Supporting information

for

Efficient Synthesis of 2,5-Disubstituted Tetrazoles *via* the Cu_2O-Catalyzed Aerobic Oxidative Direct Cross-coupling of N-H Free Tetrazoles with Boronic Acids

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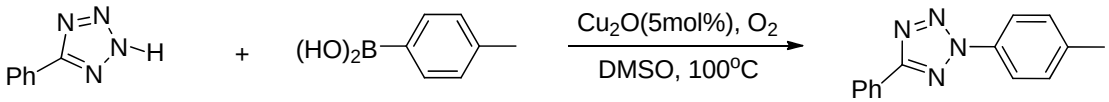
General information

All the solvents were used without further purification. The ^{1}H-NMR spectra were recorded at 600 MHz in $CDCl_3$ or DMSO-d_6, and the ^{13}C-NMR spectra were recorded at 150MHz in $CDCl_3$ or DMSO-d_6 with TMS as internal standard. All shifts were given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 100-200 mesh, 200-300 mesh.

General procedure for the synthesis of 2,5-disubstituted tetrazoles (taking coupling of 5-phenyl tetrazole and 4-methylphenylboronic acid as a representative)

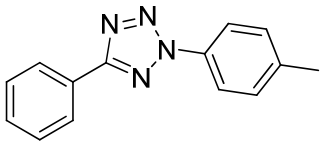
Into a 40 mL Schlenck tube was added 5-phenyl tetrazole **1a** (0.5mmol, 0.0731g), 4-methylphenylboronic acid **2a** (1mmol, 0.1360 g), Cu_2O (5mol%, 0.025mmol, 0.0036g) and DMSO (4mL). The reaction mixture was stirred under oxygen atmosphere at 100^{o}C until tetrazole had disappeared as monitored by TLC. The reaction mixture was then cooled to room temperature and diluted with 40mL ethyl acetate, washed consecutively with 5mL of 1M aqueous HCl, 5mL of brine (four times). The organic layer was separated and dried over $MgSO_4$, then concentrated under reduced pressure and purified by chromatography on silica column or purified using preparative TLC to afford the product **3a**.



1a 2a 3a

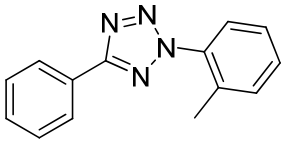
Characterization of coupling products

5-Phenyl-2-(*p*-tolyl)-2*H*-tetrazole (3a)



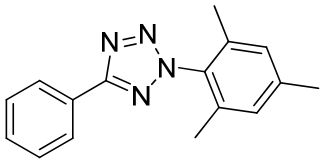
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.25 (dd, *J* = 7.9, 1.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.55–7.48 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.46 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 165.0, 139.8, 134.7, 130.4, 130.1, 128.9, 127.2, 127.0, 119.7, 21.1. HRMS: Calcd. for $C_{14}H_{13}N_4$ $[M+H]^+$: 237.1140; found: 237.1135.

5-Phenyl-2-(*o*-tolyl)-2H-tetrazole (3b)



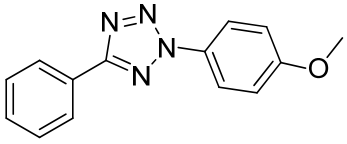
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.25 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.55–7.49 (m, 3H), 7.46 (dd, *J* = 11.3, 4.5 Hz, 1H), 7.44–7.38 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 164.9, 136.5, 133.0, 131.9, 130.4, 130.3, 128.9, 127.2, 127.0, 126.8, 125.2, 18.7. HRMS: Calcd. for $C_{14}H_{13}N_4$ $[M+H]^+$: 237.1140; found: 237.1136.

2-(2,4,6-Trimethylphenyl)-5-phenyl-2*H*-tetrazole (3c)



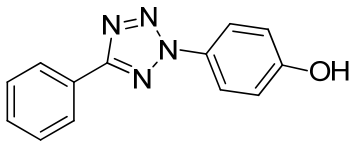
^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.25 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.55–7.48 (m, 3H), 7.04 (s, 2H), 2.39 (s, 3H), 2.02 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 165.0, 140.8, 135.0, 133.8, 130.4, 129.2, 128.9, 127.3, 126.9, 21.2, 17.3. HRMS: Calcd. for $C_{16}H_{17}N_4$ $[M+H]^+$: 265.1453; found: 265.1446.

2-(4-Methoxyphenyl)-5-phenyl-2*H*-tetrazole(3d)



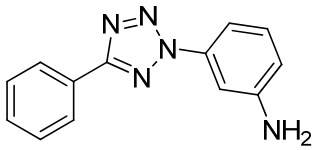
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 6.8 Hz, 2H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.55–7.47 (m, 3H), 7.07 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 165.0, 160.5, 130.5, 130.4, 128.9, 127.3, 127.0, 121.4, 114.6, 55.6. HRMS: Calcd. for $C_{14}H_{13}N_4O$ $[M+H]^+$: 253.1089; found: 253.1084.

4-(5-Phenyl-tetrazol-2-yl)phenol (Table 2, 3e)



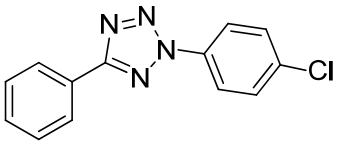
^{1}H-NMR (600 MHz, DMSO) δ 10.22 (s, 1H), 8.16 (d, *J* = 6.7 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.64–7.56 (m, 3H), 7.03 (d, *J* = 8.8 Hz, 2H). ^{13}C-NMR (151 MHz, DMSO) δ: 164.1, 159.0, 130.7, 129.2, 128.4, 126.7, 126.5, 121.7, 116.2. HRMS: Calcd. for $C_{13}H_{11}N_4O$ $[M+H]^+$: 239.0933; found: 239.0928.

3-(5-Phenyl-2*H*-tetrazol-2-yl)aniline (3f)



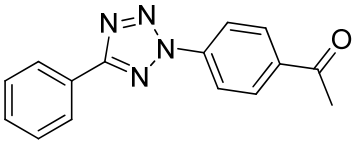
^{1}H-NMR (600 MHz, DMSO) δ: 8.16 (d, *J* = 6.6 Hz, 2H), 7.64–7.57 (m, 3H), 7.37 (t, *J* = 1.9 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.71 (s, 2H). ^{13}C-NMR (151 MHz, DMSO) δ: 164.2, 150.2, 137.0, 130.8, 130.3, 129.3, 126.6, 126.5, 115.2, 106.4, 104.2. HRMS: Calcd. for $C_{13}H_{12}N_5$ $[M+H]^+$: 238.1093; found: 238.1088.

2-(4-Chlorophenyl)-5-phenyl-2*H*-tetrazole (3g)



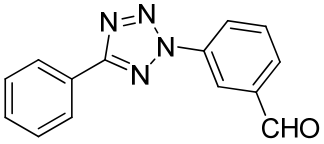
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.25 (dd, *J* = 7.7, 1.8 Hz, 2H), 8.18–8.15 (m, 2H), 7.58–7.49 (m, 5H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 165.3, 135.4, 135.3, 130.6, 129.8, 128.9, 127.0, 126.9, 121.0. HRMS: Calcd. for $C_{13}H_{10}ClN_4$ $[M+H]^+$: 257.0594; found: 257.0589.

1-(4-(5-Phenyl-2*H*-tetrazol-2-yl)phenyl)ethanone (3h)



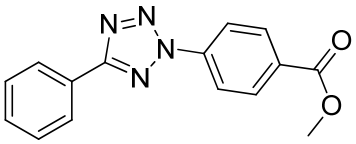
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 8.7 Hz, 2H), 8.29–8.25 (m, 2H), 8.18 (d, *J* = 8.7 Hz, 2H), 7.54 (m, 3H), 2.69 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 196.5, 165.5, 139.6, 137.5, 130.8, 129.9, 129.0, 127.1, 126.7, 119.6, 26.6. HRMS: Calcd. for $C_{15}H_{13}N_4O$ $[M+H]^+$: 265.1089; found: 265.1084.

3-(5-Phenyl-2*H*-tetrazol-2-yl)benzaldehyde (3i)



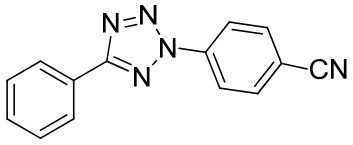
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 10.16 (s, 1H), 8.73 (s, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.30–8.25 (m, 2H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.58–7.50 (m, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 190.6, 165.5, 137.7, 137.5, 130.8, 130.6, 130.2, 129.0, 127.1, 126.8, 125.0, 120.5. HRMS: Calcd. for $C_{14}H_{11}N_4O$ $[M+H]^+$: 251.0933; found: 251.0932.

Methyl 4-(5-phenyl-2*H*-tetrazol-2-yl)benzoate (3j)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.31 (d, *J* = 8.7 Hz, 2H), 8.28–8.25 (m, 4H), 7.56–7.51 (m, 3H), 3.98 (s, 3H). HRMS: Calcd. for $C_{15}H_{13}N_4O_2$ $[M+H]^+$: 281.1039; found: 281.1034.

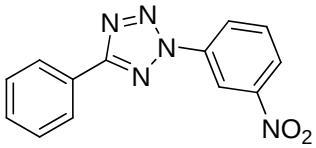
4-(5-Phenyl-2*H*-tetrazol-2-yl)benzonitrile (3k)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 8.8 Hz, 2H), 8.28–8.24 (m, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.57–7.52 (m, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 165.8, 139.3,

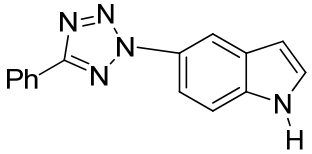
133.8, 131.0, 129.0, 127.2, 126.5, 120.2, 117.6, 113.3. HRMS: Calcd. for $C_{14}H_{10}N_5$ $[M+H]^+$: 248.0936; found: 248.0931.

2-(3-Nitrophenyl)-5-phenyl-2*H*-tetrazole (3l)



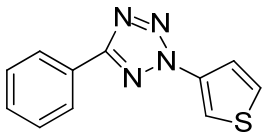
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 9.09 (t, *J* = 1.9 Hz, 1H), 8.62–8.58 (m, 1H), 8.38 (dd, *J* = 8.2, 2.0 Hz, 1H), 8.28 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.81 (t, *J* = 8.2 Hz, 1H), 7.56–7.53 (m, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 165.8, 149.0, 137.4, 131.0, 130.9, 129.0, 127.2, 126.4, 125.1, 124.0, 115.0. HRMS: Calcd. for $C_{13}H_{10}N_5O_2$ $[M+H]^+$: 268.0834; found: 268.0830.

5-(5-phenyl-2*H*-tetrazol-2-yl)-1H-indole (3m)



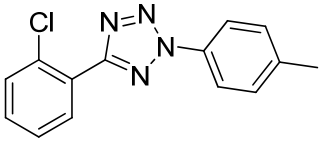
^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.40 (b, 1H), 8.28 (d, *J* = 7.1 Hz, 2H), 8.05 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.57–7.47 (m, 4H), 7.36 (t, *J* = 2.6 Hz, 1H), 6.72 (s, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 164.9, 136.0, 130.6, 130.3, 128.9, 128.0, 127.6, 127.0, 126.4, 114.8, 112.7, 111.8, 103.9. HRMS: Calcd. for $C_{15}H_{12}N_5$ $[M+H]^+$: 262.1093; found: 262.1092.

5-phenyl-2-(thiophen-3-yl)-2*H*-tetrazole (3n)



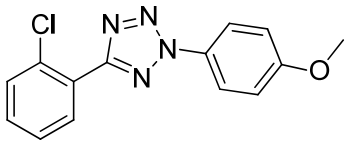
^{1}H-NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.4 Hz, 2H), 7.96 (d, *J* = 3.1 Hz, 1H), 7.78 (d, *J* = 5.2 Hz, 1H), 7.54–7.48 (m, 4H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 164.8 (s, 1C), 135.6 (s, 1C), 130.5 (s, 1C), 128.9 (s, 2C), 127.2(s, 1C), 127.0 (s, 3C), 120.4 (s, 1C), 115.5 (s, 1C). HRMS: Calcd. for $C_{11}H_9N_4S$ $[M+H]^+$: 229.0548; found: 229.0545.

5-(2-Chlorophenyl)-2-(*p*-tolyl)-2*H*-tetrazole (4a)



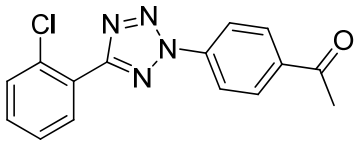
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 8.4 Hz, 2H), 8.05 (dd, *J* = 7.1, 2.3 Hz, 1H), 7.59–7.56 (m, 1H), 7.46–7.40 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.46 (s, 3H). ^{13}C-NMR (151 MHz, $cdcl_3$) δ: 163.2, 140.0, 134.6, 133.2, 131.4, 131.1, 130.9, 130.1, 126.9, 126.4, 119.8, 21.2. HRMS: Calcd. for $C_{14}H_{12}ClN_4$ $[M+H]^+$: 271.0750; found: 271.0746.

5-(2-Chlorophenyl)-2-(4-methoxyphenyl)-2*H*-tetrazole (4b)



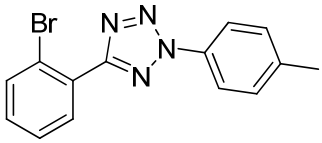
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 9.0 Hz, 2H), 8.05 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.59–7.55 (m, 1H), 7.46–7.40 (m, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 163.2, 160.6, 133.2, 131.4, 131.1, 130.9, 130.4, 126.9, 126.4, 121.5, 114.7, 55.6. HRMS: Calcd. for $C_{14}H_{12}ClN_4O$ $[M+H]^+$: 287.0700; found: 287.0695.

1-(4-(5-(2-Chlorophenyl)-2*H*-tetrazol-2-yl)phenyl)ethanone (4c)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.7 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.08 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49–7.43 (m, 2H), 2.69 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 196.5, 163.8, 139.6, 137.7, 133.3, 131.5, 131.4, 131.0, 130.0, 127.0, 125.8, 119.8, 26.7. HRMS: Calcd. for $C_{15}H_{12}ClN_4O$ $[M+H]^+$: 299.0700; found: 299.0700.

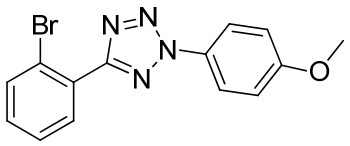
5-(2-Bromophenyl)-2-(*p*-tolyl)-2*H*-tetrazole (5a)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.36 (ddd, *J* = 9.4, 6.5, 2.3 Hz, 3H), 2.46 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 164.1, 140.0, 134.6, 134.2, 131.7,

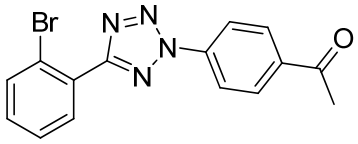
131.3, 130.2, 128.4, 127.5, 122.2, 119.8, 21.2. HRMS: Calcd. for $C_{14}H_{12}BrN_4$ $[M+H]^+$: 315.0245; found: 315.0240.

5-(2-Bromophenyl)-2-(4-methoxyphenyl)-2*H*-tetrazole (5b)



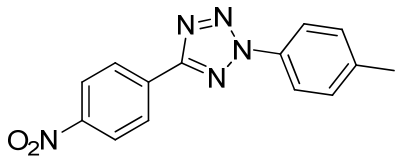
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 9.0 Hz, 2H), 7.96 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.36 (td, *J* = 7.8, 1.5 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 164.0, 160.6, 134.2, 131.7, 131.3, 130.4, 128.4, 127.4, 122.1, 121.5, 114.7, 55.6. HRMS: Calcd. for $C_{14}H_{12}BrN_4O$ $[M+H]^+$: 331.0194; found: 331.0190.

1-(4-(5-(2-Bromophenyl)-2*H*-tetrazol-2-yl)phenyl)ethanone (5c)



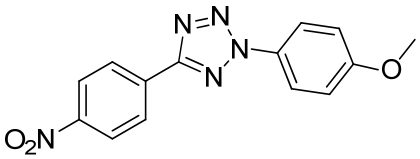
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.7 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 8.00 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.39 (td, *J* = 7.8, 1.5 Hz, 1H), 2.69 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 196.5, 164.6, 139.6, 137.7, 134.3, 131.7, 131.6, 130.0, 127.9, 127.5, 122.1, 119.8, 26.7. HRMS: Calcd. for $C_{15}H_{12}BrN_4O$ $[M+H]^+$: 343.0194; found: 343.0191.

5-(4-Nitrophenyl)-2-(*p*-tolyl)-2*H*-tetrazole (6a)



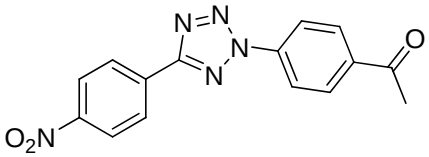
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.45 (d, *J* = 8.8 Hz, 2H), 8.39 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 163.2, 149.0, 140.5, 134.4, 133.2, 130.3, 127.8, 124.2, 119.8, 21.2. HRMS: Calcd. for $C_{14}H_{12}N_5O_2$ $[M+H]^+$: 282.0991; found: 282.0986.

2-(4-Methoxyphenyl)-5-(4-nitrophenyl)-2*H*-tetrazole (6b)



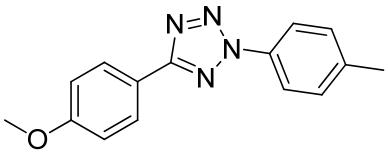
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 8.8 Hz, 2H), 8.39 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 9.1 Hz, 2H), 7.09 (d, *J* = 9.1 Hz, 2H), 3.92 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 163.1, 160.9, 149.0, 133.2, 130.1, 127.8, 124.2, 121.5, 114.8, 55.7. HRMS: Calcd. for $C_{14}H_{12}N_5O_3$ $[M+H]^+$: 298.0940; found: 298.0925.

1-(4-(5-(4-Nitrophenyl)-2*H*-tetrazol-2-yl)phenyl)ethanone (6c)



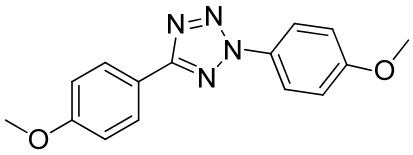
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 8.8 Hz, 2H), 8.41 (d, *J* = 8.8 Hz, 2H), 8.35 (d, *J* = 8.6 Hz, 2H), 8.21 (d, *J* = 8.6 Hz, 2H), 2.70 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 196.4, 163.7, 149.2, 139.3, 138.0, 132.6, 130.0, 128.0, 124.3, 119.9, 26.7. HRMS: Calcd. for $C_{15}H_{12}N_5O_3$ $[M+H]^+$: 310.0940; found: 310.0933.

5-(4-Methoxyphenyl)-2-(*p*-tolyl)-2*H*-tetrazole (7a)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 164.9, 161.4, 139.7, 134.7, 130.1, 128.5, 119.8, 119.6, 114.3, 55.3, 21.2. HRMS: Calcd. for $C_{15}H_{15}N_4O$ $[M+H]^+$: 267.1246; found: 267.1239.

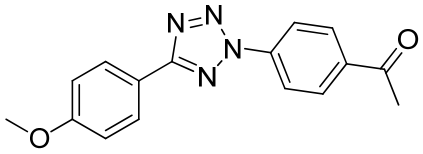
2,5-Bis(4-methoxyphenyl)-2*H*-tetrazole (7b)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 8.8 Hz, 2H), 8.09 (d, *J* = 9.0 Hz, 2H), 7.05 (dd, *J* = 13.7, 8.9 Hz, 4H), 3.89 (d, *J* = 4.6 Hz, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$)

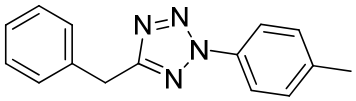
δ: 164.8, 161.3, 160.4, 130.5, 128.5, 121.3, 119.9, 114.6, 114.3, 55.6, 55.3. HRMS: Calcd. for $C_{15}H_{15}N_4O_2$ $[M+H]^+$: 283.1195; found: 283.1188.

1-(4-(5-(4-Methoxyphenyl)-2*H*-tetrazol-2-yl)phenyl)ethanone (7c)



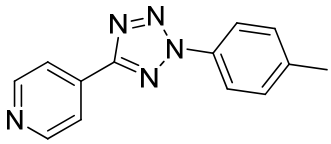
^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.32 (d, *J* = 8.6 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 2.68 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 196.5, 165.4, 161.6, 139.6, 137.4, 129.9, 128.6, 119.5, 119.2, 114.4, 55.4, 26.6. HRMS: Calcd. for $C_{16}H_{15}N_4O_2$ $[M+H]^+$: 295.1195; found: 295.1189.

5-Benzyl-2-(*p*-tolyl)-2*H*-tetrazole (8a)



^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.34–7.30 (m, 4H), 7.24 (t, *J* = 5.4 Hz, 1H), 4.33 (s, 2H), 2.42 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ: 165.6, 139.7, 136.6, 134.6, 130.0, 128.8, 128.6, 126.9, 119.7, 31.9, 21.1. HRMS: Calcd. for $C_{15}H_{15}N_4$ $[M+H]^+$: 251.1297; found: 251.1292.

4-(2-(*p*-Tolyl)-2H-tetrazol-5-yl)pyridine (9a)



^{1}H-NMR (600 MHz, DMSO) δ: 8.84 (d, *J* = 5.4 Hz, 2H), 8.10 (d, *J* = 5.3 Hz, 2H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C-NMR (151 MHz, DMSO) δ: 162.6, 150.9, 140.5, 133.8, 133.7, 130.5, 120.6, 120.0, 20.7. HRMS: Calcd. for $C_{13}H_{12}N_5$ $[M+H]^+$: 238.1093; found: 238.1086.

XPS Analysis of Catalysts under different atmosphere

1. Reaction was carried out under N_2 atmosphere: Into a 40mL Schlenck tube was added 5-phenyl-2*H*-tetrazole (0.5mmol, 0.0731g), 4-methylphenylboronic acid (1mmol, 0.1372g), Cu_2O (50mol%, 0.025mmol, 0.0355g), a magnetic bar, and DMSO (4mL). The tube was evacuated three times for 10 min under high vacuum and backfilled with N_2. The reaction mixture was stirred at 100°C for 24h under nitrogen atmosphere, then cooled to room temperature. Degassed ethyl acetate (40mL) was added. The precipitate was collected by filtration and used for XPS analysis. The results showed that Cu^{I} exist predominantly (Figure S1).

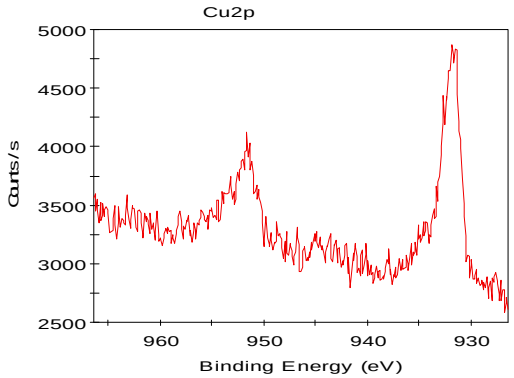


Figure S1. XPS spectroscopy of recovered catalyst under N_2

2. Reaction carried out under O_2 atmosphere: Into a 50mL round bottom flask was added 5-phenyl-2*H*-tetrazole (3mmol, 0.4360g), 4-methylphenylboronic acid (6mmol, 0.8165g), Cu_2O (5mol%, 0.15mmol, 0.0211g) and DMSO (5mL). The reaction mixture was stirred at 100°C under O_2 atmosphere until tetrazole had disappeared as monitored by TLC. The reaction mixture was cooled to room temperature and diluted with 50mL ethyl acetate and 30mL water. The precipitate was collected by filtration and used for XPS analysis. The results showed that both Cu^{I} and Cu^{II} exist in the recovered mixture (Figure S2).

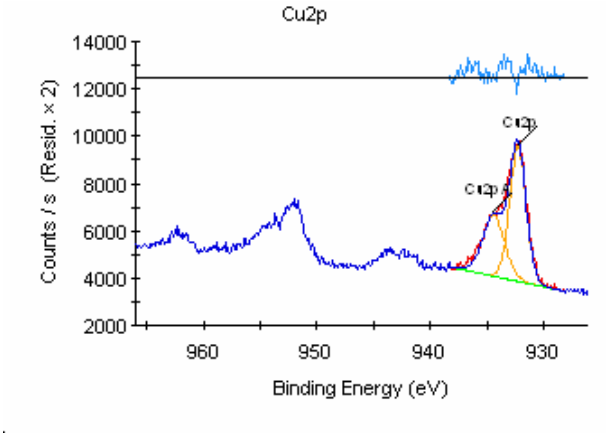


Figure S2. XPS spectroscopy of recovered catalyst under O_2

^{1}H and ^{13}C NMR Spectra of coupling products

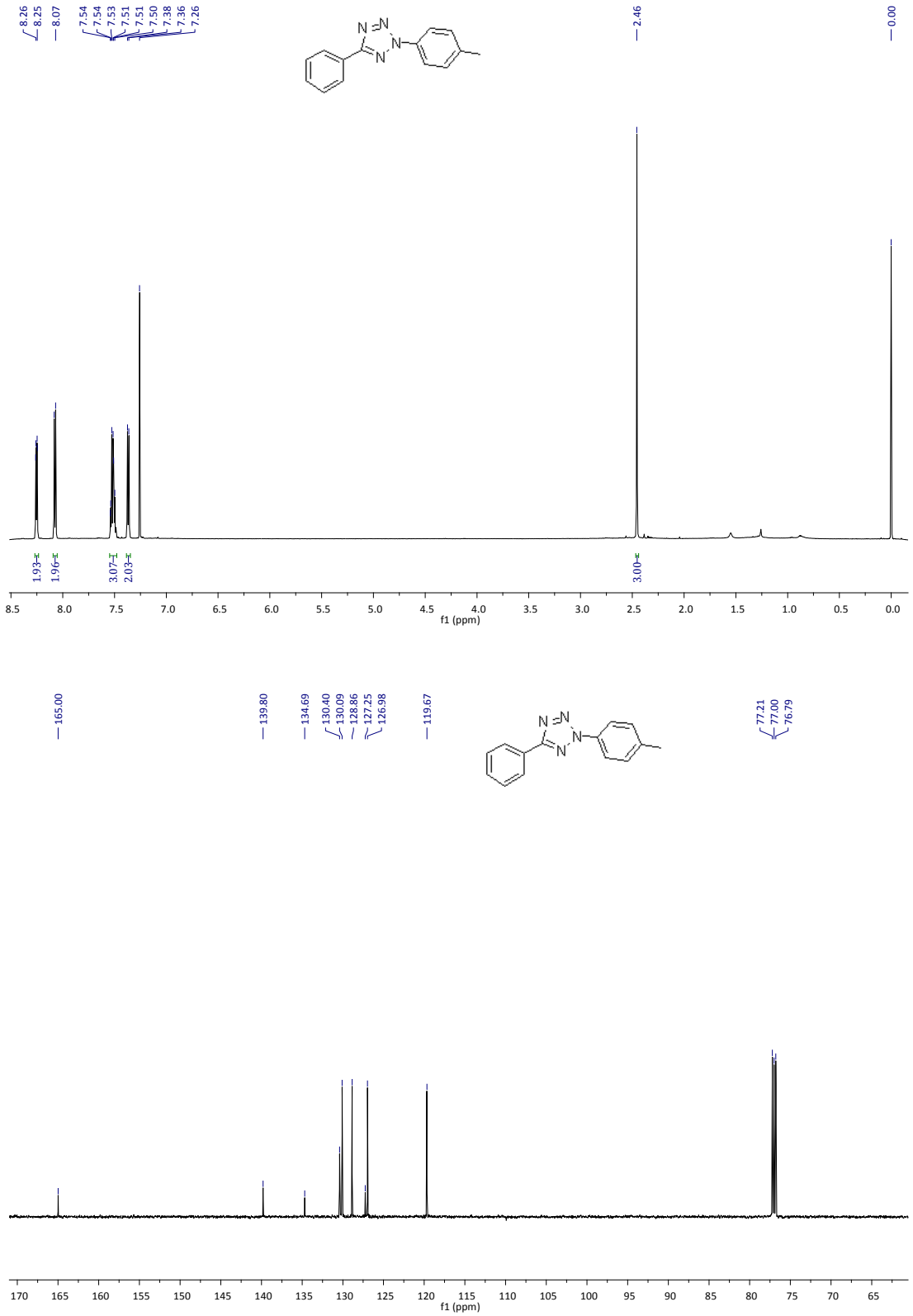


Figure S3. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3a**

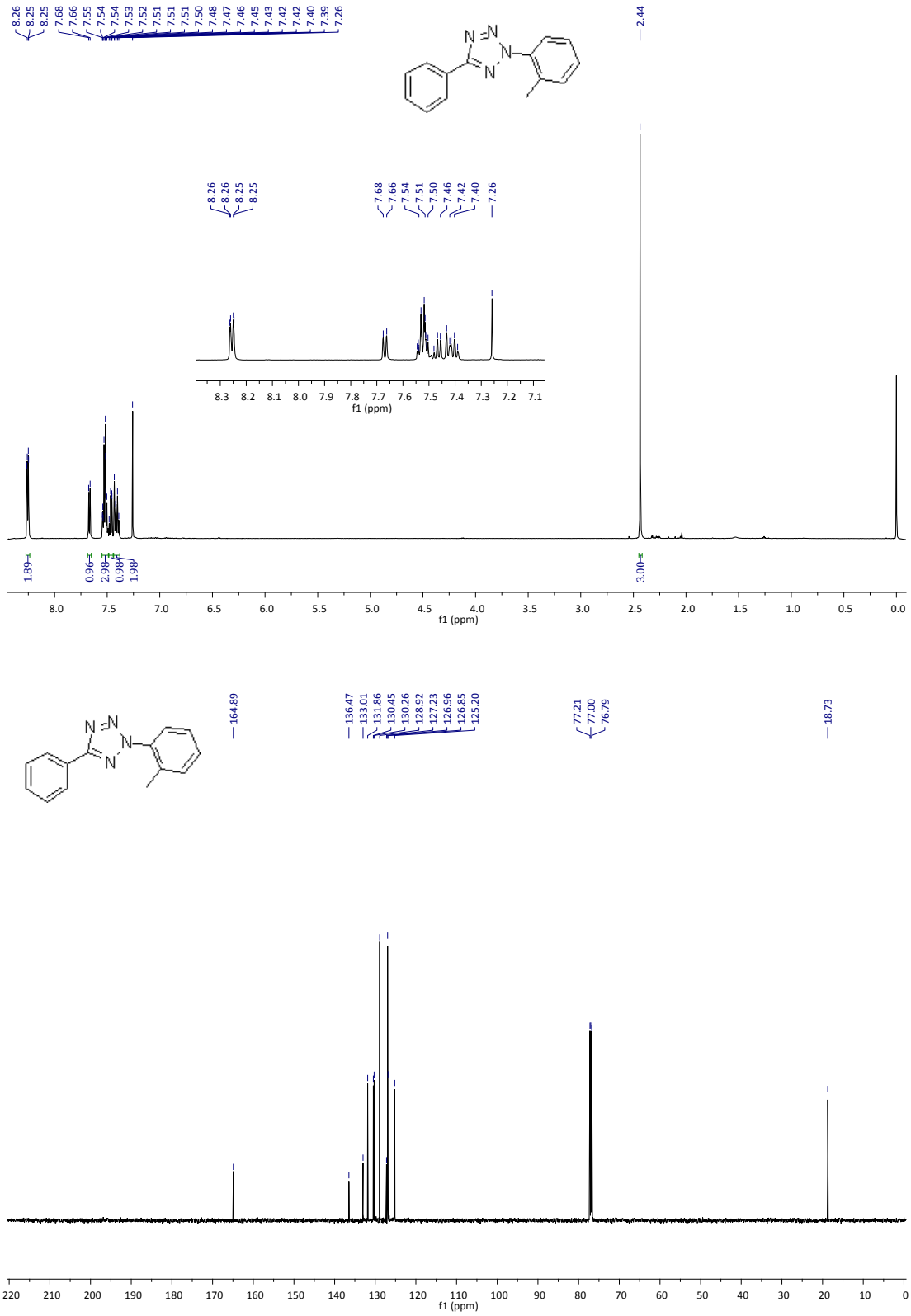


Figure S4. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3b**

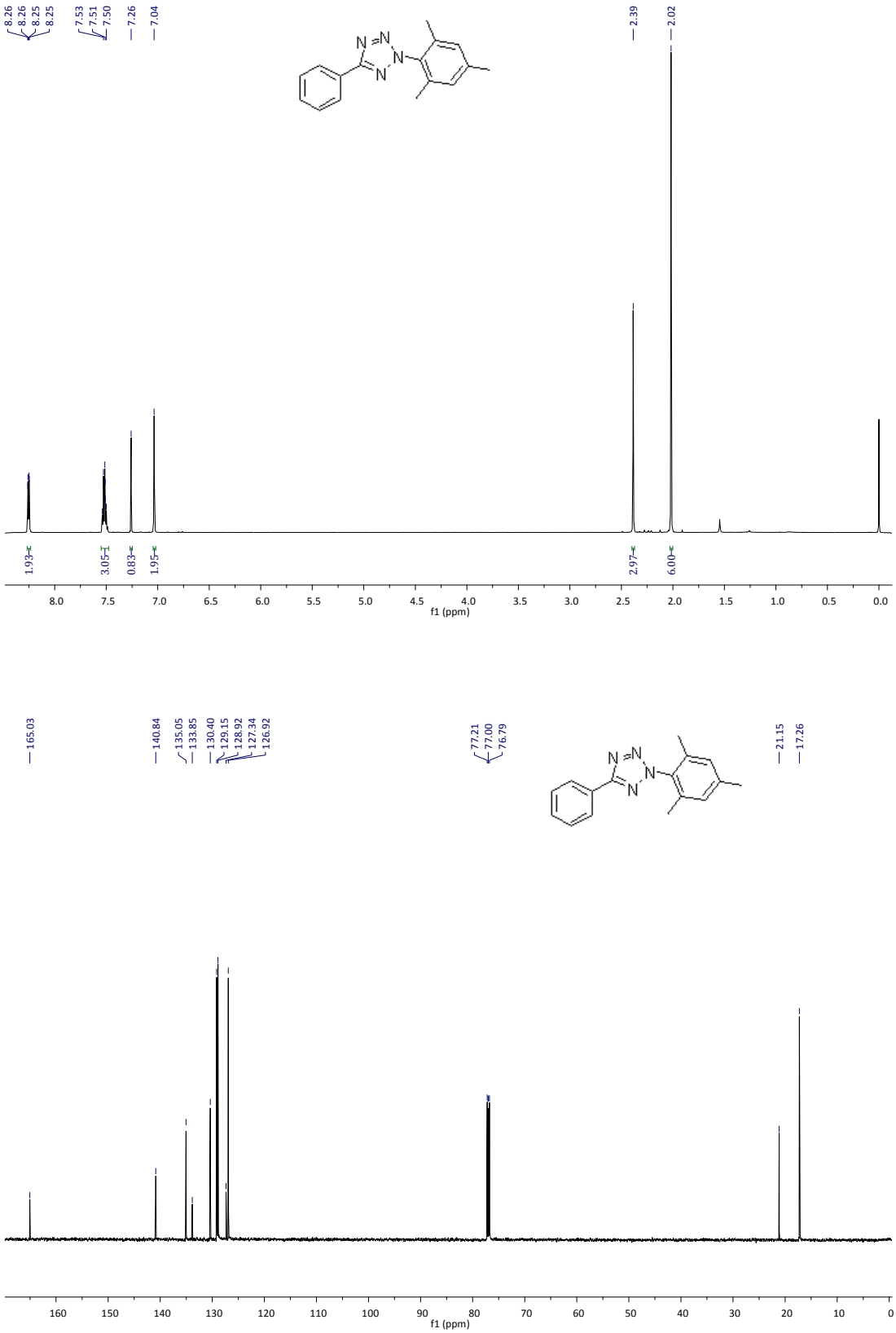


Figure S5. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3c**

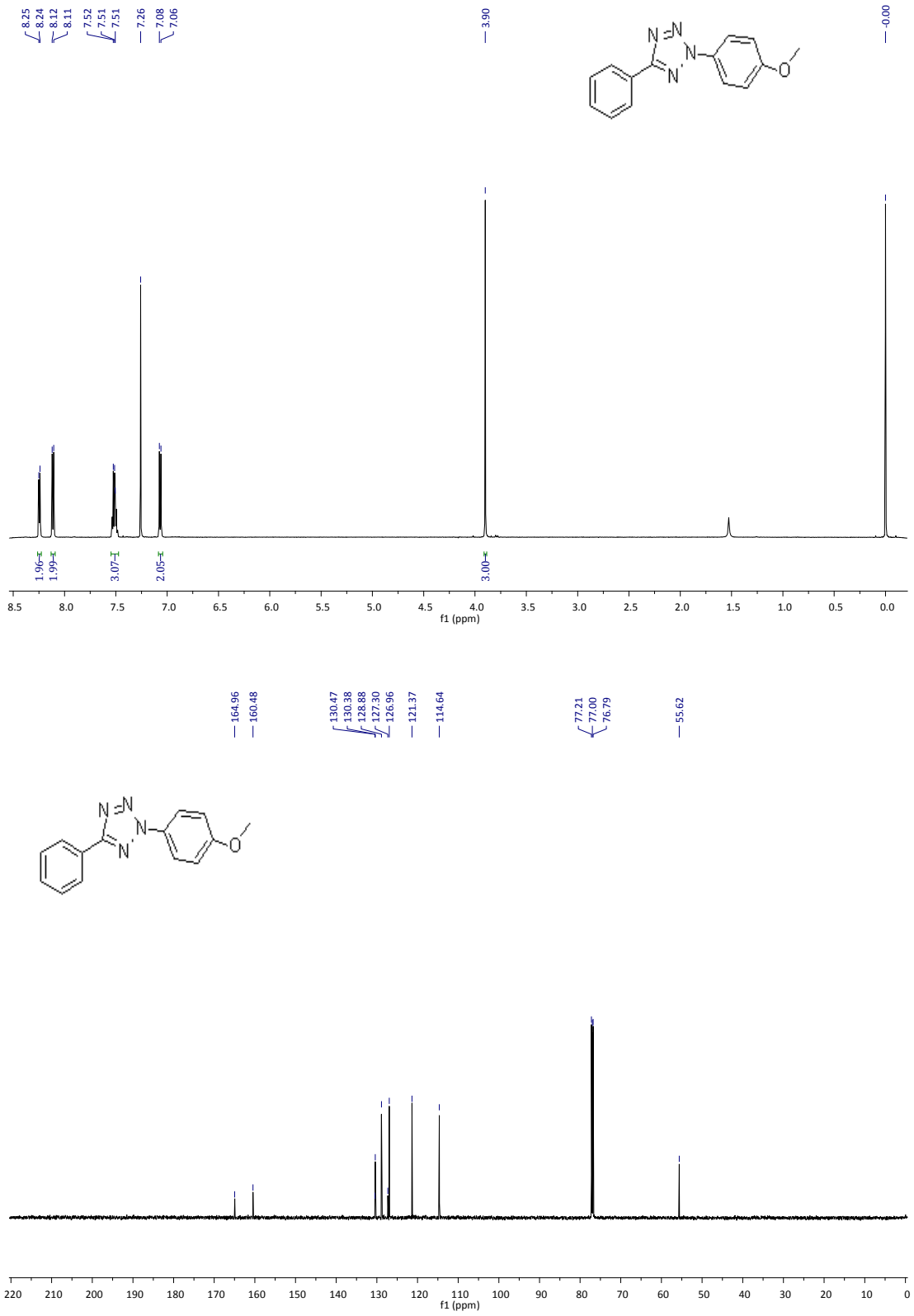


Figure S6. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3d**

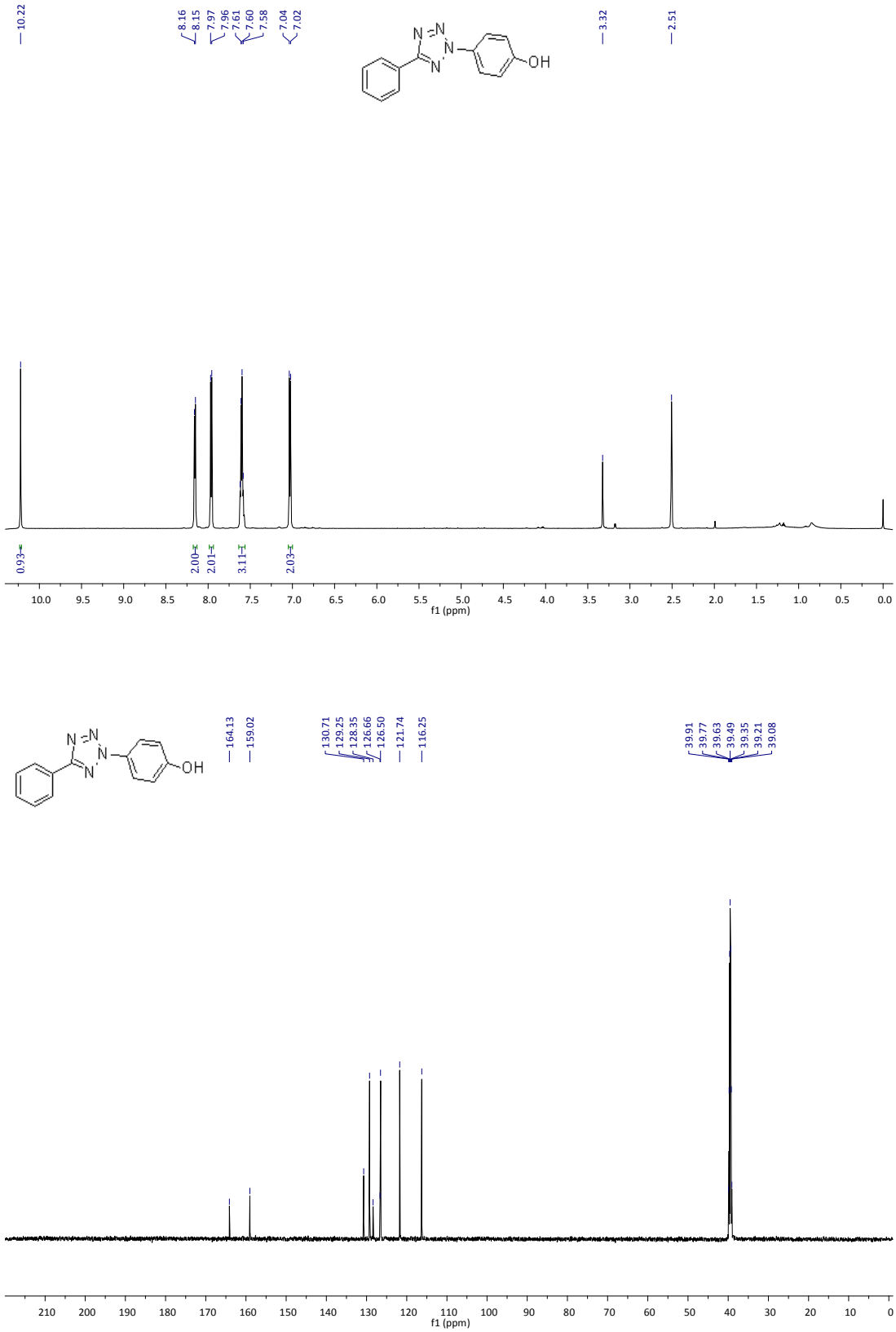


Figure S7. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3e**

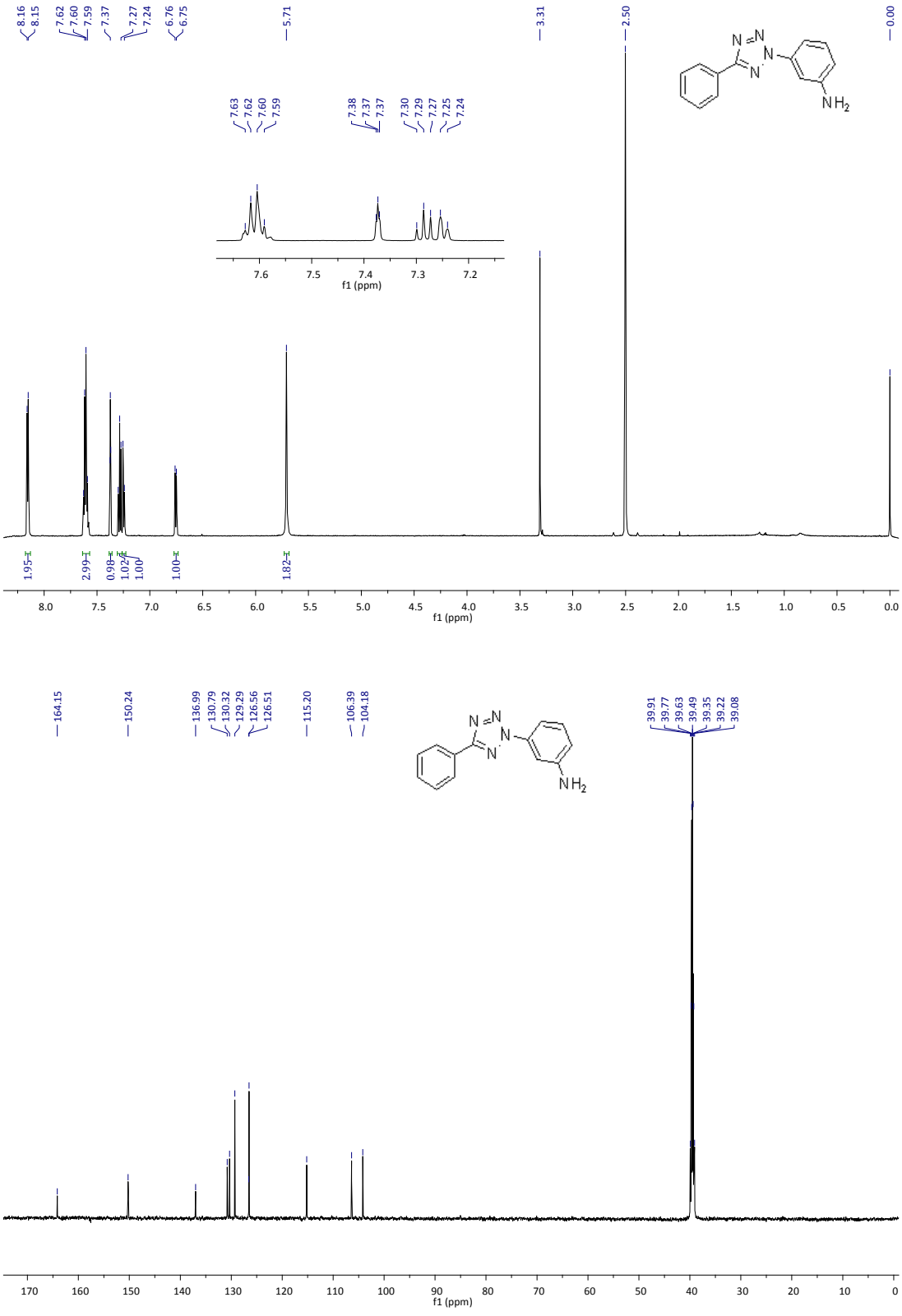


Figure S8. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3f**

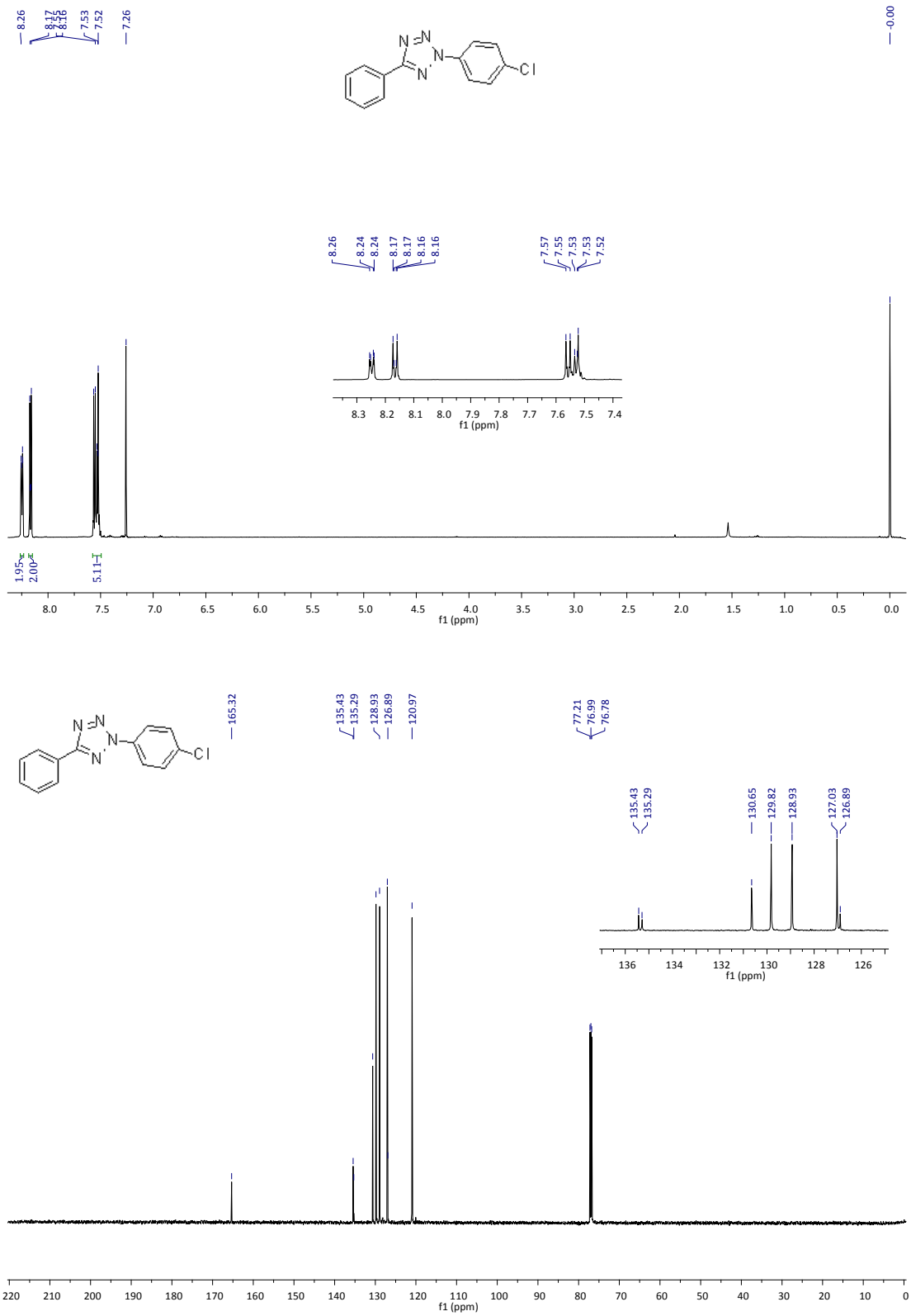


Figure S9. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3g**

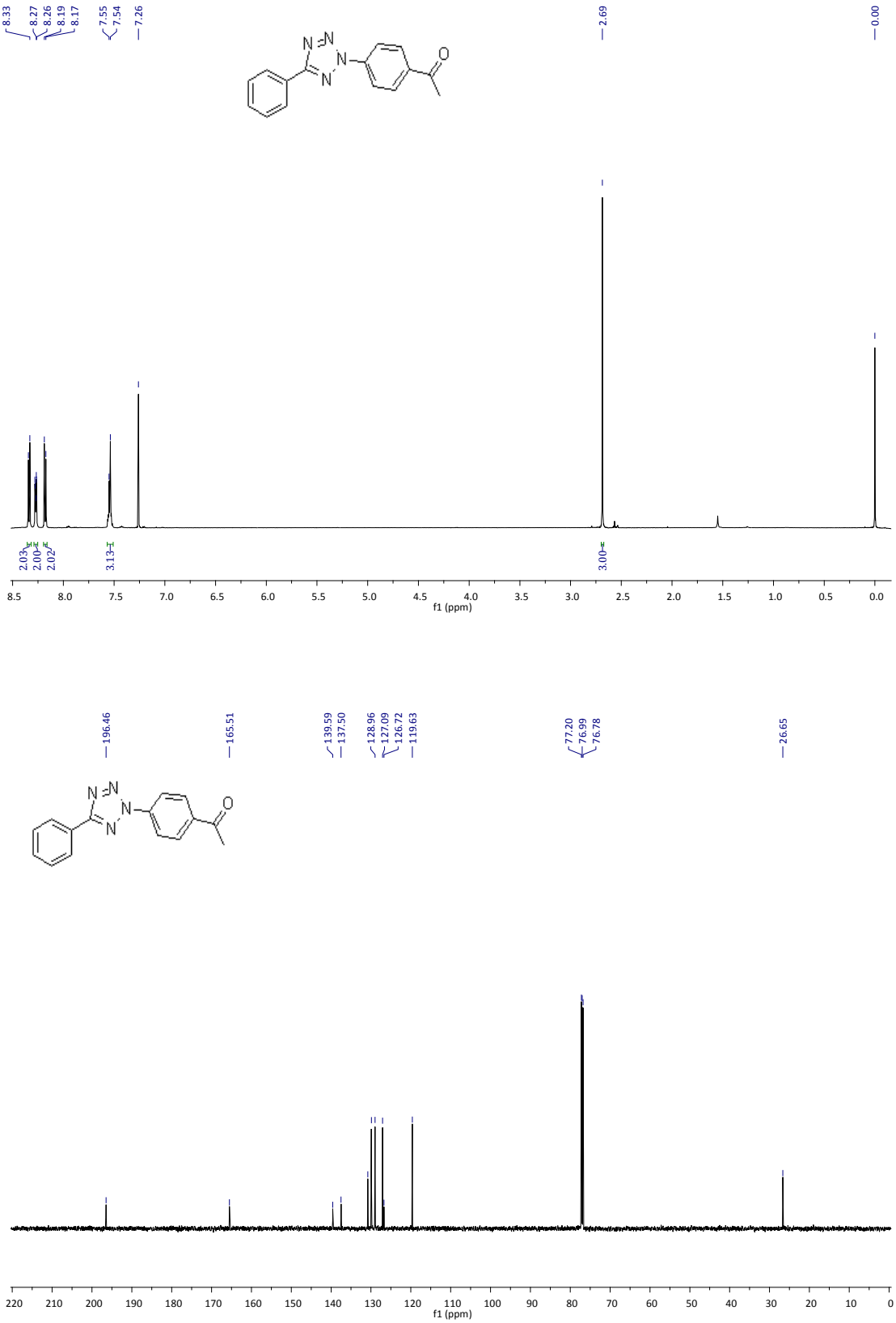


Figure S10. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3h**

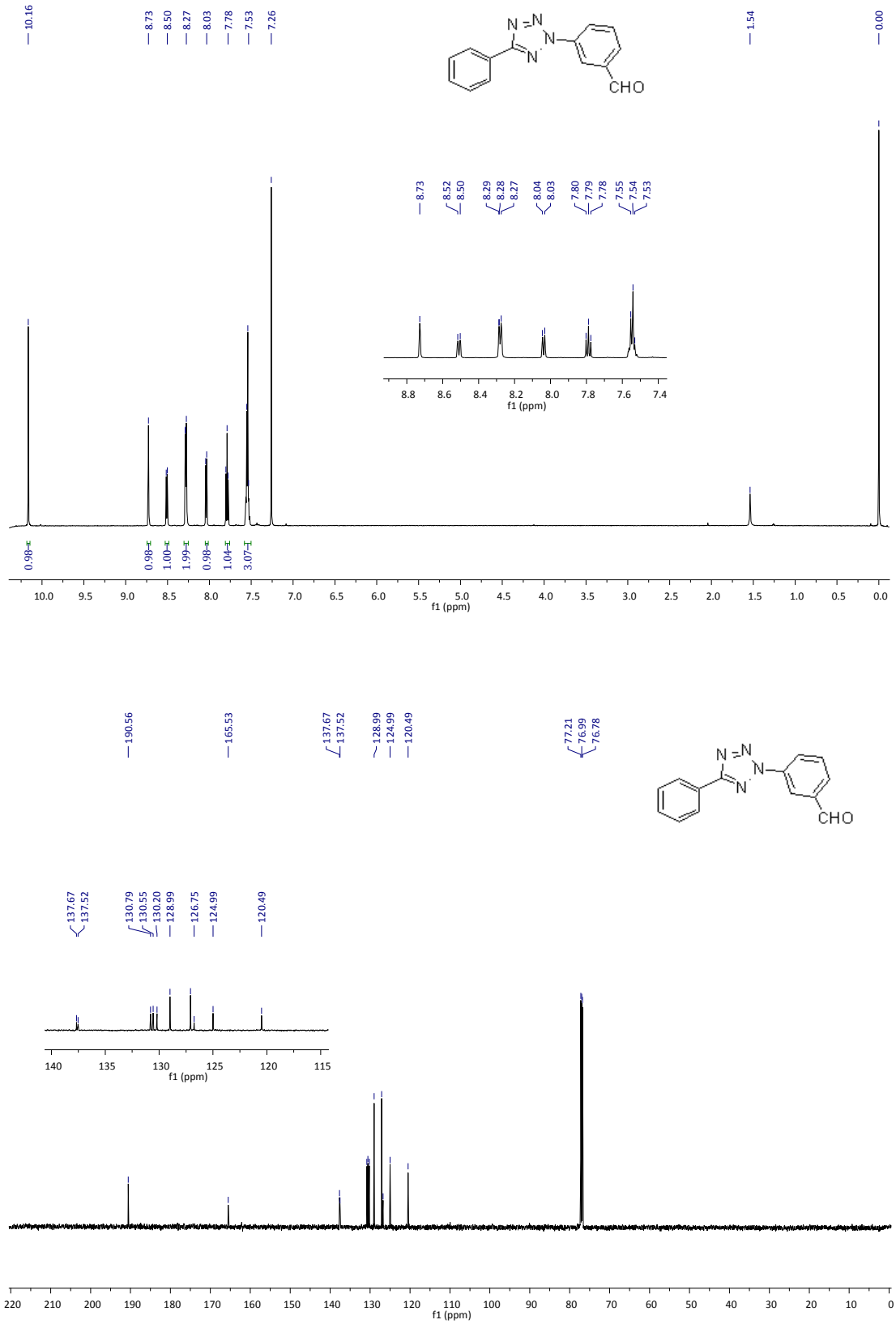


Figure S11. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3i**

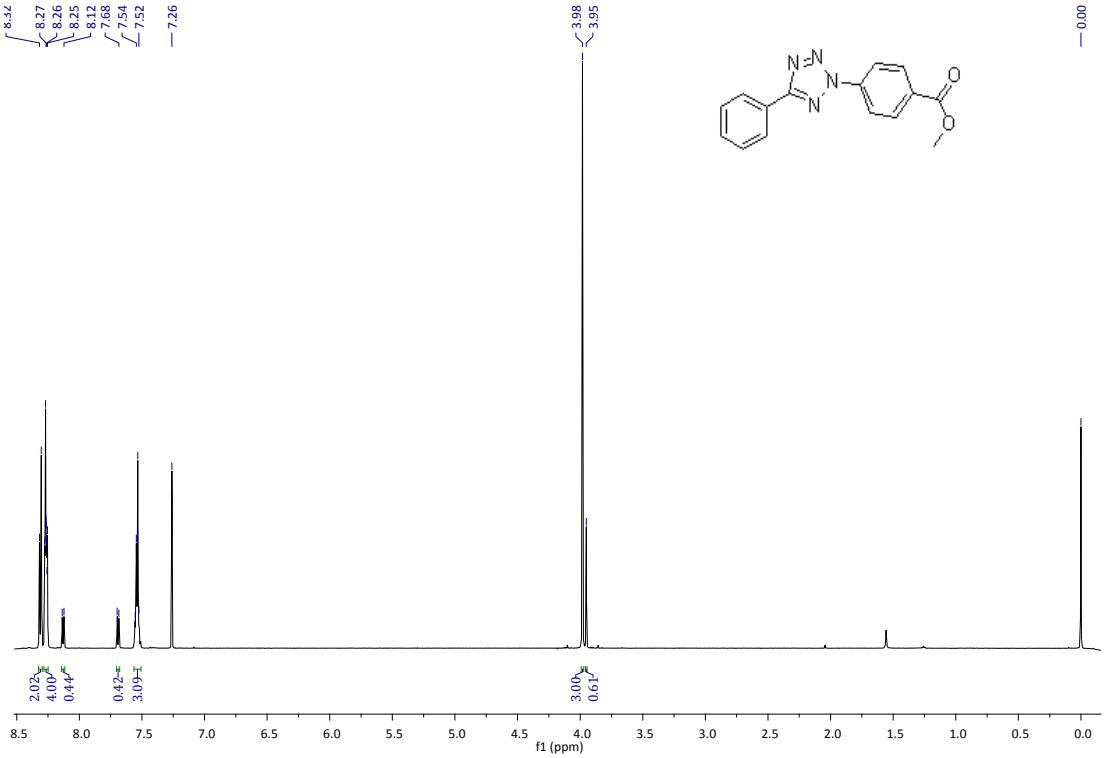


Figure S12. ^{1}H-NMR spectra of compound **3j** (containing a small amount by-product formed from the homocoupling of boromic acids)

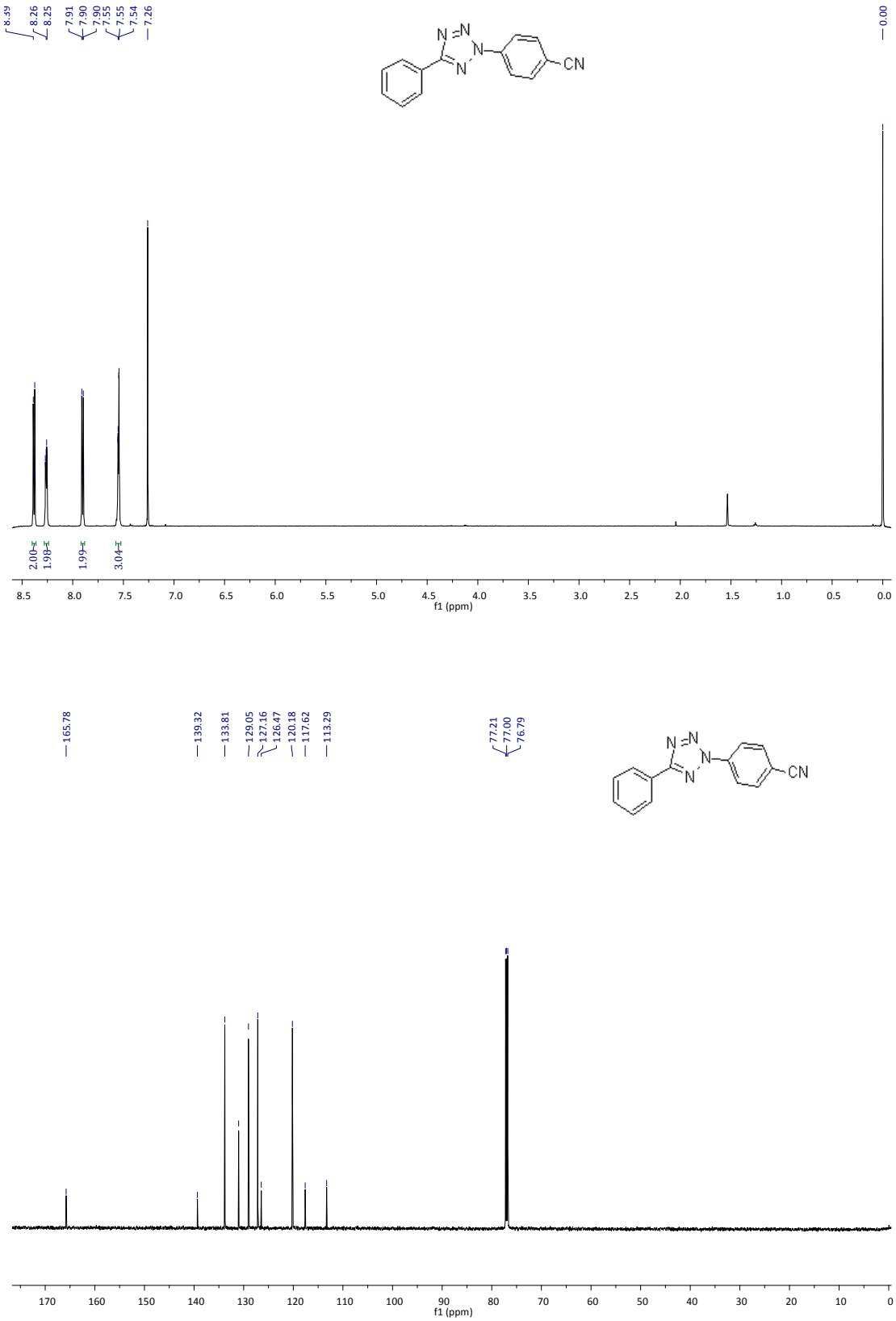


Figure S13. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3k**

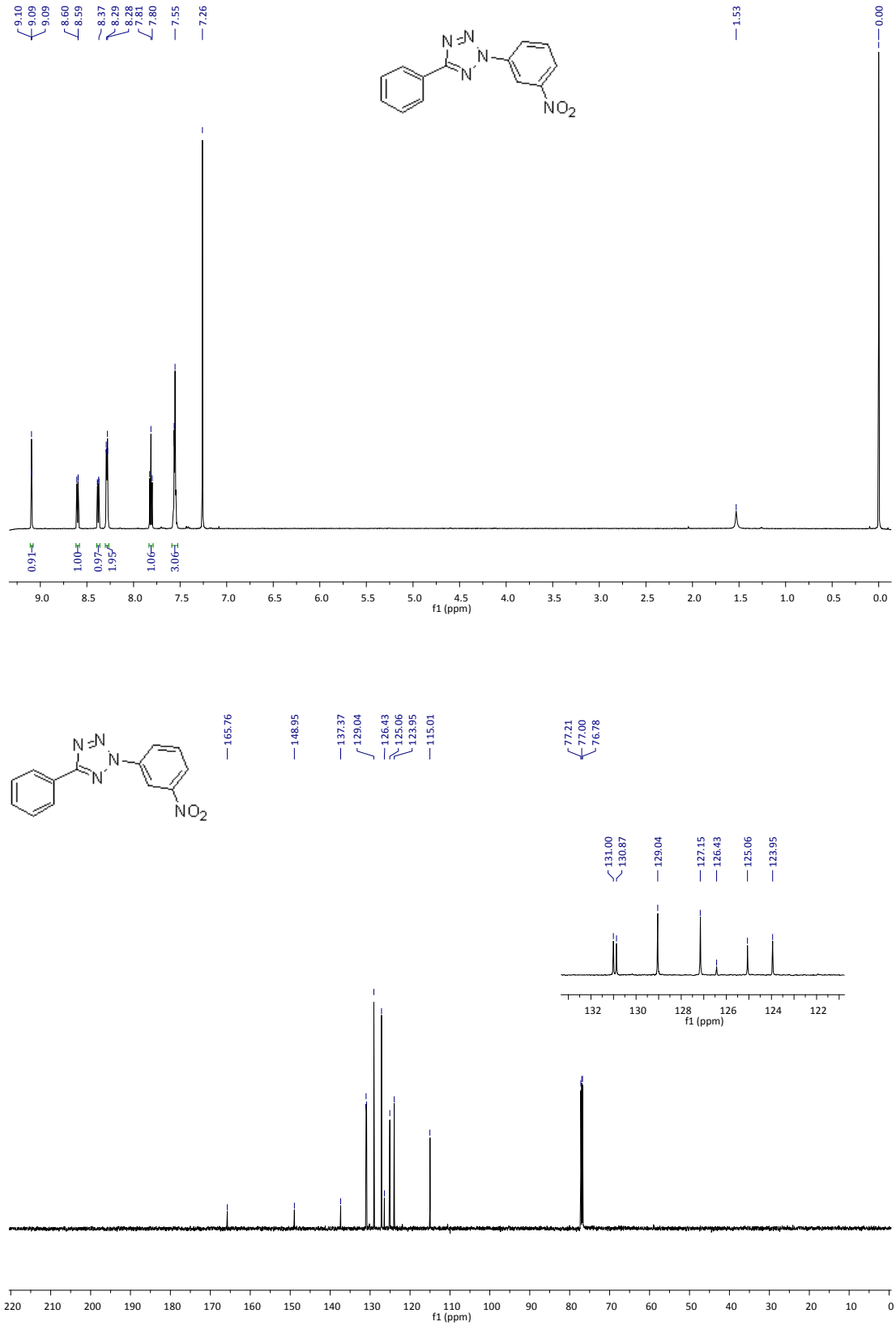


Figure S14. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3l**

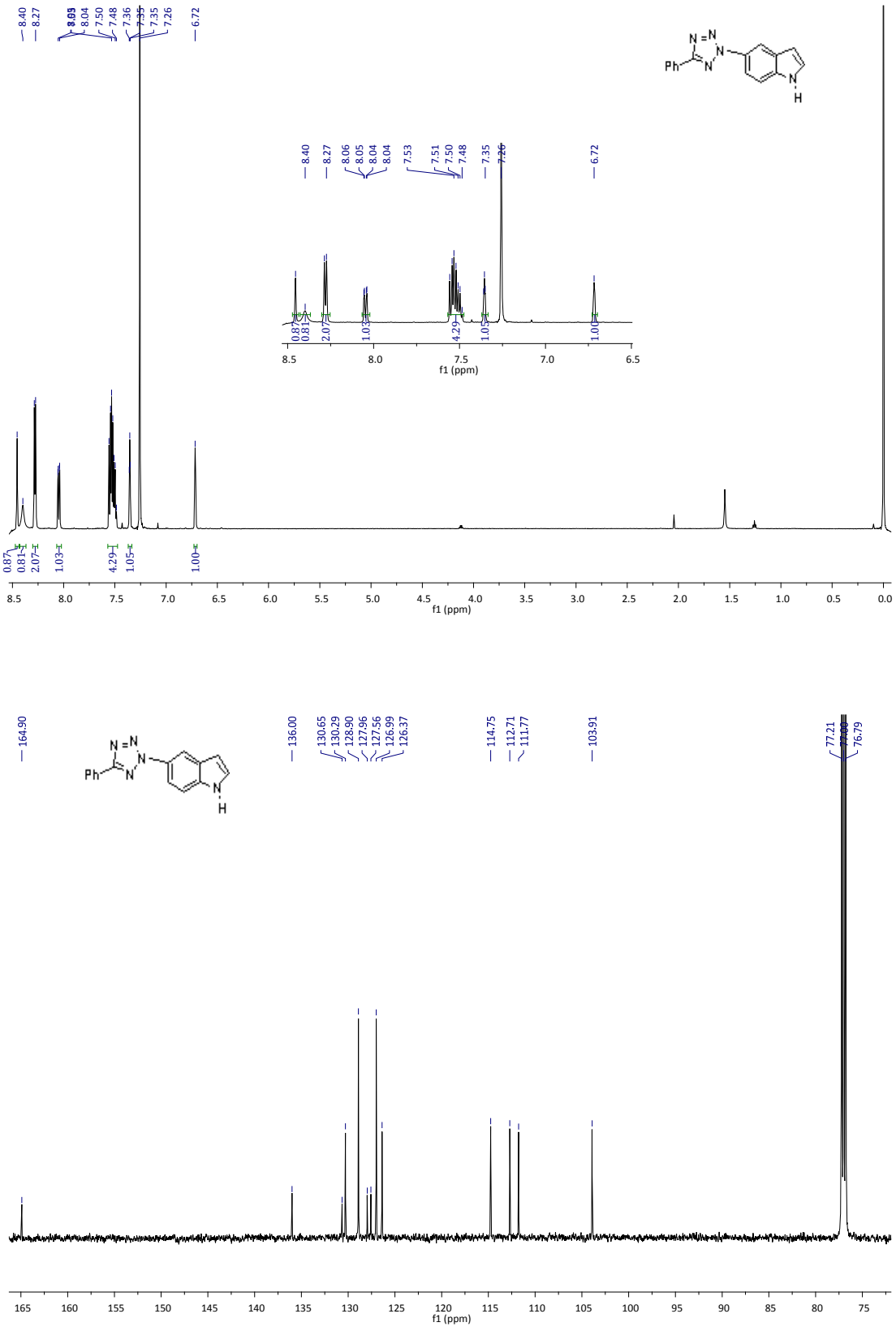
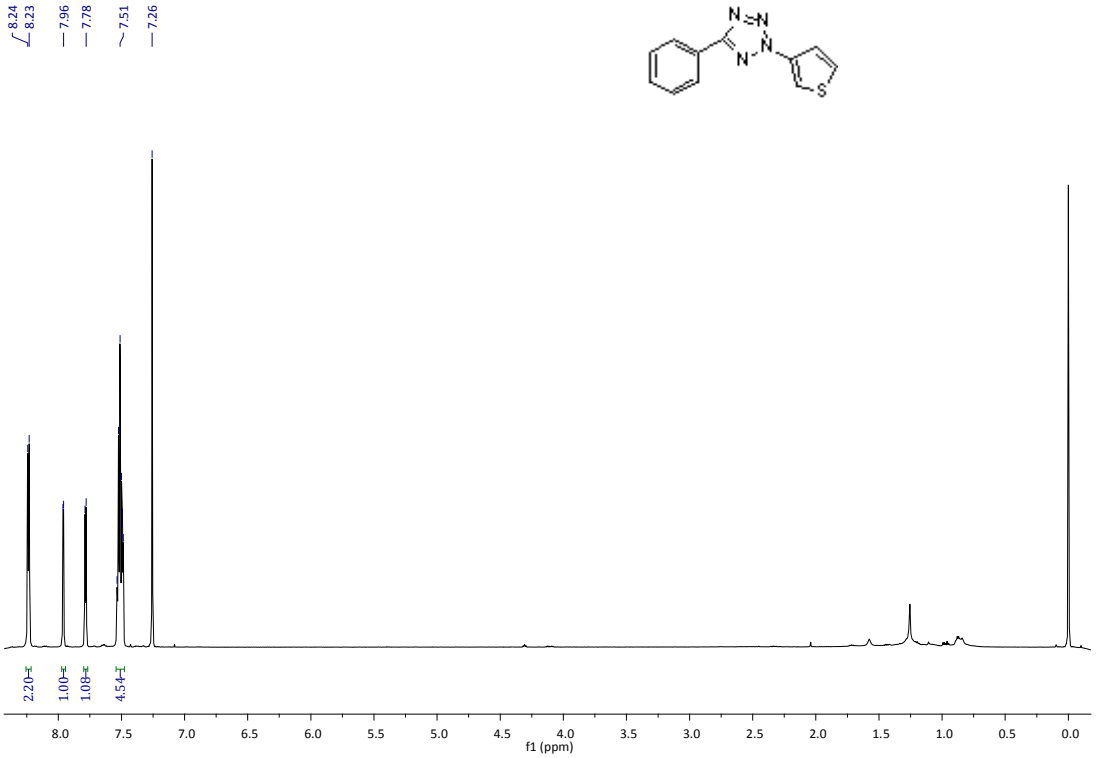


Figure S15. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3m**


8.24
8.23
7.96
7.78
7.51
7.26
2.20
1.00
1.08
4.54
f1 (ppm)

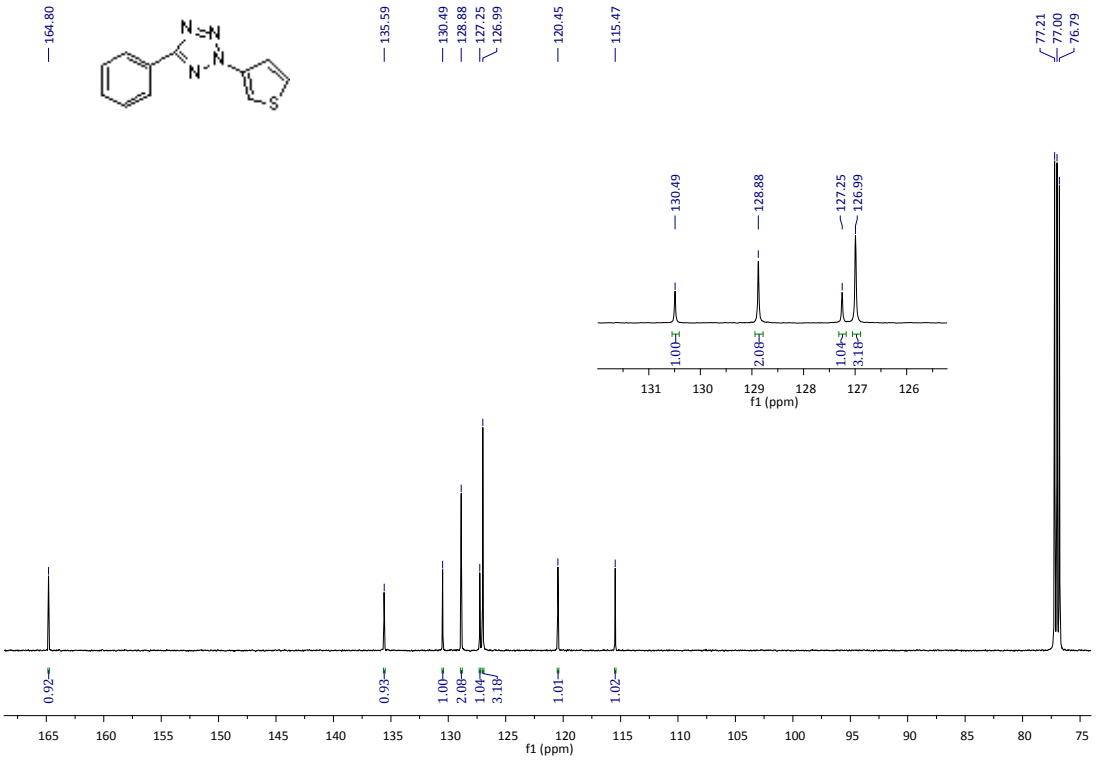
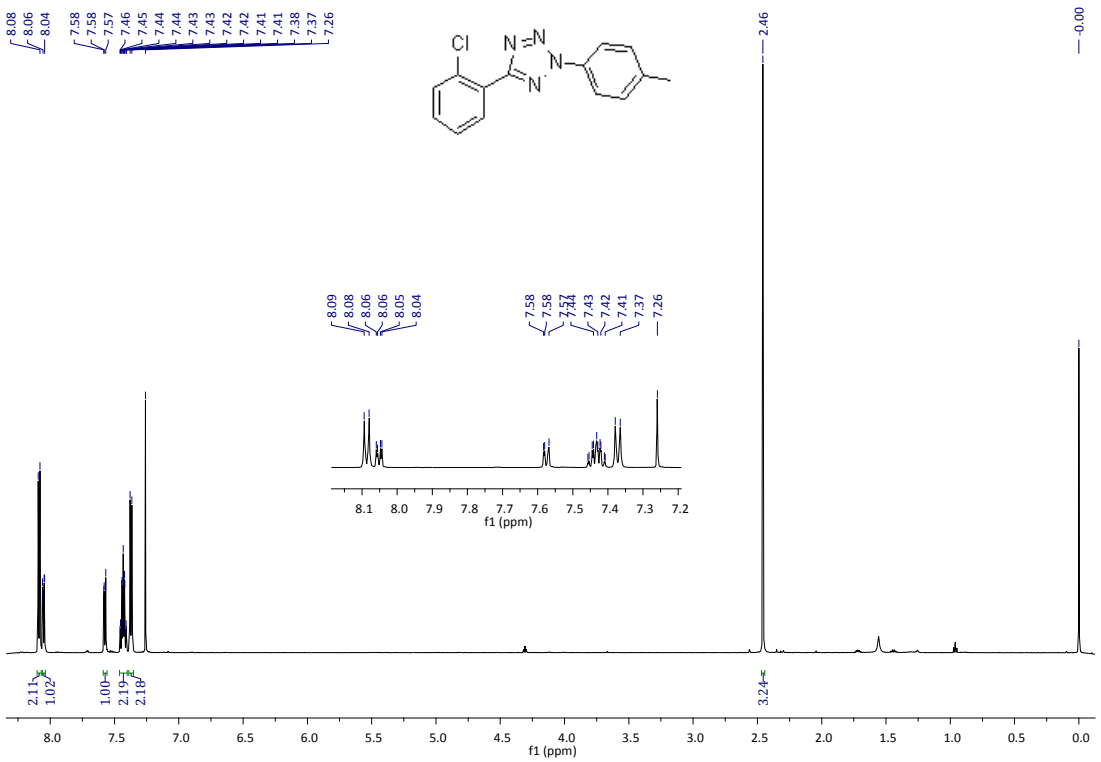

164.80
135.59
130.49
128.88
127.25
126.99
120.45
115.47
77.21
77.00
76.79
0.92
0.93
1.00
2.08
1.04
3.18
1.01
1.02
f1 (ppm)

Figure S16. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3n**



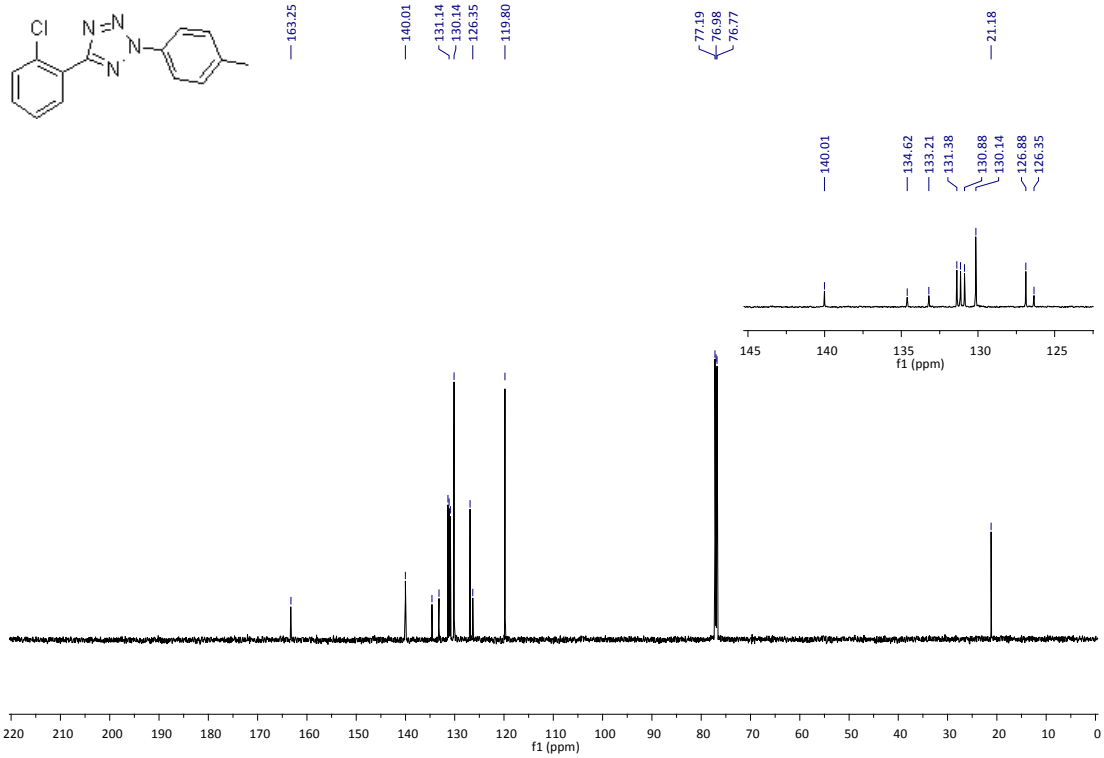


Figure S17. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4a**

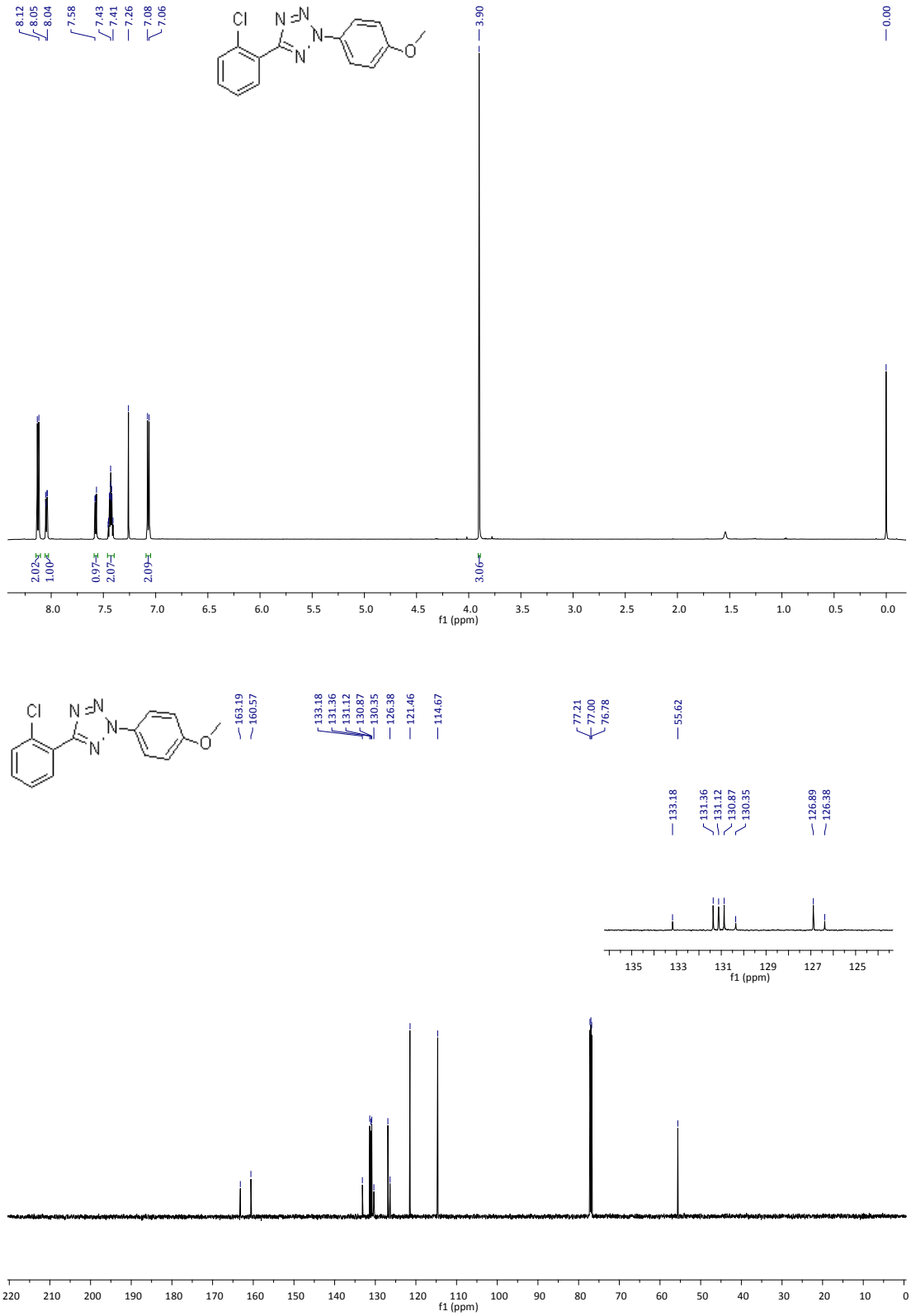


Figure S18. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4b**

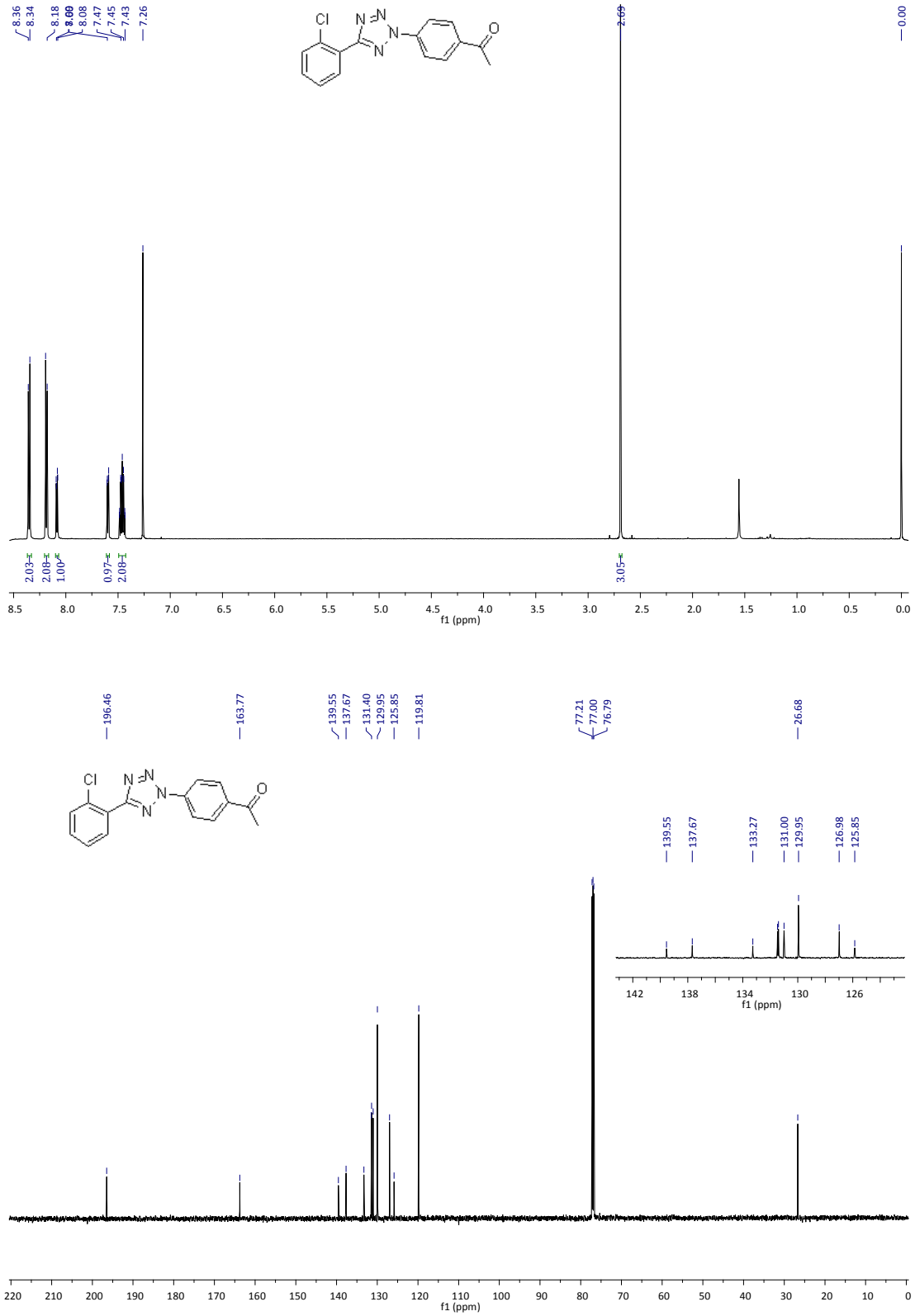


Figure S19. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4c**

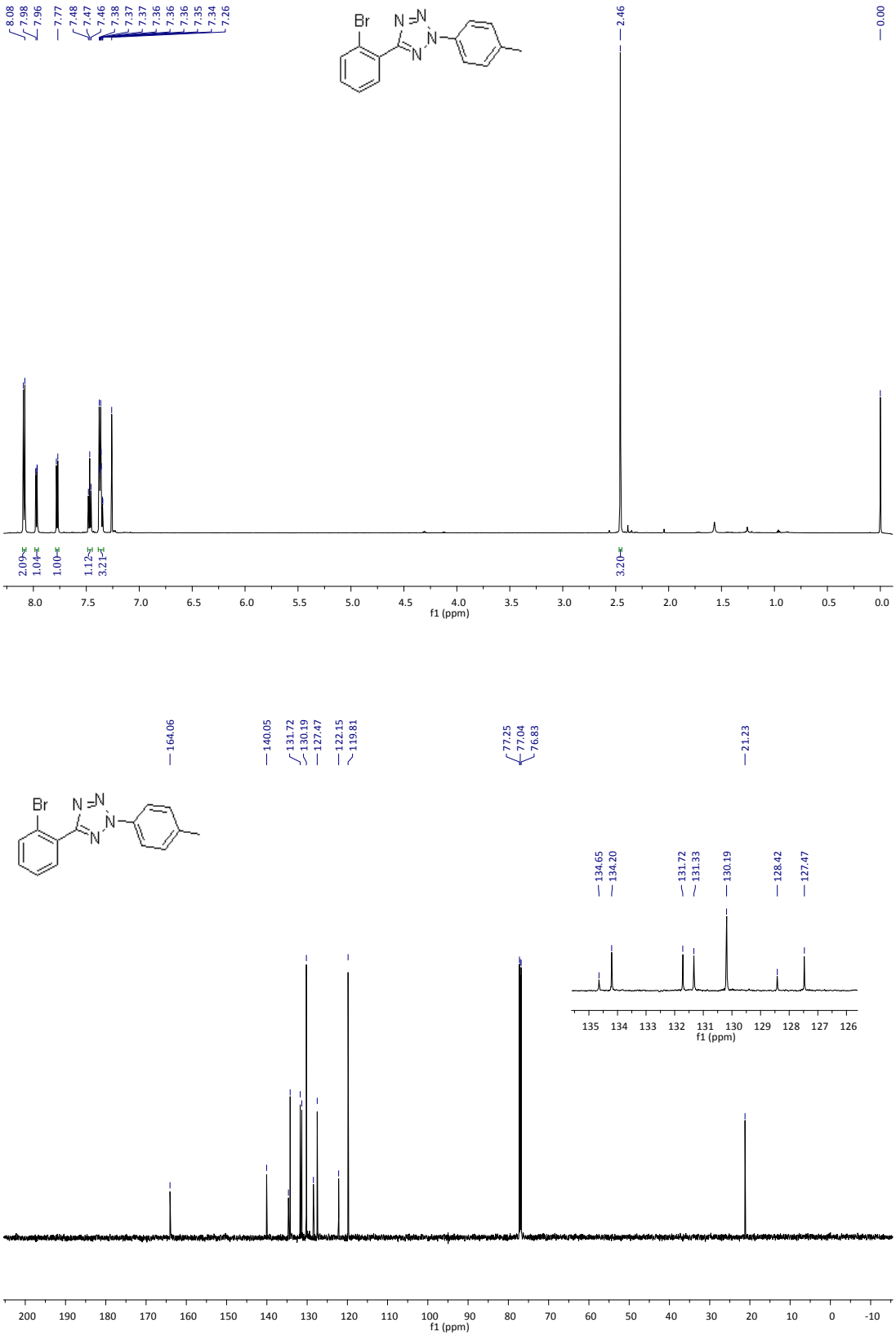


Figure S20. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **5a**

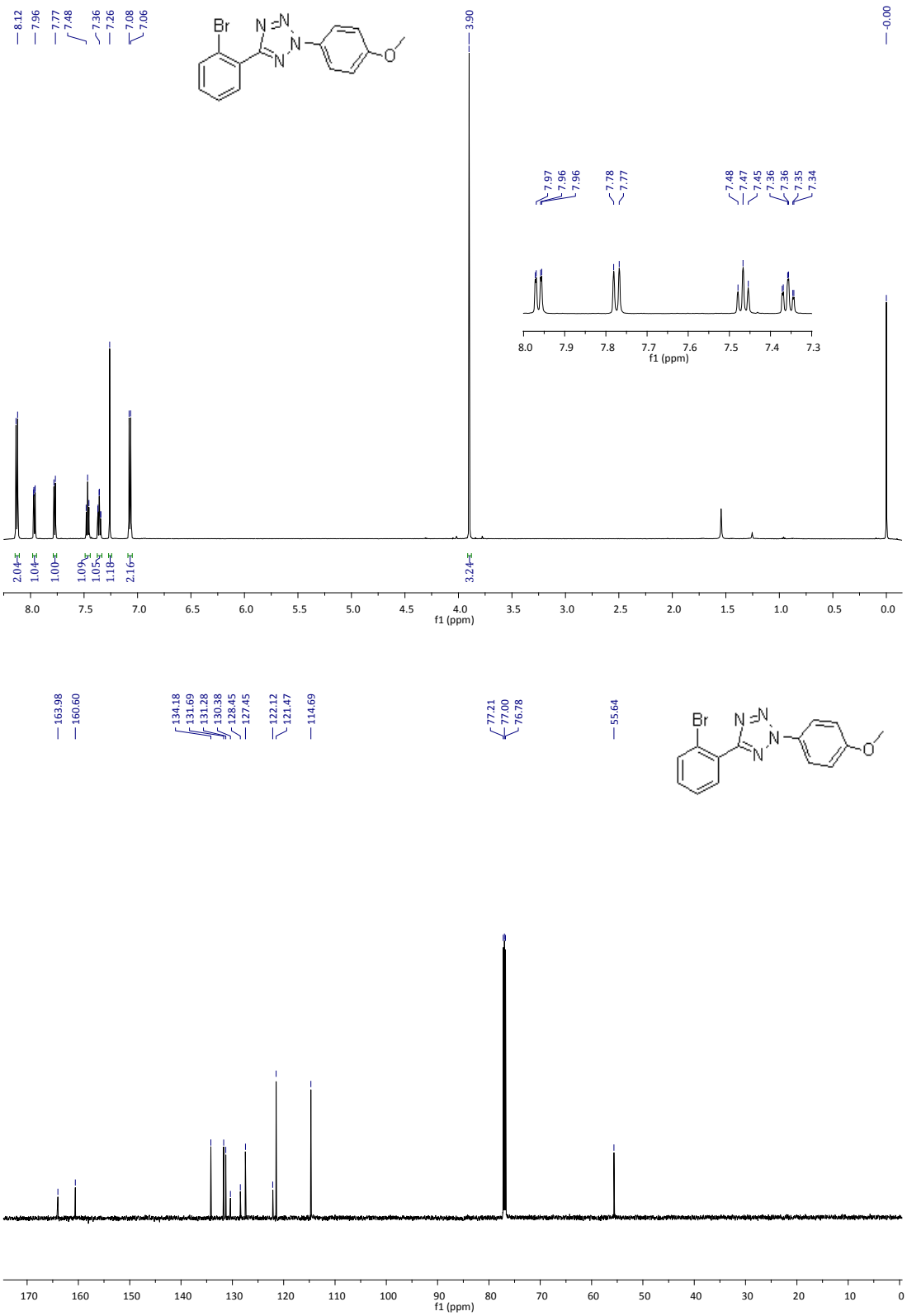


Figure S21. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **5b**

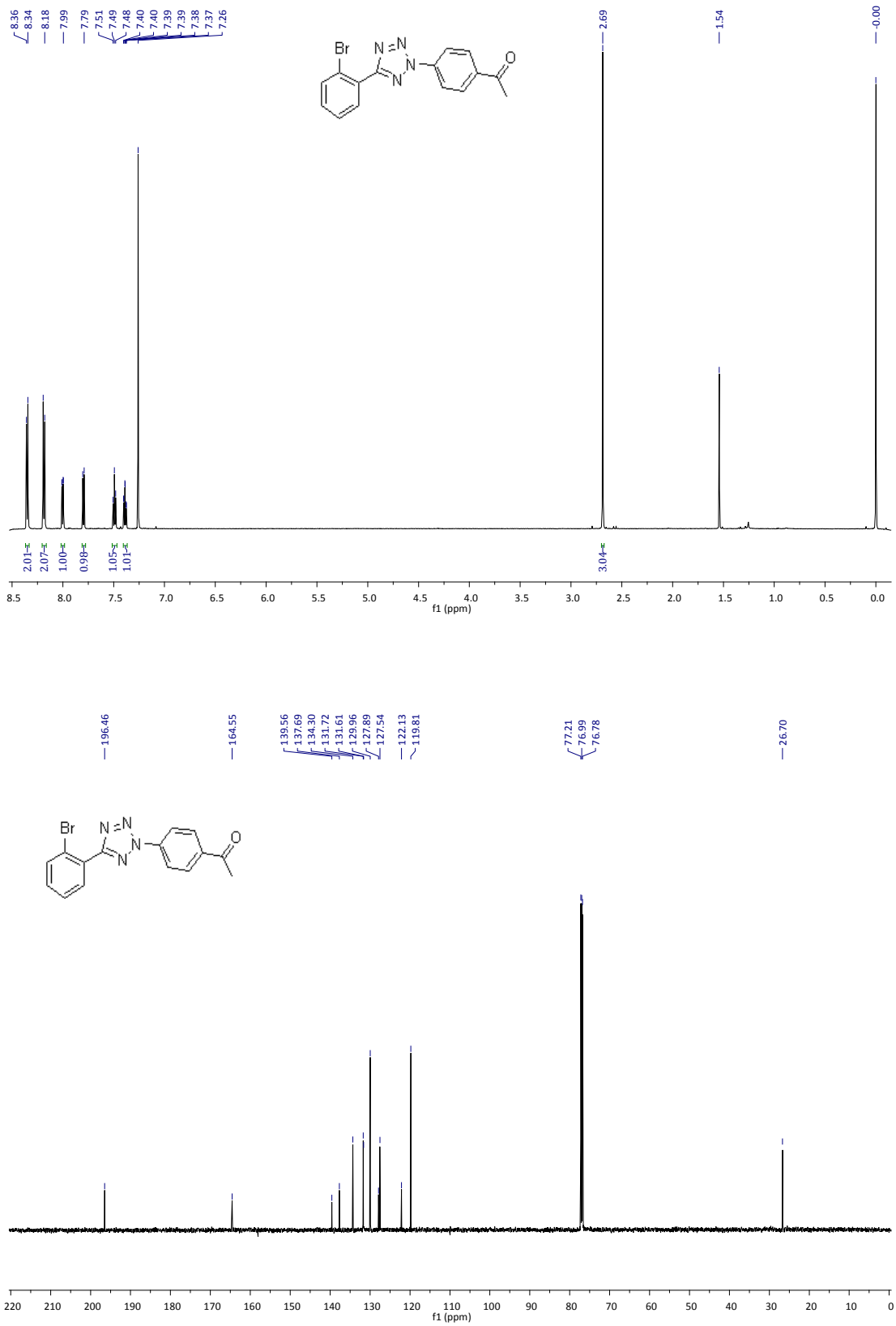


Figure S22. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **5c**

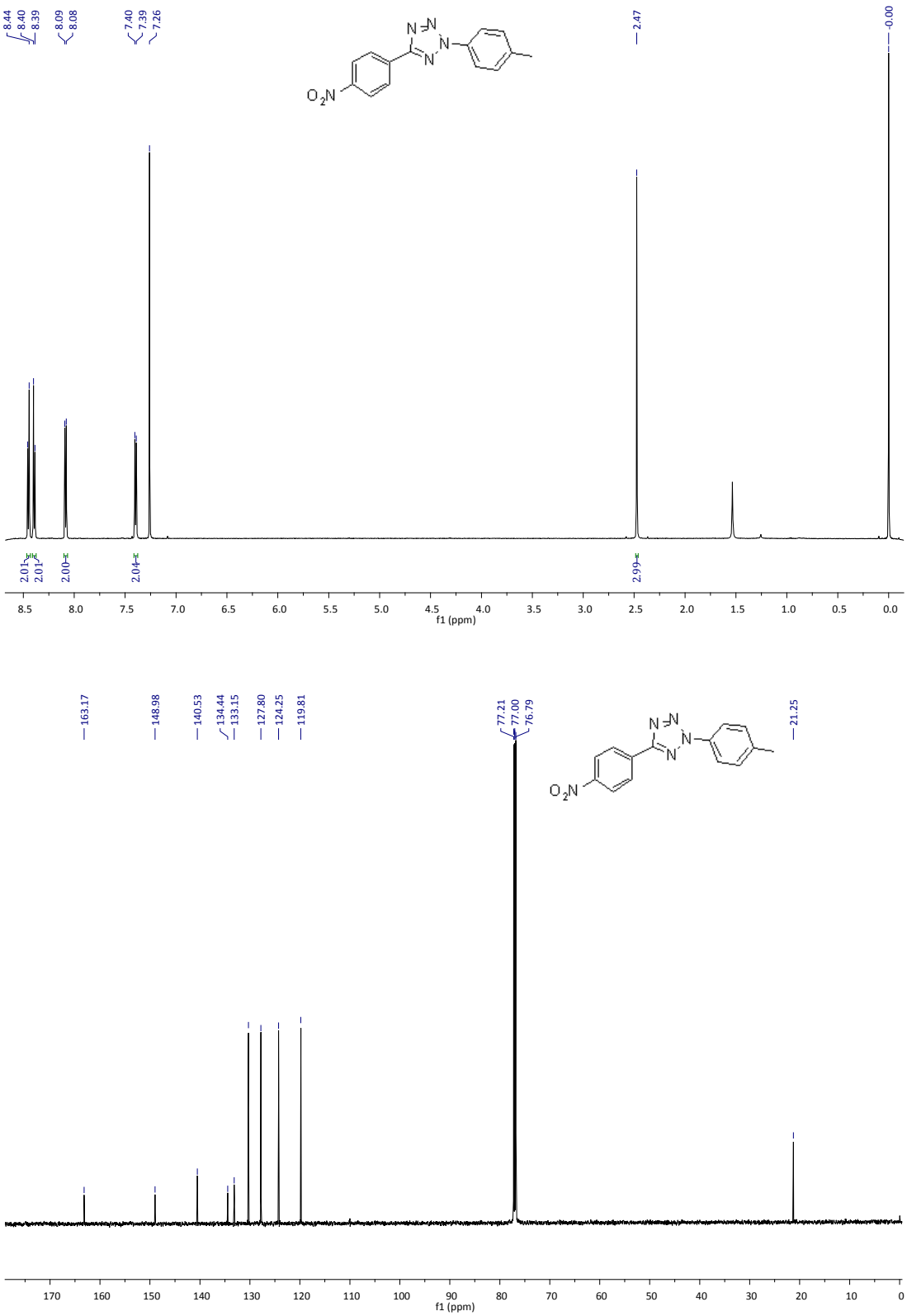


Figure S23. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6a**

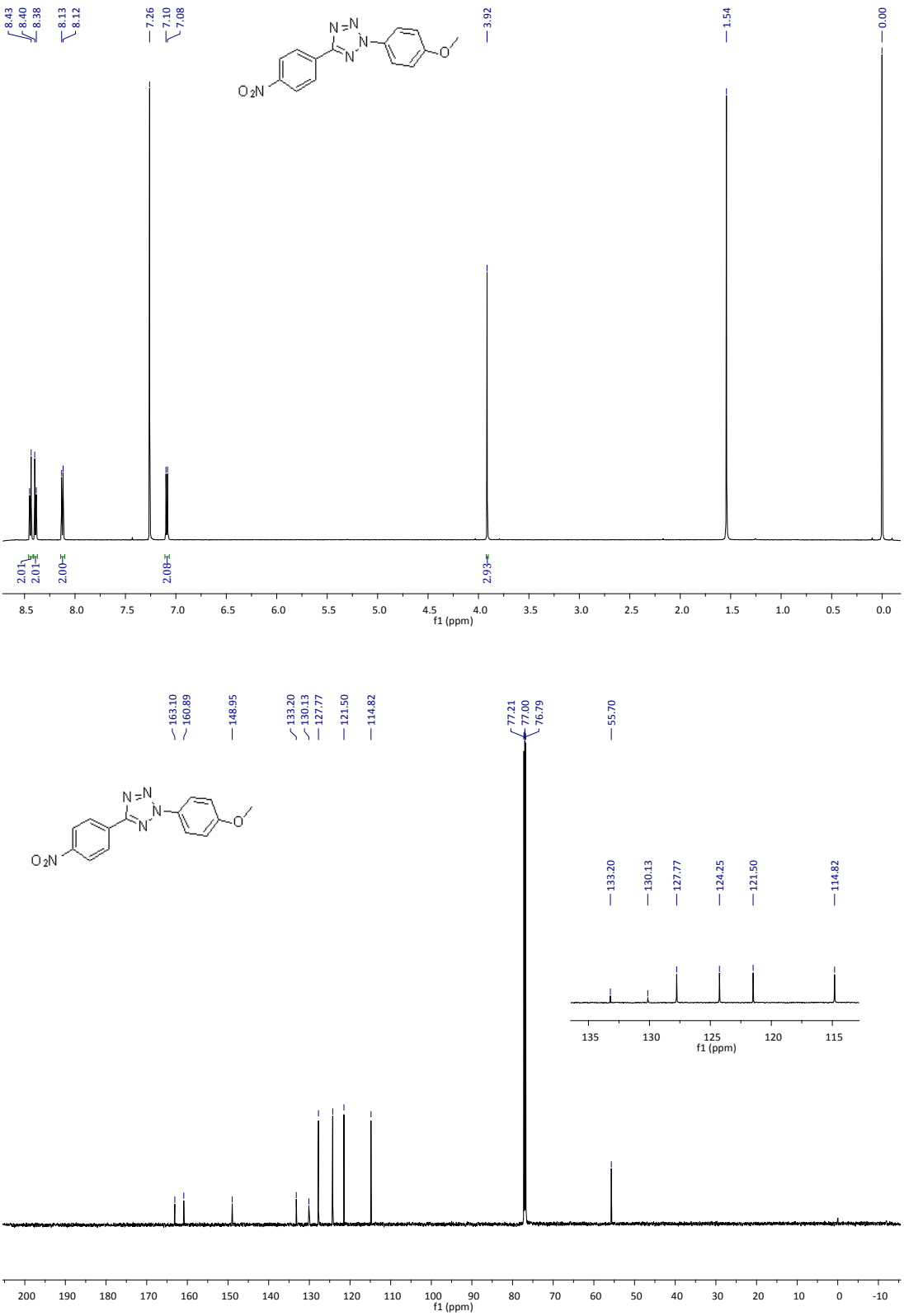


Figure S24. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6b**

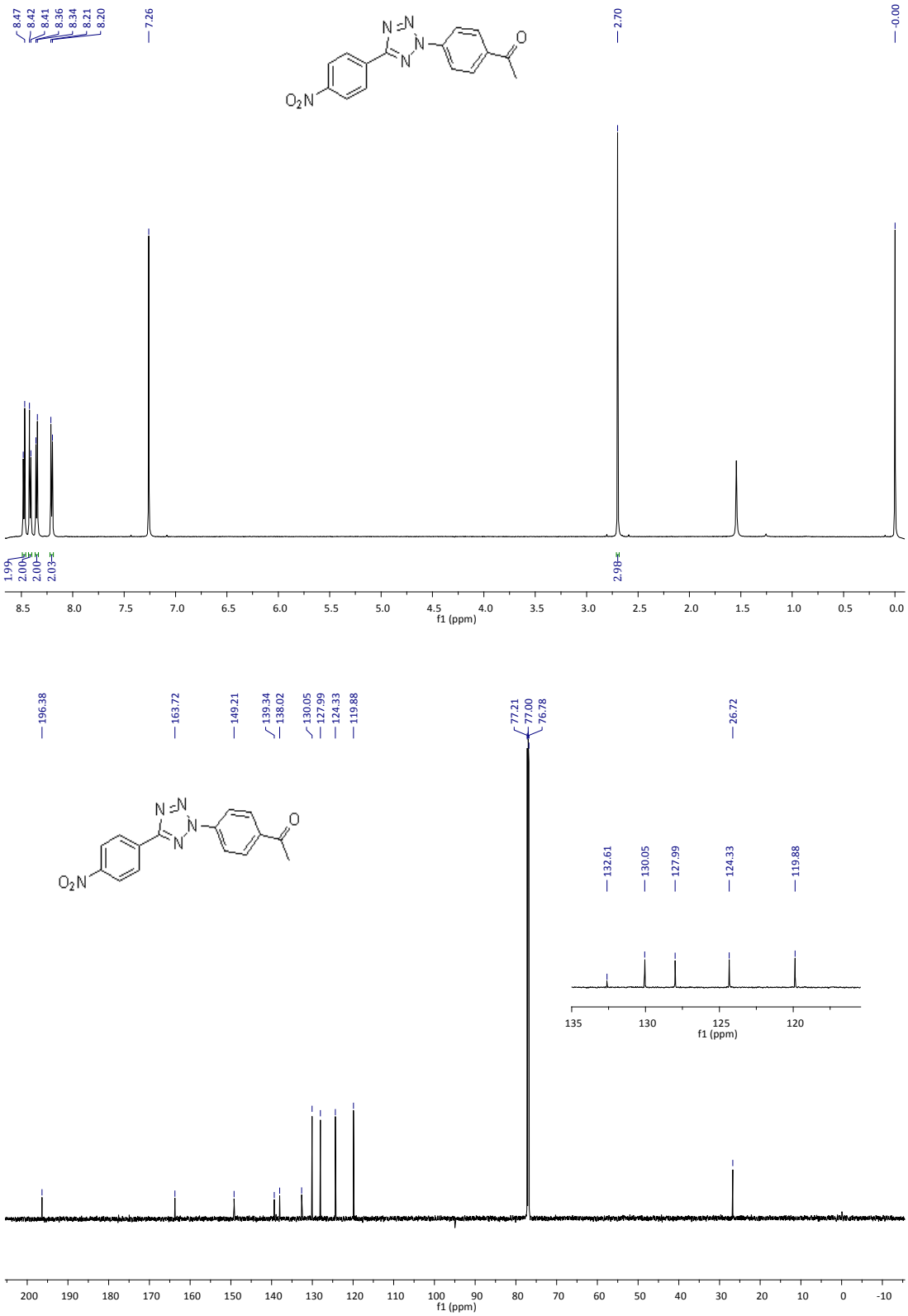


Figure S25. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6c**

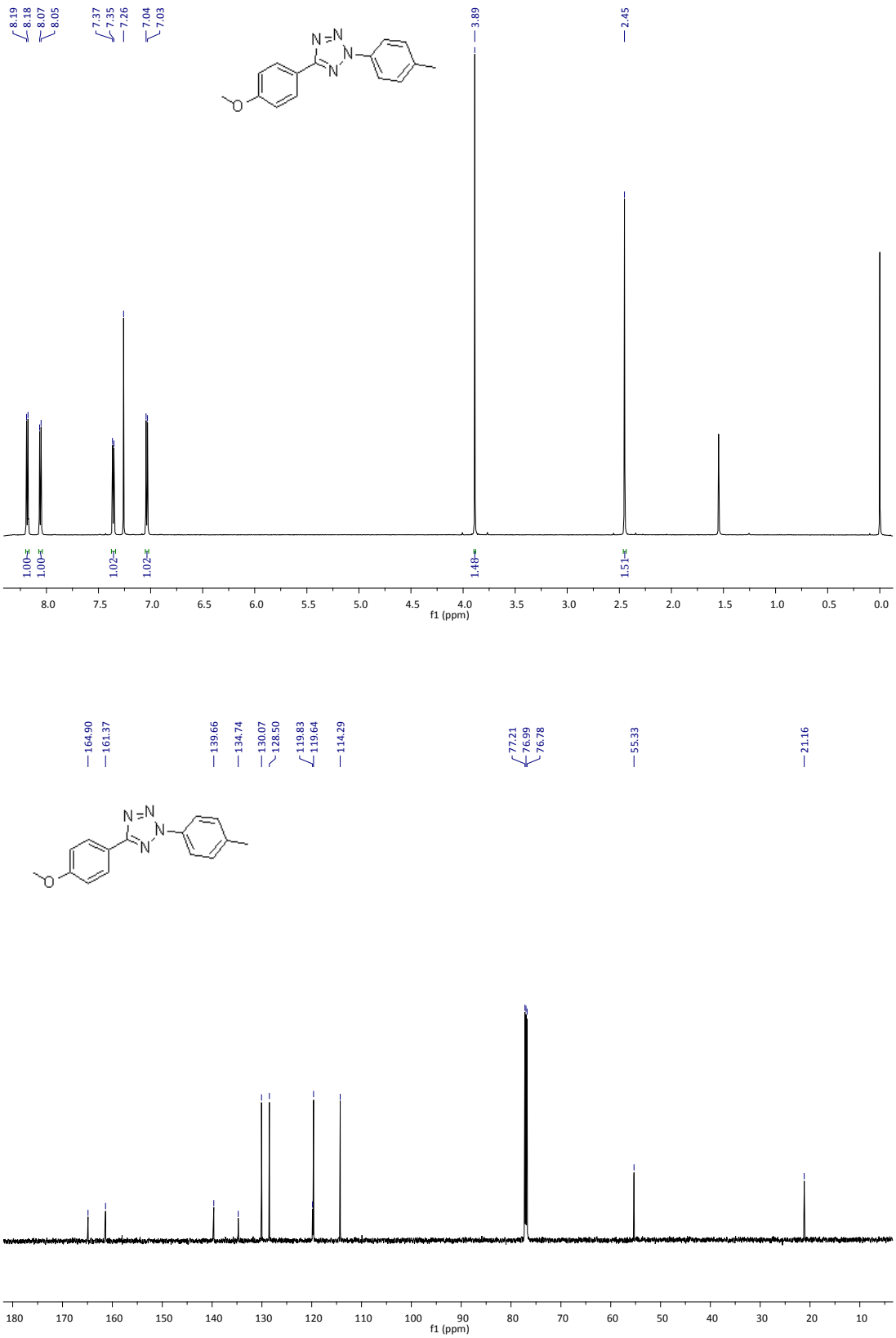


Figure S26. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **7a**

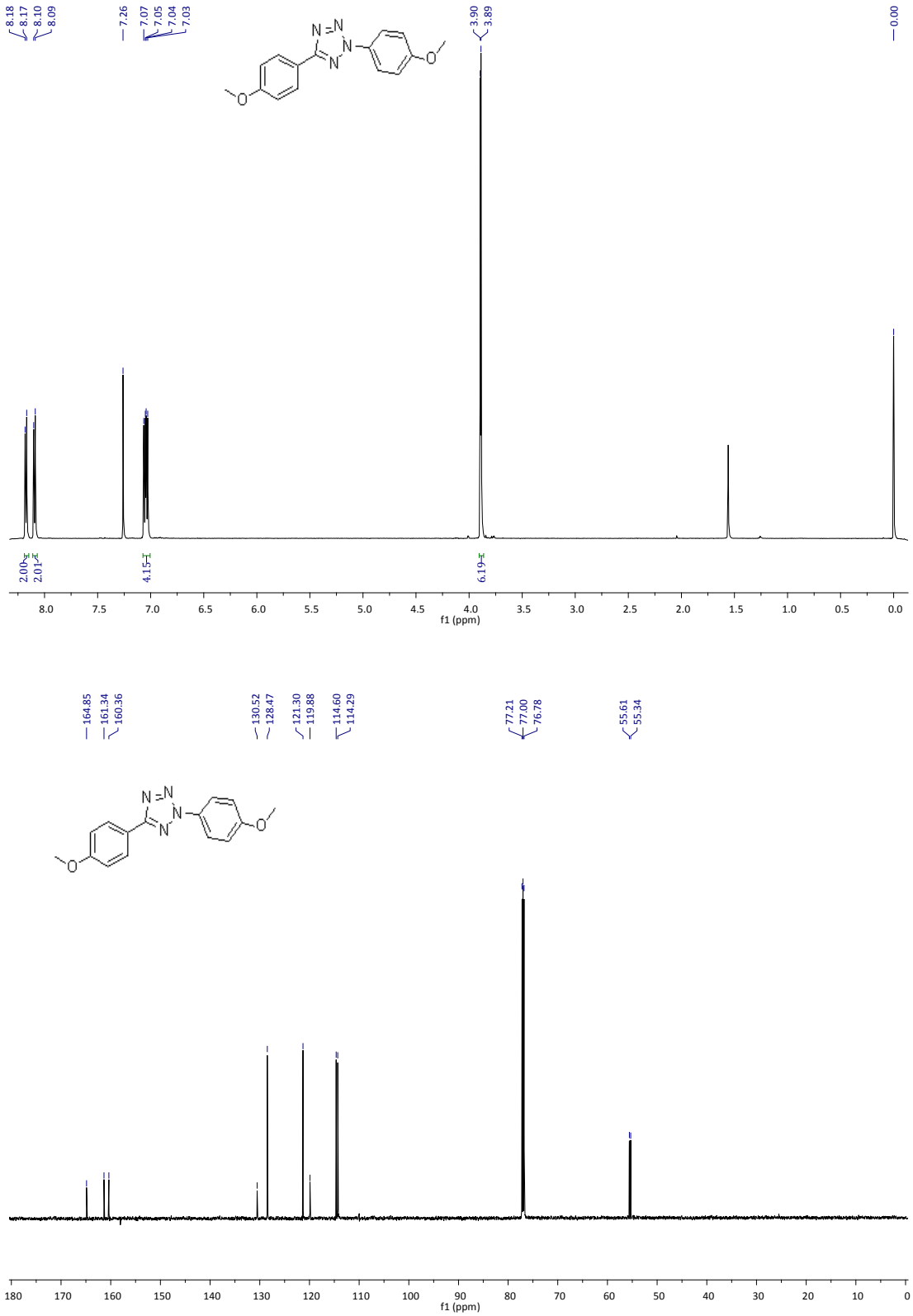


Figure S27. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **7b**

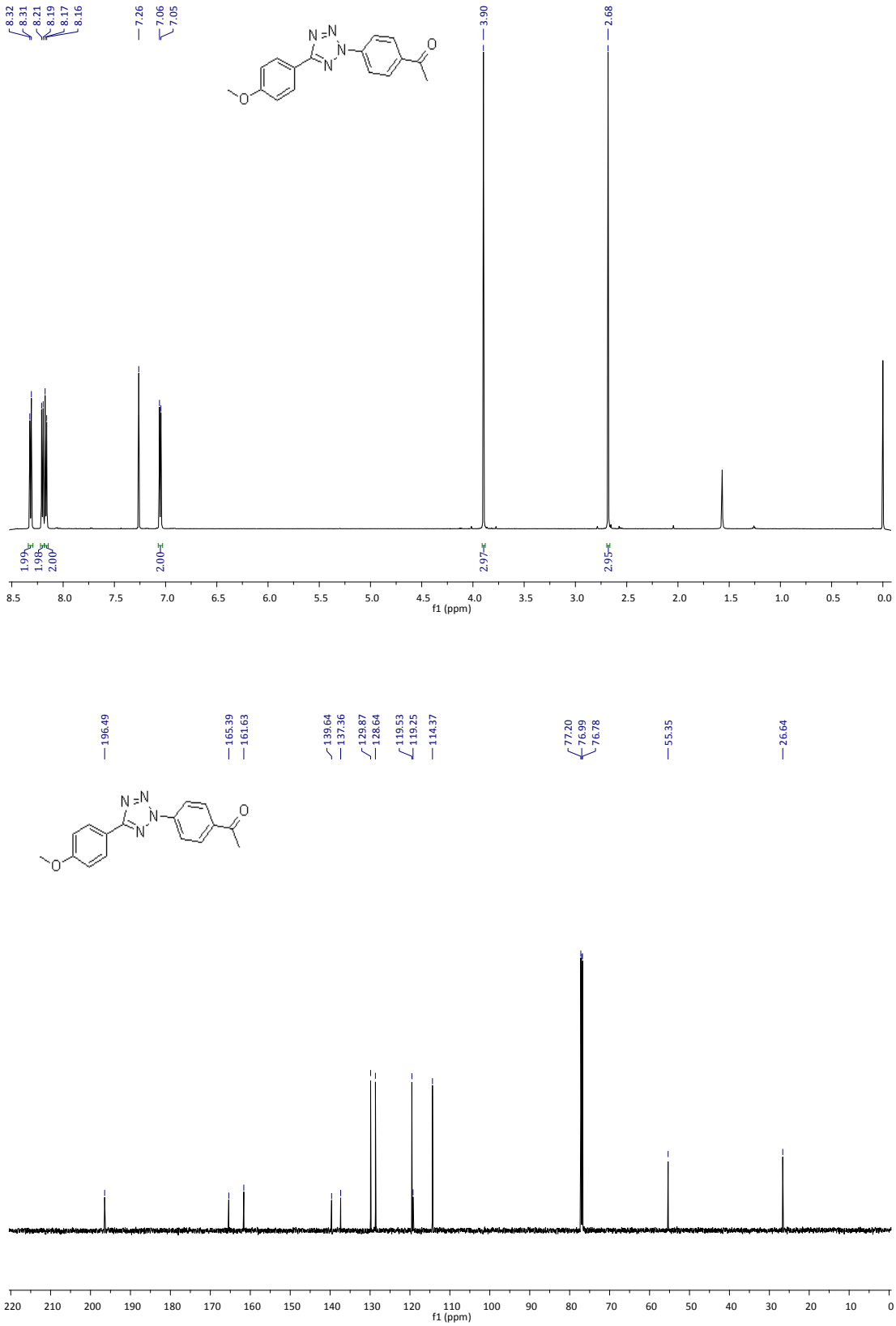


Figure S28. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **7c**

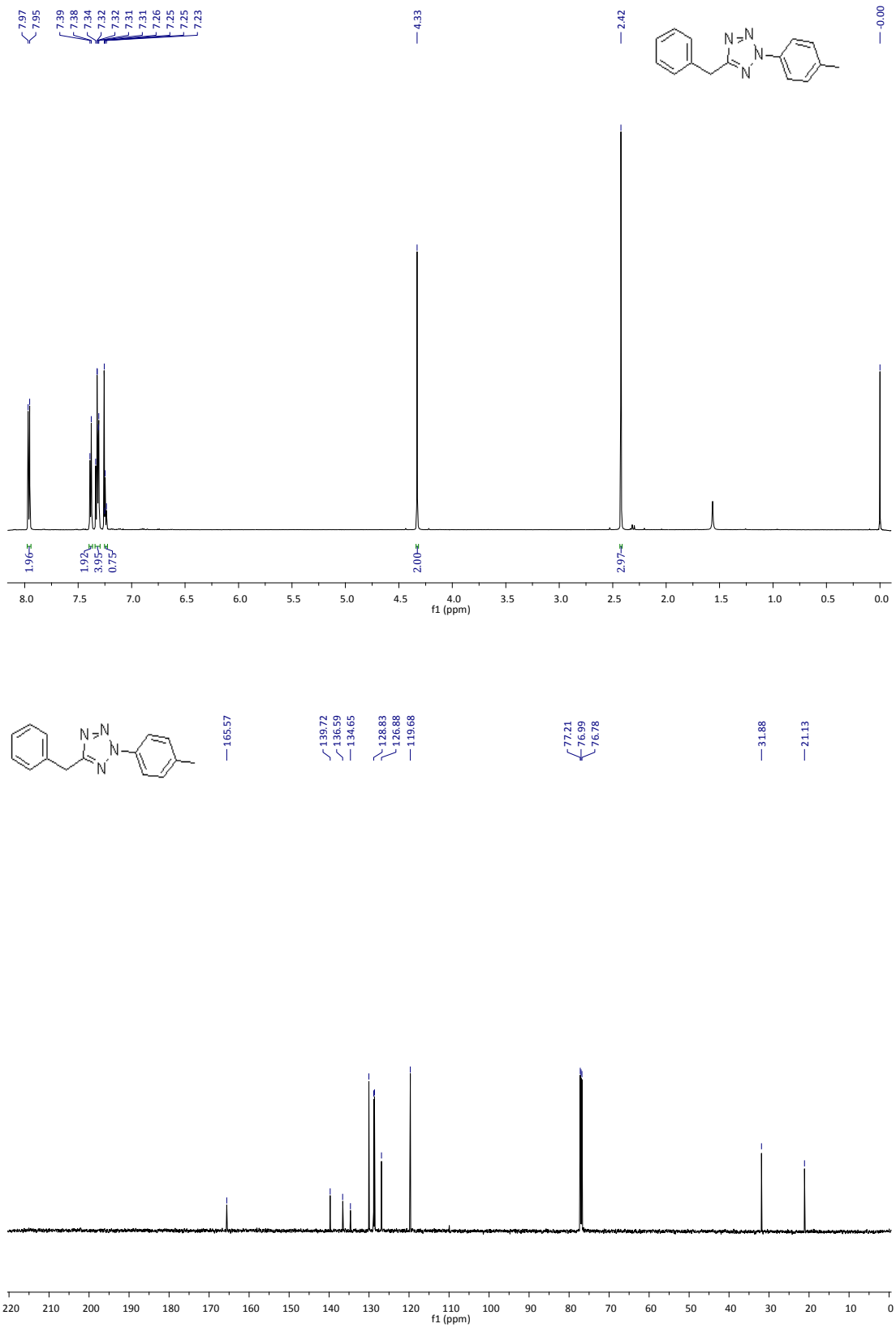


Figure S29. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **8a**

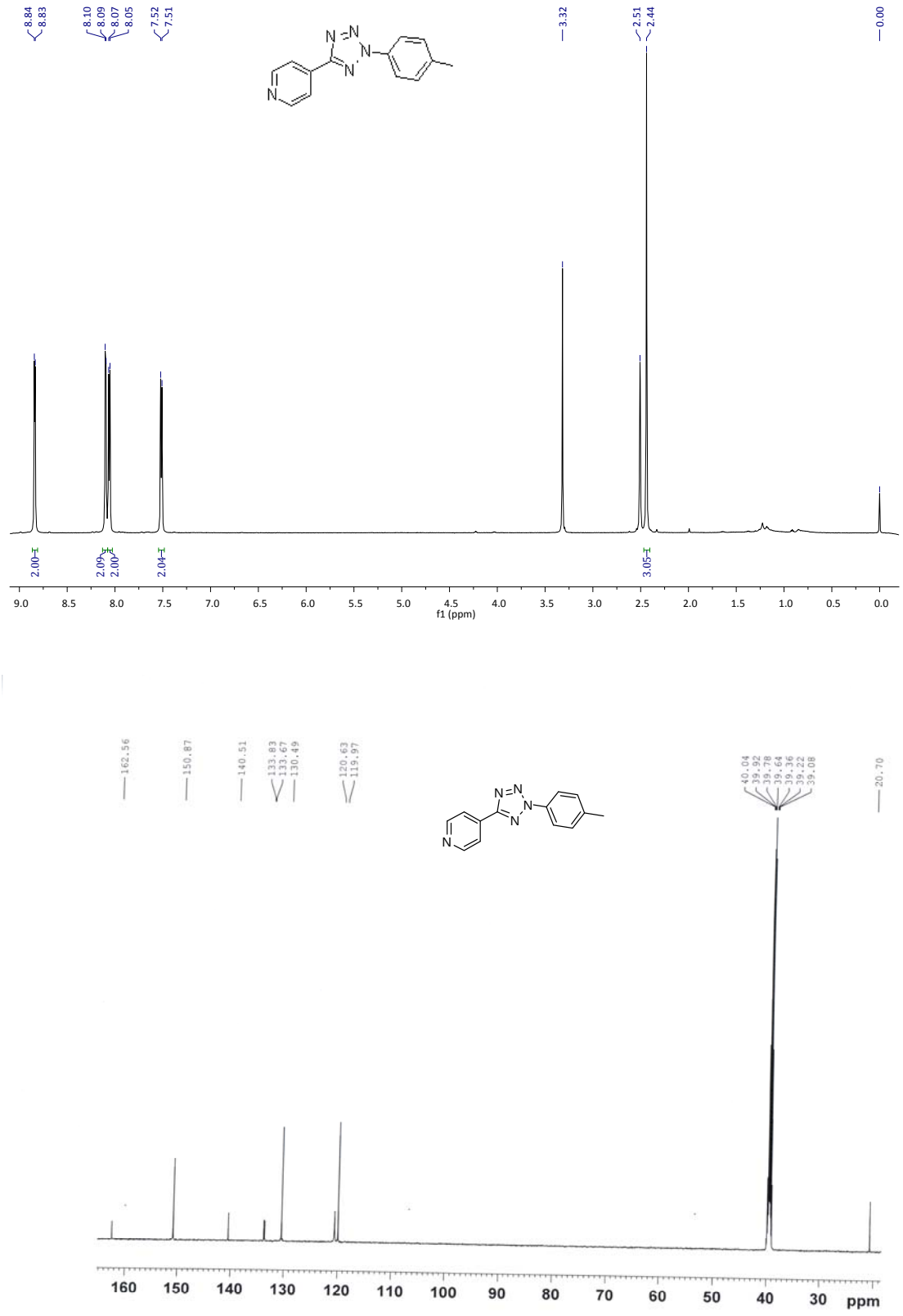


Figure S30. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **9a**