An efficient and recyclable thiourea supported copper(I) chloride catalyst for the azide–alkyne cycloaddition reactions†

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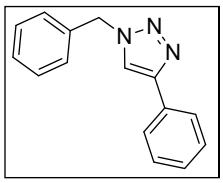
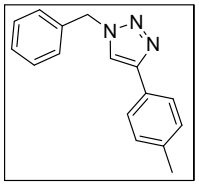
1-benzyl-4-phenyl-1H-1,2,3-triazole(4a)



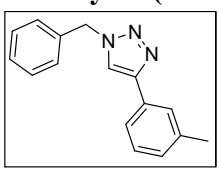
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.66 (s, 1H), 7.44 – 7.35 (m, 5H), 7.35 – 7.28 (m, 3H), 5.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 134.8, 130.6, 129.2, 128.9, 128.9, 128.2, 128.1, 125.8, 119.6, 54.3.

1-benzyl-4-(p-tolyl)-1H-1,2,3-triazole(4b)



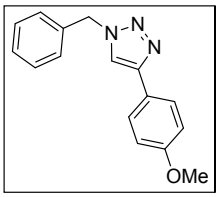
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.62 (s, 1H), 7.37 (t, *J* = 6.1 Hz, 3H), 7.32 – 7.28 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.56 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 138.2, 134.9, 129.7, 129.3, 128.9, 128.2, 127.9, 125.8, 119.3, 54.4, 21.5.

1-benzyl-4-(m-tolyl)-1H-1,2,3-triazole(4c)



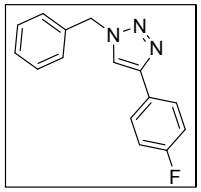
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 4.4 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 6.1 Hz, 3H), 7.30 (dd, *J* = 9.5, 4.6 Hz, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 5.57 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 134.9, 130.6, 129.3, 129.1,128.9, 128.9, 128.2, 126.5, 123.01, 119.6, 54.4, 21.6.

1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole(4d)

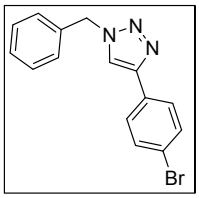


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.57 (s, 1H), 7.38 (d, *J* = 7.1 Hz, 3H), 7.31 (d, *J* = 2.2 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.56 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 148.2, 134.9, 129.2, 128.8, 128.1, 127.1, 123.4, 118.8, 114.3, 55.4, 54.3.

1-benzyl-4-(4-fluorophenyl)-1H-1,2,3-triazole(4e)

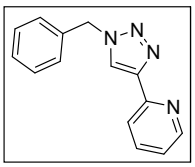


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.61 (s, 1H), 7.40-7.37 (m, 3H), 7.32-7.26(m, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 5.57 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8(d, *J* = 245Hz), 147.6, 134.8, 129.4, 129.0, 128.3, 127.6(d, *J* = 8Hz), 126.9(d, *J* = 3Hz), 119.4, 116(d, *J* = 22Hz), 54.5 ppm.



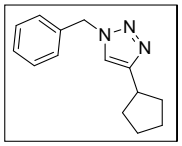
1-benzyl-4-(4-bromophenyl)-1H-1,2,3-triazole(4f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 3H), 7.53 – 7.50 (m, 2H), 7.39 (d, *J* = 7.0 Hz, 3H), 7.33 – 7.30 (m, 2H), 5.56 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 134.6, 132.1, 129.7, 129.4, 129.0, 128.3, 127.4, 122.2, 119.7, 54.5



2-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine(4g)

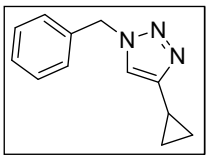
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.97 (d, *J* = 3.8 Hz, 1H), 7.74 – 7.50 (m, 1H), 7.26 (s, 1H), 6.8-6.7 (m, 4H), 6.77 – 6.73 (m, 2H), 5.02 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 146.6, 144.9, 134.4, 133.3, 129.2, 129.0, 128.2, 126.9, 123.9, 120.2, 54.4.



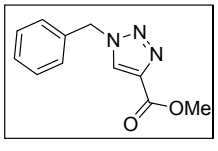
1-benzyl-4-cyclopentyl-1H-1,2,3-triazole(4h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.41 (s, 2H), 7.36 – 7.27 (m, 3H), 5.54 (s, 2H), 3.21 (s, 1H), 2.14 (s, 2H), 1.78 (d, *J* = 8.8 Hz, 2H), 1.70 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 135.0, 129.0, 128.6, 128.0, 119.6, 77.4, 77.1, 76.8, 54.0, 36.8, 33.2, 25.2.

1-benzyl-4-cyclopropyl-1H-1,2,3-triazole(4i)

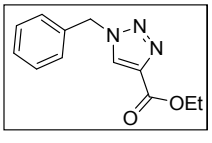


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.37 (s, 2H), 7.27 (d, *J* = 9.4 Hz, 3H), 5.48 (s, 2H), 1.95 (s, 1H), 0.95 (d, *J* = 5.0 Hz, 2H), 0.85 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 129.1, 128.9, 128.7, 128.3, 128.1, 54.2, 7.8, 6.8. HRMS calcd for $C_{12}H_{13}N_3$ $[M + H]^+$ 200.1193, found 200.1182.



methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (4j)

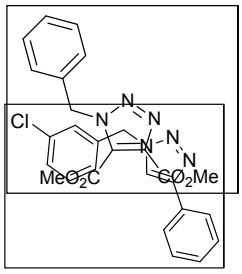
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.37 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.28 (d, *J* = 3.2 Hz, 1H), 5.56 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 133.7, 129.3, 129.2, 128.3, 127.5, 54.5, 52.2.



ethyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (4k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.34 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.25 – 7.24 (m, 1H), 4.34 (q, *J* = 7.3 Hz, 2H), 1.37 – 1.30 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 140.6, 133.8, 129.3, 129.1, 128.2, 127.4, 61.3, 54.4, 14.3.

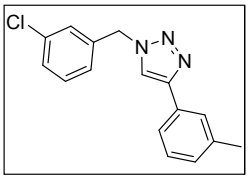
dimethyl 1-benzyl-1H-1,2,3-triazole-4,5-dicarboxylate(8a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 3H), 7.26 – 7.21 (m, 2H), 5.78 (s, 2H), 3.93 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 158.8, 140.2, 133.9, 129.8, 129.0, 128.9, 128.0, 54.0, 53.4, 52.7.

1-(3-chlorobenzyl)-4-phenyl-1H-1,2,3-triazole(4l)

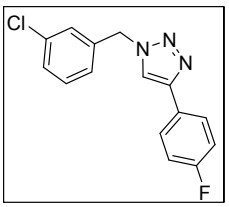
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.70 (s, 1H), 7.40 (t, *J* = 7.5 Hz, 2H),



7.33 (d, *J* = 6.8 Hz, 2H), 7.30 (d, *J* = 3.9 Hz, 2H), 7.17 (d, *J* = 6.8 Hz, 1H), 5.54 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 136.7, 135.1, 130.5, 130.5, 129.1, 128.9, 128.4, 128.1, 126.1, 125.8, 119.7, 53.6.

1-(3-chlorobenzyl)-4-(m-tolyl)-1H-1,2,3-triazole(4m)

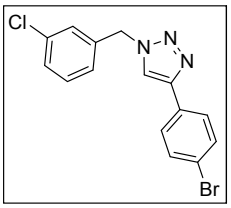
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.22 (dd, *J*



= 12.4, 5.4 Hz, 3H), 7.14 – 7.04 (m, 2H), 5.47 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 138.6, 136.7, 135.1, 130.5, 130.3, 129.2, 129.1, 128.8, 128.1, 126.5, 126.1, 122.9, 119.6, 53.6, 21.5. HRMS calcd for $C_{16}H_{14}ClN_3$ $[M + H]^+$ 284.0935, found 284.0949.

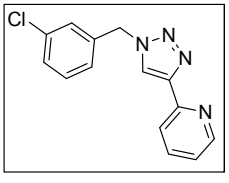
1-(3-chlorobenzyl)-4-(4-fluorophenyl)-1H-1,2,3-triazole(4n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.66 (s, 1H), 7.36 – 7.27 (m, 3H), 7.19-7.16 (m, 1H), 7.13 – 7.05 (m, 2H), 5.53 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8(d, *J* = 246Hz), 147.6, 136.6, 135.1, 130.6, 129.1, 128.2, 127.6(d, *J* = 8Hz), 126.7(d, *J* = 3Hz), 126.2, 119.4, 115.9(d, *J* = 22Hz), 53.6 ppm. HRMS calcd for $C_{15}H_{11}ClFN_3$ $[M + H]^+$ 288.0699, found 288.0698.



4-(4-bromophenyl)-1-(3-chlorobenzyl)-1H-1,2,3-triazole(4o)

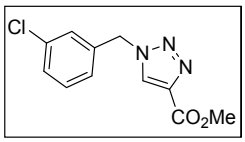
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.18 (d, *J* = 6.8 Hz, 1H), 5.54 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 135.2, 132.1, 130.6, 129.35 (d, *J* = 18.6 Hz), 128.2, 127.3, 126.2, 122.3, 119.7, 53.7; HRMS calcd for $C_{14}H_{11}ClN_4$ $[M + H]^+$ 347.9842, found 347.9898.



2-(1-(3-chlorobenzyl)-1H-1,2,3-triazol-4-yl)pyridine(4p)

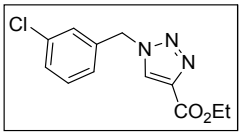
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.56 (d, *J* = 3.9 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.80 (s, 1H), 7.39 – 7.28 (m, 4H), 7.19 (d, *J* = 6.6 Hz,

1H), 5.57 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 146.9, 145.4, 136.4, 135.2, 133.3, 130.6, 129.3, 128.2, 126.7, 126.2, 124.0, 120.0, 53.8; HRMS calcd for $C_{14}H_{11}ClN_4$ $[M + H]^+$ 271.0756, found 271.0745.



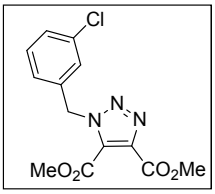
methyl 1-(3-chlorobenzyl)-1H-1,2,3-triazole-4-carboxylate(4q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.37 – 7.29 (m, 2H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.16 (d, *J* = 7.1 Hz, 1H), 5.55 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 135.7, 135.3, 130.7, 129.5, 128.4, 127.6, 126.3, 53.8, 52.3. HRMS calcd for $C_{11}H_{10}ClN_3O_2$ $[M + H]^+$ 252.0539, found 252.0534.



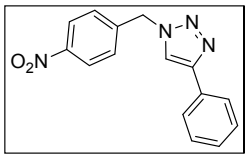
ethyl 1-(3-chlorobenzyl)-1H-1,2,3-triazole-4-carboxylate(4r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.34 – 7.07 (m, 5H), 5.55 (s, 2H), 4.38 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.37 (dd, *J* = 9.6, 4.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 135.8, 135.2, 130.6, 130.1, 129.4, 128.7, 128.3, 126.3, 61.4, 53.8, 14.3.



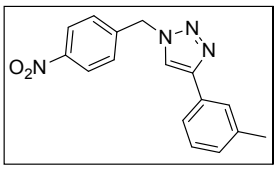
dimethyl 1-(3-chlorobenzyl)-1H-1,2,3-triazole-4,5-dicarboxylate(8c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 3H), 7.16 (d, *J* = 7.3 Hz, 1H), 5.79 (s, 2H), 3.97 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 158.7, 140.4, 135.7, 134.8, 130.2, 129.4, 129.1, 128.2, 126.2, 53.4, 53.2, 52.8.



1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole(4s)

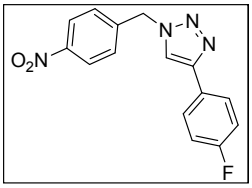
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.85 – 7.73 (m, 3H), 7.44 (s, 1H), 7.43 – 7.38 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 1H), 5.69 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 141.8, 130.2, 129.0, 128.6, 128.6, 125.8, 124.4, 119.9, 53.2.



1-(4-nitrobenzyl)-4-(m-tolyl)-1H-1,2,3-triazole(4t)

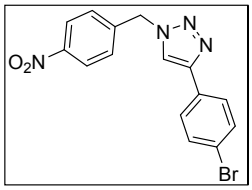
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 2H), 7.76 (s, 1H), 7.66 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.30

(t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 5.69 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 141.8, 138.8, 129.9, 129.4, 128.9, 128.7, 126.6, 124.4, 123.0, 53.3, 21.5. HRMS calcd for $C_{16}H_{14}N_4O_2$ $[M + H]^+$ 295.1178, found 295.1190.



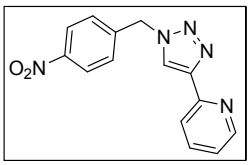
4-(4-fluorophenyl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole(4u)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 7.82 – 7.75 (m, 2H), 7.71 (s, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.10 (t, J = 8.7 Hz, 2H), 5.69 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9(d, J = 246Hz), 148.2, 148.0, 141.7, 128.7, 127.65 (d, J = 8 Hz), 126.46 (d, J = 3 Hz), 124.5, 119.5, 116.0(d, J = 22Hz), 53.3. HRMS calcd for $C_{15}H_{11}FN_4O_2$ $[M + H]^+$ 299.0924, found 299.0939.



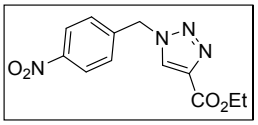
4-(4-bromophenyl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole(4v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.7 Hz, 2H), 7.77 (s, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 5.69 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 141.6, 132.2, 129.2, 128.7, 127.3, 124.5, 122.5, 53.4. HRMS calcd for $C_{15}H_{11}BrN_4O_2$ $[M + H]^+$ 359.0091, found 359.0138



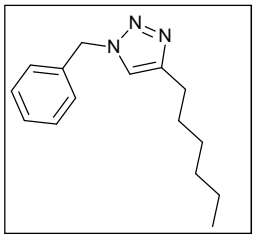
2-(1-(4-nitrobenzyl)-1H-1,2,3-triazol-4-yl)pyridine(4w)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.58 (s, 1H), 8.24 (d, J = 8.6 Hz, 2H), 8.20 (d, J = 7.9 Hz, 1H), 7.86 (s, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.37 (dd, J = 7.4, 4.9 Hz, 1H), 5.72 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 148.3, 147.1, 145.8, 141.5, 133.3, 128.8, 124.6, 124.0, 120.2, 53.5. HRMS calcd for $C_{14}H_{11}N_5O_2$ $[M + H]^+$ 282.0988, found 282.0986.



ethyl 1-(4-nitrobenzyl)-1H-1,2,3-triazole-4-carboxylate(4x)

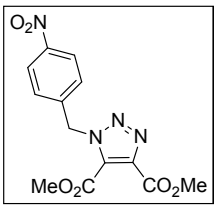
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 8.10 (s, 1H), 7.44 (d, J = 8.7 Hz, 2H), 5.71 (s, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 148.2, 140.7, 128.8, 127.6, 124.4, 124.0, 61.5, 53.3, 14.2.



1–benzyl–4–hexyl–1H–1,2,3–triazole(4y)

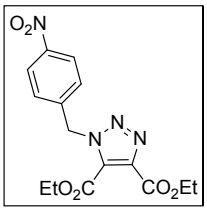
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.37 (t, J = 6 Hz, 2H), 7.28 (t, J = 4Hz, 2H), 5.51 (s, 2H), 2.70 (bs, 2H), 1.67 (bs, 2H), 1.36 – 1.26

(m, 6H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 129.1, 128.9, 128.7, 128.1, 125.8, 54.2, 31.5, 29.8, 29.1, 25.8, 22.5, 14.1 ppm.



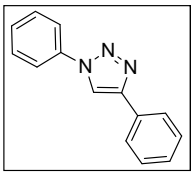
dimethyl 1-(4-nitrobenzyl)-1H-1,2,3-triazole-4,5-dicarboxylate(8d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H), 5.92 (s, 2H), 3.97 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 158.6, 148.2, 140.9, 129.2, 129.0, 124.3, 53.6, 53.1, 53.0.



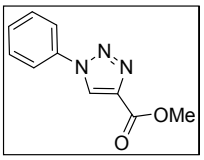
diethyl 1-(4-nitrobenzyl)-1H-1,2,3-triazole-4,5-dicarboxylate(8e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 5.92 (s, 2H), 4.43 (q, J = 7.1 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 158.3, 148.2, 141.2, 141.0, 129.3, 129.0, 124.2, 63.2, 62.2, 53.0, 14.2, 13.9. HRMS calcd for $C_{15}H_{16}N_4O_6$ $[M + H]^+$ 349.1186, found 349.1143.



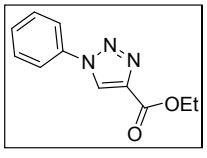
1,4-diphenyl-1H-1,2,3-triazole(6a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.92 (d, J = 7.3 Hz, 2H), 7.80 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.38 (d, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 137.2, 130.3, 129.9, 129.0, 1289, 128.5, 125.9, 120.6, 117.7.



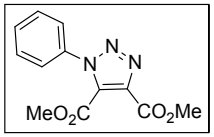
methyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (6b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.76 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.6 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 3.99 (s, 3H);). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 140.7, 136.4, 130.1, 129.7, 125.7, 120.9, 52.5.



ethyl 1-phenyl-1H-1,2,3-triazole-4-carboxylate (6c)

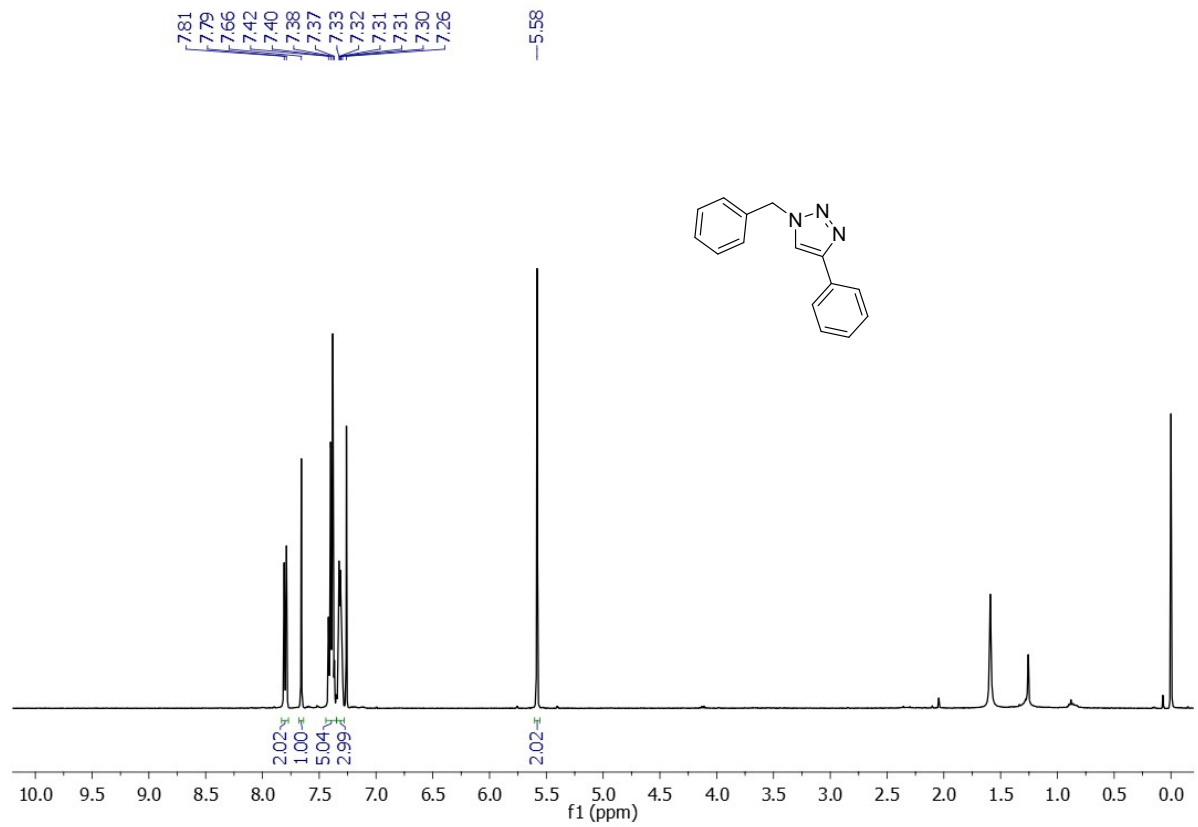
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.75 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.52 – 7.45 (m, 1H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 140.9, 136.5, 130.0, 129.6, 125.6, 120.9, 61.6, 14.4.

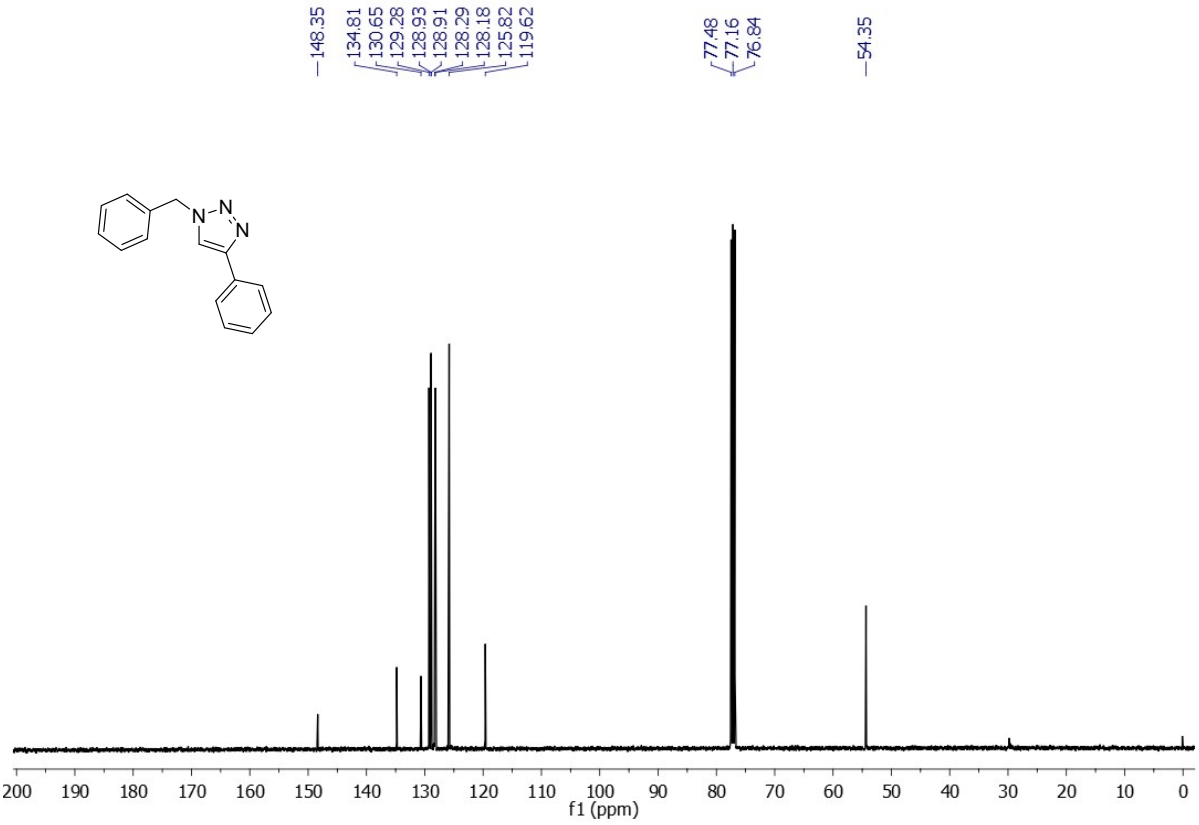


dimethyl 1-phenyl-1H-1,2,3-triazole-4,5-dicarboxylate(8b)

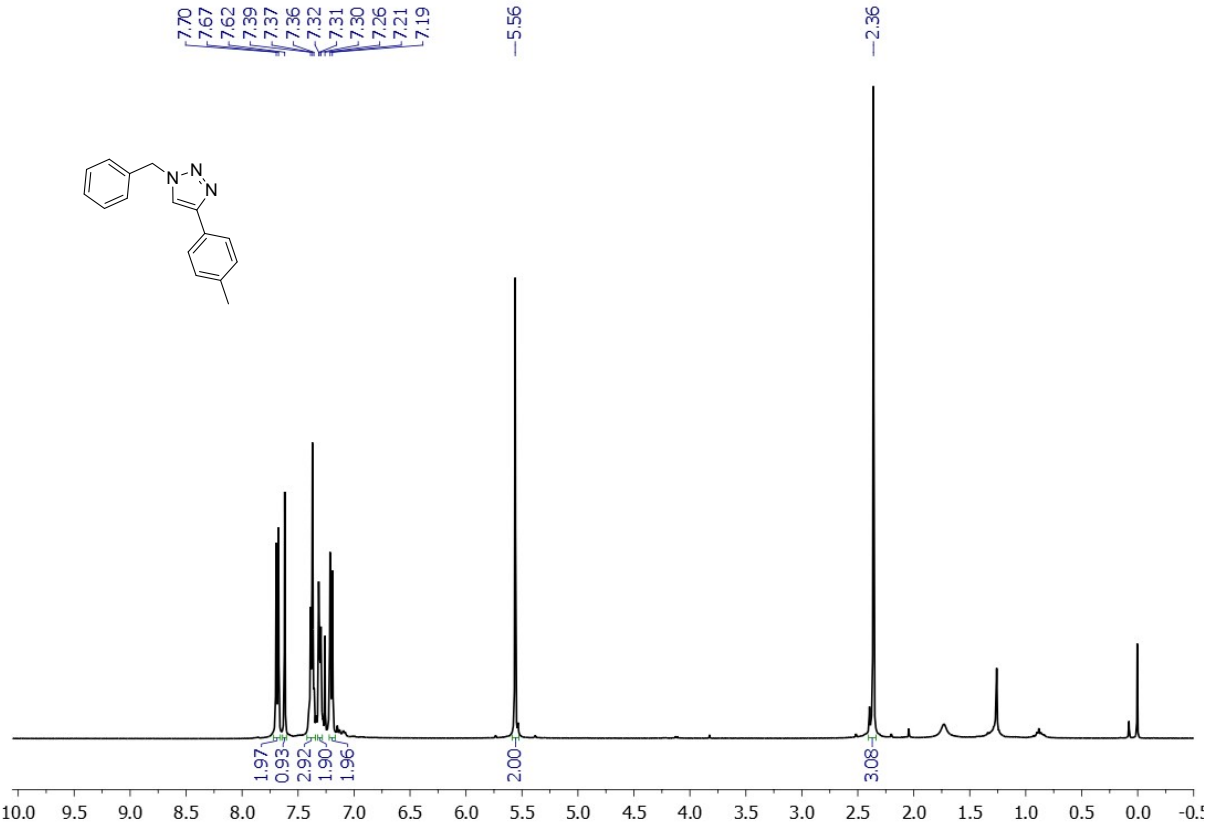
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 5H), 3.99 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 159.5, 138.8, 135.6, 132.6, 130.6, 129.7, 124.4, 53.9, 52.8.

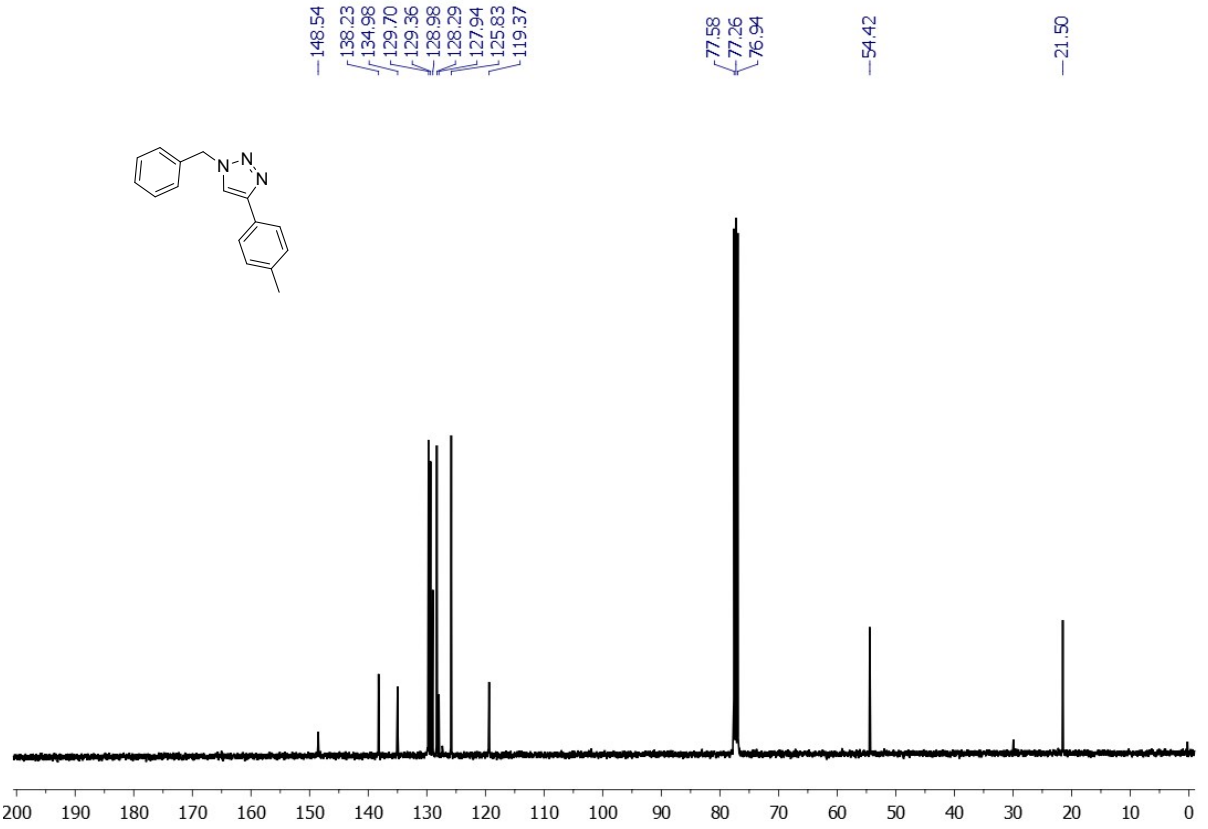
^{1}H and ^{13} C NMR spectra of compound **4a**



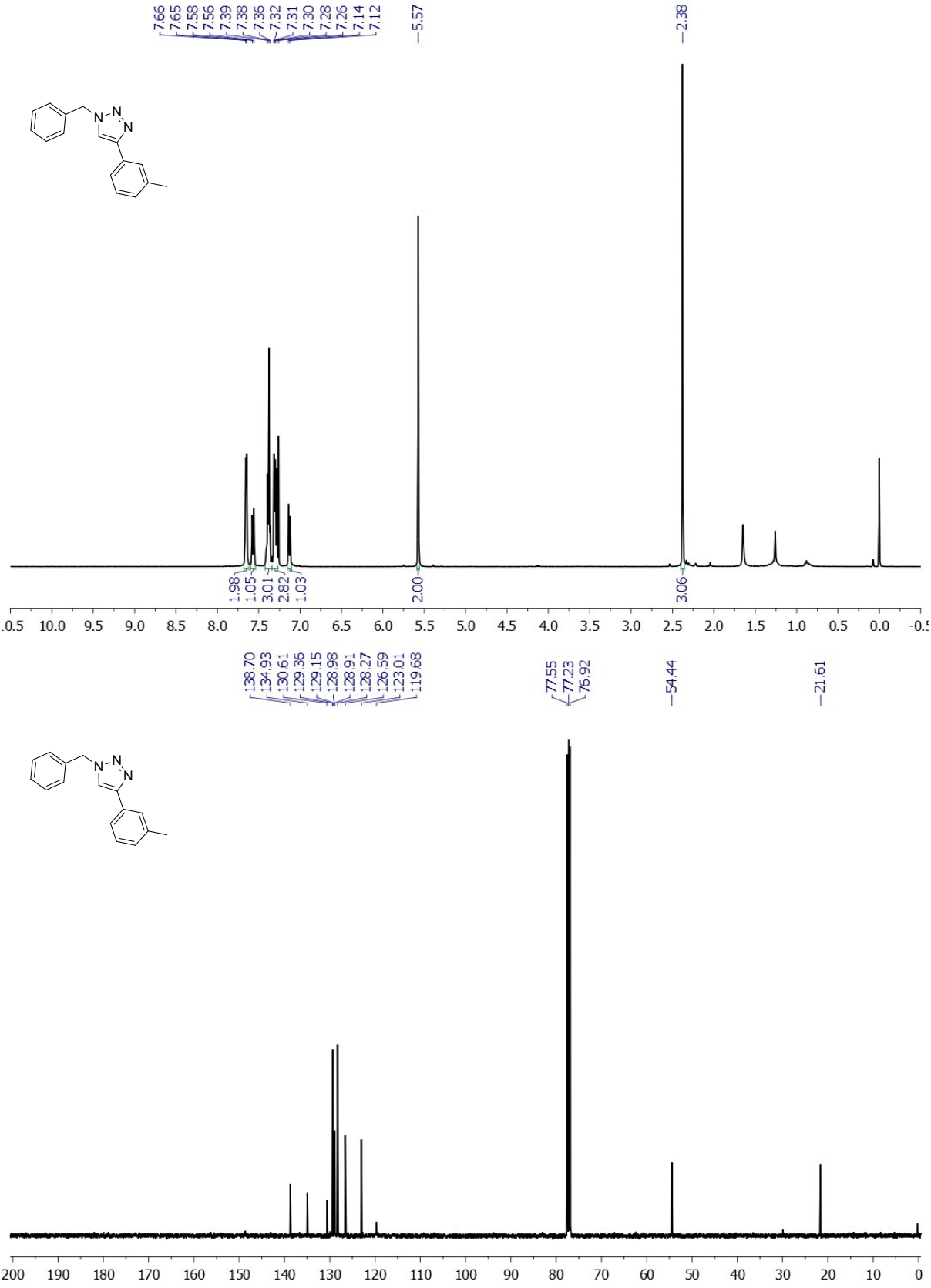


^{1}H and ^{13} C NMR spectra of compound **4b**

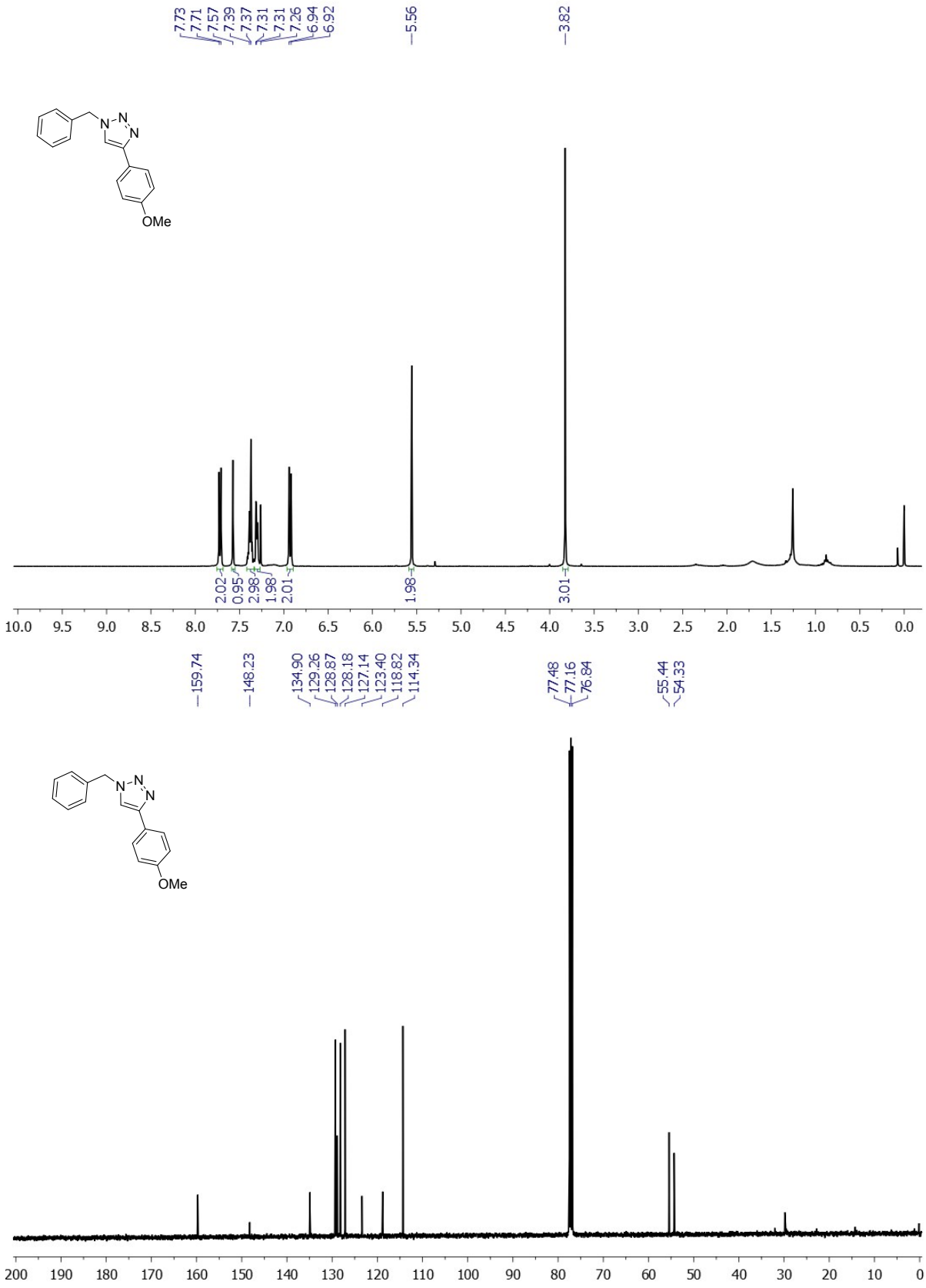




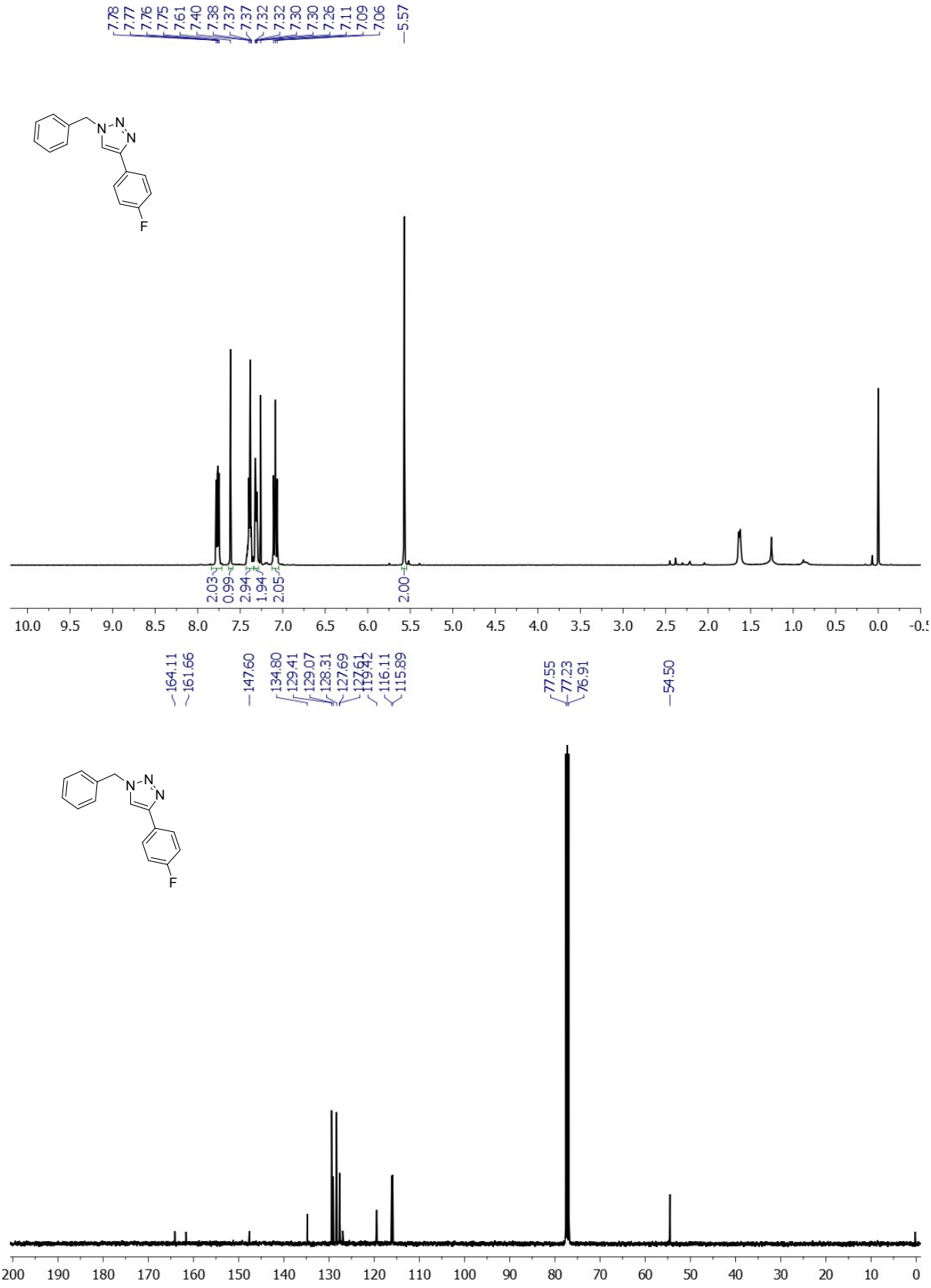
^{1}H and ^{13} C NMR spectra of compound **4c**



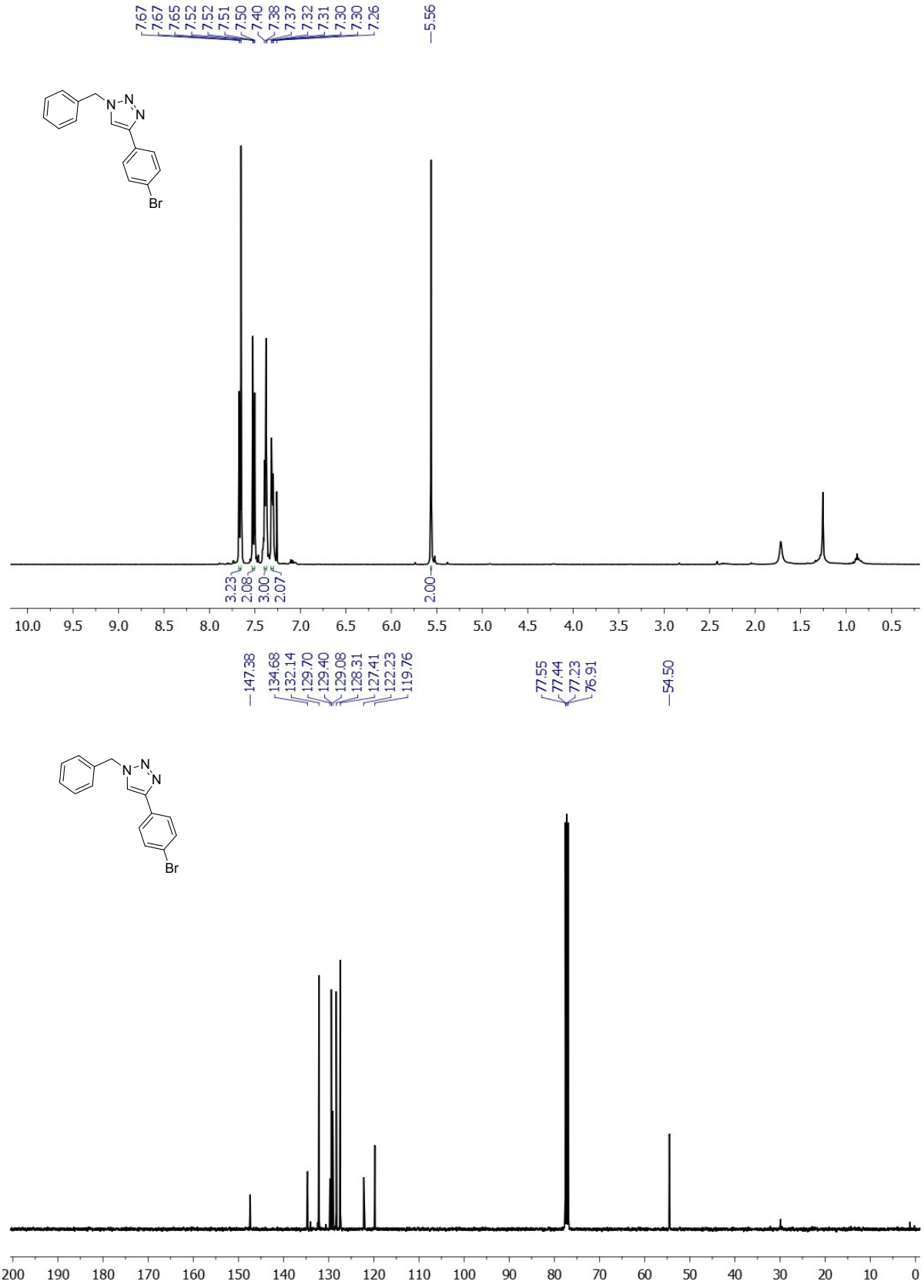
^{1}H and ^{13} C NMR spectra of compound **4d**



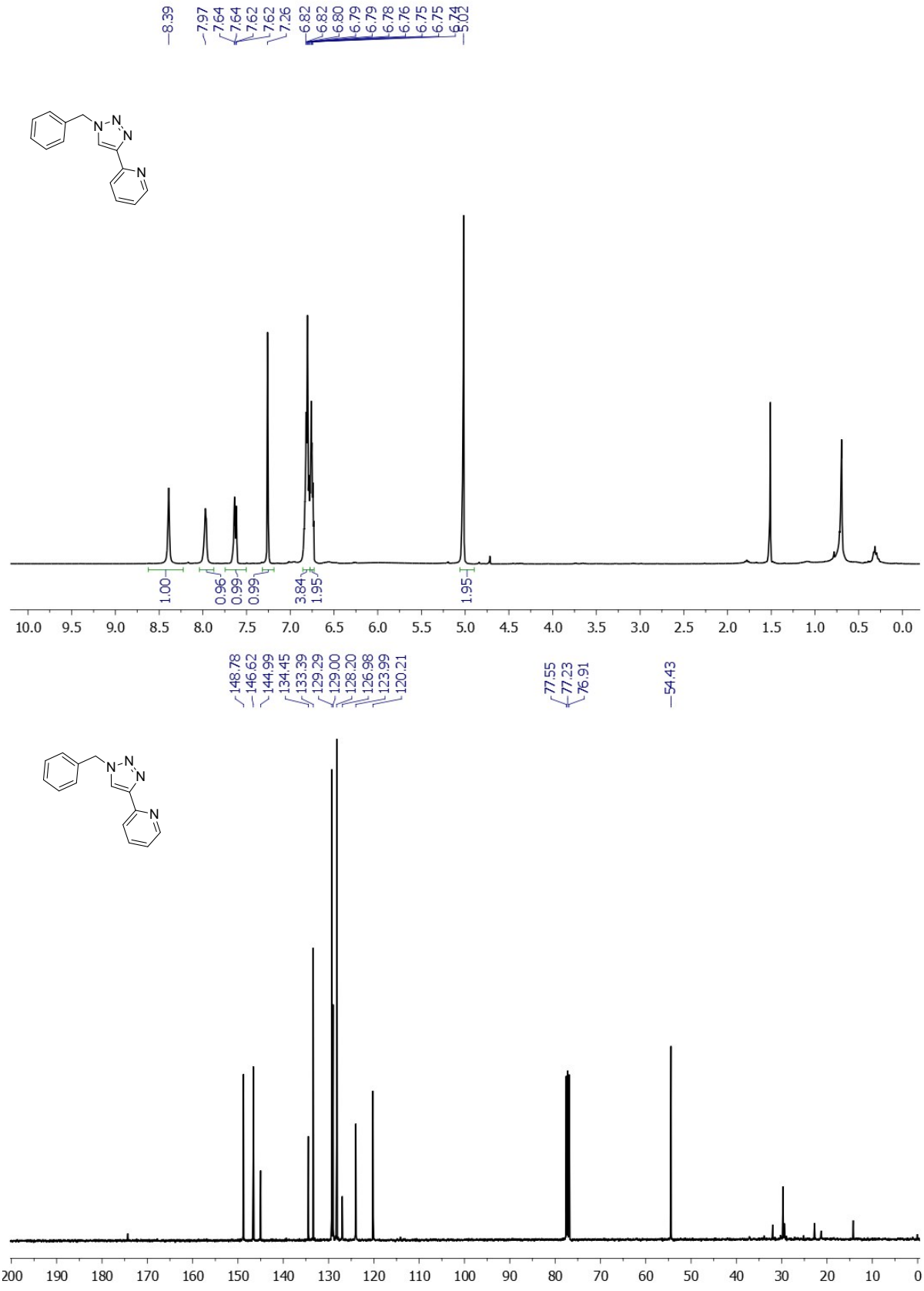
^{1}H and ^{13} C NMR spectra of compound **4e**



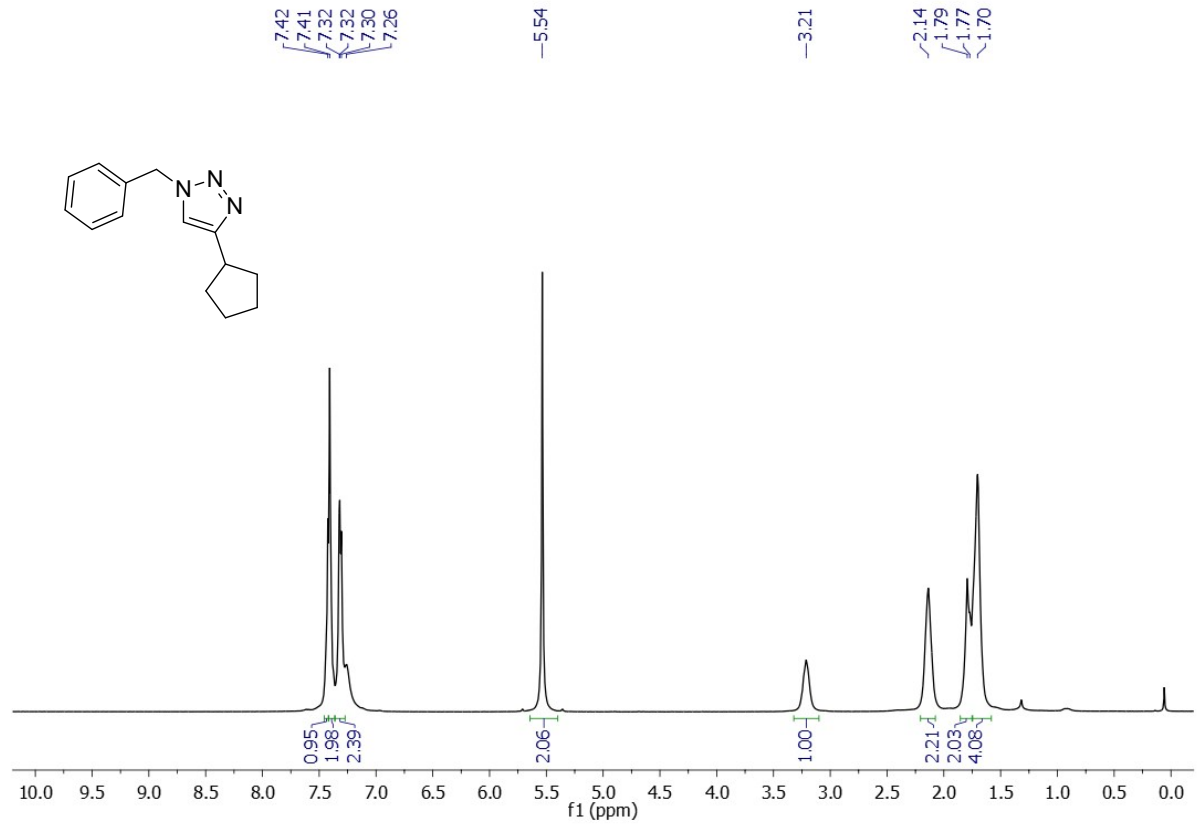
^{1}H and ^{13} C NMR spectra of compound **4f**

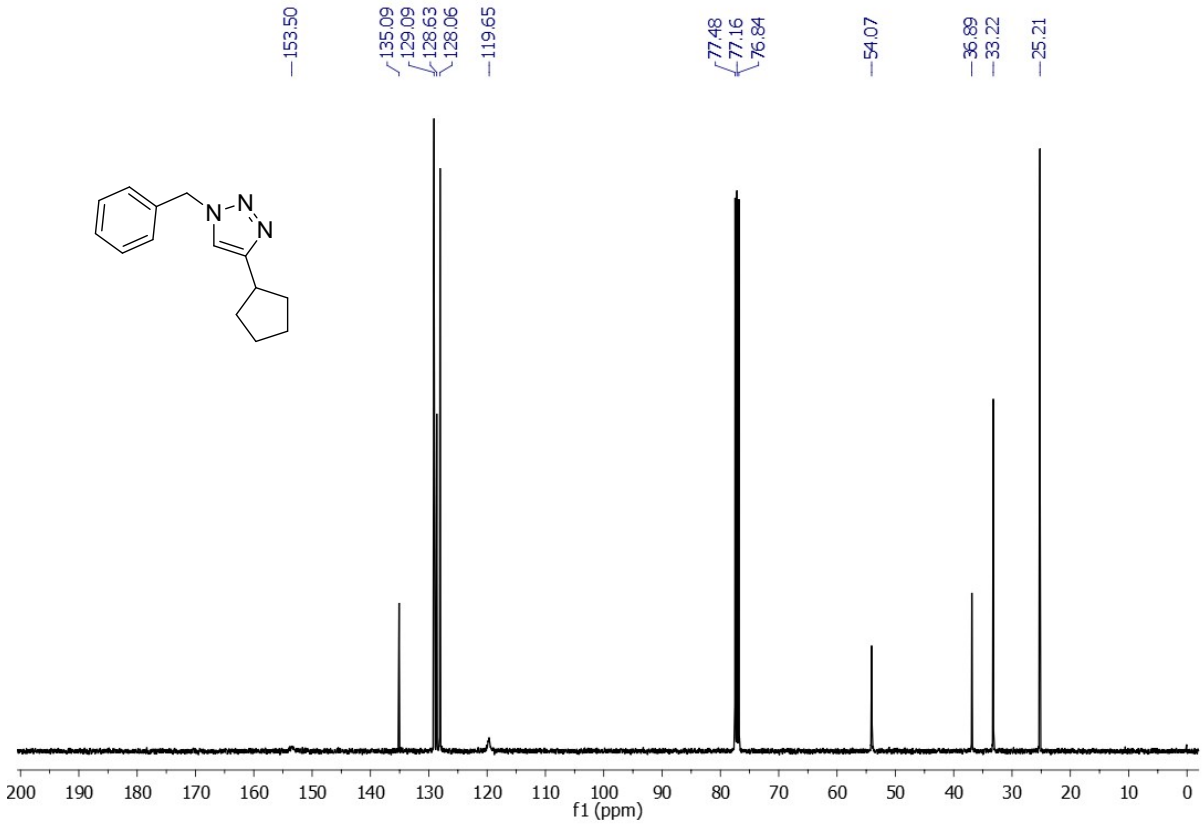


^{1}H and ^{13} C NMR spectra of compound **4g**

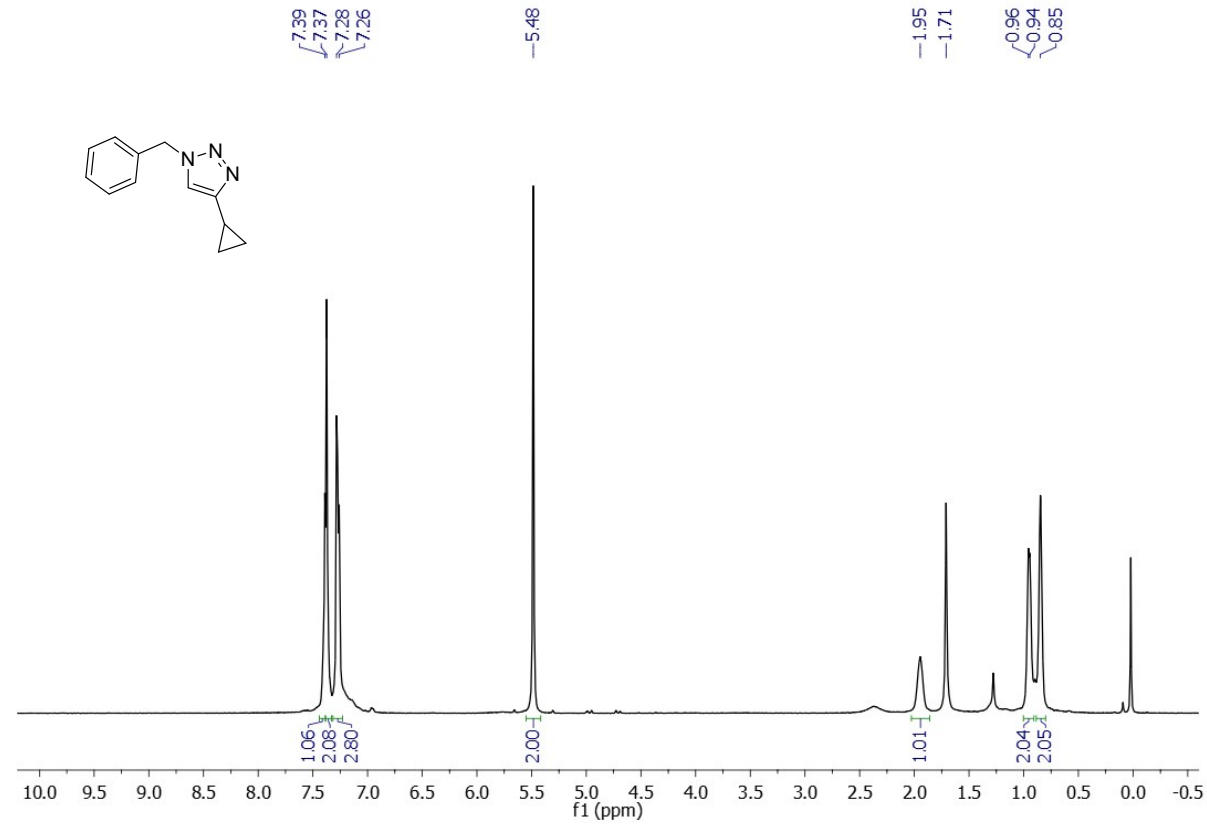


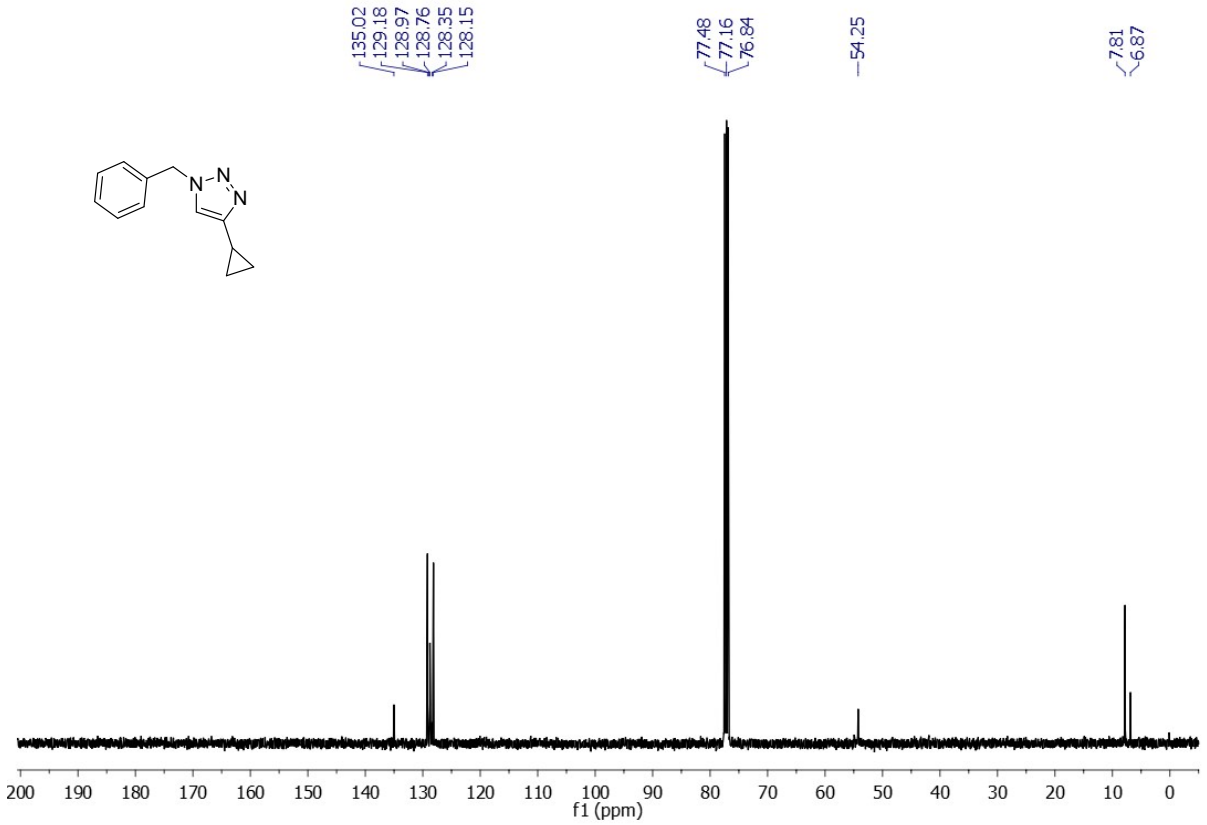
^{1}H and ^{13} C NMR spectra of compound **4h**



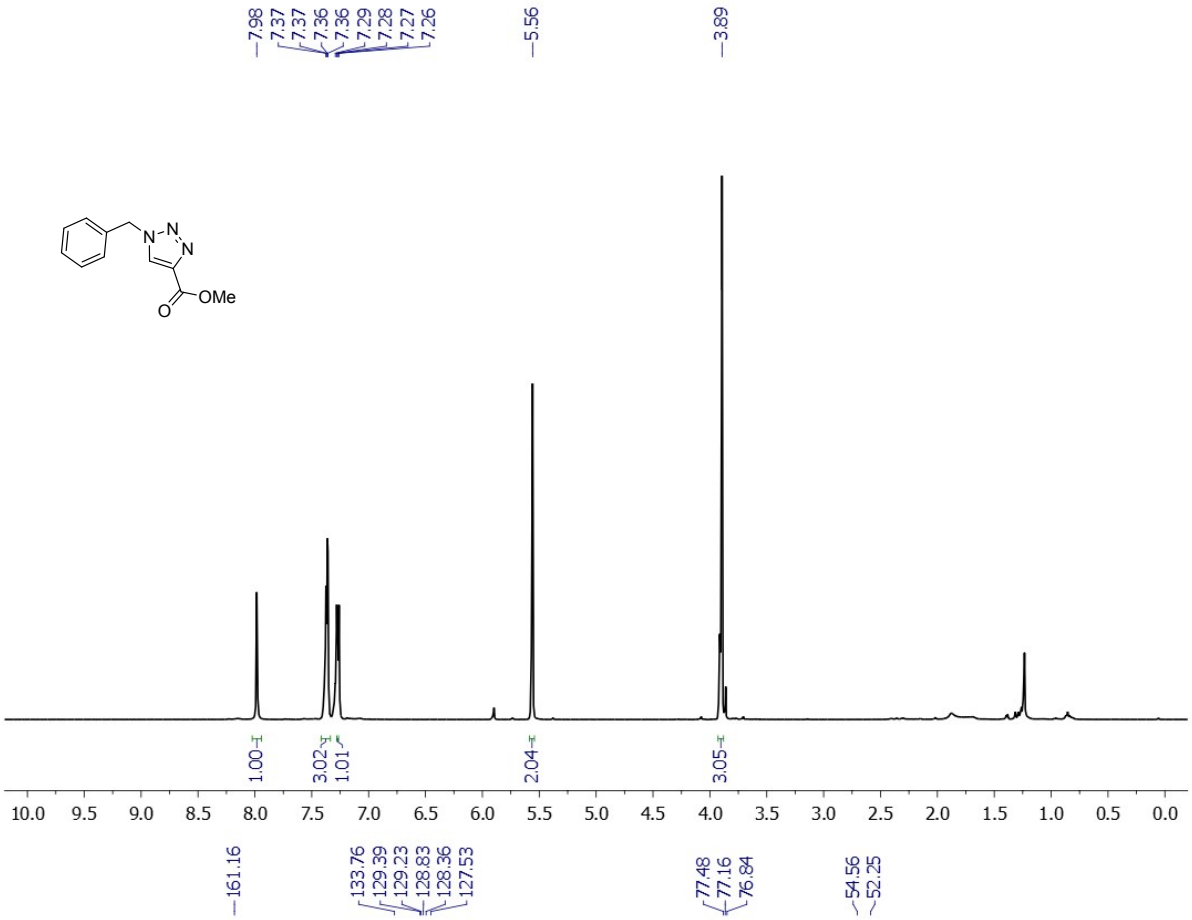


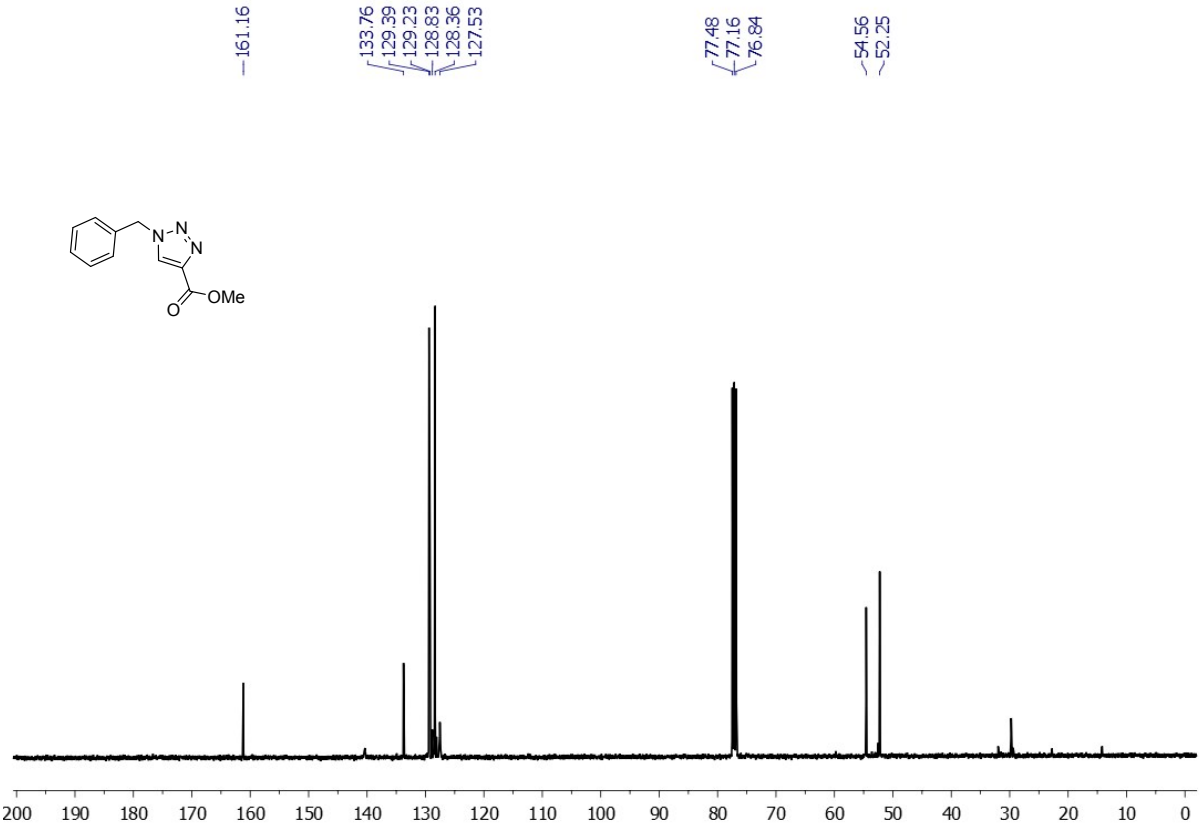
^{1}H and ^{13} C NMR spectra of compound **4i**



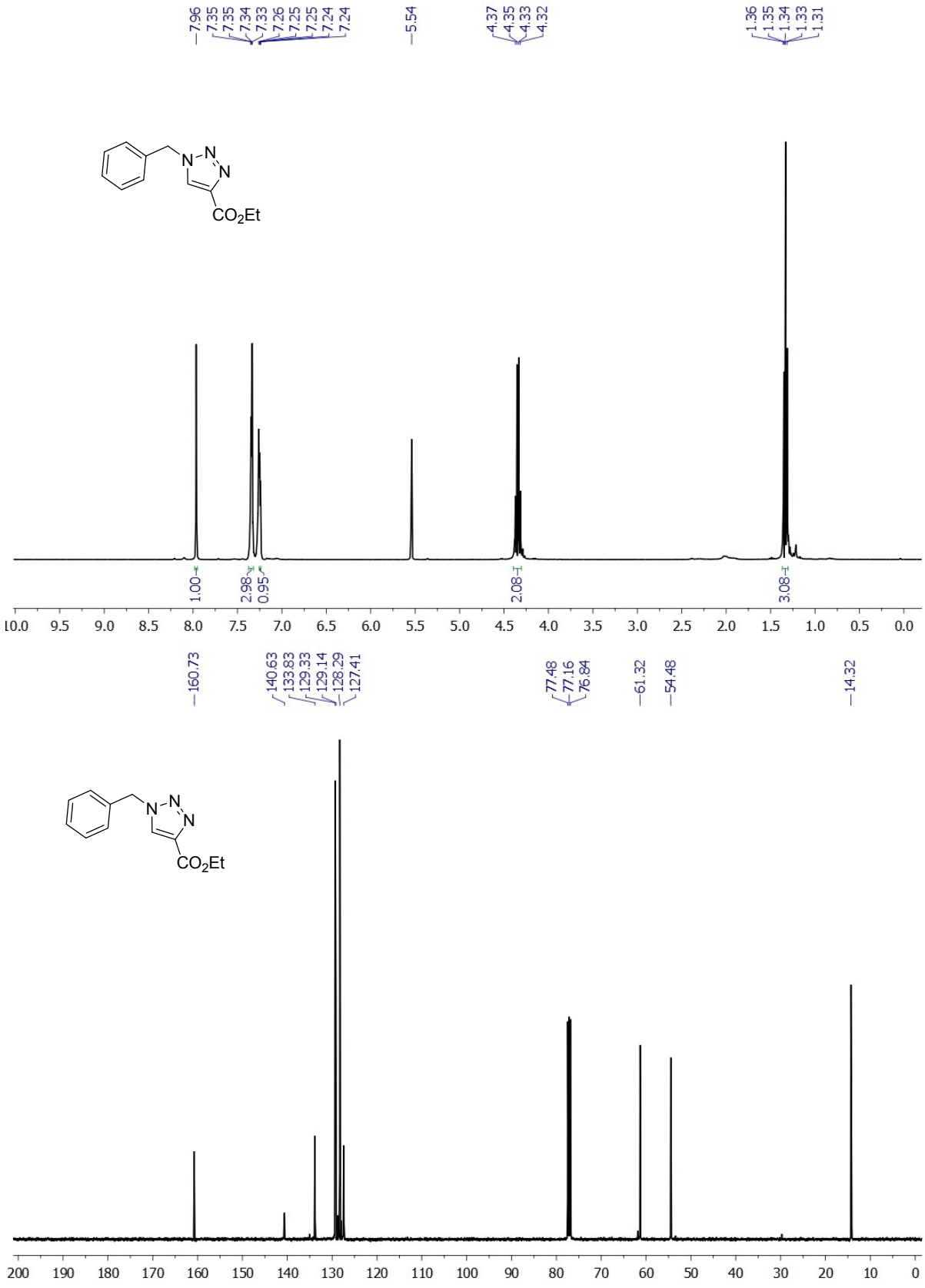


^{1}H and ^{13} C NMR spectra of compound **4j**

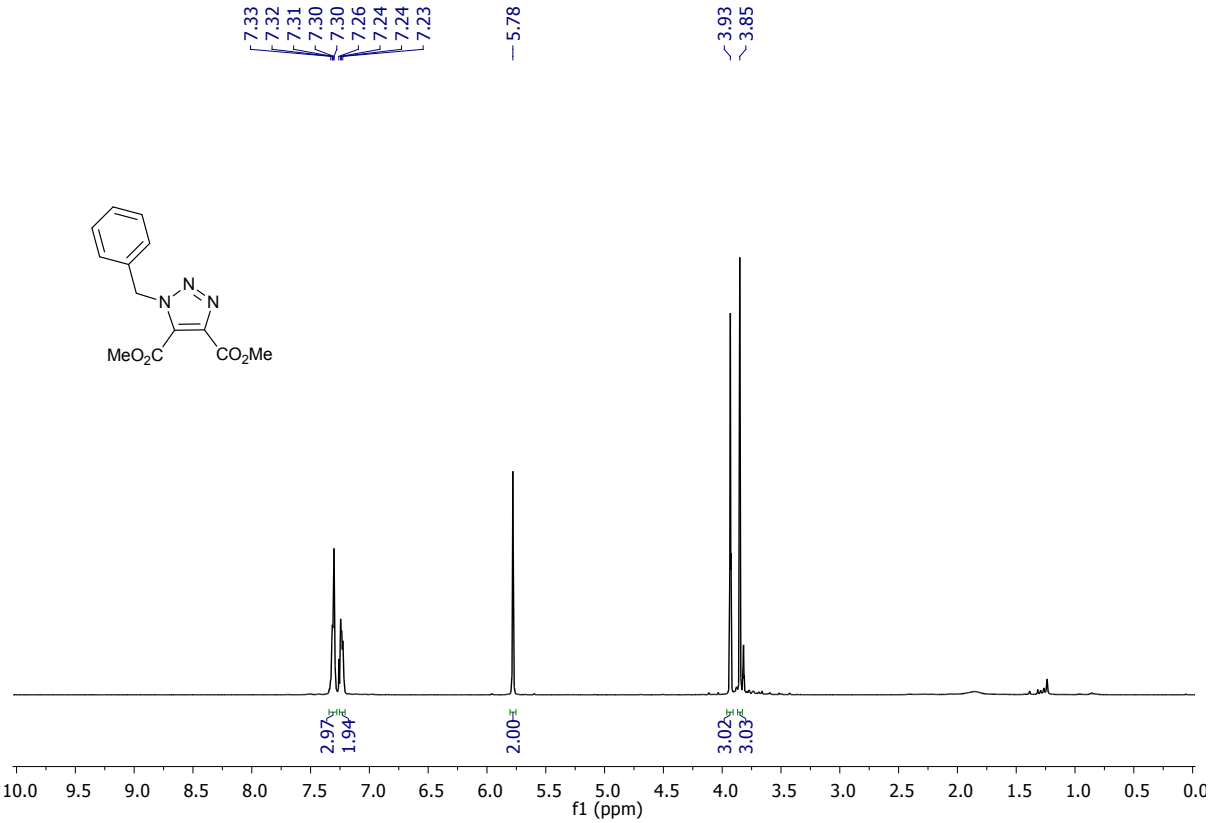


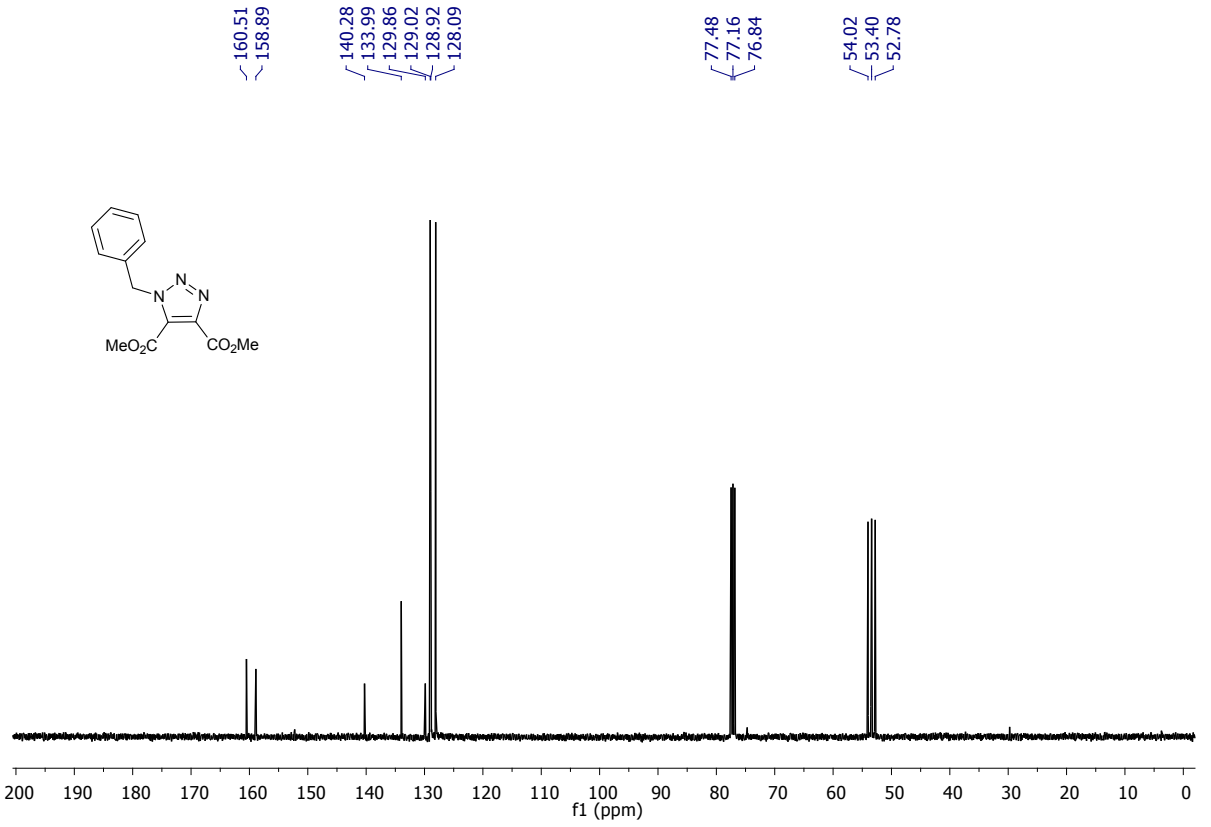


^{1}H and ^{13} C NMR spectra of compound **4k**

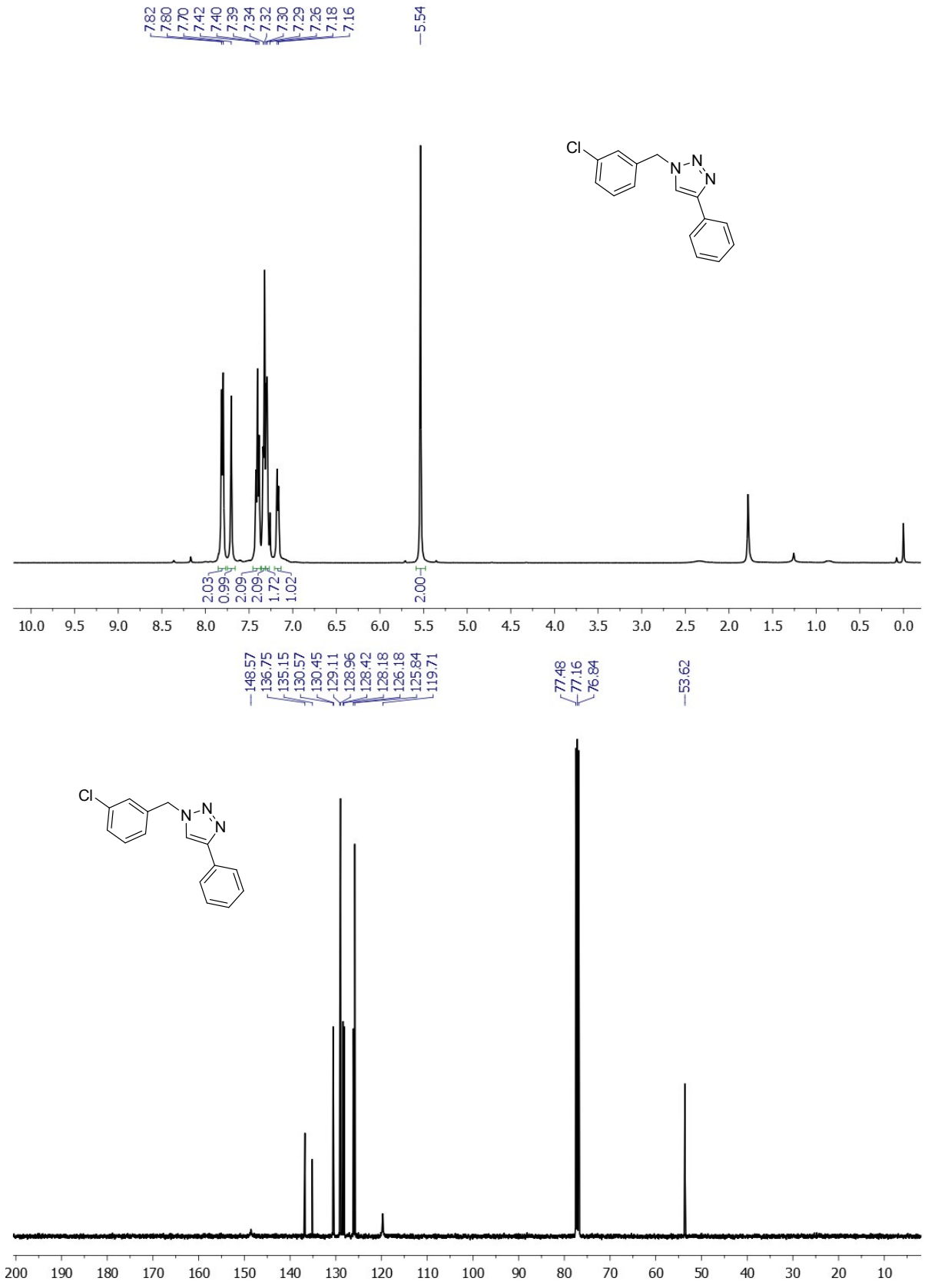


^{1}H and ^{13} C NMR spectra of compound **8a**

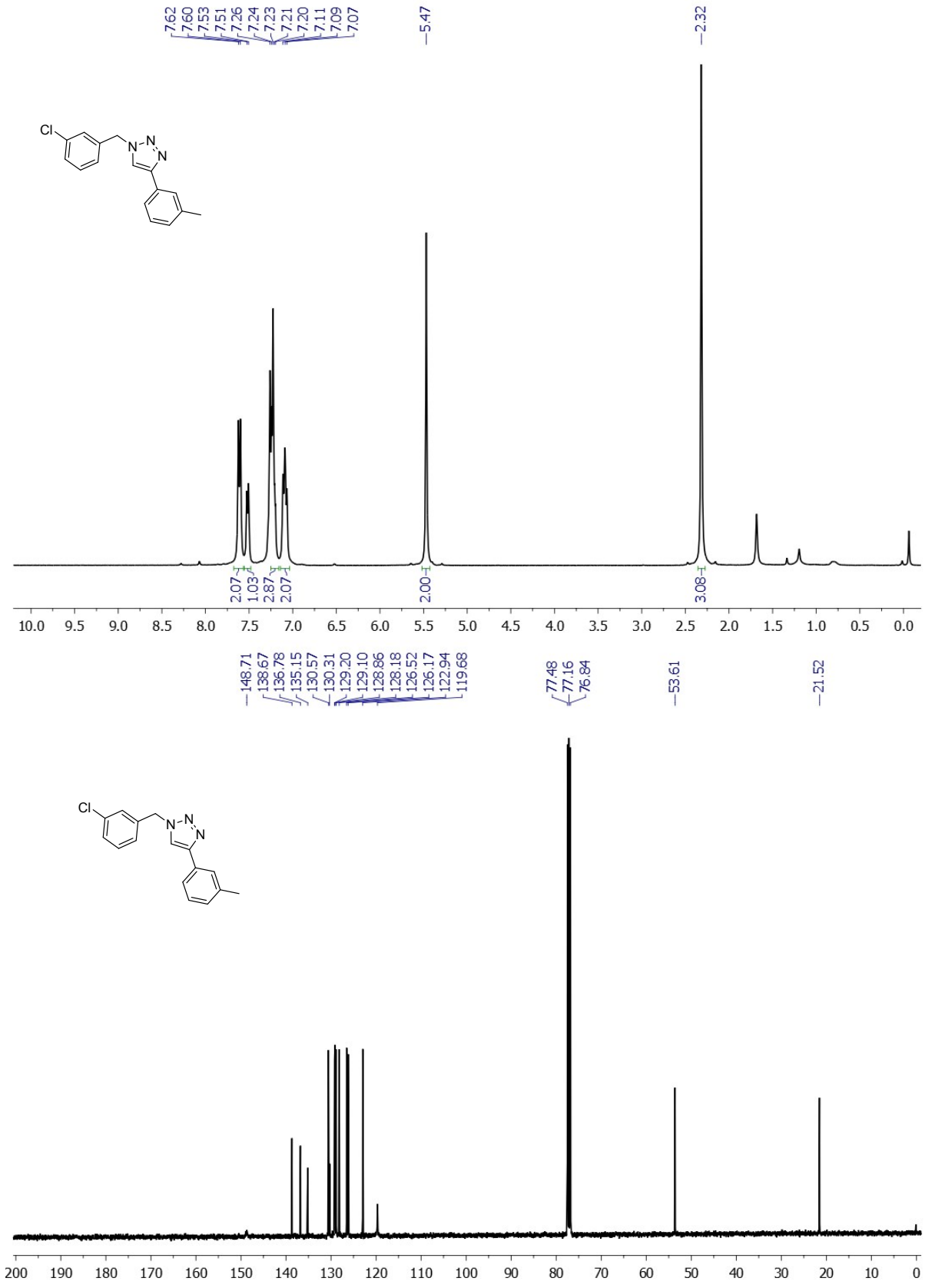




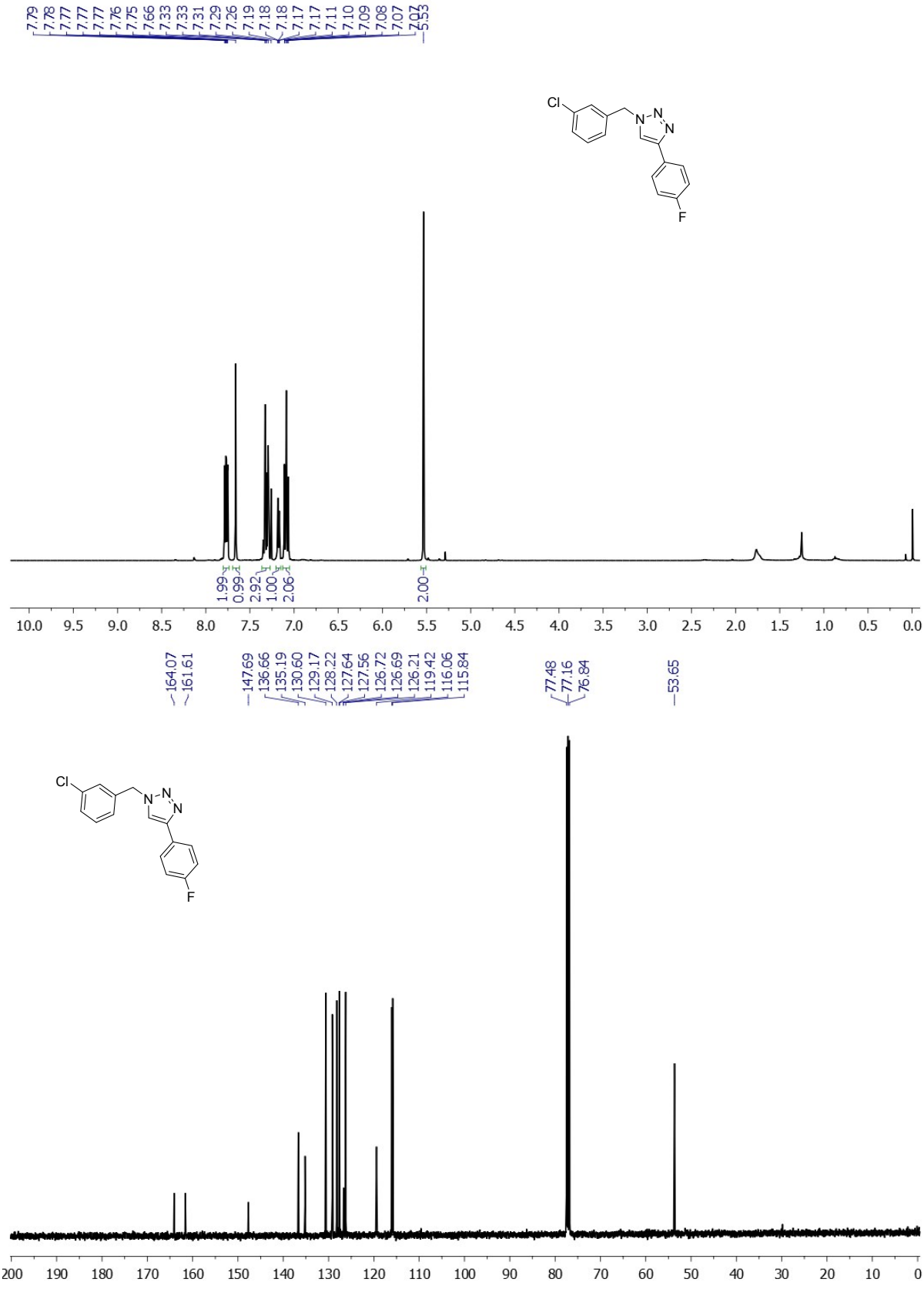
^{1}H and ^{13}C NMR spectra of compound **4l**



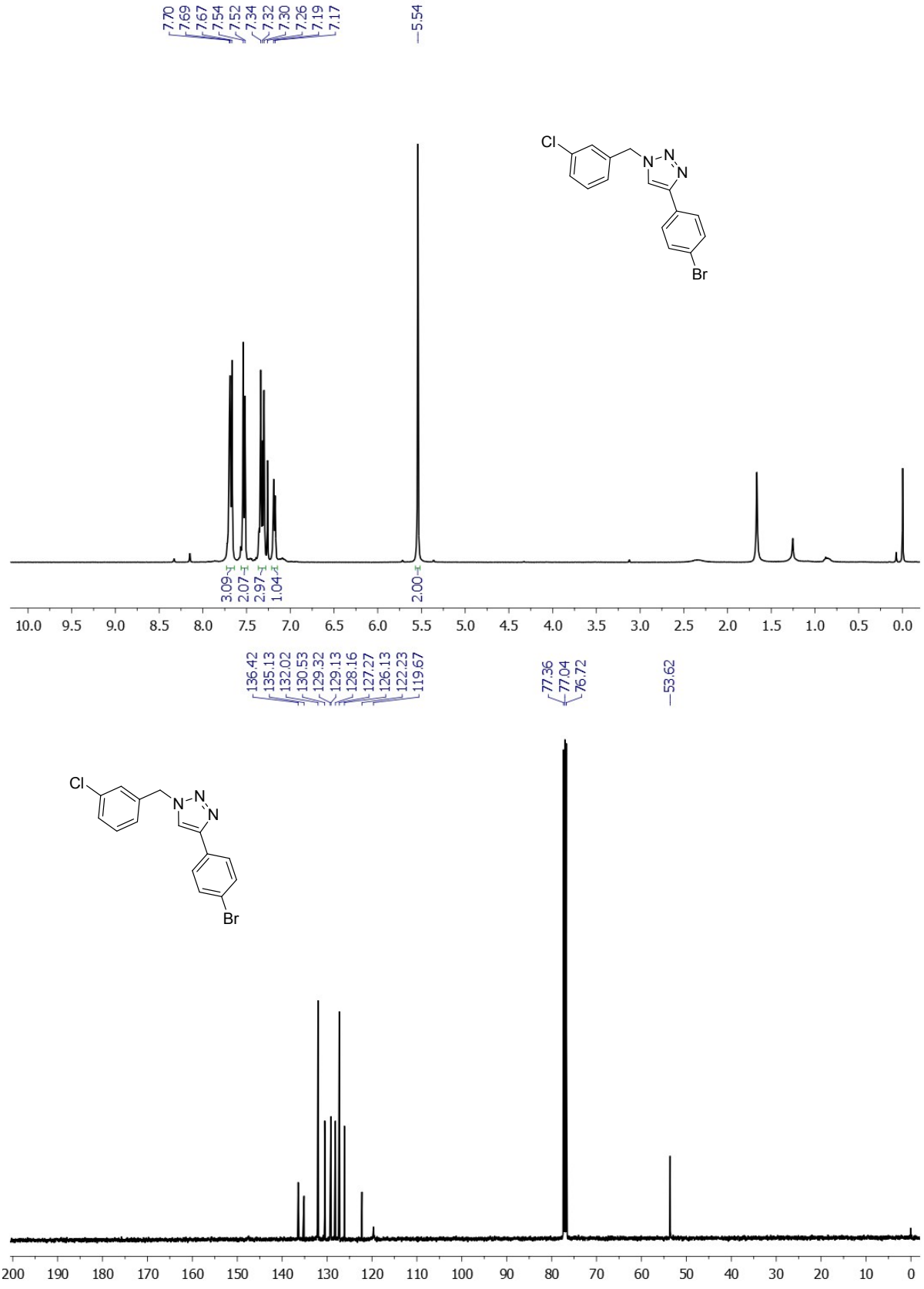
^{1}H and ^{13} C NMR spectra of compound **4m**



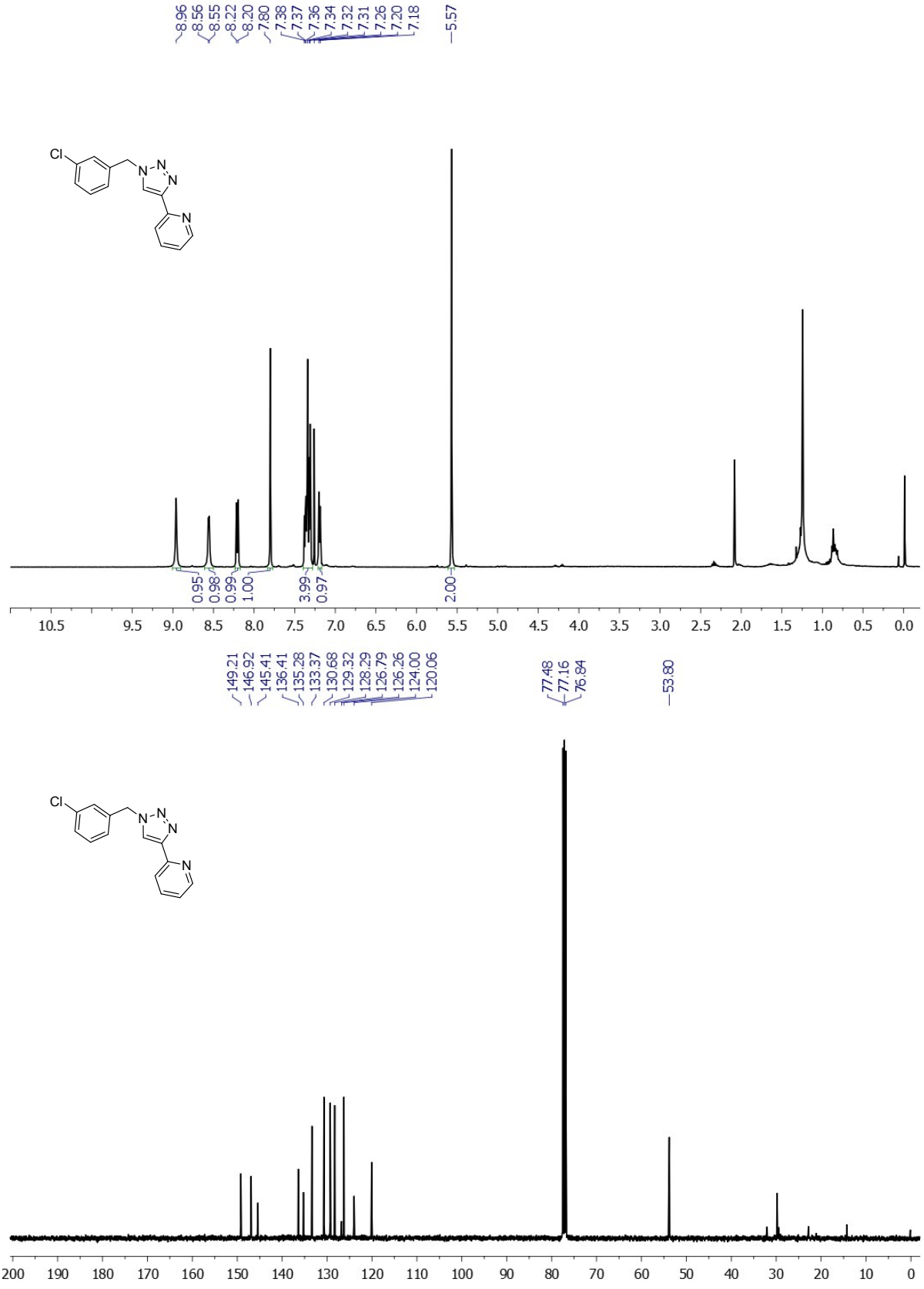
^{1}H and ^{13} C NMR spectra of compound **4n**



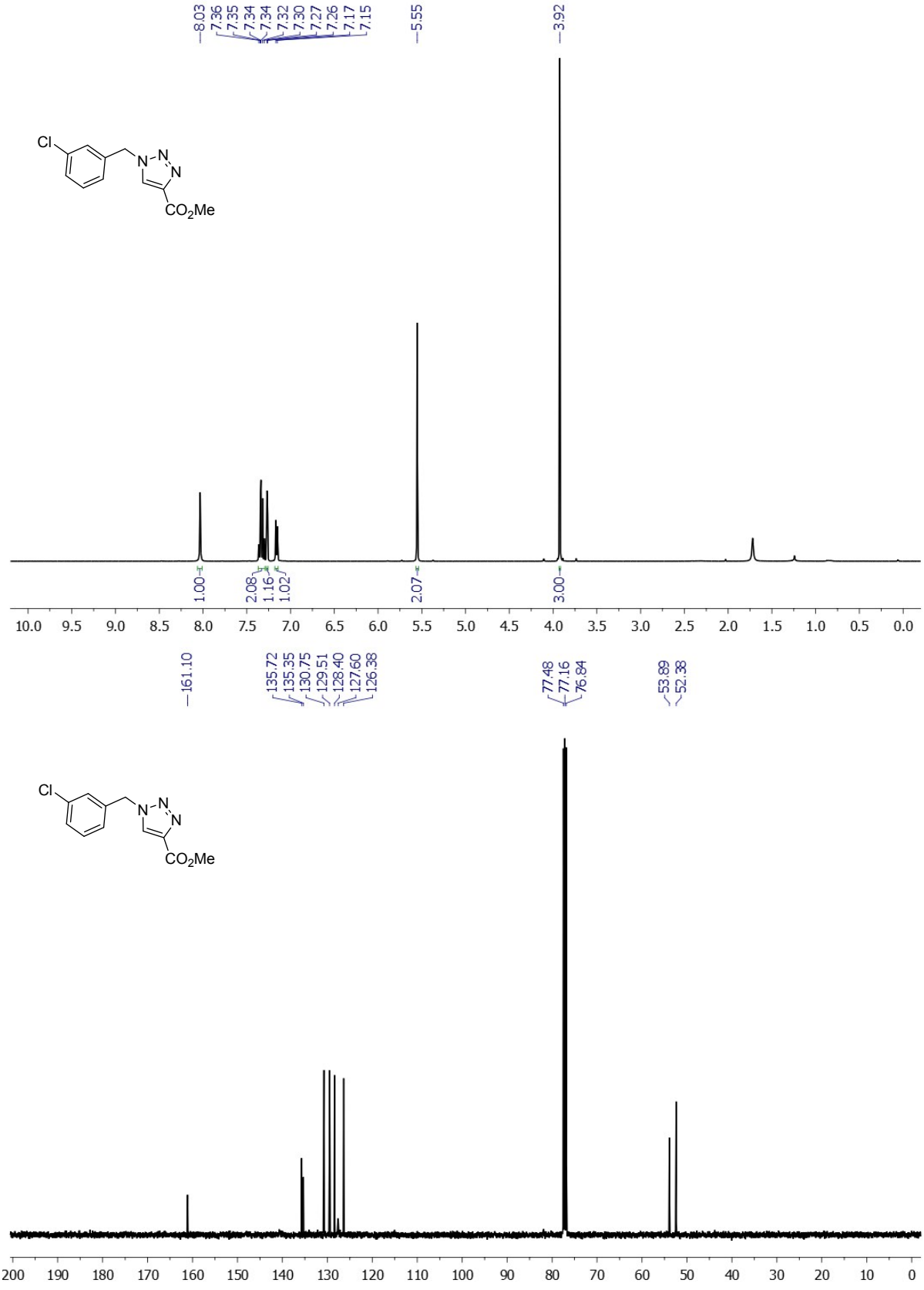
^{1}H and ^{13} C NMR spectra of compound **4o**



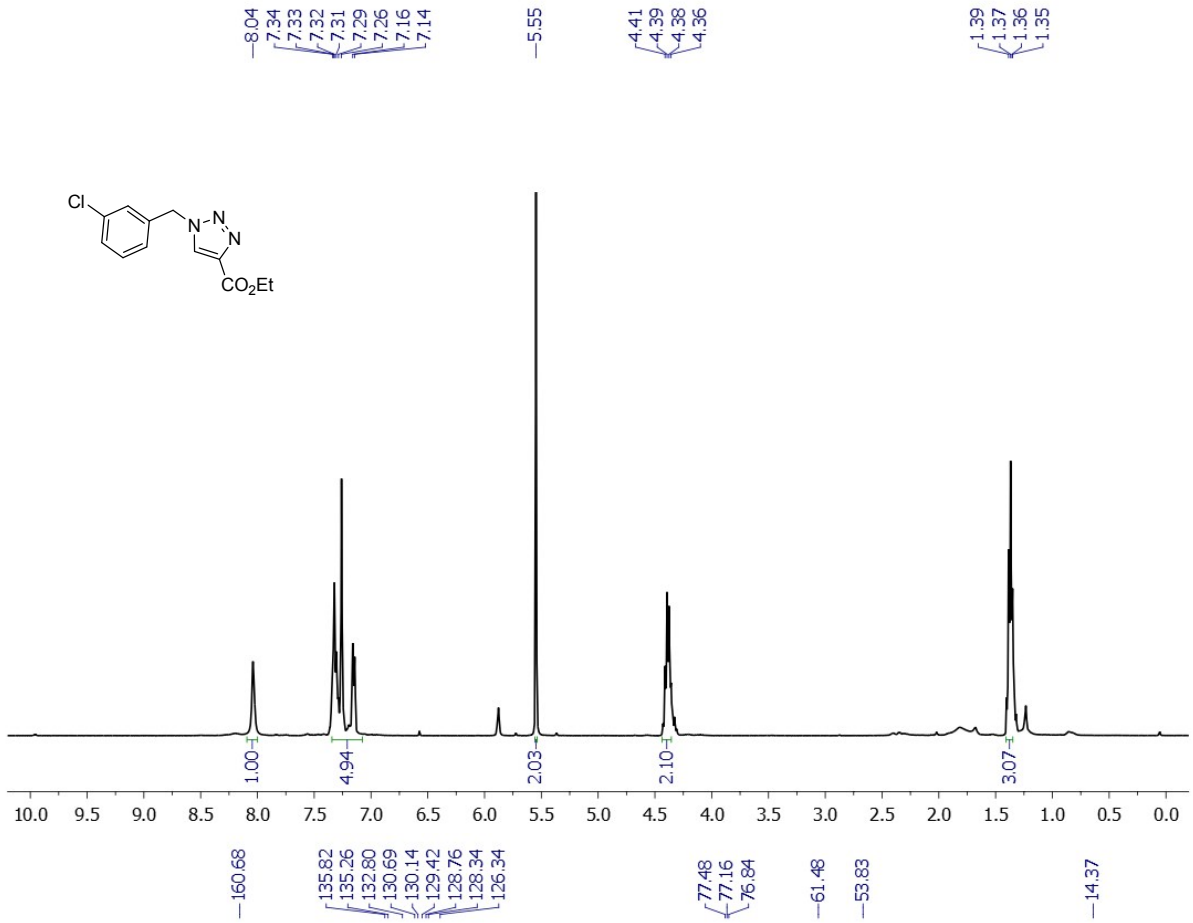
^{1}H and ^{13} C NMR spectra of compound **4p**

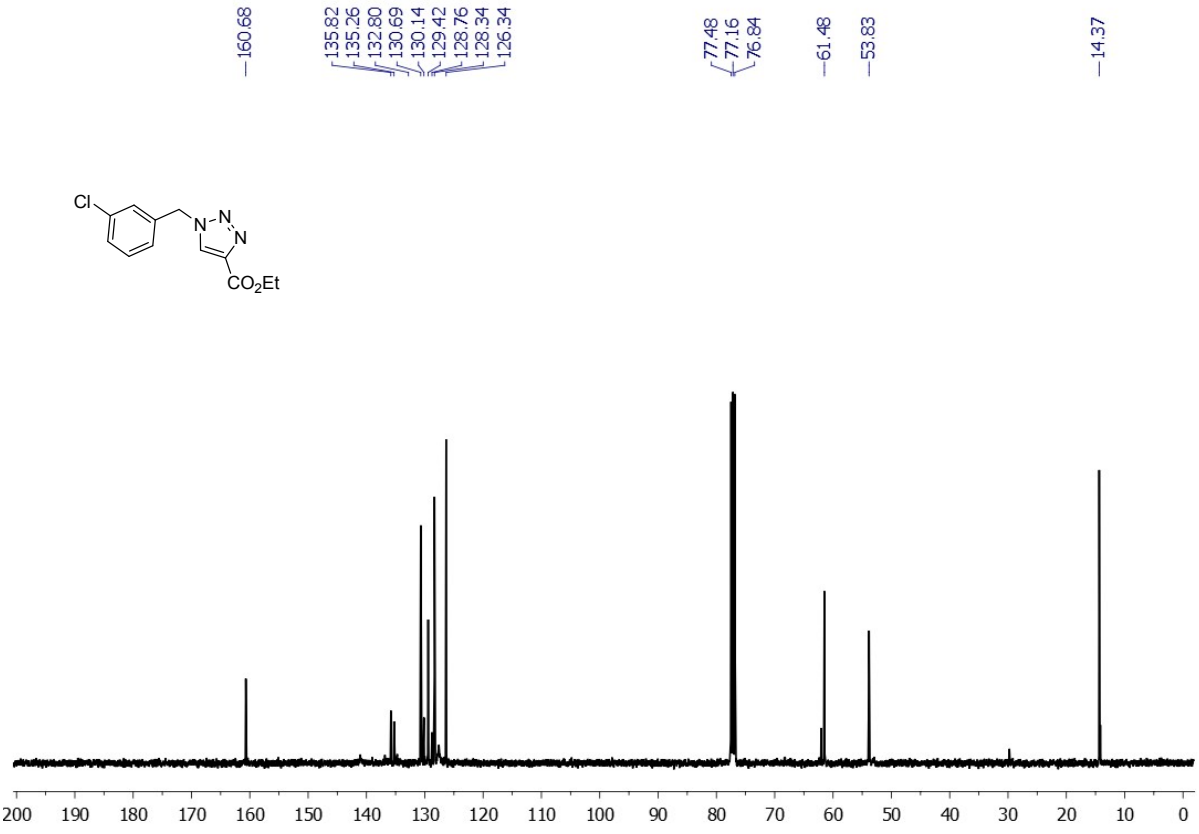


^{1}H and ^{13} C NMR spectra of compound **4q**

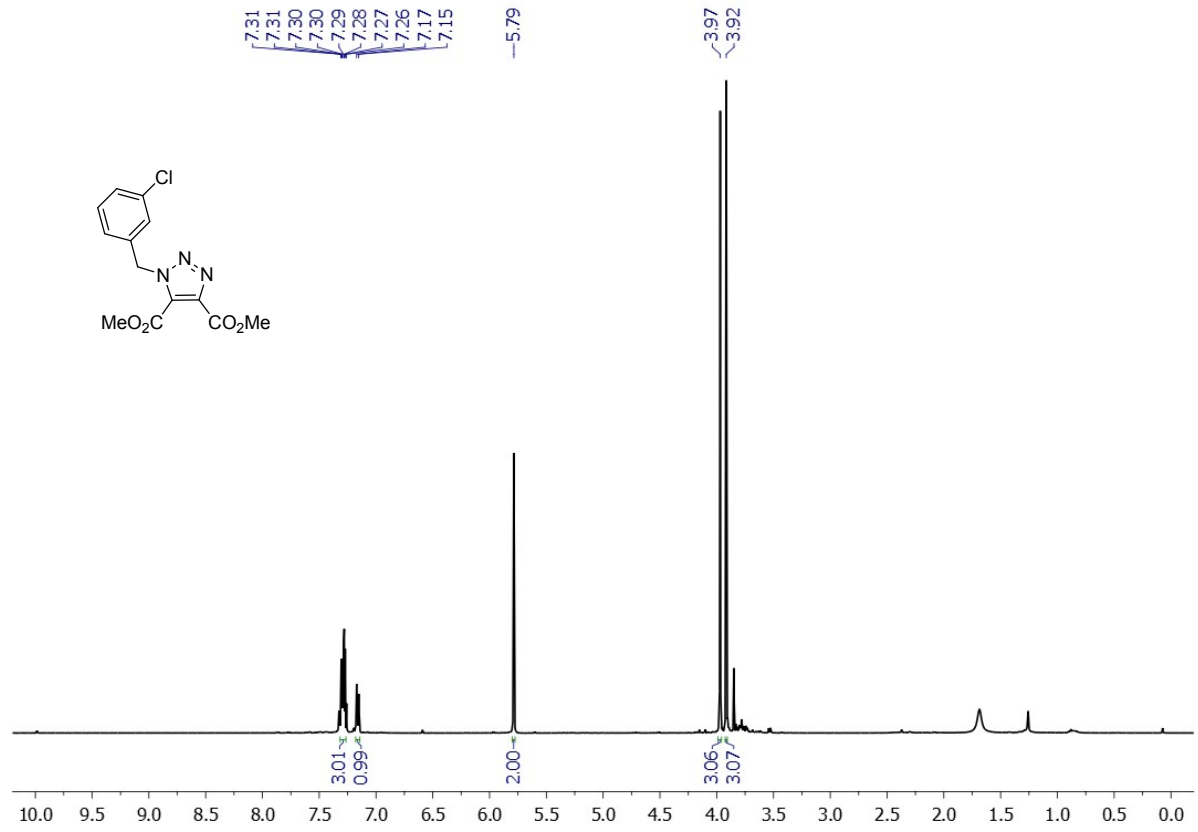


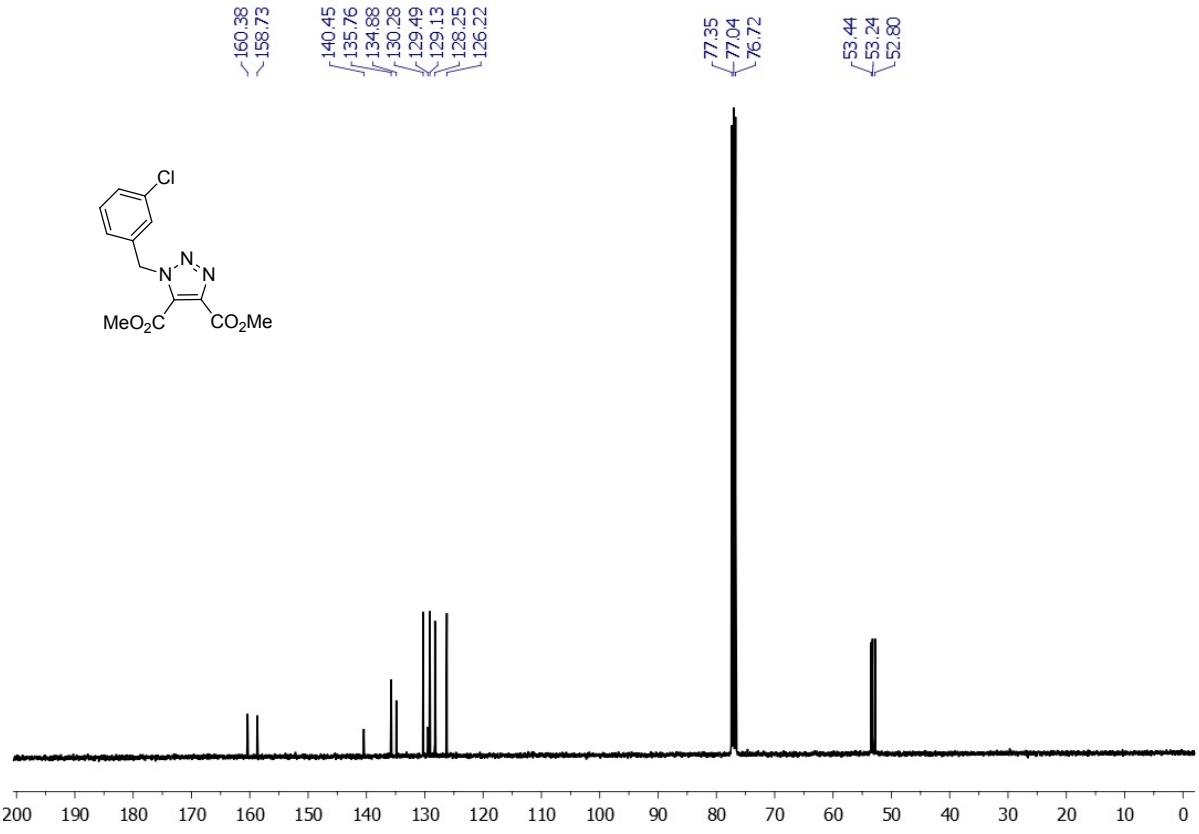
^{1}H and ^{13} C NMR spectra of compound **4r**



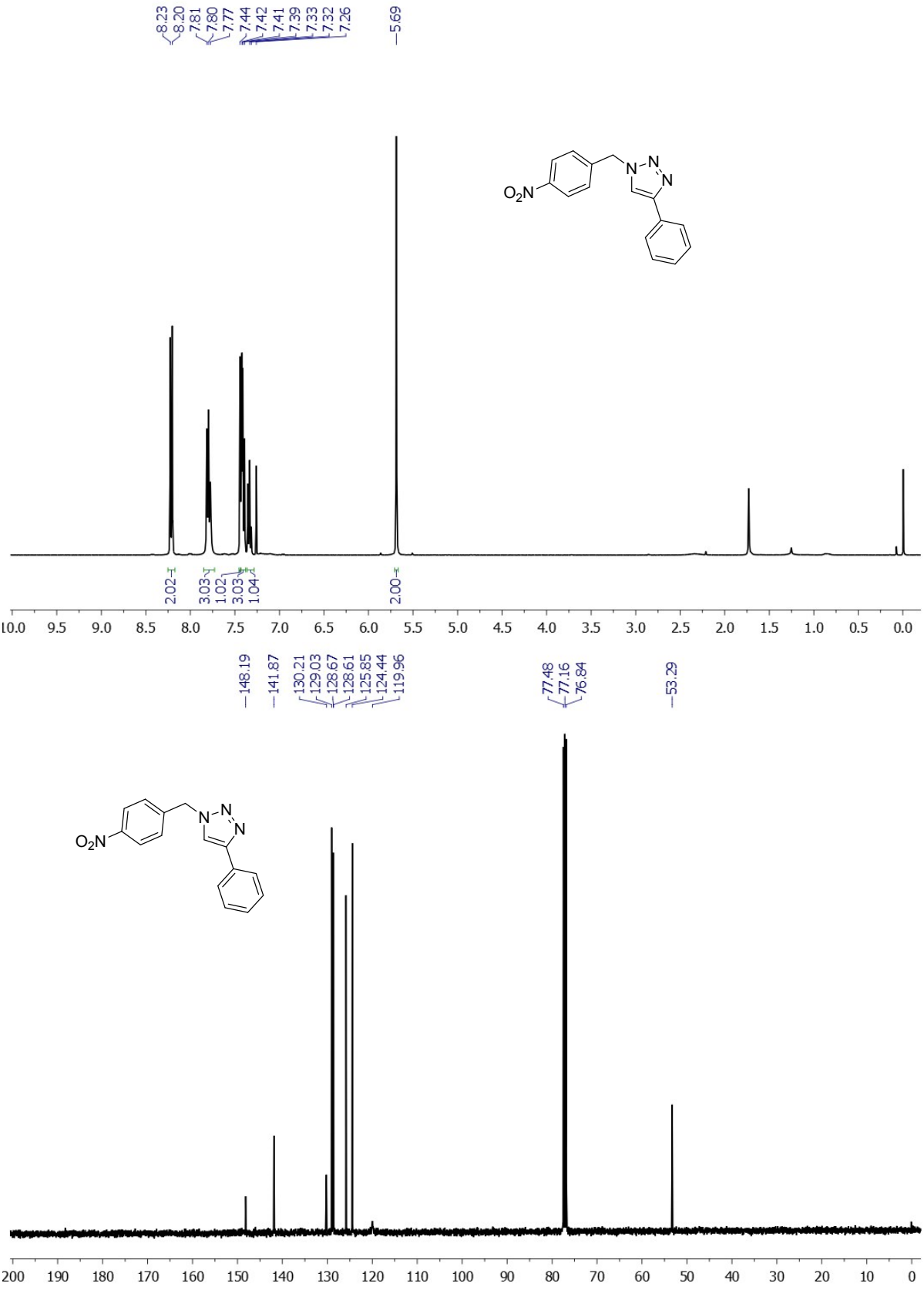


^{1}H and ^{13} C NMR spectra of compound **8c**

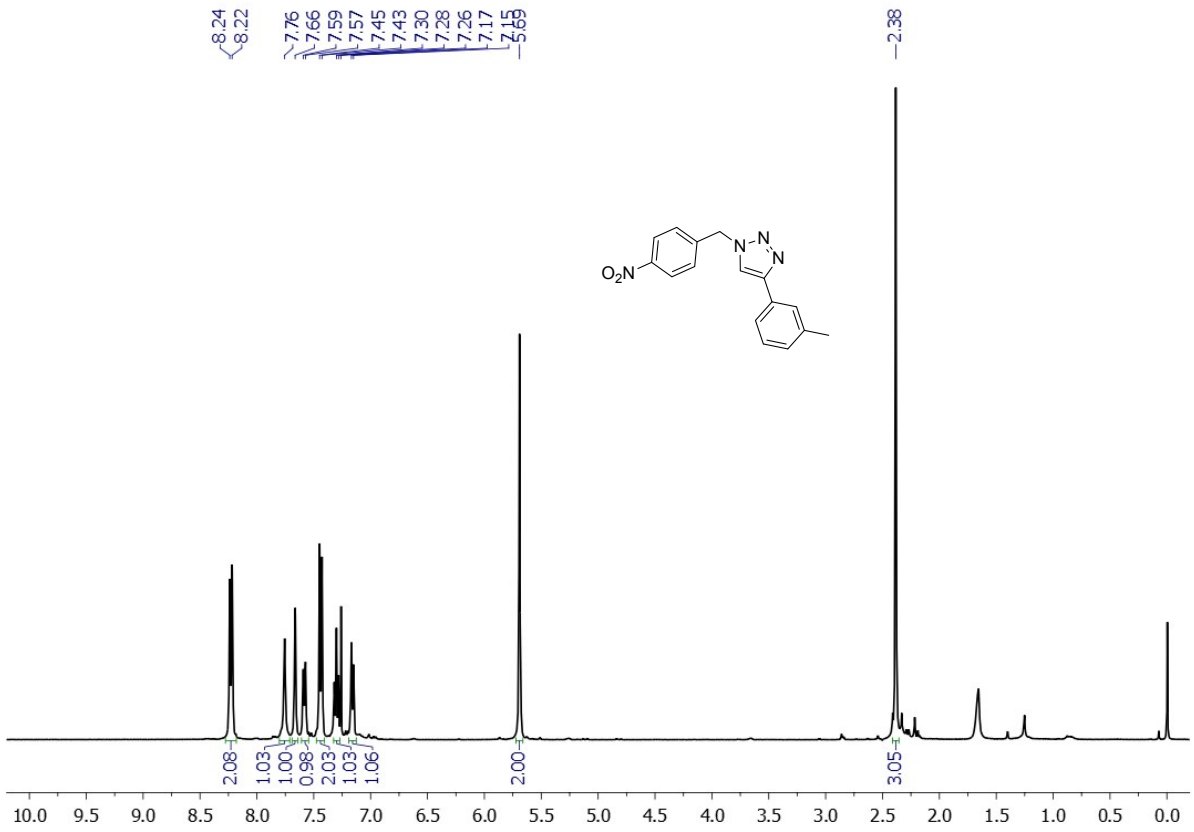


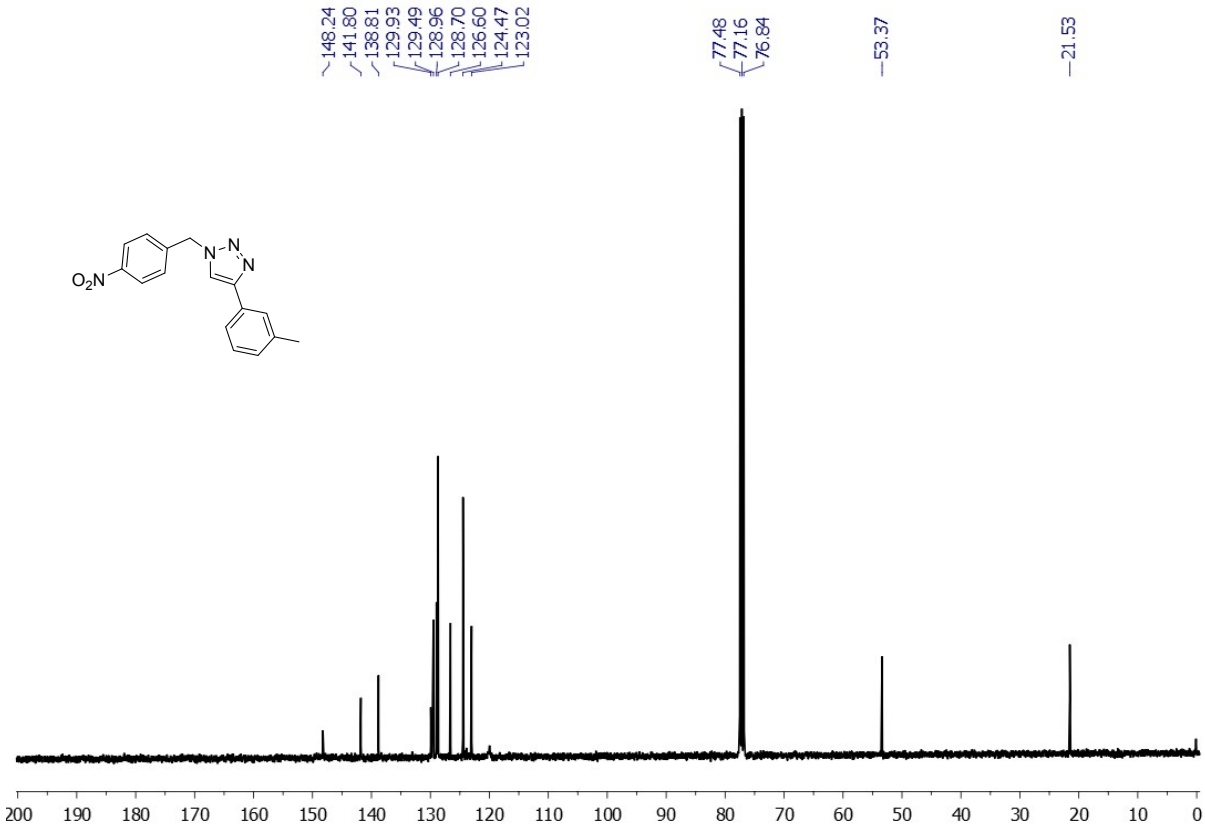


^{1}H and ^{13}C NMR spectra of compound **4s**

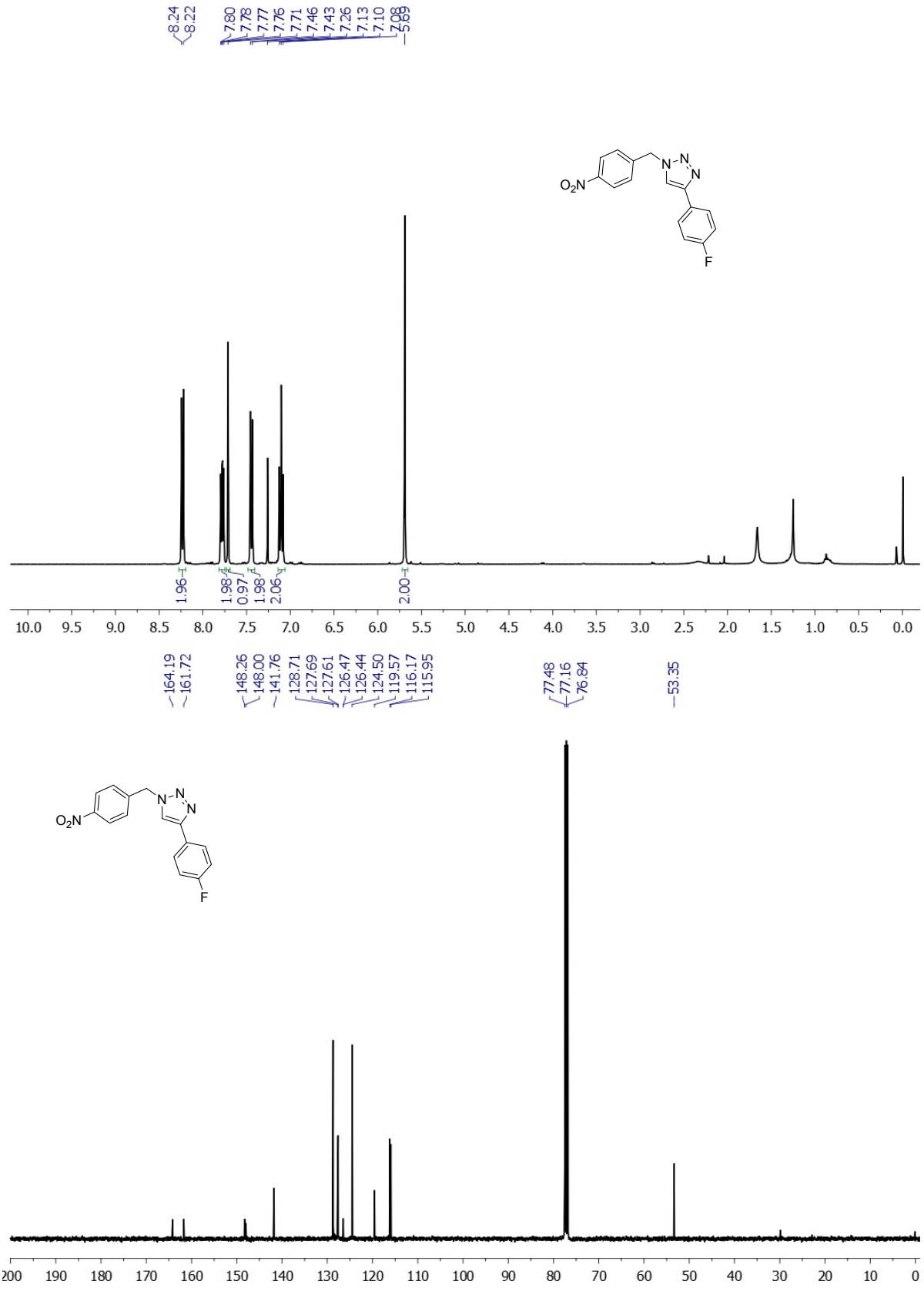


^{1}H and ^{13} C NMR spectra of compound **4t**

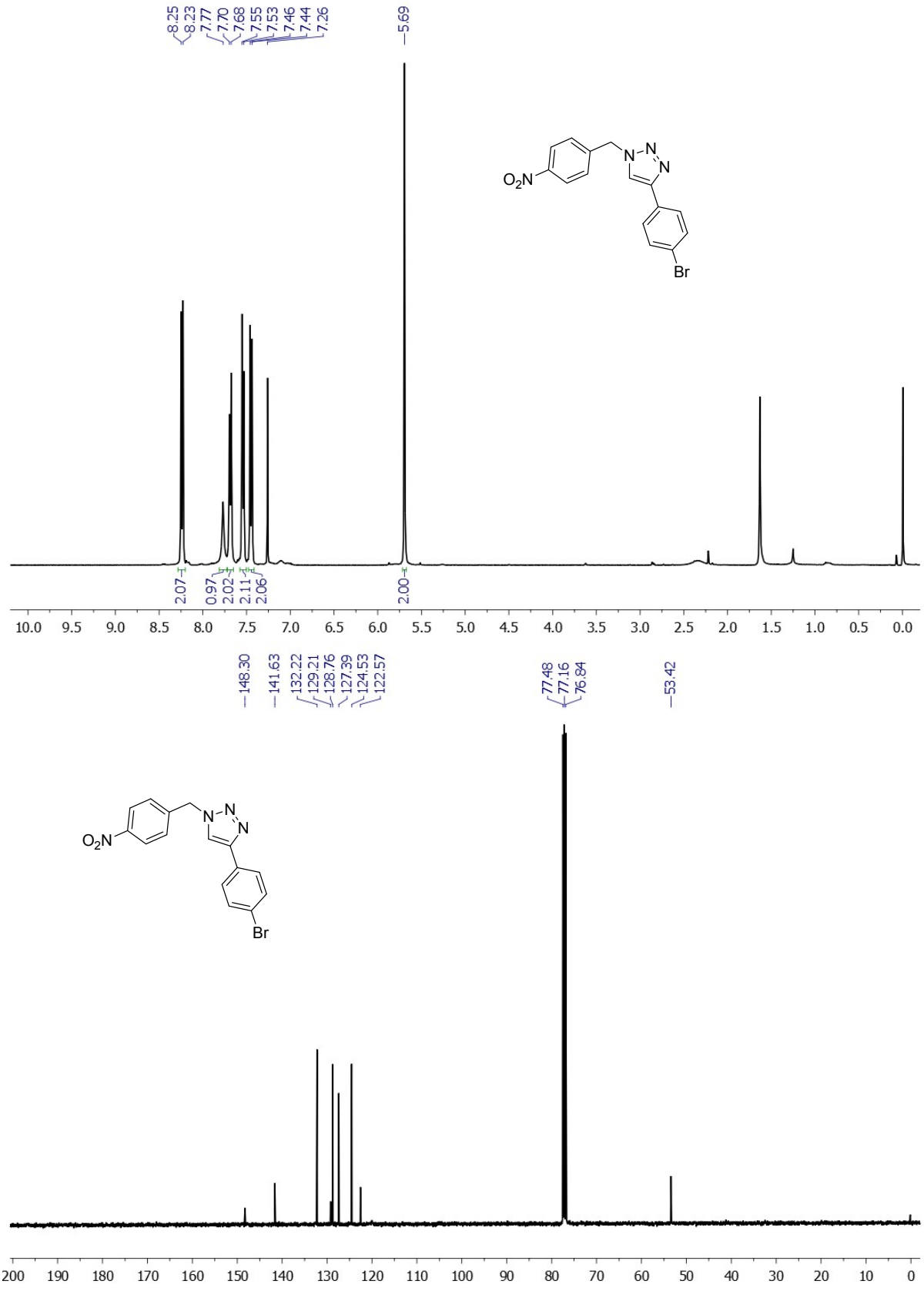




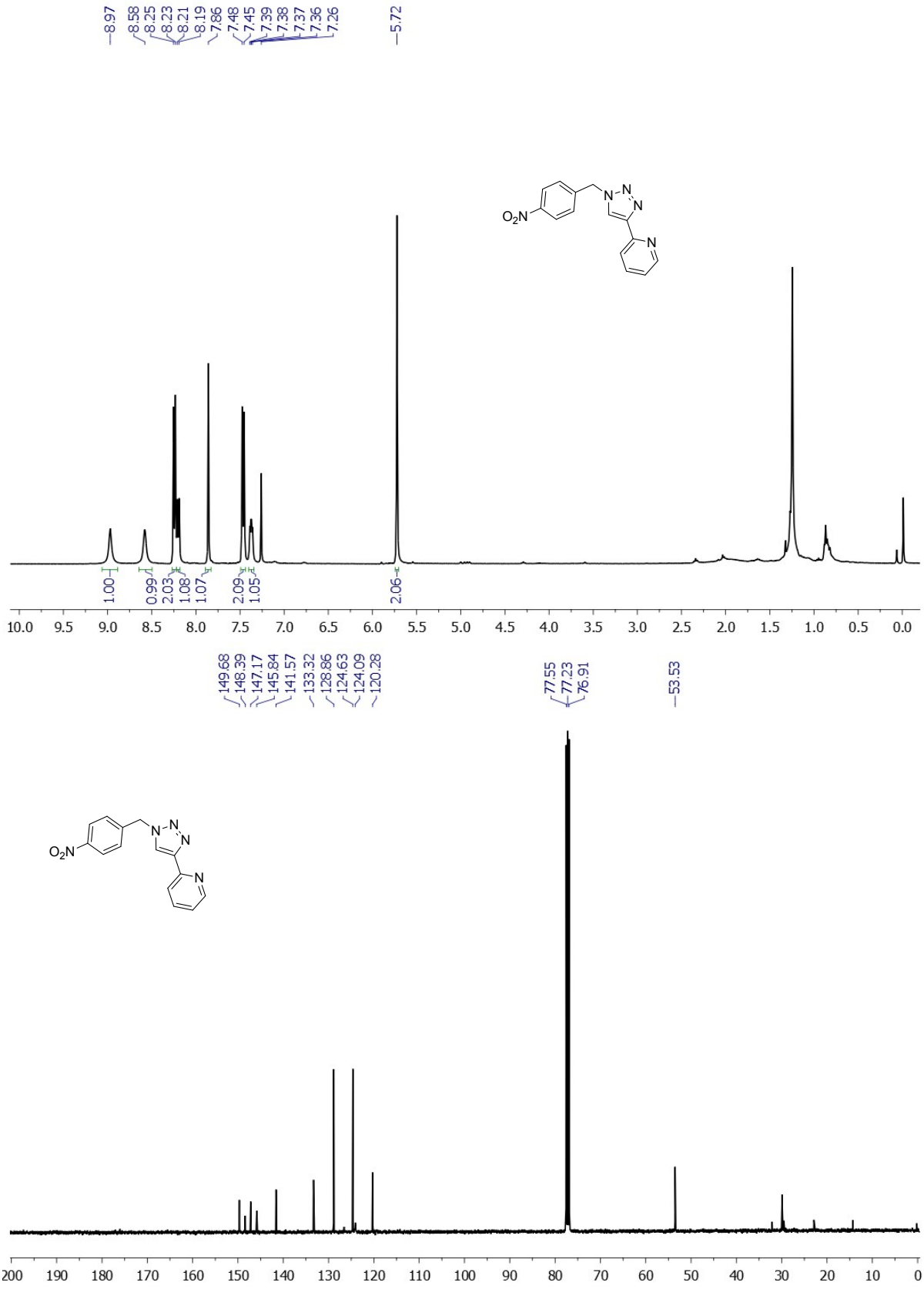
^{1}H and ^{13} C NMR spectra of compound **4u**



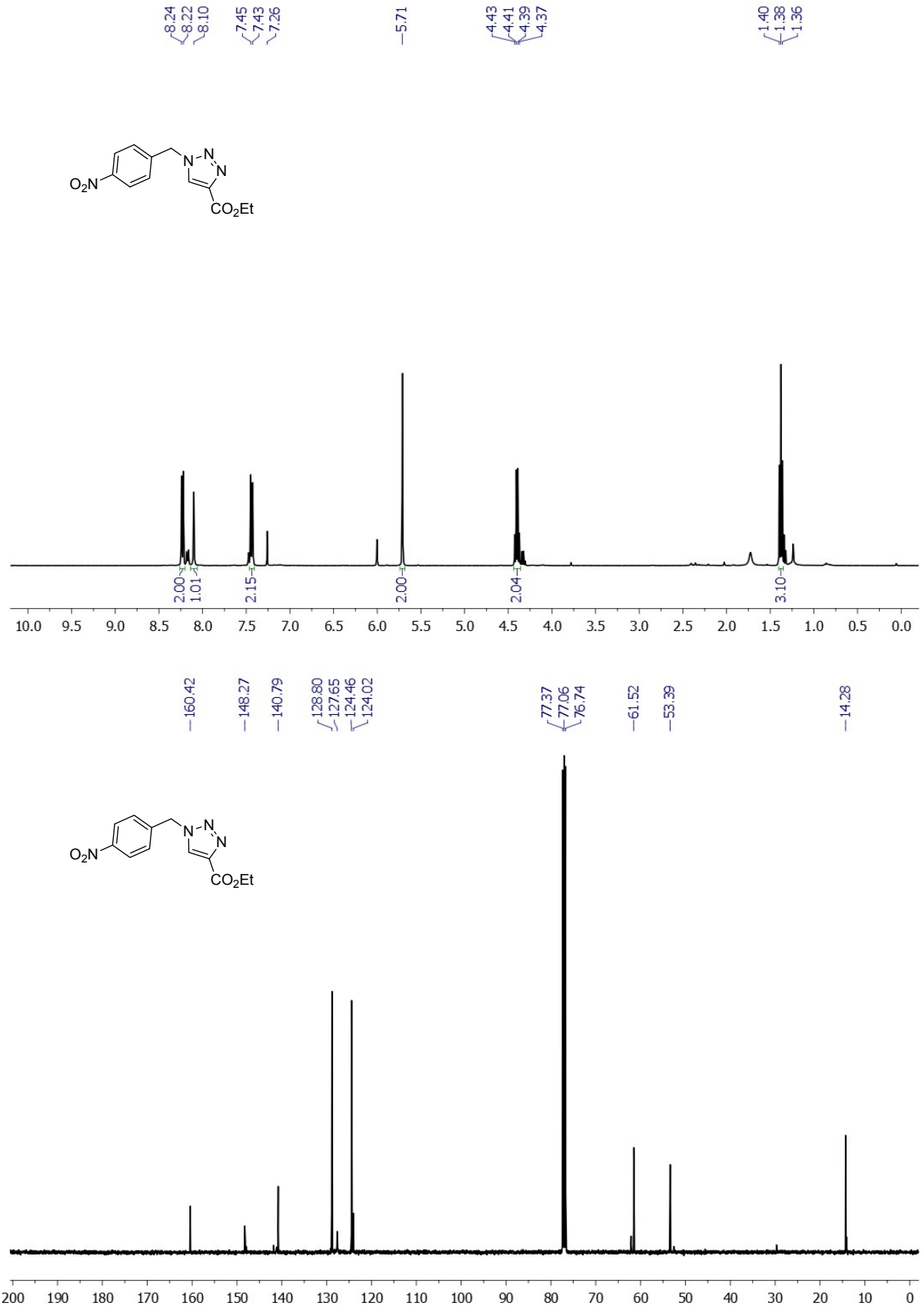
^{1}H and ^{13} C NMR spectra of compound **4v**



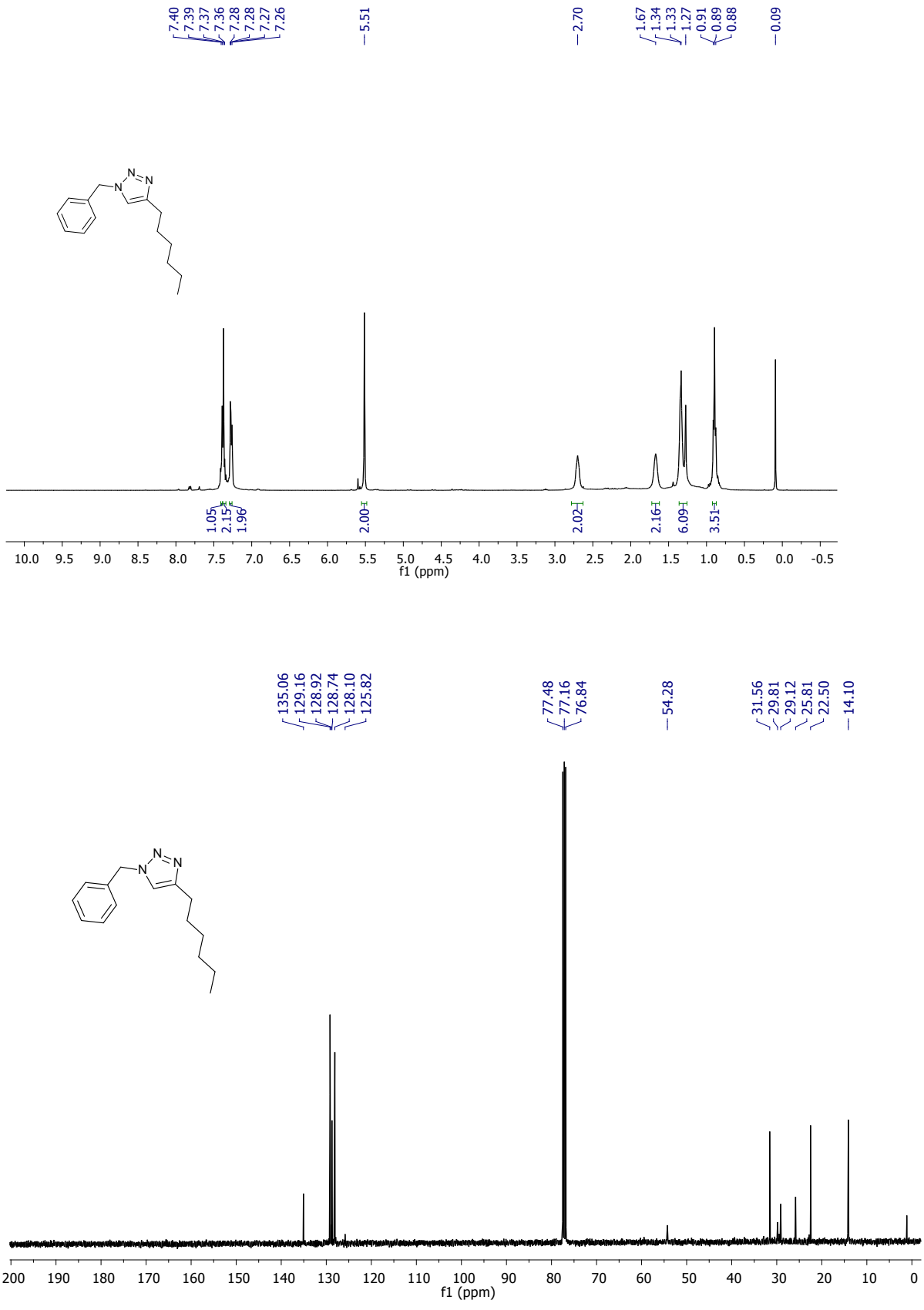
^{1}H and ^{13} C NMR spectra of compound **4w**



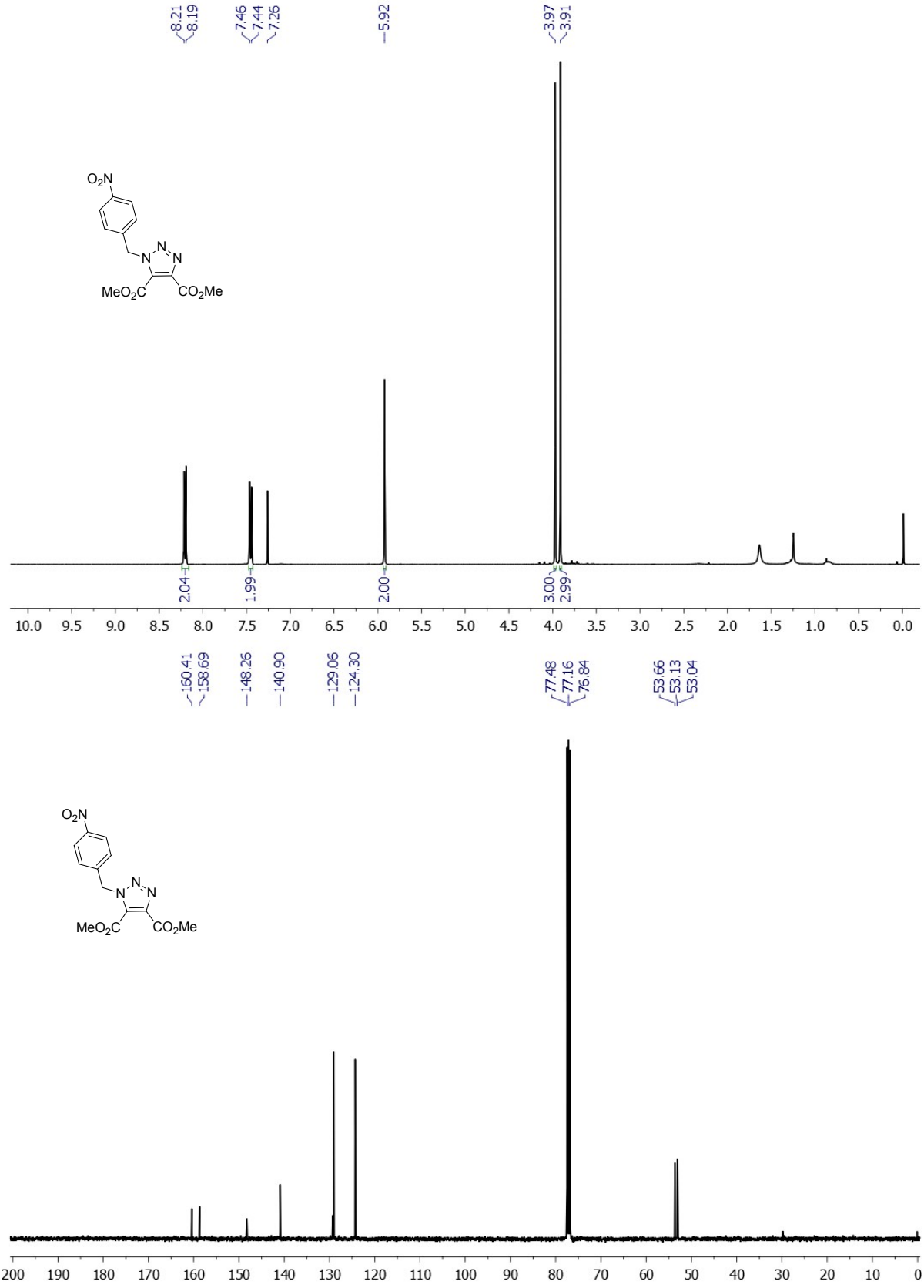
^{1}H and ^{13} C NMR spectra of compound **4x**



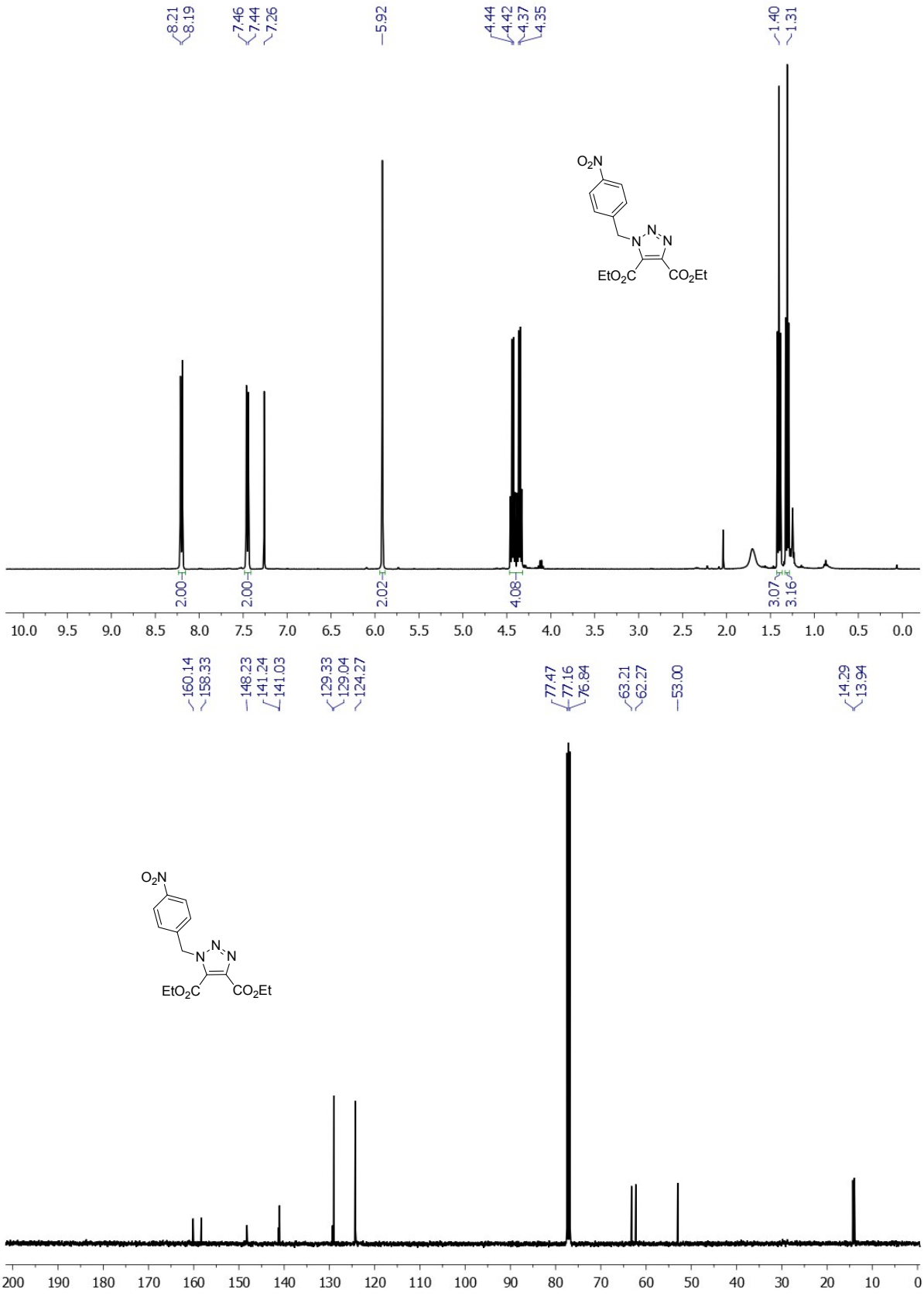
^{1}H and ^{13} C NMR spectra of compound **4y**



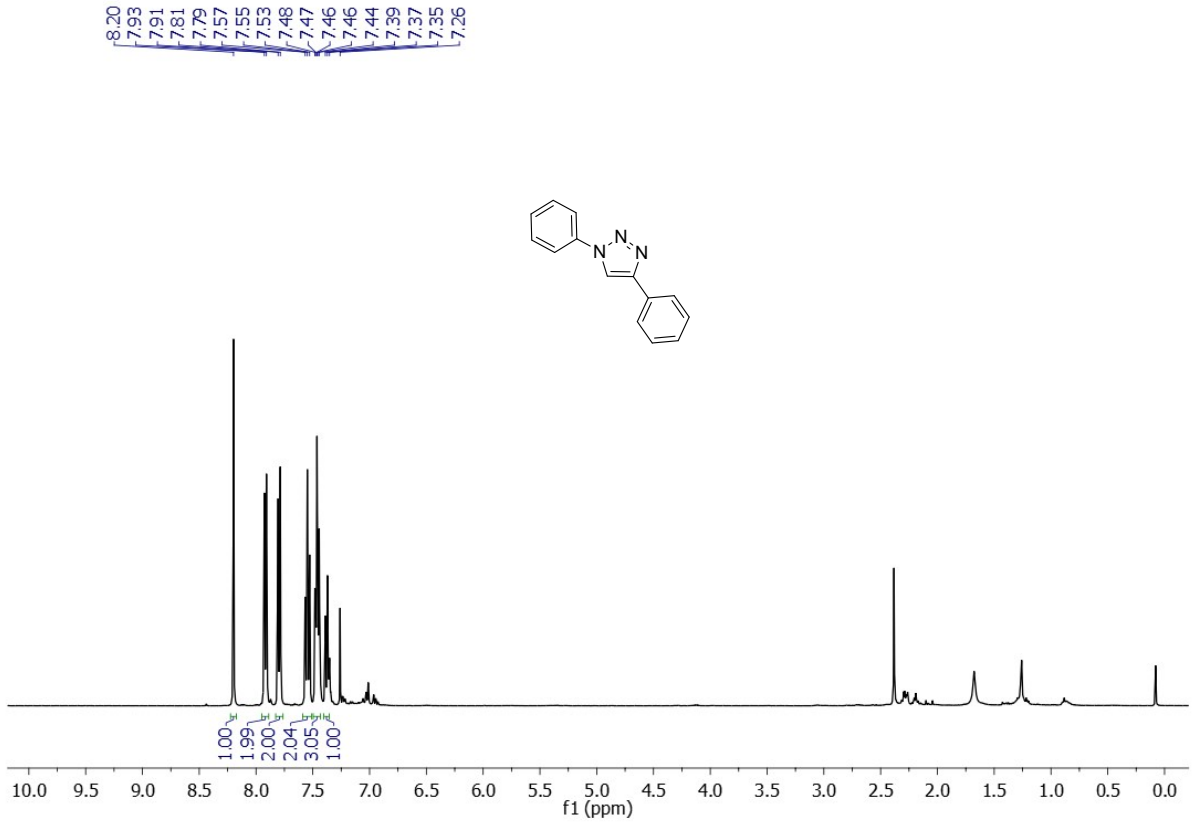
^{1}H and ^{13} C NMR spectra of compound **8d**

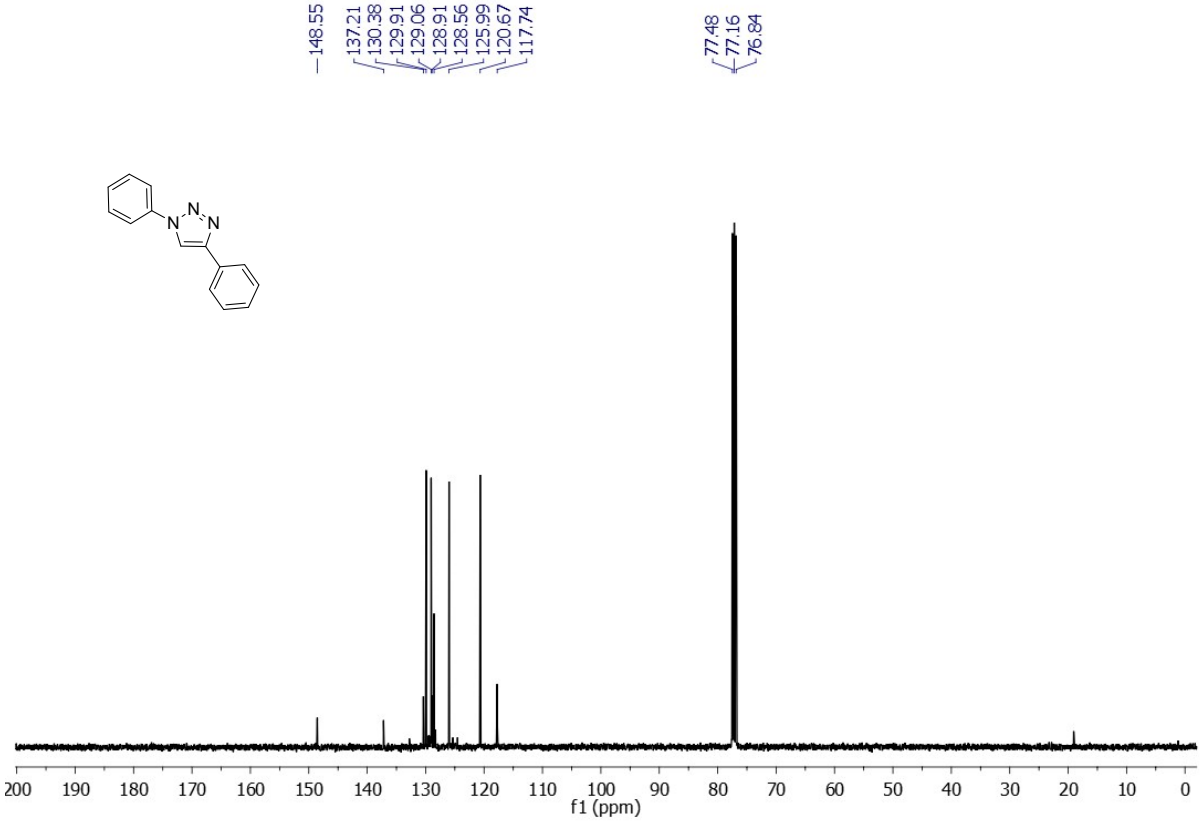


^{1}H and ^{13} C NMR spectra of compound **8e**

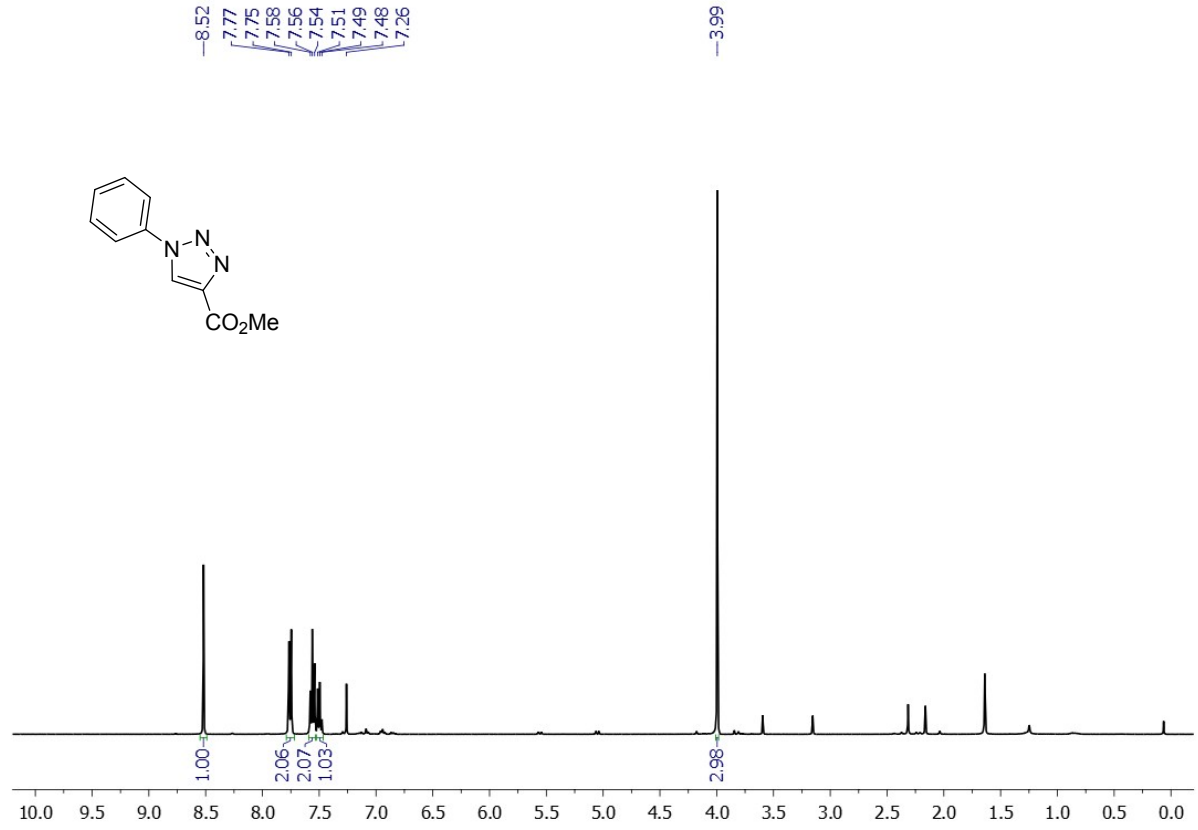


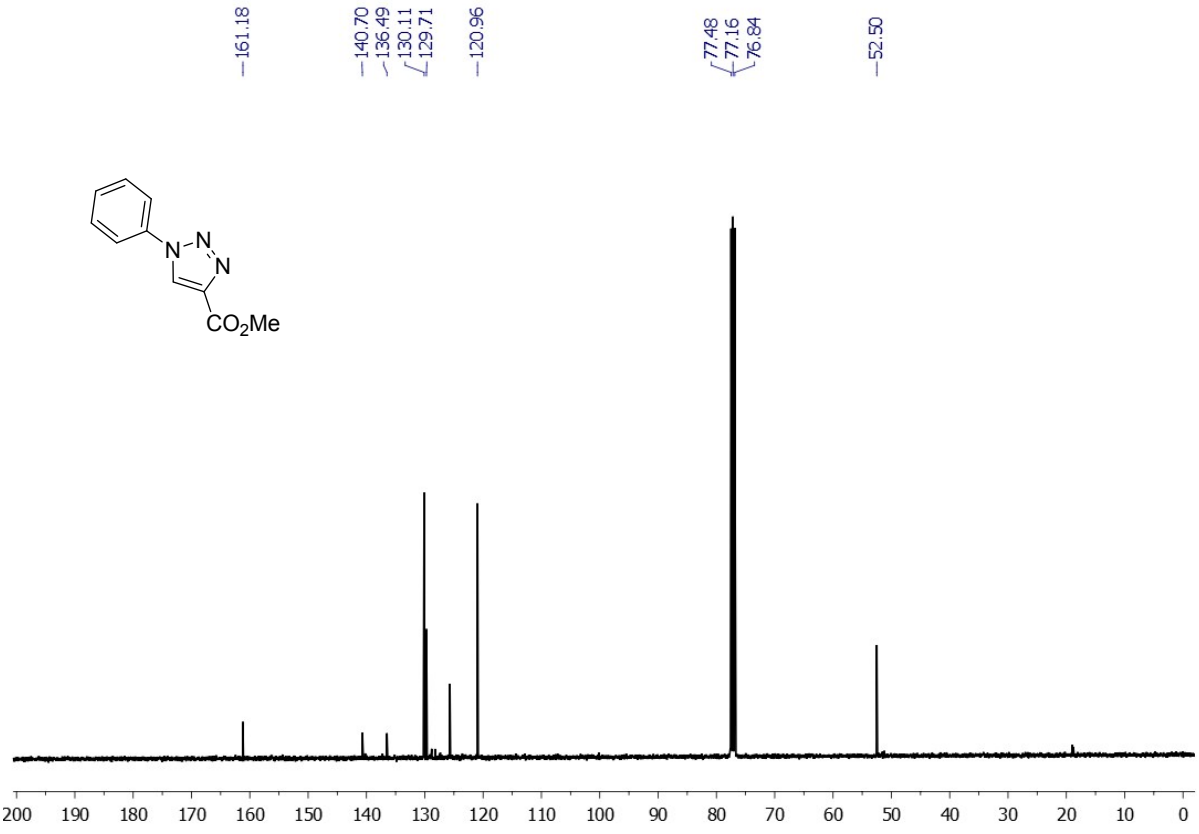
^{1}H and ^{13} C NMR spectra of compound **6a**



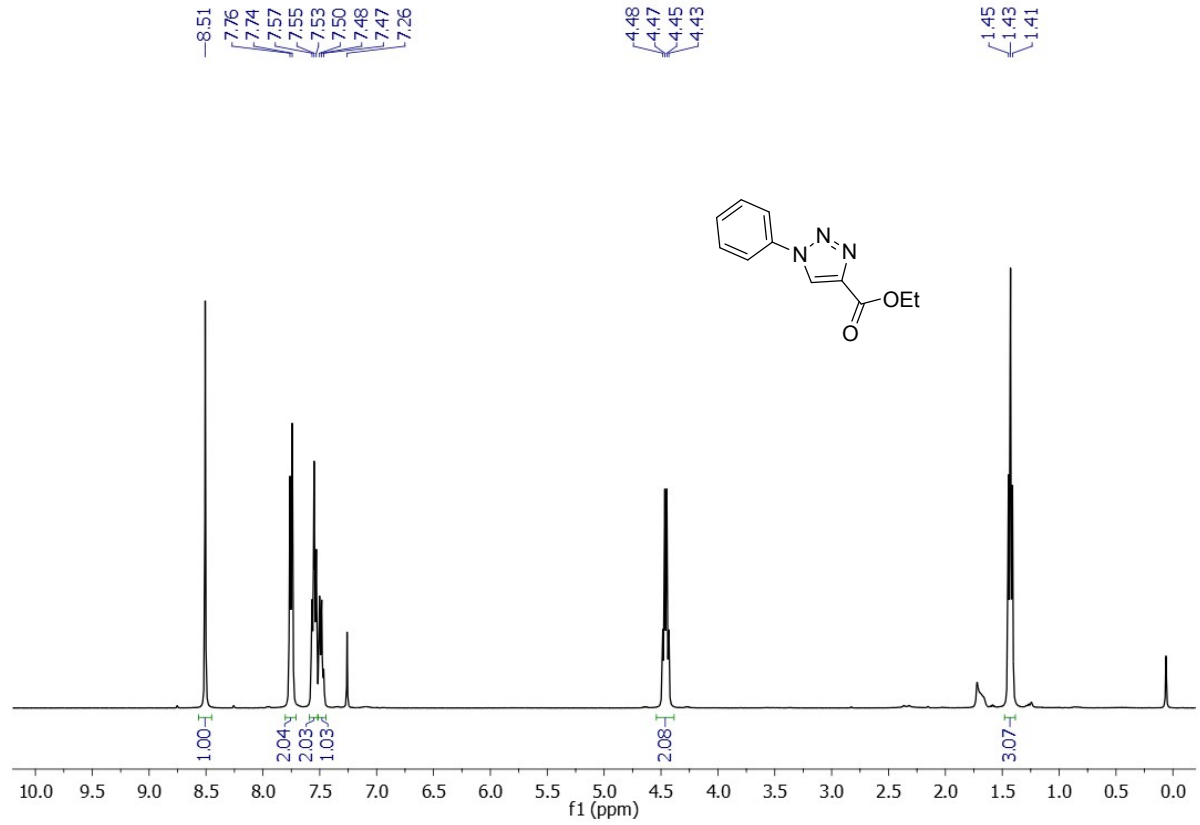


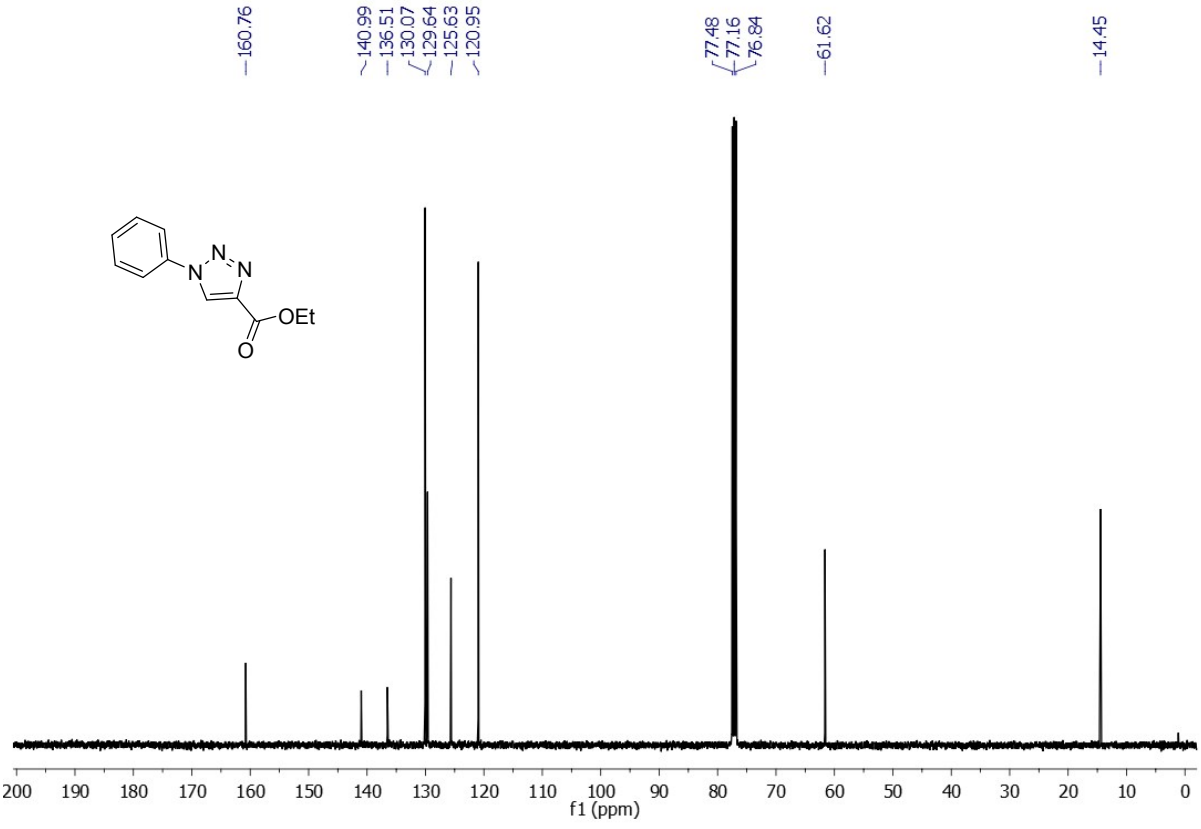
^{1}H and ^{13} C NMR spectra of compound **6b**





^{1}H and ^{13} C NMR spectra of compound **6c**





^{1}H and ^{13} C NMR spectra of compound **8b**

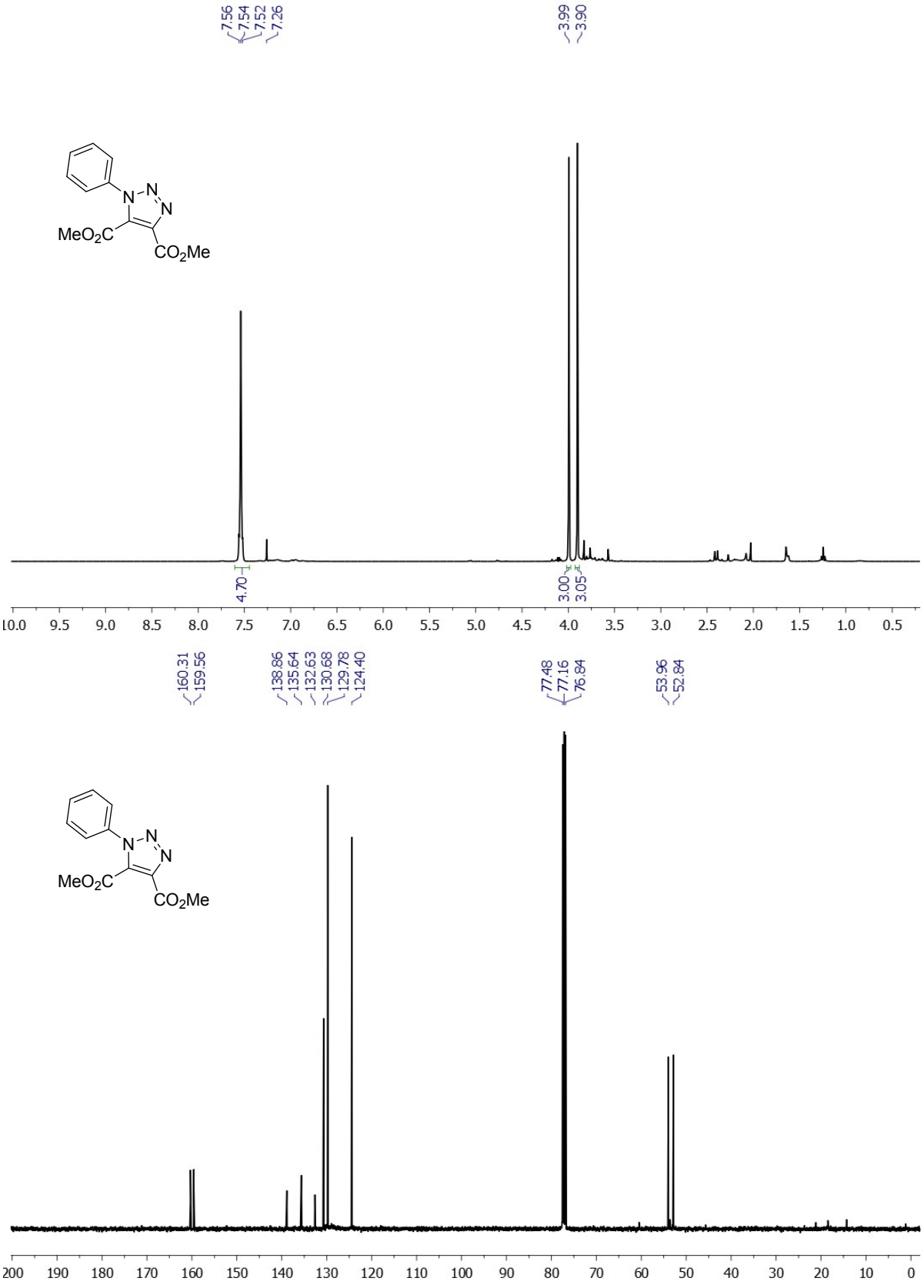


Table S1. Crystal data and structure refinement for sn_z_131_0m.

Identification code	sn_z_131_0m	
Empirical formula	C38 H48 Cl Cu N4 O S2	
Formula weight	739.91	
Temperature	100 K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.443(2) Å	α= 71.585(10)°.
	b = 12.452(3) Å	β= 84.083(10)°.
	c = 15.010(3) Å	γ = 68.386(10)°.
Volume	1886.3(13) $Å^3$	
Z	2	
Density (calculated)	1.303 Mg/m^3	
Absorption coefficient	0.795 mm^{-1}	
F(000)	780	
Crystal size	0.068 x 0.045 x 0.033 mm^3	
Theta range for data collection	1.84 to 25.50°.	
Index ranges	-13<=h<=13, -14<=k<=15, -18<=l<=18	
Reflections collected	26167	
Independent reflections	7005 [R(int) = 0.0334]	
Completeness to theta = 25.50°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7458 and 0.6589	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7005 / 0 / 432	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0919	
R indices (all data)	R1 = 0.0516, wR2 = 0.1012	
Largest diff. peak and hole	0.405 and -0.289 $e.Å^{-3}$	

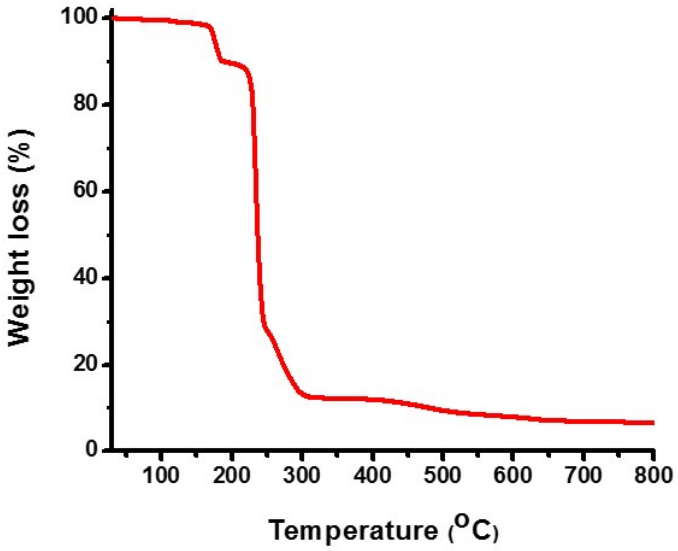


Fig. S1 Thermogravimetric analysis for LCu(Cl)L $C_{34}H_{40}ClCuN_4S_2$ (**1**).

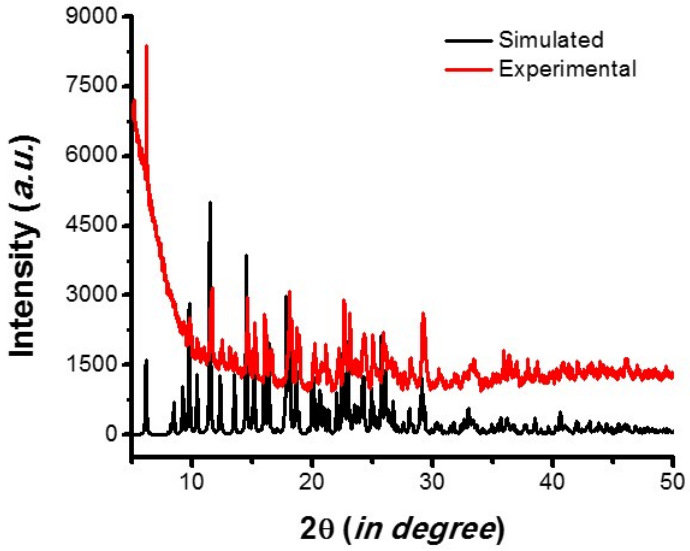


Fig. S2 PXRD pattern for LCu(Cl)L $C_{34}H_{40}ClCuN_4S_2$ (**1**).

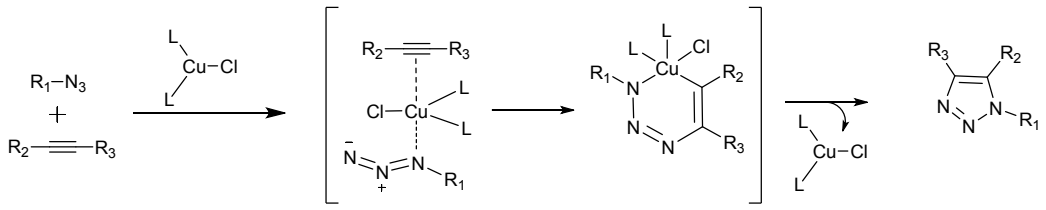


Fig. S3 Proposed mechanism for compound **1** catalysed cycloaddition of azides and internal alkynes