Supporting Information for:

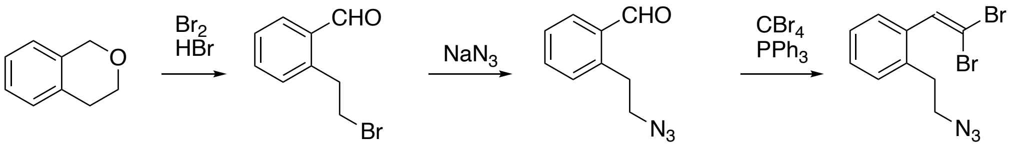
Facile preparation of polycyclic halogen-substituted 1,2,3-triazoles by using intramolecular Huisgen cycloaddition

Kazuki Kobayashi, Nozomi Kasakura, Seiya Kikukawa, Shota Matsumoto, Satoru Karasawa, and Takeshi Hata*

Department of Life Science and Technology, School of Life Science and Technology, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8501, Japan

General. ^{1}H, ^{13}C NMR spectra were taken on an Agilent 400-MR and JEOL JNM-ECZL400S spectrometers at 400 and 100 MHz, respectively. ^{19}F NMR spectra were taken on a JEOL JNM-ECZL400S spectrometer at 282 MHz. $CDCl_3$ was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^{1}H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C), or based on C_6F_6 (δ −164.9 ppm for ^{19}F) as internal standards, respectively. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in Hertz. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer and are reported in wave numbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on Bruker micrOTOF II by positive electrospray ionization (ESI) method calibrated with sodium formate and on a JEOL JMS-700 in electron impact ionization (EI) method calibrated with perfluorokerosene at the Suzukake-dai Material Analysis Center, Technical Department, Tokyo Institute of Technology. The ultraviolet−visible (UV−vis) spectra of the solutions were recorded on JASCO V760 spectrometers. The UV−vis spectra were recorded in the solid state utilizing JASCO V570 spectrometers, which were equipped with a calibrated integrating sphere system. The solid-state absorption spectra were obtained by measuring the diffuse reflectance spectra, followed by a Kubelka−Munk conversion. The fluorescence spectra and quantum yield of the solids were determined on a JASCO FP-8500 spectrofluorimeter that was equipped with a calibrated integrating sphere system. Column chromatography was performed with Silica gel [Wakogel® C-200, size 100-200 mesh (75-150 um), Cat.No. 233-00078, Wako Pure Chemical Industries, Ltd. (Japan)]. All reagents and solvents were purchased from Kanto Chemicals Co. (Japan), Sigma-Aldrich Co. LLC. (USA), Tokyo Chemical Industry Co., Ltd. (Japan), or Wako Pure Chemical Industries, Ltd. (Japan). Chemicals were purified or dried in a standard manner, if necessary. All reactions were carried out under argon.

1-(2-Azidoethyl)-2-(2,2-dibromovinyl)benzene (9). This was prepared according to the following literatures [(a) Xu, X.; Zhong, Y.; Gao, Q. X. Z.; Gou, Z.; Yu, B. *Org. Lett.* **2020**, *22*, 5176-5181; (b) Kunzer, A.; Wendt, M. D. *Tetrahedron Lett.* **2011**, *52*, 1815-1818].



Org. Lett. **2020**, *22*, 5176-5181. *Org. Lett.* **2020**, *22*, 5176-5181. *Tetrahedron Lett.* **2011**, *52*, 1815-1818.

To a stirred solution of commercially available isochroman (2.18 g, 20.0 mmol) in CCl_4 (10 mL) was added bromine (3.20 g, 20.0 mmol) dropwise at 0 °C under argon and the mixture was heated in an oil bath maintained at 90 °C under argon. After being stirred for 1.5 h at that temperature, the solution was cooled to room temperature and concentrated under reduced pressure to obtain a yellowish oil. Then, hydrobromic acid (7.10 g, 40.0 mmol) was added to the obtained yellowish oil and the mixture was heated in an oil bath maintained at 90 °C for 20 min under argon. After being cooled to room temperature, the reaction was carefully quenched with saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give 2-(2-bromoethyl)benzaldehyde as a crude brownish oil, which was essentially pure by ^{1}H NMR analysis and was used in the next step without purification.

The mixture of 2-(2-bromoethyl)benzaldehyde (958 mg, 4.30 mmol) obtained above and sodium azide (2.60 g, 40.0 mmol) in DMF (40 mL) was heated in an oil bath maintained at 80 °C for 10 h under argon. After the mixture was cooled to room temperature, water was added to the mixture and extracted with diethyl ether. The combined organic layer was successively washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude yellowish oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford give 2-(2-azidoethyl)benzaldehyde (1.53 g, 44% yield, 2 steps) as a pale yellowish oil.

To a stirred solution of CBr_4 (5.96 g, 18.0 mmol) in CH_2Cl_2 (40 mL) was added PPh_3 (9.43 g, 36.0 mmol) at 0 °C under argon and the mixture was stirred at room temperature for 10 min under argon. After the mixture was cooled to 0 °C again, 2-(2-azidoethyl)benzaldehyde (1.53 g, 8.74 mmol) obtained above in CH_2Cl_2 (5 mL) was added and the mixture was stirred at that temperature overnight. Then, the reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed successively with aqueous saturated $Na_2S_2O_4$ solution and brine, dried over Na_2SO_4, and concentrated to give a crude solid. This crude solid was crushed and immersed in hexane, filtered, and concentrated *in vacuo* to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (1.60 g, 56%) as a pale yellowish oil.

^{1}H NMR δ 2.86 (t, J = 7.2 Hz, 2H), 3.47 (t, J = 7.2 Hz, 2H), 7.24 (dd, J = 1.2, 7.2 Hz, 1H), 7.28 (dt, J = 1.2, 7.2 Hz, 1H), 7.33 (dt, J = 2.4, 7.2 Hz, 1H), 7.45 (dd, J = 2.4, 7.2 Hz, 1H), 7.55 (s, 1H).

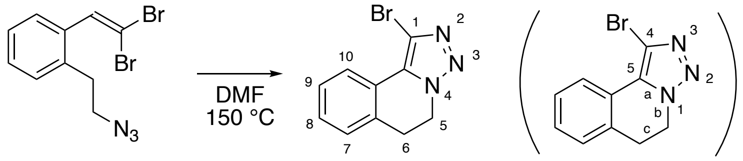
^{13}C NMR δ 32.90, 51.57, 92.94, 126.92, 128.75, 129.22, 129.58, 135.49, 135.75, 136.16.

IR (neat) 3073, 3018, 2927, 2864, 2100, 1601, 1483, 1447, 1348, 1299, 1261, 885, 859, 830, 804, 752 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_9{}^{79}Br_2N_3Na$ $[M+Na]^+$: 351.9055. Found: 351.9049.

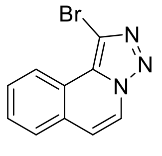
HRMS (ESI) Calcd for $C_{10}H_9{}^{79}Br{}^{81}BrN_3Na$ [M+Na]$^+$: 353.9035. Found: 353.9036.
HRMS (ESI) Calcd for $C_{10}H_9{}^{81}Br_2N_3Na$ [M+Na]$^+$: 355.9015. Found: 355.9014.

Typical procedure for Halogen-substituted Tricyclic Triazole Derivatives from 1-(ω-Azidoalkyl)-2-(2,2-dihalovinyl)arenes. 1-Bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (10).



A mixture of 1-(azidomethyl)-2-(2,2-dibromovinyl)benzene (**9**) (1.31 g, 4.00 mmol) in DMF (20 mL) was stirred in an oil bath maintained at 150 °C for 8 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (855 mg, 85%) as a white solid.
^{1}H NMR δ 3.26 (t, *J* = 7.2 Hz, 2H), 4.60 (t, *J* = 7.2 Hz, 2H), 7.34 (br dd, *J* = 1.6, 7.2 Hz, 1H), 7.38 (dt, *J* = 1.6, 7.2 Hz, 1H), 7.42 (dt, *J* = 1.6, 7.2 Hz, 1H), 8.20 (br dd, *J* = 1.6, 7.2 Hz, 1H).
^{13}C NMR δ 28.97, 49.37, 116.45, 123.42, 124.17, 127.75, 128.40, 129.72, 130.30, 132.20.
IR (KBr) 3064, 3022, 2988, 2947, 2906, 1610, 1579, 1553, 1483, 1458, 1431, 1346, 1291, 1280, 1255, 1233, 1188, 1162, 1043, 998, 946, 915, 869, 768, 740, 716, 680 cm^{-1}.
HRMS (ESI) Calcd for $C_{10}H_8{}^{79}BrN_3Na$ [M+Na]$^+$: 271.9794. Found: 271.9793.
HRMS (ESI) Calcd for $C_{10}H_8{}^{81}BrN_3Na$ [M+Na]$^+$: 273.9774. Found: 273.9774.
M.p. 88-89 °C.
The confirmation of the structure of **6** was based on the X-ray crystallographic data of **19**.

1-Bromo-[1,2,3]triazolo[5,1-*a*]isoquinoline (11).



The mixture of 1-bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (**10**) (12.5 mg, 0.050 mmol) and MnO_2 (217 mg, 2.50 mmol) in xylene (5 mL) was heated in an oil bath maintained at 160 °C under argon. After the mixture was stirred at that temperature for 24 h, the mixture was cooled to room temperature and it was filtered through Celite. The filtrate was concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (11.6 mg, 93%) as a white solid.

^{1}H NMR δ 7.25 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.91 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR δ 112.93, 117.16, 122.69, 122.76, 123.31, 127.65, 128.49, 129.02, 129.38, 129.53.

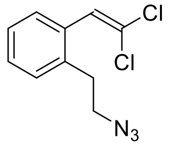
IR (KBr) 3073), 3040, 2966, 2922, 2850, 2100, 1731, 1604, 1568, 1483, 1454, 1433, 1346 1276, 1256, 1092, 1043, 1004, 878, 831, 806, 707, 566 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_6{}^{79}BrN_3Na$ [M+Na]$^+$: 269.9637. Found: 269.9637.

HRMS (ESI) Calcd for $C_{10}H_6{}^{81}BrN_3Na$ [M+Na]$^+$: 271.9617. Found: 271.9617.

M.p. 128-129 °C.

1-(2-Azidoethyl)-2-(2,2-dichlorovinyl)benzene (12).



^{1}H NMR δ 2.87 (t, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 6.97 (s, 1H), 7.24 (dd, *J* = 2.4, 7.2 Hz, 1H), 7.28 (dt, *J* = 2.4, 7.2 Hz, 1H), 7.31 (dt, *J* = 2.4, 7.2 Hz, 1H), 7.45 (dd, *J* = 2.4, 7.2 Hz, 1H).

^{13}C NMR δ 32.96, 51.72, 123.41, 126.97, 127.21, 128.78, 129.47, 129.63, 133.07, 136.22.

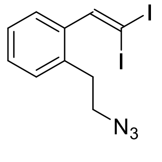
IR (neat) 3066, 3024, 2930, 2873, 2099, 1610, 1483, 1450, 1349, 1265, 1102, 1050, 952, 915, 833, 756, 653, 607 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_9{}^{35}Cl_2N_3Na$ [M+Na]$^+$: 264.0066. Found: 264.0066.

HRMS (ESI) Calcd for $C_{10}H_9{}^{35}Cl^{37}ClN_3Na$ [M+Na]$^+$: 266.0037. Found: 266.0030.

HRMS (ESI) Calcd for $C_{10}H_9{}^{37}Cl_2N_3Na$ [M+Na]$^+$: 268.0010. Found: 268.0006.

1-(2-Azidoethyl)-2-(2,2-diiodovinyl)benzene (13).



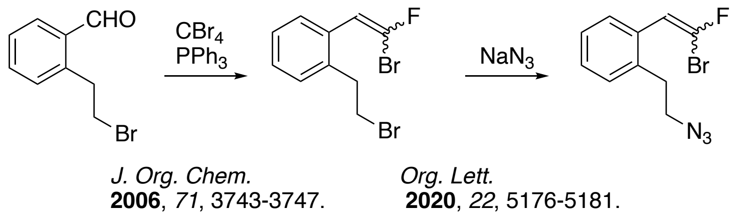
^{1}H NMR δ 2.82 (t, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 7.23 (br d, *J* = 7.2 Hz, 1H), 7.26 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.29 (dt, *J* = 1.6, 7.2 Hz, 1H), 7.35 (dt, *J* = 1.6, 7.2 Hz, 1H), 8.17 (s, 1H).

^{13}C NMR δ 32.97, 51.54, 127.14, 128.79, 128.99, 129.45, 129.77, 135.10, 140.56, 151.03.

IR (neat) 3062, 3022, 2956, 2926, 2870, 2099, 1599, 1481, 1447, 1348, 1289, 1124, 1073, 878, 852, 823, 788, 753, 706 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_9I_2N_3Na$ [M+Na]$^+$: 447.8778. Found: 447.8774.

A 52:48 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (14). This was prepared according to the following literatures [(a) Xu, J.; Burton, D. J. *J. Org. Chem.* **2006**, *71*, 3743-3747; (b) Xu, X.; Zhong, Y.; Gao, Q. X. Z.; Gou, Z.; Yu, B. *Org. Lett.* **2020**, *22*, 5176-5181].



To a stirred solution of $CFBr_3$ (0.488 mL, 18.0 mmol) in THF (5 mL) was added PPh_3 (2.62 g, 10.0 mmol) at room temperature under argon and the mixture was stirred at 70 °C for 15 min. After the mixture was cooled to room temperature again, 2-(2-bromoethyl)benzaldehyde (530 mg, 2.50 mmol) obtained above in THF (2 mL) was added and the mixture was stirred at 70 °C for 6 h. Then, the reaction was terminated with the addition of water. Hexane was added to the mixture and filtered. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to give a crude solid. This crude solid was crushed and immersed in hexane, filtered, and concentrated *in vacuo* to a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford a 54:46 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (332 mg, 43%) as a pale yellowish oil. The mixture of a 52:48 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (332 mg, 1.08 mmol) and sodium azide (140 mg, 2.16 mmol) in DMF (2 mL) was heated in an oil bath maintained at 80 °C for 10 h under argon. After the mixture was cooled to room temperature, water was added to the mixture and extracted with diethyl ether. The combined organic layer was successively washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude yellowish oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford give the title compound (131 mg, 45%) as a colorless oil.

***Z* isomer:** ^{1}H NMR δ 2.87 (t, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 6.69 (d, *J* = 12.8 Hz, 1H), 7.18-7.36 (m, 4H).

^{13}C NMR δ 33.01, 51.60, 109.78 (d, *J* = 21.5 Hz), 127.05, 128.58, 129.45 (d, *J* = 8.6 Hz), 129.60, 129.84 (d, *J* = 2.4 Hz), 135.32 (d, *J* = 0.9 Hz), 137.32 (d, *J* = 316.7 Hz).

^{19}F NMR δ –69.00.

***E* isomer:** ^{1}H NMR (characteristic peeks are shown) δ 2.89 (t, *J* = 7.2 Hz, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 6.15 (d, *J* = 31.2 Hz, 1H), 7.39 (dd, *J* = 2.0, 7.2 Hz, 1H), 7.52 (dd, *J* = 2.0, 7.2 Hz, 1H).

^{13}C NMR δ 32.91, 51.71, 110.11 (d, *J* = 7.6 Hz), 127.26, 128.32 (d, *J* = 0.9 Hz), 129.89, 130.94 (d, *J* = 3.1 Hz), 131.34 (d, *J* = 7.8 Hz), 134.37 (d, *J* = 328.2 Hz), 136.62 (d, *J* = 3.3 Hz).

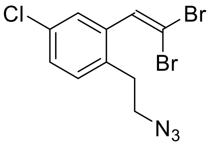
^{19}F NMR δ –72.09.

IR (ATR) 3070, 3022, 2932, 2870, 2090, 1647, 1487, 1449, 1349, 1262, 1115, 1081, 1040, 828, 753 cm^{-1} for a 52:48 *Z*/*E* mixture.

HRMS (ESI) Calcd for $C_{10}H_9{}^{79}BrFN_3Na$ $[M+Na]^+$: 291.9856. Found: 291.9860 for a 52:48 *Z*/*E* mixture.

HRMS (ESI) Calcd for $C_{10}H_9{}^{81}BrFN_3Na$ $[M+Na]^+$: 293.9836. Found: 293.9840 for a 52:48 *Z*/*E* mixture.

1-(2-Azidoethyl)-4-chloro-2-(2,2-dibromovinyl)benzene (15).



^1H NMR δ 2.82 (t, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.47 (s, 1H).

^{13}C NMR δ 32.43, 51.54, 94.29, 128.84, 129.21, 131.04, 132.74, 134.40, 134.94, 137.12.

IR (neat) 3013, 2953, 2926, 2854, 2101, 1597, 1562, 1476, 1348, 1294, 1260, 1119, 1090, 1028, 914, 887, 824, 759 cm^{-1}.

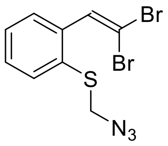
HRMS (ESI) Calcd for $C_{10}H_8{}^{79}Br_2{}^{35}ClN_3Na$ $[M+Na]^+$: 385.8666. Found: 385.8663.

HRMS (ESI) Calcd for $C_{10}H_8{}^{79}Br^{81}Br^{35}ClN_3Na$ (or $C_{10}H_8{}^{79}Br_2{}^{37}ClN_3Na$) $[M+Na]^+$: 387.8644. Found: 387.8643.

HRMS (ESI) Calcd for $C_{10}H_8{}^{81}Br_2{}^{35}ClN_3Na$ (or $C_{10}H_8{}^{79}Br^{81}Br^{37}ClN_3Na$) $[M+Na]^+$: 389.8622. Found: 389.8623.

HRMS (ESI) Calcd for $C_{10}H_8{}^{81}Br_2{}^{37}ClN_3Na$ $[M+Na]^+$: 391.8598. Found: 391.8584.

Azidomethyl 2-(2,2-dibromovinyl)phenyl sulfide (16).



^1H NMR δ 4.50 (s, 2H), 7.32-7.40 (m, 2H), 7.55-7.61 (m, 2H), 7.68 (s, 1H).

^{13}C NMR δ 55.69, 92.90, 128.04, 129.32, 129.88, 132.04, 132.21, 135.69, 137.81.

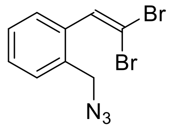
IR (neat) 3059, 3011, 2923, 2852, 2104, 1602, 1584, 1459, 1435, 1299, 1230, 1196, 1063, 1038, 859, 793, 752, 602, 559 cm^{-1}.

HRMS (ESI) Calcd for $C_9H_7{}^{79}Br_2N_3SNa$ $[M+Na]^+$: 369.8620. Found: 369.8629.

HRMS (ESI) Calcd for $C_9H_7{}^{79}Br{}^{81}BrN_3SNa$ $[M+Na]^+$: 371.8599. Found: 371.8603.

HRMS (ESI) Calcd for $C_9H_7{}^{81}Br_2N_3SNa$ $[M+Na]^+$: 373.8578. Found: 373.8558.

1-(Azidomethyl)-2-(2,2-dibromovinyl)benzene (17).



^{1}H NMR δ 4.33 (s, 2H), 7.34-7.42 (m, 3H), 7.46 (dd, *J* = 4.4, 8.0 Hz, 1H), 7.57 (s, 1H).

^{13}C NMR δ 52.67, 93.52, 128.56, 128.87, 129.31, 129.34, 133.03, 135.22, 135.54.

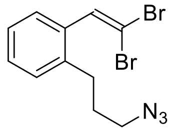
IR (neat) 3055, 3018, 2933, 2882, 2098, 1602, 1450, 1344, 1255, 1220, 895, 860, 768, 749 cm^{-1}.

HRMS (ESI) Calcd for $C_9H_7{}^{79}Br_2N_3Na$ [M+Na]$^+$: 337.8899. Found: 337.8892.

HRMS (ESI) Calcd for $C_9H_7{}^{79}Br\,{}^{81}BrN_3Na$ [M+Na]$^+$: 339.8879. Found: 339.8879.

HRMS (ESI) Calcd for $C_9H_7{}^{81}Br_2N_3Na$ [M+Na]$^+$: 341.8859. Found: 341.8859.

1-(3-Azidopropyl)-2-(2,2-dibromovinyl)benzene (18).



^{1}H NMR δ 1.85 (tt, *J* = 6.8, 8.0 Hz, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.52 (s, 1H).

^{13}C NMR δ 29.56, 30.43, 50.63, 92.50, 126.38, 128.76, 129.26 (2 peaks), 135.17, 136.47, 138.83.

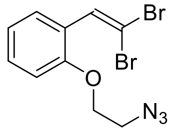
IR (neat) 3063, 3016, 2931, 2866, 2096, 1601, 1482, 1450, 1346, 1257, 888, 859, 751 cm^{-1}.

HRMS (ESI) Calcd for $C_{11}H_{11}{}^{79}Br_2N_3Na$ [M+Na]$^+$: 365.9212. Found: 365.9206.

HRMS (ESI) Calcd for $C_{11}H_{11}{}^{79}Br\,{}^{81}BrN_3Na$ [M+Na]$^+$: 367.9192. Found: 367.9192.

HRMS (ESI) Calcd for $C_{11}H_{11}{}^{81}Br_2N_3Na$ [M+Na]$^+$: 369.9172. Found: 369.9163.

1-(2-Azidoethoxy)-2-(2,2-dibromovinyl)benzene (19).



^{1}H NMR δ 3.59 (t, *J* = 4.8 Hz, 2H), 4.14 (t, *J* = 4.8 Hz), 6.83 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.69 (d, *J* = 8.0 Hz).

^{13}C NMR δ 50.19, 67.39, 90.26, 111.35, 120.94, 124.74, 129.45, 129.87, 132.67, 155.14.

IR (KBr) 3071, 3016, 2937, 2874, 2103, 1599, 1579, 1486, 1448, 1304, 1254, 1163, 1111, 1052, 1005, 922, 878, 857, 844, 807, 750, 598, 561 cm^{-1}.

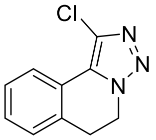
HRMS (EI) Calcd for $C_{10}H_9{}^{79}Br_2N_3O$ [M]$^+$: 344.9112. Found: 344.9113.

HRMS (EI) Calcd for $C_{10}H_9{}^{79}Br\,{}^{81}BrN_3O$ [M]$^+$: 346.9092. Found: 346.9093.

HRMS (ESI) Calcd for $C_{10}H_9{}^{81}Br_2N_3O$ [M]$^+$: 348.9071. Found: 348.9067.

M.p. 106-107 °C.

1-Chloro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (20).



A mixture of 1-(azidomethyl)-2-(2,2-dichlorovinyl)benzene (**12**) (64.8 mg, 0.267 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 8 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (54.0 mg, 98%) as a white solid.

^{1}H NMR δ 3.26 (t, J = 7.2 Hz, 2H), 4.59 (t, J = 7.2 Hz, 2H), 7.34 (dd, J = 2.0, 7.2 Hz, 1H), 7.38 (dt, J = 2.0, 7.2 Hz, 1H), 7.42 (dt, J = 2.0, 7.2 Hz, 1H), 8.07 (dd, J = 2.0, 7.2 Hz, 1H).

^{13}C NMR δ 28.95, 45.49, 123.39, 124.33, 127.94, 128.35, 128.42, 129.72, 130.91, 132.03.

IR (KBr) 3068, 3049, 2956, 2920, 2851, 1561, 1487, 1464, 1433, 1306, 1265, 1186, 1095, 1043, 1004, 802, 763, 715 cm^{-1}.

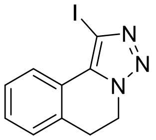
HRMS (ESI) Calcd for $C_{10}H_8{}^{35}ClN_3Na$ $[M+Na]^+$: 228.0299. Found: 228.0299.

HRMS (ESI) Calcd for $C_{10}H_8{}^{37}ClN_3Na$ $[M+Na]^+$: 230.0271. Found: 230.0268.

M.p. 86-87 °C.

The confirmation of the structure of **20** was based on the X-ray crystallographic data of **25**.

1-Iodo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (21). This is a known compound [Fiandanse, V.; Maurantonio, S.; Punzi, A.; Rafaschieri, G. G. *Org. Biomol. Chem.* **2012**, *10*, 1186].



A mixture of 1-(azidomethyl)-2-(2,2-diiodovinyl)benzene (**13**) (57.9 mg, 0.136 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 8 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32.4 mg, 80%) as a white solid.

^{1}H NMR δ 3.24 (t, J = 7.2 Hz, 2H), 4.61 (t, J = 7.2 Hz, 2H), 7.34 (dd, J = 2.0, 7.2 Hz, 1H), 7.38 (dt, J = 2.0, 7.2 Hz, 1H), 7.42 (dt, J = 2.0, 7.2 Hz, 1H), 8.35 (dd, J = 2.0, 7.2 Hz, 1H).

^{13}C NMR δ 29.16, 45.21, 83.56, 123.79, 124.09, 127.61, 128.46, 129.79, 132.49, 133.43.

IR (KBr) 3064, 3008, 2956, 2849, 1481, 1460, 1417, 1348, 1282, 1253, 1221, 1179, 1037, 994, 764 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_8IN_3Na$ [M+Na]$^+$: 319.9655. Found: 319.9655.

M.p. 98-99 °C.

These spectral properties were in good agreement with those reported in the above literature.

^{1}H NMR δ 3.21 (t, J = 7.0 Hz, 2H), 4.58 (t, J = 7.0 Hz, 2H), 7.43-7.30 (m, 3H), 8.32 (dd, J = 7.8, 1.0 Hz, 1H).

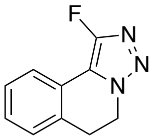
^{13}C NMR δ 29.1, 45.2, 83.5, 123.7, 124.0, 127.6, 128.4, 129.7, 132.5, 133.4.

IR (KBr) 3005, 2979, 2951, 2904, 1476, 1458, 1449, 1424, 1417, 1347, 1281, 1251, 1220, 1178, 1170, 1157, 1036, 994, 778, 758, 738, 713 cm^{-1}.

MS Calcd for $C_{10}H_8IN_3$ [M]$^+$: 297

M.p. 137-138 °C.

1-Fluoro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (22).



A mixture of a 52:48 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (**14**) (131 mg, 0.480 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 14 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (64.5 mg, 71%) as a white solid.

^{1}H NMR δ 3.27 (t, J = 7.2 Hz, 2H), 4.56 (t, J = 7.2 Hz, 2H), 7.32-7.43 (m, 3H), 8.35 (d, J = 7.2 Hz, 1H).

^{13}C NMR δ 28.67, 45.77, 116.09 (d, J = 29.7 Hz), 122.85 (d, J = 4.4 Hz), 124.31 (d, J = 3.3 Hz), 128.03, 128.38, 129.30, 131.20 (d, J = 1.5 Hz), 157.21 (d, J = 244.4 Hz).

^{19}F NMR δ –146.66.

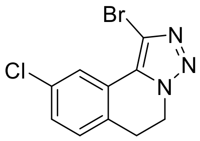
IR (ATR) 3073, 3047, 3003, 2921, 2854, 1620, 1605, 1483, 1444, 1390, 1346, 1306, 1269, 1184, 1163, 1122, 1072, 1045, 1019, 981, 950, 914, 759, 723 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_8FN_3Na$ [M+Na]$^+$: 212.0594. Found: 212.0593.

M.p. 123-125 °C.

The confirmation of the structure of **22** was based on the X-ray crystallographic data of **25**.

1-Bromo-9-chloro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (23).



A mixture of 1-(2-azidoethyl)-4-chloro-2-(2,2-dibromovinyl)benzene (**15**) (46.0 mg, 0.126 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 8 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32.8 mg, 91%) as a white solid.

^1H NMR δ 3.23 (t, J = 6.8 Hz, 2H), 4.60 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.36 (dd, J = 2.0, 8.0 Hz, 1H), 8.18 (br dd, J = 2.0 Hz, 1H).

^{13}C NMR δ 28.55, 45.33, 117.07, 124.08, 125.02, 129.37, 129.65, 129.72, 130.48, 133.77.

IR (KBr) 3073, 2956, 2922, 2850, 1604, 1568, 1483, 1433, 1346, 1276, 1256, 1229, 1092, 1043, 1004, 878, 831, 806, 707, 566 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_7{}^{79}Br_2{}^{35}ClN_3Na$ [M+Na]$^+$: 305.9404. Found: 305.9403.

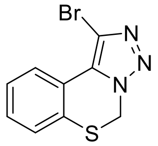
HRMS (ESI) Calcd for $C_{10}H_7{}^{81}Br^{35}ClN_3Na$ (or $C_{10}H_7{}^{79}Br^{37}ClN_3Na$) [M+Na]$^+$: 307.9382. Found: 307.9381.

HRMS (ESI) Calcd for $C_{10}H_7{}^{81}Br_2{}^{37}ClN_3Na$ [M+Na]$^+$: 309.9356. Found: 309.9349.

M.p. 146-147 °C.

The confirmation of the structure of **23** was based on the X-ray crystallographic data of **25**.

1-Bromo-5*H*-benzo[*e*][1,2,3]triazolo[1,5-*c*][1,3]thiazine (24).



A mixture of azidomethyl 2-(2,2-dibromovinyl)phenyl sulfide (**16**) (67.0 mg, 0.190 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 8 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32.5 mg, 63%) as a white solid.

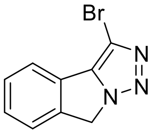
^1H NMR δ 5.51 (s, 2H), 7.38 (dt, J = 2.0, 7.2 Hz, 1H), 7.41 (dt, J = 2.0, 7.2 Hz, 1H), 7.50 (dd, J = 2.0, 7.2 Hz, 1H), 8.24 (dd, J = 2.0, 7.2 Hz, 1H).

^{13}C NMR δ 46.29, 118,05, 123.97, 126.13, 127.46, 128.59, 129.53, 129.74, 130.10 (2 peaks).

IR (KBr) 3068, 2995, 2922, 2852, 1668, 1593, 1463, 1447, 1426, 1403, 1287, 1240, 1197, 1078, 990, 942, 754, 726 cm^{-1}.

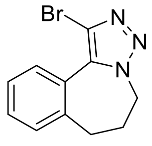
HRMS (ESI) Calcd for $C_9H_6{}^{79}BrN_3SNa$ [M+Na]$^+$: 271.9794. Found: 271.9793.
HRMS (ESI) Calcd for $C_9H_6{}^{81}BrN_3SNa$ [M+Na]$^+$: 273.9774. Found: 273.9774.
M.p. 113-114 °C.
The confirmation of the structure of **24** was based on the X-ray crystallographic data of **25**.

3-Bromo-8*H*-[1,2,3]triazolo[5,1-*a*]isoindole (25). This is a known compound [John, J.; Thomas, J.; Parekh, N.; Dehaen, W. *Eur. J. Org. Chem.* **2015**, 4922-4930].



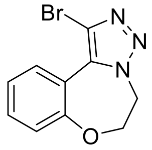
A mixture of 1-(azidomethyl)-2-(2,2-dibromovinyl)benzene (**17**) (72.0 mg, 0.228 mmol) in DMF (1.0 mL) was stirred in an oil bath maintained at 150 °C for 8 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (47.3 mg, 88%) as a white solid.
^{1}H NMR δ 5.37 (s, 2H), 7.46 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.47 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H).
^{13}C NMR δ 51.81, 110.80, 121.16, 124.11, 126.61, 128.89, 128.97, 140.43, 141.03.
IR (KBr) 3064, 2884, 1568, 1473, 1449, 1411, 1280, 1219, 1156, 1059, 1018, 996, 765, 720, 689 cm^{-1}.
HRMS (ESI) Calcd for $C_9H_6{}^{79}BrN_3Na$ [M+Na]$^+$: 257.9637. Found: 257.9637.
HRMS (ESI) Calcd for $C_9H_6{}^{81}BrN_3Na$ [M+Na]$^+$: 259.9617. Found: 259.9614.
M.p. 146-147 °C.
As these spectral properties were not in good agreement with those reported in the above literature, the structure of **25** was by determined X-ray.
^{1}H NMR δ 5.49 (s, 2H), 7.65-7.66 (m, 3H), 8.37-8.41 (m, 1H).
^{13}C NMR δ 52.4, 124.2, 125.1, 125.3, 129.8, 131.6, 140.4, 142.1.
Recrystallization was performed as follows. 3-Bromo-8*H*-[1,2,3]triazolo[5,1-*a*]isoindole (**25**) (*ca.* 5 mg) was dissolved in 0.5 mL of ethyl acetate-hexane (2:1) in a test tube. After the test tube was capped with a glass stopper and heated to melt **25**, it was allowed to stand at room temperature for 1 day. After the supernatant was removed by decantation, the remaining solid was collected to give colorless crystals of **25** (*ca.* 2 mg).
The X-ray crystallography of **25** unambiguously determined its whole structure. Its crystallographic data, ORTEP drawing, bond lengths, and bond angles of **25** were attached at the final pages. The structure of other tricyclic triazole derivatives prepared herein were assigned based on the structure of **25**.

1-Bromo-6,7-dihydro-5*H*-benzo[*c*][1,2,3]triazolo[1,5-*a*]azepine (26).



A mixture of 1-(3-azidopropyl)-2-(2,2-dibromovinyl)benzene (**18**) (70.4 mg, 0.200 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 40 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (40.5 mg, 75%) as a white solid.
^{1}H NMR δ 2.45 (quintet, J = 7.2 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 4.38 (t, J = 7.2 Hz, 2H), 7.37 (t, J = 5.2 Hz, 1H), 7.42 (d, J = 5.2 Hz, 1H), 7.43 (t, J = 5.2 Hz, 1H), 7.64 (dd, J = 2.8, 5.2 Hz, 1H).
^{13}C NMR δ 30.11, 31.02, 47.00, 118.40, 125.79, 127.27, 128.56, 129.93, 130.20, 134.88, 138.71.
IR (KBr) 3065, 2963, 2944, 2864, 1556, 1473, 1436, 1347, 1307, 1289, 1263, 1239, 1186, 1132, 1036, 994, 955, 827, 778, 742, 683 cm^{-1}.
HRMS (ESI) Calcd for $C_{11}H_{10}{}^{79}BrN_3Na$ [M+Na]$^+$: 285.9950. Found: 285.9951.
HRMS (ESI) Calcd for $C_{11}H_{10}{}^{81}BrN_3Na$ [M+Na]$^+$: 287.9930. Found: 287.9930.
M.p. 147-148 °C.
The confirmation of the structure of **26** was based on the X-ray crystallographic data of **25**.

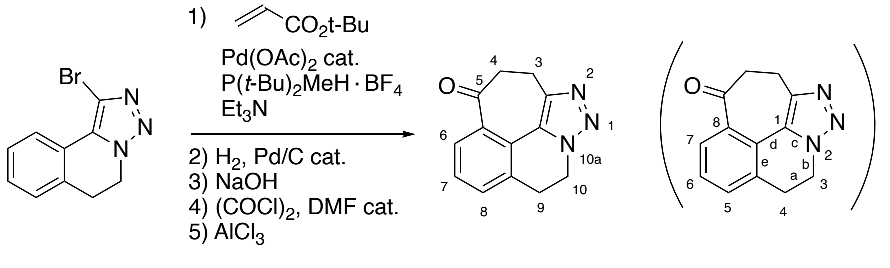
1-Bromo-5,6-dihydrobenzo[*f*][1,2,3]triazolo[1,5-*d*][1,4]oxazepine (27).



A mixture of 1-(2-azidoethoxy)-2-(2,2-dibromovinyl)benzene (**19**) (85.6 mg, 0.240 mmol) in DMF (2.0 mL) was stirred in an oil bath maintained at 150 °C for 40 h under argon. The reaction was terminated with the addition of water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (36.1 mg, 54%) as a white solid.
^{1}H NMR δ 4.60 (t, J = 5.2 Hz, 2H), 4.76 (t, J = 5.2 Hz, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H) 7.43 (dt, J = 1.6, 8.0 Hz, 1H), 8.02 (dd, J = 1.6, 8.0 Hz, 1H).
^{13}C NMR δ 50.00, 71.25, 115.75, 118.70, 122.20, 123.53, 129.21, 131.55, 132.28, 154.51.
IR (KBr) 3068, 2953, 2923, 2852, 1609, 1475, 1434, 1293, 1248, 1215, 1114, 1081, 1042, 993, 873, 795, 764 cm^{-1}.

HRMS (ESI) Calcd for $C_{10}H_8{}^{79}BrN_3ONa$ $[M+Na]^+$: 287.9743. Found: 287.9741.
HRMS (ESI) Calcd for $C_{10}H_8{}^{81}BrN_3ONa$ $[M+Na]^+$: 289.9723. Found: 289.9720.
M.p. 106-107 °C.
The confirmation of the structure of **27** was based on the X-ray crystallographic data of **25**.

3,4,9,10-Tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (28).



The mixture of 1-bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (**10**) (1.50 g, 6.00 mmol), *tert*-butyl acrylate (4.40 mL, 30.0 mmol), $Pd(OAc)_2$ (269 mg, 1.20 mmol), di-*tert*-butyl(methyl)phosphonium tetrafluoroborate (1.56 g, 2.40 mmol), and Et_3N (1.04 mL, 7.50 mmol) in DMF (30 mL) was stirred in an oil bath maintained at 100 °C for 12 h under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through Celite with aid of ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford *tert*-butyl (*E*)-3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)acrylate (1.74 g, 77%) as a white solid.

To a suspension of 10% Pd/C (300 mg) in ethyl acetate (10 mL) was added *tert*-butyl (*E*)-3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)acrylate (1.74 g, 5.80 mmol) obtained above in ethyl acetate (1 mL). After the reaction mixture was stirred at room temperature under 1 atm of H_2 for 12 h, it was filtered through Celite. The filtrate was concentrated *in vacuo* to give a crude oil of *tert*-butyl 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoate, which was directly used in the next step.

To a stirred solution of *tert*-butyl 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoate obtained above in CH_2Cl_2 (20 mL) was added CF_3CO_2H (4.43 mL, 58.0 mmol) dropwise at room temperature under argon. After stirring at room temperature for 3 h, the reaction was neutralized with aqueous saturated $NaHCO_3$ solution. The mixture was diluted with ethyl acetate and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoic acid (546 mg, 38%, 2 steps, not optimized) as a white solid.

3-(5,6-Dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoic acid**:** ^{1}H NMR δ 3.01 (t, *J* = 7.2 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 7.2 Hz, 2H), 4.57 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.38 (br t, *J* = 7.6 Hz, 1H), 7.40 (br t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H). The peaks of CO_2H was disappeared.

To a stirred solution of 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoic acid (**37**) (60.0 mg, 0.246 mmol) obtained above in CH_2Cl_2 (2 mL) were successively added DMF (1 drop) and oxalyl chloride (0.042 mL, 0.492 mmol) at room temperature. After the mixture was stirred for 1.5 h, the solvent and the excess oxalyl chloride were removed *in vacuo* to afford 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoyl chloride as a crude oil, which was pure by ^{1}H NMR spectroscopy and directly used in the next step.

To a solution of 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoyl chloride obtained above in CH_2Cl_2 (2 mL) was added pulverized $AlCl_3$ (328 mg, 2.46 mmol) at –78 °C for 1 h under argon. After the mixture was stirred at room temperature for 12 h, the reaction was terminated by the addition of aqueous saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (50.3 mg, 90%, 2 steps) as a white solid.

^{1}H NMR δ 3.10 (dd, *J* = 5.2 7.6 Hz, 2H), 3.26 (dd, *J* = 5.2 7.6 Hz, 2H), 3.34 (t, *J* = 7.2 Hz, 2H), 4.62 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.78 (dd, *J* = 0.8, 7.6 Hz, 1H).

^{13}C NMR δ 21.77, 28.84, 39.96, 44.61, 122.96, 128.41, 128.69, 129.72, 131.46, 132.23, 136.29, 144.26, 201.08.

IR (KBr) 3073, 3040, 2935, 2896, 2847, 1669, 1591, 1439, 1328, 1281, 1091, 971, 807, 769, 480, 450 cm^{-1}.

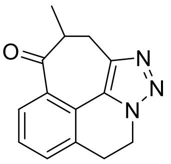
HRMS (ESI) Calcd for $C_{13}H_{11}N_3ONa$ $[M+Na]^+$: 248.0794. Found: 248.0794.

M.p. 138-139 °C.

Recrystallization was performed as follows. 3,4,9,10-Tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (**28**) (*ca.* 5 mg) was dissolved in 0.5 mL of ethyl acetate-hexane (2:1) in a test tube. After the test tube was capped with a glass stopper and heated to melt **28**, it was allowed to stand at room temperature for 1 day. After the supernatant was removed by decantation, the remaining solid was collected to give colorless crystals of **28** (*ca.* 2 mg).

The X-ray crystallography of **28** unambiguously determined its whole structure. Its crystallographic data, ORTEP drawing, bond lengths, and bond angles of **28** were attached at the final pages. The structure of other tricyclic triazole derivatives prepared herein were assigned based on the structure of **28**.

4-Methyl-3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (29).



To a stirred solution of 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)-2-methylpropanoic acid (55.0 mg, 0.214 mmol) obtained above in CH_2Cl_2 (2 mL) were successively added DMF (1 drop) and oxalyl chloride (0.036 mL, 0.428 mmol) at room temperature. After the mixture was stirred for 1.5 h, the solvent and the excess oxalyl chloride were removed *in vacuo* to afford 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)-2-methylpropanoyl chloride as a crude oil, which was pure by ^1H NMR spectroscopy and directly used in the next step.

To a solution of 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)-2-methylpropanoyl chloride obtained above in CH_2Cl_2 (2 mL) was added pulverized $AlCl_3$ (266 mg, 2.00 mmol) at –78 °C for 1 h under argon. After the mixture was stirred at room temperature for 12 h, the reaction was terminated by the addition of aqueous saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (47.0 mg, 92%, 2 steps) as a colorless oil.

^1H NMR δ 1.30 (t, J = 6.8 Hz, 3H), 3.02 (dd, J = 11.2, 16.8 Hz, 1H), 3.22-3.44 (m, 4H), 4.54 (ddd, J = 6.4, 9.2, 12.8 Hz, 1H), 4.69 (td, J = 6.4 12.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H).

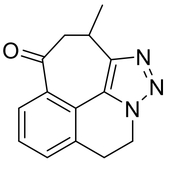
^{13}C NMR δ 16.09, 28.71, 29.76, 42.75, 44.60, 122.18, 128.35, 128.80, 129.46, 131.16, 131.74, 136.59, 142.67, 204.30.

IR (neat) 3064, 2974, 2933, 2841, 1683, 1594, 1455, 1357, 1251, 1190, 1170, 1109, 1021, 947, 907, 766 cm^{-1}.

HRMS (ESI) Calcd for $C_{14}H_{13}N_3ONa$ $[M+Na]^+$: 262.0951. Found: 262.0948.

The confirmation of the structure of **29** was based on the X-ray crystallographic data of **28**.

3-Methyl-3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (30).



To a stirred solution of 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)butanoic acid (54.2 mg, 0.210 mmol) obtained above in CH_2Cl_2 (2 mL) were successively added DMF (1 drop) and oxalyl chloride (0.036 mL, 0.420 mmol) at room temperature. After the mixture was stirred for 1.5 h, the solvent and the excess oxalyl chloride were removed *in vacuo* to afford 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)butanoyl chloride as a crude oil, which was pure by ^{1}H NMR spectroscopy and directly used in the next step.

To a solution of 3-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)butanoyl chloride obtained above in CH_2Cl_2 (2 mL) was added pulverized $AlCl_3$ (279 mg, 2.10 mmol) at –78 °C for 1 h under argon. After the mixture was stirred at room temperature for 1 h, the reaction was terminated by the addition of aqueous saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (40.2 mg, 80%, 2 steps) as a white solid.

^{1}H NMR δ 1.47 (d, J = 7.2 Hz, 3H), 3.02 (dd, J = 8.4, 12.0 Hz, 1H), 3.12 (dd, J = 3.6, 12.0 Hz, 1H), 3.34 (t, J = 7.2 Hz, 2H), 3.51 (ddq, J = 3.6, 8.4, 7.2 Hz, 1H), 4.62 (m, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.48, (dd, J = 1.2, 7.6 Hz, 1H), 7.79 (dd, J = 1.2, 7.6 Hz, 2H).

^{13}C NMR δ 19.81, 28.16, 28.82, 44.58, 47.60, 123.04, 128.19, 128.60, 128.63, 131.45, 132.19, 136.12, 148.48, 200.33).

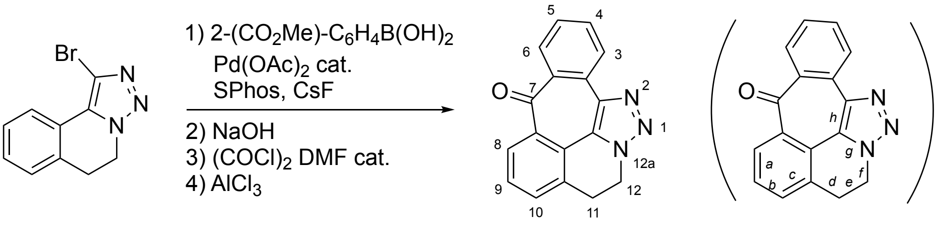
IR (KBr) 3072, 2958, 2926, 1658, 1591, 1495, 1446, 1421, 1336, 1305, 1232, 1187, 1074, 1016, 820, 775, 745 cm^{-1}.

HRMS (ESI) Calcd for $C_{14}H_{13}N_3ONa$ [M+Na]$^+$: 262.0951. Found: 262.0947.

M.p. 155-156 °C.

The confirmation of the structure of **30** was based on the X-ray crystallographic data of **28**.

11,12-Dihydro-7*H*-1,2,12a-triazacyclopenta[*gh*]pleiaden-7-one (33).



The mixture of 1-bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (**10**) (250 mg, 1.00 mmol), [2-(methoxycarbonyl)phenyl]boronic acid (414 mg, 3.00 mmol), $Pd(OAc)_2$ (22.4 mg, 0.100 mmol), SPhos (dicyclohexyl(2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phosphane) (82.0 mg, 0.200 mmol, purchased from Sigma-Aldrich Co. LLC), and CsF (453 mg, 3.00 mmol) in THF (5 mL) was stirred in an oil bath maintained at 80 °C for 10 h under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through Celite with aid of ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford methyl 2-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)benzoate (**31**) (315 mg, 100%) as a white solid.

To a solution of 2-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)benzoate (**31**) (305 mg, 1.00 mmol) obtained above in MeOH (3 mL)-water (1 mL) was added NaOH (60.0 mg, 1.50 mmol) dropwise at room temperature under argon. After stirring at that temperature for 5 h, the reaction was neutralized with aqueous 1 M HCl solution. The mixture was diluted with ethyl acetate and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford 2-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)benzoic acid (**32**) (151 mg, 52%) as a white solid.

To a stirred solution of 2-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)benzoic acid (**32**) (87.0 mg, 0.300 mmol) obtained above in CH_2Cl_2 (3 mL) were successively added DMF (1 drop) and oxalyl chloride (0.050 mL, 0.600 mmol) at room temperature. After the mixture was stirred for 1.5 h, the solvent and the excess oxalyl chloride were removed *in vacuo* to afford 2-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)benzoyl chloride as a crude oil, which was pure by ^{1}H NMR spectroscopy and directly used in the next step.

To a solution of 2-(5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)benzoyl chloride obtained above in CH_2Cl_2 (3 mL) was added pulverized $AlCl_3$ (400 mg, 3.00 mmol) at –78 °C for 1 h under argon. After the mixture was stirred at room temperature for 12 h, the reaction was terminated by the addition of aqueous saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a crude oil which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (59.2 mg, 73%, 2 steps) as a white solid.

^{1}H NMR δ 3.44 (t, J = 7.2 Hz, 2H), 4.76 (t, J = 7.2 Hz, 2H), 7.58 (t, J = 7.6 Hz, 2H) 7.61 (d, J = 7.6 Hz, 1H), 7.75 (br t, J = 7.6 Hz, 1H), 8.17 (br t, J = 7.6 Hz, 2H), 8.66 (br d, J = 7.6 Hz, 1H).

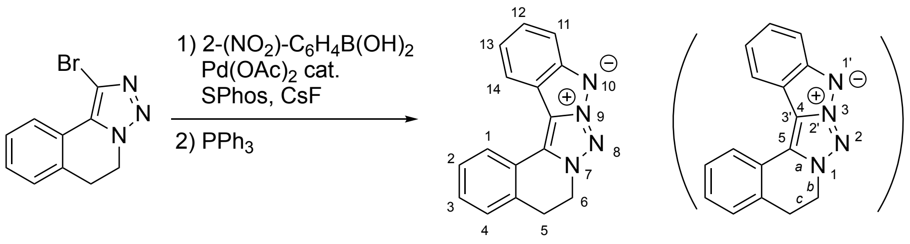
^{13}C NMR δ 29.05, 44.39, 121.87, 125.59, 128.51, 128.94, 129.33, 129.96, 130.01, 131.23, 131.33, 131.67, 132.65, 136.75, 136.91, 141.77, 192.56.

IR (KBr) 3064, 3003, 2922, 2849, 1620, 1585, 1510, 1372, 1344, 1310, 1280, 1162, 1030, 908, 745, 704 cm^{-1}.

HRMS (ESI) Calcd for $C_{17}H_{11}N_3ONa$ $[M+Na]^+$: 296.0794. Found: 296.0792.

M.p. 175-176 °C.

5,6-Dihydroindazolo[2’,3’:3,4][1,2,3]triazolo[5,1-*a*]isoquinolin-9-ium-10-ide (35).



The mixture of 1-bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (**10**) (175 mg, 0.700 mmol), (2-nitrophenyl)boronic acid (350 mg, 2.10 mmol, purchased from Sigma-Aldrich Co. LLC), Pd(OAc)$_2$ (15.6 mg, 0.070 mmol), SPhos (dicyclohexyl(2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phosphane) (57.4 mg, 0.140 mmol), and CsF (318 mg, 2.10 mmol) in THF (5 mL) was stirred in an oil bath maintained at 80 °C for 10 h under argon. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through Celite with aid of ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated *in vacuo* to give a crude solid, which was chromatographed on silica gel (hexane-ethyl acetate) to afford methyl 1-(2-nitrophenyl)-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (**34**) (174 mg, 85%) as a brownish solid.

The mixture of 1-(2-nitrophenyl)-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (**34**) (50.0 mg, 0.170 mmol) obtained above and PPh$_3$ (133 mg, 0.51 mmol) in 1,2-dicholorobenzen (2 mL) was heated in an oil bath maintained at 200 °C for 20 h under argon. After being cooled to room temperature, the reaction mixture chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (40.3 mg, 91%) as a yellowish solid.

^{1}H NMR δ 3.42 (t, *J* = 7.2 Hz, 2H), 4.74 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR δ 28.34, 46.36, 109.90, 115.02, 118.02, 119.69, 124.04, 124.42, 124.79, 125.25, 127.04, 128.33, 128.69, 129.67, 131.27, 153.60.

IR (KBr) 3050, 3027, 2998, 2951, 1508, 1488, 1466, 1442, 1383, 1344, 1255, 1194, 1177, 1136, 766, 744 cm^{-1}.

HRMS (ESI) Calcd for $C_{16}H_{12}N_4Na$ [M+Na]$^+$: 283.0954. Found: 283.0950.

M.p. > 200 °C.

Recrystallization was performed as follows. 5,6-Dihydroindazolo[2',3':3,4][1,2,3]triazolo[5,1-*a*]isoquinolin-9-ium-10-ide (**35**) (*ca*. 5 mg) was dissolved in 0.5 mL of ethyl acetate-hexane (2:1) in a test tube. After the test tube was capped with a glass stopper and heated to melt **35**, it was allowed to stand at room temperature for 1 day. After the supernatant was removed by decantation, the remaining solid was collected to give colorless crystals of **35** (*ca*. 2 mg).

The X-ray crystallography of **35** unambiguously determined its whole structure. Its crystallographic data, ORTEP drawing, bond lengths, and bond angles of **35** were attached at the final pages. The structure of other tricyclic triazole derivatives prepared herein were assigned based on the structure of **35**.

X-ray crystallographic data of 3-bromo-8*H*-[1,2,3]triazolo[5,1-*a*]isoindole (25). Crystals were obtained by recrystallization of from hexane-ethyl acetate. A single crystal was mounted in a loop.

Figure S1. ORTEP Drawing of 25.

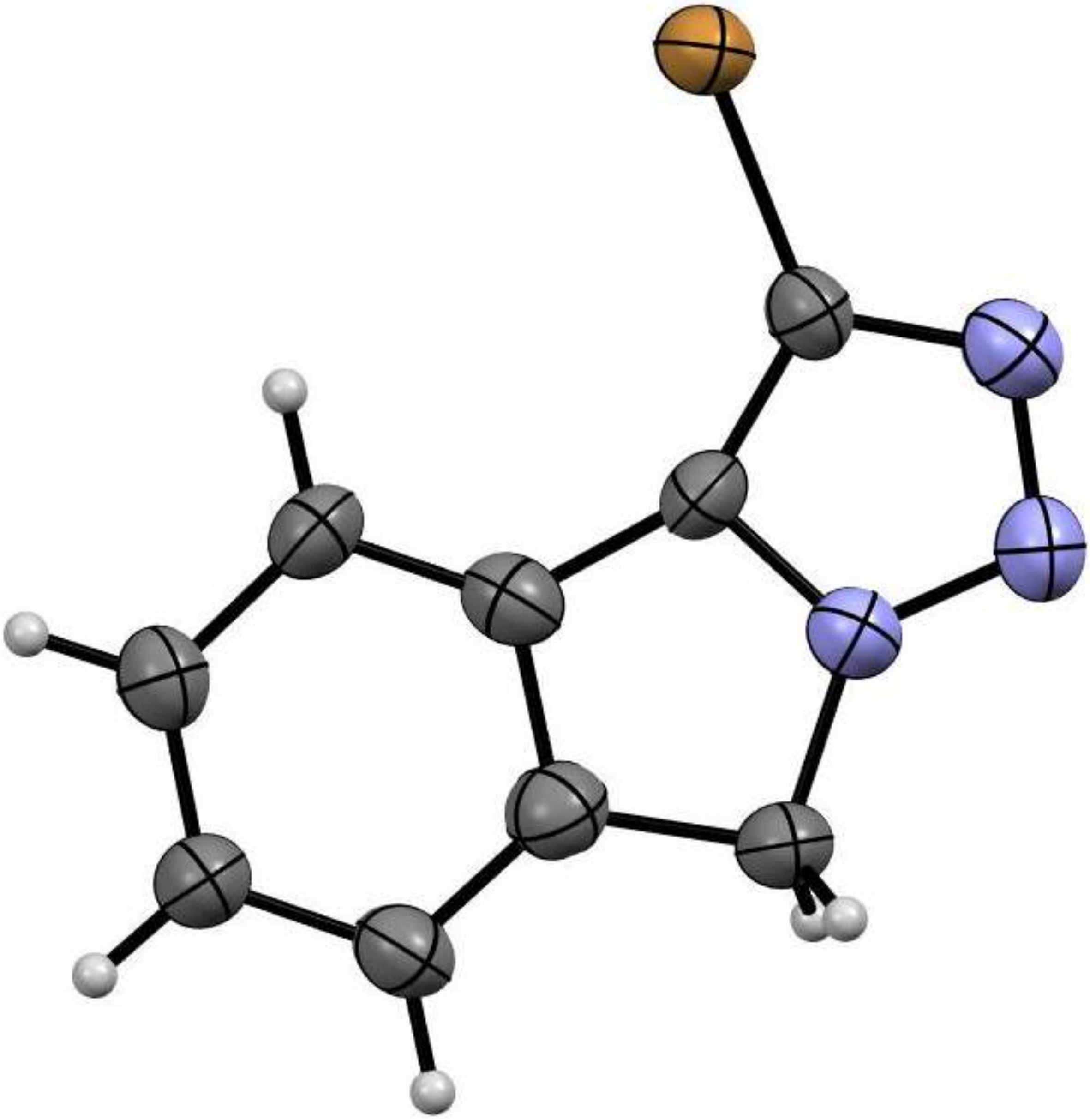


Table S1. Crystal data and structure refinement for 25.

Empirical formula	$C_9H_6BrN_3$
Formula weight	236.08
Temperature/K	90
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	4.1549(5)
b/Å	25.864(2)
c/Å	8.0655(9)
α/°	90
β/°	101.904(11)
γ/°	90
Volume/Å^3	848.11(16)
Z	4
ρ_{calc}mg/mm^3	1.849
μ/mm^{-1}	6.194
F(000)	464.0
Crystal size/mm^3	0.159 × 0.04 × 0.019
2Θ range for data collection	6.836 to 153.074°
Index ranges	$-4 \le h \le 4, -31 \le k \le 32, -10 \le l \le 10$
Reflections collected	15988
Independent reflections	1666[R(int) = 0.2096]
Data/restraints/parameters	1666/0/118
Goodness-of-fit on F^2	1.311
Final R indexes [I>=2σ (I)]	$R_1 = 0.1178$, $wR_2 = 0.2942$
Final R indexes [all data]	$R_1 = 0.1433$, $wR_2 = 0.3278$
Largest diff. peak/hole / e Å^{-3}	3.61/-1.51

Table S2. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å2$\times10^3$) for 25. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor of 25.

Atom	*x*	*y*	*z*	U(eq)
Br01	5459(2)	4494.2(3)	1586.0(11)	48.3(6)
N002	3720(18)	3143(3)	3577(9)	46.0(17)
N003	5727(17)	3396(3)	1470(9)	52(2)
N4	5052(19)	2976(3)	2279(10)	51.4(19)
C005	1530(20)	3336(3)	5893(12)	48(2)
C006	3490(19)	3664(3)	3644(12)	41.6(18)
C007	4810(20)	3819(3)	2283(10)	42.4(19)
C008	1360(20)	4275(3)	5722(12)	46(2)
C009	30(20)	4272(4)	7185(13)	48(2)
C00A	2090(20)	3804(3)	5079(11)	45(2)
C00B	-500(20)	3827(4)	7989(13)	48(2)
C00C	260(20)	3344(4)	7343(12)	49(2)
C00D	2540(20)	2872(3)	4942(11)	47(2)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for 25. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	62.3(9)	41.7(8)	44.5(9)	3.7(3)	19.0(6)	-2.5(3)
N002	59(4)	41(4)	41(4)	2(3)	17(3)	2(3)
N003	64(5)	53(5)	43(5)	1(3)	19(4)	-1(3)
N4	65(4)	45(4)	49(5)	-6(4)	22(4)	2(3)
C005	53(4)	42(5)	50(6)	0(4)	11(4)	-4(4)
C006	49(4)	27(4)	51(5)	1(4)	15(4)	3(3)
C007	55(4)	41(5)	34(4)	-3(3)	15(4)	-1(3)
C008	55(4)	31(5)	52(6)	2(4)	12(4)	5(4)
C009	56(5)	48(6)	43(5)	-5(4)	14(4)	1(4)
C00A	47(4)	51(5)	39(5)	2(4)	13(4)	-4(4)
C00B	61(5)	38(5)	49(5)	2(4)	19(4)	2(4)
C00C	54(5)	52(6)	43(5)	3(4)	19(4)	-3(4)
C00D	63(5)	36(5)	47(5)	5(4)	20(4)	-1(4)

Table S4. Bond Lengths for 25.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	C007	1.872(9)	C005	C00D	1.529(12)
N002	N4	1.353(10)	C006	C007	1.383(12)
N002	C006	1.352(10)	C006	C00A	1.445(13)
N002	C00D	1.472(10)	C008	C009	1.402(14)
N003	N4	1.329(11)	C008	C00A	1.383(12)
N003	C007	1.368(11)	C009	C00B	1.361(13)
C005	C00A	1.420(12)	C00B	C00C	1.413(13)
C005	C00C	1.380(15)			

Table S5. Bond Angles for 25.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N4	N002	C00D	132.7(7)	N003	C007	Br01	121.9(6)
C006	N002	N4	113.2(7)	N003	C007	C006	110.2(8)
C006	N002	C00D	114.1(7)	C006	C007	Br01	127.8(6)
N4	N003	C007	108.1(7)	C00A	C008	C009	117.7(8)
N003	N4	N002	106.2(7)	C00B	C009	C008	122.5(9)
C00A	C005	C00D	110.5(8)	C005	C00A	C006	106.7(8)
C00C	C005	C00A	120.4(8)	C008	C00A	C005	120.6(9)
C00C	C005	C00D	129.1(8)	C008	C00A	C006	132.6(9)
N002	C006	C007	102.3(7)	C009	C00B	C00C	120.1(9)
N002	C006	C00A	109.0(8)	C005	C00C	C00B	118.7(8)
C007	C006	C00A	148.7(8)	N002	C00D	C005	99.7(6)

Table S6. Torsion Angles for 25.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N002	C006	C007	Br01	-177.9(6)	C009	C008	C00A	C006	-179.0(9)
N002	C006	C007	N003	0.5(9)	C009	C00B	C00C	C005	-0.2(14)
N002	C006	C00A	C005	0.9(9)	C00A	C005	C00C	C00B	0.6(14)
N002	C006	C00A	C008	179.4(9)	C00A	C005	C00D	N002	0.9(9)
N4	N002	C006	C007	-0.4(9)	C00A	C006	C007	Br01	0.0(19)
N4	N002	C006	C00A	-179.2(7)	C00A	C006	C007	N003	178.4(12)
N4	N002	C00D	C005	178.3(8)	C00A	C008	C009	C00B	1.1(15)
N4	N003	C007	Br01	178.1(5)	C00C	C005	C00A	C006	178.6(8)
N4	N003	C007	C006	-0.4(10)	C00C	C005	C00A	C008	-0.1(14)
C006	N002	N4	N003	0.2(9)	C00C	C005	C00D	N002	-178.8(9)
C006	N002	C00D	C005	-0.3(9)	C00D	N002	N4	N003	-178.5(8)
C007	N003	N4	N002	0.2(9)	C00D	N002	C006	C007	178.5(7)
C007	C006	C00A	C005	-176.9(13)	C00D	N002	C006	C00A	-0.3(9)
C007	C006	C00A	C008	2(2)	C00D	C005	C00A	C006	-1.2(10)
C008	C009	C00B	C00C	-0.7(15)	C00D	C005	C00A	C008	-179.8(7)
C009	C008	C00A	C005	-0.7(14)	C00D	C005	C00C	C00B	-179.8(8)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 25.

Atom	*x*	*y*	*z*	U(eq)
H008	1744.87	4590.54	5191.4	55
H009	-522.44	4592.15	7631.92	58
H00B	-1386.68	3840.66	8984.43	58
H00C	-100.74	3031.62	7897.54	58
H00A	4305	2667.29	5661.54	57
H00D	644.21	2644.07	4490.96	57

X-ray crystallographic data of 3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (28).

Figure S2. ORTEP Drawing of 28.

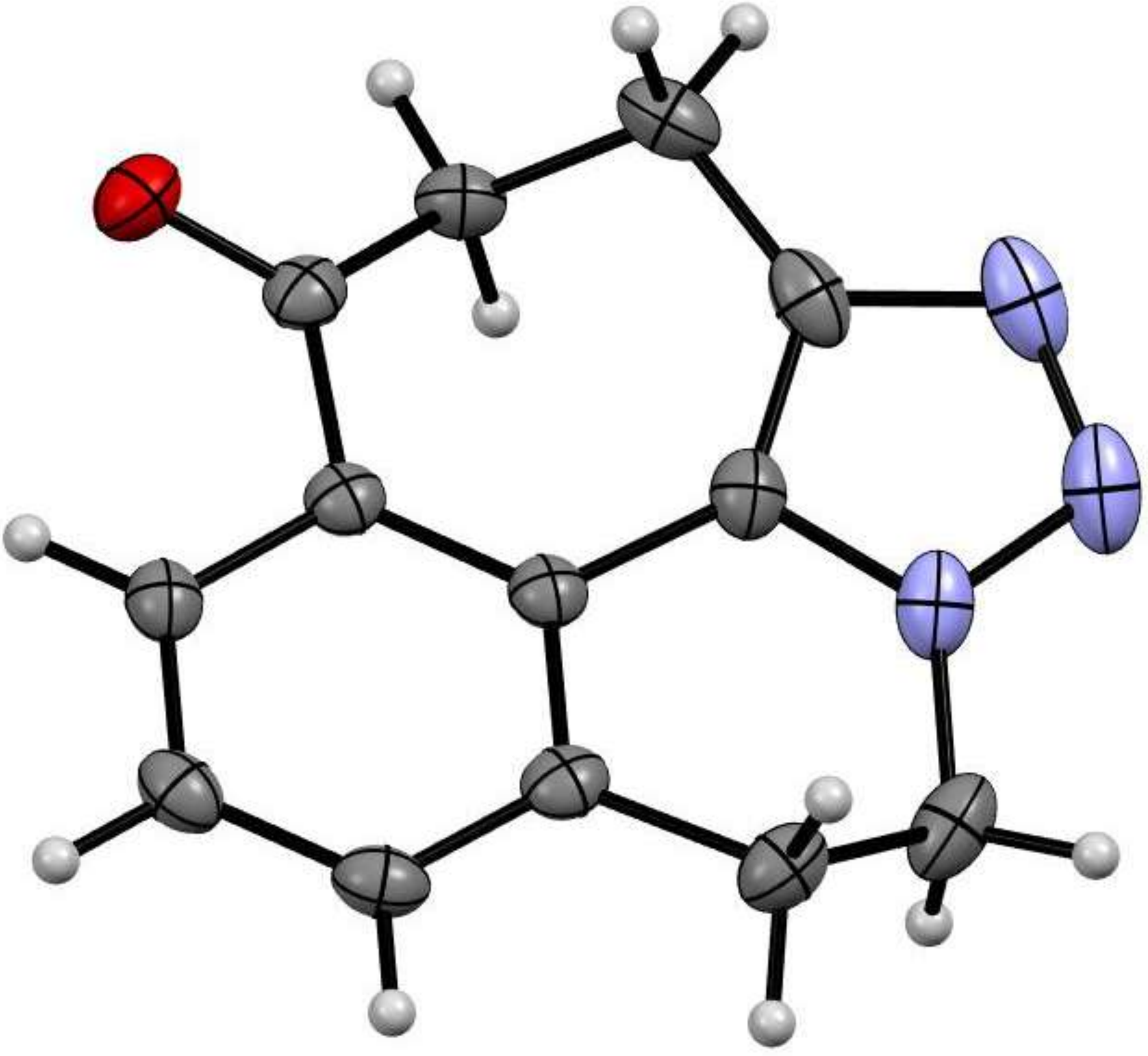


Table S8. Crystal data and structure refinement for 28.

Empirical formula	$C_{13}H_{11}N_3O$
Formula weight	225.25
Temperature/K	90
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.0182(5)
b/Å	13.7411(4)
c/Å	9.4416(5)
α/°	90
β/°	118.495(7)
γ/°	90
Volume/Å^3	1028.27(10)
Z	4
ρ_{calc}mg/mm^3	1.455
μ/mm^{-1}	0.778
F(000)	472.0
Crystal size/mm^3	0.136 × 0.029 × 0.015
2Θ range for data collection	11.17 to 148.796°
Index ranges	$-11 \le h \le 11, -17 \le k \le 16, -11 \le l \le 11$
Reflections collected	4567
Independent reflections	1928[R(int) = 0.0200]
Data/restraints/parameters	1928/0/154
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	$R_1 = 0.0399$, $wR_2 = 0.1123$
Final R indexes [all data]	$R_1 = 0.0456$, $wR_2 = 0.1162$
Largest diff. peak/hole / e Å^{-3}	0.27/-0.21

Table S9. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å2$\times10^3$) for 28. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor of 28.

Atom	*x*	*y*	*z*	U(eq)
O17	7755.6(13)	6474.4(7)	4380.5(13)	31.7(3)
N1	692.7(16)	6143.5(8)	1284.6(16)	30.7(3)
N13	-49.3(18)	6105.1(9)	-323.6(16)	38.3(4)
N12	1180.8(19)	6121.6(9)	-717.3(15)	38.5(4)
C5	3450.5(17)	6218.1(9)	3701.9(17)	22.6(3)
C14	6102.0(18)	6355.2(9)	6166.8(17)	25.2(3)
C6	5205.0(17)	6397.2(9)	4484.3(17)	22.7(3)
C4	2642.0(18)	5991.8(9)	4622.0(18)	25.1(3)
C11	2402.9(18)	6193.2(9)	1954.2(18)	25.1(3)
C16	3568.6(19)	5981.1(10)	6293.0(18)	28.0(3)
C7	6232.4(17)	6613.5(9)	3646.6(17)	25.0(3)
C15	5294.7(19)	6160.9(10)	7067.3(17)	28.0(3)
C10	2691(2)	6180.0(10)	644.6(17)	29.7(3)
C3	813.0(18)	5678.6(10)	3788.4(19)	30.2(3)
C8	5464.3(18)	7019.5(10)	1958.4(17)	27.5(3)
C9	4325(2)	6298.6(11)	646.6(18)	32.8(4)
C2	-234.4(19)	6185.2(11)	2189(2)	34.6(4)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 28. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O17	25.9(6)	31.0(5)	38.9(6)	1.1(4)	16.1(5)	3.5(4)
N1	27.8(7)	22.7(6)	31.4(7)	5.0(5)	5.8(6)	-3.0(5)
N13	37.2(8)	27.8(6)	31.2(7)	6.6(5)	1.2(6)	-8.2(5)
N12	50.3(9)	25.1(6)	25.8(7)	2.2(5)	6.6(6)	-9.8(6)
C5	25.5(7)	16.6(6)	25.3(7)	-1.2(5)	11.9(6)	1.8(5)
C14	25.8(7)	19.6(6)	26.4(8)	-1.3(5)	9.5(6)	1.1(5)
C6	25.2(7)	17.2(6)	26.0(7)	0.0(5)	12.5(6)	2.4(5)
C4	27.6(8)	17.2(6)	32.8(7)	-0.5(5)	16.4(7)	2.6(5)
C11	25.1(7)	17.6(6)	27.8(7)	0.8(5)	8.7(6)	-1.0(5)
C16	37.7(8)	22.0(6)	31.4(8)	-0.5(5)	22.2(7)	1.3(5)
C7	25.6(7)	19.2(6)	31.2(8)	-2.4(5)	14.3(7)	1.7(5)
C15	36.9(9)	22.3(6)	23.6(7)	-0.8(5)	13.4(7)	2.2(5)
C10	40.1(9)	19.4(6)	22.9(7)	-1.1(5)	9.5(7)	-3.4(6)
C3	27.6(8)	24.0(7)	41.5(9)	2.7(6)	18.5(7)	0.1(6)
C8	31.5(8)	26.1(7)	29.8(7)	0.5(5)	18.5(7)	0.7(5)
C9	48.2(10)	27.1(7)	28.3(8)	-2.2(5)	22.4(8)	1.1(6)
C2	22.5(8)	24.7(7)	51.1(10)	5.4(6)	13.0(7)	0.6(6)

Table S11. Bond Lengths for 28.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O17	C7	1.2229(16)	C14	C15	1.384(2)
N1	N13	1.3366(19)	C6	C7	1.5071(19)
N1	C11	1.3610(19)	C4	C16	1.389(2)
N1	C2	1.453(2)	C4	C3	1.512(2)
N13	N12	1.328(2)	C11	C10	1.379(2)
N12	C10	1.358(2)	C16	C15	1.390(2)
C5	C6	1.4123(19)	C7	C8	1.509(2)
C5	C4	1.4097(19)	C10	C9	1.482(2)
C5	C11	1.459(2)	C3	C2	1.515(2)
C14	C6	1.398(2)	C8	C9	1.535(2)

Table S12. Bond Angles for 28.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N13	N1	C11	111.83(13)	N1	C11	C5	120.35(13)
N13	N1	C2	123.53(13)	N1	C11	C10	103.83(13)
C11	N1	C2	124.55(13)	C10	C11	C5	135.79(14)
N12	N13	N1	106.56(12)	C4	C16	C15	120.75(13)
N13	N12	C10	109.28(13)	O17	C7	C6	118.52(13)
C6	C5	C11	123.71(13)	O17	C7	C8	118.79(12)
C4	C5	C6	119.73(13)	C6	C7	C8	122.67(12)
C4	C5	C11	116.46(13)	C14	C15	C16	119.77(13)
C15	C14	C6	121.14(13)	N12	C10	C11	108.49(14)
C5	C6	C7	125.15(13)	N12	C10	C9	123.72(14)
C14	C6	C5	118.92(13)	C11	C10	C9	127.57(14)
C14	C6	C7	115.91(12)	C4	C3	C2	113.23(12)
C5	C4	C3	119.90(13)	C7	C8	C9	114.00(11)
C16	C4	C5	119.64(13)	C10	C9	C8	110.74(12)
C16	C4	C3	120.26(13)	N1	C2	C3	107.91(12)

Table S13. Torsion Angles for 28.

Atom	*x*	*y*	*z*	U(eq)
H14	7286.31	6461.85	6700.97	30
H16	3016.52	5849.34	6913.68	34
H15	5917.71	6150.49	8210.65	34
H3A	319.56	5815.87	4505.85	36
H3B	756.66	4966.95	3605.9	36
H8A	6384.56	7227.66	1736.67	33
H8B	4794.17	7603.97	1896.96	33
H9A	4122.01	6538.47	-419.97	39
H9B	4898.16	5659.96	840.18	39
H2A	-1339.07	5856.53	1581.83	42
H2B	-437.11	6870.88	2369.52	42

X-ray crystallographic data of 5,6-dihydroindazolo[2’,3’:3,4][1,2,3]triazolo[5,1-*a*]isoquinolin-9-ium-10-ide (35).

Crystals were obtained by recrystallization of from hexane-ethyl acetate. A single crystal was mounted in a loop.

Figure S3. ORTEP Drawing of 35.

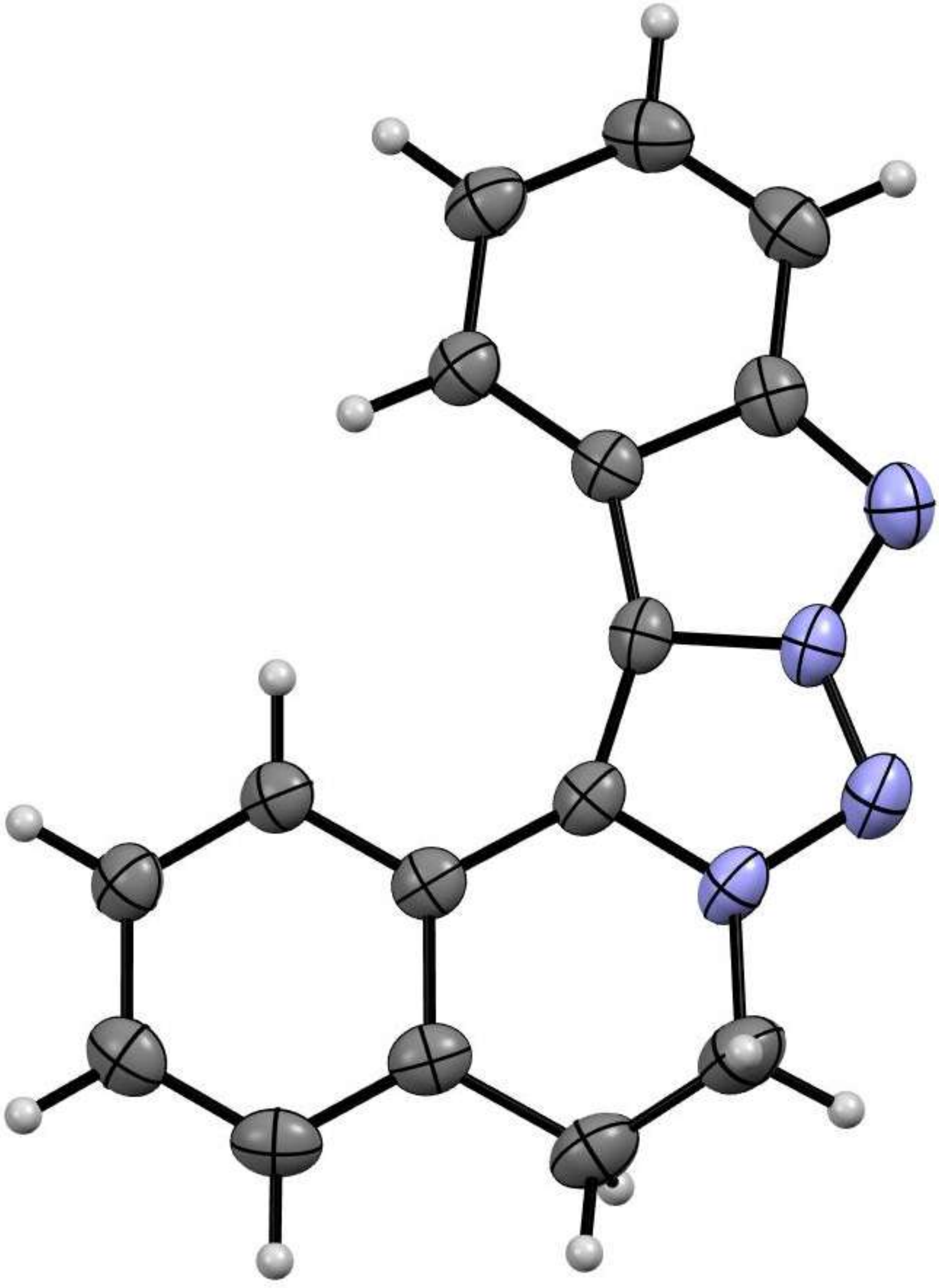


Table S14. Crystal data and structure refinement for 35.

Empirical formula	$C_{16}H_{12}N_4$
Formula weight	260.30
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a/Å	9.3536(3)
b/Å	10.4366(3)
c/Å	13.3657(4)
α/°	78.907(2)
β/°	79.540(3)
γ/°	76.410(3)
Volume/Å^3	1231.75(7)
Z	4
ρ_{calc}mg/mm^3	1.404
μ/mm^{-1}	0.694
F(000)	544.0
Crystal size/mm^3	0.414 × 0.062 × 0.017
2Θ range for data collection	6.81 to 148.726°
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-16 \le l \le 16$
Reflections collected	32072
Independent reflections	4815[R(int) = 0.0423]
Data/restraints/parameters	4815/528/361
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	$R_1 = 0.0595$, $wR_2 = 0.1376$
Final R indexes [all data]	$R_1 = 0.0699$, $wR_2 = 0.1434$
Largest diff. peak/hole / e Å^{-3}	0.51/-0.32

Table S15. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å2×10^3) for 35. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor of 35.

Atom	*x*	*y*	*z*	U(eq)
N28	6544(2)	5773.9(17)	8422.4(13)	31.9(4)
N11	7551(2)	7067.2(17)	8910.3(14)	33.8(4)
N20	5875(2)	5135.1(18)	7916.9(14)	35.5(4)
N25	3167(2)	7881.4(17)	5994.5(14)	34.9(4)
N26	1246(2)	9155.1(17)	6525.3(13)	33.9(4)
N22	4(2)	9775.7(19)	7061.9(14)	38.5(4)
N12	6870(2)	6978.9(18)	8121.0(14)	37.5(4)
N27	2055(2)	7942.0(19)	6798.5(14)	39.8(4)
C33	4233(2)	9025(2)	4374.0(15)	29.1(4)
C3	8348(2)	5977.5(19)	10552.0(15)	28.2(4)
C2	7646(2)	5994.2(19)	9665.7(15)	28.6(4)
C34	3074(2)	8973(2)	5256.4(16)	30.2(4)
C1	6976(2)	5108.1(19)	9346.1(15)	27.8(4)
C36	749(2)	11091(2)	5505.8(15)	29.0(4)
C35	1778(2)	9843(2)	5602.5(15)	29.3(4)
C19	6552(2)	3862(2)	9473.8(15)	27.8(4)
C14	5882(2)	3956(2)	8574.2(15)	31.1(4)
C18	6692(2)	2690(2)	10193.7(16)	31.7(4)
C28	5511(2)	7994(2)	4380.0(17)	33.0(5)
C40	593(2)	12276(2)	4794.6(16)	33.0(5)
C21	-294(2)	10971(2)	6424.3(16)	33.6(5)
C8	9096(2)	7013(2)	10527.3(17)	32.7(5)
C4	8323(2)	4965(2)	11393.8(16)	32.5(5)
C32	4131(2)	10079(2)	3556.0(16)	32.7(5)
C29	6647(2)	8050(2)	3547.9(18)	37.3(5)
C7	9795(2)	6993(2)	11371.6(18)	35.6(5)
C31	5287(2)	10137(2)	2759.5(16)	35.3(5)
C5	9059(2)	4943(2)	12207.7(17)	35.1(5)
C15	5327(2)	2874(2)	8420.9(17)	35.9(5)
C30	6549(3)	9112(2)	2751.8(17)	36.8(5)
C39	-577(3)	13318(2)	5010.9(18)	38.2(5)
C6	9792(2)	5966(2)	12193.7(17)	36.6(5)
C17	6184(3)	1632(2)	10008.8(17)	37.2(5)
C37	-1489(3)	12039(2)	6618.0(18)	38.9(5)
C16	5501(3)	1739(2)	9128.8(17)	38.7(5)
C38	-1605(3)	13184(2)	5919.5(18)	40.4(5)
C9	9180(3)	8046(2)	9578(2)	43.6(5)
C27	5647(3)	6929(2)	5310(2)	44.8(5)
C10	7932(3)	8308(2)	8979(2)	44.8(5)
C26	4234(3)	6642(2)	5902(2)	48.2(5)

Table S16. Anisotropic Displacement Parameters (Å^2×10^3) for 35. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+...].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N28	37.7(9)	28.7(9)	27.0(8)	-4.2(7)	-3.4(7)	-3.8(7)
N11	43.9(10)	26.1(9)	30.3(9)	-5.8(7)	-1.3(8)	-6.8(7)
N20	41.5(10)	36.9(10)	29.6(9)	-9.4(8)	-8.0(8)	-5.1(8)
N25	48.8(11)	26.7(9)	30.2(9)	-2.9(7)	-11.2(8)	-6.7(8)
N26	44.2(10)	31.7(9)	28.5(9)	-2.2(7)	-6.9(8)	-14.0(8)
N22	44.8(11)	40.7(10)	32.5(10)	-7.3(8)	-1.8(8)	-15.5(8)
N12	49.9(11)	30.4(9)	29.7(9)	-1.4(8)	-5.4(8)	-6.7(8)
N27	55.5(12)	33.3(10)	31.0(9)	-0.5(8)	-8.0(9)	-12.3(8)
C33	36.3(11)	27.7(10)	28.4(10)	-11.1(8)	-9.6(8)	-7.3(8)
C3	29.9(10)	25.1(9)	29.0(10)	-10.7(8)	1.0(8)	-3.3(8)
C2	32.4(10)	23.5(9)	28.1(10)	-6.0(8)	1.9(8)	-5.2(8)
C34	39.2(11)	27.7(10)	28.2(10)	-6.0(8)	-11.9(8)	-9.0(8)
C1	30.0(10)	27.3(10)	24.7(9)	-5.3(8)	-2.0(8)	-3.2(8)
C36	32.3(10)	32.1(10)	27.0(10)	-10.7(8)	-7.0(8)	-8.3(8)
C35	36.3(11)	30.7(10)	25.0(9)	-4.2(8)	-7.5(8)	-12.5(8)
C19	27.9(10)	30.4(10)	26.2(10)	-11.4(8)	-0.1(8)	-5.2(8)
C14	31.2(10)	35.2(11)	26.7(10)	-9.8(9)	-2.0(8)	-4.4(8)
C18	38.7(11)	32.8(10)	25.8(10)	-8.2(8)	-0.9(8)	-11.4(9)
C28	37.0(11)	27.8(10)	39.8(11)	-11.5(9)	-13.3(9)	-7.0(8)
C40	39.2(11)	33.2(11)	29.0(10)	-7.3(9)	-9.2(9)	-6.8(9)
C21	37.3(11)	38.4(11)	30.5(10)	-10.3(9)	-5.5(9)	-14.1(9)
C8	31.7(10)	26.6(10)	39.3(11)	-11.3(9)	0.9(9)	-4.9(8)
C4	38.4(11)	31.4(10)	30.2(10)	-10.2(9)	-0.5(9)	-11.1(9)
C32	38.3(11)	32.7(11)	28.6(10)	-9.8(9)	-8.1(9)	-3.8(9)
C29	36.4(11)	33.9(11)	46.1(13)	-18.8(10)	-11.2(10)	-2.2(9)
C7	33.6(11)	32.2(11)	44.8(12)	-16.1(10)	-0.5(9)	-9.8(8)
C31	43.7(12)	35.8(11)	27.9(10)	-8.4(9)	-7.1(9)	-7.3(9)
C5	44.1(12)	34.4(11)	28.4(10)	-7.7(9)	-4.2(9)	-9.5(9)
C15	35.4(11)	46.3(12)	30.7(11)	-15.8(10)	-2.8(9)	-11.2(9)
C30	39.2(12)	42.5(12)	33.7(11)	-18.5(10)	-4.3(9)	-8.9(9)
C39	47.3(13)	33.7(11)	35.3(11)	-7.8(9)	-15.5(10)	-2.5(9)
C6	37.7(11)	41.3(12)	34.6(11)	-17.6(10)	-3.7(9)	-7.5(9)
C17	49.9(13)	34.4(11)	30.2(11)	-6.1(9)	0.1(9)	-17.8(9)
C37	36.2(11)	49.6(13)	35.9(11)	-19.5(10)	-3.0(9)	-10.0(10)
C16	45.0(12)	42.7(12)	35.3(11)	-17.0(10)	2.0(10)	-19.9(10)
C38	40.1(12)	45.1(13)	39.1(12)	-20.2(10)	-10.9(10)	0.0(10)
C9	51.4(11)	31.0(9)	49.8(11)	-4.4(8)	-5.2(9)	-14.7(8)
C27	52.6(11)	30.7(9)	50.9(11)	-4.8(8)	-16.5(9)	-2.9(8)
C10	56.8(11)	31.8(9)	47.3(11)	-4.3(8)	-3.7(9)	-16.3(8)
C26	57.5(11)	34.1(9)	48.8(11)	-2.4(9)	-15.3(9)	1.5(9)

Table S17. Bond Lengths for 35.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N28	N20	1.347(2)	C36	C40	1.403(3)
N28	N12	1.333(2)	C36	C21	1.428(3)
N28	C1	1.375(3)	C19	C14	1.431(3)
N11	N12	1.355(3)	C19	C18	1.399(3)
N11	C2	1.353(3)	C14	C15	1.410(3)
N11	C10	1.445(3)	C18	C17	1.378(3)
N20	C14	1.367(3)	C28	C29	1.394(3)
N25	N27	1.353(3)	C28	C27	1.502(3)
N25	C34	1.353(3)	C40	C39	1.383(3)
N25	C26	1.448(3)	C21	C37	1.407(3)
N26	N22	1.344(3)	C8	C7	1.397(3)
N26	N27	1.334(3)	C8	C9	1.502(3)
N26	C35	1.374(3)	C4	C5	1.383(3)
N22	C21	1.369(3)	C32	C31	1.376(3)
C33	C34	1.452(3)	C29	C30	1.380(3)
C33	C28	1.408(3)	C7	C6	1.380(3)
C33	C32	1.393(3)	C31	C30	1.394(3)
C3	C2	1.451(3)	C5	C6	1.393(3)
C3	C8	1.411(3)	C15	C16	1.364(3)
C3	C4	1.388(3)	C39	C38	1.412(3)
C2	C1	1.397(3)	C17	C16	1.412(3)
C34	C35	1.396(3)	C37	C38	1.363(3)
C1	C19	1.417(3)	C9	C10	1.477(3)
C36	C35	1.425(3)	C27	C26	1.476(4)

Table S18. Bond Angles for 35.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N20	N28	C1	117.07(17)	C34	C35	C36	151.9(2)
N12	N28	N20	127.49(17)	C1	C19	C14	103.38(17)
N12	N28	C1	115.42(17)	C18	C19	C1	136.18(19)
N12	N11	C10	120.33(18)	C18	C19	C14	120.39(18)
C2	N11	N12	115.08(17)	N20	C14	C19	114.13(18)
C2	N11	C10	123.99(19)	N20	C14	C15	125.85(19)
N28	N20	C14	100.94(16)	C15	C14	C19	120.00(19)
N27	N25	C34	115.38(18)	C17	C18	C19	118.44(19)
N27	N25	C26	119.80(18)	C33	C28	C27	119.0(2)
C34	N25	C26	124.3(2)	C29	C28	C33	118.5(2)
N22	N26	C35	117.32(17)	C29	C28	C27	122.4(2)
N27	N26	N22	127.18(18)	C39	C40	C36	118.5(2)
N27	N26	C35	115.49(19)	N22	C21	C36	114.30(19)
N26	N22	C21	100.87(17)	N22	C21	C37	125.6(2)
N28	N12	N11	100.85(15)	C37	C21	C36	120.1(2)
N26	N27	N25	100.61(16)	C3	C8	C9	119.0(2)
C28	C33	C34	118.00(19)	C7	C8	C3	118.3(2)
C32	C33	C34	121.89(19)	C7	C8	C9	122.69(19)
C32	C33	C28	120.1(2)	C5	C4	C3	120.34(19)
C8	C3	C2	117.92(18)	C31	C32	C33	120.4(2)
C4	C3	C2	121.65(18)	C30	C29	C28	121.0(2)
C4	C3	C8	120.41(19)	C6	C7	C8	120.87(19)
N11	C2	C3	120.00(18)	C32	C31	C30	119.9(2)
N11	C2	C1	104.85(17)	C4	C5	C6	119.6(2)
C1	C2	C3	135.15(18)	C16	C15	C14	118.1(2)
N25	C34	C33	119.76(19)	C29	C30	C31	120.0(2)
N25	C34	C35	104.71(19)	C40	C39	C38	120.7(2)
C35	C34	C33	135.50(19)	C7	C6	C5	120.4(2)
N28	C1	C2	103.80(17)	C18	C17	C16	120.9(2)
N28	C1	C19	104.47(17)	C38	C37	C21	118.4(2)
C2	C1	C19	151.69(19)	C15	C16	C17	122.1(2)
C35	C36	C21	103.25(18)	C37	C38	C39	122.0(2)
C40	C36	C35	136.5(2)	C10	C9	C8	115.4(2)
C40	C36	C21	120.21(19)	C26	C27	C28	115.8(2)
N26	C35	C34	103.82(17)	N11	C10	C9	110.12(19)
N26	C35	C36	104.27(18)	N25	C26	C27	109.5(2)

Table S19. Torsion Angles for 35.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N28	N20	C14	C19	-0.3(2)	C1	C19	C14	C15	179.28(19)
N28	N20	C14	C15	-179.0(2)	C1	C19	C18	C17	-176.3(2)
N28	C1	C19	C14	-0.5(2)	C36	C40	C39	C38	-1.0(3)
N28	C1	C19	C18	176.8(2)	C36	C21	C37	C38	-1.0(3)
N11	C2	C1	N28	-0.4(2)	C35	N26	N22	C21	0.2(2)
N11	C2	C1	C19	176.5(4)	C35	N26	N27	N25	0.5(2)
N20	N28	N12	N11	-178.42(19)	C35	C36	C40	C39	-177.3(2)
N20	N28	C1	C2	178.83(17)	C35	C36	C21	N22	-0.1(2)
N20	N28	C1	C19	0.4(2)	C35	C36	C21	C37	178.89(18)
N20	C14	C15	C16	176.2(2)	C19	C14	C15	C16	-2.4(3)
N25	C34	C35	N26	0.2(2)	C19	C18	C17	C16	-1.7(3)
N25	C34	C35	C36	176.8(3)	C14	C19	C18	C17	0.6(3)
N26	N22	C21	C36	-0.1(2)	C14	C15	C16	C17	1.4(3)
N26	N22	C21	C37	-178.98(19)	C18	C19	C14	N20	-177.33(19)
N22	N26	N27	N25	-177.88(19)	C18	C19	C14	C15	1.5(3)
N22	N26	C35	C34	178.06(17)	C18	C17	C16	C15	0.7(4)
N22	N26	C35	C36	-0.3(2)	C28	C33	C34	N25	-7.4(3)
N22	C21	C37	C38	177.9(2)	C28	C33	C34	C35	170.1(2)
N12	N28	N20	C14	178.4(2)	C28	C33	C32	C31	-1.3(3)
N12	N28	C1	C2	0.2(2)	C28	C29	C30	C31	-1.5(3)
N12	N28	C1	C19	-178.25(17)	C28	C27	C26	N25	-42.1(3)
N12	N11	C2	C3	-179.79(18)	C40	C36	C35	N26	178.4(2)
N12	N11	C2	C1	0.4(2)	C40	C36	C35	C34	1.8(5)
N12	N11	C10	C9	-155.3(2)	C40	C36	C21	N22	-178.66(18)
N27	N25	C34	C33	178.30(17)	C40	C36	C21	C37	0.3(3)
N27	N25	C34	C35	0.1(2)	C40	C39	C38	C37	0.3(3)
N27	N25	C26	C27	-154.1(2)	C21	C36	C35	N26	0.2(2)
N27	N26	N22	C21	178.57(19)	C21	C36	C35	C34	-176.4(3)
N27	N26	C35	C34	-0.5(2)	C21	C36	C40	C39	0.7(3)
N27	N26	C35	C36	-178.82(17)	C21	C37	C38	C39	0.7(3)
C33	C34	C35	N26	-177.6(2)	C8	C3	C2	N11	-8.6(3)
C33	C34	C35	C36	-1.0(5)	C8	C3	C2	C1	171.1(2)
C33	C28	C29	C30	2.3(3)	C8	C3	C4	C5	-1.5(3)
C33	C28	C27	C26	28.9(3)	C8	C7	C6	C5	-1.6(3)
C33	C32	C31	C30	2.1(3)	C8	C9	C10	N11	-42.2(3)
C3	C2	C1	N28	179.9(2)	C4	C3	C2	N11	172.78(19)
C3	C2	C1	C19	-3.2(6)	C4	C3	C2	C1	-7.5(4)
C3	C8	C7	C6	2.0(3)	C4	C3	C8	C7	-0.4(3)
C3	C8	C9	C10	28.9(3)	C4	C3	C8	C9	176.3(2)
C3	C4	C5	C6	1.9(3)	C4	C5	C6	C7	-0.4(3)
C2	N11	N12	N28	-0.3(2)	C32	C33	C34	N25	174.93(18)
C2	N11	C10	C9	33.9(3)	C32	C33	C34	C35	-7.5(3)
C2	C3	C8	C7	-179.05(18)	C32	C33	C28	C29	-0.9(3)

C2	C3	C8	C9	-2.3(3)	C32	C33	C28	C27	175.07(19)
C2	C3	C4	C5	177.1(2)	C32	C31	C30	C29	-0.7(3)
C2	C1	C19	C14	-177.3(4)	C29	C28	C27	C26	-155.4(2)
C2	C1	C19	C18	-0.1(6)	C7	C8	C9	C10	-154.5(2)
C34	N25	N27	N26	-0.3(2)	C9	C8	C7	C6	-174.7(2)
C34	N25	C26	C27	34.8(3)	C27	C28	C29	C30	-173.5(2)
C34	C33	C28	C29	-178.56(18)	C10	N11	N12	N28	-171.83(19)
C34	C33	C28	C27	-2.6(3)	C10	N11	C2	C3	-8.6(3)
C34	C33	C32	C31	176.27(18)	C10	N11	C2	C1	171.6(2)
C1	N28	N20	C14	-0.1(2)	C26	N25	N27	N26	-172.25(19)
C1	N28	N12	N11	0.0(2)	C26	N25	C34	C33	-10.2(3)
C1	C19	C14	N20	0.5(2)	C26	N25	C34	C35	171.6(2)

Table S20. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 35.

Atom	*x*	*y*	*z*	U(eq)
H18	7126.91	2624.39	10795.84	38
H40	1276.59	12360.68	4178.1	40
H4	7796.85	4283.38	11410.89	39
H32	3258.42	10763.07	3548.03	39
H29	7500.08	7345.35	3528.64	45
H7	10277.48	7695.53	11379.61	43
H31	5224.8	10873.63	2215.49	42
H5	9065.28	4234.76	12773.15	42
H15	4845.29	2935.01	7840.9	43
H30	7342.65	9146.02	2198.15	44
H39	-690.55	14133.23	4543.24	46
H6	10293.46	5955.78	12753.73	44
H17	6295.51	819.72	10479.86	45
H37	-2198.12	11964.54	7221.52	47
H16	5152.25	996	9026.39	46
H38	-2402.36	13913.82	6047.96	48
H9A	9231.72	8893.47	9784.33	52
H9B	10115.75	7757.65	9122.56	52
H27A	6254.33	6094.54	5083.01	54
H27B	6194.65	7196.92	5776.39	54
H10A	7059.48	8891.58	9317.17	54
H10B	8216.51	8774.84	8278.54	54
H26A	3842.89	6075.59	5547.26	58
H26B	4404.68	6150.55	6595.32	58

Photophysical properties of 5,6-Dihydroindazolo[2’,3’:3,4][1,2,3]triazolo[5,1-*a*]isoquinolin-9-ium-10-ide (35).

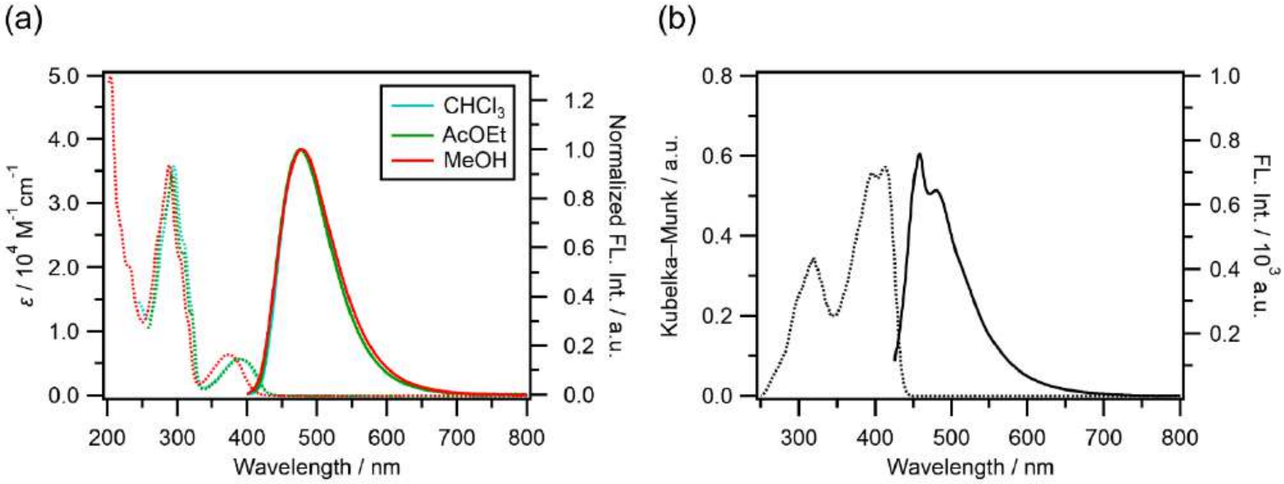
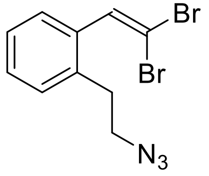
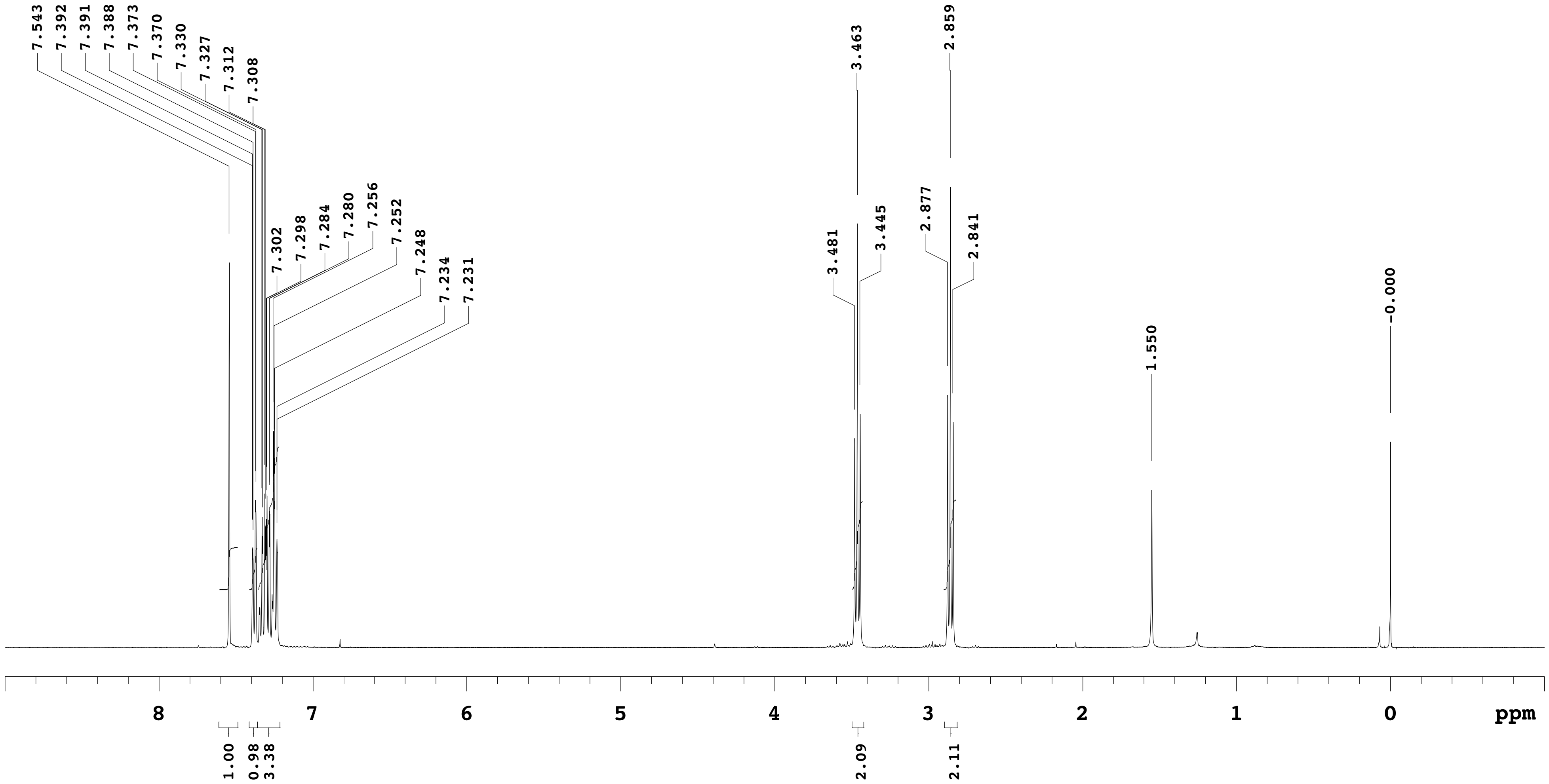


Figure S4. (a) Absorption (dotted lines on the left axis) and fluorescence (solid lines on the right axis) spectra of **35** (20 mM) in various solvents. The sky-blue, green, and red lines indicate conditions using *n*-hexane, $CHCl_3$, AcOEt, and MeOH, respectively. (b) Kubelka-Munk diffuse reflectance spectra (dotted lines on the left axis) and fluorescence (solid lines on the right axis) spectra of **35** in the solid state.

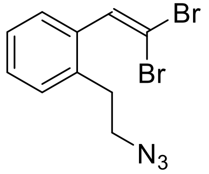
1-(2-Azidoethyl)-2-(2,2-dibromovinyl)benzene (9).

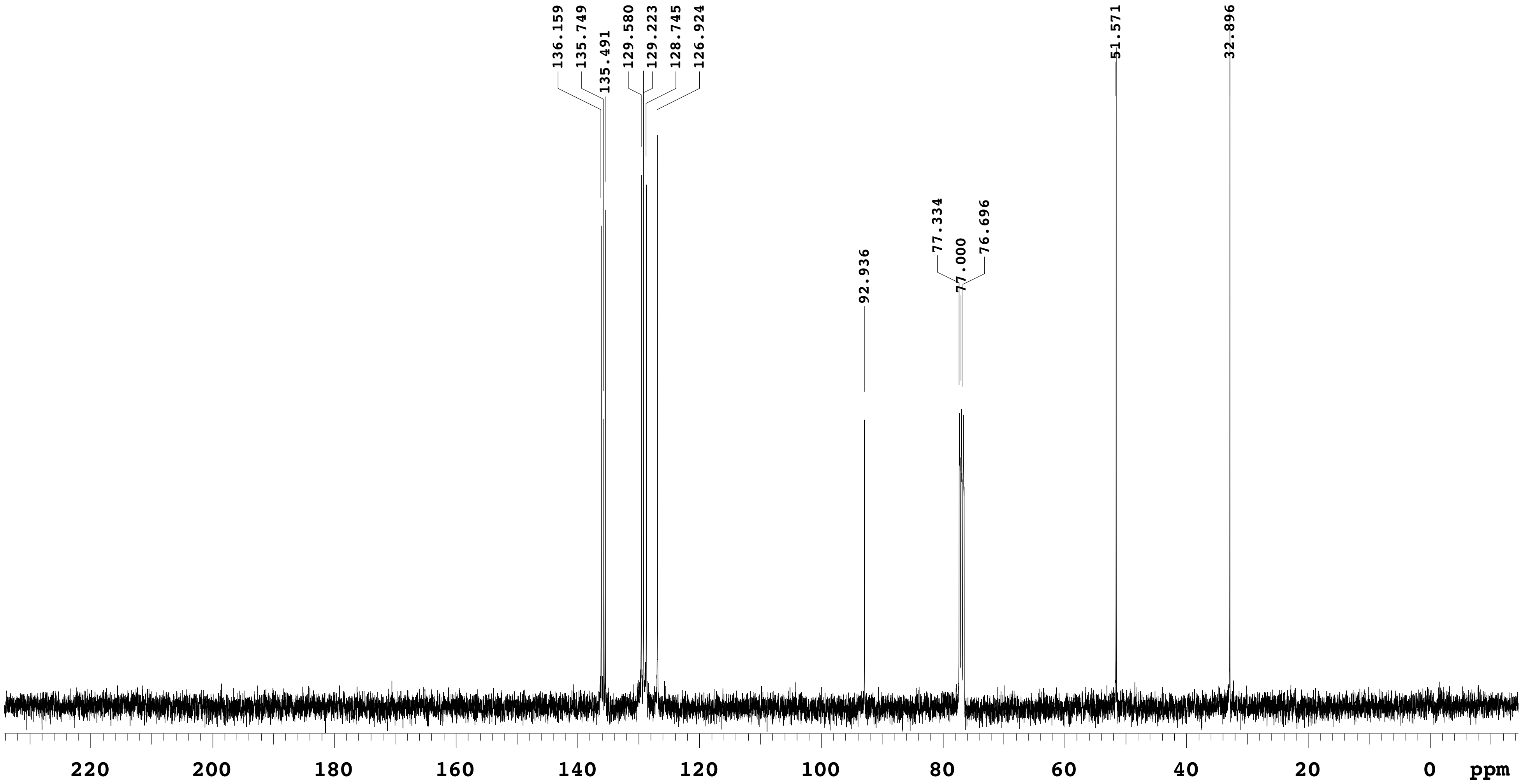
^{1}H NMR





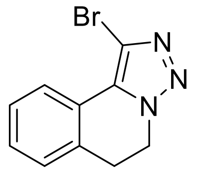
1-(2-Azidoethyl)-2-(2,2-dibromovinyl)benzene (9). ^{13}C NMR

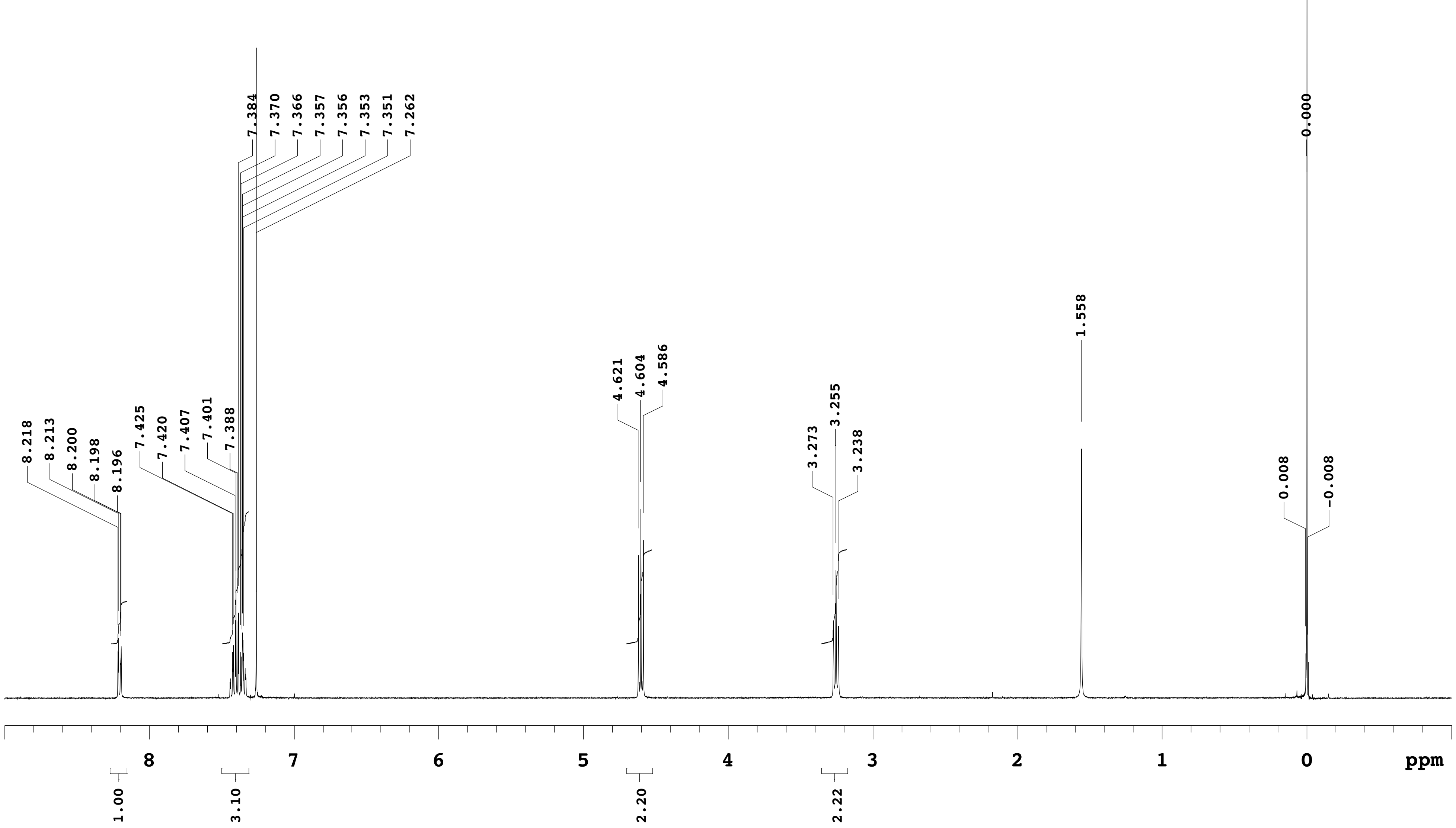




1-Bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (10).

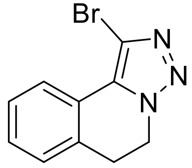
^{1}H NMR

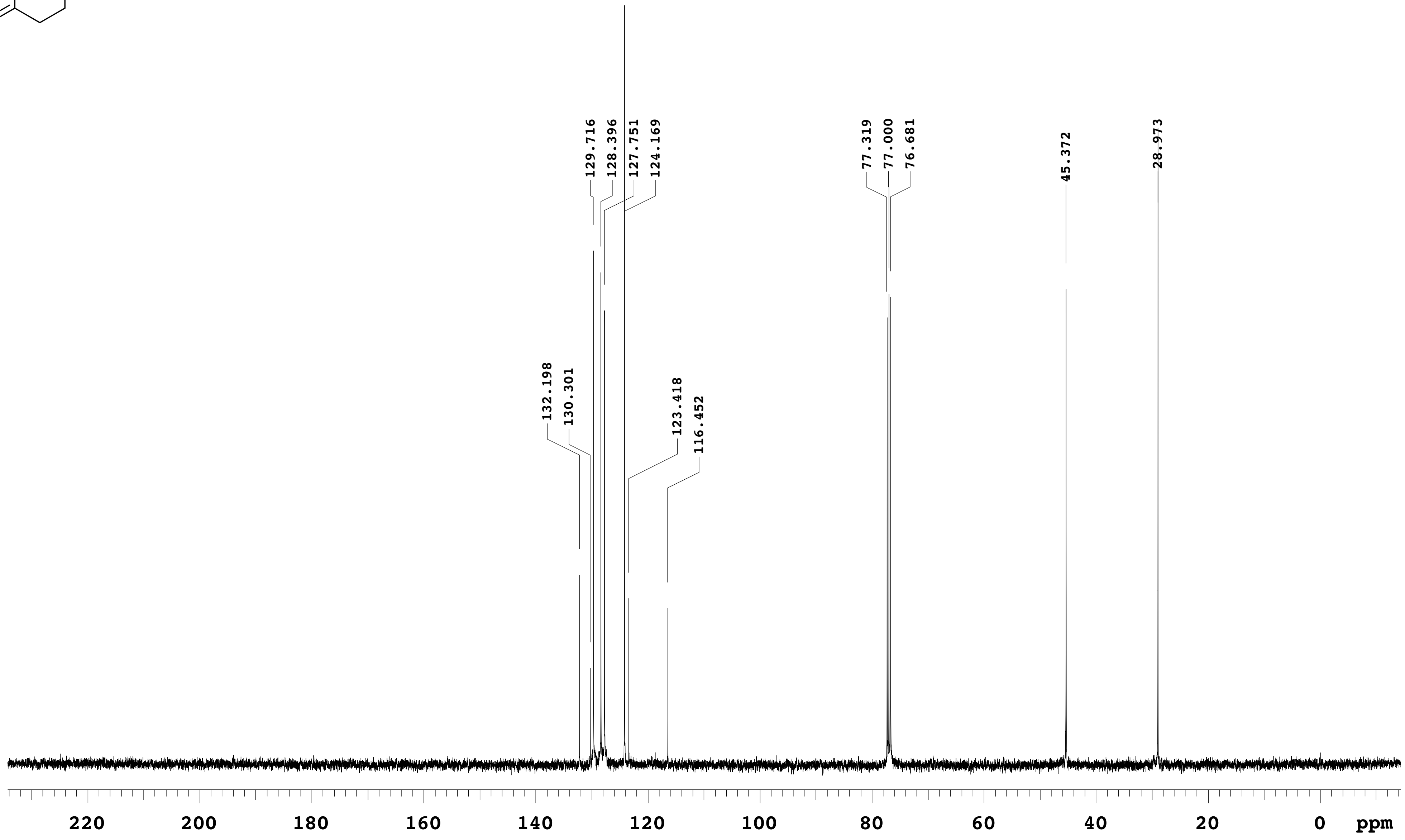




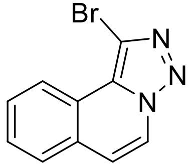
1-Bromo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (10).

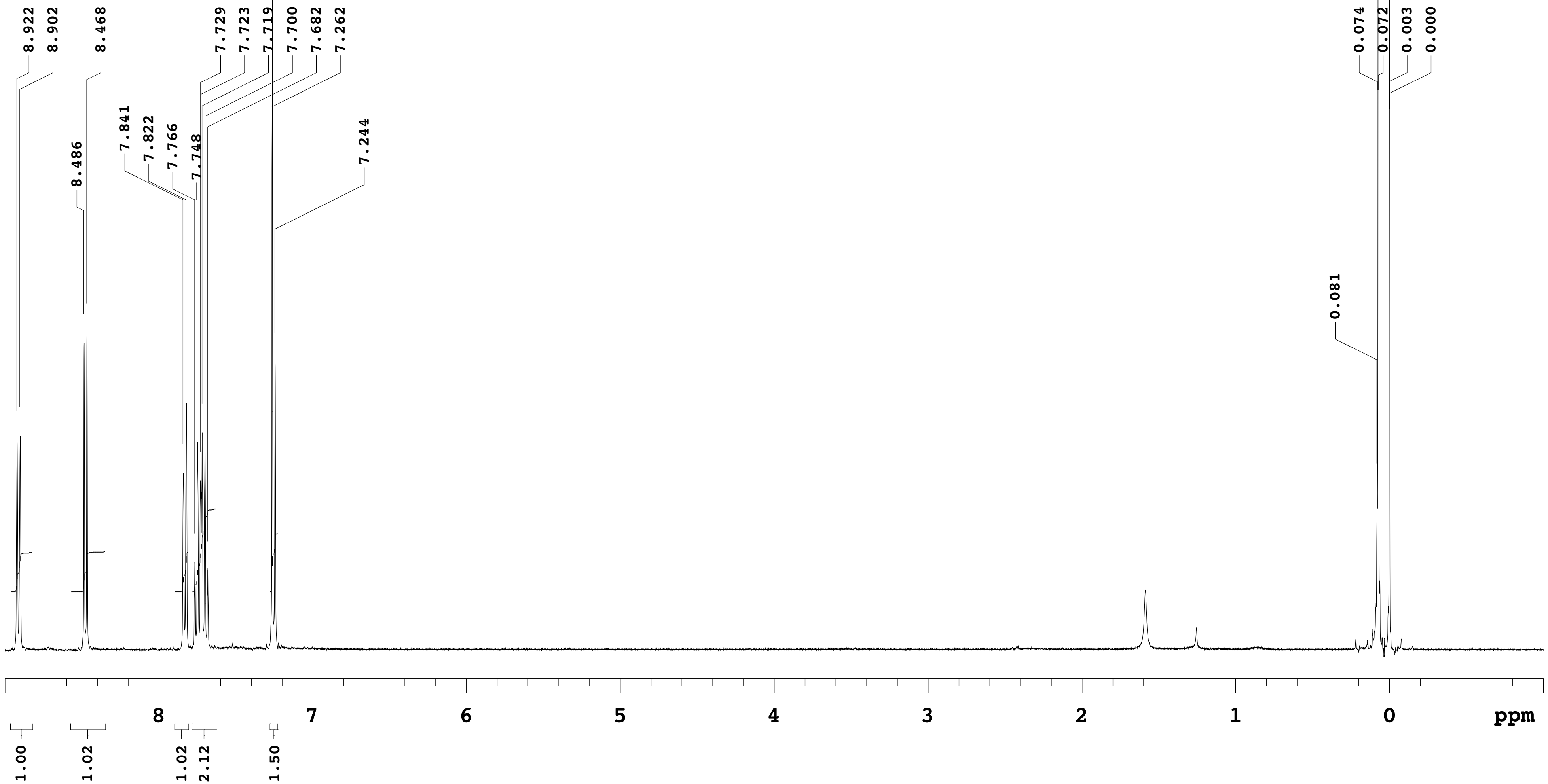
^{13}C NMR



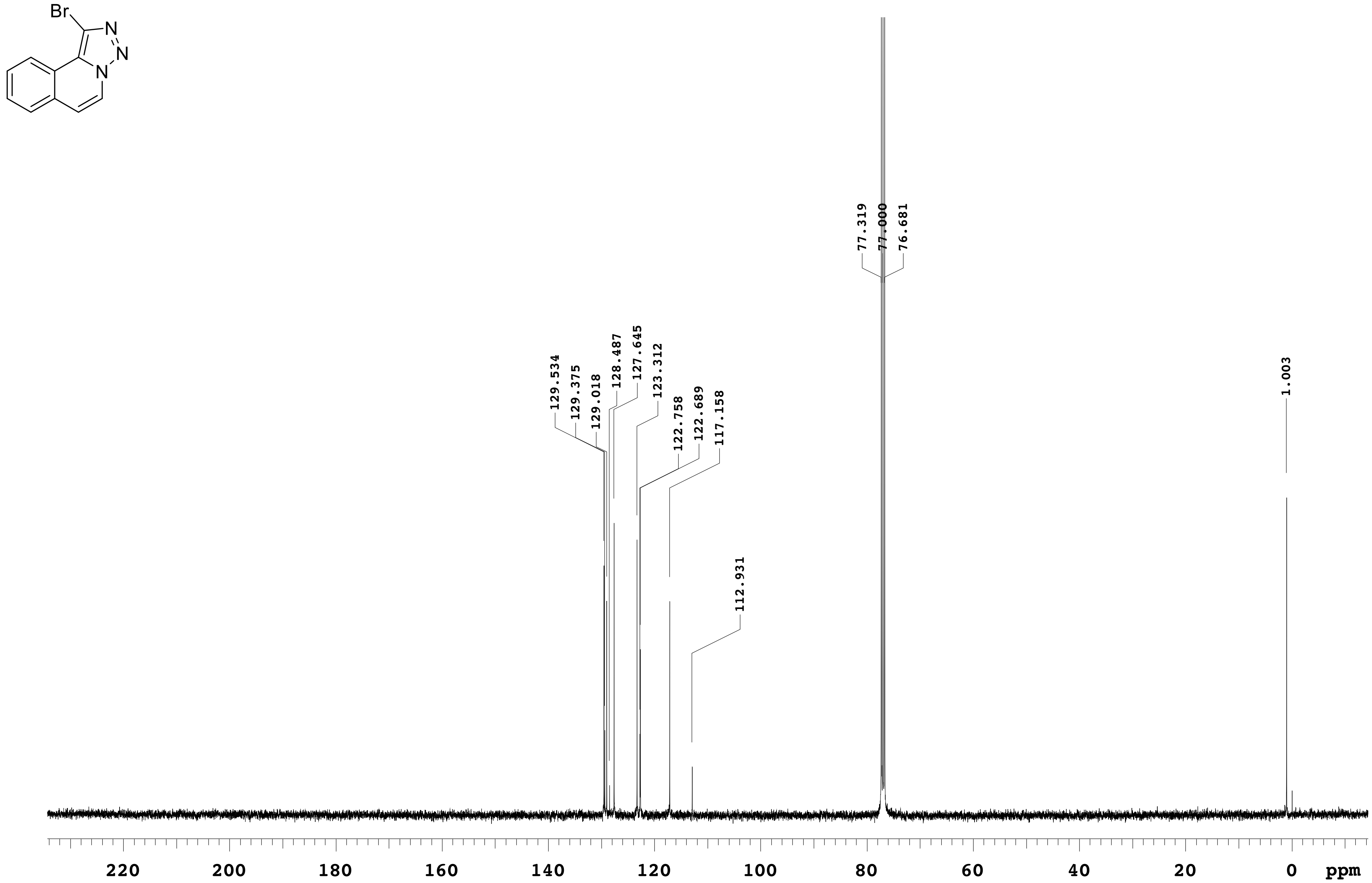


1-Bromo-[1,2,3]triazolo[5,1-*a*]isoquinoline (11). ^{1}H NMR



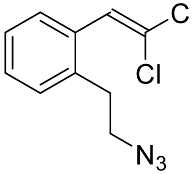


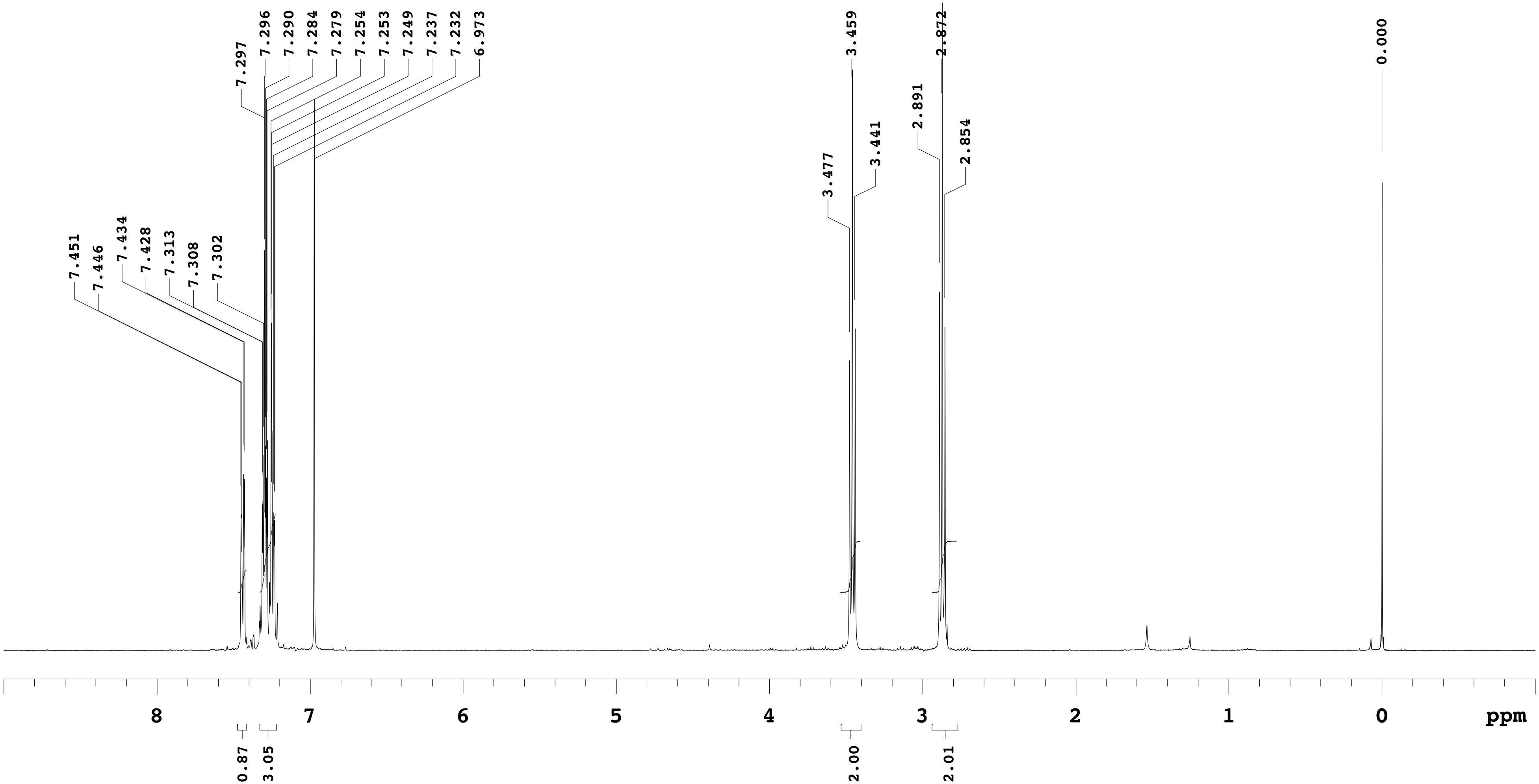
1-Bromo-[1,2,3]triazolo[5,1-*a*]isoquinoline (11). **^{13}C NMR**



1-(2-Azidoethyl)-2-(2,2-dichlorovinyl)benzene (12).

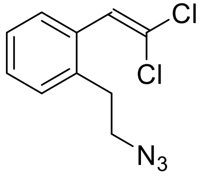
^{1}H NMR

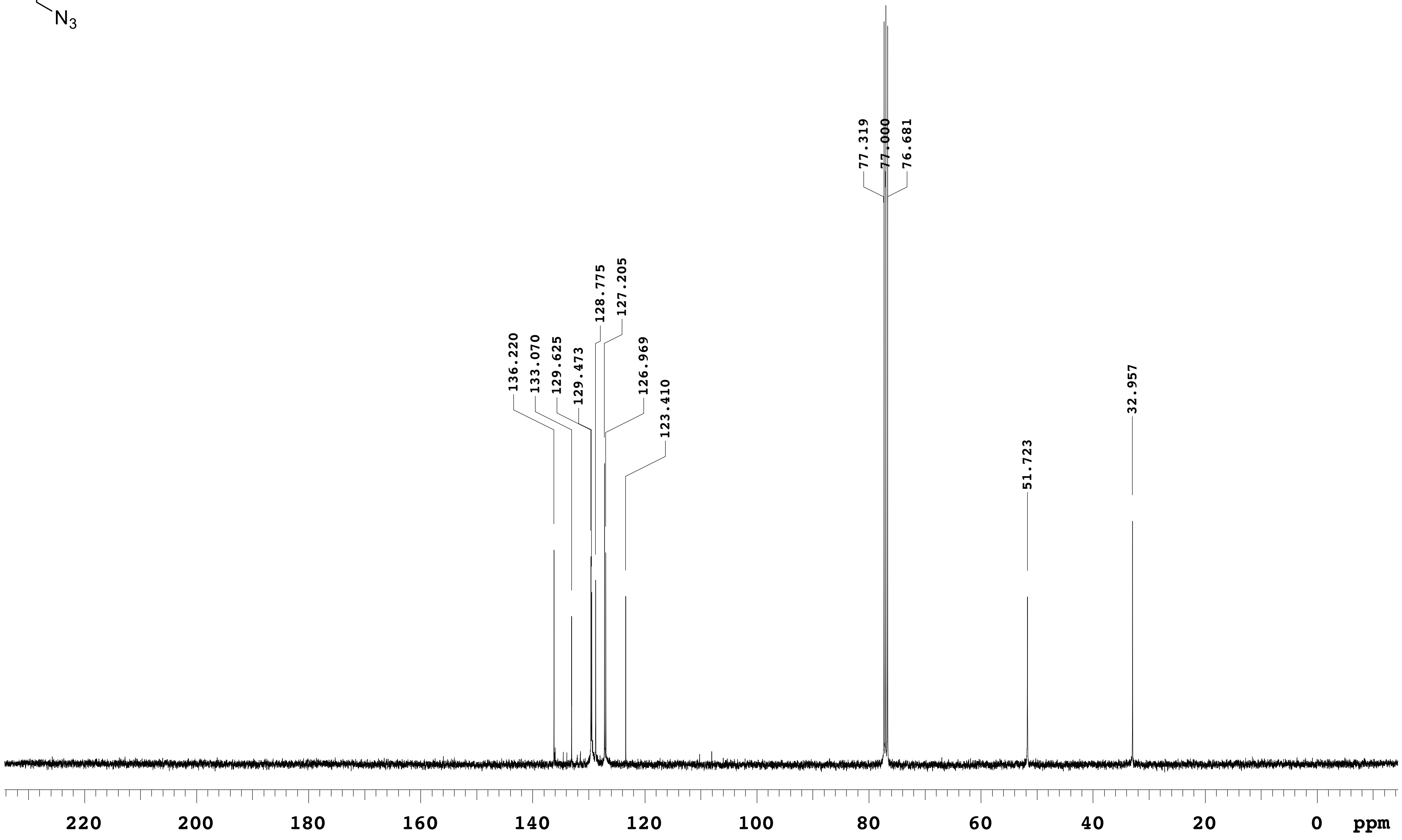




1-(2-Azidoethyl)-2-(2,2-dichlorovinyl)benzene (12).

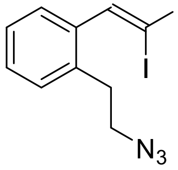
^{13}C NMR

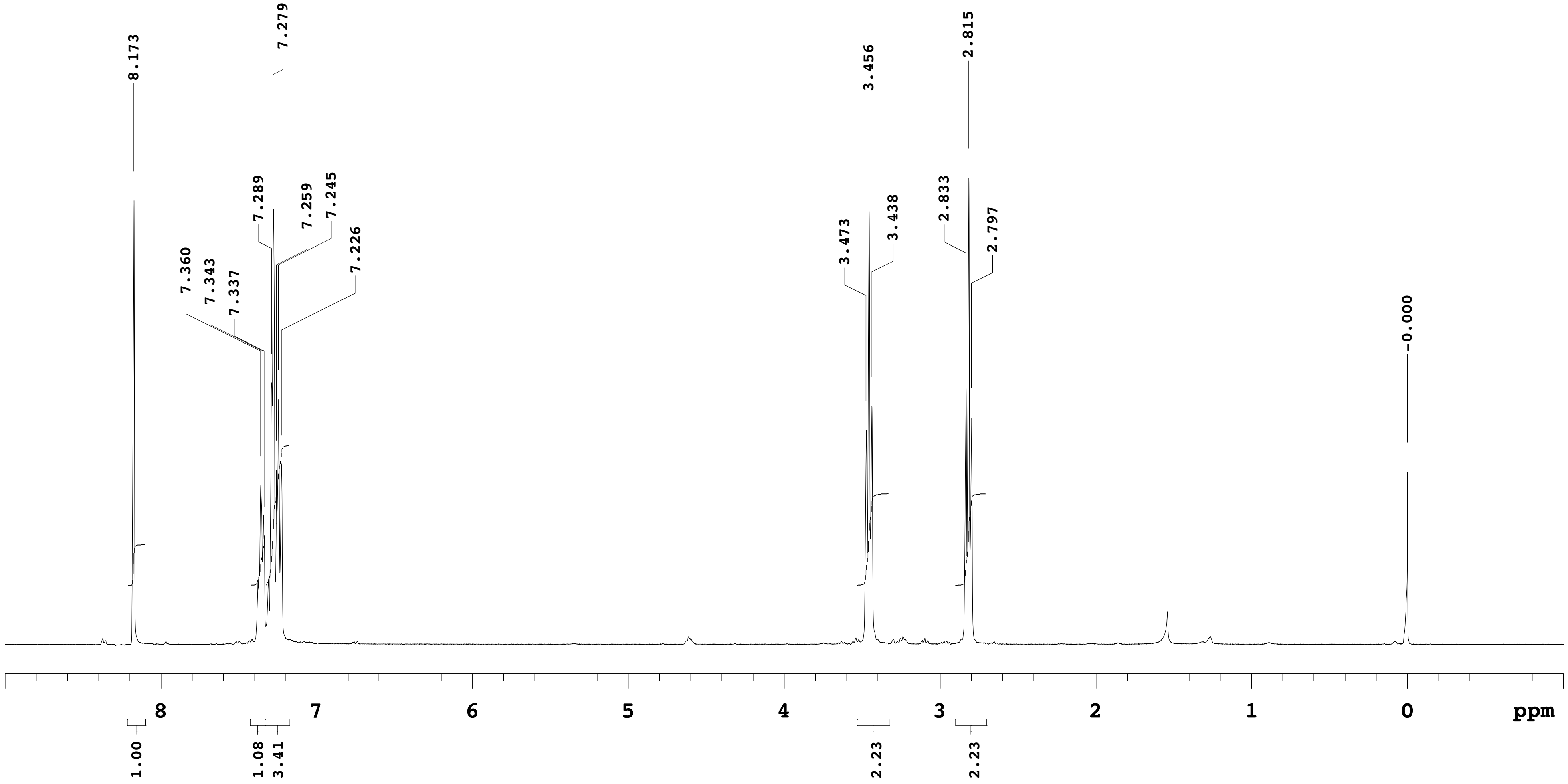




1-(2-Azidoethyl)-2-(2,2-diiodovinyl)benzene (13).

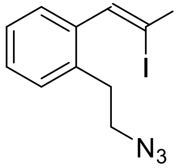
^{1}H NMR

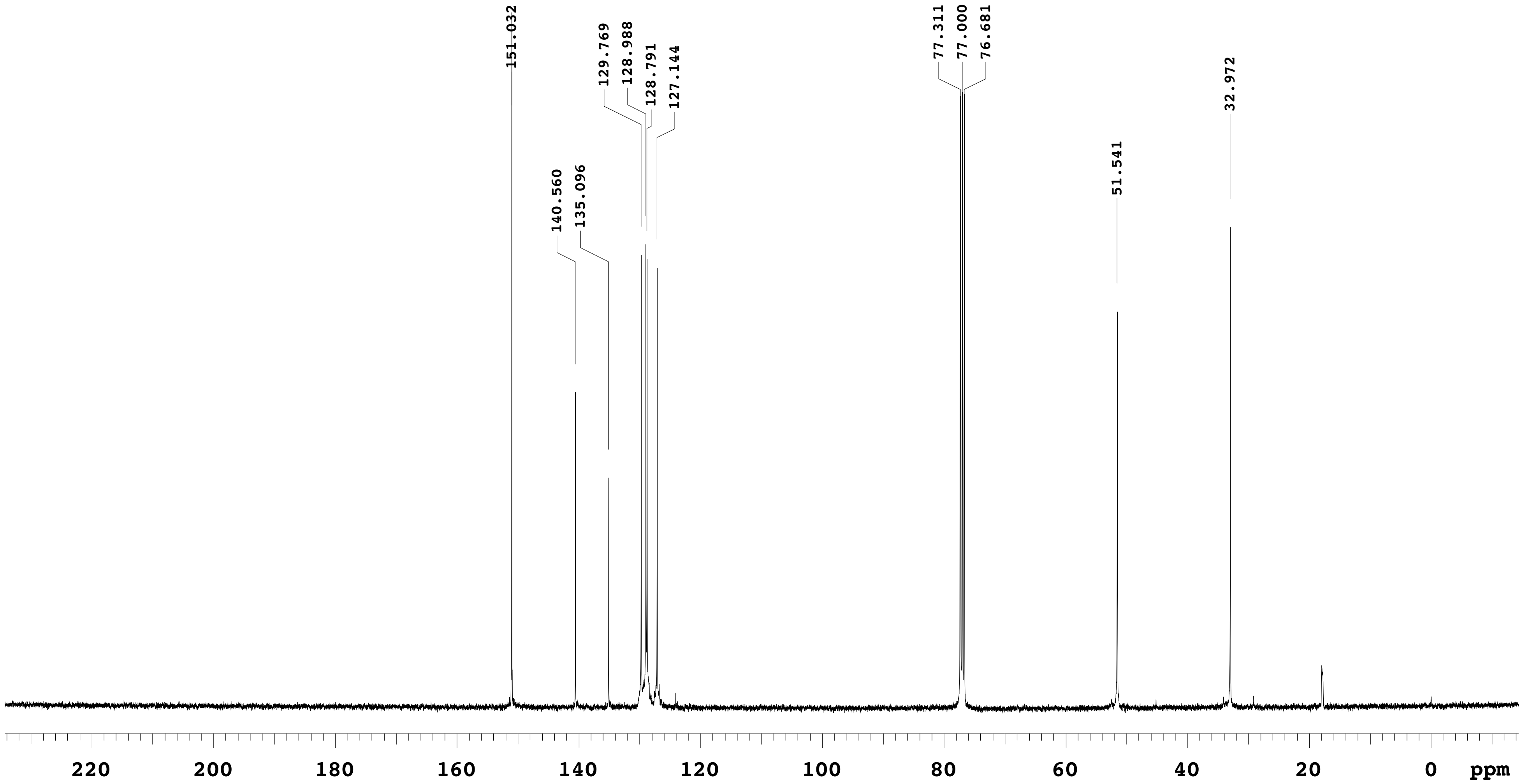




1-(2-Azidoethyl)-2-(2,2-diiodovinyl)benzene (13).

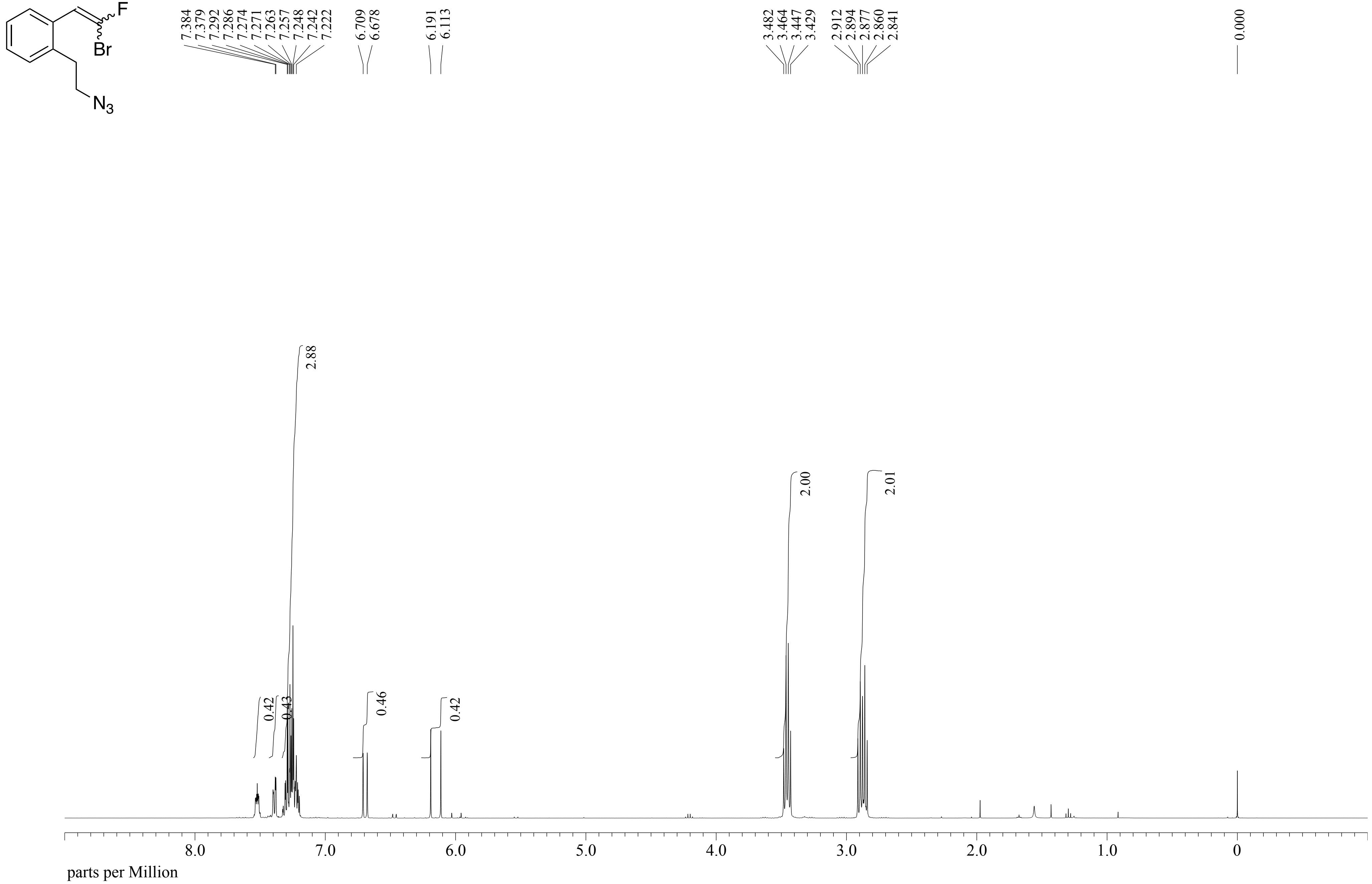
^{13}C NMR



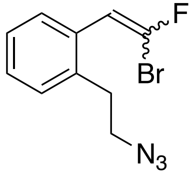


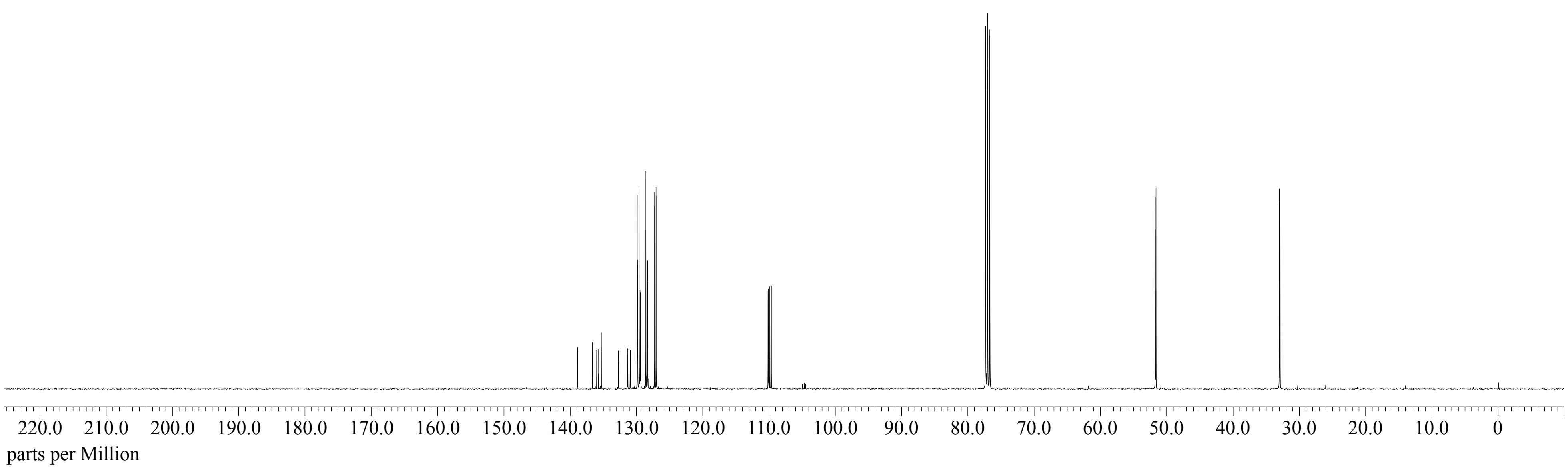
52:48 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (14).

^{1}H NMR



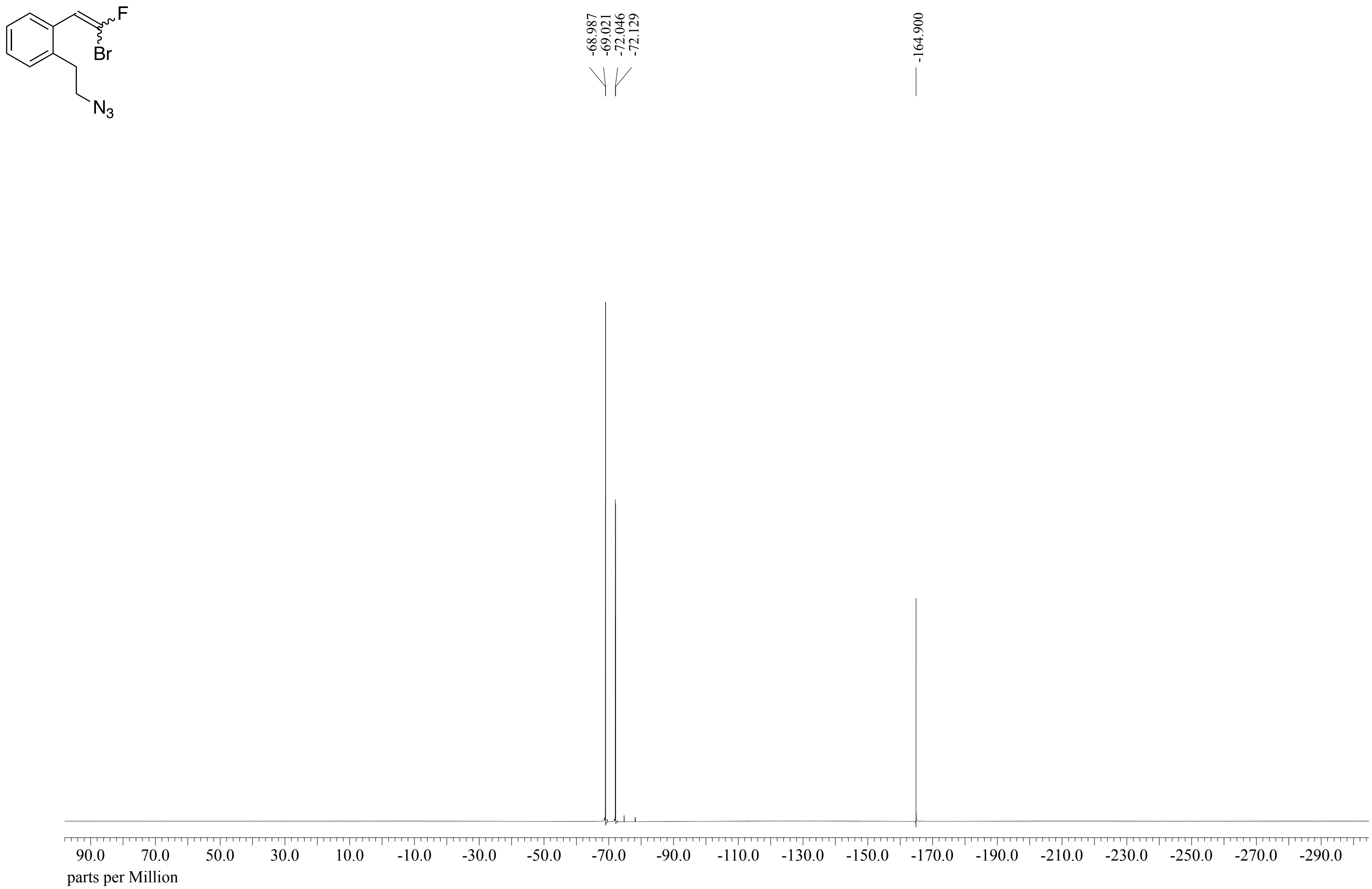
52:48 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (14). ^{13}C NMR





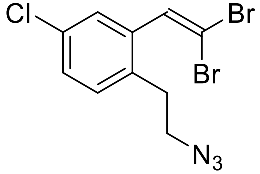
52:48 *Z*/*E* mixture of 1-(2-azidoethyl)-2-(2-bromo-2-fluorovinyl)benzene (14).

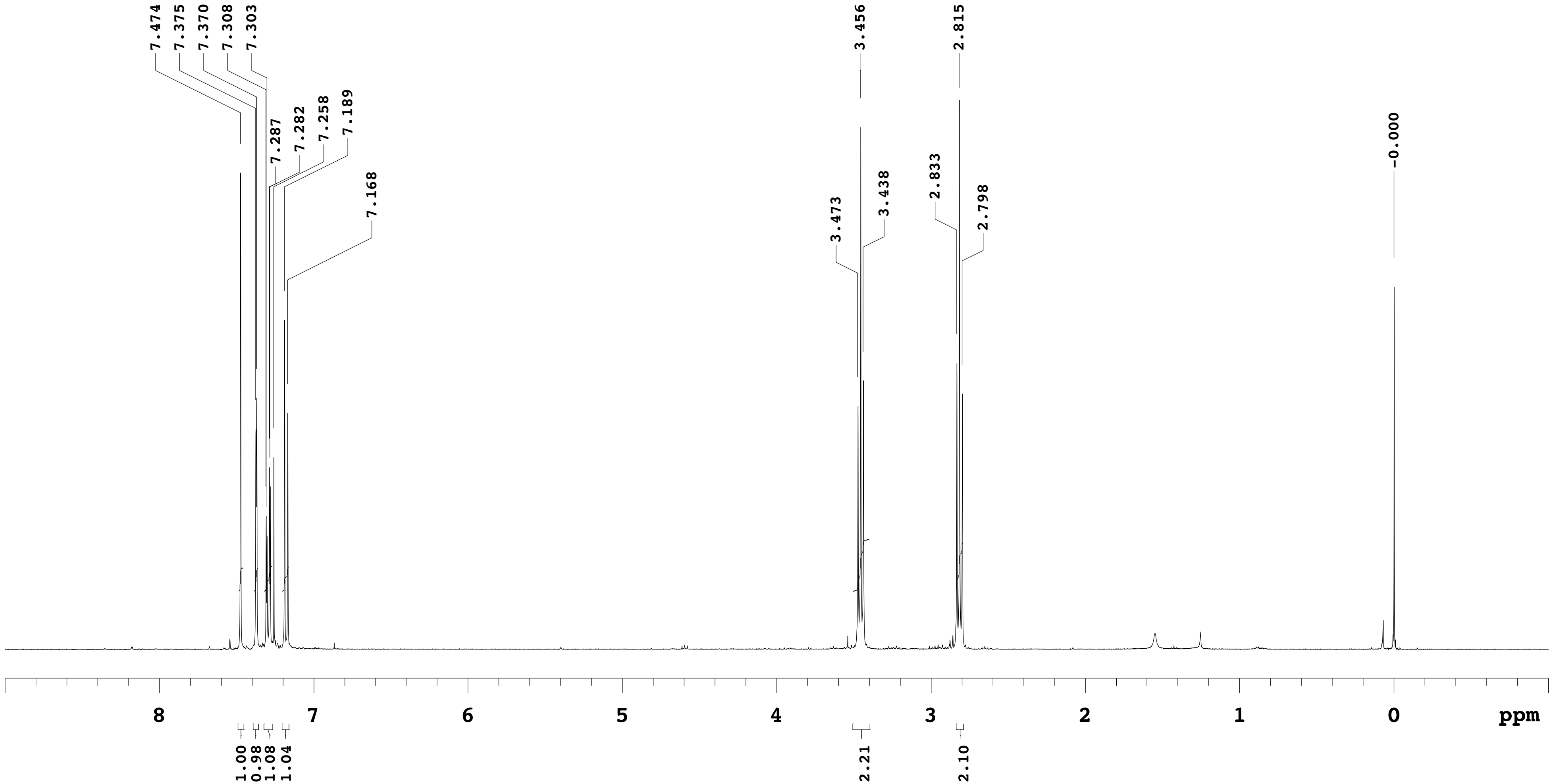
^{19}F NMR



1-(2-Azidoethyl)-4-chloro-2-(2,2-dibromovinyl)benzene (15).

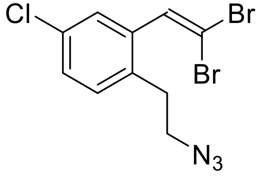
^{1}H NMR

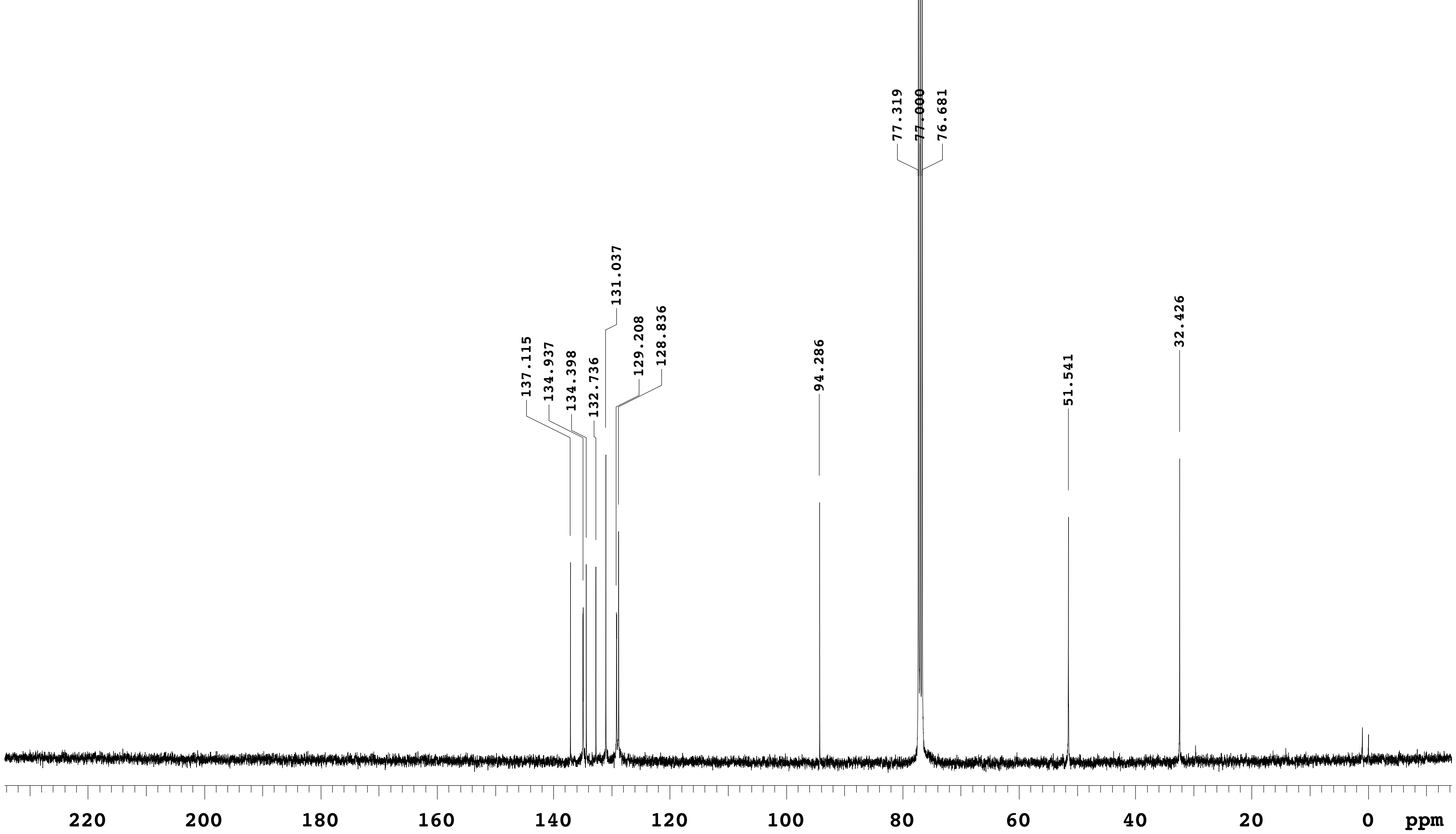




1-(2-Azidoethyl)-4-chloro-2-(2,2-dibromovinyl)benzene (15).

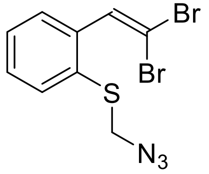
^{13}C NMR

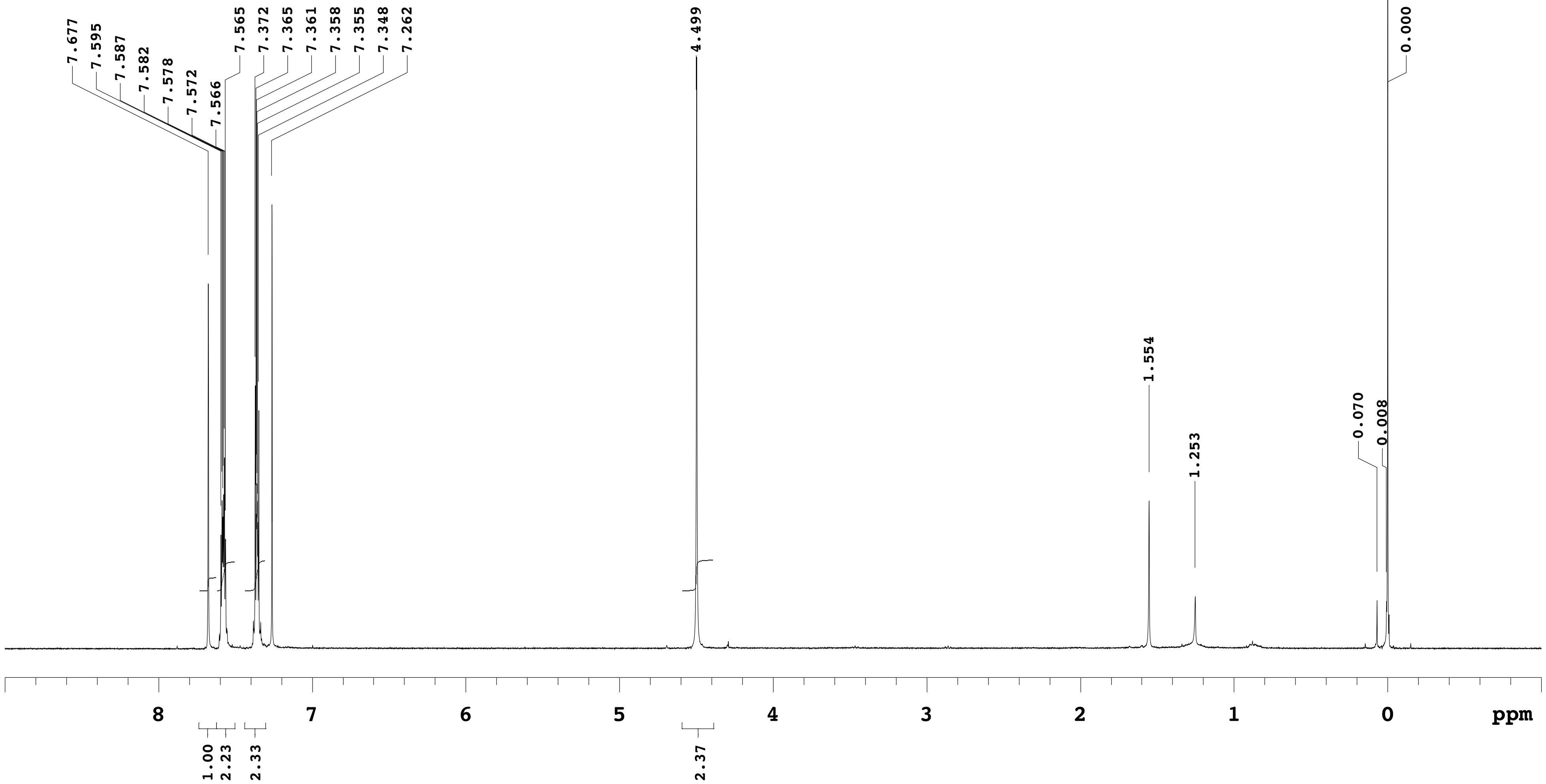




Azidomethyl 2-(2,2-dibromovinyl)phenyl sulfide (16).

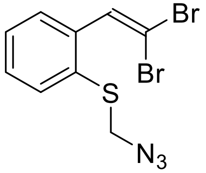
^{1}H NMR

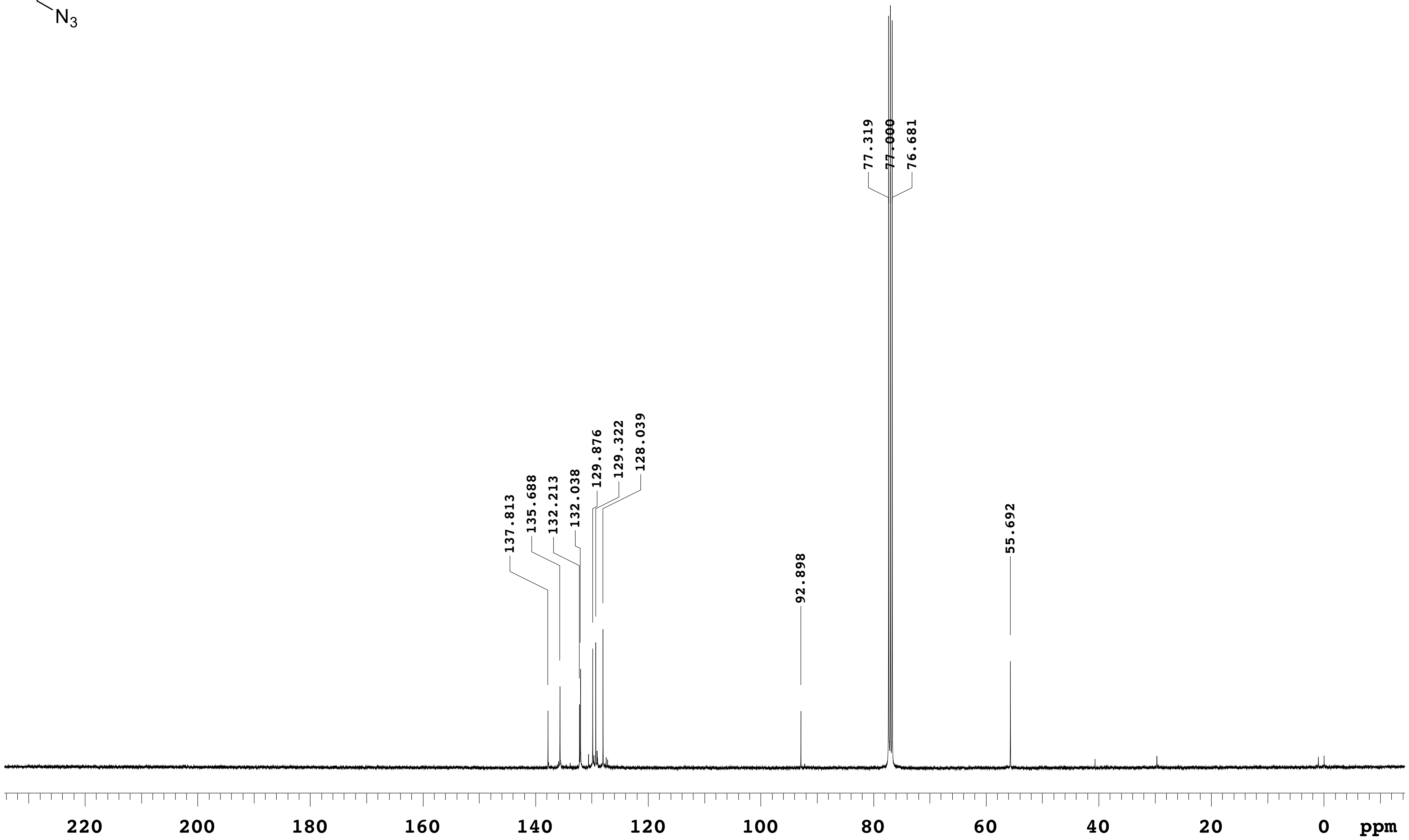




Azidomethyl 2-(2,2-dibromovinyl)phenyl sulfide (16).

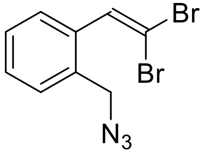
^{13}C NMR

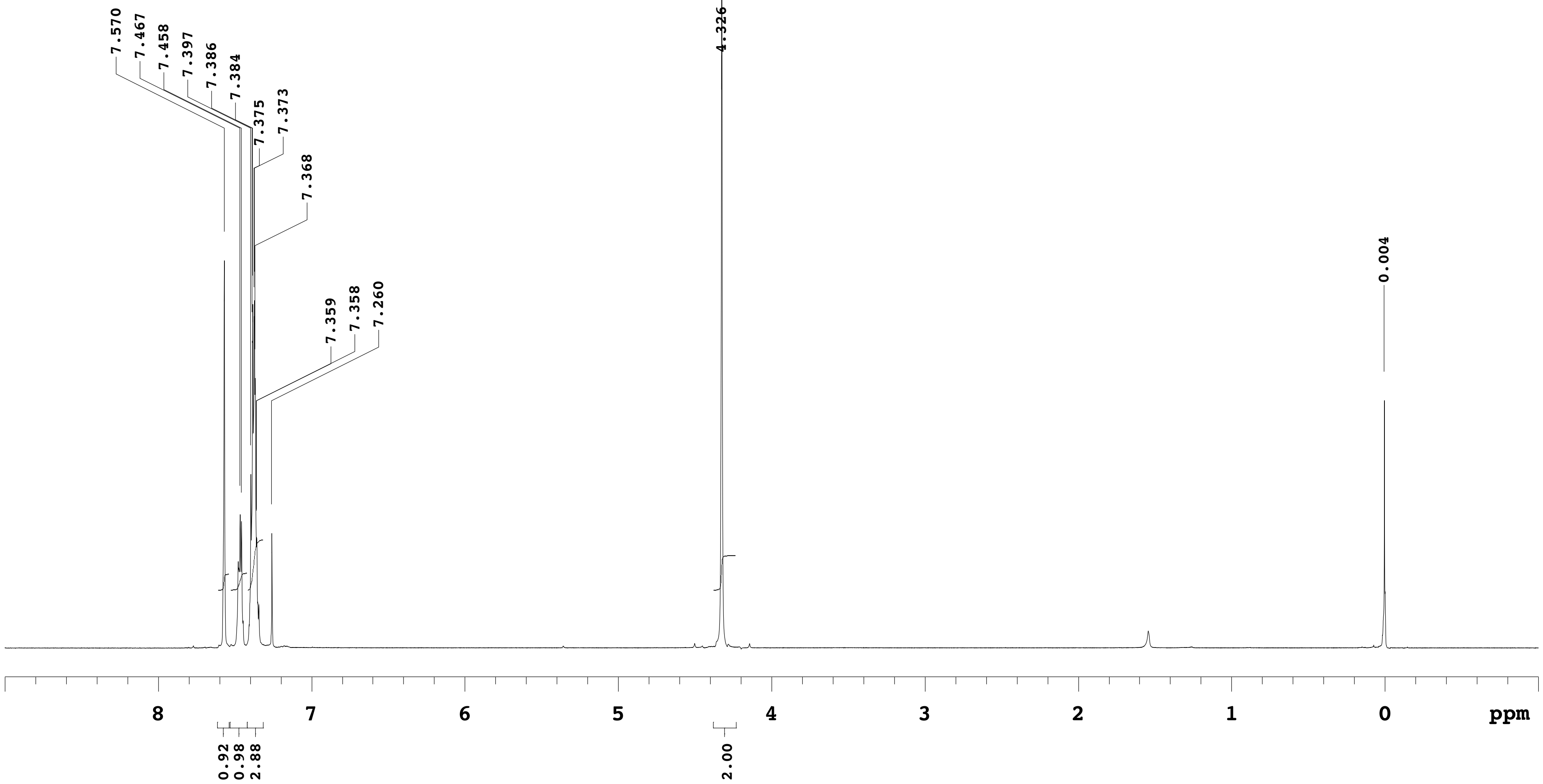




1-(Azidomethyl)-2-(2,2-dibromovinyl)benzene (17).

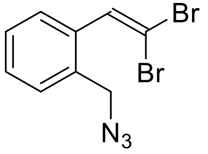
^{1}H NMR

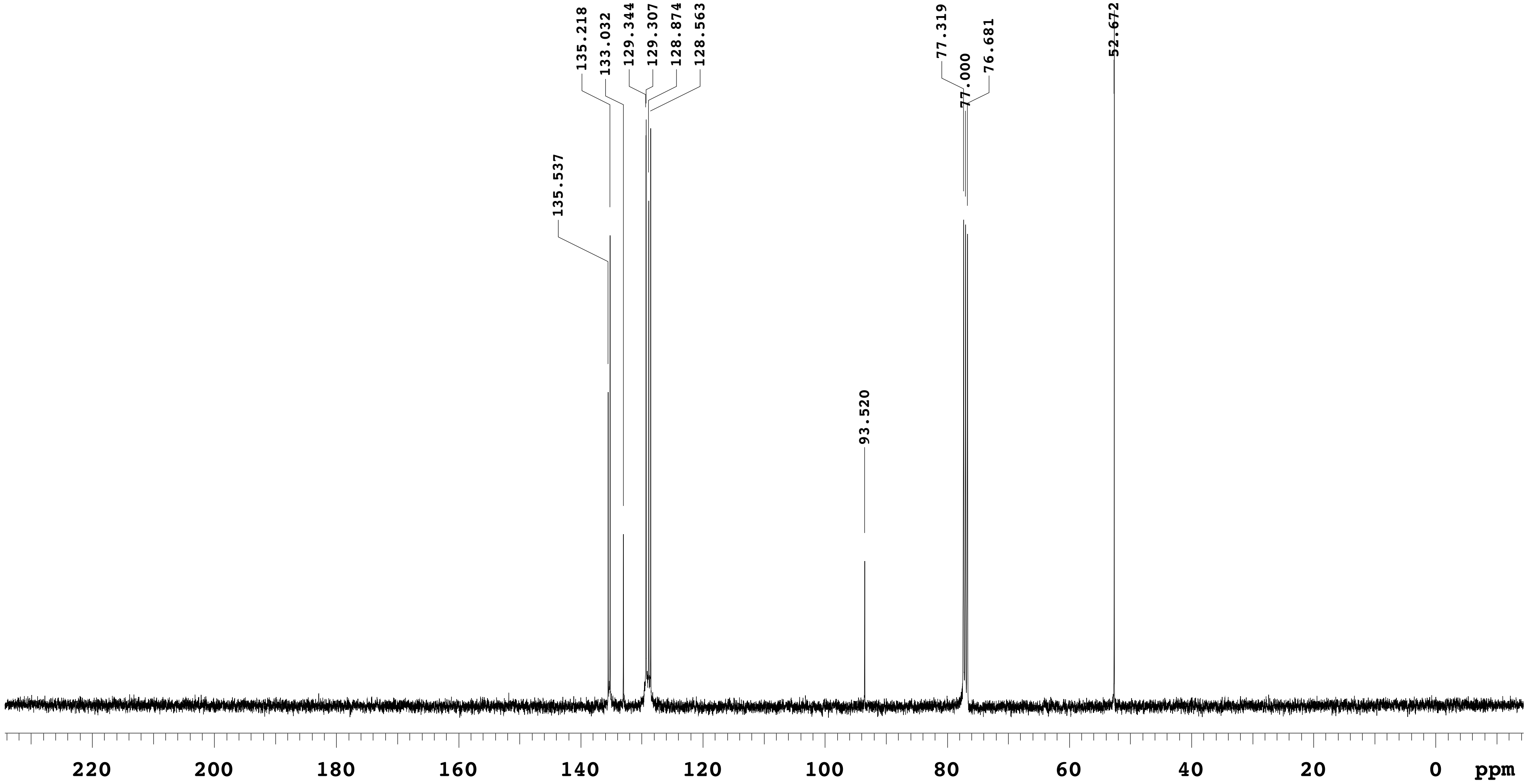




1-(Azidomethyl)-2-(2,2-dibromovinyl)benzene (17).

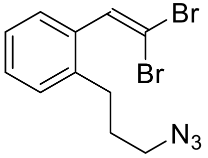
^{13}C NMR

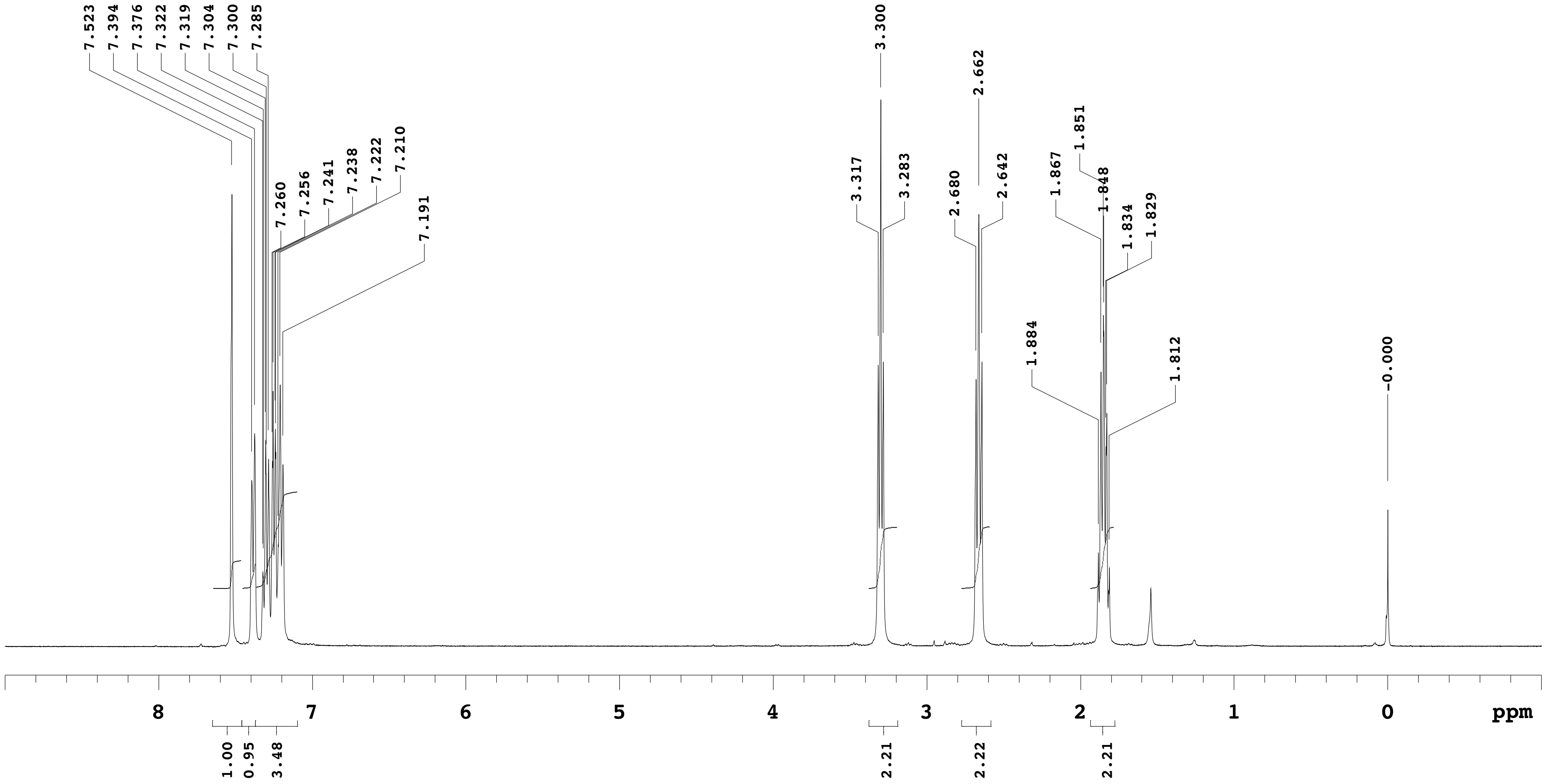




1-(3-Azidopropyl)-2-(2,2-dibromovinyl)benzene (18).

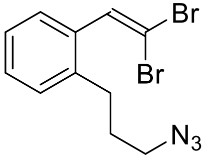
^{1}H NMR

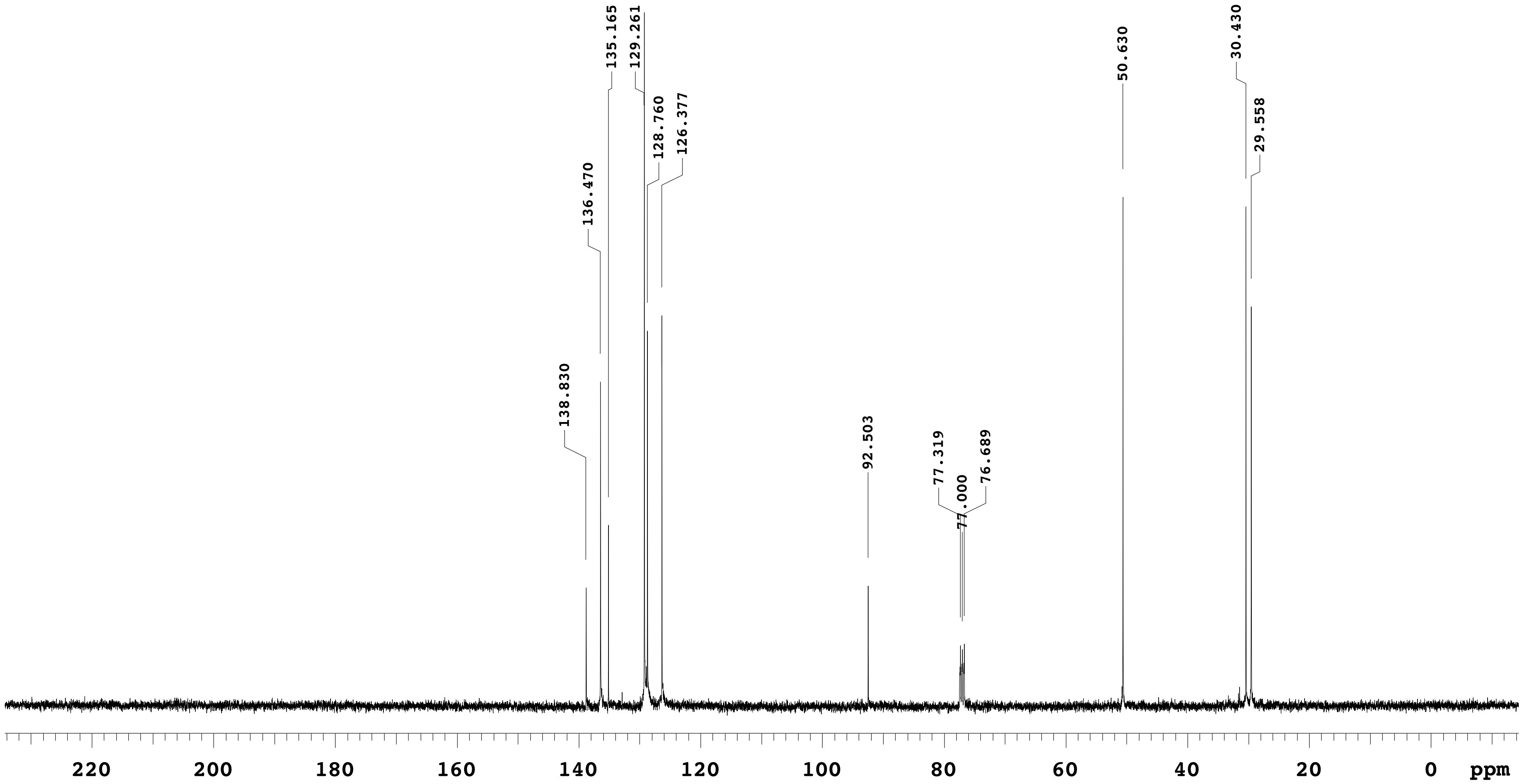




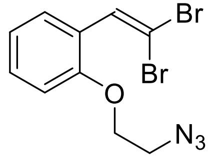
1-(3-Azidopropyl)-2-(2,2-dibromovinyl)benzene (18).

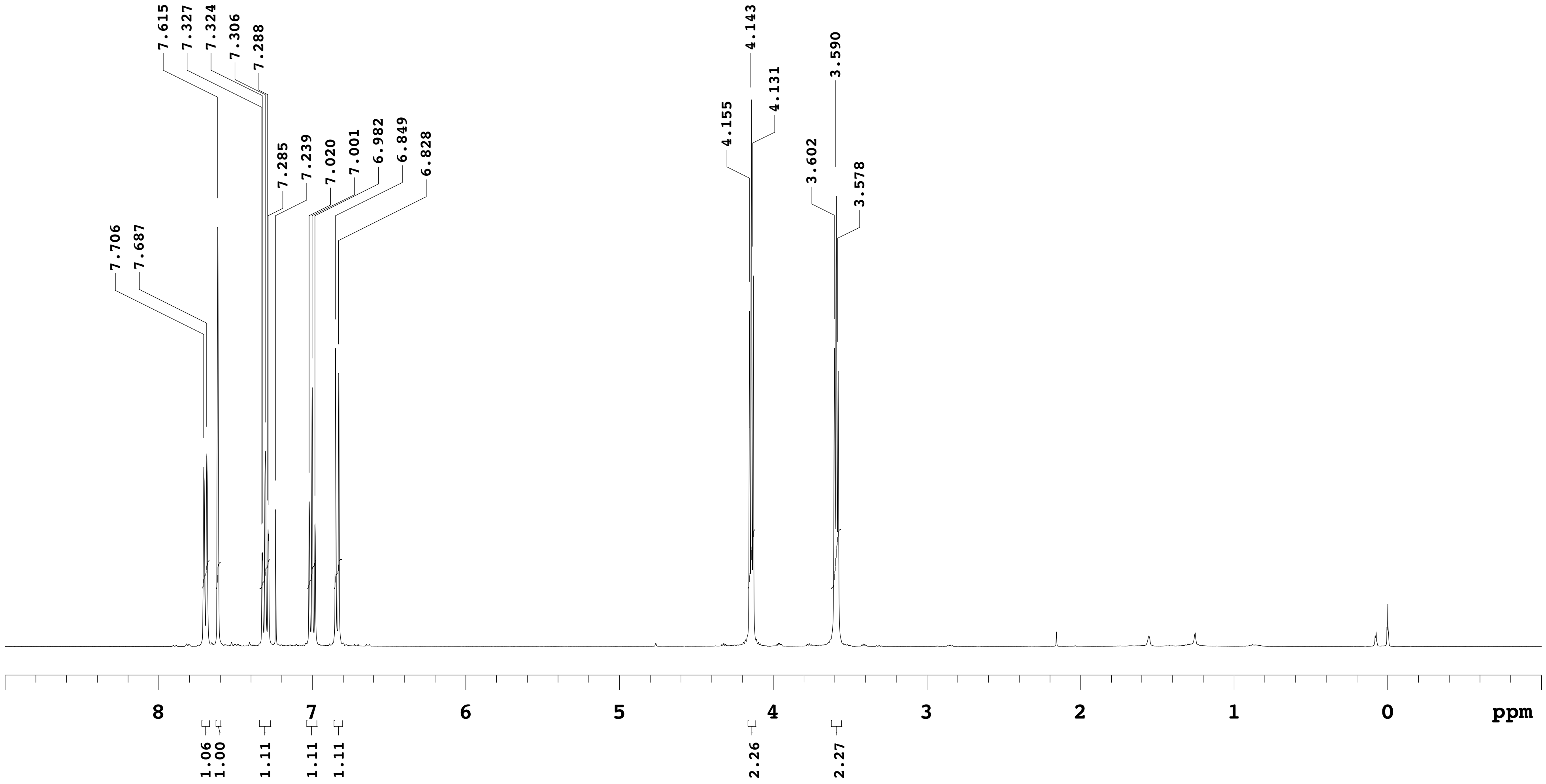
^{13}C NMR





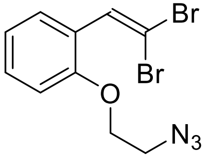
1-(2-Azidoethoxy)-2-(2,2-dibromovinyl)benzene (19). ^{1}H NMR

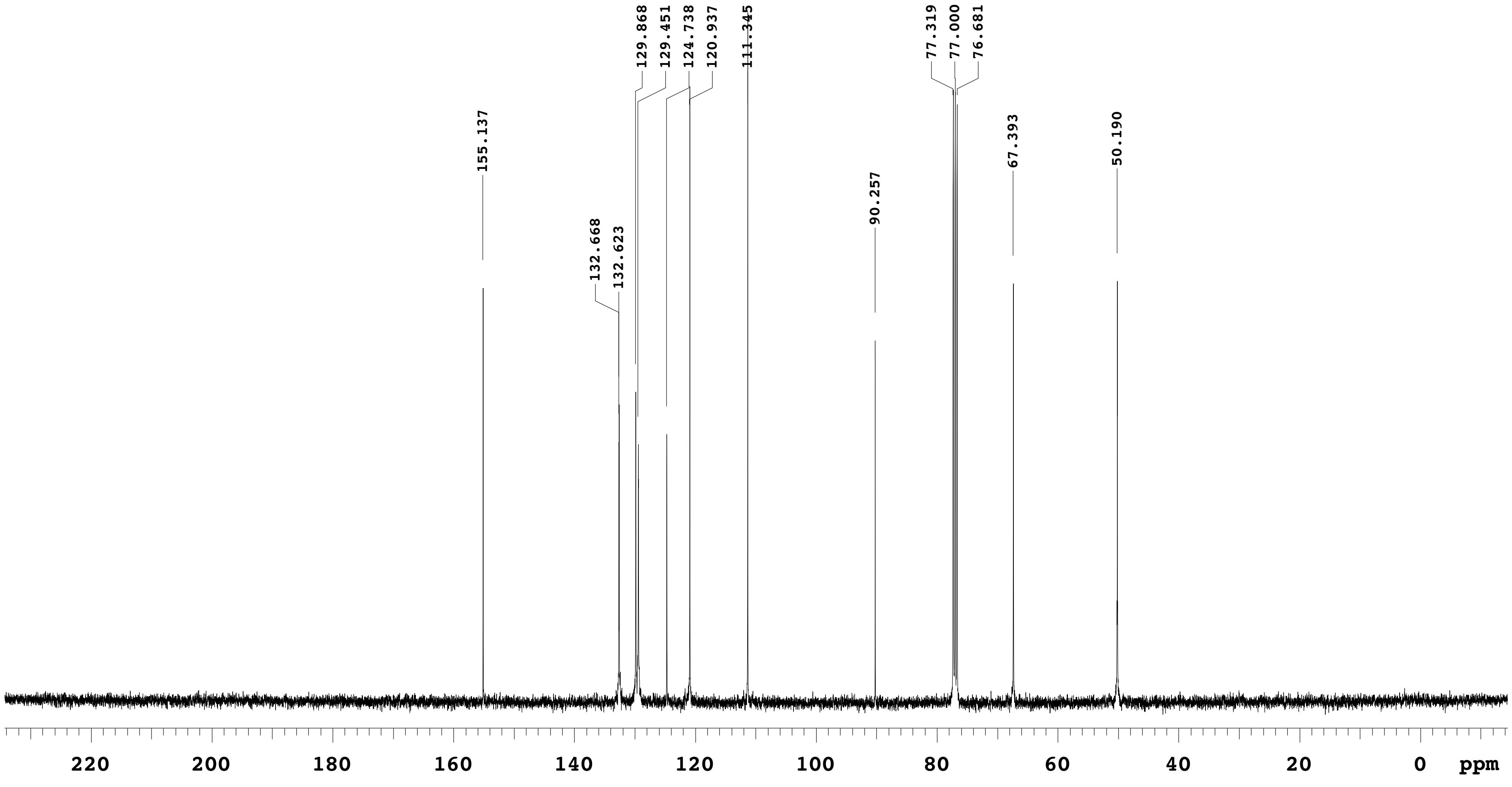




1-(2-Azidoethoxy)-2-(2,2-dibromovinyl)benzene (19).

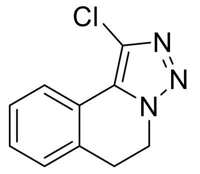
^{13}C NMR

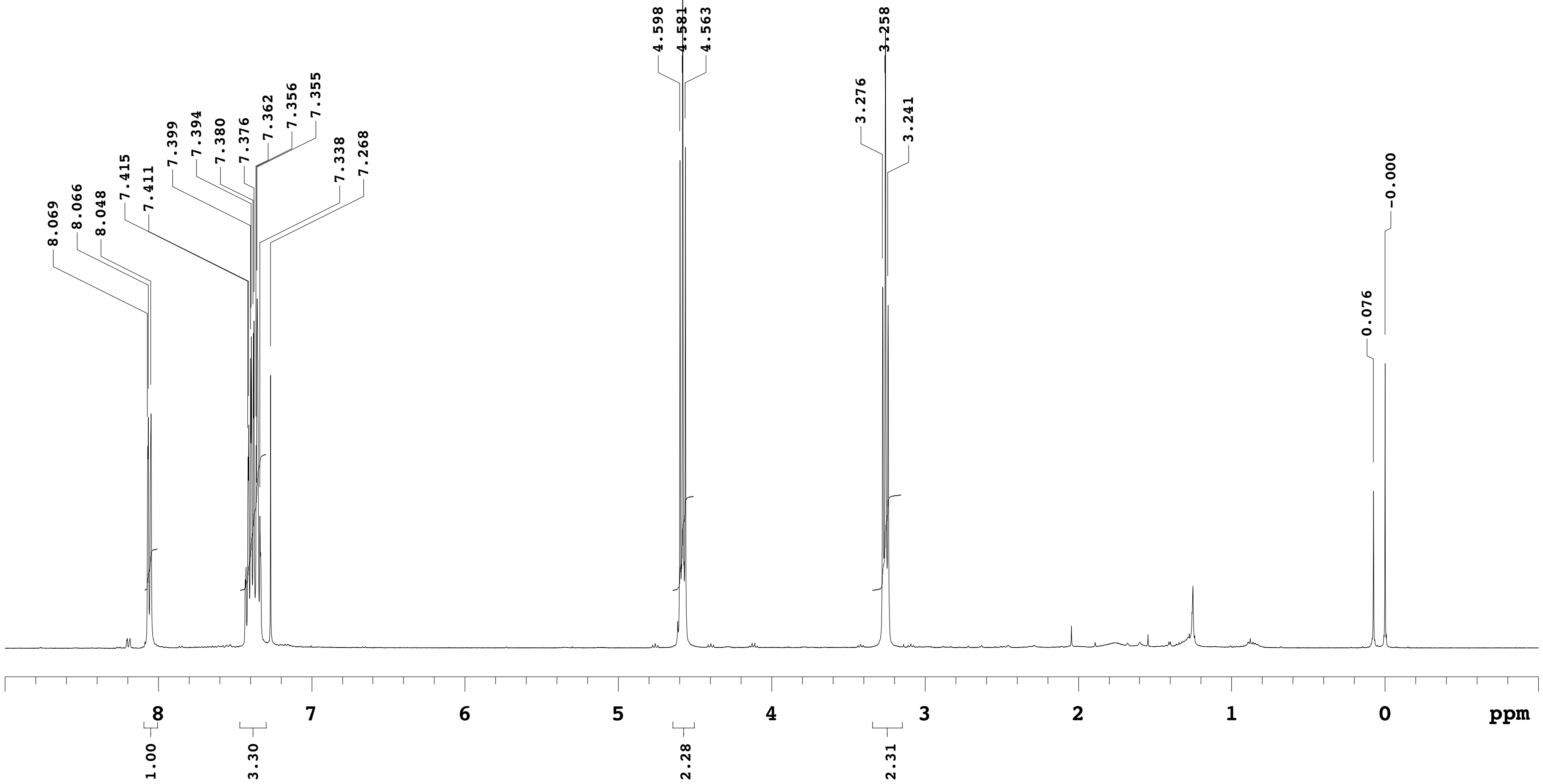




1-Chloro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (20).

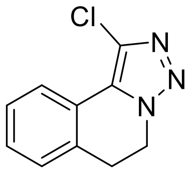
^{1}H NMR

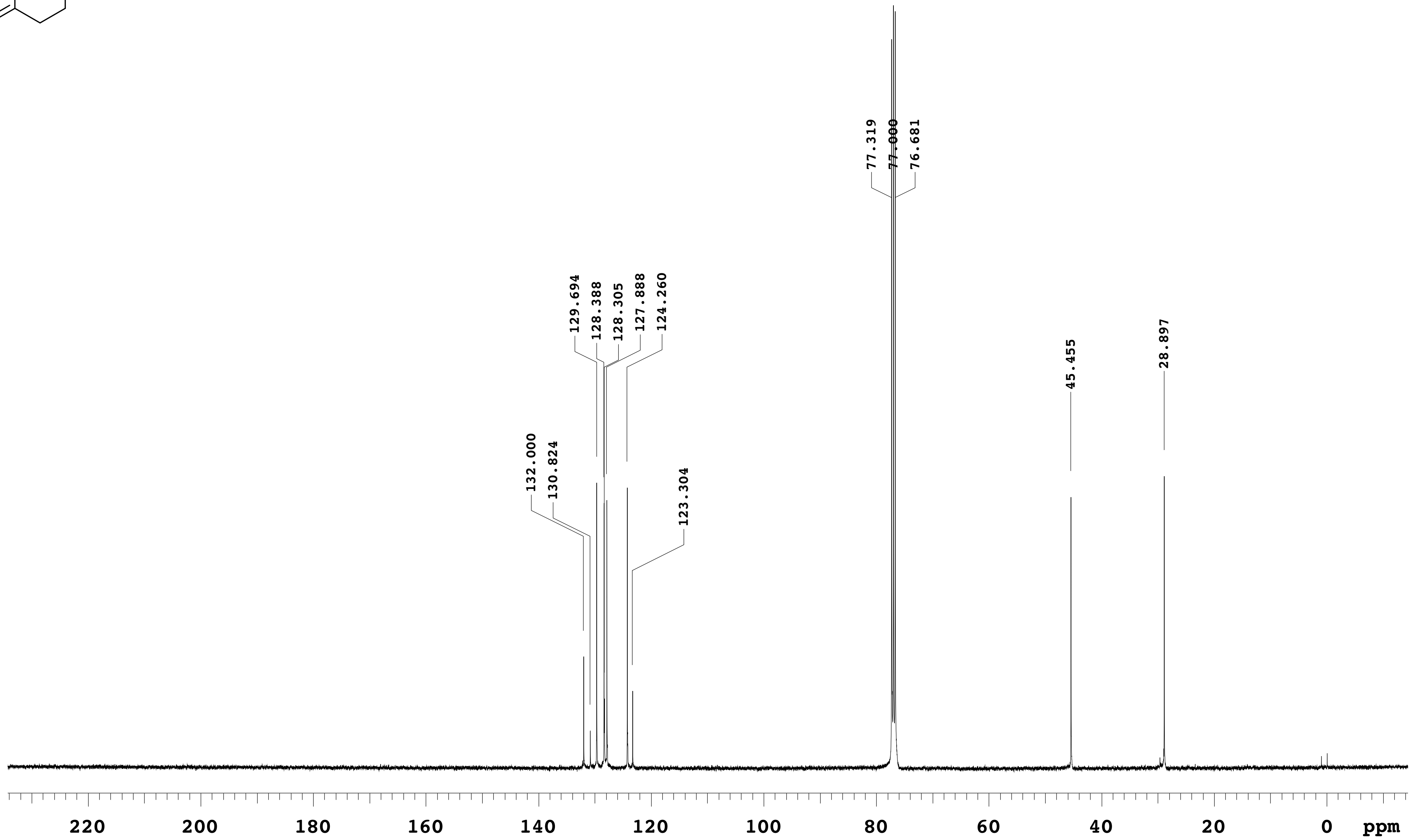




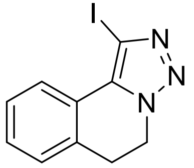
1-Chloro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (20).

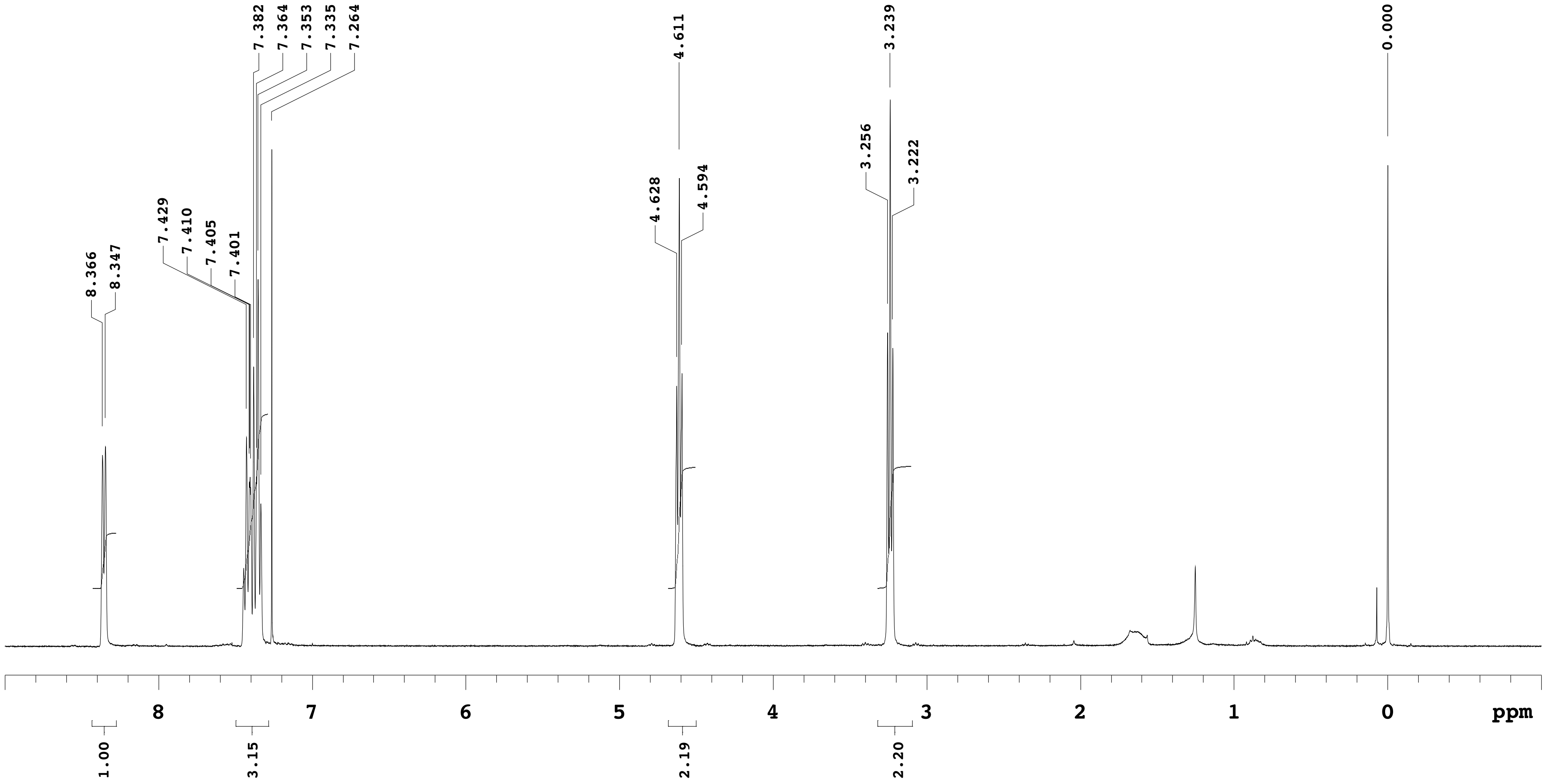
^{13}C NMR





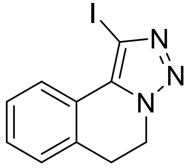
1-Iodo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (21). ^{1}H NMR

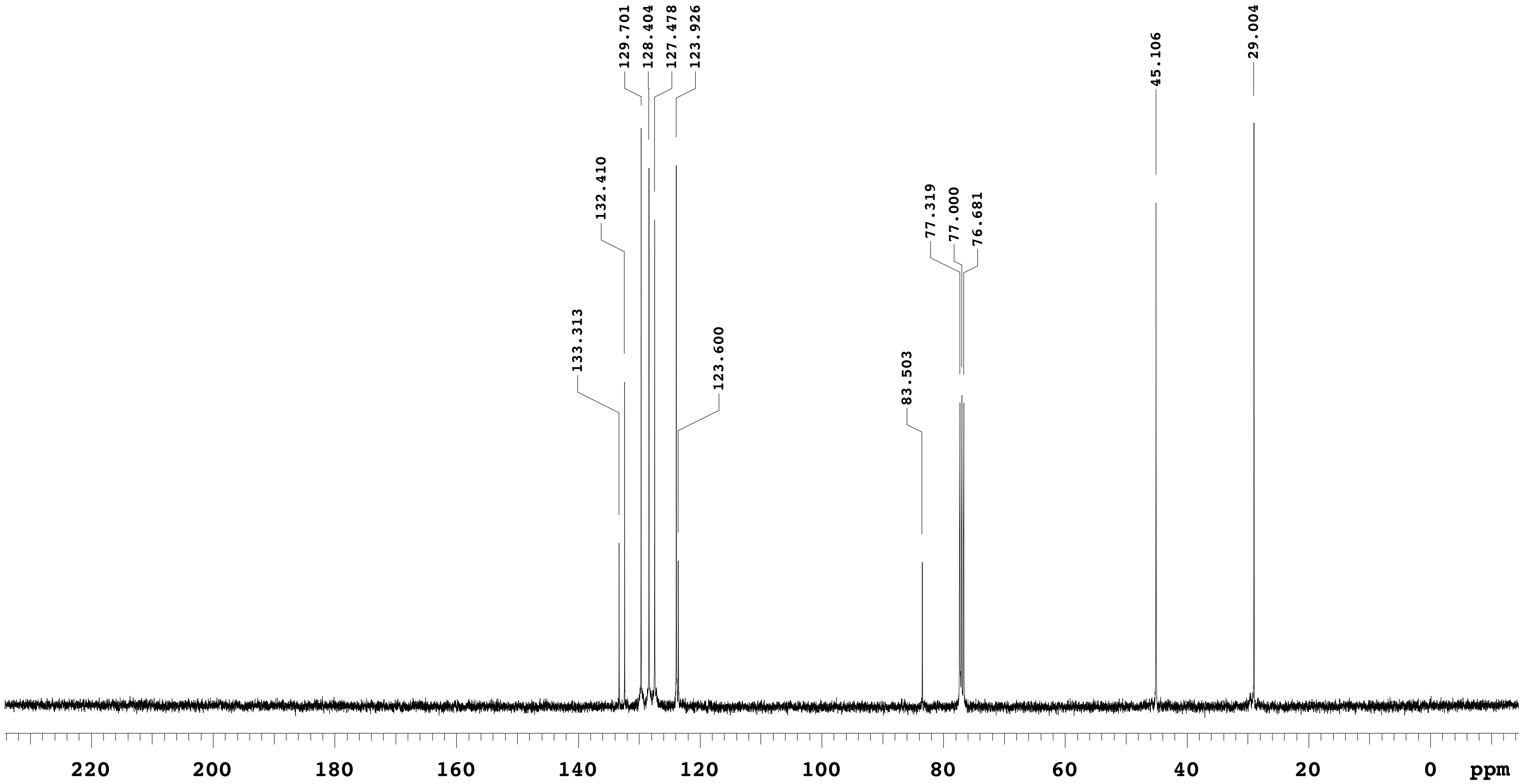




1-Iodo-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (21).

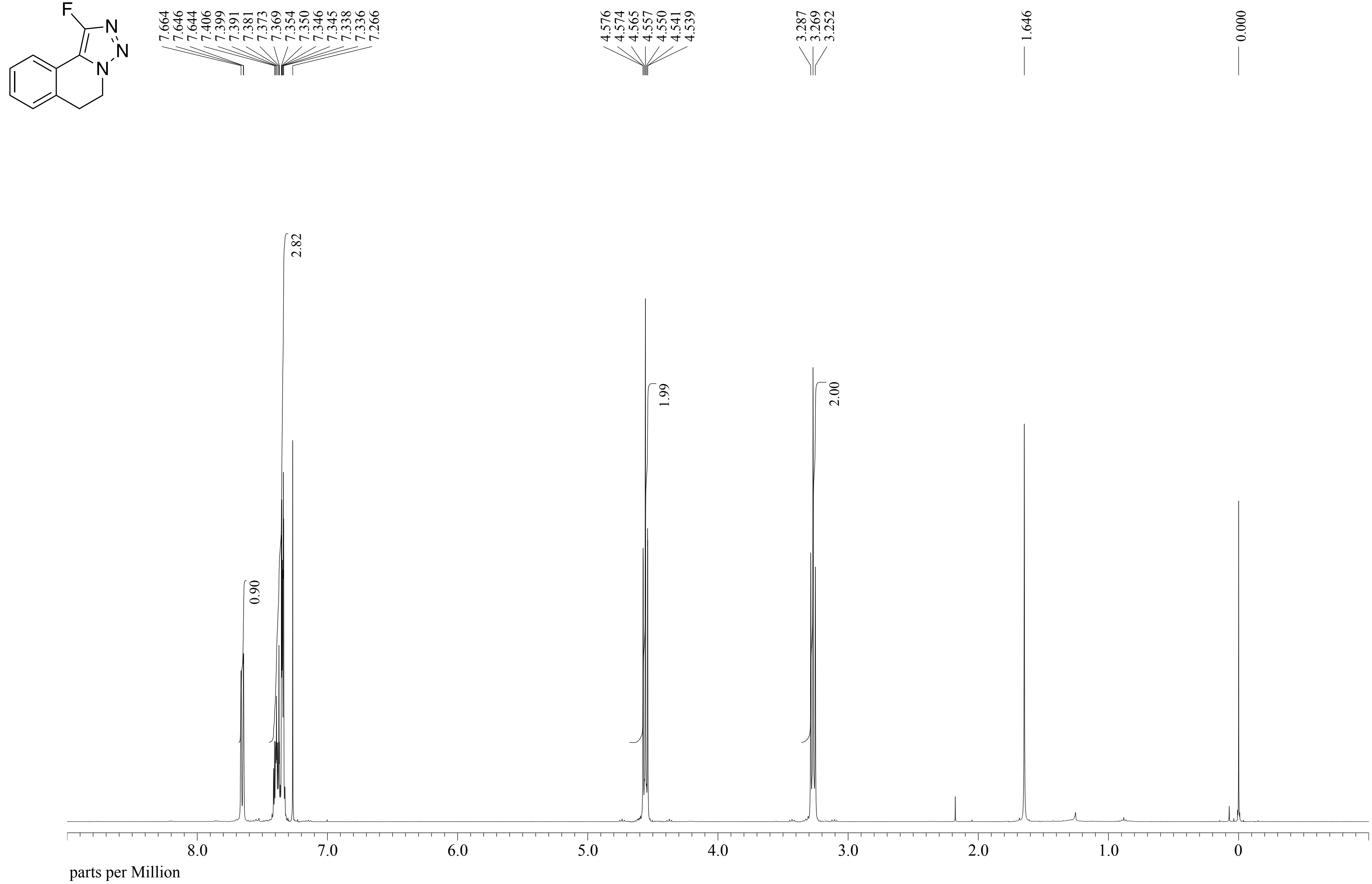
^{13}C NMR





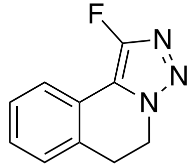
1-Fluoro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (22).

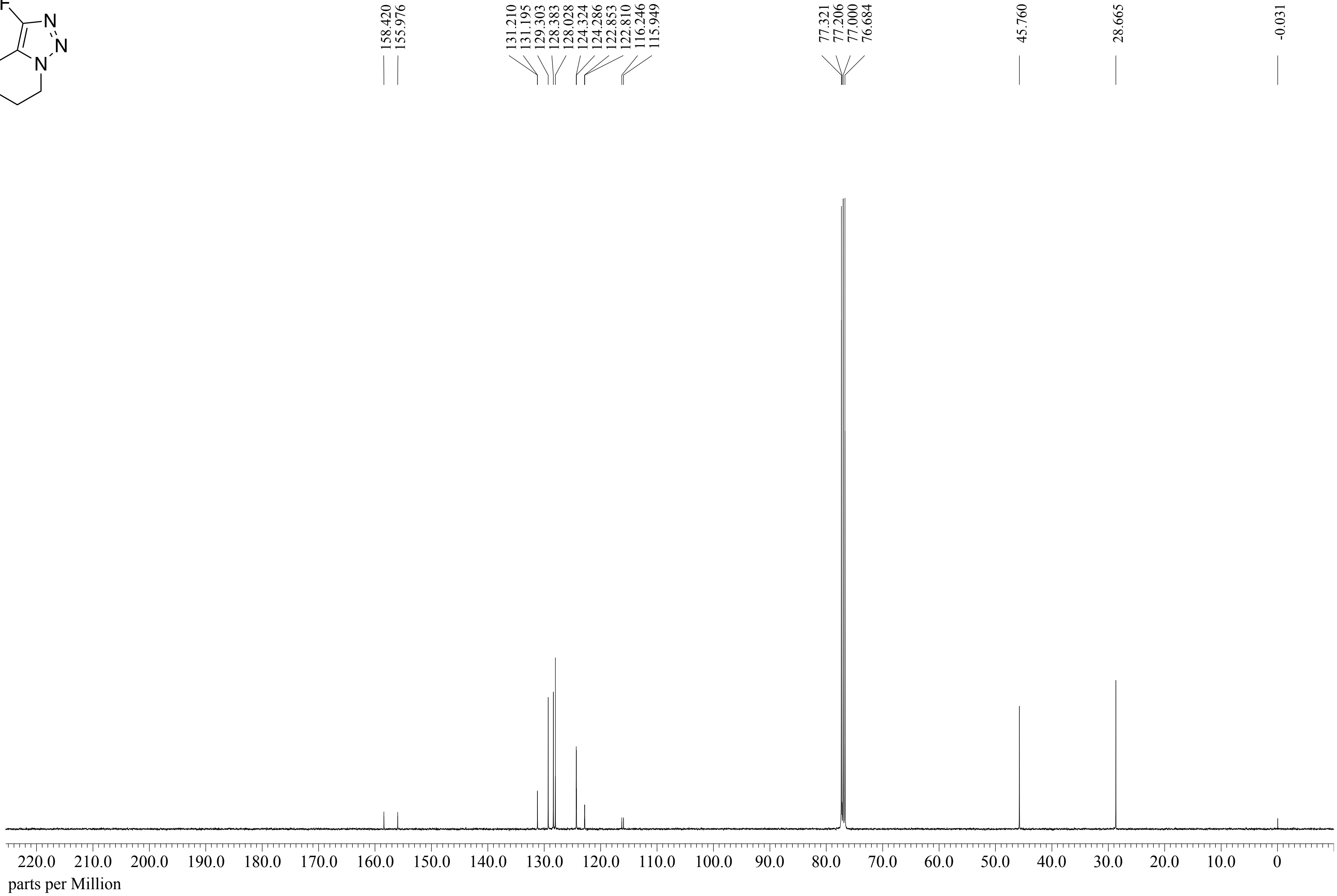
^{1}H NMR



1-Fluoro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (22).

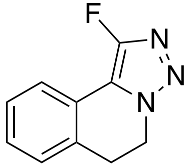
^{13}C NMR

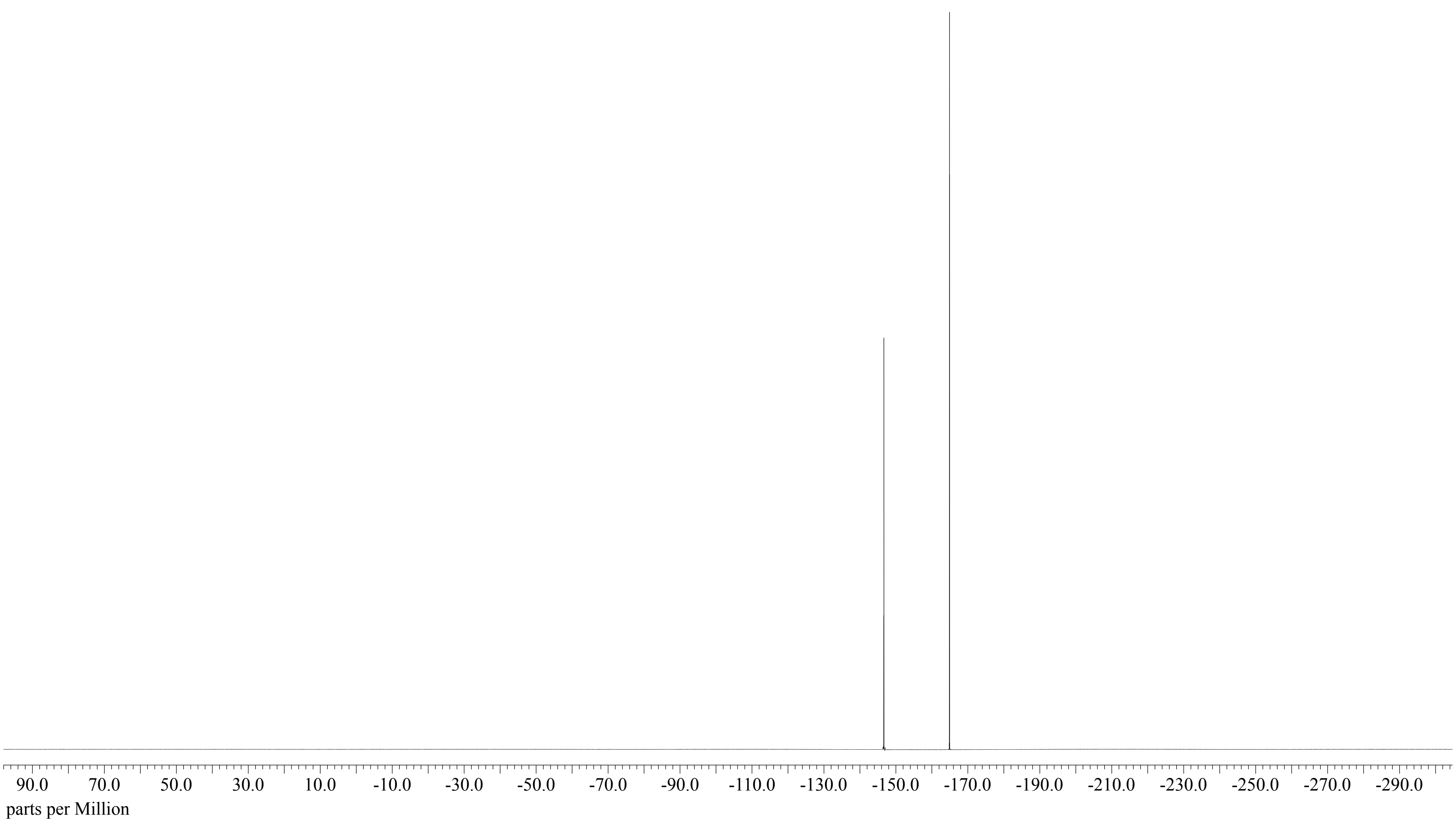




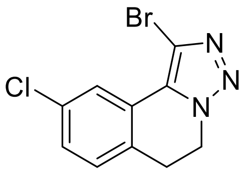
1-Fluoro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (22).

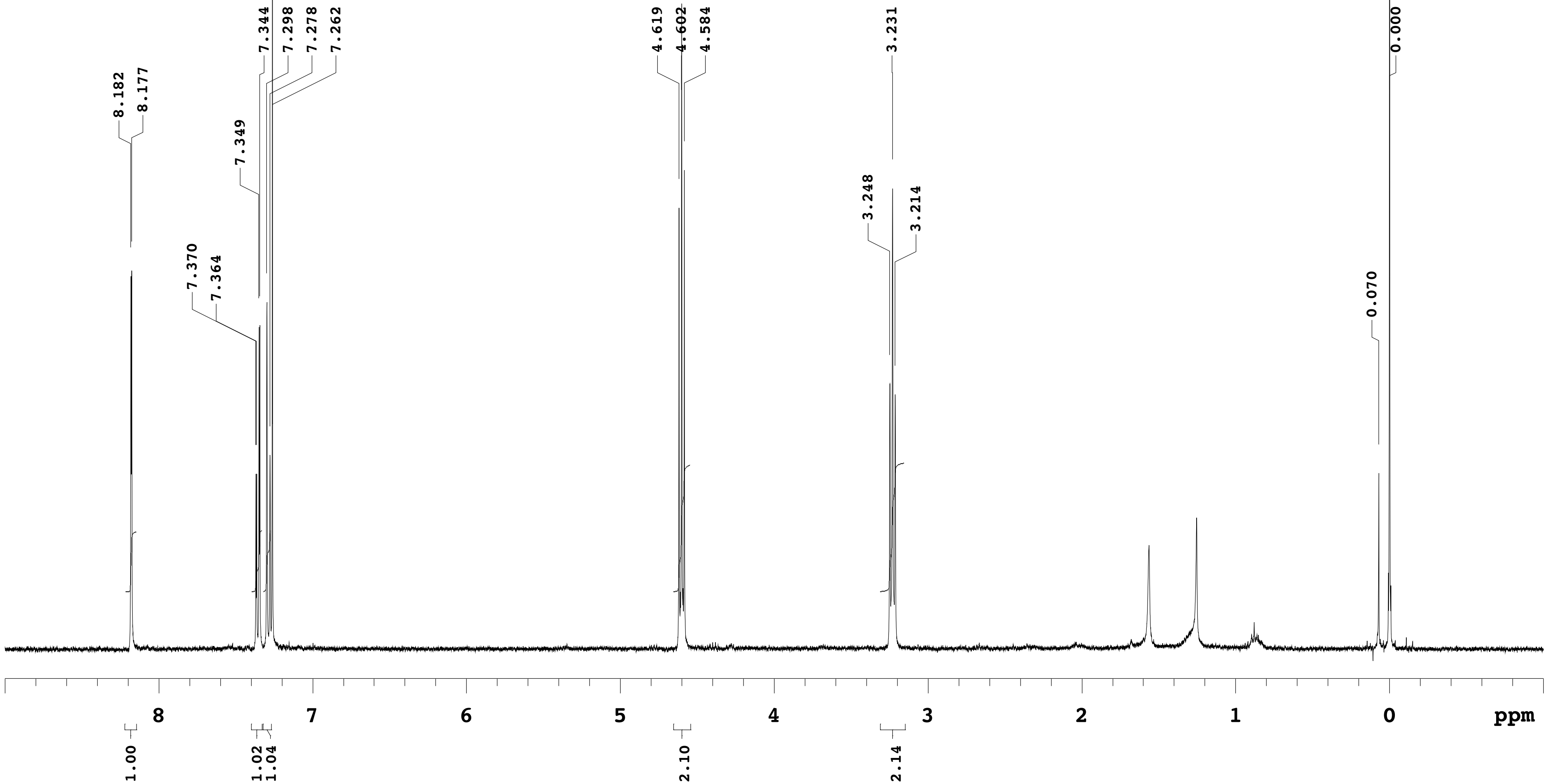
^{19}F NMR



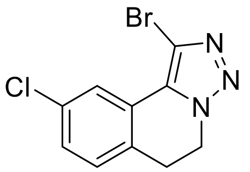


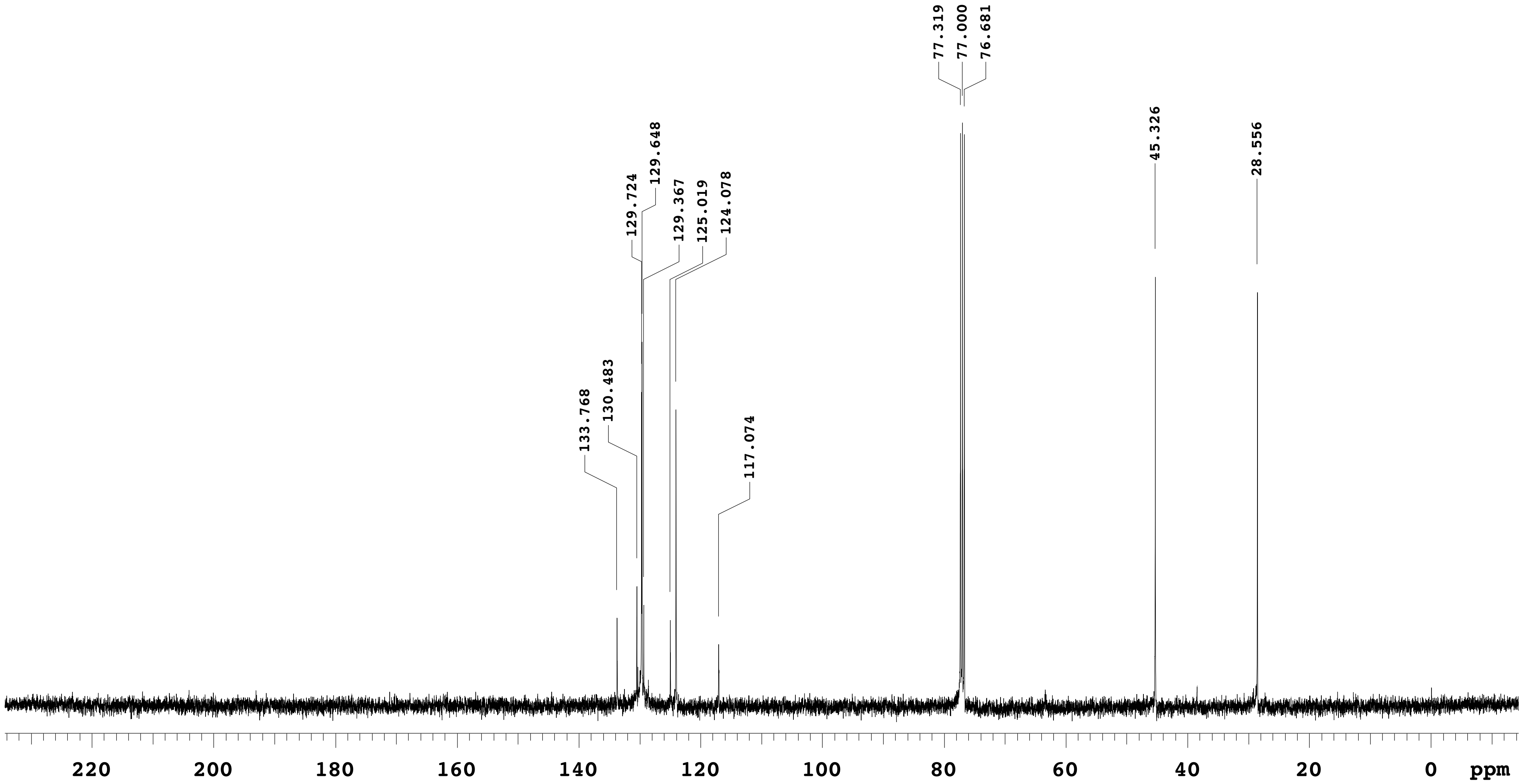
1-Bromo-9-chloro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (23). ^{1}H NMR





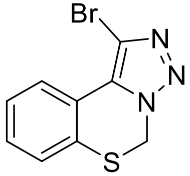
1-Bromo-9-chloro-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (23). ^{13}C NMR

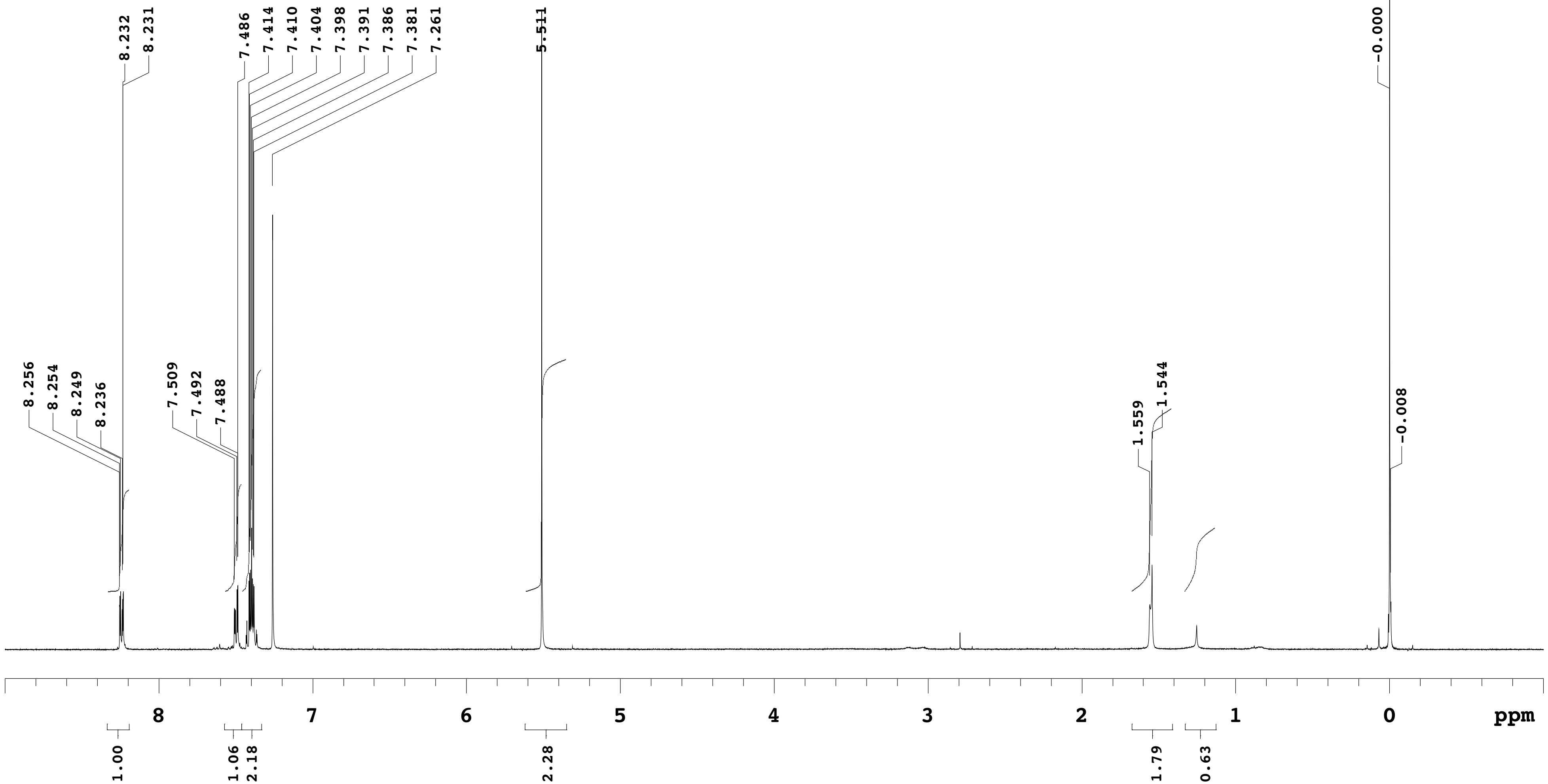




1-Bromo-5*H*-benzo[*e*][1,2,3]triazolo[1,5-*c*][1,3]thiazine (24).

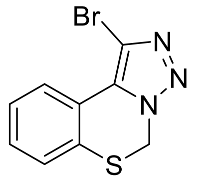
^{1}H NMR

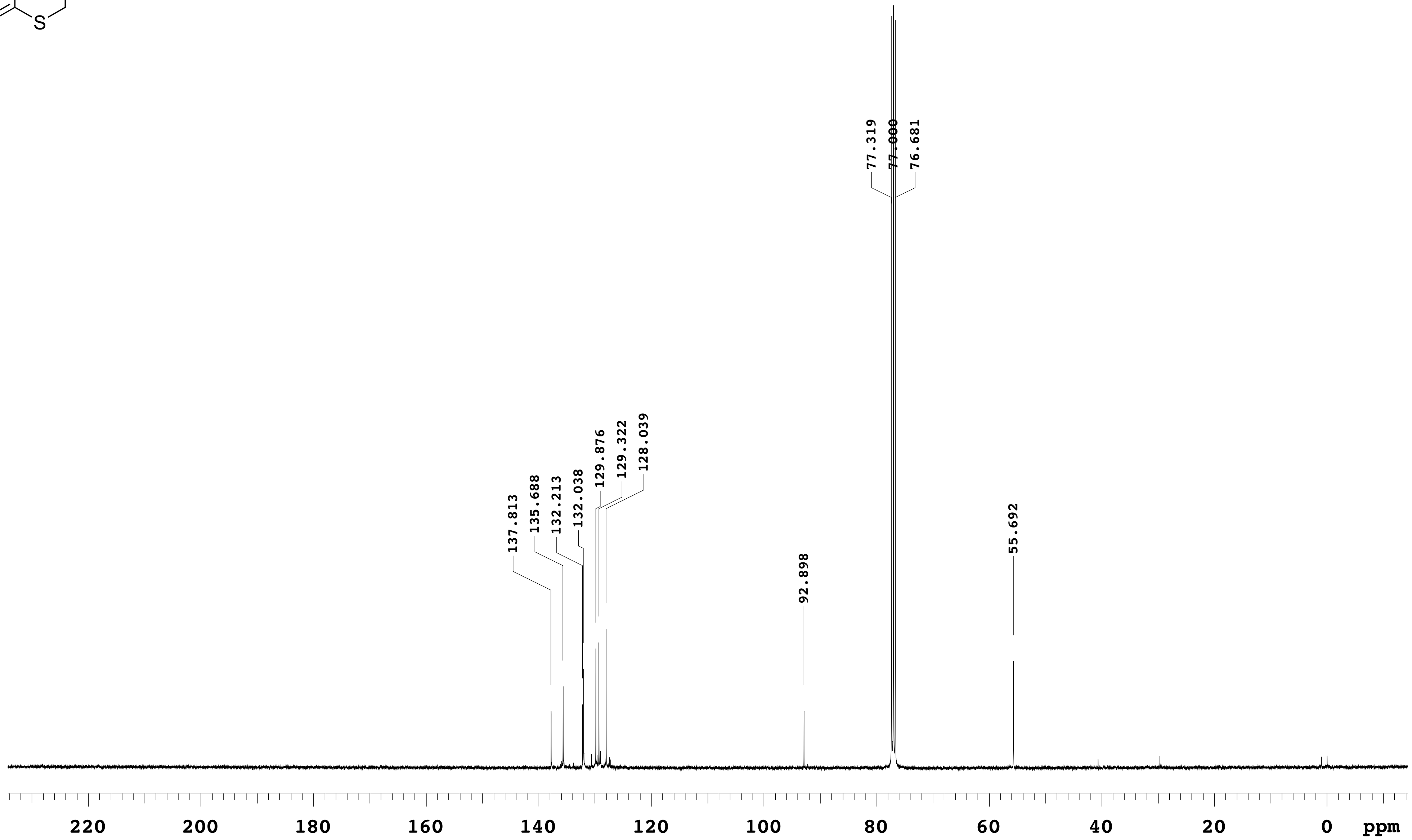




1-Bromo-5*H*-benzo[*e*][1,2,3]triazolo[1,5-*c*][1,3]thiazine (24).

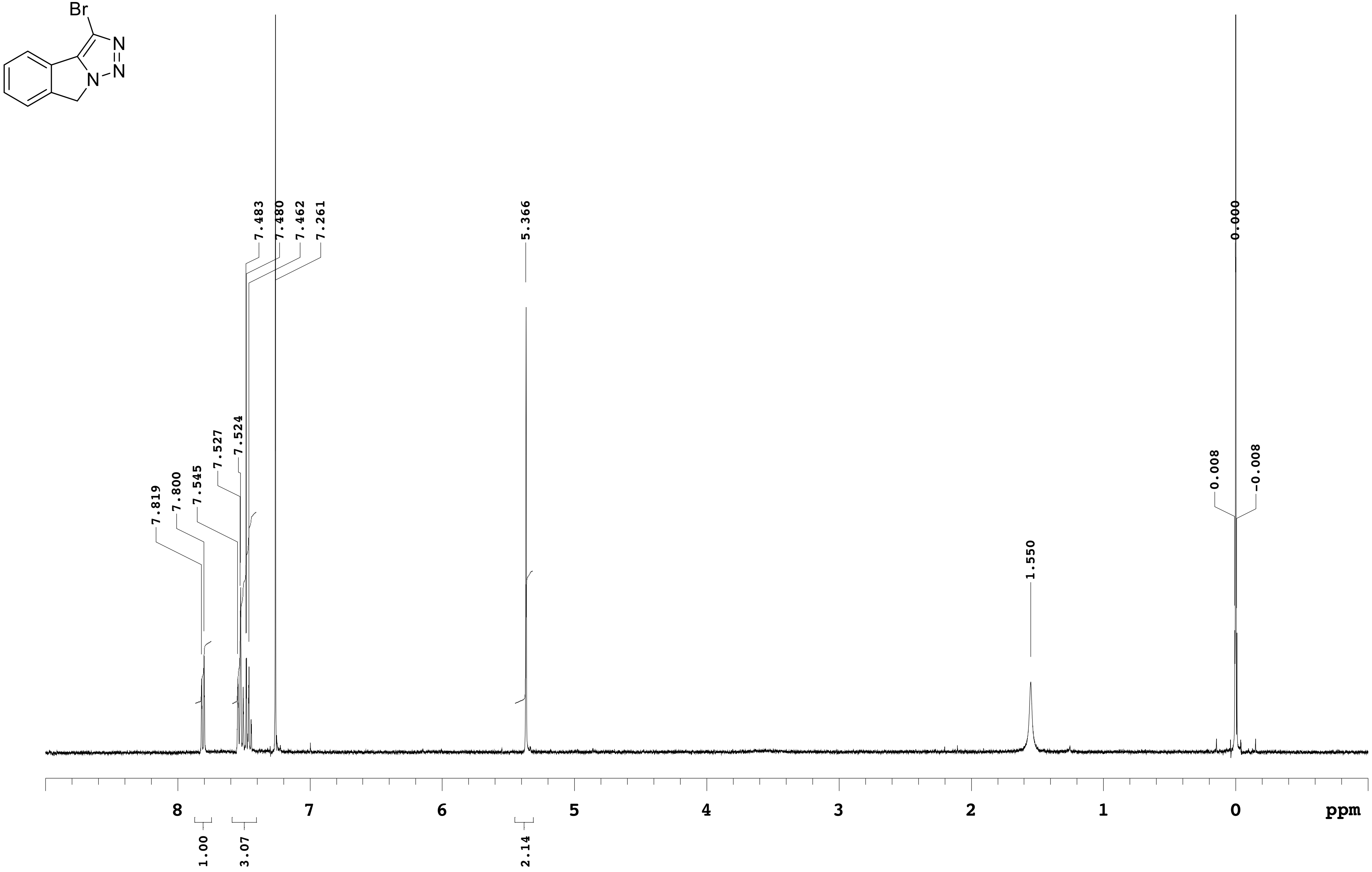
^{13}C NMR



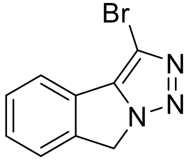


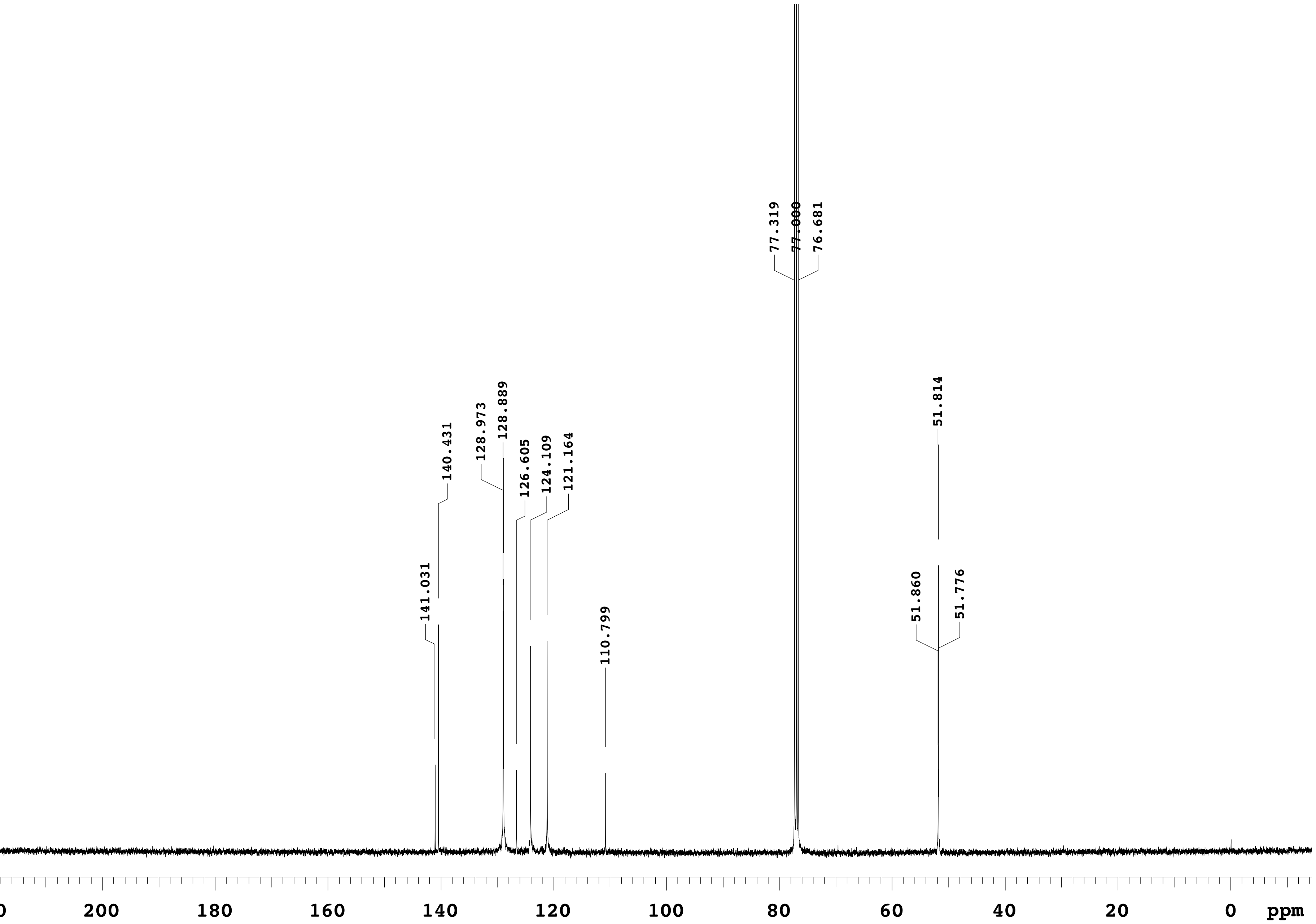
3-Bromo-8*H*-[1,2,3]triazolo[5,1-*a*]isoindole (25).

^{1}H NMR

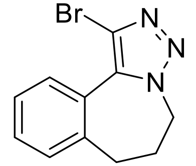


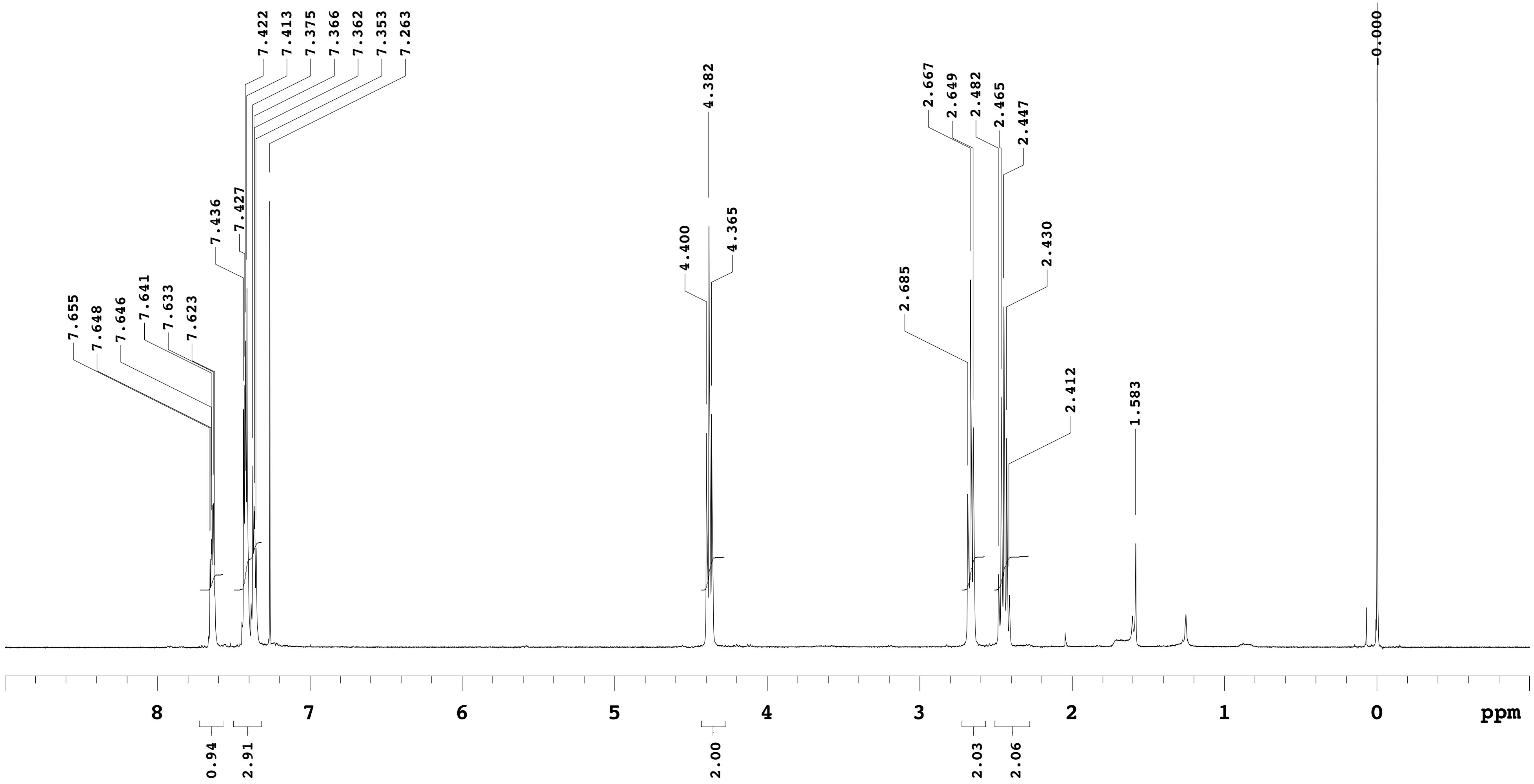
3-Bromo-8*H*-[1,2,3]triazolo[5,1-*a*]isoindole (25). **^{13}C NMR**





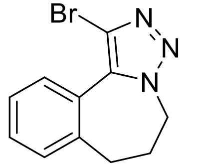
1-Bromo-6,7-dihydro-5*H*-benzo[*c*][1,2,3]triazolo[1,5-*a*]azepine (26). ^{1}H NMR

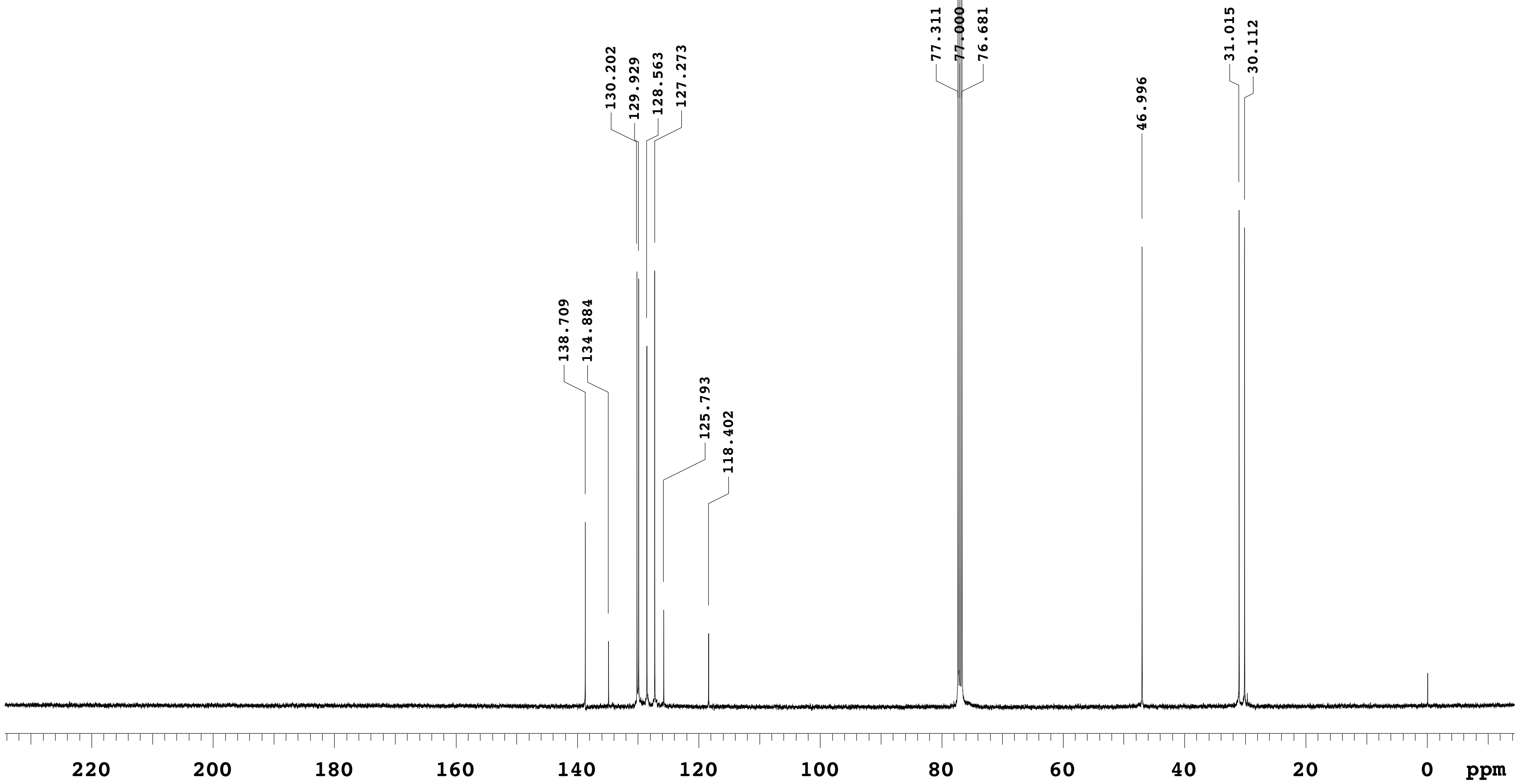




1-Bromo-6,7-dihydro-5*H*-benzo[*c*][1,2,3]triazolo[1,5-*a*]azepine (26).

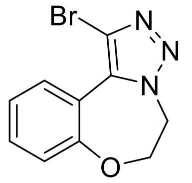
^{13}C NMR

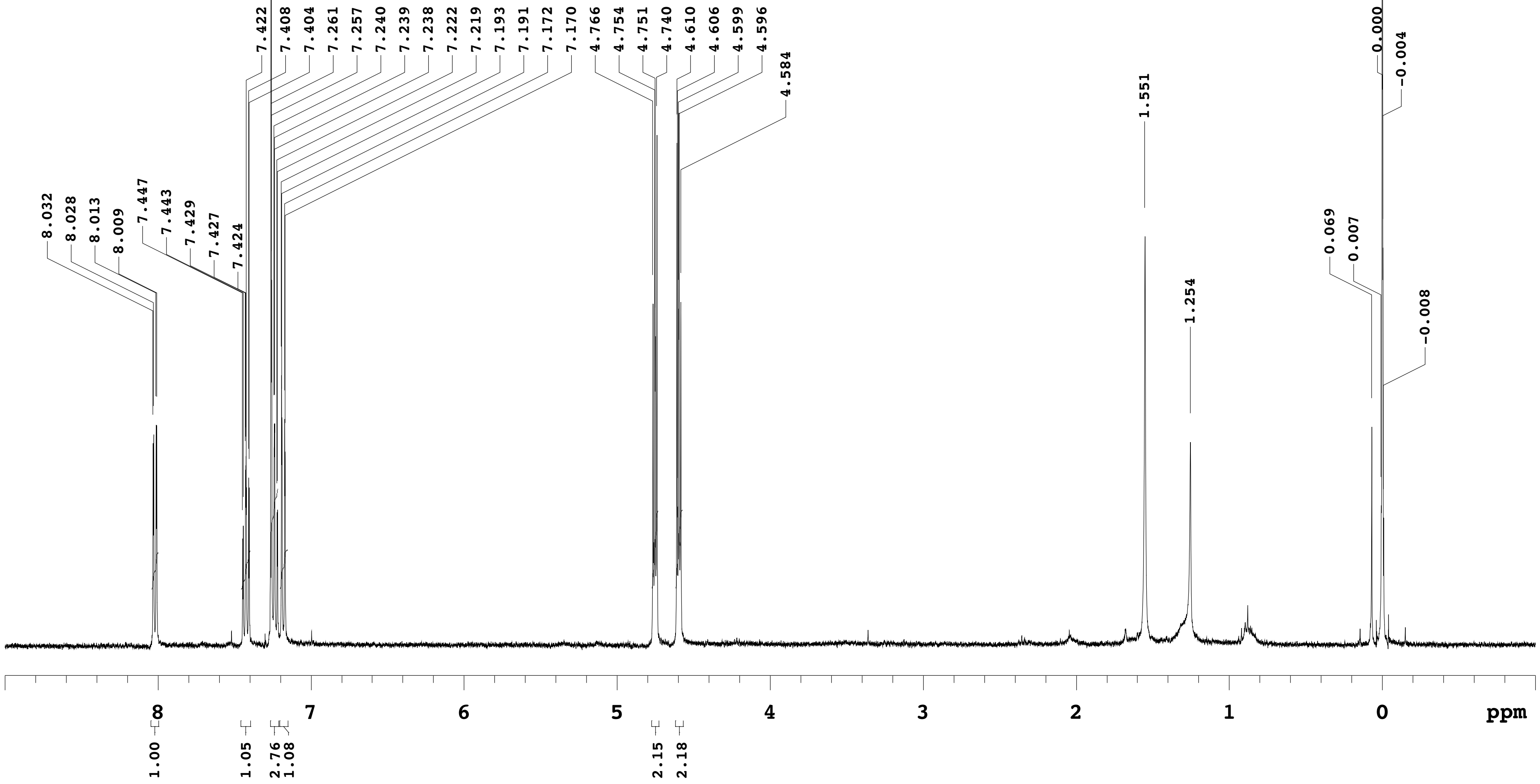




1-Bromo-5,6-dihydrobenzo[*f*][1,2,3]triazolo[1,5-*d*][1,4]oxazepine (27).

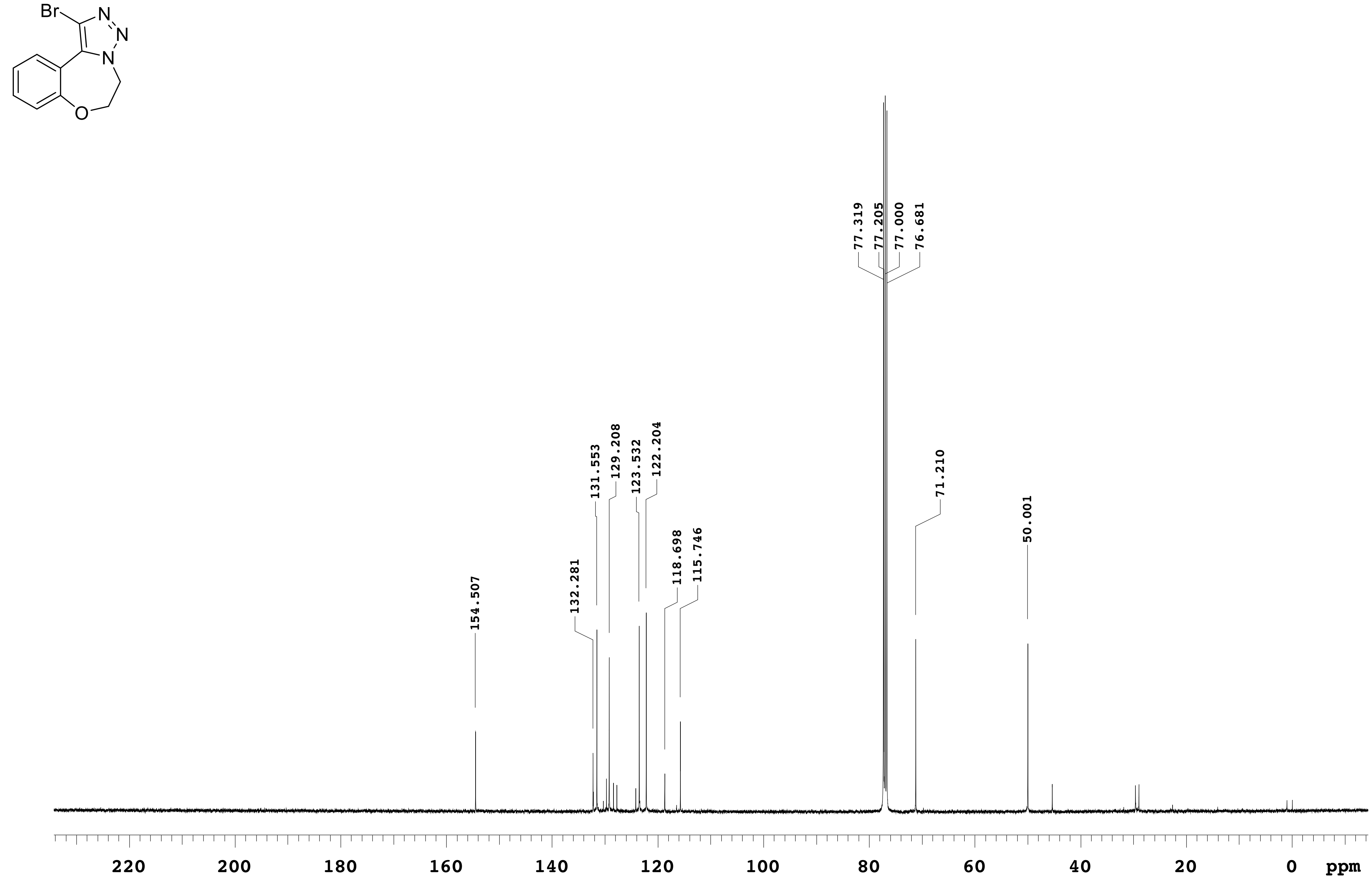
^{1}H NMR





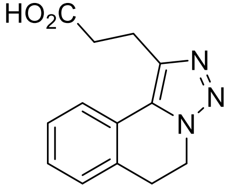
1-Bromo-5,6-dihydrobenzo[*f*][1,2,3]triazolo[1,5-*d*][1,4]oxazepine (28).

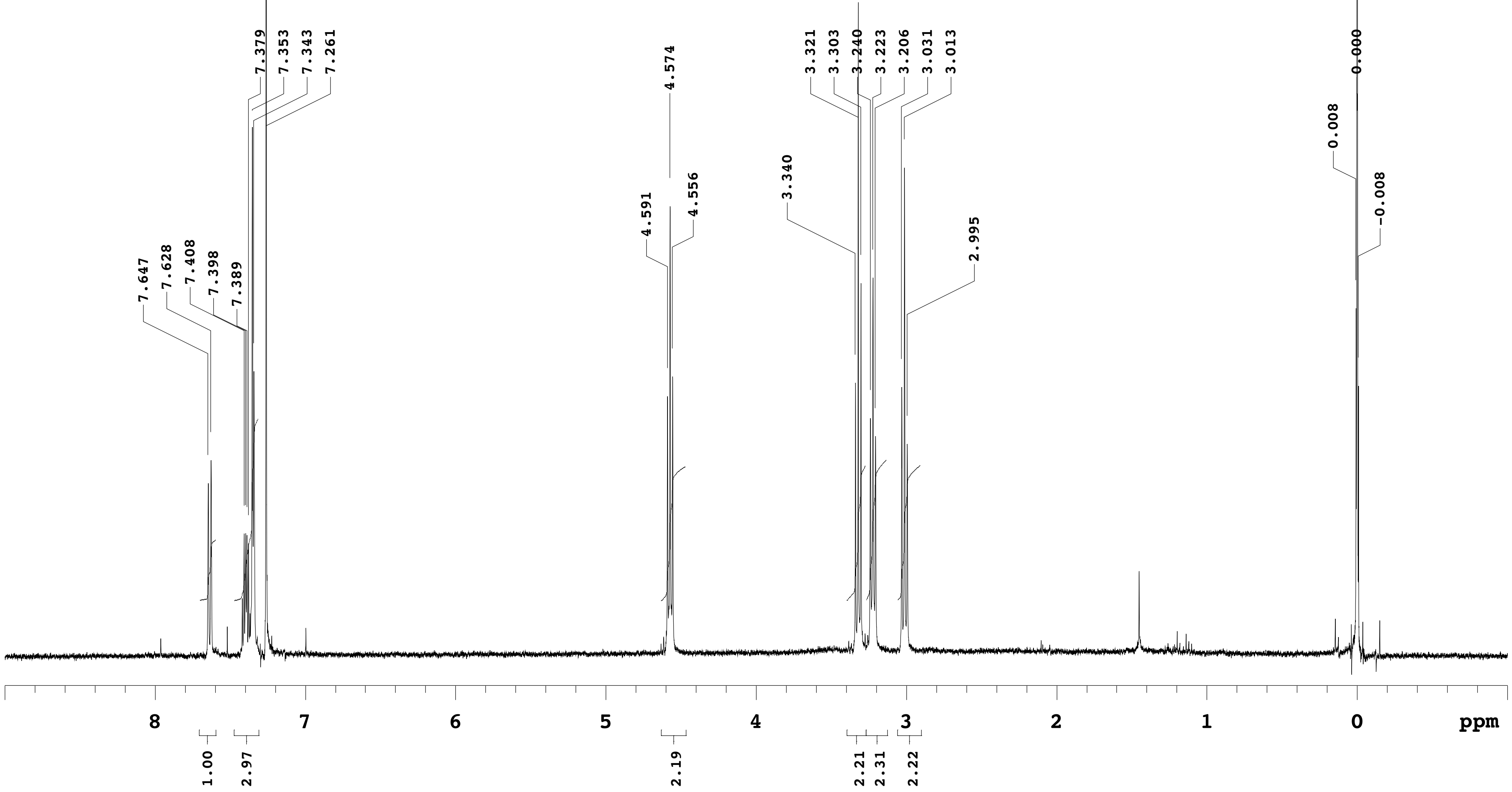
^{13}C NMR



3-(5,6-Dihydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-1-yl)propanoic acid.

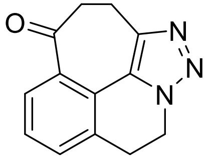
^{1}H NMR

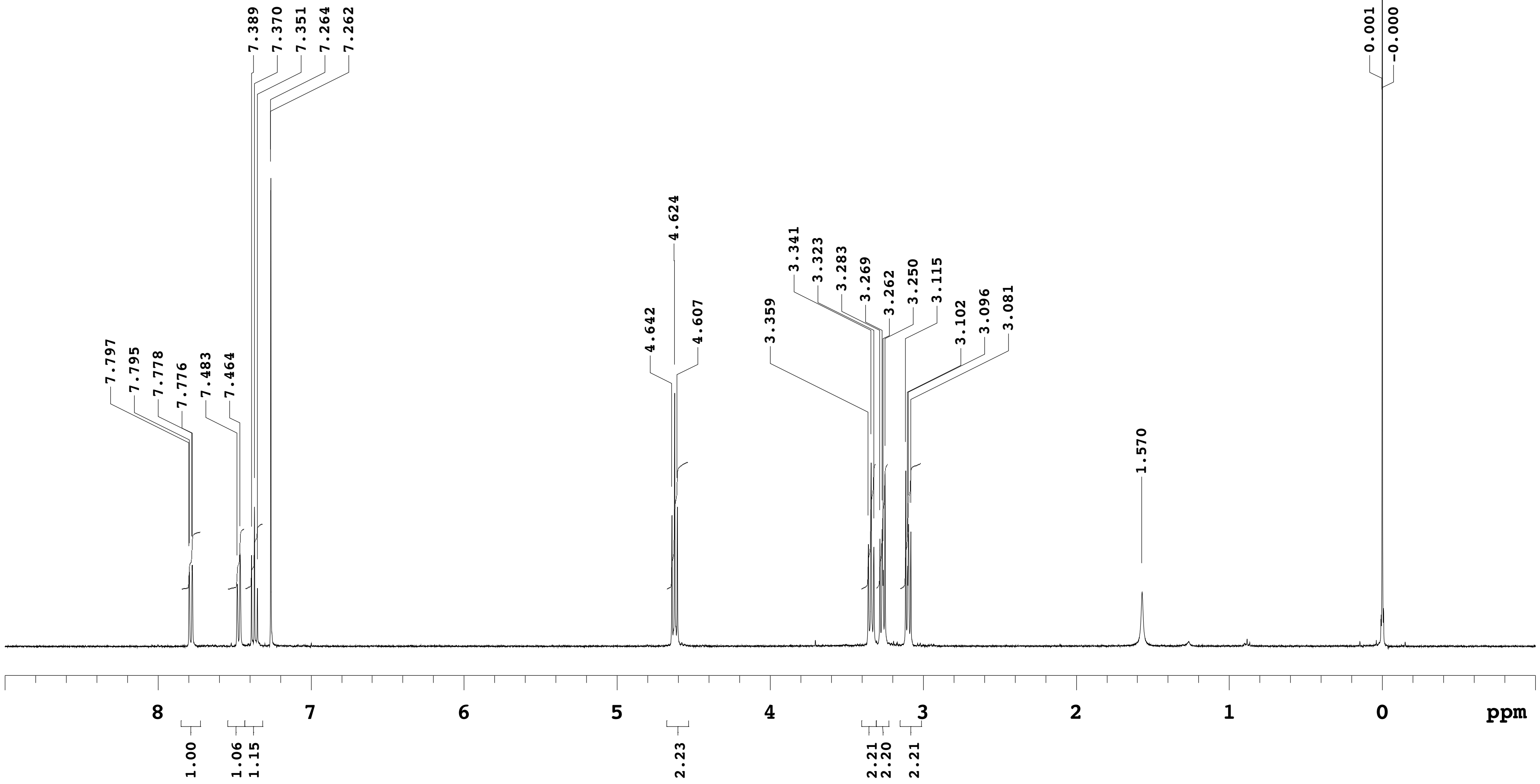




3,4,9,10-Tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (28).

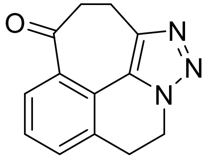
^{1}H NMR

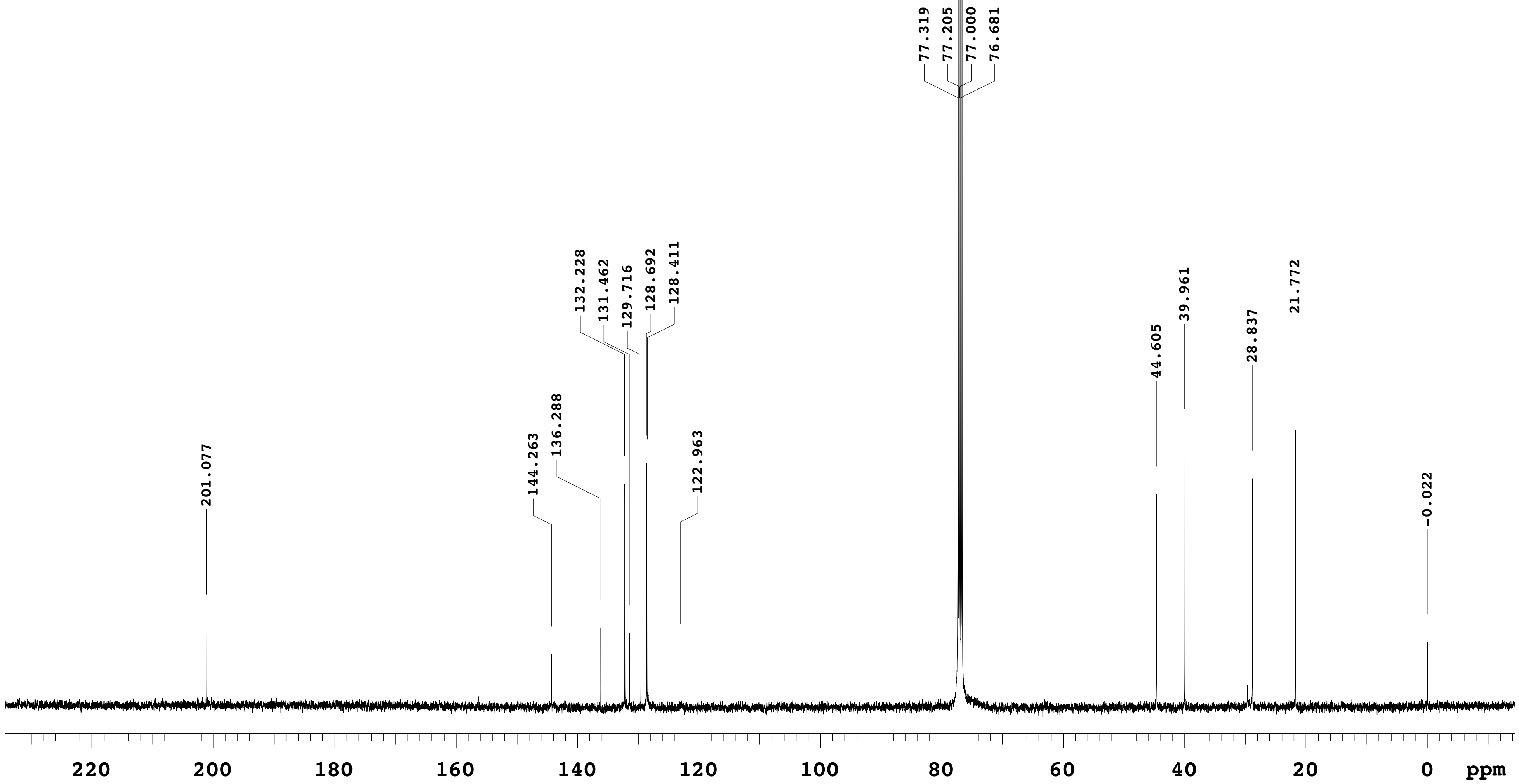




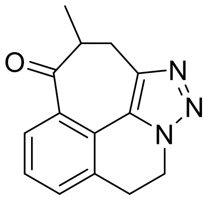
3,4,9,10-Tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (28).

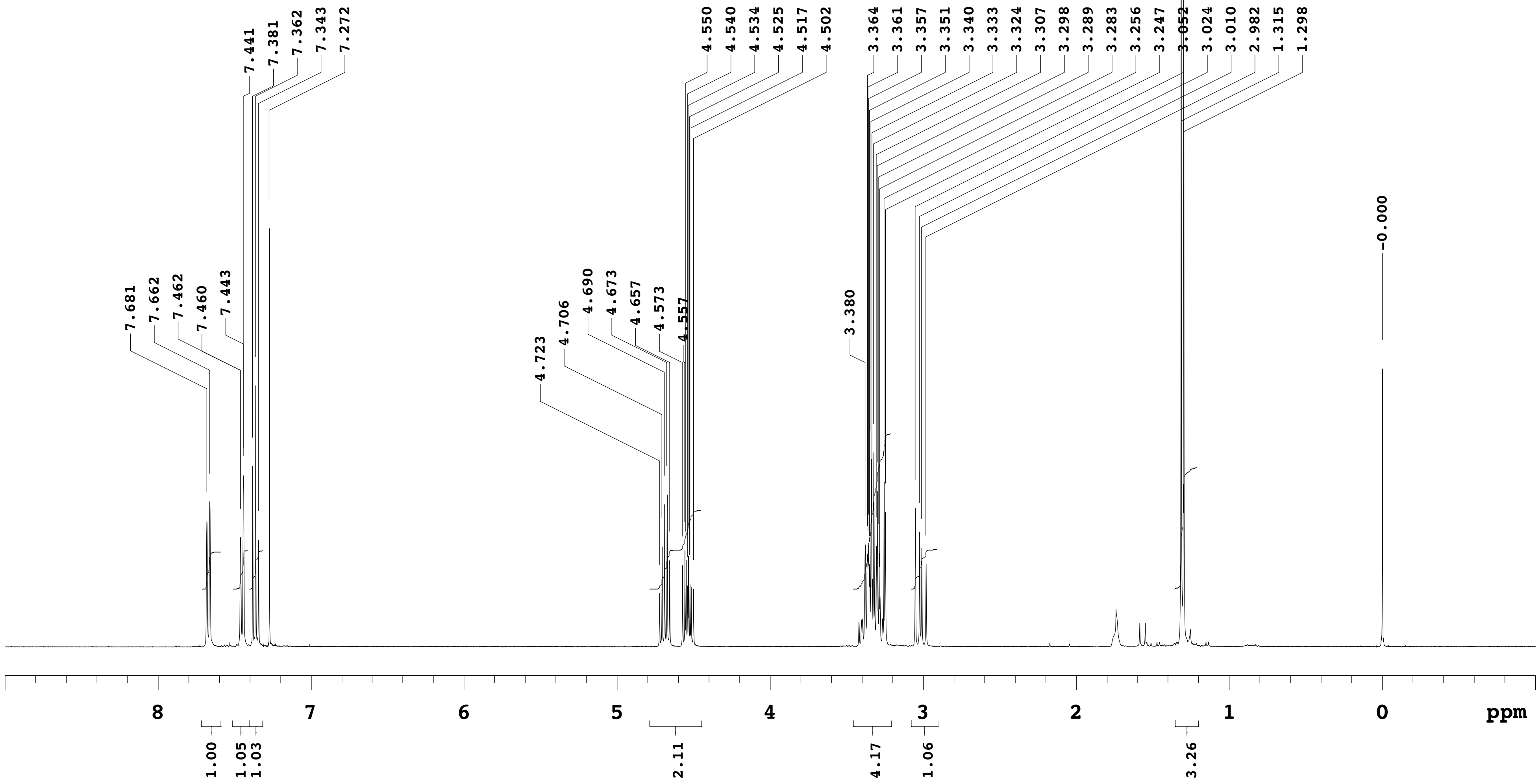
^{13}C NMR



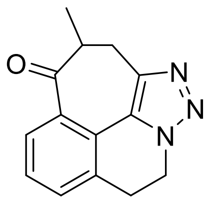


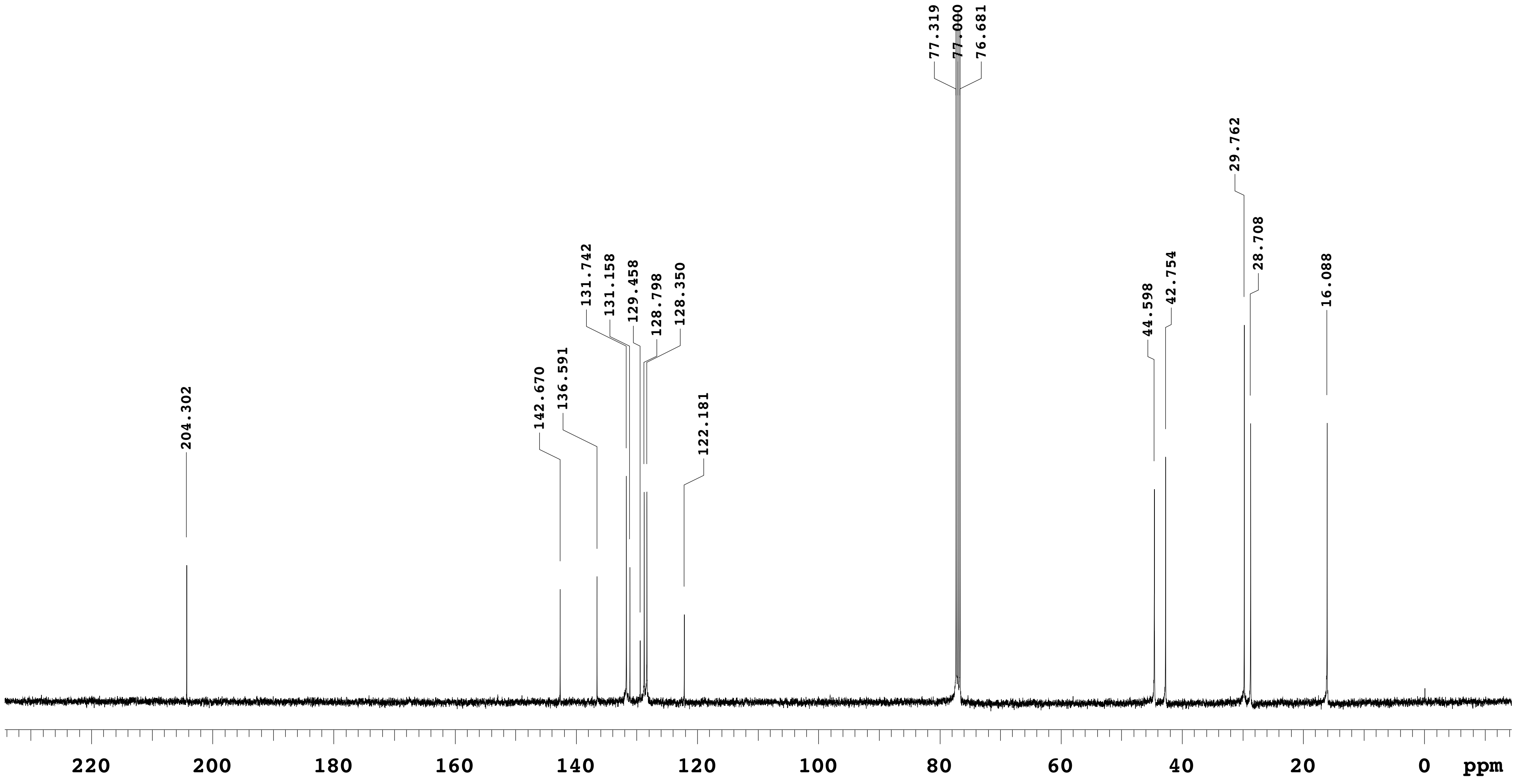
4-Methyl-3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (29). ^{1}H NMR



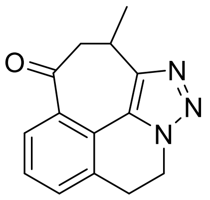


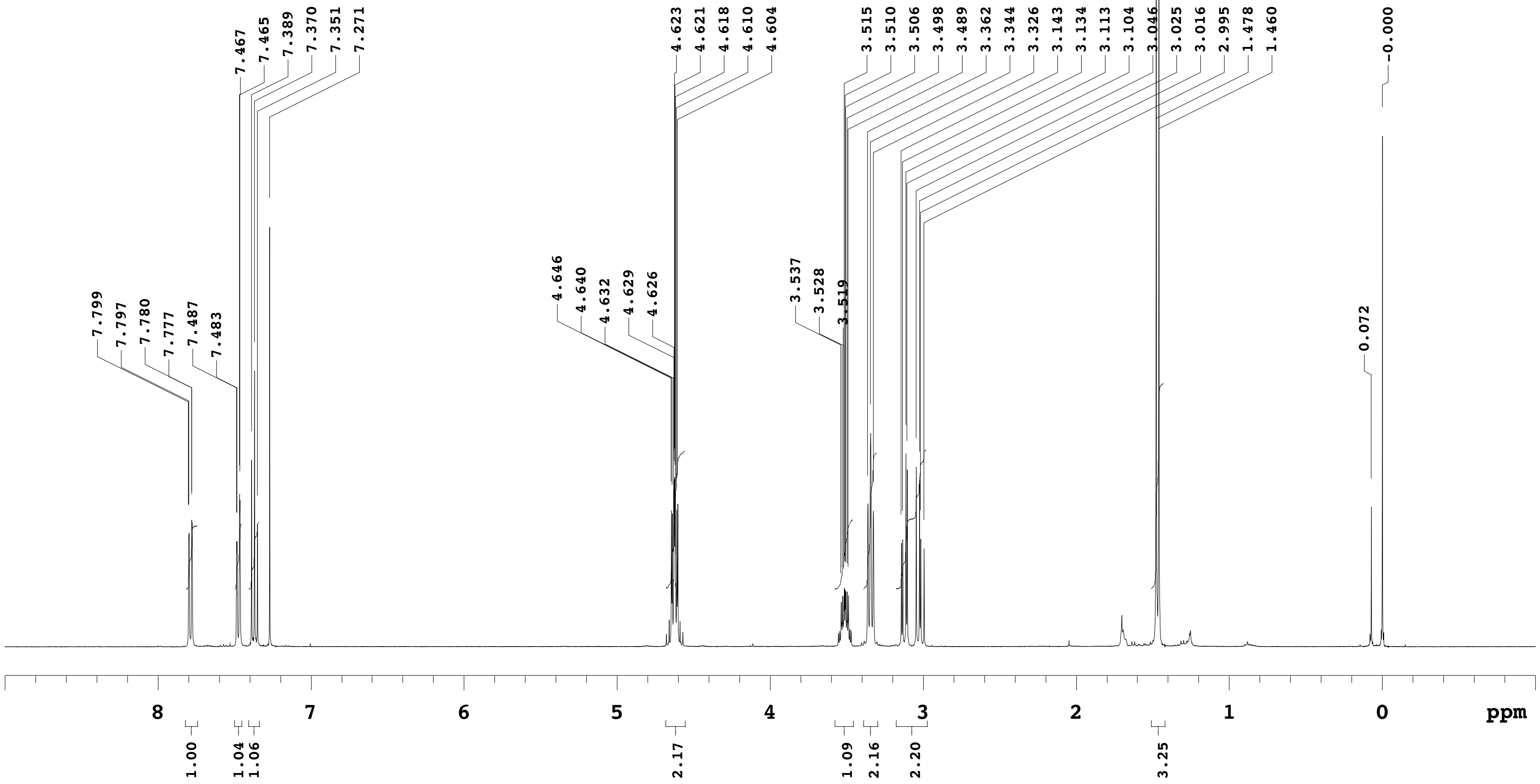
4-Methyl-3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (29). ^{13}C NMR



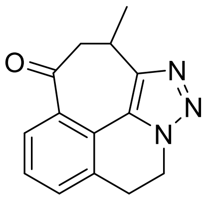


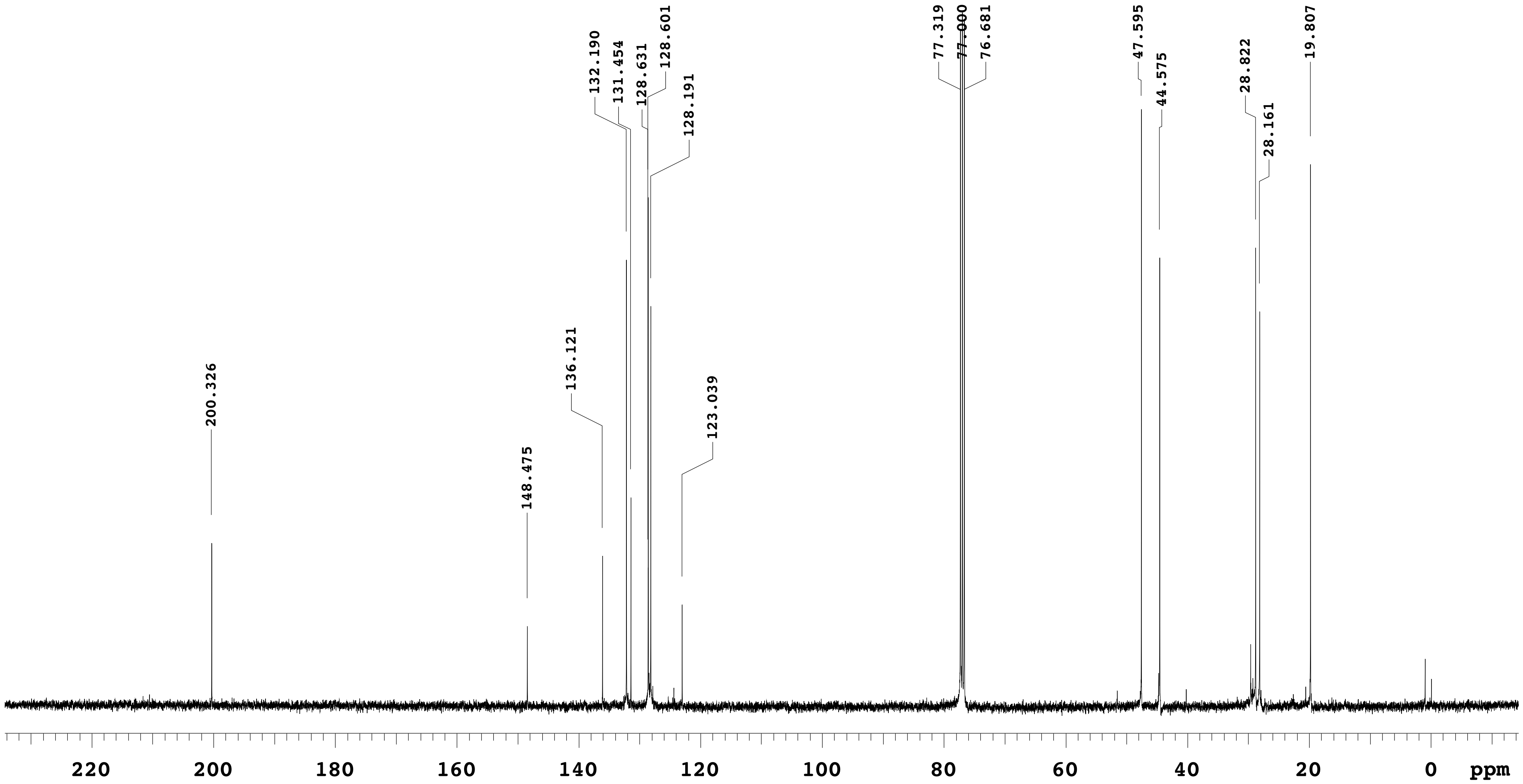
3-Methyl-3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (30). ^{1}H NMR



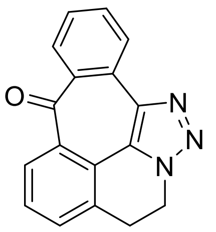


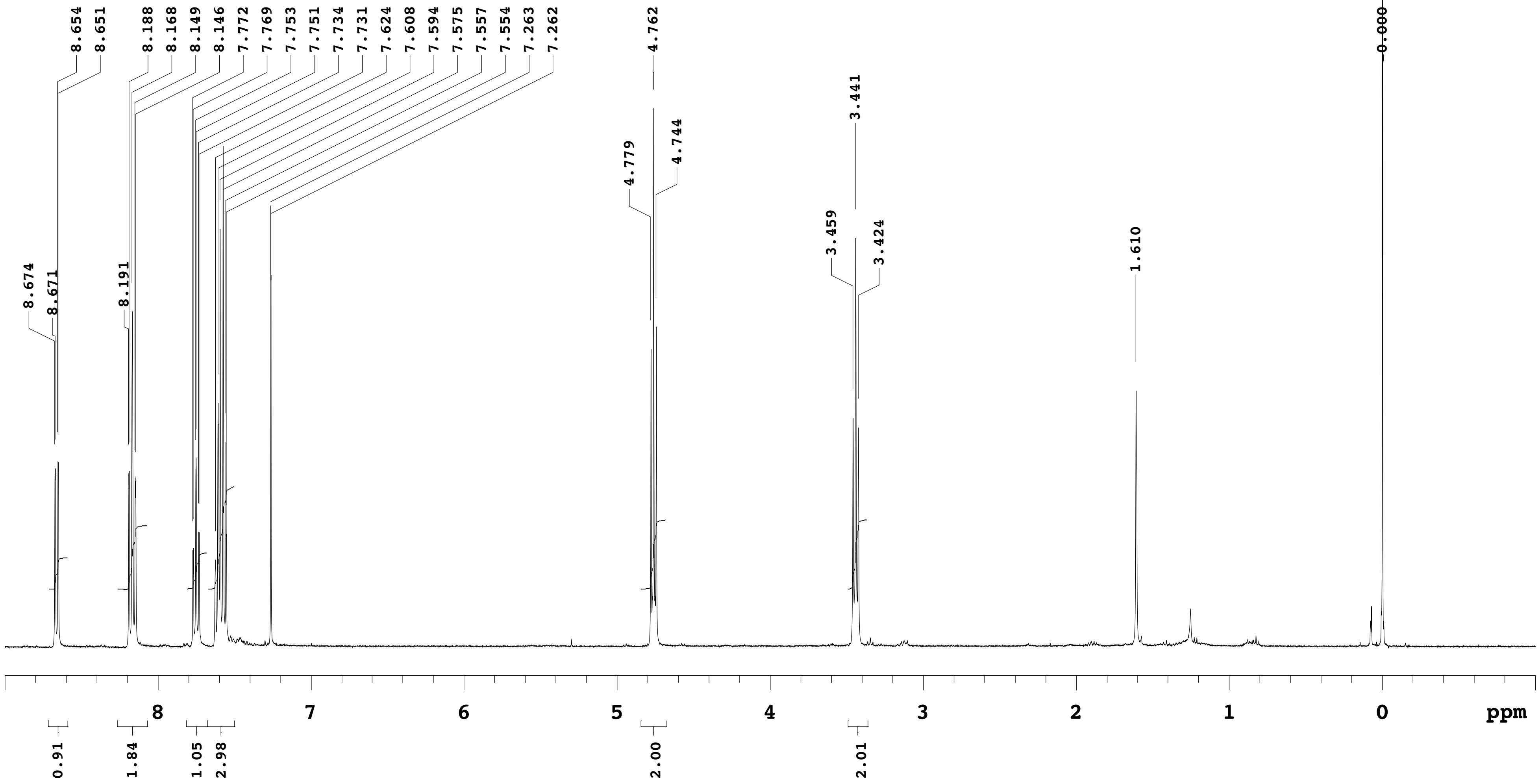
3-Methyl-3,4,9,10-tetrahydro-5*H*-1,2,10a-triazanaphtho[2,1,8-*cde*]azulen-5-one (30). **^{13}C NMR**





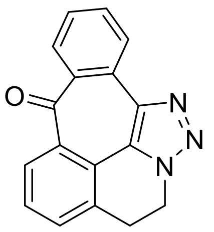
11,12-Dihydro-7*H*-1,2,12a-triazacyclopenta[*gh*]pleiaden-7-one (33). ^{1}H NMR

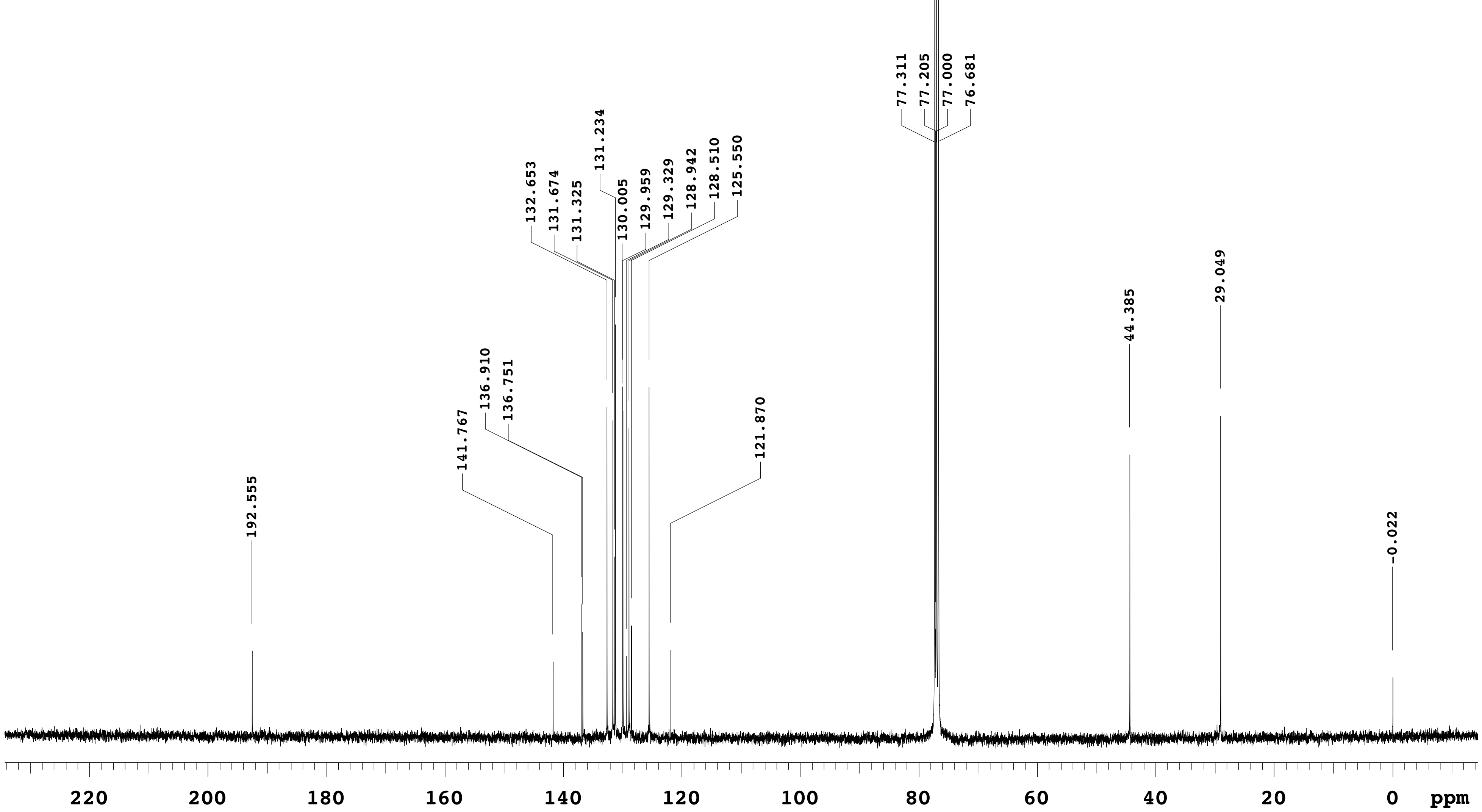




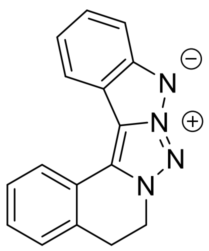
11,12-Dihydro-7*H*-1,2,12a-triazacyclopenta[*gh*]pleiaden-7-one (33).

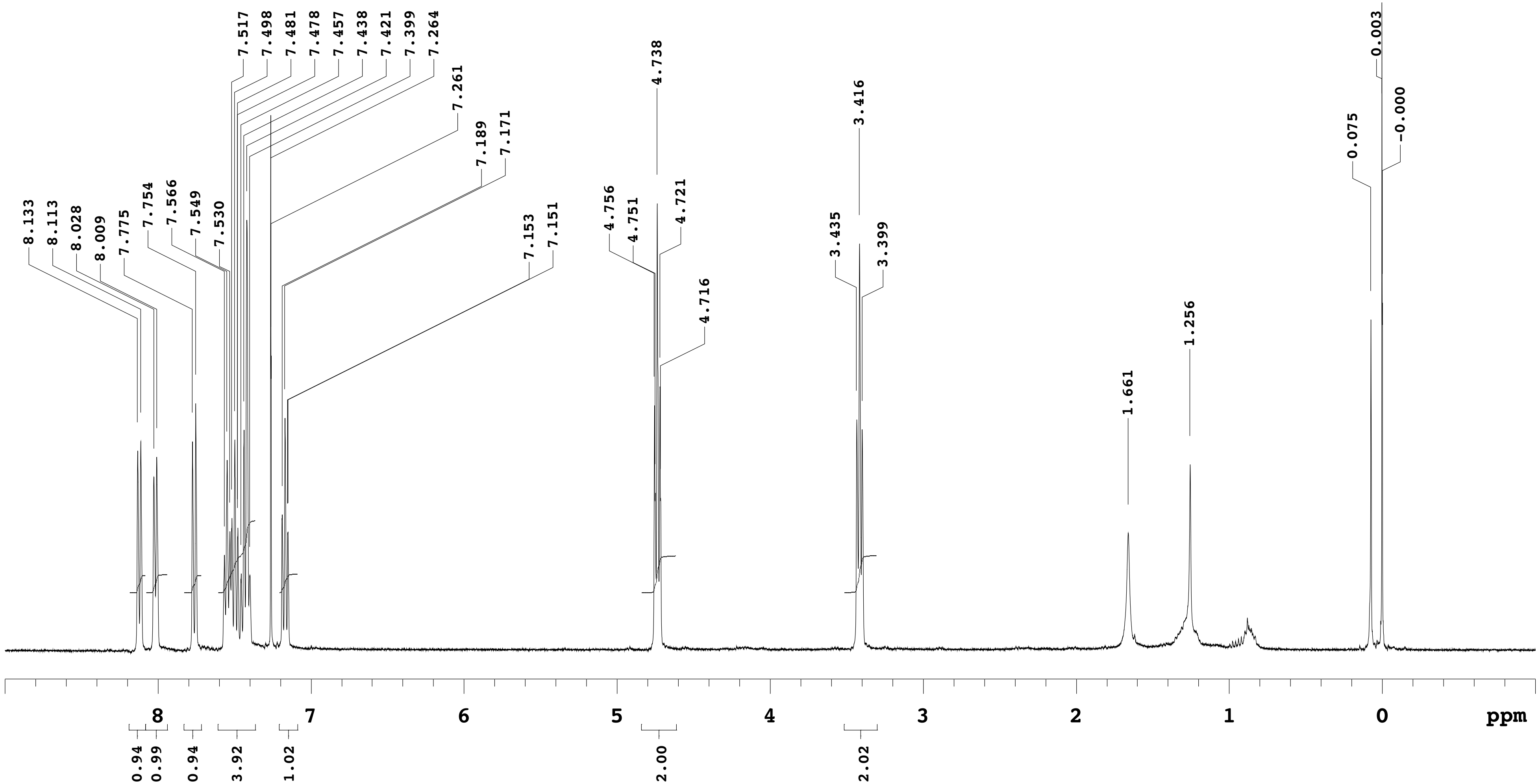
^{13}C NMR





5,6-Dihydroindazolo[2’,3’:3,4][1,2,3]triazolo[5,1-*a*]isoquinolin-9-ium-10-ide (35). ^{1}H NMR





5,6-Dihydroindazolo[2’,3’:3,4][1,2,3]triazolo[5,1-*a*]isoquinolin-9-ium-10-ide (35). ^{13}C NMR