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Please note, this ESI document has been revised since its initial publication and now includes experimental information

Ligand-free Pd/Ag-mediated dehydrogenative alkynylation of imidazole derivatives

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Supporting Information

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Experimental

General information

Melting points were recorded on a hot-stage microscope (Reichert Thermovar). Precoated silica gel PET foils (Sigma-Aldrich) were used for TLC analyses. GLC-FID analyses were performed on a Dani GC 1000 chromatograph equipped with a PTV injector, using an Agilent J&W DB-1 column (15m x 0.25mm x 0.25µm) and recorded with a Dani DDS 1000 data station. GLC-MS analyses were recorded with an Agilent 6890N gas chromatograph interfaced with an Agilent MS5973 mass detector, using an Agilent J&W DB-5ms (30m x 0.25mm x 0.25µm) column. UPLC-MS analyses were performed on an Acquity UPLC Water instrument (Phase A 95/5 H2O / ACN + 0.1% Formic Acid, Phase B 5/95 H2O / ACN + 0.1% Formic Acid; Acquity UPLC 2.1x100 mm column, BEH C18, 1.7 µm; Flow 0.6mL / min) coupled with an Acquity QDa Water mass spectrometer (Probe temperature: 600 °C; ESI capillary voltage 1.5V; Cone voltage 15V; Mass range 60-1000). Purifications by flash chromatography were performed using Merck 60 silica gel. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 and 100 MHz respectively with a Bruker 400 spectrometer using TMS as an internal standard. The following notation was used in order to report NMR spectra: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet. 1-Methyl-1*H*-imidazole (**5**), phenylacetylene (**2a**), 4-ethynylanisole (**2e**), were purified by distillation at reduced pressure over CaH_2. All the commercially available reagents and solvents were used as received.

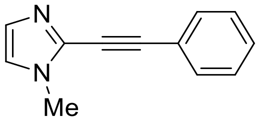
Procedure for the Screening of the Reaction Conditions for the Pd-Catalyzed C-2 dehydrogenative alkynylation of 1-Methyl-1*H*-benzimidazole (1) with phenylacetylene (2a).

To a mixture of 1-methyl-1*H*-benzimidazole (**1**) (132 mg, 1.0 mmol), palladium catalyst (0.025-0.05 mmol), Ag(I) salt (1.5-2.0 mmol), RCOOH (1.0 mmol) in the selected solvent (2 mL) was added dropwise over 45 min a solution of phenylacetylene (**2a**) (0.33 mL, 0.31 g, 3.0 mmol) in the selected solvent (2.0 mL) at the temperature reported in Table 1. The resulting reaction mixture was stirred under air (only for the reaction of entry 1, Table 1, the coupling was performed under argon) for the reaction time reported in Table 1. After cooling to room temperature, the crude reaction mixture was diluted with AcOEt, biphenyl was added as internal standard, and the resulting mixture was analyzed by GLC, GC–MS, and UPLC-MS. Table 1 summarizes the results of this screening.

General Procedure for the dehydrogenative coupling of azoles 1, 5, 7, 9, 11, 12, 15, 16 with terminal alkynes (2a-i).

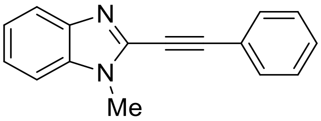
To a solution of azole (1.0 mmol), $Pd(OAc)_2$ (5.6 mg, 2.5 mol %), Ag_2CO_3 (0.55 g, 2.0 equiv), AcOH (58 µL, 60 mg, 1.0 equiv) and NMP (2.0 mL) was added dropwise a solution of terminal alkyne **2a-g** (3 equiv) in NMP (2.0 mL) over 45 min at 100 °C under air. When (triisopropylsilyl)acetylene (**2h**) and 1-octyne (**2i**) were used, they were added in one portion ad the beginning of the reaction. After 3.5h under stirring the reaction mixture was cooled at room temperature, diluted with AcOEt, filtered through a plug of Celite, and eluted with additional CH_2Cl_2 and EtOAc. The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography on silica gel. This procedure was used to prepare compounds **6a-g** and **3a-e** (Scheme 2), **8, 10a** and **10b** (Scheme 4), **13**, **14**, **17** and **18** (Scheme 5).

*1-Methyl-2-(phenylethynyl)-1H-imidazole (**6a**)*



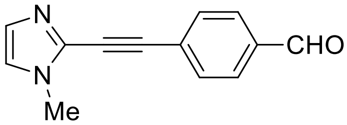
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with phenylacetylene (**2a**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of DCM and EtOAc (80:20) as eluent to give **6a** as light brown solid (135 mg, 74%), m.p. 52 - 54 °C (litt. 52 - 56 °C).[1] ESI-MS m/z 183 $[M+H]^+$. EI-MS, m/z (%): 182 (100) 181 (22) 114 (18) 183 (14) 113 (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.52 (m, 2H), 7.38 – 7.32 (m, 3H), 7.08 (s, 1H), 6.93 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.53, 131.66, 129.70, 129.02, 128.44, 121.86, 121.55, 92.64, 78.62, 33.51. The spectral properties of this compound are in agreement with those previously reported.[1]

*1-Methyl-2-(phenylethynyl)-1H-benzimidazole (**3a**)*



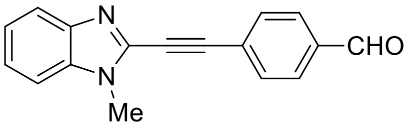
The crude reaction product obtained by the dehydrogenative coupling of 1-methyl-1*H*-benzimidazole (**1**) with phenylacetylene (**2a**) (entries 17 and 18, Table 1, and Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (85:15) as eluent to give **3a** as a yellow solid (160 mg, 69%): m.p. 131 - 133 °C. ESI-MS m/z 233 $[M+H]^+$. EI-MS, m/z (%): 232 (100) 231(32) 233 (18) 207(11) 77 (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 1H), 7.64 – 7.56 (m, 2H), 7.42 – 7.10 (m, 7H), 3.84 (s, 3H). The spectral properties of this compound are in agreement with those previously reported.[1]

*4-((1-Methyl-1H-imidazol-2-yl)ethynyl)benzaldehyde (**6b**)*



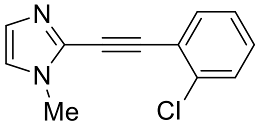
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 4-ethynylbenzaldehyde (**2b**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (x) as eluent to give **6b** as light brown solid (141 mg, 67%), m.p. 138 – 140 °C. ESI-MS m/z 211 $[M+H]^+$. EI-MS, m/z (%): 210 (100) 209 (33) 181 (20) 211 (15) 127 (7) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.89 – 7.84 (m, 2H), 7.72 – 7.67 (m, 2H), 7.12 (d, J = 1.2 Hz, 1H), 6.99 (d, J = 1.2 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.22, 135.94, 132.10, 131.82, 130.27, 129.61, 128.04, 122.09, 91.78, 82.35, 33.62. Elem. Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.31; H, 4.80; N, 13.31.

*4-((1-Methyl-1H-benzo[d]imidazol-2-yl)ethynyl)benzaldehyde imidazole (**3b**)*



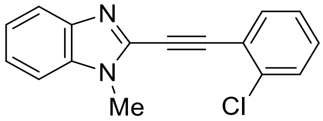
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-benzimidazole (**1**) with 4-ethynylbenzaldehyde (**2b**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (70:30) as eluent to give x as a yellow solid (188 mg, 72%), m.p. 200 – 202 °C. ESI-MS m/z 261 $[M+H]^+$. EI-MS, m/z (%):260 (100) 231 (19) 261 (19) 259 (13) 77 (8). ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.94 – 7.88 (m, 2H), 7.82 – 7.74 (m, 3H), 7.40 – 7.29 (m, 3H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.17, 143.11, 136.87, 136.42, 134.94, 132.56, 129.67, 127.26, 124.35, 123.22, 120.43, 109.59, 93.64, 82.24, 30.83. Elem. Anal. Calcd for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.46; H, 4.66; N, 10.74.

*2-((2-Chlorophenyl)ethynyl)-1-methyl-1H-imidazole (**6c**)*



The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 1-chloro-2-ethynylbenzene (**2c**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (60:40) as eluent to give x as a light brown oil (148 mg, 68%). ESI-MS m/z 217 $[M+H]^+$. EI-MS, m/z (%): 216 (100) 218 (33) 217 (15) 148 (14) 113 (9). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.3, 2.1 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.23 – 7.11 (m, 2H), 7.00 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 1.2 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.69, 133.25, 132.21, 129.99, 129.93, 129.32, 126.68, 122.04, 121.88, 89.45, 83.76, 33.64. Elem. Anal. Calcd for $C_{12}H_9ClN_2$: C, 66.52; H, 4.19; N, 12.93. Found: C, 66.50; H, 4.18; N, 12.91.

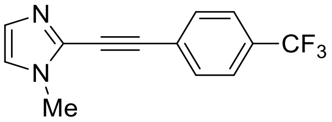
*2-((2-Chlorophenyl)ethynyl)-1-methyl-1H-benzimidazole (**3c**)*



The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-benzimidazole (**1**) with 1-chloro-2-ethynylbenzene (**2c**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (90:10) as eluent to give **3c** as a green-brown solid (192 mg, 72%), m.p. 118 - 120 °C. ESI-MS m/z 267 $[M+H]^+$. EI-MS, m/z (%): 266 (100) 268 (33) 267 (21) 231 (12) 77 (9). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 1H), 7.62 (dd, J =

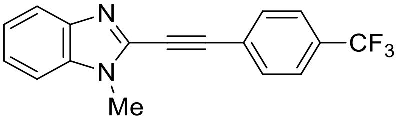
7.5, 1.9 Hz, 1H), 7.41 (dd, J = 7.8, 1.6 Hz, 1H), 7.31 – 7.20 (m, 5H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.09, 137.23, 136.16, 134.90, 133.70, 130.54, 129.40, 126.74, 124.01, 122.93, 121.42, 120.21, 109.50, 91.43, 83.79, 30.69. Elem. Anal. Calcd for $C_{16}H_{11}ClN_2$: C, 72.05; H, 4.16; N, 10.50. Found: C, 72.09; H, 4.20; N, 10.48.

*1-Methyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1H-imidazole (**6d**)*



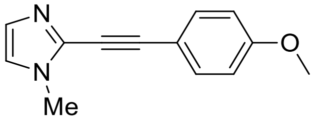
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 1-ethynyl-4-(trifluoromethyl)benzene (**2d**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (40:60) as eluent to give **6d** as a pale brown solid (163 mg, 65%), m.p. 98 - 100 °C. ESI-MS m/z 251 [M+H]$^+$. EI-MS, m/z (%): 250 (100) 182 (19) 251 (15) 181 (10) 249 (10^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 – 7.59 (m, 4H), 7.12 (d, J = 1.2 Hz, 1H), 6.97 (d, J = 1.2 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 131.96, 131.94, 130.94 (q, J = 33.0 Hz), 130.26, 125.84, 125.47 (q, J = 3.8 Hz), 123.85 (q, J = 272.2 Hz), 121.88, 91.25, 80.96, 33.59. Elem. Anal. Calcd for $C_{13}H_9F_3N_2$: C, 62.40; H, 3.63; N, 11.20. Found: C, 62.38; H, 3.63; N, 11.19.

*1-Methyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1H-benzimidazole (**3d**)*



The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-benzimidazole (**1**) with 1-ethynyl-4-(trifluoromethyl)benzene (**2d**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (90:10) as eluent to give **3d** as a green-brown solid (207 mg, 69%), m.p. 180 - 183 °C. ESI-MS m/z 301 [M+H]$^+$. EI-MS, m/z (%): 300 (100) 301 (19) 299 (16) 77 (6) 150 (5). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 – 7.77 (m, 1H), 7.75 – 7.72 (m, 2H), 7.69 – 7.64 (m, 2H), 7.38 – 7.31 (m, 3H), 3.95 (s, 3H).^{13}C NMR (100 MHz, CDCl$_3$) δ 143.08, 136.94, 134.91, 132.31, 131.33 (q, J = 32.8 Hz), 125.57 (q, J = 3.8 Hz), 125.06, 124.28, 123.71 (d, J = 271.7 Hz), 123.17, 120.41, 109.57, 93.16, 80.94, 30.82. Elem. Anal. Calcd for $C_{17}H_{11}F_3N_2$: C, 68.00; H, 3.69; N, 9.33. Found: C, 67.97; H, 3.68; N, 9.32.

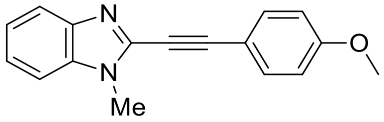
*2-((4-Methoxyphenyl)ethynyl)-1-methyl-1H-imidazole (**6e**)*



The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 1-ethynyl-4-methoxybenzene (**2e**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (35:65) as eluent to give **6e** as a light beige solid (148 mg, 70%), m.p. 88 - 90 °C (lit.62 64 °C).[5] ESI-MS m/z 213

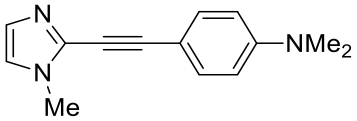
$[M+H]^+$. EI-MS, m/z (%): 212 (100) 197 (61) 213 (15) 169 (14) 198 (8). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.00 (d, J = 1.2 Hz, 1H), 6.85 (d, J = 1.2 Hz, 1H), 6.83 – 6.78 (m, 2H), 3.74 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.22, 133.25, 132.79, 129.51, 121.27, 114.13, 113.86, 92.70, 77.44, 55.31, 33.44. Elem. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.59; H, 5.71; N, 13.18. The spectral proprieties of this compound are in agreement with those previously reported.[5]

*2-((4-Methoxyphenyl)ethynyl)-1-methyl-1H-benzimidazole (**3e**)*



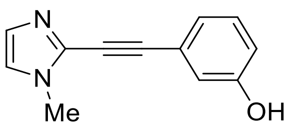
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-benzimidazole (**1**) with 1-ethynyl-4-methoxybenzene (**2e**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (80:20) as eluent to give **3e** as a light orange solid (189 mg, 72%), m.p. 154 - 156 °C. ESI-MS m/z 263 $[M+H]^+$. EI-MS, m/z (%): 262 (100) 247 (41) 263 (19) 218 (14) 219 (13). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 1H), 7.57 – 7.50 (m, 2H), 7.31 – 7.21 (m, 3H), 6.90 – 6.81 (m, 2H), 3.82 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 160.68, 143.02, 138.01, 134.81, 133.62, 123.59, 122.70, 119.90, 114.23, 113.10, 109.38, 95.29, 77.79, 55.30, 30.56. Elem. Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.82; H, 5.38; N, 10.66.

*N,N-Dimethyl-4-((1-methyl-1H-imidazol-2-yl)ethynyl)aniline (**6f**)*



The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 4-ethynyl-N,N-dimethylaniline (**2f**) (Scheme 2) was purified by flash chromatography on silica gel with EtOAc as eluent to give **6f** as a brown solid (142 mg, 63%), m.p. 70 - 73 °C. ESI-MS m/z 226 $[M+H]^+$. EI-MS, m/z (%): 225 (100) 224 (31) 209 (17) 226 (16) 210 (12). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.03 (d, J = 1.2 Hz, 1H), 6.88 (d, J = 1.2 Hz, 1H), 6.67 – 6.58 (m, 2H), 3.72 (s, 3H), 2.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.43, 133.18, 132.80, 129.05, 120.88, 111.57, 108.03, 94.11, 76.50, 39.96, 33.33. Elem. Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.59; H, 6.65; N, 18.60.

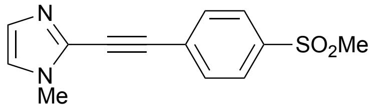
*3-((1-Methyl-1H-imidazol-2-yl)ethynyl)phenol (**6g**)*



The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 3-ethynylphenol (**2g**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of toluene and THF

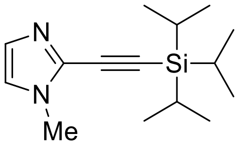
(70:30) as eluent to give **6** as an orange solid (139 mg, 70%), m.p. 174 - 145 °C. ESI-MS m/z 199 [M+H]$^+$. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (s, 1H), 7.32 (d, J = 1.2 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.06 – 7.01 (m, 1H), 7.00 (d, J = 1.2 Hz, 1H), 6.97 – 6.94 (m, 1H), 6.87 (ddd, J = 8.2, 2.5, 1.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.33, 130.86, 129.94, 128.99, 122.77, 122.16, 121.88, 117.63, 116.82, 91.86, 78.52, 33.08. Elem. Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13. Found: C, 77.72; H, 5.08; N, 14.12.

*1-Methyl-2-((4-(methylsulfonyl)phenyl)ethynyl)-1H-imidazole (**6h**)*



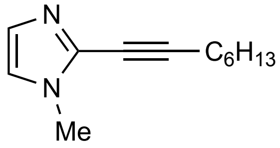
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 1-ethynyl-4-(methylsulfonyl)benzene (**2h**) (Scheme 2) was purified by flash chromatography on silica gel with a mixture of DCM and EtOAc (30:70) as eluent to give **6h** as a light yellow solid (161 mg, 62%), m.p. 135 - 137 °C. ESI-MS m/z 261 [M+H]$^+$. EI-MS, m/z (%): 260 (100), 229 (4),197 (18), 181 (41), 169 (5), 127 (12%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.90 (m,2H), 7.69-7.75 (m,2H), 7.11 (s, 1H), 6.98 (s, 1H), 3.80 (s, 3H, 3.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.31, 132.31, 132.29, 130.34, 127.71, 127.51, 122.15, 90.83, 82.36, 44.42, 33.65. Elem. Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.59; H, 6.65; N, 18.60.

*1-Methyl-2-((triisopropylsilyl)ethynyl)-1H-imidazole (**6i**)*



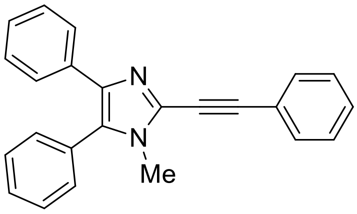
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with ethynyltriisopropylsilane (**2i**) (Scheme 3) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (70:30) as eluent to give **6i** as a yellow oil (79 mg, 30%). ESI-MS m/z 263 [M+H]$^+$. EI-MS, m/z (%): 219 (100) 191 (27) 220 (21) 149 (16) 262 (15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.89 (s, 1H), 3.74 (s, 3H), 1.17 – 1.10 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.73, 129.30, 121.20, 95.89, 95.32, 33.51, 18.62, 11.18. The physical and spectral properties of this compound are in agreement with those previously reported.[6]

*1-Methyl-2-(oct-1-yn-1-yl)-1H-imidazole (**6j**)*



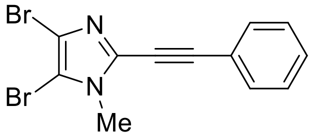
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-1*H*-imidazole (**5**) with 1-octyne (**2j**) (Scheme 3) was purified by flash chromatography on silica gel with a mixture of DCM and EtOAc (70:30) as eluent to give **6j** as a yellow oil (21 mg, 11%). ESI-MS m/z 191 [M+H]$^+$. EI-MS, m/z (%): 189 (18), 147 (16), 133 (29), 119 (48), 105 (65), 91 (100), 79 (50). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.99 (s, 1H), 6.84 (s, 1H), 3.68 (s, 3H), 2.45 (t, J = 7.1 Hz, 2H), 1.69 – 1.53 (m, 2H), 1.51 – 1.40 (m, 2H), 1.37 – 1.20 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 133.14, 128.98, 120.62, 94.50, 70.23, 33.33, 31.33, 28.59, 28.32, 22.54, 19.37, 14.04. Elem. Anal. Calcd for $C_{12}H_{18}N_2$ (190.29): C, 75.74; H, 9.53; N, 14.72; found C, 75.69; H, 9.51; N, 14.75.

*1-Methyl-4,5-diphenyl-2-(phenylethynyl)-1H-imidazole (**8**)*



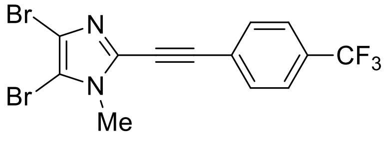
The crude reaction product obtained by the oxidative coupling reaction of 1-methyl-4,5-diphenyl-1*H*-imidazole (**7**) with phenylacetylene (**2a**) (Scheme 4) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (95:5) as eluent to give **8** as light brown solid (234 mg, 70%), m.p. 160 - 161 °C. ESI-MS m/z 335 [M+H]$^+$. EI-MS, m/z (%): 334 (100) 333 (39) 335 (25) 165 (10) 318 (8). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.56 (m, 2H), 7.54 – 7.49 (m, 2H), 7.46 – 7.40 (m, 3H), 7.37 – 7.29 (m, 5H), 7.22 – 7.08 (m, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.70, 134.02, 131.84, 131.69, 130.56, 130.36, 130.21, 129.07, 129.01, 128.87, 128.44, 128.06, 126.89, 126.63, 121.91, 93.35, 79.09, 32.11. Elem. Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 83.16; H, 5.42; N, 8.36.

*4,5-Dibromo-1-methyl-2-(phenylethynyl)-1H-imidazole (**10a**)*



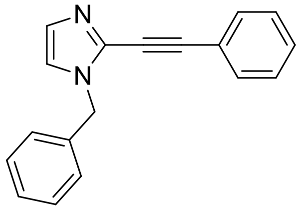
The crude reaction product obtained by the oxidative coupling reaction of 4,5-dibromo-1-methyl-1*H*-imidazole (**9**) with phenylacetylene (**2a**) (Scheme 4) was purified by flash chromatography on silica gel with toluene as eluent to give **10a** as a pale pink-orange solid (231 mg, 68%), m.p. 126 - 128 °C. ESI-MS m/z 341 [M+H]$^+$. EI-MS, m/z (%): 340 (100) 338 (52) 342 (49) 218 (34) 220 (34). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.48 (m, 2H), 7.40 – 7.30 (m, 3H), 3.71 (s, 3H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 132.51, 131.77, 129.56, 128.54, 121.02, 117.10, 105.34, 94.18, 77.44, 33.99. Elem. Anal. Calcd for $C_{12}H_8Br_2N_2$: C, 42.39; H, 2.37; N, 8.24. Found: C, 42.37; H, 2.37; N, 8.23.

*4,5-Dibromo-1-methyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1H-imidazole (**10b**)*



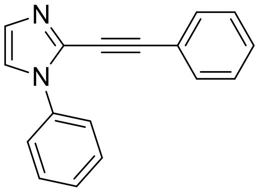
The crude reaction product obtained by the dehydrogenative coupling of 4,5-dibromo-1-methyl-1H-imidazole (**9**) with 1-ethynyl-4-(trifluoromethyl)benzene (**2d**) was purified by flash chromatography on silica gel with a mixture of DCM and petroleum ether (80:20) as eluent to give **10b** as a light brown solid (306 mg, 75%): m.p. 110 – 111 °C. ESI-MS m/z 409 [M+H]+. EI-MS, m/z (%): 408 (100) 406 (51) 410 (49) 286 (26) 288 (25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.62 (m, 4H), 3.73 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 132.02, 131.91, 131.16 (q, J = 32.8 Hz), 125.55 (q, J = 3.8 Hz), 124.90, 123.72 (q, J = 272.4 Hz), 117.55, 106.15, 92.61, 79.59, 34.16. Elem. Anal. Calcd for $C_{13}H_7Br_2F_3N_2$: C, 38.27; H, 1.73; N, 6.87. Found: C, 38.21; H, 1.71; N, 6.81.

*1-Benzyl-2-(phenylethynyl)-1H-imidazole (**13**)*



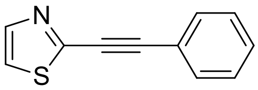
The crude reaction product obtained by the oxidative coupling reaction of 1-benzyl-1*H*-imidazole (**11**) with phenylacetylene (**2a**) (Scheme 5) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (70:30) as eluent to give x as a pale brown solid (176 mg, 68%), m.p. 60 – 62 °C (lit. 59 – 61 °C).[4] ESI-MS m/z 259 [M+H]$^+$. EI-MS, m/z (%): 258 (100) 91 (89) 257 (52) 259 (19) 65 (12). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.56 (m, 2H), 7.27 – 7.38 (m, 6H), 7.19 – 7.25 (m, 2H), 7.11 (d, J = 1.3 Hz, 1H), 6.91 (d, J = 1.3 Hz, 1H), 5.24 (s, 2H). The spectral properties of this compound are in agreement with those previously reported.[4]

*1-Phenyl-2-(phenylethynyl)-1H-imidazole (**14**)*



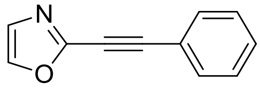
The crude reaction product obtained by the oxidative coupling reaction of 1-phenyl-1*H*-imidazole (**12**) with phenylacetylene (**2a**) (Scheme 5) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (70:30) as eluent to give **14** as light brown oil (127 mg, 52%), ESI-MS m/z 245 [M+H]$^+$. EI-MS, m/z (%): 244 (100) 243 (37) 245 (19) 77 (14) 216 (10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 4H), 7.47 – 7.44 (m, 1H), 7.43 – 7.39 (m, 2H), 7.34 – 7.30 (m, 3H), 7.24 (d, J = 1.3 Hz, 1H), 7.22 (d, J = 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.41, 131.63, 131.44, 130.43, 129.34, 129.06, 128.47, 128.42, 124.78, 121.96, 121.30, 92.25, 79.72. Elem. Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.60; H, 4.97; N, 11.46.

*2-(Phenylethynyl)thiazole (**17**)*



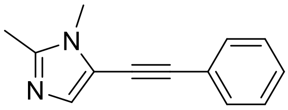
The crude reaction product obtained by the oxidative coupling reaction of thiazole (**15**) with phenylacetylene (**2a**) (Scheme 5) was purified by flash chromatography on silica gel with a mixture of toluene and EtOAc (95:5) as eluent to give **17** as a yellow solid with low melting point (89 mg, 48%). ESI-MS m/z 186 $[M+H]^+$. EI-MS, m/z (%): 185 (100) 58 (56) 186 (13) 127 (8) 187 (5). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 3.3 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.41 – 7.29 (m, 4H). The spectral properties of this compound are in agreement with those previously reported.[2]

*2-(Phenylethynyl)oxazole (**18**)*

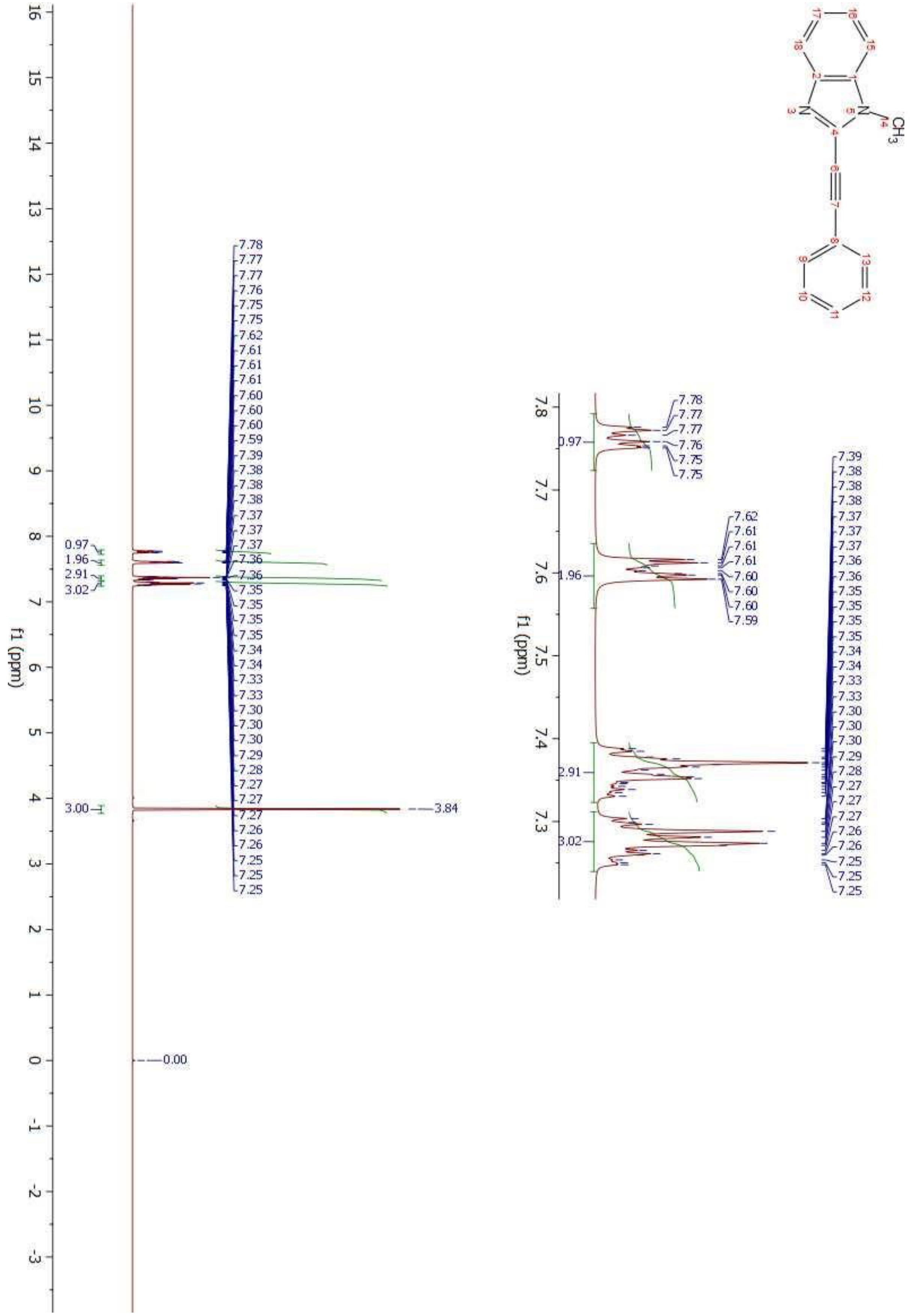


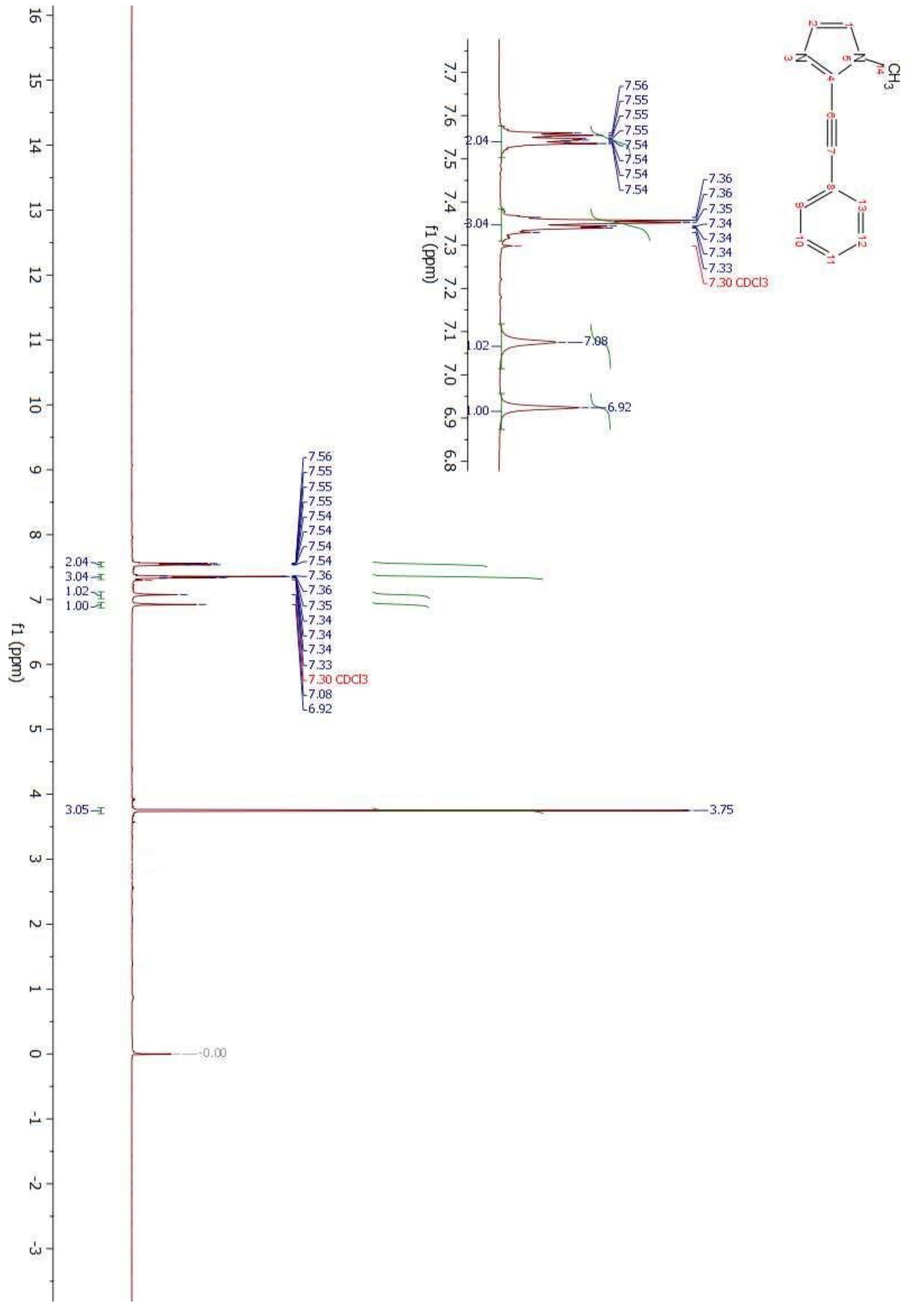
The crude reaction product obtained by the oxidative coupling reaction of oxazole (**16**) with phenylacetylene (**2a**) (Scheme 5) was purified by flash chromatography on silica gel with EtOAc as eluent to give **18** as a pale-yellow oil (71 mg, 42%). ESI-MS m/z 170 $[M+H]^+$. EI-MS, m/z (%): 114 (100) 169 (66) 113 (25) 115 (10) 63 (9). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 0.9 Hz, 1H), 7.33 – 7.46 (m, 3H), 7.57 – 7.64 (m, 2H), 7.68 (d, J = 0.9 Hz, 1H). The spectral properties of this compound are in agreement with those previously reported.[3]

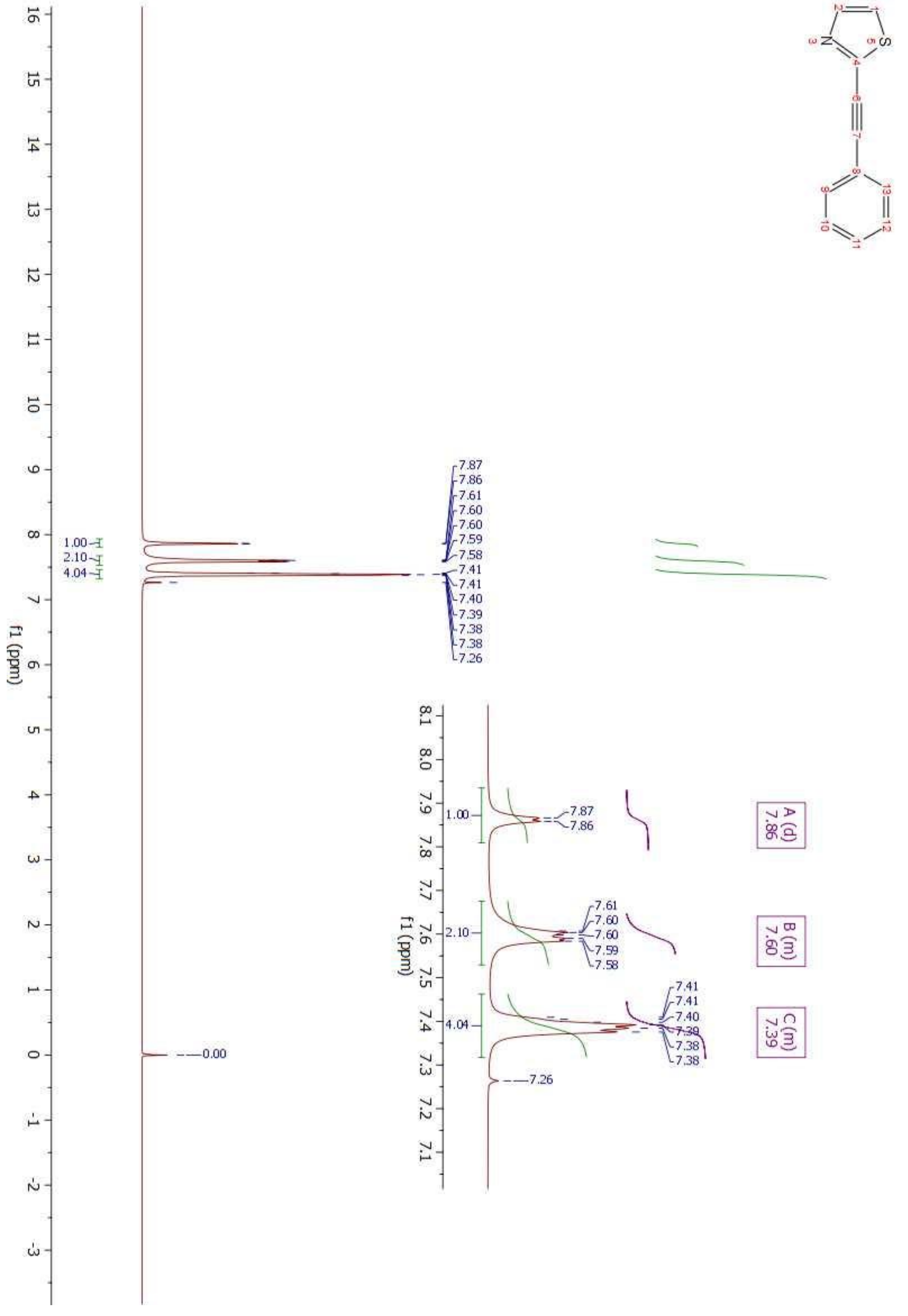
*1,2-Dimethyl-5-(phenylethynyl)-1H-imidazole (**20**)*



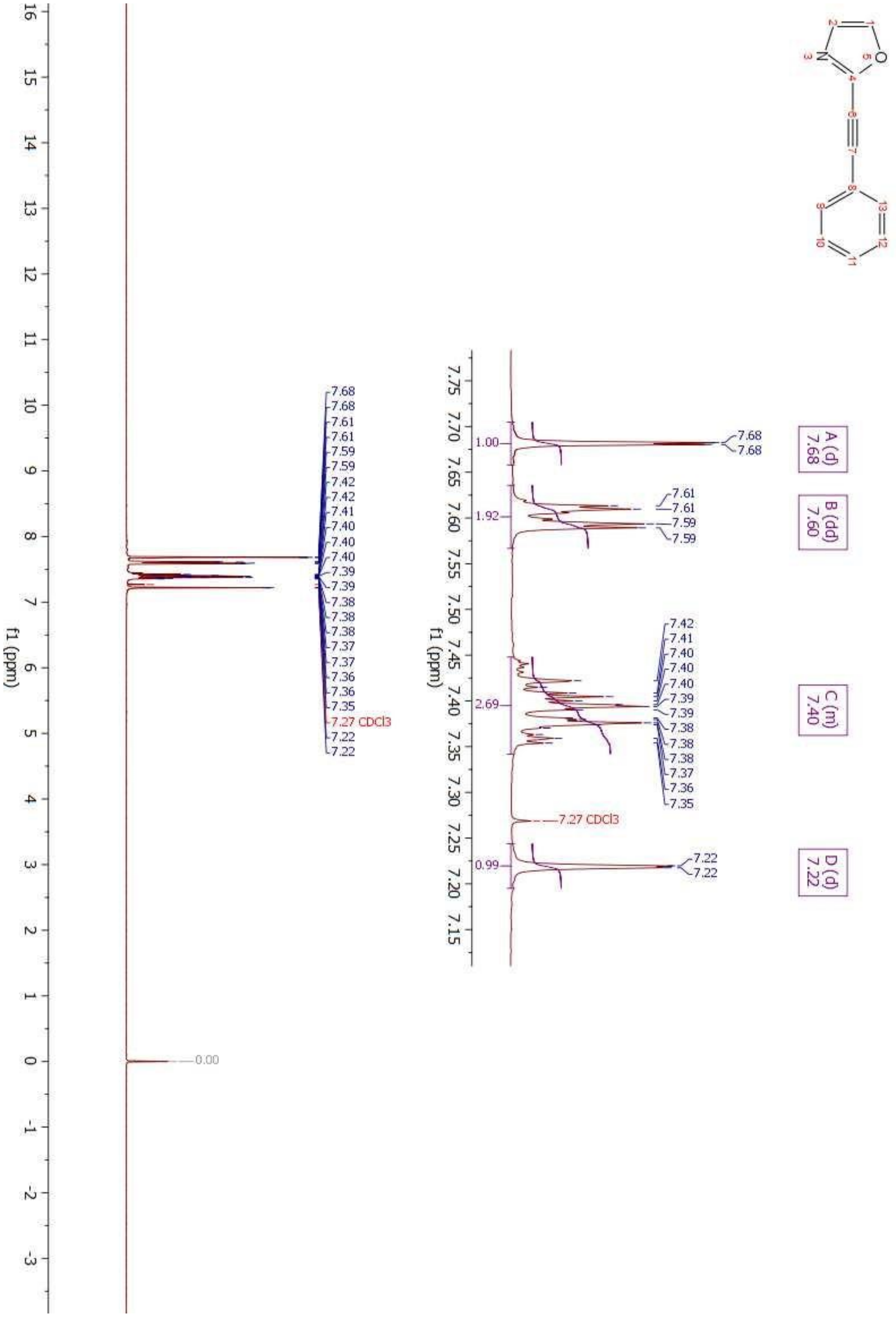
The crude reaction product obtained by the dehydrogenative coupling of 1,2-dimethyl-1H-imidazole (**19**) with phenylacetylene (**2a**) was purified by flash chromatography on silica gel with a mixture of DCM and MeOH (95:5) as eluent to give **20** as a light brown solid (82 mg, 42%): m.p. 94 – 96 °C (lit. 93 – 96 °C).[7] ESI-MS m/z 197 [M+H]+. EI-MS m/z (%): 196 (100) 128 (45) 195 (20) 127 (18) 197 (15). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.40 – 7.29 (m, 3H), 7.23 (s, 1H), 3.62 (s, 3H), 2.41 (s, 3H). The physical and spectral properties of this compound are in agreement with those previously reported.[7]

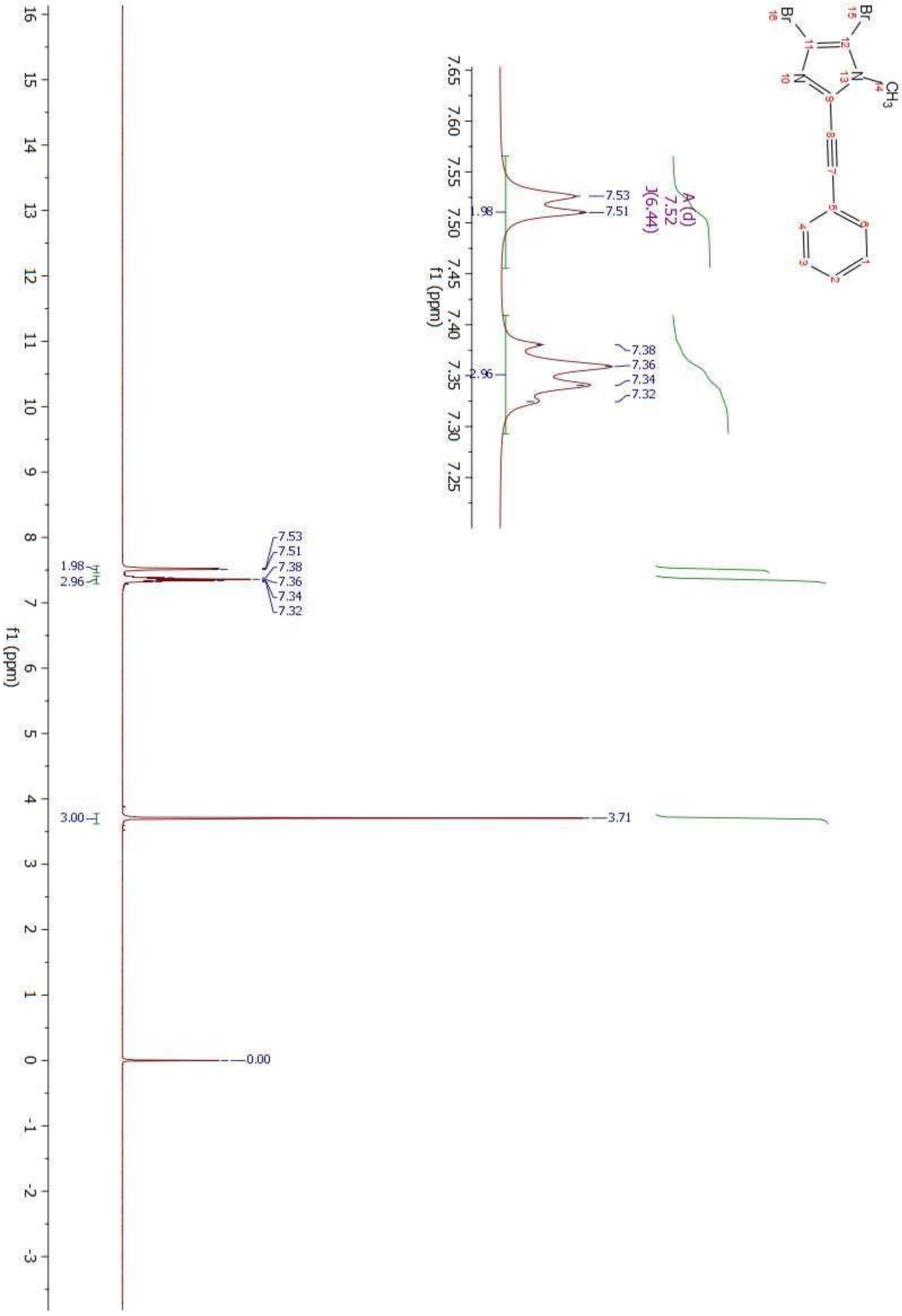

CH3
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
0.97
1.96
2.91
3.02
3.00
7.78 7.77 7.77 7.76 7.75 7.75 7.62 7.61 7.61 7.61 7.60 7.60 7.60 7.59 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.30 7.30 7.30 7.29 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.25 7.25
3.84
0.00
7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)


CH3
N
N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
7.56
7.55
7.55
7.55
7.54
7.54
7.54
7.54
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.30 CDCl3
7.08
6.92
3.75
0.00
2.04
3.04
1.02
1.00
3.05
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8



S
N
1
2
3
4
5
6
7
8
9
10
11
12
13
7.87
7.86
7.61
7.60
7.60
7.59
7.58
7.41
7.41
7.40
7.39
7.38
7.38
7.26
1.00
2.10
4.04
0.00
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
A (d) 7.86
B (m) 7.60
C (m) 7.39


O
1
2
N
3
4
5
6
7
8
9
10
11
12
13
A (d)
7.68
B (dd)
7.60
C (m)
7.40
D (d)
7.22
7.68
7.68
7.61
7.61
7.59
7.59
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.36
7.35
7.27 CDCl3
7.22
7.22
1.00
1.92
2.69
0.99
f1 (ppm)
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
7.68
7.68
7.61
7.61
7.59
7.59
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.27 CDCl3
7.22
7.22
0.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Br
Br
N
N
CH3
7.53
7.51
A (d)
7.52
J(6.44)
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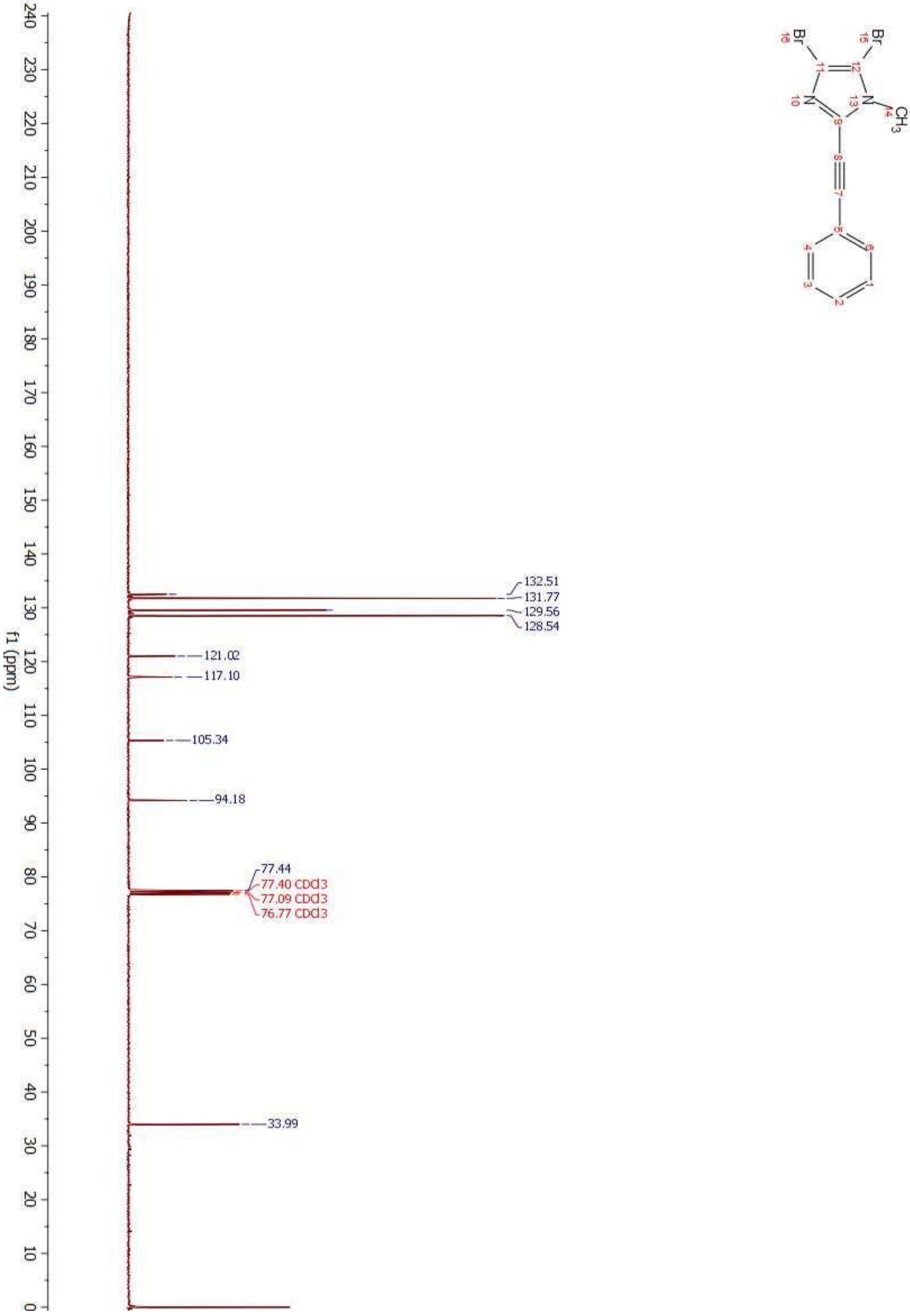
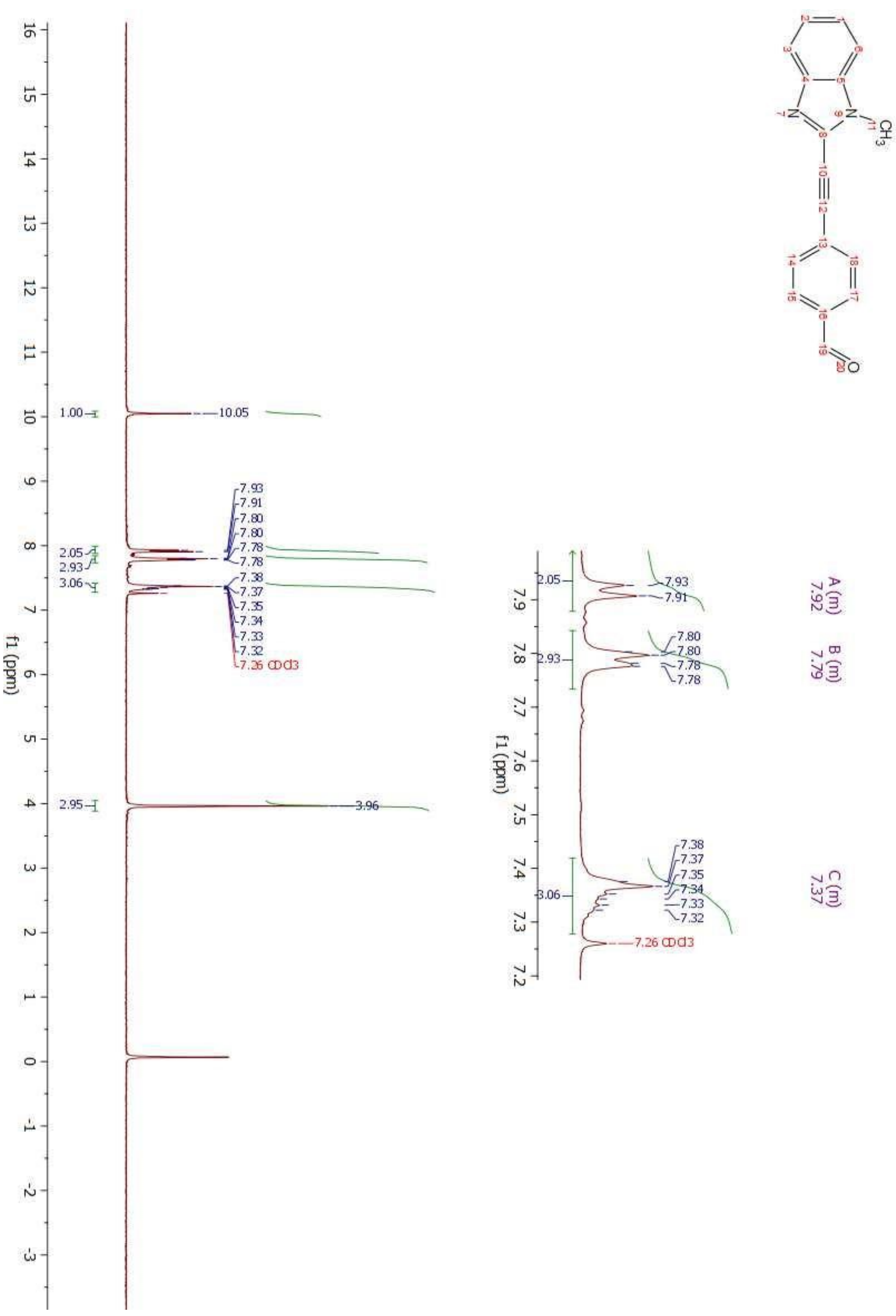
7.38
7.36
7.34
7.32
2.96
3.00
3.71
0.00
f1 (ppm)


Br
16
Br
15
11
12
10
N
13
N
CH3
14
9
8
7
5
6
4
1
3
2
132.51
131.77
129.56
128.54
121.02
117.10
105.34
94.18
77.44
77.40 CDCl3
77.09 CDCl3
76.77 CDCl3
33.99
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
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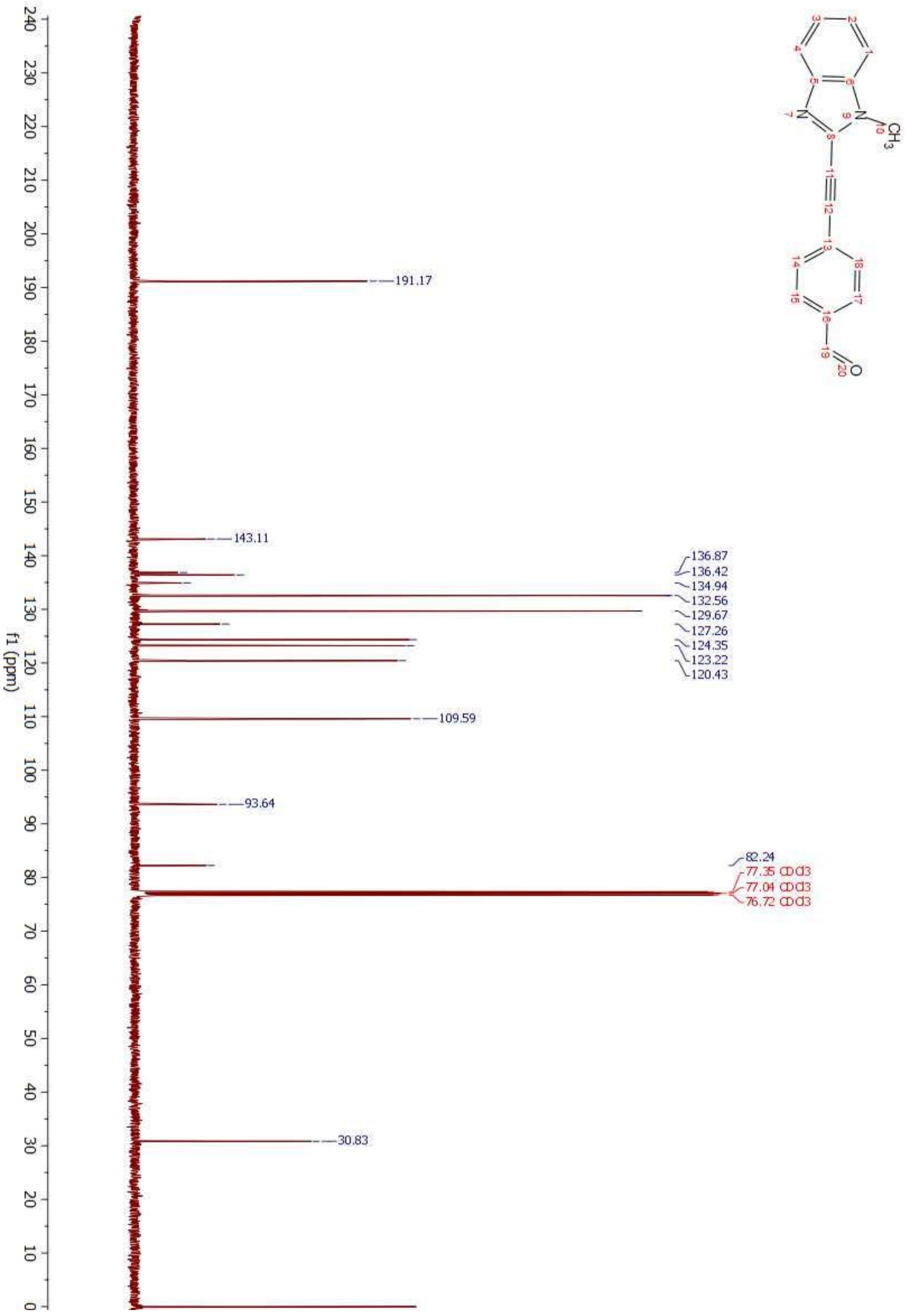
7.91
7.80
7.80
7.78
7.78
7.38
7.37
7.35
7.34
7.33
7.32
7.26 CDCl3
3.96
1.00
2.05
2.93
3.06
2.95
f1 (ppm)
A (m) 7.92
B (m) 7.79
C (m) 7.37


240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
191.17
143.11
136.87
136.42
134.94
132.56
129.67
127.26
124.35
123.22
120.43
109.59
93.64
82.24
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
30.83
CH3
N
N
O
1
2
3
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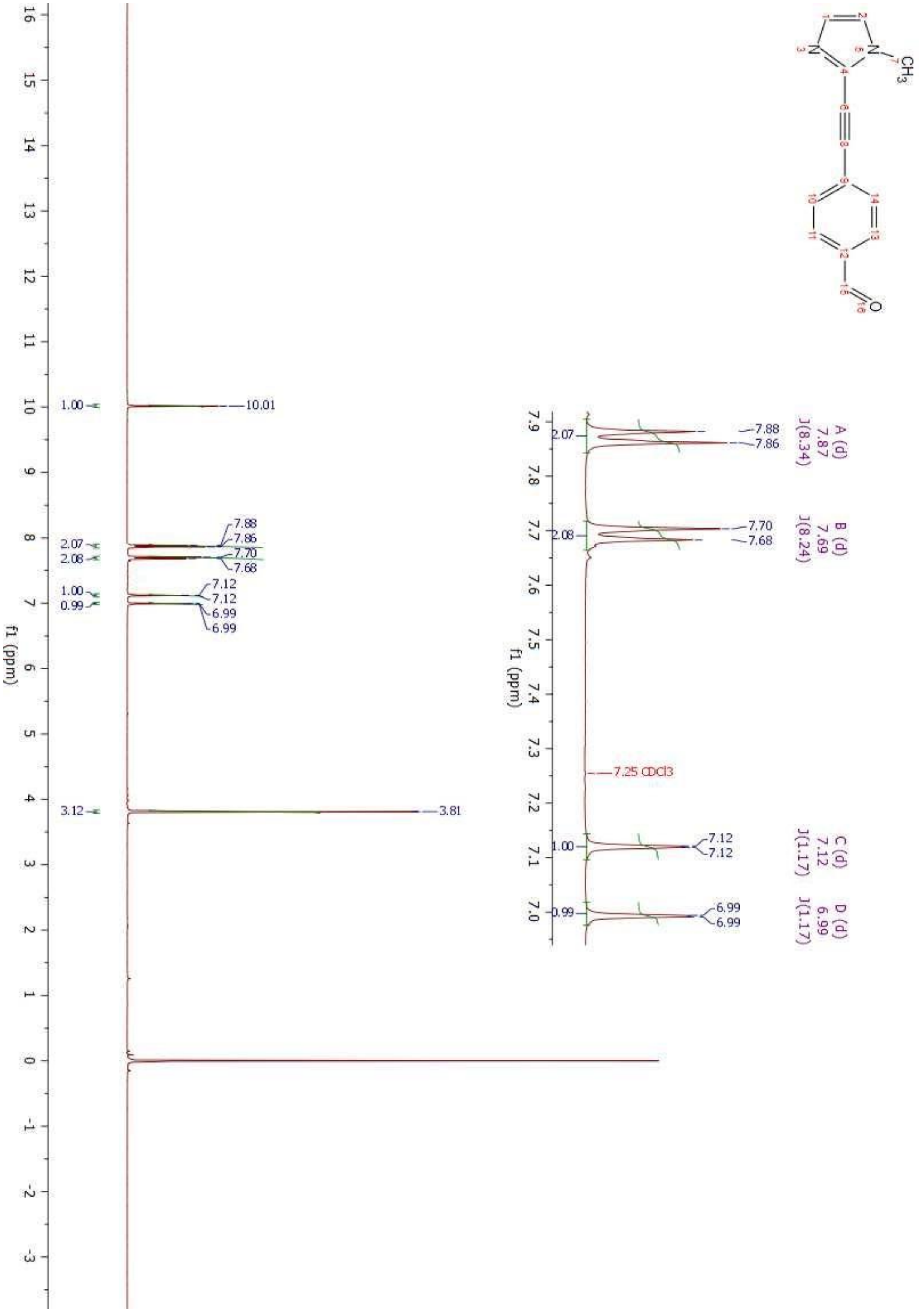
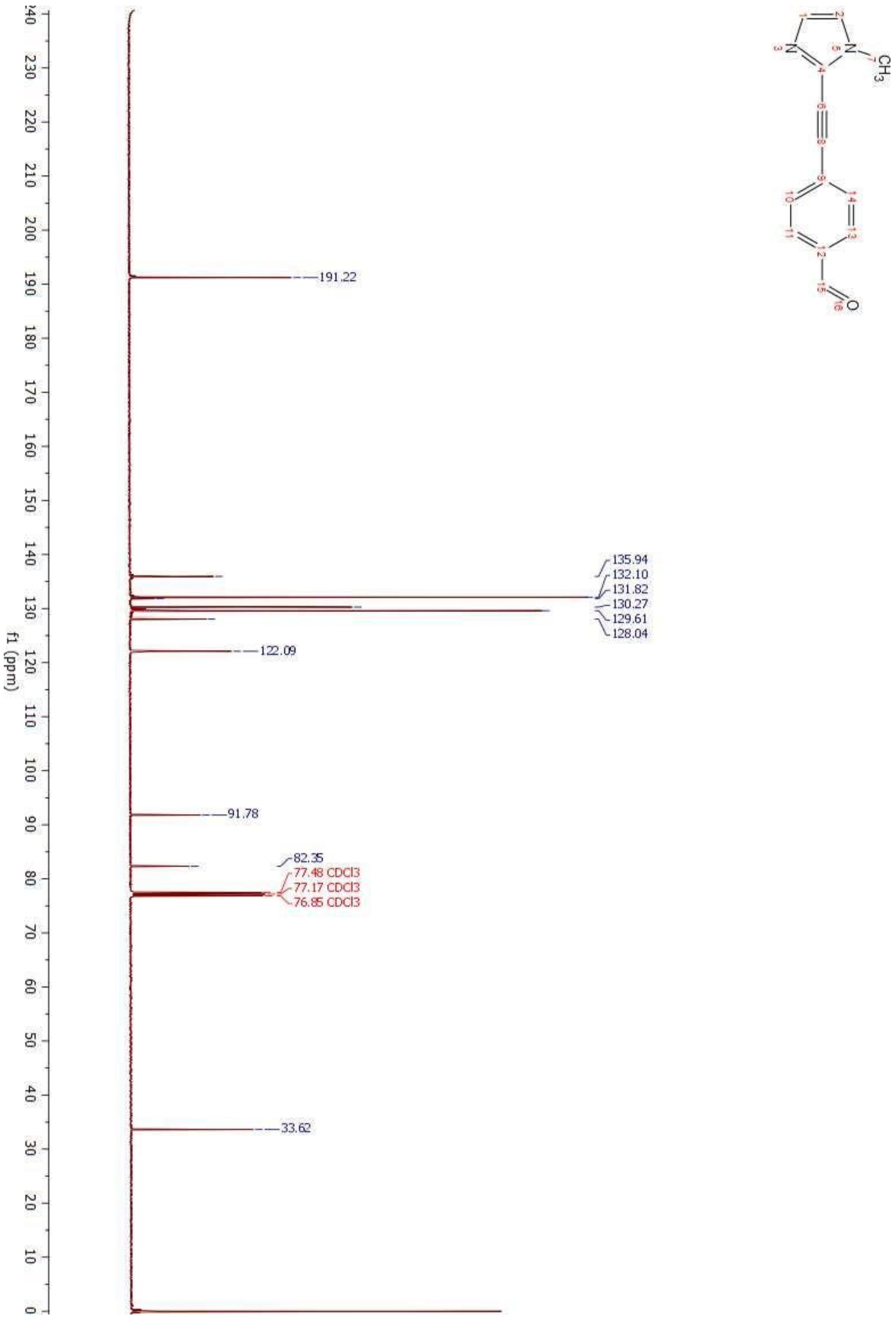
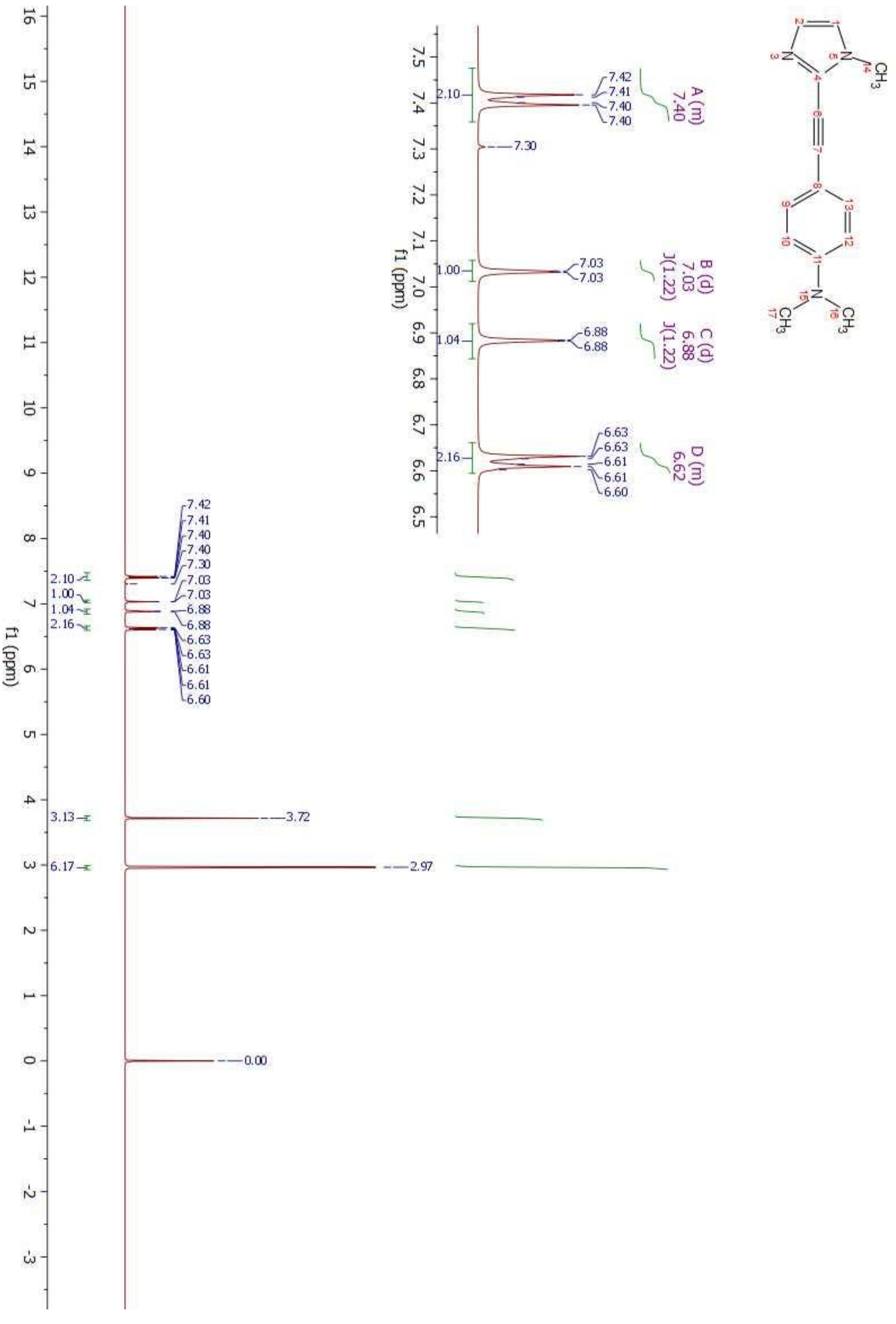
15
16
17
18
19
20



10.01
7.88
7.86
7.70
7.68
7.12
7.12
6.99
6.99
3.81
1.00
2.07
2.08
1.00
0.99
3.12
f1 (ppm)
7.25 CDCl3
A (d) 7.87 J(8.34)
B (d) 7.69 J(8.24)
C (d) 7.12 J(1.17)
D (d) 6.99 J(1.17)
CH3
N
N
O


191.22
135.94
132.10
131.82
130.27
129.61
128.04
122.09
91.78
82.35
77.48 CDCl3
77.17 CDCl3
76.85 CDCl3
33.62
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N
CH3
O



CH3
N
N
A (m)
7.40
B (d)
7.03
J(1.22)
C (d)
6.88
J(1.22)
D (m)
6.62
7.42
7.41
7.40
7.40
7.30
7.03
7.03
6.88
6.88
6.63
6.63
6.61
6.61
6.60
3.72
2.97
0.00
2.10
1.00
1.04
2.16
3.13
6.17
f1 (ppm)
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
16
15
14
13
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11
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9
8
7
6
5
4
3
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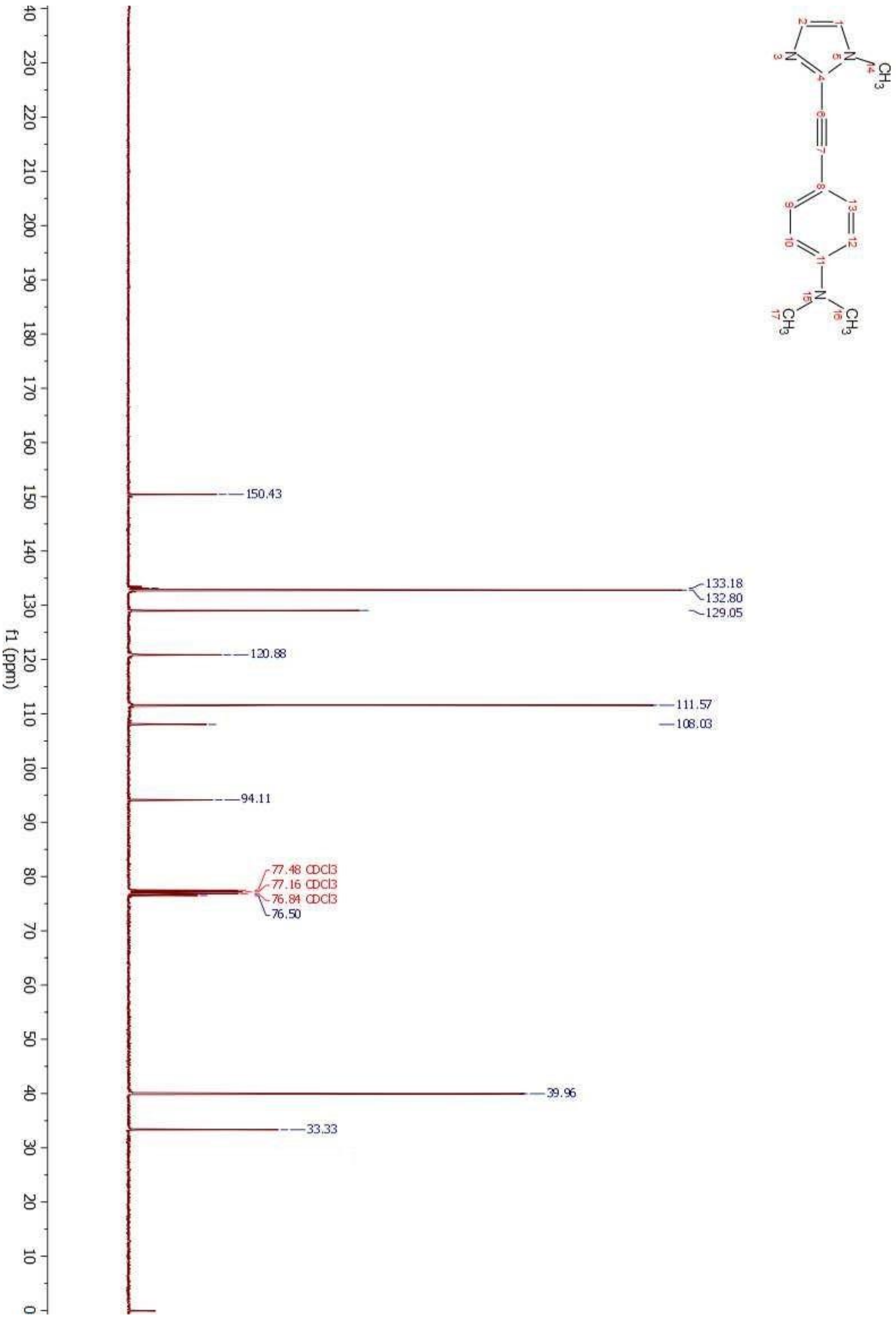
1
0
-1
-2
-3



CH3
N
N
CH3
CH3
f1 (ppm)
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133.18
132.80
129.05
120.88
111.57
108.03
94.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.50
39.96
33.33
240
230
220
210
200
190
180
170
160
150
140
130
120
110
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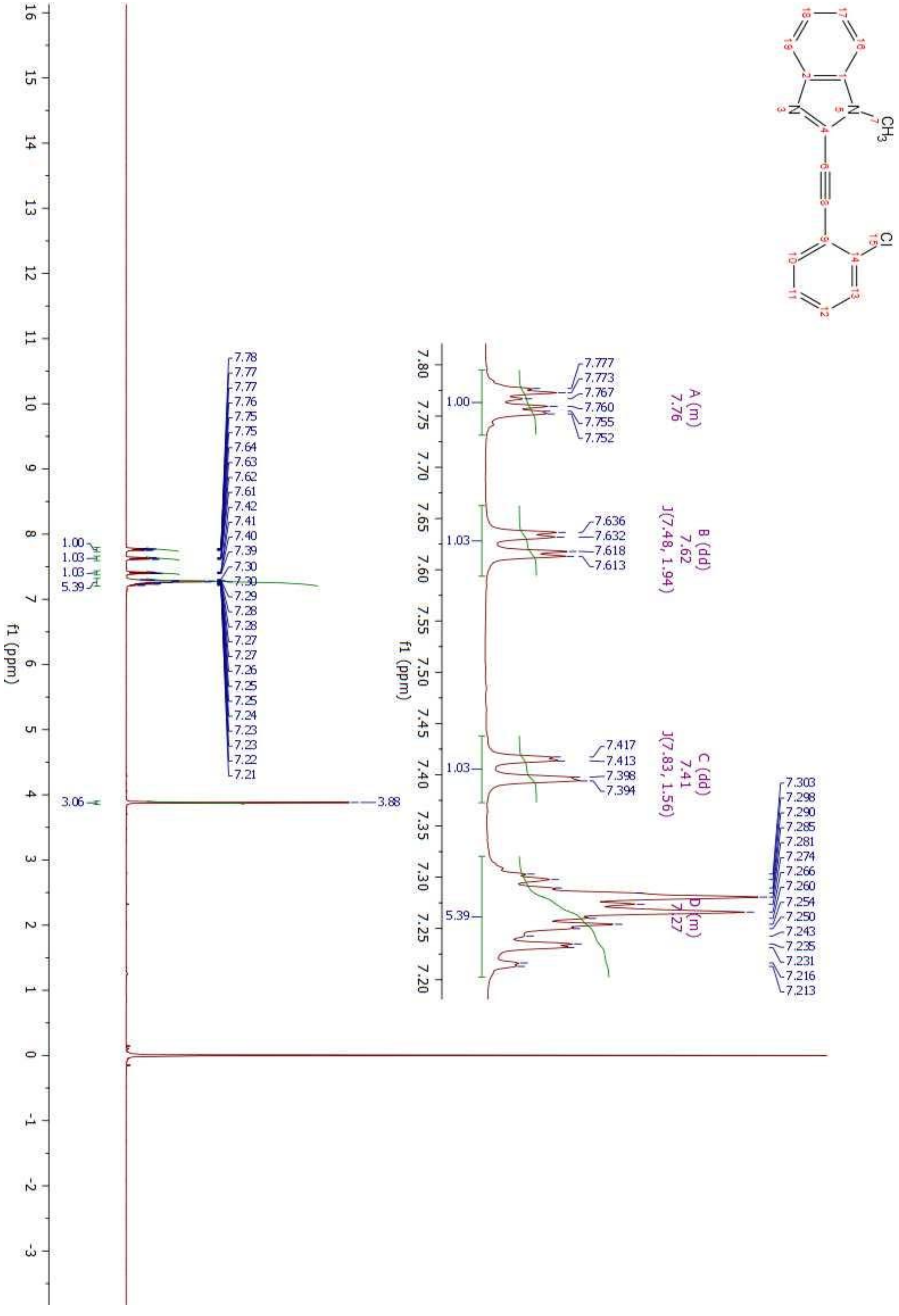
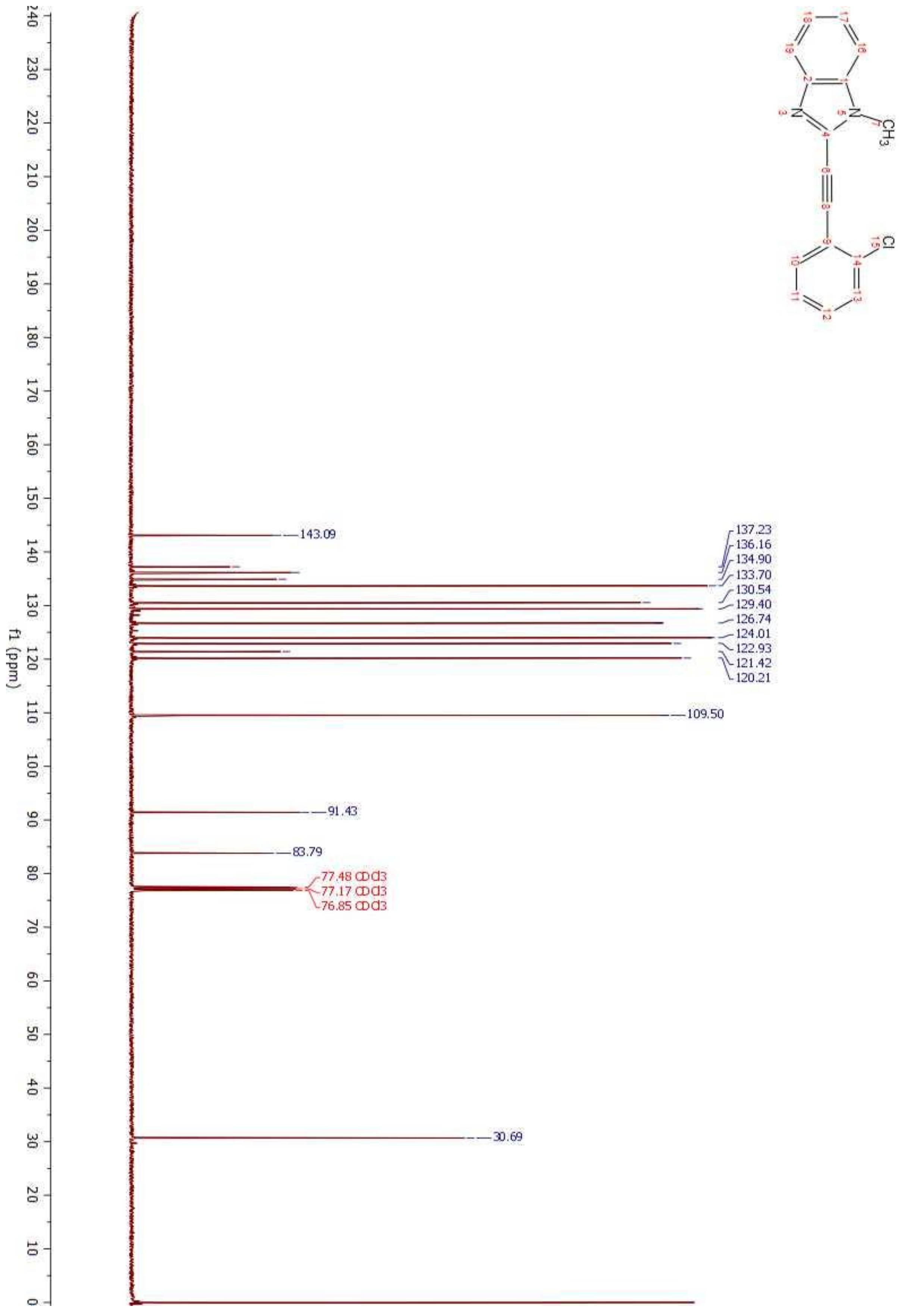
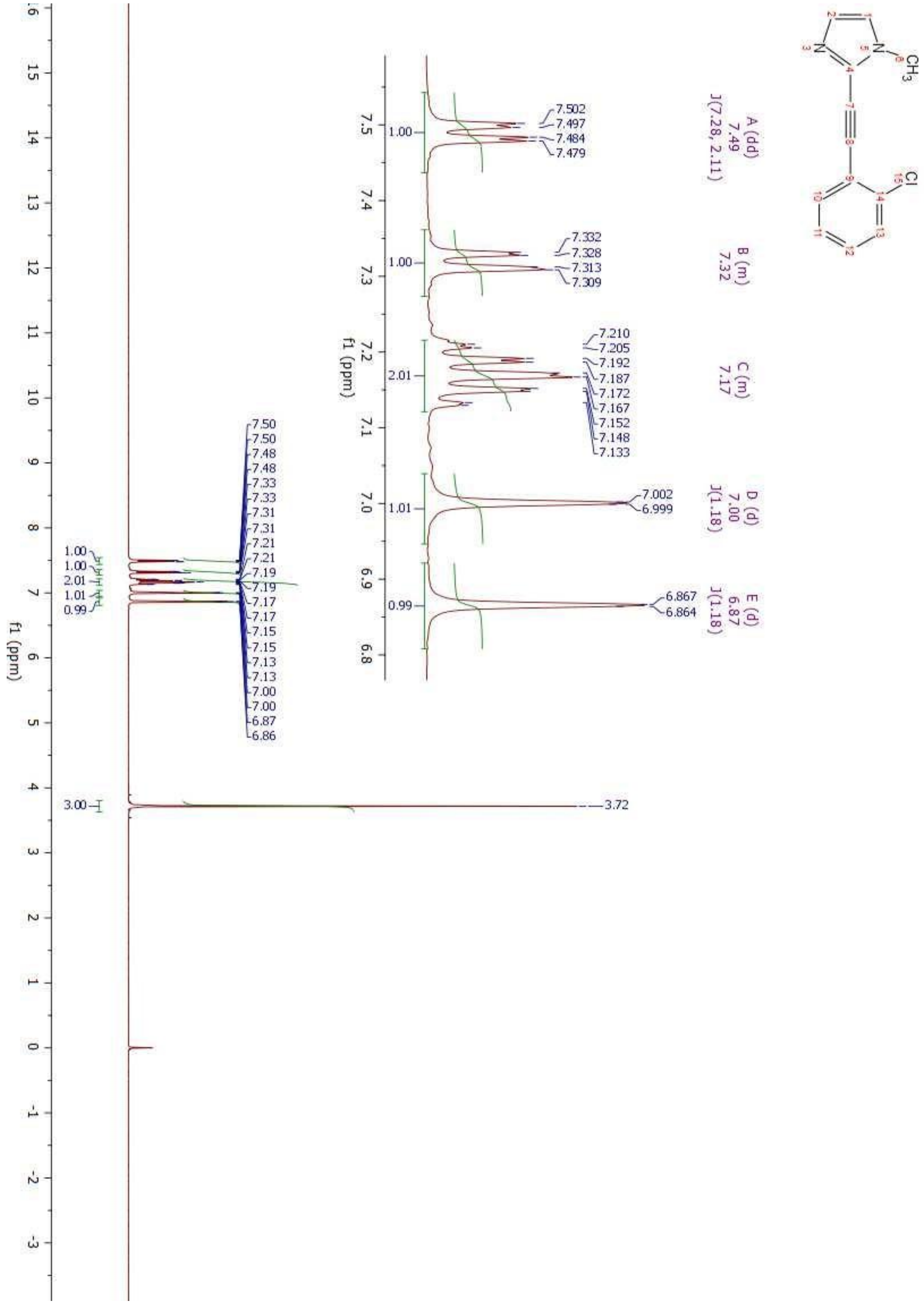
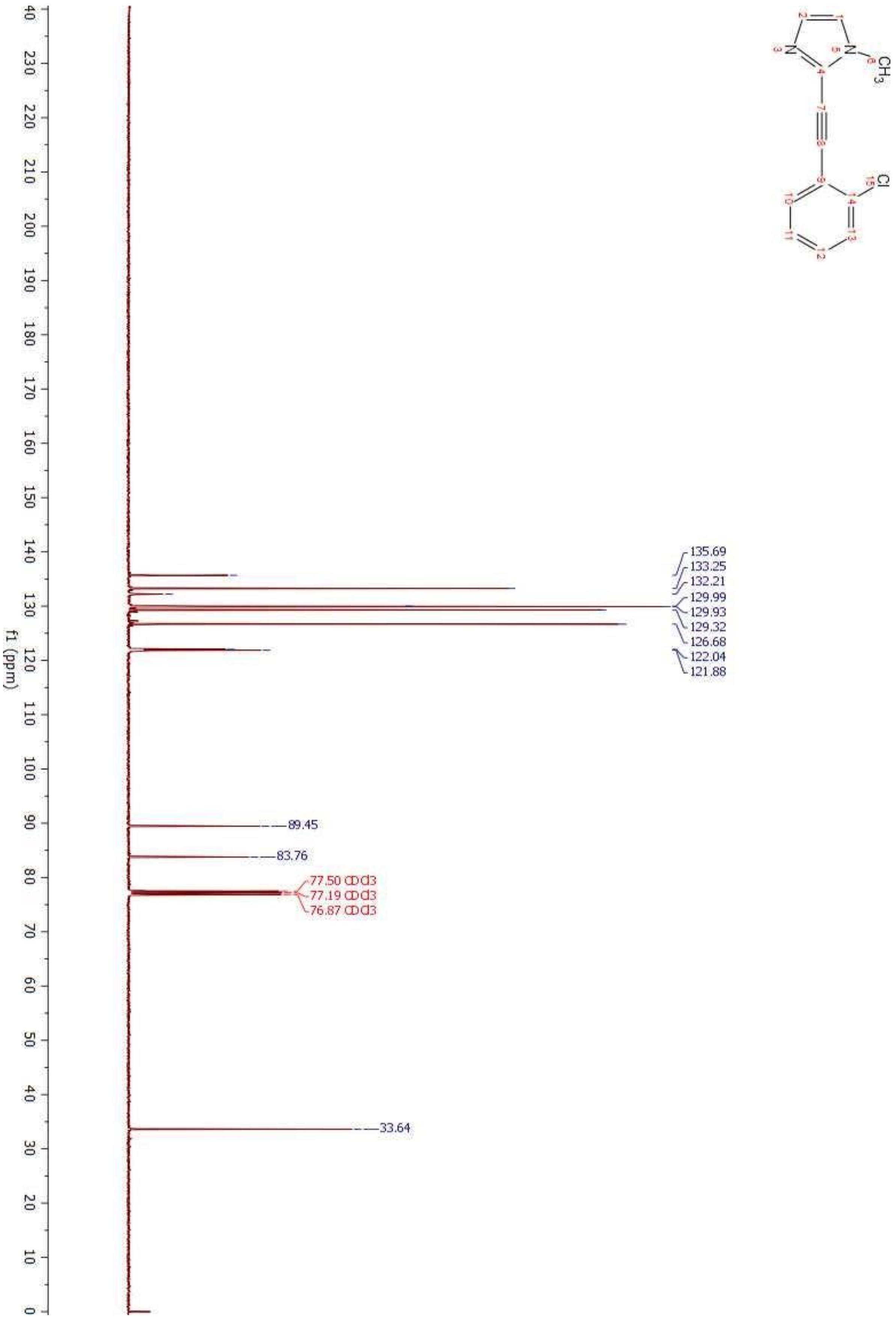
50
40
30
20
10
0


CH3
Cl
N
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
1.00
1.03
1.03
5.39
3.06
3.88
7.78
7.77
7.77
7.76
7.75
7.75
7.64
7.63
7.62
7.61
7.42
7.41
7.40
7.39
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.21
A (m)
7.76
B (dd)
7.62
J(7.48, 1.94)
C (dd)
7.41
J(7.83, 1.56)
D (m)
7.27
7.777
7.773
7.767
7.760
7.755
7.752
7.636
7.632
7.618
7.613
7.417
7.413
7.398
7.394
7.303
7.298
7.290
7.285
7.281
7.274
7.266
7.260
7.254
7.250
7.243
7.235
7.231
7.216
7.213
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20

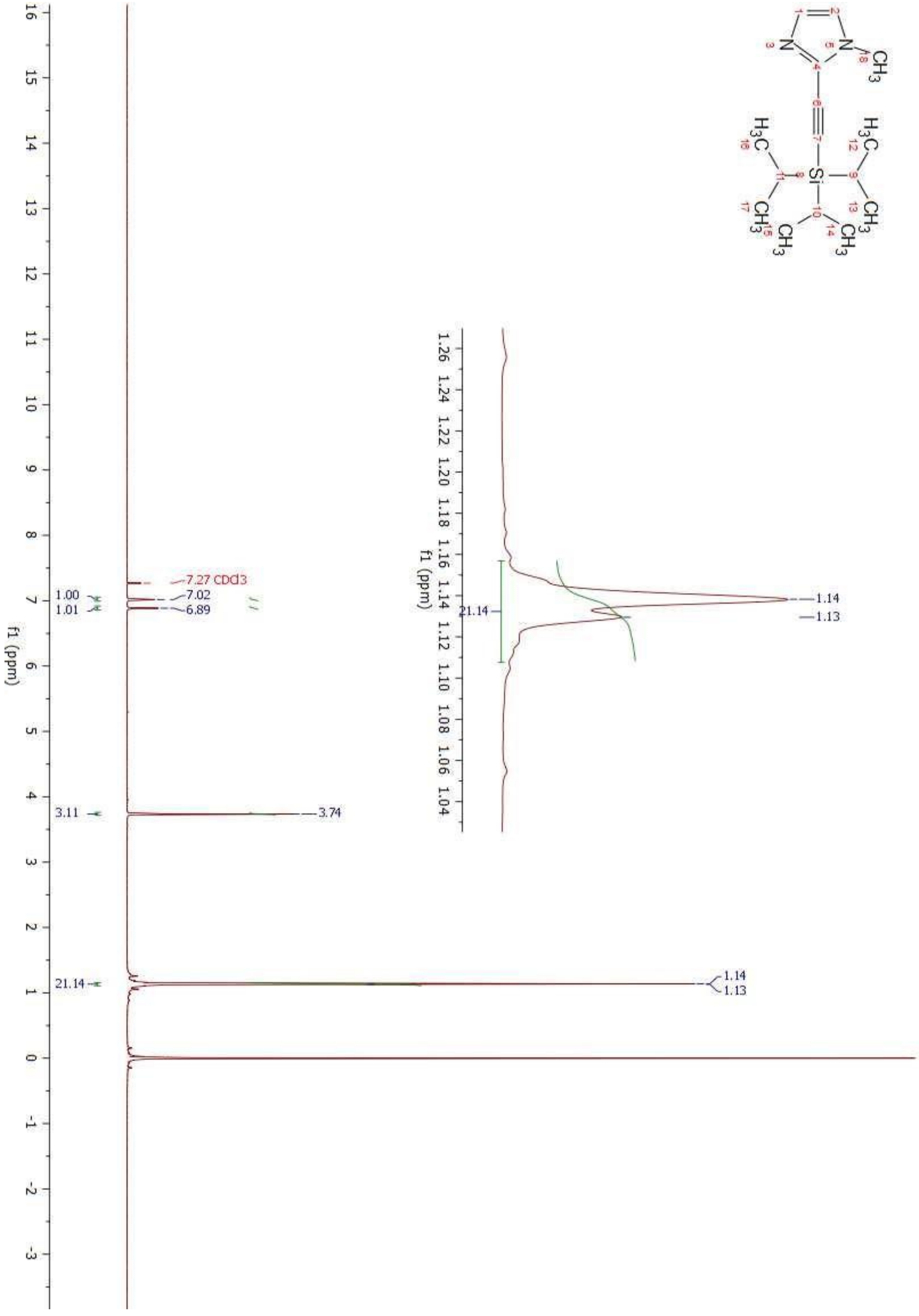

143.09
137.23
136.16
134.90
133.70
130.54
129.40
126.74
124.01
122.93
121.42
120.21
109.50
91.43
83.79
77.48 CDCl3
77.17 CDCl3
76.85 CDCl3
30.69
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
N
N
CH3
Cl



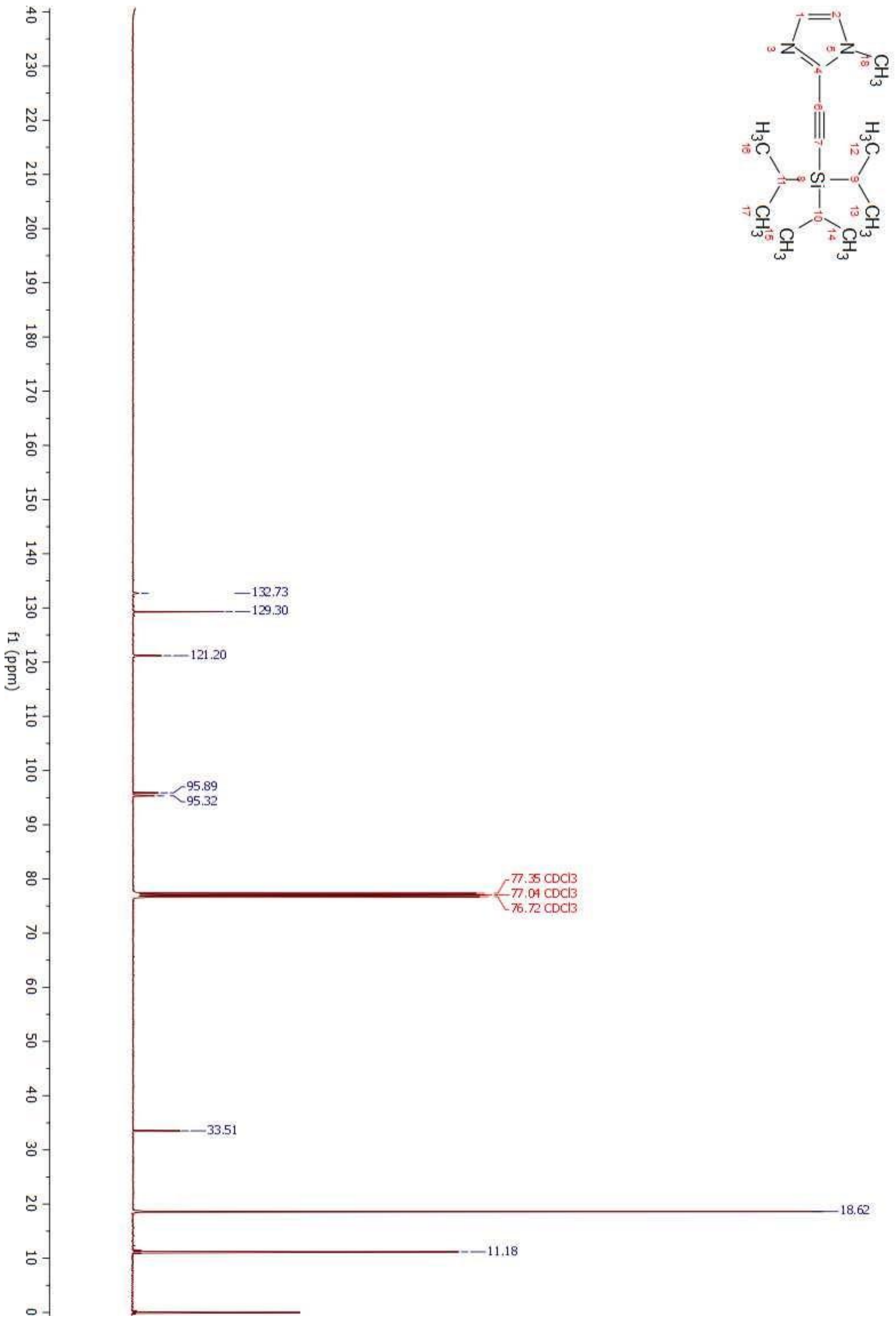
CH3
Cl
N
N
A (dd) 7.49 J(7.28, 2.11)
B (m) 7.32
C (m) 7.17
D (d) 7.00 J(1.18)
E (d) 6.87 J(1.18)
7.502
7.497
7.484
7.479
7.332
7.328
7.313
7.309
7.210
7.205
7.192
7.187
7.172
7.167
7.152
7.148
7.133
7.002
6.999
6.867
6.864
1.00
1.00
2.01
1.01
0.99
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
7.50
7.50
7.48
7.48
7.33
7.33
7.31
7.31
7.21
7.21
7.19
7.19
7.17
7.17
7.15
7.15
7.13
7.13
7.00
7.00
6.87
6.86
3.72
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)



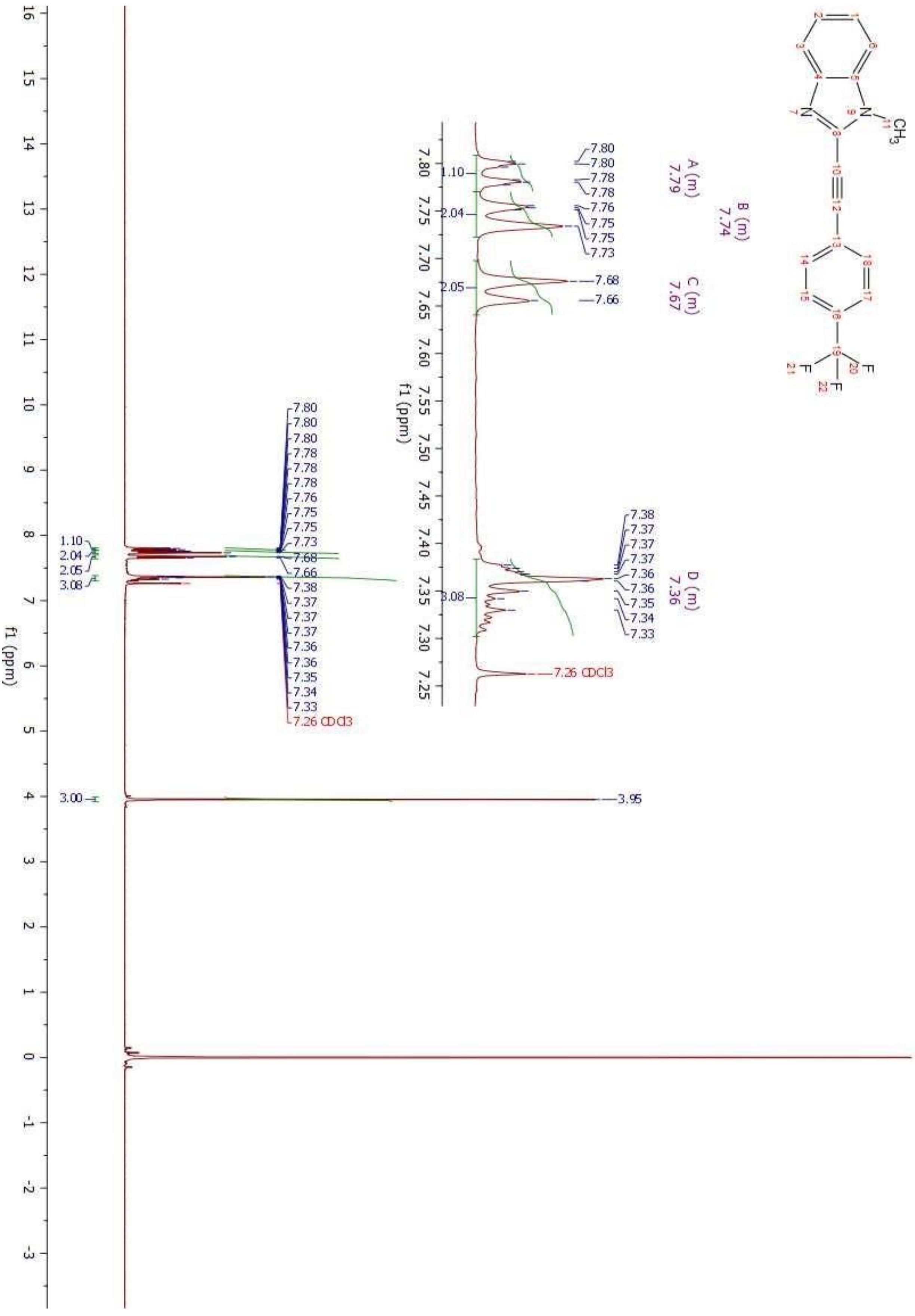
135.69
133.25
132.21
129.99
129.93
129.32
126.68
122.04
121.88
89.45
83.76
77.50 CDCl3
77.19 CDCl3
76.87 CDCl3
33.64
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N
CH3
Cl
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15



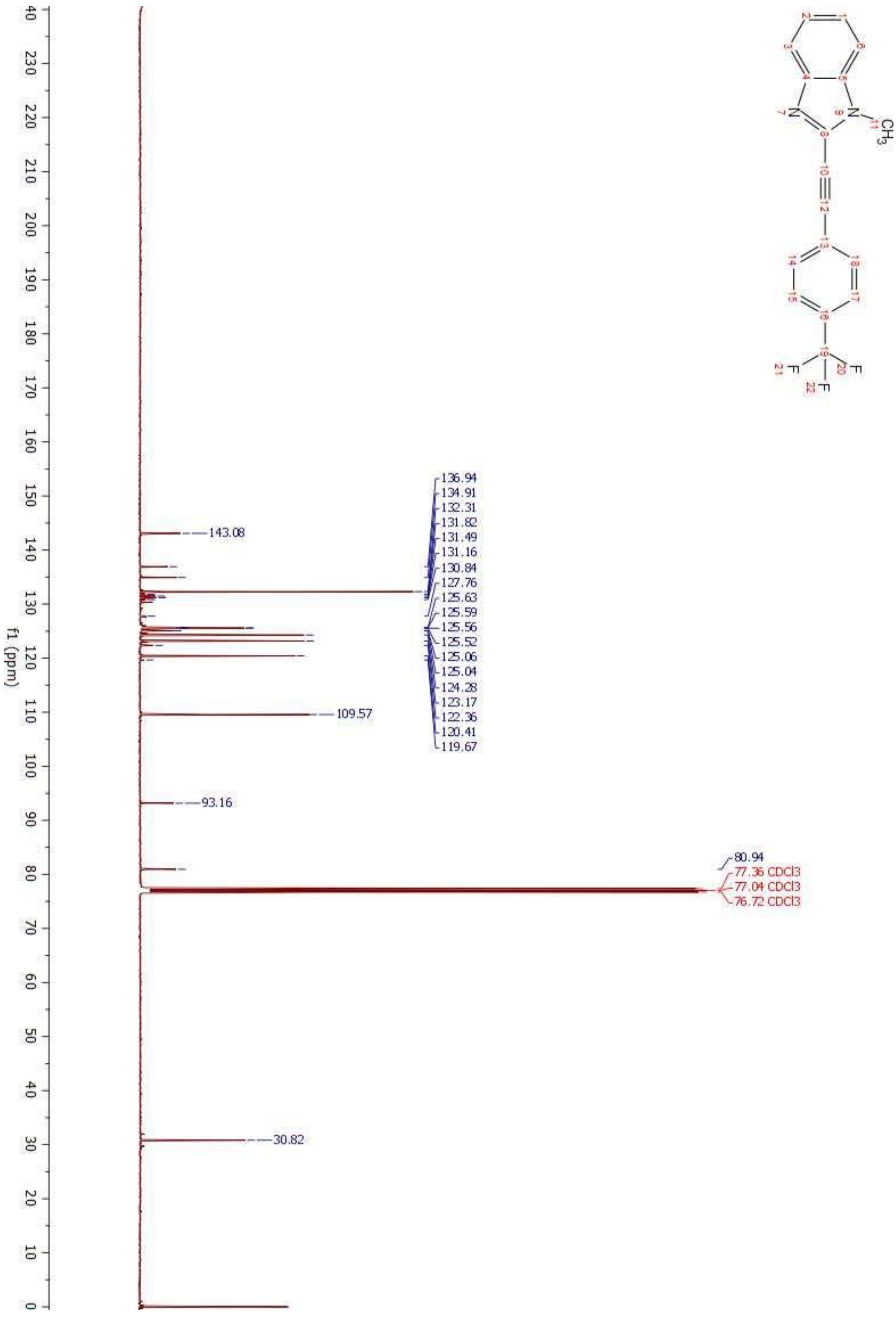
CH3
H3C
CH3
CH3
H3C
CH3
CH3
N
N
Si
7.27 CDCl3
7.02
6.89
3.74
1.14
1.13
1.00
1.01
3.11
21.14
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
1.26
1.24
1.22
1.20
1.18
1.16
1.14
1.12
1.10
1.08
1.06
1.04

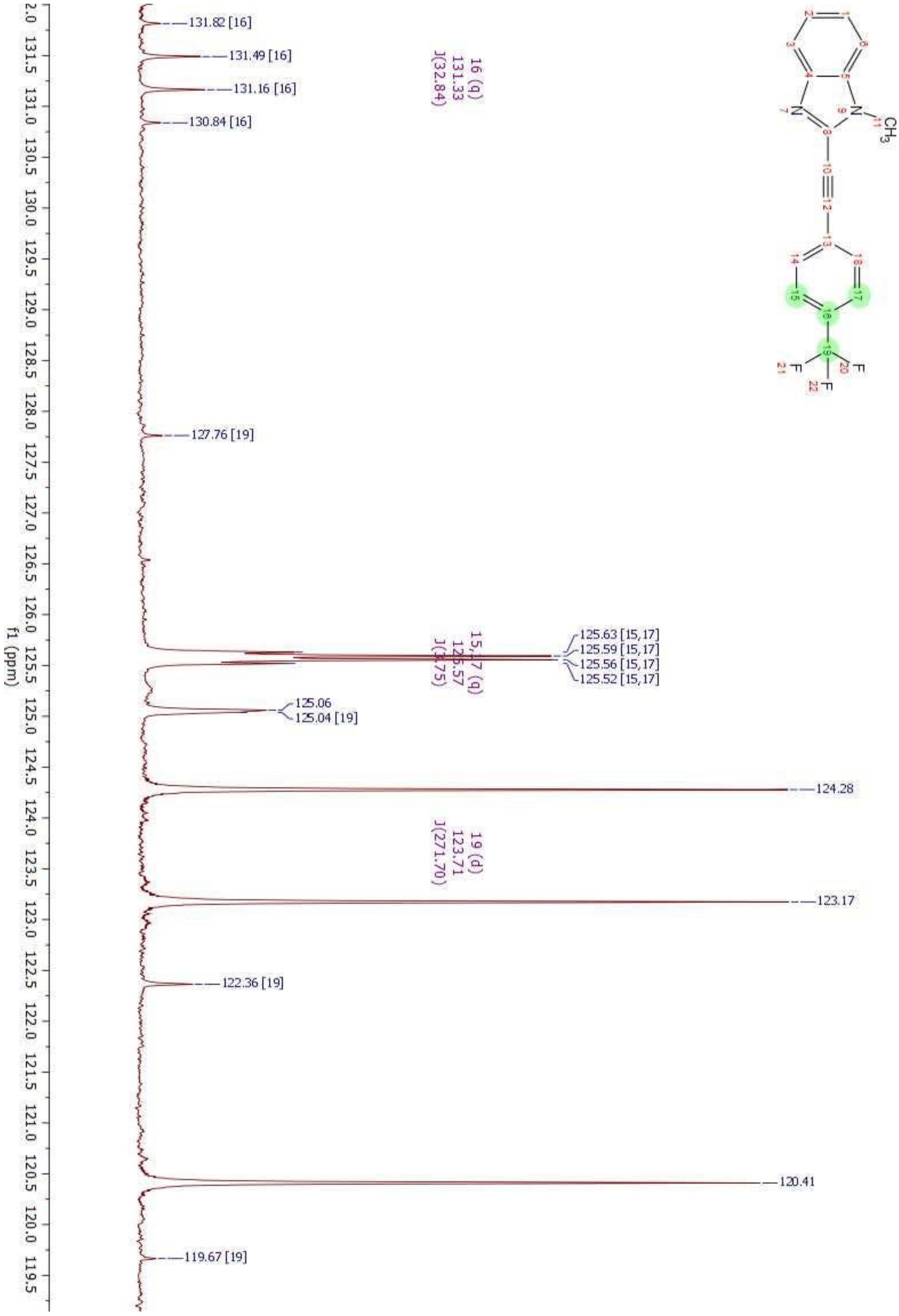


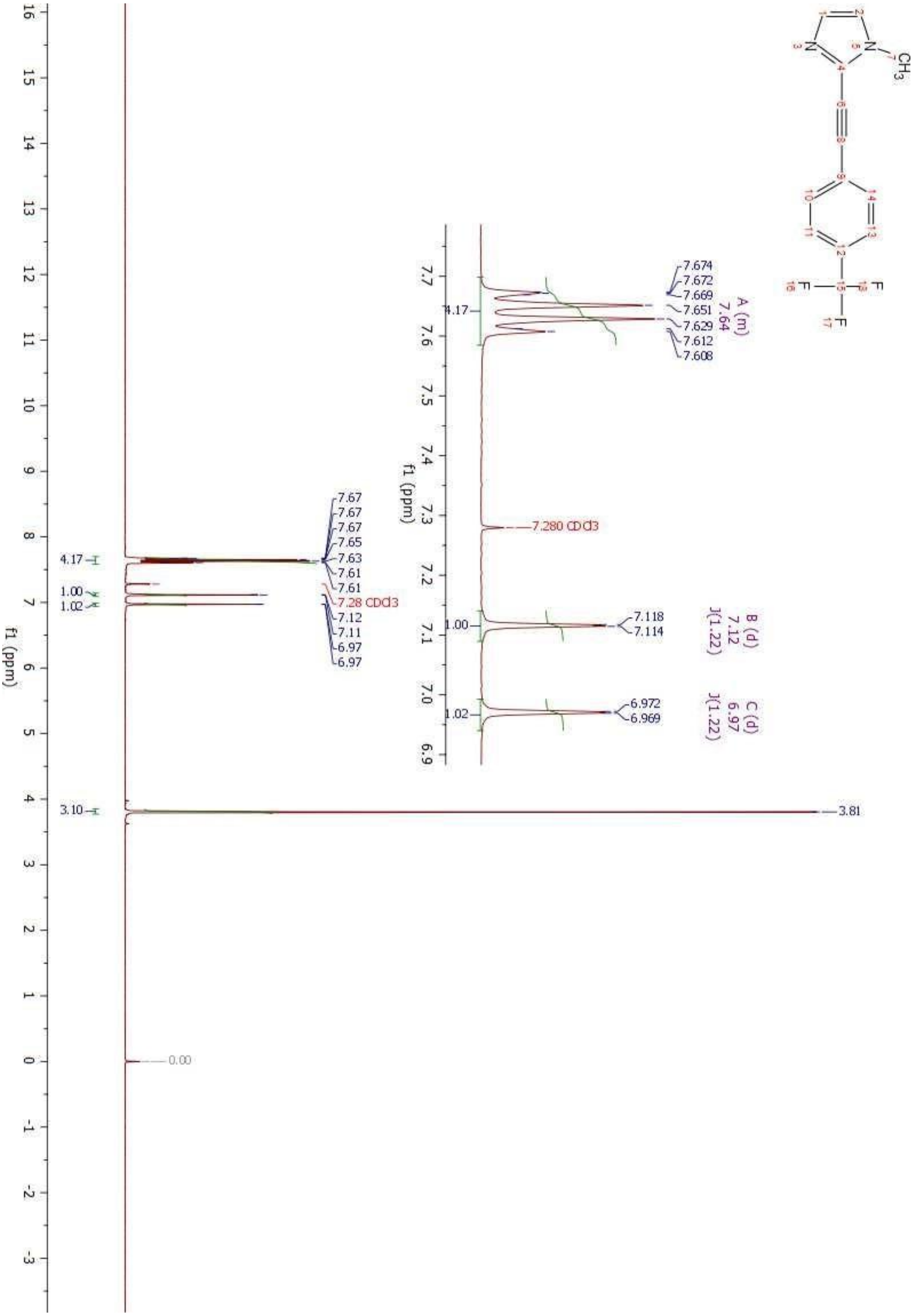
CH3
N
N
Si
H3C
CH3
H3C
CH3
CH3
CH3
132.73
129.30
121.20
95.89
95.32
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
33.51
18.62
11.18
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

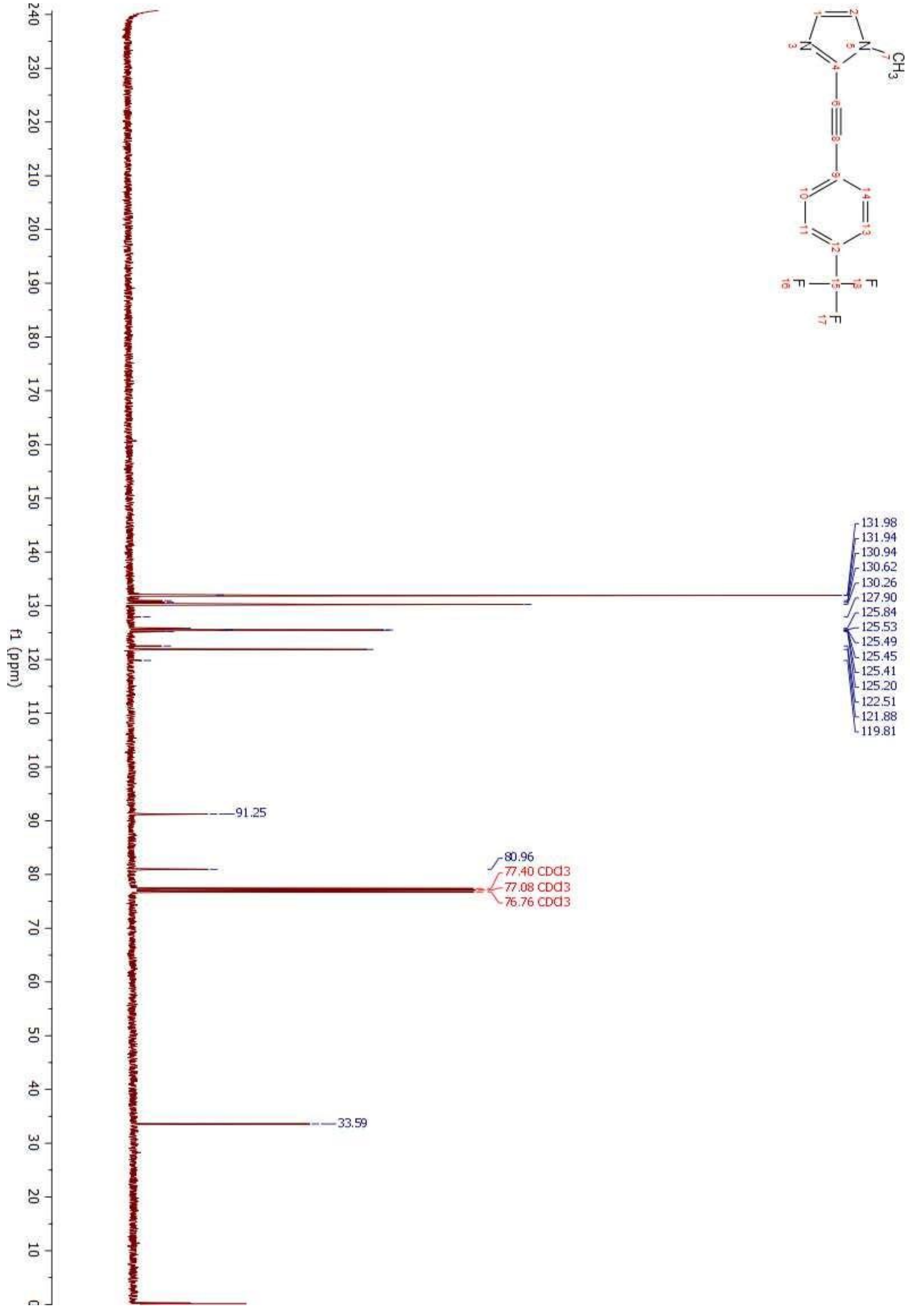


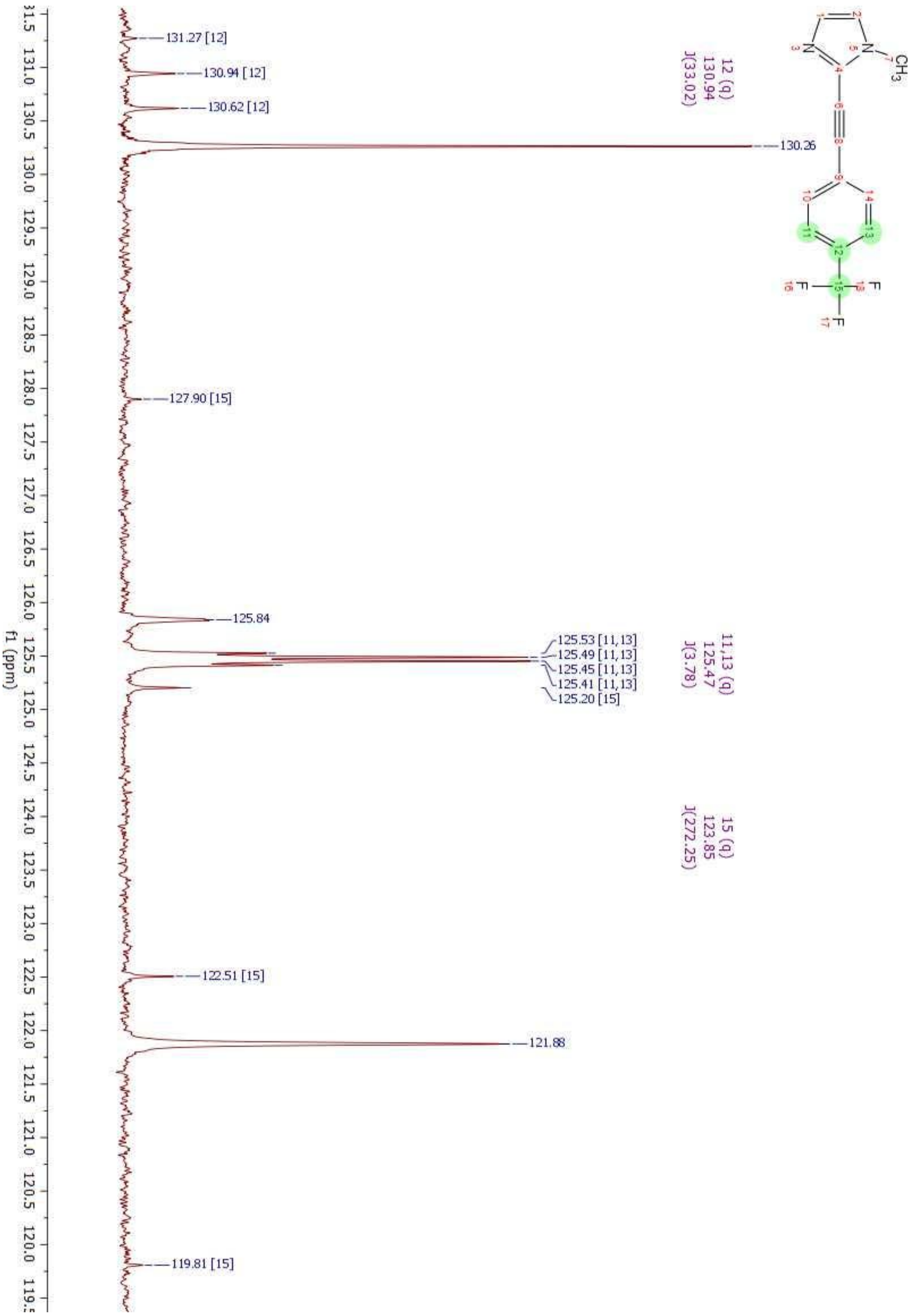
CH3
F
F
F
N
N
A (m)
7.79
B (m)
7.74
C (m)
7.67
D (m)
7.36
7.80
7.80
7.78
7.78
7.76
7.75
7.75
7.73
7.68
7.66
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.26 CDCl3
3.95
1.10
2.04
2.05
3.08
3.00
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25

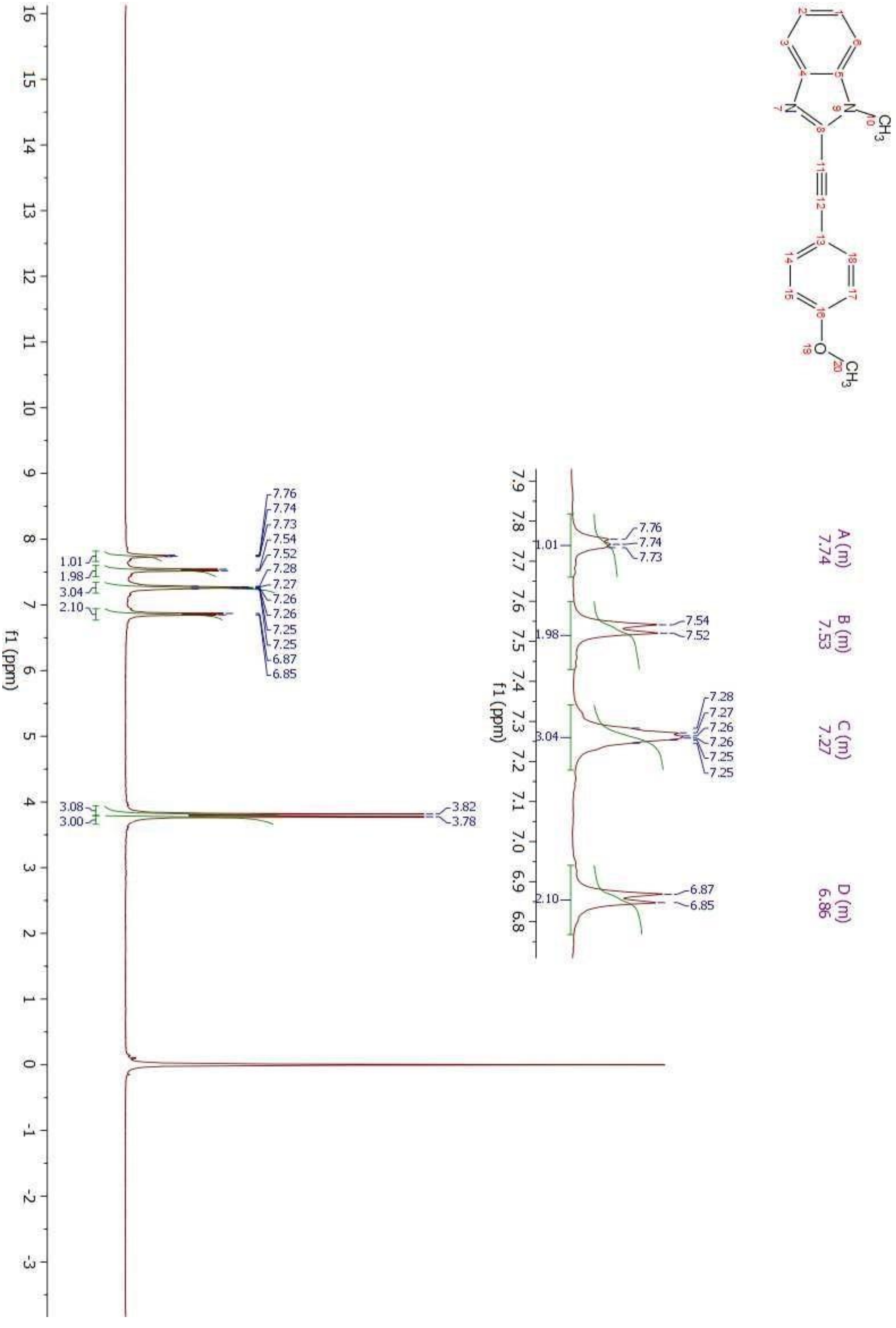

CH3
N
N
F
F
F
143.08
136.94
134.91
132.31
131.82
131.49
131.16
130.84
127.76
125.63
125.59
125.56
125.52
125.06
125.04
124.28
123.17
122.36
120.41
119.67
109.57
93.16
80.94
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
30.82
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
N
N
F
F
F
131.82 [16]
131.49 [16]
131.16 [16]
130.84 [16]
16 (q)
131.33
J(32.84)
127.76 [19]
125.63 [15,17]
125.59 [15,17]
125.56 [15,17]
125.52 [15,17]
15,17 (q)
125.57
J(3.75)
125.06
125.04 [19]
124.28
19 (q)
123.71
J(271.70)
123.17
122.36 [19]
120.41
119.67 [19]
f1 (ppm)
132.0
131.5
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
123.5
123.0
122.5
122.0
121.5
121.0
120.5
120.0
119.5

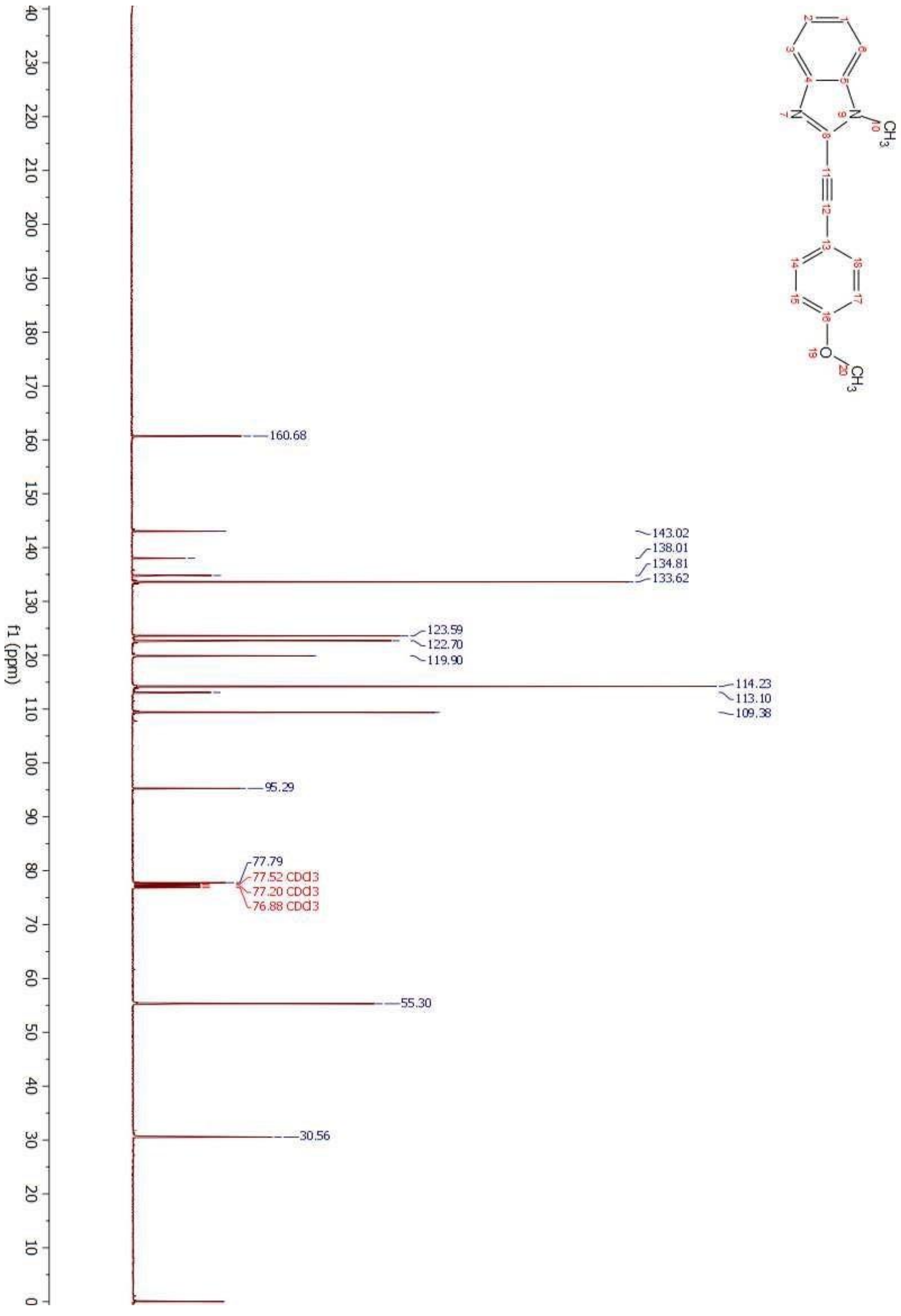

CH3
N
N
F
F
F
7.674
7.672
7.669
7.651
7.629
7.612
7.608
A (m)
7.64
4.17
7.280 CDCl3
7.118
7.114
B (d)
7.12
J(1.22)
1.00
6.972
6.969
C (d)
6.97
J(1.22)
1.02
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
7.67
7.67
7.67
7.65
7.63
7.61
7.61
7.28 CDCl3
7.12
7.11
6.97
6.97
4.17
1.00
1.02
3.10
3.81
0.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

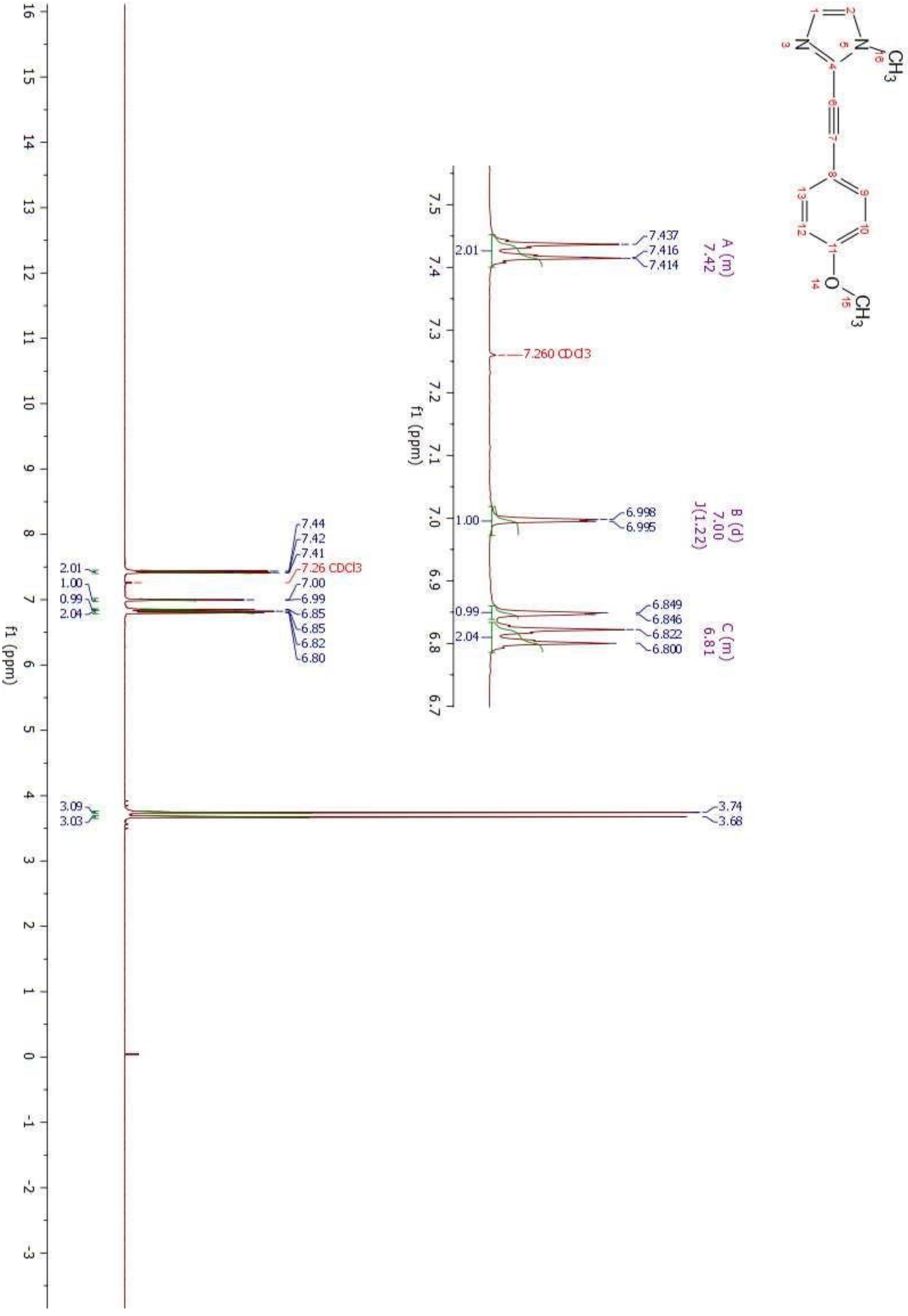

CH3
N
N
F
F
F
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
131.98
131.94
130.94
130.62
130.26
127.90
125.84
125.53
125.49
125.45
125.41
125.20
122.51
121.88
119.81
91.25
80.96
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
33.59
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

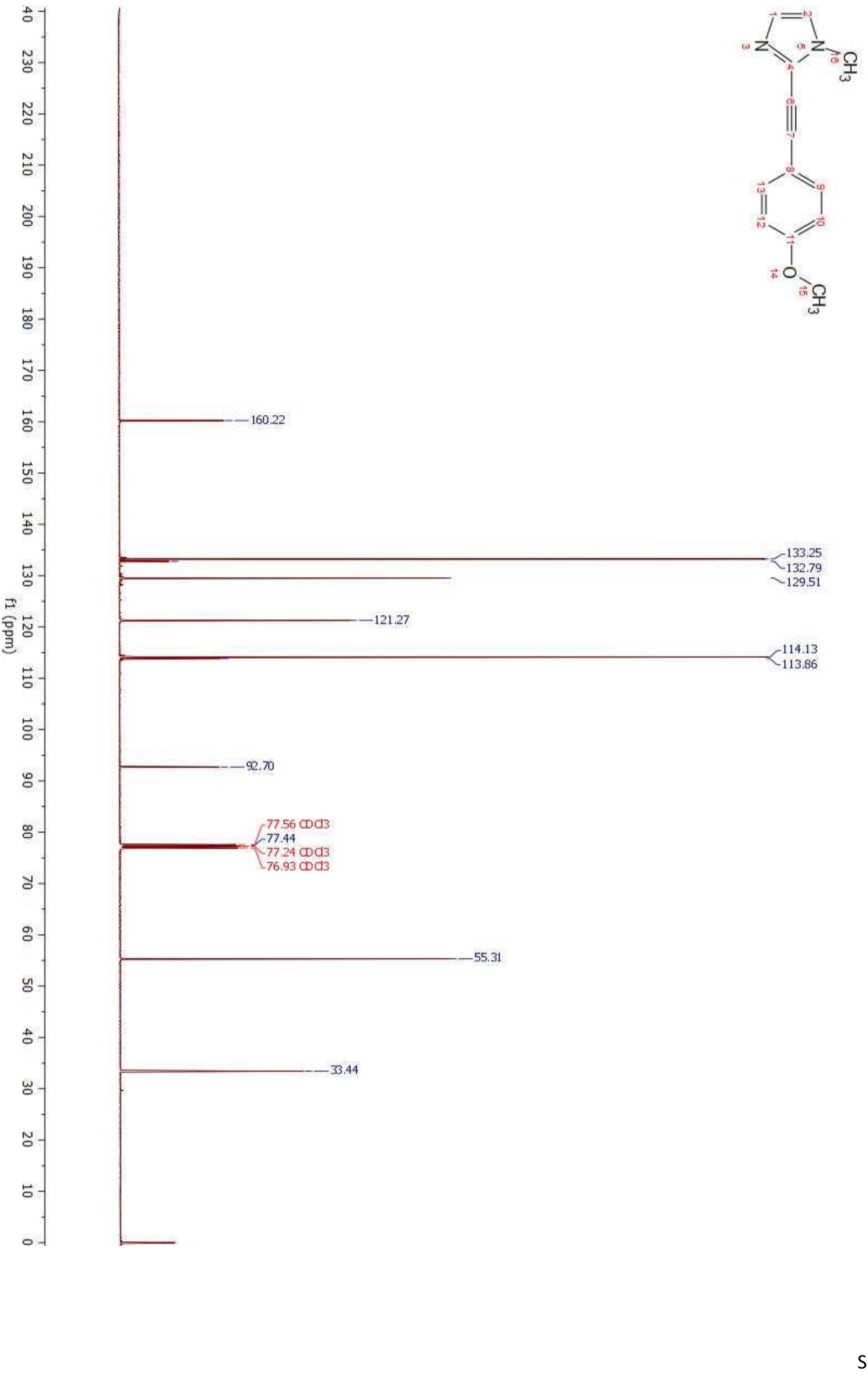

131.27 [12]
130.94 [12]
130.62 [12]
130.26
127.90 [15]
125.84
125.53 [11,13]
125.49 [11,13]
125.45 [11,13]
125.41 [11,13]
125.20 [15]
122.51 [15]
121.88
119.81 [15]
12 (q)
130.94
J(33.02)
11,13 (q)
125.47
J(3.78)
15 (q)
123.85
J(272.25)
CH3
N
N
F
F
F
f1 (ppm)
131.5
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
123.5
123.0
122.5
122.0
121.5
121.0
120.5
120.0
119.5



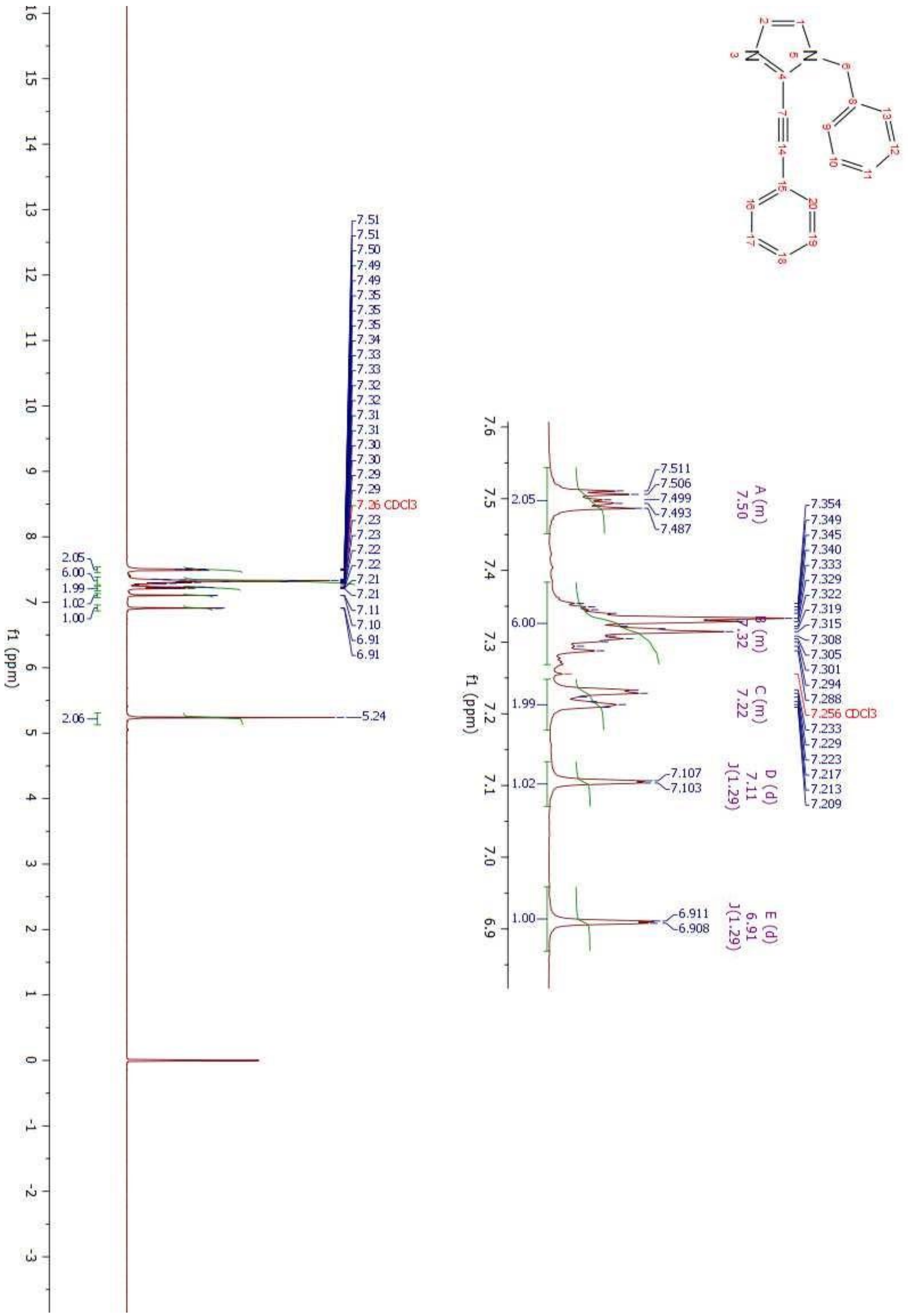
CH3
N
N
A (m)
7.74
B (m)
7.53
C (m)
7.27
D (m)
6.86
7.76
7.74
7.73
7.54
7.52
7.28
7.27
7.26
7.26
7.25
7.25
6.87
6.85
3.82
3.78
1.01
1.98
3.04
2.10
3.08
3.00
f1 (ppm)


160.68
143.02
138.01
134.81
133.62
123.59
122.70
119.90
114.23
113.10
109.38
95.29
77.79
77.52 CDCl3
77.20 CDCl3
76.88 CDCl3
55.30
30.56
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N
CH3
O
CH3

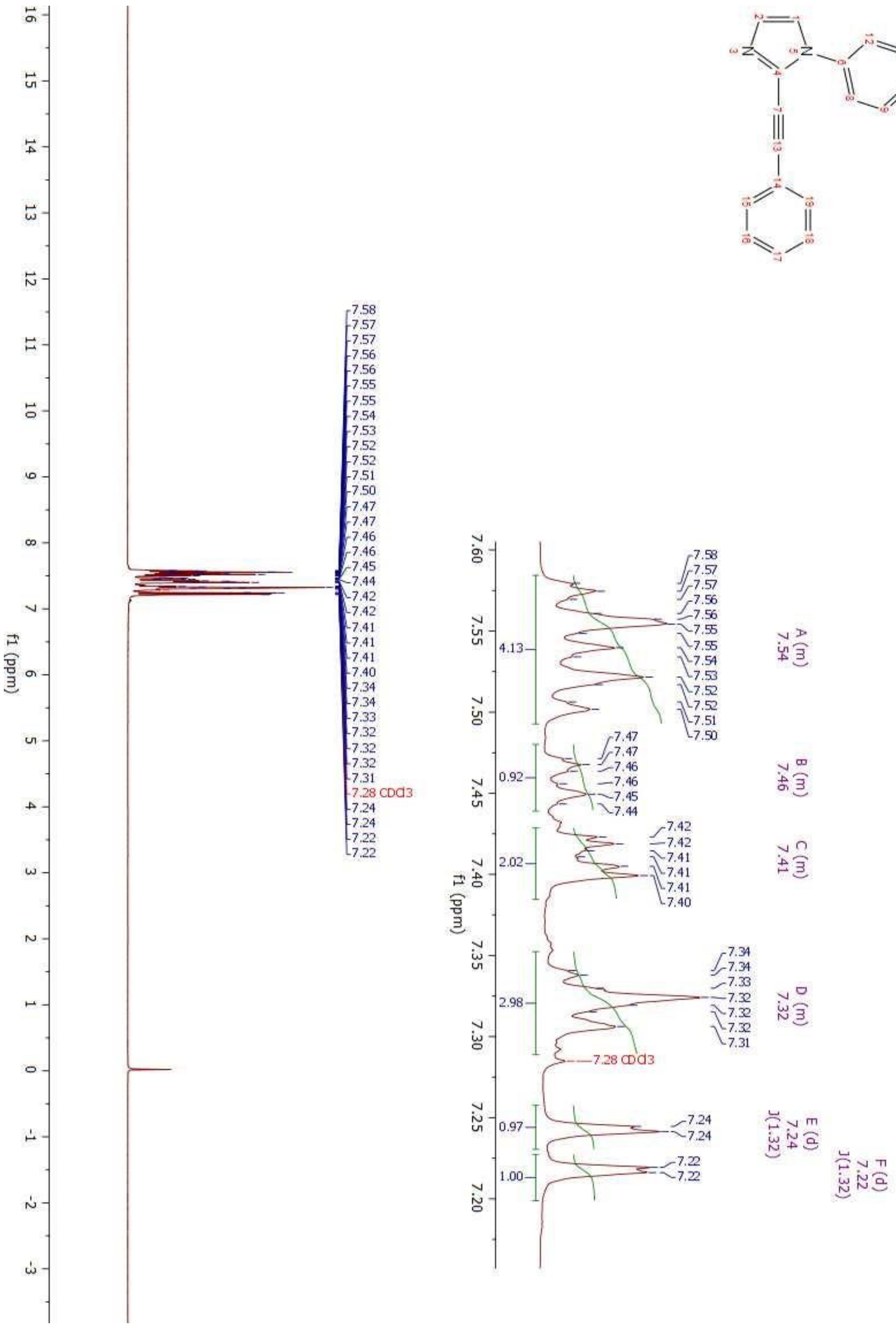

CH3
N
N
CH3
O
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
A (m)
7.42
7.437
7.416
7.414
2.01
7.260 CDCl3
B (d)
7.00
J(1.22)
6.998
6.995
1.00
C (m)
6.81
6.849
6.846
6.822
6.800
0.99
2.04
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
7.44
7.42
7.41
7.26 CDCl3
7.00
6.99
6.85
6.85
6.82
6.80
2.01
1.00
0.99
2.04
3.74
3.68
3.09
3.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)



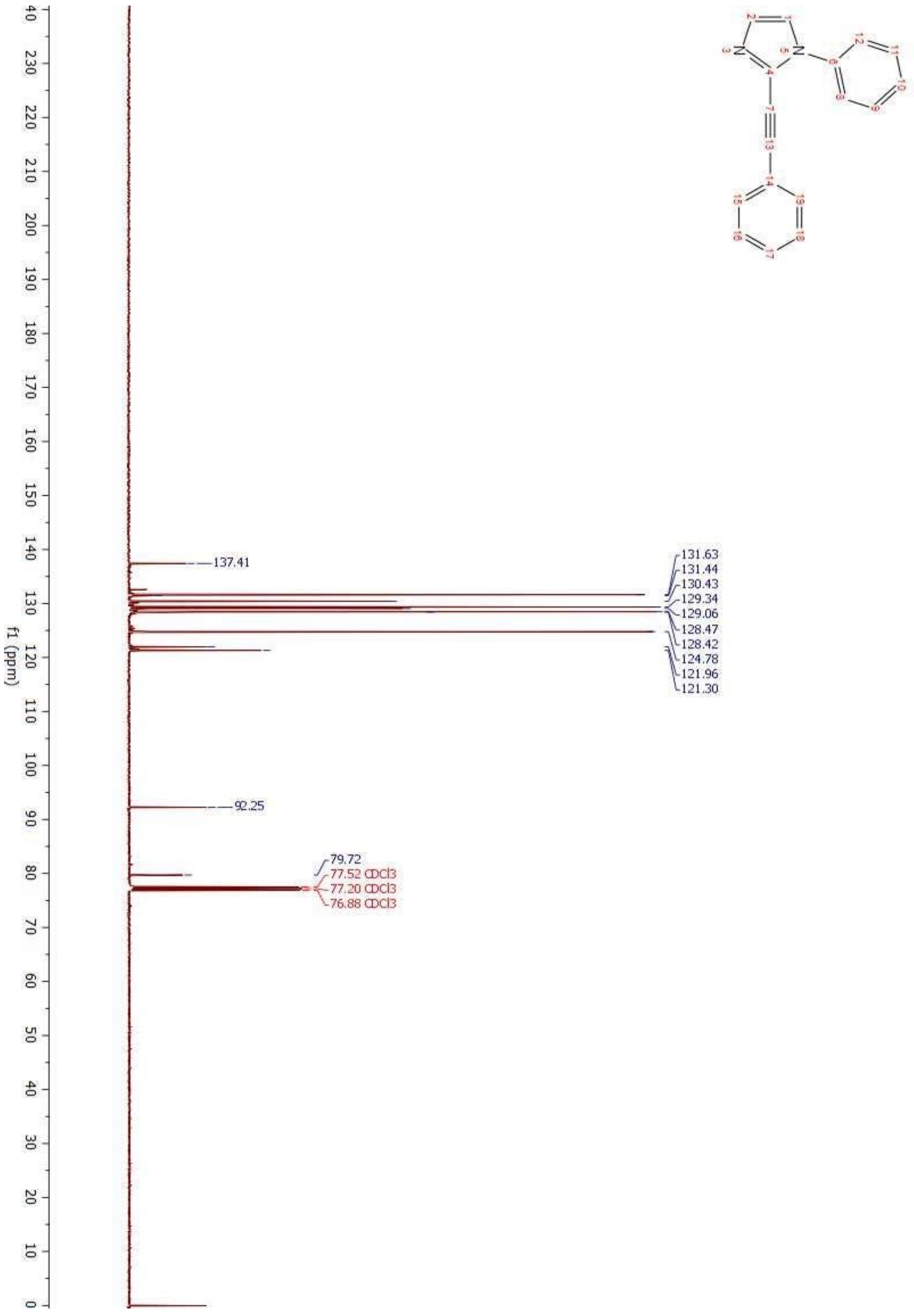
CH3
N
N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
O
CH3
160.22
133.25
132.79
129.51
121.27
114.13
113.86
92.70
77.56 CDCl3
77.44
77.24 CDCl3
76.93 CDCl3
55.31
33.44
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

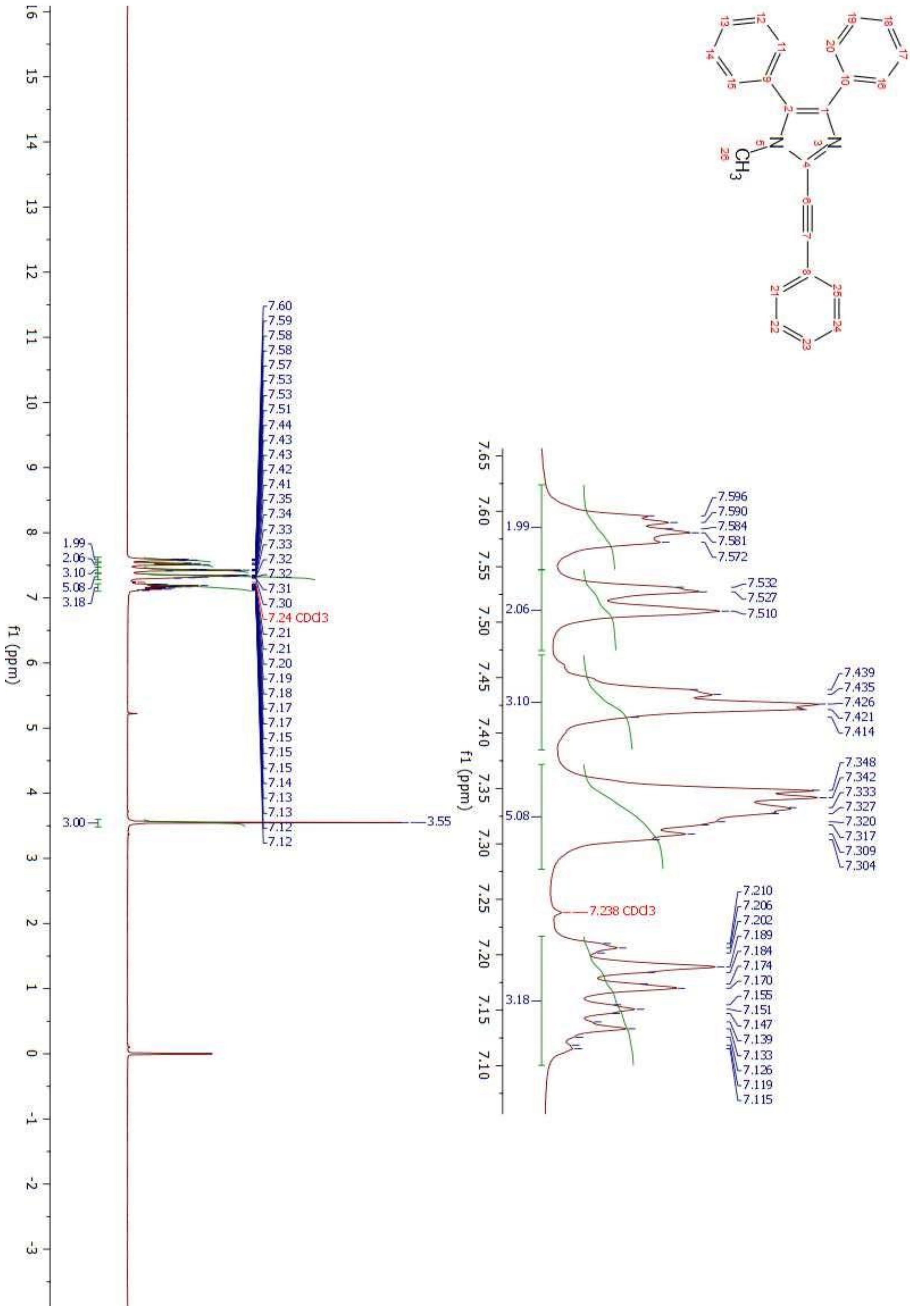


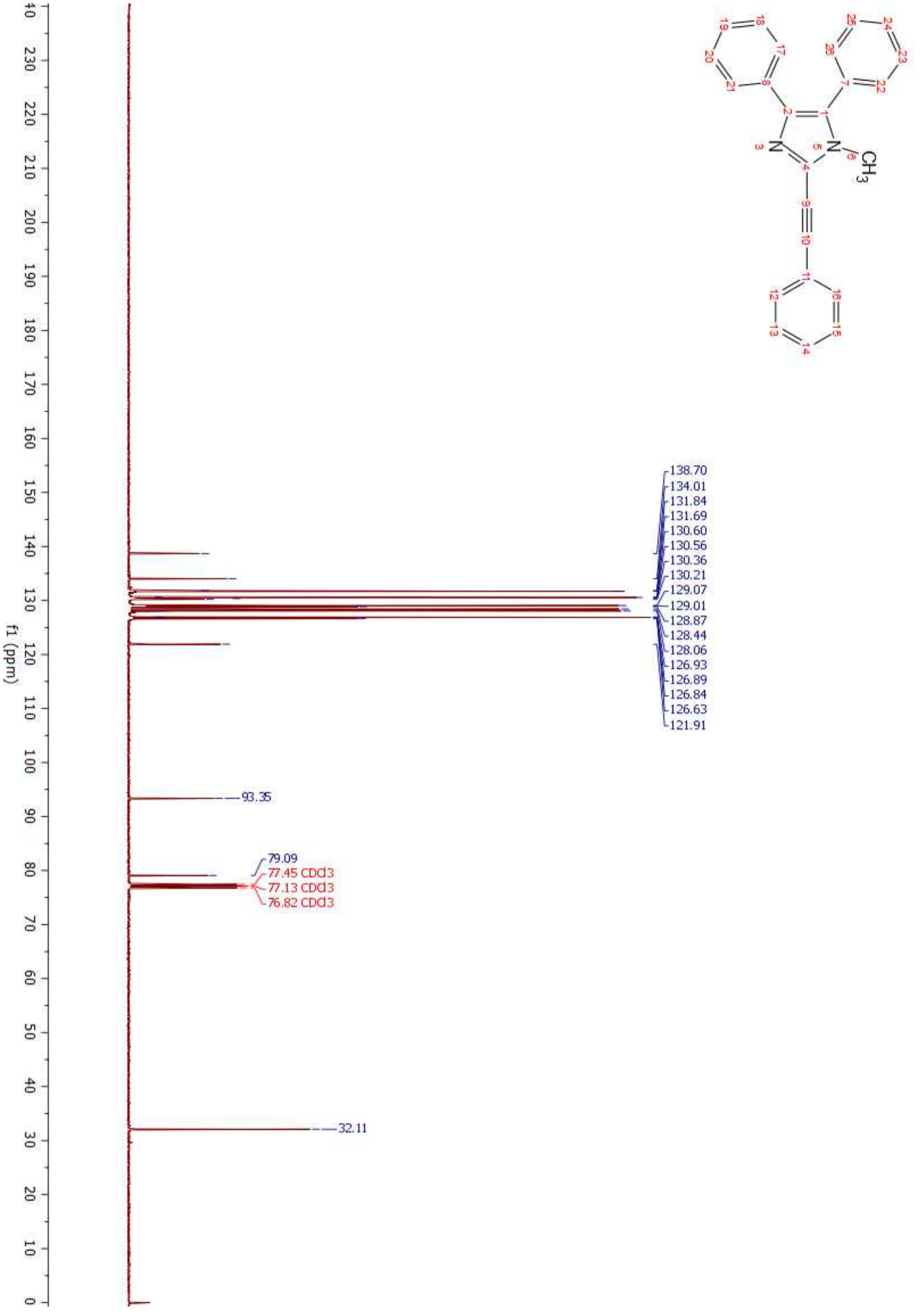
f1 (ppm)
7.51
7.51
7.50
7.49
7.49
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.26 CDCl3
7.23
7.23
7.22
7.22
7.21
7.21
7.11
7.10
6.91
6.91
5.24
2.05
6.00
1.99
1.02
1.00
2.06
A (m)
7.50
B (m)
7.32
C (m)
7.22
D (d)
7.11
J(1.29)
E (d)
6.91
J(1.29)
7.511
7.506
7.499
7.493
7.487
7.354
7.349
7.345
7.340
7.333
7.329
7.322
7.319
7.315
7.308
7.305
7.301
7.294
7.288
7.256 CDCl3
7.233
7.229
7.223
7.217
7.213
7.209
7.107
7.103
6.911
6.908
N
N



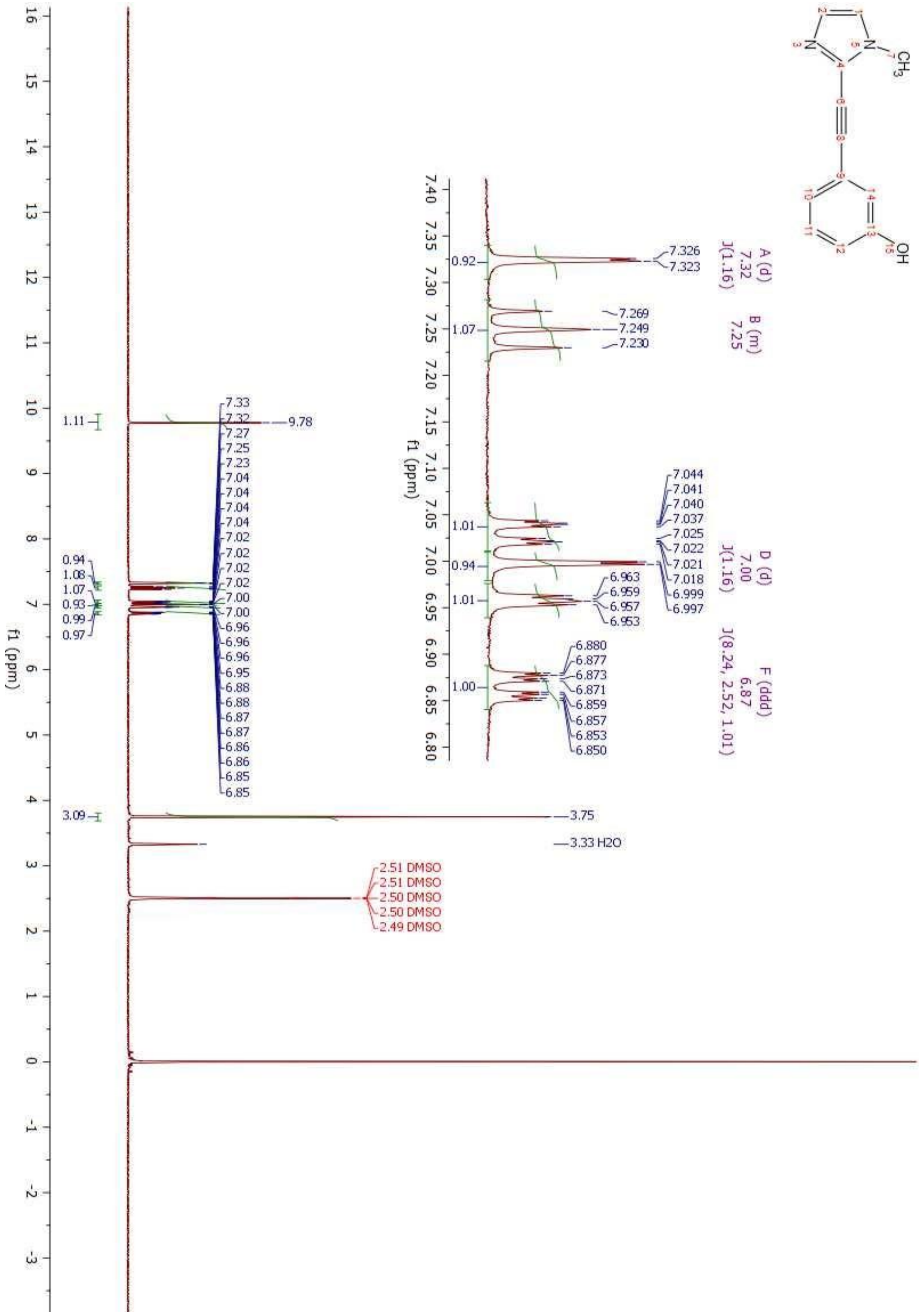
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.53
7.52
7.52
7.51
7.50
7.47
7.47
7.46
7.46
7.45
7.44
7.42
7.42
7.41
7.41
7.41
7.40
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.28 CDCl3
7.24
7.24
7.22
7.22
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
4.13
0.92
2.02
2.98
0.97
1.00
A (m)
7.54
B (m)
7.46
C (m)
7.41
D (m)
7.32
E (d)
7.24
J(1.32)
F (d)
7.22
J(1.32)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
N
N


40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
137.41
131.63
131.44
130.43
129.34
129.06
128.47
128.42
124.78
121.96
121.30
92.25
79.72
77.52 CDCl3
77.20 CDCl3
76.88 CDCl3
N
N

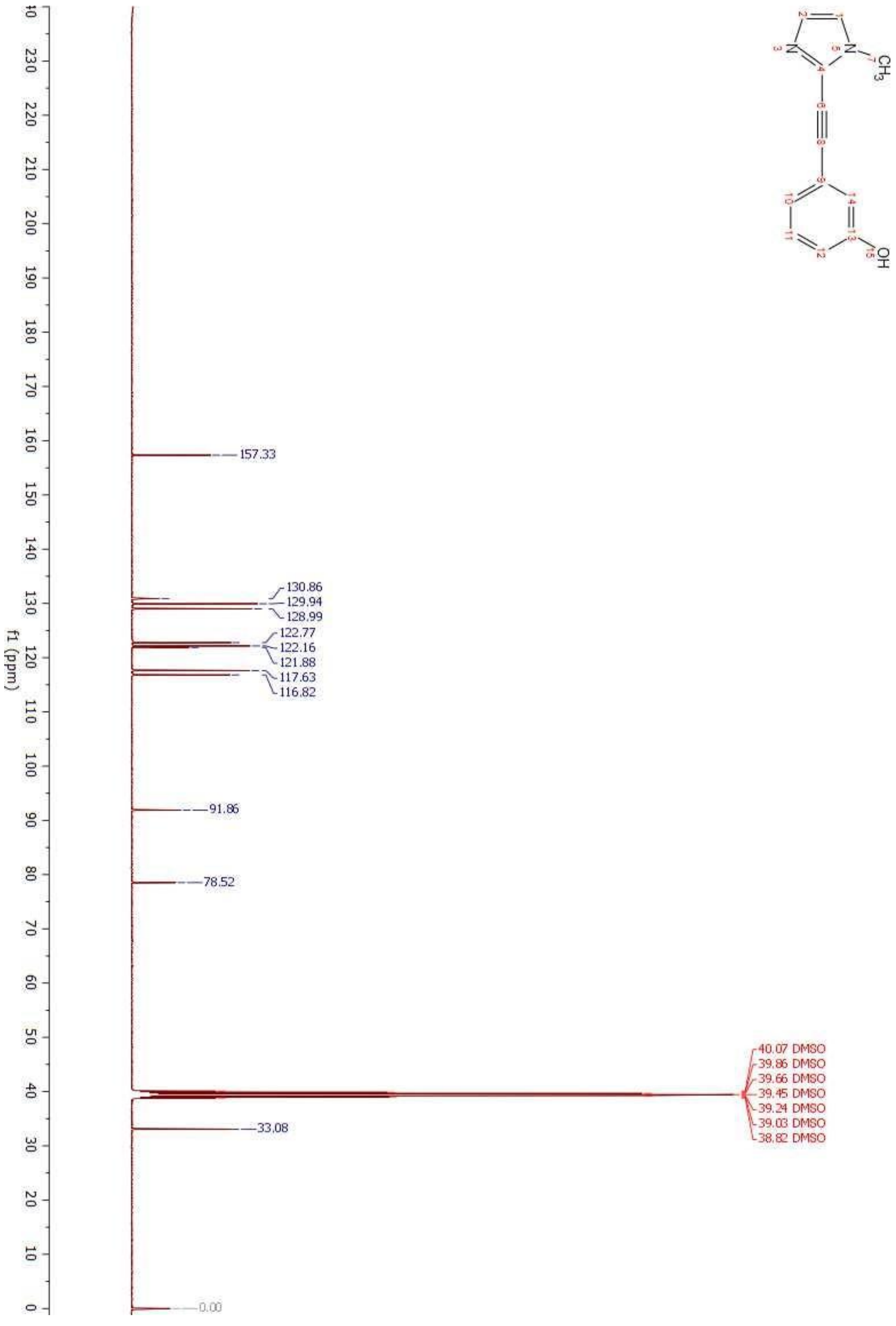

7.60
7.59
7.58
7.58
7.57
7.53
7.53
7.51
7.44
7.43
7.43
7.42
7.41
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.24 CDCl3
7.21
7.21
7.20
7.19
7.18
7.17
7.17
7.15
7.15
7.15
7.14
7.13
7.13
7.12
7.12
3.55
1.99
2.06
3.10
5.08
3.18
3.00
f1 (ppm)
7.596
7.590
7.584
7.581
7.572
7.532
7.527
7.510
7.439
7.435
7.426
7.421
7.414
7.348
7.342
7.333
7.327
7.320
7.317
7.309
7.304
7.238 CDCl3
7.210
7.206
7.202
7.189
7.184
7.174
7.170
7.155
7.151
7.147
7.139
7.133
7.126
7.119
7.115
CH3
N
N

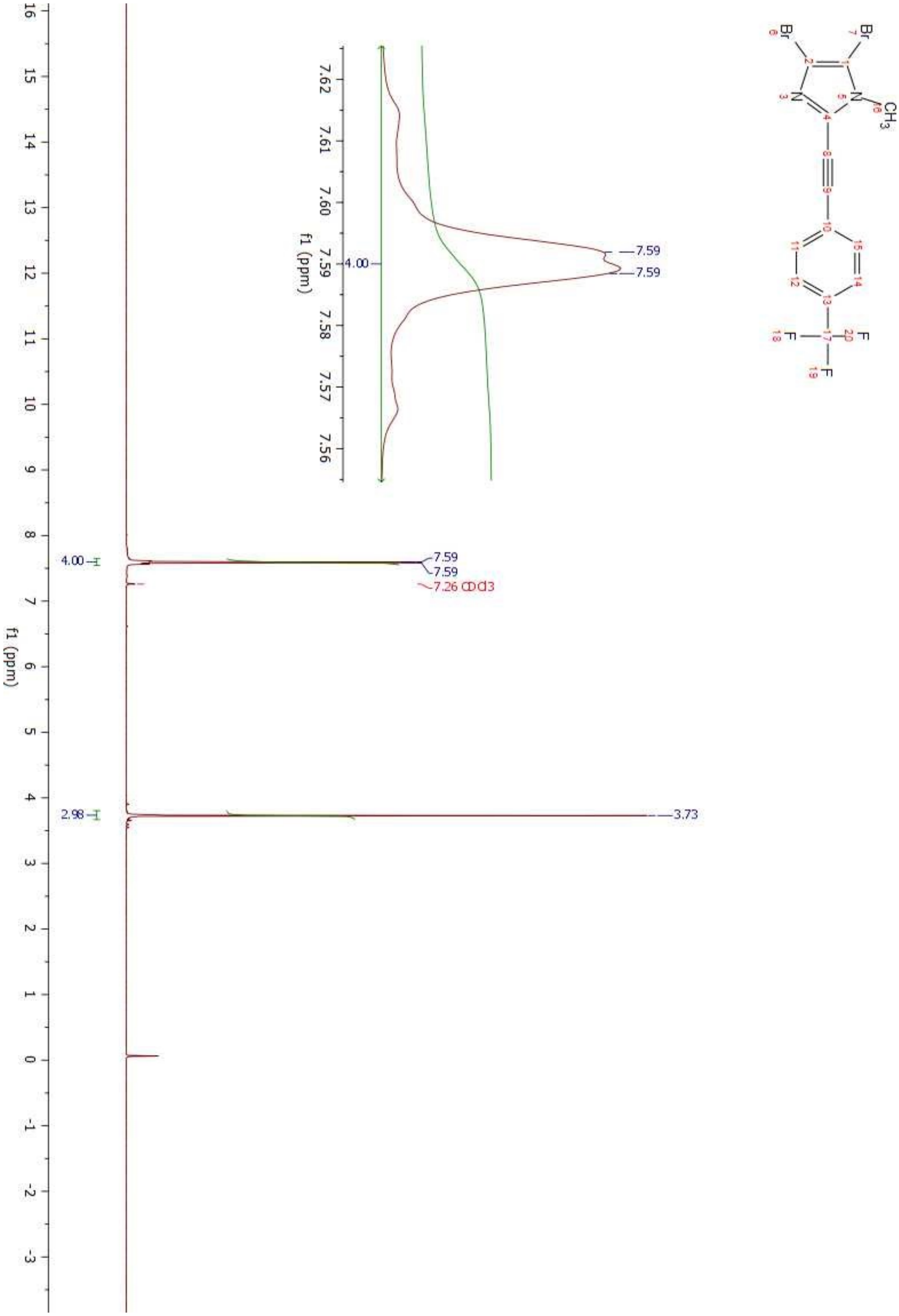


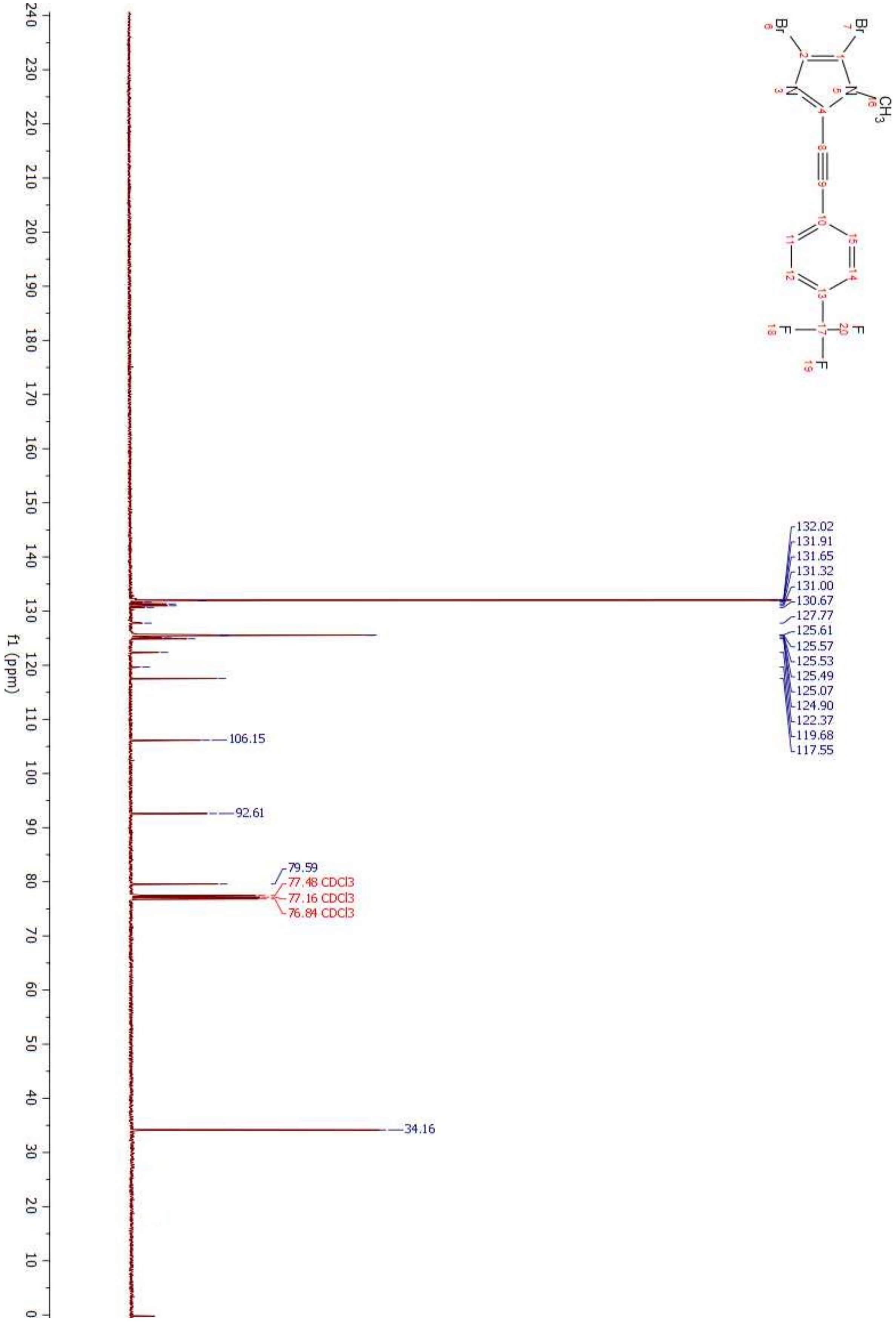
138.70
134.01
131.84
131.69
130.60
130.56
130.36
130.21
129.07
129.01
128.87
128.44
128.06
126.93
126.89
126.84
126.63
121.91
93.35
79.09
77.45 CDCl3
77.13 CDCl3
76.82 CDCl3
32.11
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
N
CH3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26



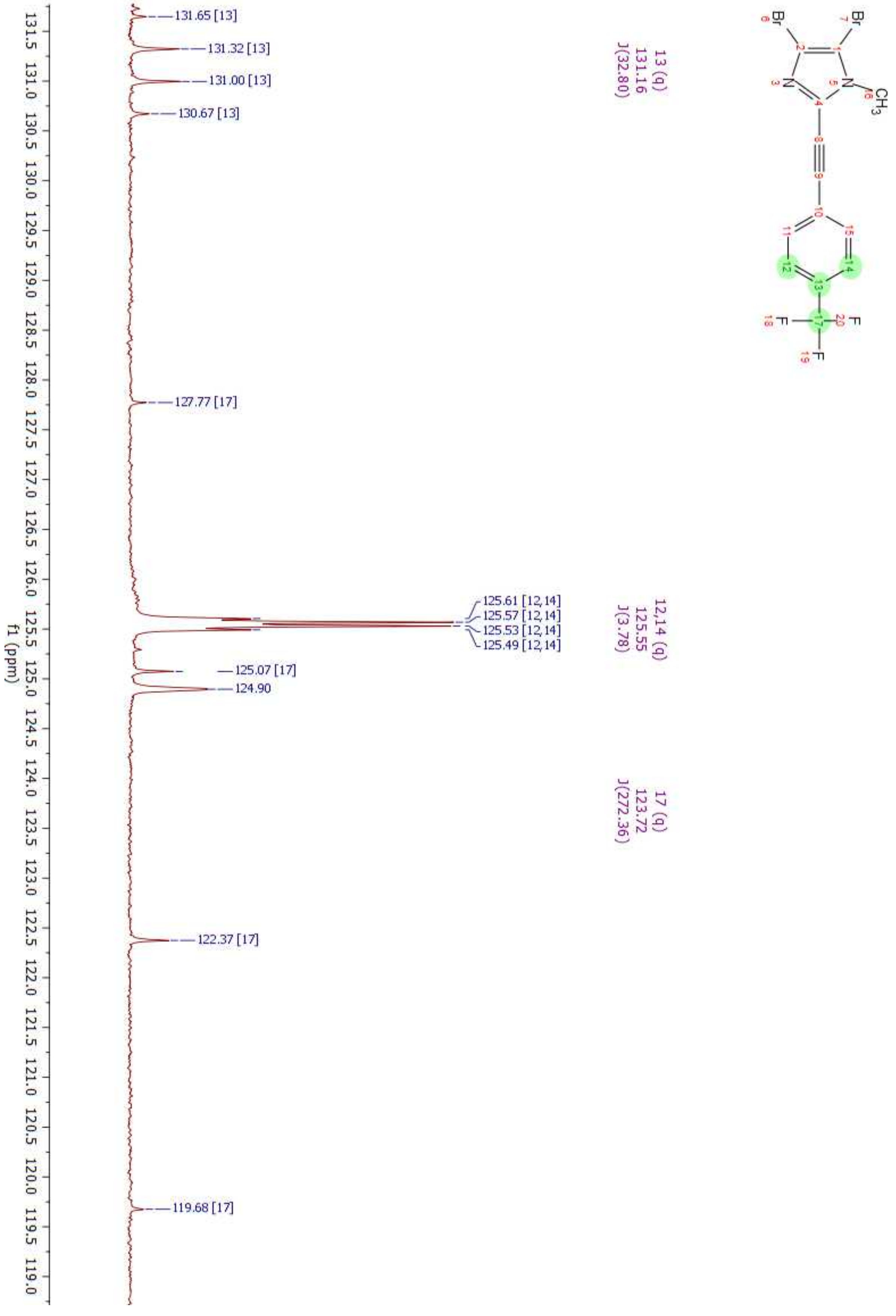
CH3
OH
A (d)
7.32
J(1.16)
7.326
7.323
B (m)
7.25
7.269
7.249
7.230
D (d)
7.00
J(1.16)
7.044
7.041
7.040
7.037
7.025
7.022
7.021
7.018
6.999
6.997
6.963
6.959
6.957
6.953
F (ddd)
6.87
J(8.24, 2.52, 1.01)
6.880
6.877
6.873
6.871
6.859
6.857
6.853
6.850
0.92
1.07
1.01
0.94
1.01
1.00
f1 (ppm)
9.78
1.11
0.94
1.08
1.07
0.93
0.99
0.97
3.75
3.09
3.33 H2O
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO

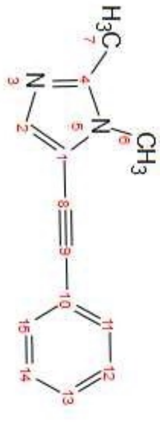

CH3
OH
N
N
157.33
130.86
129.94
128.99
122.77
122.16
121.88
117.63
116.82
91.86
78.52
40.07 DMSO
39.86 DMSO
39.66 DMSO
39.45 DMSO
39.24 DMSO
39.03 DMSO
38.82 DMSO
33.08
0.00
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

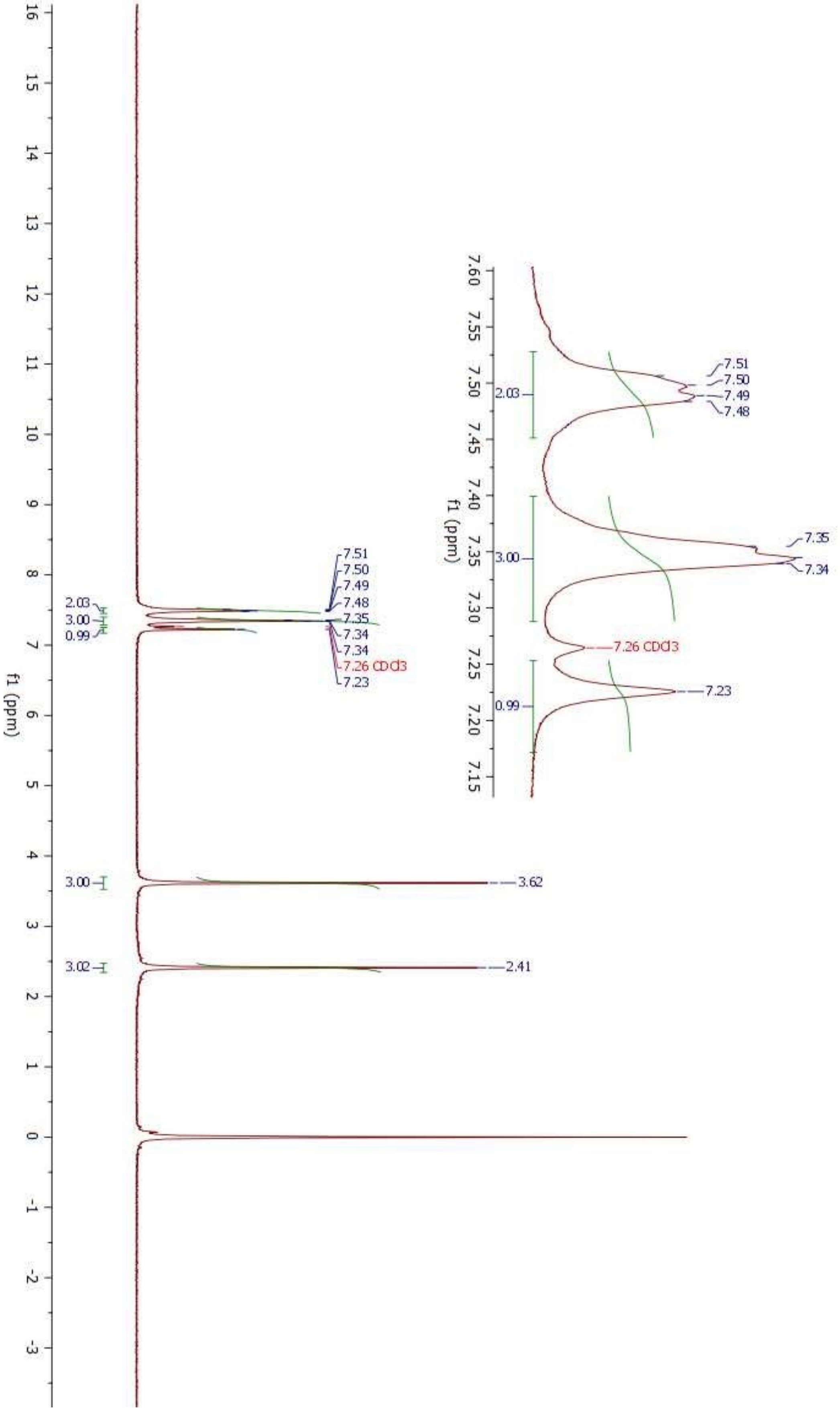

Br
Br
N
N
CH3
F
F
F
7.59
7.59
4.00
7.62
7.61
7.60
7.59
7.58
7.57
7.56
f1 (ppm)
4.00
7.59
7.59
7.26 CDCl3
2.98
3.73
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

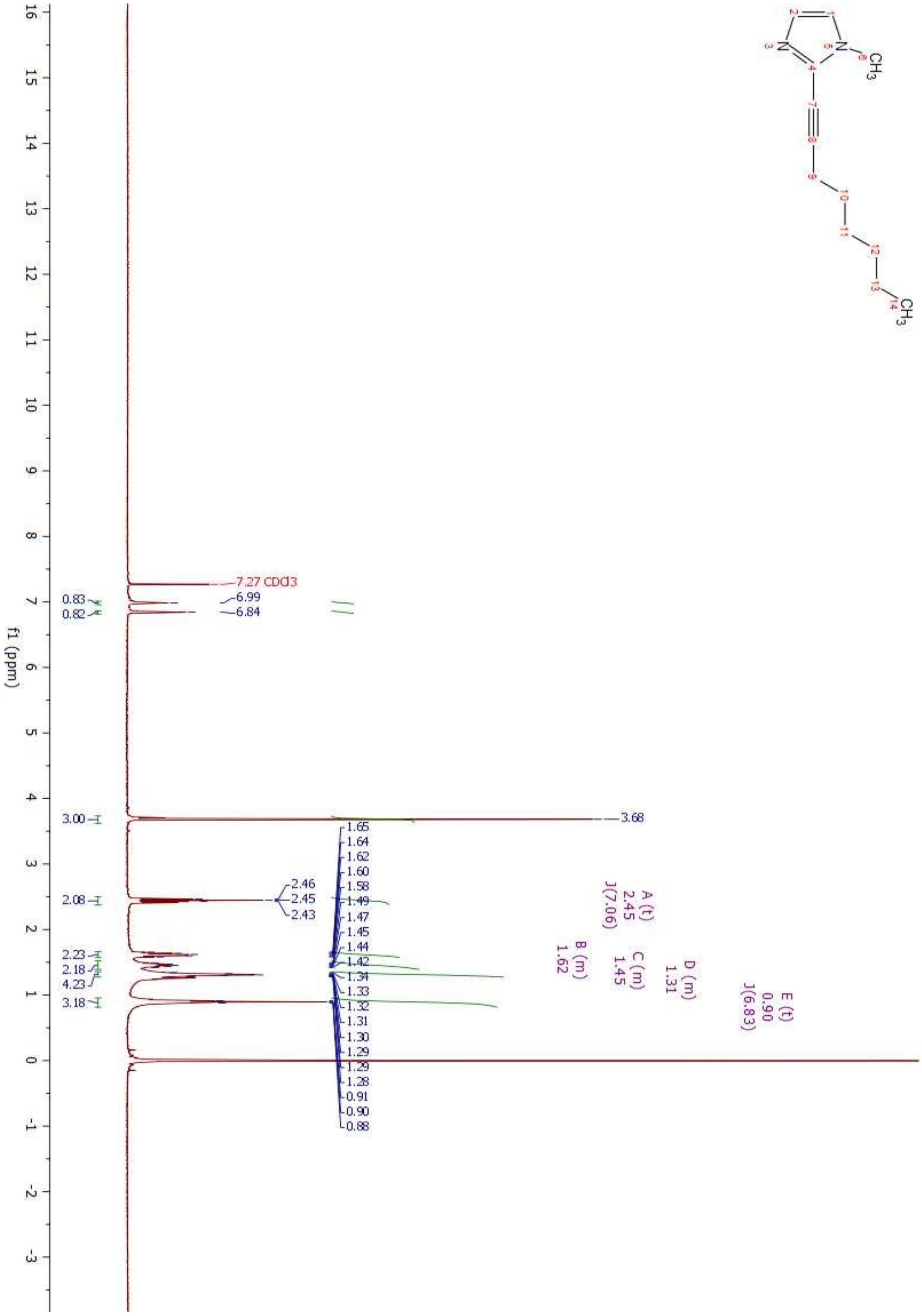


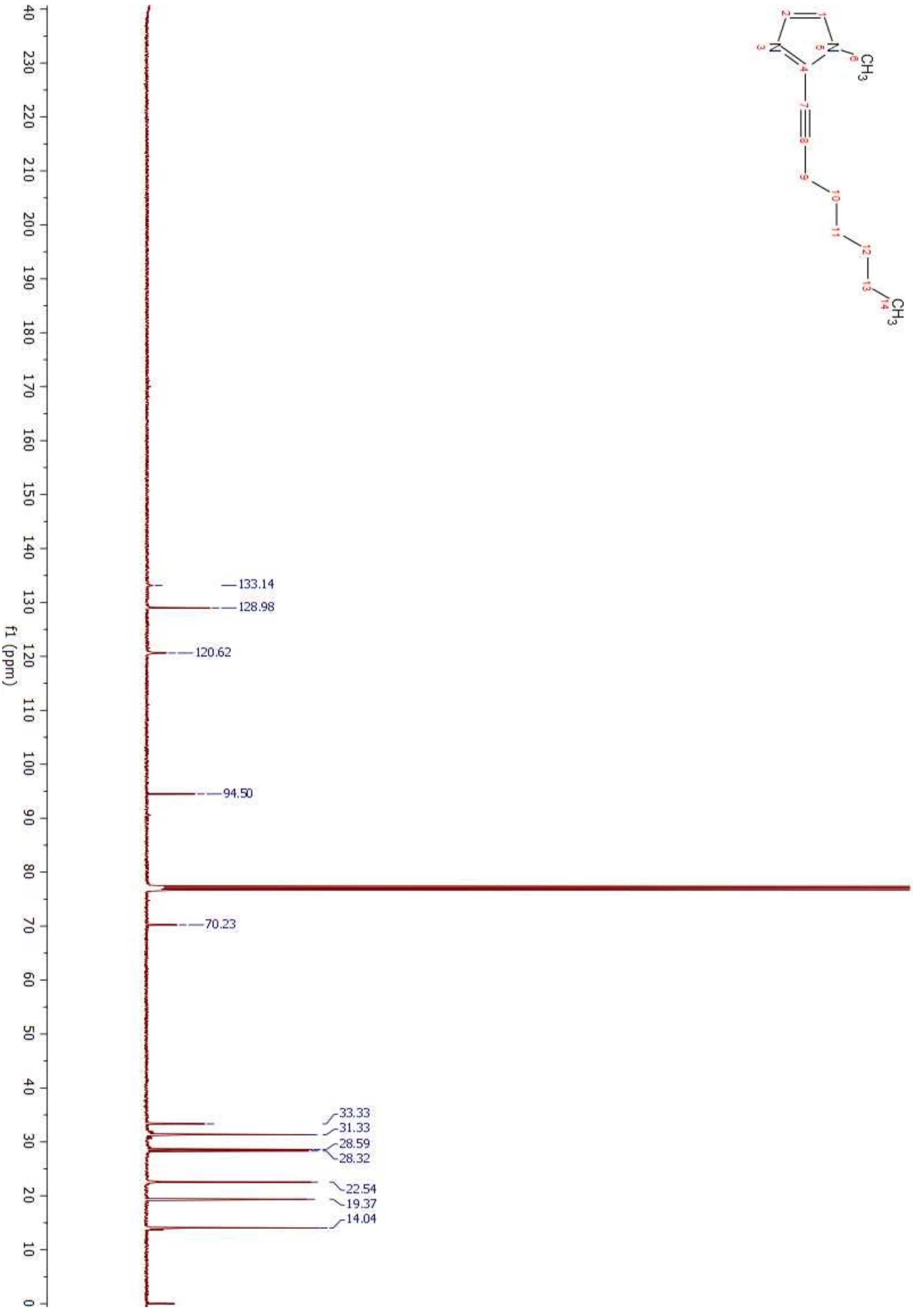
Br
Br
N
N
CH3
F
F
F
132.02
131.91
131.65
131.32
131.00
130.67
127.77
125.61
125.57
125.53
125.49
125.07
124.90
122.37
119.68
117.55
106.15
92.61
79.59
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
34.16
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

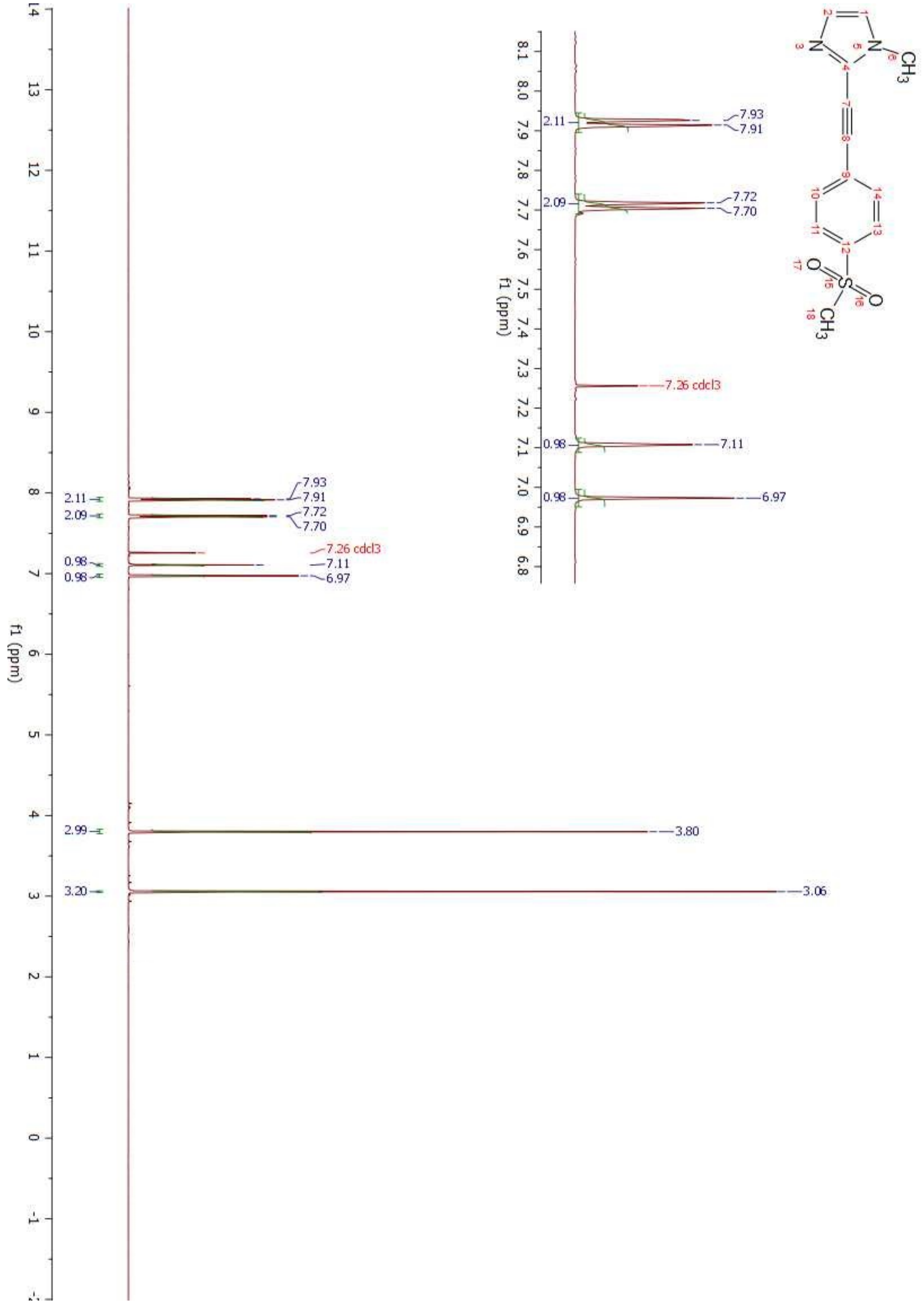

Br 7
Br 6
CH3 16
N 5
N 3
F 18
F 19
F 20
13 (q)
131.16
J(32.80)
12,14 (q)
125.55
J(3.78)
17 (q)
123.72
J(272.36)
131.65 [13]
131.32 [13]
131.00 [13]
130.67 [13]
127.77 [17]
125.61 [12,14]
125.57 [12,14]
125.53 [12,14]
125.49 [12,14]
125.07 [17]
124.90
122.37 [17]
119.68 [17]
f1 (ppm)
131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5 121.0 120.5 120.0 119.5 119.0


H3C
CH3
N
N
N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

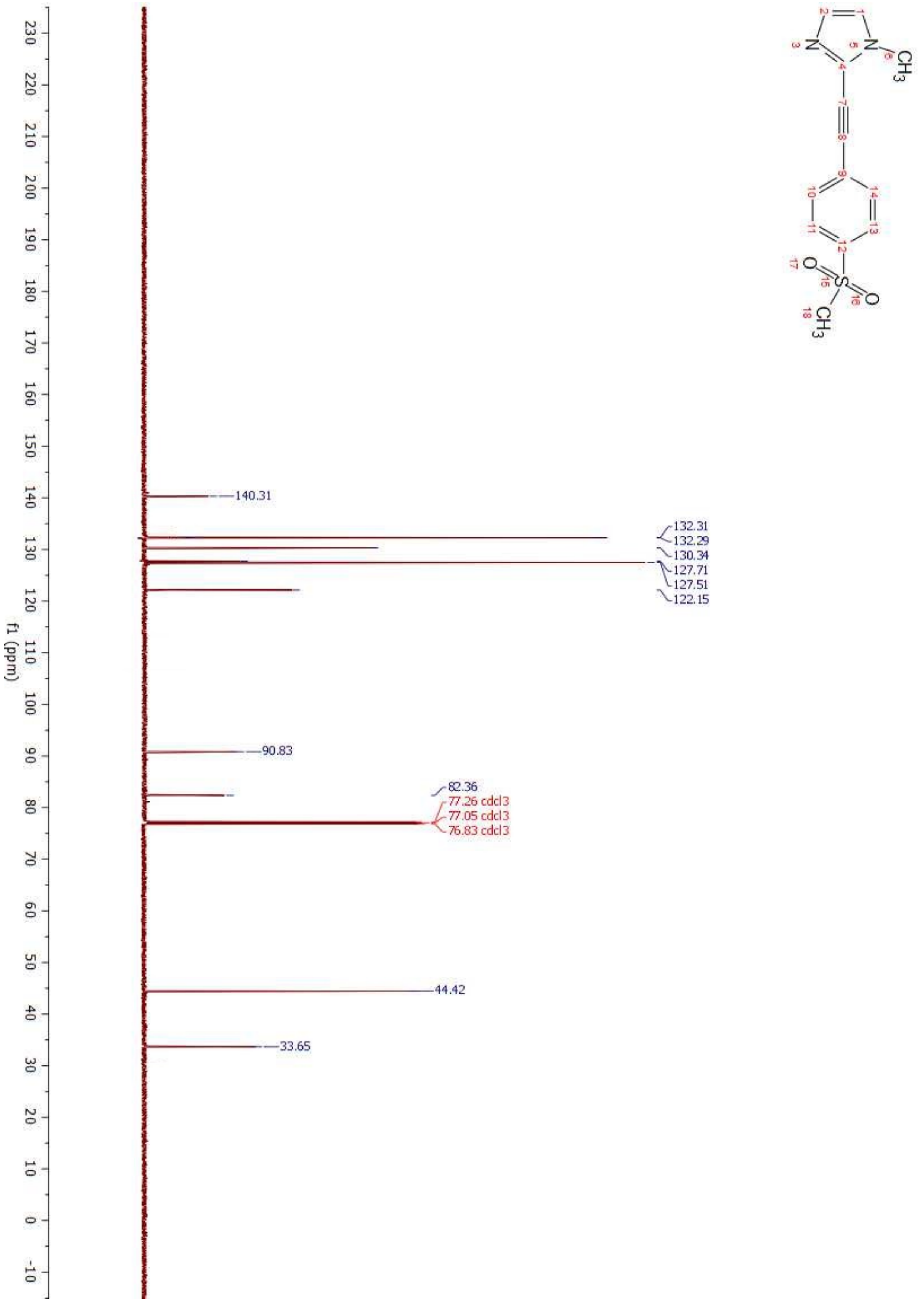

7.51
7.50
7.49
7.48
7.35
7.34
7.34
7.26 CDCl3
7.23
3.62
2.41
2.03
3.00
0.99
3.00
3.02
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15


CH3
CH3
7.27 CDCl3
6.99
6.84
3.68
2.46
2.45
2.43
1.65
1.64
1.62
1.60
1.58
1.49
1.47
1.45
1.44
1.42
1.34
1.33
1.32
1.31
1.30
1.29
1.29
1.28
0.91
0.90
0.88
A (t)
2.45
J(7.06)
B (m)
1.62
C (m)
1.45
D (m)
1.31
E (t)
0.90
J(6.83)
0.83
0.82
3.00
2.08
2.23
2.18
4.23
3.18
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3


CH3
CH3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
N
N
133.14
128.98
120.62
94.50
70.23
33.33
31.33
28.59
28.32
22.54
19.37
14.04
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



7.93
7.91
7.72
7.70
7.26 cdcl3
7.11
6.97
3.80
3.06
2.11
2.09
0.98
0.98
2.99
3.20
f1 (ppm)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
CH3
N
N
O
S
O
CH3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18



140.31
132.31
132.29
130.34
127.71
127.51
122.15
90.83
82.36
77.26 cdcl3
77.05 cdcl3
76.83 cdcl3
44.42
33.65
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
N
N
CH3
O
S
O
CH3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

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