Supporting Information for

Ruthenium-Catalyzed Cycloaddition of Alkynes and Organic Azides

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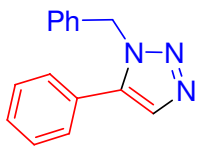
Experimental procedures

Reactions 1-7 were carried out under nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Reactions 8-11 were performed in tightly capped vials flushed with nitrogen. ^{1}H and ^{13}C NMR chemical shifts are relative to TMS. Mass Spectra were collected on a Finnigan TSQ 7000 Spectrometer and LC-MS data were obtained on an Agilent 1100 ESI-MS system.

General procedure for Cp*RuCl(PPh$_3$)$_2$ catalyzed cycloadditions. A mixture of azide, alkyne and Cp*RuCl(PPh$_3$)$_2$ in organic solvent (8-20 mL, 0.07–0.2M in reactants) was stirred at a given temperature for a period of time indicated in the Table 1. The progress of the reaction was monitored by ^{1}H NMR or GC. In most cases the azide was completely consumed at the end of the reaction. The solvent was removed under vacuum and the product was purified by silica gel chromatography. The unreacted alkyne and traces of side products were first eluted out with hexane, followed by 1/1 hexane/ether. The pure 1,5-disubstututed triazole product was then obtained by elution with ether or chloroform.

1-benzyl-5-phenyl-1H-1,2,3-triazole (1a).



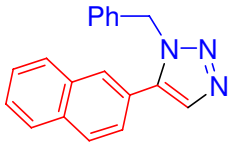
(a) Benzylazide (0.400 g, 3.00 mmol), phenylacetylene (0.500 mL, 4.55 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, benzene; reaction temperature, 80 °C, reaction time, 2 h; yield, 0.56 g (80%).

(b) Benzylazide (0.200 g, 1.50 mmol), phenylacetylene (0.300 mL, 2.73 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, tetrahydrofuran; reaction temperature, 65 °C; reaction time, 3 h; yield, 0.26 g (74%).

(c) Benzylazide (0.100 g, 0.751 mmol), phenylacetylene (0.150 mL, 1.37 mmol), Cp*RuCl(PPh_3)$_2$ (30 mg, 0.038 mmol). Solvent, benzene; reaction temperature, r.t.; reaction time, 24 h; yield, 0.13 g (75%).

^{1}H NMR ($CDCl_3$): δ 5.54 (s, 2H), 7.07 (t, 2H, J = 3.6 Hz), 7.23 – 7.27 (m, 5H), 7.37 – 7.46 (m, 3H), 7.73 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 51.85, 126.93, 127.22, 128.22, 128.92, 129.08, 129.64, 133.26, 133.34, 135.66, 138.26. EI-MS: m/z 236 [M + 1].

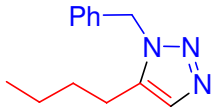
1-benzyl-5-(2-naphthyl)-1H-1,2,3-triazole (2a)



Benzylzaide (0.400 g, 3.00 mmol), 2-ethynylnaphthalene (0.503 g, 3.31 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 4 h; yield, 0.80 g (93%).

^{1}H NMR ($CDCl_3$): δ = 5.55 (s, 2H), 7.10 (t, 2H, J = 3.6 Hz), 7.24 – 7.33 (m, 4H), 7.47 – 7.54 (m, 2H), 7.68 – 7.74 (m, 2H), 7.83 (t, 3H, J = 7.35 Hz). ^{13}C NMR ($CDCl_3$): δ 52.06, 124.21, 125.93, 125.98, 127.16, 127.34, 127.42, 127.96, 128.32, 128.65, 128.72, 128.99, 133.03, 133.38, 133.57, 133.64, 135.81, 138.34. EI-MS: m/z 285 [M^+].

1-benzyl-5-butyl-1H-1,2,3-triazole (3a).



Benzylazide (0.340 g, 2.55 mmol), 1-hexyne (0.580 ml, 5.05 mmol), Cp*RuCl(PPh_3)$_2$ (50 mg, 0.063 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 3 h; yield, 0.45 g (82%).

^{1}H NMR ($CDCl_3$): δ = 0.768 (t, 3H, J = 7.2 Hz), 1.15 – 1.27 (m, 2H), 1.36 – 1.46, (m, 2H), 2.44 (t, 2H, J = 7.8 Hz), 5.41 (s, 2H), 7.07 (t, 2H, J = 3.8 Hz), 7.18 – 7.27 (m, 3H), 7.39 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.16, 22.69, 23.35, 30.42, 52.13, 127.62, 128.78, 129.46, 133.05, 133.11, 135.63, 137.99. EI-MS: m/z 216 [M+1].

1-benzyl-5-(*tert*-butyl)-1H-1,2,3-triazole (4a).

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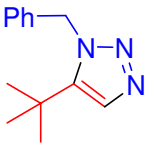
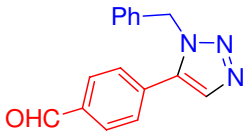


Benzylazide (0.400 g, 3.00 mmol), 3,3-dimethyl-1-butyne (0.556 ml, 4.51 mmol), Cp*RuCl(PPh_3)$_2$ (50 mg, 0.063 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 4 h; yield, 0.54 g (83%).

^{1}H NMR ($CDCl_3$): δ = 0.974 (s, 9H), 5.42 (s, 2H), 6.77 (d, 2H, J = 7.0 Hz), 6.87 – 7.00 (m, 3H), 7.14 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 29.72, 29.99, 52.60, 126.32, 127.68, 128.61, 131.26, 131.37, 136.37, 146.00. EI-MS: m/z 216 [M+1].

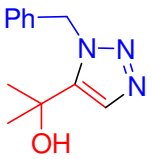
4-(1-benzyl-1H-1,2,3-triazol-5-yl)benzaldehyde (5a).



Benzylazide (0.200 g, 1.50 mmol), 4-ethynylbenzaldehyde (0.200 g, 1.54 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 2 h; yield, 0.32 g (81%).

^{1}H NMR ($CDCl_3$): δ 5.59 (s, 2H), 7.06 (t, 2H, J = 3.3 Hz), 7.27 (dd, 4H, J = 3.1 Hz), 7.43 (d, 2H, J = 8 Hz), 7.81 (s, 1H), 7.91 (d, 2H, 8.2 Hz), 10.05 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 52.33, 127.13, 128.52, 129.08, 129.48, 129.54, 130.20, 132.84, 133.91, 133.98, 135.17, 136.76, 137.04. EI-MS: m/z 264 [M+1].

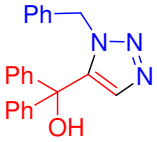
2-(1-benzyl-1H-1,2,3-triazol-5-yl)propan-2-ol (6a).



Benzylazide (0.400 g, 3.00 mmol), 2-methyl-3-butyn-2-ol (0.290 ml, 3.00 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 2.5 h; yield, 0.63 g (96%).

^{1}H NMR ($CDCl_3$): δ 1.43 (s, 6H), 5.23 (s**,** 1H), 5.74 (s, 2H), 7.11 – 7.26 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 30.90, 52.94, 67.63, 127.82, 128.15, 128.91, 130.58, 130.66, 136.62, 144.16. EI-MS: m/z 218 [M+1].

(1-benzyl-1H-1,2,3-triazol-5-yl)diphenylmethanol (7a).



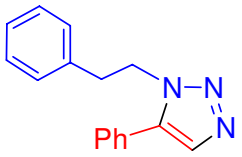
(a) Benzylazide (0.400 g, 3.00 mmol), 1,1-diphenyl-2-propyn-1-ol (0.688 g, 3.31 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 4 h; yield, 0.89 g (87%).

(b) Benzylazide (0.200 g, 1.50 mmol), 1,1-diphenyl-2-propyn-1-ol (0.344 g, 1.65 mmol), Cp*RuCl(PPh_3)$_2$ (60 mg, 0.75 mmol). Solvent, benzene; reaction temperature, r.t.; reaction time, 24 h; yield, 0.43 g (83%).

(c) Benzylazide (0.200 g, 1.50 mmol), 1,1-diphenyl-2-propyn-1-ol (0.344 g, 1.65 mmol), Cp*RuCl(PPh_3)$_2$ (12 mg, 0.015 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 4 h; yield, 0.39 g (75%). The reaction was performed under air.

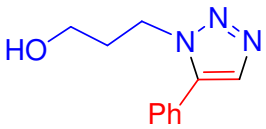
^{1}H NMR ($CDCl_3$): δ 4.14 (s, 1H), 5.36 (s, 2H), 6.82 (s, 1H), 7.02 – 7.05 (m, 2H), 7.13 –7.30 (m, 13H). ^{13}C NMR ($CDCl_3$): δ 53.04, 127.00, 127.88, 128.17, 128.42, 134.92, 135.01, 135.32, 142.34, 143.94. EI-MS: m/z 342 [M+1].

1-phenethyl-5-phenyl-1H-1,2,3-triazole (8a)



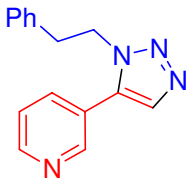
Phenethyl azide (148 mg, 1 mmol), phenylacetylene (113 mg, 1.1mmol), Cp*RuCl(PPh_3)$_2$ (8 mg, 0.01 mmol, 1 mol%). Solvent: THF, 10 mL, 60 ^{o}C, 2 h. Off-white product obtained in 89% yield (221 mg). ^{1}H NMR (DMSO- d_6): δ 4.31 (t, J = 8.1 Hz, 2H), 5.52 (t, J = 8.1 Hz, 2H), 7.09 (m, 2H), 7.21 – 7.29 (m, 5H), 7.37 – 7.46 (m, 3H), 7.71 (s, 1H). ^{13}C NMR (DMSO- d_6): δ 36.6, 57.3, 127.0, 127.2, 128.6, 128.9, 129.3, 129.7, 133.42, 133.49, 137.6, 139.3. ESI-MS: m/z 250, [M+H].

3-(5-phenyl-1H-1,2,3-triazol-1-yl)propan-1-ol (9a).



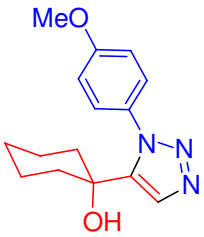
3-Azidopropanol (101 mg, 1 mmol), phenylacetylene (113 mg, 1.1 mmol), Cp*RuCl(PPh_3)$_2$ (8 mg, 0.01 mmol, 1 mol%). Solvent: THF, 10 mL, 60 ^{o}C, 2 h. White microcrystalline product obtained in 82% yield (167 mg). ^{1}H NMR (DMSO- d_6): δ 1.91 (m, 2H), 3.53 (t, J = 7.1 Hz, 2H), 3.81 (t, J = 8.2 Hz, 2H), 7.22 – 7.36 (m, 5H), 7.67 (s, 1H). ^{13}C NMR (DMSO- d_6): δ 31.1, 45.5, 61.2, 127.5, 129.4, 128.6, 129.1, 133.3, 142.2. ESI-MS: m/z 204, [M+H].

3-(1-phenethyl-1H-1,2,3-triazol-5-yl)pyridine (10a)



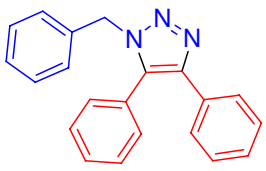
Phenethyl azide (148 mg, 1 mmol), 3-propynyl pyridine (111 mg, 1.1 mmol), Cp*RuCl(PPh_3)$_2$ (8 mg, 0.02 mmol, 2 mol%). Solvent: dioxane, 10 mL, 60^{o}C, 12 h. Product obtained as off-white powder in 80% yield (200 mg). ^{1}H NMR ($CDCl_3$): δ = 3.23 (t, 2H, J = 6.7 Hz), 4.56 (t, 2H, J = 6.7 Hz), 6.84 (d, 2H), 7.21 (m, 3H), 7.30 (m, 1H), 7.42 (m, 1H), 7.69 (s, 1H), 8.22 (s, 1H), 8.69 (br. s, 1H). ^{13}C NMR ($CDCl_3$): δ 36.5, 49.4, 122.9, 123.4, 126.9, 128.53, 128.59, 133.2, 135.0, 136.0, 136.6, 148.9, 150.1. ESI-MS: m/z 251, [M+H].

1-(1-(4-methoxyphenyl)-1H-1,2,3-triazol-5-yl)cyclohexanol (11a)



4-Azido anisole (149 mg, 1 mmol), 1-ethynylcyclohexanol (136 mg, 1.1mmol), Cp*RuCl(PPh_3)$_2$ (16 mg, 0.02 mmol, 2 mol%). Solvent: dioxane, 10 mL, 60^{o}C, 6 h. Slightly yellow product obtained in 94% yield (257mg). ^{1}H NMR ($CDCl_3$): δ = 1.24 (m,1H), 1.46-1.59 (m, 5H), 1.79 (m, 4H), 2.49 (br. s, 1H), 3.89 (s, 3H), 6.9 (d, 2H, J = 7.2 Hz), 7.43 (d, 2H, J = 7.2 Hz), 7.63 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 21.6, 25.0, 37.1, 55.6, 68.8, 114.0, 128.5, 130.5, 131.1, 144.5, 160.5. ESI-MS: m/z 274, [M+H].

1-benzyl-4,5-diphenyl-1H-1,2,3-triazole (12).



Benzylazide (0.400 g, 3.00 mmol), diphenylacetylene (0.588 g, 3.30 mmol), Cp*RuCl(PPh_3)$_2$ (25 mg, 0.031 mmol). Solvent, benzene; reaction temperature, 80 °C; reaction time, 2 h; yield, 0.75 g (80 %).

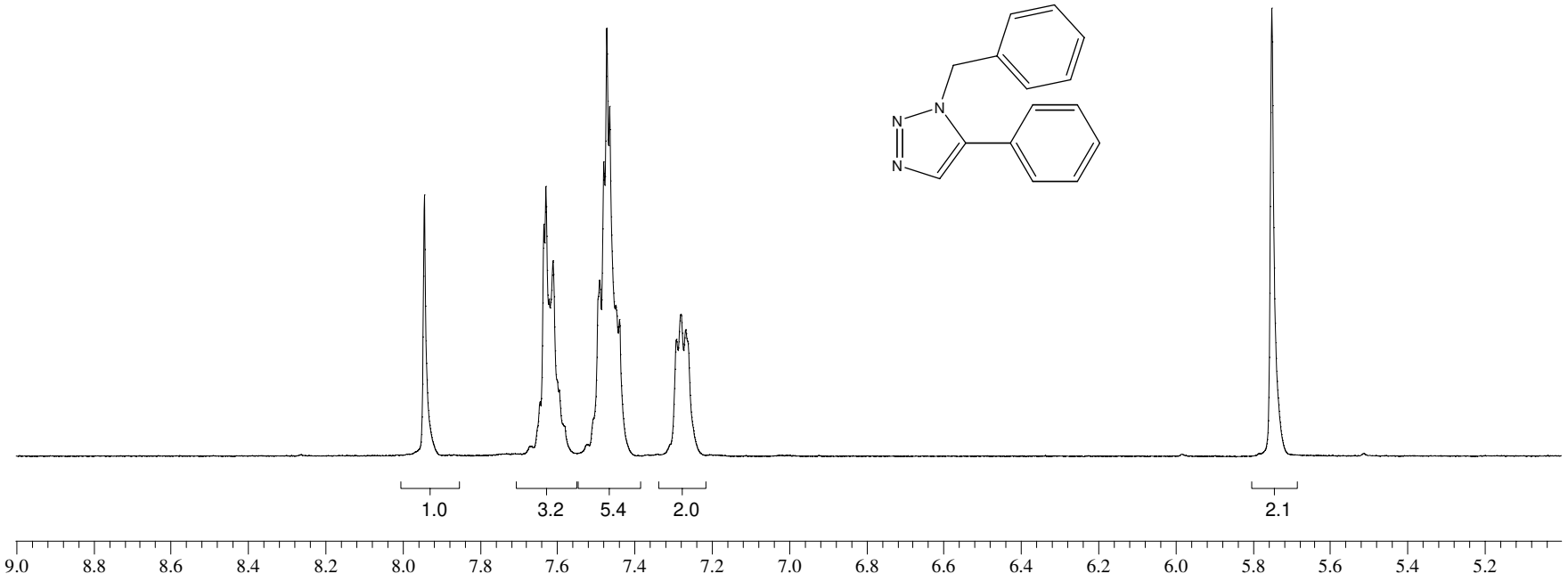
^{1}H NMR ($CDCl_3$): δ = 5.41 (s, 2H), 7.02 (t, 2H, J = 3.5 Hz,), 7.13 – 7.16 (m, 2H), 7.24 – 7.26 (m, 7H), 7.39 – 7.44 (m, 3H), 7.46 – 7.58 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 52.15, 126.83, 127.61, 127.80, 127.98, 128.26, 128.56, 128.81, 129.29, 129.80, 130.22, 131.05, 134.00, 135.49, 144.64. EI-MS: m/z 312 [M+1].

Ru(OAc)$_2$(PPh$_3$)$_2$ catalyzed reactions. A mixture of benzylazide, phenylacetylene and Ru(OAc)$_2$(PPh_3)$_2$ was refluxed in 20 mL of benzene for 4 h. The progress of the reaction was monitored by ^{1}H NMR. The azide was consumed completely at the end of the reaction, as confirmed by NMR. The solvent was removed under reduced pressure and the product was purified by silica gel column chromatography. The unreacted phenylacetylene and the side products were first eluted out with hexane, and 2/1 hexane/ether. The pure 1,4-substututed triazole was then obtained by elution with 1/1 hexane/ether.

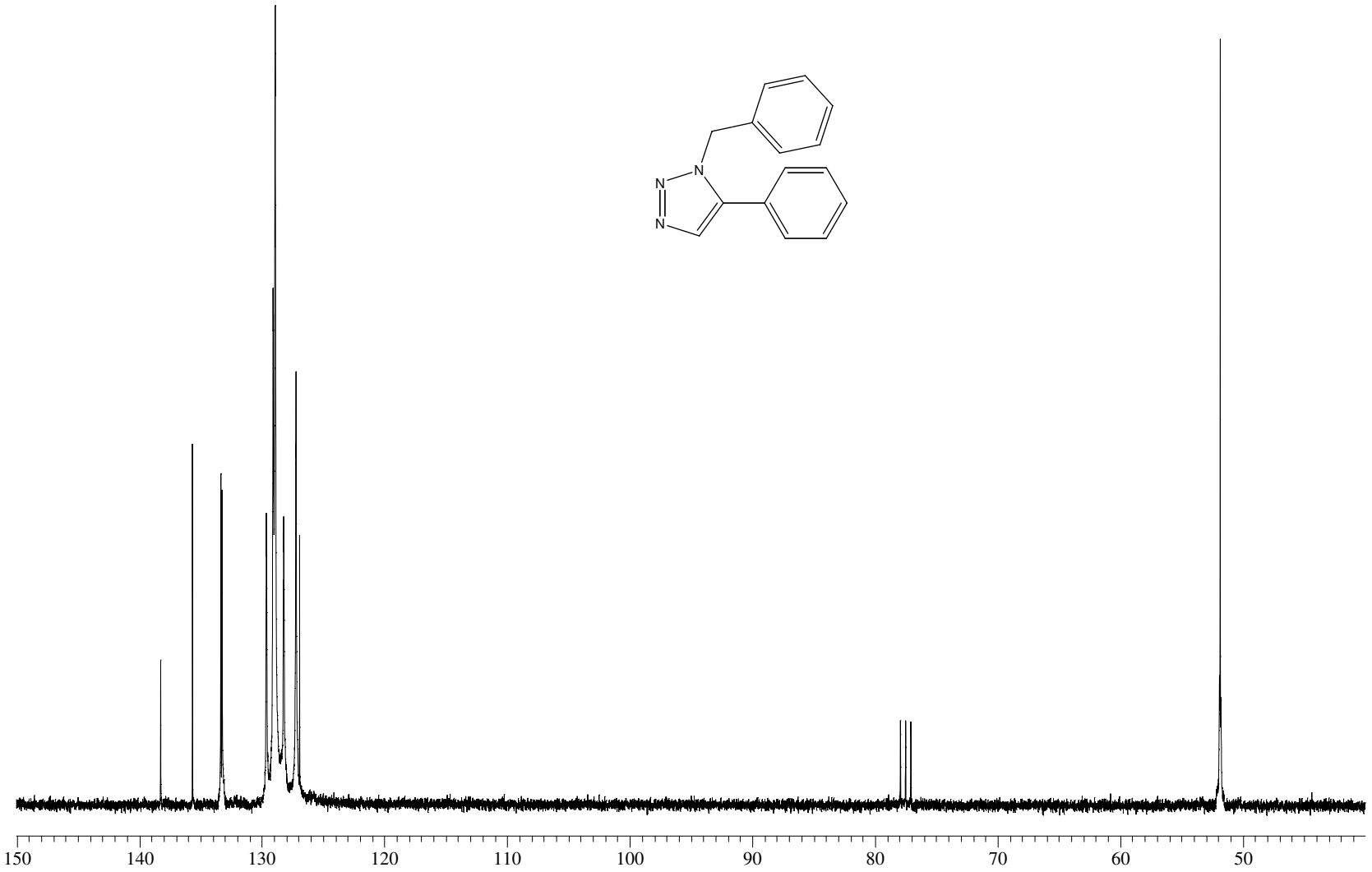
CpRu(PPh$_3$)$_2$Cl catalyzed reactions. A mixture of benzylazide (0.200 g, 1.50 mmol), phenylacetylene (0.250 mL, 2.25 mmol) and CpRu(PPh_3)$_2$Cl (54.54 mg, 0.0751 mmol) was refluxed in 20 mL of benzene for 8 h. The progress of the reaction was monitored by ^{1}H NMR. The azide was consumed completely at the end of the reaction, as confirmed by NMR. The solvent was removed under vacuum and the product was purified by silica gel column chromatography. The unreacted phenylacetylene and the side products were first eluted out with hexane, and 2/1 hexane/ether. The 1:5.8 mixed 1,4-/1,5- disubstututed triazoles were then obtained by elution with 1/1 hexane/ether.

Selected NMR spectra of 1, 5- and 1,4-disubstituted traizoles.

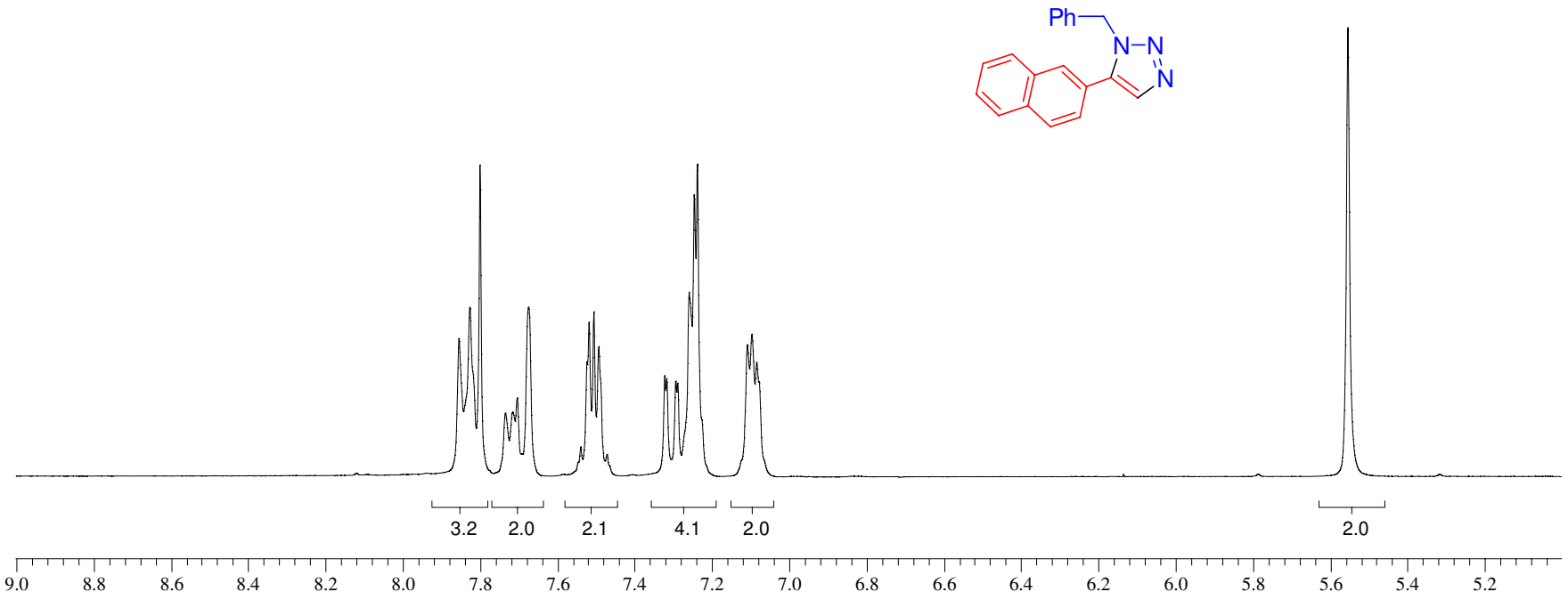
The ^{1}H NMR spectrum of **1a** in $CDCl_3$.



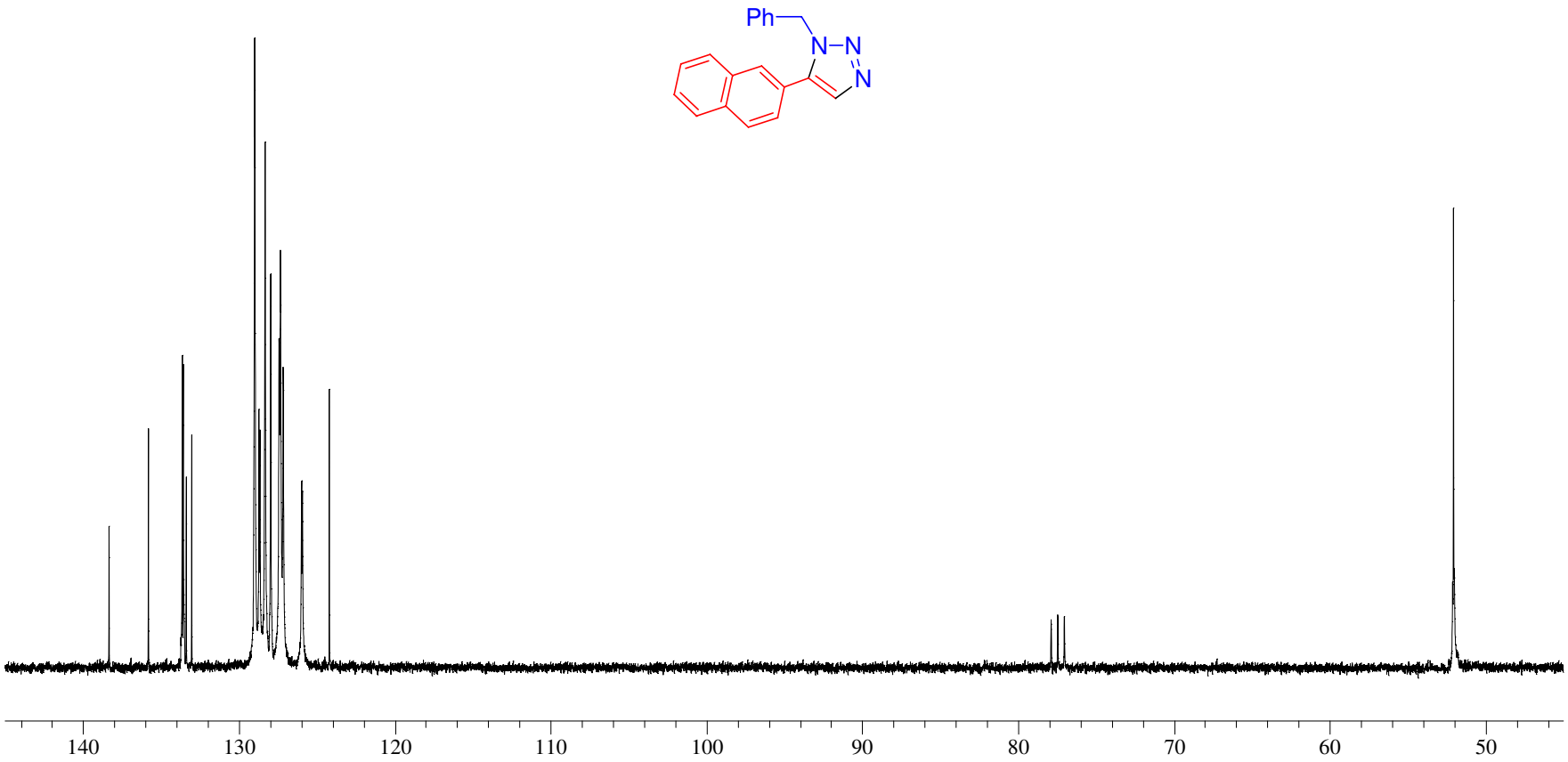
The ^{13}C NMR spectrum of **1a** in $CDCl_3$.



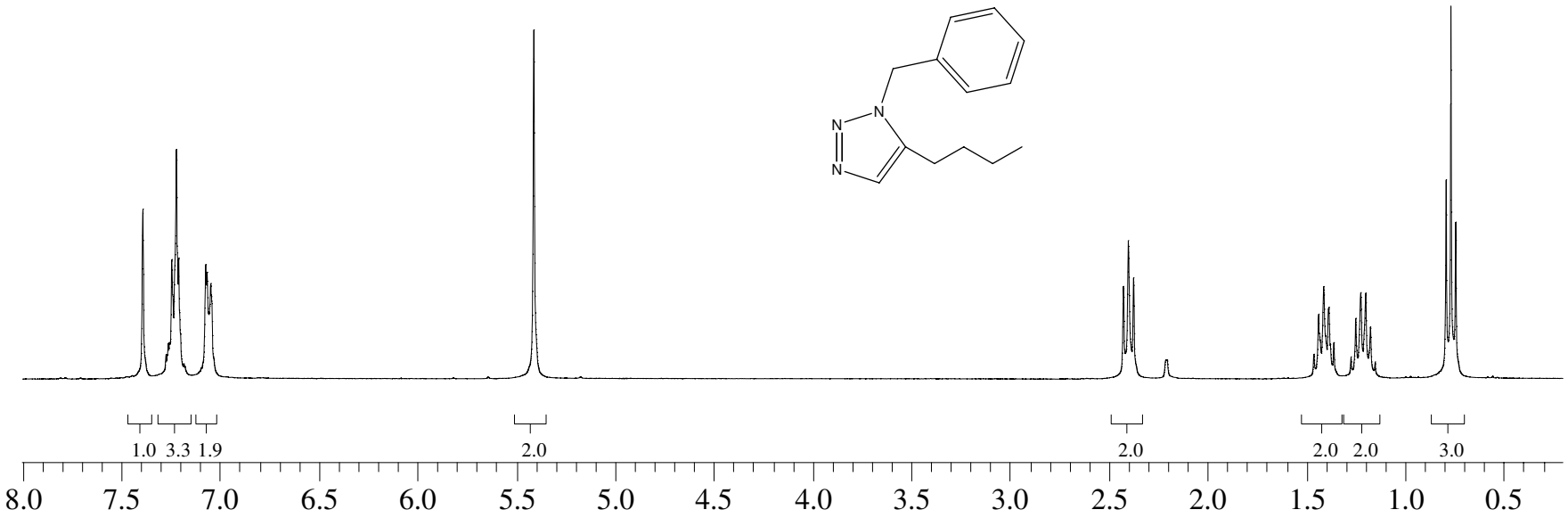
The ^{1}H NMR spectrum of **2a** in $CDCl_3$.



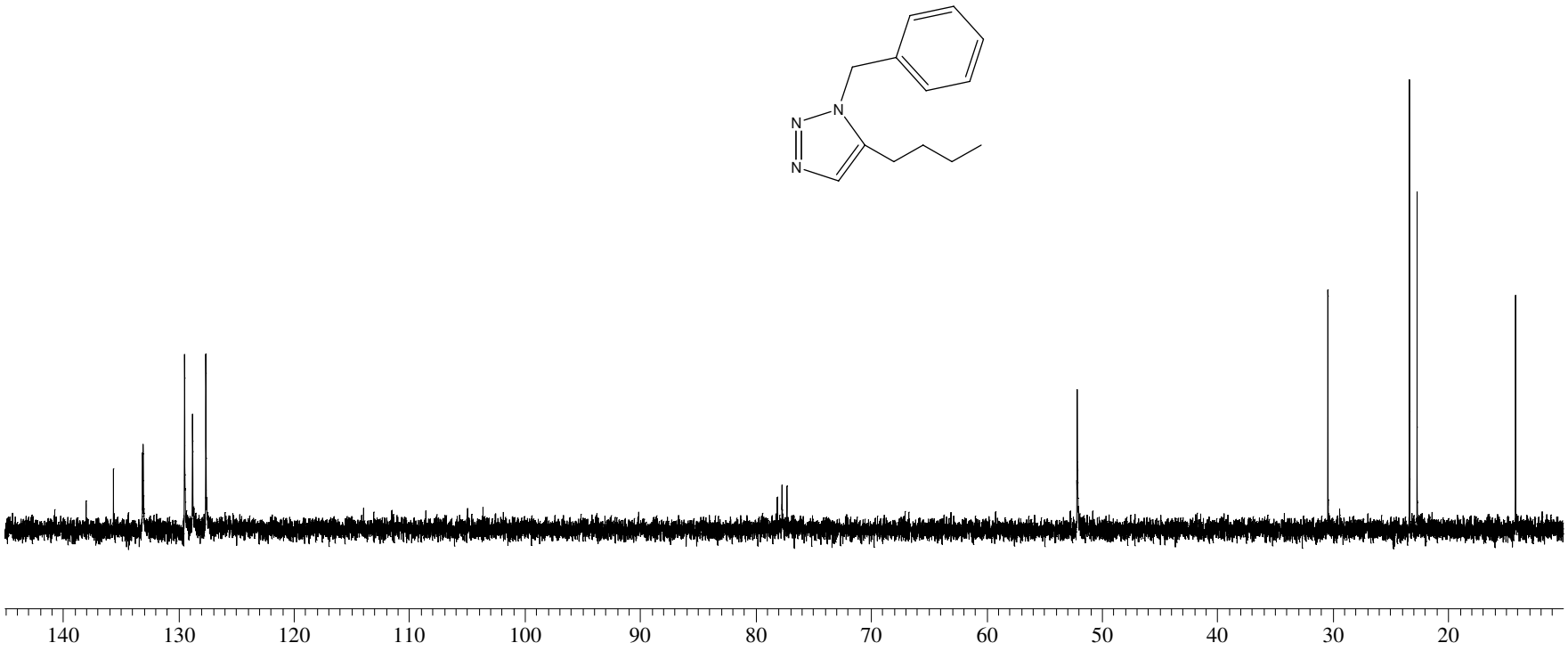
The ^{13}C NMR spectrum of **2a** in $CDCl_3$.



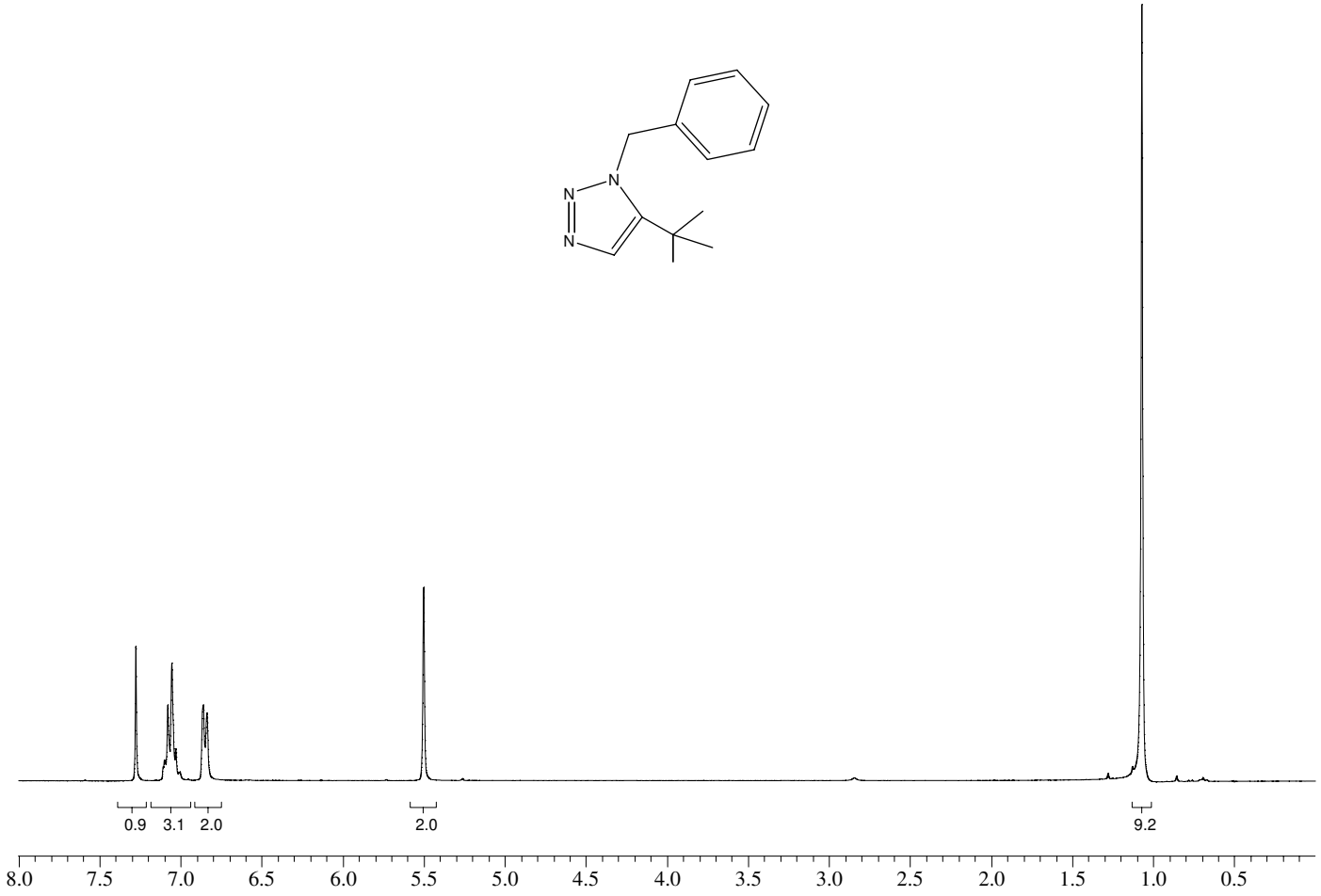
The ^{1}H NMR spectrum of **3a** in $CDCl_3$.



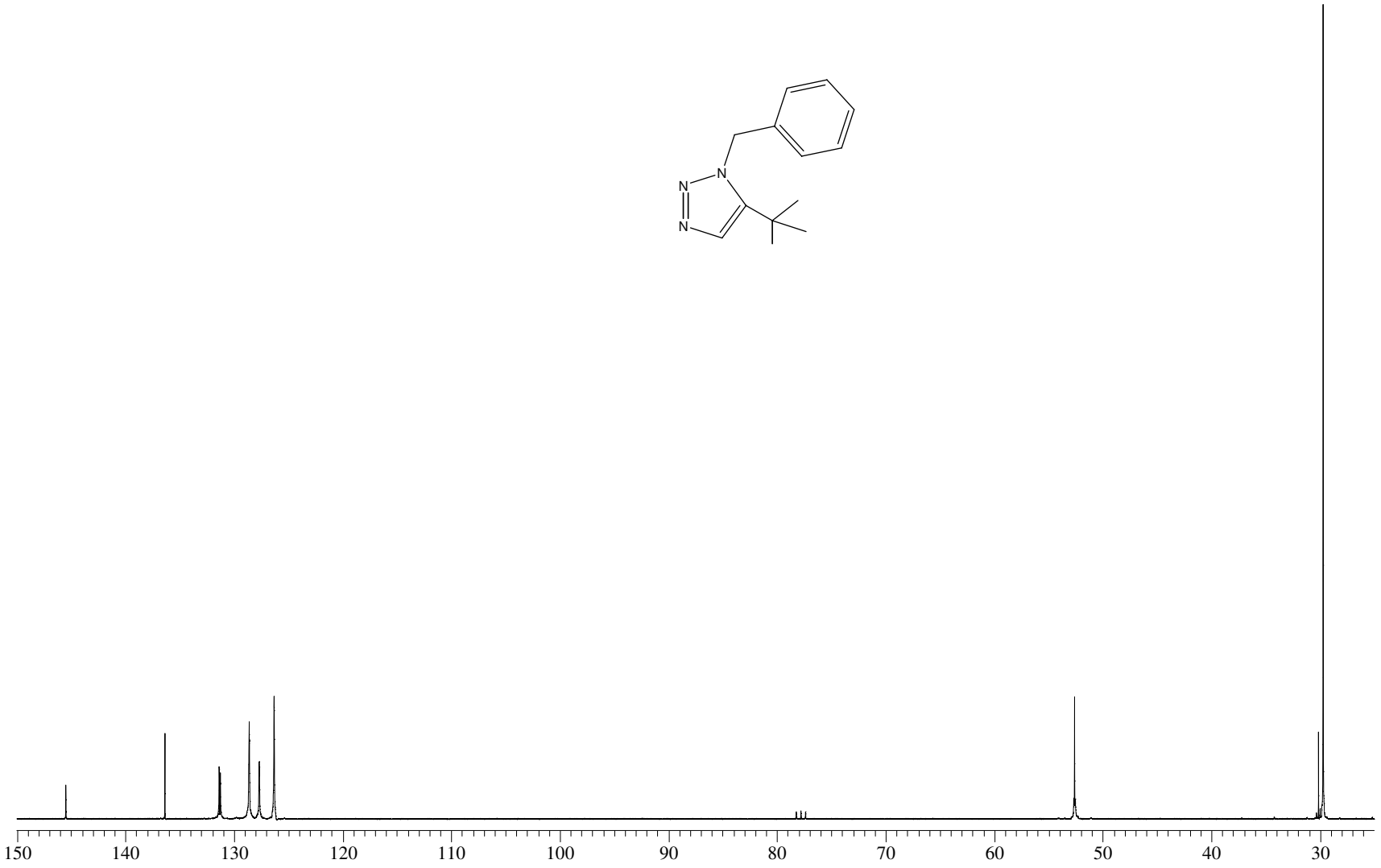
The ^{13}C NMR spectrum of **3a** in $CDCl_3$.



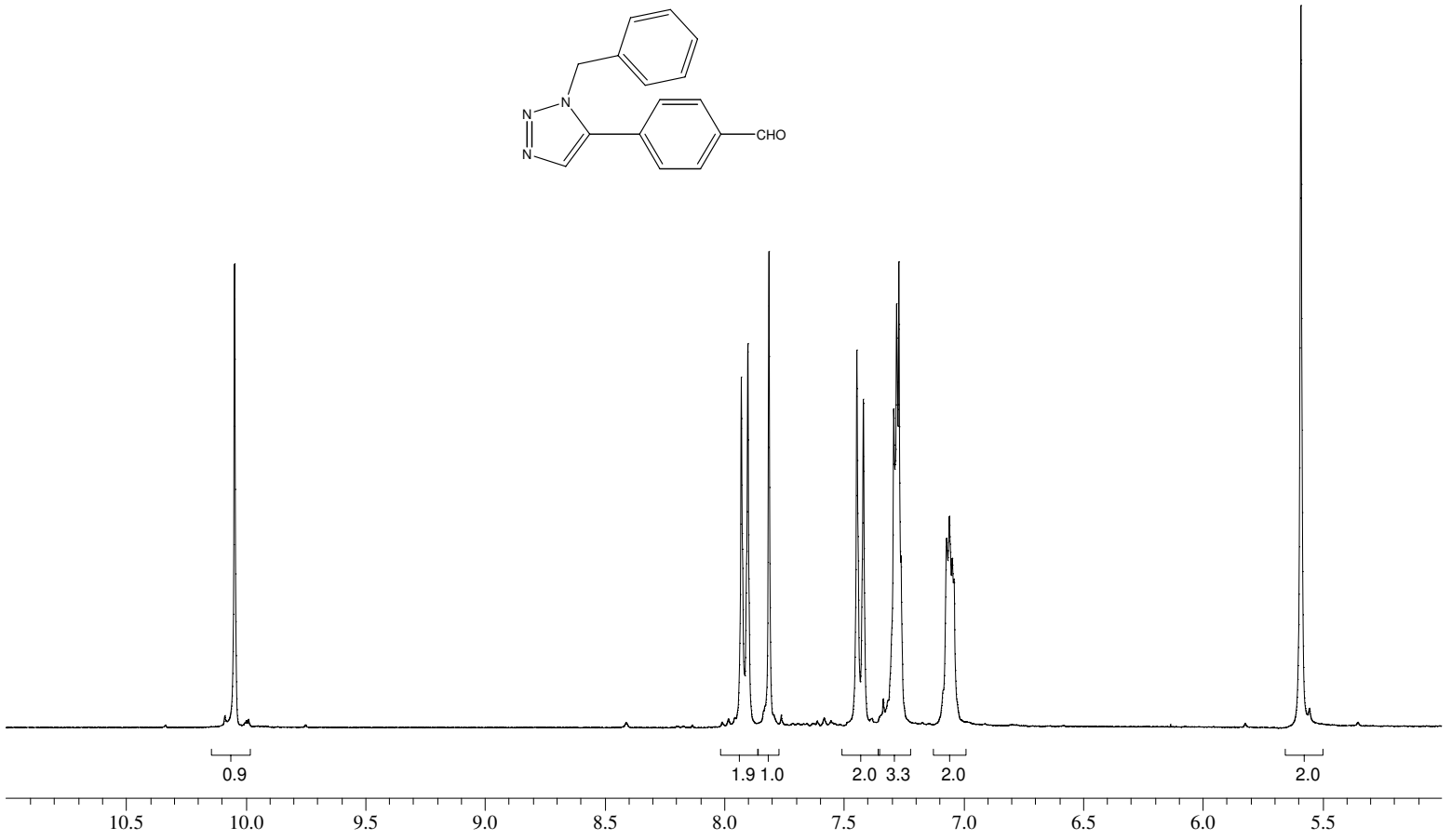
The ^{1}H NMR spectrum of **4a** in $CDCl_3$.



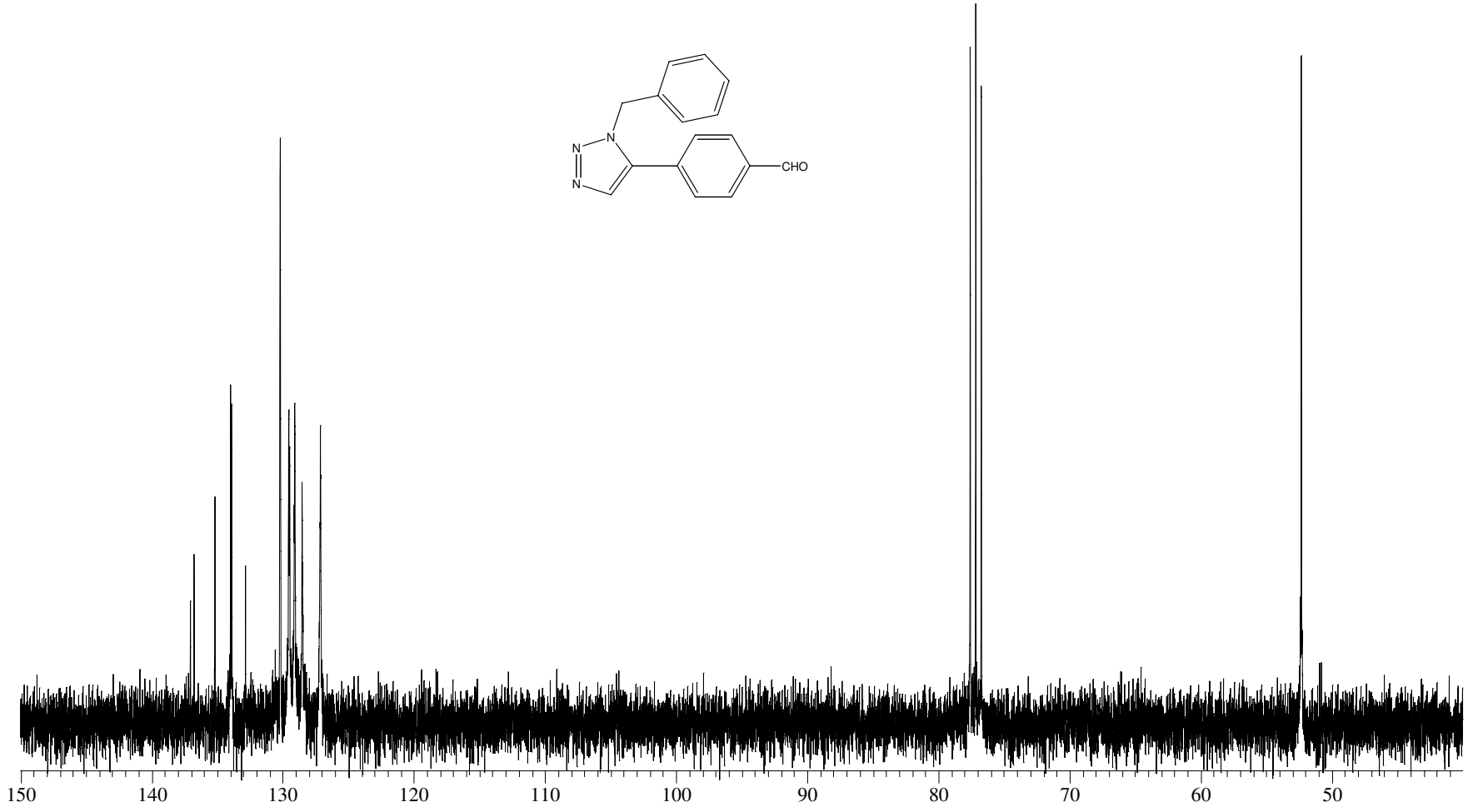
The ^{13}C NMR spectrum of **4a** in $CDCl_3$.



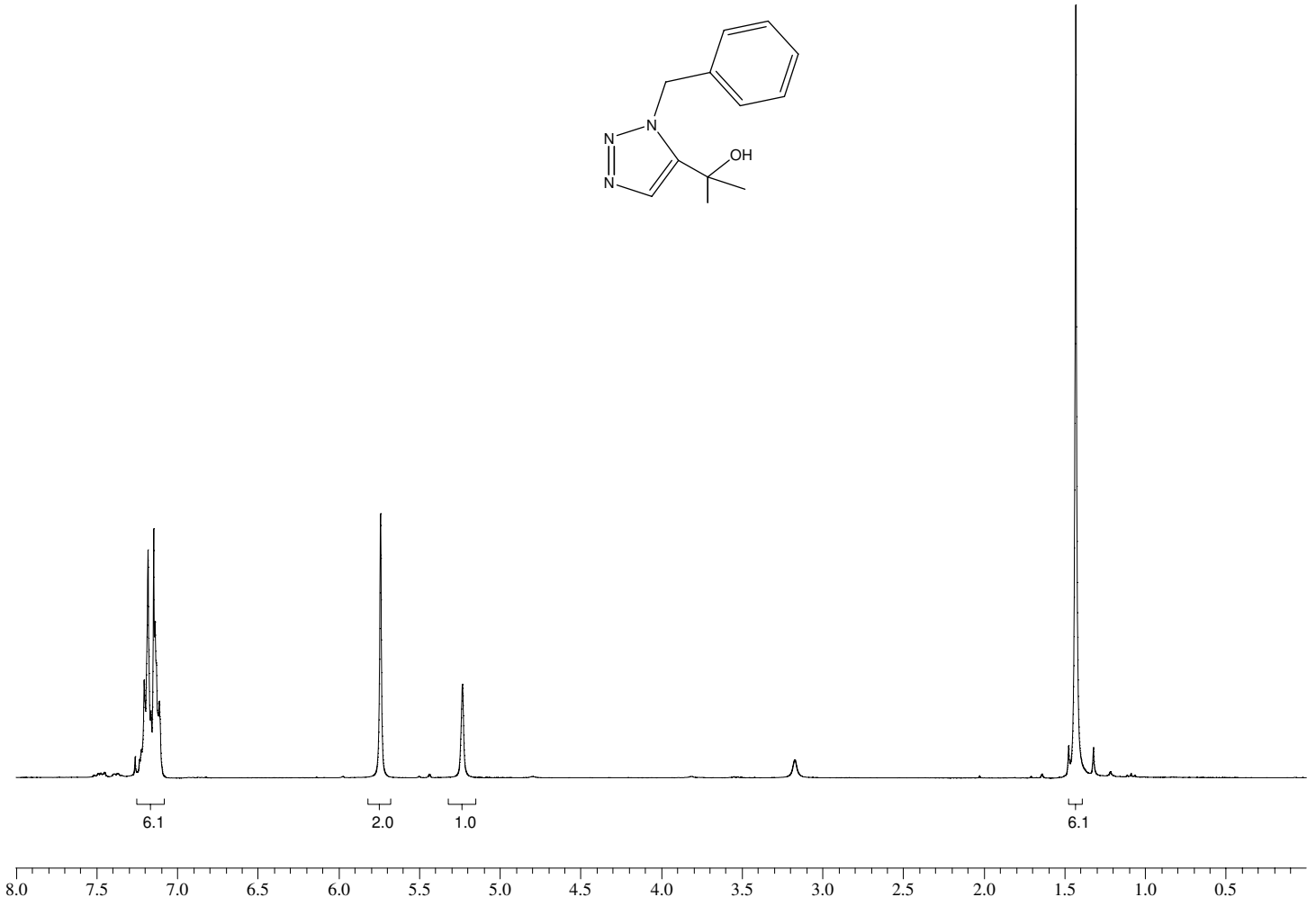
The ^{1}H NMR spectrum of **5a** in $CDCl_3$.



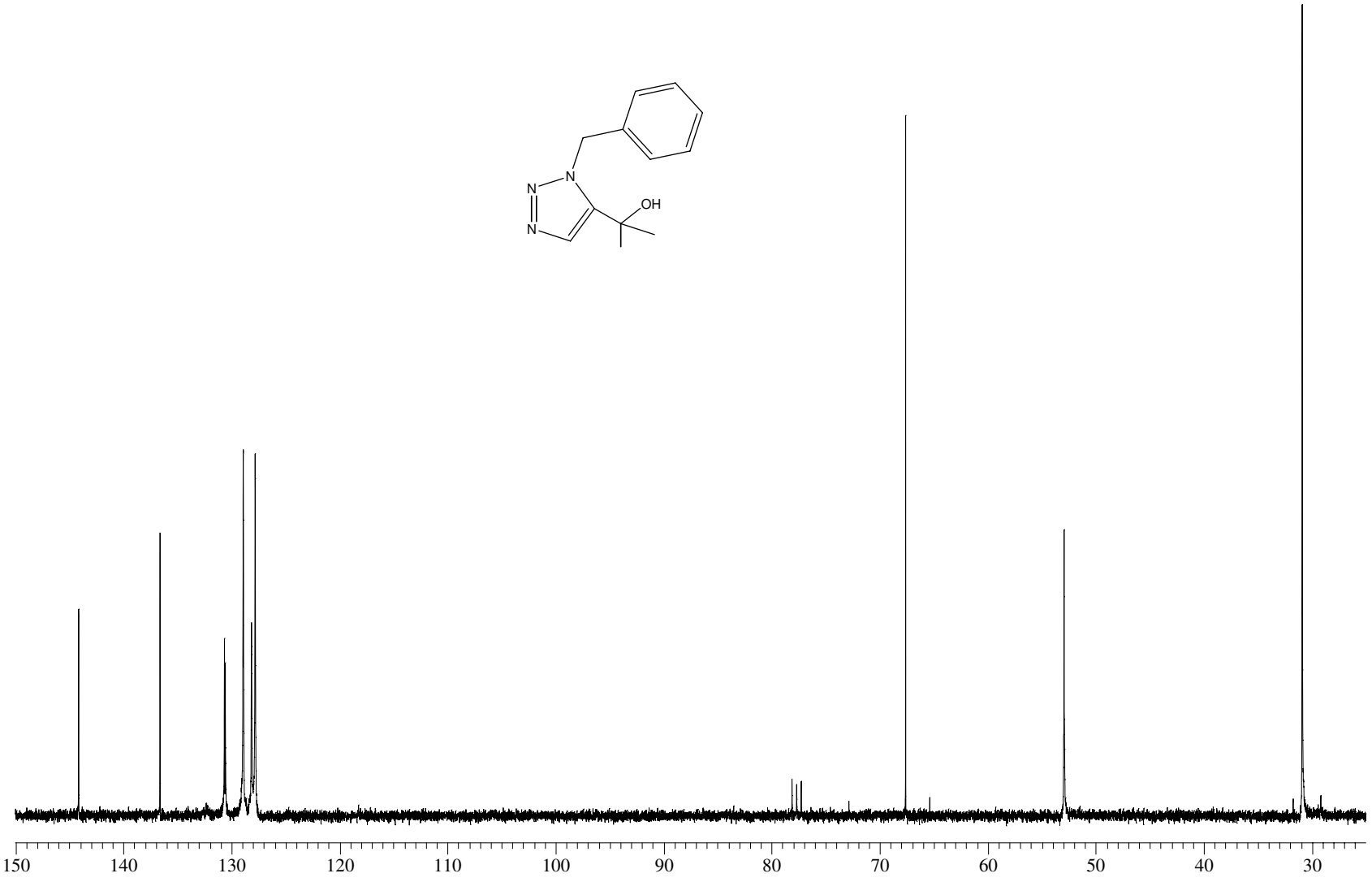
The ^{13}C NMR spectrum of **5a** in $CDCl_3$.



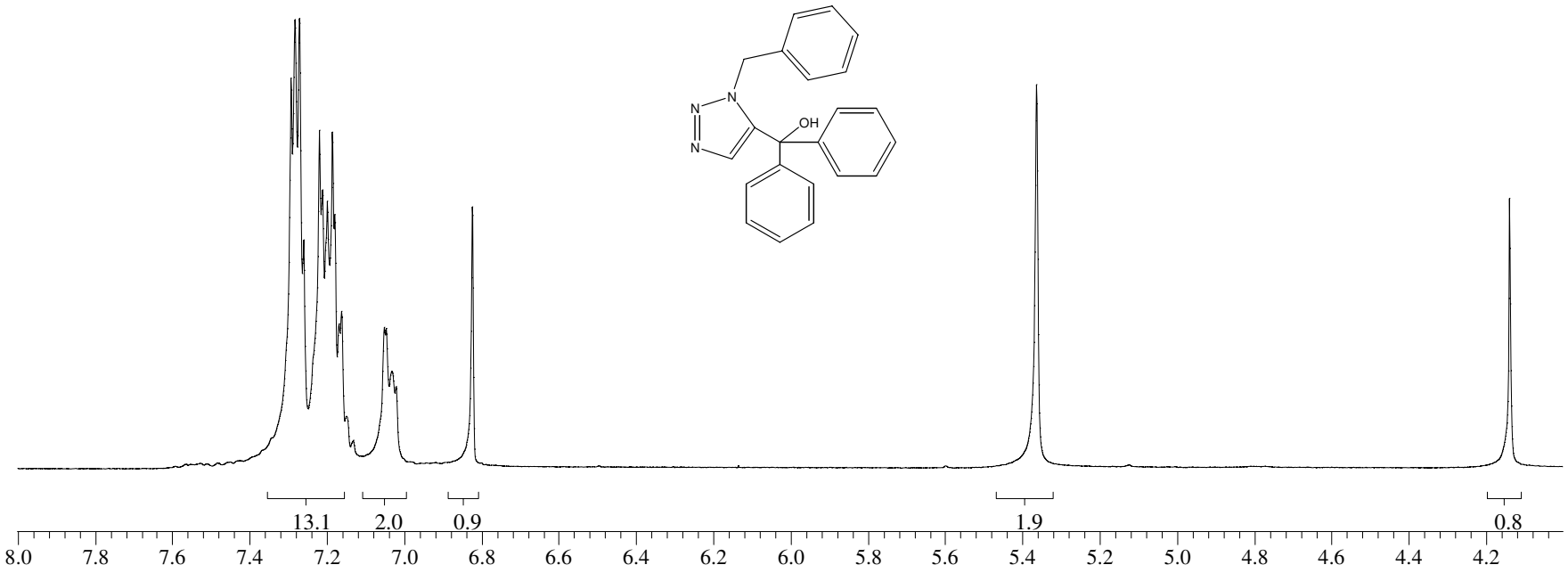
The ^{1}H NMR spectrum of **6a** in $CDCl_3$.



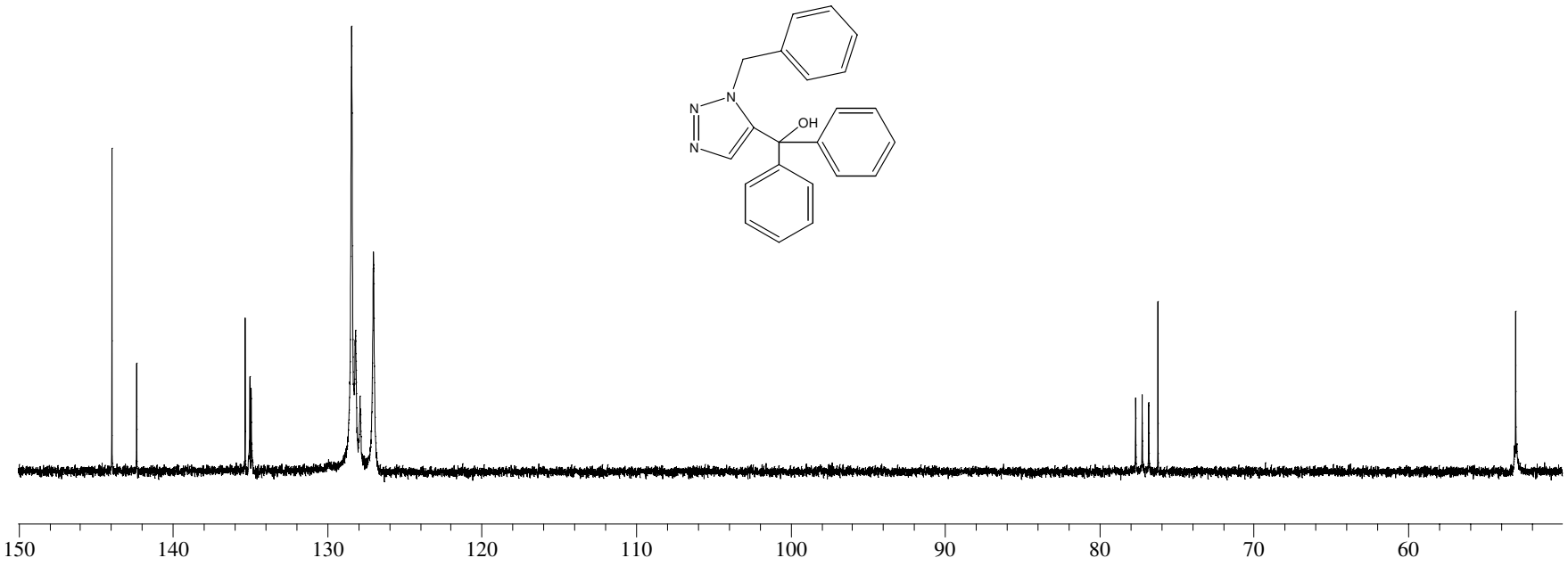
The ^{13}C NMR spectrum of **6a** in $CDCl_3$.



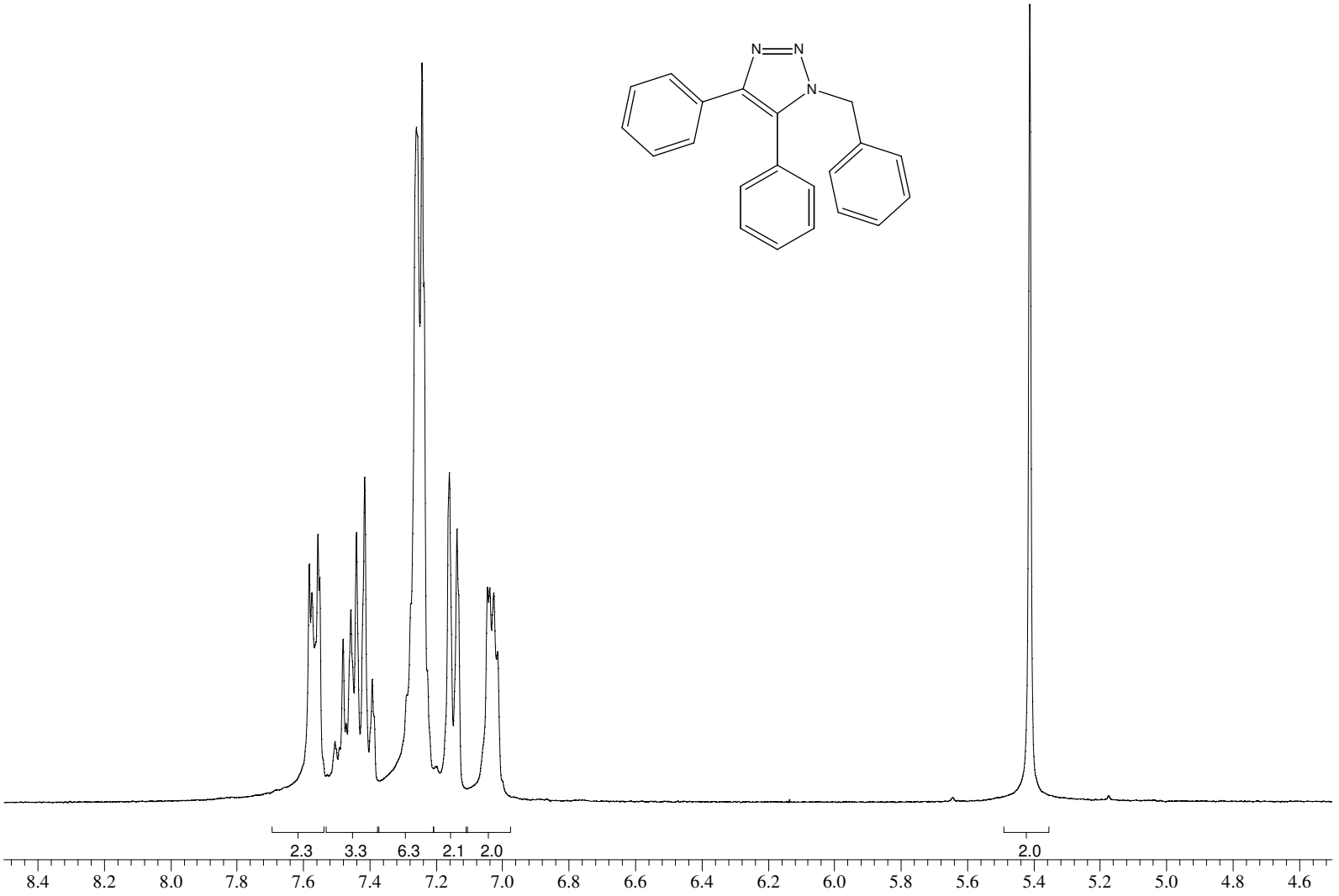
The ^{1}H NMR spectrum of **7a** in $CDCl_3$.



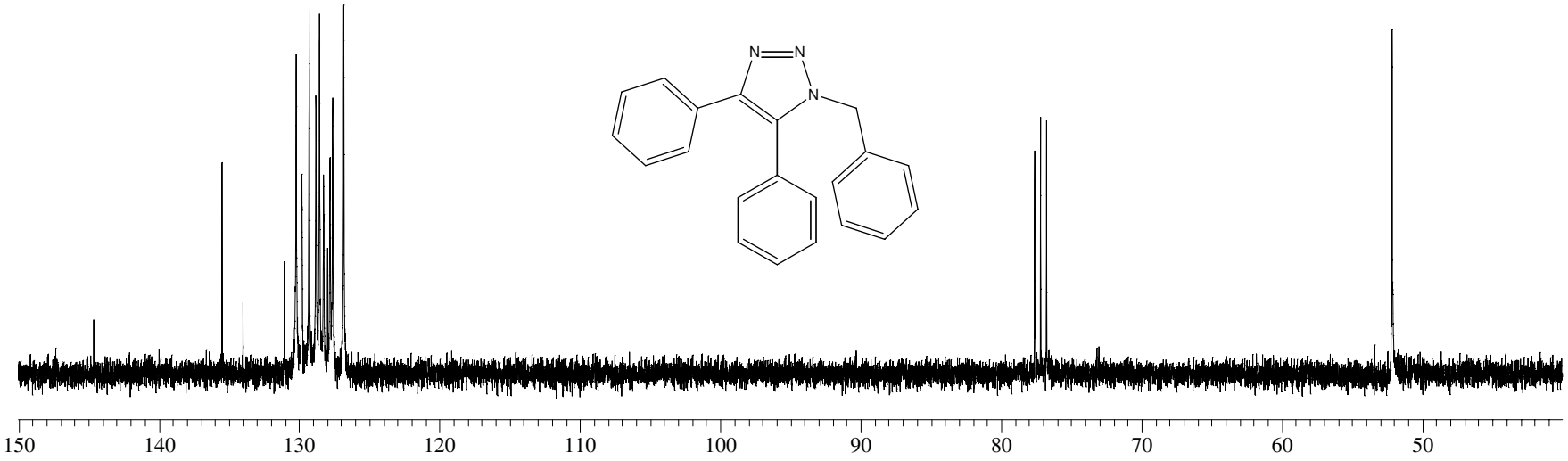
The ^{13}C NMR spectrum of **7a** in $CDCl_3$.



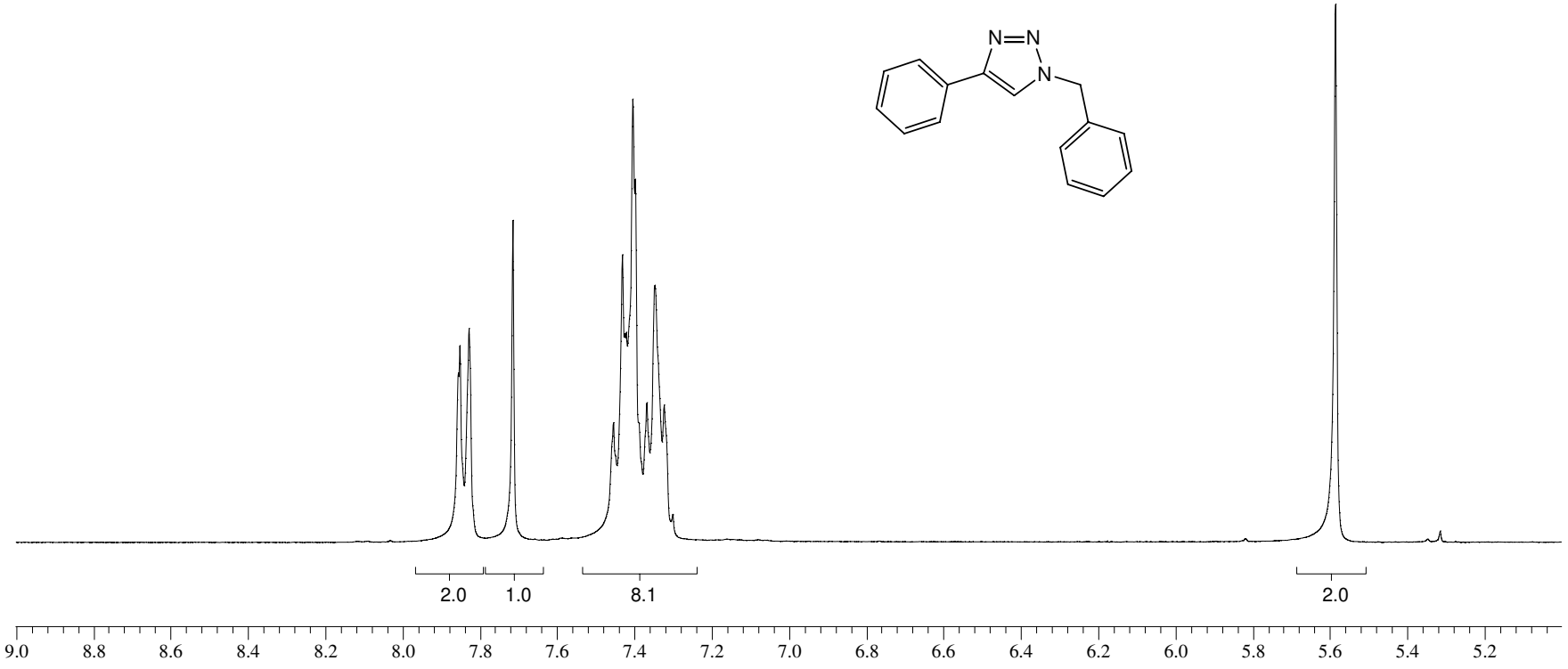
The ^{1}H NMR spectrum of **12** in $CDCl_3$.



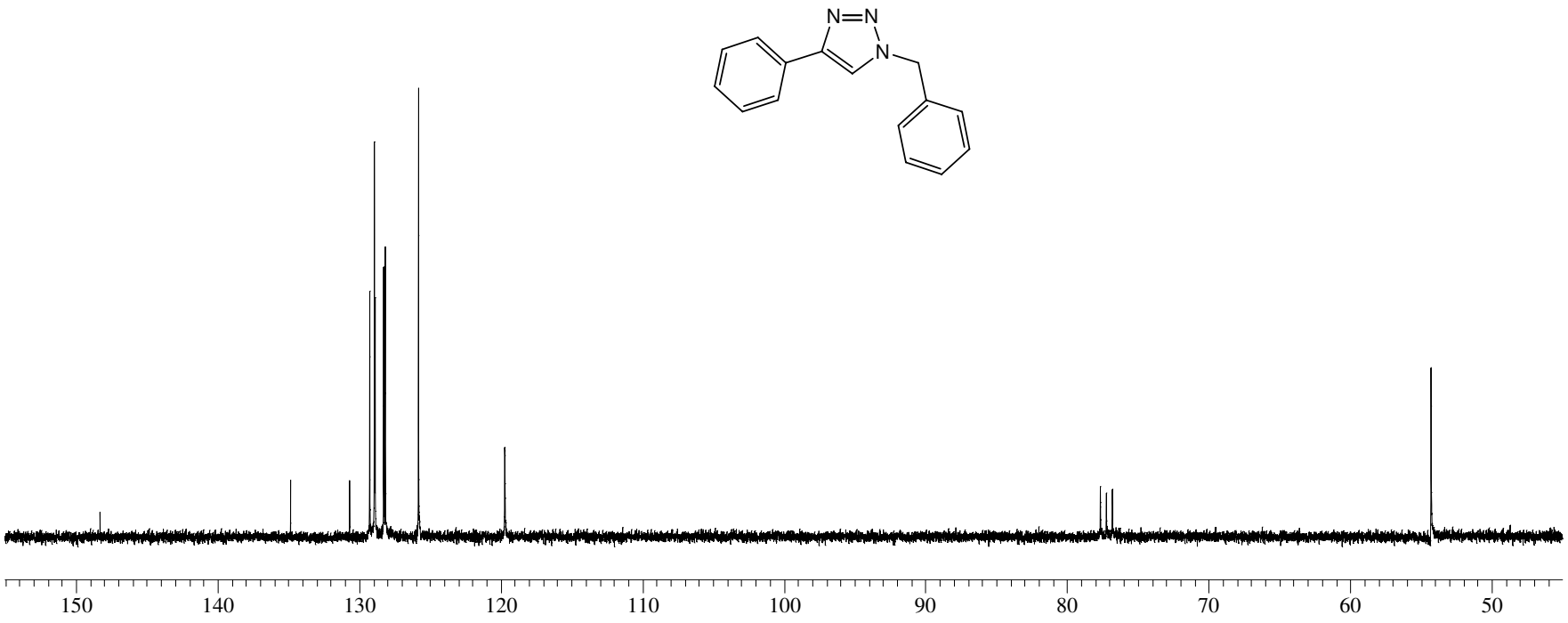
The ^{13}C NMR spectrum of **12** in $CDCl_3$.



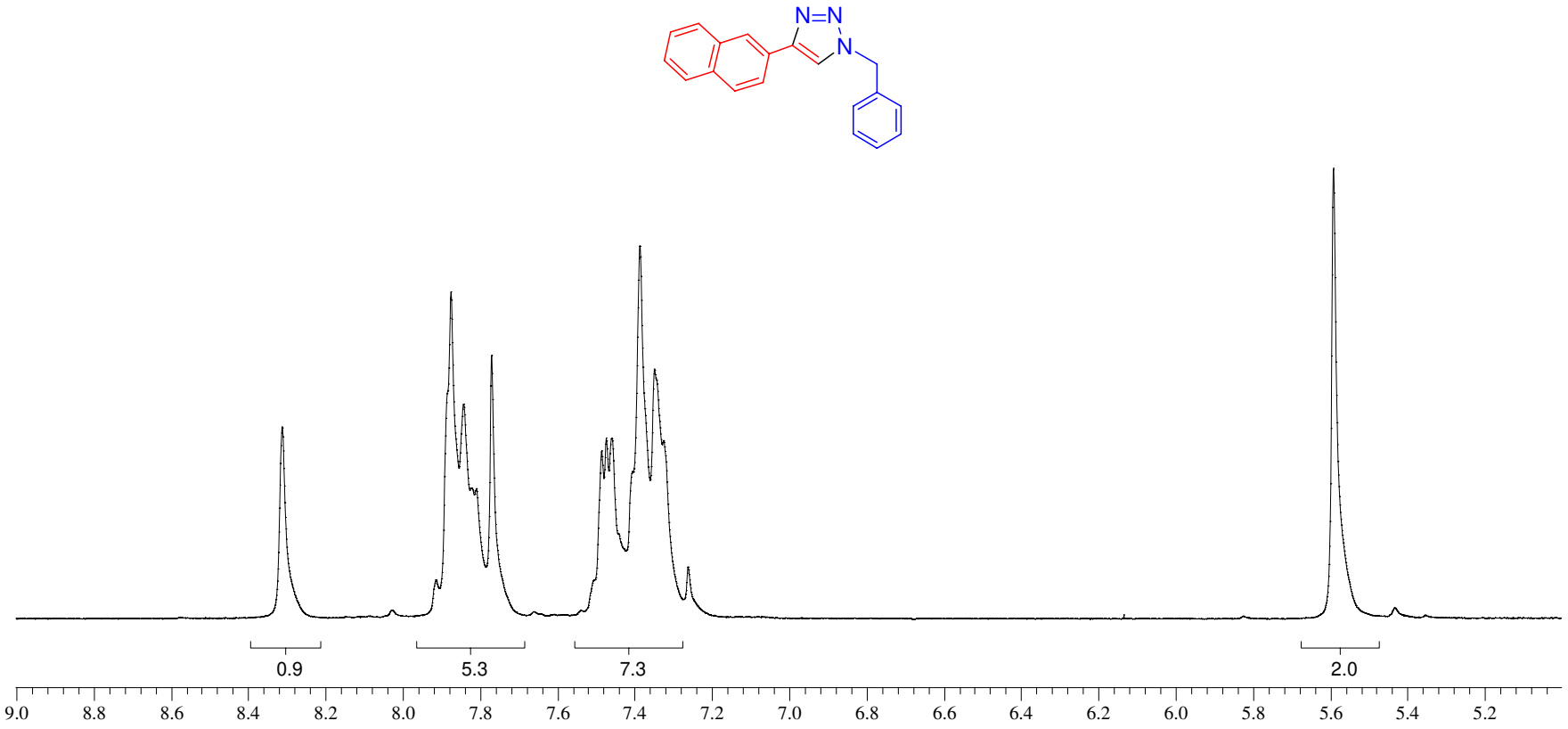
The ^{1}H NMR spectrum of **1b** in $CDCl_3$.



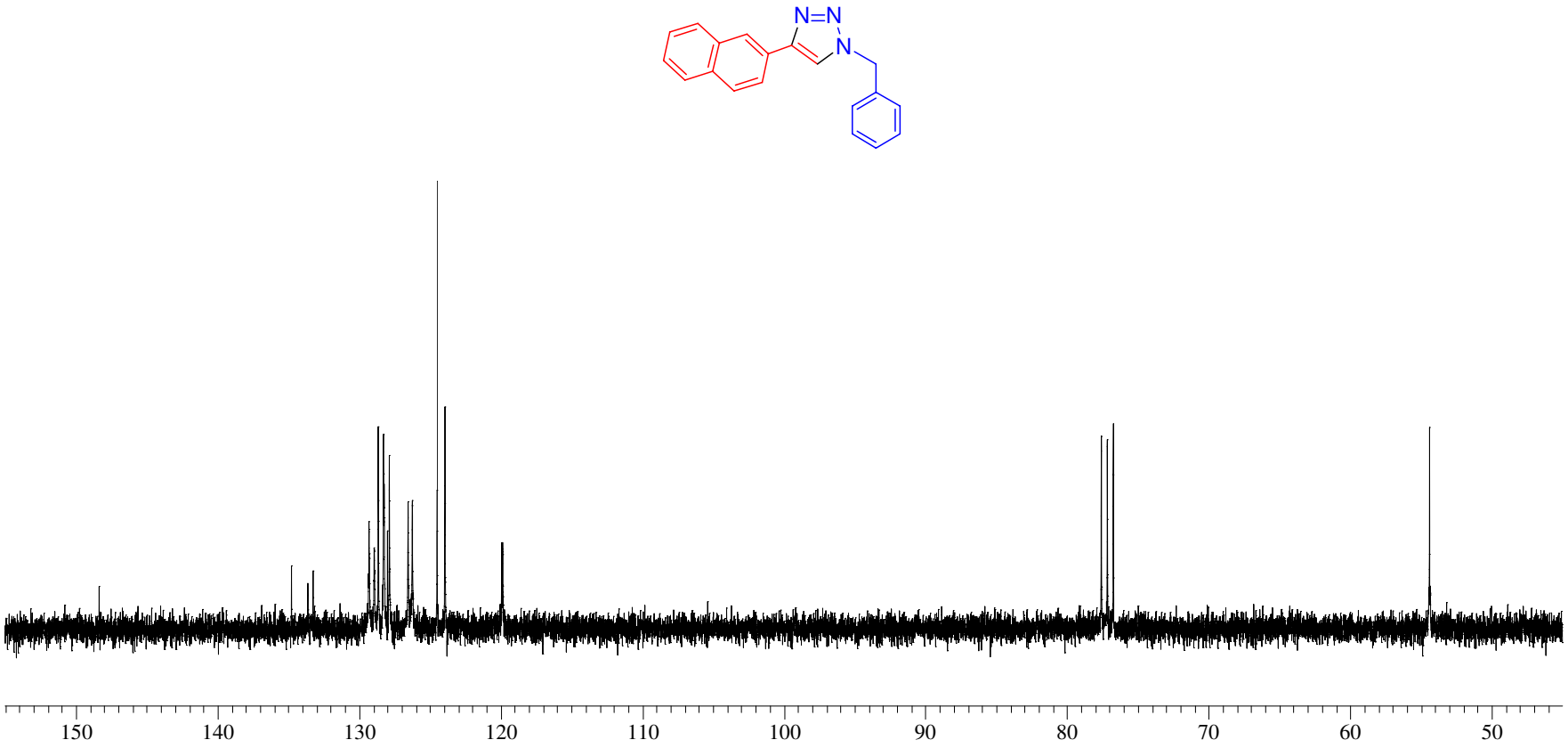
The ^{13}C NMR spectrum of **1b** in $CDCl_3$.



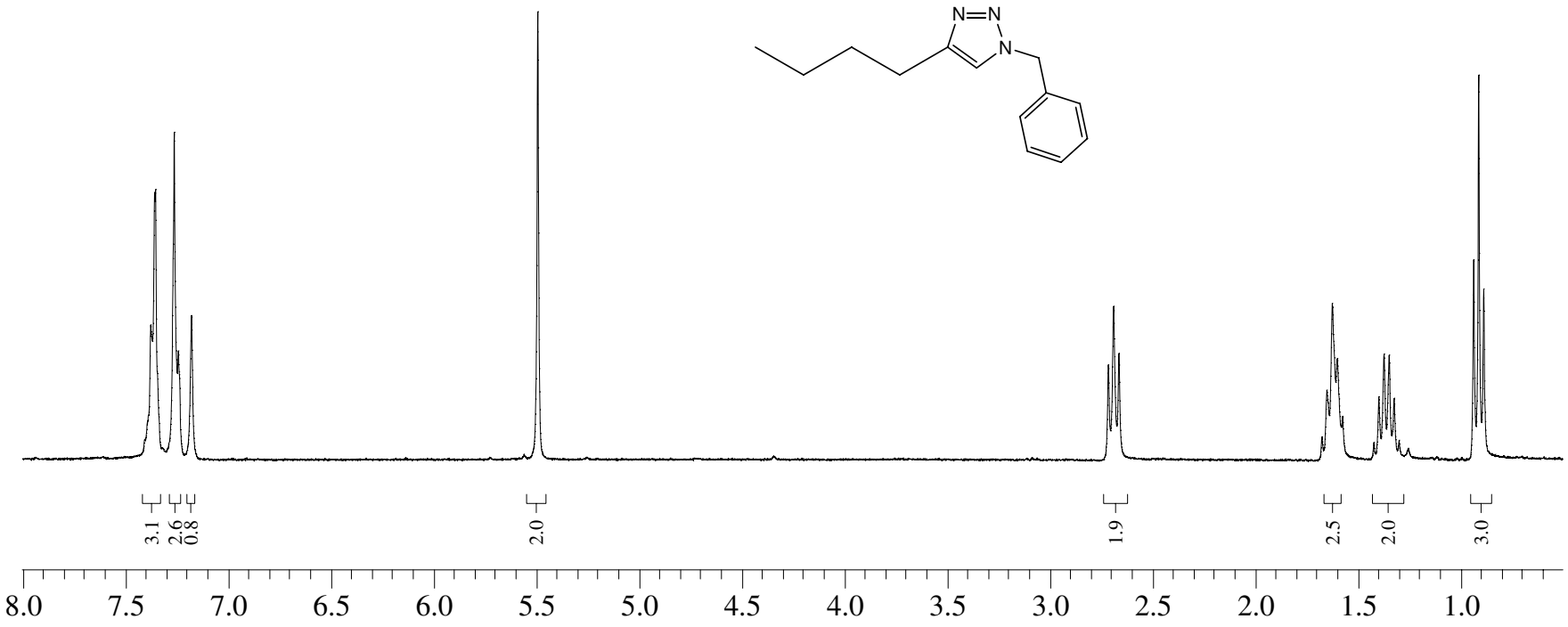
The ^{1}H NMR spectrum of **2b** in $CDCl_3$.



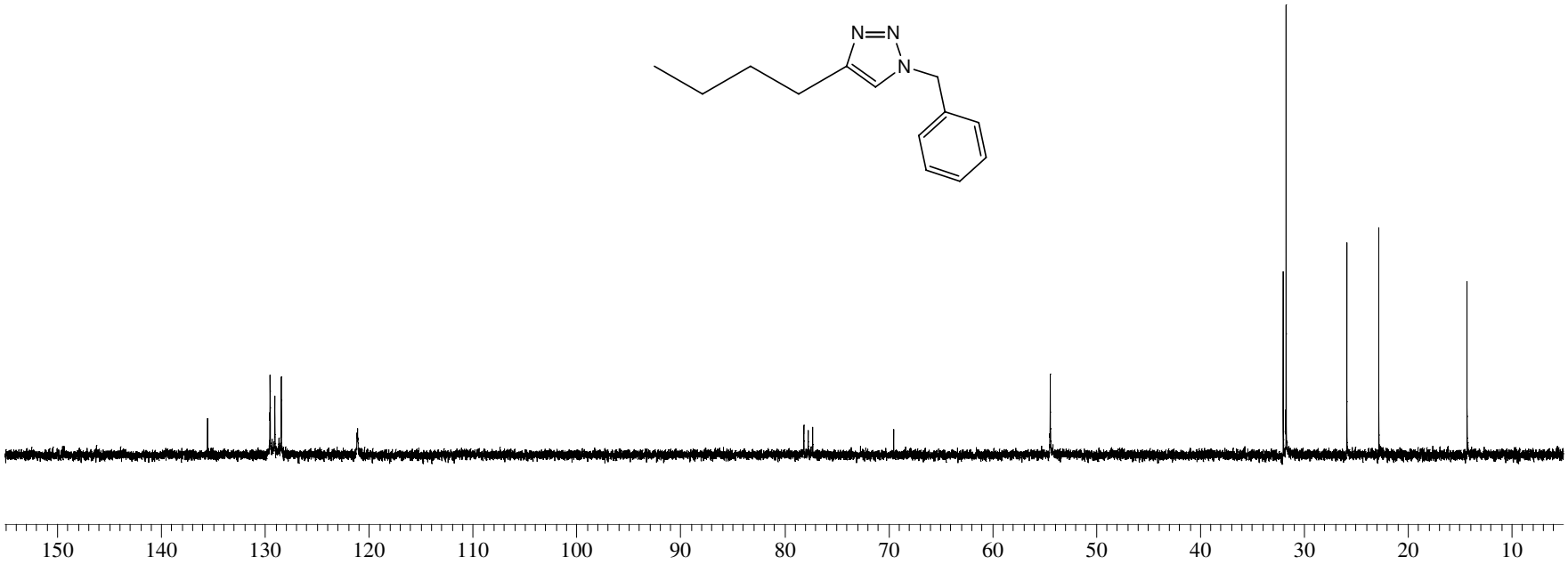
The ^{13}C NMR spectrum of **2b** in $CDCl_3$.



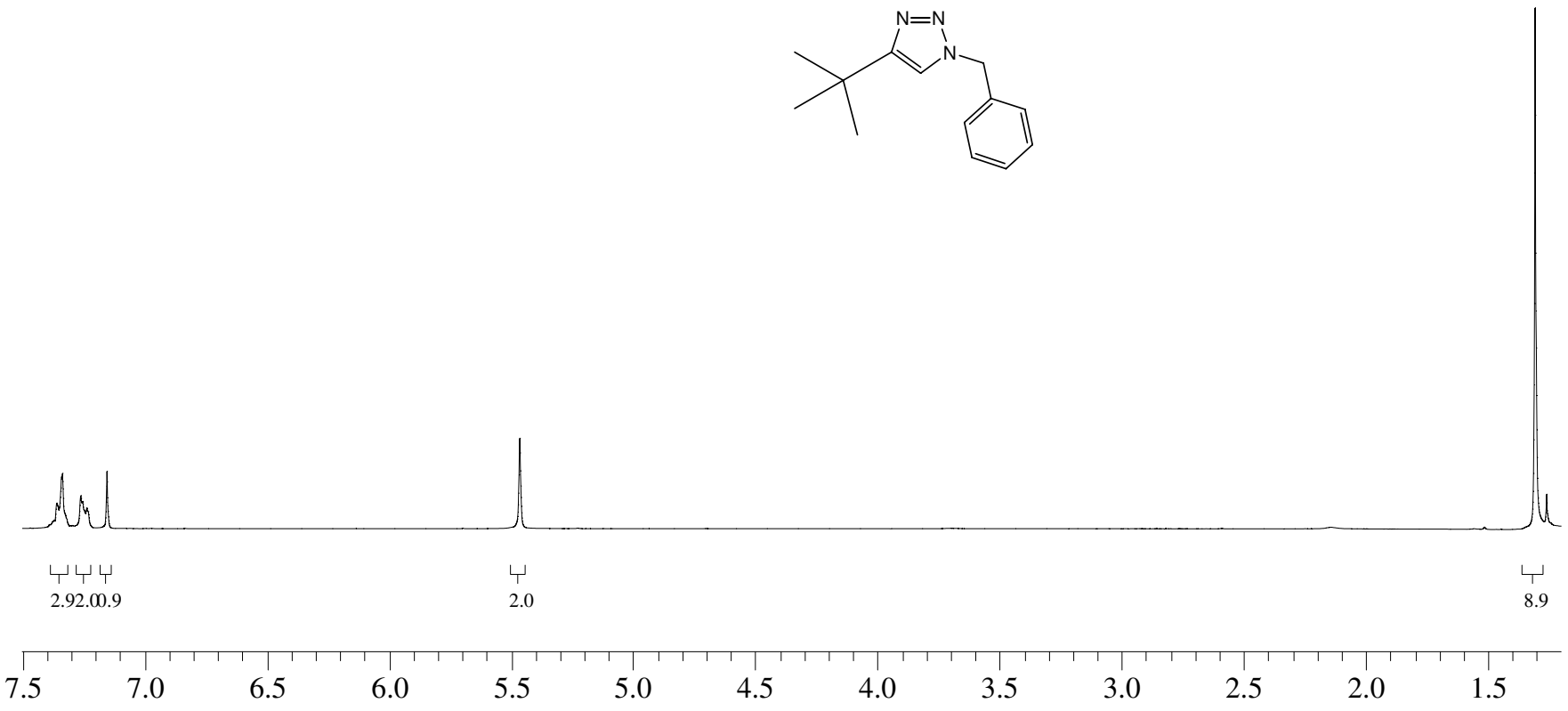
The ^{1}H NMR spectrum of **3b** in $CDCl_3$.



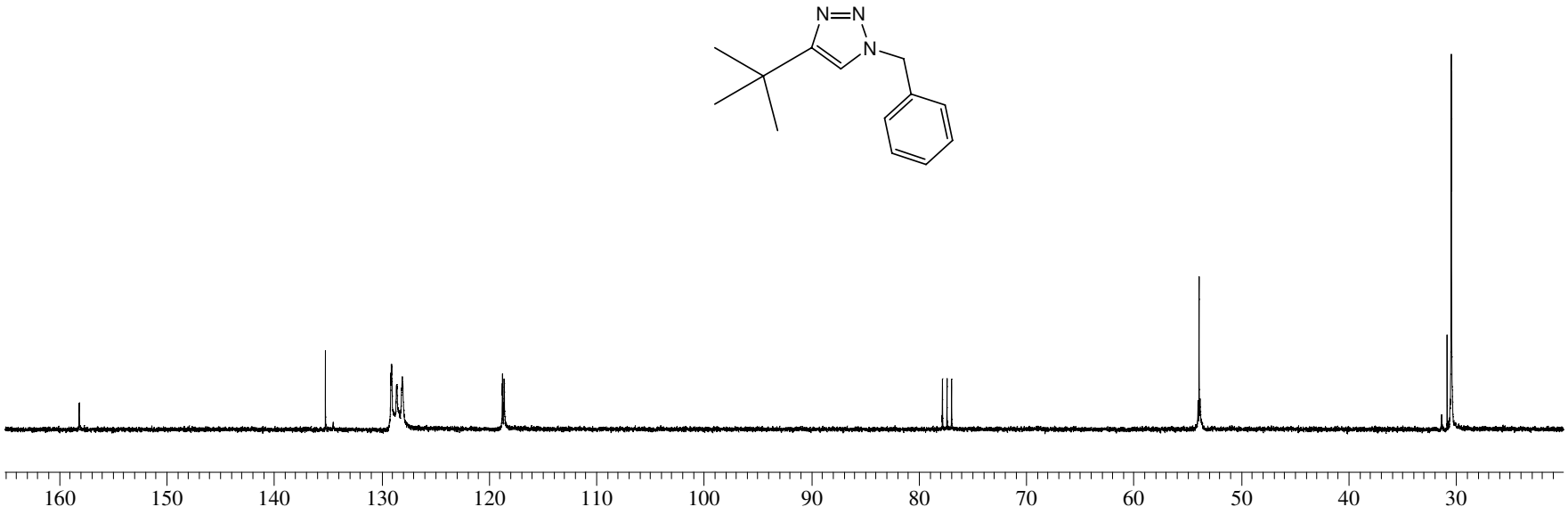
The ^{13}C NMR spectrum of **3b** in $CDCl_3$.



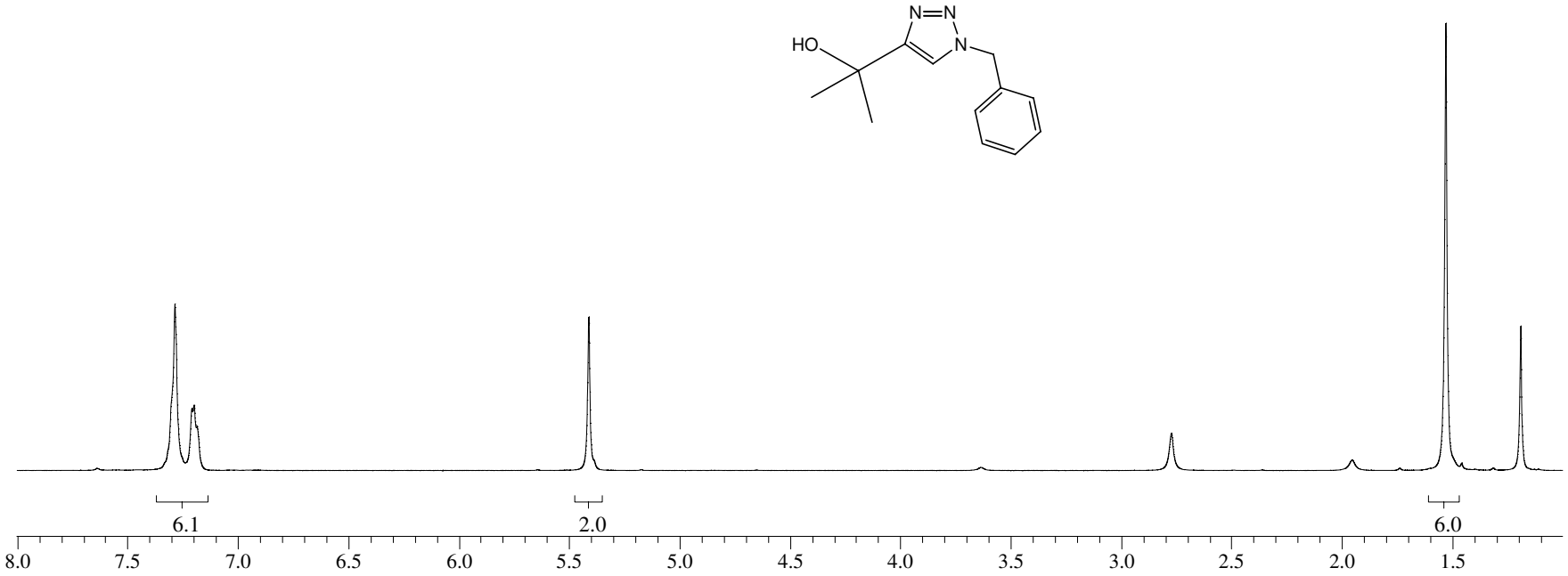
The ^{1}H NMR spectrum of **4b** in $CDCl_3$.



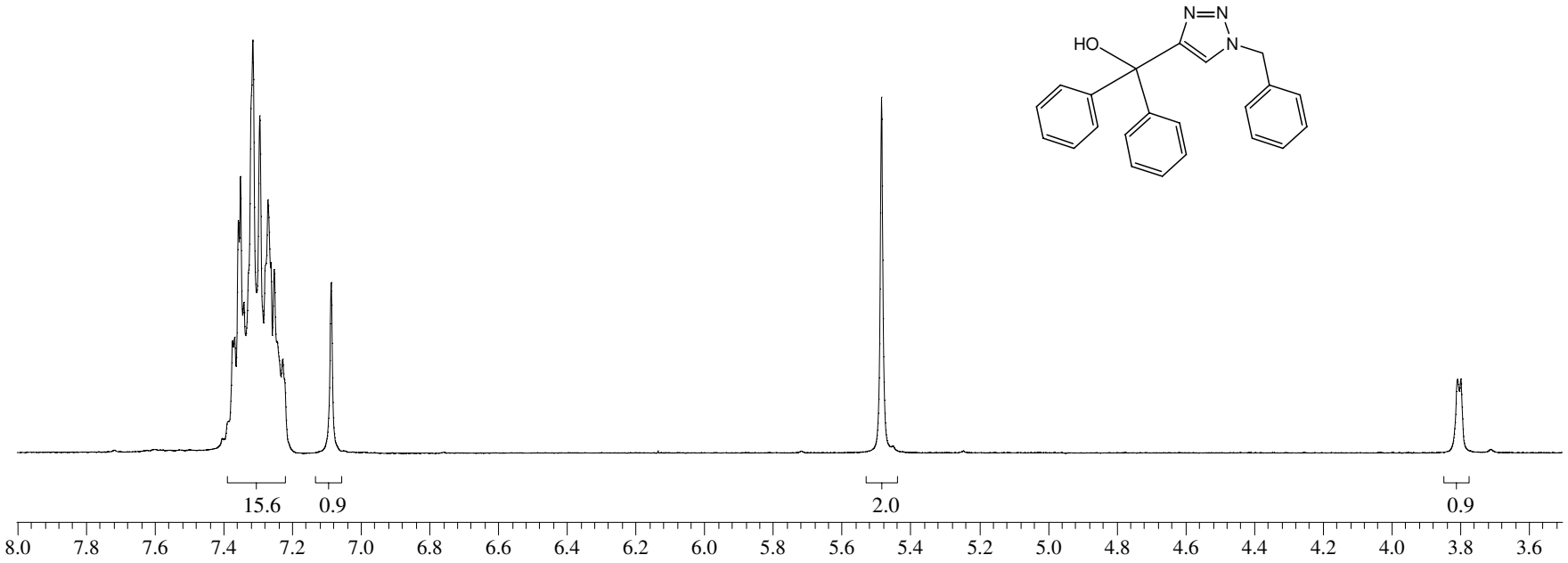
The ^{13}C NMR spectrum of **4b** in $CDCl_3$.



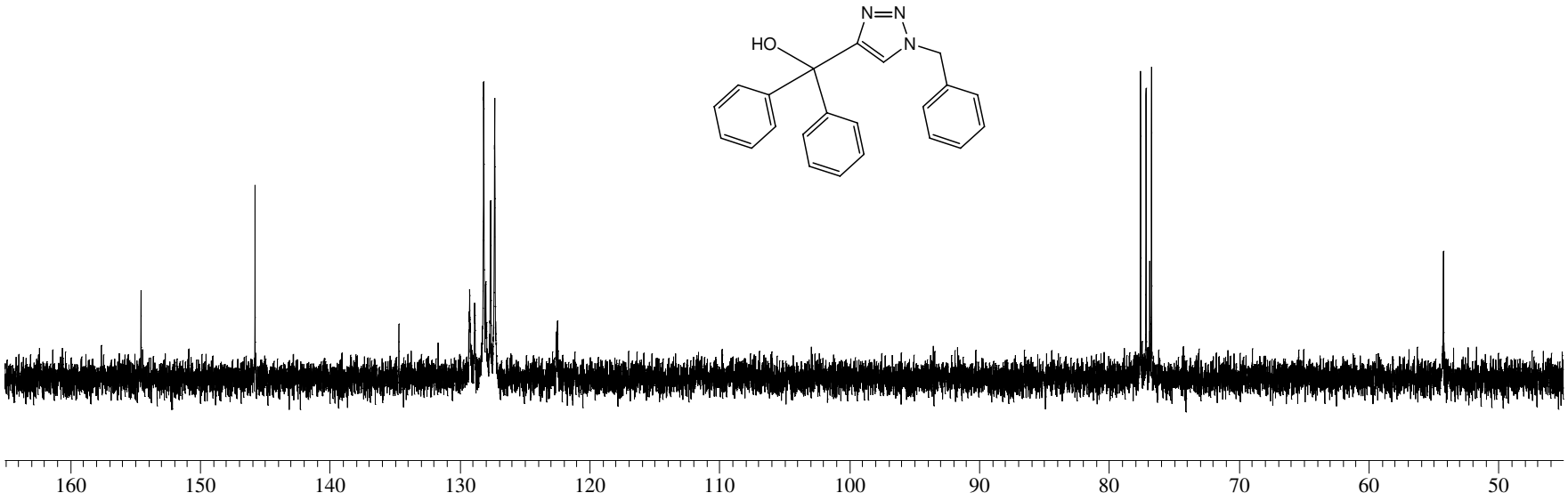
The ^{1}H NMR spectrum of **6b** in $CDCl_3$.



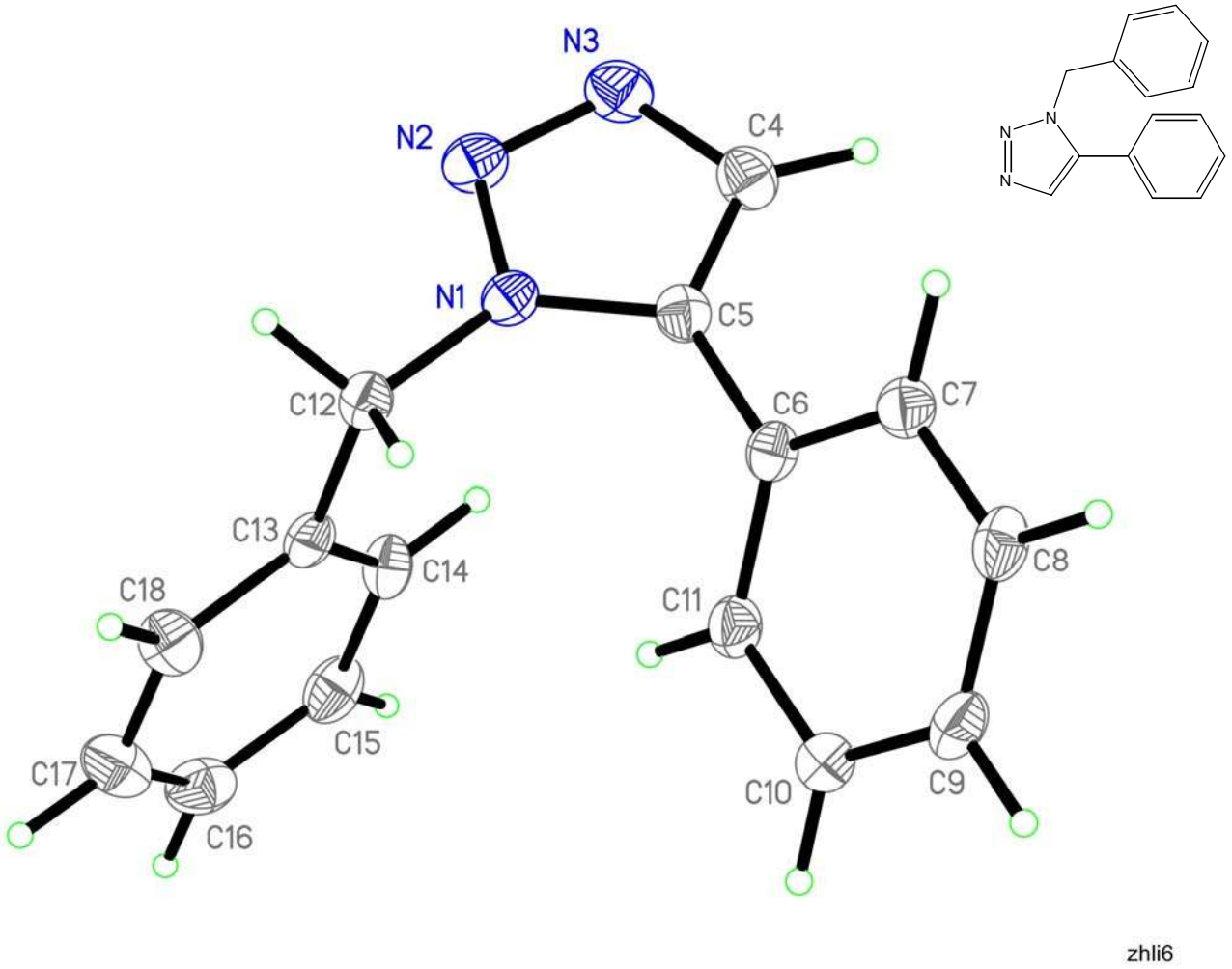
The ^{1}H NMR spectrum of **7b** in $CDCl_3$.



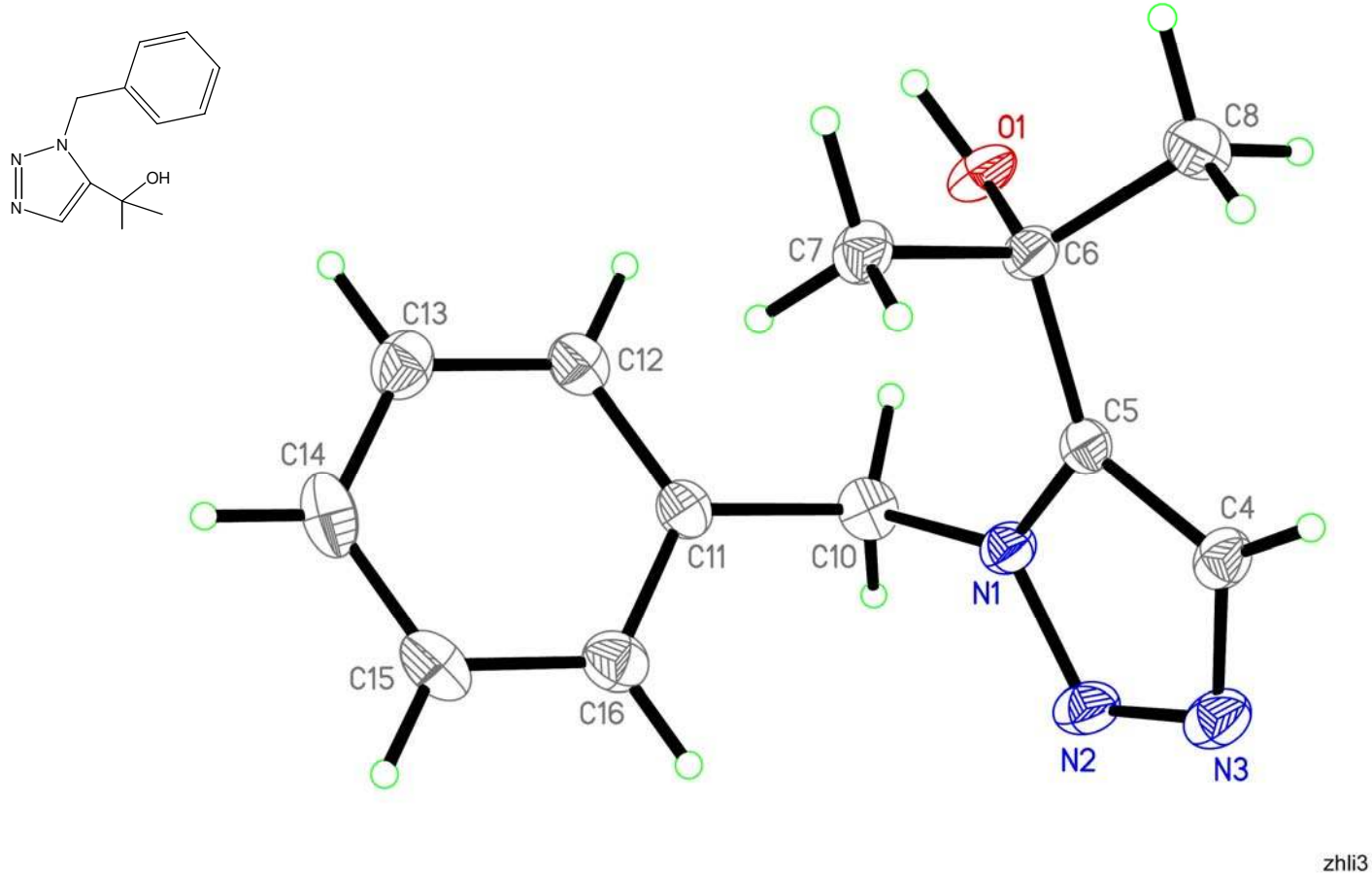
The ^{13}C NMR spectrum of **7b** in $CDCl_3$.



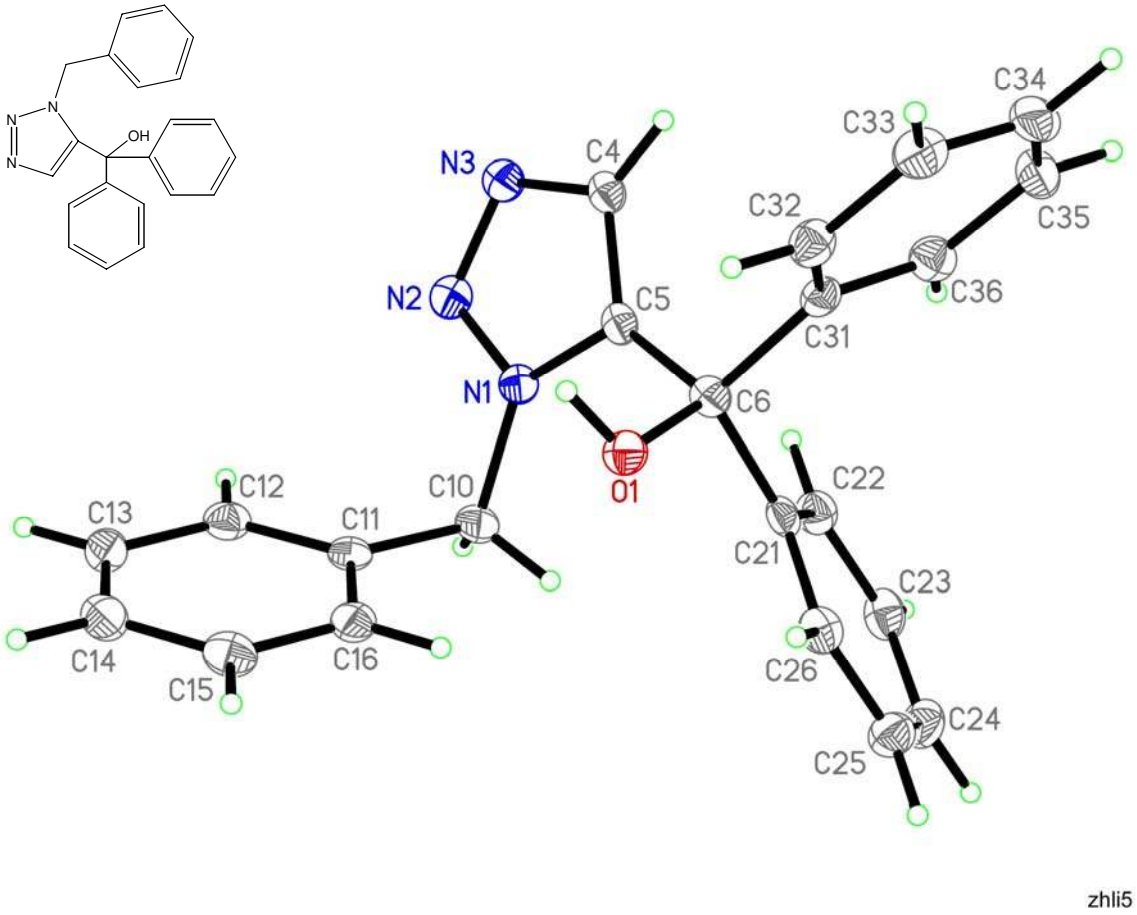
The X-ray structure of **1a.**



The X-ray structure of **6a**.



The X-ray structure of **7a**.



The X-ray structure of **12**.