

Supporting Online Material for

**Carboxylic Acids Promoted Cu(I)-catalyzed
azide-alkyne cycloaddition**

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Page 03-10: Materials and Methods.

Page 10-11: References.

Page 12-45: the ^1H NMR and ^{13}C NMR spectra for compounds **3a-3q**.

Page 46: The ^1H NMR comparison between **3a** and **3a-d₁**

List of ^1H NMR and ^{13}C NMR spectra for compounds 3a-3q.

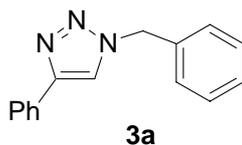
Page 12	^1H NMR of 3a	Page 13	^{13}C NMR of 3a
Page 14	^1H NMR of 3b	Page 15	^{13}C NMR of 3b
Page 16	^1H NMR of 3c	Page 17	^{13}C NMR of 3c
Page 18	^1H NMR of 3d	Page 19	^{13}C NMR of 3d
Page 20	^1H NMR of 3e	Page 21	^{13}C NMR of 3e
Page 22	^1H NMR of 3f	Page 23	^{13}C NMR of 3f
Page 24	^1H NMR of 3g	Page 25	^{13}C NMR of 3g
Page 26	^1H NMR of 3h	Page 27	^{13}C NMR of 3h
Page 28	^1H NMR of 3i	Page 29	^{13}C NMR of 3i
Page 30	^1H NMR of 3j	Page 31	^{13}C NMR of 3j
Page 32	^1H NMR of 3k	Page 33	^{13}C NMR of 3k
Page 34	^1H NMR of 3l	Page 35	^{13}C NMR of 3l
Page 36	^1H NMR of 3m	Page 37	^{13}C NMR of 3m
Page 38	^1H NMR of 3n	Page 39	^{13}C NMR of 3n
Page 40	^1H NMR of 3o	Page 41	^{13}C NMR of 3o
Page 42	^1H NMR of 3p	Page 43	^{13}C NMR of 3p
Page 44	^1H NMR of 3q	Page 45	^{13}C NMR of 3q

Materials and Methods

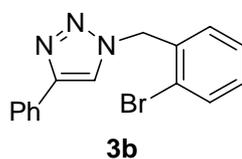
General Method: All melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer. The ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a JEOL JNM-ECA 300 spectrometer in CDCl_3 with TMS as internal reference. The J values are given in Hz. MS were recorded on a VG-ZAB-MS spectrometer with 70 eV. Elementary analysis data were obtained on a Perkin-Elmer-241C apparatus.

A typical benzoic acid promoted CuAAC procedure for the preparation of 1-benzyl-4-phenyl-1*H*-[1,2,3]triazole (3a): To a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5.0 mg, 0.02 mmol), sodium ascorbate (7.9 mg, 0.04 mmol) and PhCO_2H (24.4 mg, 0.2 mmol) in $t\text{-BuOH}/\text{H}_2\text{O}$ (1:2 by v/v, 2.0 mL) was added a mixture of phenylethyne (**1a**, 204 mg, 2 mmol) and benzyl azide (**2a**, 280 mg, 2.1 mmol) at room temperature. The resultant mixture was stirred continuously until the reaction system solidified completely (*ca.* 4 min). Then CH_2Cl_2 (20 mL) was added to dissolve the crude product. The organic layer was washed with H_2O and brine, and dried over anhydrous Na_2SO_4 . Removal of the solvent yielded a residue, which was purified by a short chromatography (silica gel, EtOAc:PE = 1:3) to give **3a** (461 mg, 98%) as an off-white solid.

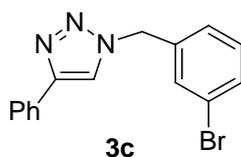
The similar procedure was used in the preparation of products **3b~3q**.



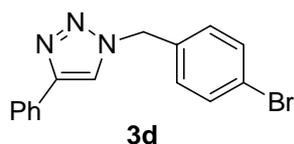
1-Benzyl-4-phenyl-1H-1,2,3-triazole (3a):¹ White solid, mp: 130-132 °C (PE-EtOAc) (lit.¹ mp: 129-129.5 °C). ¹H NMR: δ 7.85-7.78 (m, 2H), 7.65 (s, 1H), 7.40-7.21 (m, 8H), 5.54 (s, 2H). ¹³C NMR: δ 148.1, 134.7, 130.5, 129.0 (2C), 128.7 (2C), 128.6, 128.1, 128.0 (2C), 125.6 (2C), 119.5, 54.1.



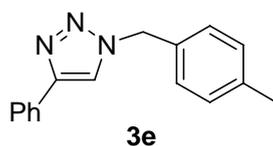
1-(2-Bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3b):² White solid, mp: 102-103 °C (PE-EtOAc) (lit.² mp: 105-106 °C). ¹H NMR: δ 7.85-7.78 (m, 3H), 7.62-7.58 (m, 1H), 7.42-7.06 (m, 6H), 5.66 (s, 2H); ¹³C NMR: δ 147.9, 134.1, 133.0, 130.4, 130.2, 130.1, 128.7 (2C), 128.1, 128.0, 125.6 (2C), 123.0, 119.8, 53.7.



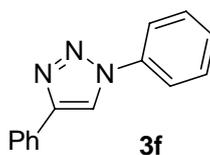
1-(3-Bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3c):² White solid, mp: 93-94 °C (PE-EtOAc) (lit.² 94-95 °C). ¹H NMR: δ 7.81-7.77 (m, 2H), 7.72 (s, 1H), 7.44-7.16 (m, 6H), 5.50 (s, 2H); ¹³C NMR: δ 148.2, 136.8, 131.8, 130.8, 130.6, 130.3, 128.7 (2C), 128.2, 126.4, 125.6 (2C), 122.9, 119.6, 53.3.



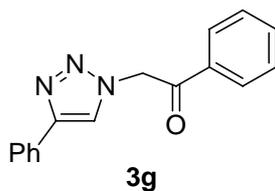
1-(4-Bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3d):¹ White solid, mp: 150-152 °C (PE-EtOAc) (lit.¹ mp: 152-152.5 °C). ¹H NMR: δ 7.80-7.77 (m, 2H), 7.68 (s, 1H), 7.51-7.46 (m, 2H), 7.43-7.29 (m, 3H), 7.16-7.13 (m, 2H), 5.48 (s, 2H). ¹³C NMR: δ 148.2, 133.7, 132.2 (2C), 130.3, 129.5 (2C), 128.8 (2C), 128.2 (2C), 125.6 (2C), 122.8, 119.5, 53.4.



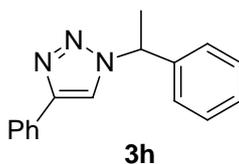
1-[4-Methylbenzyl]-4-phenyl-1H-1,2,3-triazole (3e):² White solid, mp: 93-94 °C (PE-EtOAc) (lit.² 95-97 °C). ¹H NMR: 7.79-7.76 (m, 2H), 7.63 (s, 1H), 7.38-7.25 (m, 3H), 7.20-7.16 (m, 4H), 5.47 (s, 2H), 2.32 (s, 3H); ¹³C NMR: 147.9, 138.5, 131.6, 130.5, 129.6 (2C), 128.6 (2C), 128.0 (3C), 125.5 (2C), 119.4, 53.7, 21.0.



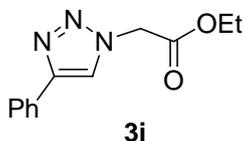
1,4-Diphenyl-1H-1,2,3-triazole (3f):³ Yellowish solid, mp: 183-184 °C (PE-DCM) (lit.³ mp: 184-186 °C). ¹H NMR: δ 8.80 (s, 1H), 7.94-7.90 (m, 2H), 7.81-7.78 (m, 2H), 7.60-7.26 (m, 6H). ¹³C NMR (DMSO-*d*₆): δ 147.3, 136.6, 130.3, 130.0 (2C), 129.0 (2C), 128.7, 128.2, 125.3 (2C), 120.0 (2C), 119.6.



1-Phenacyl-4-phenyl-1H-1,2,3-triazole (3g):⁴ Yellow solid, mp: 166-167 °C (PE-DCM) (lit.⁴ mp: 172-175 °C). ¹H NMR (DMSO-*d*₆): δ 8.54 (s, 1H), 8.13-8.10 (m, 2H), 7.91-7.88 (m, 2H), 7.75-7.70 (m, 1H), 7.65-7.60 (m, 2H), 7.50-7.45 (m, 2H), 7.39-7.32 (m, 1H), 6.28 (s, 2H). ¹³C NMR (DMSO-*d*₆): δ 192.2, 146.3, 134.3, 134.1, 130.9, 129.0 (2C), 128.9 (2C), 128.2 (2C), 127.9, 125.2 (2C), 123.1, 56.0.

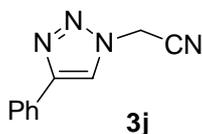


4-Phenyl-1-(1-phenylethyl)-1H-1,2,3-triazole (3h):⁵ White solid, mp: 80-81 °C (PE-EtOAc). ¹H NMR: δ 7.78-7.80 (m, 2H), 7.68 (s, 1H), 7.27-7.34 (m, 8H), 5.79 (q, *J* = 6.9 Hz, 1H), 1.95 (d, *J* = 7.2 Hz, 3H); ¹³C NMR: δ 147.4, 139.8, 130.5, 128.8(2C), 128.6(2C), 128.3, 127.8, 126.3(2C), 125.4(2C), 118.4, 60.0, 21.1.

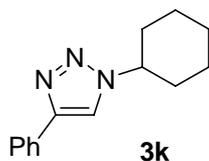


Ethyl 2-(4-phenyl-1H-1,2,3-triazol-1-yl)acetate (3i):⁶ White solid, mp: 93-95 °C (PE-EtOAc) (lit.⁶ mp: 94-95 °C). ¹H NMR: δ 7.95 (s, 1H), 7.82-7.79 (m, 2H), 7.40-7.35 (m, 2H), 7.31-7.28 (m, 1H), 5.14 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ¹³C NMR: δ 166.1, 147.6, 130.1, 128.5 (2C), 127.8, 125.4 (2C), 121.1, 62.0, 50.5,

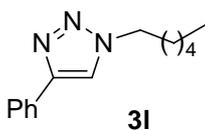
13.7.



2-(4-Phenyl-1H-1,2,3-triazol-1-yl)acetonitrile (3j):^{7,8} White solid, mp: 98-99 °C (PE-EtOAc) (lit.⁷ mp: 69-71 °C). ¹H NMR: δ 7.99 (s, 1H), 7.81-7.79 (m, 2H), 7.42-7.38 (m, 3H), 5.38 (s, 2H); ¹³C NMR: δ 148.9, 129.4, 128.9 (2C), 128.8, 125.8 (2C), 120.0, 112.7, 37.5.

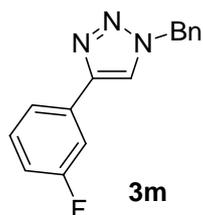


1-Cyclohexyl-4-phenyl-1H-1,2,3-triazole (3k):⁶ White solid, mp: 109-111 °C (PE-EtOAc) (lit.⁶ mp: 105.8-110 °C). ¹H NMR: δ 7.85-7.81 (m, 3H), 7.40-7.27 (m, 2H), 7.33-7.24 (m, 1H), 4.42-4.37 (m, 1H), 2.21-2.11 (m, 2H), 1.84-1.65 (m, 5H), 1.43-1.25 (m, 3H); ¹³C NMR: δ 146.8, 130.7, 128.4 (2C), 127.6, 125.3 (2C), 117.3, 59.8, 33.2 (2C), 24.8 (2C), 24.7.

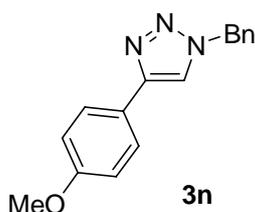


1-Hexyl-4-phenyl-1H-1,2,3-triazole (3l):⁹ White solid, mp: 67-68 °C (PE-EtOAc) (lit.^{9a} mp: 77-79 °C). ¹H NMR: δ 7.84-7.81 (m, 2H), 7.75 (s, 1H), 7.43-7.38 (m, 2H),

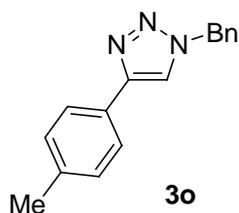
7.33-7.27 (m, 1H), 4.36 (t, $J = 5.5$ Hz, 2H), 1.94-1.89 (m, 2H), 1.31 (m, 6H), 0.90-0.85 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR: δ 147.6, 130.7, 128.7 (2C), 127.9, 125.6 (2C), 119.4, 50.3, 31.1, 30.2, 26.1, 22.3, 13.8.



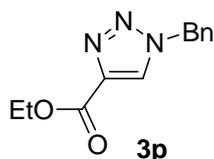
1-Benzyl-4-(3-fluorophenyl)-1H-1,2,3-triazole (3m): Yellowish solid, mp: 109-110 °C (PE-EtOAc). IR (KBr): ν 3090, 1584, 1461, 1223, 1165, 864 cm^{-1} . ^1H NMR: δ 7.70 (s, 1H), 7.53-7.50 (m, 2H), 7.40-7.22 (m, 6H), 7.01-6.92 (m, 1H), 5.54 (s, 2H). ^{13}C NMR: δ 163.0 ($J = 243.0$ Hz), 147.0, 134.4, 132.6 ($J = 8.6$ Hz), 130.3 ($J = 7.9$ Hz), 129.1 (2C), 128.7, 128.0 (2C), 121.2 ($J = 2.9$ Hz), 119.9, 114.8 ($J = 20.8$ Hz), 112.5 ($J = 23.0$ Hz), 54.1. HRMS Calcd. For $\text{C}_{15}\text{H}_{12}\text{FN}_3$: 253.1015. Found: 253.1021.



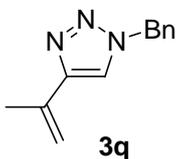
1-Benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (3n):³ White solid, mp: 141-142 °C (PE-EtOAc) (lit.³ mp: 143-144 °C). ^1H NMR: δ 7.72-7.69 (m, 2H), 7.59-7.57 (m, 1H), 7.34-7.20 (m, 5H), 6.91-6.89 (m, 2H), 5.50 (s, 2H), 3.78 (s, 3H); ^{13}C NMR: δ 159.4, 147.9, 134.7, 128.9 (2C), 128.5, 127.9 (2C), 126.8 (2C), 123.2, 118.7, 114.1 (2C), 55.1, 53.9.



1-Benzyl-4-p-tolyl-1H-1,2,3-triazole (3o):¹⁰ White solid, mp: 150-152 °C (PE-EtOAc) (lit.¹⁰ mp: 155-157 °C). ¹H NMR: δ 7.68-7.62 (m, 3H), 7.40-7.12 (m, 7H), 5.50 (s, 2H), 2.33 (s, 3H); ¹³C NMR: δ 148.1, 137.8, 134.7, 129.3 (2C), 128.9 (2C), 128.5, 127.9 (2C), 127.6, 125.4 (2C), 119.2, 53.9, 21.1.



Ethyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (3p):³ Yellowish solid, mp: 80-81 °C (PE-EtOAc) (lit.³ mp: 83-85 °C). ¹H NMR: δ 8.12 (s, 1H), 7.40-7.25 (m, 5H), 5.60 (s, 2H), 4.37 (q, $J = 7.2$ Hz, 2H), 1.35 (t, $J = 7.2$ Hz, 3H). ¹³C NMR: δ 160.2, 140.0, 133.7, 128.8 (2C), 128.5, 127.8 (2C), 127.2, 60.8, 53.9, 13.9.



1-Benzyl-4-(prop-1-en-2-yl)-1H-1,2,3-triazole (3q):¹¹ White solid. mp: 90-92 °C (PE/EtOAc) (lit.^{11b} mp: 95-96 °C). ¹H NMR: δ 7.41-7.24 (m, 6H), 5.68 (s, 1H), 5.51 (s, 2H), 5.08-5.07 (m, 1H), 2.10 (s, 3H); ¹³C NMR: δ 149.2, 134.7, 133.5, 129.0 (2C),

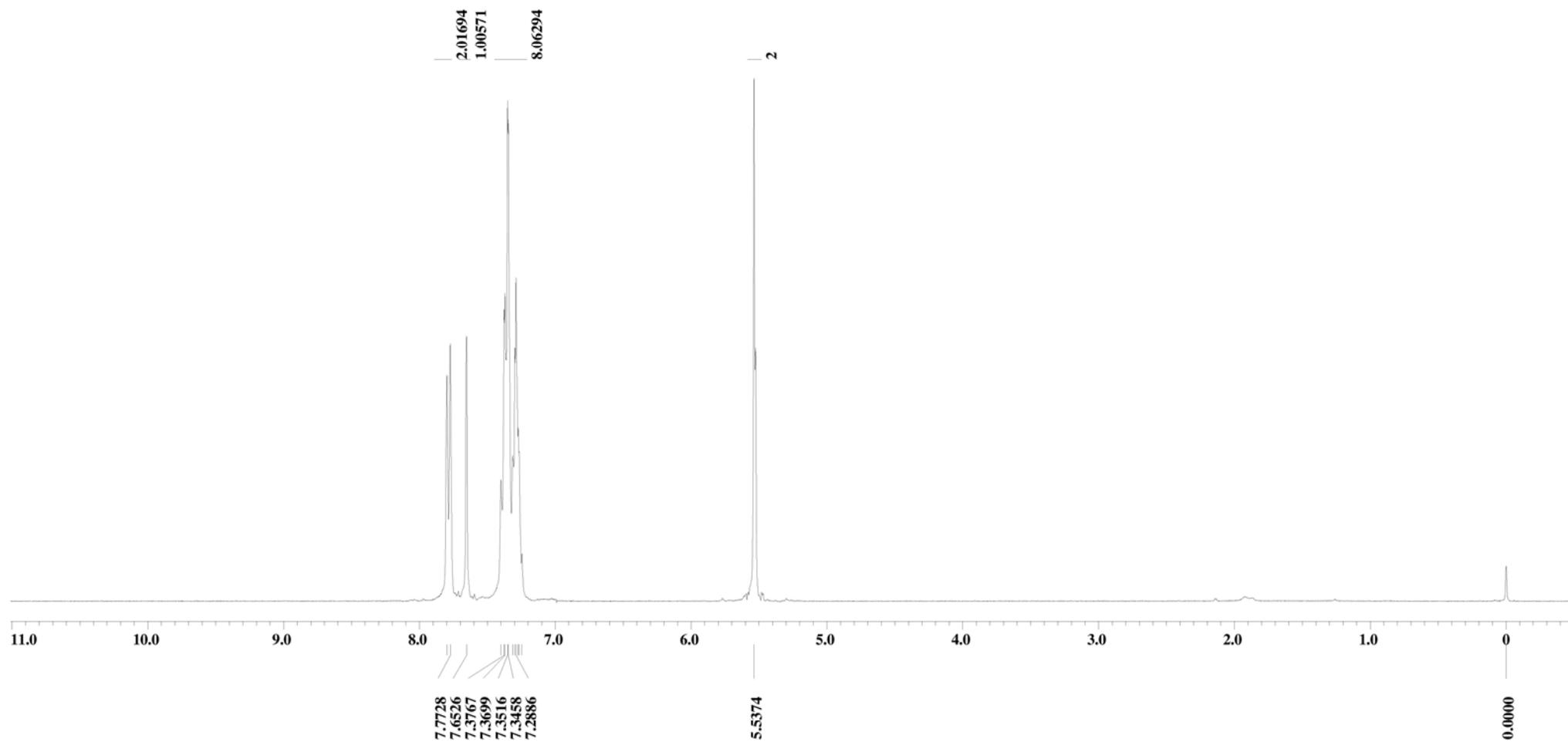
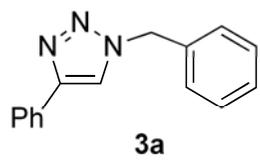
128.6, 127.9 (2C), 119.4, 112.4, 54.0, 20.5.

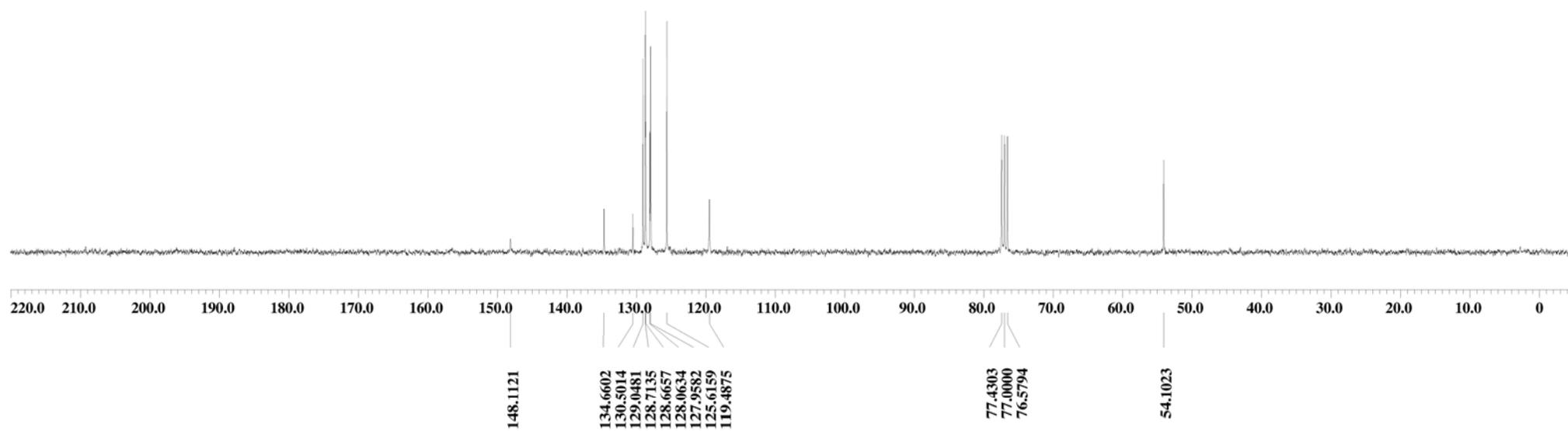
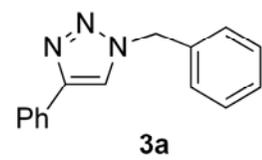
A deuterium labeling CuAAC for the preparation of 1-benzyl-4-phenyl-5-D-1H-[1,2,3]triazole (3a-d₁): To a mixture of PhC≡CCu (164 mg, 1 mmol) and BnN₃ (146 mg, 1.1 mmol) in C₆H₁₂ (5 mL) was added DOAc (98 atom% D, 57.6 μL, 1.0 mmol) at room temperature. The resultant mixture was stirred continuously until the yellow solid was completely converted into white solid (*ca.* 5 min). Then CH₂Cl₂ (20 mL) was added to dissolve the crude product. The organic layer was washed with H₂O and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent yielded a residue, which was purified by a short chromatography (silica gel, EtOAc:PE = 1:3) to give **3a-d₁** (232 mg, 98%, 97% D) as an off-white solid.

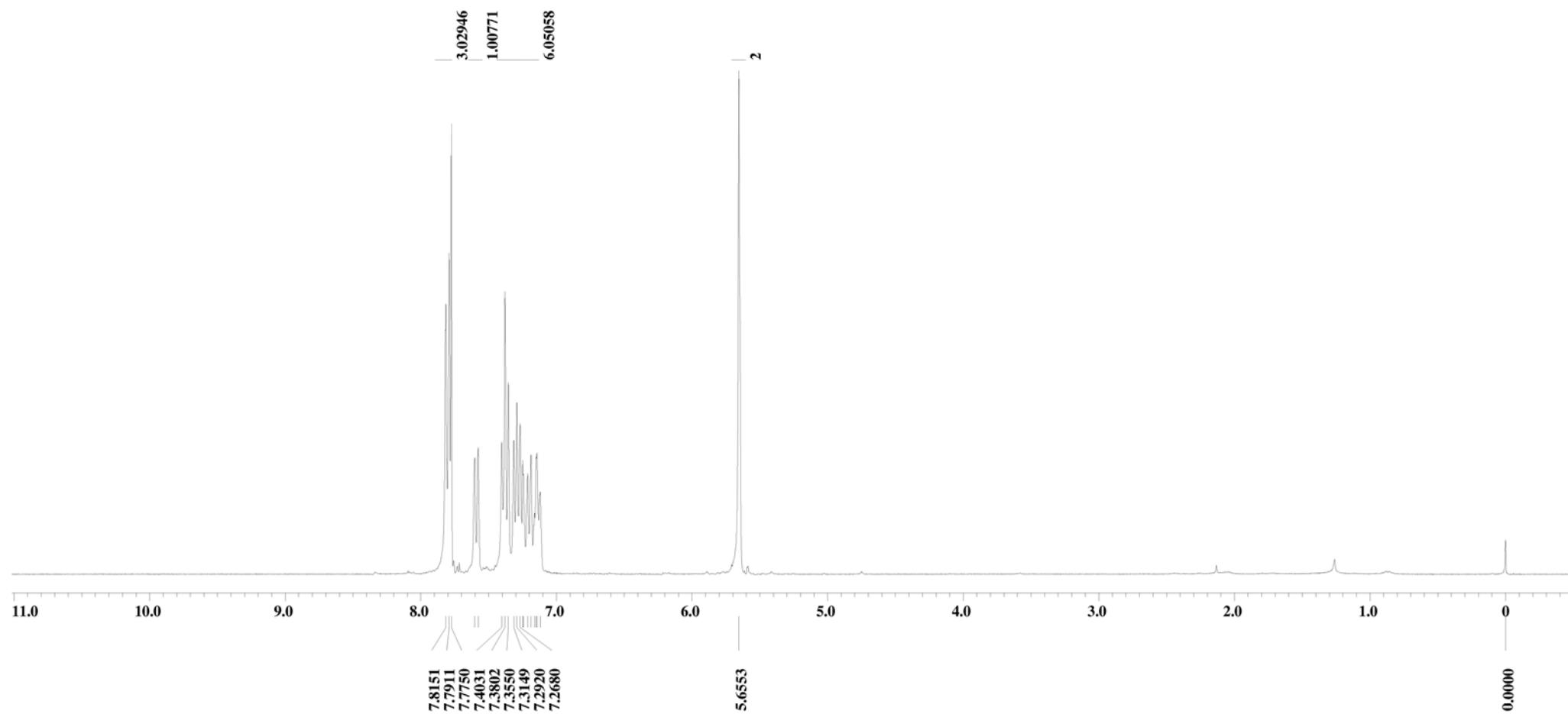
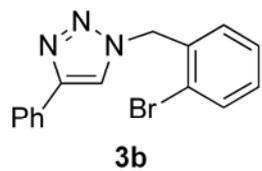
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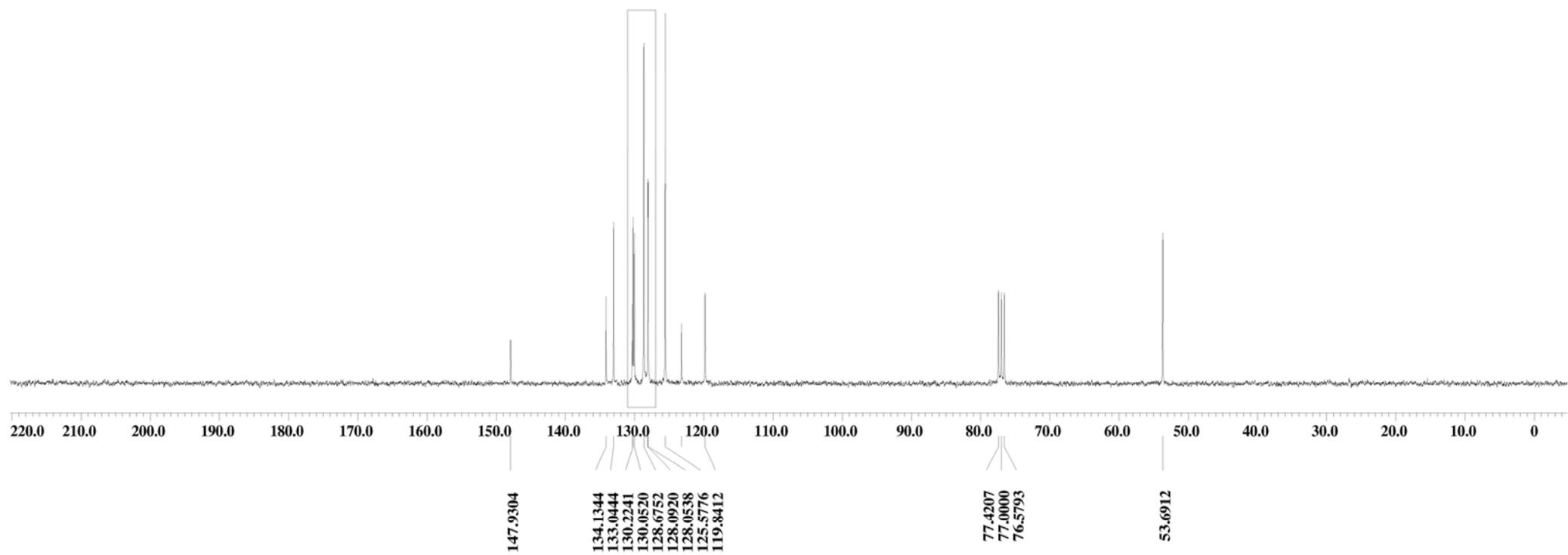
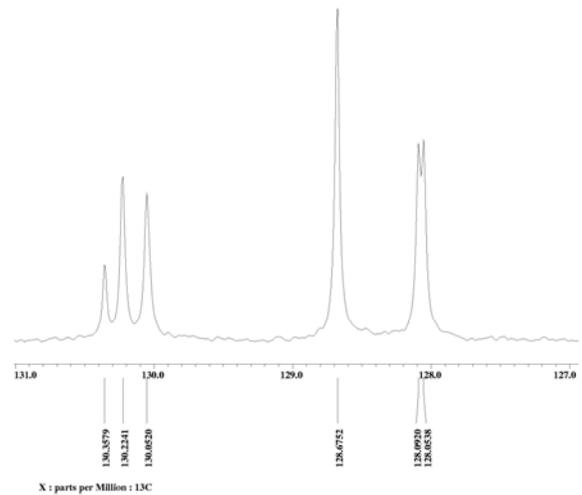
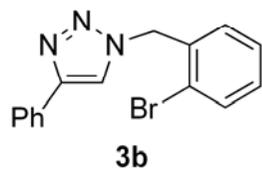
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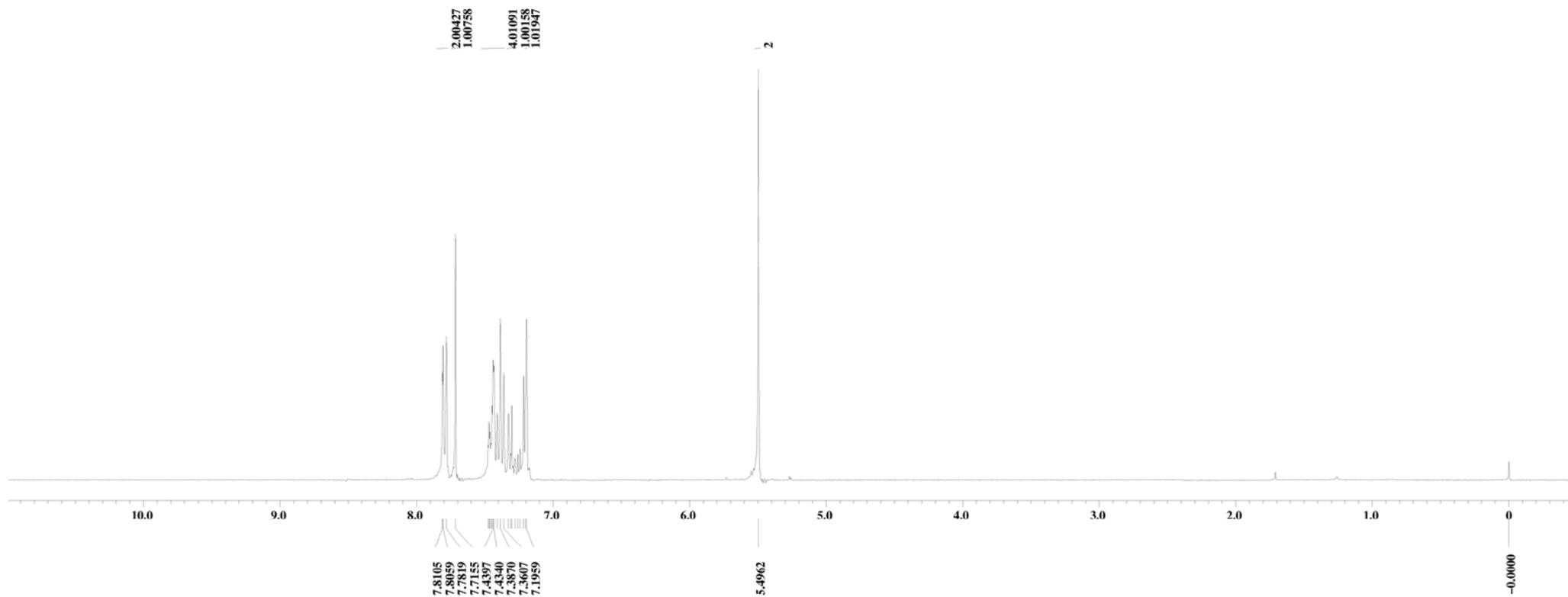
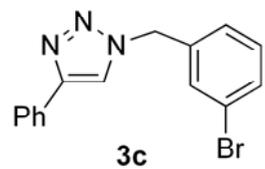
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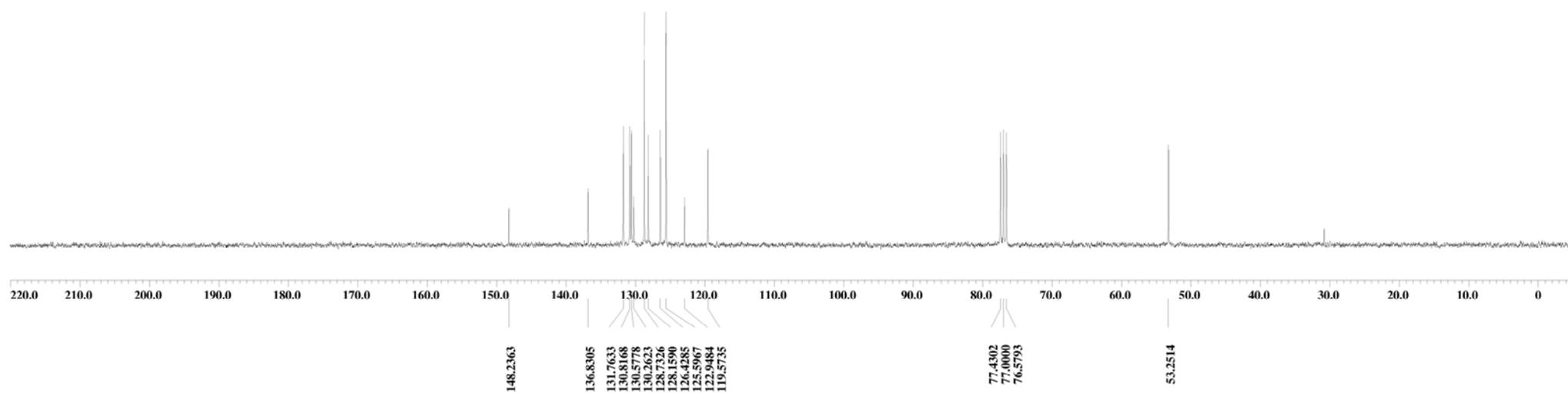
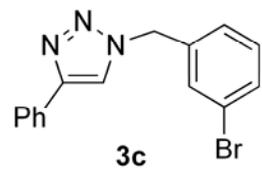




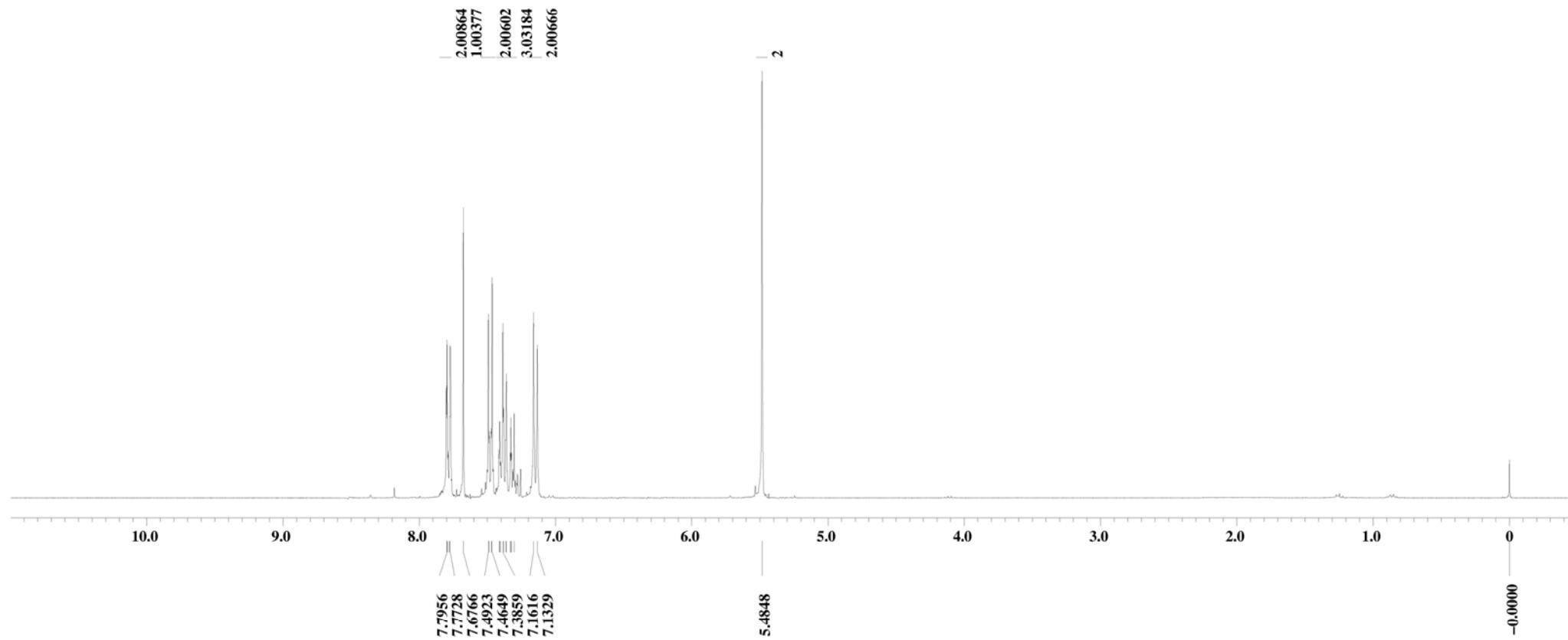
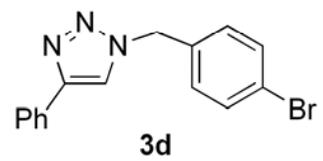


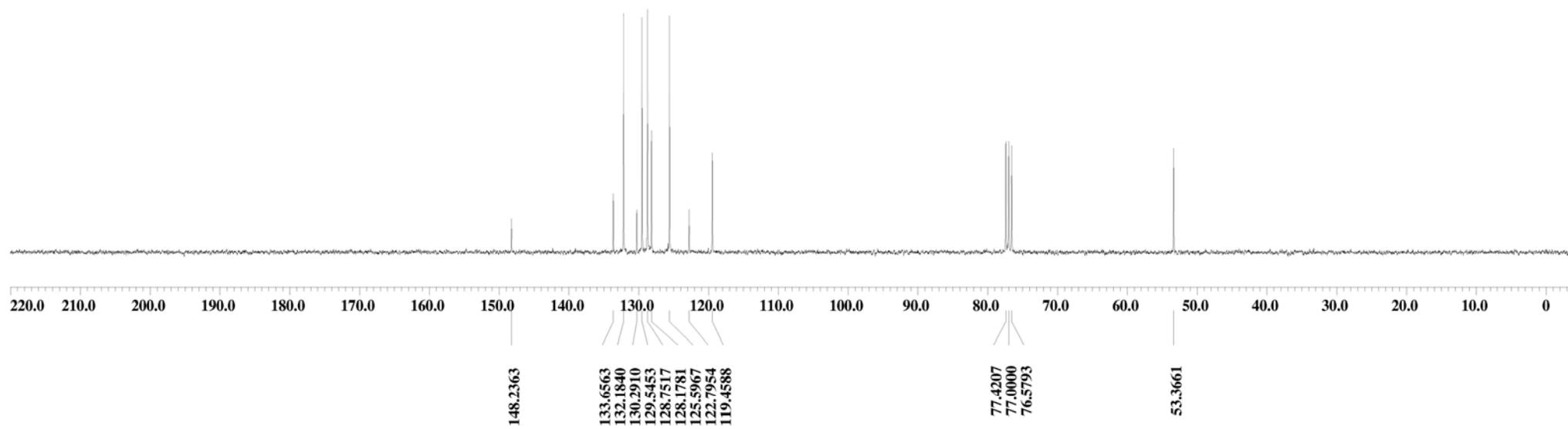
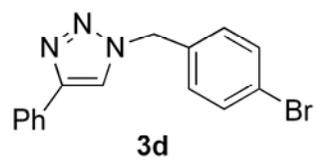


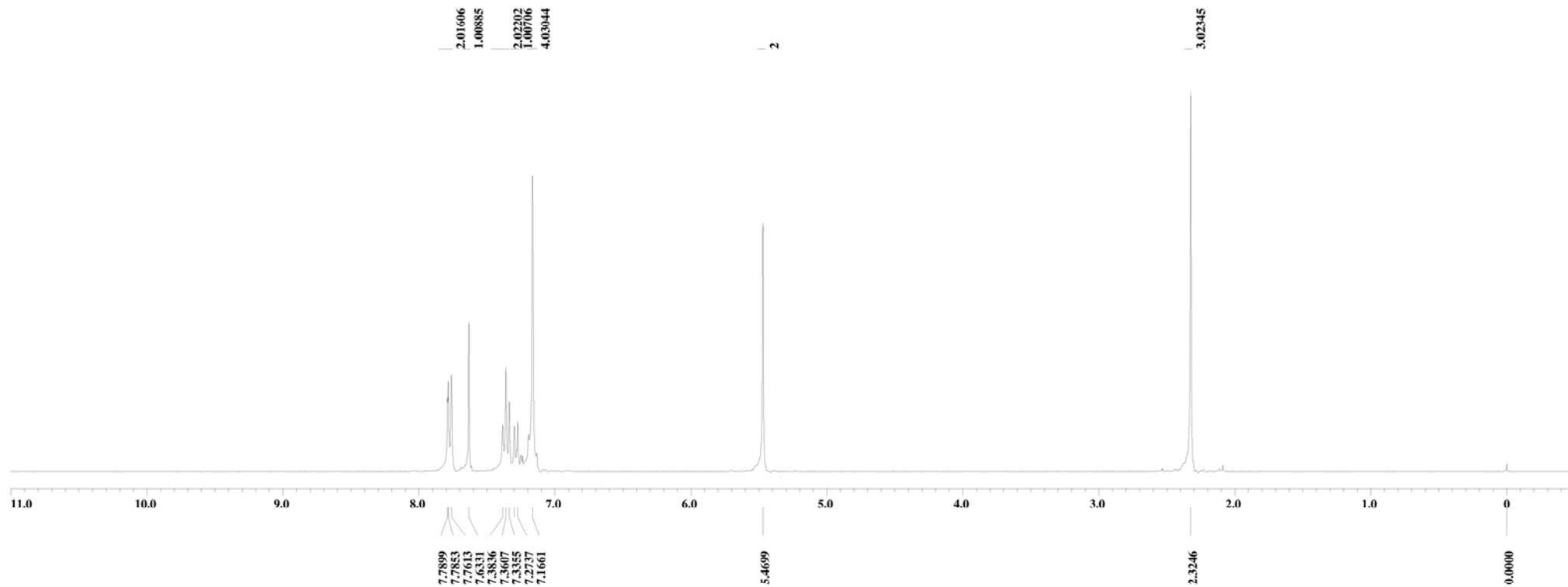
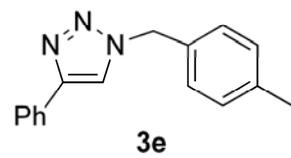
X : parts per Million : 1H



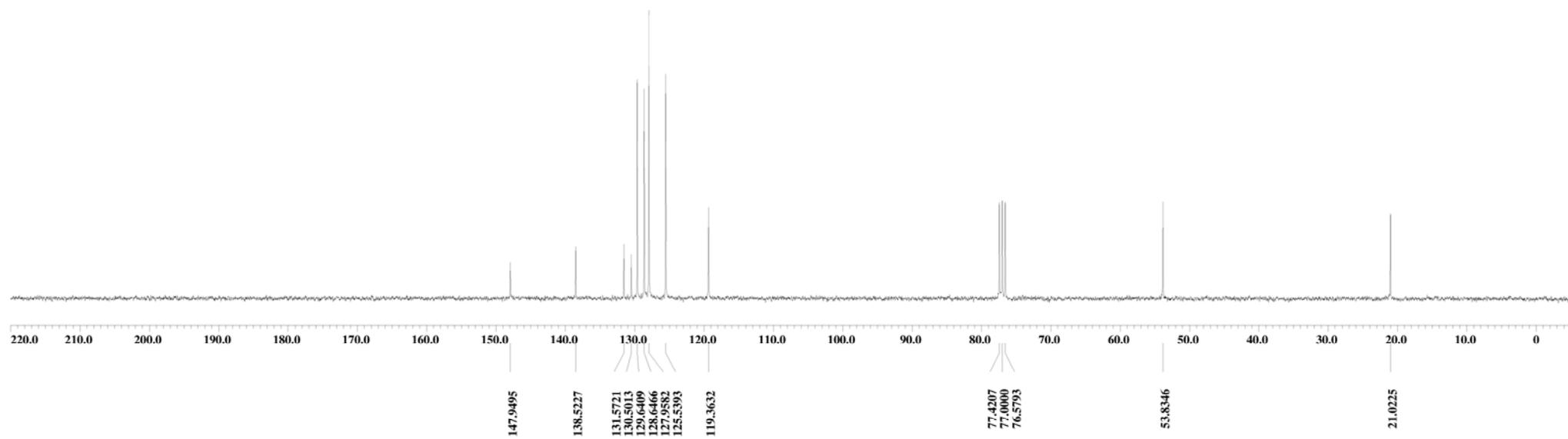
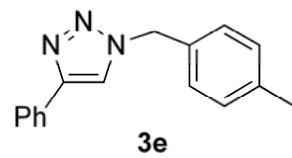
X : parts per Million : 13C

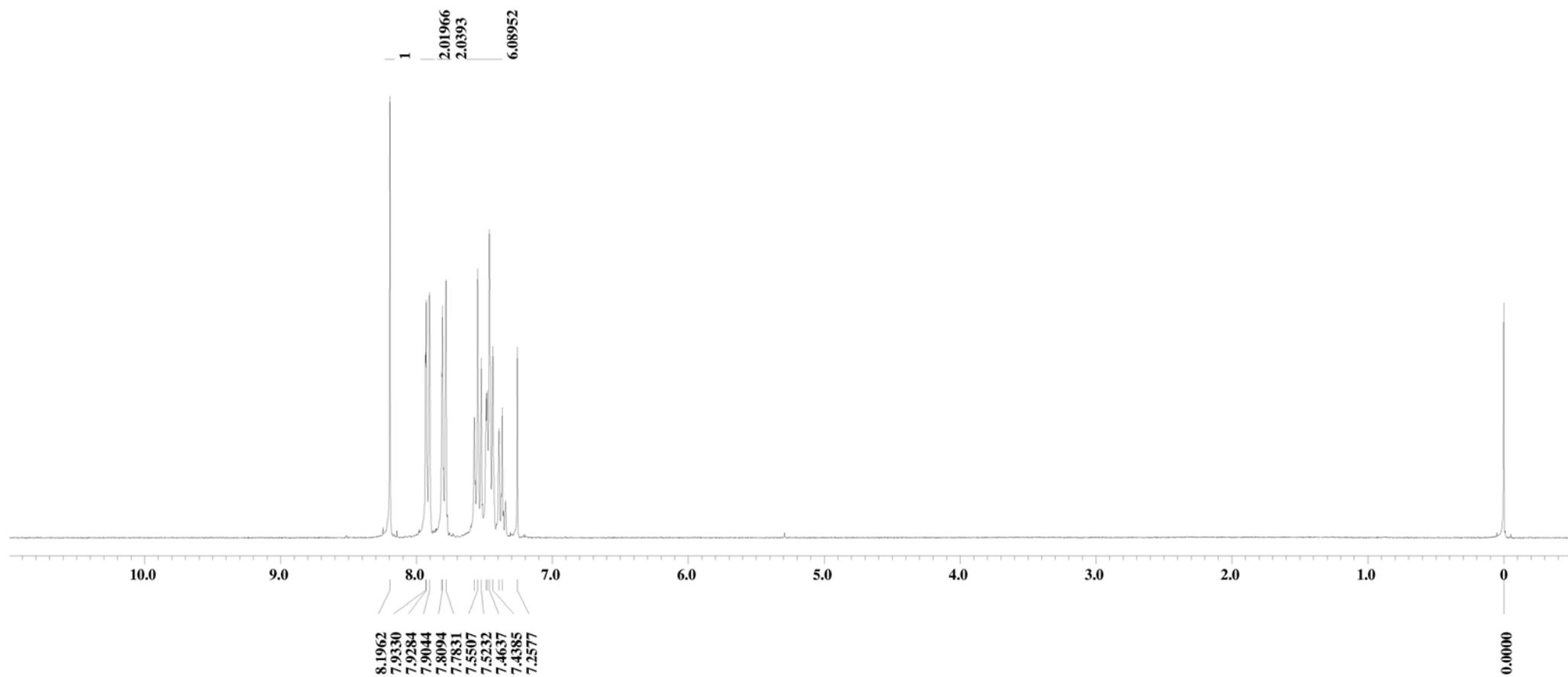
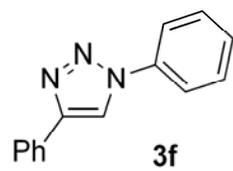


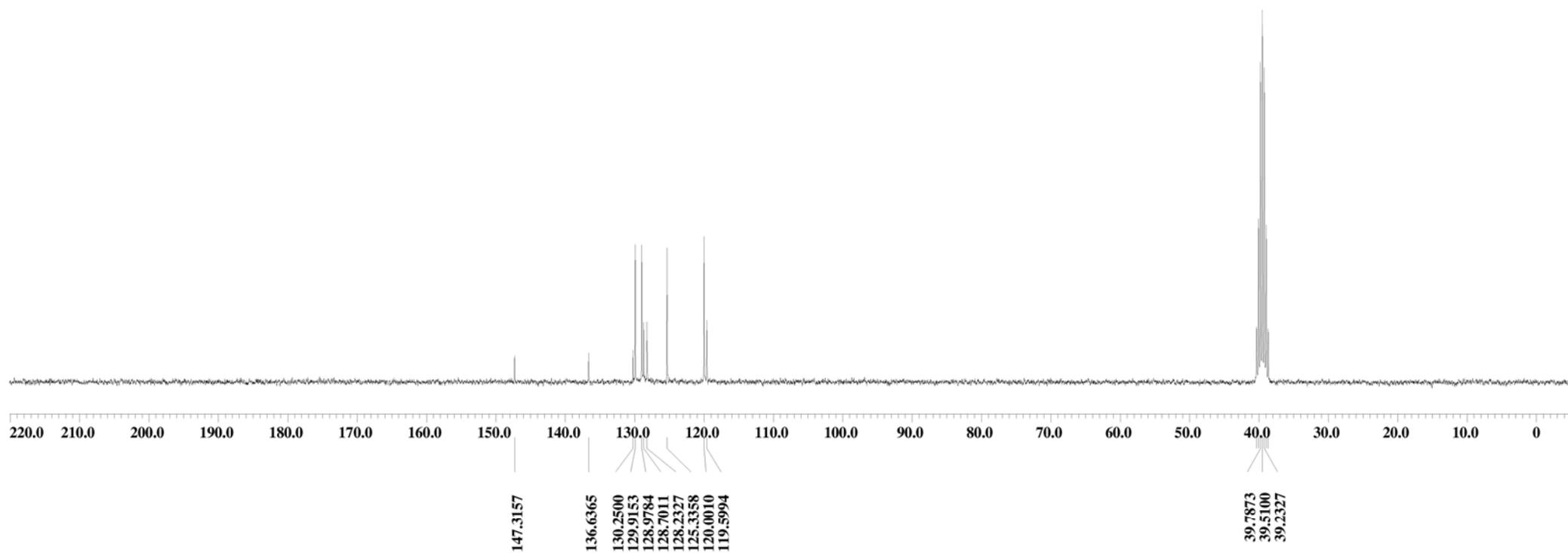
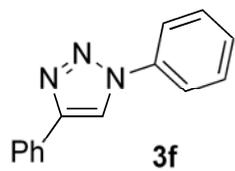


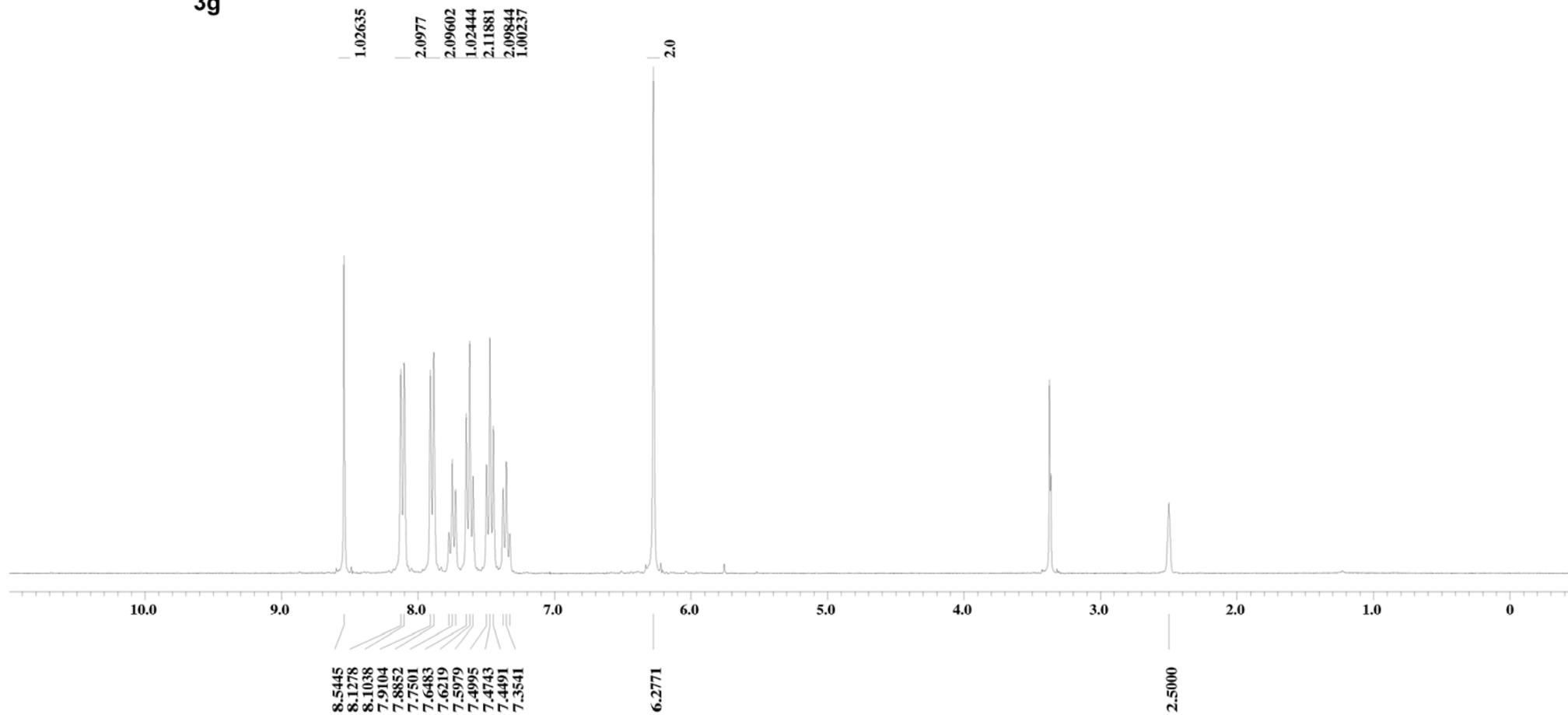
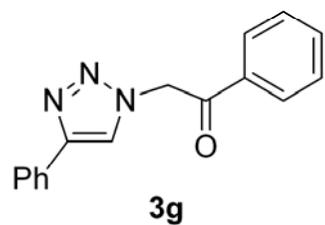


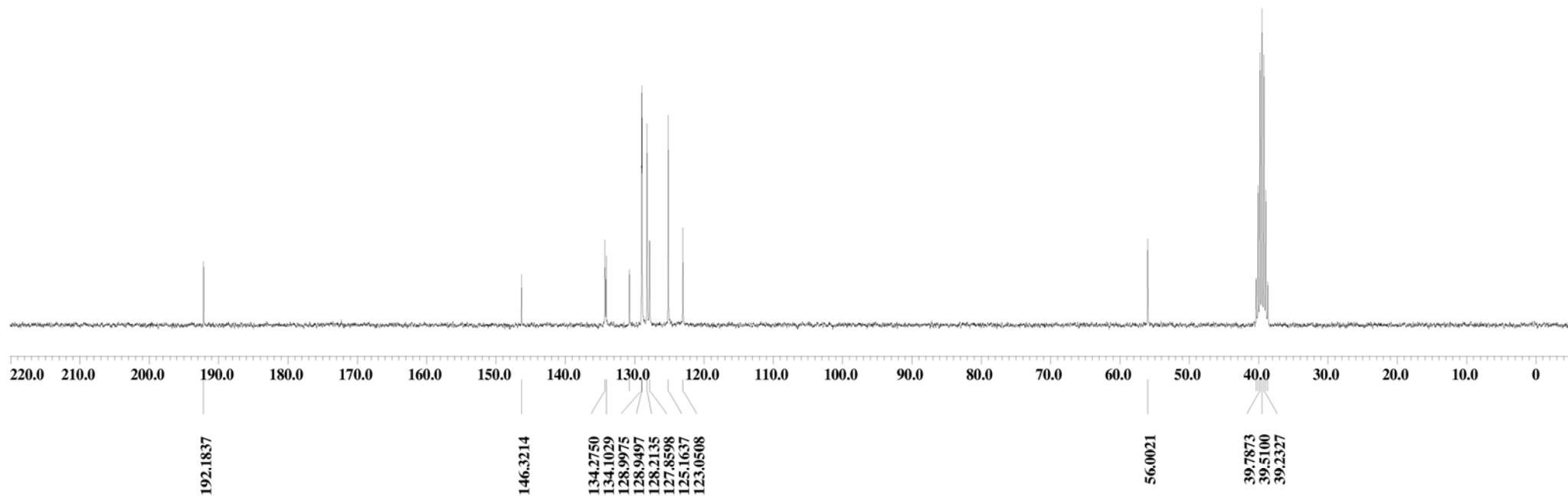
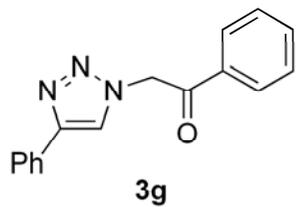
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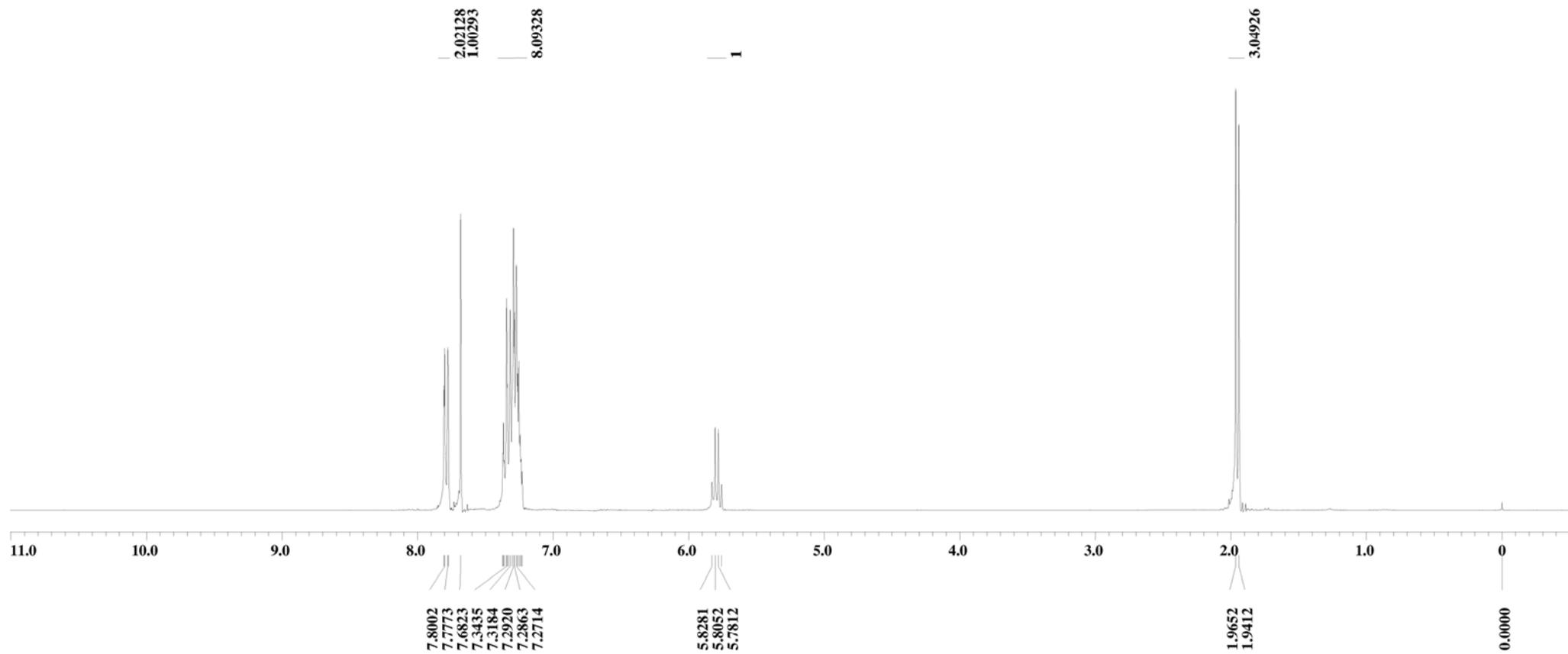
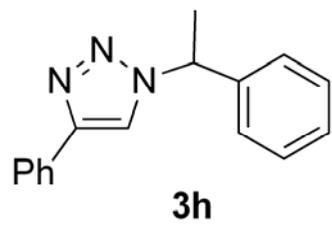


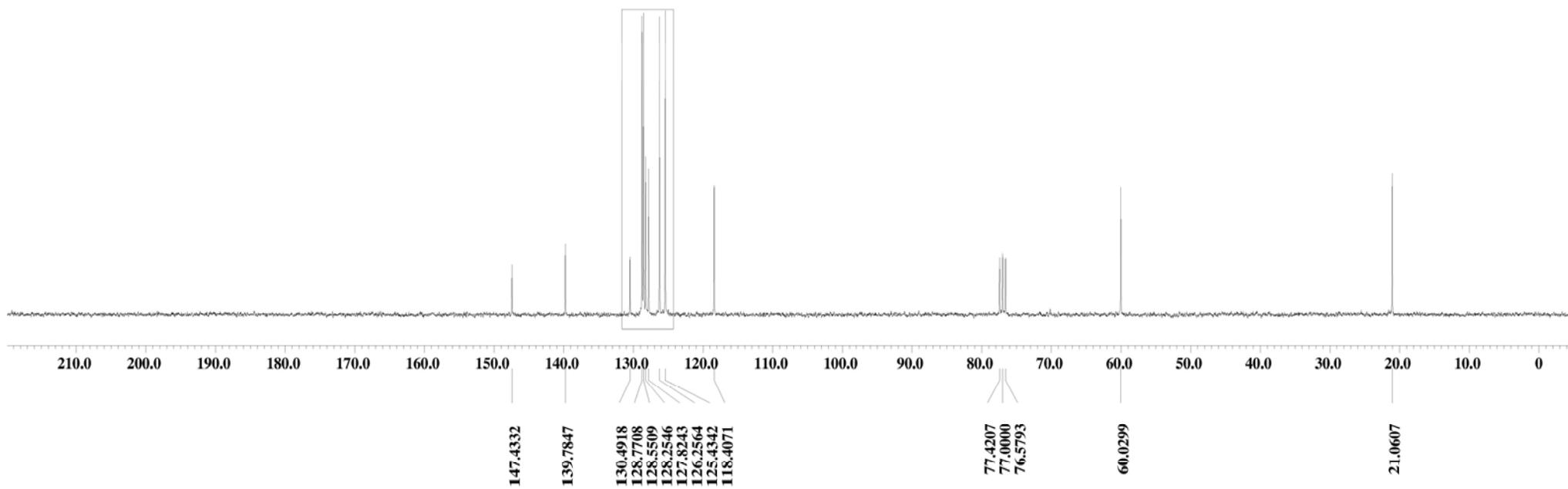
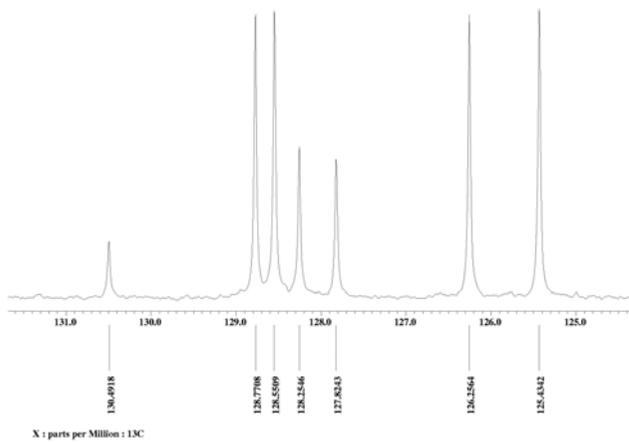
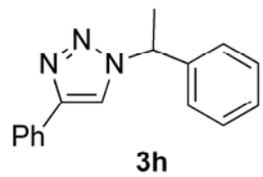


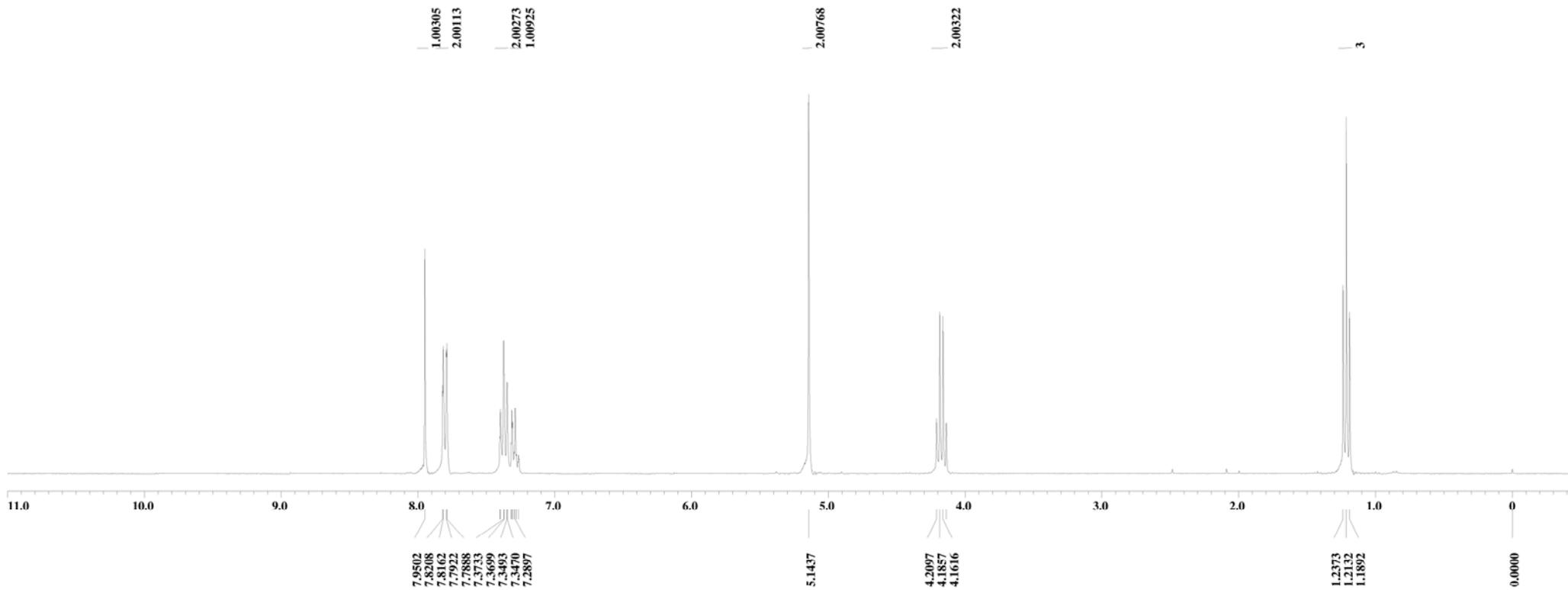
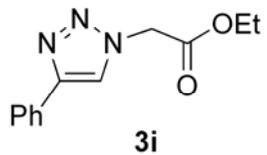




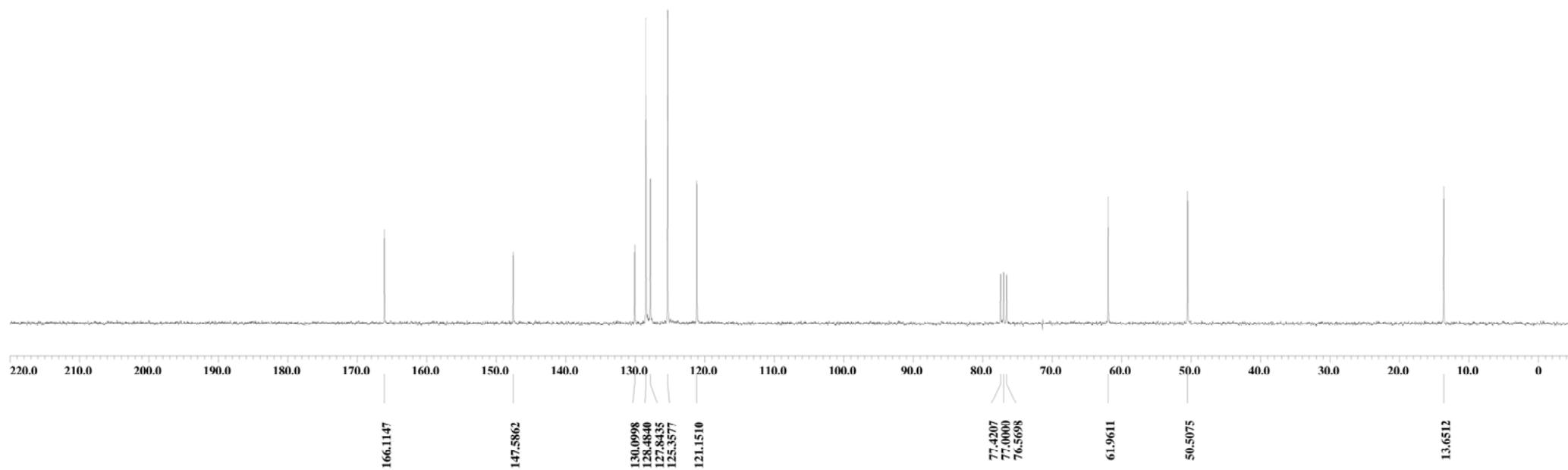
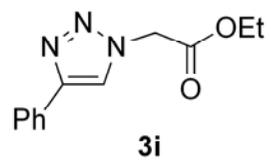




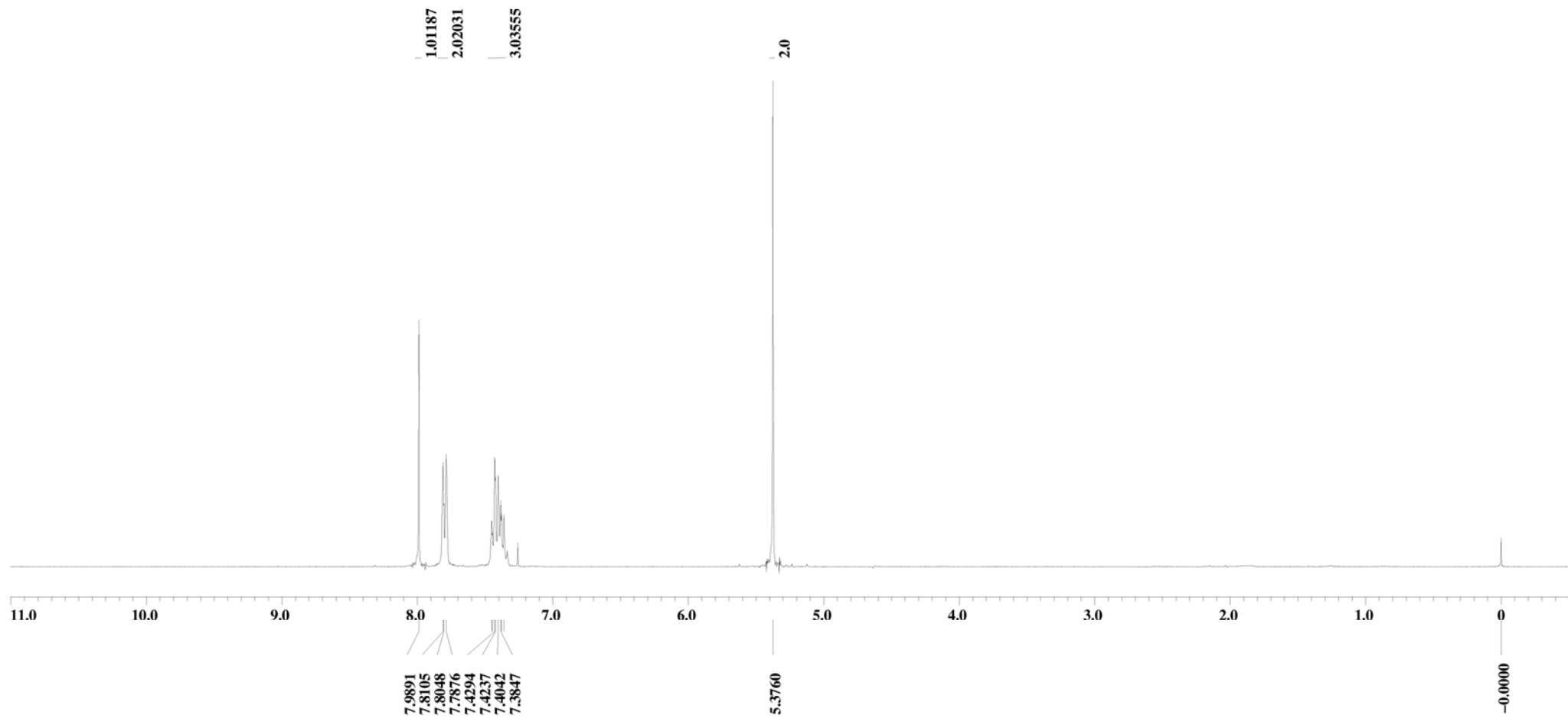
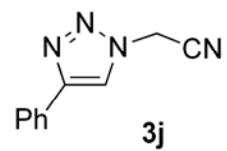


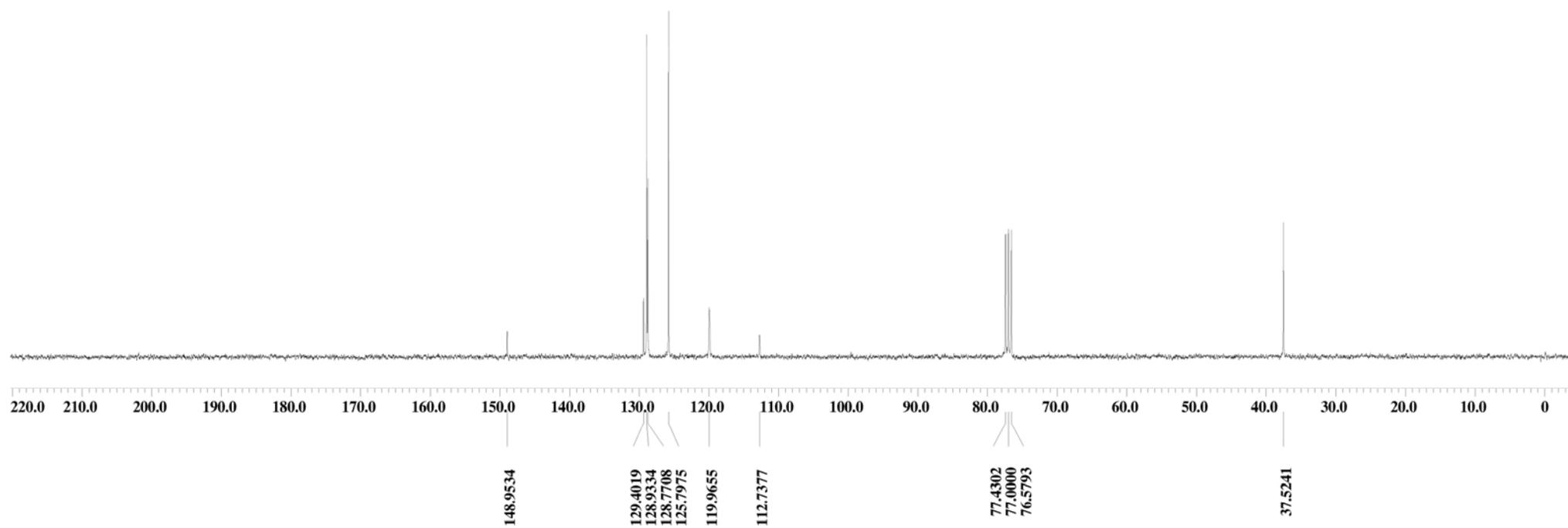
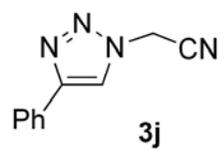


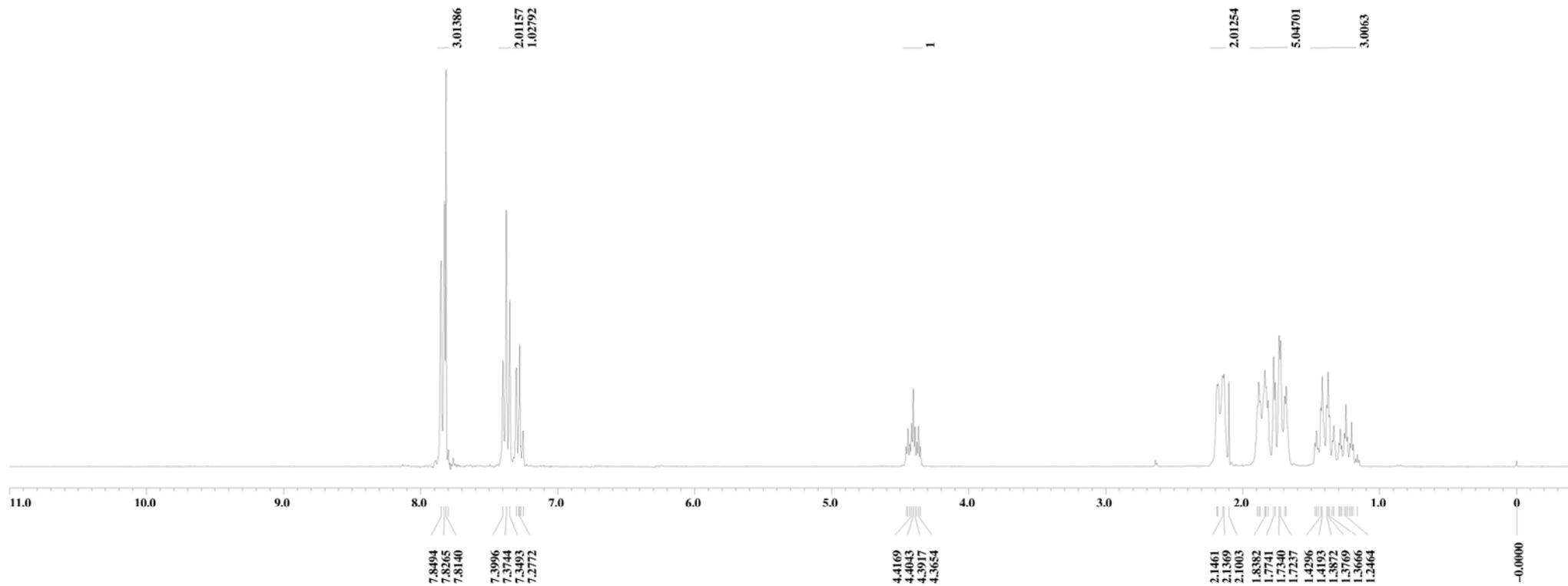
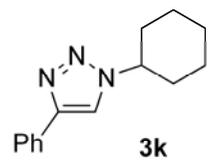
X : parts per Million : 1H



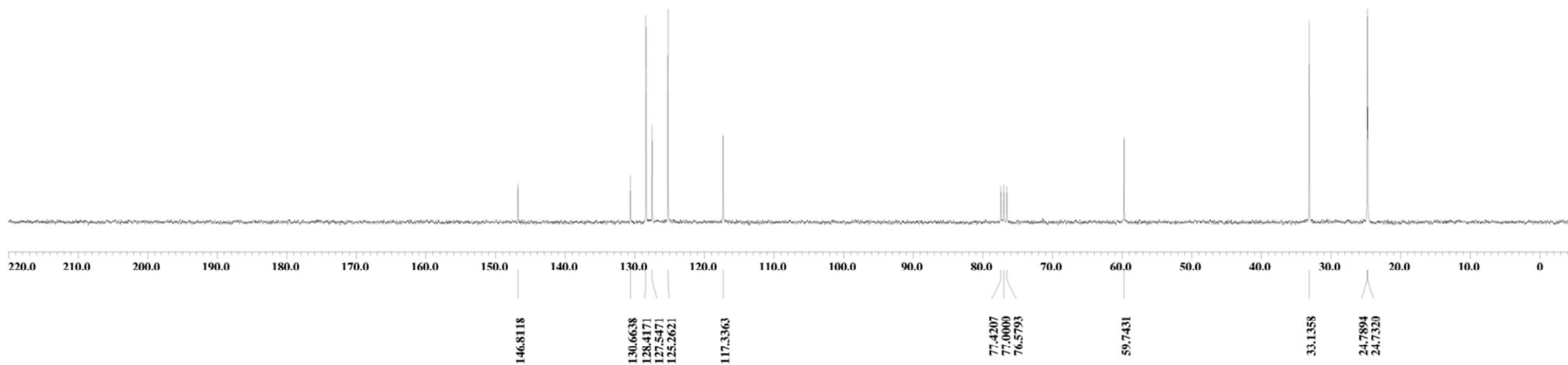
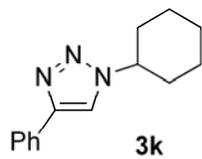
X : parts per Million : 13C







X : parts per Million : 1H



X : parts per Million : 13C

