

Supporting Information
for
Effect of the *ortho*-hydroxy group of salicylaldehyde in the
A³ coupling reaction: A metal-catalyst-free synthesis of
propargylamine

Sujit Ghosh, Kinkar Biswas, Suchandra Bhattacharya, Pranab Ghosh and Basudeb Basu*

Address: Department of Chemistry, University of North Bengal, Darjeeling 734013, India

Email: Basudeb Basu - basu_nbu@hotmail.com

*Corresponding author

Experimental procedure, characterization data and scan copies of
¹H and ¹³C NMR spectra (3a–t)

Table of contents

I.	General information	S2
II.	General procedure of the A³ coupling reaction	S2
III.	Characterization data of different propargylamine derivatives (3a–t)	S2–S7
IV.	References	S7
V.	Scanned spectra (¹H and ¹³C NMR) of propargylamine derivatives (3a–t)	S8–S47

I. General information

o-Vanillin, phenylacetylene, *p*-tolylacetylene, *o*-bromophenylacetylene, *p*-bromophenylacetylene and 4-benzylpiperidine were purchased from Sigma–Aldrich and used directly as obtained. Salicylaldehyde was purchased from SD Fine Chemical Limited, India. Morpholine, piperidine and pyrrolidine were purchased from Lancaster and used after distillation. All the products were purified by column chromatography on 60–120 mesh silica gels (SRL, India). For TLC, Merck plates coated with silica gel 60, F₂₅₄ were used. FTIR spectra were recorded in Perkin Elmer FTIR spectrometer using KBr pellets for solid compounds and under neat condition for liquid compounds. The peak patterns in FTIR spectra were denoted by s (sharp), m (medium), w (weak) and br (broad). The ¹H and ¹³C NMR spectra were recorded at 300 MHz and 75 MHz, respectively on a Bruker AV 300 spectrometer in CDCl₃. Splitting patterns of protons were described as s (singlet), d (doublet), t (triplet), br (broad) and m (multiplet). Chemical shifts (δ) were reported in parts per million (ppm) relative to TMS as internal standard. *J* values (coupling constant) were reported in Hz (Hertz). ¹³C NMR spectra were recorded with complete proton decoupling (CDCl₃: δ 77.0 ppm). High resolution mass spectra (HRMS) were done under ESI (positive mode) in a Micromass Q-TOF Spectrometer at Indian Association for the Cultivation of Science, Kolkata, India or in a Bruker Maxis Spectrometer at National Institute of Pharmaceutical Education and Research, Mohali, India. Melting points were determined by heating the solid sample in a sealed capillary tube taken in concentrated H₂SO₄ bath and are uncorrected.

II. General procedure of the A³ coupling reaction

An equimolar mixture of salicylaldehyde, amine and acetylene (1 mmol of each component) was magnetically stirred (oil bath temp. 80 °C or 90 °C) in a Teflon-capped sealed tube for 4–8 h. After completion of the reaction (disappearance of the alkyne spot on TLC), the reaction mixture was cooled to room temperature, CH₂Cl₂ (2 mL) was added and adsorbed with silica gel. After evaporation of the solvent, the resulting dry mass was placed on a silica gel column and elution with light petroleum–ethyl acetate (in varying proportion) afforded the desired propargylamine.

III. Characterization data for different propargylamine derivatives (3a–t)

2-(1-Morpholino-3-phenylprop-2-ynyl)phenol, ¹ (3a): Yellow solid (mp 94–96 °C); FTIR (KBr): 3414 (m, br), 3044 (s), 2970 (s), 2838 (s), 2369 (w), 1586 (s), 1487 (s), 1236 (s), 1115 (s), 755 (s), 692 (s) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 2.78 (s, 4H, 2 x OCH₂), 3.80 (s, 4H, 2 x NCH₂), 5.10 (s, 1H, CH), 6.86–6.91 (m, 2H, ArH), 7.22–7.27 (m, 1H, ArH), 7.35–7.37 (m, 3H, ArH), 7.53–7.58 (m, 3H, ArH), 10.76 (s, br, 1H, OH); ¹³C NMR (CDCl₃, 75 MHz): δ 47.8 (NCH₂), 59.6 (CH), 65.7 (OCH₂), 80.5 (acetylenic carbon), 89.3 (acetylenic carbon), 115.4, 118.3, 119.5, 121.2, 127.3, 127.61, 127.63, 128.6, 130.8, 155.9 (aromatic carbons).

2-(1-Morpholino-3-*p*-tolylprop-2-ynyl)phenol (3b): Yellow solid (mp 88–90 °C); FTIR (KBr): 3415 (m, br), 2915 (s), 2846 (s), 2361 (w), 1582 (s), 1454 (s), 1278 (s), 1114 (s), 812 (s), 754 (s), 560 (s) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 2.38 (s, 3H, CH₃), 2.78 (s, 4H, 2 x OCH₂), 3.80 (s, 4H, 2 x NCH₂), 5.08 (s, 1H, CH), 6.85–6.97 (m, 2H, ArH), 7.15–7.26 (m,

3H, ArH), 7.42–7.52 (m, 2H, ArH), 7.56–7.64 (m, 1H, ArH), 10.80 (s, br, 1H, OH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.5 (CH_3), 48.5 (NCH_2), 60.8 (CH), 66.9 (OCH_2), 80.8 (acetylenic carbon), 90.6 (acetylenic carbon), 116.5, 119.2, 119.4, 120.7, 128.8, 129.2, 129.7, 131.8, 139.0, 157.0 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{20}\text{H}_{21}\text{NO}_2\text{Na}$) 330.1470, found 330.1466.

2-(3-(2-Bromophenyl)-1-morpholinoprop-2-ynyl)phenol (3c): Off-white solid (mp 102–104 °C); FTIR (KBr): 3416 (m, br), 2942 (s), 2849 (s), 2364 (w), 1584 (s), 1470 (s), 1242 (s), 1114 (s), 756 (s), 574 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 2.84 (s, 4H, 2 x OCH_2), 3.81 (s, 4H, 2 x NCH_2), 5.16 (s, 1H, CH), 6.86–6.92 (m, 2H, ArH), 7.19–7.34 (m, 3H, ArH), 7.57–7.67 (m, 3H, ArH), 10.74 (s, br, 1H, OH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 49.1 (NCH_2), 60.8 (CH), 66.9 (OCH_2), 86.5 (acetylenic carbon), 88.7 (acetylenic carbon), 116.5, 119.5, 120.3, 124.6, 125.6, 127.1, 128.9, 129.8, 129.9, 132.6, 133.8, 157.0 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{19}\text{H}_{18}\text{BrNO}_2\text{Na}$) 394.0419, found 394.0419.

2-(3-(4-Bromophenyl)-1-morpholinoprop-2-ynyl)phenol (3d): Yellow sticky solid; FTIR (KBr): 3408 (w, br), 2842 (m), 2364 (w), 1584 (s), 1471 (s), 1270 (s), 1115 (s), 1073 (s), 999 (s), 844 (s), 746 (s), 584 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 2.74 (s, 4H, 2 x OCH_2), 3.77 (s, 4H, 2 x NCH_2), 5.05 (s, 1H, CH), 6.86–6.91 (m, 2H, ArH), 7.21–7.27 (m, 1H, ArH), 7.37–7.54 (m, 5H, ArH), 10.69 (s, 1H, br, OH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 48.6 (NCH_2), 60.4 (CH), 66.5 (OCH_2), 82.7 (acetylenic carbon), 89.0 (acetylenic carbon), 116.3, 119.2, 120.0, 120.9, 122.8, 128.4, 129.6, 131.4, 133.0, 156.7 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{19}\text{H}_{18}\text{BrNO}_2\text{Na}$) 394.0419, found 394.0421.

2-(3-Phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenol,² (3e): Yellow liquid; FTIR (Neat): 3055 (w), 2936 (s), 2853 (s), 2221 (w), 1692 (s), 1590 (s), 1464 (s), 1277 (s), 1108 (s), 1084 (s), 974 (s), 754 (s), 691 (s), 670 (s), 543 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.52 (s, br, 2H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 1.68 (s, 4H, 2 x NCH_2CH_2), 2.72 (t, $J = 5.1$ Hz, 4H, 2 x NCH_2), 5.09 (s, 1H, CH), 6.83–6.88 (m, 2H, ArH), 7.20–7.25 (m, 1H, ArH), 7.34–7.38 (m, 3H, ArH), 7.52–7.57 (m, 3H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 24.0 ($\text{N}(\text{CH}_2)_2\text{CH}_2$), 26.0 (NCH_2CH_2), 50.0 (NCH_2), 61.1 (CH), 82.4 (acetylenic carbon), 89.8 (acetylenic carbon), 116.4, 119.0, 121.3, 122.7, 128.42, 128.45, 128.6, 129.4, 131.9, 157.7 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd ($\text{C}_{20}\text{H}_{22}\text{NO}$) 292.1701, found 292.1693.

2-(1-(Piperidin-1-yl)-3-*p*-tolylprop-2-ynyl)phenol (3f): Yellow viscous liquid; FTIR (Neat): 3416 (m, br), 3028 (s), 2935 (s), 2854 (s), 2830 (s), 2361 (w), 2217 (w), 1690 (s), 1607 (s), 1586 (s), 1509 (s), 1465 (s), 1278 (s), 1084 (s), 976 (s), 816 (s), 754 (s), 530 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.59 (s, br, 2H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 1.75 (s, 4H, 2 x NCH_2CH_2), 2.44 (s, 3H, CH_3), 2.79 (s, 4H, 2 x NCH_2), 5.15 (s, 1H, CH), 6.91–6.96 (m, 2H, ArH), 7.22–7.32 (m, 3H, ArH), 7.53 (d, $J = 8.07$ Hz, 2H, ArH), 7.64–7.68 (m, 1H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.6 (CH_3), 24.1 ($\text{N}(\text{CH}_2)_2\text{CH}_2$), 26.1 (NCH_2CH_2), 49.8 (NCH_2), 61.2 (CH), 81.7 (acetylenic carbon), 90.0 (acetylenic carbon), 116.4, 119.1, 119.6, 121.5, 128.6, 129.2, 129.4, 131.9, 138.8, 157.8 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd ($\text{C}_{21}\text{H}_{24}\text{NO}$) 306.1858, found 306.1854.

2-(3-(2-Bromophenyl)-1-(piperidin-1-yl)prop-2-ynyl)phenol (3g): Pale yellow liquid; FTIR (Neat): 3054 (s), 2936 (s), 2862 (s), 2223 (w), 1690 (s), 1592 (s), 1466 (s), 1243 (s), 1156 (s), 1083 (s), 973 (s), 751 (s), 675 (s), 560 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.52 (s, br, 2H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 1.68 (s, 4H, 2 x NCH_2CH_2), 2.78 (s, 4H, 2 x NCH_2), 5.15 (s, 1H, CH), 6.84–6.88 (m, 2H, ArH), 7.18–7.34 (m, 3H, ArH), 7.56–7.65 (m, 3H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 24.0 ($\text{N}(\text{CH}_2)_2\text{CH}_2$), 26.0 (NCH_2CH_2), 49.6 (NCH_2), 61.2 (CH), 87.4 (acetylenic carbon), 88.1 (acetylenic carbon), 116.4, 119.1, 121.1, 124.9, 125.6, 127.1, 128.6, 129.4, 129.7, 132.5, 133.8, 157.7 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd ($\text{C}_{20}\text{H}_{21}\text{BrNO}$) 370.0807, found 370.0804.

2-(1-(4-Benzylpiperidin-1-yl)-3-phenylprop-2-ynyl)phenol (3h): Yellow viscous liquid; FTIR (Neat): 3365 (w), 3025 (m), 2923 (s), 2849 (s), 2216 (w), 1693 (s), 1605 (s), 1463 (s), 1375 (s), 1276 (s), 1259 (s), 753 (s), 698 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.27–1.49 (m, 2H), 1.57–1.81 (m, 3H), 2.33–2.40 (m, 1H), 2.54 (d, $J = 6.8$ Hz, 2H), 2.65–2.74 (m, 2H), 3.01–3.04 (m, 1H), 5.10 (s, 1H, CH), 6.82–6.87 (m, 2H, ArH), 7.12 (d, $J = 7$ Hz, 2H, ArH), 7.17–7.28 (m, 4H, ArH), 7.33–7.35 (m, 3H, ArH), 7.49–7.55 (m, 3H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 31.9 (NCH_2CH_2), 32.6 (NCH_2CH_2), 37.7 ($\text{NCH}_2\text{CH}_2\text{CH}$), 43.0 (NCH_2), 46.4 (PhCH_2), 52.0 (NCH_2), 60.7 (CH), 82.2 (acetylenic carbon), 89.9 (acetylenic carbon), 116.4, 119.1, 121.3, 122.6, 126.0, 128.3, 128.4, 128.6, 129.1, 129.4, 131.9, 140.3, 157.6 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd ($\text{C}_{27}\text{H}_{28}\text{NO}$) 382.2171, found 382.2164.

2-(1-(4-Benzylpiperidin-1-yl)-3-*p*-tolylprop-2-ynyl)phenol (3i): Yellow viscous liquid; FTIR (Neat): 3414 (m, br), 2923 (s), 2853 (s), 2219 (w), 1586 (s), 1509 (s), 1463 (s), 1377 (s), 1277 (s), 816 (s), 752 (s), 700 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.32–1.50 (m, 3H), 1.62–1.83 (m, 3H), 2.34 (s, 3H, CH_3), 2.54–2.56 (m, 2H), 2.66–2.74 (m, 2H), 3.02–3.06 (m, 1H), 5.11 (s, 1H, CH), 6.83–6.88 (m, 2H, ArH), 7.12–7.31 (m, 8H, ArH), 7.40–7.43 (m, 2H, ArH), 7.53–7.57 (m, 1H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.5 (CH_3), 31.9 (NCH_2CH_2), 32.6 (NCH_2CH_2), 37.7 ($\text{NCH}_2\text{CH}_2\text{CH}$), 43.0 (NCH_2), 46.4 (PhCH_2), 52.0 (NCH_2), 60.7 (CH), 81.5 (acetylenic carbon), 90.0 (acetylenic carbon), 116.3, 119.0, 119.5, 121.5, 126.0, 128.3, 128.5, 129.07, 129.14, 129.4, 131.8, 138.8, 140.3, 157.7 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{28}\text{H}_{29}\text{NONa}$) 418.2147, found 418.2140.

2-(3-Phenyl-1-(pyrrolidin-1-yl)prop-2-ynyl)phenol,³ (3j): Pale yellow semisolid (Lit.³ reported as pale yellow oil); FTIR (Neat): 3367 (m), 3056 (s), 2967 (s), 2845 (s), 2268 (w), 1591 (s), 1489 (s), 1466 (s), 1276 (s), 1095 (s), 1258 (s), 754 (s), 691 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.88–1.90 (m, 4H, 2 x NCH_2CH_2), 2.79–2.88 (m, 4H, 2 x NCH_2), 5.28 (s, 1H, CH), 6.83–6.88 (m, 2H, ArH), 7.20–7.27 (m, 2H, ArH), 7.35–7.43 (m, 3H, ArH), 7.52–7.55 (m, 3H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 23.9 (NCH_2CH_2), 49.0 (NCH_2), 57.1 (CH), 83.1 (acetylenic carbon), 89.1 (acetylenic carbon), 116.3, 119.0, 122.2, 122.6, 127.9, 128.4, 128.6, 129.4, 131.9, 157.6 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd ($\text{C}_{19}\text{H}_{20}\text{NO}$) 278.1545, found 278.1537.

2,4-Dibromo-6-(1-morpholino-3-phenylprop-2-ynyl)phenol (3k): Light yellow solid (mp 63–65 °C); FTIR (KBr): 3456 (s, br), 3056 (w), 2958 (s), 2849 (s), 2219 (w), 1633 (m), 1597 (m), 1441 (s), 1245 (s), 1117 (s), 754 (s), 707 (s), 690 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.92 (s, 4H, 2 x OCH_2), 2.93 (s, 4H, 2 x NCH_2), 4.18 (s, 1H, CH), 6.47–6.53 (m, 3H, ArH), 6.66–6.69 (m, 2H, ArH), 6.74–6.75 (m, 2H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 48.2 (NCH_2), 59.8 (CH), 65.9 (OCH_2), 79.2 (acetylenic carbon), 90.7 (acetylenic carbon), 110.4, 110.6, 120.9, 122.5, 127.8, 128.5, 130.1, 131.2, 134.5, 152.6 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{19}\text{H}_{17}\text{Br}_2\text{NO}_2\text{Na}$) 471.9524, found 471.9523.

2,4-Dibromo-6-(1-morpholino-3-*p*-tolylprop-2-ynyl)phenol (3l): Light yellow solid (mp 68–70 °C); FTIR (KBr): 3447 (m, br), 3073 (w), 2952 (s), 2848 (s), 2219 (w), 1636 (w), 1509 (s), 1447 (s), 1247 (s), 1116 (s), 815 (s), 706 (s), 557 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 2.39 (s, 3H, CH_3), 2.79 (s, 4H, 2 x OCH_2), 3.81 (s, 4H, 2 x NCH_2), 5.05 (s, 1H, CH), 7.19 (d, $J = 7.5$ Hz, 2H, ArH), 7.43–7.45 (m, 2H, ArH), 7.62 (s, 2H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.6 (CH_3), 48.7 (NCH_2), 60.6 (CH), 66.6 (OCH_2), 79.2 (acetylenic carbon), 91.6 (acetylenic carbon), 111.1, 111.3, 118.5, 123.4, 129.3, 130.9, 131.9, 135.2, 139.5, 153.3 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{20}\text{H}_{19}\text{Br}_2\text{NO}_2\text{Na}$) 485.9681, found 485.9679.

2-Methoxy-6-(1-morpholino-3-phenylprop-2-ynyl)phenol,⁴ (3m): Yellow solid (mp 130–132 °C); FTIR (KBr): 3438 (m, br), 2935 (m), 2846 (s), 1584 (m), 1457 (s), 1243 (s), 1116 (s), 1072 (s), 988 (s), 855 (s), 753 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 2.71 (s, 4H, 2 x OCH_2), 3.76 (s, 4H, 2 x NCH_2), 3.80 (s, 3H, OCH_3), 6.72–6.82 (m, 2H, ArH), 7.10–7.12 (m, 1H, ArH), 7.23–7.29 (m, 3H, ArH), 7.42–7.44 (m, 2H, ArH), 10.97 (s, br, 1H, OH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 48.9 (NCH_2), 56.0 (OCH_3), 60.6 (CH), 66.8 (OCH_2), 81.7 (acetylenic carbon), 90.1 (acetylenic carbon), 111.9, 118.9, 120.6, 120.8, 122.2, 128.4, 128.7, 131.9, 146.4, 148.0 (aromatic carbons).

2-Methoxy-6-(1-morpholino-3-*p*-tolylprop-2-ynyl)phenol (3n): White solid (mp 172–174 °C); FTIR (KBr): 3402 (w), 2921 (s), 2837 (s), 2211 (m), 1584 (s), 1466 (s), 1238 (s), 1112 (s), 1075 (s), 987 (s), 820 (s), 749 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 2.39 (s, 3H, CH_3), 2.80 (s, 4H, 2 x OCH_2), 3.81 (s, 4H, 2 x NCH_2), 3.90 (s, 3H, OCH_3), 5.11 (s, 1H, CH), 6.82–6.91 (m, 2H, ArH), 7.16–7.23 (m, 3H, ArH), 7.45 (d, $J = 7.8$ Hz, 2H, ArH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.5 (CH_3), 48.9 (NCH_2), 55.9 (OCH_3), 60.6, 66.8 (OCH_2), 80.9 (acetylenic carbon), 90.2 (acetylenic carbon), 111.8, 118.8, 119.1, 120.7, 120.9, 129.1, 131.7, 138.9, 146.3, 148.0 (aromatic carbons).

2-(3-(2-Bromophenyl)-1-morpholinoprop-2-ynyl)-6-methoxyphenol (3o): Orange sticky solid; FTIR (KBr): 3413 (m), 2924 (s), 2851 (s), 2230 (w) 1586 (m), 1467 (s), 1240 (w), 1116 (s), 1082 (s), 991 (s), 747 (s), 567 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 2.85 (s, 4H, 2 x OCH_2), 3.81 (s, 4H, 2 x NCH_2), 3.89 (s, 3H, OCH_3), 5.17 (s, 1H, CH), 6.81–6.91 (m, 2H, ArH), 7.19–7.33 (m, 3H, ArH), 7.56–7.64 (m, 2H, ArH), 10.98 (s, br, 1H, OH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 49.1 (NCH_2), 56.0 (OCH_3), 60.7 (CH), 66.9 (OCH_2), 86.6 (acetylenic

carbon), 88.4 (acetylenic carbon), 111.9, 118.9, 120.5, 120.8, 124.5, 125.5, 127.1, 129.9, 132.5, 133.7, 146.3, 148.0 (aromatic carbons).

2-(3-(4-Bromophenyl)-1-morpholinoprop-2-ynyl)-6-methoxyphenol (3p): Pale yellow solid (mp 156–158 °C); FTIR (KBr): 3428 (m), 2931 (s), 2847 (s), 2207 (w), 1594 (m), 1459 (s), 1240 (s), 1115 (s), 1070 (s), 982 (s), 822 (s), 744 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 2.78 (s, 4H, 2 x OCH_2), 3.80 (s, 4H, 2 x NCH_2), 3.89 (s, 3H, OCH_3), 5.08 (s, 1H, CH), 6.80–6.91 (m, 2H, ArH), 7.12–7.15 (m, 1H, ArH), 7.37–7.41 (m, 2H, ArH), 7.47–7.50 (m, 2H, ArH), 10.92 (s, br, 1H, OH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 49.0 (NCH_2), 56.0 (OCH_3), 60.6 (CH), 66.8 (OCH_2), 83.06 (acetylenic carbon), 89.0 (acetylenic carbon), 111.9, 118.9, 120.5, 120.6, 121.1, 123.0, 131.7, 133.3, 146.3, 148.1 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{20}\text{H}_{20}\text{BrNO}_3\text{Na}$) 424.0524, found 424.0525.

2-(1-(4-Benzylpiperidin-1-yl)-3-phenylprop-2-ynyl)-6-methoxyphenol (3q): Pale yellow solid (mp 118–119 °C); FTIR (KBr): 3428 (m), 2930 (s), 2827 (s), 1587 (m), 1497 (s), 1375 (s), 1324 (s), 1242 (s), 1073 (s), 832 (s), 749 (s), 697 (s), 590 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.28–1.41 (m, 2H), 1.51–1.62 (m, 2H), 1.72–1.76 (m, 1H), 2.29–2.36 (m, 1H), 2.46 (d, $J = 6.78$ Hz, 2H), 2.59–2.71 (m, 2H), 2.96–3.00 (m, 1H), 3.83 (s, 3H, OCH_3), 5.07 (s, 1H, CH), 6.71–6.82 (m, 2H), 7.05–7.07 (m, 2H), 7.10–7.14 (m, 2H, ArH), 7.18–7.22 (m, 2H, ArH), 7.26–7.30 (m, 3H, ArH), 7.44–7.47 (m, 2H, ArH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 31.7 (NCH_2CH_2), 32.6 (NCH_2CH_2), 37.6 ($\text{NCH}_2\text{CH}_2\text{CH}$), 42.9 (NCH_2), 46.4 (PhCH_2), 52.0 (NCH_2), 56.0 (OCH_3), 60.6 (CH), 82.2 (acetylenic carbon), 89.6 (acetylenic carbon), 111.6, 118.4, 120.3, 121.5, 122.5, 125.9, 128.2, 128.4, 128.6, 129.0, 131.8, 140.3, 147.1, 148.1 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{28}\text{H}_{29}\text{NO}_2\text{Na}$) 434.2096, found 434.2092.

2-(1-(4-Benzylpiperidin-1-yl)-3-*p*-tolylprop-2-ynyl)-6-methoxyphenol (3r): White solid (mp 155–156 °C); FTIR (KBr): 3407 (m, br), 2929 (s), 2837 (s), 1594 (m), 1458 (s), 1237 (s), 1075 (s), 989 (s), 820 (s), 731 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.27–1.38 (m, 2H), 1.52–1.61 (m, 2H), 1.71–1.76 (m, 1H), 2.30–2.35 (m, 4H), 2.46 (d, $J = 6.9$ Hz, 2H), 2.60–2.70 (m, 2H), 2.95–2.99 (m, 1H), 3.82 (s, 3H, OCH_3), 5.05 (s, 1H, CH), 6.70–6.81 (m, 2H), 7.04–7.13 (m, 6H), 7.18–7.22 (m, 2H, ArH), 7.34 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.5 (CH_3), 31.7 (NCH_2CH_2), 32.5 (NCH_2CH_2), 37.6 ($\text{NCH}_2\text{CH}_2\text{CH}$), 42.9 (NCH_2), 46.3 (PhCH_2), 51.9 (NCH_2), 56.0 (OCH_3), 60.6 (CH), 81.5 (acetylenic carbon), 89.7 (acetylenic carbon), 111.6, 118.3, 119.4, 120.4, 121.6, 125.9, 128.2, 129.0, 129.1, 131.7, 138.7, 140.3, 147.1, 148.0 (aromatic carbons).

2-Methoxy-6-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenol (3s): White solid (mp 132–134 °C); FTIR (KBr): 3417 (w, br), 2930 (s), 2837 (s), 1584 (m), 1458 (s), 1239 (s), 1074 (s), 985 (s), 742 (s), 587 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.51 (s, 2H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 1.66–1.69 (m, 4H, 2 x NCH_2CH_2), 2.73 (s, 4H, 2 x NCH_2), 3.89 (s, 3H, OCH_3), 5.10 (s, 1H, CH), 6.77–6.89 (m, 2H, ArH), 7.17–7.20 (m, 1H, ArH), 7.34–7.37 (m, 3H, ArH), 7.53–7.56 (m, 2H, ArH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 24.0 ($\text{N}(\text{CH}_2)_2\text{CH}_2$), 25.9 (NCH_2CH_2), 49.7 (NCH_2), 56.0 (OCH_3), 61.0 (CH), 82.4 (acetylenic carbon), 89.5 (acetylenic carbon), 111.6, 118.3, 120.4, 121.5, 122.6, 128.4, 128.5, 131.8, 147.1, 148.0 (aromatic carbons).

2-Methoxy-6-(1-(piperidin-1-yl)-3-*p*-tolylprop-2-ynyl)phenol (3t): Yellowish white solid (mp 152–154 °C); FTIR (KBr): 3423 (w), 2916 (s), 2832 (s), 1594 (m), 1466 (s), 1240 (s), 1078 (s), 987 (s), 822 (s), 741 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.43 (s, 2H, $\text{N}(\text{CH}_2)_2\text{CH}_2$), 1.61 (s, 4H, 2 x NCH_2CH_2), 2.29 (s, 4H, 2 x NCH_2), 2.65 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 5.01 (s, 1H, CH), 6.67–6.80 (m, 2H, ArH), 6.98–7.29 (m, 3H, ArH), 7.35 (d, 2H, $J = 8.1$ Hz, ArH), 7.35 (d, 2H, $J = 8.1$ Hz ArH). ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.5 (CH_3), 24.0 ($\text{N}(\text{CH}_2)_2\text{CH}_2$), 25.9 (NCH_2CH_2), 49.5 (NCH_2), 55.9 (OCH_3), 61.0 (CH), 81.6 (acetylenic carbon), 89.6 (acetylenic carbon), 111.5, 118.3, 119.5, 120.4, 121.6, 129.1, 131.7, 138.7, 147.1, 148.0 (aromatic carbons). HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd ($\text{C}_{22}\text{H}_{25}\text{NO}_2\text{Na}$) 358.1783, found 358.1779.

IV. References

1. Namitharan, K.; Pitchumani, K. *Eur. J. Org. Chem.* **2010**, 411–415. doi: 10.1002/ejoc.200901084
2. Borah, B. J.; Borah, S. J.; Saikia, K.; Dutta D. K. *Catal. Sci. Technol.* **2014**, 4, 4001–4009. doi:10.1039/C4CY00666F
3. Trose, M.; Dell'Acqua, M.; Pedrazzini, T.; Pirovano, V.; Gallo, E.; Rossi, E.; Caselli, A.; Abbiati, G. *J. Org. Chem.* **2014**, 79, 7311–7320. doi:10.1021/jo500981r
4. Mirabedini, M.; Motamedi, E.; Kassaee, M. Z. *Chin. Chem. Lett.* **2015**, 26, 1085–1090. doi:10.1016/j.cclet.2015.05.021

V. Scanned spectra (^1H and ^{13}C NMR) of propargylamine derivatives (3a–t)













































































