 132.7, 132.4, 131.3, 131.1, 130.7, 130.1, 129.6, 129.4, 128.91, 128.86, 128.3, 127.5, 126.7, 123.5, 123.0, 122.8, 118.2 (q, J = 320.8 Hz), 52.3, 21.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -73.65; IR (KBr): ν_{max} 2922, 1720, 1616, 1420, 1292, 1262, 1209, 1139, 1005, 823, 755, 598, 505 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{18}F_3O_5S^+$ 475.0822, found 475.0820.

10-(p-tolyl)-2-(trifluoromethyl)phenanthren-9-yl trifluoromethanesulfonate (2u)



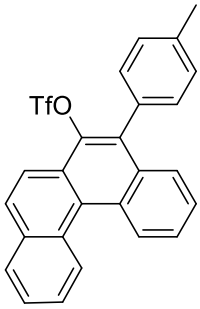
349 mg, 72% yield; White solid; Mp 141.2–142.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 8.8 Hz, 1H), 8.69 (d, J = 8.1 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.87–7.73 (m, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 2.58 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 139.2, 132.0, 131.8, 131.4, 131.0, 130.6, 129.5, 129.4, 129.3 (q, J = 32.6 Hz), 128.9, 128.4, 126.6, 125.3 (q, J = 4.4 Hz), 124.1 (q, J = 273.7 Hz), 123.7, 123.5 (q, J = 3.4 Hz), 123.2, 122.9, 118.3 (q, J = 320.8 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.24, -73.61; IR (KBr): ν_{max} 3031, 2928, 1624, 1515, 1406, 1281, 1131, 1082, 965, 836, 605, 506 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{23}H_{14}F_6O_3S^+$ 484.0562, found 484.0560.

10-(naphthalen-2-yl)phenanthren-9-yl trifluoromethanesulfonate (2v)



389 mg, 86% yield; White solid; Mp 188.9–189.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83–8.78 (m, 2H), 8.39–8.36 (m, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.02–7.94 (m, 3H), 7.84–7.79 (m, 2H), 7.75–7.69 (m, 2H), 7.65–7.52 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 133.3, 133.2, 131.8, 131.7, 131.6, 130.9, 130.8, 129.9, 128.7, 128.24, 128.16, 128.12, 128.08, 128.0, 127.9, 127.8, 127.6, 126.8, 126.6, 125.9, 123.0, 122.9, 122.8, 118.2 (q, J = 320.8 Hz), ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.69; IR (KBr): ν_{max} 3056, 1597, 1400, 1223, 1134, 1009, 960, 830, 799, 754, 619, 506, 478 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{25}H_{15}F_3O_3S^+$ 452.0689, found 452.0687.

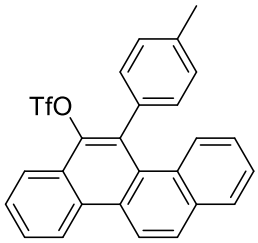
5-(p-tolyl)benzo[c]phenanthren-6-yl trifluoromethanesulfonate (2w)



364 mg, 78% yield; White solid; Mp 174.4–175.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17–9.06 (m, 2H), 8.31 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.3 Hz, 1H), 7.78–7.68 (m, 3H), 7.61–7.57 (m, 1H), 7.49 (s, 4H), 2.60 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.3, 138.6, 133.6, 132.8, 132.0, 131.3, 130.6, 129.8, 129.5, 129.4, 129.3, 128.9, 128.7, 128.32, 128.25, 127.8, 127.0, 126.92, 126.87, 124.5, 119.6, 118.4 (q, J = 319.0 Hz), 21.5; ^{19}F NMR

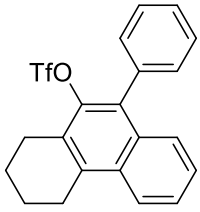
(376 MHz, $CDCl_3$) δ -73.47; IR (KBr): ν_{max} 3056, 2923, 1510, 1474, 1408, 1330, 1209, 1134, 1006, 920, 844, 818, 760, 631 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{26}H_{17}F_3O_3S^+$ 466.0845, found 466.0843.

5-(p-tolyl)chrysen-6-yl trifluoromethanesulfonate (2x)



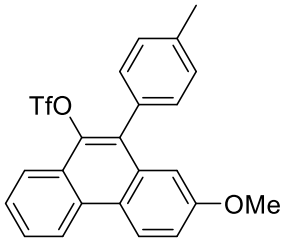
285 mg, 61% yield; White solid; Mp 212.9–213.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56–8.50 (m, 1H), 8.43 (d, *J* = 9.0 Hz, 1H), 8.21–8.14 (m, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.62–7.51 (m, 2H), 7.31–7.13 (m, 6H), 6.94–6.90 (m, 1H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 142.7, 138.6, 134.1, 133.7, 132.1, 131.3, 131.1, 130.0, 129.7, 129.5, 128.34, 128.27, 128.1, 128.0, 127.8, 126.2, 125.6, 125.1, 123.6, 122.5, 120.7, 118.3 (q, *J* = 320.9 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.44; IR (KBr): ν_{max} 3067, 2923, 1606, 1515, 1413, 1208, 1140, 1069, 932, 832, 821, 752, 699, 498 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{26}H_{17}F_3O_3S^+$ 466.0845, found 466.0845.

10-phenyl-5,6,7,8-tetrahydrophenanthren-9-yl trifluoromethanesulfonate (2y)



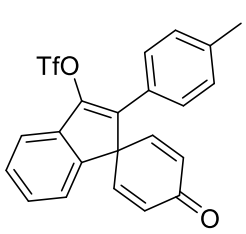
256 mg, 63% yield; White solid; Mp 155.8–156.4 °C; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.58–7.47 (m, 5H), 7.42–7.36 (m, 3H), 3.22 (t, *J* = 6.5 Hz, 2H), 2.98 (t, *J* = 6.2 Hz, 2H), 2.04–1.98 (m, 2H), 1.94–1.88 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 144.5, 135.9, 134.2, 132.1, 132.0, 131.7, 131.0, 128.8, 128.7, 128.67, 127.6, 127.2, 126.6, 123.5, 118.5 (q, *J* = 320.3 Hz), 26.7, 25.9, 22.8, 22.6; ^{19}F NMR (376 MHz, CD_2Cl_2) δ -74.37; IR (KBr): ν_{max} 3066, 2943, 2866, 1403, 1205, 1131, 957, 854, 810, 762, 753, 703, 640, 578 cm^{-1}; HRMS(EI-TOF) *m/z* calculated for $(M)^+$ $C_{21}H_{17}F_3O_3S^+$ 406.0845, found 406.0844.

2-methoxy-10-(p-tolyl)phenanthren-9-yl trifluoromethanesulfonate (2z)



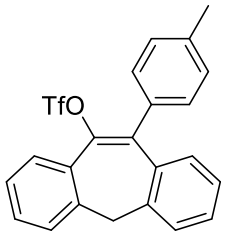
103 mg, 23% yield; White solid; Mp 144.2–145.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.75–8.58 (m, 2H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.85–7.66 (m, 2H), 7.40 (s, 4H), 7.36 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 3.78 (s, 3H), 2.53 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.8, 141.8, 138.5, 133.4, 131.5, 131.4, 131.0, 130.5, 129.2, 128.0, 126.8, 124.7, 124.4, 124.1, 122.6, 122.4, 118.3 (q, *J* = 320.9 Hz), 116.67, 109.1, 55.3, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.69; IR (KBr): ν_{max} 3034, 2963, 2837, 1616, 1407, 1222, 1135, 1108, 1046, 867, 821, 756, 593 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{18}F_3O_4S^+$ 447.0872, found 447.0867.

4-oxo-2'-(p-tolyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-3'-yl trifluoromethanesulfonate (2z')



272 mg, 63% yield; White solid; Mp 131.2–132.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 1H), 7.38–7.35 (m, 1H), 7.30–7.25 (m, 3H), 7.14–6.98 (m, 3H), 6.47 (s, 4H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 185.5, 147.3, 145.1, 139.9, 138.4, 137.2, 135.8, 131.6, 129.6, 129.3, 128.4, 127.7, 127.3, 123.9, 119.6, 118.4 (q, J = 320.5 Hz), 57.8, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.62; IR (KBr): ν_{max} 2935, 1668, 1425, 1212, 1180, 1140, 886, 861, 844, 829, 794, 756, 744 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{22}H_{16}F_3O_4S^+$ 433.0716, found 433.0713.

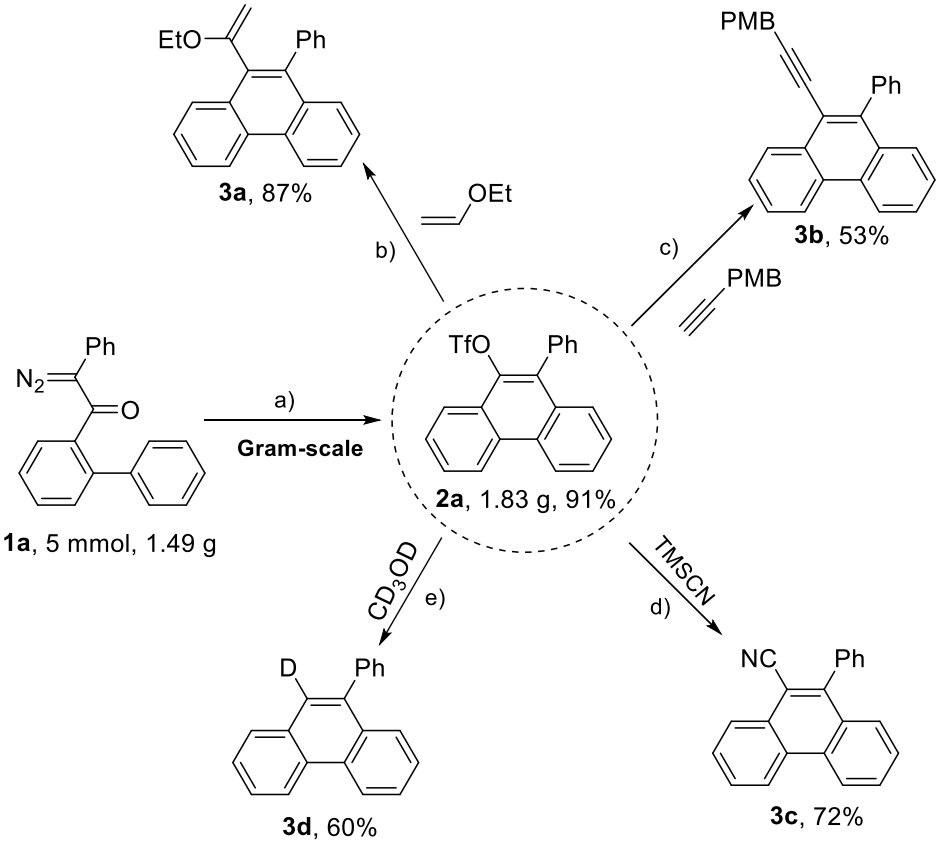
11-(p-tolyl)-5H-dibenzo[a,d][7]annulen-10-yl trifluoromethanesulfonate (2aa)



301 mg, 70% yield; White solid; Mp 199.5–200.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.0, 1.2 Hz, 1H), 7.49–7.33 (m, 8H), 7.14–7.10 (m, 1H), 7.00 (dd, J = 7.9, 1.3 Hz, 1H), 4.00 (d, J = 3.3 Hz, 2H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.2, 141.3, 140.7, 138.4, 136.9, 134.9, 134.7, 131.0, 130.9, 130.7, 130.6, 129.6, 129.0, 127.2, 126.9, 126.6, 126.4, 126.0, 118.1 (q, J = 320.7 Hz), 40.9, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.79; IR (KBr): ν_{max} 2959, 1510, 1405, 1239, 1206, 1137, 994, 920, 818, 762, 613, 577 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{18}F_3O_3S^+$ 431.0923, found 431.0920.

5 Gram-scale reaction and synthetic applications of 2a

5.1 Procedure for obtaining products 3a–3d

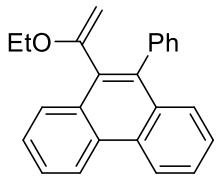


Reaction conditions: a) standard conditions; b) **2a** (0.5 mmol), Ethyl vinyl ether (1.2 equiv.), $Pd(OAc)_2$ (5 mol%), dppp (5 mol%), Et_3N (1.2 equiv.), DMF, N_2, 90 ℃; c) **2a** (0.5 mmol), 4-Ethynylanisole (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), Et_3N (2.0 equiv.), DMF, N_2, 100 ℃; d) **2a** (0.5 mmol), TMSCN (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol%), Et_3N, N_2, 90 ℃; e) **2a** (0.5 mmol), 10% Pd/C (10 wt% of **2a**), Mg (2.0 equiv.), CH_3OD, N_2, rt. PMB = *p*-methoxyphenyl, dppp = 1,3-bis(diphenylphosphino)propane.

The synthetic utility of this cationic annulation method was evaluated. A gram-scale reaction involving diazoketone **1a** was conducted using standard conditions, obtaining phenanthrenyl triflates **2a** in 91% yield (1.83 g). Furthermore, phenanthrenyl triflate **2a** demonstrated its versatility by participating in transition-metal-catalyzed coupling reactions to form more complex molecules. The substrate proportions were slightly adjusted, referring to the procedure described in the literature. Treatment of phenanthrenyl triflate **2a** on Heck[5] or Sonogashira[6] coupling reaction conditions afforded the corresponding products **3a** and **3d** in 87% and 53% yield, respectively. Additionally, phenanthrenyl triflate **2a** could transform to cyanated product **3c** catalyzed by $Pd(PPh_3)_4$,[7] or convert to 9-phenylphenanthrene-10-*d* catalyzed by Pd/C.[8]

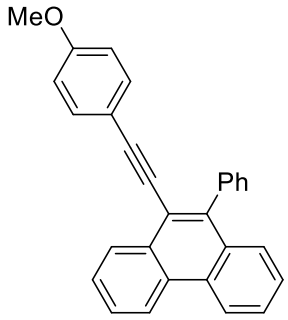
5.2 Characterization data of 3a–3d

9-(1-ethoxyvinyl)-10-phenylphenanthrene (3a)



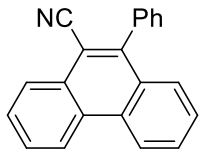
141 mg, 87% yield; White solid; Mp 139.5–141.1 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.75 (dd, J = 8.3, 3.6 Hz, 2H), 8.14 (d, J = 8.0 Hz, 1H), 7.79–7.58 (m, 3H), 7.54 (d, J = 8.2 Hz, 1H), 7.51–7.16 (m, 6H), 4.31 (s, 1H), 4.01 (s, 1H), 3.85 (s, 1H), 3.53 (s, 1H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 158.4, 139.5, 137.7, 133.5, 131.6, 130.5, 130.3, 129.8, 128.0, 127.0, 126.94, 126.85, 126.7, 126.51, 126.47, 122.5, 122.4, 88.4, 63.0, 14.2; IR (KBr): ν_{max} 3072, 2977, 2926, 1651, 1617, 1488, 1447, 1255, 1061, 759, 725, 701 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{24}H_{20}ONa^+$ 347.1406, found 347.1406.

9-((4-methoxyphenyl)ethynyl)-10-phenylphenanthrene (3b)



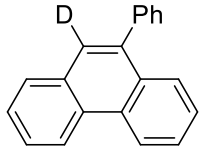
102 mg, 53% yield; White solid; Mp 172.8–173.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69–8.66 (m, 2H), 8.63 (dd, J = 8.0, 1.5 Hz, 1H), 7.71–7.65 (m, 2H), 7.63 (dd, J = 8.3, 1.3 Hz, 1H), 7.60–7.57 (m, 1H), 7.55–7.46 (m, 5H), 7.45–7.43 (m, 1H), 7.15 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 159.7, 142.4, 140.0, 133.0, 131.5, 130.84, 130.82, 130.1, 129.8, 128.1, 127.7, 127.51, 127.50, 127.3, 127.08, 127.06, 126.8, 122.74, 122.70, 119.5, 115.7, 114.0, 98.5, 86.7, 55.3; IR (KBr): ν_{max} 2957, 2932, 2835, 2203, 1604, 1508, 1248, 1169, 1031, 830, 757, 724 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{29}H_{20}ONa^+$ 407.1406, found 407.1402.

10-phenylphenanthrene-9-carbonitrile (3c)[9]



101 mg, 72% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96–8.68 (m, 2H), 8.53–8.32 (m, 1H), 7.99–7.77 (m, 3H), 7.74 (d, J = 8.2 Hz, 1H), 7.68–7.45 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.4, 137.1, 131.8, 130.2, 130.0, 129.7, 129.5, 129.0, 128.9, 128.74, 128.70, 128.4, 128.1, 127.4, 126.5, 122.9, 117.3, 109.7.

9-phenylphenanthrene-10-d (3d)[10]



77 mg, 60% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.3 Hz, 1H), 8.76 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.93 (dd, J = 7.7, 1.6 Hz, 1H), 7.80–7.64 (m, 3H), 7.63–7.41 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.9, 138.8, 131.6, 131.3, 130.8, 130.2, 130.1, 128.7, 128.4, 127.5, 127.0, 126.97, 126.7, 126.6, 126.57, 123.0, 122.7.

6 References

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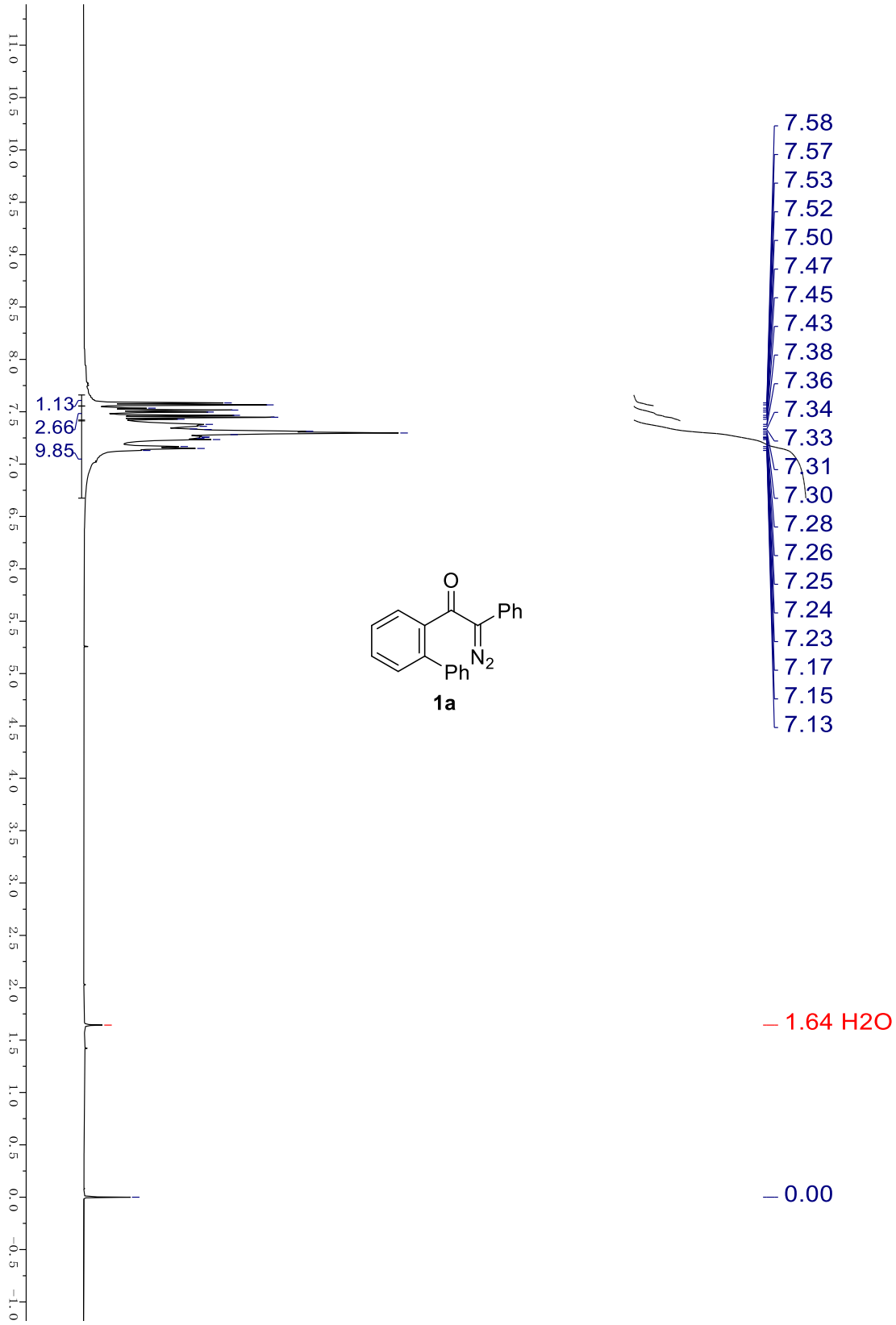
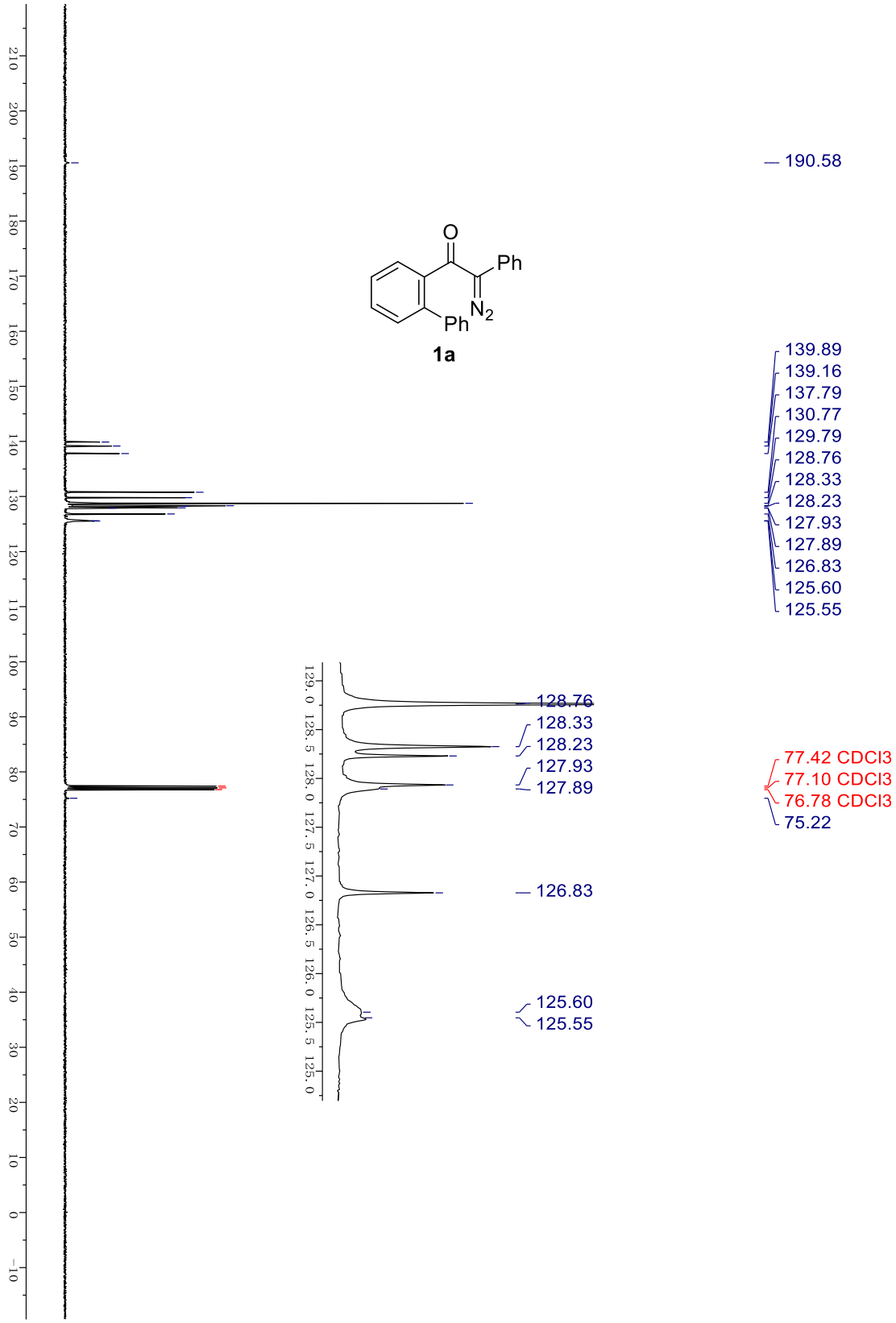
7 Copies of NMR spectra

7.1 NMR spectra of diazoketones 1

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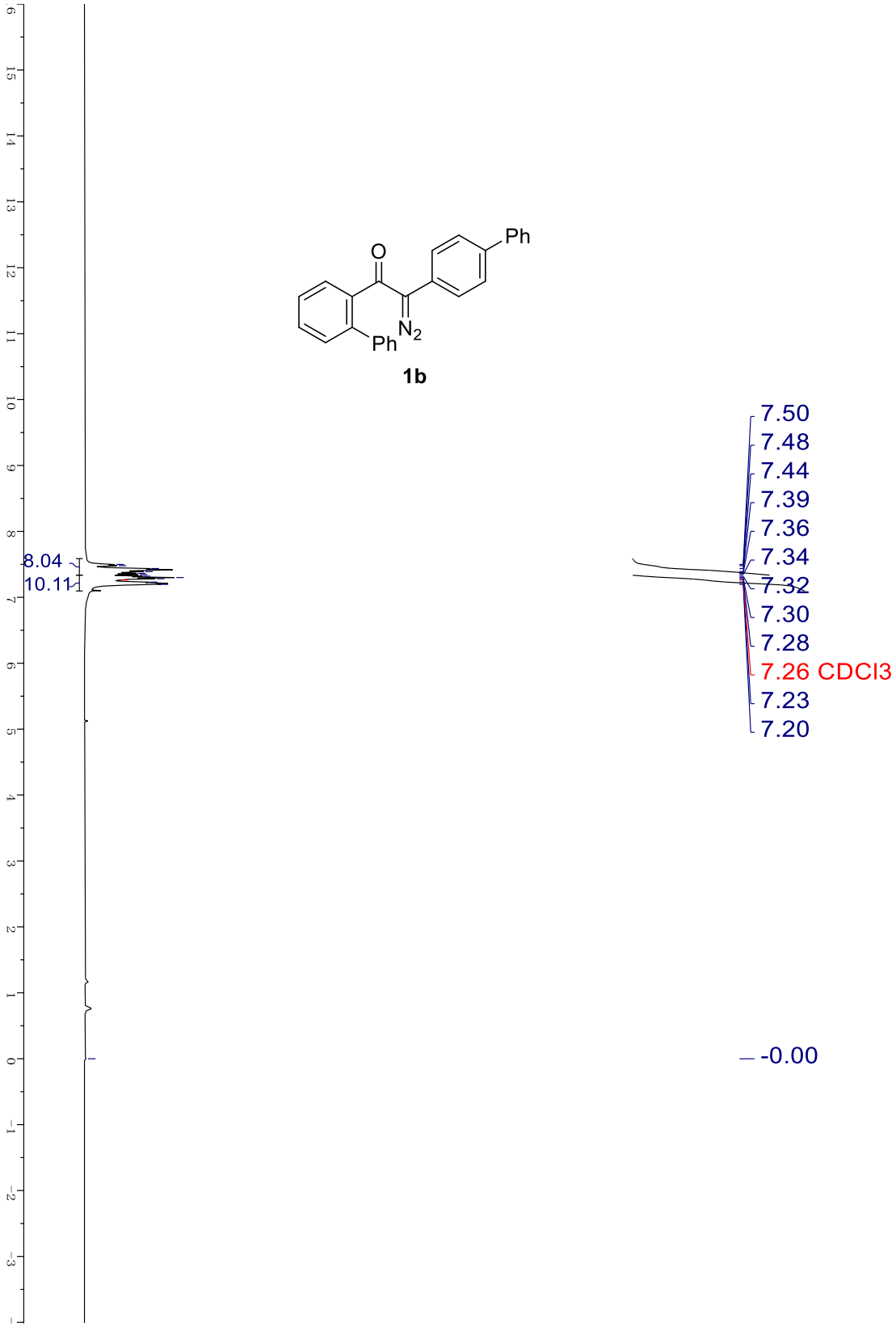
76.78 CDCl3
75.22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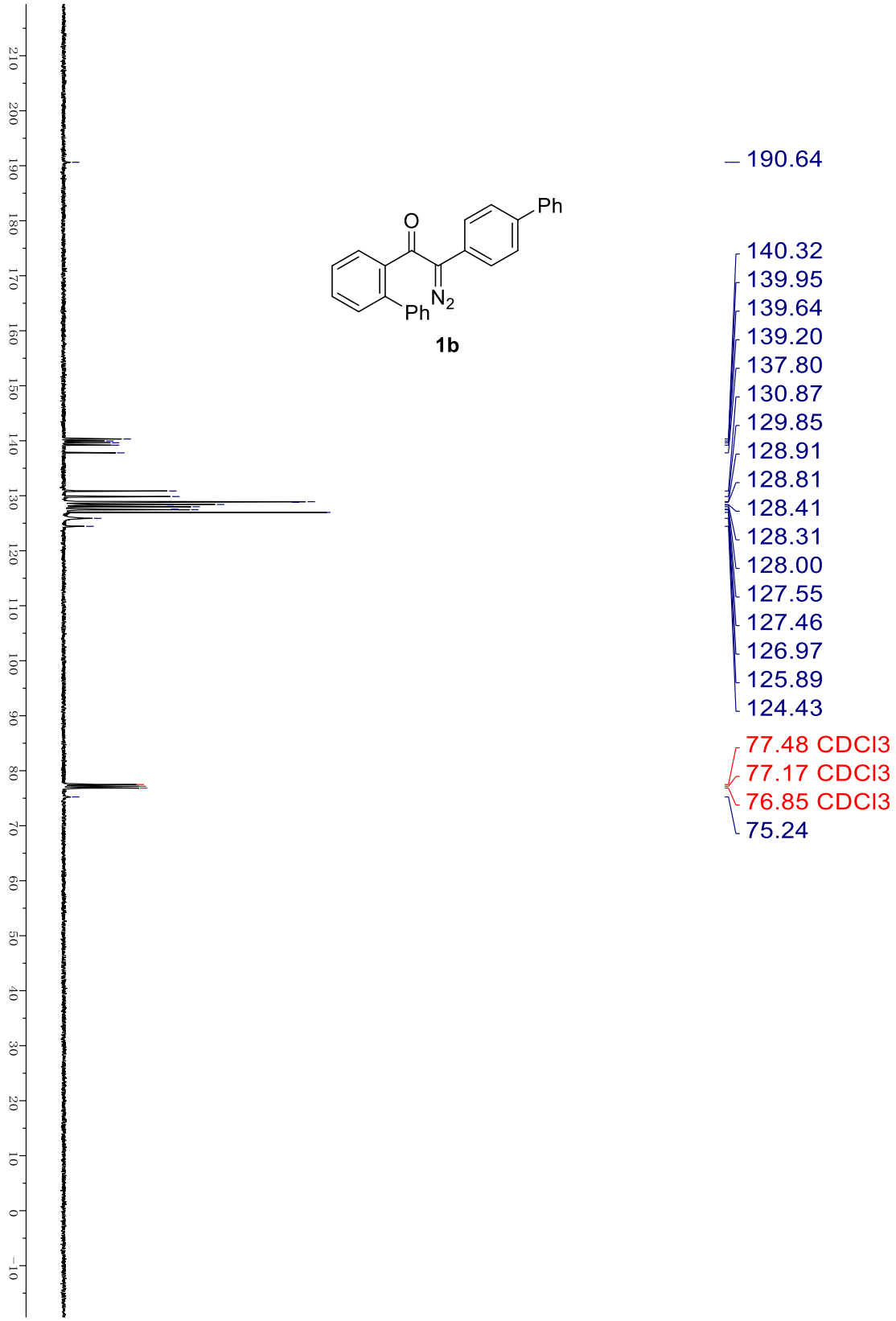
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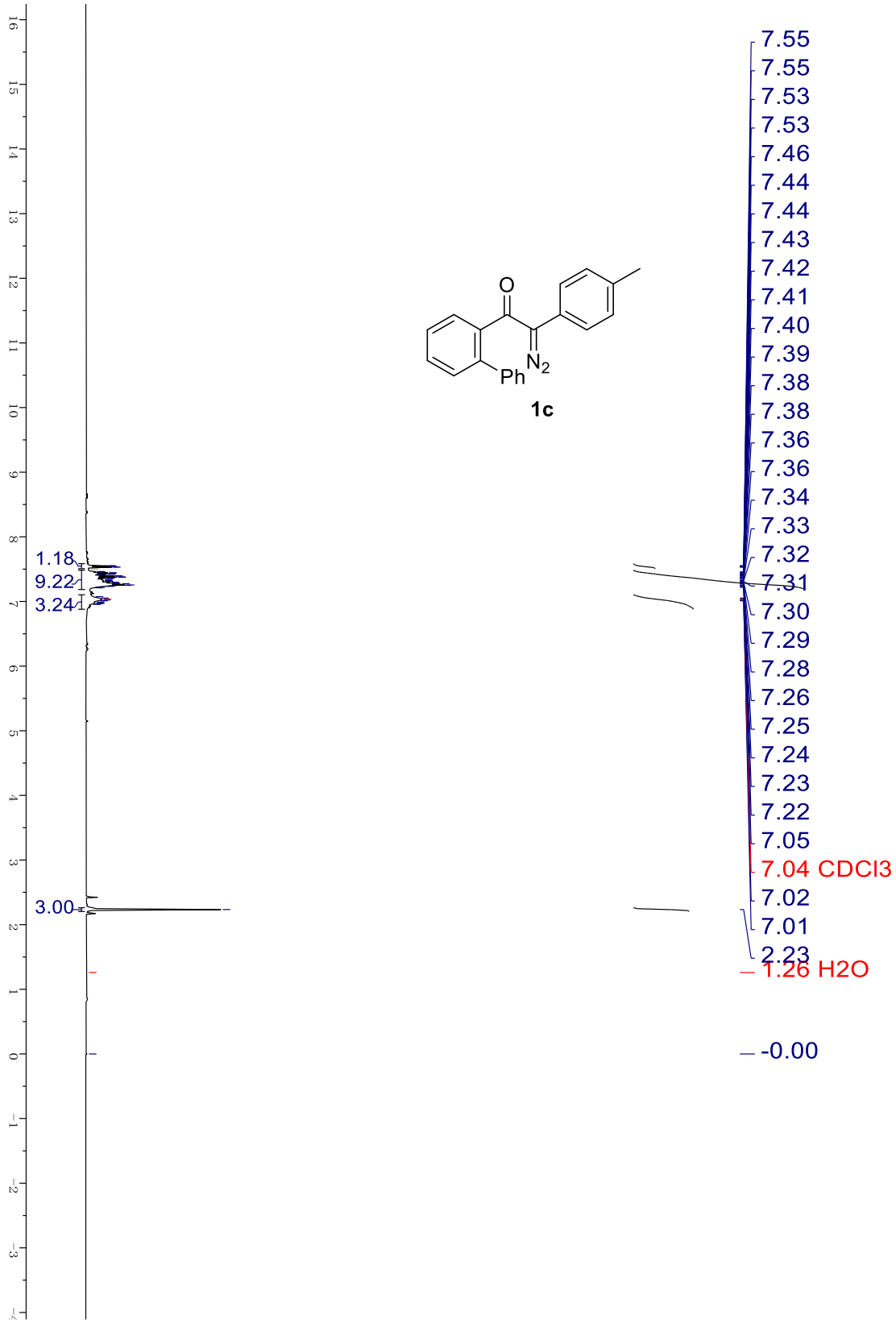
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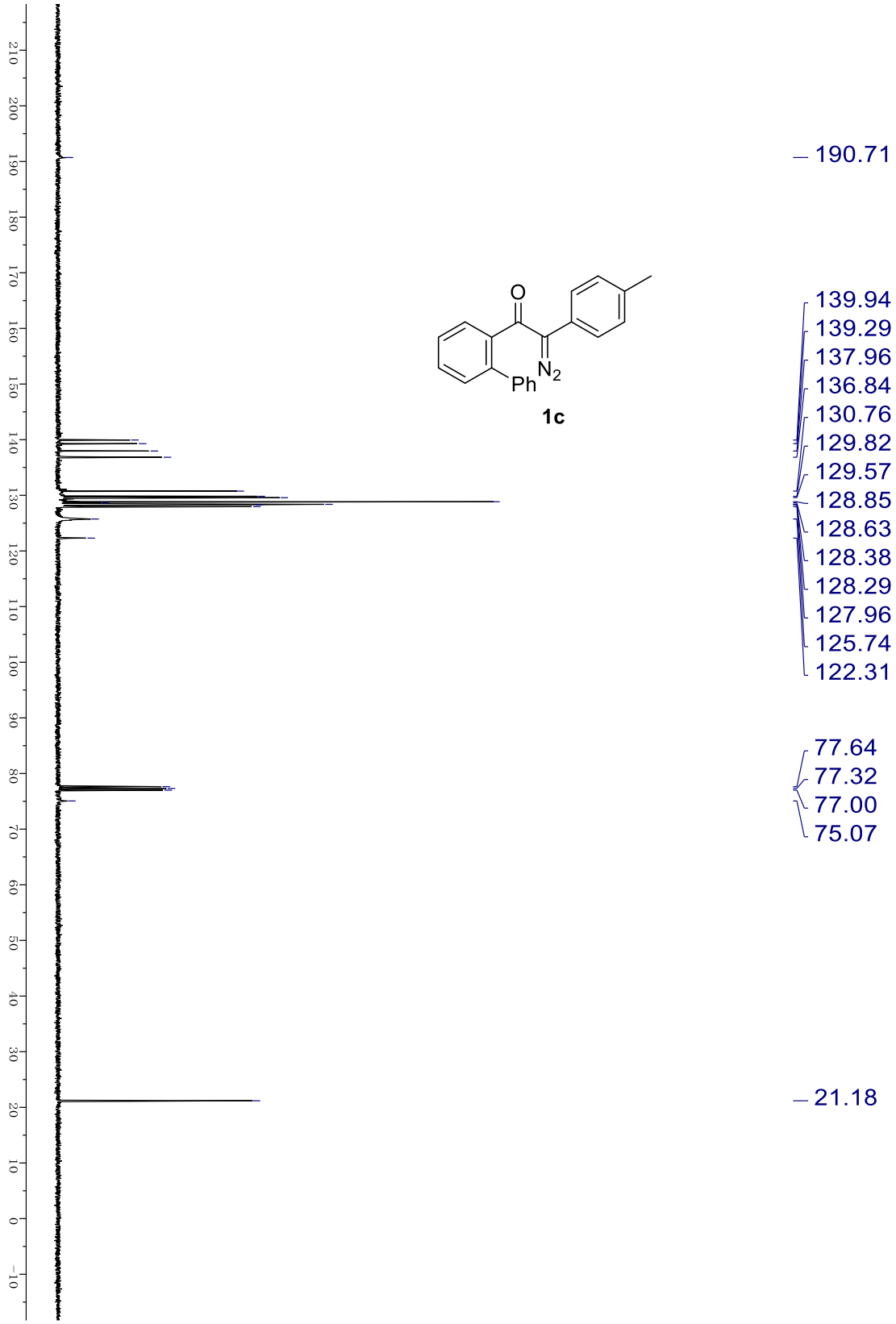
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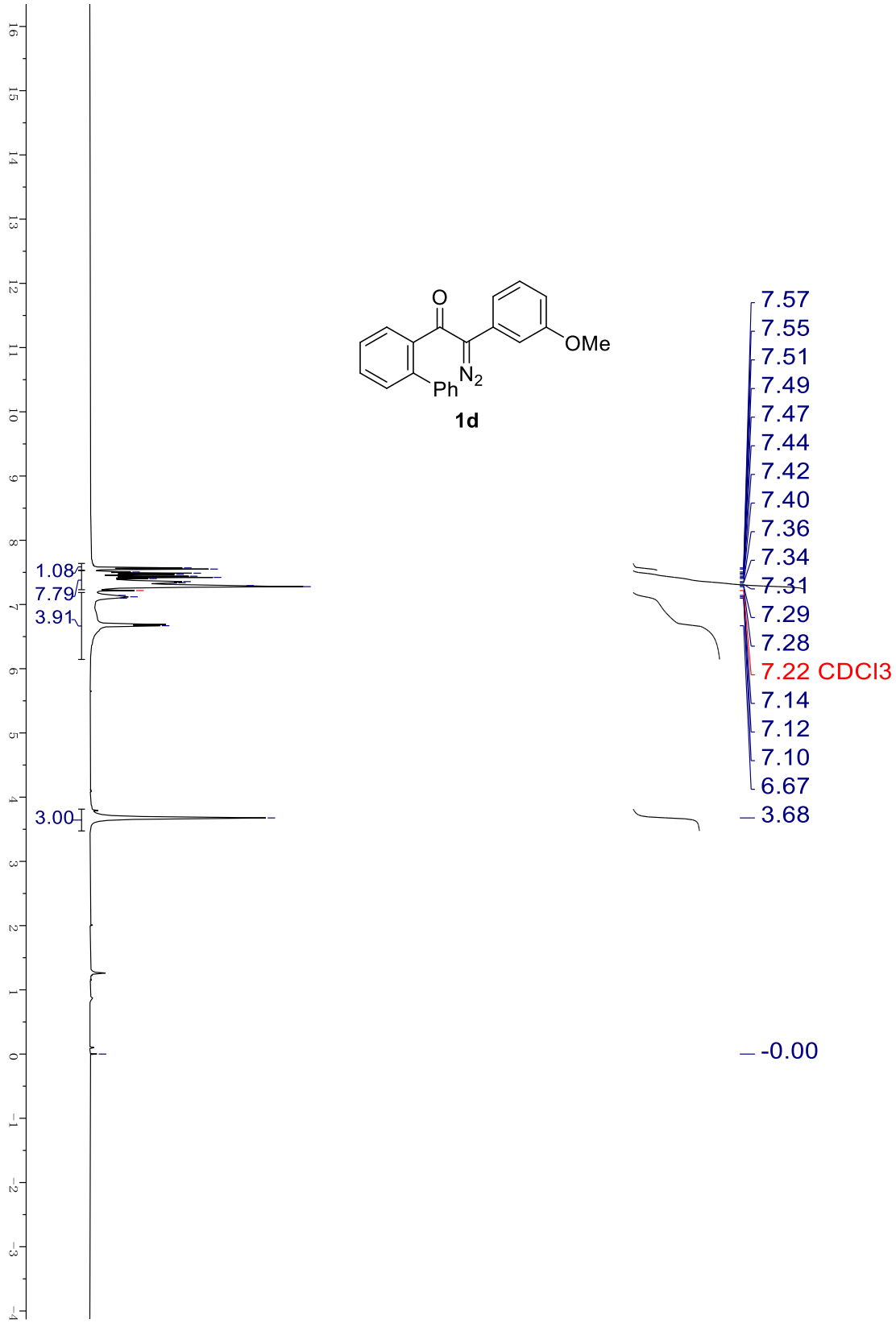
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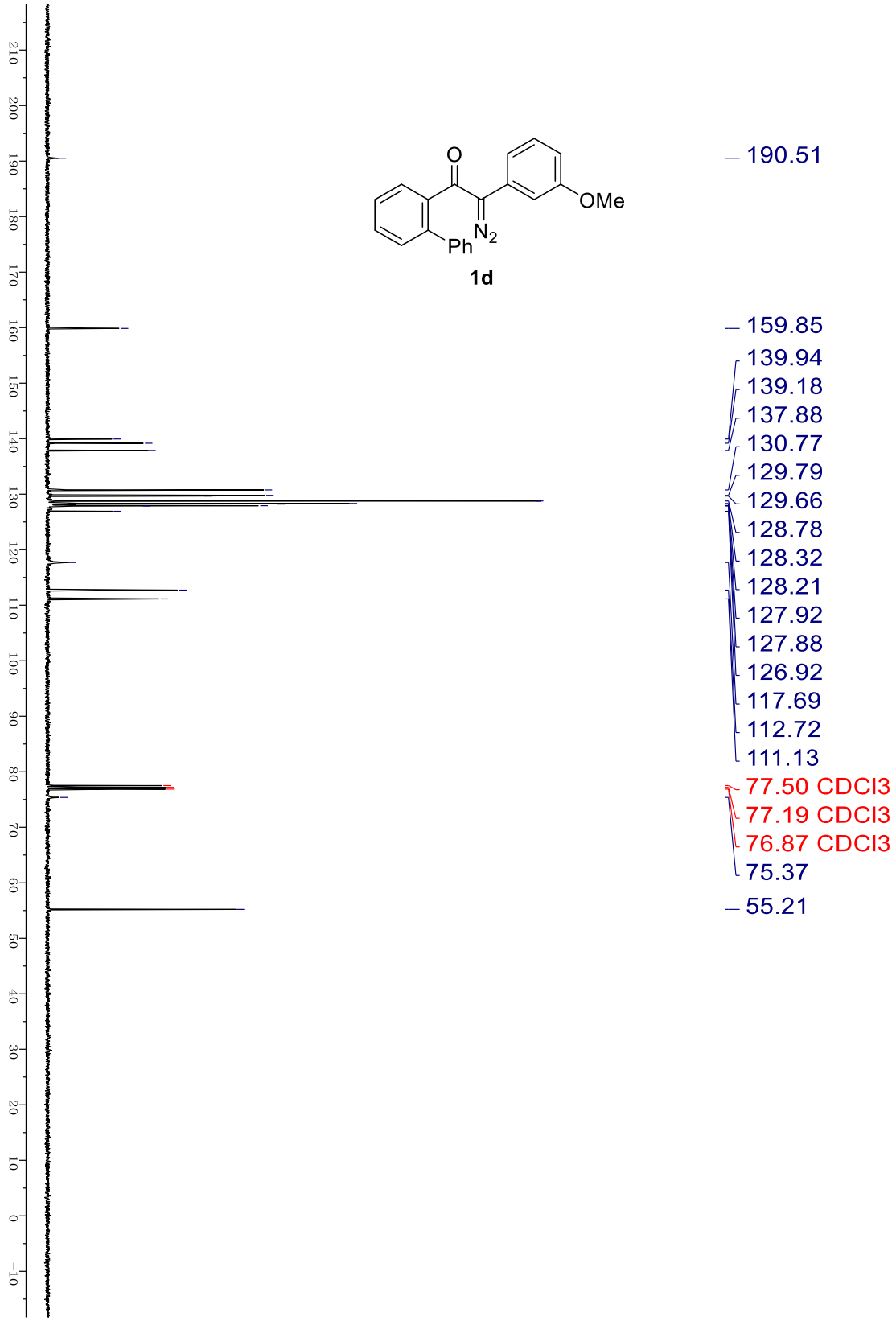
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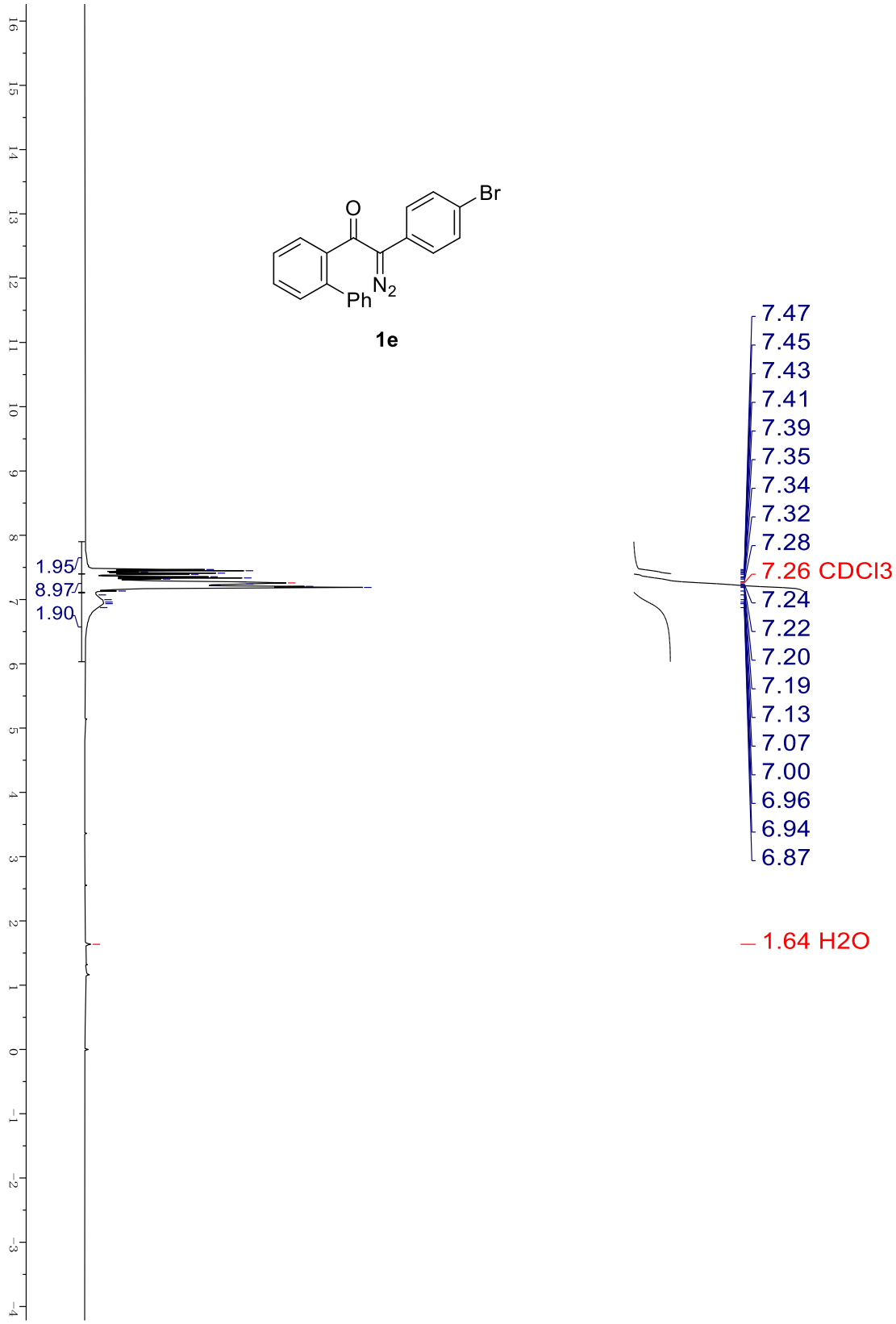
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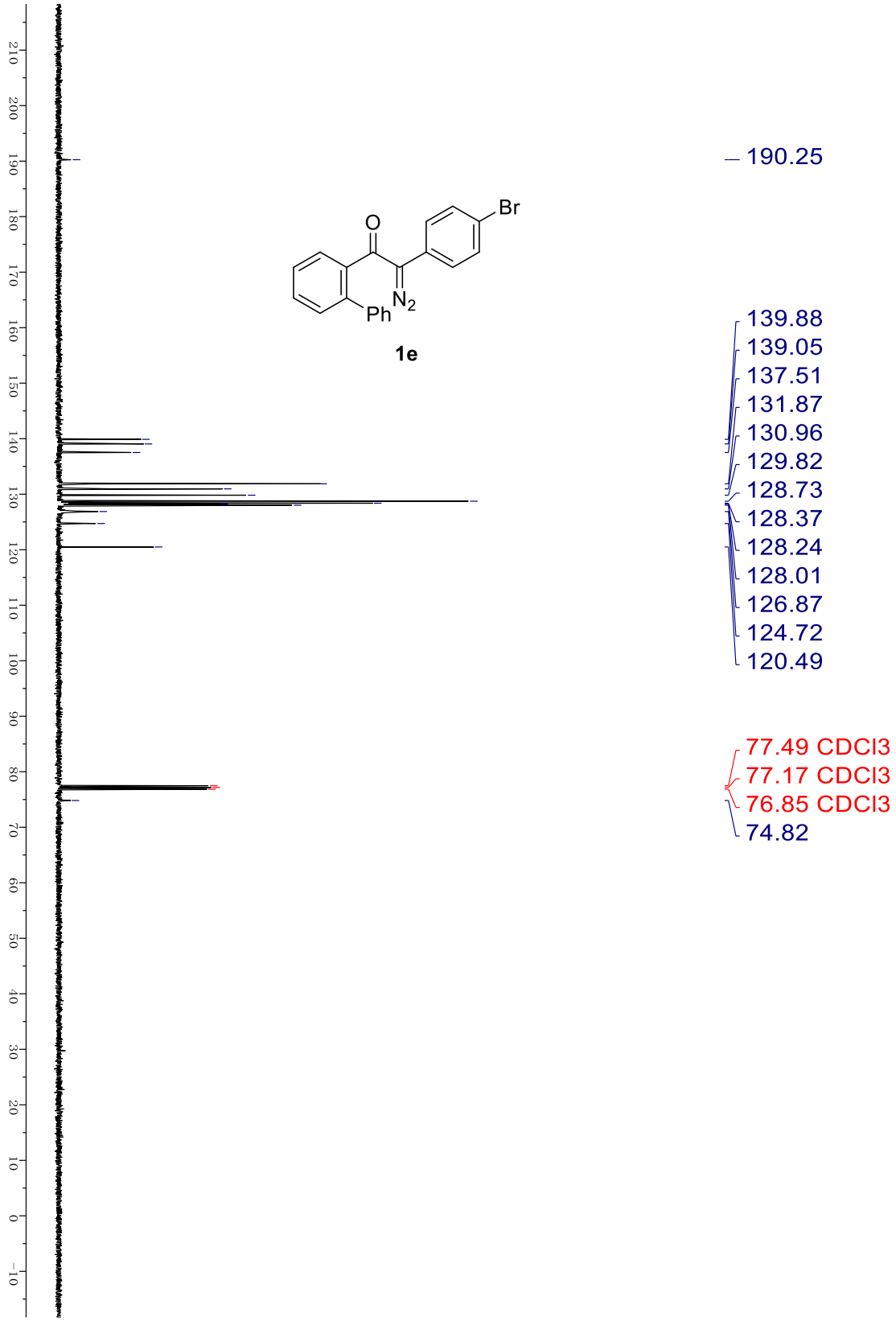
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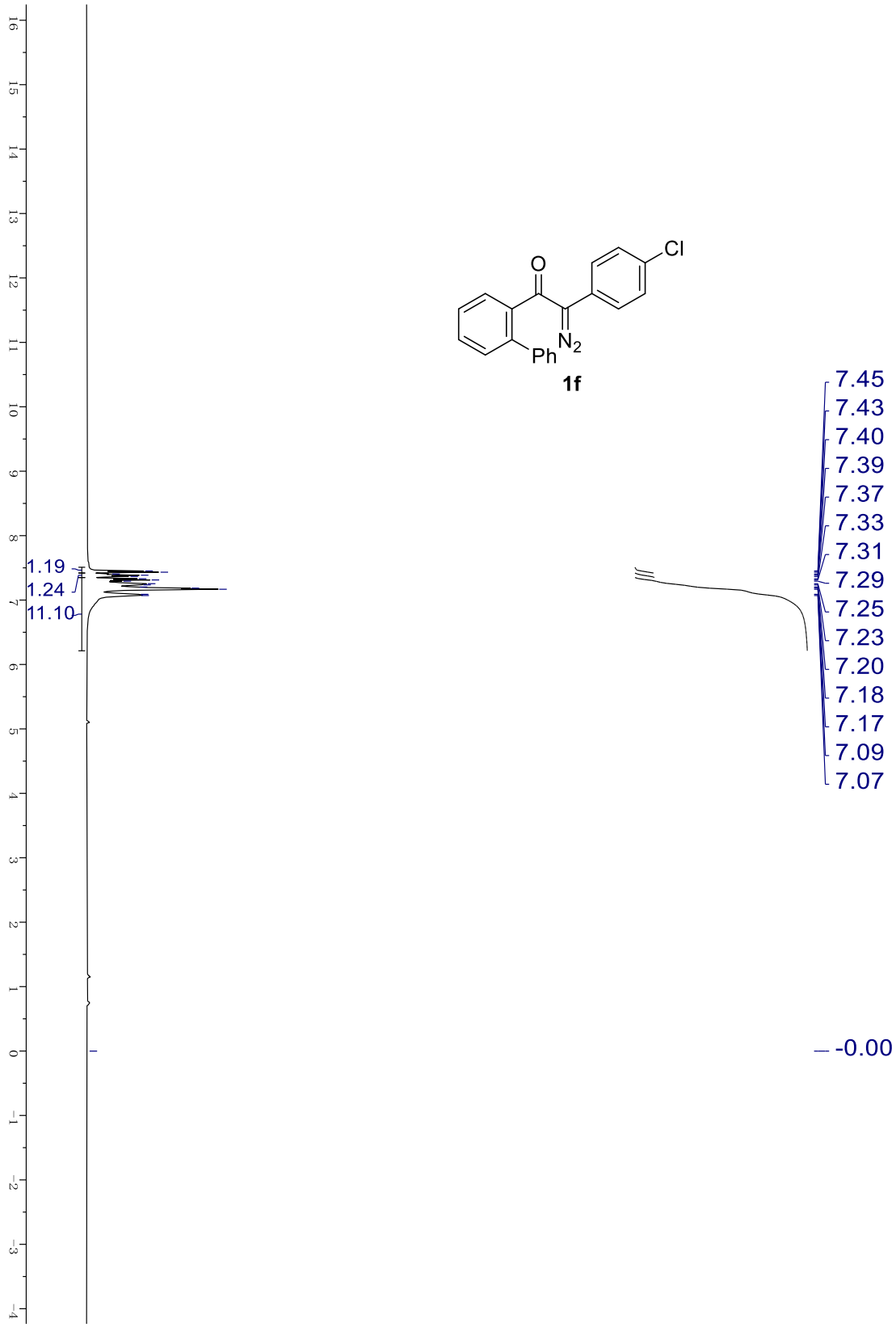
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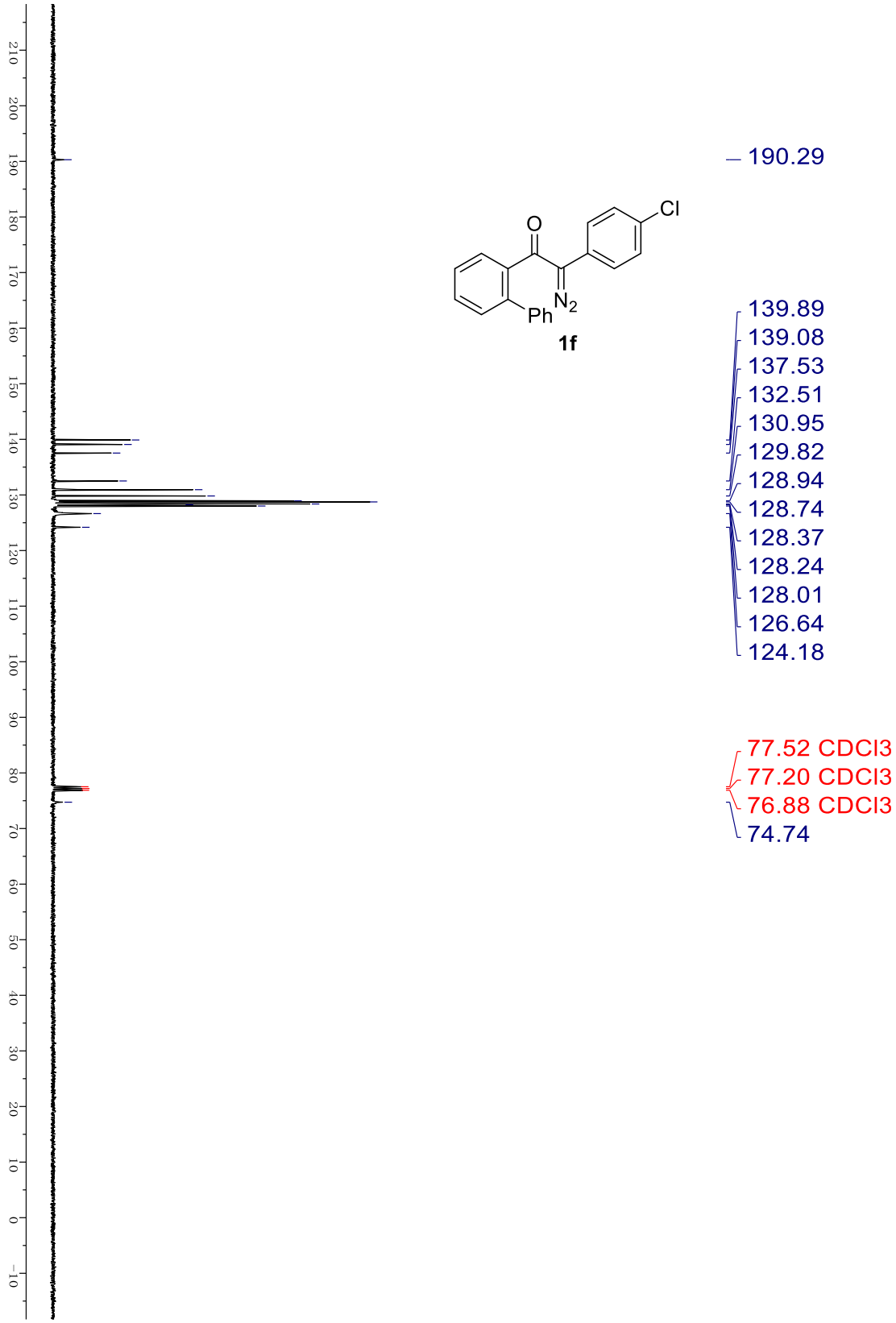
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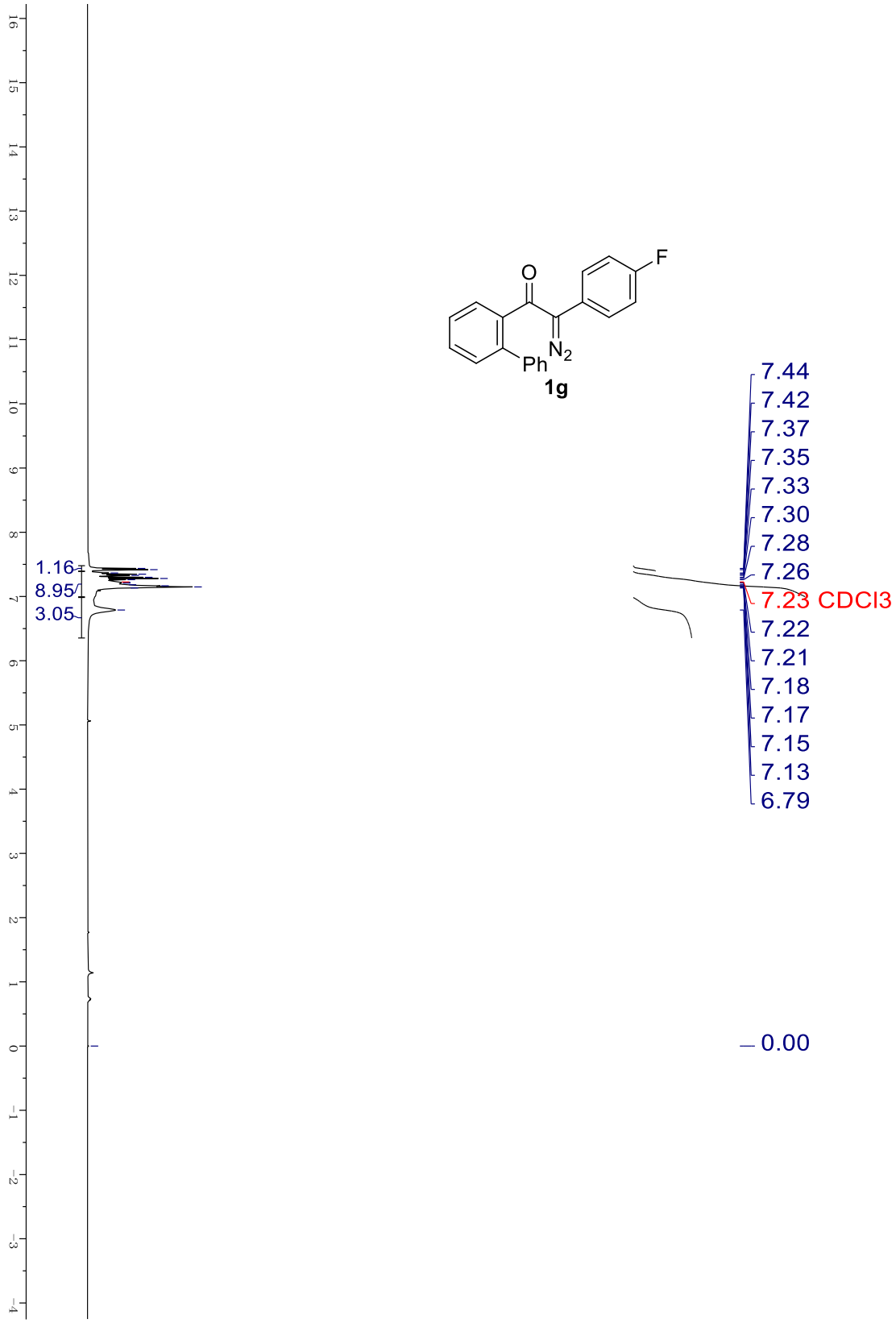
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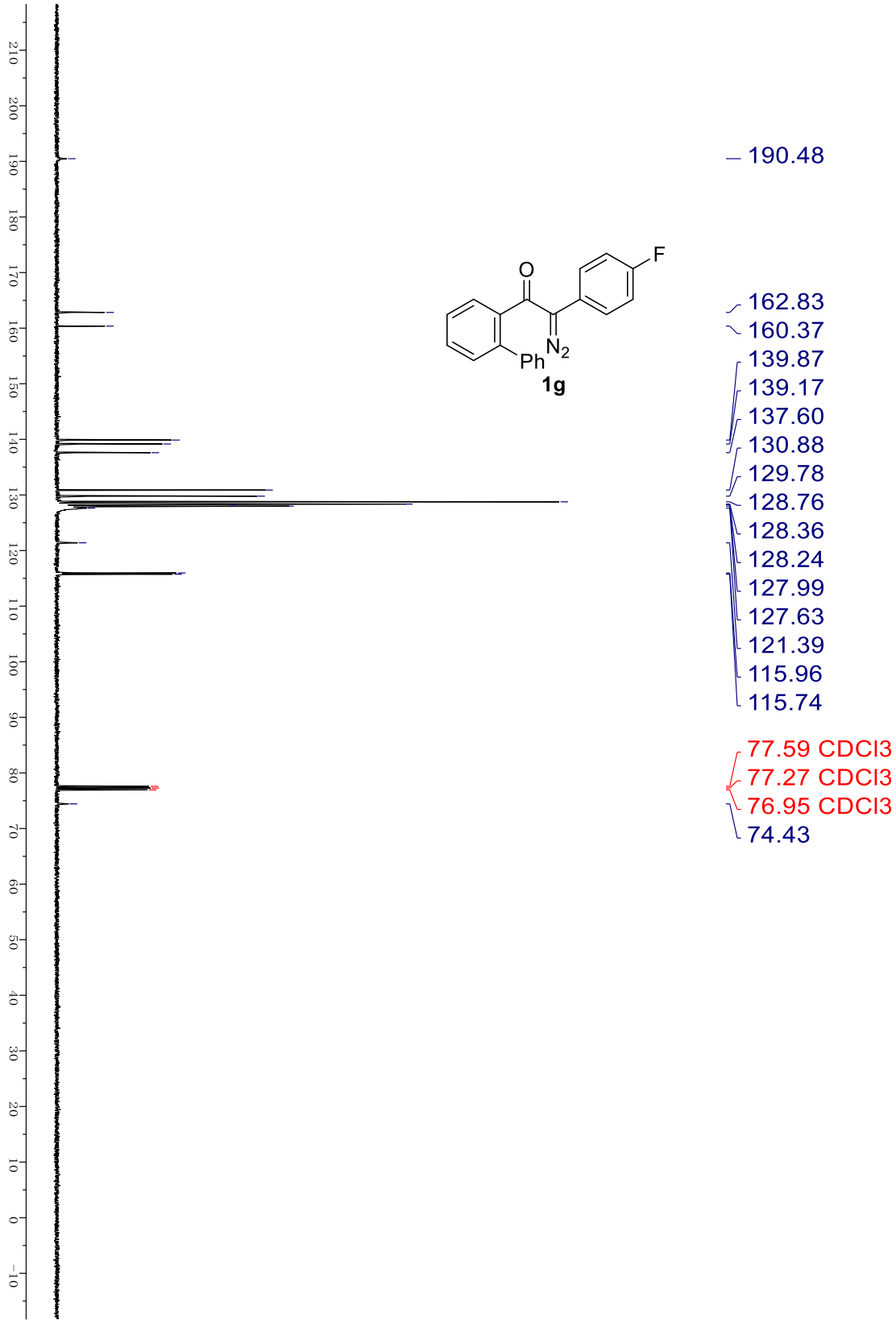
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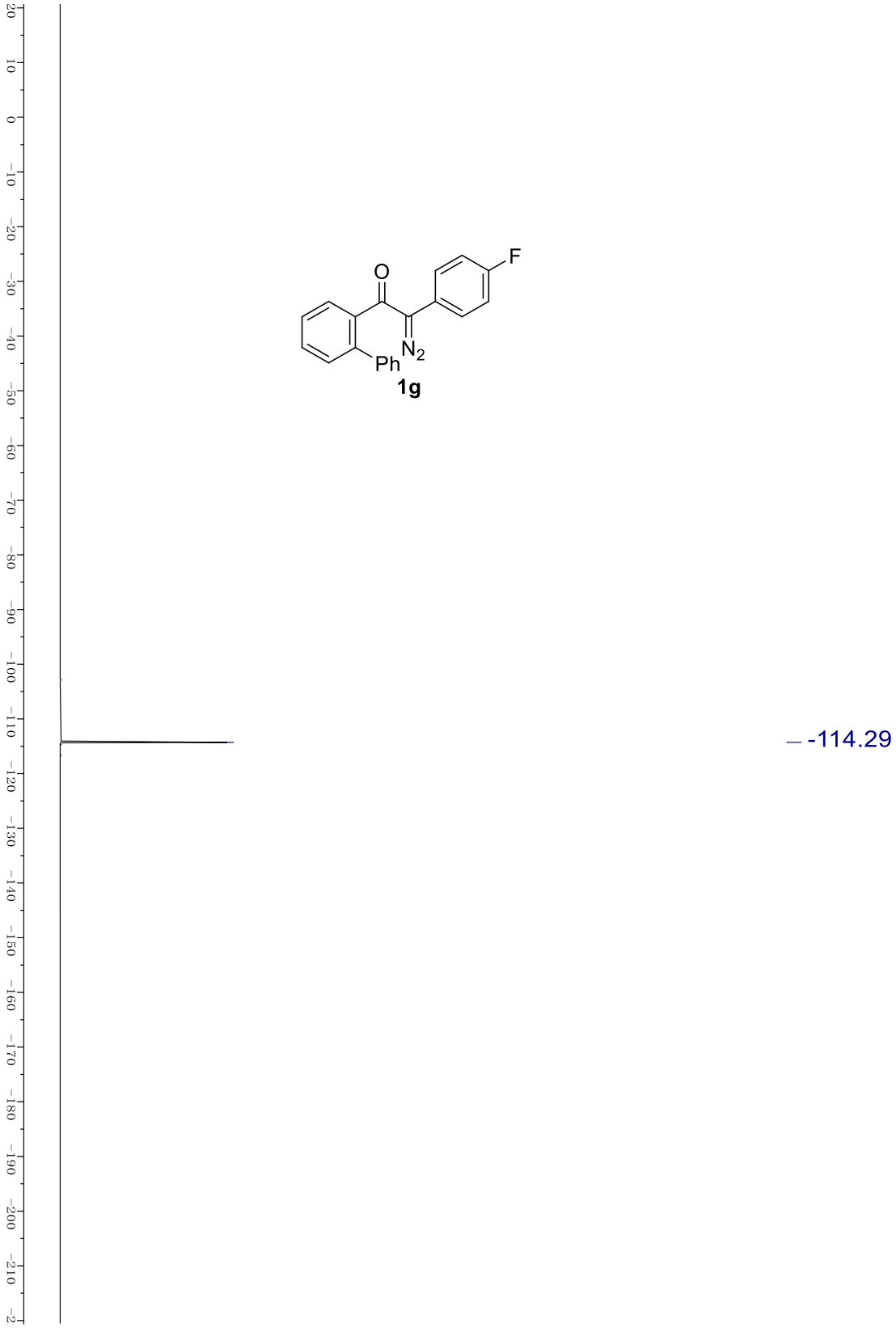
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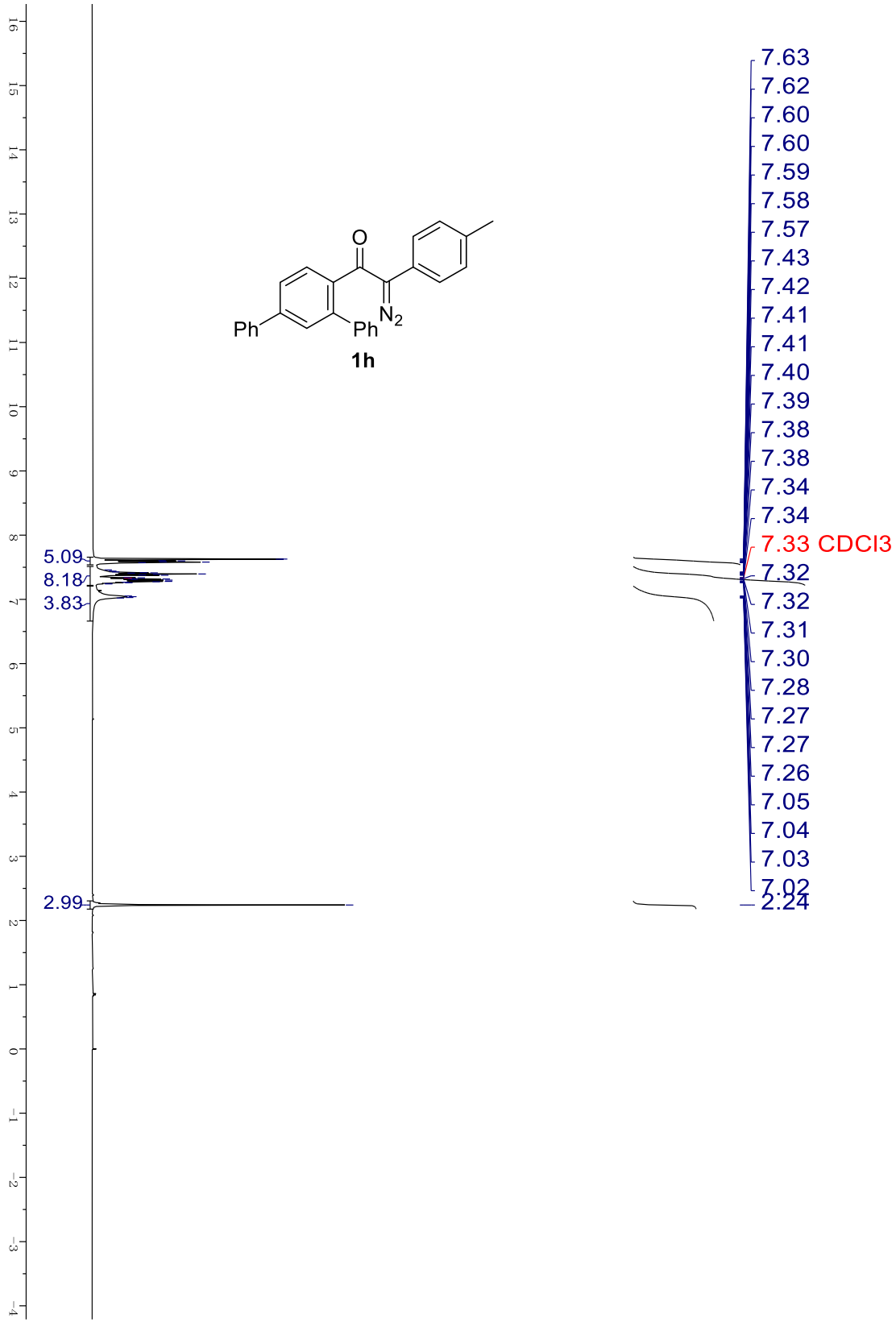
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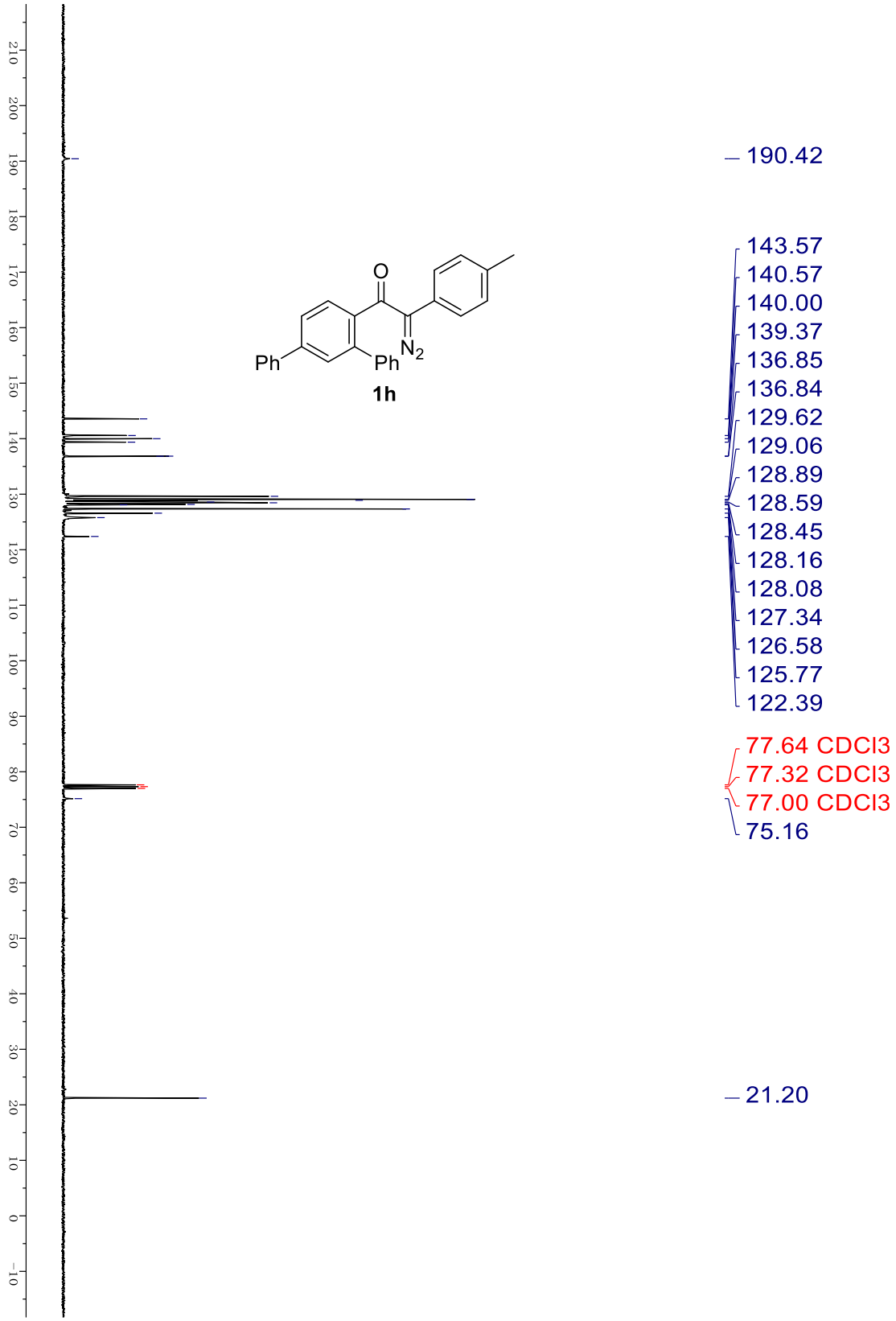
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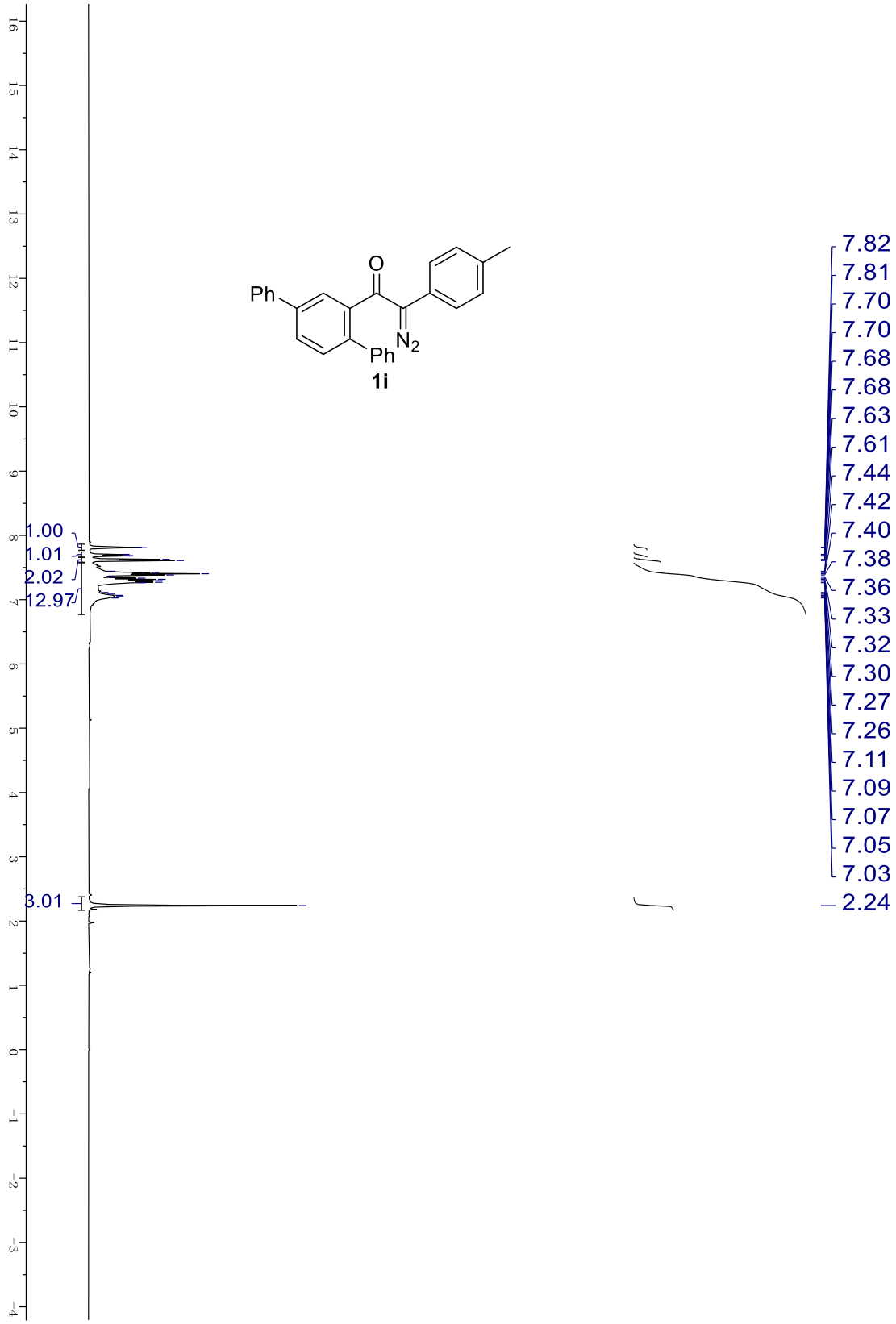
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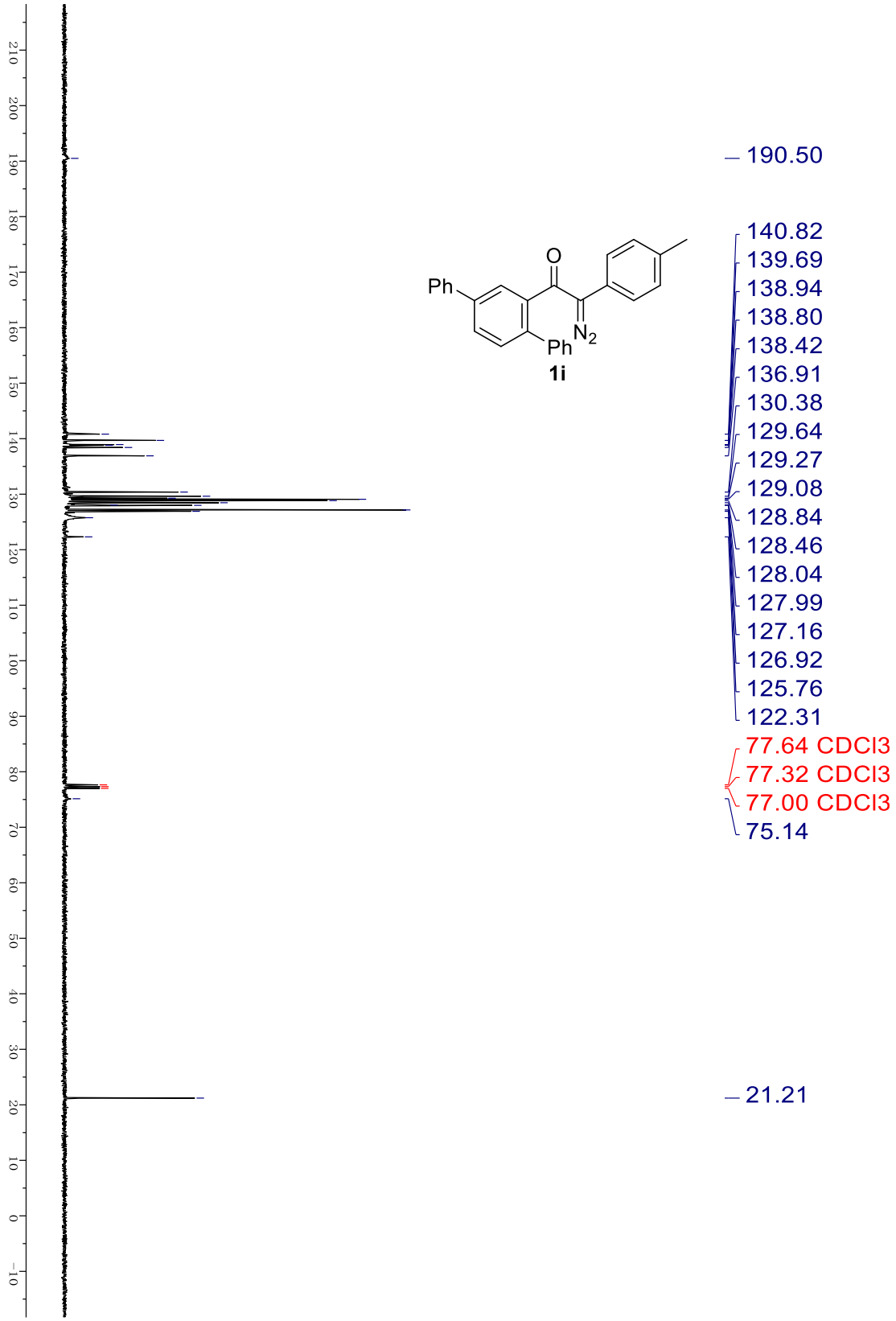
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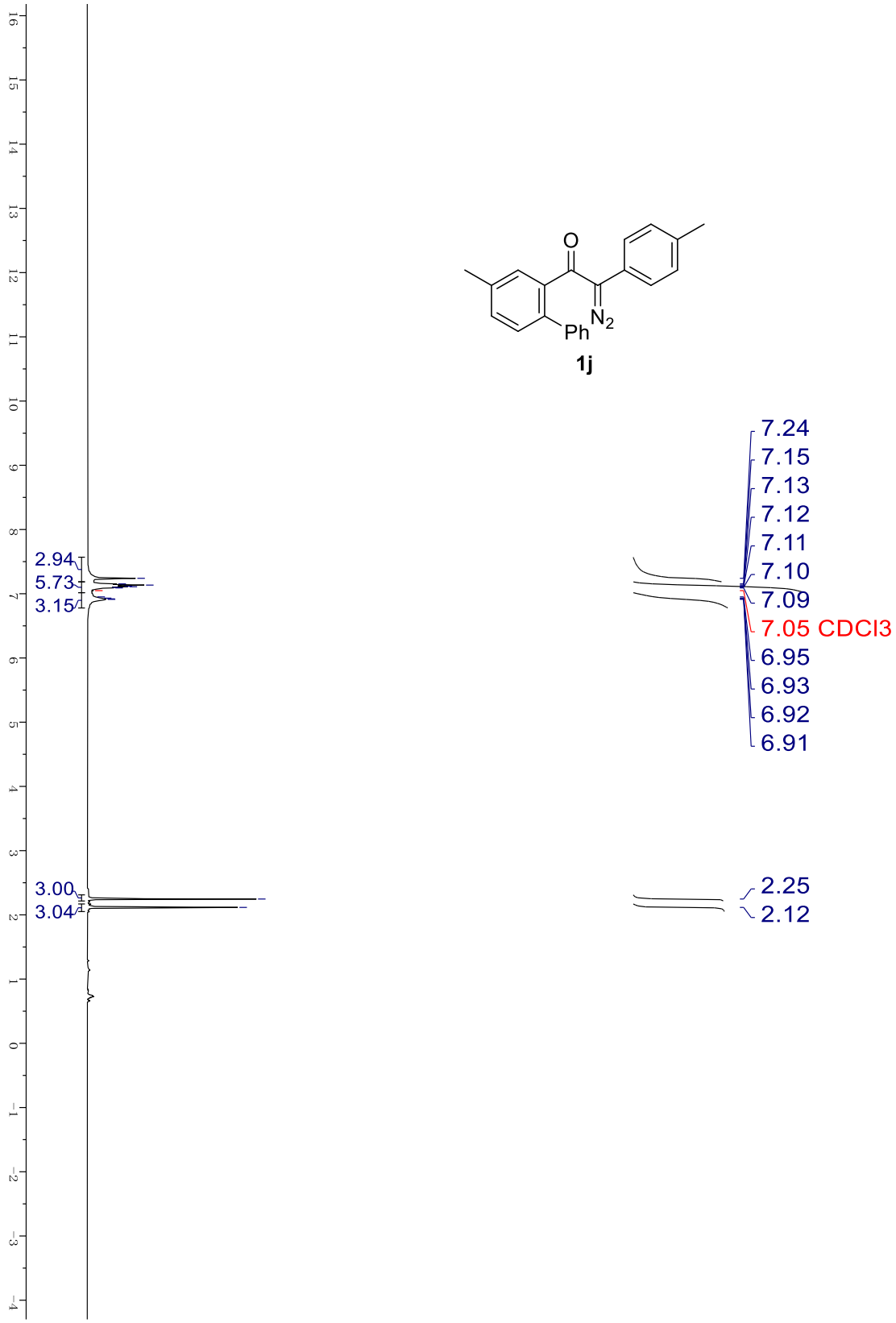
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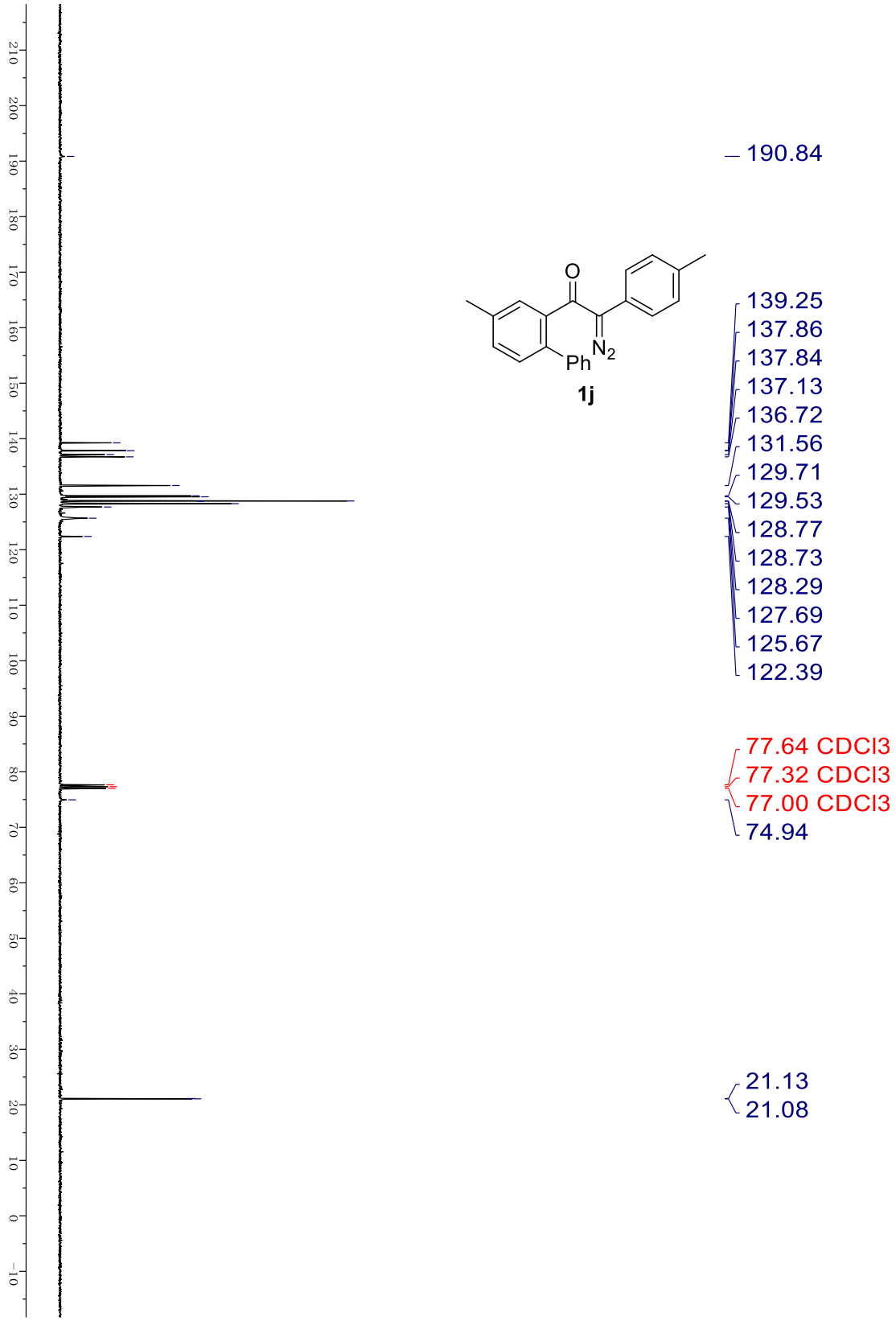
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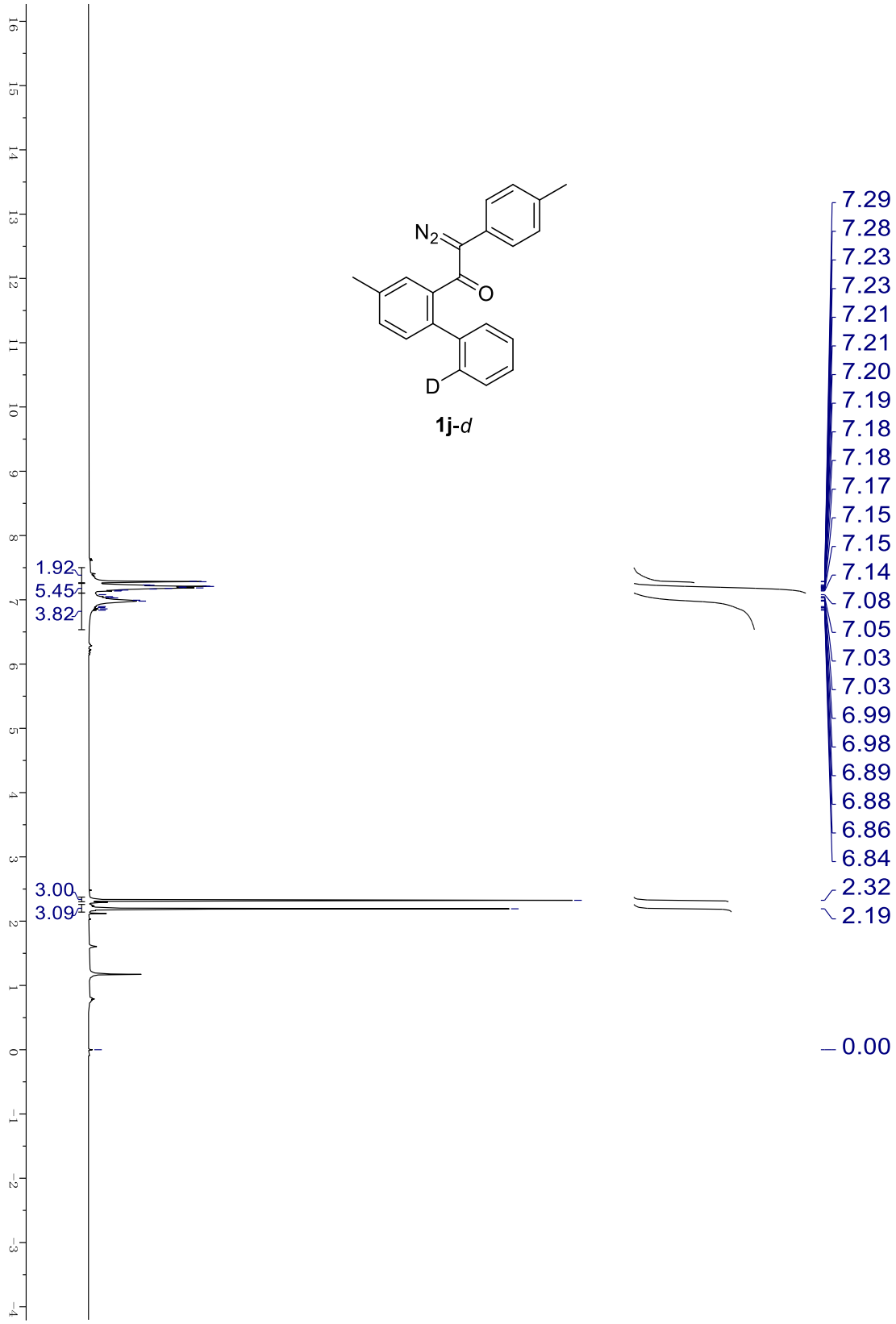
1j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7.18
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7.15
7.15
7.14
7.08
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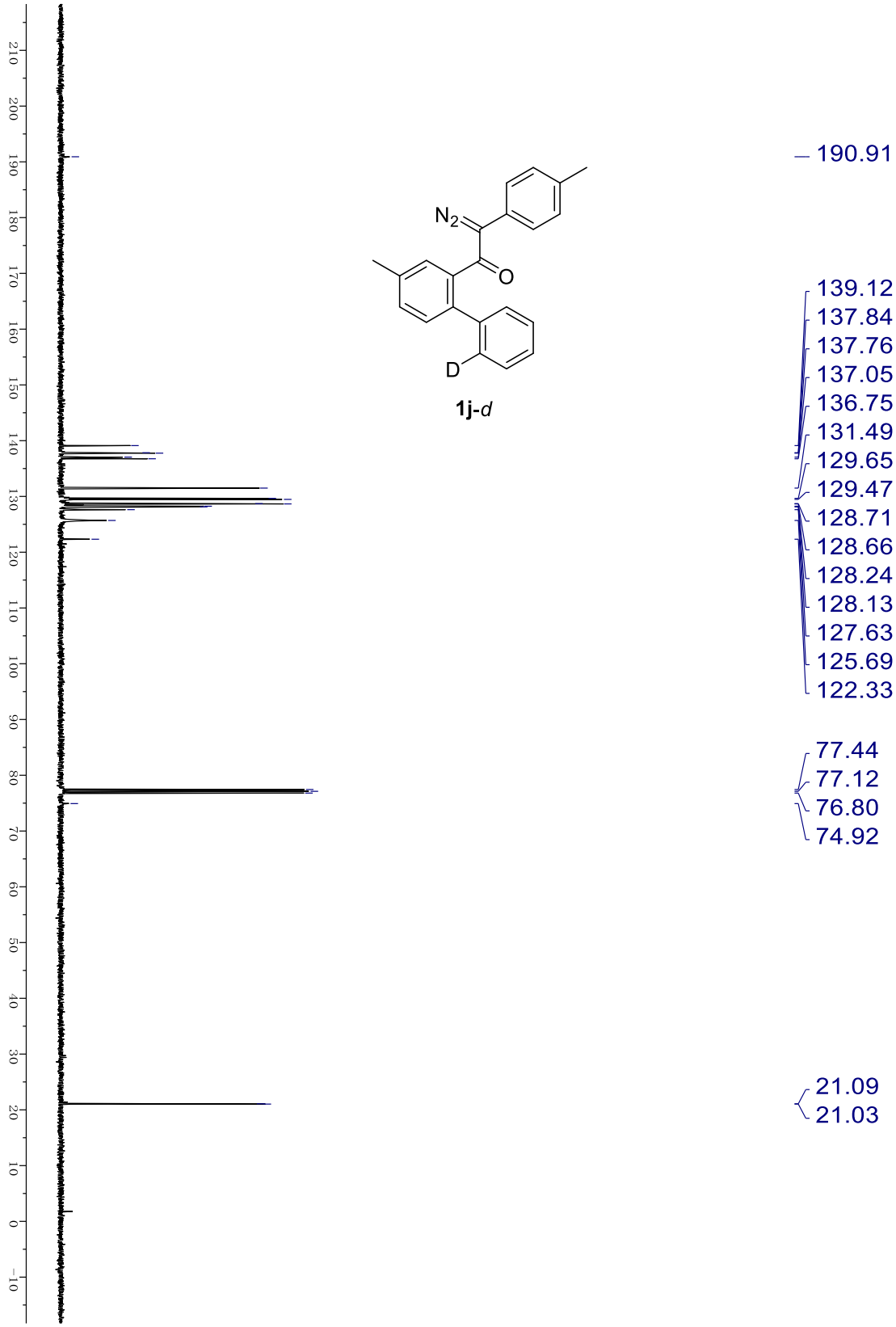
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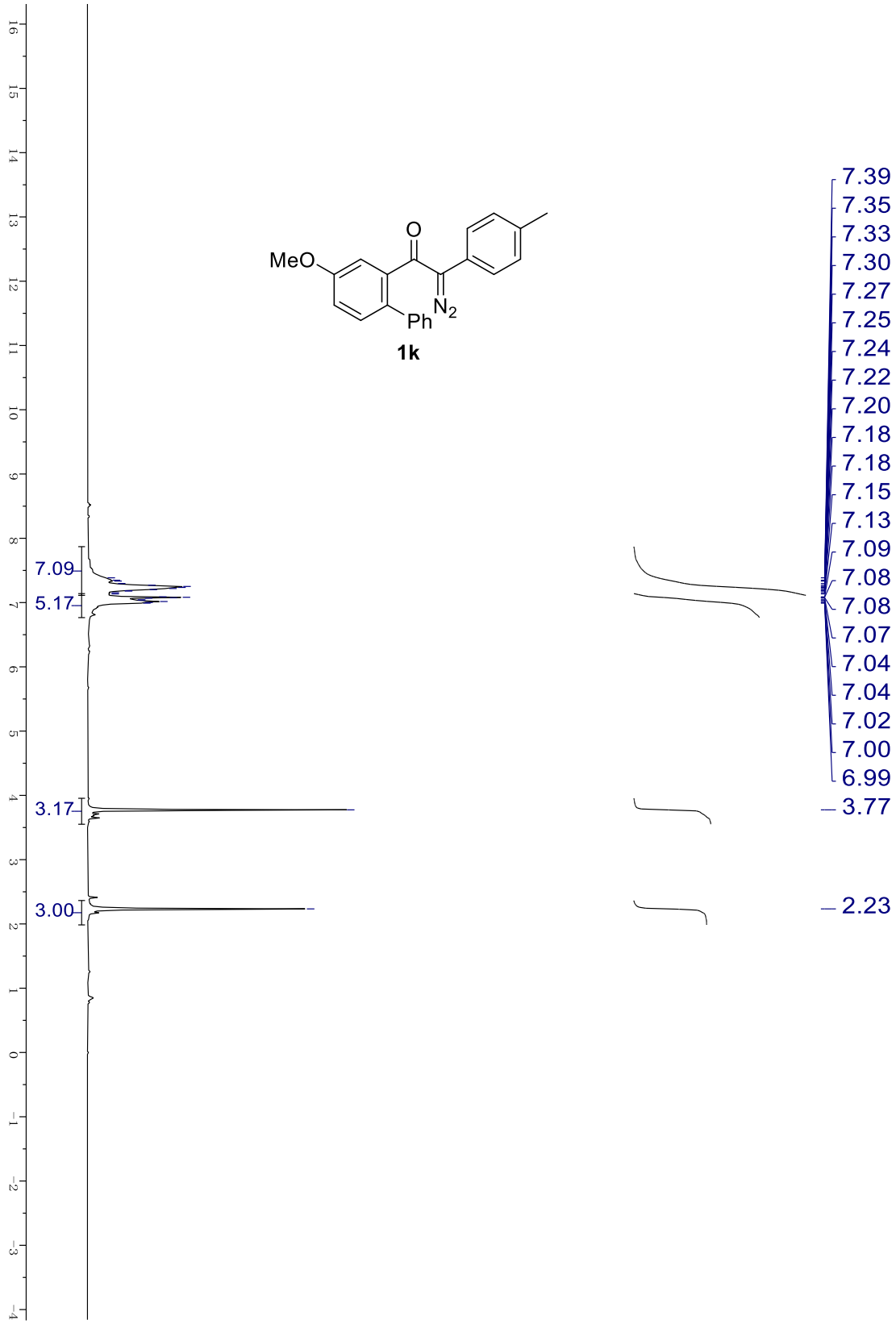
21.03

1j-*d*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7.27
7.25
7.24
7.22
7.20
7.18
7.18
7.15
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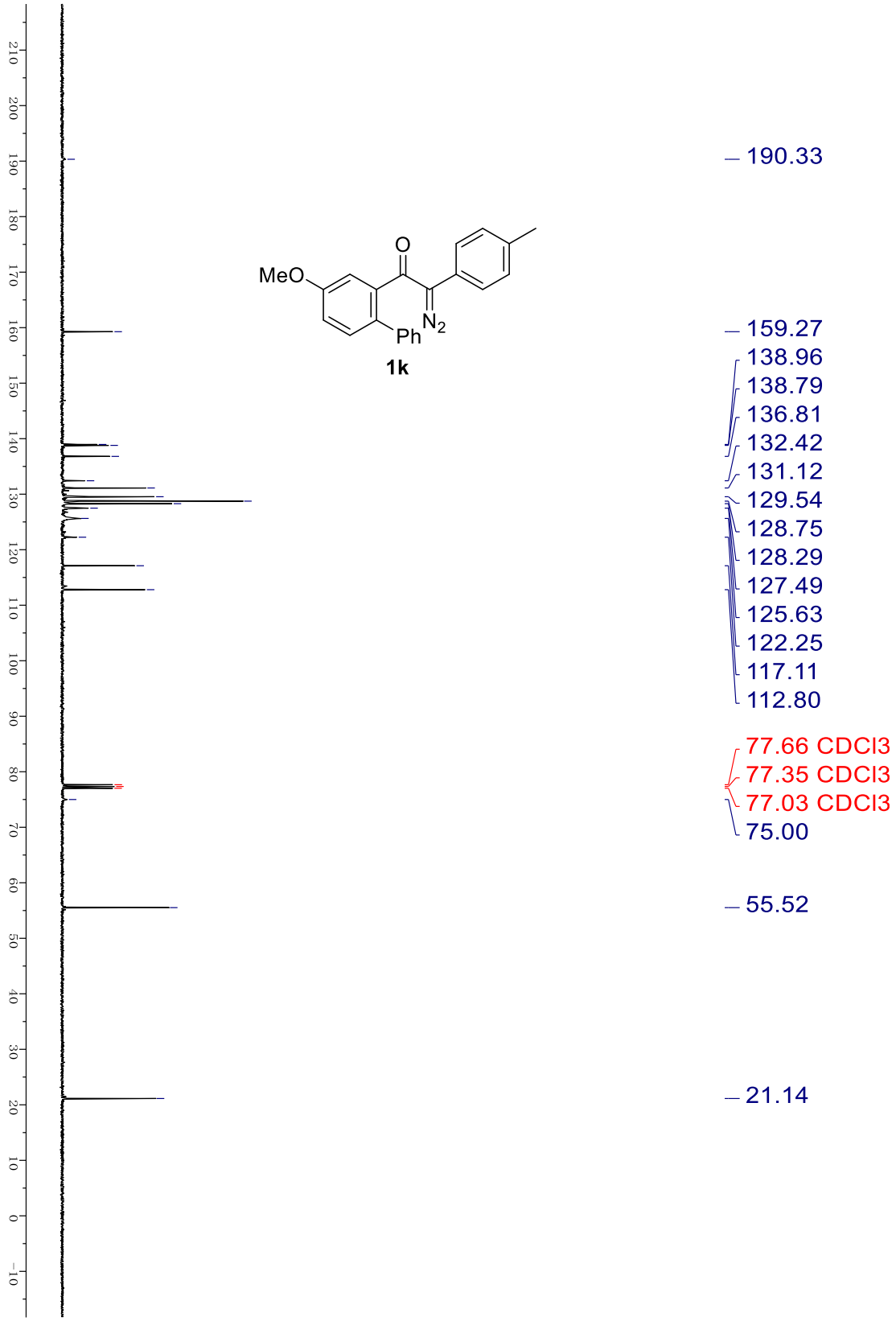
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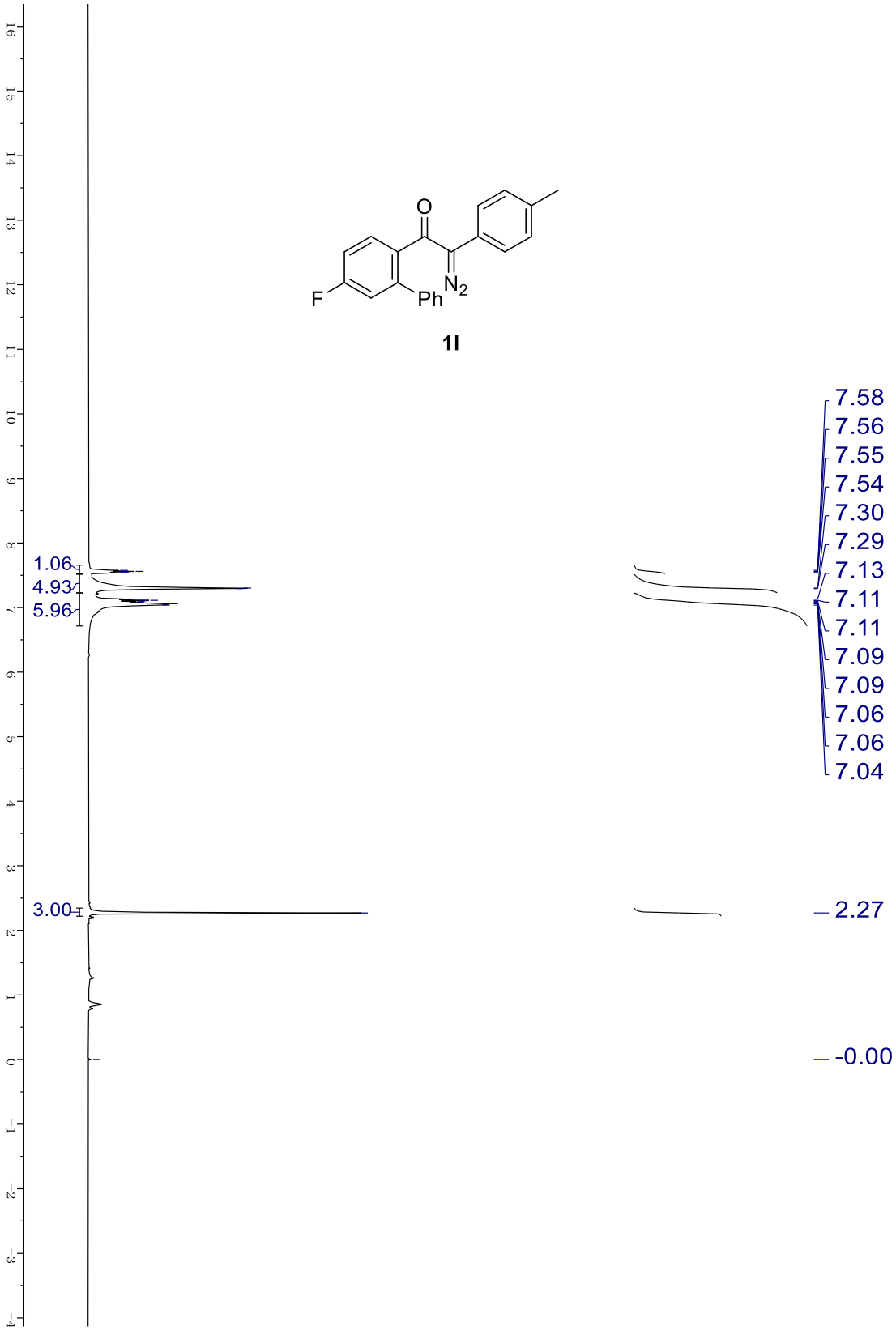
21.14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7.13
7.11
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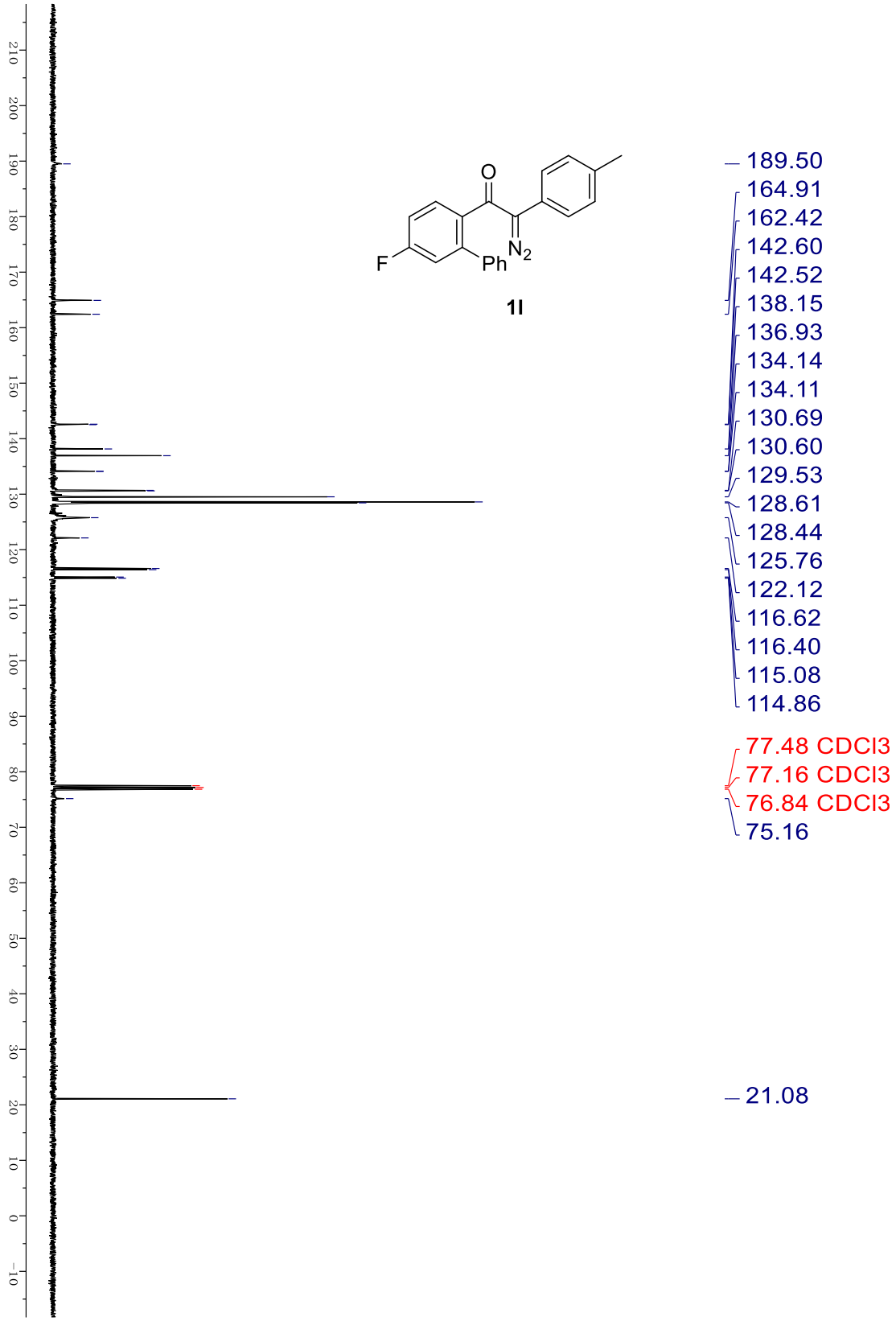
-0.00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F
Ph
1l
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162.42
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142.52
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130.69
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128.44
125.76
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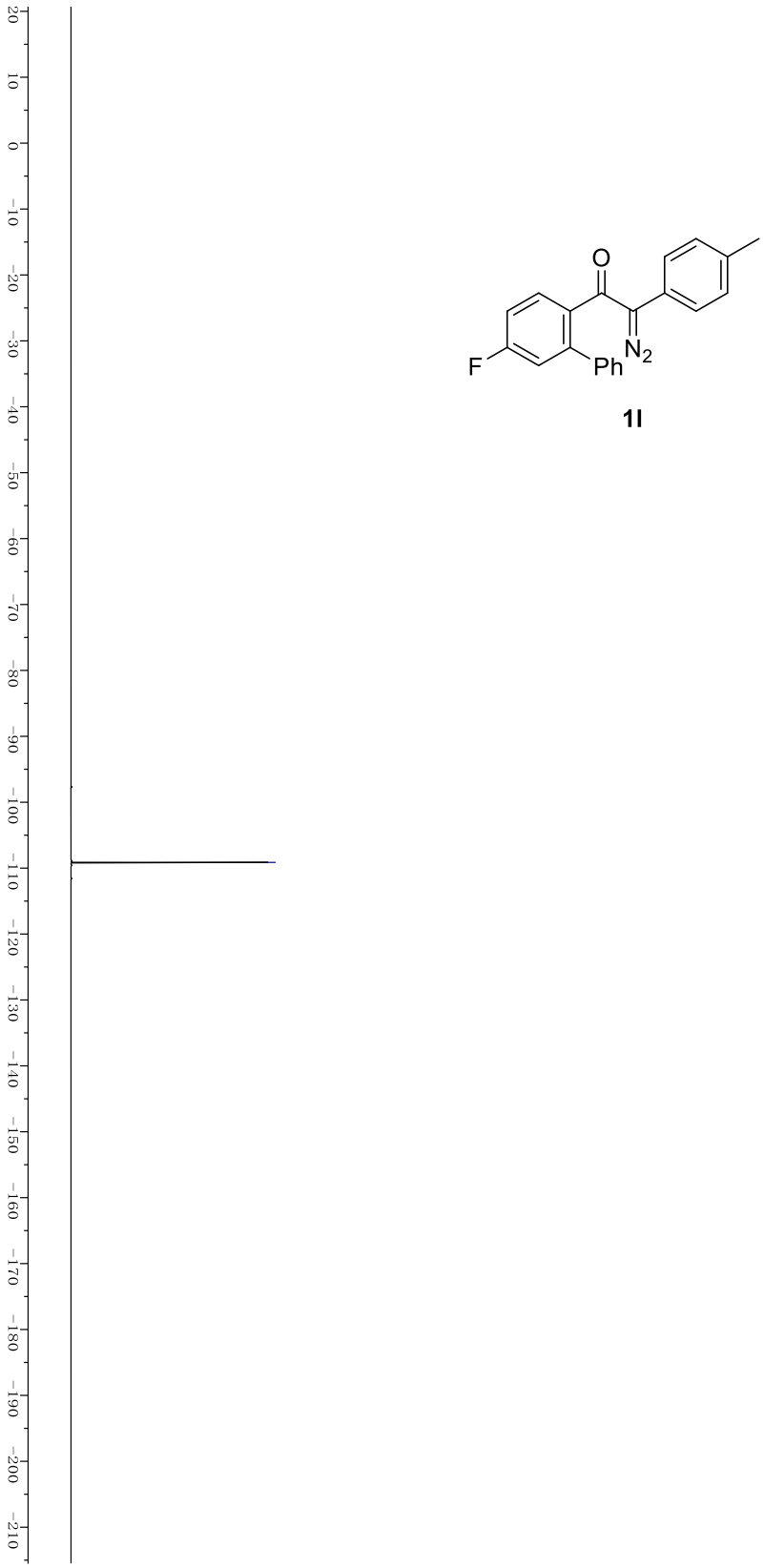
75.16
21.08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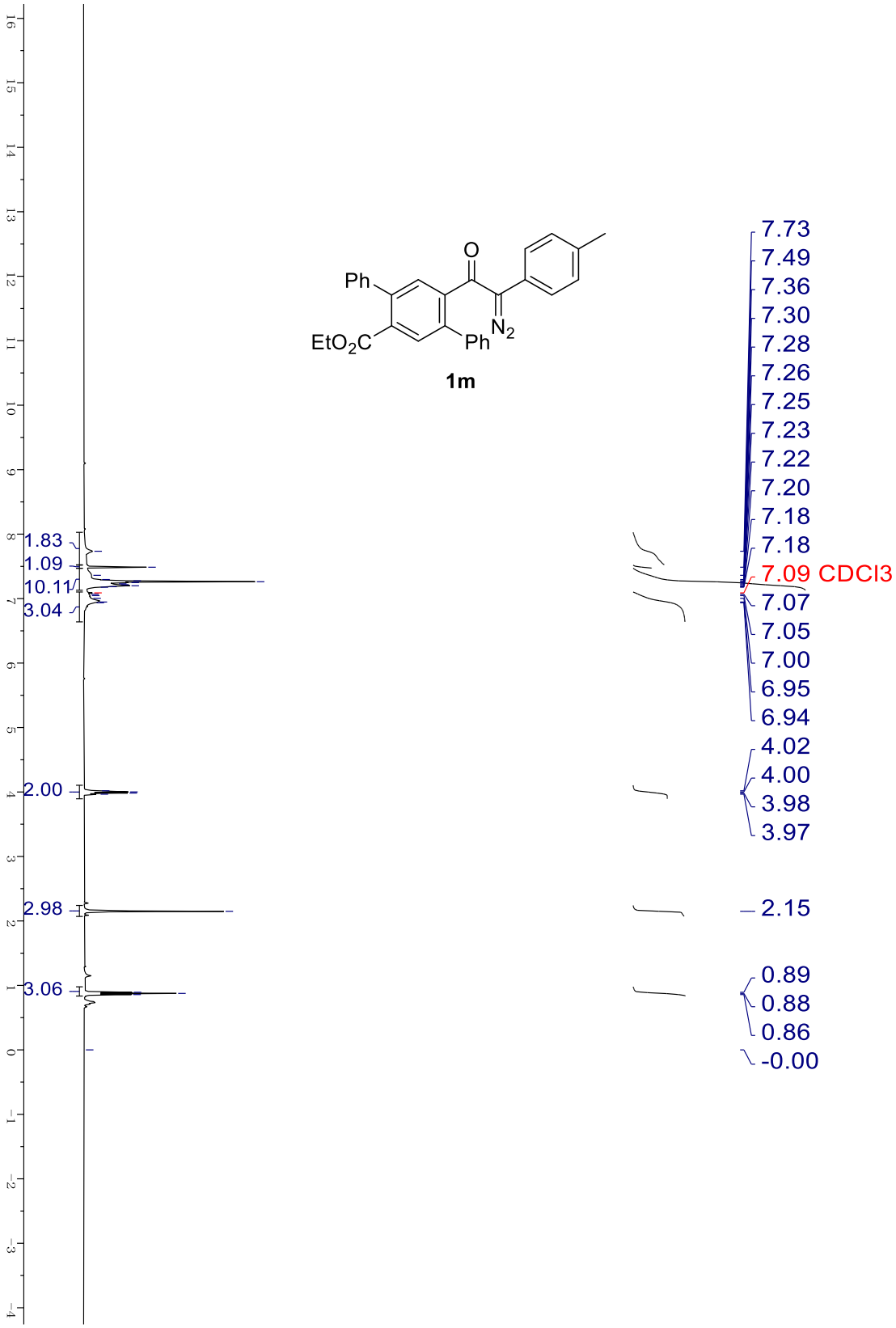
N2
F
Ph
-109.13

1l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Ph
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EtO2C
Ph
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2.00
2.98
3.06
7.73
7.49
7.36
7.30
7.28
7.26
7.25
7.23
7.22
7.20
7.18
7.18
7.09 CDCl3
7.07
7.05
7.00
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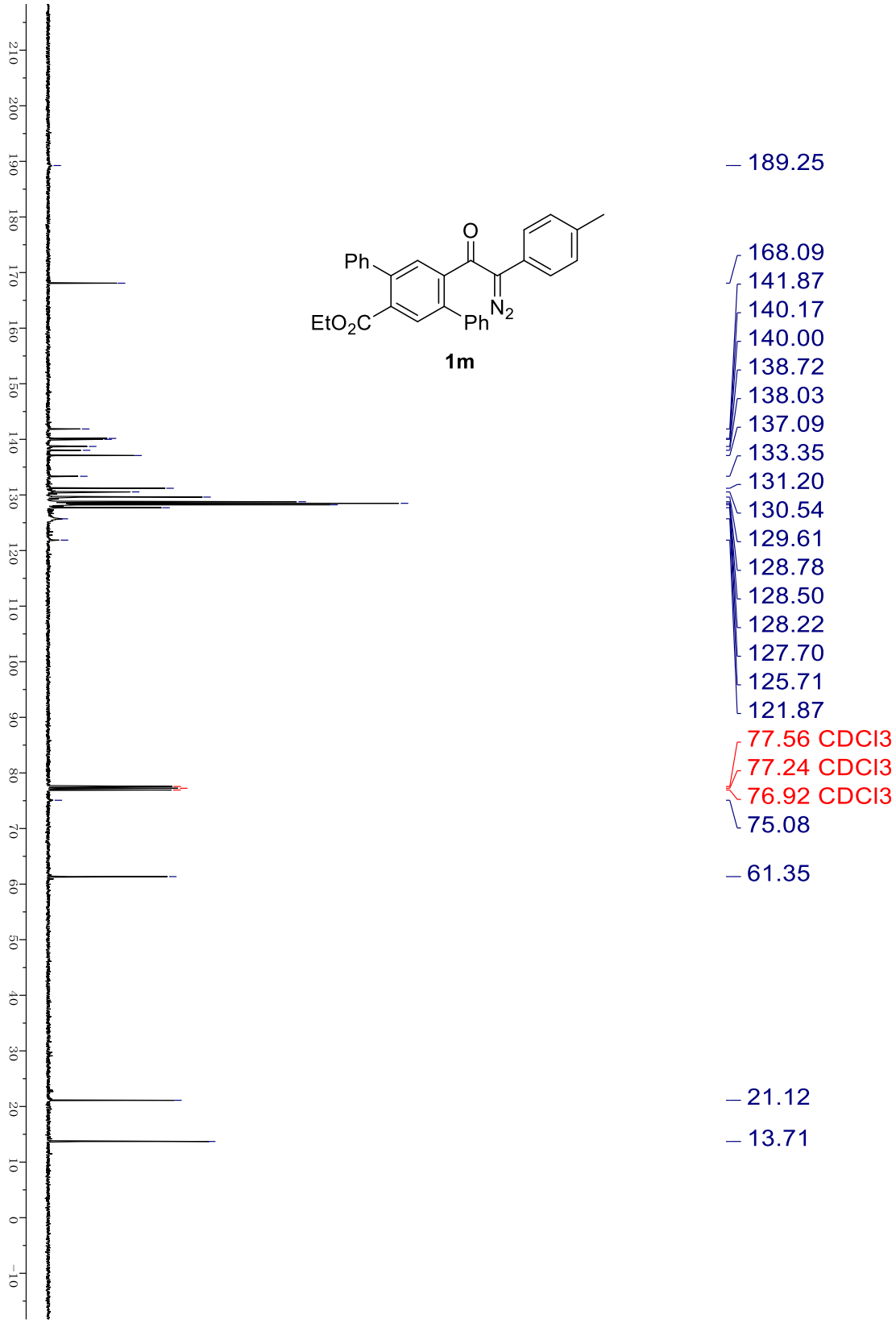
4.02
4.00
3.98
3.97
2.15
0.89
0.88
0.86
-0.00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128.50
128.22
127.70
125.71
121.87
77.56 CDCl3
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61.35
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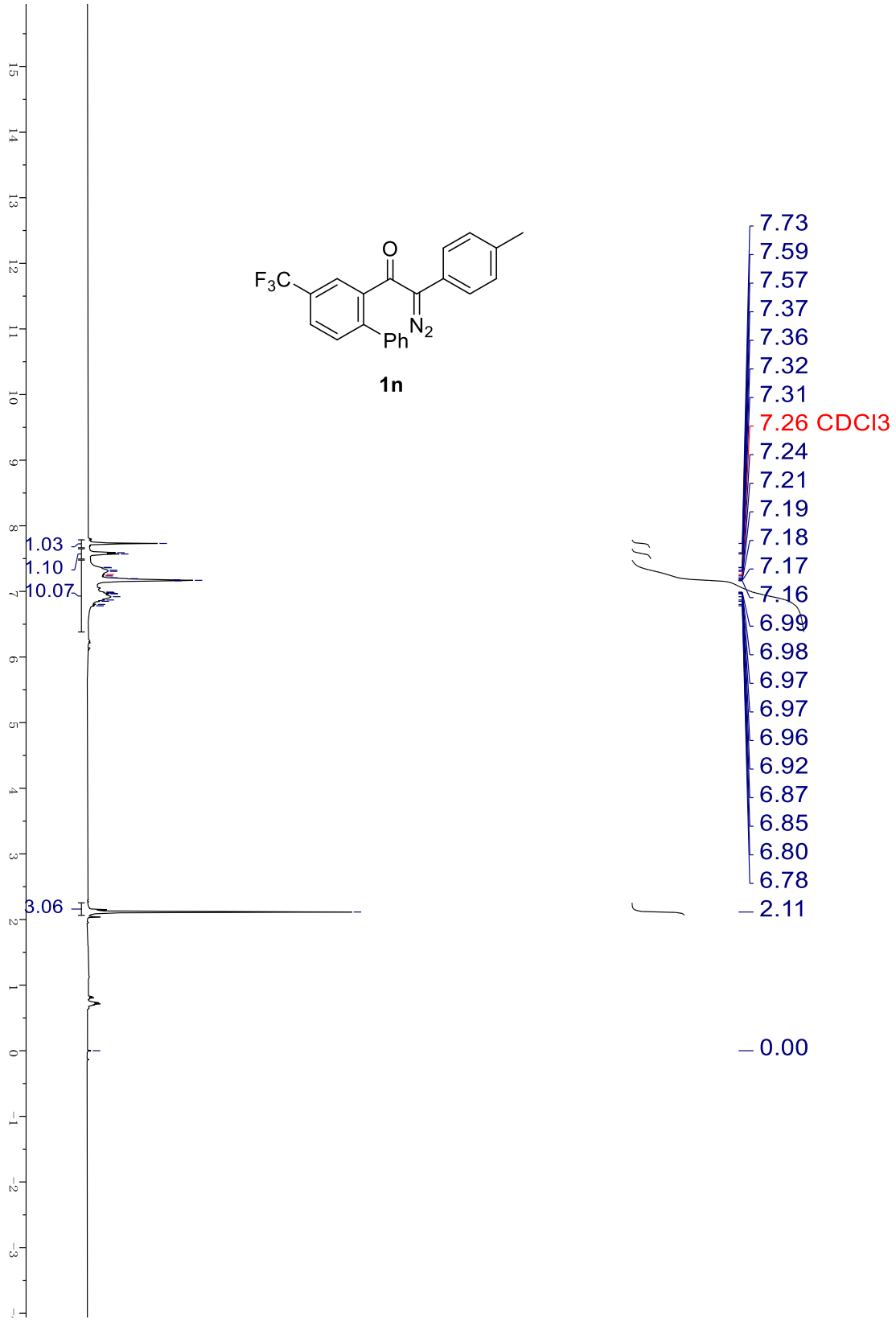
13.71
Ph
O
N2
EtO2C
Ph
1m


F3C
O
N2
Ph
1n
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1.10
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3.06
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7.59
7.57
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7.36
7.32
7.31
7.26 CDCl3
7.24
7.21
7.19
7.18
7.17
7.16
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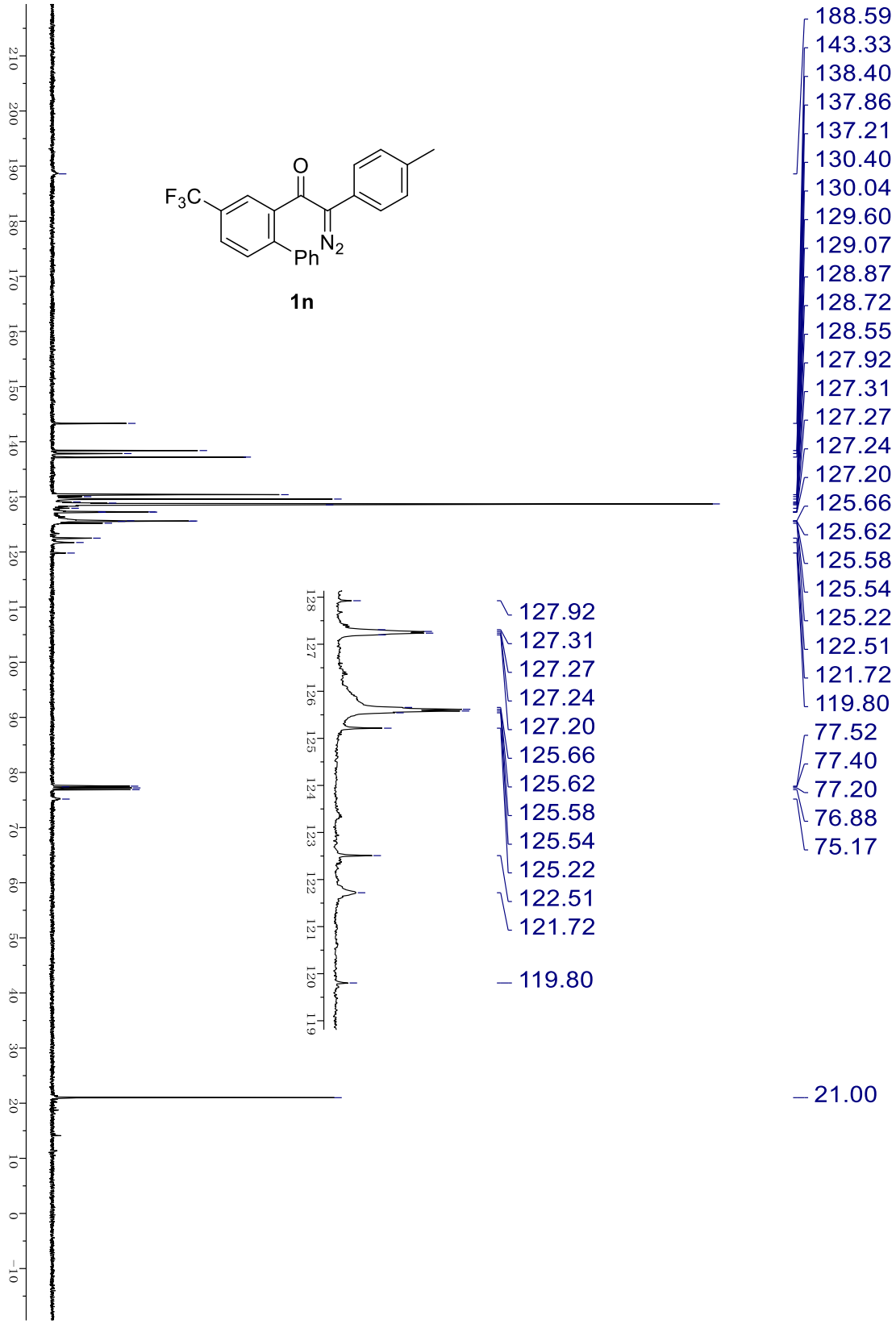
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1n
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129.07
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127.27
127.24
127.20
125.66
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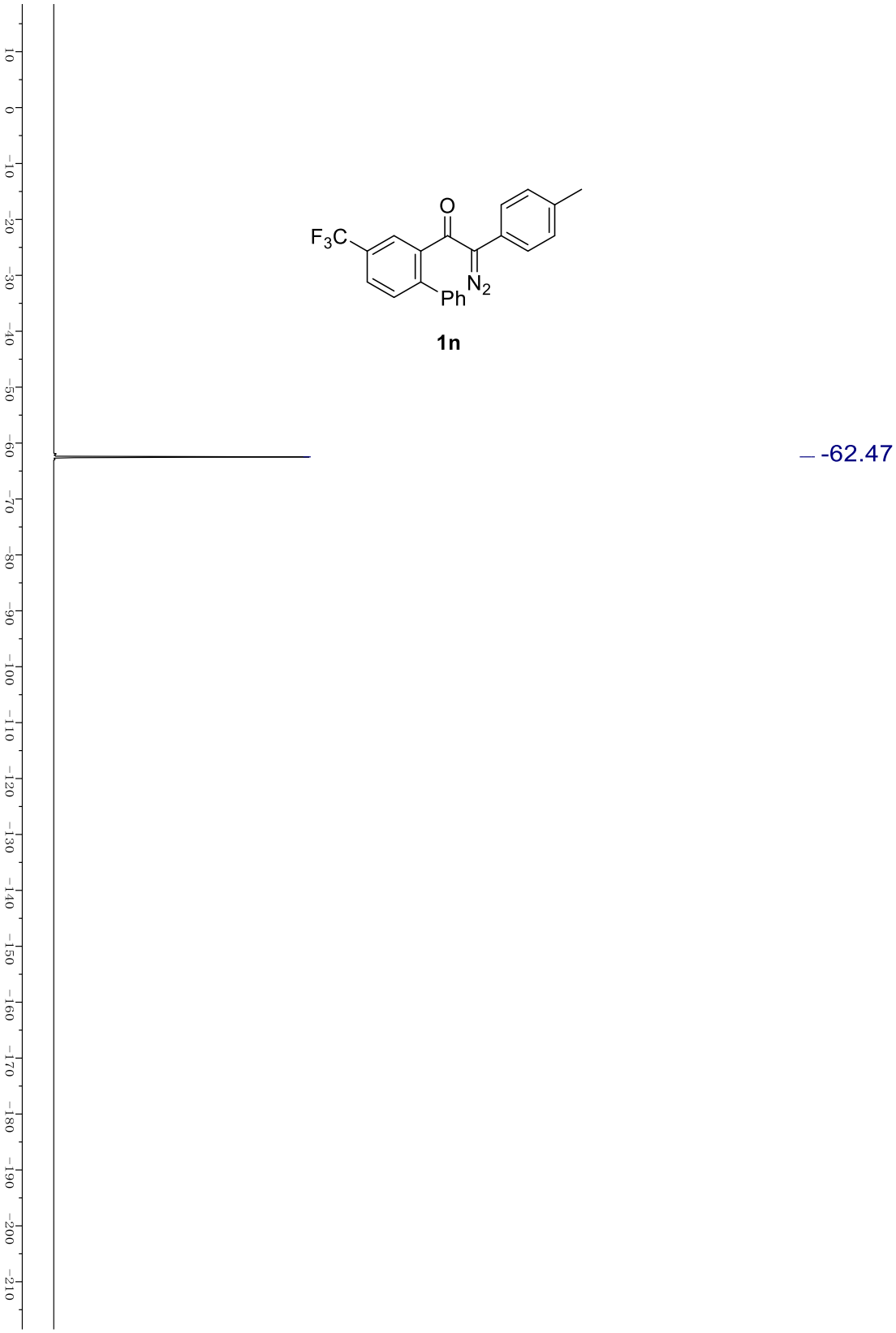
76.88
75.17
21.00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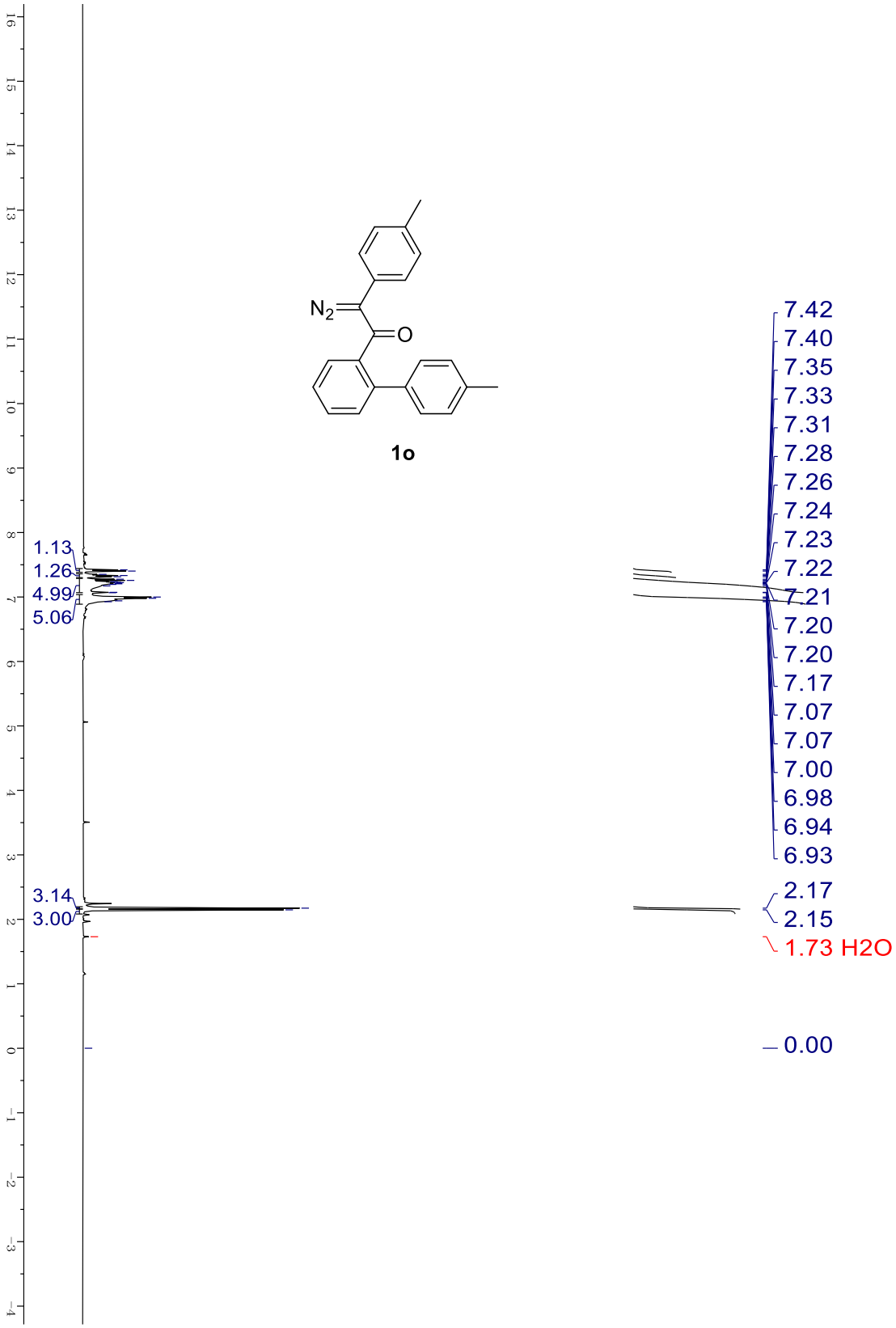
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3.00
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7.31
7.28
7.26
7.24
7.23
7.22
7.21
7.20
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2.17
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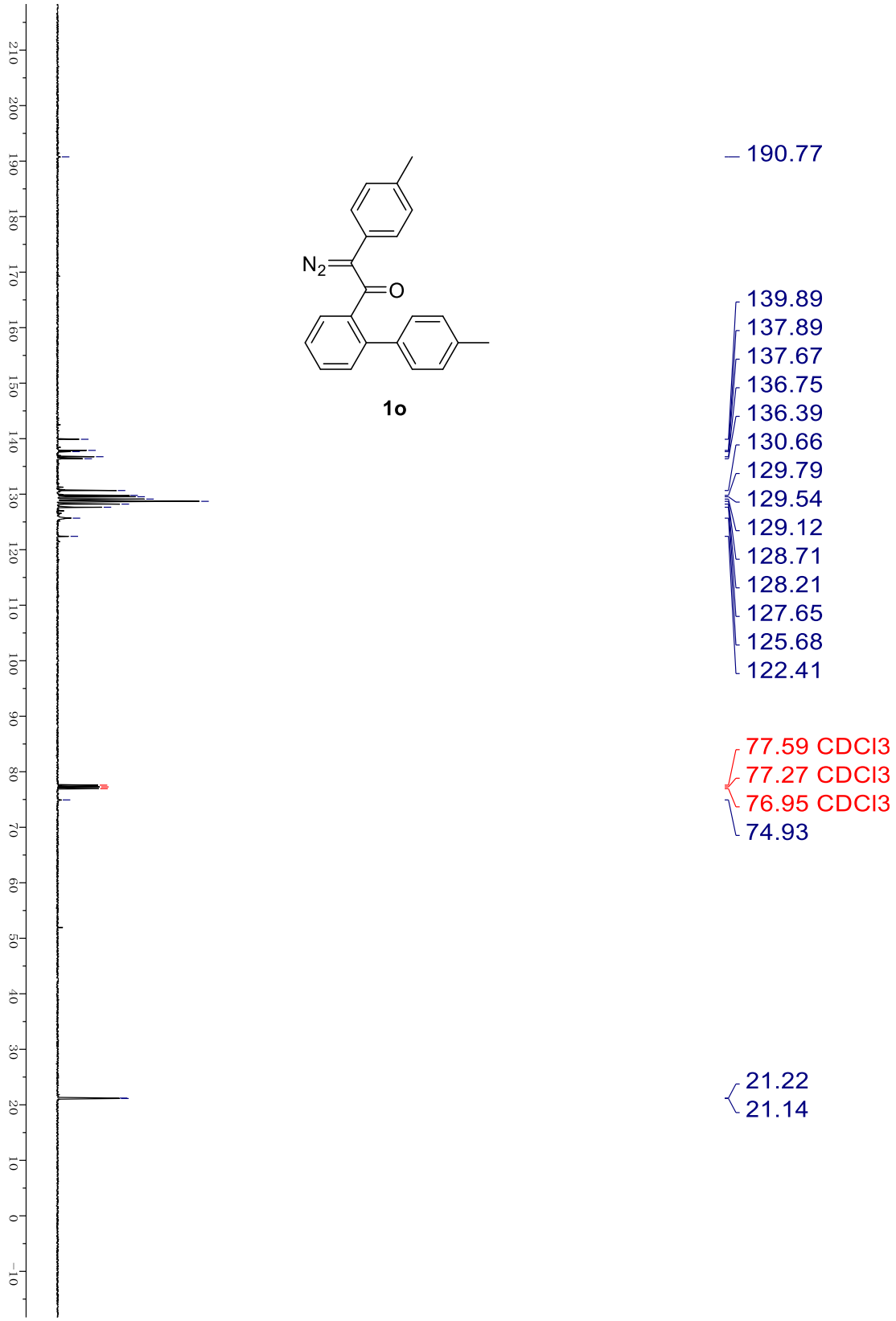
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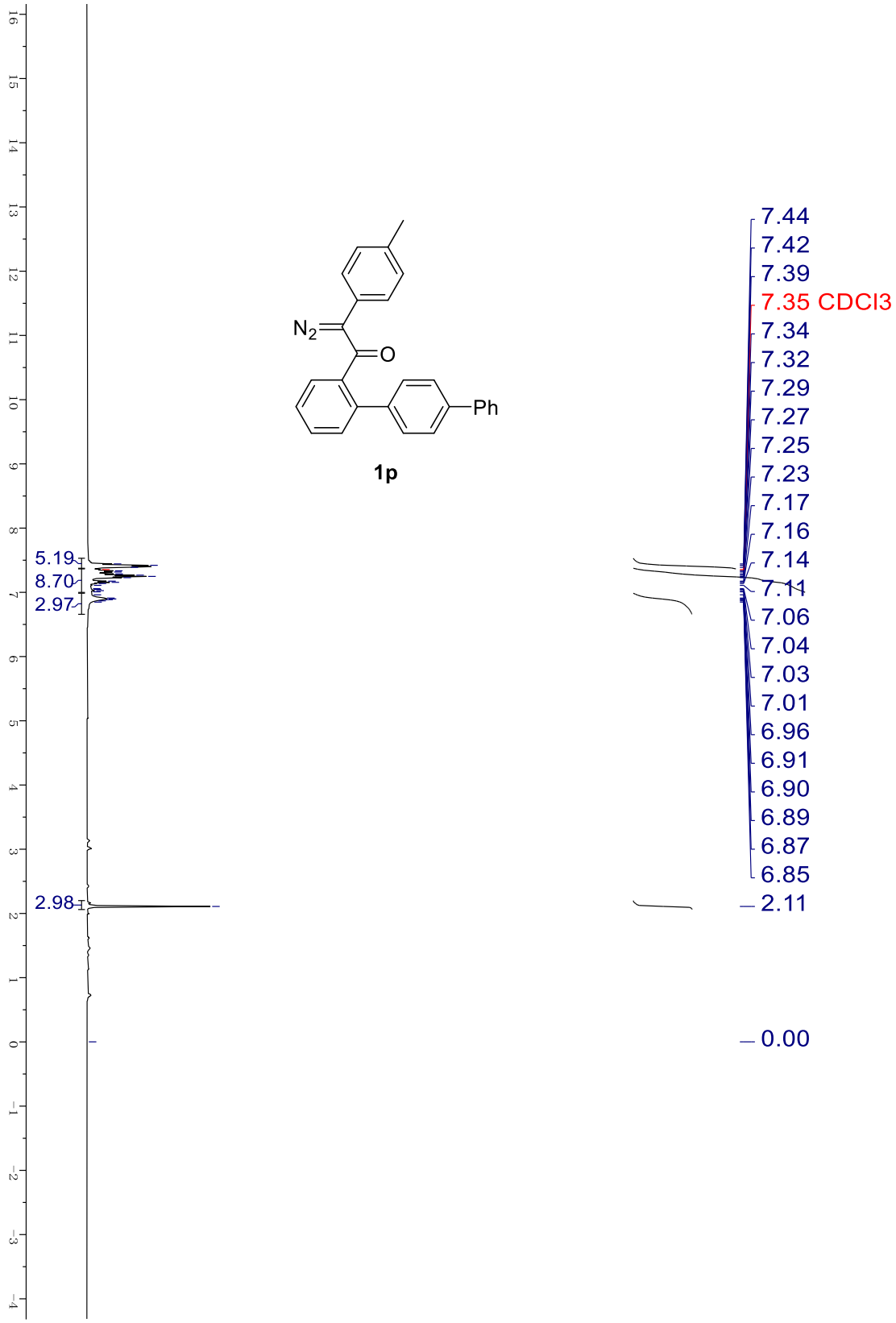
74.93
21.22
21.14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7.29
7.27
7.25
7.23
7.17
7.16
7.14
7.11
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6.90
6.89
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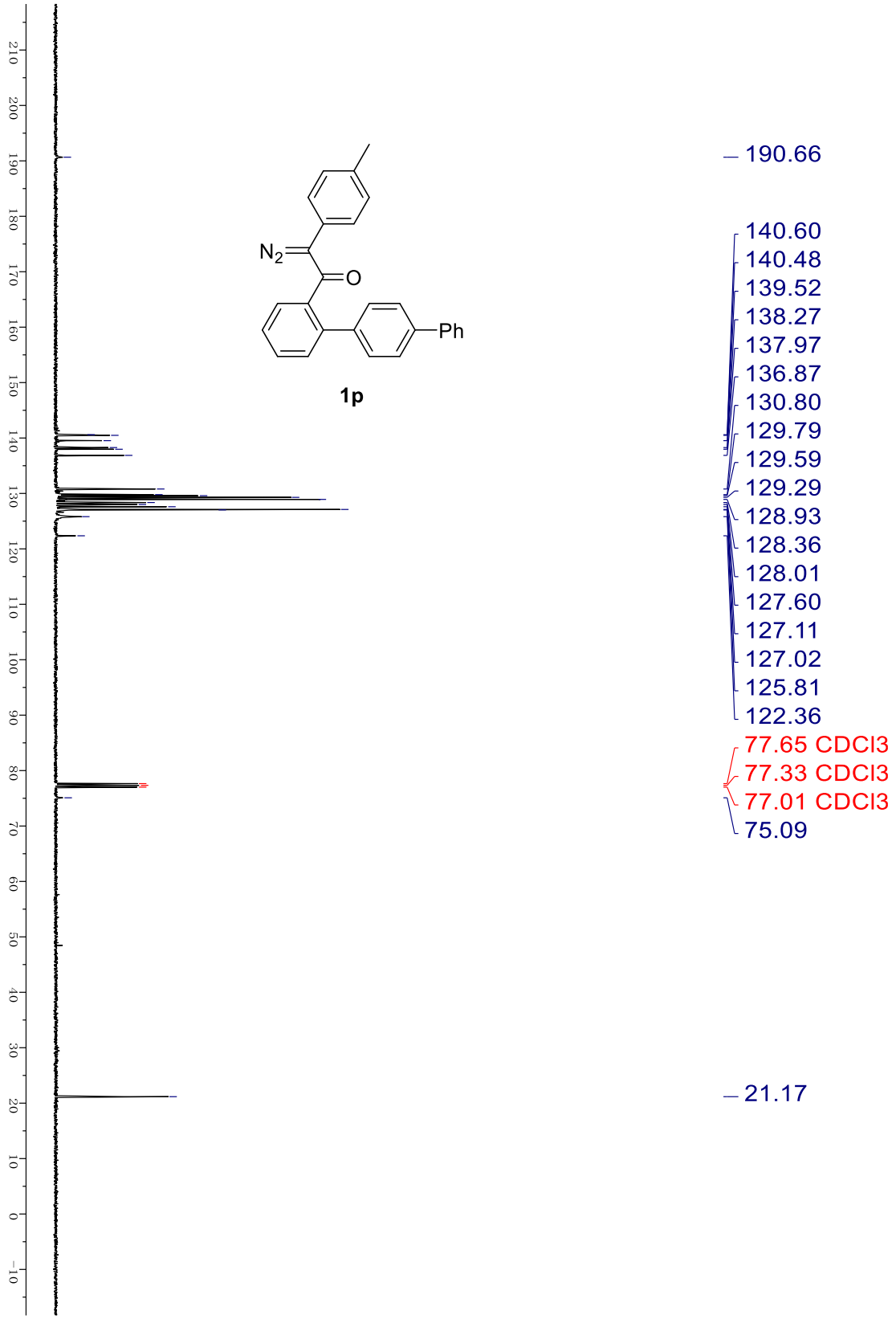
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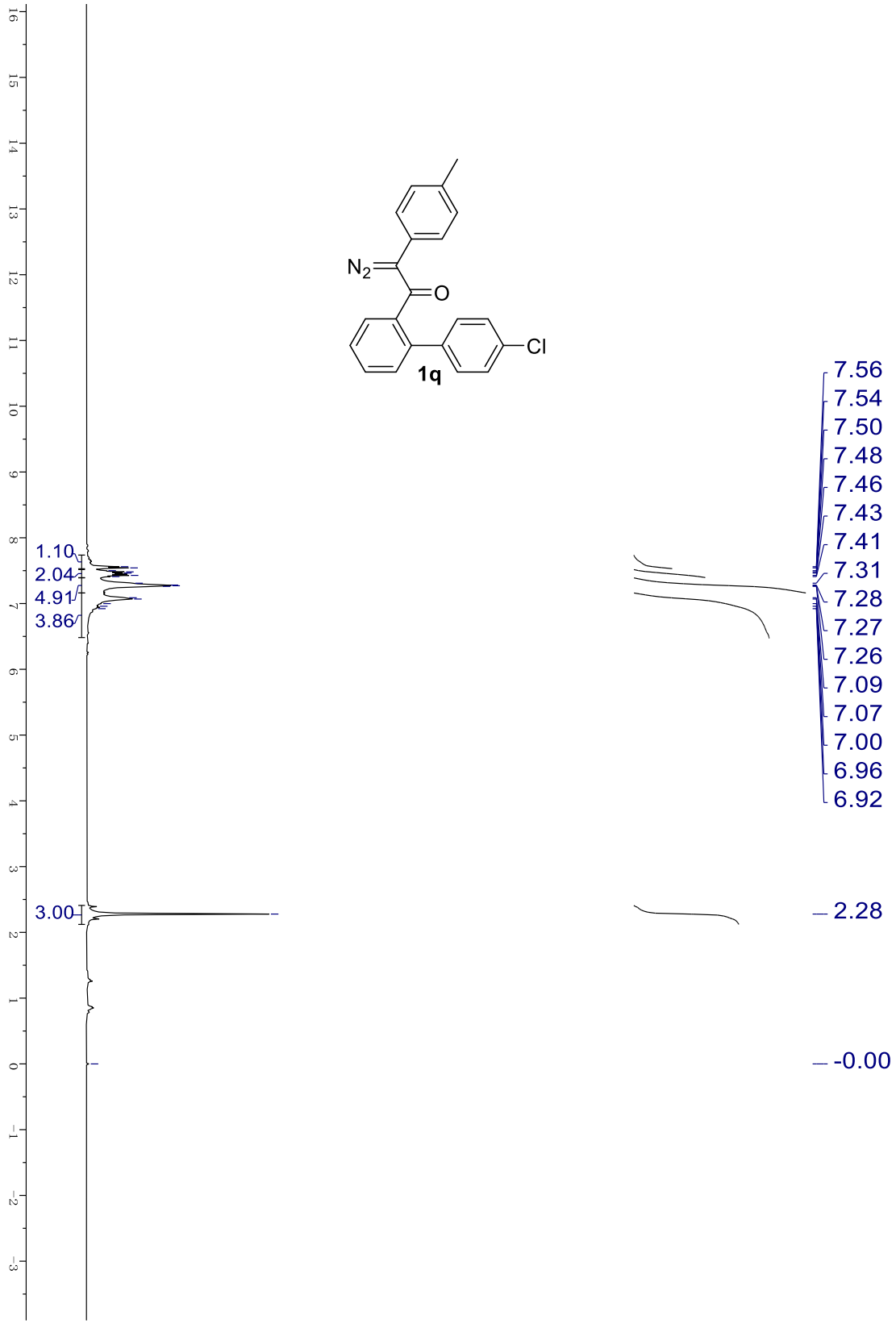
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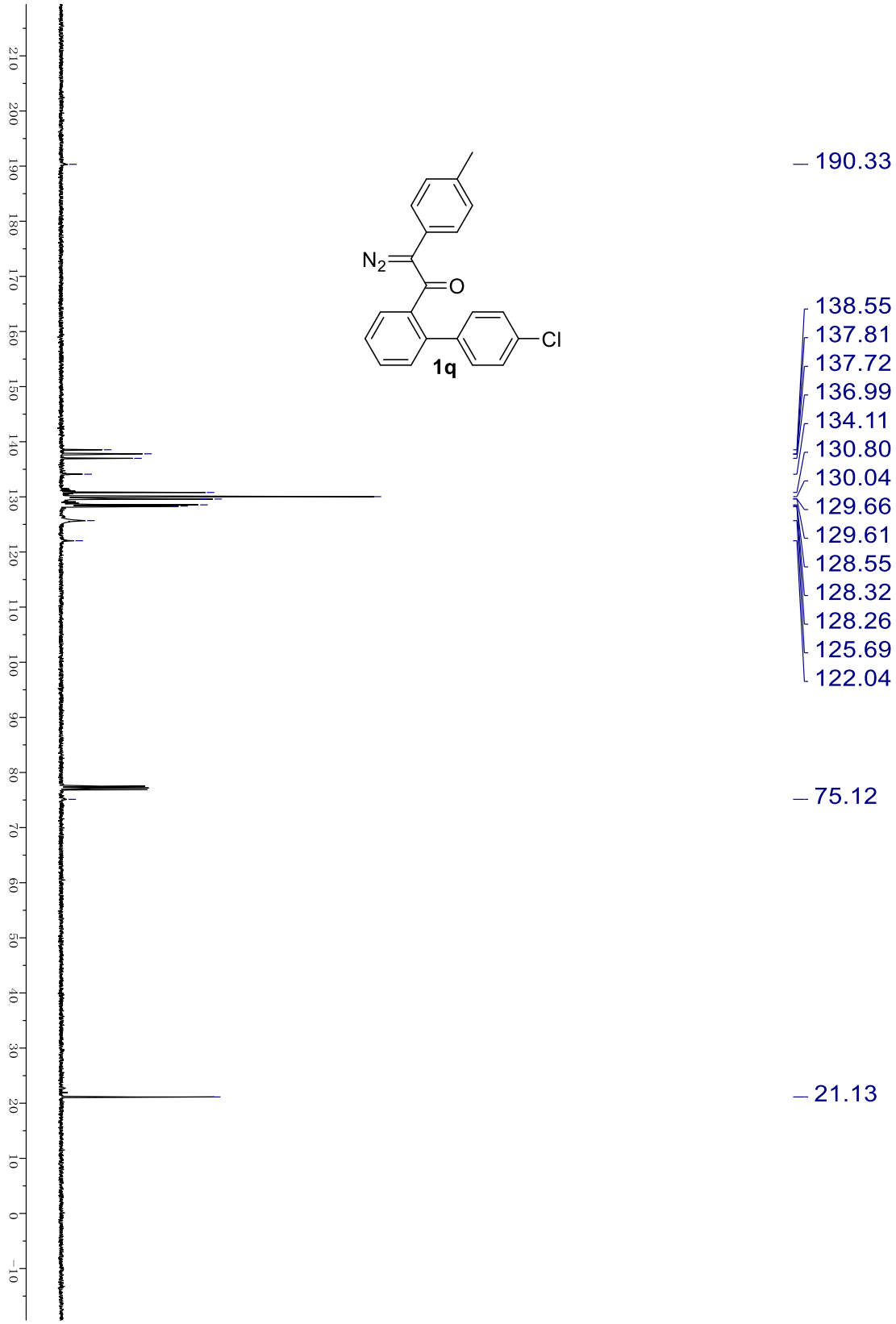
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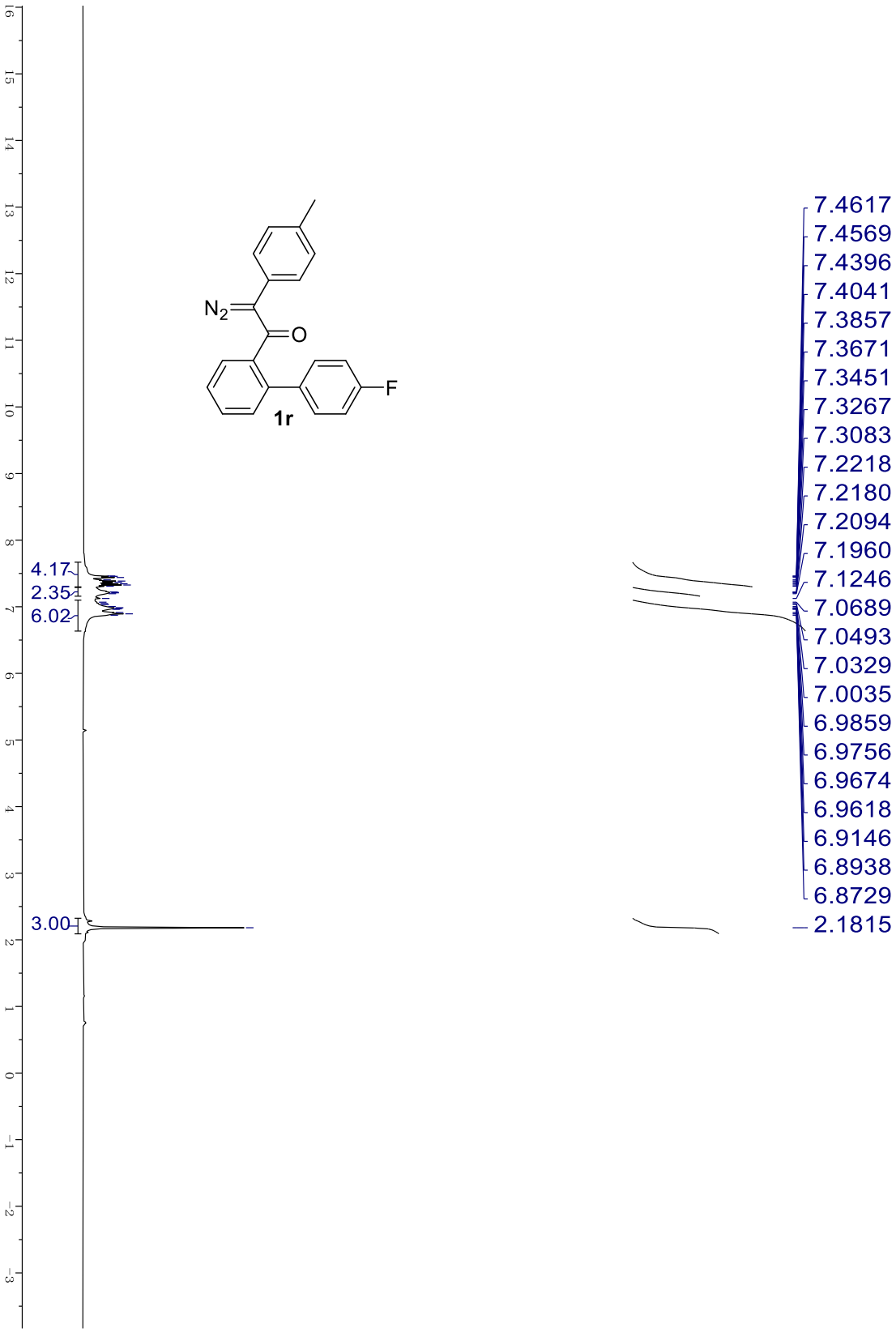
Cl
1q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6.8729
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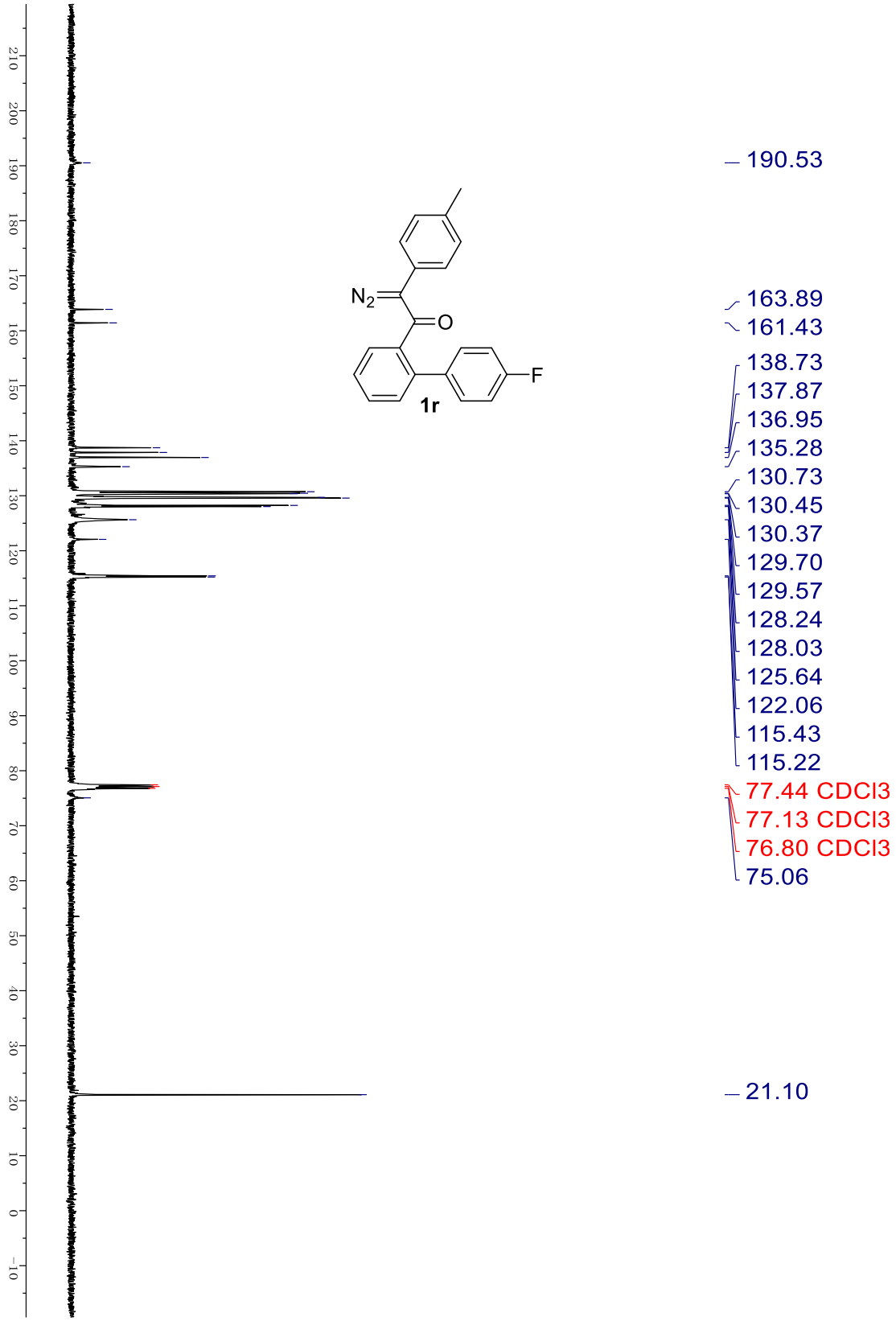
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77.13 CDCl3
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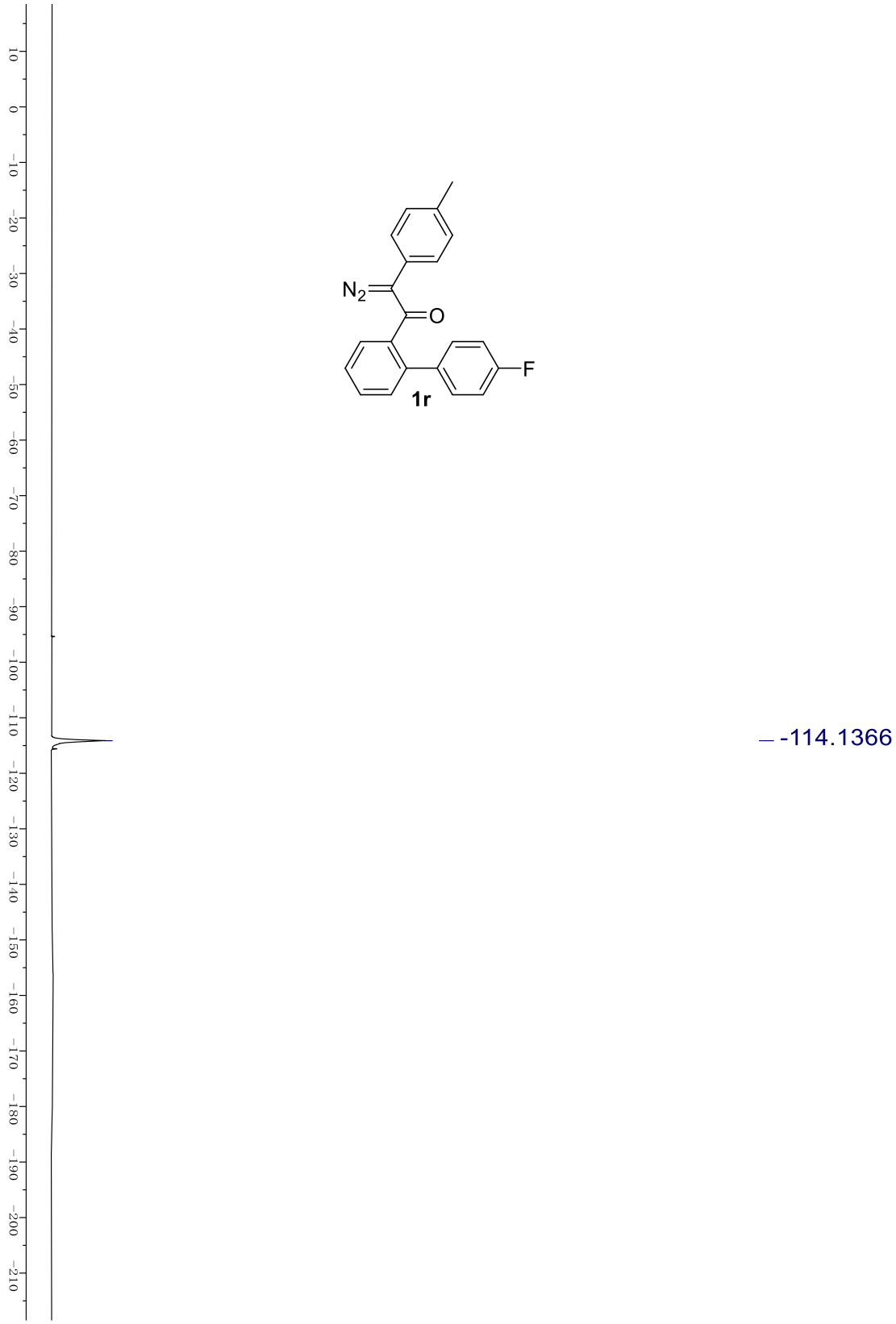
75.06
21.10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-210
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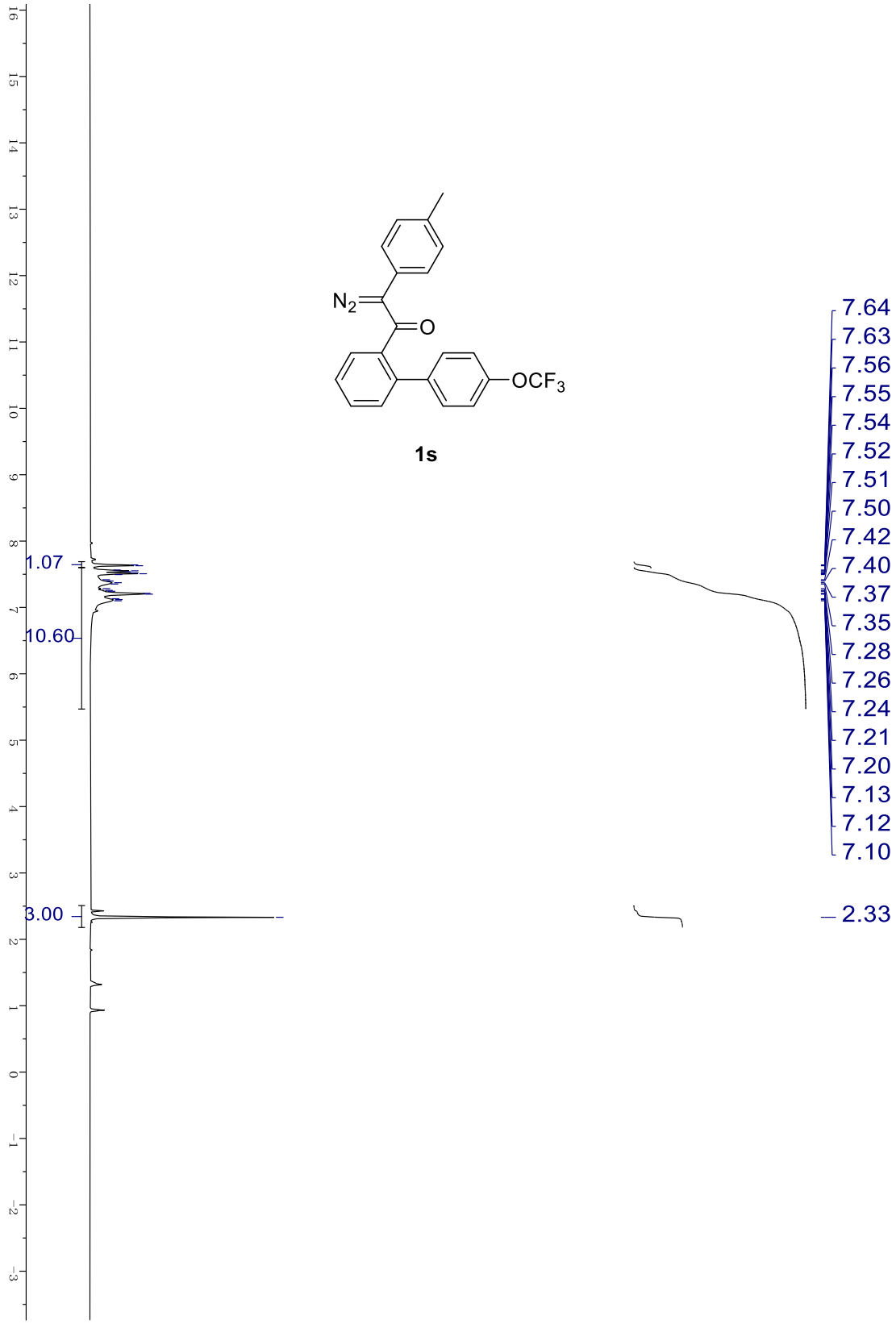
1r
-114.1366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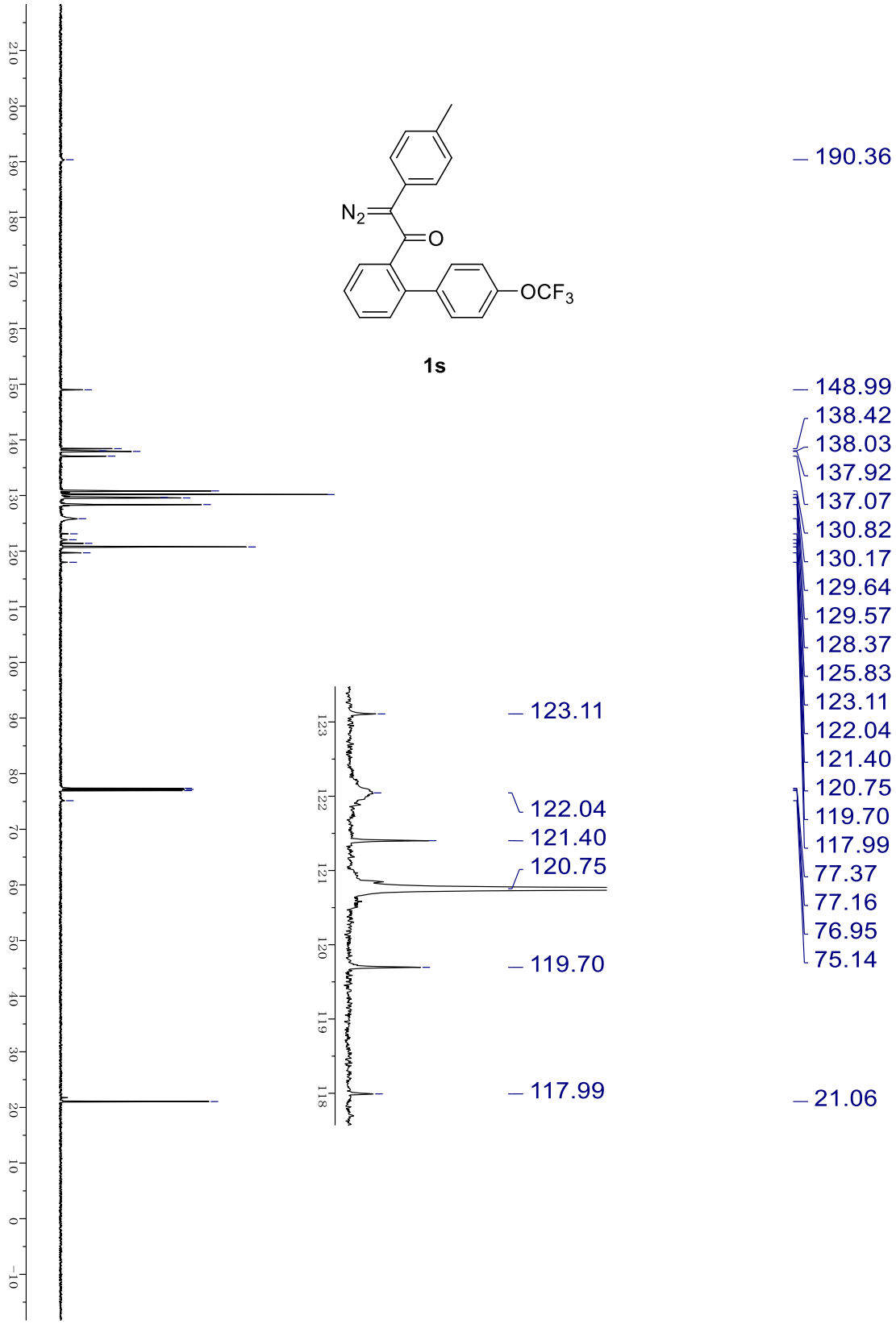
3.00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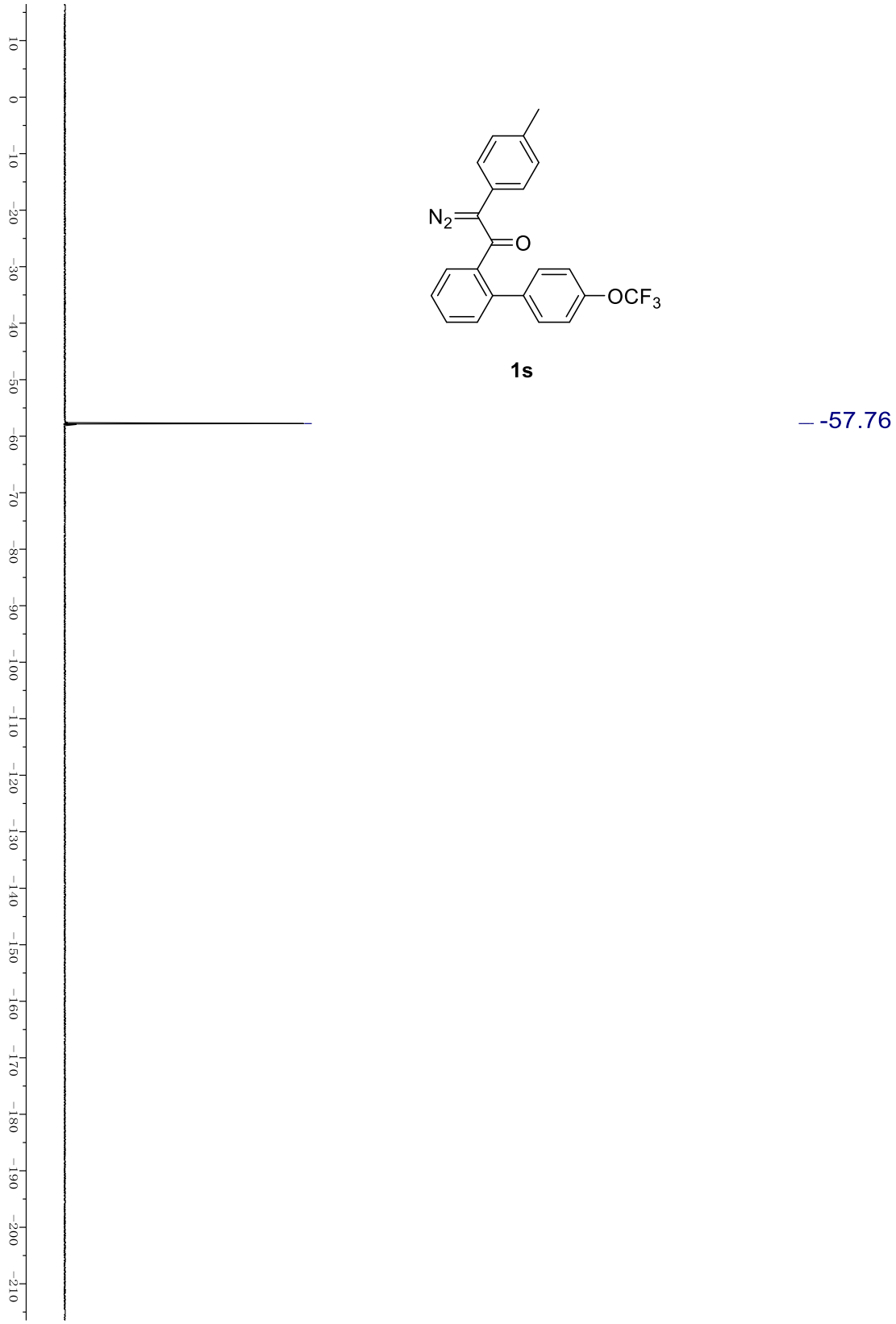
21.06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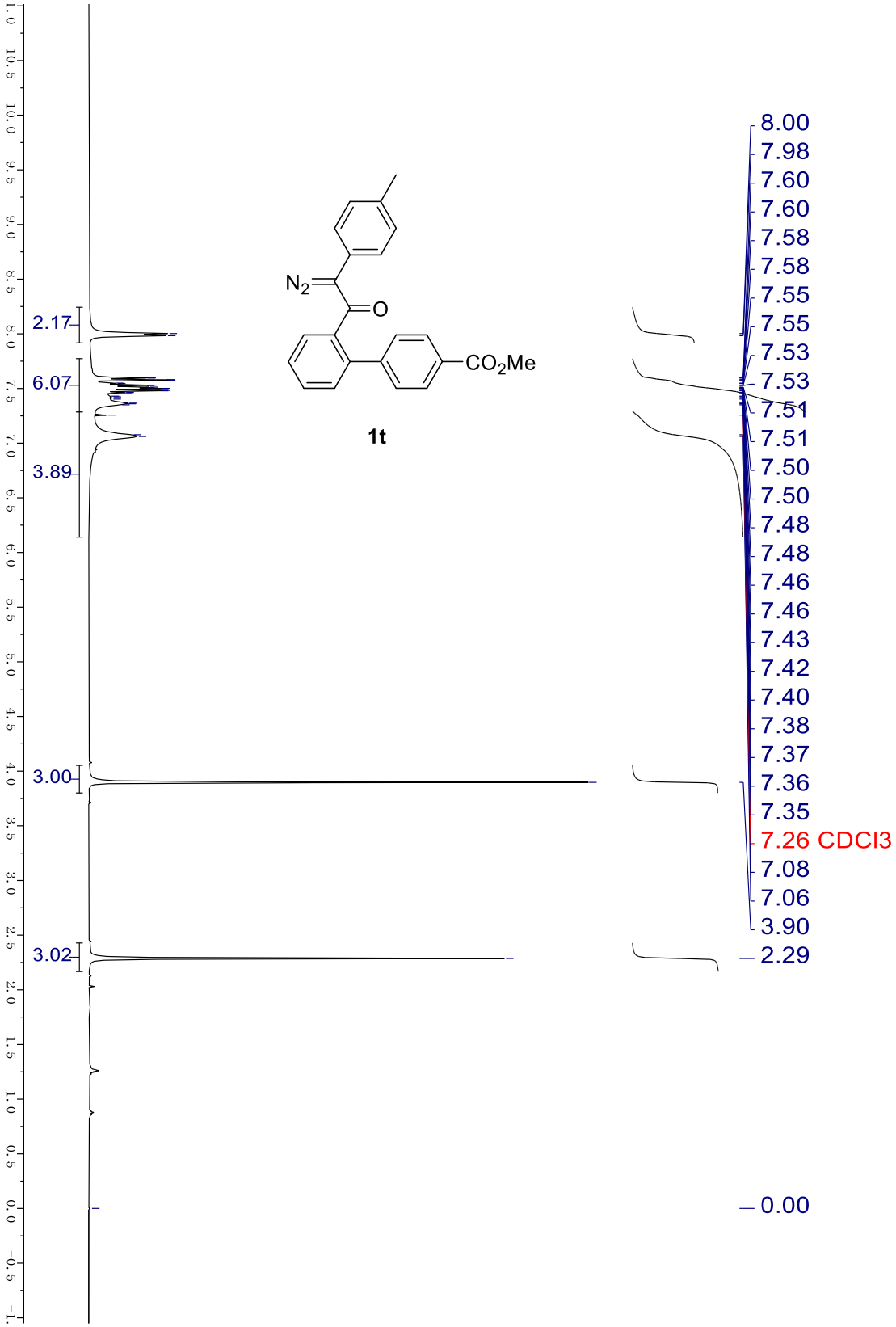
1s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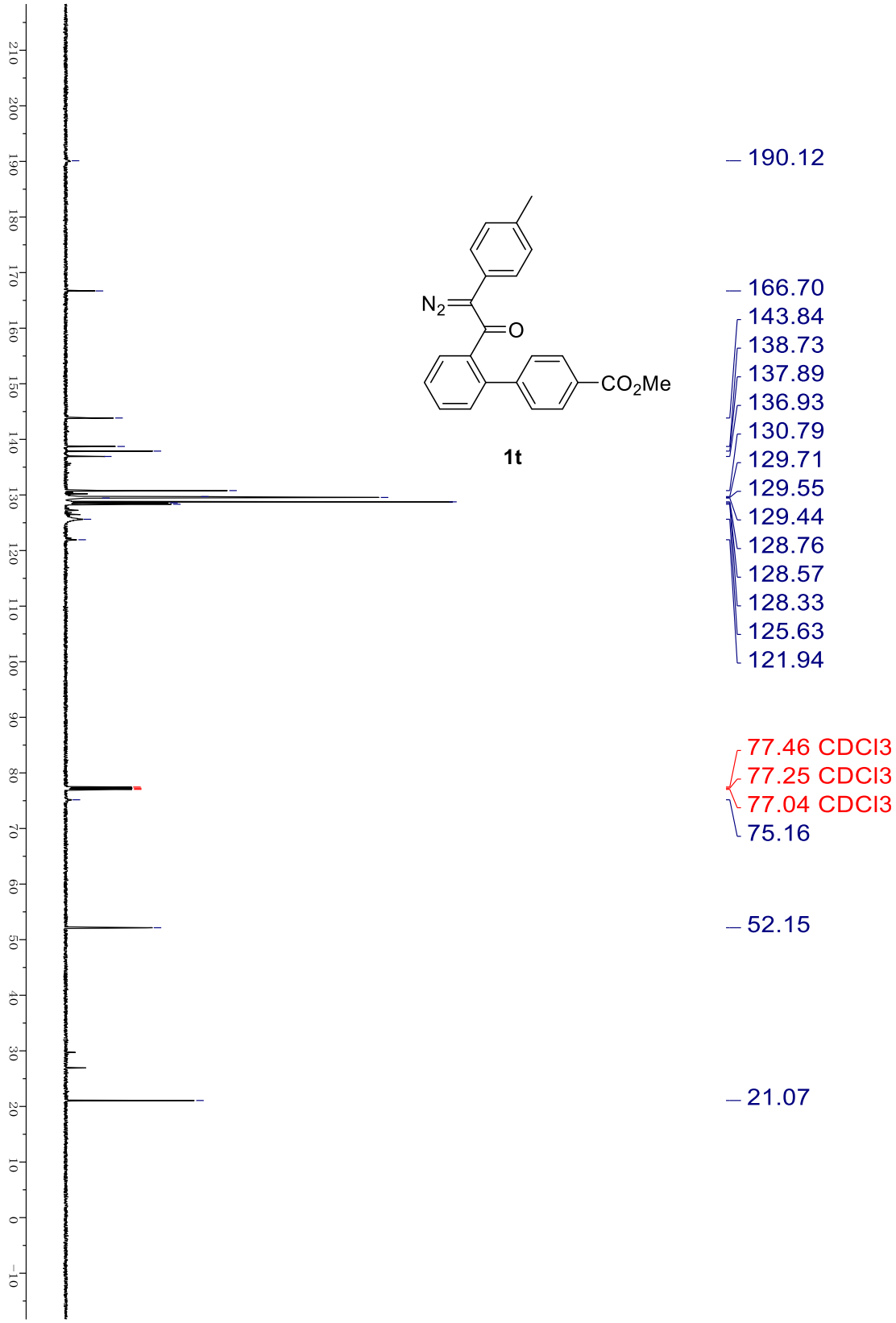
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77.04 CDCl3
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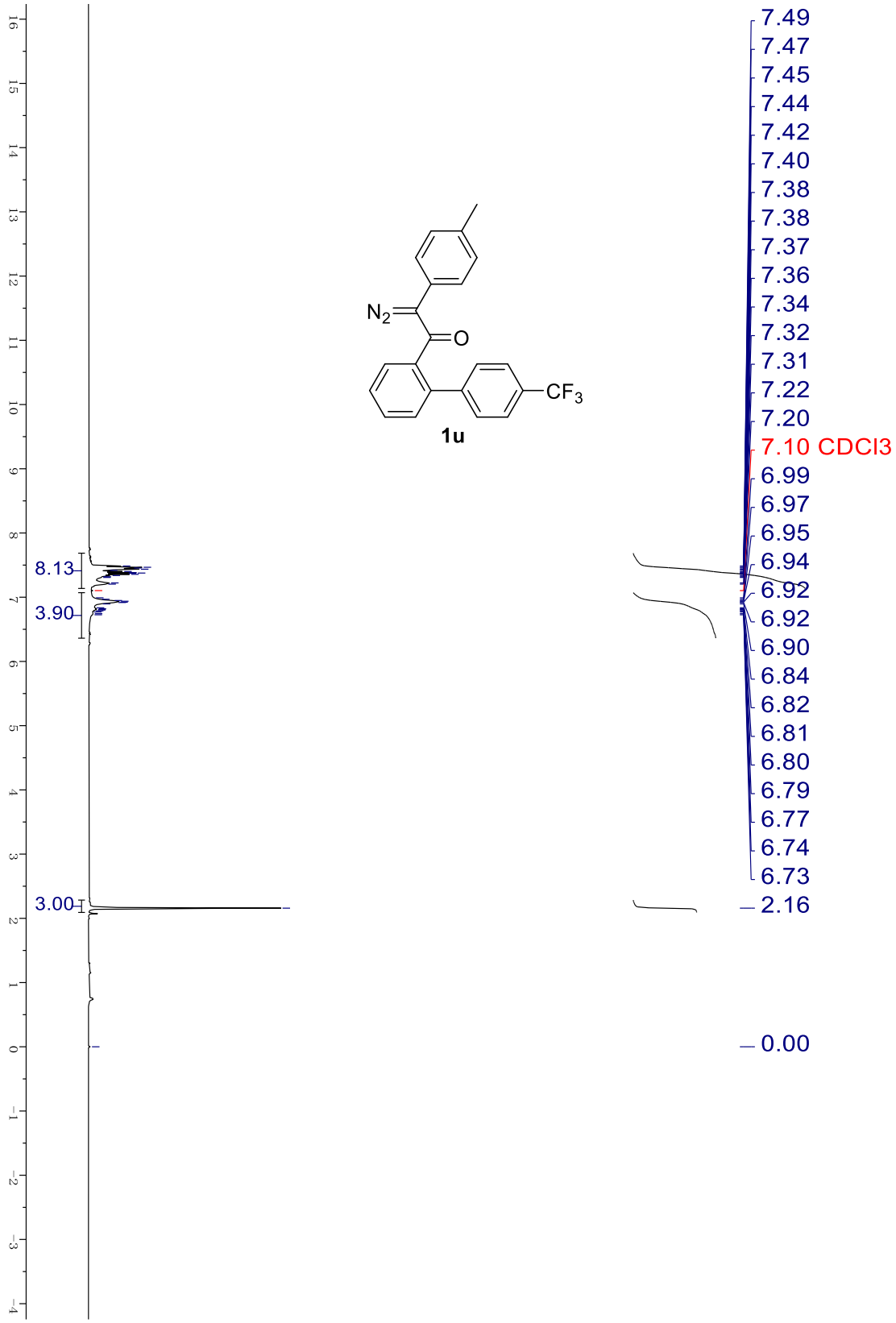
CO2Me
1t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7.10 CDCl3
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6.95
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CF3
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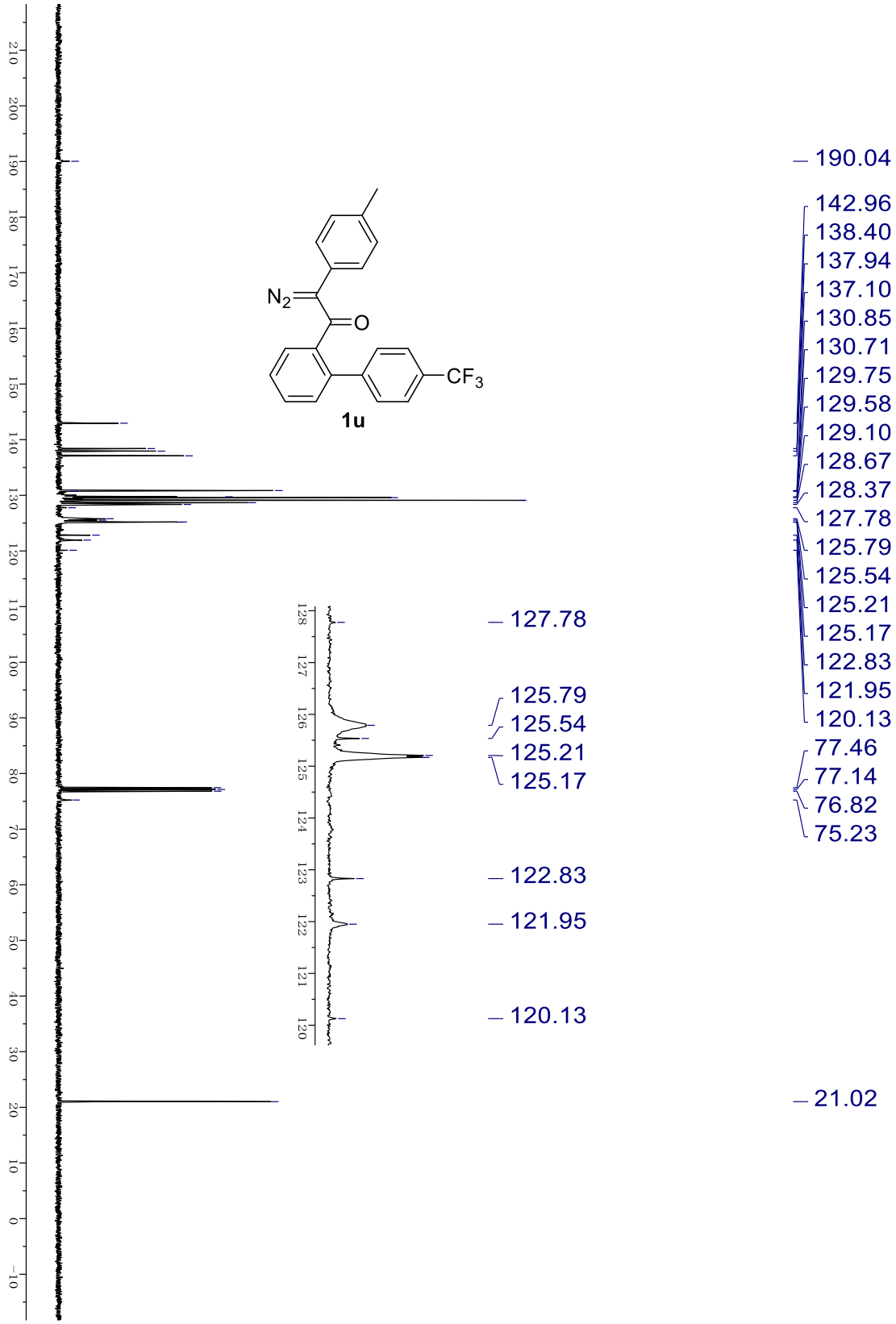
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CF3
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129.10
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128.37
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76.82
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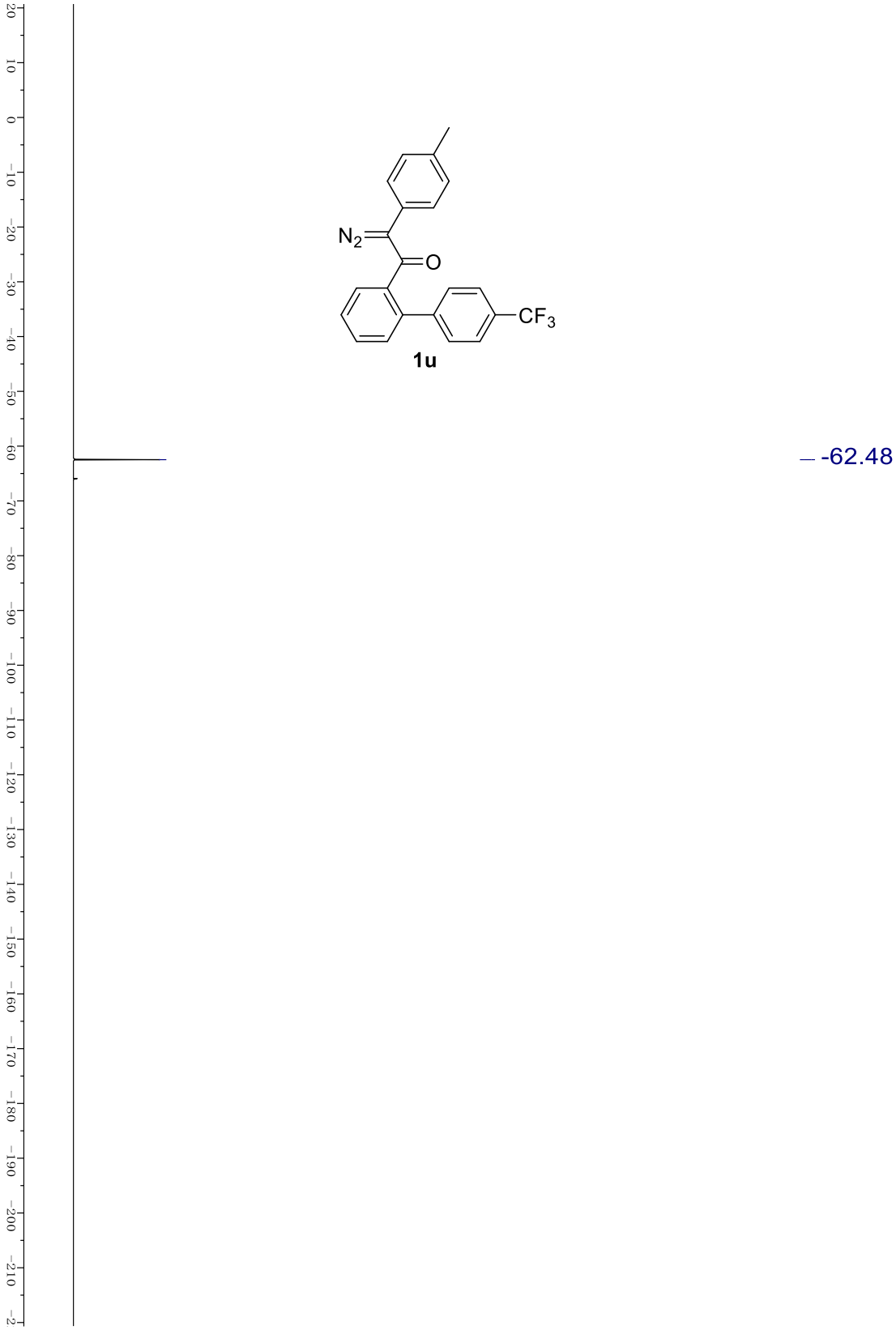
21.02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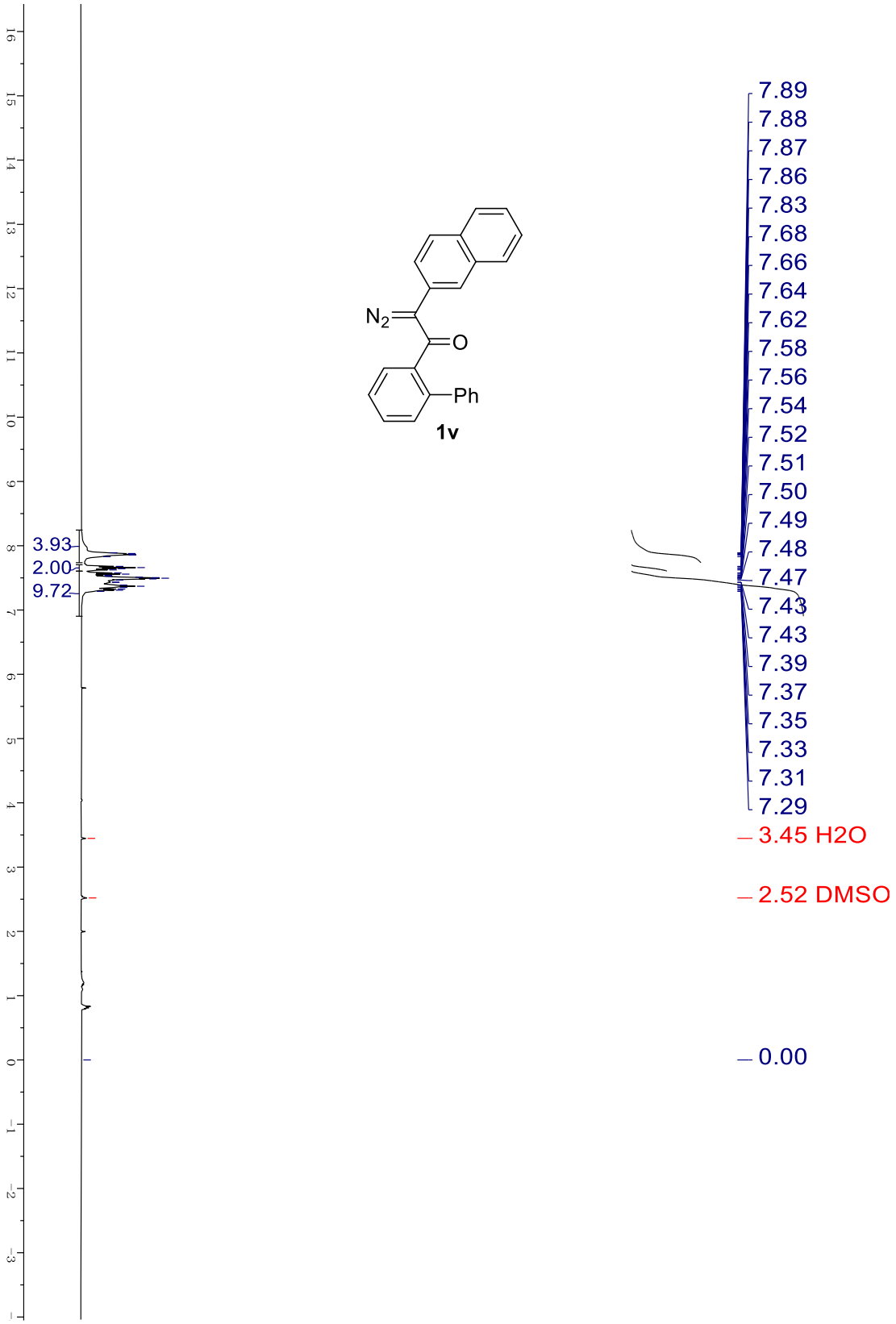
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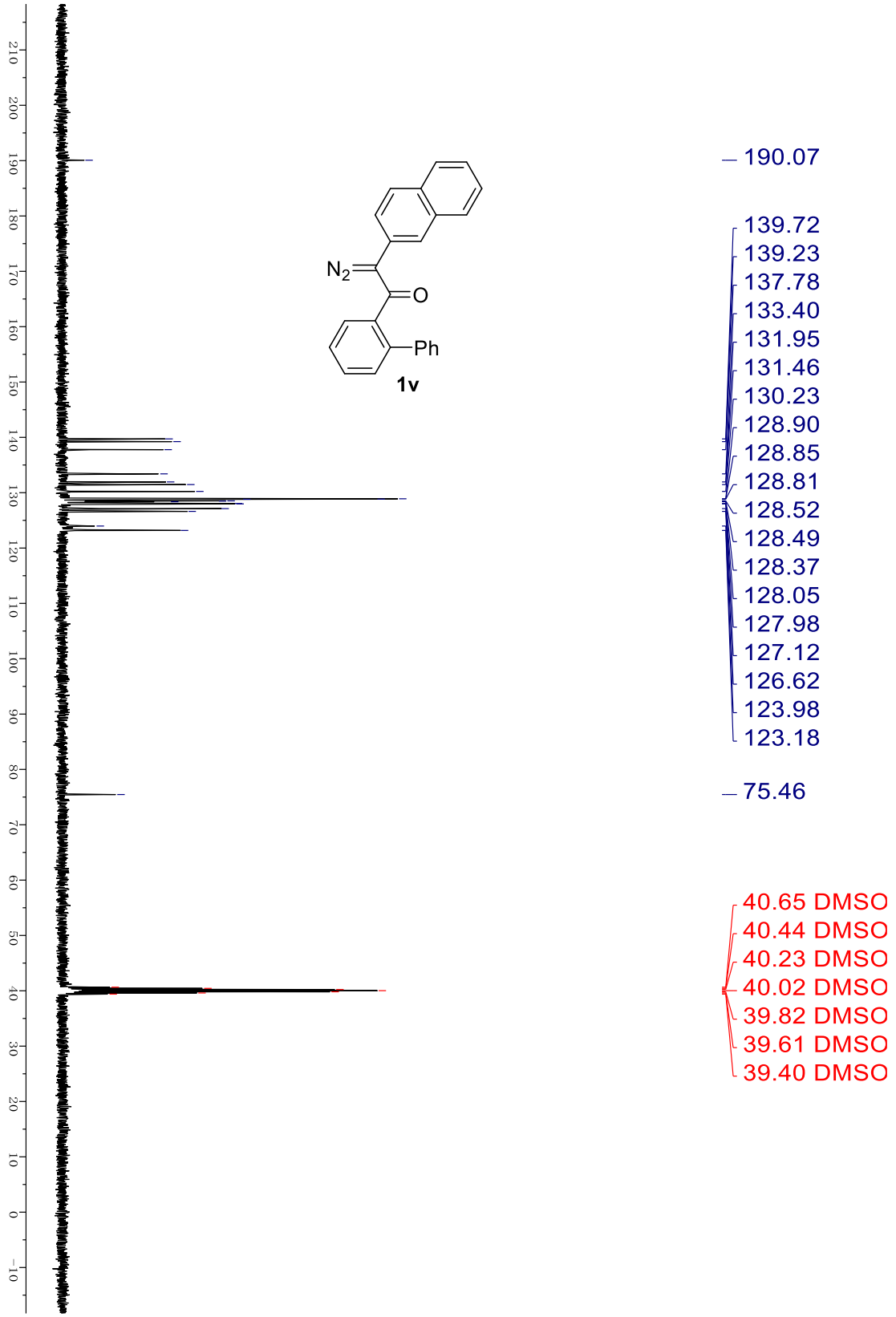
7.88
7.87
7.86
7.83
7.68
7.66
7.64
7.62
7.58
7.56
7.54
7.52
7.51
7.50
7.49
7.48
7.47
7.43
7.43
7.39
7.37
7.35
7.33
7.31
7.29
3.45 H2O
2.52 DMSO
0.00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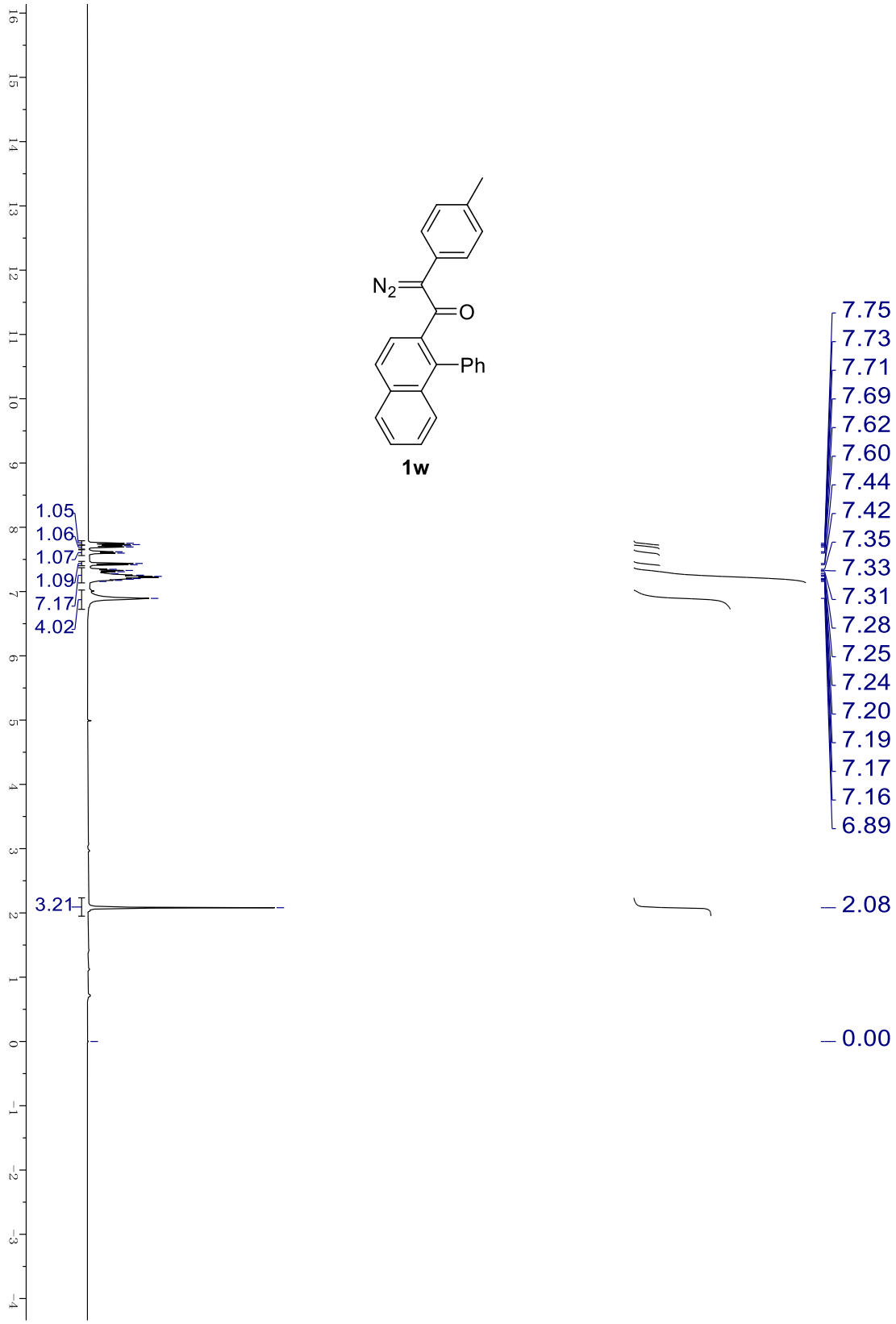
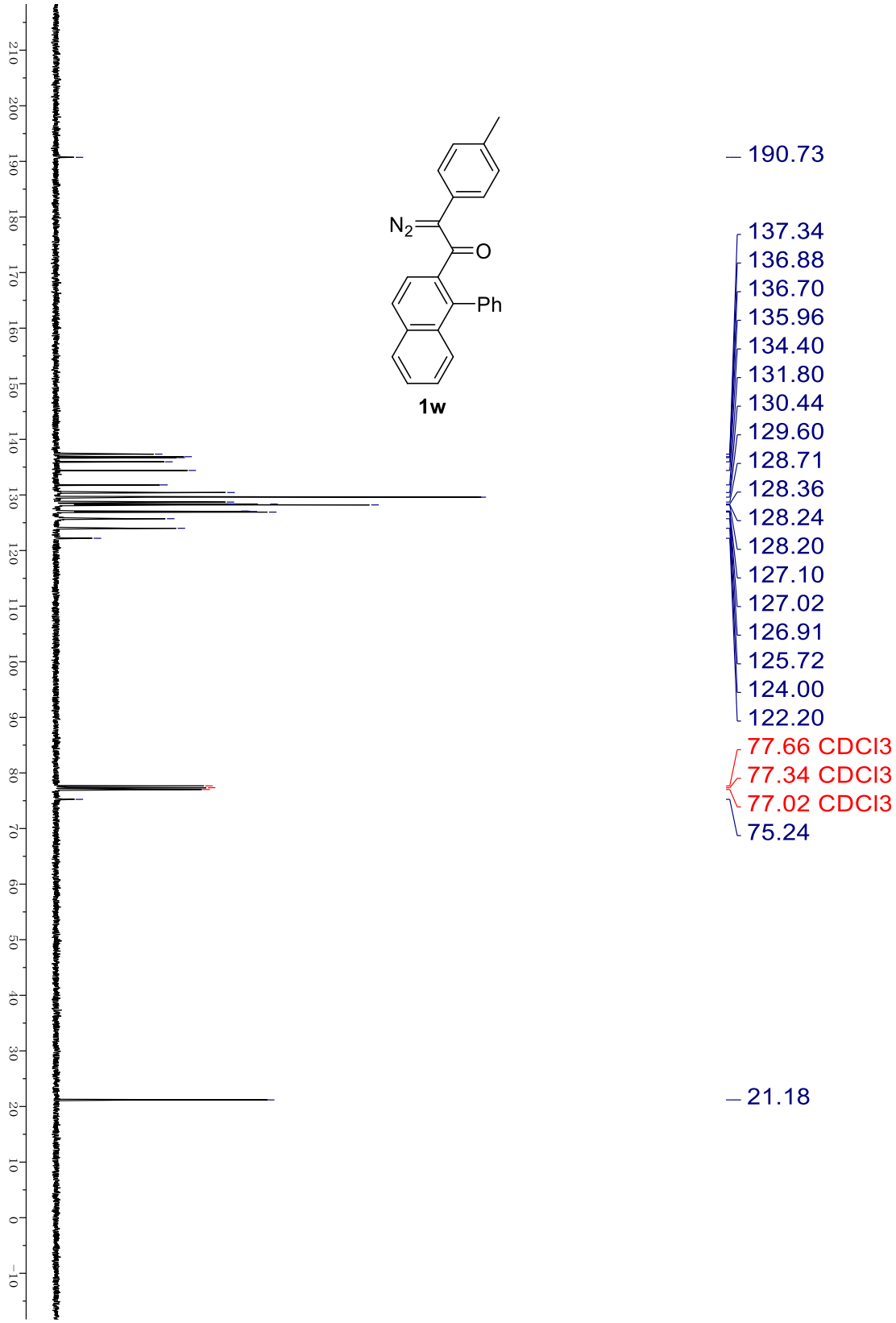
O
Ph
1v
190.07
139.72
139.23
137.78
133.40
131.95
131.46
130.23
128.90
128.85
128.81
128.52
128.49
128.37
128.05
127.98
127.12
126.62
123.98
123.18
75.46
40.65 DMSO
40.44 DMSO
40.23 DMSO
40.02 DMSO
39.82 DMSO
39.61 DMSO
39.40 DMSO


N2
O
Ph
1w
1.05
1.06
1.07
1.09
7.17
4.02
3.21
7.75
7.73
7.71
7.69
7.62
7.60
7.44
7.42
7.35
7.33
7.31
7.28
7.25
7.24
7.20
7.19
7.17
7.16
6.89
2.08
0.00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O
Ph
1w
190.73
137.34
136.88
136.70
135.96
134.40
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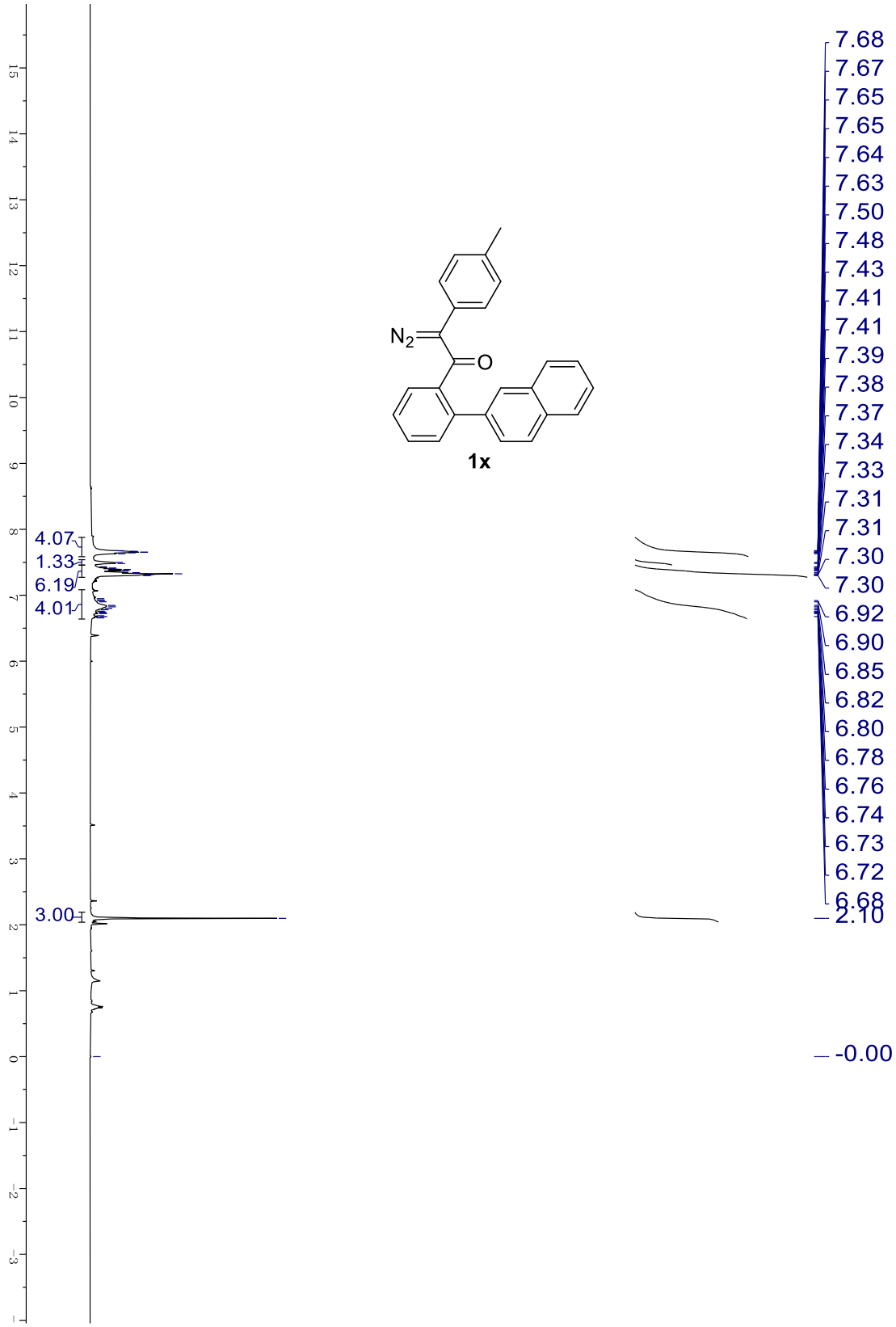
130.44
129.60
128.71
128.36
128.24
128.20
127.10
127.02
126.91
125.72
124.00
122.20
77.66 CDCl3
77.34 CDCl3
77.02 CDCl3
75.24
21.18


N2
O
1x
4.07
1.33
6.19
4.01
3.00
7.68
7.67
7.65
7.65
7.64
7.63
7.50
7.48
7.43
7.41
7.41
7.39
7.38
7.37
7.34
7.33
7.31
7.31
7.30
7.30
6.92
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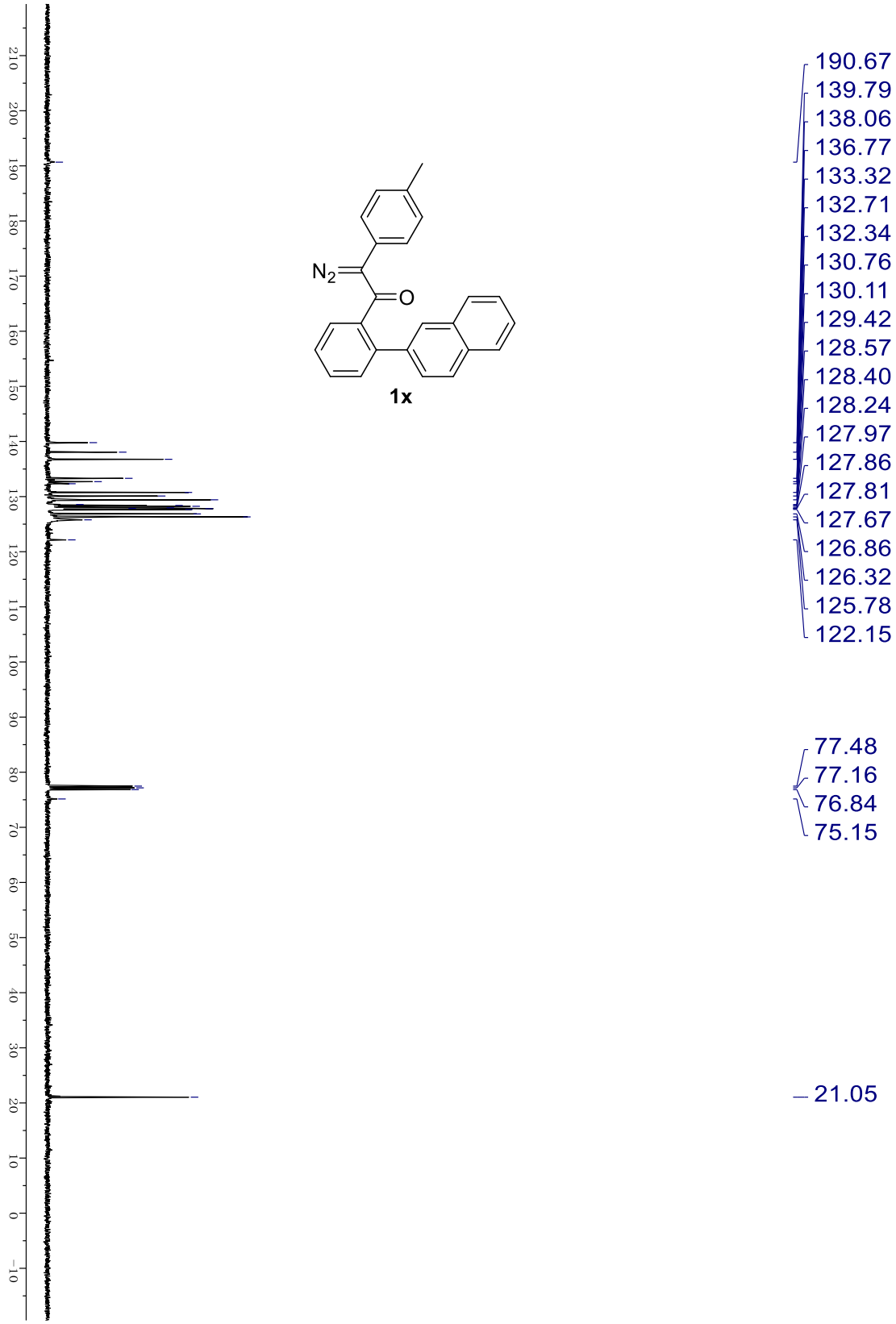
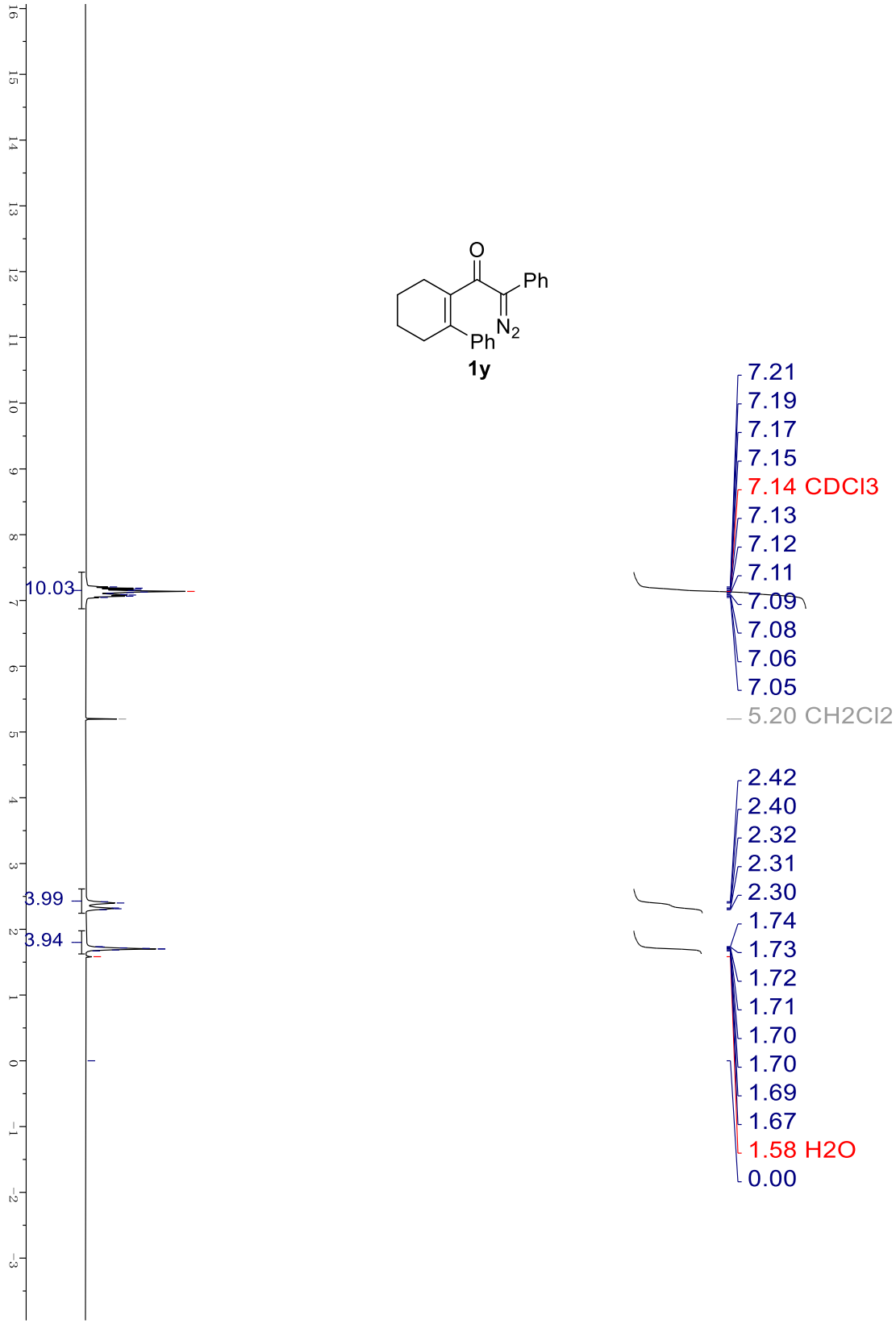
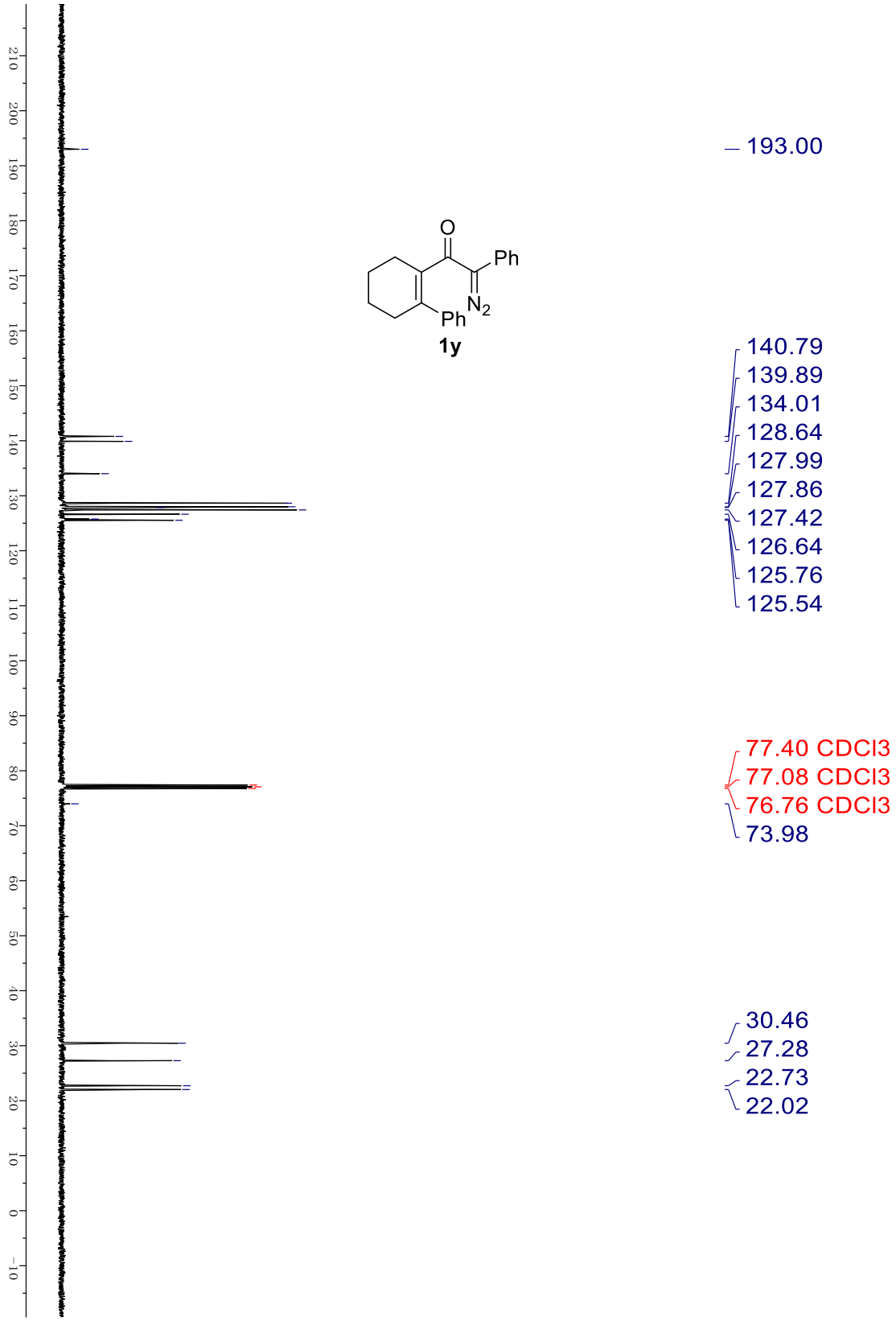
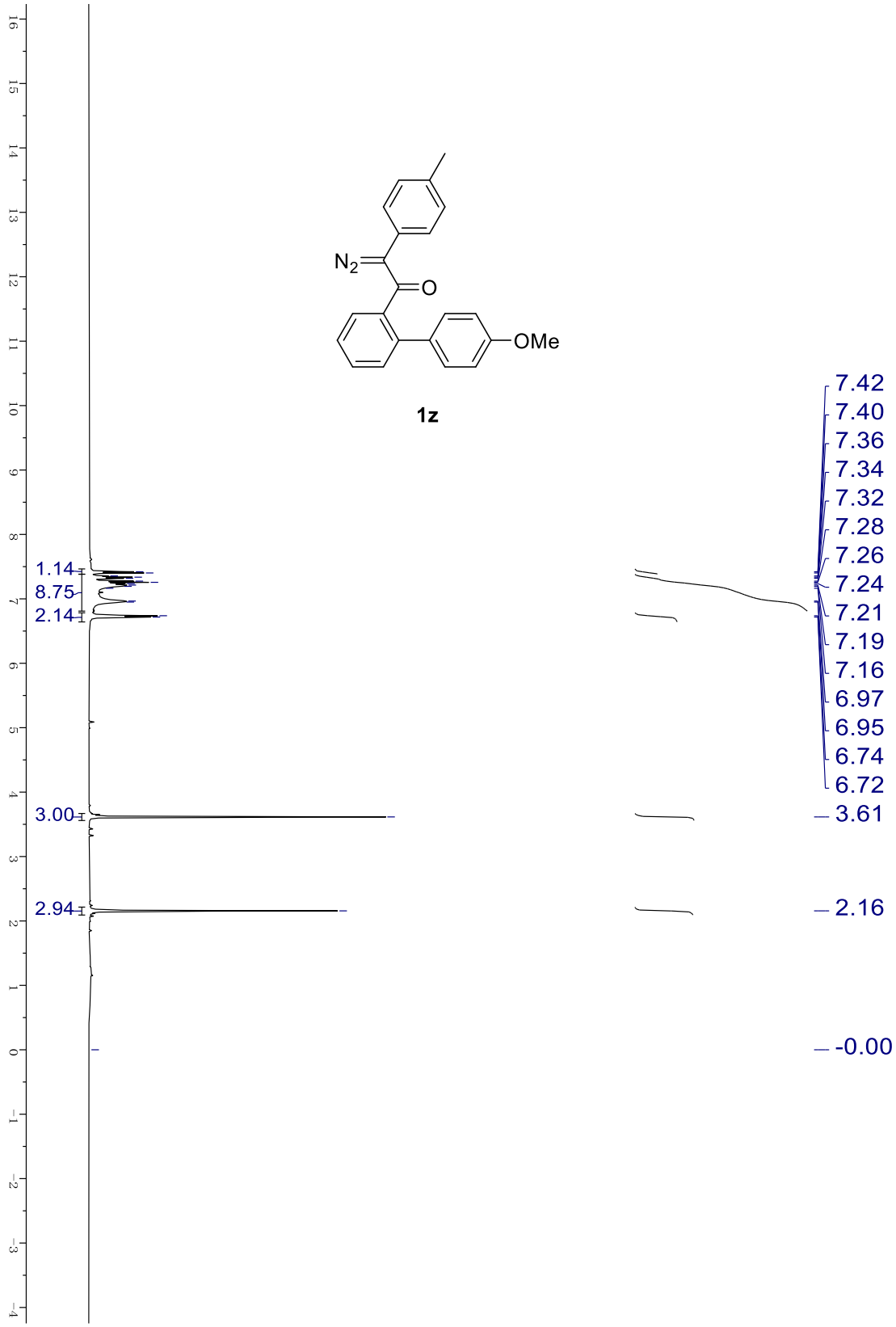
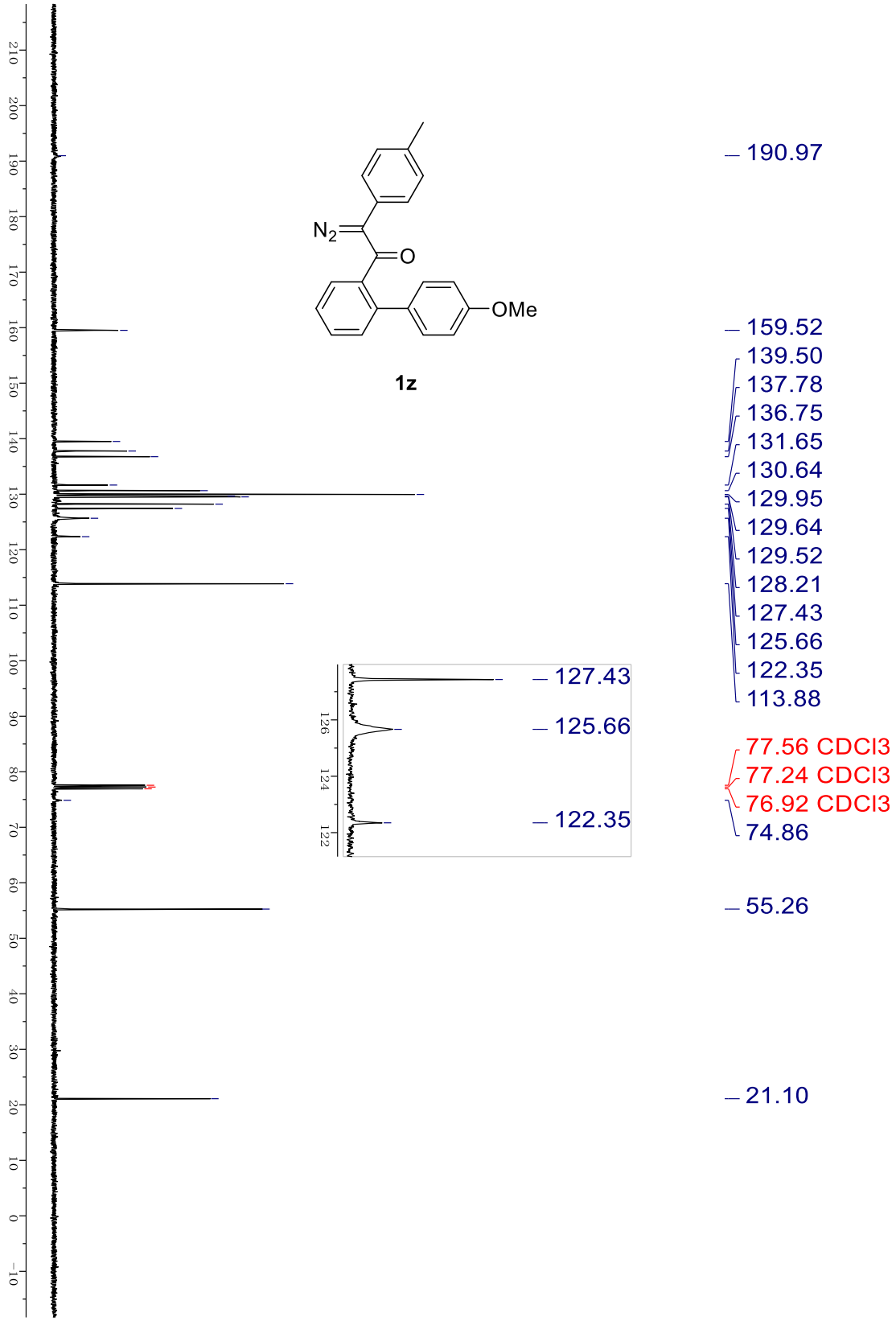
6.73
6.72
6.68
2.10
-0.00

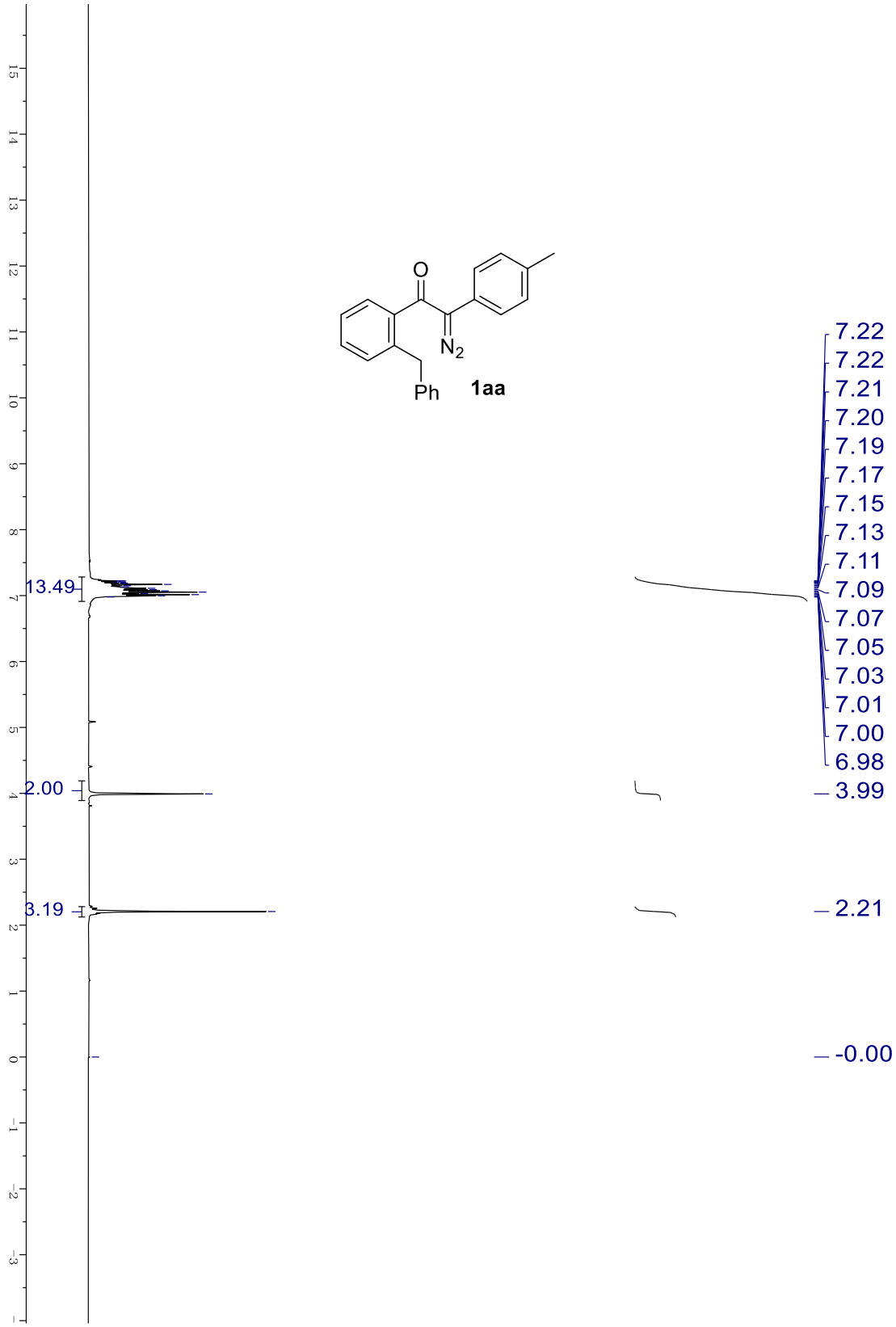

190.67
139.79
138.06
136.77
133.32
132.71
132.34
130.76
130.11
129.42
128.57
128.40
128.24
127.97
127.86
127.81
127.67
126.86
126.32
125.78
122.15
77.48
77.16
76.84
75.15
21.05
N2
O
1x


O
Ph
N2
Ph
1y
7.21
7.19
7.17
7.15
7.14 CDCl3
7.13
7.12
7.11
7.09
7.08
7.06
7.05
5.20 CH2Cl2
2.42
2.40
2.32
2.31
2.30
1.74
1.73
1.72
1.71
1.70
1.70
1.69
1.67
1.58 H2O
0.00
10.03
3.99
3.94


193.00
O
Ph
N2
Ph
1y
140.79
139.89
134.01
128.64
127.99
127.86
127.42
126.64
125.76
125.54
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
73.98
30.46
27.28
22.73
22.02


N2
O
OMe
1z
7.42
7.40
7.36
7.34
7.32
7.28
7.26
7.24
7.21
7.19
7.16
6.97
6.95
6.74
6.72
3.61
2.16
-0.00
1.14
8.75
2.14
3.00
2.94


N2
O
OMe
1z
190.97
159.52
139.50
137.78
136.75
131.65
130.64
129.95
129.64
129.52
128.21
127.43
125.66
122.35
113.88
77.56 CDCl3
77.24 CDCl3
76.92 CDCl3
74.86
55.26
21.10


O
N2
Ph
1aa
13.49
2.00
3.19
7.22
7.22
7.21
7.20
7.19
7.17
7.15
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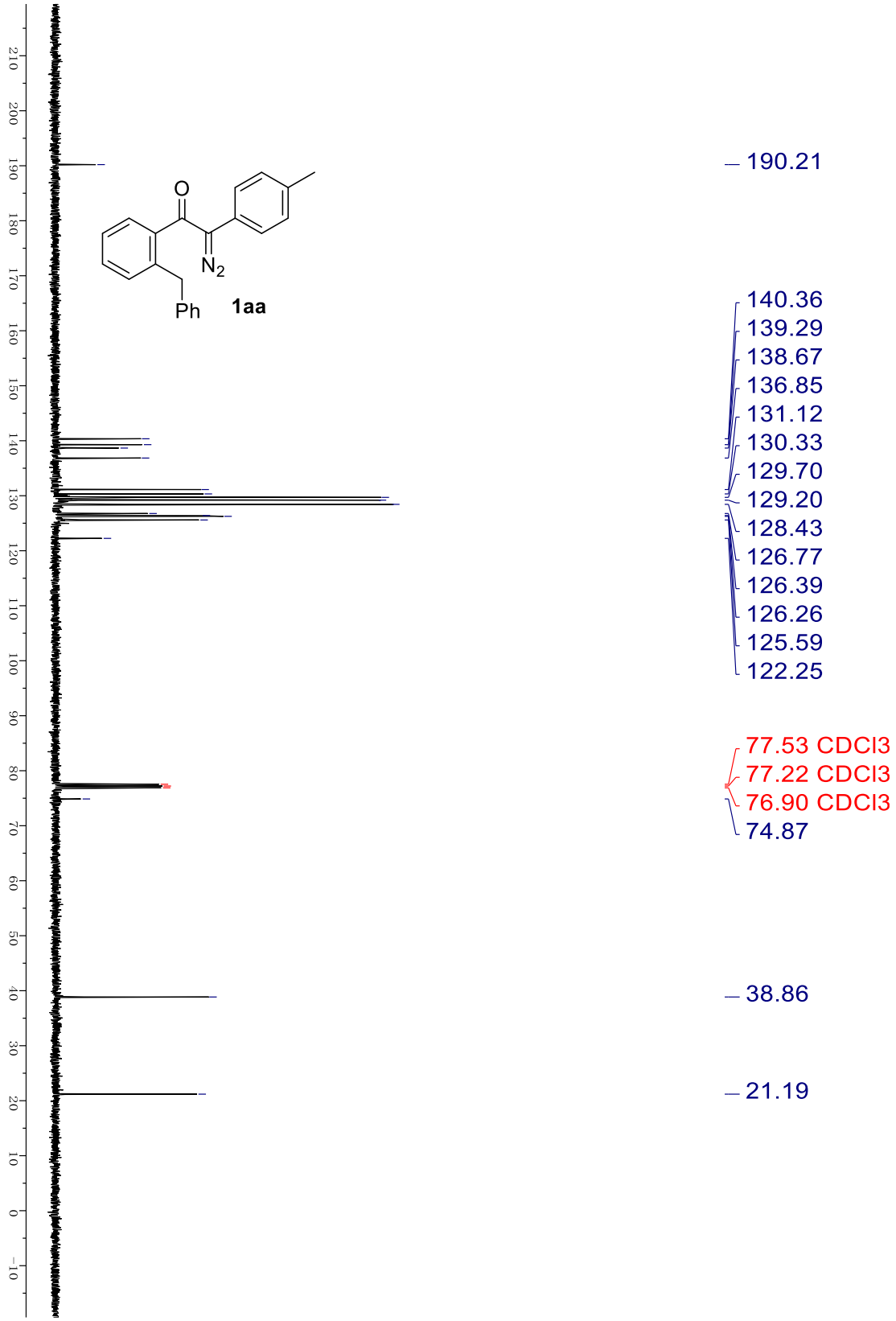
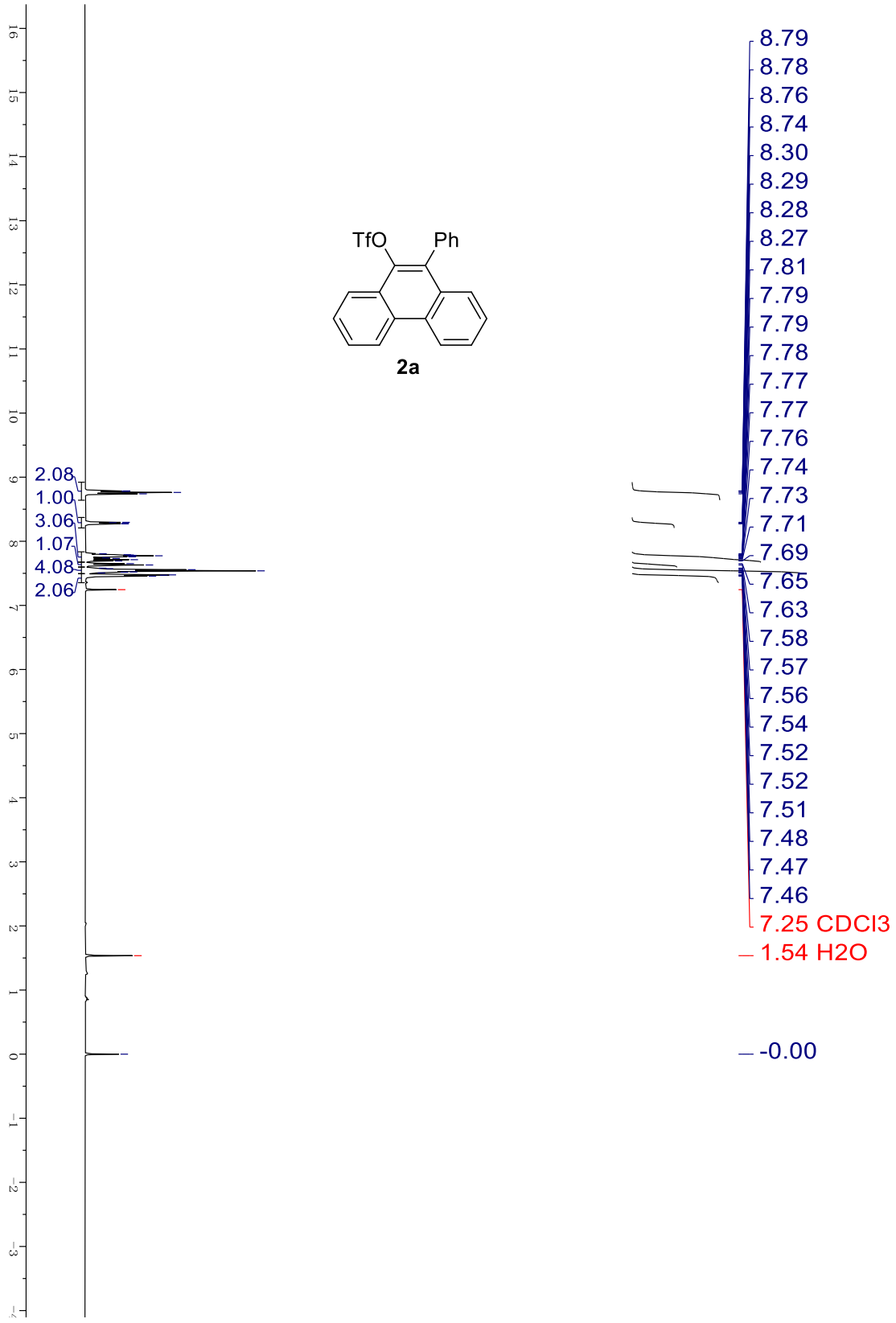
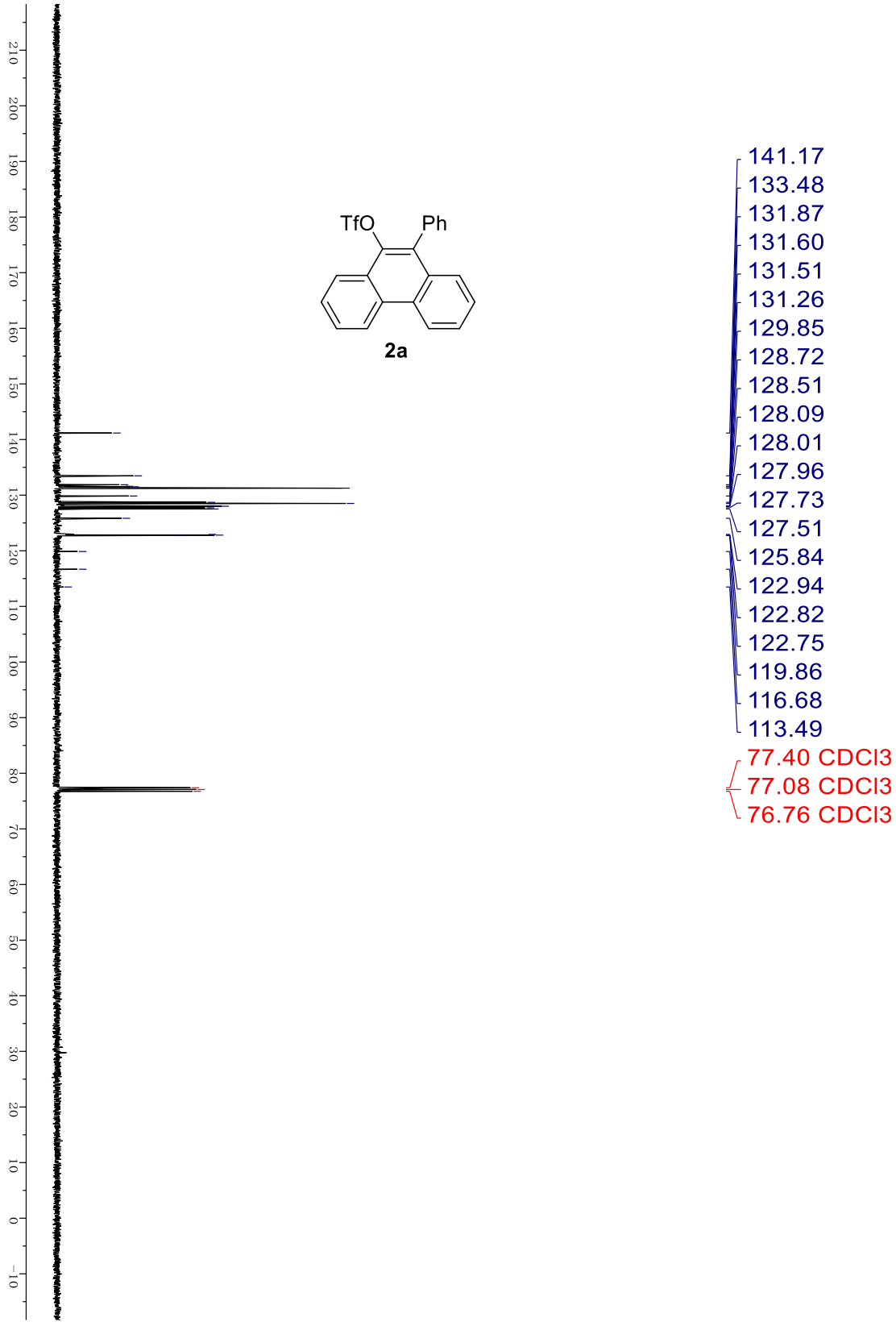
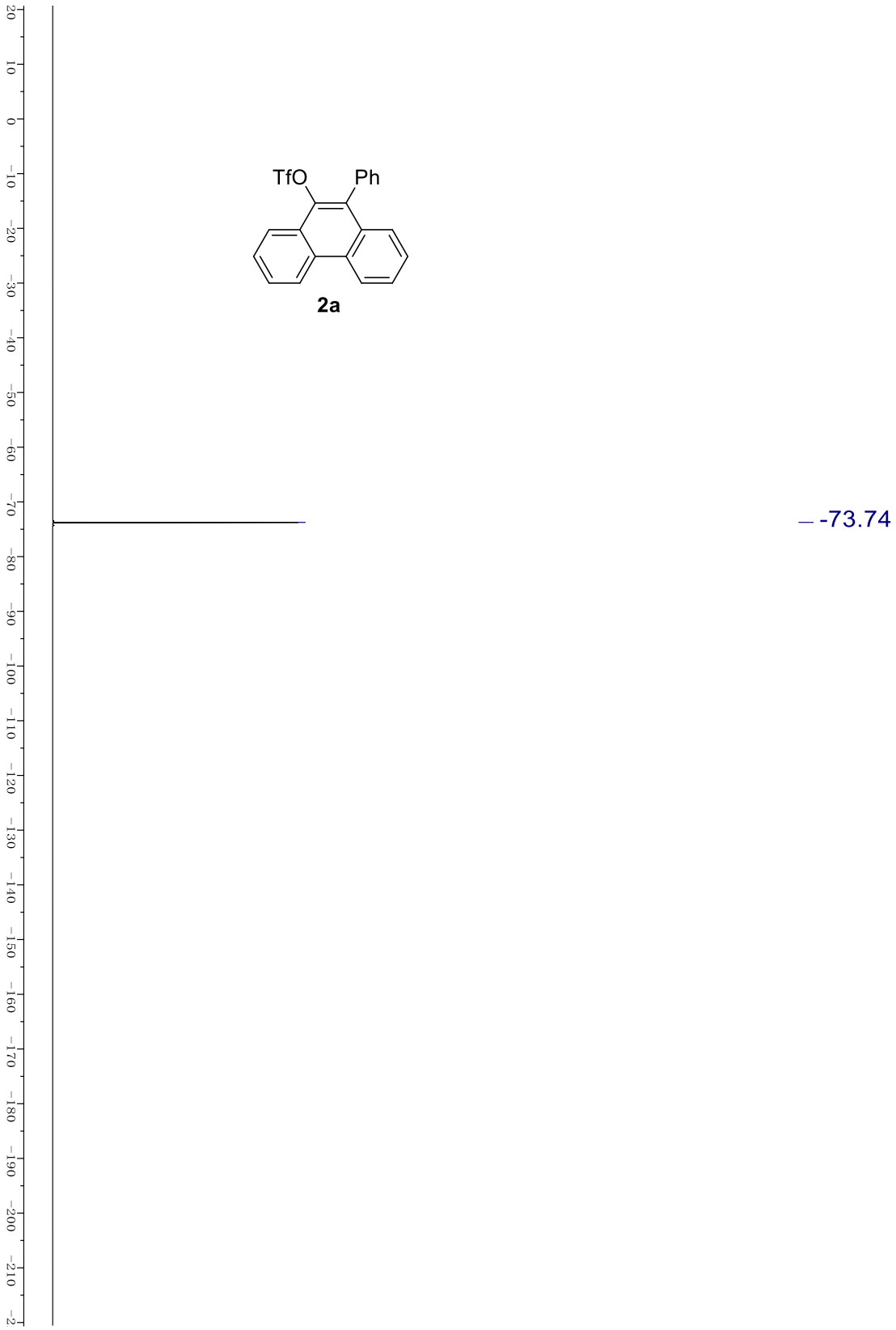
7.00
6.98
3.99
2.21
-0.00

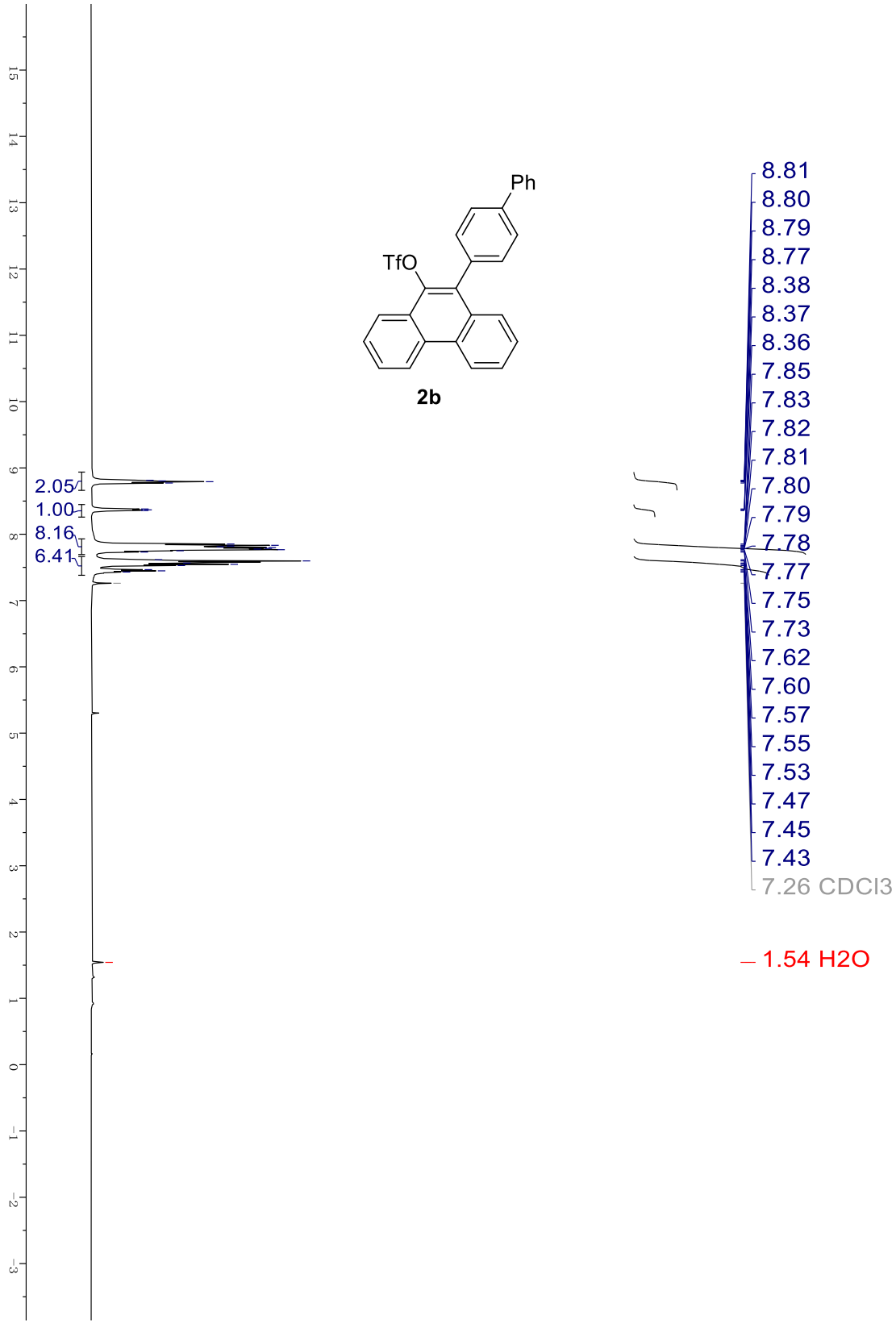

O
N2
Ph
1aa
190.21
140.36
139.29
138.67
136.85
131.12
130.33
129.70
129.20
128.43
126.77
126.39
126.26
125.59
122.25
77.53 CDCl3
77.22 CDCl3
76.90 CDCl3
74.87
38.86
21.19

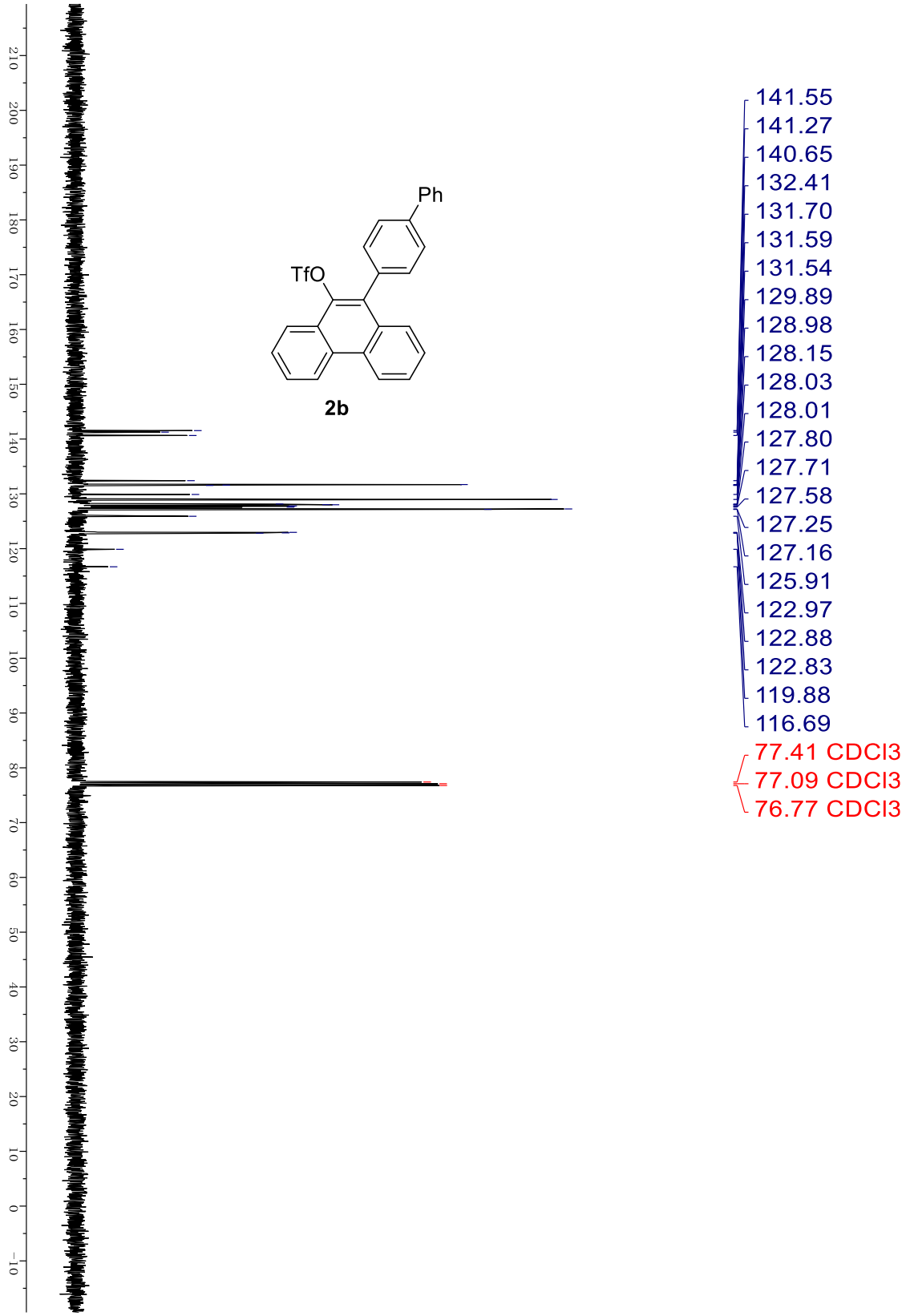
7.2 NMR spectra of compounds 2a–2z, 2z', 2aa and 2j-*d*

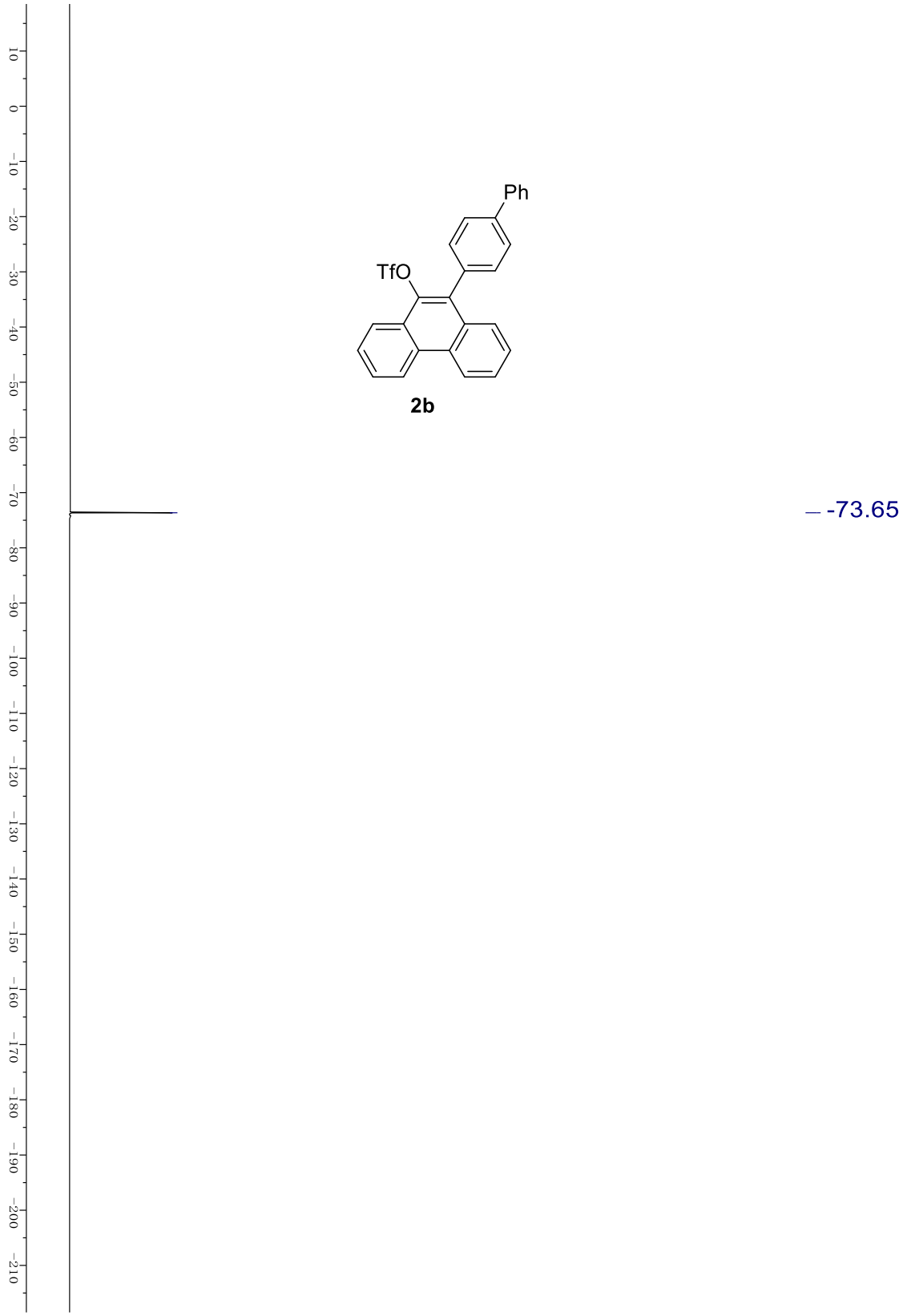



TfO
Ph
2a
141.17
133.48
131.87
131.60
131.51
131.26
129.85
128.72
128.51
128.09
128.01
127.96
127.73
127.51
125.84
122.94
122.82
122.75
119.86
116.68
113.49
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3

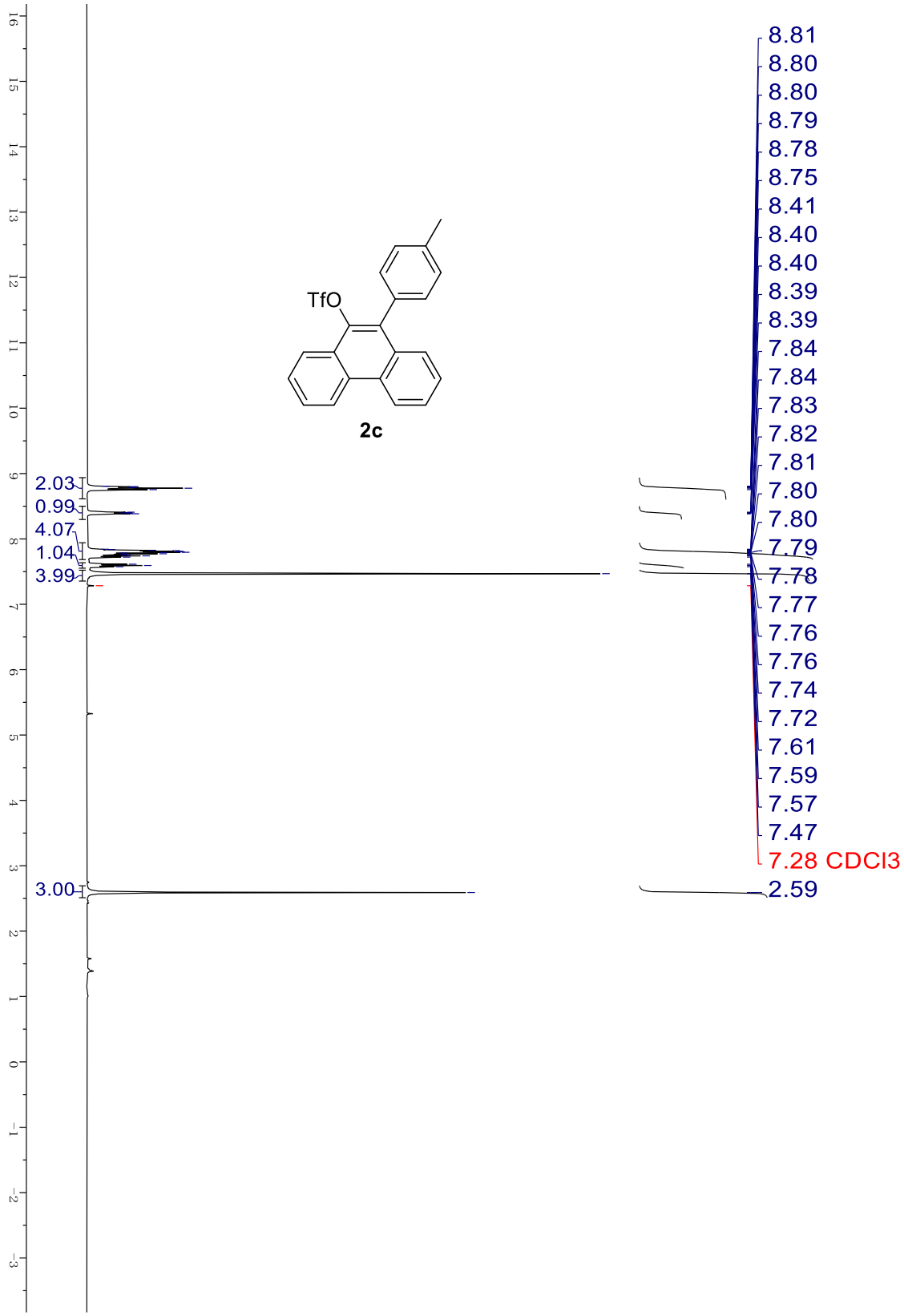

TfO
Ph
2a
-73.74
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


Ph
TfO
2b
2.05
1.00
8.16
6.41
8.81
8.80
8.79
8.77
8.38
8.37
8.36
7.85
7.83
7.82
7.81
7.80
7.79
7.78
7.77
7.75
7.73
7.62
7.60
7.57
7.55
7.53
7.47
7.45
7.43
7.26 CDCl3
1.54 H2O


Ph
TfO
2b
141.55
141.27
140.65
132.41
131.70
131.59
131.54
129.89
128.98
128.15
128.03
128.01
127.80
127.71
127.58
127.25
127.16
125.91
122.97
122.88
122.83
119.88
116.69
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3



2b


TfO
2c
2.03
0.99
4.07
1.04
3.99
3.00
8.81
8.80
8.80
8.79
8.78
8.75
8.41
8.40
8.40
8.39
8.39
7.84
7.84
7.83
7.82
7.81
7.80
7.80
7.79
7.78
7.77
7.76
7.76
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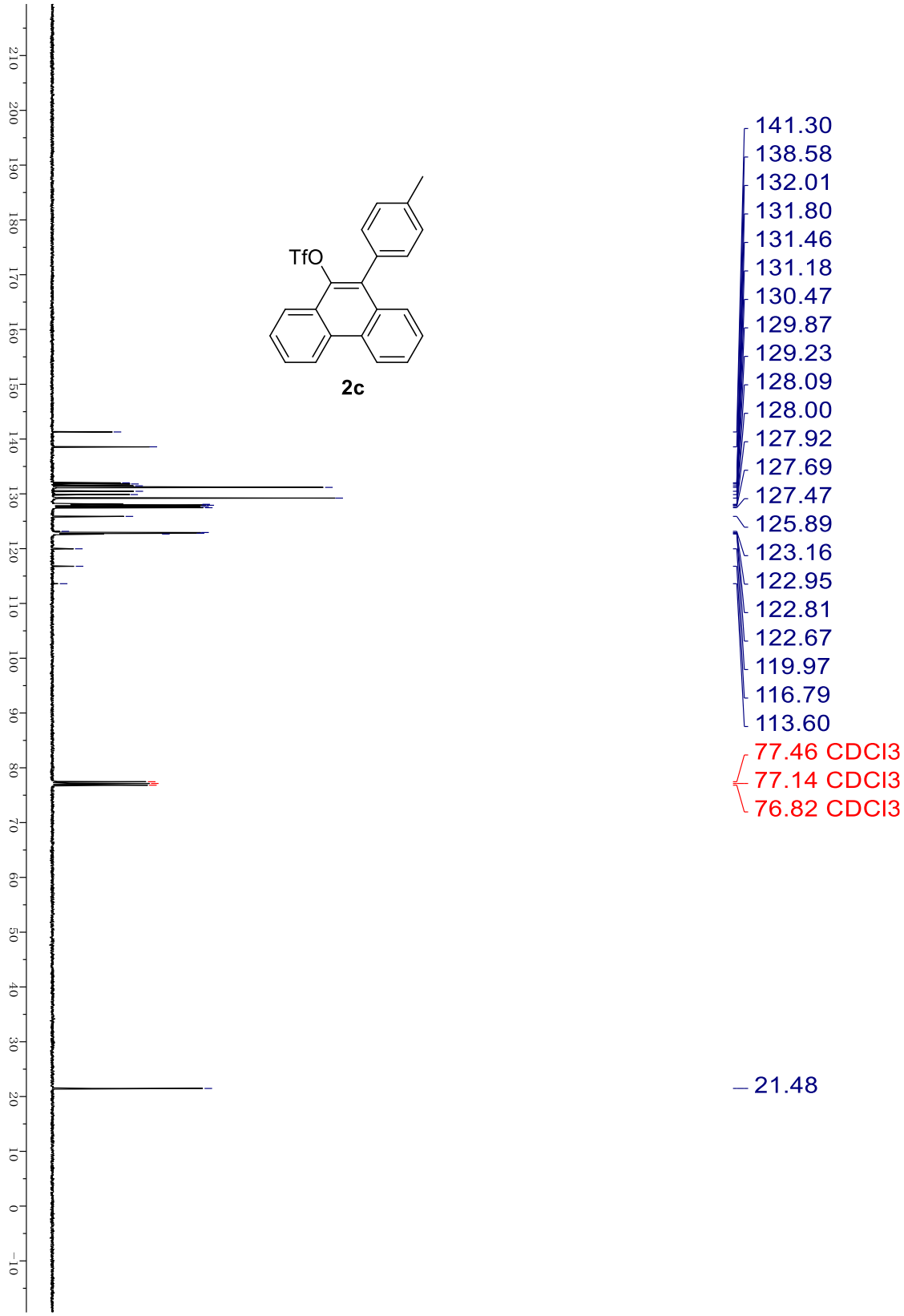
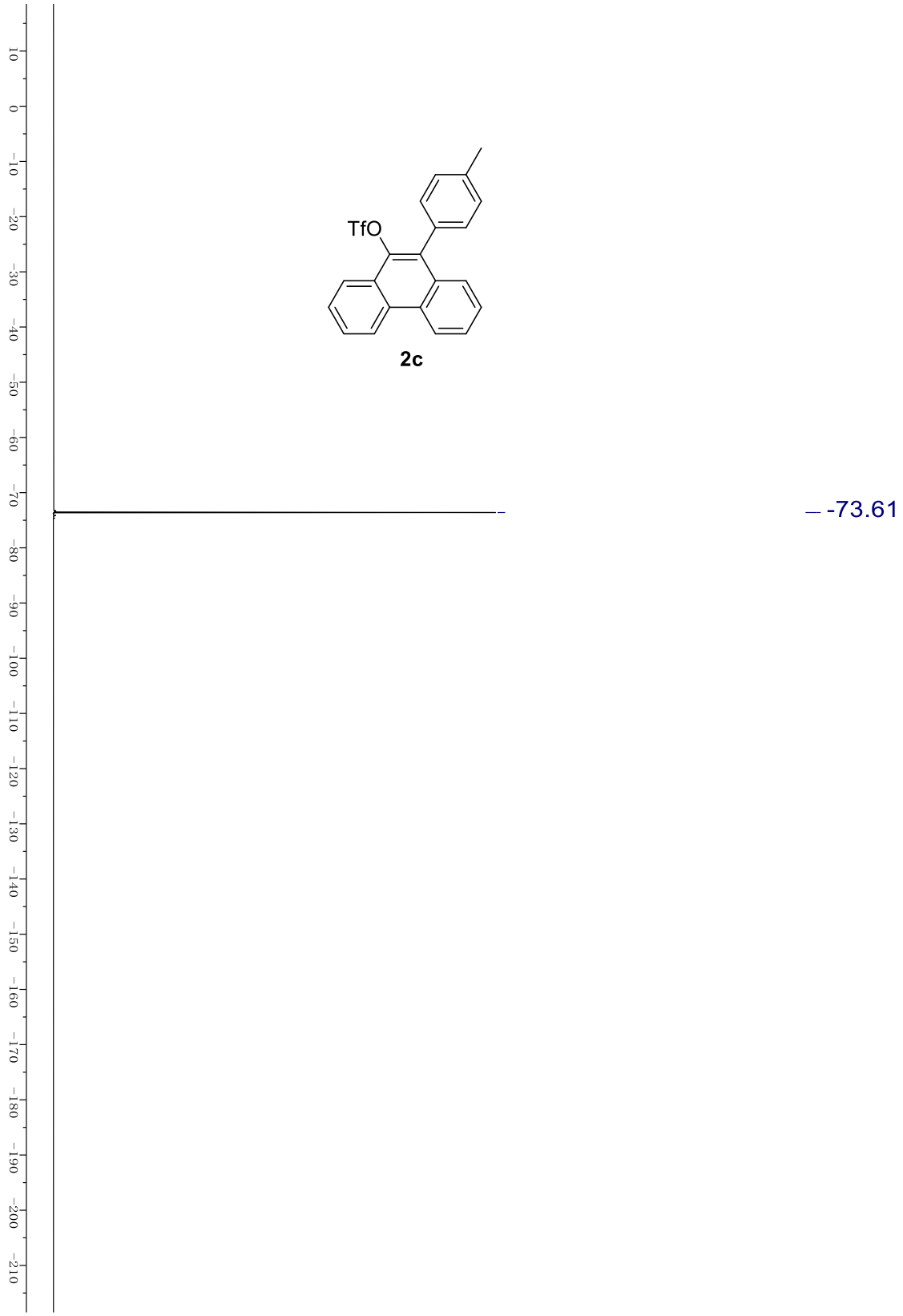
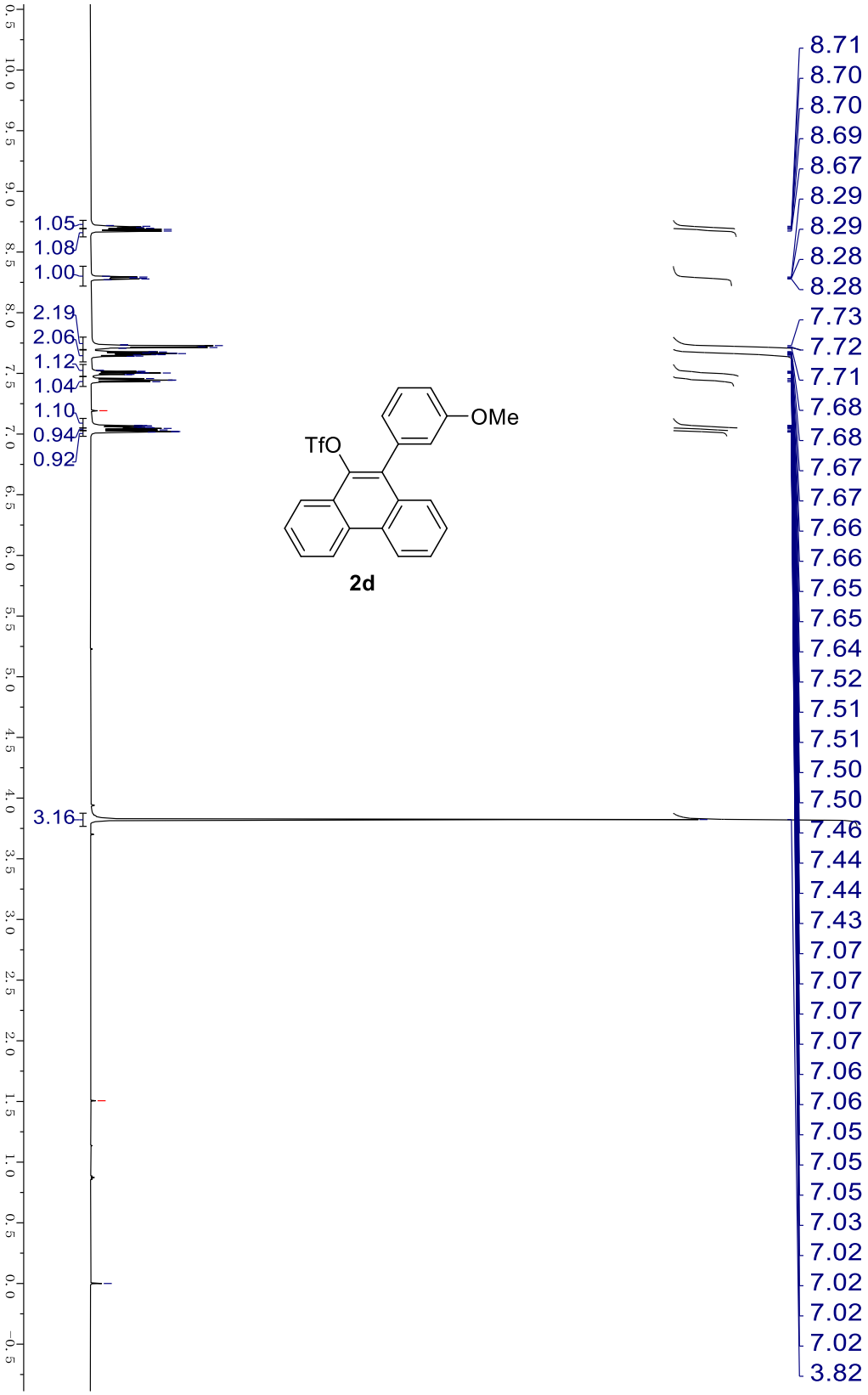
7.59
7.57
7.47
7.28 CDCl3
2.59


TfO
2c
141.30
138.58
132.01
131.80
131.46
131.18
130.47
129.87
129.23
128.09
128.00
127.92
127.69
127.47
125.89
123.16
122.95
122.81
122.67
119.97
116.79
113.60
77.46 CDCl3
77.14 CDCl3
76.82 CDCl3
21.48



2c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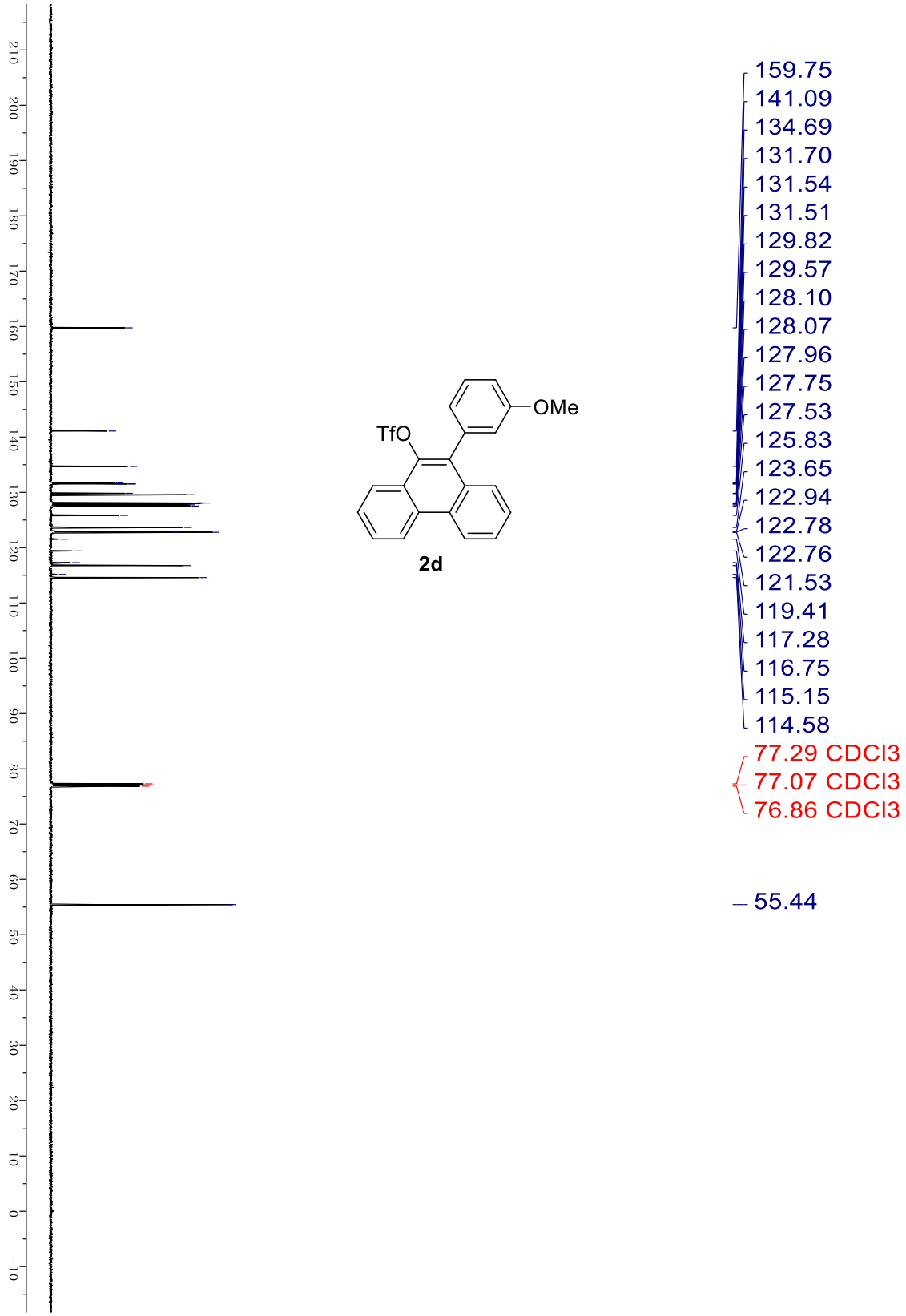
8.70
8.70
8.69
8.67
8.29
8.29
8.28
8.28
7.73
7.72
7.71
7.68
7.68
7.67
7.67
7.66
7.66
7.65
7.65
7.64
7.52
7.51
7.51
7.50
7.50
7.46
7.44
7.44
7.43
7.07
7.07
7.07
7.07
7.06
7.06
7.05
7.05
7.05
7.03
7.02
7.02
7.02
7.02
3.82
1.05
1.08
1.00
2.19
2.06
1.12
1.04
1.10
0.94
0.92
3.16
TfO
OMe
2d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141.09
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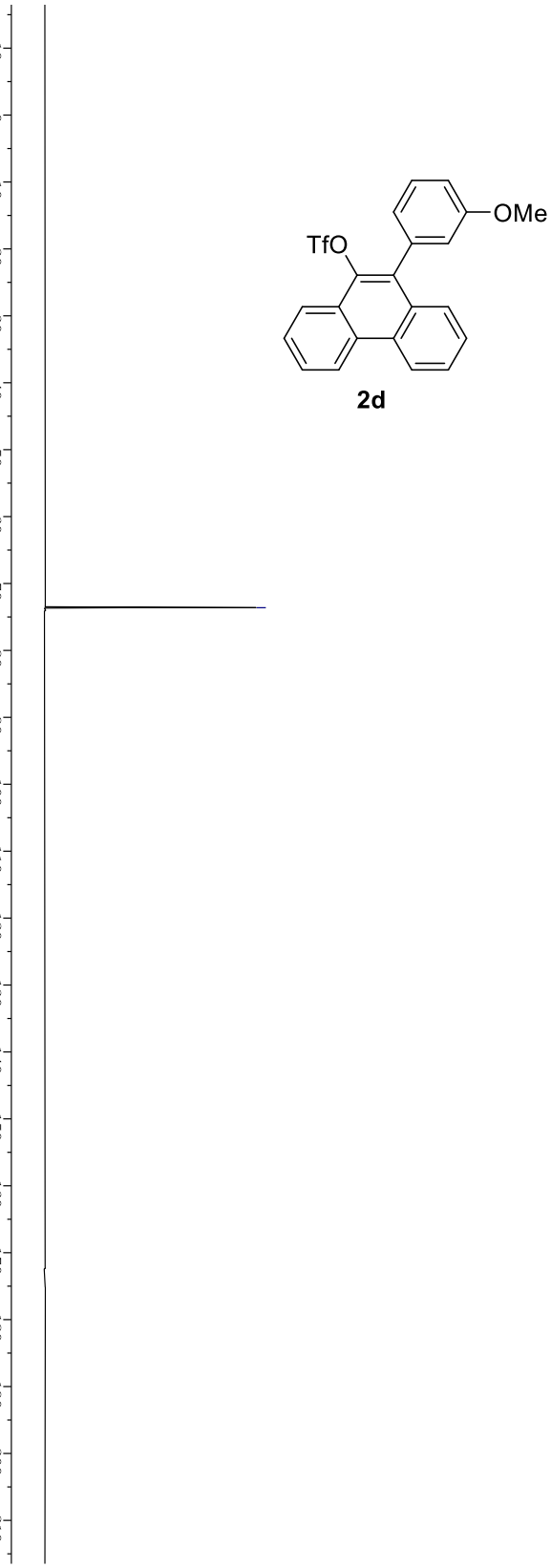
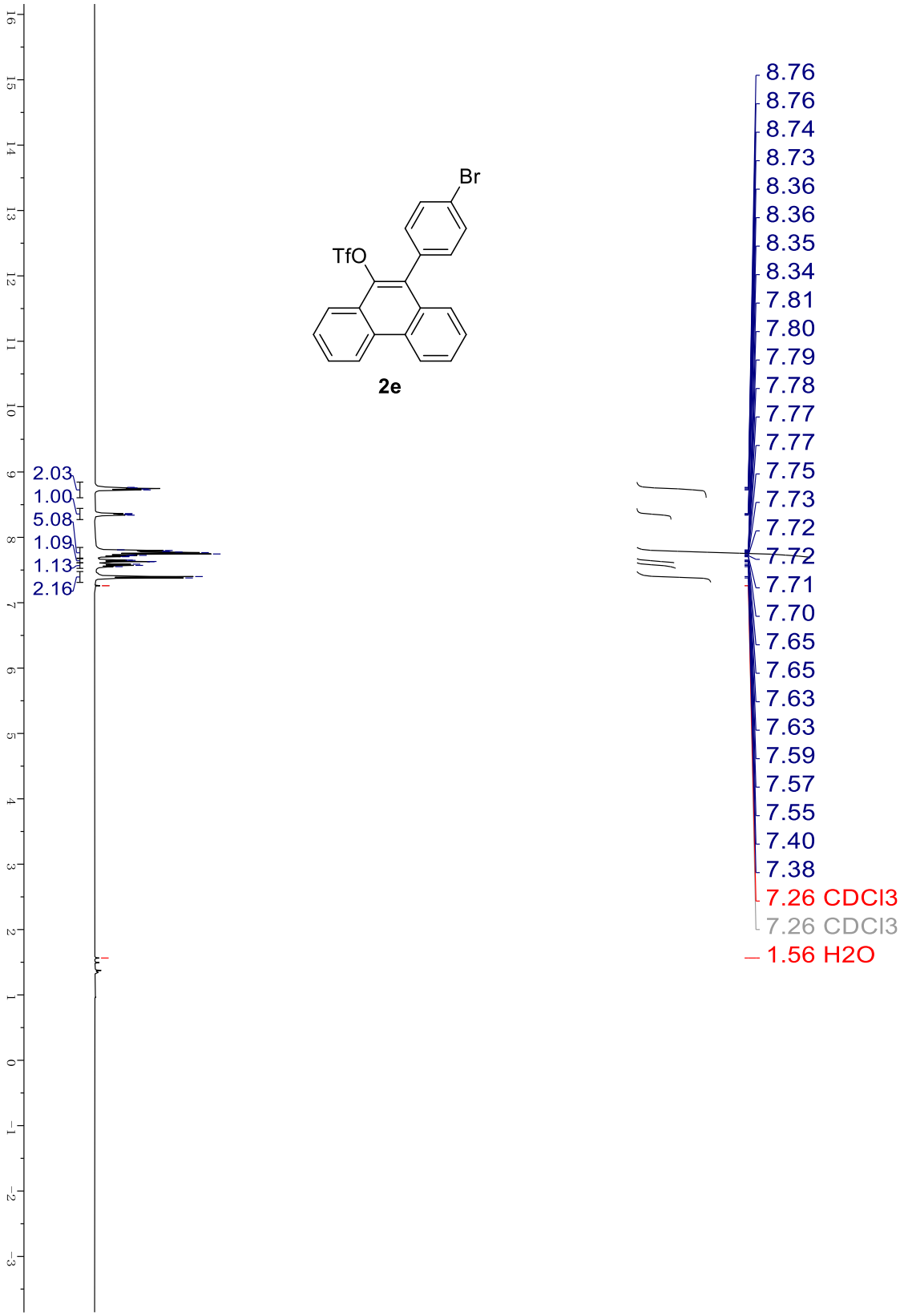
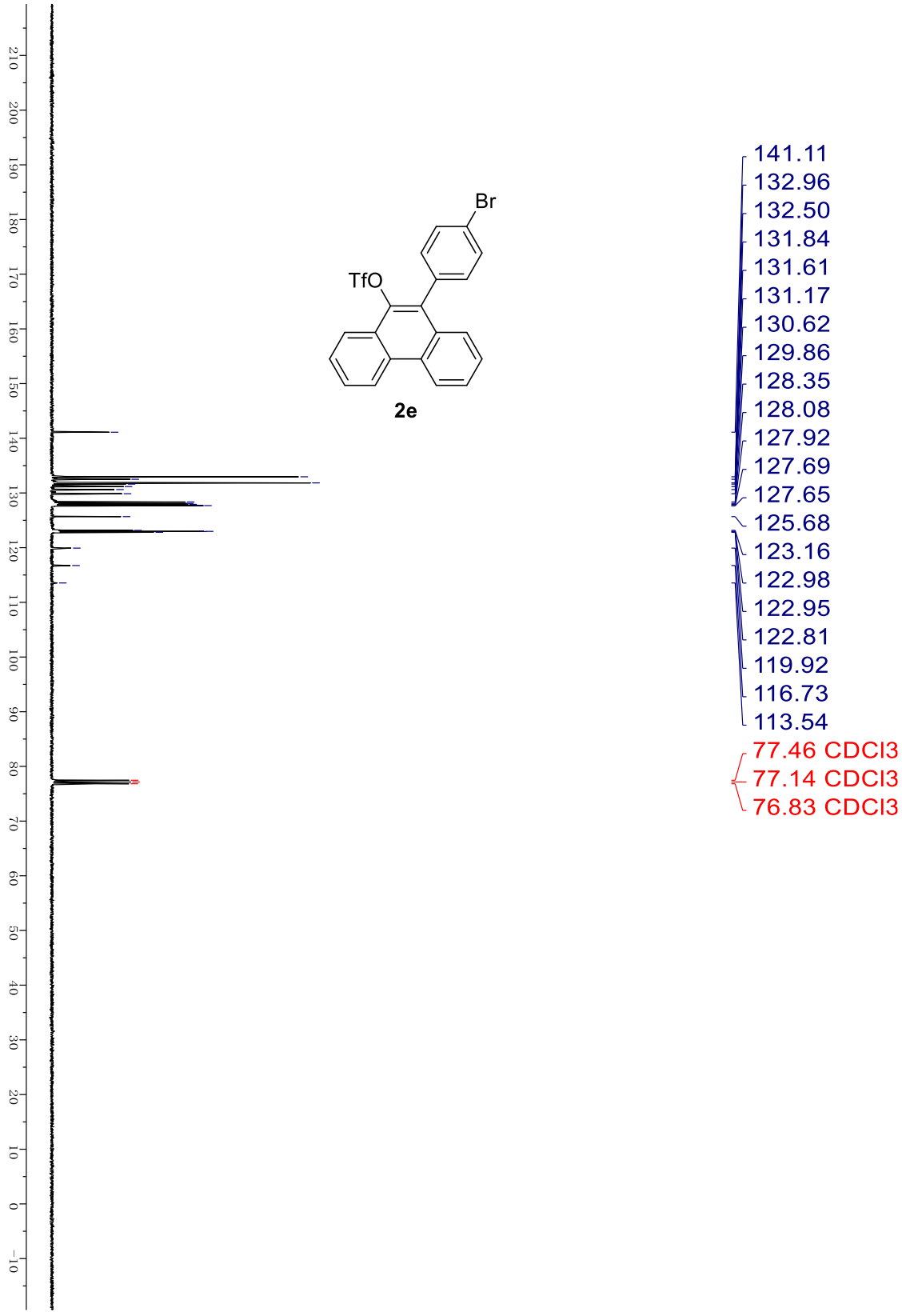
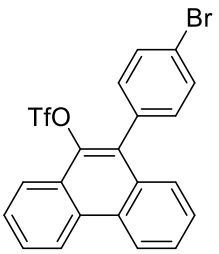
131.70
131.54
131.51
129.82
129.57
128.10
128.07
127.96
127.75
127.53
125.83
123.65
122.94
122.78
122.76
121.53
119.41
117.28
116.75
115.15
114.58
77.29 CDCl3
77.07 CDCl3
76.86 CDCl3
55.44
TfO
OMe
2d

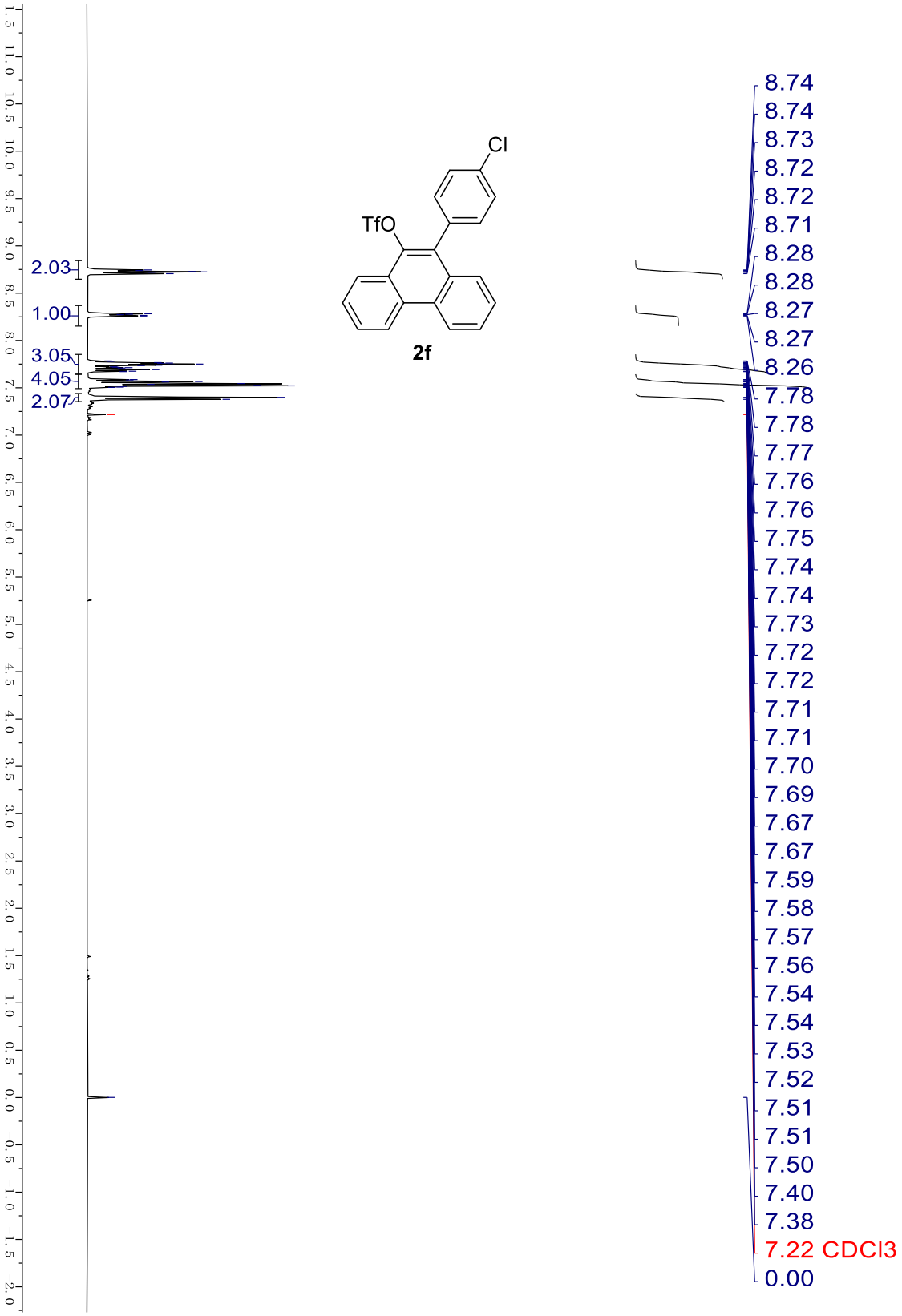

10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
TfO
OMe
2d
-73.61

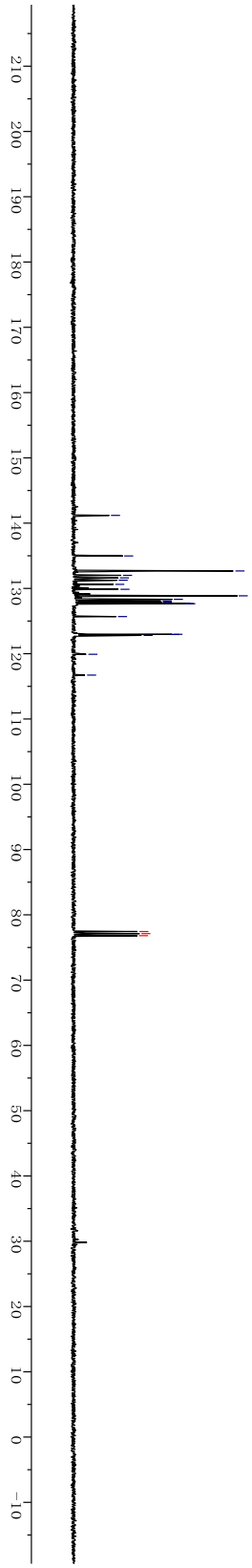

Br
TfO
2e
2.03
1.00
5.08
1.09
1.13
2.16
8.76
8.76
8.74
8.73
8.36
8.36
8.35
8.34
7.81
7.80
7.79
7.78
7.77
7.77
7.75
7.73
7.72
7.72
7.71
7.70
7.65
7.65
7.63
7.63
7.59
7.57
7.55
7.40
7.38
7.26 CDCl3
7.26 CDCl3
1.56 H2O

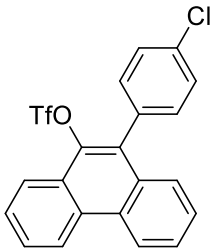

Br
TfO
2e
141.11
132.96
132.50
131.84
131.61
131.17
130.62
129.86
128.35
128.08
127.92
127.69
127.65
125.68
123.16
122.98
122.95
122.81
119.92
116.73
113.54
77.46 CDCl3
77.14 CDCl3
76.83 CDCl3



2e


Cl
TfO
2f
2.03
1.00
3.05
4.05
2.07
8.74
8.74
8.73
8.72
8.72
8.71
8.28
8.28
8.27
8.27
8.26
7.78
7.78
7.77
7.76
7.76
7.75
7.74
7.74
7.73
7.72
7.72
7.71
7.71
7.70
7.69
7.67
7.67
7.59
7.58
7.57
7.56
7.54
7.54
7.53
7.52
7.51
7.51
7.50
7.40
7.38
7.22 CDCl3
0.00





2f

141.19
134.98
132.68
132.00
131.61
131.26
130.62
129.87
128.87
128.33
128.07
127.90
127.68
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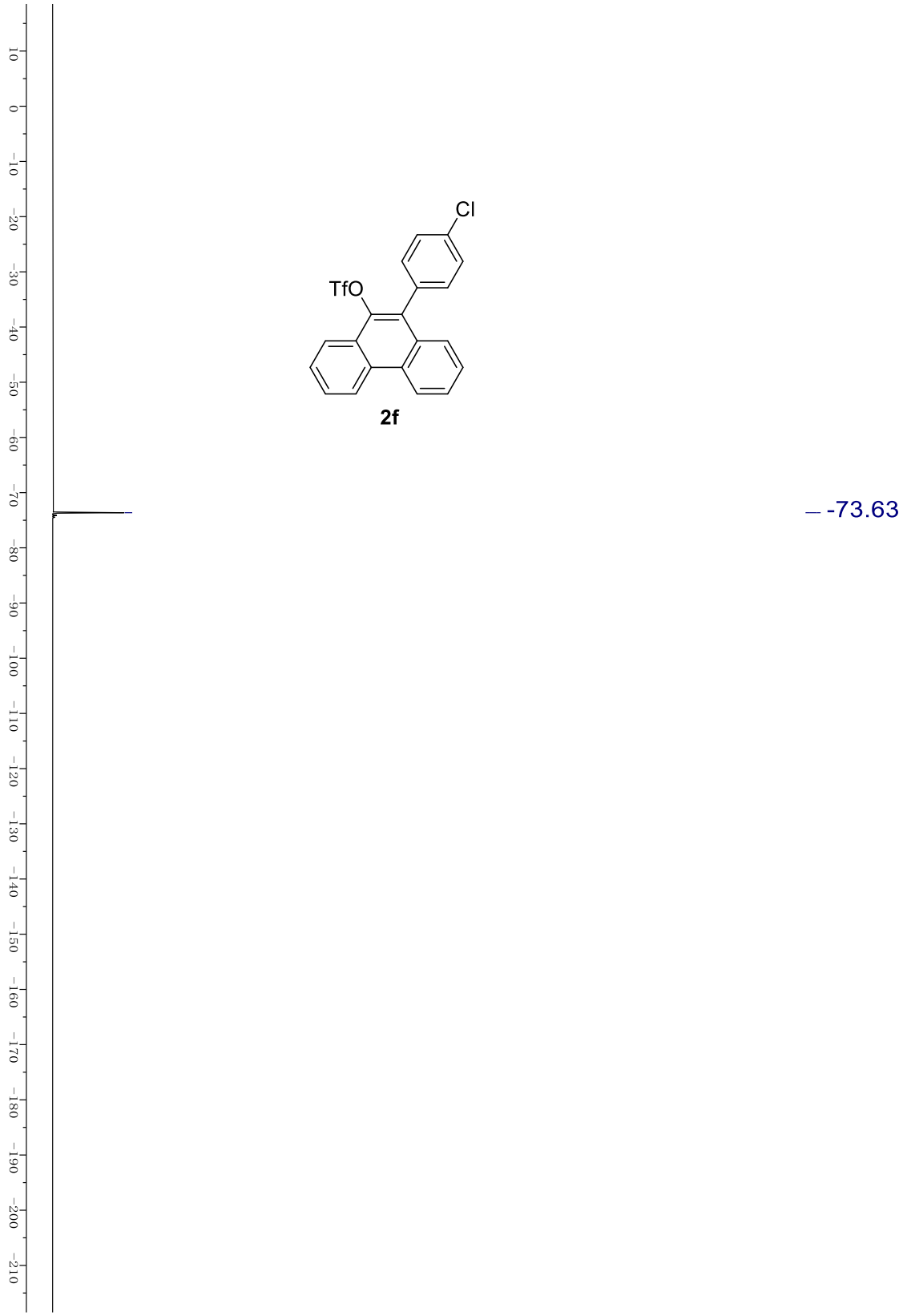
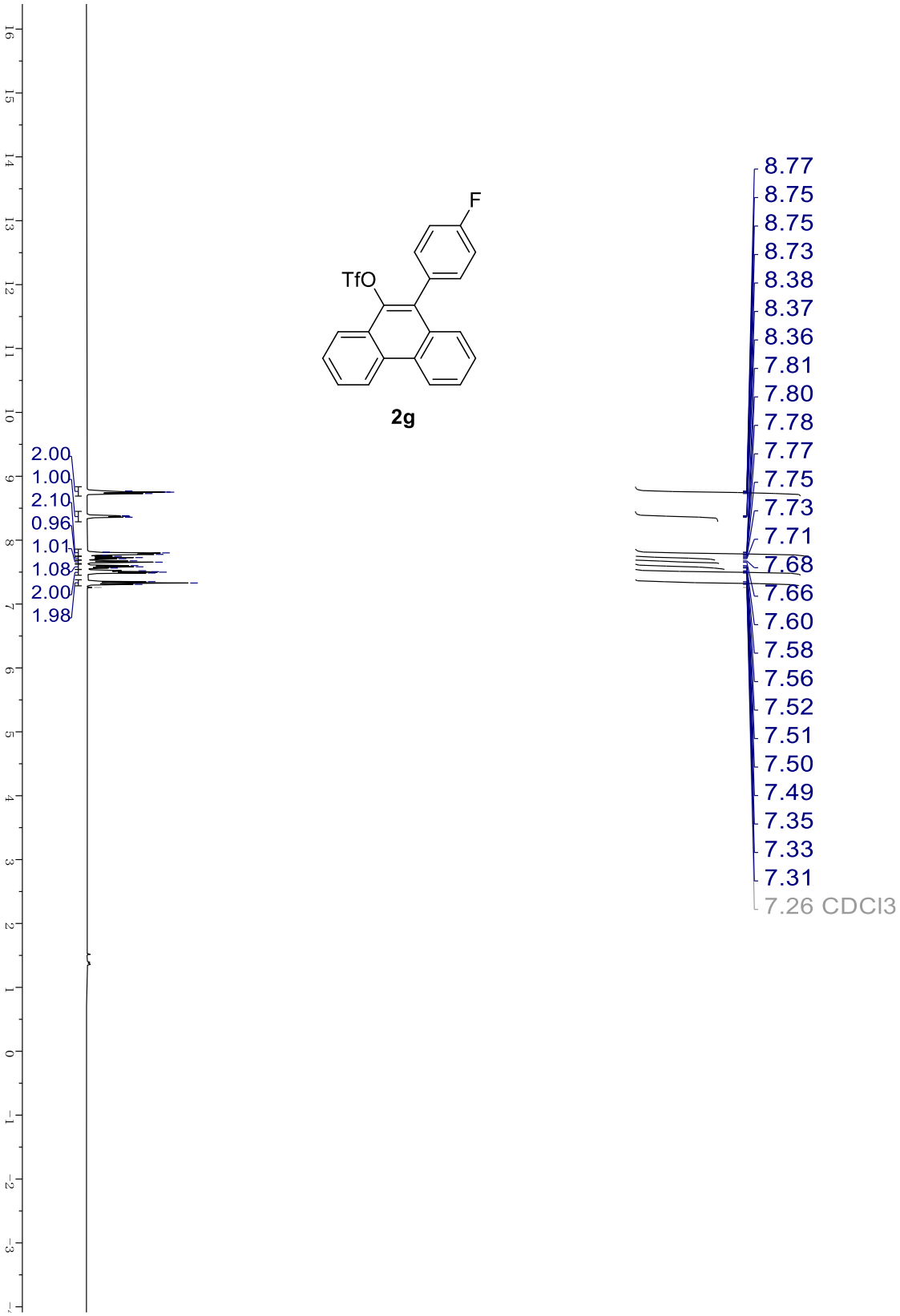
116.72
77.44 CDCl3
77.12 CDCl3
76.80 CDCl3


Cl
TfO
2f
-73.63
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


F
TfO
2g
2.00
1.00
2.10
0.96
1.01
1.08
2.00
1.98
8.77
8.75
8.75
8.73
8.38
8.37
8.36
7.81
7.80
7.78
7.77
7.75
7.73
7.71
7.68
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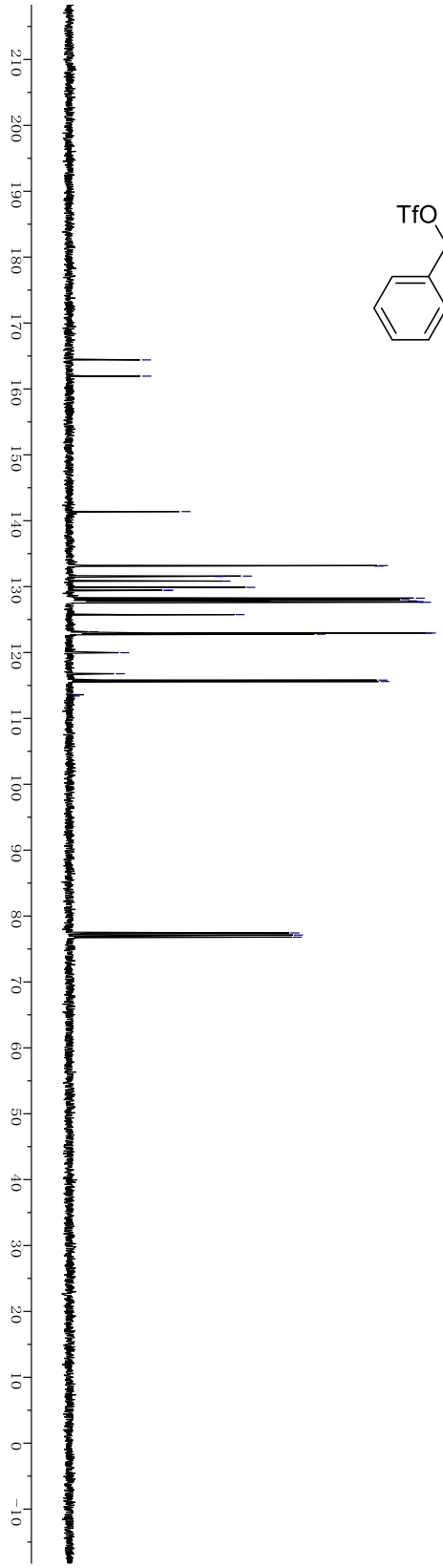
7.51
7.50
7.49
7.35
7.33
7.31
7.26 CDCl3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200
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100
90
80
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60
50
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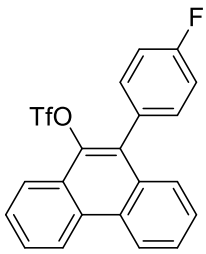
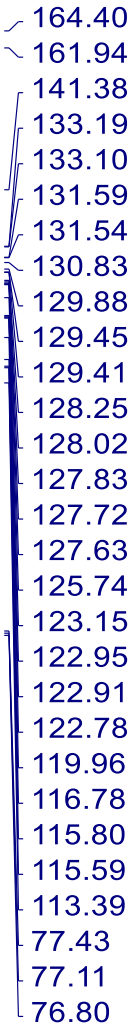
20
10
0
−10


F
TfO

2g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133.10
131.59
131.54
130.83
129.88
129.45
129.41
128.25
128.02
127.83
127.72
127.63
125.74
123.15
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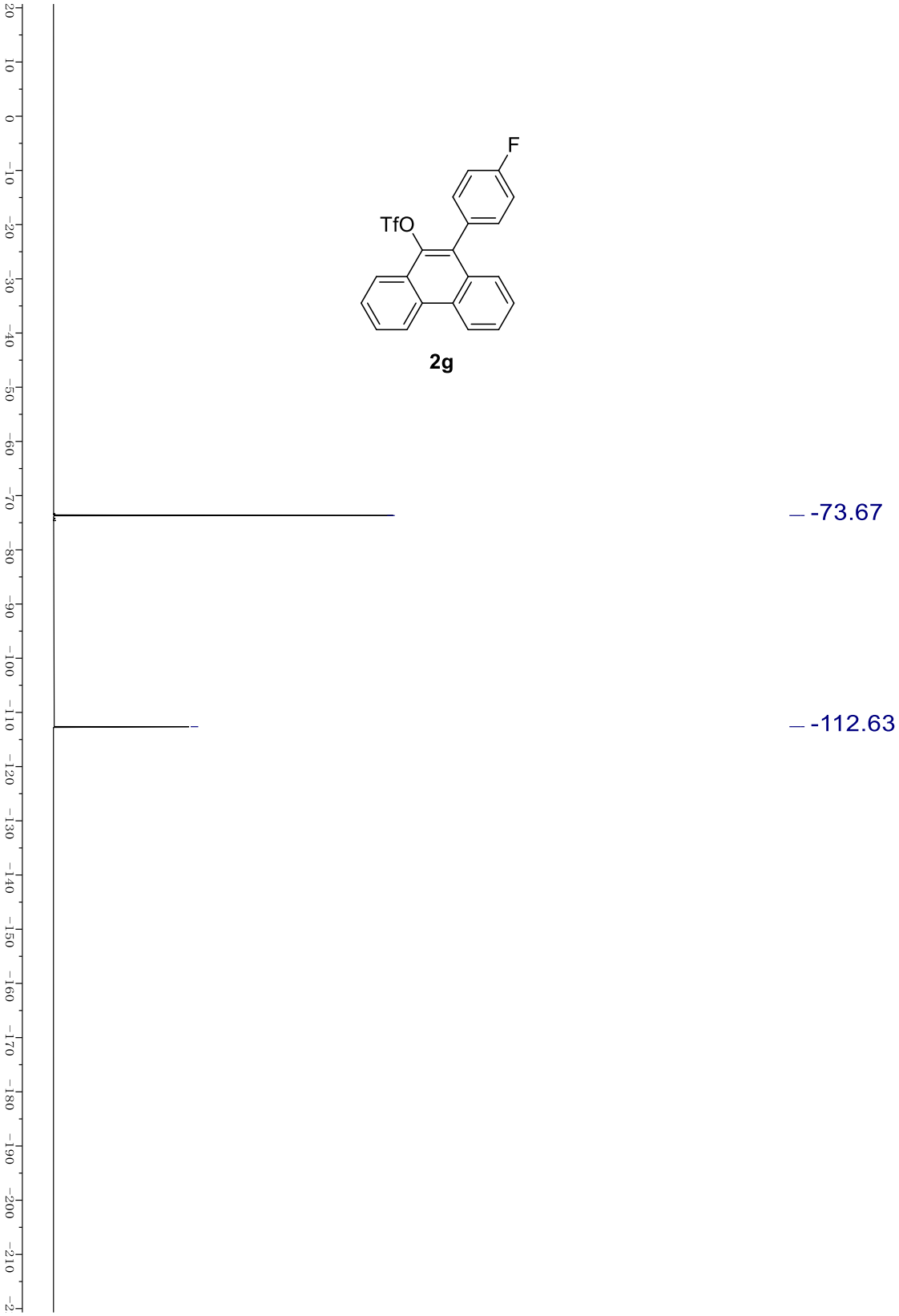
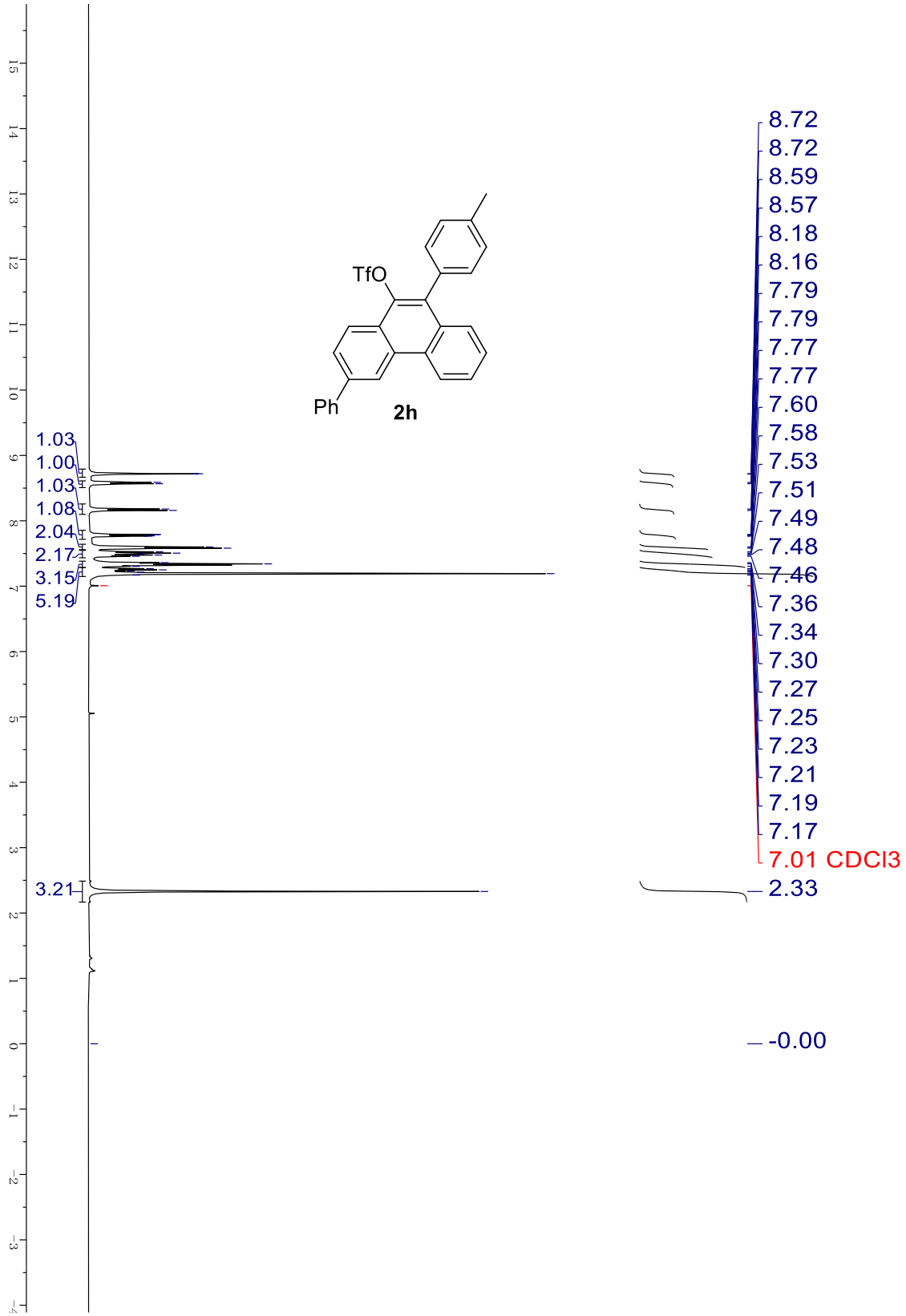
122.91
122.78
119.96
116.78
115.80
115.59
113.39
77.43
77.11
76.80


F
TfO
2g
-73.67
-112.63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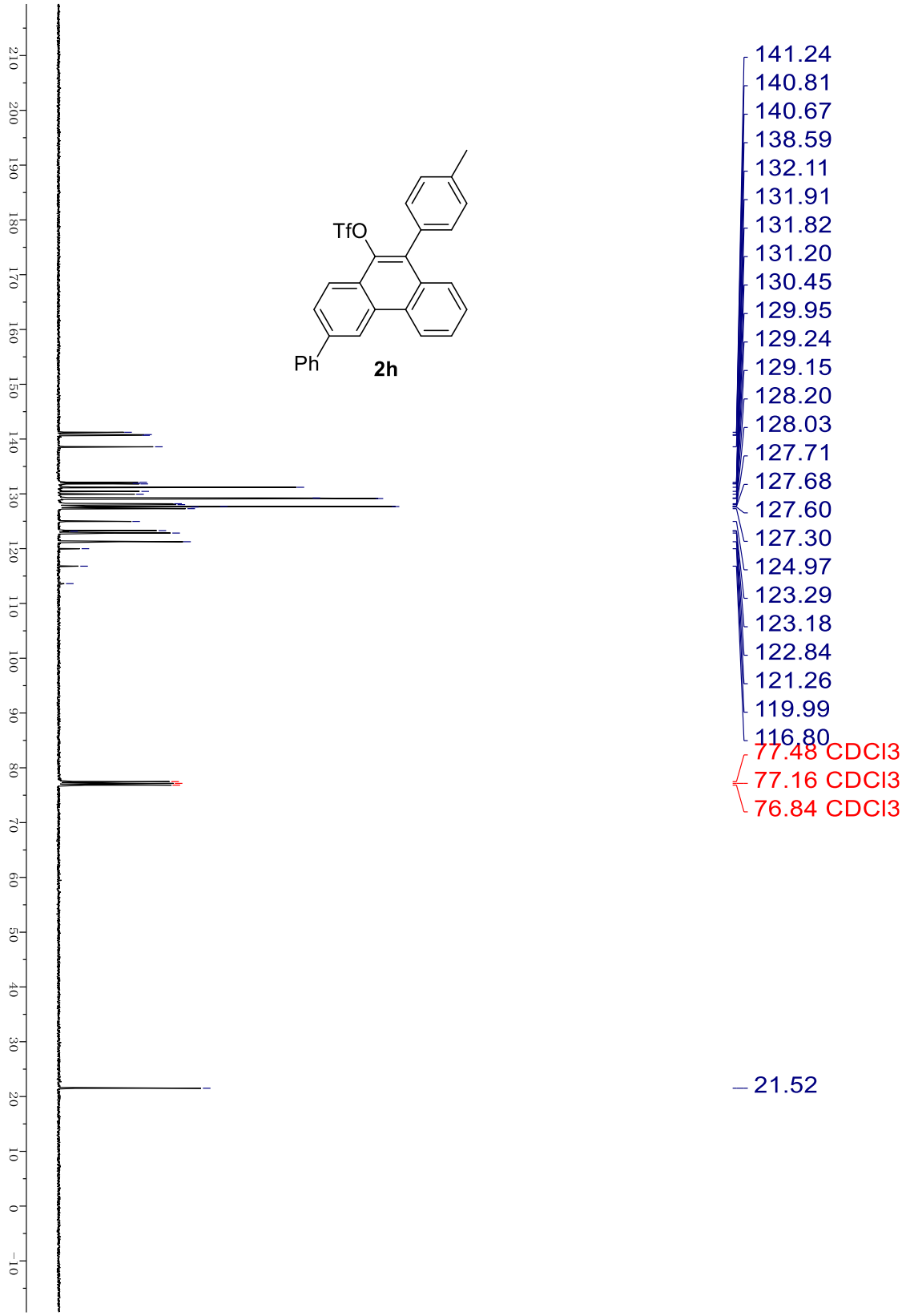
Ph
2h
1.03
1.00
1.03
1.08
2.04
2.17
3.15
5.19
3.21
8.72
8.72
8.59
8.57
8.18
8.16
7.79
7.79
7.77
7.77
7.60
7.58
7.53
7.51
7.49
7.48
7.46
7.36
7.34
7.30
7.27
7.25
7.23
7.21
7.19
7.17
7.01 CDCl3
2.33
-0.00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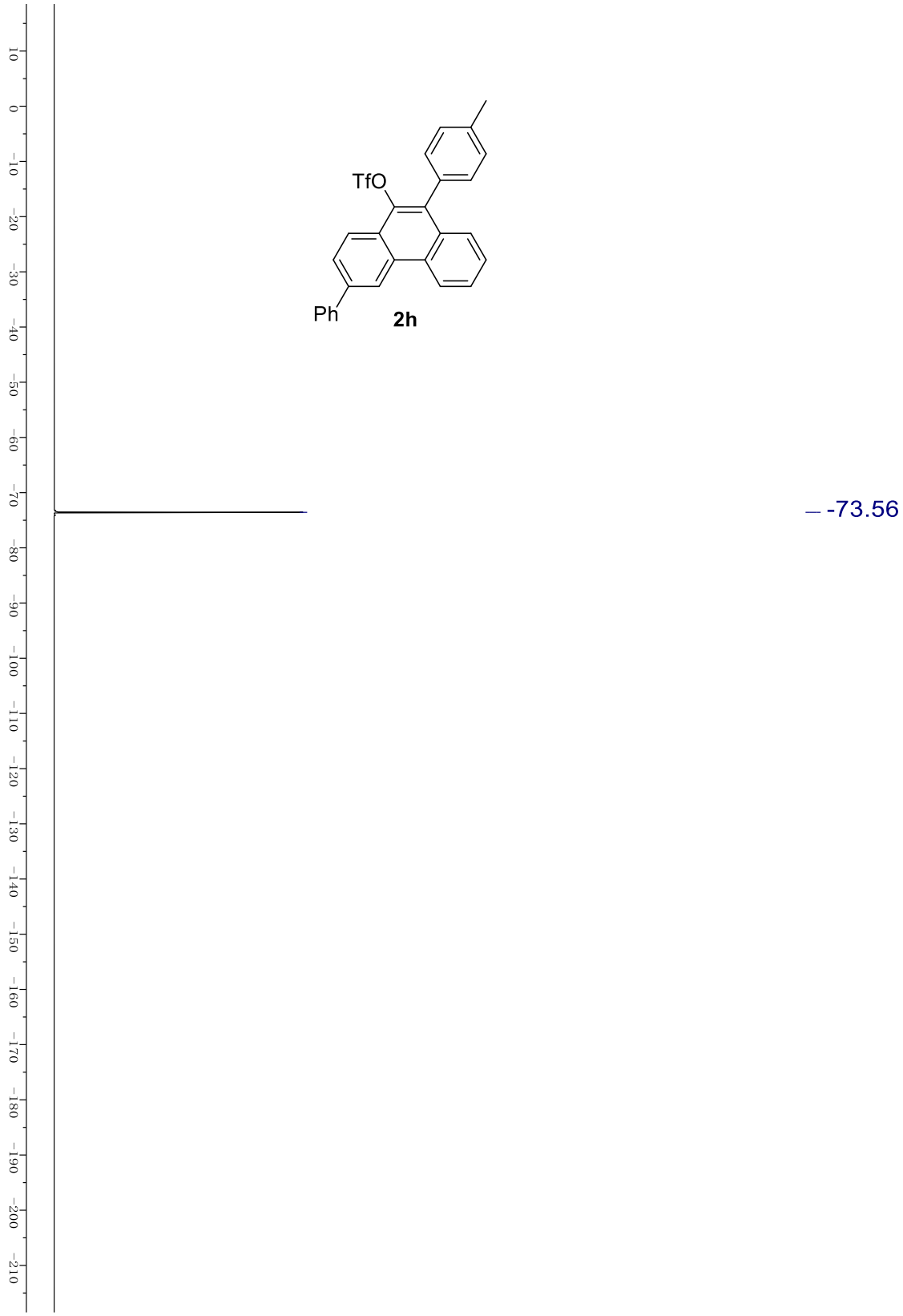
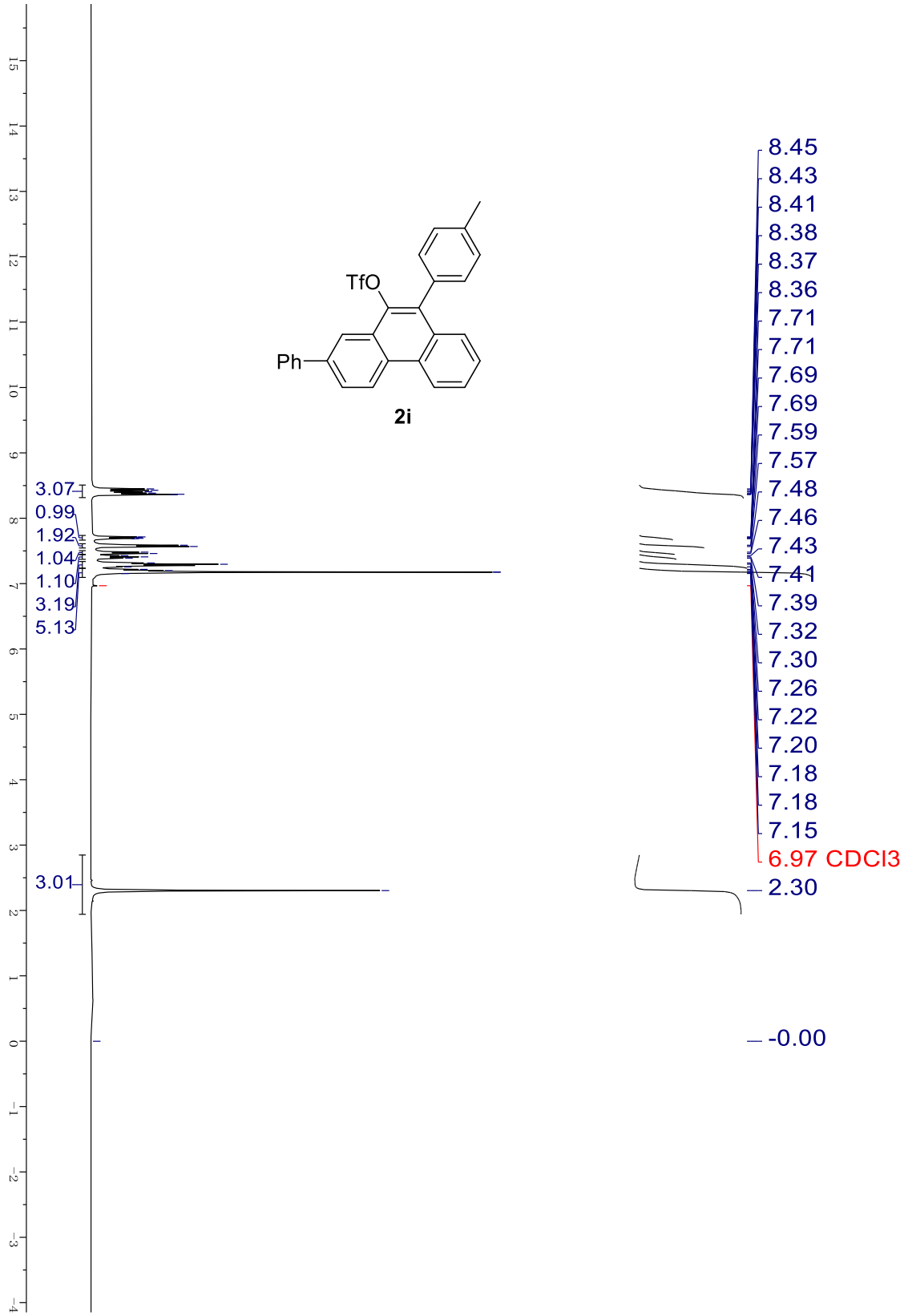
Ph
2h
141.24
140.81
140.67
138.59
132.11
131.91
131.82
131.20
130.45
129.95
129.24
129.15
128.20
128.03
127.71
127.68
127.60
127.30
124.97
123.29
123.18
122.84
121.26
119.99
116.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.52


TfO
Ph
2h
-73.56
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


TfO
Ph
2i
3.07
0.99
1.92
1.04
1.10
3.19
5.13
3.01
8.45
8.43
8.41
8.38
8.37
8.36
7.71
7.71
7.69
7.69
7.59
7.57
7.48
7.46
7.43
7.41
7.39
7.32
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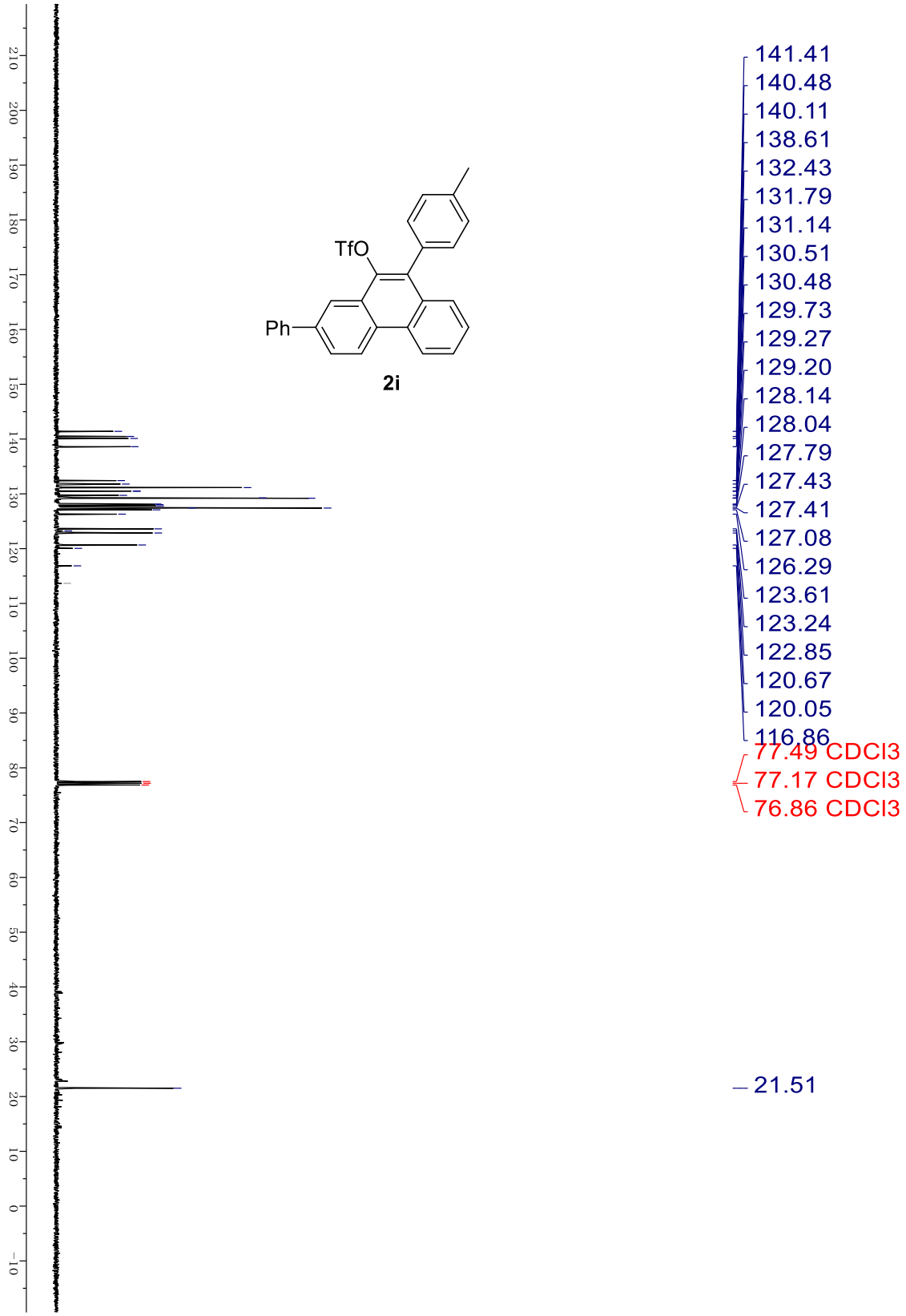
7.26
7.22
7.20
7.18
7.18
7.15
6.97 CDCl3
2.30
-0.00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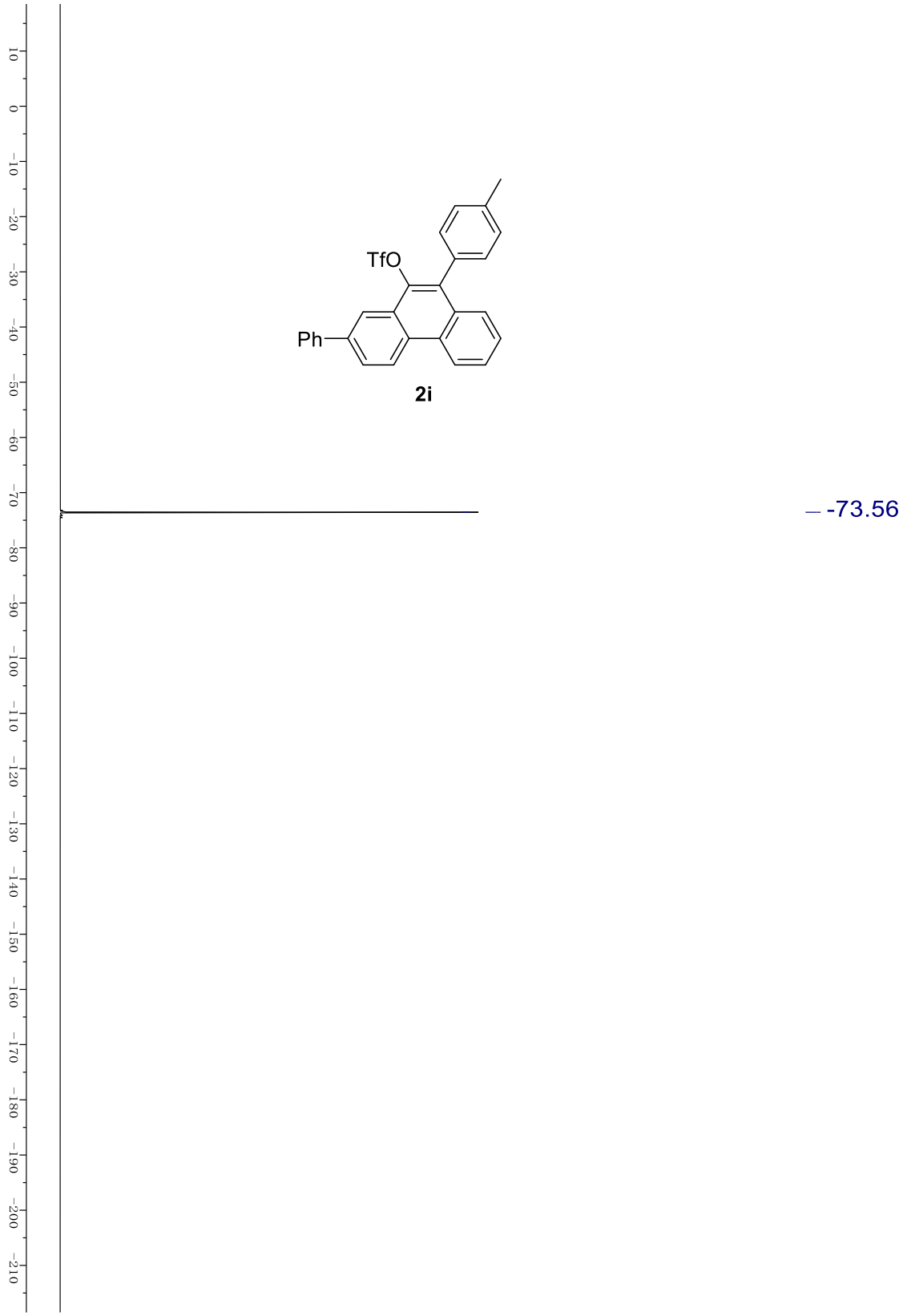
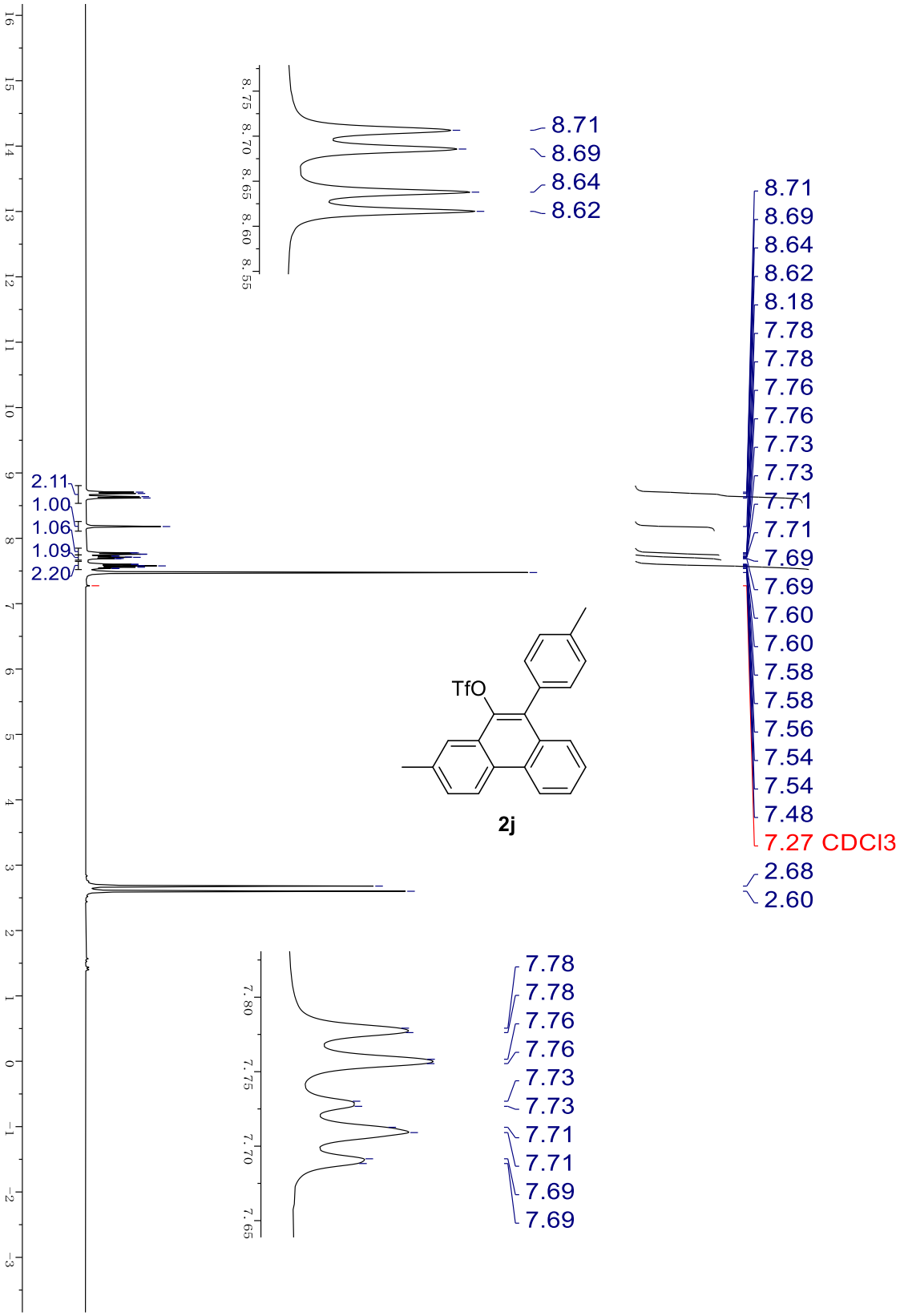
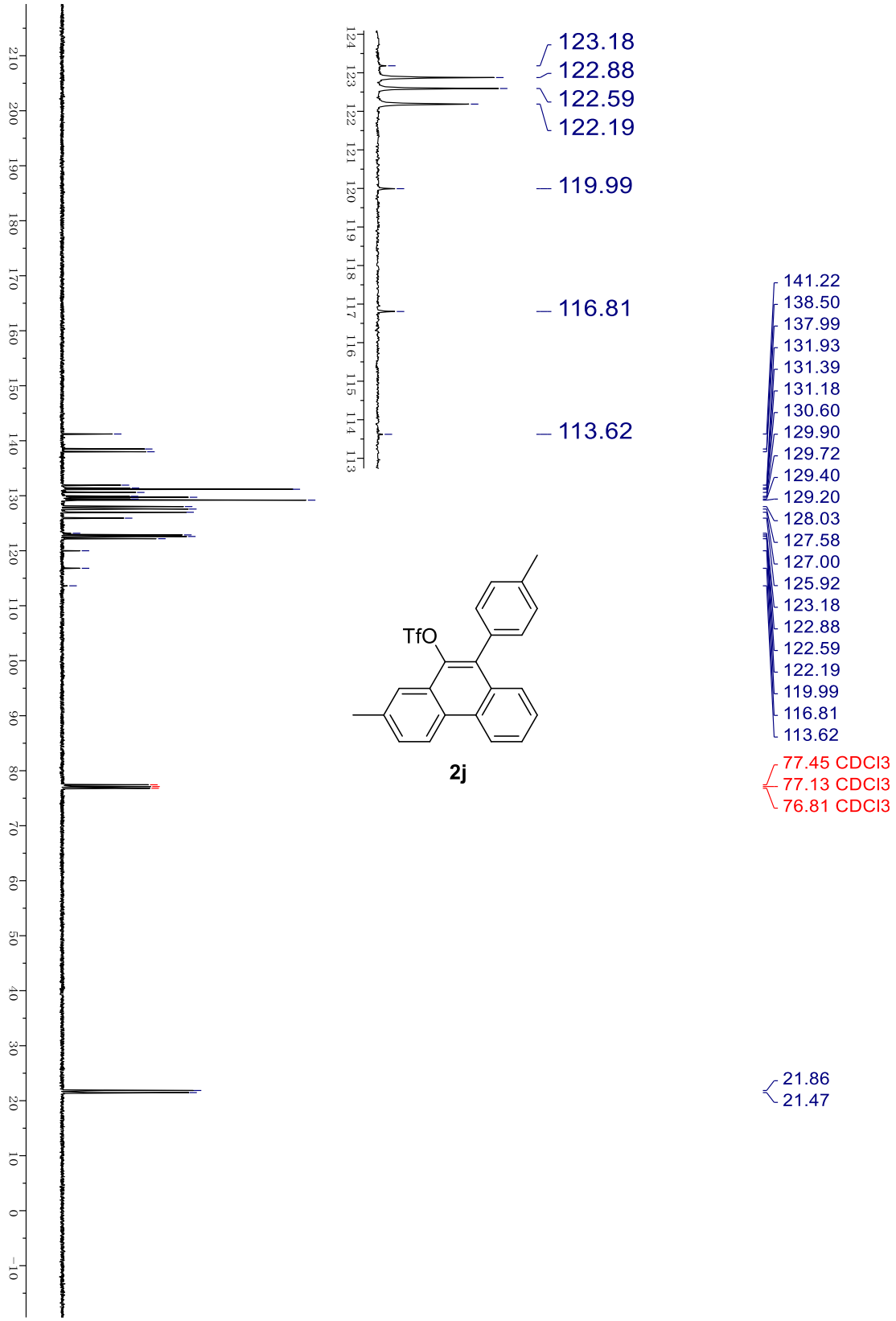
Ph
2i
141.41
140.48
140.11
138.61
132.43
131.79
131.14
130.51
130.48
129.73
129.27
129.20
128.14
128.04
127.79
127.43
127.41
127.08
126.29
123.61
123.24
122.85
120.67
120.05
116.86
77.49 CDCl3
77.17 CDCl3
76.86 CDCl3
21.51



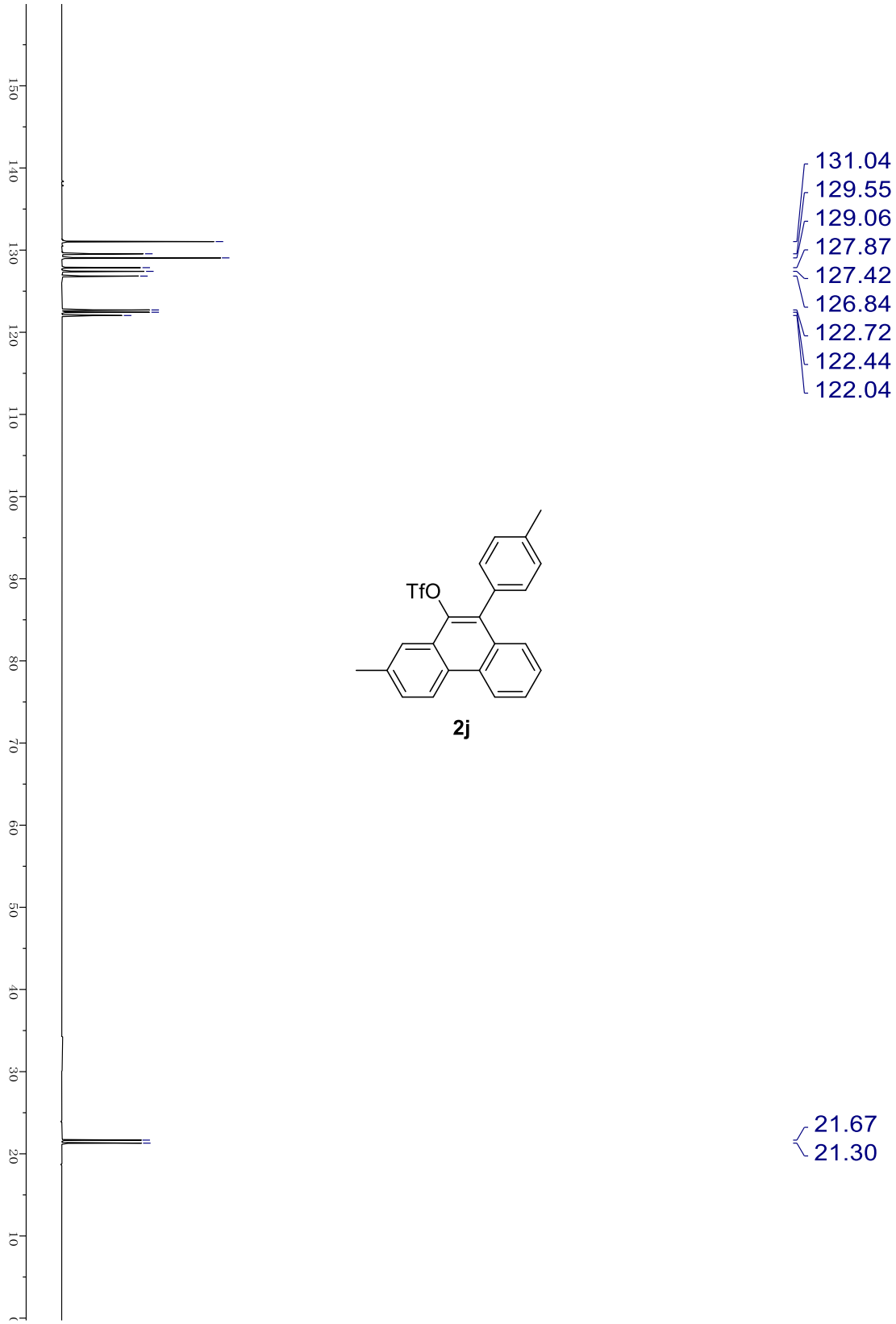
2i



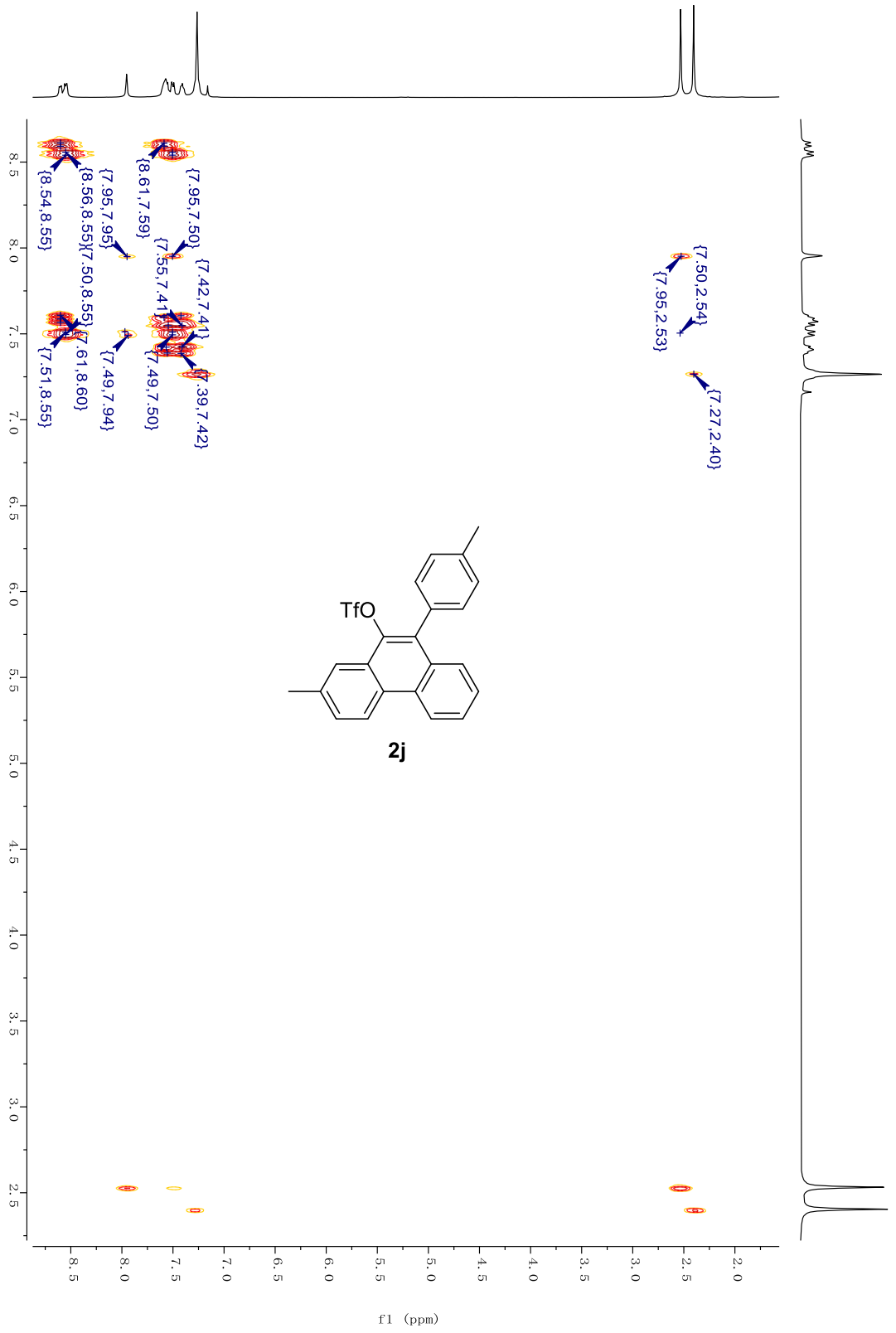
^{1}H NMR spectrum of compound **2j**



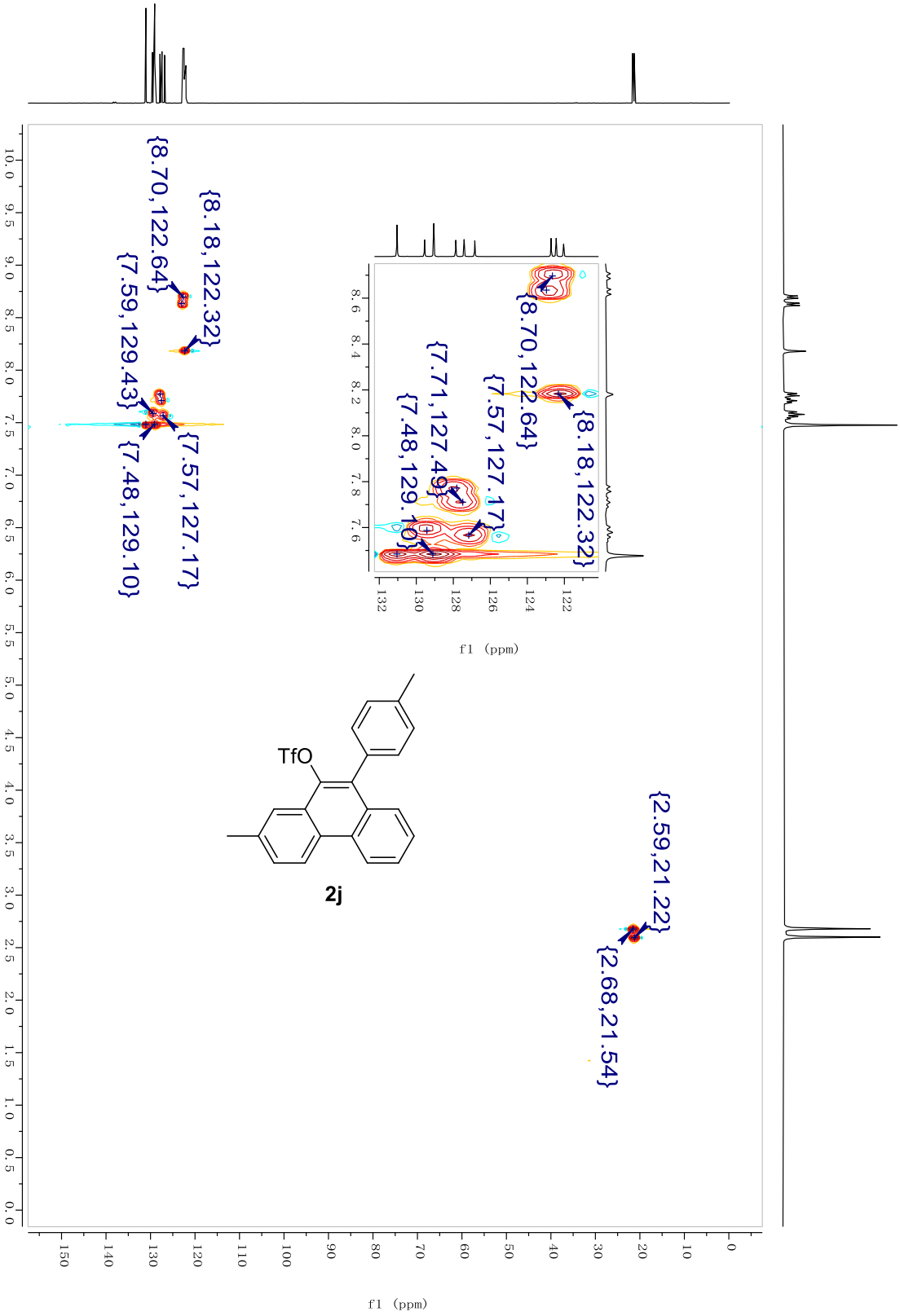
^{13}C NMR spectrum of compound **2j**



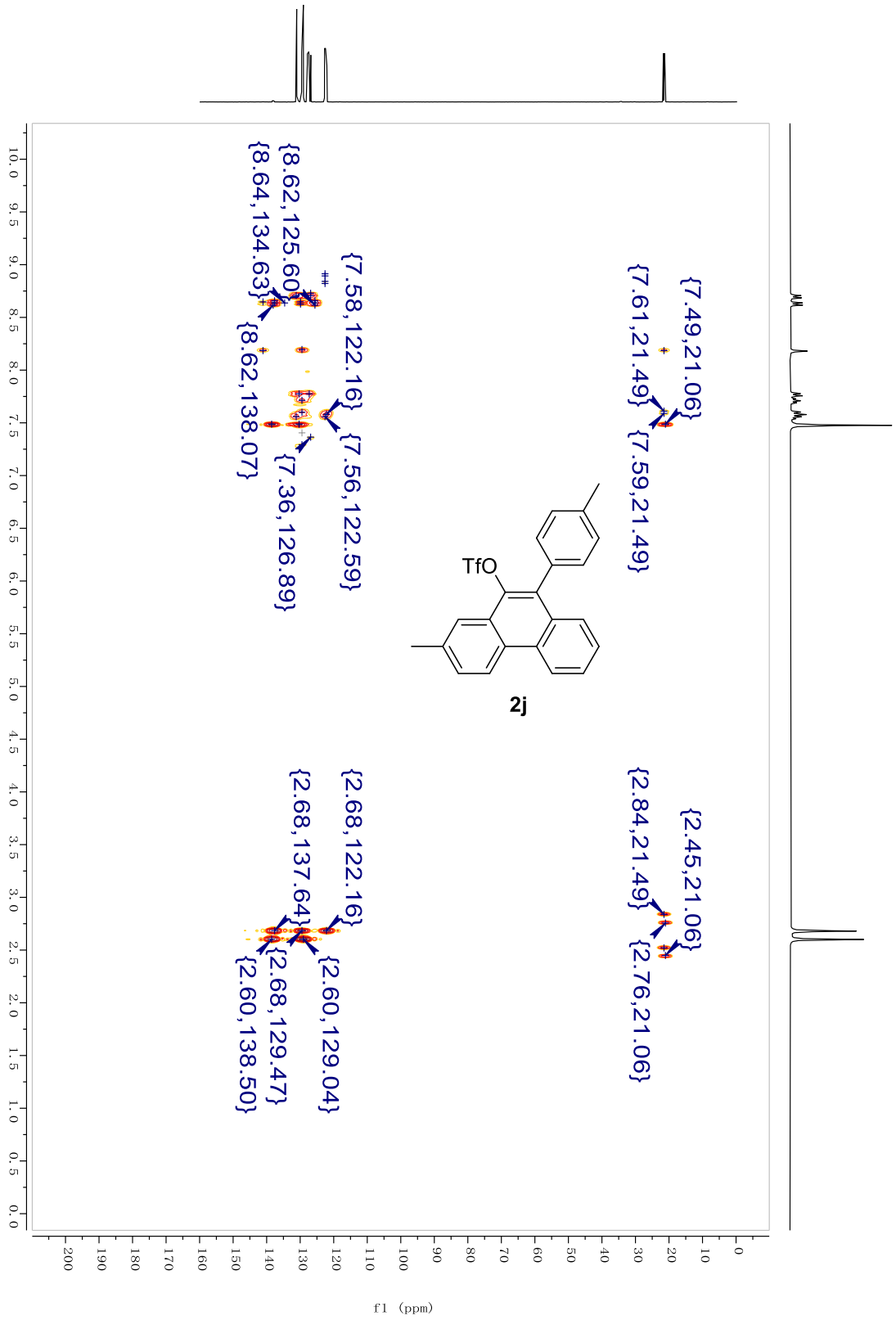
DEPT 135 spectrum of compound **2j**



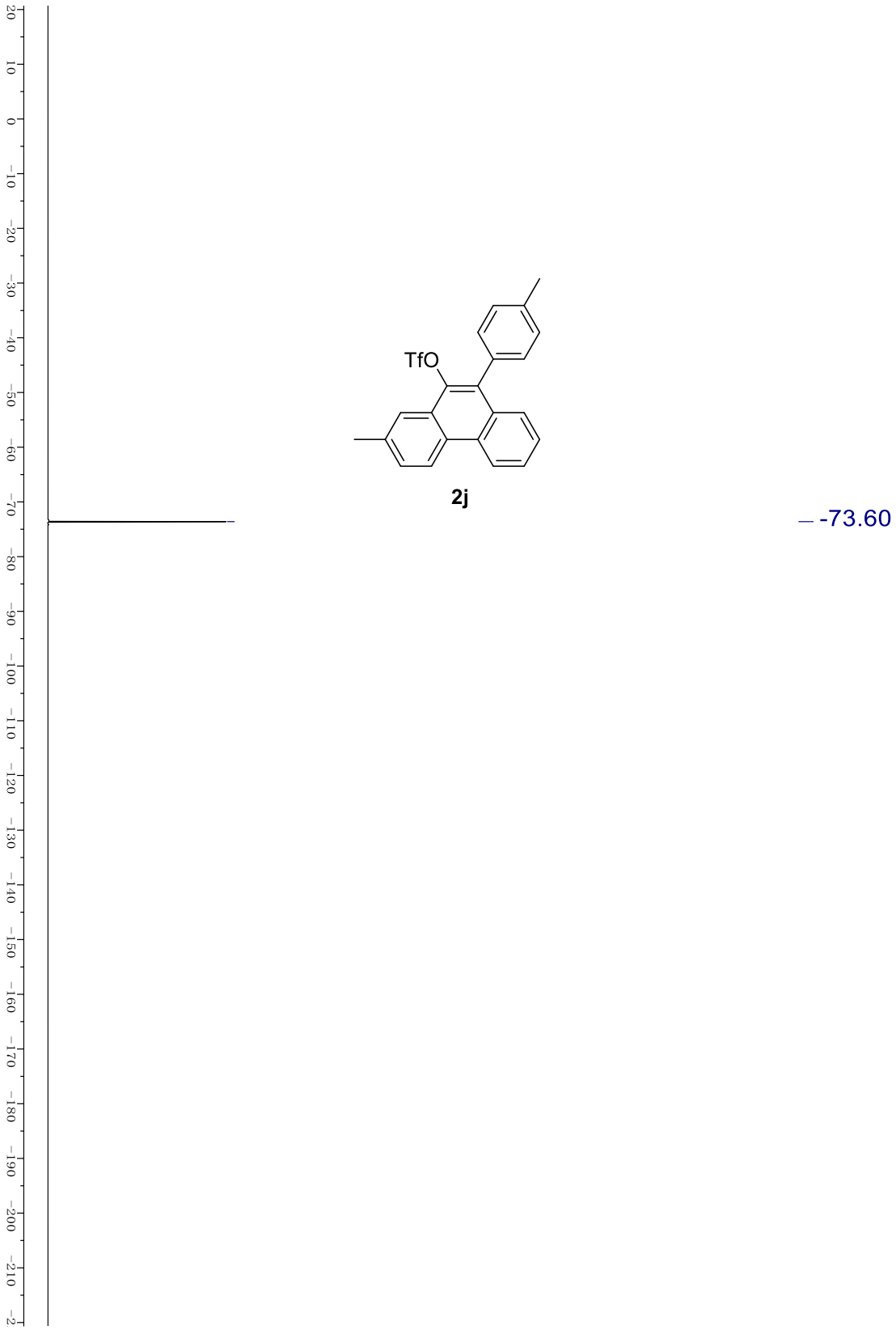
H-H COSY spectrum of compound **2j**



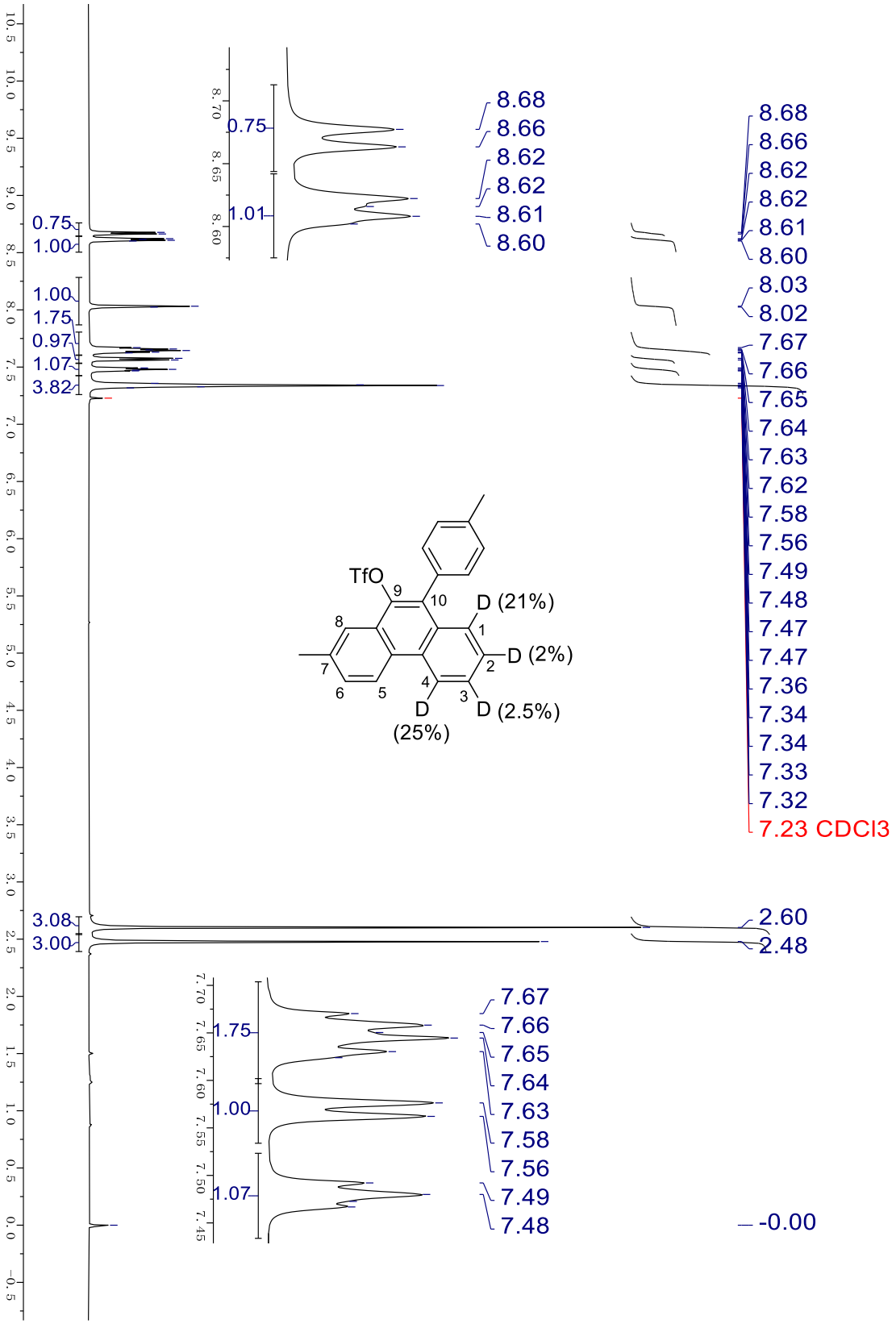
HSQC spectrum of compound **2j**



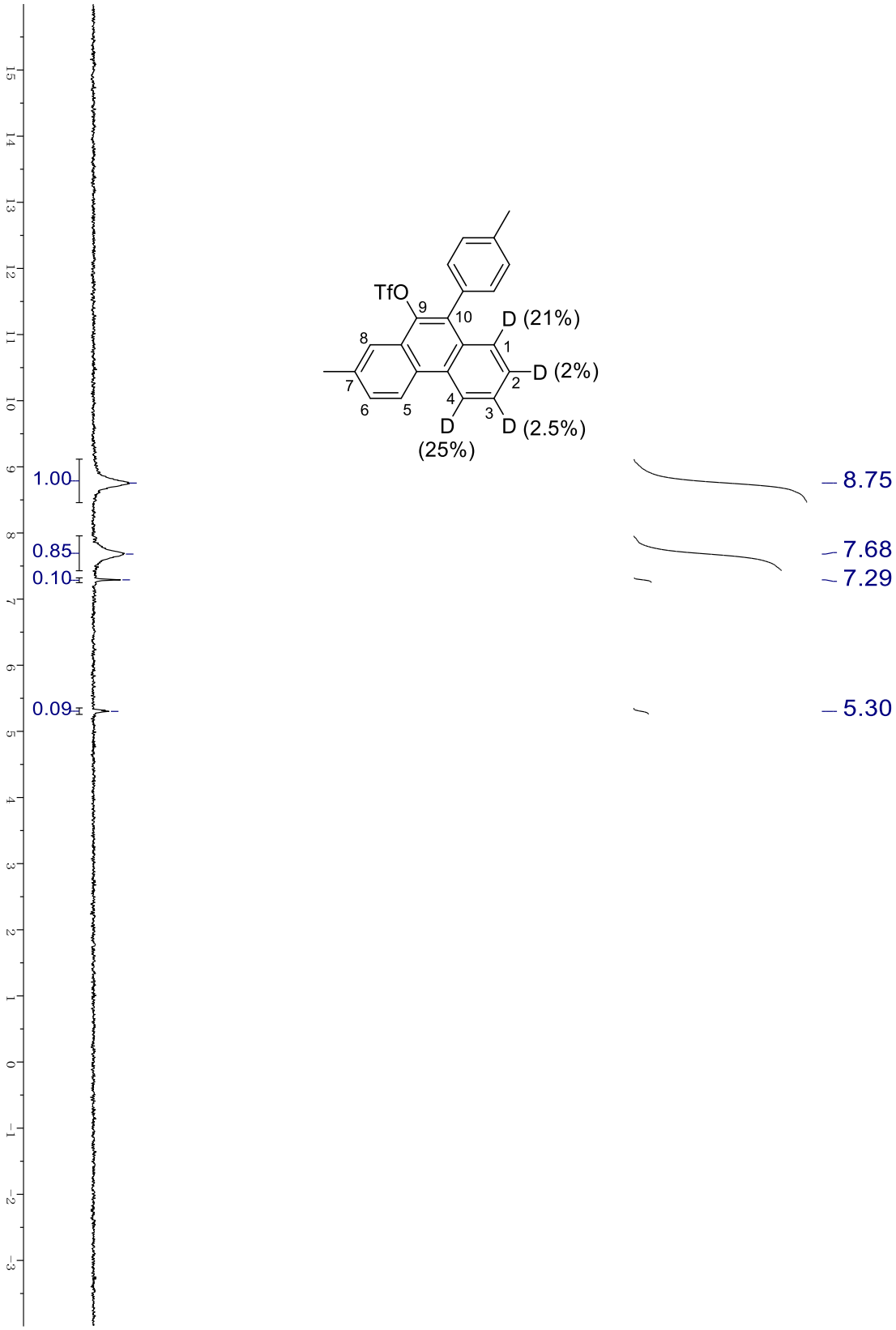
HMBC spectrum of compound **2j**



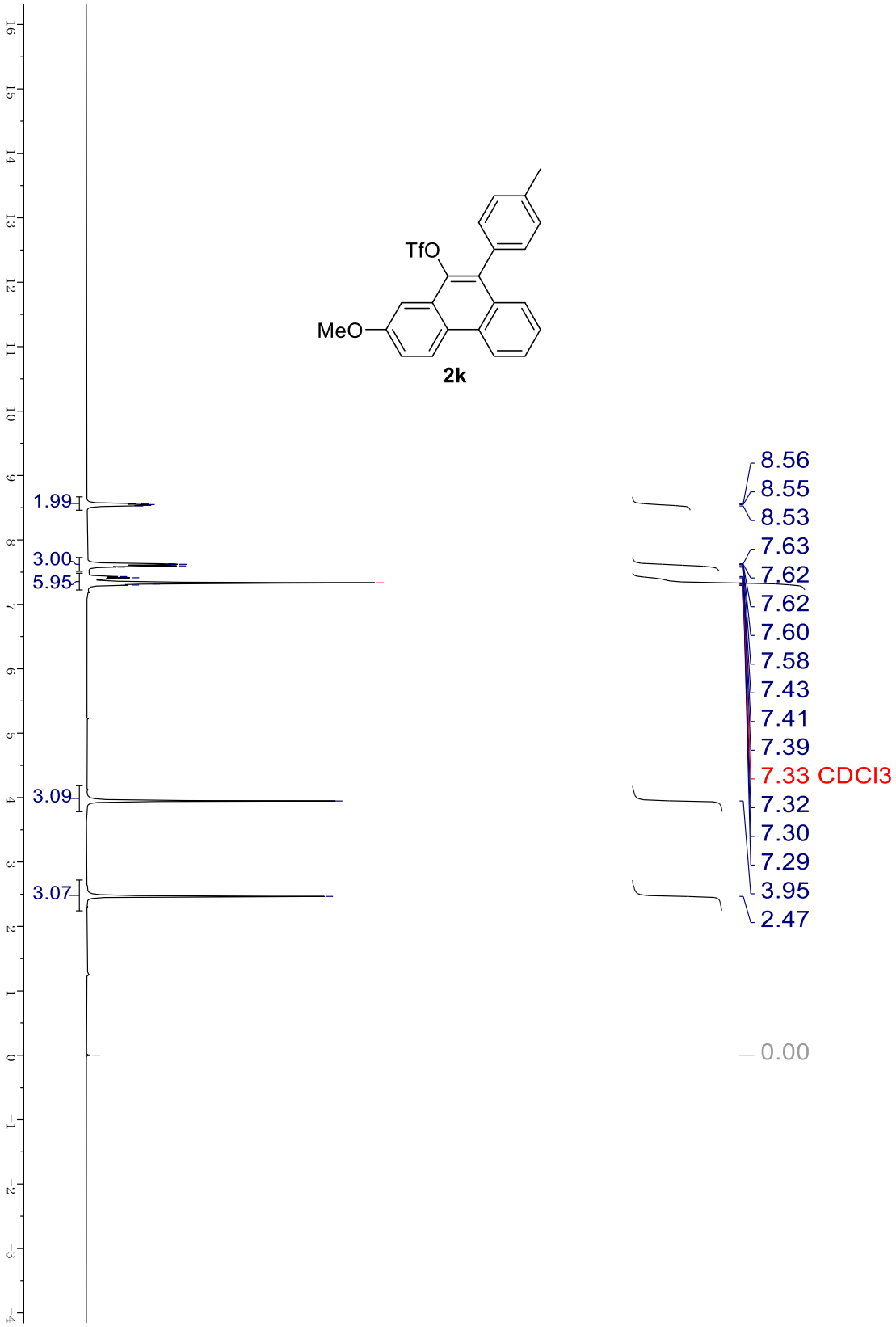
^{19}F NMR spectrum of compound **2j**

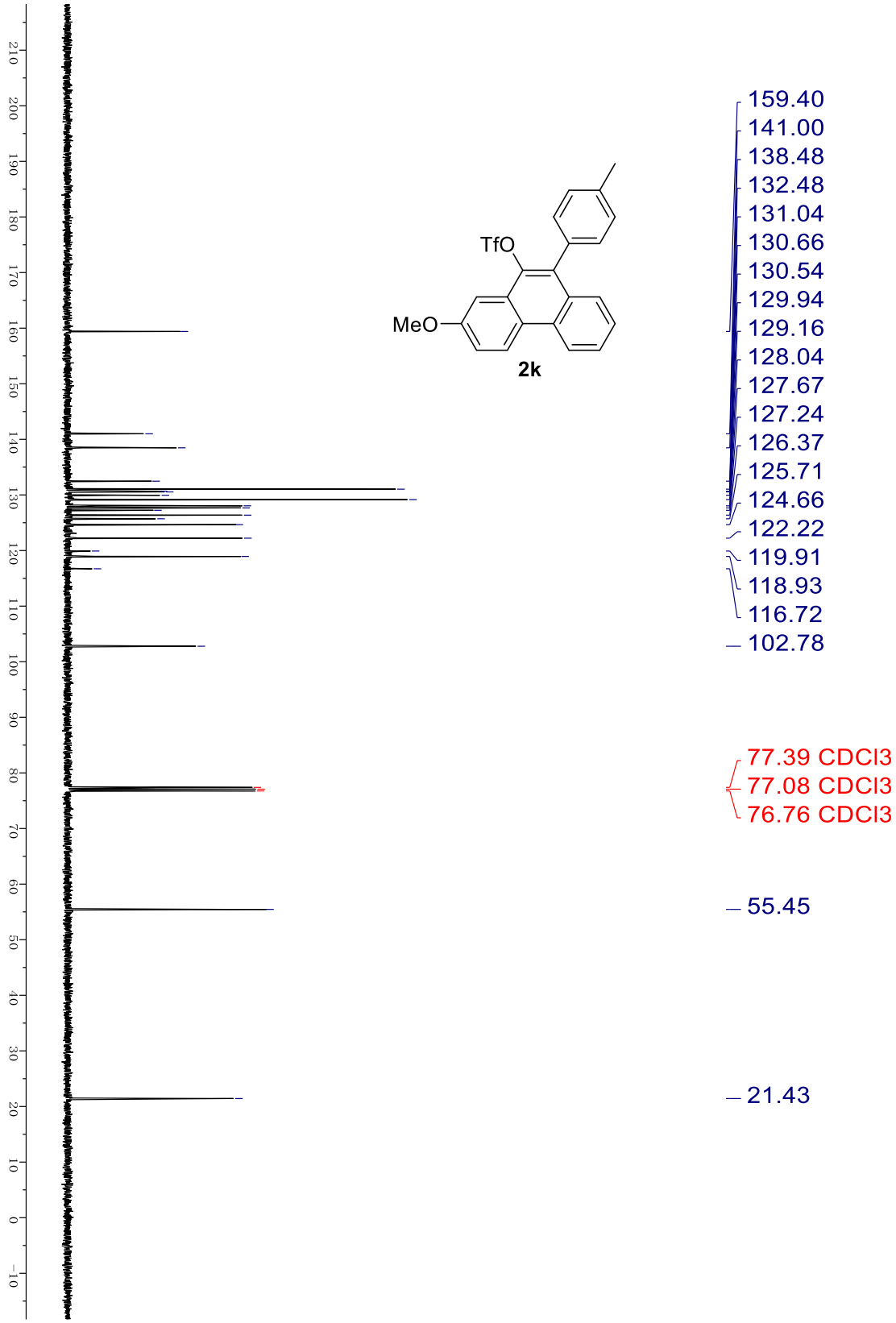


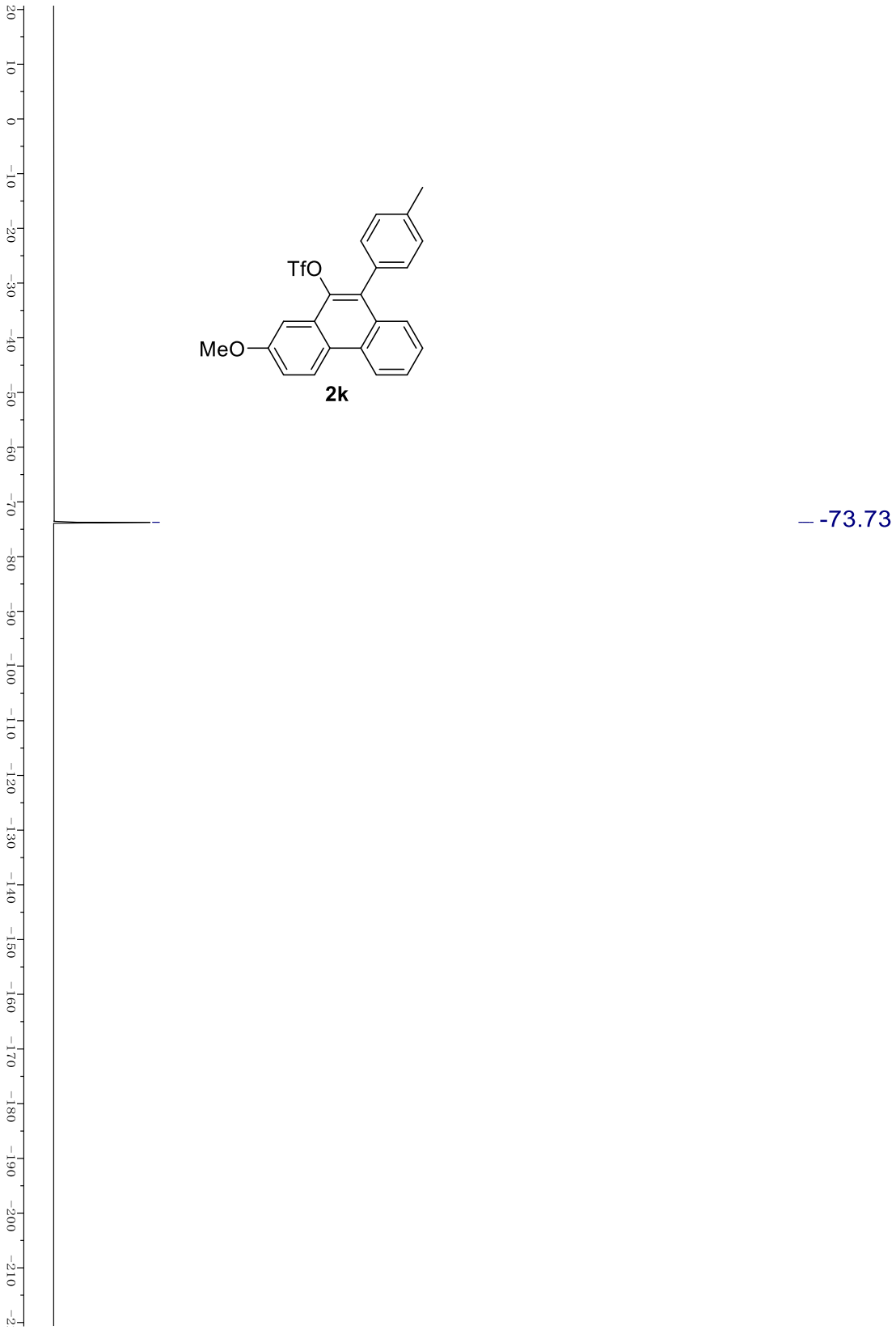
^{1}H NMR spectrum of compound **2j**-*d*

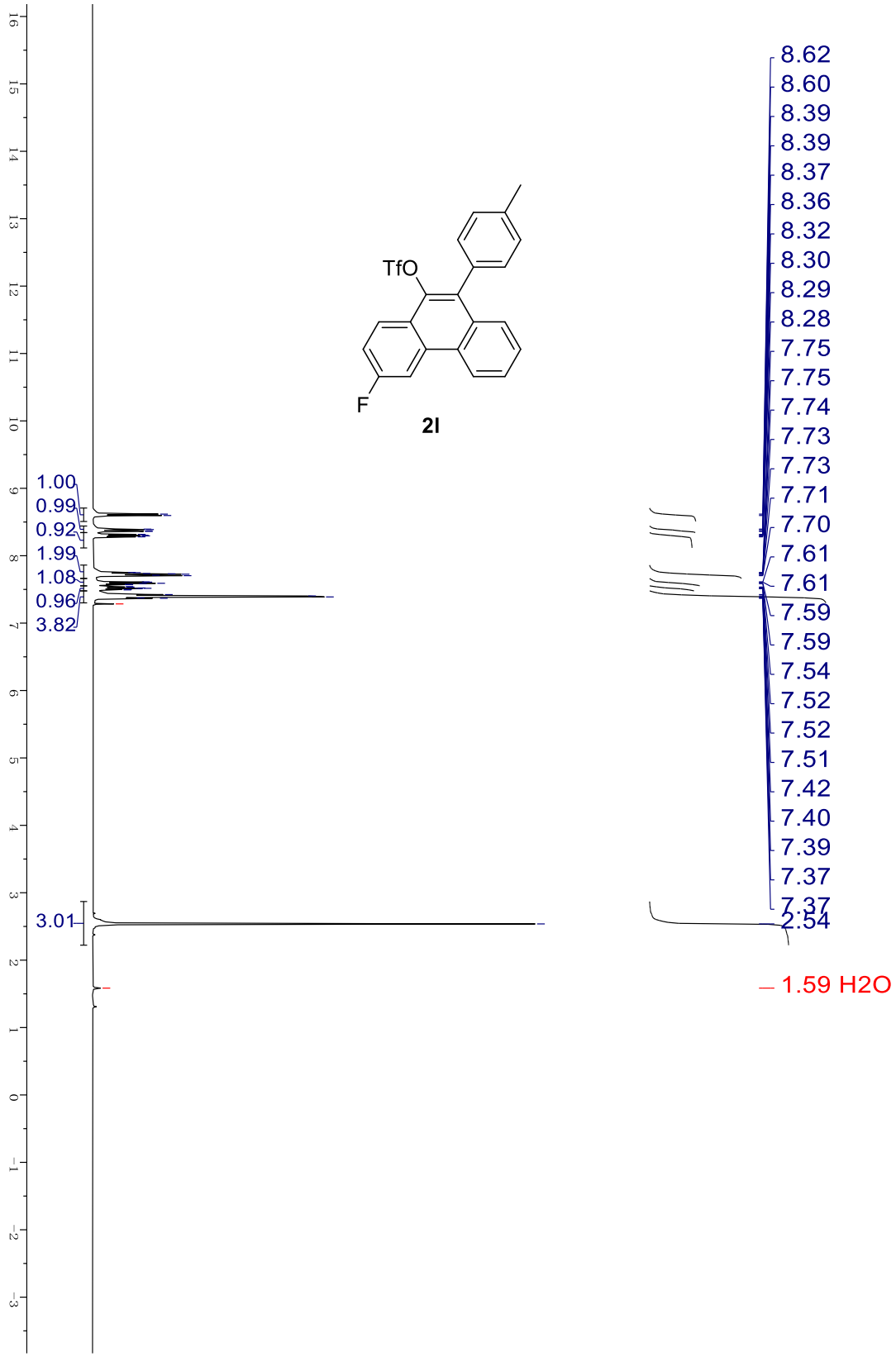


^{2}H NMR spectrum of compound **2j**-*d*


TfO
MeO
2k
1.99
3.00
5.95
3.09
3.07
8.56
8.55
8.53
7.63
7.62
7.62
7.60
7.58
7.43
7.41
7.39
7.33 CDCl3
7.32
7.30
7.29
3.95
2.47
0.00


TfO
MeO
2k
159.40
141.00
138.48
132.48
131.04
130.66
130.54
129.94
129.16
128.04
127.67
127.24
126.37
125.71
124.66
122.22
119.91
118.93
116.72
102.78
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
55.45
21.43


TfO
MeO
2k
-73.73


TfO
F
2l
1.00
0.99
0.92
1.99
1.08
0.96
3.82
3.01
8.62
8.60
8.39
8.39
8.37
8.36
8.32
8.30
8.29
8.28
7.75
7.75
7.74
7.73
7.73
7.71
7.70
7.61
7.61
7.59
7.59
7.54
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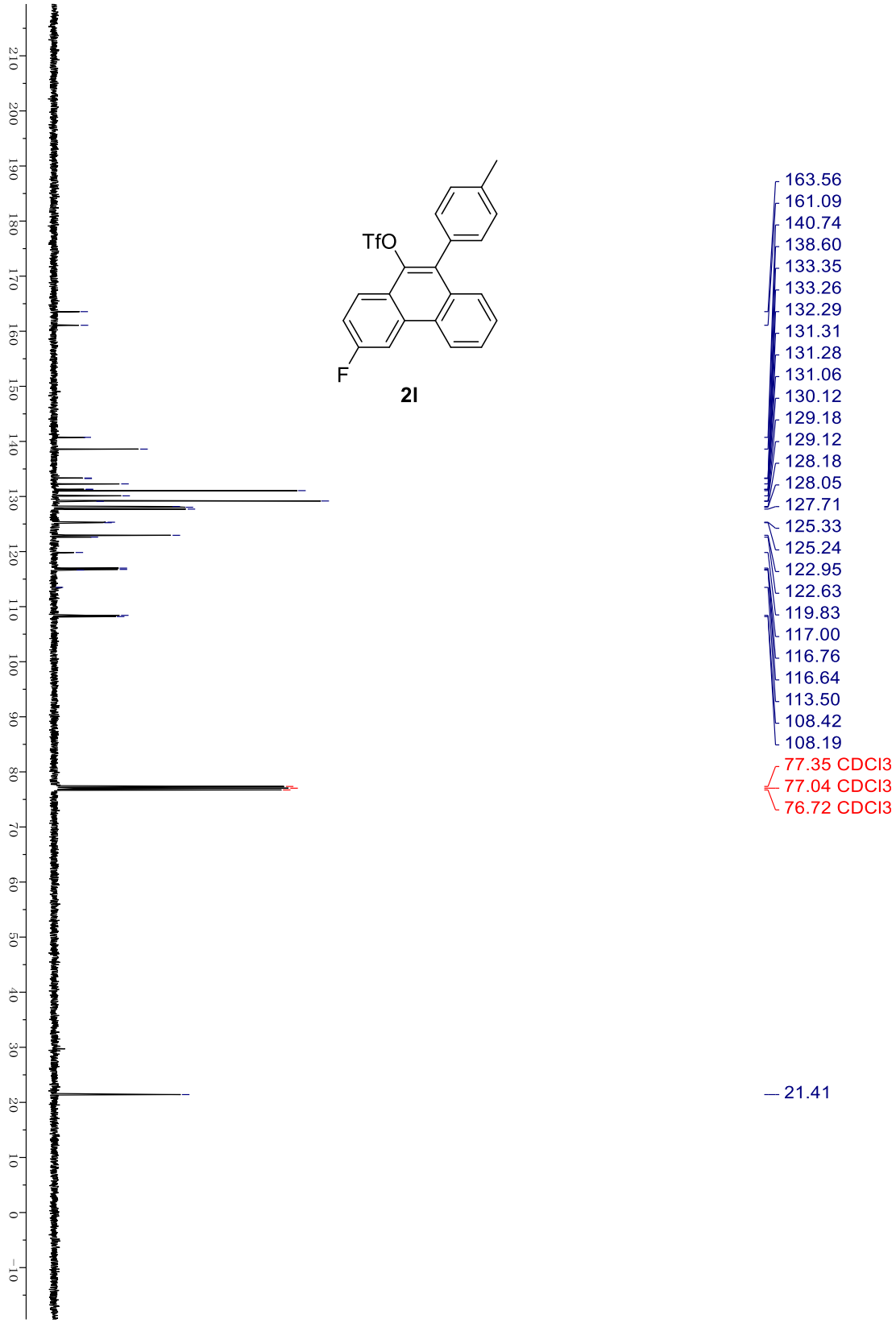
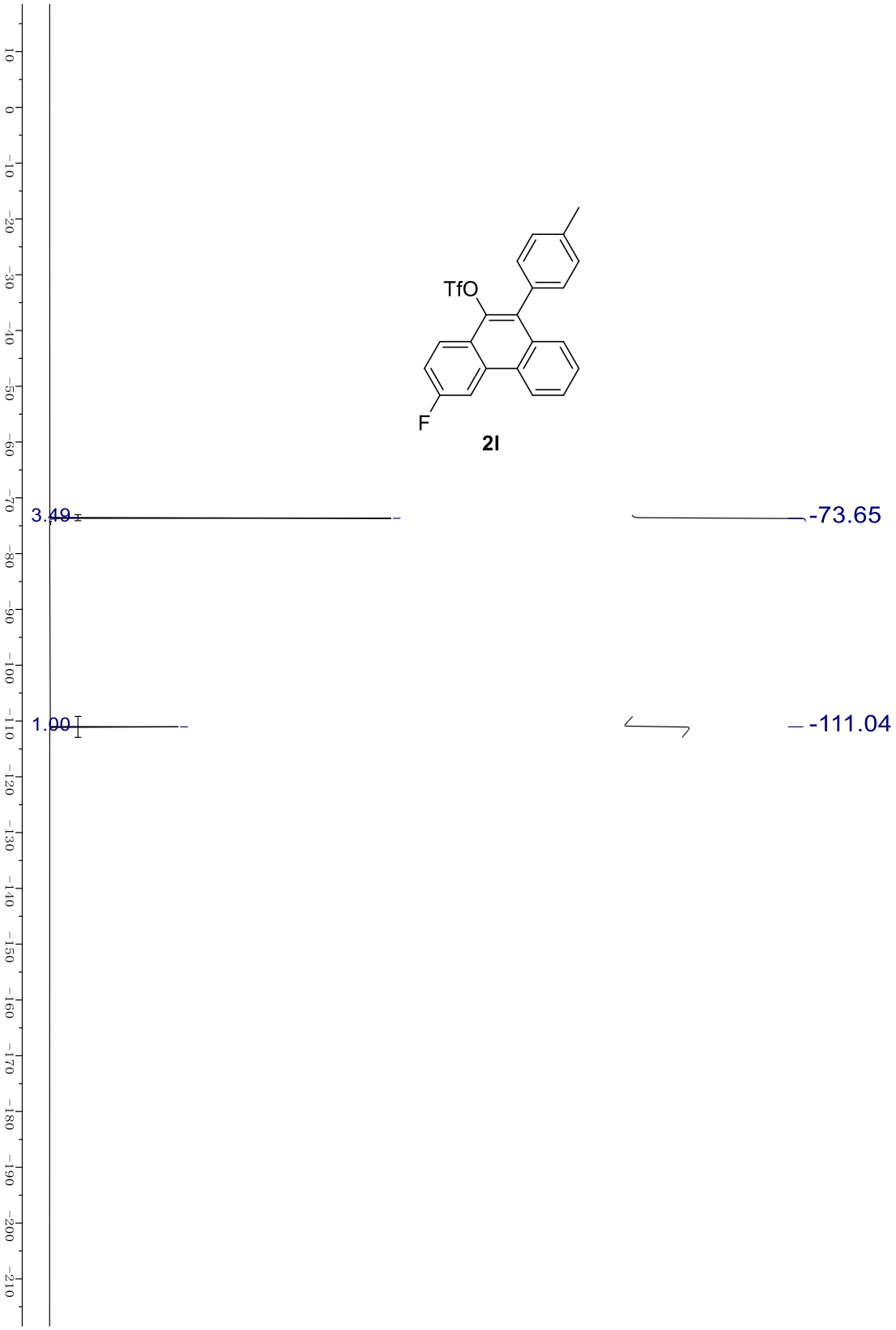
7.39
7.37
7.37
2.54
1.59 H2O


TfO
F
2l
163.56
161.09
140.74
138.60
133.35
133.26
132.29
131.31
131.28
131.06
130.12
129.18
129.12
128.18
128.05
127.71
125.33
125.24
122.95
122.63
119.83
117.00
116.76
116.64
113.50
108.42
108.19
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
21.41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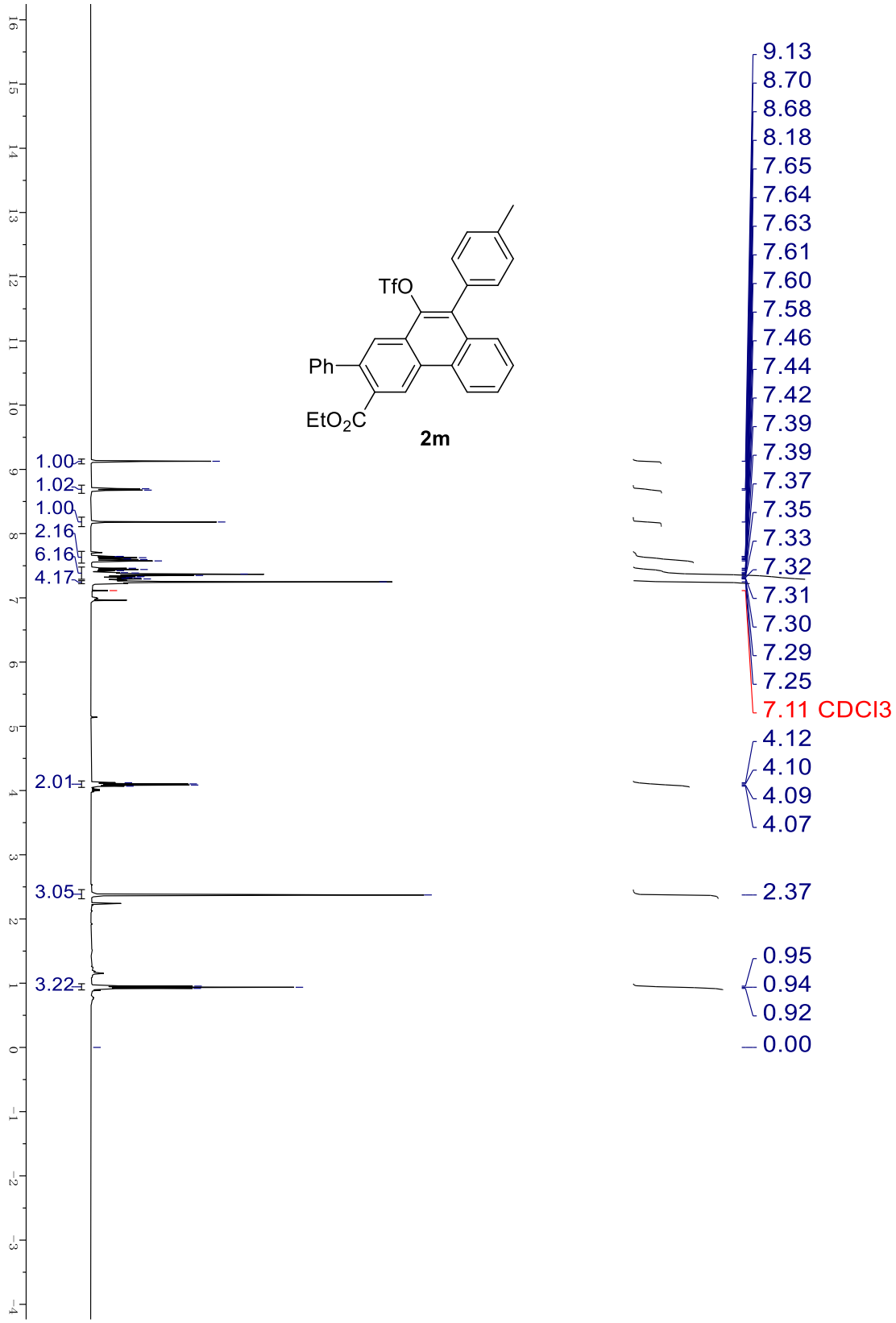
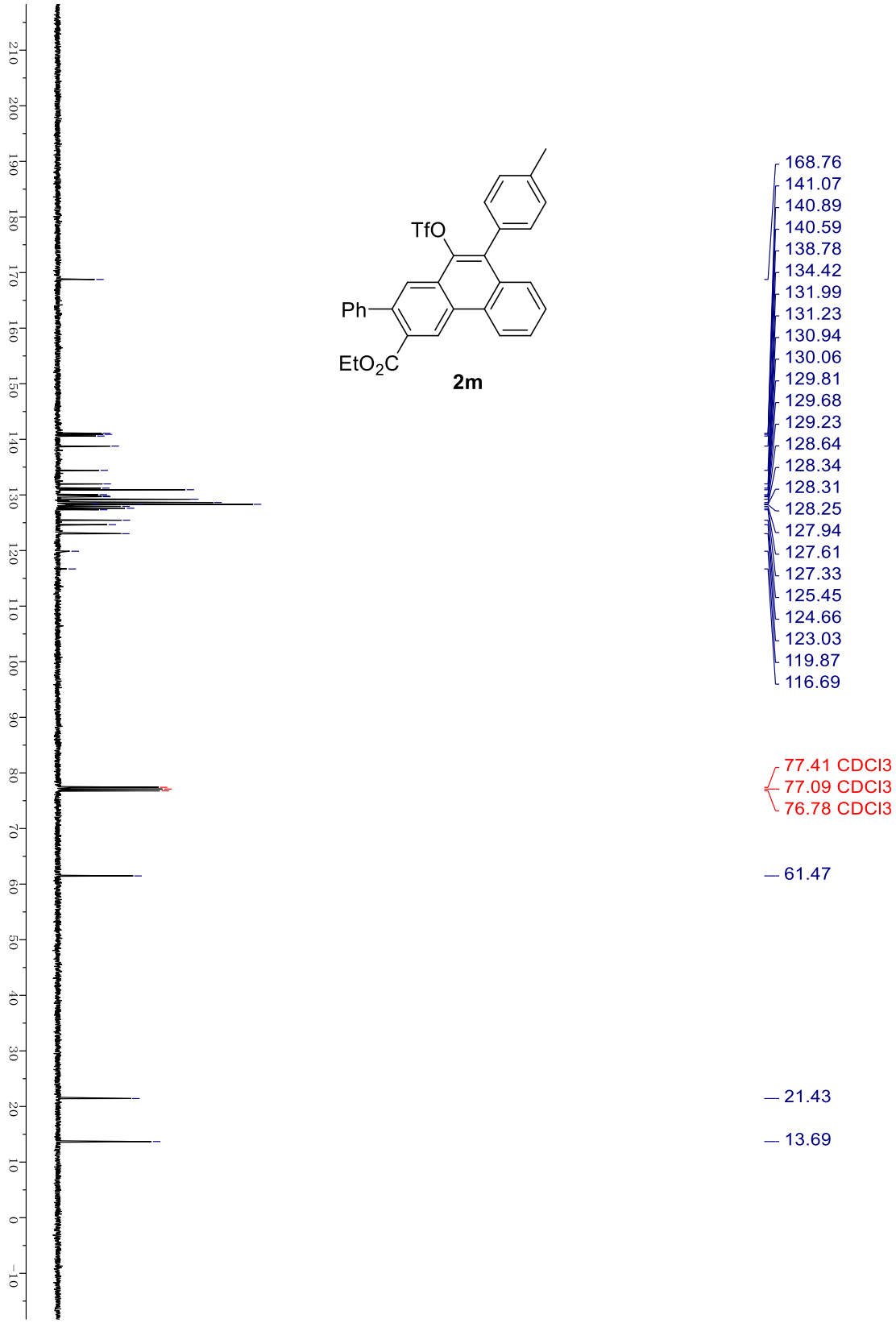
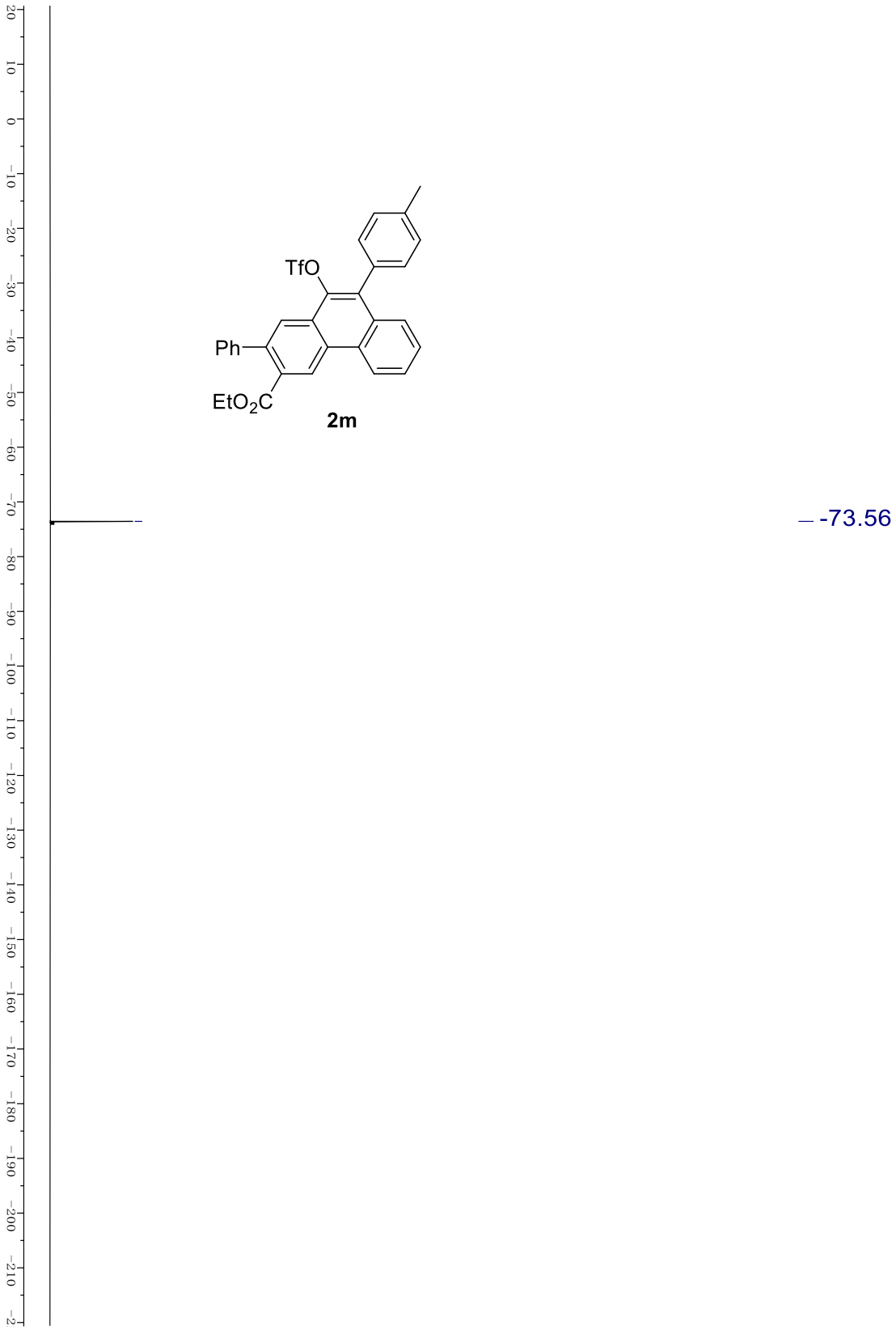
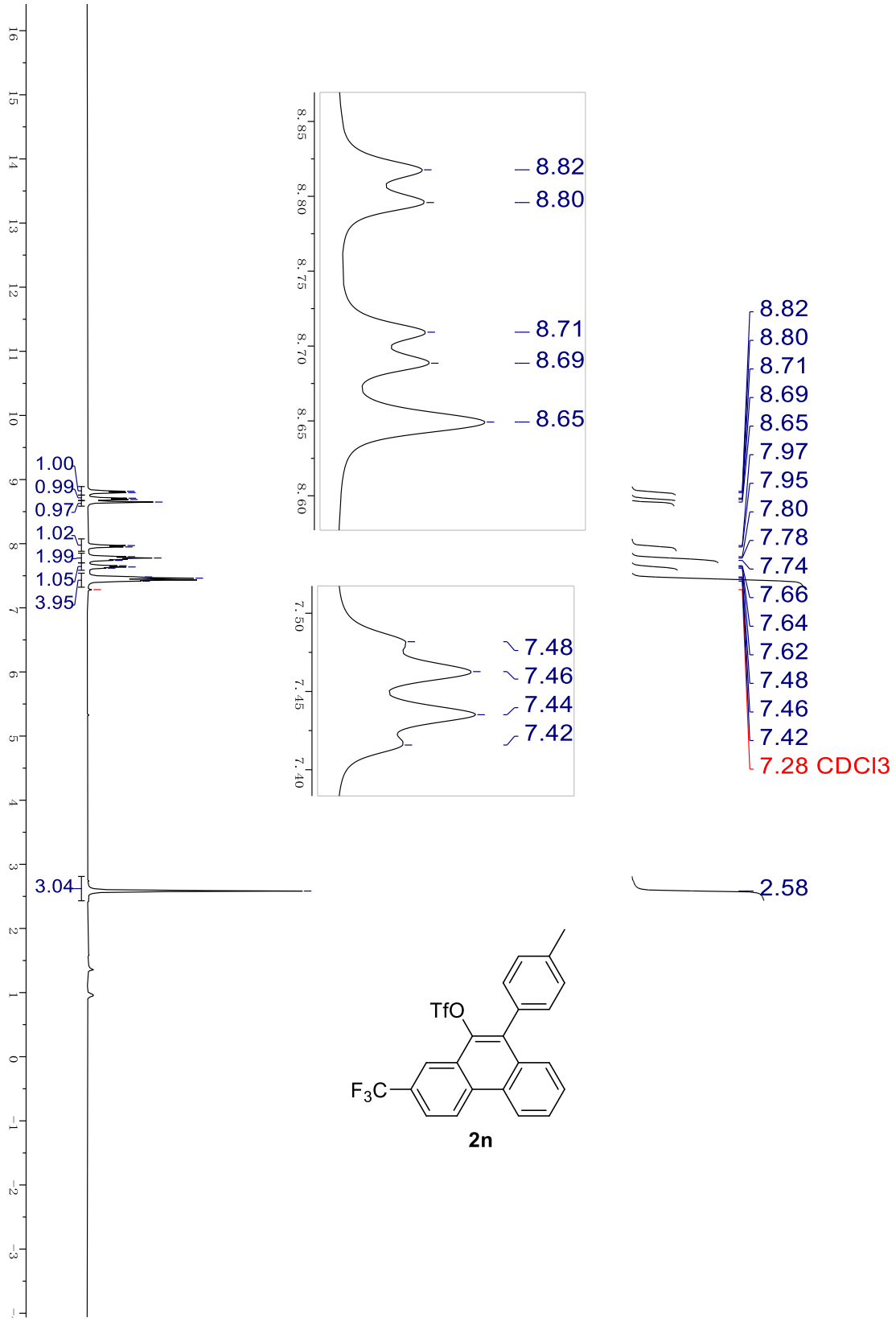
F
2l
3.49
1.00
-73.65
-111.04


TfO
Ph
EtO2C
2m
1.00
1.02
1.00
2.16
6.16
4.17
2.01
3.05
3.22
9.13
8.70
8.68
8.18
7.65
7.64
7.63
7.61
7.60
7.58
7.46
7.44
7.42
7.39
7.39
7.37
7.35
7.33
7.32
7.31
7.30
7.29
7.25
7.11 CDCl3
4.12
4.10
4.09
4.07
2.37
0.95
0.94
0.92
0.00


TfO
Ph
EtO2C
2m
168.76
141.07
140.89
140.59
138.78
134.42
131.99
131.23
130.94
130.06
129.81
129.68
129.23
128.64
128.34
128.31
128.25
127.94
127.61
127.33
125.45
124.66
123.03
119.87
116.69
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3
61.47
21.43
13.69


TfO
Ph
EtO2C
2m
-73.56


1.00
0.99
0.97
1.02
1.99
1.05
3.95
3.04
8.82
8.80
8.71
8.69
8.65
7.48
7.46
7.44
7.42
8.82
8.80
8.71
8.69
8.65
7.97
7.95
7.80
7.78
7.74
7.66
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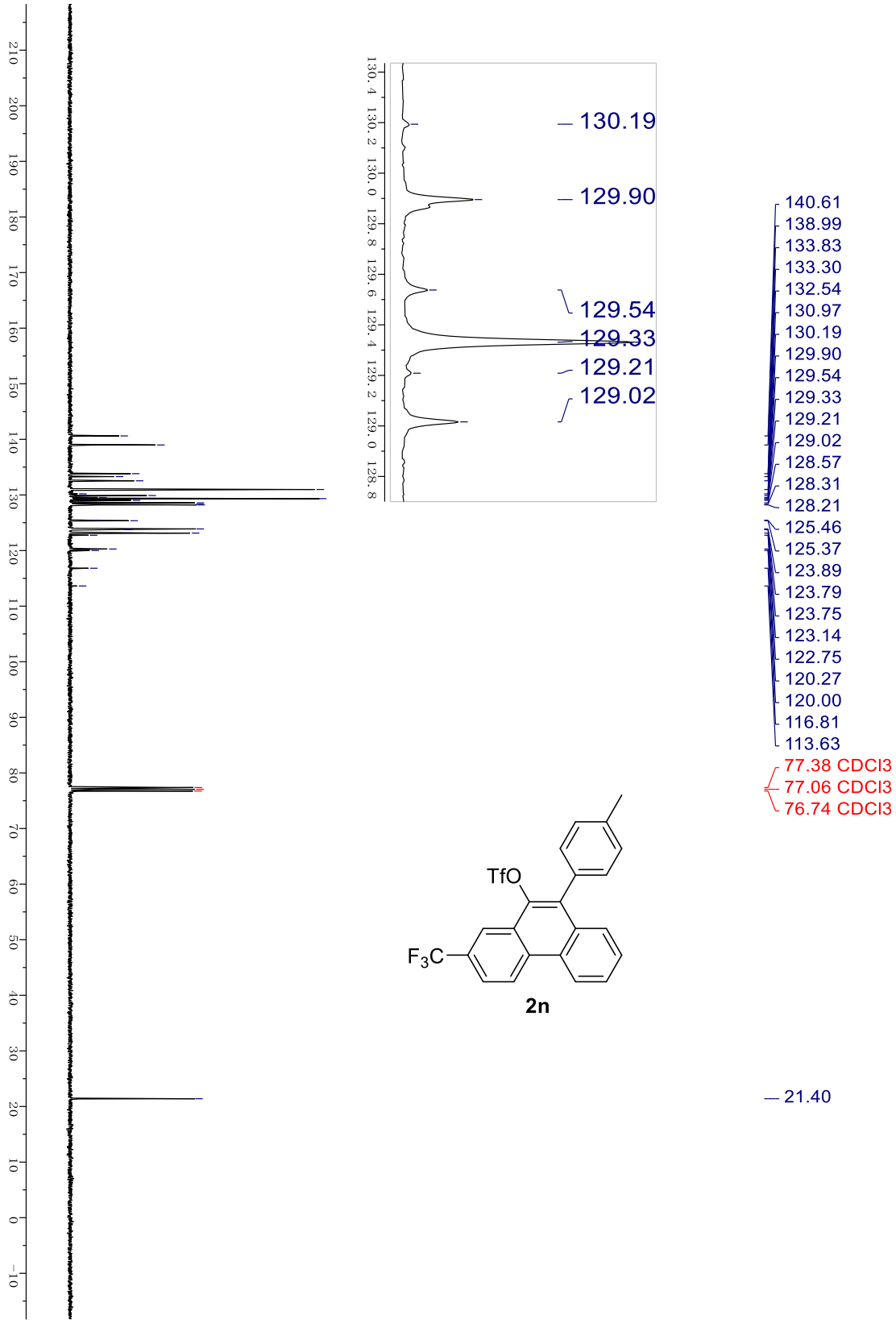
7.62
7.48
7.46
7.42
7.28 CDCl3
2.58
TfO
F3C

2n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138.99
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133.30
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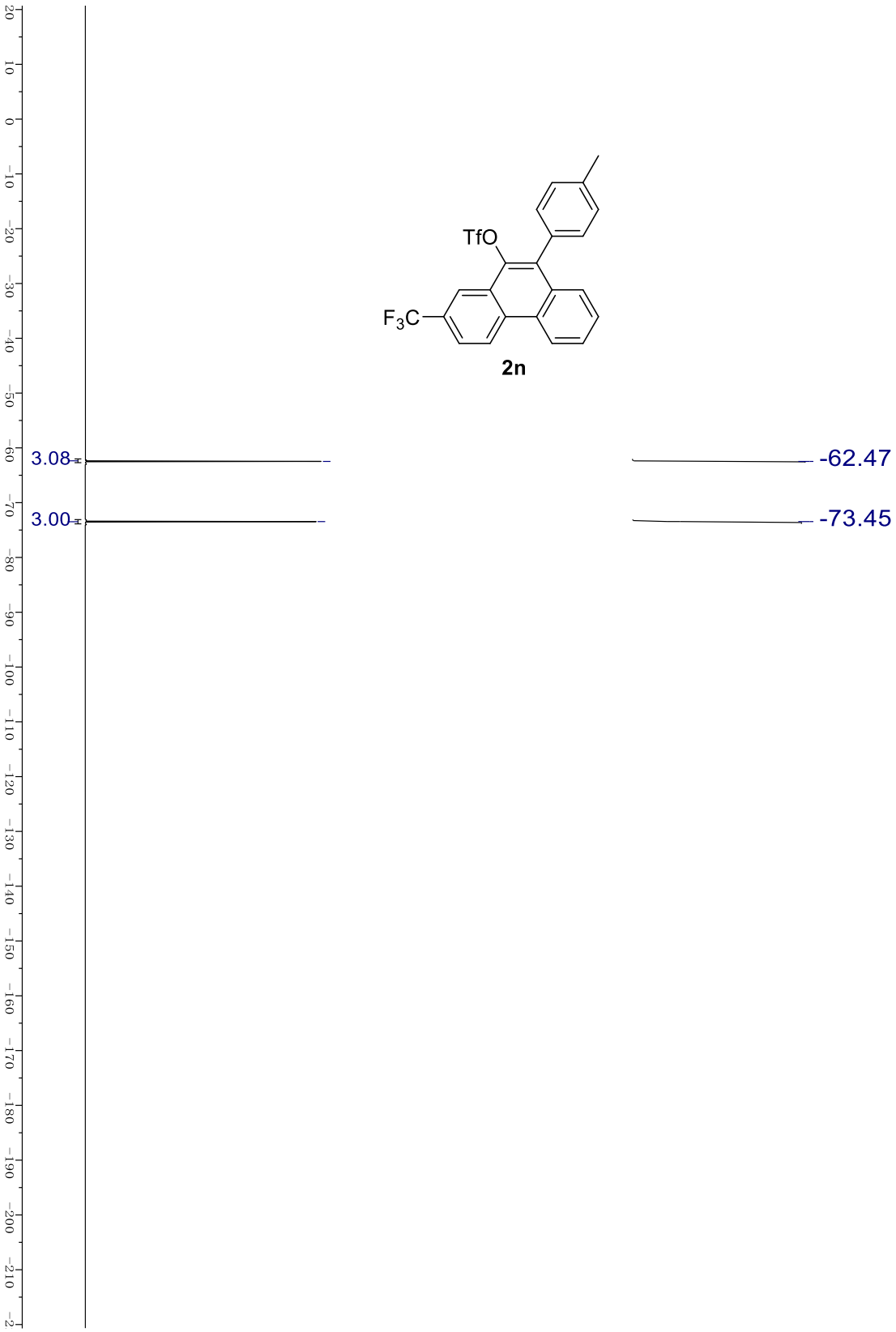
130.19
129.90
129.54
129.33
129.21
129.02
128.57
128.31
128.21
125.46
125.37
123.89
123.79
123.75
123.14
122.75
120.27
120.00
116.81
113.63
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
21.40
TfO
F3C
2n


TfO
F3C
2n
3.08
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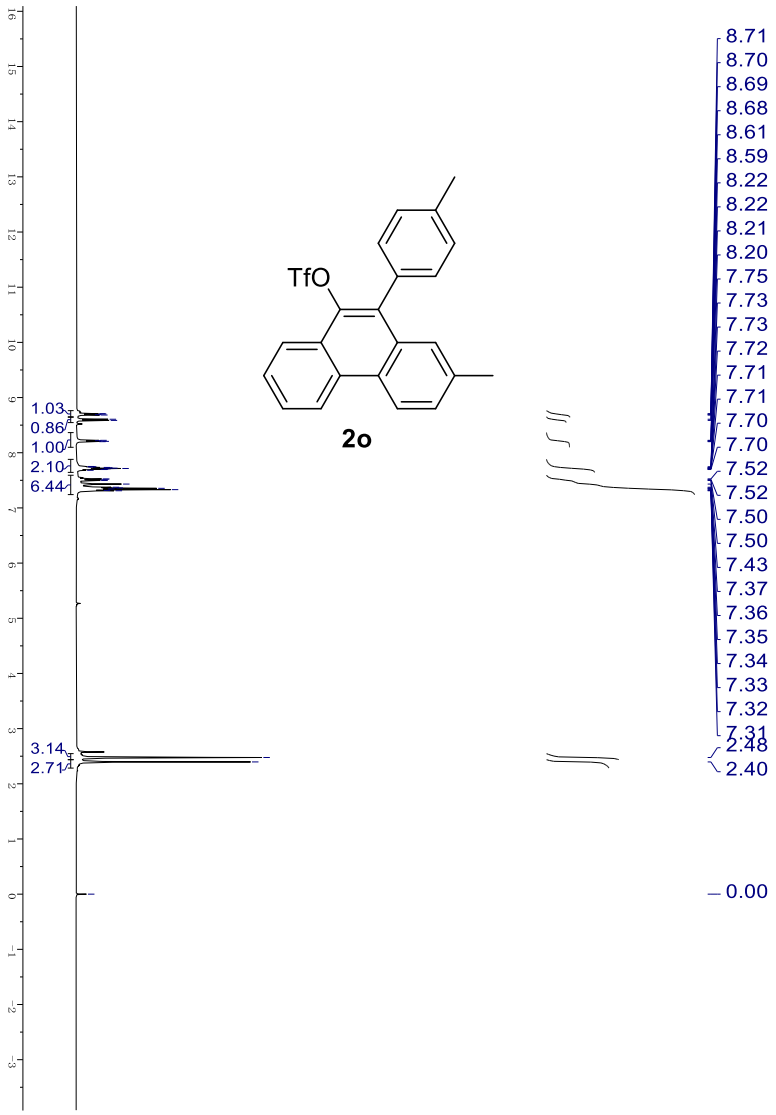
-62.47
-73.45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2o
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1.00
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3.14
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8.71
8.70
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8.68
8.61
8.59
8.22
8.22
8.21
8.20
7.75
7.73
7.73
7.72
7.71
7.71
7.70
7.70
7.52
7.52
7.50
7.50
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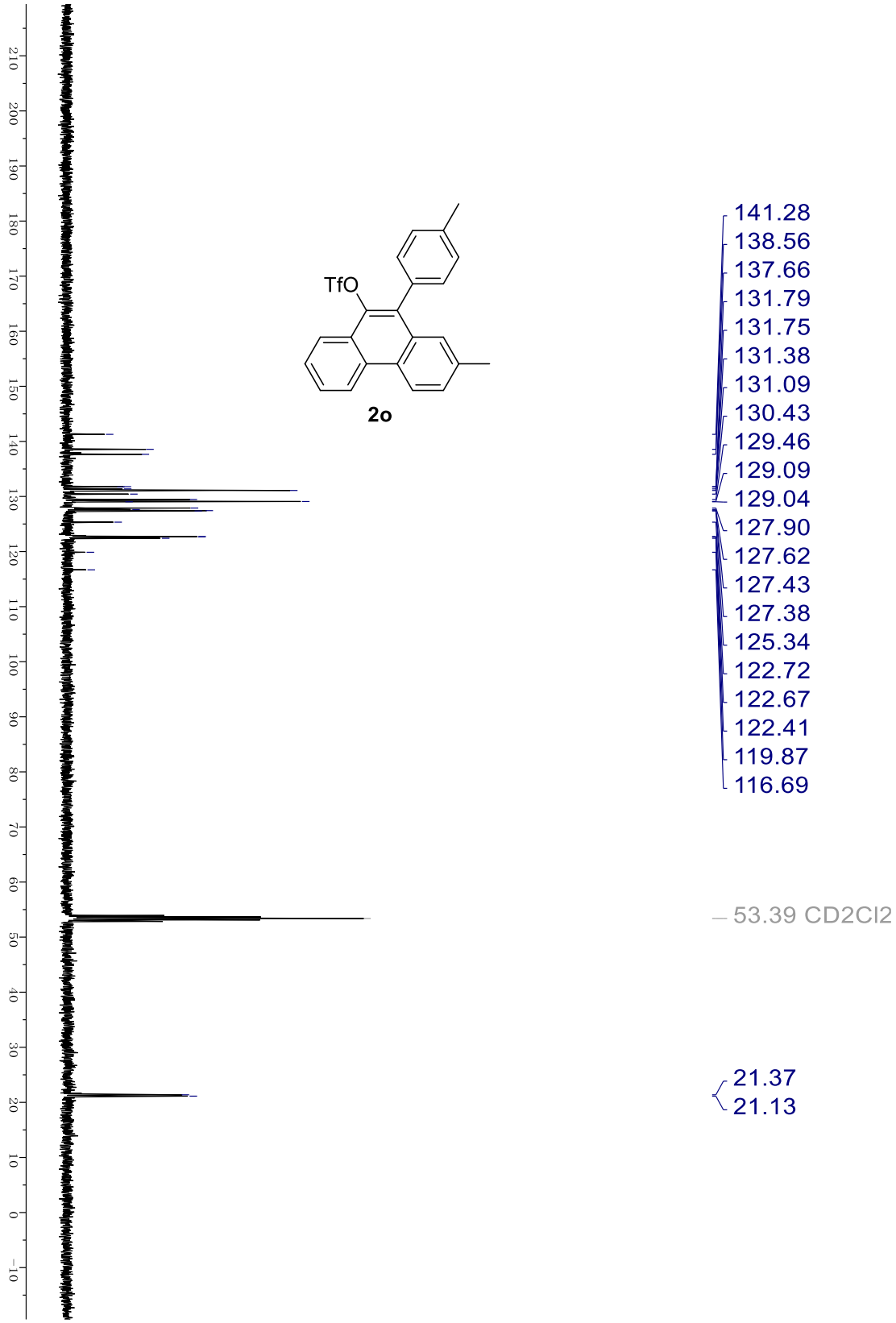
7.34
7.33
7.32
7.31
2.48
2.40
0.00


TfO
2o
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137.66
131.79
131.75
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129.04
127.90
127.62
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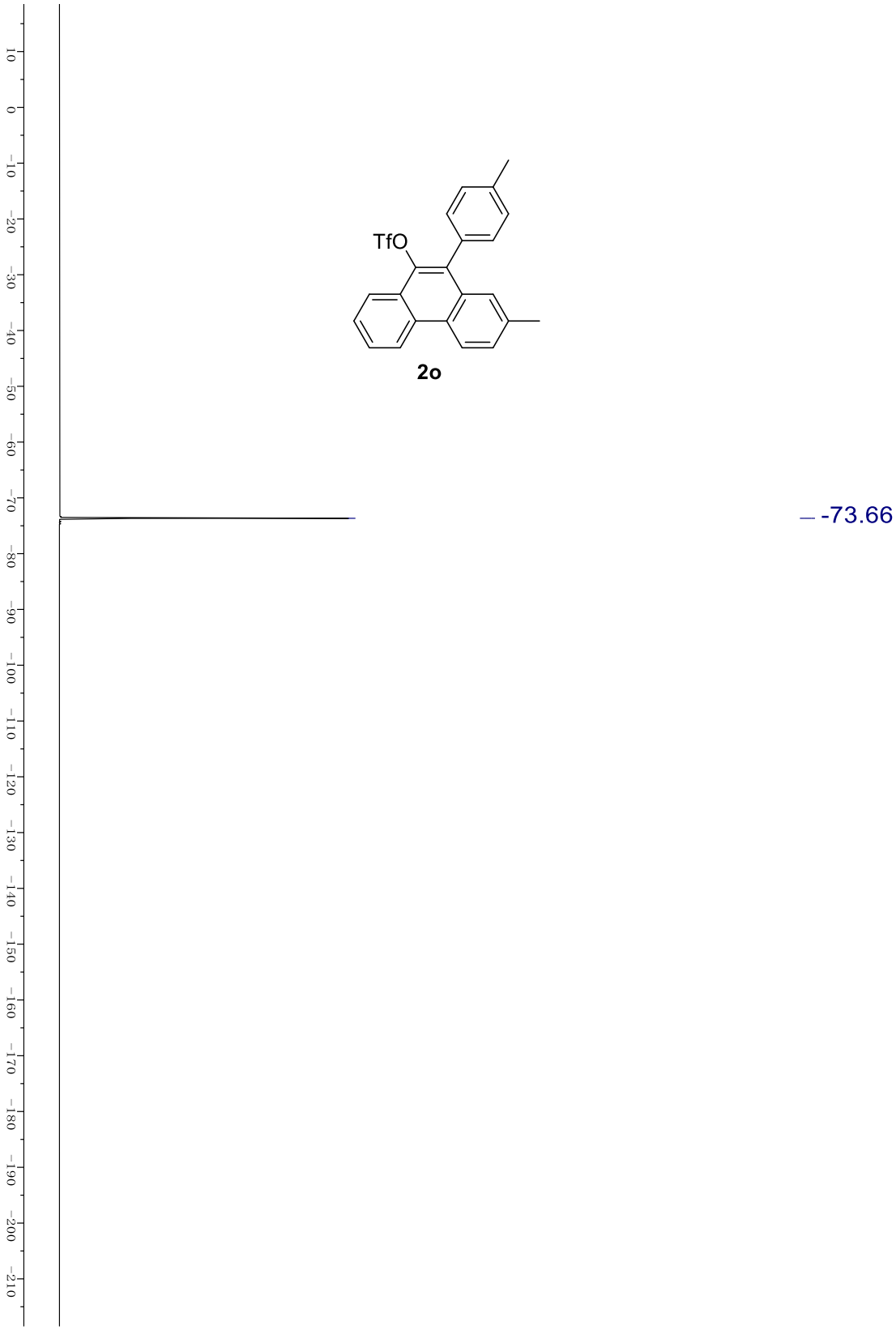
125.34
122.72
122.67
122.41
119.87
116.69
53.39 CD2Cl2
21.37
21.13


TfO
2o
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10
0
-10
-20
-30
-40
-50
-60
-70
-80
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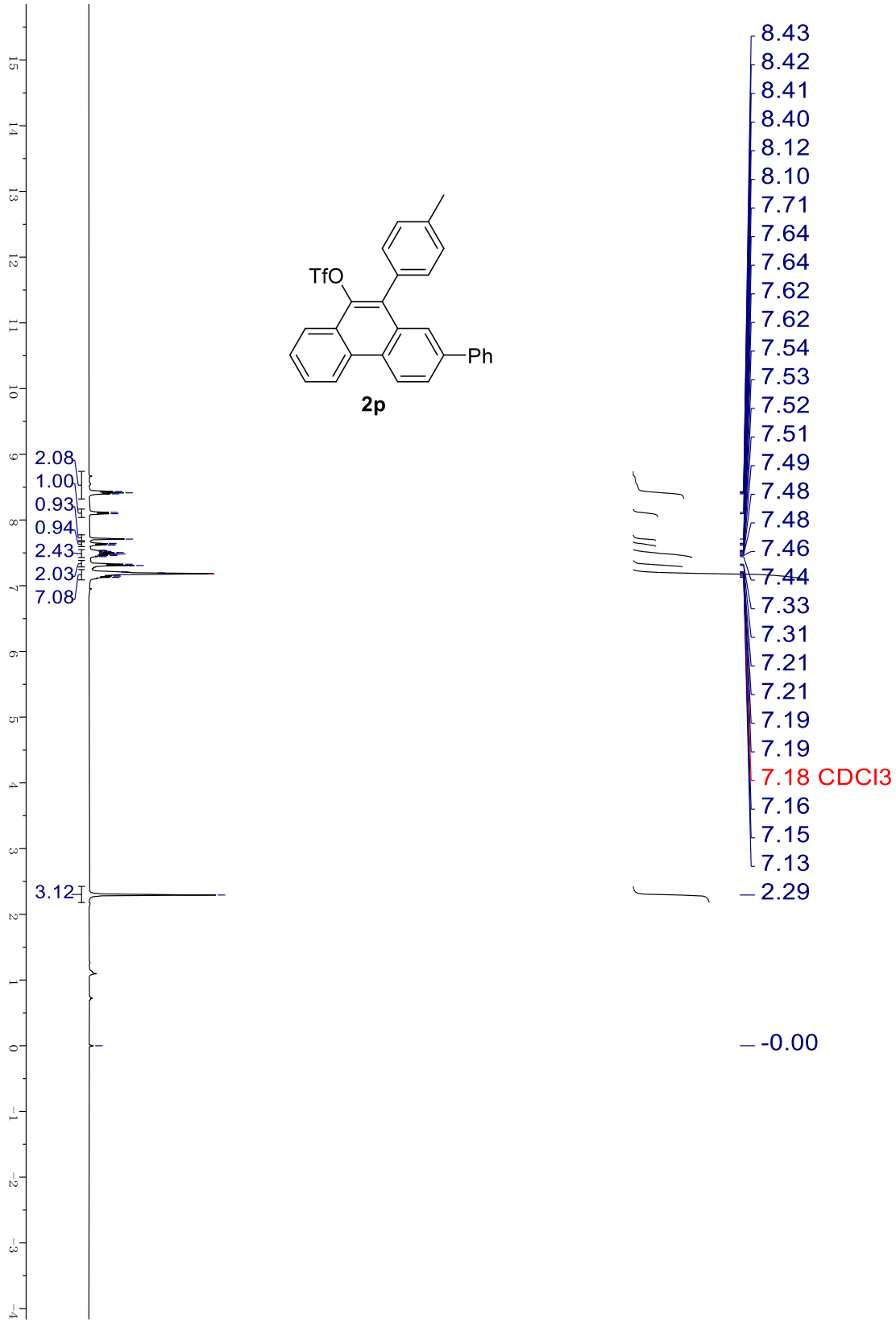
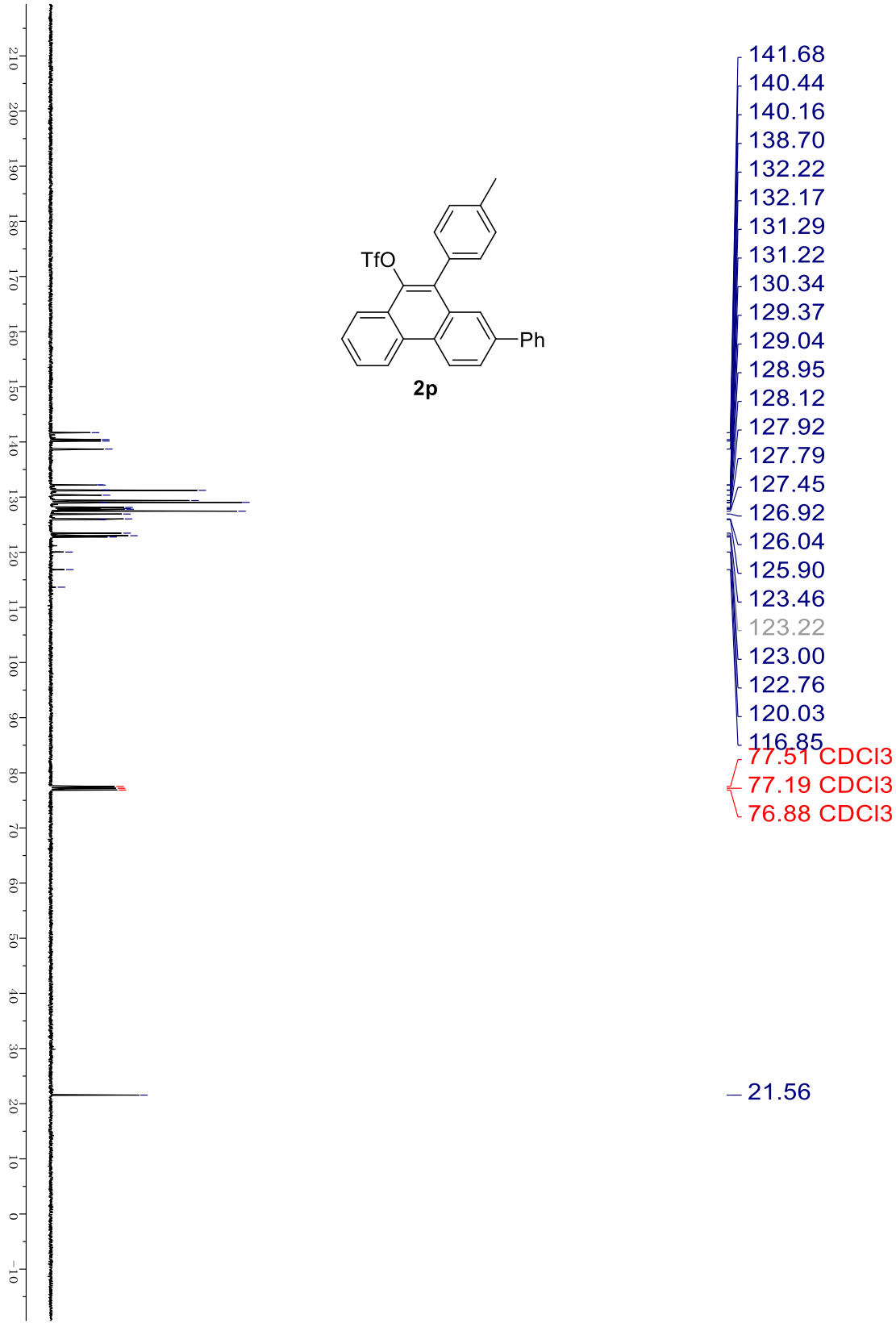
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


TfO
Ph
2p
2.08
1.00
0.93
0.94
2.43
2.03
7.08
3.12
8.43
8.42
8.41
8.40
8.12
8.10
7.71
7.64
7.64
7.62
7.62
7.54
7.53
7.52
7.51
7.49
7.48
7.48
7.46
7.44
7.33
7.31
7.21
7.21
7.19
7.19
7.18 CDCl3
7.16
7.15
7.13
2.29
-0.00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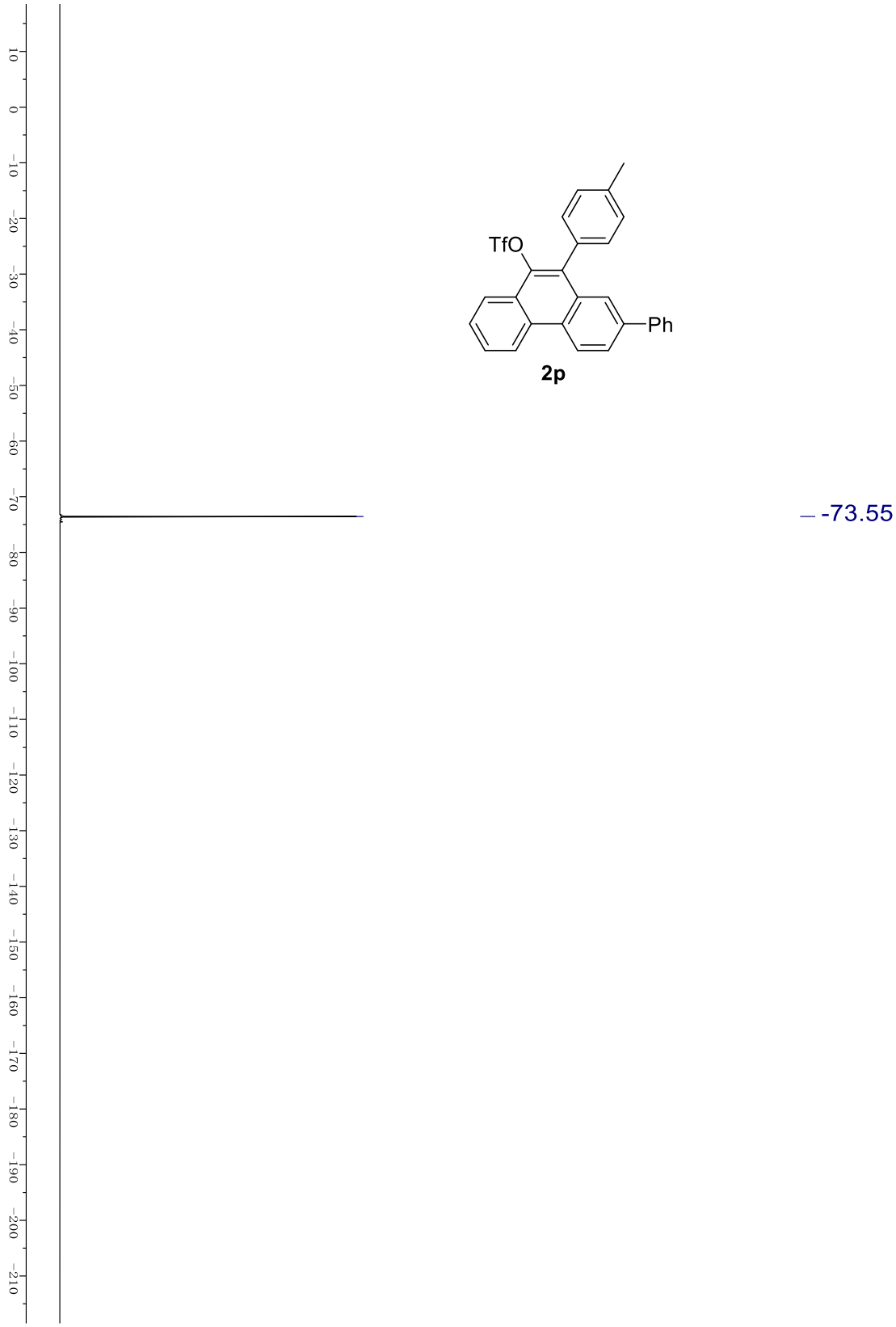
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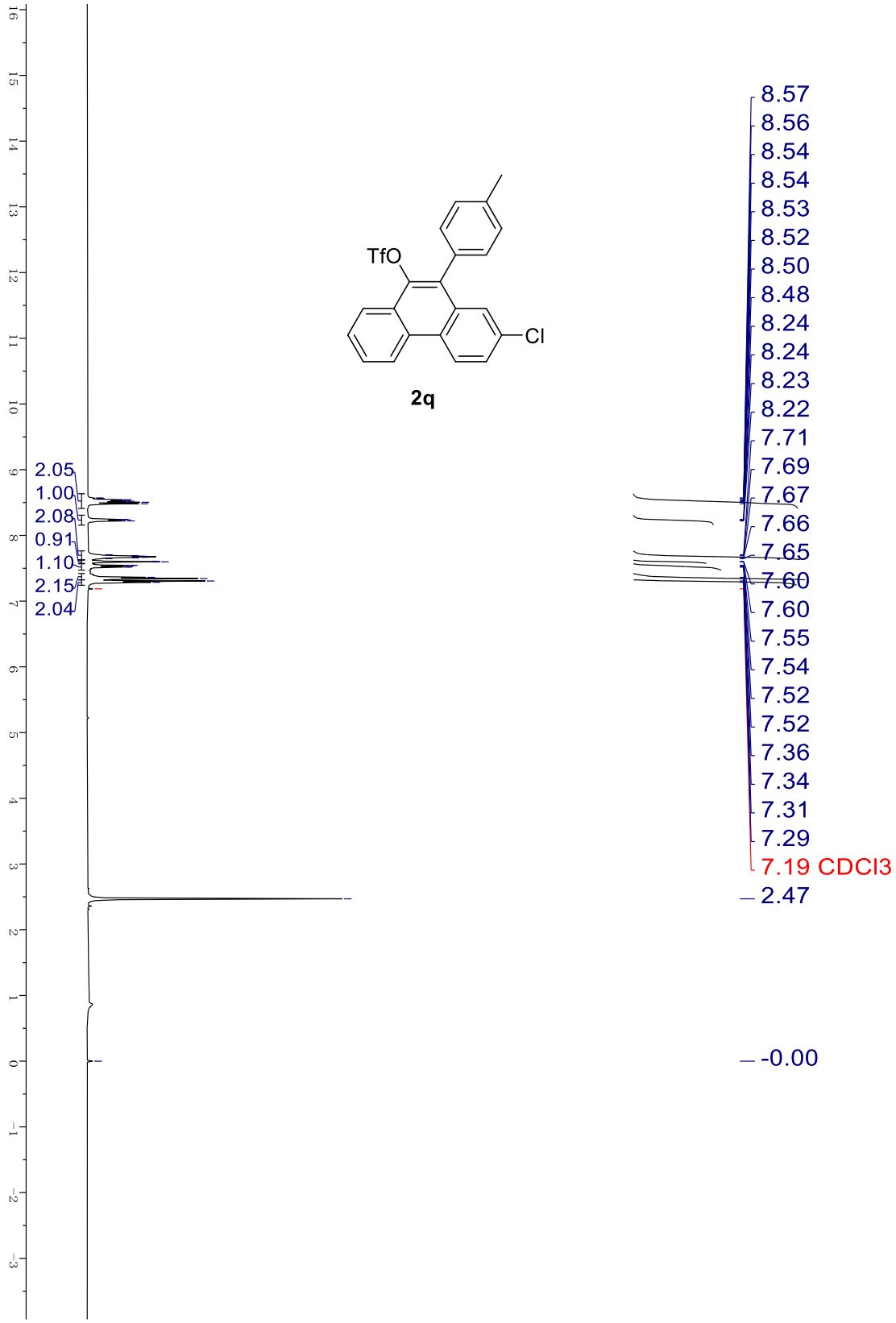
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8.53
8.52
8.50
8.48
8.24
8.24
8.23
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7.65
7.60
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7.31
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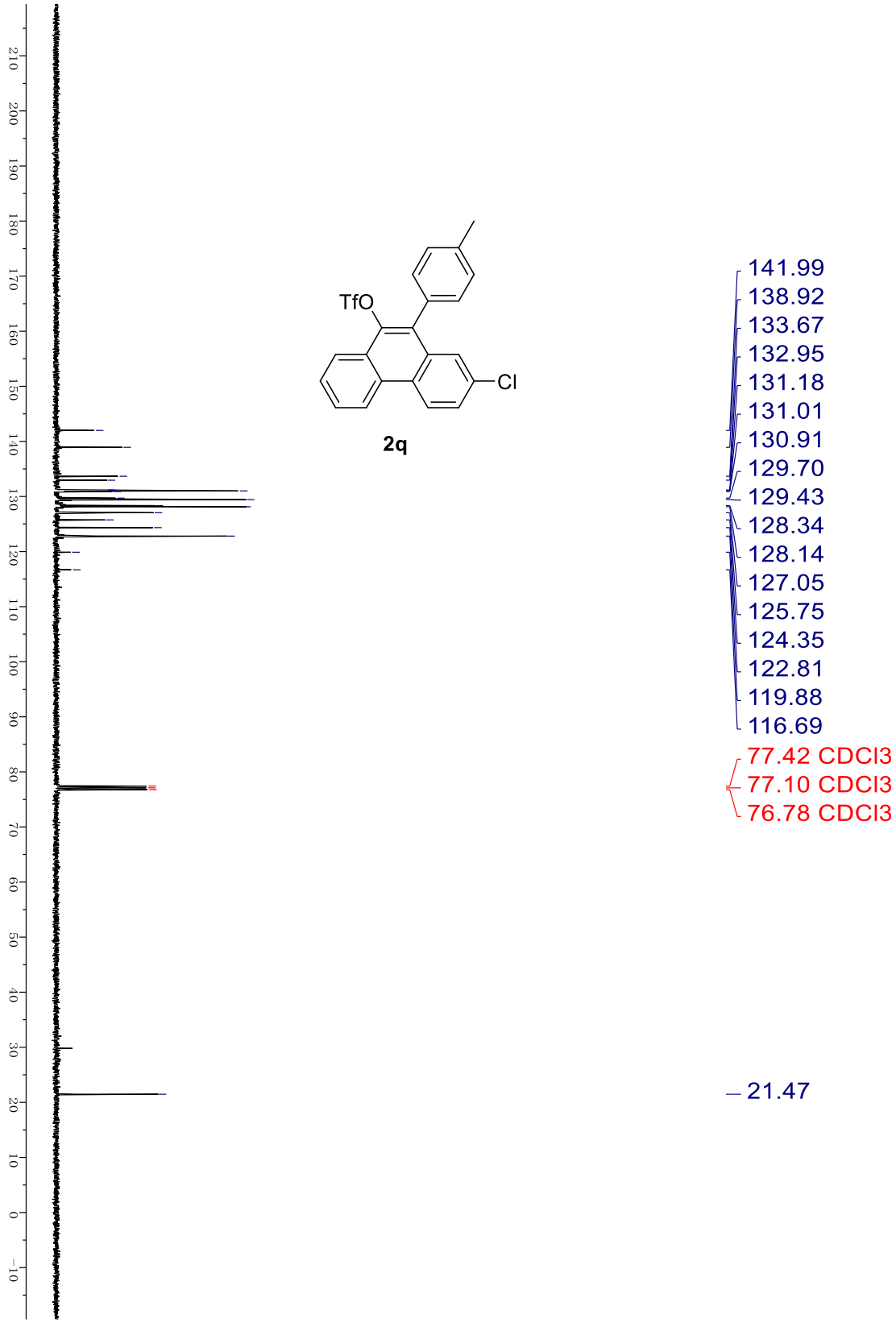
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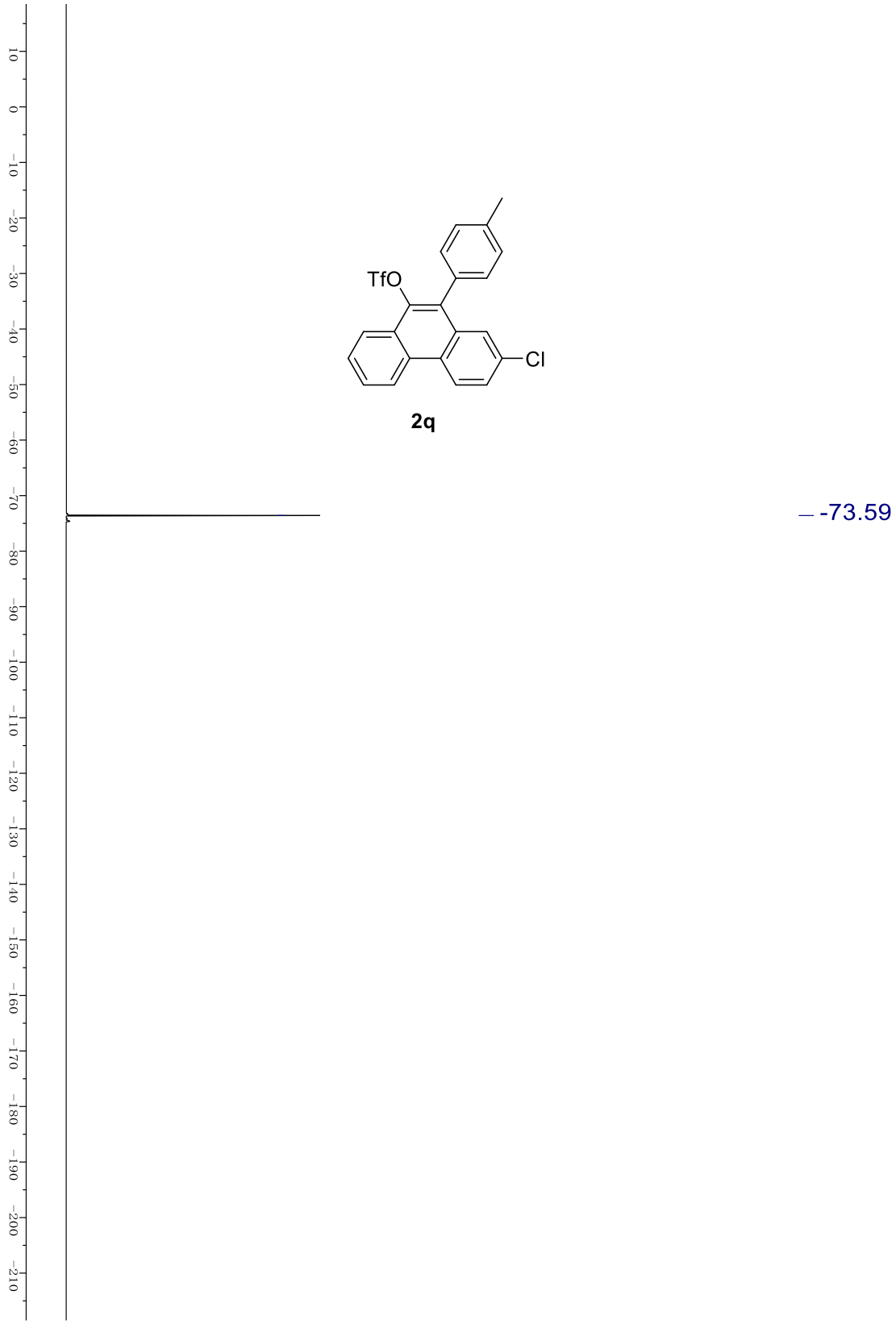
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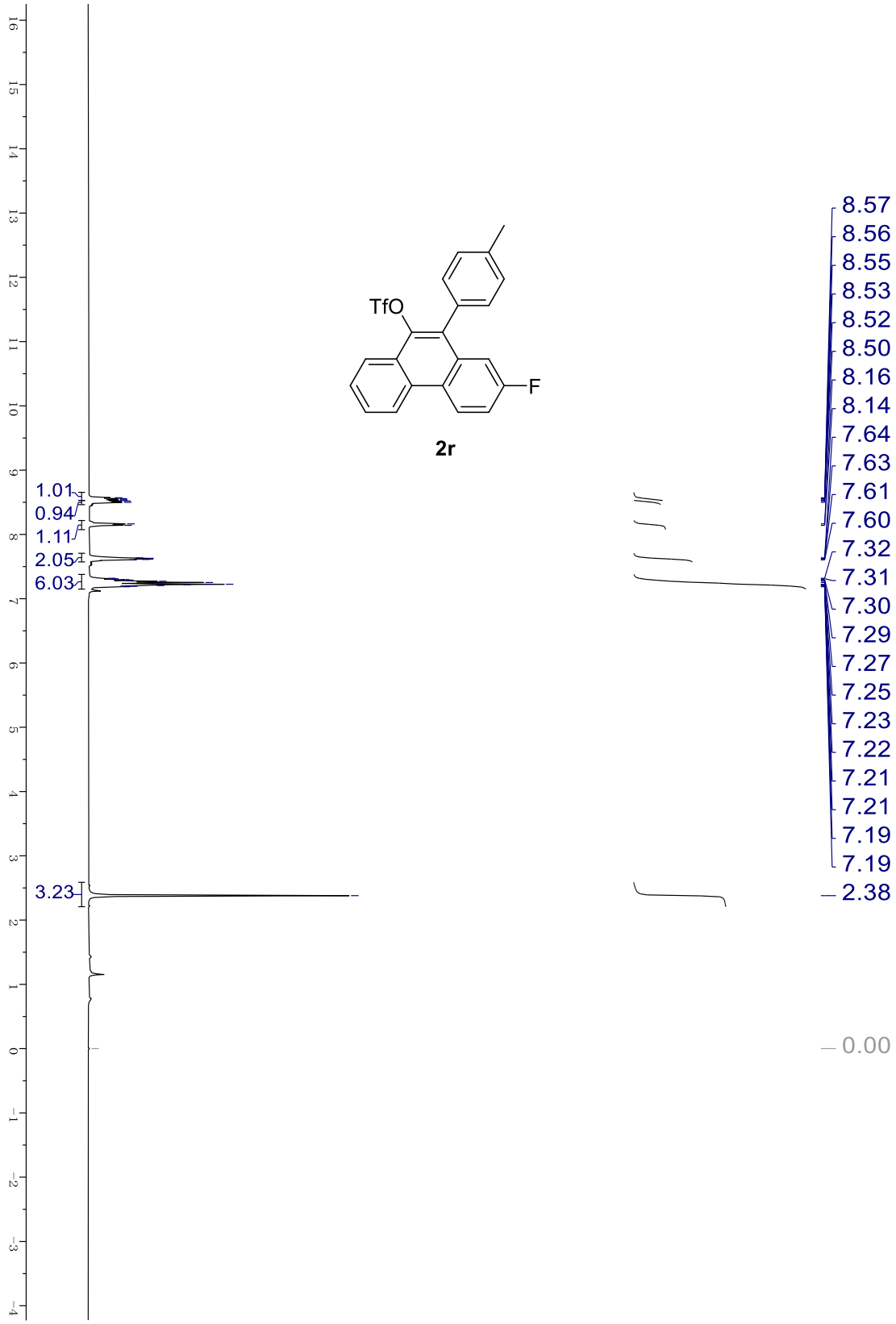
2q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8.50
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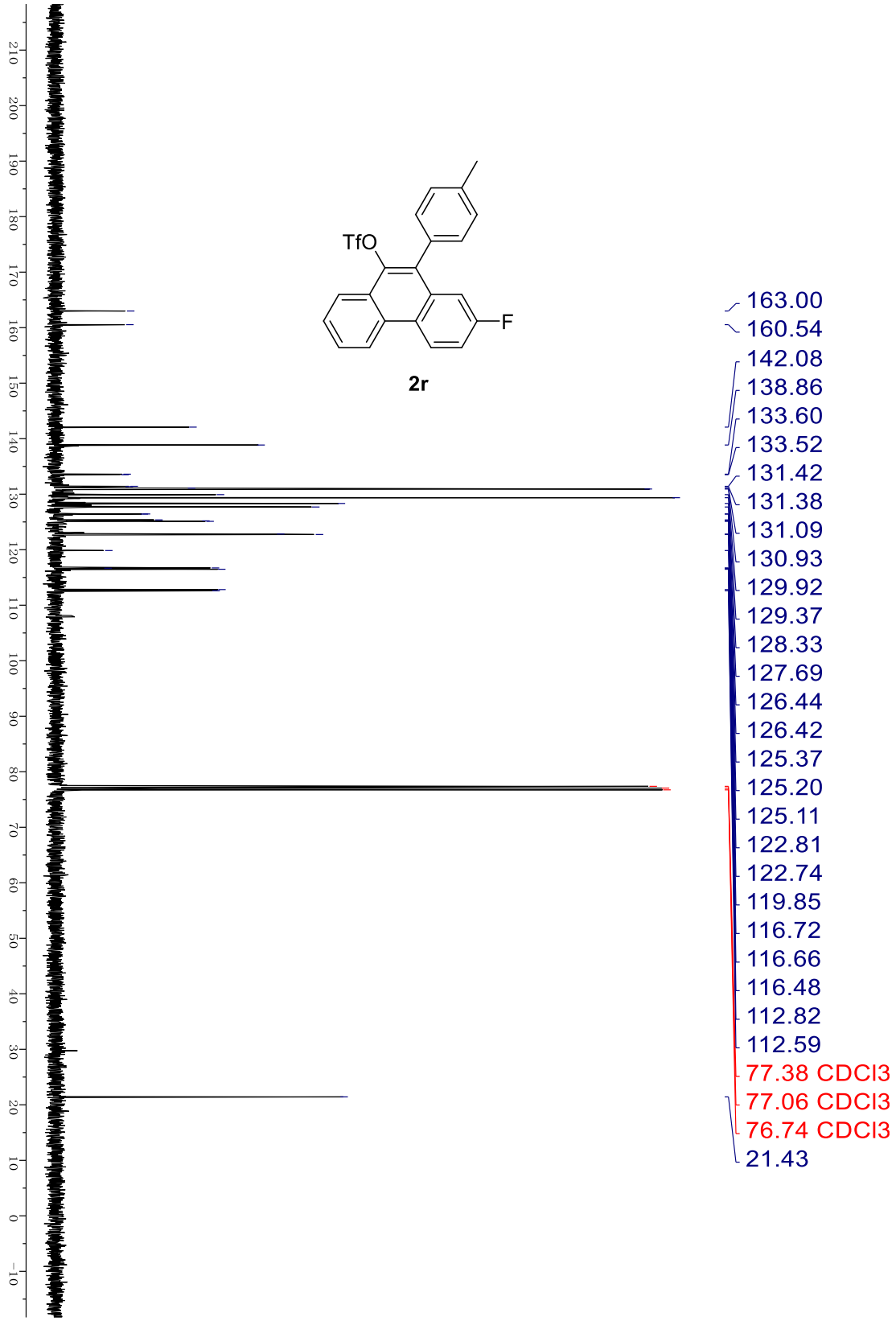
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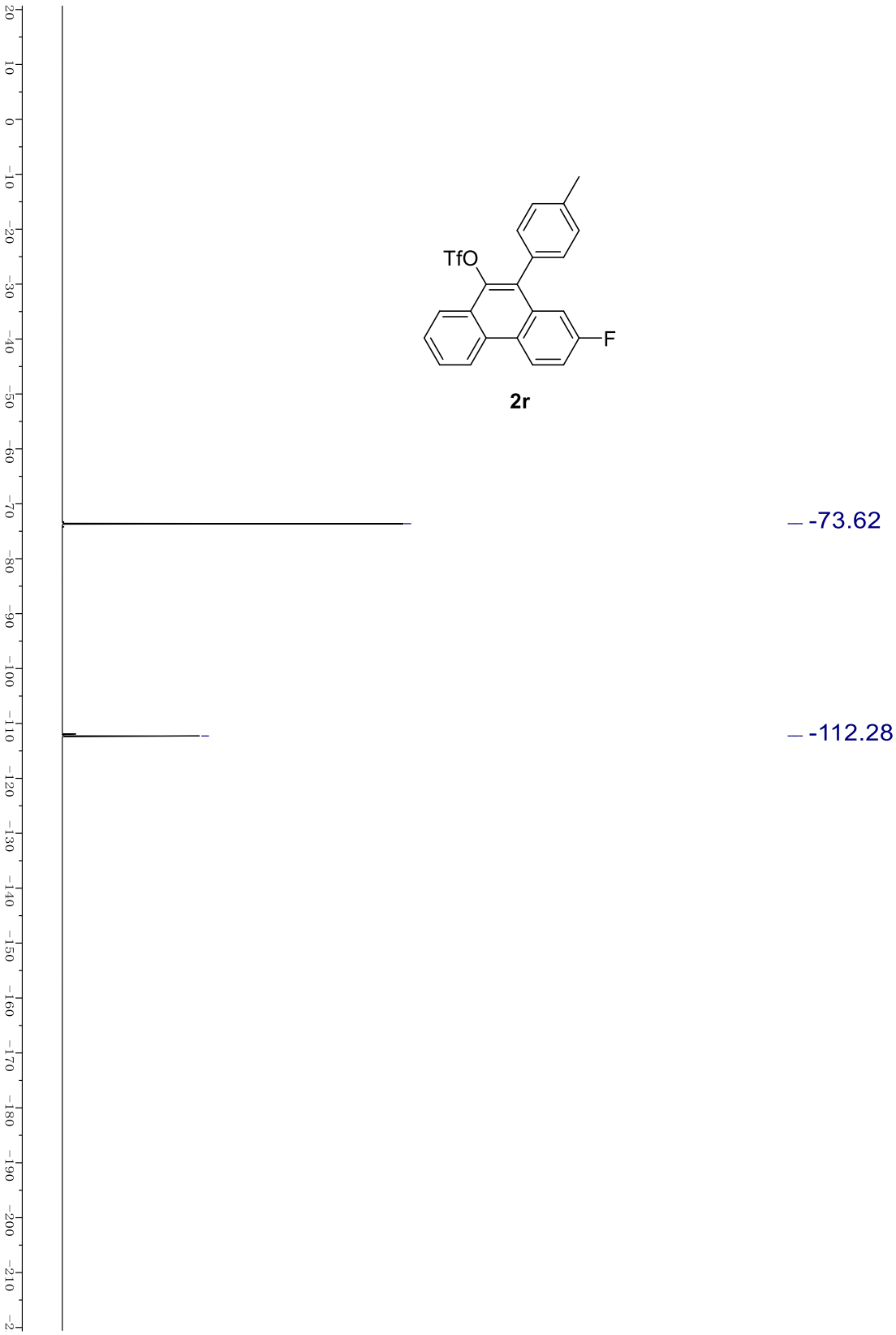
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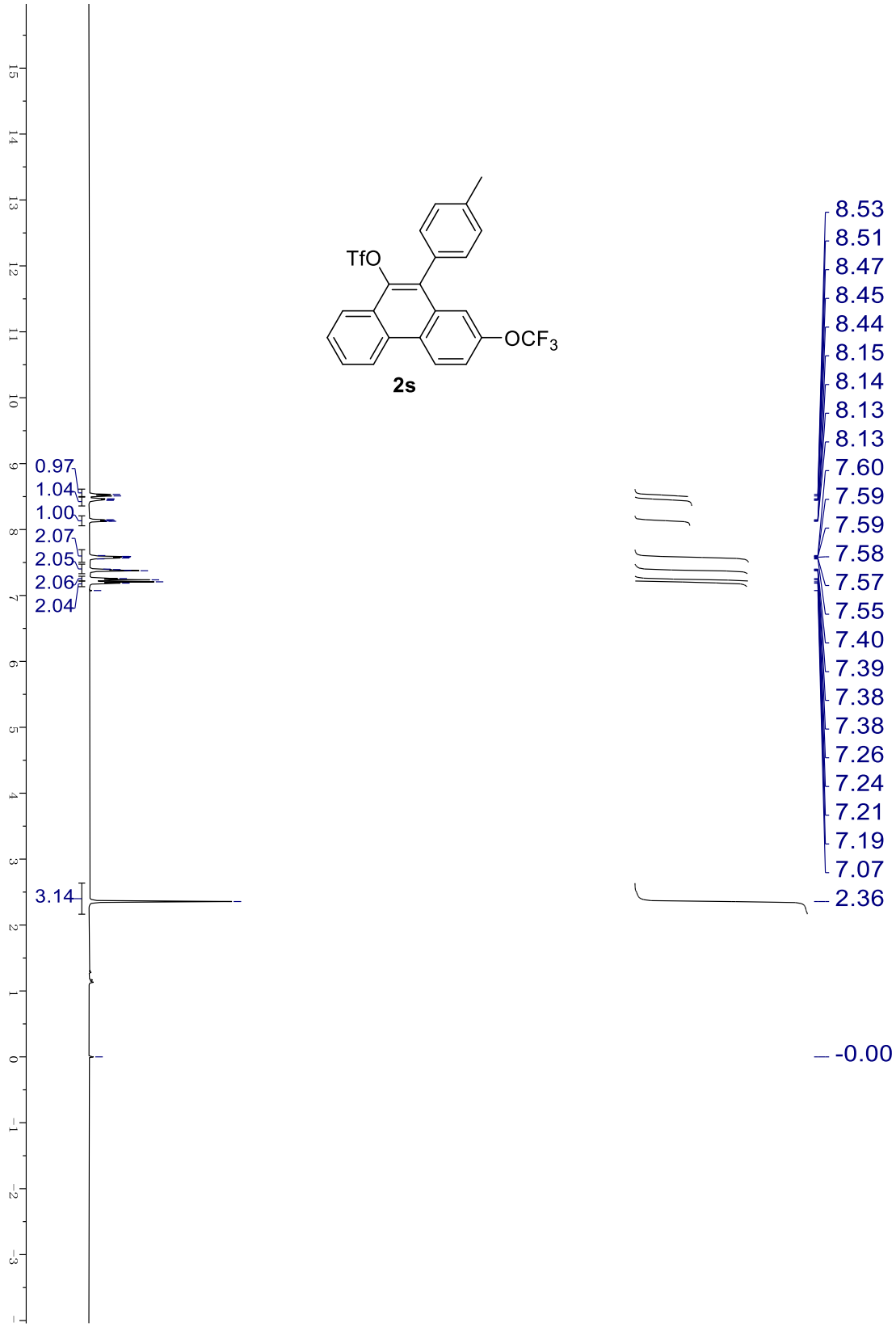
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8.47
8.45
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8.15
8.14
8.13
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7.58
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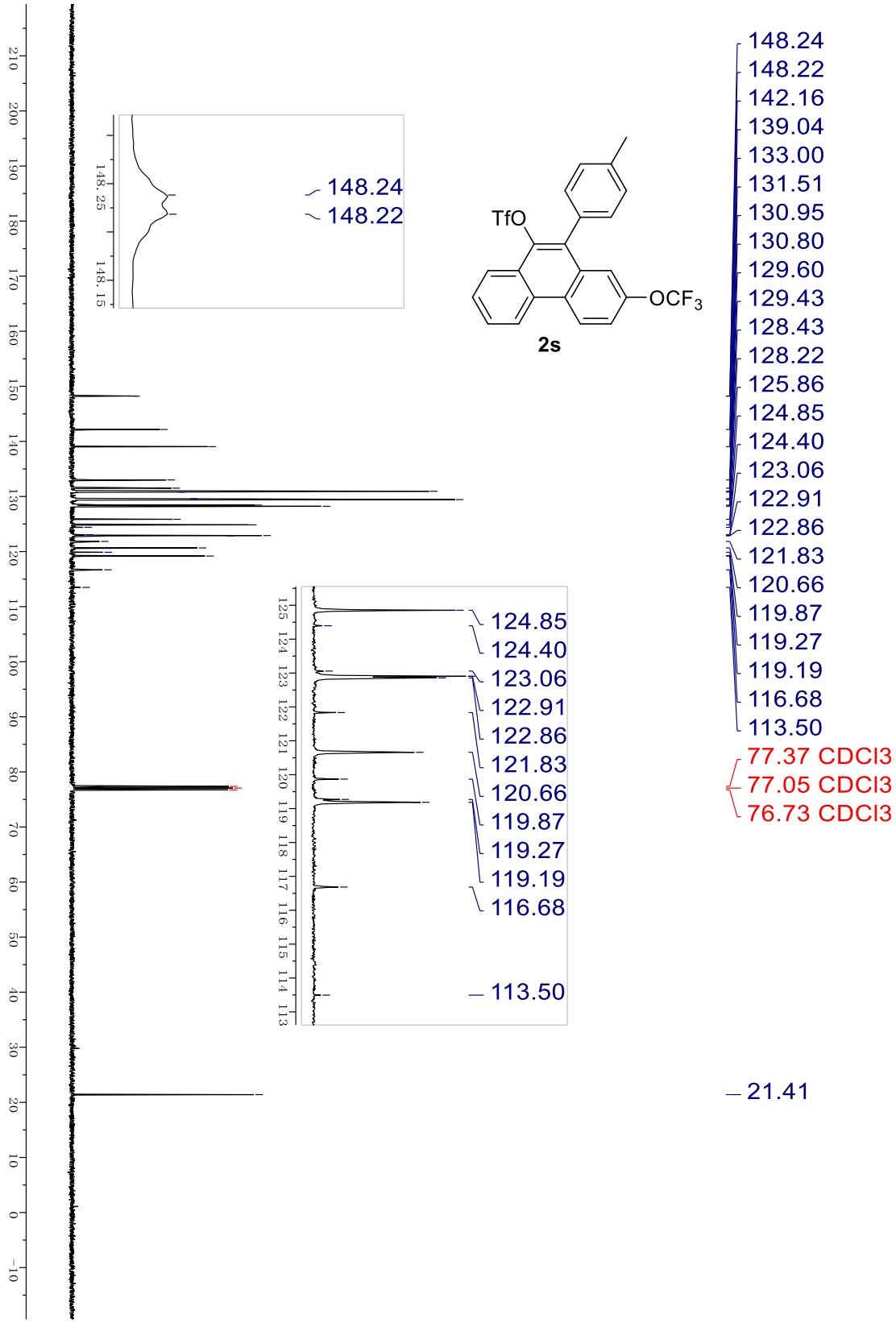
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123.06
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119.87
119.27
119.19
116.68
113.50
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
124.85
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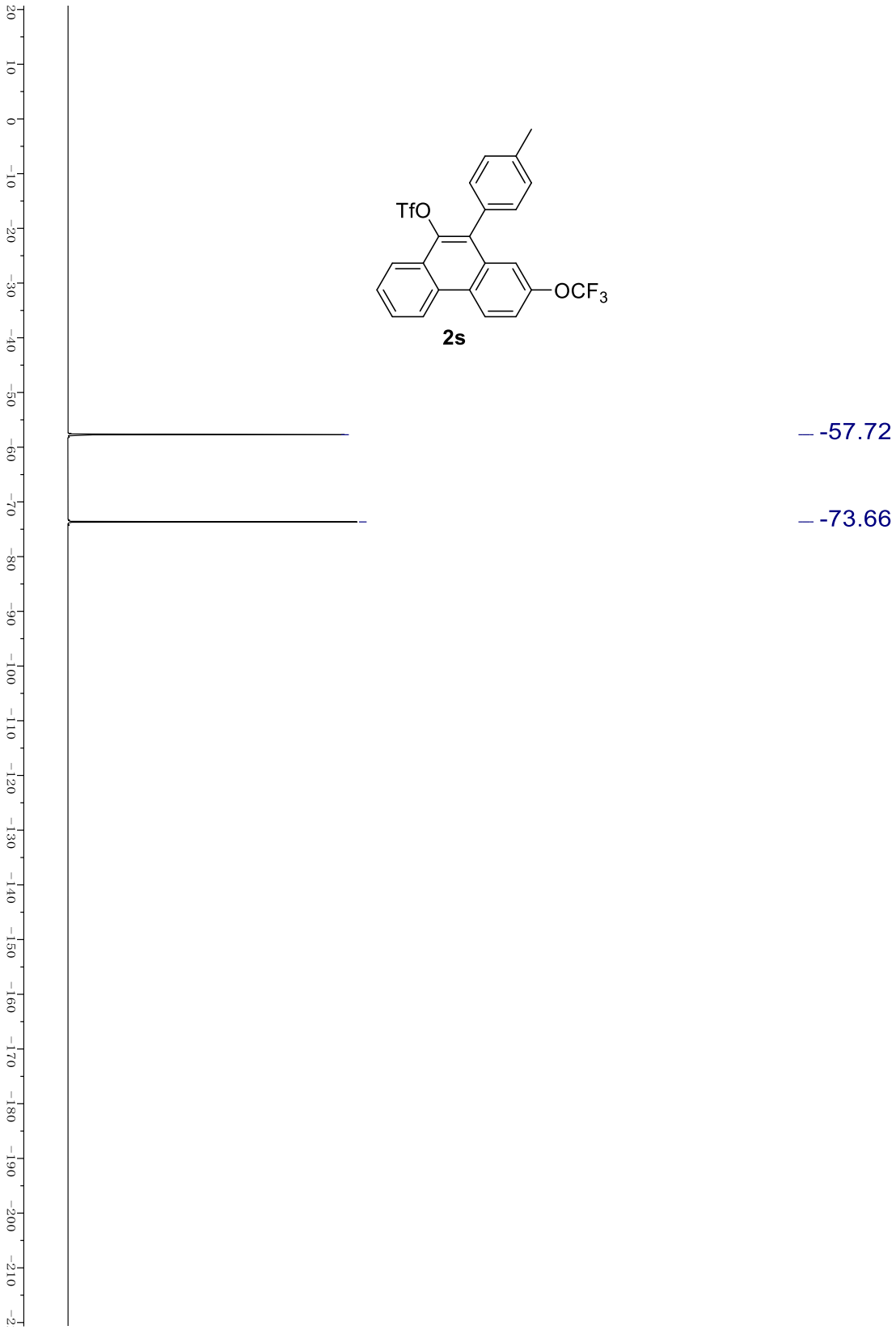
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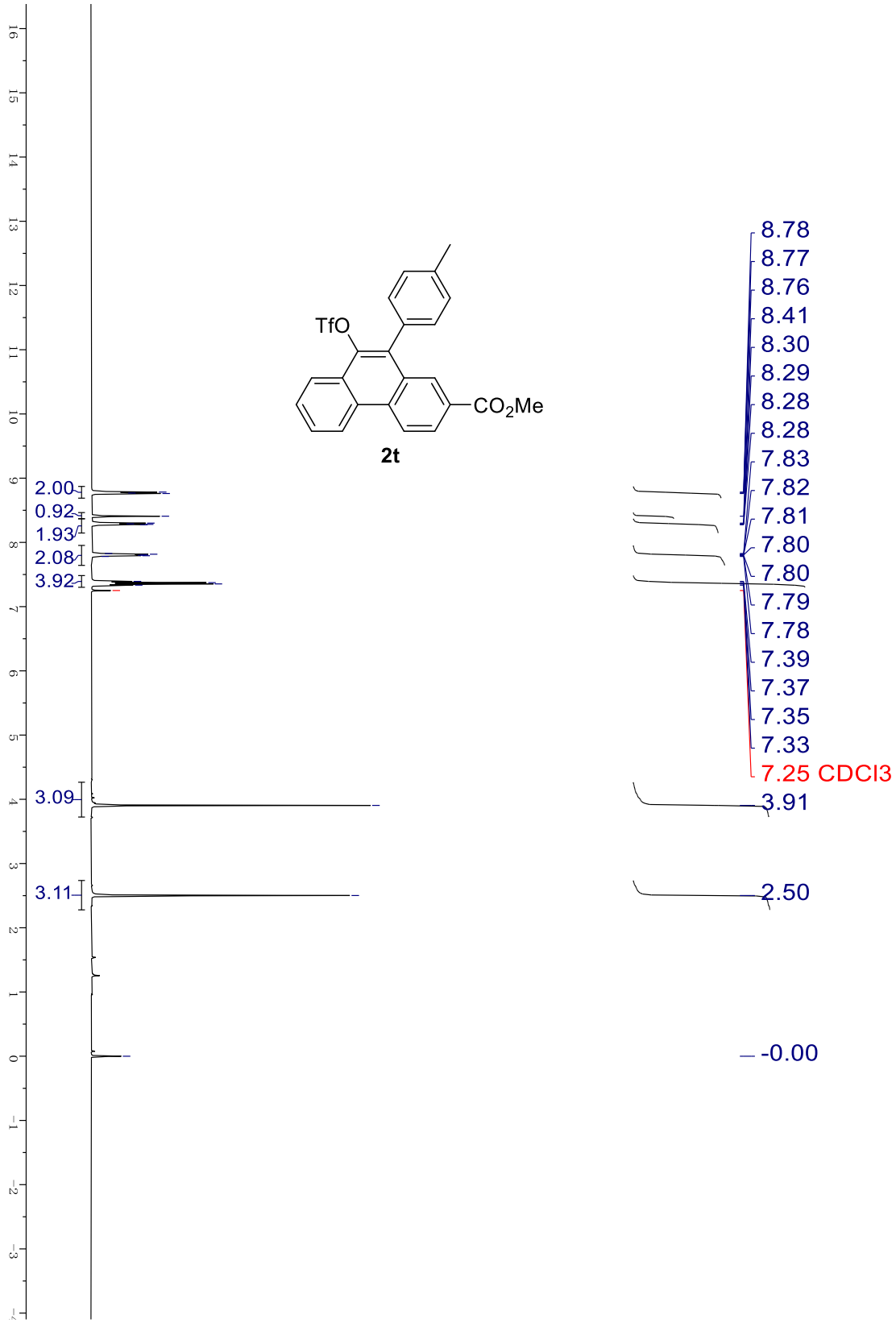
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7.82
7.81
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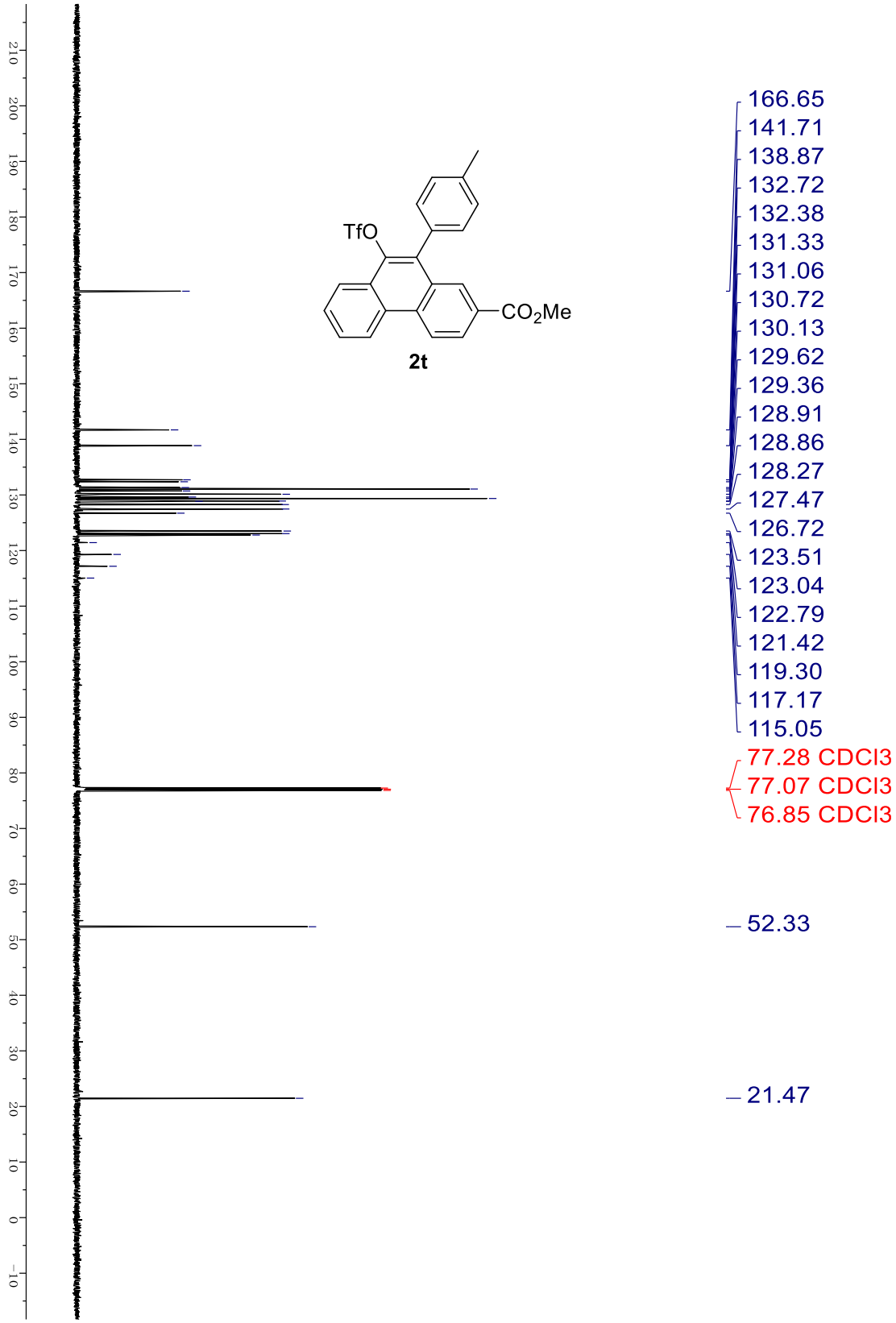
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123.51
123.04
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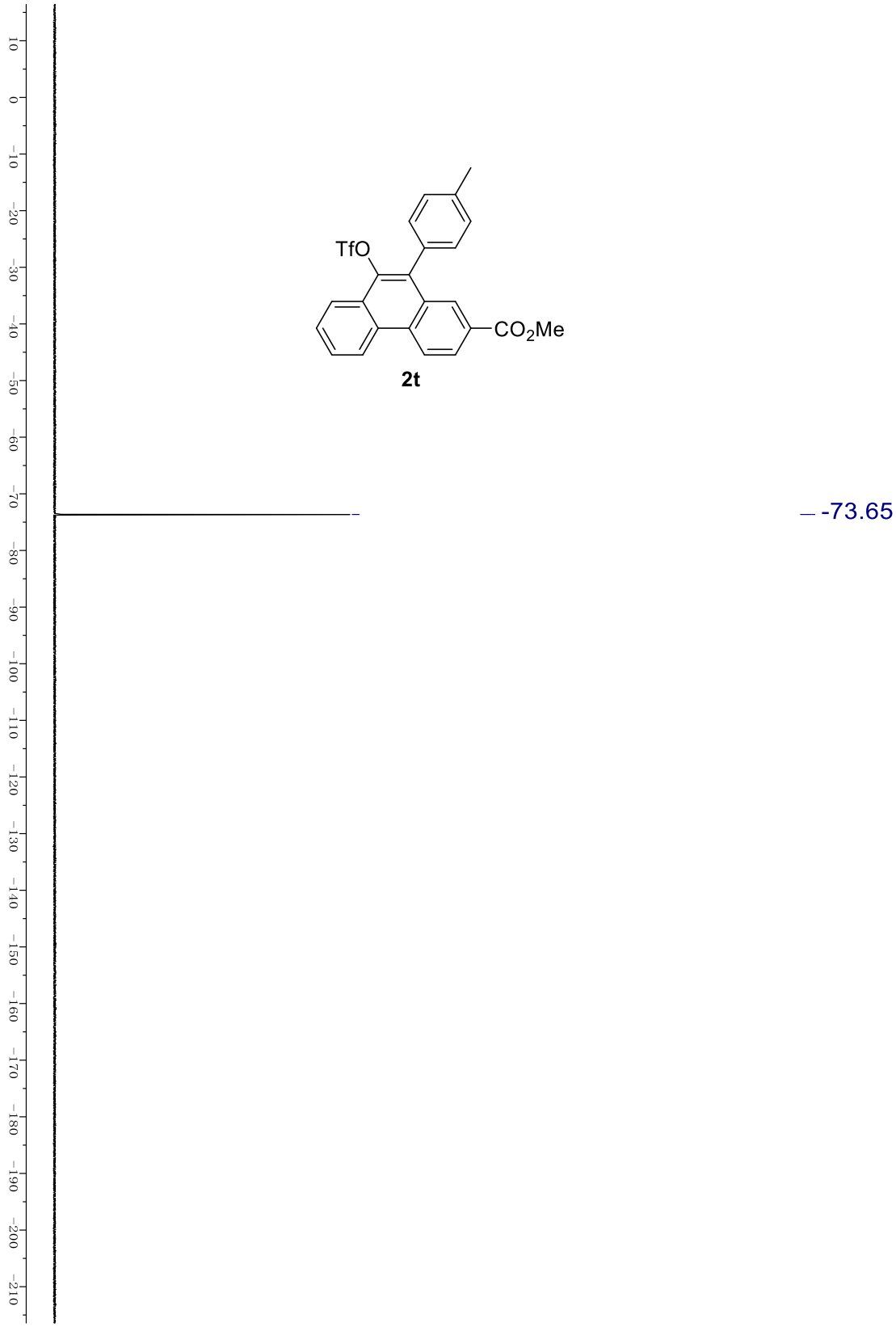
21.47



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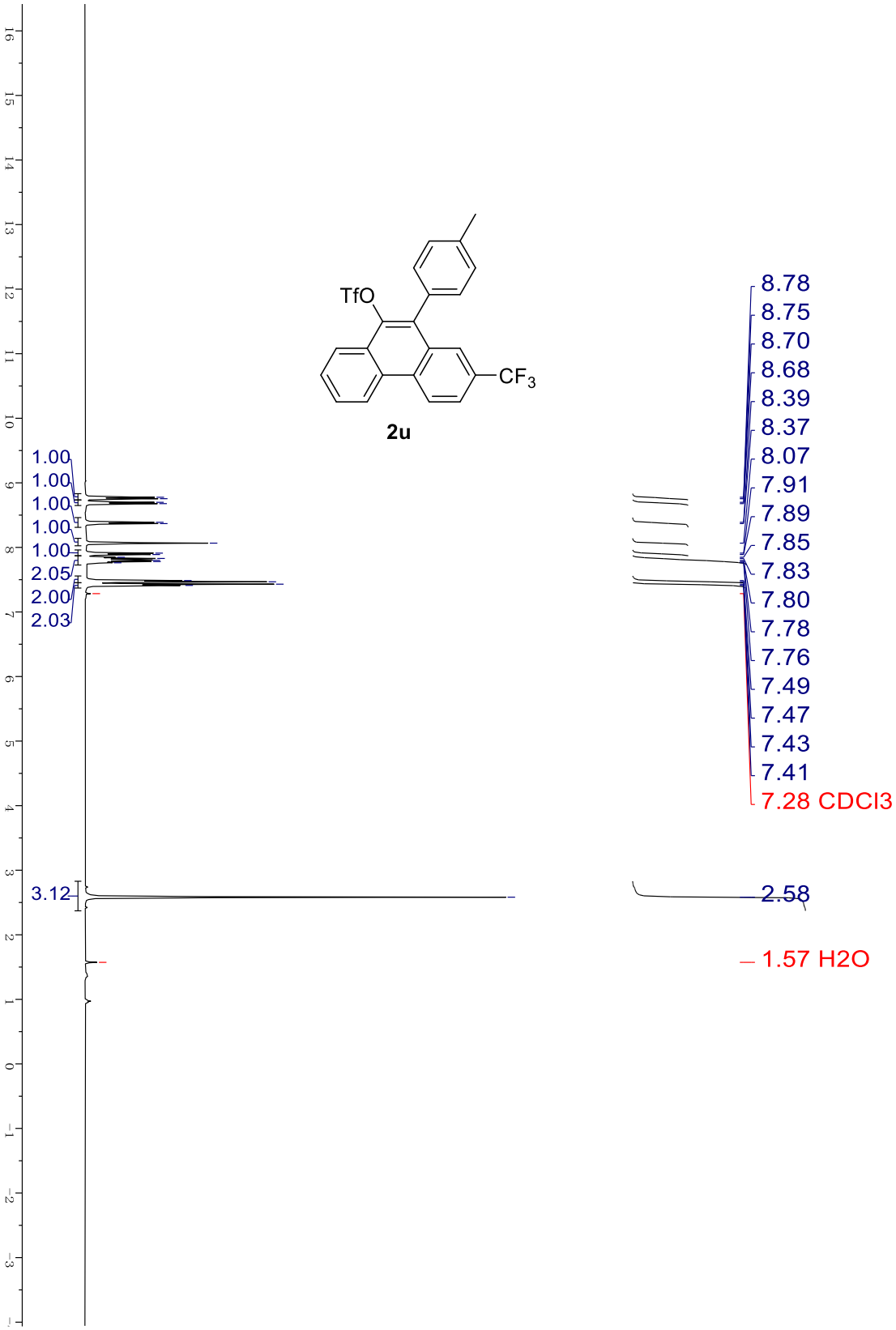
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8.75
8.70
8.68
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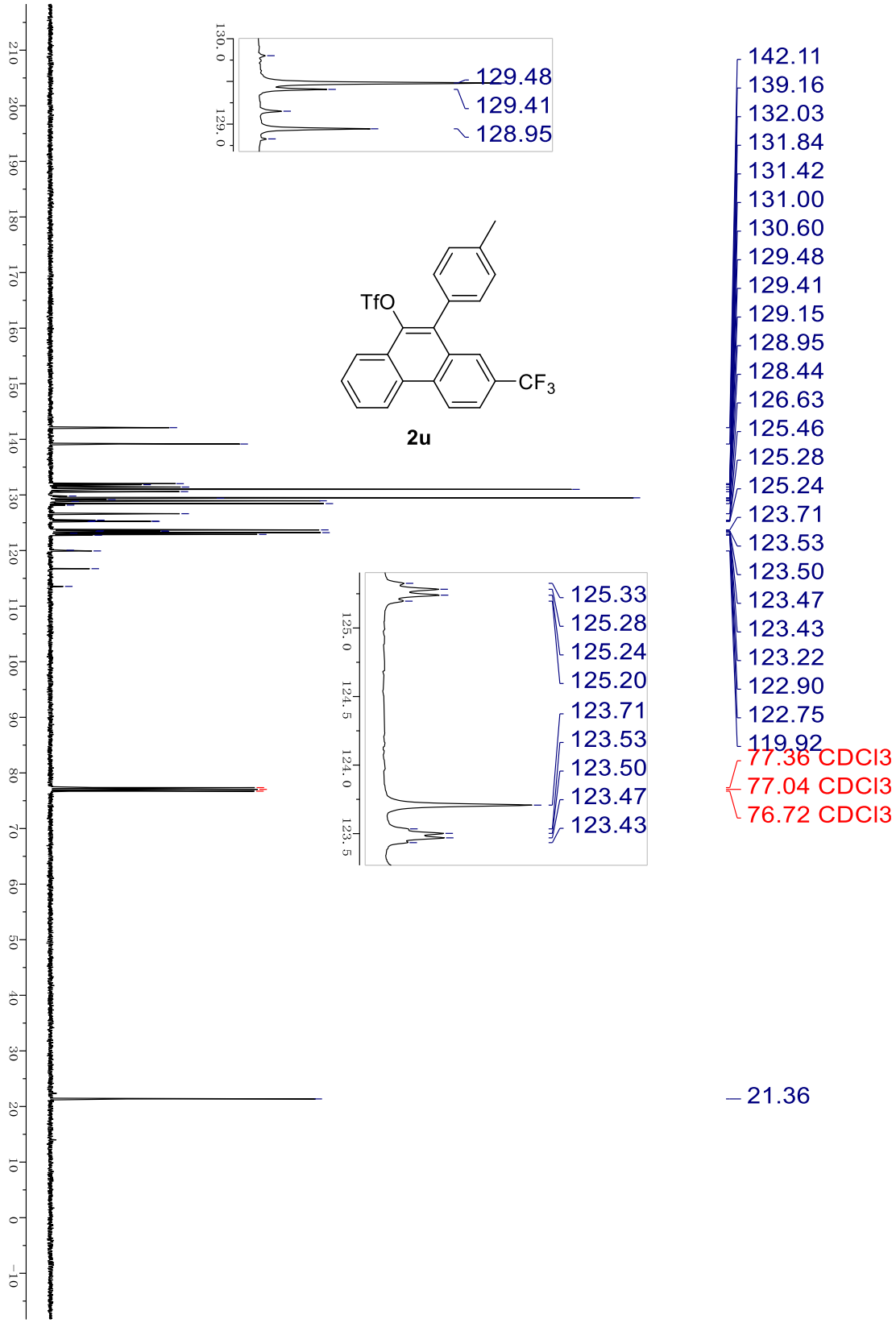
1.57 H2O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123.43
123.22
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77.04 CDCl3
76.72 CDCl3
21.36
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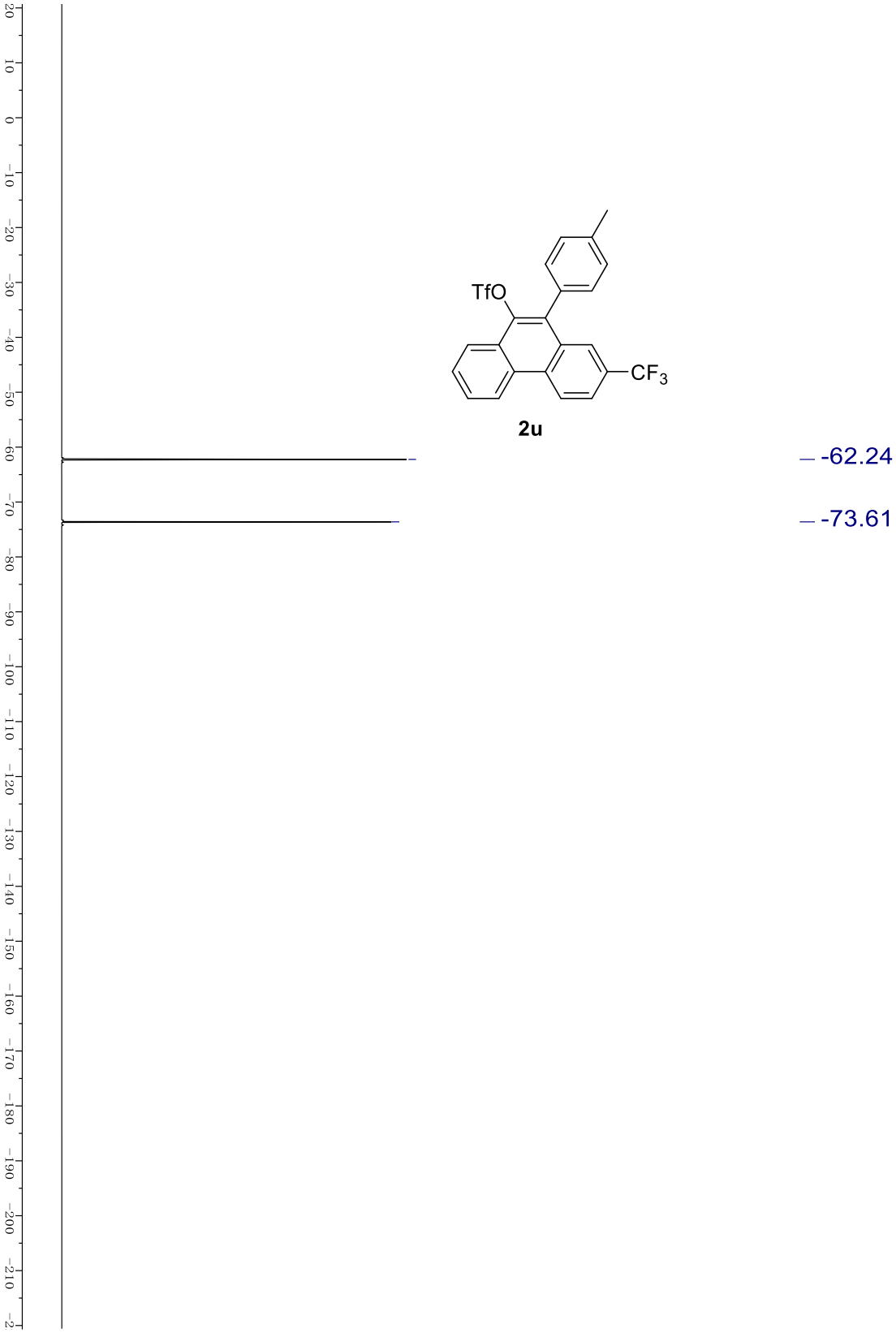
CF3
2u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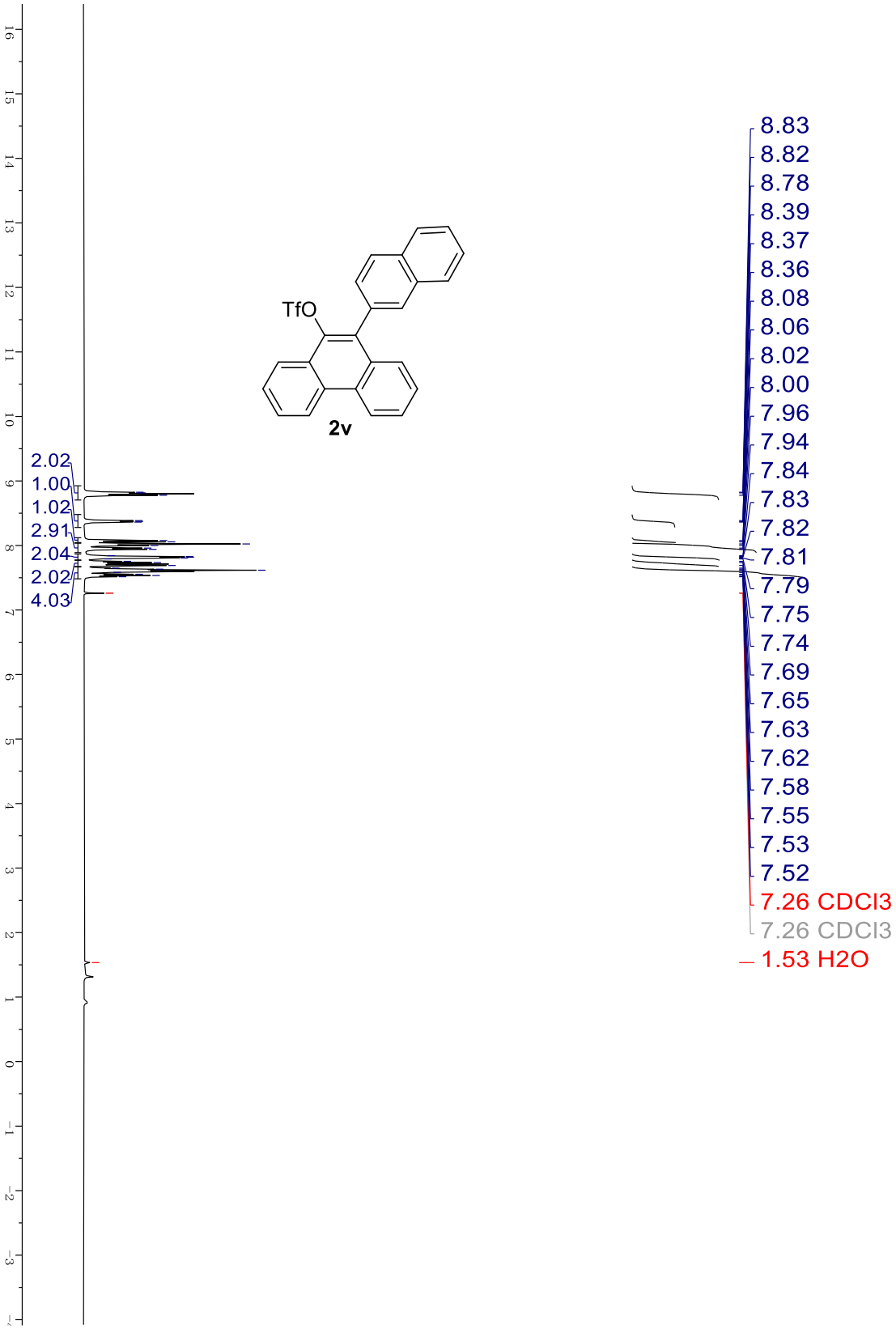
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8.37
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8.00
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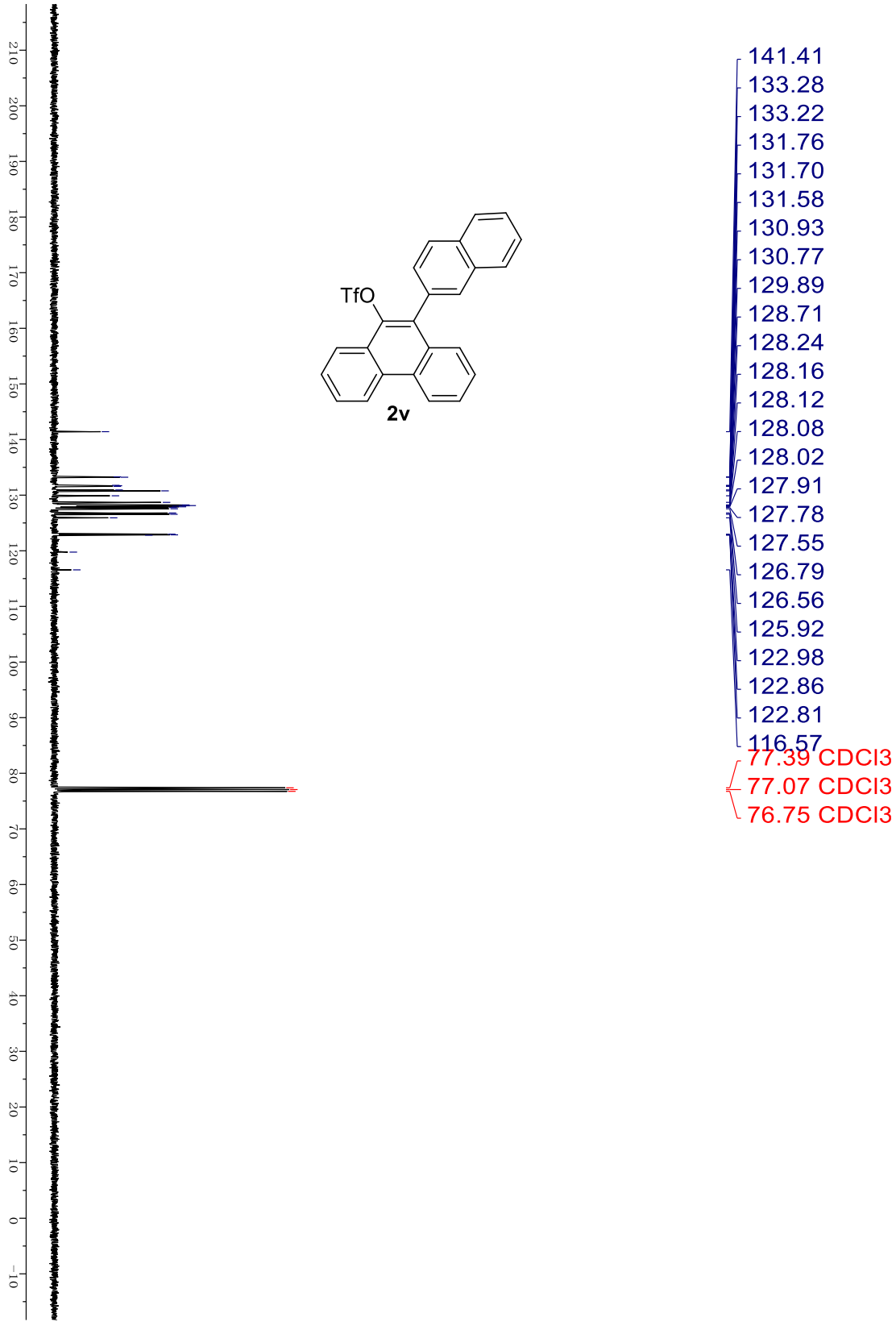
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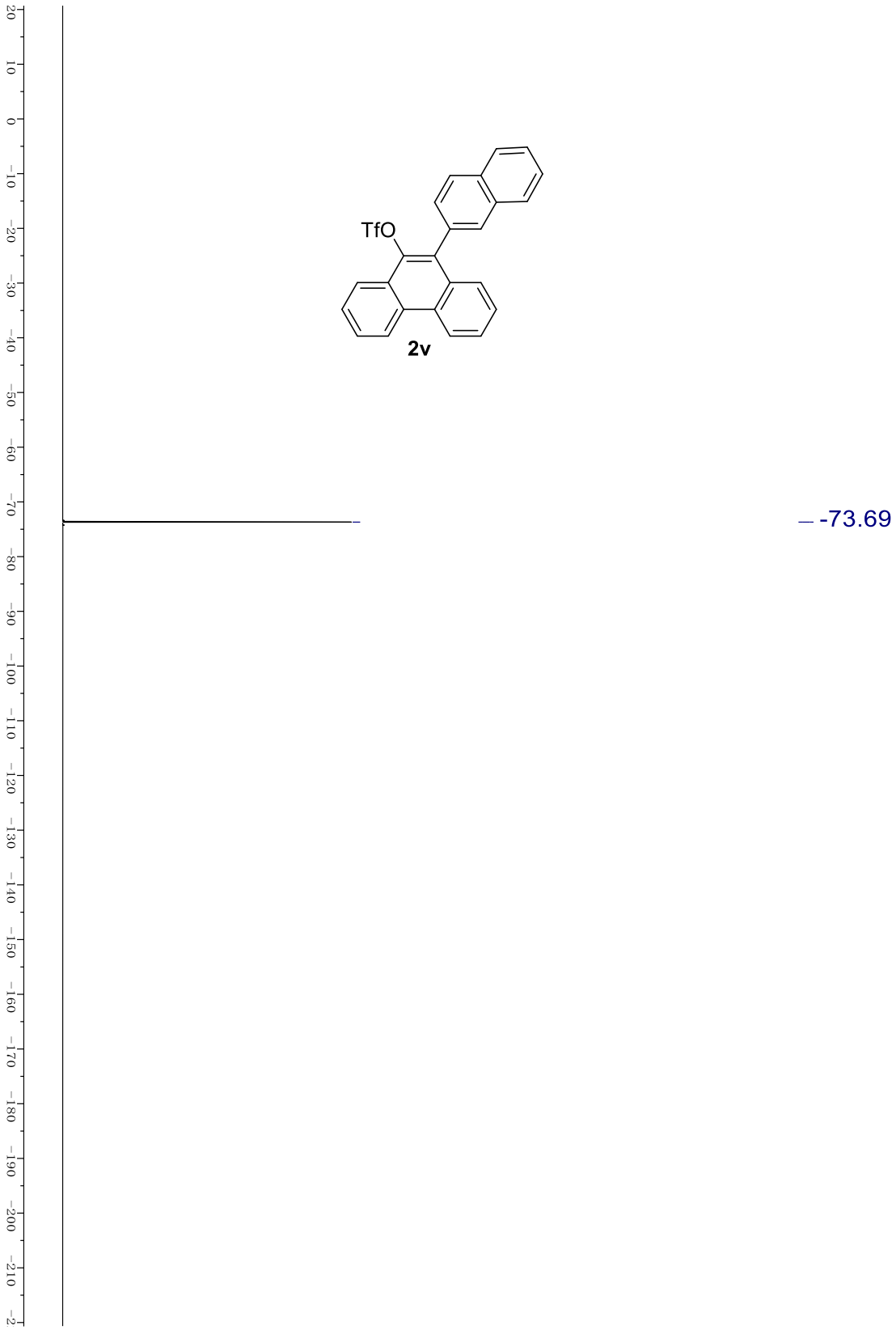
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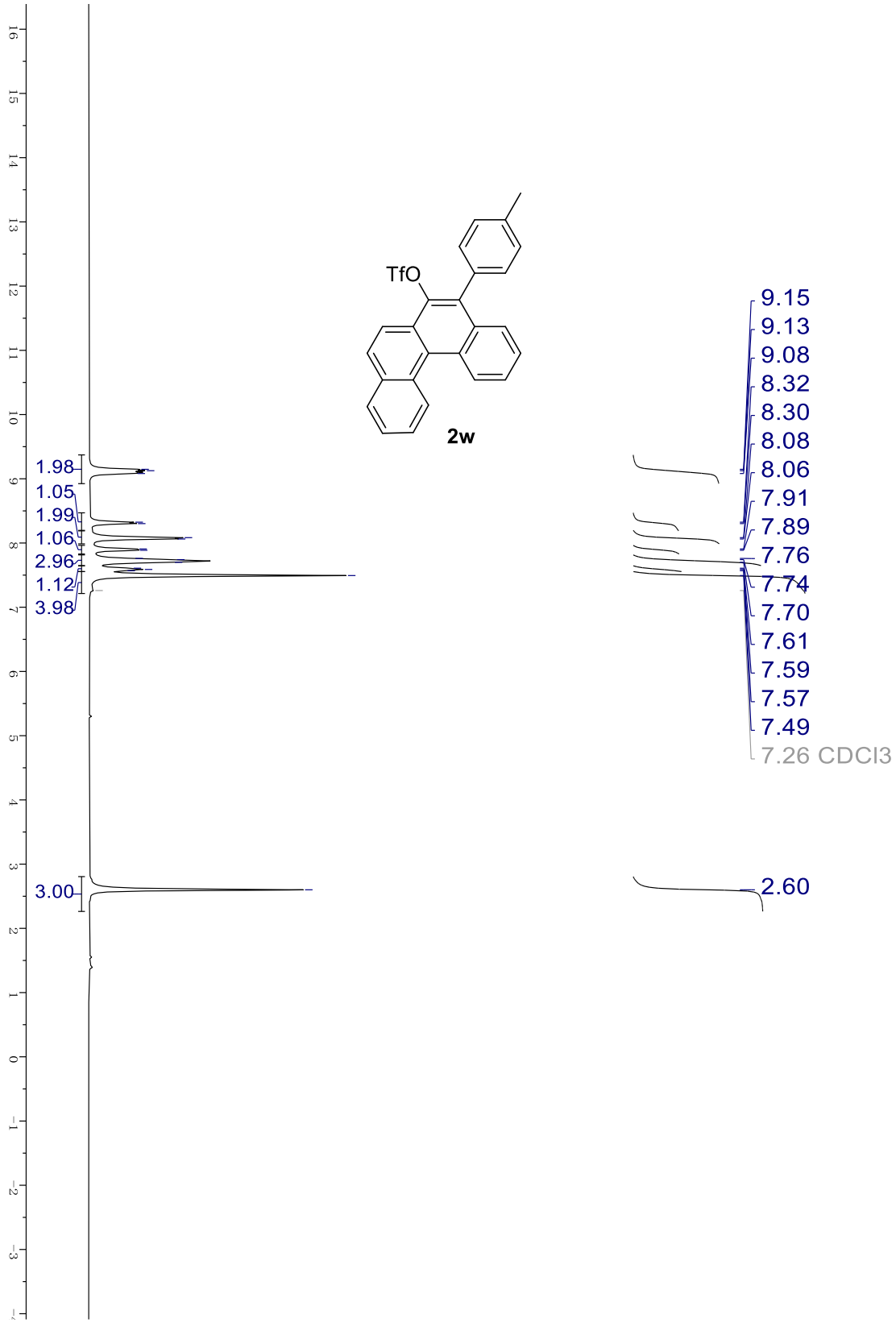
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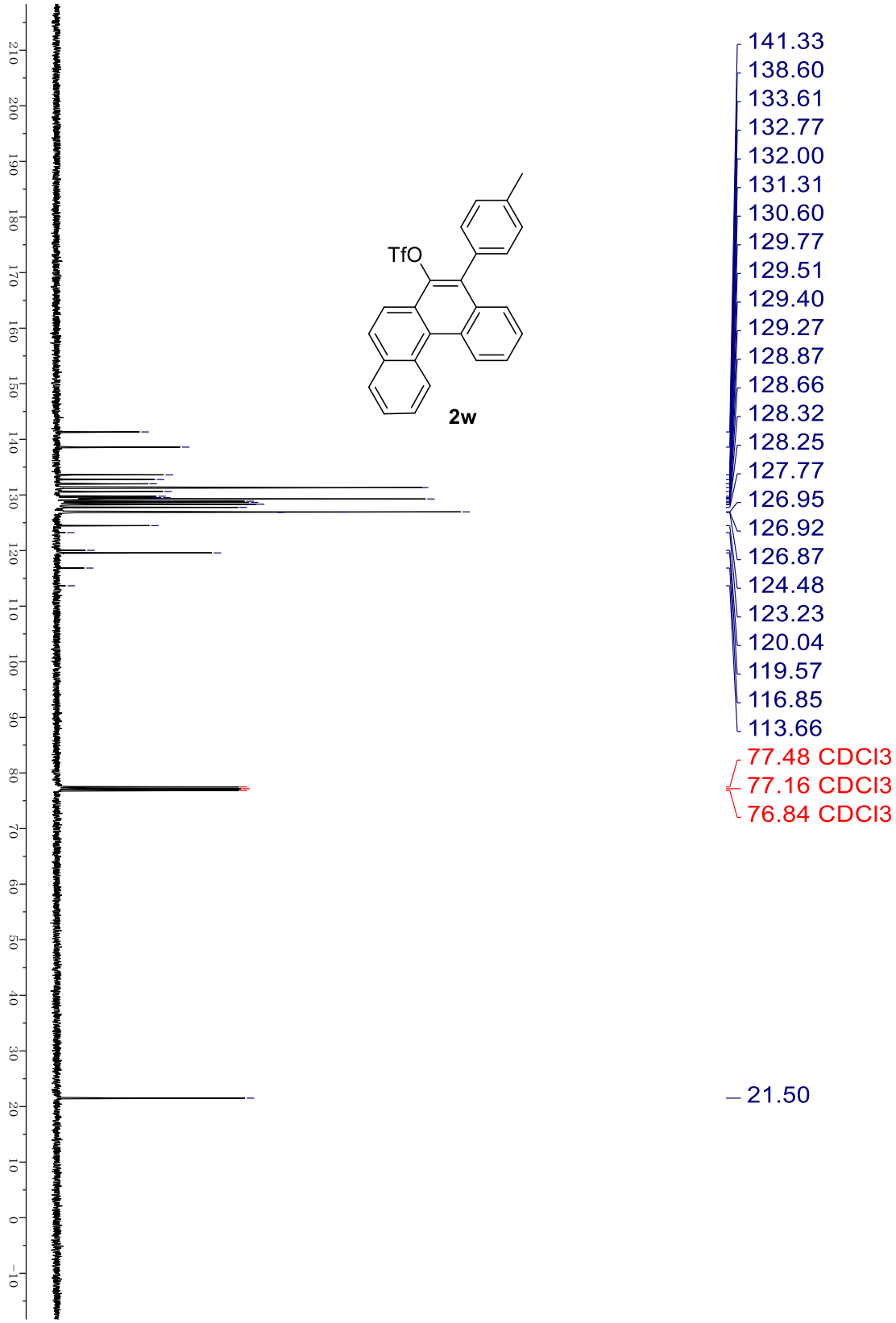
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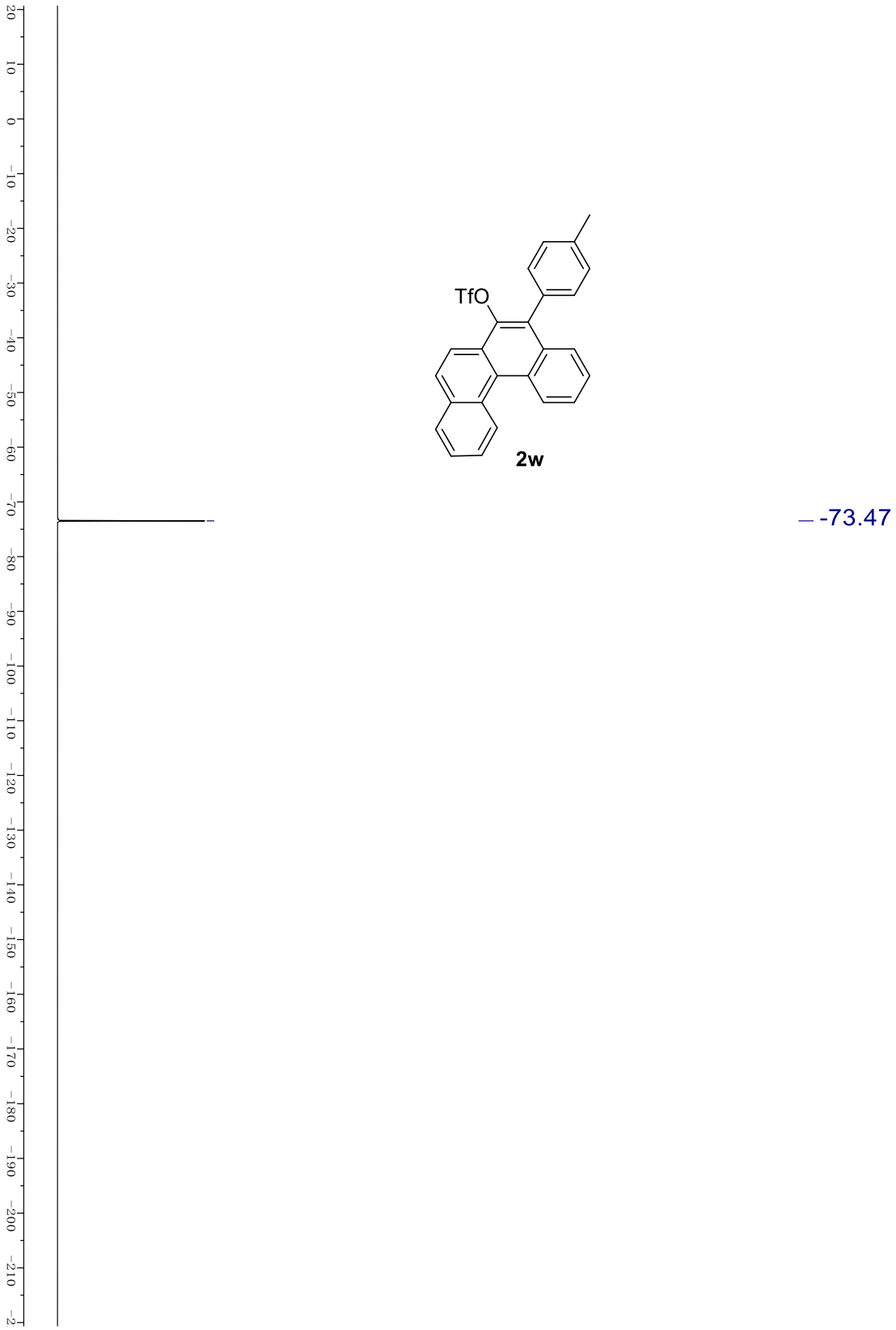
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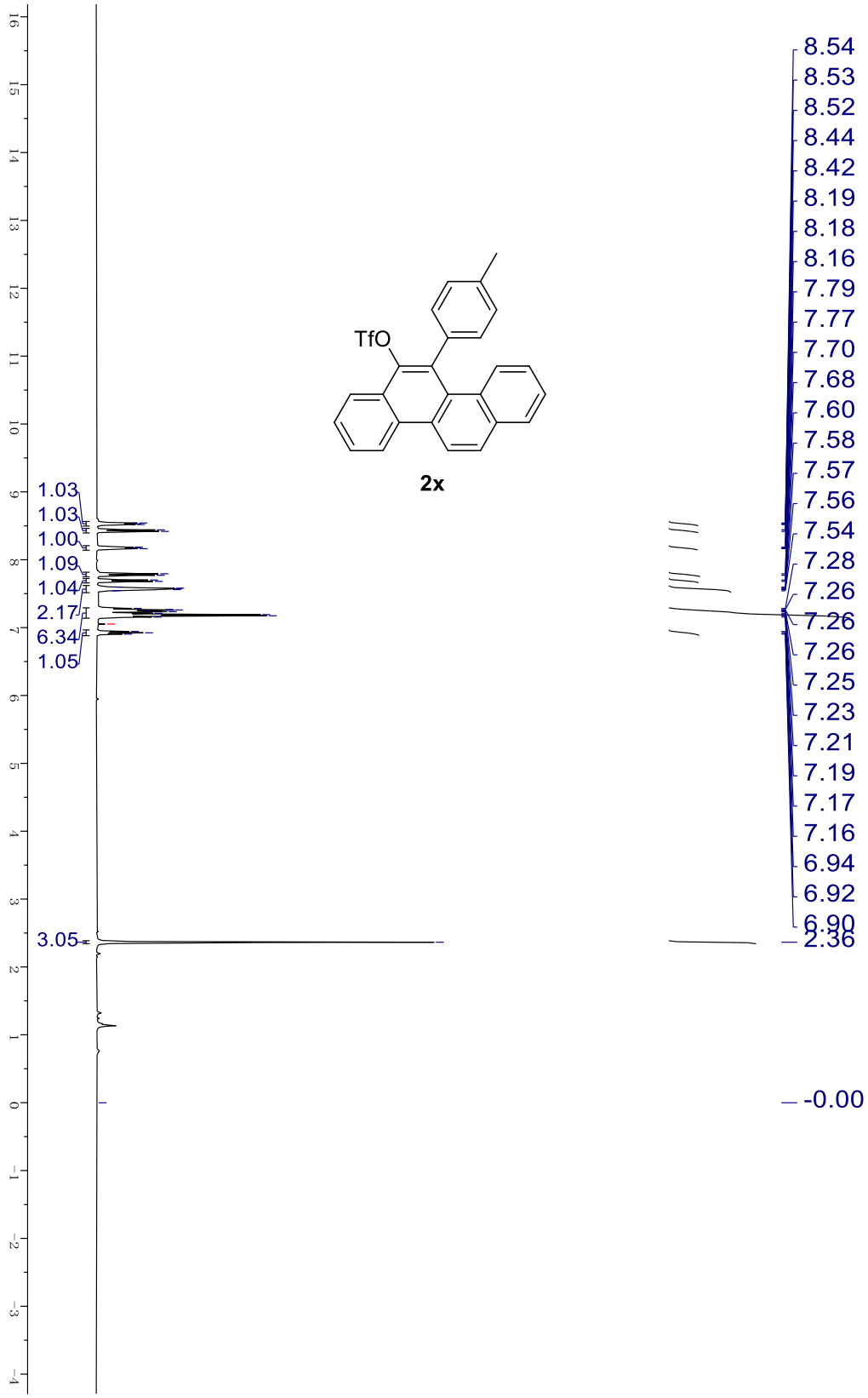
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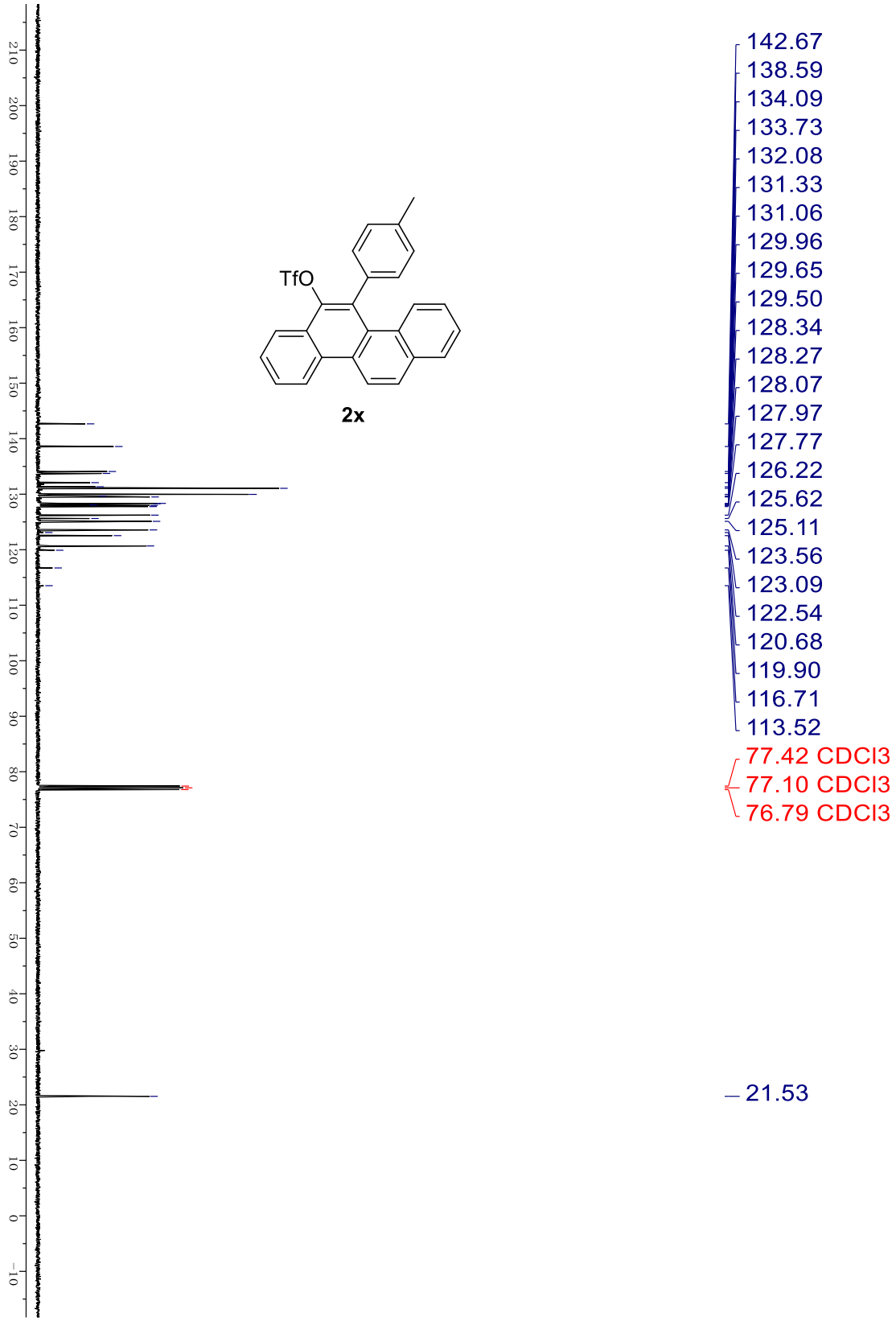
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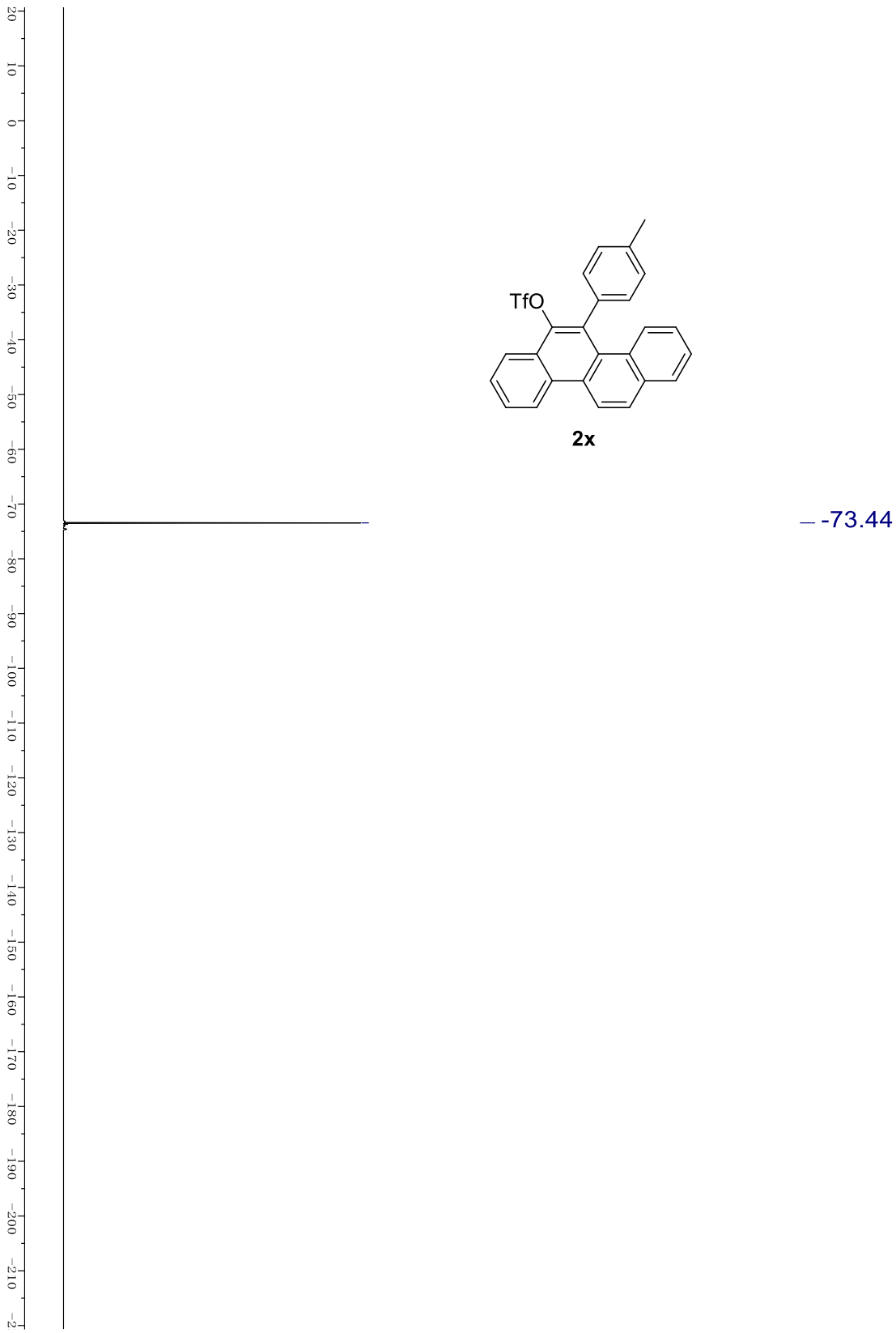
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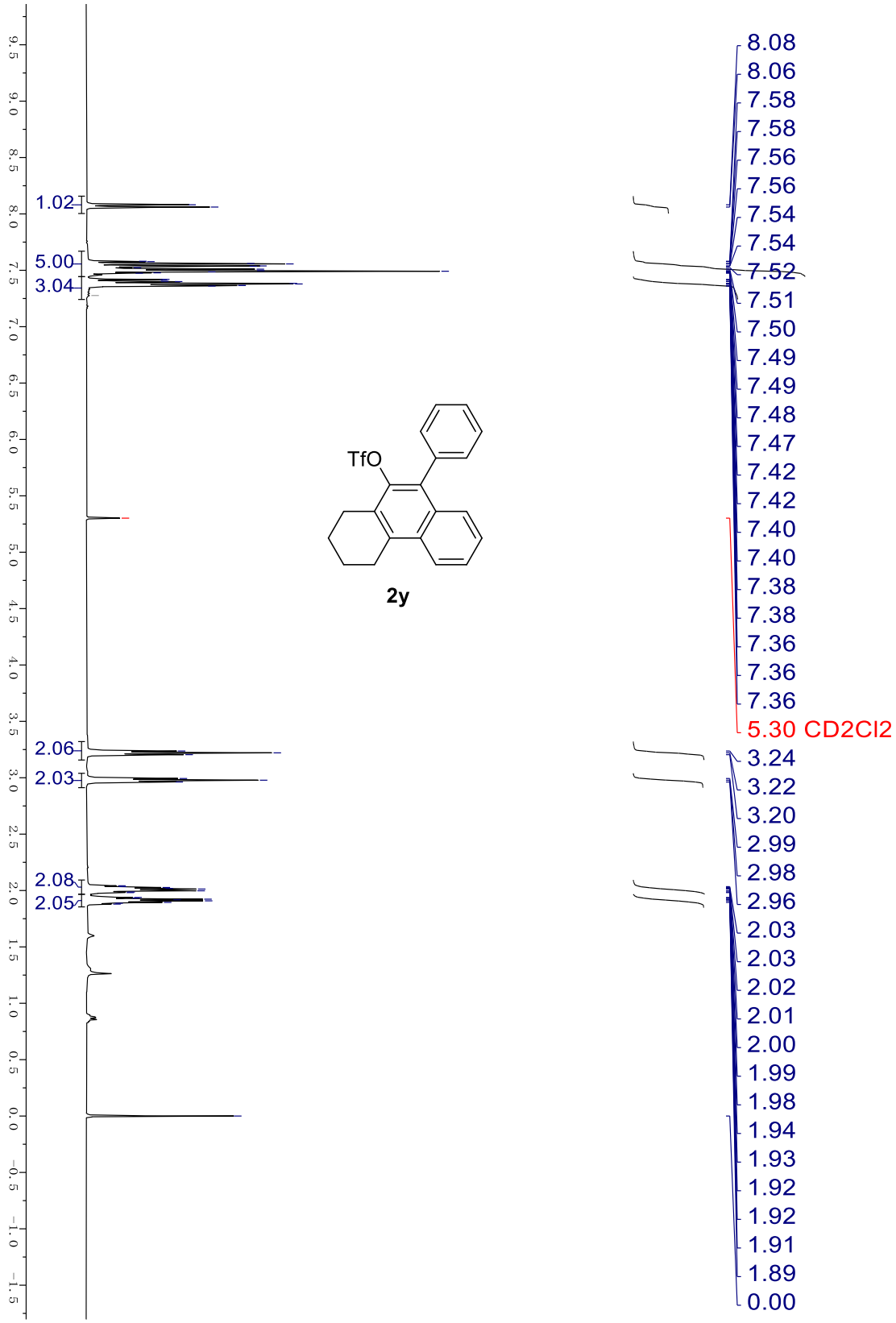
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2.03
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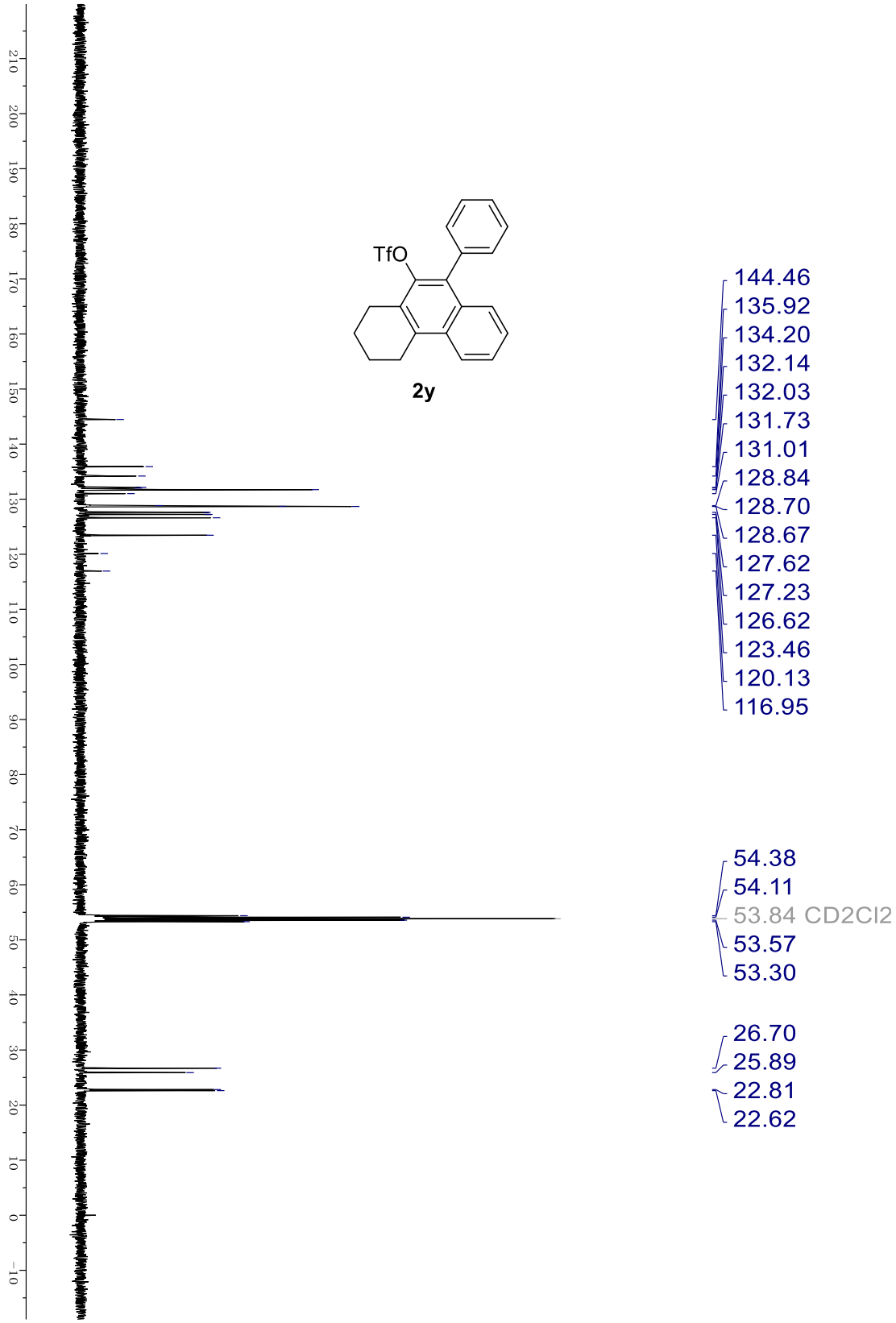
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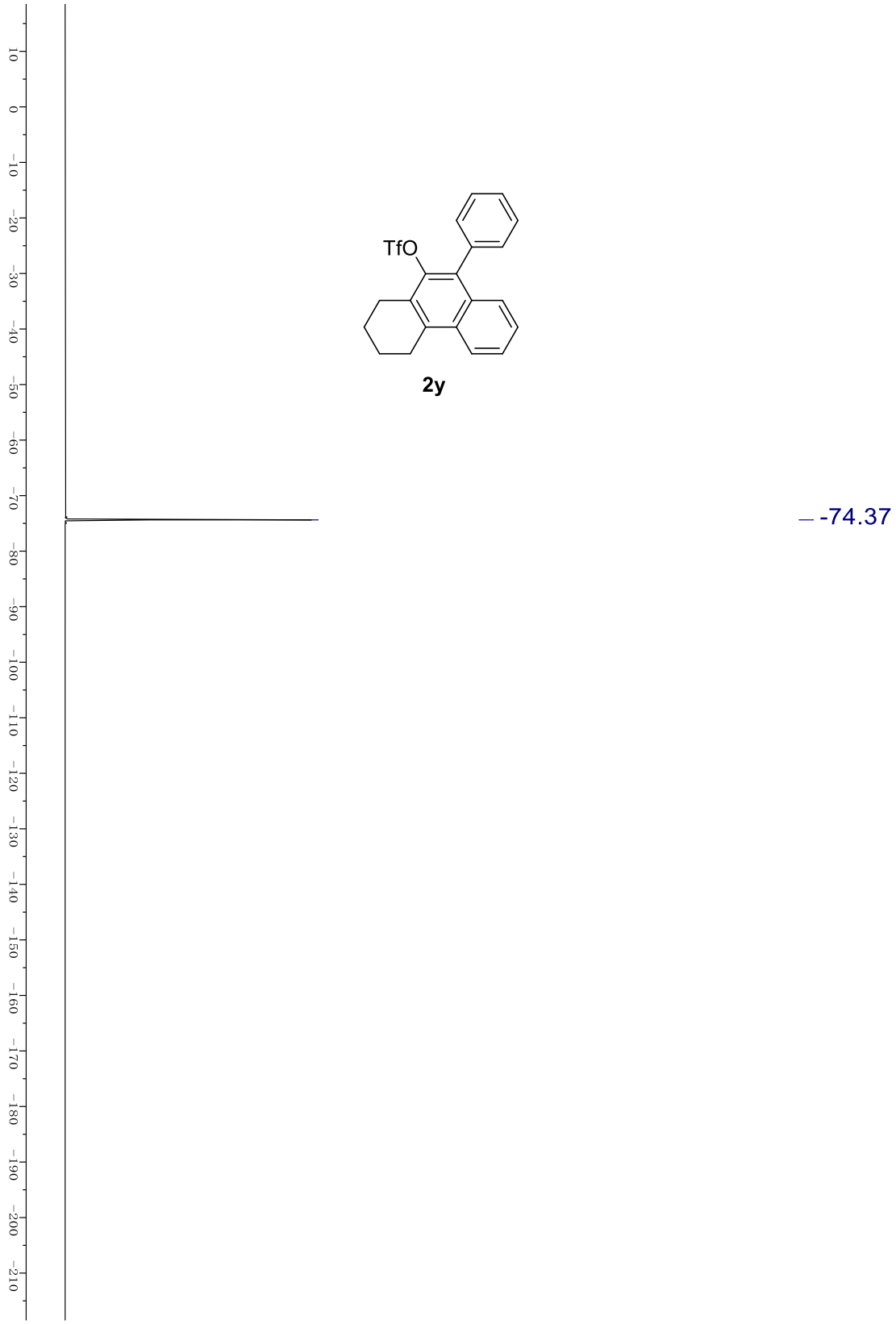
22.62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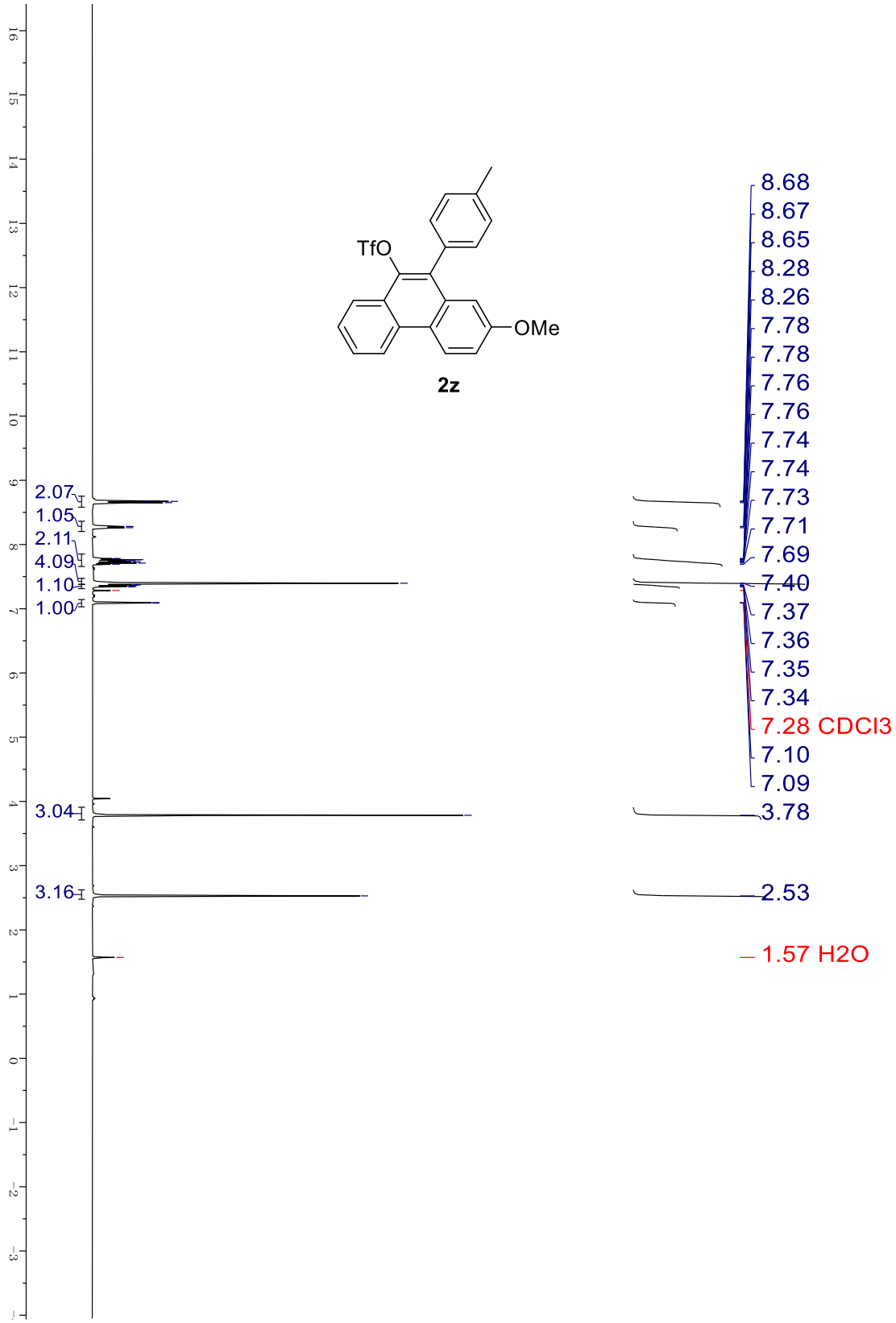
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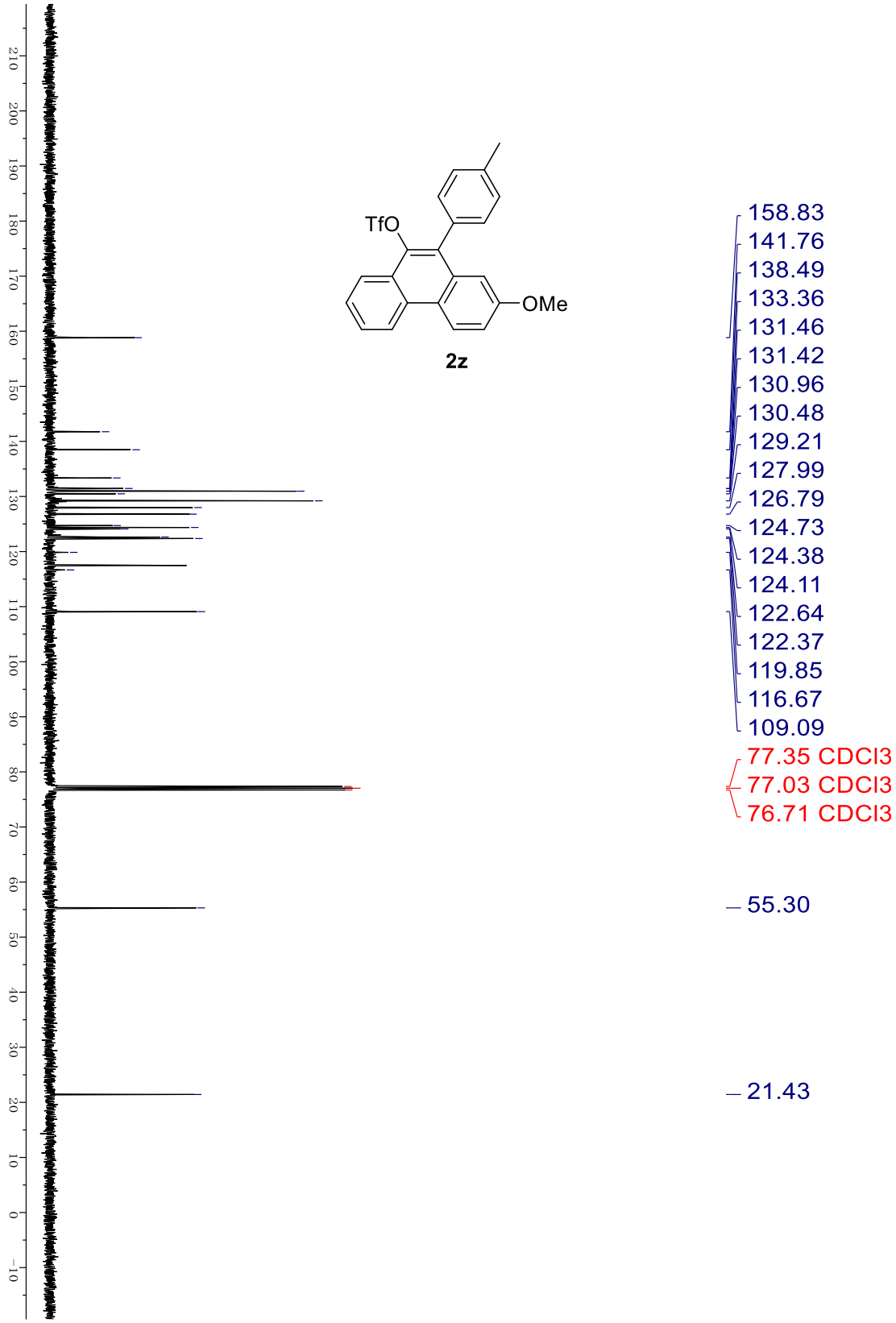
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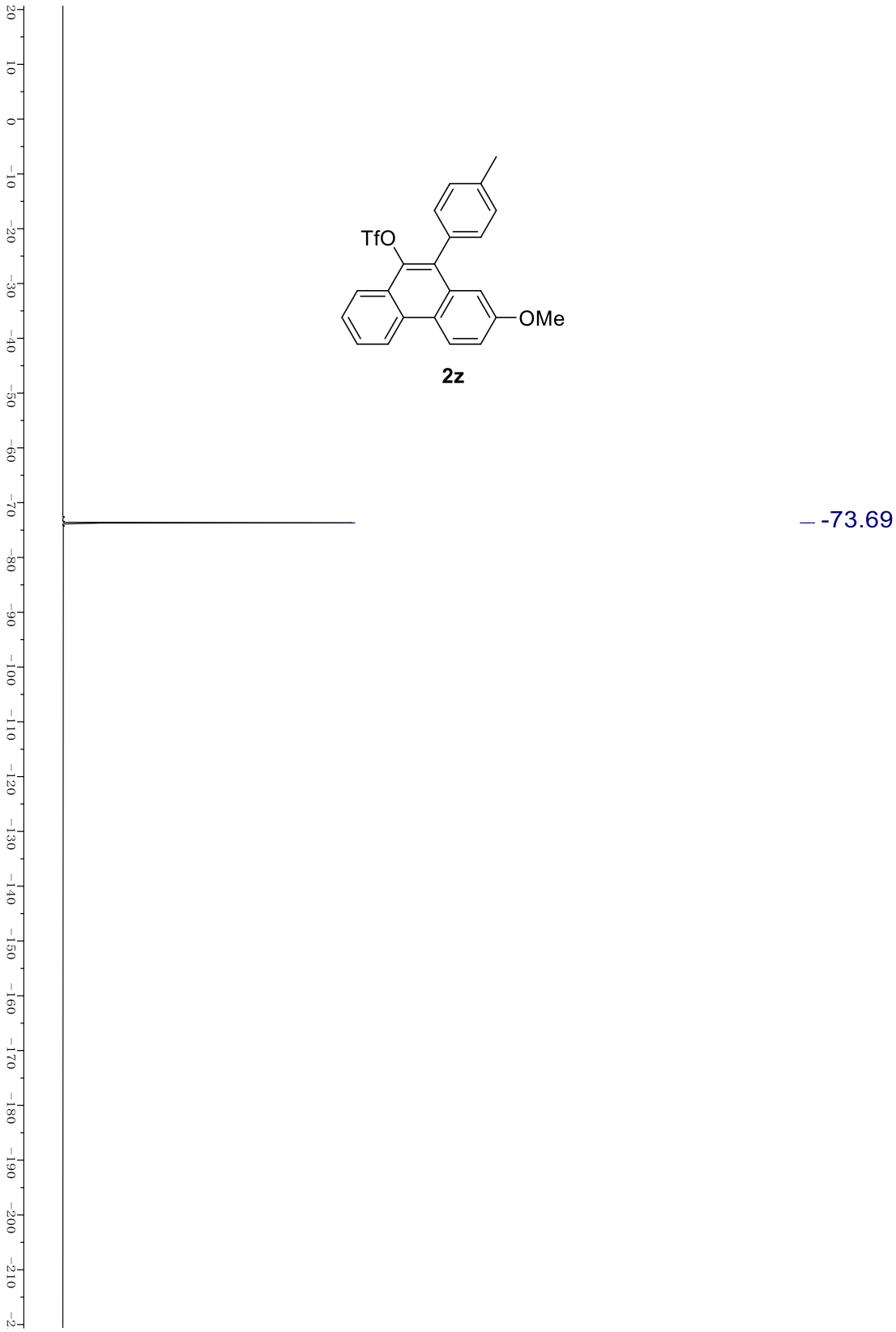
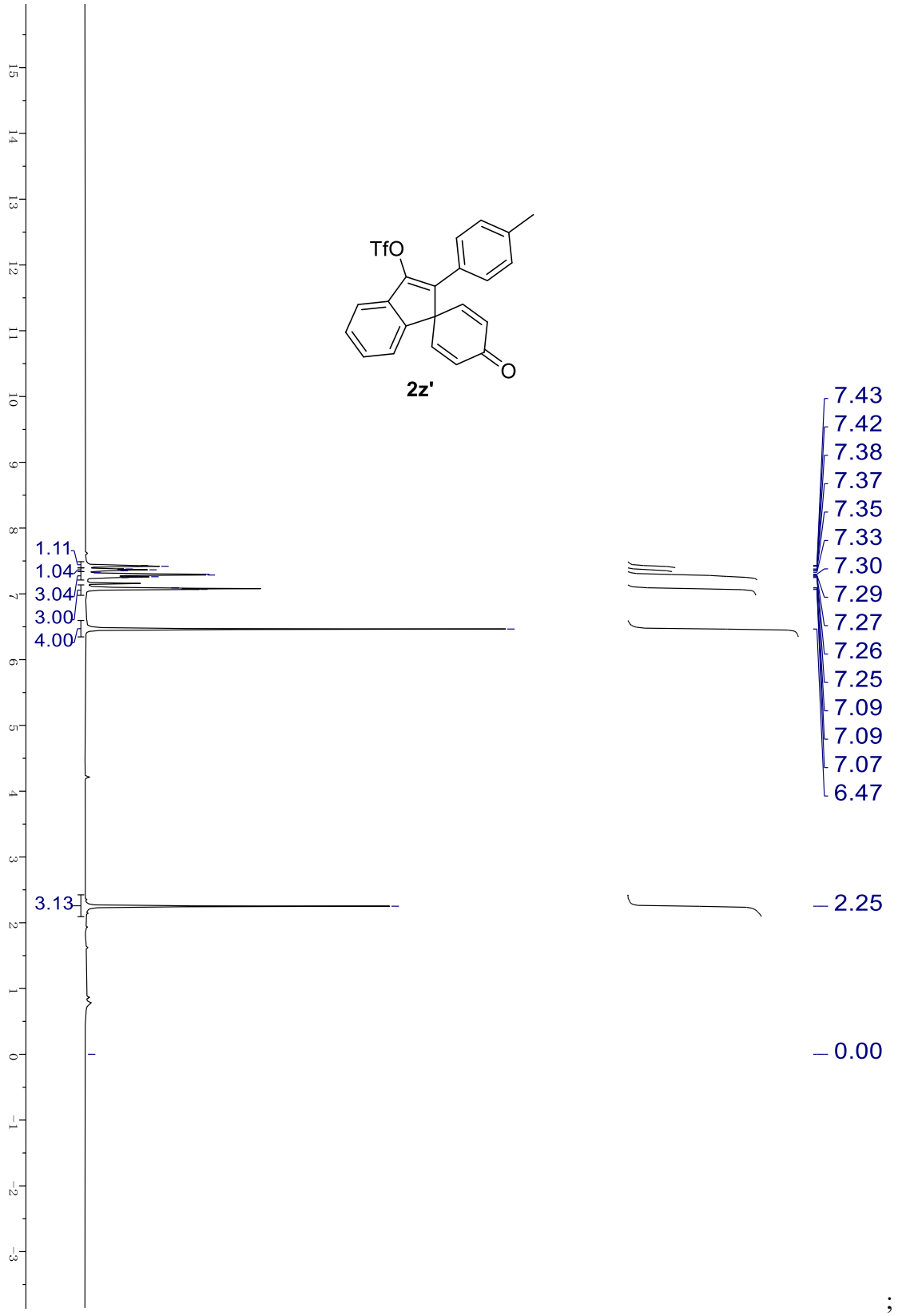
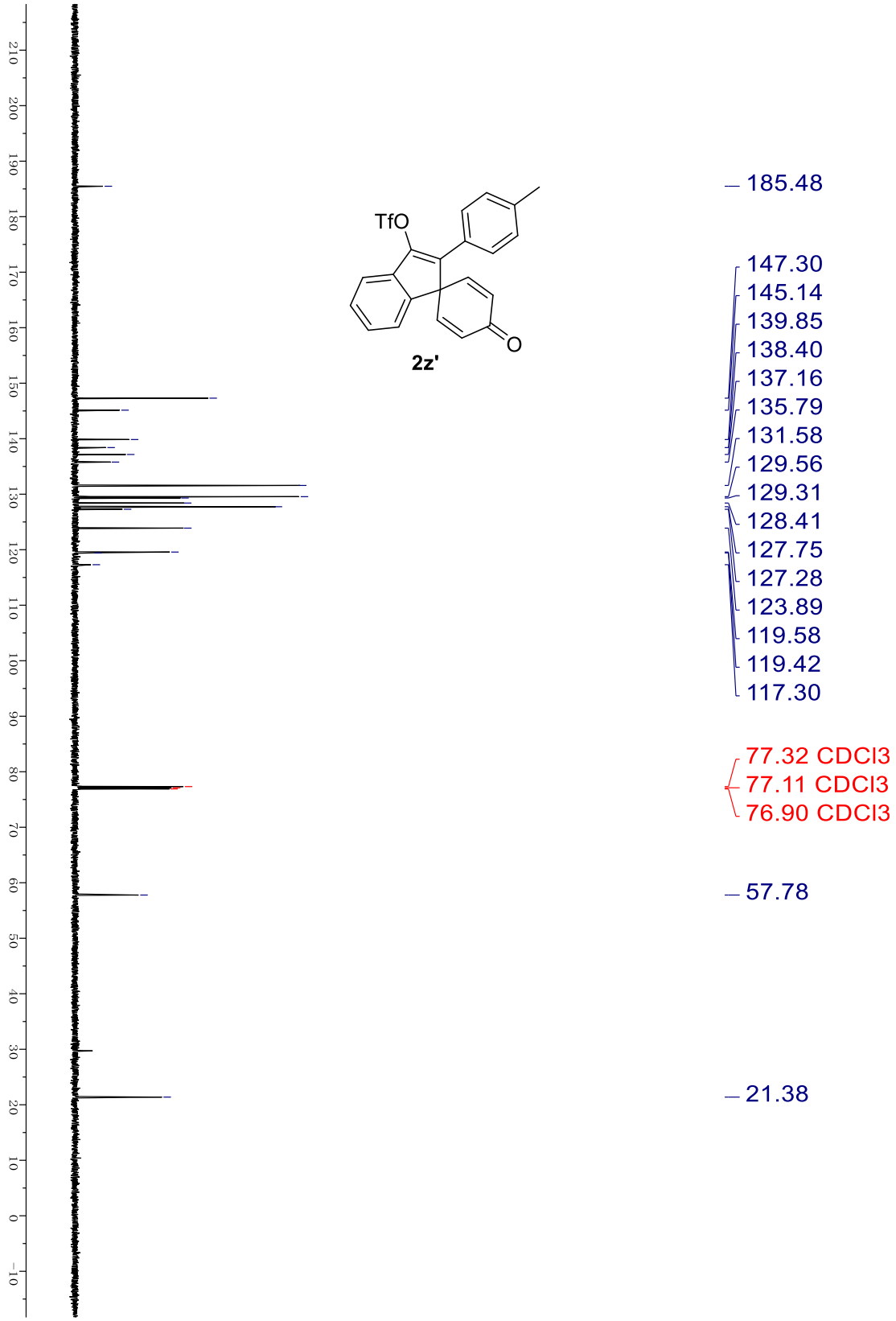
116.67
109.09
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
55.30
21.43

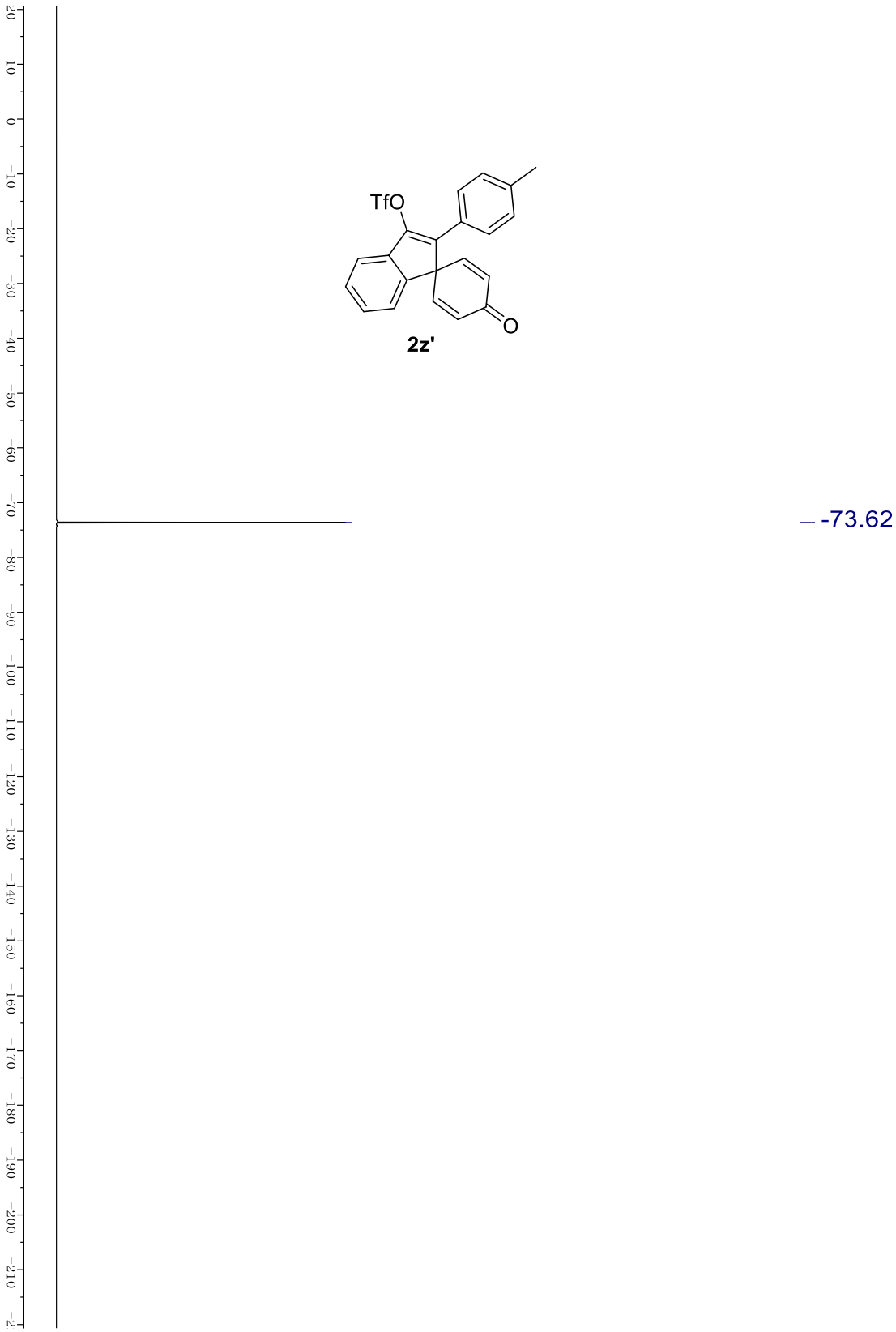

TfO
OMe
-73.69
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2

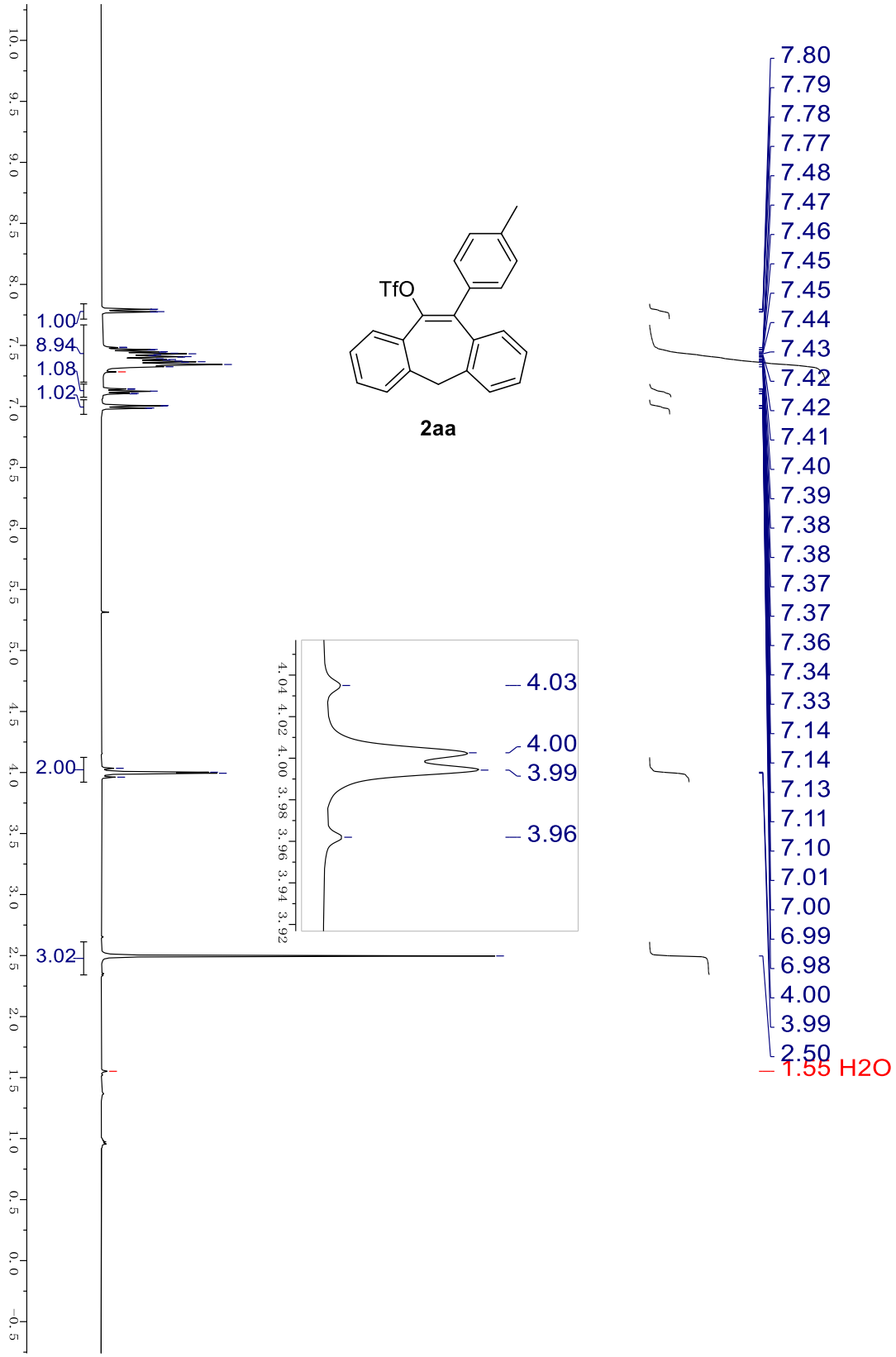
2z

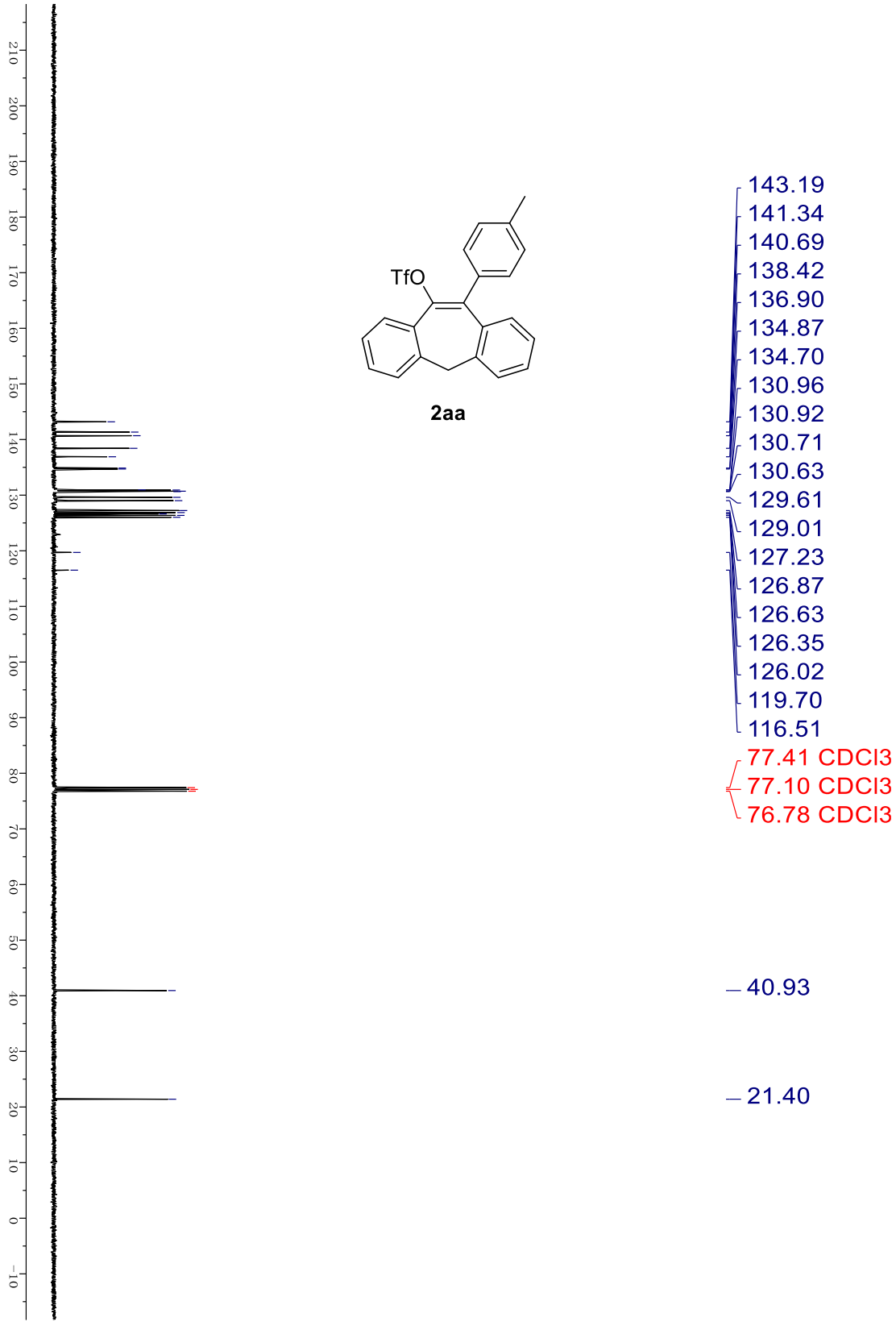

TfO
O
2z'
1.11
1.04
3.04
3.00
4.00
3.13
7.43
7.42
7.38
7.37
7.35
7.33
7.30
7.29
7.27
7.26
7.25
7.09
7.09
7.07
6.47
2.25
0.00

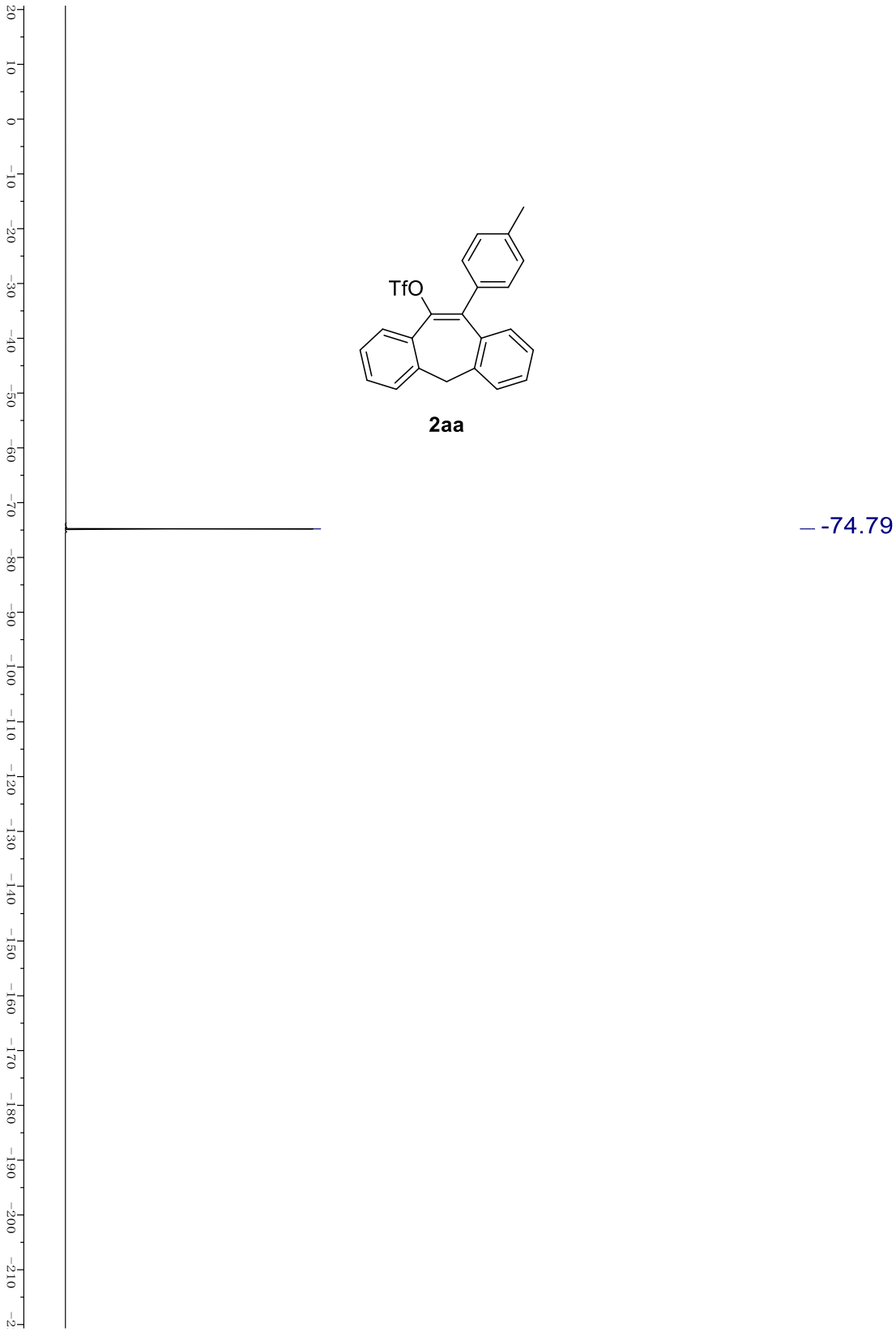
;


TfO
O
2z'
185.48
147.30
145.14
139.85
138.40
137.16
135.79
131.58
129.56
129.31
128.41
127.75
127.28
123.89
119.58
119.42
117.30
77.32 CDCl3
77.11 CDCl3
76.90 CDCl3
57.78
21.38


TfO
O
2z'
-73.62
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2

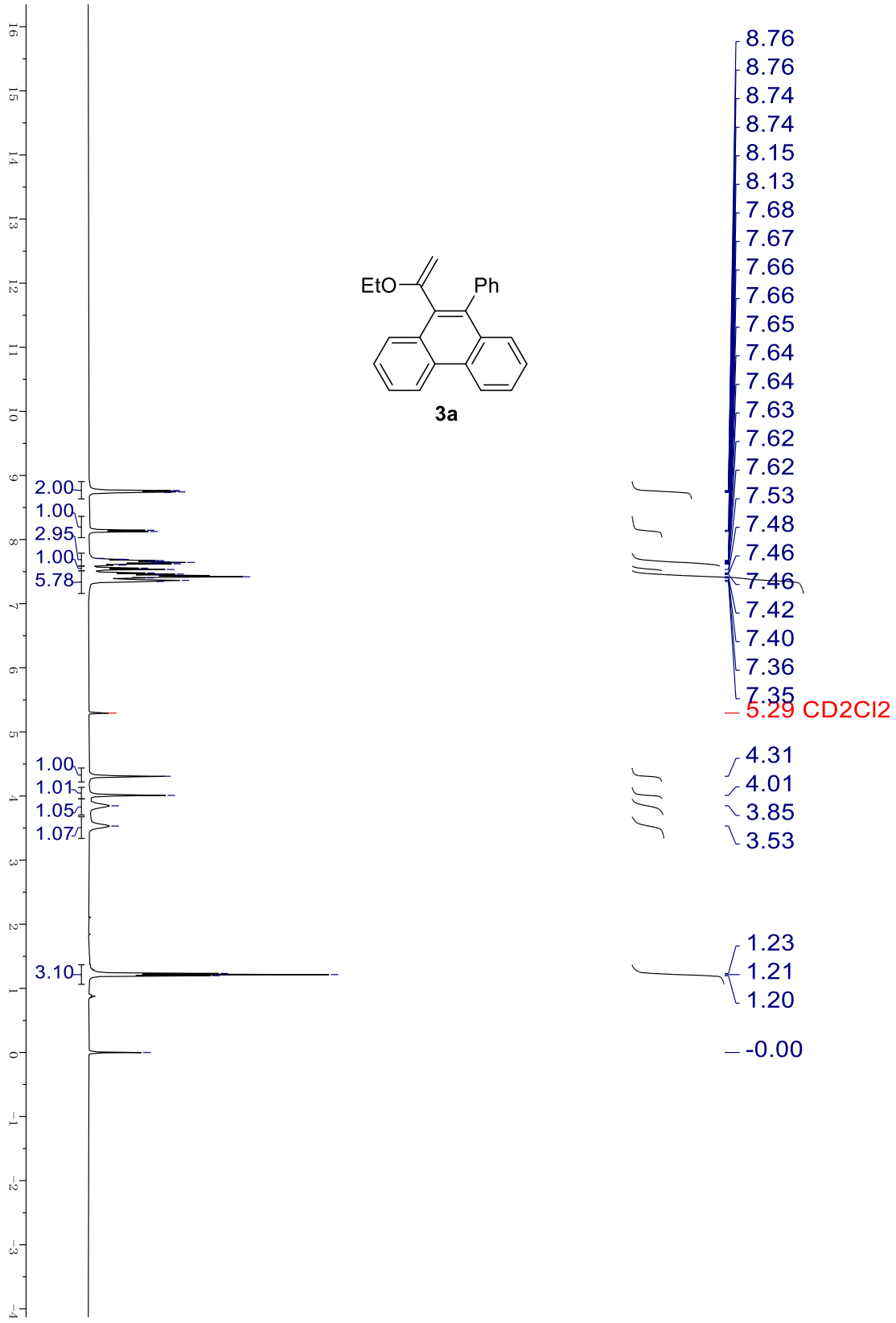

TfO
2aa
1.00
8.94
1.08
1.02
2.00
3.02
4.03
4.00
3.99
3.96
7.80
7.79
7.78
7.77
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.34
7.33
7.14
7.14
7.13
7.11
7.10
7.01
7.00
6.99
6.98
4.00
3.99
2.50
1.55 H2O

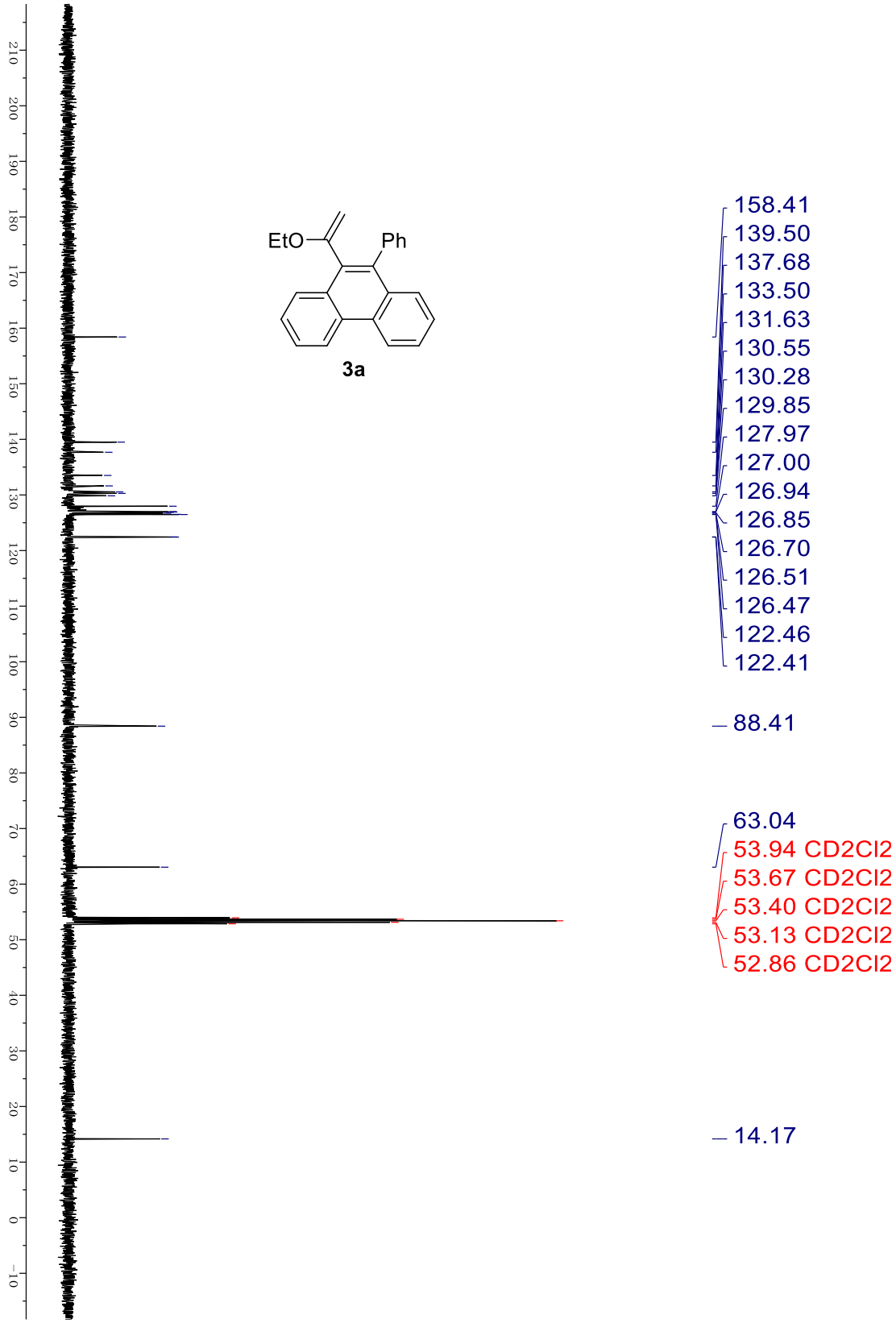

TfO
2aa
143.19
141.34
140.69
138.42
136.90
134.87
134.70
130.96
130.92
130.71
130.63
129.61
129.01
127.23
126.87
126.63
126.35
126.02
119.70
116.51
77.41 CDCl3
77.10 CDCl3
76.78 CDCl3
40.93
21.40

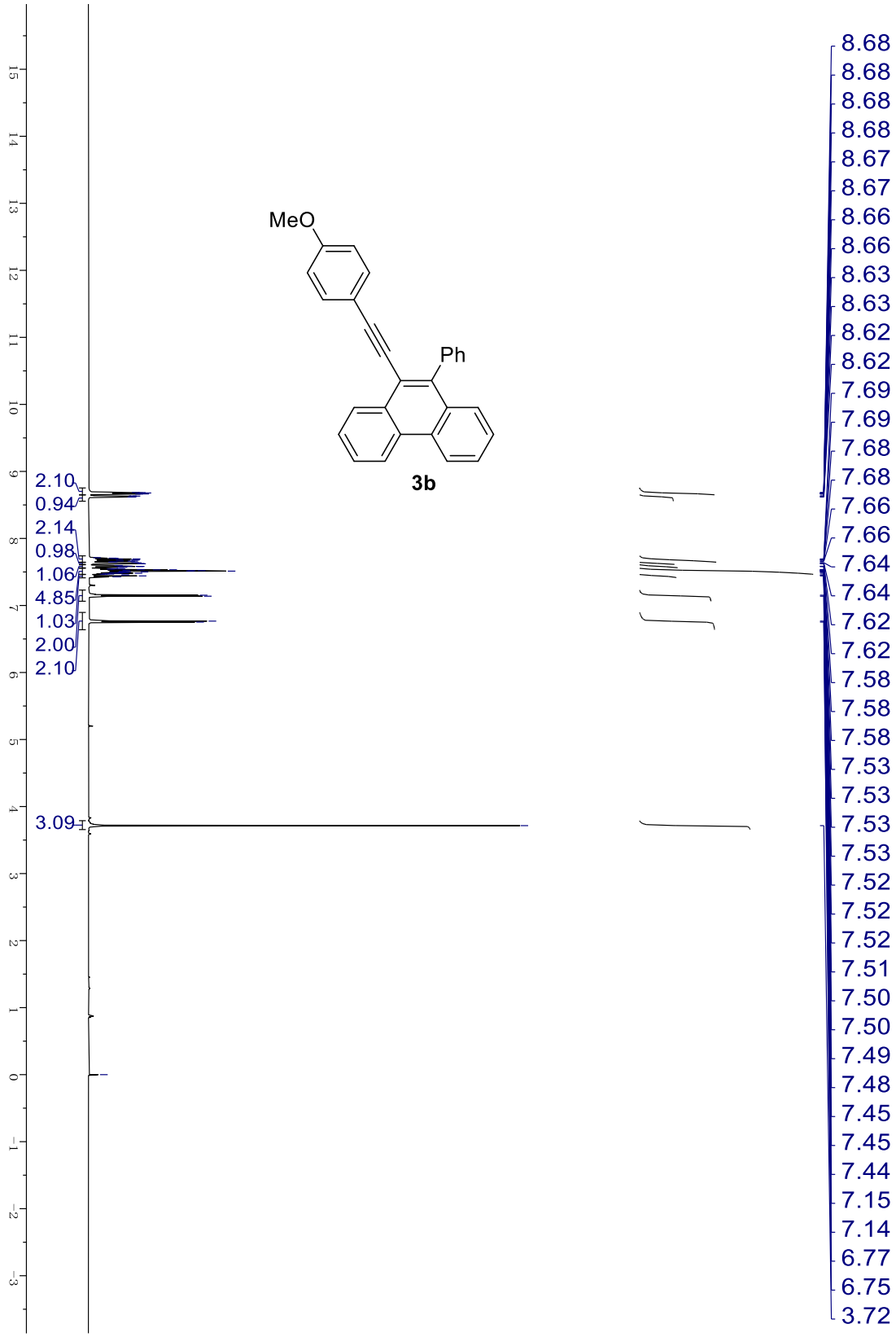


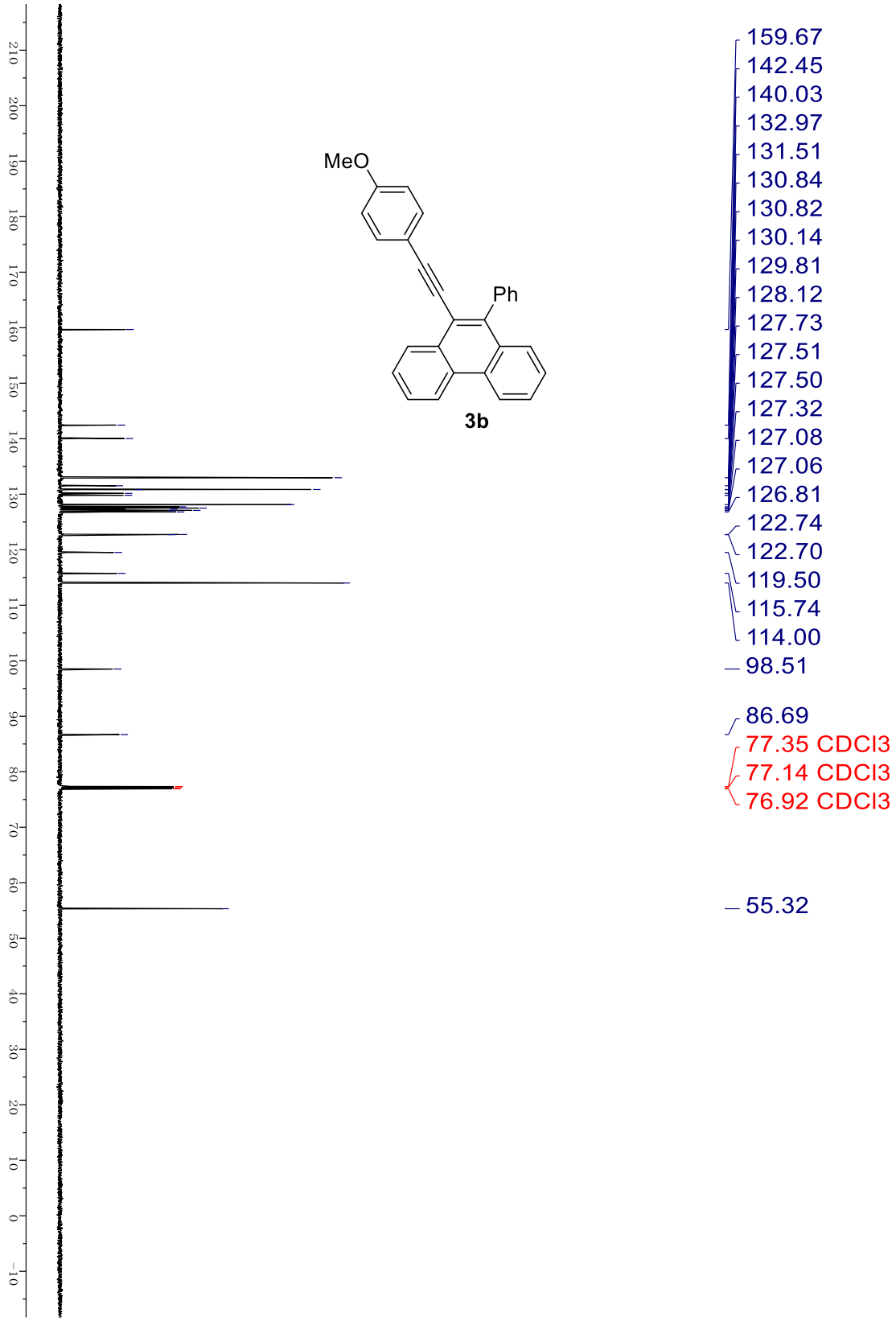
2aa

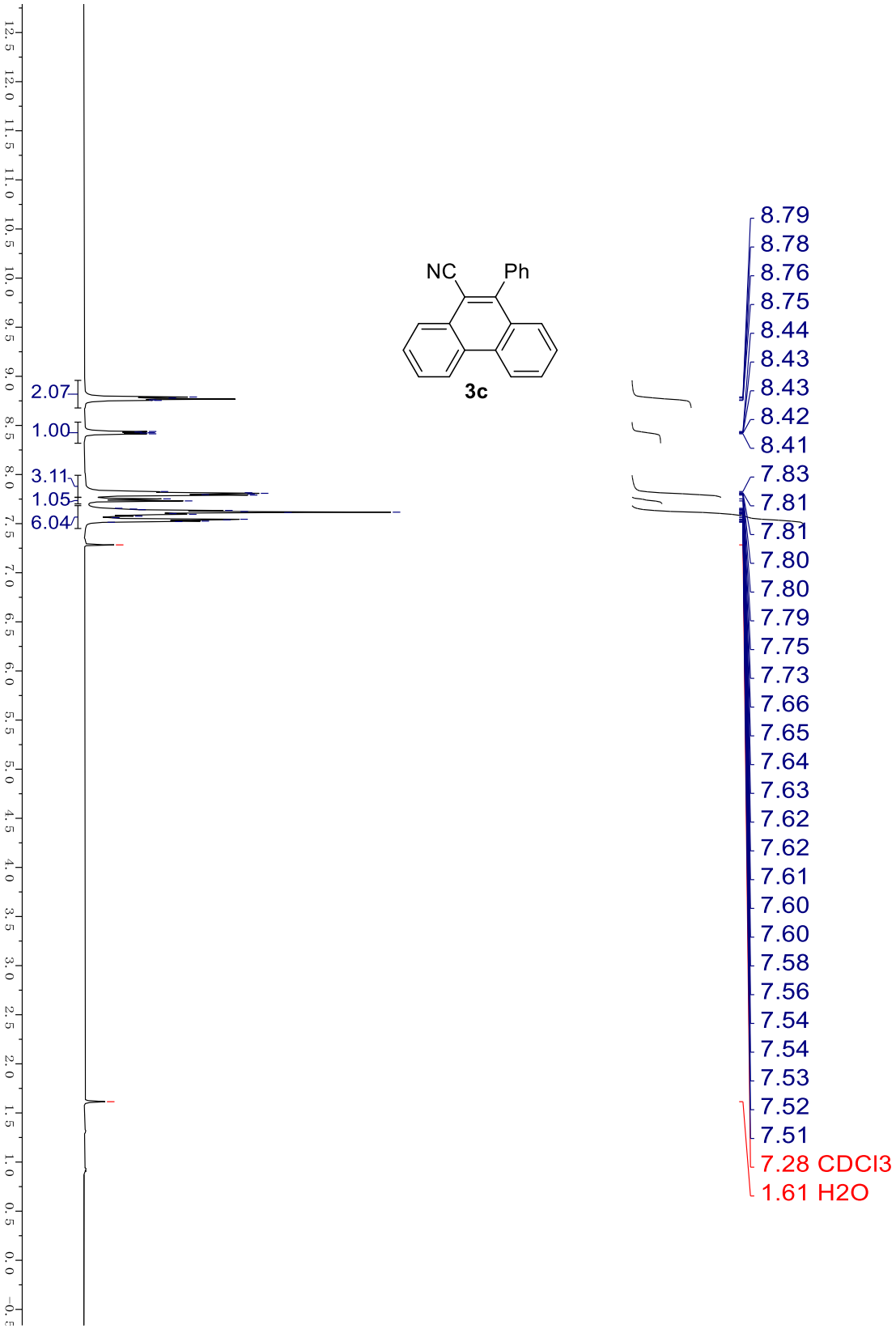
7.3 NMR spectra of compounds 3a–3d

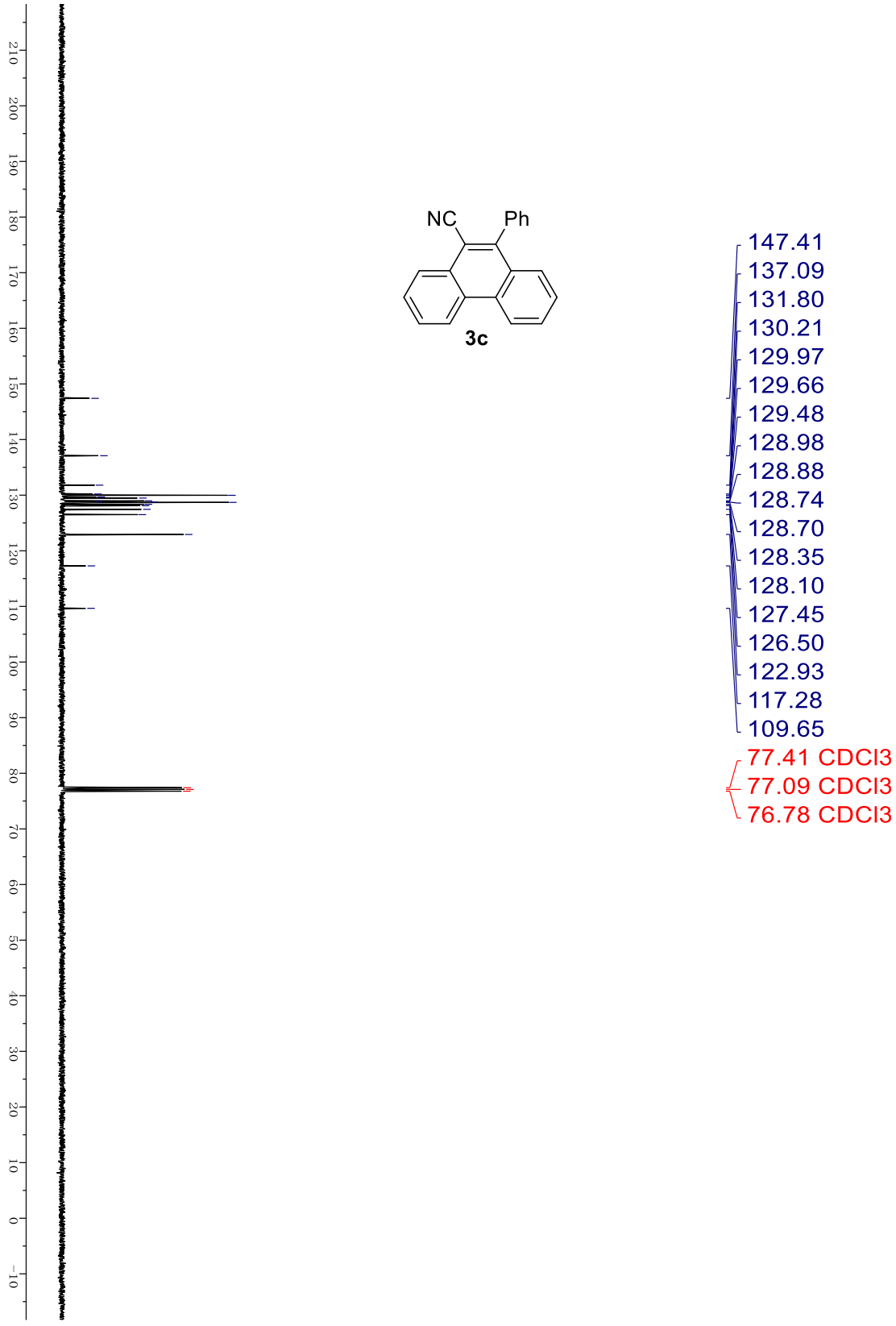



EtO
Ph
3a
158.41
139.50
137.68
133.50
131.63
130.55
130.28
129.85
127.97
127.00
126.94
126.85
126.70
126.51
126.47
122.46
122.41
88.41
63.04
53.94 CD2Cl2
53.67 CD2Cl2
53.40 CD2Cl2
53.13 CD2Cl2
52.86 CD2Cl2
14.17


MeO
Ph
3b
2.10
0.94
2.14
0.98
1.06
4.85
1.03
2.00
2.10
3.09
8.68
8.68
8.68
8.68
8.67
8.67
8.66
8.66
8.63
8.63
8.62
8.62
7.69
7.69
7.68
7.68
7.66
7.66
7.64
7.64
7.62
7.62
7.58
7.58
7.58
7.53
7.53
7.53
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.45
7.45
7.44
7.15
7.14
6.77
6.75
3.72


MeO
Ph
3b
159.67
142.45
140.03
132.97
131.51
130.84
130.82
130.14
129.81
128.12
127.73
127.51
127.50
127.32
127.08
127.06
126.81
122.74
122.70
119.50
115.74
114.00
98.51
86.69
77.35 CDCl3
77.14 CDCl3
76.92 CDCl3
55.32


NC
Ph
3c
2.07
1.00
3.11
1.05
6.04
8.79
8.78
8.76
8.75
8.44
8.43
8.43
8.42
8.41
7.83
7.81
7.81
7.80
7.80
7.79
7.75
7.73
7.66
7.65
7.64
7.63
7.62
7.62
7.61
7.60
7.60
7.58
7.56
7.54
7.54
7.53
7.52
7.51
7.28 CDCl3
1.61 H2O


NC
Ph
3c
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137.09
131.80
130.21
129.97
129.66
129.48
128.98
128.88
128.74
128.70
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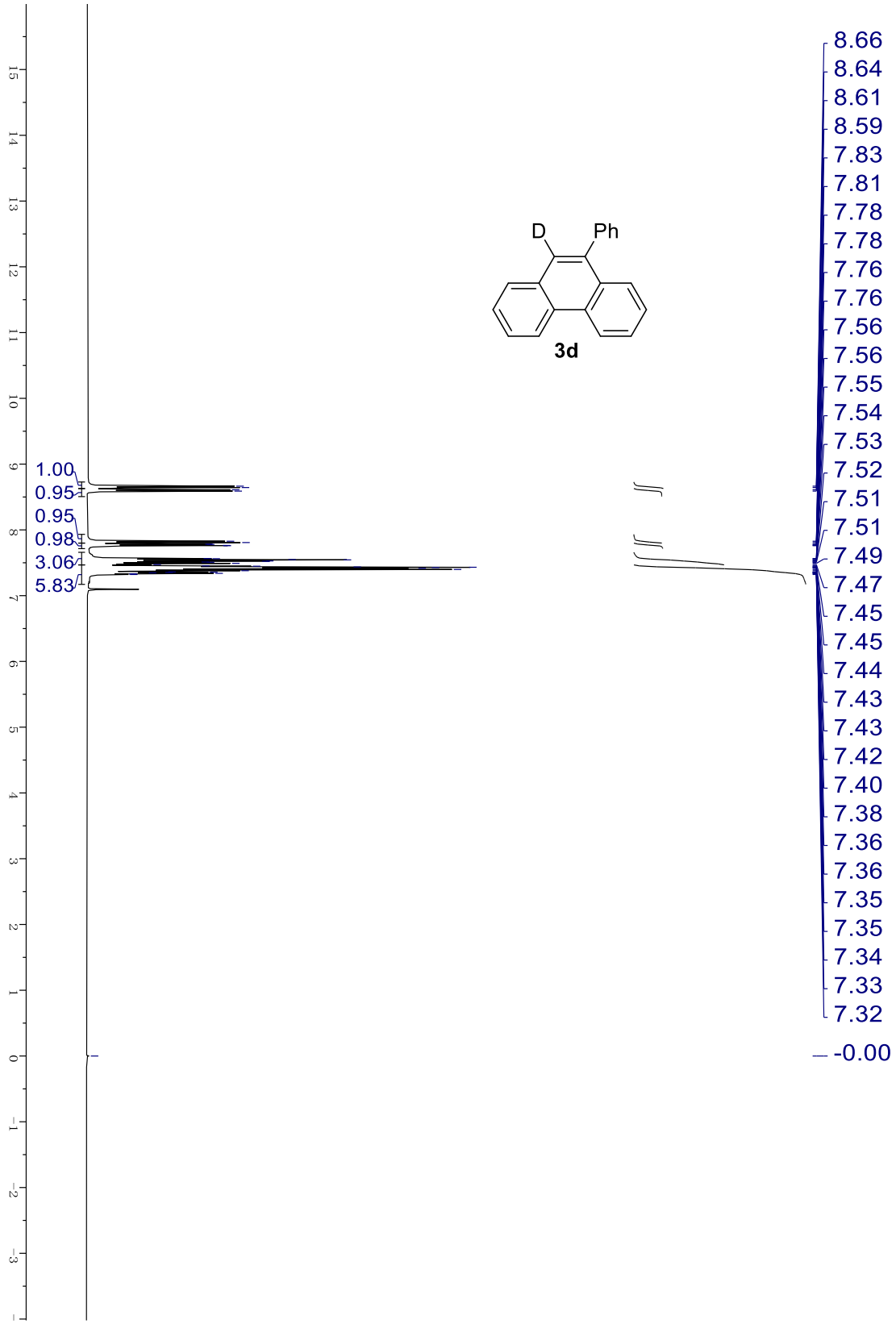
109.65
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3


D
Ph
3d
1.00
0.95
0.95
0.98
3.06
5.83
8.66
8.64
8.61
8.59
7.83
7.81
7.78
7.78
7.76
7.76
7.56
7.56
7.55
7.54
7.53
7.52
7.51
7.51
7.49
7.47
7.45
7.45
7.44
7.43
7.43
7.42
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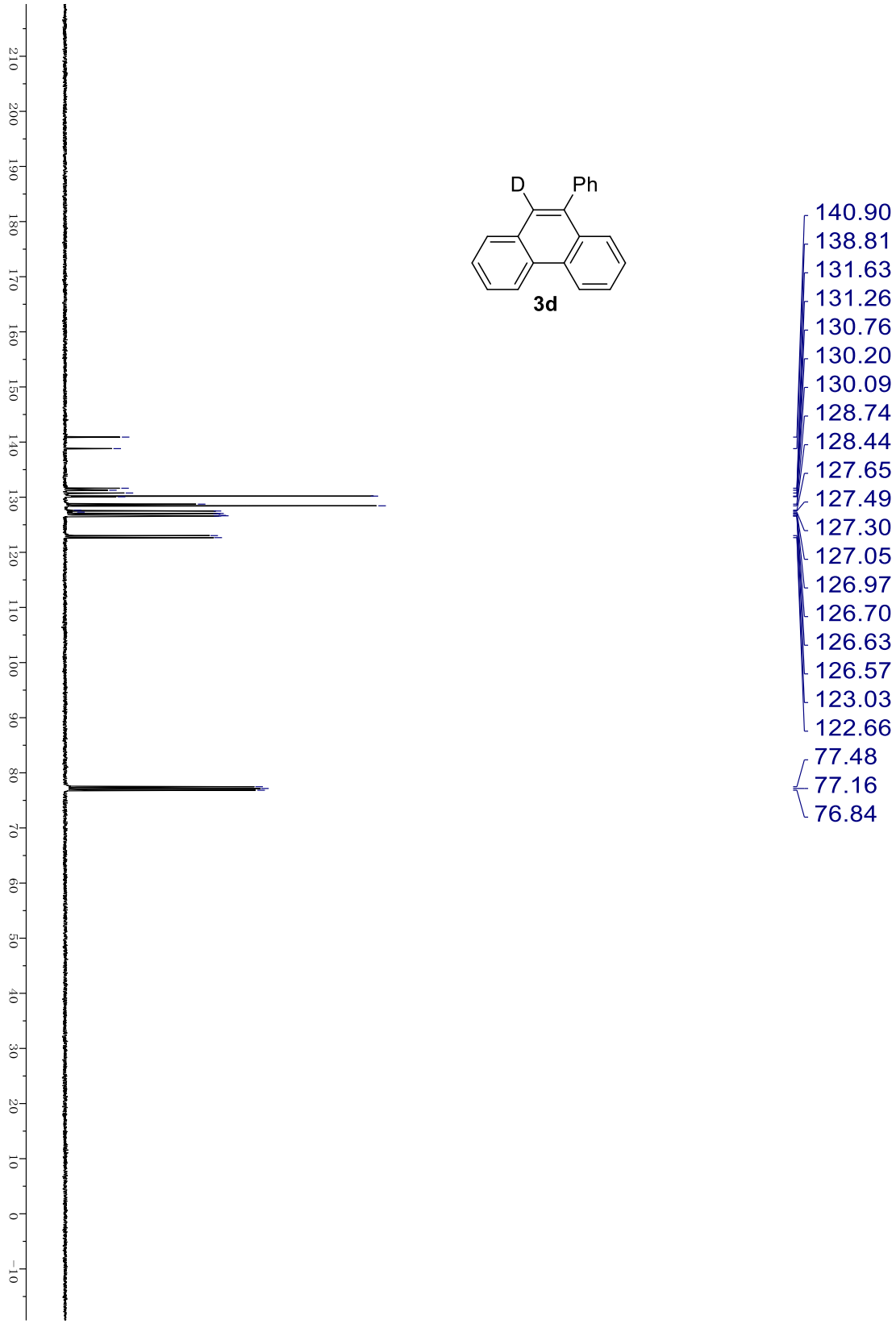
7.35
7.35
7.34
7.33
7.32
-0.00


D
Ph
3d
140.90
138.81
131.63
131.26
130.76
130.20
130.09
128.74
128.44
127.65
127.49
127.30
127.05
126.97
126.70
126.63
126.57
123.03
122.66
77.48
77.16
76.84