Electronic Supplementary Information

Synthesis of bicyclic vinyl triazenes by Ficini-type reactions

Carl Thomas Bormann, Farzaneh Fadaei-Tirani, Rosario Scopelliti, and Kay Severin*

Contents

General Information

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk and glovebox techniques in oven-dried glassware with dry solvents except indicated otherwise. Cyclopentenone and cyclohexenone were dried over molecular sieves prior to use. Dry solvents were obtained using a solvent purification system from Innovative Technologies. Iodomethane was degassed using standard freeze-pump-thaw technique.

Microwave assisted synthesis was carried out in a Biotage Initiator+.

Flash column chromatography was performed with Silicycle silica gel 60 (0.040–0.063 μm grade). For the purification of the triazenes, the silica was deactivated prior to use by treating it with DCM containing 5–10 vol.-% NEt_3 and removal of the solvent under reduced pressure. Residual NEt_3 was removed either by repeated co-evaporation with pentane or by addition of pentane and freeze-drying.

1-Alkynyltriazenes[1], α-unsaturated β-ketoesters,[2] and phenyl vinyl ketone[3] were synthesized as described in the literature.

NMR spectra were recorded on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm (^{1}H); t 77.16 ppm (^{13}C)). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet, br, broad or combinations of those.

High resolution mass are given in *m/z*. Electrospray-ionization (ESI) HRMS data were acquired on a Xevo G2-S QTOF (Waters) or an Agilent LC-MS TOF operated in the positive ionization mode. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo-ionization (APPI) HR-MS measurements were performed on a LTQ–Orbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. Data were processed using the XCalibur v2.2 software. Atmospheric-pressure chemical ionization (APCI) HR-MS data were acquired on a Xevo G2-S QTOF (Waters) operated in the positive ionization mode. Data were processed using MassLynx 4.1 software.

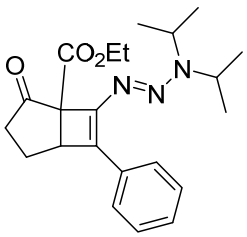
IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

The X-ray analyses were performed by Dr. R. Scopelliti and Dr. F. Fadaei-Tirani at EPFL, Lausanne.

Melting points were acquired using a Edmund Bueler SP6 apparatus and are uncorrected.

Synthesis of the vinyl triazenes **1a**–**1g**

Ethyl 7-(3,3-diisopropyltriaz-1-en-1-yl)-2-oxo-6-phenylbicyclo[3.2.0]hept-6-ene-1-carboxylate (**1a**)



$CuOTf{\cdot}C_6H_6$ (13.0 mg, 25.8 µmol, 2.5 mol%), ethyl 5-oxocyclopent-1-ene-1-carboxylate (156 mg, 1.01 mmol, 1 eq.), and 3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (280 mg, 1.21 mmol, 1.2 eq.) were dissolved in dichloromethane (10 mL). The mixture was stirred at RT under exclusion of light. The reaction was determined complete by TLC after 2 h 15 min. The mixture was filtered over cotton and the solvent was removed under vacuum. Purification by flash chromatography with a gradient of 5–10% EtOAc in pentane gave the product as a yellow solid. (327 mg, 853 µmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.1, 1.5 Hz, 2H, $C_{Ph}H$), 7.37 (t, *J* = 7.7 Hz, 2H, $C_{Ph}H$), 7.25 – 7.19 (m, 1H, $C_{Ph}H$), 5.27 (br s, 1H, $C_{i\mathrm{Pr}}H$), 4.33 – 4.08 (m, 2H, $C_{Et}H_2$), 3.95 (s, 1H, $C_{i\mathrm{Pr}}H$), 3.83 – 3.72 (m, 1H, $C_{sp3}H$), 2.89 (ddd, *J* = 18.0, 12.0, 9.4 Hz, 1H, $C_{sp3}HH$), 2.42 – 2.09 (m, 3H, $C_{sp3}H_2$), 1.39 – 1.25 (m, 12H, $C_{i\mathrm{Pr}}H_3$), 1.22 (t, *J* = 7.1 Hz, 4H, $C_{Et}H_3$).

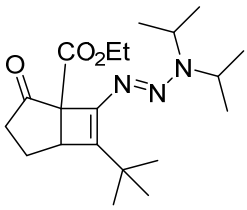
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4 (CO), 169.4 (COOEt), 142.0 (C_{sp2}-$N_3i\mathrm{Pr}_2$), 133.9 (C_{sp2}-Ph), 128.6 ($C_{Ph}H$), 127.2 ($C_{Ph}H$), 127.0 ($C_{Ph,q}$), 63.1 ($C_{sp3,q}$), 60.8 ($C_{Et}H_2$), 49.8 ($C_{i\mathrm{Pr}}H$), 46.9 ($C_{i\mathrm{Pr}}H$), 45.8 ($C_{sp3}H$), 36.1 ($C_{sp3}H_2$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 21.6 ($C_{sp3}H_2$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 14.4 ($C_{Et}H_3$).

IR (ν_{max}, cm^{-1}) 2974 (s), 2934 (s), 2873 (s), 1744 (s), 1732 (s), 1636 (s), 1407 (s), 1377 (s), 1338 (s), 1292 (s), 1249 (s), 1156 (s), 1023 (s), 913 (s), 753 (s), 729 (s).

Mp: 107 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{22}H_{29}N_3NaO_3^+$ 406.2101; Found 406.2103.

Ethyl 6-(tert-butyl)-7-(3,3-diisopropyltriaz-1-en-1-yl)-2-oxobicyclo[3.2.0]hept-6-ene-1-carboxylate (**1b**)



1b was synthesized analogously to **1a** from ethyl 5-oxocyclopent-1-ene-1-carboxylate (15.4 mg, 100 µmol, 1 eq.) and 1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (26mg, 124 µmol, 1.2 eq.) within 4 h 30 min. The product was obtained as a yellow solid (27.2 mg, 74.8 µmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (hept, *J* = 6.9 Hz, 1H, $C_{i\mathrm{Pr}}H$), 4.25 – 4.03 (m, 2H, $C_{Et}H_2$), 3.85 (hept, *J* = 6.7 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.43 – 3.34 (m, 1H, $C_{sp3}H$), 2.92 (ddd, *J* = 17.6, 12.2, 9.3 Hz, 1H, $C_{sp3}HH$), 2.29 – 2.15 (m, 1H, $C_{sp3}HH$), 2.12 – 2.01 (m, 2H, $C_{sp3}H$), 1.27 (dd, *J* = 22.4, 6.3 Hz, 5H), 1.26 (s, 9H, $C_{t\mathrm{Bu}}H_3$), 1.21 (t, *J* = 7.1 Hz, 3H $C_{Et}H_3$)., 1.15 (dd, *J* = 6.8, 3.9 Hz, 6H), 1.30 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.26 (s, 9H, $C_{t\mathrm{Bu}}H_3$), 1.24 (d, *J* = 6.0 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.21 (t, *J* = 7.1 Hz, 3H, $C_{Et}H_3$), 1.15 (d, *J* = 6.7 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.14 (d, J = 6.3 Hz, 3H, $C_{i\mathrm{Pr}}H_3$).

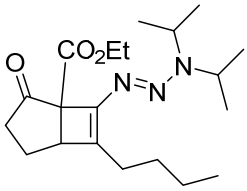
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1 (CO), 169.7 (CO_2Et), 140.9 (C_{sp2}-$N_3i\mathrm{Pr}_2$), 139.1 (C_{sp2}-*t*Bu), 62.1 ($C_{sp3,q}$), 60.5 ($C_{Et}H_2$), 49.4 ($C_{i\mathrm{Pr}}H$), 46.6 ($C_{sp3}H$), 46.4 ($C_{i\mathrm{Pr}}H$), 35.8 ($C_{sp3}H_2$), 34.1 ($C_{t\mathrm{Bu},q}$), 29.2 ($C_{t\mathrm{Bu}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 22.8 ($C_{sp3}H_2$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 19.2 ($C_{i\mathrm{Pr}}H_3$), 14.4 ($C_{Et}H_3$).

IR (ν_{max}, cm^{-1}) 2968 (s), 2933 (s), 2870 (s), 1735 (s), 1463 (s), 1408 (s), 1365 (s), 1312 (s), 1290 (s), 1244 (s), 1197 (s), 1158 (s), 1111 (s), 1072 (s), 1029 (s), 961 (s).

Mp: 35 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{33}N_3NaO_3^+$ 386.2414; Found 386.2409.

Ethyl 6-butyl-7-(3,3-diisopropyltriaz-1-en-1-yl)-2-oxobicyclo[3.2.0]hept-6-ene-1-carboxylate **1c**

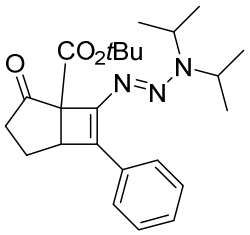


1c was synthesized analogously to **1a** from ethyl 5-oxocyclopent-1-ene-1-carboxylate (14.9 mg, 96.8 µmol, 1 eq.) and 1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (25.2 mg, 120 µmol, 1.2 eq.) within 2 h 30 min. The product was obtained as a yellow solid (20.5 mg, 56.4 µmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (br s, 1H, $C_{i\mathrm{Pr}}H$), 4.25 – 4.02 (m, 2H, $C_{Et}H_2$), 3.84 (br s, 1H, $C_{i\mathrm{Pr}}H$), 3.33 (d, *J* = 6.7 Hz, 1H, $C_{sp3}H$), 2.87 (ddd, *J* = 17.8, 11.9, 9.4 Hz, 1H, $C_{sp3}HH$), 2.39 (dt, *J* = 15.5, 7.7 Hz, 1H, C_{sp3}-C*H*H), 2.33 – 2.19 (m, 2H, $C_{sp3}HH$ + C_{sp2}-C*H*H), 2.12 –

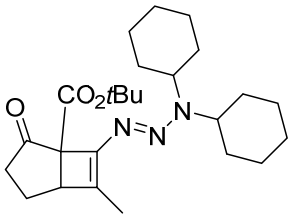
1.91 (m, 2H, $C_{sp3}CH_2$), 1.62 (p, *J* = 7.4 Hz, 2H, C_{sp2}-CH_2-C*H*$_2$), 1.41 (hd, *J* = 7.3, 2.1 Hz, 2H, C_{sp2}-CH_2-CH_2-C*H*$_2$), 1.34 – 1.04 (m, 12H, $C_{i\mathrm{Pr}}H_3$), 1.22 (t, *J* = 7.1 Hz, 3H, $C_{\mathrm{Et}}H_3$), 0.93 (t, *J* = 7.3 Hz, 3H, $C_{n\mathrm{Bu}}H_3$).
^{13}C NMR (101 MHz, CDCl3) δ 209.1 (CO), 169.6 (COOEt), 142.7 (C_{sp2}-N_3*i*Pr_2), 132.5 (C_{sp2}-*n*Bu), 63.0 ($C_{sp3,q}$), 60.6 ($C_{\mathrm{Et}}H_2$), 49.1 ($C_{i\mathrm{Pr}}H$), 47.5 ($C_{sp3}H$), 45.9 ($C_{i\mathrm{Pr}}H$), 36.0 ($C_{sp3}H_2$), 29.4 (C_{sp2}-CH_2-*C*H_2), 26.8 (C_{sp2}-*C*H_2-CH_2), 23.4 ($C_{i\mathrm{Pr}}H_3$), 22.9 (C_{sp2}-CH_2-CH_2-C*H*$_2$), 21.2 ($C_{sp3}H_2$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 14.4 ($C_{\mathrm{Et}}H_3$), 14.0 ($C_{n\mathrm{Bu}}H_3$).
IR (ν_{max}, cm^{-1}) 2969 (s), 2933 (s), 2873 (s), 1735 (s), 1467 (s), 1408 (s), 1366 (s), 1246 (s), 1157 (s), 1118 (s), 1032 (s).
Mp: 47 °C.
HRMS (ESI/QTOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{33}N_3NaO_3^+$ 386.2414; Found 386.2432.

tert-Butyl 7-(3,3-diisopropyltriaz-1-en-1-yl)-2-oxo-6-phenylbicyclo[3.2.0]hept-6-ene-1-carboxylate (**1d**)



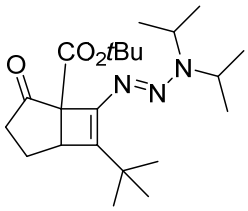
1d was synthesized analogously to **1a** from tert-butyl 5-oxocyclopent-1-ene-1-carboxylate (18.4 mg, 101 µmol, 1 eq.) and 3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (26.7 mg, 116 µmol, 1.2 eq.) within 2 h 10 min. The product was obtained as a yellow solid (37.4 mg, 90.9 µmol, 90%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H, $C_{\mathrm{Ph}}H$), 7.36 (dd, *J* = 7.7 Hz, 2H, $C_{\mathrm{Ph}}H$), 7.25 – 7.19 (m, 1H, $C_{\mathrm{Ph}}H$), 5.31 – 5.15 (br m, 1H, $C_{i\mathrm{Pr}}H$), 3.95 (br s, 1Hz, $C_{i\mathrm{Pr}}H$), 3.72 (dd, *J* = 6.2, 1.5 Hz, 1H, $C_{sp3}H$), 2.85 (ddd, *J* = 17.4, 11.6, 9.3 Hz, 1H, C_{sp3}*H*H), 2.33 – 2.12 (m, 3H, C_{sp3}*H*H + $C_{sp3}H_2$), 1.44 (s, 9H, $C_{t\mathrm{Bu}}H_3$), 1.36 (d, *J* = 6.3 Hz, 6H, $C_{i\mathrm{Pr}}H_3$), 1.25 (d, *J* = 6.8 Hz, 6H, $C_{i\mathrm{Pr}}H_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7 (CO), 168.6 (CO_2*t*Bu), 142.3 (C_{sp2}-N_3*i*Pr_2), 134.1 (C_{sp2}-Ph), 128.5 ($C_{\mathrm{Ph}}H$), 127.0 ($C_{\mathrm{Ph}}H$), 126.9 ($C_{\mathrm{Ph}}H$), 126.9 ($C_{\mathrm{Ph},q}$), 80.8 ($C_{t\mathrm{Bu},q}$), 64.3 ($C_{sp3,q}$), 49.9 ($C_{i\mathrm{Pr}}H$), 46.8 ($C_{i\mathrm{Pr}}H$), 45.9 ($C_{sp3}H$), 36.2 ($C_{sp3}H_2$), 28.2 ($C_{t\mathrm{Bu}}H_3$), 23.6 ($C_{i\mathrm{Pr}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 21.6 ($C_{sp3}H_2$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 19.2 ($C_{i\mathrm{Pr}}H_3$).
IR (ν_{max}, cm^{-1}) 2974 (w), 2934 (w), 2872 (w), 1730 (m), 1368 (s), 1340 (m), 1300 (m), 1250 (s), 1148 (s), 1082 (m), 1024 (m), 910 (m), 730 (s).
Mp: 116–119 °C.
HRMS (ESI/QTOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{24}H_{33}N_3NaO_3^+$ 434.2414; Found 434.2424.

tert-Butyl 7-(3,3-dicyclohexyltriaz-1-en-1-yl)-6-methyl-2-oxobicyclo[3.2.0]hept-6-ene-1-carboxylate (**1e**)



1e was synthesized analogously to **1a** from *tert*-butyl 5-oxocyclopent-1-ene-1-carboxylate (17.8 mg, 97.7 µmol, 1 eq.) and 3,3-dicyclohexyl-1-(prop-1-yn-1-yl)triaz-1-ene (29.3 mg, 118 µmol, 1.2 eq.) within 2 h 10 min. The product was obtained as a yellow solid (36.7 mg, 85.4 µmol, 87%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (br s, 1H, $C_{\mathrm{Cy}}H$), 3.33 (m, 1H, $C_{\mathrm{Cy}}H$), 3.23 (d, *J* = 6.8 Hz, 1H, $C_{sp3}H$), 2.82 (ddd, *J* = 17.8, 11.7, 9.4 Hz, 1H, C_{sp3}*H*H), 2.21 (ddd, *J* = 17.7, 8.4, 1.7 Hz, 1H, C_{sp3}*H*H), 2.07 – 1.93 (m, 2H, $C_{sp3}H_2$), 1.91 (d, *J* = 1.3 Hz, 3H, CH_3), 1.87 – 1.57 (m, 12H, $C_{\mathrm{Cy}}H_2$), 1.42 (s, 9H, $C_{t\mathrm{Bu}}H_3$), 1.41 – 1.07 (m, 8H, $C_{\mathrm{Cy}}H_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4 (CO), 168.9 (CO_2*t*Bu), 143.3 (C_{sp2}-N_3Cy_2), 127.8 (C_{sp2}-Me), 80.5 ($C_{t\mathrm{Bu},q}$), 64.8 ($C_{sp3,q}$), 57.8 ($C_{\mathrm{Cy}}H$), 53.6 ($C_{\mathrm{Cy}}H$), 48.7 ($C_{sp3}H$), 36.0 ($C_{sp3}H_2$), 34.0 ($C_{\mathrm{Cy}}H_2$), 33.69 ($C_{\mathrm{Cy}}H_2$), 30.0 ($C_{\mathrm{Cy}}H_2$), 29.9 ($C_{\mathrm{Cy}}H_2$), 28.2 ($C_{t\mathrm{Bu}}H_3$), 26.3 ($C_{\mathrm{Cy}}H_2$), 25.9 ($C_{\mathrm{Cy}}H_2$), 25.5 ($C_{\mathrm{Cy}}H_2$), 20.6 ($C_{sp3}H_2$), 11.7 ($C_{\mathrm{Me}}H_3$).
IR (ν_{max}, cm^{-1}) 2930 (m), 2854 (w), 1732 (m), 1452 (m), 1408 (s), 1368 (m), 1338 (m), 1302 (m), 1254 (s), 1210 (m), 1146 (s), 910 (m), 798 (m), 730 (s).
Mp: 74 °C.
HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{40}N_3O_3^+$ 430.3064; Found 430.3064.

tert-Butyl 6-(tert-butyl)-7-(3,3-diisopropyltriaz-1-en-1-yl)-2-oxobicyclo[3.2.0]hept-6-ene-1-carboxylate (**1f**)



1f was synthesized analogously to **1a** from *tert*-butyl 5-oxocyclopent-1-ene-1-carboxylate (17.9 mg, 98.2 µmol, 1 eq.) and 1-(3,3-dimethylbut-1-yn-1-yl)-3,3-diisopropyltriaz-1-ene (24.7 mg, 118 µmol, 1.2 eq.) within 2 h 15 min. The product was obtained as a yellow solid (28.0 mg, 71.5 µmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 – 4.84 (m, 1H, $C_{i\mathrm{Pr}}H$), 3.90 – 3.78 (m, 1H, $C_{i\mathrm{Pr}}H$), 3.32 (dd, *J* = 5.3, 2.1 Hz, 1H, $C_{sp3}H$), 2.89 (ddd, *J* = 17.4, 11.9, 9.5 Hz, 1H, $C_{sp3}HH$), 2.27 – 2.14 (m, 1H, $C_{sp3}HH$), 2.11 – 1.97 (m, 2H, $C_{sp3}H_2$), 1.41 (s, 9H, $C_{O\text{-}t\mathrm{Bu}}H_3$), 1.30 (d, *J* = 5.9 Hz, 6H, $C_{i\mathrm{Pr}}H_3$), 1.25 (s, 9H, $C_{t\mathrm{Bu}}H_3$), 1.15 (d, *J* = 6.9 Hz, 6H, $C_{i\mathrm{Pr}}H_3$).

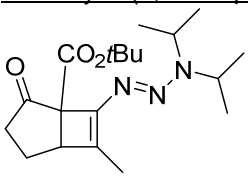
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3 (CO), 168.9 (CO_2tBu), 141.1 (C_{sp2}-$N_3i\mathrm{Pr}_2$), 139.1 (C_{sp2}-*t*Bu), 80.3 ($C_{O\text{-}t\mathrm{Bu},q}$), 63.0 ($C_{sp3,q}$), 49.6 ($C_{i\mathrm{Pr}}H$), 46.7 ($C_{sp3}H$), 46.5 ($C_{i\mathrm{Pr}}H$), 36.0 ($C_{sp3}H_2$), 34.0 ($C_{t\mathrm{Bu},q}$), 29.2 ($C_{t\mathrm{Bu}}H_3$), 28.2 ($C_{O\text{-}t\mathrm{Bu}}H_3$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 22.8 ($C_{sp3}H_2$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 19.2 ($C_{i\mathrm{Pr}}H_3$).

IR (ν_{max}, cm^{-1}) 2968 (m), 2932 (w), 2870 (w), 1732 (s), 1460 (w), 1406 (s), 1366 (m), 1296 (m), 1244 (s), 1152 (s), 1110 (s), 1074 (m), 1028 (m), 998 (m), 964 (w), 920 (w), 874 (w), 844 (w), 818 (w), 732 (w).

Mp: 44 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{22}H_{37}N_3NaO_3^+$ 414.2727; Found 414.2721.

tert-Butyl 7-(3,3-diisopropyltriaz-1-en-1-yl)-6-methyl-2-oxobicyclo[3.2.0]hept-6-ene-1-carboxylate (**1g**)



1g was synthesized analogously to **1a** from *tert*-butyl 5-oxocyclopent-1-ene-1-carboxylate (18.1 mg, 99.3 µmol, 1 eq.) and 3,3-diisopropyl-1-(prop-1-yn-1-yl)triaz-1-ene (20.2 mg, 121 µmol, 1.22 eq.) within 2 h 10 min. The product was obtained as a yellow oil (28.0 mg, 71.5 µmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (br s, 1H, $C_{i\mathrm{Pr}}H$), 3.84 (br s, 1H, $C_{i\mathrm{Pr}}H$), 3.24 (d, *J* = 6.8 Hz, 1H, $C_{sp3}H$), 2.82 (ddd, *J* = 17.8, 11.8, 9.4 Hz, 1H, $C_{sp3}HH$), 2.21 (ddd, *J* = 17.9, 8.3, 1.7 Hz, 1H, $C_{sp3}HH$), 2.07 – 1.92 (m, 2H), 1.90 (d, *J* = 1.4 Hz, 3H, $C_{\mathrm{Me}}H_3$), 1.42 (s, 9H, $C_{t\mathrm{Bu}}H_3$), 1.28 (d, *J* = 6.4 Hz, 6H, $C_{i\mathrm{Pr}}H_3$), 1.14 (d, *J* = 6.7 Hz, 6H, $C_{i\mathrm{Pr}}H_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3 (CO), 168.8 (CO_2tBu), 143.3 (C_{sp2}-$N_3i\mathrm{Pr}_2$), 128.1 (C_{sp2}-Me), 80.5 ($C_{t\mathrm{Bu},q}$), 64.7 ($C_{sp3,q}$), 48.9 ($C_{i\mathrm{Pr}}H$), 48.7 ($C_{sp3}H$), 45.4 ($C_{i\mathrm{Pr}}H$), 36.0 ($C_{sp3}H_2$), 28.2 ($C_{t\mathrm{Bu}}H_3$), 23.6 ($C_{i\mathrm{Pr}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 20.5 ($C_{sp3}H_2$), 19.5 ($C_{i\mathrm{Pr}}H_3$), 19.6 ($C_{i\mathrm{Pr}}H_3$), 11.6 ($C_{\mathrm{Me}}H_3$).

IR (ν_{max}, cm^{-1}) 2973 (w), 2933 (w), 2874 (w), 1731 (s), 1408 (s), 1366 (m), 1303 (m), 1248 (s), 1146 (s), 1116 (s), 1092 (m), 1028 (m), 1002 (m), 967 (m), 917 (w), 842 (w), 803 (w), 773 (w), 731 (m).

HRMS (ESI/QTOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{19}H_{31}N_3NaO_3^+$ 372.2258; Found 372.2269.

Structure of the vinyl triazenes 1a–1g

The structure of products **1a**–**1g** was corroborated by ^{1}H-^{13}C-HSQC spectroscopy. In **1b**, for example, the protons from both the CH_2-group adjacent to the bridgehead (2.12 – 2.01 ppm (m, 2H)) and the *t*Bu-group (1.26 ppm (s, 9H)) couple to the same vinylic carbon (139.1 ppm) (Figure S1). Such a coupling pattern requires the reported isomer **A**. For the hypothetical isomer **B**, the respective protons would each couple to different vinylic carbons (139.1 ppm and 140.9 ppm), which is not observed.

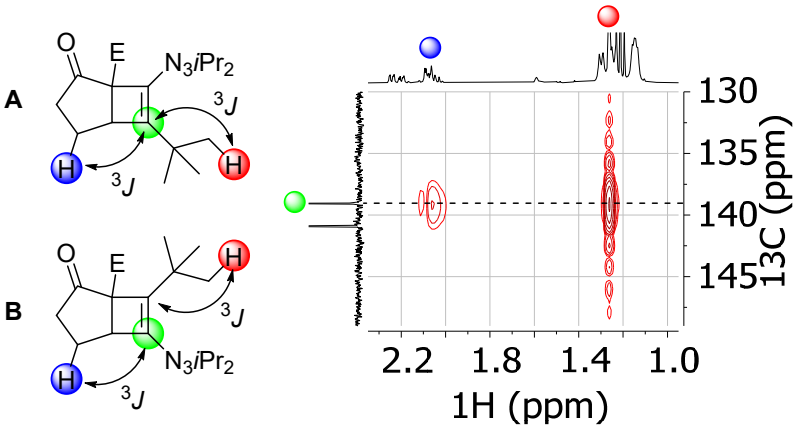
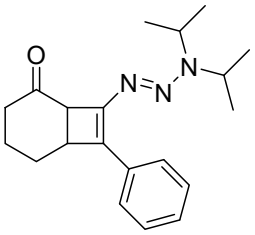


Figure S1. Left: Possible regioisomers and coupling partners of the vinylic carbons of **1b**. E = CO_2Et Right: Section of the ^{1}H-^{13}C-HSQC spectrum showing the actual coupling pattern.

Synthesis of the vinyl triazenes **2a**–**2j**

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-phenylbicyclo[4.2.0]oct-7-en-2-one (**2a**)



Tris(pentafluorophenyl)borane (5.6 mg, 11 µmol, 2.5 mol%.), (*E*)-3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (100 mg, 437 µmol, 1 eq.) and 2-cyclohexen-1-one (106 µL, 1.09 mmoles, 2.5 eq.) were dissolved in toluene (2 mL). The mixture was stirred at RT for 24 h. K_2CO_3 (sat. aq., 5.4 µL) was added and the mixture was stirred vigorously for 20 min. The mixture was then filtered over a plug of $MgSO_4$ and basic alumina and eluted with Et_2O. The solvent was removed under vacuum. Purification by flash chromatography with a gradient of 0–15% Et_2O in pentane gave the product in the form of a yellow solid (139 mg, 428 µmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H, $C_{Ph}H$), 7.35 (t, *J* = 7.7 Hz, 2H, $C_{Ph}H$), 7.25 – 7.15 (m, 1H, $C_{Ph}H$), 5.23 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.92 (hept, *J* = 6.6 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.76 (dd, *J* = 4.8, 1.8 Hz, 1H, $C_{CO\text{-}sp3}H$), 3.58 (td, *J* = 4.8, 2.0 Hz, 1H, $C_{sp3}H$), 2.55 – 2.44 (m, 1H, $C_{sp3}HH$), 2.28 – 2.17 (m, 2H, 2 x $C_{sp3}HH$), 2.16 – 2.00 (m, 1H, $C_{sp3}HH$), 1.77 – 1.61 (m, 2H, $C_{sp3}H_2$), 1.33 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.29 – 1.20 (m, 9H, $C_{i\mathrm{Pr}}H_3$).

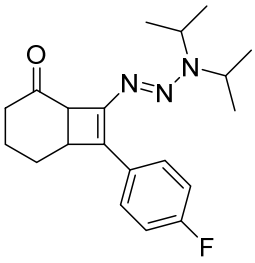
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8 (CO), 142.6 (C_{sp2}-$N_3i\mathrm{Pr}_2$), 134.6 ($C_{Ph,q}$), 128.5 ($C_{Ph}H$), 127.2 (C_{sp2}-Ph), 126.9 ($C_{Ph}H$), 126.6 ($C_{Ph}H$), 53.8 ($C_{CO\text{-}sp3}H$), 49.6 ($C_{i\mathrm{Pr}}H$), 46.7 ($C_{i\mathrm{Pr}}H$), 38.9 ($C_{sp3}H_2$), 38.2 ($C_{sp3}H$), 25.2 ($C_{sp3}H_2$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.3 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 18.3 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 2973 (w), 2933 (w), 2905 (w), 2876 (w), 2852 (w), 1699 (s), 1633 (w), 1492 (w), 1448 (m), 1379 (s), 1338 (m), 1249 (s), 1155 (s), 1114 (m), 1095 (m), 1031 (m), 977 (m), 758 (s).

Mp: 97 °C.

HRMS (ESI/QTOF) *m*/*z*: [M + H]+ Calcd for C20H28N3O+ 326.2227; Found 326.2229.

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(4-fluorophenyl)bicyclo[4.2.0]oct-7-en-2-one (**2b**)



2b was synthesized analogously to **2a** from 1-((4-fluorophenyl)ethynyl)-3,3-diisopropyltriaz-1-ene (59.5 mg, 241 µmol, 1 eq.) and 2-cyclohexen-1-one (58 µL, 599 µmol, 2.5 eq.). The product was obtained as a highly viscous yellow liquid (70.0 mg, 203 µmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H, $C_{Ph}H$), 7.11 – 6.97 (m, 2H, $C_{Ph}H$), 5.21 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.92 (hept, *J* = 6.6 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.75 (dd, *J* = 4.8, 1.7 Hz, 1H, $C_{CO\text{-}sp3}H$), 3.54 (td, *J* = 4.6, 4.2, 1.8 Hz, 1H, $C_{sp3}H$), 2.54 – 2.42 (m, 1H, $C_{sp3}HH$), 2.29 – 2.14 (m, 2H2 x $C_{sp3}HH$), 2.14 – 1.97 (m, 1H, $C_{sp3}HH$), 1.78 – 1.60 (m, 2H, $C_{sp3}H_2$), 1.32 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.28 – 1.18 (m, 9H, $C_{i\mathrm{Pr}}H_3$).

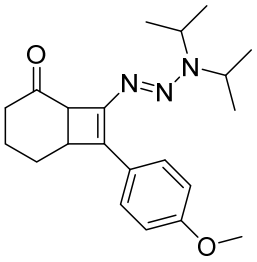
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.5 (CO), 161.7 (d, *J* = 246.7 Hz, $C_{Ph}F$), 142.0 (d, *J* = 2.8 Hz, C_{sp2}-$N_3i\mathrm{Pr}_2$), 131.0 (d, *J* = 3.4 Hz, $C_{Ph,q}$), 128.5 (d, *J* = 7.7 Hz, $C_{Ph}H$), 126.1 (d, *J* = 1.4 Hz, C_{sp2}-Ph), 115.5 (d, *J* = 21.5 Hz, $C_{Ph}H$), 53.7 ($C_{CO\text{-}sp3}H$), 49.6 ($C_{i\mathrm{Pr}}H$), 46.6 ($C_{i\mathrm{Pr}}H$), 38.9 ($C_{sp3}H_2$), 38.2 ($C_{sp3}H$), 25.1 ($C_{sp3}H_2$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.3 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 18.3 ($C_{sp3}H_2$).

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.6.

IR (ν_{max}, cm^{-1}) 2974 (w), 2935 (w), 2907 (w), 2878 (w), 1700 (m), 1636 (w), 1506 (s), 1380 (s), 1331 (s), 1251 (s), 1232 (s), 1154 (s), 1113 (m), 1095 (m), 979 (m), 839 (s), 731 (m).

HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{27}FN_3O^+$ 344.2133; Found 344.2125.

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(4-methoxyphenyl)bicyclo[4.2.0]oct-7-en-2-one (**2c**)



2c was synthesized analogously to **2a** from 3,3-diisopropyl-1-((4-methoxyphenyl)ethynyl)triaz-1-ene (62.3 mg, 240 µmol, 1 eq.) and cyclohexen-1-one (58 µL, 599 µmol, 2.5 eq.) using tris(pentafluorophenyl)-borane (6.1 mg, 12 µmol, 5 mol%). The product was obtained as a yellow solid (68.1 mg, 192 µmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H, $C_{Ph}H$), 6.95 – 6.87 (m, 2H, $C_{Ph}H$), 5.21 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.91 (hept, *J* = 6.6 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.83 (s, 3H, O-$C_{Me}H_3$), 3.74 (dd, *J* = 4.8, 1.7 Hz, 1H, $C_{CO\text{-}sp3}H$), 3.53 (m, 1H, $C_{sp3}H$), 2.48 (dd, *J* = 18.4, 7.6 Hz, 1H, $C_{sp3}HH$), 2.21 (m, 2H 2 x $C_{sp3}HH$), 2.08 (dddd, *J* = 18.1, 16.7, 9.4, 4.0 Hz, 1H, $C_{sp3}HH$), 1.72 (dt, *J* = 13.5, 3.9 Hz, 1H, $C_{sp3}HH$), 1.68 – 1.58 (m, 1H, $C_{sp3}HH$), 1.32 (d, *J* = 6.5 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.24 (m, 9H, $C_{i\mathrm{Pr}}H_3$).

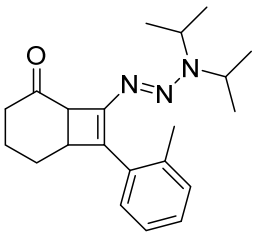
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.0 (CO), 158.5 (C_{Ph}-OMe), 140.5 (C_{sp2}-N_3iPr_2), 128.3 ($C_{Ph}H$), 127.7 ($C_{Ph,q}$), 127.1 (C_{sp2}-Ph), 114.1 ($C_{Ph}H$), 55.4 (O-$C_{Me}H_3$), 53.8 ($C_{CO\text{-}sp3}H$), 49.4 ($C_{i\mathrm{Pr}}H$), 46.4 ($C_{i\mathrm{Pr}}H$), 38.9 ($C_{sp3}H_2$), 38.2 ($C_{sp3}H$), 25.2 ($C_{sp3}H_2$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.3 ($C_{i\mathrm{Pr}}H_3$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 18.3 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 2972 (w), 2933 (w), 2837 (w), 1700 (m), 1605 (w), 1508 (m), 1392 (m), 1333 (m), 1243 (s), 1157 (m), 1034 (m), 979 (m), 836 (m).

Mp: 91 °C.

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{30}N_3O_2^+$ 356.2333; Found 356.2346.

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(o-tolyl)bicyclo[4.2.0]oct-7-en-2-one (**2d**)



2d was synthesized analogously to **2a** from (E)-3,3-diisopropyl-1-(o-tolylethynyl)triaz-1-ene (58.3 mg, 240 µmol, 1 eq.) and 2-cyclohexen-1-one (58 µL, 599 µmol, 2.5 eq.). The product was obtained as a yellow, highly viscous resin (60.8 mg 179 µmol, 75%).

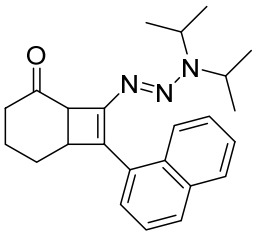
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 1H, $C_{Ph}H$), 7.24 – 7.10 (m, 3H, $C_{Ph}H$), 5.13 (hept, *J* = 6.9 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.90 (hept, *J* = 6.5 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.78 (dd, *J* = 4.8, 1.8 Hz, 1H, $C_{CO\text{-}sp3}H$), 3.70 (td, *J* = 3.8, 3.2, 1.4 Hz, 1H, $C_{sp3}H$), 2.54 (s, 3H, $C_{Ph\text{-}Me}H_3$), 2.57 – 2.46 (m, 1H, $C_{sp3}HH$), 2.22 (dddd, *J* = 18.5, 10.3, 8.5, 1.9 Hz, 1H, $C_{sp3}HH$), 2.15 – 1.91 (m, 2H, $C_{sp3}H_2$), 1.72 – 1.58 (m, 2H, $C_{sp3}H_2$), 1.32 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.26 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.20 (d, *J* = 6.8 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.16 (d, *J* = 6.8 Hz, 3H, $C_{i\mathrm{Pr}}H_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.9 (CO), 142.4 (C_{sp2}-N_3iPr_2), 136.4 ($C_{Ph,q}$), 133.7 (C_{Ph}-Me), 130.9 ($C_{Ph}H$), 129.1 ($C_{Ph}H$), 128.4 (C_{sp2}-Ph), 127.1 ($C_{Ph}H$), 125.6 ($C_{Ph}H$), 53.4 ($C_{CO\text{-}sp3}H$), 49.4 ($C_{i\mathrm{Pr}}H$), 46.6 ($C_{i\mathrm{Pr}}H$), 40.2 ($C_{sp3}H$), 38.9 ($C_{sp3}H_2$), 25.2 ($C_{sp3}H_2$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 21.6 ($C_{Ph\text{-}Me}H_3$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 19.2 ($C_{i\mathrm{Pr}}H_3$), 18.5 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 2972 (w), 2933 (w), 2874 (w), 2852 (w), 1696 (m), 1392 (s), 1380 (s), 1316 (m), 1249 (s), 1156 (s), 1103 (m), 1034 (m), 977 (m), 908 (m), 753 (s), 731 (s).

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{30}N_3O^+$ 340.2383; Found 340.2374.

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(naphthalen-1-yl)bicyclo[4.2.0]oct-7-en-2-one (**2e**)

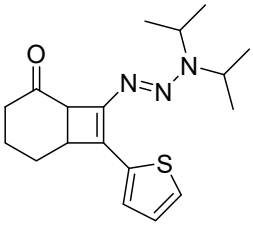


2e was synthesized analogously to **2a** from 3,3-diisopropyl-1-(naphthalen-1-ylethynyl)triaz-1-ene (150 mg, 538 µmol, 1 eq.) and cyclohexen-1-one (130 µL, 1.34 mmol, 2.5 eq.) using tris(pentafluorophenyl)-borane (13.8 mg, 27.0 µmol, 5 mol%) within 16 h. The product was obtained as a yellow solid (135 mg, 359 µmol, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 – 8.63 (m, 1H, $C_{Naph}H$), 7.87 – 7.83 (m, 1H $C_{Naph}H$), 7.78 – 7.73 (m, 1H $C_{Naph}H$), 7.63 (dd, *J* = 7.3, 1.2 Hz, 1H $C_{Naph}H$), 7.48 (m, 3H $C_{Naph}H$), 5.14 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.96 (hept, *J* = 6.6 Hz, 1H, overlapping with following m), 3.91 – 3.86 (m, 2H, $C_{CO\text{-}sp3}H$, $C_{sp3}H$), 2.65 – 2.52 (m, 1H, $C_{sp3}HH$), 2.26 (dddd, *J* = 18.3, 10.1, 8.5, 1.7 Hz, 1H, $C_{sp3}HH$), 2.17 – 2.01 (m, 2H, 2 x $C_{sp3}HH$), 1.71 (tt, *J* = 13.6, 3.5 Hz, 1H, $C_{sp3}HH$), 1.66 – 1.59 (m, 1H, $C_{sp3}HH$), 1.35 (d, *J* = 6.5 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.30 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.28 (d, *J* = 6.8 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.18 (d, *J* = 6.8 Hz, 3H, $C_{i\mathrm{Pr}}H_3$).

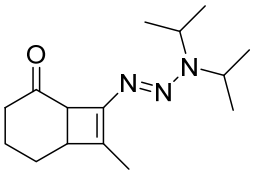
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8 (CO), 142.6 (C_{sp2}-N_3*i*Pr_2), 134.2 ($C_{Naph,q}$), 132.1 ($C_{Naph,q}$), 131.2 ($C_{Naph,q}$), 128.4 (C_{Naph}H), 127.9 (C_{Naph}H), 127.5 (C_{Naph}H), 127.1 (C_{sp2}-Naph), 126.3 (C_{Naph}H), 125.9 (C_{Naph}H), 125.8 (C_{Naph}H), 125.6 (C_{Naph}H), 53.2 ($C_{CO\text{-}sp3}$H), 49.8 ($C_{i\text{Pr}}$H), 47.1 ($C_{i\text{Pr}}$H), 39.8 (C_{sp3}H), 39.0 ($C_{sp3}H_2$), 24.9 ($C_{sp3}H_2$), 23.5 ($C_{i\text{Pr}}H_3$), 23.4 ($C_{i\text{Pr}}H_3$), 19.4 ($C_{i\text{Pr}}H_3$), 19.2 ($C_{i\text{Pr}}H_3$), 18.6 ($C_{sp3}H_2$).
IR (ν_{max}, cm^{-1}) 3044 (w), 2973 (w), 2934 (w), 2874 (w), 2853 (w), 1700 (m), 1404 (s), 1391 (s), 1379 (s), 1366 (m), 1314 (m), 1253 (s), 1156 (m), 1129 (m), 1102 (m), 1033 (m), 803 (m), 779 (s).
Mp: 58 °C.
HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{30}N_3O^+$ 376.2383; Found 376.2385.

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(thiophen-2-yl)bicyclo[4.2.0]oct-7-en-2-one (**2f**)



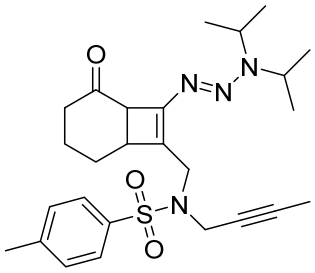
2f was synthesized analogously to **2a** from 3,3-diisopropyl-1-(thiophen-2-ylethynyl)triaz-1-ene (56.5 mg, 240 µmol, 1 eq.) and 2-cyclohexen-1-one (58 µL, 600 µmol, 2.5 eq.) using tris(pentafluorophenyl)borane (12.3 mg, 24.0 µmol, 10 mol%). The product was obtained as a yellow-brown oil (41.5 mg, 125 µmol, 52%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H, C_{Thioph}H), 7.10 – 7.06 (m, 1H, C_{Thioph}H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H, C_{Thioph}H), 5.18 (hept, *J* = 6.7 Hz, 1H, $C_{i\text{Pr}}$H), 3.93 (hept, *J* = 6.6 Hz, 1H, $C_{i\text{Pr}}$H), 3.78 (dd, *J* = 4.8, 1.7 Hz, 1H, $C_{CO\text{-}sp3}$H), 3.55 (dt, *J* = 6.5, 3.5 Hz, 1H, C_{sp3}H), 2.63 – 2.41 (m, 1H, C_{sp3}*H*H), 2.31 – 2.01 (m, 3H, 3 x C_{sp3}*H*H), 1.78 – 1.62 (m, 2H 2 x C_{sp3}*H*H), 1.32 (d, *J* = 6.6 Hz, 3H, $C_{i\text{Pr}}H_3$), 1.29 – 1.21 (m, 9H, $C_{i\text{Pr}}H_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0 (CO), 139.3 (C_{sp2}-N_3*i*Pr_2), 136.8 ($C_{Thioph,q}$), 127.3 (C_{Thioph}H), 125.7 (C_{Thioph}H), 123.8 (C_{Thioph}H), 122.1 (C_{sp2}-Thioph), 54.0 ($C_{CO\text{-}sp3}$H), 49.9 ($C_{i\text{Pr}}$H), 47.0 ($C_{i\text{Pr}}$H), 39.4 (C_{sp3}H), 39.0 ($C_{sp3}H_2$), 25.2 ($C_{sp3}H_2$), 23.5 ($C_{i\text{Pr}}H_3$), 23.3 ($C_{i\text{Pr}}H_3$), 19.3 ($C_{i\text{Pr}}H_3$), 19.3 ($C_{i\text{Pr}}H_3$), 18.2 ($C_{sp3}H_2$).
IR (ν_{max}, cm^{-1}) 3103 (w), 3070 (w), 2972 (w), 2933 (w), 2874 (w), 2852 (w), 1699 (s), 1637 (w), 1405 (s), 1391 (s), 1380 (s), 1314 (m), 1253 (s), 1157 (m), 1033 (m).
HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{26}N_3OS^+$ 332.1791; Found 332.1797.

8-(3,3-Diisopropyltriaz-1-en-1-yl)-7-methylbicyclo[4.2.0]oct-7-en-2-one (**2g**)



2g was synthesized analogously to **2a** from 3,3-diisopropyl-1-(prop-1-yn-1-yl)triaz-1-ene (500 mg, 2.99 mmol, 1 eq.) and 2-cyclohexen-1-one (720 µL, 7.44 mmol, 2.5 eq.) using tris(pentafluorophenyl)borane (12.3 mg, 24.0 µmol, 10 mol%). The product was obtained as a yellow solid (477 mg, 1.81 mmol, 61%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (br s, 1H, $C_{i\text{Pr}}$H), 3.82 (br s, 1H, $C_{i\text{Pr}}$H), 3.60 (dt, *J* = 4.2, 2.1 Hz, 1H, $C_{CO\text{-}sp3}$H), 3.04 (dtq, *J* = 4.2, 2.6, 1.3 Hz, 1H, C_{sp3}H), 2.50 – 2.37 (m, 1H, C_{sp3}*H*H), 2.15 (dddd, *J* = 18.0, 10.0, 8.2, 1.8 Hz, 1H, C_{sp3}*H*H), 2.09 – 1.95 (m, 1H, C_{sp3}*H*H), 1.96 – 1.86 (m, 1H, C_{sp3}*H*H), 1.85 (t, *J* = 1.8 Hz, 3H $C_{Me}H_3$), 1.73 – 1.50 (m, 2H, 2 x C_{sp3}*H*H), 1.35 – 1.06 (m, 12H, $C_{i\text{Pr}}H_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3 (CO), 142.7 (C_{sp2}-N_3*i*Pr_2), 128.3 (C_{sp2}-Me), 54.2 ($C_{CO\text{-}sp3}$H), 48.7 ($C_{i\text{Pr}}$H), 45.3 ($C_{i\text{Pr}}$H), 40.4 (C_{sp3}H), 38.6 ($C_{sp3}H_2$), 24.4 ($C_{sp3}H_2$), 23.4 ($C_{i\text{Pr}}H_3$), 19.5 ($C_{i\text{Pr}}H_3$), 18.2 ($C_{sp3}H_2$), 11.3 ($C_{Me}H_3$).
IR (ν_{max}, cm^{-1}) 2971 (w), 2932 (m), 2905 (w), 2849 (w), 1700 (s), 1407 (s), 1366 (m), 1294 (m), 1235 (s), 1159 (m), 1128 (m), 1105 (s), 1028 (s).
Mp: 48–52 °C.
HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{26}N_3O^+$ 264.2070; Found 264.2069.

N-(But-2-yn-1-yl)-N-((8-(3,3-diisopropyltriaz-1-en-1-yl)-2-oxobicyclo[4.2.0]oct-7-en-7-yl)methyl)-4-methylbenzenesulfonamide (**2h**)



2h was synthesized analogously to **2a** from N-(but-2-yn-1-yl)-N-(3-(3,3-diisopropyltriaz-1-en-1-yl) prop-2-yn-1-yl)-4-methylbenzenesulfonamide (50 mg, 129 µmol, 1 eq.) and 2-cyclohexen-1-one (31.2 µL, 322 µmol, 2.5 eq.) using tris(pentafluorophenyl)borane (6.6 mg, 12.9 µmol, 10 mol%~~0.1 eq.~~). The product was obtained as an off-white solid (41.0 mg, 84.6 µmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (d, *J* = 8.3 Hz, 2H, $C_{Ph}H$), 7.28 (d, *J* = 8.1 Hz, 2H, $C_{Ph}H$), 5.00 (hept, *J* = 7.0 Hz, 1H, $C_{i\mathrm{Pr}}H$), 4.22 (dq, *J* = 18.0, 2.4 Hz, 1H, NC*H*H), 4.11 – 3.95 (m, 3H, NC*H*H + NCH_2), 3.86 (hept, *J* = 7.6, 6.9 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.60 – 3.55 (m, 1H, $C_{CO\text{-}sp3}H$), 3.16 – 3.09 (m, 1H, $C_{sp3}H$), 2.42 (s, 3H, $C_{Ph\text{-}Me}H_3$), 2.47 – 2.35 (m, 1H, C_{sp3}*H*H), 2.16 (dddd, *J* = 18.3, 10.1, 8.2, 1.7 Hz, 1H, C_{sp3}*H*H), 2.09 – 1.93 (m, 2H, 2 x C_{sp3}*H*H), 1.75 – 1.66 (m, 1H, C_{sp3}*H*H), 1.65 – 1.55 (m, 1H, C_{sp3}*H*H), 1.56 – 1.52 (m, 3H, $C_{C\equiv CMe}H_3$), 1.28 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.20 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 1.18 – 1.10 (m, 6H, $C_{i\mathrm{Pr}}H_3$).

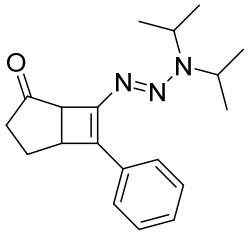
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0 (CO), 146.5 (C_{sp2}-N_3*i*Pr_2), 143.2 (C_{Ph}-Me), 136.6 ($C_{Ph,q}$), 129.3 ($C_{Ph}H$), 128.0 ($C_{Ph}H$), 123.6 (*C*$_{sp2}$-CH_2), 81.4 (C≡C), 72.3 (C≡C), 53.9 ($C_{CO\text{-}sp3}H$), 49.5 ($C_{i\mathrm{Pr}}H$), 46.4 ($C_{i\mathrm{Pr}}H$), 41.8 (C_{sp2}-*C*H_2), 39.1 ($C_{sp3}H$), 39.0 ($C_{sp3}H_2$), 37.5 (NCH_2), 24.6 ($C_{sp3}H_2$), 23.5 ($C_{i\mathrm{Pr}}H_3$), 23.2 ($C_{i\mathrm{Pr}}H_3$), 21.7 ($C_{Ph\text{-}Me}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 18.4 ($C_{sp3}H_2$), 3.4 ($C_{C\equiv CMe}H_3$).

IR (ν_{max}, cm^{-1}) 2972 (w), 2934 (w), 2876 (w), 2854 (w), 1700 (m), 1406 (m), 1346 (m), 1304 (m), 1248 (m), 1160 (s), 1094 (m), 994 (w), 902 (w), 740 (w).

Mp: 110 °C.

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{37}N_4O_3S^+$ 485.2581; Found 485.2584.

7-(3,3-Diisopropyltriaz-1-en-1-yl)-6-phenylbicyclo[3.2.0]hept-6-en-2-one (**2i**)



2i was synthesized analogously to **2a** from 3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (54.9 mg, 239 µmol, 1 eq.) and 2-cyclopentenone (50.2 µL, 599 µmol, 2.5 eq.). The product was obtained as a yellow solid (60.8 mg, 195 µmol, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H, $C_{Ph}H$), 7.36 (t, *J* = 7.6 Hz, 2H, $C_{Ph}H$), 7.20 (t, *J* = 7.4 Hz, 1H, $C_{Ph}H$), 5.21 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.97 (hept, *J* = 6.6 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.67 – 3.52 (m, 2H, $C_{CO\text{-}sp3}H$ + $C_{sp3}H$), 2.86 (ddd, *J* = 15.3, 11.2, 8.8 Hz, 1H, C_{sp3}*H*H), 2.26 (dd, *J* = 12.3, 9.0 Hz, 1H, C_{sp3}*H*H), 2.15 – 1.99 (m, 2H, $C_{sp3}H_2$), 1.37 (dd, *J* = 6.6, 1.9 Hz, 6H, $C_{i\mathrm{Pr}}H_3$), 1.25 (dd, *J* = 6.9, 3.9 Hz, 6H, $C_{i\mathrm{Pr}}H_3$).

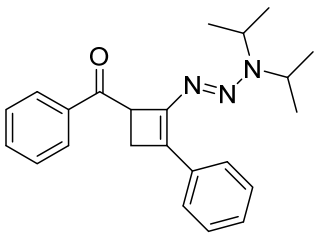
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1 (CO), 143.8 (C_{sp2}-N_3*i*Pr_2), 134.6 ($C_{Ph,q}$), 128.6 ($C_{Ph}H$), 127.5 (C_{sp2}-Ph), 126.8 ($C_{Ph}H$), 126.6 ($C_{Ph}H$), 52.4 ($C_{CO\text{-}sp3}H$), 49.8 ($C_{i\mathrm{Pr}}H$), 46.8 ($C_{i\mathrm{Pr}}H$), 37.7 ($C_{sp3}H$), 35.0 ($C_{sp3}H_2$), 23.6 ($C_{i\mathrm{Pr}}H_3$), 23.4 ($C_{i\mathrm{Pr}}H_3$), 22.4 ($C_{sp3}H_2$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$).

IR (ν_{max}, cm^{-1}) 2973 (w), 2933 (w), 2871 (w), 1733 (s), 1628 (w), 1407 (m), 1390 (s), 1379 (s), 1341 (m), 1251 (s), 1154 (s), 975 (m), 752 (m).

Mp: 81 °C.

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{26}N_3O^+$ 312.2070; Found 312.2061.

(2-(3,3-Diisopropyltriaz-1-en-1-yl)-3-phenylcyclobut-2-en-1-yl)(phenyl)methanone (**2j**)



2j was synthesized analogously to **2a** from (E)-3,3-diisopropyl-1-(phenylethynyl)triaz-1-ene (55.0 mg, 240 µmol, 1 eq.) and phenyl vinyl ketone (79.5 mg, 602 µmol, 2.5 eq.). The product was obtained as a yellow solid (35.5 mg, 98.2 mmol, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H, $C_{Ph\text{-}CO}H$), 7.70 – 7.62 (m, 2H, $C_{Ph}H$), 7.57 – 7.51 (m, 1H, $C_{Ph\text{-}CO}H$), 7.50 – 7.41 (m, 2H, $C_{Ph\text{-}CO}H$), 7.38 – 7.30 (m, 2H, $C_{Ph}H$), 7.22 – 7.16 (m, 1H, $C_{Ph}H$), 5.23 (hept, *J* = 6.8, 6.3 Hz, 1H, $C_{i\mathrm{Pr}}H$), 4.89 (dd, *J* = 5.3, 2.3 Hz, 1H, $C_{CO\text{-}sp3}H$), 3.76 (hept, *J* = 6.6 Hz,

1H, $C_{i\mathrm{Pr}}H$), 2.93 (dd, *J* = 12.0, 5.3 Hz, 1H, $C_{sp3}H\mathit{H}$), 2.80 (dd, *J* = 12.0, 2.3 Hz, 1H, $C_{sp3}H\mathit{H}$), 1.25 – 1.17 (m, 6H, $C_{i\mathrm{Pr}}H_3$), 1.07 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$), 0.83 (d, *J* = 6.6 Hz, 3H, $C_{i\mathrm{Pr}}H_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8 (CO), 145.0 (C_{sp2}-$N_3i\mathrm{Pr}_2$), 137.8 ($C_{\mathrm{Ph\text{-}CO,q}}$), 135.2 ($C_{\mathrm{Ph,q}}$), 132.7 ($C_{\mathrm{Ph\text{-}CO}}H$), 128.6 ($C_{\mathrm{Ph\text{-}CO}}H$), 128.5 ($C_{\mathrm{Ph\text{-}CO}}H$), 128.3 ($C_{\mathrm{Ph}}H$), 126.9 ($C_{\mathrm{Ph}}H$), 126.5 ($C_{\mathrm{Ph}}H$), 125.7 ($C_{sp2}$-Ph), 49.0 ($C_{i\mathrm{Pr}}H$), 46.8 ($C_{i\mathrm{Pr}}H$), 45.3 ($C_{\mathrm{CO\text{-}sp3}}H$), 29.1 ($C_{sp3}H_2$), 23.3 ($C_{i\mathrm{Pr}}H_3$), 22.9 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$).
IR (ν_{max}, cm^{-1}) 3058 (w), 3024 (w), 2974 (w), 2930 (w), 2912 (w), 2870 (w), 1252 (s), 1674 (m), 1344 (s), 1214 (s), 1154 (m), 1022 (m), 760 (m), 1378 (s), 1390 (m), 1406 (m), 1448 (m), 1596 (w).
Mp: 137 °C.
HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{28}N_3O^+$ 362.2227; Found 362.2226.

Structure of the vinyl triazenes 2a–2j

The structure of the vinyl triazenes **2a**–**1j** was corroborated by ^{1}H-^{13}C-HSQC spectroscopy. In **2b**, for example, one of the protons from the CH_2-group adjacent to the bridgehead (part of the multiplet 1.78 – 1.60 ppm (m, 2H)) and two of the protons from the Ph-group (7.69 – 7.58 ppm (m, 2H)) couple to the same vinylic carbon (126.1 ppm (d, *J* = 1.4 Hz)) (Figure S2). Such a coupling pattern requires the reported isomer **A**. For the hypothetical isomer **B**, the respective protons would each couple to different vinylic carbons (126.1 ppm (d, *J* = 1.4 Hz) and ppm 142.0 (d, *J* = 2.8 Hz)), which is not observed.

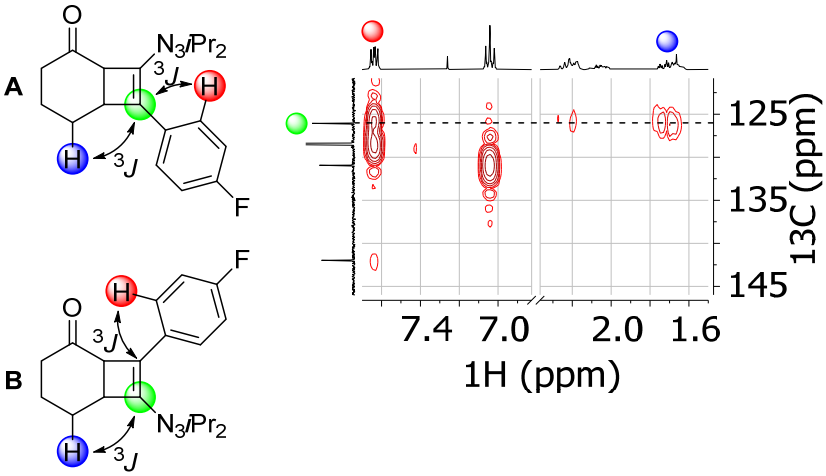
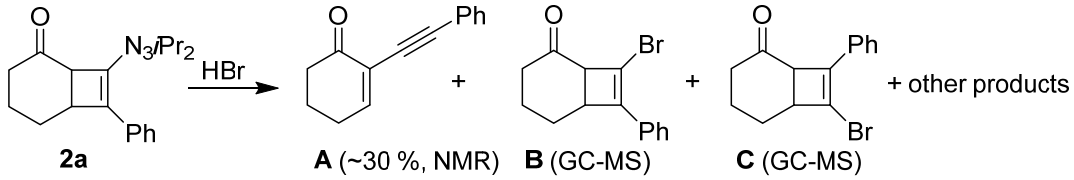


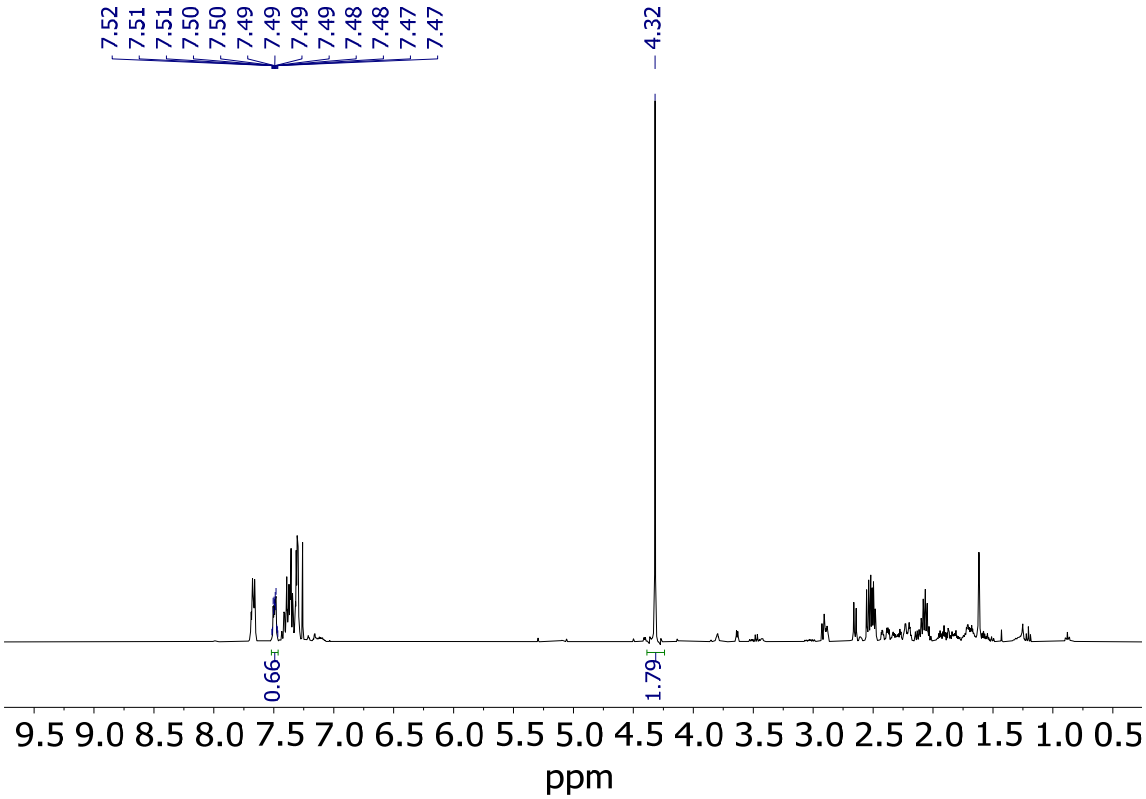
Figure S2. Left: Possible regioisomers and coupling partners of the vinylic carbons of **2b**. Right: Section of the ^{1}H-^{13}C-HSQC spectrum showing the actual coupling pattern.

Reaction of **2a** with HBr

A solution of **2a** (15.0 mg, 46.1 µmol, 1 eq.) in Et_2O (0.46 mL) was cooled to 0 °C. HBr (47% aq., 32.0 µL, 275 µmol, 6 eq.) was added and the mixture was stirred at 0 °C for 1 h. The ice bath was removed and stirring was continued for additional 2 h. The reaction mixture was quenched with K_2CO_3 (38.5 mg, 279 µmol, 6 eq.) and stirred vigorously for 15 min. The mixture was filtered over a plug of silica (rinsed with Et_2O), and the solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ (ca. 0.5 mL) and the solution was transferred into an NMR tube. After addition of nitromethane (1.5 µL, 27.5 µmol, 0.597 eq.) as internal standard, ^1H and ^{13}C NMR spectra were recorded.



The presence of alkyne **A** was evidenced by ^{13}C NMR signals at 92.2 and 83.9 ppm,[4] and the yield of **A** was estimated by integration of the ^1H NMR signal at 7.52 – 7.47 (m).



^1H NMR spectrum (400 MHz, $CDCl_3$) of crude product with $MeNO_2$ as internal standard

The crude product was also analyzed by GC-MS, and the results are summarized below:

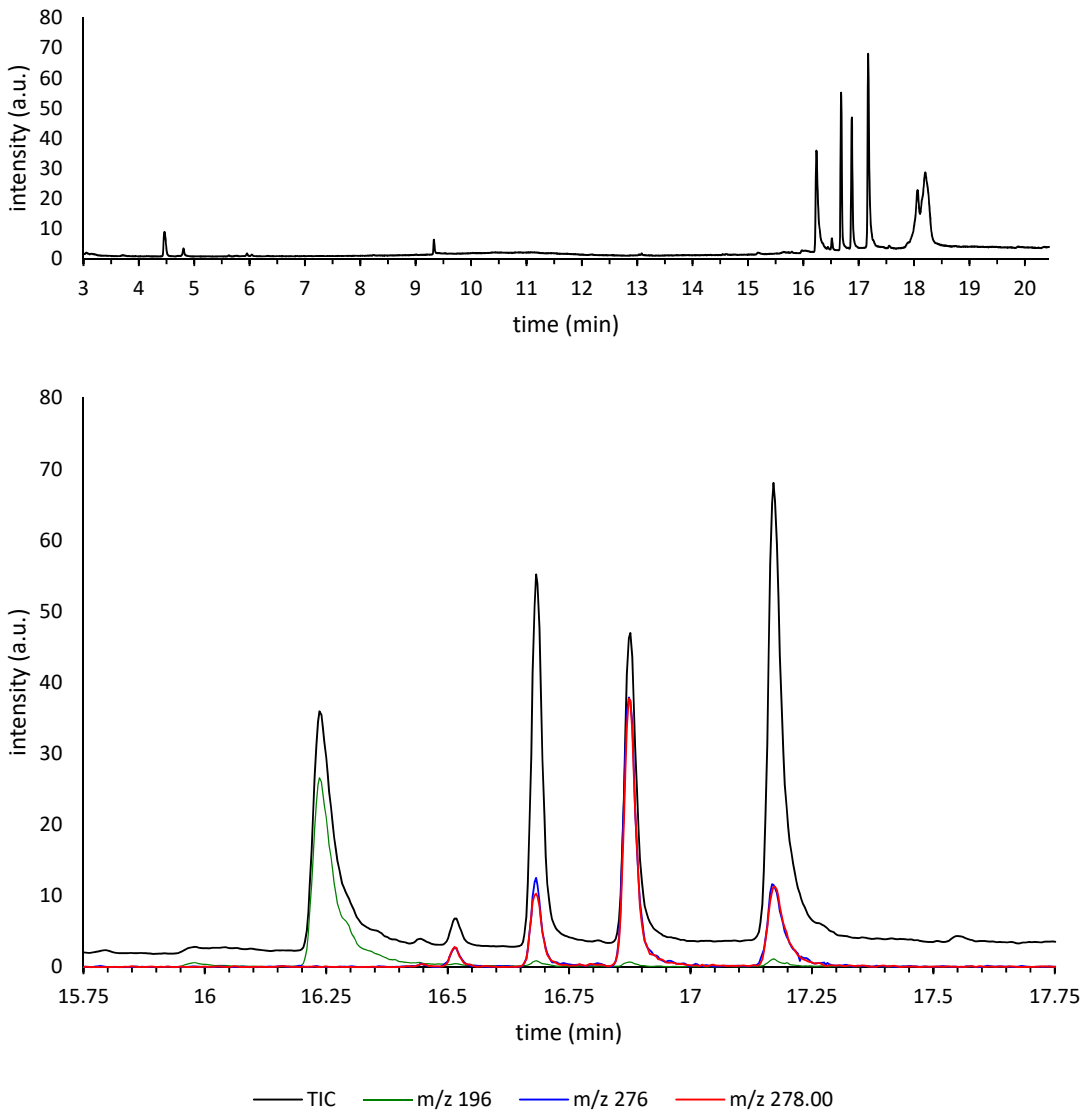
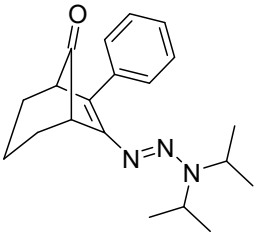


Figure S3. Full GC-MS chromatogram of the product mixture (top) and enlarged view on signals with *m*/*z* = 196 (green trace, mass of alkyne **A**) or *m*/*z* = 276, 278 (blue and red trace, mass of brominated products such as **B** and **C**). The compounds responsible for the signals at 18 – 18.5 min could not be identified.

Synthesis of the vinyl triazenes **3a**–**3e** and **4**

6-(3,3-Diisopropyltriaz-1-en-1-yl)-7-phenylbicyclo[3.2.1]oct-6-en-8-one (**3a**)



A solution of **2a** (200 mg, 615 µmol, 1 eq.) in toluene (1 mL) was dried over molecular sieves (10 – 20 vol%) overnight. The solution was diluted with more toluene (8 mL), dimethylaluminium chloride (0.9 M in hexanes, 140 µL, 126 µmol, 0.2 eq.) was added, and the mixture was heated to 50 °C under exclusion of light for 4 h. The mixture was allowed to cool to RT and filtered over a plug of deactivated silica (eluent: Et_2O). The solvent was removed under vacuum. Purification by flash column chromatography on deactivated silica (NEt_3) with 5% Et_2O in pentane gave the product in the form of a yellow solid (161 mg, 495 µmol, 81%).

Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H, $C_{Ph}H$), 7.35 (dd, *J* = 8.5, 7.1 Hz, 2H, $C_{Ph}H$), 7.23 – 7.17 (m, 1H, $C_{Ph}H$), 5.21 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 4.00 (hept, *J* = 6.6 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.56 (dt, *J* = 4.2, 2.0 Hz, 1H, $C_{sp3}H$), 3.42 (dt, *J* = 4.0, 1.9 Hz, 1H, $C_{sp3}H$), 2.21 – 2.09 (m, 1H, $C_{sp3}HH$), 2.04 – 1.96 (m, 1H, $C_{sp3}HH$), 1.89 (dddd, *J* = 13.4, 11.9, 5.9, 2.1 Hz, 1H, $C_{sp3}HH$), 1.79 (tdd, *J* = 12.7, 5.9, 2.3 Hz, 1H, $C_{sp3}HH$), 1.72 – 1.51 (m, 2H, $C_{sp3}H_2$), 1.38 – 1.22 (m, 12H, $C_{i\mathrm{Pr}}H_3$).

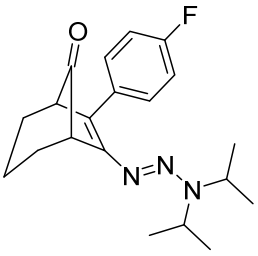
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9 (CO), 145.1 (C_{sp2}-N_3iPr_2), 135.3 ($C_{Ph,q}$), 128.4 ($C_{Ph}H$), 128.3 ($C_{Ph}H$), 126.3 ($C_{Ph}H$), 121.1 (C_{sp2}-Ph), 53.4 ($C_{sp3}H$), 51.1 ($C_{sp3}H$), 49.2 ($C_{i\mathrm{Pr}}H$), 47.1 ($C_{i\mathrm{Pr}}H$), 30.2 ($C_{sp3}H_2$), 29.3 ($C_{sp3}H_2$), 23.9 ($C_{i\mathrm{Pr}}H_3$), 23.7 ($C_{i\mathrm{Pr}}H_3$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 18.4 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 2974 (m), 2939 (m), 2858 (w), 1760 (s), 1493 (w), 1446 (w), 1396 (m), 1354 (m), 1252 (s), 1155 (m), 1033 (w), 770 (w).

Mp: 86 °C.

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{28}N_3O^+$ 326.2227; Found 326.2222.

6-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(4-fluorophenyl)bicyclo[3.2.1]oct-6-en-8-one (**3b**)



3b was synthesized analogously to **3a** from a dried solution of **2b** (25.0 mg, 72.8 µmol, 1 eq.) in toluene (1.1 mL). The product was obtained as a yellow solid (19.7 mg, 57.4 µmol, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.5, 5.6 Hz, 2H, $C_{Ph}H$), 7.04 (t, *J* = 8.6 Hz, 2H, $C_{Ph}H$), 5.18 (hept, *J* = 6.8 Hz, 1H, $C_{i\mathrm{Pr}}H$), 4.00 (hept, *J* = 6.7 Hz, 1H, $C_{i\mathrm{Pr}}H$), 3.55 (dd, *J* = 4.4, 2.1 Hz, 1H, $C_{sp3}H$), 3.37 (dd, *J* = 3.6, 1.7 Hz, 1H, $C_{sp3}H$), 2.12 (dt, *J* = 13.3, 3.9 Hz, 1H, $C_{sp3}HH$), 1.99 (dt, *J* = 12.9, 4.1 Hz, 1H, $C_{sp3}HH$), 1.88 (td, *J* = 12.2, 7.3 Hz, 1H, $C_{sp3}HH$), 1.79 (td, *J* = 12.0, 7.4 Hz, 1H, $C_{sp3}HH$), 1.66 – 1.53 (m, 2H, $C_{sp3}H_2$), 1.35 – 1.20 (m, 12H, $C_{i\mathrm{Pr}}H_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.5 (CO), 161.4 (d, *J* = 247.0 Hz, $C_{Ph}F$), 144.6 (d, *J* = 2.2 Hz, C_{sp2}-N_3iPr_2), 131.5 (d, *J* = 3.3 Hz, $C_{Ph,q}$), 129.9 (d, *J* = 7.4 Hz, $C_{Ph}H$), 120.1 (C_{sp2}-Ph), 115.2 (d, *J* = 21.2 Hz, $C_{Ph}H$), 53.4 ($C_{sp3}H$), 50.9 ($C_{sp3}H$), 49.2 ($C_{i\mathrm{Pr}}H$), 47.1 ($C_{i\mathrm{Pr}}H$), 30.1 ($C_{sp3}H_2$), 29.2 ($C_{sp3}H_2$), 23.9 ($C_{i\mathrm{Pr}}H_3$), 23.7 ($C_{i\mathrm{Pr}}H_3$), 19.3 ($C_{i\mathrm{Pr}}H_3$), 19.3, 18.4 ($C_{sp3}H_2$).

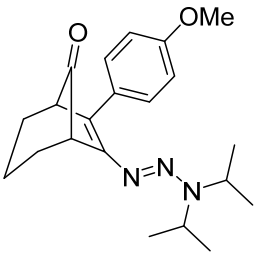
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6.

IR (ν_{max}, cm^{-1}) 2974 (w), 2938 (m), 2860 (w), 1756 (s), 1506 (s), 1394 (s), 1382 (m), 1354 (s), 1248 (s), 1156 (s), 836 (m).

Mp: 113 °C.

HRMS (nanochip-ESI/LTQ-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}FN_3NaO^+$ 366.1952; Found 366.1961.

6-(3,3-Diisopropyltriaz-1-en-1-yl)-7-(4-methoxyphenyl)bicyclo[3.2.1]oct-6-en-8-one (**3c**)



3c was synthesized analogously to **3a** from a dried solution of **2c** (25.1 mg, 70.6 µmol, 1 eq.) in toluene (1 mL) within 6.5 h. The product was obtained as a yellow solid (14.8 mg, 41.6 µmol, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H, $C_{Ph}H$), 6.91 (d, *J* = 8.4 Hz, 2H, $C_{Ph}H$), 5.28 – 5.11 (m, 1H, $C_{i\mathrm{Pr}}H$), 4.05 – 3.91 (m, 1H, $C_{i\mathrm{Pr}}H$), 3.83 (s, 3H, $C_{OMe}H_3$), 3.57 – 3.50 (m, 1H, $C_{sp3}H$), 3.38 (s, 1H, $C_{sp3}H$), 2.17 – 2.06 (m, 1H, $C_{sp3}HH$), 2.00 (dd, *J* = 12.4, 5.9 Hz, 1H, $C_{sp3}HH$), 1.87 (td, *J* = 12.4, 5.6 Hz, 1H, $C_{sp3}HH$), 1.77 (td, *J* = 12.3, 5.7 Hz, 1H, $C_{sp3}HH$), 1.66 – 1.52 (m, 2H, $C_{sp3}H_2$), 1.38 – 1.19 (m, 12H, $C_{i\mathrm{Pr}}H_3$).

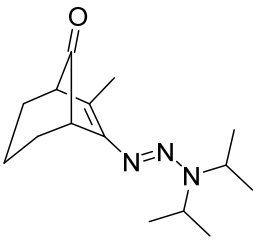
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9 (CO), 158.2(C_{Ph}-OMe), 143.2 (C_{sp2}-N_3iPr_2), 129.6 ($C_{Ph}H$), 128.1 ($C_{Ph,q}$), 121.0 (C_{sp2}-Ph), 113.9 ($C_{Ph}H$), 55.4 ($C_{OMe}H_3$), 53.4 ($C_{sp3}H$), 50.9 ($C_{sp3}H$), 49.0 ($C_{i\mathrm{Pr}}H$), 46.9 ($C_{i\mathrm{Pr}}H$), 30.1 ($C_{sp3}H_2$), 29.2 ($C_{sp3}H_2$), 24.0 ($C_{i\mathrm{Pr}}H_3$), 23.7 ($C_{i\mathrm{Pr}}H_3$), 19.4 ($C_{i\mathrm{Pr}}H_3$), 18.4 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 2972 (w), 2936 (w), 2856 (w), 2836 (w), 1756 (m), 1604 (w), 1508 (m), 1396 (m), 1354 (m), 1248 (s), 1180 (m), 1154 (m), 1032 (m), 832 (m).

Mp: 91–95 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{30}N_3O_2^+$ 356.2333; Found 356.2333.

6-((*E*)-3,3-Diisopropyltriaz-1-en-1-yl)-7-methylbicyclo[3.2.1]oct-6-en-8-one (**3d**)



3d was synthesized analogously to **3a** from a dried solution of **2g** (25.0 mg, 94.9 µmol, 1 eq.) in toluene (1.4 mL). The product was obtained as a yellow solid (16.1 mg, 61.1 µmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (br, 1H, $C_{i\mathrm{Pr}}H$), 3.91 (br, 1H, $C_{i\mathrm{Pr}}H$), 3.24 (t, *J* = 3.2 Hz, 1H, $C_{sp3}H$), 2.73 (dt, *J* = 3.8, 1.7 Hz, 1H, $C_{sp3}H$), 2.01 (s, 3H, $C_{Me}H_3$), 1.95 – 1.84 (m, 2H, $C_{sp3}H_2$), 1.76 – 1.60 (m, 2H, $C_{sp3}H_2$), 1.57 – 1.43 (m, 2H, $C_{sp3}H_2$), 1.27 – 1.18 (m, 12H, $C_{i\mathrm{Pr}}H_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.7 (CO), 143.6 (C_{sp2}-N_3iPr_2), 122.3 (C_{sp2}-Me), 55.3 ($C_{sp3}H$), 49.5 ($C_{sp3}H$), 28.8 ($C_{sp3}H_2$), 28.7 ($C_{sp3}H_2$), 18.3 ($C_{sp3}H_2$), 11.4 ($C_{Me}H_3$).[1]

IR (ν_{max}, cm^{-1}) 2974 (m), 2931 (m), 2858 (w), 1755 (s), 1409 (s), 1244 (s), 1214 (s), 1155 (m), 1103 (s), 1379 (m), 1367 (m), 1331 (m), 1140 (m), 1015 (m), 1034 (m), 1128 (m).

Mp: 61–64 °C.

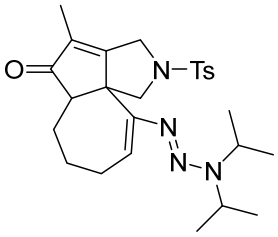
HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{26}N_3O^+$ 264.2070; Found 264.2073.

10-(3,3-Diisopropyltriaz-1-en-1-yl)-4-methyl-2-tosyl-2,3,5a,6,7,8-hexahydroazuleno[1,8a-c]pyrrol-5(1H)-one (**4**) and N-(But-2-yn-1-yl)-N-(((1S,5R)-7-(3,3-diisopropyltriaz-1-en-1-yl)-8-oxobicyclo[3.2.1]oct-6-en-6-yl)methyl)-4-methylbenzenesulfonamide (**3e**)

4 and **3e** were obtained as a separable mixture of isomers analogously to **3a** from a dried solution of **2h** (50 mg, 103 µmol, 1 eq.) in toluene (1.6 mL) and dimethylaluminium chloride (0.9 M in hexanes, 34.4 µL, 31.0 µmol, 0.3 eq.) within 6 h. The products were obtained as colorless solids (**4**: 17.0 mg, 35.1 mmol, 34%, **3e**: 15.3 mg, 31.6 mmol, 31%).

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of **4** in toluene.

[1] The signals of $C_{i\mathrm{Pr}}H$ and $C_{i\mathrm{Pr}}H_3$ are strongly broadened. They can tentatively be assigned to broad peaks at 48.4 ppm, 46.0 ppm and 23.6 ppm, 19.6 ppm respectively (see below for spectra).



4:

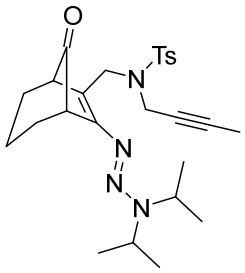
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H, $C_{Ph}H$), 7.25 (d, *J* = 8.3 Hz, 2H, $C_{Ph}H$), 5.30 (t, *J* = 7.9 Hz, 1H, $C_{sp2}H$), 4.34 (dd, *J* = 14.0, 1.6 Hz, 1H, NC*H*H), 4.22 (d, *J* = 8.7 Hz, 1H, NC*H*H), 3.99 (d, *J* = 14.0 Hz, 1H, NC*H*H), 2.96 (d, *J* = 8.8 Hz, 1H, NC*H*H), 2.39 (s, 3H, $C_{Ph\text{-}Me}H_3$), 2.19 (td, *J* = 8.6, 5.7 Hz, 2H, $C_{sp3}H_2$), 2.07 (m, 2H, C_{sp3}*H*H + C_{sp3}H), 1.64 (d, *J* = 1.3 Hz, 3H, $C_{Me}H_3$), 1.61 – 1.47 (m, 2H, $C_{sp3}H_2$), 1.44 – 1.31 (m, 1 H, C_{sp3}*H*H) 1.19 (br, 12H, $C_{i\text{Pr}}H_3$). [2]

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3 (CO), 173.0 (C_{sp2}), 152.6 (C_{sp2}-N_3*i*Pr_2), 143.5 (C_{Ph}-Me), 134.6 ($C_{Ph,q}$), 133.4 (C_{sp2}-Me), 129.7 ($C_{Ph}H$), 127.6 ($C_{Ph}H$), 106.1 ($C_{sp2}H$), 61.7 (NCH_2), 57.7 (C_{sp3}), 52.9 ($C_{sp3}H$), 48.6 (NCH_2), 24.4 ($C_{sp3}H_2$), 23.0 ($C_{sp3}H_2$), 21.7 ($C_{Ph\text{-}Me}H_3$), 20.9 ($C_{sp3}H_2$), 8.9 ($C_{Me}H_3$).[3]

IR (ν_{max}, cm^{-1}) 2972 (w), 2936 (w), 2864 (w), 1712 (m), 1680 (m), 1404 (m), 1346 (m), 1222 (m), 1156 (s), 1094 (m), 1036 (m), 732 (m), 814 (w), 914 (w).

Mp: 130 °C (decomposition).

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{37}N_4O_3S^+$ 485.2581; Found 485.2580.



3e:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H, $C_{Ph}H$), 7.29 (d, *J* = 8.1 Hz, 2H, $C_{Ph}H$), 5.11 (hept, *J* = 6.1 Hz, 1H, $C_{i\text{Pr}}H$), 4.28 (s, 2H, NCH_2), 4.02 (dq, *J* = 7.0, 2.4 Hz, 2H, NCH_2), 3.89 (hept, *J* = 7.5, 7.0 Hz, 1H, $C_{i\text{Pr}}H$), 3.29 (dt, *J* = 4.1, 1.9 Hz, 1H, $C_{sp3}H$), 2.98 (dt, *J* = 3.8, 1.8 Hz, 1H, $C_{sp3}H$), 2.42 (s, 3H, $C_{Ph\text{-}Me}H_3$), 2.06 – 1.96 (m, 1H, C_{sp3}*H*H), 1.94 – 1.85 (m, 1H, C_{sp3}*H*H), 1.79 – 1.65 (m, 2H, $C_{sp3}H_2$), 1.56 – 1.47 (m, 5H, $C_{sp3}H_2$ + $C_{C\equiv CMe}H_3$), 1.26 (d, *J* = 6.3 Hz, 6H, $C_{i\text{Pr}}H_3$), 1.17 (d, *J* = 6.8 Hz, 3H, $C_{i\text{Pr}}H_3$), 1.14 (d, *J* = 6.7 Hz, 3H, $C_{i\text{Pr}}H_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9 (CO), 148.6 (C_{sp2}-N_3*i*Pr_2), 143.2 (C_{Ph}-Me), 136.9 ($C_{Ph,q}$), 129.3 ($C_{Ph}H$), 128.0 ($C_{Ph}H$), 119.1 (C_{sp2}-CH_2), 80.8 (C≡C), 72.7 (C≡C), 52.4 ($C_{sp3}H$), 49.9 ($C_{sp3}H$), 49.1 ($C_{i\text{Pr}}H$), 46.3 ($C_{i\text{Pr}}H$), 42.0 (NCH_2), 37.1 (NCH_2), 29.6 ($C_{sp3}H_2$), 28.8 ($C_{sp3}H_2$), 23.8 ($C_{i\text{Pr}}H_3$), 23.6 ($C_{i\text{Pr}}H_3$), 21.7 ($C_{Ph\text{-}Me}H_3$), 19.4 ($C_{i\text{Pr}}H_3$), 18.5 ($C_{sp3}H_2$), 3.4 ($C_{C\equiv CMe}H_3$).

IR (ν_{max}, cm^{-1}) 2970 (w), 2926 (w), 2858 (w), 1756 (m), 1406 (m), 1346 (m), 1246 (m), 1158 (s), 1094 (m), 900 (m).

Mp: 140 °C.

HRMS (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{37}N_4O_3S^+$ 485.2581; Found 485.2592.

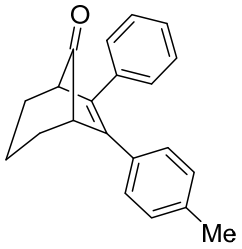
[2] The signals of $C_{i\text{Pr}}H$ are strongly broadened. They can tentatively be assigned to broad peaks at 4.50 ppm and 3.85 ppm respectively (see below for spectra).

[3] The signals of $C_{i\text{Pr}}H$ and $C_{i\text{Pr}}H_3$ are not detected, presumably due to broadening.

Pd-Catalyzed Cross-Coupling Reactions with **3a**

The compounds **5a**–**5c** were synthesized in analogy to a published procedure, in which aryl triazenes are used as substrates.[6]

6-Phenyl-7-(p-tolyl)bicyclo[3.2.1]oct-6-en-8-one (**5a**)



BF_3*OEt_2 (19.0 µL, 154 µmol, 2 eq.) was added to a solution of **3a** (25.0 mg, 76.8 µmol, 1 eq.), 4-tolylboronic acid (21.3 mg, 157 µmol, 2.04 eq.) and $Pd(PPh_3)_4$ (9.0 mg, 7.8 µmol, 0.1 eq.) in DME (0.77 mL), and the mixture was stirred at for 4 h. The reaction was quenched with NaOH (1 M, 0.5 mL), and the product was extracted with Et_2O (3 x 1.5 mL). The combined organic phases were dried over $MgSO_4$, filtered over celite, and the solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 0 – 5% Et_2O in pentane gave the product in the form of a yellow solid (14.7 mg, 51.0 µmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 5H, $C_{Ph}H$), 7.15 (d, *J* = 8.2 Hz, 2H, $C_{Tol}H$), 7.06 (d, *J* = 7.9 Hz, 2H, $C_{Tol}H$), 3.22 (s, 1H, $C_{sp3}H$), 3.21 (s, 1H, $C_{sp3}H$), 2.32 (s, 3H, $C_{Ph\text{-}Me}H_3$), 2.15 – 2.06 (m, 2H, $C_{sp3}H_2$), 1.97 – 1.85 (m, 3H, $C_{sp3}H_2$ + $C_{sp3}H$*H*), 1.67 (dtd, *J* = 7.9, 5.9, 5.4, 2.7 Hz, 1H, $C_{sp3}H$*H*).

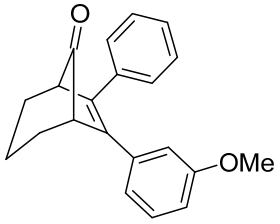
^{13}C NMR (101 MHz, $CDCl_3$) δ 216.1 (CO), 137.6 (C_{Ph}-Me), 136.2 ($C_{Ph,q}$), 134.9 (C_{sp2}-Tol), 134.2 (C_{sp2}-Ph), 132.8 ($C_{Tol,q}$), 129.3 ($C_{Tol}H$), 128.6 ($C_{Ph}H$), 128.1 ($C_{Ar}H$), 128.0 ($C_{Ar}H$), 127.6 ($C_{Ph}H$), 56.3 ($C_{sp3}H$), 56.2 ($C_{sp3}H$), 30.0 ($C_{Ph\text{-}Me}H_3$), 21.4 ($C_{sp3}H_2$)[4], 18.1 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 3078 (w), 3052 (w), 3026 (w), 2940 (w), 2858 (w), 1758 (s), 1512 (w), 1444 (w), 1268 (w), 1228 (w), 1076 (w), 828 (w), 818 (w), 768 (w).

Mp: 109 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{21}O^+$ 289.1587; Found 289.1585.

6-(3-Methoxyphenyl)-7-phenylbicyclo[3.2.1]oct-6-en-8-one (**5b**)



5b was synthesized analogously to **5a** from **3a** (25.0 mg, 76.8 µmol, 1 eq.) and 3-methoxyphenylboronic acid (23.2 mg, 153 µmol, 2 eq.). The product was obtained as a light yellow solid (15.1 mg, 49.6 µmol, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 5H, $C_{Ph}H$), 7.20 – 7.15 (m, 1H, $C_{PhOMe}H$), 6.83 (dt, *J* = 7.7, 1.3 Hz, 1H, $C_{PhOMe}H$), 6.78 (t, *J* = 2.9 Hz, $C_{PhOMe}H$), 6.77 (d, *J* = 1.6 Hz, $C_{PhOMe}H$), 3.64 (s, 3H, $C_{OMe}H_3$), 3.23 (s, 1H, $C_{sp3}H$), 3.22 (s, 1H, $C_{sp3}H$), 2.17 – 2.05 (m, 2H, $C_{sp3}H_2$), 1.98 – 1.85 (m, 3H, $C_{sp3}H_2$ + $C_{sp3}H$*H*), 1.69 (dd, *J* = 9.2, 5.3 Hz, 1H, $C_{sp3}H$*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.9 (CO), 159.6 (C_{Ph}-OMe), 137.1 ($C_{PhOMe,q}$), 136.0 ($C_{Ph,q}$), 135.2 (C_{sp2}-Ph), 134.7 (C_{sp2}PhOMe), 129.7 ($C_{PhOMe}H$), 128.7 ($C_{Ph}H$), 128.1 ($C_{Ph}H$), 127.8 ($C_{Ph}H$), 120.5 ($C_{PhOMe}H$), 113.5 ($C_{PhOMe}H$), 113.5 ($C_{PhOMe}H$), 56.4 ($C_{sp3}H$), 56.2 ($C_{sp3}H$), 55.2 ($C_{OMe}H_3$), 30.0 ($C_{sp3}H_2$), 30.0 ($C_{sp3}H_2$), 18.1 ($C_{sp3}H_2$).

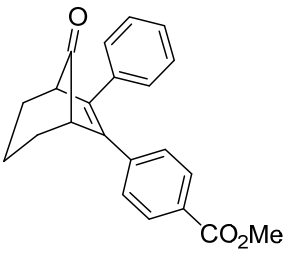
IR (ν_{max}, cm^{-1}) 3076 (w), 3054 (w), 3028 (w), 3000 (w), 2940 (w), 2858 (w), 2834 (w), 1762 (s), 1598 (w), 1576 (w), 1444 (w), 1288 (w), 1260 (w), 788 (w), 768 (w).

Mp: 87–90 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{21}O_2^+$ 305.1536; Found 305.1530.

[4] The signals for the two $C_{sp3}H_2$ adjacent to the bridgehead are not resolved.

Methyl 4-(8-oxo-7-phenylbicyclo[3.2.1]oct-6-en-6-yl)benzoate (**5c**)



5c was synthesized analogously to **5a** from **3a** (25.0 mg, 76.8 µmol, 1 eq.) and 4-methoxycarbonylphenylboronic acid (27.6 mg, 153 µmol, 2 eq.). The product was obtained as a light yellow solid (14.7 mg, 44.2 µmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H, $C_{PhCO2Me}H$), 7.33 – 7.29 (m, 2H, $C_{PhCO2Me}H$), 7.29 – 7.20 (m, 5H, $C_{Ph}H$), 3.90 (s, 3H, $C_{OMe}H_3$), 3.26 (s, 1H, $C_{sp3}H$), 3.25 (s, 1H, $C_{sp3}H$), 2.15 – 2.07 (m, 2H, $C_{sp3}H_2$), 2.01 – 1.84 (m, 3H, $C_{sp3}H_2$ + $C_{sp3}H$*H*), 1.75 – 1.67 (m, 1H, $C_{sp3}H$*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3 (CO), 166.8 (CO_2Me), 140.6 (*C*$_{Ph}$-CO_2Me), 137.3 (C_{sp2}-Ph), 135.4 ($C_{Ar,q}$), 134.0 (*C*s_{p2}-PhCO2Me), 129.9 ($C_{PhCO2Me}H$), 129.1 ($C_{Ar,q}$), 128.8 ($C_{Ar}H$), 128.1 ($C_{Ph}H$), 128.1 ($C_{Ar}H$), 128.0 ($C_{Ar}H$), 56.5 ($C_{sp3}H$), 56.1 ($C_{sp3}H$), 30.1 ($C_{sp3}H_2$), 30.0 ($C_{sp3}H_2$), 18.1 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 3076 (w), 3054 (w), 3022 (w), 2996 (w), 2946 (w), 2860 (w), 1762 (s), 1720 (s), 1606 (m), 1436 (m), 1276 (s), 1182 (w), 1110 (m), 770 (m).

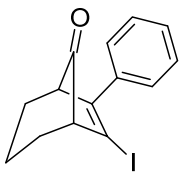
Mp: 104–107 °C.

HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{22}H_{21}O_3^+$ 333.1485; Found 333.1480.

Synthesis of Iodo-Bicyclooctenone and Derivatization

6 was synthesized in analogy to a published procedure.[7] The cross-coupling products **7** and **8** were synthesized according to modified literature procedures.[8,9]

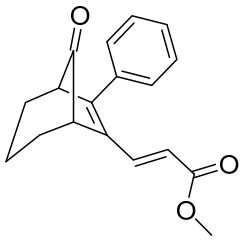
6-Iodo-7-phenylbicyclo[3.2.1]oct-6-en-8-one (**6**)



In a microwave-vial, **3a** (50 mg, 154 µmol, 1 eq.) and iodine (7.8 mg, 30.7 µmol, 0.2 eq.) were dissolved in dry, degassed iodomethane (3 mL). The vial was sealed and heated in the microwave to 130 °C for 4 h. The mixture was allowed to cool to RT, diluted with Et_2O (15 mL), and washed with $Na_2S_2O_3$ (sat. aq., 5 mL) and NaCl (sat. aq., 5 mL). The organic phase was dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by flash column chromatography on silica with a gradient of 4–6% Et_2O in pentane gave the product in the form of a light yellow solid (44.3 mg, 137 µmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H, $C_{Ph}H$), 7.47 – 7.31 (m, 3H, $C_{Ph}H$), 3.17 (dt, *J* = 4.5, 1.6 Hz, 1H, $C_{sp3}H$), 3.06 (m, 1H, $C_{sp3}H$), 2.14 – 2.00 (m, 2H, 2 x C_{sp3}*H*H), 1.85 – 1.60 (m, 4H, 2 x C_{sp3}*H*H + $C_{sp3}H_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.8 (CO), 144.0 (C_{sp2}-Ph), 135.5 ($C_{Ph,q}$), 128.7 ($C_{Ph}H$), 128.6 ($C_{Ph}H$), 127.2 ($C_{Ph}H$), 87.2 (C_{sp2}-I), 62.6 ($C_{sp3}H$), 56.2 ($C_{sp3}H$), 29.9 ($C_{sp3}H_2$), 28.4 ($C_{sp3}H_2$), 17.5 ($C_{sp3}H_2$).
IR (ν_{max}, cm^{-1}) 2940 (w), 2857 (w), 1762 (s), 1491 (w), 1443 (w), 1279 (w), 1267 (w), 1073 (w), 764 (m), 694 (m).
Mp: 48 °C.
HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}IO^+$ 325.0084; Found 325.0096.

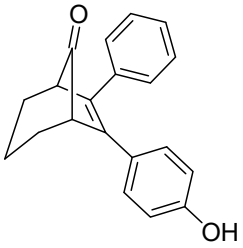
Methyl (*E*)-3-(8-oxo-7-phenylbicyclo[3.2.1]oct-6-en-6-yl)acrylate (**7**)



A solution of $Pd(OAc)_2$ (1.7 mg, 7.6 µmol, 0.1 eq.) in DMF (0.3 mL) was added to a solution containing **6** (25.0 mg, 77.1 µmol, 1 eq.), methyl acrylate (10.4 µL, 116 µmol, 1.5 eq.) and triethylamine (16.1 µL, 116 µmol, 1.5 eq.) in DMF (0.5 mL). The mixture was heated to 50 °C for 14 h. The mixture was allowed to cool to RT, diluted with Et_2O (15 mL), and washed with H_2O (3 x 5 mL). The combined aqueous phases were extracted with Et_2O (2 x 15 mL). The combined organic phases were washed with NaCl (sat. aq., 2 x 15 mL), dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by flash column chromatography on silica with 20% Et_2O in pentane gave the product in the form of a light yellow, highly viscous liquid, which solidified upon standing (19.1 mg, 67.7 µmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 15.8 Hz, 1H, CO-C*H*=CH), 7.48 – 7.32 (m, 5H, C_{Ph}-H), 5.92 (d, *J* = 15.7 Hz, 1H, CO-CH=C*H*), 3.76 (s, 3H, CH_3), 3.29 (dd, *J* = 4.2, 2.0 Hz, 1H, $C_{sp3}H$), 3.23 (dd, *J* = 4.1, 2.0 Hz, 1H, $C_{sp3}H$), 2.11 – 2.00 (m, 2H, 2 x C_{sp3}*H*H), 1.98 – 1.81 (m, 2H, 2 x C_{sp3}*H*H), 1.70 – 1.53 (m, 2H, $C_{sp3}H_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8 (CO), 167.6 (CO_2Me), 145.4 (C_{sp2}-Ph), 136.9 (CO-*C*H=CH), 134.5 ($C_{Ph,q}$), 132.0 (*C*$_{sp2}$-CH=CH-CO), 129.0 (C_{Ph}-H), 129.0 (C_{Ph}-H), 128.5 (C_{Ph}-H), 120.4 (CO-CH=*C*H), 56.7 ($C_{sp3}H$), 51.9 (CH_3), 51.6 ($C_{sp3}H$), 30.1 ($C_{sp3}H_2$), 29.6 ($C_{sp3}H_2$), 17.8 ($C_{sp3}H_2$).
IR (ν_{max}, cm^{-1}) 2946 (w), 2860 (w), 1760 (s), 1710 (s), 1615 (m), 1444 (m), 1435 (m), 1324 (m), 1306 (m), 1272 (s), 1166 (s), 984 (m), 768 (m).
Mp: 95 °C.
HRMS (APCI/QTOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}O_3^+$ 283.1329; Found 283.1325.

6-(4-Hydroxyphenyl)-7-phenylbicyclo[3.2.1]oct-6-en-8-one (**8**)



6 (25.0 mg, 77.1 µmol, 1 eq.), 4-hydroxyphenylboronic acid (21.3 mg, 154 µmol, 2 eq.), potassium carbonate (21.3 mg, 154 µmol, 2 eq.), and $Pd(OAc)_2$ (1.7 mg, 7.6 µmol, 0.1 eq.) were dissolved in DMF (1.2 mL) and water (0.3 mL) and purged with N_2 at RT for 30 min. The mixture was heated to 85 °C for 6 h. The mixture was allowed to cool to RT, diluted with Et_2O (15 mL), washed with LiCl (10% aq., 2 x 5 mL) H_2O (1 x 5 mL) and NaCl (sat. aq., 2 x 4 mL), dried over $MgSO_4$, and the solvent was removed under vacuum. Purification by flash column chromatography on silica with 18% EtOAc in pentane gave the product in the form of an off-white solid (21.1 mg, 72.7 µmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 5H, C_{Ph}-H), 7.17 – 7.07 (m, 2H, $C_{Ph\text{-}OH}$-H), 6.84 – 6.66 (m, 2H, Ph_{OH}-H), 5.08 (s, 1H, OH), 3.26 – 3.16 (m, 2H, C_{sp3}H), 2.15 – 2.06 (m, 2H, 2 x C_{sp3}*H*H), 1.96 – 1.83 (m, 3H, 3 x C_{sp3}*H*H), 1.71 – 1.63 (m, 1H, C_{sp3}*H*H).

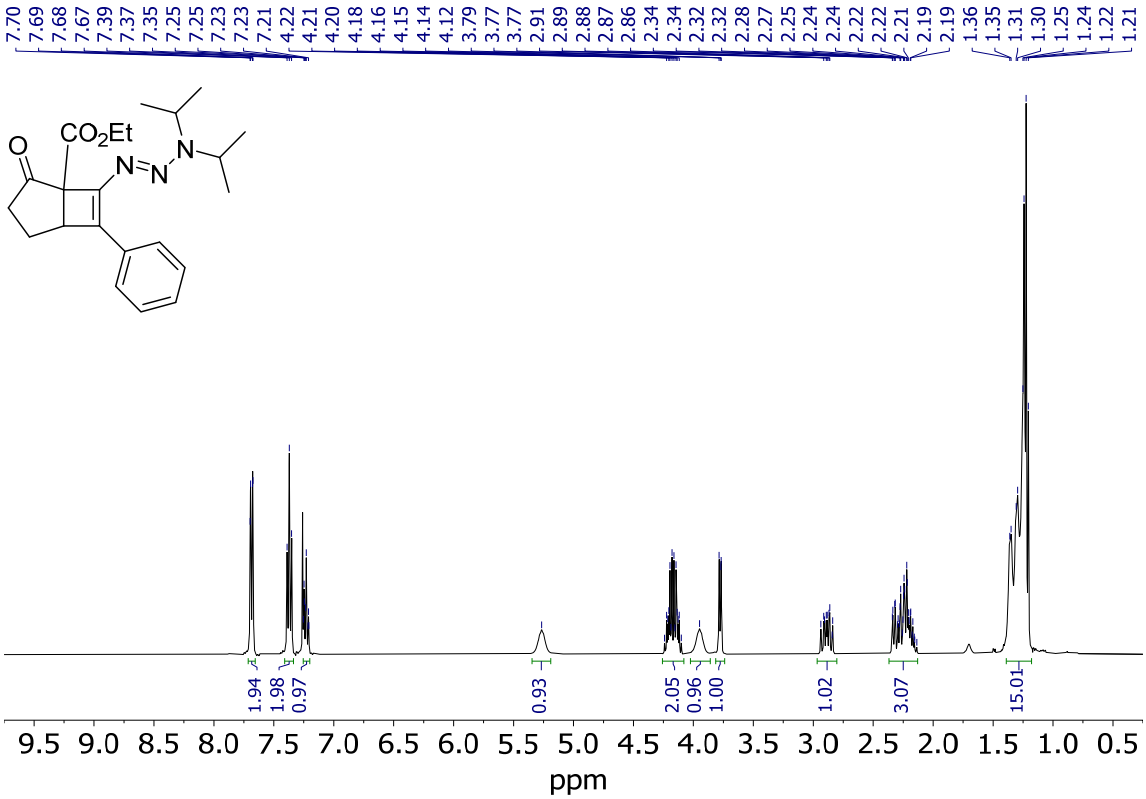
^{13}C NMR (101 MHz, $CDCl_3$) δ 216.4 (CO), 155.2 (C_{Ph}-OH), 136.2 ($C_{Ph,q}$), 134.4 (C_{sp2}-Ph-OH), 133.5 (C_{sp2}-Ph), 129.6 ($C_{Ph\text{-}OH}$-H), 128.7 (C_{Ph}-H), 128.3 ($C_{Ph\text{-}OH,q}$), 128.1 (C_{Ph}-H), 127.6 (C_{Ph}-H), 115.6 ($C_{Ph\text{-}OH}$-H), 56.3 (C_{sp3}H), 56.1 (C_{sp3}H), 30.0 ($C_{sp3}H_2$), 30.0 ($C_{sp3}H_2$), 18.1 ($C_{sp3}H_2$).

IR (ν_{max}, cm^{-1}) 3346 (w), 2941 (m), 2858 (w), 1743 (s), 1609 (m), 1513 (s), 1443 (m), 1267 (m), 1217 (m), 1173 (m), 837 (m), 731 (m).

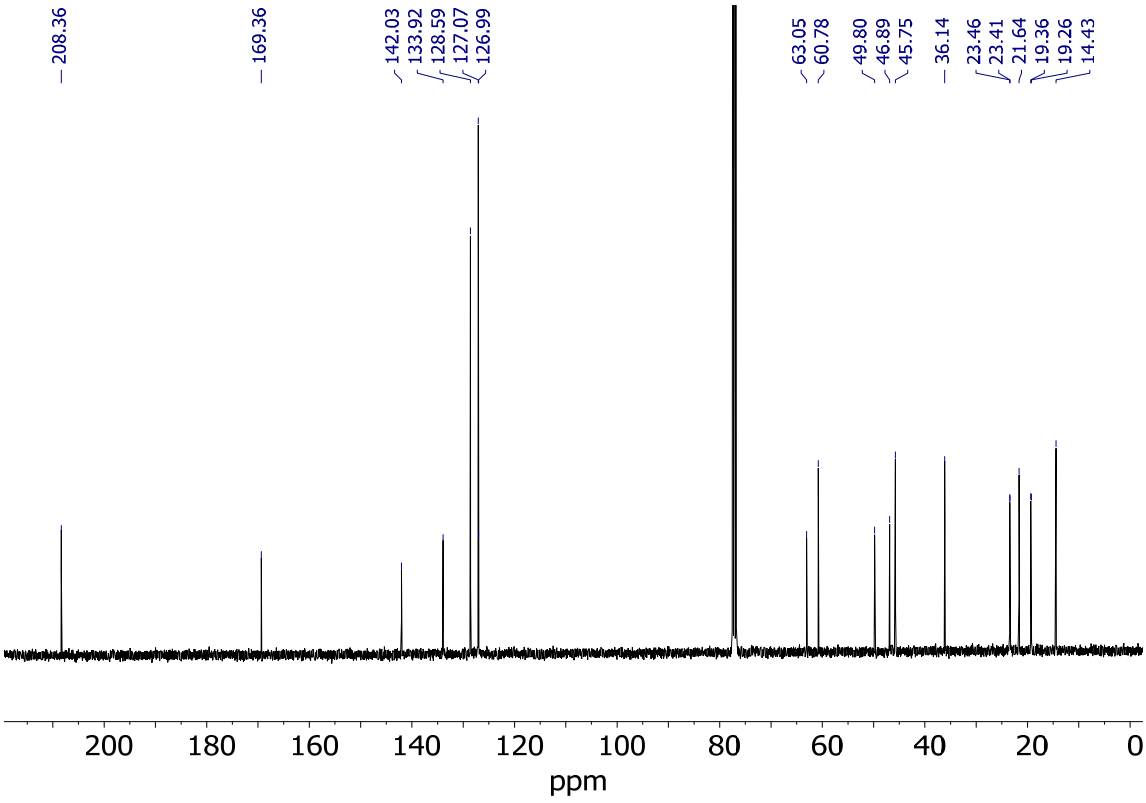
Mp: 149 °C (decomposition).

HRMS (ESI/QTOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{19}O_2^+$ 291.1380; Found 291.1366.

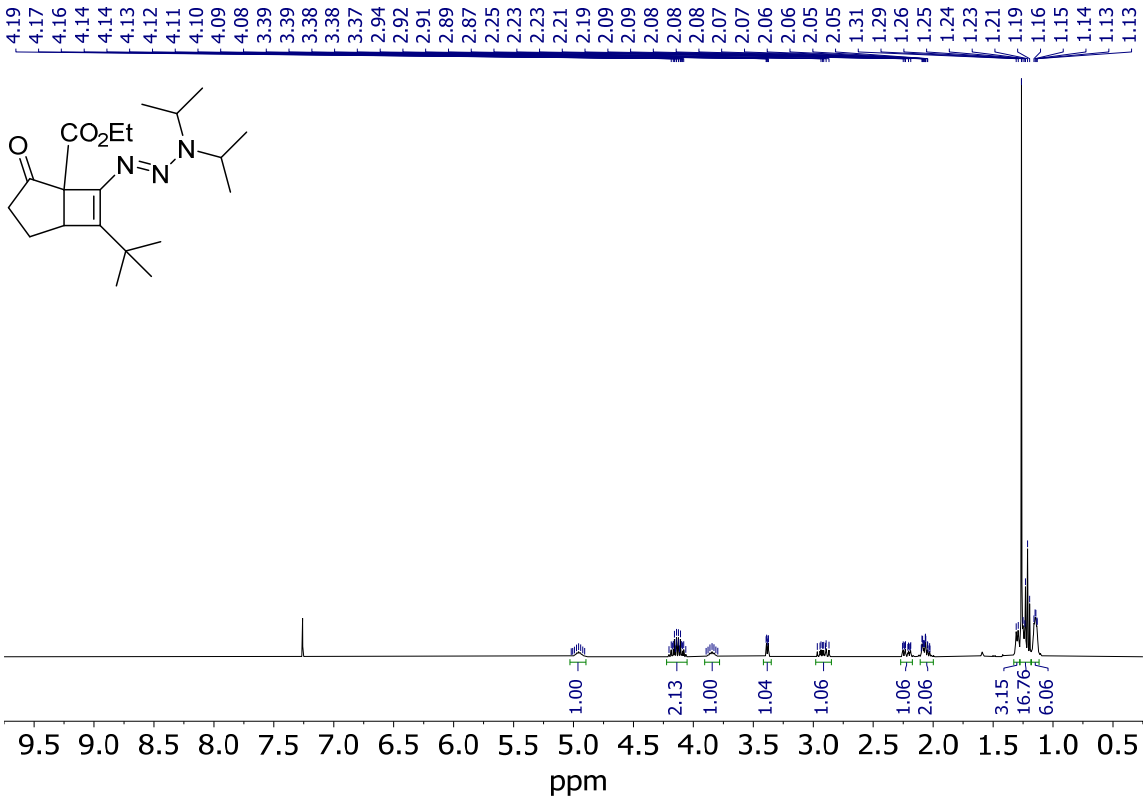
NMR-Spectra



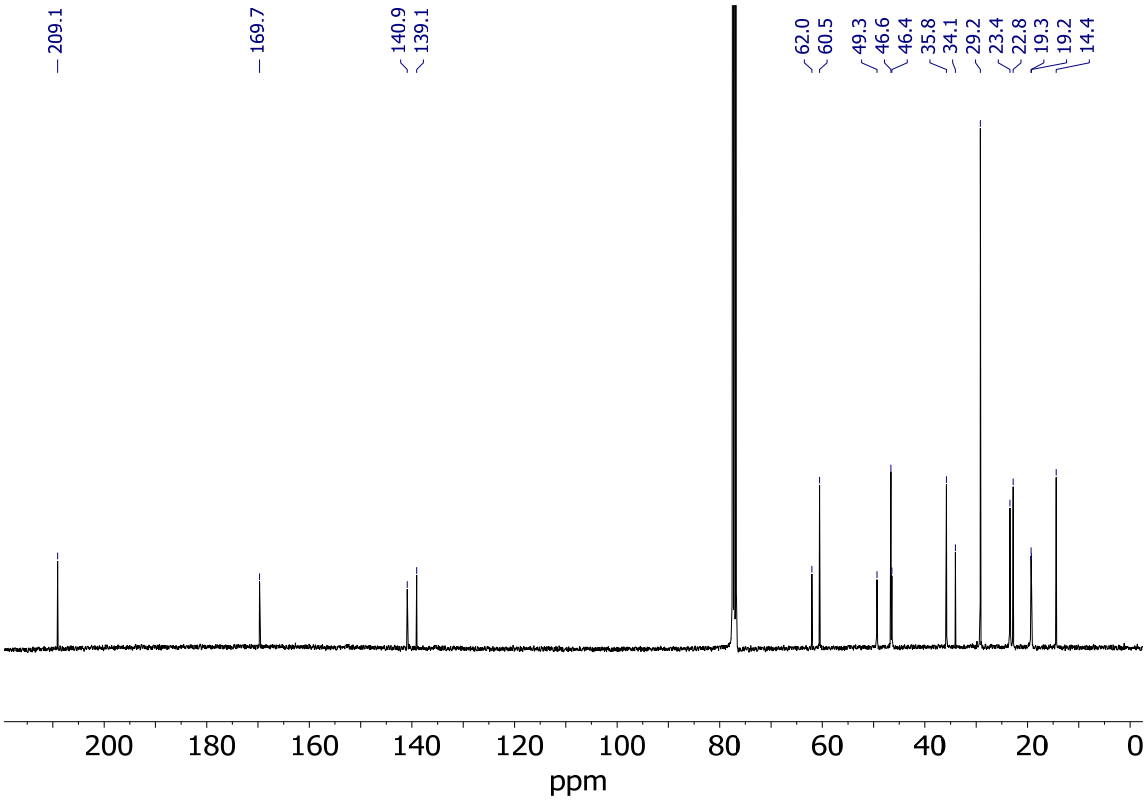
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1a**.



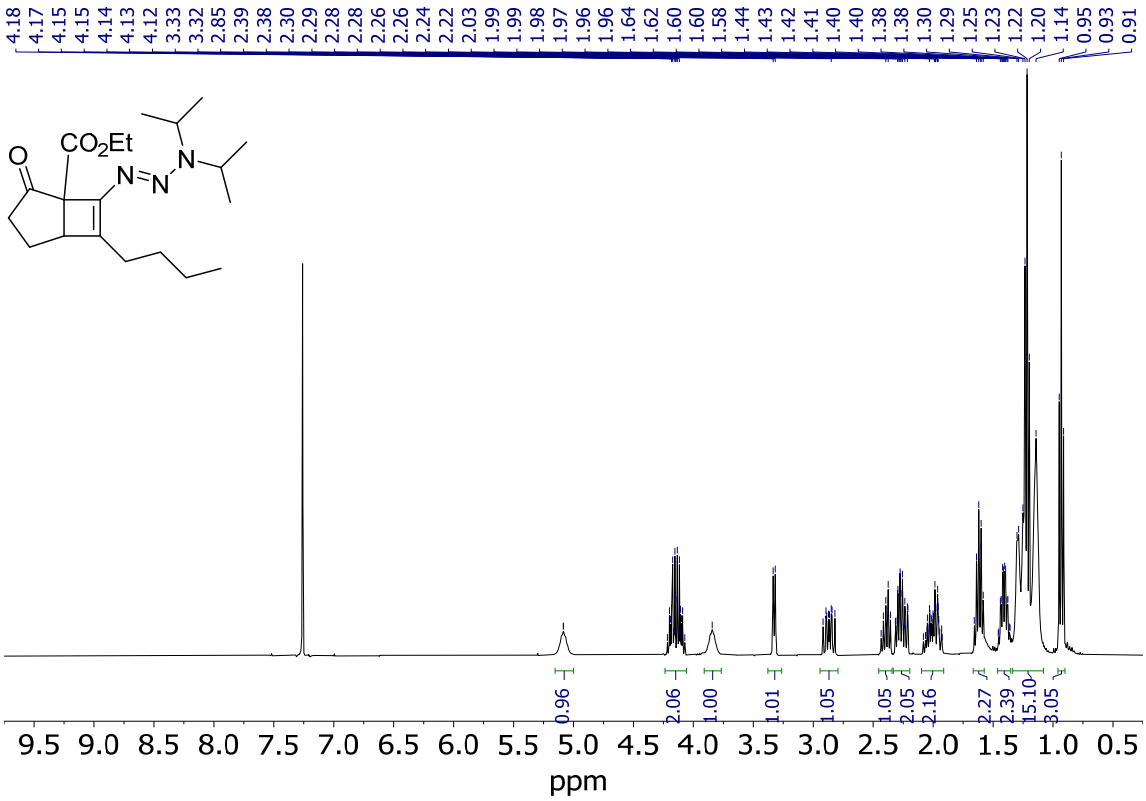
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1a**.



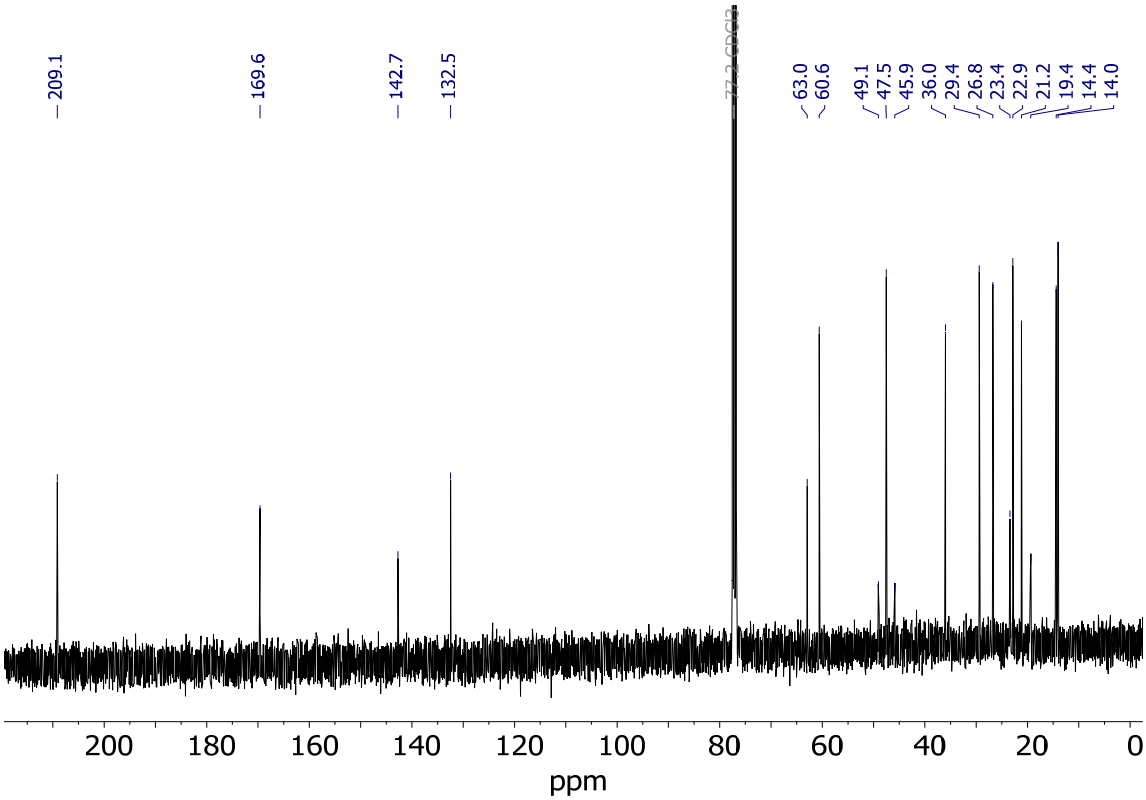
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1b**.



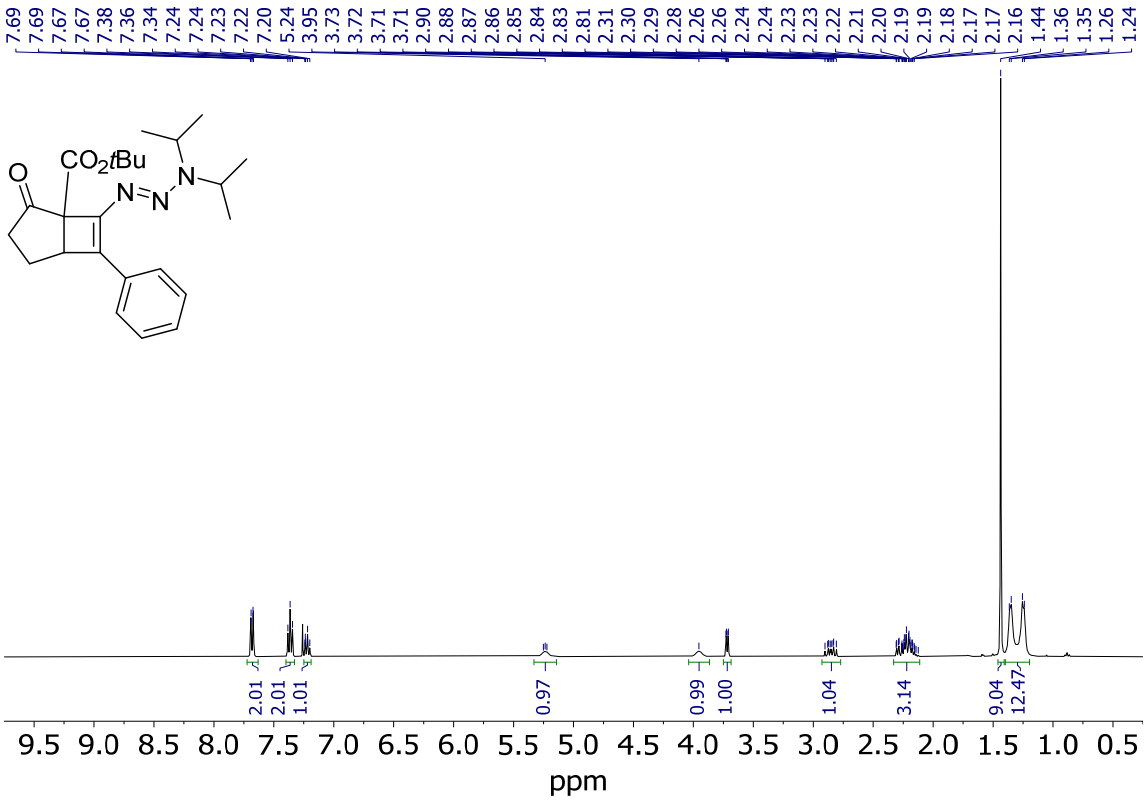
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1b**.



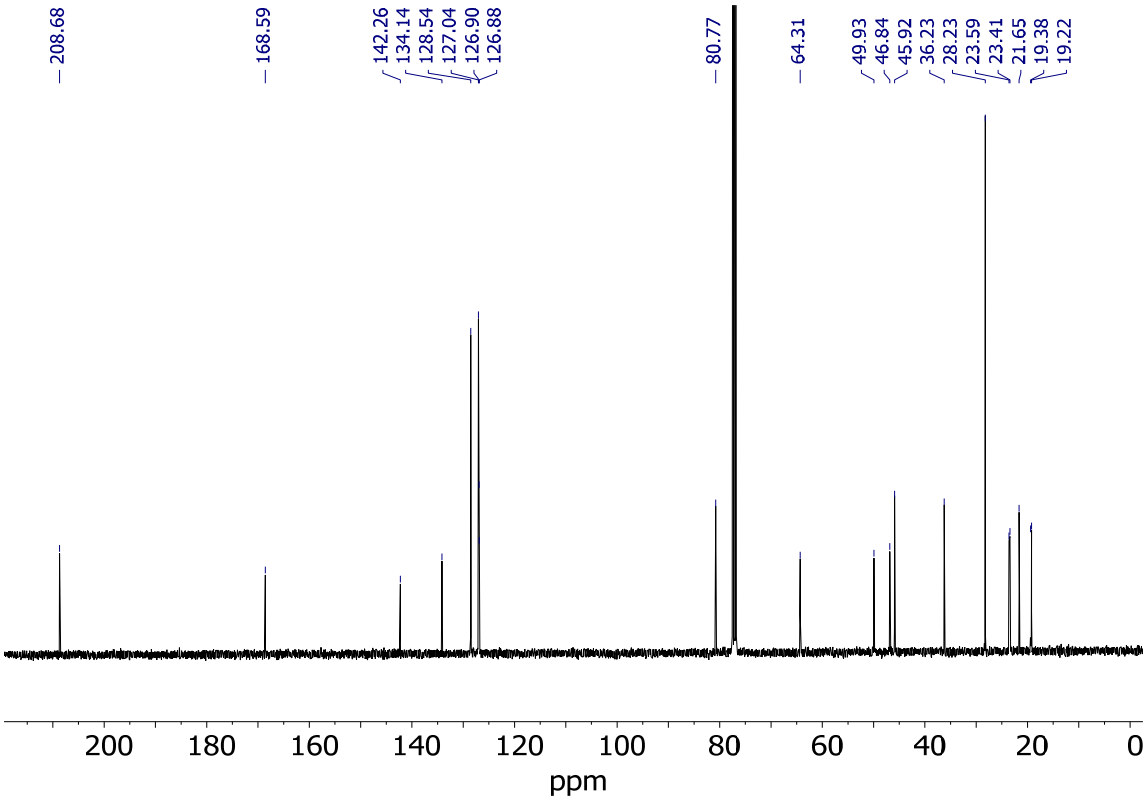
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1c**.



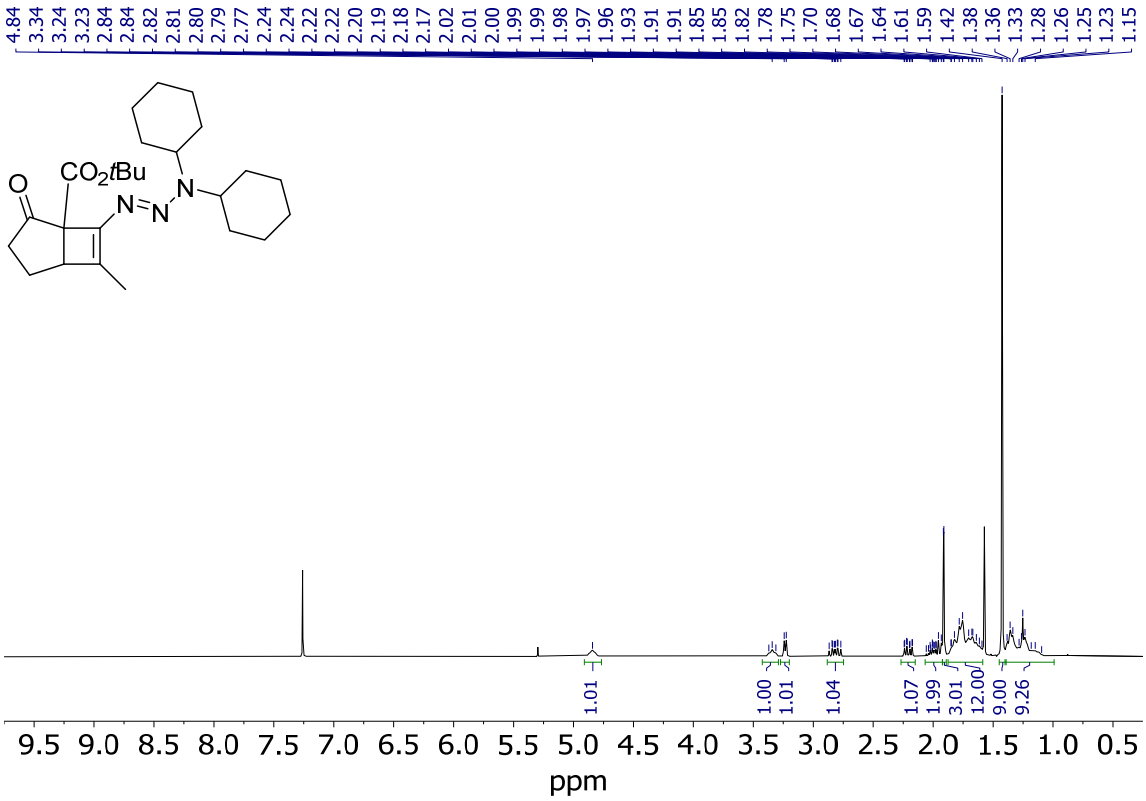
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1c**.



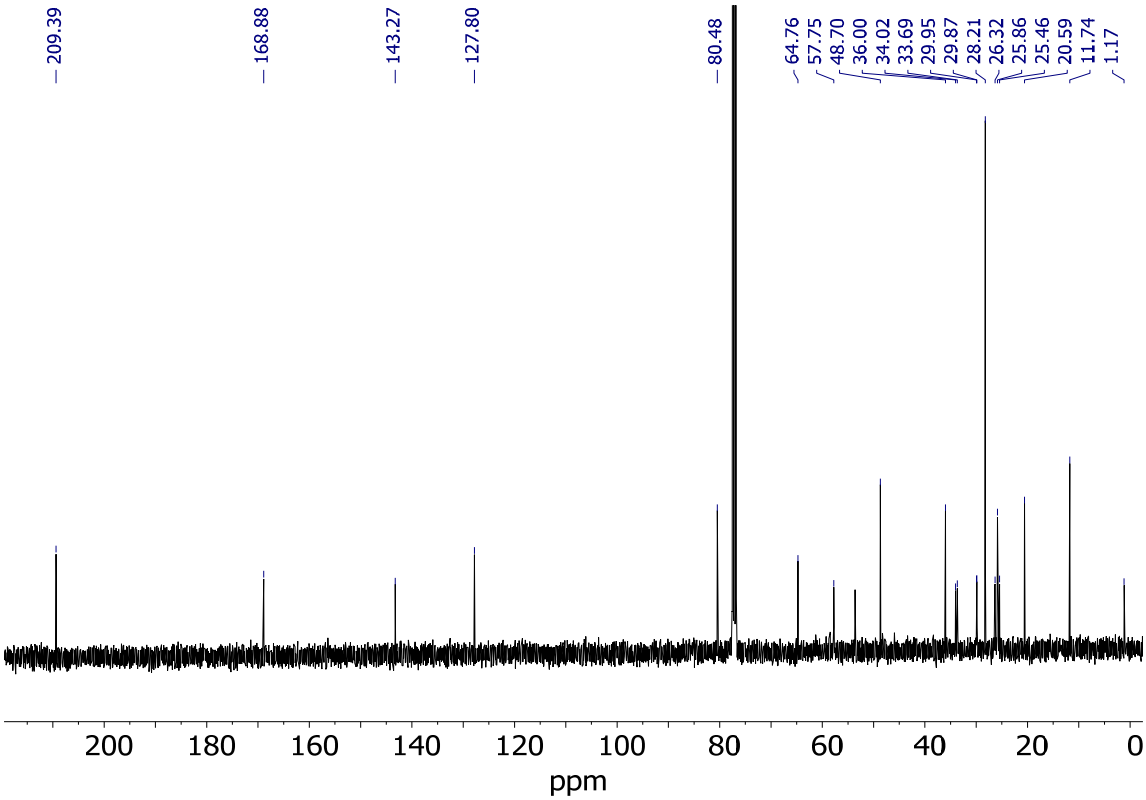
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1d**.



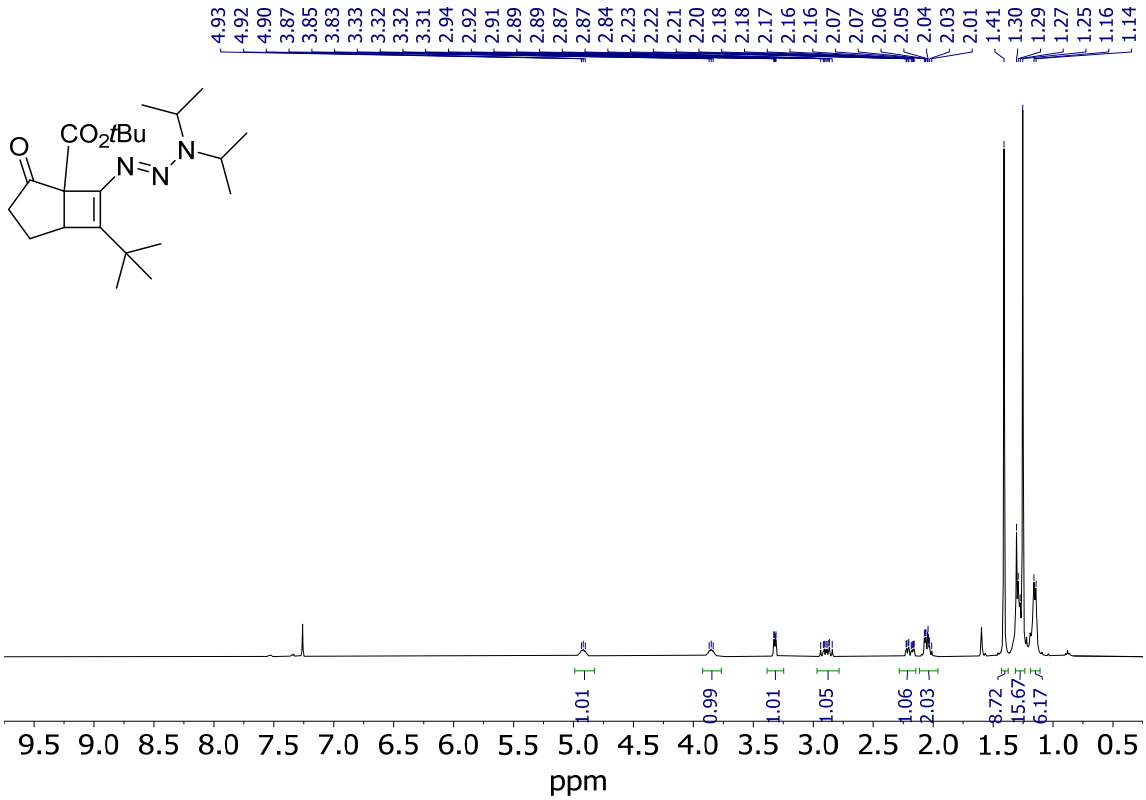
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1d**.



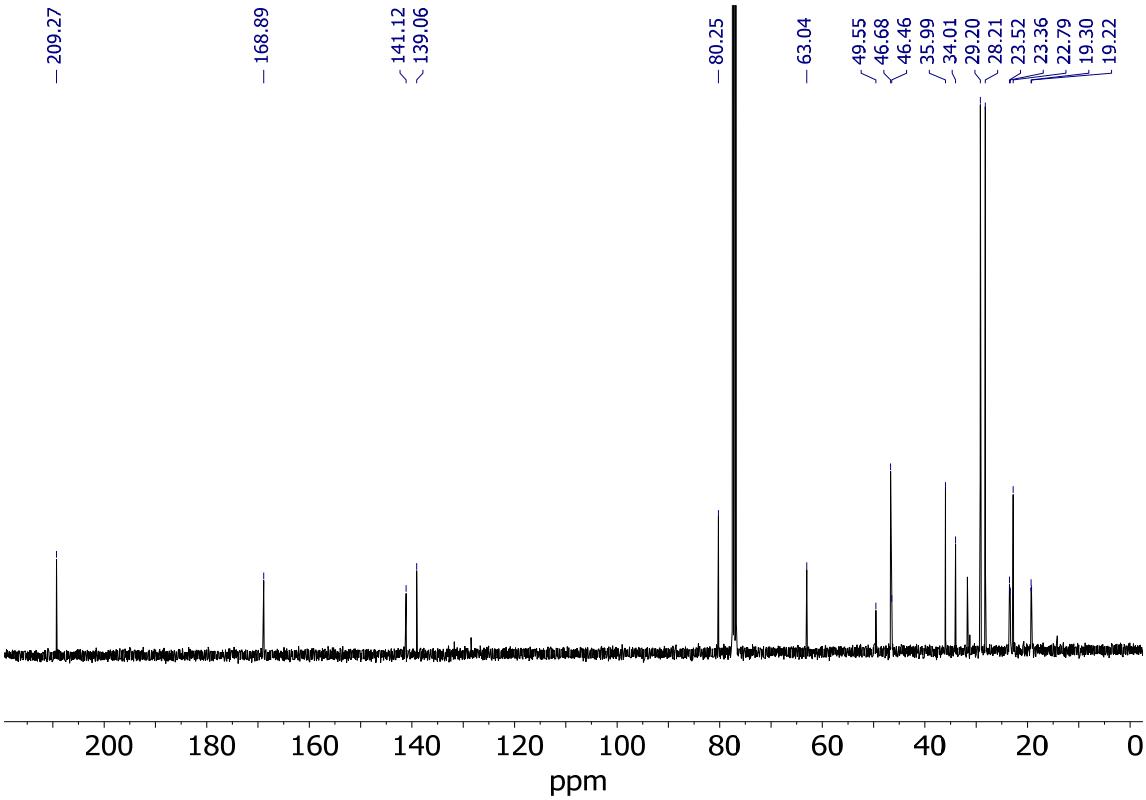
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1e**.



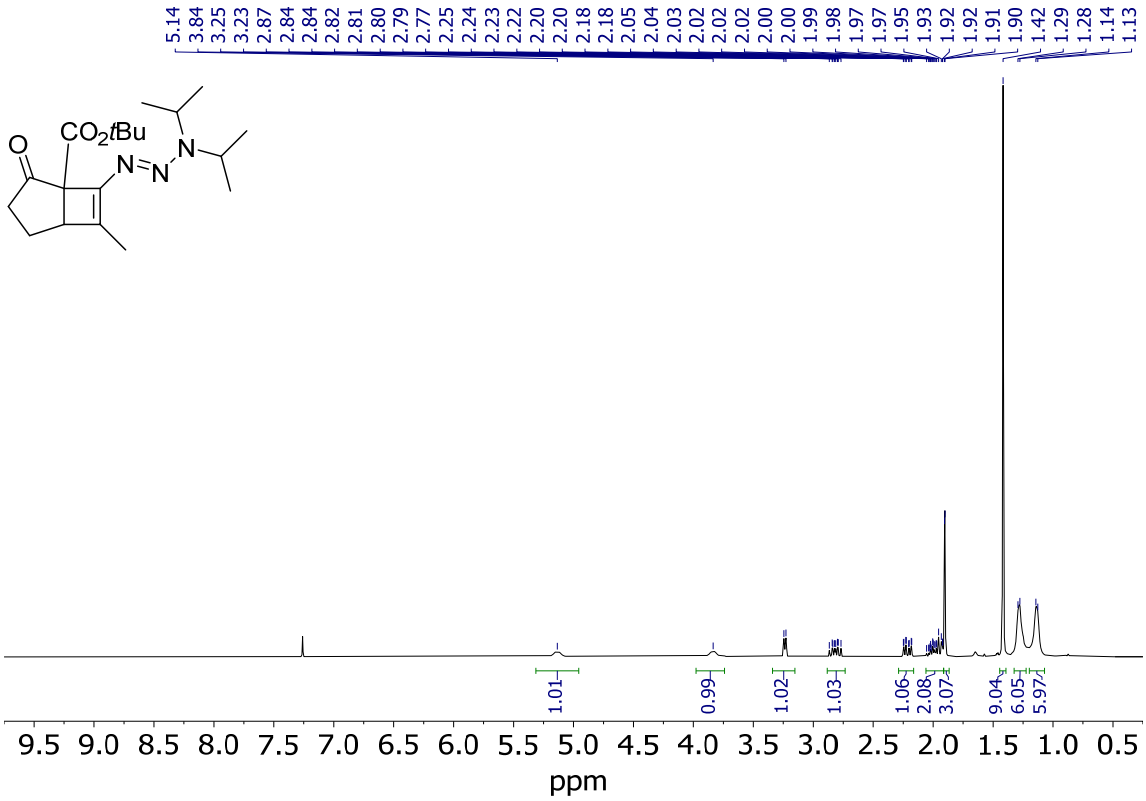
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1e**.



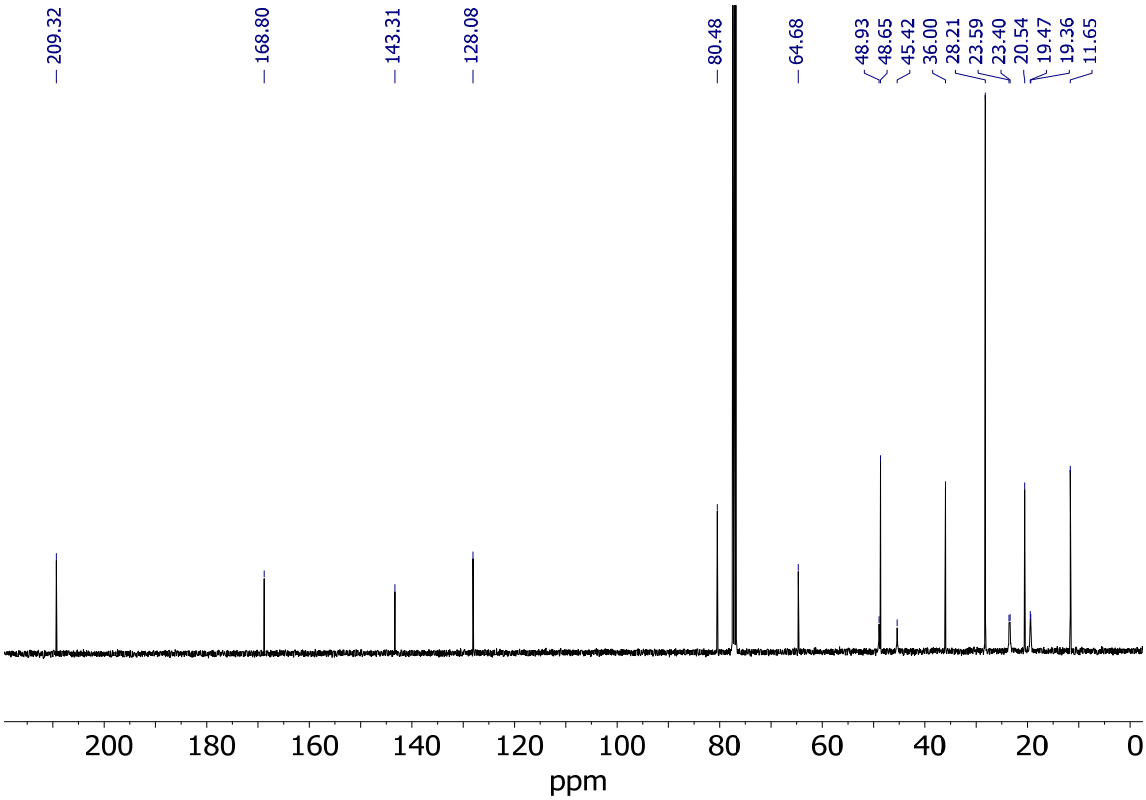
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1f**.



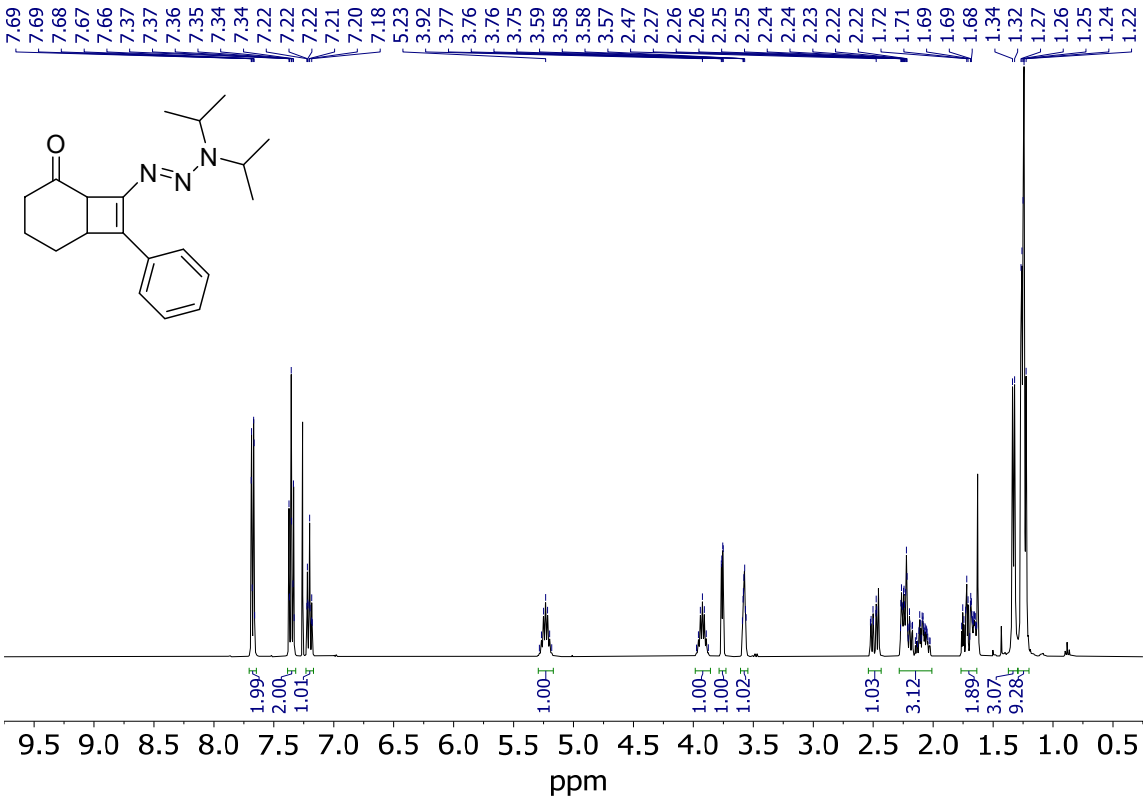
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1f**.



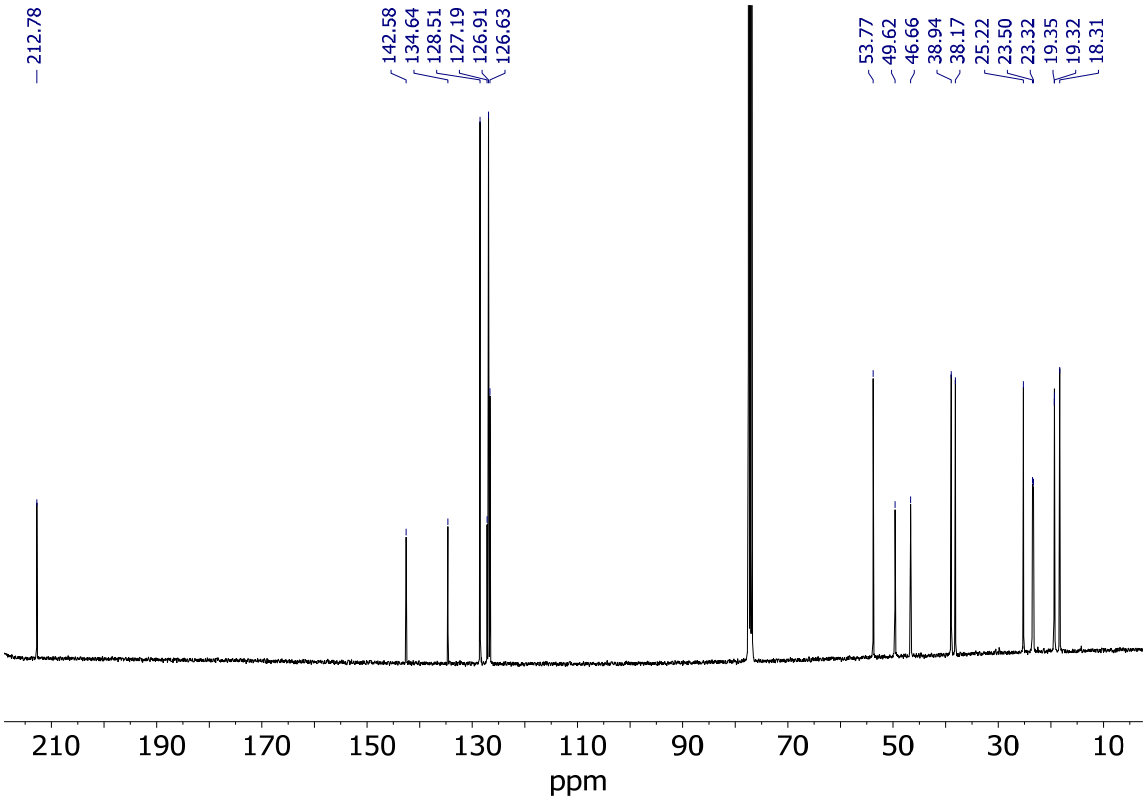
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1g**.



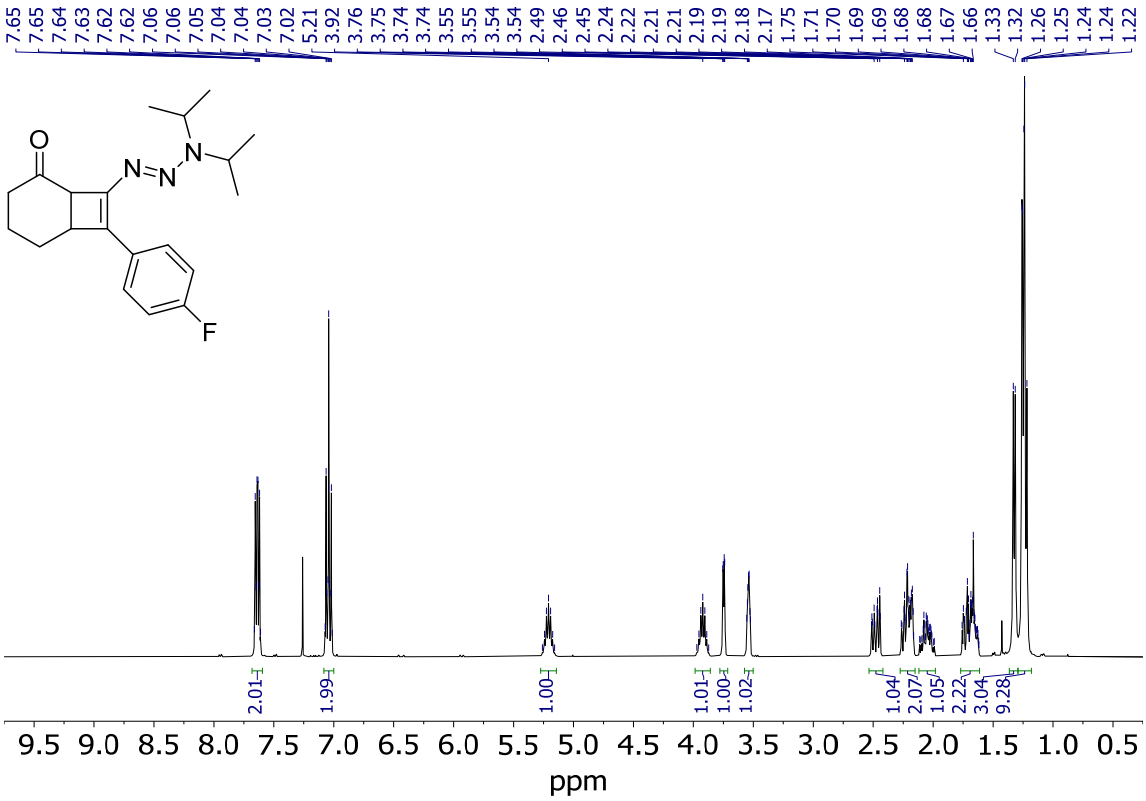
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **1g**.



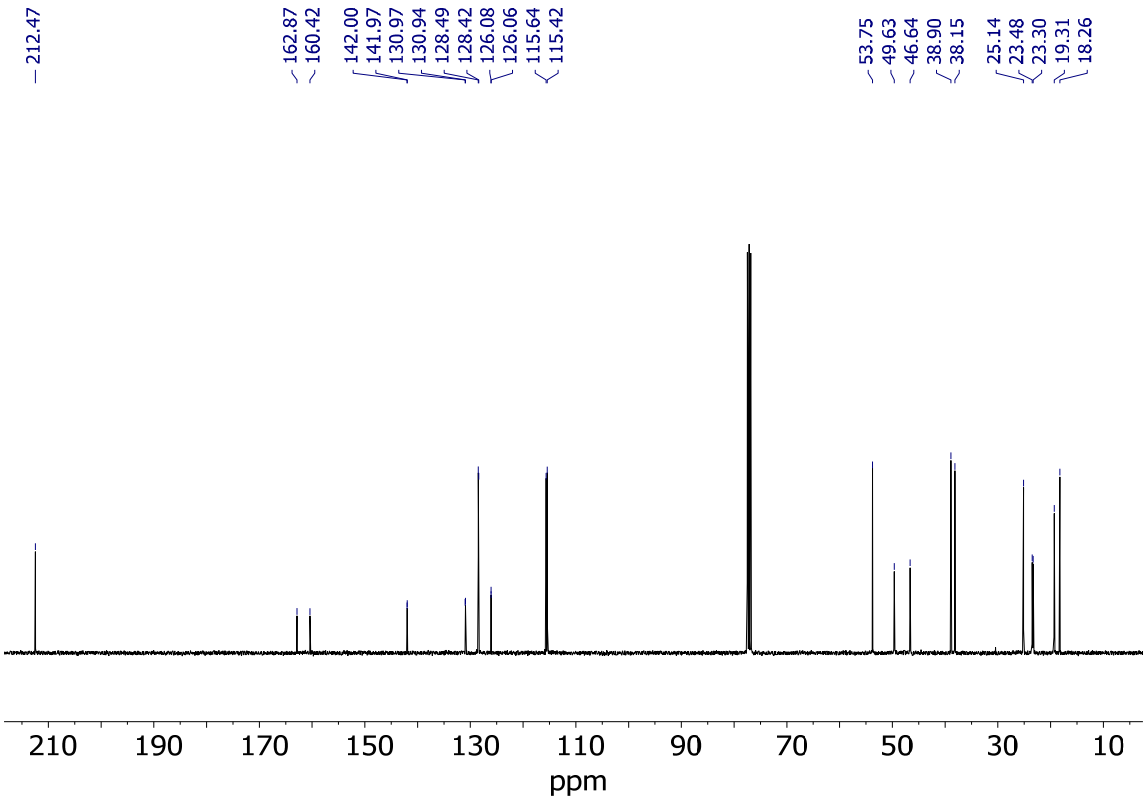
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2a**.



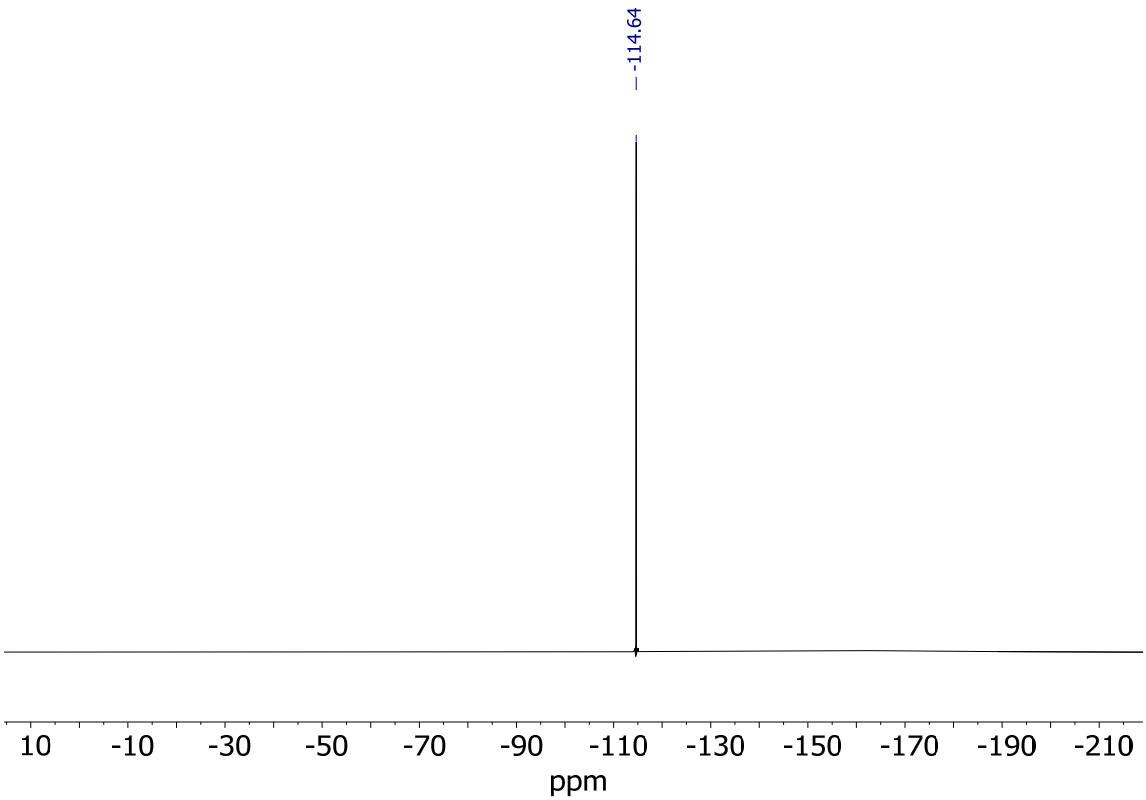
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2a**.



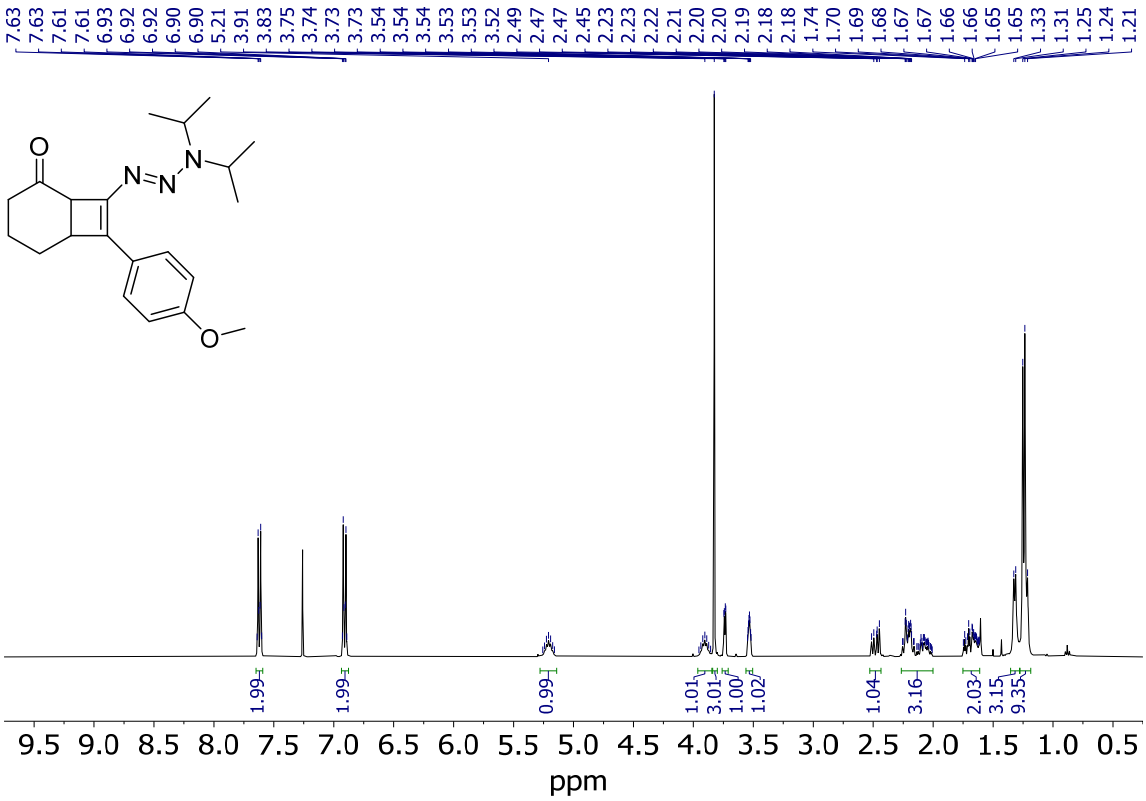
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2b**.



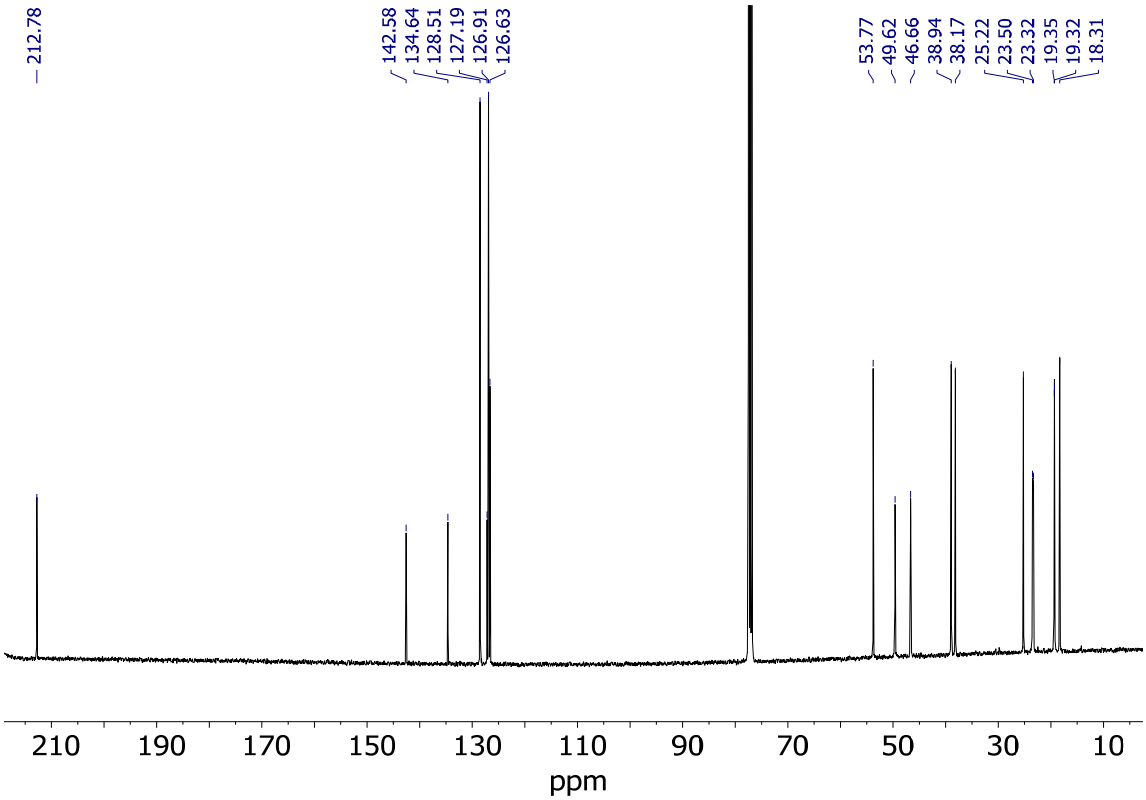
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2b**.



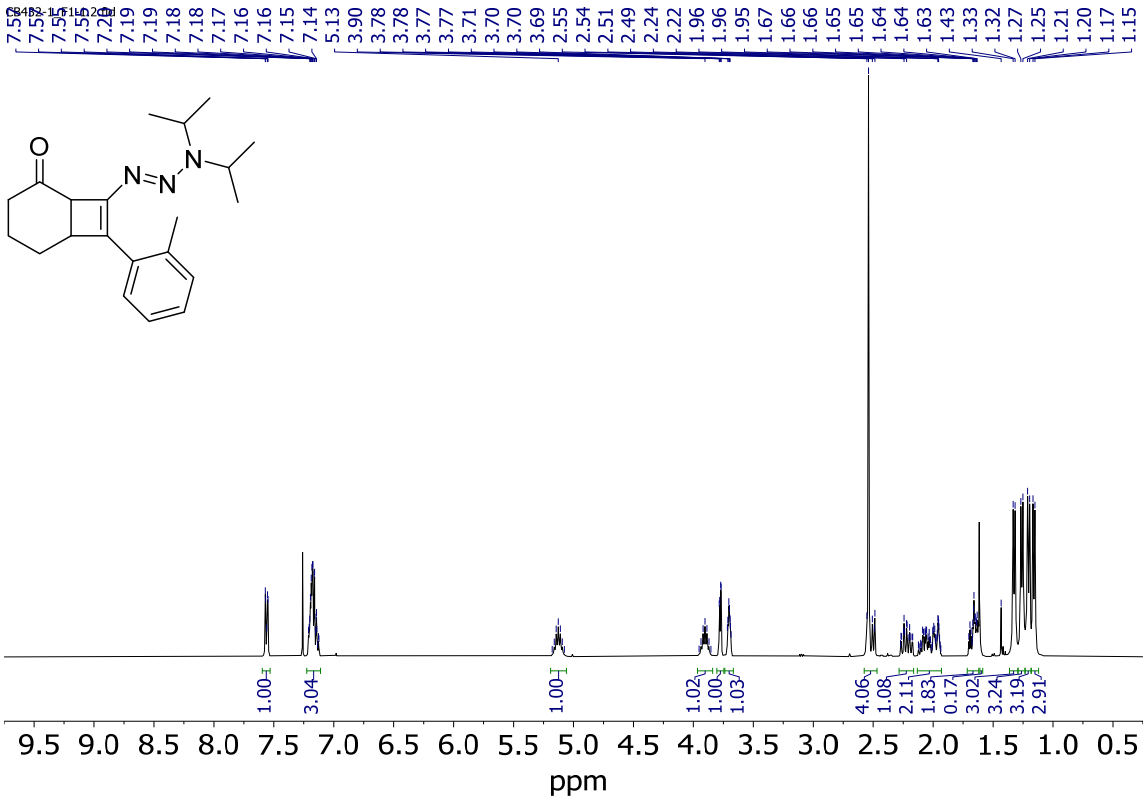
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **2b**.



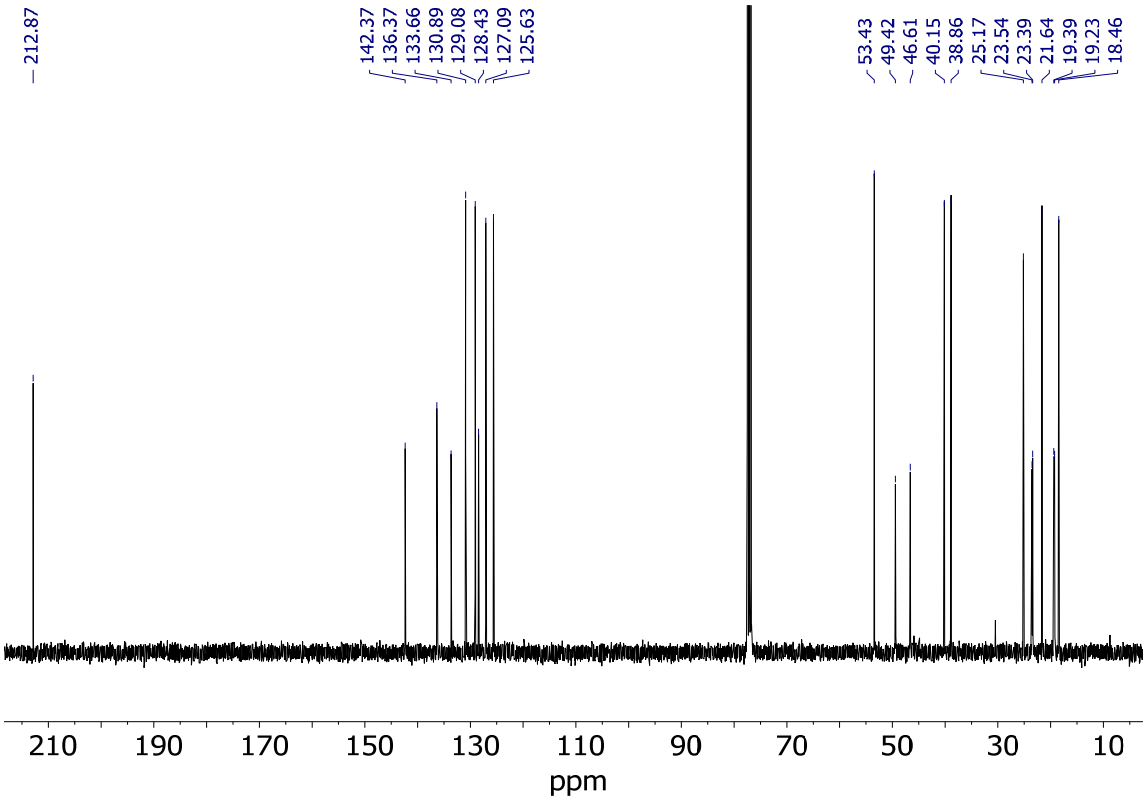
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2c**.



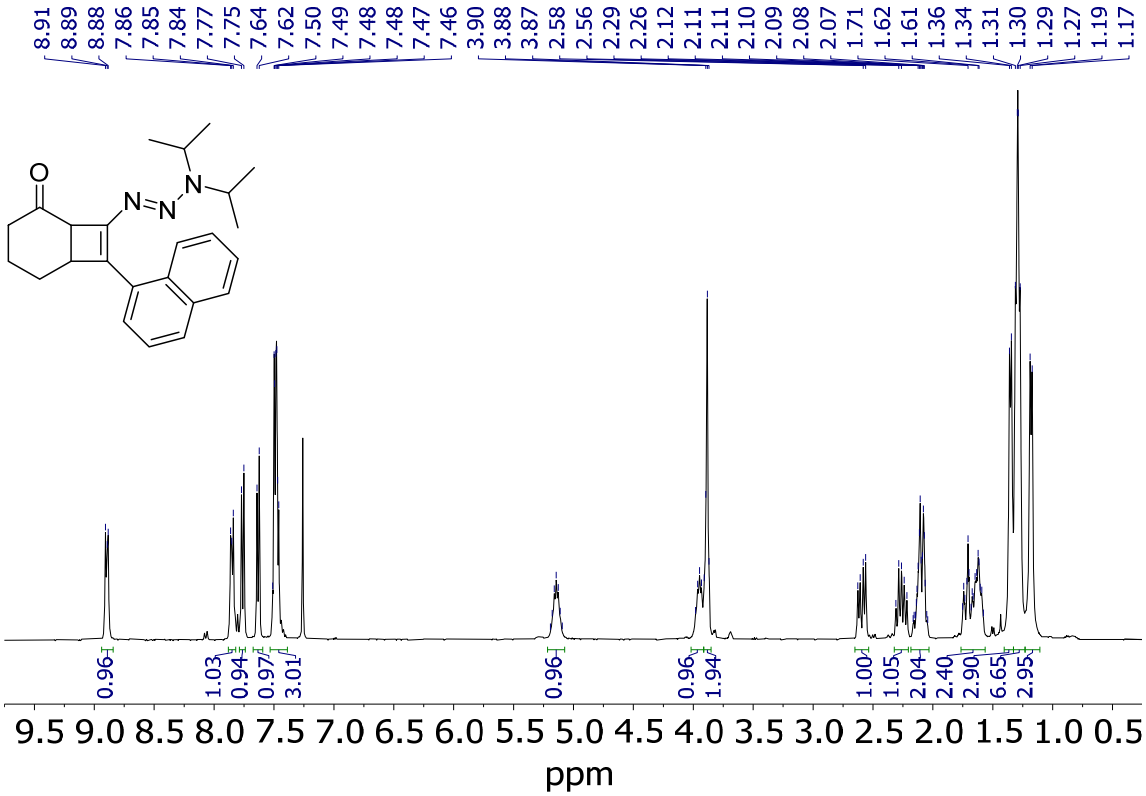
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2c**.



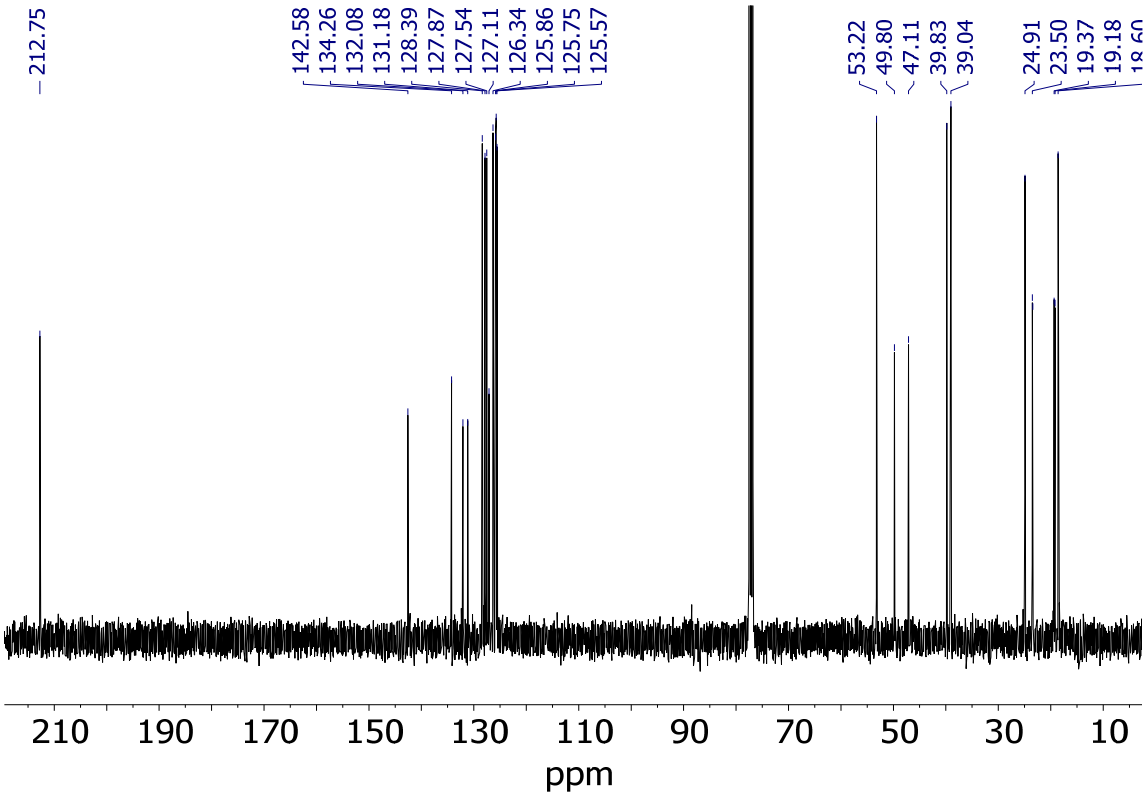
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2d**.



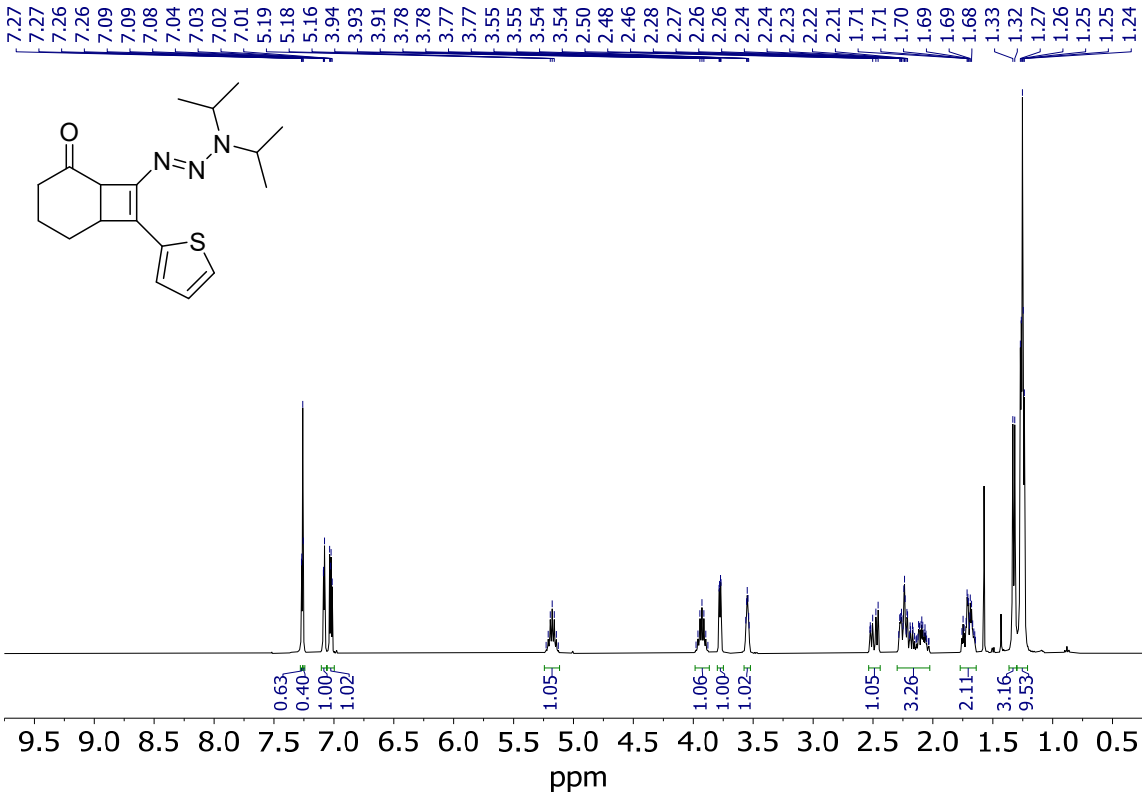
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2d**.



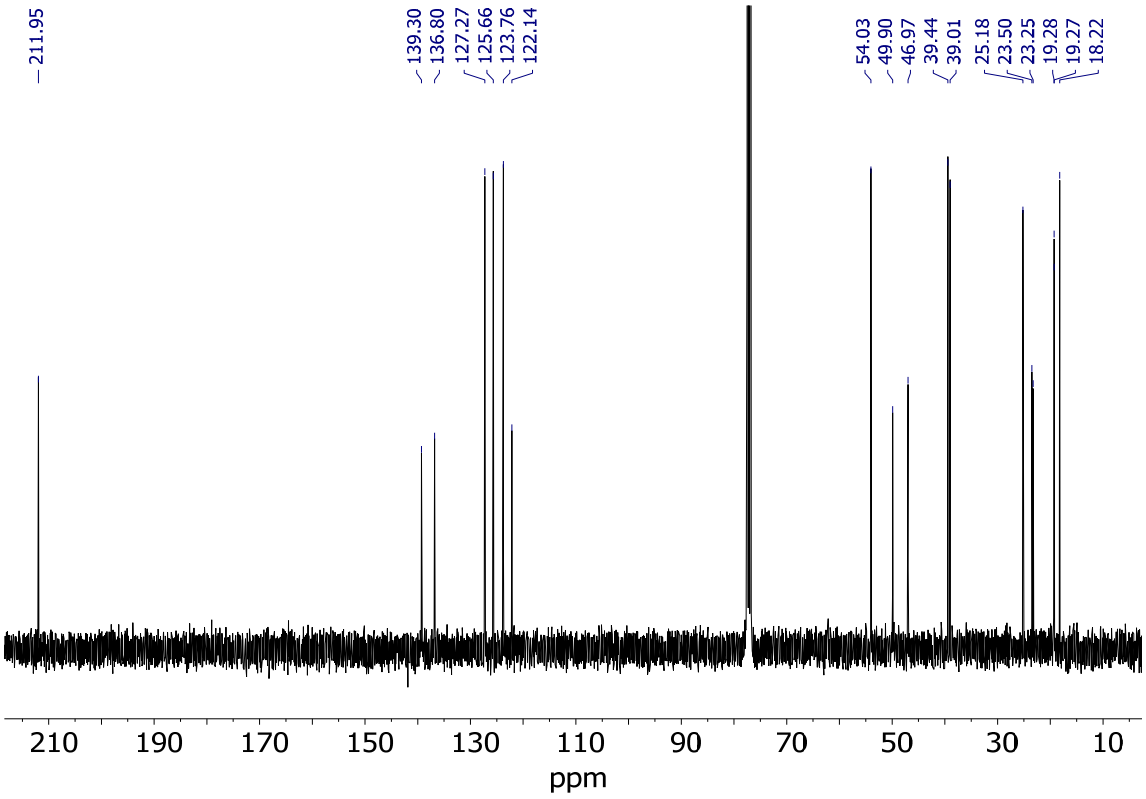
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2e**.



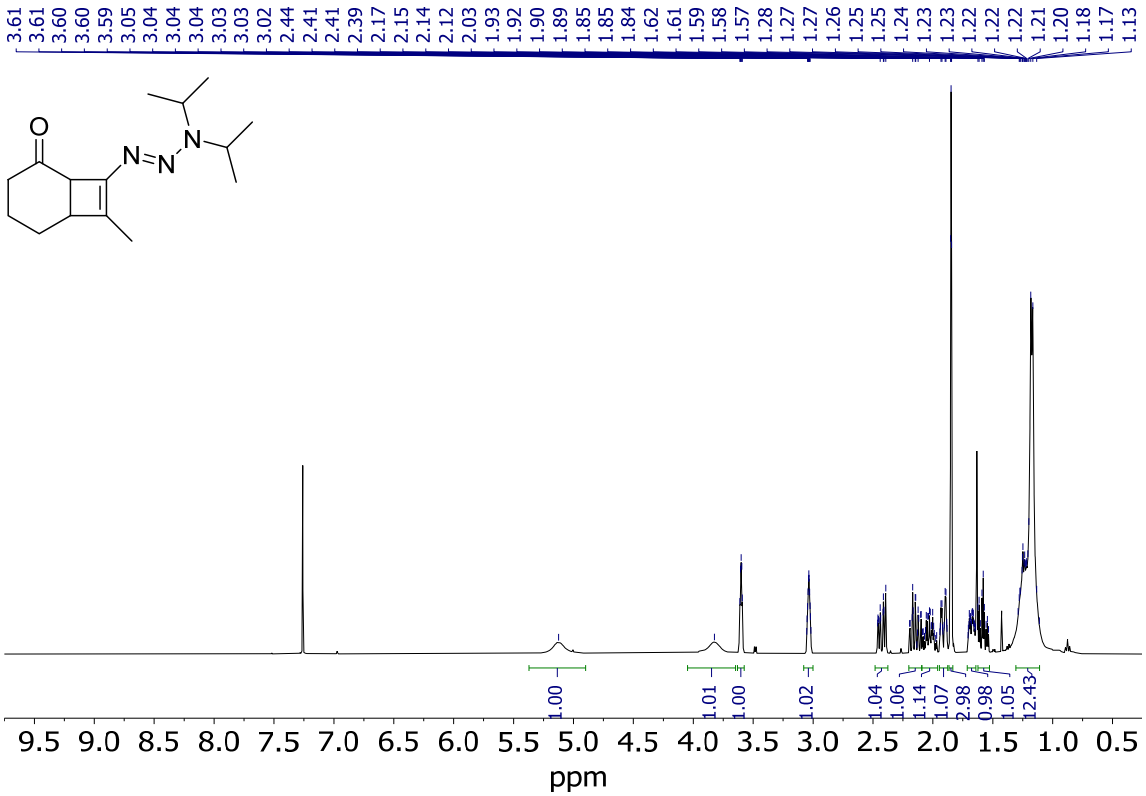
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2e**.



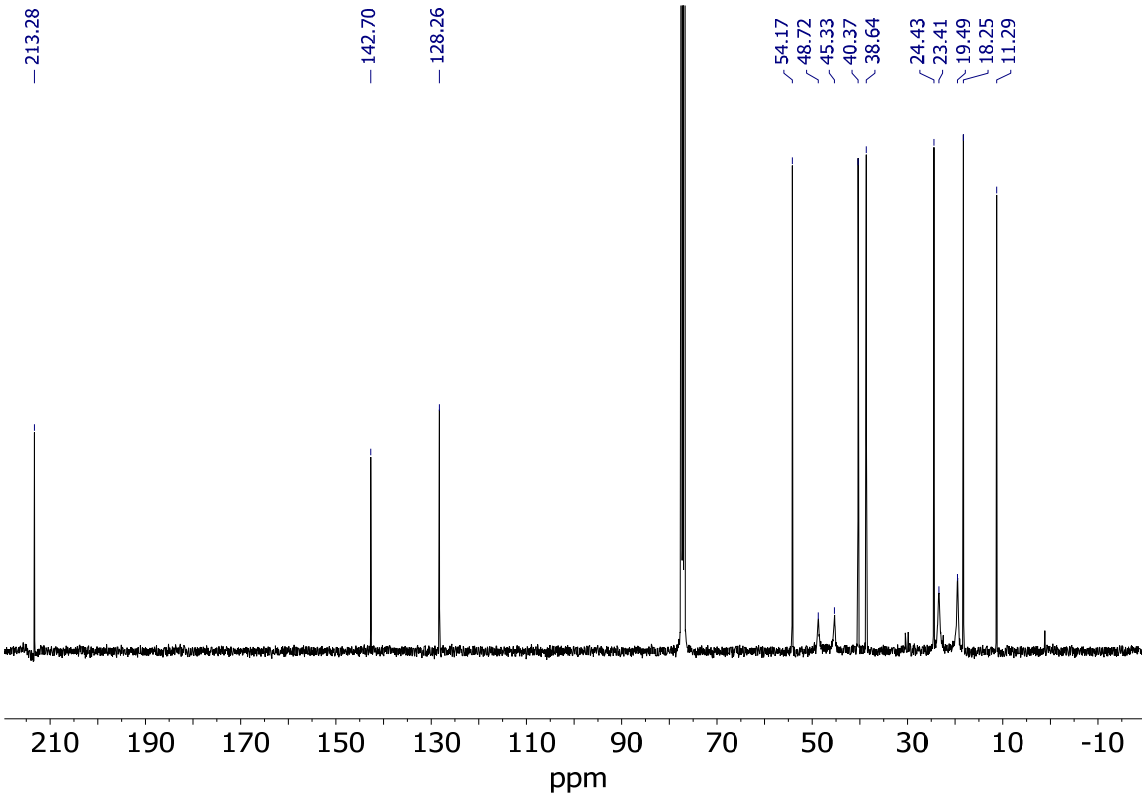
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2f**.



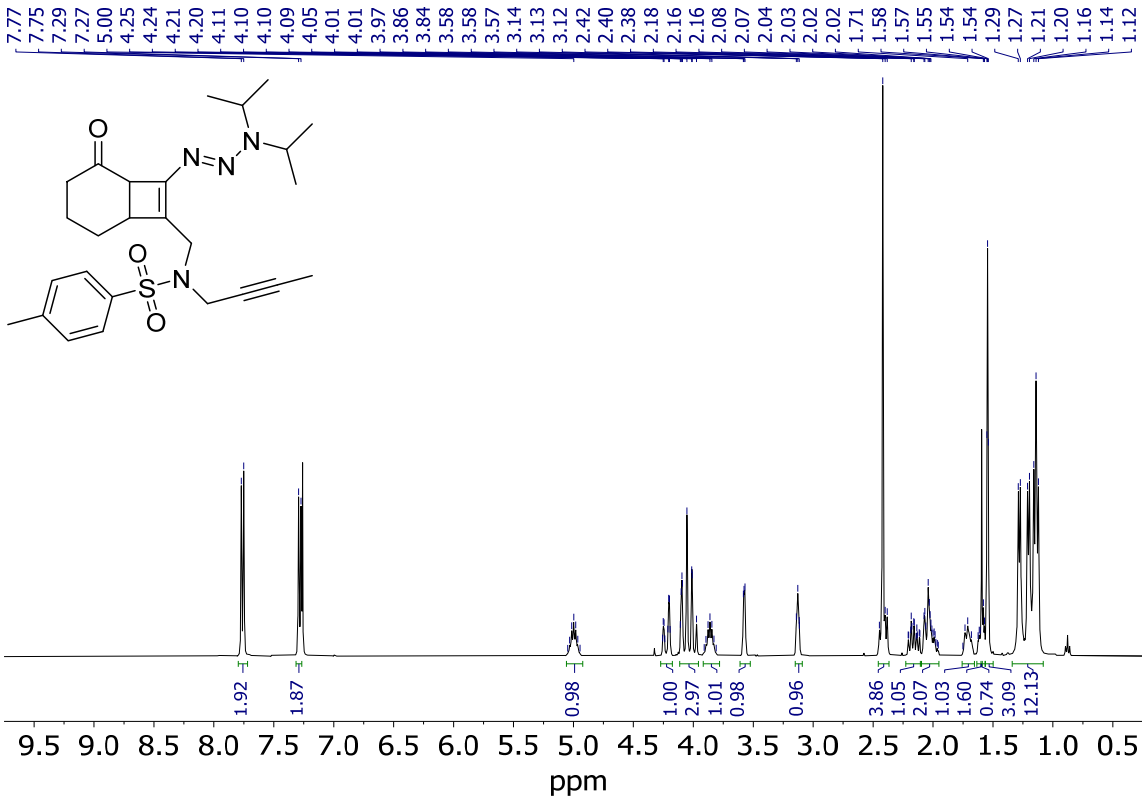
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2f**.



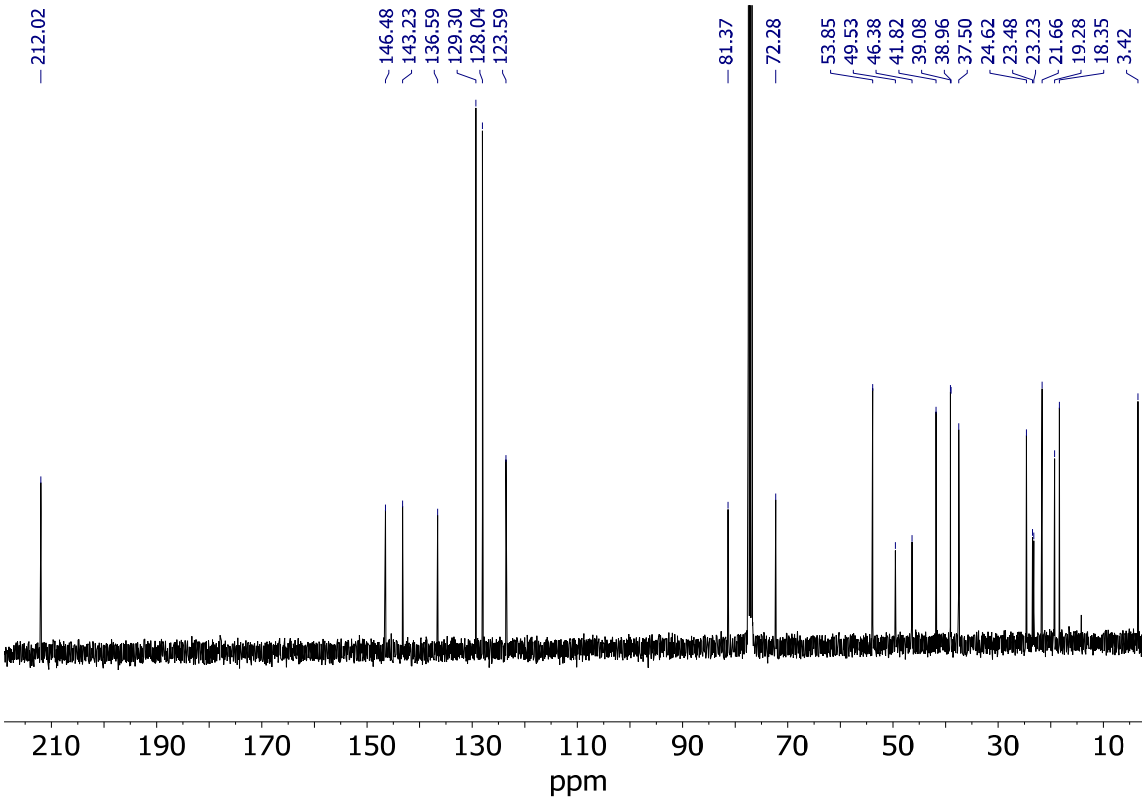
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2g**.



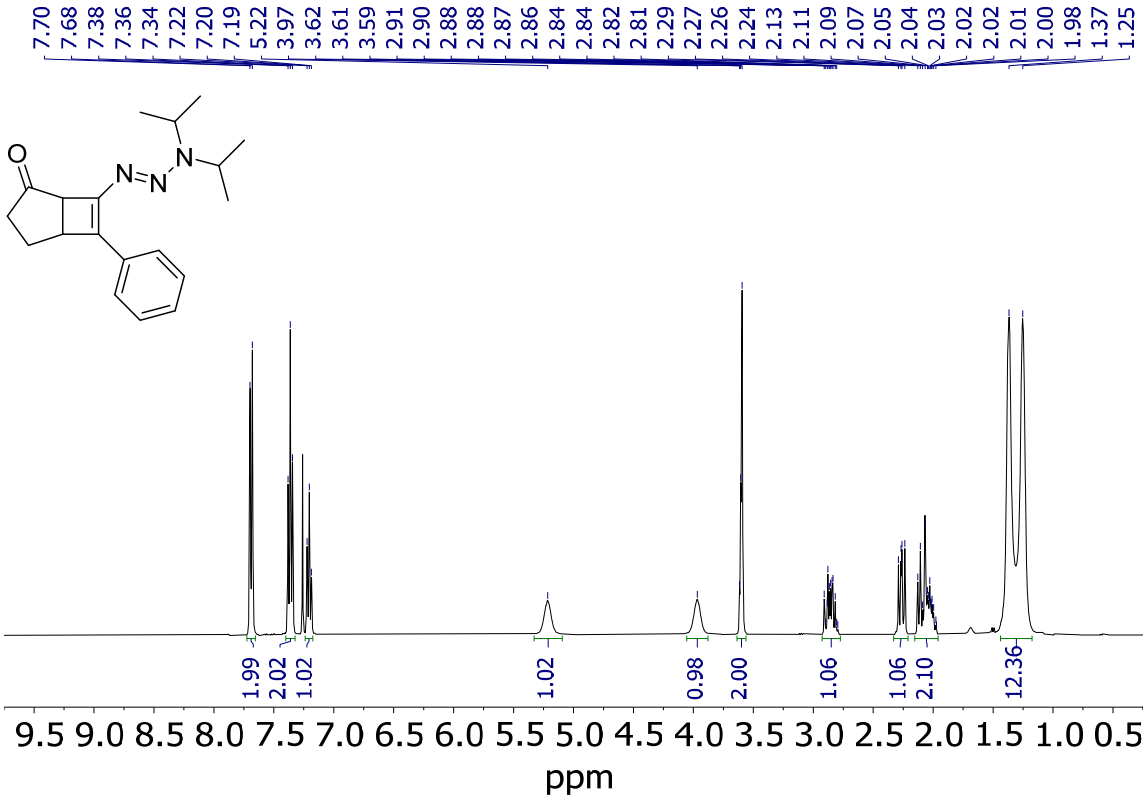
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2g**.



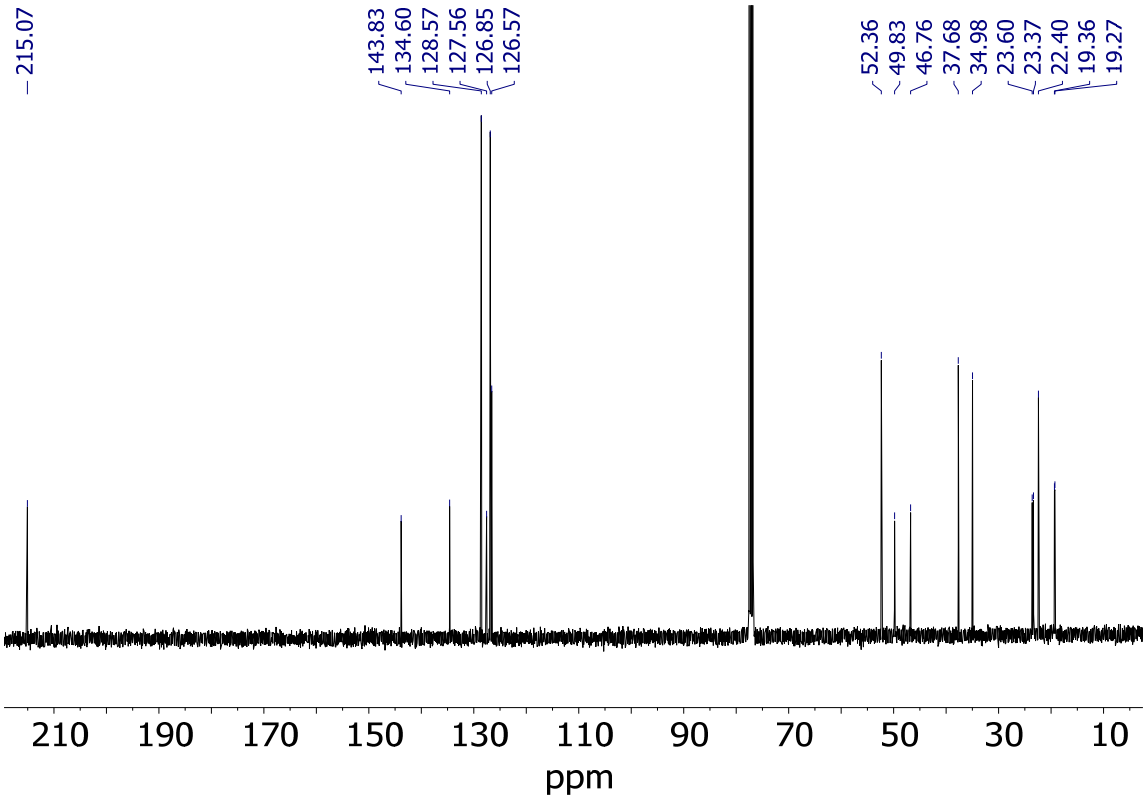
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2h**.



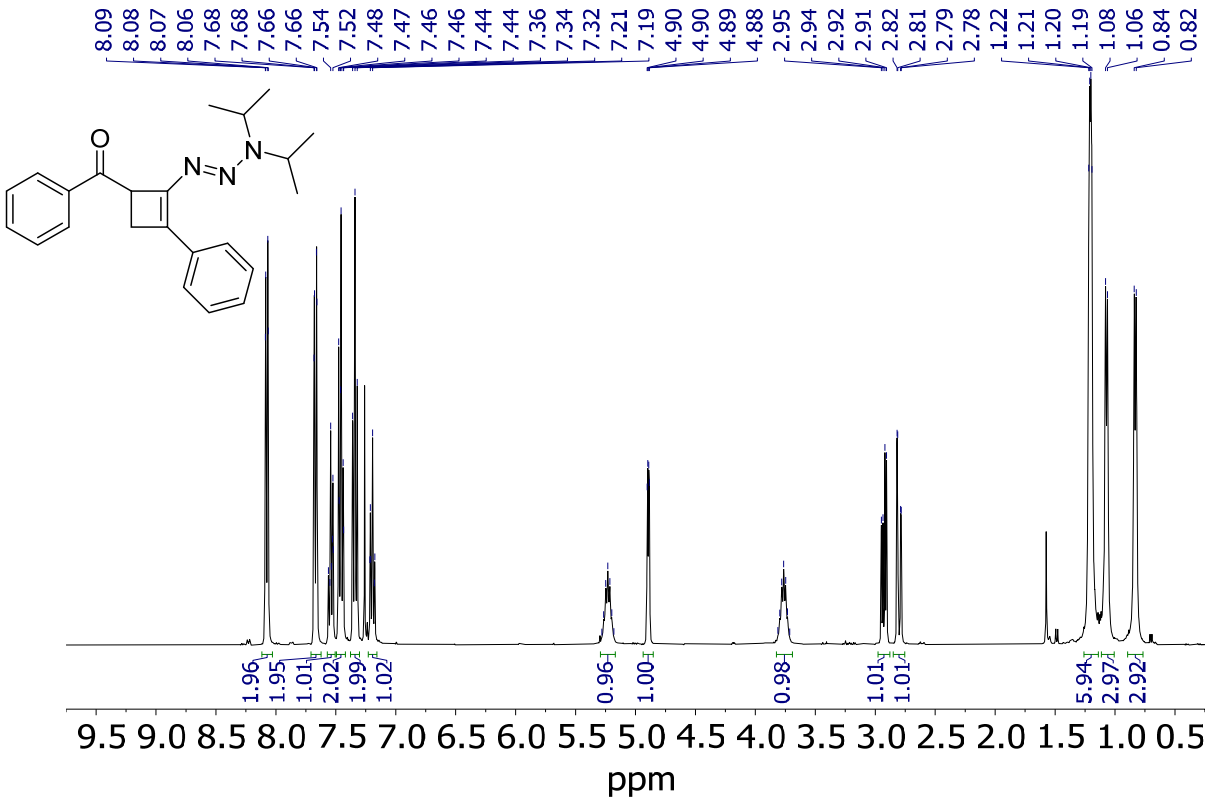
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2h**.



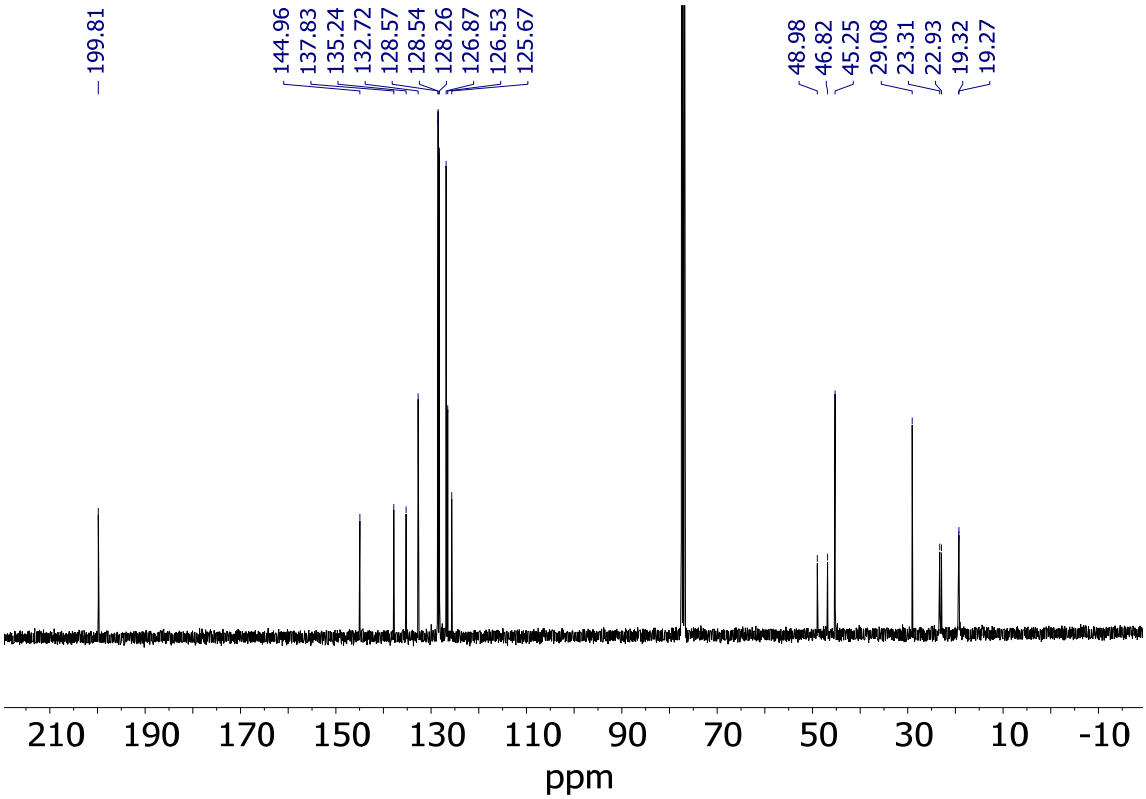
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2i**.



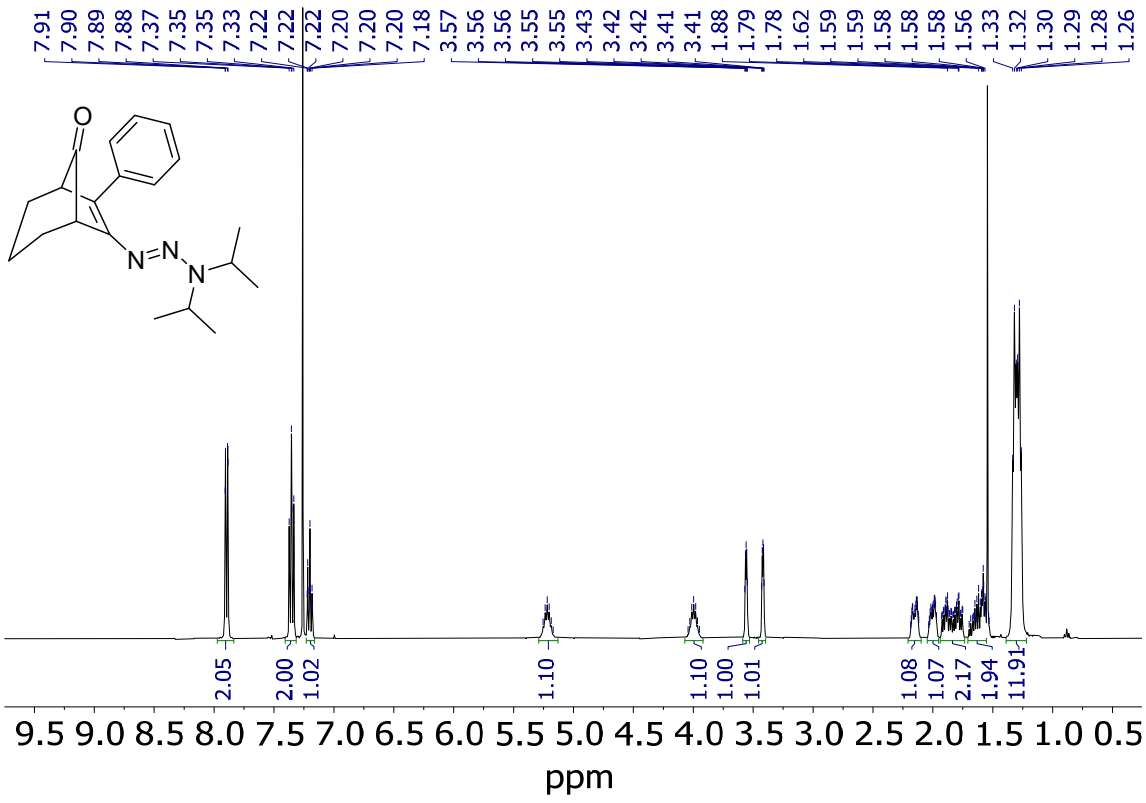
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2i**.



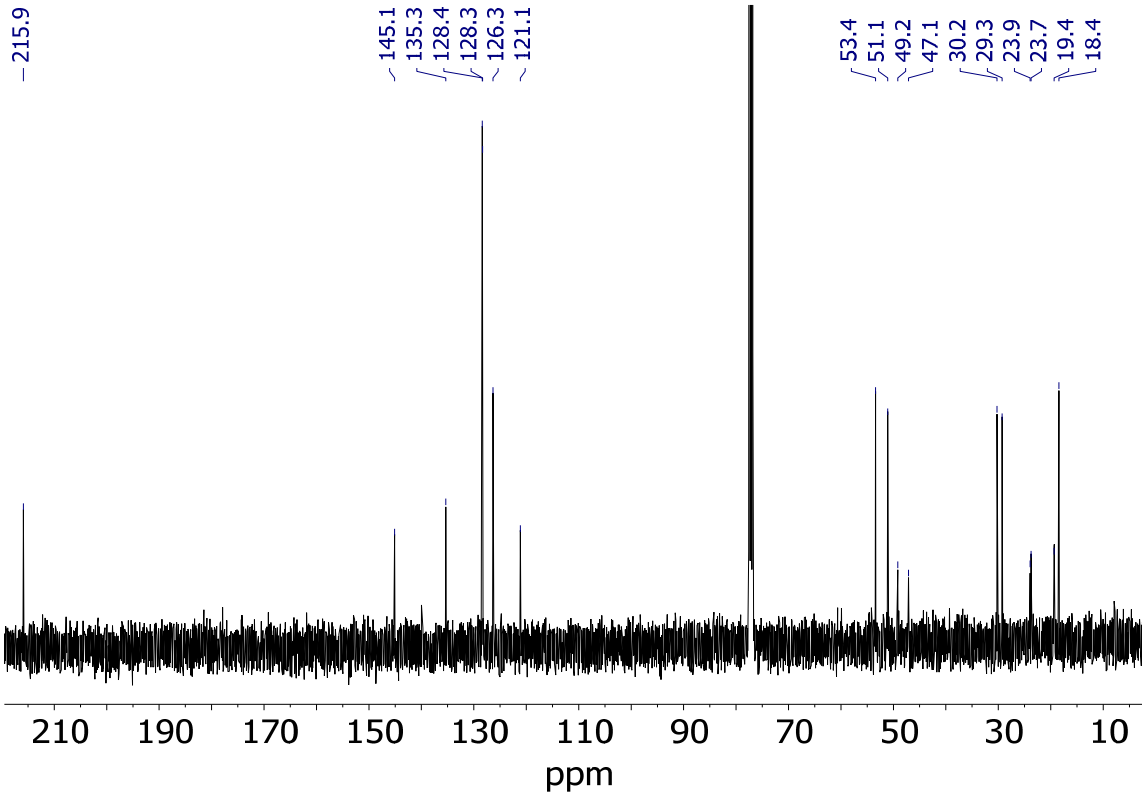
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **2j**.



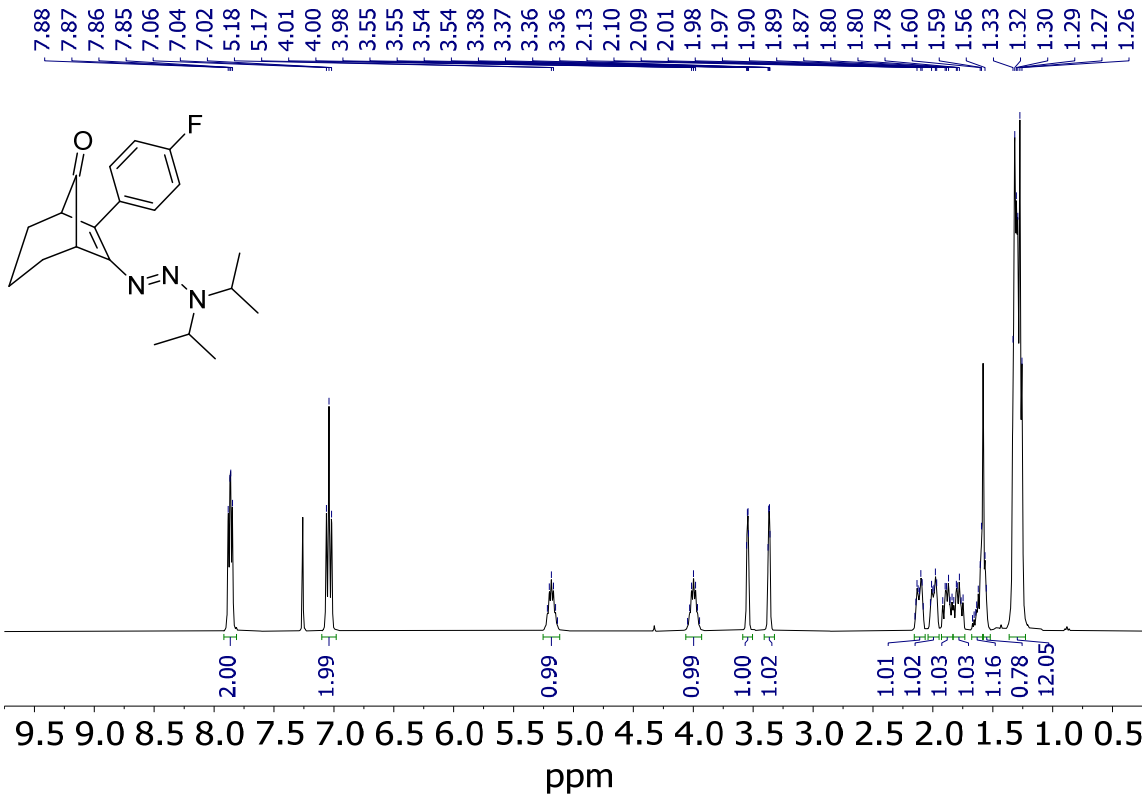
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **2j**.



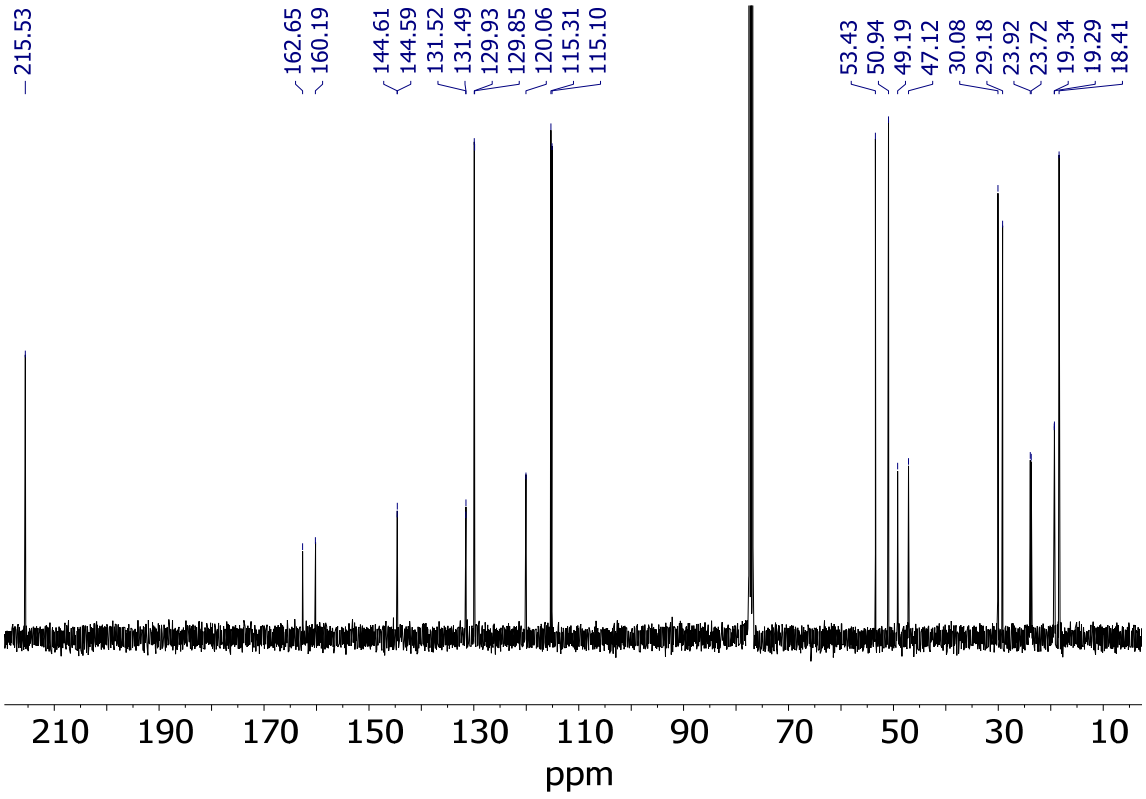
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**.



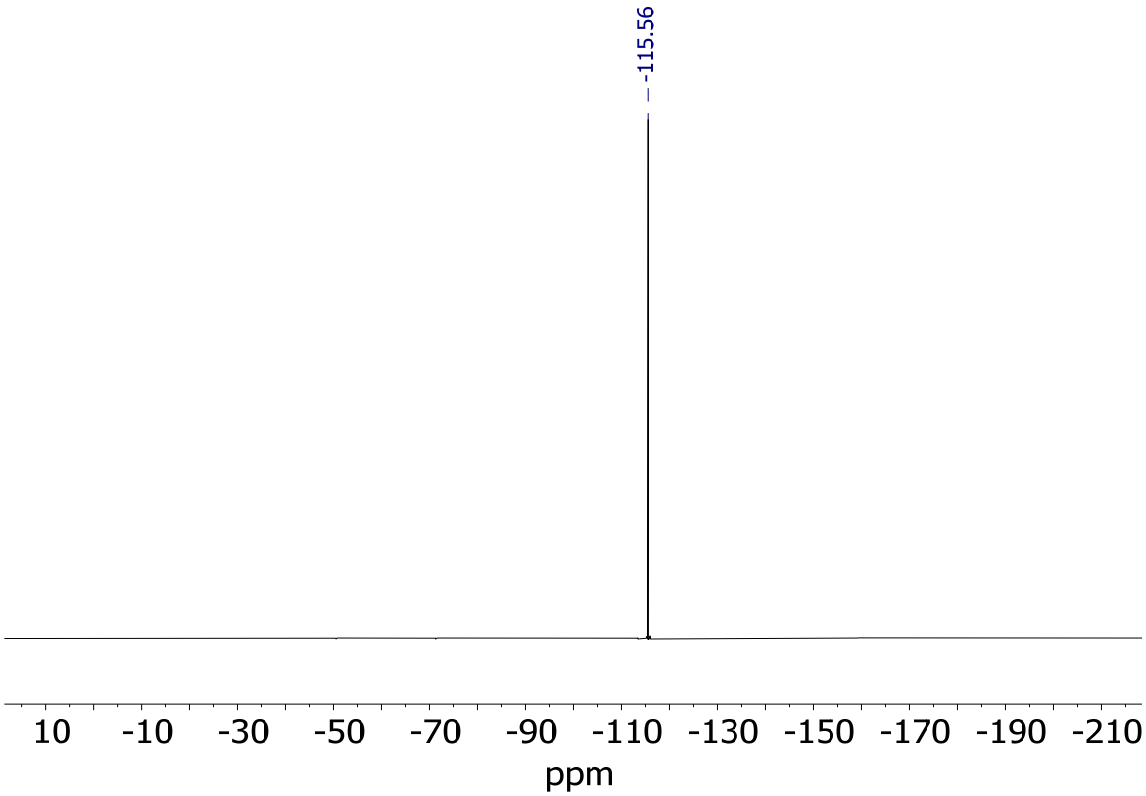
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **3a**.



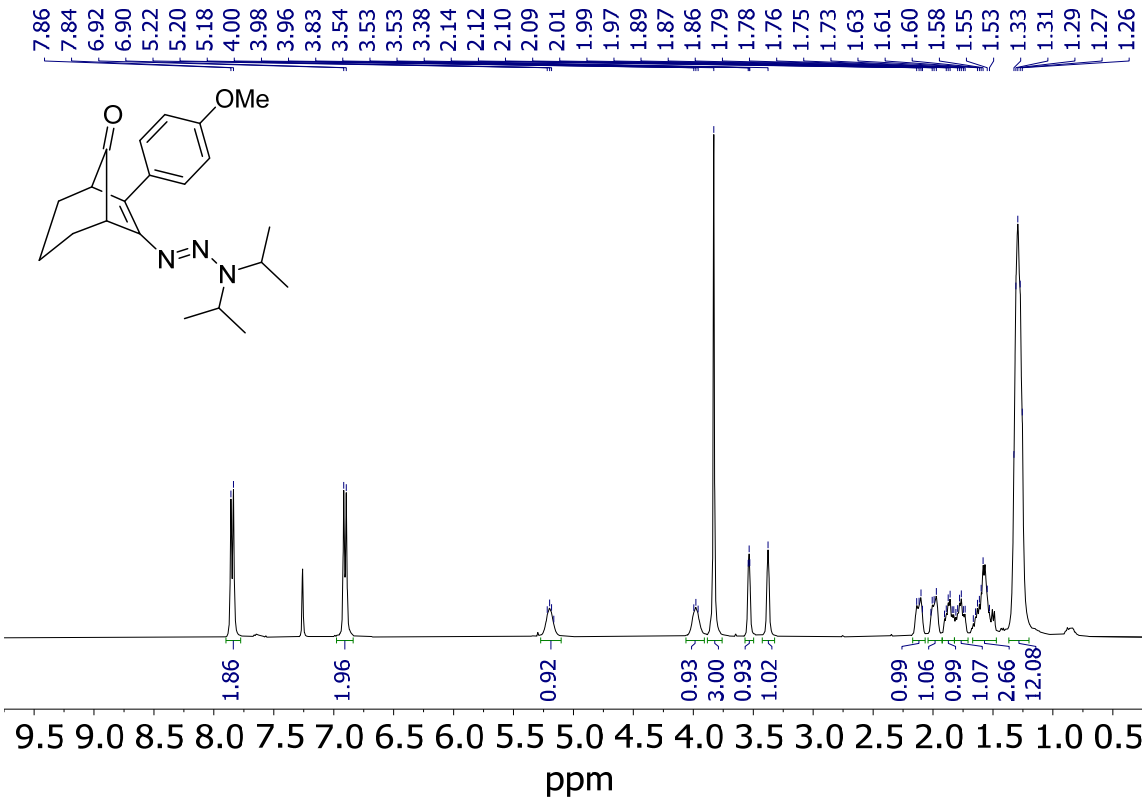
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3b**.



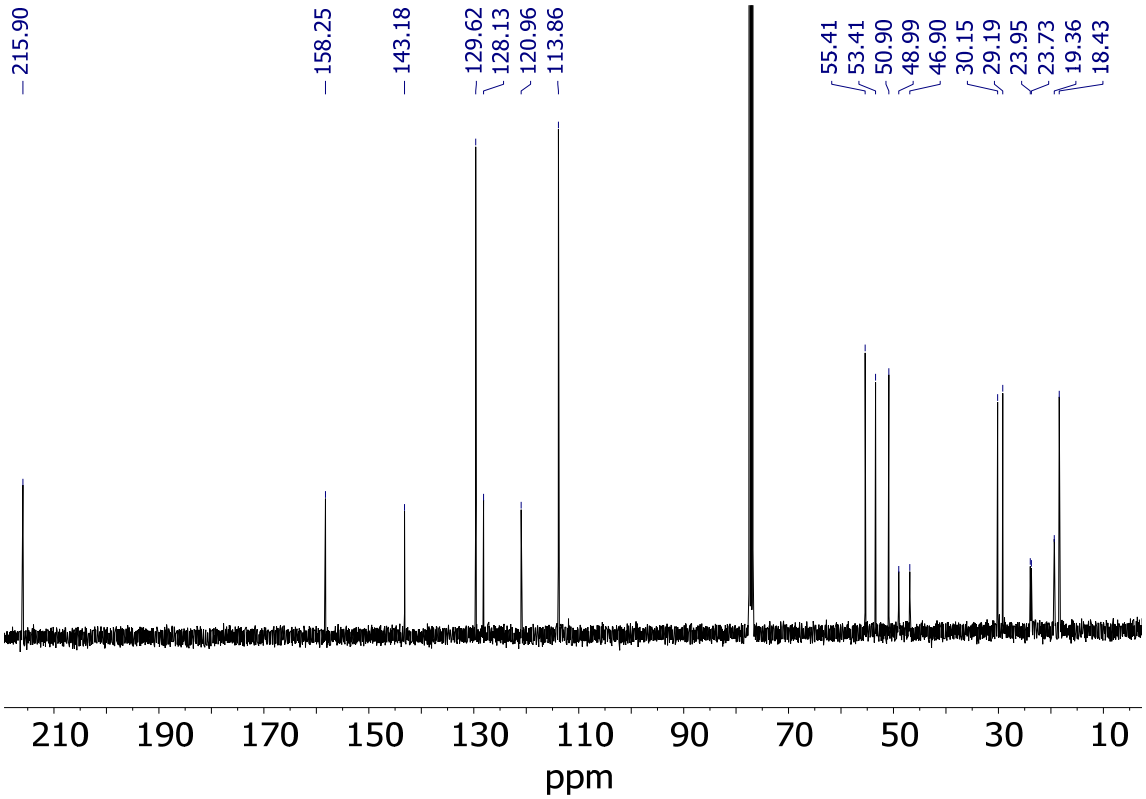
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **3b**.



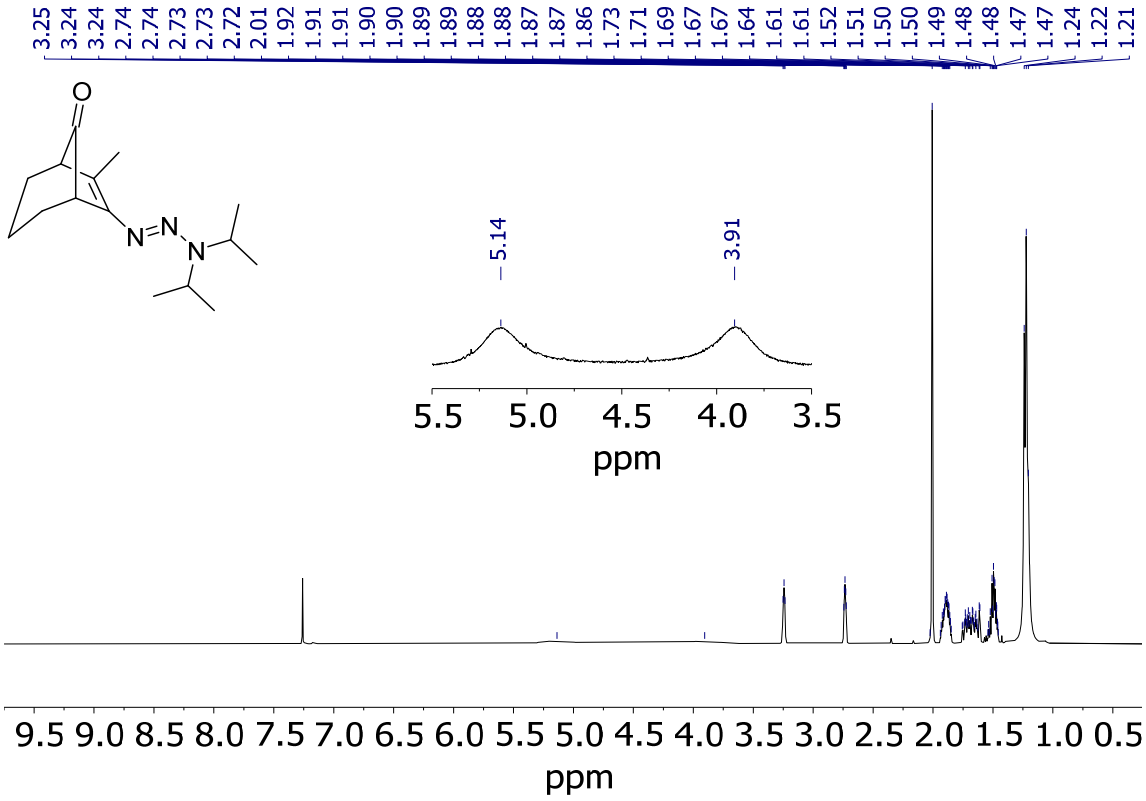
^{19}F NMR spectrum (377 MHz, $CDCl_3$) of compound **3b**.



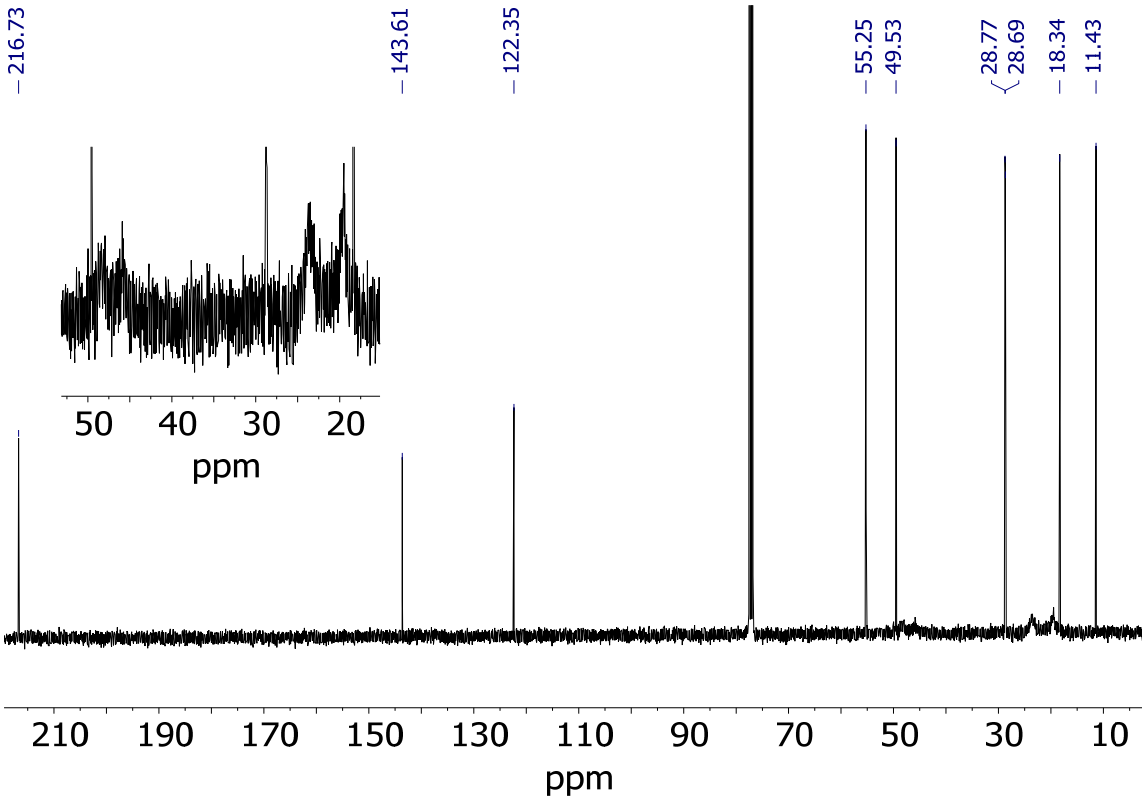
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3c**.



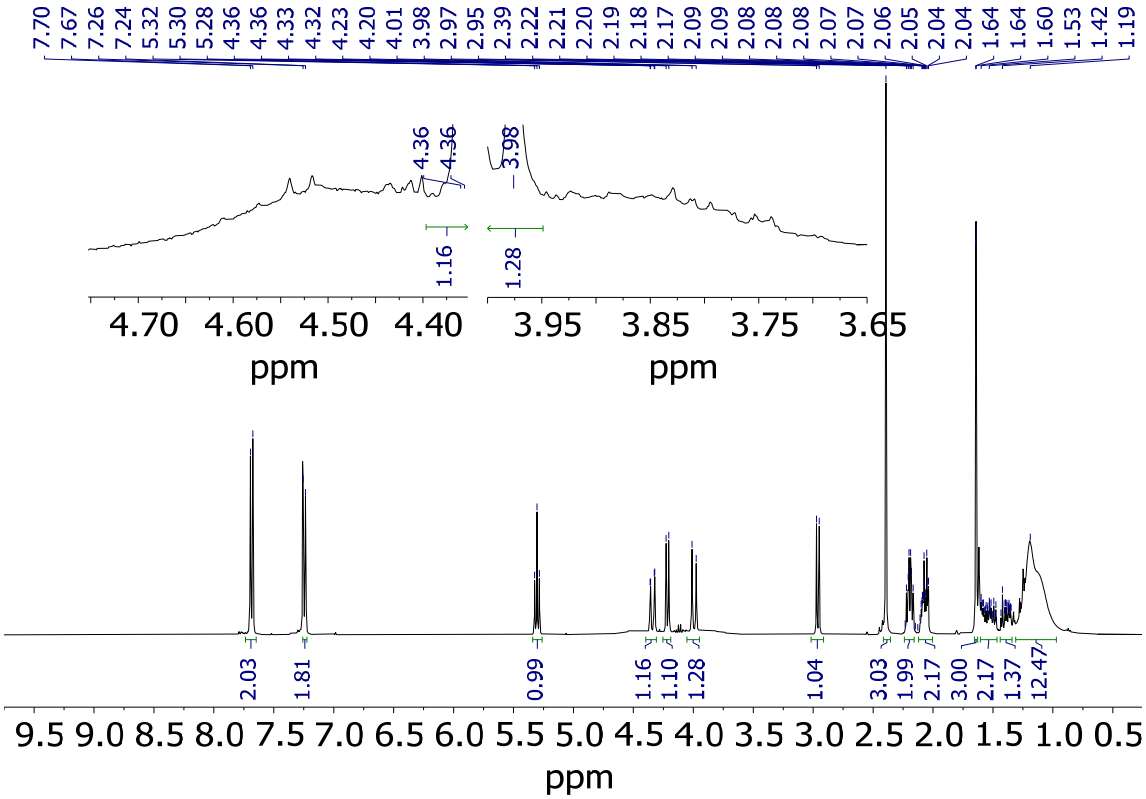
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **3c**.



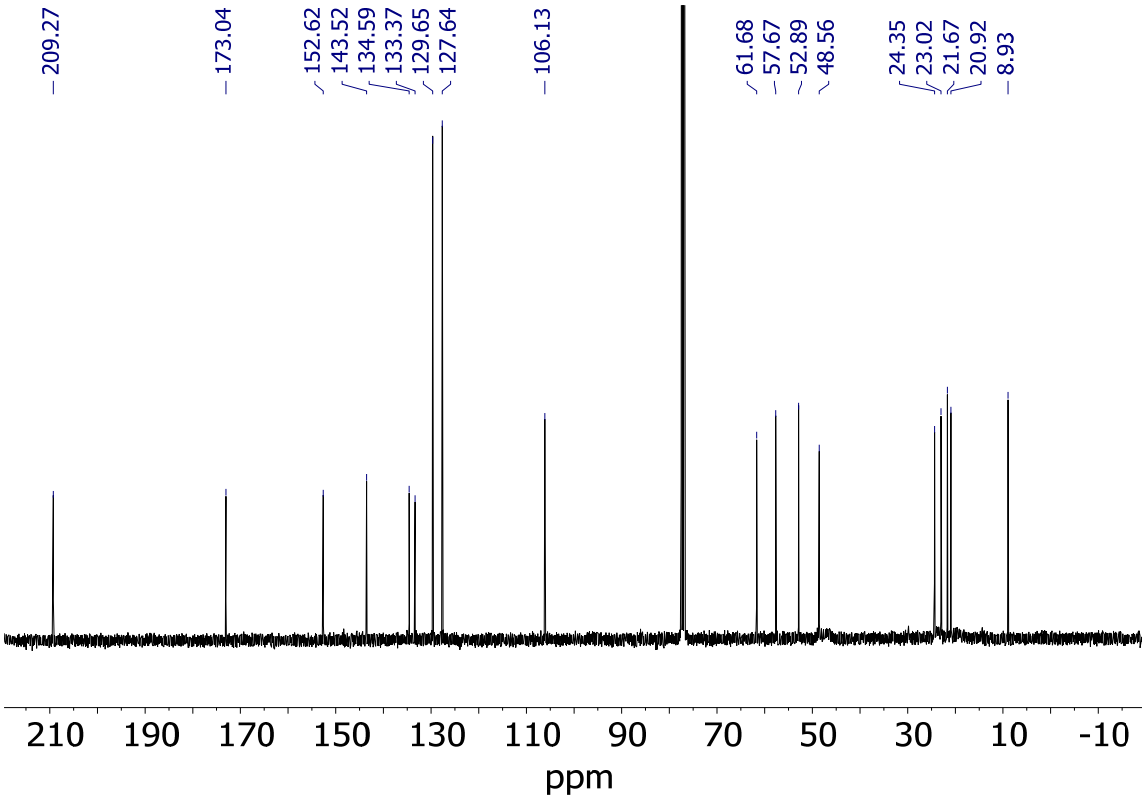
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**.



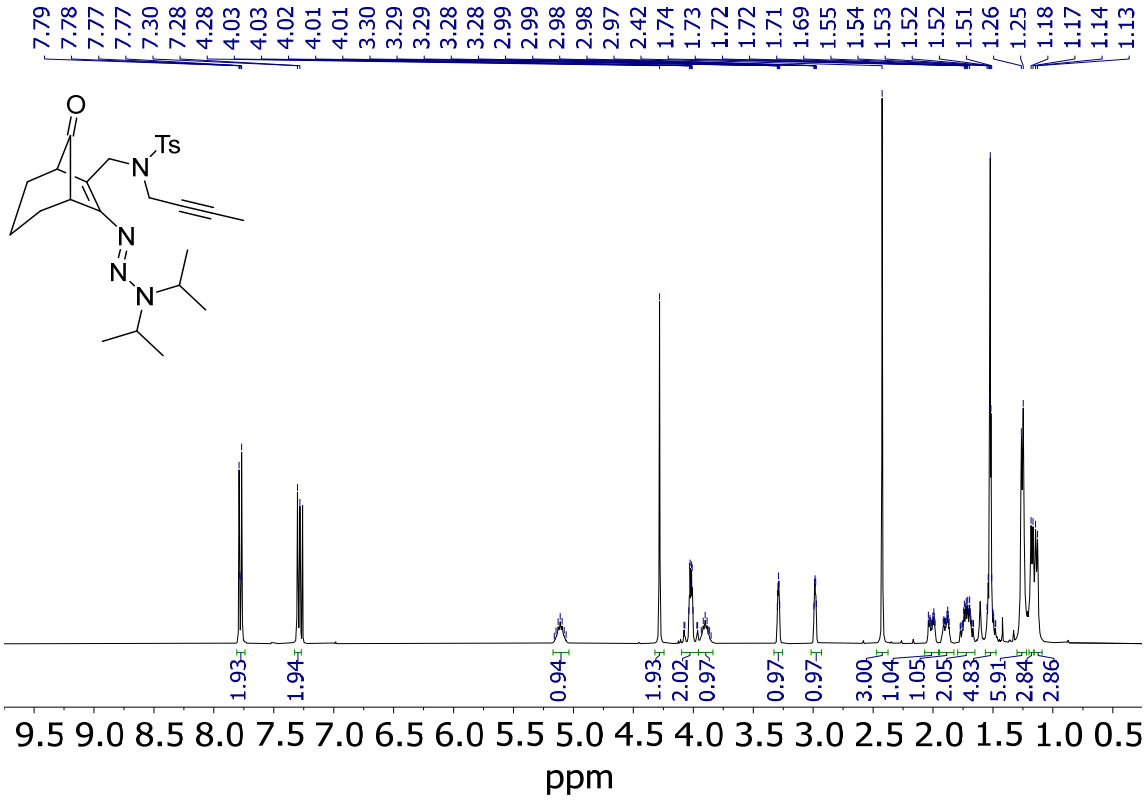
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **3d**.



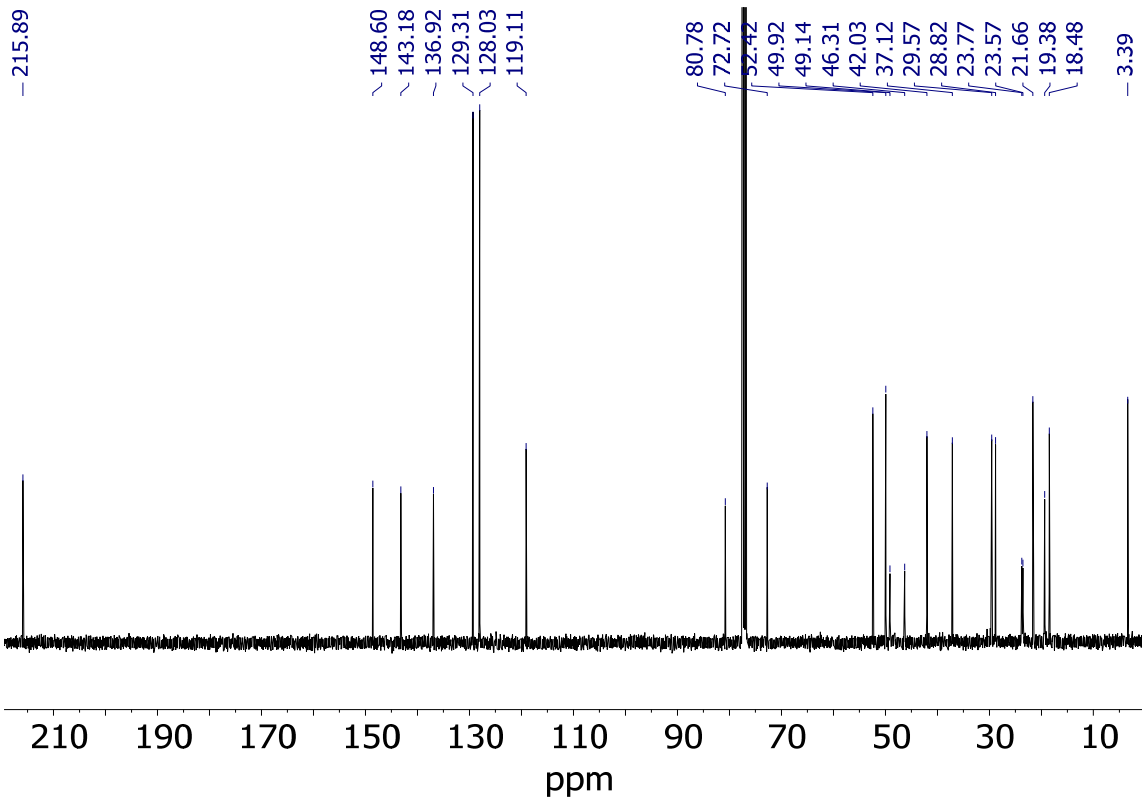
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.



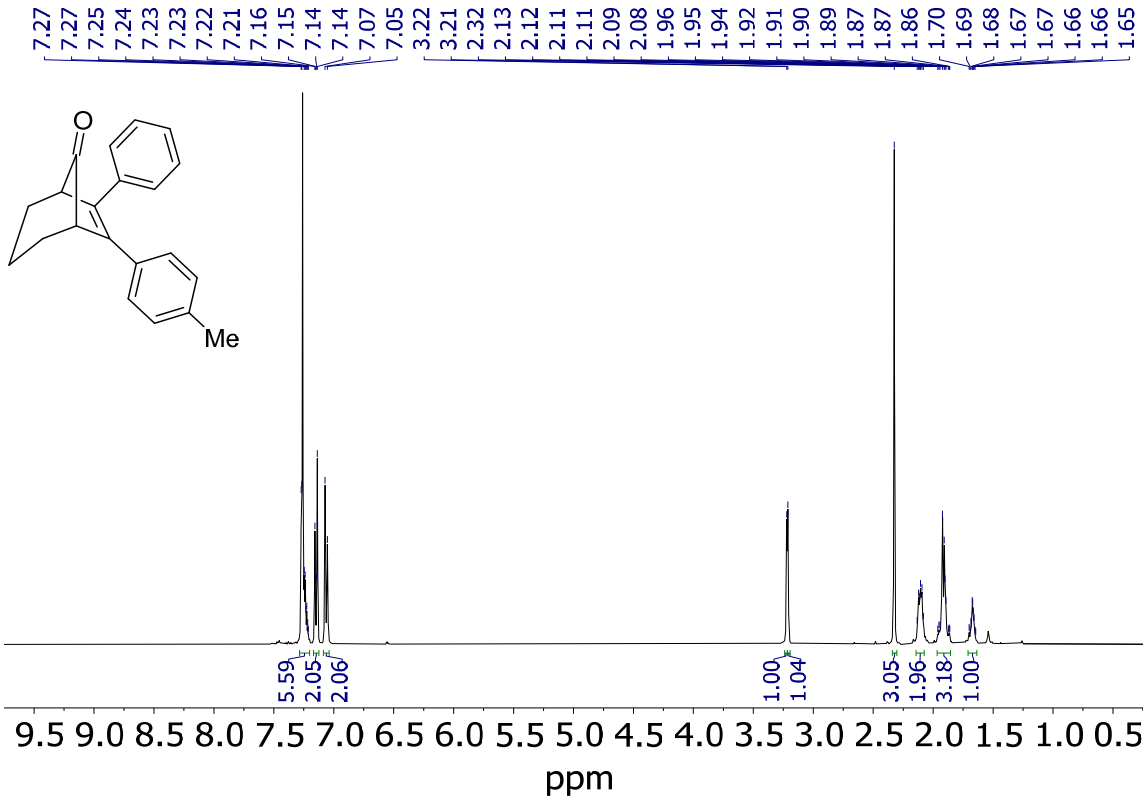
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4**.



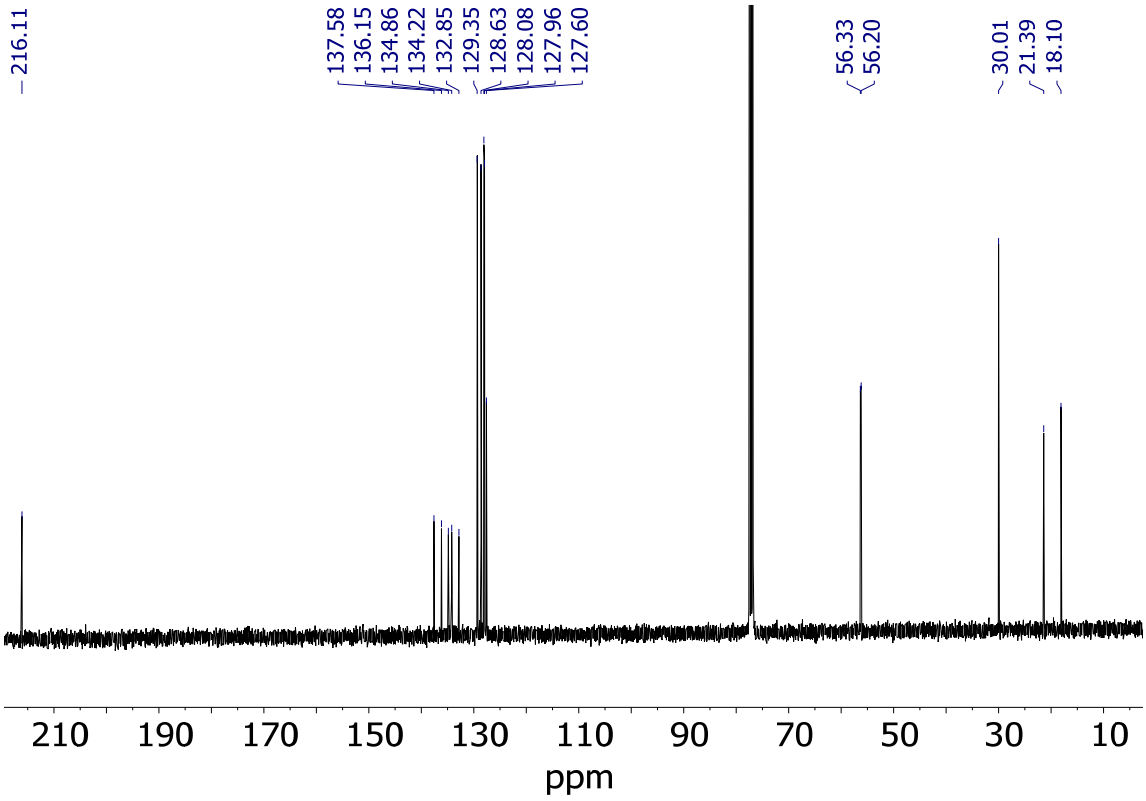
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3e**.



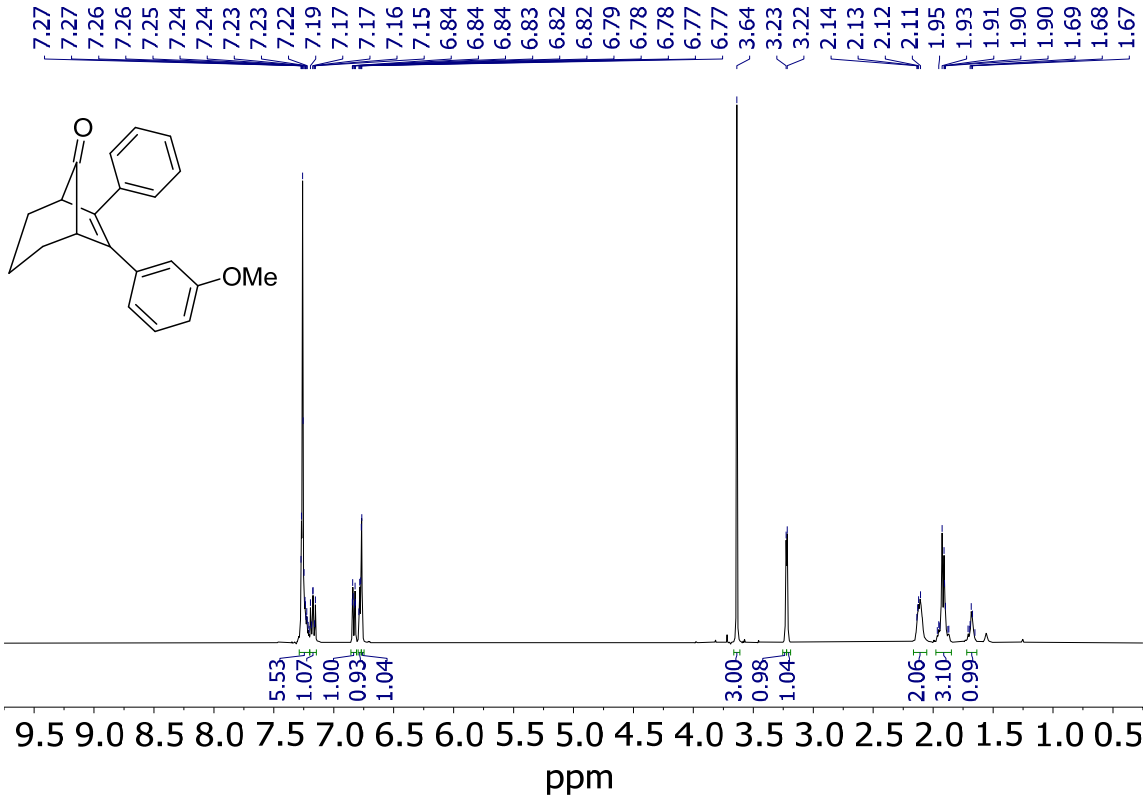
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **3e**.



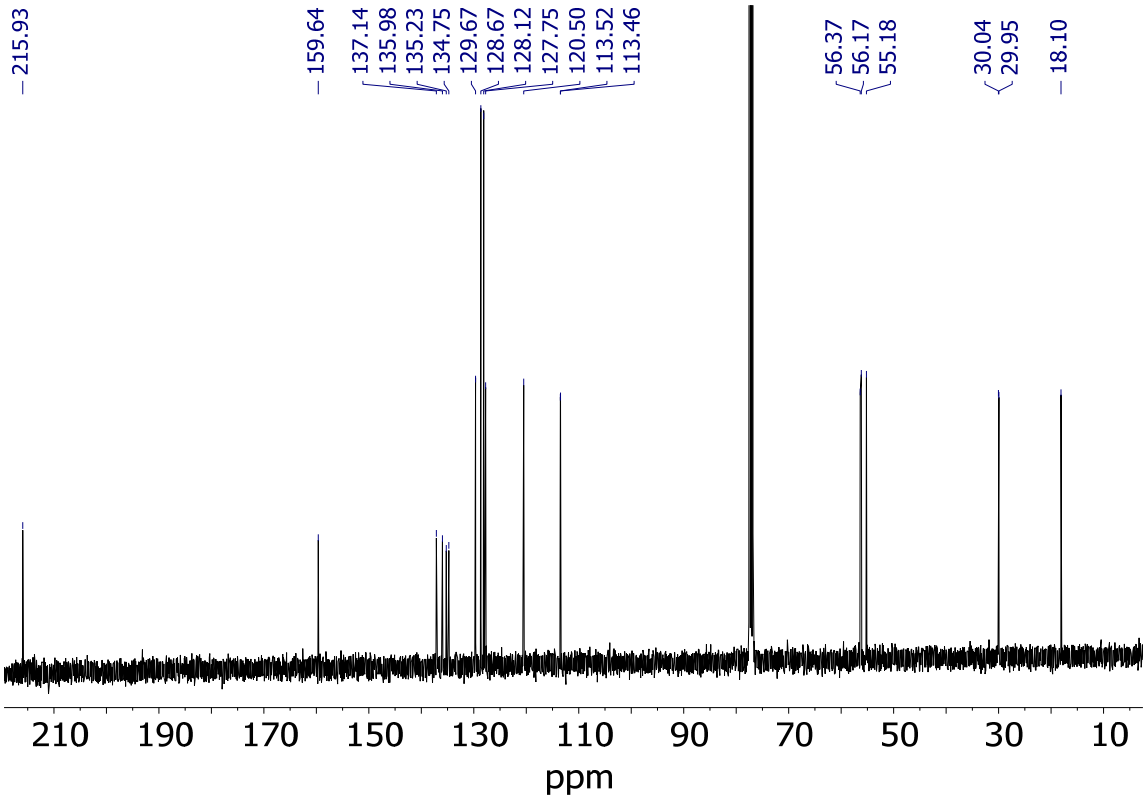
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5a1**.



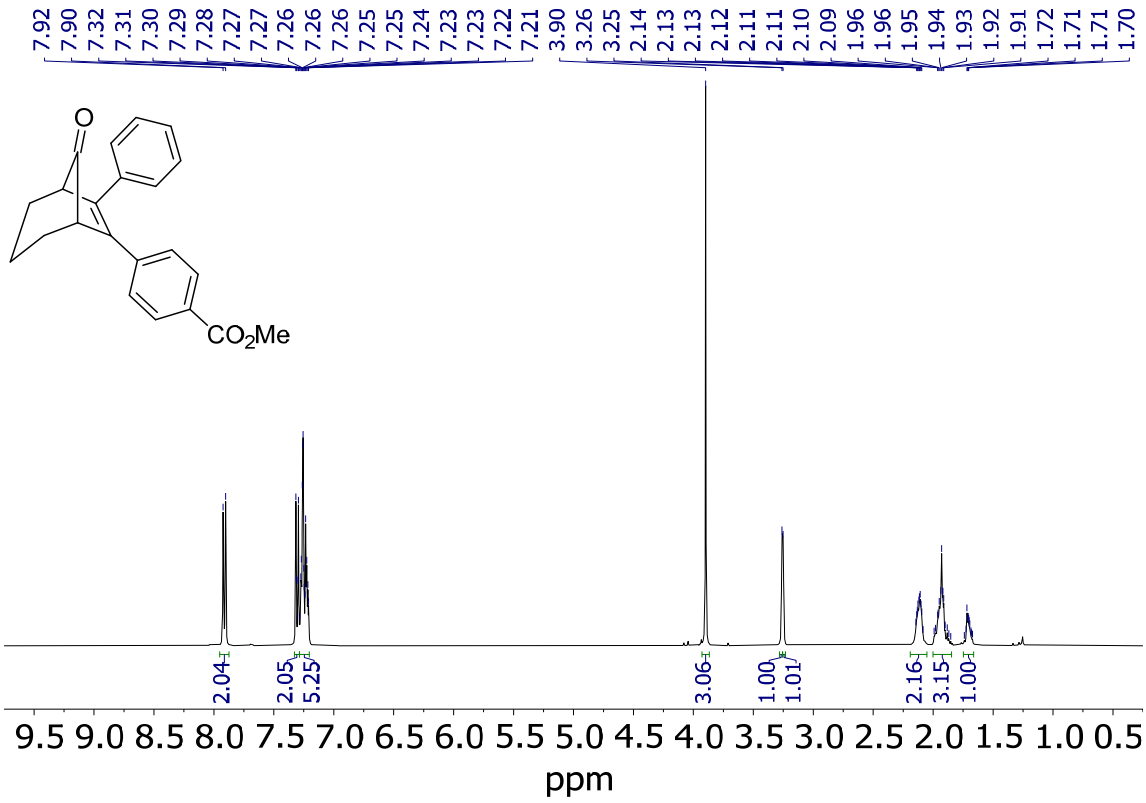
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **5a**.



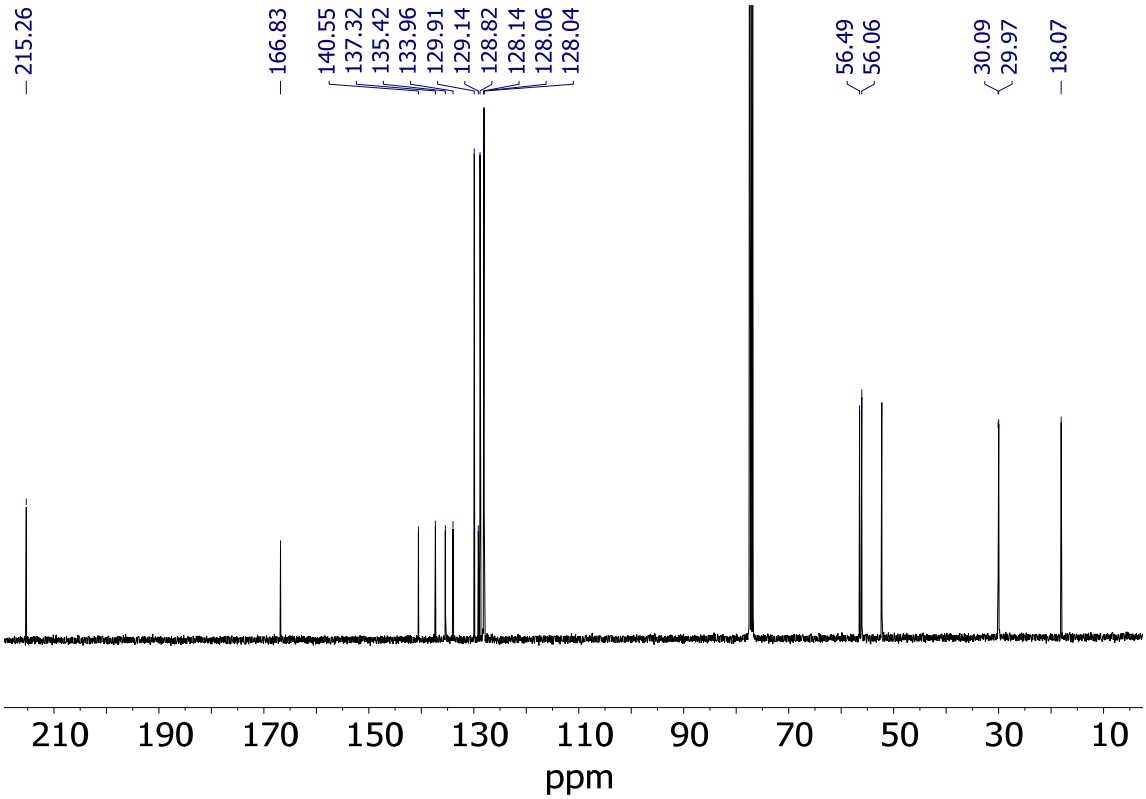
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5b**.



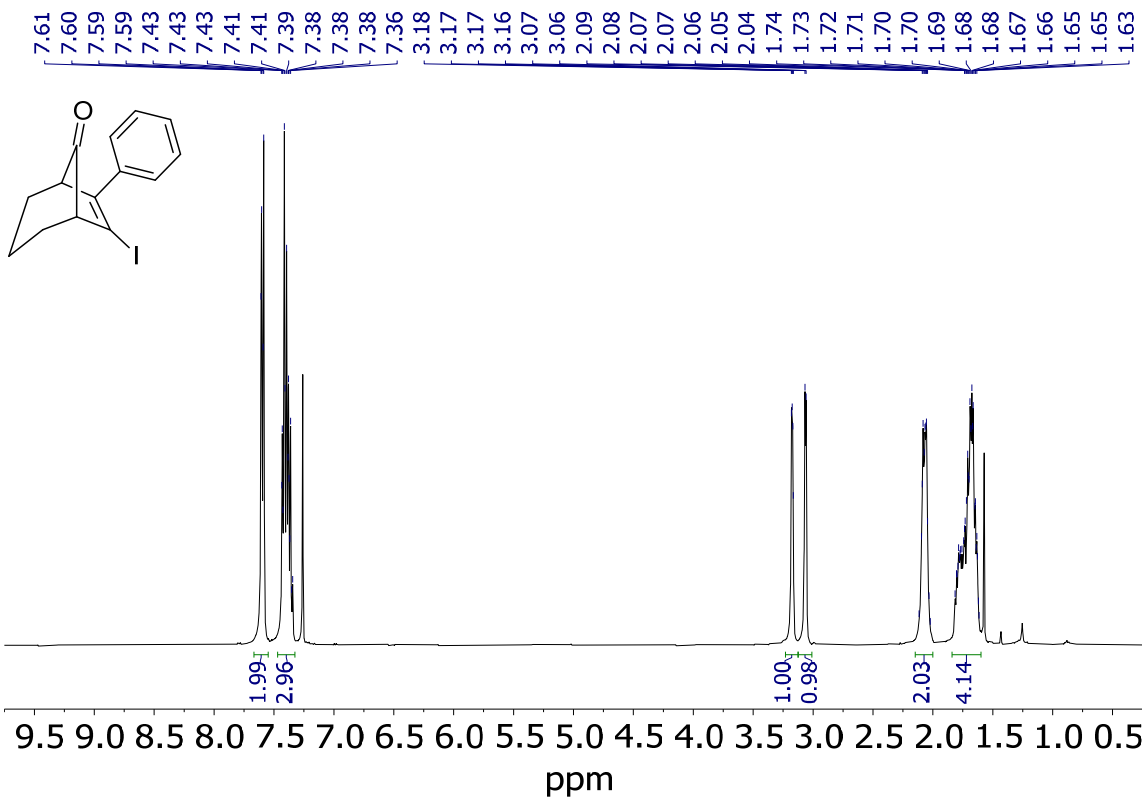
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **5b**.



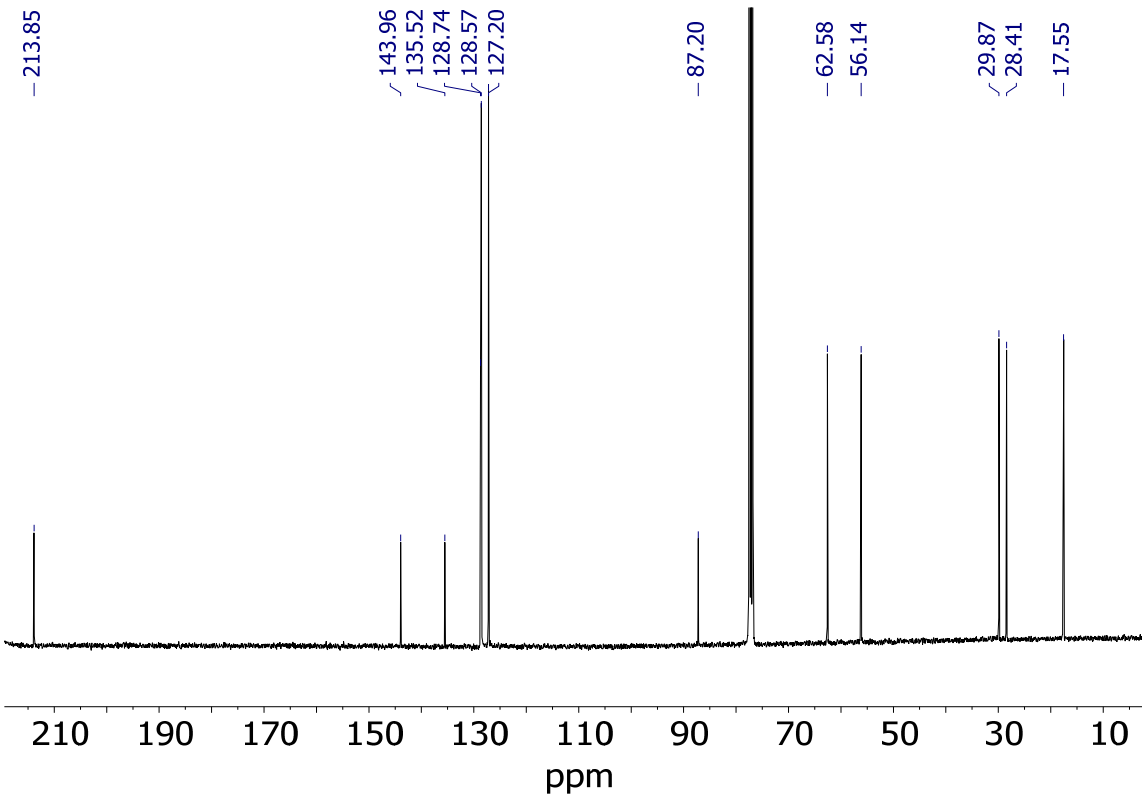
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5c**.



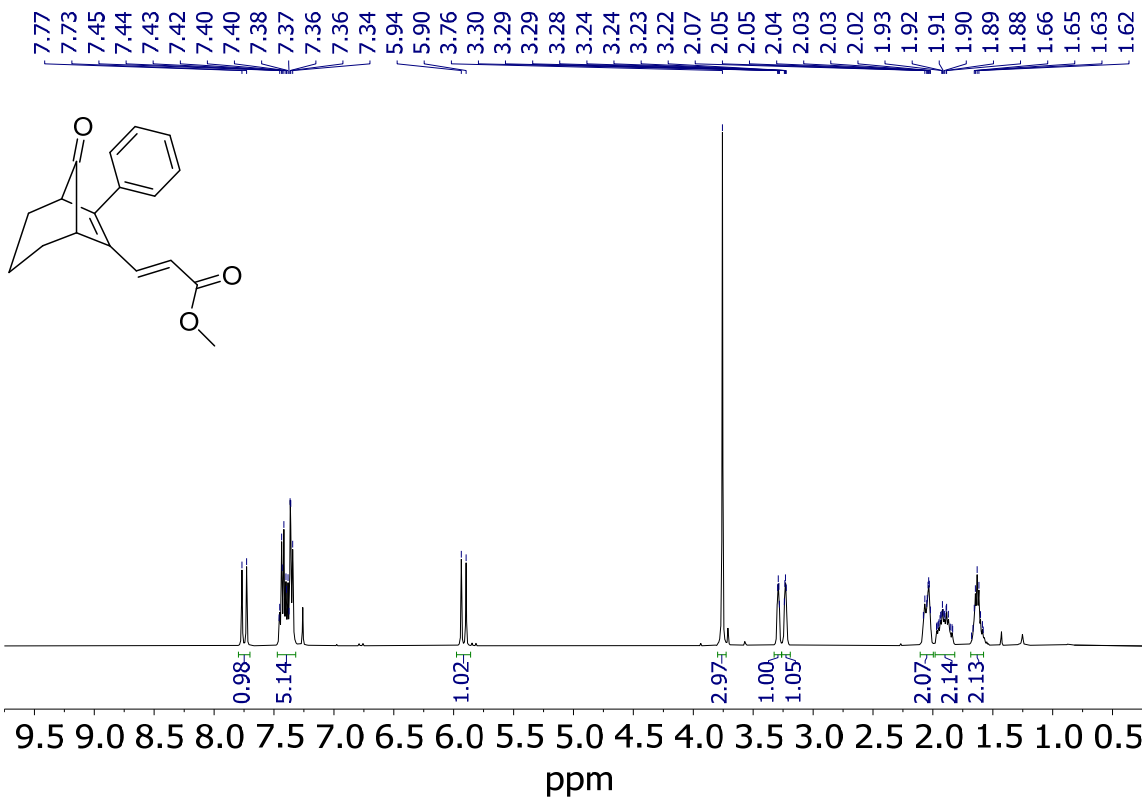
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **5c**.



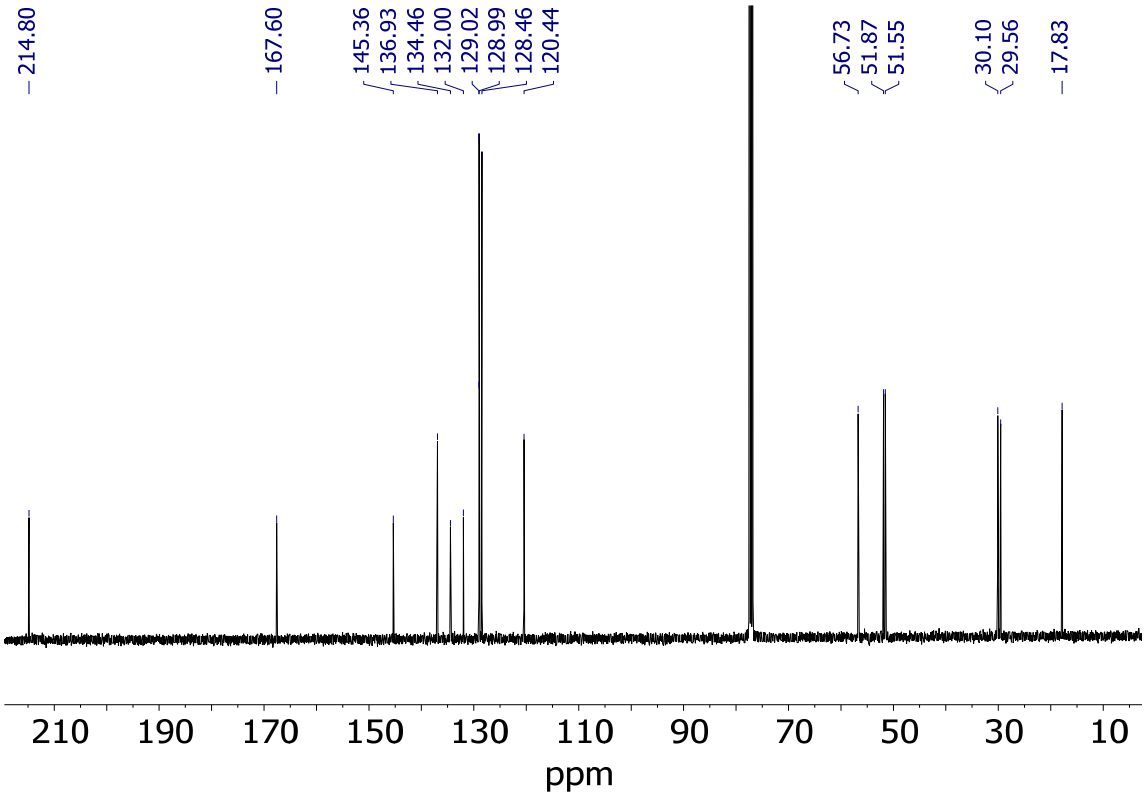
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**.



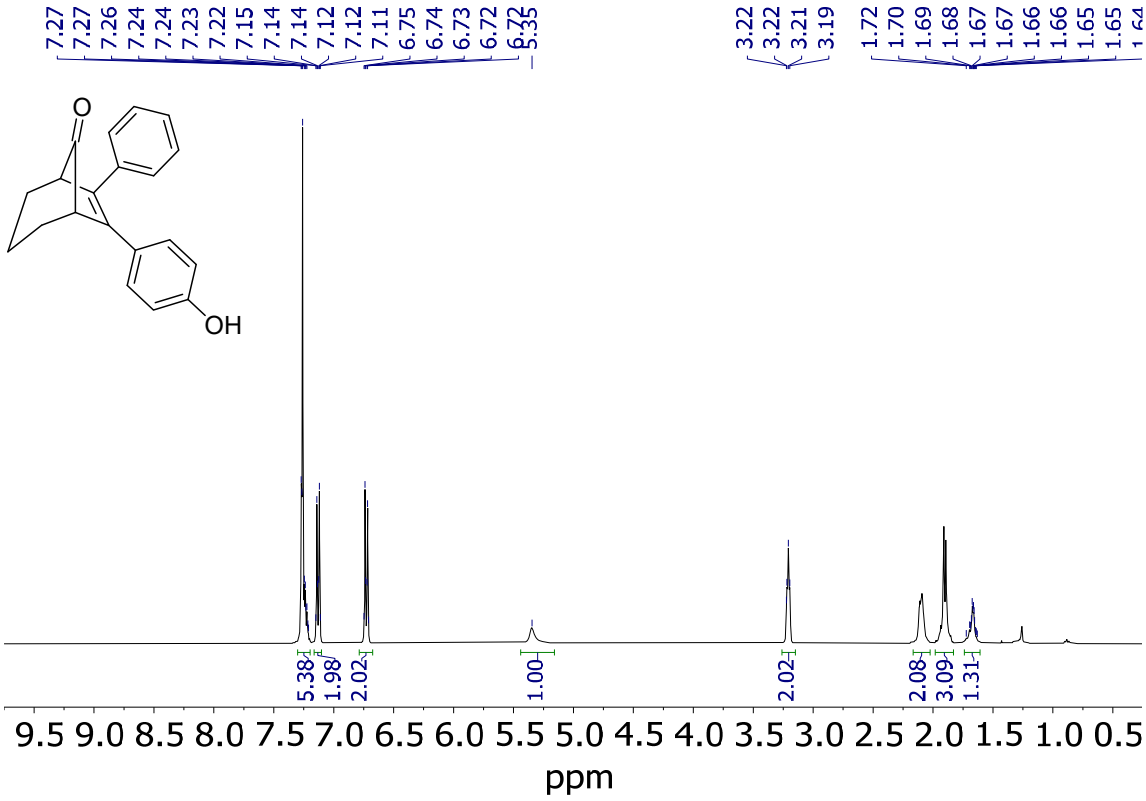
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6**.



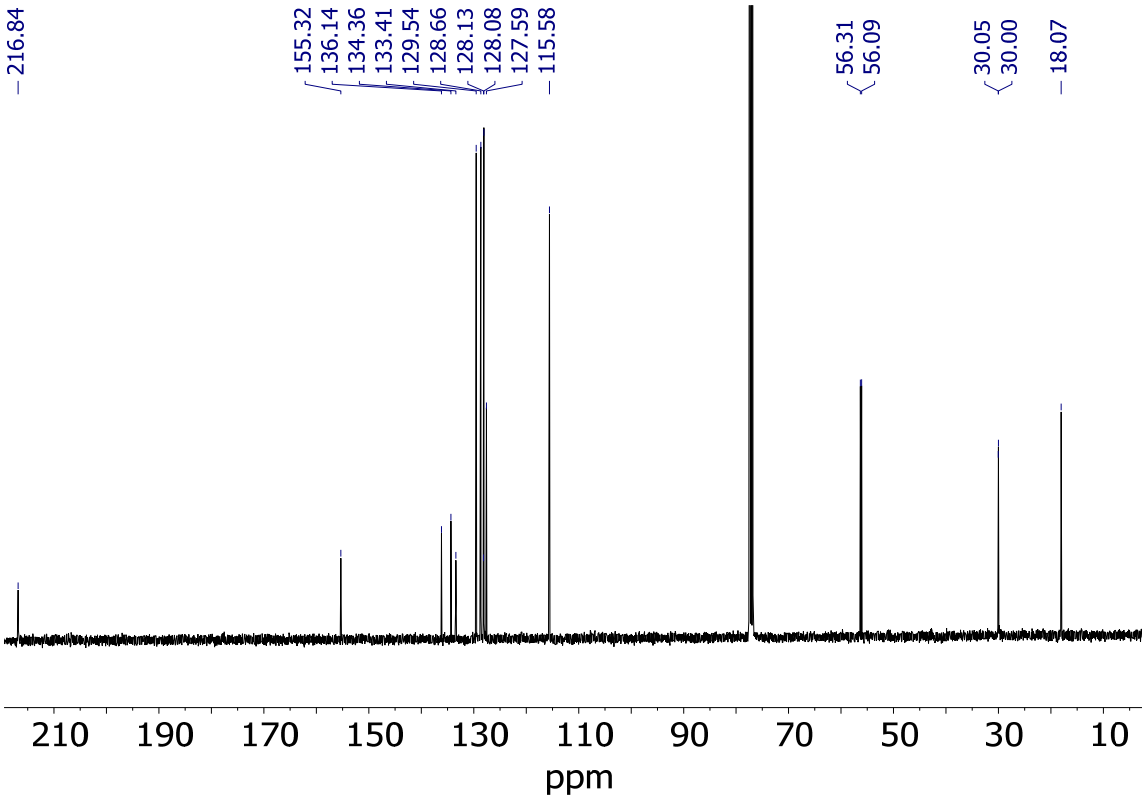
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**.



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **7**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**.



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **8**.

X-Ray Crystallography

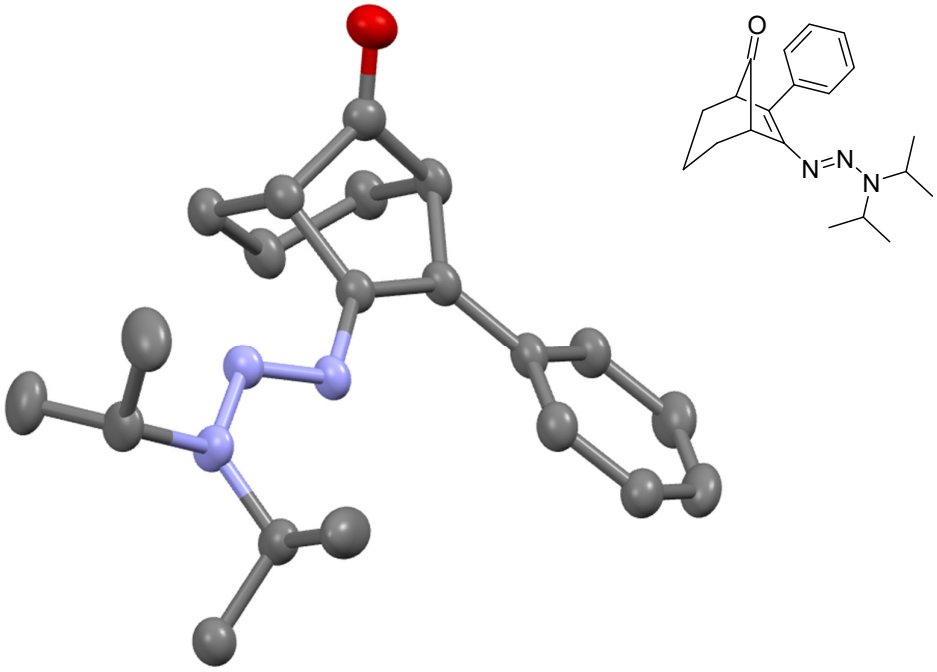
Bragg-intensities of **3a** and **4** were collected at low temperature (See Table S1) using Cu*K*α radiation (*λ* = 1.54184 Å) on a Rigaku SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis*^{Pro}.[10]

The solutions and refinements of the structures were performed by the latest available version of ShelXT[11] and *ShelXL*.[12] and by using Olex2[13] as the graphical interface. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the riding model.

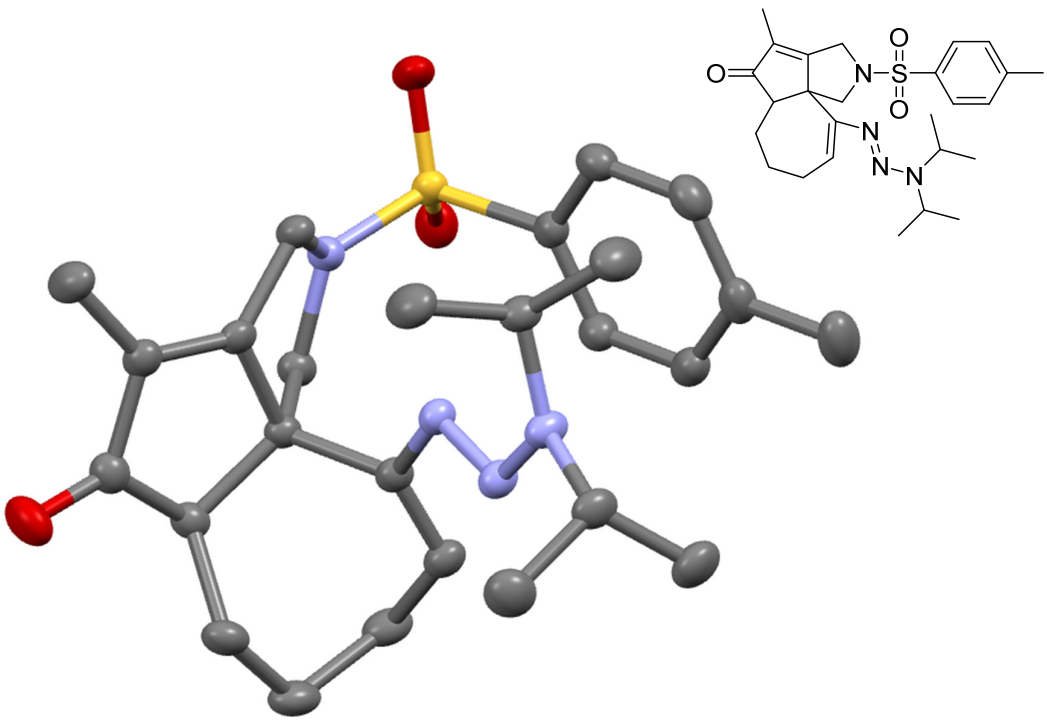
Crystallographic and refinement data are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and correspond to the following codes: **3a** (2101091), **4** (2101092). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1: X-Ray Crystallographic Data for compounds 3a and 4.

Compound	**3a**	**4**
Formula	$C_{20}H_{27}N_3O$	$C_{26}H_{36}N_4O_3S$
$D_{calc.}$/ g cm^{-3}	1.171	1.261
μ/mm^{-1}	0.572	1.400
Formula Weight	325.44	484.65
Colour	clear pale colourless	colourless
Shape	prism	plate
Size/mm^3	0.46×0.17×0.12	0.26×0.18×0.03
T/K	140.15	140.00(10)
Crystal System	triclinic	monoclinic
Space Group	$P\bar{1}$	$P2_1/c$
a/Å	10.9301(7)	7.80574(8)
b/Å	12.0124(11)	34.1537(3)
c/Å	16.8138(12)	9.62710(9)
α/°	69.946(8)	90
β/°	72.758(6)	95.7493(9)
γ/°	64.698(8)	90
V/Å^3	1845.4(3)	2553.62(4)
Z	4	4
Z'	2	1
Wavelength/Å	1.54184	1.54184
Radiation type	Cu$K\alpha$	Cu$K\alpha$
Θ_{min}/°	2.842	4.795
Θ_{max}/°	72.866	72.655
Measured Refl's.	7640	20995
Indep't Refl's	7640	5004
Refl's I≥2σ(I)	6257	4698
R_{int}	n/a	0.0222
Parameters	442	314
Restraints	0	0
Largest Peak/e Å^{-3}	0.512	0.303
Deepest Hole/e Å^{-3}	-0.406	-0.348
GooF	1.048	1.022
wR_2 (all data)	0.2503	0.0816
wR_2	0.2450	0.0799
R_1 (all data)	0.0883	0.0330
R_1	0.0810	0.0310
CCDC number	2101091	2101092



Molecular structure of compound **3a** determined by X-ray diffraction. Ellipsoids are set at a 50% probability level. Color-coding: C: grey, N: blue, O: red. Hydrogen atoms and second molecule in the unit cell are omitted for clarity.



Molecular structure of compound **4** determined by X-ray diffraction. Ellipsoids are set at a 50% probability level. Color-coding: C: grey, N: blue, O: red, S: yellow. Hydrogen atoms are omitted for clarity.

References

1 G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti and K. Severin, *Angew. Chem. Int. Ed.*, 2015, **54**, 302–305.
2 S. V. Ley, P. J. Murray and B. D. Palmer, *Tetrahedron*, 1985, **41**, 4765–4769.
3 S. Chanthamath, S. Takaki, K. Shibatomi and S. Iwasa, *Angew. Chem. Int. Ed.*, 2013, **52**, 5818–5821.
4 T. Yao, X. Zhang and R. C. Larock, *J. Am. Chem. Soc.*, 2004, **126**, 11164–11165.
5 X.-N. Wang, E. H. Krenske, R. C. Johnston, K. N. Houk and R. P. Hsung, *J. Am. Chem. Soc.*, 2015, **137**, 5596–5601.
6 T. Saeki, E.-C. Son and K. Tamao, *Org. Lett.*, 2004, **6**, 617–619.
7 Z. Wu and J. S. Moore, *Tetrahedron Lett.*, 1994, **35**, 5539–5542.
8 M. Shi, L.-P. Liu and J. Tang, *J. Org. Chem.*, 2005, **70**, 10420–10425.
9 S. Archana, R. Geesala, N. B. Rao, S. Satpati, G. Puroshottam, A. Panasa, A. Dixit, A. Das and A. K. Srivastava, *Bioorg. Med. Chem. Lett.*, 2015, **25**, 680–684.
10 CrysAlis^{Pro} Software System, Rigaku Oxford Diffraction, releases V1.171.41.93a, 2020 and V1.171.41.105a, 2021.
11 G. M. Sheldrick, *Acta Cryst.*, 2015, A**71**, 3–8.
12 G. M. Sheldrick, *Acta Cryst.*, 2015, C**71**, 3–8.
13 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.