

Acid Catalysed Rearrangement of Isobenzofurans to Angularly Fused Phthalides

Bhavani Shankar Chinta,^[a] Soniya Gandhi^[a] and Beeraiah Baire*^[a]

Department of Chemistry

Indian Institute of Technology Madras, Chennai

Tamilnadu, INDIA-600036

E-mail: beeru@iitm.ac.in

Experimental section

General procedure A: Synthesis of propargylic alcohols

To an ice-cold solution of aldehyde (1 equiv.) in anhydrous THF under nitrogen atmosphere was added (phenylethynyl) lithium (or) RMgX (1.3 eq., in THF), and the reaction mixture was stirred for 2 h at 0 °C. Reaction progress was monitored by thin layer chromatography (TLC) analysis. Reaction mixture was diluted with saturated aq. NH₄Cl (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (10 mL) and dried over Na₂SO₄. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (4:1, hexane:EtOAc) gave the corresponding propargylic alcohols in 65–98% yields.

General procedure B: Synthesis of bispropargylic ethers

An ice cold solution of alcohol (1 equiv.) in anhydrous THF under nitrogen atmosphere was added to a suspension of sodium hydride 60% (2 equiv.) in THF at 0 °C. After 30 minutes propargyl bromide (1.3 equiv. in THF) was added slowly and the reaction mixture was stirred at room temperature for 12 h. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. Reaction mixture was diluted water (10 mL) and extracted with ethyl acetate (2 x 20 mL). The combined organic layer was washed with brine (10 mL), and dried over Na₂SO₄. Evaporation of the solvent and purification of the crude by flash column chromatography (9:1, hexane: EtOAc) gave the corresponding bispropargyl ethers in 50–85% yields.

General procedure C: Synthesis of esters

To an ice-cold solution of alkyne (1 equiv.) in anhydrous THF under nitrogen atmosphere was added ⁿBuLi (1.3 equiv., in THF). After 30 minutes, was added ethyl chloroformate (3 equiv. in THF) and the reaction mixture was stirred for 1-3 h at 0°C. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. Reaction mixture was diluted with saturated aq. NH₄Cl (10 mL) and extracted with ethyl acetate (2x20 mL). The combined organic layer was washed with brine (10 mL) and dried over Na₂SO₄. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (9:1, hexane: EtOAc) gave the corresponding alkynoates in 55–80% yields.

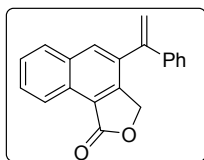
General procedure D: the Sonogashira cross-coupling reaction

The propargylic alcohol (1 equiv.) and iodo compound (1.2 equiv.) were dissolved in anhydrous THF, and added DIPA under nitrogen atmosphere at 0 °C. Subsequently, CuI (0.15 equiv.), and Pd(PPh₃)₂Cl₂ (1 mol%) were added to the reaction flask, then after 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature (RT) and continued the stirring at the same temperature for 14 h. Reaction progress was monitored by the thin layer chromatography (TLC) analysis. After complete consumption of the iodocompound, reaction was quenched with saturated NH₄Cl and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried over Na₂SO₄. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (4:1, hexane: EtOAc) gave the corresponding coupled product in 50–90% yields.

General procedure E: for the synthesis of angularly fused isonaphthofuranones

To an ice-cold solution of isobenzofuran (1 equiv.) in anhydrous 1,2-DCE (3mL/0.1mmol) under nitrogen atmosphere was added TfOH (0.2 equiv) at 0 °C. Then reaction mixture was stirred at 100 °C for 1-20 h. Reaction progress was monitored by thin layer chromatography (TLC) analysis. Reaction mixture was diluted with saturated aq. NaHCO₃ (10 mL) and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic layer was washed with brine (10 mL) and dried over Na₂SO₄. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (9:1, hexane: EtOAc) gave the corresponding phthalide derivatives in 45–98% yields.

4-(1-Phenylvinyl)naphtho[1,2-*c*]furan-1(3*H*)-one (2a)



Followed procedure E: To an ice cold solution of cyclised product¹ **1a** (30 mg, 0.09 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.018 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C for 20 min and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **2a** (23 mg, 0.084 mmol, 93%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 9.02 (1 H, d, J = 8.2 Hz), 8.14 (1 H, s), 7.99 (1 H, d, J = 8.1 Hz), 7.73 (1 H, t, J = 7.2 Hz), 7.65 (1 H, t, J = 7.5 Hz), 7.30-7.36 (5 H, m), 5.75 (1 H, s), 5.53 (1 H, s), 4.82 (2 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 147.7, 146.7, 139.5, 134.6, 133.9, 133.8, 129.1, 128.97, 129.94, 128.8, 128.6, 127.6, 127.5, 123.4, 120.4, 117.3 and 69.1 ppm.

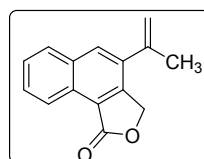
IR (neat): 3055, 2928, 2854, 1752, 1630, 1502, 1441, 1263, 1104, 1024, 735 cm⁻¹.

HR ESI-MS: [C₂₀H₁₅O₂]⁺ = [M+H]⁺ requires 287.1067; found 287.1099

M.P : 142-145 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Prop-1-en-2-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (2b)



Followed procedure E: To an ice cold solution of cyclised product **1b** (30 mg, 0.111 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.02 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C for 2 h. Evaporation of the solvent. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the **2b** angularly fused isonaphthafuranone (23 mg, 0.102 mmol, 93%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 9.01 (1 H, d, J = 8.3 Hz), 8.05 (1 H, s), 7.95 (1 H, d, J = 8.1 Hz), 7.70 (1 H, ddd, J = 1.2, 7.0 & 8.2 Hz), 7.62 (1 H, ddd, J = 1.2, 6.6 & 8.5 Hz), 5.56 (2 H, s), 5.40 (1 H, t, J = 1.1 Hz), 5.20 (1 H, s), 2.26 (3 H, d, J = 0.4 Hz) ppm.

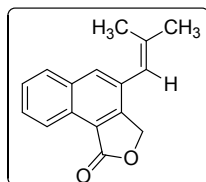
¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 146.6, 141.2, 134.2, 133.6, 132.6, 128.9, 128.6, 128.5, 127.6, 123.3, 120.5, 116.5, 69.7 and 23.3 ppm.

IR (neat): 3056, 2986, 2926, 2863, 1748, 1610, 1431, 1266, 1162, 1099, 1032, 897, 743 and 422 cm^{-1}

HR ESI-MS: $[\text{C}_{15}\text{H}_{12}\text{O}_2\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 247.0730; found 247.0761

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(2-Methylprop-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (2c)



Followed procedure E: To an ice cold solution of cyclised product¹ **1c** (30 mg, 0.105 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.02 mmol, 2 μL) at 0 $^\circ\text{C}$. Then reaction mixture was stirred at 100 $^\circ\text{C}$ for 4 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **2c** (25 mg, 0.087 mmol, 98%) as a yellow semi solid.

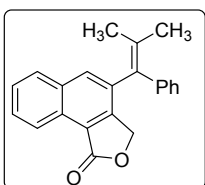
¹H NMR (400 MHz, CDCl_3): $\delta = 8.95$ (1 H, d, $J = 8.2$ Hz), 7.92 (2 H, d, $J = 9.9$ Hz), 7.66 (1 H, t, $J = 7.2$ Hz), 7.59 (1 H, t, $J = 7.7$ Hz), 6.19 (1 H, s), 5.27 (2 H, s), 1.99 (3 H, s), 1.90 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl_3): $\delta = 171.8, 148.6, 140.2, 133.9, 133.7, 130.3, 128.4, 128.3, 127.9, 127.3, 123.2, 119.8, 119.2, 69.0, 26.7$ and 19.8 ppm.

IR (neat): 3059, 2974, 2930, 2852, 1756, 1628, 1516, 1446, 1342, 1265, 1184, 1105, 1029, 967, 905, 845, 741, 492 and 439 cm^{-1} .

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(2-Methyl-1-phenylprop-1-en-1-yl) naphtho [1, 2-*c*] furan-1(3*H*)-one (2d)



Followed procedure E: To an ice cold solution of cyclised product **1d** (30 mg, 0.083 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.017 mmol, 2 μL) at 0 $^\circ\text{C}$. Then reaction mixture was stirred at 100 $^\circ\text{C}$ for 2 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **2d** (22 mg, 0.07 mmol, 84%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.97 (1 H, d, *J* = 8.2 Hz), 7.99 (1 H, s), 7.96 (1 H, d, *J* = 8.1 Hz), 7.68 (1 H, td, *J* = 1.2 & 7.0 Hz), 7.61 (1 H, td, *J* = 1.2 & 8.2 Hz), 7.27-7.31 (2 H, m), 7.20-7.25 (1 H, m), 7.12-7.17 (2 H, m), 4.78 (2 H, s), 1.95 (3 H, s), 1.83 (3 H, s) ppm.

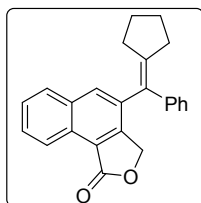
¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 148.9, 140.5, 135.5, 134.86, 134.83, 133.6, 132.8, 129.9, 128.6, 128.4, 128.3, 127.3, 127.3, 127.1, 123.3, 117.8, 69.2, 22.9 and 22.3 ppm.

IR (neat): 3057, 2984, 2927, 2863, 1753, 1631, 1509, 1444, 1371, 1266, 1182, 1111, 1061, 1026, 969, 894, 741, 541 and 446 cm⁻¹.

HR ESI-MS: [C₂₂H₁₈O₂Na]⁺ = [M+Na]⁺ requires 337.1199; found 337.1199

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

4-(Cyclopentylidene(phenyl)methyl)naphtho[1,2-*c*]furan-1(3*H*)-one (2e)



Followed procedure E: To an ice cold solution of cyclised product **1e** (30 mg, 0.077 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.016 mmol, 2 μL) at 0 °C. Then reaction mixture was stirred at 100 °C for 4 h. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **2e** (22 mg, 0.064 mmol, 84%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.88 (1 H, d, *J* = 8.2 Hz), 8.10 (1 H, s), 7.97 (1 H, d, *J* = 8.1 Hz), 7.69 (1 H, t, *J* = 7.0 Hz), 7.62 (1 H, t, *J* = 7.0 Hz), 7.20-7.29 (5 H, m), 4.75 (2 H, s), 2.59 (2 H, t, *J* = 6.9 Hz), 2.36 (2 H, t, *J* = 6.9 Hz), 1.69-1.77 (4 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 148.8, 147.2, 140.7, 135.1, 135.0, 133.7, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 127.3, 127.0, 123.3, 120.4, 69.2, 33.6, 33.2, 27.1 and 26.6 ppm.

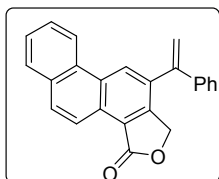
IR (neat): 3057, 2951, 2851, 1754, 1510, 1420, 1347, 1266, 1101, 1027, 743, 503 and 442 cm⁻¹.

HR ESI-MS: [C₂₄H₂₁O₂]⁺ = [M+H]⁺ requires 341.1536; found 341.1549

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

11-(1-Phenylvinyl)phenanthro[1,2-*c*]furan-3(1*H*)-one (2f)

Followed procedure E: To an ice cold solution of cyclised product **1f** (30 mg, 0.078 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid



(0.016 mmol, 2 μ L) at 0 $^{\circ}$ C. Then reaction mixture was stirred at 100 $^{\circ}$ C for 2 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **2f** (25 mg, 0.074 mmol, 95%) as a yellow oil.

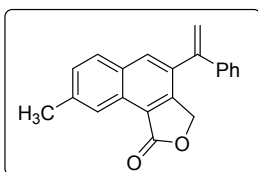
1 H NMR (400 MHz, CDCl_3): δ = 9.03 (1 H, d, J = 7.3 Hz), 8.99 (1 H, s), 8.71 (1 H, d, J = 6.6 Hz), 7.98-8.02 (2 H, m), 7.67-7.74 (2 H, m), 7.33-7.39 (5 H, m), 5.82 (1 H, d, J = Hz), 5.60 (1 H, d, J = 0.6 Hz), 4.87 (2 H, s) ppm.

13 C NMR (100 MHz, CDCl_3): δ = 171.6, 147.2, 146.5, 139.6, 134.1, 133.5, 132.3, 130.9, 130.4, 129.8, 129.2, 129.1, 129.0, 128.9, 128.8, 127.57, 127.53, 122.9, 120.9, 120.8, 117.4 and 68.9 ppm.

IR (neat): 3057, 2986, 2930, 2857, 1753, 1610, 1424, 1344, 1266, 1173, 1080, 1028, 905, 837, 746, 568, 452 and 419 cm^{-1} .

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

8-Methyl-4-(1-phenylvinyl)naphtho[1,2-c]furan-1(3H)-one (**2g**)



Followed procedure E: To an ice cold solution of cyclised product **1g** (30 mg, 0.086 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.017 mmol, 2 μ L) at 0 $^{\circ}$ C. Then reaction mixture was stirred at 100 $^{\circ}$ C for 2 h. Evaporation of the solvent. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **2g** (25 mg, 0.083 mmol, 97%) as a yellow solid.

1 H NMR (400 MHz, CDCl_3): δ = 8.80 (1 H, s), 8.08 (1 H, s), 7.88 (1 H, d, J = 8.4 Hz), 7.47 (1 H, dd, J = 1.5 & 8.4 Hz), 7.29-7.36 (5 H, m), 5.33 (1 H, d, J = 0.9 Hz), 5.50 (1 H, d, J = 0.8 Hz), 4.80 (2 H, s), 2.60 (3 H, s) ppm.

13 C NMR (100 MHz, CDCl_3): δ = 171.7, 149.2, 147.7, 146.8, 139.6, 134.5, 132.8, 132.0, 129.8, 129.1, 128.9, 128.7, 128.4, 127.5, 122.5, 119.6, 117.1, 69.1 and 22.2 ppm.

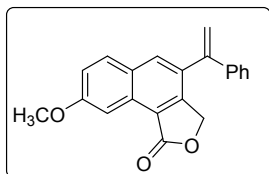
IR (neat): 3057, 2931, 2856, 1753, 1634, 1509, 1443, 1346, 1265, 1173, 1108, 1026, 973, 898, 740 and 503 cm^{-1} .

HR ESI-MS: $[\text{C}_{21}\text{H}_{17}\text{O}_2]^+ = [\text{M}+\text{H}]^+$ requires 301.1223 ; found 301.1256.

M.P : 116 -118 $^{\circ}$ C

TLC: $R_f = 0.5$ (9:1; hexane: EtOAc).

8-Methoxy-4-(1-phenylvinyl)naphtho[1,2-*c*]furan-1(3*H*)-one (2h)



Followed procedure E: To an ice cold solution of cyclised product **1h** (30 mg, 0.08 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.016 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **2h** (22 mg, 0.069 mmol, 87%) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.36$ (1 H, s), 8.05 (1 H, s), 7.86 (1 H, d, $J = 9.0$ Hz), 7.25-7.36 (6 H, m), 5.71 (1 H, s), 5.49 (1 H, s), 4.82 (2 H, s), 4.02 (3 H, s) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.9, 160.5, 148.0, 146.8, 139.8, 134.5, 131.3, 130.8, 130.1, 129.1, 128.9, 128.7, 127.5, 120.5, 119.1, 116.8, 101.7, 69.1$ and 55.8 ppm.

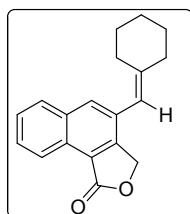
IR (neat): 3058, 2932, 2860, 1750, 1611, 1474, 1404, 1347, 1265, 1160, 1100, 1066, 1027, 908, 740 and 504 cm^{-1} .

HR ESI-MS: $[\text{C}_{21}\text{H}_{17}\text{O}_3]^+ = [\text{M}+\text{H}]^+$ requires 317.1172 ; found 317.1174

M.P : 110 -112 °C

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(Cyclohexylidenemethyl)naphtho[1,2-*c*]furan-1(3*H*)-one (2i)



Followed procedure E: To an ice cold solution of cyclised product¹ **1i** (30 mg, 0.096 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.014 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C for 8 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **2i** (20 mg, 0.0719 mmol, 75%) as a yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.96$ (1 H, d, $J = 6.5$ Hz), 7.91 (1 H, d, $J = 6.3$ Hz), 7.87 (1 H, s), 7.67 (1 H, td, $J = 0.8$ & 5.6 Hz), 7.60 (1 H, td, $J = 0.9$ & 5.6 Hz), 5.50 (1 H, s), 5.30 (2 H, s), 2.34 (1 H, t, $J = 4.3$ Hz), 2.03-2.04 (2 H, m), 1.87 (2 H, s), 1.54-1.64 (5 H, m) ppm.

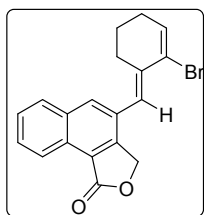
^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.8, 148.9, 134.7, 133.8, 131.5, 128.3, 128.2, 128.0, 127.3, 124.6, 123.3, 120.0, 116.1, 68.7, 41.7, 28.2, 25.4, 22.8$ and 22.3 ppm.

IR (neat): 3056, 2983, 2929, 2856, 1754, 1517, 1432, 1346, 1265, 1175, 1105, 1027, 965, 898, 743, 503 and 419 cm^{-1} .

M.P:132-134 $^\circ\text{C}$

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(E)-4-((2-Bromocyclohex-2-en-1-ylidene)methyl)naphtho[1,2-c]furan-1(3H)-one (2j)



Followed procedure E: To an ice cold solution of tricyclic compound⁵ **1j** (30 mg, 0.074 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.015 mmol, 2 μL) at $0\text{ }^\circ\text{C}$. Then reaction mixture was stirred at $100\text{ }^\circ\text{C}$ for 2 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused

isonaphthafuranone **2j** (22 mg, 0.061 mmol, 84%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.97$ (1 H, d, $J = 8.2$ Hz), 7.94 (2 H, d, $J = 5.2$ Hz), 7.70 (1 H, t, $J = 7.4$ Hz), 7.62 (1 H, t, $J = 7.4$ Hz), 6.86 (1 H, s), 6.54 (1 H, s), 5.35 (2 H, s), 2.77 (2 H, t, $J = 5.9$ Hz), 2.34 (2 H, q, $J = 5.0$ Hz), 1.74-1.80 (2 H, m) ppm.

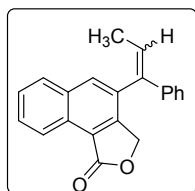
^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.6, 148.7, 138.2, 136.1, 134.2, 133.5, 128.97, 128.91, 128.5, 128.2, 127.5, 123.4, 123.3, 123.2, 120.2, 68.9, 28.59, 28.51$ and 22.3 ppm.

IR (neat): 3056, 2985, 2933, 2857, 1756, 1429, 1265, 1173, 1102, 1027, 969, 897, 743 and 495 cm^{-1} .

HR ESI-MS: $[\text{C}_{19}\text{H}_{15}\text{BrO}_2\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 377.0148; found 377.0128

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(1-Phenylprop-1-en-1-yl)naphtho[1,2-c]furan-1(3H)-one (2k)



Followed procedure E: To an ice cold solution of cyclised product¹ **1k** (25 mg, 0.072 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.015 mmol, 2 μL) at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at $100\text{ }^\circ\text{C}$ for 6 h. And purification of the crude mixture by column

chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone (*E:Z*; 1:0.6) **2k** (15 mg, 0.05 mmol, 69%) as a yellow oil.

Data for major *E* isomer : $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.98$ (1 H, d, $J = 8.2$ Hz), 8.10 (1 H, s), 7.96-8.00 (1 H, d, $J = 8.8$ Hz), 7.60-7.70 (2 H, m), 7.33-7.41 (2 H, m), 7.19-7.29 (3 H, m), 6.20 (1 H, q, $J = 7.1$ Hz), 4.58 (2 H, s), 1.94 (3 H, d, $J = 7.1$ Hz) ppm.

Data for minor *Z* isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 9.03$ (0.6 H, d, $J = 8.3$ Hz), 7.60-7.70 (1 H, m), 7.33-7.41 (2 H, m), 7.19-7.29 (3 H, m), 6.41 (0.6 H, q, $J = 7.0$ Hz), 4.85 (1.2 H, s), 1.84 (1.84 H, d, $J = 7.0$ Hz) ppm

Data for both mixture of (*E:Z*; 1:0.6)

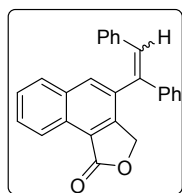
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.6, 148.8, 147.9, 140.4, 139.6, 138.3, 138.2, 135.98, 135.95, 133.8, 133.7, 133.5, 131.4, 129.9, 129.84, 129.80, 128.9, 128.8, 128.7, 128.5, 128.48, 128.42, 128.0, 127.7, 127.59, 127.50, 127.1, 127.0, 126.6, 125.8, 125.3, 123.4, 123.3, 120.2, 69.3, 69.1, 15.9$ and 15.8 ppm.

IR (neat): 3056, 2983, 2930, 2860, 1753, 1605, 1501, 1431, 1350, 1265, 1177, 1104, 1027, 898, 743 and 436 cm^{-1} .

HR ESI-MS: $[\text{C}_{21}\text{H}_{17}\text{O}_2]^+ = [\text{M}+\text{H}]^+$ requires 301.1223; found 301.1234

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(1,3-Diphenylprop-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (**2l**)



Followed procedure E: To an ice cold solution of cyclised product¹ **1l** (20 mg, 0.049 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.01 mmol, 1 μL) at $0\text{ }^\circ\text{C}$. Then reaction mixture was stirred at $100\text{ }^\circ\text{C}$ for 6 h and purification of the crude mixture by column

chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone (*E:Z* ; 1:1) **2l** (12 mg, 0.033 mmol, 68%) as a yellow solid.

Data for both mixture of (*E: Z*; 1:1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 9.03$ (2 H, dd, $J = 0.8$ & 9.1 Hz), 8.23 (1 H, s), 8.00 (2 H, d, $J = 10.0$ Hz), 7.88 (1 H, d, $J = 8.2$ Hz), 7.69-7.76 (2 H, m), 7.60-7.66 (2 H, m), 7.28-7.34 (8 H, m), 7.18-7.25 (6 H, m), 7.10-7.15 (5 H, m), 6.98-7.01 (3 H, m), 4.80 (2 H, s), 4.56 (2 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 171.5, 148.5, 147.9, 141.8, 139.7, 138.8, 137.5, 136.7, 136.4, 136.2, 134.0, 133.9, 133.8, 132.3, 131.5, 130.6, 130.1, 129.9, 129.28, 129.21, 129.0, 128.96, 128.90, 128.86, 128.82, 128.7, 128.69, 128.63, 128.63, 128.60, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 127.3, 123.49, 123.45, 120.9, 120.5, 69.4 and 69.2 ppm.

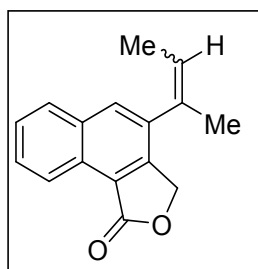
IR (neat): 3057, 2928, 2858, 1754, 1508, 1442, 1351, 1265, 1174, 1106, 1026, 903, 740 and 512 cm⁻¹.

HR ESI-MS: [C₂₆H₁₉O₂]⁺ = [M+H]⁺ requires 363.1380; found 363.1370

M.P: 160-162 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

4-(But-2-en-2-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (**2m**) (1:0.3; *E/Z* mixture)



To an ice cold solution of cyclised product **1m** (30 mg, 0.11 mmol) was dissolved in DCM (3 mL) then added trifluoromethanesulfonic acid (2.4 mg, 0.022 mmol, 2 μL) at 0 °C. The reaction was stirred at room temperature for 45 min. Evaporation of the solvent. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **2m** (20 mg, 0.086 mmol, 78%) as a yellow solid.

major diastereomer ¹H NMR (400 MHz, CDCl₃): δ = 8.98 (1 H, d, *J* = 8.3 Hz), 7.93 (1 H, s), 7.90 (1 H, d, *J* = 7.8 Hz), 7.66 (1 H, t, *J* = 7.4 Hz), 7.59 (1 H, t, *J* = 7.1 Hz), 5.74 (1 H, q, *J* = 7.2 Hz), 5.38 (2 H, s), 2.10 (3 H, s) and 1.87 (3 H, d, *J* = 6.7 Hz) ppm.

minor diastereomer ¹H NMR (400 MHz, CDCl₃): δ = 8.98 (1 H, d, *J* = 8.3 Hz), 7.94 (1 H, d, *J* = 7.8 Hz), 7.85 (1 H, s), 7.66 (1 H, t, *J* = 7.2 Hz), 7.58 (1 H, t, *J* = 7.1 Hz), 5.74 (1 H, q, *J* = 7.2 Hz), 5.23 (2 H, s), 2.06 (3 H, s) and 1.48 (3 H, d, *J* = 6.7 Hz) ppm.

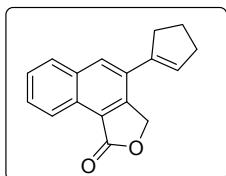
¹³C NMR (100 MHz, CDCl₃): δ (mixture of *E/Z*) = 171.6, 147.5, 146.8, 136.9, 133.9, 133.8, 133.7, 133.1, 132.9, 132.3, 128.5, 128.3, 128.2, 128.1, 127.3, 126.3, 124.7, 123.3, 123.2, 120.2, 69.4, 69.0, 29.7, 24.8, 16.7, 15.0 and 14.3 ppm.

IR (neat): 2967, 2924, 2853, 2364, 1715, 1593, 1453, 1429, 1221, 1143, 1034, 872, 752 and 612 cm^{-1} .

HR ESI-MS: $[\text{C}_{16}\text{H}_{15}\text{O}_2]^+ = [\text{M}+\text{H}]^+$ requires 239.1067; found 239.1074

TLC: $R_f = 0.6$ (19:1, Hex/EtOAc).

4-(Cyclopent-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (4a)



Followed procedure E: To an ice cold solution of cyclised product **3a** (30 mg, 0.101 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.02 mmol, 2 μL) at 0 $^\circ\text{C}$. Then reaction mixture was stirred at 100 $^\circ\text{C}$ for 6 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **4a** (24 mg, 0.096 mmol, 95%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.91$ (1 H, d, $J = 8.1$ Hz), 7.87 (1 H, s), 7.84 (1 H, d, $J = 8.2$ Hz), 7.58 (1 H, t, $J = 7.8$ Hz), 7.52 (1 H, t, $J = 7.9$ Hz), 5.91 (1 H, s), 5.35 (2 H, s), 2.81 (2 H, t, $J = 6.6$ Hz), 2.58 (2 H, t, $J = 6.7$ Hz), 1.96-2.03 (2 H, m) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.6, 146.9, 139.9, 133.7, 132.2, 130.8, 129.0, 128.6, 128.5, 128.0, 127.5, 123.3, 120.3, 70.2, 34.6, 34.3$ and 22.7 ppm.

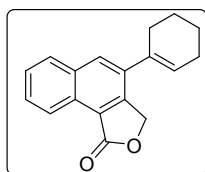
IR (neat): 3057, 2984, 2931, 2857, 1752, 1428, 1265, 1110, 1032, 898, 752 and 467 cm^{-1} .

HR ESI-MS: $[\text{C}_{17}\text{H}_{15}\text{O}_2]^+ = [\text{M}+\text{H}]^+$ requires; 251.1067 found 251.1074

M.P : 158 -160 $^\circ\text{C}$

TLC: $R_f = 0.5$ (9:1; hexane: EtOAc).

4-(Cyclohex-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (4b)



Followed procedure E: To an ice cold solution of cyclised product¹ **3b** (30 mg, 0.096 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.019 mmol, 2 μL) at 0 $^\circ\text{C}$. Then reaction was stirred at 100 $^\circ\text{C}$ for 2 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **4b** (22 mg, 0.083 mmol, 87%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.98 (1 H, d, *J* = 7.7 Hz), 7.94 (1 H, s), 7.90 (1 H, d, *J* = 7.7 Hz), 7.65 (1 H, t, *J* = 7.6 Hz), 7.58 (1 H, t, *J* = 7.5 Hz), 5.96 (1 H, s), 5.39 (2 H, s), 2.40-2.42 (2 H, m), 2.24-2.26 (2 H, m), 1.81-1.84 (2 H, m), 1.71-1.74 (2 H, m) ppm.

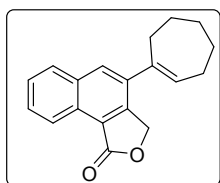
¹³C NMR (100 MHz, CDCl₃): δ = 171.1, 146.8, 135.7, 134.9, 133.8, 131.8, 128.6, 128.4, 128.3, 128.2, 127.3, 123.3, 120.3, 69.6, 28.8, 25.8, 23.0 and 21.9 ppm.

IR (neat): 3057, 2924, 2861, 1751, 1639, 1510, 1418, 1348, 1263, 1186, 1111, 1036, 963, 911, 829, 752, 694, 654, 607, 514 and 450 cm⁻¹.

HR ESI-MS: [C₁₈H₁₇O₂]⁺ = [M+H]⁺ requires 265.1223; found 265.1221

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

4-(Cyclohept-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (4c)



Followed procedure E: To an ice cold solution of cyclised product **3c** (30 mg, 0.09 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.018 mmol, 2 μL) at 0 °C. Then reaction mixture was stirred at 100 °C for 4 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **4c** (23 mg, 0.082 mmol, 92%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.96 (1 H, d, *J* = 8.2 Hz), 7.90 (1 H, d, *J* = 8.1 Hz), 7.88 (1 H, s), 7.65 (1 H, td, *J* = 1.1 & 8.1 Hz), 7.58 (1 H, td, *J* = 1.1 & 8.1 Hz), 6.07 (1 H, t, *J* = 6.6 Hz), 5.35 (2 H, s), 2.59 (2 H, t, *J* = 5.4 Hz), 2.32-2.37 (2 H, m), 1.88-1.90 (2 H, m), 1.67-1.71 (2 H, m), 1.60-1.63 (2 H, m) ppm.

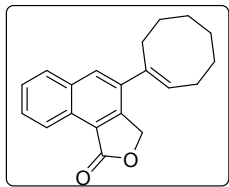
¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 146.9, 142.2, 137.8, 133.9, 133.8, 132.1, 128.35, 128.30, 128.1, 127.3, 123.2, 120.1, 69.3, 33.8, 32.6, 29.1, 27.1 and 26.8 ppm.

IR (neat): 3056, 2981, 2927, 2853, 1753, 1512, 1442, 1350, 1265, 11009, 1030, 958, 898, 742, 507 and 443 cm⁻¹.

HR ESI-MS: [C₁₉H₁₈O₂Na]⁺ = [M+Na]⁺ requires 301.1199; found 301.1199

TLC: R_f = 0.5 (9:1; hexane: EtOAc).

(*E*)-4-(Cyclooct-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (4d)



Followed procedure E: To an ice cold solution of cyclised product **3d** (30 mg, 0.088 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.0176 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C for 2 h and purification of the crude mixture by column chromatography (9:1, hexane:EtOAc) gave the angularly fused isonaphthafuranone **4d** (23 mg, 0.078 mmol, 90%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.99 (1 H, d, J = 8.3 Hz), 7.95 (1 H, s), 7.92 (1 H, d, J = 8.2 Hz), 7.66 (1 H, t, J = 7.0 Hz), 7.60 (1 H, t, J = 7.1 Hz), 5.86 (1 H, t, J = 8.2 Hz), 5.41 (2 H, s), 2.63-2.66 (2 H, m), 2.33-2.37 (2 H, m), 1.63-1.67 (8 H, m) ppm.

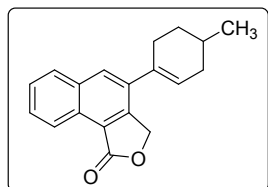
¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 146.8, 143.5, 139.8, 138.9, 138.3, 135.2, 133.5, 128.8, 128.5, 127.4, 123.1, 116.4, 68.6, 29.5, 25.0, 22.7 and 22.3 ppm.

IR (neat): 3056, 2980, 2928, 2858, 1754, 1511, 1437, 1353, 1265, 1179, 1109, 1030, 899, 738 and 508 cm⁻¹.

HR ESI-MS: [C₂₀H₂₀O₂Na]⁺ = [M+Na]⁺ requires 315.1356; found 315.1359

TLC: R_f = 0.5 (9:1; hexane: EtOAc).

4-(4-Methylcyclohex-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (**4e**)



Followed procedure E: To an ice cold solution of cyclised product **3e** (30 mg, 0.09 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.018 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C for 4 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **4e** (22 mg, 0.079 mmol, 88%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 9.0 (1 H, d, J = 7.9 Hz), 7.96 (1 H, s), 7.92 (1 H, d, J = 8.2 Hz), 7.66 (1 H, t, J = 7.2 Hz), 7.60 (1 H, t, J = 7.4 Hz), 5.94 (1 H, s), 5.42 (2 H, s), 2.34-2.48 (3 H, m), 1.82-1.90 (4 H, m), 1.06 (3 H, d, J = 6.1 Hz) ppm.

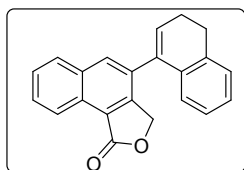
¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 146.8, 135.5, 134.6, 133.8, 131.9, 128.4, 128.3, 128.2, 127.4, 123.3, 120.3, 117.4, 69.6, 34.3, 31.2, 28.9, 28.0 and 21.7 ppm.

IR (neat): 3056, 2925, 1754, 1513, 1440, 1350, 1265, 1188, 1113, 1031, 898, 740 and 504 cm⁻¹.

HR ESI-MS: $[C_{19}H_{19}O_2]^+ = [M+H]^+$ requires 279.1380; found 279.1385.

M.P: 110-112 °C **TLC:** $R_f = 0.5$ (9:1; hexane: EtOAc).

4-(3,4-Dihydronaphthalen-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (4f)



Followed procedure E: To an ice cold solution of cyclised product **3f** (30 mg, 0.083 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.0166 mmol, 2 μ L) at 0 °C. The reaction mixture was stirred at 100 °C for 2 h and purification of the crude mixture

by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **4f** (20 mg, 0.057 mmol, 70%) as a yellow solid.

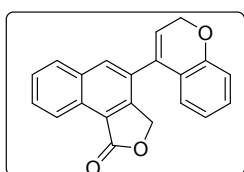
¹H NMR (400 MHz, CDCl₃): $\delta = 9.04$ (1 H, d, $J = 8.3$ Hz), 8.06 (1 H, s), 7.97 (1 H, d, $J = 8.2$ Hz), 7.73 (1 H, t, $J = 7.9$ Hz), 7.65 (1 H, t, $J = 7.8$ Hz), 7.24 (1 H, d, $J = 5.0$ Hz), 7.20 (1 H, t, $J = 6.7$ Hz), 7.08 (1 H, t, $J = 7.4$ Hz), 6.71 (1 H, d, $J = 7.6$ Hz), 6.22 (1 H, t, $J = 4.5$ Hz), 5.08 (2 H, s), 2.92 (2 H, t, $J = 7.8$ Hz), 2.47-2.52 (2 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 171.8, 148.3, 136.3, 136.1, 135.0, 133.5, 132.8, 130.3, 129.7, 128.8, 128.4, 128.1, 128.0, 127.5, 126.8, 124.7, 123.4, 120.2, 115.4, 69.2, 28.1$ and 23.5 ppm. **IR** (neat): 3056, 2984, 2930, 2858, 1752, 1600, 1429, 1265, 1106, 1027, 899, 745 and 500 cm^{-1} .

HR ESI-MS: $[C_{22}H_{17}O_2]^+ = [M+H]^+$ requires : 313.1223 ; found : 313.1206,

M.P : 168 -170 °C

4-(2*H*-Chromen-4-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (4g)



Followed procedure E: To an ice cold solution of cyclised product **3g** (30 mg, 0.083 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.0166 mmol, 2 μ L) at 0 °C. Then reaction mixture was stirred at 100 °C for 2 h and purification of the crude mixture

by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **4g** (20 mg, 0.063 mmol, 77%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): $\delta = 9.04$ (1 H, d, $J = 8.3$ Hz), 8.07 (1 H, s), 7.99 (1 H, d, $J = 8.2$ Hz), 7.76 (1 H, ddd, $J = 1.2, 2.4$ & 7.0 Hz), 7.67 (1 H, ddd, $J = 1.2, 2.4$ & 6.9 Hz), 7.20 (1 H, dd,

$J = 1.6$ & 8.0 Hz), 6.95 (1 H, dd, $J = 0.9$ & 8.1 Hz), 6.82 (1 H, td, $J = 1.1$ & 7.6 Hz), 6.70 (1 H, dd, $J = 1.5$ & 7.6 Hz), 5.93 (1 H, t, $J = 3.9$ Hz), 5.13 (2 H, s), 4.94 (2 H, d, $J = 4.0$ Hz) ppm.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.4, 154.9, 147.8, 135.1, 133.8, 133.6, 130.3, 130.2, 129.2, 128.9, 128.5, 127.7, 125.2, 123.5, 122.35, 123.31, 121.7, 120.5, 116.8, 69.0$ and 65.2 ppm.

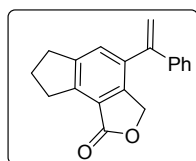
IR (neat): $3056, 2981, 2926, 2854, 1754, 1607, 1424, 1265, 1090, 1029, 896, 743, 527$ and 413 cm^{-1} .

HR ESI-MS: $[\text{C}_{21}\text{H}_{14}\text{O}_3\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 337.0835 ; found 337.0825

M.P : $164 -166$ $^\circ\text{C}$

TLC: $R_f = 0.4$ (9:1; hexane: EtOAc).

4-(1-Phenylvinyl)-3,6,7,8-tetrahydro-1H-indeno[4,5-c]furan-1-one (15a)



Followed procedure E: To an ice cold solution of cyclised product **14a** (30 mg, 0.09 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.018 mmol, 2 μL) at 0 $^\circ\text{C}$. Then reaction mixture was stirred at 100 $^\circ\text{C}$ for 2 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **15a** (21 mg, 0.076 mmol, 85%) as a yellow semi solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.49$ (1 H, s), $7.33-7.35$ (3 H, m), $7.25-7.28$ (2 H, m), 5.64 (1 H, d, $J = 1.0$ Hz), 5.37 (1 H, d, $J = 0.9$ Hz), 4.76 (2 H, s), 3.28 (2 H, t, $J = 7.5$ Hz), 2.99 (2 H, t, $J = 7.6$ Hz), $2.18-2.25$ (2 H, m) ppm.

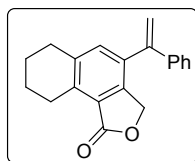
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.4, 147.1, 147.0, 143.8, 143.4, 139.9, 134.8, 130.1, 128.8, 128.5, 127.5, 121.8, 116.4, 69.8, 32.2, 30.5$ and 25.6 ppm.

IR (neat): $3056, 2950, 2857, 1763, 1611, 1479, 1444, 1369, 1312, 1271, 1176, 1087, 1017, 911, 779, 739, 704, 631, 569, 521$ and 446 cm^{-1} .

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(1-Phenylvinyl)-6,7,8,9-tetrahydronaphtho[1,2-c]furan-1(3H)-one (15b)

Followed procedure E: To an ice cold solution of cyclised product **14b** (30 mg, 0.089 mmol) was dissolved in 1,2-DCE (3 mL) then added trifluoromethanesulfonic acid (0.017 mmol, 2 μL)



at 0 °C. Then reaction mixture was stirred at 100 °C for 2 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **15b** (20 mg, 0.068 mmol, 77%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.32-7.34 (4 H, m), 7.26-7.28 (2 H, m), 5.62 (1 H, s), 5.36 (1 H, s), 4.69 (2 H, s), 3.24 (2 H, t, *J* = 5.0 Hz), 2.86 (2 H, t, *J* = 5.7 Hz), 1.85 (4 H, t, *J* = 3.2 Hz) ppm.

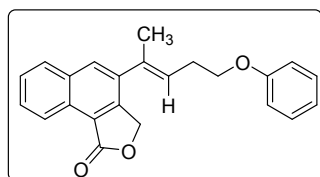
¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 146.8, 143.5, 139.8, 138.9, 138.3, 135.2, 133.5, 128.8, 128.5, 127.4, 123.1, 116.4, 68.9, 29.5, 25.0, 22.7 and 22.3 ppm.

IR (neat): 3055, 2934, 2864, 1717, 1599, 1447, 1260, 1184, 1026, 908, 874, 742 and 544 cm⁻¹

HR ESI-MS: [C₂₀H₁₉O₂]⁺ = [M+H]⁺ requires 291.1380 ; found 291.1367

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Z)-4-(5-Phenoxy-pent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one



(6a)

Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) and Phenol (47 mg 0.505 mmol) were dissolved in DCM (3 mL) then added CF₃SO₃H (7.6 mg, 0.05 mmol, 4 μL) at 0 °C The reaction was stirred at room temperature for 23 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **6a** (20 mg, 0.058 mmol, 57%) as a yellow oil. (4:1, hexane: EtOAc) gave Hydroxy trapped angularly fused isonaphthofuranone **6a'** (5 mg, 0.018 mmol, 18%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.99 (1 H, d, *J* = 8.2 Hz), 7.96 (1 H, s), 7.93 (1 H, d, *J* = 8.1 Hz), 7.67 (1 H, ddd, *J* = 1.2, 7.0 & 8.2 Hz), 7.60 (1 H, ddd, *J* = 1.2, 7.0 & 8.2 Hz), 7.30 (2 H, dd, *J* = 1.2 & 7.4 Hz), 6.92-6.98 (3 H, m), 5.78 (1 H, td, *J* = 1.2 & 7.0 Hz), 5.39 (2 H, s), 4.12 (2 H, t, *J* = 6.4 Hz), 2.76 (2 H, q, *J* = 6.5 Hz), 2.16 (3 H, d, *J* = 0.8 Hz) ppm.

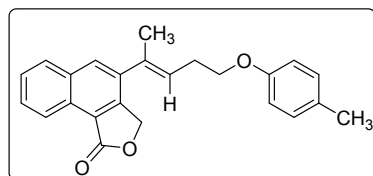
¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 158.8, 146.8, 136.6, 134.7, 133.7, 132.5, 129.6, 128.6, 128.4, 128.3, 127.8, 127.5, 123.3, 121.0, 120.4, 114.5, 69.4, 66.9, 29.0 and 17.4 ppm.

IR (neat): 3058, 2985, 2931, 2871, 1754, 1638, 1497, 1430, 1263, 1110, 1034, 897, 741 and 502 cm^{-1} .

HR ESI-MS: $[\text{C}_{23}\text{H}_{20}\text{O}_3\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires : 367.1305; found : 367.1323

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(E)-4-(5-(P-tolyloxy)pent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one (6b)



Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) para cresol (54 mg, 0.505 mmol) were dissolved in DCM (3 mL) then added $\text{CF}_3\text{SO}_3\text{H}$ (0.05 mmol, 4 μL) at 0 $^\circ\text{C}$ The reaction was stirred at room temperature for 25 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **6b** (15 mg, 0.04 mmol, 41%) as a yellow oil. (4:1, hexane: EtOAc) gave Hydroxy trapped angularly fused isonaphthofuranone **6a'** (10 mg, 0.037 mmol, 37%)

^1H NMR (400 MHz, CDCl_3): $\delta = 9.00$ (1 H, d, $J = 8.0$ Hz), 7.95 (1 H, s), 7.93 (1 H, d, $J = 8.0$ Hz), 7.67 (1 H, t, $J = 6.6$ Hz), 7.60 (1 H, t, $J = 7.2$ Hz), 7.09 (2 H, t, $J = 7.8$ Hz), 6.82 (2 H, d, $J = 8.1$ Hz), 5.78 (1 H, t, $J = 5.8$ Hz), 5.38 (2 H, s), 4.09 (2 H, t, $J = 6.1$ Hz), 2.73 (2 H, d, $J = 6.3$ Hz), 2.29 (3 H, s), 2.15 (3 H, s) ppm.

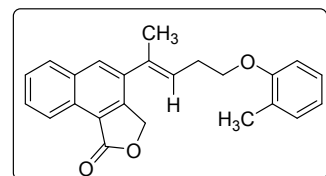
^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.6, 156.8, 146.8, 136.7, 134.6, 133.8, 132.5, 131.8, 130.3, 130.1, 128.6, 128.4, 127.9, 127.5, 123.3, 120.4, 114.5, 69.4, 67.2, 29.0, 20.6$ and 17.4 ppm.

IR (neat): 3056, 2985, 2932, 2871, 1754, 1600, 1512, 1429, 1264, 1110, 1033, 898, 740 and 422 cm^{-1} .

HR ESI-MS: $[\text{C}_{24}\text{H}_{23}\text{O}_3]^+ = [\text{M}+\text{H}]^+$ requires 359.1642; found 359.1659

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(E)-4-(5-(O-tolyloxy)pent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one (6c)



Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) and ortho cresol (54 mg, 0.505 mmol) were dissolved in DCM (3 mL) then added $\text{CF}_3\text{SO}_3\text{H}$ (0.05 mmol, 4 μL) at 0 $^\circ\text{C}$ The reaction was stirred at room temperature for 21 h and purification of

the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **6c** (20 mg, 0.055 mmol, 54%) as a yellow oil. (9:1, hexane: EtOAc) gave Hydroxyl trapped angularly fused isonaphthofuranone **6a'** (5 mg, 0.018 mmol, 18%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 9.00 (1 H, d, *J* = 8.3 Hz), 7.96 (1 H, s), 7.93 (1 H, d, *J* = 8.0 Hz), 7.68 (1 H, ddd, *J* = 1.3, 2.5 & 7.0 Hz), 7.61 (1 H, ddd, *J* = 1.3, 2.4 & 6.8 Hz), 7.15 (2 H, d, *J* = 7.4 Hz), 6.84-6.89 (2 H, m), 5.79-5.83 (1 H, m), 5.39 (2 H, s), 4.12 (2 H, t, *J* = 6.3 Hz), 2.78 (2 H, q, *J* = 6.4 Hz), 2.24 (3 H, s), 2.17 (3 H, d, *J* = 1.0 Hz) ppm.

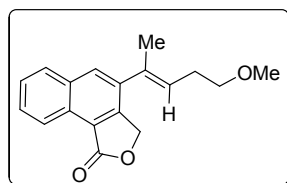
¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 157.0, 146.8, 136.7, 134.7, 133.8, 132.5, 130.9, 128.6, 128.4, 128.1, 127.5, 126.9, 126.8, 123.4, 120.7, 110.0, 69.4, 67.0, 29.2, 17.3 and 16.4 ppm.

IR (neat): 3056, 2978, 2929, 2860, 1752, 1595, 1432, 1264, 1113, 1033, 896, 741 and 545 cm⁻¹.

HR ESI-MS: [C₂₄H₂₃O₃]⁺ = [M+H]⁺ requires 359.1642; found 359.1653

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Z)-4-(5-Methoxypent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one (6d)



Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) was dissolved in DCM (3 mL) then added MeOH (0.1 mL) at 0 °C. The reaction was stirred at room temperature for 12 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave methoxy trapped angularly fused isonaphthofuranone **6d** (23 mg, 0.088 mmol, 87%) as a yellow oil.

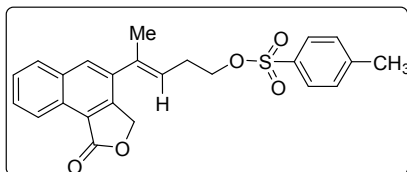
¹H NMR (400 MHz, CDCl₃): δ = 8.99 (1 H, d, *J* = 8.2 Hz), 7.96 (1 H, s), 7.91-7.93 (1 H, m), 7.65-7.69 (1 H, m), 7.60 (1 H, td, *J* = 1.1 & 8.1 Hz), 5.70 (1 H, td, *J* = 1.3 & 7.0 Hz), 5.40 (2 H, s), 3.52 (2 H, t, *J* = 6.6 Hz), 3.39 (3 H, s), 2.55 (2 H, q, *J* = 6.5 Hz), 2.12 (3 H, d, *J* = 0.8 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 146.9, 136.8, 134.0, 133.8, 132.5, 130.6, 128.5, 128.3, 128.2, 127.5, 127.4, 123.3, 72.0, 69.4, 58.9, 29.4 and 17.2 ppm.

IR (neat): 3056, 2984, 2930, 2866, 1753, 1430, 1265, 1113, 1029, 897, 744 and 500 cm⁻¹.

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Z)-4-(1-Oxo-1,3-dihydronaphtho[1,2-c]furan-4-yl)pent-3-en-1-yl 4-methylbenzenesulfonate (6e)



Followed procedure E: To a solution of cyclised product¹ **5a** (15 mg, 0.05 mmol) was dissolved in DCM (3 mL) then added *p*-TSA (12 mg, 0.06 mmol,) at 55 °C for 2 h and purification of the crude mixture by column chromatography (9:1, hexane:

EtOAc) gave the tosyl trapped angularly fused isonaphthafuranone **6e** (15 mg, 0.035 mmol, 71%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.99 (1 H, d, *J* = 8.2 Hz), 7.92 (2 H, d, *J* = 11.1 Hz), 7.80 (2 H, d, *J* = 8.2 Hz), 7.69 (1 H, t, *J* = 7.1 Hz), 7.62 (1 H, t, *J* = 8.0 Hz), 7.32 (2 H, d, *J* = 8.1 Hz), 5.52 (1 H, t, *J* = 6.9 Hz), 5.28 (2 H, s), 4.18 (2 H, t, *J* = 6.4 Hz), 2.64 (2 H, q, *J* = 6.6 Hz), 2.41 (3 H, s), 2.08 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 146.5, 145.1, 136.1, 136.0, 133.7, 133.1, 132.6, 130.0, 128.7, 128.4, 127.9, 127.6, 125.6, 123.3, 120.4, 69.38, 69.31, 28.5, 21.7 and 17.3 ppm.

IR (neat): 3058, 2986, 2926, 2868, 1754, 1639, 1426, 1352, 1265, 1175, 1027, 965, 908, 738 and 580 cm⁻¹.

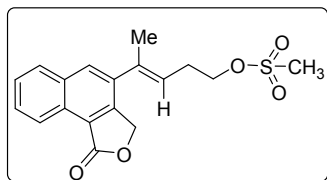
HR ESI-MS: [C₂₄H₂₂O₅SNa]⁺ = [M+Na]⁺ requires 445.1080; found 445.1115

M.P: 100-102 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Z)-4-(1-Oxo-1,3-dihydronaphtho[1,2-c]furan-4-yl)pent-3-en-1-yl methanesulfonate (6f)

Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) was



dissolved in DCM (3 mL) then added MeSO₃H (12 mg, 0.12 mmol, 0.008 mL) at 55 °C for 2.5 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **6f** (28 mg, 0.085 mmol, 85%) as a pale

yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.96 (1 H, d, *J* = 8.1 Hz), 7.94 (1 H, s), 7.92 (1 H, d, *J* = 6.4 Hz), 7.67 (1 H, t, *J* = 8.1 Hz), 7.60 (1 H, t, *J* = 7.5 Hz), 5.66 (1 H, t, *J* = 7.0 Hz), 5.38 (2 H, s), 4.37 (2 H, t, *J* = 6.3 Hz), 3.05 (3 H, s), 2.73 (2 H, q, *J* = 6.6 Hz), 2.14 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 146.5, 136.3, 136.1, 133.6, 132.6, 128.7, 128.4, 128.3, 127.5, 125.3, 123.2, 120.3, 69.3, 68.7, 37.7, 28.8 and 17.4 ppm.

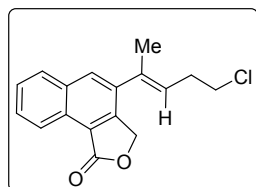
IR (neat): 3057, 2986, 1755, 1604, 1428, 1357, 1265, 1177, 1106, 1028, 971, 905, 740, 557 and 502 cm⁻¹.

HR ESI-MS: [C₁₈H₁₉O₅S]⁺ = [M+H]⁺ requires 347.0948; found 347.0942.

M.P: 102-104 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Z)-4-(5-Chloropent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one (6g)



Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) was dissolved in DCM (3 mL) then added BiCl₃ (18 mg, 0.15 mmol,) at 55 °C for 1 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **6g** (28 mg, 0.097 mmol, 97%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.91 (1 H, d, *J* = 8.3 Hz), 7.88 (1 H, s), 7.85 (1 H, d, *J* = 8.4 Hz), 7.60 (1 H, t, *J* = 8.0 Hz), 7.53 (1 H, t, *J* = 7.3 Hz), 5.60 (1 H, t, *J* = 7.0 Hz), 5.32 (2 H, s), 3.60 (2 H, t, *J* = 6.5 Hz), 2.67 (2 H, q, *J* = 6.7 Hz), 2.06 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 146.7, 136.4, 135.4, 133.7, 132.5, 128.7, 128.4, 127.59, 127.55, 123.3, 120.5, 69.4, 44.1, 31.7 and 17.4 ppm.

IR (neat): 3057, 2981, 2874, 1754, 1513, 1440, 1352, 1265, 1158, 1110, 1031, 899, 740 and 464 cm⁻¹.

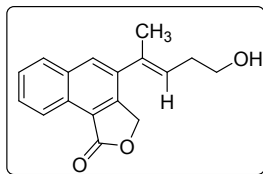
HR ESI-MS: [C₁₇H₁₆ClO₂]⁺ = [M+H]⁺ requires 287.0833; found 287.0818.

M.P: 130-132 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(E)-4-(5-Hydroxypent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one (6a')

Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) was dissolved in DCM (3 mL) then added FeCl₃ (19 mg, 0.12 mmol,) at 55 °C for 1 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthafuranone **6a'** (20 mg, 0.075 mmol, 75%) as a yellow solid.



¹H NMR (400 MHz, CDCl₃): δ = 8.99 (1 H, d, *J* = 8.1 Hz), 7.97 (1 H, s), 7.93 (1 H, d, *J* = 7.8 Hz), 7.68 (1 H, t, *J* = 6.4 Hz), 7.61 (1 H, t, *J* = 7.4 Hz), 5.31 (1 H, t, *J* = 5.8 Hz), 5.41 (2 H, s), 3.81 (2 H, t, *J* = 6.1 Hz), 2.56 (2 H, d, *J* = 6.4 Hz), 2.14 (3 H, s) ppm.

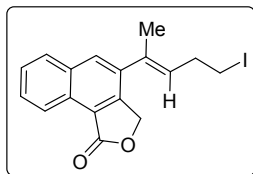
¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 146.7, 136.7, 134.9, 133.8, 132.5, 128.6, 128.4, 128.3, 128.1, 127.5, 123.3, 120.4, 69.4, 62.5, 32.2 and 17.3 ppm.

IR (neat): 3417, 3059, 2928, 1746, 1511, 1446, 1355, 1257, 1109, 1033, 969, 798, 753, 608, 501 and 461 cm⁻¹

M.P: 106-108 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(Z)-4-(5-Iodopent-2-en-2-yl)naphtho[1,2-c]furan-1(3H)-one (6h)



Followed procedure E: To a solution of cyclised product **5a** (30 mg, 0.101 mmol) was dissolved in DCM (3 mL) then added I₂ (31 mg, 0.121 mmol,) at 55 °C for 4 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone **6h** (36 mg, 0.095 mmol, 94%) as a brown solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.99 (1 H, d, *J* = 8.2 Hz), 7.96 (1 H, s), 7.93 (1 H, d, *J* = 8.1 Hz), 7.68 (1 H, t, *J* = 7.0 Hz), 7.60 (1 H, t, *J* = 7.1 Hz), 5.60 (1 H, t, *J* = 7.0 Hz), 5.44 (2 H, s), 3.30 (2 H, t, *J* = 6.7 Hz), 2.88 (2 H, q, *J* = 6.8 Hz), 2.12 (3 H, s), ppm.

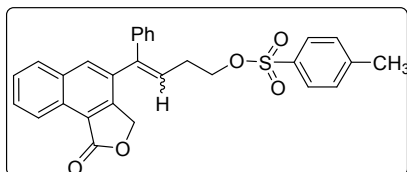
¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 146.7, 136.3, 135.0, 133.7, 132.5, 130.3, 129.0, 128.7, 128.4, 127.5, 123.3, 120.4, 69.6, 32.2, 17.5, 5.40 ppm.

IR (neat): 3056, 2983, 2936, 2865, 1755, 1605, 1513, 1430, 1350, 1263, 1165, 1111, 1032, 963, 898, 739 and 441 cm⁻¹.

HR ESI-MS: [C₁₇H₁₅O₂NaI]⁺ = [M+Na]⁺ requires : 401.0009; found : 401.0041

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(E)-4-(1-oxo-1,3-dihydronaphtho[1,2-c]furan-4-yl)-4-phenylbut-3-en-1-yl-4-methylbenzenesulfonate (7a)



Followed procedure E: To a solution of cyclised product **5b** (30 mg, 0.083 mmol) was dissolved in DCM (3 mL) then added *p*-TSA (19 mg, 0.10 mmol) at 55 °C for 8 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone (*E:Z*; 1:0.74) **7a** (18 mg, 0.037 mmol, 45%) as a yellow oil.

Data for major E isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.97$ (1 H, d, $J = 8.2$ Hz), 8.03 (1 H, s), 7.94-7.99 (1 H, m), 7.72-7.78 (1 H, m), 7.67-7.70 (2 H, m), 7.60-7.65 (1 H, m), 7.36-7.38 (2 H, m), 7.27-7.29 (2 H, m), 7.22 (1 H, d, $J = 8.0$ Hz), 7.14-7.17 (2 H, m), 5.98 (1 H, t, $J = 7.3$ Hz), 4.55 (2 H, s), 4.19 (2 H, t, $J = 6.3$ Hz), 2.65 (2 H, q, $J = 7.2$ Hz), 2.38 (3 H, s) ppm.

Data for minor Z isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 9.01$ (0.74 H, d, $J = 8.3$ Hz), 7.94-7.99 (1.47 H, m), 7.72-7.78 (1.81 H, m), 7.67-7.70 (1.11 H, m), 7.36-7.38 (1.05 H, m), 7.27-7.29 (2.50 H, m), 7.22 (1.60 H, d, $J = 8.0$ Hz), 7.14-7.17 (1.50 H, m), 6.17 (0.74 H, t, $J = 7.5$ Hz), 4.75 (1.43 H, s), 4.12 (1.53 H, t, $J = 6.4$ Hz), 2.45 (1.59 H, q, $J = 7.4$ Hz), 2.38 (2.08 H, s) ppm.

Data for both mixture of (E: Z; 1:0.74)

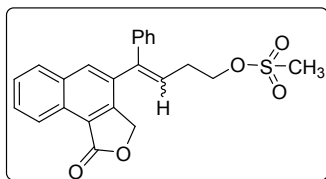
$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.39, 171.34, 148.4, 147.5, 145.08, 145.04, 142.1, 140.9, 139.5, 137.8, 135.5, 135.0, 133.7, 133.6, 133.2, 133.0, 130.7, 129.9, 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.67, 128.60, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.2, 126.8, 126.1, 123.4, 123.3, 120.8, 120.4, 69.5, 69.2, 69.1, 68.8, 29.7, 29.4$ and 21.6 ppm.

IR (neat): 3058, 2986, 2926, 2868, 1754, 1639, 1426, 1352, 1265, 1175, 1027, 965, 908, 738, 517 and 420 cm^{-1} .

HRESI-MS: $[\text{C}_{29}\text{H}_{25}\text{O}_5\text{S}]^+ = [\text{M}+\text{H}]^+$ requires 485.1417; found 485.1423.

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(E)-4-(1-Oxo-1,3-dihydronaphtho[1,2-c]furan-4-yl)-4-phenylbut-3-en-1-yl methanesulfonate (7b)



Followed procedure E: To a solution of cyclized product **5b** (30 mg, 0.083 mmol) was dissolved in DCM (3 mL) then added MeSO₃H (9.6 mg, 0.10 mmol, 0.006 mL) at 55 °C for 10 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone (*E:Z*; 1:0.7) **7b** (30 mg, 0.073 mmol, 88%) as a yellow oil.

Data for major *E* isomer: ¹H NMR (400 MHz, CDCl₃): δ = 8.98 (1 H, d, *J* = 8.2 Hz), 8.12 (1 H, s), 8.00 (1 H, d, *J* = 8.0 Hz), 7.63-7.75 (2 H, m), 7.38-7.42 (2 H, m), 7.30 (1 H, t, *J* = 6.2 Hz), 7.21-7.23 (2 H, m), 6.11 (1 H, t, *J* = 7.3 Hz), 4.60 (2 H, s), 4.37 (2 H, t, *J* = 6.3 Hz), 3.01 (3 H, s), 2.77 (2 H, q, *J* = 6.5 Hz) ppm.

Data for minor *Z* isomer : ¹H NMR (400 MHz, CDCl₃): δ = 9.02 (0.71 H, d, *J* = 8.2 Hz), 8.00 (1.49 H, d, *J* = 8.0 Hz), 7.63-7.75 (1.88 H, m), 7.38-7.42 (1.20 H, m), 7.30 (1.15 H, t, *J* = 6.2 Hz), 7.21-7.23 (2.69 H, m), 6.30 (0.7 H, t, *J* = 7.4 Hz), 4.82 (1.41 H, s), 4.32 (1.43 H, t, *J* = 6.2 Hz), 2.98 (2.16 H, s), 2.0 (1.46 H, q, *J* = 7.1 Hz) ppm.

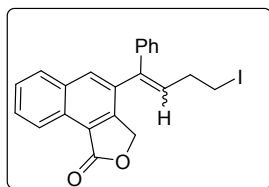
Data for mixture of (*E:Z*; 1:0.7)

¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 148.4, 147.5, 142.5, 141.2, 139.5, 137.8, 135.5, 135.0, 133.8, 133.6, 130.7, 129.5, 129.2, 129.1, 129.0, 128.9, 128.86, 128.81, 128.67, 128.62, 128.5, 127.8, 127.6, 126.9, 125.9, 123.4, 123.3, 120.9, 120.5, 68.9, 68.8, 37.78, 37.71, 30.1 and 29.7 ppm.

IR (neat): 3054, 2972, 2905, 2846, 1728, 1612, 1425, 1332, 1218, 1153, 1048, 962, 878, 719 and 512 cm⁻¹

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

(*E*)-4-(4-Iodo-1-phenylbut-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (7c)



Followed procedure E: To a solution of cyclized product **5b** (30 mg, 0.083 mmol) was dissolved in DCM (3 mL) then added I₂ (25 mg, 0.099 mmol) at 55 °C for 4 h and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone (*E:Z*; 1:0.6) **7c** (32 mg, 0.072 mmol, 87%) as a yellow oil.

Data for major *E* isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 9.01$ (1 H, d, $J = 8.2$ Hz), 8.03 (1 H, s), 8.00 (1 H, t, $J = 8.7$ Hz), 7.73-7.76 (1 H, m), 7.61-7.70 (1 H, m), 7.39-7.40 (1 H, m), 7.30-7.32 (2 H, m), 7.21-7.26 (2 H, m), 6.21 (1 H, t, $J = 7.3$ Hz), 4.84 (2 H, s), 3.23 (2 H, t, $J = 6.6$ Hz), 2.74 (2 H, q, $J = 6.7$ Hz) ppm.

Data for minor *Z* isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.99$ (0.61 H, d, $J = 8.3$ Hz), 8.13 (0.69 H, s), 8.00 (0.59 H, t, $J = 8.7$ Hz), 7.61-7.70 (0.65 H, m), 7.39-7.40 (1.80 H, m), 7.30-7.32 (1.34 H, m), 7.21-7.26 (1.96 H, m), 6.03 (0.6 H, t, $J = 7.2$ Hz), 4.66 (1.20 H, s), 3.28 (1.22 H, t, $J = 6.8$ Hz), 2.88 (1.25 H, q, $J = 7.0$ Hz) ppm.

Data for both mixture of (*E*:*Z*; 1:0.6)

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.4, 148.5, 147.6, 141.1, 139.9, 139.7, 138.1, 135.5, 135.2, 133.8, 133.7, 133.6, 131.8, 131.0, 130.8, 129.5, 129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 127.7, 127.6, 126.9, 125.6, 123.5, 123.3, 120.8, 120.4, 69.3, 69.0, 33.0, 32.8, 5.54$ and 5.41 ppm.

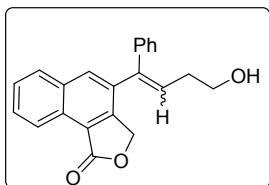
IR (neat): 3442, 3057, 2983, 2862, 1753, 1637, 1425, 1265, 1162, 1107, 1028, 898, 739 and 463 cm^{-1} .

HR ESI-MS: $[\text{C}_{22}\text{H}_{18}\text{IO}_2]^+ = [\text{M}+\text{H}]^+$ requires 441.0346; found 442.0383

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(*E*)-4-(4-Hydroxy-1-phenylbut-1-en-1-yl)naphtho[1,2-*c*]furan-1(3*H*)-one (7d)

Followed procedure E: To a solution of cyclized product **5b** (30 mg, 0.083 mmol) was dissolved in DCM (3 mL) then added FeCl_3 (16 mg, 0.10 mmol) at $55\text{ }^\circ\text{C}$ 1 h and purification of the crude mixture by column chromatography (4:1, hexane: EtOAc) gave the angularly fused isonaphthofuranone (*E*:*Z*; 1:0.62) **7d** (25 mg, 0.075 mmol, 91%) as a yellow oil.



Data for major *E* isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.91$ (1 H, d, $J = 8.2$ Hz), 8.02 (1 H, s), 7.89-7.94 (1 H, m), 7.61 (1 H, t, $J = 7.5$ Hz), 7.54 (1 H, t, $J = 7.9$ Hz), 7.29-7.33 (2 H, m), 7.21-7.23 (1 H, m), 7.14-7.17 (2 H, m), 6.05 (1 H, t, $J = 7.2$ Hz), 4.57 (2 H, s), 3.60 (2 H, t, $J = 6.5$ Hz), 2.70 (2 H, q, $J = 6.7$ Hz) ppm.

Data for minor *Z* isomer: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.95$ (0.62 H, d, $J = 8.3$ Hz), 7.96 (0.66 H, s), 7.89-7.94 (1.23 H, m), 7.61 (0.53 H, t, $J = 7.5$ Hz), 7.29-7.33 (1.22 H, m), 7.21-7.23

(1.11 H, m), 7.14-7.17 (2.02 H, m), 6.24 (0.62 H, t, $J = 7.2$ Hz), 4.76 (1.25 H, s), 3.54 (1.17 H, t, $J = 6.4$ Hz), 2.53 (1.27 H, q, $J = 6.8$ Hz) ppm

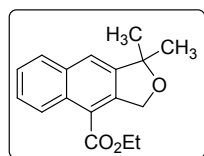
Data for both mixture of (*E*:*Z*; 1:0.62)

^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.3, 148.4, 147.5, 141.6, 140.2, 139.5, 138.0, 135.4, 135.1, 133.6, 133.5, 130.9, 129.4, 129.07, 129.01, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.8, 127.6, 126.7, 123.3, 123.2, 120.7, 120.4, 69.1, 68.8, 44.1, 32.7$ and 32.4 ppm.

IR (neat): 3056, 2932, 2868, 1754, 1426, 1265, 1104, 1028, 898, 742 and 459 cm^{-1}

TLC: $R_f = 0.5$ (4:1; hexane:EtOAc).

Ethyl 1,1-dimethyl-1,3-dihydronaphtho[2,3-*c*]furan-4-carboxylate (1b**)**



To a solution of ester **S**₂ (200 mg, 0.74 mmol) and phenol (661 mg, 7.04 mmol) in 1,2-DCB (7 mL) was taken in a reaction tube. The reaction tube was kept at $150\text{ }^\circ\text{C}$. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **1b** (125 mg, 0.46 mmol, 62%) as a yellow oil.

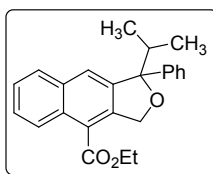
^1H NMR (400 MHz, CDCl_3): $\delta = 8.82$ (1 H, d, $J = 8.6$ Hz), 7.85 (1 H, d, $J = 8.0$ Hz), 7.69 (1 H, s), 7.57 (1 H, t, $J = 7.9$ Hz), 7.50 (1 H, t, $J = 7.6$ Hz), 5.38 (2 H, s), 4.48 (2 H, q, $J = 7.1$ Hz), 1.59 (6 H, s), 1.46 (3 H, t, $J = 7.1$ Hz) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 167.1, 145.9, 142.3, 134.0, 131.2, 128.5, 127.4, 126.1, 125.8, 123.7, 120.9, 84.7, 71.7, 61.3, 28.5$ and 14.5 ppm.

IR (neat): 3056, 2979, 2935, 2868, 1710, 1598, 1468, 1374, 1303, 1263, 1228, 1028, 891, 859, 742, 515 and 456 cm^{-1} .

TLC: $R_f = 0.4$ (9:1; hexane: EtOAc).

Ethyl 1-isopropyl-1-phenyl-1,3-dihydronaphtho[2,3-*c*]furan-4-carboxylate (1d**)**



To a solution of ester **S**₅ (150 mg, 0.416 mmol) and phenol (391 mg, 4.16 mmol) in 1,2-DCB (10 mL) was taken in a reaction tube. The reaction tube was kept at $150\text{ }^\circ\text{C}$. After 30 minutes, the reaction mixture was directly

poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **1d** (100 mg, 0.277 mmol, 67%) as a yellow oil.

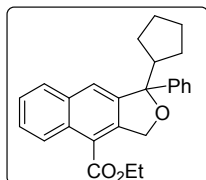
¹H NMR (400 MHz, CDCl₃): δ = 8.80 (1 H, d, J = 8.6 Hz), 7.94 (1 H, s), 7.88 (1 H, d, J = 8.0 Hz), 7.60 (2 H, dd, J = 1.2 & 7.1 Hz), 7.54 (1 H, td, J = 1.2 & 8.4 Hz), 7.48 (1 H, td, J = 1.0 & 8.0 Hz), 7.32 (2 H, t, J = 7.7 Hz), 7.19 (1 H, t, J = 7.1 Hz), 5.50 (2 H, q, J = 6.8 Hz), 4.41-4.50 (2 H, m), 2.66-2.72 (1 H, m), 1.44 (3 H, t, J = 7.2 Hz), 0.90 (3 H, d, J = 7.9 Hz), 0.86 (3 H, d, J = 6.7 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.0, 144.8, 143.5, 142.9, 134.0, 131.3, 128.8, 128.4, 127.5, 126.8, 126.0, 125.8, 125.24, 125.20, 120.8, 93.2, 73.5, 61.2, 38.0, 17.47, 17.40 and 14.5 ppm. **IR** (neat): 3056, 2974, 2873, 1712, 1595, 1491, 1452, 1381, 1266, 1224, 1160, 1033, 890, 859, 740, 515 and 431 cm⁻¹.

M.P: 78-80 °C

TLC: R_f = 0.4 (9:1; hexane: EtOAc).

Ethyl 1-cyclopentyl-1-phenyl-1,3-dihydronaphtho[2,3-*c*]furan-4-carboxylate (**1e**)



To a solution of ester **S₈** (150 mg, 0.388 mmol) and phenol (364 mg, 3.88 mmol) in 1,2-DCB (10 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **1e** (110 mg, 0.284 mmol, 73%) as a yellow oil.

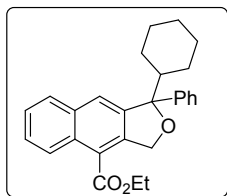
¹H NMR (400 MHz, CDCl₃): δ = 8.80 (1 H, d, J = 6.9 Hz), 7.95 (1 H, s), 7.88 (1 H, d, J = 6.4 Hz), 7.61 (2 H, d, J = 6.5 Hz), 7.53 (1 H, t, J = 5.6 Hz), 7.48 (1 H, t, J = 5.8 Hz), 7.31 (2 H, t, J = 6.1 Hz), 7.18 (1 H, t, J = 5.8 Hz), 5.50 (2 H, q, J = 11.2 Hz), 4.41-4.50 (2 H, m), 2.99-3.04 (1 H, m), 1.39-1.61 (5 H, m), 1.25-1.31 (3 H, m), 0.91 (3 H, t, J = 5.5 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.0, 145.3, 144.1, 142.8, 134.1, 131.4, 128.8, 128.3, 127.5, 126.8, 126.0, 125.8, 125.2, 120.8, 91.7, 73.4, 61.2, 50.2, 39.1, 27.7, 27.6, 26.2, 25.8 and 14.2 ppm.

IR (neat): 3056, 2955, 2868, 1712, 1443, 1265, 1225, 1164, 1033, 897, 741 and 499 cm⁻¹.

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 1-cyclohexyl-1-phenyl-1,3-dihydronaphtho[2,3-*c*]furan-4-carboxylate (**1f**)



To a solution of ester **S**₁₁ (160 mg, 0.4 mmol) and phenol (376 mg, 4.0 mmol) in 1,2-DCB (8 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **1f** (120 mg, 0.30 mmol, 75%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.79 (1 H, d, *J* = 8.5 Hz), 7.94 (1 H, s), 7.90 (1 H, d, *J* = 7.5 Hz), 7.59 (2 H, dd, *J* = 1.2 & 8.5 Hz), 7.47-7.55 (2 H, m), 7.32 (2 H, t, *J* = 8.0 Hz), 7.23 (1 H, d, *J* = 6.5 Hz), 5.48 (2 H, q, *J* = 9.8 Hz), 4.42-4.47 (2 H, m), 2.25-2.28 (1 H, m), 1.62-1.71 (4 H, m), 1.44 (3 H, t, *J* = 7.2 Hz), 1.13-1.36 (6 H, m) ppm.

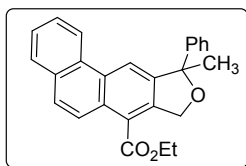
¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 144.4, 143.1, 142.9, 134.0, 131.3, 128.8, 128.4, 127.5, 126.8, 126.0, 125.8, 125.2, 120.6, 115.4, 93.2, 73.5, 61.3, 47.9, 27.3, 27.2, 26.8, 26.6, 26.4 and 14.5 ppm.

IR (neat): 3057, 2983, 2932, 2859, 1712, 1590, 1445, 1265, 1167, 1035, 890, 742 and 515 cm⁻¹.

HR ESI-MS: [C₂₇H₂₈O₃Na]⁺ = [M+Na]⁺ requires 423.1931; found 423.1922

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 10-methyl-10-phenyl-8,10-dihydrophenanthro[2,3-*c*]furan-7-carboxylate (**1g**)



To a solution of ester **S**₁₇ (150 mg, 0.392 mmol) and phenol (369 mg, 3.92 mmol) in 1,2-DCB (10 mL) was taken in a reaction tube. The reaction tube was kept at 150°C. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **1g** (90 mg, 0.235 mmol, 60%) as a yellow oil.

1g (90 mg, 0.235 mmol, 60%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.68 (2 H, m), 7.91 (1 H, d, *J* = 7.6 Hz), 7.83 (1 H, d, *J* = 9.4 Hz), 7.61-7.69 (2 H, m), 7.55 (2 H, d, *J* = 7.8 Hz), 7.34 (2 H, t, *J* = 7.4 Hz), 7.25 (2 H, t, *J* = 7.1 Hz), 5.47 (2 H, q, *J* = 14.4 Hz), 4.47-4.54 (2 H, m), 2.03 (3 H, s), 1.47 (3 H, t, *J* = 7.1 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.3, 145.3, 145.0, 141.3, 131.7, 130.1, 129.7, 128.67, 128.63, 128.5, 127.5, 127.2, 126.9, 125.5, 123.8, 122.8, 120.7, 119.5, 115.4, 88.4, 72.4, 61.5, 28.7 and 14.5 ppm.

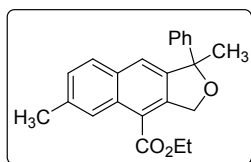
IR (neat): 3054, 2980, 2927, 2859, 1713, 1600, 1492, 1449, 1367, 1310, 1225, 1176, 1115, 1067, 1027, 872, 827, 748 and 501 cm^{-1} .

HR ESI-MS: $[\text{C}_{26}\text{H}_{23}\text{O}_3]^+ = [\text{M}+\text{H}]^+$ requires : 383.1642; found 383.1636

M.P: 98-100 $^\circ\text{C}$

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

Ethyl 1,6-dimethyl-1-phenyl-1,3-dihydronaphtho[2,3-c]furan-4-carboxylate (**1h**)



To a solution of ester **S**₂₀ (100 mg, 0.289 mmol) and phenol (271 mg, 2.89 mmol) in 1,2-DCB (6 mL) was taken in a reaction tube. The reaction tube was kept at 150 $^\circ\text{C}$. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan

1i (75 mg, 0.216 mmol, 75%) as a yellow oil.

¹H NMR (400 MHz, CDCl_3): $\delta = 8.61$ (1 H, s), 7.79 (1 H, s), 7.76 (1 H, d, $J = 8.4$ Hz), 7.52 (2 H, dd, $J = 0.7$ & 7.9 Hz), 7.30-7.35 (3 H, m), 7.21-7.25 (1 H, m), 5.34 (2 H, q, $J = 15.0$ Hz), 4.42-4.50 (2 H, m), 2.53 (3 H, s), 1.94 (3 H, s), 1.44 (3 H, t, $J = 7.1$ Hz) ppm.

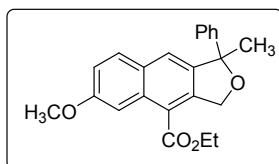
¹³C NMR (100 MHz, CDCl_3): $\delta = 167.1, 145.3, 143.6, 142.4, 137.6, 132.2, 131.7, 131.5, 128.5, 128.4, 127.3, 125.4, 125.0, 124.9, 120.2, 87.6, 72.3, 61.2, 28.8, 22.3$ and 14.5 ppm.

IR (neat): 3056, 2984, 2931, 2861, 1712, 1610, 1431, 1265, 1177, 1031, 895, 741 and 439 cm^{-1}

HR ESI-MS: $[\text{C}_{23}\text{H}_{22}\text{O}_3\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 369.1467; found 369.1467

TLC: $R_f = 0.4$ (9:1; hexane:EtOAc).

Ethyl 6-methoxy-1-methyl-1-phenyl-1,3-dihydronaphtho[2,3-c]furan-4-carboxylate (**1i**)



To a solution of ester **S**₂₃ (100 mg, 0.276 mmol) and phenol (259 mg, 2.76 mmol) in 1,2-DCB (6 mL) was taken in a reaction tube. The reaction tube was kept at 150 $^\circ\text{C}$. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan

1j (65 mg, 0.179 mmol, 65%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.38 (1 H, s), 7.75 (2 H, d, *J* = 9.3 Hz), 7.51 (2 H, d, *J* = 7.6 Hz), 7.32 (2 H, t, *J* = 7.4 Hz), 7.23 (1 H, t, *J* = 7.5 Hz), 7.17 (1 H, dd, *J* = 1.9 & 8.9 Hz), 5.45 (2 H, q, *J* = 15.0 Hz), 4.42-4.50 (2 H, m), 3.95 (3 H, s), 1.94 (3 H, s), 1.46 (3 H, t, *J* = 7.1 Hz) ppm.

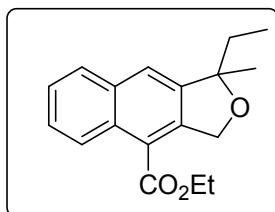
¹³C NMR (100 MHz, CDCl₃): δ = 167.2, 159.3, 145.5, 143.5, 142.4, 133.2, 133.0, 130.0, 129.5, 128.4, 127.3, 125.4, 119.1, 119.0, 104.6, 87.6, 72.8, 61.1, 55.4, 28.8 and 14.5 ppm.

IR (neat): 3056, 2984, 2933, 2858, 1708, 1620, 1503, 1433, 1374, 1265, 1180, 1032, 895, 743, 471 and 422 cm⁻¹.

HR ESI-MS: [C₂₃H₂₃O₄]⁺ = [M+H]⁺ requires 363.1591 ; found 363.1613

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 1-ethyl-1-methyl-1,3-dihydro[2,3-*c*]furan-4-carboxylate (**1n**)



To a solution of ester S11 (120 mg, 0.422 mmol) and phenol (397 mg, 4.22 mmol) in 1,2-DCB (12 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 minutes, the reaction further purified by column chromatography (19:1, hexane:EtOAc) gave the furan **1n** (59 mg, 0.21 mmol, 50%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.84 (1 H, d, *J* = 8.6 Hz), 7.86 (1 H, d, *J* = 8.4 Hz), 7.65 (1 H, s), 7.57 (1 H, t, *J* = 8.3 Hz), 7.50 (1 H, t, *J* = 7.7 Hz), 5.40 (2 H, s), 4.48 (2 H, q, *J* = 7.0 Hz), 1.97-1.87 (2 H, m), 1.55 (3 H, s), 1.46 (3 H, t, *J* = 7.1 Hz) and 0.85 (3 H, t, *J* = 7.2 Hz) ppm.

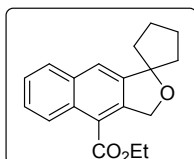
¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 144.6, 143.1, 134.0, 131.4, 128.6, 127.4, 126.0, 125.9, 124.1, 120.8, 87.7, 72.7, 61.3, 34.5, 27.2, 14.5 and 8.6 ppm.

IR (neat): 2967, 2924, 2853, 2364, 1715, 1593, 1453, 1429, 1221, 1143, 1034, 872, 752 and 612 cm⁻¹.

HR ESI-MS: [C₁₈H₂₁O₃]⁺ = [M+H]⁺ requires 285.1485; found 285.1498

TLC: R_f = 0.4 (19:1, Hex/EtOAc).

Ethyl 3'-*H*-spiro[cyclopentane-1,1'-naphtho[2,3-*c*]furan]-4'-carboxylate (**3a**)



To a solution of ester **S**₂₆ (100 mg, 0.337 mmol) and phenol (317 mg, 3.37 mmol) in 1,2-DCB (8 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 min, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **3a** (60 mg, 0.202 mmol, 60%) as a yellow oil.

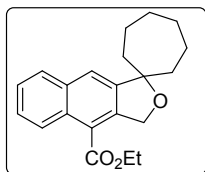
¹H NMR (400 MHz, CDCl₃): δ = 8.82 (1 H, d, *J* = 7.2 Hz), 7.83 (1 H, t, *J* = 6.6 Hz), 7.69 (1 H, d, *J* = 7.8 Hz), 7.53-7.55 (1 H, m), 7.48 (1 H, t, *J* = 6.3 Hz), 5.33 (2 H, s), 4.47 (2 H, q, *J* = 5.7 Hz), 2.12-2.15 (2 H, m), 1.90-1.96 (6 H, m), 1.45 (3 H, t, *J* = 5.7 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 144.4, 143.2, 134.1, 131.2, 128.5, 127.3, 126.0, 125.9, 123.6, 120.6, 95.0, 71.8, 61.2, 40.7, 25.0 and 14.5 ppm.

IR (neat): 3057, 2969, 2872, 1713, 1609, 1433, 1265, 1226, 1158, 1034, 895, 741 and 541 cm⁻¹.

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 3'*H*-spiro[cycloheptane-1,1'-naphtho[2,3-*c*]furan]-4'-carboxylate (3c**)**



To a solution of ester **S**₃₂ (150 mg, 0.462 mmol) and phenol (435 mg, 4.62 mmol) in 1,2-DCB (10 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **3c** (100 mg, 0.308 mmol, 67%) as a yellow oil.

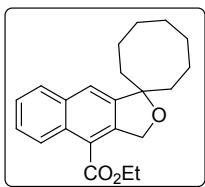
¹H NMR (400 MHz, CDCl₃): δ = 8.80 (1 H, d, *J* = 8.4 Hz), 7.85 (1 H, d, *J* = 7.8 Hz), 7.74 (1 H, s), 7.55 (1 H, t, *J* = 6.8 Hz), 7.49 (1 H, t, *J* = 6.9 Hz), 5.33 (2 H, s), 4.47 (2 H, q, *J* = 7.1 Hz), 2.03-2.04 (2 H, m), 1.96 (2 H, t, *J* = 10.0 Hz), 1.61-1.82 (4 H, m), 1.39-1.47 (2 H, m), 1.25-1.31 (2 H, m), 0.91 (3 H, t, *J* = 7.0 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 147.7, 142.6, 134.0, 131.2, 128.6, 127.3, 126.0, 125.8, 123.5, 89.4, 71.4, 61.2, 40.9, 29.7, 23.0 and 14.5 ppm.

IR (neat): 3058, 2862, 1716, 1455, 1376, 1224, 1158, 1032, 896, 859, 746 and 519 cm⁻¹.

TLC: R_f = 0.4 (9:1; hexane: EtOAc).

Ethyl 3'*H*-spiro[cyclooctane-1,1'-naphtho[2,3-*c*]furan]-4'-carboxylate (3d**)**



To a solution of ester **S**₃₂ (120 mg, 0.355 mmol) and phenol (333 mg, 3.55 mmol) in 1,2-DCB (6 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan

3d (60 mg, 0.177 mmol, 50%) as a yellow oil.

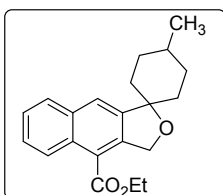
¹H NMR (400 MHz, CDCl₃): δ = 8.79 (1 H, d, *J* = 8.6 Hz), 7.86 (1 H, dd, *J* = 1.1 & 8.5 Hz), 7.71 (1 H, s), 7.56 (1 H, ddd, *J* = 1.4, 3.2 & 6.8 Hz), 7.49 (1 H, td, *J* = 1.2 & 8.1 Hz), 5.31 (2 H, s), 4.47 (2 H, q, *J* = 7.2 Hz), 2.07-2.14 (1 H, m), 1.92-1.98 (1 H, m), 1.71-1.80 (3 H, m), 1.59-1.62 (1 H, m), 1.39-1.46 (4 H, m), 1.25-1.31 (4 H, m), 0.91 (3 H, t, *J* = 6.8 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 146.1, 142.9, 133.7, 131.2, 128.6, 127.3, 126.0, 125.8, 124.0, 121.0, 89.1, 71.4, 61.2, 39.1, 35.7, 25.7, 23.4 and 14.2 ppm.

IR (neat): 3056, 2981, 2930, 2862, 1712, 1429, 1265, 1228, 1162, 1032, 897 and 743 cm⁻¹.

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 4-methyl-3'*H*-spiro[cyclohexane-1,1'-naphtho[2,3-*c*]furan]-4'-carboxylate (**3e**)



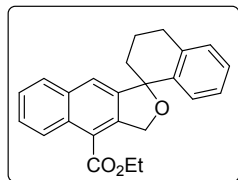
To a solution of ester **S**₃₅ (110 mg, 0.339 mmol) and phenol (319 mg, 3.39 mmol) in 1,2-DCB (8 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 min, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **3e** (65 mg, 0.20 mmol, 59%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.78 (1 H, d, *J* = 8.5 Hz), 7.86-7.89 (2 H, m), 7.56 (1 H, t, *J* = 8.0 Hz), 7.50 (1 H, t, *J* = 7.5 Hz), 5.35 (2 H, s), 4.48 (2 H, q, *J* = 5.8 Hz), 1.85-1.98 (5 H, m), 1.75-1.80 (2 H, m), 1.51-1.59 (2 H, m), 1.43-1.47 (3 H, m), 1.12 (3 H, d, *J* = 6.6 Hz) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ = 167.2, 145.5, 143.2, 133.7, 131.2, 128.7, 127.4, 126.0, 125.7, 124.5, 121.0, 85.8, 71.3, 61.2, 34.3, 29.7, 29.0, 19.7 and 14.5 ppm.

IR (neat): 3057, 2932, 2865, 1714, 1610, 1450, 1377, 1265, 1228, 1169, 1034, 890, 614 and 429 cm⁻¹.

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 3,4-dihydro-2*H*,3'*H*-spiro[naphthalene-1,1'-naphtho[2,3-*c*]furan]-4'-carboxylate (**3f**)



To a solution of ester **S₃₈** (150 mg, 0.418 mmol) and phenol (393 mg, 4.18 mmol) in 1,2-DCB (10 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 min, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **3f** (100 mg, 0.279 mmol, 67%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.86 (1 H, d, *J* = 8.7 Hz), 7.76 (1 H, d, *J* = 8.0 Hz), 7.55-7.58 (2 H, m), 7.48 (1 H, t, *J* = 7.3 Hz), 7.19-7.20 (2 H, m), 7.03-7.07 (1 H, m), 6.88 (1 H, d, *J* = 7.8 Hz), 5.44-5.57 (2 H, m), 4.49-4.54 (2 H, m), 2.95-2.97 (2 H, m), 2.27-2.32 (1 H, m), 1.99-2.17 (3 H, m), 1.49 (3 H, t, *J* = 7.1 Hz) ppm.

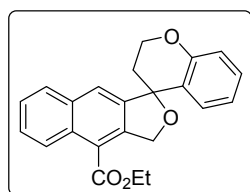
¹³C NMR (100 MHz, CDCl₃): δ = 167.2, 146.0, 143.1, 139.2, 137.8, 134.1, 131.4, 129.5, 129.0, 128.7, 128.4, 127.9, 127.6, 126.4, 126.1, 125.8, 120.7, 86.5, 72.2, 61.4, 37.0, 29.7, 19.7 and 14.5 ppm.

IR (neat): 3056, 2985, 2938, 2864, 1713, 1607, 1430, 1265, 1029, 896, 741, 507 and 436 cm⁻¹.

HR ESI-MS: [C₂₄H₂₃O₃]⁺ = [M+H]⁺ requires 359.1642; found 359.1647

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 3'*H*-spiro [chromane-4,1'-naphtho[2,3-*c*]furan]-4'-carboxylate (**3g**)



To a solution of ester **S₄₄** (100 mg, 0.27 mmol) and phenol (253 mg, 2.70 mmol) in 1,2-DCB (6 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 min, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **3g** (60 mg, 0.166 mmol, 62%) as a yellow oil.

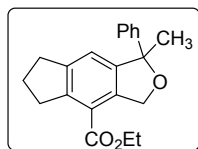
¹H NMR (400 MHz, CDCl₃): δ = 8.88 (1 H, d, *J* = 8.7 Hz), 7.79 (1 H, d, *J* = 8.1 Hz), 7.60 (2 H, t, *J* = 10.0 Hz), 7.50 (1 H, t, *J* = 7.7 Hz), 7.21 (1 H, t, *J* = 8.2 Hz), 6.93 (1 H, d, *J* = 8.7 Hz), 6.81 (2 H, t, *J* = 7.6 Hz), 5.57 (1 H, d, *J* = 15.0 Hz), 5.45 (1 H, d, *J* = 15.0 Hz), 4.42-4.55 (4 H, m), 2.28-2.38 (2 H, m), 1.49 (3 H, t, *J* = 7.2 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 167.0, 155.2, 143.6, 143.1, 134.1, 131.6, 130.0, 129.77, 129.72, 126.3, 125.9, 125.8, 125.2, 120.9, 120.7, 117.2, 115.4, 82.5, 72.0, 63.4, 61.5, 36.1 and 14.5 ppm.

IR (neat): 3056, 2985, 2932, 2862, 1712, 1604, 1428, 1265, 1162, 1028, 898, 743 and 442 cm^{-1} .

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

Ethyl 1-methyl-1-phenyl-3,5,6,7-tetrahydro-1*H*-indeno[5,6-*c*]furan-4-carboxylate (20a)



To a solution of ester **S**₄₉ (80 mg, 0.25 mmol) in 1,2-DCB (5 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 15 min, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **20a** (50 mg, 0.156 mmol, 62%) as a white solid.

¹H NMR (400 MHz, CDCl_3): $\delta = 7.47$ (2 H, dd, $J = 1.4$ & 8.6 Hz), 7.30 (2 H, t, $J = 7.3$ Hz), 7.20-7.24 (2 H, m), 5.40 (2 H, q, $J = 14.3$ Hz), 4.31-4.36 (2 H, m), 3.17-3.31 (2 H, m), 2.89 (2 H, t, $J = 7.5$ Hz), 2.03-2.13 (2 H, m), 1.85 (3 H, s), 1.38 (3 H, t, $J = 7.1$ Hz) ppm.

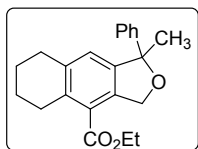
¹³C NMR (100 MHz, CDCl_3): $\delta = 166.7, 146.7, 146.2, 146.1, 145.8, 139.5, 128.4, 127.1, 125.2, 121.8, 121.2, 87.8, 73.1, 60.8, 33.8, 32.5, 28.50, 25.58$ and 14.5 ppm.

IR (neat): 3056, 2980, 2862, 1711, 1598, 1440, 1261, 1181, 1027, 895, 749, 543, 490 and 425 cm^{-1}

M.P: 98-100 °C

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

Ethyl 1-methyl-1-phenyl-1,3,5,6,7,8-hexahydronaphtho[2,3-*c*]furan-4-carboxylate (20b)



To a solution of ester **S**₅₁ (150 mg, 0.449 mmol) and phenol (422 mg, 4.49 mmol) in 1,2-DCB (10 mL) was taken in a reaction tube. The reaction tube was kept at 150°C. After 15 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **20b** (90 mg, 0.269 mmol, 60%) as a yellow oil.

¹H NMR (400 MHz, CDCl_3): $\delta = 7.45$ -7.48 (2 H, m), 7.30 (2 H, t, $J = 8.3$ Hz), 7.21 (1 H, t, $J = 7.2$ Hz), 7.06 (1 H, s), 5.23-5.32 (2 H, m), 4.30-4.35 (2 H, m), 2.95-3.07 (2 H, m), 2.75-2.80 (2 H, m), 1.83 (3 H, s), 1.72-1.76 (4 H, m), 1.36 (3 H, t, $J = 7.1$ Hz) ppm.

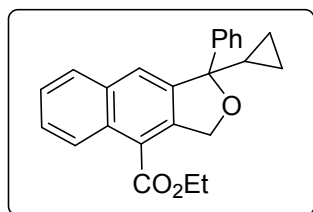
^{13}C NMR (100 MHz, CDCl_3): δ = 167.4, 145.9, 143.9, 138.1, 138.0, 137.7, 128.3, 127.1, 125.7, 125.1, 124.8, 88.1, 72.5, 60.8, 30.5, 28.4, 27.9, 23.2, 22.4 and 14.4 ppm.

IR (neat): 3055, 2934, 2864, 1717, 1599, 1447, 1260, 1184, 1026, 908, 874, 742 and 544 cm^{-1} .

HR ESI-MS: $[\text{C}_{22}\text{H}_{24}\text{O}_3\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 359.1618 ; found 359.1609

TLC: R_f = 0.4 (9:1; hexane:EtOAc).

Ethyl 1-cyclopropyl-1-phenyl-1,3-dihydronaphtho[2,3-*c*]furan-4-carboxylate (**5b**)



To a solution of ester **S**₄₇ (400 mg, 0.10 mmol) and phenol (97 mg, 1.03 mmol) in 1,2-DCB (15 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 30 minutes, the reaction mixture was directly poured inside the column eluted with (9:1, hexane: EtOAc) gave the furan **5b** (300 mg, 0.06 mmol, 62%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): δ = 8.84 (1 H, d, J = 8.7 Hz), 7.85 (1 H, d, J = 7.8 Hz), 7.84 (1 H, s), 7.58 (2 H, dd, J = 1.3 & 9.2 Hz), 7.53-7.56 (1 H, m), 7.44-7.50 (1 H, m), 7.31 (2 H, t, J = 7.24 Hz), 7.21-7.25 (1 H, m), 5.42 (2 H, q, J = 12.7 Hz), 4.43-4.49 (2 H, m), 1.62-1.69 (1 H, m), 1.44 (3 H, t, J = 7.1 Hz), 0.58-0.63 (1 H, m), 0.40-0.52 (3 H, m) ppm.

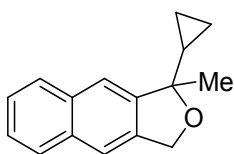
^{13}C NMR (100 MHz, CDCl_3): δ = 167.0, 144.2, 143.7, 143.0, 133.9, 131.4, 128.8, 128.2, 127.6, 127.4, 126.5, 126.1, 126.0, 125.9, 120.8, 89.2, 73.1, 61.3, 20.7, 14.5, 1.58 and 1.32 ppm. IR (neat): 3059, 2988, 2932, 2863, 1712, 1600, 1496, 1446, 1376, 1266, 1223, 1162, 1031, 901, 754, 513 and 428 cm^{-1}

HR ESI-MS: $[\text{C}_{24}\text{H}_{23}\text{O}_3]^+ = [\text{M}+\text{H}]^+$ requires 359.1642 ; found 359.1663

M.P: 90-92 °C

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

1-Cyclopropyl-1-methyl-1,3-dihydronaphtho[2,3-*c*]furan (**8b**)



To a solution of ester **S**₁₁ (120 mg, 0.535 mmol) and phenol (503 mg, 5.35 mmol) in 1,2-DCB (12 mL) was taken in a reaction tube. The reaction tube was kept at 150 °C. After 24 h, the reaction further

purified by column chromatography (19:1, hexane:EtOAc) gave the furan 10 (45 mg, 0.20 mmol, 38%) as **8b** a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.85-7.80 (2 H, m), 7.61 (1 H, s), 7.55 (1 H, s), 7.45-7.33 (2 H, m), 5.17 (2 H, s), 1.59 (3 H, s), 1.33-1.27 (1 H, m), 0.48-0.44 (1 H, m), 0.38-0.33 (1 H, m) and 0.29-0.22 (1 H, m) ppm.

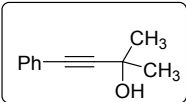
¹³C NMR (100 MHz, CDCl₃): δ = 144.5, 138.8, 133.4, 133.2, 128.2, 127.9, 125.8, 125.7, 119.7, 119.3, 86.8, 71.0, 26.5, 21.1, 1.3, and 0.77 ppm.

IR (neat): 2958, 2925, 2852, 2366, 1602, 1456, 1367, 1270, 1101, 1045, 1021, 873, 750 and 615 cm⁻¹.

HR ESI-MS: [C₁₆H₁₇O]⁺ = [M+H]⁺ requires 225.1274; found 225.1279

TLC: R_f = 0.6 (19:1, Hex/EtOAc).

2-Methyl-4-phenylbut-3-yn-2-ol (**S₀**)

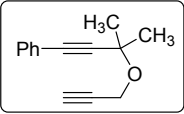
Followed procedure A: To an ice-cold solution of aldehyde (300 mg, mmol) in THF (5 mL) was added, the solution of (phenylethynyl)  5.17 lithium [3 mL in THF 1.3 eq., 6.72 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C for 2 h. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₀** (420 mg, 2.62 mmol, 51%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.40-7.42 (2 H, m), 7.29-7.30 (3 H, m), 2.14 (1 H, br, s), 1.62 (6 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.7, 128.4, 128.3, 122.8, 93.8, 82.2, 65.7 and 31.6 ppm **IR** (neat): 3401, 3052, 2983, 2928, 1438, 1252, 1035, 894 and 736 cm⁻¹

TLC: R_f = 0.4 (4:1; hexane:EtOAc).

(3-Methyl-3-(prop-2-yn-1-yloxy)but-1-yn-1-yl)benzene (**S₁**)

Followed procedure B: To an ice cold solution of alcohol **S₀** (350 mg, 2.18 mmol) was added to  a suspension of sodium hydride 60% (175 mg, 4.37 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (334 mg, 2.83 mmol,

and 0.2 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₁** (270 mg, 1.36 mmol, 62%) as a yellow oil.

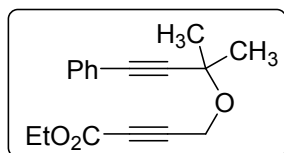
¹H NMR (400 MHz, CDCl₃): δ = 7.42 (2 H, dd, *J* = 1.8 & 6.0 Hz), 7.30 (3 H, dd, *J* = 1.8 & 4.3 Hz), 4.34 (2 H, d, *J* = 2.0 Hz), 2.43 (1 H, t, *J* = 2.0 Hz), 1.59 (6 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.8, 128.5, 128.4, 122.6, 90.2, 85.2, 81.1, 73.7, 71.9, 52.7 and 29.0 ppm.

IR (neat): 3300, 3051, 2985, 1604, 1502, 1432, 1264, 1112, 1068, 895 and 716 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

Ethyl 4-((2-methyl-4-phenylbut-3-yn-2-yl)oxy)but-2-ynoate (**S₂**)



Followed procedure C: To an ice-cold solution of alkyne **S₁** (260 mg, 1.33 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (1.73 mmol, 1.0 mL) after 30 minutes added Ethyl chloroformate (470 mg, 3.99 mmol, 0.4 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S₂** (220 mg, 0.81 mmol, 61%) as a yellow oil.

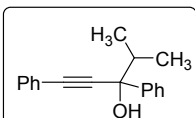
¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.43 (2 H, m), 7.30-7.31 (3 H, dd, *J* = 1.4 & 4.0 Hz), 4.46 (2 H, s), 4.21 (2 H, q, *J* = 5.7 Hz), 1.59 (6 H, s), 1.29 (3 H, t, *J* = 5.7 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 131.8, 128.6, 128.4, 122.4, 89.8, 85.7, 84.8, 77.3, 72.4, 62.1, 52.5, 28.9 and 14.1 ppm.

IR (neat): 3060, 2985, 2934, 2241, 1715, 1597, 1454, 1373, 1256, 1152, 1051, 869, 753, 694, 623, 546 and 488 cm⁻¹.

TLC: R_f = 0.5 (9:1; hexane: EtOAc).

4-Methyl-1,3-diphenylpent-1-yn-3-ol (**S₃**)



Followed procedure A: To an ice-cold solution of 1,3-diphenylprop-2-yn-1-one² (500 mg, 2.42 mmol) in THF (5 mL) was added, the solution of isopropylmagnesium bromide [3 mL in THF 1.3 eq., 14.7 mmol freshly

prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₃** (550 mg, 2.2 mmol, 91%) as a yellow oil.

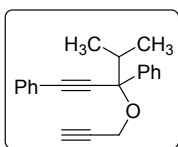
¹H NMR (400 MHz, CDCl₃): δ = 7.67 (2 H, d, *J* = 8.1 Hz), 7.48-7.51 (2 H, m), 7.30-7.38 (6 H, m), 2.43 (1 H, br, s), 2.16-2.22 (1 H, m), 1.14 (3 H, d, *J* = 6.5 Hz), 0.88 (3 H, d, *J* = 6.7 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 139.2, 135.6, 131.9, 128.7, 128.4, 128.3, 122.4, 119.4, 87.1, 85.6, 60.7, 40.4, 30.1 and 21.5 ppm.

IR (neat): 3430, 3060, 2968, 2931, 2878, 1597, 1486, 1451, 1375, 1335, 1266, 1173, 1007, 926, 862, 753, 696 and 509 cm⁻¹.

TLC: R_f = 0.4 (4:1; hexane:EtOAc).

(3-Methyl-3-(prop-2-yn-1-yloxy)but-1-yn-1-yl)benzene (S₄**)**



Followed procedure B: To an ice cold solution of alcohol **S₃** (300 mg, 1.2 mmol) was added to a suspension of sodium hydride 60% (96 mg, 2.4 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (184 mg, 1.56 mmol, and 0.1 mL) in THF (3 mL) was added slowly at 0 °C, and

the reaction mixture was stirred at room temperature for 12 h. Evaporation of the solvent. And purification of the crude by flash column chromatography (9:1 hexane:EtOAc) gave the alkyne **S₄** (250 mg, 0.868 mmol, 72%) as a yellow oil.

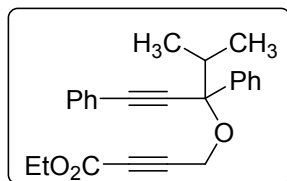
¹H NMR (400 MHz, CDCl₃): δ = 7.62 (2 H, dd, *J* = 1.3 & 8.4 Hz), 7.53-7.56 (2 H, m), 7.31-7.39 (6 H, m), 4.32 (1 H, dd, *J* = 2.4 & 14.8 Hz), 3.80 (1 H, dd, *J* = 2.4 & 14.8 Hz), 2.38 (1 H, t, *J* = 2.4 Hz), 2.18-2.25 (1 H, m), 1.23 (3 H, d, *J* = 6.6 Hz), 0.74 (3 H, d, *J* = 6.8 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 140.5, 131.9, 128.7, 128.5, 128.2, 128.1, 127.3, 122.6, 90.1, 86.1, 85.1, 80.8, 53.4, 40.7, 18.3 and 18.1 ppm.

IR (neat): 3303, 3056, 2979, 2930, 2875, 1601, 1485, 1438, 1379, 1328, 1265, 1060, 976, 899, 642 and 435 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

Ethyl 4-((4-methyl-1,3-diphenylpent-1-yn-3-yl)oxy)but-2-ynoate (S₅**)**



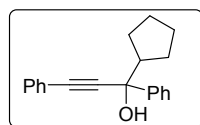
Followed procedure C: To an ice-cold solution of alkyne **S₄** (200 mg, 0.694 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.902 mmol, 0.6 mL) after 30 minutes added Ethyl chloroformate (106 mg, 0.902 mmol, 0.1 mL) 2 mL in THF at 0 °C for 3 h. Evaporation of the solvent. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S₅** (160 mg, 0.444 mmol, 64%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.61 (2 H, d, *J* = 7.4 Hz), 7.52-7.55 (2 H, m), 7.30-7.39 (6 H, m), 4.40 (1 H, d, *J* = 16.0 Hz), 4.20 (2 H, d, *J* = 7.1 Hz), 3.96 (1 H, d, *J* = 16.0 Hz), 2.17-2.24 (1 H, m), 1.28 (3 H, t, *J* = 6.7 Hz), 1.20 (3 H, d, *J* = 6.4 Hz), 0.74 (3 H, d, *J* = 6.7 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 140.1, 131.9, 128.8, 128.5, 128.3, 127.3, 125.8, 122.4, 90.6, 85.7, 85.5, 84.5, 62.0, 53.1, 40.6, 39.1, 18.2, 18.1 and 14.1 ppm.

IR (neat): 3056, 2974, 2874, 1713, 1600, 1446, 1374, 1261, 1051, 901, 741 and 536 cm⁻¹. **TLC:** R_f = 0.5 (9:1; hexane:EtOAc).

1-Cyclopentyl-1,3-diphenylprop-2-yn-1-ol (**S₆**)



Followed procedure A: To an ice-cold solution of (1,3-diphenylprop-2-yn-1-one)² (300 mg, 1.45 mmol) in THF (5 mL) was added, the solution of cyclopentylmagnesium bromide [3 mL in THF 1.3 eq., 1.89 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)] at 0 °C for 2 h. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₆** (250 mg, 0.905 mmol, 62%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.70 (2 H, dd, *J* = 1.4 & 7.2 Hz), 7.48-7.50 (2 H, m), 7.31-7.38 (5 H, m), 7.28 (1 H, ddd, *J* = 1.3, 2.6 & 6.4 Hz), 2.43-2.49 (2 H, m), 1.79-1.85 (2 H, m), 1.42-1.72 (5 H, m) ppm.

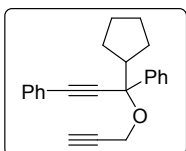
¹³C NMR (100 MHz, CDCl₃): δ = 144.9, 131.9, 128.5, 128.4, 128.1, 127.7, 126.0, 122.9, 90.8, 86.6, 76.9, 52.9, 29.0, 28.3, 26.1 and 25.9 ppm.

IR (neat): 3441, 3055, 2957, 1441, 1266, 1023, 901, 752, 605, 548, 500 and 455 cm⁻¹.

TLC: R_f = 0.4 (4:1; hexane:EtOAc).

(3-Cyclopentyl-3-(prop-2-yn-1-yloxy)prop-1-yne-1,3-diyl)dibenzene (**S**₇)

Followed procedure B: To an ice cold solution of alcohol **S**₆ (220 mg, 0.797 mmol) was added to a suspension of sodium hydride 60% (64 mg, 1.59 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (122 mg, 1.03 mmol, and 0.1 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S**₇ (190 mg, 0.605 mmol, 76%) as a yellow oil.



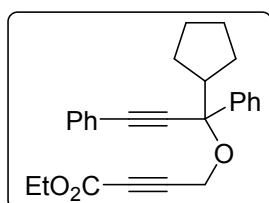
¹H NMR (400 MHz, CDCl₃): δ = 7.65 (2 H, dd, *J* = 1.4 & 7.1 Hz), 7.52-7.54 (2 H, m), 7.35-7.39 (5 H, m), 7.30 (1 H, ddd, *J* = 1.3, 2.7 & 6.2 Hz), 4.32 (1 H, dd, *J* = 2.4 & 14.8 Hz), 3.81 (1 H, dd, *J* = 2.5 & 14.8 Hz), 2.44-2.53 (1 H, m), 2.37 (1 H, t, *J* = 2.5 Hz), 1.89-1.97 (2 H, m), 1.55-1.717 (2 H, m), 1.35-1.44 (2 H, m), 1.21-1.27 (2 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 141.4, 131.9, 128.7, 128.5, 128.3, 128.0, 127.0, 122.7, 89.7, 86.8, 84.5, 80.8, 73.5, 53.3, 52.6, 29.0, 28.8, 26.0 and 25.7 ppm.

IR (neat): 3303, 3056, 2962, 2869, 1595, 1434, 1266, 1057, 898, 723, 542 and 422 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

Ethyl 4-((1-cyclopentyl-1,3-diphenylprop-2-yn-1-yl)oxy)but-2-ynoate (**S**₈)



Followed procedure C: To an ice-cold solution of alkyne **S**₇ (170 mg, 0.541 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.703 mmol, 0.22 mL) after 30 minutes added Ethyl chloroformate (191mg, 1.62 mmol, 0.2 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S**₈ (160 mg, 0.414 mmol, 77%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.63 (2 H, dd, *J* = 1.5 & 7.0 Hz), 7.52-7.54 (2 H, m), 7.34-7.39 (5 H, m), 7.31 (1 H, ddd, *J* = 1.3, 2.7 & 6.1 Hz), 4.42 (1 H, d, *J* = 16.0 Hz), 4.20 (2 H, q, *J* = 7.2 Hz), 3.97 (1 H, d, *J* = 16.0 Hz), 2.44-2.52 (1 H, m), 1.90-1.93 (2 H, m), 1.36-1.43 (3 H, m), 1.22-1.32 (5 H, m), 0.90 (3 H, t, *J* = 6.9 Hz) ppm.

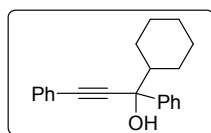
¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 140.9, 132.0, 128.8, 128.5, 128.4, 128.2, 127.0, 122.4, 90.1, 86.3, 84.9, 84.6, 74.5, 62.1, 53.0, 39.1, 28.9, 28.8, 26.1, 25.7 and 14.1 ppm.

IR (neat): 3056, 2957, 2869, 1712, 1601, 1444, 1372, 1262, 1042, 900, 740 and 520 cm^{-1} .

HR ESI-MS: $[\text{C}_{26}\text{H}_{26}\text{O}_3\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 409.1780; found 409.1779

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

1-Cyclohexyl-1,3-diphenylprop-2-yn-1-ol (**S₉**)



Followed procedure A: To an ice-cold solution of 1,3-diphenylprop-2-yn-1-one (500 mg, 2.42 mmol) in THF (5 mL) was added, the solution of cyclohexylmagnesium bromide [3 mL in THF 1.3 eq., 3.15 mmol freshly prepared from phenyl acetylene and $n\text{BuLi}$ (1.6 M in hexane)]. The reaction was stirred at 0 $^\circ\text{C}$. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₉** (650 mg, 2.24 mmol, 92%) as a yellow oil.

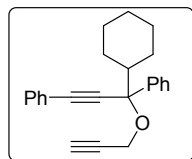
¹H NMR (400 MHz, CDCl_3): $\delta = 7.64\text{-}7.67$ (2 H, m), 7.46-7.49 (2 H, m), 7.27-7.36 (6 H, m), 2.60 (1 H, d, $J = 16.2$ Hz), 2.03 (1 H, d, $J = 11.2$ Hz), 1.77-1.79 (2 H, m), 1.54-1.68 (3 H, m), 1.11-1.32 (5 H, m) ppm.

¹³C NMR (100 MHz, CDCl_3): $\delta = 143.9, 131.8, 128.4, 128.3, 127.9, 127.6, 126.3, 122.8, 91.0, 86.8, 77.0, 50.2, 28.0, 27.6, 26.36$ and 26.30 ppm.

IR (neat): 3412, 3056, 2985, 2932, 2857, 1600, 1430, 1265, 1167, 1015, 897, 743 and 465 cm^{-1} .

TLC: $R_f = 0.5$ (4:1; hexane:EtOAc).

(3-Cyclohexyl-3-(prop-2-yn-1-yloxy)prop-1-yne-1,3-diyl)dibenzene (**S₁₀**)



Followed procedure B: To an ice cold solution of alcohol **S₉** (260 mg, 0.896 mmol) was added to a suspension of sodium hydride 60% (72 mg, 1.79 mmol) in THF (5 mL) anhydrous at 0 $^\circ\text{C}$. After 30 minutes propargyl bromide (137 mg, 1.16 mmol, and 0.1 mL) in THF (3 mL) was added slowly at 0 $^\circ\text{C}$. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₁₀** (220 mg, 0.67 mmol, 75%) as a yellow oil.

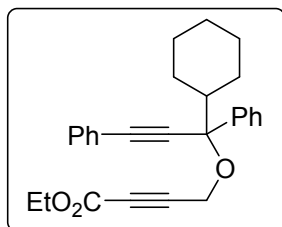
¹H NMR (400 MHz, CDCl_3): $\delta = 7.61$ (2 H, d, $J = 8.4$ Hz), 7.53-7.55 (2 H, m), 7.29-7.39 (6 H, m), 4.30 (1 H, dd, $J = 2.4$ & 14.8 Hz), 3.80 (1 H, dd, $J = 2.4$ & 14.8 Hz), 2.38 (1 H, t, $J = 2.4$ Hz), 2.28 (1 H, d, $J = 10.5$ Hz), 1.77-1.89 (2 H, m), 1.61-1.63 (2 H, m), 1.23-1.37 (3 H, m), 1.07-1.12 (3 H, m) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 140.5, 131.9, 128.7, 128.5, 128.2, 128.0, 127.3, 122.7, 90.0, 86.9, 84.5, 80.8, 73.5, 53.2, 50.3, 28.3, 28.0, 26.5, 26.4$ and 26.2 ppm.

IR (neat): 3303, 3056, 2984, 2931, 2859, 1600, 1437, 1265, 985, 897, 743, 532 and 447 cm^{-1} .

TLC: $R_f = 0.6$ (9:1; hexane:EtOAc).

Ethyl 4-((1-cyclohexyl-1,3-diphenylprop-2-yn-1-yl)oxy)but-2-ynoate (S_{11})



Followed procedure C: To an ice-cold solution of alkyne S_{10} (190 mg, 0.579 mmol) in THF (3 mL) was added $n\text{BuLi}$ in hexane (1.6 M) (0.75 mmol, 0.47 mL) after 30 minutes added Ethyl chloroformate (204 mg, 1.73 mmol, 0.2 mL) 2 mL in THF at 0°C . And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the

ester S_{11} (175 mg, 0.437 mmol, 75%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): $\delta = 7.59$ (2 H, d, $J = 7.5$ Hz), 7.54 (2 H, dd, $J = 2.4$ & 6.0 Hz), 7.29-7.39 (6 H, m), 4.40 (1 H, d, $J = 16.0$ Hz), 4.20 (2 H, q, $J = 7.1$ Hz), 3.95 (1 H, d, $J = 16.0$ Hz), 2.26 (1 H, d, $J = 12.2$ Hz), 1.78-1.84 (2 H, m), 1.61-1.63 (3 H, m), 1.22-1.32 (8 H, m) ppm.

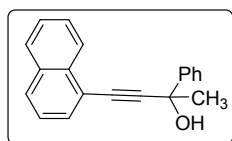
^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.4, 140.1, 131.9, 128.8, 128.5, 128.28, 128.24, 127.3, 125.9, 122.4, 90.4, 86.4, 84.8, 84.6, 62.1, 52.9, 50.2, 28.2, 28.0, 26.4, 26.3, 26.2$ and 14.1 ppm.

IR (neat): 3057, 2985, 2932, 2859, 1712, 1600, 1431, 1370, 1264, 1045, 895, 743, 709 and 432 cm^{-1} .

HR ESI-MS: $[\text{C}_{27}\text{H}_{28}\text{O}_3\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 423.1936; found 423.1934

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(Naphthalen-1-yl)-2-phenylbut-3-yn-2-ol (S_{12})



Followed procedure D: To a solution of 2-phenylbut-3-yn-2-ol (300 mg, 2.05 mmol) and 1-iodonaphthalene⁴ (878 mg, 2.46 mmol) in dry THF (10 mL) and DIPA (4 mL) were added $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ (14 mg, 0.0205 mmol) and CuI (58 mg, 0.307 mmol) 0°C . And purification of the crude mixture

by column chromatography (4:1, hexane: EtOAc) gave the alcohol S_{12} (400 mg, 1.47 mmol, 72%) as a yellow oil.

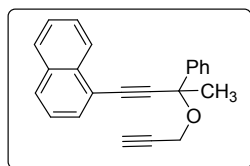
¹H NMR (400 MHz, CDCl₃): δ = 8.31 (1 H, d, *J* = 8.0 Hz), 7.78-7.80 (4 H, m), 7.67 (1 H, d, *J* = 6.8 Hz), 7.45-7.53 (2 H, m), 7.37 (3 H, t, *J* = 6.6 Hz), 7.29 (1 H, t, *J* = 7.0 Hz), 2.83 (1 H, br, s), 1.96 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 145.8, 133.4, 133.2, 129.0, 128.5, 128.4, 127.8, 126.9, 126.5, 126.1, 125.24, 125.20, 125.1, 120.2, 97.5, 83.1, 70.7 and 33.6 ppm.

IR (neat): 3426, 3056, 2986, 2930, 1591, 1498, 1447, 1397, 1327, 1268, 1147, 1085, 1026, 928, 898, 740, 560 and 443 cm⁻¹.

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

1-(3-Phenyl-3-(prop-2-yn-1-yloxy)but-1-yn-1-yl)naphthalene (S₁₃)



Followed procedure B: To an ice cold solution of alcohol S₁₂ (220 mg, 0.808 mmol) was added to a suspension of sodium hydride 60% (67 mg, 1.61 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (123 mg, 1.05 mmol, and 0.1 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne S₁₃ (200 mg, 0.645 mmol, 80%) as a yellow oil.

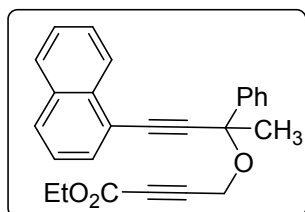
¹H NMR (400 MHz, CDCl₃): δ = 8.35 (1 H, d, *J* = 8.1 Hz), 7.86 (2 H, d, *J* = 7.8 Hz), 7.77 (3 H, d, *J* = 6.8 Hz), 7.53-7.59 (2 H, m), 7.40-7.47 (3 H, m), 7.34 (1 H, t, *J* = 6.8 Hz), 4.45 (1 H, d, *J* = 14.7 Hz), 4.02 (1 H, d, *J* = 14.8 Hz), 2.42 (1 H, s), 1.98 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 142.3, 133.5, 133.3, 131.0, 129.3, 128.7, 128.5, 128.3, 127.1, 126.6, 126.2, 126.1, 125.3, 120.1, 93.4, 86.5, 80.5, 77.6, 73.9, 53.6 and 33.2 ppm.

IR (neat): 3295, 3057, 2984, 2928, 2862, 1733, 1589, 1496, 1449, 1379, 1228, 1082, 915, 770, 697, 633 and 567 cm⁻¹

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

Ethyl 4-((4-(naphthalen-1-yl)-2-phenylbut-3-yn-2-yl)oxy)but-2-ynoate (S₁₄)



Followed procedure C: To an ice-cold solution of alkyne S₁₃ (180 mg, 0.580 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.75 mmol, 0.47 mL) after 30 minutes added Ethyl chloroformate (205 mg, 1.74 mmol, 0.1 mL) 2 mL in THF at 0 °C. And purification

of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S₁₄** (155 mg, 0.405 mmol, 70%) as a yellow oil.

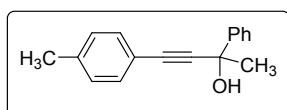
¹H NMR (400 MHz, CDCl₃): δ = 8.32 (1 H, d, *J* = 7.9 Hz), 7.87 (2 H, d, *J* = 8.0 Hz), 7.76 (3 H, d, *J* = 6.8 Hz), 7.52-7.60 (2 H, m), 7.35-7.47 (4 H, m), 4.54 (1 H, d, *J* = 16.0 Hz), 4.10-4.21 (3 H, m), 1.97 (3 H, s), 1.25 (3 H, t, *J* = 7.1 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.3, 141.9, 133.4, 133.3, 131.1, 129.4, 128.7, 128.54, 128.51, 127.2, 126.6, 126.2, 126.0, 125.3, 119.9, 92.9, 87.0, 84.1, 78.0, 77.5, 62.1, 53.2, 33.0 and 14.0 ppm.

IR (neat): 3057, 2985, 2934, 2863, 1713, 1445, 1374, 1262, 1178, 1080, 1032, 740 and 478 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

2-Phenyl-4-(p-tolyl)but-3-yn-2-ol (**S₁₅**)



Followed procedure D: To a solution of 2-phenylbut-3-yn-2-ol (300 mg, 2.05 mmol) and 4-iodo toluene (536 mg, 2.46 mmol) in dry THF (10 mL) and DIPA (4 mL) were added [(Ph₃P)₂PdCl₂] (14 mg, 0.0205 mmol) and CuI (58 mg, 0.307 mmol) at 0 °C. And purification of the crude mixture by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₁₅** (400 mg, 1.69 mmol, 83%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.72 (2 H, d, *J* = 7.2 Hz), 7.36-7.39 (4 H, m), 7.30 (1 H, t, *J* = 7.0 Hz), 7.12 (2 H, d, *J* = 7.7 Hz), 2.48 (1 H, br, s), 2.35 (3 H, s), 1.85 (3 H, s) ppm.

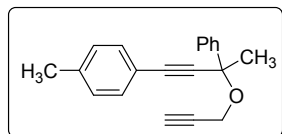
¹³C NMR (100 MHz, CDCl₃): δ = 145.9, 138.7, 131.7, 129.1, 128.4, 127.8, 125.1, 119.5, 91.8, 85.2, 70.5, 33.4 and 21.6 ppm

IR (neat): 3435, 3055, 2986, 2931, 1508, 1441, 1327, 1266, 1134, 1084, 1038, 934, 896, 818 and 741 cm⁻¹.

TLC: R_f = 0.4 (4:1; hexane: EtOAc).

1-Methyl-4-(3-phenyl-3-(prop-2-yn-1-yloxy)but-1-yn-1-yl)benzene (**S₁₆**)

Followed procedure B: To an ice cold solution of alcohol **S₁₅** (350 mg, 1.48 mmol) was added to a suspension of sodium hydride 60% (118 mg, 2.96 mmol) in THF (7



mL) anhydrous at 0 °C. After 30 minutes propargylic bromide (227 mg, 1.92 mmol, and 0.13 mL) in THF (3 mL) was added slowly at 0 °C. And Purification of the crude by flash column chromatography (9:1 hexane:EtOAc) gave the alkyne **S**₁₆ (300 mg, 1.08 mmol, 73%) as a yellow oil.

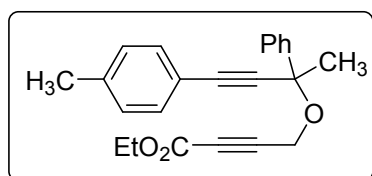
¹H NMR (400 MHz, CDCl₃): δ = 7.68 (2 H, d, *J* = 7.4 Hz), 7.37-7.43 (4 H, m), 7.32 (1 H, t, *J* = 7.2 Hz), 7.15 (2 H, d, *J* = 7.8 Hz), 4.34 (1 H, dd, *J* = 2.4 & 15.0 Hz), 3.84 (1 H, dd, *J* = 2.4 & 14.7 Hz), 2.41 (1 H, t, *J* = 2.4 Hz), 2.37 (3 H, s), 1.85 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 142.3, 138.9, 131.8, 129.2, 128.5, 128.2, 126.1, 119.3, 87.6, 80.5, 77.2, 76.8, 73.8, 53.3, 33.0 and 27.0 ppm.

IR (neat): 3303, 3056, 2987, 2931, 2865, 1507, 1432, 1266, 1151, 1082, 895, 742 and 529 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

Ethyl 4-((2-phenyl-4-(p-tolyl)but-3-yn-2-yl)oxy)but-2-ynoate **S₁₇**



Followed procedure C: To an ice-cold solution of alkyne **S**₁₆ (200 mg, 0.729 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.948 mmol, 0.6 mL) after 30 minutes added Ethyl chloroformate (258 mg, 2.18 mmol, 0.24 mL) 2 mL in THF at 0

°C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S**₁₇ (180 mg, 0.52 mmol, 71%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.66 (2 H, dd, *J* = 1.4 & 8.5 Hz), 7.37-7.43 (4 H, m), 7.32 (1 H, ddd, *J* = 1.3, 2.6 & 6.2 Hz), 7.16 (2 H, d, *J* = 7.8 Hz), 4.43 (1 H, d, *J* = 16.0 Hz), 4.20 (2 H, q, *J* = 7.1 Hz), 4.01 (1 H, d, *J* = 16.0 Hz), 2.37 (3 H, s), 1.85 (3 H, s), 1.28 (3 H, t, *J* = 7.1 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.3, 141.8, 139.1, 131.8, 129.2, 128.6, 128.3, 126.2, 119.1, 89.0, 87.2, 84.2, 77.6, 77.3, 62.1, 53.0, 32.8, 21.6 and 14.1 ppm.

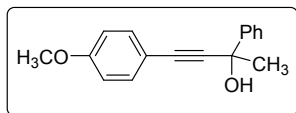
IR (neat): 3052, 2984, 2927, 2816, 1706, 1602, 1498, 1432, 1369, 1263, 1165, 1070, 1028, 890, 842, 738 and 442 cm⁻¹

HR ESI-MS: [C₂₃H₂₂O₃Na]⁺ = [M+Na]⁺ requires 369.1461; found 370.1506

TLC: R_f = 0.5 (9:1; hexane:EtOAc).

4-(4-Methoxyphenyl)-2-phenylbut-3-yn-2-ol (**S**₁₈)

Followed procedure D: To a solution of 2-phenylbut-3-yn-2-ol (300 mg, 2.05 mmol) and 4-iodo anisole (575 mg, 2.46 mmol) in dry THF (10 mL) and DIPA (4 mL) were added [(Ph₃P)₂PdCl₂] (14 mg, 0.0205 mmol) and CuI (58 mg, 0.307 mmol) at 0 °C. And purification of the crude mixture by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S**₁₈ (420 mg, 1.66 mmol, 81%) as a yellow oil.



¹H NMR (400 MHz, CDCl₃): δ = 7.72 (2 H, d, *J* = 7.3 Hz), 7.36-7.42 (4 H, m), 7.30 (1 H, t, *J* = 7.3 Hz), 6.84 (2 H, d, *J* = 8.7 Hz), 3.80 (3 H, s), 2.50 (1 H, br, s), 1.85 (3 H, s) ppm.

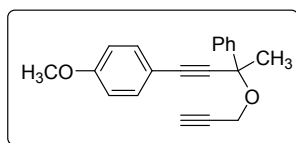
¹³C NMR (100 MHz, CDCl₃): δ = 159.8, 145.9, 133.3, 128.4, 127.8, 125.1, 114.7, 114.0, 91.1, 84.9, 70.5, 55.4 and 33.5 ppm.

IR (neat): 3431, 3056, 2986, 2842, 1606, 1509, 1445, 1262, 1173, 1138, 1086, 1033, 896, 832, 618, 532 and 445 cm⁻¹.

HR ESI-MS: [C₁₇H₁₆O₂Na]⁺ = [M+Na]⁺ requires 275.1043; found 275.1049

TLC: R_f = 0.5 (4:1; hexane:EtOAc).

1-Methoxy-4-(3-phenyl-3-(prop-2-yn-1-yloxy)but-1-yn-1-yl)benzene (**S**₁₉)



Followed procedure B: To an ice cold solution of alcohol **S**₁₈ (300 mg, 1.19 mmol) was added to a suspension of sodium hydride 60% (95 mg, 2.38 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (182 mg, 1.54 mmol, and 0.12 mL) in THF (3 mL) was added slowly at 0 °C. Evaporation of the solvent, and Purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S**₁₉ (250 mg, 0.862 mmol, 72%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.68 (2 H, d, *J* = 6.3 Hz), 7.46 (2 H, d, *J* = 7.0 Hz), 7.38 (2 H, t, *J* = 5.9 Hz), 7.31 (1 H, t, *J* = 6.0 Hz), 6.86 (2 H, d, *J* = 7.0 Hz), 4.34 (1 H, dd, *J* = 1.7 & 11.8 Hz), 3.86 (1 H, dd, *J* = 1.8 & 11.8 Hz), 3.80 (3 H, s), 2.41 (1 H, t, *J* = 2.4 Hz), 1.85 (3 H, s) ppm.

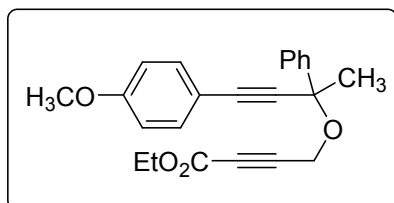
¹³C NMR (100 MHz, CDCl₃): δ = 160.0, 142.4, 133.3, 128.5, 128.1, 126.1, 114.5, 114.0, 88.3, 86.9, 80.6, 77.2, 73.7, 55.3, 53.2 and 33.0 ppm.

IR (neat): 3302, 3056, 2987, 2846, 1606, 1509, 1434, 1263, 1155, 1082, 1039, 896, 831, 721 and 455 cm^{-1} .

HR ESI-MS: $[\text{C}_{20}\text{H}_{18}\text{O}_2\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 313.1199 ; found 313.1206

TLC: $R_f = 0.6$ (9:1; hexane:EtOAc).

Ethyl 4-((4-(4-methoxyphenyl)-2-phenylbut-3-yn-2-yl)oxy)but-2-ynoate (**S**₂₀)



Followed procedure C: To an ice-cold solution of alkyne **S**₁₉ (150 mg, 0.517 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.672 mmol, 0.4 mL) after 30 minutes added ethyl chloroformate (183 mg, 1.55 mmol, 0.2 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column

chromatography (9:1, hexane: EtOAc) gave the ester **S**₂₀ (135 mg, 0.372 mmol, 72%) as a yellow oil.

¹H NMR (400 MHz, CDCl_3): $\delta = 7.66$ (2 H, dd, $J = 1.4$ & 8.5 Hz), 7.46 (2 H, d, $J = 8.9$ Hz), 7.38 (2 H, ddd, $J = 1.2, 3.0$ & 8.2 Hz), 7.32 (1 H, ddd, $J = 1.2, 2.6$ & 6.2 Hz), 6.87 (2 H, d, $J = 8.8$ Hz), 4.43 (1 H, d, $J = 16.0$ Hz), 4.19 (2 H, q, $J = 7.2$ Hz), 4.00 (1 H, d, $J = 16.0$ Hz), 3.82 (3 H, s), 1.84 (3 H, s), 1.28 (3 H, t, $J = 7.2$ Hz) ppm.

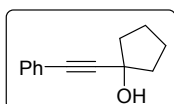
¹³C NMR (100 MHz, CDCl_3): $\delta = 160.1, 153.3, 141.9, 133.4, 128.6, 128.3, 126.2, 125.3, 114.1, 88.8, 86.6, 84.3, 77.7, 77.3, 62.0, 55.4, 53.0, 32.8$ and 14.1 ppm.

IR (neat): 3057, 2986, 2935, 2848, 1711, 1607, 1506, 1434, 1373, 1263, 1174, 1080, 1033, 895, 839, 742 and 442 cm^{-1} .

HR ESI-MS: $[\text{C}_{23}\text{H}_{22}\text{O}_4\text{Na}]^+ = [\text{M}+\text{Na}]^+$ requires 385.1410; found 385.1423

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

1-(Phenylethynyl)cyclopentan-1-ol (**S**₂₁)



Followed procedure A: To an ice-cold solution of aldehyde (300 mg, 3.57 mmol) in THF (5 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 4.64 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S**₂₁ (420 mg, 2.25 mmol, 63%) as a yellow oil.

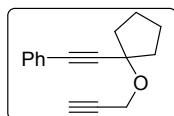
¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.43 (2 H, m), 7.30 (3 H, t, *J* = 6.0 Hz), 2.09-2.14 (2 H, m), 1.89-1.94 (2 H, m), 1.58-1.67 (4 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.7, 128.3, 128.2, 123.0, 93.0, 83.2, 75.0, 42.6 and 23.6 ppm.

IR (neat): 3442, 3048, 2926, 2859, 1661, 1542, 1418, 1375, 1252, 1108, 972, 736, 612, 518 and 415 cm⁻¹.

TLC: R_f = 0.5 (4:1; hexane: EtOAc).

((1-(Prop-2-yn-1-yloxy)cyclopentyl)ethynyl)benzene (S₂₂)



Followed procedure B: To an ice cold solution of alcohol S₂₁ (290 mg, 1.55 mmol) was added to a suspension of sodium hydride 60% (124 mg, 3.11 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (237 mg, 2.01 mmol, and 0.15 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane:EtOAc) gave the alkyne S₂₂ (250 mg, 1.16 mmol, 72%) as a yellow oil.

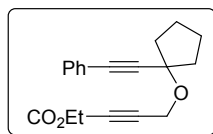
¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.44 (2 H, m), 7.29-7.31 (3 H, m), 4.32 (2 H, d, *J* = 2.4 Hz), 2.41 (1 H, t, *J* = 2.4 Hz), 2.12-2.18 (2 H, m), 1.96-2.04 (2 H, m), 1.75-1.85 (4 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.8, 128.43, 128.40, 122.8, 89.8, 85.9, 81.9, 81.1, 73.6, 53.2, 39.8 and 23.5 ppm.

IR (neat): 3303, 3055, 2975, 2873, 1435, 1373, 1194, 1064, 896, 741 and 496 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

((1-(Pent-2-yn-1-yloxy)cyclopentyl)ethynyl)benzene (S₂₃)



Followed procedure C: To an ice-cold solution of alkyne S₂₂ (230 mg, 1.02 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (1.33 mmol, 0.83 mL) after 30 minutes added Ethyl chloroformate (361mg, 3.06 mmol, 0.35 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester S₂₃ (200 mg, 0.675 mmol, 66%) as a yellow oil.

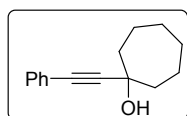
¹H NMR (400 MHz, CDCl₃): δ = 7.42 (2 H, dd, *J* = 2.0 & 5.6 Hz), 7.30-7.31 (3 H, m), 4.44 (2 H, s), 4.22 (2 H, q, *J* = 7.1 Hz), 2.11-2.13 (2 H, m), 1.97-2.03 (2 H, m), 1.76-1.83 (4 H, m), 1.29 (3 H, t, *J* = 7.1 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 131.8, 128.5, 128.4, 122.6, 89.3, 86.4, 84.7, 82.4, 62.1, 52.9, 39.8, 23.4 and 14.1 ppm.

IR (neat): 3057, 2980, 2872, 1711, 1665, 1433, 1049, 897, 741 and 520 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

1-(Phenylethynyl)cycloheptan-1-ol (S₂₄)



Followed procedure A: To an ice-cold solution of aldehyde (300 mg, 2.67 mmol) in THF (5 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 3.48 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol S₂₄ (480 mg, 2.24 mmol, 84%) as a yellow oil.

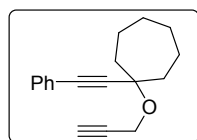
¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.44 (2 H, m), 7.29-7.30 (3 H, m), 2.09-2.14 (2 H, m), 1.89-1.94 (2 H, m), 1.58-1.67 (8 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.7, 128.3, 128.2, 123.0, 93.9, 83.7, 72.3, 43.3, 28.0 and 24.4 ppm.

IR (neat): 3438, 3046, 2942, 2852, 1648, 1540, 1415, 1372, 1245, 1102, 948, 718, 625, 516 and 412 cm⁻¹.

TLC: R_f = 0.5 (4:1; hexane:EtOAc).

1-(Phenylethynyl)-1-(prop-2-yn-1-yloxy) cycloheptane (S₂₅)



Followed procedure B: To an ice cold solution of alcohol S₂₄ (270 mg, 1.26 mmol) was added to a suspension of sodium hydride 60% (100 mg, 2.52 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes, propargyl bromide (193 mg, 1.63 mmol, and 0.12 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne S₂₅ (280 mg, 1.11 mmol, 88%) as a yellow oil.

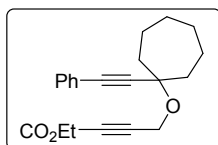
¹H NMR (400 MHz, CDCl₃): δ = 7.42-7.44 (2 H, m), 7.30-7.31 (3 H, m), 4.34 (2 H, d, *J* = 2.4 Hz), 2.41 (1 H, t, *J* = 2.4 Hz), 2.07-2.13 (2 H, m), 1.95-2.03 (2 H, m), 1.68-1.74 (2 H, m), 1.60-1.62 (6 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.8, 128.45, 128.41, 122.9, 90.7, 86.4, 81.4, 78.8, 73.4, 52.3, 40.2, 28.4 and 22.2 ppm.

IR (neat): 3302, 3056, 2932, 2863, 1599, 1444, 1362, 1266, 1185, 1059, 897, 672, 535 and 449 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

1-(Pent-2-yn-1-yloxy)-1-(phenylethynyl) cycloheptane (S₂₆)



Followed procedure C: To an ice-cold solution of alkyne S₂₅ (250 mg, 1.11 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (1.44 mmol, 0.9 mL) after 30 minutes added Ethyl chloroformate (392 mg, 3.33 mmol, 0.4 mL) 2 mL in THF at 0 °C for 3 h. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester S₂₆ (260 mg, 0.802 mmol, 72%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.42-7.43 (2 H, m), 7.30-7.32 (3 H, m), 4.46 (2 H, s), 4.22 (2 H, q, *J* = 7.0 Hz), 1.95-2.11 (4 H, m), 1.60-1.70 (8 H, m), 1.29 (3 H, t, *J* = 7.0 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 131.8, 128.5, 128.3, 122.6, 90.2, 86.8, 85.1, 79.2, 77.1, 62.0, 52.0, 40.2, 28.3, 22.1 and 14.0 ppm.

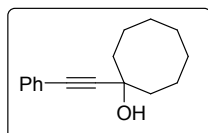
IR (neat): 3057, 2983, 2935, 2862, 1712, 1607, 1433, 1374, 1047, 895, 742 and 431 cm⁻¹.

HR ESI-MS: [C₂₁H₂₅O₃]⁺ = [M+H]⁺ requires 325.1798; found 325.1804

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

1-(Phenylethynyl) cyclooctan-1-ol (S₂₇)

Followed procedure A: To an ice-cold solution of cyclooctanone (300 mg, 2.38 mmol) in THF (5 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 3.09 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in



hexane)] at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₂₇** (320 mg, 1.403 mmol, 59%) as a yellow oil.

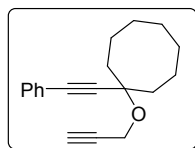
¹H NMR (400 MHz, CDCl₃): δ = 7.40-7.42 (2 H, m), 7.28-7.30 (3 H, m), 2.40 (1 H, t, *J* = 6.2 Hz), 2.00-2.08 (4 H, m), 1.84-1.90 (1 H, m), 1.63-1.71 (5 H, m), 1.50-1.55 (3 H, m), 1.33-1.39 (1 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.7, 128.3, 128.2, 123.0, 93.8, 83.3, 71.8, 42.0, 38.4, 28.0 and 22.2 ppm.

IR (neat): 3438, 3046, 2942, 2852, 1648, 1540, 1415, 1372, 1245, 1102, 948, 718, 625, 516 and 412 cm⁻¹

TLC: R_f = 0.5 (4:1; hexane:EtOAc).

1-(Phenylethynyl)-1-(prop-2-yn-1-yloxy)cyclooctane (**S₂₈**)



Followed procedure B: To an ice cold solution of alcohol **S₃₀** (300 mg, 1.31 mmol) was added to a suspension of sodium hydride 60% (105 mg, 2.63 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (200 mg, 1.70 mmol, and 0.13 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₂₈** (180 mg, 0.676 mmol, 52%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.44 (2 H, m), 7.30 (3 H, t, *J* = 6.1 Hz), 4.32 (2 H, d, *J* = 2.3 Hz), 2.41 (1 H, t, *J* = 2.4 Hz), 1.98-2.09 (4 H, m), 1.52-1.70 (10 H, m) ppm.

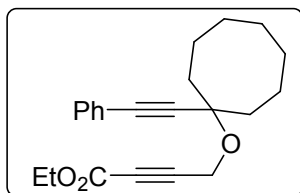
¹³C NMR (100 MHz, CDCl₃): δ = 131.8, 128.4, 128.3, 122.7, 90.4, 86.1, 81.3, 78.5, 73.4, 52.0, 34.9, 28.0, 24.6 and 21.8 ppm.

IR (neat): 3302, 3056, 2927, 2862, 1702, 1601, 1448, 1363, 1266, 1120, 1064, 911, 741, 651 and 453 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

Ethyl 4-((1-(phenylethynyl)cyclooctyl)oxy)but-2-ynoate (**S₂₉**)

Followed procedure C: To an ice-cold solution of alkyne **S₂₈** (140 mg, 0.526 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.68 mmol, 0.42 mL)



after 30 minutes added Ethyl chloroformate (186 mg, 1.57 mmol, 0.2 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S₂₉** (130 mg, 0.384 mmol, 73%) as a yellow oil.

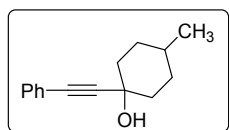
¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.43 (2 H, m), 7.30-7.32 (3 H, m), 4.45 (2 H, s), 4.22 (2 H, q, *J* = 7.1 Hz), 2.06-2.10 (1 H, m), 1.93-1.99 (1 H, m), 1.62-1.67 (3 H, m), 1.51-1.54 (1 H, m), 1.39-1.43 (2 H, m), 1.25-1.33 (6 H, m), 0.91 (3 H, t, *J* = 6.7 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 131.8, 128.5, 128.4, 122.6, 90.3, 86.6, 85.1, 79.1, 62.1, 51.9, 39.1, 34.9, 28.0, 23.4, 21.8 and 14.2 ppm.

IR (neat): 3056, 2931, 2864, 1712, 1600, 1453, 1373, 1265, 1143, 1049, 897, 741, 707 and 491 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc).

4-Methyl-1-(phenylethynyl)cyclohexan-1-ol (**S₃₀**)



Followed procedure A: To an ice-cold solution of aldehyde (300 mg, 2.67 mmol) in THF (5 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 3.48 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₃₀** (450 mg, 2.10 mmol, 78%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.43 (2 H, dd, *J* = 2.9 & 6.9 Hz), 7.31 (3 H, t, *J* = 6.4 Hz), 2.04-2.08 (2 H, m), 1.69-1.73 (2 H, m), 1.59-1.65 (2 H, m), 1.32-1.38 (3 H, m), 0.93 (3 H, d, *J* = 5.8 Hz) ppm.

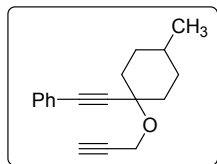
¹³C NMR (100 MHz, CDCl₃): δ = 131.8, 128.38, 128.35, 123.0, 92.4, 85.1, 69.9, 40.2, 32.6, 31.8 and 21.9 ppm.

IR (neat): 3430, 3052, 2930, 2863, 1680, 1586, 1432, 1330, 1262, 1116, 975, 738, 614, 525 and 420 cm⁻¹.

TLC: R_f = 0.5 (4:1; hexane:EtOAc).

((4-Methyl-1-(prop-2-yn-1-yloxy)cyclohexyl)ethynyl)benzene (**S₃₁**)

Followed procedure B: To an ice cold solution of alcohol **S₃₀** (140 mg, 0.65 mmol) was added to a suspension of sodium hydride 60% (52 mg, 1.30 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (100 mg, 0.84 mmol) in THF (3 mL) was added slowly at 0 °C. And Purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₃₁** (150 mg, 0.595 mmol, 91%) as a yellow oil.



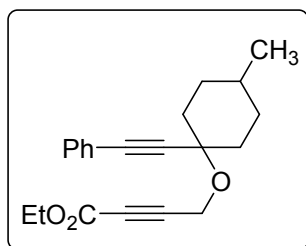
¹H NMR (400 MHz, CDCl₃): δ = 7.43-7.45 (2 H, m), 7.29-7.32 (3 H, m), 4.39 (2 H, d, *J* = 2.4 Hz), 2.41 (1 H, t, *J* = 2.4 Hz), 2.14-2.17 (2 H, m), 1.70-1.73 (2 H, m), 1.57-1.63 (2 H, m), 1.32-1.38 (3 H, m), 0.92 (3 H, d, *J* = 6.0 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 131.8, 128.4, 128.3, 122.8, 89.0, 87.8, 81.3, 76.4, 73.6, 51.9, 37.5, 32.2, 32.0 and 21.9 ppm.

IR (neat): 3302, 3056, 2939, 2862, 1600, 1489, 1448, 1371, 1322, 1267, 1156, 1066, 994, 904, 717 and 554 cm⁻¹

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

Ethyl 4-((4-methyl-1-(phenylethynyl)cyclohexyl)oxy)but-2-ynoate (S₃₂**)**



Followed procedure C: To an ice-cold solution of alkyne **S₃₁** (135 mg, 0.535 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.69 mmol, 0.43 mL) after 30 minutes added Ethyl chloroformate (189 mg, 1.60 mmol, 0.2 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc)

gave the ester **S₃₂** (110 mg, 0.416 mmol, 78%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.42-7.45 (2 H, m), 7.30-7.34 (3 H, m), 4.51 (2 H, s), 4.21 (2 H, q, *J* = 7.1 Hz), 2.14 (2 H, d, *J* = 12.0 Hz), 1.73 (2 H, d, *J* = 12.1 Hz), 1.59 (2 H, t, *J* = 13.0 Hz), 1.27-1.39 (6 H, m), 0.92 (3 H, t, *J* = 2.4 Hz) ppm.

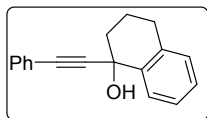
¹³C NMR (100 MHz, CDCl₃): δ = 153.4, 131.8, 128.6, 128.4, 122.6, 88.6, 88.3, 85.0, 77.2, 76.9, 62.0, 51.8, 37.4, 32.2, 31.9, 21.8 and 14.1 ppm.

IR (neat): 3058, 2935, 2862, 1713, 1483, 1451, 1373, 1314, 1254, 1156, 1087, 1056, 923, 859, 746 and 698 cm⁻¹.

HR ESI-MS: $[C_{21}H_{25}O_3]^+ = [M+H]^+$ requires 325.1798; found 325.1804

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

1-(Phenylethynyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**S₃₃**)



Followed procedure A: To an ice-cold solution of aldehyde (300 mg, 2.05 mmol) in THF (8 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 2.66 mmol freshly prepared from phenyl acetylene and n BuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₃₃** (450 mg, 1.81 mmol, 88%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.84$ (1 H, dd, $J = 2.1$ & 7.8 Hz), 7.42 (2 H, dd, $J = 2.2$ & 5.9 Hz), 7.22-7.29 (5 H, m), 7.11 (1 H, dd, $J = 1.7$ & 6.9 Hz), 2.82-2.86 (2 H, m), 2.47 (1 H, s), 2.28-2.31 (2 H, m), 1.95-2.08 (2 H, m) ppm.

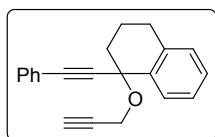
¹³C NMR (100 MHz, CDCl₃): $\delta = 139.2, 136.1, 131.7, 129.2, 128.4, 128.3, 128.2, 128.0, 126.7, 122.8, 93.4, 84.3, 68.3, 39.1, 29.3$ and 19.2 ppm.

IR (neat): 3432, 3048, 2965, 2932, 1603, 1474, 1448, 1372, 1299, 1251, 1212, 1104, 1028, 942, 848, 755 and 419 cm^{-1}

TLC: $R_f = 0.5$ (4:1; hexane: EtOAc).

1-(Phenylethynyl)-1-(prop-2-yn-1-yloxy)-1,2,3,4-tetrahydronaphthalene (**S₃₄**)

Followed procedure B: To an ice cold solution of alcohol **S₃₃** (400 mg, 1.61 mmol) was added to a suspension of sodium hydride 60% (1.28 mg, 3.22 mmol) in THF (8 mL) anhydrous at 0 °C. After 30 minutes, propargyl bromide (246 mg, 2.09 mmol, and 0.16 mL) in THF (4 mL) was added slowly at 0 °C. And Purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₃₄** (350 mg, 1.22 mmol, 76%) as a yellow oil.



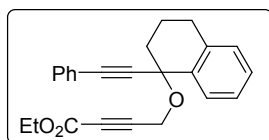
¹H NMR (400 MHz, CDCl₃): $\delta = 7.76$ (1 H, dd, $J = 1.7$ & 6.5 Hz), 7.44-7.46 (2 H, m), 7.29-7.31 (3 H, m), 7.21-7.23 (2 H, m), 7.11 (1 H, dd, $J = 3.1$ & 8.6 Hz), 4.43 (1 H, dd, $J = 2.4$ & 15.0 Hz), 4.26 (1 H, dd, $J = 2.4$ & 15.0 Hz), 2.77-2.92 (2 H, m), 2.45-2.50 (1 H, m), 2.38 (1 H, t, $J = 2.4$ Hz), 2.14-2.19 (2 H, m), 1.84-1.89 (1 H, m) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 136.8, 136.3, 131.8, 129.3, 129.1, 128.6, 128.4, 128.3, 125.9, 122.6, 89.9, 87.2, 81.0, 74.4, 73.6, 52.5, 35.5, 29.0$ and 18.4 ppm.

IR (neat): 3300, 3057, 2943, 2869, 1684, 1600, 1489, 1443, 1361, 1268, 1163, 1052, 925, 746, 692, 644 and 442 cm^{-1} .

TLC: $R_f = 0.6$ (9:1; hexane: EtOAc).

Ethyl 4-((1-(phenylethynyl)-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)but-2-ynoate (S_{35})



Followed procedure C: To an ice-cold solution of alkyne S_{34} (250 mg, 0.874 mmol) in THF (6 mL) was added $n\text{BuLi}$ in hexane (1.6 M) (1.13 mmol, 0.7 mL) after 30 minutes added Ethyl chloroformate (309 mg, 2.62 mmol, 0.3 mL) 2 mL in THF at $0\text{ }^\circ\text{C}$. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester S_{35} (200 mg, 0.558 mmol, 64%) as a yellow oil.

^1H NMR (400 MHz, CDCl_3): $\delta = 7.75$ (1 H, dd, $J = 1.8$ & 6.3 Hz), 7.44-7.46 (2 H, m), 7.30 (3 H, dd, $J = 2.0$ & 5.2 Hz), 7.21-7.24 (2 H, m), 7.11 (1 H, dd, $J = 2.9$ & 7.2 Hz), 4.55 (1 H, d, $J = 16.3$ Hz), 4.38 (1 H, d, $J = 16.3$ Hz), 4.19 (2 H, q, $J = 7.1$ Hz), 2.81-2.91 (2 H, m), 2.43-2.47 (1 H, m), 2.11-2.22 (2 H, m), 1.85-1.89 (1 H, m), 1.26 (3 H, t, $J = 7.2$ Hz) ppm.

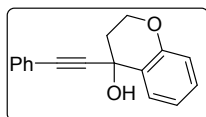
^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.3, 136.9, 135.9, 131.8, 129.3, 129.0, 128.7, 128.6, 128.4, 126.0, 122.4, 89.4, 87.7, 84.7, 77.2, 74.8, 62.0, 52.3, 35.6, 28.9, 18.4$ and 14.0 ppm.

IR (neat): 3057, 2980, 2943, 2872, 1712, 1601, 1444, 1371, 1262, 1039, 911, 742 and 562 cm^{-1} .

HR ESI-MS: $[\text{C}_{24}\text{H}_{23}\text{O}_3]^+ = [\text{M}+\text{H}]^+$ requires 359.1642; found 359.1637

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

4-(Phenylethynyl)chroman-4-ol (S_{36})



Followed procedure A: To an ice-cold solution of aldehyde (300 mg, 2.02 mmol) in THF (5 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 2.63 mmol freshly prepared from phenyl acetylene and $n\text{BuLi}$ (1.6 M in hexane)]. at $0\text{ }^\circ\text{C}$. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol S_{36} (450 mg, 1.8 mmol, 89%) as a yellow oil.

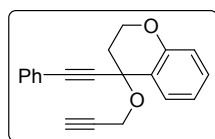
¹H NMR (400 MHz, CDCl₃): δ = 7.75 (1 H, dd, *J* = 7.7 Hz), 7.44-7.46 (2 H, m), 7.29-7.32 (3 H, m), 7.21-7.25 (1 H, m), 6.97 (1 H, t, *J* = 7.6 Hz), 6.85 (1 H, d, *J* = 8.3 Hz), 4.36-4.39 (2 H, m), 2.60 (1 H, br, s), 2.43-2.49 (1 H, m), 2.36-2.40 (1 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.6, 131.8, 130.3, 128.7, 128.4, 125.3, 122.4, 121.0, 117.4, 91.5, 84.9, 64.3, 62.5 and 37.3 ppm

IR (neat): 3428, 3063, 2971, 2937, 1600, 1487, 1452, 1374, 1309, 1258, 1225, 1109, 1056, 958, 864, 757 and 425 cm⁻¹

TLC: R_f = 0.5 (4:1; hexane:EtOAc).

4-(Phenylethynyl)-4-(prop-2-yn-1-yloxy) chromane (S₃₇)



Followed procedure B: To an ice cold Solution of alcohol S₃₆ (350 mg, 1.4 mmol) was added to a suspension of sodium hydride 60% (112 mg, 2.8 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargylic bromide (214 mg, 1.82 mmol, and 0.13 mL) in THF (3 mL) was added slowly at 0 °C. And Purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne S₃₇ (320 mg, 1.11 mmol, 79%) as a yellow oil.

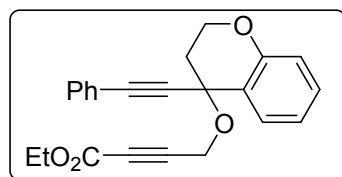
¹H NMR (400 MHz, CDCl₃): δ = 7.64 (1 H, dd, *J* = 1.2 & 6.2 Hz), 7.46-7.48 (2 H, m), 7.30-7.35 (3 H, m), 7.24 (1 H, td, *J* = 1.3 & 5.7 Hz), 6.93 (1 H, td, *J* = 0.8 & 6.1 Hz), 6.86 (1 H, d, *J* = 6.6 Hz), 4.46-4.52 (2 H, m), 4.32 (1 H, dt, *J* = 2.8 & 6.0 Hz), 4.21 (1 H, dd, *J* = 2.0 & 11.9 Hz), 2.53 (1 H, dt, *J* = 2.0 & 4.6 Hz), 2.37-2.43 (2 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 154.0, 131.9, 130.6, 129.8, 128.9, 128.4, 122.2, 121.3, 120.0, 117.5, 87.9, 87.6, 80.6, 73.8, 70.1, 52.5 and 34.9 ppm.

IR (neat): 3301, 3056, 2968, 2873, 1739, 1597, 1484, 1451, 1375, 1266, 1054, 922, 748, 534 and 456 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane: EtOAc)

Ethyl 4-((4-(phenylethynyl)chroman-4-yl)oxy)but-2-ynoate (S₃₈)



Followed procedure C: To an ice-cold solution of alkyne S₃₇ (200 mg, 0.694 mmol) in THF (6 mL) was added ⁿBuLi in hexane (1.6 M) (0.90 mmol, 0.6 mL) after 30 minutes added Ethyl

chloroformate (245 mg, 2.08 mmol, 0.25 mL) 2 mL in THF at 0 °C for 2 h. Evaporation of the solvent. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S₃₈** (180 mg, 0.5 mmol, 72%) as a yellow oil.

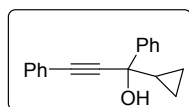
¹H NMR (400 MHz, CDCl₃): δ = 7.63 (1 H, d, *J* = 6.2 Hz), 7.47-7.48 (2 H, m), 7.30-7.34 (3 H, m), 7.25 (1 H, ddd, *J* = 1.3, 1.6 & 6.1 Hz), 6.93 (1 H, t, *J* = 6.0 Hz), 6.86 (1 H, d, *J* = 6.6 Hz), 4.60 (1 H, d, *J* = 13.0 Hz), 4.46 (1 H, td, *J* = 2.0 & 9.2 Hz), 4.30-4.35 (2 H, m), 4.17-4.21 (2 H, m), 2.50 (1 H, dt, *J* = 2.2 & 11.3 Hz), 2.37-2.43 (1 H, m), 1.27 (3 H, t, *J* = 5.7 Hz) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ = 154.0, 153.2, 131.9, 130.8, 129.7, 129.0, 128.4, 122.0, 120.8, 120.0, 117.6, 88.0, 87.4, 84.1, 70.4, 62.1, 61.9, 52.2, 34.9 and 14.2 ppm.

IR (neat): 3057, 2985, 1712, 1601, 1485, 1437, 1374, 1263, 1046, 898, 742, 522 and 456 cm⁻¹.

HR ESI-MS: [C₂₃H₂₀O₄Na]⁺ = [M+Na]⁺ requires 383.1254; found 383.1259

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

1-cyclopropyl-1,3-diphenylprop-2-yn-1-ol (**S₃₉**)



Followed procedure A: To an ice-cold solution of aldehyde (1 gm, 11.3 mmol) in THF (5 mL) was added, the solution of (phenylethynyl) lithium [3 mL in THF 1.3 eq., 14.7 mmol freshly prepared from phenyl acetylene and ⁿBuLi (1.6 M in hexane)]. The reaction was stirred at 0 °C. And purified by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₃₉** (800 mg, 4.10 mmol, 36%) as a yellow oil.

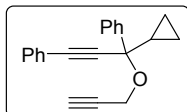
¹H NMR (400 MHz, CDCl₃): δ = 7.73 (2 H, dd, *J* = 1.2 & 8.2 Hz), 7.43-7.45 (2 H, m), 7.36-7.40 (2 H, m), 7.29-7.33 (4 H, m), 2.51 (1 H, s), 1.42-1.49 (1 H, m), 0.85-0.89 (1 H, m), 0.69-0.74 (1 H, m), 0.57-0.64 (2 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 144.9, 131.9, 128.6, 128.4, 128.3, 127.8, 125.5, 122.5, 89.1, 86.1, 75.0, 23.9, 3.40 and 2.55 ppm.

IR (neat): 3440, 3056, 2997, 1490, 1440, 1266, 1167, 1030, 911, 740, 507 and 420 cm⁻¹.

TLC: R_f = 0.5 (4:1; hexane:EtOAc).

(3-Cyclopropyl-3-(prop-2-yn-1-yloxy)prop-1-yne-1,3-diyl)dibenzene (**S₄₀**)



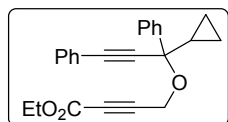
Followed procedure B: To an ice cold solution of alcohol **S₃₉** (700 mg, 2.27 mmol) was added to a suspension of sodium hydride 60% (181 mg, 4.54 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (348 mg, 2.95 mmol, and 0.22 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₄₀** (550 mg, 1.17 mmol, 52%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.68 (2 H, d, *J* = 8.0 Hz), 7.47-7.50 (2 H, m), 7.32-7.40 (6 H, m), 4.38 (1 H, dd, *J* = 2.4 & 14.8 Hz), 4.00 (1 H, dd, *J* = 2.4 & 14.8 Hz), 2.39 (1 H, t, *J* = 2.4 Hz), 1.43-1.46 (1 H, m), 0.91-0.93 (1 H, m), 0.63-0.66 (1 H, m), 0.43-0.53 (2 H, m) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ = 142.0, 131.9, 128.8, 128.5, 128.4, 128.1, 126.4, 122.2, 89.3, 85.1, 82.4, 80.7, 73.7, 53.3, 22.8, 3.95 and 2.29 ppm.

IR (neat): 3302, 3057, 2924, 2865, 1668, 1599, 1489, 1439, 1367, 1266, 1055, 904, 708 and 541 cm⁻¹.

TLC: R_f = 0.6 (9:1; hexane:EtOAc).

Ethyl 4-((1-cyclopropyl-1,3-diphenylprop-2-yn-1-yl)oxy)but-2-ynoate (**S₄₁**)



Followed procedure C: To an ice-cold solution of alkyne **S₄₀** (500 mg, 0.28 mmol) in THF (3 mL) was added *n*BuLi in hexane (1.6 M) (0.36 mmol, 0.22 mL) after 30 minutes added Ethyl chloroformate (91mg, 0.84 mmol, 0.1 mL)

2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the ester **S₄₁** (420 mg, 0.11 mmol, 41%) as a yellow oil.

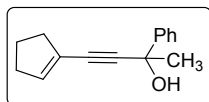
¹H NMR (400 MHz, CDCl₃): δ = 7.67 (2 H, d, *J* = 7.5 Hz), 7.48-7.51 (2 H, m), 7.30-7.40 (6 H, m), 4.48 (1 H, d, *J* = 16.1 Hz), 4.14-4.22 (3 H, m), 1.42-1.48 (1 H, m), 1.27 (3 H, t, *J* = 7.2 Hz), 0.90-0.95 (1 H, m), 0.63-0.69 (1 H, m), 0.43-0.55 (2 H, m) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 153.3, 141.6, 132.0, 129.0, 128.5, 128.3, 128.0, 126.4, 122.0, 89.8, 84.7, 84.4, 82.8, 62.0, 53.0, 22.6, 14.0, 3.95 and 2.33 ppm.

IR (neat): 3056, 2992, 2918, 2961, 1718, 1592, 1488, 1054, 742 and 532 cm⁻¹

TLC: R_f = 0.6 (9:

4-(Cyclopent-1-en-1-yl)-2-phenylbut-3-yn-2-ol (**S₄₂**)



Followed procedure D: To a solution of 2-phenylbut-3-yn-2-ol (200 mg, 1.36 mmol) and cyclopent-1-en-1-yl trifluoromethanesulfonate⁷ (355 mg, 1.64 mmol) in dry THF (10 mL) and DIPA (3 mL) were added [(Ph₃P)₂PdCl₂] (10 mg, 0.0136 mmol) and CuI (39 mg, 0.204 mmol) at 0 °C. And Evaporation of the solvent and purification of the crude mixture by column chromatography (4:1, hexane: EtOAc) gave the alcohol **S₄₂** (160 mg, 0.75 mmol, 55%) as a yellow oil.

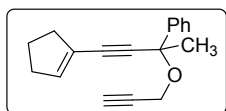
¹H NMR (400 MHz, CDCl₃): δ = 7.65 (2 H, dd, *J* = 3.3 & 7.2 Hz), 7.35 (2 H, td, *J* = 1.7 & 7.1 Hz), 7.27 (1 H, ddd, *J* = 1.2, 2.4 & 6.4 Hz), 6.07-6.09 (1 H, m), 2.40-2.49 (4 H, m), 1.87-1.95 (2 H, m), 1.78 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 145.9, 138.5, 128.3, 127.7, 125.1, 124.0, 93.7, 82.4, 70.5, 36.5, 33.4, 33.3 and 23.4 ppm.

IR (neat): 3393, 3057, 2935, 2856, 1672, 1610, 1444, 1409, 1328, 1265, 1075, 1038, 907, 704, 592 and 468 cm⁻¹.

TLC: R_f = 0.5 (9:1; hexane: EtOAc).

(4-(Cyclopent-1-en-1-yl)-2-(prop-2-yn-1-yloxy)but-3-yn-2-yl)benzene (S₄₃)



Followed procedure B: To an ice cold solution of alcohol **S₄₂** (150 mg, 0.707 mmol) was added to a suspension of sodium hydride 60% (57 mg, 1.41 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (108 mg, 0.919 mmol, and 0.06 mL) in THF (3 mL) was added slowly at 0 °C. And purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₄₃** (110 mg, 0.44 mmol, 62%) as a yellow oil.

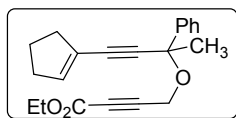
¹H NMR (400 MHz, CDCl₃): δ = 7.61 (2 H, dd, *J* = 1.5 & 8.6 Hz), 7.36 (2 H, ddd, *J* = 1.1, 2.9 & 8.2 Hz), 7.30 (1 H, ddd, *J* = 1.3, 2.6 & 6.2 Hz), 6.13-6.16 (1 H, m), 4.26 (1 H, dd, *J* = 2.4 & 14.7 Hz), 3.77 (1 H, dd, *J* = 2.5 & 14.7 Hz), 2.50-2.55 (2 H, m), 2.44-2.48 (2 H, m), 2.39 (1 H, t, *J* = 2.5 Hz), 1.90-1.98 (2 H, m), 1.78 (3 H, s) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 142.3, 138.9, 128.5, 128.1, 126.1, 123.8, 89.4, 85.8, 80.6, 77.3, 73.7, 53.2, 36.5, 33.4, 33.0 and 23.4 ppm.

IR (neat): 3301, 3056, 2980, 2936, 2864, 1681, 1608, 1443, 1372, 1266, 1081, 1048, 895, 744, 632 and 487 cm^{-1} .

TLC: $R_f = 0.6$ (9:1; hexane:EtOAc).

Ethyl 4-((4-(cyclopent-1-en-1-yl)-2-phenylbut-3-yn-2-yl)oxy)but-2-ynoate (S₄₄)



Followed procedure C: To an ice-cold solution of alkyne **S₄₃** (100 mg, 0.4 mmol) in THF (3 mL) was added ⁿBuLi in hexane (1.6 M) (0.50 mmol, 0.32 mL) after 30 minutes added Ethyl chloroformate (141 mg, 1.2 mmol, 0.12 mL) 2 mL in THF at 0 °C. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave mixture of product ester & cyclised (1:0.7) **S₄₄** (85 mg, 0.26 mmol, 66%) as a yellow oil.

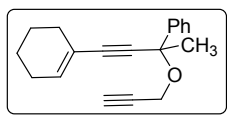
¹H NMR (400 MHz, CDCl₃): $\delta = 7.59$ (2 H, dd, $J = 1.5$ & 8.4 Hz), 7.30-7.38 (3 H, m), 6.15-6.16 (1 H, m), 4.35 (1 H, d, $J = 16.0$ Hz), 4.21 (2 H, q, $J = 7.2$ Hz), 3.94 (1 H, d, $J = 16.0$ Hz), 2.44-2.54 (4 H, m), 1.92-1.96 (2 H, m), 1.78 (3 H, s), 1.29 (3 H, t, $J = 7.1$ Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 153.4, 141.9, 139.1, 128.5, 128.3, 126.2, 123.7, 89.0, 86.3, 84.3, 77.3, 62.1, 52.9, 36.5, 33.4, 32.8, 23.4$ and 14.1 ppm.

IR (neat): 3052, 2978, 2860, 1707, 1589, 1436, 1212, 1175, 1021, 878, 725, 542, 478 and 420 cm^{-1}

TLC: $R_f = 0.5$ (9:1; hexane:EtOAc).

(1-(Cyclohex-1-en-1-yl)-3-methylhepta-1,6-diyn-3-yl)benzene (S₄₅)



Followed procedure B: To an ice cold solution of 4-(cyclohex-1-en-1-yl)-2-phenylbut-3-yn-2-ol⁸ (280 mg, 2.27 mmol) was added to a suspension of sodium hydride 60% (181 mg, 4.54 mmol) in THF (5 mL) anhydrous at 0 °C. After 30 minutes propargyl bromide (348 mg, 2.95 mmol, and 0.22 mL) in THF (3 mL) was added slowly at 0 °C. And Purification of the crude by flash column chromatography (9:1 hexane: EtOAc) gave the alkyne **S₄₅** (220 mg, 1.17 mmol, 52%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.61$ (2 H, dd, $J = 1.5$ & 8.5 Hz), 7.34-7.38 (2 H, m), 7.29 (1 H, ddd, $J = 1.4, 2.7$ & 6.3 Hz), 6.20-6.23 (1 H, m), 4.25 (1 H, dd, $J = 2.5$ & 14.7 Hz), 3.75 (1 H,

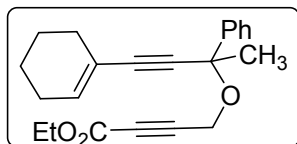
dd, $J = 2.5$ & 14.7 Hz), 2.39 (1 H, t, $J = 2.5$ Hz), 2.18-2.21 (2 H, m), 2.10-2.14 (2 H, m), 1.77 (3 H, s), 1.58-1.69 (4 H, m) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 142.5, 135.8, 128.4, 128.0, 126.1, 120.1, 90.3, 85.5, 80.6, 77.1, 73.7, 53.1, 33.1, 29.3, 25.7, 22.3$ and 21.5 ppm.

IR (neat): 3302, 3057, 2986, 2943, 2869, 1722, 1673, 1608, 1427, 1265, 1083, 897, 740 and 462 cm^{-1} .

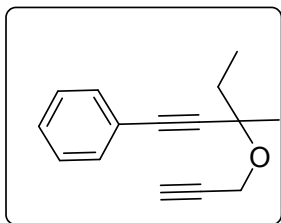
TLC: $R_f = 0.6$ (9:1; hexane:EtOAc).

Ethyl 4-((4-(cyclohex-1-en-1-yl)-2-phenylbut-3-yn-2-yl)oxy)but-2-ynoate (S_{46})



Followed procedure C: To an ice-cold solution of alkyne S_{45} (200 mg, 0.757 mmol) in THF (3 mL) was added $n\text{BuLi}$ in hexane (1.6 M) (0.98 mmol, 0.6 mL) after 30 minutes added Ethyl chloroformate (267 mg, 2.2 mmol, 0.25 mL) 2 mL in THF at $0\text{ }^\circ\text{C}$. And purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave mixture of cyclised & ester (1:0.25) S_{46} (170 mg, 0.508 mmol, 67%) as a yellow oil.

(3-Methyl-3-(prop-2-yn-1-yloxy)pent-1-yn-1-yl)benzene (S_{47})



To an ice cold Solution of alcohol⁹ (250 mg, 1.44 mmol) was added to a suspension of sodium hydride 60% (118 mg, 2.96 mmol) in THF (7 mL) anhydrous at $0\text{ }^\circ\text{C}$. After 30 minutes propargylic bromide (227 mg, 1.92 mmol, and 0.13 mL) in THF (3 mL) was added slowly at $0\text{ }^\circ\text{C}$, and the reaction mixture was stirred at room temperature for 12 h. Evaporation of the solvent. And Purification of the crude by flash column chromatography (19:1 hexane:EtOAc) gave the alkyne S_{47} (220mg, 1.05 mmol, 73%) as a yellow oil.

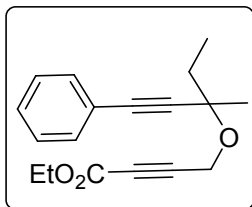
^1H NMR (400 MHz, CDCl_3): $\delta = 7.45\text{-}7.40$ (2 H, m), $7.33\text{-}7.28$ (3 H, m), 4.35 (2 H, d, $J = 2.2$ Hz), 2.42 (1 H, t, $J = 2.2$ Hz), 1.91-1.74 (2 H, m), 1.53 (3 H, s) and 1.06 (3 H, t, $J = 7.4$ Hz) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 131.9, 131.8, 128.5, 128.4, 128.4, 128.3, 122.7, 89.5, 86.3, 81.2, 75.6, 73.6, 52.6, 34.6, 25.9$ and 8.9 ppm.

IR (neat): 2956, 2925, 2852, 2366, 1651, 1445, 1425, 1380, 1121, 1089 and 1023 cm^{-1} .

TLC: $R_f = 0.6$ (19:1, Hex/EtOAc).

Ethyl 4-((3-methyl-1-phenylpent-1-yn-3-yl)oxy)but-2-ynoate (**S₄₈**)



To an ice-cold solution of alkyne **S₄₇** (200 mg, 0.94 mmol) in THF (3 mL) was added nBuLi in hexane (1.6 M) (1.226 mmol, 0.8 mL) after 30 minutes added Ethyl chloroformate (265 mg, 2.82 mmol, 0.25 mL) 2 mL in THF at 0 °C for 2 h. Evaporation of the solvent. And purification of the crude mixture by column chromatography (19:1, hexane: EtOAc) gave the ester **S₄₈** (187 mg, 0.66 mmol, 70%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.45\text{-}7.40$ (2 H, m), $7.33\text{-}7.29$ (3 H, m), 4.46 (2 H, s), 4.22 (2 H, q, $J = 7.1$ Hz), 1.90-1.73 (2 H, m), 1.53 (3 H, s), 1.29 (3 H, t, $J = 7.1$ Hz) and 1.06 (3 H, t, $J = 7.4$ Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 153.4, 131.8, 128.6, 128.4, 122.5, 89.1, 86.8, 84.9, 76.1, 62.1, 52.4, 34.6, 25.9, 14.1$ and 8.9 ppm.

IR (neat): 2980, 2926, 2241, 1714, 1489, 1459, 1372, 1303, 1253, 1082, 1051, 755 and 692 cm⁻¹.

HR ESI-MS: [C₁₈H₂₀NaO₃]⁺ = [M+Na]⁺ requires 307.1305; found 307.1311

TLC: $R_f = 0.6$ (19:1, Hex/EtOAc).

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