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Supporting Information

Synthesis of 1-Aryl-1*H*-1,2,3-triazoles through the One-pot Cascade Reactions of Alkynes with Aliphatic Azides and Allenic Ketones

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Table of Contents

I. General Experimental Information

Reagents and solvents were purchased from commercial suppliers and used without further purification. 1-Aryl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,[1] which were prepared through zinc promoted propargylation of aldehydes.[2] 1,4-Disubsituted allenic ketones were prepared from the reaction of 1-(triphenylphosphoranylidene)-2-propanone or 2-(triphenylphosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.[3] The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm from the internal standard tetramethylsilane. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. Coupling constants were given in hertz. High-resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental Procedures and Spectroscopic Data

1. Typical procedure for the synthesis of 4a and spectroscopic data of 4a-4gg

To a flask containing ethynyl-3-methylbenzene (**1a**, 56.1 mg, 0.55 mmol) and ethyl 4-azido-3-oxobutanoate (**2**, 85.5 mg, 0.5 mmol) in *t*-BuOH/H_2O (5 mL, v/v = 1/1) were added $CuSO_4·5H_2O$ (aqueous solution, 25 μL, 1 M, 0.025 mmol) and sodium ascorbate (9.9 mg, 0.05 mmol). The mixture was stirred at room temperature for 12 h. Upon completion as monitored by TLC, the flask was charged with 1-phenylbuta-2,3-dien-1-one (**3a**, 79.2 mg, 0.55mmol) and NaOH (40.0 mg, 1.0 mmol). The mixture was stirred at 80 ℃ for 1.5 h. After being cooled to room temperature, it was quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give **4a** (128.0 mg, 64%). Other 1-aryl-1*H*-1,2,3-triazole derivatives **4b-4dd** were obtained in a similar manner.

Ethyl 3-hydroxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4a)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (128.0 mg, 64%); Mp: 144-145 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 7.2 Hz, 3H), 2.69 (s, 3H), 4.50 (q, *J* = 7.6 Hz, 2H), 6.93 (s, 1H), 7.20-7.16 (m, 2H), 7.25-7.22 (m, 3H), 7.32-7.28 (m, 1H), 7.40-7.37 (m, 2H), 7.70 (s, 1H), 7.81-7.78 (m, 2H), 12.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 62.4, 112.4, 122.0, 122.9, 124.3, 125.8, 128.1, 128.0, 128.5, 128.7, 130.5, 136.5, 143.5, 144.6, 147.1, 158.7, 171.2. HRMS (ESI): calcd for $C_{24}H_{22}N_3O_3$ $[M+H]^+$: 400.1656; found: 400.1663.

Ethyl 2'-bromo-3-hydroxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4b) Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (143.1 mg, 60%); Mp: 168-169 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 6.8 Hz, 3H), 2.69 (s, 3H), 4.52 (q, *J* = 7.2 Hz, 2H), 6.82 (s, 1H), 7.10 (7, *J* = 7.6 Hz, 1H), 7.31-7.18 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.89 (s, 1H), 12.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 62.5, 113.2, 121.9, 122.6, 122.8, 124.5, 125.8, 127.2, 128.0, 128.7, 130.0, 130.6, 130.8, 132.4, 137.4, 143.2, 144.0, 146.5, 158.1, 171.2. HRMS (ESI): calcd for $C_{24}H_{21}BrN_3O_3$ $[M+H]^+$: 478.0761; found: 478.0768.

Ethyl 3-hydroxy-4',5-dimethyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4c)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (130.1 mg, 63%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 6.8 Hz, 3H), 2.27 (s, 3H), 2.68 (s, 3H), 4.49 (q, *J* = 6.8 Hz, 2H), 6.92 (s, 1H), 7.08- 7.02 (m, 4H), 7.32-7.28 (m, 1H), 7.41-7.38 (m, 2H), 7.71 (s, 1H), 7.83-7.80 (m, 2H), 12.06 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.2, 24.4, 62.4, 112.1, 121.9, 122.9, 124.3, 125.8, 127.98, 128.0, 128.7, 129.3, 130.6, 133.5, 138.5, 143.4, 144.7, 147.1, 158.8, 171.3. HRMS (ESI): calcd for $C_{25}H_{24}N_3O_3$ $[M+H]^+$: 414.1812; found: 414.1811.

Ethyl 3-hydroxy-3',4'-dimethoxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4d)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (149.6 mg, 65%); Mp: 170-171 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (t, *J* = 6.8 Hz, 3H), 2.67 (s, 3H), 3.65 (s, 3H), 3.79 (s, 3H), 4.47 (q, *J* = 6.8 Hz, 2H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.30-7.26 (m, 1H), 6.93 (s, 1H), 7.39-7.35 (m, 2H), 7.67 (s, 1H), 7.78-7.76 (m, 2H), 12.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 55.8, 55.9, 62.4, 111.0, 111.9, 120.9, 121.7, 122.9, 123.9, 125.8, 128.1, 128.77, 128.8, 130.4, 143.6, 144.2, 147.3, 148.7, 149.3, 159.0, 171.3. HRMS (ESI): calcd for $C_{26}H_{26}N_3O_5$ $[M+H]^+$: 460.1867; found: 460.1877.

Ethyl 2'-bromo-3-hydroxy-5'-methoxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4e)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (152.4 mg, 60%); Mp: 180-182 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 7.2 Hz, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 4.51 (q, *J* = 7.2 Hz, 2H), 6.65 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.78 (d, *J* = 2.8 Hz, 1H), 7.41-7.29 (m, 4H), 6.82 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 1H), 12.08 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 55.5, 62.5, 112.1, 113.2, 115.8, 116.5, 122.7, 124.4, 125.8, 128.0, 128.8, 130.5, 133.1, 138.0, 143.2, 143.9, 146.6, 158.2, 158.5, 171.2. HRMS (ESI): calcd for $C_{25}H_{23}BrN_3O_4$ $[M+H]^+$: 508.0866; found: 508.0878.

Ethyl 2-(4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4f)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (149.7 mg, 69%); Mp: 151-152 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 7.2 Hz, 3H), 2.69 (s, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 6.93 (s, 1H), 7.17-7.15 (m,

2H), 7.25-7.22 (m, 3H), 7.36-7.33 (m, 2H), 7.68 (s, 1H), 7.74-7.70 (m, 2H), 12.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 62.5, 112.4, 121.9, 122.9, 124.3, 127.1, 128.1, 128.5, 128.6, 128.9, 133.8, 136.4, 143.7, 144.6, 146.0, 158.6, 171.2. HRMS (ESI): calcd for $C_{24}H_{21}ClN_3O_3$ $[M+H]^+$: 434.1266; found: 434.1276.

Ethyl 2'-bromo-2-(4-(4-chlorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5'-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4g)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (165.3 mg, 61%); Mp: 177-179 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, J = 6.8 Hz, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 4.50 (q, J = 7.2 Hz, 2H), 6.65 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.77 (d, J = 3.2 Hz, 1H), 6.81 (s, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.90 (s, 1H), 12.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 55.5, 62.6, 112.1, 113.2, 115.9, 116.5, 122.5, 122.8, 124.5, 127.0, 128.9, 129.1, 133.1, 133.7, 138.0, 143.4, 143.8, 145.5, 158.1, 158.5, 171.2. HRMS (ESI): calcd for $C_{25}H_{22}BrClN_3O_4$ $[M+H]^+$: 542.0477; found: 542.0473.

Ethyl 2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4h)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (142.2 mg, 68%); Mp: 154-155 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, J = 7.6 Hz, 3H) , 2.69 (s, 3H), 4.49 (q, J = 7.6 Hz, 2H), 6.92 (s, 1H), 7.08-7.04 (m, 2H), 7.18-7.16 (m, 2H), 7.24-7.22 (m, 3H), 7.66 (s, 1H), 7.76-7.73 (m, 2H), 12.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 62.5, 112.4, 115.7 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 121.9, 122.6, 124.3, 126.8 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 127.5 (d, $^3J_{C\text{-}F}$ = 7.4 Hz), 128.1, 128.5, 136.5, 143.6, 144.6, 146.2, 158.7, 162.6 (d, $^1J_{C\text{-}F}$ = 245.8 Hz), 171.2. HRMS (ESI): calcd for $C_{24}H_{21}FN_3O_3$ $[M+H]^+$: 418.1561; found: 418.1562.

Ethyl 2'-bromo-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4i)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (153.8 mg, 62%); Mp: 171-172 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, J = 7.2 Hz, 3H), 2.69 (s, 3H), 4.51 (q, J = 6.8 Hz, 2H), 6.81 (s, 1H), 7.12-7.04 (m, 3H), 7.26-7.19 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.75-7.72 (m, 2H), 7.85 (s, 1H), 12.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 62.5, 113.2, 115.7 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 121.9, 122.4, 122.7, 124.5, 126.7 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 127.2, 127.5 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 129.9, 130.8, 132.4, 137.4, 143.2, 143.9, 145.7, 158.1,

162.6 (d, $^{1}J_{C\text{-}F}$ = 245.6 Hz), 171.2. HRMS (ESI): calcd for $C_{24}H_{20}BrFN_3O_3$ $[M+H]^+$: 496.0667; found: 496.0678.

Ethyl 2'-bromo-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5'-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4j)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (147.3 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 7.2 Hz, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 6.66 (dd, J_1 = 8.8 Hz, J_2 = 3.6 Hz, 1H), 6.77 (d, *J* = 2.8 Hz, 1H), 6.81 (s, 1H), 7.05-7.09 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.72-7.76 (m, 2H), 7.86 (s, 1H), 12.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 55.5, 62.6, 112.1, 113.2, 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 115.9, 116.5, 122.5, 122.6, 124.4, 126.7 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 127.5 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 133.1, 138.1, 143.3, 143.8, 145.7, 158.1, 158.5, 162.6 (d, $^{1}J_{C\text{-}F}$ = 245.5 Hz), 171.2. HRMS (ESI): calcd for $C_{25}H_{22}BrFN_3O_4$ $[M+H]^+$: 526.0772; found: 526.0777.

Ethyl 2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4k)

Eluent: ethyl acetate/petroleum ether (1/8); Brown solid (169.7 mg, 71%); Mp: 162-164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 7.2 Hz, 3H), 2.68 (s, 3H), 4.49 (q, *J* = 7.6 Hz, 2H), 6.92 (s, 1H), 7.17-7.14 (m, 2H), 7.24-7.21 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.70 (s, 1H), 12.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 62.5, 112.4, 121.9, 124.3, 123.0, 127.3, 128.1, 128.53, 128.56, 129.5, 131.9, 136.4, 143.7, 144.6, 146.1, 158.6, 171.2. HRMS (ESI): calcd for $C_{24}H_{21}BrN_3O_3$ $[M+H]^+$: 478.0761; found: 478.0770.

Ethyl 2'-bromo-2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4l)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow solid (147.3 mg, 53%); Mp: 165-166 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 7.6 Hz, 3H), 2.69 (s, 3H), 4.51 (q, *J* = 7.6 Hz, 2H), 6.82 (s, 1H), 7.12-7.08 (m, 1H), 7.26-7.18 (m, 2H), 7.50-7.46 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.89 (s, 1H), 12.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 62.6, 113.2, 121.8, 121.9, 122.6, 122.7, 124.5, 127.2, 127.3, 129.5, 129.9, 130.8, 131.9, 132.4, 137.3, 143.3, 143.9, 145.5, 158.0, 171.2. HRMS (ESI): calcd for $C_{24}H_{20}Br_2N_3O_3$ $[M+H]^+$: 555.9866; found: 555.9876.

Ethyl 2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (4m)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (180.2 mg, 66%); Mp: 169-170 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 6.8 Hz, 3H), 2.70 (s, 3H), 4.51 (q, *J* = 7.2 Hz, 2H), 6.90 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.52-7.49 (m, 4H), 7.86-7.66 (m, 2H), 7.80 (s, 1H), 12.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 62.7, 113.0, 121.9, 122.1, 122.9, 124.2, 127.9 (q, $^{1}J_{C\text{-}F}$ = 270.0 Hz), 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 127.3, 128.6, 129.3, 130.2 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 131.9, 140.2, 143.0, 144.0, 146.3, 158.5, 171.1. HRMS (ESI): calcd for $C_{25}H_{20}BrF_3N_3O_3$ $[M+H]^+$: 546.0635; found: 546.0631.

Ethyl 3-hydroxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4n)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (130.5 mg, 63%); Mp: 120-122 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 2.69 (s, 3H), 4.50 (q, *J* = 7.6 Hz, 2H), 6.93 (s, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.18-7.16 (m, 2H), 7.25-7.22 (m, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.69 (s, 1H), 12.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.4, 24.4, 62.4, 112.4, 122.0, 122.87, 122.93, 124.3, 126.5, 128.1, 128.5, 128.7, 128.9, 129.1, 130.2, 136.5, 138.4, 143.5, 144.6, 147.1, 158.7, 171.2. HRMS (ESI): calcd for $C_{25}H_{24}N_3O_3$ $[M+H]^+$: 414.1812; found: 414.1823.

Ethyl 2'-bromo-3-hydroxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4o)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (147.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (t, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 2.69 (s, 3H), 4.51 (q, *J* = 7.2 Hz, 2H), 6.81 (s, 1H), 7.11-7.07 (m, 2H), 7.28-7.17 (m, 3H), 7.47 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.64 (s, 1H), 7.88 (s, 1H), 12.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.4, 24.3, 62.5, 113.2, 121.9, 122.6, 122.8, 122.9, 124.5, 126.4, 127.2, 128.6, 128.8, 129.9, 130.3, 130.8, 132.4, 137.4, 138.4, 143.2, 144.0, 146.6, 158.1, 171.2. HRMS (ESI): calcd for $C_{25}H_{23}BrN_3O_3$ $[M+H]^+$: 492.0917; found: 492.0927.

Ethyl 2'-bromo-3-hydroxy-5'-methoxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4p)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (187.9 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ:

1.46 (t, J = 7.6 Hz, 3H), 2.36 (s, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 4.49 (q, J = 7.6 Hz, 2H), 6.64 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1H), 6.78 (d, J = 2.8 Hz, 1H), 6.81 (s, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.32-7.24 (m, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.65 (s, 1H), 7.90 (s, 1H), 12.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.4, 24.3, 55.5, 62.5, 112.1, 113.2, 115.8, 116.5, 122.67, 122.70, 122.9, 124.4, 126.4, 128.7, 128.8, 130.4, 133.0, 138.1, 138.4, 143.2, 143.9, 146.7, 158.2, 158.5, 171.2. HRMS (ESI): calcd for $C_{26}H_{25}BrN_3O_4$ $[M+H]^+$: 522.1023; found: 522.1033.

Ethyl 2'-bromo-3-hydroxy-5-methyl-2-(4-(p-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4q)

Eluent: ethyl acetate/petroleum ether (1/3). Brown solid (172.2 mg, 70%); Mp: 145-146 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, J = 7.0 Hz, 3H), 2.34 (s, 3H), 2.68 (s, 3H), 4.49 (q, J = 7.2 Hz, 2H), 6.81 (s, 1H), 7.10-7.06 (m, 1H), 7.22-7.17 (m, 4H), 7.46 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.85 (s, 1H), 12.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.3, 24.3, 62.5, 113.2, 121.9, 122.3, 122.8, 124.5, 125.7, 127.2, 127.7, 129.4, 129.9, 130.8, 132.4, 137.4, 137.8, 143.1, 143.9, 146.6, 158.1, 171.2. HRMS (ESI): calcd for $C_{25}H_{23}BrN_3O_3$ $[M+H]^+$: 492.0917; found: 492.0925.

Ethyl 2'-bromo-3-hydroxy-5'-methoxy-2-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)-5-methyl–[1,1'-biphenyl]-4-carboxylate (4r)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (147.9 mg, 55%); Mp: 162-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, J = 7.2 Hz, 3H), 2.68 (s, 3H), 3.67 (s, 3H), 3.81 (s, 3H), 4.50 (q, J = 6.8 Hz, 2H), 6.65 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1H), 6.77 (d, J = 3.2 Hz, 1H), 6.81 (s, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.79 (s, 1H), 12.06 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 55.3, 55.5, 62.5, 112.2, 113.2, 114.2, 115.8, 116.6, 121.8, 122.7, 123.2, 124.4, 127.1, 133.1, 138.1, 143.1, 143.9, 146.4, 158.2, 158.5, 159.5, 171.2. HRMS (ESI): calcd for $C_{26}H_{25}BrN_3O_5$ $[M+H]^+$: 538.0972; found: 538.0980.

Ethyl 3-hydroxy-2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4s)

Eluent: ethyl acetate/petroleum ether (1/1). Yellow solid (138.1 mg, 78%); Mp: 120-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, J = 7.2 Hz, 3H), 2.68 (s, 3H), 2.77 (s, 1H), 4.49 (q, J = 7.6 Hz, 2H), 4.73 (s, 2H),

6.90 (s, 1H), 7.14-7.09 (m, 2H), 7.25-7.21 (m, 3H), 7.46 (s, 1H), 12.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 56.4, 62.4, 112.4, 121.9, 124.3, 125.1, 128.0, 128.51, 128.53, 136.4, 143.6, 144.6, 146.9, 158.6, 171.2. HRMS (ESI): calcd for $C_{19}H_{20}N_3O_4$ $[M+H]^+$: 354.1448; found: 354.1442.

Ethyl 2'-bromo-3-hydroxy-2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4t)

Eluent: ethyl acetate/petroleum ether (1/1). Yellow solid (159.8 mg, 74%); Mp: 129-130 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 6.8 Hz, 3H), 2.66 (s, 3H), 2.82 (s, 1H), 4.49 (q, *J* = 6.8 Hz, 2H), 4.65 (s, 2H), 6.78 (s, 1H), 7.10-7.06 (m, 1H), 7.17-7.14 (m, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.61 (s, 1H), 11.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.2, 56.4, 62.5, 113.3, 121.9, 122.7, 124.5, 124.7, 127.1, 129.9, 130.7, 132.4, 137.3, 143.1, 143.9, 146.5, 158.0, 171.1. HRMS (ESI): calcd for $C_{19}H_{19}BrN_3O_4$ $[M+H]^+$: 432.0553; found: 432.0560.

Ethyl 2'-bromo-5'-fluoro-3-hydroxy-2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4u)

Eluent: ethyl acetate/petroleum ether (1/1). White solid (171.0 mg, 76%); Mp: 135-136 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 6.8 Hz, 3H), 2.67 (s, 3H), 2.70 (s, 1H), 4.50 (q, *J* = 6.8 Hz, 2H), 4.71 (s, 2H), 6.76 (s, 1H), 6.83-6.86 (m, 1H), 6.95 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 7.39-7.42 (m, 1H), 7.68 (s, 1H), 12.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.2, 56.5, 62.6, 113.6, 116.3 (d, $^4J_{C\text{-}F}$ = 3.9 Hz), 117.2 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 118.1 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 122.6, 124.1, 124.8, 133.7 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 139.2 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 142.6, 143.4, 146.5, 157.8, 161.3 (d, $^1J_{C\text{-}F}$ = 247.6 Hz), 171.0. HRMS (ESI): calcd for $C_{19}H_{18}BrFN_3O_4$ $[M+H]^+$: 450.0459; found: 450.0470.

Ethyl 3-hydroxy-2-(4-(hydroxy(phenyl)methyl)-1H-1,2,3-triazol-1-yl)-5-methyl-[1,1'-biphenyl]-4-carboxylate (4v)

Eluent: ethyl acetate/petroleum ether (1/2). White solid (150.6 mg, 70%); Mp: 140-142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (t, *J* = 7.2 Hz, 3H), 2.65 (s, 3H), 3.52 (s, 1H), 4.46 (q, *J* = 7.6 Hz, 2H), 5.93 (s, 1H), 6.87 (s, 1H), 7.04-7.02 (m, 2H), 7.14 (s, 1H), 7.28-7.18 (m, 8H), 11.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 62.4, 68.9, 112.5, 121.9, 124.0, 124. , 126.78, 127.8, 128.0, 128.36, 128.44, 128.5, 136.4, 141.9, 143.6, 144.6, 150.7, 158.5, 171.2. HRMS (ESI): calcd for $C_{25}H_{24}N_3O_4$ $[M+H]^+$: 430.1761;

found: 430.1767.

Ethyl 2-(4-(2-(2-bromophenyl)-1-hydroxyethyl)-1H-1,2,3-triazol-1-yl)-3-hydroxy-5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (4w)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (203.5 mg, 69%); Mp: 88-90 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46 (d, *J* = 7.2 Hz, 3H), 2.67 (s, 3H), 2.94-2.99 (m, 1H), 3.21-3.25 (m, 1H), 3.74 (s, 1H), 4.49 (q, *J* = 7.6 Hz, 2H), 5.30 (s, 1H), 6.87 (s, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.25-7.20 (m, 3H), 7.31 (s, 1H), 7.49-7.44 (m, 4H), 12.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 24.3, 33.1, 62.6, 71.9, 113.1, 121.6, 124.0, 125.4 (q, $^{3}J_{C\text{-}F}$ = 3.2 Hz), 126.6 (q, $^{1}J_{C\text{-}F}$ = 271.4 Hz), 127.5, 127.6, 128.5, 128.8, 130.4 (q, $^{2}J_{C\text{-}F}$ = 31.0 Hz), 132.5, 140.2, 142.2, 142.9, 143.9, 158.5, 171.1. HRMS (ESI): calcd for $C_{27}H_{24}BrF_3N_3O_4$ $[M+H]^+$: 590.0897; found: 590.0906.

Ethyl 2-(4-benzyl-1H-1,2,3-triazol-1-yl)-3-hydroxy-3',4'-dimethoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (4x)

Eluent: ethyl acetate/petroleum ether (1/3). White solid (151.7 mg, 64%); Mp: 100-101 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (t, J = 7.2 Hz, 3H), 2.65 (s, 3H), 3.58 (s, 3H), 3.85 (s, 3H), 4.06 (s, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 6.48 (s, 1H), 6.74 (s, 2H), 6.88 (s, 1H), 7.07-7.05 (m, 3H), 7.23-7.14 (m, 3H), 11.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.3, 31.9, 55.78, 55.82, 62.3, 110.9, 111.0, 120.8, 123.8, 124.9, 126.3, 128.4, 128.5, 129.1, 143.3, 144.3, 148.7, 149.3, 158.8, 171.2. HRMS (ESI): calcd for $C_{27}H_{28}N_3O_5$ $[M+H]^+$: 474.2023; found: 474.2030.

Ethyl 3-hydroxy-5,6-dimethyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4y)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow oil (119.9 mg, 56%); Mp: 133-135 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 7.6 Hz, 3H) , 2.04 (s, 3H) , 2.35 (s, 3H) , 2.58 (s, 3H) , 4.50 (q, *J* = 7.2 Hz, 2H) , 7.09-7.06 (m, 3H) , 7.25-7.19 (m, 4H) , 7.45 (d, *J* = 7.2 Hz, 1H) , 7.50 (s, 1H) , 7.56 (s, 1H), 10.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 17.7, 19.4, 21.4, 62.3, 115.4, 122.61, 122.64, 122.8, 126.4, 127.6, 127.9, 128.2, 128.6, 128.7, 128.8, 130.3, 136.3, 138.4, 141.4, 144.7, 146.7, 153.9, 170.6. HRMS (ESI): calcd for $C_{26}H_{26}N_3O_3$ $[M+H]^+$: 428.1969; found: 428.1979.

Ethyl 4-benzyl-2-hydroxy-5,6-dimethyl-3-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)benzoate (4z)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (128.2 mg, 58%); Mp: 110-112 ℃. ^{1}H NMR (400

MHz, $CDCl_3$) δ: 1.45 (t, *J* = 7.2 Hz, 3H), 2.18 (s, 3H), 2.38 (s, 3H), 2.57 (s, 3H), 3.84 (s, 2H), 4.48 (q, *J* = 7.2 Hz, 2H), 6.95-6.93 (m, 2H), 7.22-7.12 (m, 4H), 7.28 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.65 (s, 1H), 10.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 16.4, 19.7, 21.5, 34.9, 62.4, 113.9, 122.9, 123.2, 123.9, 126.3, 126.6, 128.0, 128.6, 128.7, 128.8, 130.4, 138.4, 138.7, 141.8, 142.4, 147.2, 154.8, 171.0. HRMS (ESI): calcd for $C_{27}H_{28}N_3O_3$ $[M+H]^+$: 442.2125; found: 442.2129.

Ethyl 5-benzyl-3-hydroxy-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4aa)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (127.1 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, *J* = 6.8 Hz, 3H), 2.38 (s, 3H), 4.34 (q, *J* = 6.8 Hz, 2H), 4.47 (s, 2H), 6.95 (s, 1H), 7.17-7.11 (m, 5H), 7.24-7.21 (m, 4H), 7.32-7.28 (m, 3H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.67 (s, 1H), 7.72 (s, 1H), 11.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 21.4, 41.9, 62.4, 122.7, 122.8, 122.9, 124.9, 126.2, 126.5, 128.1, 128.2, 128.53, 128.56, 128.59, 128.7, 128.8, 130.4, 136.4, 138.5, 140.3, 144.7, 147.3, 158.8, 170.6. HRMS (ESI): calcd for $C_{31}H_{28}N_3O_3$ $[M+H]^+$: 490.2125; found: 490.2130.

Ethyl 6-benzyl-2-hydroxy-4-methyl-3-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)benzoate (4bb)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (113.5 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 7.2 Hz, 3H), 2.16 (s, 3H), 2.43 (s, 3H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.40 (s, 2H), 6.05 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.23-7.17 (m, 2H), 7.36-7.28 (m, 3H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.80 (s, 1H), 7.98 (s, 1H), 12.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 18.2, 21.5, 41.8, 62.3, 111.3, 122.5, 122.9, 124.1, 125.4, 126.1, 126.6, 128.2, 128.5, 128.8, 129.0, 130.4, 138.6, 140.5, 142.5, 144.4, 147.4, 158.4, 170.8. HRMS (ESI): calcd for $C_{26}H_{26}N_3O_3$ $[M+H]^+$: 428.1969; found: 428.1977.

Ethyl 4-benzyl-3-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-2-hydroxy-6-methylbenzoate (4cc)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow oil (147.6 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (t, *J* = 7.6 Hz, 3H), 2.61 (s, 3H), 3.83 (s, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 6.01 (s, 1H), 6.94-6.92 (m, 2H), 7.16-7.13 (m, 3H), 7.55-7.53 (m, 3H), 7.68-7.66 (m, 2H), 12.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 37.8, 62.3, 111.7, 121.9, 123.2, 124.6, 126.5, 127.4, 128.5, 128.8, 129.57, 129.6, 130.7, 131.9, 138.4, 143.7, 144.9, 146.1, 158.3, 171.3. HRMS (ESI): calcd for $C_{25}H_{23}BrN_3O_3$ $[M+H]^+$: 492.0917; found: 492.0923.

Ethyl 2-hydroxy-6-methyl-4-phenethyl-3-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)benzoate (4dd)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (141.5 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 2.64 (s, 3H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 6.78 (s, 1H), 6.95-6.94 (m, 2H), 7.22-7.16 (m, 4H), 7.34 (dd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 1H), 7.38 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 11.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.5, 24.3, 33.7, 37.0, 62.2, 111.2, 122.9, 123.4, 123.8, 126.2, 126.5, 128.5, 28.6, 128.7, 128.8, 130.5, 138.4, 140.6, 143.2, 145.5, 147.2, 158.2, 171.3. HRMS (ESI): calcd for $C_{27}H_{28}N_3O_3$ $[M+H]^+$: 442.2125; found: 442.2131.

Ethyl 3-hydroxy-3',4'-dimethoxy-5-methyl-2-(4-(thiophen-3-yl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4ee)

Eluent: ethyl acetate/petroleum ether (1/3). White soild (158.4 mg, 68%); Mp: 160-161 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 6.8 Hz, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 3.83 (s, 3H), 4.50 (q, *J* = 6.8 Hz, 2H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.85-6.76 (m, 2H), 6.94 (s, 1H), 7.36-7.34 (m, 1H), 7.41-7.39 (m, 1H), 7.57 (s, 1H), 7.65 (dd, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 12.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 24.4, 55.78, 55.87, 62.4, 110.9, 111.0, 111.9, 120.9, 121.2, 121.7, 122.6, 123.9, 125.9, 126.2, 128.9, 131.6, 143.5, 143.6, 144.2, 148.7, 149.3, 159.0, 171.2. HRMS (ESI): calcd for $C_{24}H_{24}N_3O_5S$ $[M+H]^+$: 466.1431; found: 466.1435.

Ethyl 3-hydroxy-4',5-dimethyl-2-(4-(thiophen-3-yl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4ff)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (128.1 mg, 61%); Mp: 100-101 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.47 (t, *J* = 7.2 Hz, 3H), 2.27 (s, 3H), 2.68 (s, 3H), 4.49 (q, *J* = 6.8 Hz, 2H), 6.91 (s, 1H), 7.05 (dd, J_1 = 11.6 Hz, J_2 = 8.4 Hz, 4H), 7.36-7.34 (m, 1H), 7.43-7.41 (m, 1H), 7.61 (s, 1H), 7.66 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1H), 12.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.2, 24.4, 62.4, 112.1, 121.1, 121.9, 122.6, 124.3, 126.0, 126.1, 128.0, 129.3, 131.8, 133.5, 138.5, 134.3, 143.4, 144.7, 158.8, 171.3. HRMS (ESI): calcd for $C_{23}H_{22}N_3O_3S$ $[M+H]^+$: 420.1376; found: 420.1380.

Ethyl 3-hydroxy-4',5-dimethyl-2-(4-(pyridin-3-yl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (4gg)

Eluent: ethyl acetate/petroleum ether (1/2). Yellow oil (22.3 mg, 11%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48

(t, *J* = 6.8 Hz, 3H), 2.28 (s, 3H), 2.68 (s, 3H), 4.51 (q, *J* = 6.8 Hz, 2H), 6.93 (s, 1H), 7.05 (s, 4H), 7.37-7.34 (m, 1H), 7.78 (s, 1H), 8.23-8.20 (m, 1H), 8.55(d, *J* = 3.6 Hz, 1H), 8.93 (s, 1H), 12.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 21.2, 24.4, 62.4, 112.1, 121.7, 123.2, 123.7, 124.3, 128.0, 129.3, 133.1, 133.4, 138.6, 143.7, 144.0, 144.7, 147.1, 149.1, 158.7, 171.3. HRMS (ESI): calcd for $C_{24}H_{23}N_4O_3$ $[M+H]^+$: 415.1765; found: 415.1775.

2. Typical procedure for the synthesis of 7a and spectroscopic data of 7a-7e.

To a flask containing **4b** (238.5 mg, 0.5 mmol) and K_2CO_3 (138.0 mg, 1 mmol) in CH_3CN (5 mL) was added CH_3I (355.0 mg, 2.5 mmol). The mixture was stirred at 80 ^{o}C for 2 h. After being cooled to room temperature, it was quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/8) as eluent to give **7a** (223.4 mg, 91%). **7b-7e** were obtained in a similar manner.

Ethyl 2'-bromo-3-methoxy-5-methyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7a)

Eluent: ethyl acetate/petroleum ether (1/8). White solid (223.9 mg, 91%); Mp: 109-111 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.42 (t, *J* = 6.8 Hz, 3H), 2.45 (s, 3H), 3.52 (s, 3H), 4.47 (q, *J* = 6.8 Hz, 2H), 7.05 (s, 1H), 7.08 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.18 (dd, J_1 = 7.6 Hz, J_2 = 7.2 Hz, 1H), 7.22 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.28 (dd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 1H), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 61.8, 62.9, 122.4, 122.7, 125.6, 127.1, 127.4, 128.1, 128.2, 128.8, 129.5, 129.8, 130.2, 131.1, 132.3, 137.3, 138.5, 140.9, 146.8, 152.3, 166.7. HRMS (ESI): calcd for $C_{25}H_{23}BrN_3O_3$ $[M+H]^+$: 492.0917; found: 492.0924.

Ethyl 2'-bromo-2-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)-3-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (7b)

Eluent: ethyl acetate/petroleum ether (1/5). White solid (262.2 mg, 92%); Mp: 123-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.41 (t, *J* = 6.8 Hz, 3H), 2.43 (s, 3H), 3.50 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.04 (s, 1H), 7.07 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.21-7.15 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 61.8, 63.0, 121.9,

122.4, 122.8, 127.1, 127.2, 127.3, 128.1, 129.2, 129.5, 129.8, 131.1, 131.9, 132.3, 137.3, 138.6, 140.8, 145.8, 152.2, 166.6. HRMS (ESI): calcd for $C_{25}H_{22}Br_2N_3O_3$ $[M+H]^+$: 570.0022; found: 570.0023.

Ethyl 2'-bromo-3-methoxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7c)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow soild (225.2 mg, 89%); Mp: 99-101 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (t, *J* = 8.0 Hz, 3H), 2.37 (s, 3H), 2.45 (s, 3H) , 3.51 (s, 3H), 4.48 (qd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.06 (s, 1H), 7.14-7.07 (m, 2H), 7.25-7.18 (m, 2H), 7.28 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 21.3, 61.7, 62.8, 122.4, 122.6, 122.7, 126.3, 127.1, 127.4, 128.0, 128.7, 128.9, 129.4, 129.8, 130.1, 131.1, 132.3, 137.3, 138.4, 138.5, 140.9, 146.8, 152.2, 166.7. HRMS (ESI): calcd for $C_{26}H_{25}BrN_3O_3$ $[M+H]^+$: 506.1079; found: 506.1075.

Ethyl 2-(4-benzyl-1H-1,2,3-triazol-1-yl)-2'-bromo-3-methoxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (7d)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow soild (227.7 mg, 90%); Mp: 89-91 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 3.49 (s, 3H), 3.97 (s, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.98 (s, 1H), 7.22-7.07 (m, 6H), 7.28 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.4, 31.7, 61.7, 62.9, 122.4, 124.8, 126.3, 127.0, 127.8, 128.3, 128.4, 129.6, 129.7, 130.9, 132.2, 137.3, 138.2, 138.9, 140.9, 146.4, 152.3, 166.7. HRMS (ESI): calcd for $C_{26}H_{25}BrN_3O_3$ $[M+H]^+$: 506.1074; found: 506.1068.

Ethyl 2'-bromo-3,5'-dimethoxy-5-methyl-2-(4-(m-tolyl)-1H-1,2,3-triazol-1-yl)-[1,1'-biphenyl]-4-carboxylate (7e)

Eluent: ethyl acetate/petroleum ether (1/5). White solid (249.3 mg, 93%); Mp: 120-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.39 (t, *J* = 6.8 Hz, 3H), 2.33 (s, 3H), 2.42 (s, 3H), 3.50 (s, 3H), 3.62 (s, 3H), 4.44 (qd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 2H), 6.60 (dd, J_1= 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 7.03 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.63 (s, 1H), 7.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 21.3, 55.4, 61.7, 62.9, 112.6, 116.2, 116.3, 122.7, 126.3, 127.4, 127.9, 128.7, 128.9, 129.5, 130.1, 132.9, 138.0, 138.5, 140.8, 146.9,

152.3, 158.4, 166.6. HRMS (ESI): calcd for $C_{27}H_{27}BrN_3O_4$ $[M+H]^+$: 536.1179; found: 536.1185.

3. Typical procedure for the synthesis of 8a and spectroscopic data of 8a-8e.

A suspension of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PCy_3 (11.2 mg, 0.04 mmol), K_2CO_3 (138.0 mg, 1.0 mmol) and **7a** (245.5 mg, 0.5 mmol) in toluene (3 mL) was stirred at 120 ^oC under N_2 for 24 h. Upon completion, it was cooled to room temperature, treated with H_2O (10 mL). The resulting mixture was then extracted with EtOAc (3×10 mL). The combined organic layers were washed with brine (2×10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether, v/v = 1/8) to afford **8a** (185.0mg, 90%) as a white solid. Other triazolophenanthridine derivatives **8b-8e** were obtained in a similar manner.

Ethyl 11-methoxy-9-methyl-3-phenyl-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8a)

Eluent: ethyl acetate/petroleum ether (1/8). White solid (185.4 mg, 90%); Mp: 191-192 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.45 (t, *J* = 7.2 Hz, 3H), 2.48 (s, 3H), 4.01 (s, 3H), 4.50 (q, *J* = 6.8 Hz, 2H), 7.32 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H), 7.55-7.47 (m, 4H), 7.72-7.70 (m, 2H), 7.98 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 61.8, 63.4, 120.4, 122.9, 123.4, 123.8, 123.9, 125.2, 126.9, 127.7, 128.78, 128.82, 129.2, 129.8, 131.9, 132.2, 134.3, 140.9, 148.2, 167.1. HRMS (ESI): calcd for $C_{25}H_{22}N_3O_3$ $[M+H]^+$: 412.1656; found: 412.1659.

Ethyl 3-(4-bromophenyl)-11-methoxy-9-methyl-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8b)

Eluent: ethyl acetate/petroleum ether (1/8). White solid (217.6 mg, 89%); Mp: 198-201 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 8.0 Hz, 3H), 2.53 (s, 3H), 4.09 (s, 3H), 4.52 (q, *J* = 6.8 Hz, 2H), 7.45 (dd, J_1 = 8.0 Hz, J_2 = 7.6 Hz, 1H), 7.64-7.61 (m, 3H), 7.71-7.68 (m, 2H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.08 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 61.8, 63.4, 120.5, 122.8, 123.1, 123.6, 123.8, 123.9, 125.2, 127.2, 127.9, 128.9, 129.4, 131.3, 131.5, 132.1, 134.5, 139.8, 148.4, 167.1. HRMS (ESI): calcd for $C_{25}H_{21}BrN_3O_3$ $[M+H]^+$: 490.0761; found: 490.0766.

Ethyl 11-methoxy-9-methyl-3-(m-tolyl)-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8c)

Eluent: ethyl acetate/petroleum ether (1/8). White solid (198.2 mg, 93%); Mp: 184-185 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.46 (t, *J* = 7.2 Hz, 3H), 2.46 (s, 3H), 2.53 (s, 3H), 4.10 (s, 3H), 4.52 (q, *J* = 7.2 Hz, 2H),

7.33 (d, *J* = 7.6 Hz, 1H), 7.46-7.40 (m, 2H), 7.62-7.52 (m, 3H), 8.08 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 21.4, 61.7, 63.4, 120.4, 123.1, 123.4, 123.9, 124.1, 125.2, 126.8, 127.0, 127.7, 128.6, 128.8, 129.2, 129.6, 130.5, 131.9, 132.1, 134.2, 138.6, 141.1, 148.3, 167.2. HRMS (ESI): calcd for $C_{26}H_{24}N_3O_3$ $[M+H]^+$: 426.1812; found: 426.1821.

Ethyl 3-benzyl-11-methoxy-9-methyl-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8d)

Eluent: ethyl acetate/petroleum ether (1/5). White solid (196.1 mg, 92%); Mp: 174-176 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (t, *J* = 8.0 Hz, 3H), 2.46 (s, 3H), 4.08 (s, 3H), 4.59 (d, *J* = 7.2 Hz, 2H), 4.63 (s, 2H), 7.17-7.14 (m, 1H), 7.28-7.23 (m, 4H), 7.45-7.38 (m, 2H), 7.86 (s, 1H), 7.90-7.89 (m, 1H), 8.11 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.4, 33.3, 61.7, 63.4, 120.3, 122.9, 123.2, 123.9, 124.2, 125.0, 126.5, 126.6, 128.25, 128.33, 128.62, 128.64, 129.1, 131.9, 134.1, 137.9, 138.7, 148.1, 167.1. HRMS (ESI): calcd for $C_{26}H_{24}N_3O_3$ $[M+H]^+$: 426.1812; found: 426.1817.

Ethyl 6,11-dimethoxy-9-methyl-3-(m-tolyl)-[1,2,3]triazolo[1,5-f]phenanthridine-10-carboxylate (8e)

Eluent: ethyl acetate/petroleum ether (1/5). White solid (207.5 mg, 91%); Mp: 193-194 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (t, *J* = 7.6 Hz, 3H), 2.42 (s, 3H), 2.47 (s, 3H), 3.88 (s, 3H), 4.07 (s, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 6.93 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.39 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.62 (s, 1H), 7.88 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.4, 21.4, 55.5, 61.7, 63.3, 106.7, 116.50, 116.54, 120.4, 124.0, 124.9, 125.6, 126.7, 127.8, 128.6, 128.7, 129.4, 130.5, 132.0, 132.3, 134.0, 138.5, 139.8, 148.2, 160.1, 167.1. HRMS (ESI): calcd for $C_{27}H_{26}N_3O_4$ $[M+H]^+$: 456.1918; found: 456.1920.

III. Control experiments (I)

1. Reaction of 1a with 2 leading to the formation of intermediate A

To a flask containing 4-azido-3-oxobutanoate (**2**, 171.2 mg, 1.0 mmol) and ethynylbenzene (**1a**, 102.0 mg, 1.0 mmol) in *t*-BuOH/H_2O (4 mL) were added $CuSO_4 \cdot 5H_2O$ (aqueous solution, 1 M, 50 μL, 0.05 mmol) and sodium ascorbate (19.8 mg, 0.1 mmol). The resulting mixture was stirred at room temperature for 12 h. Then, it was diluted with cold water (15 mL) and 10% aqueous ammonia (2 mL). After being stirred for another 5 min, it was extracted with dichloromethane (3×5 mL). The combined organic phases were dried, filtered and concentrated under reduced pressure. The residue was purified by column chromatography over

silica gel using ethyl acetate/petroleum ether (v/v = 1:2) as eluent to give 3-*oxo*-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate as a mixture of ketone and enol tautomers (4/1) (**A**, 235.1 mg, 85%).

3-Oxo-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (A)

Eluent: ethyl acetate/petroleum ether (1/2). Yellow oil (235.1 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$), Enol tautomer: δ: 1.27 (t, *J* = 6.8 Hz, 3H), 4.20 (q, *J* = 6.8 Hz, 2H), 5.02 (s, 1H), 5.11 (s, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 9.2 Hz, 2H), 7.89 (s, 1H), 12.17 (s, 1H). Ketone tautomer: δ: 1.29 (t, *J* = 7.2 Hz, 3H), 3.58 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 5.43 (s, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 9.2 Hz, 2H), 7.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 14.11, 46.5, 58.1, 60.7, 62.1, 91.4, 120.5, 121.3, 125.8, 128.4, 128.41, 128.9, 130.3, 148.4, 166.4, 194.5. HRMS (ESI): calcd for $C_{14}H_{16}N_3O_3$ $[M+H]^+$: 274.1186; found: 274.1189.

2. Reaction of A with 3a leading to the formation of 4a

To a flask containing 3-oxo-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butanoate (**A**, 136.5 mg, 0.5 mmol) and 1-phenylbuta-2,3-dien-1-one (**3a**, 72.0 mg, 0.5 mmol) were added NaOH (40.0 mg, 1.0 mmol). The mixture was stirred at 80 ℃ for 1.5 h. After being cooled to room temperature, it was quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated uner reduced pressure. The resulting residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give **4a** (157.6 mg, 79%).

IV. Control experiments (II)

1. Preparation of 5 from the reaction of 2 and 3a

To a flask containing 4-azido-3-oxobutanoate (**2**, 85.6 mg, 0.5 mmol) and 1-phenylbuta-2,3-dien-1-one (**3a**, 72.0 mg, 0.5 mmol) in *t*-BuOH/H_2O (5 mL, v/v = 1/1) were added NaOH (40.0 mg, 1.0 mmol). The mixture was stirred 80 ^{o}C for 2 h. Upon completion, it was quenched with aqueous NH_4Cl and extracted with ethyl acetate (3×5 mL). The combined organic phases were dried, filtered and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (v/v = 1/30) as eluent to give ethyl 2-azido-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (**5**, 92.2 mg, 31%).

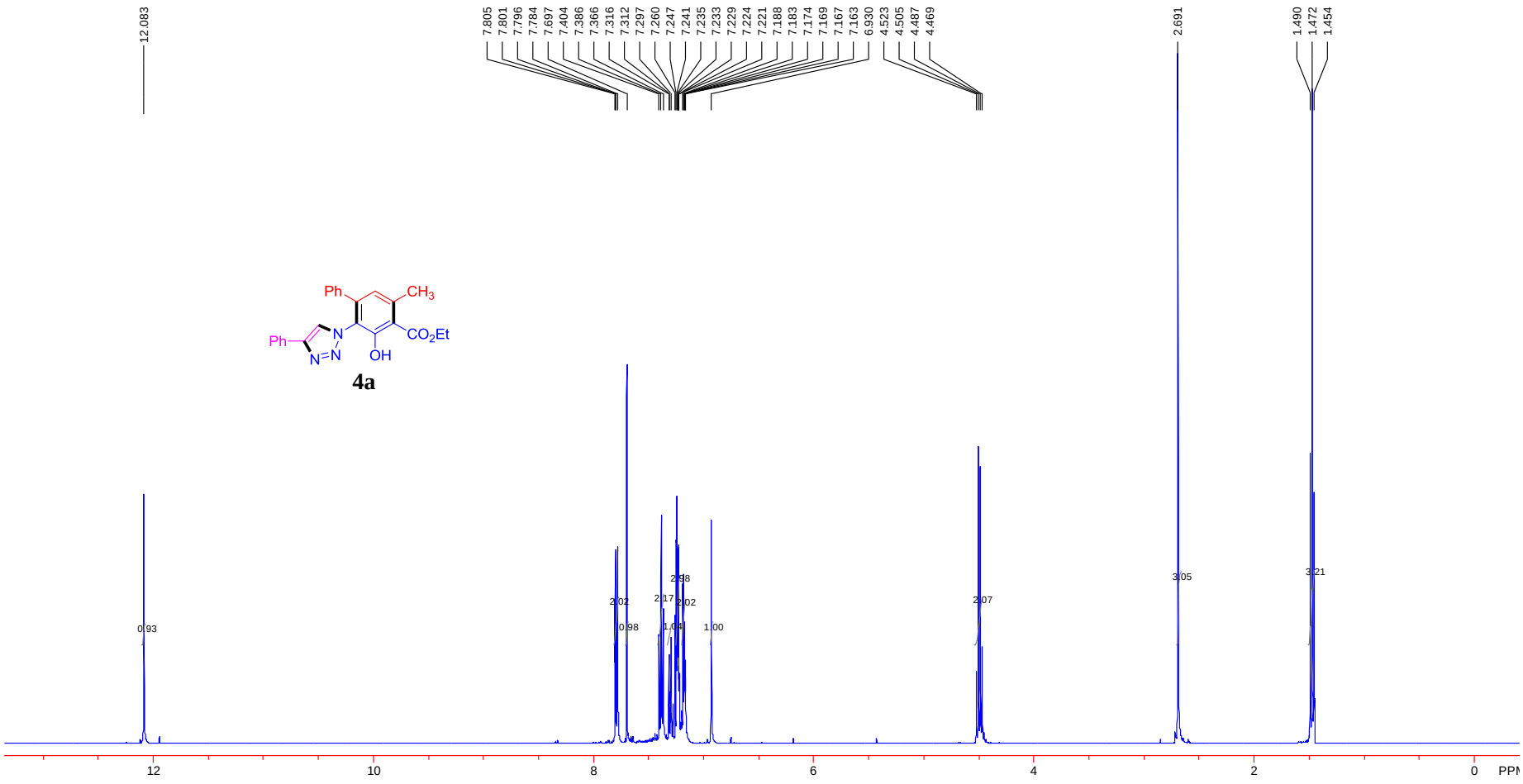
Ethyl 2-azido-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (5)

Eluent: ethyl acetate/petroleum ether (1/30). Yellow solid (92.2 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.44 (t, *J* = 7.2 Hz, 3H), 2.54 (s, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 6.68 (s, 1H), 7.46-7.37 (m, 5H), 12.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 23.9, 62.1, 111.6, 123.1, 124.4, 128.1, 128.2, 129.2, 137.1, 137.8, 139.1, 157.8, 171.8. HRMS (ESI): calcd for $C_{16}H_{16}N_3O_3$ $[M+H]^+$: 298.1186; found: 298.1193.

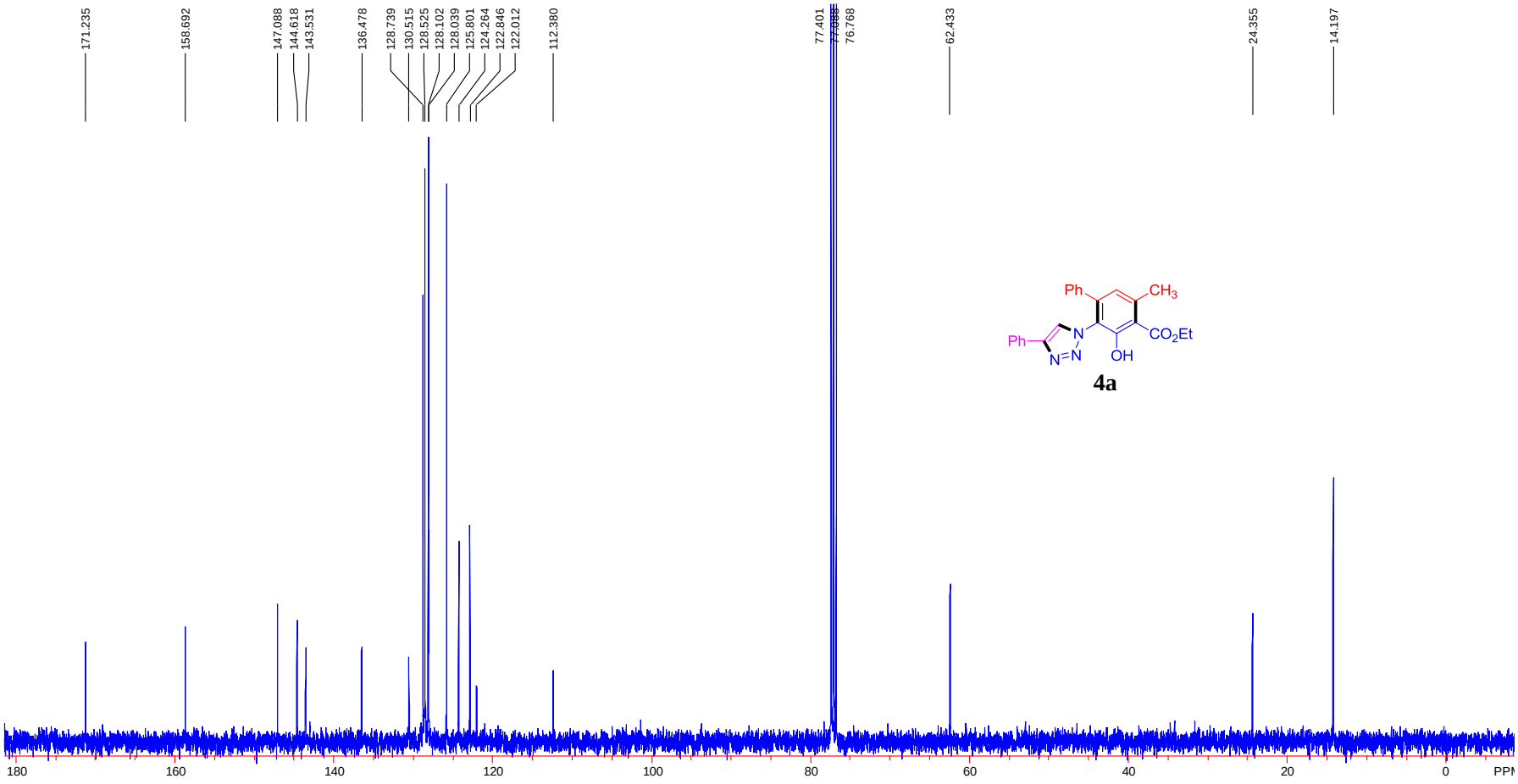
2. Preparation of 4a from the reaction of 5 and 1a

To a flask containing ethynyl-3-methylbenzene (**1a**, 56.1 mg, 0.55 mmol) and ethyl 2-azido-3-hydroxy-5-methyl-[1,1'-biphenyl]-4-carboxylate (**5**, 148.5 mg, 0.5 mmol) in *t*-BuOH/H_2O (5 mL, v/v = 1/1) were added $CuSO_4 \cdot 5H_2O$ (aqueous solution, 1 M, 25 μL, 0.025 mmol) and sodium ascorbate (9.9 mg, 0.05 mmol). The mixture was stirred at room temperature for 12 h. Upon completion, it was cooled to room temperature, quenched with water and extracted with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v = 1/5) as the eluent to give **4a** (73.8 mg, 37%).

III. Copies of 1H and 13C NMR spectra of 4a-4gg



4a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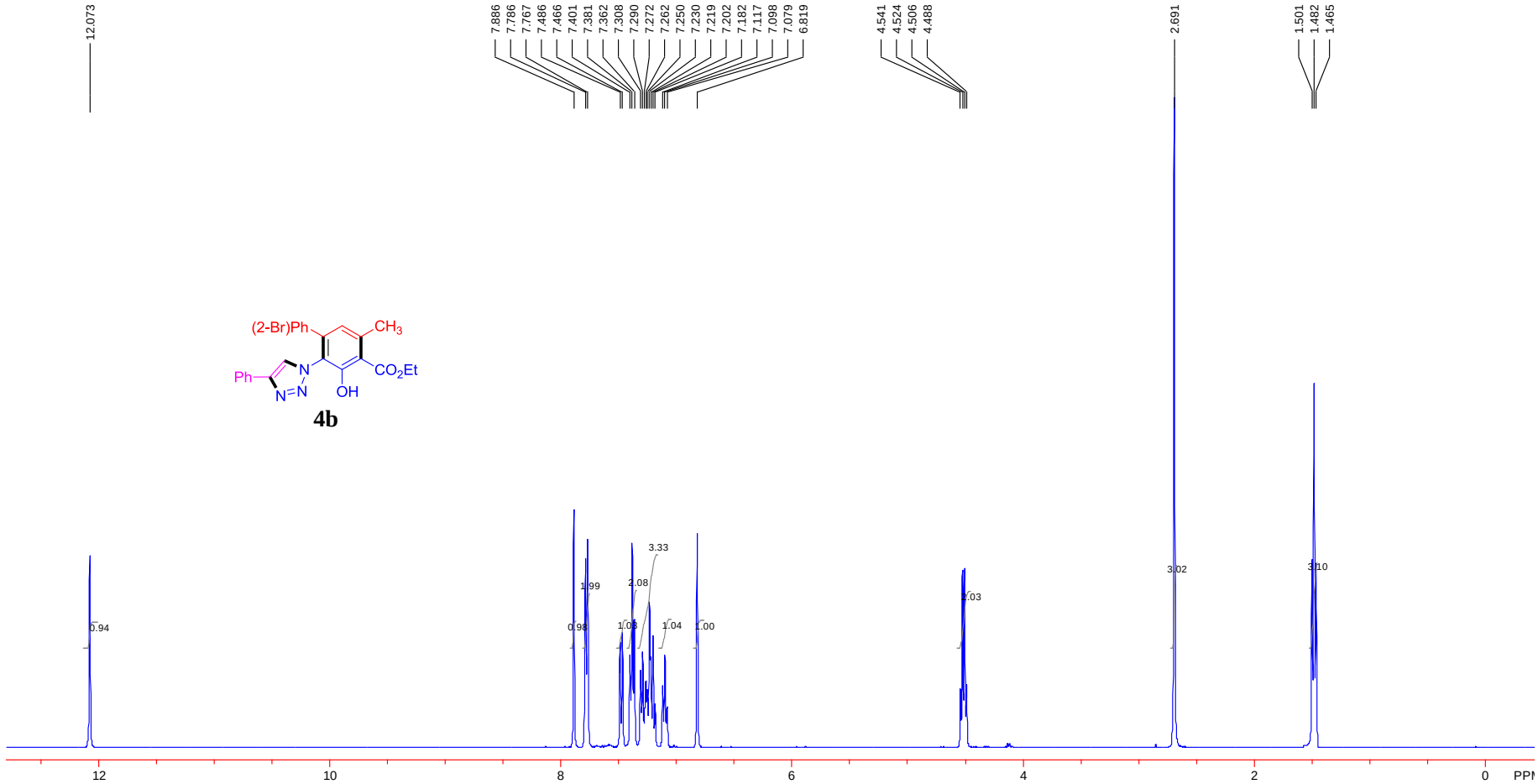
4a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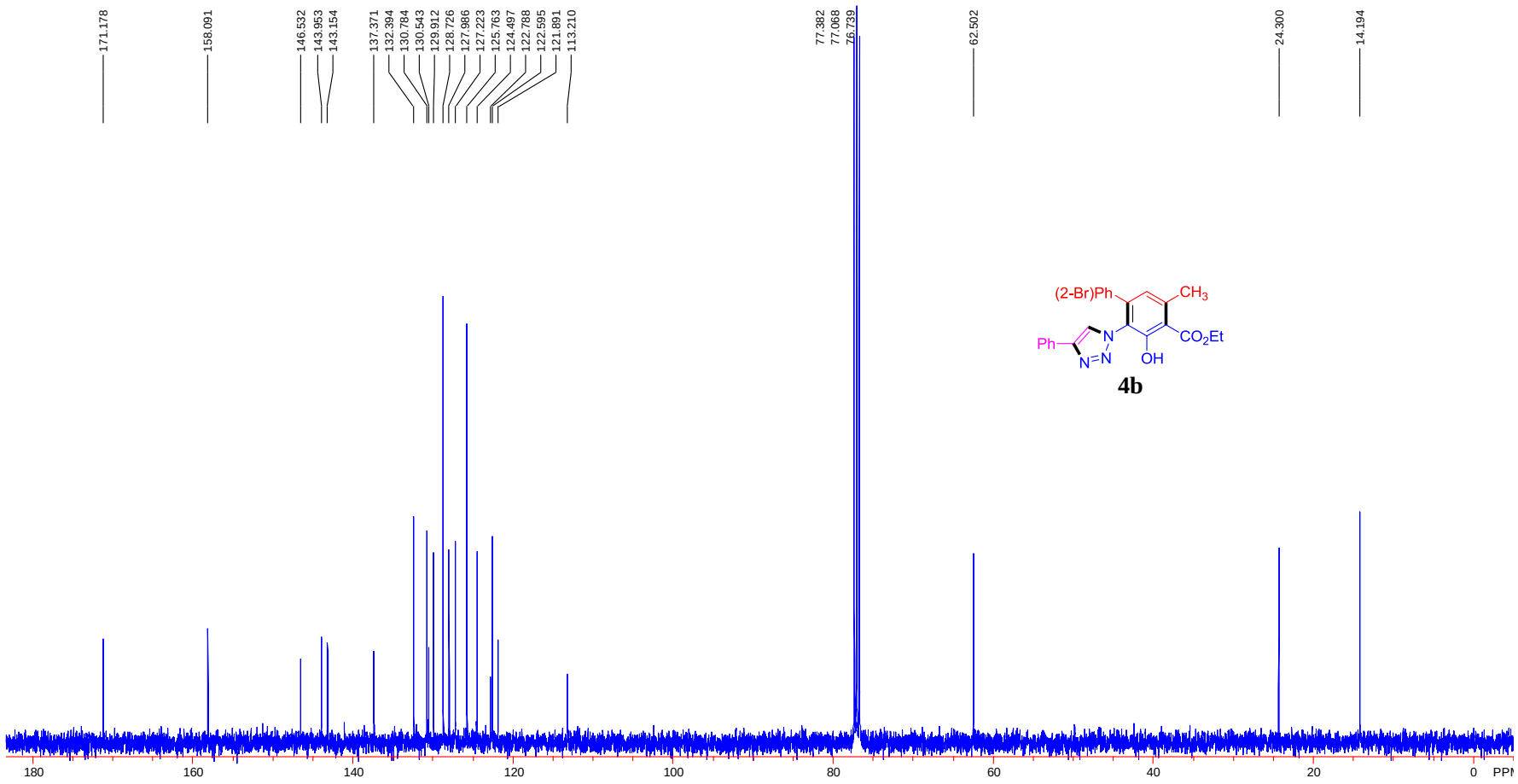
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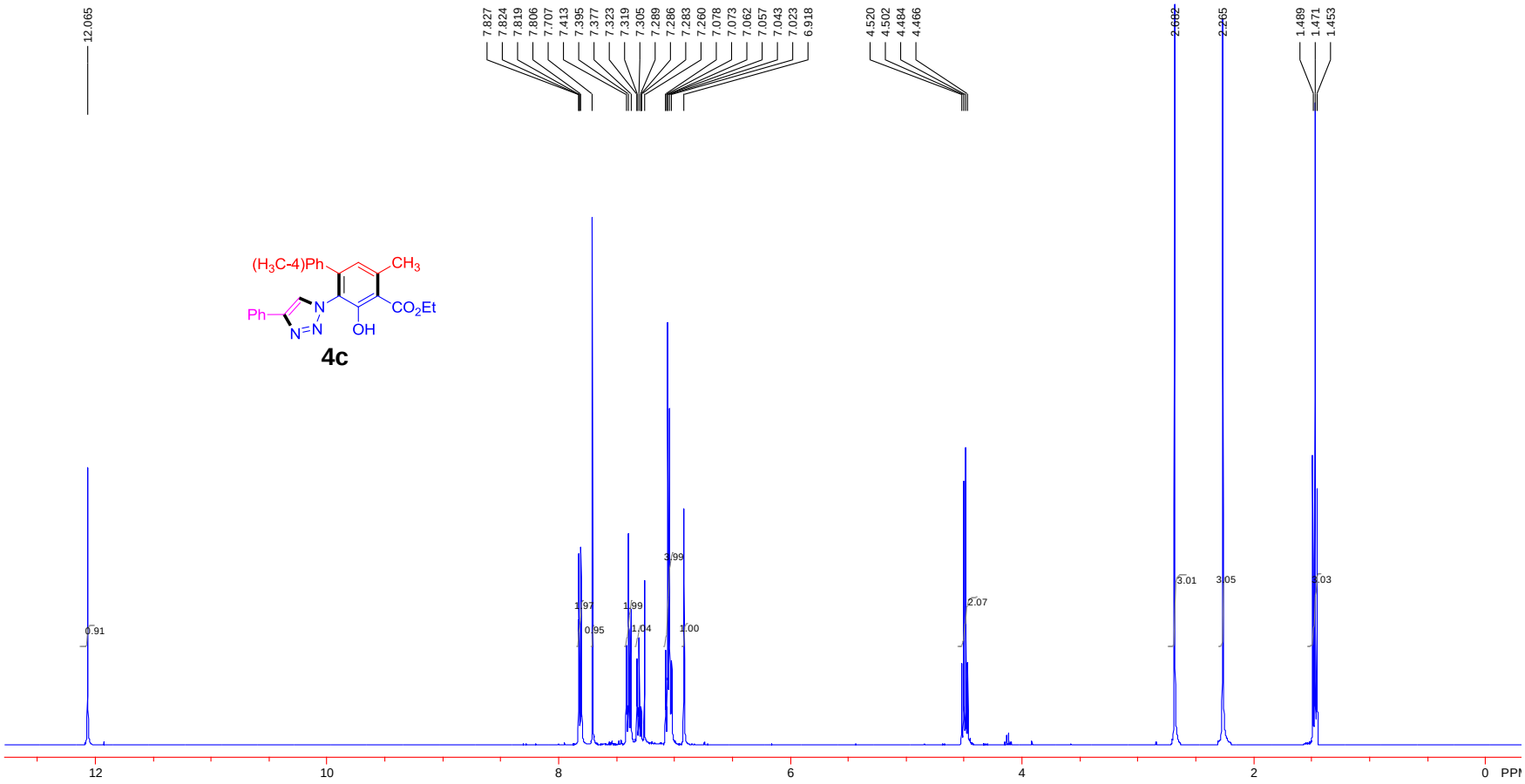
4b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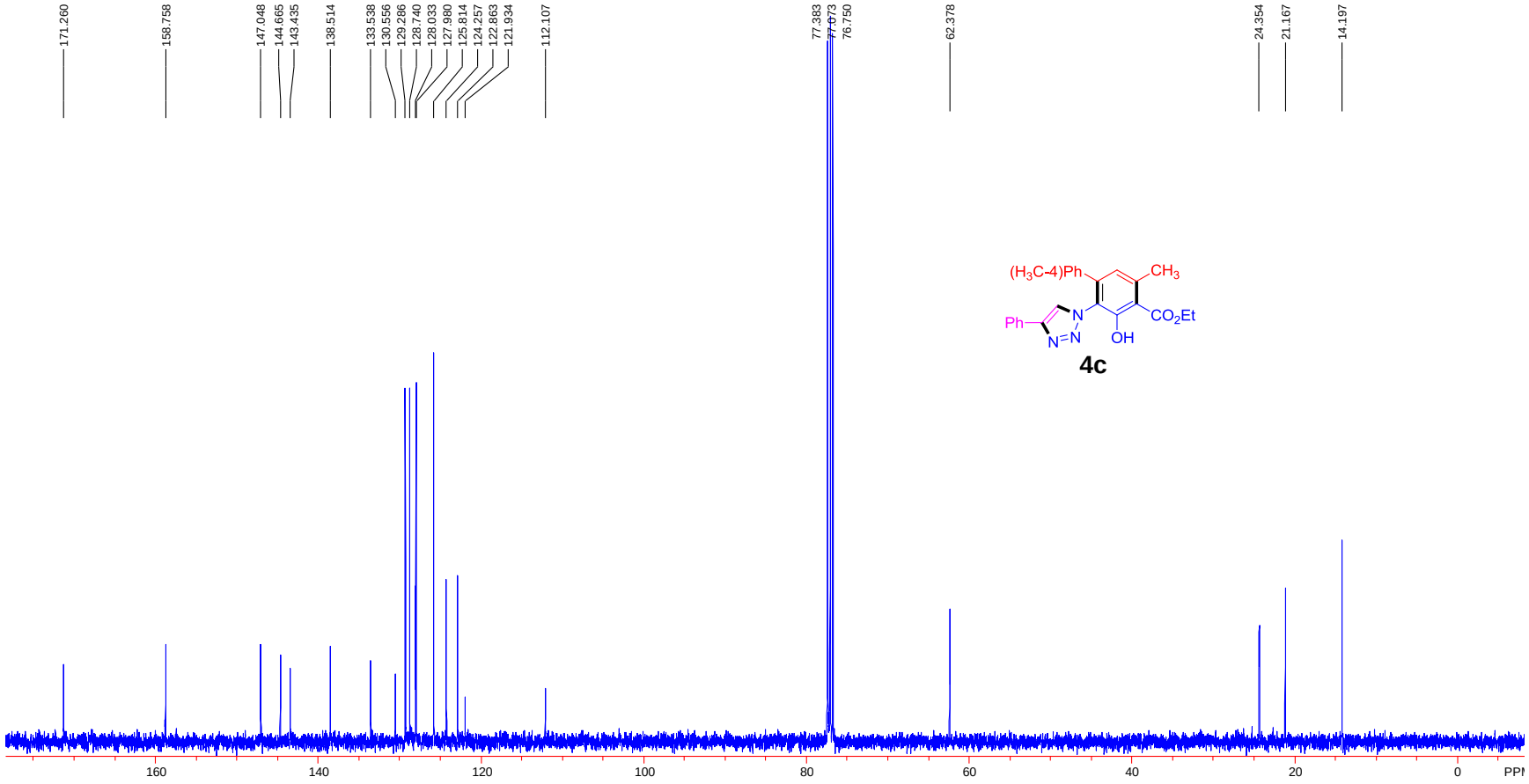
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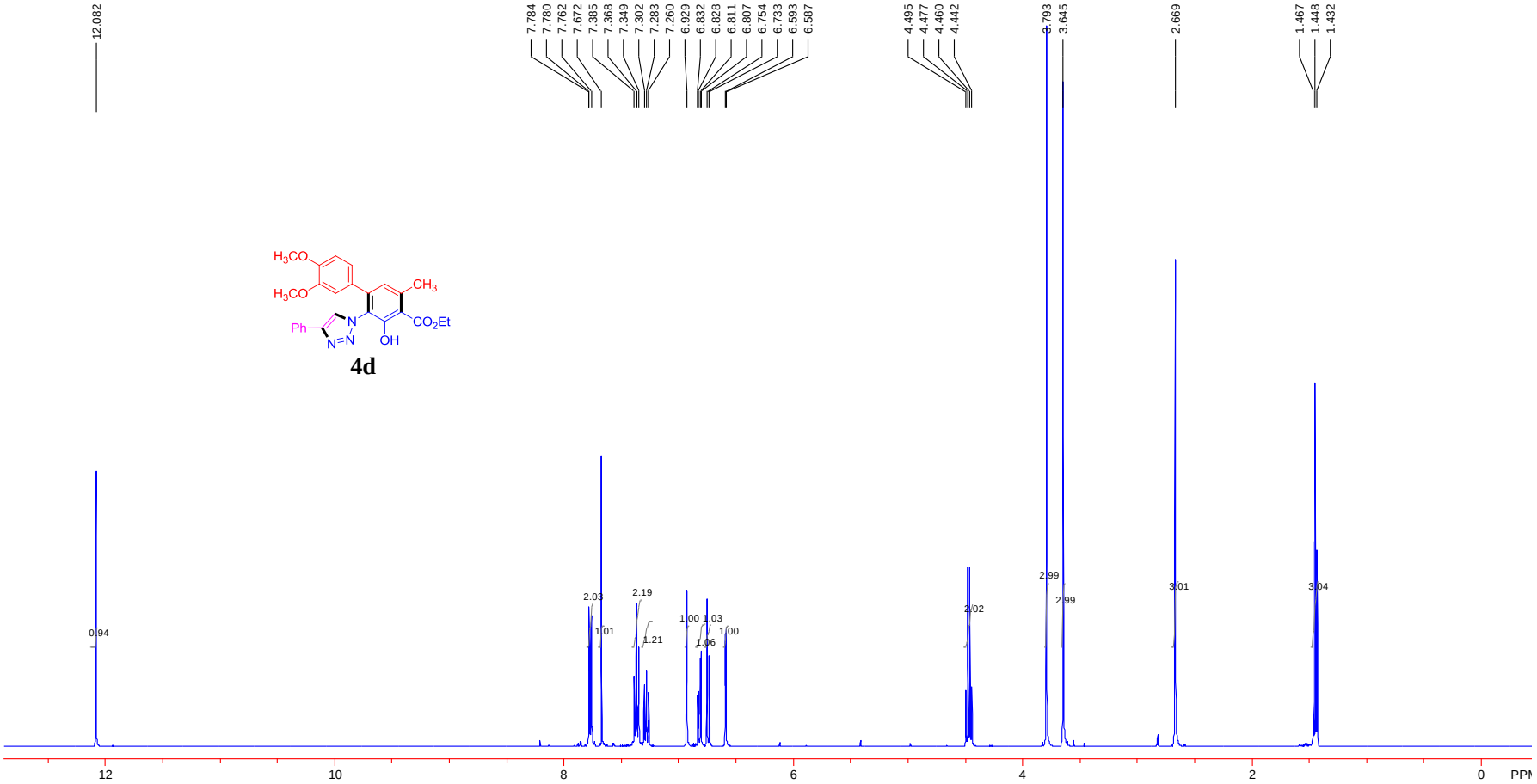
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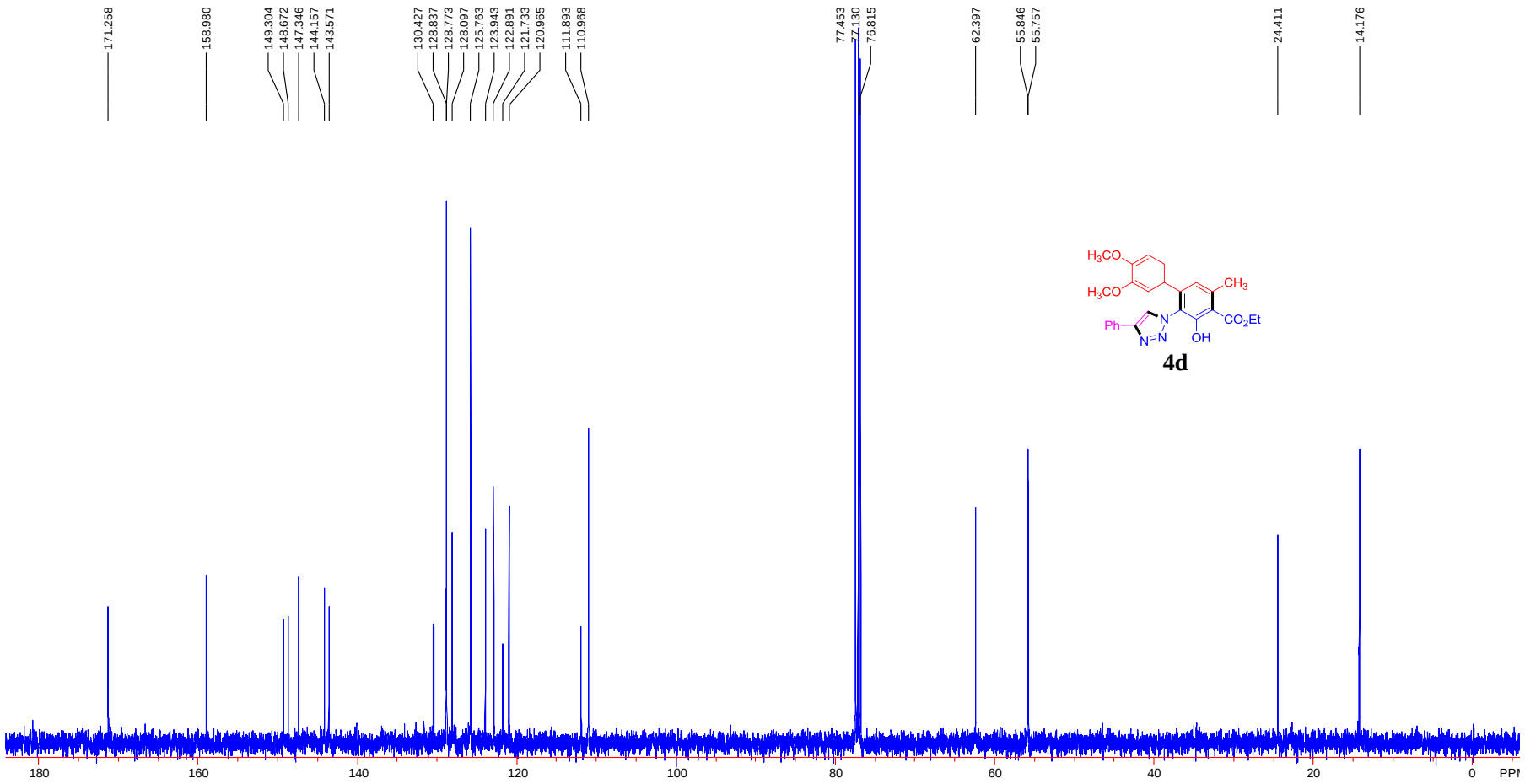
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14.176
H3CO
H3CO
CH3
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Ph
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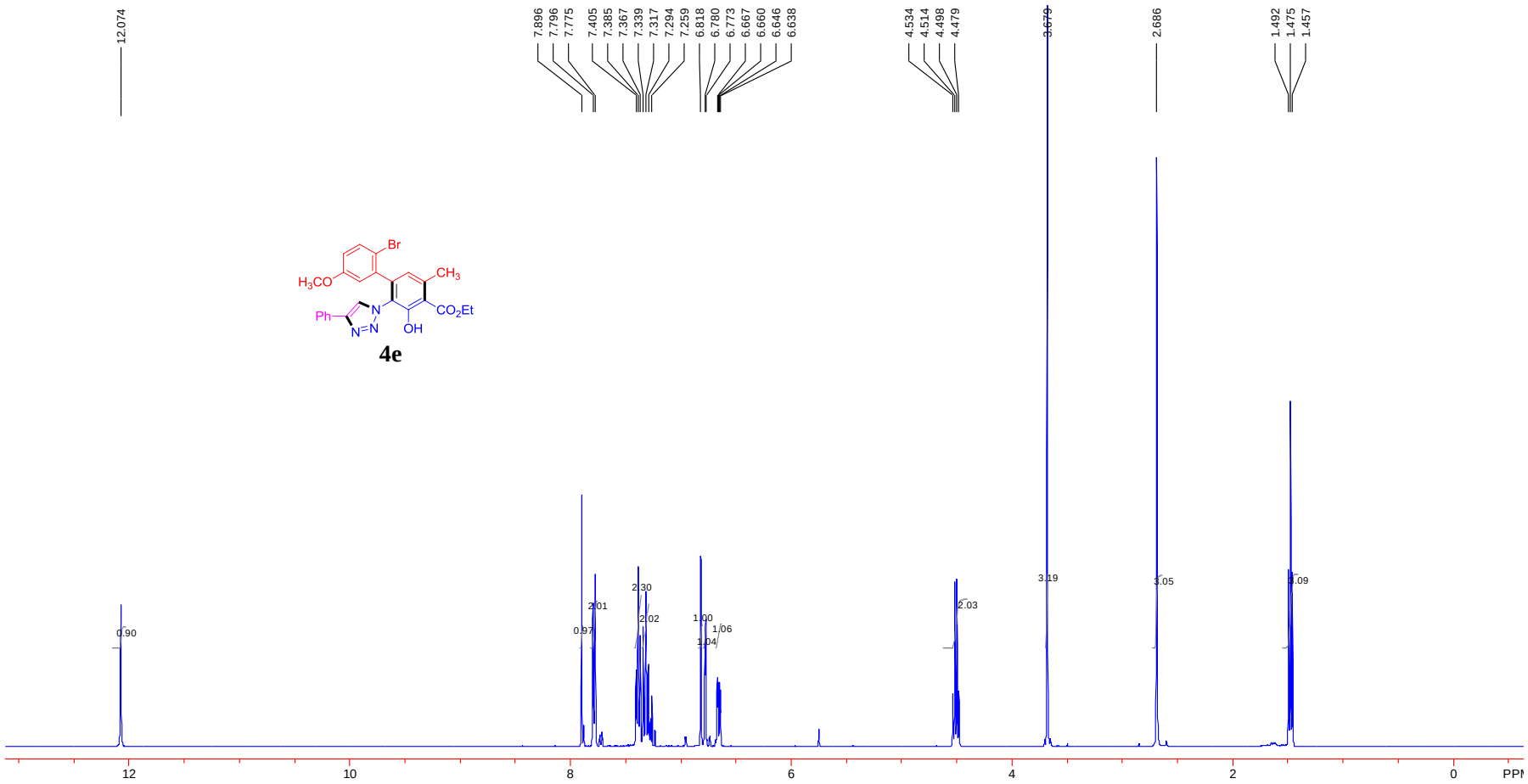
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1.457
Br
H3CO
CH3
Ph
N
N=N
OH
CO2Et
4e
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0.97
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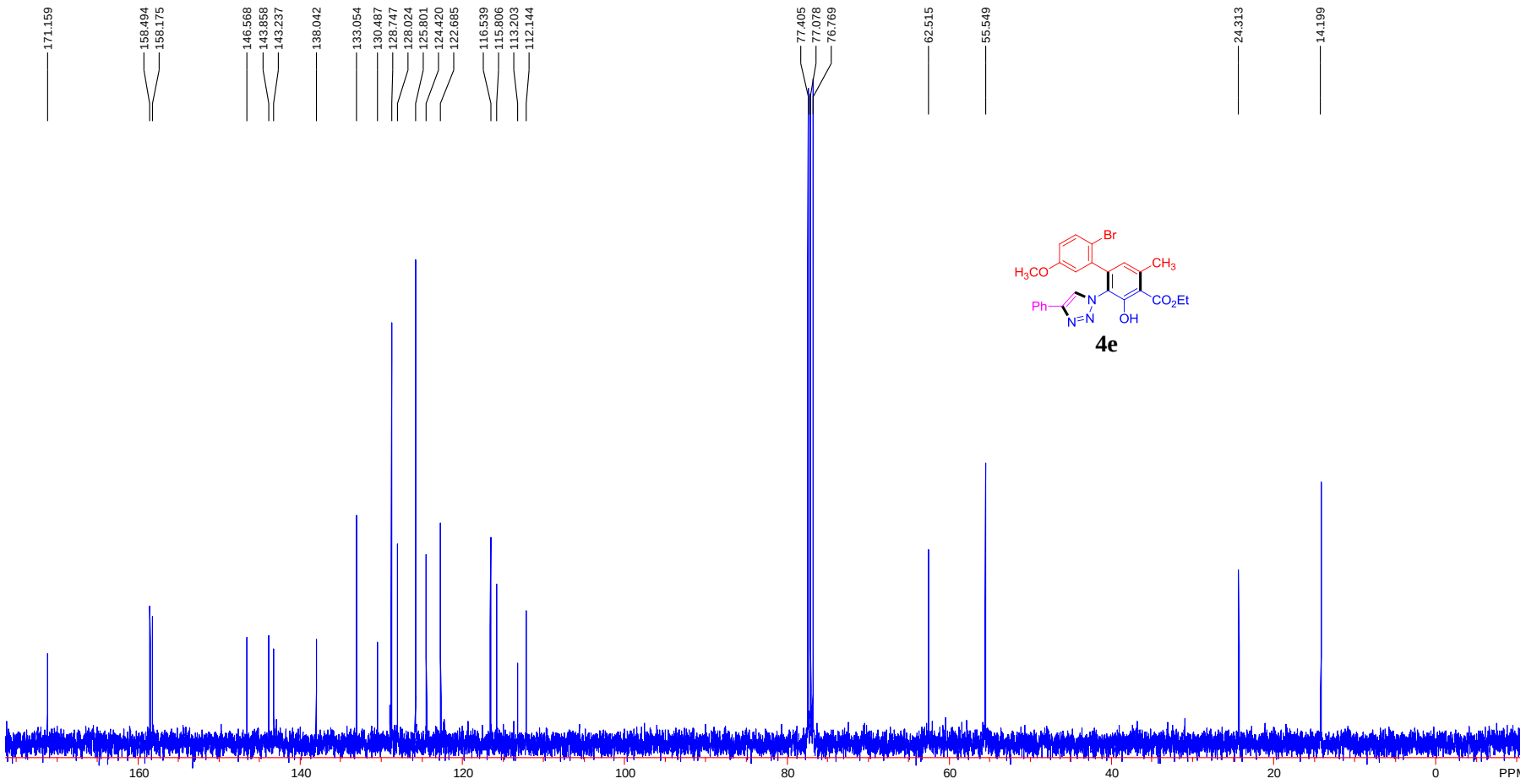
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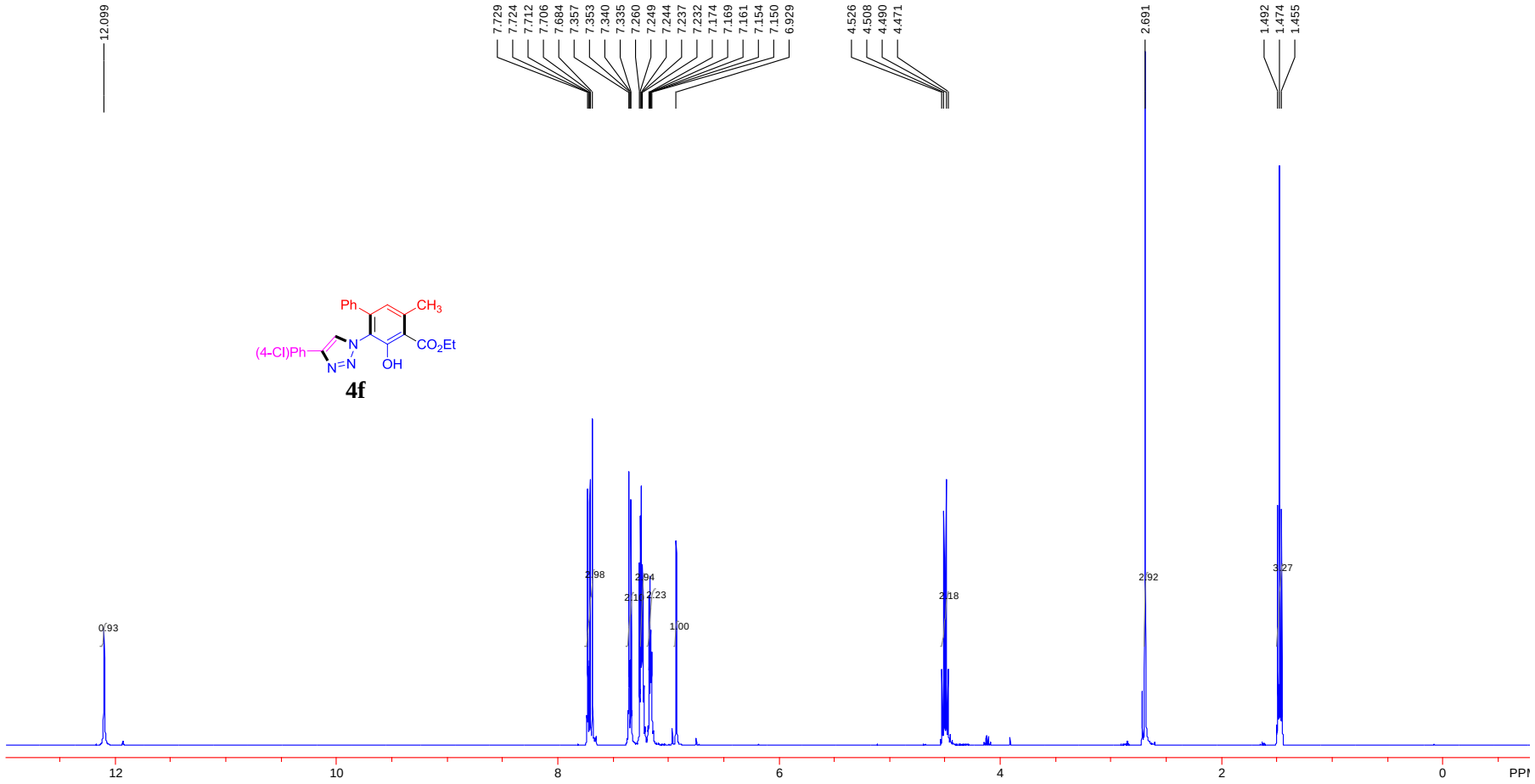
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7.244
7.237
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7.174
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7.161
7.154
7.150
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4.490
4.471
2.691
1.492
1.474
1.455
Ph
CH3
(4-Cl)Ph
N
N=N
OH
CO2Et
4f
0.93
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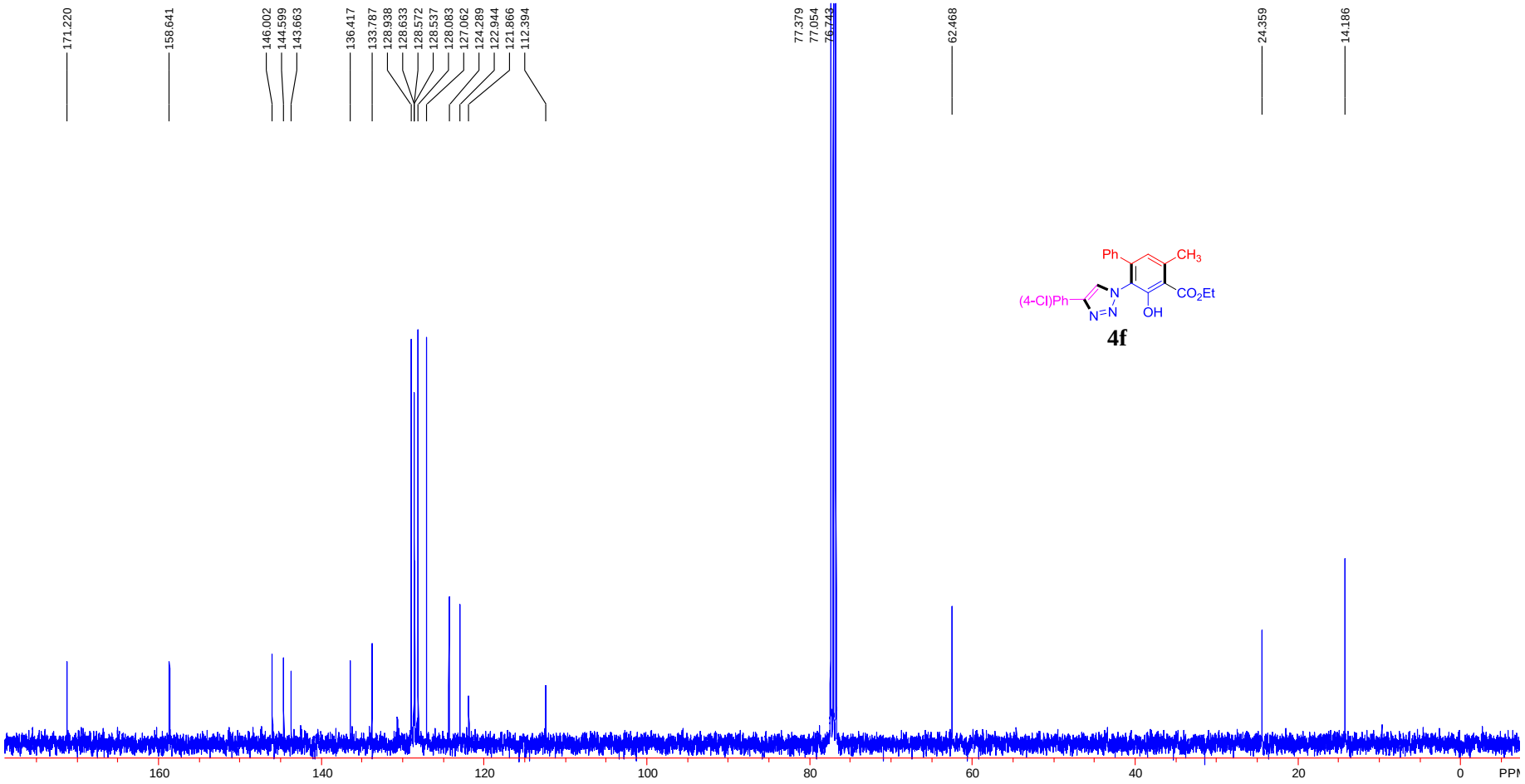
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14.186
Ph
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N=N
CO2Et
OH
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80
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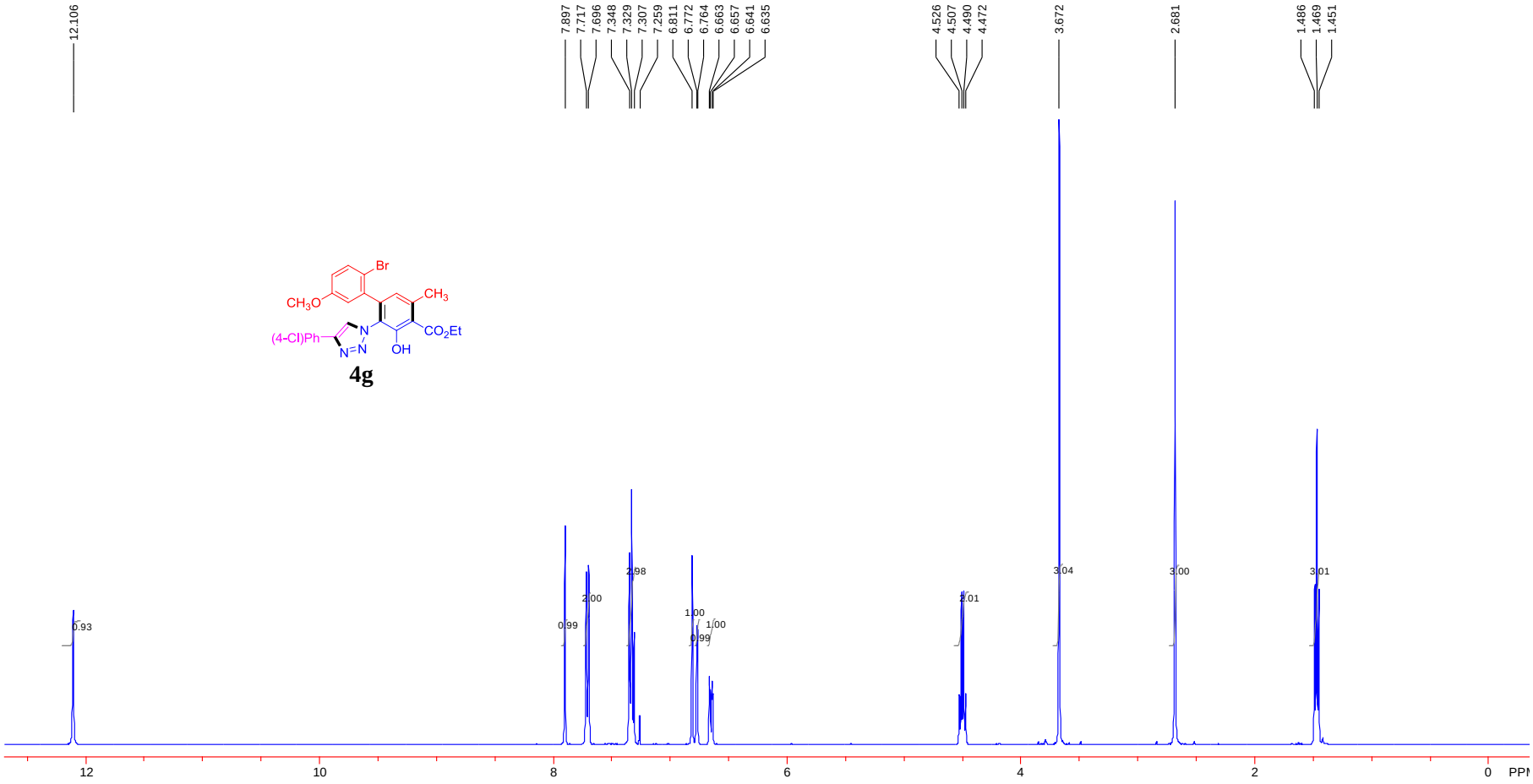
PPM

4f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6.641
6.635
4.526
4.507
4.490
4.472
3.672
2.681
1.486
1.469
1.451
Br
CH3O
CH3
(4-Cl)Ph
N
N=N
OH
CO2Et
4g
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0.99
2.00
2.98
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1.00
2.01
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3.00
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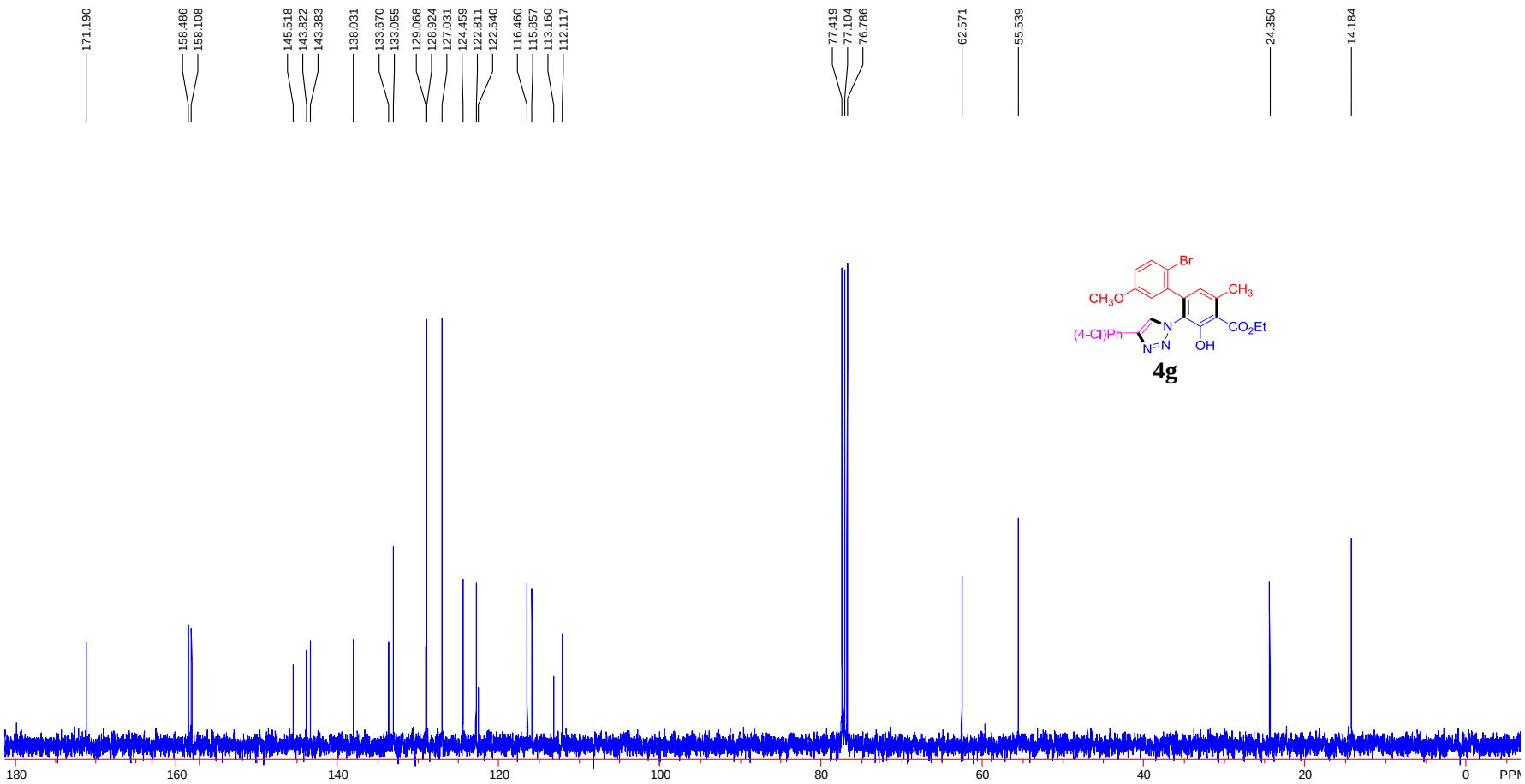
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122.811
122.540
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115.857
113.160
112.117
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77.104
76.786
62.571
55.539
24.350
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Br
CH3O
CH3
CO2Et
(4-Cl)Ph
N
N=N
OH
4g
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120
100
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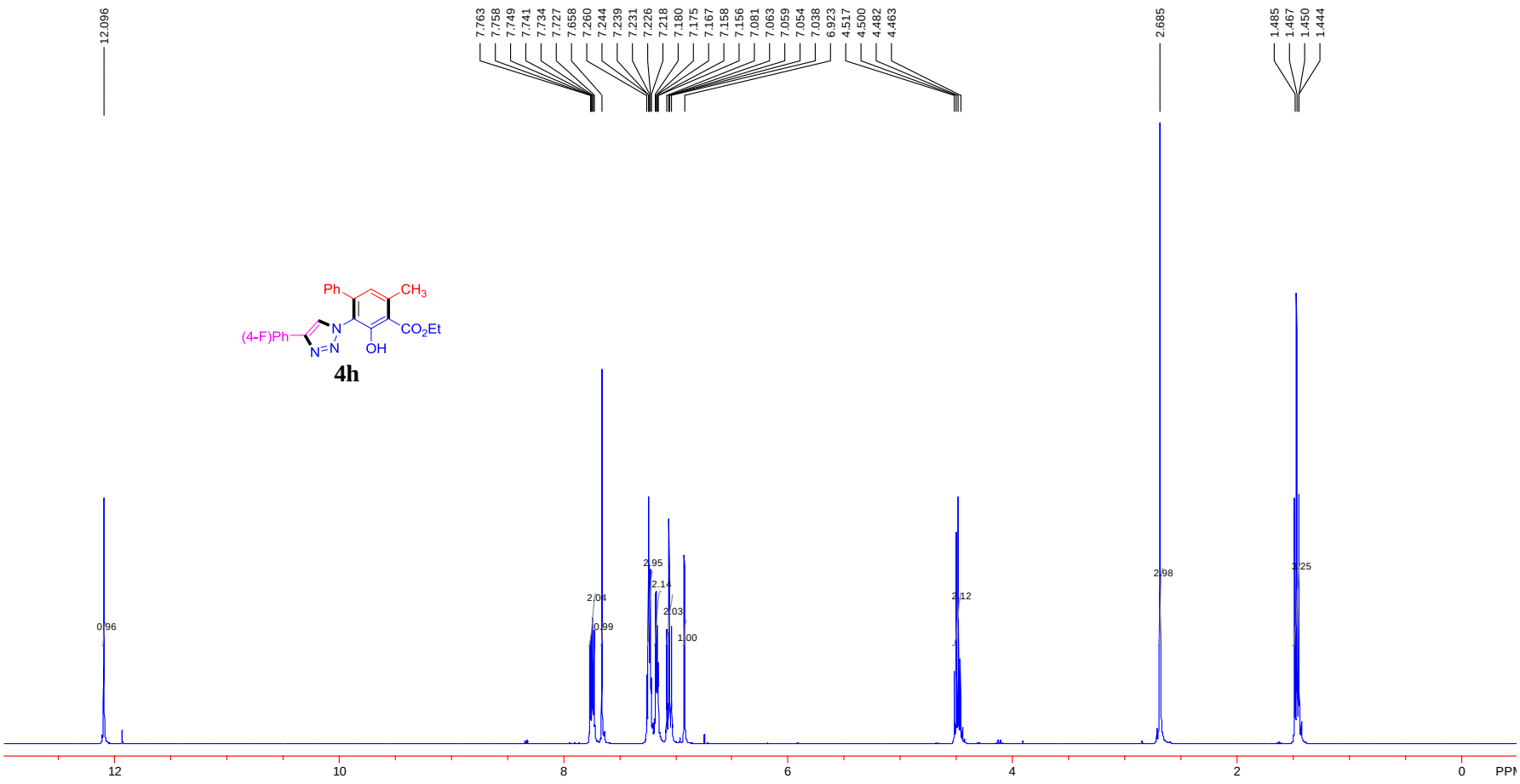
PPM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7.231
7.226
7.218
7.180
7.175
7.167
7.158
7.156
7.081
7.063
7.059
7.054
7.038
6.923
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4.500
4.482
4.463
2.685
1.485
1.467
1.450
1.444
Ph
CH3
(4-F)Ph
N
N
OH
CO2Et
4h
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2.04
0.99
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10
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6
4
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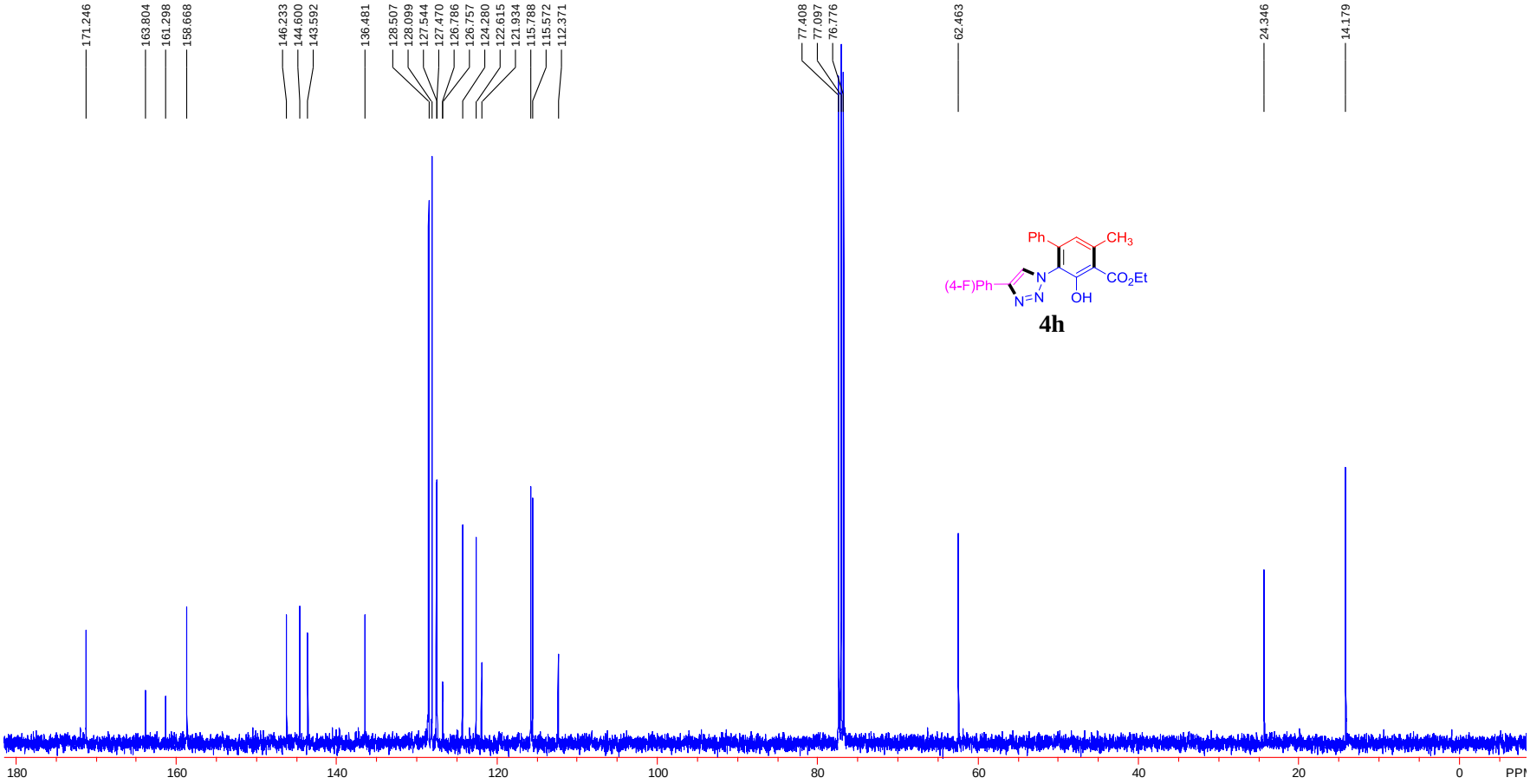
PPM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126.757
124.280
122.615
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115.572
112.371
77.408
77.097
76.776
62.463
24.346
14.179
Ph
CH3
(4-F)Ph
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N=N
CO2Et
OH
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140
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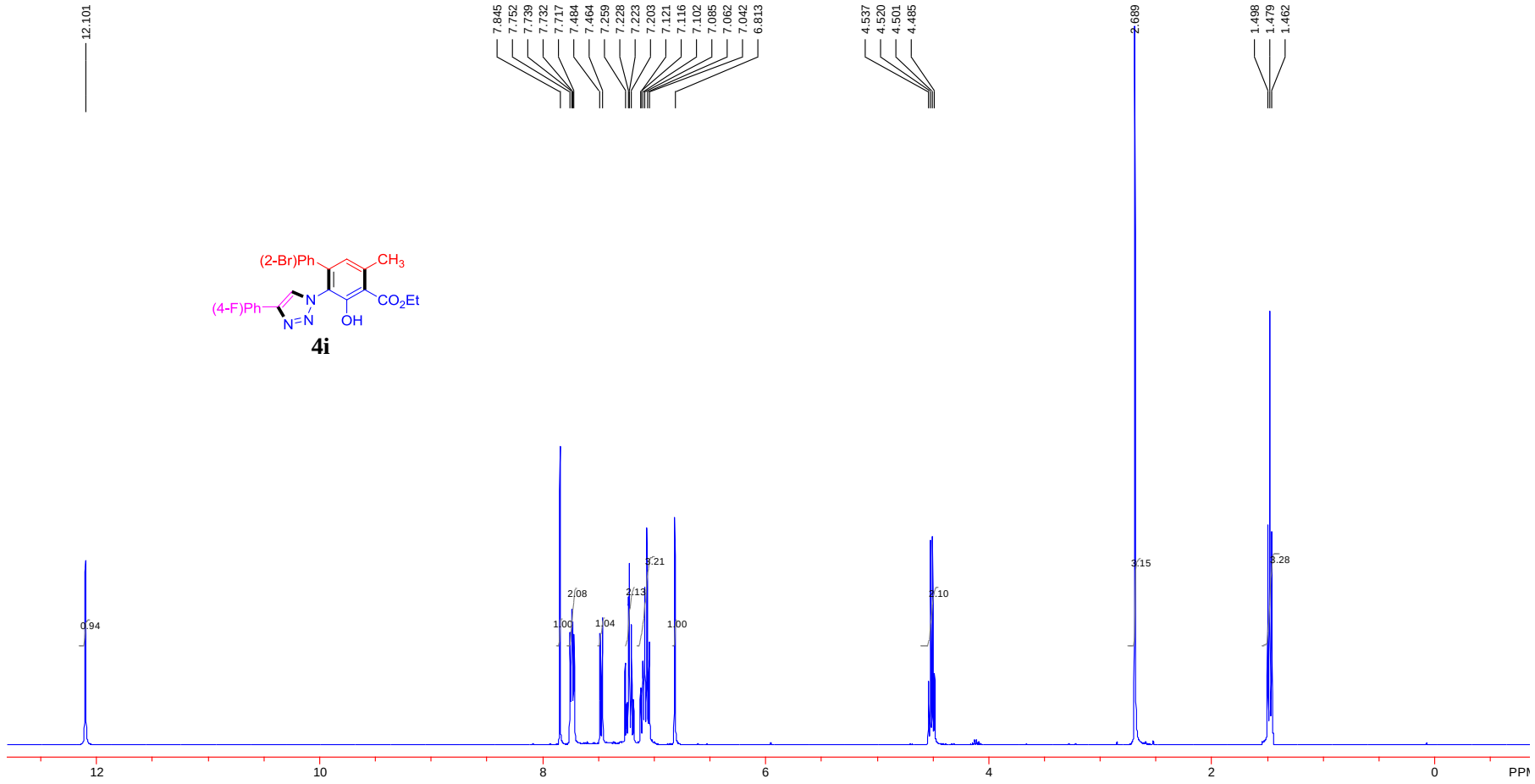
100
80
60
40
20
0
PPM

4h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7.116
7.102
7.085
7.062
7.042
6.813
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4.520
4.501
4.485
2.689
1.498
1.479
1.462
(2-Br)Ph
CH3
(4-F)Ph
N
N=N
OH
CO2Et
4i
0.94
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2.08
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1.00
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12
10
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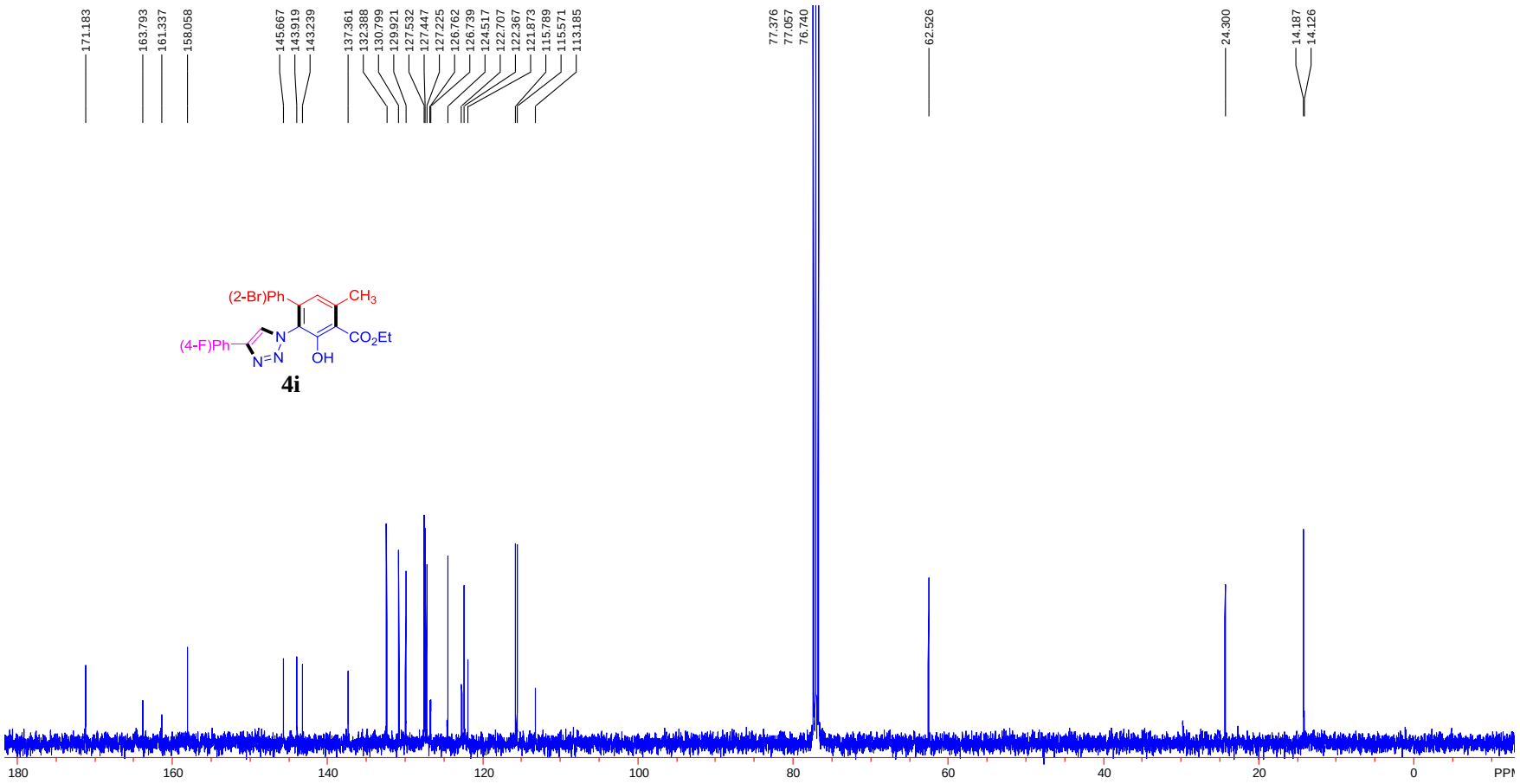
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126.739
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113.185
77.376
77.057
76.740
62.526
24.300
14.187
14.126
(2-Br)Ph
CH3
(4-F)Ph
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N
N
OH
CO2Et
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80
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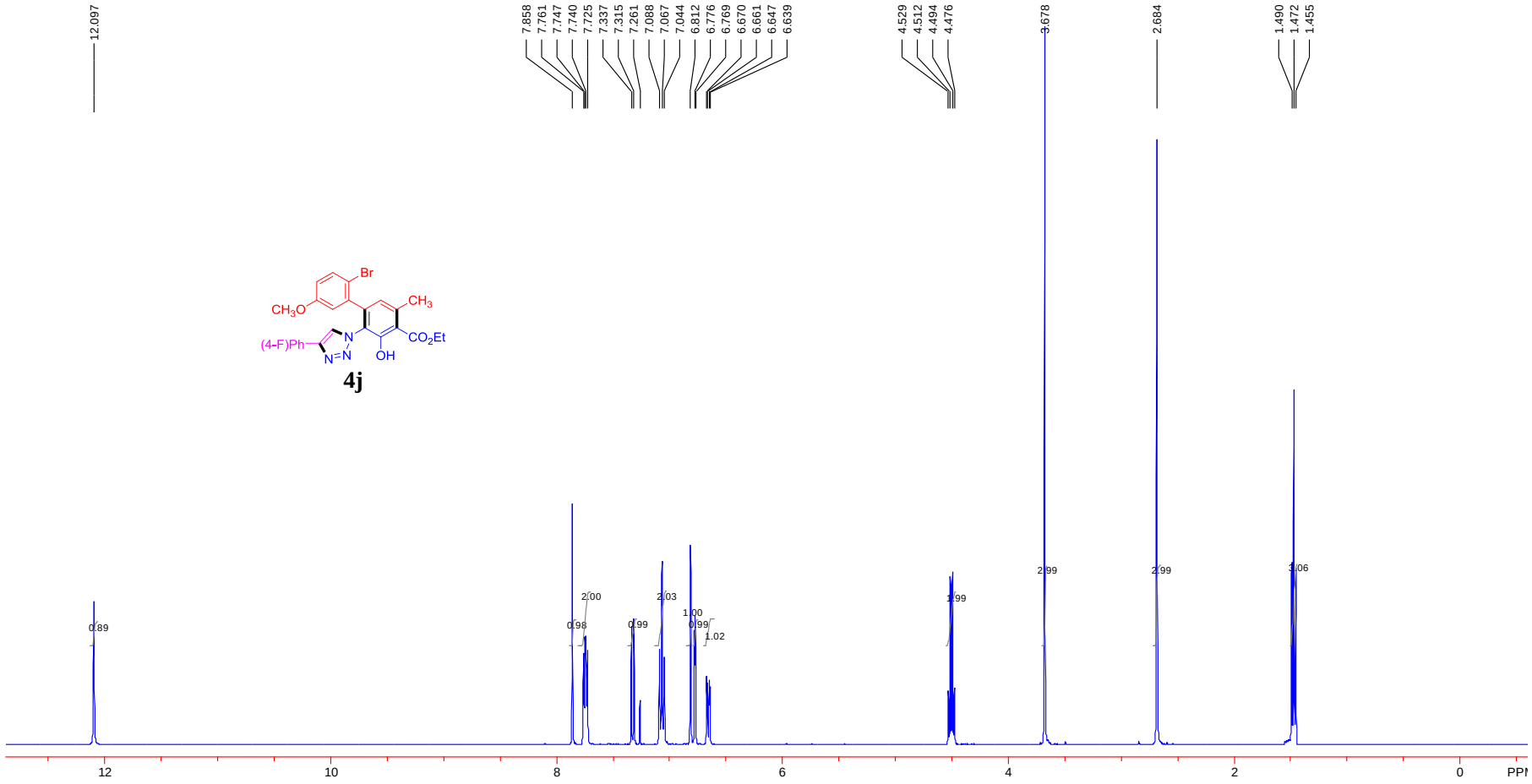
40
20
0
PPM

4i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6.776
6.769
6.670
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4.512
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4.476
3.678
2.684
1.490
1.472
1.455
Br
CH3O
CH3
(4-F)Ph
N
N=N
CO2Et
OH
4j
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0.98
0.99
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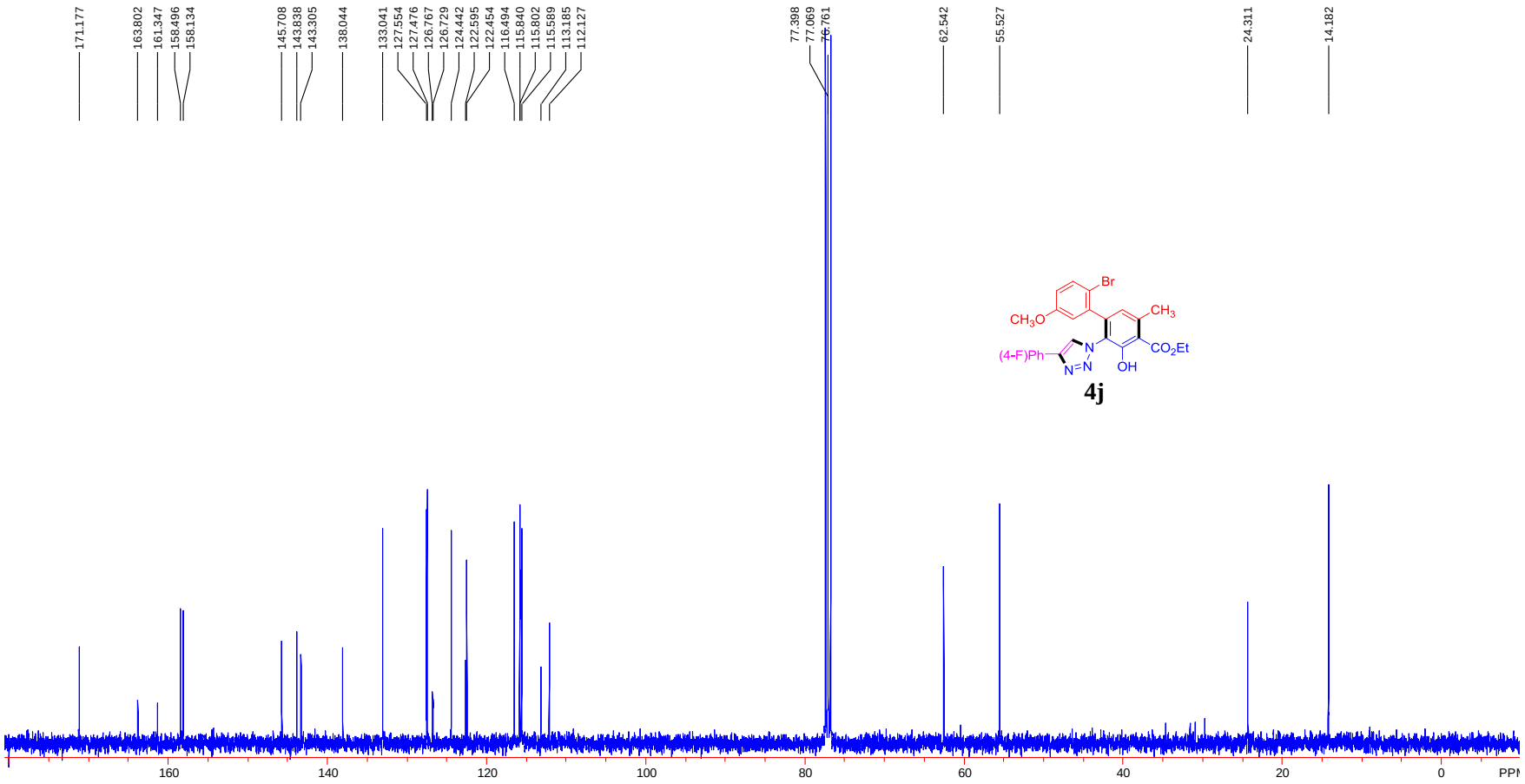
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77.069
76.761
62.542
55.527
24.311
14.182
Br
CH3O
CH3
(4-F)Ph
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N
N
CO2Et
OH
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80
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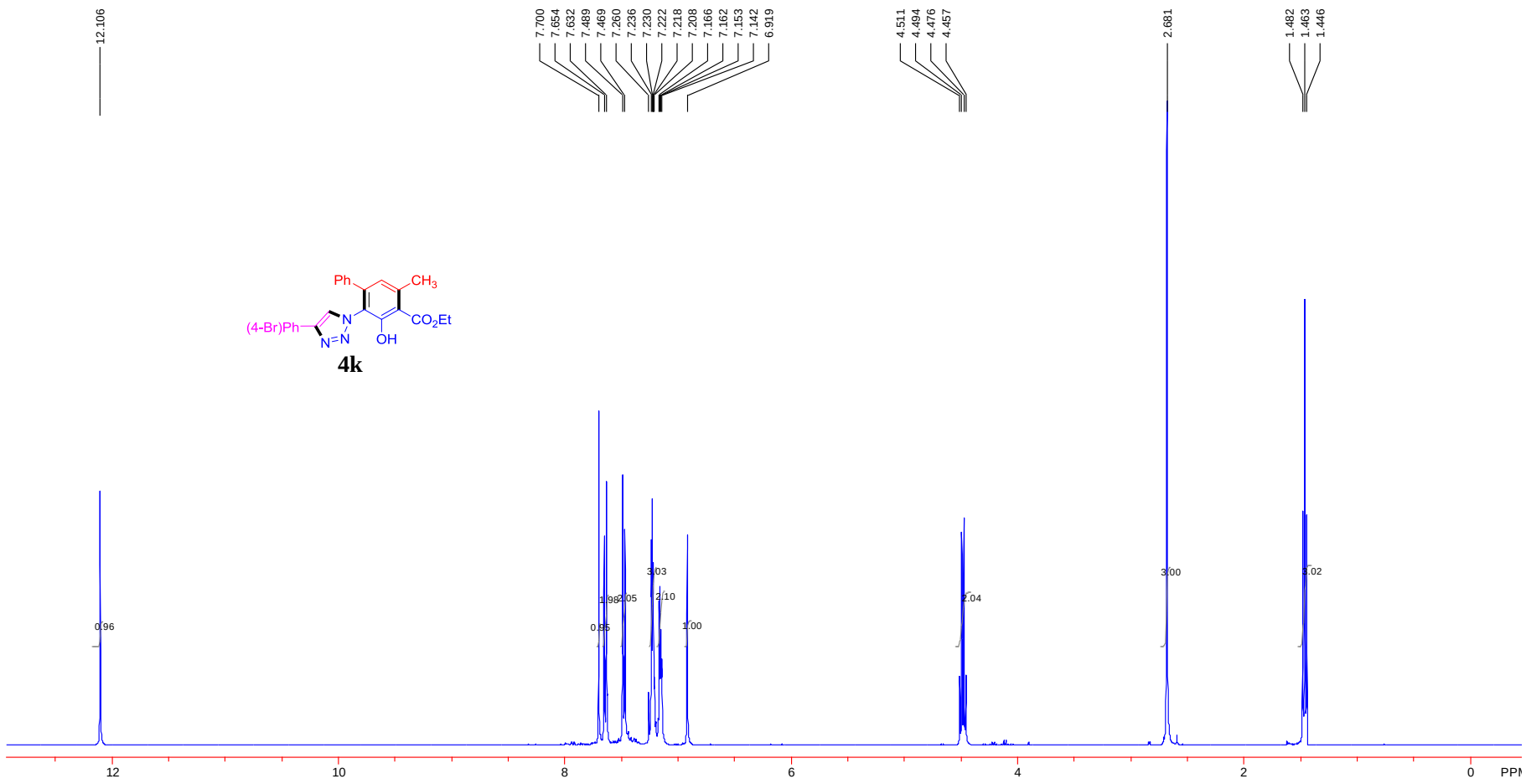
PPM

4j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7.166
7.162
7.153
7.142
6.919
4.511
4.494
4.476
4.457
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1.482
1.463
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Ph
CH3
(4-Br)Ph
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N=N
OH
CO2Et
4k
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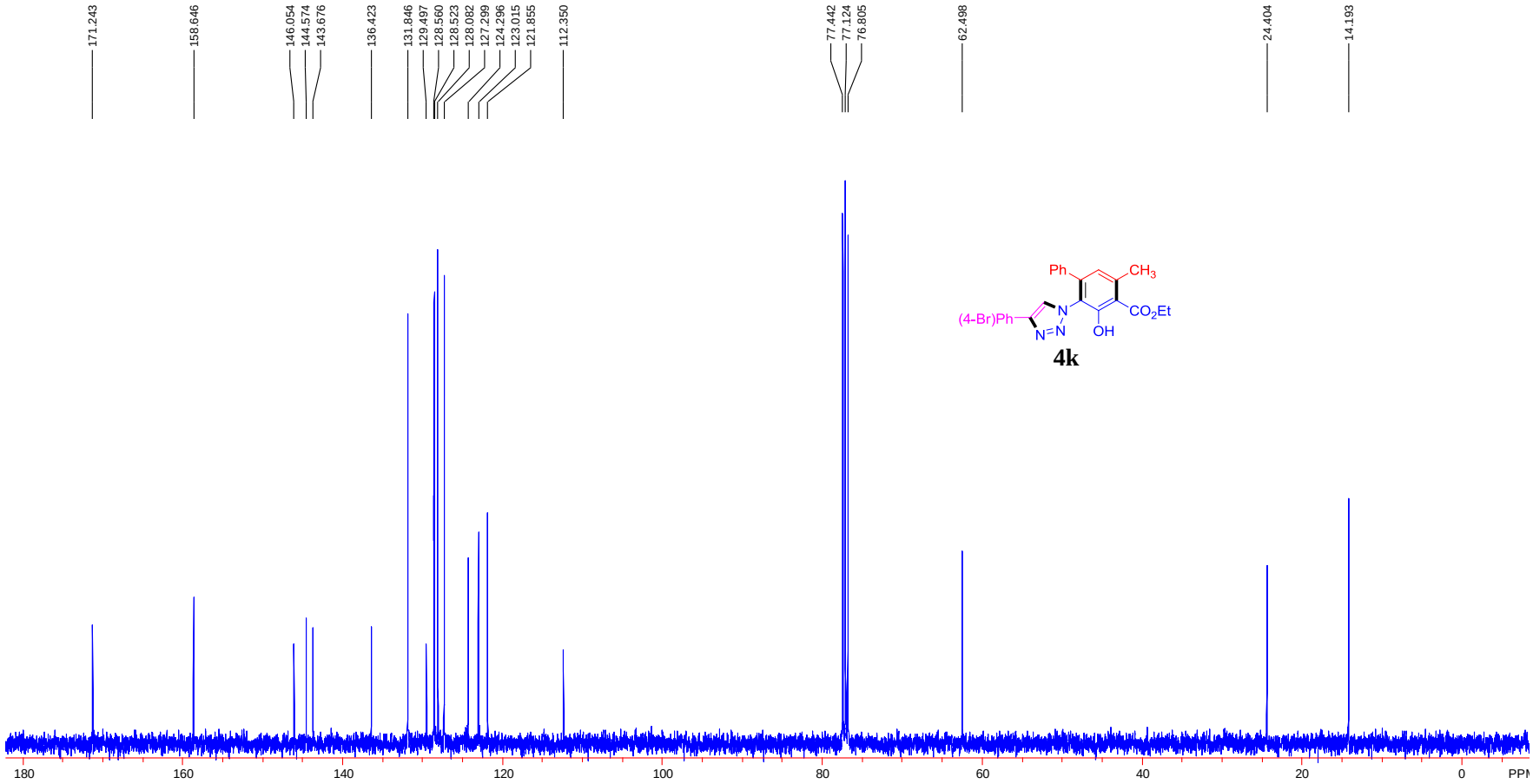
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Ph
CH3
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OH
CO2Et
4k
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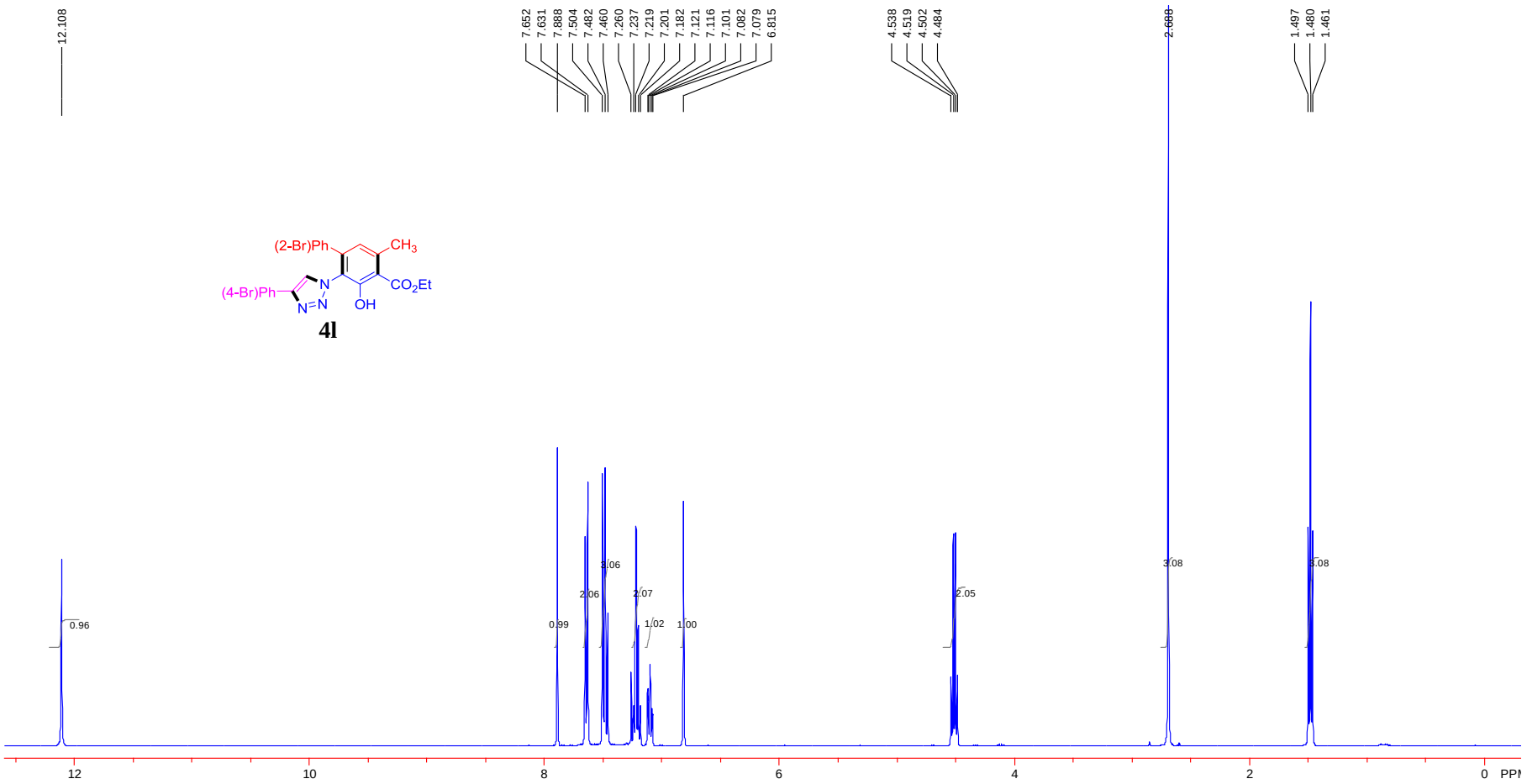
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1.497
1.480
1.461
(2-Br)Ph
CH3
(4-Br)Ph
N
N=N
OH
CO2Et
0.96
0.99
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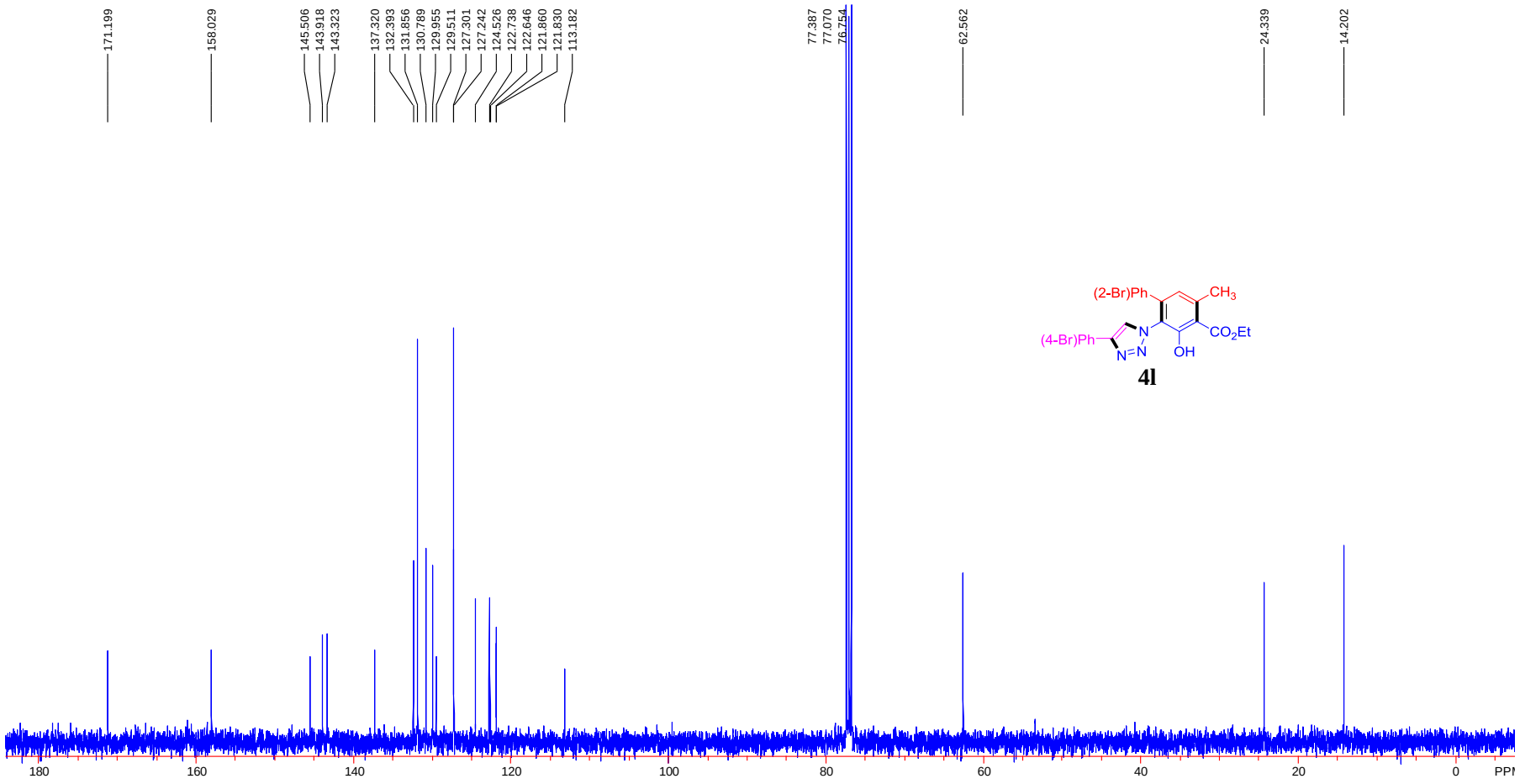
4l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76.754
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14.202
(2-Br)Ph
CH3
(4-Br)Ph
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N
N
CO2Et
OH
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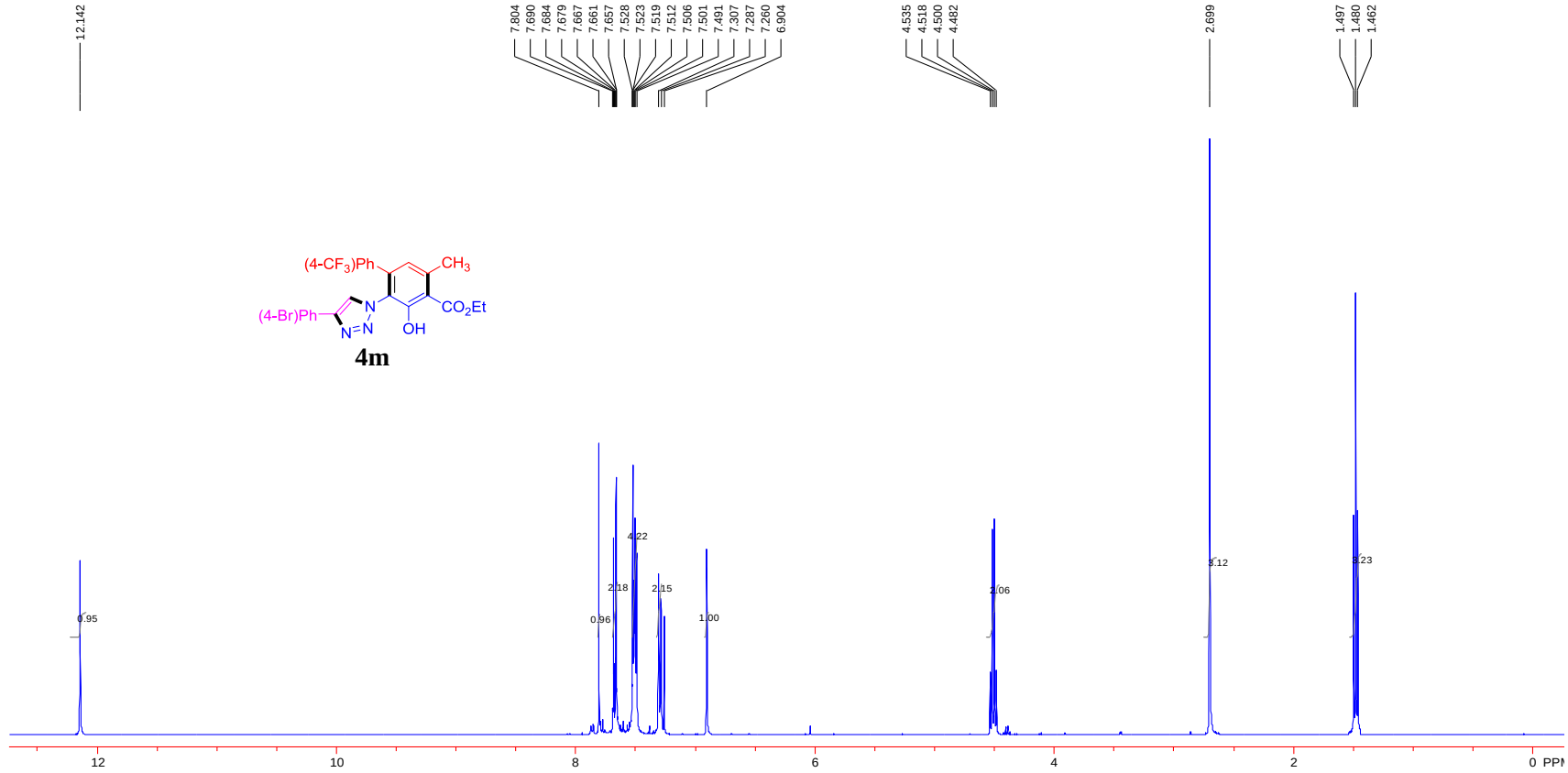
80
60
40
20
0
PPM

4l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7.491
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7.287
7.260
6.904
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4.518
4.500
4.482
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1.497
1.480
1.462
(4-CF3)Ph
CH3
(4-Br)Ph
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N=N
OH
CO2Et
4m
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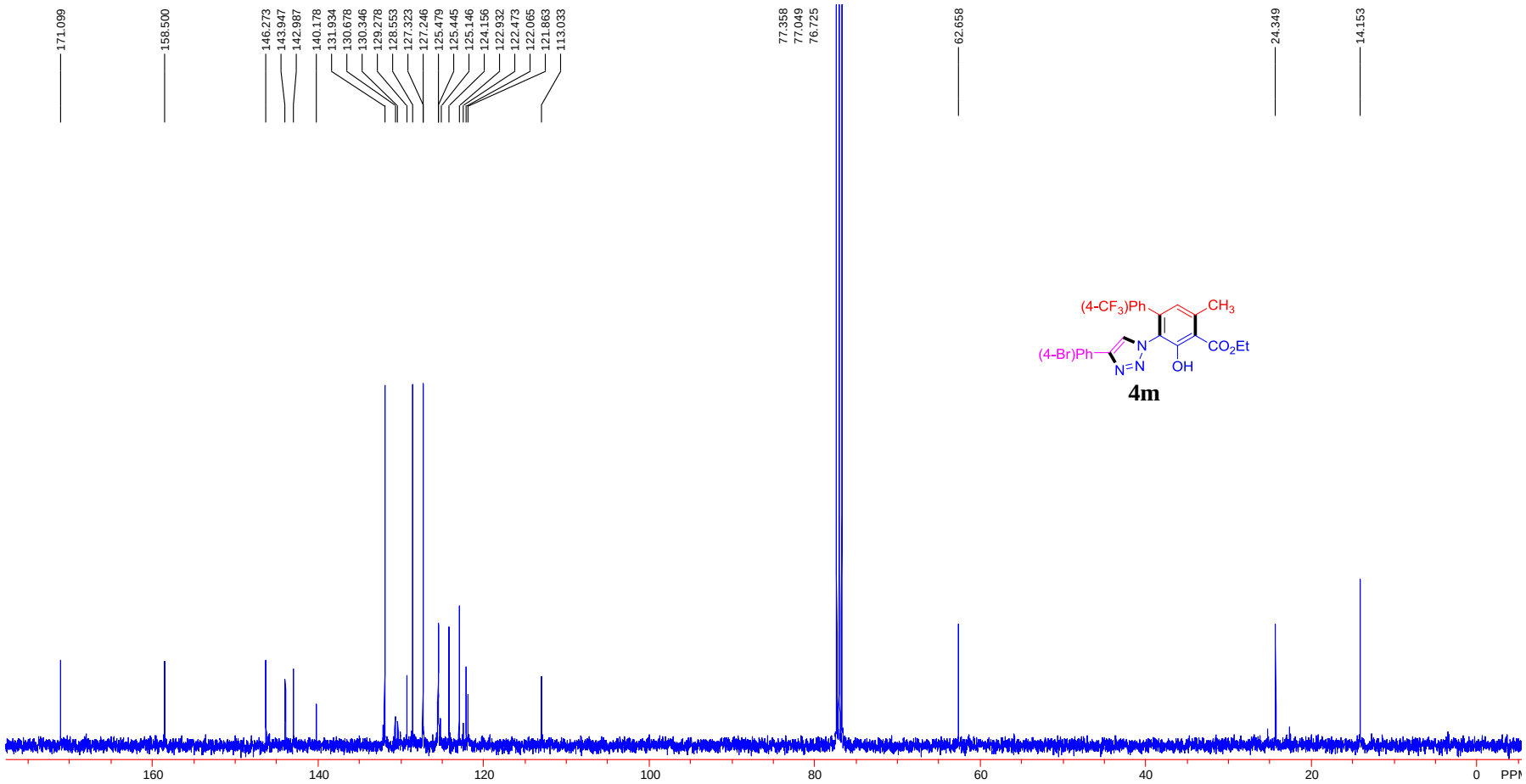
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122.932
122.473
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121.863
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77.049
76.725
62.658
24.349
14.153
(4-CF3)Ph
CH3
(4-Br)Ph
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N=N
CO2Et
OH
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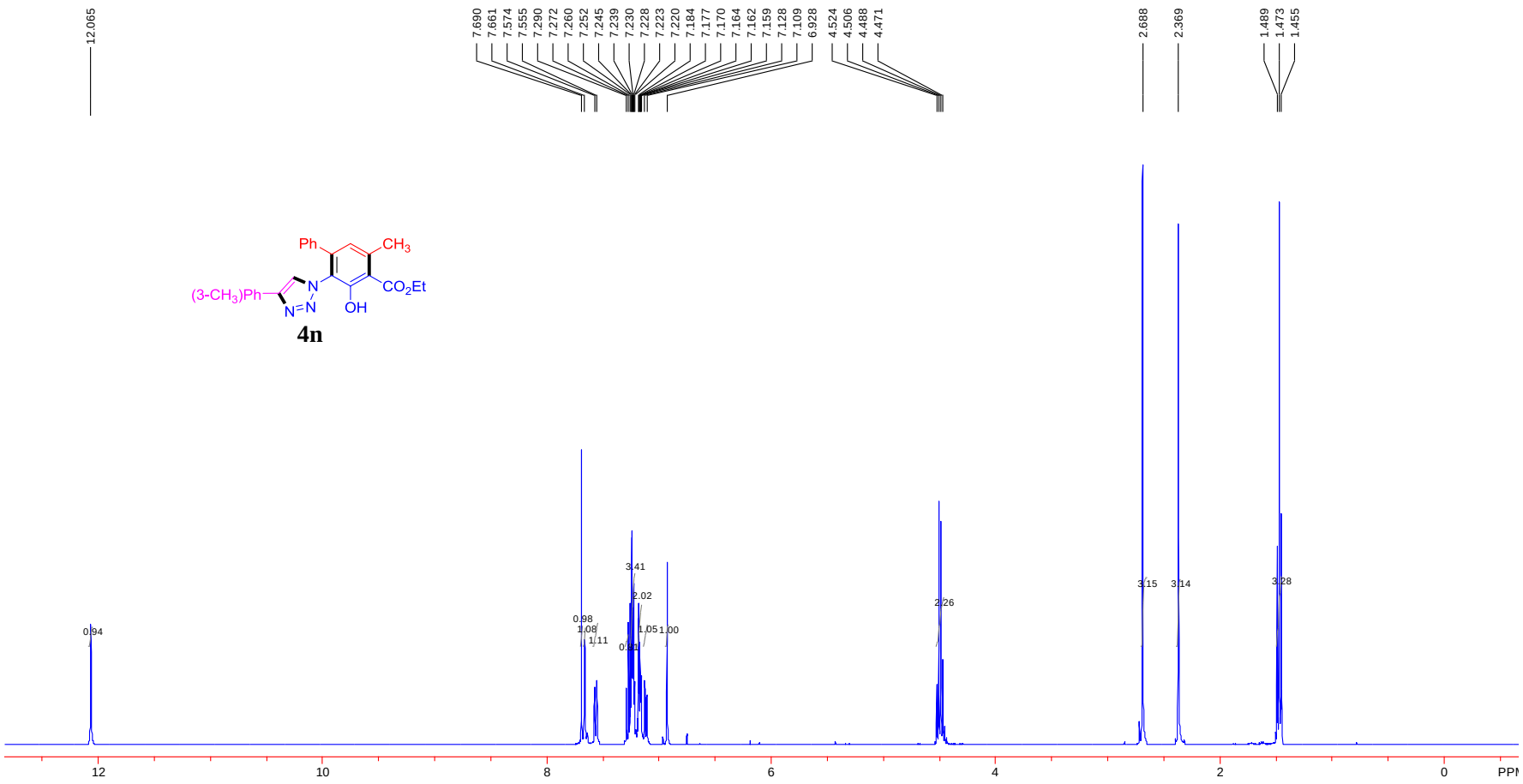
140
120
100
80
60
40
20
0
PPM

4m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7.223
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7.177
7.170
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7.159
7.128
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6.928
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4.488
4.471
2.688
2.369
1.489
1.473
1.455
Ph
CH3
(3-CH3)Ph
N
N=N
OH
CO2Et
4n
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0.98
1.08
1.11
3.41
2.02
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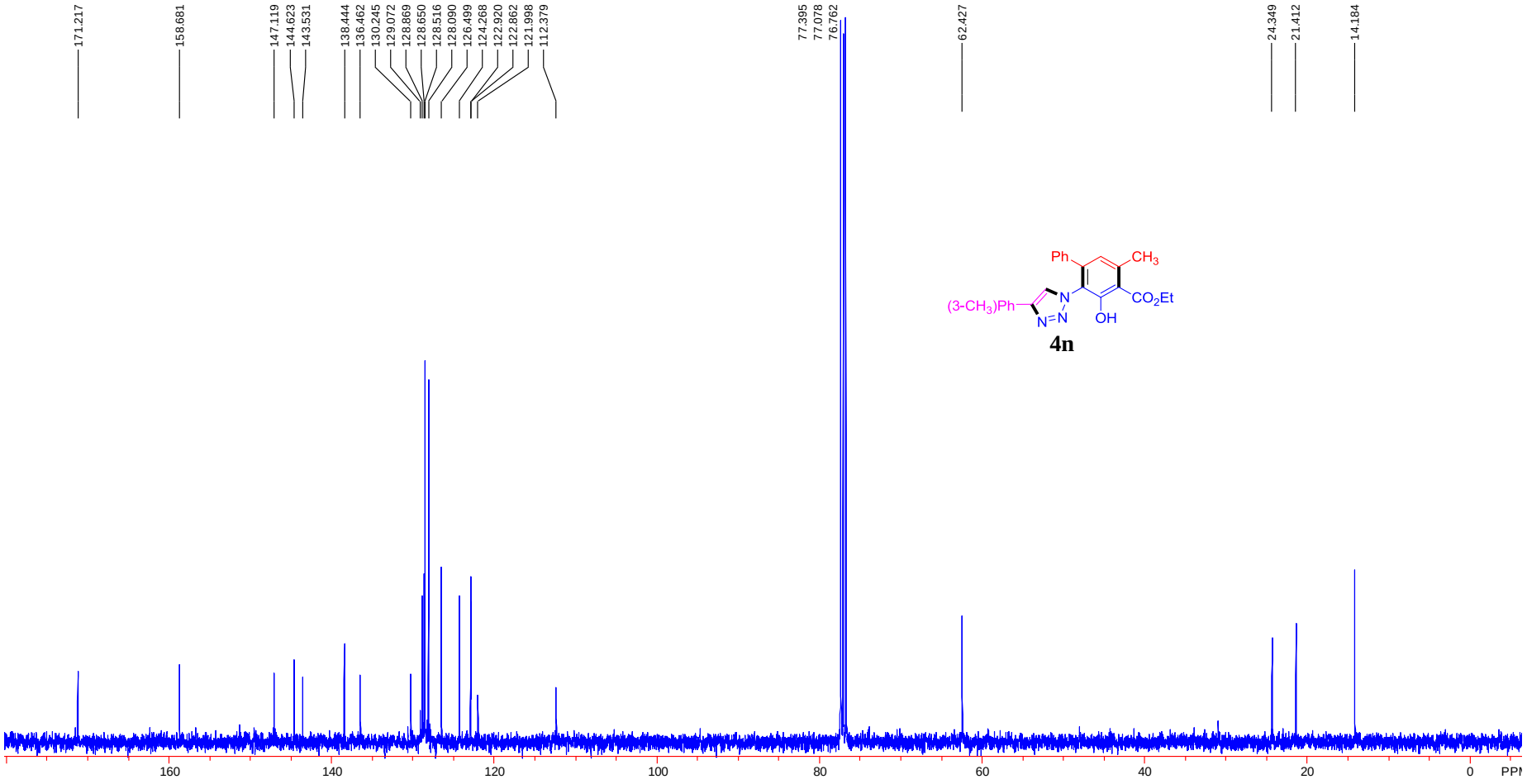
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CH3
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CO2Et
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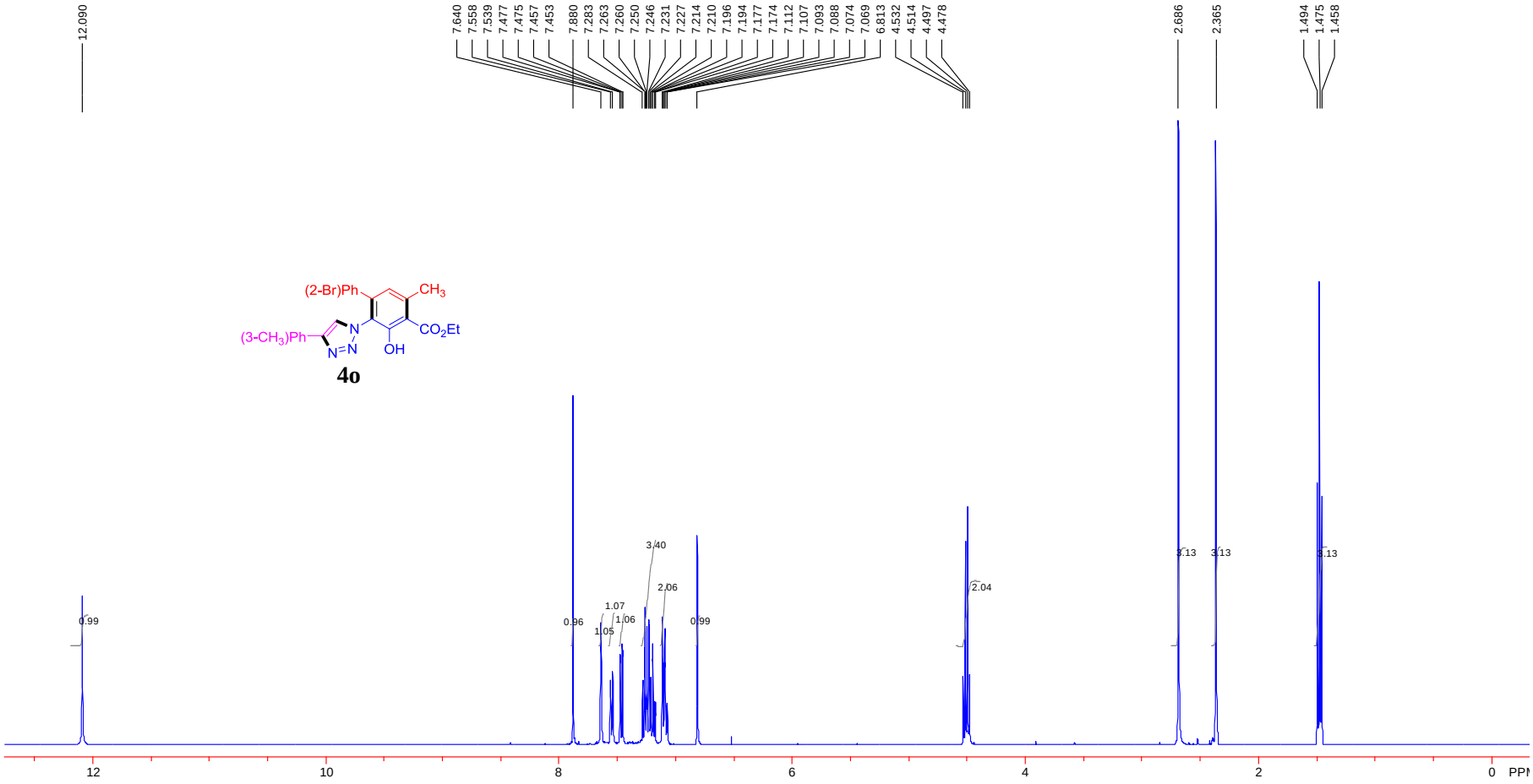
PPM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4.497
4.478
2.686
2.365
1.494
1.475
1.458
(2-Br)Ph
CH3
(3-CH3)Ph
N
N=N
OH
CO2Et
4o
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1.07
1.06
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10
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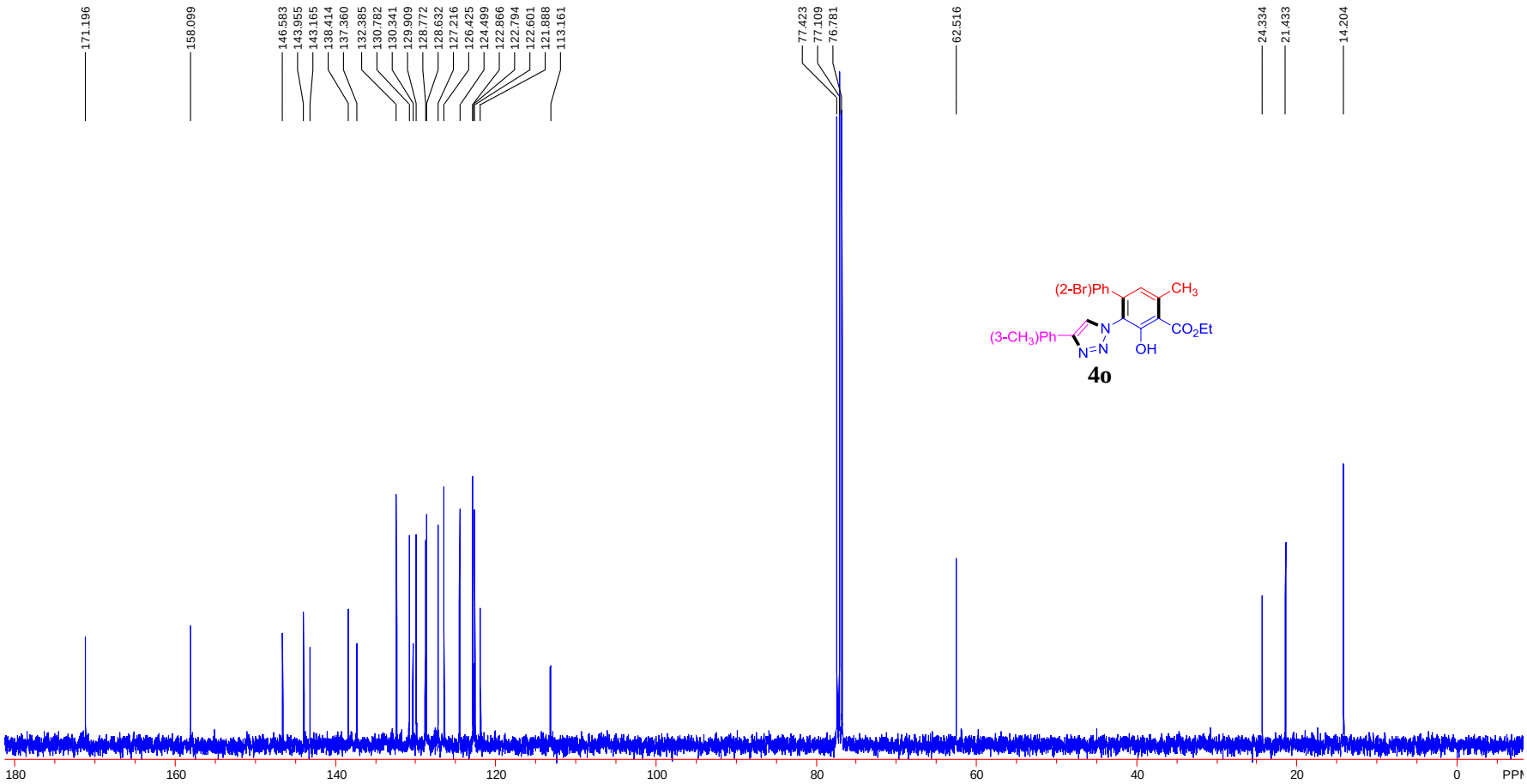
PPM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121.888
113.161
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77.109
76.781
62.516
24.334
21.433
14.204
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CH3
(3-CH3)Ph
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CO2Et
OH
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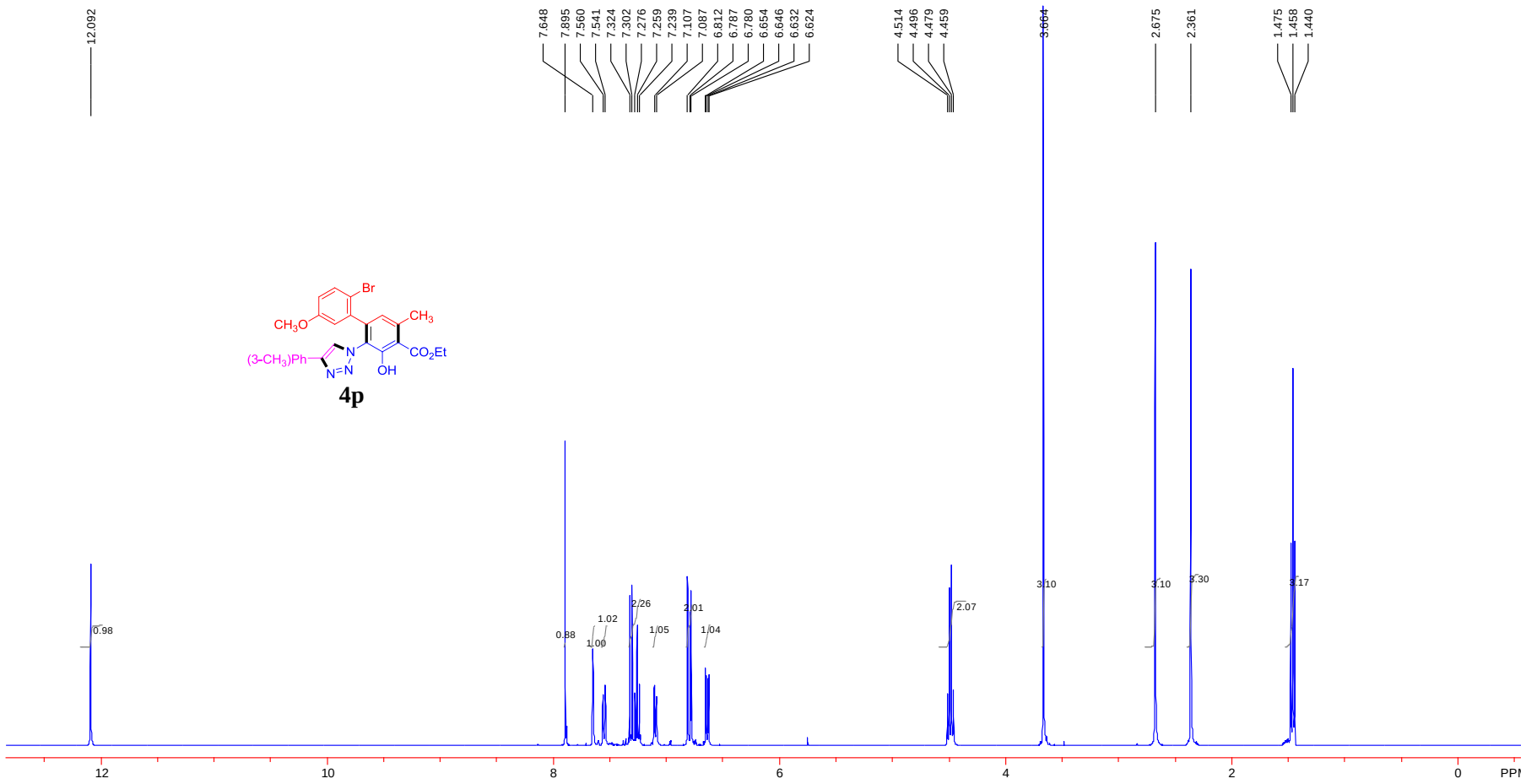
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4.496
4.479
4.459
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1.440
Br
CH3O
CH3
(3-CH3)Ph
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N
N
OH
CO2Et
4p
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1.02
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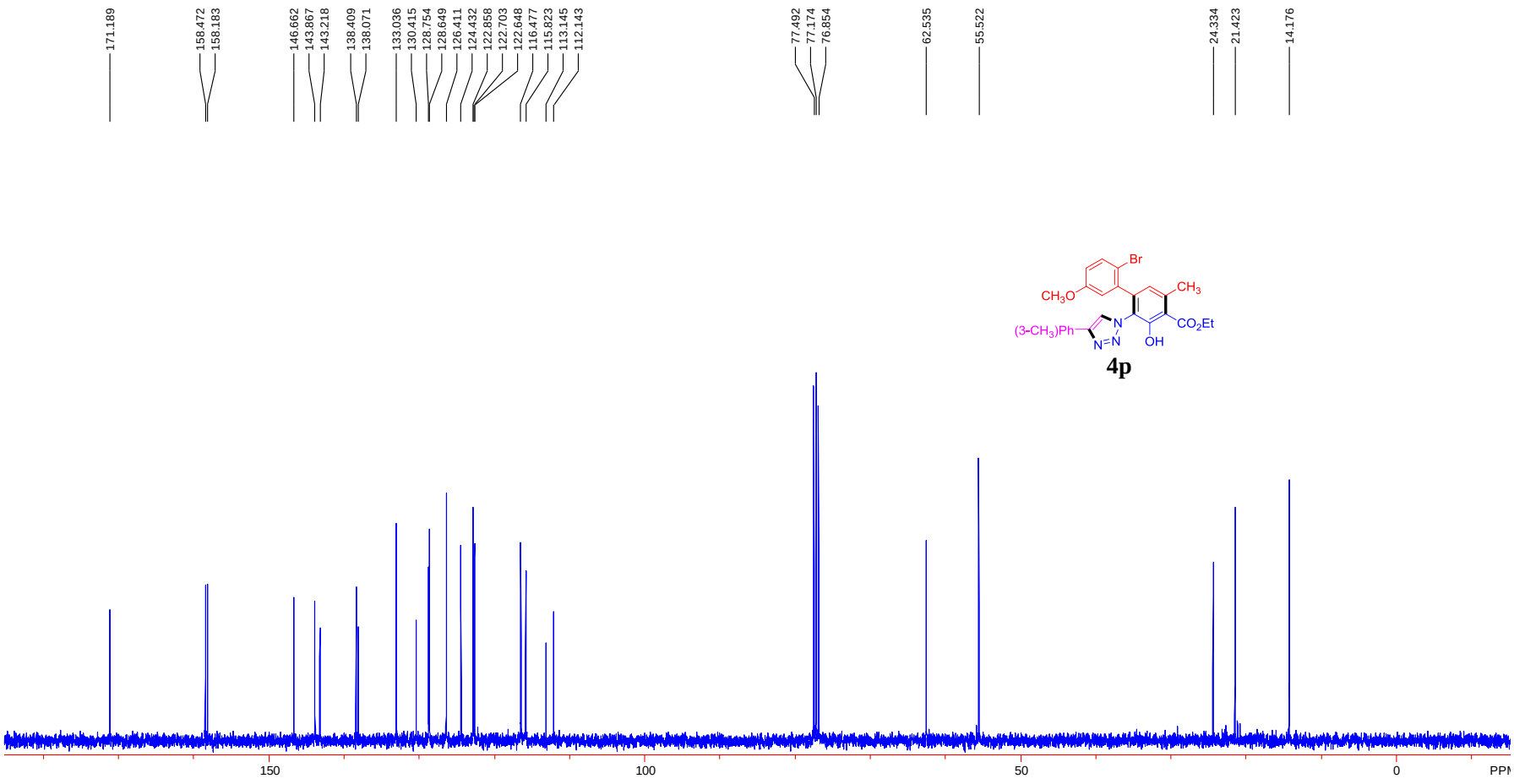
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24.334
21.423
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CO2Et
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OH
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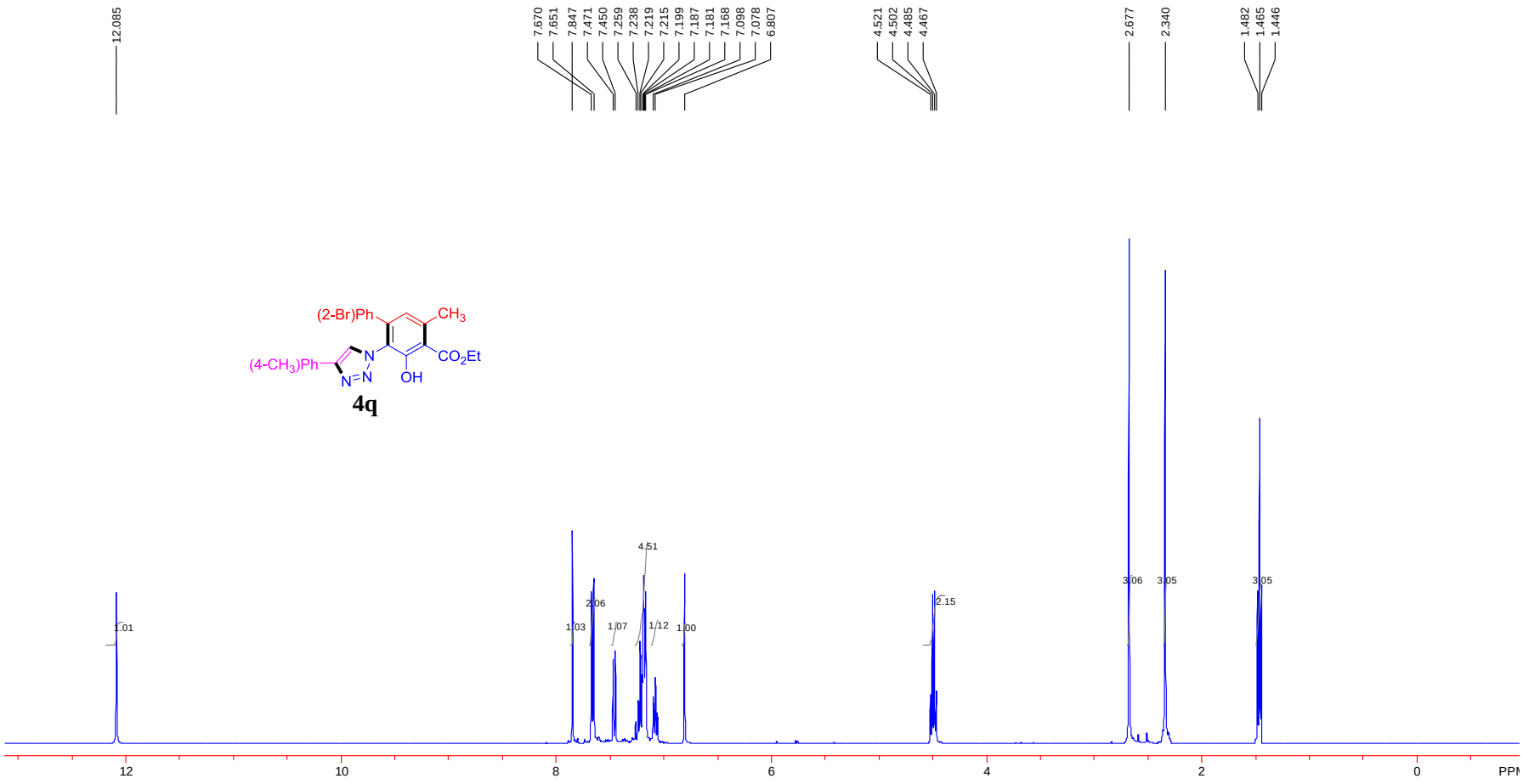
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1.465
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CH3
(4-CH3)Ph
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N=N
CO2Et
OH
4q
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1.03
2.06
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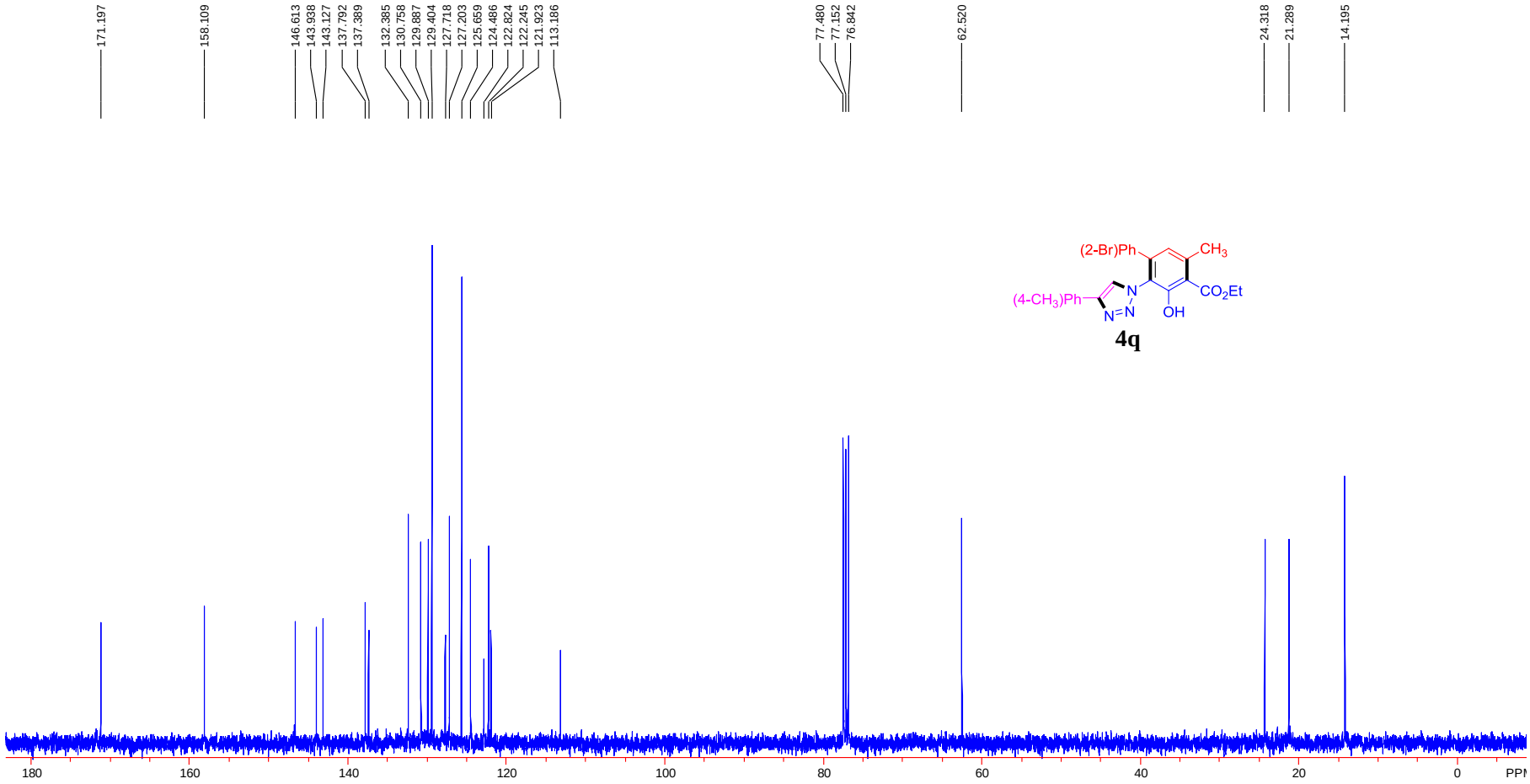
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127.203
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124.486
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77.152
76.842
62.520
24.318
21.289
14.195
(2-Br)Ph
CH3
(4-CH3)Ph
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CO2Et
OH
4q
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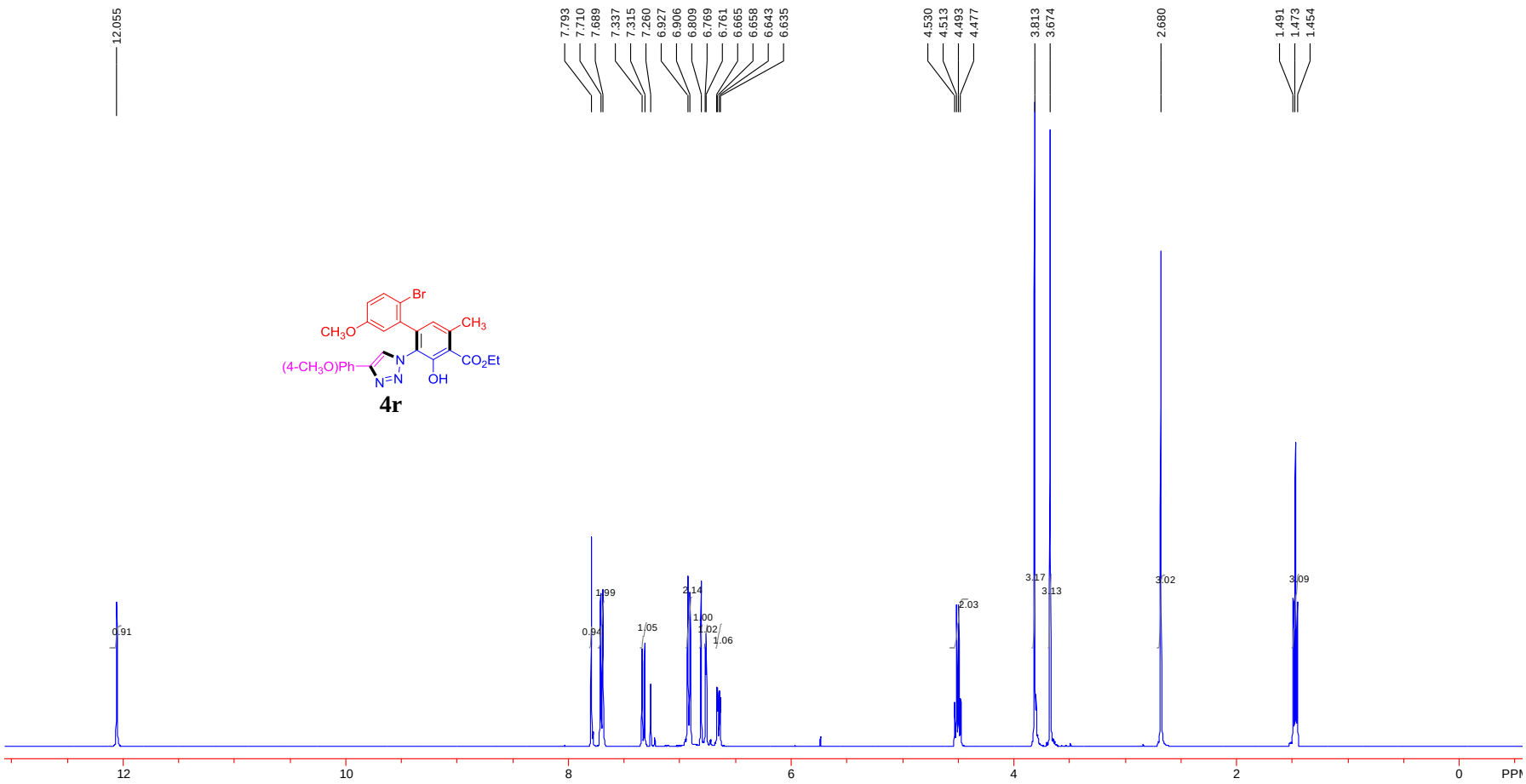
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6.761
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6.658
6.643
6.635
4.530
4.513
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4.477
3.813
3.674
2.680
1.491
1.473
1.454
Br
CH3O
CH3
(4-CH3O)Ph
N
N=N
OH
CO2Et
4r
0.91
1.99
0.94
1.05
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1.00
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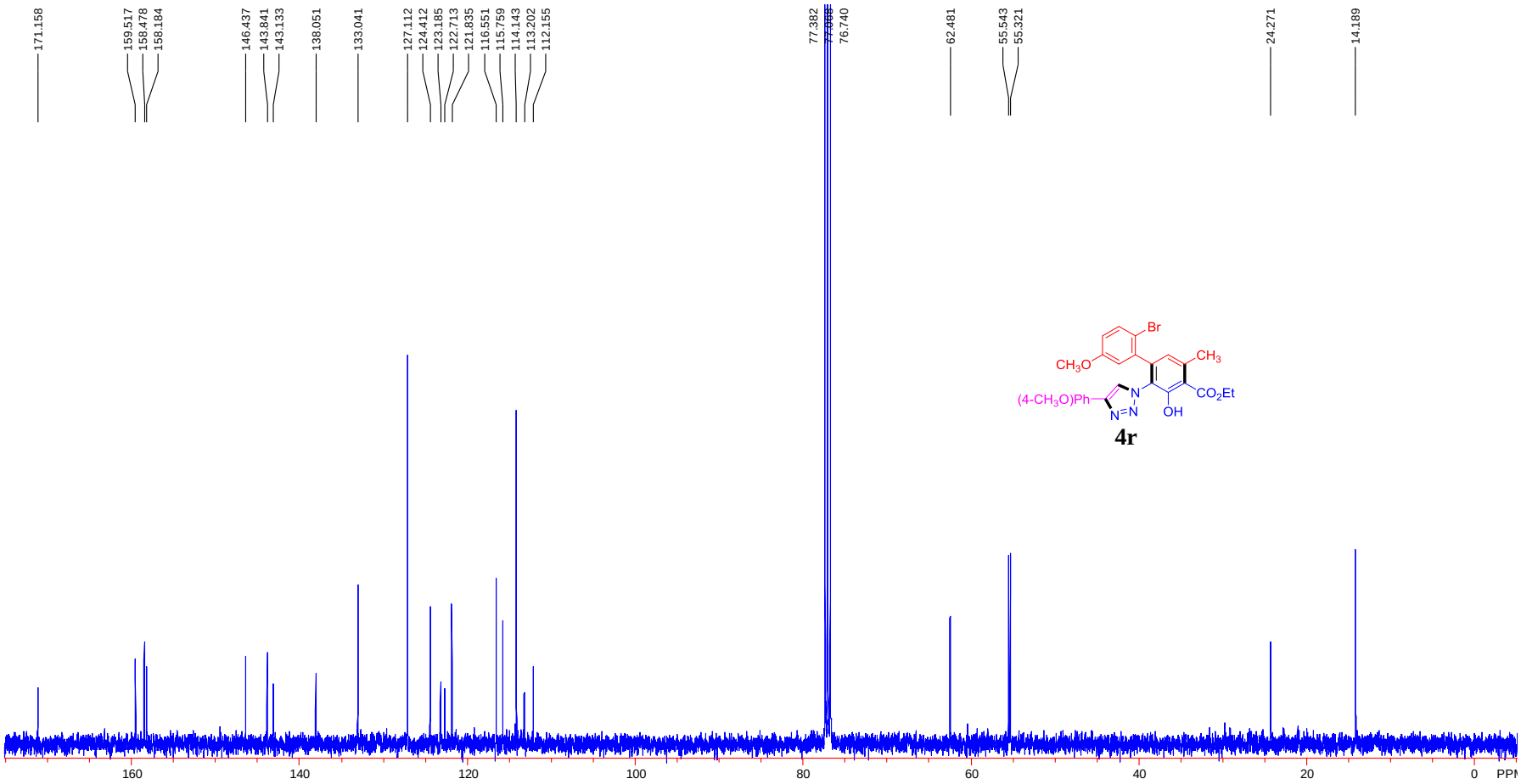
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138.051
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114.143
113.202
112.155
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77.068
76.740
62.481
55.543
55.321
24.271
14.189
Br
CH3O
CH3
(4-CH3O)Ph
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N=N
OH
CO2Et
4r
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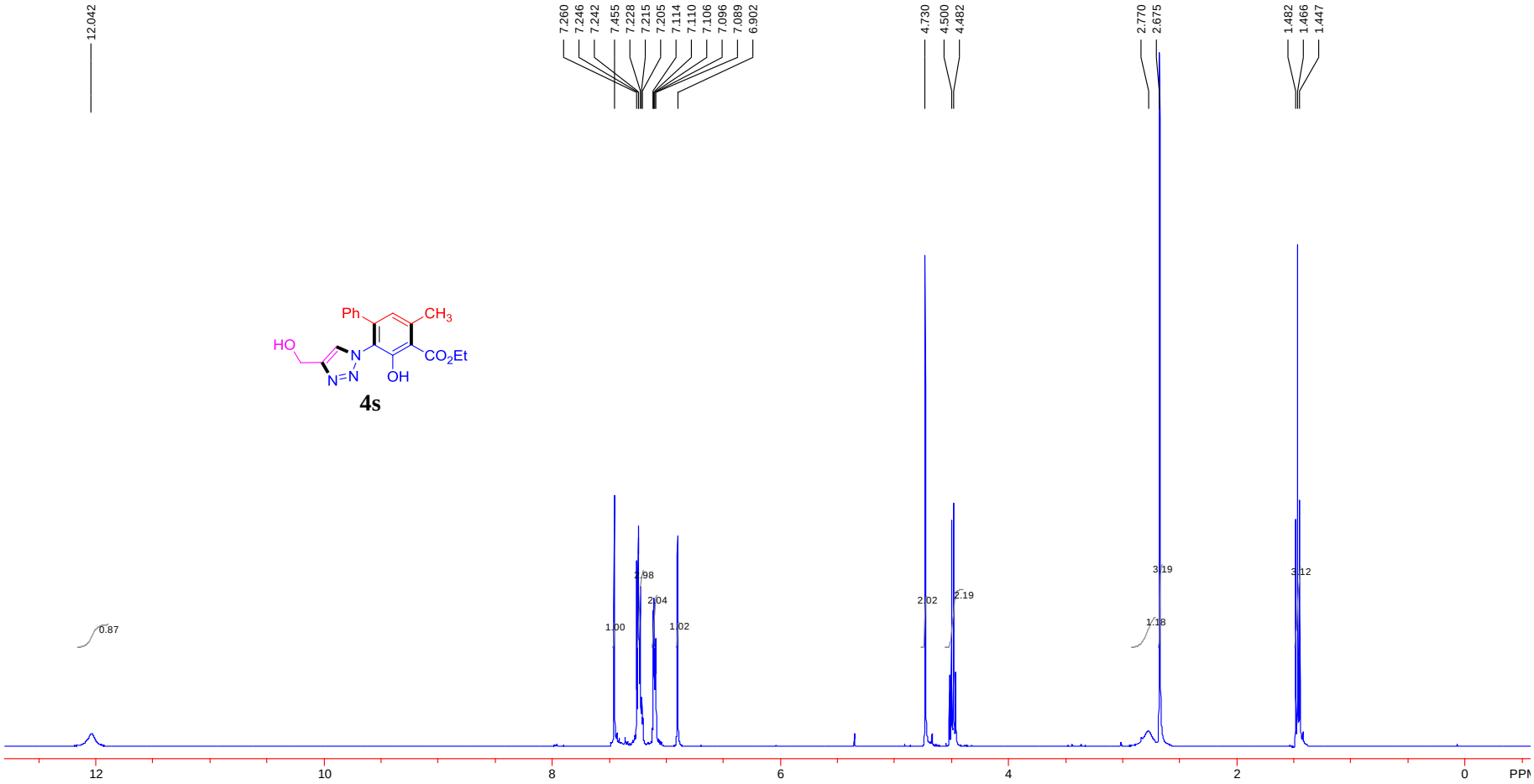
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7.096
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6.902
4.730
4.500
4.482
2.770
2.675
1.482
1.466
1.447
Ph
CH3
HO
N
N=N
CO2Et
OH
4s
0.87
1.00
2.98
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10
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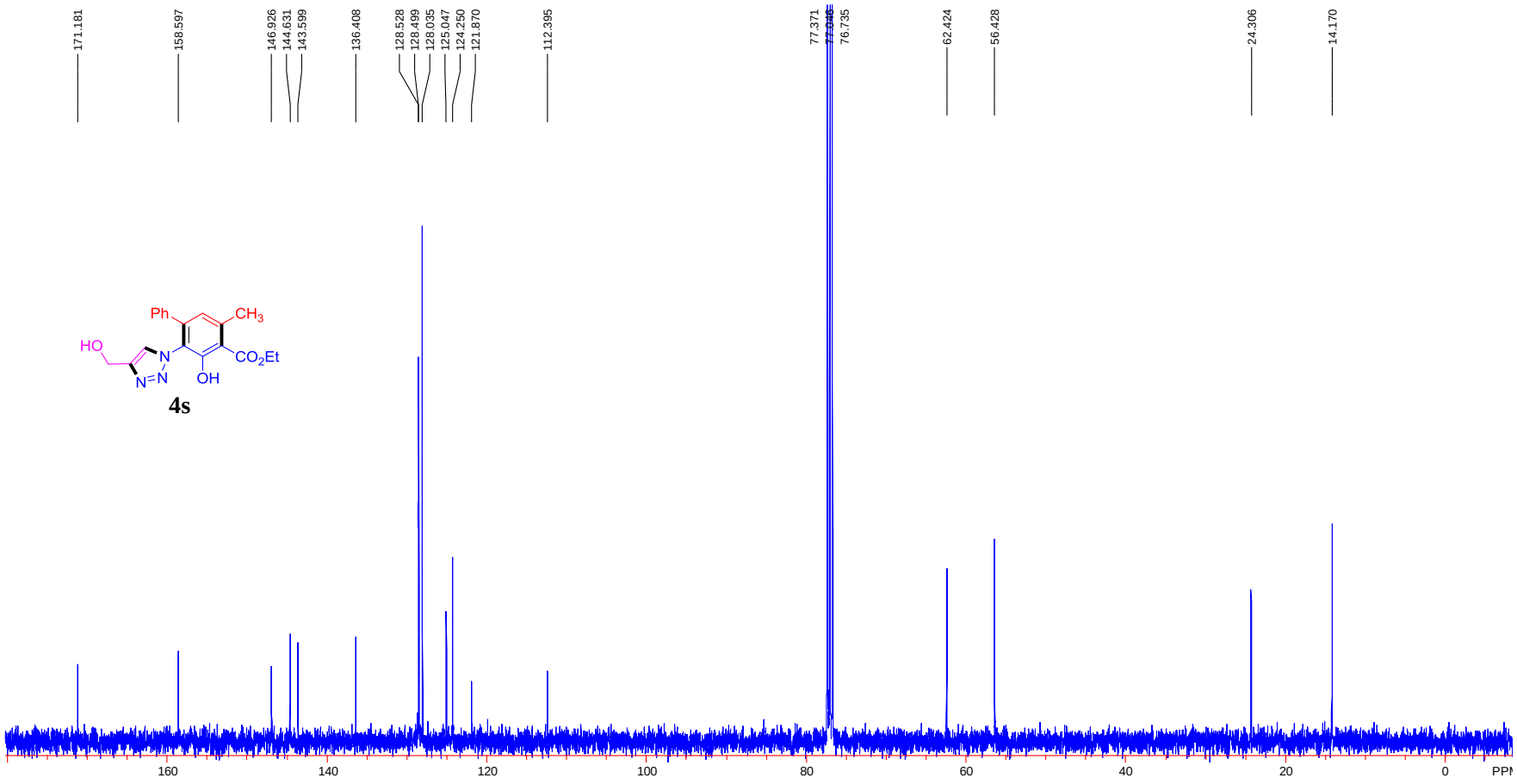
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76.735
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14.170
Ph
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N=N
OH
CO2Et
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140
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100
80
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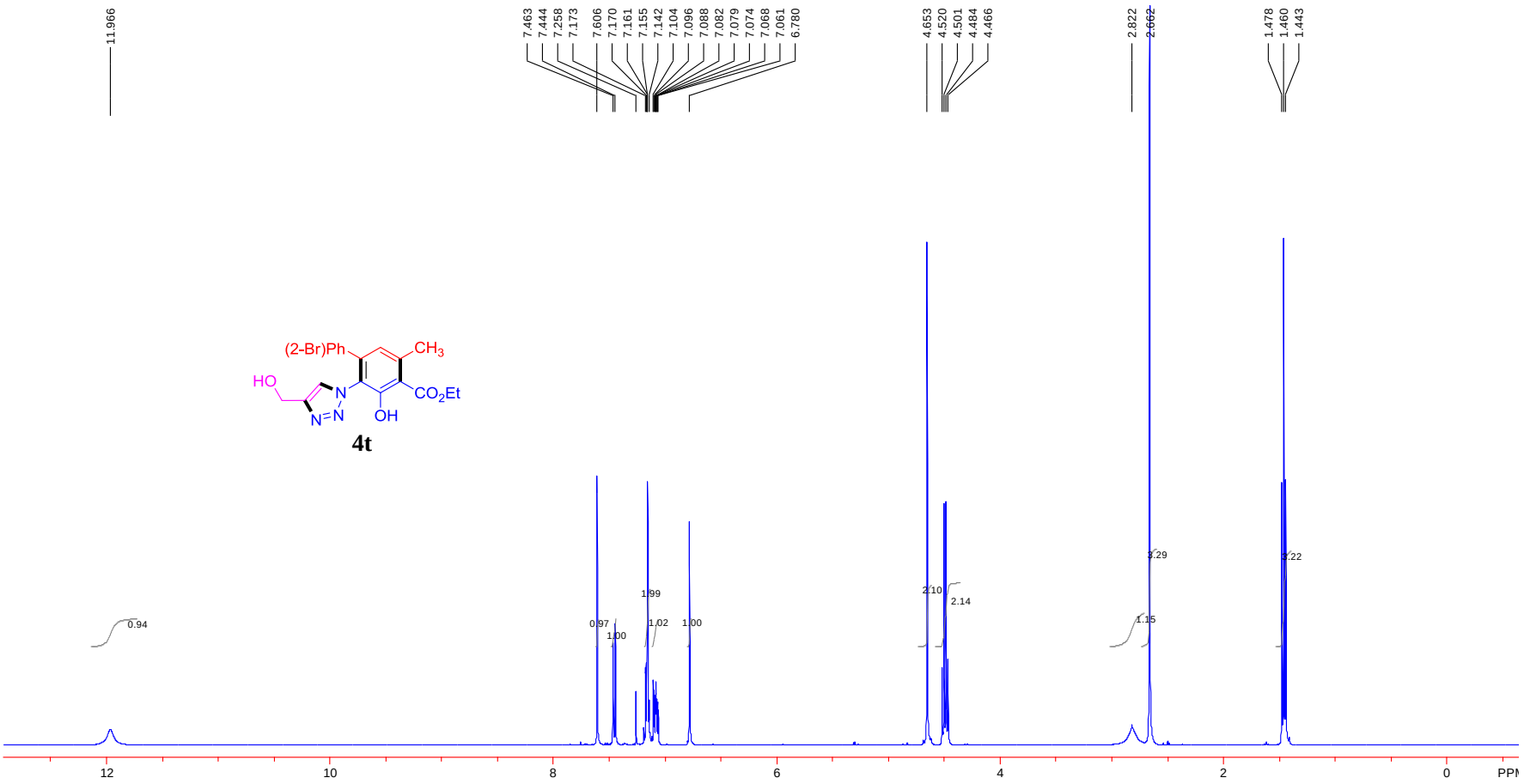
40
20
0
PPM

4s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7.088
7.082
7.079
7.074
7.068
7.061
6.780
4.653
4.520
4.501
4.484
4.466
2.822
2.662
1.478
1.460
1.443
(2-Br)Ph
CH3
HO
CO2Et
OH
N
N=N
4t
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0.97
1.00
1.99
1.02
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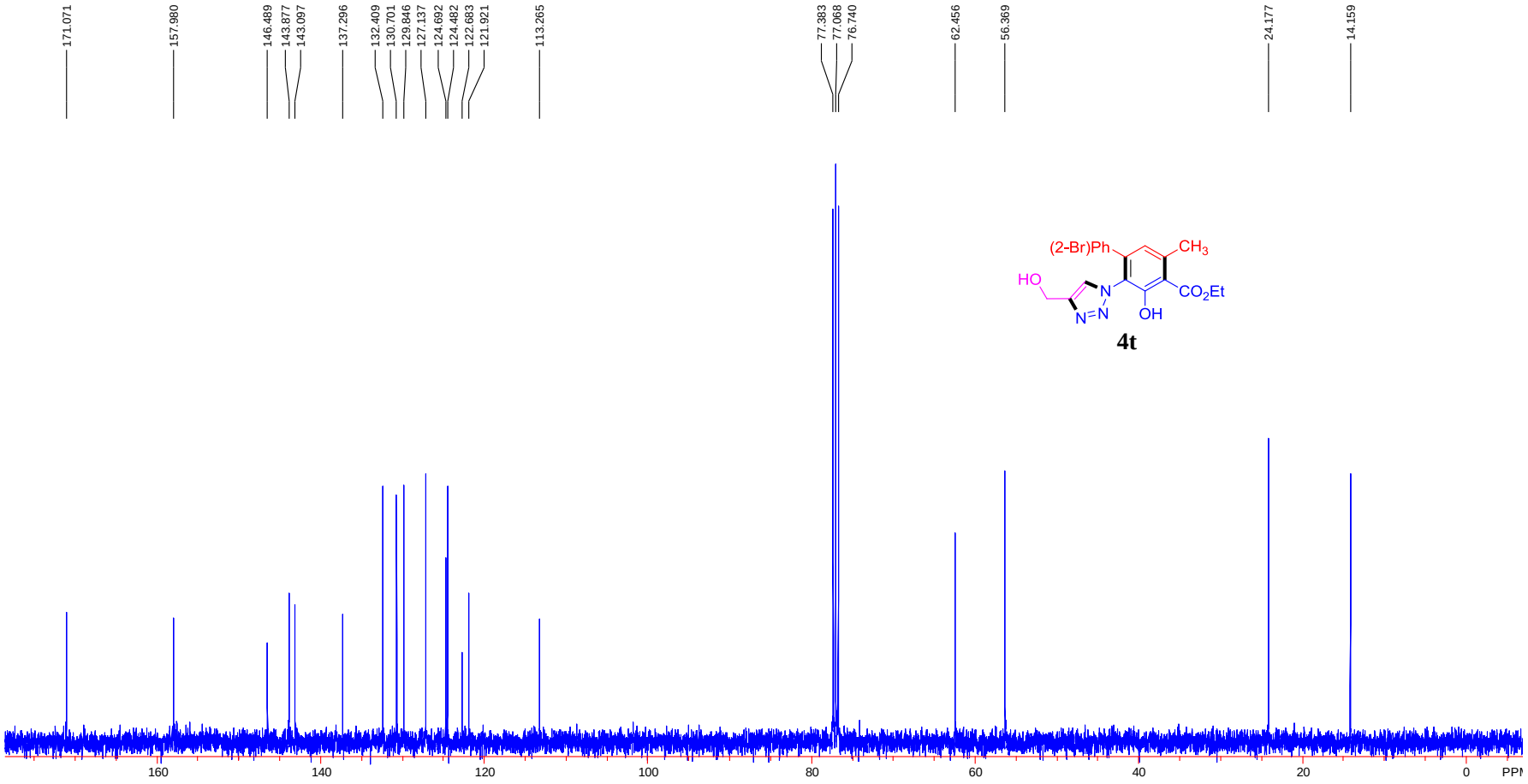
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77.068
76.740
62.456
56.369
24.177
14.159
(2-Br)Ph
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HO
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N=N
CO2Et
OH
160
140
120
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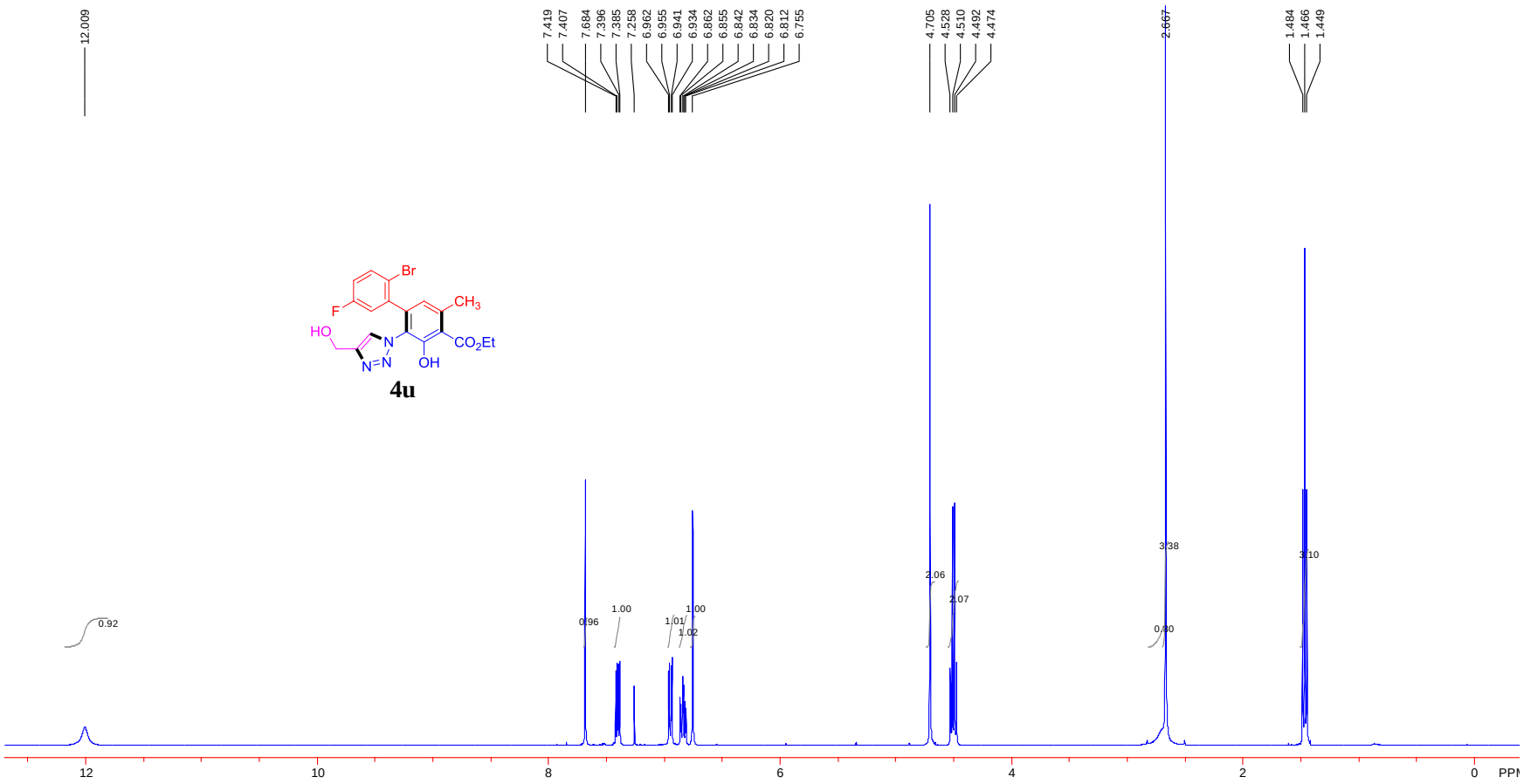
80
60
40
20
0
PPM

4t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6.812
6.755
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4.510
4.492
4.474
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1.484
1.466
1.449
Br
F
CH3
HO
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OH
CO2Et
4u
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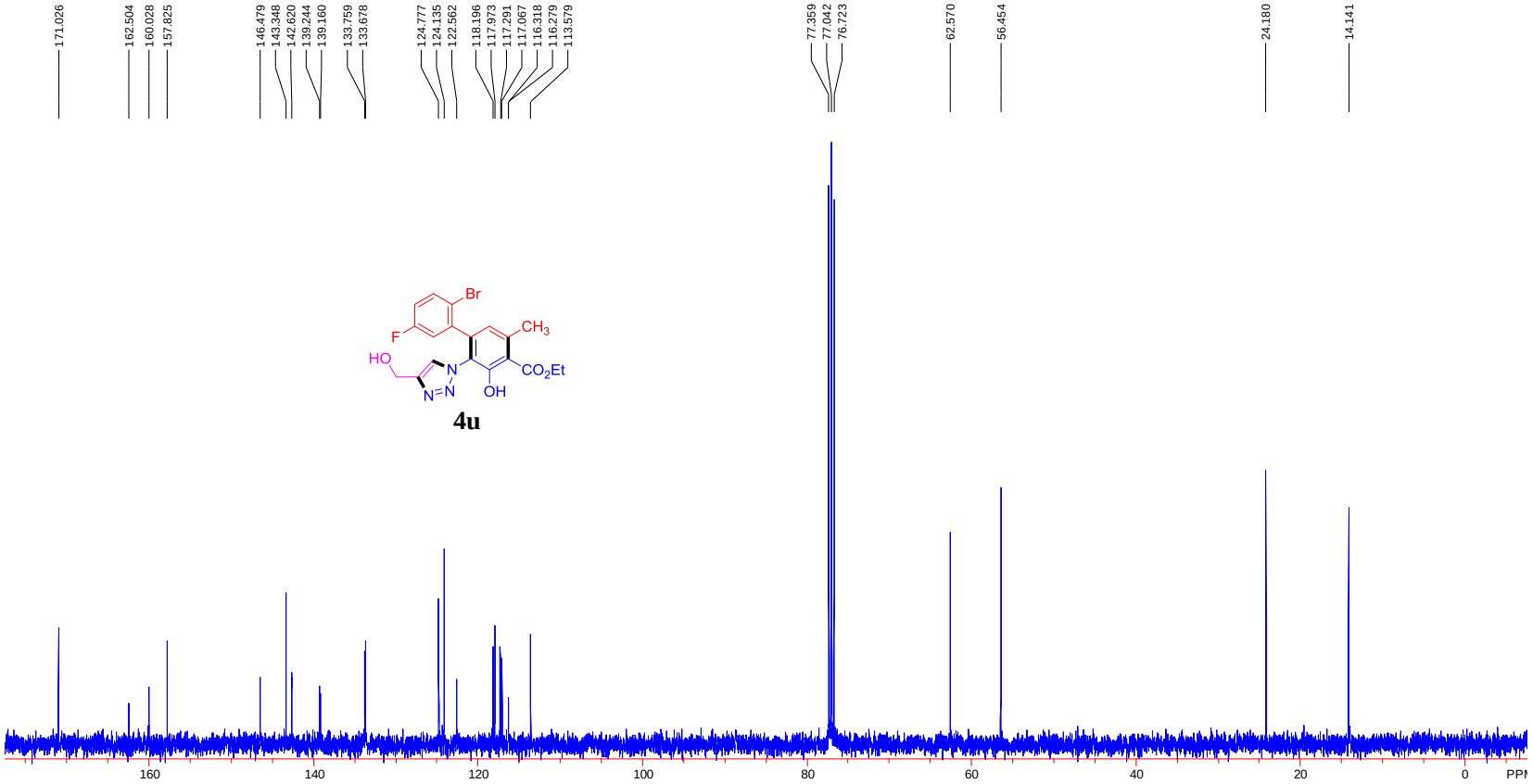
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62.570
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Br
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80
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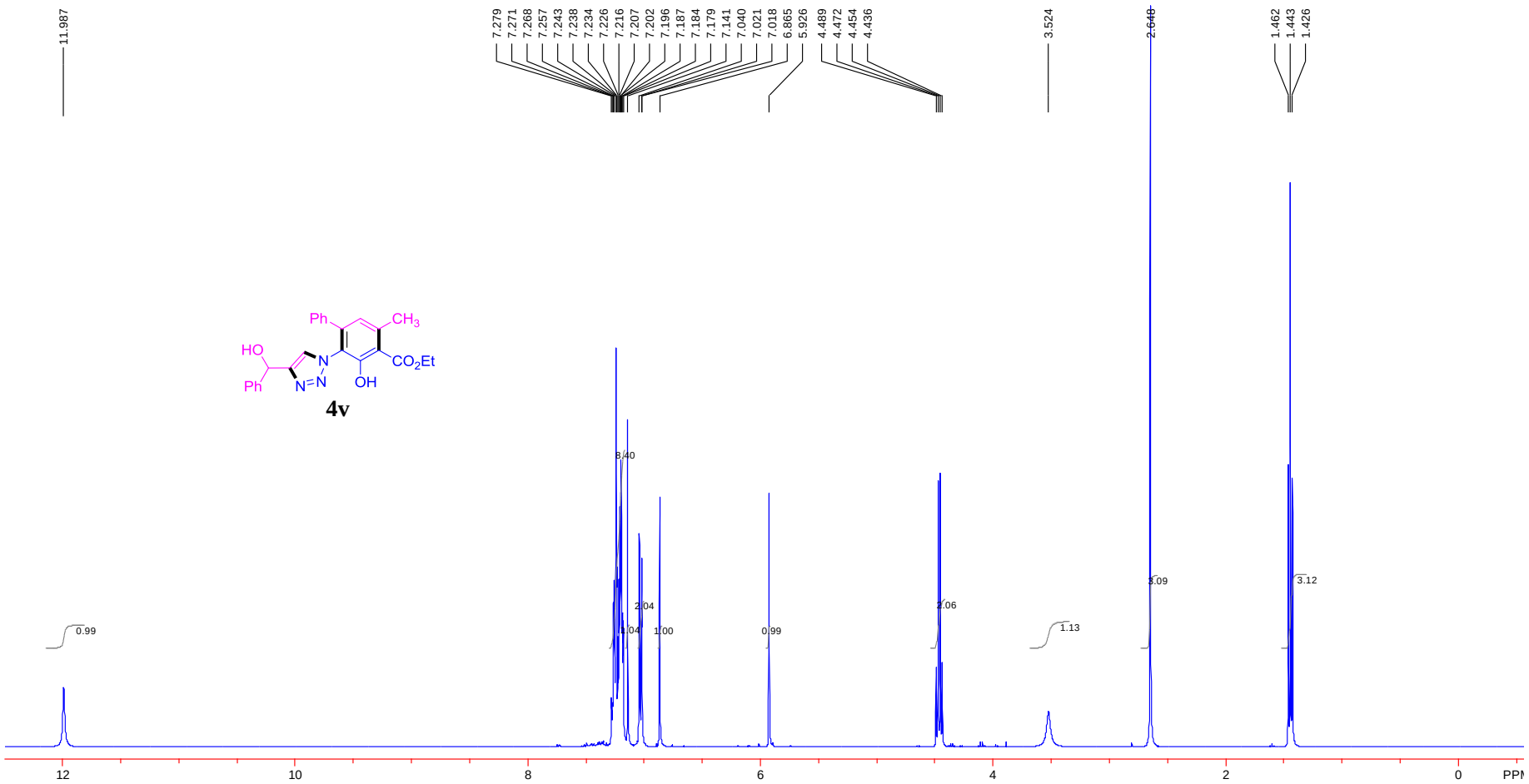
PPM

4u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7.234
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7.187
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7.018
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5.926
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3.524
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1.443
1.426
Ph
CH3
HO
CO2Et
Ph
N
N=N
OH
4v
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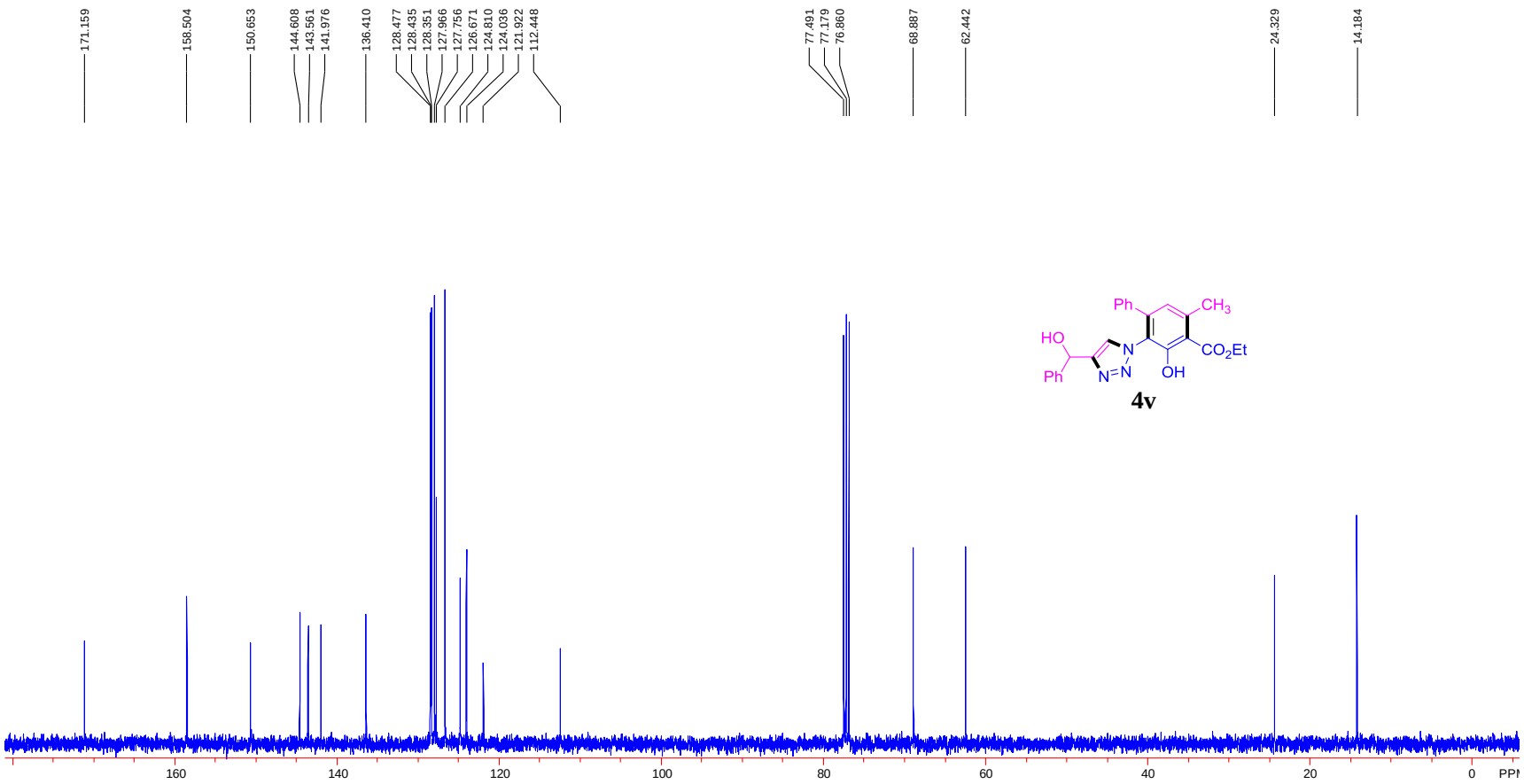
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24.329
14.184
Ph
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CO2Et
Ph
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OH
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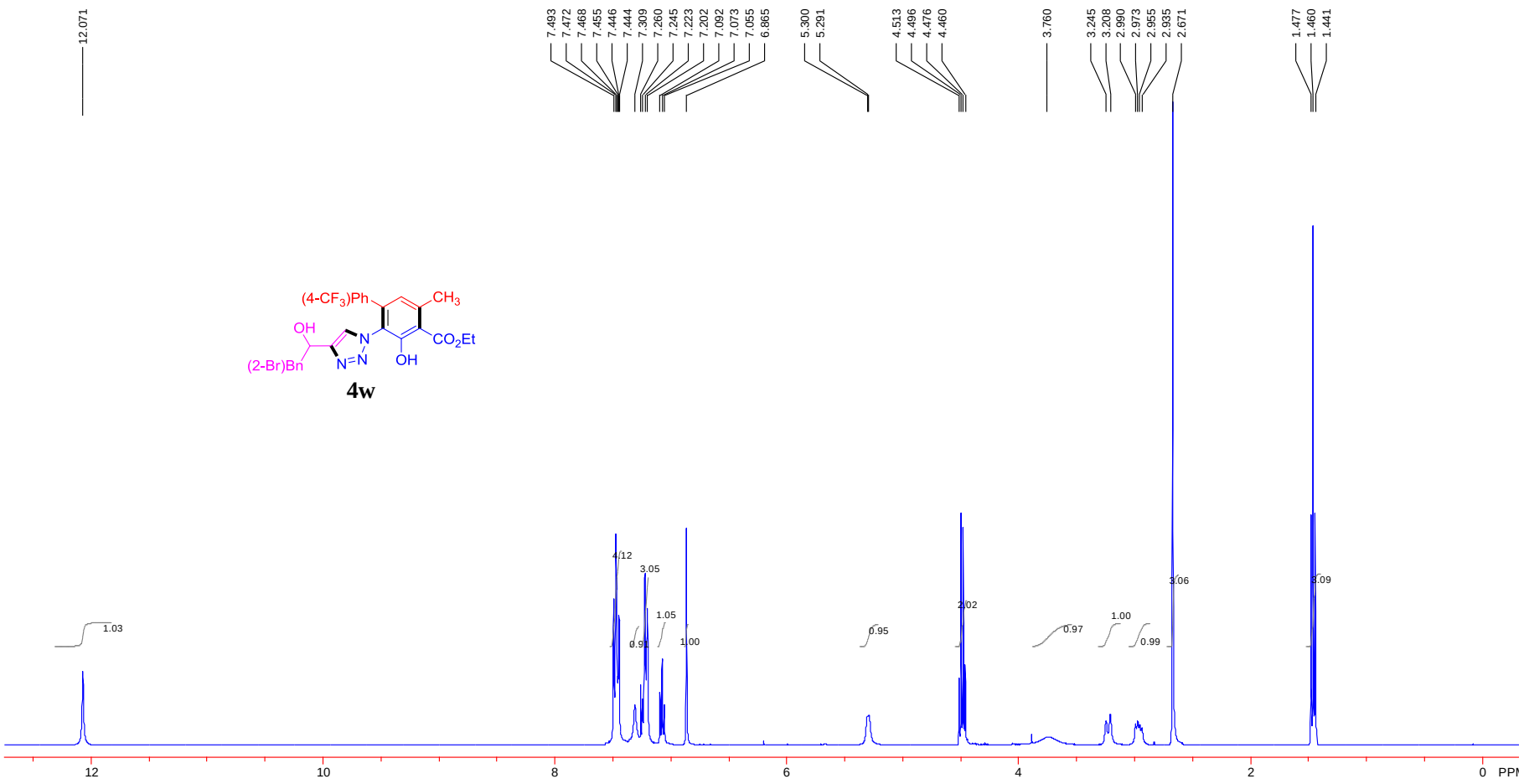
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CO2Et
(2-Br)Bn
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OH
4w
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1.00
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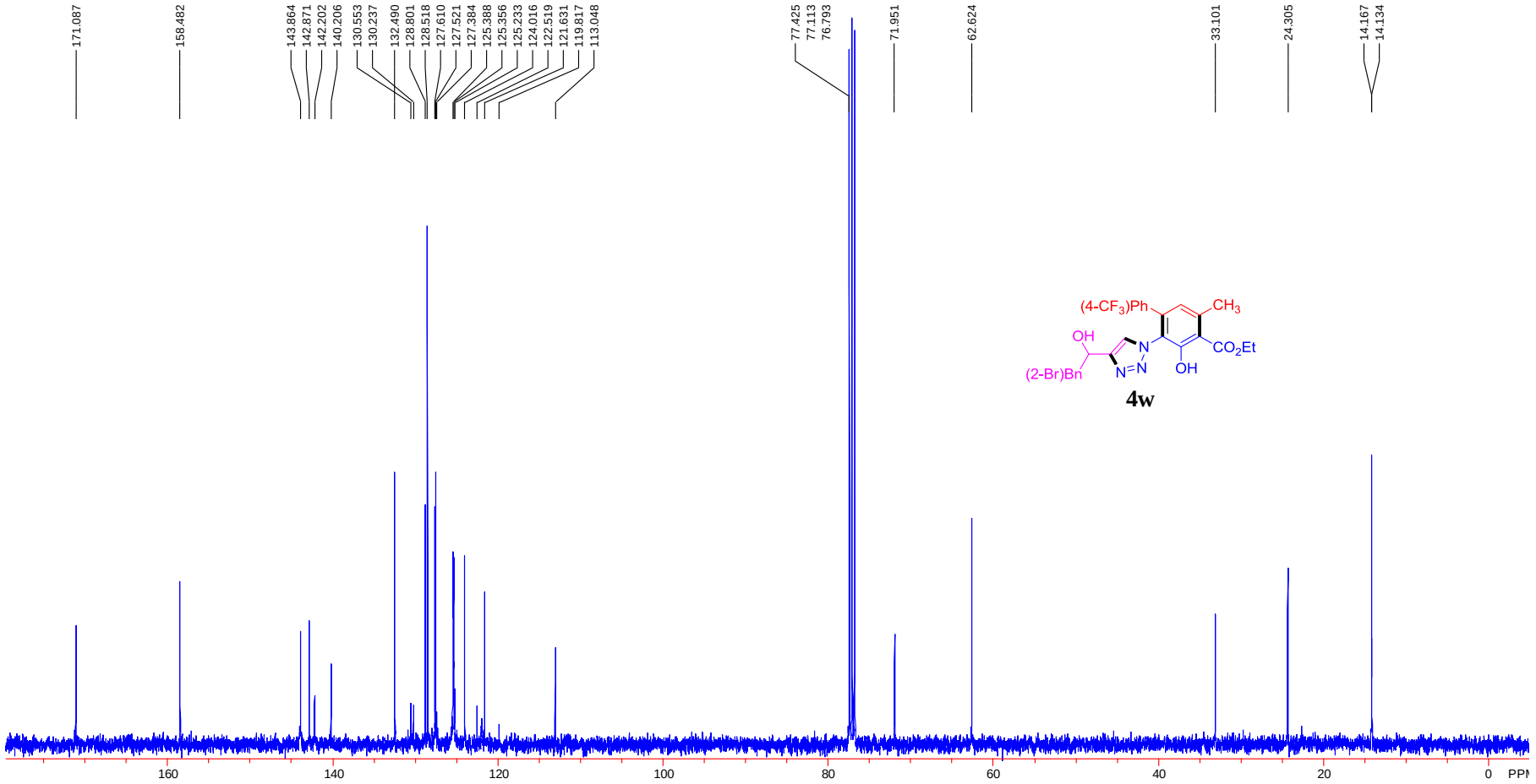
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(4-CF3)Ph
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OH
CO2Et
(2-Br)Bn
OH
4w
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20
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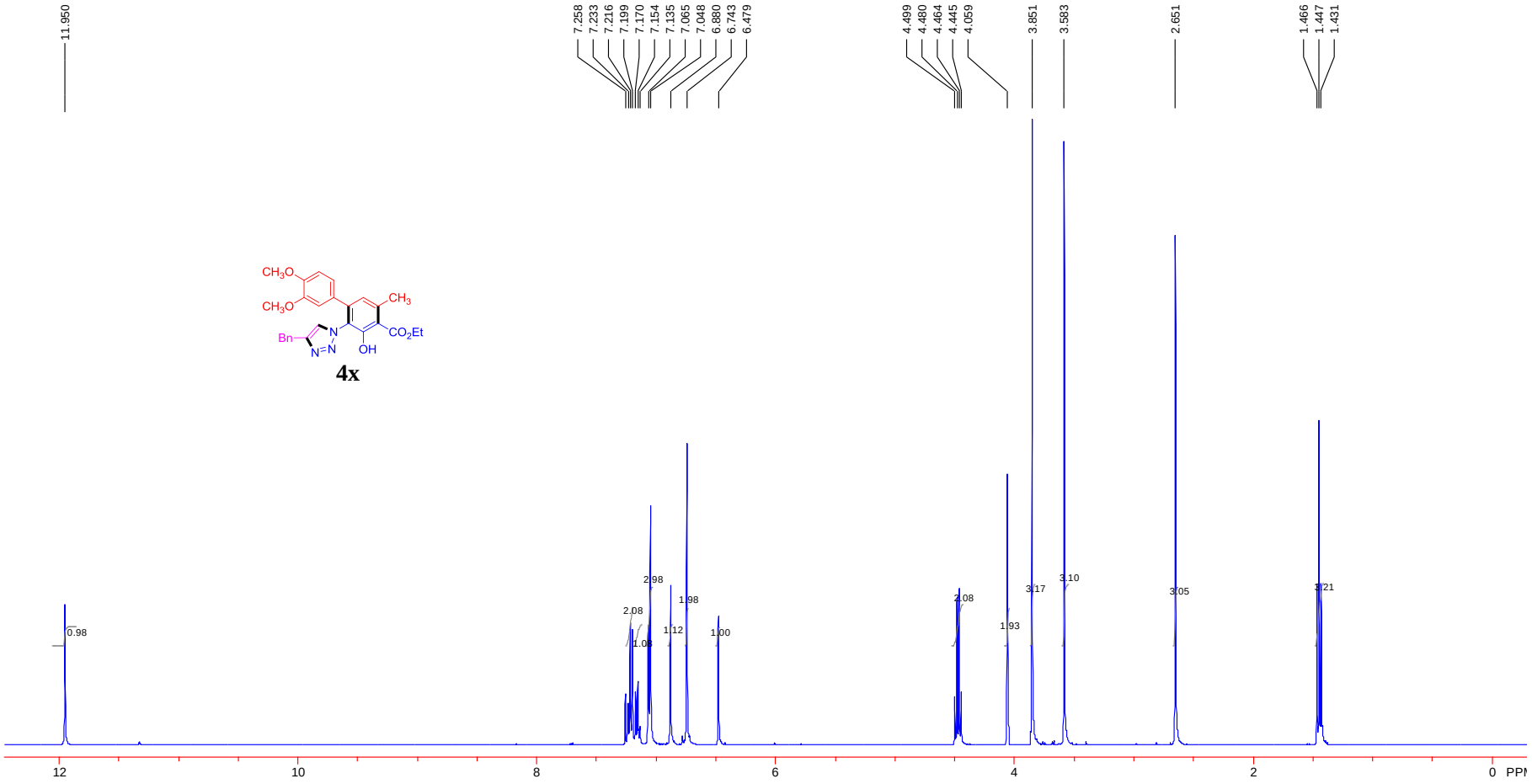
PPM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3.851
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1.447
1.431
CH3O
CH3O
CH3
Bn
N
N=N
OH
CO2Et
4x
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2.08
2.98
1.08
1.12
1.98
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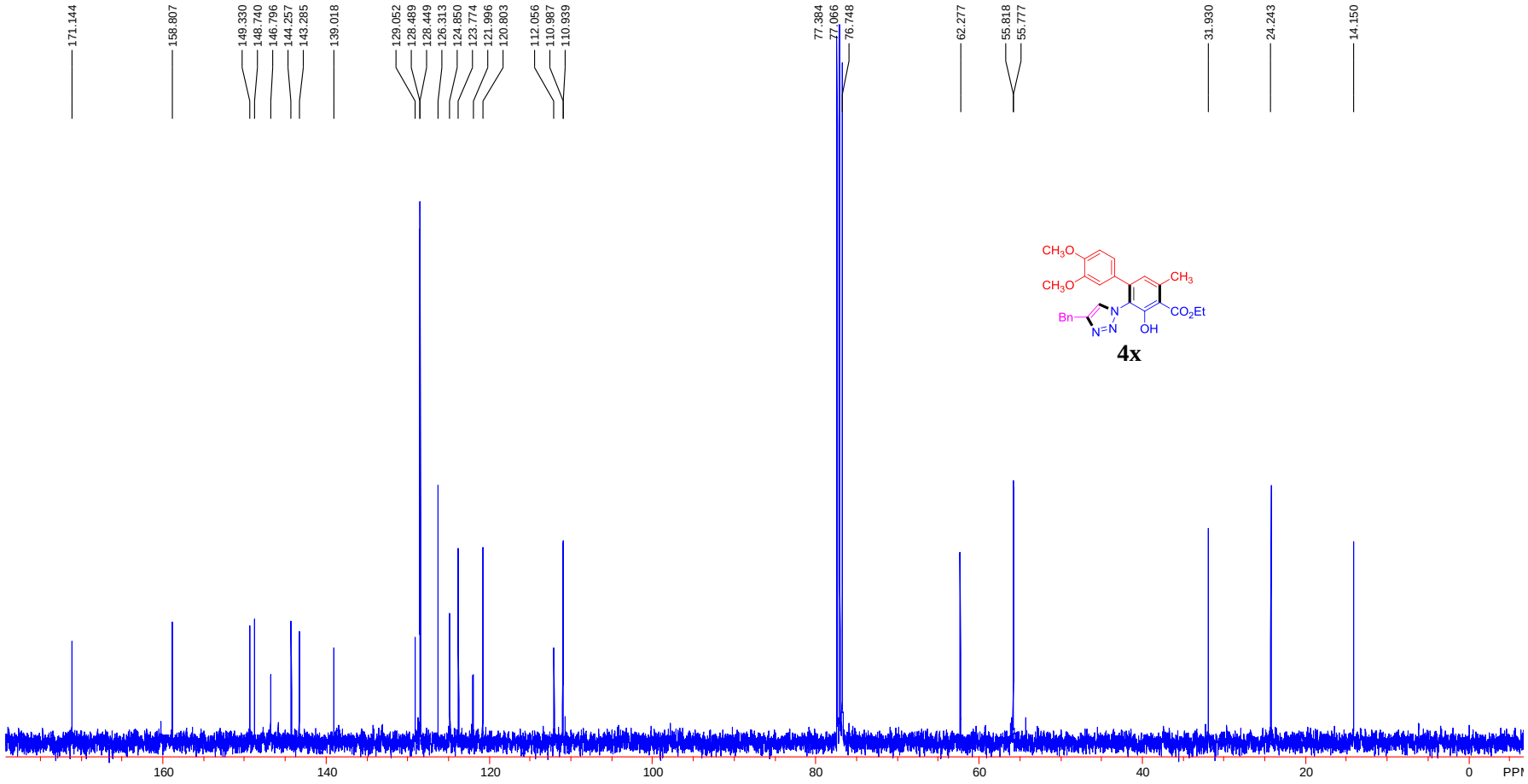
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77.066
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62.277
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55.777
31.930
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CH3O
CH3O
CH3
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N=N
OH
CO2Et
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80
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0
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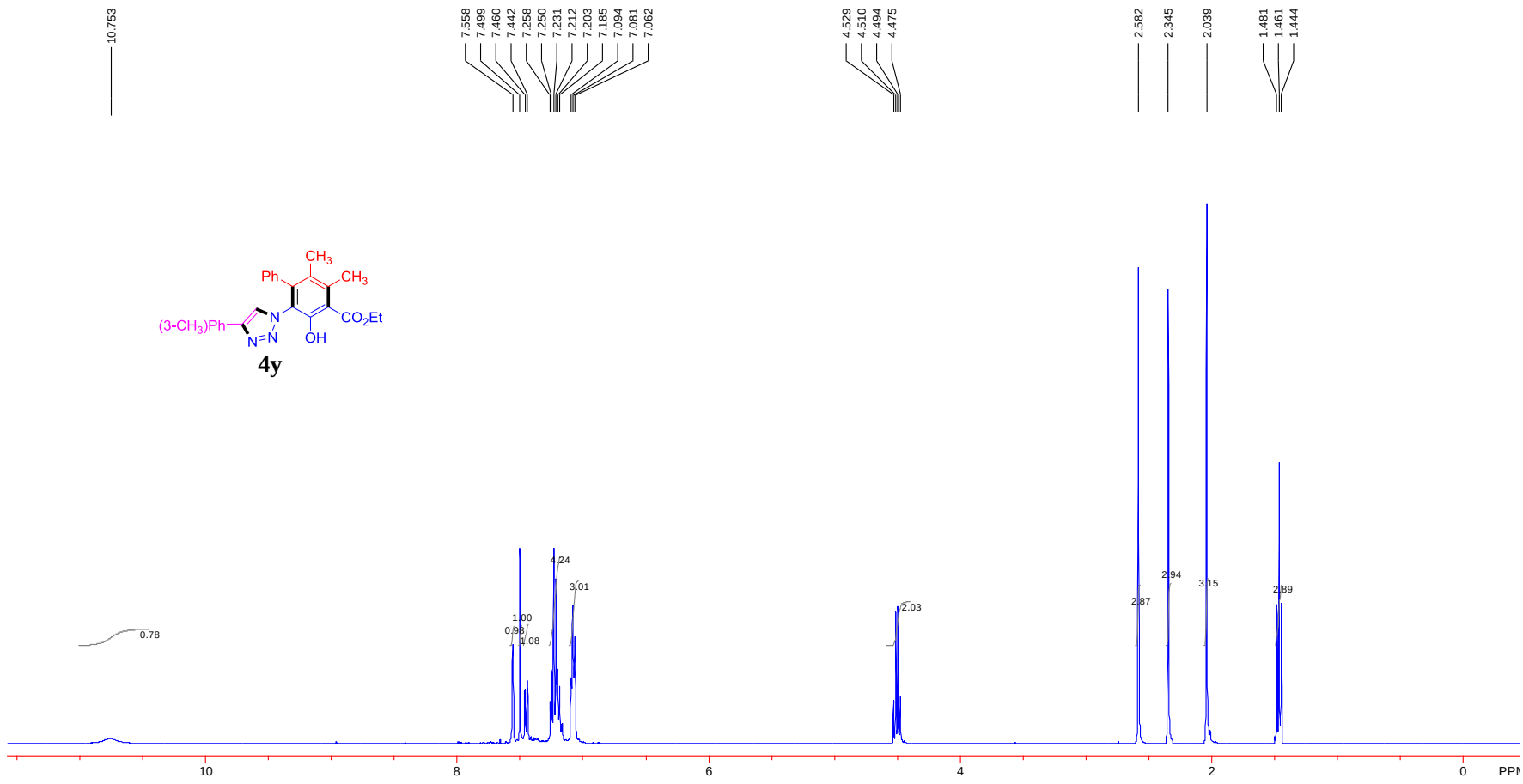
4x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4.475
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CH3
Ph
CH3
(3-CH3)Ph
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CO2Et
OH
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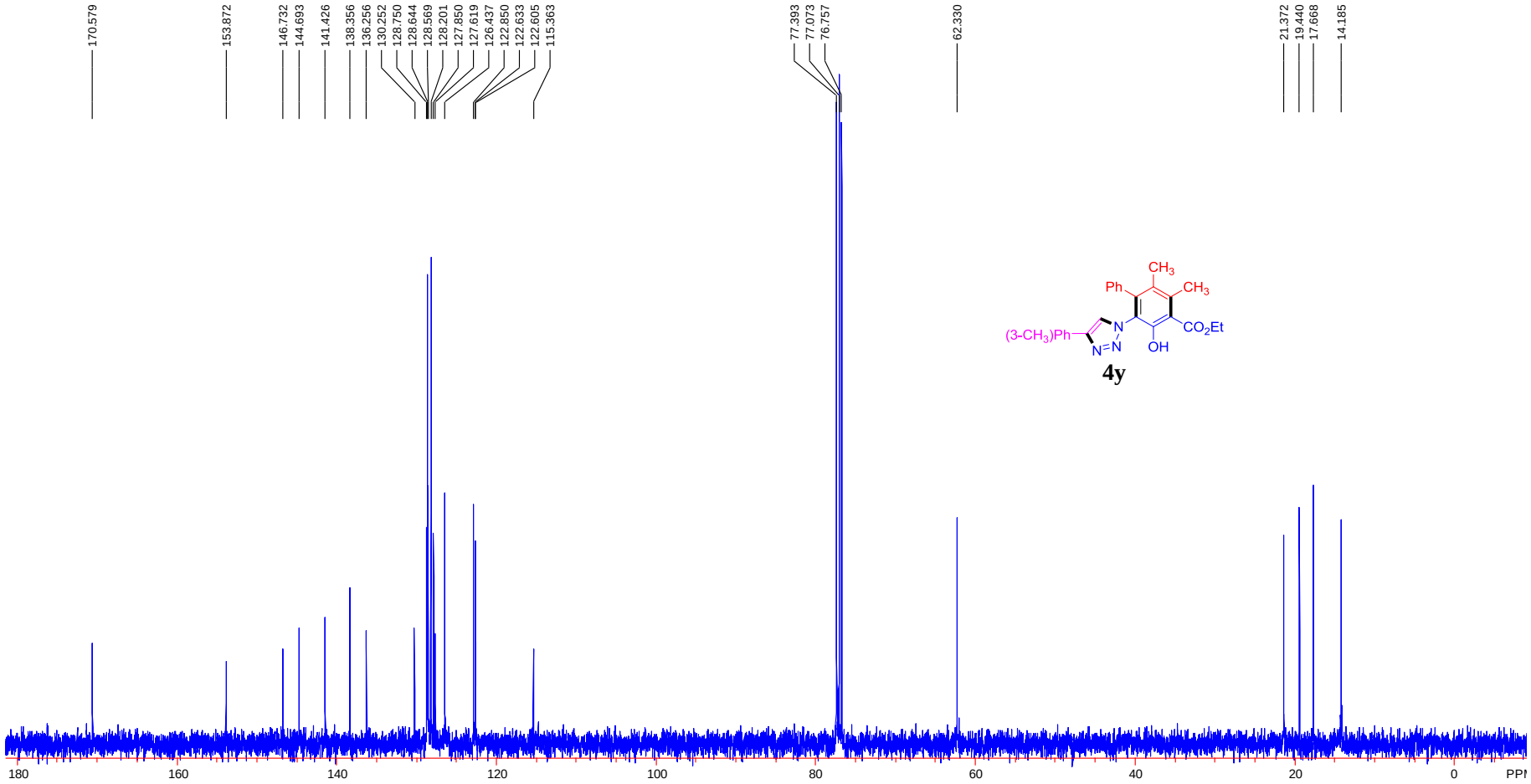
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21.372
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CH3
Ph
CH3
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CO2Et
OH
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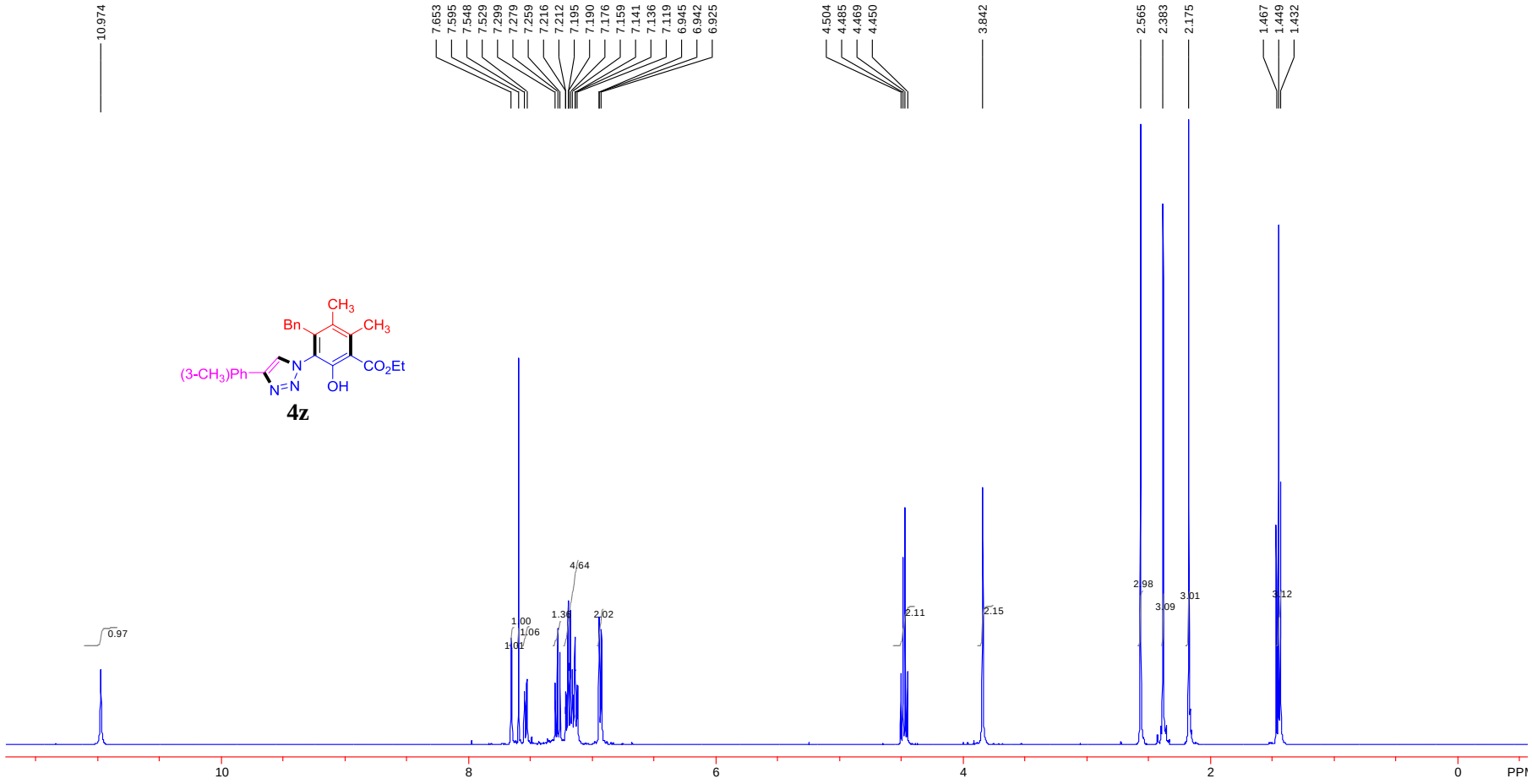
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3.842
2.565
2.383
2.175
1.467
1.449
1.432
CH3
Bn
CH3
(3-CH3)Ph
N
N=N
CO2Et
OH
4z
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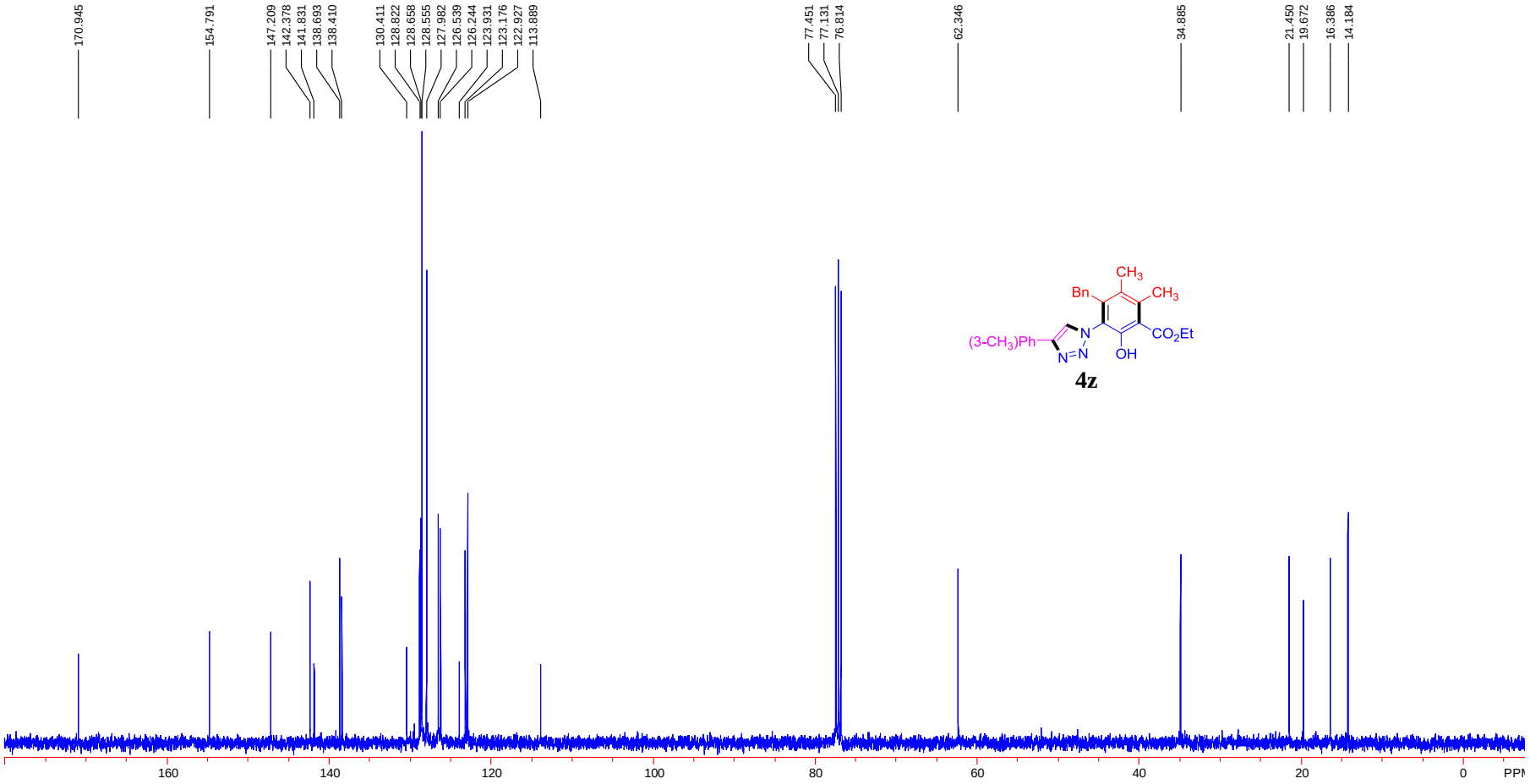
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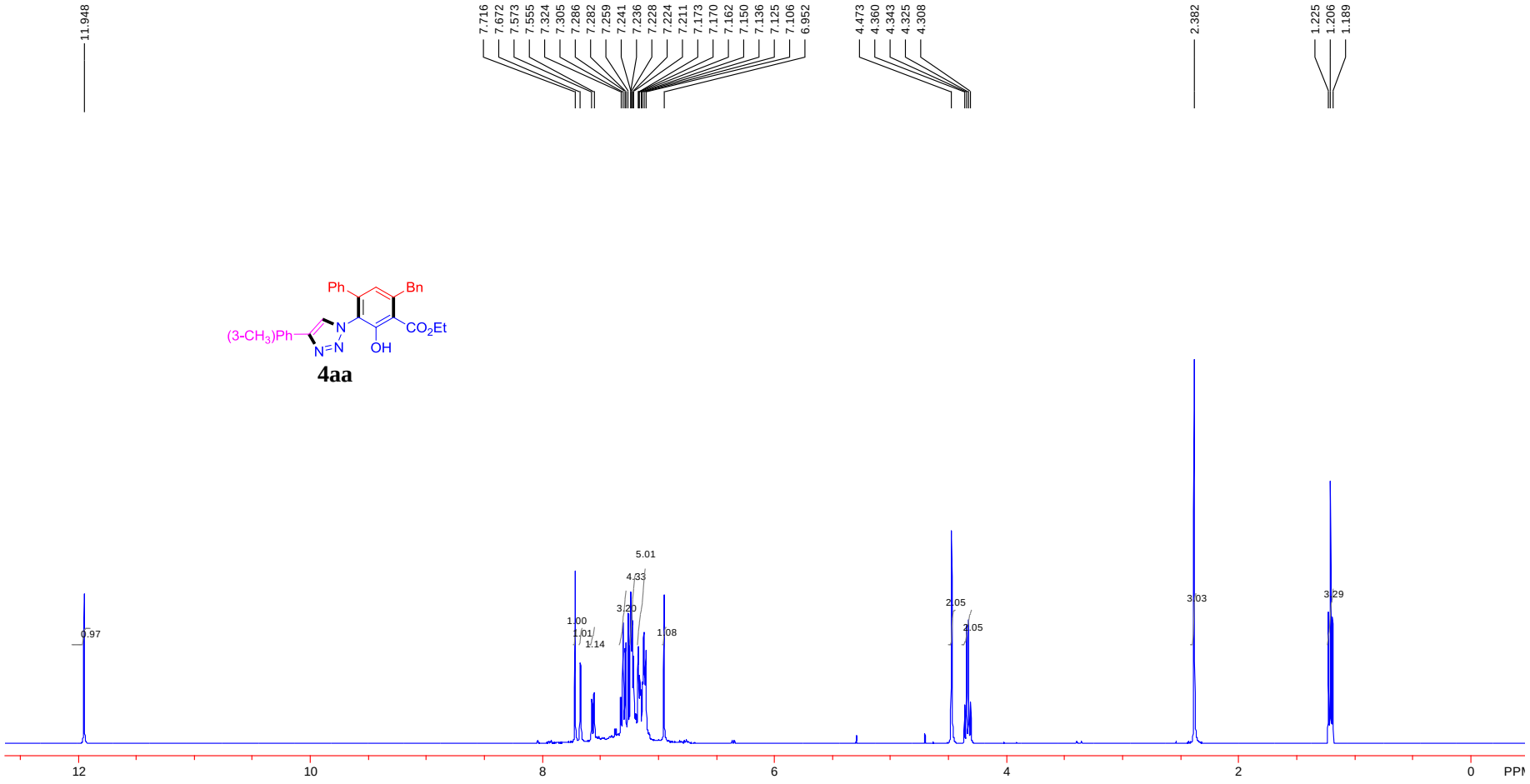
76.814
62.346
34.885
21.450
19.672
16.386
14.184
CH3
Bn
CH3
(3-CH3)Ph
N
N
N
CO2Et
OH
160
140
120
100
80
60
40
20
0
PPM

4z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7.286
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7.241
7.236
7.228
7.224
7.211
7.173
7.170
7.162
7.150
7.136
7.125
7.106
6.952
4.473
4.360
4.343
4.325
4.308
2.382
1.225
1.206
1.189
Ph
Bn
(3-CH3)Ph
CO2Et
OH
4aa
0.97
1.00
1.01
1.14
3.20
4.33
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1.08
2.05
2.05
3.03
3.29
12
10
8
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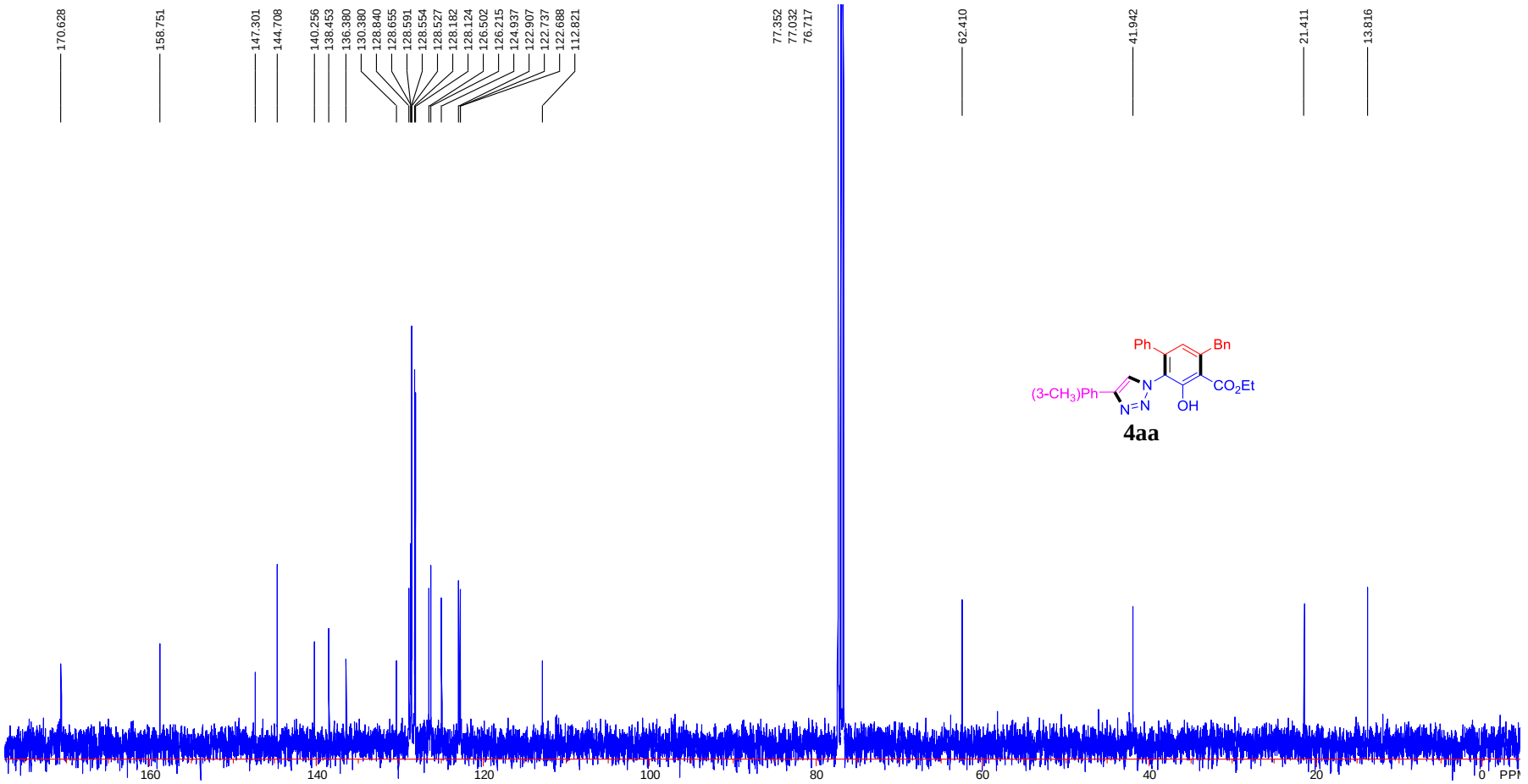
0
PPM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144.708
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138.453
136.380
130.380
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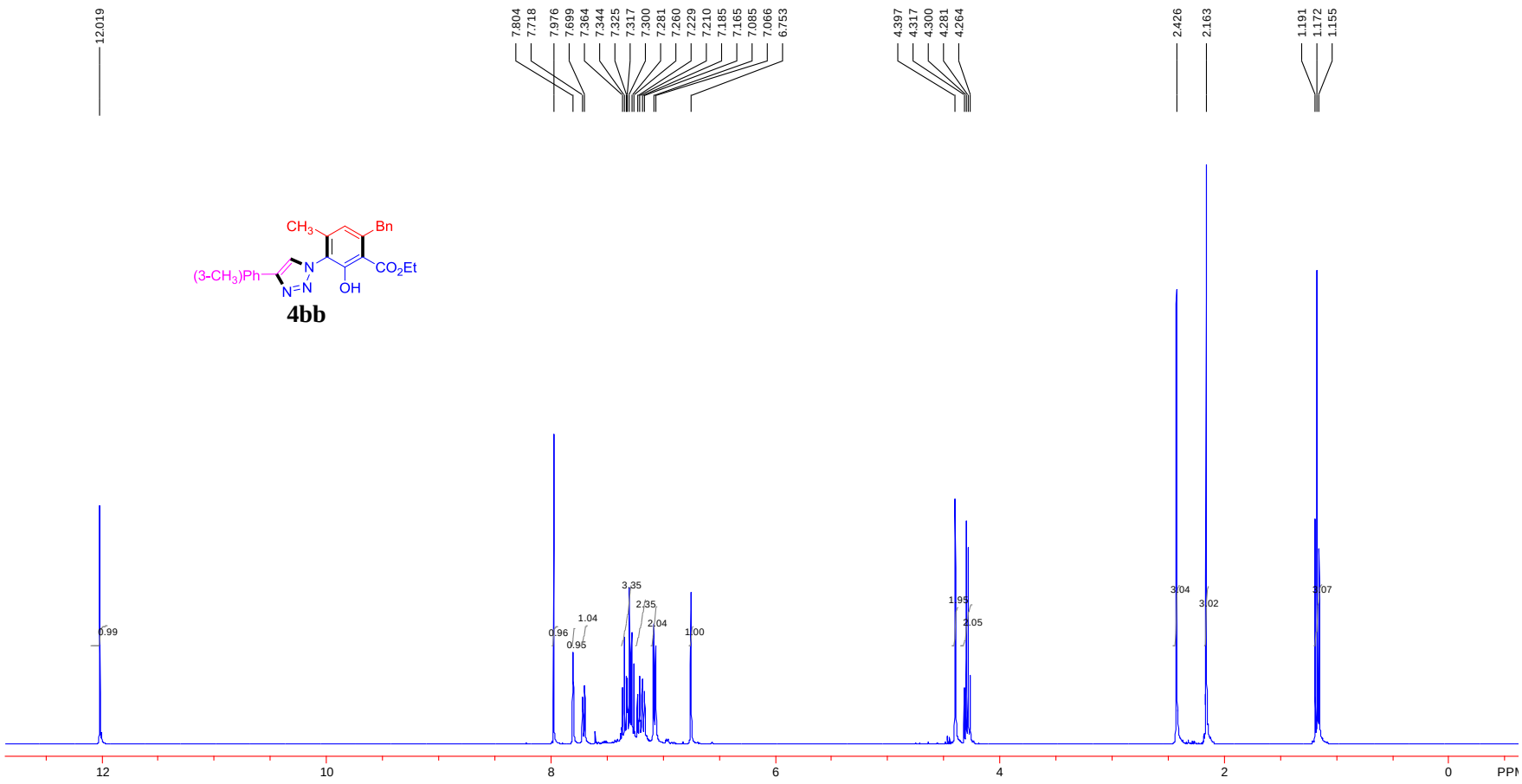
128.591
128.554
128.527
128.182
128.124
126.502
126.215
124.937
122.907
122.737
122.688
112.821
77.352
77.032
76.717
62.410
41.942
21.411
13.816
Ph
Bn
(3-CH3)Ph
N
N
N
OH
CO2Et
160
140
120
100
80
60
40
20
0
PPM

4aa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7.718
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7.699
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7.344
7.325
7.317
7.300
7.281
7.260
7.229
7.210
7.185
7.165
7.085
7.066
6.753
4.397
4.317
4.300
4.281
4.264
2.426
2.163
1.191
1.172
1.155
CH3
Bn
(3-CH3)Ph
N
N=N
OH
CO2Et
4bb
0.99
0.96
1.04
0.96
3.35
2.35
2.04
1.00
1.95
2.05
3.04
3.02
3.07
12
10
8
6
4
2
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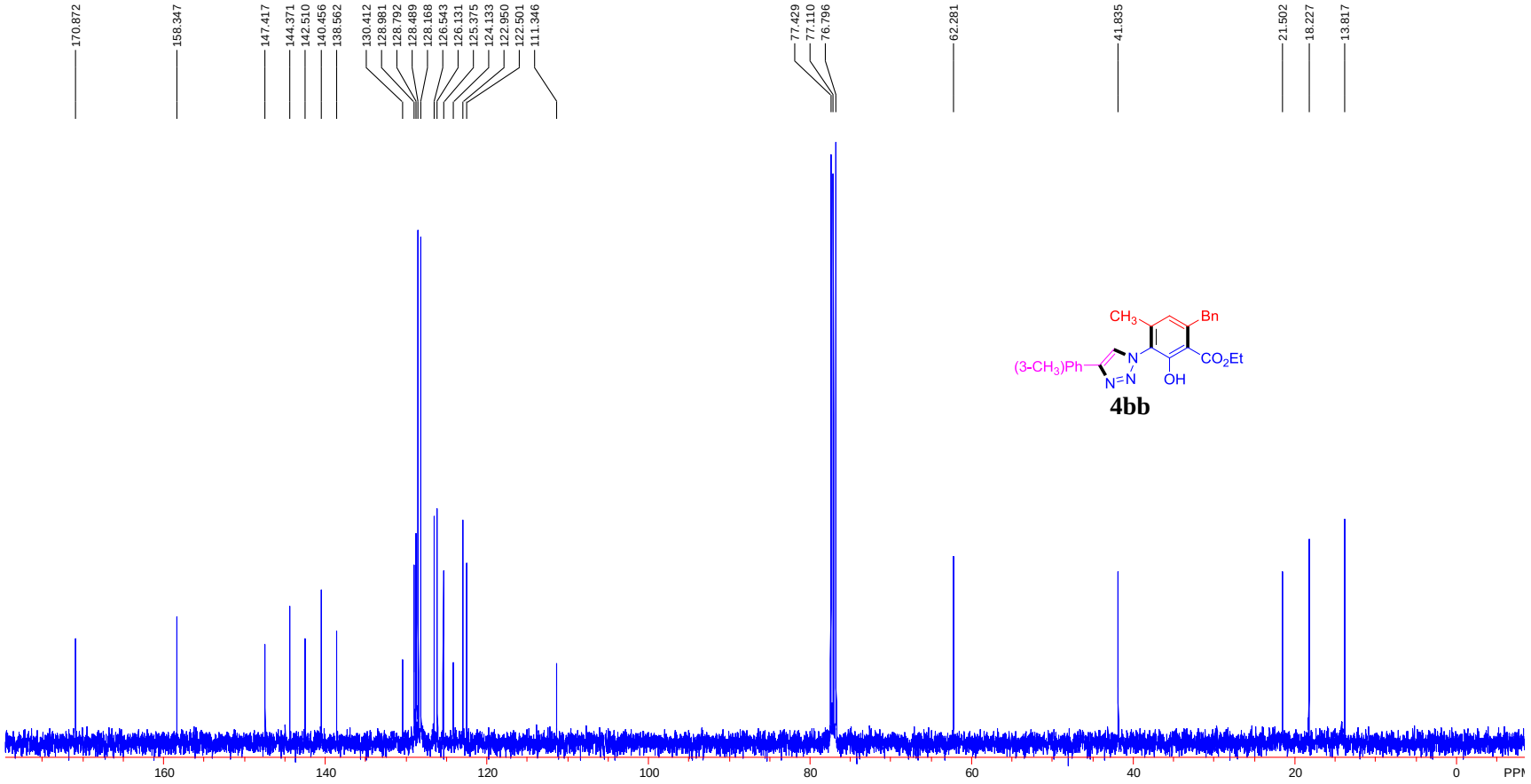
PPM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147.417
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140.456
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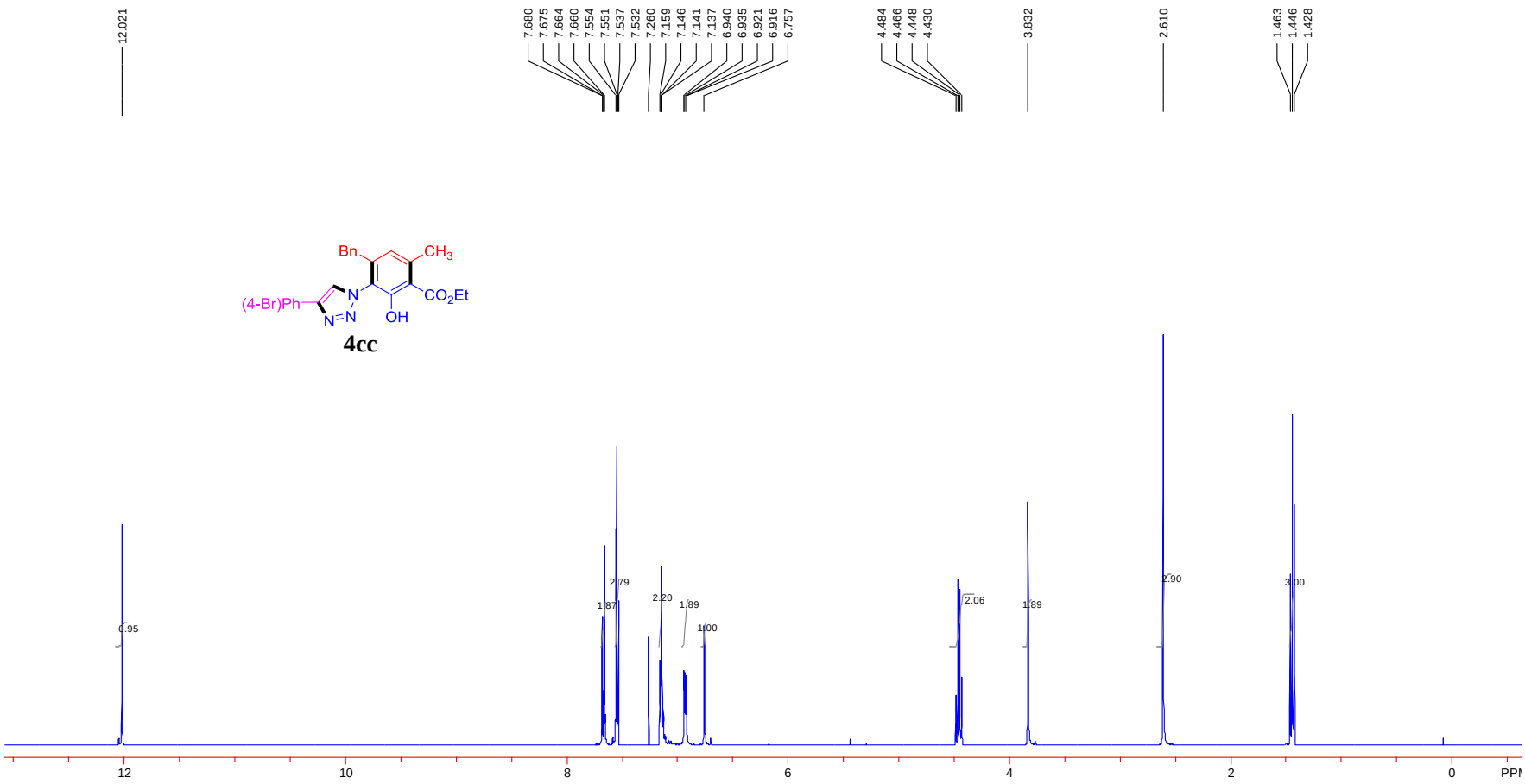
130.412
128.981
128.792
128.489
128.168
126.543
126.131
125.375
124.133
122.950
122.501
111.346
77.429
77.110
76.796
62.281
41.835
21.502
18.227
13.817
CH3
Bn
(3-CH3)Ph
N
N=N
OH
CO2Et
160
140
120
100
80
60
40
20
0
PPM

4bb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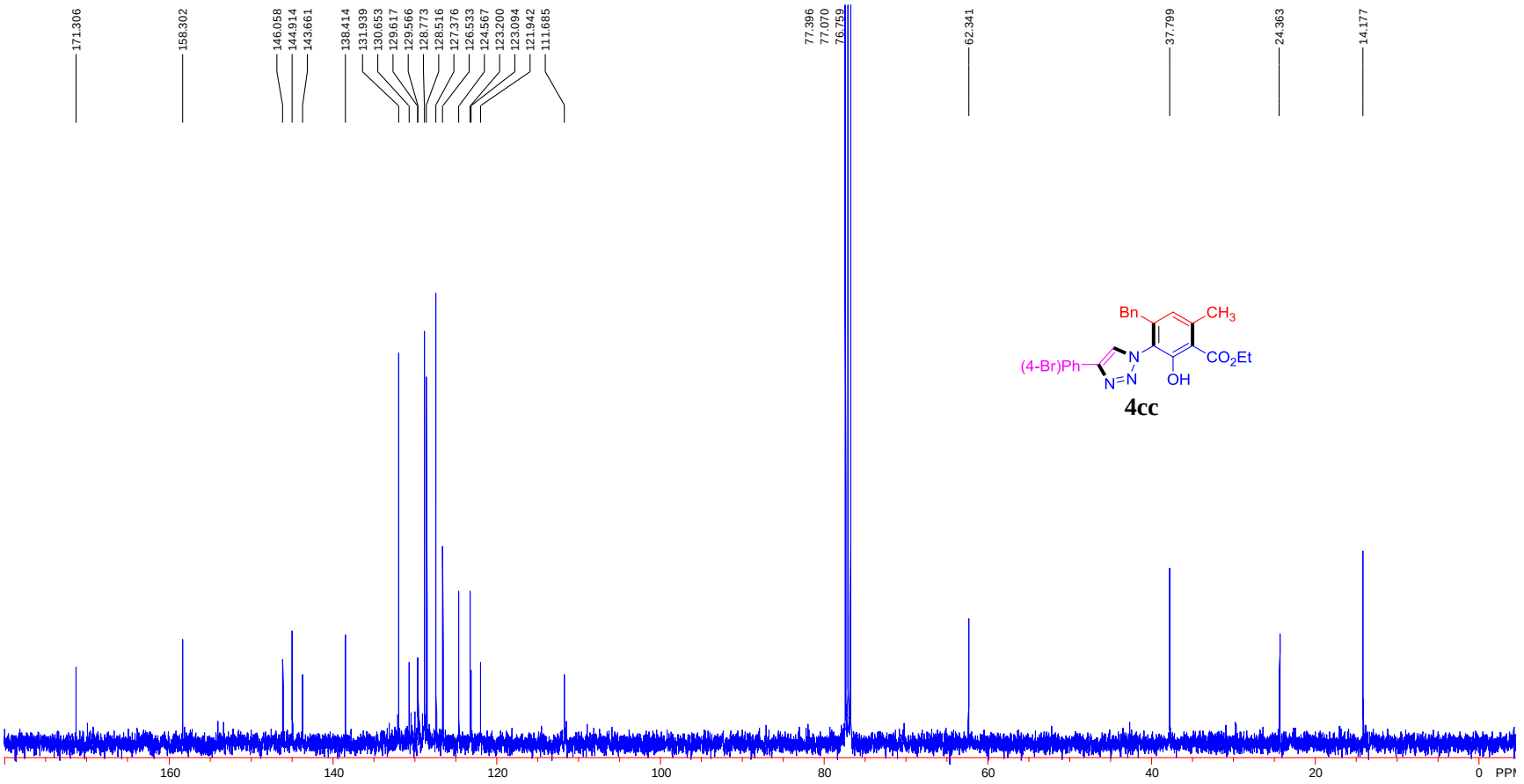
7.680
7.675
7.664
7.660
7.554
7.551
7.537
7.532
7.260
7.159
7.146
7.141
7.137
6.940
6.935
6.921
6.916
6.757
4.484
4.466
4.448
4.430
3.832
2.610
1.463
1.446
1.428
Bn
CH3
(4-Br)Ph
N
N=N
OH
CO2Et
4cc
0.95
1.87
2.79
2.20
1.89
1.00
2.06
1.89
2.90
3.00
12
10
8
6
4
2
0
PPM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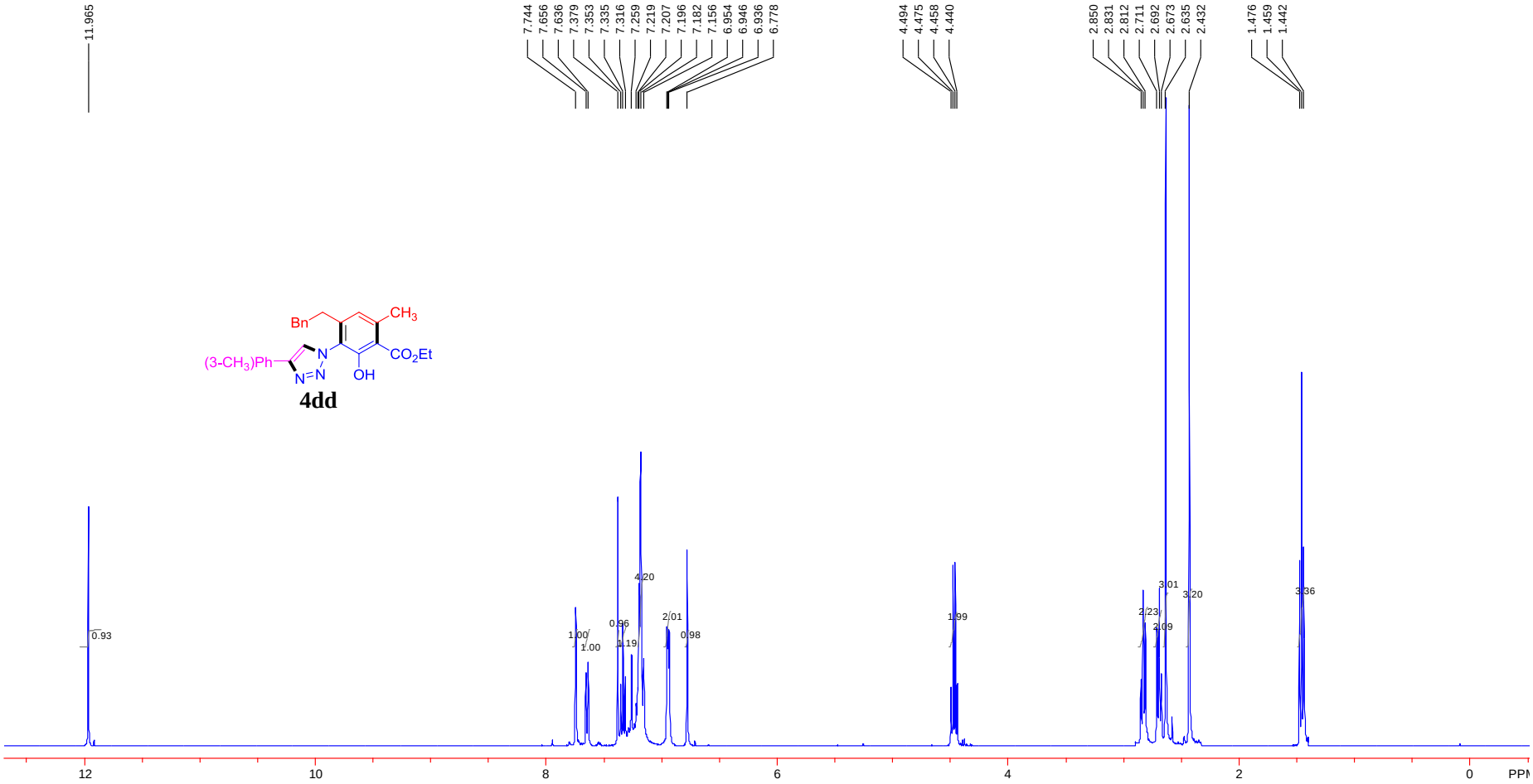
158.302
146.058
144.914
143.661
138.414
131.939
130.653
129.617
129.566
128.773
128.516
127.376
126.533
124.567
123.200
123.094
121.942
111.685
77.396
77.070
76.759
62.341
37.799
24.363
14.177
Bn
CH3
(4-Br)Ph
N
N=N
CO2Et
OH
160
140
120
100
80
60
40
20
0
PPM

4cc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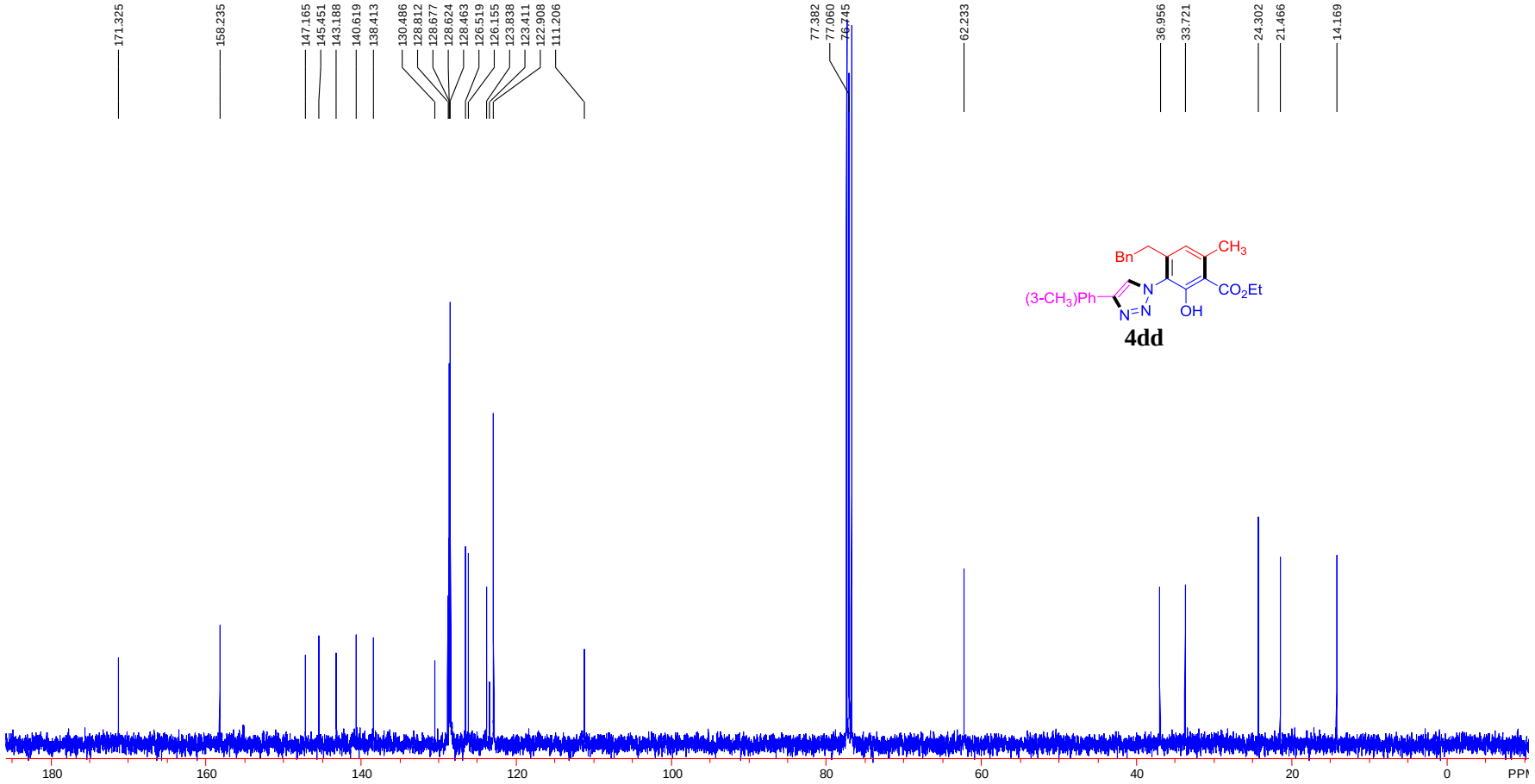
7.656
7.636
7.379
7.353
7.335
7.316
7.259
7.219
7.207
7.196
7.182
7.156
6.954
6.946
6.936
6.778
4.494
4.475
4.458
4.440
2.850
2.831
2.812
2.711
2.692
2.673
2.635
2.432
1.476
1.459
1.442
Bn
CH3
(3-CH3)Ph
N
N=N
OH
CO2Et
4dd
0.93
1.00
1.00
0.96
1.19
4.20
2.01
0.98
1.99
2.23
2.09
3.01
3.20
3.36
12
10
8
6
4
2
0
PPM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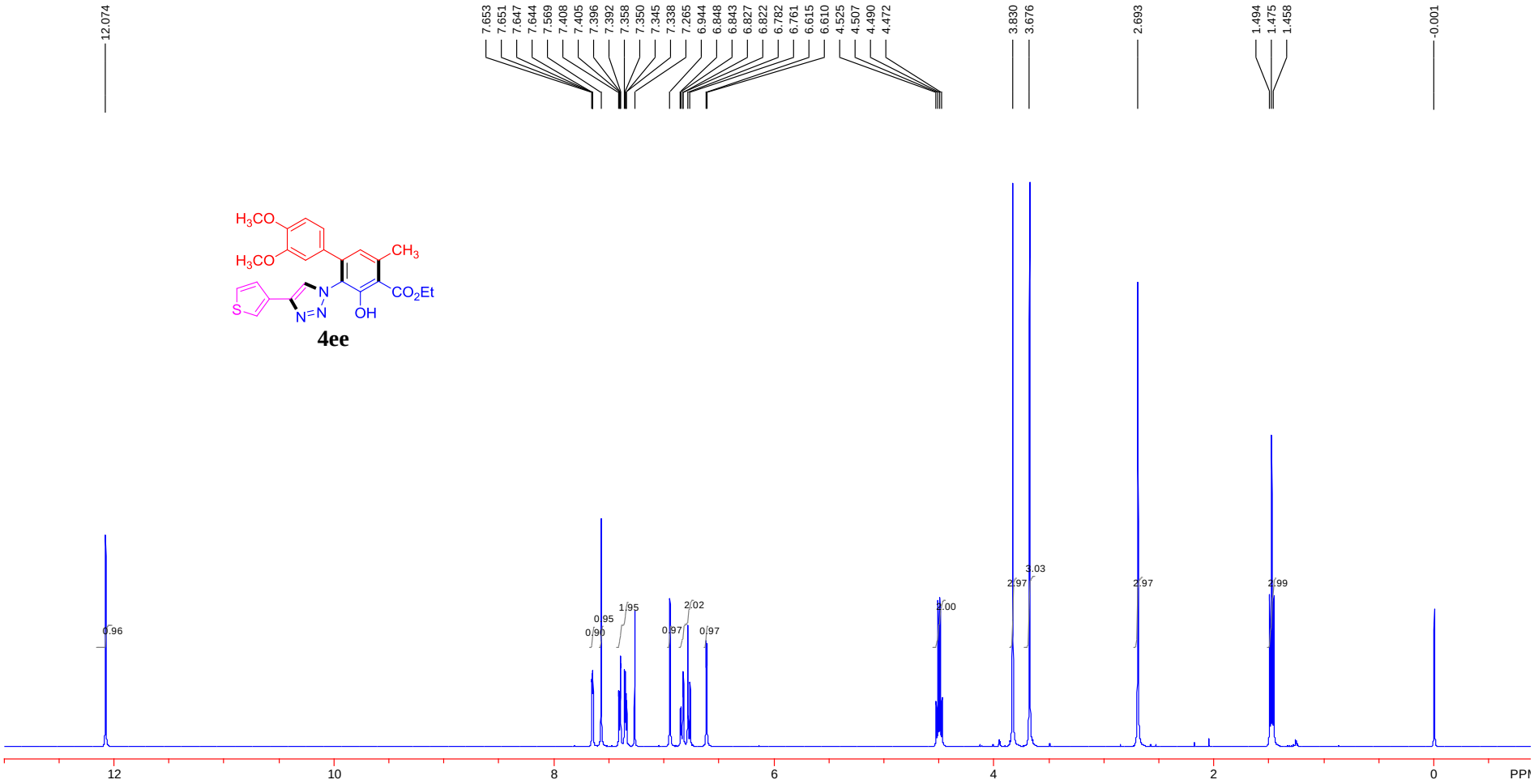
158.235
147.165
145.451
143.188
140.619
138.413
130.486
128.812
128.677
128.624
128.463
126.519
126.155
123.838
123.411
122.908
111.206
77.382
77.060
76.745
62.233
36.956
33.721
24.302
21.466
14.169
Bn
CH3
(3-CH3)Ph
N
N=N
OH
CO2Et
4dd
180
160
140
120
100
80
60
40
20
0
PPM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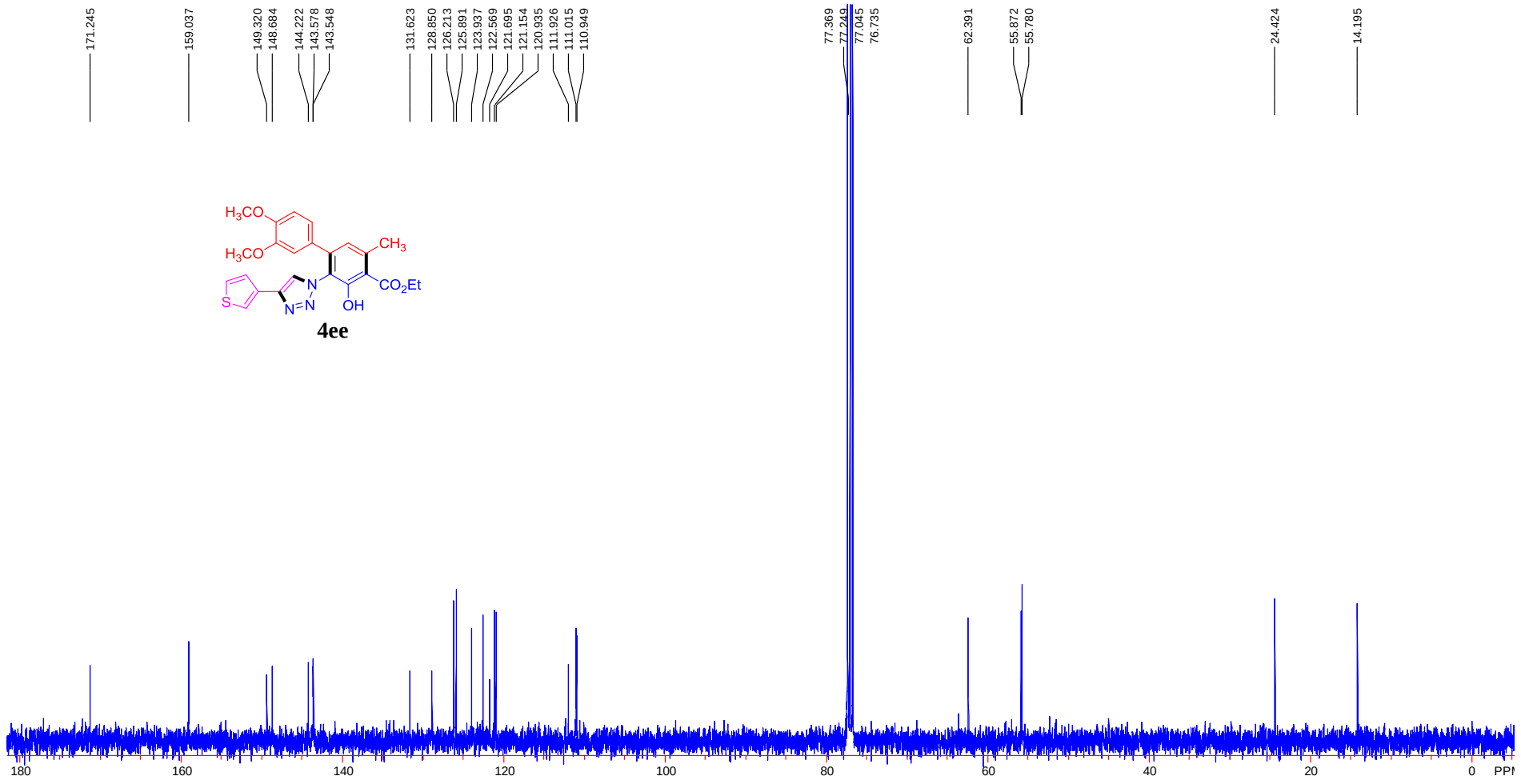
7.651
7.647
7.644
7.569
7.408
7.405
7.396
7.392
7.358
7.350
7.345
7.338
7.265
6.944
6.848
6.843
6.827
6.822
6.782
6.761
6.615
6.610
4.525
4.507
4.490
4.472
3.830
3.676
2.693
1.494
1.475
1.458
-0.001
H3CO
H3CO
CH3
CO2Et
OH
N
N=N
S
4ee
0.96
0.90
0.95
1.95
0.97
2.02
0.97
2.00
2.97
3.03
2.97
2.99
12
10
8
6
4
2
0
PPM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149.320
148.684
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143.578
143.548
131.623
128.850
126.213
125.891
123.937
122.569
121.695
121.154
120.935
111.926
111.015
110.949
77.369
77.249
77.045
76.735
62.391
55.872
55.780
24.424
14.195
H3CO
H3CO
CH3
CO2Et
OH
N
N=N
S
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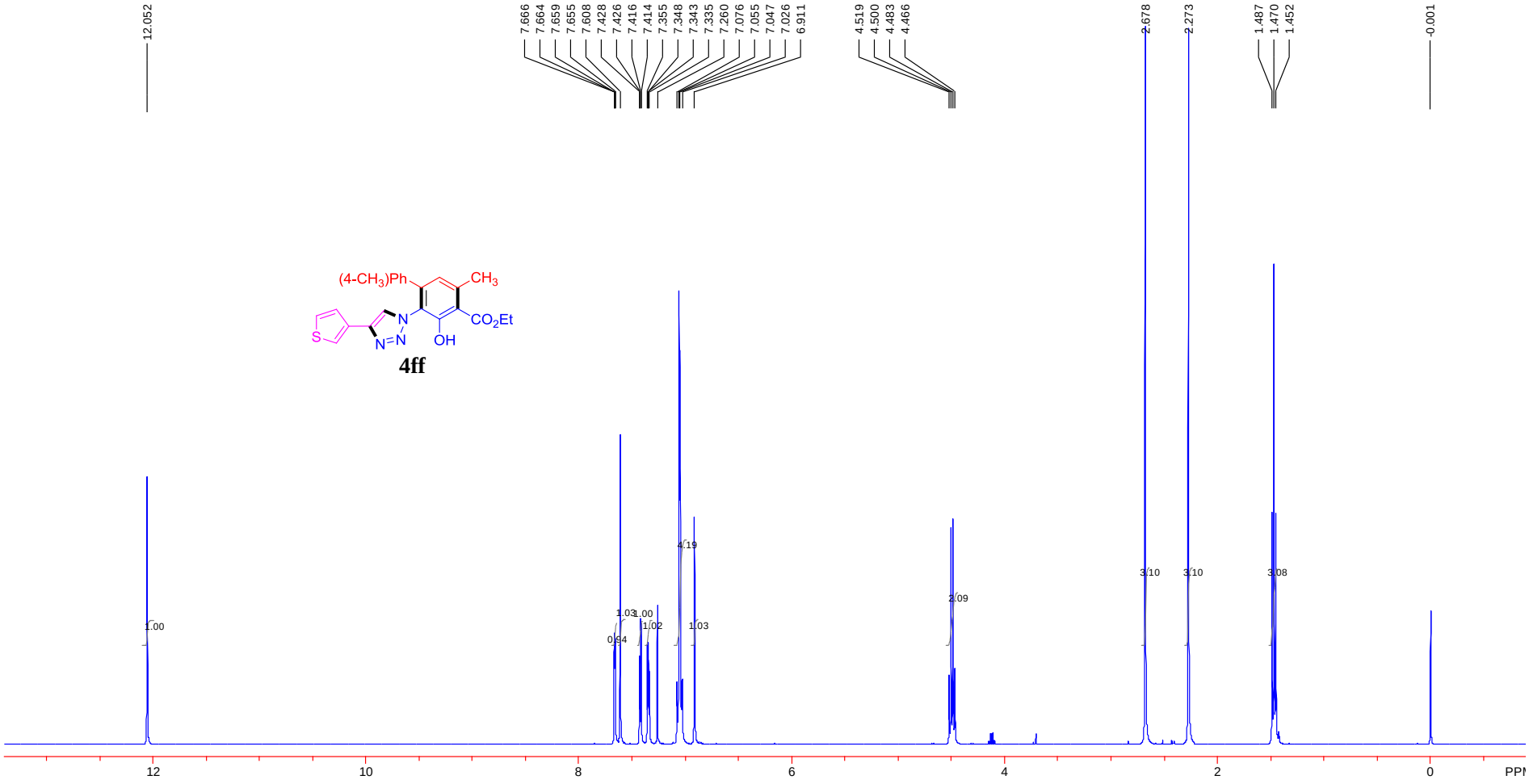
160
140
120
100
80
60
40
20
0
PPM

4ee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7.664
7.659
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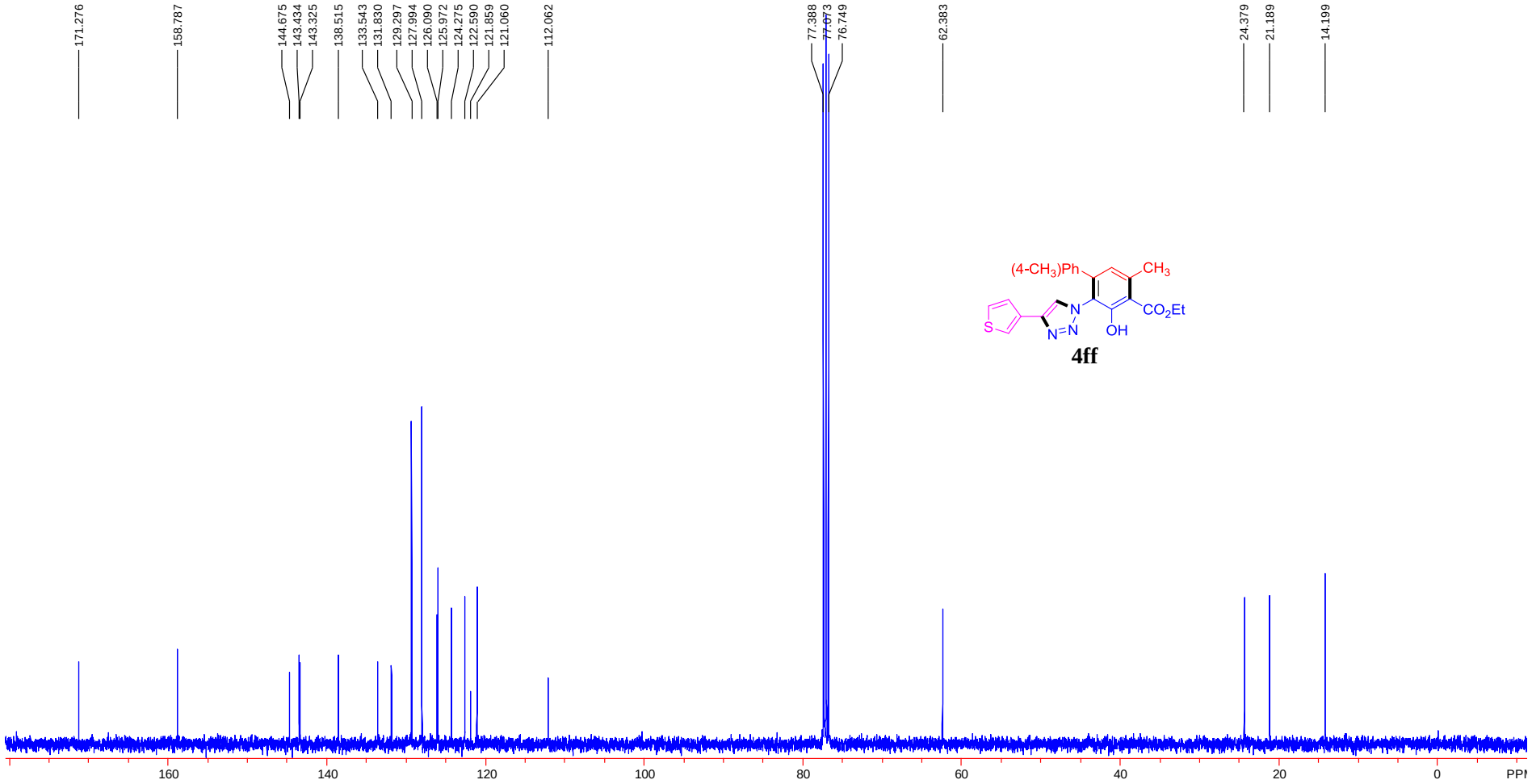
7.608
7.428
7.426
7.416
7.414
7.355
7.348
7.343
7.335
7.260
7.076
7.055
7.047
7.026
6.911
4.519
4.500
4.483
4.466
2.678
2.273
1.487
1.470
1.452
0.001
(4-CH3)Ph
CH3
CO2Et
OH
S
N
N=N
4ff
1.00
1.03
1.00
0.94
1.02
4.19
1.03
2.09
3.10
3.10
3.08
12
10
8
6
4
2
0
PPM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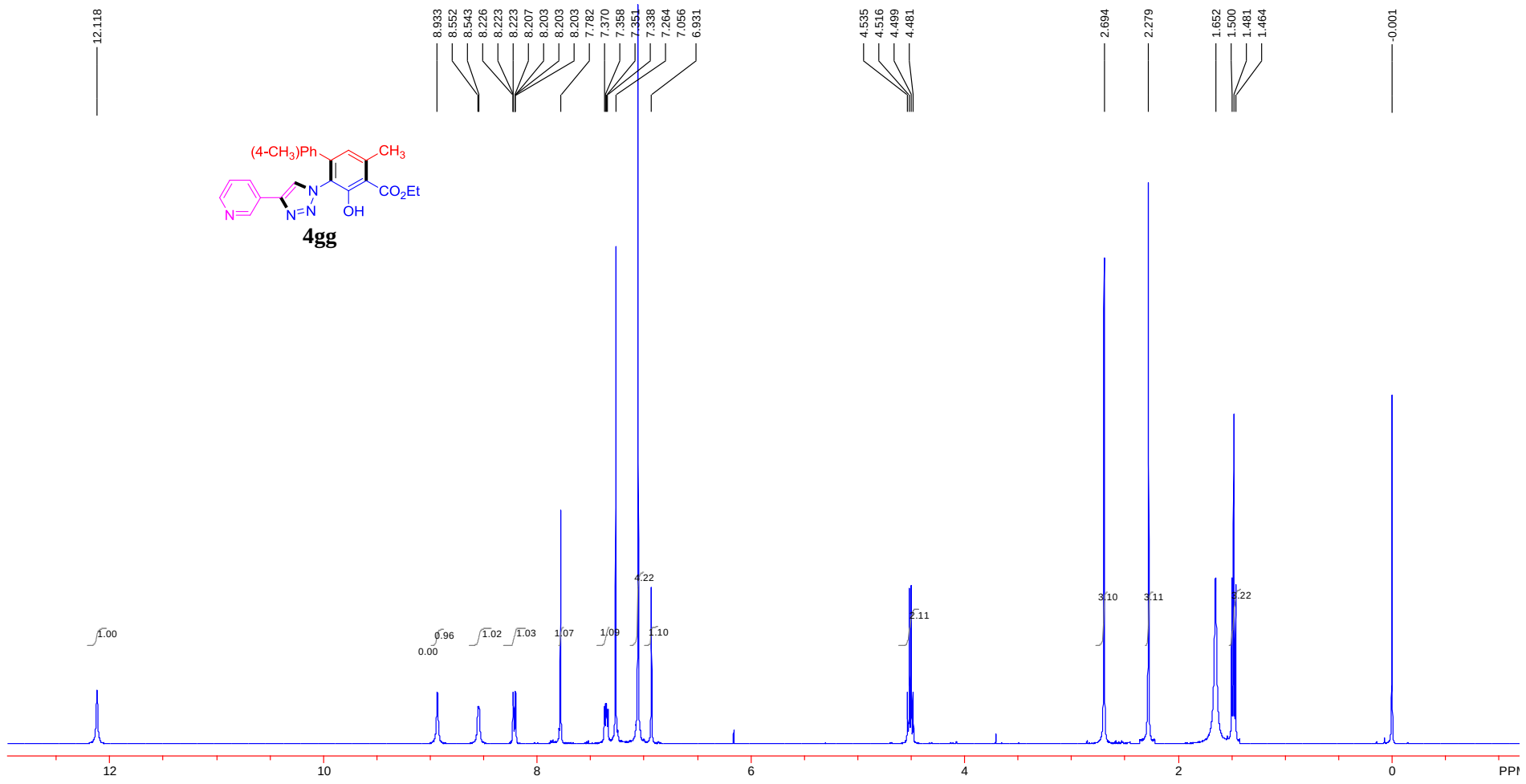
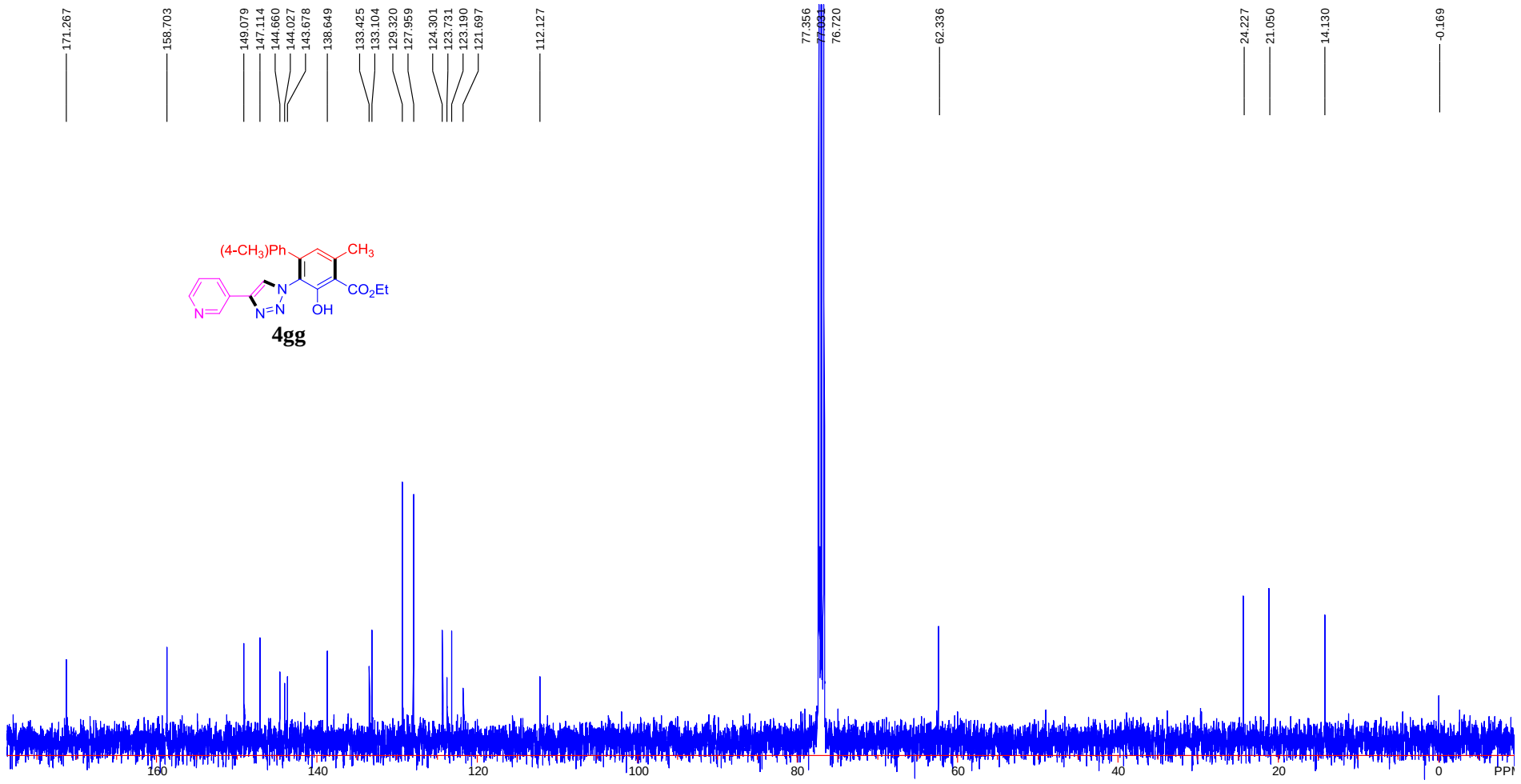
158.787
144.675
143.434
143.325
138.515
133.543
131.830
129.297
127.994
126.090
125.972
124.275
122.590
121.859
121.060
112.062
77.388
77.073
76.749
62.383
24.379
21.189
14.199
(4-CH3)Ph
CH3
CO2Et
OH
S
N
N
N
160
140
120
100
80
60
40
20
0
PPM

4ff


12.118
8.933
8.552
8.543
8.226
8.223
8.223
8.207
8.203
8.203
8.203
7.782
7.370
7.358
7.351
7.338
7.264
7.056
6.931
4.535
4.516
4.499
4.481
2.694
2.279
1.652
1.500
1.481
1.464
-0.001
(4-CH3)Ph
CH3
CO2Et
OH
N
N=N
4gg
1.00
0.96
0.00
1.02
1.03
1.07
1.09
4.22
1.10
2.11
3.10
3.11
3.22
12
10
8
6
4
2
0
PPM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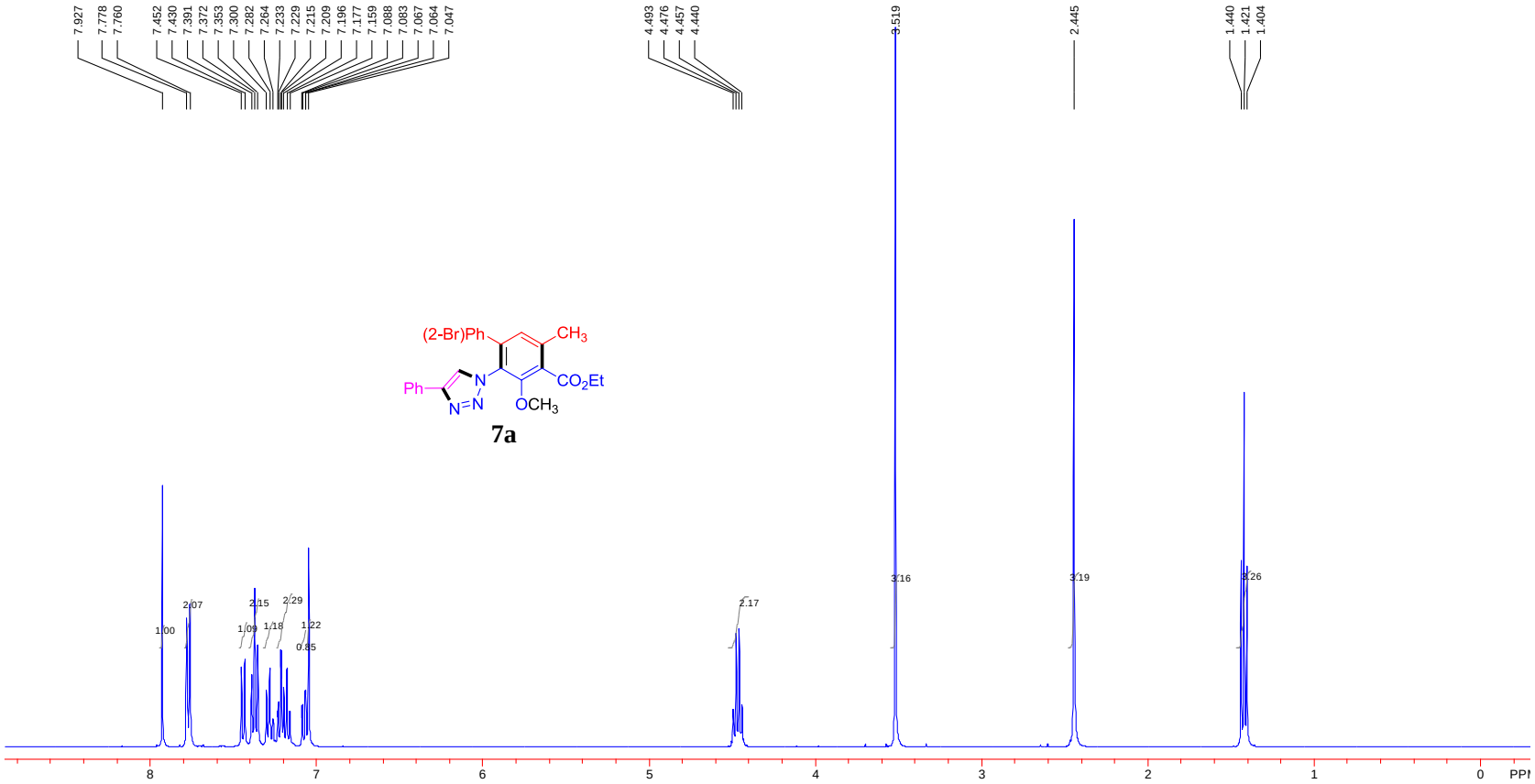
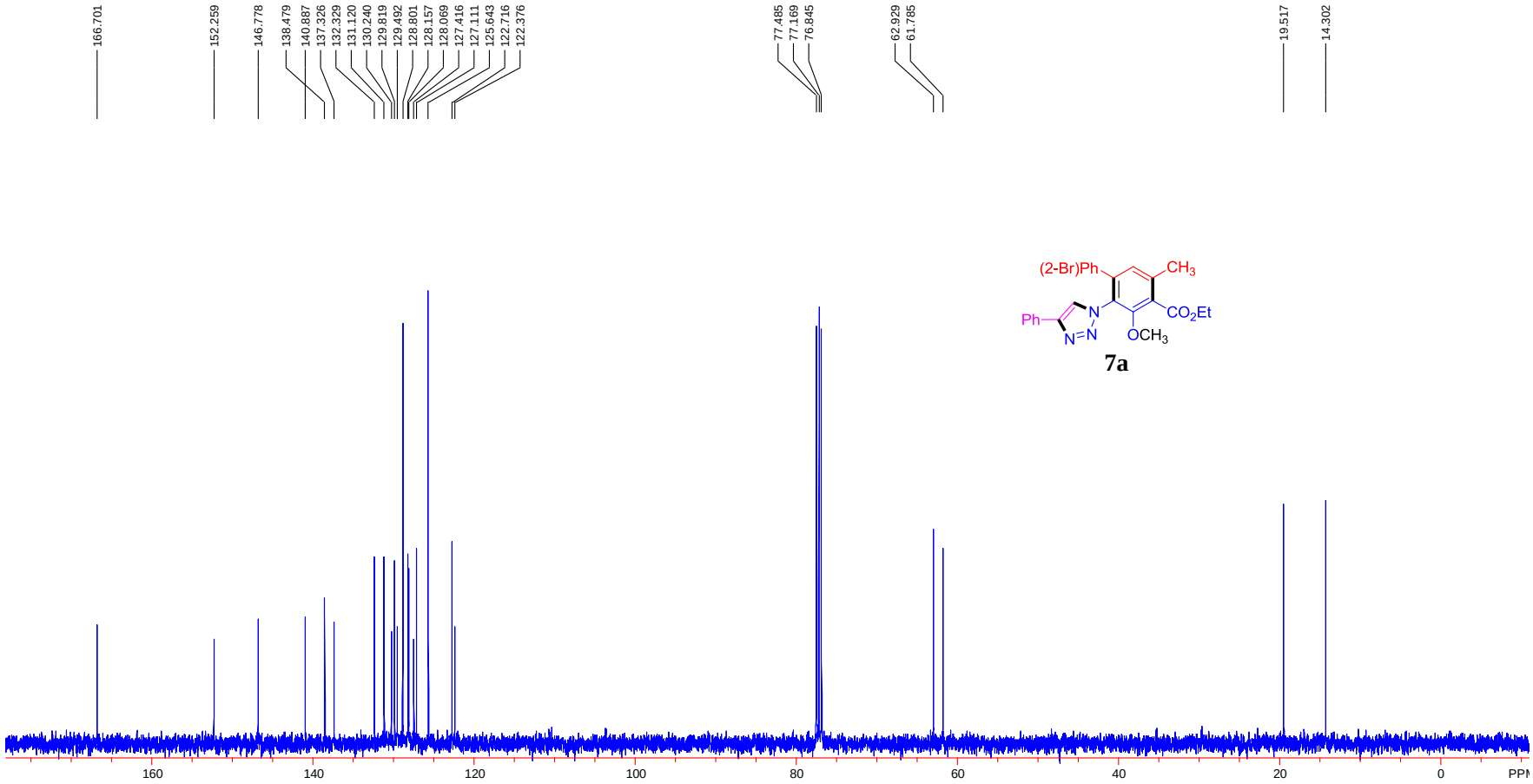
144.660
144.027
143.678
138.649
133.425
133.104
129.320
127.959
124.301
123.731
123.190
121.697
112.127
77.356
77.031
76.720
62.336
24.227
21.050
14.130
-0.169
(4-CH3)Ph
CH3
CO2Et
OH
N
N
N
160
140
120
100
80
60
40
20
0
PPM

4gg

IV. Copies of ^{1}H and ^{13}C NMR spectra of 7a-7e

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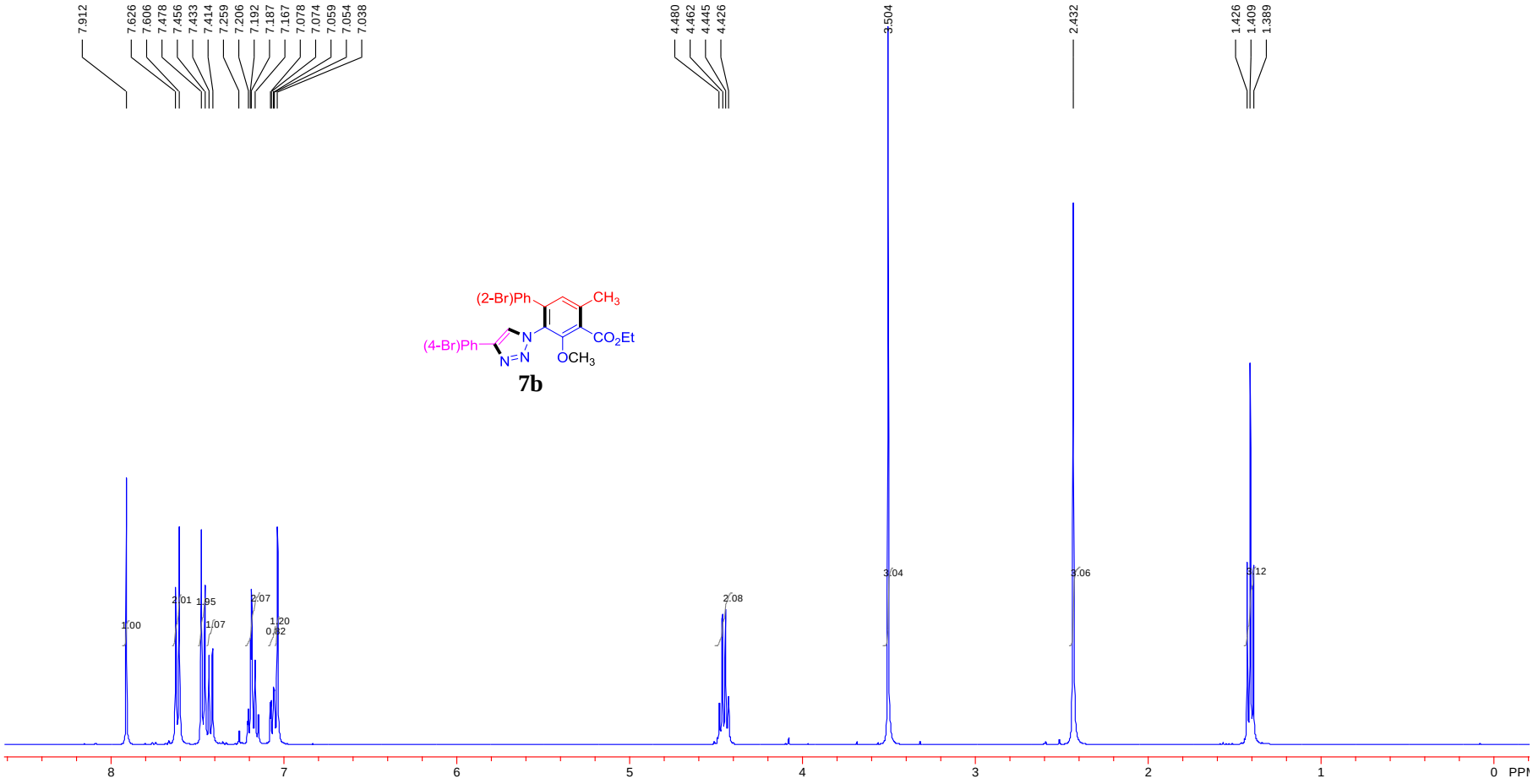
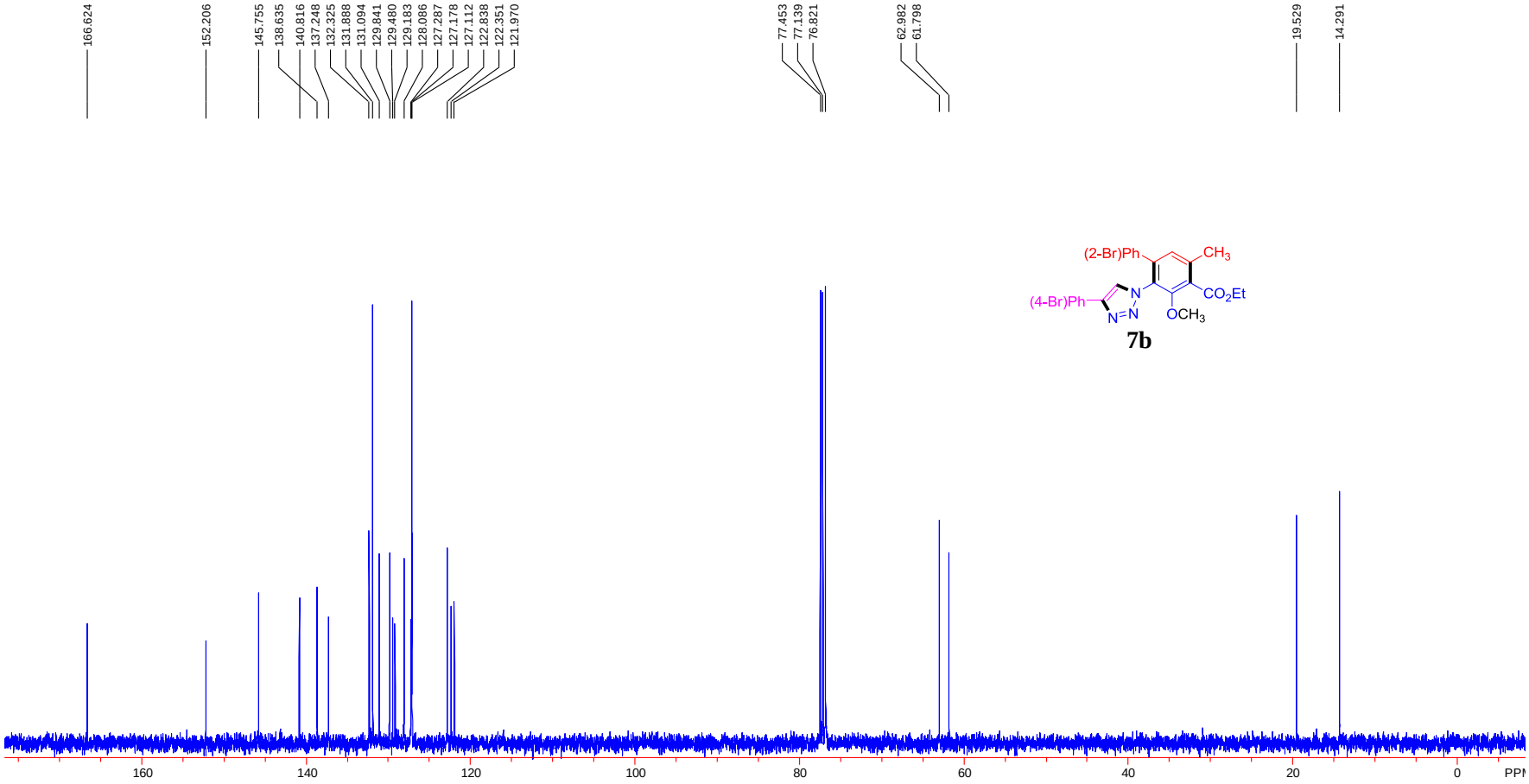
140.887
137.326
132.329
131.120
130.240
129.819
129.492
128.801
128.157
128.069
127.416
127.111
125.643
122.716
122.376
77.485
77.169
76.845
62.929
61.785
19.517
14.302
(2-Br)Ph
CH3
Ph
N
N=N
CO2Et
OCH3
160
140
120
100
80
60
40
20
0
PPM

7a


7.912
7.626
7.606
7.478
7.456
7.433
7.414
7.259
7.206
7.192
7.187
7.167
7.078
7.074
7.059
7.054
7.038
4.480
4.462
4.445
4.426
3.504
2.432
1.426
1.409
1.389
(2-Br)Ph
CH3
(4-Br)Ph
N
N=N
CO2Et
OCH3
7b
1.00
2.01
1.95
1.07
2.07
1.20
0.92
2.08
3.04
3.06
3.12
8
7
6
5
4
3
2
1
0
PPM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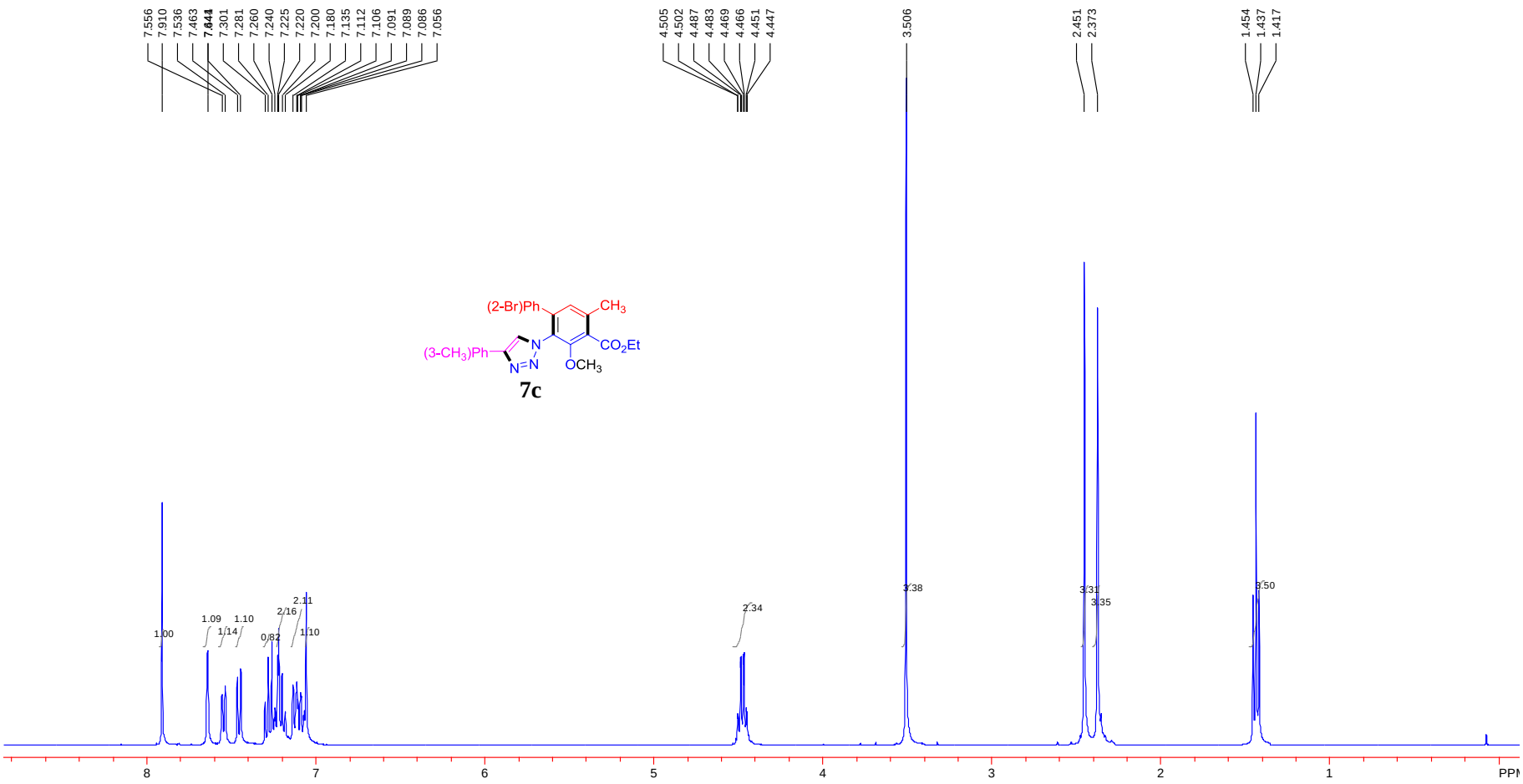
145.755
138.635
140.816
137.248
132.325
131.888
131.094
129.841
129.480
129.183
128.086
127.287
127.178
127.112
122.838
122.351
121.970
77.453
77.139
76.821
62.982
61.798
19.529
14.291
(2-Br)Ph
CH3
(4-Br)Ph
N
N
N
CO2Et
OCH3
160
140
120
100
80
60
40
20
0
PPM

7b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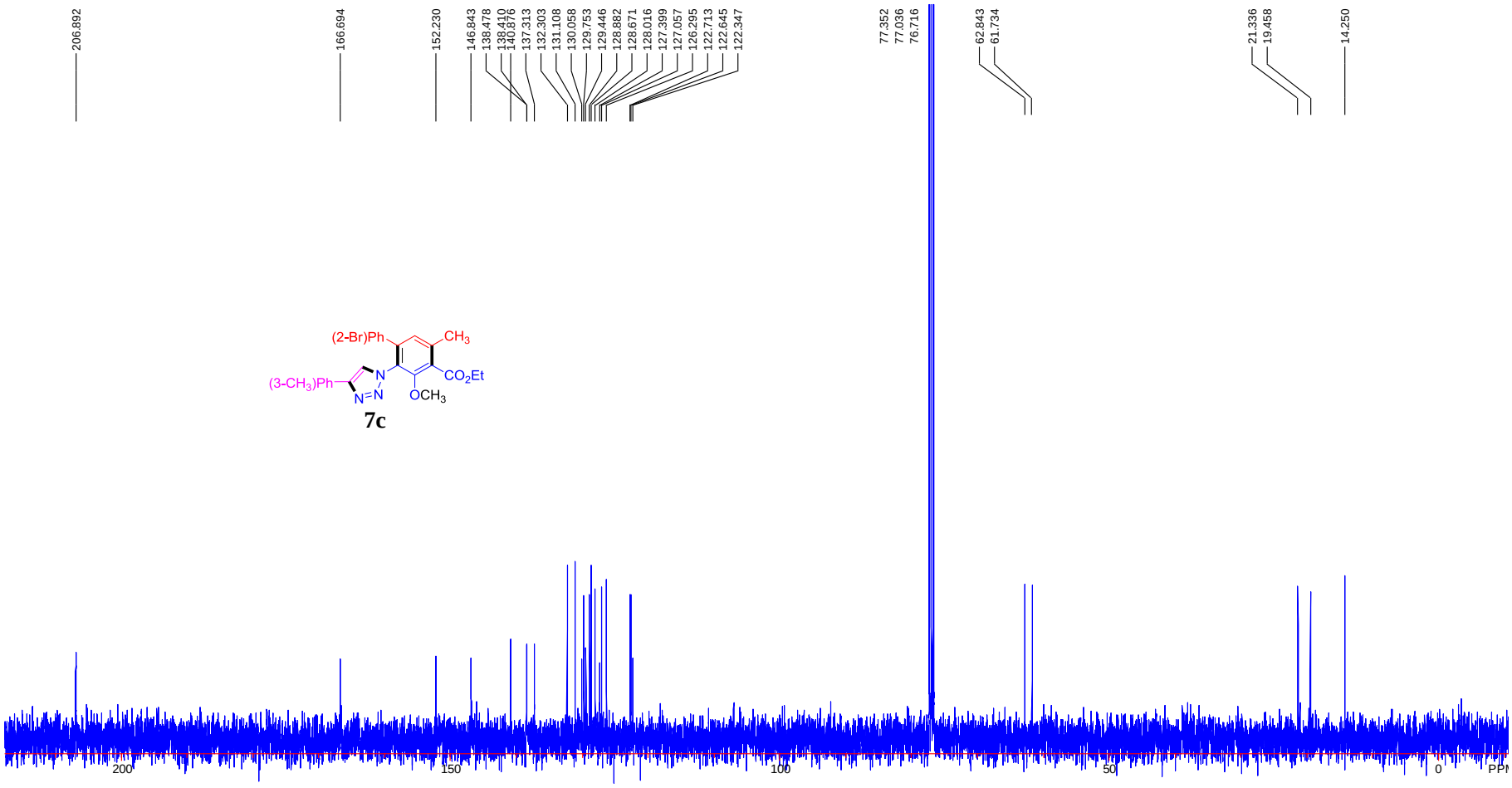
7.536
7.463
7.444
7.301
7.281
7.260
7.240
7.225
7.220
7.200
7.180
7.135
7.112
7.106
7.091
7.089
7.086
7.056
4.505
4.502
4.487
4.483
4.469
4.466
4.451
4.447
3.506
2.451
2.373
1.454
1.437
1.417
(2-Br)Ph
CH3
(3-CH3)Ph
CO2Et
OCH3
7c
1.00
1.09
1.14
1.10
0.82
2.16
2.11
1.10
2.34
3.38
3.31
3.35
3.50
8
7
6
5
4
3
2
1
PPM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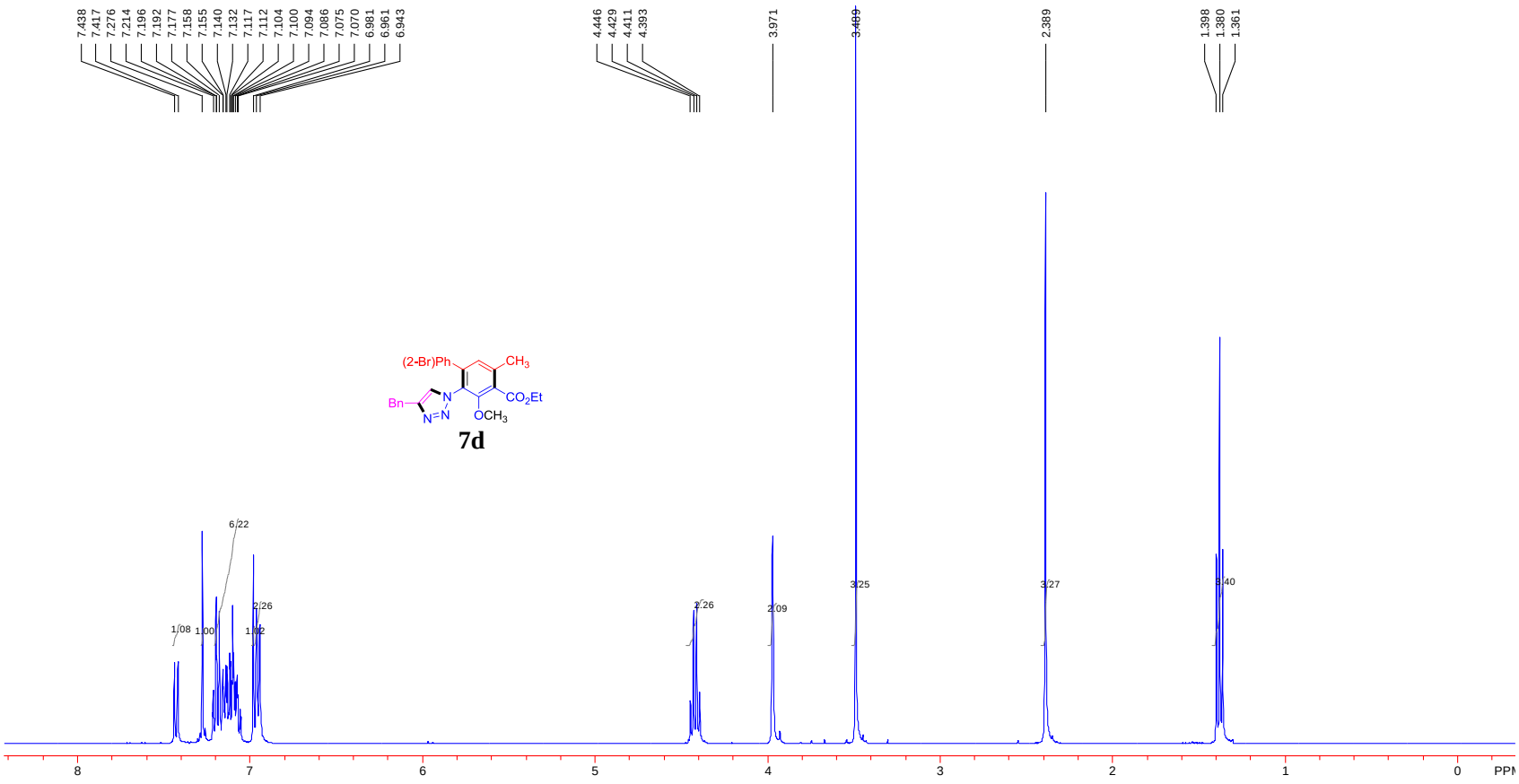
138.478
138.410
140.876
137.313
132.303
131.108
130.058
129.753
129.446
128.882
128.671
128.016
127.399
127.057
126.295
122.713
122.645
122.347
77.352
77.036
76.716
62.843
61.734
21.336
19.458
14.250
(2-Br)Ph
CH3
(3-CH3)Ph
N
N=N
CO2Et
OCH3
200
150
100
50
0
PPM

7c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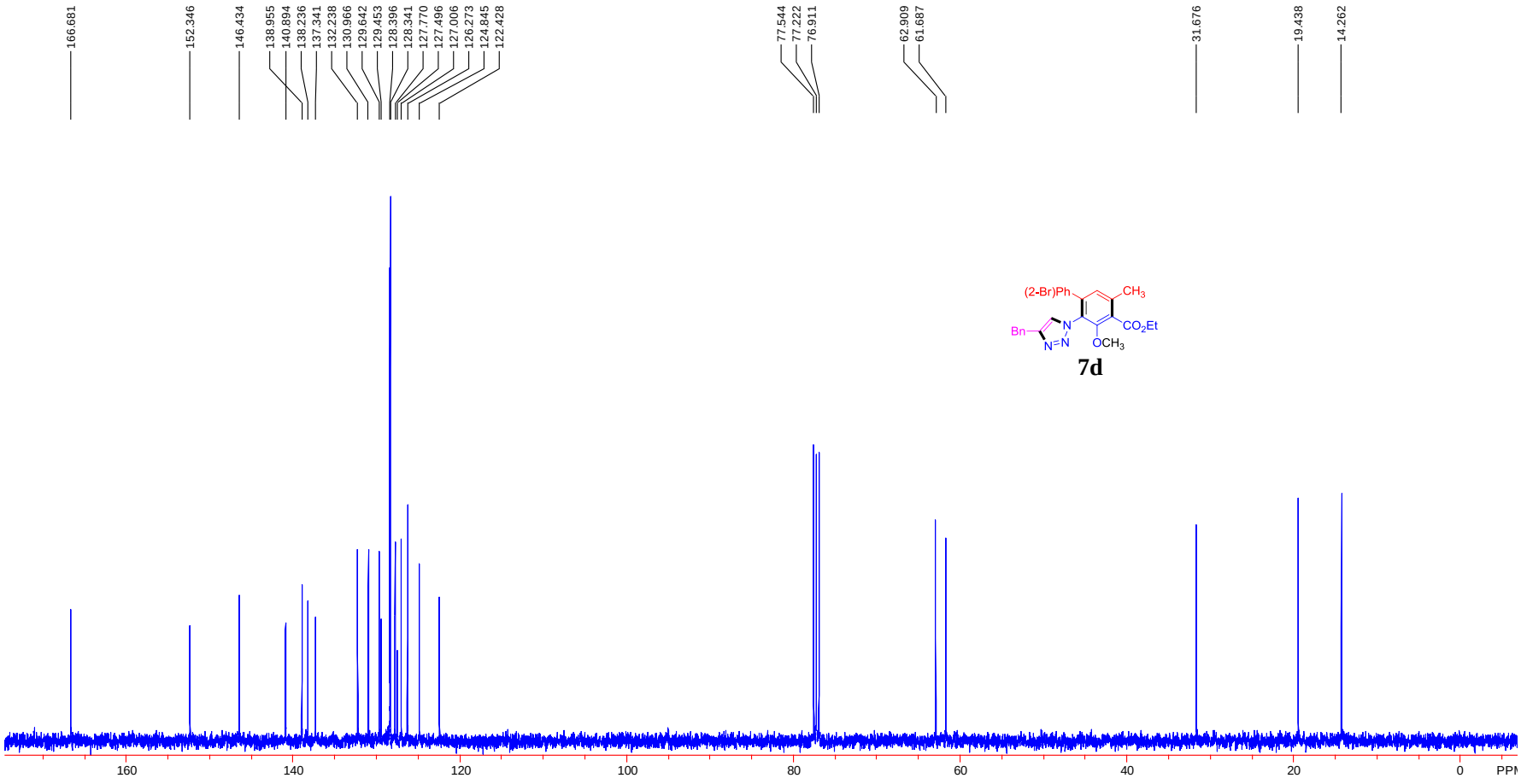
7.276
7.214
7.196
7.192
7.177
7.158
7.155
7.140
7.132
7.117
7.112
7.104
7.100
7.094
7.086
7.075
7.070
6.981
6.961
6.943
4.446
4.429
4.411
4.393
3.971
3.489
2.389
1.398
1.380
1.361
(2-Br)Ph
CH3
Bn
N
N
N
CO2Et
OCH3
7d
6.22
2.26
1.08
1.00
1.02
2.26
2.09
3.25
3.27
3.40
8
7
6
5
4
3
2
1
0
PPM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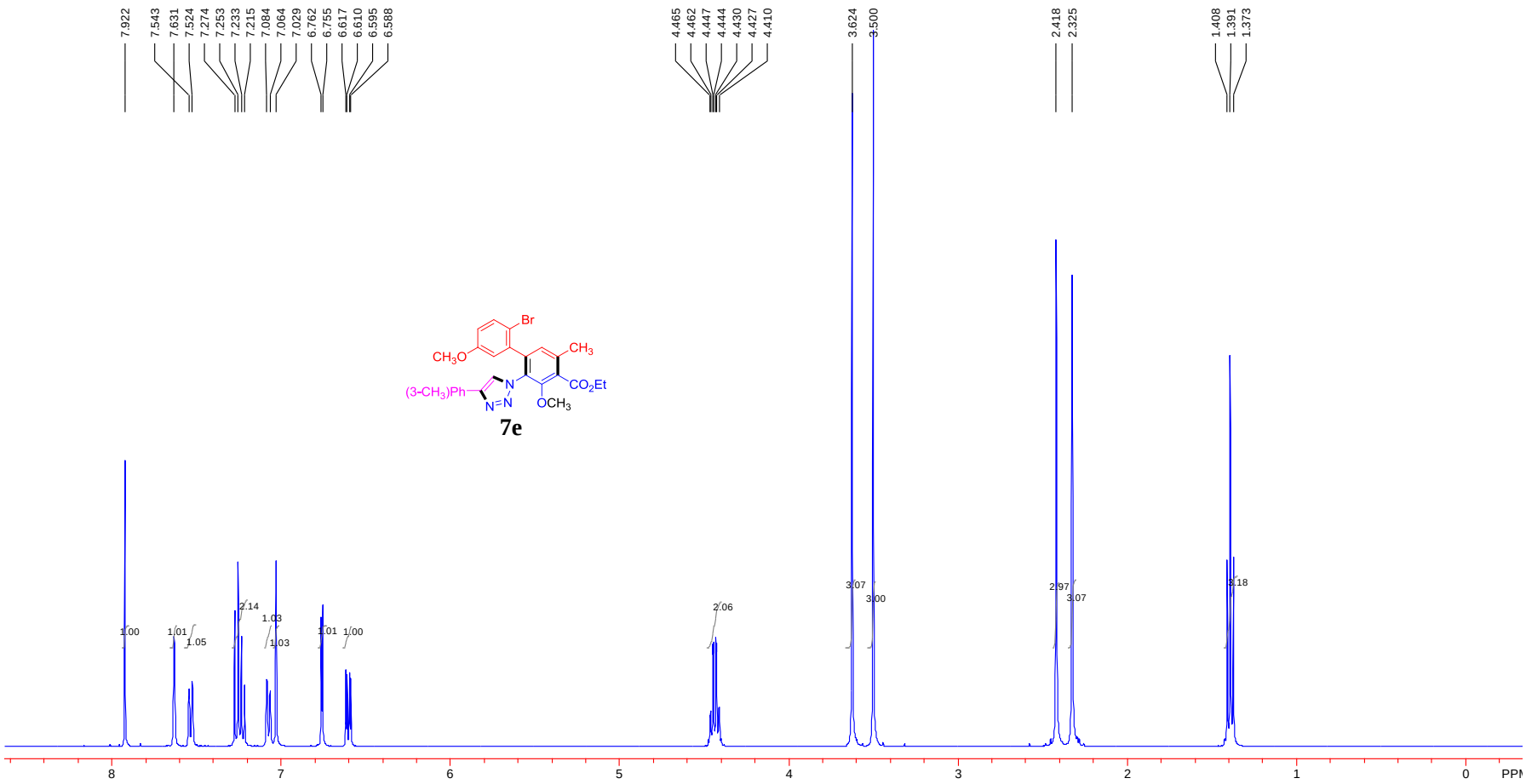
138.955
140.894
138.236
137.341
132.238
130.966
129.642
129.453
128.396
128.341
127.770
127.496
127.006
126.273
124.845
122.428
77.544
77.222
76.911
62.909
61.687
31.676
19.438
14.262
(2-Br)Ph
CH3
Bn
N
N=N
CO2Et
OCH3
160
140
120
100
80
60
40
20
0
PPM

7d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7.543
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7.524
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7.253
7.233
7.215
7.084
7.064
7.029
6.762
6.755
6.617
6.610
6.595
6.588
4.465
4.462
4.447
4.444
4.430
4.427
4.410
3.624
3.500
2.418
2.325
1.408
1.391
1.373
Br
CH3O
CH3
(3-CH3)Ph
N
N=N
CO2Et
OCH3
7e
1.00
1.01
1.05
2.14
1.03
1.03
1.01
1.00
2.06
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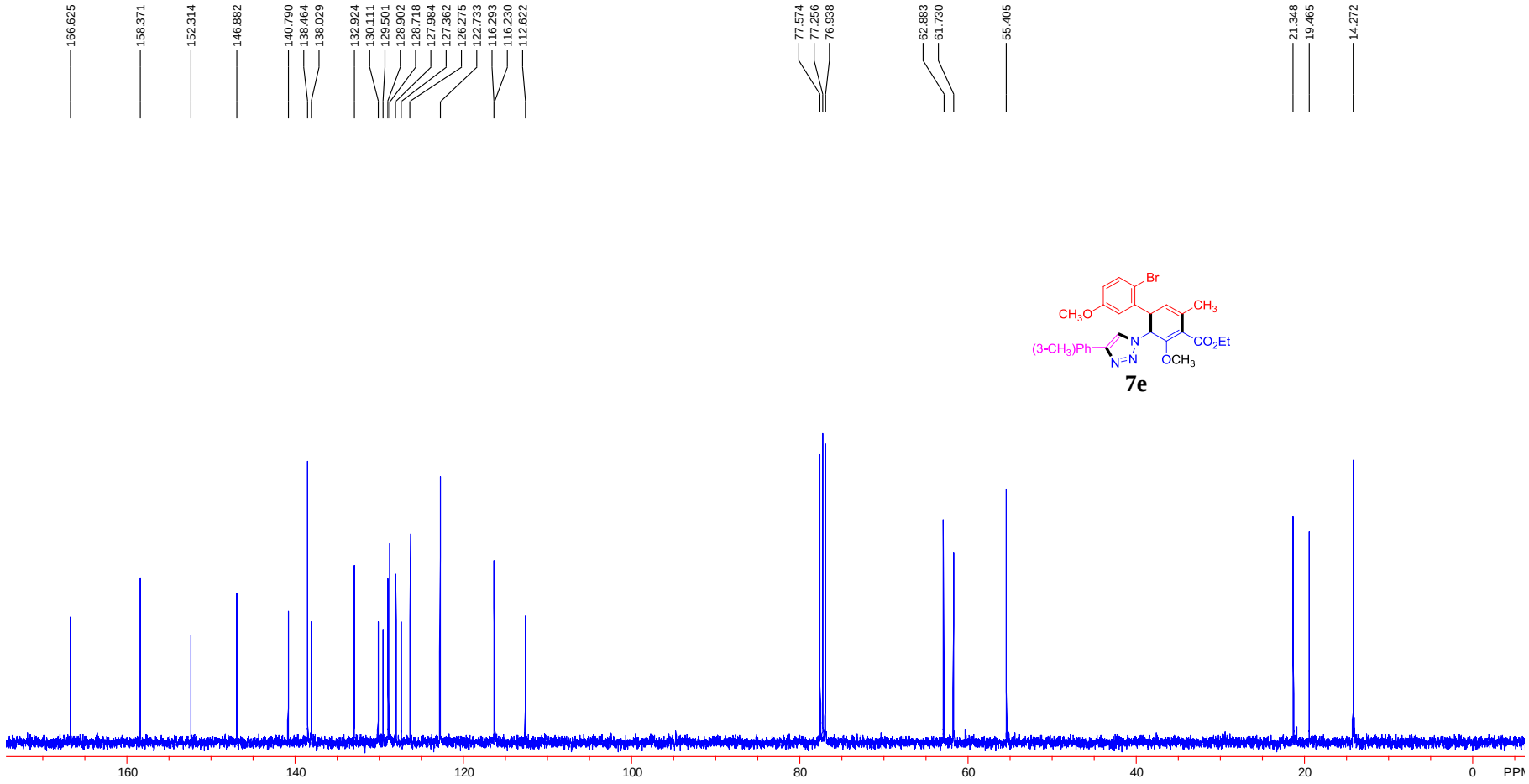
6
5
4
3
2
1
0
PPM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127.362
126.275
122.733
116.293
116.230
112.622
77.574
77.256
76.938
62.883
61.730
55.405
21.348
19.465
14.272
Br
CH3O
CH3
(3-CH3)Ph
N
N=N
CO2Et
OCH3
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140
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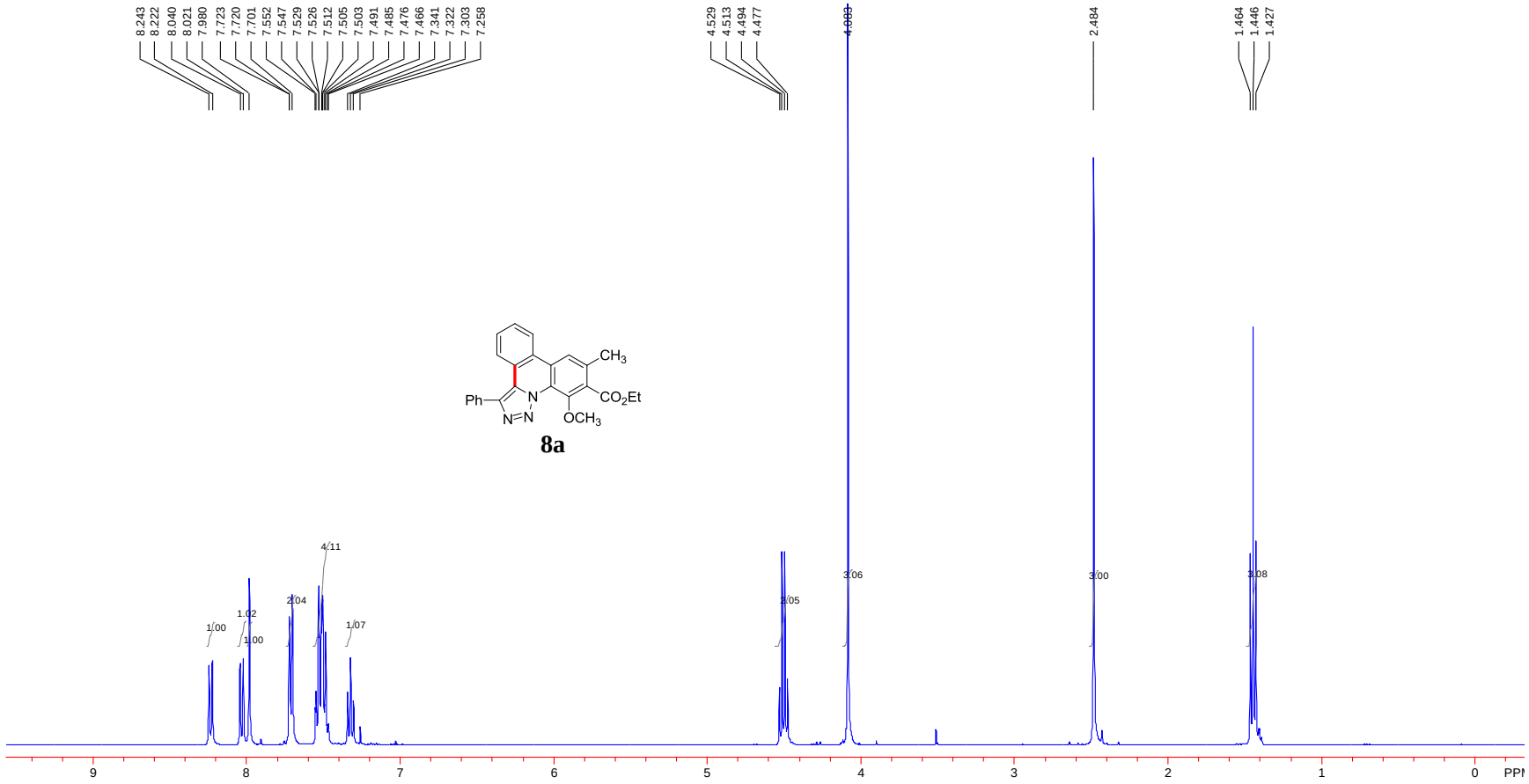
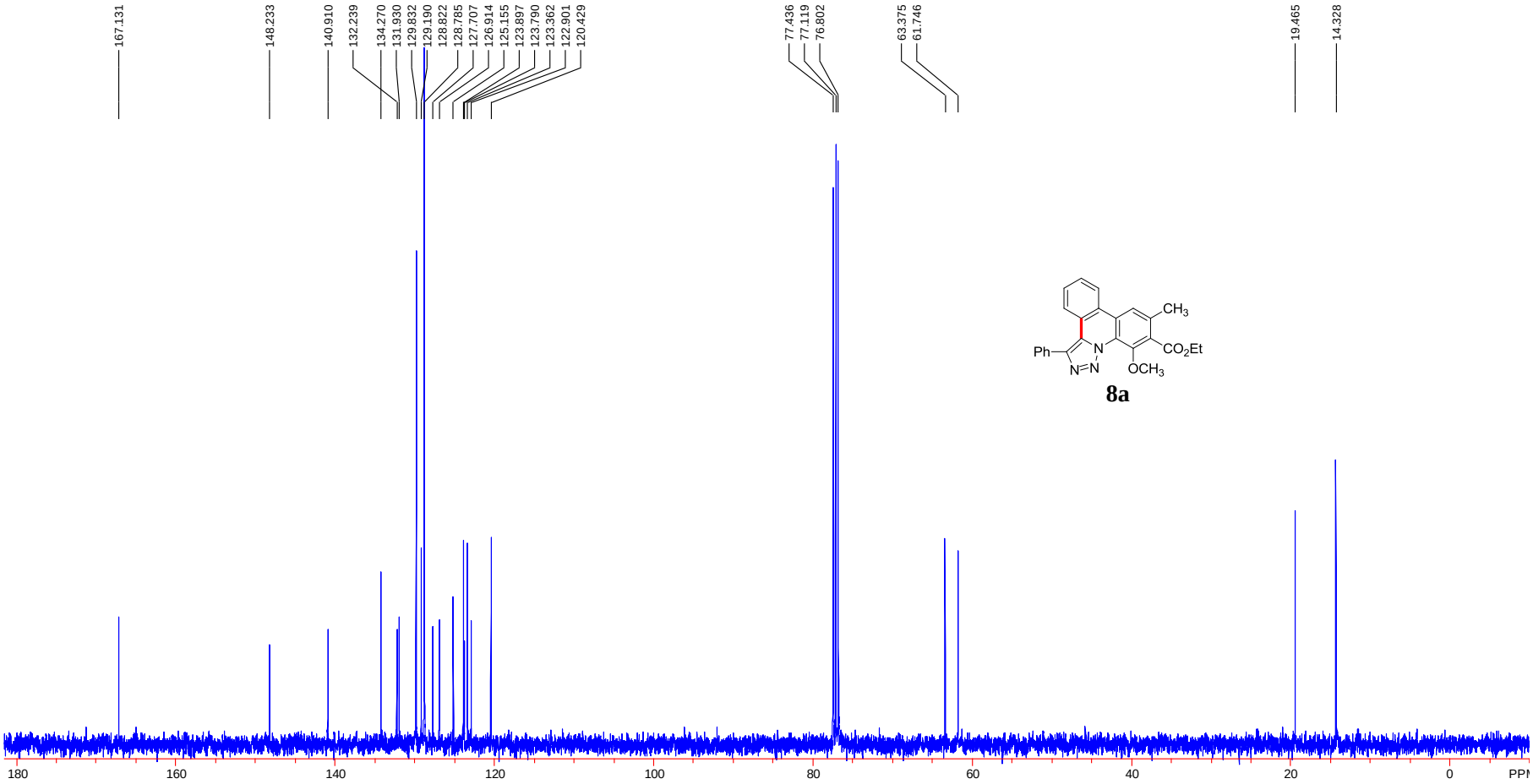
100
80
60
40
20
0
PPM

7e

V. Copies of ^{1}H and ^{13}C NMR spectra of 8a-8e

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132.239
134.270
131.930
129.832
129.190
128.822
128.785
127.707
126.914
125.155
123.897
123.790
123.362
122.901
120.429
77.436
77.119
76.802
63.375
61.746
19.465
14.328
CH3
Ph
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CO2Et
OCH3
180
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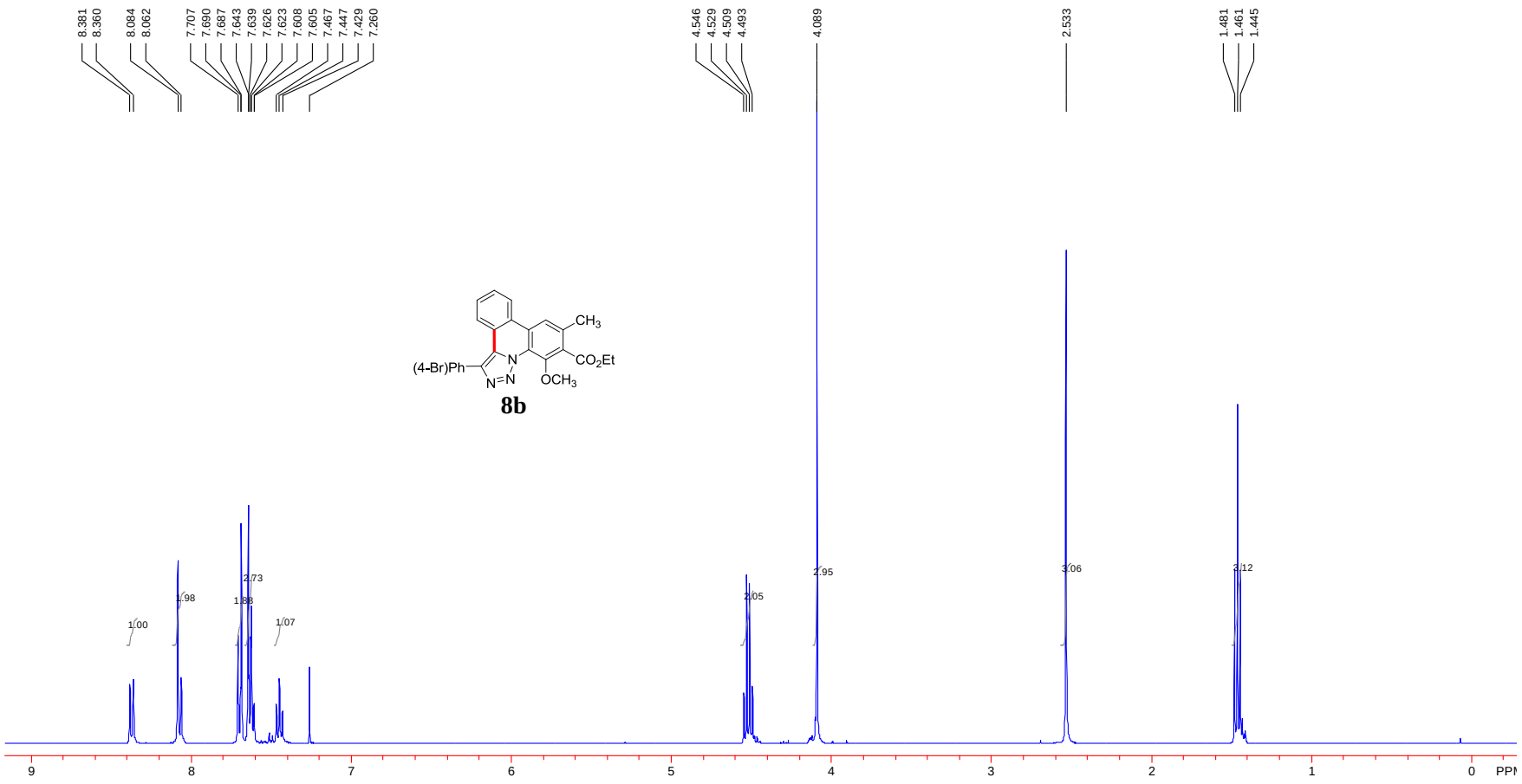
140
120
100
80
60
40
20
0
PPM

8a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8.360
8.084
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7.643
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7.626
7.623
7.608
7.605
7.467
7.447
7.429
7.260
4.546
4.529
4.509
4.493
4.089
2.533
1.481
1.461
1.445
CH3
CO2Et
(4-Br)Ph
N
N=N
OCH3
8b
1.00
1.98
2.73
1.88
1.07
2.05
2.95
3.06
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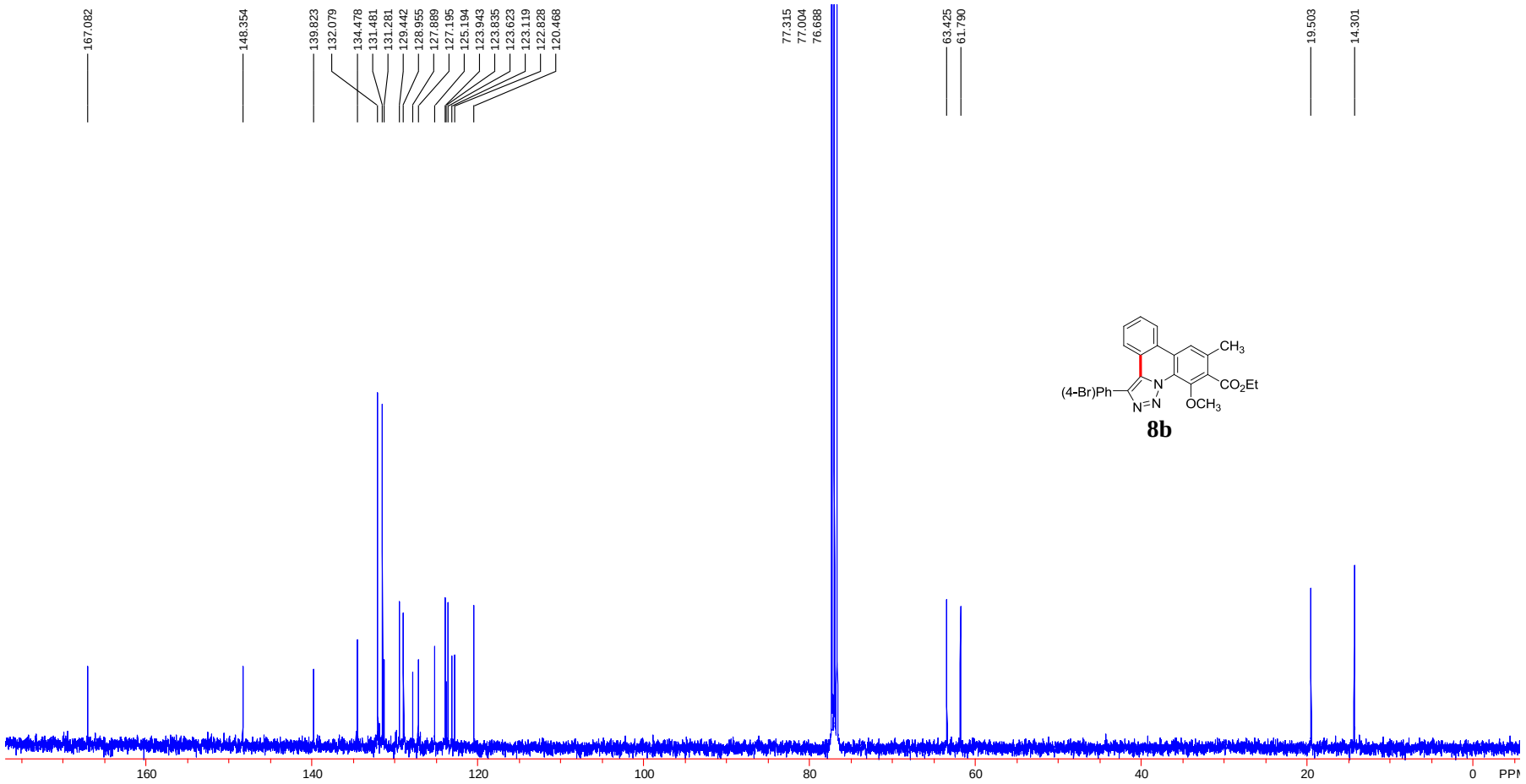
9
8
7
6
5
4
3
2
1
0
PPM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139.823
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134.478
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129.442
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127.889
127.195
125.194
123.943
123.835
123.623
123.119
122.828
120.468
77.315
77.004
76.688
63.425
61.790
19.503
14.301
CH3
CO2Et
(4-Br)Ph
N
N=N
OCH3
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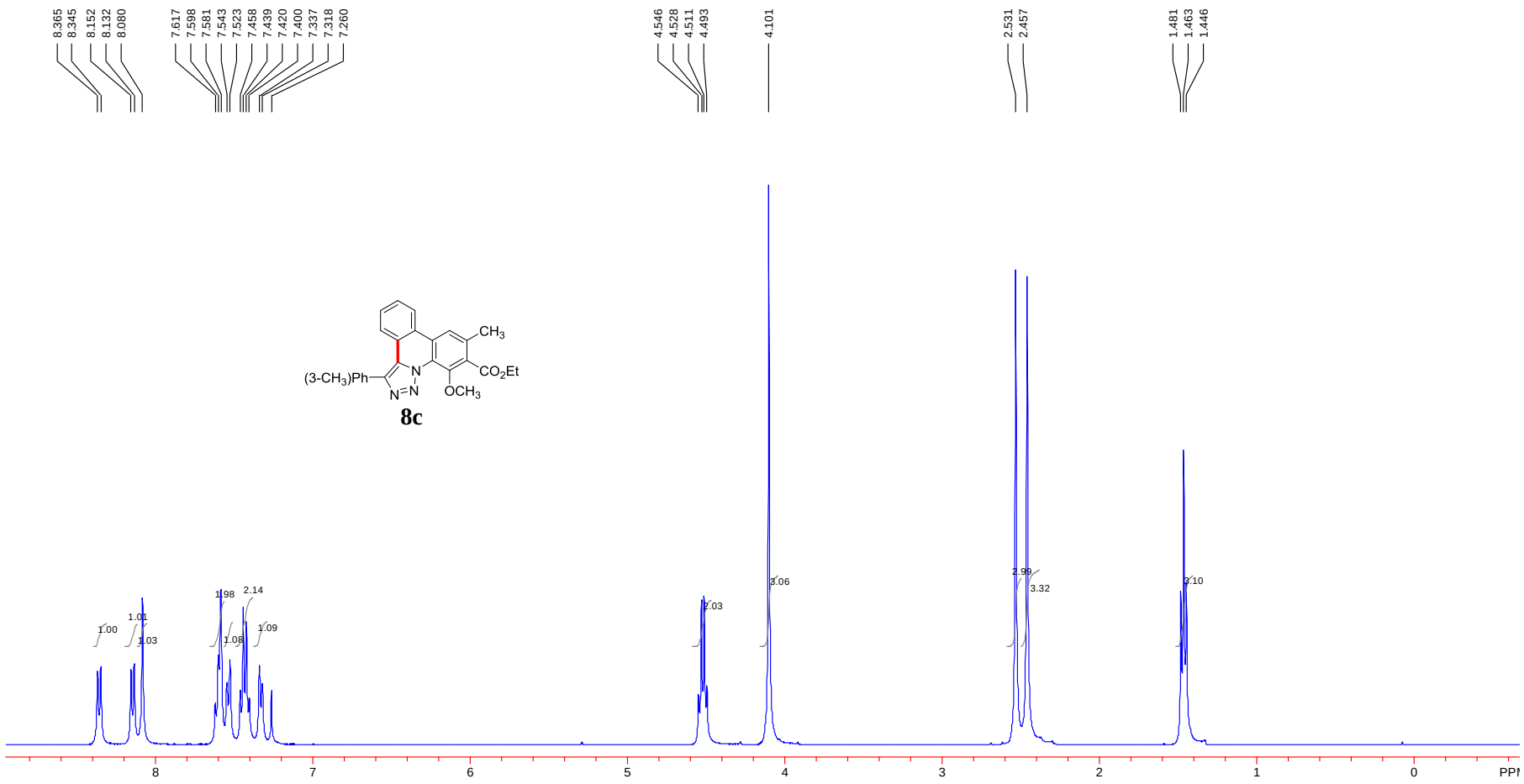
140
120
100
80
60
40
20
0
PPM

8b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8.152
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7.523
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7.420
7.400
7.337
7.318
7.260
4.546
4.528
4.511
4.493
4.101
2.531
2.457
1.481
1.463
1.446
CH3
CO2Et
(3-CH3)Ph
N
N
OCH3
8c
1.00
1.01
1.03
1.98
2.14
1.08
1.09
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3.06
2.99
3.32
3.10
8
7
6
5
4
3
2
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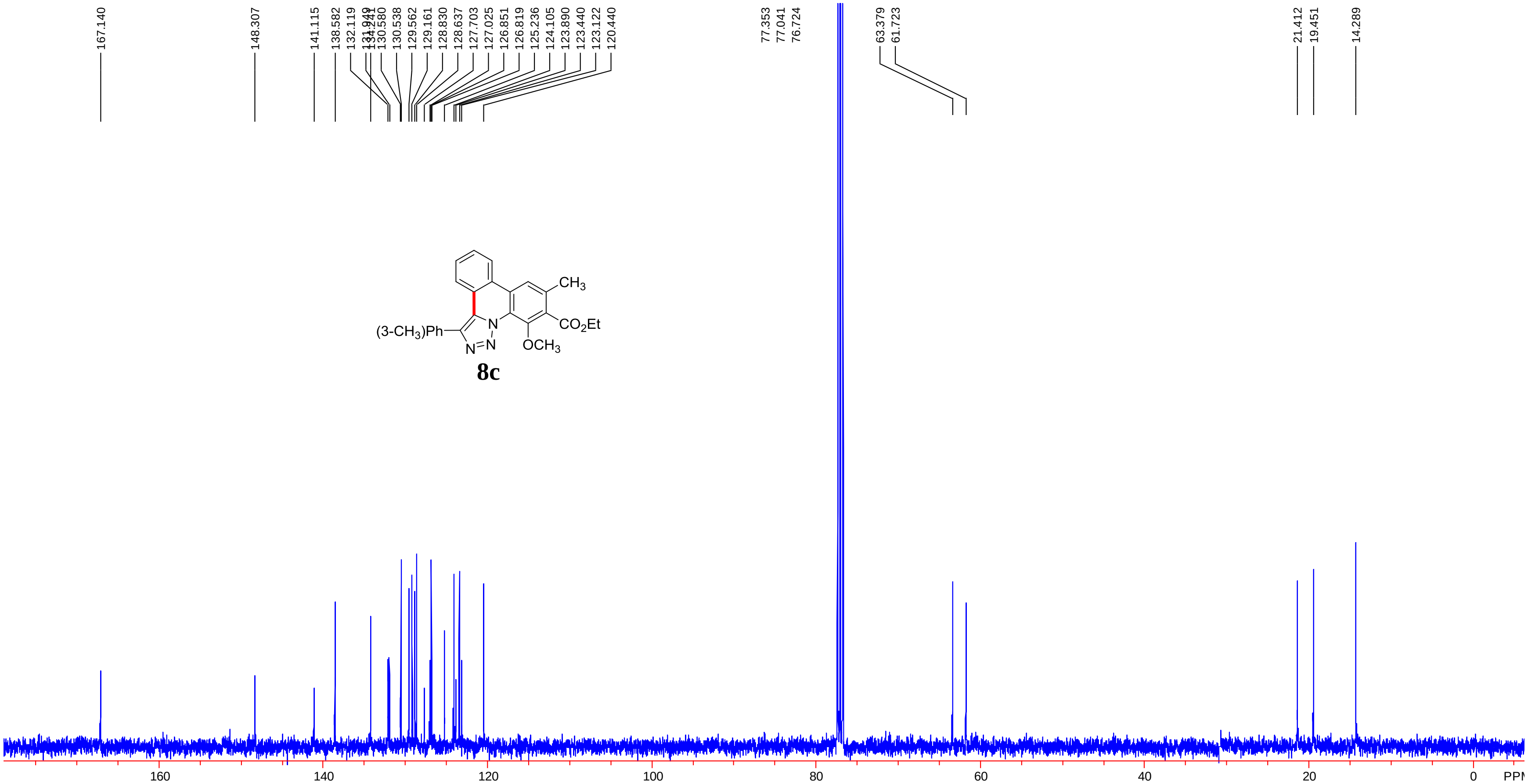
PPM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132.119
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129.562
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127.025
126.851
126.819
125.236
124.105
123.890
123.440
123.122
120.440
77.353
77.041
76.724
63.379
61.723
21.412
19.451
14.289
CH3
CO2Et
OCH3
(3-CH3)Ph
N
8c
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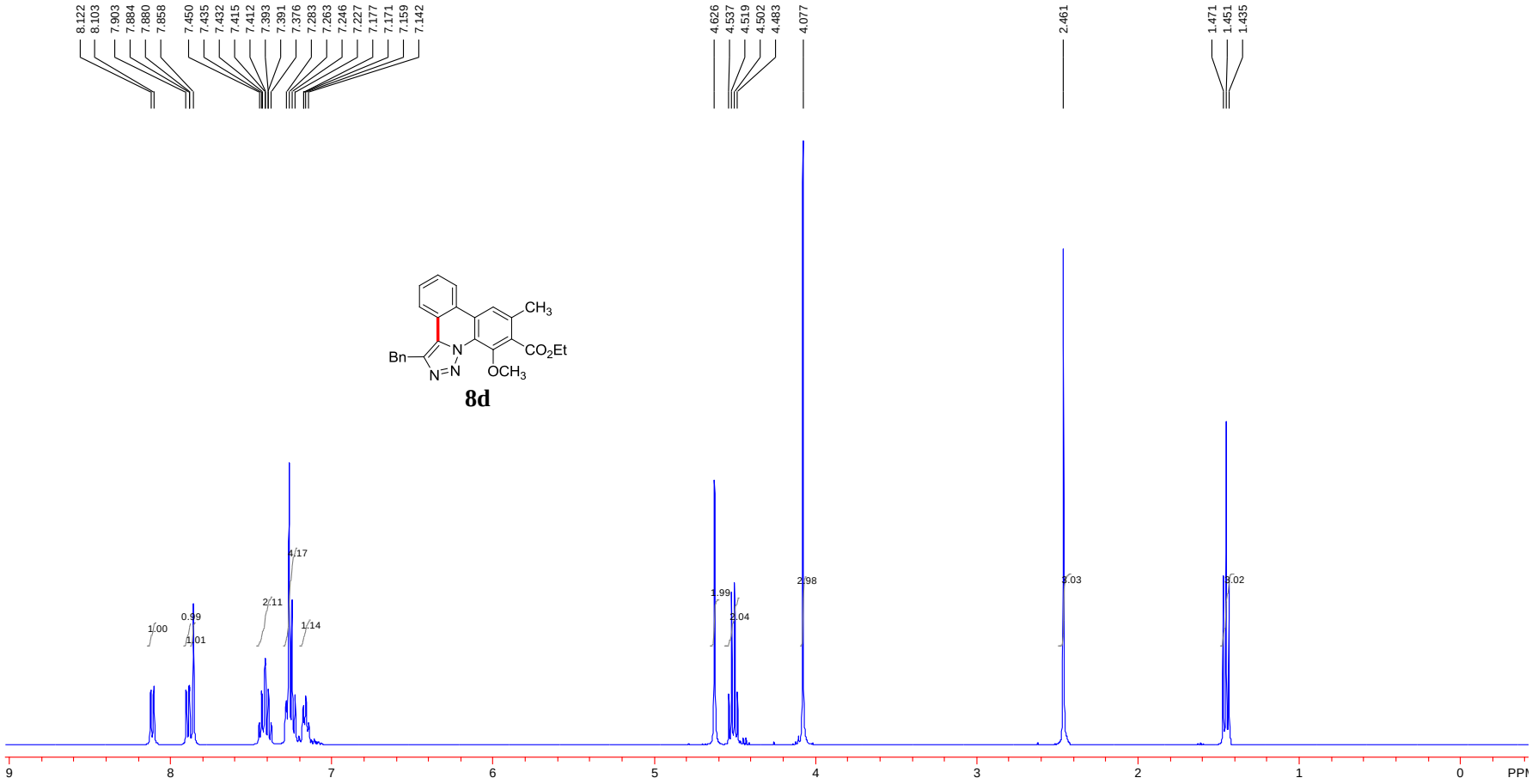
140
120
100
80
60
40
20
0
PPM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7.880
7.858
7.450
7.435
7.432
7.415
7.412
7.393
7.391
7.376
7.283
7.263
7.246
7.227
7.177
7.171
7.159
7.142
4.626
4.537
4.519
4.502
4.483
4.077
2.461
1.471
1.451
1.435
CH3
CO2Et
Bn
N
N=N
OCH3
8d
1.00
0.99
1.01
2.11
4.17
1.14
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3.03
3.02
9
8
7
6
5
4
3
2
1
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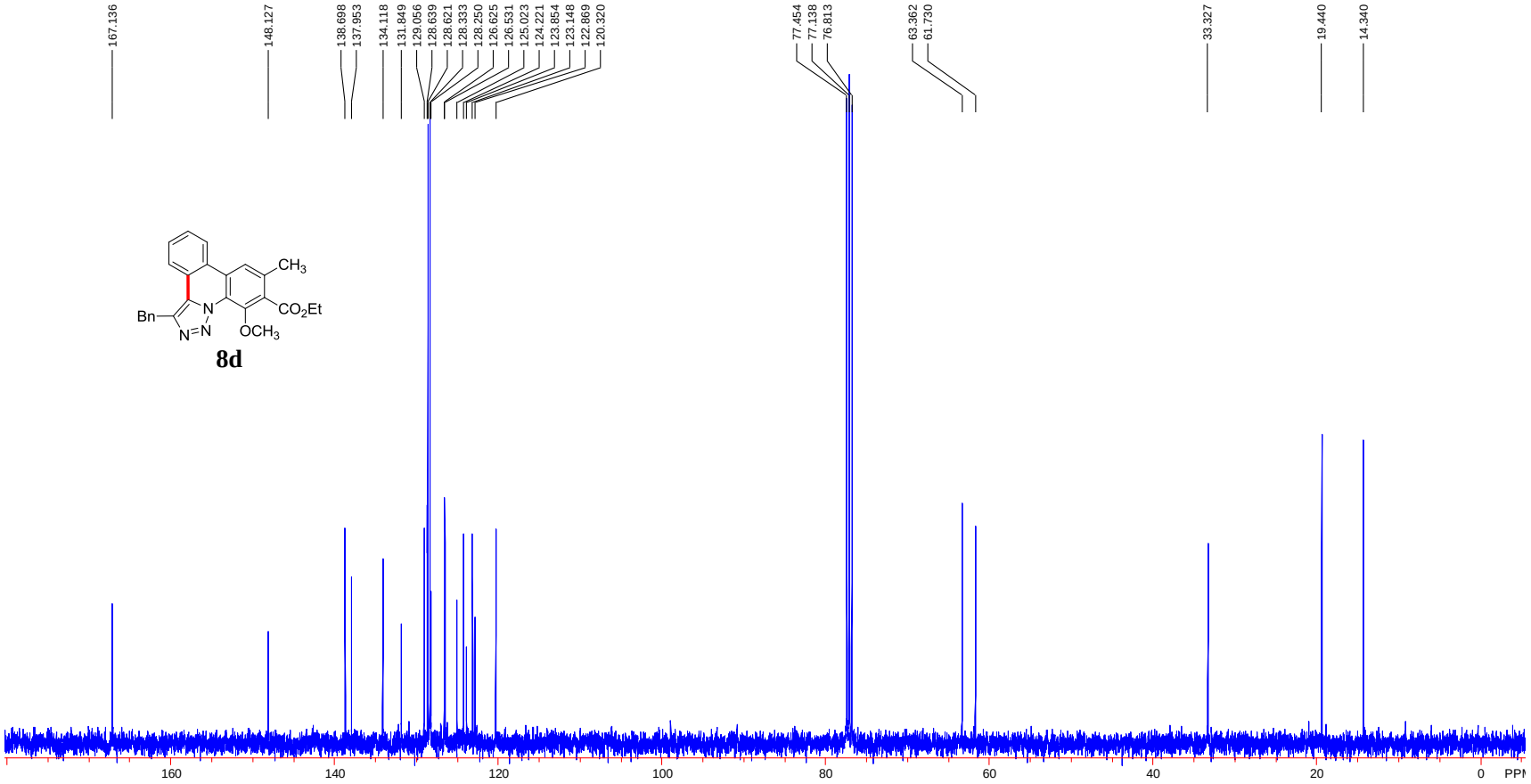
PPM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131.849
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128.639
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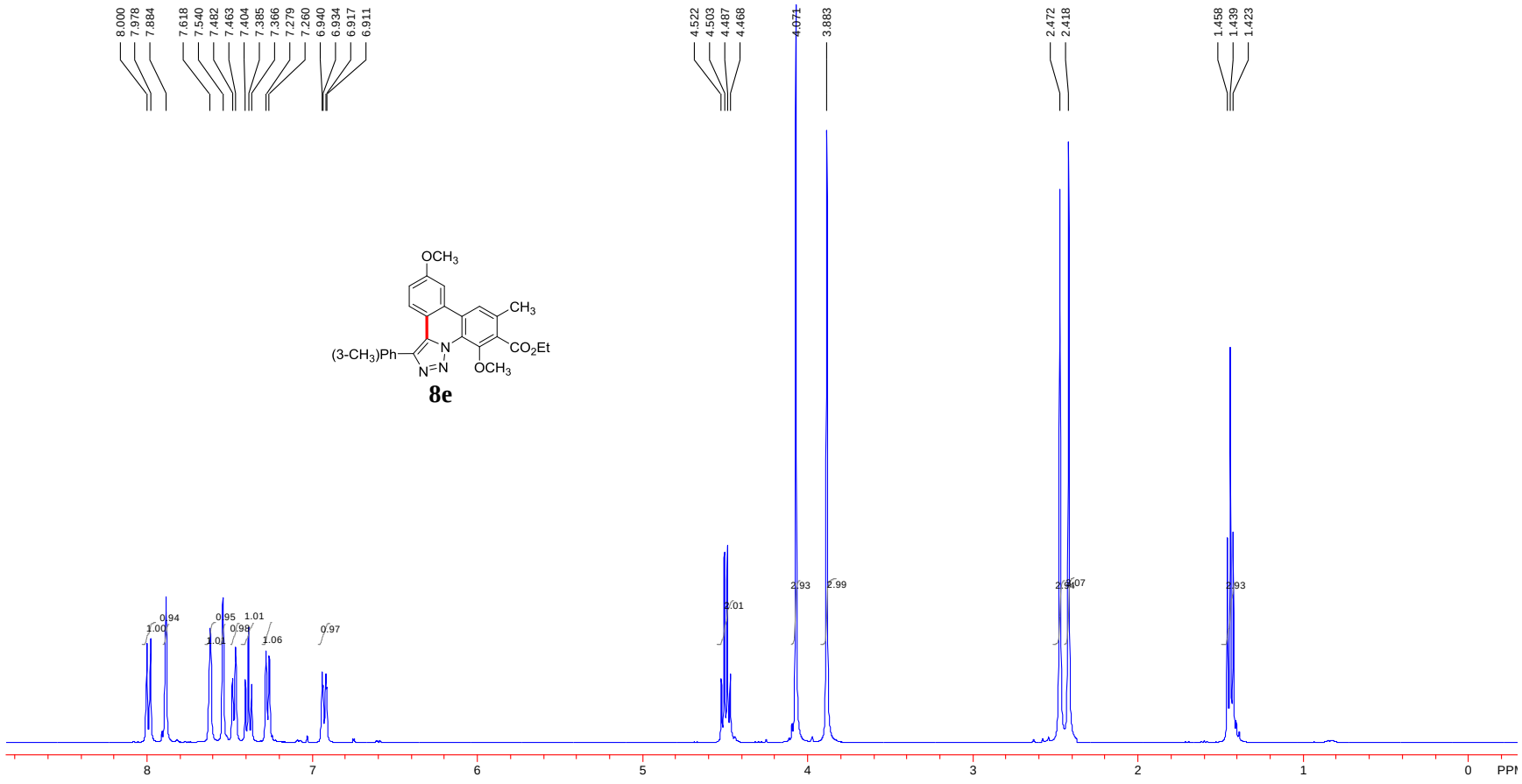
128.250
126.625
126.531
125.023
124.221
123.854
123.148
122.869
120.320
77.454
77.138
76.813
63.362
61.730
33.327
19.440
14.340
CH3
CO2Et
Bn
N
N=N
OCH3
160
140
120
100
80
60
40
20
0
PPM

8d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7.482
7.463
7.404
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7.366
7.279
7.260
6.940
6.934
6.917
6.911
4.522
4.503
4.487
4.468
4.071
3.883
2.472
2.418
1.458
1.439
1.423
OCH3
CH3
CO2Et
(3-CH3)Ph
N
N
OCH3
8e
1.00
0.94
1.04
0.95
0.98
1.01
1.06
0.97
2.01
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7
6
5
4
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2
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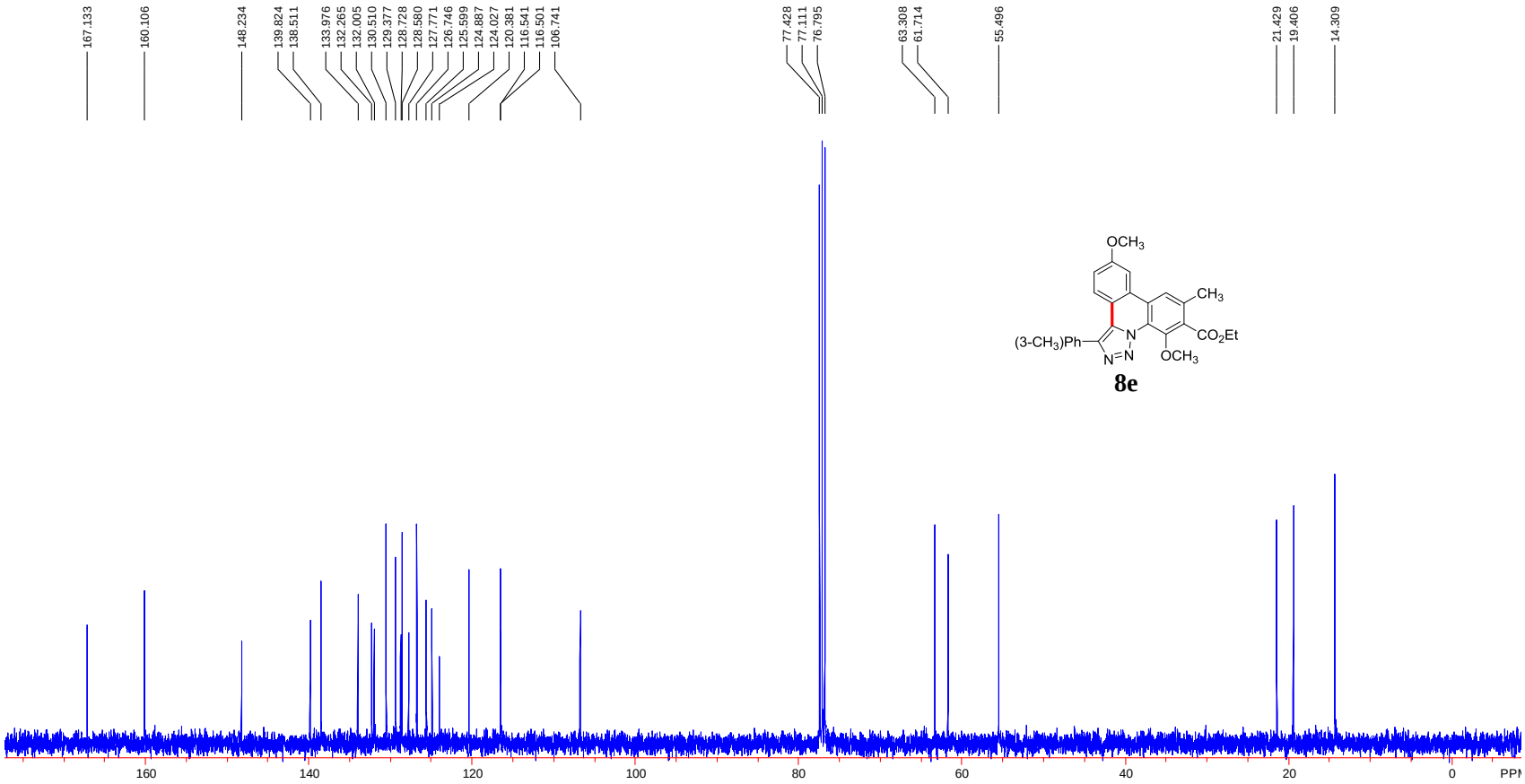
PPM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148.234
139.824
138.511
133.976
132.265
132.005
130.510
129.377
128.728
128.580
127.771
126.746
125.599
124.887
124.027
120.381
116.541
116.501
106.741
77.428
77.111
76.795
63.308
61.714
55.496
21.429
19.406
14.309
OCH3
CH3
(3-CH3)Ph
N
N=N
CO2Et
OCH3
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140
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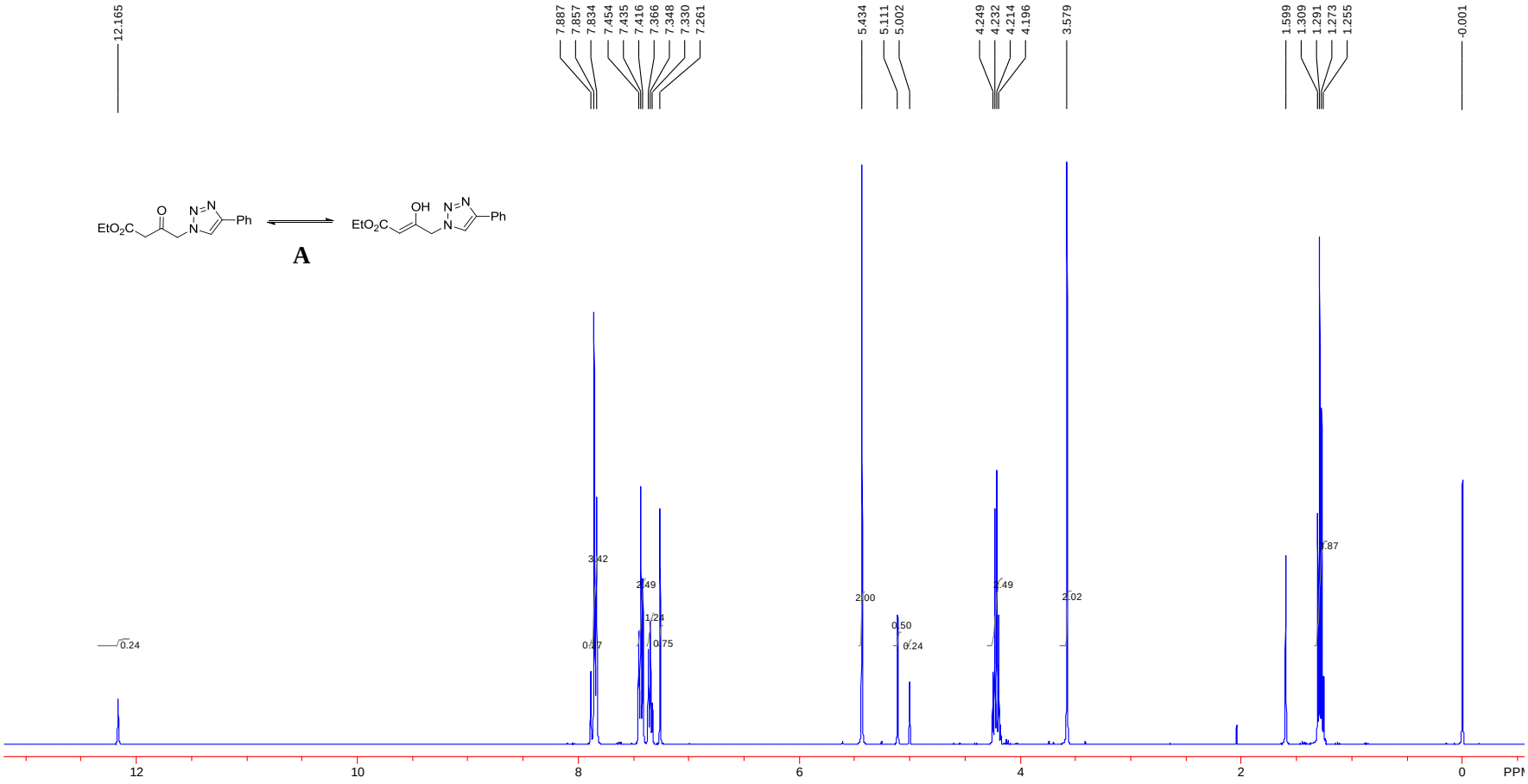
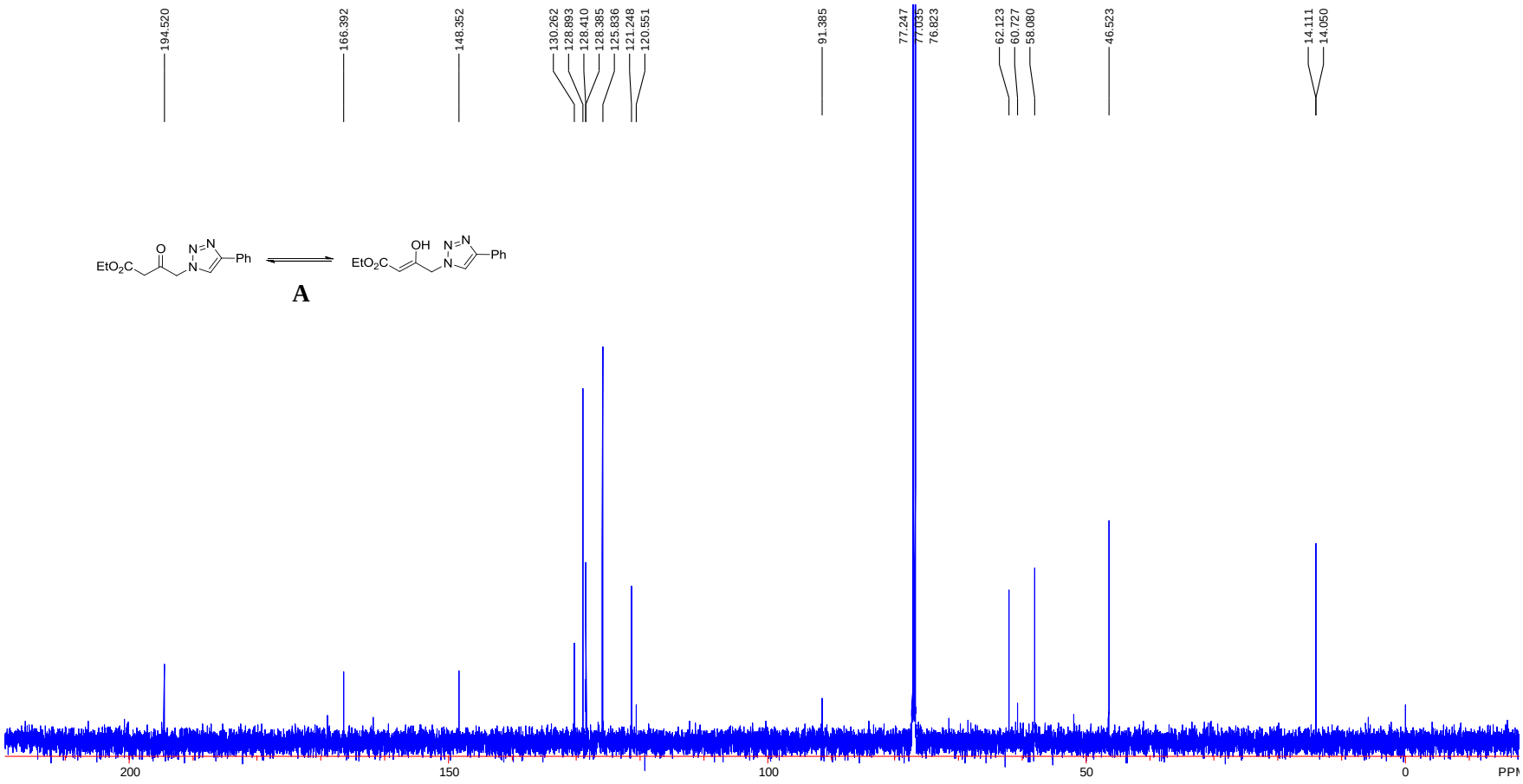
100
80
60
40
20
0
PPM

VI. Copies of ^{1}H and ^{13}C NMR spectra of A and 5

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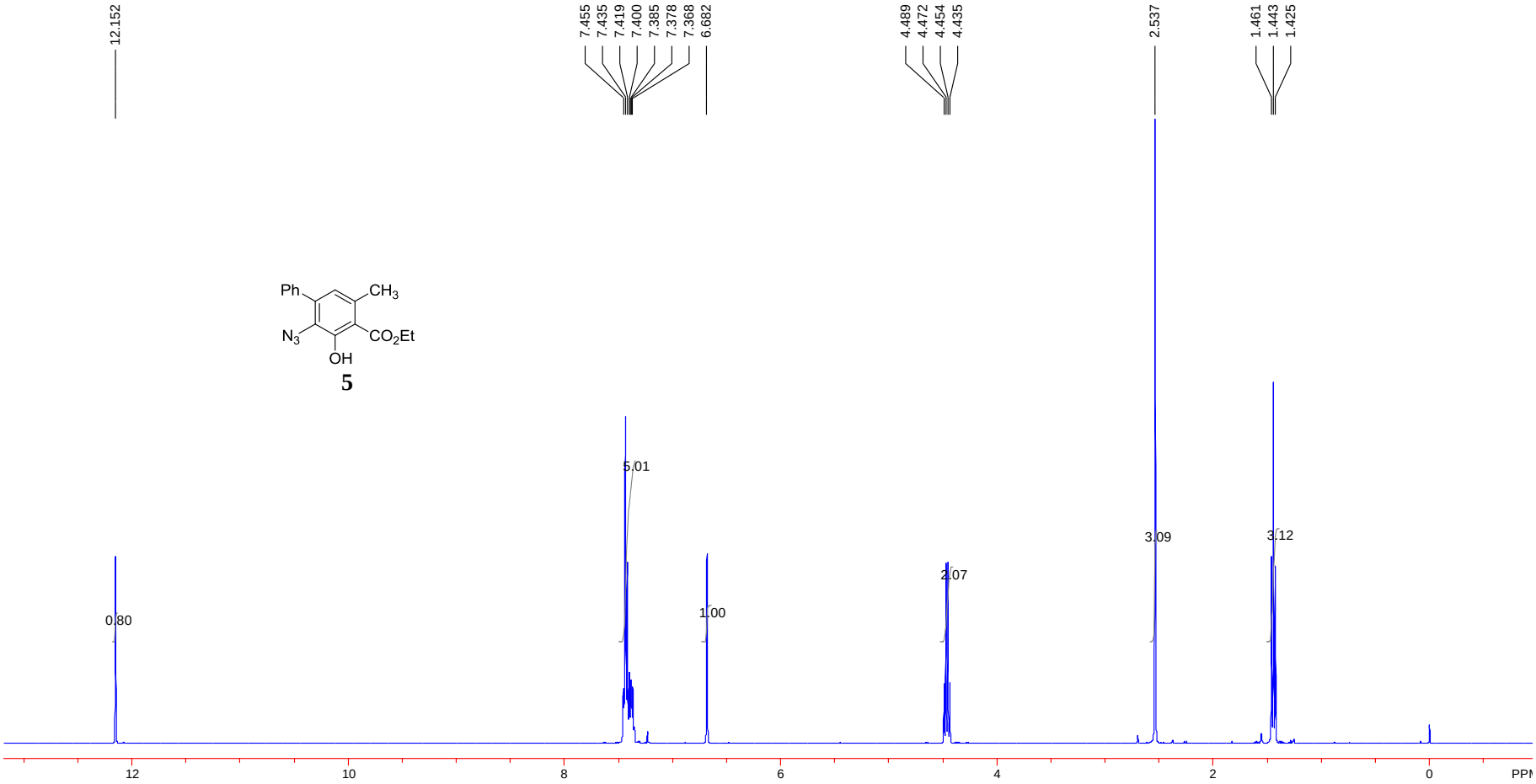
166.392
148.352
130.262
128.893
128.410
128.385
125.836
121.248
120.551
91.385
77.247
77.035
76.823
62.123
60.727
58.080
46.523
14.111
14.050
EtO2C
O
N
N
Ph
OH
A
200
150
100
50
0
PPM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7.435
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7.400
7.385
7.378
7.368
6.682
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4.472
4.454
4.435
2.537
1.461
1.443
1.425
Ph
CH3
N3
CO2Et
OH
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1.00
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12
10
8
6
4
2
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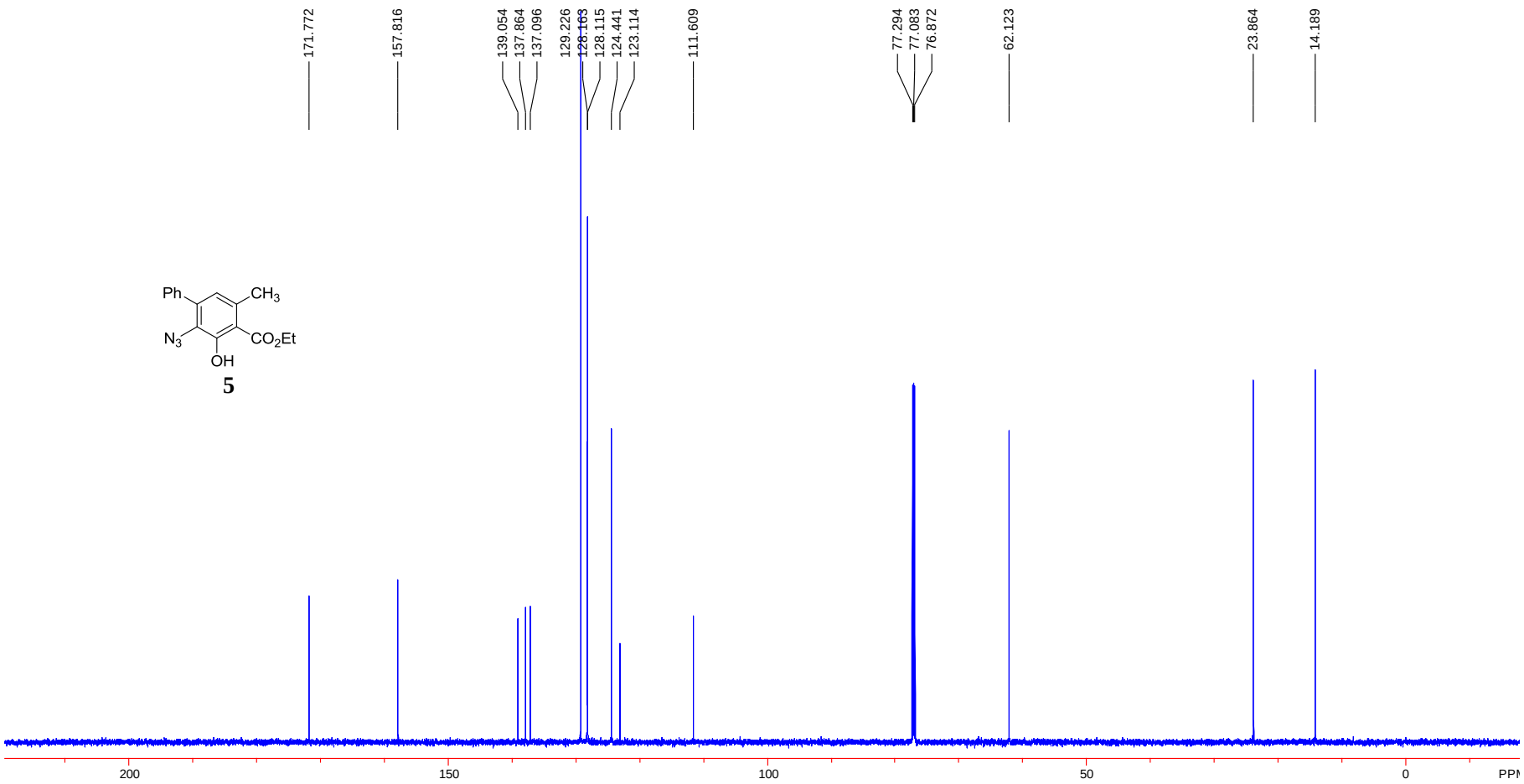
PPM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76.872
62.123
23.864
14.189
Ph
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OH
5
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150
100
50
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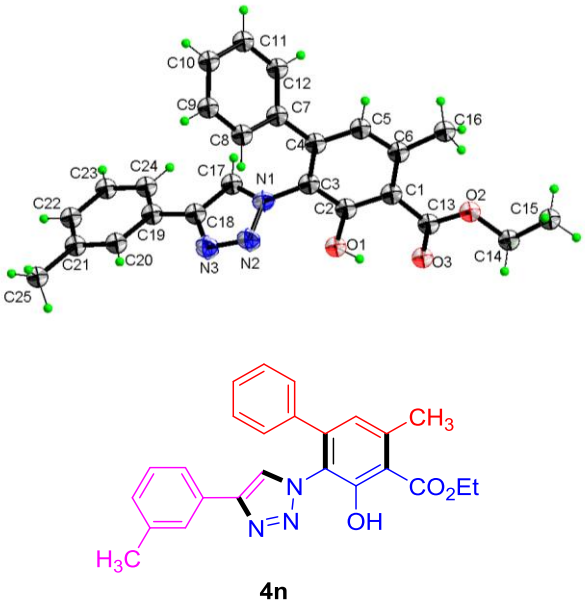
PPM

VII. X-ray crystal structure and data of 4n



Fiure 1 The X-ray crystal structure of of 4n

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a $CHCl_3$ solution of **4n**. Crystal data collection and refinement parameters of **4n** are summarized in Table 1. Intensity data were collected at 290 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. The crystallographic data (excluding structure factors) for **4n** has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1536564 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystallographic data and structure refinement results of **3g**

Empirical formula	$C_{25}H_{23}N_3O_3$
Formula weight	413.46
Temp, K	296 (2)
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	9.4549(11)
b, Å	10.7640 (12)
c, Å	21.279 (3)
α (°)	90
β (°)	98.778(2)
γ (°)	90
Volume, Å^3	2140.2(4)
Z	4
d_{calc}, g cm^{-3}	1.283
λ, Å	0.71073
μ, mm^{-1}	0.086
No. of data collected	11223
No. of unique data	3756
R_{int}	0.0507
Goodness-of-fit on F^2	1.004
R_1, wR_2 ($I > 2\sigma(I)$)	0.0498, 0.1102
R_1, wR_2 (all data)	0.1068, 0.1408

VIII. References

1 A. Sniady, M. S. Morreale and R. Dembinski, *Org. Synth*., 2007, **84**, 199.

2 W.-L. Wu, Z.-J. Yao, Y.-L. Li, J.-C. Li, Y. Xia and Y.-L. Wu, *J. Org. Chem*., 1995, **60**, 3257.

3 N. A. Petasis and K. A. Teets, *J. Am. Chem. Soc*., 1992, **114**, 10328.