Synthesis and crystal structures of salen-type Cu(II) and Ni(II) Schiff base complexes: Application in [3+2]-Cycloaddition and A^3-coupling reactions

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Contents

Synthesis of Salen type Schiff base ligand (H_2L)

The Salen type Schiff base ligand H_2L was prepared by the reported method.[1] The ligand was prepared by refluxing a mixture of 4-(diethylamino)-2-hydroxybenzaldehyde (0.193 g, 1 mmol) and trans-cyclohexane-1,2-diamine (0.057g, 0.5 mmol) in 10 mL of ethanol for 6 h. The reaction mixture was cooled to room temperature and the resulting off-white precipitate was filtered, washed with cold ethanol and dried in vacuum over anhydrous $CaCl_2$. Yield: 89%, FT-IR (KBr), cm^{-1}: 3298 ν (OH) , 1620 ν (C=N), 2850-2931 ν (CH_2), 1340 ν ($C=C_{ring}$). ^1H NMR ($CDCl_3$, 25 ^0C, 400 MHz): δ 13.79 (s, 2H, O*H*), δ7.93 (s, 2H, *H*-CN), δ6.88 (d, 2H, J = 4 Hz, Ar *H*), δ6.08 (d, 2H, *J* = 2.4, Ar *H*), δ3.32 (q, *J*= 2.4 Hz, 2H, -CH_2), δ3.14 (m, 2H, cyclohexane ring), δ1.94 (d, 2H, *J* = 14, cyclohexane ring), δ1.83 (d, 2H, J = 8.8, cyclohexane ring), δ1.63 (m, 2H, cyclohexane ring), δ1.42 (m, 2H, cyclohexane ring), δ1.16-1.13 (t, *J* = 7.2 Hz, 12 H, -CH_3) .

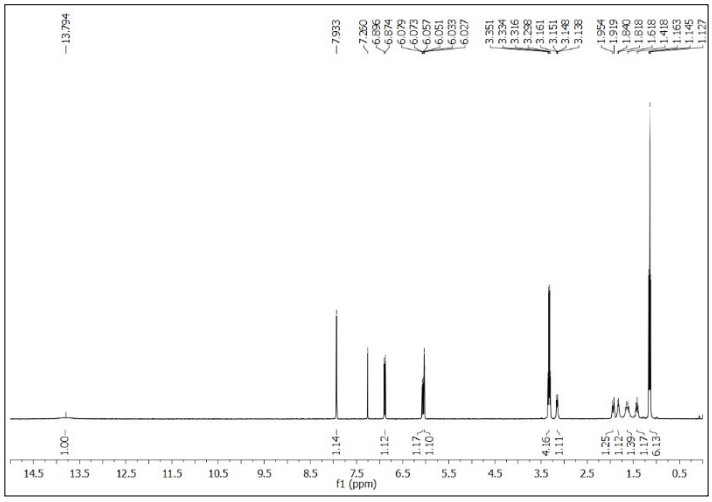


Fig.S1 ^1H NMR of salen-type Schiff base ligand

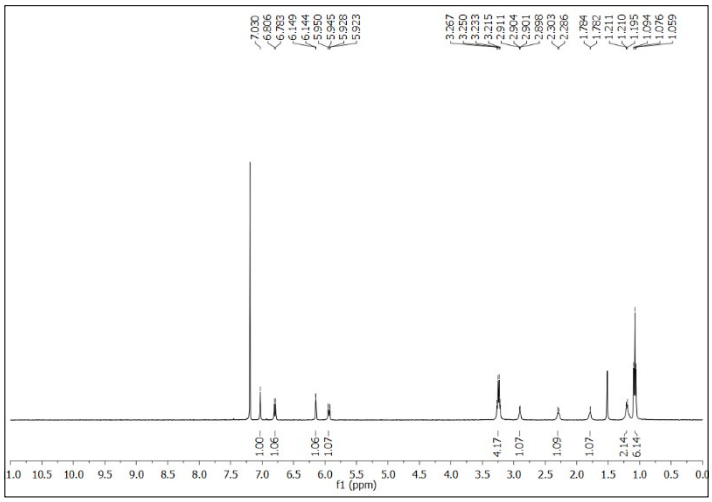


Fig. S2 ^1H NMR of Ni(II) Salen-type Schiff base complex

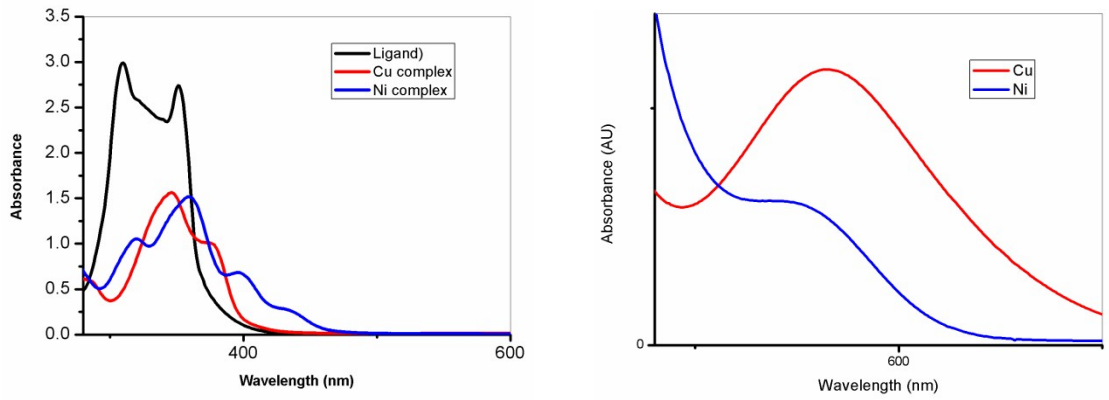
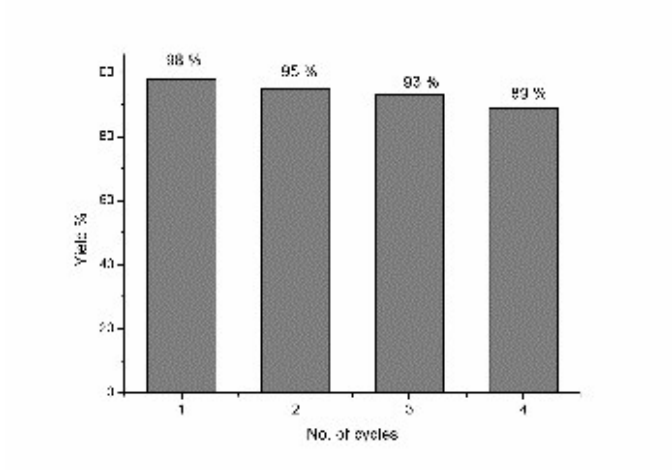


Fig. S3 UV-vis spectra of (a) Ligand (b) Cu complex (c) Ni complex

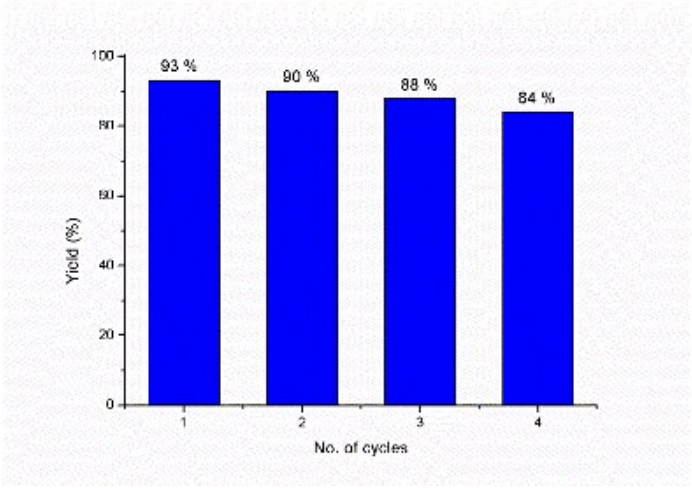
Table 1S Selected bond distances (Å) and bond angles (°) for [Cu(L)].0.5H_2O and [Ni(L)] Salen-type Schiff base complexes.

[Cu(L)].*0.5*H_2O	Bond distance	[Ni(L)]	Bond distance
Cu(1)-O(1)	1.903(3)	Ni(1)-O(1)	1.840(3)
Cu(1)-O(2)	1.910(3)	Ni(1)-O(2)	1.856(3)
Cu(1)-N(1)	1.925(4)	Ni(1)-N(1)	1.851(4)
Cu(1)-N(2)	1.928(4)	Ni(1)-N(2)	1.850(3)

[Cu(L)].*0.5*H_2O	Bond angle	[Ni(L)]	Bond angle
O(1)-Cu(1)-O(2)	90.17(15)	O(1)-Ni(1)-O(2)	85.0(1)
O(1)-Cu(1)-N(1)	93.81(18)	O(1)-Ni(1)-N(1)	95.0(2)
O(2)-Cu(1)-N(1)	169.75(16)	O(2)-Ni(1)-N(1)	176.5(2)
O(1)-Cu(1)-N(2)	165.92(16)	O(1)-Ni(1)-N(2)	178.0(2)
O(2)-Cu(1)-N(2)	93.76(17)	O(2)-Ni(1)-N(2)	94.3(2)
N(1)-Cu(1)-N(2)	84.64(19)	N(1)-Ni(1)-N(2)	85.7(2)



(a)



(b)

Fig. S4 Recyclability test of the complex **1** in (a) 5-substituted 1*H*-tetrazole and (b) propargylamines

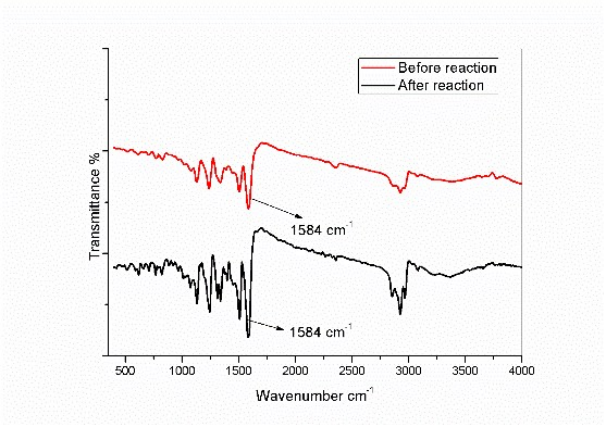


Fig. S5 FTIR plot of Cu(II) Complex **1** before and after use of it in 5-substituted 1*H*-tetrazole

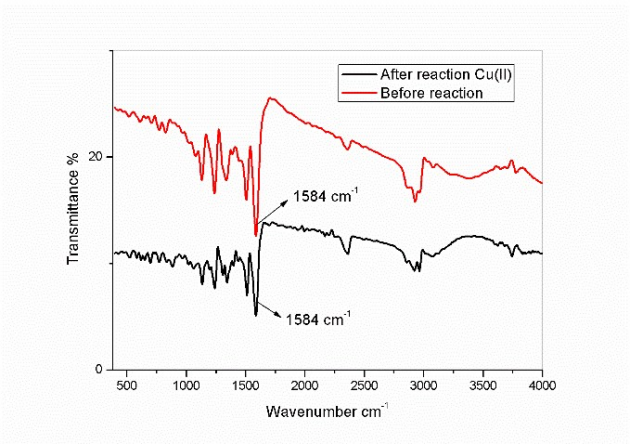
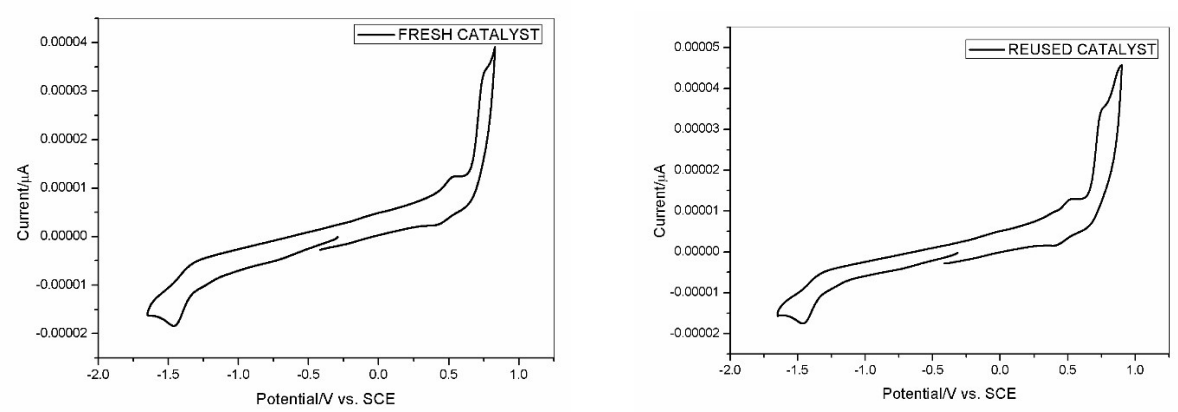


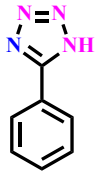
Fig. S6 FTIR plot of Cu(II) Complex **1** before and after use of it in propargylamines reaction



(a) **(b)**

Fig. S7 CV plot of (a) Cu(II) Complex 1 of the fresh and (b) used catalysts in propargylamines reaction

Spectral data and spectra of isolated 5-substituted 1 *H*-tetrazoles products



***5-phenyl-1H-tetrazole (3a)*:** Off-white solid, m.p. 214-216°C, eluent: ethylacetate/ pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 8.06 (d, 2H, J= 8 Hz), 7.58-7.56 (m, 3H); ^{13}C NMR (DMSO-d6): δ 155.87, 131.86, 130.07, 127.56 and 124.79.

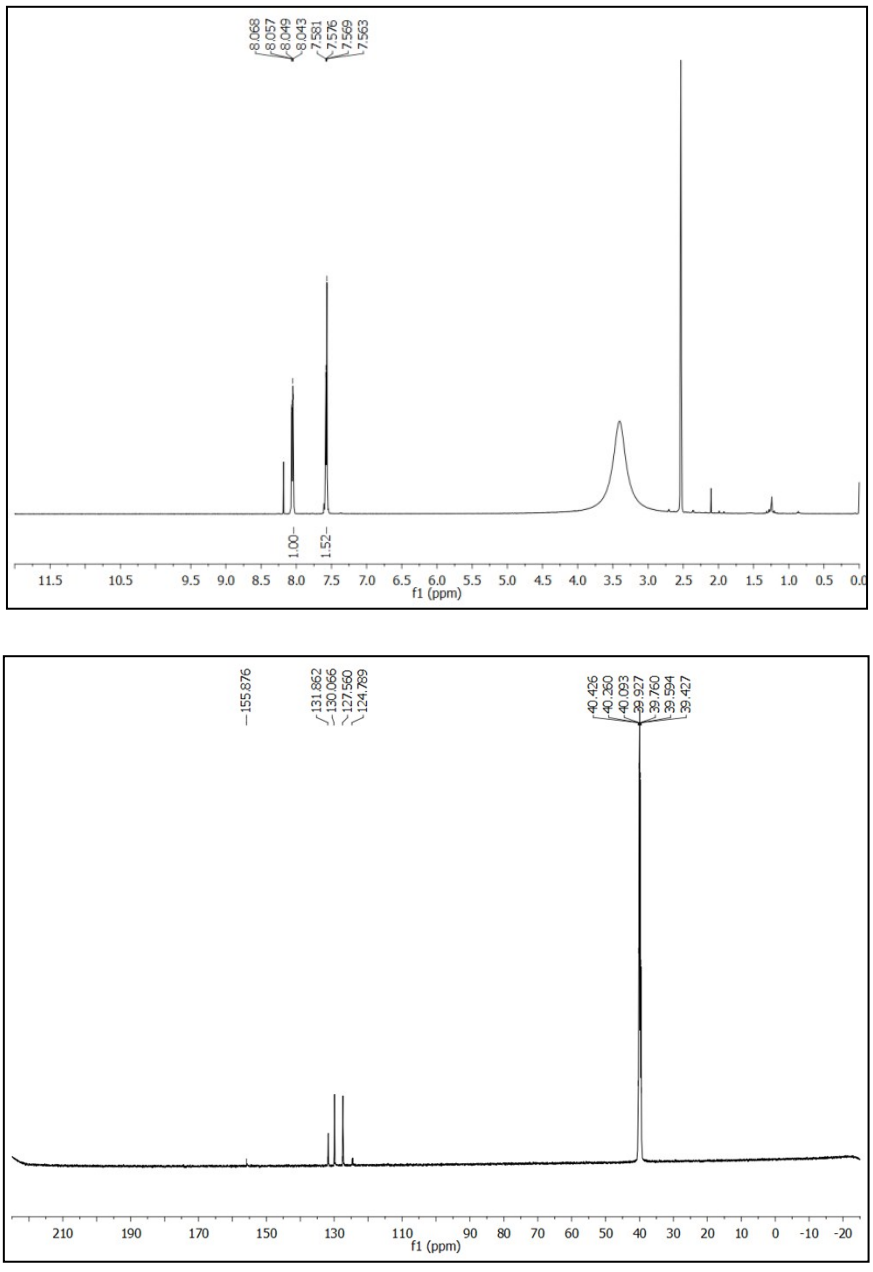
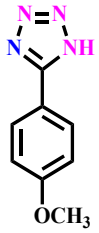


Fig. S8 ^{1}H NMR and ^{13}C of 5-phenyl-1H-tetrazole



***5-(4-methoxyphenyl)-1H-tetrazole (3b)*:** Off-white solid, m.p. 230-232°C, eluent: ethylacetate/pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 7.99 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8 Hz, 2H), 3.86 (s, 3H).

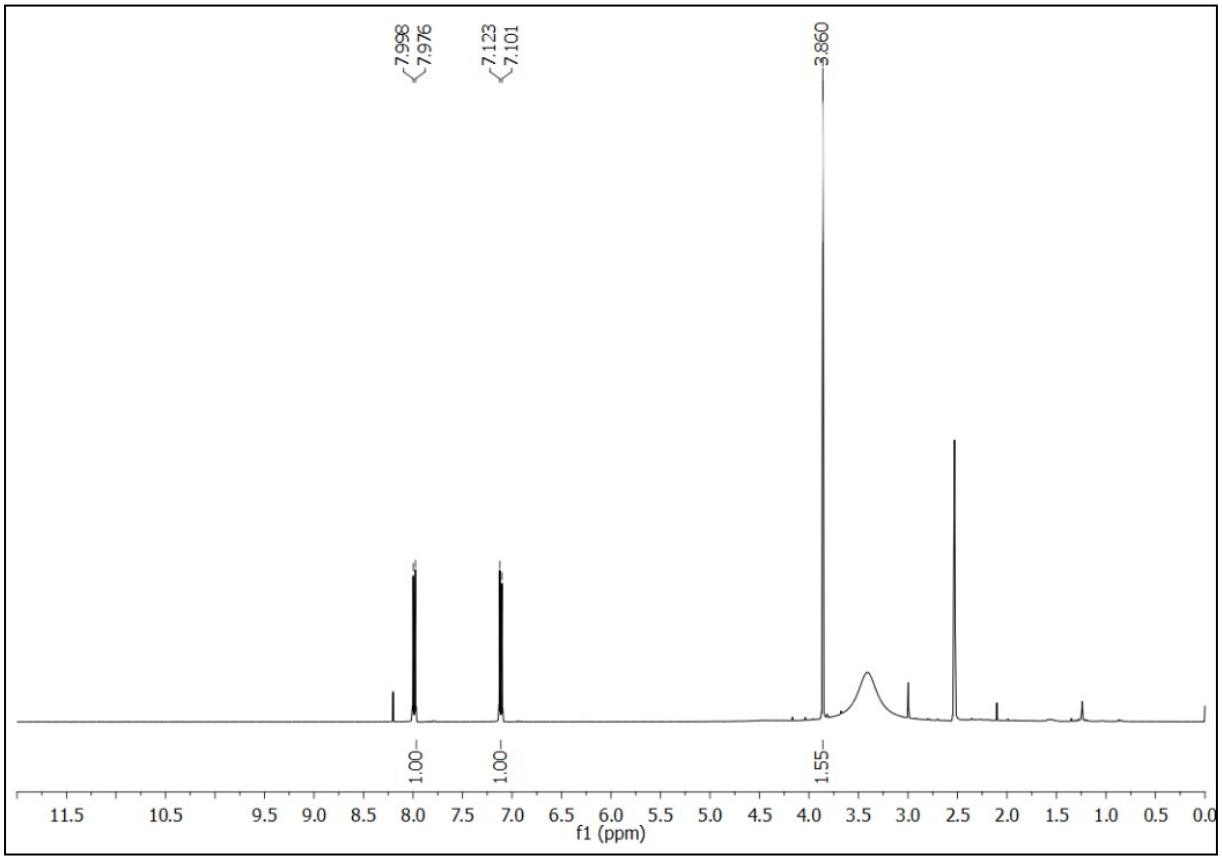
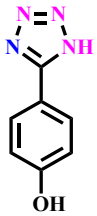


Fig. S9 ^{1}*H NMR of 5-(4-methoxyphenyl)-1H-tetrazole*



5-(4-hydroxyhenyl)-1H-tetrazole **(3c):** Off-white solid, yield: 94%, m.p. 218-220°C, eluent: ethylacetate/ pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 9.87 (br s, 1H), 7.83 (d, 2H, J = 12 Hz), 6.88 (d, 2H, J = 8 Hz).

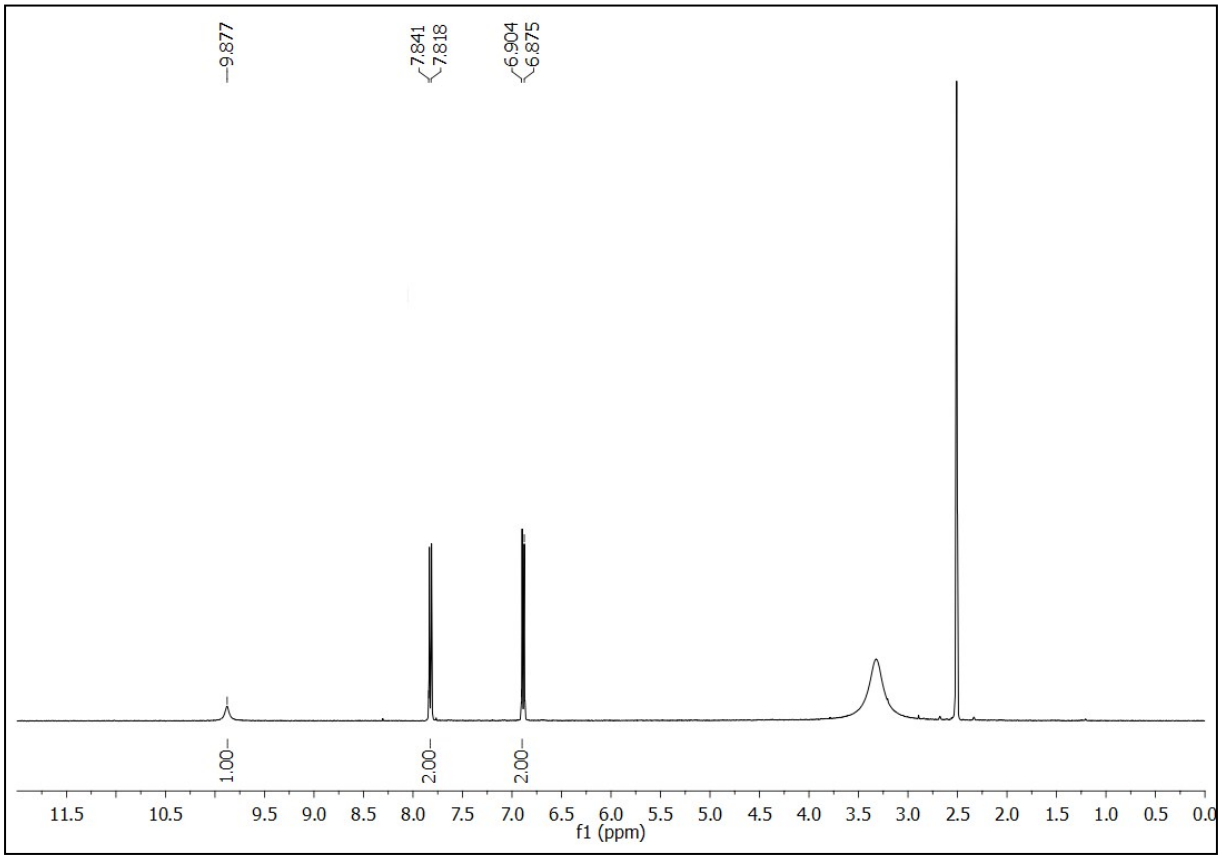
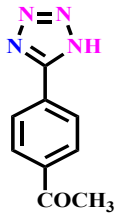


Fig. S10 ^{1}H NMR of 5-(4-hydroxyhenyl)-1H-tetrazole



5-(4-acetyl)-1H-tetrazole **(3d):** White solid, m.p. 218-220°C, eluent: ethylacetate/pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 8.22 (d, 2H, J = 8 Hz), 8.11 (d, 2H, J = 8 Hz), 2.65 (s, 3H).

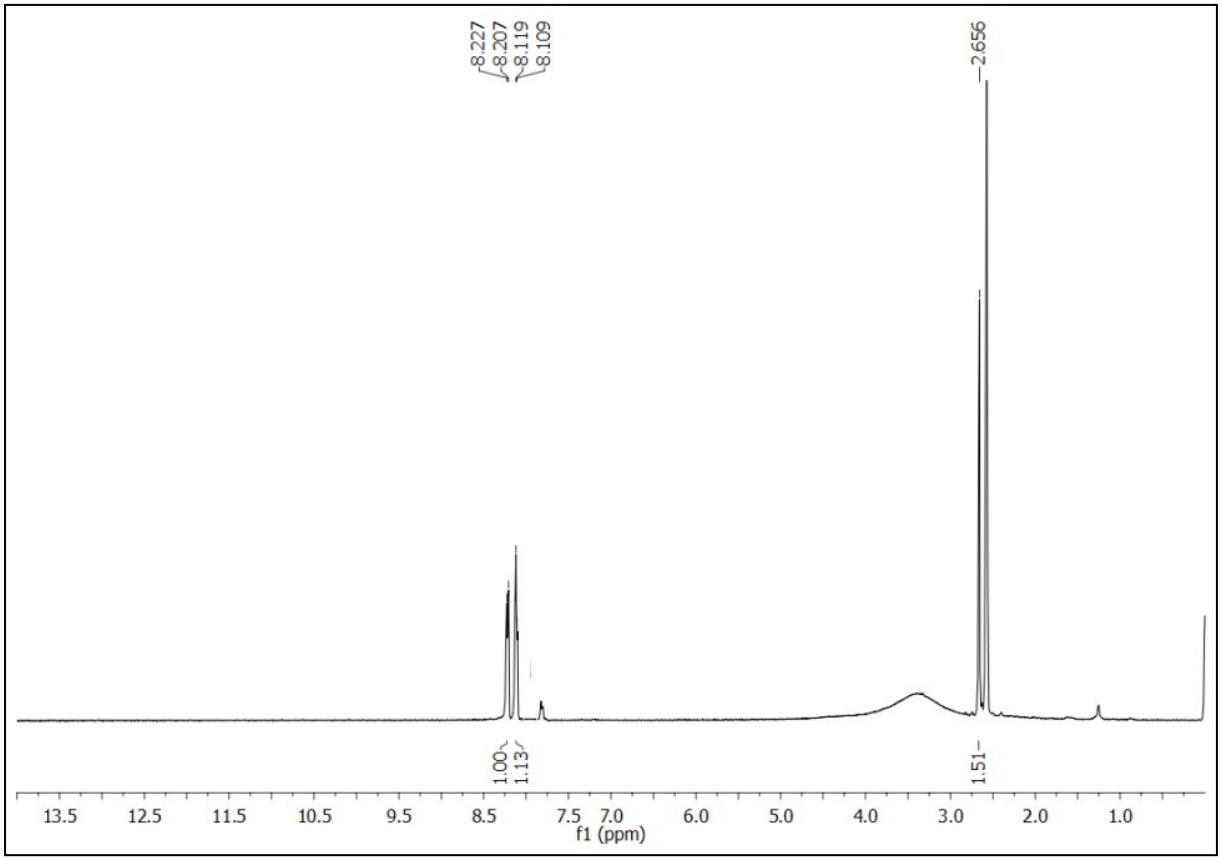
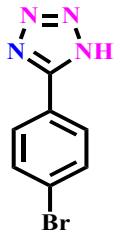


Fig. S11 ^{1}H NMR of 5-(4-acetyl)-1H-tetrazole



5-(4-bromohenyl)-1H-tetrazole **(3e):** White solid, m.p. 264-266°C, eluent: ethylacetate/ pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 7.96 (d, 2H, J = 8 Hz), 7.69 (d, 2H, J = 8 Hz).

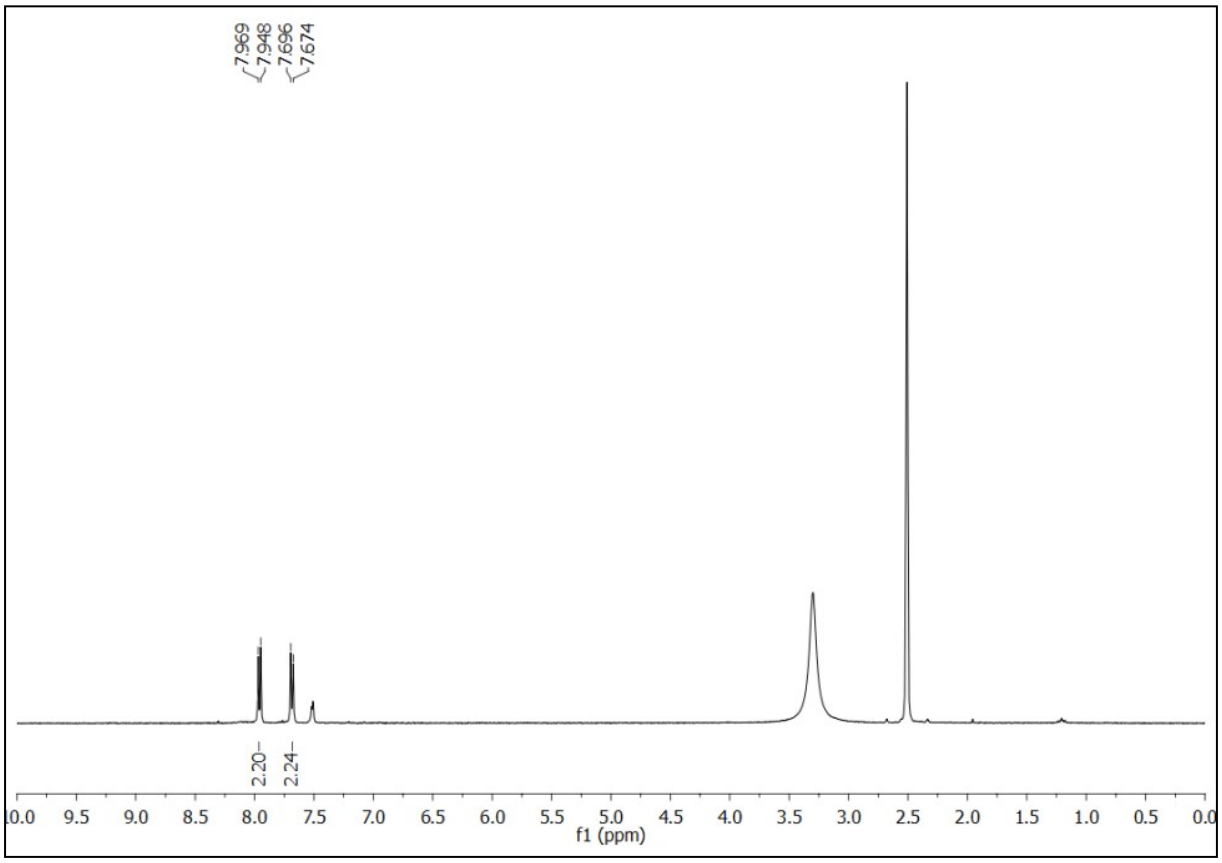
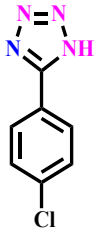


Fig. S12 ^{1}H NMR of 5-(4-bromohenyl)-1H-tetrazole



5-(4-chlorohenyl)-1H-tetrazole **(3f):** White solid, m.p = 262-264^{o}C, eluent: ethylacetate/pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 8.06 (d, 2H, J = 8 Hz), 7.56 (d, 2H, J = 8 Hz).

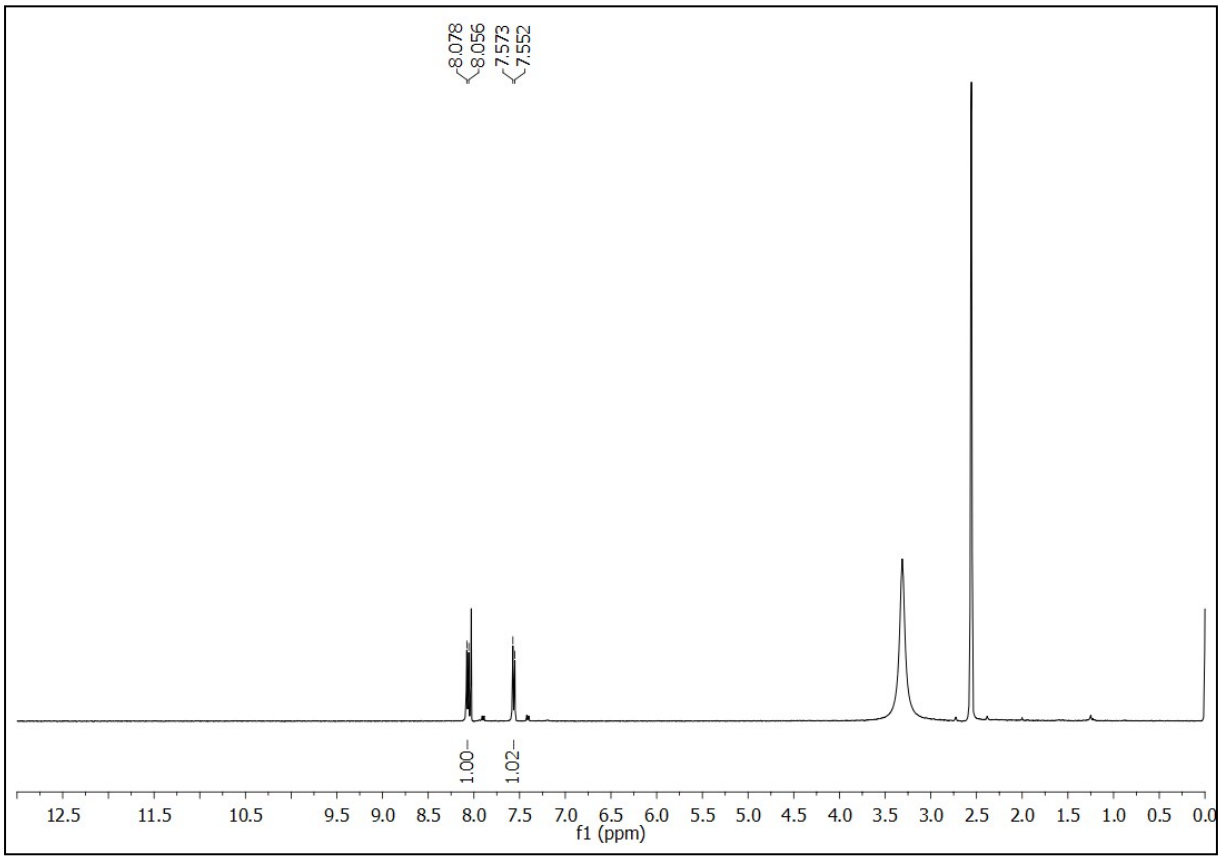
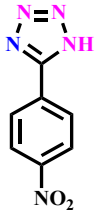


Fig. S13 ^{1}H NMR of *5-(4-chlorohenyl)-1H-tetrazole*



5-(4-nitrophenyl)-1H-tetrazole **(3g):** Light yellow solid, m.p. 218-220°C, eluent: ethylacetate/pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 7.99 (d, 2H, J = 8 Hz), 7.11 (d, 2H, J= 8 Hz).

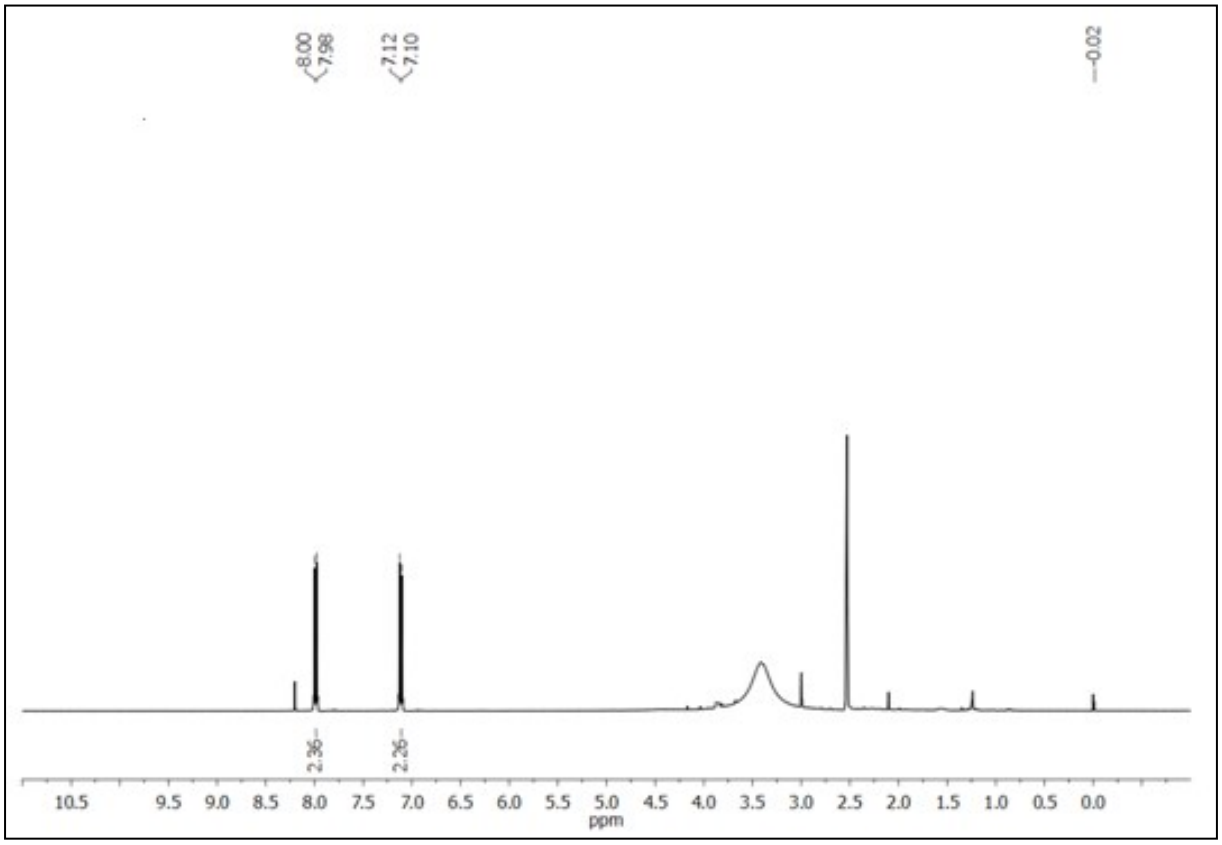
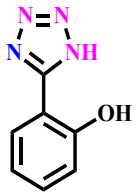


Fig. S14 ^{1}H NMR of 5-(4-nitrophenyl)-1H-tetrazole



5-(2-hydroxyhenyl)-1H-tetrazole **(3h):** White solid, m.p. 218-220^{o}C, eluent: ethylacetate/ pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 10.78 (br s, 1H), 8.05 (d, 1H, J =6.8 Hz), 7.37 (d, 1H, J = 8 Hz), 7.07 (d, 1H, J = 8 Hz), 6.99-6.96 (m, 1H). ^{13}C NMR (DMSO-d6): δ 155.89, 152.31, 133.21, 129.39, 120.57, 116.67, 111.01.

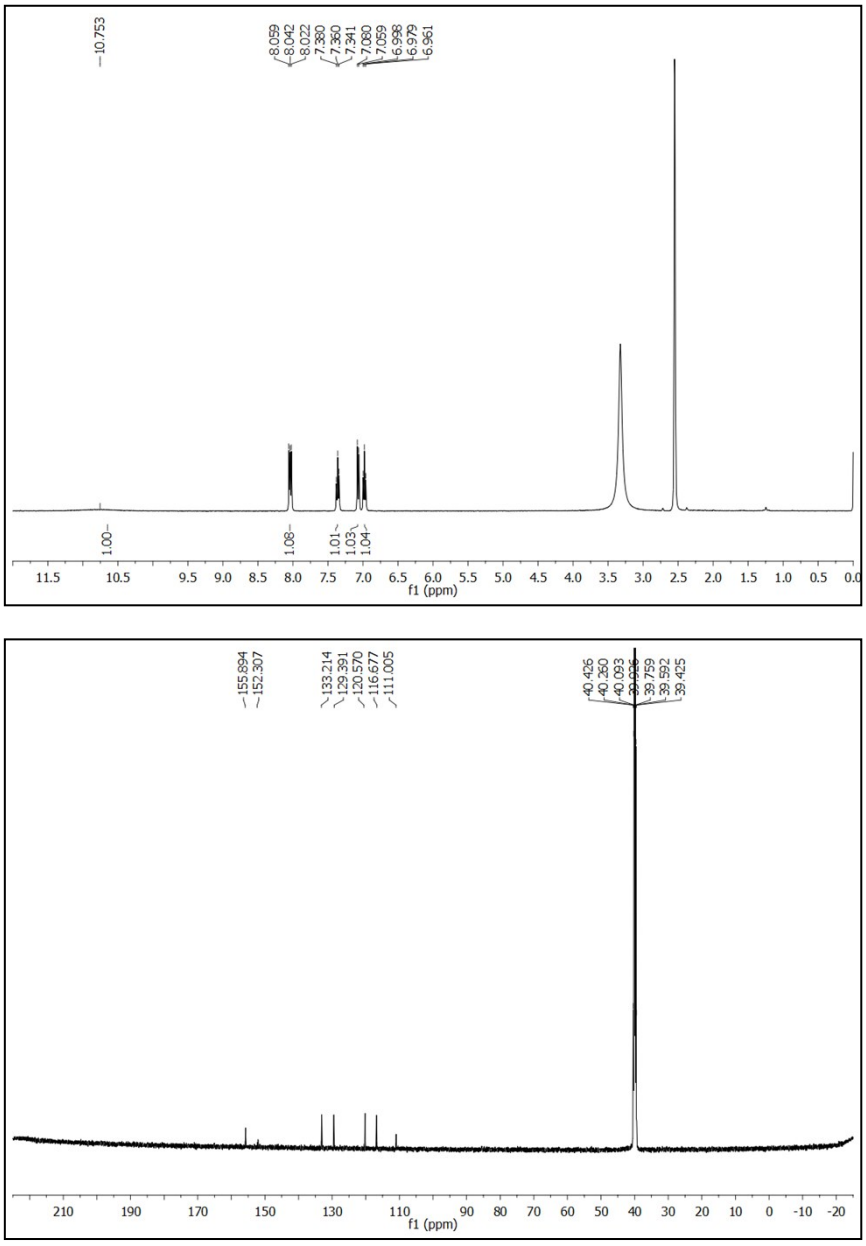
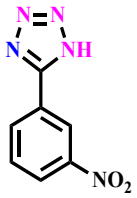


Fig. S15 ^{1}H NMR and ^{13}C NMR of 5-(2-hydroxyhenyl)-1H-tetrazole



5-(3-nitrophenyl)-1H-tetrazole **(3i):** Light yellow solid, m.p. 154-156^{o}C, eluent: ethylacetate/ pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 8.90 (s, 1H), 8.50 (d, 1H, J = 12 Hz), 8.38 (d, 1H, J = 8 Hz), 7.87-7.83 (m, 1H).

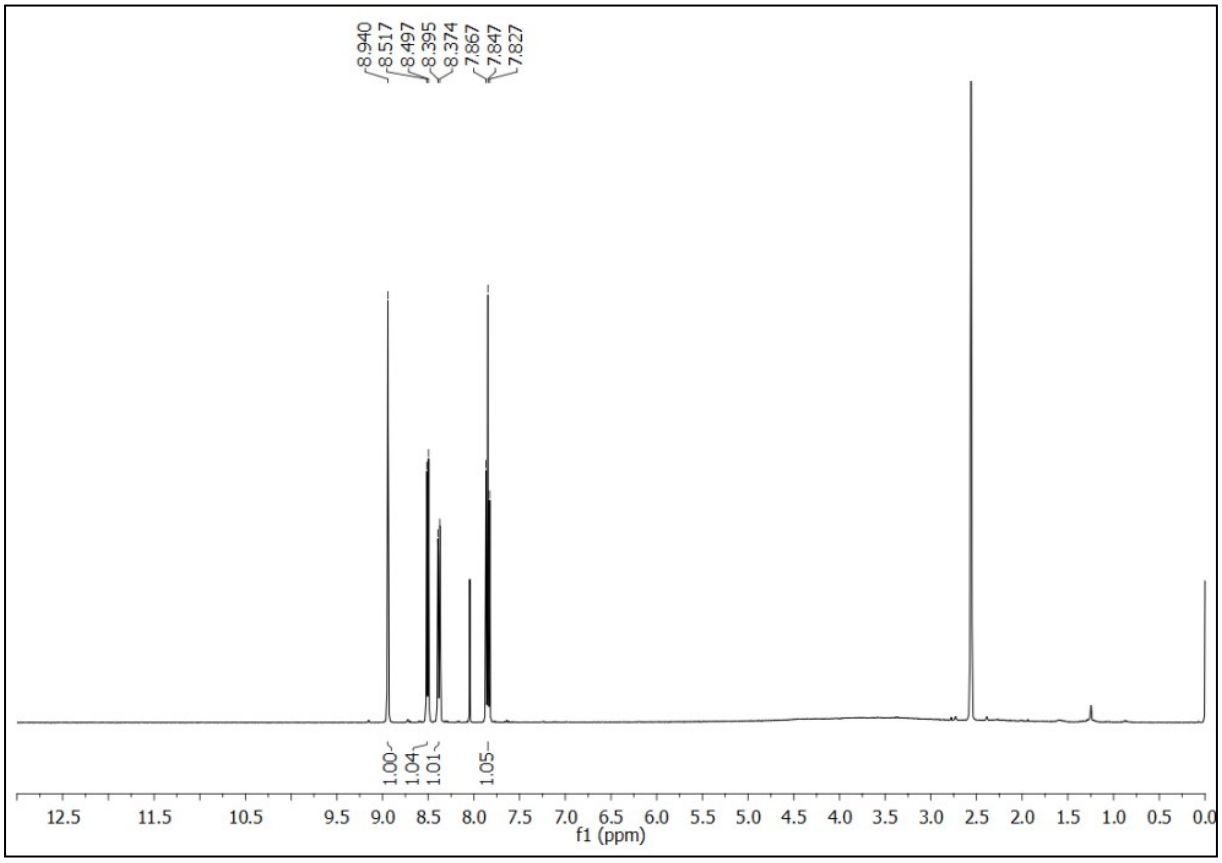
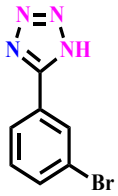


Fig. S16 ^{1}H NMR of 5-(3-nitrophenyl)-1H-tetrazole



5-(3-bromohenyl)-1H-tetrazole **(3j):** Off-white solid, m.p. 154-156^{o}C, eluent: ethylacetate/pet ether (8:2). ^{1}H NMR (DMSO-d6): δ (ppm) 8.01 (s, 1H), 7.95-7.90 (m, 1H, J = 8 Hz), 7.64 (d, 1H, J = 8 Hz), 7.49 (d, 1H, J =4 Hz).

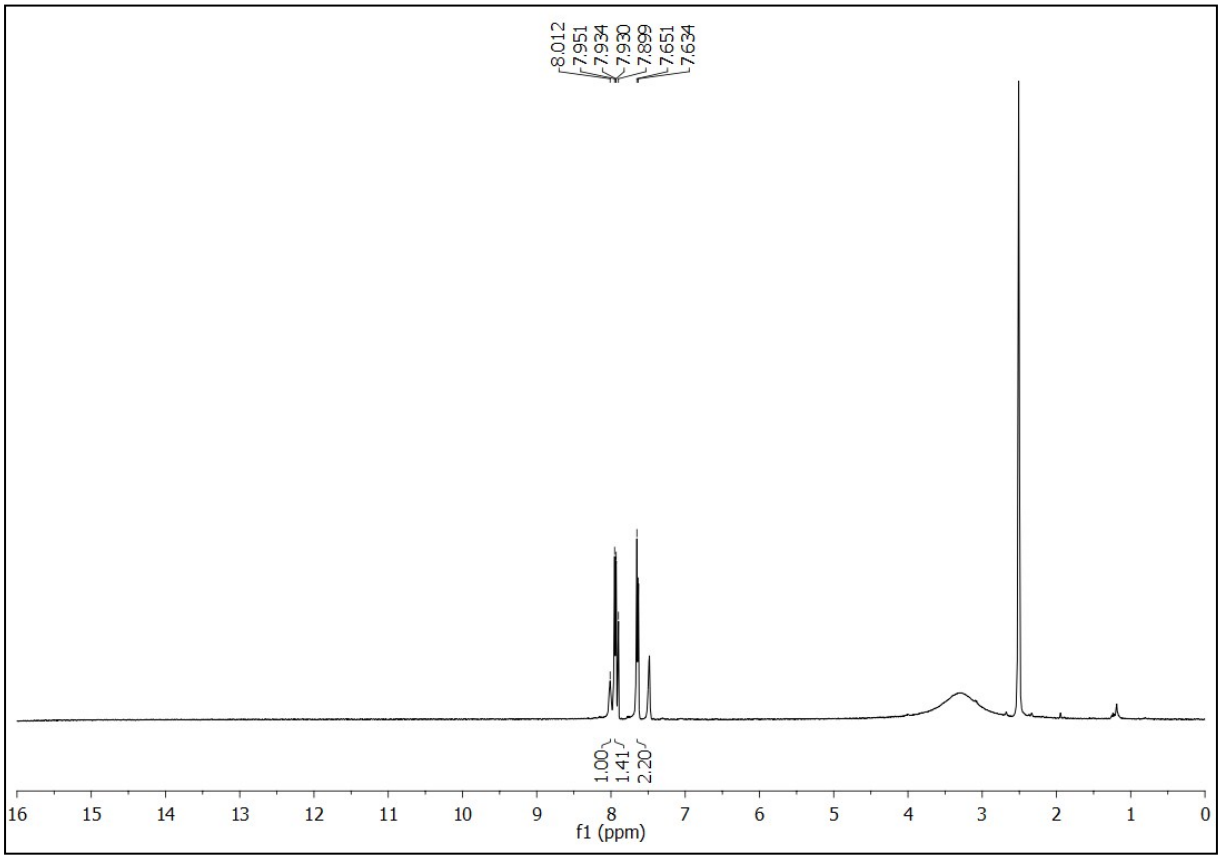
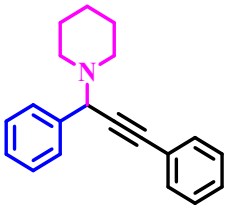


Fig. S17 ^{1}H NMR of 5-(3-bromohenyl)-1H-tetrazole

Spectral data and spectra of isolated A^3 coupling products



1-(1,3-diphenylprop-2-ynyl)piperidine (4a)

Yellow oily liquid; FT-IR (cm^{-1}): 3045, 2981, 1611, 1520, 1432, 1320, 1162; ^1H NMR (400 MHz, $CDCl_3$, ppm δ): 7.70-7.69 (m, 2H), 7.59-7.57 (m, 2H), 7.43-7.33 (m, 6H), 4.86 (s, 1H), 2.63 (t, 4H), 1.70-1.61 (m, 4H), 1.51-1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 138.17, 132.29, 129.69, 128.29, 127.63, 123.26, 88.01, 85.96, 62.11, 50.41, 26.30, 24.24.

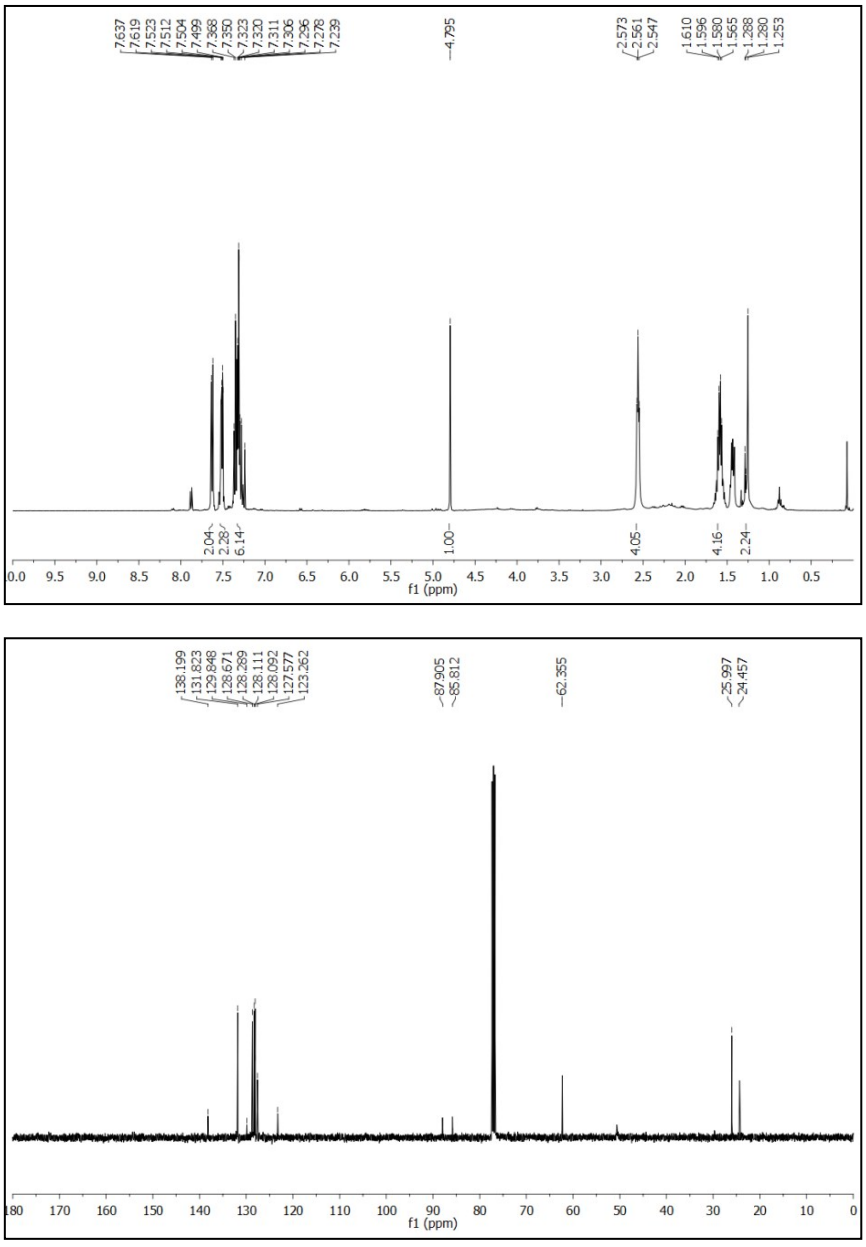
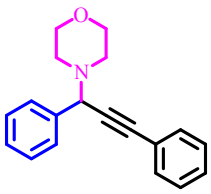


Fig. S18 ^1H and ^{13}C NMR of 1-(1, 3-diphenylprop-2-ynyl)piperidine



4-(1, 3-diphenylprop-2-ynyl)morpholine (4b)

Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm δ): 7.58-7.62 (m, 2H), 7.49-7.52 (m, 2H), 7.19-7.41 (m, 6H), 4.79 (s, 1H), 3.62- 3.85 (m, 4H), 2.61 (t, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 137.82, 131.84, 129.90, 128.65, 128.27, 123.15, 88.54, 84.94, 67.15, 61.97, 49.87.

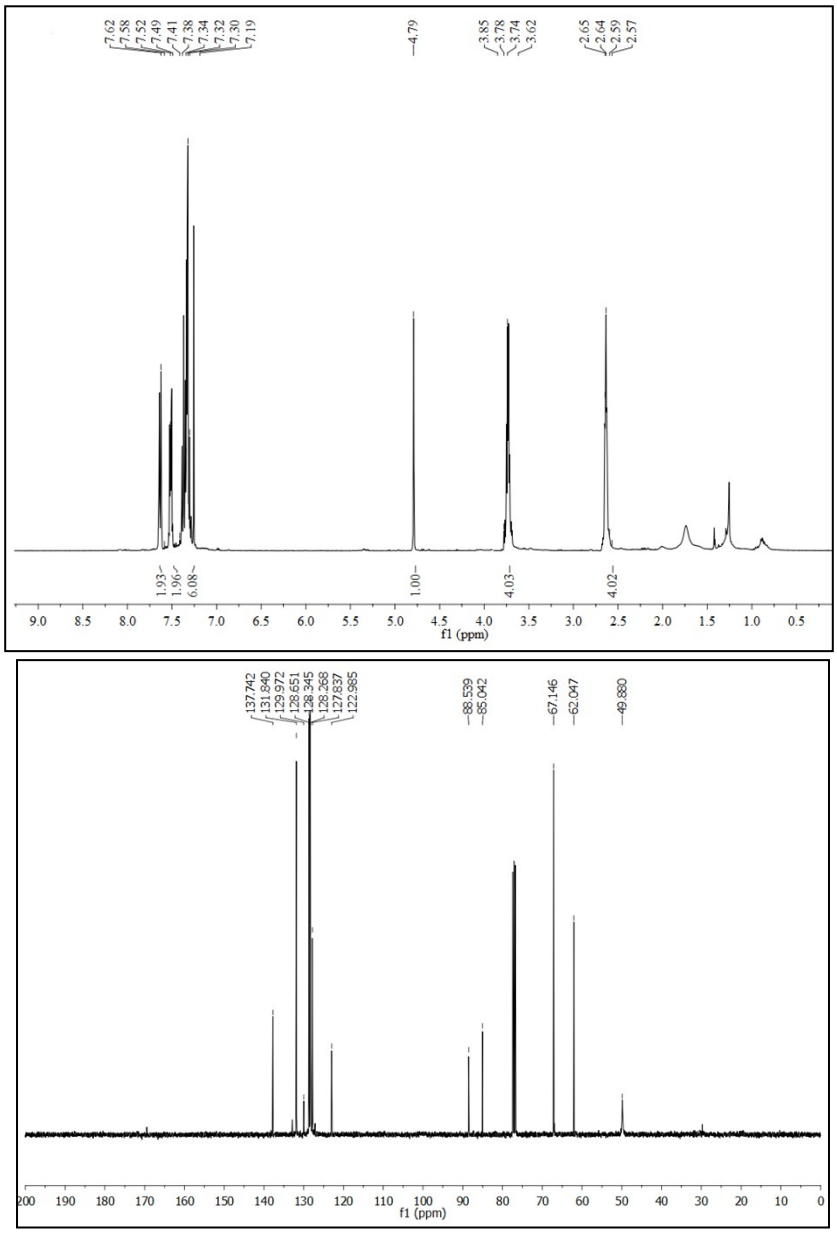
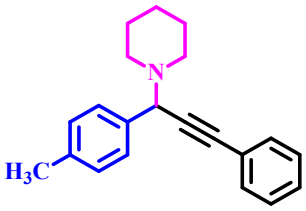
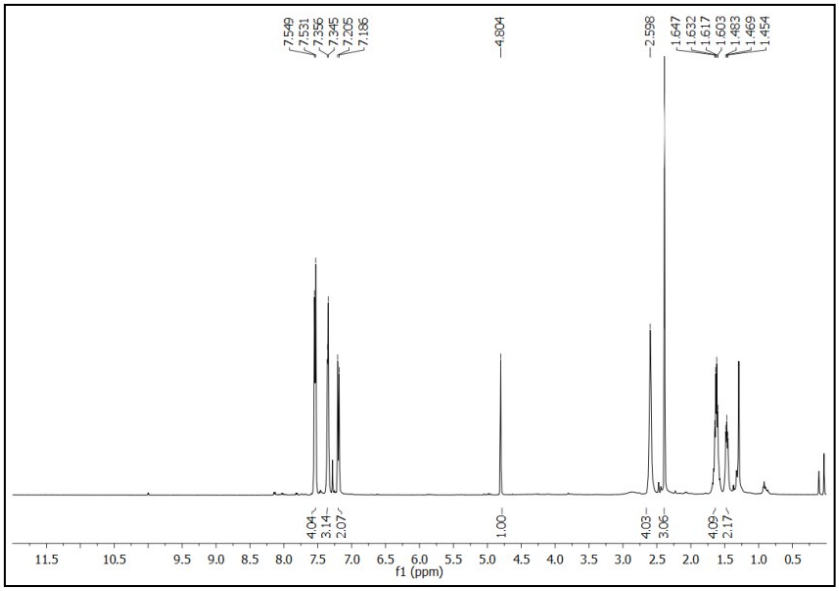


Fig. S19 ^{1}H and ^{13}C NMR of 4-(1, 3-diphenylprop-2-ynyl)morpholine



1-(3-phenyl-1-p-tolylprop-2-ynyl)piperidine (4c)

Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.53-7.46 (m, 4H), 7.28-7.22 (m, 3H), 7.09-7.07 (m, 2H), 4.69 (s, 1H), 2.61-2.55 (m, 4H), 2.27 (s, 3H), 1.58-1.50 (m, 4H), 1.35-1.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 137.22, 135.48, 131.876, 128.84, 128.61, 128.33, 128.08, 123.47, 87.70, 86.38, 62.16, 50.72, 26.18, 24.50, 21.31



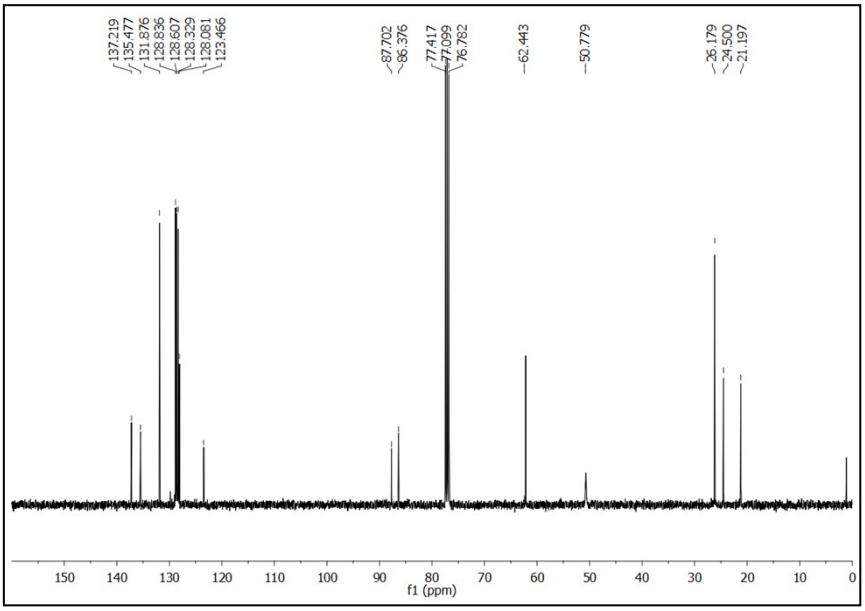
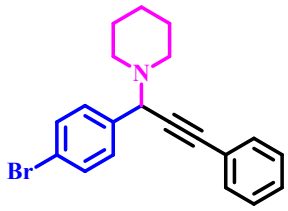


Fig. S20 ^{1}H and ^{13}C NMR of *1-(3-phenyl-1-p-tolylprop-2-ynyl)piperidine*



1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) piperidine(4d)

Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.80-7.59 (m, 1H), 7.55-7.46 (m, 1H), 7.40-7.22 (m, 5H), 7.18-7.17 (m, 2H), 4.67 (s, 1H), 2.46-2.39 (m, 4H), 1.63-1.52 (m, 4H), 1.32-1.28 (m, 2H); ^{13}C NMR (75 MHz, CDCl3, ppm, δ): 145..45, 137.82, 131.96, 131.82, 131.17, 130.74, 130.22, 129.03, 128.33, 123.08, 121.36, 88.15, 85.22, 61.78, 50.58, 26.00, 24.31.

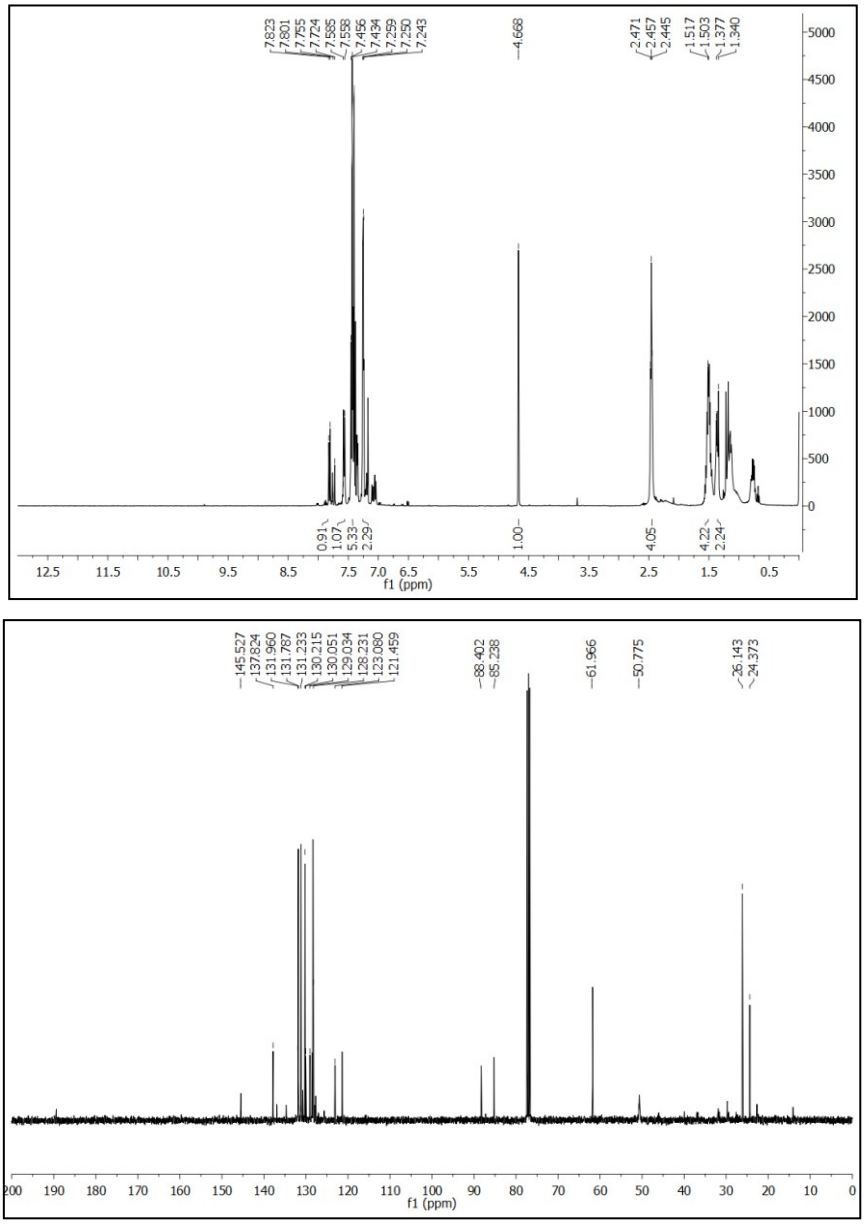
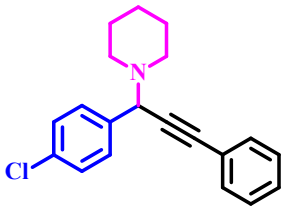


Fig. S21 ^{1}H and ^{13}C NMR of *1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) piperidine*



1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (4e)

Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.47-7.51 (m, 2H), 7.41-7.51 (m, 2H), 7.16-7.25 (m, 4H), 7.08 (m, 1H), 4.70 (s, 1H), 2.45-2.53 (m, 4H), 1.47-1.57 (m, 4H), 1.32-1.34 (m, 2H); ^{13}C NMR (75 MHz, CDCl3, ppm, δ): 139.47, 137.19, 133.14, 131.82, 129.86, 128.69, 128.33, 128.08, 127.74, 123.07, 88.01, 85.11, 61.25, 50.46, 26.10, 23.67.

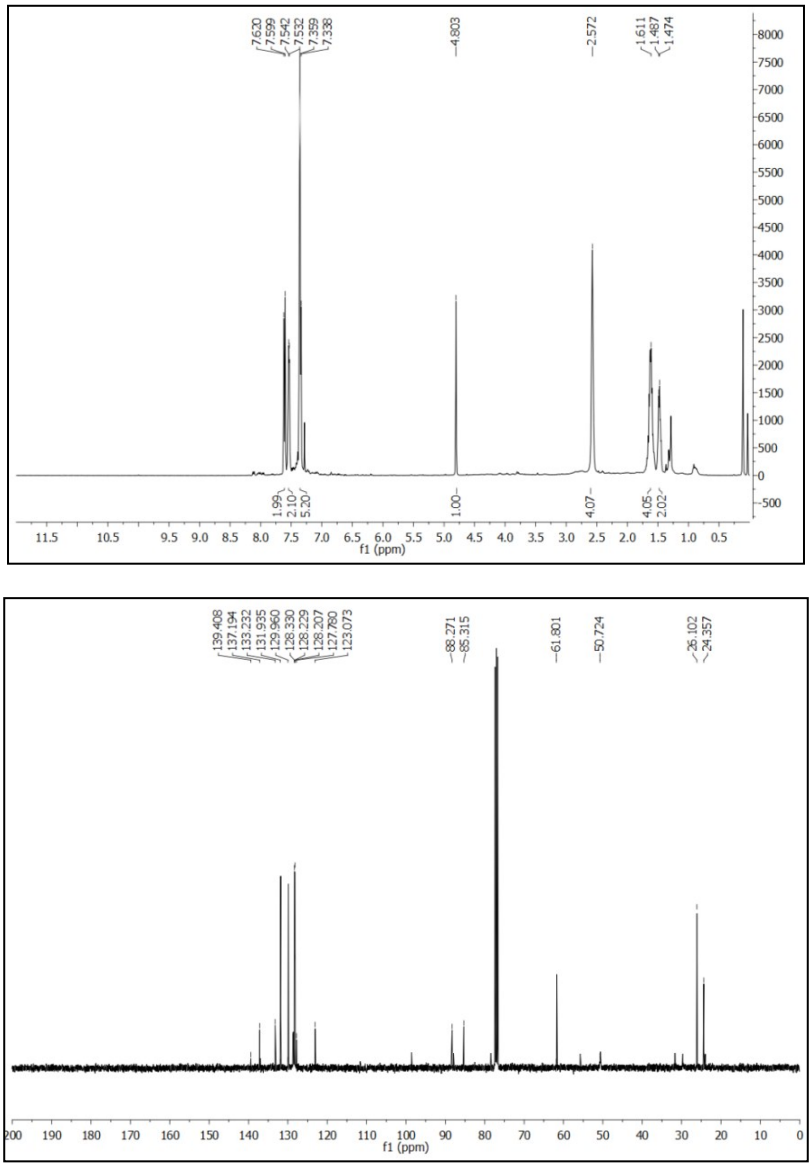
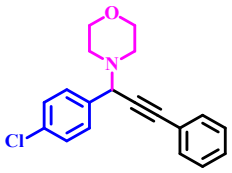
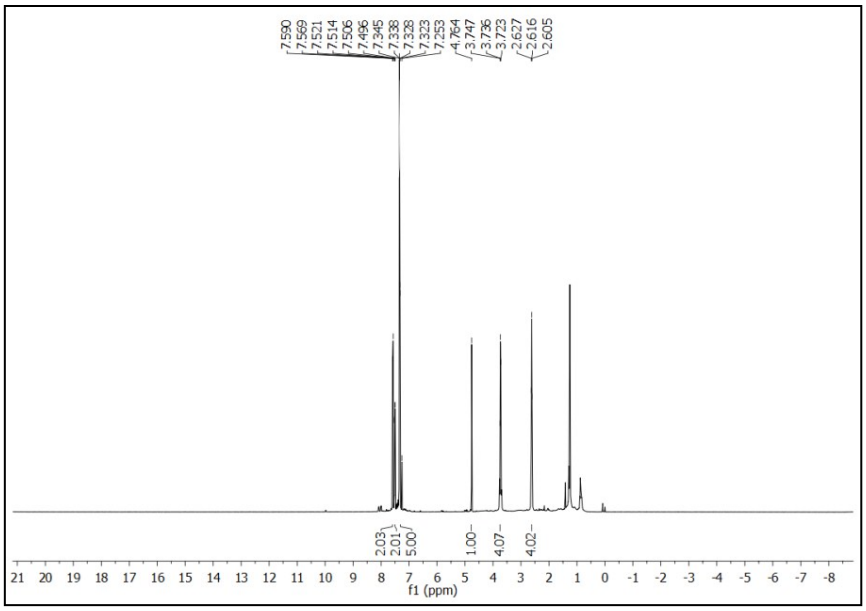


Fig. S22 ^{1}H and ^{13}C NMR of *1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine*



1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) morpholine (4f)

Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm δ): 7.59-7.57 (m, 2H), 7.50-7.34 (m, 2H), 7.30-7.18 (m, 5H), 4.76 (s, 1H), 3.76- 3.68 (m, 4H), 2.71-2.60 (m, 4H).



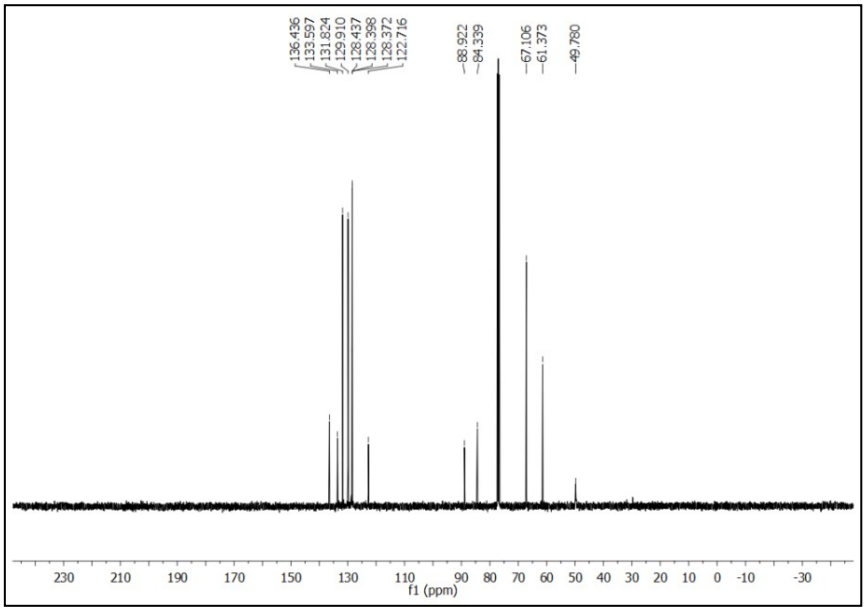
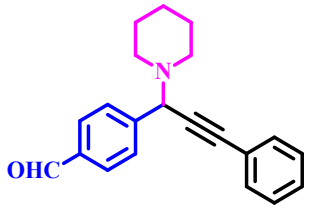


Fig. S23 ^{1}H and ^{13}C NMR of *1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine*



4-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)benzaldehyde (4g)

Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 10.00 (s, 1H), 8.00-7.42 (m, 5H), 7.41-7.29 (m, 3H), 4.79 (s, 1H), 2.56-2.55 (m, 4H), 1.60-1.51 (m, 6H).

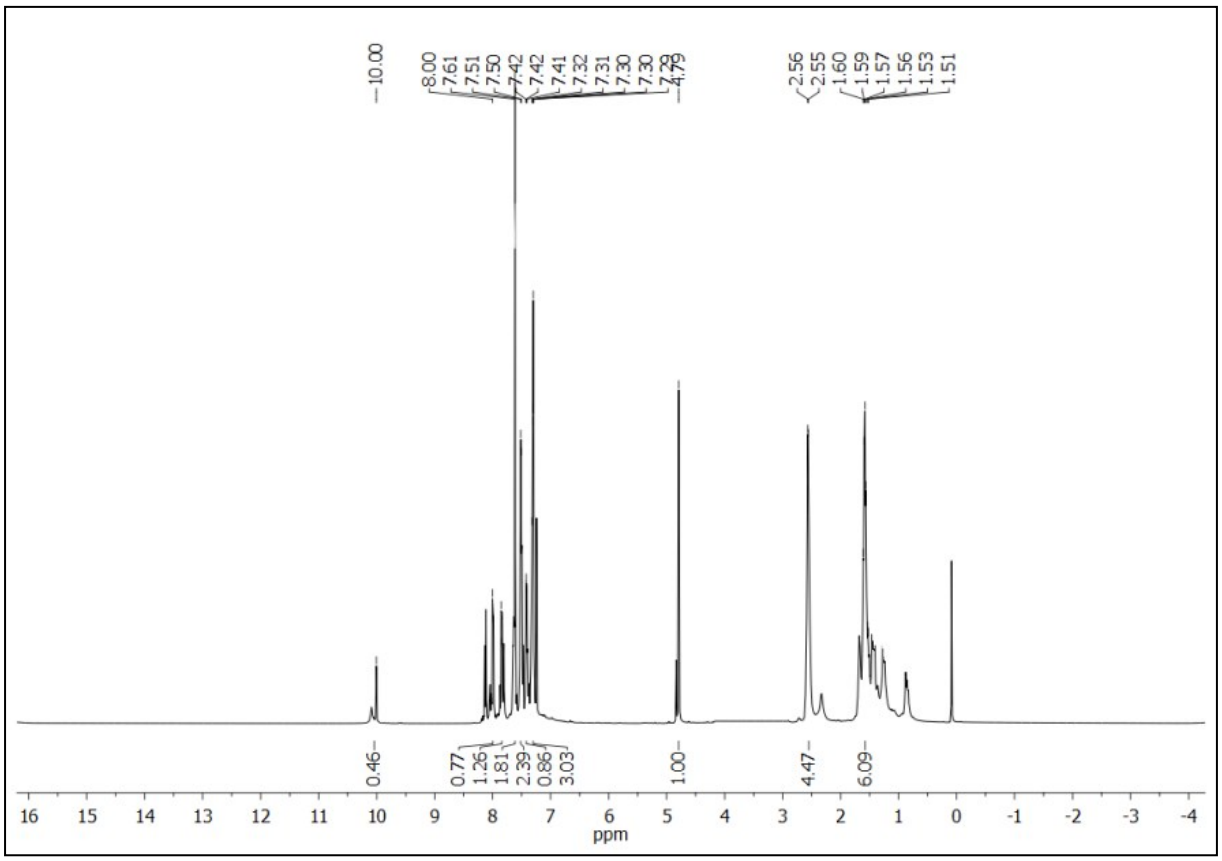
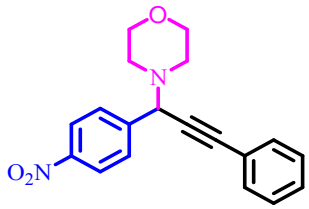


Fig. S24 ^{1}H NMR of *4-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)benzaldehyde*



4-(1-(4-nitrophenyl)-3-phenylprop-2-yn-1-yl)morpholine (4h)

Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 8.21-8.17 (m, 2H), 7.87-7.85 (m, 2H), 7.54-7.53 (m, 2H), 7.36-7.34 (m, 3H), 4.88 (s,1H), 3.71-3.64 (m, 4H), 2.66-2.61 (m, 4H).

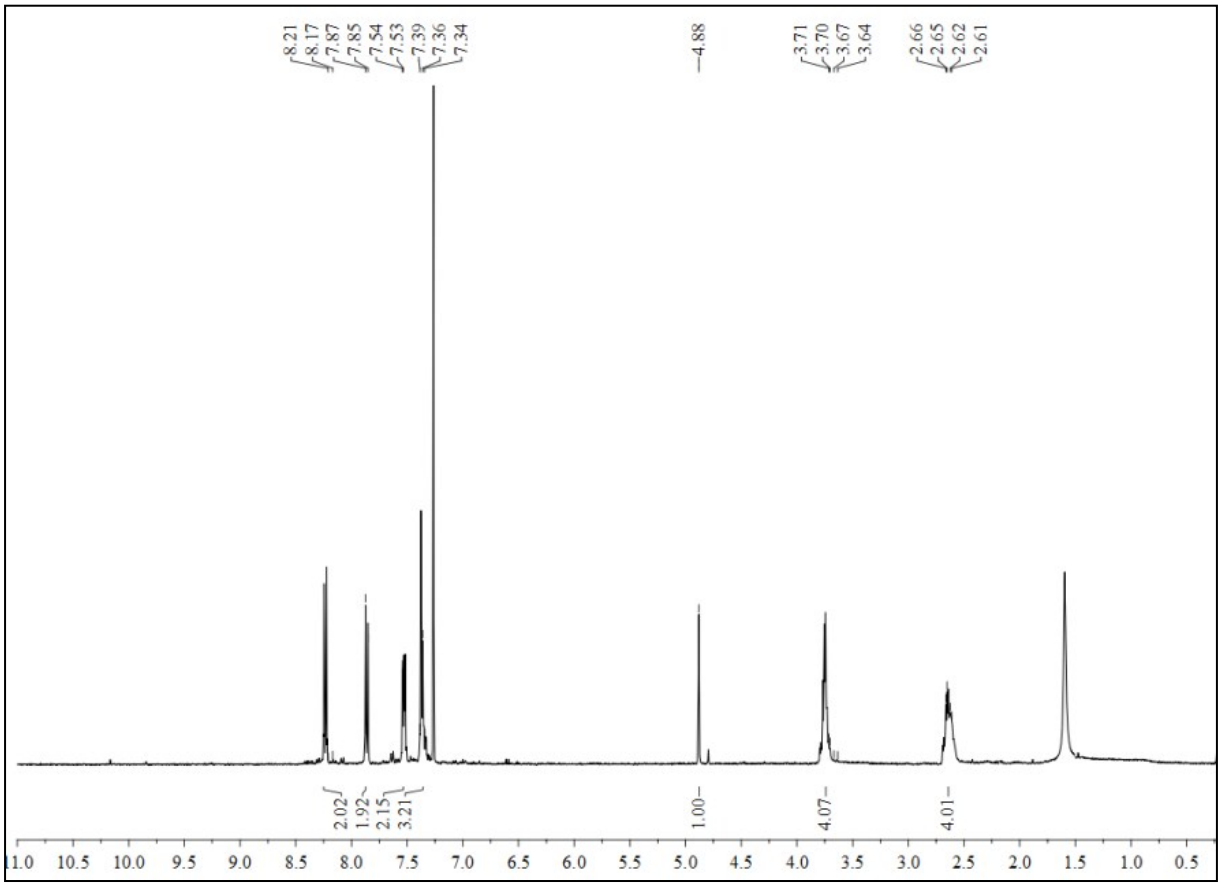
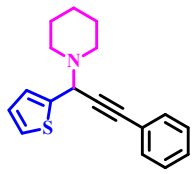


Fig.S25 *^{1}H NMR of 4-(1-(4-nitrophenyl)-3-phenylprop-2-yn-1-yl)morpholine*



4-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)piperdiene (4i)

Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm δ): 7.54-7.51 (m, 2H), 7.34-7.32 (m, 3H), 7.27-7.26 (m, 1H), 7.23-7.22 (m, 1H), 6.98-6.96 (m, 1H), 4.99 (s, 1H), 2.64-2.60 (m, 4H), 1.65-1.61 (m, 4H), 1.48-1.45(m, 2H).

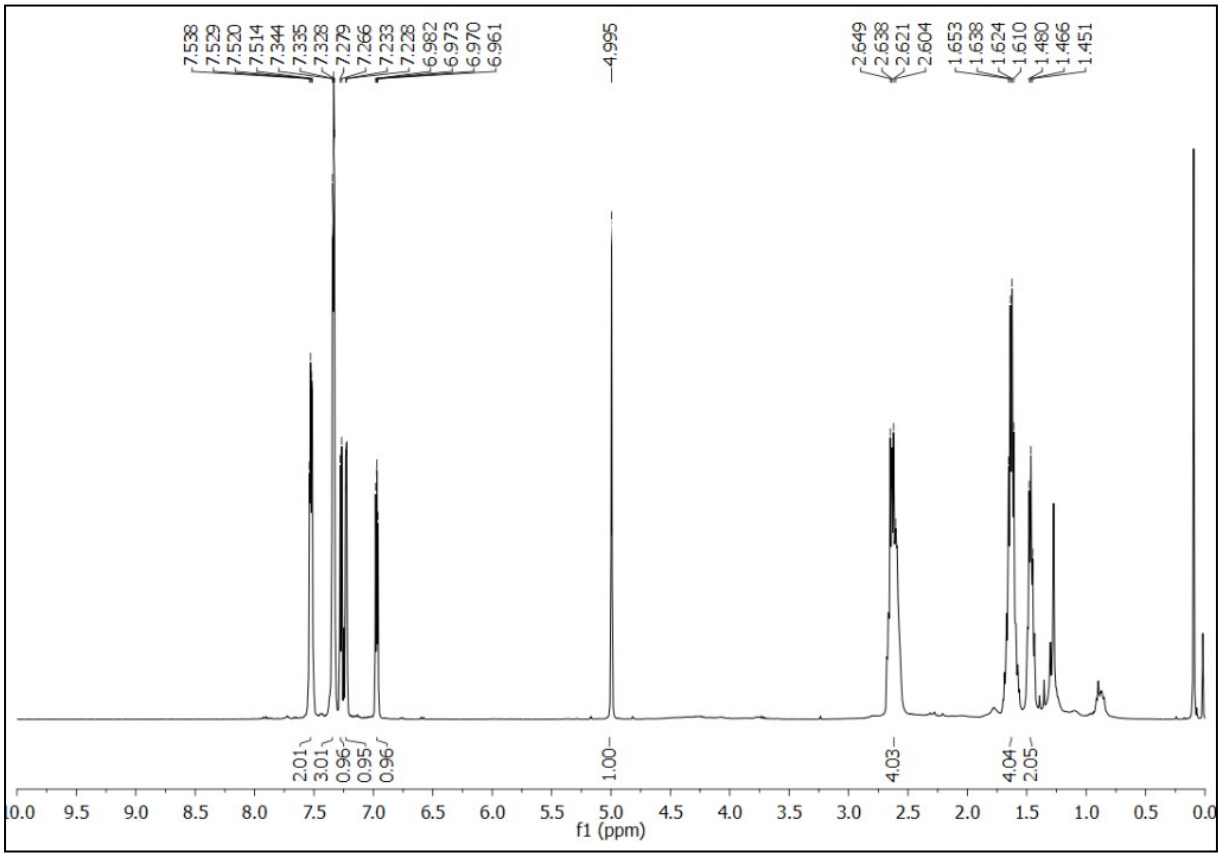
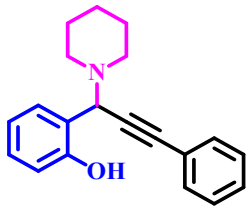


Fig. S26 ^{1}H NMR of *4-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)piperdiene*



2-(3-phenyl-1(piperdin-1-yl)prop-2yn-1-yl)phenol (4j)

^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.60-7.57 (m,3H), 7.40-7.39 (m, 3H), 7.28-7.24 (m, 1H), 6.89-6.88 (m,2H), 5.13 (s, 1H), 2.78-2.74(m, 2H), 1.72 (m, 5H), 1.46 (m, 1H), 1.33-1.29 (m, 2H).

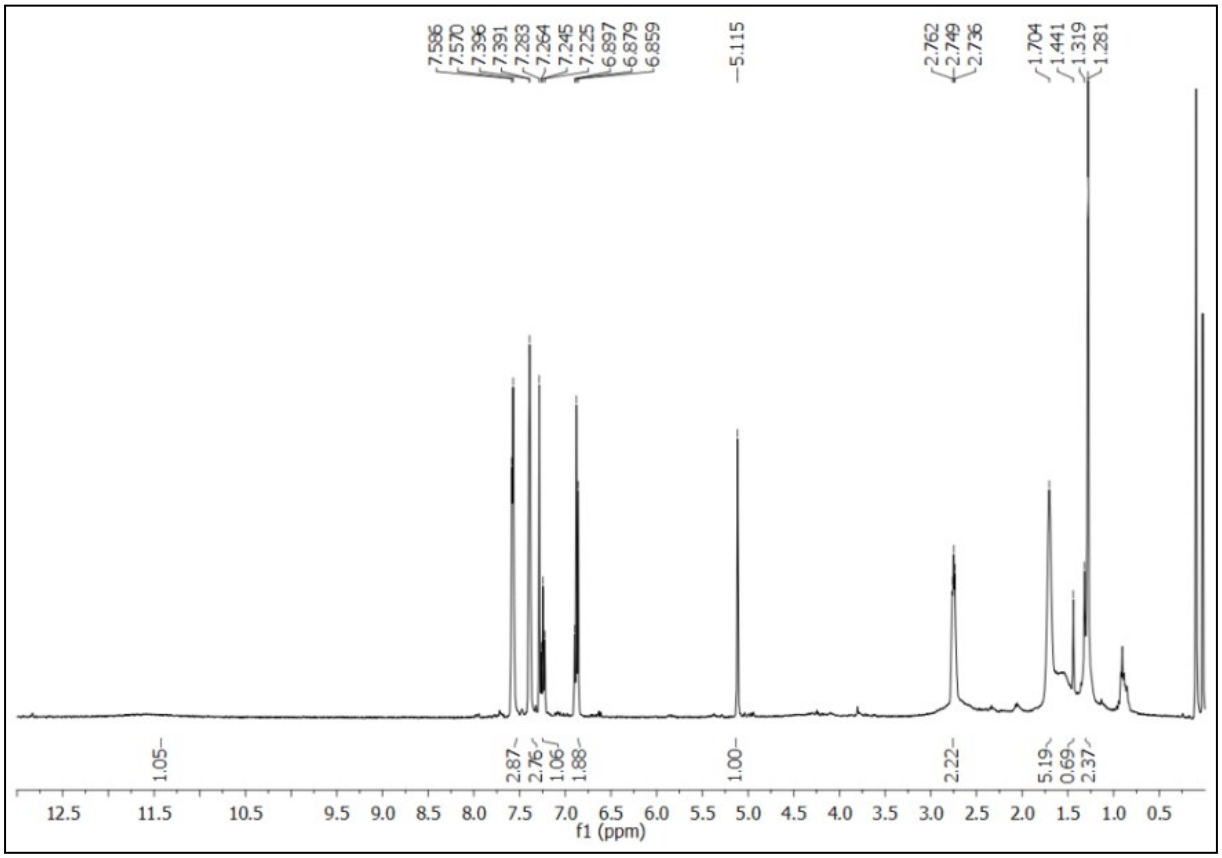
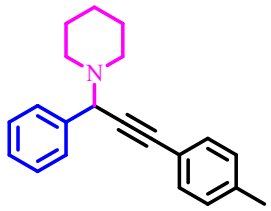


Fig. S27 ^{1}H NMR of *2-(3-phenyl-1(piperdin-1-yl)prop-2yn-1-yl)phenol*



1-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)piperidine (4k)

Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.69-7.67 (m, 2H), 7.46 (br, 2H), 7.45-7.40 (m, 2H), 7.37 (t, 1H), 7.17 (d, 2H), 4.84 (s, 1H), 2.62-2.59 (m, 4H), 2.40 (s, 3H), 1.67-1.61 (m, 4H), 1.49-1.47 (m, 2H).

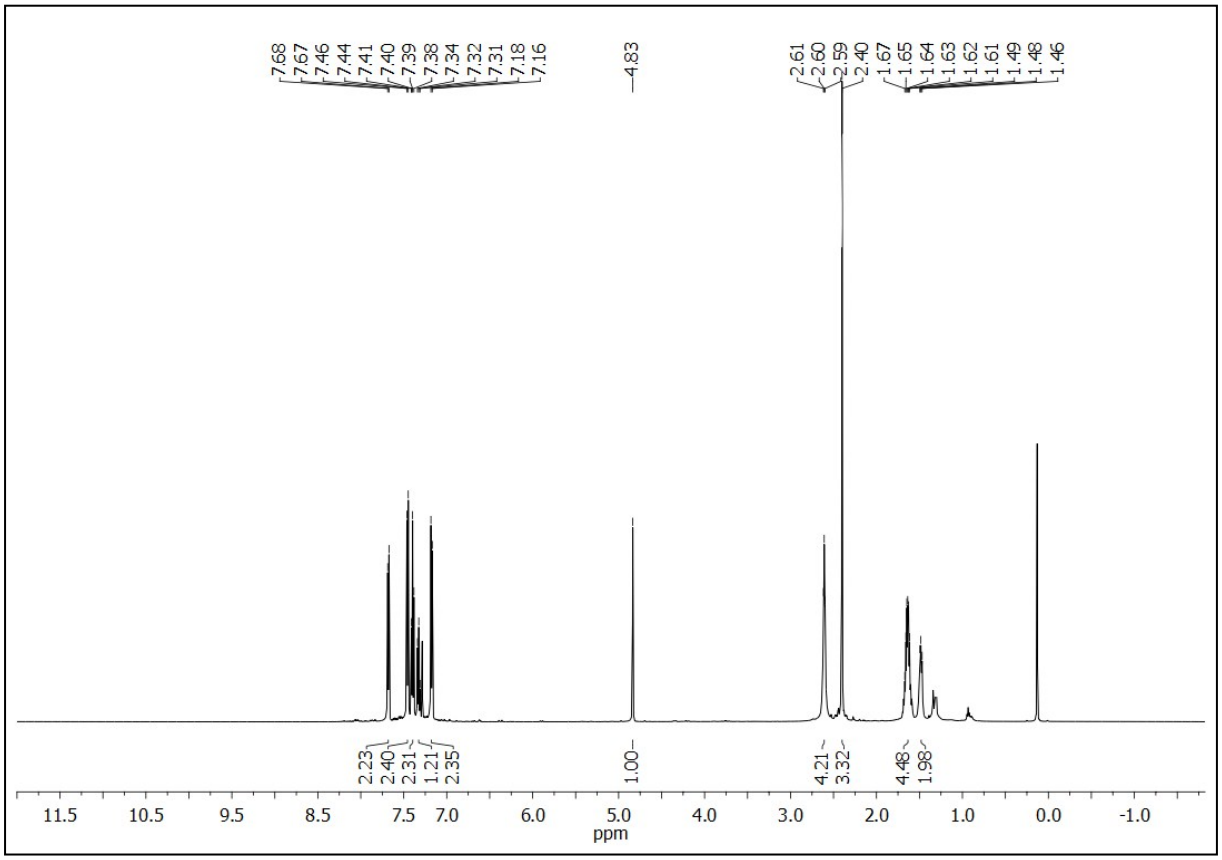
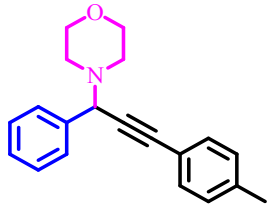


Fig. S28 *^{1}H NMR of1-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)piperidine*



4-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)morpholine (4l)

Yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.71-7.69 (m, 2H), 7.48-7.42 (m, 2H), 7.40-7.36 (m, 2H), 7.35-7.33(m, 1H), 7.19-7.18 (m, 2H), 4.84 (s, 1H), 3.82-3.75 (m, 4H), 2.69 (s, 3H), 2.41 (m, 4H).

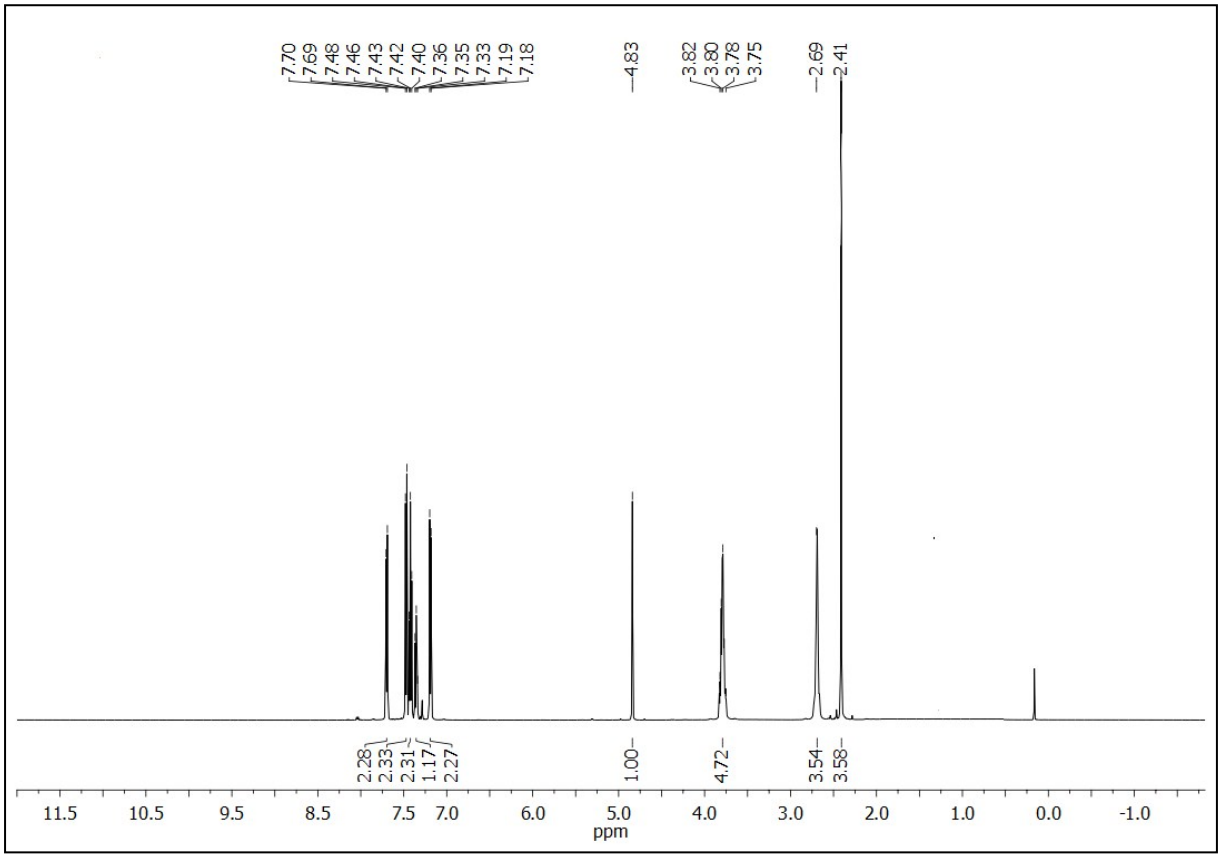
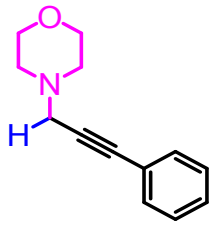


Fig.S29 *^{1}H NMR of 4-(1-phenyl-3-(p-tolyl)prop-2-yn-1-yl)morpholine*



4-(3-phenylprop-2-yn-1-yl)morpholine(4m)

^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): δ 7.43-7.40 (m, 2H), 7.29-7.27 (t, 3H), 3.77 -3.75 (m, 4H), 3.50 (s, 2H), 2.64 - 2.62 (m, 4H).

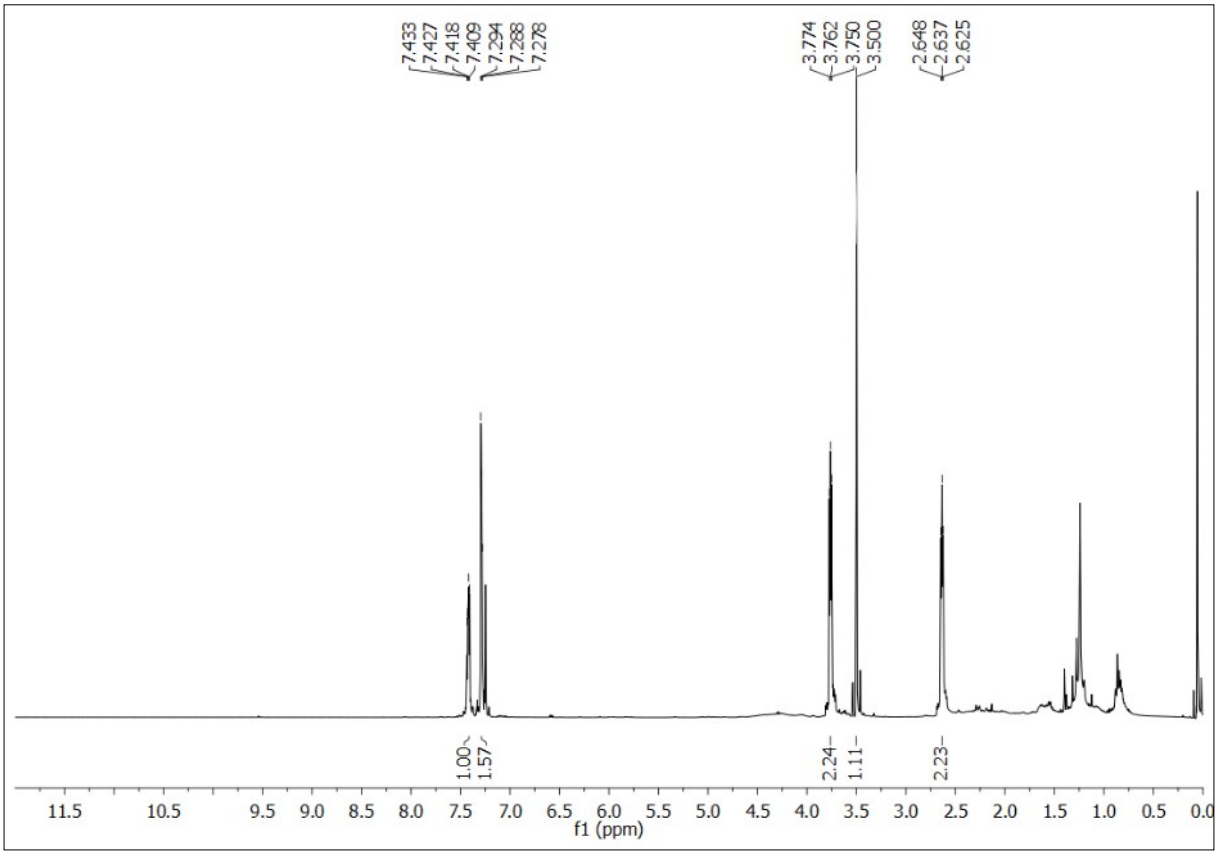


Fig. S 30 *^{1}HNMR of 4-(3-phenylprop-2-yn-1-yl)morpholine*

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