Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 139–141

Synthesis and crystal structure of the first amino-1,3a,4,6a-tetraazapentalenes

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Contents

Experimental Section

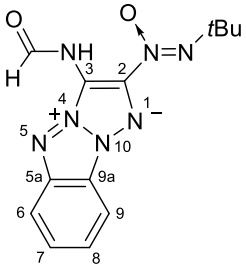
General Remarks: ^{1}H, ^{13}C and ^{14}N NMR spectra were recorded with Bruker DRX-500 (500.1, 125.8, 36.1 MHz, respectively) and Bruker AV600 (600.1, 150.9, 43.4, respectively) spectrometers. *Chemical shifts* are reported in delta (δ) *units*, parts per million (ppm) downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, negative values of δ_N correspond to upfield shifts). The IR spectra were recorded with a Bruker ALPHA-T spectrometer in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}) as pellets with KBr. High-resolution ESI mass spectra (HRMS) were recorded with a Bruker micrOTOF II instrument. Melting points were determined with a Kofler melting point apparatus and are uncorrected. Thermal behavior was studied using Mettler Toledo DSC 822e in nitrogen flow. A sample of ca. 0.5 mg was placed in closed aluminium crucibles with pierced lids and heated linearly at 10 K/min rate up to 450 °C. Silica gel 60 Merck (15–40 μm) was used for preparative thin-layer and column chromatography. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254. All reagents were purchased from Acros and Sigma-Aldrich. *Solvents were purified* before use, according to standard procedures. All other reagents were used without further purification. 4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-(2-azidophenyl)-2H-1,2,3-triazole (**2**) and 5-(*tert*-butyl-*NNO*-azoxy)-4-formylamino-(2'-azidophenyl)-2H-1,2,3-triazole (**4**) were prepared according to the reported procedures.[1]

[3-(*tert*-Butyl-*NNO*-azoxy)-1,5-dehydro-1H,5H-[1,2,3]triazolo[2,1-*a*][1,2,3]-benzotriazol-2-yl]formamide (6a) and [3-(*tert*-Butyl-*NNO*-azoxy)-1,5-dehydro-1H,5H-[1,2,3]triazolo[2,1-a][1,2,3]-benzotriazol-3-yl]formamide (6b). The solution of triazole **4** (198 mg, 0.6 mmol) in 1,2-dichlorobenzene (14 mL) was stirred at 180 °C for 1 h. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography (CH_2Cl_2/ethyl acetate, 2:1) to give tetraazapentalene **6a** (94 mg, 52%) as a yellow solid (m.p. 201–203 °C) and tetraazapentalene **6b** (56 mg, 31%) as a yellow solid (m.p. 250–253 °C).

Data for tetraazapentalene 6a: ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ = 1.56 (s, 9 H, CMe_3), 7.47 (t, J =7.9 Hz, 1 H, H-8), 7.58 (t, J =7.9 Hz, 1 H, H-7), 7.91–7.93 (m, 2 H, H-6 and H-9), 9.28 (br. s, 2 H, NH and CHO) ppm. ^{1}H NMR (500.1 MHz, [D_6]DMSO): δ = 1.50 (s, 9 H, CMe_3), 7.48 (t, J = 7.6 Hz, 1 H, H-8), 7.61 (t, J = 7.6 Hz, 1 H, H-7), 7.96 (d, J = 8.5 Hz, 1 H, H-6), 8.09 (d, J = 8.5 Hz, 1 H, H-9), 8.90 (br m, 1 H, CHO), 10.30 (br. m, 1 H, NH) ppm. ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 26.4 (C*Me*$_3$), 60.4 (*C*Me$_3$), 110.3 (C-9), 111.9 (br., C-3), 117.9 (C-6), 119.5 (C-9a), 124.7 (C-8), 127.6 (C-7), 141.4 (C-2), 145.4 (C-5a), 160.2 (CHO) ppm. ^{13}C NMR (125.8 MHz, [D_6]DMSO): δ = 25.9 (C*Me*$_3$), 59.2 (*C*Me$_3$), 110.2 (C-9), 113.5 (br., C-3), 116.8 (C-6), 118.7 (C-9a), 123.7 (C-8), 127.1 (C-7), 139.8 (C-2), 144.2 (C-5a), 160.1 (CHO) ppm. ^{14}N NMR (36.14 MHz, CD_2Cl_2): δ = –66 (N→O, $\Delta\nu_{½}$ = 110 Hz). IR (KBr): ν = 3334 (m), 3087 (w), 2972 (m), 2923 (m), 2853 (w), 1708 (s), 1571 (s), 1530 (s), 1490 (s), 1357 (s), 1292 (s), 1210 (s), 1187 (s) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{13}H_{15}N_7O_2$ $[M + Na]^+$ 324.1179; found 324.1184.

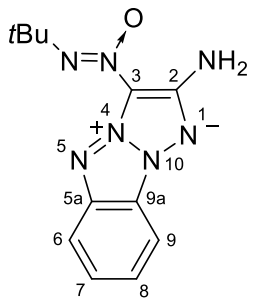
[1] A. A. Konnov, M. S. Klenov, A. M. Churakov, Yu. A. Strelenko, A. O. Dmitrienko, L. N. Puntus, K. A. Lyssenko, V. A. Tartakovsky, *Asian J. Org. Chem.*, 2018, **7**, 2534.

Data for tetraazapentalene 6b:



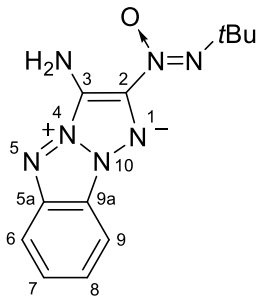
^{1}H NMR (500.1 MHz, [D$_6$]DMSO): δ = 1.45 (s, 9 H, CMe$_3$), 7.41 (t, J = 7.9 Hz, 1 H, H-8), 7.63 (t, J = 7.9 Hz, 1 H, H-7), 7.85 (d, J = 8.5 Hz, 1 H, H-6), 8.19 (d, J = 8.5 Hz, 1 H, H-9), 8.46 (s, 1 H, CHO), 10.90 (br. s, 1 H, NH) ppm. ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 25.3 (C*Me*$_3$), 59.5 (*C*Me$_3$), 105.6 (C-3), 111.1 (C-9), 115.9 (C-6), 118.7 (C-9a), 121.9 (C-8), 127.8 (C-7), 145.2 (C-5a), 145.3 (br., C-2), 160.6 (CHO) ppm. ^{14}N NMR (36.14 MHz, [D$_6$]DMSO): δ = –65 (N→O, $\Delta\nu_{½}$ = 115 Hz) ppm. IR (KBr): ν = 3410 (m), 3262 (m), 2976 (w), 2931 (w), 2894 (w), 1713 (s), 1598 (w), 1483 (m), 1468 (m), 1404 (m), 1390 (m), 1365 (m), 1232 (m) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{13}H_{15}N_7O_2$ [M + Na]$^+$ 324.1179; found 324.1178.

[3-(*tert*-Butyl-*NNO*-azoxy)-1,5-dehydro-1H,5H-[1,2,3]triazolo[2,1-a][1,2,3]-benzotriazol-2-amine (5a). Method A. The solution of aminotriazole **2** (301 mg, 0.1 mmol) in 1,2-dichlorobenzene (30 mL) was stirred at 150 °C for 3.5 h and then concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 2:1 then 1:1) to give tetraazapentalene **5a** (190 mg, 70%) as a yellowish solid, m.p. 235–239 °C. **Method B.** MeSO$_3$H (0.375 mL, 5.6 mmol) was added to a stirred suspension of tetraazapentalene **6a** (36 mg, 5.6 mmol) in MeOH (2 mL) at 50 °C. The reaction mixture was stirred at this temperature for 30 min and then poured out into water (15 mL). The solution was extracted with CH_2Cl_2 (4 × 30 mL). The combined organic extracts were washed with water (100 mL), dried (MgSO$_4$) and concentrated under reduced pressure to give tetraazapentalene **5a** (32 mg, 98%) as a yellowish solid, m.p. 235–239 °C.



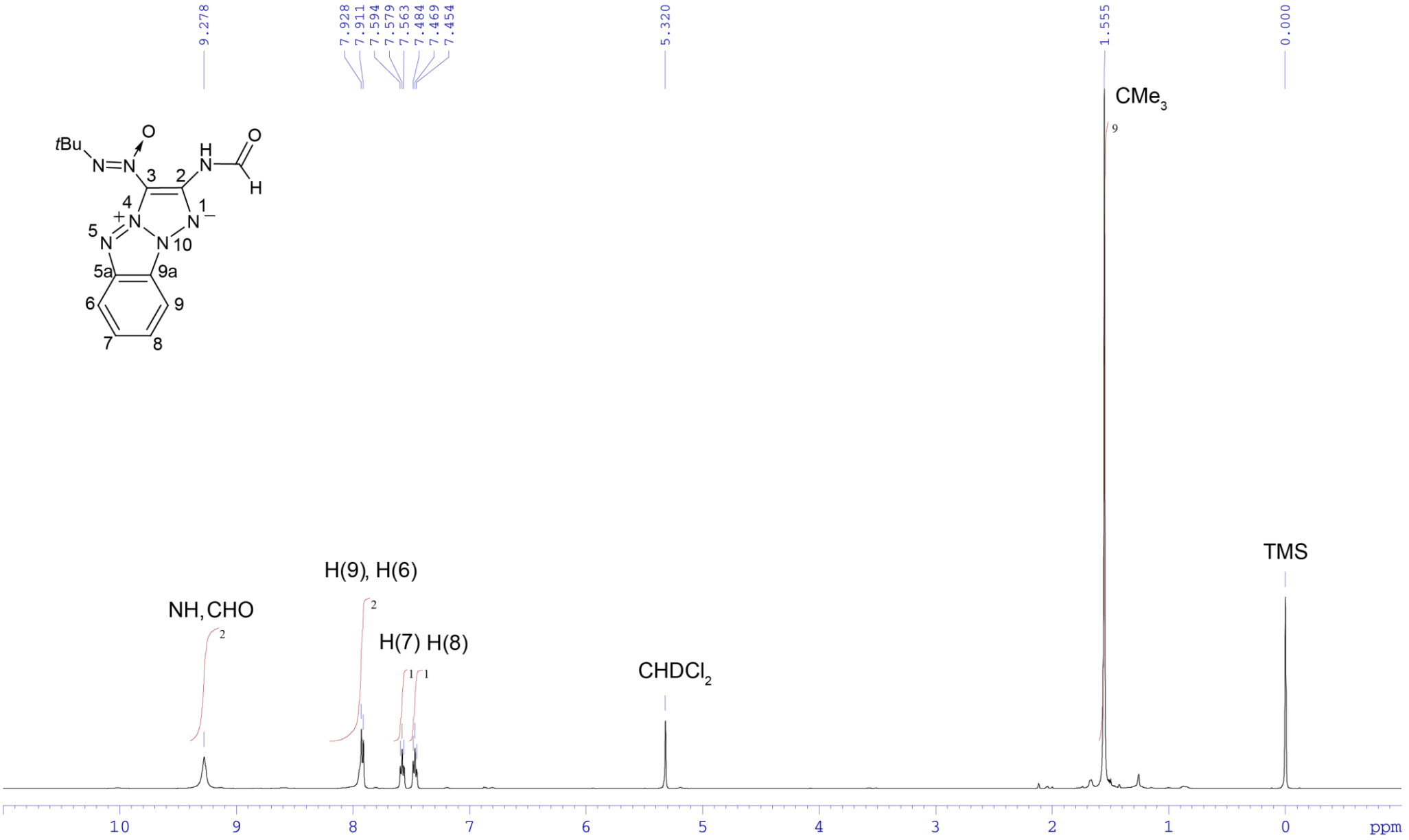
^{1}H NMR (600.1 MHz, CDCl$_3$): δ = 1.55 (s, 9 H, CMe$_3$), 5.56 (br. s, 2 H, NH$_2$), 7.35 (t, J =8.1 Hz, Ar), 7.47 (t, J =8.1 Hz, 1 H, Ar), 7.80 (d, J = 8.8 Hz, 1 H, Ar), 7.87 (d, J = 8.8 Hz, 1 H, Ar) ppm. ^{13}C NMR (150.8 MHz, CDCl$_3$): δ = 26.5 (C*Me*$_3$), 59.4 (*C*Me$_3$), 109.5 (CH$_{Ar}$), 112.1 (br., C-3), 117.4 (CH$_{Ar}$), 119.1 (C$_{Ar}$), 123.4 (CH$_{Ar}$), 126.3 (CH$_{Ar}$), 144.7, 148.4 ppm. ^{14}N NMR (43.4 MHz, CDCl$_3$): δ = –65 (N→O, $\Delta\nu_{½}$ = 100 Hz). IR (KBr): ν = 3431 (s), 3272 (s), 2970 (w), 2929 (w), 1621 (m), 1599 (s), 1539 (m), 1516 (m), 1489 (m), 1420 (m), 1383 (m), 1328 (m), 1223 (m), 1171 (w) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}N_7O$ [M + Na]$^+$ 296.1233; found 296.1230.

[2-(*tert*-Butyl-*NNO*-azoxy)-1,5-dehydro-1H,5H-[1,2,3]triazolo[2,1-a][1,2,3]-benzotriazol-3-amine (5b). MeSO$_3$H (0.375 mL, 5.6 mmol) was added to a stirred suspension of tetraazapentalene **6b** (56 mg, 0.19 mmol) in MeOH (3 mL) at 50 °C. The reaction mixture was stirred at this temperature for 30 min and then poured out into water (15 mL). The solution was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were dried (MgSO$_4$) and concentrated under reduced pressure to give tetraazapentalene **5b** (49 mg, 96%) as an orange solid, m.p. 181–183 °C. ^{1}H NMR (600.1 MHz, [D$_6$]DMSO): δ = 1.49 (s, 9 H, CMe$_3$), 6.57 (br. s, 2 H, NH$_2$), 7.19 (t, J =7.3 Hz, H-8), 7.51 (t, J =7.3 Hz, 1 H, H-7), 7.65 (d, J = 8.8 Hz, 1 H, H-6), 8.04 (d, J = 8.8 Hz, 1 H, H-9) ppm. ^{13}C NMR (150.8 MHz, [D$_6$]DMSO): δ = 25.7 (C*Me*$_3$), 58.9 (*C*Me$_3$), 111.0 (C-9), 114.3 (C-6), 117.5 (C-9a), 119.2 (C-8), 121.4 (C-3), 127.6 (C-7), 135.5 (br., C-2), 146.4 (C-5a) ppm. ^{14}N

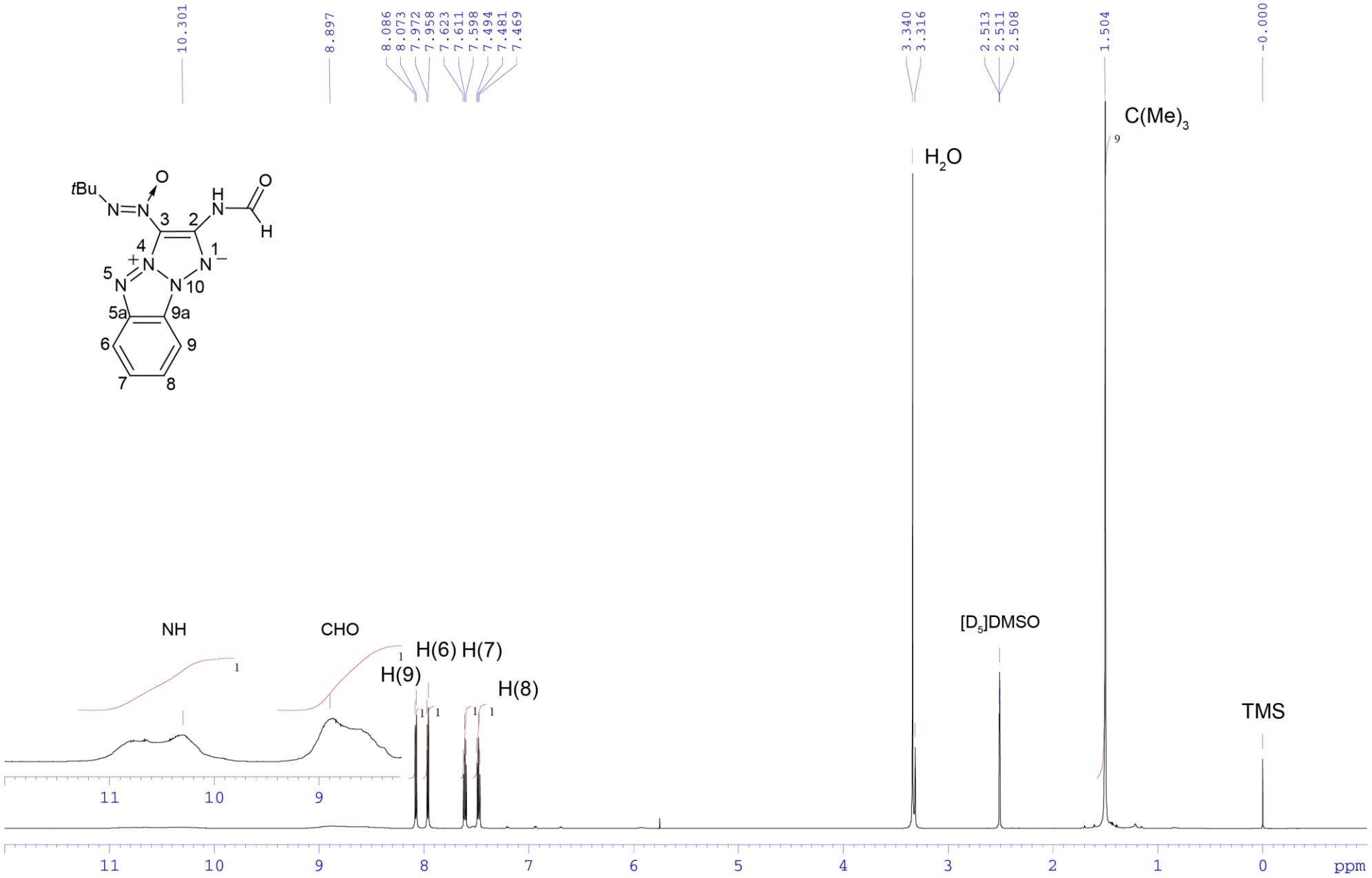


NMR (43.4 MHz, [D_6]DMSO): δ = –61 (N→O, $\Delta\nu_{½}$ = 110 Hz). IR (KBr): ν = 3422 (s), 3274 (s), 3096 (w), 2972 (m), 1629 (s), 1579 (w), 1435 (s), 1373 (s), 1265 (s), 1232 (m) cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}N_7O$ $[M + H]^+$ 274.1411; found 274.1412.

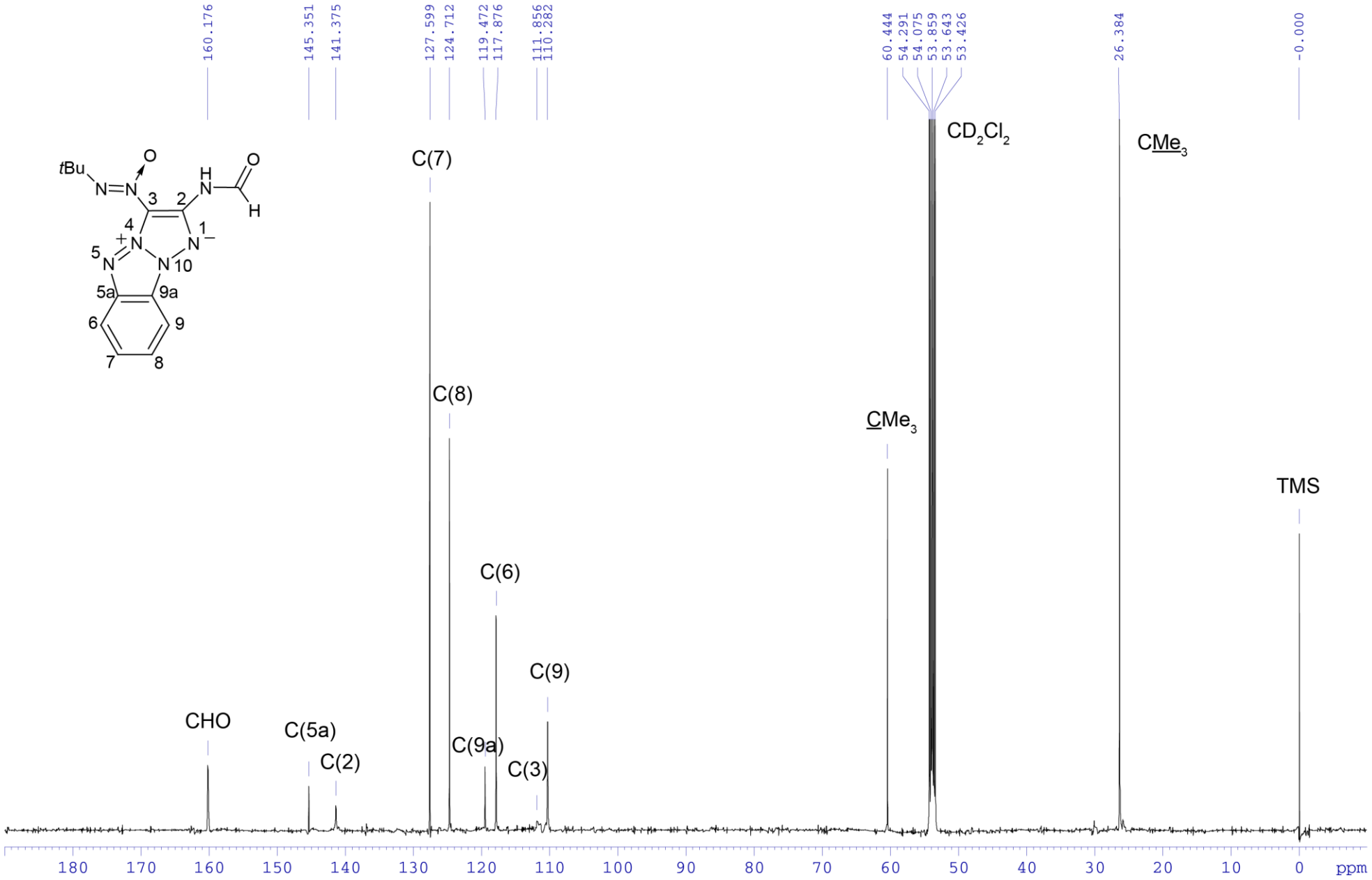
^{1}H NMR (600.1 MHz, CD_2Cl_2) of compound 6a



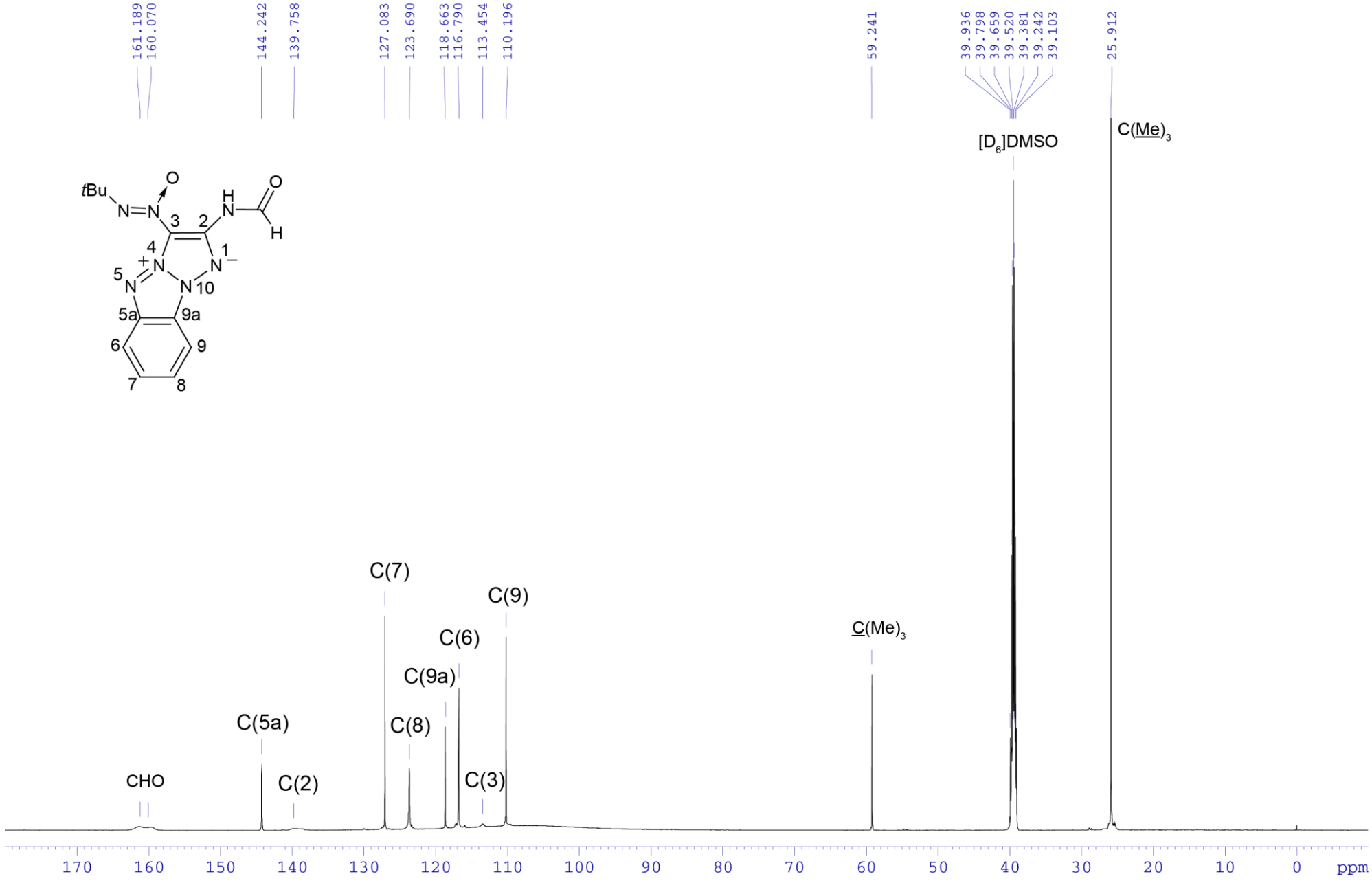
^{1}H NMR (600.1 MHz, [D$_6$]DMSO) of compound 6a



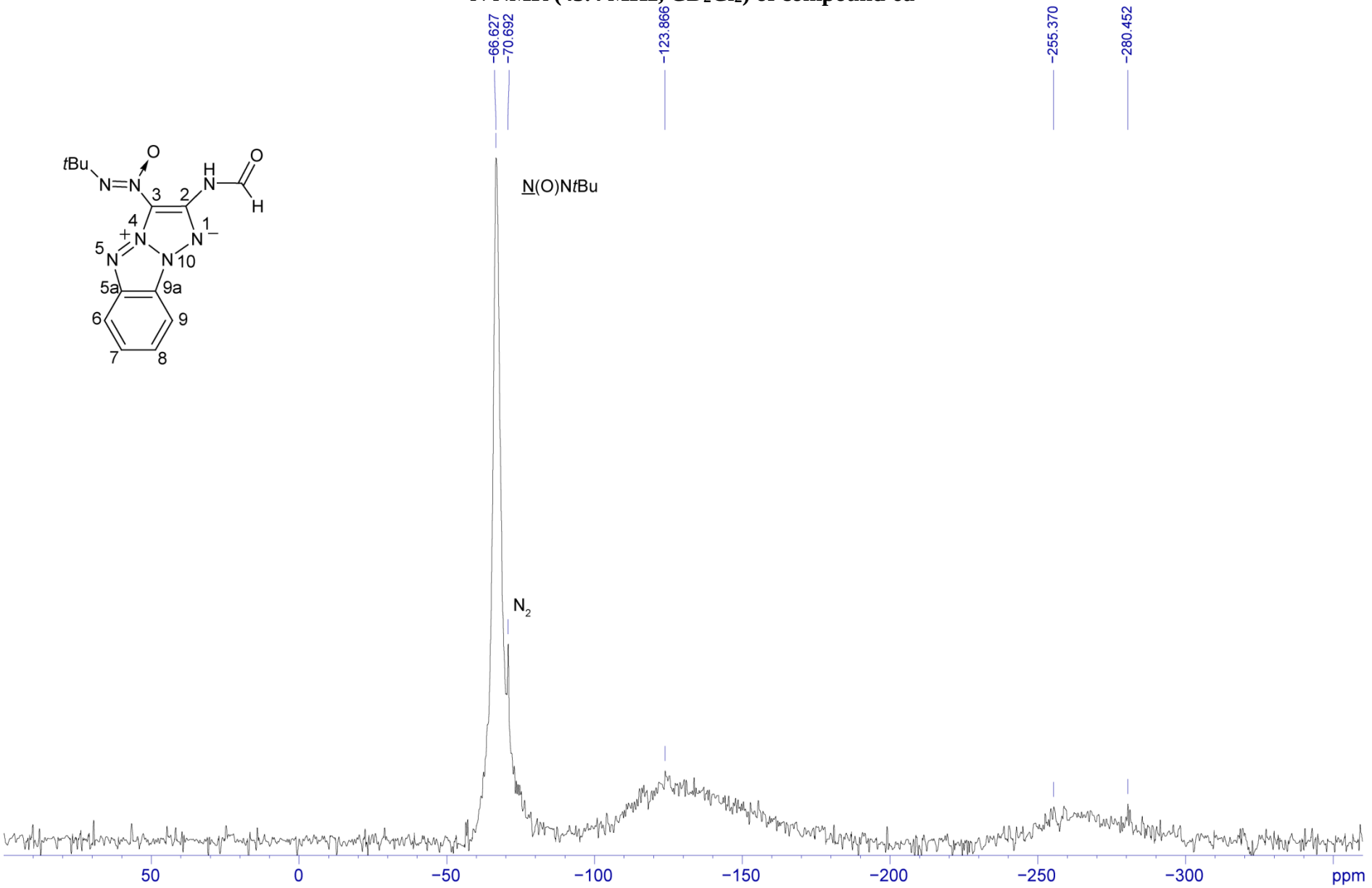
^{13}C NMR (150.9 MHz, CD_2Cl_2) of compound 6a



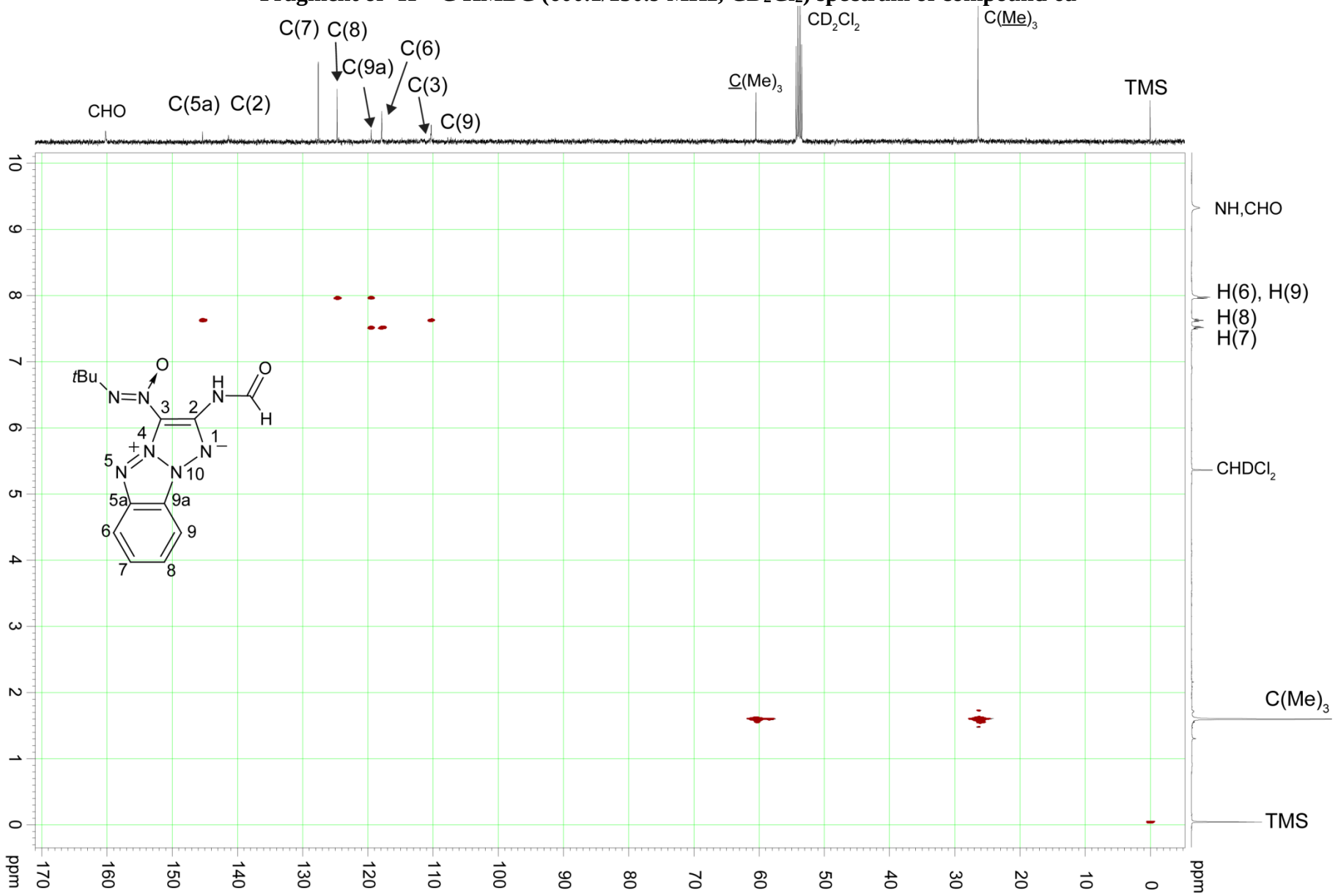
^{13}C NMR (150.9 MHz, [D$_6$]DMSO) of compound 6a



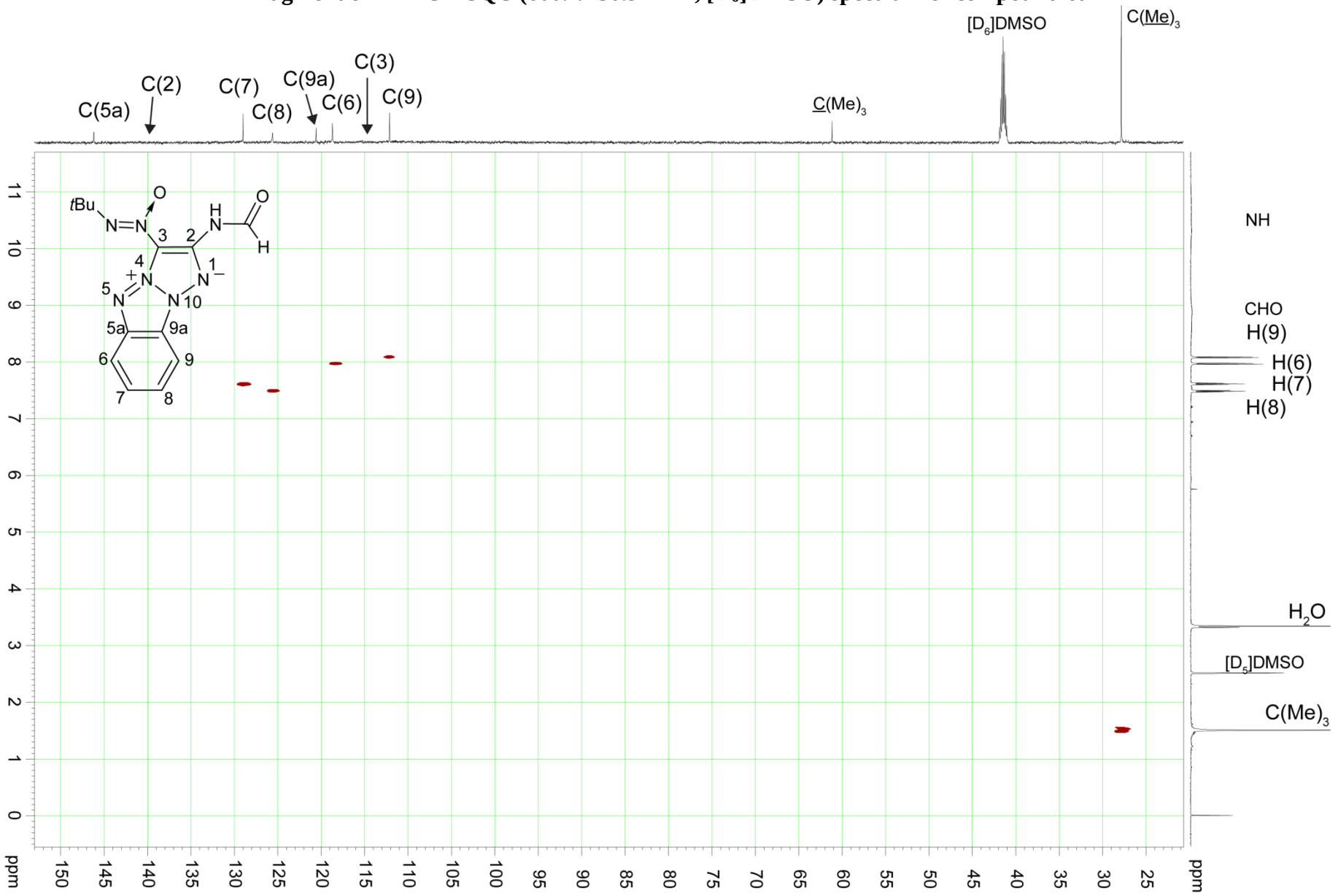
^{14}N NMR (43.4 MHz, CD_2Cl_2) of compound 6a



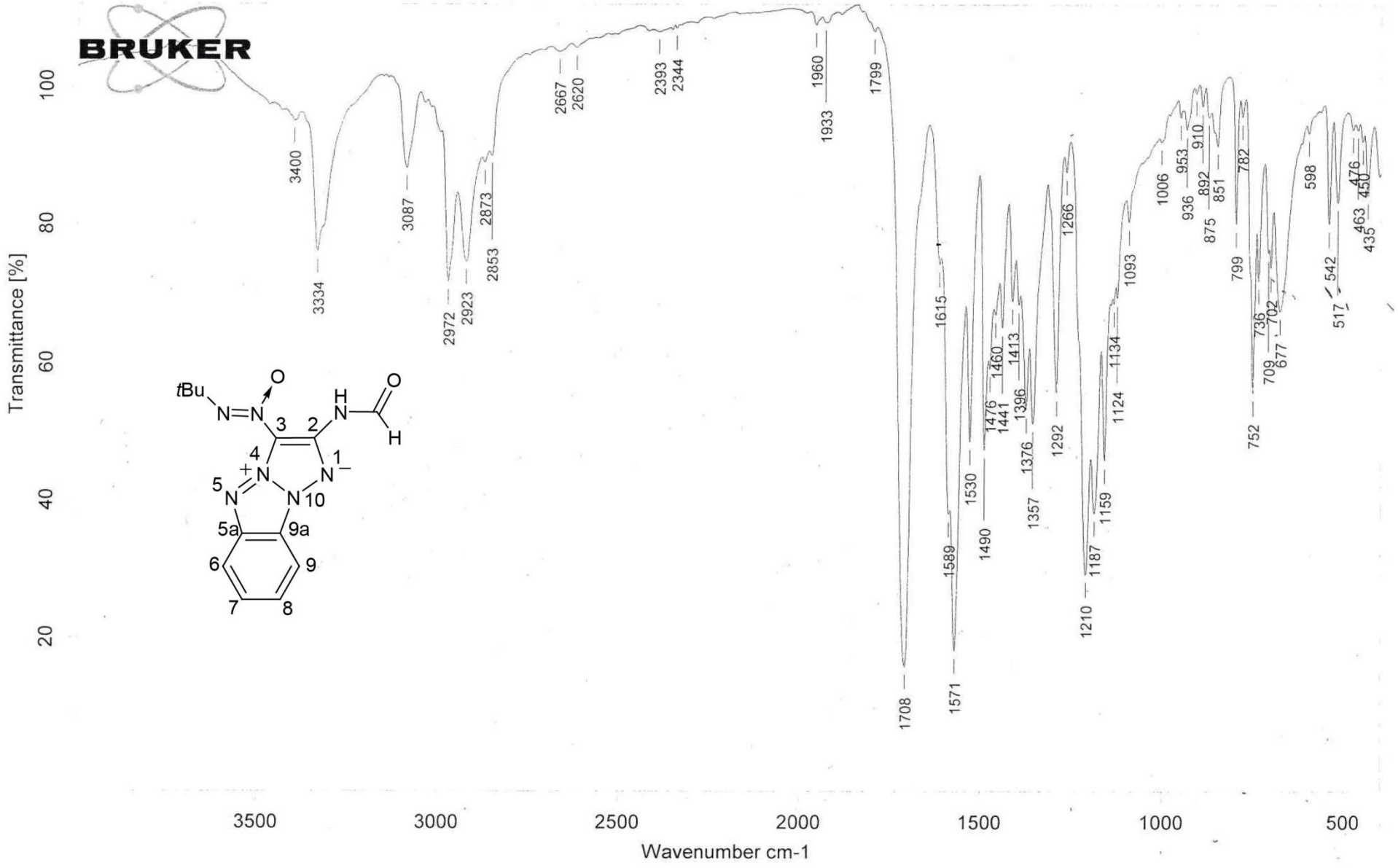
Fragment of ^{1}H-^{13}C HMBC (600.1/150.9 MHz, CD_2Cl_2) spectrum of compound 6a



Fragment of ^{1}H-^{13}C HSQC (600.1/150.9 MHz, [D_6]DMSO) spectrum of compound 6a



IR of compound 6a



HRMS of compound 6a

Acquisition Parameter

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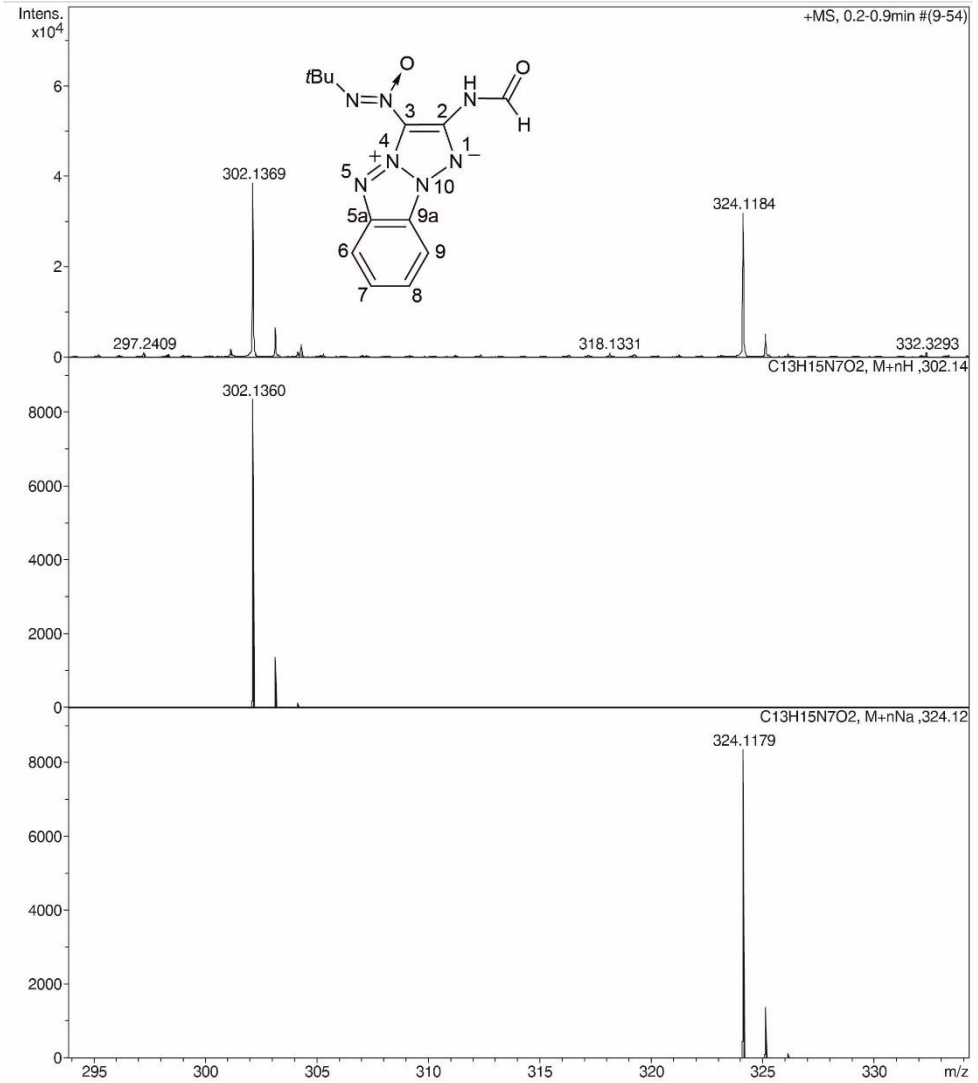
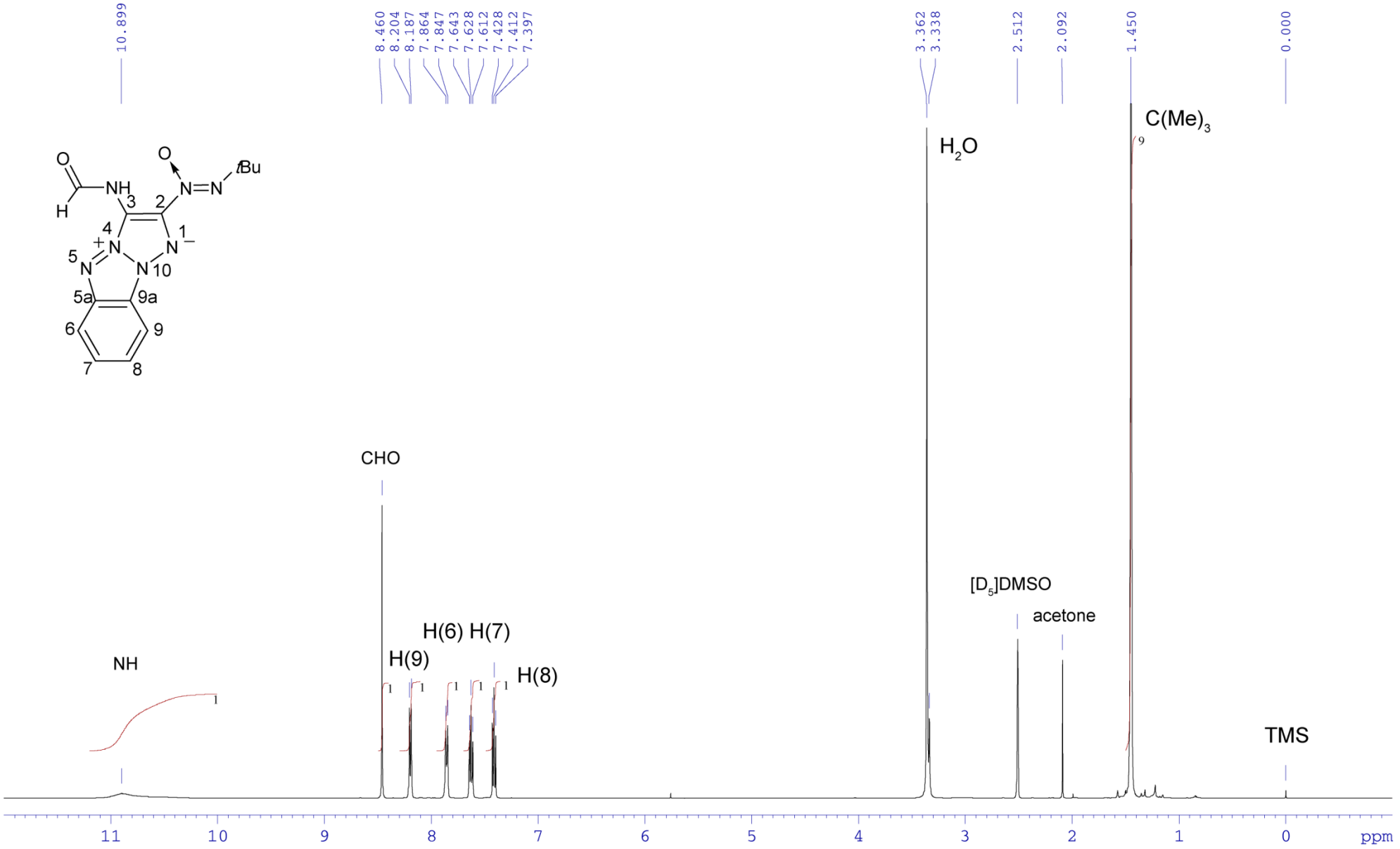
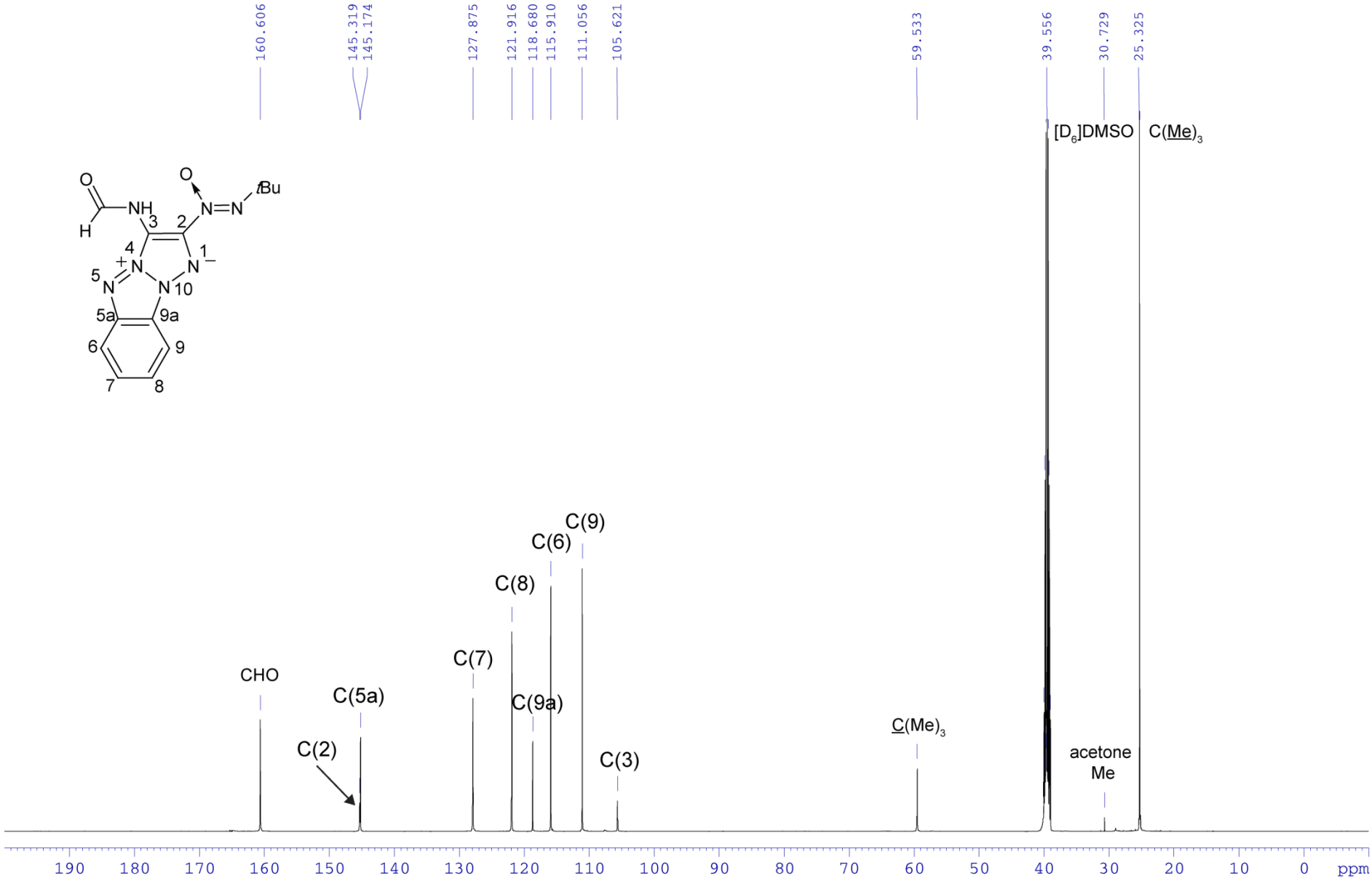


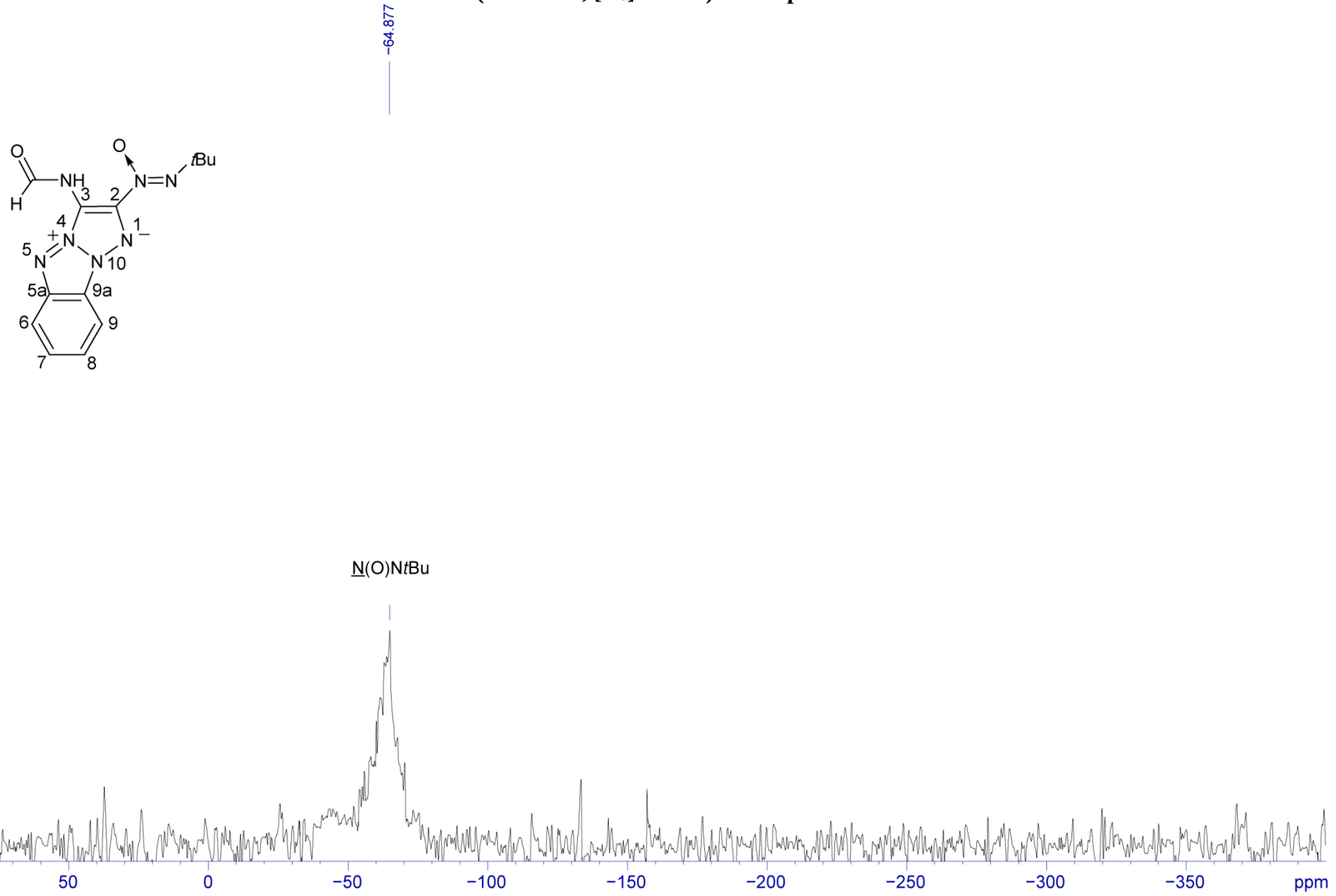
^{1}H NMR (500.1 MHz, [D$_6$]DMSO) of compound 6b



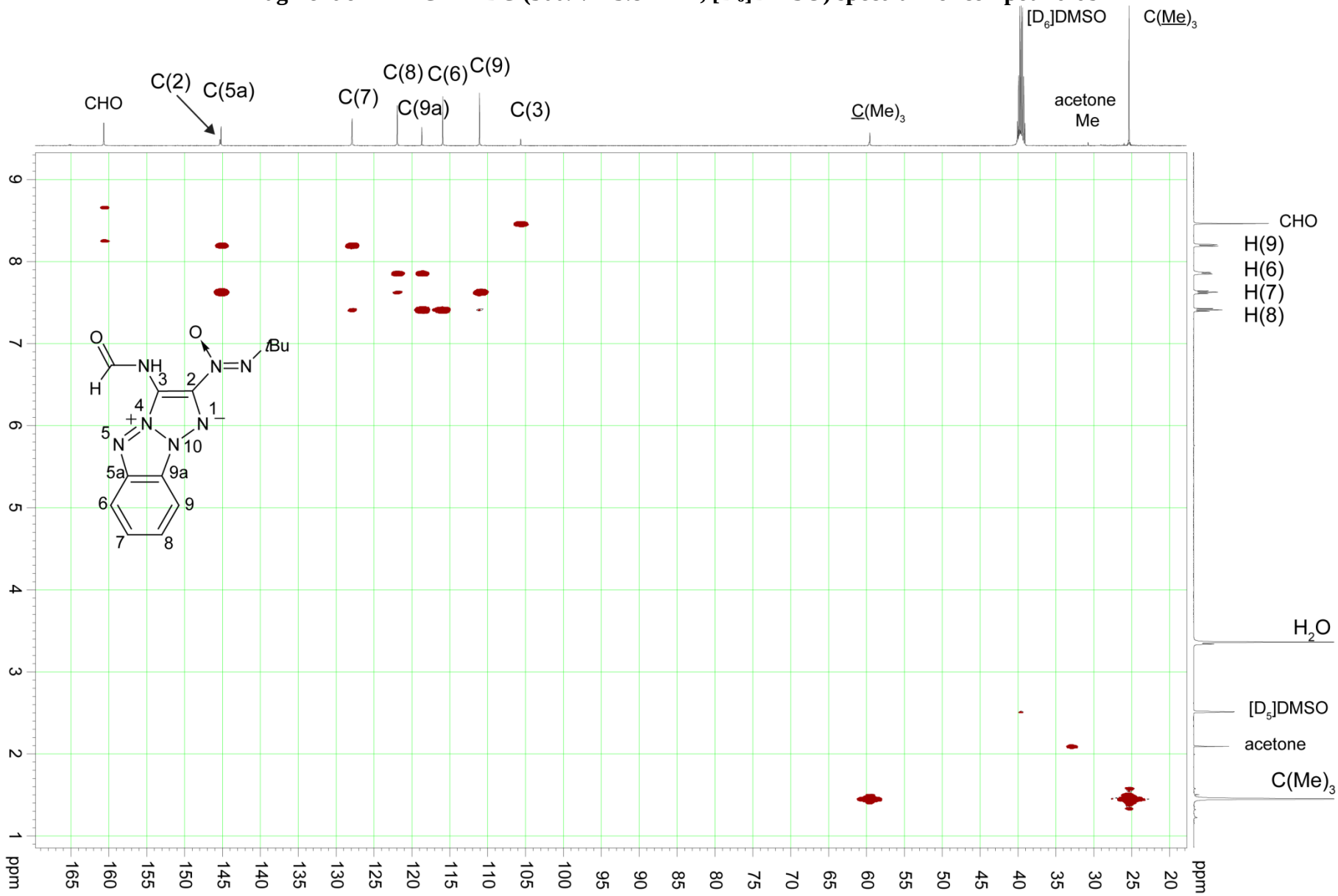
^{13}C NMR (125.8 MHz, [D$_6$]DMSO) of compound 6b



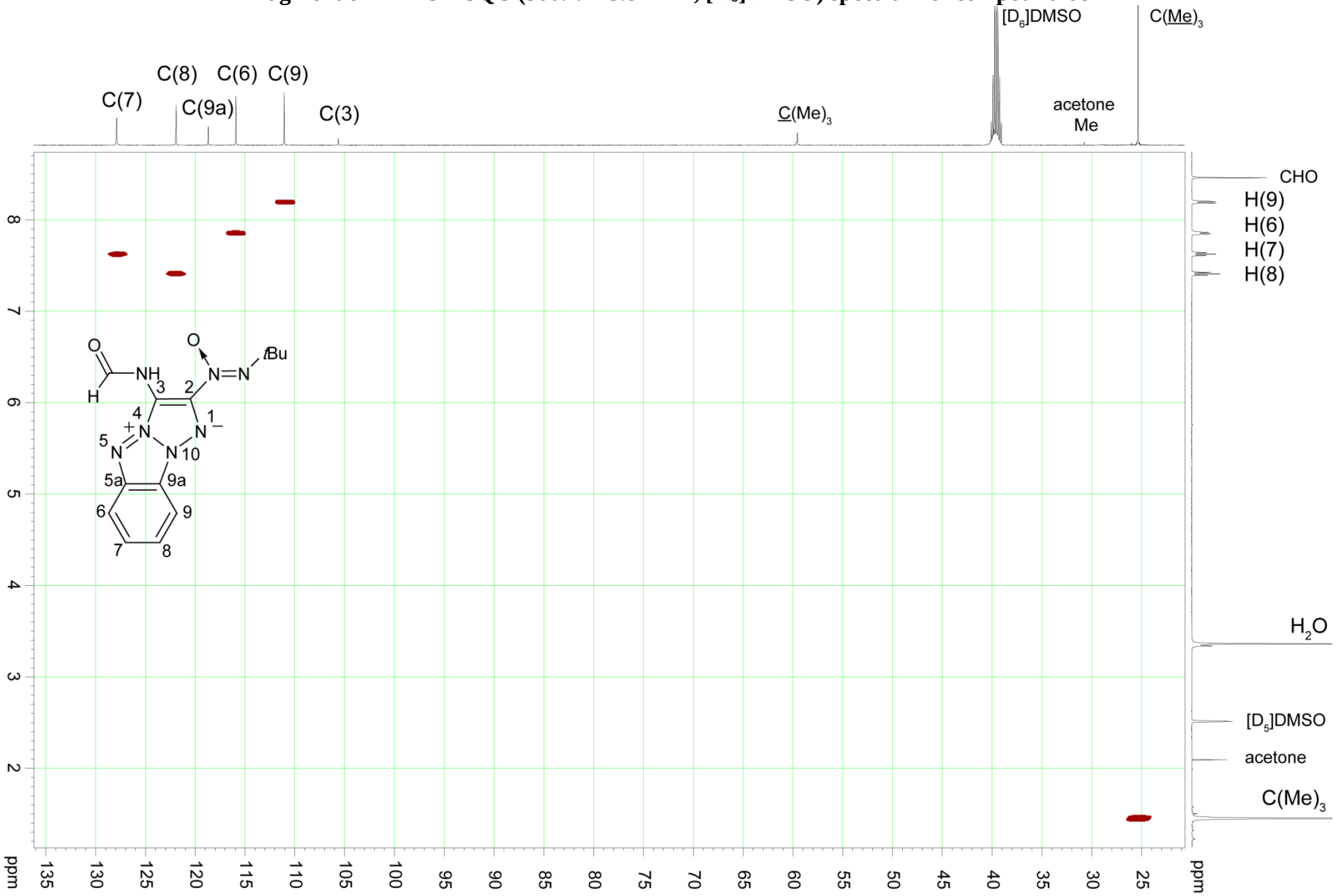
^{14}N NMR (36.1 MHz, [D$_6$]DMSO) of compound 6b



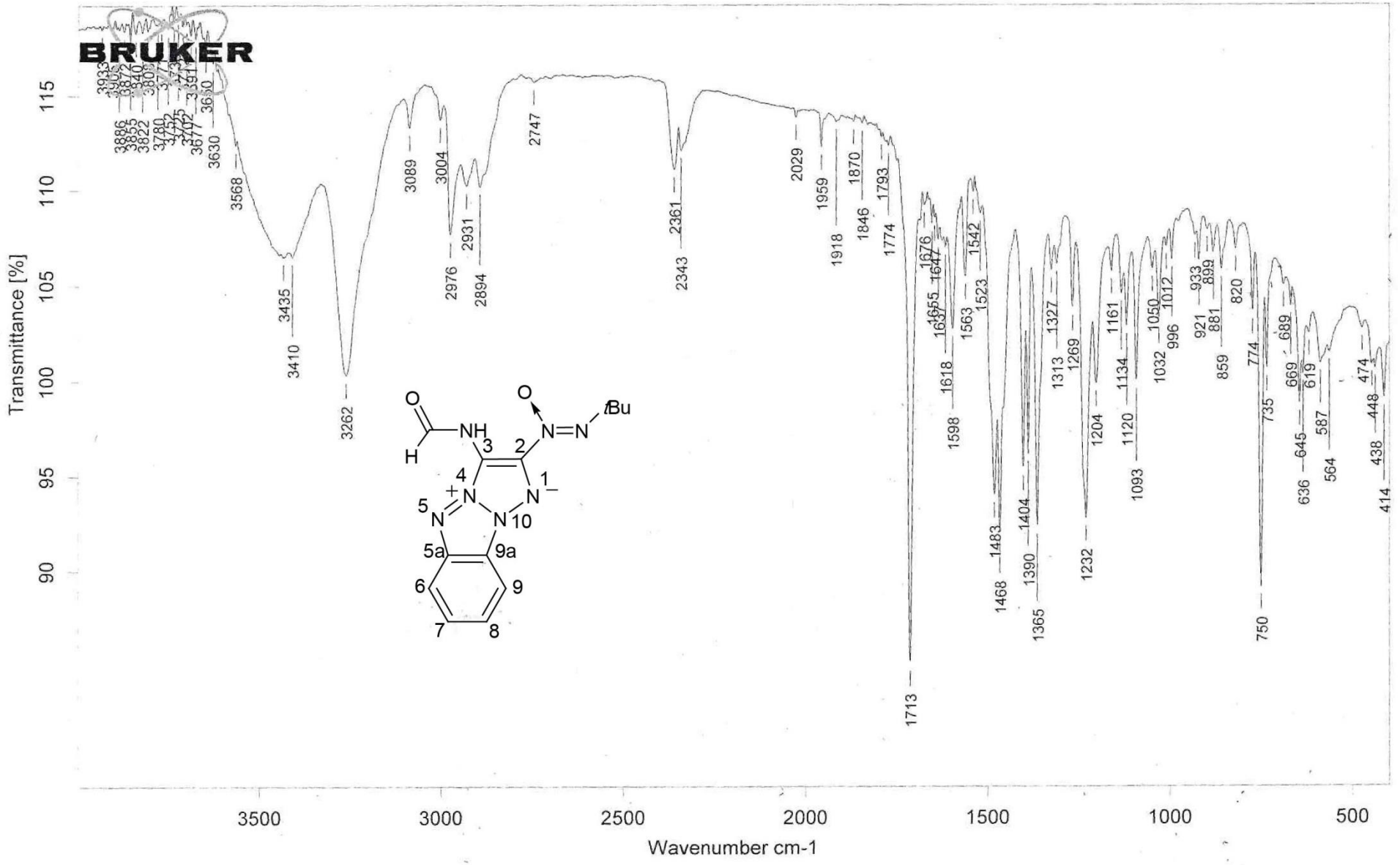
Fragment of ^{1}H-^{13}C HMBC (500.1/125.8 MHz, [D_6]DMSO) spectrum of compound 6b



Fragment of ^{1}H-^{13}C HSQC (500.1/125.8 MHz, [D_6]DMSO) spectrum of compound 6b



IR of compound 6b



HRMS of compound 6b

Acquisition Parameter

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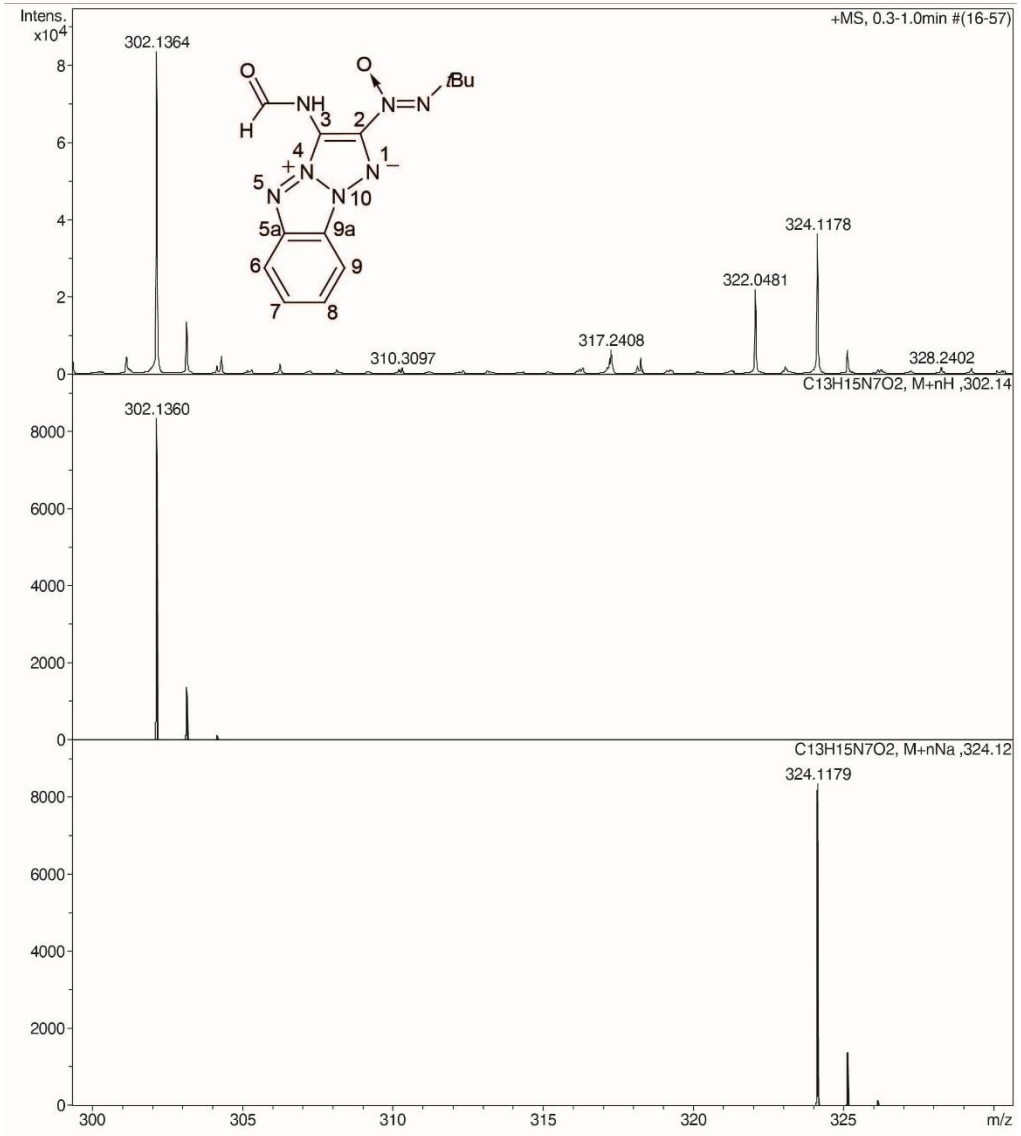
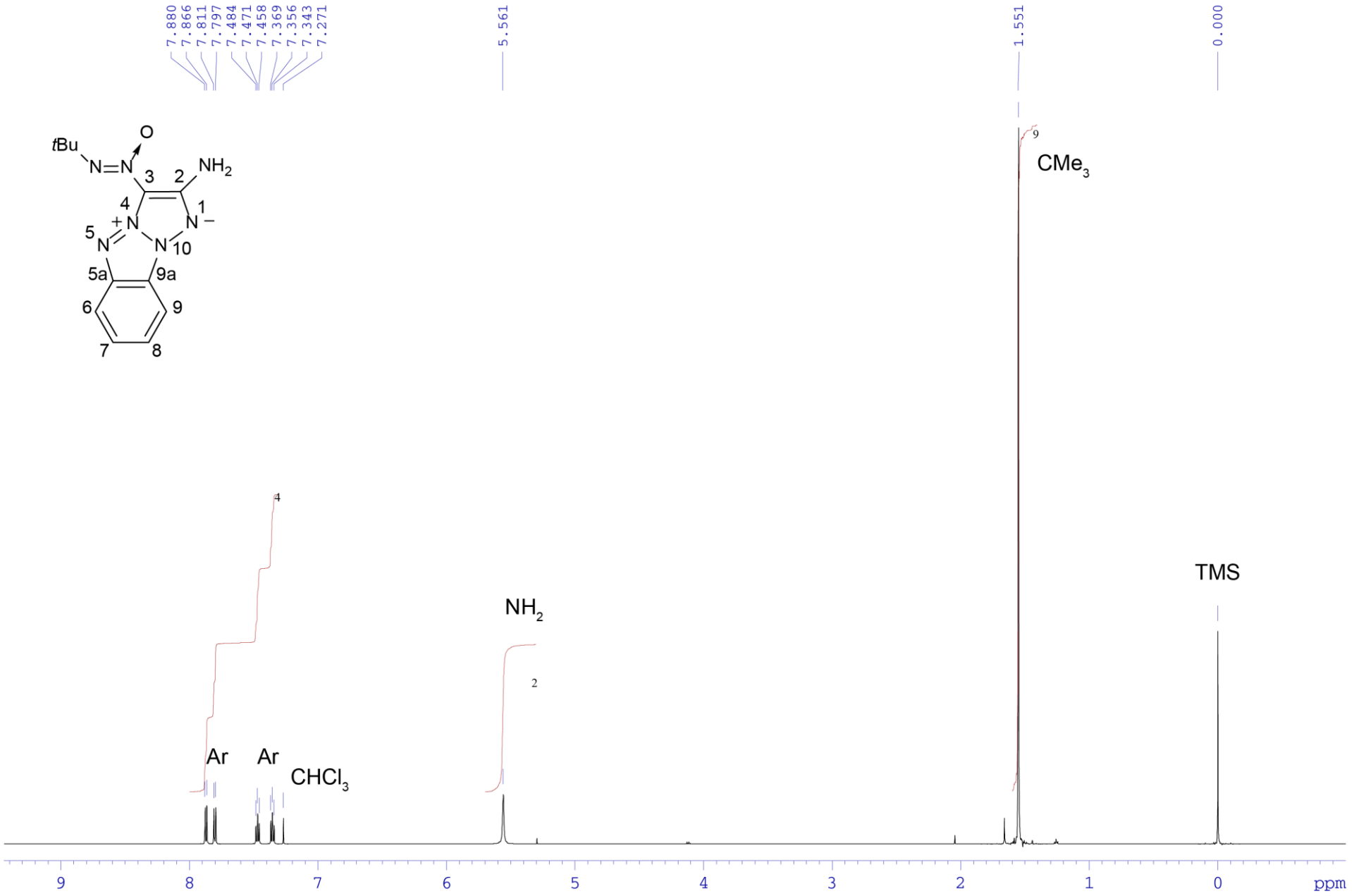
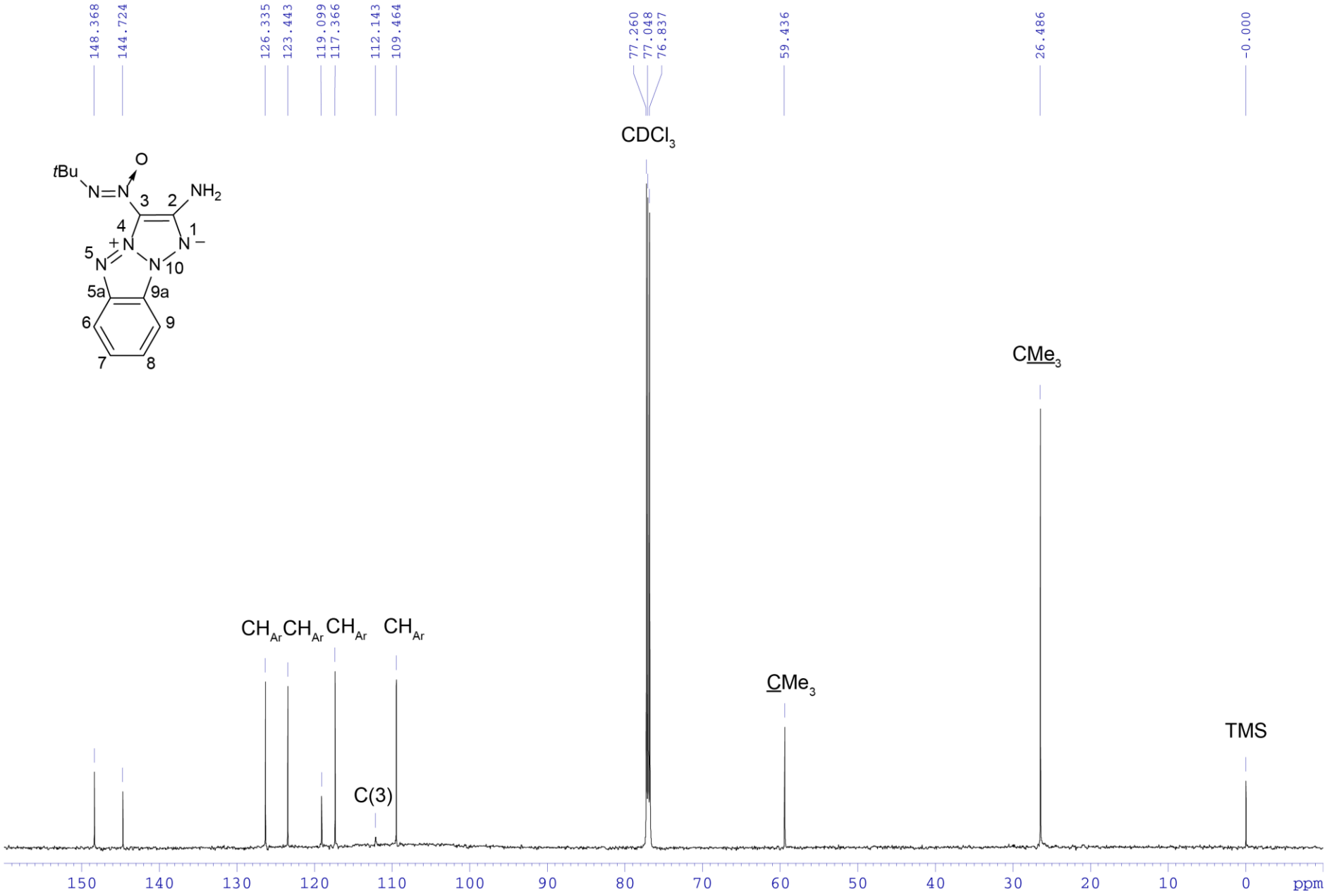


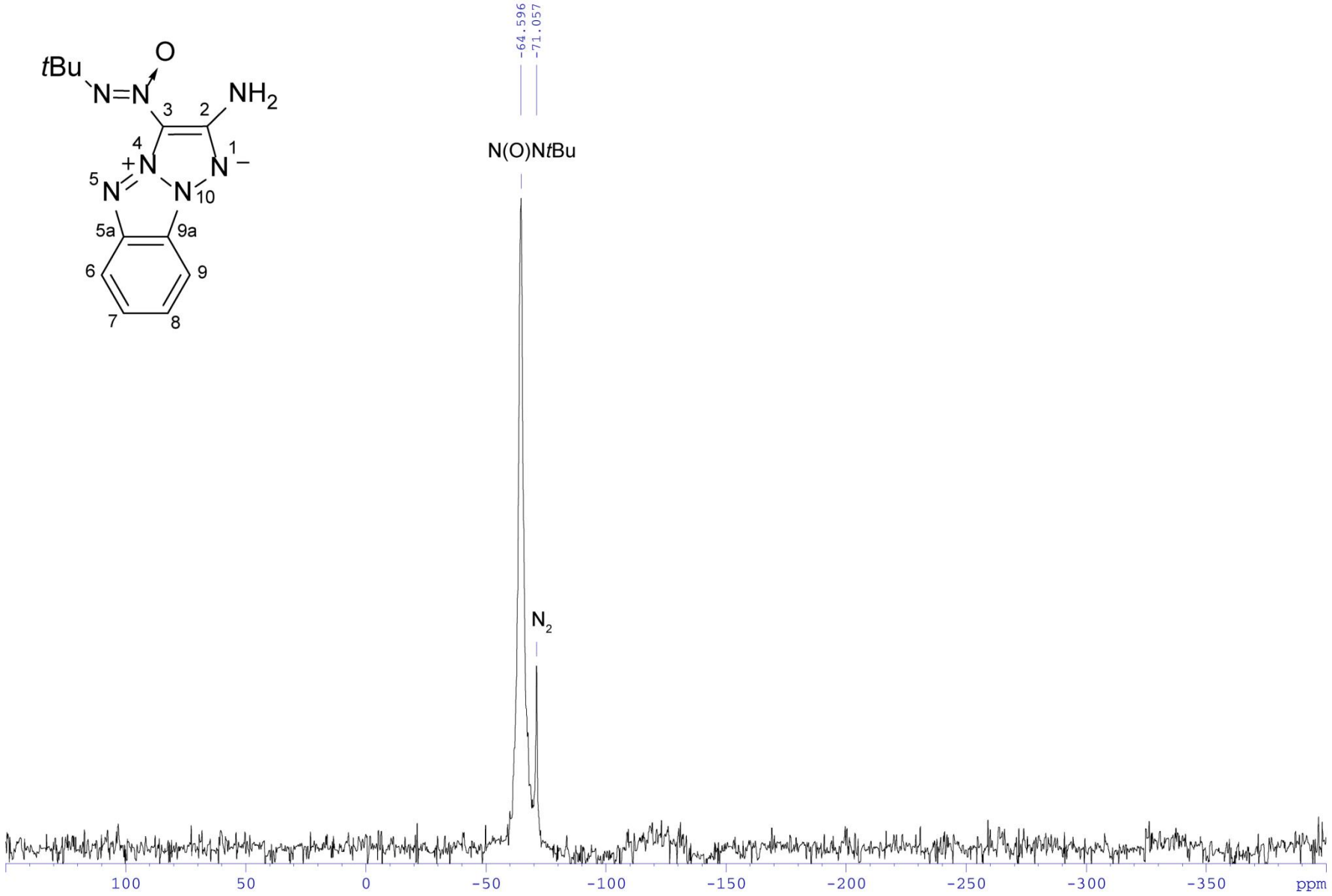
^{1}H NMR (600.1 MHz, $CDCl_3$) of compound 5a



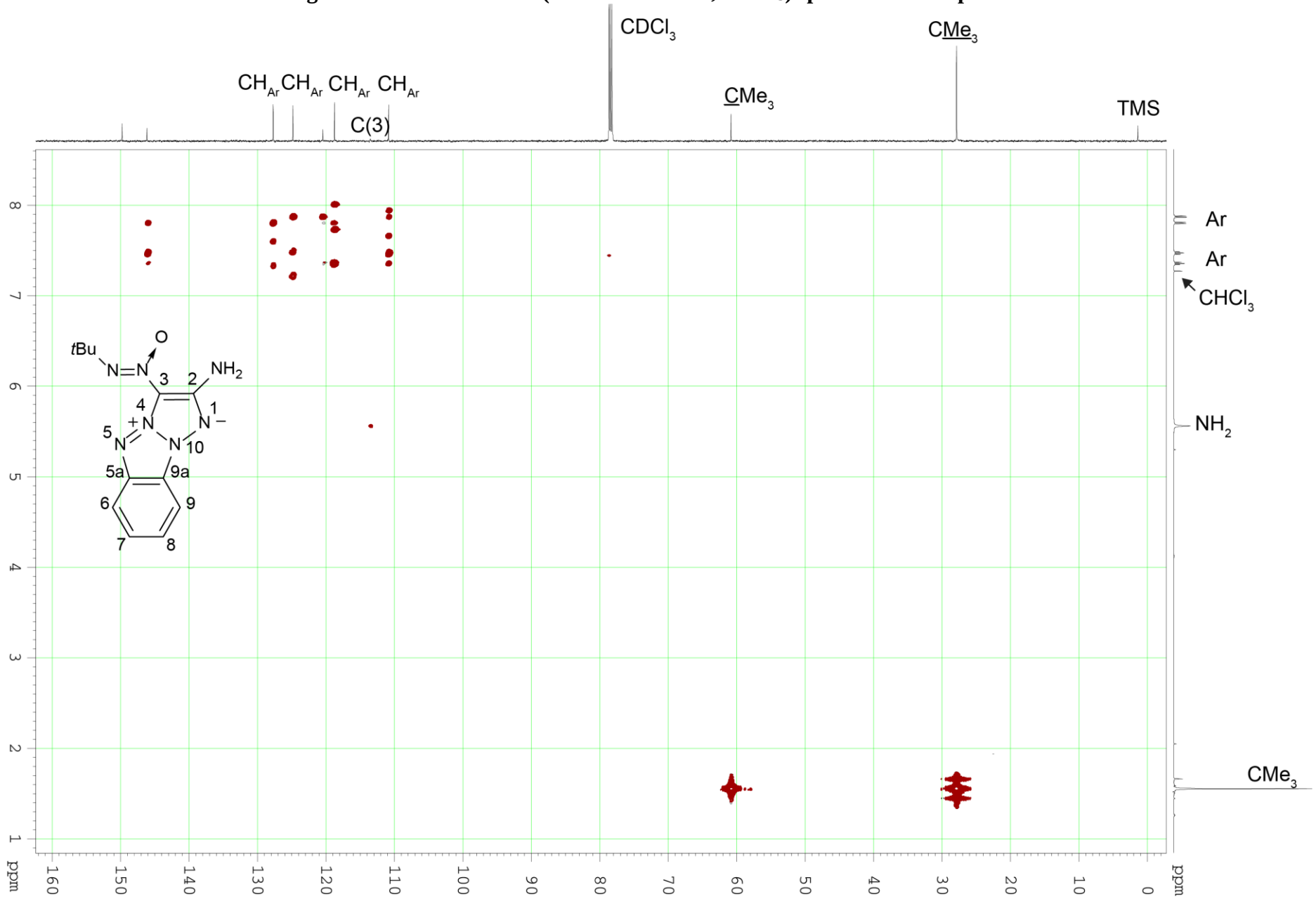
^{13}C NMR (150.9 MHz, $CDCl_3$) of compound 5a



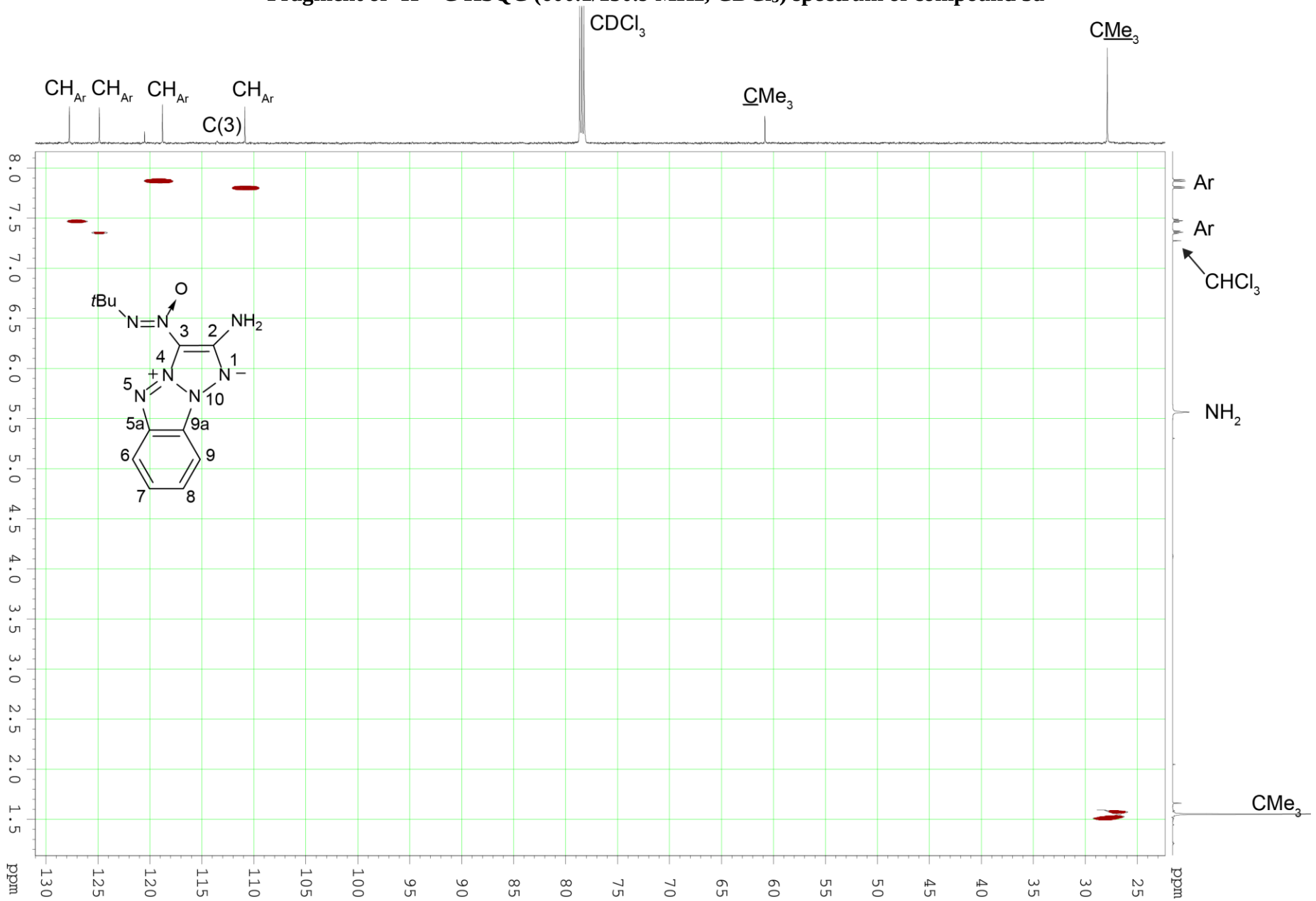
^{14}N NMR (43.4 MHz, $CDCl_3$) of compound 5a



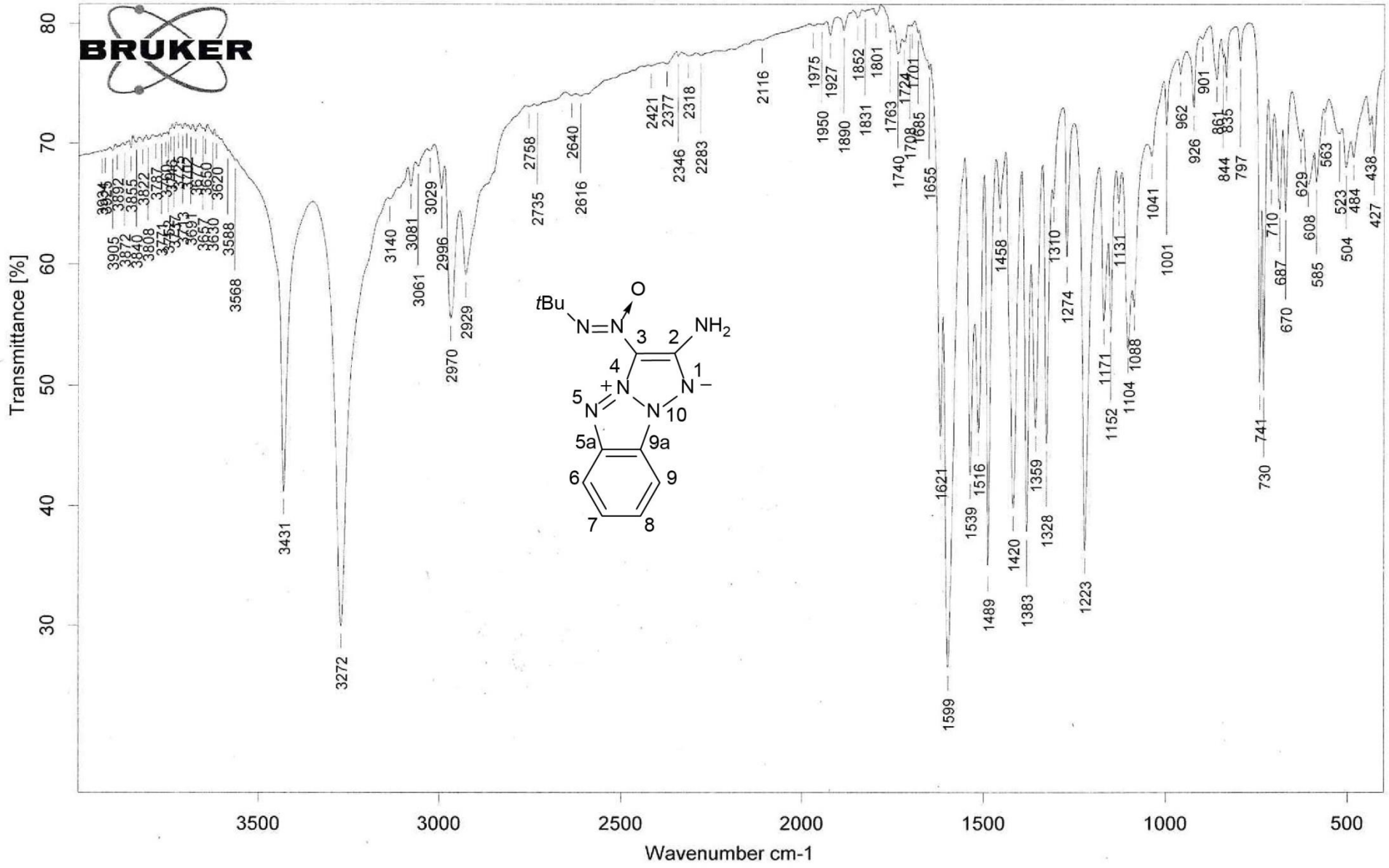
Fragment of ^{1}H-^{13}C HMBC (600.1/150.9 MHz, $CDCl_3$) spectrum of compound 5a



Fragment of ^{1}H-^{13}C HSQC (600.1/150.9 MHz, $CDCl_3$) spectrum of compound 5a



IR of compound 5a



HRMS of compound 5a

Acquisition Parameter

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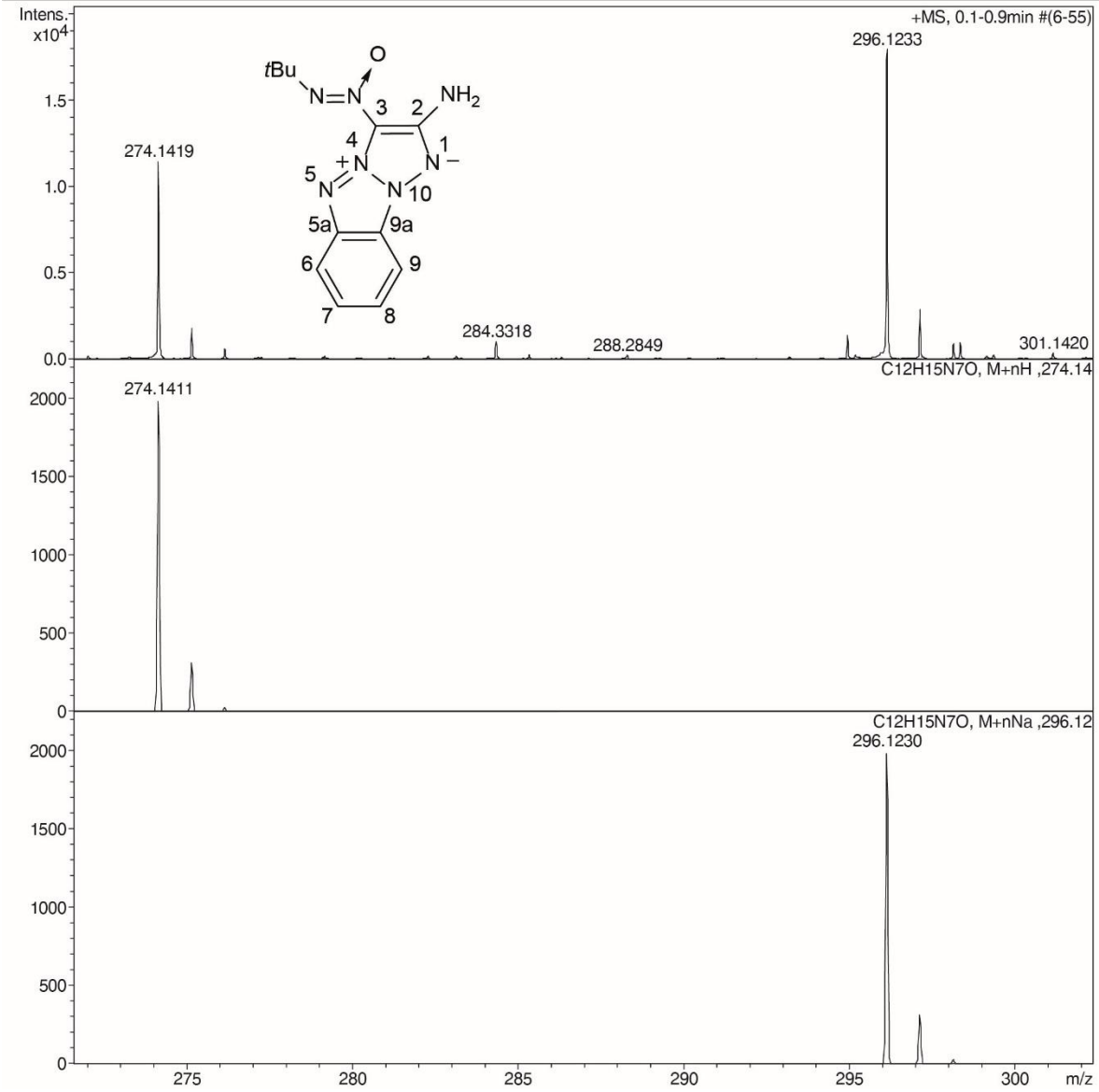
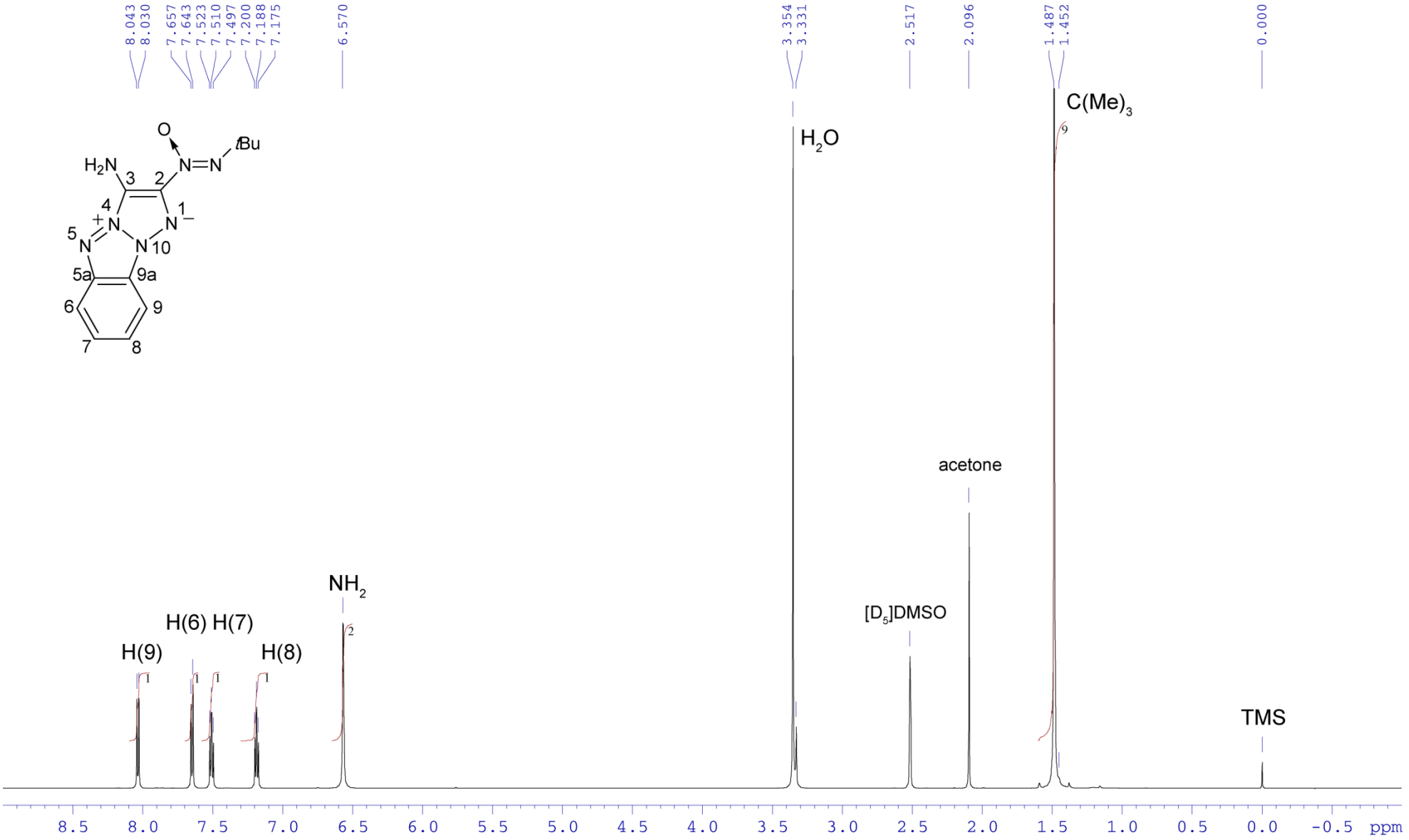
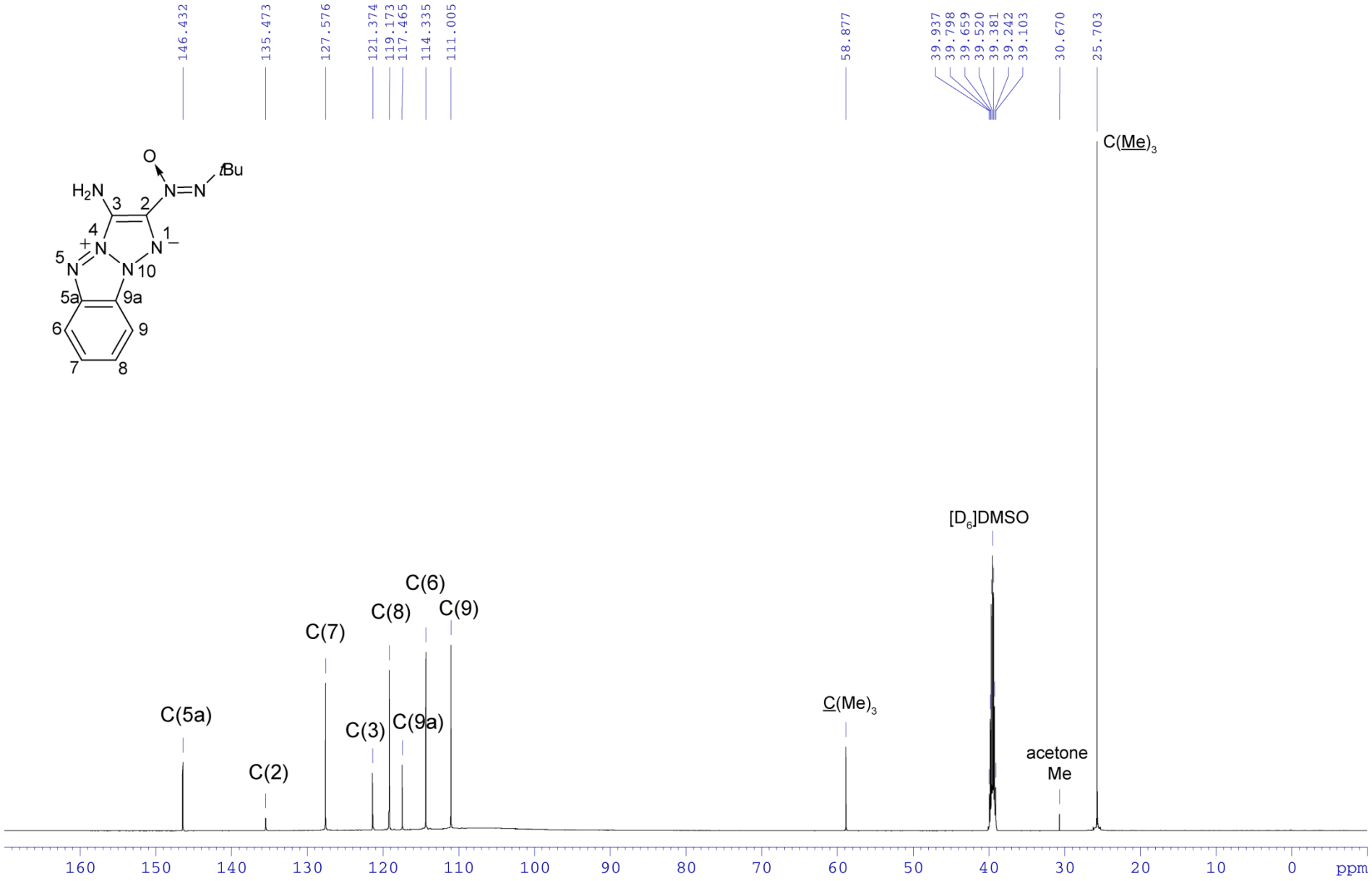


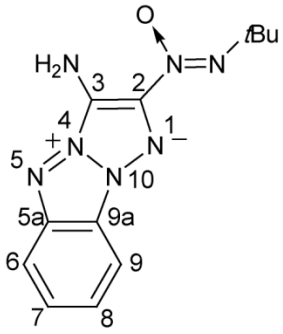
^{1}H NMR (600.1 MHz, [D$_6$]DMSO) of compound 5b



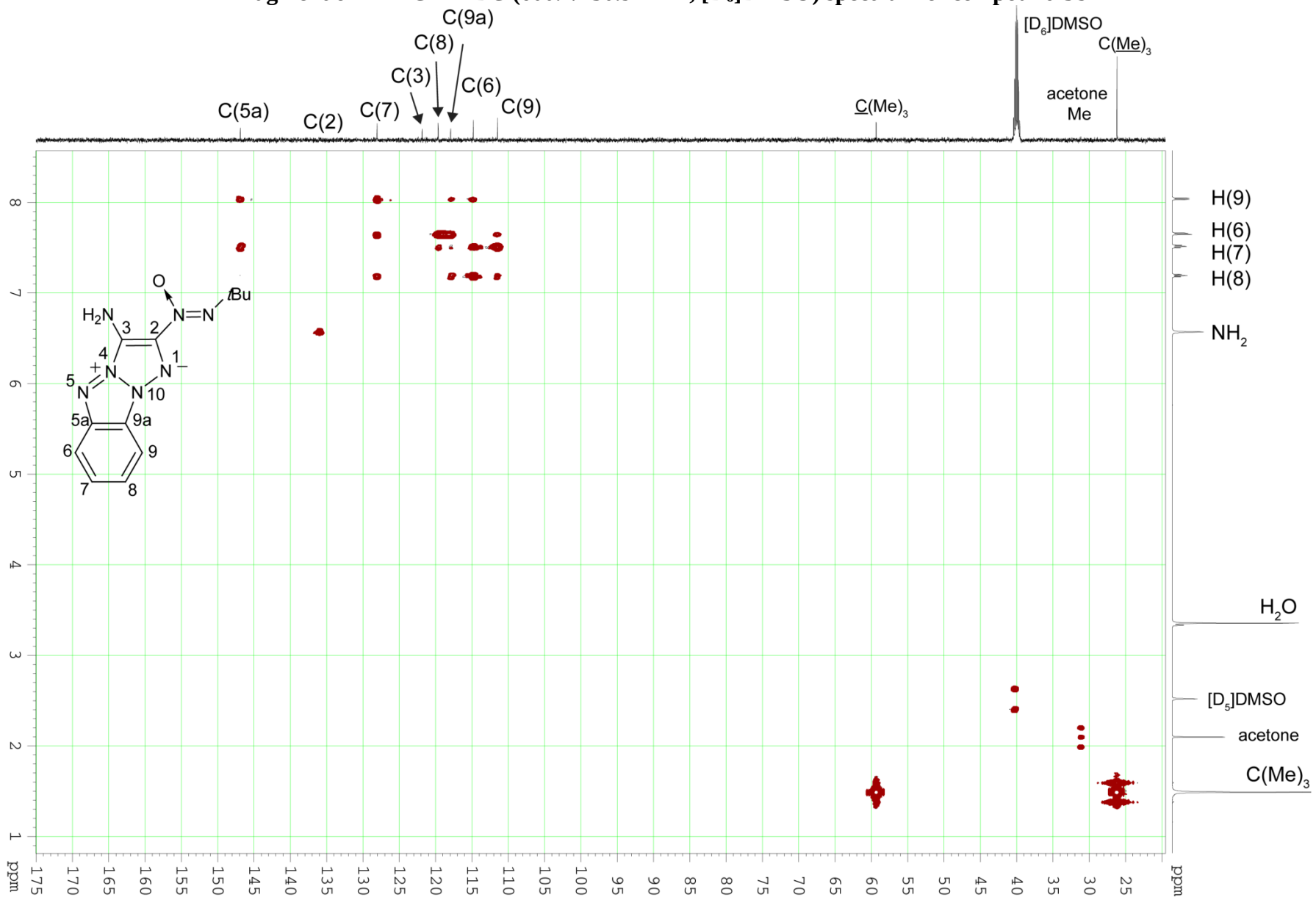
^{13}C NMR (150.9 MHz, [D$_6$]DMSO) of compound 5b



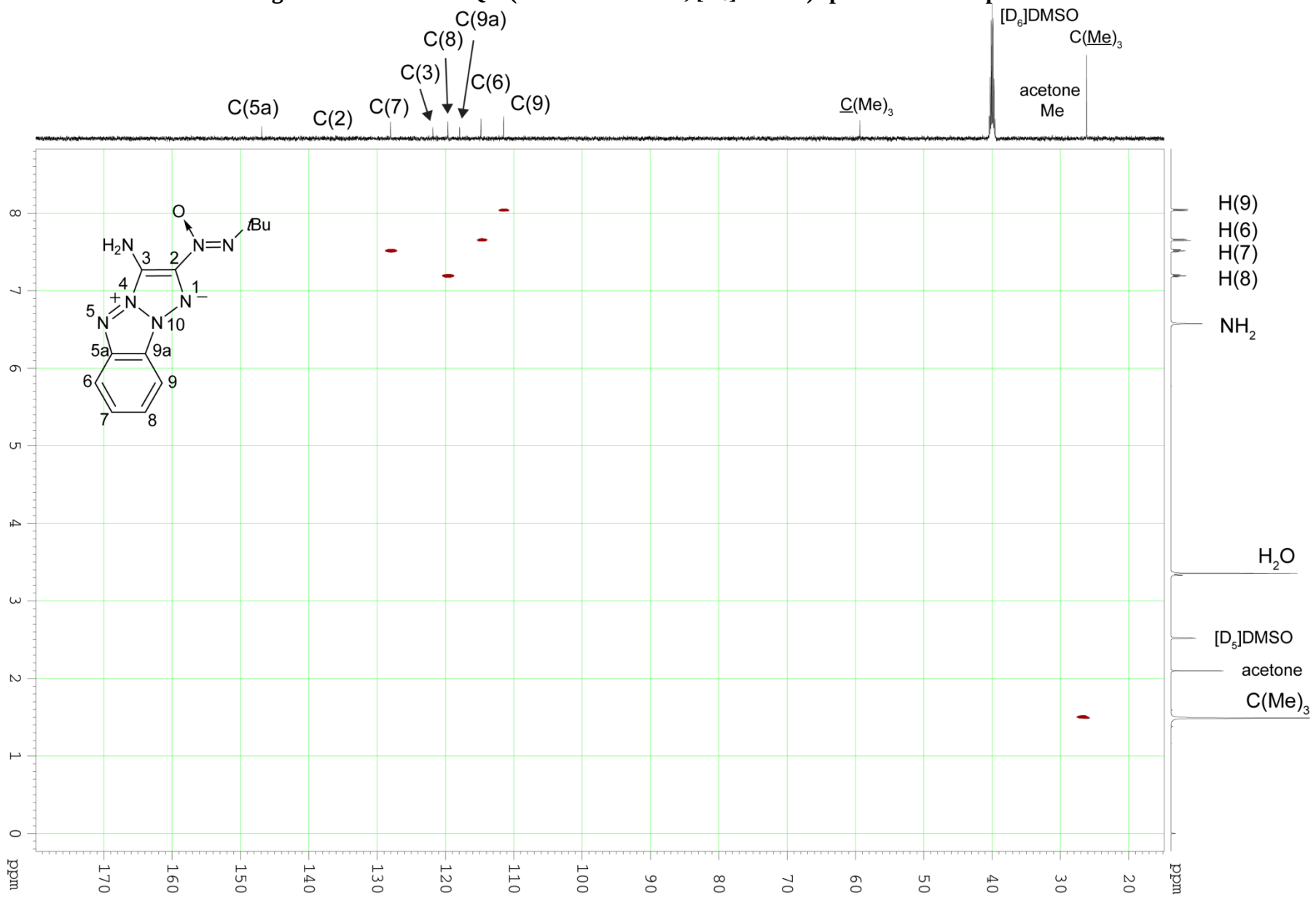
^{14}N NMR (43.4 MHz, [D$_6$]DMSO) of compound 5b



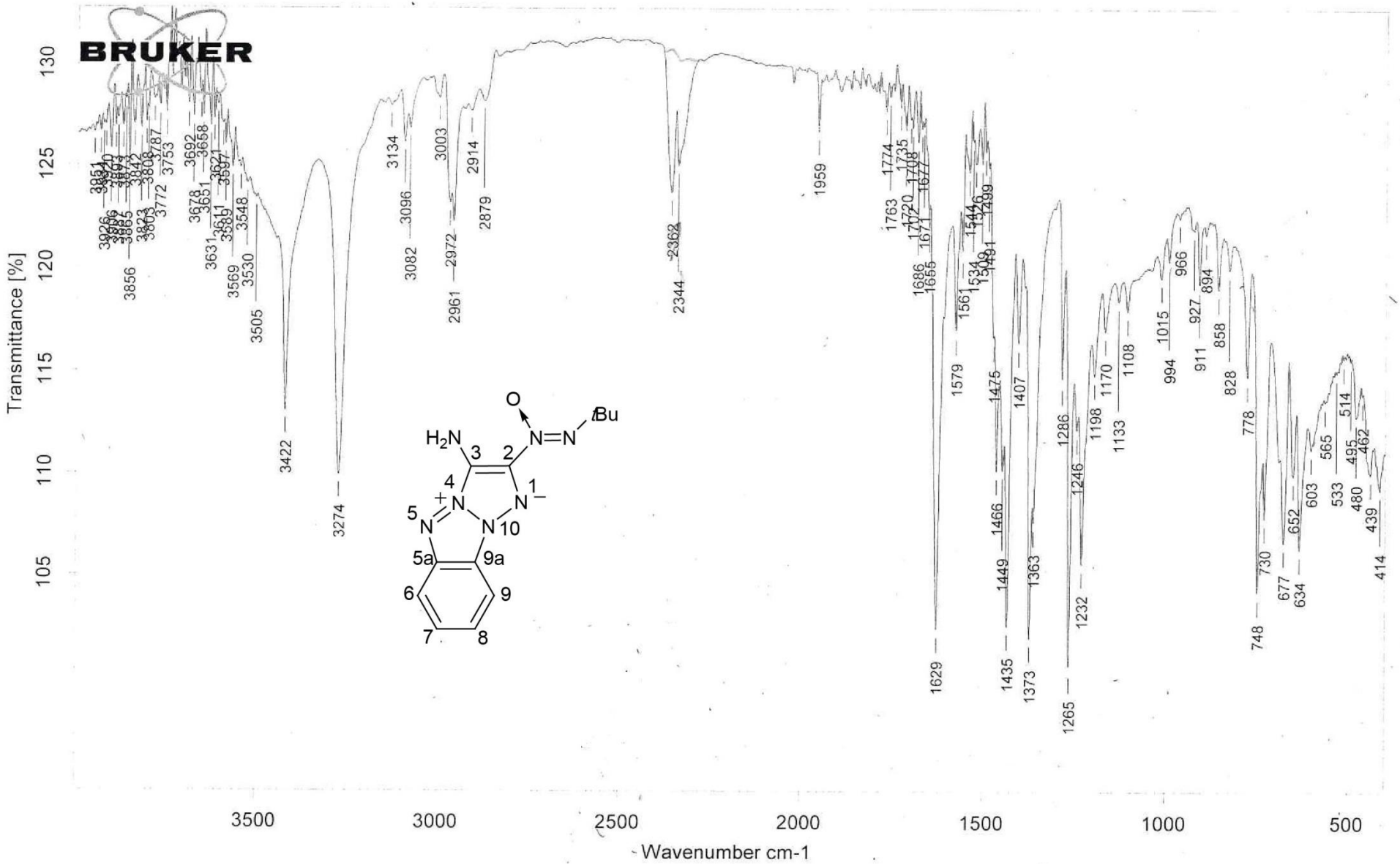
Fragment of ^{1}H-^{13}C HMBC (600.1/150.9 MHz, [D_6]DMSO) spectrum of compound 5b



Fragment of ^{1}H-^{13}C HSQC (600.1/150.9 MHz, [D_6]DMSO) spectrum of compound 5b



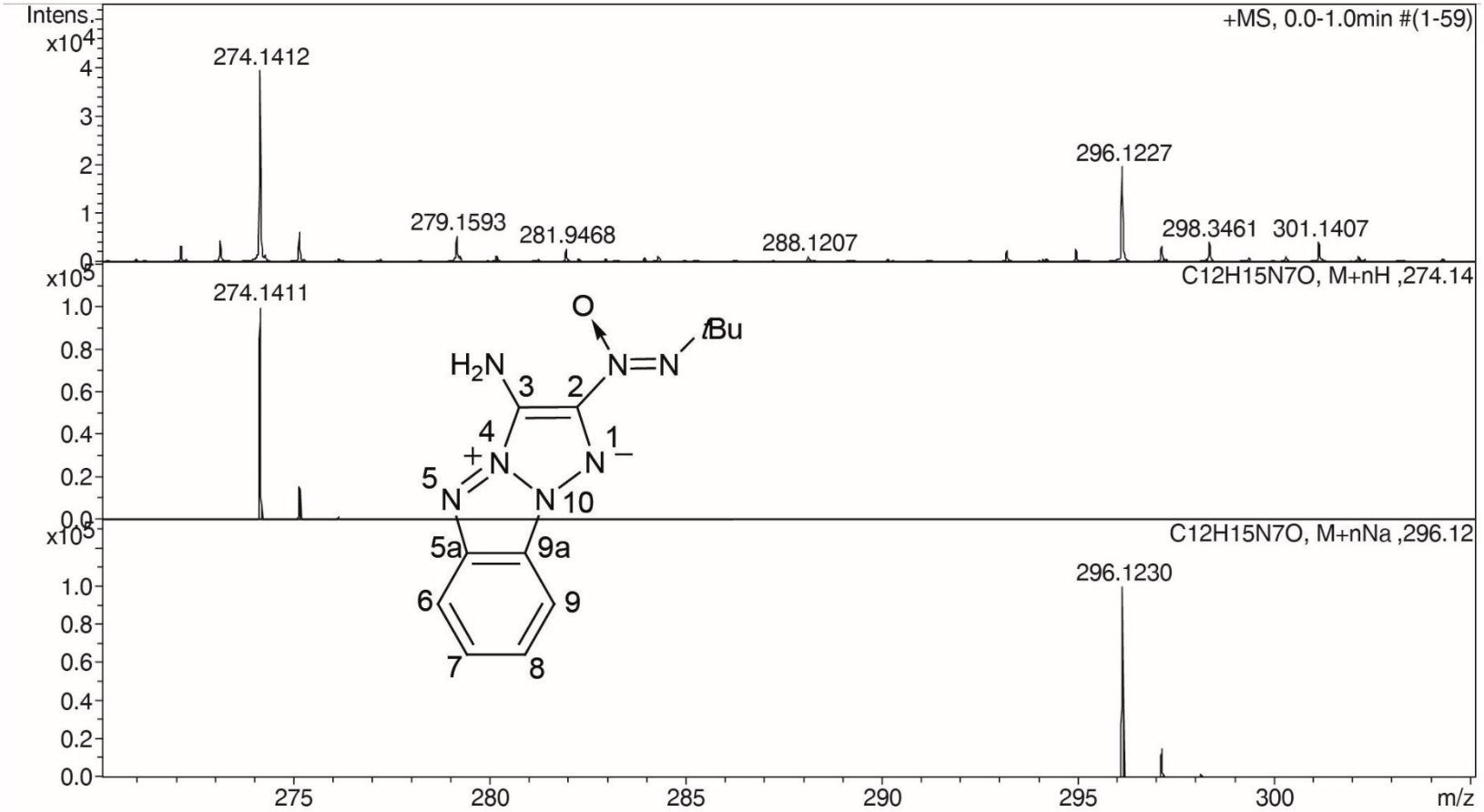
IR of compound 5b



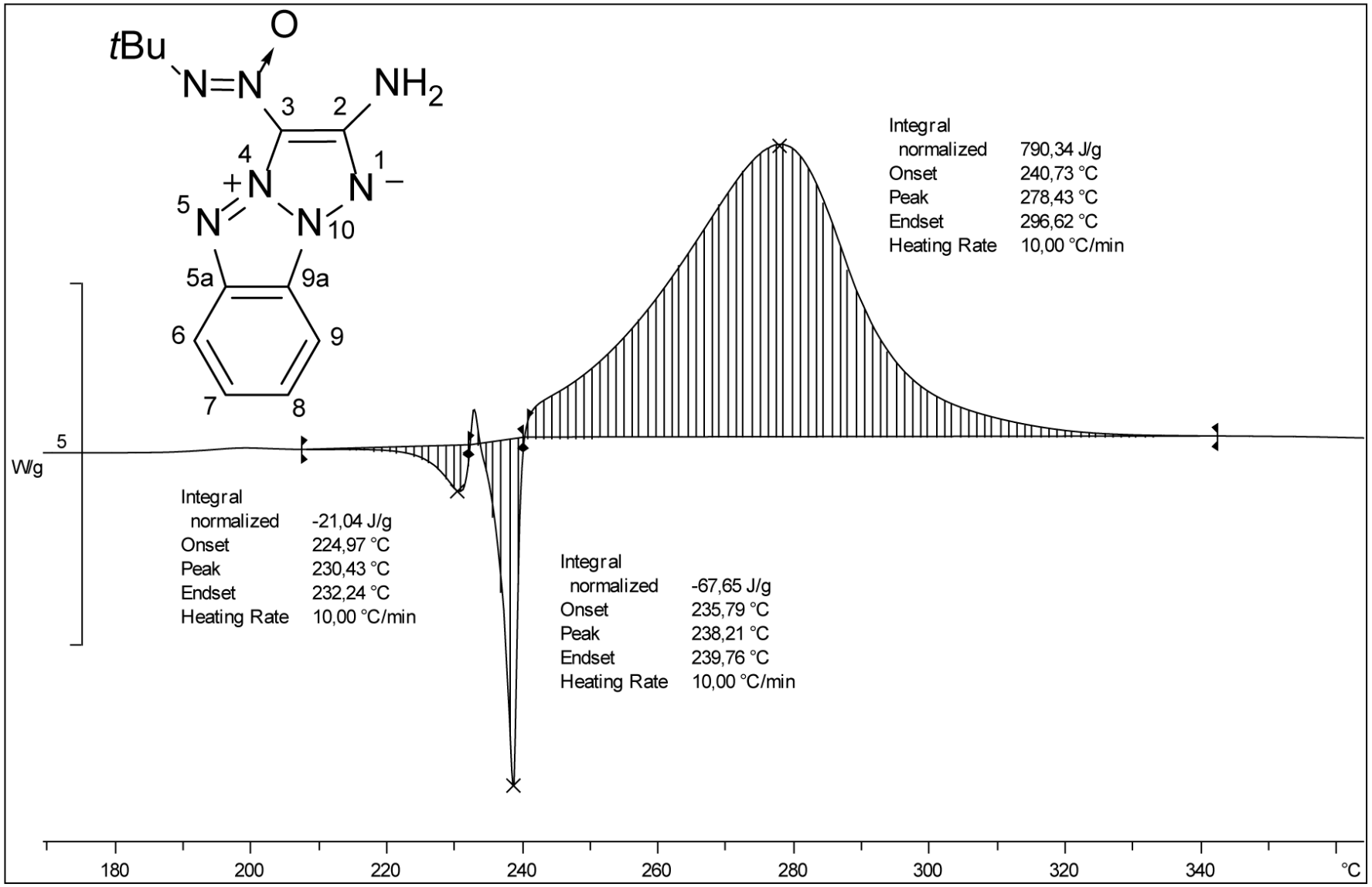
HRMS of compound 5b

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



DSC of compound 5a



DSC of compound 5b